Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Hydroboration of Internal Alkynes Catalyzed by $FeH(CO)(NO)(PPh_3)_2$: a Case of Boron-Source controlled Regioselectivity

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Contents

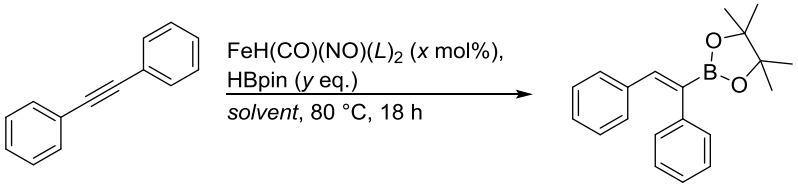
1. General Remarks

All reactions that are sensitive towards moisture or air were performed by application of standard Schlenk techniques under dry nitrogen. Solvents were purified and dried prior to use. All chemicals were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar, ChemPUR or TCI and used as received. Pinacolborane (HBpin, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 97%) was purchased from Sigma Aldrich and stored in a 10 mL-screw cap Schlenk tube at -18 °C. *Bis*(pinacolato)diboron (B_2pin_2) was purchased from ChemPUR and used as received. Commercial substrates for the catalysis were bought from the aforementioned suppliers and used without further purification. The catalysts $[Fe(CO)_3(NO)][NBu_4]$ and **1b-d** were prepared as described in the literature.[1] NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz (^{1}H NMR), 122 MHz (^{31}P NMR) and 75 MHz (^{13}C NMR), a Bruker Ascend 400 spectrometer at 400 MHz (^{1}H NMR), 162 MHz (^{31}P NMR), 128 MHz (^{11}B NMR) and 101 MHz (^{13}C NMR) or a Bruker Avance 500 spectrometer at 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR). Chemical shifts are reported in ppm and were corrected with tetramethylsilane as internal standard or with the residual NMR solvent peaks. The sp^2-carbon atoms directly attached to the boronate were not visible in the ^{13}C-NMR spectra due to quadrupolar relaxation. IR spectrometry was performed on a FT-IR spectrometer in ATR mode. Band intensities are abbreviated as follows: weak (w), medium (m), strong (s) and very strong (vs). Mass spectra including high resolution mass spectrometry were measured on a Bruker micrOTOF-Q ESI spectrometer or on a Finnigan MAT-95 EI spectrometer. For high performance liquid chromatography (HPLC) a Knauer K-501 pump, Knauer RI-detector K 2400 and a Macherey-Nagel VP250/21 Nucleodur 100-5 column were used. Unless otherwise stated, the flow rate was set to 10 mL/min. X-ray structures were measured on a Bruker Kappa APEXII Duo diffractometer.

2. General Optimisation

2.1 Reaction optimisation – HBpin as boron source

Table S1: Reaction optimisation.



2 (*Z*)/(*E*)-**3**

Entry[a]	Catalyst (*x* mol%)	Solvent	*y* eq.	Yield / %[b,c]
1	**1a** (5)	THF	2.0	70
2	**1a** (1)	THF	2.0	32
3	**1a** (2)	THF	2.0	29
4[d]	**1a** (5)	THF	2.0	16
5	**1a** (5)	PhMe	2.0	80
6	**1a** (5)	1,4-dioxane	2.0	21
7	**1a** (5)	DME	2.0	25
8	**1a** (5)	DMF	2.0	26
9	**1a (5)**	**PhMe**	**2.2**	**85 (85)[e]**
10	-	PhMe	2.2	0
11	PPh_3 (10)	PhMe	2.2	0
12	$[Fe(CO)_3(NO)][NBu_4]$	PhMe	2.2	68
13	**1b** (5)	PhMe	2.2	9
14	**1c** (5)	PhMe	2.2	26
15	**1d** (5)	PhMe	2.2	67
16[f]	**1a** (5)	PhMe	2.2	26

[a] Reactions were run on 0.3 mmol scale. [b] (*Z*)/(*E*) ratio was determined by ^{1}H NMR and was always >95/5. [c] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [d] With NEt_3 (0.5 eq.) as additive. [e] Isolated yield. [f] Reaction under air and with wet toluene.

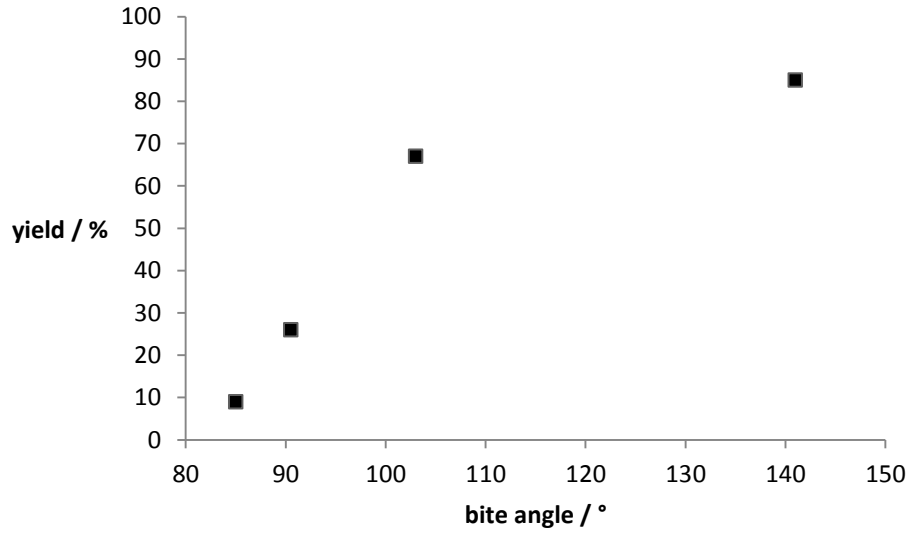
During the optimisation of the reaction, we observed a correlation between the bite angle of the phosphine ligand attached to the iron centre of the complex and the corresponding yields

(see Table S1, entries 9 and 13-15). The ligand bite angles for complexes **1a-d** are as follows:

- $FeH(CO)(NO)(PPh_3)_2$ **1a** – 141° [2]
- FeH(CO)(NO)(dppe) **1b** – 85° [3]
- FeH(CO)(NO)(dppp) **1c** – 90.5° [1b]
- FeH(CO)(NO)(dppf) **1d** – 103° [4]

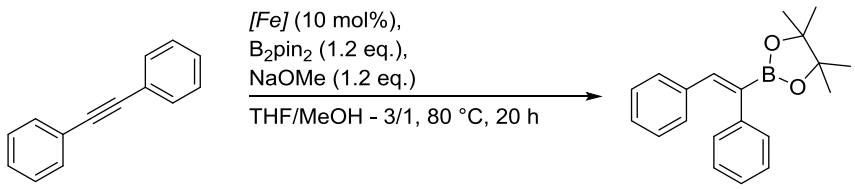
This correlation is summarised in Figure S1.

Figure S1: Correlation between the bite angle of the phosphine ligand in complexes **1a-d** and the corresponding yield in the hydroboration of tolane **2**.



2.2 Reaction optimisation – B_2pin_2 as boron source

Table S2: Catalyst Screening.



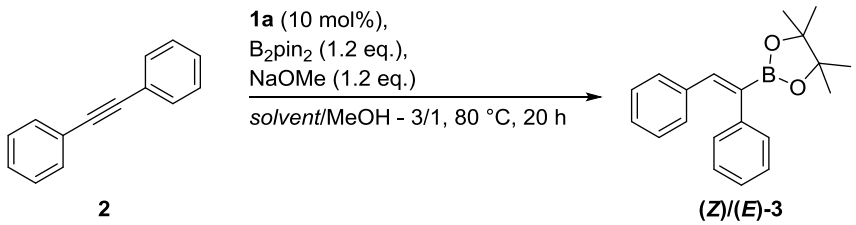
2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**1a**	**84**	**99/1**
2	**1b**	74	99/1
3	**1c**	71	99/1

4	**1d**	83	99/1
5	$[Fe(CO)_3(NO)][NBu_4]$	85	99/1
6	Bu_4NBr	3	n. d.
7	dppf	64	99/1
8	$FeCp_2$	4	n. d.
9	$Fe(acac)_3$	61	95/5
10	$FeCl_2$ x $4H_2O$	44	99/1
11	$FeCl_3$	90	>99/1
12	no catalyst	2	n. d.
13	PPh_3 (20 mol%)	4	n. d.

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S3: Solvent Screening.

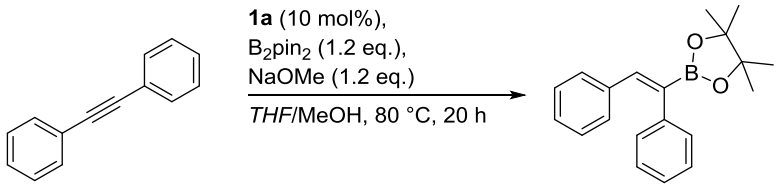


Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**THF (standard conditions)**	**85**	**99/1**
2	MeCN	63	94/6
3	*n*-pentane	66	99/1
4	PhMe	88	99/1
5	CH_2Cl_2	52	98/2
6	MeOH	84	99/1
7	1,2-dichlorobenzene	81	98/2
8	DMF	23	89/11
9	DMSO	57	76/24

10	NEt_3	86	99/1
11	Et_2O	64	99/1
12	1,4-dioxane	86	99/1
13	tetrahydropyran	78	99/1
14	MTBE	84	99/1
15	dimethoxyethane	87	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S4: Concentration Screening - THF.

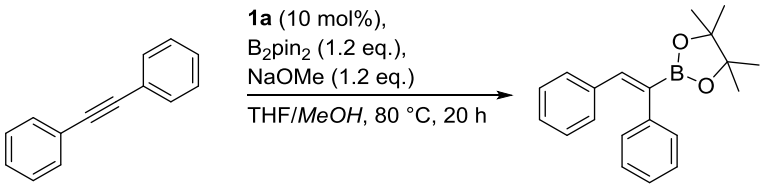


2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	***c* = 0.67 M (standard conditions)**	**83**	**99/1**
2	*c* = 1.0 M	89	99/1
3	*c* = 1.5 M	89	99/1
4	*c* = 0.4 M	85	99/1
5	*c* = 0.2 M	84	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S5: Methanol Equivalents Screening.

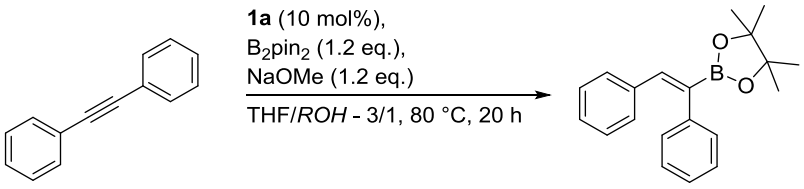


2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**12.0 eq., 0.15 mL (standard conditions)**	**86**	**99/1**
2	0.5 eq., 0.006 mL	29	98/2
3	1.0 eq., 0.012 mL	70	98/2
4	2.0 eq., 0.024 mL	76	99/1
5	3.0 eq., 0.037 mL	77	99/1
6	4.0 eq., 0.049 mL	81	99/1
7	5.0 eq., 0.061 mL	83	99/1
8	6.0 eq., 0.073 mL	88	99/1
9	24.0 eq., 0.30 mL	85	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S6: Alcohol Screening.



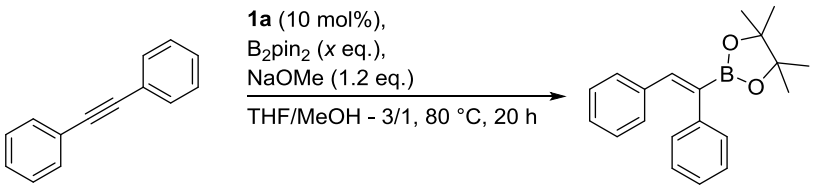
2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**MeOH (standard conditions)**	**87**	**99/1**
2	*i*-PrOH	74	99/1

3	1-butanol	83	99/1
4	*t*-amyl alcohol	64	>99/1
5	trifluoroethanol	72	99/1
6	H_2O	20	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S7: Equivalents of B_2pin_2.

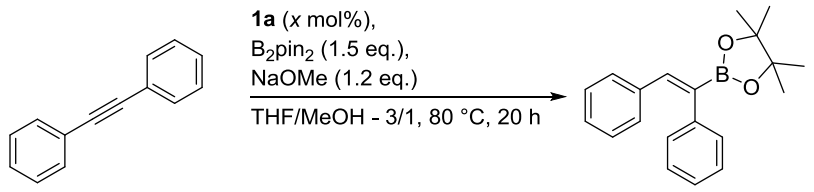


2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	1.2 eq. (standard conditions)	82	99/1
2	0.7 eq.	38	n. d.
3	1.0 eq.	76	99/1
4	**1.5 eq.**	**93**	**99/1**
5	2.0 eq.	quant.	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S8: Catalyst Loading.



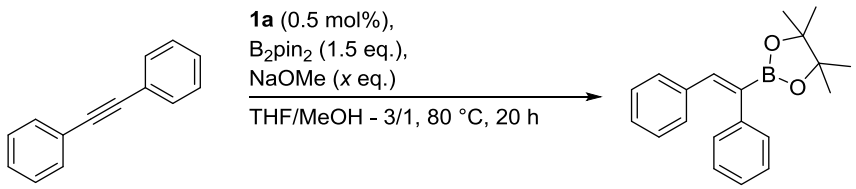
2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	10 mol% (standard conditions)	92	99/1
2	5 mol%	92	99/1

3	2.5 mol%	85	99/1
4	1 mol%	86	99/1
5	**0.5 mol%**	**92 (87)[d]**	**99/1**
6	0.1 mol%	77	99/1
7	0.05 mol%	69	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration. [d] Isolated yield.

Table S9: Equivalents of NaOMe.

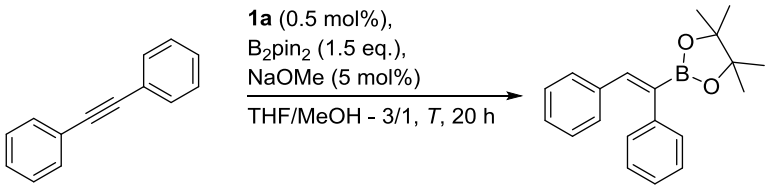


2 (***Z***)/(***E***)**-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	1.2 eq. (standard conditions)	88	99/1
2	0.7 eq.	87	99/1
3	0.5 eq.	87	99/1
4	0.3 eq.	88	99/1
5	0.1 eq.	92 (90)[d]	99/1
6	**0.05 eq.**	**quant. (quant.)[d]**	**98/2**
7	0.01 eq.	94	98/2
8	0.005 eq.	96	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration. [d] Isolated yield.

Table S10: Temperature Screening.

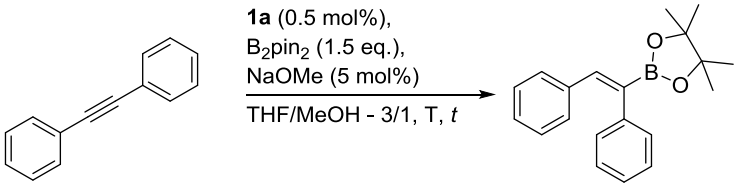


2 (***Z***)/(***E***)-**3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**80 °C (standard conditions)**	**98**	**98/2**
2	60 °C	49	98/2
3	40 °C	6	n. d.
4	room temperature	3	n. d.

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

Table S11: Reaction Time Screening.

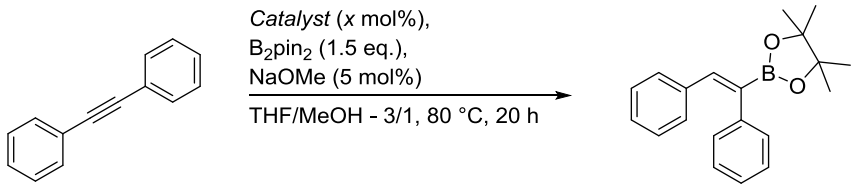


2 (***Z***)/(***E***)-**3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	6 hours	85	98/2
2	**9 hours**	**96 (91)[d]**	**98/2**
3	3 hours, *c* = 1.2 M	41	99/1
4	6 hours, *c* = 1.2 M	74	99/1
5	9 hours, *c* = 1.2 M	92	98/2
6	6 hours, 10 mol% NaOMe	75	99/1
7	9 hours, 10 mol% NaOMe	94	99/1

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration. [d] Isolated yield.

Table S12: Final reaction conditions – reactions without catalyst.



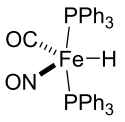
2 **(*Z*)/(*E*)-3**

Entry[a]	Conditions	Yield / %[b]	(*Z*)/(*E*)[c]
1	**1a** (0.5 mol%)	96	98/2
2	no catalyst	0	n. d.
3	PPh_3 (5 mol%)	8	n. d.

[a] Reactions were run on 0.3 mmol scale. [b] Yield was determined by ^{1}H NMR integration with 1,3,5-trimethylbenzene (1.0 eq.) as internal standard. [c] Determined by GC integration.

3. Preparation of Catalyst 1a and Fe-Catalysed Hydroborations

3.1 Preparation of $FeH(CO)(NO)(PPh_3)_2$ 1a



1a

A 500 mL three-necked flask equipped with a reflux condenser and an argon T-piece was charged with sodium nitrite (2.59 g, 37.60 mmol, 1.01 eq.) and sodium methoxide (4.7 g, 87.10 mmol, 2.34 eq.). Methanol (200 mL, degassed in a N_2 stream for 20 minutes) and iron pentacarbonyl (>99.99% Fe, 5.00 mL, 1.00 eq.) were added. The reaction mixture was heated to reflux for three hours. Afterwards, the mixture was cooled to 30 °C and the solvent was evaporated under reduced pressure with an ether bridge connected to a liquid N_2-cooled trap. The obtained red-orange solid was dried under high vacuum for 16 hours. The solid was dissolved again in diethyl ether (550 mL, degassed in a N_2 stream for 20 minutes) and filtered over a sintered-glass frit under nitrogen atmosphere. Triphenylphosphine (39.00 g, 148.80 mmol, 4.00 eq.) was added to this solution. After cooling to 0 °C, trifluoroacetic acid (4.30 mL, 55.80 mmol, 1.50 eq.) was added dropwise followed by stirring for two hours at room temperature. The orange precipitate was filtered over a sintered-glass frit under nitrogen atmosphere, washed with N_2-degassed diethyl ether (50 mL) and dried under high vacuum for three hours. The crude product was dissolved in benzene (250 mL, degassed in

a N_2-stream for 20 minutes) and this solution was concentrated to dryness at 30 °C under reduced pressure using an ether bridge with a liquid N_2-cooled trap. After drying under high vacuum for 16 hours, the title complex was obtained in a yield of 12.42 g (19.43 mmol, 52%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55-7.52 (m, 12 H), 7.39-7.29 (m, 18 H), -4.97 (t, J = 77.8 Hz, 1 H) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 76.9 (d, J = 78.4 Hz) ppm.

The analytical data are in good accordance with those published in the literature.[1c]

3.2 General procedure for the hydroboration of internal alkynes with HBpin as boron source (GP-1)

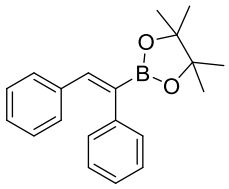
A 10 mL-screw cap Schlenk tube was briefly dried with a heat gun and charged with $FeH(CO)(NO)(PPh_3)_2$ **1a** (16.0 mg, 0.025 mmol, 5 mol%). In case the starting material was solid, the catalyst was dissolved in dry toluene (0.67 mL) and the alkyne (0.5 mmol, 1.0 eq.) was added. If the starting material was liquid, it was transferred to the Schlenk tube with a Pasteur pipette which was rinsed with dry toluene (0.67 mL) afterwards. Pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) was added and the reaction mixture was stirred at 80 °C for 18 hours. After cooling to room temperature, the mixture was filtered over a pad of silica gel (eluent: diethyl ether). The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate mixtures as eluent.

3.3 General procedure for the hydroboration of internal alkynes with B_2pin_2 as boron source (GP-2)

A 10 mL-screw cap Schlenk tube was dried with a heat gun and charged with $FeH(CO)(NO)(PPh_3)_2$ **1a** (0.75 mL of a catalyst stock solution in dry THF, c = 3.35 mmol/L, 1.6 mg, 2.5 µmol, 0.5 mol%). The alkyne (0.5 mmol, 1.0 eq.) was added (liquid alkynes were transferred *via* Pasteur pipette), followed by sodium methoxide (0.25 mL of a stock solution in dry methanol, c = 0.1 mol/L, 0.025 mmol, 5 mol%) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.). The reaction mixture was stirred at 80 °C for 9 hours. After cooling to room temperature, the mixture was filtered over a pad of silica gel (eluent: diethyl ether). The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate mixtures as eluent.

Remarks: The catalyst stock solution was prepared freshly for every reaction by dissolving $FeH(CO)(NO)(PPh_3)_2$ (10.7 mg, 0.0167 mmol) in dry THF (5 mL). The sodium methoxide stock solution was prepared freshly every week by dissolving sodium methoxide (27.0 mg, 0.5 mmol) in dry methanol (5 mL).

3.4 Preparation of (*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3



3

Method A (HBpin as boron source):

According to GP-1, diphenylacetylene (89.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **3** was isolated in a yield of 130.1 mg (0.42 mmol, 85%) as a colourless solid, (*Z*)/(*E*)-95/5.

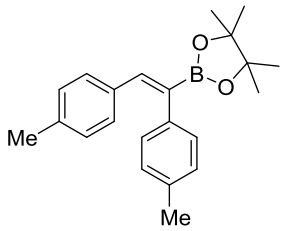
Method B (B_2pin_2 as boron source):

According to GP-2, diphenylacetylene (89.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **3** was isolated in a yield of 141.1 mg (0.46 mmol, 92%) as a colourless solid, (*Z*)/(*E*)-98/2.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37 (s, 1H), 7.29-7.03 (m, 10H), 1.31 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 143.2, 140.4, 136.9, 129.9, 128.8, 128.2, 127.8, 127.6, 126.2, 83.8, 24.8 ppm; **IR** (in $CDCl_3$) ν = 3055 (w), 3022 (w), 2977 (w), 2930 (w), 1605 (w), 1493 (m), 1446 (m), 1370 (m), 1340 (s), 1315 (s), 1269 (m), 1168 (m), 1140 (s), 981 (m), 858 (s), 762 (m), 693 (s), 581 (w), 561 (m), 498 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 329 (100); **HRMS** (ESI): calcd for $C_{20}H_{23}BO_2Na^+$: 329.1687; found: 329.1682; $\boldsymbol{R_f}$ = 0.31 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those reported in the literature.[5]

3.5 Preparation of (*Z*)-2-(1,2-di-*p*-tolylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4



4

Method A (HBpin as boron source):

According to GP-1, 1,2-di-*p*-tolylethyne **S2** (103.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **4** was isolated in a yield of 145.8 mg (0.44 mmol, 87%) as a colourless solid, (*Z*)/(*E*)-97/3.

Method B (B_2pin_2 as boron source):

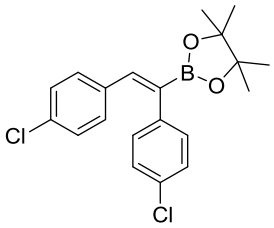
According to GP-2, 1,2-di-*p*-tolylethyne **S2** (103.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **4** was isolated in a yield of 157.7 mg (0.47 mmol, 94%) as a colourless solid, (*Z*)/(*E*)-98/2.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (s, 1 H), 7.07 (s, 4 H), 6.99-6.92 (m, 4 H), 2.34 (s, 3 H), 2.26 (s, 3 H), 1.30 (s, 12 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.9, 137.7, 137.6, 135.8, 134.4, 130.1, 129.2, 128.9, 128.7, 83.8, 24.9, 21.4, 21.3 ppm; **IR** (neat) ν = 2980 (w), 2818 (w), 1904 (w), 1605 (w), 1563 (w), 1508 (m), 1462 (w), 1438 (w), 1390 (m), 1376 (s), 1363 (m), 1337 (s), 1318 (vs), 1305 (s), 1281 (m), 1265 (m), 1209 (m), 1182 (w), 1167 (m), 1141 (s), 1111 (m), 1022 (w), 1006 (w), 982 (m), 958 (w), 911 (w), 861 (m), 845 (m), 810 (s), 777 (w), 717 (m), 691 (m), 675 (m), 638 (w), 579 (w), 539 (m), 512 (w), 492 (s) cm^{-1}; **MS** (ESI): *m*/*z* (%): 357 (100), 301 (81), 279 (47); **HRMS** (ESI): calcd for $C_{22}H_{27}BO_2Na^+$: 357.2000; found: 357.2006; $\boldsymbol{R_f}$ = 0.36 (petroleum ether/ethyl acetate – 40/1).

The X-Ray structure of **4** is deposited at the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under CCDC 184 8842.

The analytical data are in good accordance with those reported in the literature.[6]

3.6 Preparation of (*Z*)-2-(1,2-*bis*(4-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5



5

Method A (HBpin as boron source):

According to GP-1, 1,2-*bis*(4-chlorophenyl)ethyne **S5** (123.6 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **5** was isolated in a yield of 150.2 mg (0.40 mmol, 80%) as a colourless solid, (*Z*)/(*E*)-77/23.

Method B (B_2pin_2 as boron source):

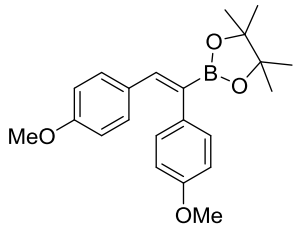
According to GP-2, 1,2-*bis*(4-chlorophenyl)ethyne **S5** (123.6 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 40/1), vinylboronate **5** was isolated in a yield of 82.5 mg (0.22 mmol, 44%) as a colourless solid, (*Z*)/(*E*)-98/2.

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.35 (s, 1 H), 7.29-7.25 (m, 2 H), 7.17-7.07 (m, 4 H), 7.04-6.99 (m, 2 H), 1.31 (s, 12 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 142.7, 139.3, 135.7, 133.9, 132.6, 131.6, 130.7, 128.9, 128.6, 84.5, 25.0 ppm; **IR** (neat) ν = 2985 (w), 1609 (w), 1589 (w), 1487 (s), 1464 (w), 1403 (m), 1390 (m), 1376 (m), 1322 (vs), 1296 (m), 1264 (m), 1210 (w), 1170 (m), 1139 (s), 1091 (s), 1013 (m), 983 (m), 959 (w), 909 (w), 857 (m), 840 (m), 814 (s), 772 (m), 746 (m), 716 (w), 685 (m), 642 (w), 611 (w), 578 (w), 565 (w), 511 (w), 493 (s), 442 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 374 (100), 359 (7), 274 (9), 258 (48), 253 (17), 203 (17), 176 (7), 152 (5), 139 (9); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{21}BCl_2O_2^+$: 374.1015; found: 374.1004; R_f = 0.33 (petroleum ether/ethyl acetate – 40/1).

The X-Ray structure of **5** is deposited at the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under CCDC 184 8840.

The analytical data are in good accordance with those reported in the literature.[6]

3.7 Preparation of (*Z*)-2-(1,2-*bis*(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 6



6

Method A (HBpin as boron source):

According to GP-1, 1,2-*bis*(4-methoxyphenyl)ethyne **S8** (119.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 20/1), vinylboronate **6** was isolated in a yield of 157.5 mg (0.43 mmol, 86%) as a colourless solid, (*Z*)/(*E*)-98/2.

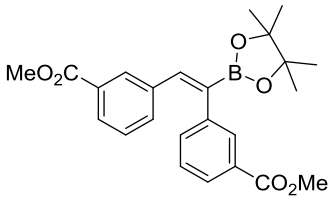
Method B (B_2pin_2 as boron source):

According to GP-2, 1,2-*bis*(4-methoxyphenyl)ethyne **S8** (119.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 20/1), vinylboronate **6** was isolated in a yield of 172.8 mg (0.47 mmol, 94%) as a colourless solid, (*Z*)/(*E*)-97/3.

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.26 (s, 1 H), 7.09-7.02 (m, 4 H), 6.87-6.83 (m, 2 H), 6.70-6.65 (m, 2 H), 3.81 (s, 3 H), 3.74 (s, 3 H), 1.30 (s, 12 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 159.6, 158.6, 142.8, 133.6, 131.8, 130.3, 130.1, 114.1, 113.7, 84.0, 55.5, 55.4, 24.9 ppm; **IR** (neat) ν = 2976 (w), 2933 (w), 2835 (w), 1714 (w), 1601 (m), 1570 (w), 1507 (s), 1462 (m), 1442 (w), 1418 (w), 1370 (m), 1338 (s), 1314 (m), 1304 (m), 1284 (s), 1242 (s), 1167 (s), 1140 (vs), 1110 (m), 1032 (s), 982 (m), 954 (w), 861 (m), 828 (s), 805 (m), 779 (m), 738 (w), 712 (w), 695 (w), 676 (w), 579 (w), 548 (m), 519 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 366 (100), 250 (19), 135 (11); **HRMS** (EI, 70 eV): calcd for $C_{22}H_{27}BO_4^+$: 366.2006; found: 366.2000; R_f = 0.22 (petroleum ether/ethyl acetate – 20/1).

The analytical data are in good accordance with those reported in the literature.[6]

3.8 Preparation of dimethyl 3,3'-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)ethene-1,2-diyl)(*Z*)-dibenzoate 7



7

Method A (HBpin as boron source):

According to GP-1, dimethyl 3,3'-(ethyne-1,2-diyl)dibenzoate **S12** (147.2 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 10/1 to 7/1), vinylboronate **7** was isolated in a yield of 51.9 mg (0.12 mmol, 25%) as a colourless solid, (*Z*)/(*E*)-77/23. The isomers were separated by HPLC (petroleum ether/ethyl acetate – 7/1).

Method B (B_2pin_2 as boron source):

According to GP-2, dimethyl 3,3'-(ethyne-1,2-diyl)dibenzoate **S12** (147.2 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 7/1) and subsequent HPLC (petroleum ether/ethyl acetate – 5/1), vinylboronate **7** was isolated in a yield of 183.9 mg (0.44 mmol, 87%) as a yellow oil, (*Z*)/(*E*)-97/3.

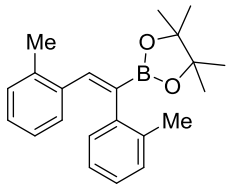
Analytical data for (*Z*)-7:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.89 (m, 1 H), 7.84-7.83 (m, 1 H), 7.81-7.78 (m, 2 H), 7.44 (s, 1 H), 7.36-7.29 (m, 2 H), 7.16-7.09 (m, 2 H), 3.87 (s, 3 H), 3.82 (s, 3 H), 1.31 (s, 12 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.3, 166.9, 142.9, 140.5, 136.9, 133.9, 133.5, 131.4, 130.5, 130.2, 130.1, 128.9, 128.6, 128.1, 127.9, 84.2, 52.1, 24.9 ppm; **IR** (in $CDCl_3$) *v* = 2980 (w), 2952 (w), 2254 (w), 1719 (s), 1610 (w), 1579 (w), 1438 (m), 1372 (m), 1334 (m), 1284 (s), 1266 (s), 1203 (m), 1167 (m), 1140 (s), 1107 (m), 1083 (m), 1012 (w), 972 (w), 908 (s), 853 (m), 755 (m), 726 (vs), 684 (m), 648 (m), 574 (w), 513 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 445 (100), 391 (64); **HRMS** (ESI): calcd for $C_{24}H_{27}BO_6Na^+$: 445.1797; found: 445.1793; R_f = 0.28 (petroleum ether/ethyl acetate – 7/1), yellow oil.

Analytical data for (*E*)-7:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18-8.15 (m, 2 H), 7.98-7.93 (m, 2 H), 7.68-7.63 (m, 2 H), 7.44-7.40 (m, 2 H), 7.34 (s, 1 H), 3.92 (s, 6 H), 1.32 (s, 12 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.2, 167.0, 142.7, 140.8, 138.9, 133.3, 131.4, 130.6, 130.3, 129.2, 129.1, 128.7, 128.6, 128.4, 128.3, 84.5, 52.3, 52.2, 25.0 ppm; **IR** (in $CDCl_3$) v = 2979 (w), 2951 (w), 2257 (w), 1719 (vs), 1601 (w), 1580 (w), 1482 (w), 1438 (m), 1380 (m), 1280 (s), 1215 (s), 1167 (m), 1139 (s), 1107 (s), 1083 (m), 999 (w), 969 (m), 913 (m), 856 (m), 819 (w), 755 (s), 730 (s), 692 (m), 669 (m), 647 (w), 578 (w), 548 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 445 (100), 391 (20); **HRMS** (ESI): calcd for $C_{24}H_{27}BO_6Na^+$: 445.1797; found: 445.1791; $\boldsymbol{R_f}$ = 0.26 (petroleum ether/ethyl acetate – 7/1), colourless solid.

3.9 Preparation of (*Z*)-2-(1,2-di-*o*-tolylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8



8

Method A (HBpin as boron source):

According to GP-1, 1,2-di-*o*-tolylethyne **S15** (103.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **8** was isolated in a yield of 89.9 mg (0.27 mmol, 54%) as a colourless solid, (*Z*)/(*E*)-99/1.

Method B (B_2pin_2 as boron source):

According to GP-2, 1,2-di-*o*-tolylethyne **S15** (103.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **8** was isolated in a yield of 114.4 mg (0.34 mmol, 68%) as a colourless solid, (*Z*)/(*E*)-99/1.

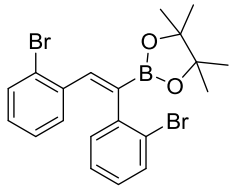
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.60 (s, 1 H), 7.13-7.01 (m, 5 H), 6.92-6.89 (m, 1 H), 6.82-6.77 (m, 1 H), 6.67-6.64 (m, 1 H), 2.41 (s, 3 H), 2.18 (s, 3 H), 1.34 (s, 12 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 142.5, 140.3, 136.7, 136.6, 135.5, 129.9, 129.2, 129.1, 127.5, 126.4, 125.7, 125.2, 83.7, 24.9, 20.1, 20.0 ppm; **IR** (neat) v = 3065 (w), 3016 (w), 2981 (m), 2925 (w), 1604 (w), 1568 (w), 1478 (m), 1458 (m), 1373 (s), 1329 (vs), 1286 (m), 1267 (m), 1214 (m), 1145 (vs), 1107 (m), 1047 (w), 1007 (w), 983 (m), 956 (w), 907 (w), 859 (m), 845 (m),

797 (w), 766 (m), 745 (s), 729 (s), 720 (m), 692 (m), 680 (m), 592 (w), 579 (m), 540 (w), 515 (w), 487 (w), 447 (m) cm^{-1}; **MS** (ESI): *m*/*z* (%): 357 (100); **HRMS** (ESI): calcd for $C_{22}H_{27}BO_2Na^+$: 357.2000; found: 357.1988; $\boldsymbol{R_f}$ = 0.31 (petroleum ether/ethyl acetate – 40/1).

The X-Ray structure of **8** is deposited at the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under CCDC 184 8841.

The analytical data are in good accordance with those reported in the literature.[6]

3.10 Preparation of (*Z*)-2-(1,2-*bis*(2-bromophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9



9

Method A (HBpin as boron source):

According to GP-1, 1,2-*bis*(2-bromophenyl)ethyne **S18** (168.0 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **9** was isolated in a yield of 91.4 mg (0.19 mmol, 39%) as a yellow solid, (*Z*)/(*E*)-99/1.

Method B (B_2pin_2 as boron source):

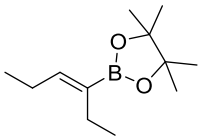
According to GP-2, 1,2-*bis*(2-bromophenyl)ethyne **S18** (168.0 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **9** was isolated in a yield of 164.4 mg (0.35 mmol, 71%) as a yellow solid, (*Z*)/(*E*)-98/2.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56-7.49 (m, 3 H), 7.09-7.02 (m, 2 H), 7.00-6.95 (m, 1 H), 6.93-6.85 (m, 2 H), 6.73-6.71 (m, 1 H), 1.34 (s, 12 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 143.0, 141.3, 137.4, 132.4, 132.3, 130.9, 130.7, 128.9, 128.2, 127.5, 126.8, 124.3, 124.0, 84.2, 24.9 ppm; **IR** (neat) *v* = 3067 (w), 2977 (m), 2930 (w), 1611 (w), 1559 (w), 1460 (m), 1433 (m), 1393 (m), 1369 (vs), 1265 (m), 1214 (w), 1181 (m), 1143 (s), 1110 (m), 1046 (m), 1023 (s), 981 (m), 955 (m), 854 (s), 838 (m), 769 (m), 755 (m), 737 (s), 694 (s), 653 (m), 581 (m), 559 (w), 511 (w), 447 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 464 (100), 448 (12), 377 (6),

363 (10), 347 (28), 327 (6), 299 (11), 285 (20), 267 (14), 246 (28), 204 (38), 176 (14); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{21}BBr_2O_2^+$: 463.9986; found: 463.9980; $\boldsymbol{R_f}$ = 0.33 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those reported in the literature.[6]

3.11 Preparation of (*Z*)-2-(hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 10



10

Method A (HBpin as boron source):

According to GP-1, 3-hexyne (57 µL, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **10** was isolated in a yield of 57.7 mg (0.27 mmol, 54%) as a yellow oil, (*Z*)/(*E*)-98/2.

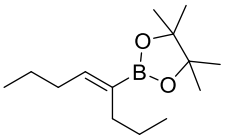
Method B (B_2pin_2 as boron source):

According to GP-2, 3-hexyne (57 µL, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **10** was isolated in a yield of 66.9 mg (0.32 mmol, 64%) as a yellow oil, (*Z*)/(*E*)-99/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.26 (t, *J* = 7.0 Hz, 1 H), 2.18-2.10 (m, 4 H), 1.26 (s, 12 H), 1.00 (t, *J* = 7.6 Hz, 3 H), 0.94 (t, *J* = 7.5 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 147.1, 83.1, 24.9, 21.8, 21.6, 15.0, 13.9 ppm; **IR** (neat) *v* = 2964 (m), 2932 (w), 2872 (w), 1629 (m), 1459 (w), 1409 (m), 1381 (m), 1366 (s), 1346 (s), 1299 (s), 1254 (m), 1214 (w), 1141 (s), 1096 (w), 968 (m), 900 (w), 856 (m), 795 (w), 691 (m) cm^{-1}; **MS** (ESI): *m*/*z* (%): 233 (100); **HRMS** (ESI): calcd for $C_{12}H_{23}BO_2Na^+$: 233.1685; found: 233.1682; $\boldsymbol{R_f}$ = 0.33 (petroleum ether/ethyl acetate – 50/1).

The analytical data are in good accordance with those reported in the literature.[7]

3.12 Preparation of (*Z*)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane 11



11

Method A (HBpin as boron source):

According to GP-1, 4-octyne (73 µL, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **11** was isolated in a yield of 82.1 mg (0.34 mmol, 69%) as a yellow oil, (*Z*)/(*E*)-99/1.

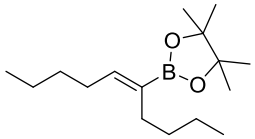
Method B (B_2pin_2 as boron source):

According to GP-2, 4-octyne (73 µL, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **11** was isolated in a yield of 102.6 mg (0.43 mmol, 86%) as a colourless oil, (*Z*)/(*E*)-99/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.29 (t, *J* = 7.1 Hz, 1 H), 2.13-2.08 (m, 4 H), 1.46-1.31 (m, 4 H), 1.25 (s, 12 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 146.1, 83.1, 30.8, 30.7, 24.9, 23.4, 22.6, 14.23, 14.19 ppm; **IR** (in $CDCl_3$) *v* = 2959 (m), 2930 (m), 2871 (w), 1628 (w), 1464 (w), 1409 (m), 1378 (s), 1349 (m), 1301 (m), 1229 (w), 1142 (s), 1115 (w), 1103 (w), 974 (w), 862 (w), 691 (m), 542 (m) cm^{-1}; **MS** (ESI): *m*/*z* (%): 261 (100); **HRMS** (ESI): calcd for $C_{14}H_{27}BO_2Na^+$: 261.1999; found: 261.1996; $\boldsymbol{R_f}$ = 0.32 (petroleum ether/ethyl acetate – 50/1).

The analytical data are in good accordance with those reported in the literature.[8]

3.13 Preparation of (*Z*)-2-(dec-5-en-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 12



12

Method A (HBpin as boron source):

According to GP-1, 5-decyne (90 µL, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **12** was isolated in a yield of 90.4 mg (0.34 mmol, 68%) as an orange oil, (*Z*)/(*E*)-99/1.

Method B (B_2pin_2 as boron source):

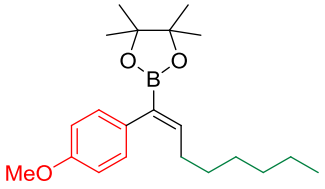
According to GP-2, 5-decyne (90 µL, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and

B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **12** was isolated in a yield of 115.2 mg (0.43 mmol, 87%) as a yellow oil, (*Z*)/(*E*)-99/1.

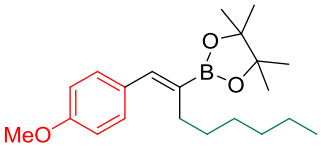
^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.27 (t, *J* = 7.1 Hz, 1 H), 2.16-2.09 (m, 4 H), 1.43-1.28 (m, 8 H), 1.25 (s, 12 H), 0.93-0.87 (m, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 146.1, 83.1, 32.6, 31.6, 28.4, 28.3, 24.9, 22.8, 22.7, 14.3, 14.1 ppm; **IR** (in $CDCl_3$) *v* = 2956 (m), 2927 (m), 2859 (w), 1627 (w), 1466 (w), 1409 (m), 1377 (s), 1348 (m), 1299 (s), 1273 (m), 1212 (m), 1141 (s), 1116 (m), 1014 (w), 969 (w), 860 (m), 692 (m), 542 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 289 (100); **HRMS** (ESI): calcd for $C_{16}H_{31}BO_2Na^+$: 289.2312; found: 289.2312; R_f = 0.35 (petroleum ether/ethyl acetate – 50/1).

The analytical data are in good accordance with those reported in the literature.[9]

3.14 Preparation of (*Z*)-2-(1-(4-methoxyphenyl)oct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 13A and (*Z*)-2-(1-(4-methoxyphenyl)oct-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 13B



13A



13B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S19** (108.2 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **13** was isolated in a yield of 142.5 mg (0.41 mmol, 83%) as a yellow oil as a regioisomeric mixture of **13A**/**13B**-74/26.

Method B (B_2pin_2 as boron source):

According to GP-2, arylalkylalkyne **S19** (108.2 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1 to 40/1), vinylboronate **13** was isolated in a yield of 140.7 mg (0.41 mmol, 82%) as a regioisomeric mixture of **13A**/**13B**-18/82. The regioisomers were separated by HPLC (petroleum ether/ethyl acetate – 50/1).

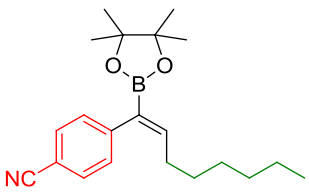
Analytical data for 13A:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.05-7.02 (m, 2 H), 6.88-6.83 (m, 2 H), 6.52 (t, *J* = 7.3 Hz, 1 H), 3.79 (s, 3 H), 2.13 (q, *J* = 7.4 Hz, 2 H), 1.41-1.35 (m, 2 H), 1.31-1.19 (m, 6 H), 1.26 (s, 12 H), 0.86 (t, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 158.3, 148.6, 133.2, 130.5, 113.5, 83.8, 55.6, 32.1, 30.3, 29.8, 29.5, 25.0, 23.0, 14.3 ppm; **IR** (in CD_2Cl_2) *v* = 2956 (w), 2927 (m), 2855 (w), 1673 (w), 1601 (m), 1575 (w), 1510 (s), 1456 (m), 1372 (m), 1338 (s), 1306 (m), 1285 (m), 1244 (s), 1169 (s), 1144 (vs), 1032 (m), 1009 (w), 981 (m), 952 (w), 926 (w), 852 (m), 833 (m), 752 (w), 726 (w), 672 (m), 633 (w), 609 (w), 579 (w), 517 (w), 450 (w) cm^{-1}; **MS** (EI, 70 eV): *m/z* (%): 344 (100), 329 (10), 315 (1), 301 (1), 287 (43), 273 (14), 260 (44), 247 (29), 229 (37), 217 (25), 202 (9), 187 (14), 173 (38), 160 (28), 147 (28), 135 (28), 115 (36), 101 (63), 83 (36); **HRMS** (EI, 70 eV): calcd for $C_{21}H_{33}BO_3^+$: 344.2527; found: 344.2527; R_f = 0.24 (petroleum ether/ethyl acetate – 50/1), yellow oil.

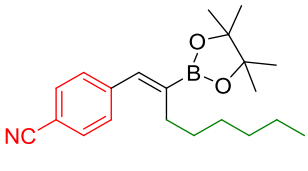
Analytical data for 13B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.30-7.27 (m, 2 H), 7.09 (s, 1 H), 6.89-6.86 (m, 2 H), 3.80 (s, 3 H), 2.37-2.33 (m, 2 H), 1.51-1.44 (m, 2 H), 1.37-1.29 (m, 6 H), 1.28 (s, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 159.2, 141.4, 131.0, 130.9, 113.9, 83.7, 55.6, 32.2, 30.3, 29.9, 29.8, 25.0, 23.1, 14.3 ppm; **IR** (in CD_2Cl_2) *v* = 2976 (w), 2955 (m), 2927 (m), 2857 (w), 1605 (m), 1573 (w), 1509 (s), 1465 (m), 1417 (w), 1404 (w), 1372 (m), 1348 (s), 1305 (s), 1287 (m), 1271 (m), 1248 (s), 1213 (w), 1175 (m), 1146 (s), 1129 (s), 1037 (m), 964 (w), 867 (m), 834 (m), 769 (w), 722 (w), 690 (w), 660 (w), 579 (w), 538 (w) cm^{-1}; **MS** (EI, 70 eV): *m/z* (%): 344 (100), 329 (6), 301 (1), 287 (3), 273 (33), 260 (29), 244 (8), 229 (32), 216 (17), 187 (17), 173 (52), 159 (18), 145 (27), 134 (17), 121 (52), 101 (49), 83 (39); **HRMS** (EI, 70 eV): calcd for $C_{21}H_{33}BO_3^+$: 344.2527; found: 344.2523; R_f = 0.29 (petroleum ether/ethyl acetate – 50/1), yellow oil.

3.15 Preparation of (*Z*)-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)benzonitrile 14A and (*Z*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)benzonitrile 14B



14A



14B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S20** (105.7 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **14** was isolated in a yield of 41.7 mg (0.12 mmol, 25%) as a regioisomeric mixture of **14A**/**14B**-87/13. The regiosomers were separated by HPLC (petroleum ether/ethyl acetate – 40/1).

Method B (B_2pin_2 as boron source):

According to GP-2, arylalkylalkyne **S20** (105.7 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 20/1) and subsequent HPLC (petroleum ether/ethyl acetate – 20/1), vinylboronate **14** was isolated in a yield of 109.1 mg (0.32 mmol, 64%) as a colourless solid as a regioisomeric mixture of **14A**/**14B**-4/96.

Analytical data for 14A:

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.62-7.59 (m, 2 H), 7.25-7.22 (m, 2 H), 6.65 (t, *J* = 7.4 Hz, 1 H), 2.08 (q, *J* = 7.4 Hz, 2 H), 1.44-1.34 (m, 2 H), 1.33-1.19 (m, 6 H), 1.25 (s, 12 H), 0.85 (t, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 150.7, 146.2, 132.0, 130.2, 119.6, 109.9, 84.1, 32.0, 30.3, 29.5, 29.4, 24.9, 22.9, 14.2 ppm; **IR** (in CD_2Cl_2) *v* = 2977 (m), 2957 (m), 2927 (m), 2857 (m), 2227 (m), 1606 (m), 1504 (w), 1467 (w), 1379 (s), 1342 (vs), 1317 (s), 1271 (w), 1213 (w), 1166 (w), 1145 (s), 1111 (w), 1009 (w), 975 (w), 856 (m), 752 (w), 723 (w), 691 (w), 668 (w), 569 (w), 549 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 339 (41), 324 (7), 296 (1), 282 (47), 268 (1), 255 (45), 239 (13), 224 (3), 211 (14), 182 (8), 169 (24), 154 (10), 130 (10), 116 (3), 101 (100), 83 (16); **HRMS** (EI, 70 eV): calcd for $C_{21}H_{30}BNO_2^+$: 339.2373; found: 339.2371; $\boldsymbol{R_f}$ = 0.36 (petroleum ether/ethyl acetate – 20/1), yellow oil.

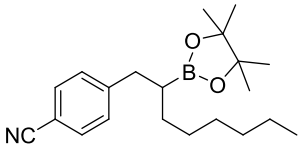
Analytical data for 14B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.64-7-62 (m, 2 H), 7.41-7.39 (m, 2 H), 7.15 (s, 1 H), 2.33-2.29 (m, 2 H), 1.49-1.42 (m, 2 H), 1.32-1.21 (m, 6 H), 1.29 (s, 12 H), 0.87 (t, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 143.1, 139.7, 132.4, 129.9, 119.3, 110.8, 84.1, 32.1, 30.1, 29.9, 29.8, 25.0, 23.0, 14.2 ppm; **IR** (in CD_2Cl_2) *v* = 2977 (m), 2956 (m), 2928 (m), 2857 (w), 2227 (m), 1603 (w), 1502 (w), 1467 (w), 1408 (m), 1373 (s), 1316 (s), 1271 (m), 1213 (w), 1166 (m), 1146 (s), 1132 (s), 1054 (w), 964 (w), 896 (w), 865 (m), 840 (w), 689 (w), 578 (w), 548 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 339 (42), 324 (14), 310 (1), 296 (1), 282 (23), 268 (5), 255 (60), 240 (25), 224 (7), 211 (41), 196 (11), 182 (20), 169 (100), 154 (42), 142 (36),

129 (22), 116 (17), 101 (80), 84 (61); **HRMS** (EI, 70 eV): calcd for $C_{21}H_{30}BNO_2^+$: 339.2373; found: 339.2369; $\boldsymbol{R_f}$ = 0.42 (petroleum ether/ethyl acetate – 20/1), colourless solid.

4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)benzonitrile S1

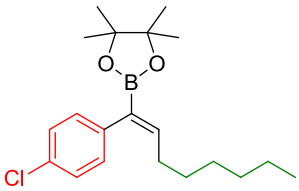
This compound was isolated as a side product (15.5 mg, 0.05 mmol, 9%) when Method B was employed for the hydroboration of arylalkylalkyne **S20**.



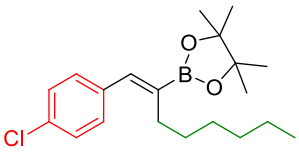
S1

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.55-7.53 (m, 2 H), 7.33-7.31 (m, 2 H), 2.77-2.67 (m, 2 H), 1.48-1.24 (m, 11H), 1.13 (d, J = 7.0 Hz, 12 H), 0.87 (t, J = 6.8 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 149.0, 132.3, 130.1, 119.6, 109.8, 83.5, 37.9, 32.2, 31.6, 29.9, 29.3, 25.0, 23.0, 14.3 ppm; **IR** (in CD_2Cl_2) ν = 2977 (w), 2957 (w), 2925 (m), 2855 (m), 2228 (w), 1607 (w), 1505 (w), 1459 (w), 1411 (w), 1381 (s), 1322 (s), 1252 (w), 1235 (w), 1214 (w), 1166 (w), 1143 (s), 1021 (w), 968 (w), 846 (m), 816 (w), 685 (w), 671 (w), 560 (w) cm^{-1}; **MS** (EI, 70 eV): *m/z* (%): 341 (3), 326 (16), 284 (45), 258 (9), 241 (11), 225 (2), 213 (7), 170 (28), 156 (10), 144 (12), 130 (20), 116 (37), 101 (33), 84 (100); **HRMS** (EI, 70 eV): calcd for $C_{21}H_{32}BNO_2^+$: 341.2530; found: 341.2527; $\boldsymbol{R_f}$ = 0.34 (petroleum ether/ethyl acetate – 20/1), colourless solid.

3.16 Preparation of (*Z*)-2-(1-(4-chlorophenyl)oct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 15A and (*Z*)-2-(1-(4-chlorophenyl)oct-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 15B



15A



15B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S21** (110.4 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate

– 50/1), vinylboronate **15** was isolated in a yield of 130.5 mg (0.37 mmol, 75%) as a yellow oil as a regioisomeric mixture of **15A**/**15B**-84/16.

Method B (B_2pin_2 as boron source):

According to GP-2, alkylarylalkyne **S21** (110.4 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 40/1), the vinylboronate **15** was isolated in a yield of 148.7 mg (0.43 mmol, 85%) as a regioisomeric mixture of **15A**/**15B**-19/81. The regioisomers were separated by HPLC (petroleum ether/ethyl acetate – 200/1).

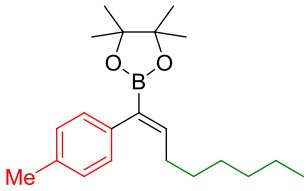
Analytical data for 15A:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.30-7.26 (m, 2 H), 7.07-7.05 (m, 2 H), 6.58 (t, *J* = 7.3 Hz, 1 H), 2.09 (q, *J* = 7.4 Hz, 2 H), 1.41-1.34 (m, 2 H), 1.30-1.19 (m, 6 H), 1.25 (s, 12 H), 0.85 (t, *J* = 7.0 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 149.7, 139.6, 131.8, 130.8, 128.2, 84.0, 32.0, 30.3, 29.6, 29.5, 24.9, 23.0, 14.2 ppm; **IR** (in CD_2Cl_2) *v* = 2977 (m), 2957 (m), 2926 (m), 2856 (m), 1615 (w), 1890 (m), 1467 (w), 1408 (m), 1378 (s), 1372 (s), 1339 (vs), 1309 (s), 1271 (m), 1214 (w), 1196 (w), 1145 (s), 1110 (w), 1090 (m), 1015 (m), 975 (m), 856 (m), 829 (m), 778 (w), 732 (w), 707 (w), 683 (w), 579 (w), 555 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 348 (52), 333 (6), 313 (3), 291 (66), 277 (1), 264 (29), 249 (4), 221 (7), 191 (5), 164 (10), 139 (14), 115 (7), 101 (100), 83 (17); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{30}BClO_2^+$: 348.2031; found: 348.2022; $\boldsymbol{R}_f$ = 0.41 (petroleum ether/ethyl acetate –40/1), colourless oil.

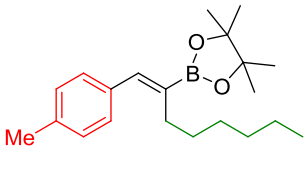
Analytical data for 15B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.33-7.31 (m, 2 H), 7.27-7.25 (m, 2 H), 7.11 (s, 1 H), 2.33-2.29 (m, 2 H), 1.49-1.42 (m, 2 H), 1.33-1.21 (m, 6 H), 1.28 (s, 12 H), 0.88 (t, *J* = 7.0 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 140.4, 137.0, 133.0, 130.7, 128.7, 83.9, 32.1, 30.2, 29.83, 29.81, 25.0, 23.0, 14.3 ppm; **IR** (in CD_2Cl_2) *v* = 2977 (m), 2956 (m), 2927 (m), 2857 (w), 1615 (w), 1489 (m), 1467 (m), 1407 (m), 1372 (s), 1342 (s), 1311 (s), 1268 (m), 1214 (m), 1146 (vs), 1130 (s), 1093 (s), 1054 (w), 1013 (m), 963 (m), 896 (w), 865 (m), 835 (m), 728 (w), 688 (m), 617 (w), 579 (w), 499 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 348 (100), 333 (7), 313 (24), 291 (8), 277 (3), 264 (32), 233 (9), 220 (21), 185 (16), 178 (22), 164 (10), 151 (16), 138 (41), 115 (14), 101 (80), 85 (39); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{30}BClO_2^+$: 348.2031; found: 348.2024; $\boldsymbol{R}_f$ = 0.46 (petroleum ether/ethyl acetate –40/1), colourless oil.

3.17 Preparation of (*Z*)-4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)oct-1-en-1-yl)-1,3,2-dioxaborolane 16A and (*Z*)-4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)oct-1-en-2-yl)-1,3,2-dioxaborolane 16B



16A



16B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **23** (100.2 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **16** was isolated in a yield of 134.7 mg (0.41 mmol, 82%) as a yellow oil as an inseparable regioisomeric mixture of **16A**/**16B**-75/25.

Method B (B_2pin_2 as boron source):

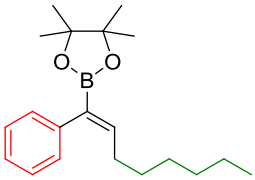
According to GP-2, alkylarylalkyne **23** (100.2 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), the vinylboronate **16** was isolated in a yield of 131.8 mg (0.40 mmol, 80%) as a yellow oil as an inseparable regioisomeric mixture of **16A**/**16B**-24/76.

Analytical data for the mixture of 16A/16B according to Method A:

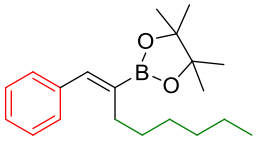
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24-7.21 (m, 0.7 H, minor), 7.17 (s, 0.3 H, minor), 7.14-7.10 (m, 2.6 H, major and minor), 7.04-7.02 (m, 2 H, major), 6.55 (t, *J* = 7.2 Hz, 1 H, major), 2.33 (s, 4 H, major and minor), 2.17-2.11 (m, 2 H, major), 1.51-1.27 (m, 6.1 H, major and minor), 1.30 (s, 4 H, minor), 1.26 (s, 12 H, major), 1.25-1.14 (m, 6.5 H, major and minor), 0.88-0.83 (m, 4 H, major and minor) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 148.3, 141.7, 137.4, 136.8, 135.3, 129.1, 129.0, 128.9, 128.8, 128.6, 83.5, 83.4, 31.9, 31.8, 30.1, 30.0, 29.6, 29.5, 29.4, 29.2, 24.9, 24.8, 22.7, 22.6, 21.3, 21.2, 14.2, 14.1 ppm; **IR** (in $CDCl_3$) *v* = 2977 (w), 2956 (w), 2923 (m), 2855 (w), 1612 (w), 1512 (w), 1466 (w), 1407 (m), 1377 (s), 1339 (s), 1303 (s), 1270 (m), 1214 (w), 1145 (vs), 1111 (m), 1008 (w), 974 (m), 856 (m), 819 (m), 748 (w), 723 (w), 693 (m), 579 (w), 542 (w), 495 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 351 (100); **HRMS** (ESI):

calcd for $C_{21}H_{33}BO_2Na^+$: 351.2470; found: 351.2461; R_f = 0.33 (petroleum ether/ethyl acetate –50/1).

3.18 Preparation of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenyloct-1-en-1-yl)-1,3,2-dioxaborolane 17A and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenyloct-1-en-2-yl)-1,3,2-dioxaborolane 17B



17A



17B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S22** (93.2 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **17** was isolated in a yield of 133.1 mg (0.42 mmol, 85%) as a regioisomeric mixture of **17A**/**17B**-82/18. The regioisomers were separated by HPLC (petroleum ether/ethyl acetate – 100/1, flow rate: 15 mL/min).

Method B (B_2pin_2 as boron source):

According to GP-2, alkylarylalkyne **S22** (93.2 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 40/1), vinylboronate **17** was isolated in a yield of 78.0 mg (0.25 mmol, 50%) as a yellow oil as a regioisomeric mixture of **17A**/**17B**-24/76.

Analytical data for 17A:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.32-7.28 (m, 2 H), 7.22-7.18 (m, 1 H), 7.11-7.09 (m, 2 H), 6.56 (t, *J* = 7.3 Hz, 1H), 2.11 (q, *J* = 7.4 Hz, 2 H), 1.42-1.35 (m, 2 H), 1.31-1.18 (m, 6 H), 1.26 (s, 12 H), 0.86 (t, *J* = 7.0 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 149.0, 141.1, 129.4, 128.1, 126.2, 83.8, 32.1, 30.3, 29.7, 29.5, 24.9, 23.0, 14.2 ppm; **IR** (in CD_2Cl_2) *v* = 3079 (w), 3054 (w), 2977 (w), 2967 (w), 2925 (m), 2855 (w), 1937 (w), 1688 (w), 1614 (w), 1494 (w), 1467 (w), 1405 (m), 1378 (s), 1341 (s), 1306 (s), 1271 (m), 1214 (w), 1196 (w), 1145 (vs), 1111 (w), 1073 (w), 1008 (w), 974 (m), 909 (w), 855 (m), 777 (w), 761 (w), 700 (s), 677 (w), 621 (w), 580 (w), 553 (w), 492 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 337 (100), 315 (23); **HRMS**

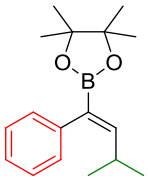
(ESI): calcd for $C_{20}H_{32}BO_2^+$: 315.2493; found: 315.2468; $\boldsymbol{R_f}$ = 0.34 (petroleum ether/ethyl acetate – 50/1), yellow oil.

Analytical data for 17B:

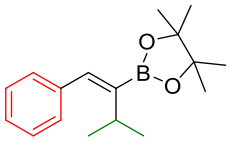
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.36-7.30 (m, 4 H), 7.28-7.21 (m, 1 H), 7.16 (s, 1 H), 2.36-2.32 (m, 2 H), 1.51-1.44 (m, 2 H), 1.40-1.26 (m, 6 H), 1.29 (s, 12 H), 0.88 (t, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 141.8, 138.5, 129.4, 128.5, 127.4, 83.8, 32.2, 30.3, 29.88, 29.87, 25.0, 23.1, 14.3 ppm; **IR** (in CD_2Cl_2) ν = 3056 (w), 3023 (w), 2977 (w), 2956 (w), 2926 (m), 2856 (w), 1615 (w), 1599 (w), 1574 (w), 1493 (w), 1466 (w), 1446 (w), 1405 (m), 1371 (s), 1348 (s), 1308 (s), 1271 (m), 1213 (m), 1145 (vs), 1131 (s), 1074 (w), 1054 (w), 1004 (w), 964 (w), 924 (w), 865 (m), 838 (w), 751 (m), 725 (w), 698 (m), 580 (w), 554 (w), 522 (w), 488 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 337 (100), 315 (22); **HRMS** (ESI): calcd for $C_{20}H_{32}BO_2^+$: 315.2493; found: 315.2478; $\boldsymbol{R_f}$ = 0.39 (petroleum ether/ethyl acetate – 50/1), yellow oil.

The analytical data are in good accordance with those published in the literature.[10]

3.19 Preparation of (*Z*)-4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane 18A and (*Z*)-4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane 18B



18A



18B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S23** (72.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **18** was isolated in a yield of 75.2 mg (0.28 mmol, 55%) as an orange solid as a regioisomeric mixture of **18A**/**18B**-90/10.

Method B (B_2pin_2 as boron source):

According to GP-2, the arylalkylalkyne **S23** (72.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 50/1),

vinylboronate **18** was isolated in a yield of 61.1 mg (0.22 mmol, 45%) as a regioisomeric mixture of **18A**/**18B**-31/69. Here, the corresponding (*E*)-isomers were also formed, the total ratio was **18A**/**18B**/(***E***)**-18A**/(***E***)**-18B**-30/68/1/1. The regioisomers **18A** and **18B** were separated by HPLC (petroleum ether/ethyl acetate – 50/1).

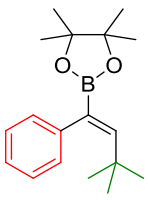
Analytical data for 18A:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.32-7.28 (m, 2 H), 7.22-7.18 (m, 1 H), 7.10-7.08 (m, 2 H), 6.33 (d, *J* = 10.1 Hz, 1 H), 2.60-2.48 (m, 1 H), 1.26 (s, 12 H), 0.95 (d, *J* = 6.6 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 155.3, 141.3, 129.2, 128.2, 126.1, 83.9, 28.8, 24.9, 22.8 ppm; **IR** (in CD_2Cl_2) *v* = 3079 (w), 3054 (w), 2976 (m), 2962 (m), 2929 (w), 2867 (w), 1616 (w), 1494 (w), 1464 (w), 1443 (w), 1406 (m), 1372 (s), 1344 (vs), 1308 (s), 1271 (m), 1214 (w), 1197 (m), 1145 (s), 1111 (w), 1072 (w), 1006 (w), 978 (m), 940 (w), 909 (w), 860 (m), 844 (w), 775 (w), 761 (w), 702 (s), 682 (w), 580 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 272 (32), 257 (14), 229 (3), 215 (21), 172 (35), 157 (38), 144 (61), 129 (66), 115 (14), 101 (100), 91 (13), 83 (29), 77 (13); **HRMS** (EI, 70 eV): calcd for $C_{17}H_{25}BO_2^+$: 272.1951; found: 272.1950; $\boldsymbol{R_f}$ = 0.43 (petroleum ether/ethyl acetate – 40/1), colourless oil.

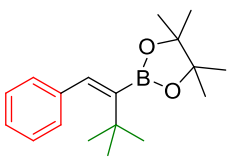
Analytical data for 18B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.35-7.31 (m, 2 H), 7.27-7.21 (m, 3 H), 7.11 (s, 1 H), 3.00 (sept, *J* = 6.8 Hz, 1 H), 1.29 (s, 12 H), 1.12 (d, *J* = 6.8 Hz, 6 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 140.3, 138.7, 129.2, 128.4, 127.2, 83.5, 29.1, 25.0, 22.5 ppm; **IR** (in CD_2Cl_2) *v* = 3099 (w), 3080 (w), 3056 (w), 3022 (w), 2977 (m), 2931 (w), 2871 (w), 1612 (w), 1597 (w), 1574 (w), 1493 (w), 1467 (w), 1445 (w), 1401 (m), 1380 (m), 1366 (s), 1299 (s), 1269 (m), 1214 (w), 1165 (m), 1140 (vs), 1110 (w), 1074 (w), 1030 (w), 1006 (w), 987 (w), 958 (w), 922 (w), 892 (w), 862 (w), 831 (w), 755 (m), 698 (m), 673 (w), 581 (w), 488 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 272 (70), 257 (27), 229 (3), 215 (28), 172 (81), 157 (67), 144 (57), 129 (100), 115 (17), 101 (73), 91 (22), 84 (45), 77 (12); **HRMS** (EI, 70 eV): calcd for $C_{17}H_{25}BO_2^+$: 272.1951; found: 272.1951; $\boldsymbol{R_f}$ = 0.45 (petroleum ether/ethyl acetate – 40/1), colourless solid.

3.20 Preparation of (*Z*)-2-(3,3-dimethyl-1-phenylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 19A and (*Z*)-2-(3,3-dimethyl-1-phenylbut-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 19B



19A



19B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S24** (79.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **19** was isolated in a yield of 120.1 mg (0.42 mmol, 84%) as a yellow solid as a regioisomeric mixture of **19A**/**19B**-94/6.

Method B (B_2pin_2 as boron source):

According to GP-2, arylalkylalkyne **S24** (79.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 40/1), vinylboronate **19** was isolated in a yield of 78.4 mg (0.27 mmol, 55%) as a regioisomeric mixture of **19A**/**19B**-59/41. Here, the corresponding (*E*)-isomers were also formed, the total ratio was **19A**/**19B**/(***E***)**-19A**/(***E***)**-19B**-55/39/3/3. The regioisomers **19A** and **19B** were separated by HPLC (petroleum ether/ethyl acetate – 50/1).

Analytical data for 19A:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.27-7.23 (m, 2 H), 7.20-7.16 (m, 1 H), 7.05-7.03 (m, 2 H), 6.47 (s, 1 H), 1.22 (s, 12 H), 0.90 (s, 9 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 156.6, 142.4, 129.2, 127.7, 125.9, 83.9, 35.9, 31.0, 24.9 ppm; **IR** (in CD_2Cl_2) ν = 3050 (w), 2988 (m), 2954 (m), 2901 (w), 2866 (w), 1614 (w), 1596 (w), 1494 (w), 1474 (w), 1441 (w), 1403 (w), 1390 (w), 1377 (m), 1365 (m), 1338 (s), 1315 (s), 1270 (w), 1256 (w), 1210 (w), 1167 (w), 1146 (s), 1113 (w), 1071 (w), 1028 (w), 1007 (w), 979 (w), 958 (w), 917 (w), 855 (w), 833 (w), 769 (w), 702 (m), 687 (m), 619 (w), 579 (w), 565 (w), 493 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 286 (33), 271 (20), 229 (27), 186 (26), 171 (70), 158 (100), 143 (77), 129 (43), 117 (24), 101 (79), 84 (36), 77 (10), 57 (21); **HRMS** (EI, 70 eV): calcd for $C_{18}H_{27}BO_2^+$: 286.2107; found: 286.2102; R_f = 0.31 (petroleum ether/ethyl acetate – 50/1), yellow solid.

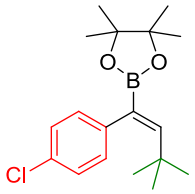
Analytical data for 19B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.28-7.24 (m, 2 H), 7.21-7.14 (m, 3 H), 7.10 (s, 1 H), 1.29 (s, 12 H), 1.03 (s, 9 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 141.8, 138.9, 128.6, 127.9, 126.5, 83.7, 36.5, 31.7, 24.9 ppm; **IR** (in CD_2Cl_2) ν = 2977 (m), 2953 (w), 2868 (w), 1615 (w), 1592 (w), 1489 (w), 1481 (w), 1466 (w), 1443 (w), 1371 (s), 1326 (s), 1299 (s), 1272 (m), 1238 (w), 1214 (w), 1198 (w), 1145 (vs), 1109 (w), 1072 (w), 1044 (m), 1030 (w), 1007 (w), 991 (m), 958 (w), 915 (w), 865 (m), 845 (w), 830 (w), 756 (m), 738 (w), 699 (s), 669 (w), 580 (w), 560 (w), 484 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 286 (49), 271 (32), 243 (6), 229 (6), 186 (59), 171

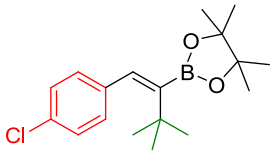
(100), 158 (58), 143 (80), 129 (47), 117 (22), 101 (56), 84 (47), 77 (11), 69 (6), 57 (16); **HRMS** (EI, 70 eV): calcd for $C_{18}H_{27}BO_2^+$: 286.2107; found: 286.2102; $\boldsymbol{R_f}$ = 0.36 (petroleum ether/ethyl acetate – 50/1), colourless oil.

The analytical data are in good accordance with those published in the literature.[11]

3.21 Preparation of (*Z*)-2-(1-(4-chlorophenyl)-3,3-dimethylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 20A and (*Z*)-2-(1-(4-chloro-phenyl)-3,3-dimethylbut-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 20B



20A



20B

Method A (HBpin as boron source):

According to GP-1, arylalkylalkyne **S25** (96.3 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **20** was isolated in a yield of 139.7 mg (0.44 mmol, 87%) as a colourless solid as a regioisomeric mixture of **20A**/**20B**-94/6.

Method B (B_2pin_2 as boron source):

According to GP-2, arylalkylalkyne **S25** (96.3 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 100/0 to 40/1), vinylboronate **20** was isolated in a yield of 82.3 mg (0.26 mmol, 51%) as a regioisomeric mixture of **20A**/**20B**-58/42. Here, the corresponding (*E*)-isomers were also formed, the total ratio was **20A**/**20B**/(***E***)**-20A**/(***E***)**-20B**-55/39/3/3. The regioisomers **20A** and **20B** were separated by HPLC (petroleum ether/ethyl acetate – 100/1).

Analytical data for 20A:

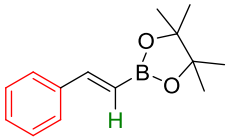
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.25-7-23 (m, 2 H), 7.01-6.99 (m, 2 H), 6.48 (s, 1 H), 1.22 (s, 12 H), 0.91 (s, 9 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 157.3, 141.0, 131.6, 130.7, 127.8, 84.0, 35.9, 31.0, 24.9 ppm; **IR** (in CD_2Cl_2) ν = 2987 (m), 2956 (m), 2929 (w), 2901 (w), 2866

(w), 1617 (w), 1588 (w), 1489 (m), 1469 (w), 1403 (w), 1390 (w), 1378 (m), 1356 (m), 1337 (s), 1314 (s), 1258 (w), 1212 (w), 1167 (w), 1145 (s), 1113 (w), 1091 (m), 1014 (w), 958 (w), 916 (w), 857 (m), 826 (w), 791 (w), 756 (w), 734 (w), 701 (w), 685 (w), 625 (w), 570 (w), 519 (w), 501 (w), 430 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 320 (72), 305 (13), 285 (11), 263 (24), 237 (3), 220 (9), 205 (27), 193 (18), 185 (21), 157 (32), 143 (10), 115 (3), 101 (100), 83 (21), 69 (5), 57 (12); **HRMS** (EI, 70 eV): calcd for $C_{18}H_{26}BClO_2^+$: 320.1718; found: 320.1716; $\boldsymbol{R_f}$ = 0.23 (petroleum ether/ethyl acetate – 100/1), colourless solid.

Analytical data for 20B:

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.25-7-23 (m, 2 H), 7.11-7.09 (m, 2 H), 7.01 (s, 1 H), 1.28 (s, 12 H), 1.02 (s, 9 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 140.3, 137.5, 132.2, 130.1, 128.0, 83.7, 36.6, 31.7, 24.9 ppm; **IR** (in CD_2Cl_2) ν = 2981 (m), 2954 (m), 2905 (w), 2865 (w), 1611 (w), 1484 (m), 1462 (w), 1446 (w), 1371 (s), 1325 (s), 1307 (s), 1271 (m), 1212 (w), 1167 (w), 1143 (s), 1110 (w), 1088 (m), 1045 (m), 1014 (m), 991 (w), 958 (w), 864 (m), 843 (w), 830 (w), 805 (m), 750 (w), 698 (m), 579 (w), 503 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 320 (76), 305 (17), 285 (54), 263 (14), 241 (2), 220 (19), 205 (36), 185 (92), 157 (43), 143 (21), 128 (16), 115 (6), 101 (100), 83 (38), 67 (6), 57 (16); **HRMS** (EI, 70 eV): calcd for $C_{18}H_{26}BClO_2^+$: 320.1718; found: 320.1714; $\boldsymbol{R_f}$ = 0.24 (petroleum ether/ethyl acetate – 100/1), colourless solid.

3.22 Preparation of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane 21



21

Method A (HBpin as boron source):

According to GP-1, phenylacetylene (55 µL, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **21** was isolated as a single regioisomer in a yield of 14.4 mg (0.06 mmol, 13%) as a yellow oil.

Method B (B_2pin_2 as boron source):

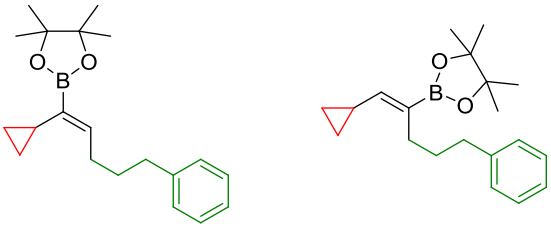
According to GP-2, phenylacetylene (55 µL, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After

column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **21** was isolated as a single regioisomer in a yield of 40.3 mg (0.18 mmol, 35%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.48 (m, 2 H), 7.41 (d, J = 18.5 Hz, 1 H), 7.36-7.27 (m, 3 H), 6.18 (d, J = 18.4 Hz, 1 H), 1.32 (s, 12 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 149.6, 137.6, 129.0, 128.7, 127.2, 83.5, 24.9 ppm; **IR** (in $CDCl_3$) ν = 3060 (w), 3026 (w), 2978 (w), 2929 (w), 1624 (m), 1450 (w), 1386 (m), 1352 (s), 1324 (m), 1272 (w), 1210 (m), 1144 (s), 998 (w), 970 (w) cm^{-1}; **MS** (ESI): *m/z* (%): 253 (100), 231 (14); **HRMS** (ESI): calcd for $C_{14}H_{19}BO_2Na^+$: 253.1373; found: 253.1374; $\boldsymbol{R_f}$ = 0.44 (petroleum ether/ethyl acetate – 20/1).

The analytical data are in good accordance with those reported in the literature.[6]

3.23 Preparation of (*Z*)-2-(1-cyclopropyl-5-phenylpent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 22A and (*Z*)-2-(1-cyclopropyl-5-phenylpent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 22B



22A **22B**

Method A (HBpin as boron source):

According to GP-1, cyclopropylalkyne **S27** (92.1 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **22** was isolated in a yield of 132.4 mg (0.42 mmol, 85%) as a regioisomeric mixture of **22A**/**22B**-61/39. The regioisomers were separated by HPLC (petroleum ether/ethyl acetate – 50/1).

Method B (B_2pin_2 as boron source):

According to GP-2, cyclopropylalkyne **S27** (92.1 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **22** was isolated in a yield of 141.1 mg (0.45 mmol, 90%) as a colourless oil as a regioisomeric mixture of **22A**/**22B**-32/68.

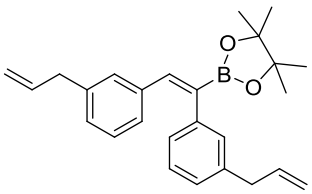
Analytical data for 22A:

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.31-7.14 (m, 5 H), 6.29 (t, J = 6.9 Hz, 1 H), 2.69-2.64 (m, 2 H), 2.35-2.28 (m, 2 H), 1.82-1.72 (m, 2 H), 1.54-1.45 (m, 1 H), 1.21 (s, 12 H), 0.72-0.65 (m, 2 H), 0.64-0.58 (m, 2 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 145.8, 143.0, 128.9, 128.6, 126.0, 83.1, 36.0, 31.3, 28.7, 24.9, 11.6, 6.5 ppm; **IR** (in $CDCl_3$) v = 3084 (w), 3062 (w), 3025 (w), 2977 (w), 2930 (w), 2858 (w), 1609 (w), 1496 (w), 1454 (w), 1401 (m), 1361 (s), 1297 (s), 1273 (m), 1214 (w), 1141 (vs), 1111 (w), 1051 (w), 1021 (w), 1006 (w), 983 (m), 960 (w), 905 (w), 857 (m), 814 (w), 746 (m), 698 (s), 687 (s), 580 (w), 542 (w), 494 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 312 (45), 297 (7), 284 (19), 227 (14), 212 (28), 184 (69), 169 (10), 151 (17), 144 (31), 131 (22), 117 (26), 101 (74), 91 (100), 84 (43), 67 (17); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{29}BO_2^+$: 312.2264; found: 312.2259; $\boldsymbol{R_f}$ = 0.31 (petroleum ether/ethyl acetate – 50/1), colourless oil.

Analytical data for 22B:

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.29-7.12 (m, 5 H), 5.61 (d, J = 10.2 Hz, 1 H), 2.66-2.61 (m, 2 H), 2.31-2.26 (m, 2 H), 1.79-1.69 (m, 2 H), 1.68-1.56 (m, 1 H), 1.23 (s, 12 H), 0.83-0.78 (m, 2 H), 0.49-0.44 (m, 2 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 151.1, 143.5, 128.8, 128.5, 125.9, 83.3, 36.1, 32.4, 28.9, 24.9, 11.4, 7.9 ppm; **IR** (in $CDCl_3$) v = 3083 (w), 3062 (w), 3025 (w), 2977 (w), 2930 (w), 2860 (w), 1626 (m), 1496 (w), 1454 (w), 1409 (m), 1370 (s), 1333 (m), 1298 (s), 1271 (m), 1212 (w), 1189 (w), 1141 (vs), 1109 (w), 1086 (m), 1048 (w), 1022 (w), 965 (m), 944 (m), 917 (w), 867 (m), 851 (m), 808 (w), 747 (m), 696 (s), 579 (w), 520 (w), 493 (w), 460 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 312 (52), 297 (7), 284 (14), 270 (17), 255 (3), 227 (14), 212 (28), 184 (41), 165 (10), 156 (19), 131 (19), 121 (26), 104 (100), 91 (87), 84 (48); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{29}BO_2^+$: 312.2264; found: 312.2258; $\boldsymbol{R_f}$ = 0.26 (petroleum ether/ethyl acetate – 50/1).

3.24 Preparation of (*Z*)-2-(1,2-*bis*(3-allylphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 25



25

Method A (HBpin as boron source):

According to GP-1, **24** (129.2 mg, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 3 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **25** was

isolated in a yield of 153.1 mg (0.40 mmol, 79%) as a yellow oil, (*Z*)/(*E*)-97/3; alkyne/alkene-96/4.

Method B (B_2pin_2 as boron source):

According to GP-2, **24** (129.2 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 50/1), vinylboronate **25** was isolated in a yield of 110.7 mg (0.29 mmol, 57%) as a yellow oil, (*Z*)/(*E*)-99/1; alkyne/alkene-88/12.

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.31 (s, 1 H), 7.24-7.20 (m, 1 H), 7.07-7.03 (m, 2 H), 6.97-6.95 (m, 3 H), 6.90-6.87 (m, 2 H), 5.97-5.87 (m, 1 H), 5.83-5.73 (m, 1 H), 5.09-4.93 (m, 4 H), 3.32 (d, *J* = 6.6 Hz, 2 H), 3.18 (d, *J* = 6.8 Hz, 2 H), 1.30 (s, 12 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 143.5, 141.4, 140.5, 140.1, 138.1, 137.6, 137.4, 130.6, 129.4, 128.8, 128.4, 128.3, 128.1, 126.9, 126.7, 115.9, 115.7, 84.2, 40.5, 40.3, 24.9 ppm; **IR** (in $CDCl_3$) *v* = 3076 (w), 3056 (w), 2978 (m), 2928 (w), 1639 (w), 1601 (w), 1581 (w), 1480 (w), 1432 (w), 1378 (m), 1371 (m), 1337 (vs), 1317 (m), 1271 (m), 1215 (w), 1142 (s), 1111 (w), 1012 (w), 994 (m), 964 (w), 913 (m), 853 (m), 794 (w), 721 (w), 698 (m), 670 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 386 (100), 371 (2), 346 (8), 286 (3), 270 (16), 230 (4), 202 (3), 143 (3), 101 (7); **HRMS** (EI): calcd for $C_{26}H_{31}BO_2$: 386.2422; found: 386.2419; R_f = 0.30 (petroleum ether/ethyl acetate – 50/1).

4. Preparation of the Starting Materials

4.1 General procedure for the Sonogashira reactions towards aryl-TMS-alkynes or arylalkylalkynes GP-3

The procedure was taken from a literature reference.[12] In a heat gun-dried two-necked flask the respective iodobenzene derivative (1.0 eq.), $PdCl_2(PPh_3)_2$ (2 mol%) and copper(I)-iodide (6 mol%) were suspended in triethylamine (0.33 M) under a nitrogen atmosphere. After stirring for five minutes at room temperature, the terminal alkyne (1.2 eq.) was added. The reaction mixture was stirred overnight (reaction times are given for the individual compounds at their corresponding entries) and then filtered over a pad of celite (10 mL ethyl acetate per mmol of iodobenzene derivative as eluent). The organic layer was washed with dilute hydrochloric acid (1 N, 10 mL/mmol of substrate). After phase separation, the aqueous phase was extracted with ethyl acetate (3 x 2 mL/mmol of substrate). The combined organic phases were dried over sodium sulphate and the solvent was removed under reduced

pressure. Purification of the crude material was achieved *via* column chromatography on silica gel with petroleum ether/ethyl acetate mixtures as eluent.

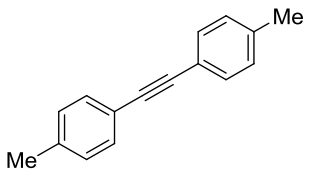
4.2 General procedure for the desilylation of TMS-alkynes GP-4

The deprotection of TMS-alkynes was performed in analogy to a literature-known procedure.[12] The aryl-TMS-alkyne (1.0 eq.) was dissolved under air in methanol (0.5 M, not absolute). Potassium carbonate (1.5 eq.) was added and the reaction mixture was stirred for 2 hours. The reaction was quenched by addition of demineralised water (9 mL/mmol of substrate). After extraction with ethyl acetate or diethyl ether (3 ml/mmol of substrate) the combined organic phases were dried over sodium sulphate and the solvent was removed at a rotary evaporator. The products were isolated by purification with silica gel column chromatography (eluent: petroleum ether/ethyl acetate mixtures or *n*-pentane/diethyl ether mixtures).

4.3 General procedure for the Sonogashira reaction towards *bis*arylalkynes GP-5

In a heat gun-dried two-necked flask, the corresponding iodoaryl compound (1.0 eq.), $PdCl_2(PPh_3)_2$ (2 mol%) and copper(I)-iodide (6 mol%) were suspended in triethylamine (0.33 M) under a nitrogen atmosphere. After a period of stirring of five minutes at room temperature, the terminal alkyne (1.0 eq.) was added and the reaction mixture was stirred at room temperature overnight (reaction times are indicated at the corresponding entries for each compound). Unless otherwise specified, the mixture was filtered over a pad of celite (20 mL ethyl acetate as eluent per mmol of starting material) and quenched by addition of dilute hydrochloric acid (1 N, 10 mL/mmol of substrate). Extraction of the aqueous layer after phase separation with ethyl acetate (3 x 3 mL/mmol of starting material) and drying of the combined organic phases over sodium sulphate followed by removal of the solvent under reduced pressure gave the crude product, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate mixtures as eluent).

4.4 Preparation of 1,2-di-*p*-tolylethyne S2



S2

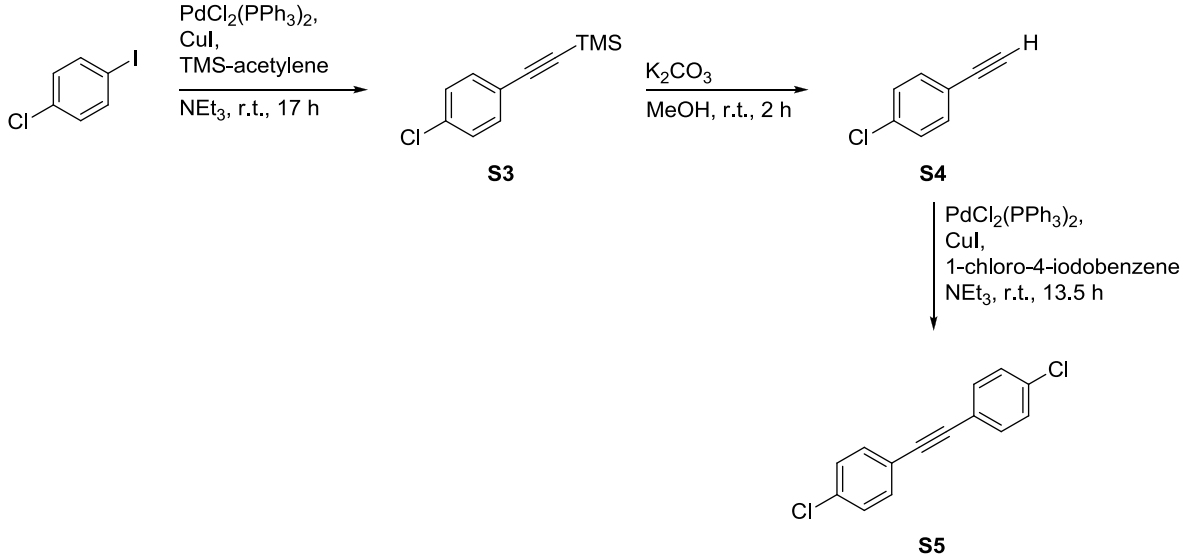
This compound was prepared in analogy to a literature procedure.[13] In a two-necked flask, 4-Iodotoluene (1.74 g, 8.0 mmol, 2.0 eq.), $PdCl_2(PPh_3)_2$ (280.8 mg, 0.4 mmol, 10 mol%) and copper(I)-iodide (152.4 mg, 0.8 mmol, 20 mol%) were suspended in toluene (6.9 mL). After addition of demineralised water (73 µL, 4.0 mmol, 1.0 eq.), DBU (7.2 mL, 48.0 mmol, 12 eq.) and TMS-acetylene (570 µL, 4.0 mmol, 1.0 eq.) the reaction mixture was heated to 65 °C for

17 hours. The mixture was cooled to room temperature and quenched with dilute aqueous hydrochloric acid (2 N, 15 mL). After phase separation, the aqueous phase was extracted with diethyl ether (3 x 15 mL). The combined organic phases were washed with 1 N aqueous hydrochloric acid (15 mL) and a saturated aqueous sodium chloride solution (15 mL). Subsequent drying over magnesium sulphate and removal of the solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 – 20/1). The title compound was isolated in a yield of 370.0 mg (1.8 mmol, 45%) as a colourless solid.

^{1}H NMR (300 MHz,$CDCl_3$) δ = 7.43-7.40 (m, 4 H), 7.16-7.14 (m, 4 H), 2.37 (s, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 138.3, 131.6, 129.2, 120.5, 89.0, 21.7 ppm; **IR** (neat) ν = 3024 (w), 2919 (w), 2859 (w), 1908 (w), 1657 (w), 1541 (w), 1513 (s), 1441 (m), 1409 (m), 1309 (w), 1211 (w), 1183 (w), 1123 (m), 1035 (m), 1019 (m), 947 (w), 907 (w), 855 (w), 839 (w), 812 (vs), 734 (m), 707 (w), 643 (w), 513 (s), 470 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 206 (100), 189 (10); **HRMS** (EI, 70 eV): calcd for $C_{16}H_{14}^+$: 206.1096; found: 206.1098; R_f = 0.46 (petroleum ether/CH_2Cl_2 – 20/1).

The analytical data are in good accordance with those published in the literature.[14]

4.5 Preparation of 1,2-*bis*(4-chlorophenyl)ethyne S5



((4-chlorophenyl)ethynyl)trimethylsilane S3:

According to GP-3, 1-chloro-4-iodobenzene (2.39 g, 10.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%) and copper(I)-iodide (114.3 mg, 0.6 mmol, 6 mol%) were suspended in triethylamine (30 mL). After addition of TMS-acetylene (1.71 mL, 12.0 mmol, 1.2 eq.) the reaction mixture was stirred for 17 hours at room temperature. Silica gel column

chromatography (petroleum ether) after the work-up gave product **S3** in a yield of 1.503 g (7.2 mmol, 72%) as a colourless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.37 (m, 2 H), 7.29-7.25 (m, 2 H), 0.25 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 134.6, 133.3, 128.7, 121.8, 103.9, 95.5, 0.0 ppm; **IR** (in $CDCl_3$) ν = 2959 (w), 2899 (w), 2160 (m), 1591 (w), 1487 (m), 1340 (w), 1249 (m), 1217 (w), 1090 (m), 1015 (w), 857 (s), 839 (s), 823 (vs), 758 (s), 684 (s), 622 (w), 531 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 208 (17), 193 (100); **HRMS** (EI, 70 eV): calcd for $C_{11}H_{13}ClSi^+$: 208.0475; found: 208.0474; $\boldsymbol{R_f}$ = 0.59 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[15]

1-chloro-4-ethynylbenzene S4:

According to GP-4, the suspension of aryl-TMS-acetylene **S3** (1.48 g, 7.1 mmol, 1.0 eq.) and potassium carbonate (1.47 g, 10.7 mmol, 1.5 eq.) in methanol (14 mL) was stirred for 2 hours at room temperature. Aqueous work-up, extraction with diethyl ether and subsequent column chromatography (*n*-pentane) gave terminal alkyne **S4** in a yield of 853.7 mg (6.3 mmol, 88%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.40 (m, 2 H), 7.32-7.28 (m, 2 H), 3.10 (s, 1 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 135.1, 133.5, 128.8, 120.7, 82.7, 78.3 ppm; **IR** (in $CDCl_3$) ν = 3296 (w), 3263 (m), 3084 (w), 2924 (w), 2854 (w), 2106 (w), 1903 (w), 1775 (w), 1650 (w), 1591 (w), 1487 (s), 1472 (m), 1396 (m), 1375 (w), 1248 (w), 1088 (s), 1014 (m), 824 (vs), 780 (w), 705 (m), 676 (m), 631 (m), 590 (m), 525 (s), 413 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 136 (100), 101 (20), 75 (11); **HRMS** (EI, 70 eV): calcd for $C_8H_5Cl^+$: 136.0080; found: 136.0082; $\boldsymbol{R_f}$ = 0.56 (*n*-pentane).

The analytical data are in good accordance with those published in the literature.[16]

1,2-*bis*(4-chlorophenyl)ethyne S5:

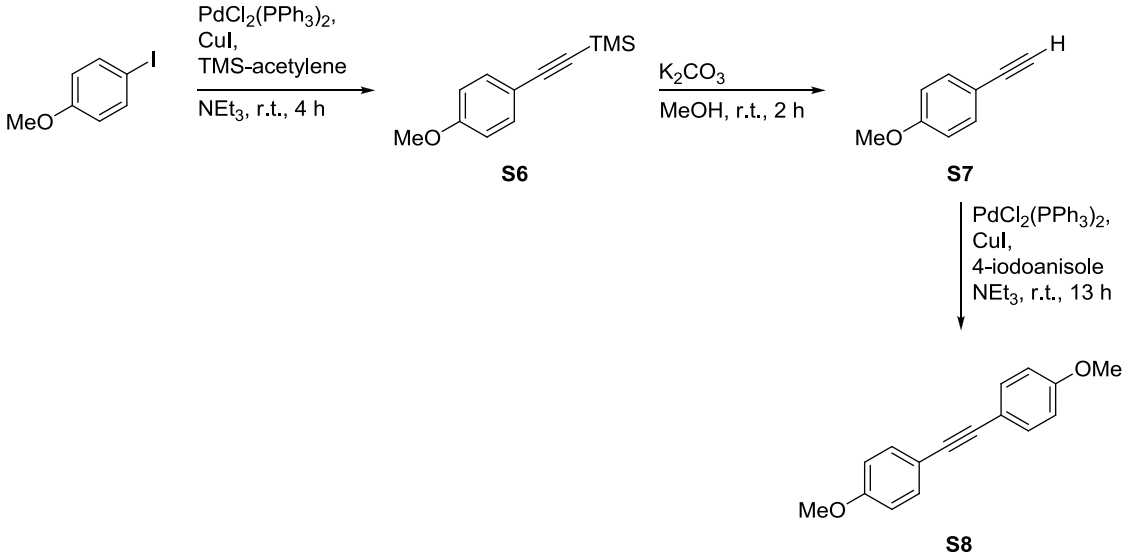
According to GP-5, 1-chloro-4-iodobenzene (1.46 g, 6.12 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (85.9 mg, 0.12 mmol, 2 mol%) and copper(I)-iodide (69.9 mg, 0.37 mmol, 6 mol%) were suspended in triethylamine (18 mL). After addition of the terminal alkyne **S4** (835.7 mg, 6.12 mmol, 1.0 eq.), the reaction mixture was stirred for 13.5 hours. Work-up was performed as described in the general procedure, to one exception: the crude product was taken up in acetone (40 mL) and then filtered over celite with acetone (200 mL) and diethyl ether (200 mL) as eluents. Silica gel was added (ca. 1 g) and the solvent was evaporated. The dry product/silica mixture was subjected to column chromatography on silica gel (petroleum

ether/ethyl acetate – 100/1 to 40/1). The title compound was isolated in a yield of 981.6 mg (3.97 mmol, 65%) as a colourless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.47-7.43 (m, 4 H), 7.35-7.31 (m, 4 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 134.7, 132.9, 128.9, 121.6, 89.3 ppm; **IR** (neat) ν = 1911 (m), 1657 (w), 1593 (w), 1489 (s), 1399 (m), 1259 (w), 1172 (w), 1155 (w), 1086 (s), 1052 (m), 1009 (s), 823 (vs), 770 (m), 653 (s), 635 (m), 512 (s), 474 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 246 (100), 210 (3), 176 (25); $\boldsymbol{R_f}$ = 0.53 (petroleum ether/ethyl acetate –100/1).

The analytical data are in good accordance with those published in the literature.[17]

4.6 Preparation of 1,2-*bis*(4-methoxyphenyl)ethyne S8



((4-methoxyphenyl)ethynyl)trimethylsilane S6:

According to GP-3, 4-iodoanisole (1.17 g, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of TMS-acetylene (854 µL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 4 hours at room temperature. Silica gel column chromatography (petroleum ether/ethyl acetate – 20/1) after the work-up gave product **S6** in a yield of 943.9 mg (4.6 mmol, 92%) as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43-7.38 (m, 2 H), 6.84-6.79 (m, 2 H), 3.80 (s, 3 H), 0.24 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 159.9, 133.6, 115.4, 113.9, 105.3, 92.6, 55.4, 0.21 ppm; **IR** (in $CDCl_3$) ν = 2958 (w), 2899 (w), 2838 (w), 2155 (m), 1606 (m), 1571 (w), 1507 (s), 1464 (w), 1442 (w), 1410 (w), 1292 (m), 1247 (s), 1171 (m), 1107 (w), 1034 (m), 863 (s), 832 (vs), 756 (s), 699 (w), 633 (w), 541 (w), 464 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 204 (39), 189 (100), 174 (6), 159 (3), (6); **HRMS** (EI, 70 eV): calcd for $C_{12}H_{16}OSi^+$: 204.0970; found: 204.0980; $\boldsymbol{R_f}$ = 0.57 (petroleum ether/ethyl acetate – 20/1).

The analytical data are in good accordance with those published in the literature.[18]

1-ethynyl-4-methoxybenzene S7:

According to GP-4, the suspension of aryl-TMS-acetylene **S6** (920.8 mg, 4.5 mmol, 1.0 eq.) and potassium carbonate (934.2 mg, 6.8 mmol, 1.5 eq.) in methanol (9.0 mL) was stirred for 2 hours at room temperature. Aqueous work-up, extraction with ethyl acetate and subsequent column chromatography (petroleum ether/ethyl acetate – 20/1) gave terminal alkyne **S7** in a yield of 506.1 mg (3.8 mmol, 85%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.42 (m, 2 H), 6.86-6.83 (m, 2 H), 3.81 (s, 3 H), 3.00 (s, 1 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.1, 133.7, 114.3, 114.1, 83.8, 75.9, 55.4 ppm; **IR** (neat) ν = 3285 (m), 3005 (w), 2960 (w), 2838 (w), 2540 (w), 2106 (w), 1893 (w), 1605 (s), 1571 (w), 1504 (s), 1464 (m), 1441 (m), 1415 (w), 1289 (s), 1245 (vs), 1169 (s), 1107 (m), 1028 (s), 829 (s), 811 (m), 685 (m), 657 (m), 640 (m), 604 (m), 535 (s), 486 (m), 449 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 132 (100), 117 (27), 102 (4), 89 (31), 75 (3), 63 (10); **HRMS** (EI, 70 eV): calcd for $C_9H_8O^+$: 132.0575; found: 132.0574; R_f = 0.50 (petroleum ether/ethyl acetate – 20/1).

The analytical data are in good accordance with those published in the literature.[19]

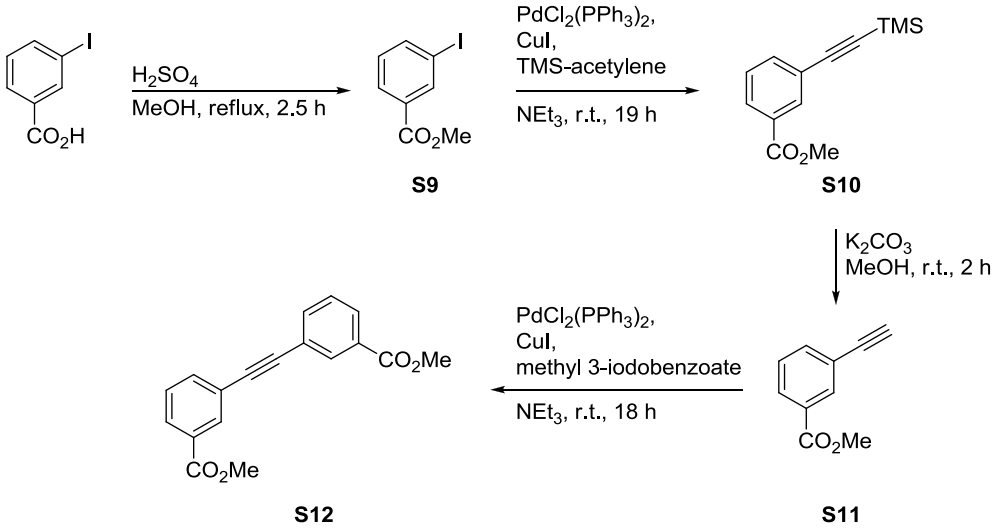
1,2-*bis*(4-methoxyphenyl)ethyne S8:

According to GP-5, 4-iodoanisole (889.3 mg, 3.80 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (53.3 mg, 0.08 mmol, 2 mol%) and copper(I)-iodide (43.3 mg, 0.23 mmol, 6 mol%) were suspended in triethylamine (11.4 mL). After addition of the terminal alkyne **S7** (500.8 mg, 3.80 mmol, 1.0 eq.), the reaction mixture was stirred for 13 hours at room temperature. Work-up and subsequent purification by silica gel column chromatography (petroleum ether/ethyl acetate – 5/1) gave a still impure product. An additional recrystallisation from acetone (5 mL) and a second recrystallisation from the mother liquor (1 mL of acetone) yielded 422.5 mg of the title compound as colourless needle-shaped crystals (1.77 mmol, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47-7.44 (m, 4 H), 6.89-6.85 (m, 4 H), 3.82 (s, 6 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.5, 133.0, 115.9, 114.1, 88.1, 55.4 ppm; **IR** (neat) ν = 2933 (w), 2838 (w), 2037 (w), 1897 (w), 1605 (s), 1567 (m), 1506 (s), 1457 (m), 1439 (m), 1414 (m), 1316 (w), 1303 (w), 1285 (m), 1243 (s), 1170 (s), 1106 (s), 1023 (s), 832 (vs), 821 (s), 748 (m), 640 (w), 525 (s), 463 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 238 (100), 223 (50), 195 (7); **HRMS** (EI, 70 eV): calcd for $C_{16}H_{14}O_2^+$: 238.0994; found: 238.0995; R_f = 0.59 (petroleum ether/ethyl acetate – 5/1).

The analytical data are in good accordance with those published in the literature.[20]

4.7 Preparation of dimethyl 3,3'-(ethyne-1,2-diyl)dibenzoate S12



methyl 3-iodobenzoate S9:

The compound was prepared according to the literature.[21] A two-necked flask was evacuated for ten minutes, refilled with nitrogen and charged with 3-iodobenzoic acid (7.44 g, 30.0 mmol, 1.0 eq.). Methanol (186 mL, not dried) was added and the mixture was stirred at room temperature until the carboxylic acid was completely dissolved. Concentrated sulphuric acid (96%, 18.5 mL) was added slowly. The reaction mixture was heated to reflux for 2.5 hours. After cooling to room temperature, the mixture was diluted with diethyl ether (186 mL) and washed with demineralised water (2 x 186 mL), a saturated aqueous sodium bicarbonate solution (186 mL) and a saturated aqueous sodium chloride solution (186 mL). The organic layer was dried over sodium sulphate and the solvent was evaporated under reduced pressure, yielding product **S9** in a yield of 5.97 g (22.8 mmol, 76%) as a colourless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.38 (t, J = 1.7 Hz, 1 H), 8.01-7.98 (m, 1 H), 7.89-7.86 (m, 1 H), 7.18 (t, J = 7.8 Hz, 1 H), 3.92 (s, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 165.7, 141.9, 138.6, 132.1, 130.2, 128.9, 93.9, 52.5 ppm; **IR** (in $CDCl_3$) ν = 3063 (w), 2996 (w), 2950 (w), 2842 (w), 1721 (s), 1565 (m), 1471 (w), 1435 (m), 1415 (w), 1279 (s), 1257 (vs), 1193 (w), 1170 (w), 1117 (m), 1082 (w), 1060 (w), 998 (w), 970 (w), 901 (w), 831 (w), 810 (w), 743 (s), 705 (m), 673 (w), 646 (w) cm^{-1}; **MS** (EI, 70 eV): *m/z* (%): 262 (100), 230 (83), 202 (21), 135 (3), 76 (15).

The analytical data are in good accordance with those published in the literature.[21]

methyl 3-((trimethylsilyl)ethynyl)benzoate S10:

According to GP-3, methyl 3-iodobenzoate **S9** (2.62 g, 10.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%) and copper(I)-iodide (114.3 mg, 0.6 mmol, 6 mol%) were suspended in triethylamine (30 mL). After addition of TMS-acetylene (1.71 mL, 12.0 mmol, 1.2 eq.) the reaction mixture was stirred for 19 hours at room temperature. Silica gel column chromatography (petroleum ether/ethyl acetate – 40/1) after work-up gave product **S10** in a yield of 2.18 g (9.4 mmol, 94 %) as a brown solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.13 (t, *J* = 1.6 Hz, 1 H), 7.97 (dt, *J* = 7.7 Hz, 1.4 Hz, 1 H), 7.63 (dt, *J* = 7.6 Hz, 1.3 Hz, 1 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 3.91 (s, 3 H), 0.25 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 166.5, 136.1, 133.3, 130.5, 129.6, 128.5, 123.7, 104.0, 95.5, 52.4, 0.0 ppm; **IR** (neat) *v* = 2956 (w), 2900 (w), 2157 (w), 2067 (w), 1725 (s), 1597 (w), 1576 (w), 1483 (w), 1429 (m), 1416 (w), 1296 (s), 1248 (m), 1240 (m), 1207 (m), 1102 (m), 1087 (w), 1072 (w), 973 (m), 907 (m), 841 (s), 811 (m), 797 (m), 761 (s), 749 (s), 703 (m), 681 (m), 643 (m), 560 (w), 465 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 232 (17), 217 (100), 201 (3), 187 (3); R_f = 0.38 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those published in the literature.[22]

methyl 3-ethynylbenzoate S11:

According to GP-4, the suspension of aryl-TMS-acetylene **S10** (2.15 g, 9.25 mmol, 1.0 eq.) and potassium carbonate (1.92 g, 13.87 mmol, 1.5 eq.) in methanol (18.5 mL) was stirred for 2 hours at room temperature. Aqueous work-up, extraction with diethyl ether and subsequent column chromatography (petroleum ether/ethyl acetate – 40/1) gave terminal alkyne **S11** in a yield of 1.28 g (7.99 mmol, 86%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (t, *J* = 1.6 Hz, 1 H), 8.01 (dt, *J* = 7.8 Hz, 1.4 Hz, 1 H), 7.66 (dt, *J* = 7.7 Hz, 1.4 Hz, 1 H), 7.40 (t, *J* = 7.7 Hz, 1 H), 3.92 (s, 3 H), 3.12 (s, 1 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 166.4, 136.4, 133.4, 130.6, 129.9, 128.6, 122.7, 82.7, 78.3, 52.4 ppm; **IR** (in $CDCl_3$) *v* = 3254 (s), 2954 (m), 2842 (w), 2107 (w), 1903 (w), 1713 (vs), 1598 (w), 1580 (m), 1482 (w), 1461 (w), 1432 (m), 1292 (vs), 1239 (m), 1195 (s), 1166 (m), 1100 (s), 1079 (s), 999 (w), 967 (m), 906 (m), 883 (w), 813 (w), 778 (m), 749 (s), 714 (s), 663 (s), 541 (m), 437 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 160 (72), 129 (100), 101 (45), 75 (13); R_f = 0.36 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those published in the literature.[23]

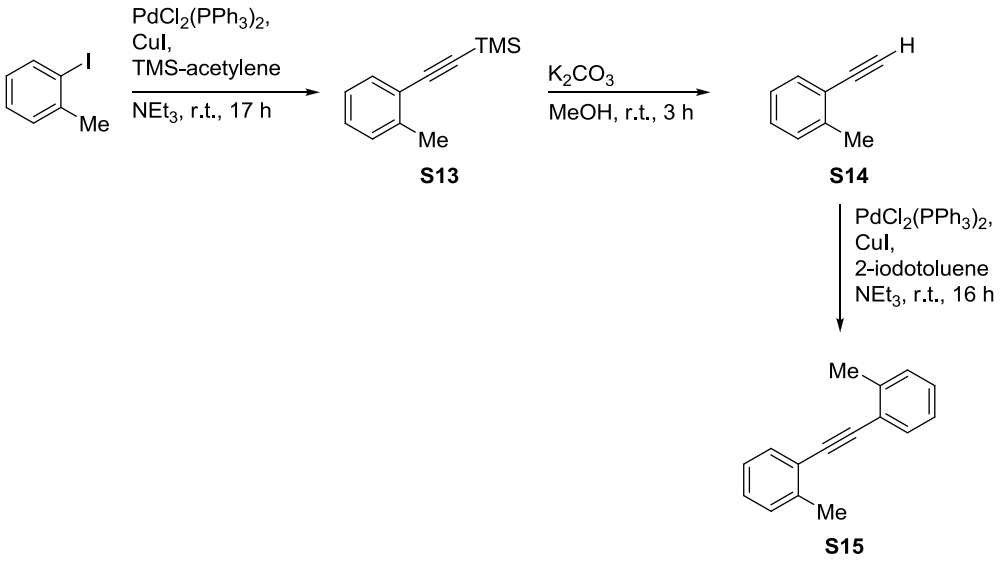
dimethyl 3,3'-(ethyne-1,2-diyl)dibenzoate S12:

According to GP-5, methyl 3-iodobenzoate (2.05 g, 7.84 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (110.1 mg, 0.16 mmol, 2 mol%) and copper(I)-iodide (89.6 mg, 0.47 mmol, 6 mol%) were suspended in triethylamine (23.5 mL). After the addition of the terminal alkyne **S11** (1.26 mg, 7.84 mmol, 1.0 eq.), the reaction mixture was stirred for 18 hours at room temperature. As the product was not soluble in ethyl acetate, it was dissolved in dichloromethane (40 mL) and transferred to a separation funnel. The reaction was quenched by addition of dilute aqueous hydrochloric acid (2 N, 50 mL). After phase separation, the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic phases were dried over sodium sulphate and the solvent was removed under vacuum. The crude material was dissolved in boiling dichloromethane (40 mL) and crystallised by layering the hot solution with *n*-pentane (110 mL). Crystallisation was complete after 16 hours at 4 °C. Filtration of the solid and a second recrystallisation (30 mL of dichloromethane and 75 mL of *n*-pentane) gave the title compound **S12** in a yield of 1.23 g (4.18 mmol, 53%) as a colourless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (t, *J* = 1.5 Hz, 2 H), 8.02 (dt, *J* = 7.8 Hz, 1.3 Hz, 2 H), 7.71 (dt, *J* = 7.7 Hz, 1.3 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 3.94 (s, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 166.5, 135.9, 132.9, 130.7, 129.7, 128.7, 123.5, 89.3, 52.5 ppm; **IR** (neat) *v* = 3082 (w), 3019 (w), 2953 (w), 2840 (w), 1728 (s), 1715 (s), 1599 (m), 1577 (m), 1489 (w), 1435 (m), 1326 (s), 1303 (m), 1287 (m), 1241 (vs), 1192 (m), 1169 (m), 1101 (s), 1085 (m), 997 (w), 972 (m), 910 (m), 828 (m), 818 (m), 802 (m), 750 (vs), 679 (s), 539 (m), 515 (w), 436 (w), 418 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 294 (100), 263 (46), 235 (7), 220 (2), 176 (10), 116 (10), 102 (7); R_f = 0.59 (petroleum ether/ethyl acetate – 4/1).

The analytical data are in good accordance with those published in the literature.[24]

4.8 Preparation of 1,2-di-*o*-tolylethyne S15



trimethyl(*o*-tolylethynyl)silane S13:

According to GP-3, 2-iodotoluene (1.28 mL, 10.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%) and copper(I)-iodide (114.3 mg, 0.6 mmol, 6 mol%) were suspended in triethylamine (30 mL). After addition of TMS-acetylene (1.71 mL, 12.0 mmol, 1.2 eq.) the reaction mixture was stirred for 17 hours at room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **S13** in a yield of 1.88 g (9.98 mmol, quantitative) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.42 (m, 1 H), 7.23-7.09 (m, 3 H), 2.44 (s, 3 H), 0.26 (s, 9 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.8, 132.2, 129.5, 128.6, 125.6, 123.1, 104.2, 98.3, 20.8, 0.2 ppm; **IR** (neat) ν = 3022 (w), 2959 (w), 2155 (m), 2068 (w), 1483 (w), 1456 (w), 1409 (w), 1380 (w), 1249 (w), 1227 (w), 1194 (w), 1111 (w), 1044 (w), 866 (s), 834 (vs), 754 (vs), 715 (m), 699 (m), 646 (m), 556 (w), 507 (w), 456 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 188 (29), 173 (100); **HRMS** (EI, 70 eV): calcd for $C_{12}H_{16}Si^+$: 188.1021; found: 188.1022; $\boldsymbol{R_f}$ = 0.58 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[25]

1-ethynyl-2-methylbenzene S14:

According to GP-4, the suspension of aryl-TMS-acetylene **S13** (1.85 g, 9.8 mmol, 1.0 eq.) and potassium carbonate (2.03 g, 14.7 mmol, 1.5 eq.) in methanol (20 mL) was stirred for 3 hours at room temperature. Aqueous work-up, extraction with diethyl ether and subsequent column chromatography (*n*-pentane) gave terminal alkyne **S14** in a yield of 986.2 mg (8.5 mmol, 87%) as a colourless oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.45-7.43 (m, 1 H), 7.27-7.21 (m, 2 H), 7.16-7.12 (m, 1 H), 3.32 (s, 1 H), 2.44 (s, 3 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 141.2, 132.8, 129.9, 129.2, 125.9, 122.3, 82.7, 81.3, 20.7 ppm; **IR** (in CD_2Cl_2) ν = 3289 (w), 3064 (w), 3022 (w), 2923 (w), 2104 (w), 1922 (w), 1483 (m), 1456 (w), 1380 (w), 1230 (w), 1159 (w), 1108 (w), 1043 (w), 945 (w), 866 (w), 820 (w), 754 (vs), 716 (m), 646 (m), 610 (s), 550 (w), 531 (w), 453 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 115 (100, $[M-H]^+$), 89 (7), 63 (7); **HRMS** (EI, 70 eV): calcd for $C_9H_8^+$: 116.0626; found: 116.0628; $\boldsymbol{R_f}$ = 0.59 (*n*-pentane).

The analytical data are in good accordance with those published in the literature.[26]

1,2-di-*o*-tolylethyne S15:

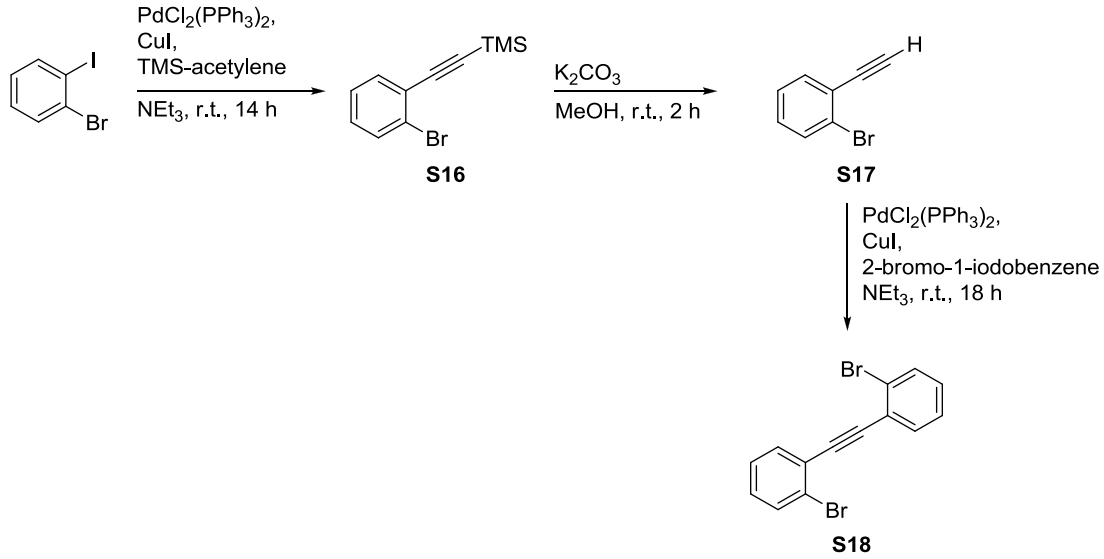
According to GP-5, 2-iodotoluene (1.02 mL, 7.98 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (112.0 mg, 0.16 mmol, 2 mol%) and copper(I)-iodide (91.2 mg, 0.48 mmol, 6 mol%) were suspended in triethylamine (24 mL). After addition of terminal alkyne **S14** (926.7 mg, 7.98 mmol, 1.0 eq.),

the reaction mixture was stirred for 16 hours. Work-up and subsequent purification by silica gel column chromatography (petroleum ether) gave the title compound in a yield of 987.0 mg (4.78 mmol, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52-7.50 (m, 2 H), 7.24-7.22 (m, 4 H), 7.20-7.15 (m, 2 H), 2.53 (s, 6 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.1, 132.0, 129.6, 128.3, 125.7, 123.5, 92.5, 21.1 ppm; **IR** (neat) ν = 3059 (w), 3021 (w), 2945 (w), 2919 (w), 2854 (w), 2318 (w), 2212 (w), 1951 (w), 1915 (w), 1836 (w), 1802 (w), 1728 (w), 1696 (w), 1599 (w), 1570 (w), 1490 (m), 1455 (m), 1378 (w), 1309 (w), 1275 (w), 1197 (w), 1157 (w), 1114 (w), 1097 (w), 1042 (w), 985 (w), 941 (w), 908 (w), 864 (w), 750 (vs), 714 (s), 587 (w), 566 (w), 538 (w), 489 (w), 445 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 206 (100), 191 (22), 178 (11), 165 (9), 115 (7), 101 (7), 89 (8); **HRMS** (EI, 70 eV): calcd for $C_{16}H_{14}^+$: 206.1096; found: 206.1089; $\boldsymbol{R_f}$ = 0.55 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[27]

4.9 Preparation of 1,2-*bis*(2-bromophenyl)ethyne S18



((2-bromophenyl)ethynyl)trimethylsilane S16:

According to GP-3, 2-bromo-1-iodobenzene (1.29 mL, 10.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%) and copper(I)-iodide (114.3 mg, 0.6 mmol, 6 mol%) were suspended in triethylamine (30 mL). After addition of TMS-acetylene (1.71 mL, 12.0 mmol, 1.2 eq.) the reaction mixture was stirred for 14 hours at room temperature. Silica gel column chromatography (*n*-pentane) after the work-up gave product **S16** in a yield of 2.48 g (9.8 mmol, 98%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.60-7.57 (m, 1 H), 7.52-7.49 (m, 1 H), 7.28-7.23 (m, 1 H), 7.20-7.14 (m, 1 H), 0.30 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 133.7, 132.5, 129.7,

127.0, 125.9, 125.4, 103.2, 99.8, 0.0 ppm; **IR** (neat) ν = 2959 (w), 2898 (w), 2162 (w), 1585 (w), 1558 (w), 1465 (m), 1434 (w), 1249 (m), 1220 (w), 1120 (w), 1046 (w), 1027 (m), 945 (w), 860 (s), 838 (vs), 750 (vs), 711 (m), 700 (m), 669 (m), 640 (m), 593 (w), 548 (w), 448 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 254 (25), 239 (100), 208 (5), 172 (2), 157 (2), 143 (10), 128 (5), 115 (9); $\boldsymbol{R_f}$ = 0.60 (*n*-pentane).

The analytical data are in good accordance with those published in the literature.[28]

1-bromo-2-ethynylbenzene S17:

According to GP-4, the suspension of aryl-TMS-acetylene **S16** (2.33 g, 9.2 mmol, 1.0 eq.) and potassium carbonate (1.91 g, 13.8 mmol, 1.5 eq.) in methanol (18.5 mL) was stirred for 2 hours at room temperature. Aqueous work-up, extraction with diethyl ether and subsequent column chromatography (*n*-pentane) gave terminal alkyne **S17** in a yield of 1.44 g (8.0 mmol, 87%) as a dark orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.59 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.52 (dd, J = 7.5 Hz, 1.9 Hz, 1 H), 7.29-7.17 (m, 2 H), 3.37 (s, 1 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 134.2, 132.6, 130.1, 127.2, 125.7, 124.4, 82.0, 81.9 ppm; **IR** (in $CDCl_3$) ν = 3290 (m), 3066 (w), 2113 (w), 1924 (w), 1808 (w), 1589 (w), 1559 (w), 1465 (s), 1434 (m), 1422 (w), 1257 (w), 1161 (w), 1119 (w), 1044 (m), 1026 (m), 947 (w), 901 (w), 864 (w), 750 (vs), 712 (w), 659 (s), 621 (s), 540 (m), 496 (w), 446 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 180 (100), 101 (48), 75 (23); $\boldsymbol{R_f}$ = 0.55 (*n*-pentane).

The analytical data are in good accordance with those published in the literature.[29]

1,2-*bis*(2-bromophenyl)ethyne S18:

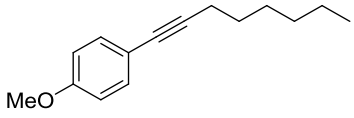
According to GP-5, 2-bromo-1-iodobenzene (1.0 mL, 7.79 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (109.3 mg, 0.16 mmol, 2 mol%) and copper(I)-iodide (89.0 mg, 0.47 mmol, 6 mol%) were suspended in triethylamine (23.4 mL). After addition of terminal alkyne **S17** (1.41 g, 7.79 mmol, 1.0 eq.), the reaction mixture was stirred for 18 hours. Work-up and subsequent purification by silica gel column chromatography (petroleum ether) gave the title compound in a yield of 2.18 g (6.49 mmol, 83%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.60 (m, 4 H), 7.31 (dt, J = 7.6 Hz, 1.2 Hz, 2 H), 7.20 (dt, J = 7.7 Hz, 1.6 Hz, 2 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 133.8, 132.7, 129.9, 127.2, 125.7, 125.3, 92.4 ppm; **IR** (neat) ν = 3059 (w), 3043 (w), 1957 (w), 1922 (w), 1889 (w), 1839 (w), 1805 (w), 1728 (w), 1700 (w), 1618 (w), 1591 (w), 1556 (w), 1511 (w), 1479 (s), 1433 (m), 1323 (w), 1272 (w), 1248 (m), 1160 (w), 1118 (w), 1047 (m), 1019 (m), 980 (w), 945 (m), 914 (w), 865 (w), 855 (w), 843 (w), 745 (vs), 709 (m), 663 (m), 554 (m), 508 (m), 439 (m)

cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 335 (100), 176 (35), 167 (5), 150 (5); $\boldsymbol{R_f}$ = 0.39 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[6]

4.10 Preparation of 1-methoxy-4-(oct-1-yn-1-yl)benzene S19



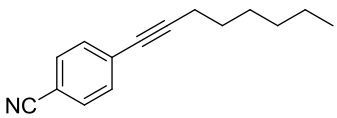
S19

According to GP-3, 4-iodoanisole (1.17 g, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of 1-octyne (0.88 mL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 15 hours at room temperature. Silica gel column chromatography after work-up (petroleum ether/ethyl acetate – 40/1) gave product **S19** as a dark brown oil. The colour was removed by dissolving the product in ethyl acetate (10 mL) followed by washing with a saturated aqueous ammonium chloride solution (3 x 5 mL) and an aqueous ammonia solution (25%, 2 x 5 mL). The organic layer was dried over sodium sulphate, the solvent was removed under reduced pressure and the residue was filtered over a pad of celite (eluent: petroleum ether/ethyl acetate – 20/1). Product **S19** was obtained in a yield of 1.06 g (4.9 mmol, 98%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35-7.30 (m, 2 H), 6.83-6.79 (m, 2 H), 3.80 (s, 3 H), 2.38 (t, *J* = 7.0 Hz, 2 H), 1.64-1.57 (m, 2 H), 1.50-1.40 (m, 2 H), 1.37-1.28 (m, 4 H), 0.90 (t, *J* = 7.0 Hz, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 159.1, 133.0, 116.4, 113.9, 88.9, 80.4, 55.4, 31.5, 29.0, 28.8, 22.7, 19.6, 14.2 ppm; **IR** (in $CDCl_3$) *v* = 2954 (w), 2929 (m), 2857 (w), 1607 (m), 1569 (w), 1508 (s), 1463 (m), 1441 (w), 1378 (w), 1288 (m), 1243 (vs), 1171 (m), 1105 (w), 1034 (m), 829 (s), 808 (w), 725 (w), 649 (w), 631 (w), 533 (m) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 216 (100), 201 (3), 187 (28), 173 (53), 159 (25), 147 (92), 134 (10), 121 (23), 115 (13), 102 (13), 91 (7); $\boldsymbol{R_f}$ = 0.35 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those published in the literature.[30]

4.11 Preparation of 4-(oct-1-yn-1-yl)benzonitrile S20



S20

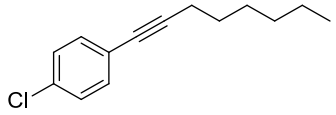
According to GP-3, 4-iodobenzonitrile (1.15 g, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in

triethylamine (15 mL). After addition of 1-octyne (0.88 mL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 12.5 hours at room temperature. Silica gel column chromatography (petroleum ether/ethyl acetate – 50/1) after work-up gave product **S20** as a brown oil. The colour was removed by dissolving the product in ethyl acetate (10 mL) followed by washing with a saturated aqueous ammonium chloride solution (3 x 5 mL) and an aqueous ammonia solution (25%, 2 x 5 mL). The organic layer was dried over sodium sulphate, the solvent was removed under reduced pressure and the residue was filtered over a pad of celite (eluent: petroleum ether/ethyl acetate – 20/1). Product **S20** was obtained in a yield of 988.2 mg (4.7 mmol, 94%) as a light brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58-7.55 (m, 2 H), 7.46-7.44 (m, 2 H), 2.42 (t, J = 7.0 Hz, 2 H), 1.66-1.58 (m, 2 H), 1.49-1.29 (m, 6 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 132.2, 132.0, 129.3, 118.8, 110.9, 95.9, 79.6, 31.4, 28.7, 28.5, 22.7, 19.6, 14.2 ppm; **IR** (in $CDCl_3$) ν = 2955 (m), 2929 (m), 2858 (m), 2226 (s), 1604 (m), 1500 (m), 1466 (w), 1429 (w), 1405 (w), 1379 (w), 1330 (w), 1271 (w), 1177 (w), 1105 (w), 1018 (w), 838 (vs), 725 (w), 555 (s) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 211 (62), 196 (3), 182 (67), 168 (100), 154 (53), 140 (67), 127 (30), 116 (31), 95 (16); $\boldsymbol{R_f}$ = 0.28 (petroleum ether/ethyl acetate – 50/1).

The analytical data are in good accordance with those published in the literature.[31]

4.12 Preparation of 1-chloro-4-(oct-1-yn-1-yl)benzene S21



S21

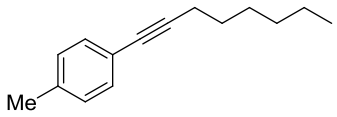
According to GP-3, 1-chloro-4-iodobenzene (768.4 mg, 3.22 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (45.2 mg, 0.06 mmol, 2 mol%) and copper(I)-iodide (36.8 mg, 0.19 mmol, 6 mol%) were suspended in triethylamine (9.8 mL). After addition of 1-octyne (0.57 mL, 3.86 mmol, 1.2 eq.) the reaction mixture was stirred for 14.5 hours at room temperature. Silica gel column chromatography (petroleum ether/ethyl acetate – 40/1) after work-up gave product **S21** as a brown oil. The colour was removed by dissolving the product in ethyl acetate (10 mL) followed by washing with a saturated aqueous ammonium chloride solution (3 x 5 mL) and an aqueous ammonia solution (25%, 2 x 5 mL). The organic layer was dried over sodium sulphate, the solvent was removed under reduced pressure and the residue was filtered over a pad of celite (eluent: petroleum ether/ethyl acetate – 20/1). Product **S21** was obtained in a yield of 595.3 mg (2.70 mmol, 84%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2 H), 7.26-7.22 (m, 2 H), 2.38 (t, J = 6.9 Hz, 2 H), 1.64-1.54 (m, 2 H), 1.49-1.39 (m, 2 H), 1.34-1.29 (m, 4 H), 0.90 (t, J = 6.8 Hz, 3 H)

ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 133.5, 132.9, 128.6, 122.8, 91.7, 79.6, 31.5, 28.8, 28.7, 22.7, 19.5, 14.2 ppm; **IR** (in $CDCl_3$) ν = 2955 (m), 2928 (m), 2857 (m), 2229 (w), 1897 (w), 1649 (w), 1593 (w), 1488 (s), 1465 (m), 1429 (w), 1396 (w), 1378 (w), 1330 (w), 1259 (w), 1174 (w), 1090 (s), 1014 (m), 825 (vs), 725 (w), 706 (w), 639 (w), 580 (w), 523 (m), 412 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 220 (72), 205 (2), 191 (20), 177 (63), 163 (12), 151 (100), 149 (61), 142 (26), 136 (19), 129 (38), 115 (26); $\boldsymbol{R_f}$ = 0.77 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those published in the literature.[32]

4.13 Preparation of 1-methyl-4-(oct-1-yn-1-yl)benzene 23



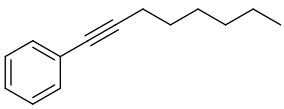
23

According to GP-3, 4-iodotoluene (1.09 g, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of 1-octyne (0.88 mL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 16.5 hours at room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **23** in a yield of 911.7 mg (4.6 mmol, 91%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.28 (m, 2 H), 7.09-7.07 (m, 2 H), 2.39 (t, *J* = 7.1 Hz, 2 H), 2.33 (s, 3 H), 1.64-1.56 (m, 2 H), 1.49-1.42 (m, 2 H), 1.37-1.28 (m, 4 H), 0.91 (t, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.5, 131.6, 129.1, 121.2, 89.8, 80.7, 31.5, 29.0, 28.8, 22.7, 21.5, 19.6, 14.2 ppm; **IR** (in $CDCl_3$) ν = 3027 (w), 2955 (m), 2927 (m), 2857 (m), 1509 (m), 1457 (w), 1378 (w), 1330 (w), 1180 (w), 1106 (w), 1021 (w), 943 (w), 815 (vs), 725 (w), 709 (w), 525 (m), 412 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 200 (69), 185 (5), 171 (20), 157 (61), 143 (38), 131 (100), 129 (95), 115 (25), 105 (24), 91 (9); $\boldsymbol{R_f}$ = 0.66 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[33]

4.14 Preparation of oct-1-yn-1-ylbenzene S22



S22

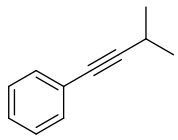
According to GP-3, iodobenzene (0.56 mL, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of 1-octyne (0.88 mL, 6.0 mmol, 1.2 eq.) the reaction

mixture was stirred for 15.5 hours at room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **S22** in a yield of 939.4 mg (5.0 mmol, quantitative) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.38 (m, 2 H), 7.29-7.25 (m, 3 H), 2.40 (t, J = 7.4 Hz, 2 H), 1.64-1.57 (m, 2 H), 1.49-1.42 (m, 2 H), 1.36-1.29 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 131.7, 128.3, 127.6, 124.3, 90.6, 80.7, 31.5, 28.9, 28.8, 22.7, 19.6, 14.2 ppm; **IR** (in $CDCl_3$) ν = 2955 (w), 2928 (m), 2857 (m), 2227 (w), 1598 (w), 1489 (m), 1465 (w), 1442 (w), 1378 (w), 1330 (w), 1069 (w), 1028 (w), 912 (w), 753 (vs), 726 (w), 690 (s), 524 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 186 (30), 171 (2), 157 (15), 143 (52), 129 (54), 115 (100), 102 (18), 91 (23), 77 (7); $\boldsymbol{R_f}$ = 0.58 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[34]

4.15 Preparation of (3-methylbut-1-yn-1-yl)benzene S23



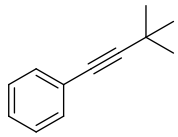
S23

The compound was prepared by a slightly modified general procedure GP-3. Iodobenzene (0.56 mL, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After cooling to 0 °C, *iso*-propylacetylene (0.71 mL, 7.0 mmol, 1.4 eq.) was added and the reaction mixture was stirred for 11.5 hours at 0 °C to room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **S23** in a yield of 707.0 mg (4.90 mmol, 98%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.37 (m, 2 H), 7.31-7.25 (m, 3 H), 2.78 (sept, J = 6.9 Hz, 1H), 1.27 (d, J = 6.8 Hz, 6 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 131.7, 128.3, 127.6, 124.2, 95.9, 79.8, 23.2, 21.3 ppm; **IR** (in $CDCl_3$) ν = 3082 (w), 3058 (w), 2969 (m), 2933 (w), 2871 (w), 2229 (w), 1599 (w), 1489 (m), 1464 (w), 1442 (w), 1383 (w), 1363 (w), 1321 (m), 1158 (w), 1101 (w), 1070 (w), 1027 (w), 942 (w), 913 (w), 754 (vs), 691 (s), 545 (w), 513 (w), 479 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 144 (28), 129 (100), 115 (17), 102 (15), 77 (17); $\boldsymbol{R_f}$ = 0.54 (petroleum ether).

The analytical data are in good accordance with those reported in the literature.[34]

4.16 Preparation of (3,3-dimethylbut-1-yn-1-yl)benzene S24



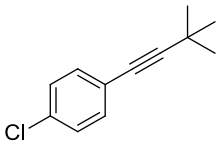
S24

According to GP-3, iodobenzene (0.56 mL, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of *tert*-butylacetylene (0.74 mL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 4 hours at room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **S24** in a yield of 781.9 mg (4.94 mmol, 99%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.37 (m, 2 H), 7.32-7.25 (m, 3 H), 1.33 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 131.7, 128.3, 127.5, 124.2, 98.7, 79.2, 31.2, 28.1 ppm; **IR** (in $CDCl_3$) ν = 3057 (w), 2968 (m), 2927 (w), 2901 (w), 2868 (w), 2238 (w), 1598 (w), 1573 (w), 1489 (w), 1475 (m), 1456 (w), 1443 (w), 1391 (w), 1362 (w), 1289 (m), 1244 (w), 1201 (w), 1070 (w), 1029 (w), 913 (w), 787 (w), 754 (vs), 690 (s), 552 (m), 510 (w), 480 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 158 (28), 143 (100), 128 (59), 115 (31), 102 (9), 77 (12); $\boldsymbol{R_f}$ = 0.59 (petroleum ether).

The analytical data are in good accordance with those reported in the literature.[6]

4.17 Preparation of 1-chloro-4-(3,3-dimethylbut-1-yn-1-yl)benzene S25



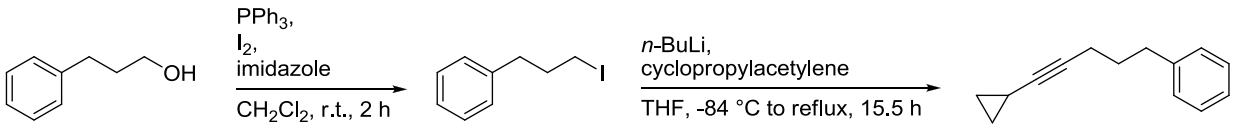
S25

According to GP-3, 1-chloro-4-iodobenzene (1.19 g, 5.0 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol, 2 mol%) and copper(I)-iodide (57.1 mg, 0.3 mmol, 6 mol%) were suspended in triethylamine (15 mL). After addition of *tert*-butylacetylene (0.74 mL, 6.0 mmol, 1.2 eq.) the reaction mixture was stirred for 12 hours at room temperature. Silica gel column chromatography (petroleum ether) after work-up gave product **S25** in a yield of 927.3 mg (4.81 mmol, 96%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2 H), 7.26-7.21 (m, 2 H), 1.31 (s, 9 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 133.4, 132.9, 128.5, 122.7, 99.7, 78.2, 31.1, 28.1 ppm; **IR** (in $CDCl_3$) ν = 2968 (m), 2927 (w), 2901 (w), 2865 (w), 2238 (w), 1897 (w), 1649 (w), 1593 (w), 1488 (s), 1475 (m), 1456 (m), 1397 (w), 1362 (m), 1290 (m), 1244 (w), 1202 (m), 1088 (m),

1015 (m), 915 (m), 825 (s), 702 (m), 549 (m), 511 (m), 482 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 192 (35), 177 (100), 162 (11), 157 (18), 149 (8), 142 (52), 137 (5), 126 (10), 115 (17), 101 (6), 75 (7); **HRMS** (EI, 70 eV): calcd for $C_{12}H_{13}Cl^+$: 192.0706; found: 192.0710 $\boldsymbol{R_f}$ = 0.63 (petroleum ether).

4.18 Preparation of (6,6-dimethylhept-4-yn-1-yl)benzene S27



S26 **S27**

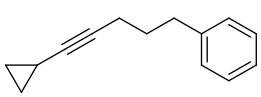
(3-iodopropyl)benzene S26:

The substance was prepared according to a published procedure.[35] A solution of triphenylphosphine (7.87 g, 30.0 mmol, 1.5 eq.) and iodine (7.61 g, 30.0 mmol, 1.5 eq.) in dichloromethane (136 mL, not dried) was stirred for 10 minutes at room temperature. After addition of imidazole (3.40 g, 50.0 mmol, 2.5 eq.), the mixture was stirred for another 10 minutes, then 3-phenyl-1-propanol (2.70 mL, 20.0 mmol, 1.0 eq.) was added and stirring was continued for 2 hours. The reaction was quenched with a saturated aqueous sodium metabisulphite solution (90 mL). Separation of the layers and extraction of the aqueous layer with dichloromethane (3 x 45 mL) followed by drying of the combined organic layers over magnesium sulphate and removal of the solvent in the vacuum gave the crude product. The purified product was isolated after silica gel column chromatography (petroleum ether/ethyl acetate – 20/1) in a yield of 4.89 g (19.9 mmol, 99%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.32-7.18 (m, 5 H), 3.17 (t, *J* = 6.9 Hz, 2 H), 2.73 (t, *J* = 7.3 Hz, 2 H), 2.18-2.08 (m, 2 H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 140.5, 128.7, 128.6, 126.3, 36.4, 35.0, 6.5 ppm; **IR** (in $CDCl_3$) *v* = 3084 (w), 3061 (w), 3025 (w), 2932 (w), 2853 (w), 1603 (w), 1495 (m), 1453 (m), 1424 (w), 1348 (w), 1263 (w), 1213 (m), 1166 (w), 1074 (w), 1029 (w), 955 (w), 908 (w), 851 (w), 792 (w), 741 (m), 698 (vs), 615 (w), 589 (w), 576 (w), 552 (w), 488 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 246 (52), 154 (2), 119 (19), 91 (100), 77 (3); $\boldsymbol{R_f}$ = 0.71 (petroleum ether/ethyl acetate – 20/1).

The analytical data are in good accordance with those published in the literature.[36]

Preparation of (5-cyclopropylpent-4-yn-1-yl)benzene S27

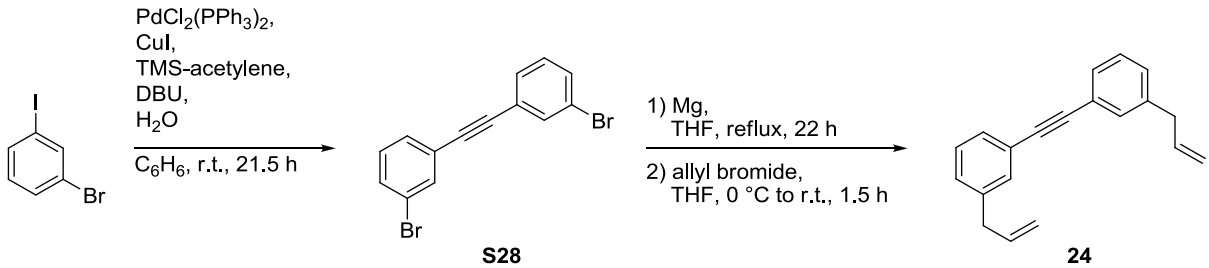


S27

The substance was prepared in analogy to a literature-known procedure.[37] The solution of cyclopropylacetylene (0.51 mL, 6.0 mmol, 1.2 eq.) in tetrahydrofuran (21 mL) in a 50 mL-round-bottomed Schlenk flask was cooled to -84 °C (ethyl acetate/liquid nitrogen-slush bath). A *n*-butyllithium solution (3.75 mL, 6.0 mmol, 1.2 eq., 1.6 M in hexanes) was added dropwise followed by warming to room temperature and addition of (3-iodopropyl)benzene **S26** (0.80 mL, 5.0 mmol, 1.0 eq.). The reaction mixture was heated to reflux for 15.5 hours, then cooled to 0 °C and quenched with a saturated aqueous ammonium chloride solution (15 mL). After phase separation, the aqueous layer was extracted with diethyl ether (3 x 15 mL) and the combined organic layers were washed with demineralised water (15 mL) and dried over sodium sulphate. The solvent was removed under reduced pressure and the product was isolated by silica gel column chromatography (petroleum ether/ethyl acetate – 40/1) in a yield of 912.9 mg (4.95 mmol, 99%) as a colourless oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.29-7.25 (m, 2 H), 7.19-7.15 (m, 3 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 2.12 (dt, *J* = 7.0 Hz, 1.9 Hz, 2 H), 1.79-1.72 (m, 2 H), 1.24-1.16 (m, 1 H), 0.73-0.68 (m, 2 H), 0.60-0.56 (m, 2 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 142.4, 128.9, 128.7, 126.2, 84.0, 75.4, 35.2, 31.2, 18.5, 8.2, -0.2 ppm; **IR** (in CD_2Cl_2) *v* = 3087 (w), 3025 (w), 2938 (w), 2858 (w), 1603 (w), 1496 (w), 1454 (m), 1361 (w), 1202 (w), 1080 (w), 1050 (w), 1028 (w), 960 (w), 908 (w), 881 (w), 811 (w), 744 (m), 698 (vs), 597 (w), 568 (w), 488 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 184 (15), 169 (69), 155 (69), 141 (58), 128 (41), 115 (17), 104 (55), 91 (100), 77 (46), 65 (21); **HRMS** (EI, 70 eV): calcd for $C_{14}H_{16}^+$: 184.1252; found: 184.1245; R_f = 0.50 (petroleum ether/ethyl acetate – 40/1).

4.19 Preparation of 1,2-*bis*(3-allylphenyl)ethyne 24



1,2-*bis*(3-bromophenyl)ethyne S28:

The compound was prepared according to a literature-known procedure.[38] $PdCl_2(PPh_3)_2$ (842.0 mg, 1.2 mmol, 6 mol%) and copper(I)-iodide (381.0 mg, 2.0 mmol, 10 mol%) were suspended in benzene (100 mL) followed by addition of 1-bromo-2-iodobenzene (2.6 mL, 20.0 mmol, 1.0 eq.) and DBU (17.9 mL, 120.0 mmol, 6.0 eq.). After dropwise addition of TMS-acetylene (1.42 mL, 10.0 mmol, 0.5 eq.) and demineralised water (0.14 mL, 8.0 mmol, 0.4 eq.) the reaction vessel was completely covered in aluminium foil. The reaction mixture

was stirred for 21.5 hours at room temperature and was then taken up in a mixture of diethyl ether/tetrahydrofuran/water – 100 mL/180 mL/100 mL. After phase separation, the organic layer was washed with aqueous hydrochloric acid (10%, 3 x 80 mL) and saturated aqueous sodium chloride solution (80 mL). The organic layer was dried over sodium sulphate and the volatiles were removed under reduced pressure. The crude product was purified by adsorbing on silica gel followed by silica gel column chromatography (eluent: petroleum ether/ethyl acetate – 100/0 to 40/1), the title compound was obtained in a yield of 2.95 g (8.78 mmol, 88%) as a colourless solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.69 (t, J = 1.7 Hz, 2 H), 7.53-7.46 (m, 4 H), 7.26 (t, J = 7.9 Hz, 2 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 134.7, 132.2, 130.7, 130.4, 125.1, 122.5, 89.3 ppm; **IR** (in $CDCl_3$) ν = 3062 (w), 2009 (w), 1593 (s), 1557 (m), 1479 (s), 1453 (w), 1403 (w), 1289 (w), 1148 (w), 1088 (w), 1072 (w), 995 (w), 890 (m), 780 (vs), 710 (w), 679 (s) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 336 (100), 176 (58), 150 (17); $\boldsymbol{R_f}$ = 0.70 (petroleum ether).

The analytical data are in good accordance with those published in the literature.[38]

1,2-*bis*(3-allylphenyl)ethyne 24:

Aryl bromide **S28** was dissolved in tetrahydrofuran (12 mL) under nitrogen atmosphere and was added dropwise to a suspension of magnesium turnings (189.0 mg, 7.75 mmol, 2.1 eq., oxide coating was removed by washing with 1 N hydrochloric acid, demineralised water and acetone) in tetrahydrofuran (6 mL). This mixture was heated to reflux for 22 hours. After cooling to 0 °C, allyl bromide (1.3 mL, 14.75 mmol, 4.0 eq.) was added. After warming to room temperature, the reaction mixture was stirred for 1.5 hours. The reaction was quenched by addition of a saturated aqueous ammonium chloride solution (20 mL). After phase separation, the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over sodium sulphate and the solvents were removed under reduced pressure. Purification by silica gel column chromatography (eluent: petroleum ether) gave the product **24** in a yield of 539.4 mg (2.1 mmol, 57%) as a colourless oil.

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.38-7-35 (m, 4 H), 7.32-7.27 (m, 2H), 7.20-7.17 (m, 2 H), 6.06-5.92 (m, 2 H), 5.15-5.08 (m, 4 H), 3.40 (d, J = 6.7 Hz, 4 H) ppm; **^{13}C NMR** (75 MHz, CD_2Cl_2) δ = 140.9, 137.5, 132.1, 129.7, 129.2, 128.9, 123.6, 116.3, 89.6, 40.3 ppm; **IR** (in $CDCl_3$) ν = 3078 (w), 3059 (w), 3039 (w), 3005 (w), 2978 (w), 2904 (w), 2851 (w), 1639 (m), 1601 (s), 1579 (m), 1488 (m), 1432 (m), 1170 (w), 1088 (w), 993 (m), 969 (w), 915 (vs), 790 (s), 765 (m), 710 (m), 691 (s), 660 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 258 (100), 241 (8), 228 (11), 215 (39), 202 (25), 189 (14), 141 (5), 115 (11); **HRMS** (EI, 70 eV): calcd for $C_{20}H_{18}^+$: 258.1409; found: 258.1408; $\boldsymbol{R_f}$ = 0.37 (petroleum ether).

5. Competition Experiments

5.1 Comparison to Different Catalytic Systems

For benchmarking purposes, we compared our catalytic systems to established procedures, namely those of Tsuji *et al.*[39] and Knochel and coworkers.[40] We started with substrate **S29** that was also used in the aforementioned publications. Experimental conditions as detailed in the respective publication were used for these experiments. The synthesis and analytical data of the two ligands employed in Tsuji's conditions are given below. With our conditions, we obtained the vinylboronates **S30A** and **S30B** in moderate to good yields and regioselectivities (Table S13, entries 1 and 4). Control reactions in absence of catalyst or in presence of free phosphine ligand were negative (entries 2, 3, 5 and 6), therefore we can exclude a possible uncatalysed background reaction as exemplified by Knochel's work.[40] When reacting substrate **S29** with *in-situ* formed pinacolborane, the products were isolated in a yield of 40% in a ratio of regioisomers of **S30A/S30B** – 73/27 (entry 7). Concerning the regioselectivity, this result is comparable to our HBpin-conditions, further highlighting that the observed regioselectivity is caused by the nature of the substrate rather than the catalyst itself. Control reactions in which commercial pinacolborane was used did not give any conversion to the products, regardless of the concentration of the reaction mixture (entries 8 and 9). Dimethylsulfide as additive also gave a negative result (entry 10). These findings imply that the method by Knochel *et al.*[40] is not completely uncatalysed, which is backed up by a ^{11}B NMR investigation of the *in-situ* formed pinacolborane (see figure S2). This NMR shows two additional peaks besides the signal for pinacolborane. The absence of any apparent multiplet structure of those signals suggest the formation of higher boronate aggregates that might act as the catalyst. When using Tsuji's B_2pin_2-conditions[39], we were able to reproduce the published results for the regioselectivity although we obtained a slightly higher yield (entry 11). For the related HBpin-conditions with the MeAr-Xantphos ligand, product was only formed in traces (entry 12).

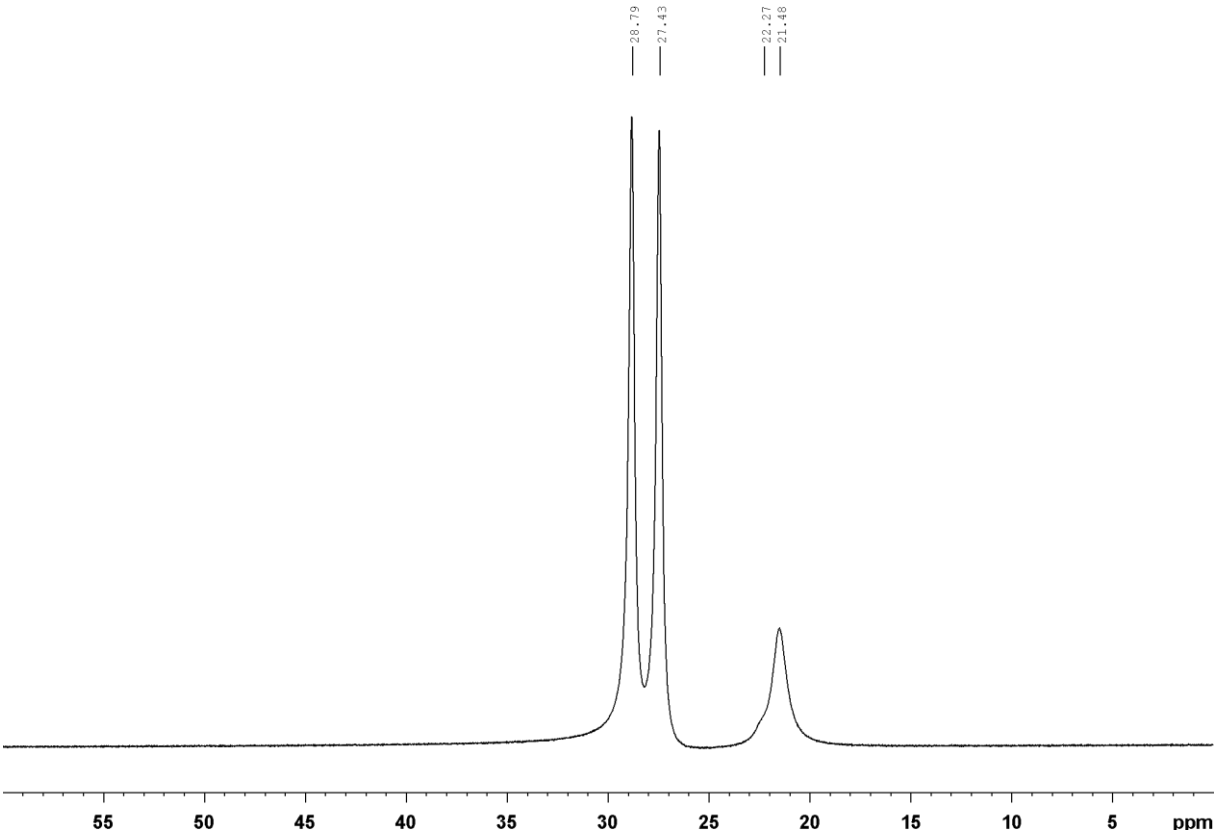
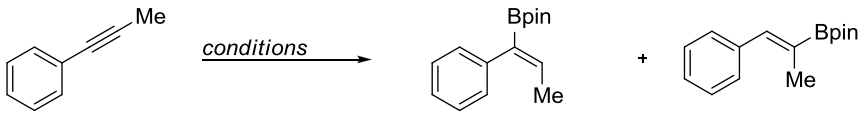


Figure S2: ^{11}B NMR spectrum (128 MHz, CD_2Cl_2) of the *in-situ* formed HBpin according to Knochel's procedure. The HBpin doublet appears at δ = 28.1 ppm, *J* = 174.5 Hz. The hypothetically catalytically active impurities appear at δ = 22.8 ppm (broad shoulder) and 21.5 ppm, respectively.

Table S13: Method Comparison – Phenylpropyne **S29**.



S29 **S30A** **S30B**

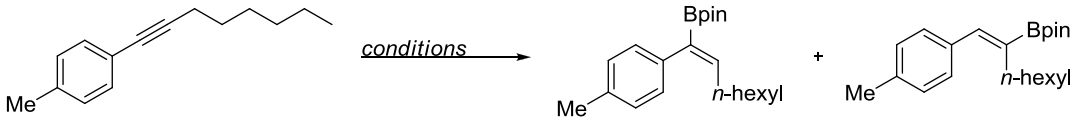
Entry[a]	Conditions	Yield / %[b]	**A/B**[c]
1	**1a** (5 mol%), HBpin (2.2 eq.), PhMe, 80 °C, 18 h	87	76/24
2	HBpin (2.2 eq.), PhMe, 80 °C, 18 h	0	--
3	PPh_3 (10 mol%), HBpin (2.2 eq.), PhMe, 80 °C, 18 h	0	--
4	**1a** (0.5 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	52	11/89

5	B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	0	--
6	PPh_3 (10 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	0	--
7	Pinacol (2 eq.), BH_3*Me_2S (2 eq.), CH_2Cl_2, 0 °C – r.t., 8 h	40	73/27
8	HBpin (2 eq.), CH_2Cl_2 (5.0 M), 0 °C – r.t., 8 h	0	--
9	HBpin (2 eq.), CH_2Cl_2 (2.5 M), 0 °C – r.t., 8 h	0	--
10	HBpin (2 eq.), CH_2Cl_2 (5.0 M), Me_2S (5.0 M), 0 °C – r.t., 8 h	0	--
11	CuCl (2 mol%), CF_3Ar-Xan (2 mol%), NaO*t*-Bu (12 mol%), B_2pin_2 (1.2 eq.), PhMe, r.t. – 28 °C, 3 h	98	>1/99
12	CuCl (2 mol%), MeAr-Xan (2 mol%), NaO*t*-Bu (12 mol%), HBpin (1.5 eq.), PhMe, 0 °C – r.t., 20 h	<5	60/40[d]

[a] Reactions were run on 0.5 mmol scale. [b] Isolated yield. [c] Determined by GC integration. [d] Due to low signal/noise ratio, an exact integration of the GC peaks was not possible.

In addition, we used the arylalkylalkyne **23** of our substrate scope as a second reference point. The results for our method can be found in the manuscript. To further exclude a non-catalysed pathway, we again perfomed control reactions (Table S14, entries 1 to 4). We did not observe product formation in any case. Knochel's conditions[40] gave moderate amounts of product in comparable regioselectivity to our method (**16A**/**16B** – 82/18 vs. 75/25, entry 5). Again, control reactions with commercial HBpin in absence or presence of dimethylsulfide did not result in any conversion to the vinylboronate products (entries 6 and 7). Tsuji's conditions[39] with B_2pin_2 and HBpin led to isolated yields of 83% of **16B** and 45% of **16A** in nearly exclusive regioselectivity. We also tested KO*t*-Bu instead of NaO*t*-Bu as base, with identical result (entry 9). To probe the influence of the Xantphos-type ligands and the boron source on the outcome of the reaction, we decided to set up two experiments in which the ligands were exchanged (entries 11 and 12). For both reactions, yields were quite low. In the case of CF_3Ar-Xan and HBpin, we also observed a lower regioselectivity (entry 11), but for MeAr-Xan/B_2pin_2 product formation occurred in almost exclusive regioselectivity (entry 12). These reactions show that the chosen ligand is mostly responsible for achieving high yields. The observed regioselectivities are still very high, regardless of the ligand. Rather, the regioselectivity of the reaction is dictated by the boron source used which is in line with our findings as well. The use of HBpin leads to preferential formation of products **A**, whereas with B_2pin_2 as boron source the products **B** are obtained.

Table S14: Method Comparison – Alkyne **23**.



23 **16A** **16B**

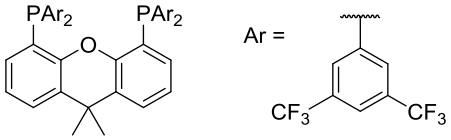
Entry[a]	Conditions	Yield / %[b]	**A/B**[c]
1	HBpin (2.2 eq.), PhMe, 80 °C, 18 h	0	--
2	PPh_3 (10 mol%), HBpin (2.2 eq.), PhMe, 80 °C, 18 h	0	--
3	B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	0	--
4	PPh_3 (10 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	0	--
5	Pinacol (2 eq.), BH_3*Me_2S (2 eq.), CH_2Cl_2, 0 °C – r.t., 8 h	42	82/18
6	HBpin (2 eq.), CH_2Cl_2 (5.0 M), 0 °C – r.t., 8 h	0	--
7	HBpin (2 eq.), CH_2Cl_2 (5.0 M), Me_2S (5.0 M), 0 °C – r.t., 8 h	0	--
8	CuCl (2 mol%), CF_3Ar-Xan (2 mol%), NaO*t*-Bu (12 mol%), B_2pin_2 (1.2 eq.), PhMe, r.t. – 28 °C, 3 h	83	2/98
9	CuCl (2 mol%), CF_3Ar-Xan (2 mol%), KO*t*-Bu (12 mol%), B_2pin_2 (1.2 eq.), PhMe, r.t. – 28 °C, 3 h	88	2/98
10	CuCl (2 mol%), MeAr-Xan (2 mol%), NaO*t*-Bu (12 mol%), HBpin (1.5 eq.), PhMe, 0 °C – r.t., 20 h	45	92/8
11	CuCl (2 mol%), CF_3Ar-Xan (2 mol%), NaO*t*-Bu (12 mol%), HBpin (1.5 eq.), PhMe, 0 °C – r.t., 20 h	34	87/13
12	CuCl (2 mol%), MeAr-Xan (2 mol%), NaO*t*-Bu (12 mol%), B_2pin_2 (1.2 eq.), PhMe, r.t. – 28 °C, 3 h	24	3/97

[a] Reactions were run on 0.5 mmol scale. [b] Isolated yield. [c] Determined by GC integration.

5.2 Preparation of the Xantphos ligands

Both CF_3Ar-Xan and MeAr-Xan were prepared in accordance to the procedure published by Tsuji.[39]

Preparation of CF_3Ar-Xan

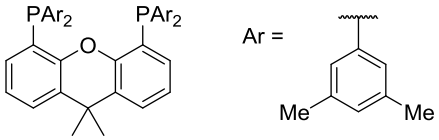


A solution of 9,9-dimethylxanthene (159.9 mg, 0.73 mmol, 1.0 eq.) and TMEDA (0.28 mL, 1.83 mmol, 2.5 eq.) in diethyl ether (2.4 mL) was cooled to 0 °C. At this temperature, a solution of *n*-butyl lithium (0.73 mL, 1.83 mmol, 2.5 eq. 2.5 M in hexanes) was added dropwise. The resulting red reaction mixture was stirred overnight (16 hours) while gradually warming up to room temperature. The mixture was cooled to -84 °C (ethyl acetate/liq. N_2-slush bath) and a solution of *bis*(3,5-di(trifluoromethyl)phenyl)chlorophosphine (1.00 g, 2.04 mmol, 2.8 eq.) in diethyl ether (3.0 mL) was added. After warming to room temperature, the reaction mixture was stirred for 24 hours. The solvent was removed under reduced pressure and the crude product was taken up in dichlormethane (4.0 mL). After washing with demineralised water (4.0 mL), the layers were separated. The organic layer was again washed with demineralised water (2 x 4.0 mL) and the combined organic phases were dried over magnesium sulphate. After removal of the solvent at the rotary evaporator, the crude product was purified by silica gel column chromatography (petroleum ether) and subsequent HPLC (petroleum ether/ethyl acetate – 100/1). The product was obtained in a yield of 551.9 mg (0.49 mmol, 67%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (s, 4 H), 7.61 (s, 8 H), 7.57 (d, J = 7.6 Hz, 2 H), 7.12 (t, J = 7.7 Hz, 2 H), 6.40 (dd, J = 7.5 Hz, 1.7 Hz, 2 H), 1.67 (s, 6 H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -63.1 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ = -14.5 ppm; **IR** (in $CDCl_3$) ν = 2978 (m), 2919 (m), 2850 (m), 1647 (w), 1446 (w), 1371 (s), 1323 (s), 1259 (m), 1214 (w), 1144 (vs), 1010 (m), 1080 (m), 1009 (m), 911 (m), 894 (m), 869 (w), 847 (m), 680 (w) cm^{-1}; **MS** (EI, 70 eV): *m*/*z* (%): 1122 (100), 1107 (77), 631 (6), 561 (14), 412 (8); **HRMS** (ESI): calcd for $C_{47}H_{24}F_{24}OP_2$: 1122.0919; found: 1122.0930; $\boldsymbol{R_f}$ = 0.32 (petroleum ether/ethyl acetate – 90/1).

The analytical data are in good accordance with those reported in the literature.[39]

Preparation of MeAr-Xan

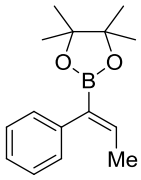


A solution of 9,9-dimethylxanthene (282.6 mg, 1.29 mmol, 1.0 eq.) and TMEDA (0.49 mL, 3.23 mmol, 2.5 eq.) in diethyl ether (4.3 mL) was cooled to 0 °C. At this temperature, a solution of *n*-butyl lithium (1.29 mL, 3.23 mmol, 2.5 eq., 2.5 M in hexanes) was added dropwise. The reaction mixture was stirred overnight (18 hours) while gradually warming to room temperature. After cooling to -84 °C (ethyl acetate/liq. N_2-slush bath) a solution of *bis*(3,5-dimethylphenyl)chlorophosphine (1.00 g, 3.61 mmol, 2.8 eq.) in diethyl ether (5.3 mL) was added. After warming to room temperature, the mixture was stirred for 29.5 hours. The solvent was evaporated under reduced pressure and the crude residue was taken up in dichloromethane (7.0 mL). The organic phase was washed with demineralised water (7.0 mL) and the layers were separated. The organic layer was washed again with demineralised water (2 x 7.0 mL) and the combined organic phases were dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane – 10/1 to 7/1 to 3/1) followed by HPLC (petroleum ether/ethyl acetate – 100/1). The title compound was obtained in a yield of 53.4 mg (0.08 mmol, 6%) as a colourless foamy solid.

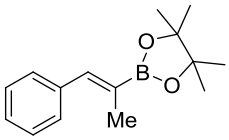
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (dd, J = 7.7 Hz, 1.0 Hz, 2 H), 6.97 (t, J = 7.6 Hz, 2 H), 6.85 (s, 4 H), 6.80 (t, J = 3.2 Hz, 8 H), 6.58-6.56 (m, 2 H), 2.18 (s, 24 H), 1.65 (s, 6 H) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ = -17.2 ppm; **IR** (in $CDCl_3$) ν = 3022 (w), 2979 (w), 2917 (w), 2858 (w), 1599 (w), 1582 (w), 1563 (w), 1461 (w), 1433 (w), 1401 (vs), 1283 (w), 1237 (m), 1198 (w), 1146 (w), 1126 (w), 1068 (w), 1037 (w), 994 (w), 908 (m), 882 (w), 846 (m), 787 (w), 731 (m), 692 (m), 642 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 691 (100), 467 (19), 381 (15); **HRMS** (ESI): calcd for $C_{47}H_{49}OP_2^+$: 691.3253; found: 691.3254; $\boldsymbol{R_f}$ = 0.48 (petroleum ether/dichloromethane – 3/1).

The analytical data are in good accordance with those reported in the literature.[39]

5.3 Preparation of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane S30A and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane S30B



S30A



S30B

Method A (HBpin as boron source):

According to GP-1, 1-phenyl-1-propyne (62 µL, 0.5 mmol, 1.0 eq.), **1a** (16.0 mg, 0.025 mmol, 5 mol%) and pinacolborane (160 µL, 1.1 mmol, 2.2 eq.) were stirred for 18 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **S30** was isolated in a yield of 106.0 mg (0.43 mmol, 87%) as a colourless oil as a regioisomeric mixture of **S30A**/**S30B**-76/24.

Method B (B_2pin_2 as boron source):

According to GP-2, 1-phenyl-1-propyne (62 mg, 0.5 mmol, 1.0 eq.), **1a** (0.75 mL of the stock solution in dry THF, 0.5 mol%), sodium methoxide (0.25 mL of the stock solution in dry methanol) and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 eq.) were stirred for 9 hours at 80 °C. After column chromatography on silica gel (petroleum ether/ethyl acetate – 40/1), vinylboronate **S30** was isolated in a yield of 64.0 mg (0.26 mmol, 52%) as a colourless oil as a regioisomeric mixture of **S30A**/**S30B**-11/89. The regioisomers **S30A** and **S30B** were separated by HPLC (petroleum ether/ethyl acetate – 100/0 to 100/1).

Analytical data for S30A:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.30 (m, 2H), 7.22-7.14 (m, 3H), 6.72 (q, *J* = 7.0 Hz, 1H), 1.77 (d, *J* = 7.0 Hz, 3H), 1.27 (s, 12H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.8, 140.0, 129.2, 127.9, 126.0, 83.6, 24.9, 16.1 ppm; **IR** (in $CDCl_3$) ν = 2977 (m), 2932 (w), 1618 (w), 1600 (w), 1494 (m), 1469 (w), 1439 (w), 1407 (m), 1386 (s), 1370 (m), 1334 (s), 1304 (s), 1271 (m), 1214 (w), 1192 (m), 1144 (vs), 1104 (w), 1074 (w), 1032 (w), 1007 (m), 985 (m), 958 (w), 920 (w), 855 (s), 833 (w), 778 (w), 758 (m), 699 (s), 675 (m), 620 (w), 579 (w), 552 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 267 (40), 245 (12), 225 (4), 201 (6), 189 (11), 177 (17), 159 (10), 145 (100), 133 (15), 117 (29), 101 (14); **HRMS** (ESI): calcd for $C_{15}H_{21}BO_2Na^+$: 267.1530; found: 267.1527; R_f = 0.46 (petroleum ether/ethyl acetate – 40/1).

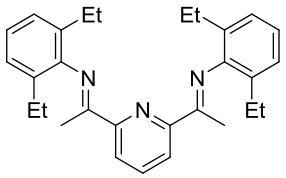
Analytical data for S30B:

^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.40-7.32 (m, 4H), 7.27-7.21 (m, 1H), 7.18 (d, *J* = 1.5 Hz, 1H), 1.95 (d, *J* = 1.7 Hz, 3H), 1.29 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 142.5, 138.1, 129.6, 128.2, 1267.2, 83.7, 25.0, 16.1 ppm; **IR** (in CD_2Cl_2) *v* = 2978 (m), 2928 (w), 2861 (w), 1617 (w), 1574 (w), 1491 (w), 1448 (w), 1405 (m), 1367 (vs), 1346 (s), 1311 (s), 1271 (m), 1208 (w), 1146 (s), 1105 (s), 1031 (w), 984 (w), 960 (w), 924 (w), 865 (m), 838 (w), 752 (m), 699 (m), 668 (m), 522 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%):267 (12(, 240(2), 227 (4), 217 (9), 145 (16), 131 (9), 117 (100), 101 (2); **HRMS** (ESI): calcd for $C_{15}H_{21}BO_2Na^+$: 267.1530; found: 267.1530; R_f = 0.46 (petroleum ether/ethyl acetate – 40/1).

The analytical data are in good accordance with those reported in the literature.[39]

5.4 Selectivity – Alkyne vs. Alkene

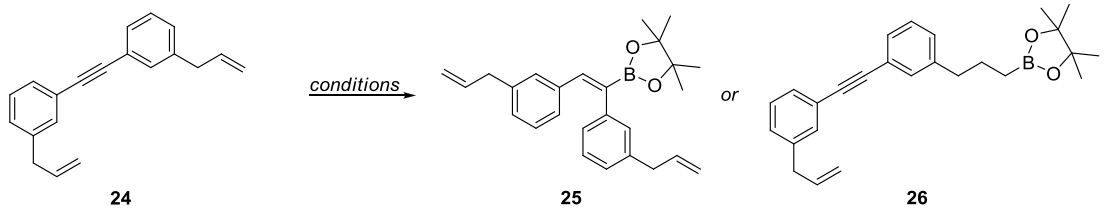
To test the performance of our catalytic system in terms of selectivity towards different unsaturated carbon-carbon bonds, we subjected the *bis*(allyl)alkyne **24** to the catalytic conditions published by Enthaler *et al.*[41] and Thomas,[42] the reactions were carried out as described in the respective publication. The diketiminato ligand **L** (Figure S3) used by Thomas *et al.* was prepared according to their published procedure.[42] The results of this study are summarised in table S15.



L

Figure S3: Diketiminato-ligand **L** as used by Thomas.[42]

Table S15: Competition experiments – alkyne vs. alkene.



24 **25** **26**

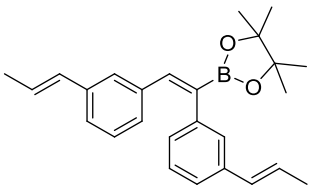
Entry[a]	Conditions	Yield / %[b]	**25/26**[c]
1	**1a** (5 mol%), HBpin (2.2 eq.), PhMe, 80 °C, 3 h	79	94/6
2	**1a** (0.5 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	57	88/12

3[d]	$FeCl_2$ (5 mol%), **L** (5 mol%), EtMgBr (15 mol%), HBpin (1.1 eq.), THF, r.t., 45.5 h	52	95/5[e]
4	$Fe_2(CO)_9$ (2.5 mol%), HBpin (1.25 eq.), PhMe, 100 °C, 24 h	0	-

[a] Reactions were run on 0.5 mmol scale, (*Z*)/(*E*) was ≥97/3 in all cases. [b] Isolated yields. [c] Determined by GC integration. [d] Reaction on 0.7 mmol scale. [e] Determined by isolation of the compounds.

Table S15, entries 1 and 2 repeat the results using our catalytic conditions, either with HBpin as boron source (Table S15, entry 1), or with B_2pin_2 (Table S15, entry 2). With HBpin, the ratio of **25**/**26** shows a clear preference for the alkyne as reactive centre, although statistics and sterics thoroughly favour the alkene. Therefore, a ratio of 94/6 in favour of an addition of the borane to the alkyne is a quite remarkable result. With B_2pin_2, the amount of alkene addition product **26** is a little bit higher compared to HBpin, but still shows a preferential reaction at the alkyne moiety.

In terms of yield, Thomas' conditions (Table S15, entry 3) give a result comparable to our B_2pin_2-protocol. Interestingly, **25** is formed as the major product, although for this method mostly alkene hydroboration was reported, with only two examples of internal alkynes as substrates. Nevertheless, the selectivity towards the alkyne in presence of the two allyl groups was very high. Under Enthaler's conditions (Table S15, entry 4), a mixture of products was obtained in an isolated yield of 85% in a ratio of 88/6/6. Neither **25** nor **26** were formed as the major product, but instead compound **24**, arising from hydroboration of the alkyne and isomerisation of the terminal alkenes to the thermodynamically more stable internal isomers (Figure S4). Unfortunately, we were not able to separate and analyse the side products formed in this reaction.



27

Figure S4: Major product for hydroboration of **24** under Enthalers' conditions.

Analytical data for 27:

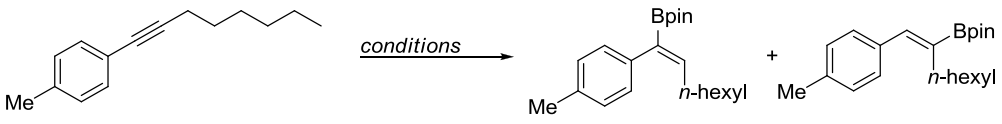
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.34 (s, 1 H), 7.24-7.23 (m, 2 H), 7.14-7.09 (m, 3 H), 7.06-7.02 (m, 1 H), 6.98-6.95 (m, 1 H), 6.90-6.88 (m, 1 H), 6.38 (dq, *J* = 15.8 Hz, 1.5 Hz, 1 H), 6.24-6.15 (m, 2 H), 6.04-5.95 (m, 1 H), 1.86 (dd, *J* = 6.6 Hz, 1.5 Hz, 3 H), 1.81 (dd, *J* = 6.6 Hz, 1.6 Hz, 3 H), 1.32 (s, 12 H) ppm; **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 143.5, 141.6, 138.5, 138.0, 137.5, 131.4, 130.9, 128.9, 128.8, 128.4, 127.8, 127.5, 126.6, 126.4, 126.0,

125.8, 124.1, 84.3, 25.0, 18.6, 18.5 ppm; **IR** (in CD_2Cl_2) ν = 3019 (w), 2977 (w), 2931 (w), 2913 (w), 2852 (w), 1656 (w), 1595 (w), 1575 (w), 1476 (w), 1372 (m), 1335 (s), 1313 (s), 1269 (m), 1215 (w), 1165 (m), 1141 (vs), 1111 (w), 1013 (w), 995 (w), 961 (s), 924 (w), 903 (w), 853 (m), 813 (w), 772 (m), 719 (w), 686 (m), 669 (w) cm^{-1}; **MS** (ESI): *m*/*z* (%): 409 (100), 387 (12), 331 (19), 287 (18), 269 (4), 259 (4), 213 (43); **HRMS** (ESI): calcd for $C_{26}H_{31}BO_2Na^+$: 409.2314; found: 409.2314; R_f = 0.28 (petroleum ether/ethyl acetate – 50/1).

5.5 Selectivity – Unsymmetrical Internal Alkynes

As a second step, we set out to explore the performance of the abovementioned catalytic systems towards unsymmetrical internal alkynes. We chose alkyne **23** for those experiments, because it showed good yields and regioselectivities when used under our conditions. A summary of these investigations can be found in Table S16.

Table S16: Selectivity – unsymmetrical internal alkynes.



23 **16A** **16B**

Entry[a]	Conditions	Yield[b]	**A/B**[c]	***cis*/*trans***[c]
1	**1a** (5 mol%), HBpin (2.2 eq.), PhMe, 80 °C, 18 h	82%	75/25	>99/1
2	**1a** (0.5 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	80%	24/76	>99/1
3	$Fe_2(CO)_9$ (2.5 mol%), HBpin (1.25 eq.), PhMe, 100 °C, 24 h	85%	complex mixture	--
4	$Fe_2(CO)_9$ (0.25 mol%), B_2pin_2 (1.5 eq.), NaOMe (5 mol%), THF/MeOH – 3/1, 80 °C, 9 h	78%	25/75	98/2
5[d]	$FeCl_2$ (5 mol%), **L** (5 mol%), EtMgBr (15 mol%), HBpin (1.1 eq.), THF, r.t., 4 h	92%	24/76	>99/1
6[d]	$FeCl_2$ (0.5 mol%), **L** (0.5 mol%), EtMgBr (1.5 mol%), NaOMe (5 mol%), B_2pin_2 (1.5 eq.), THF/MeOH – 3/1, 80 °C, 9 h	28%	27/73	93/7

[a] Reactions were run on 0.3 mmol scale. [b] Isolated yield. [c] Determined by GC integration. [d] Reaction on 0.7 mmol scale.

As a reference, our results obtained with **1a** and HBpin/B_2pin_2 as detailed in the manuscript are also given (Table S16, entries 1 and 2). In addition to only adapting Enthaler's and Thomas' protocols (Table S16, entries 3 and 5), we also tested their catalysts under our B_2pin_2-conditions (0.5 mol% Fe-source, 1.5 eq. B_2pin_2, THF/MeOH as solvent). The latter

experiments were not only designed to find out if the same reversed regioselectivity as observed by us can be achieved with different catalytic systems when changing the boron source, but also to obtain further insight into possible reactive intermediates (Table S16, entries 4 and 6).

Enthaler's standard protocol using $Fe_2(CO)_9$ and HBpin unfortunately does not lead to selective product formation when employed together with substrate **23**. Instead, a complex mixture of various hydroboration products is obtained according to GC and GC/MS. Based on the result for the symmetrical internal alkyne **24**, those products might arise from triple bond hydroboration and subsequent double-bond isomerisation of the vinylboronate moiety. With B_2pin_2 as the boron source, hydroboration works smoothly with both regioselectivity and yield identical to our B_2pin_2-conditions.

Using Thomas' standard conditions (Table S16, entry 5), alkyne hydroboration is achieved in an excellent yield and regioselectivity as compared to our B_2pin_2-conditions. This suggests that the same catalytic intermediate is present under those reaction conditions. Thomas' catalytic system together with B_2pin_2, NaOMe and THF/MeOH leads to a rather low yield of 28%, but conserved regioselectivity again favouring the isomer **16B** (Table S16, entry 6). For this experiment however, we cannot exclude that the observed product formation stems from the presence of iron-salt based species formed by degradation of the active species as proposed by Thomas. Such a degradation might take place due to the presence of methanol in the reaction mixture.

As a conclusion, the observed regioselectivity in absolute numbers arises rather from the stereoelectronic properties of the starting material than from an influence of the tested catalytic species themselves. In this context, it is noteworthy that among the catalysts used in these experiments, our catalytic system is the only one for which we observed switchable regioselectivity. Therefore, a selective access to either isomers **A** or **B** can be achieved.

6. Literature

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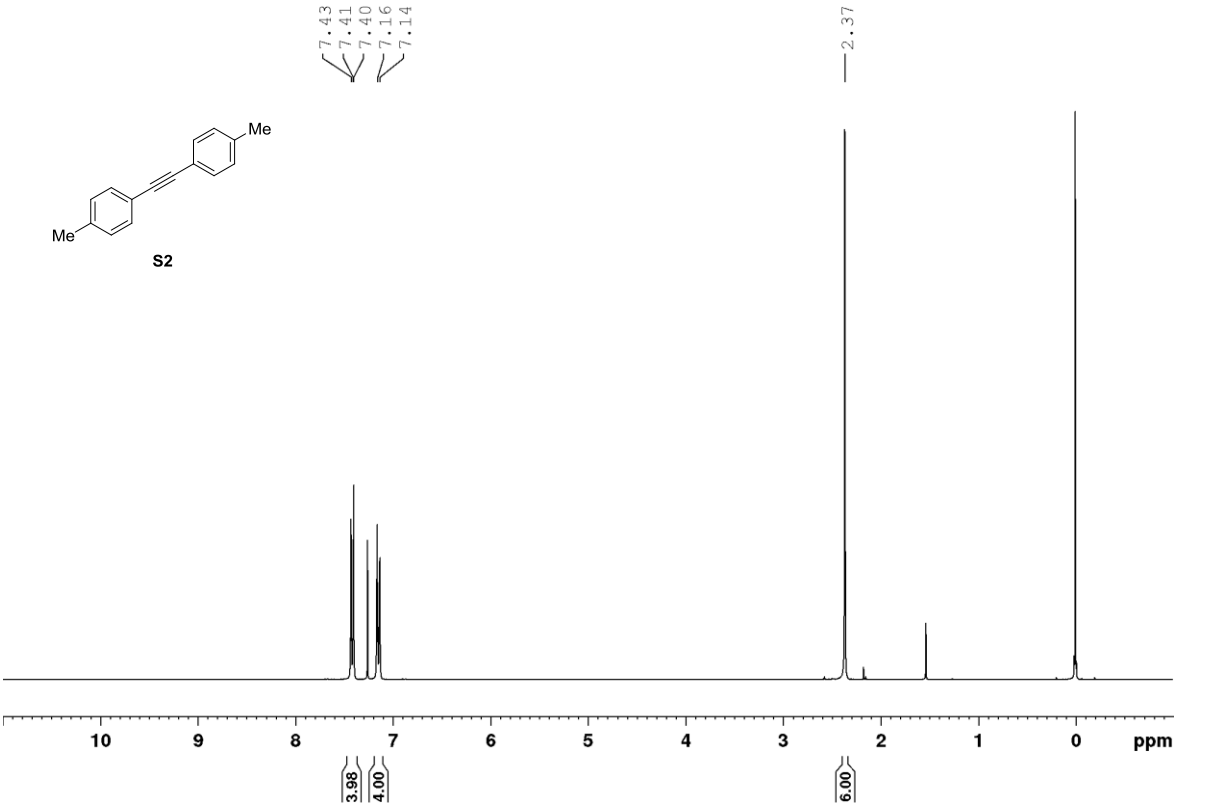
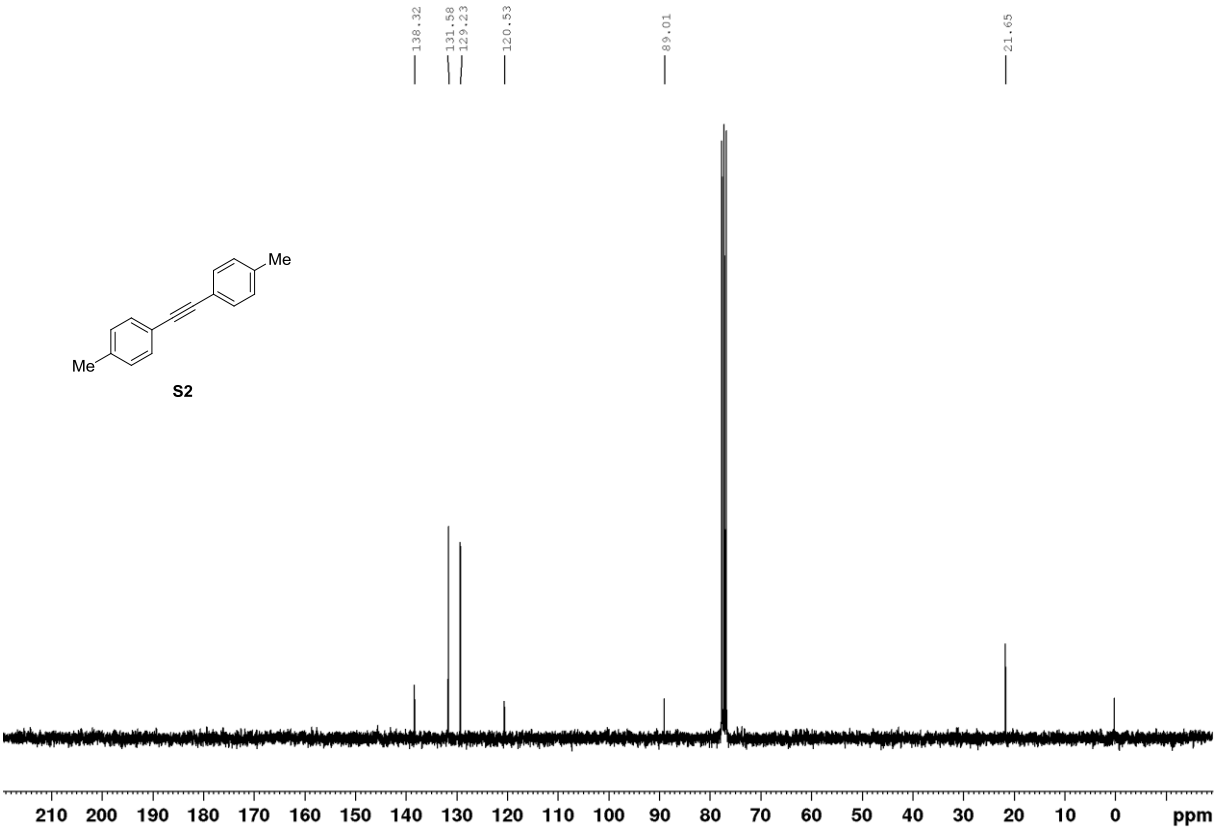
7. NMR Data for Starting Materials and Hydroboration Products

7.1 NMR data for the starting materials

NMR spectra of S2:





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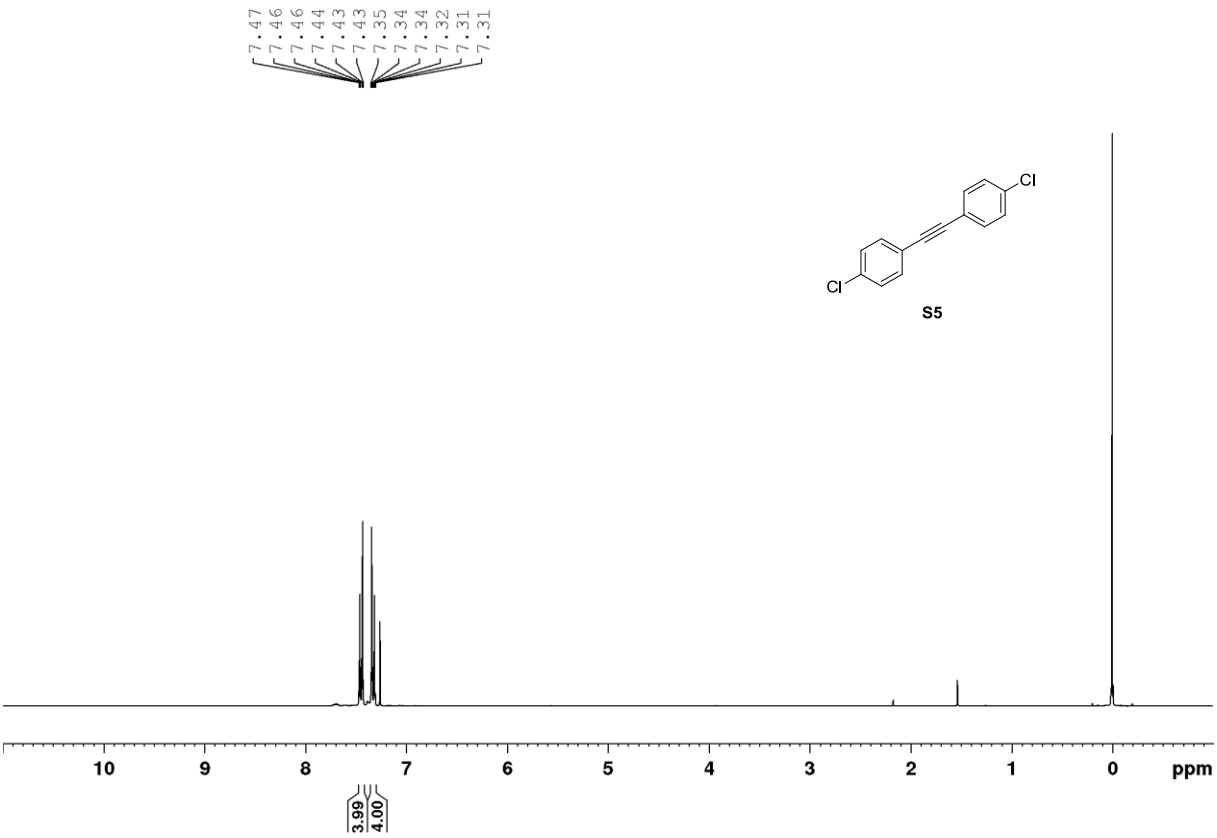

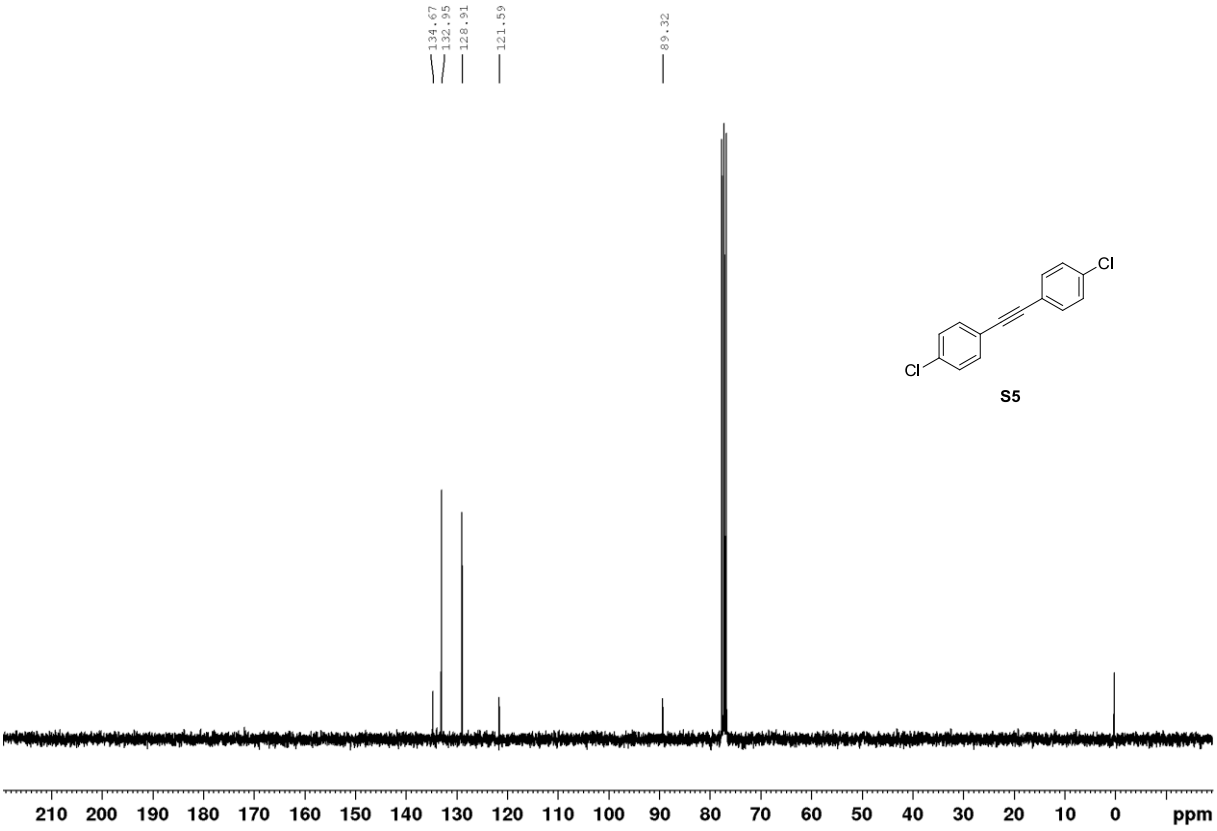

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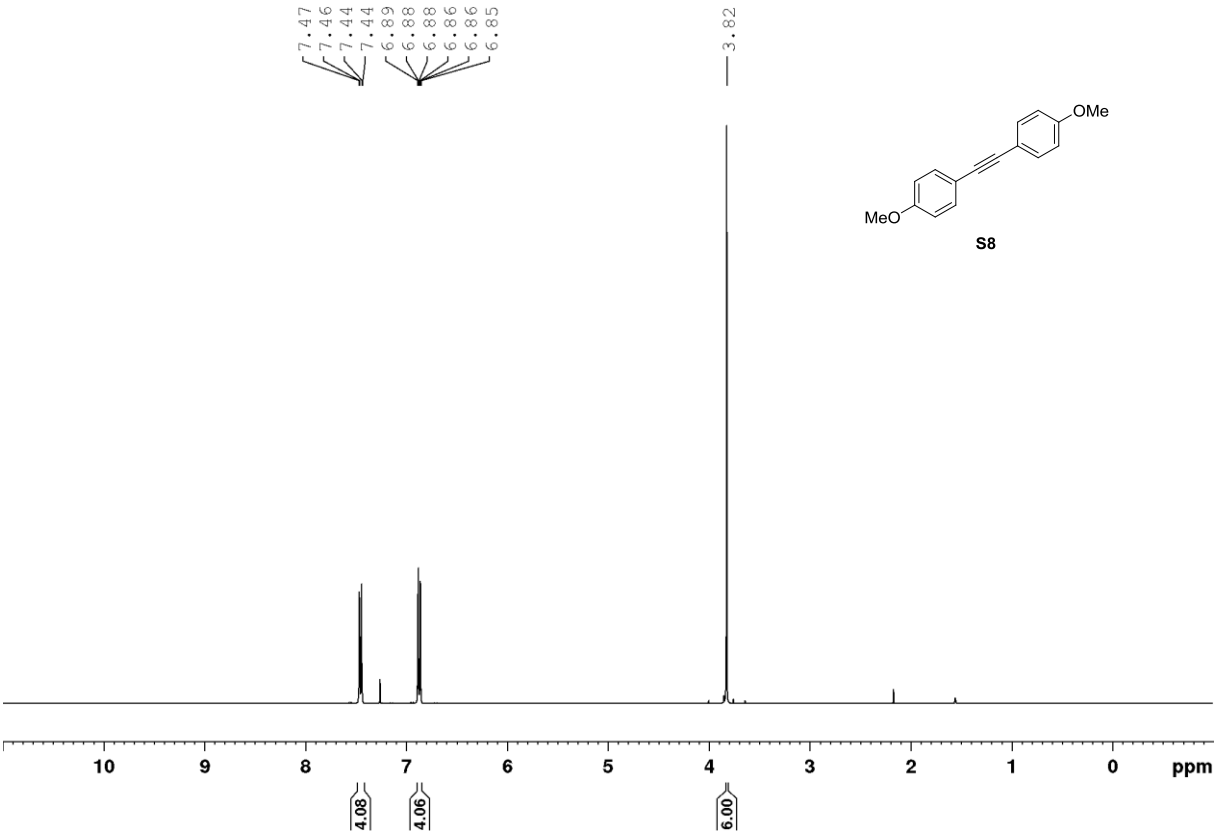

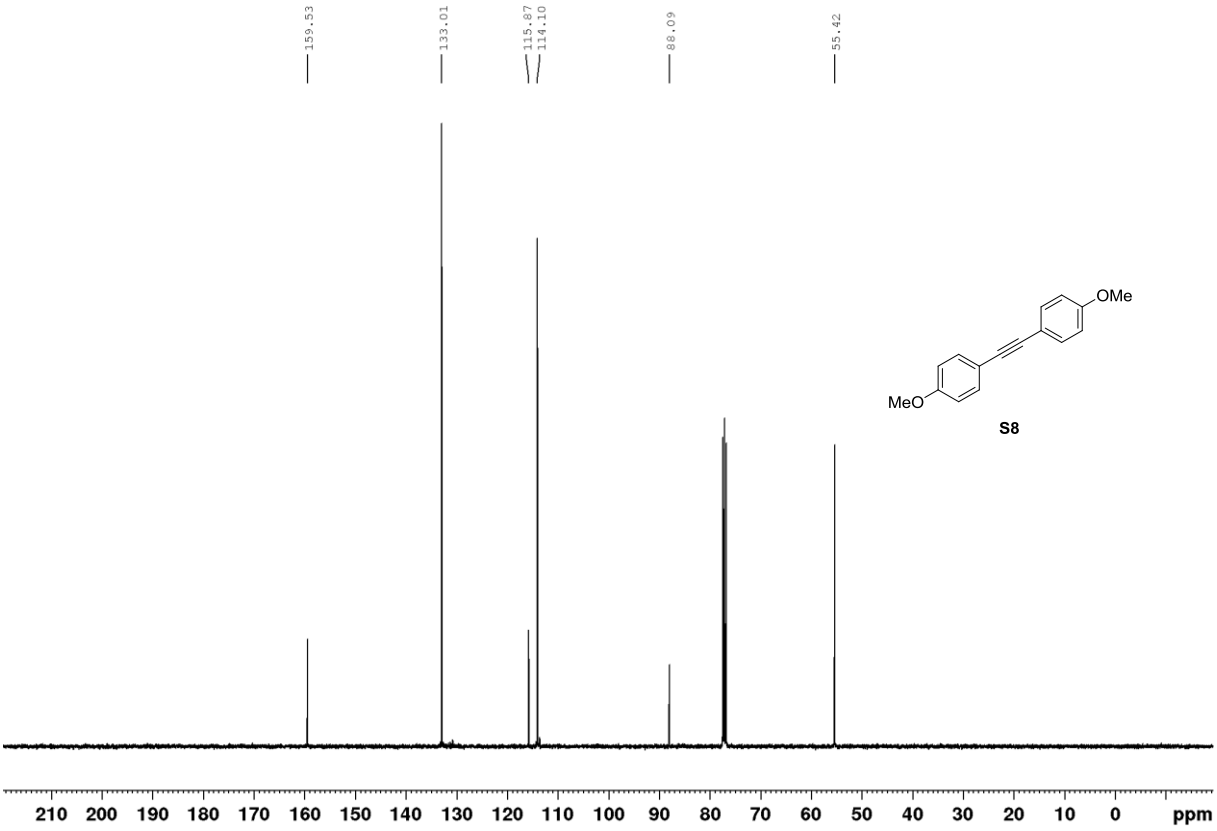

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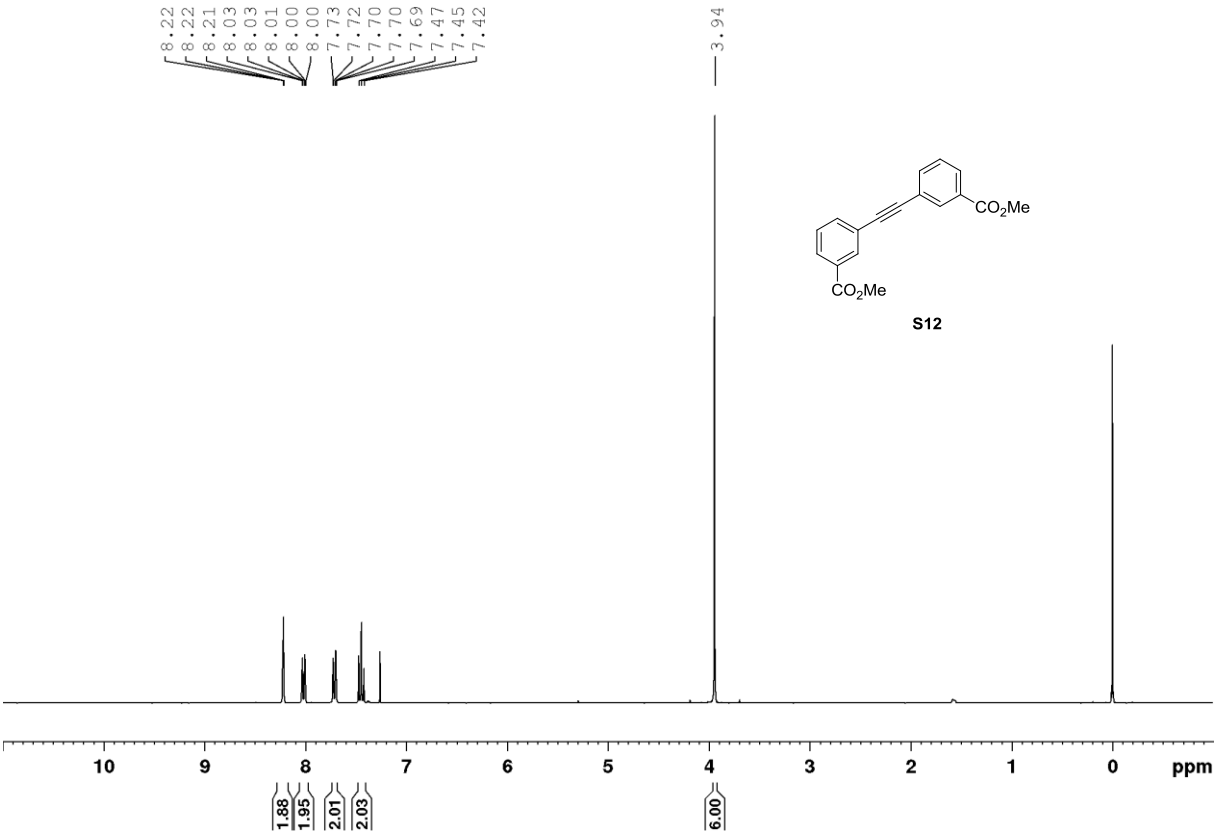

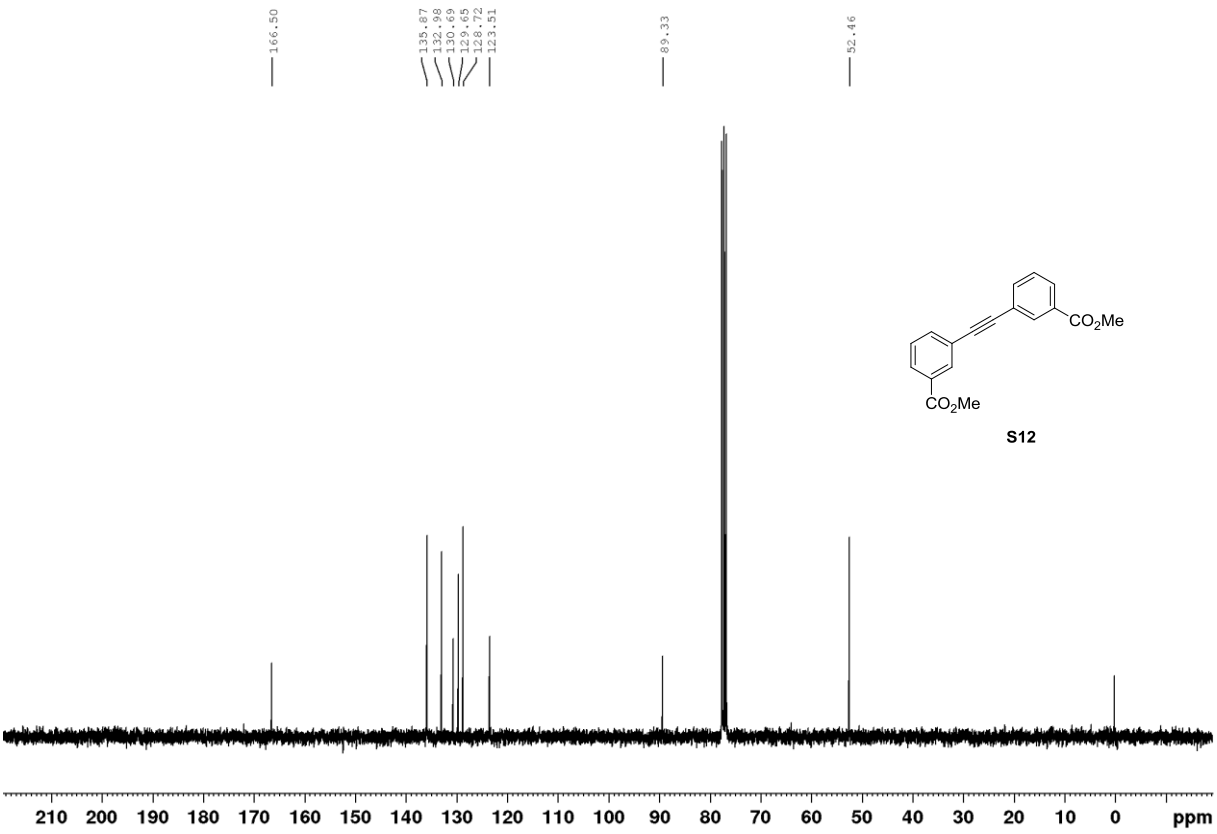

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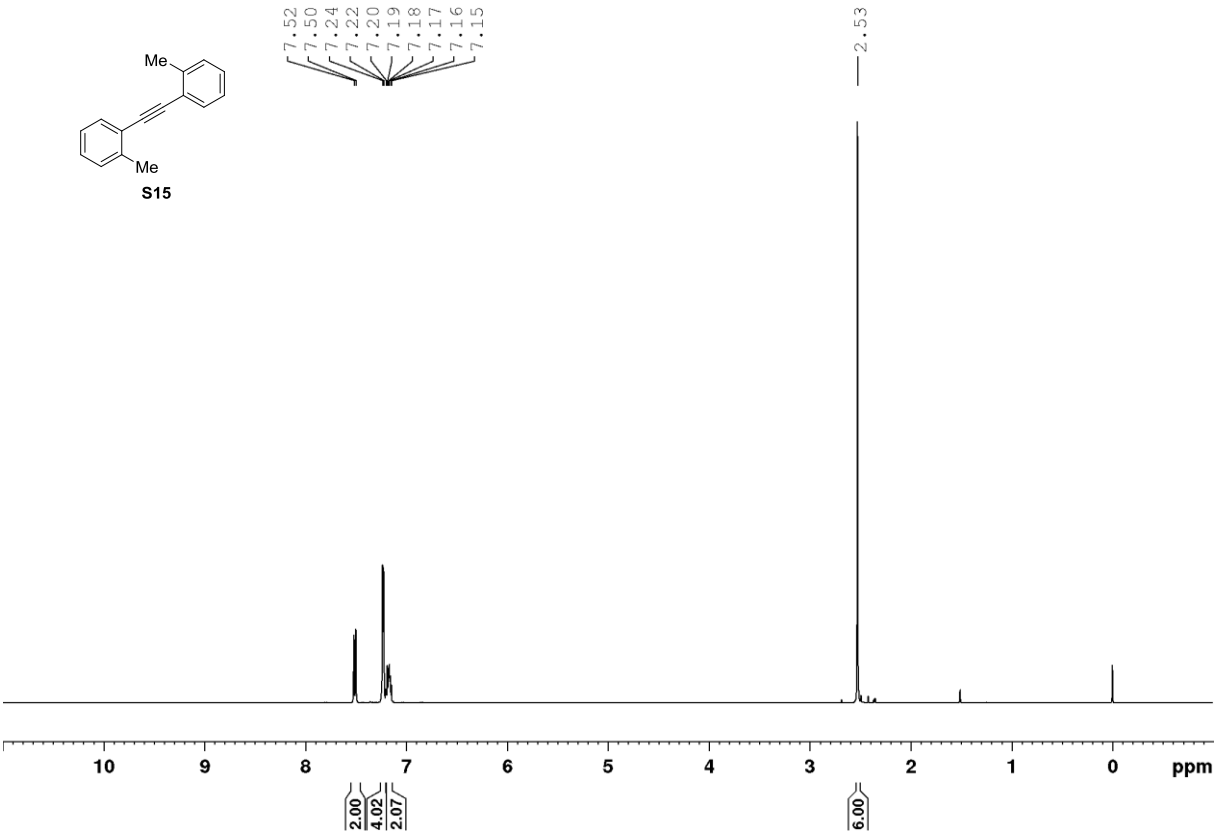

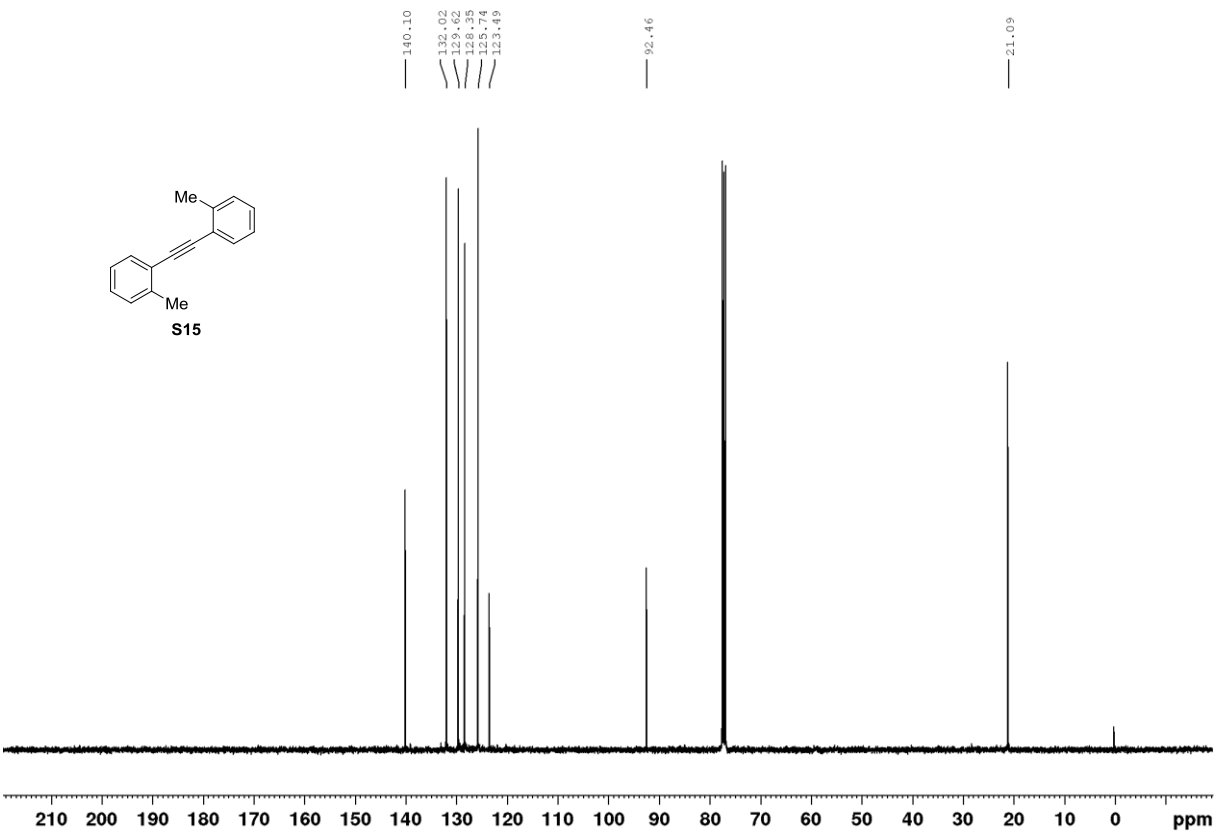

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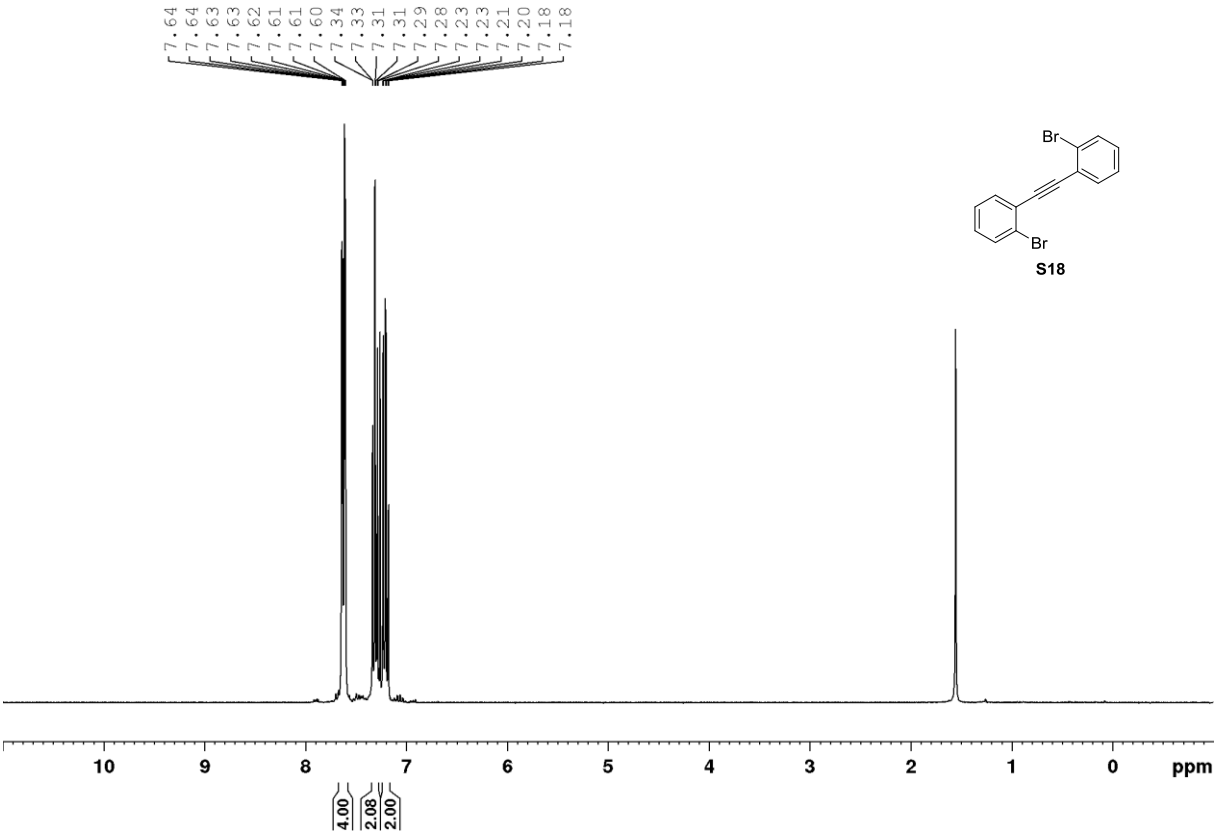

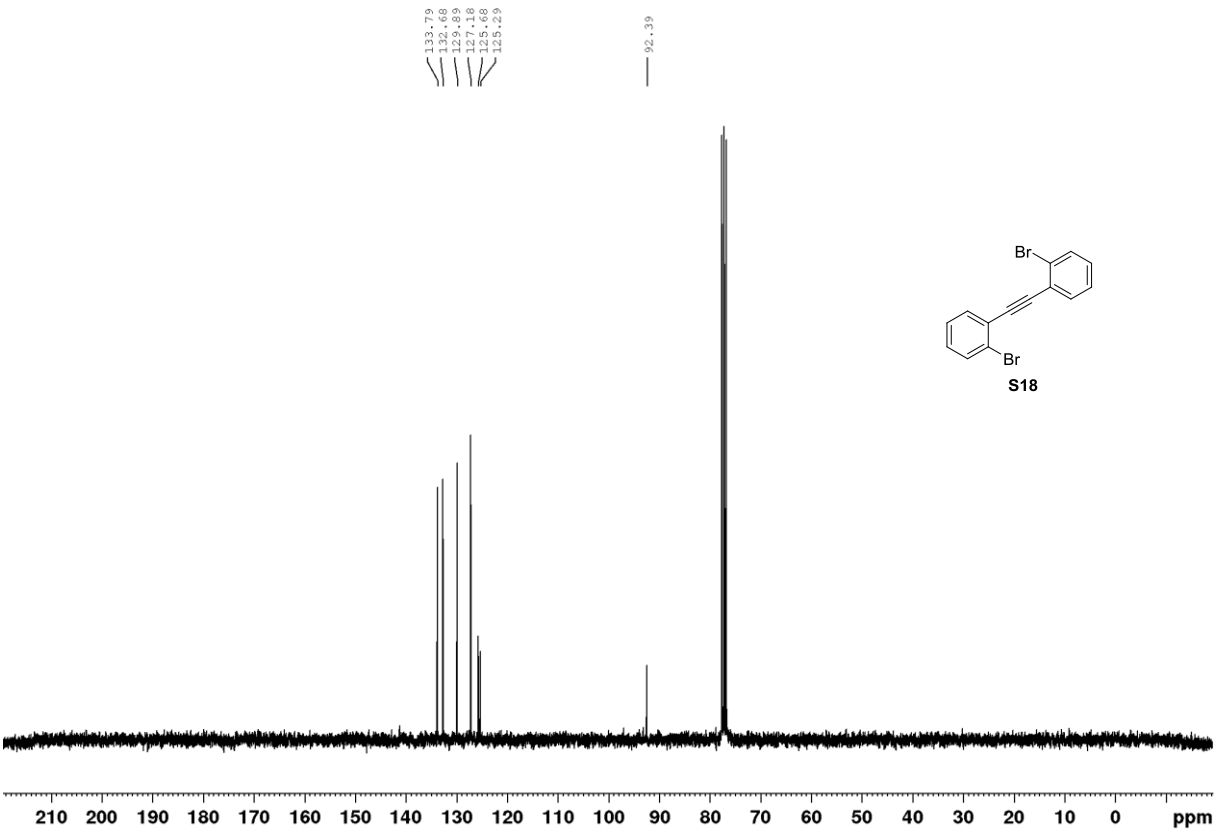

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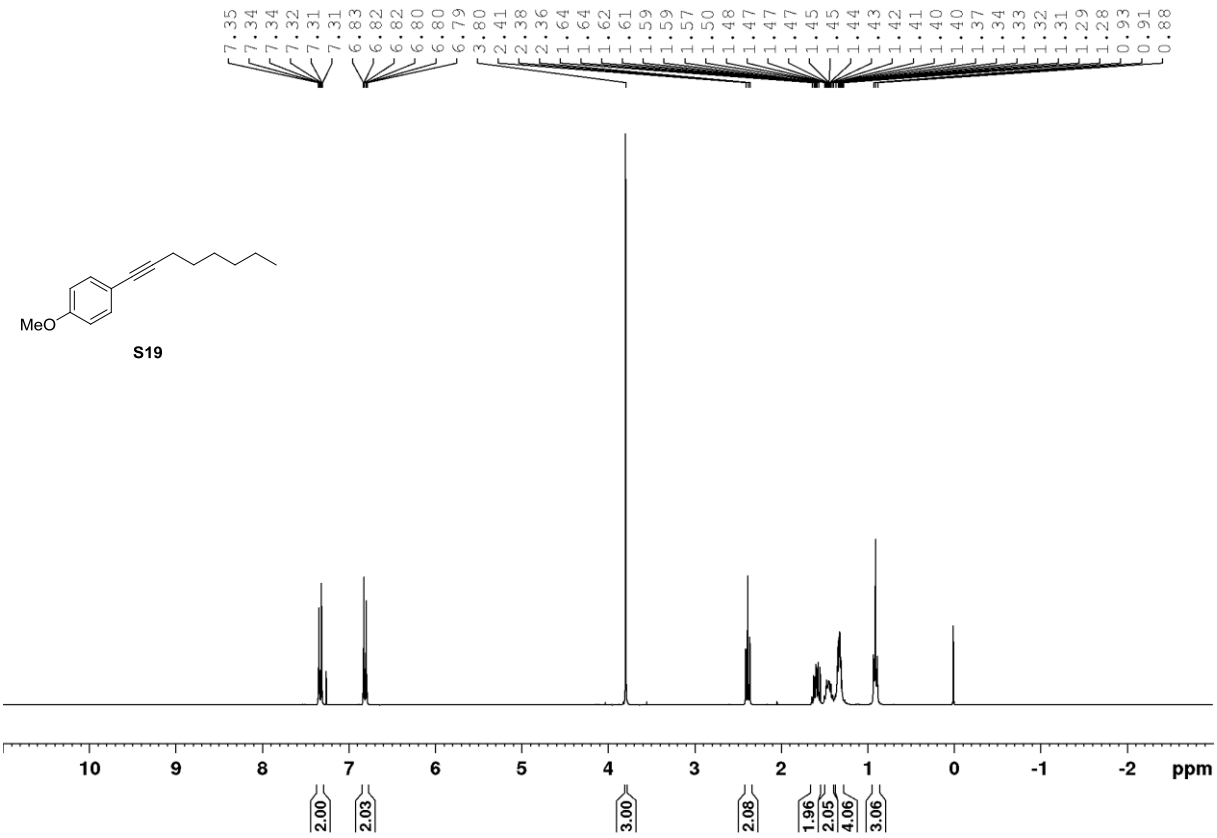

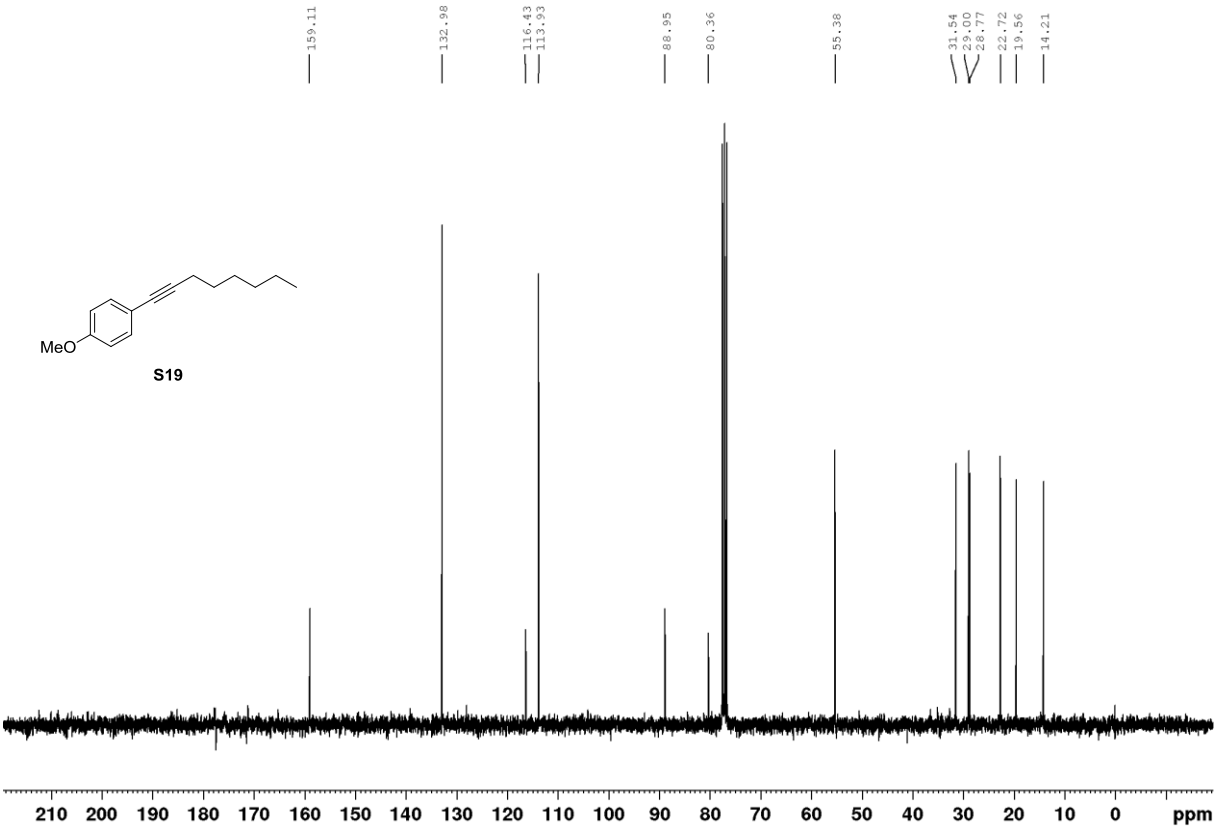

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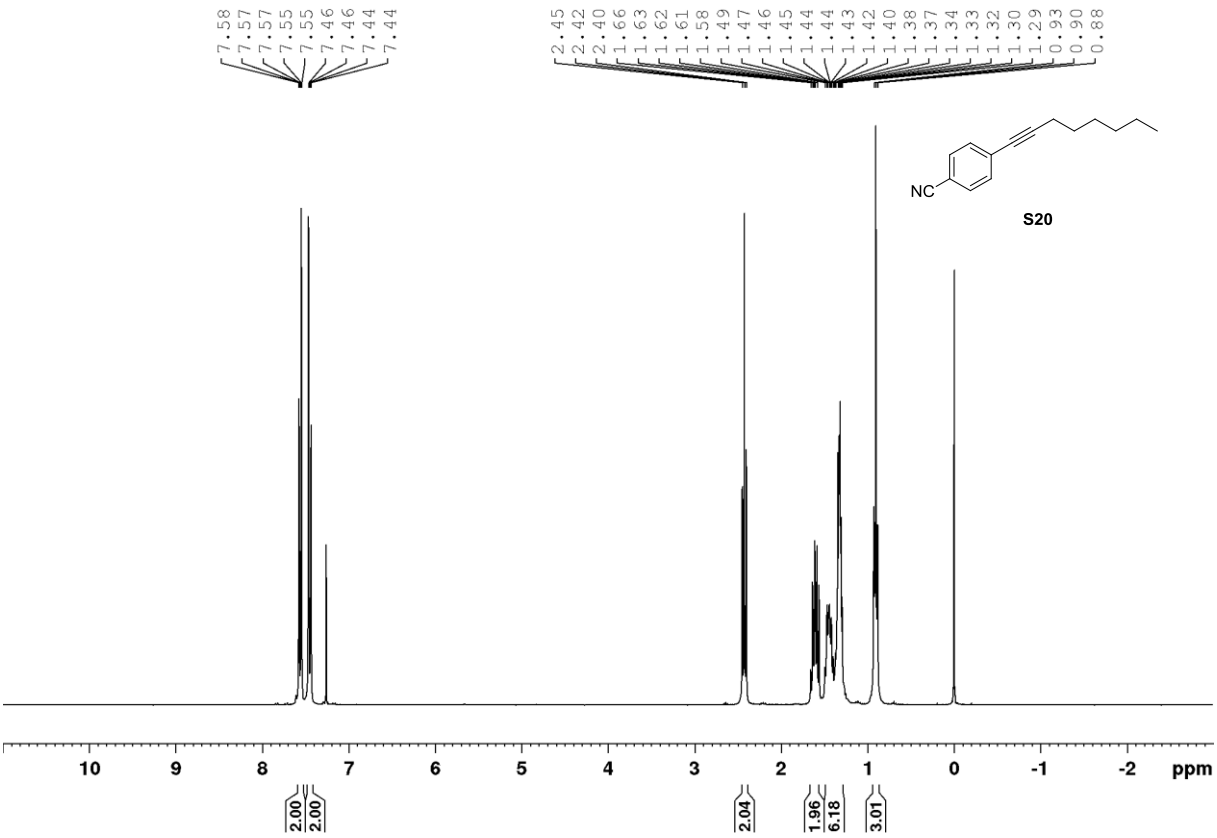

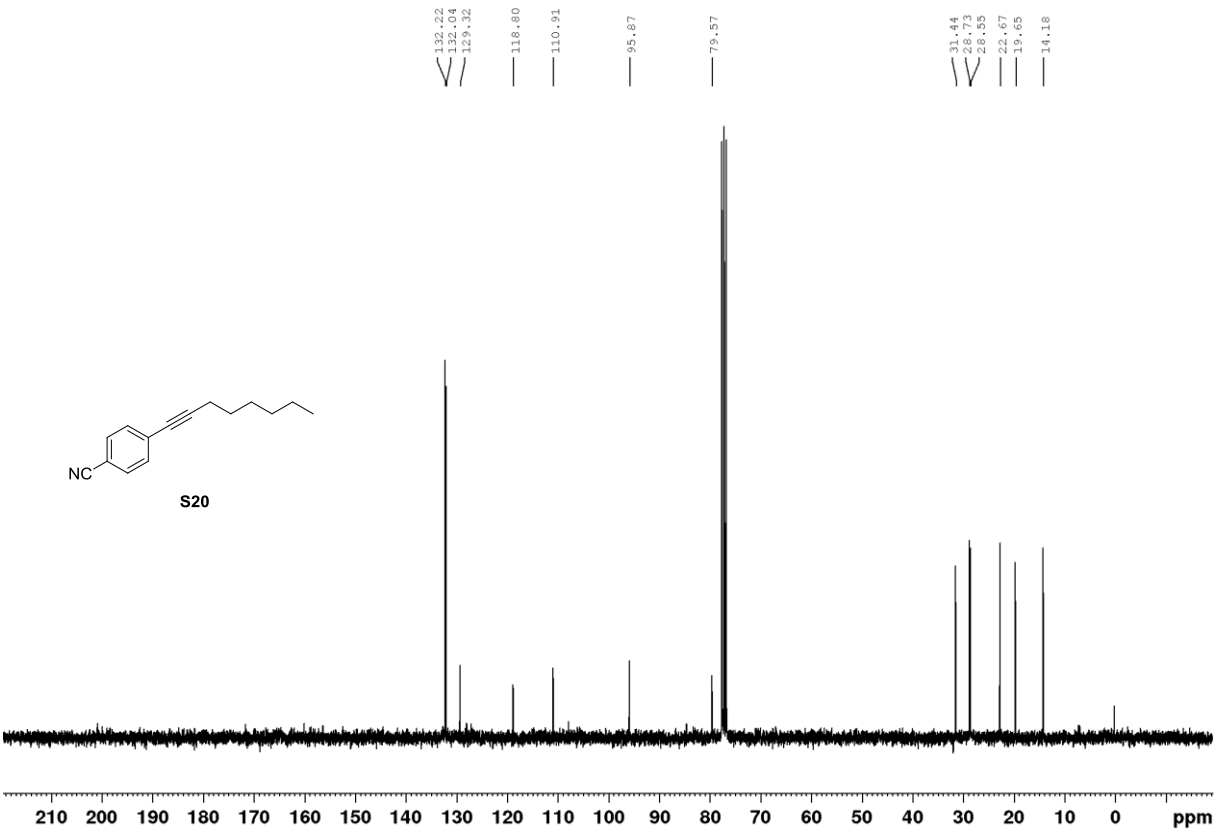

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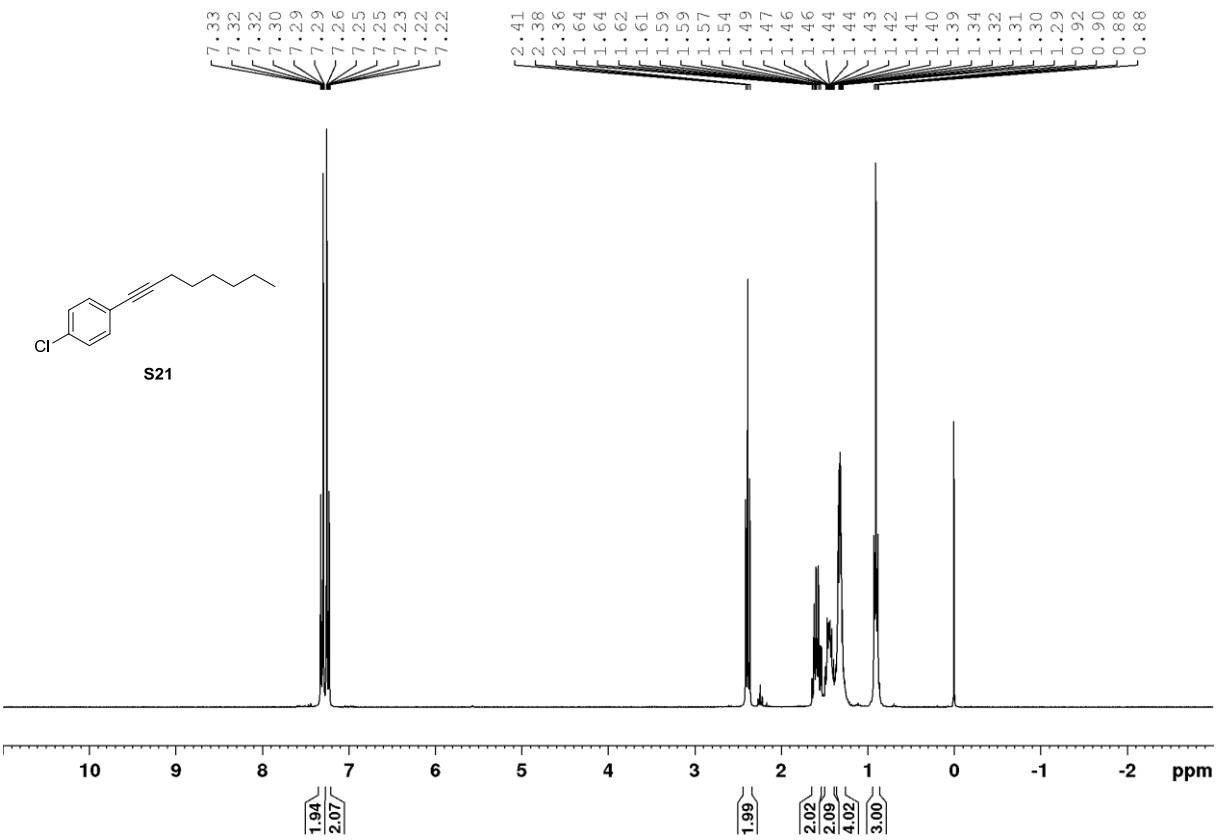

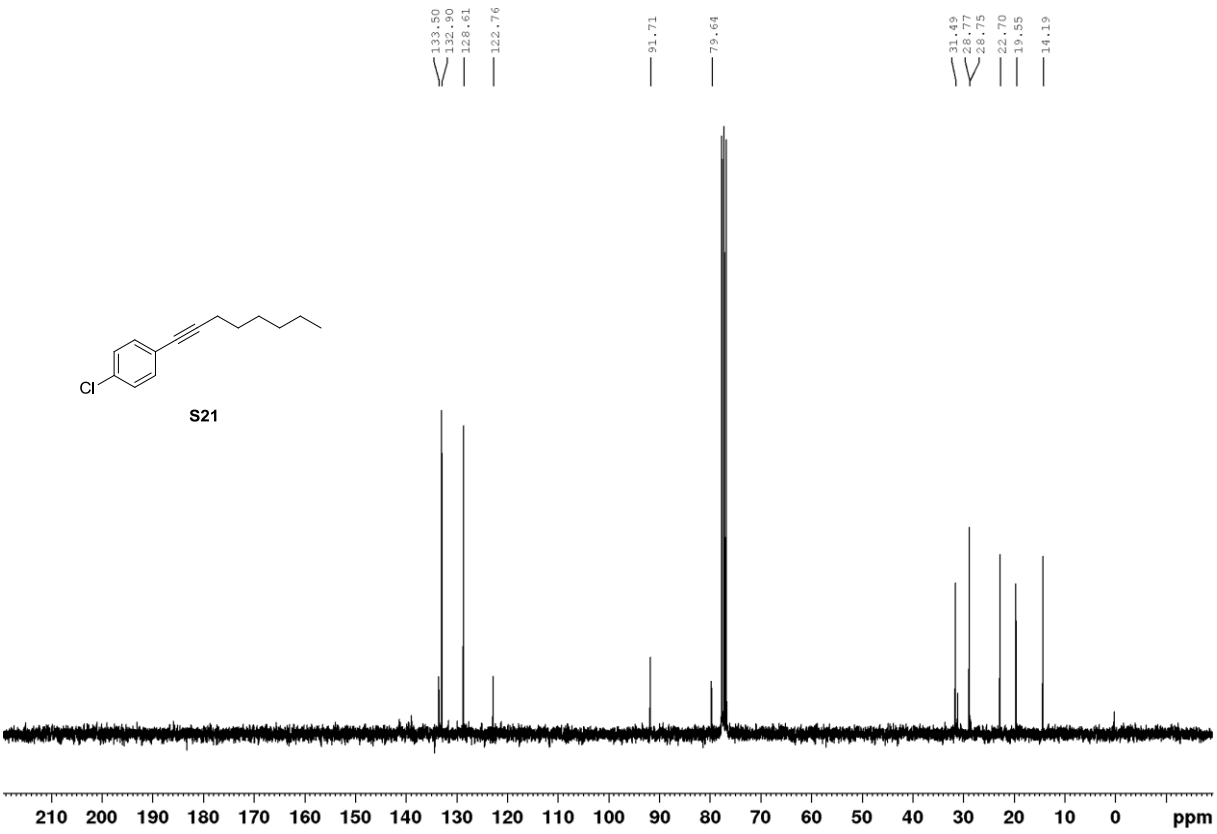

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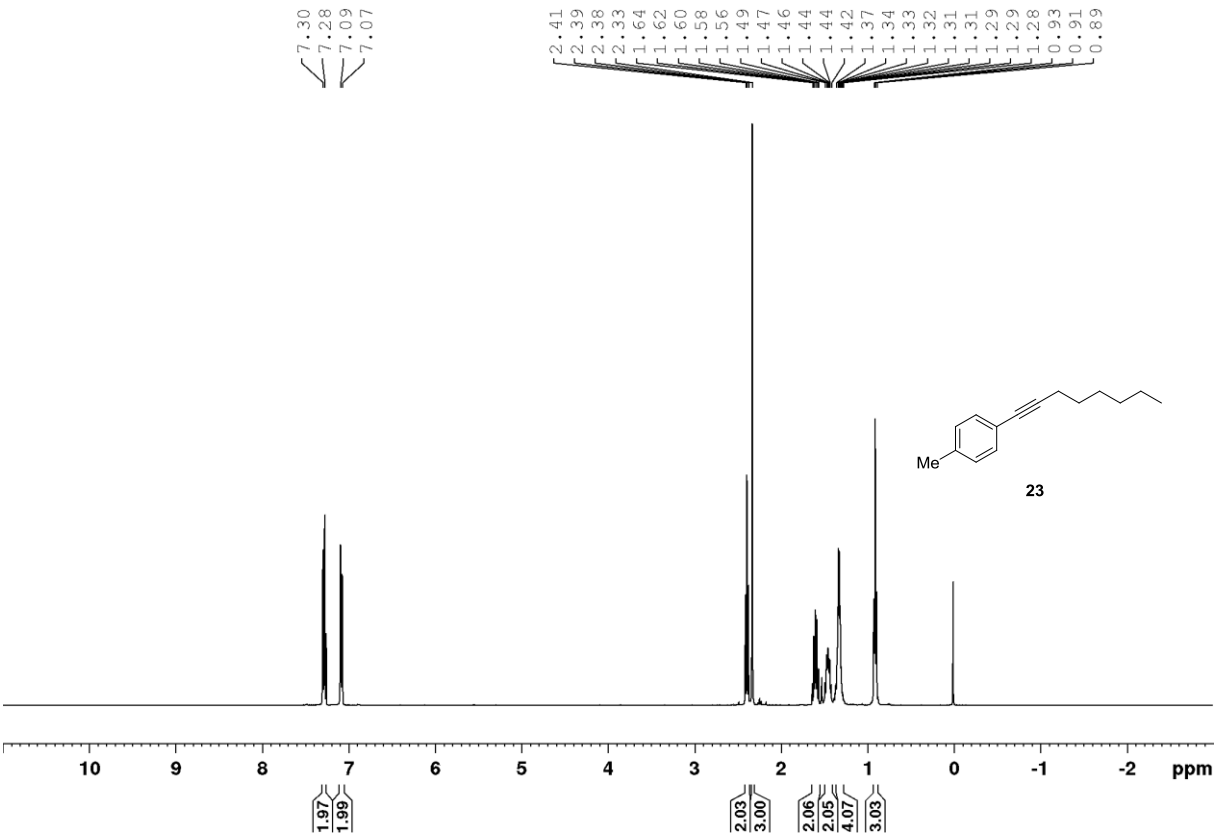

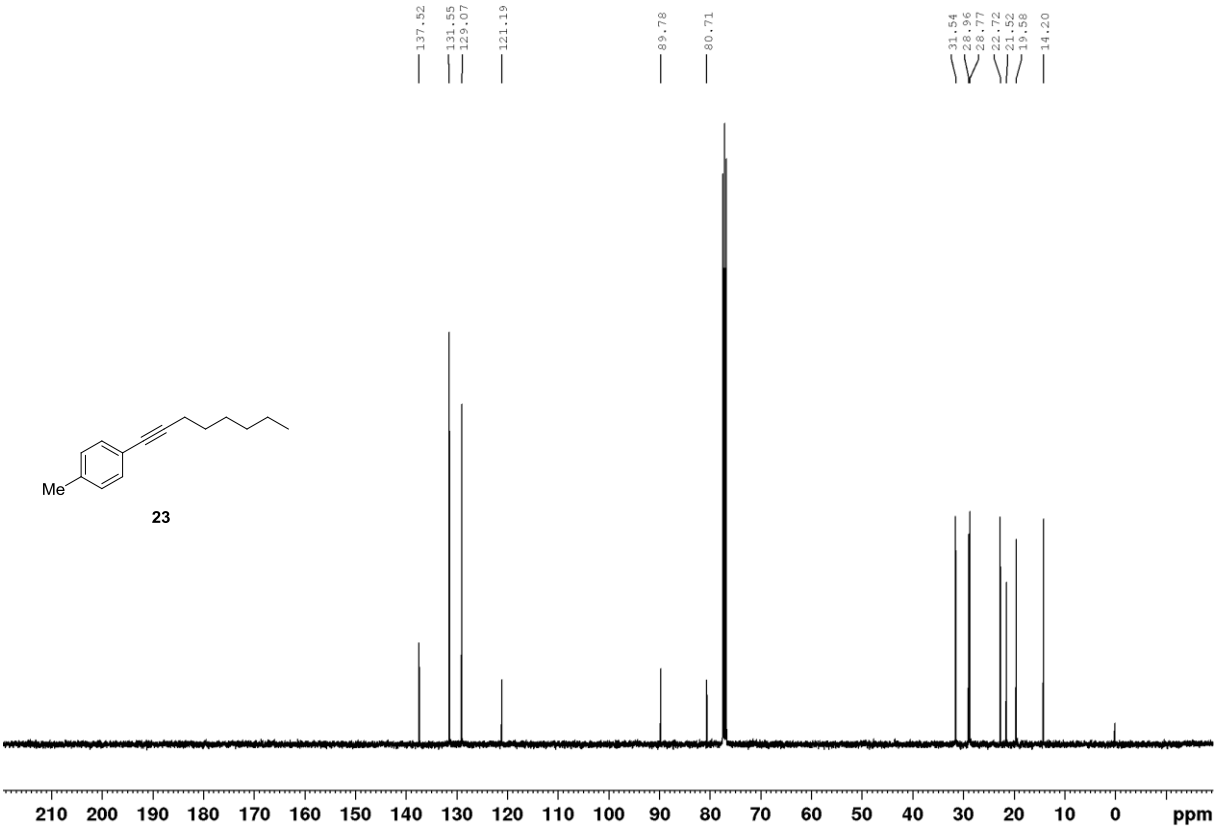

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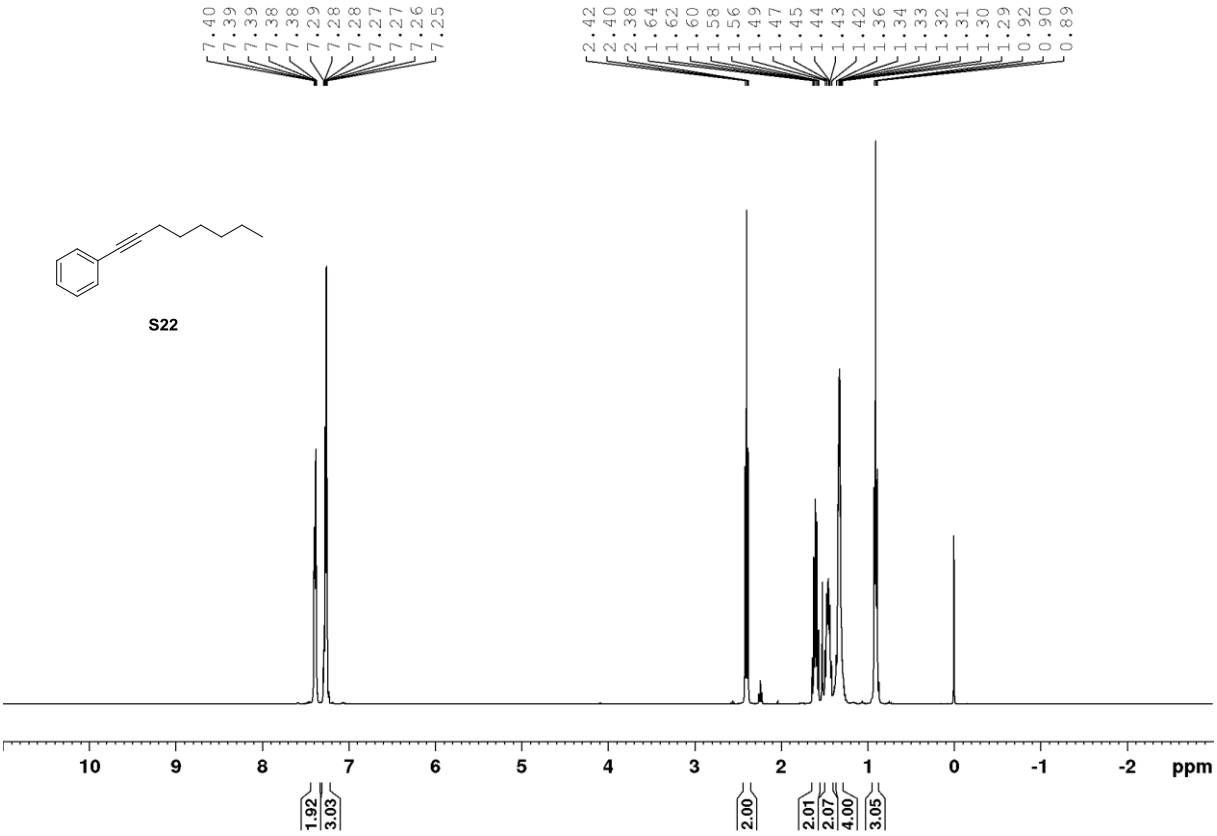

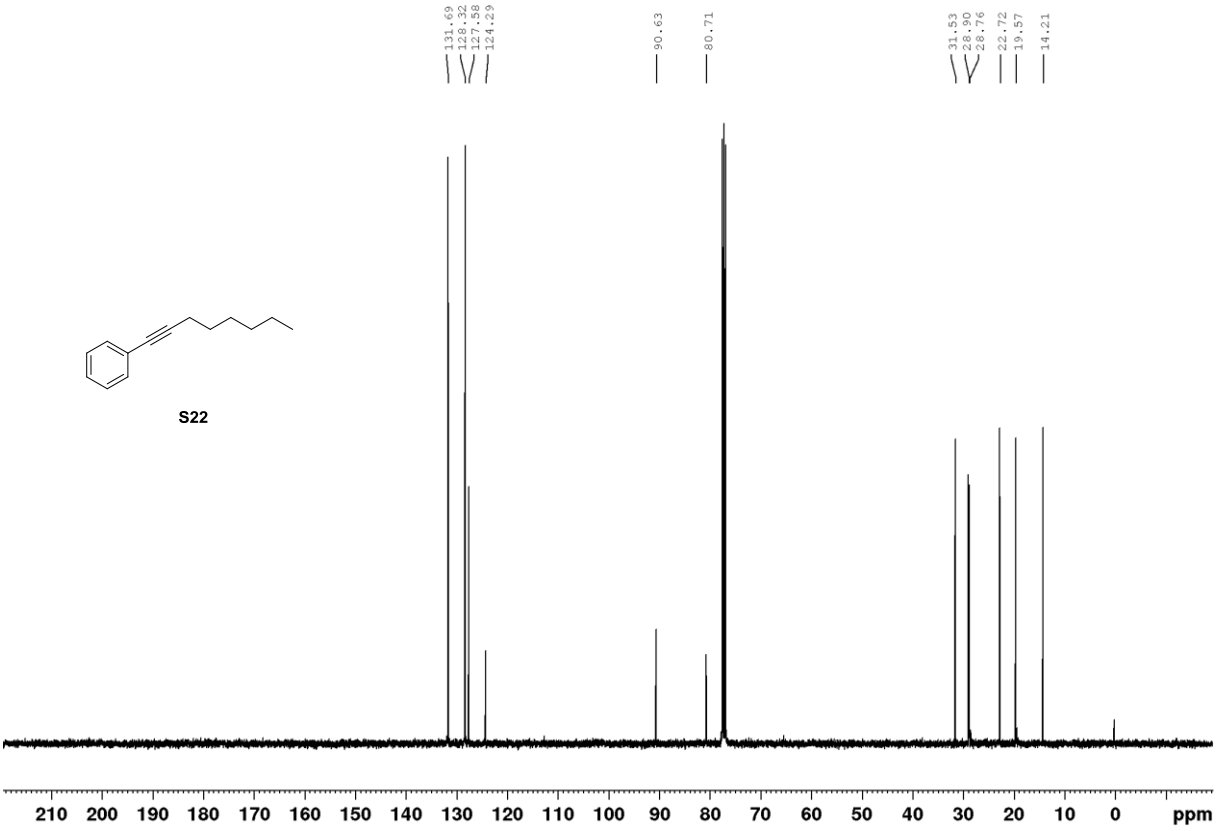

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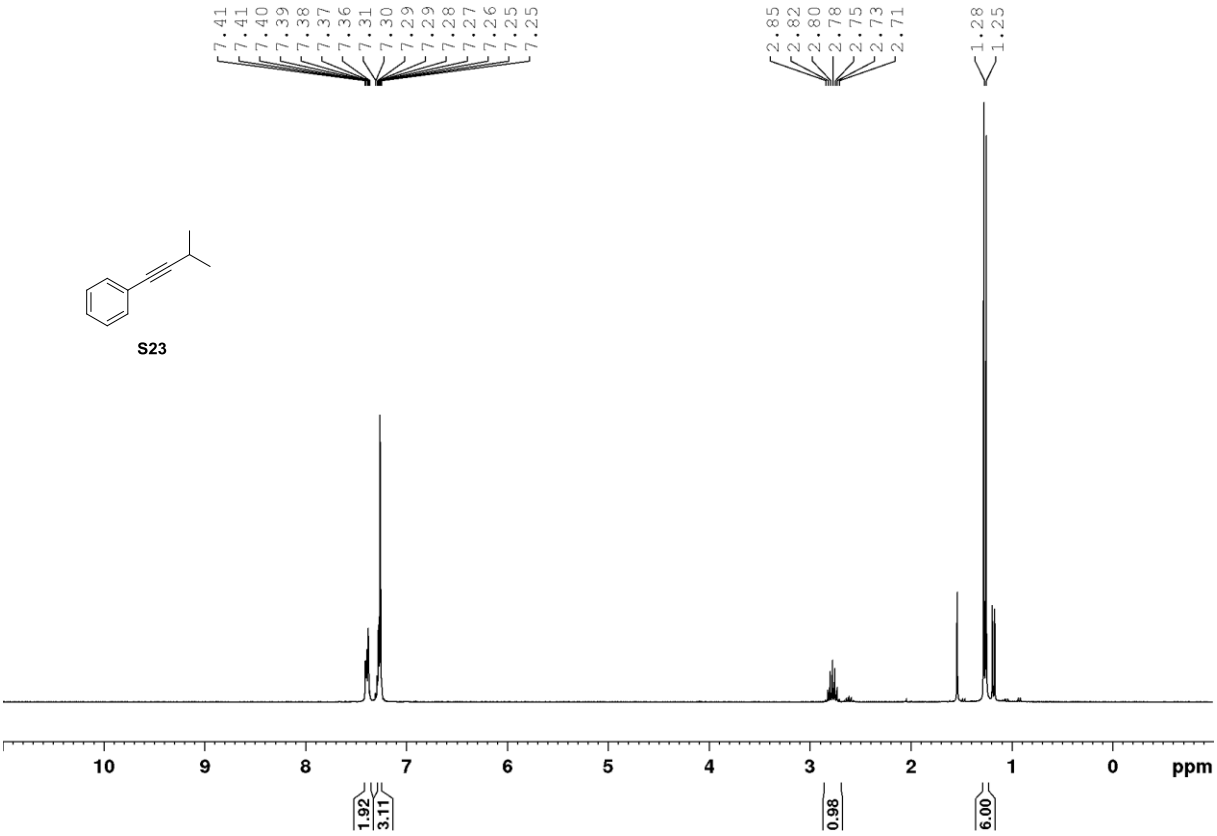

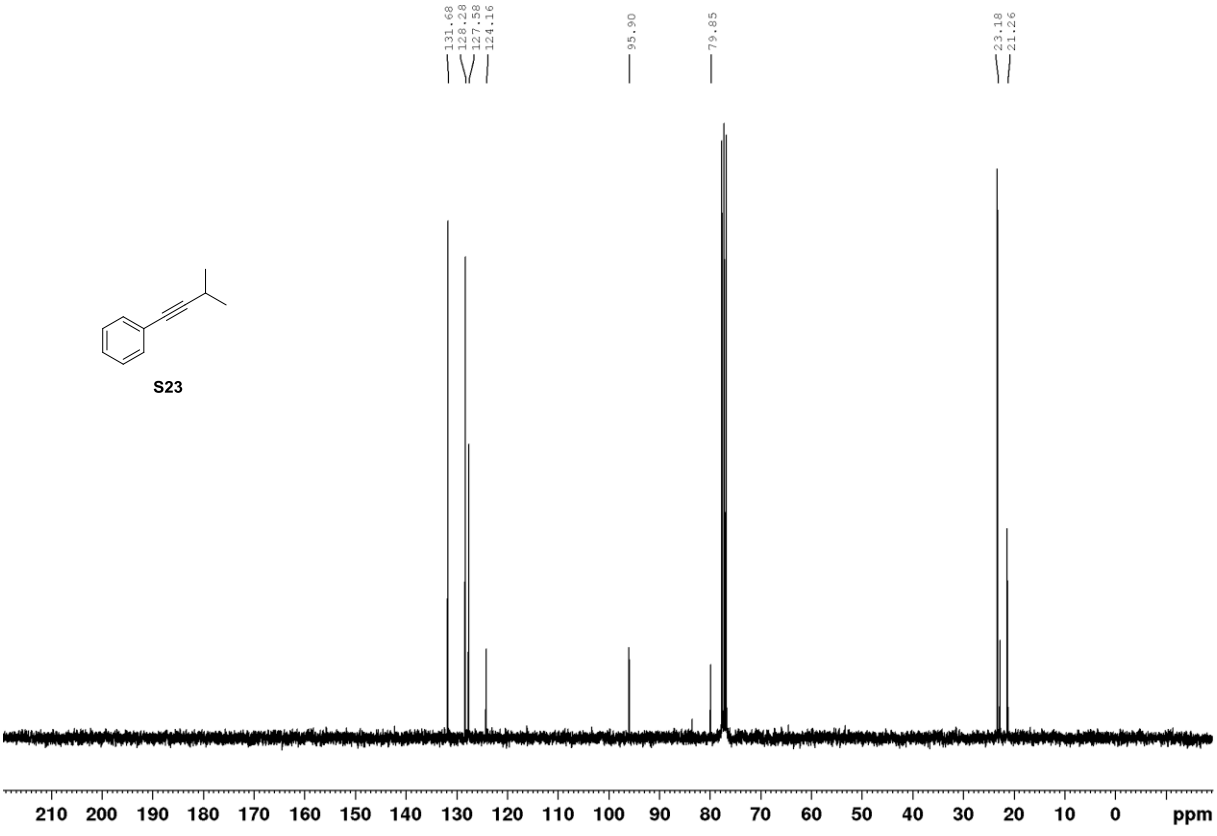

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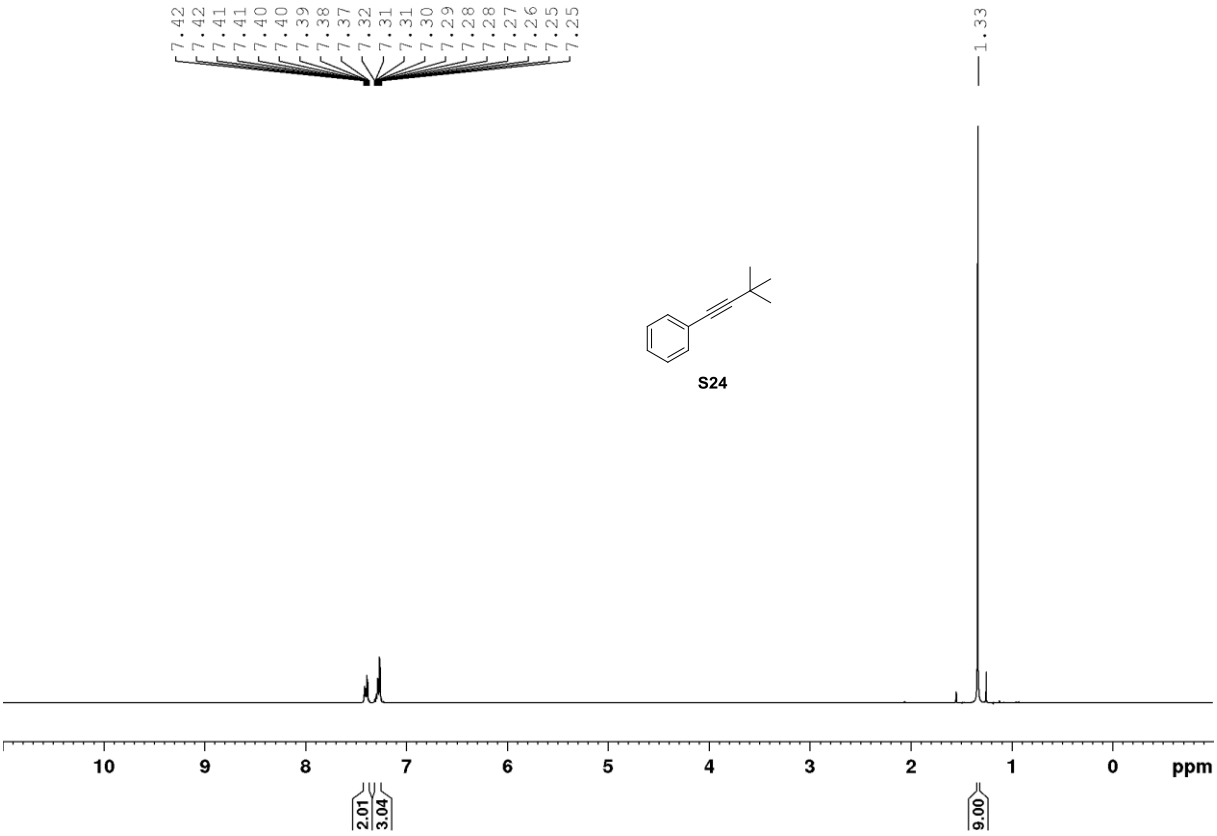

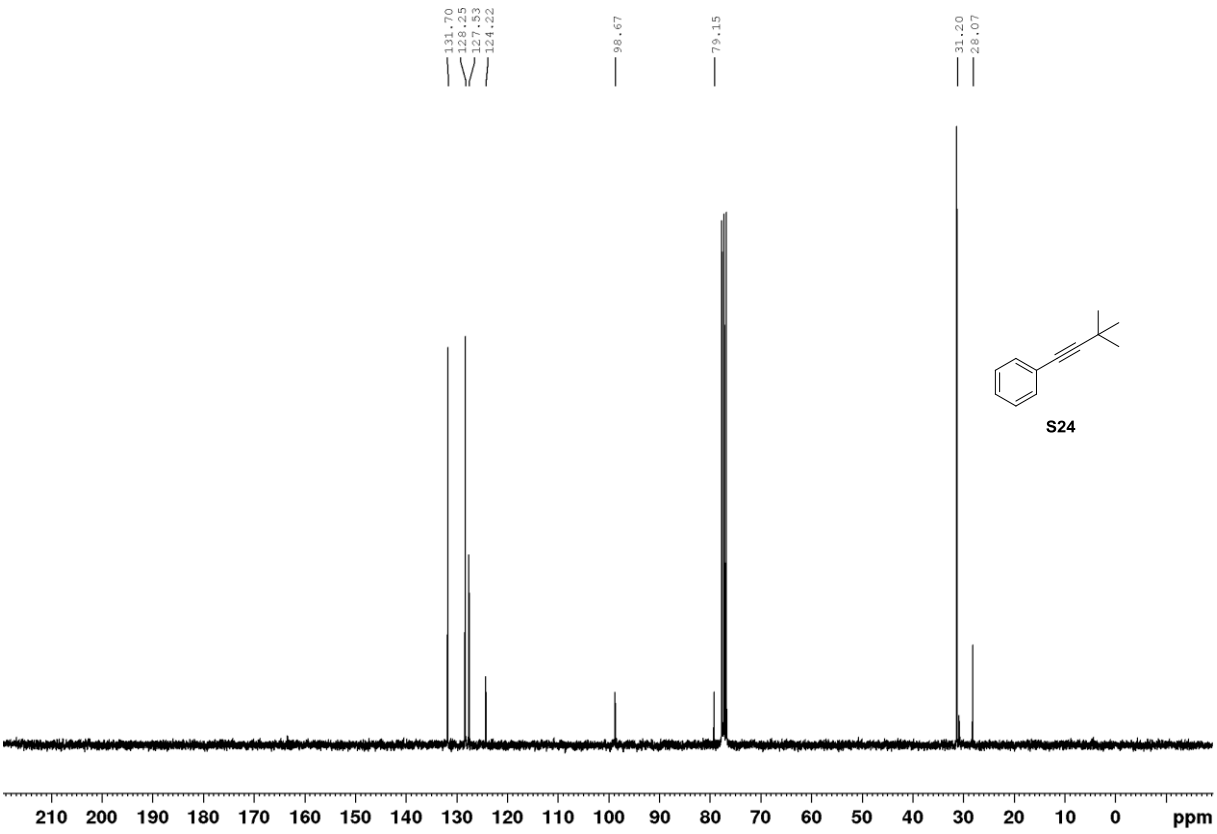

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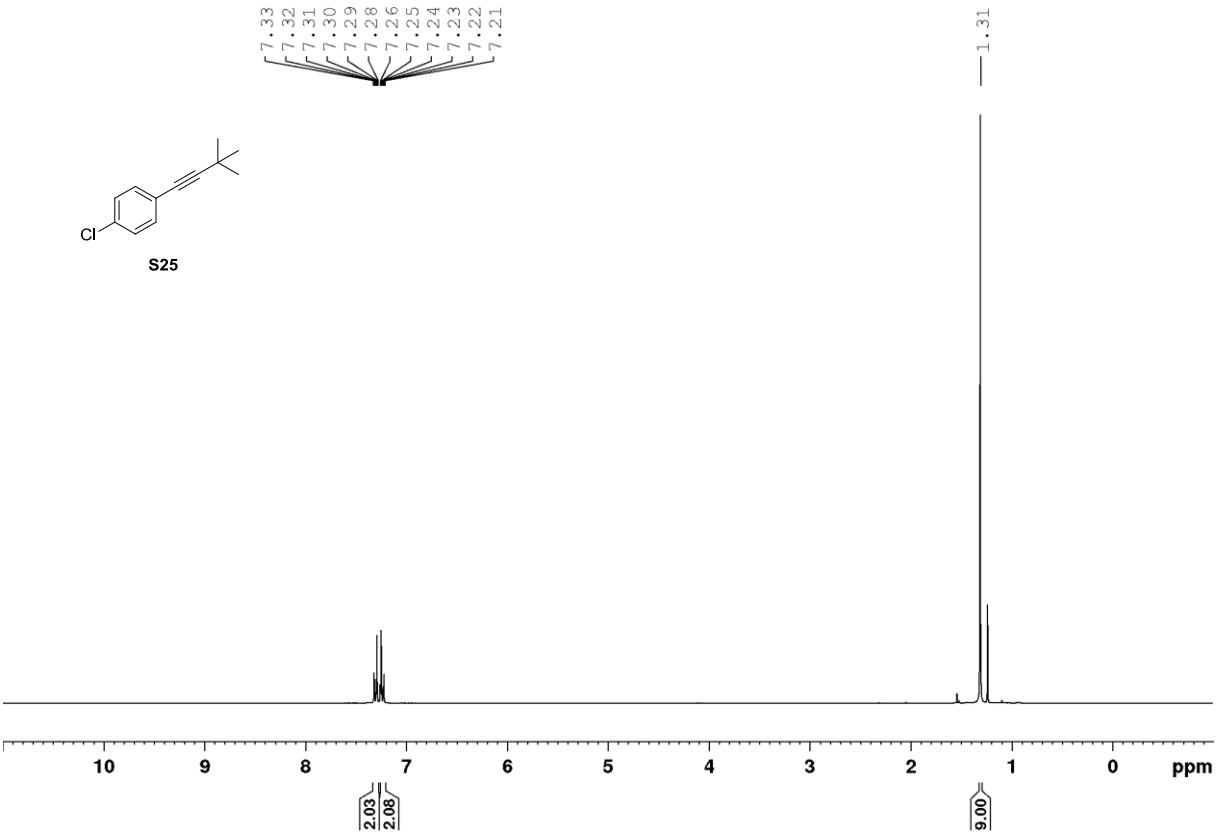

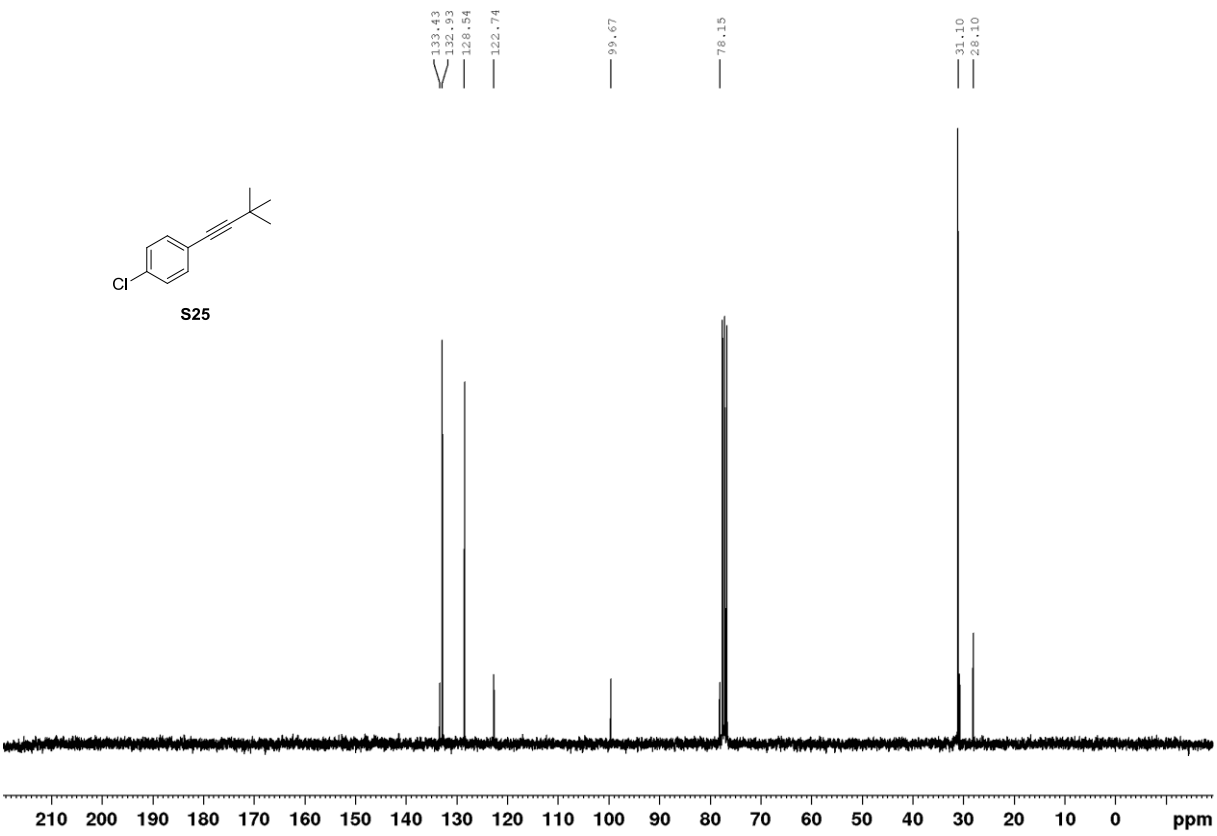

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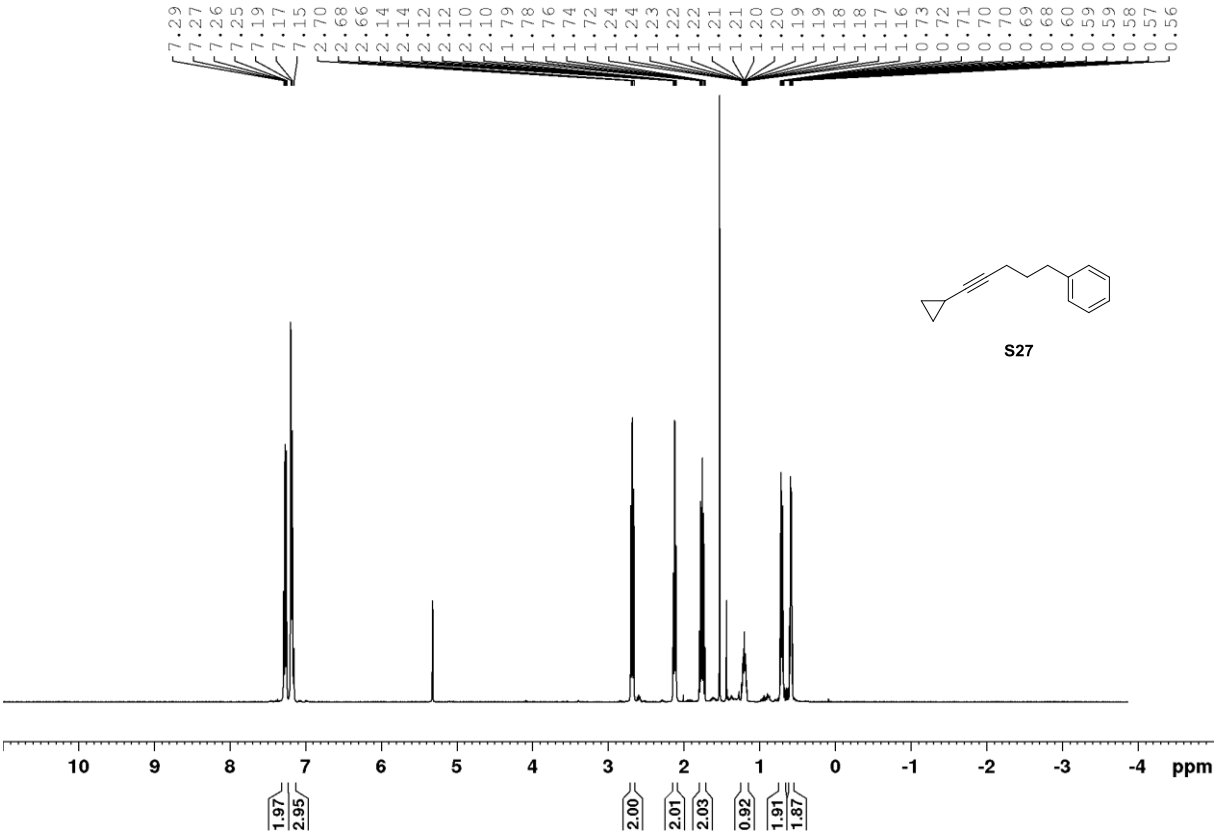

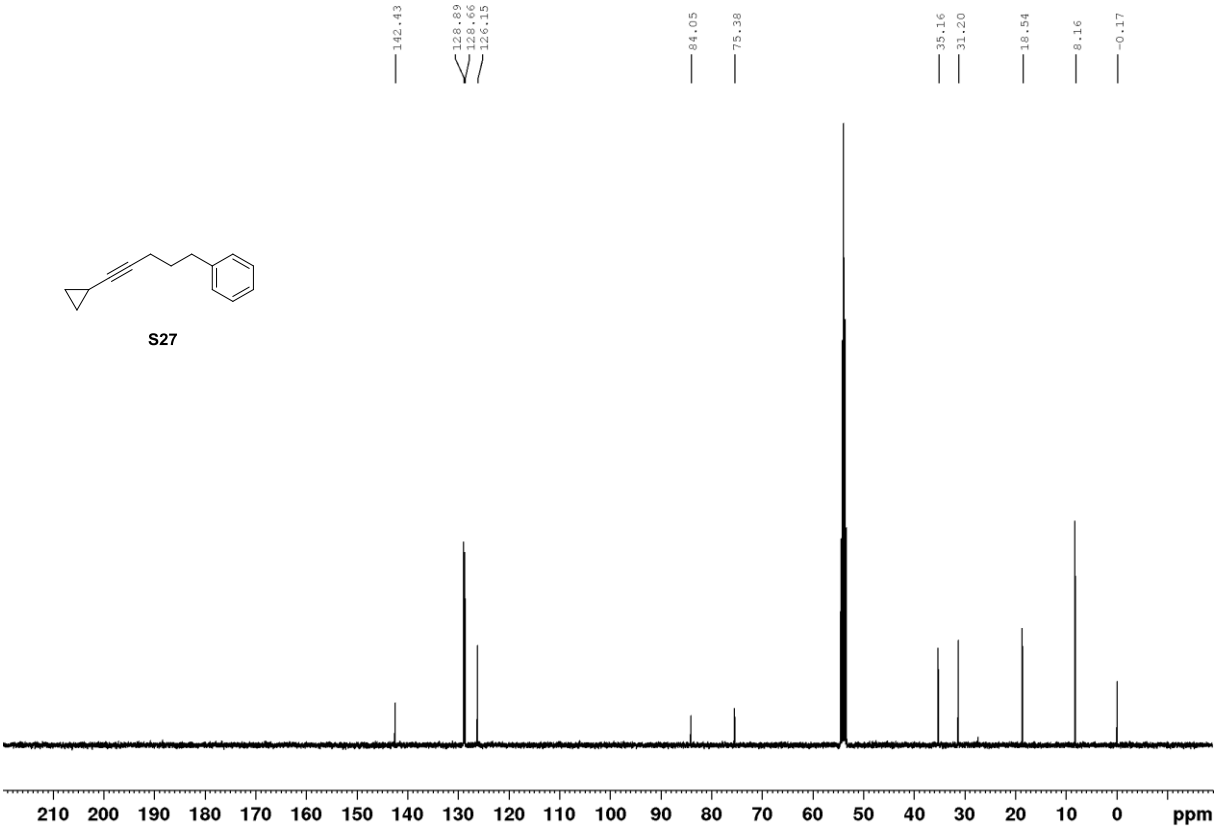

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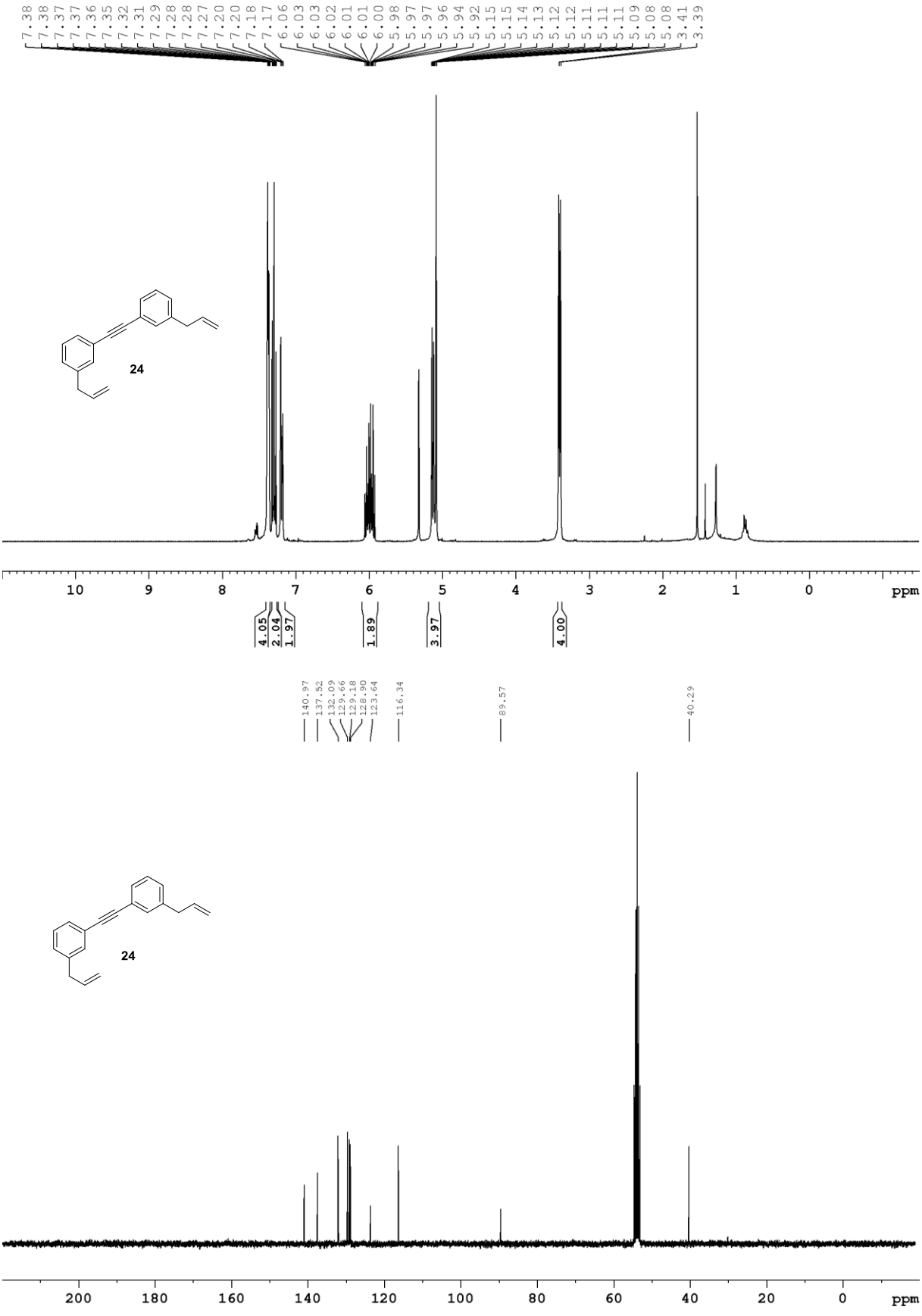

7.2 NMR data for the hydroboration products

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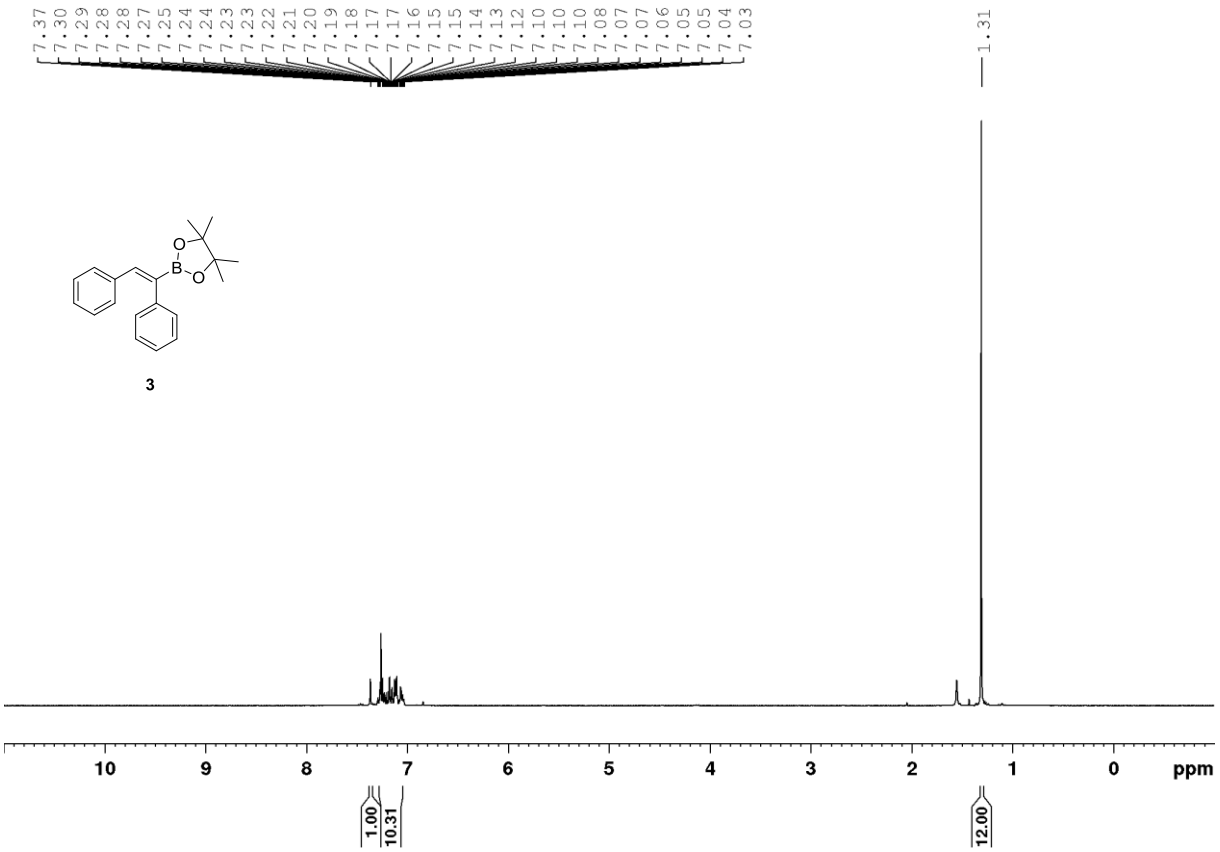

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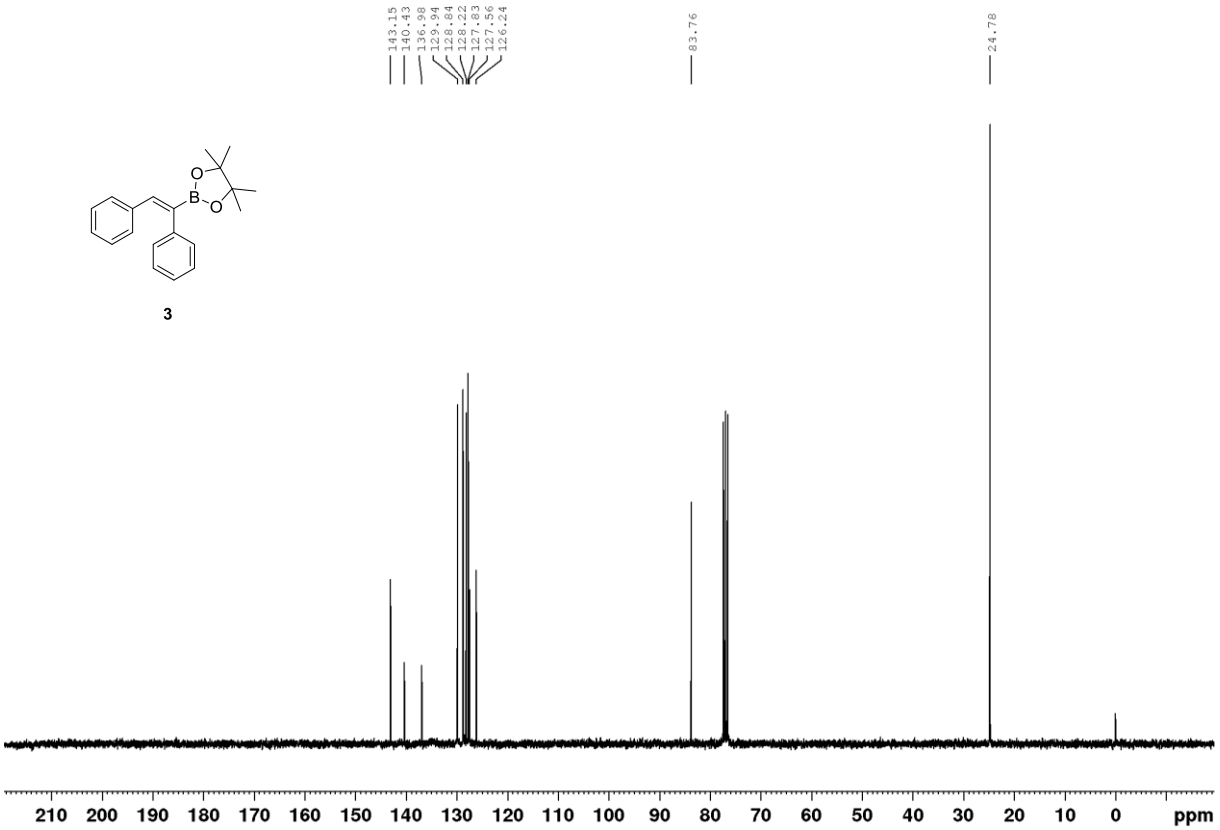

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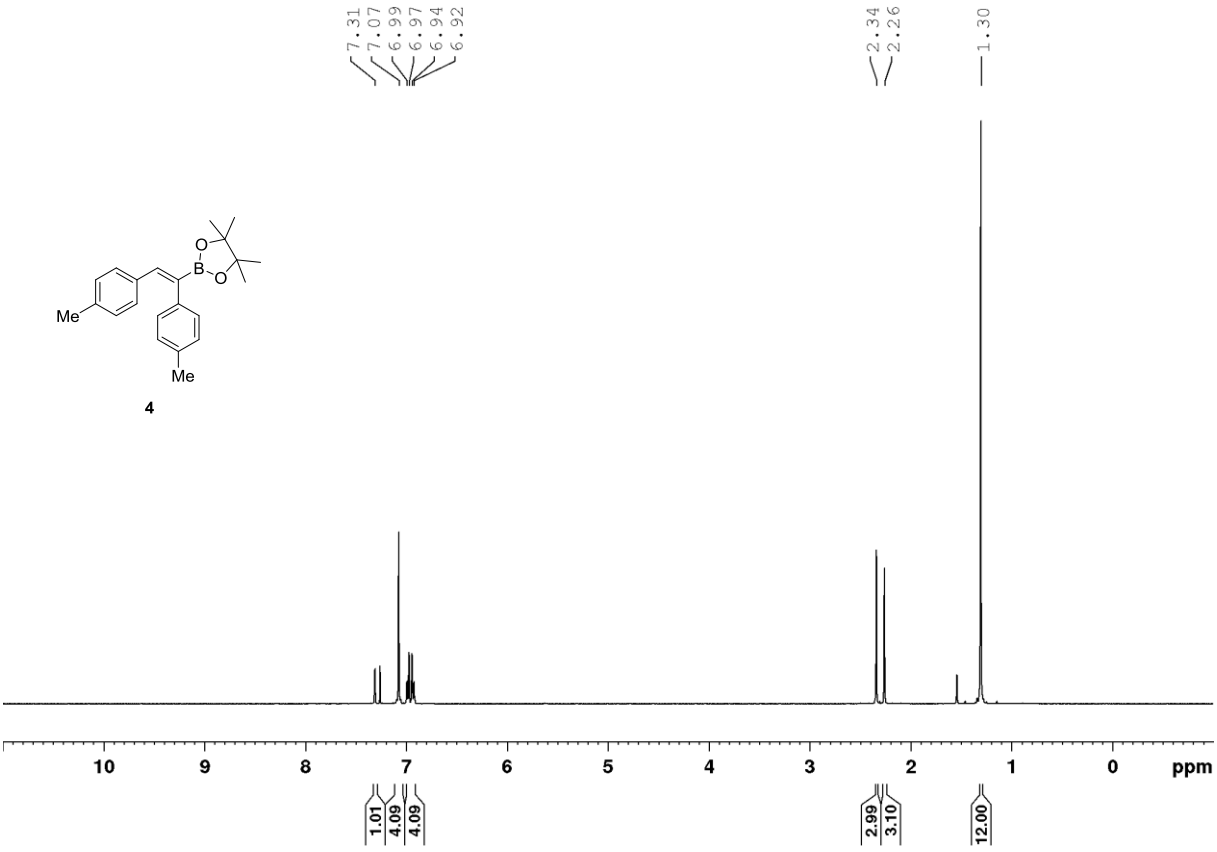
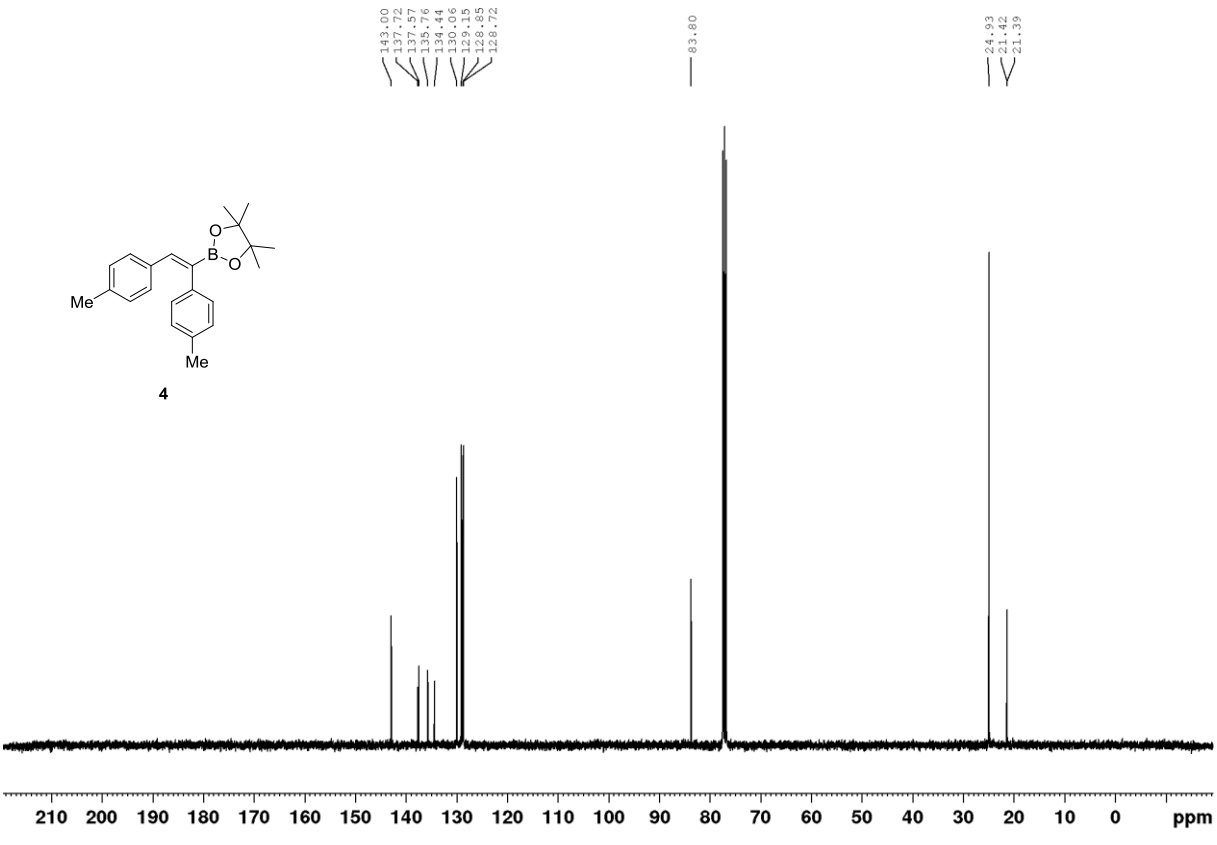
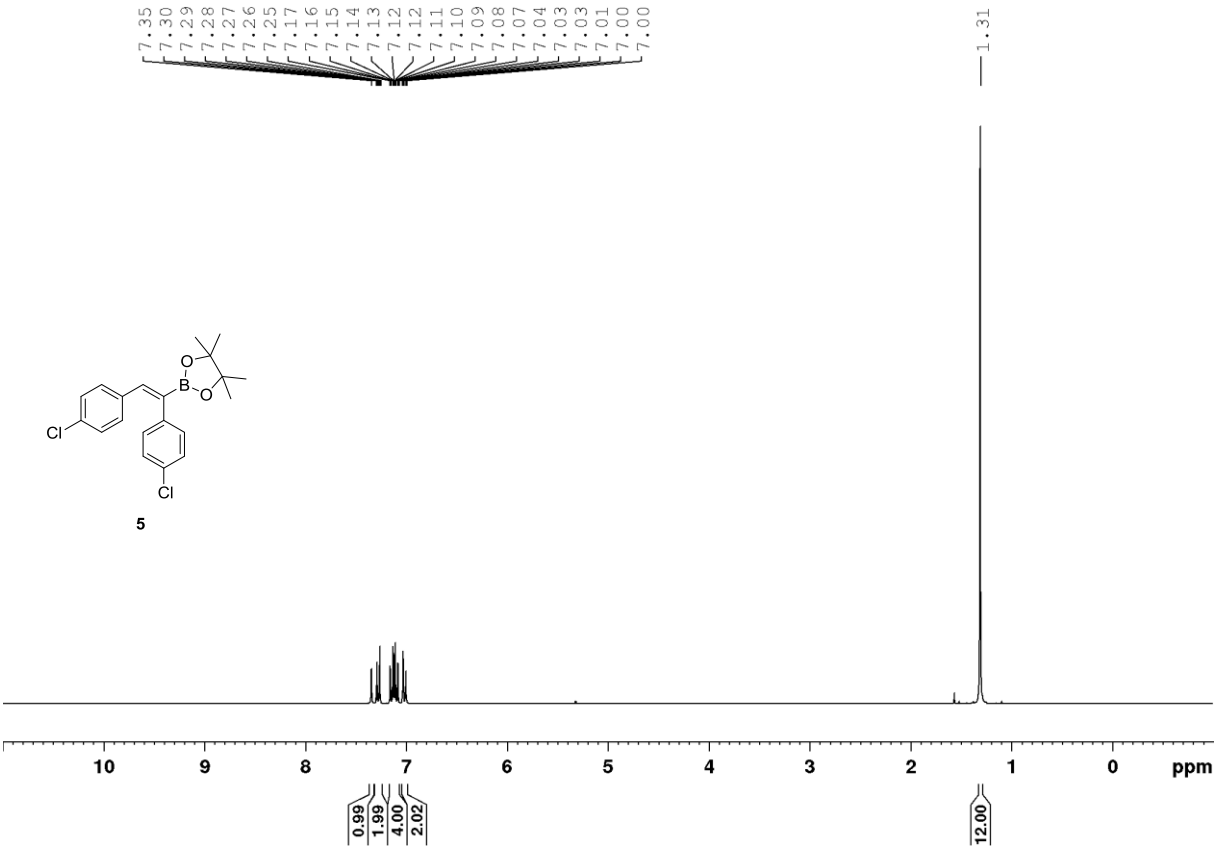
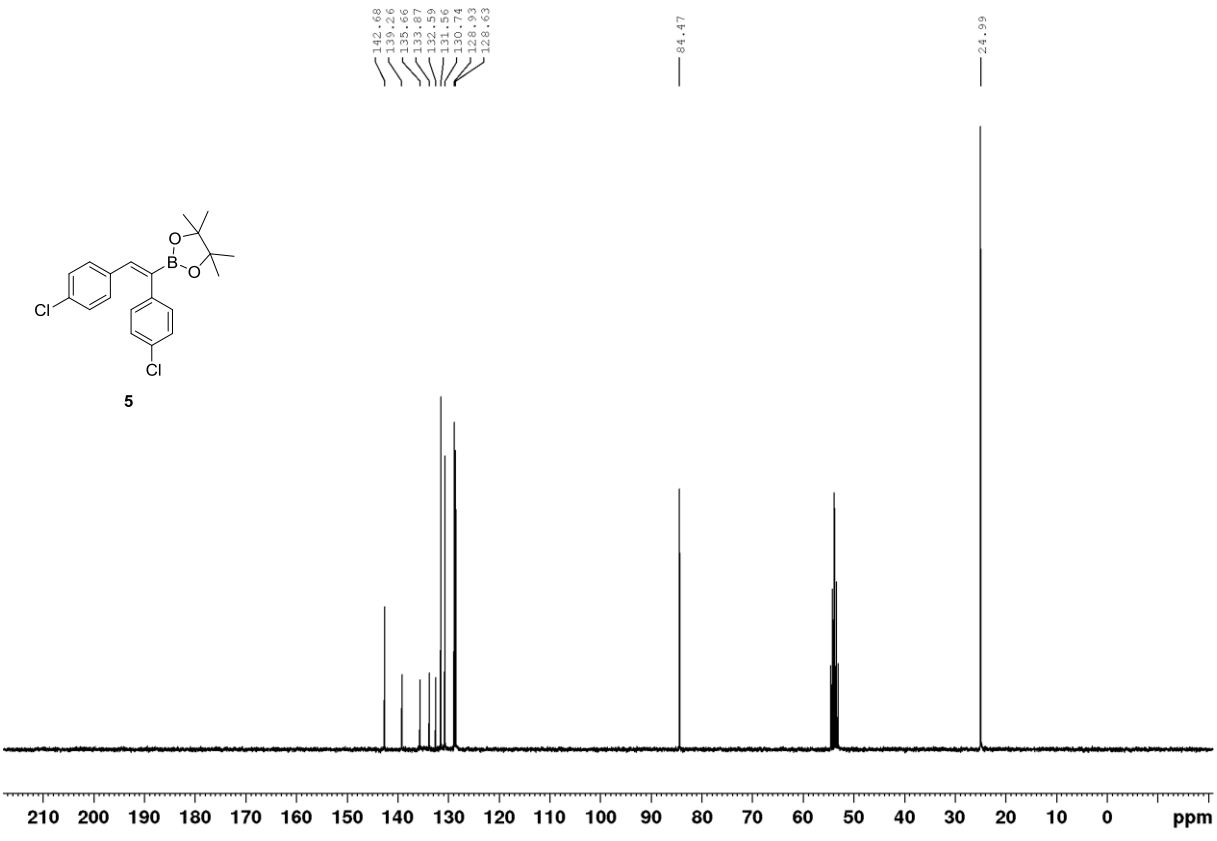


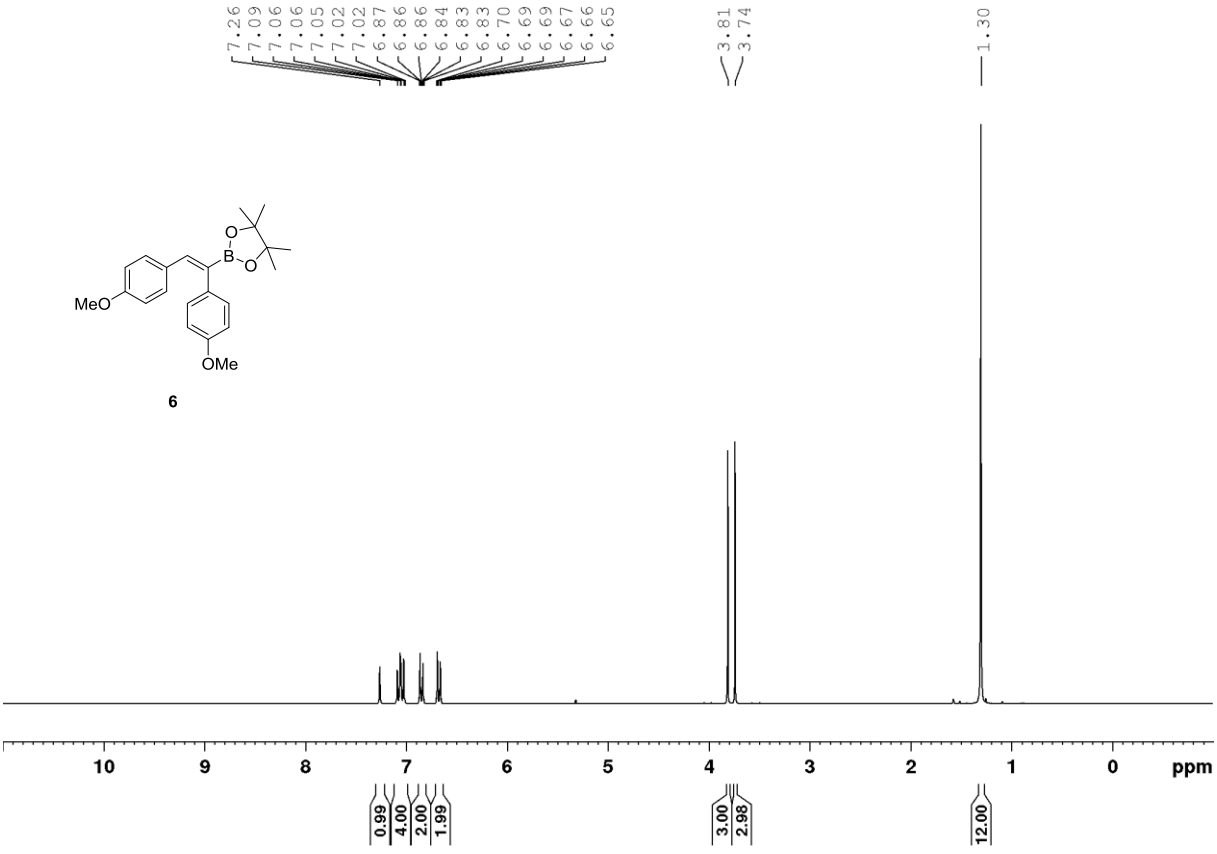


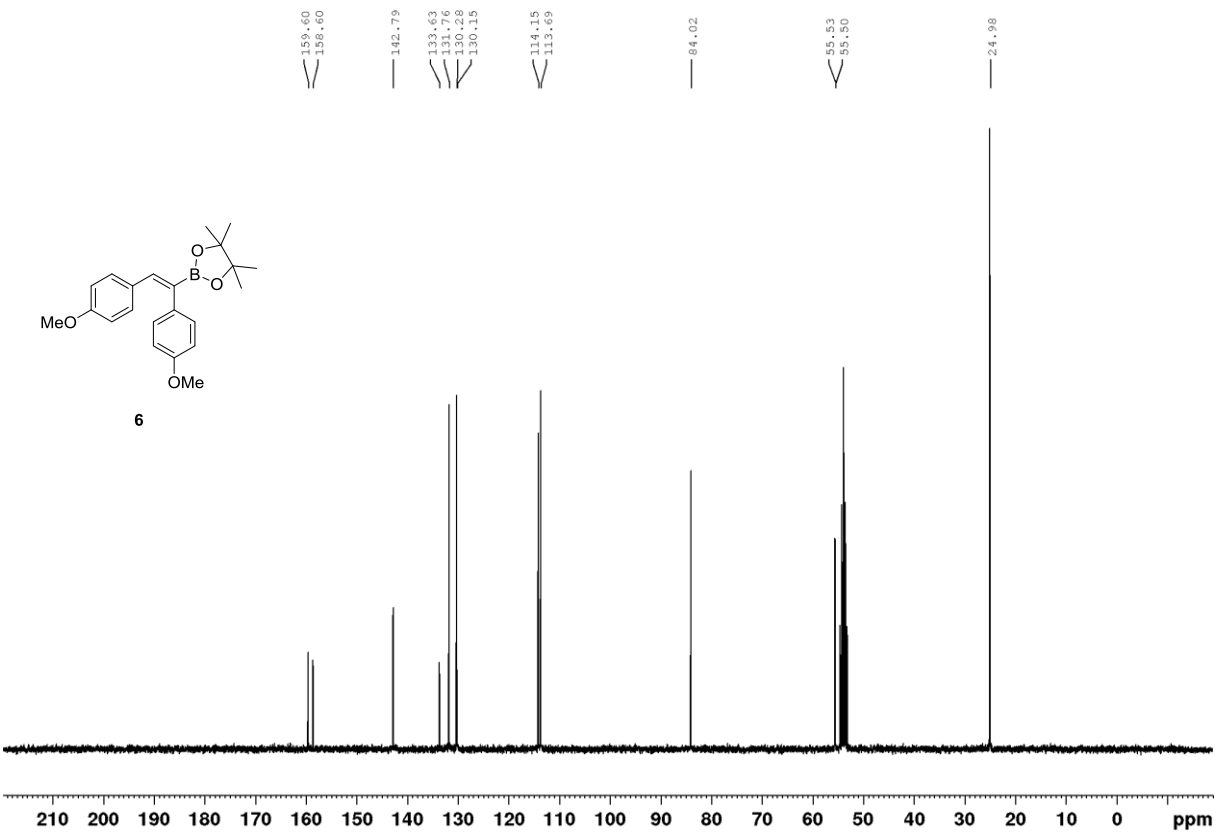
NMR spectra of 5:



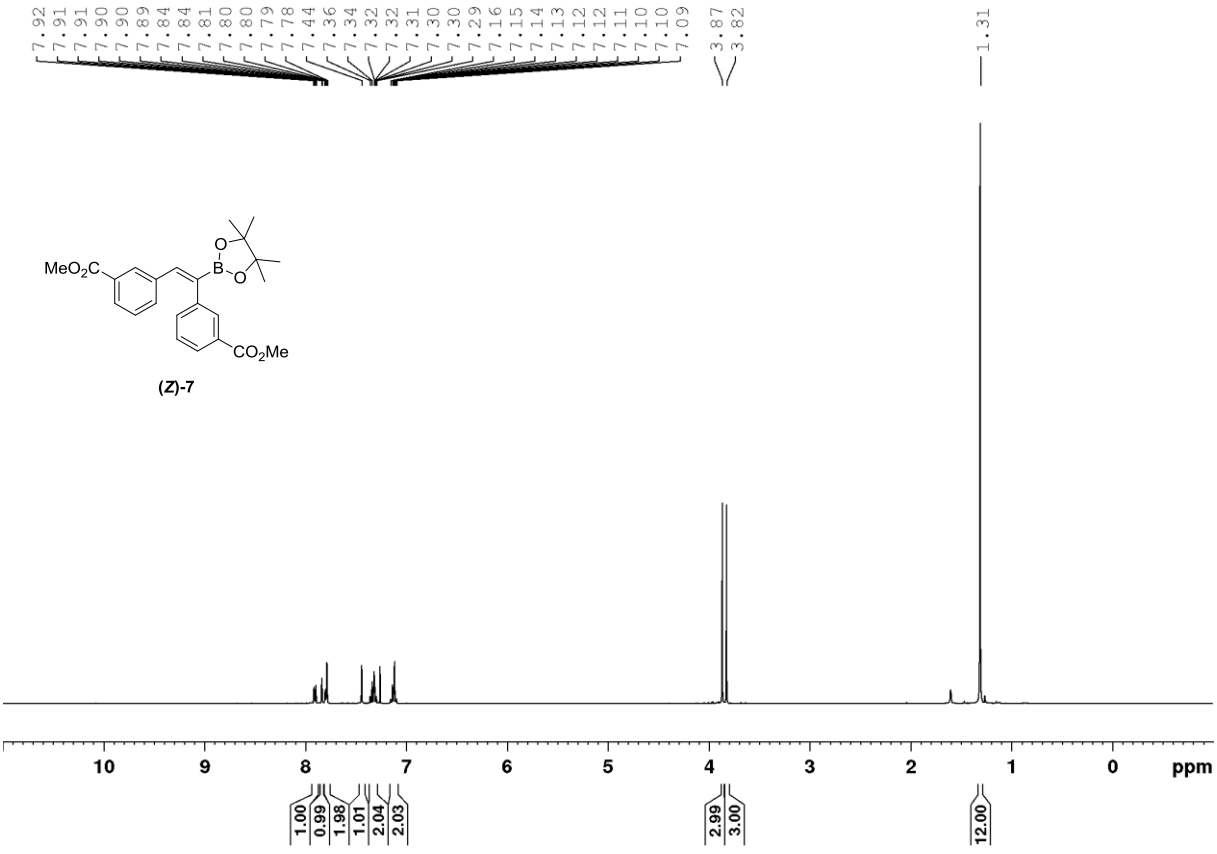


NMR spectra of 6:

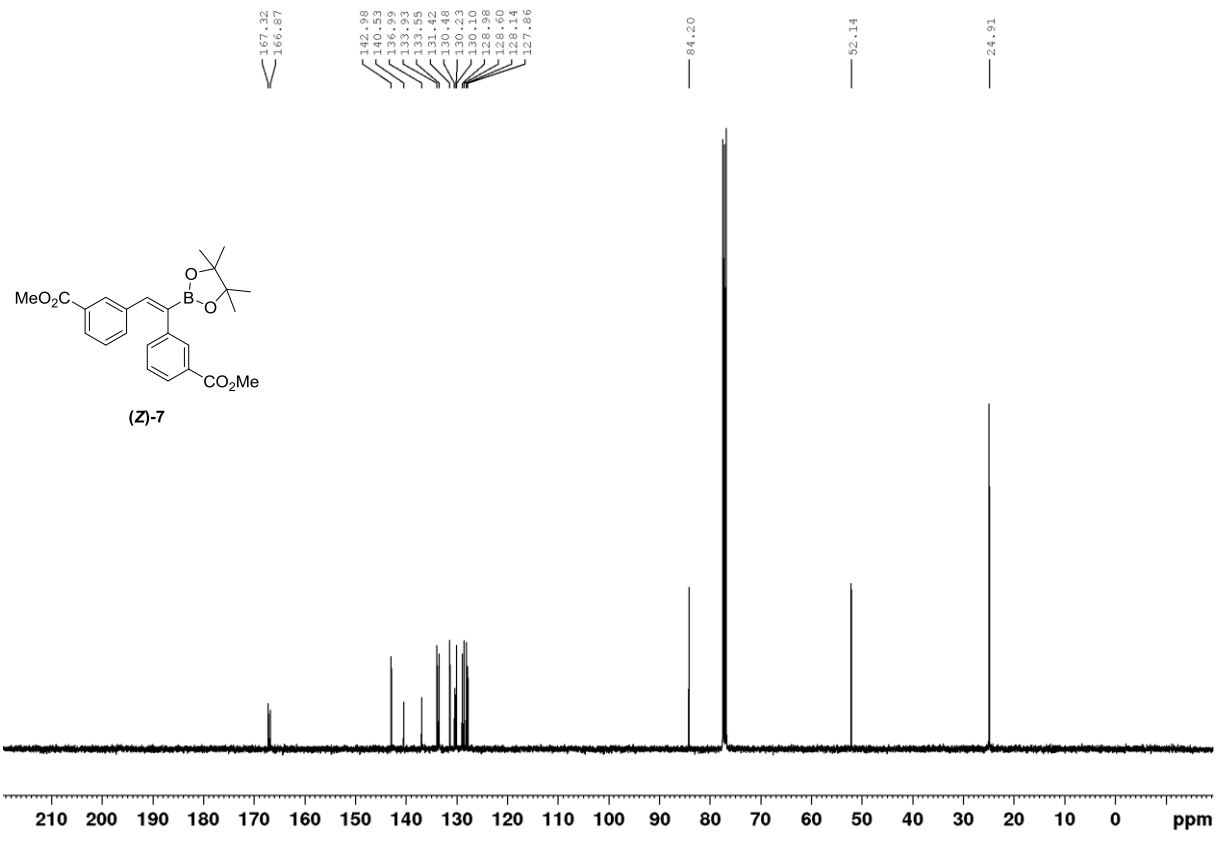




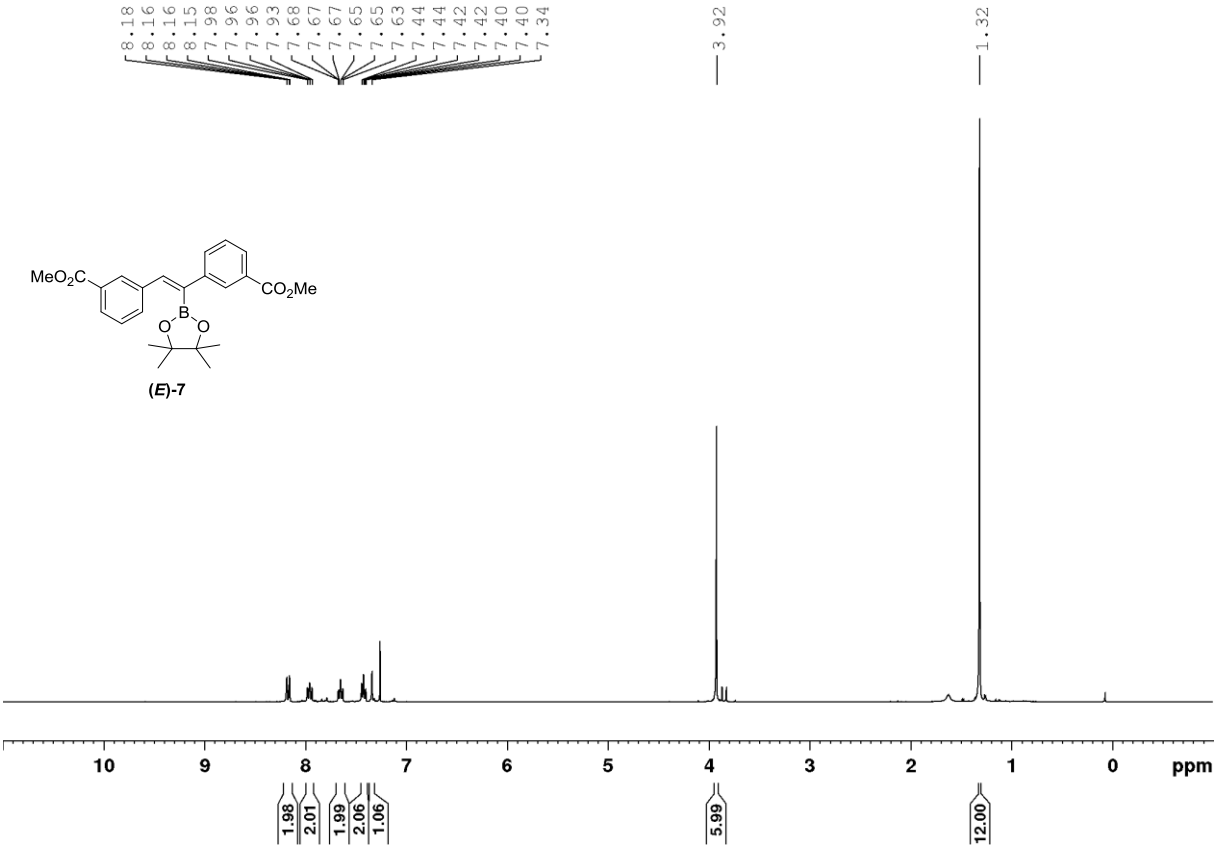
NMR spectra of 7:



(*Z*)-7



(*Z*)-7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7.96
7.93
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7.67
7.67
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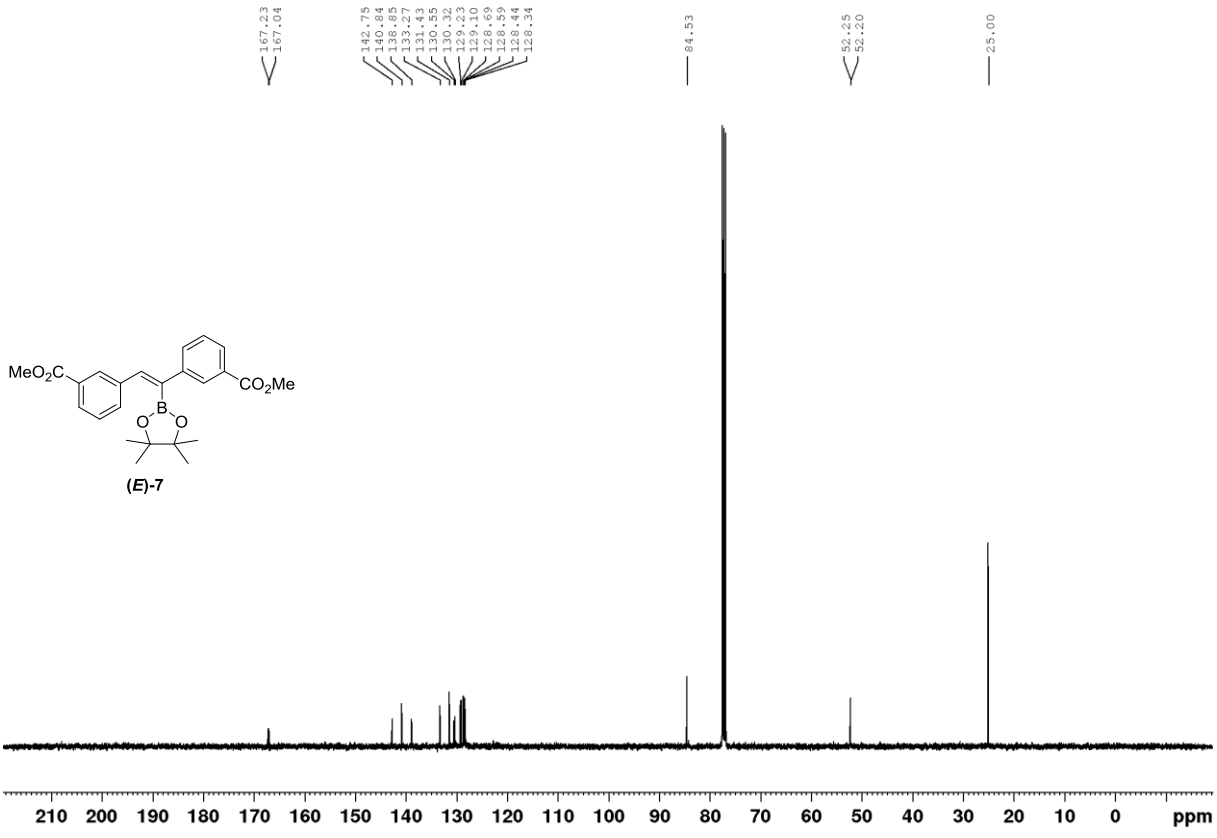
7.65
7.63
7.44
7.44
7.42
7.42
7.40
7.40
7.34
3.92
1.32
MeO2C
CO2Me
B
O
O
(E)-7
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
2.01
1.99
2.06
1.06
5.99
12.00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128.44
128.34
84.53
52.25
52.20
25.00
MeO2C
CO2Me
B
O
O
(E)-7
210
200
190
180
170
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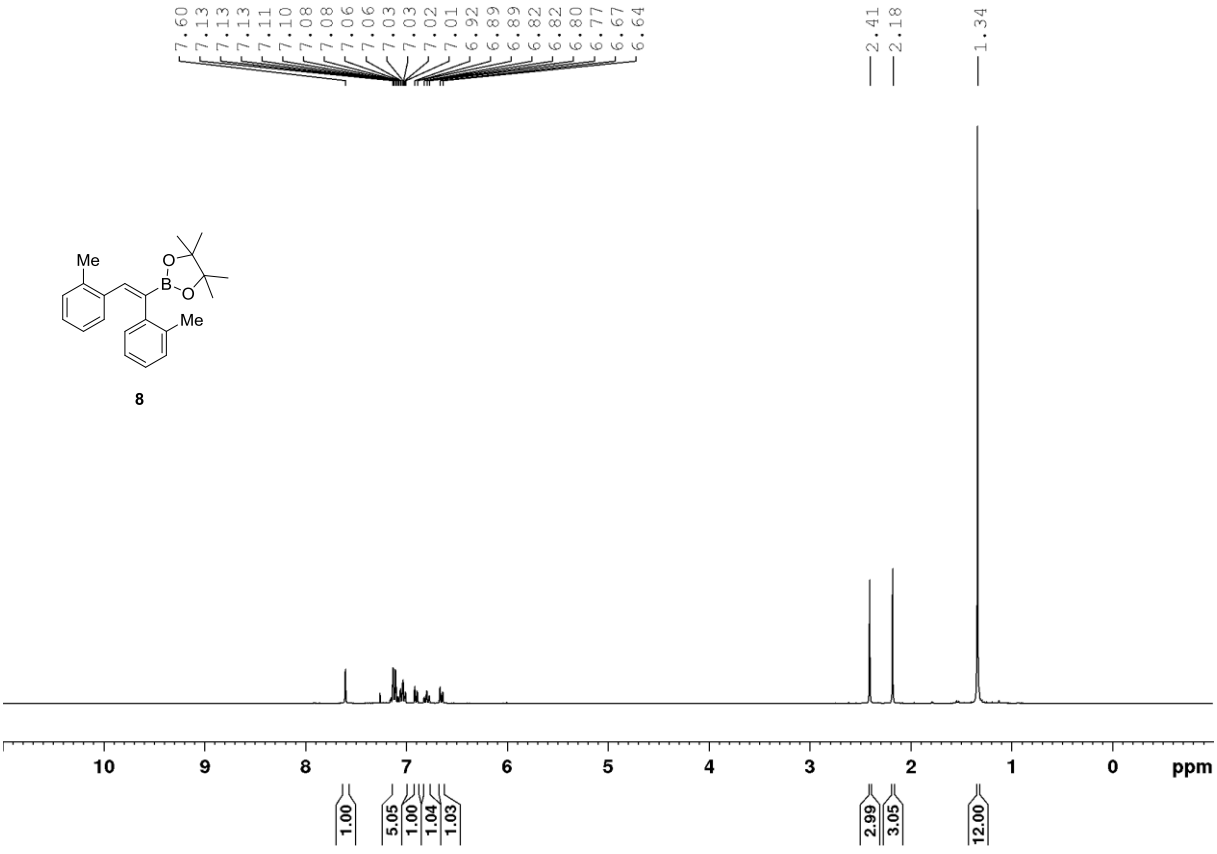
0
ppm

NMR spectra of 8:



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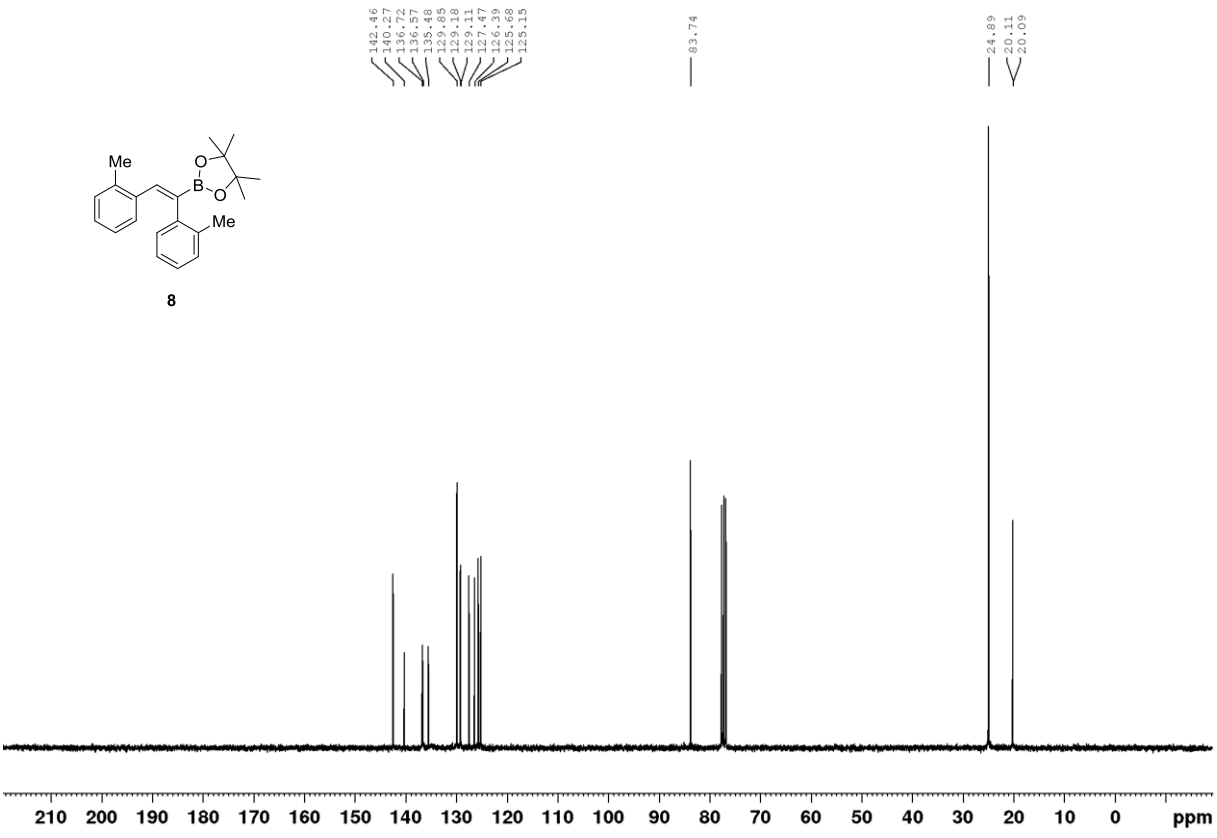
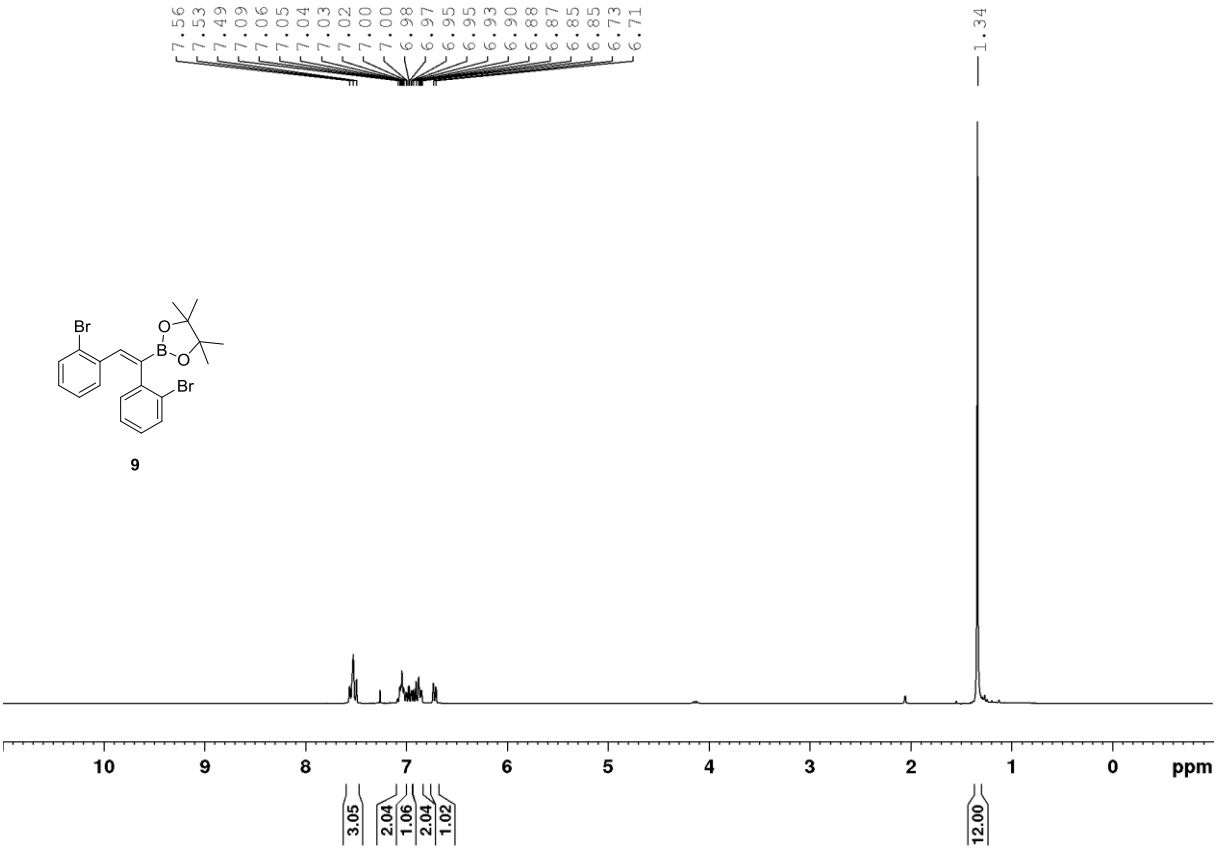
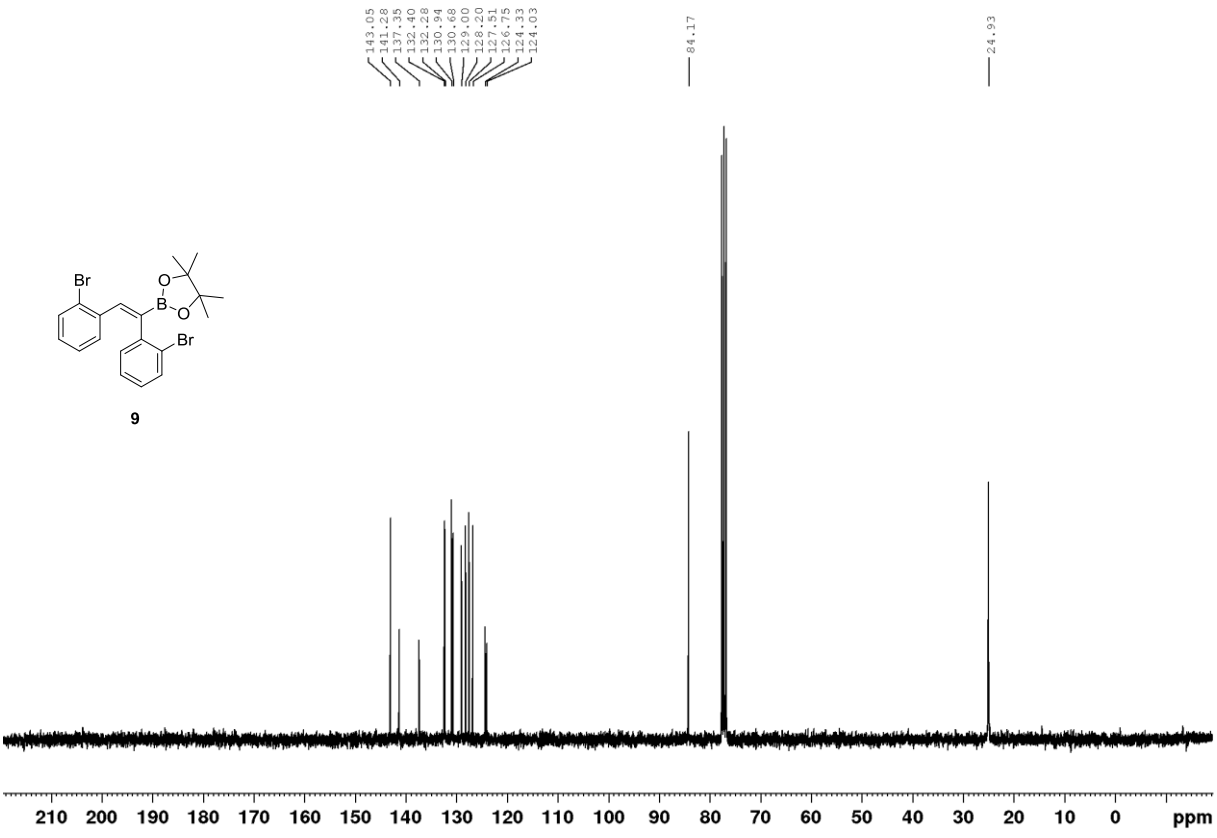


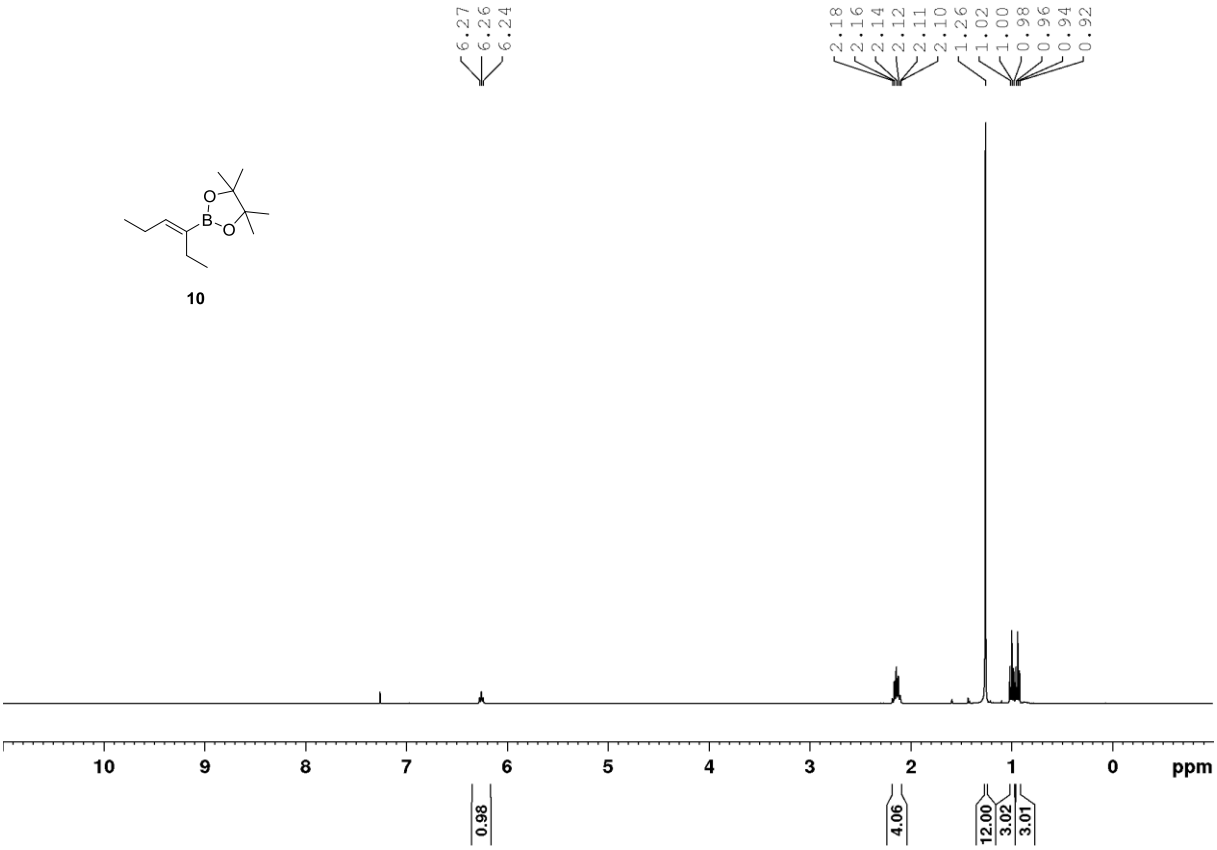
8

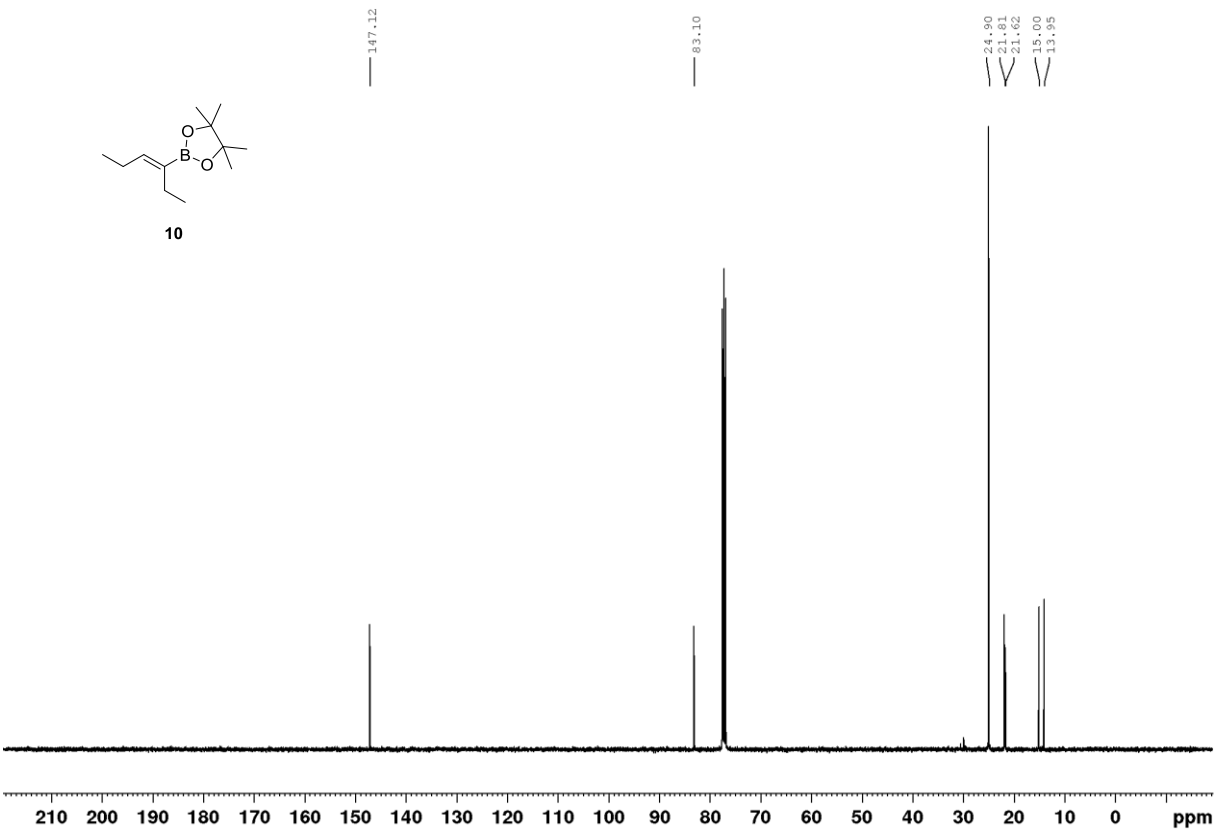
NMR spectra of 9:



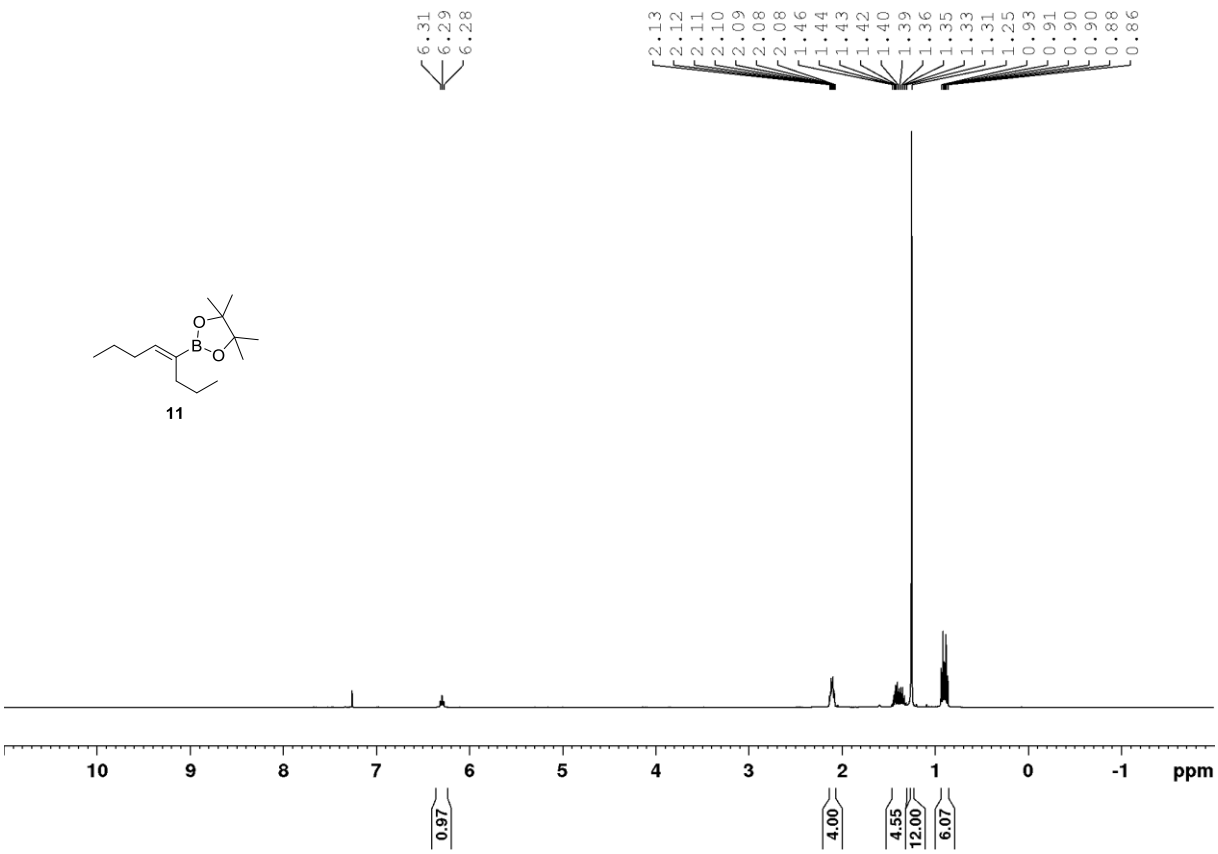


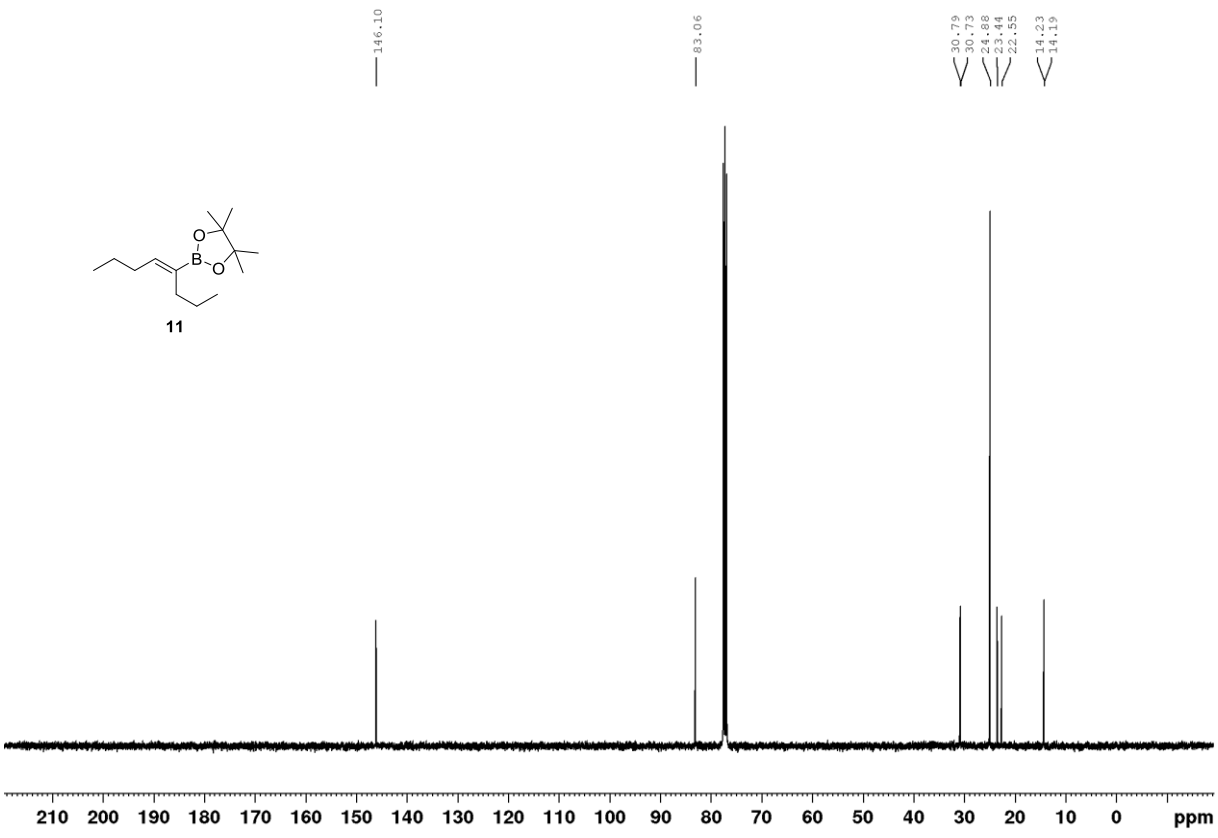
NMR spectra of 10:



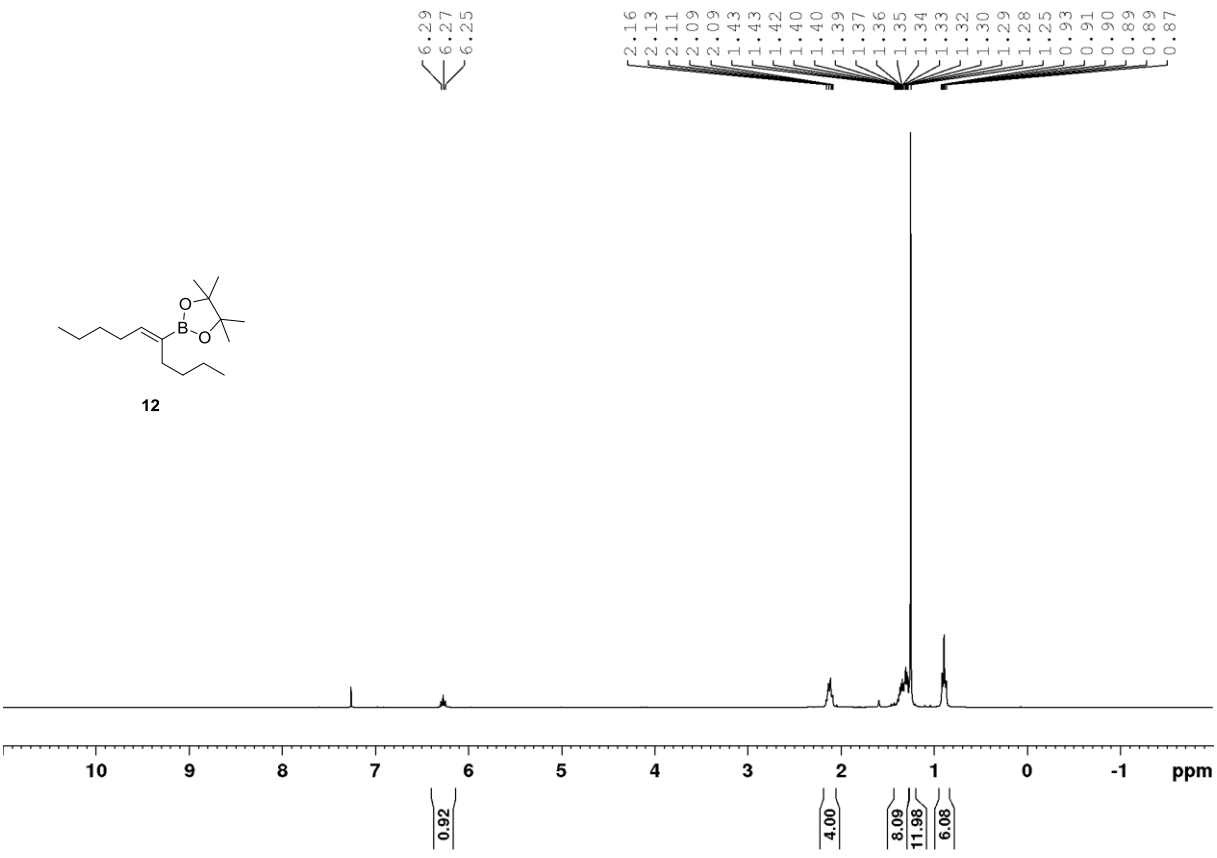


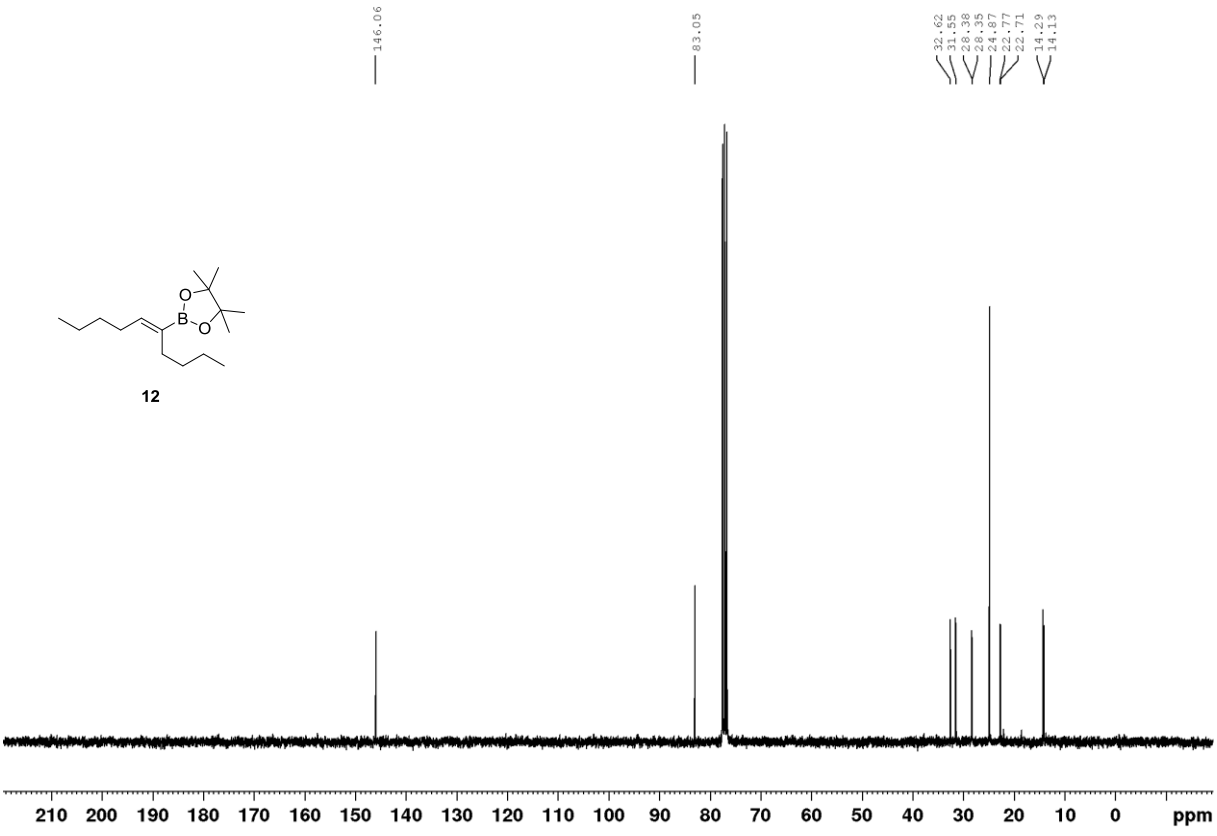
NMR spectra of 11:



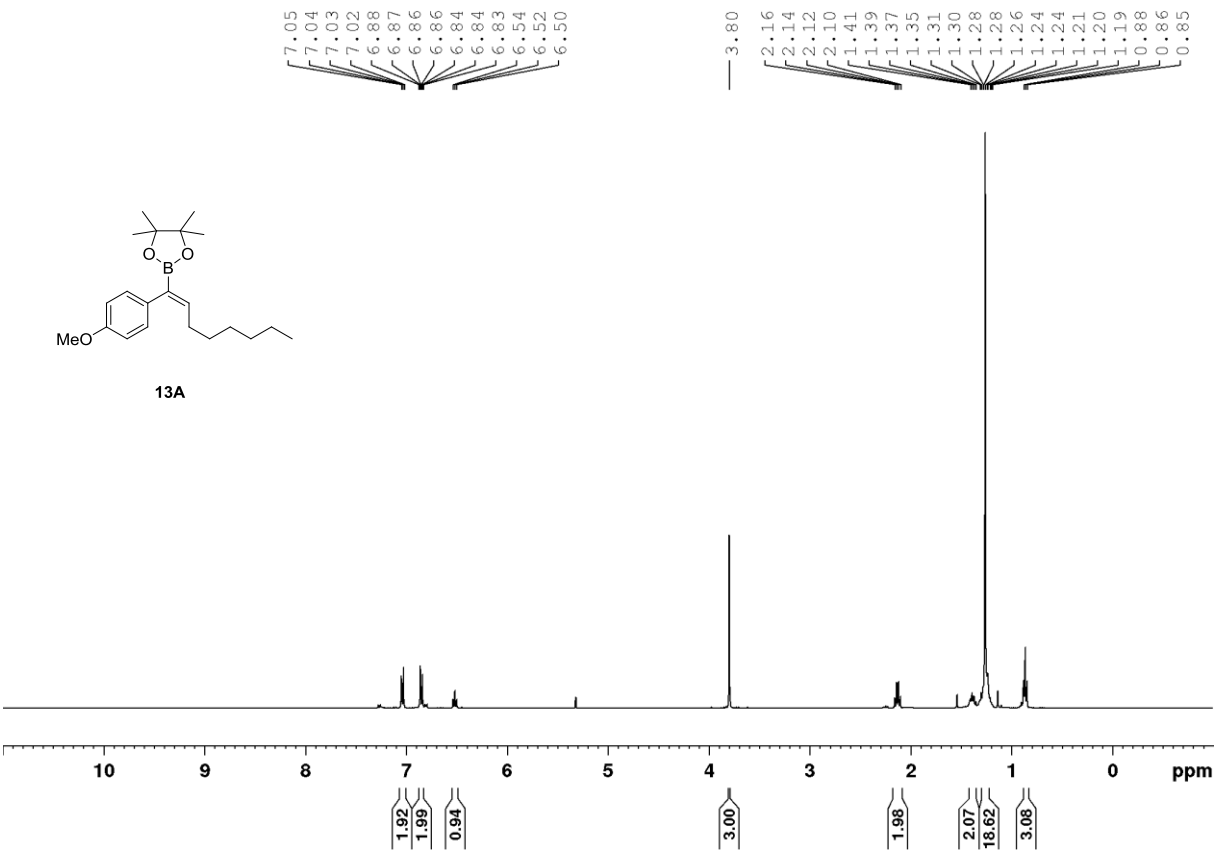


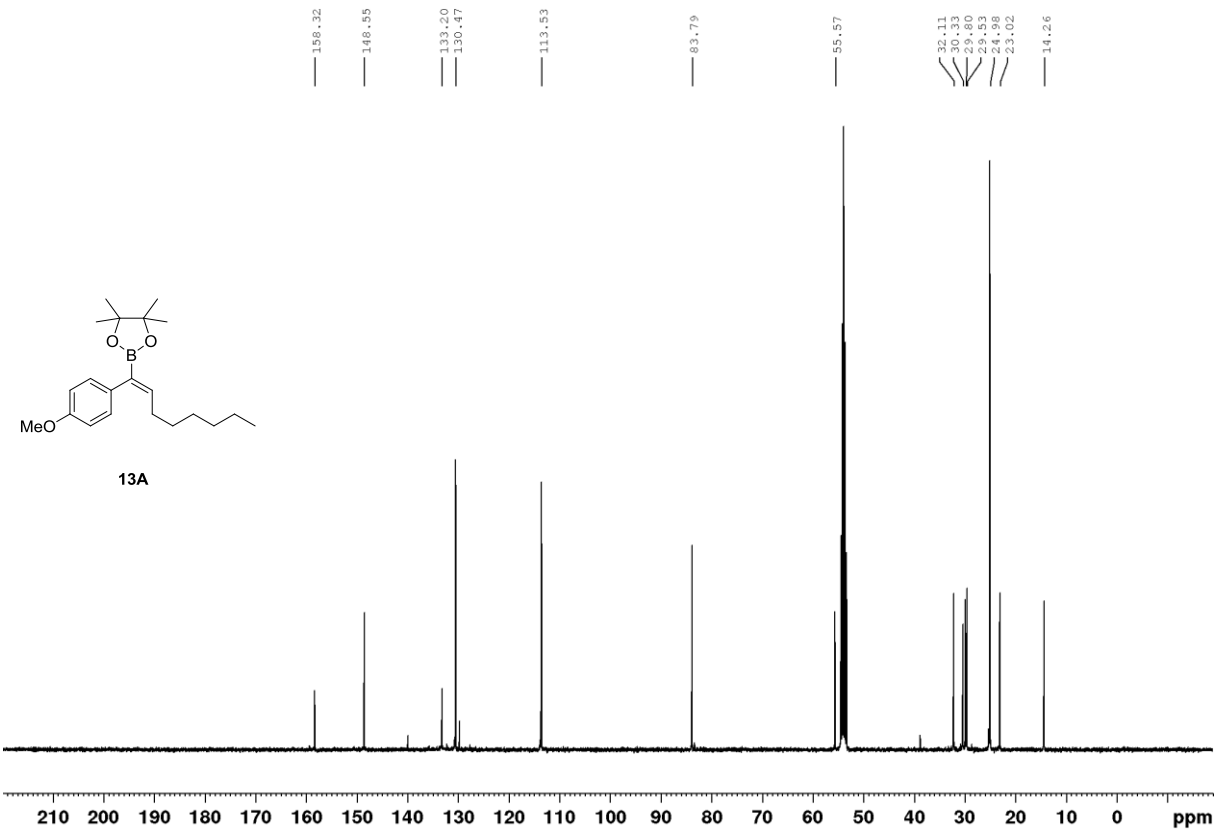
NMR spectra of 12:



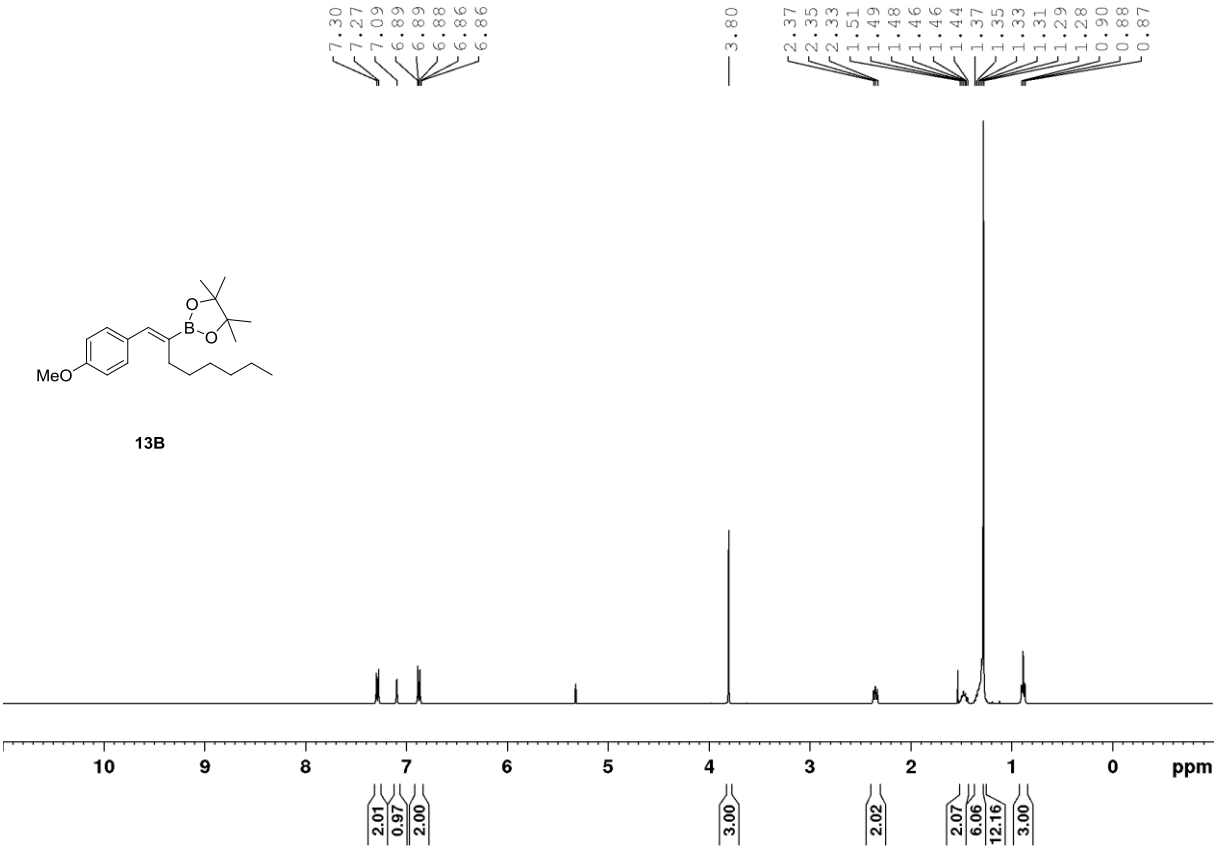


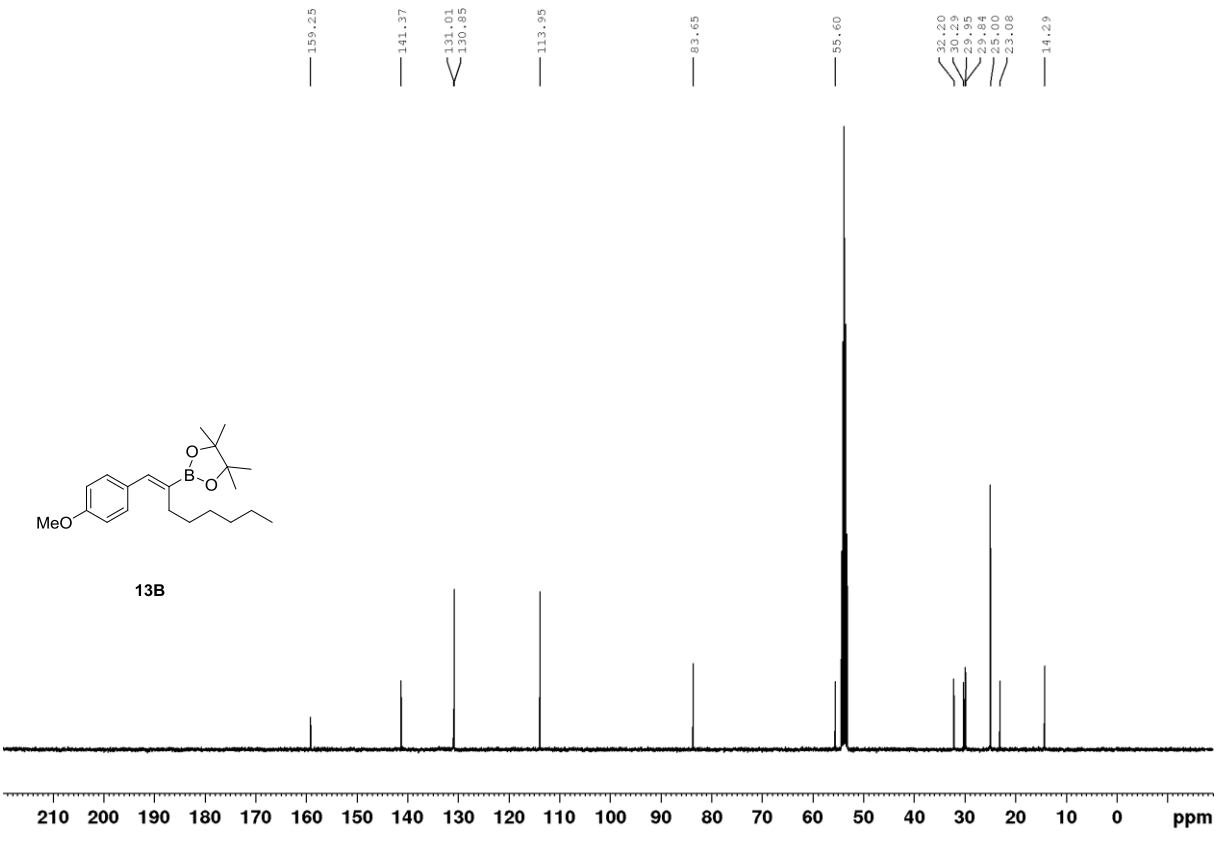
NMR spectra of 13A:



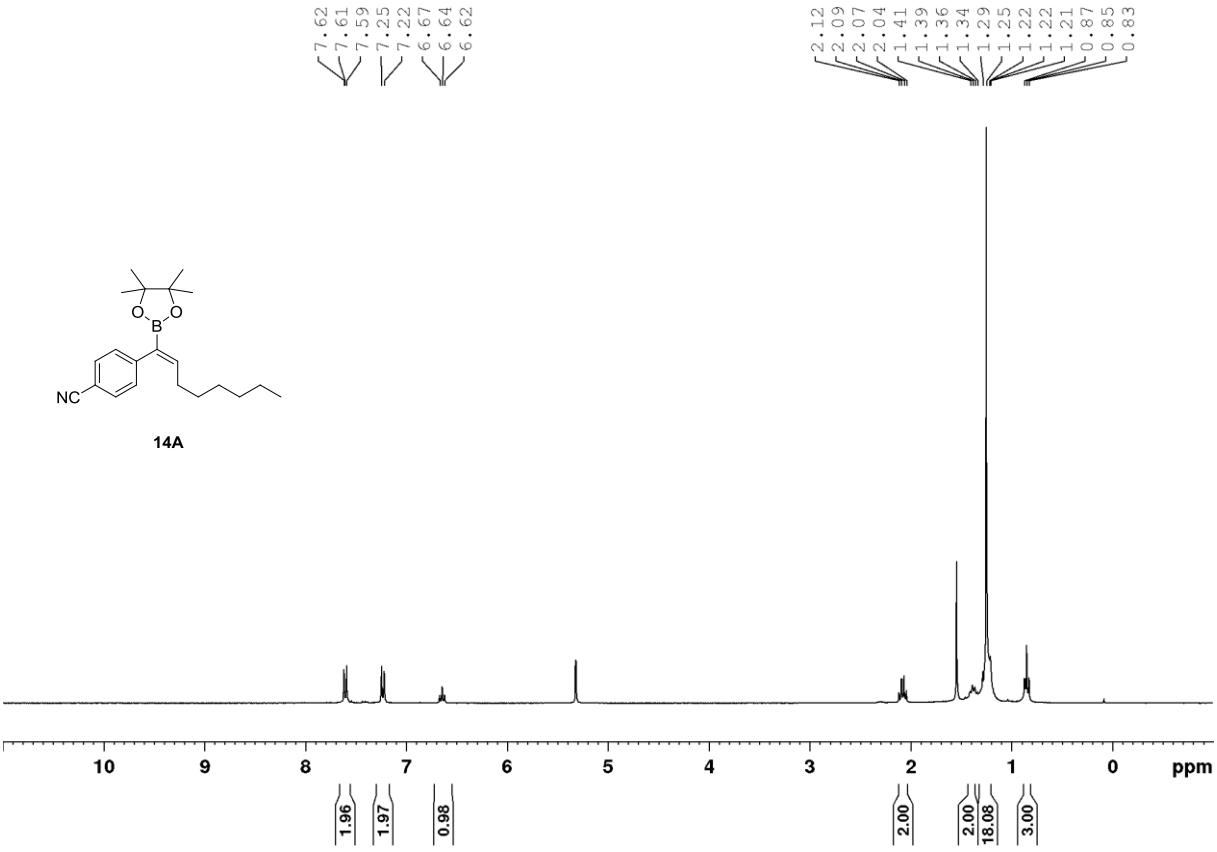


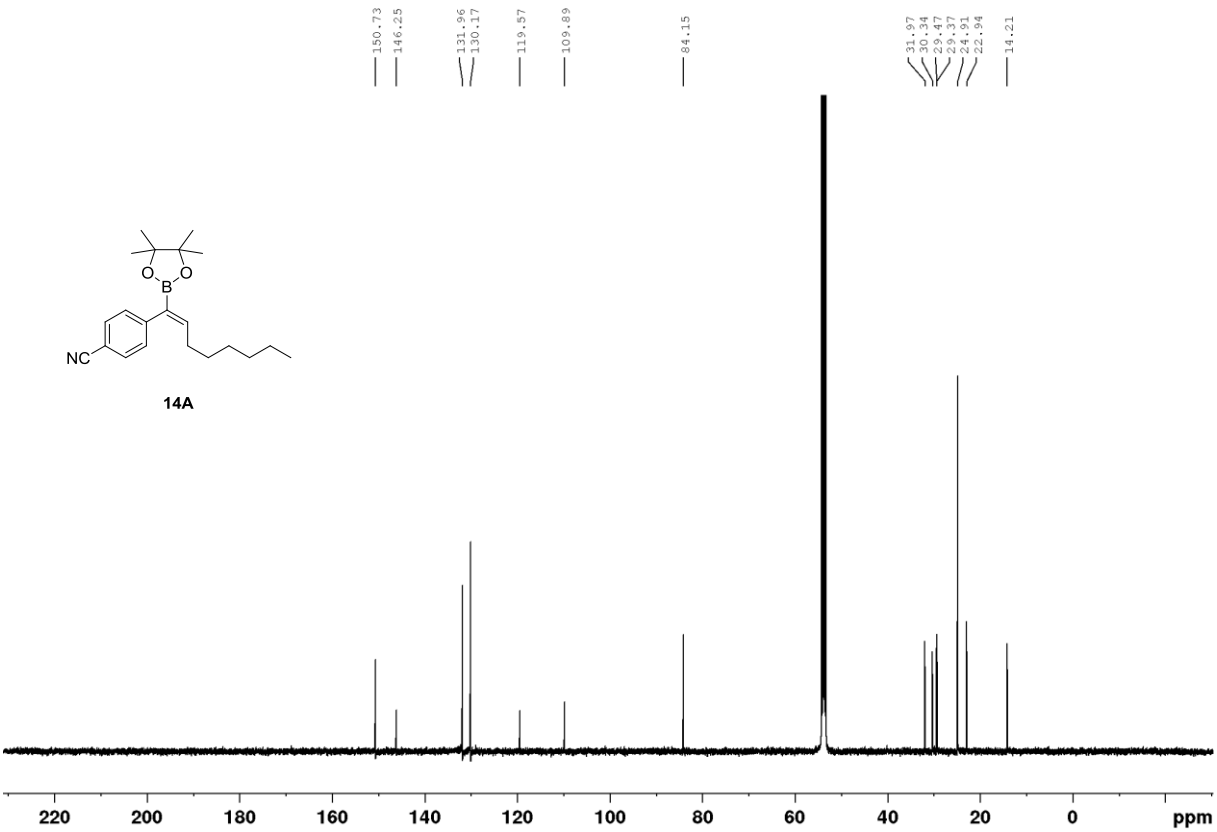
NMR spectra of 13B:



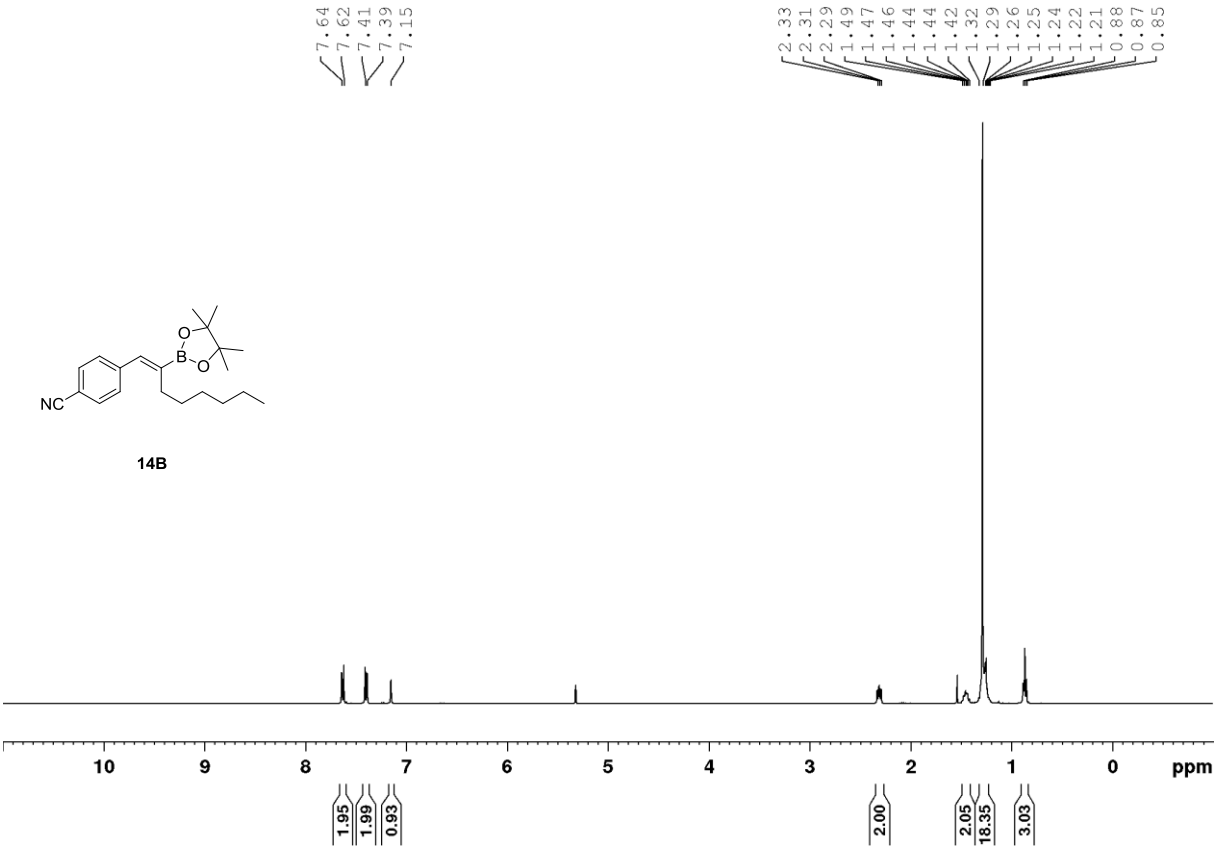


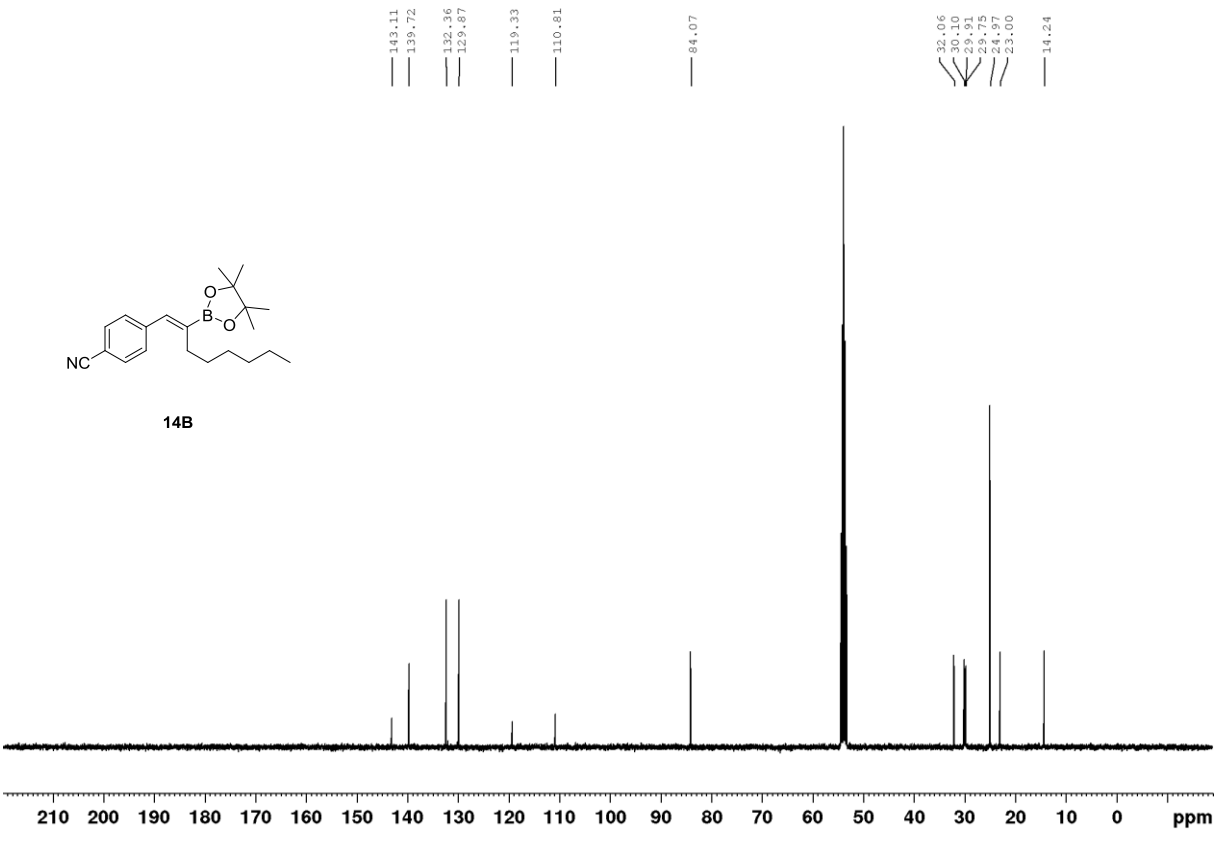
NMR spectra of 14A:



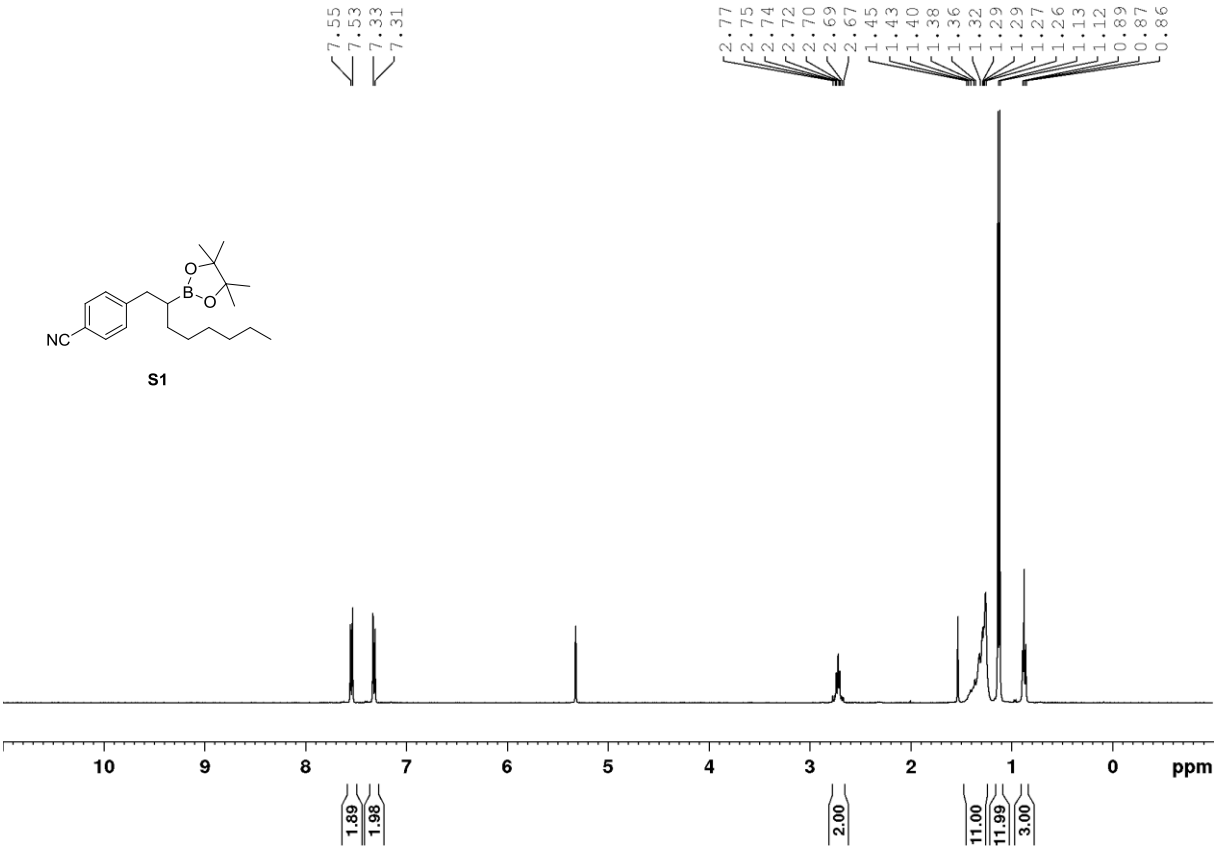


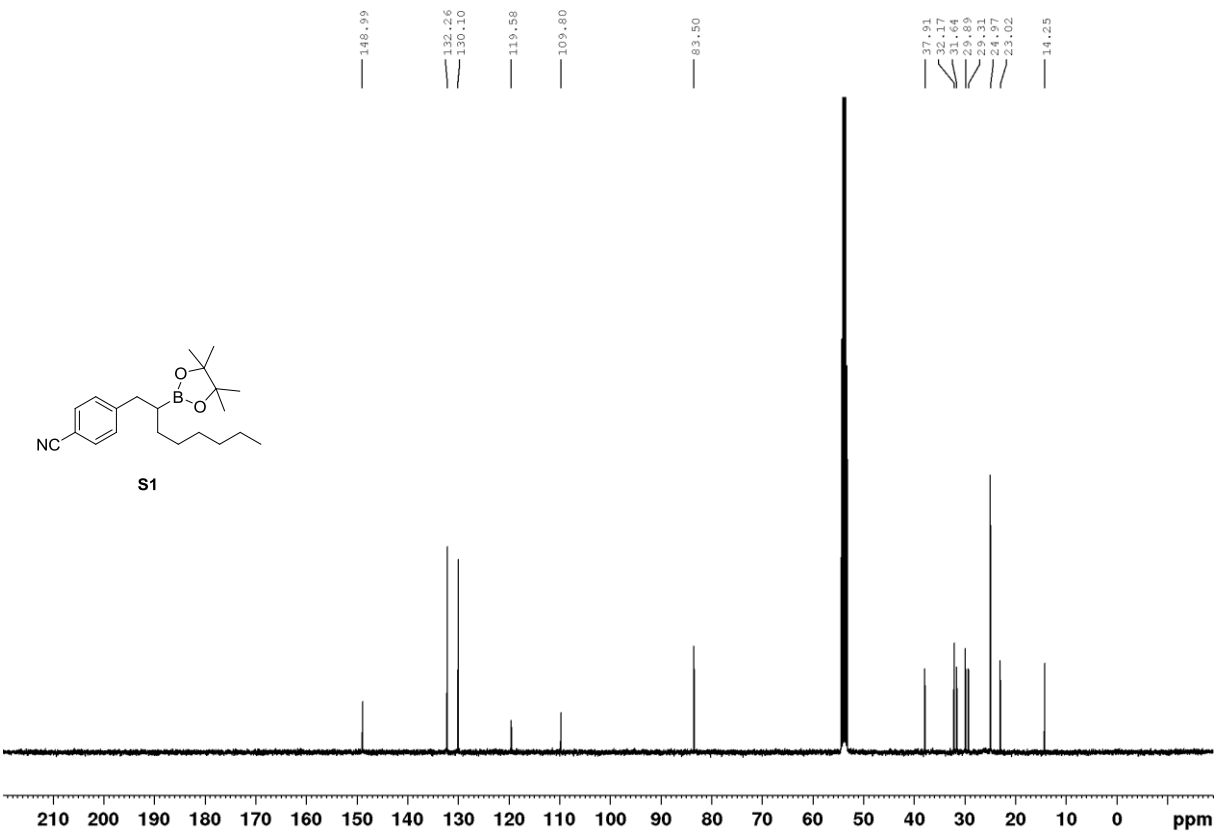
NMR spectra of 14B:



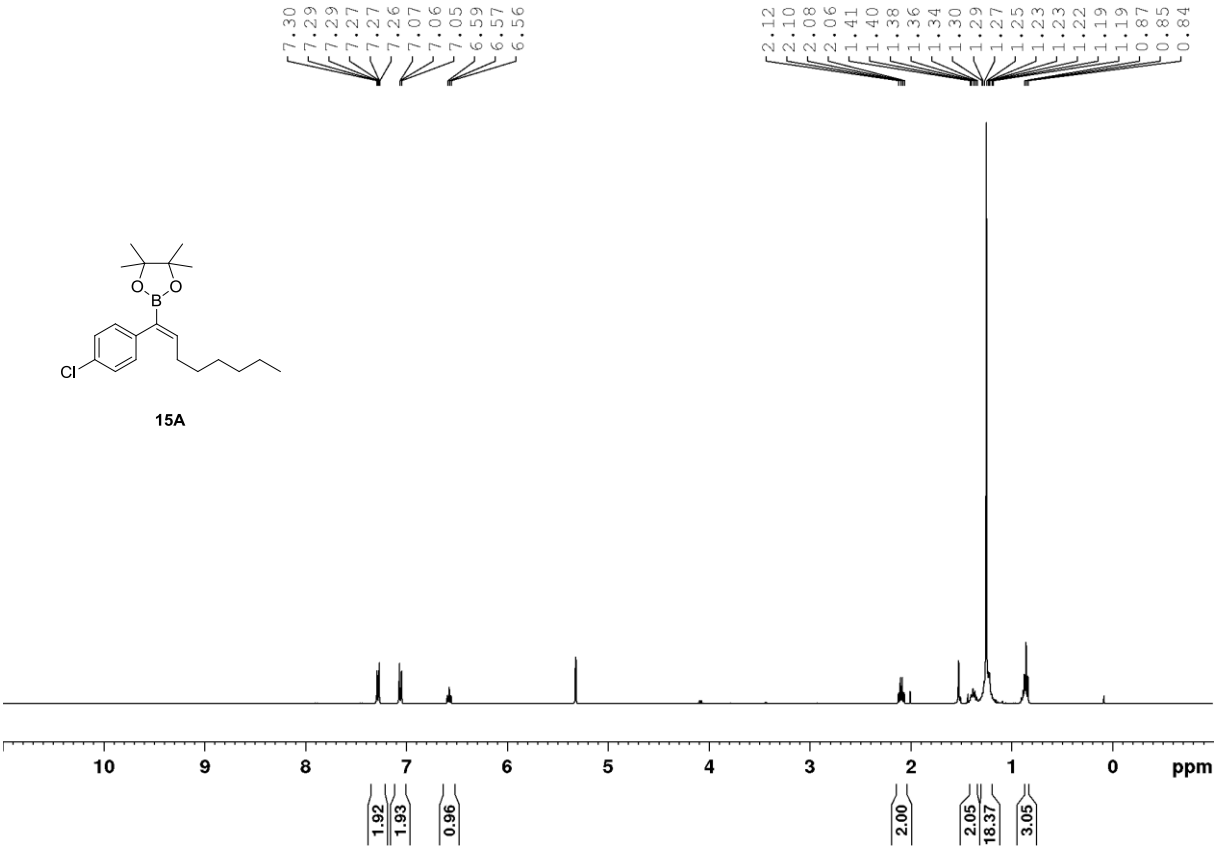


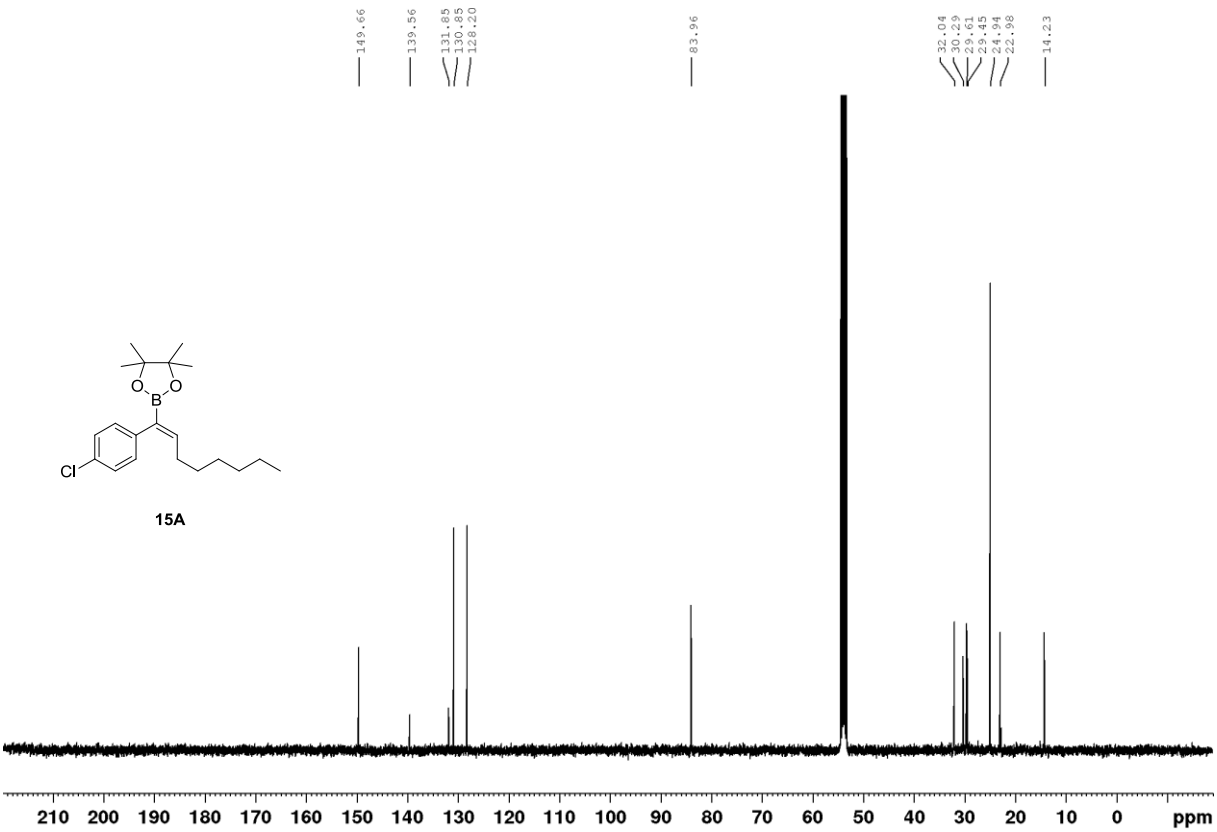
NMR spectra of S1:



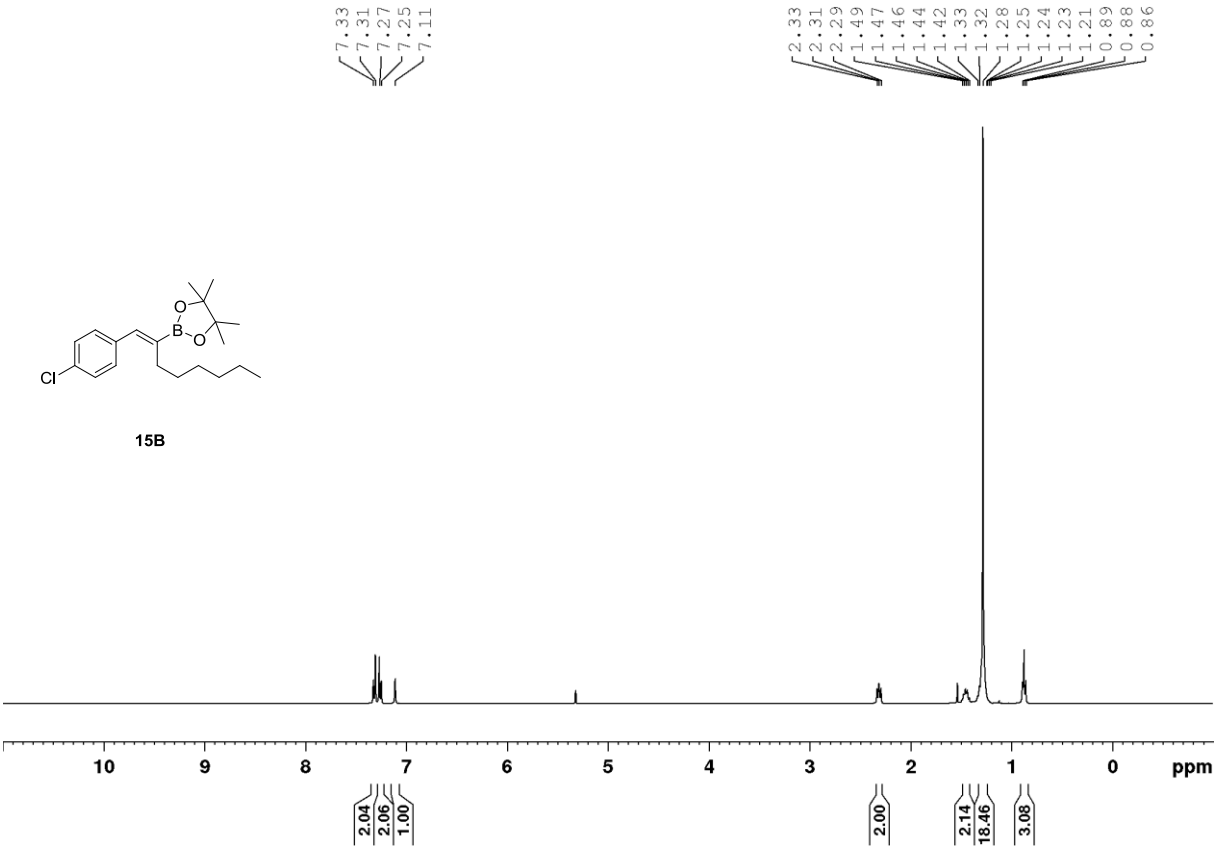


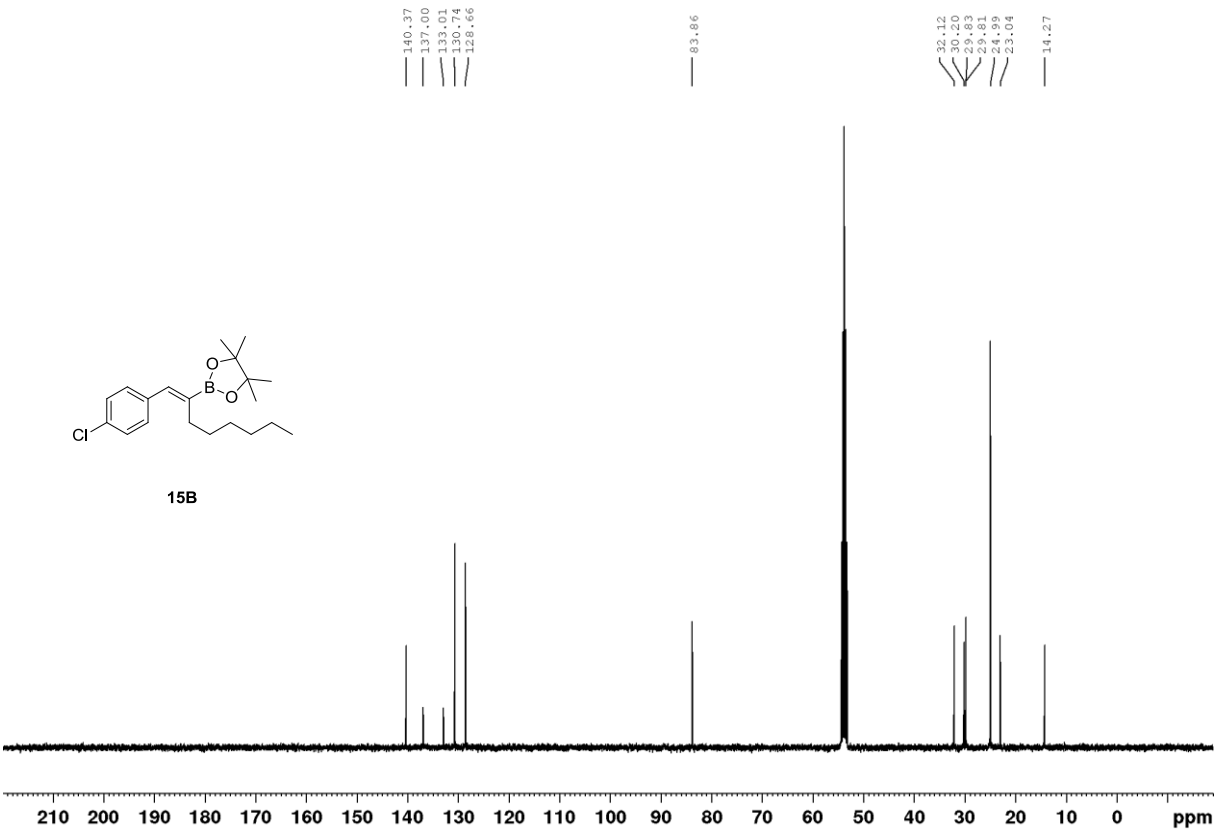
NMR spectra of 15A:



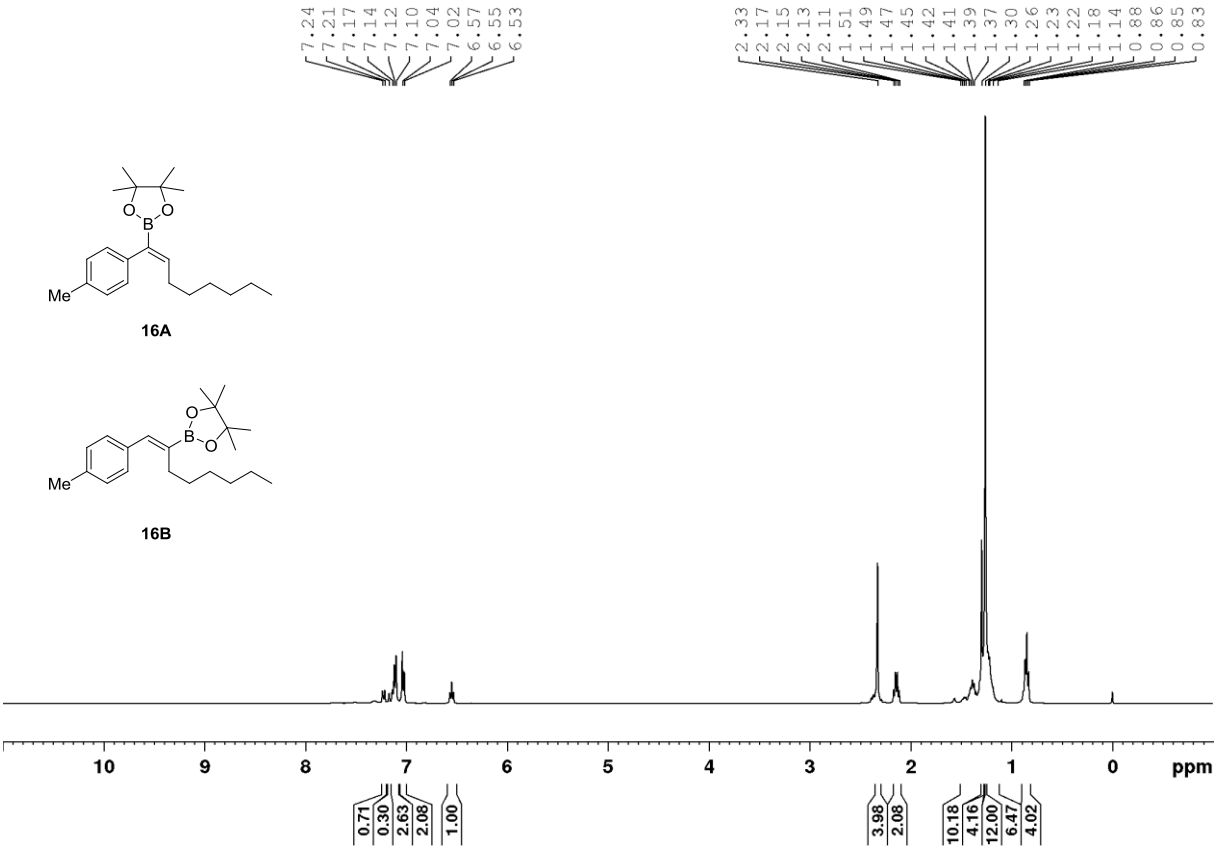


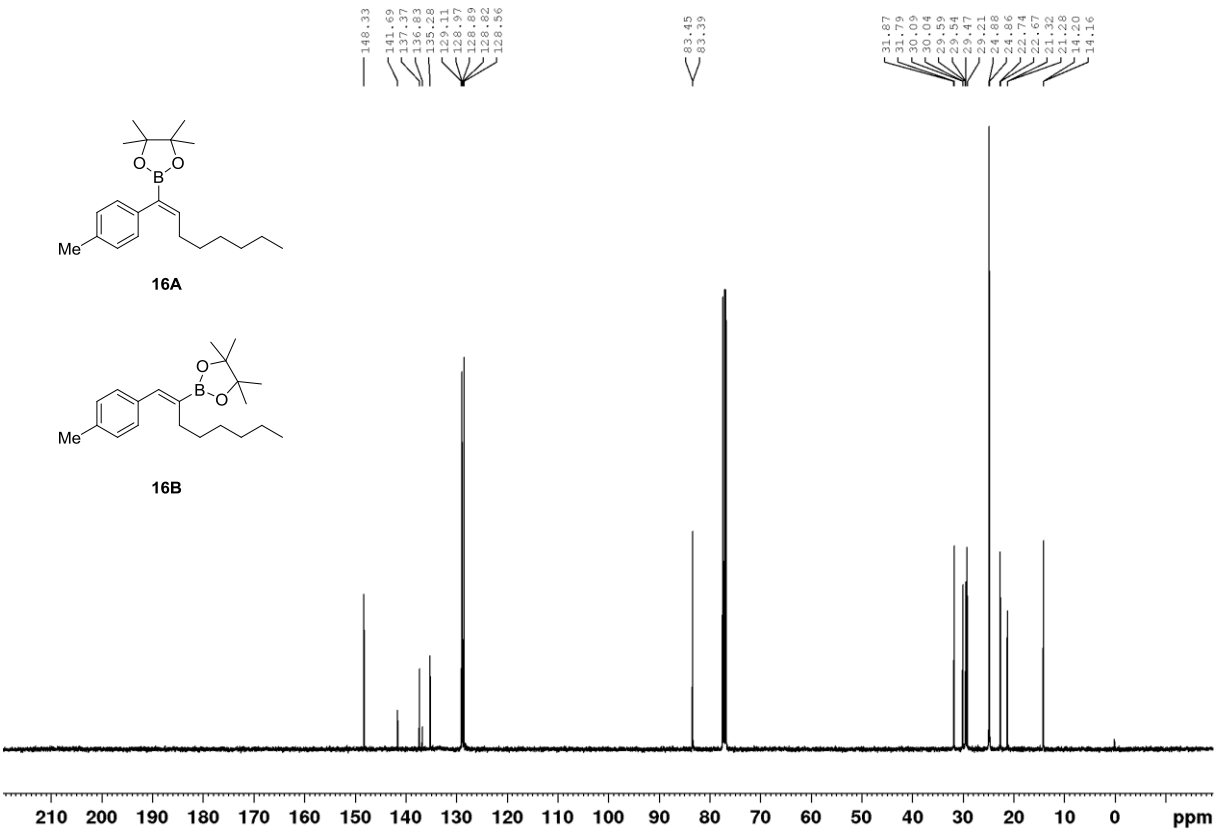
NMR spectra of 15B:



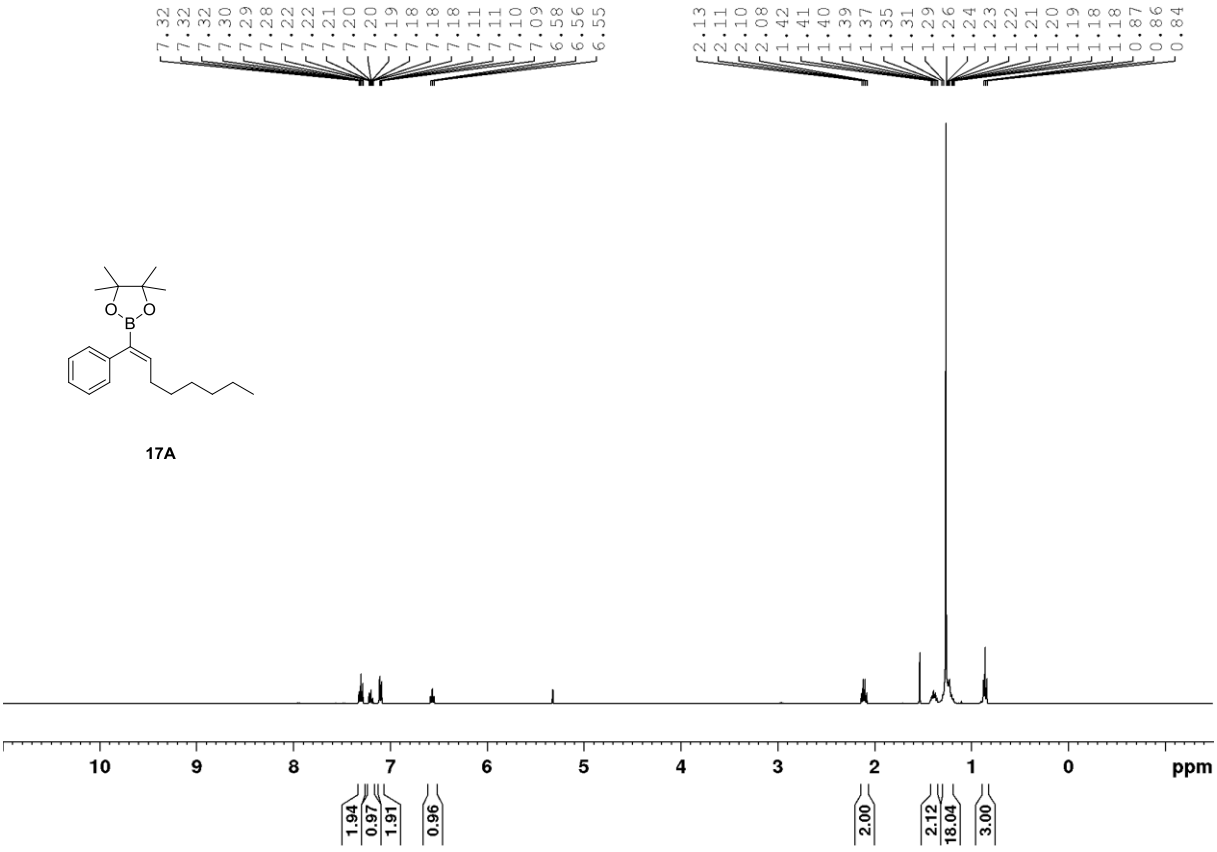


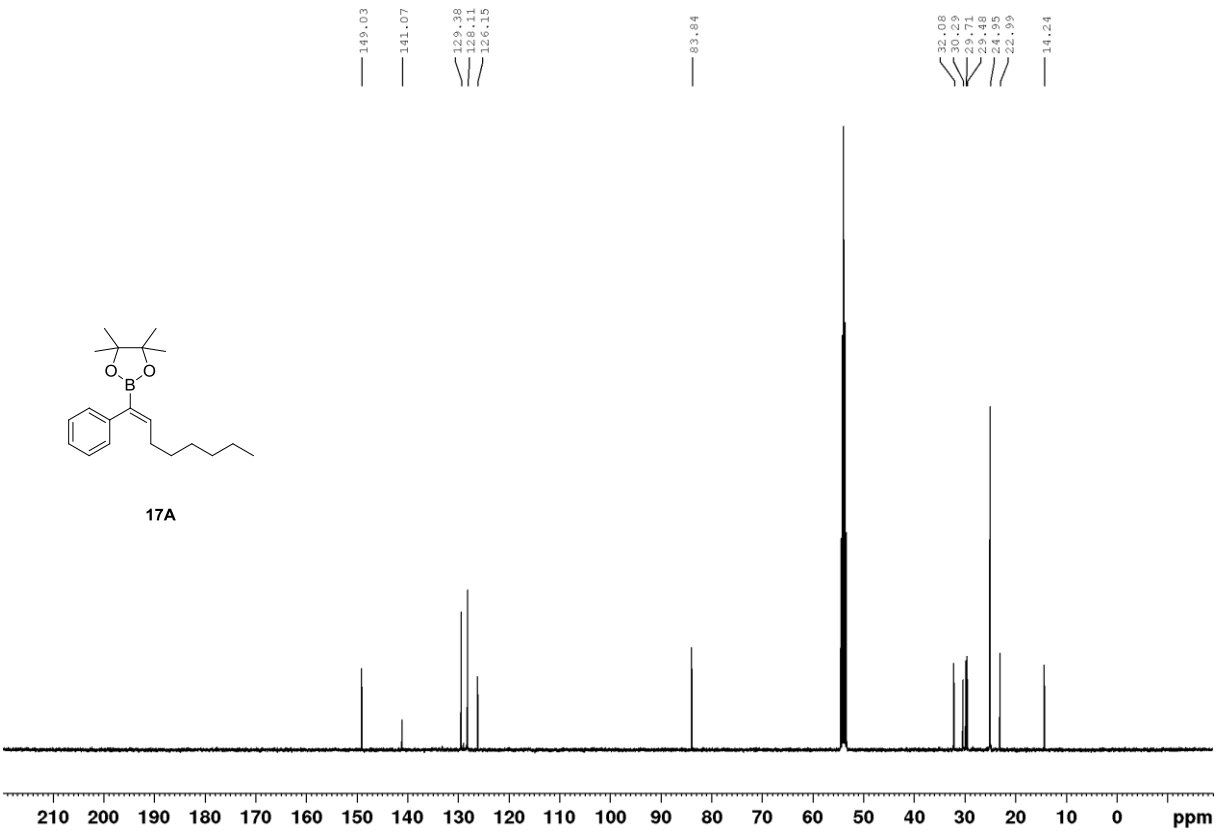
NMR spectra of 16A/16B:



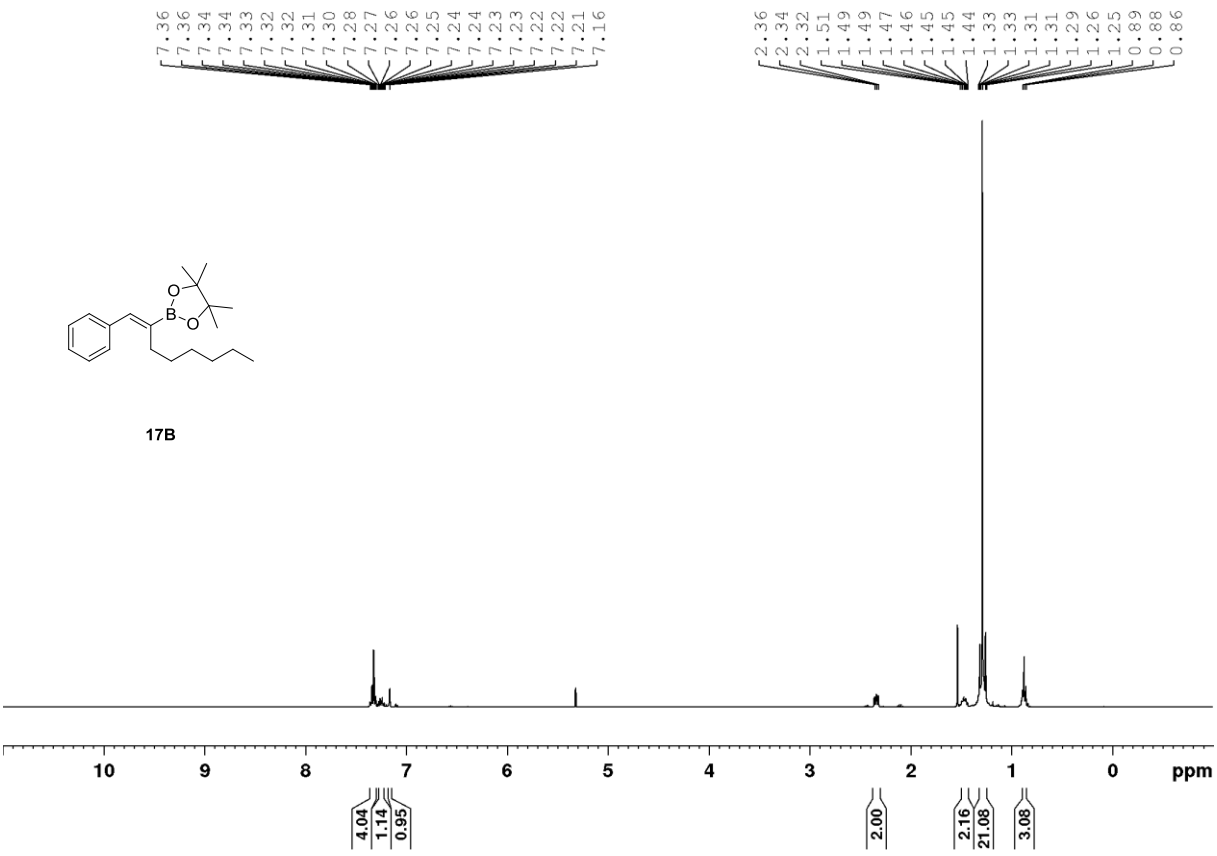


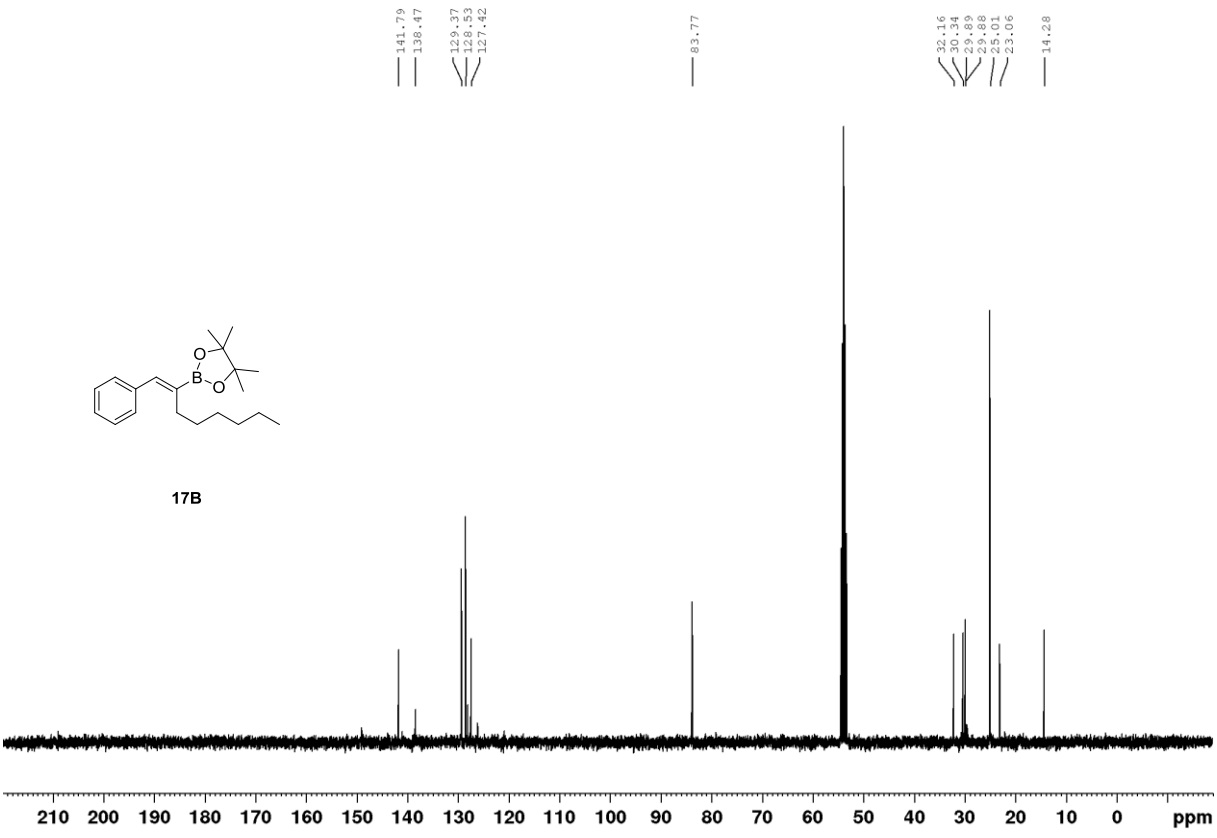
NMR spectra of 17A:



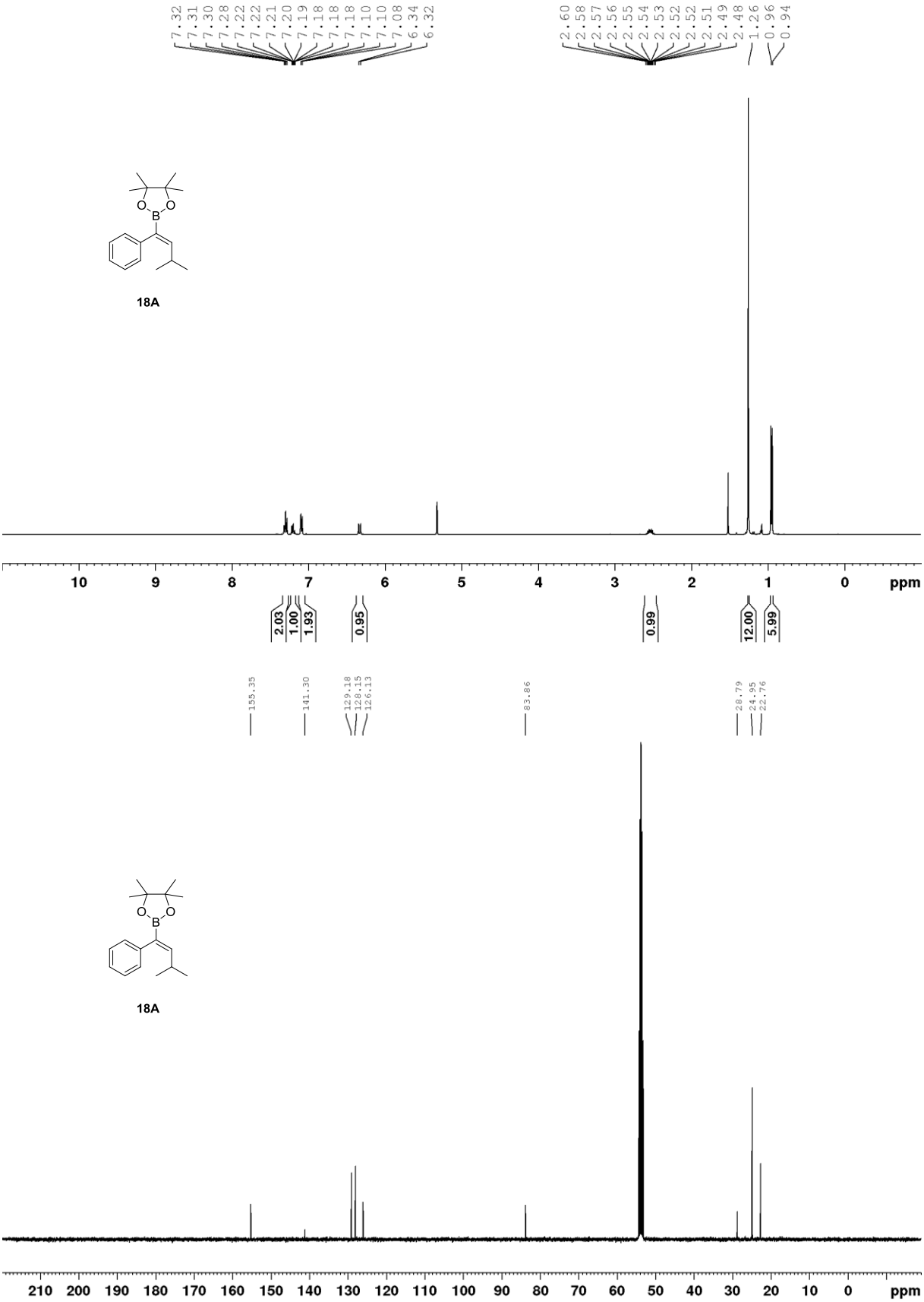


NMR spectra of 17B:

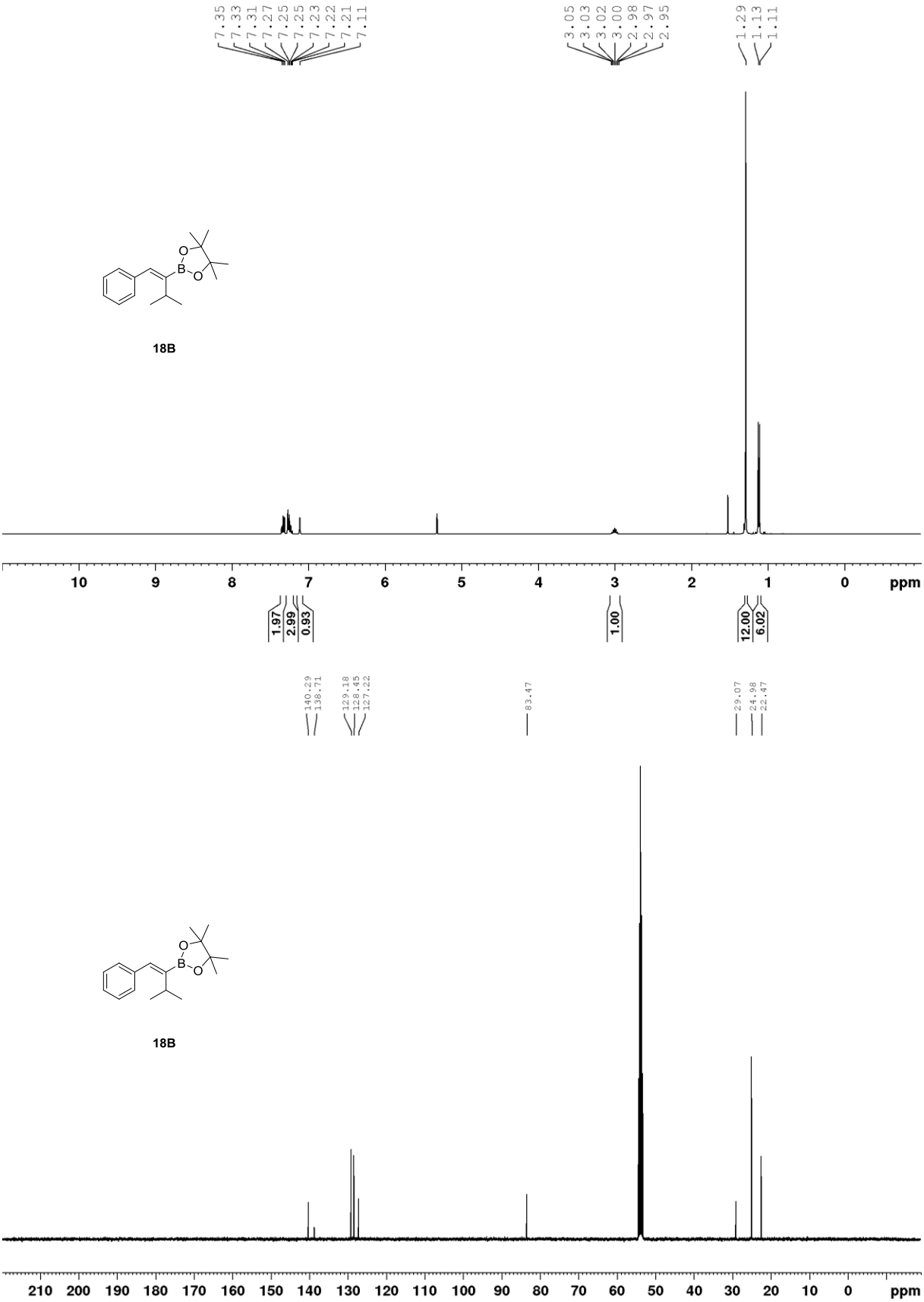




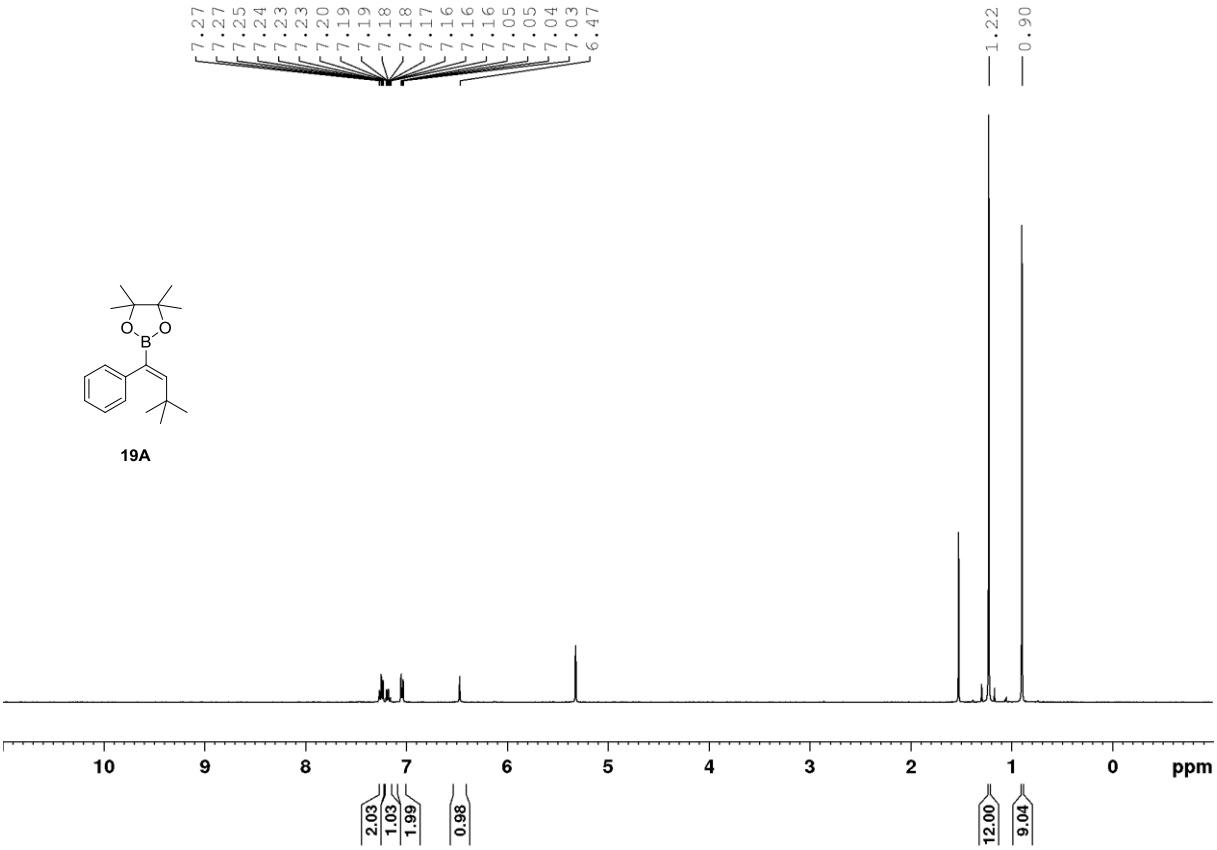
NMR spectra of 18A:

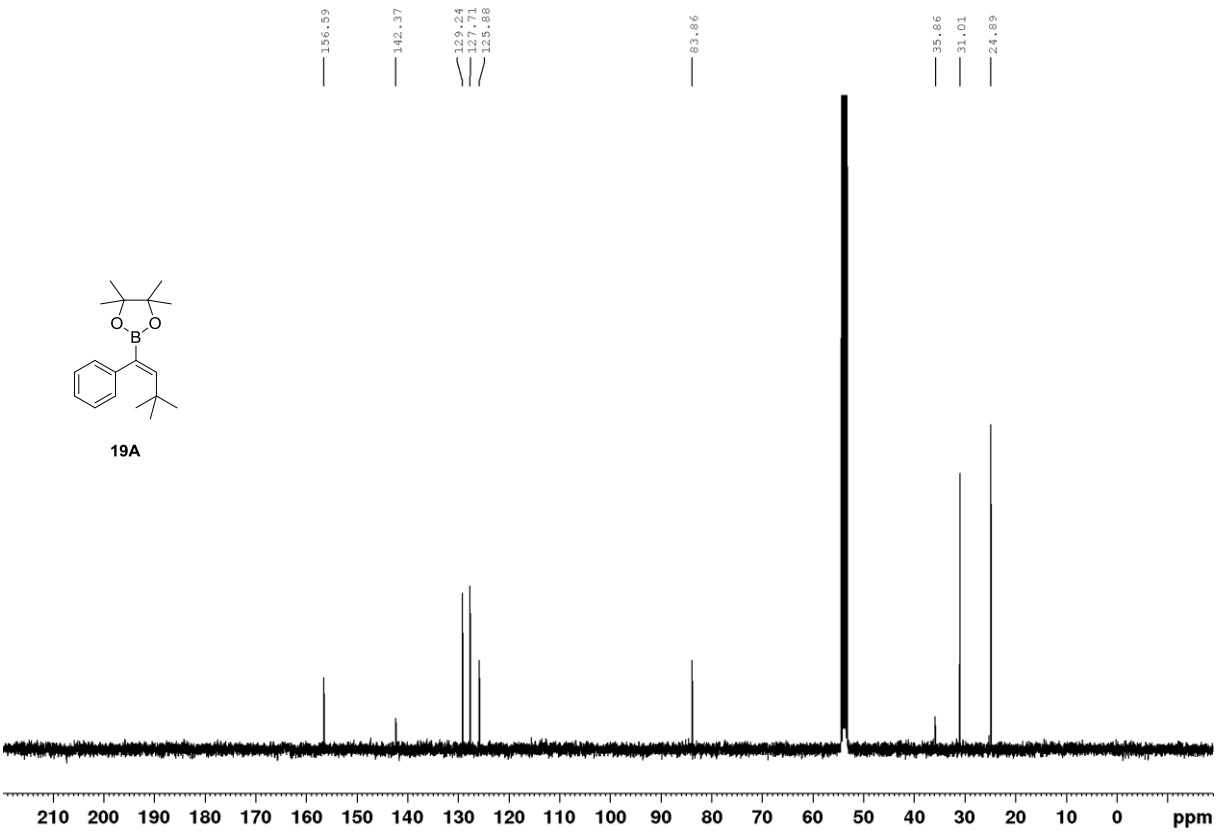


NMR spectra of 18B:

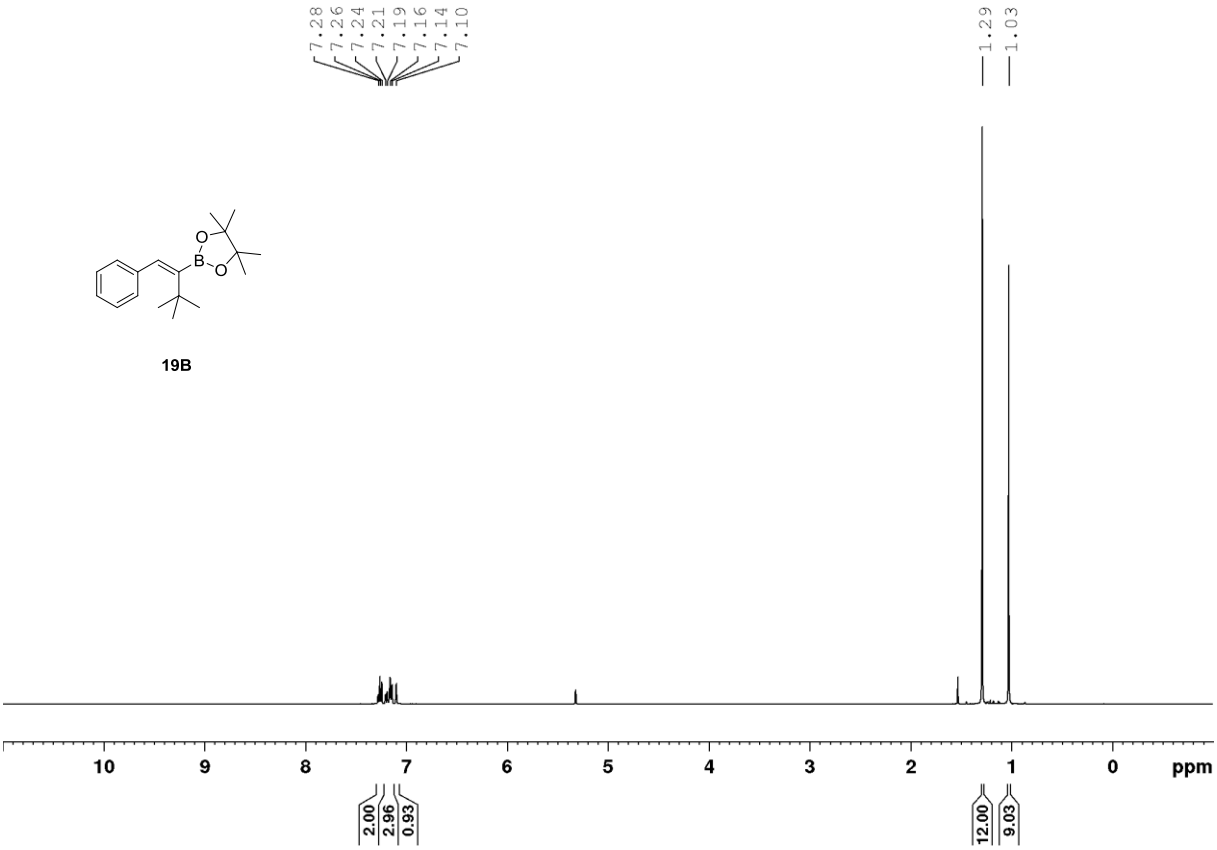


NMR spectra of 19A:

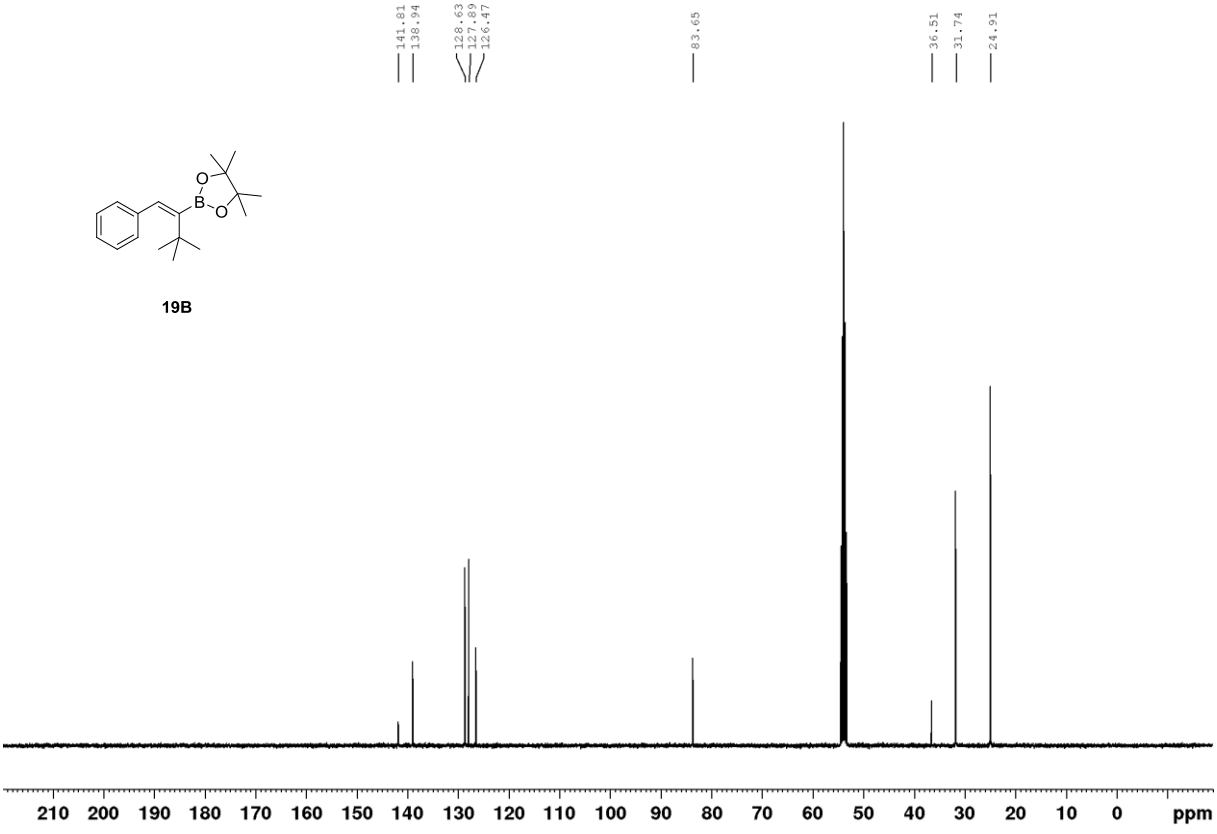




NMR spectra of 19B:

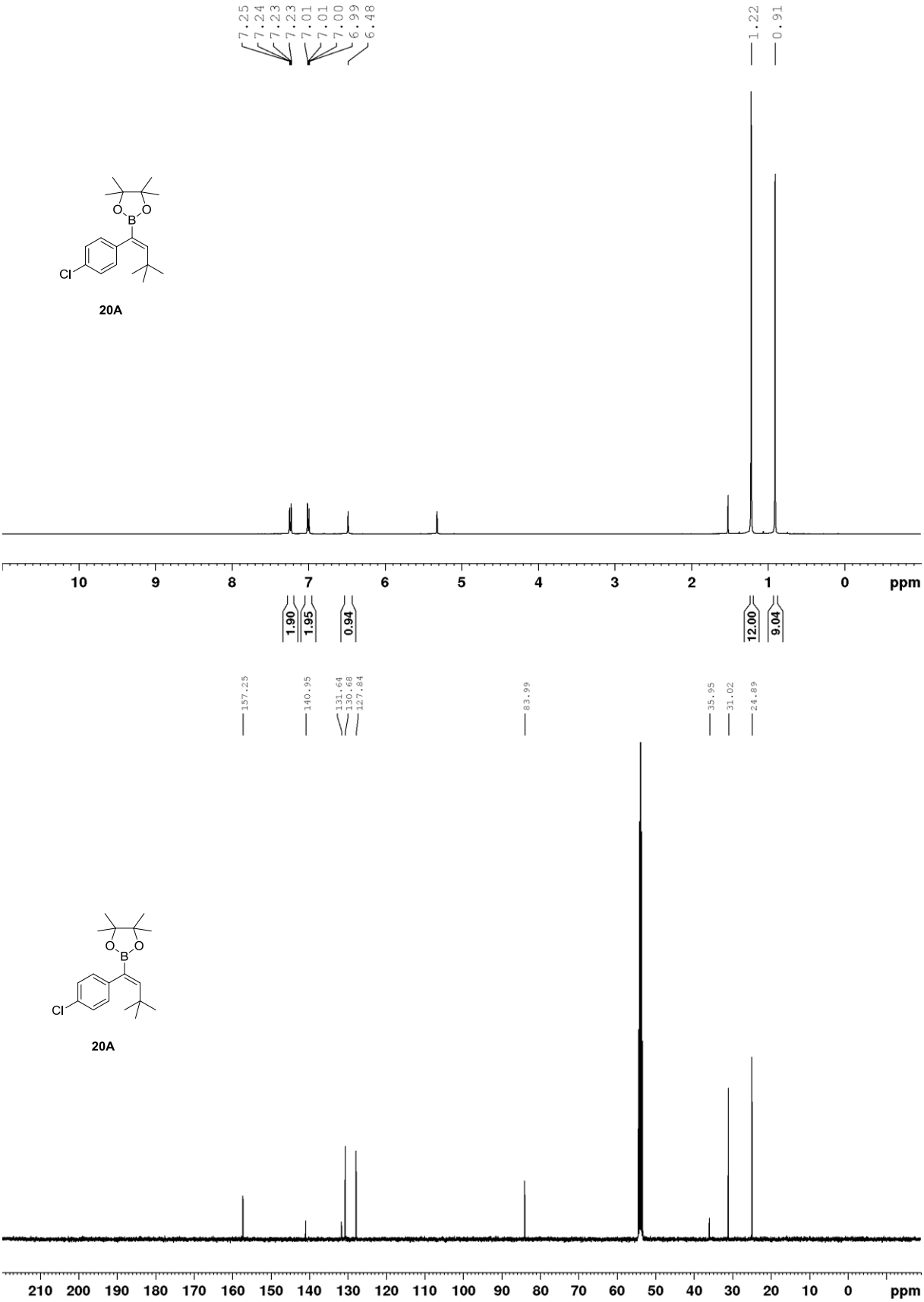


19B

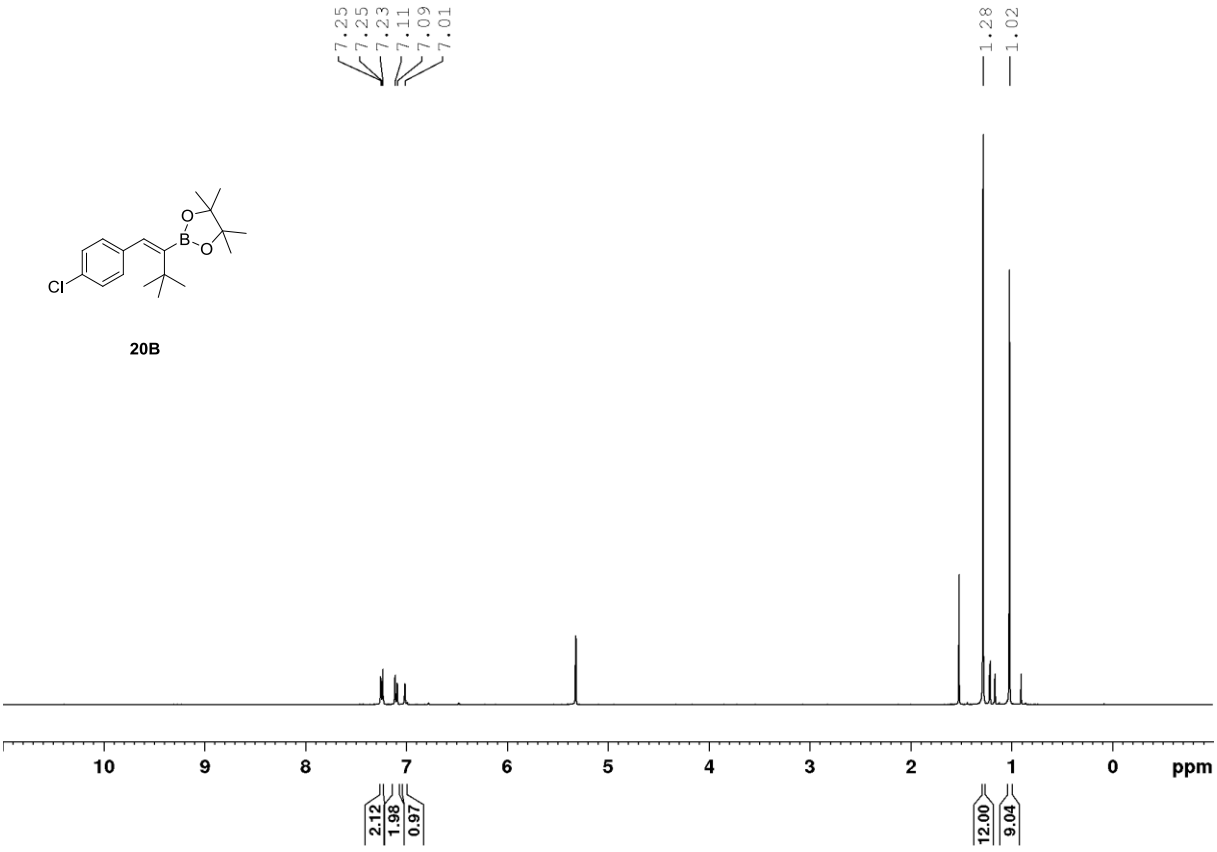


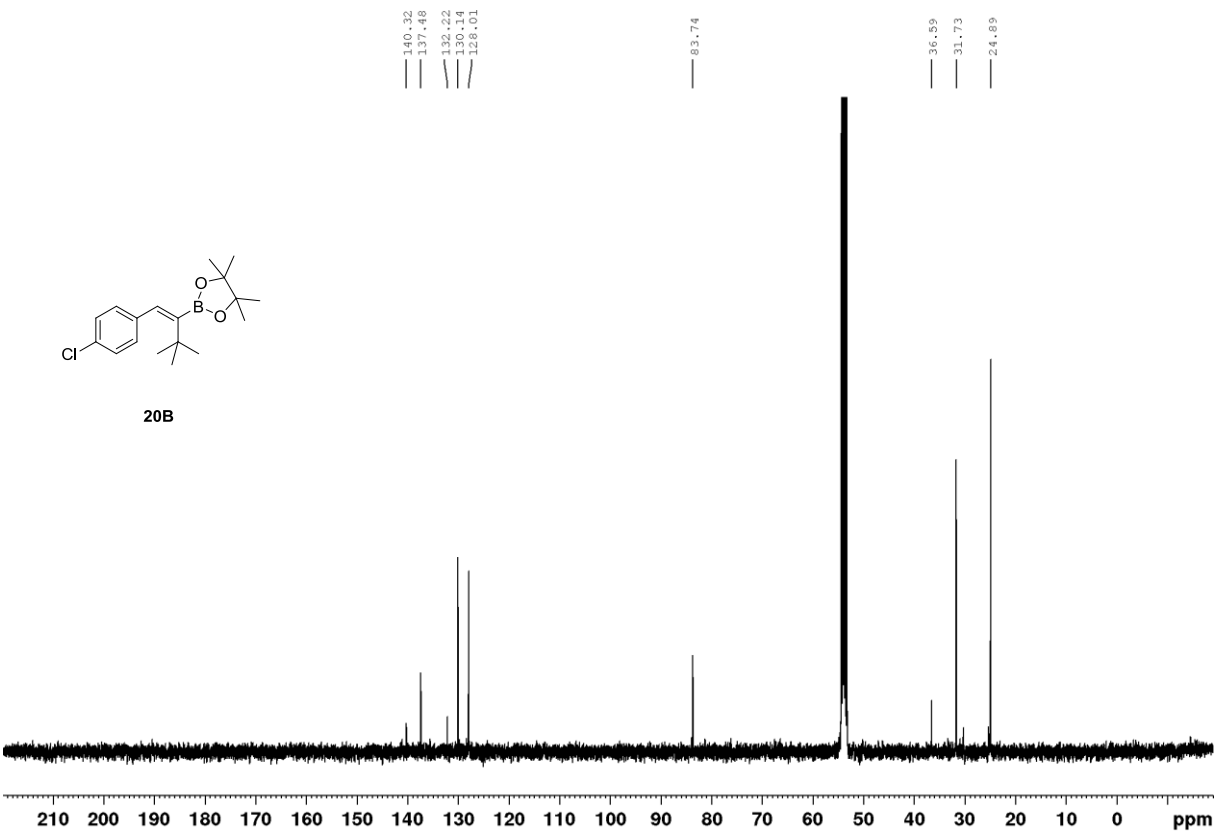
19B

NMR spectra of 20A:

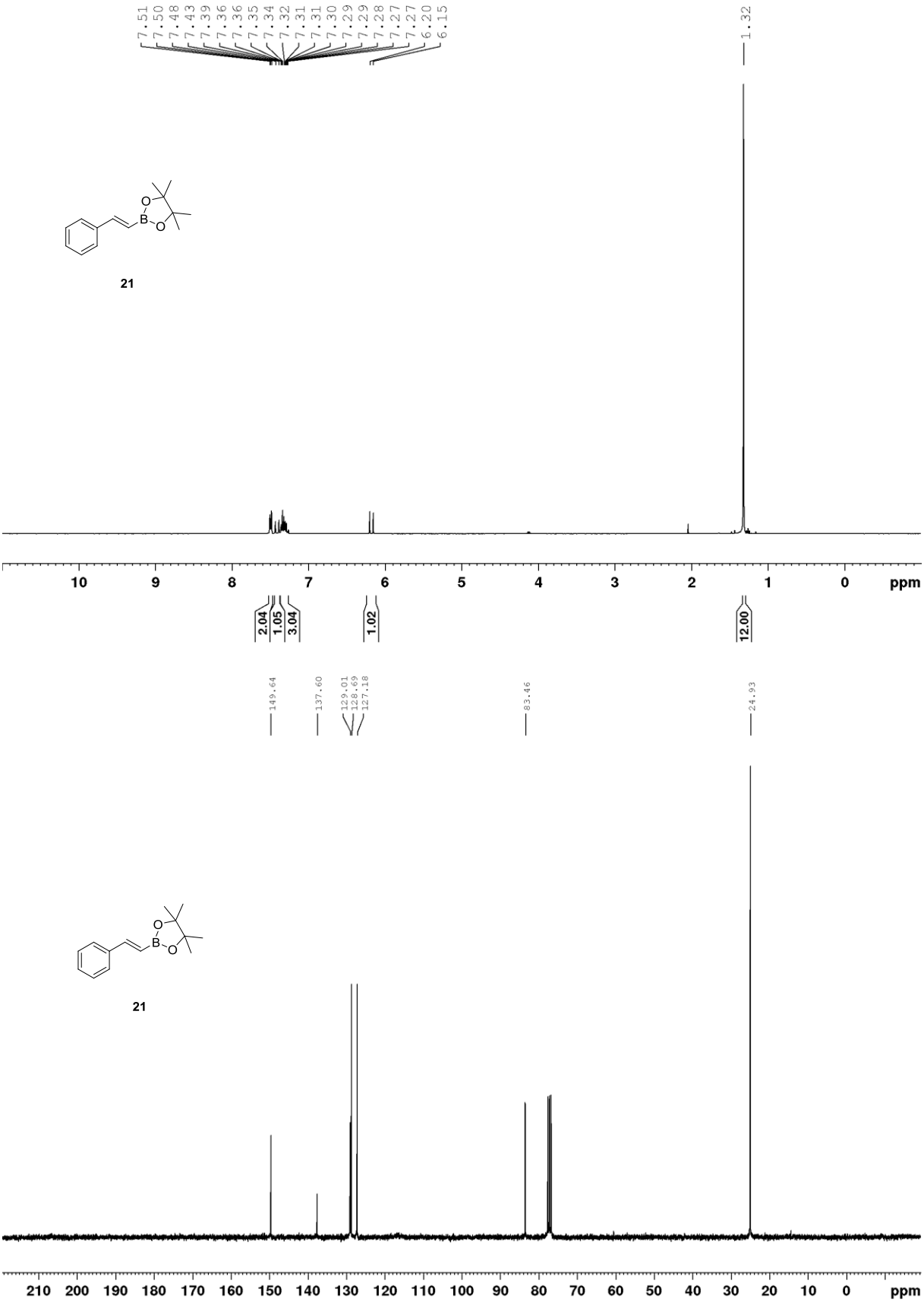


NMR spectra of 20B:

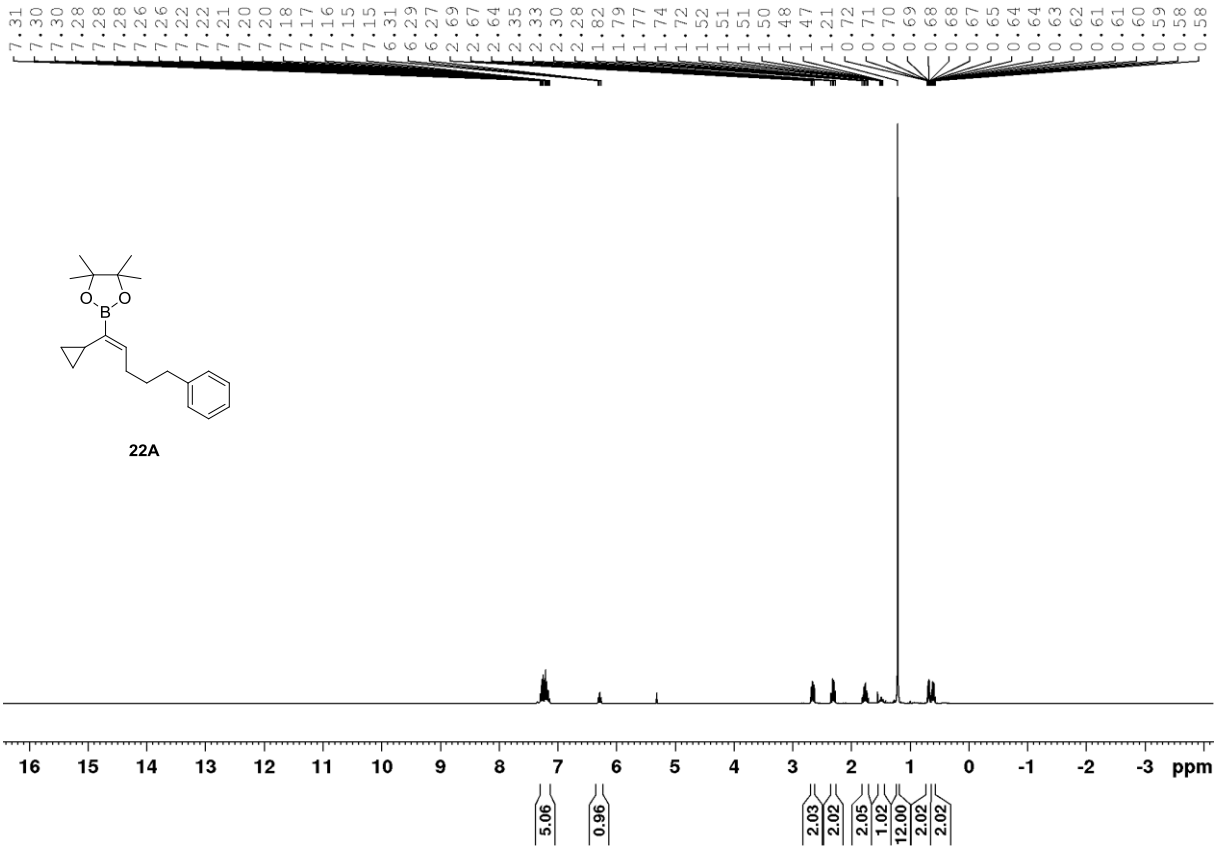


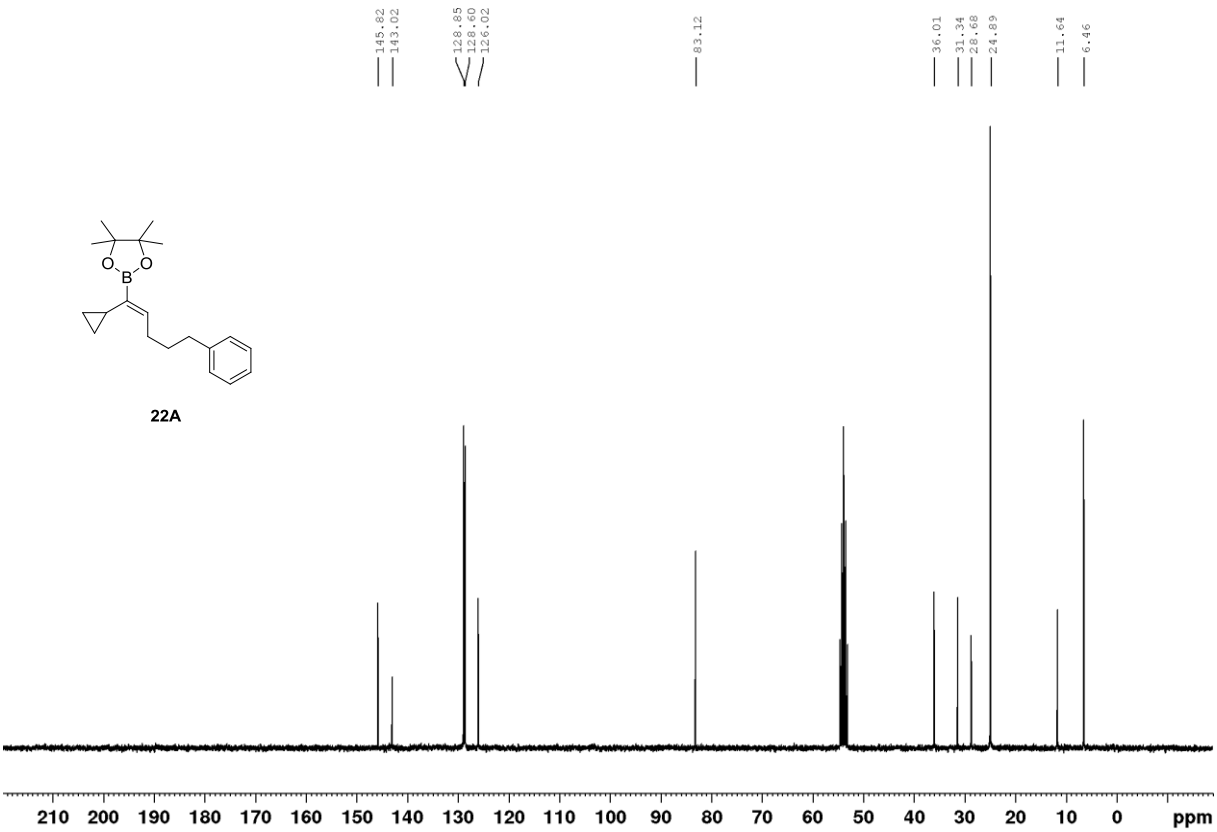


NMR spectra of 21:

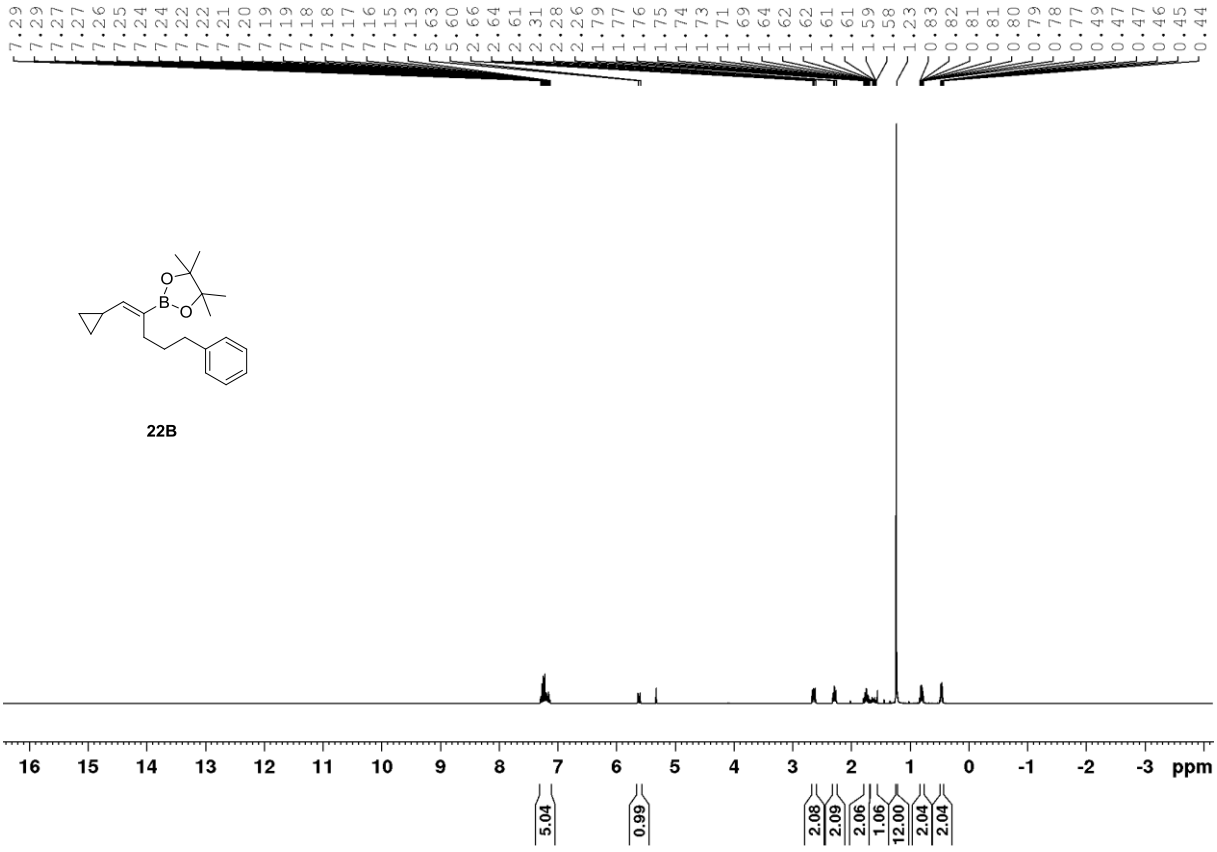


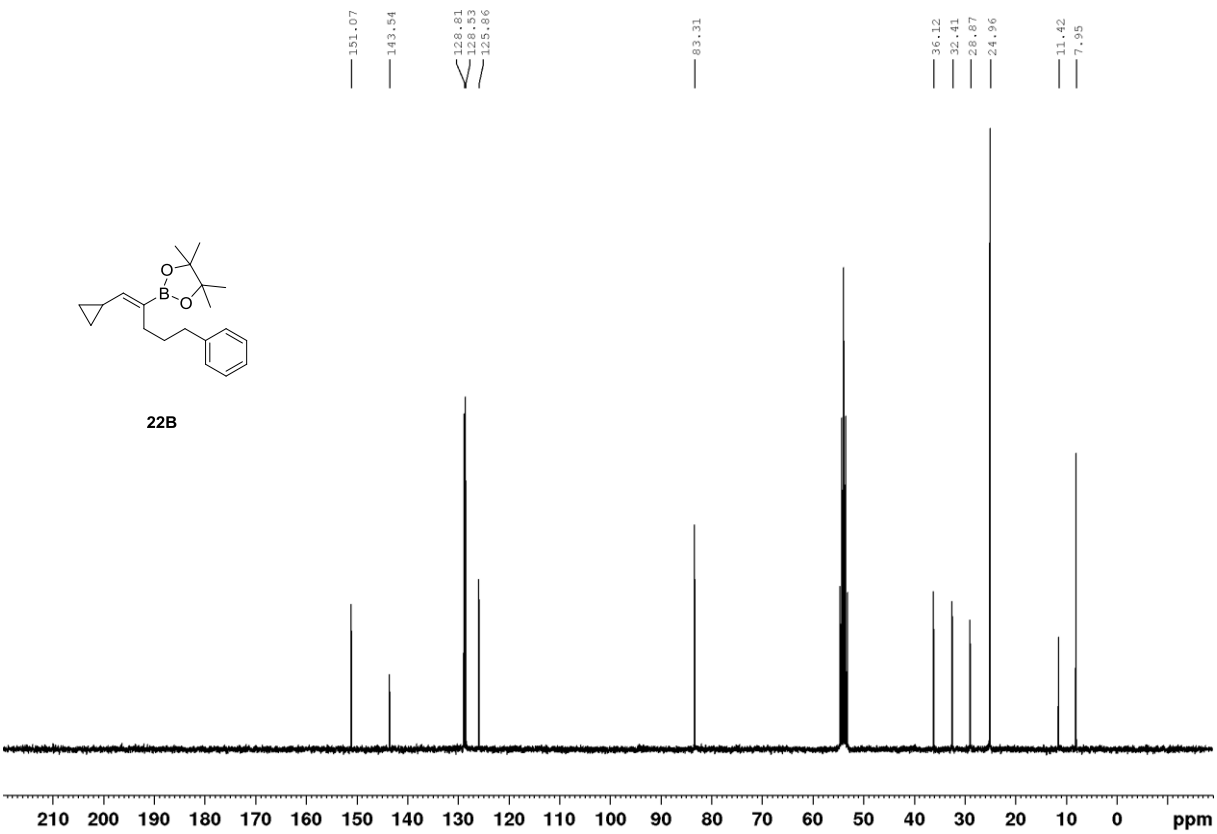
NMR spectra of 22A:



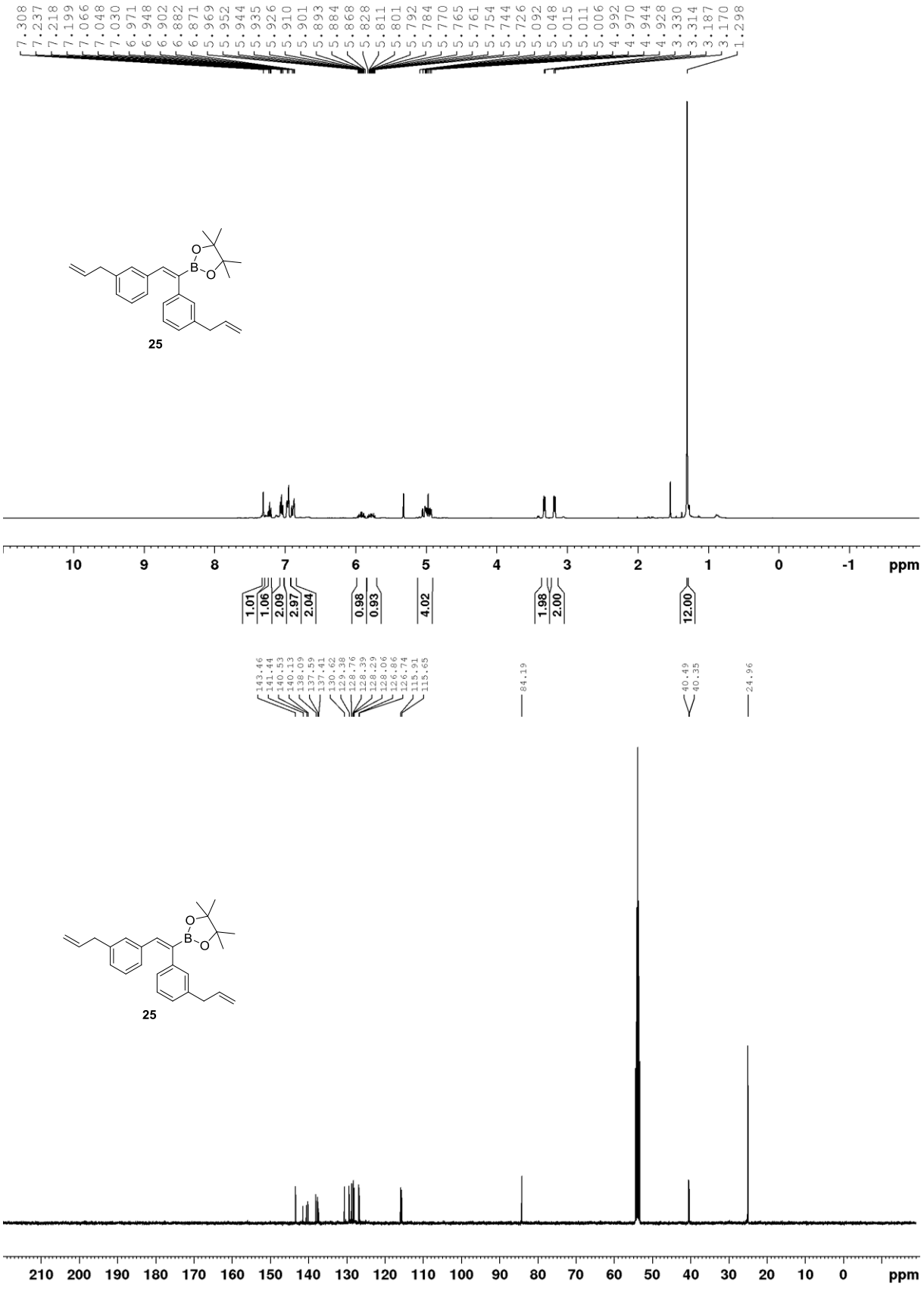


NMR spectra of 22B:

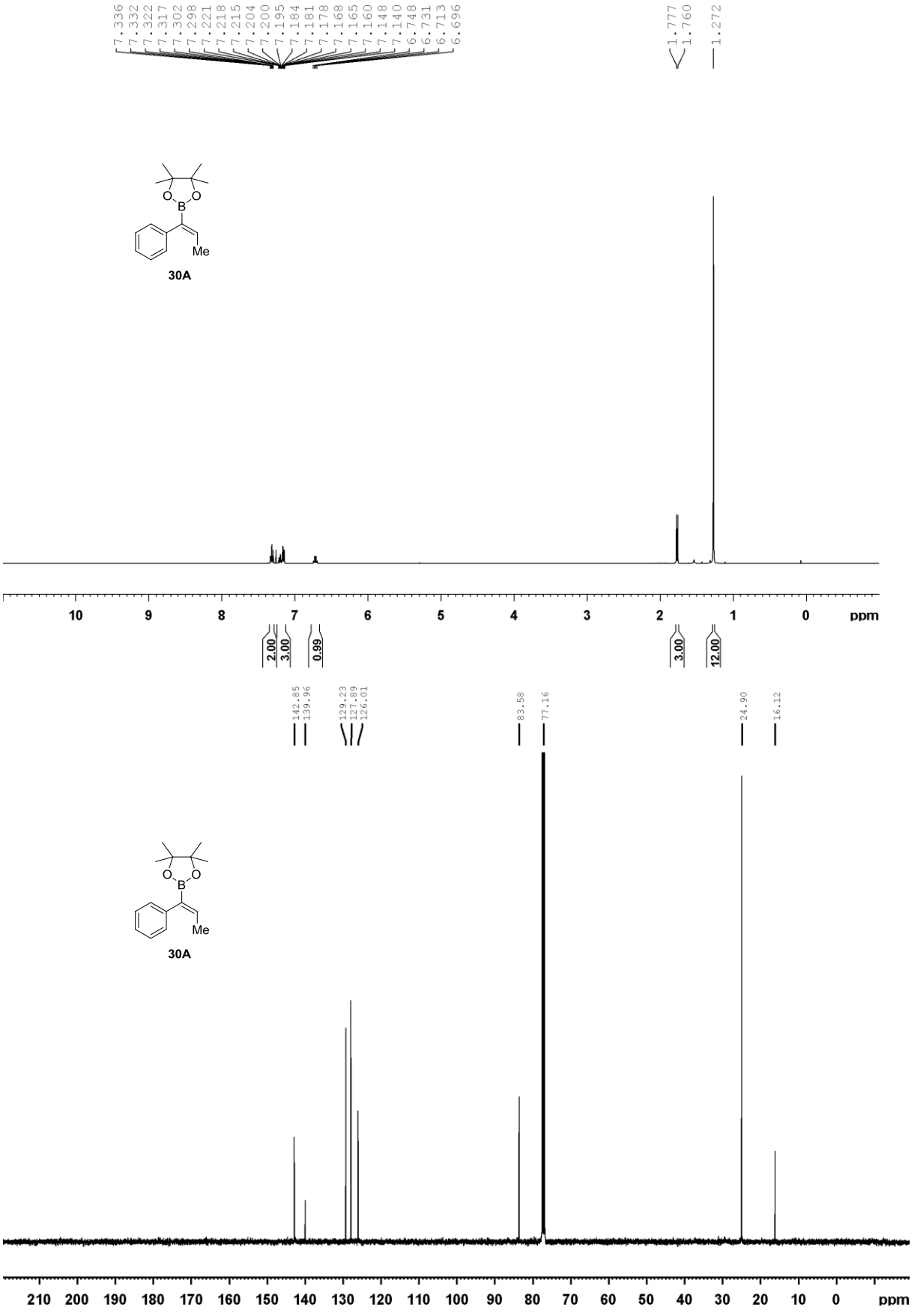




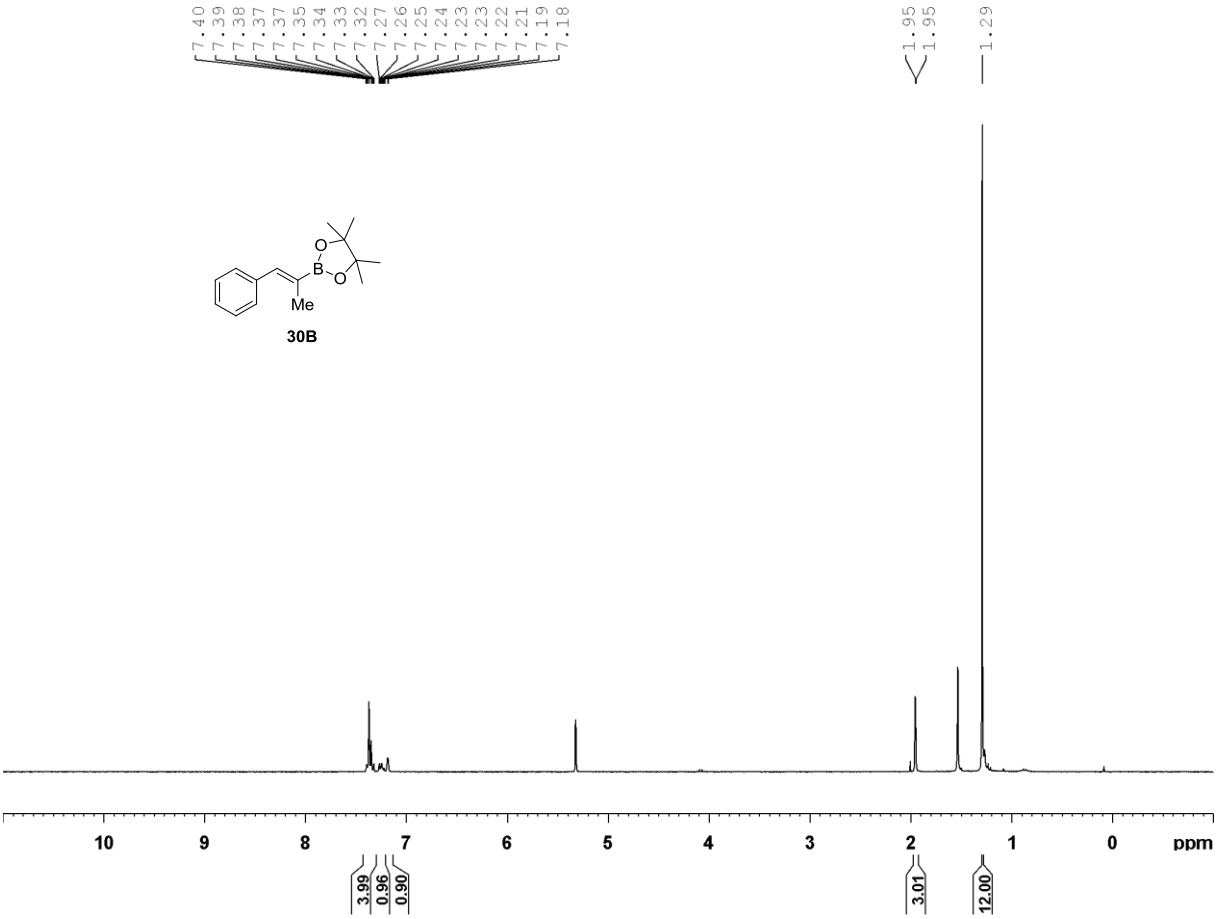
NMR spectra of 25:

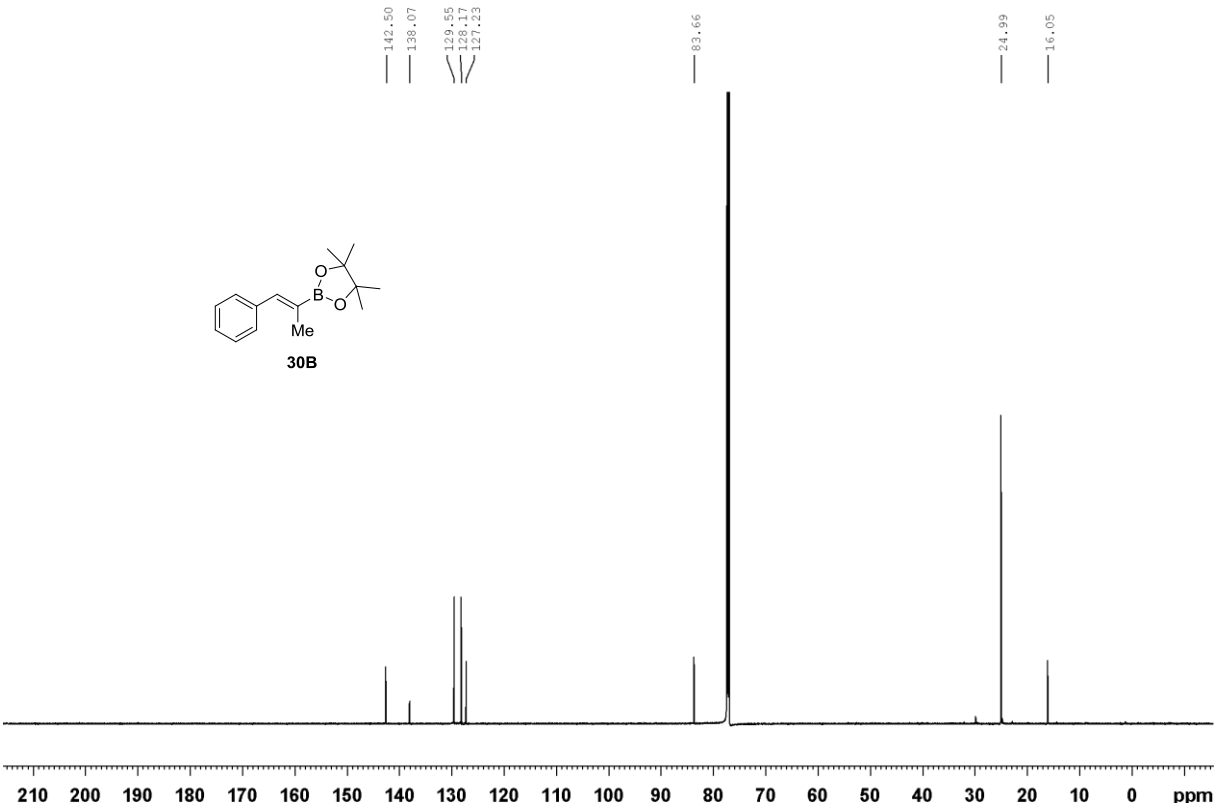


NMR spectra of 30A:



NMR spectra of 30B:





NMR spectra of 27: