Supporting Information

Cu^{I}/Pd^{0} cooperative catalysis enabled regioselective C(sp^2)-carboboration of 1,3-diynes

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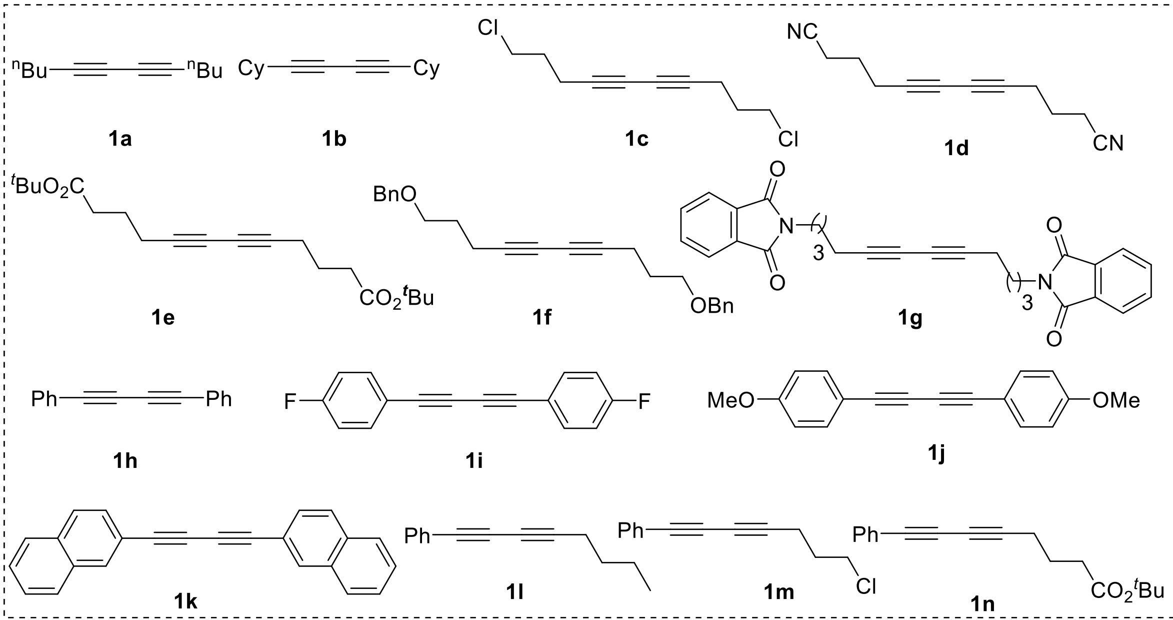
1. General experimental details:

All air and water-sensitive reactions were carried out in flame-dried glassware under a nitrogen/argon atmosphere using the standard Schlenk manifold technique. Bulk solutions were evaporated under reduced pressure using a Büchi rotary evaporator. All solvents were commercially supplied, and dry solvents were prepared using the standard protocol. THF was dried using sodium metal and benzophenone. All reactions requiring heating were set up using a heating block unless stated explicitly. Petroleum ether (hexanes) refers to the fraction collected between 40-60 °C. Unless noted, all other reagents were purchased from commercial sources and used as sold. Flash column chromatography (FCC) was performed using silica gel (60 Å, 230-400 mesh size). All reactions were followed by thin-layer chromatography (TLC) using Merck Kieselgel 60 F254 fluorescent-treated silica, visualized under UV light (254 nm), or staining with aqueous basic potassium permanganate solution. The NMR spectra were recorded on BRUKER ULTRA SHIELD (400 MHz) and BRUKER ASCEND EVO (400 MHz and 500 MHz) instruments. Chemical shifts for ^{1}H NMR were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, dd= doublet of doublet, td= triplet of doublet, ddd= doublet of doublet of doublet, ttt= triplet of triplet of triplet, m= multiplet. Coupling constants, *J*, were reported in hertz (Hz). ^{13}C NMR spectra were fully decoupled by broadband proton decoupling. ^{13}C chemical shifts were reported in ppm referenced to the center of a triplet at 77.16 ppm of $CDCl_3$ or the center of a septet at 39.52 ppm of DMSO-d_6. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. Infrared (IR) spectra were recorded using a Spectrum BX FT-IR instrument from Perkin Elmer. Frequencies are given in reciprocal centimeters (cm^{-1}), and only selected transmittance peaks are reported. High-resolution mass spectra (HRMS) were recorded in the ESI-TOF (+ve) method using a time-of-flight (TOF) mass analyzer (Agilent AdvanceBio 6545XT LC/Q-S3 TOF). The single-crystal XRD was done with the BRUKER D8 QUEST instrument. Unless otherwise noted, materials were obtained from commercial suppliers or prepared according to standard procedures. Substrates that are not commercially available were synthesized according to the reported procedures. (pin)B-B(dan) was synthesized using the previous literature procedure.[1]

2. Preparation of symmetrical and unsymmetrical diynes:



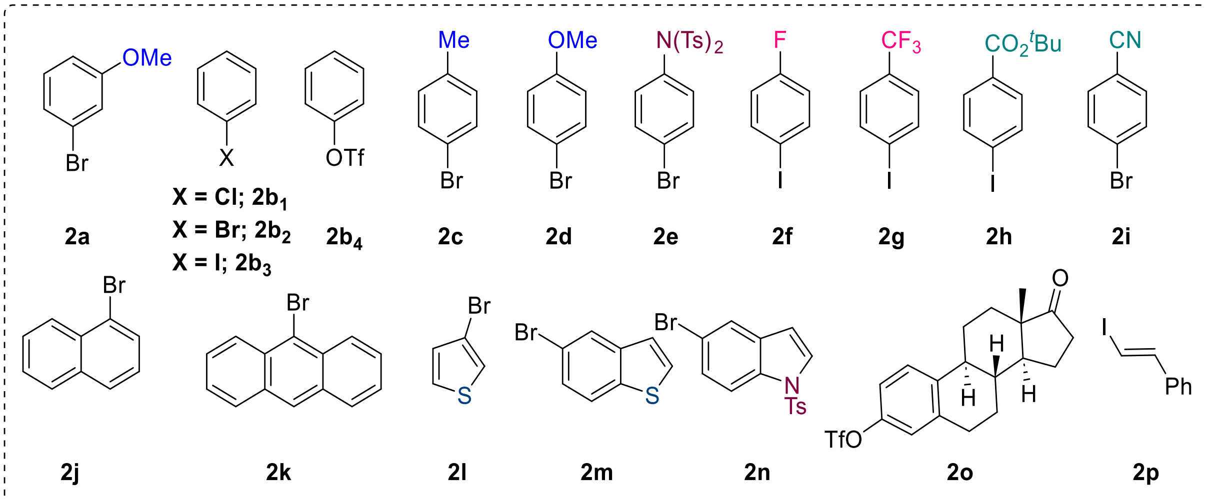
The symmetrical diynes were synthesized via procedure **2A** or procedure **2B**. Unsymmetrical diynes were synthesized using procedures **2B** and **2C**.

Procedure 2A[2]: To an oven-dried round-bottom flask, were added terminal alkynes (1 equiv.), benzotriazole (5.0 mol%), CuI (5.0 mol%), and K_2CO_3 (1 equiv.) suspended in DMF (1 M) in the open air. The reaction mixture was vigorously stirred at room temperature. The progress of the reaction was monitored by TLC periodically. After the completion of the reaction, diethyl ether was added to the reaction mixture and washed with brine. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mass thus obtained was subjected to purification by flash column chromatography (SiO_2) using *n*-hexane/EtOAc to afford symmetrical diynes in good yields.

Procedure 2B[3]: A mixture of the terminal alkyne (1 equiv.), TMEDA (20 mol%), CuI (5 mol%), and $NiCl_2.6H_2O$ (5 mol%) in THF (0.5 M) were stirred in the open air at room temperature. After completion of the reaction, as indicated by TLC, the mixture was concentrated in vacuo, and the crude product was purified by column chromatography on silica gel to afford the desired symmetrical and unsymmetrical diynes.

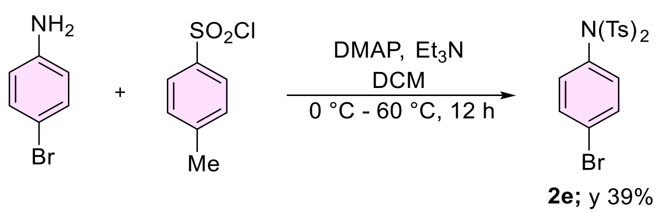
Procedure 2C:[4] To a flame-dried Schlenk tube, under nitrogen atmosphere, were added alkyl/aryl bromoethyne (1 equiv.), CuI (5 mol%), and $Pd(PPh_3)_2Cl_2$ (5 mol%). Triethylamine (0.15 M) and terminal alkyne (1 equiv.) were added to this mixture sequentially via a syringe. Then, the reaction mixture was stirred at 55 °C for 6 h, the solvent was evaporated to dryness under reduced pressure, and the residue was further purified by column chromatography with hexanes/ethyl acetate as the eluent to afford unsymmetrical diynes.

3. Synthesis of C(sp^2)-X electrophiles employed in carboboration:



Compounds **2b₄**[5] and **2o**[6] were synthesized using standard literature procedures.

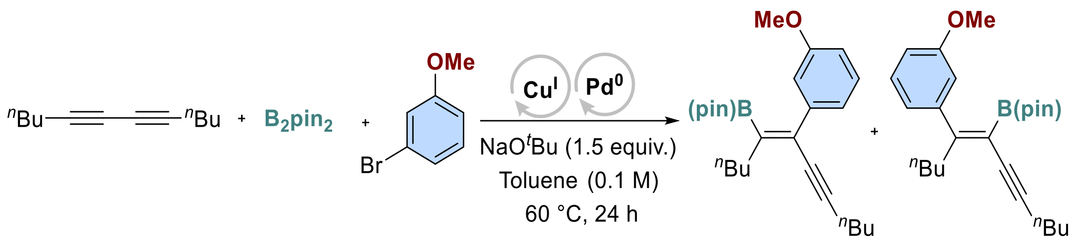
Synthesis of compound 2e:



The above compound was synthesized using a modified literature procedure.[7] 4-Bromoaniline (0.3 g, 1.74 mmol, 1 equiv.) was dissolved in dry DCM. Then, triethylamine (0.36 mL, 2.62 mmol, 1.5 equiv.) was added dropwise to the mixture at 0 °C. After 10 min of stirring at 0 °C, freshly purified TsCl (1.0 g, 5.23 mmol, 3 equiv.) was added portion-wise, followed by the addition of DMAP (5 mol%, 10.7 mg, 0.087 mmol) in a catalytic amount. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with water (5 mL), and the mixture was extracted with dichloromethane (2 × 20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification was done by silica gel flash chromatography using 10-30%

ethyl acetate in hexanes as the eluent to obtain the desired product **2e** (318 mg, 38%) as a white solid. **mp** 218-219 °C; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2923, 1596, 1485, 1169, 907; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 2.47 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 136.5, 133.6, 133.2, 132.6, 129.8, 128.7, 124.9, 21.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}BrN2O_2S_2$ 499.0179; Found: 499.0198.

4A. Optimization Table for Arylative Borylation of Aliphatic 1,3-Diynes:

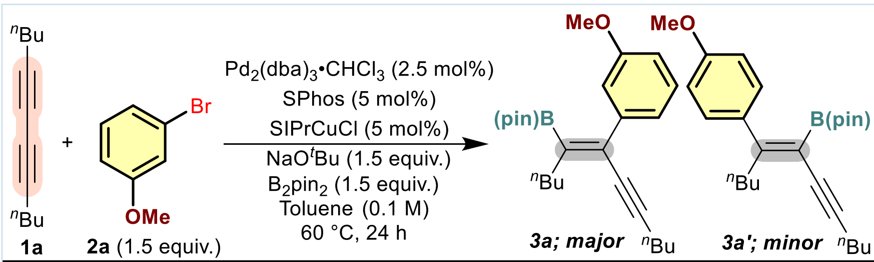


1a **2a** **3a**; Major **3a'**; Minor

SN	Pd salt (2.5 mol%)	Ligand (5 mol%	Cu salt (5 mol%)	Ligand (8 mol%)	Total yield	*rr*
1	-	-	CuCl	PCy_3	SM	-
1	$Pd_2(dba)_3.CHCl_3$	XPhos	SIPrCuCl	-	75	72:28
2	$Pd_2(dba)_3.CHCl_3$	XPhos	SXylCuCl	-	57	65:35
3	$Pd_2(dba)_3.CHCl_3$	XPhos	CuCl	SiItBu.HCl	61	65:35
4	$Pd_2(dba)_3.CHCl_3$	XPhos	IMesCuCl		32	66:33
5	$Pd_2(dba)_3.CHCl_3$	XPhos	SiMesCuCl		68	63:37
6	$Pd_2(dba)_3.CHCl_3$	XPhos	CuCl	$IBn.HBF_4$	48	67:33
7	$Pd_2(dba)_3.CHCl_3$	XPhos	CuCl	$ICy.HBF_4$	33	77:23
8	$Pd_2(dba)_3.CHCl_3$	XPhos	CuCl	SIAd.HCl	66	78:22
9	$Pd_2(dba)_3.CHCl_3$	XPhos	DippCuCl	-	SM	-
10	$Pd_2(dba)_3.CHCl_3$	PCy_3	SIPrCuCl	-	56	76:24
11	$Pd_2(dba)_3.CHCl_3$	SPhos	SIPrCuCl	-	81 (78%)	90:10
12	$Pd_2(dba)_3.CHCl_3$	Johnphos	SIPrCuCl	-	57	77:13
13	$Pd_2(dba)_3.CHCl_3$	CyJohnphos	SIPrCuCl	-	58	80:20
14	$Pd_2(dba)_3.CHCl_3$	dppf	SIPrCuCl	-	50	80:20
15	$Pd_2(dba)_3.CHCl_3$	dppe	SIPrCuCl	-	59	71:29
16	$Pd_2(dba)_3.CHCl_3$	PCy_2Ph	SIPrCuCl	-	41	68:32
17	$Pd_2(dba)_3.CHCl_3$	(*p*-anisyl)$_3$P	SIPrCuCl	-	24	61:39
18	$Pd(OAc)_2$	Sphos	SIPrCuCl	-	59	86:14
19	$Pd(PPh_3)_4$	Sphos	SIPrCuCl	-	<5	ND[e]
20	$PdCl_2(PPh_3)_2$	Sphos	SIPrCuCl	-	68	83:17
21	$Pd(OCOCF_3)_2$	Sphos	SIPrCuCl	-	75	90:10
22[a]	$Pd_2(dba)_3.CHCl_3$	SPhos	SIPrCuCl	-	30	80:20
23[b]	$Pd_2(dba)_3.CHCl_3$	SPhos	SIPrCuCl	-	SM	-
24[c]	$Pd_2(dba)_3.CHCl_3$	SPhos	SIPrCuCl	-	56	86:14
25[d]	$Pd_2(dba)_3.CHCl_3$	SPhos	SIPrCuCl	-	35	>90:10
26	$Pd_2(dba)_3.CHCl_3$	SPhos	-	-	SM	-

Standard conditions: 1 (1 equiv.), Pd-catalyst (2.5 mol%), Phosphine (5 mol%), Cu salt (5 mol%), NHC·HX (8 mol%), Base (1.5 equiv.), solvent (0.1 M), 60 °C, 24 h; [a]KO^{t}Bu was used; [b]Cs_2CO_3 was used; [c]Toluene: THF (1:1); [d]Toluene: DMF (1:1) was used; [e]ND = Not determined; SM indicates starting material recovery.

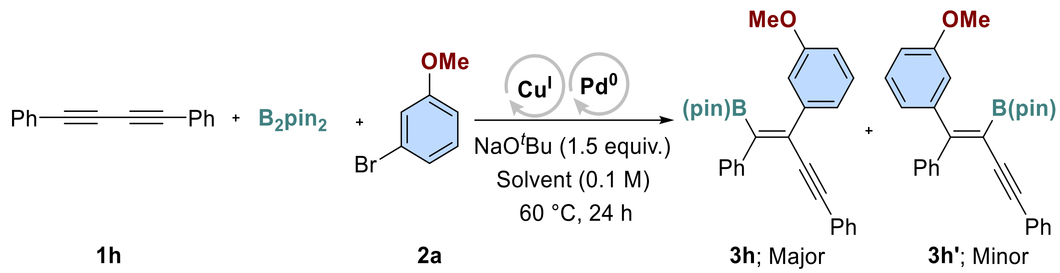
Deviations from Standard Conditions: We began our investigation by using dibutyl buta-1,3-diyne (**1a**) as the standard substrate with B_2pin_2 and 3-bromoanisole as the aryl electrophile. Various Pd^0/phosphine and Cu^IL_n combinations were studied to facilitate the desired arylboration of **1a**. The best results were obtained with SIPrCuCl/$Pd_2(dba)_3{\cdot}CHCl_3$/SPhos catalyst combination, operating cooperatively to deliver the desired product **3a** in 81% NMR yield with *rr* 90:10 (isolated yield: 78%; entry 1). In the absence of either Pd^0 or Cu^I catalyst, **1a** remained unreacted, suggesting the cooperative involvement of both metal complexes in the catalytic cycle. Screening other Pd sources showed moderate reactivity (y 59-75%; entry 3). Bases like KO^{t}Bu and Cs_2CO_3 were incompatible for arylboration, delivering poor yields of **3a** (0-30%; entry 4). A variety of phosphines like Johnphos, CyJohnphos, dppf, dppe, PCy_2Ph, and P(*p*-anisyl)$_3$ were studied; however, the desired product **3a** was obtained only in moderate yields and regioselectivity (y 24-59%; *rr* up to 80:20, entry 5).



Entry	*Deviations from Std. Cond.*	*Yield%; (rr)*[b]
1	None	81 (78)[c]; (90:10)
2	absence of $Pd_2(dba)_3{\cdot}CHCl_3$ *or* SIPrCuCl	NR[d]
3	$Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, or $Pd(TFA)_2$	59-75; (up to 90:10)
4	Cs_2CO_3, KO^{t}Bu	0, 30; (80:20)
5	Johnphos, dppf, dppe, XPhos, and P(*p*-anisyl)$_3$	24-59; (up to 80:20)

[a]**Standard Conditions:** Diyne **1a** (0.15 mmol, 1 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%), SPhos (5 mol%), SIPrCuCl (5 mol%), NaO^{t}Bu (1.5 equiv.), ArBr (1.5 equiv.), toluene (0.1 M), 60 °C, 24 h; [b]^{1}H NMR yields and *rr* were determined using 1,1,2,2-tetrachloroethane as int. std.; [c]Isolated yield; [d]NR = no reaction.

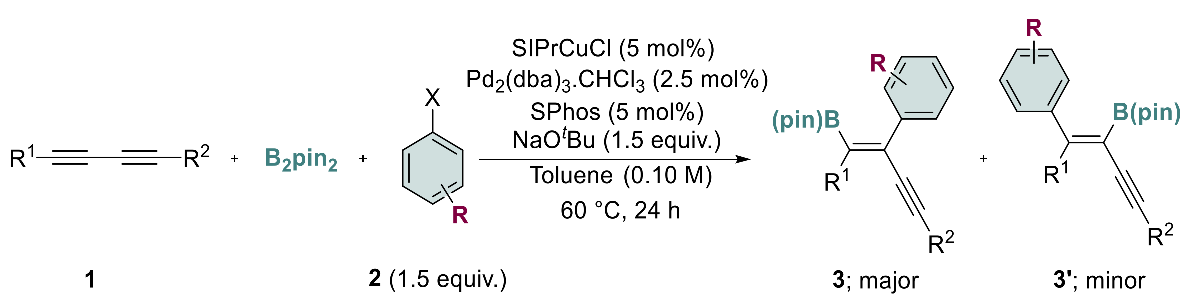
4B. Optimization Table for Arylative Borylation of Aromatic 1,3-Diynes:



SN	Cu salt (5 mol%)	Ligand (8 mol%)	Base (1.5 equiv.)	Solvent	Total yield	*rr*
1	SIPrCuCl	-	NaO^{t}Bu	Toluene	23	90:10
2	CuCl	SIAd.HCl	NaO^{t}Bu	Toluene	<5%	-
3	IMesCuCl	-	NaO^{t}Bu	Toluene	<5%	-
4	SIPrCuCl	-	NaO^{t}Bu	Toluene	<5%	-
6	SXylCuCl	-	NaO^{t}Bu	Toluene	<5%	-
7	SXylCuCl	-	NaO^{t}Am	Hexane	-	-
8	CuCl	I^{t}Bu	NaO^{t}Bu	Toluene	-	-
9	CuCl	SPhos	NaO^{t}Bu	Toluene	-	-
10	CuCl	PCy_3	NaO^{t}Bu	Toluene	-	-
11	CuCl	IPr	NaO^{t}Bu	Toluene	30	90:10
12	CuCl	IPr	NaO^{t}Am	Hexane (RT)	SM	-
13	CuCl	IPr	NaO^{t}Am	Hexane (60 °C)	SM	-
14	SIPrCuCl	-	NaO^{t}Bu	THF	-	-
15	SIPrCuCl	-	NaO^{t}Bu	DMF	SM	
16	SIPrCuCl	-	NaO^{t}Bu	DCM (50 °C)	44	90:10
17	SIPrCuCl	-	NaO^{t}Bu	CH_3CN	<5%	-

Standard conditions: **1** (1 equiv.), $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%), SPhos (5 mol%), Cu salt (5 mol%), NHC·HX (8 mol%), Base (1.5 equiv.), solvent (0.1 M), 60 °C, 24 h; SM indicates starting material recovery.

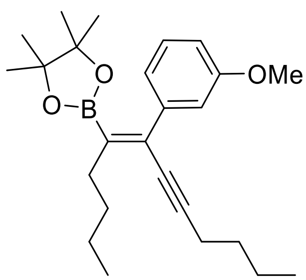
4C. General Procedure for Arylative Borylation of 1,3-Diynes:



To a flame-dried Schlenk tube, SIPrCuCl (3.9 mg, 0.0075 mmol, 5 mol%), B_2pin_2 (56 mg, 0.225 mmol, 1.5 equiv.), diyne (0.15 mmol, 1 equiv.) were added, and dissolved in dry toluene (1.0 mL) under an inert atmosphere. To this reaction mixture, NaO^{t}Bu solution (0.125 mL, 0.225 mmol, 1.5 equiv, 2 M in THF) was added sequentially at room temperature. In another Schlenk tube, $Pd_2(dba)_3 \cdot CHCl_3$ (3.7 mg, 0.0037 mmol, 2.5 mol%) and SPhos (3.1 mg, 0.0075 mmol, 5 mol%)

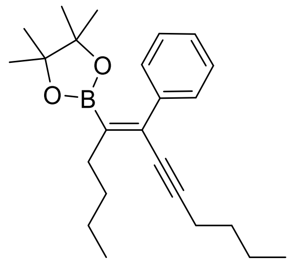
were weighed, and dry toluene (0.5 mL) was added under an inert atmosphere and stirred for 10 minutes. Then, the catalyst was transferred to the reaction mixture under an inert atmosphere. Then ArX (0.225 mmol, 1.5 equiv.) was added, and the mixture was stirred at 60 °C for 24 h. After completion of the reaction, the mixture was cooled to room temperature, decanted into the separating funnel, and diluted with ethyl acetate (30 mL). The organic layer was washed with distilled water (2×20 mL) and brine (20 mL). Then the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated in vacuo to provide a crude mixture. The mixture was analyzed by ^{1}H NMR with 1,1,2,2-tetrachloroethane (1 equiv.) as an internal standard to determine the NMR yield and regioselectivity. Further purification by flash column chromatography using ethyl acetate-hexanes/ toluene-hexanes was performed rapidly (preferably within 10 minutes). (**Note.** Pinacol boronate esters are unstable under the column and ambient atmosphere and need to be stored under 2-8 ^{o}C).

5. Characterization Data for the Synthesis of Aryl-substituted Boryl Enynes (3/4):

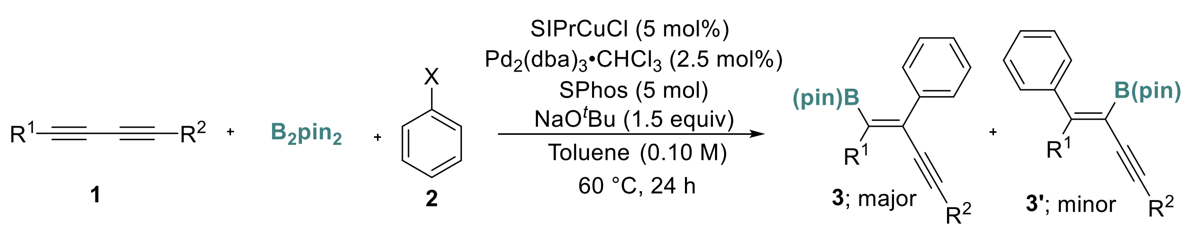


(*Z*)-2-(6-(3-Methoxyphenyl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a): Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2a** (42.08 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **3a** (47.6 mg; 78%; *rr* 90:10) as a colorless liquid after chromatographic purification with 40-50% toluene in hexanes, $\mathbf{R_f}$ (5% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 1739, 1606, 1510, 1467, 1247, 1046; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.16 (m, 1H), 6.99-6.97 (m, 2H), 6.84-6.74 (m, 1H), 3.81 (s, 3H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.48-2.36 (m, 2H), 1.62-1.38 (m, 8H), 1.16 (d, *J* = 1.1 Hz, 12H), 1.01-0.88 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 143.2, 132.4, 128.8, 121.1, 114.0, 113.2, 97.3, 83.5, 80.3, 55.3, 34.9, 31.5, 31.0, 24.7, 22.9, 22.1, 19.5, 14.1, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{38}BO_3$ 397.2909; Found: 397.2931.

(*Z*)-4,4,5,5-Tetramethyl-2-(6-phenyldodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane (3b): Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3b** (92.2 mg; 84%; *rr* 85:15) as colorless viscus liquid after chromatographic purification with 30-40% toluene in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2931, 2874, 1712, 1596, 1456, 1360, 1016; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.16-7.09 (m, 3H), 2.49-2.39 (m, 2H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.47-1.39 (m, 2H), 1.39-1.32 (m, 4H), 1.32-1.27 (m, 2H), 1.02 (s, 12H), 0.82 (t, *J* = 6.04, 3H), 0.80 (t, *J* = 6.04, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 132.8, 128.5, 127.8, 127.4, 97.4, 83.5, 80.4, 35.0, 31.6, 31.1, 24.7, 22.9, 22.1, 19.5, 14.2, 13.7 [Note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{36}BO_2$ 367.2803; Found: 367.2815.

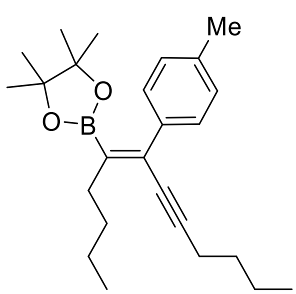


Screening of Different Aryl Halide:



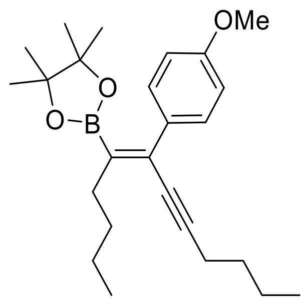
Electrophiles	Yields and *rr*	*Electrophiles*	Yields and *rr*
PhCl	y 59%; *rr* 90:10	PhI	y 57%; *rr* 80:20
PhBr	y 84%; *rr 85:15*	PhOTf	y 39%; *rr* 80:20

(*Z*)-4,4,5,5-Tetramethyl-2-(6-(*p*-tolyl)dodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane (3c): Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using 4-bromotoluene **2c** (76.96 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3c** (74.9 mg; 66%; *rr* 90:10) as colorless viscus liquid after chromatographic purification with 30-40% toluene in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2933, 2873, 1711, 1671, 1610, 1459, 1178; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 2.54-2.47 (m, 2H), 2.35 (t, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 1.54-1.46 (m, 2H), 1.46-1.40 (m, 4H), 1.40-1.33 (m, 2H), 1.11 (s, 12H), 0.90 (t, *J* = 7.0, 3H), 0.88 (t, *J* = 7.1, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 132.8,



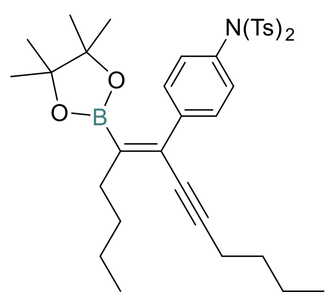
128.5, 127.8, 127.4, 97.4, 83.5, 80.4, 35.0, 31.6, 31.1, 25.0, 24.7, 22.9, 22.1, 19.5, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{38}BO_2$ 381.2959; Found: 381.2969.

(Z)-2-(6-(4-Methoxyphenyl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



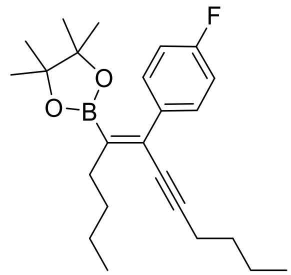
(3d): Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2d** (42.08 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **3d** (44.58 mg; 75%; *rr* 90:10) as colorless viscus liquid after chromatographic purification with 30-40% toluene in hexanes; **R_f** (5% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2958, 2924, 2851, 1739, 1246, 1176; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.60-2.45 (m, 2H), 2.39 (t, *J* = 6.9 Hz, 2H), 1.58-1.52 (m, 2H), 1.49-1.42 (m, 4H), 1.40-1.33 (m, 2H), 1.15 (s, 12H), 0.93 (t, *J* = 6.7 Hz, 3H), 0.91 (q, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 134.5, 132.4, 129.7, 113.2, 97.2, 83.5, 80.6, 55.4, 35.0, 31.6, 31.1, 24.7, 22.9, 22.1, 19.5, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{38}BO_3$ 397.2909; Found: 397.2931.

(*Z*)-2-(6-(Benzo[b]thiophen-5-yl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-



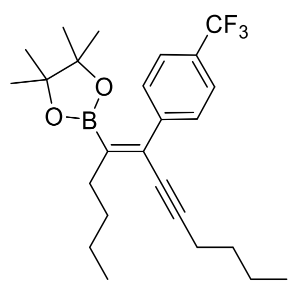
dioxaborolane (3e): Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2e** (165 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3e** (81.9 mg; 74%; *rr* 90:10) as colorless liquid after chromatographic purification with 15% ethyl acetate in hexanes, **R_f** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2958, 2930, 1710, 1597, 1456, 1378, 1168, 913; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 2H), 2.60-2.49 (m, 2H), 2.45 (s, 6H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.60-1.50 (m, 2H), 1.50-1.36 (m, 4H), 1.36-1.22 (m, 2H), 1.15 (s, 12H), 0.95 (t, *J* = 6.5 Hz, 3H), 0.93 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 143.6, 136.9, 133.3, 131.9, 131.0, 129.6, 129.3, 128.6, 98.2, 83.7, 79.9, 35.0, 31.4, 30.9, 24.7, 22.9, 22.0, 21.8, 19.5, 14.1, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.7; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{38}H_{52}BN_2O_6S_2$; 707.3354; Found: 707.3368.

(*Z*)-2-(6-(4-fluorophenyl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f):



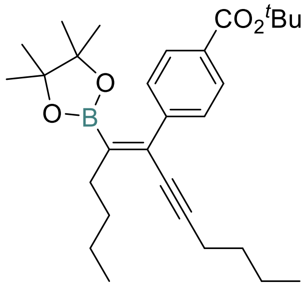
Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2f** (78.75 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3f** (66.2 mg, 58%; *rr* 85:15) as colorless liquid after chromatographic purification with 30-40% toluene in hexanes; **R_f** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2958, 2860, 1602, 1507, 1346, 1304; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.34 (m, 2H), 7.00-6.96 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 6.8 Hz, 2H), 1.54-1.50 (m, 8H), 1.18 (s, 12H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.5 Hz), 137.8 (d, *J* = 3.6 Hz), 131.9, 130.2 (d, *J* = 8.0 Hz), 114.6 (d, *J* = 21.4 Hz); 97.8, 83.6, 80.4, 35.0, 31.6, 31.0, 24.7, 22.9, 22.1, 19.5, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 36.0; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -115.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{35}BFO_2$ 385.2709; Found: 385.2721.

(*Z*)-4,4,5,5-tetramethyl-2-(6-(4-(trifluoromethyl)phenyl)dodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane (3g):



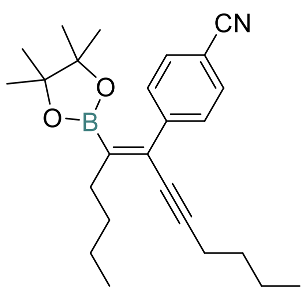
Starting diyne **1a** (48.6 mg, 0.30 mmol) was reacted according to the above general procedure using **2g** (122.4 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3g** (61.6 mg; 71%; *rr* 85:15) as colorless viscus liquid after chromatographic purification with 30-40% toluene in hexanes; **R_f** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2919, 2851, 736, 1618, 1467, 1325, 1129, 1067; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 8.8 Hz, 2H), 7.49 (t, *J* = 8.9 Hz, 2H), 2.59-2.53 (m, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.57-1.49 (m, 3H), 1.50-1.46 (m, 5H), 1.12 (s, 12H), 0.95 (t, *J* = 7.05 Hz, 3H), 0.92 (t, *J* = 7.04 Hz, 3H), ; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.4, 131.9, 129.4 (d, *J* = 32.4 Hz), 129.0, 124.7 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 272.4 Hz), 98.4, 83.7, 80.0, 35.1, 31.5, 31.0, 24.7, 22.9, 22.1, 19.5, 14.1, 13.7; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{35}BF_3O_2$ 435.2677; Found: 435.2648.

(*Z*)-4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-yn-6-*tert*-butyl)benzoate (3h):



Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2h** (115.7 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3h** (95.7 mg; 69%; *rr* 90:10) as colorless liquid after chromatographic purification with 5% ethyl acetate in hexanes; **R_f** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2988, 2943, 1735, 1376, 1233; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.82 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 2.47 (d, J = 7.6 Hz, 2H), 2.41 (t, J = 6.7 Hz, 2H), 1.54 (s, 9H), 1.54-1.45 (m, 8H), 1.09 (s, 12H), 0.90 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.8, 145.0, 131.3, 130.3, 128.7, 128.1, 98.0, 83.5, 80.8, 79.7, 34.6, 30.8, 30.3, 27.8, 24.4, 22.1, 21.4, 18.6, 13.8, 13.4 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 40.2; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{44}BO_4$ 467.3327; Found: 467.3317.

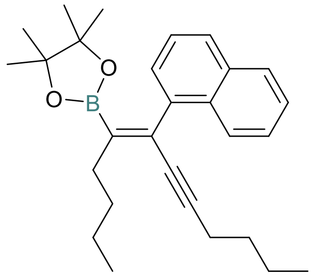
(*Z*)-4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-yn-6-yl)benzonitrile (3i):



Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2i** (82 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3i** (86.7 mg; 74%; *rr* 90:10) as a colorless liquid after chromatographic purification with 5% ethyl acetate in hexanes; **R_f** (5% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2968, 2932, 2232, 1717, 1554, 1378; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 2.50-2.40 (m, 2H), 2.28 (t, J = 7.0 Hz, 2H), 1.46-1.25 (m, 8H), 1.02 (s, 12H), 0.93 (t, J = 7.5 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 131.6, 131.5, 129.4, 119.2, 110.7, 98.6, 83.7, 79.5, 35.1, 31.3, 30.8, 24.6, 22.8, 22.0, 19.4, 14.1, 13.6 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{25}H_{38}BN_2O_2$ 409.3021; Found: 409.3020.

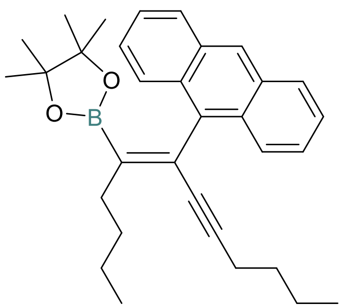
Minor isomer (3i'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 2.30 (t, J = 7.1 Hz, 2H), 2.14 – 2.07 (t, J = 7.2, 2H), 1.46-1.25 (m, 8H), 1.35 (s, 12H), 0.81-0.76 (m, 6H).

(*E*)-4,4,5,5-Tetramethyl-2-(6-(naphthalen-1-yl)dodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane



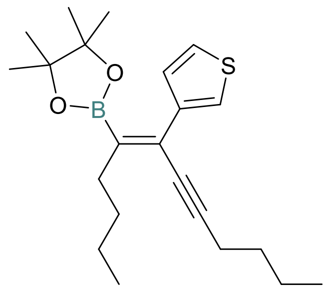
(3j): Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2j** (93.18 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3j** (97.4 mg; 78%; *rr* >95:5) as colorless liquid after chromatographic purification with 2-3% ethyl acetate in hexanes; **R**$_f$ (5% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2922, 2862, 1731, 1544; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.72-7.68 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.39-7.33 (m, 2H), 7.32-7.25 (m, 2H), 2.66-2.49 (m, 2H), 2.25 (t, *J* = 6.9 Hz, 2H), 1.53-1.45 (m, 2H), 1.44-1.37 (m, 4H), 1.36-1.30 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.70 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.7, 133.7, 132.1, 130.9, 127.9, 127.4, 126.5, 126.5, 125.7, 125.5, 125.2, 98.2, 83.1, 80.7, 34.1, 31.8, 31.0, 24.3, 22.9, 22.0, 19.6, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{38}BO_2$ 417.2959; Found: 417.2984.

(*E*)-2-(6-(Anthracen-9-yl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



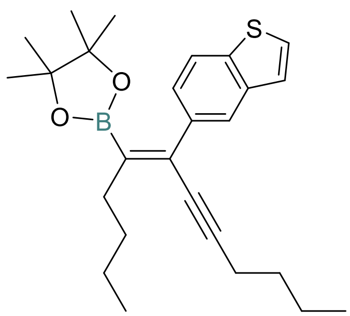
(3k): Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2k** (115.70 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3k** (95.1 mg; 68%; *rr* >95:5) as colorless liquid after chromatographic purification with 2-3% ethyl acetate in hexanes; **R**$_f$ (5% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2917, 2857, 1742, 1468, 1246; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.50-7.40 (m, 4H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 6.9 Hz, 2H), 1.75-1.65 (m, 2H), 1.63-1.57 (m, 2H), 1.56-1.49 (m, 2H), 1.48-1.38 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.51 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.2, 131.6, 130.0, 129.20, 128.16, 127.0, 125.9, 125.1, 124.9, 98.4, 82.7, 80.9, 34.0, 32.0, 31.0, 24.0, 23.1, 22.0, 19.7, 14.3, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.7; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{40}BO_2$; 467.3116; Found: 467.3140.

(*E*)-4,4,5,5-Tetramethyl-2-(6-(thiophen-3-yl)dodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane (3l):



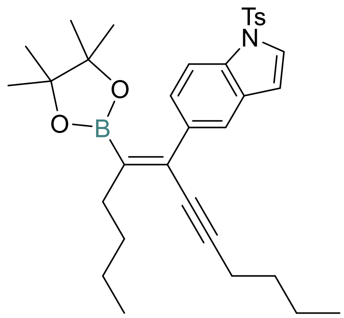
Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2l** (48.90 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3l** (61.9 mg; 56%; *rr* 90:10) as colorless liquid after chromatographic purification with 30% toluene in hexanes, **R$_f$** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2961, 2920, 1600, 1460, 1378, 1033; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.35 (m, 1H), 7.32-7.25 (m, 2H), 2.66-2.59 (m, 2H), 2.49 (t, *J* = 6.9 Hz, 2H), 1.68-1.61 (m, 2H), 1.60-1.45 (m, 6H), 1.30 (s, 12H), 1.04 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 128.4, 126.6, 124.6, 122.9, 96.5, 83.6, 80.0, 34.7, 31.5, 31.0, 24.8, 22.9, 22.1, 19.5, 14.1, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{34}BO_2S$; 373.2367; Found: 373.2375.

(*Z*)-2-(6-(Benzo[b]thiophen-5-yl)dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m):



Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2m** (95.89 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3m** (64.10 mg; 50%; *rr* 90:10) as colorless liquid after chromatographic purification with 50% toluene in hexanes, **R$_f$** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2920, 2852, 1734, 1467, 1374, 1243; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.65 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.3, 1H), 7.24 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 5.7 Hz, 1H), 2.49-2.39 (m, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 1.43-1.35 (m, 4H), 1.35-1.25 (m, 4H), 0.94 (s, 12H), 0.81 (dt, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.4, 138.8, 138.3, 132.7, 126.5, 125.3, 124.0, 123.4, 121.8, 97.6, 83.5, 80.6, 35.1, 31.6, 31.1, 24.7, 22.9, 22.1, 19.5, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.0; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{36}BO_2S$; 423.2524; Found: 423.2537.

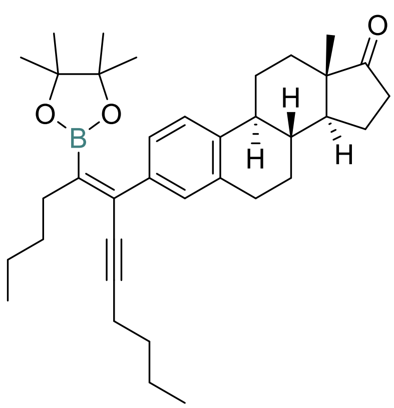
(*Z*)-5-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-yn-6-yl)-1-tosyl-1H-



indole (3n): Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2n** (78.8 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **3n** (55 mg; 51%; *rr* 85:15) as colorless liquid after chromatographic purification with 15% ethyl acetate in hexanes; **R$_f$** (15% EtOAc/hexanes): 0.35; **IR** (film)ν_{max}/cm^{-1}: 2920, 2851, 1734, 1457, 1374, 1245; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.55-7.50 (m, 2H), 7.35 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 3.6 Hz, 1H), 2.59-2.49 (m, 2H), 2.43-2.35 (m, 2H), 2.32 (s, 3H), 1.60-1.52 (m, 2H), 1.51-1.43 (m, 4H), 1.43-1.38 (m, 2H), 1.02 (s, 12H), 0.94 (t, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 137.4, 135.4, 134.4, 132.5, 130.6, 129.9, 126.9, 126.8, 125.5, 121.3, 112.9, 109.5, 97.6, 83.4, 80.5, 35.0, 31.5, 31.0, 24.7, 22.9, 22.1, 21.6, 19.5, 14.2, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{43}BNO_4S$; 560.3000; Found: 560.3018.

Minor isomer (3n'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.72 (s, 2H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.66 – 6.62 (m, 1H), 2.34 (s, 2H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.56-1.33 (m, 8H), 1.25 (d, *J* = 2.1 Hz, 12H), 0.94-0.88 (m, 6H).

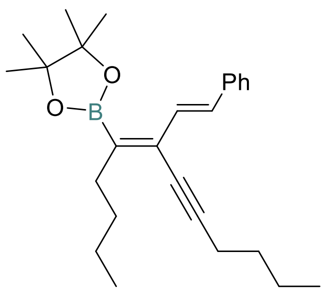
(*8R,9S,13S,14S*)-13-Methyl-3-((*Z*)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-



en-7-yn-6-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3o): Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2o** (120.72 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3o** (67.1 mg; 62%; *rr* >95:5) as colorless liquid after chromatographic purification with 10% ethyl acetate in hexanes, **R$_f$** (10% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2931, 2861, 1716, 1599, 1457, 1294, 1016, 860; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 1.0 Hz, 2H), 7.12 (s, 1H), 2.88 (dd, *J* = 8.7, 4.1 Hz, 2H), 2.59-2.50 (m, 2H), 2.41-2.36 (m, 2H), 2.28 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.22-1.93 (m, 4H), 1.64-1.34 (m, 16H), 1.15 (d, *J* = 1.7 Hz, 12H), 0.95-0.91 (m, 6H), 0.90 (s, 3H); **^{13}C NMR** (126

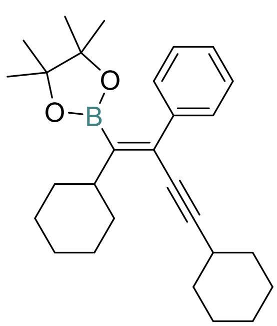
MHz, $CDCl_3$) δ 221.2, 139.2, 138.9, 135.7, 132.6, 128.9, 126.0, 124.8, 97.2, 83.5, 80.5, 50.7, 48.1, 44.6, 38.4, 36.0, 35.0, 31.7, 31.6, 31.1, 29.6, 26.7, 25.9, 24.8, 24.8, 24.7, 22.9, 22.0, 21.7, 19.5, 14.2, 14.0, 13.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 36.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{36}H_{52}BO_3$; 543.4004; Found: 543.4003.

4,4,5,5-Tetramethyl-2-((*Z*)-6-((*E*)-styryl)dodec-5-en-7-yn-5-yl)-1,3,2-dioxaborolane (3p):



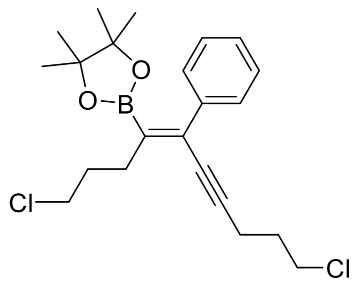
Starting diyne **1a** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2p** (103 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **3p** (29.4 mg; 25%; *rr* 90:10) as colorless liquid after chromatographic purification with 15% ethyl acetate in hexanes, **R_f** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2931, 2861, 1716, 1599, 1457, 1294, 1016, 860; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.6 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.40-7.36 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 15.7 Hz, 1H), 2.64-2.55 (m, 4H), 1.78-1.53 (m, 6H), 1.49 (dd, *J* = 10.2, 5.6 Hz, 2H), 1.44 (s, 12H), 1.05-0.98 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 134.6, 132.0, 129.5, 128.6, 127.4, 126.9, 99.2, 83.5, 77.3, 34.5, 32.2, 31.1, 25.0, 22.9, 22.1, 19.5, 14.3, 13.8 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.3; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{26}H_{38}BO_2$; 393.2959; Found: 393.2978.

(*Z*)-2-(1,4-Dicyclohexyl-2-phenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-



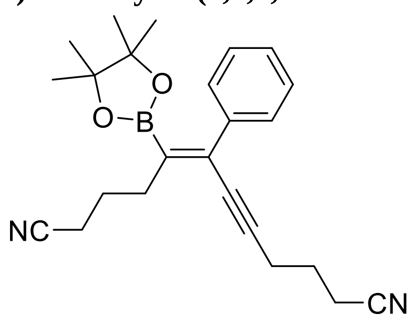
dioxaborolane (4b): Starting diyne **1b** (64.3 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using bromobenzene **2b$_2$** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **4b** (93.4 mg; 74%; *rr* 85:15) as colorless liquid after chromatographic purification with 40% toluene in hexanes, **R_f** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2931, 2861, 1716, 1599, 1457, 1294, 1016, 860; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.31-6.98 (m, 3H), 2.91-2.86 (m, 1H), 2.59-2.55 (m, 1H), 1.86-1.59 (m, 8H), 1.59-1.37 (m, 4H), 1.40-1.23 (m, 8H), 1.07 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 130.1, 128.6, 127.9, 127.3, 100.8, 83.6, 80.5, 45.2, 32.8, 32.3, 29.9, 26.9, 26.4, 26.2, 25.0, 24.7 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{40}BO_2$; 419.3116; Found: 419.3138.

(*Z*)-2-(1,10-Dichloro-5-phenyldec-4-en-6-yn-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



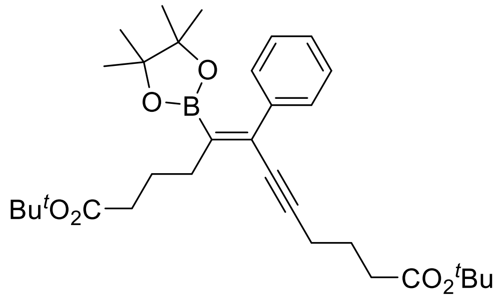
(4c): Starting diyne **1c** (0.061g, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **4c** (66 mg; 54%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 2-5% EtOAc in hexanes; **R_f** (5% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2926, 2854, 1711, 1588, 1356, 1307, 1141, 956; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.24 (m, 5H), 3.68-3.65 (m, 2H), 3.63-3.59 (m, 2H), 2.69-2.65 (m, 2H), 2.62-2.59 (m, 2H), 2.01 (t, *J* = 6.6 Hz, 2H), 2.00 (t, *J* = 6.5 Hz, 2H), 1.14 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 133.8, 128.3, 127.84, 127.6, 95.8, 83.69, 80.8, 44.9, 43.7, 32.3, 32.3, 31.4, 24.6, 17.2. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.5; **HRMS** (ESI-TOF): $[M+NH_4]^+$ Calcd for $C_{22}H_{33}BCl_2NO_2$; 424.1976; Found: 424.1949.

(*Z*)-6-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-ynedinitrile (4d):

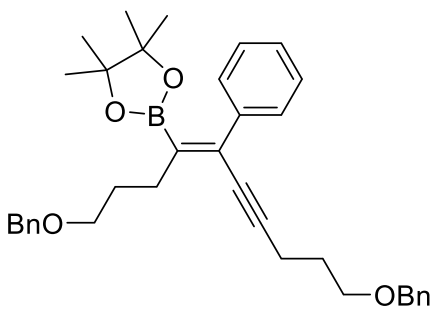


Starting diyne **1d** (27.6 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (35.32 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **4d** (50.1 mg; 86%; *rr* 85:15) as pale yellow liquid after chromatographic purification with 10-15% EtOAc in hexanes; **R_f** (15% EtOAc/hexanes): 0.25; **IR** (film)ν_{max}/cm^{-1}: 2977, 2932, 2247, 1672, 1588, 1356, 963; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.22-7.17 (m, 3H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 2.42-2.38 (m, 2H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.87-1.79 (m, 4H), 1.04 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 134.7, 128.6, 128.4, 128.1, 128.0, 126.1, 95.5, 83.9, 81.6, 33.7, 25.3, 24.7, 24.7, 19.0, 16.9, 16.4 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the 11B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.8; **HRMS** (ESI-TOF): Calculated for $[M+NH_4]^+$ $C_{24}H_{33}BN_3O_2$ 406.2660; Found: 406.2683.

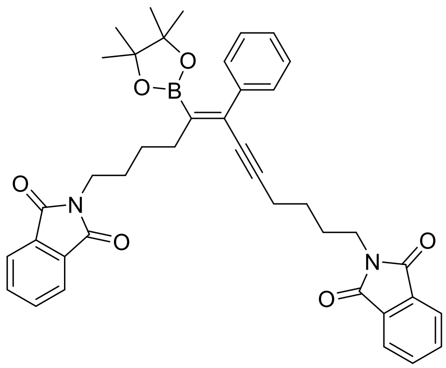
Di-*tert*-butyl (*Z*)-6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-ynedioate (4e): Starting diyne **1e** (29 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (35.32 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **4e** (26 mg; 56%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 2-3% EtOAc in hexanes; **IR** (film)ν_{max}/cm^{-1}: 2980, 2932, 1730, 1455, 1372, 1160; **R$_f$** (5% EtOAc/hexanes): 0.5; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.36-7.32 (m, 5H), 2.59-2.45 (m, 4H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.81-1.69 (m, 4H), 1.45 (m, 9H), 1.45 (m, 9H), 1.15 (s, 12H); **^{13}C NMR** (101 MHz, DMSO-d$_6$) δ 171.9, 171.7, 140.5, 132.2, 127.9, 127.9, 127.7, 96.7, 83.3, 80.4, 79.6, 79.4, 34.7, 34.1, 33.6, 27.8, 27.7, 24.4, 24.3, 23.9, 18.3 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 39.3; **HRMS** (ESI-TOF): Calcd for $[M+NH_4]^+$ $C_{32}H_{51}BNO_6$; 556.3804; Found: 556.3825.



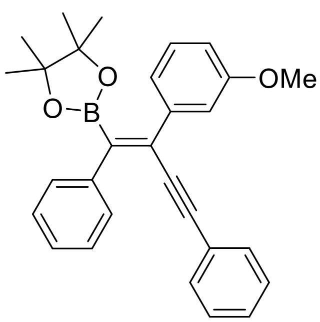
(*Z*)-2-(1,10-*bis*(Benzyloxy)-5-phenyldec-4-en-6-yn-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f): Starting diyne **1f** (103.95 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **4f** (74.32 mg; 45%, *rr* 85:15) as pale yellow liquid after chromatographic purification with 2-3% EtOAc in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.5; **IR** (film)ν_{max}/cm^{-1}: 2961, 2932, 1588, 1465, 1351, 1298, 964; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.05 (m, 15H), 4.38 (d, *J* = 17.3 Hz, 4H), 3.43 (t, *J* = 6.5 Hz, 4H), 2.51 (d, *J* = 7.4 Hz, 2H), 2.38 (d, *J* = 7.0 Hz, 2H), 1.79-1.67 (m, 4H), 1.01 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 138.9, 138.5, 133.3, 128.4, 128.4, 128.3, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 97.0, 83.5, 80.5, 73.0, 72.7, 70.4, 69.0, 31.7, 29.2, 29.1, 24.6, 16.6 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.3; **HRMS** (ESI-TOF): Calcd for $[M+NH_4]^+$ $C_{36}H_{47}BNO_4$; 568.3593; Found: 568.3607.



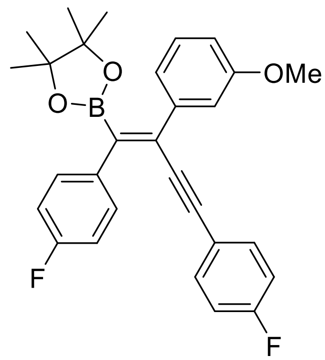
(*Z*)-2,2'-(6-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodec-5-en-7-yne-1,12-diyl)*bis*(isoindoline-1,3-dione) (4g): Starting diyne **1g** (103.95 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2b₂** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **4g** (135.92 mg; 69%; *rr* 85:15) as pale yellow liquid after chromatographic purification with 30% EtOAc in hexanes; **R$_f$** (30% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2979, 2931, 2859, 1711, 1710, 1615, 1396; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.69 (m, 4H), 7.67-7.65 (m, 4H), 7.35-7.33 (m, 2H), 7.23-7.19 (m, 3H), 3.70 (t, *J* = 7.1 Hz, 4H), 2.61-2.51 (m, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.86-1.70 (m, 4H), 1.64-1.48 (m, 4H), 1.08 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 168.5, 141.5, 133.9, 133.8, 133.3, 132.3, 132.2, 128.5, 127.8, 127.4, 123.2, 123.2, 96.9, 83.5, 80.8, 38.1, 37.6, 34.7, 28.5, 28.0, 26.5, 26.2, 24.7, 19.4 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.7; **HRMS** (ESI-TOF): $[M+NH_4]^+$ Calculated for $C_{40}H_{45}BN_3O_6$; 674.3396; Found: 674.3418.



(*Z*)-2-(2-(3-Methoxyphenyl)-1,4-diphenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h): Starting diyne **1h** (30.44, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2a** (42.08 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **4h** (29 mg; 44%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 2-3% EtOAc in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2963, 2928, 1713, 1605, 1510, 1464, 1175, 1034; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71-7.63 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.33-7.20 (m, 9H), 6.94-6.84 (m, 1H), 3.87 (s, 3H), 1.16 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 142.7, 140.9, 131.7, 131.5, 130.2, 129.3, 129.0, 128.3, 128.0, 127.3, 123.6, 121.2, 114.3, 114.0, 95.1, 90.4, 84.2, 55.4, 24.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{40}BO_2$; 437.2283; Found: 437.2303.

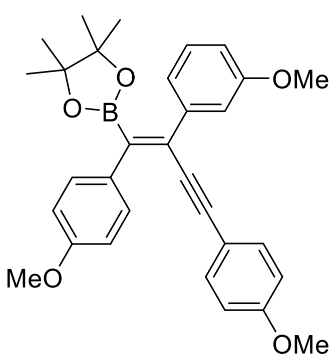


(*Z*)-2-(2-(3-Methoxyphenyl)-1,4-diphenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i):



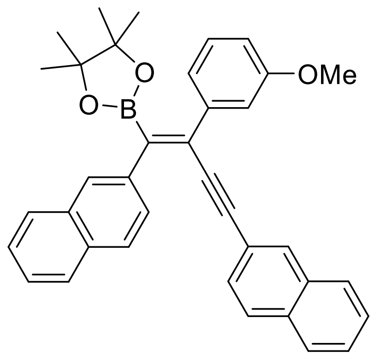
1i (47.6, 0.20 mmol, 1 equiv.) was reacted according to the above general procedure using **2a** (56.10 mg, 0.30 mmol, 1.5 equiv.) to afford the title product **4i** (31.4 mg; 33%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 2-3% EtOAc in hexanes; Rf (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2958, 2925, 1737, 1663, 1598, 1506, 1368; **^{1}H NMR** (500 MHz, CDCl3) δ 7.65-7.56 (m, 2H), 7.32-7.15 (m, 5H), 7.09 (dd, *J* = 8.8 Hz, *J* = 8.8 Hz, 2H), 6.96 (dd, *J* = 8.7 Hz, *J* = 8.7 Hz, 2H), 6.90 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.86 (s, 3H), 1.15 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.4 (d, *J* = 58.9 Hz), 161.5 (d, *J* = 55.4 Hz), 159.6, 142.3, 136.8 (d, *J* = 3.3 Hz), 133.5 (d, *J* = 8.4 Hz), 131.6, 130.7 (d, *J* = 8.0 Hz), 129.4, 127.3, 119.5 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.1 Hz), 114.9 (d, *J* = 21.3 Hz), 114.3, 113.9, 94.2, 89.8, 84.3, 55.4, 24.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -110.6, -114.8; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.8; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}BF_2O_3$; 473.2094; Found: 473.2107.

(*Z*)-2-(2-(3-Methoxyphenyl)-1,4-diphenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4j):

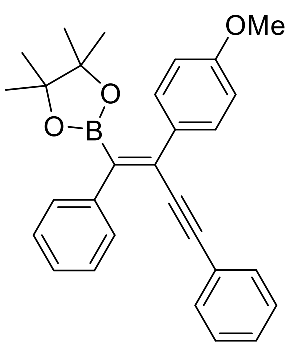


Starting diyne **1j** (52.4, 0.20 mmol, 1 equiv.) was reacted according to the above general procedure using **2a** (56.10 mg, 0.30 mmol, 1.5 equiv.) to afford the title product **4j** (47.7 mg; 48%; *rr* 85:15) as pale yellow liquid after chromatographic purification with 15% EtOAc in hexanes; **R_f** (15% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2983, 2913, 1736, 1604, 1448, 1373, 1234; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.60-7.50 (m, 2H), 7.33 (dd, *J* = 7.9 Hz, *J* = 7.9 Hz, 1H), 7.27-7.22 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.05-6.98 (m, 3H), 6.96-6.91 (m, 3H), 3.79 (d, *J* = 1.0 Hz, 6H), 3.75 (s, 3H), 1.09 (s, 12H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.6, 159.1, 158.7, 142.1, 132.7, 132.5, 129.8, 129.5, 128.7, 120.4, 114.5, 114.4, 113.9, 113.5, 113.3, 94.4, 89.2, 83.8, 55.3, 55.2, 55.2, 24.4 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{34}BO_5$; 497.2494; Found: 497.2516.

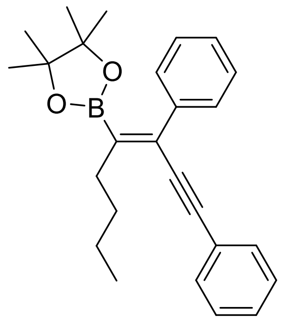
(*Z*)-2-(2-(3-Methoxyphenyl)-1,4-di(naphthalen-2-yl)but-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k): Starting diyne **1k** (61 mg, 0.20 mmol) was reacted according to the above general procedure using **2a** (56.10 mg, 0.30 mmol, 1.5 equiv.) to afford the title product **4k** (22.3 mg; 22%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 2-3% EtOAc in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2919, 2851, 1744, 1465, 1373, 1238, 1046; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.92-7.80 (m, 4H), 7.73-7.65 (m, 2H), 7.64-7.55 (m, 2H), 7.51-7.43 (m, 2H), 7.43-7.37 (m, 2H), 7.35-7.20 (m, 4H), 6.89-6.87 (m, 1H), 3.85 (s, 3H), 1.15 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 148.6, 142.6, 138.5, 133.5, 133.0, 132.9, 131.8, 131.7, 129.4, 128.4, 128.3, 128.1, 127.9, 128.0, 127.8, 127.8, 127.4, 127.4, 126.7, 126.5, 126.0, 124.1, 121.2, 120.8, 114.2, 114.0, 95.8, 90.9, 84.3, 55.5, 24.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.2; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{37}H_{34}BO_3$; 537.2596; Found: 537.2613.



(*Z*)-2-(2-(4-Methoxyphenyl)-1,4-diphenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l): Starting diyne **1h** (81.1 mg, 0.40 mmol, 1 equiv.) was reacted according to the above general procedure using **2d** (75 µL, 0.6 mmol, 1.5 equiv.) to afford the title product **4l** (36.2 mg; 22%; *rr* 85:15) as pale yellow liquid after chromatographic purification with 5% EtOAc in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2958, 2923, 1600, 1509, 1249, 988; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69-7.63 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.41 (dd, *J* = 7.7 Hz, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.26 (s, 5H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 1.19 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 141.3, 133.9, 131.6, 131.5, 130.0, 129.0, 128.3, 128.2, 127.9, 127.1, 123.7, 113.6, 94.9, 90.8, 84.1, 55.5, 24.8 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.7; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{40}BO_2$; 437.2283; Found: 437.2302.

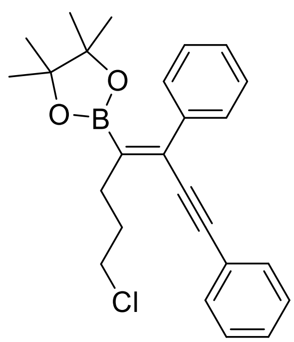


(*Z*)-2-(1,3-Diphenyloct-3-en-1-yn-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m):



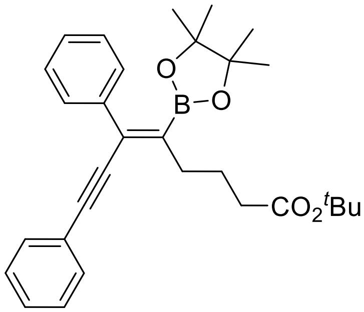
Starting diyne **1l** (48.6 mg, 0.30 mmol, 1 equiv.) was reacted according to the above general procedure using **2b** (70.65 mg, 0.45 mmol, 1.5 equiv.) to afford the title product **4m** (61.42 mg; 53%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 5% EtOAc in hexanes; **R_f** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2979, 2923, 1560, 1362, 1135; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.42 (m, 4H), 7.35-7.25 (m, 6H), 2.76-2.62 (m, 2H), 1.56 (d, *J* = 7.6 Hz, 2H), 1.46 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.15 (s, 12H), 0.96 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 132.0, 131.5, 128.5, 128.3, 128.1, 127.8, 127.5, 123.8, 95.8, 89.2, 83.6, 35.1, 31.4, 24.6, 22.8, 14.1 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{32}BO_2$; 387.2490; Found: 387.2497.

(*Z*)-2-(7-chloro-1,3-diphenylhept-3-en-1-yn-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



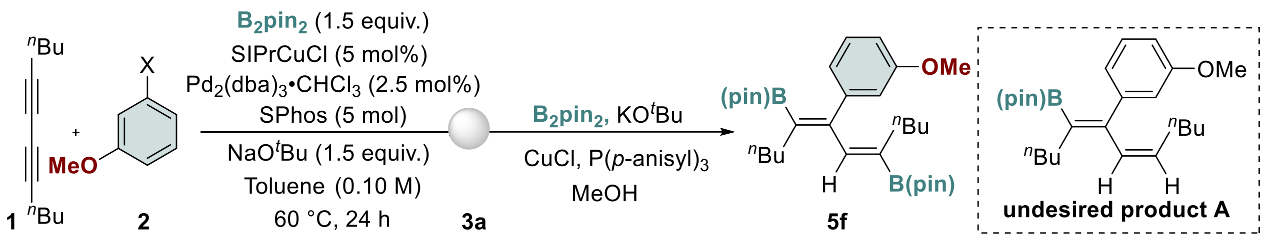
(4n): Starting diyne **1m** (60.8 mg, 0.30 mmol) was reacted according to the above general procedure using **2b** (40 µL, 0.45 mmol, 1.5 equiv.) to afford the title product **4n** (64.5 mg; 53%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 5% EtOAc in hexanes; **R_f** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2251, 2125, 1660, 1355, 1053, 1027; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.49-7.48 (m, 2H), 7.43-7.28 (m, 8H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.80-2.63 (m, 2H), 1.99-1.92 (m, 2H), 1.12 (s, 12H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 139.7, 132.1, 131.3, 128.9, 128.9, 128.7, 128.1, 128.0, 122.4, 96.1, 88.4, 83.6, 45.1, 32.2, 31.8, 24.4 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{29}BClO_2$; 407.1944; Found: 407.1963.

***tert*-Butyl (*Z*)-6,8-diphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-5-en-7-ynoate (4o)**: Starting diyne **1n** (41.2 mg, 0.153 mmol) was reacted according to the above general procedure using bromobenzene (36.03 mg, 0.229 mmol, 1.5 equiv.) to afford the title product **4o** (47.7 mg; 66%; *rr* 90:10) as pale yellow liquid after chromatographic purification with 5% EtOAc in hexanes; **R_f** (5% EtOAc/hexanes): 0.3; **IR** (film)ν_{max}/cm^{-1}: 2256, 2156, 1665, 1490, 1353, 1047,



1024; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.58-7.49 (m, 2H), 7.47-7.37 (m, 8H), 2.72-2.60 (m, 2H), 2.36-2.27 (m, 2H), 1.84-1.74 (m, 2H), 1.42 (s, 9H), 1.17 (s, 12H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.0, 139.9, 131.6, 131.3, 128.9, 128.7, 128.1, 128.0, 128.0, 122.4, 95.9, 88.5, 83.6, 79.5, 34.6, 34.3, 27.8, 24.4, 24.2 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{30}H_{41}BNO_4$; 490.3123; Found: 490.3125.

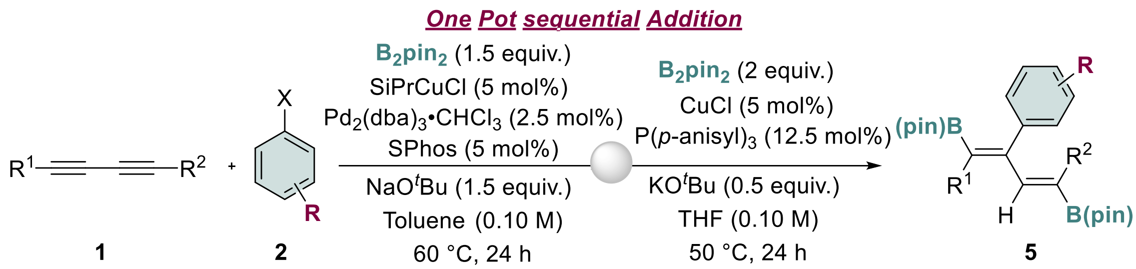
6A. Optimization Table for the synthesis of pentasubstituted Diene:



Entry	Reagent for the second step	Starting Compound	Process	Yield % (5f)	*rr*
1[a]	B_2pin_2, MeOH, KO^{t}Bu,	1a	In the same pot	3a	-
2[a]	B_2pin_2, MeOH, KO^{t}Bu, THF (1 mL)	1a	In the same pot	**A** (21%)	-
3[b]	CuCl, P(p-anisyl)$_3$ KO^{t}Bu, MeOH, THF	1a	Workup was done after the first step	50	>95:5
4[b]	CuCl, P(p-anisyl)$_3$ KO^{t}Bu, MeOH, THF	1a	In the same pot	51	>95:5
5[b]	CuCl, P(p-anisyl)$_3$, KO^{t}Bu, MeOH, THF	3a	Isolation after the first step via column chromatography	70	>95:5

Reaction Conditions: diyne (0.15 mmol, 1 equiv.), SIPrCuCl (5 mol%), $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%), SPhos (5 mol%), NaO^{t}Bu (1.5 equiv.), RX (1.5 equiv.), toluene (0.10 M), 60 °C, 24 h; [a]KO^{t}Bu (50 mol%), B_2pin_2 (2 equiv.), MeOH (4 equiv.); [b]CuCl (5 mol%), P(p-anisyl)$_3$ (12.5 mol%), KO^{t}Bu (50 mol%), B_2pin_2 (2 equiv.), MeOH (4 equiv.), THF (1 mL), 50 °C, 18 h;

6B. One-Pot Synthesis of Penta-Substituted Dienes:

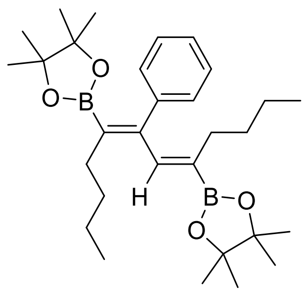


To a flame-dried Schlenk tube A, SIPrCuCl (3.9 mg, 0.0075 mmol, 5 mol%), B_2pin_2 (56 mg, 0.225 mmol, 1.5 equiv.), diyne (0.15 mmol, 1 equiv.) were added and stirred in dry toluene (1.0 mL) under an inert atmosphere. To this mixture, NaO^{t}Bu solution (0.125 mL, 0.225 mmol, 1.5 equiv, 2M in THF) was added sequentially at room temperature. To another Schlenk tube B, $Pd_2(dba)_3.CHCl_3$ (3.7 mg, 0.0037 mmol, 2.5 mol%), SPhos (3.1 mg, 0.0075 mmol, 5 mol%), and toluene (0.5 mL) were added and stirred for 10 minutes under an inert atmosphere. Then, this catalyst mixture in the Schlenk tube B was transferred to the Schlenk tube A. Then, to Schlenck tube A, ArX (0.225 mmol, 1.5 equiv.) was added, and the mixture was stirred at 60 °C for 24 h.

Protoboration: After completion of the first step, CuCl (0.8 mg, 0.0075 mmol, 5 mol%), P(*p*-anisyl)$_3$ (6.4 mg, 0.019 mmol, 12.5 mol%), B_2Pin_2 (76 mg, 0.3 mmol, 2 equiv.) and dry THF (1 mL, 0.15 M) were added to Schlenk tube A and stirred for 10 minutes at room temperature. Then, KO^{t}Bu (0.076 mL, 0.075 mmol, 0.5 equiv, 1 M in THF) was MeOH (25 µL, 0.6 mmol, 4 equiv.) was sequentially added to this reaction mixture. The reaction was stirred at 50 ^{o}C for 24 h. After completion of the reaction, the mixture was cooled to room temperature, decanted into the separating funnel, and diluted with ethyl acetate (30 mL). The organic layer was washed with distilled water (2×20 mL) and brine (20 mL). Then the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated in vacuo to provide a crude mixture. The mixture was analyzed by ^{1}H NMR with 1,1,2,2-tetrachloroethane (1 equiv.) as an internal standard to determine the NMR yield and regioselectivity. Further purification by flash column chromatography using ethyl acetate-hexanes/ toluene-hexanes was performed rapidly (preferably within 10 minutes). (**Note.** Pinacol boronate esters are unstable under the column and ambient atmosphere and need to be stored under 2-8 ^{o}C).

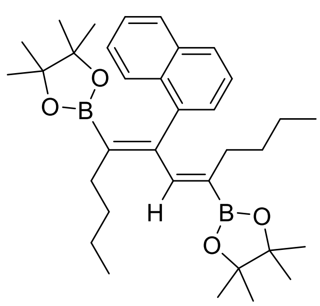
7. Characterization Data of Penta-Substituted Dienes

2,2'-((*5E,7Z*)-6-Phenyldodeca-5,7-diene-5,8-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5a):



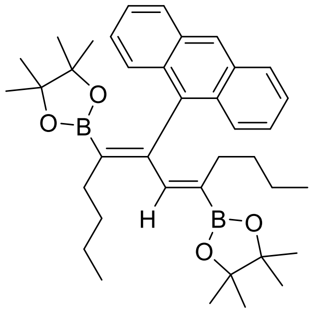
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2b** (35.32 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5a** (44.7 mg; 60%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 70-80% toluene in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.20; **IR** (film)ν_{max}/cm^{-1}: 2983, 2928, 1741, 1595, 1379, 1240, 1046; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.14 (m, 5H), 7.01 (s, 1H), 2.29-2.21 (m, 2H), 1.85 (t, *J* = 7.1 Hz, 2H), 1.45-1.32 (m, 4H), 1.25 (s, 12H), 1.09 (s, 12H), 1.07-1.00 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 144.2, 142.0, 129.0, 127.7, 126.6, 83.2, 83.2, 32.6, 31.6, 31.4, 30.3, 24.8, 24.7, 23.0, 22.9, 14.2, 14.1 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{49}B_2O_4$ 495.3811; Found: 495.3836.

2,2'-((*5E,7Z*)-6-(Naphthalen-1-yl)dodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5b):



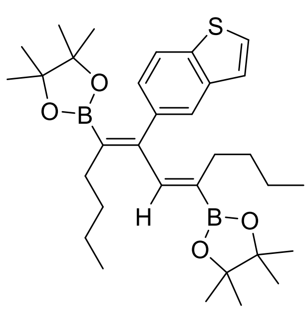
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using 1-bromonapthalene **2j** (46.6 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5b** (47.4 mg; 58%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 70-80% toluene in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2981, 2925, 1745, 1605, 1372, 1240, 1131, 1046; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03-7.94 (m, 1H), 7.80-7.74 (m, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.43-7.29 (m, 4H), 7.13 (s, 1H), 2.49-2.38 (m, 2H), 1.80 (t, *J* = 7.3 Hz, 2H), 1.53-1.50 (m, 2H), 1.45-1.41 (m, 2H), 1.23 (s, 12H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.95-0.86 (m, 4H), 0.71 (d, *J* = 16.3 Hz, 12H), 0.62 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.0, 142.0, 140.7, 133.8, 132.7, 127.9, 127.0, 127.0, 126.9, 125.5, 125.4, 125.2, 83.2, 82.8, 32.1, 32.0, 31.8, 30.3, 24.8, 24.3, 23.1, 23.0, 14.2, 14.1 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.9; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{51}B_2O_4$ 545.3968; Found: 545.3995.

2,2'-((5*E*,7*Z*)-6-(Anthracen-9-yl)dodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5c):



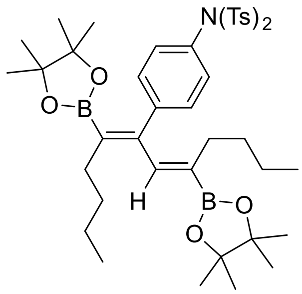
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2k** (57.8 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5c** (35.9 mg; 41%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 60-80% toluene in hexanes; $\mathbf{R_f}$ (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2981, 2923, 1740, 1555, 1373, 1278; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.09 (dd, *J* = 5.7, 4.3 Hz, 2H), 7.96-7.86 (m, 2H), 7.43-7.33 (m, 4H), 7.29 (s, 1H), 2.70-2.59 (m, 2H), 1.66-1.59 (m, 2H), 1.54-1.45 (m, 4H), 1.21 (s, 12H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.72-0.60 (m, 2H), 0.61-0.51 (m, 2H), 0.41 (s, 12H), 0.39 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 138.7, 138.6, 131.6, 130.6, 128.1, 127.7, 125.7, 124.9, 124.8, 83.2, 82.5, 32.2, 32.2, 31.7, 30.3, 24.8, 24.0, 23.2, 23.0, 14.2, 13.9 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.9; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{53}B_2O_4$ 595.4124; Found: 595.4154.

2,2'-((5*E*,7*Z*)-6-(Benzo[b]thiophen-5-yl)dodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5d):



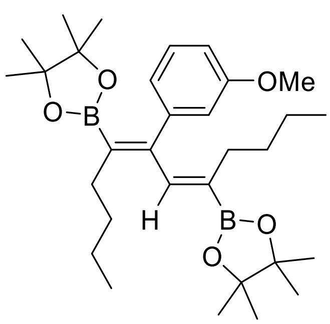
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2m** (48 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5d** (52 mg; 62%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 20% ethyl acetate in hexanes; $\mathbf{R_f}$ (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2978, 2929, 2858, 1740, 1592, 1466, 1047; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.57 (m, 2H), 7.36 (d, *J* = 5.4 Hz, 1H), 7.27-7.15 (m, 2H), 7.06 (s, 1H), 2.35-2.20 (m, 2H), 1.97-1.77 (m, 2H), 1.46-1.30 (m, 4H), 1.24 (s, 12H), 1.01 (s, 12H), 1.01-0.98 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.62 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 142.0, 140.7, 139.4, 138.1, 126.2, 125.8, 123.9, 123.7, 121.6, 83.2, 83.2, 32.7, 31.6, 31.4, 30.3, 25.0, 24.8, 24.7, 22.9, 14.1, 14.0 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.2; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{49}B_2O_4S$ 551.3532; Found: 551.3564.

N-(4-((*5E,7Z*)-5,8-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-5,7-dien-6-yl)phenyl)-4-methyl-N-tosylbenzenesulfonamide (5e):



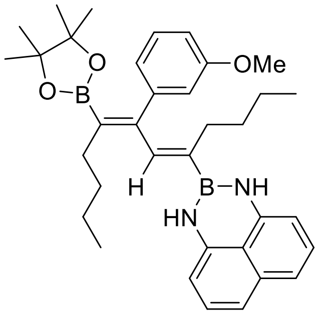
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using amine derivative **2e** (82.5 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5e** (98.5 mg; 81%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 20% ethyl acetate in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2924, 2855, 1740, 1604, 1496, 1373, 1239; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 4H), 7.30 (d, *J* = 8.3 Hz, 4H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.97 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 6H), 2.31-2.17 (m, 2H), 1.86 (d, *J* = 6.6 Hz, 2H), 1.46-1.31 (m, 6H), 1.26 (s, 12H), 1.14-1.09 (m, 2H), 1.12 (s, 12H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 4.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.2, 146.1, 144.9, 141.3, 137.1, 132.8, 131.0, 129.6, 129.6, 128.6, 83.5, 83.3, 32.7, 31.5, 31.3, 30.3, 24.8, 24.7, 23.0, 22.8, 21.8, 14.2, 14.0 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 36.6; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{44}H_{65}B_2N_2O_8S_2$ 835.4363; Found: 835.4405.

2,2'-((*5E,7Z*)-6-(3-methoxyphenyl)dodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5f):



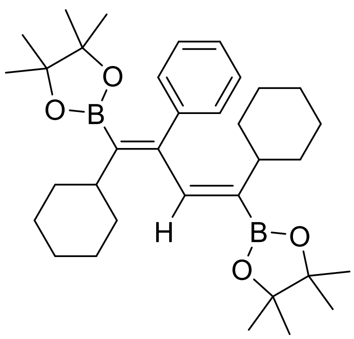
Starting diyne **1a** (24.3 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2a** (42.08 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5f** (39.5 mg; 51%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 80% toluene in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2958, 2930, 1576, 1466, 1371, 1300, 1215; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.9 Hz, *J* = 7.9 Hz, 1H), 7.07 (s, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.87-6.83 (m, 1H), 6.80 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.84 (s, 3H), 2.35-2.27 (m, 2H), 1.94 (t, *J* = 7.1 Hz, 2H), 1.52-1.37 (m, 4H), 1.32 (s, 12H), 1.17 (s, 12H), 1.17-1.14 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 146.7, 145.7, 141.7, 128.7, 121.6, 114.5, 112.3, 83.2, 83.2, 55.3, 32.5, 31.6, 31.4, 30.3, 24.8, 24.7, 23.0, 22.9, 14.2, 14.1 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 31.4; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{51}B_2O_5$ 525.3917; Found: 525.3952.

2-((*5Z,7E*)-7-(3-Methoxyphenyl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-5,7-dien-5-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (5g):



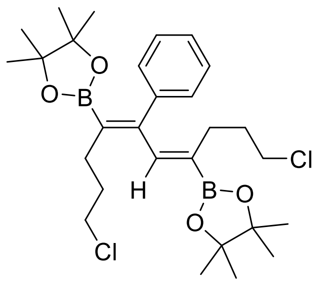
Starting diyne **1a** (24.3 mg, 0.15 mmol) was reacted according to the above general procedure using **2a** (42.08 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5g** (39.5 mg; 52%; *rr* 85:15) as colorless viscus liquid after chromatographic purification with 5% ethyl acetate in hexanes; $\mathbf{R_f}$ (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2927, 2857, 1739, 1602, 1507, 1373, 1247, 1145; ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.19-7.16 (m, 1H), 7.12-7.09 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.77 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.74 (s, 1H), 6.34 (d, *J* = 7.3 Hz, 2H), 5.72 (s, 2H), 3.80 (s, 3H), 2.33-2.26 (m, 2H), 1.98 (t, *J* = 6.8 Hz, 2H), 1.49-1.42 (m, 2H), 1.40 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.25 (d, *J* = 6.4 Hz, 2H), 1.14-1.12 (m 2H), 1.13 (s, 12H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 6.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 159.2, 146.4, 145.8, 141.3, 136.5, 136.3, 128.9, 127.7, 121.5, 119.9, 117.6, 114.7, 112.4, 105.9, 83.4, 55.3, 32.8, 31.8, 31.5, 30.5, 24.8, 23.2, 23.1, 14.2, 14.1 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 30.7; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{35}H_{47}B_2N_2O_3$ 565.3767; Found: 565.3797.

2,2'-((*1E,3Z*)-1,4-Dicyclohexyl-2-phenylbuta-1,3-diene-1,4-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5h):

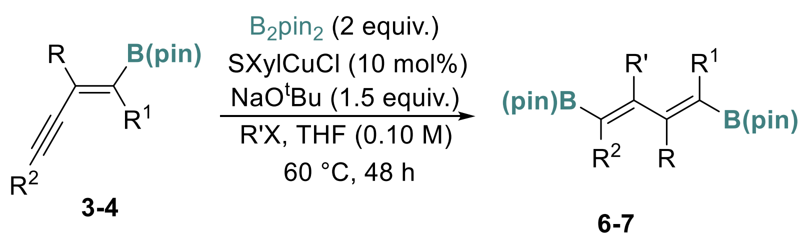


Starting diyne **1b** (32.15 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using $\mathbf{2b_2}$ (35.32 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5h** (28.1 mg; 35%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 80% toluene in hexanes; R_f (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 2925, 2854, 1745, 1605, 1373, 1240; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.18-7.14 (m, 2H), 7.17-7.13 (m, 2H), 7.06 (dd, *J* = 8.4, 5.8 Hz, 1H), 6.77 (s, 1H), 2.35-2.33 (m, 1H), 2.17-2.13 (m, 1H), 1.61 (dd, *J* = 32.3, 15.1 Hz, 6H), 1.49 (d, *J* = 13.1 Hz, 3H), 1.42-1.32 (m, 3H), 1.25-1.18 (m, 4H), 1.16 (s, 12H), 1.09-1.07 (m, 3H), 1.04 (dd, *J* = 11.9, 3.4 Hz, 1H), 0.98 (s, 12H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 147.1, 144.2, 142.0, 129.0, 127.7, 126.6, 83.2, 83.2, 32.6, 31.6, 31.4, 30.3, 24.8, 24.7, 23.0, 22.9, 14.2, 14.1 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{11}**B NMR** (160 MHz, $CDCl_3$) δ 35.9; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{53}B_2O_4$ 547.4124; Found: 547.4256.

2,2'-((*4E,6Z*)-1,10-Dichloro-5-phenyldeca-4,6-diene-4,7-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5i): Starting diyne **1c** (30.4 mg, 0.15 mmol, 1 equiv.) was reacted according to the above general procedure using **2b** (35.32 mg, 0.225 mmol, 1.5 equiv.) to afford the title product **5i** (74.3 mg; 64%; *rr* >95:5) as colorless viscus liquid after chromatographic purification with 5% ethyl acetate in hexanes; **R$_f$** (5% EtOAc/hexanes): 0.40; **IR** (film)ν_{max}/cm^{-1}: 3027, 2922, 1604, 1495, 1379, 1081; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 5.0 Hz, 5H), 7.05 (s, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.47-2.25 (m, 2H), 1.88-1.84 (m, *J* = 7.3 Hz, 4H), 1.61-1.42 (m, 3H), 1.18 (s, 12H), 1.02 (s, 12H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 148.4, 143.7, 142.9, 128.9, 127.9, 127.1, 83.5, 83.5, 45.0, 45.0, 32.4, 32.3, 30.1, 28.1, 24.9, 24.8 [note: the carbons attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{11}**B NMR** (128 MHz, $CDCl_3$) δ 30.1; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{46}B_2Cl_2NO_4$ 552.2985; Found: 552.2999.

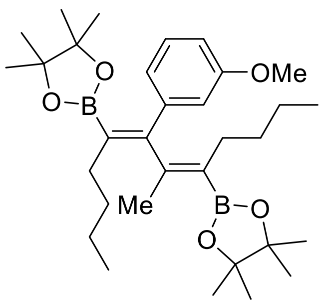


8. General Procedure and Characterization Data of Hexa-Substituted Dienes:



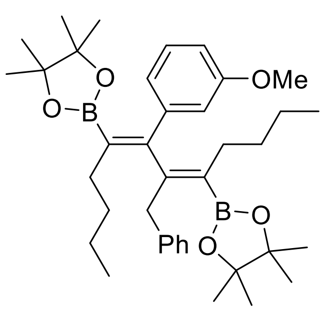
To a flame-dried Schlenk tube, (SXyl)CuCl (10 mol%) and B_2pin_2 (2 equiv.) were added and stirred in dry THF (0.10 M) under an inert atmosphere. To this mixture, enyne **3-4** (1 equiv., soluble with 0.5 mL dry THF) was added to the schlenk tube. Then, NaO^{t}Bu solution (1.5 equiv., 2 M in THF), and R'X (1.5-6 equiv.) were added sequentially at room temperature and allowed to stir at 60 °C for 48 h. After completion of the reaction, the mixture was cooled to room temperature, decanted into the separating funnel, and diluted with ethyl acetate (30 mL). The organic layer was washed with distilled water (2×20 mL) and brine (20 mL). Then the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated in vacuo to provide a crude mixture. The mixture was analyzed by ^{1}H NMR with 1,1,2,2-tetrachloroethane (1 equiv.) as an internal standard to determine the NMR yield and regioselectivity. Further purification by flash column chromatography using ethyl acetate-hexanes/ toluene-hexanes was performed rapidly to obtain the desired products **6** and **7** (preferably within 10 minutes). (**Note.** Pinacol boronate esters are unstable under the column and ambient atmosphere and need to be stored under 2-8 °C).

2,2'-((*5Z,7Z*)-6-(3-Methoxyphenyl)-7-methyldodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**6**): Starting enyne **3a** (91 mg, 0.23 mmol, 1 equiv.) was reacted according to the above general procedure using MeI (86 µL, 1.37 mmol, 6 equiv.) as electrophile to afford the title product **6** (29.6 mg; 71%, *rr* >95:5) as a viscus liquid after chromatographic purification with 5% ethyl acetate in hexanes; **R**



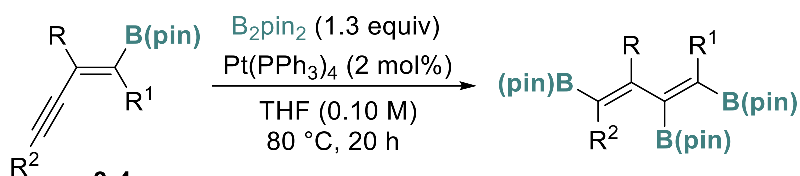
R_f (5% EtOAc/hexanes): 0.20; **IR** (film)ν_{max}/cm^{-1}: 2931, 2862, 1741, 1594, 1465, 1350, 1291; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17-7.14 (m, 1H), 7.11-7.04 (m, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.74 (s, 3H), 2.11-2.09 (m, 2H), 2.05-1.88 (m, 2H), 1.63 (s, 3H), 1.41-1.26 (m, 8H), 1.20 (s, 12H), 1.20 (s, 12H), 0.86 (d, *J* = 6.1 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 156.0, 152.2, 142.5, 128.3, 122.2, 114.3, 113.2, 83.0, 82.8, 55.1, 32.9, 32.6, 32.0, 31.3, 25.2 (all pinacol –CH_3 peaks are merging), 23.2, 22.9, 18.2, 14.3, 14.2 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.6; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{53}B_2O_5$ 539.4074; Found: 539.4100.

2,2'-((*5Z,7Z*)-6-(3-Methoxyphenyl)-7-methyldodeca-5,7-diene-5,8-diyl)*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**7**): Starting enyne **3a** (36 mg, 0.091 mmol, 1 equiv.) was reacted according to the above general procedure using Benzyl bromide (23.29 mg, 0.137 mmol, 1.5 equiv.) as electrophile to afford the title product **7** (14 mg; 25%, *rr* >95:5) as a viscus liquid after chromatographic purification with 2-5% ethyl acetate in hexanes; **R_f** (5% EtOAc/hexanes): 0.45; **IR** (film)ν_{max}/cm^{-1}:



2955, 2925, 1739, 1594, 1359, 1234; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.99-6.87 (m, 3H), 6.88-6.80 (m, 3H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.63 (s, 3H), 3.37 (dd, *J* = 52.9, 11.9 Hz, 2H), 2.14 (dd, *J* = 35.0, 9.6 Hz, 2H), 1.84 (t, *J* = 7.8 Hz, 2H), 1.40-0.99 (m, 8H), 1.30 (s, 12H), 1.30 (s, 12H), 0.81 (t, J = 7.1 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H); ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 155.7, 152.8, 142.4, 140.7, 129.7, 128.3, 127.5, 125.1, 122.4, 114.4, 113.1, 83.0, 82.9, 55.1, 38.7, 32.9, 32.8, 32.0, 31.5, 25.6, 24.6, 23.2, 23.2, 14.3, 14.2 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.0; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{38}H_{57}B_2O_5$ 615.4387; Found: 615.4421.

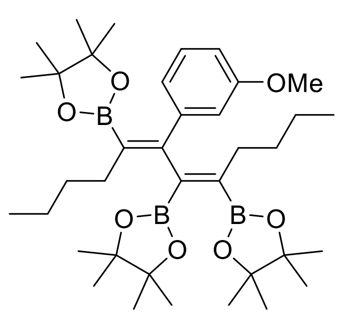
9. Platinum-Catalyzed Diborylation of Boryl Enynes:



3-4 **8-9**

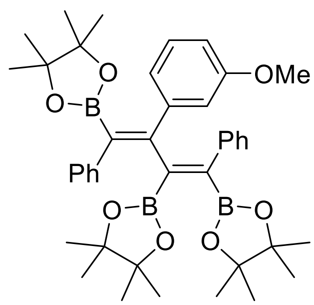
To a flame-dried Schlenk tube, 1,3-enyne boronates **3-4** (1 equiv.), $Pt(PPh_3)_4$ (2 mol%), and $B_2(pin)_2$ (1.3 equiv.) were added and stirred in dry THF (0.10 M) under an inert atmosphere. Then, the reaction mixture was stirred at 80 °C for 20 h to complete the conversion. After the reaction was completed, the reaction mixture was directly subjected to flash column chromatography to give the corresponding triborotate products as a viscus liquid.

2,2',2''-((*5Z,7E*)-7-(3-Methoxyphenyl)dodeca-5,7-diene-5,6,8-triyl)*tris*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**8**): Starting enyne **3a** (39.6 mg, 0.10 mmol, 1 equiv.) was reacted according to the above general procedure to afford the title product **8** (48.4 mg; 71%) as a viscus liquid after chromatographic purification with 2-5% ethyl acetate in hexanes; **R_f** (5% EtOAc/hexanes): 0.45; **IR** (film)ν_{max}/cm^{-1}: 2921, 2852, 1740, 1457, 1237, 1047; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06-7.02 (m, 1H), 6.92-6.77 (m, 2H), 6.65 (dd, J = 8.0, 1.9 Hz, 1H), 3.74 (s, 3H), 2.33-2.32 (m, 1H), 2.23-2.21 (m, 1H), 2.18-2.07 (m, 2H), 1.45-1.31 (m, 3H), 1.29 (s, 12H), 1.29-1.28 (m, 2H), 1.22 (d, J = 2.9 Hz, 12H), 1.20-1.14 (m, 2H), 1.12 (s, 6H), 1.06 (s, 6H), 1.00-0.91 (m, 1H), 0.86 (t, J = 6.9 Hz, 3H), 0.76 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 149.5, 146.3, 128.4, 121.6, 114.6, 112.0, 83.5, 83.4, 83.0, 55.1, 34.0, 33.3, 31.6, 30.7, 25.2, 25.1, 25.0, 24.9, 24.7, 24.6, 23.3, 23.2,



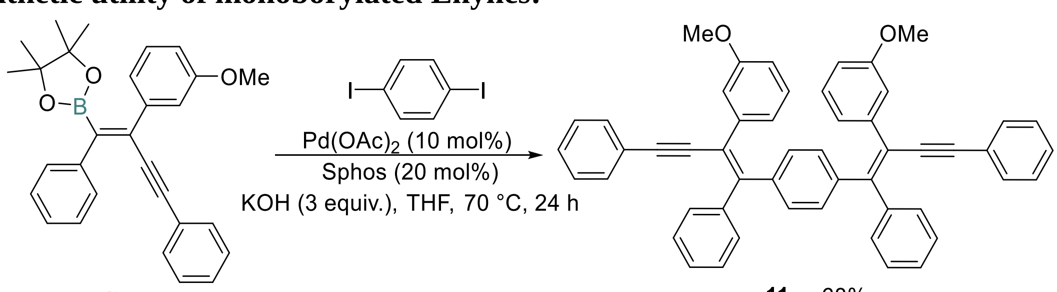
14.3, 14.2 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.6; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{37}H_{65}B_3NO_7$ 668.5035; Found: 668.5072.

2,2',2''-((*1Z,3E*)-3-(3-Methoxyphenyl)-1,4-diphenylbuta-1,3-diene-1,2,4-triyl)*tris*(4,4,5,5-

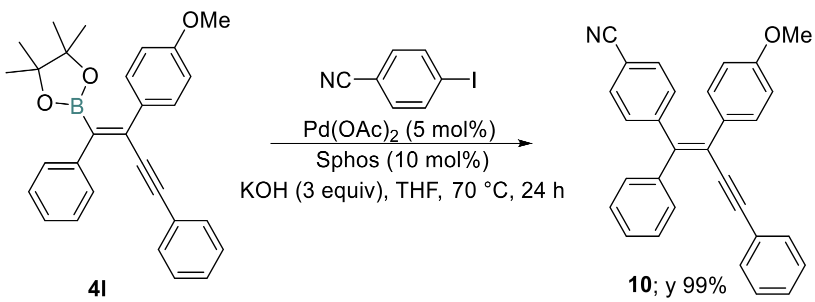


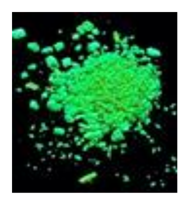
tetramethyl-1,3,2-dioxaborolane) (9): Starting enyne **4h** (43.9 mg, 0.10 mmol, 1 equiv.) was reacted according to the above general procedure to afford the title product **9** (53.4 mg; 82%) as a viscus liquid after chromatographic purification with 2-5% ethyl acetate in hexanes; R_f (10% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2978, 2926, 1739, 1597, 1456, 1330; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.24-7.21 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.06-6.98 (m, 3H), 6.95-6.86 (m, 3H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.59-6.51 (m, 1H), 6.48-6.43 (m, 1H), 3.63 (s, 3H), 1.21 (d, *J* = 9.3 Hz, 12H), 1.11 (s, 6H), 0.98 (s, 12H), 0.98 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.5, 150.8, 146.5, 142.6, 141.7, 129.4, 128.2, 128.0, 127.6, 127.6, 126.1, 126.0, 121.7, 114.9, 112.4, 83.7, 83.6, 83.4, 55.1, 25.1, 24.8, 24.5, 24.5, 24.4 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.1; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{41}H_{57}B_3NO_7$ 708.4409; Found: 708.4444.

10. Synthetic utility of monoborylated Enynes:



The coupling reaction was performed using our previous literature procedure.[4] Under an argon atmosphere, a 10 mL Schlenk tube was charged with pinacol boronate ester **4h** (99 mg, 0.22 mmol, 2.2 equiv.), 1,4-diiodobenzene (39.29 mg, 0.10 mmol, 1 equiv.), a 1.5 M KOH aqueous solution (400 µL, 0.60 mmol, 6 equiv.), and THF (1 mL). After degassing by three freeze-pump-thaw cycles, $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%) and SPhos (8.2 mg, 0.02 mmol, 10 mol%) were added to this reaction mixture, and the resulting mixture was stirred at 70 ºC for 24 h. Then, H_2O (10 mL) was added to the mixture, and the organic phase was extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent, followed by purification via column chromatography (10% ethyl acetate in hexane) to deliver the desired product 10 as a yellow solid (47.5 mg; y 68%). **R_f** (5% EtOAc/hexanes): 0.20; **mp** 187-188 ºC; **IR** (film)ν_{max}/cm^{-1}: 2925, 2854, 2597, 1488, 1259, 1034; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.43 (d, J = 6.5 Hz, 3H), 7.31-7.23 (m, 6H), 7.19-7.08 (m, 9H), 7.06-7.00 (m, 4H), 6.82 (d, J = 7.0 Hz, 4H), 6.72 (s, 3H), 6.64 (d, J = 7.3 Hz, 2H), 3.61 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 148.8, 142.6, 141.0, 140.6, 131.5, 130.7, 130.6, 129.0, 128.3, 128.1, 128.1, 127.8, 123.8, 122.6, 121.7, 115.4, 113.4, 93.4, 92.4, 55.3; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{52}H_{42}NO_2$ 712.3210; Found: 712.3215.

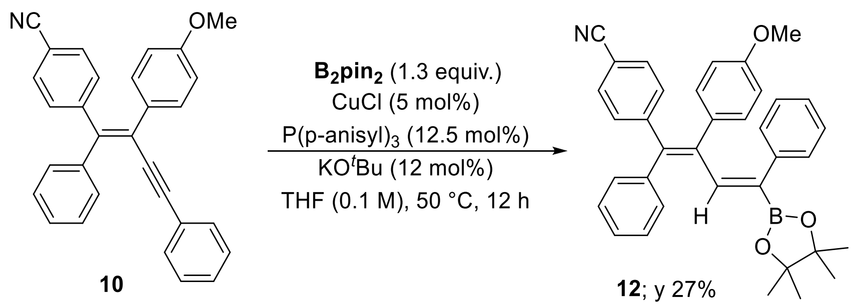




The coupling reaction was performed using our previous literature procedure.[4] Under an argon atmosphere, a 10 mL Schlenk tube was charged with pinacol boronate ester **4l** (32 mg, 0.073 mmol, 1 equiv.), ArI (20.1 mg, 0.088 mmol, 1.2 equiv.), a 1.5 M KOH aqueous solution (147 µL, 0.219 mmol, 3 equiv.), and THF (1 mL). After degassing by three freeze-pump-thaw cycles, $Pd(OAc)_2$ (1.0 mg, 0.0036 mmol, 5 mol%) and SPhos (3.0 mg, 0.0073 mmol, 10 mol%) were added to this reaction mixture, and the resulting mixture was stirred at 70 ºC for 24 h. Then, H_2O (10 mL) was added to the mixture, and the organic phase was extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Filtration through a cotton plug and evaporation of the solvent, followed by purification via column chromatography (10% ethyl acetate in hexane) to deliver the desired product 11 as a yellow solid (29.9 mg, 99%). **R_f** (5% EtOAc/hexanes): 0.40; **mp** 138-139 ºC; **IR** (film)ν_{max}/cm^{-1}:

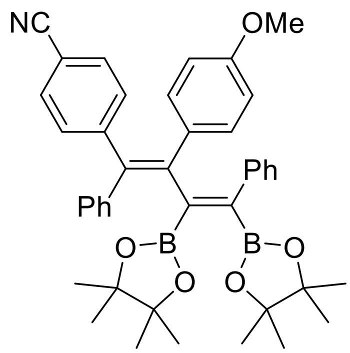
2919, 2850, 2227, 1737, 1603, 1508; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.38-7.33 (m, 2H), 7.33-7.25 (m, 3H), 7.19-7.16 (m, 7H), 7.05 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 146.8, 145.6, 141.9, 131.9, 131.6, 131.5, 131.2, 131.0, 130.5, 128.3, 128.3, 128.2, 128.0, 123.5, 123.3, 118.9, 113.7, 110.5, 94.5, 91.8, 55.3; **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{22}NO$ 412.1696; Found: 412.1699.

Synthesis of Compound 12:

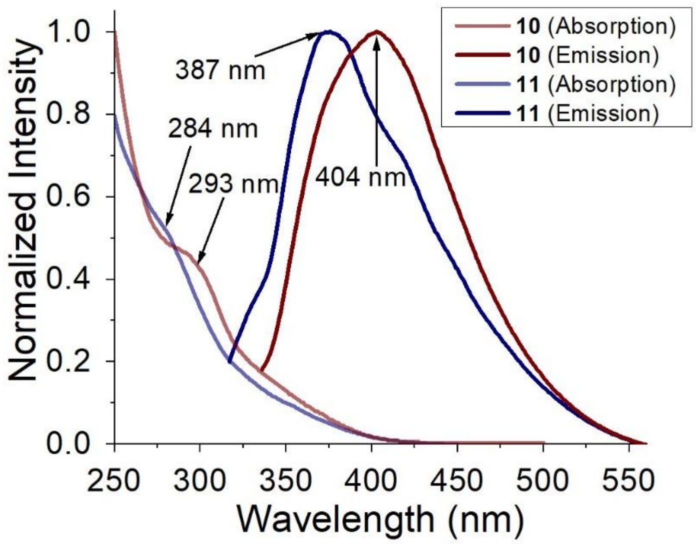


Compound **12** was synthesized using a modified literature procedure.[8] To a flame-dried Schlenk tube, CuCl (0.5 mg, 0.0027 mmol, 5 mol%), P(*p*-anisyl)$_3$ (2.43 mg, 0.0069 mmol, 12.5 mol%), B_2Pin_2 (27.7 mg, 0.011 mmol, 2 equiv.) were added and stirred in dry THF (0.5 mL, 0.10 M) under an inert atmosphere. To this reaction mixture, KO^{t}Bu (6 µL, 0.075 mmol, 12 mol%, 1 M in THF) was added and stirred for 10 minutes at room temperature. Then, enyne **10** (22.5 mg, 0.055 mmol, 1 equiv.) and MeOH (10 µL, 0.22 mmol, 4 equiv.) were added sequentially and heated for 12 h at 50 °C. After completion of the reaction, the mixture was cooled to room temperature, decanted into the separating funnel, and diluted with ethyl acetate (30 mL). The organic layer was washed with distilled water (2×20 mL) and brine (20 mL). Then the organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated in vacuo to provide a crude mixture. Further purification by flash column chromatography using 10% ethyl acetate in hexanes delivered the desired product **12** (8 mg, 27%; *rr* 90:10) as a yellow liquid. **R_f** (10% EtOAc/hexanes): 0.30; **IR** (film)ν_{max}/cm^{-1}: 2984, 2944, 1737, 1444, 1373, 1044; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.17 (s, 2H), 7.05 – 6.99 (m, 3H), 6.99 – 6.93 (m, 4H), 6.93 – 6.87 (m, 3H), 6.79 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 8.8 Hz, 2H), 3.66 (s, 3H), 1.23 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 148.4, 145.6, 142.1, 141.2, 139.7, 139.5, 132.4, 132.3, 131.9, 131.4, 131.14, 128.8, 127.8, 127.7, 127.3, 126.0, 119.2, 113.1, 109.8, 83.8, 55.3, 24.7 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.7; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{36}H_{38}BN_2O_3$ 557.2970; Found: 557.2986.

4-((*1Z,3Z*)-2-(4-Methoxyphenyl)-1,4-diphenyl-3,4-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)benzonitrile (**13**): Starting enyne **10** (27 mg, 0.065 mmol, 1 equiv.) was reacted according to the above general diborylation procedure **9** to afford the title product **13** (32.9 mg; 75%) as a yellow viscus liquid after chromatographic purification with 2-5% ethyl acetate in hexanes; **R_f** (10% EtOAc/hexanes): 0.20; **IR** (film)ν_{max}/cm^{-1}: 2961, 2921, 1735, 1604, 1463, 1378, 1248, 1144; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.14 – 6.88 (m, 10H), 6.84 – 6.70 (m, 4H), 6.61 – 6.52 (m, 2H), 3.71 (s, 3H), 1.21 (s, 12H), 1.02 (s, 6H), 0.99 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 149.7, 142.9, 142.3, 141.8, 137.1, 133.8, 132.6, 132.3, 131.3, 131.2, 127.9, 127.5, 127.3, 126.6, 126.1, 119.4, 113.1, 109.3, 83.8, 83.7, 55.3, 25.1, 24.8, 24.6, 24.5 [note: the carbon attached to boron were not observed due to quadrupole broadening caused by the ^{11}B nucleus, methyl groups in the Bpin unit showed different chemical shift due to its skew geometry]; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.7; **HRMS** (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{42}H_{49}B_2N_2O_5$ 683.3822; Found: 683.3835.



11. UV Vis and Fluorescence Spectrum:



UV-vis and Fluorescence spectra were recorded in $CHCl_3$ at a concentration of 10^{-5} M.

12. X-ray Crystallography Data:

*Single Crystal XRD Data for the compound **10**:* The crystals were grown by layering hexane onto a solution of compound **10** in a minimum amount of diethyl ether in a glass vial. Slow evaporation of the solvent mixture provided colorless block-shaped crystals. A crystal was selected from the mother liquor, immersed in paratone oil, and then mounted on a loop. Single crystal X-ray data were collected on a Rigaku XtaLAB Synergy, Dualflex four-circle diffractometer with HyPix3000 detector and Cu-Kα radiation at 100 K.

CCDC No. - 2444264 (Ellipsoid Contour Probability at 50%)

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: gv_sg_605_0m_a

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Bond precision:   C-C = 0.0034 A          Wavelength=0.71073

Cell:              a=9.762(2)     b=19.290(4)          c=13.150(3)
                   alpha=90       beta=110.326(6)      gamma=90
Temperature:       301 K

                 Calculated                  Reported
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Space group      P 21/c                      P 1 21/c 1
Hall group       -P 2ybc                     -P 2ybc
Moiety formula   C30 H21 N O                 C30 H21 N O
Sum formula      C30 H21 N O                 C30 H21 N O
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Dx,g cm-3        1.177                       1.177
Z                4                           4
Mu (mm-1)        0.071                       0.071
F000             864.0                       864.0
F000'            864.34
h,k,lmax         11,22,15                    11,22,15
Nref             4092                        4088
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Tmin'            0.972

Correction method= # Reported T Limits: Tmin=0.627 Tmax=0.745
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                                                     0.1507( 4088)
S = 1.080                    Npar= 291
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The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
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Alert level C

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PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C18 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C16 Check
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Alert level G

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PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C7        - C30      .       1.43 Ang.
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C15       - C16      .       1.43 Ang.
PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res ..       50.0 Degree
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   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
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Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

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# start Validation Reply Form
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;
PROBLEM: High   'MainMol' Ueq as Compared to Neighbors of        C18 Check
RESPONSE: ...
;
_vrf_PLAT242_gv_sg_605_0m_a
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of        C16 Check
RESPONSE: ...
;
# end Validation Reply Form
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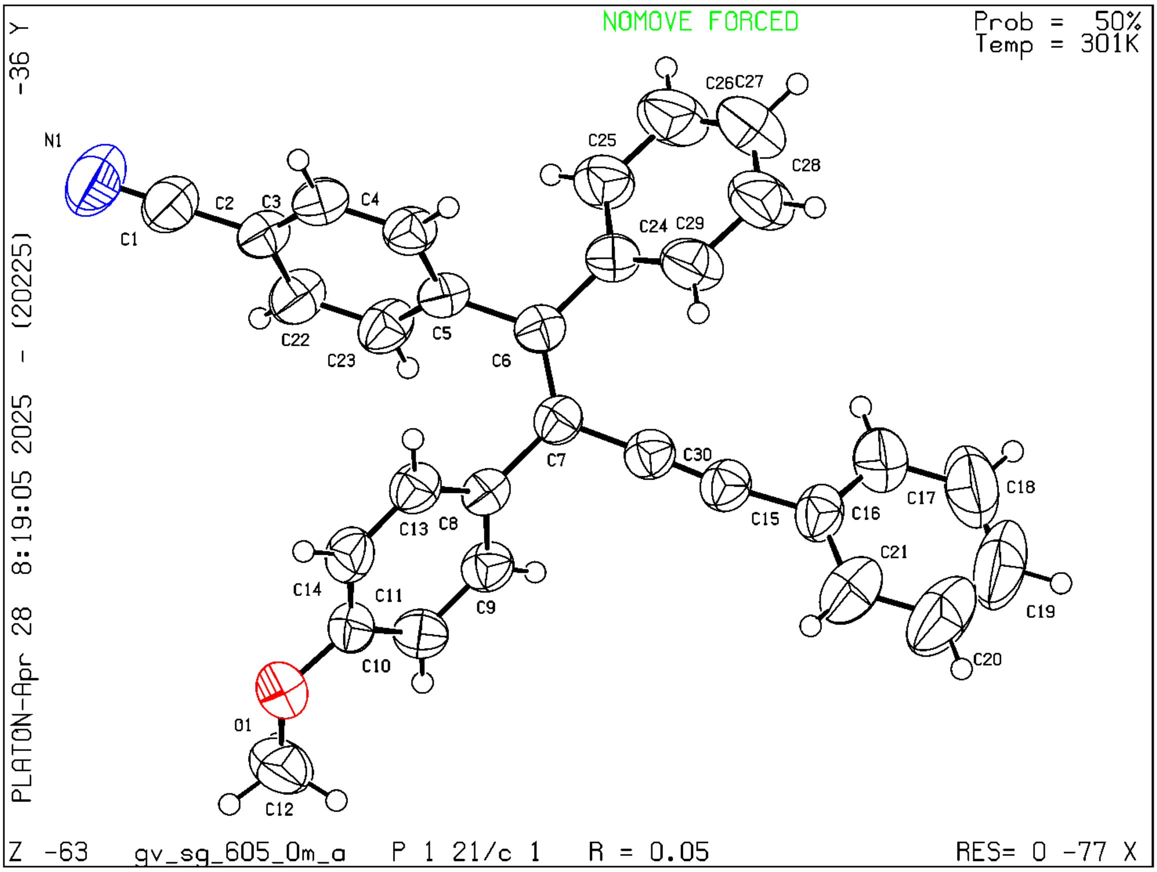
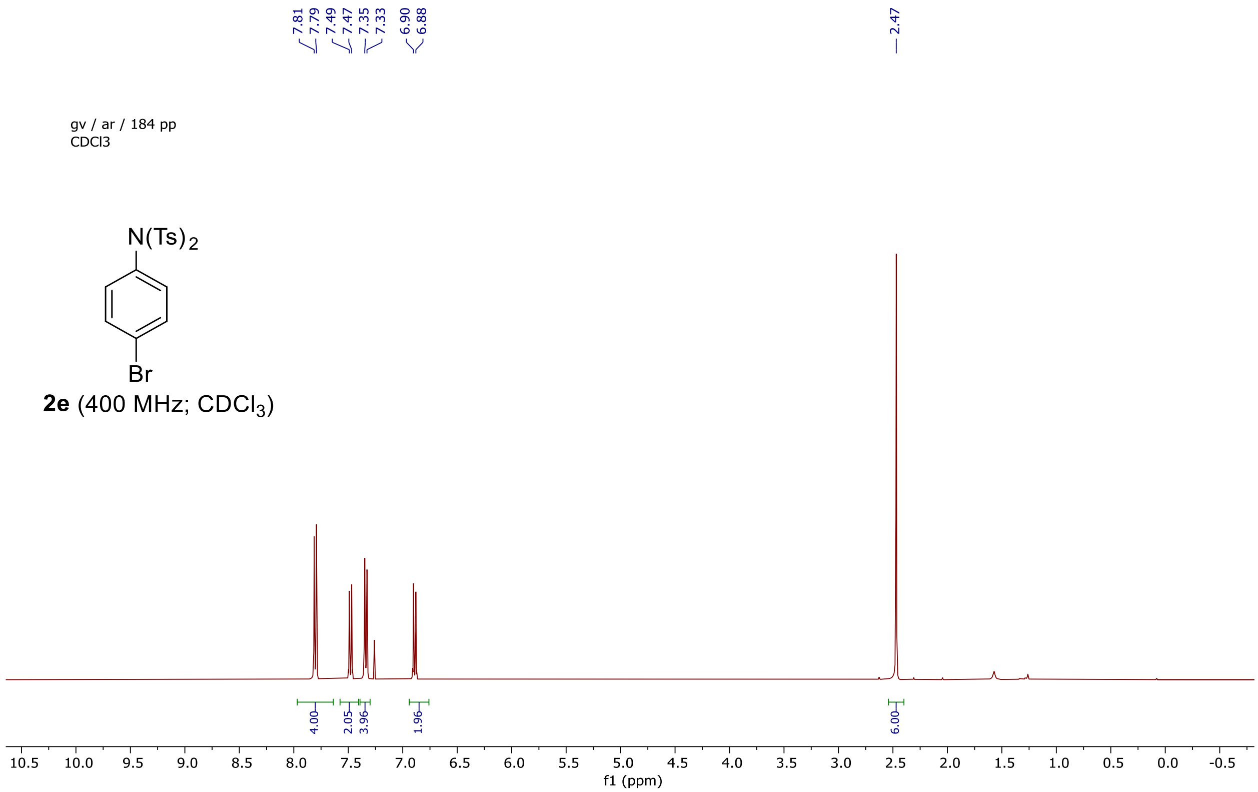
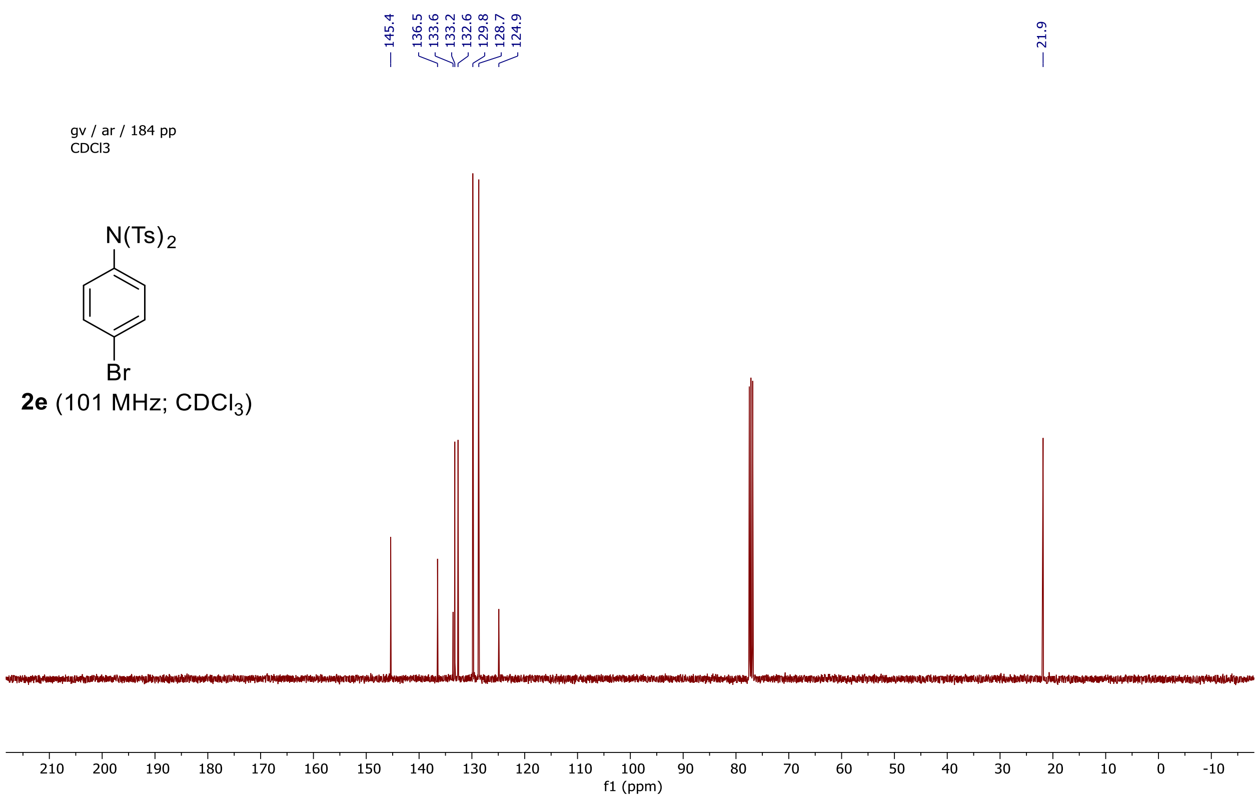
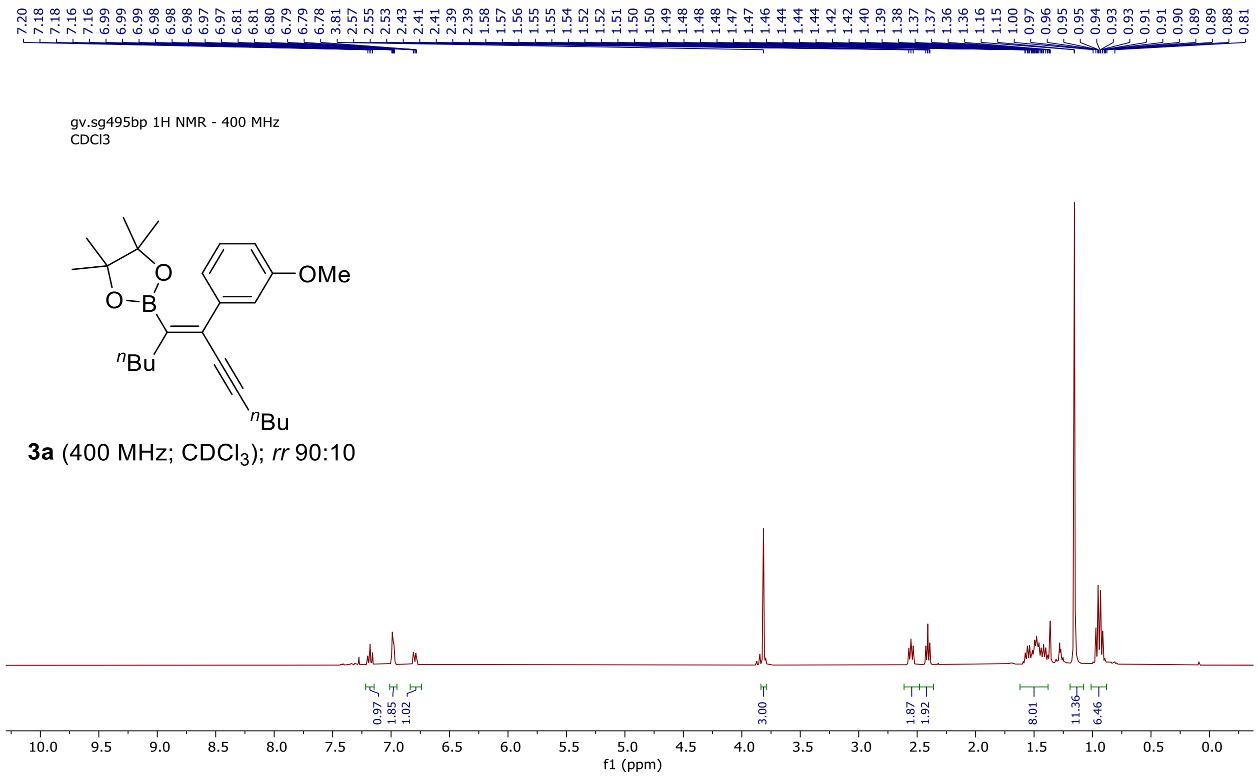
Datablock gv_sg_605_0m_a - ellipsoid plot



13. Copies of ^{1}H, ^{13}C, ^{11}B, ^{19}F, 2D NMR



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OMe
O
O
B
^{n}Bu
^{n}Bu
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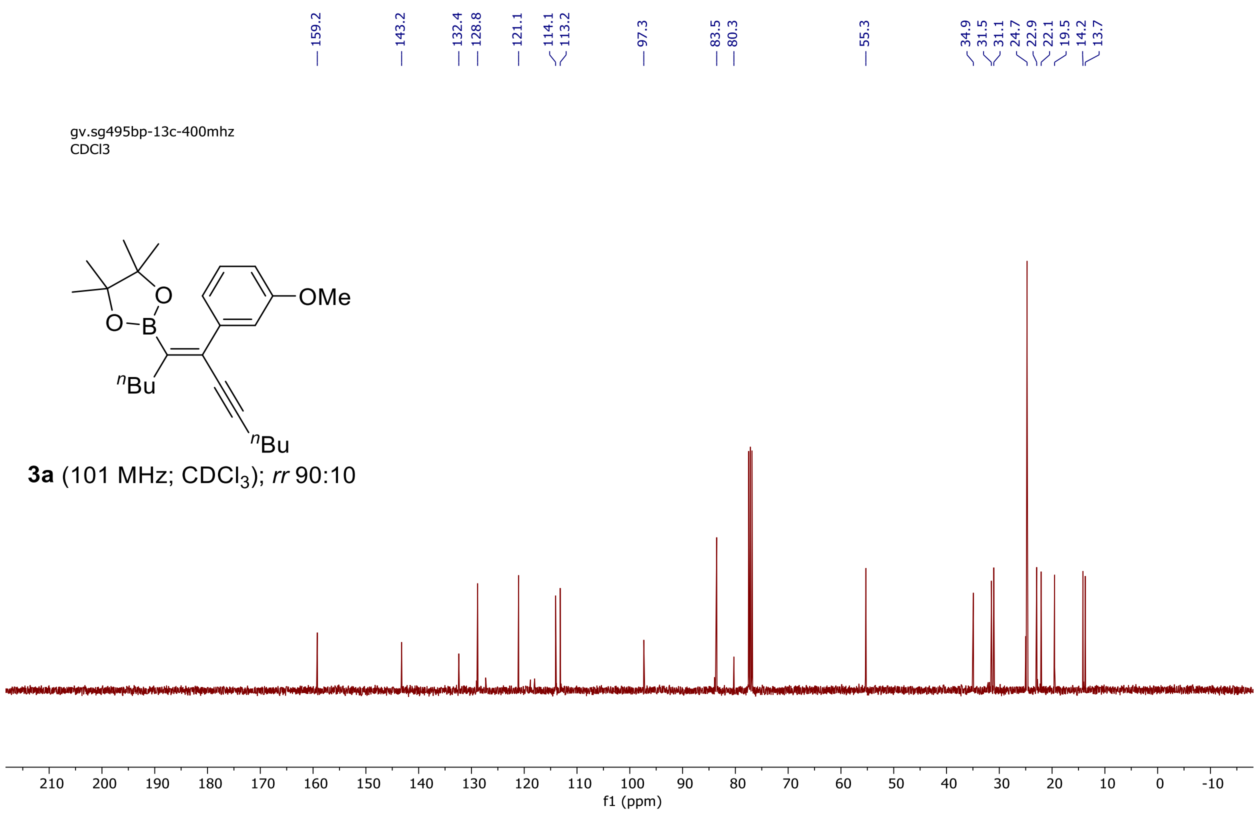
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CDCl3
OMe
O
O
B
^{n}Bu
^{n}Bu
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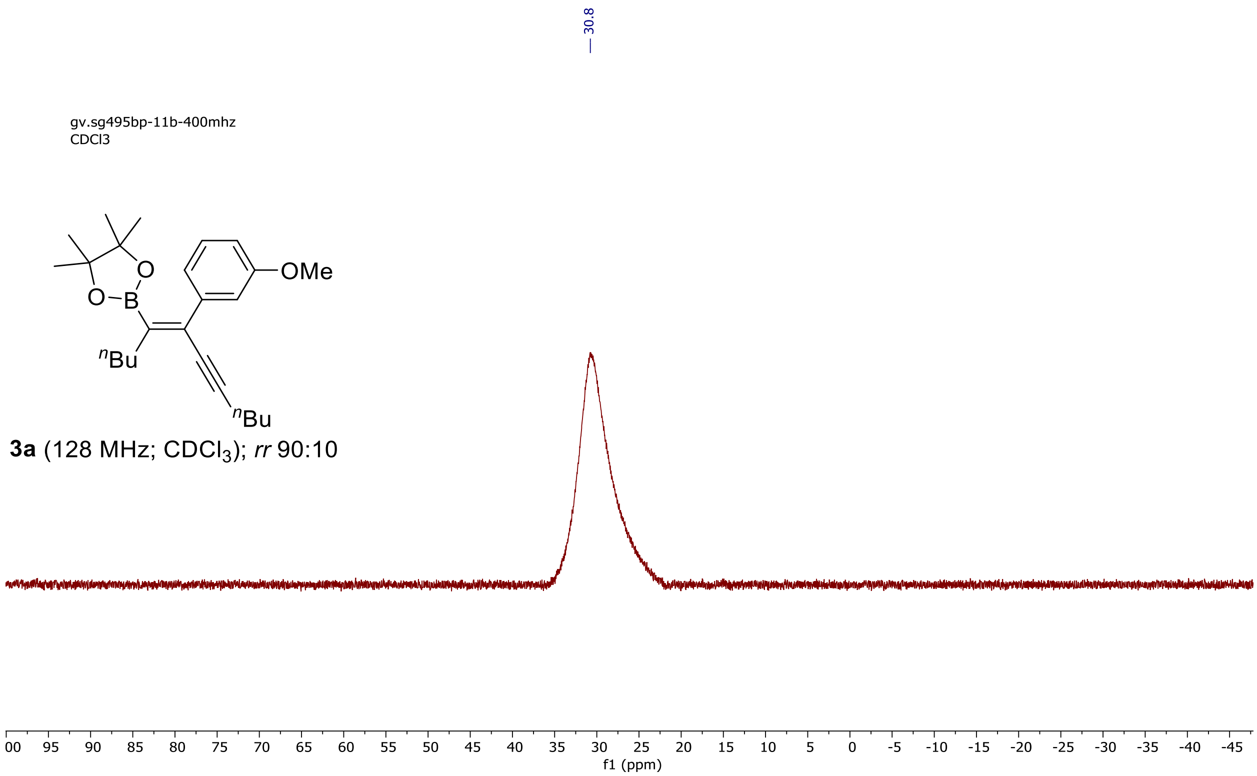
f1 (ppm)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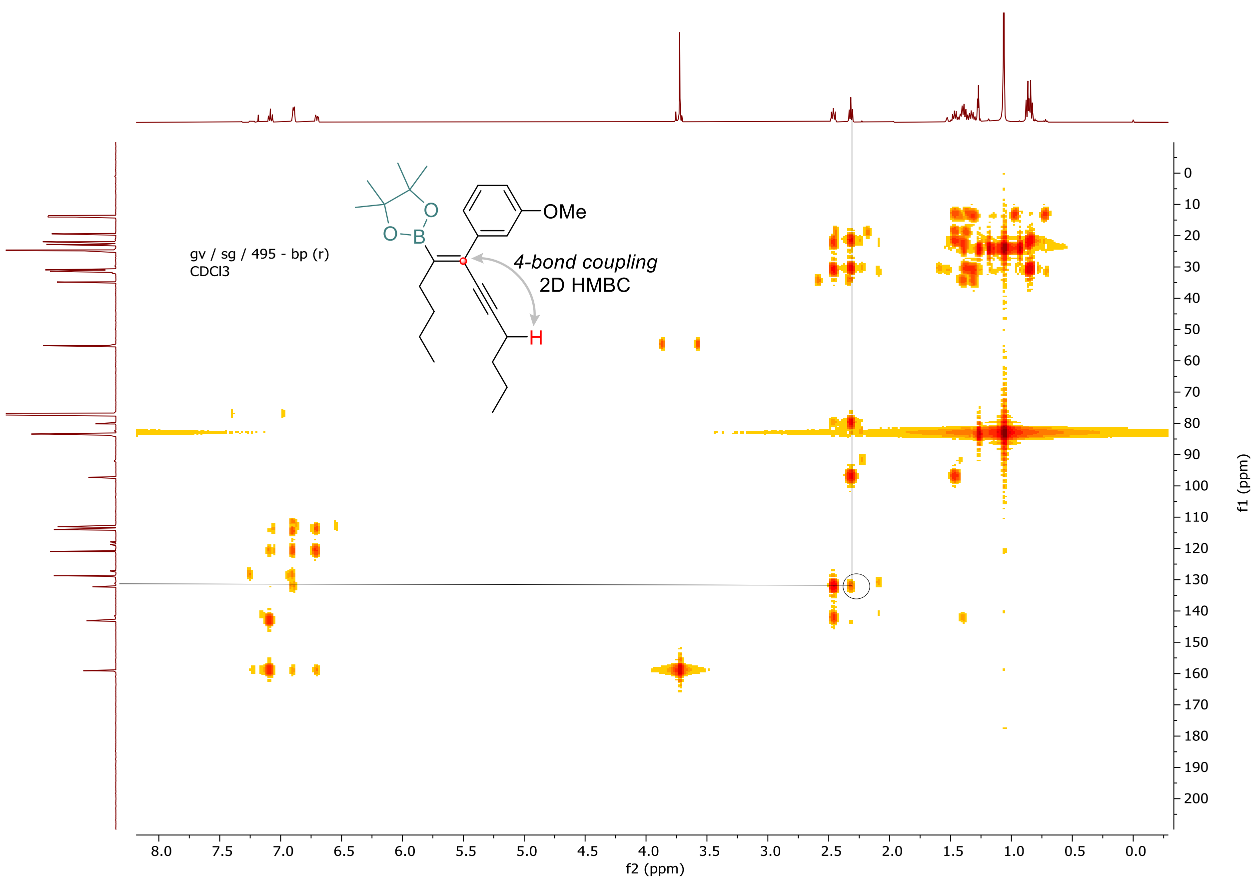
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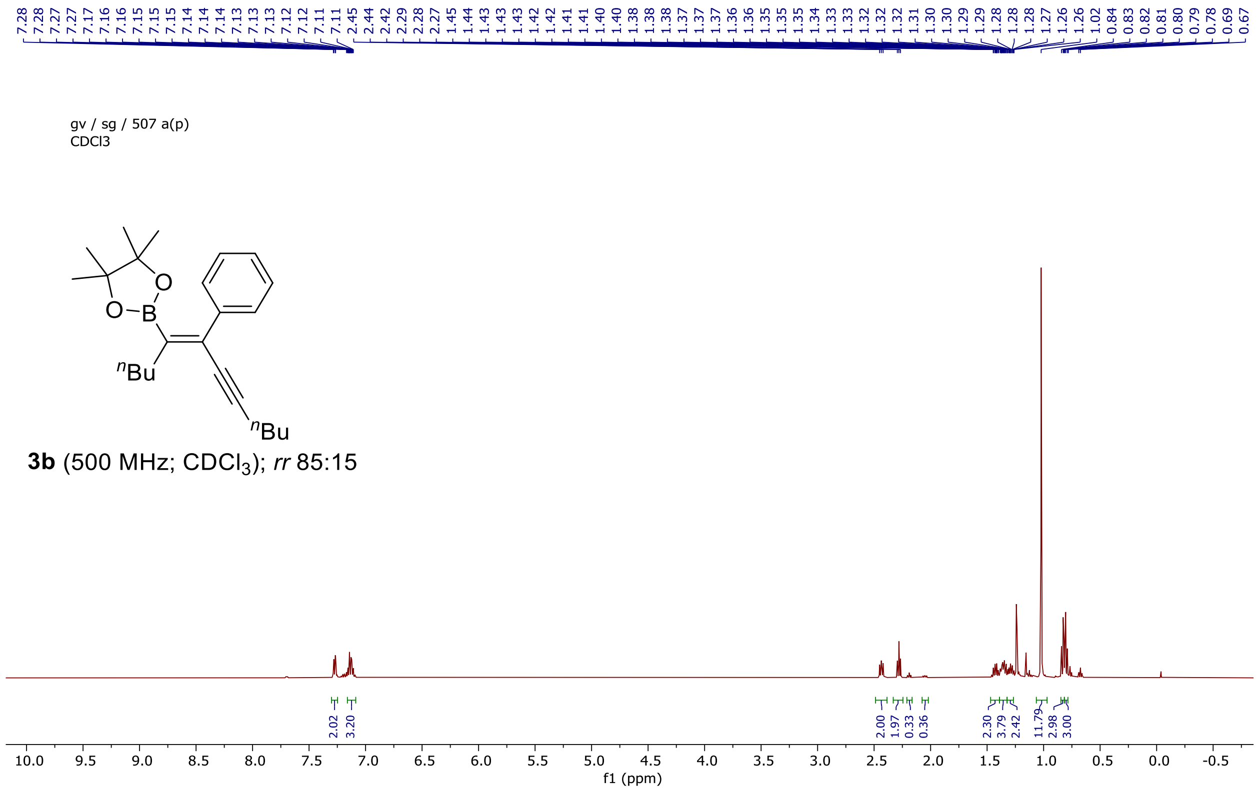
2D HMBC
H
f2 (ppm)
f1 (ppm)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gv / sg / 507 a(p)
CDCl3
O
O
B
^{n}Bu
^{n}Bu
3b (500 MHz; $CDCl_3$); *rr* 85:15
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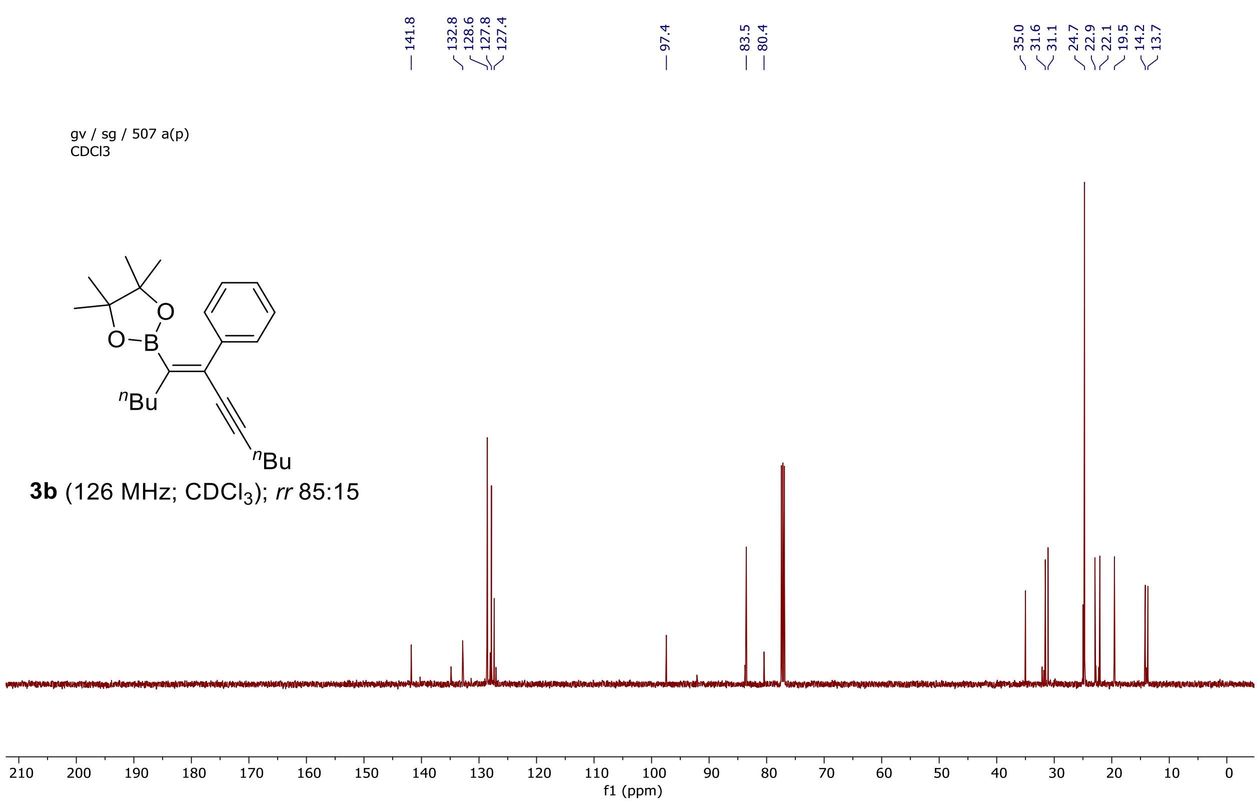
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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gv / sg / 507 a(p)
CDCl3
O
O
B
^{n}Bu
^{n}Bu
3b (126 MHz; $CDCl_3$); *rr* 85:15
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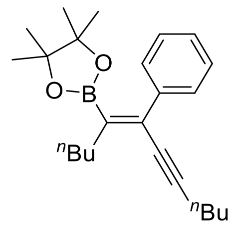
f1 (ppm)

gv.sg507ap-11b-400mhz
CDCl3



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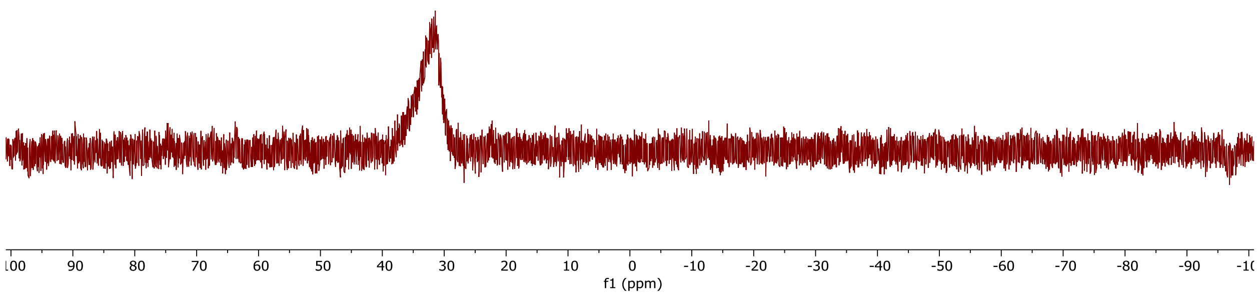
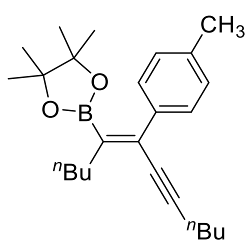
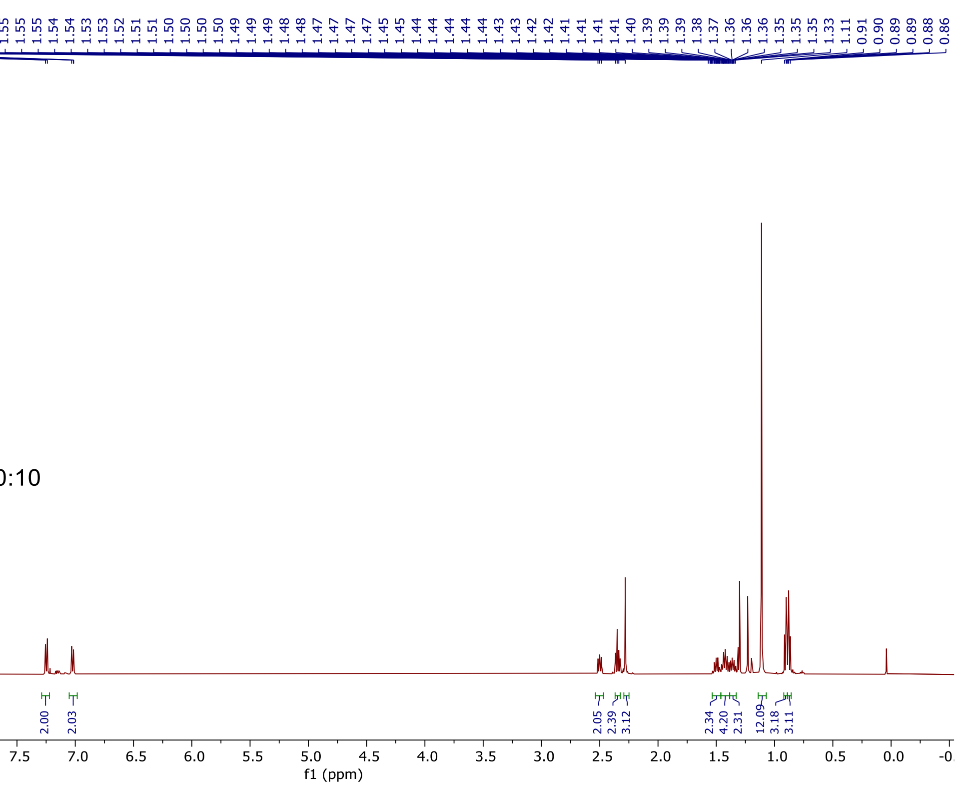
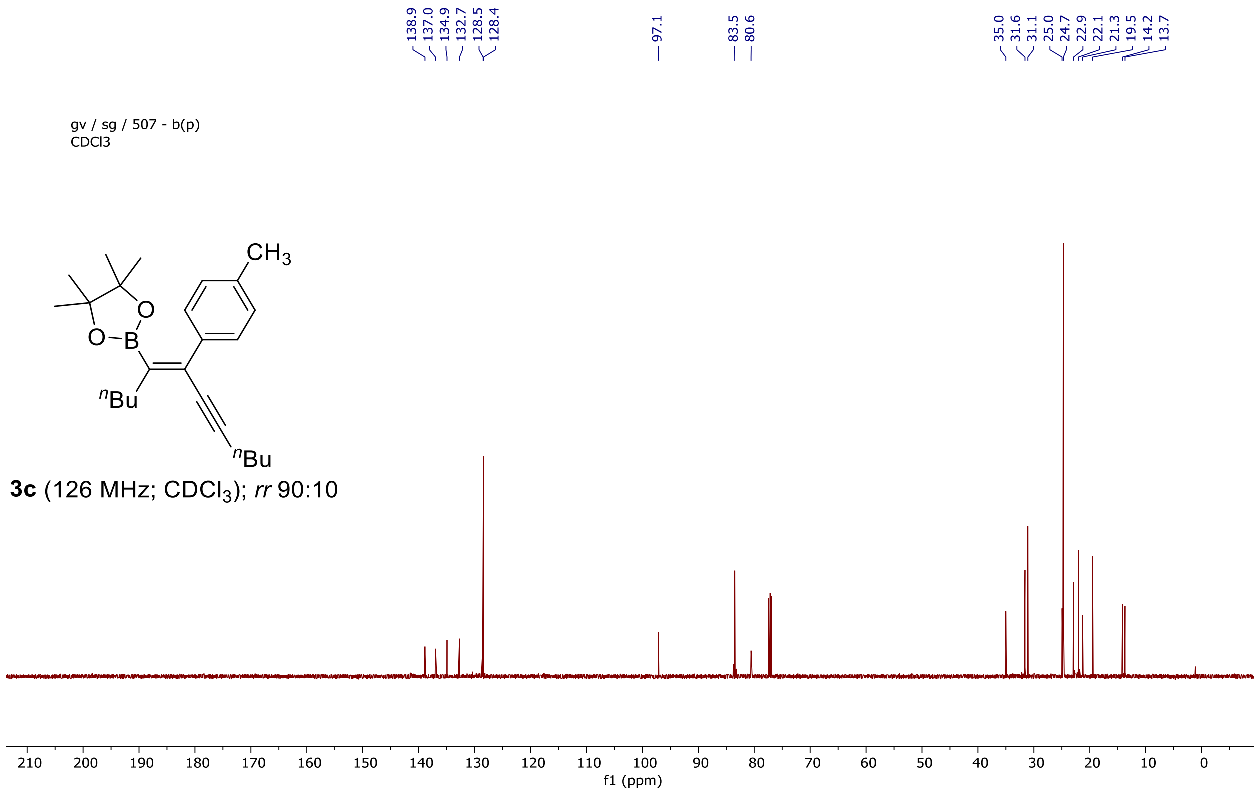


gv / sg / 507 - b(p)
CDCl3



3c (500 MHz; $CDCl_3$); *rr* 90:10





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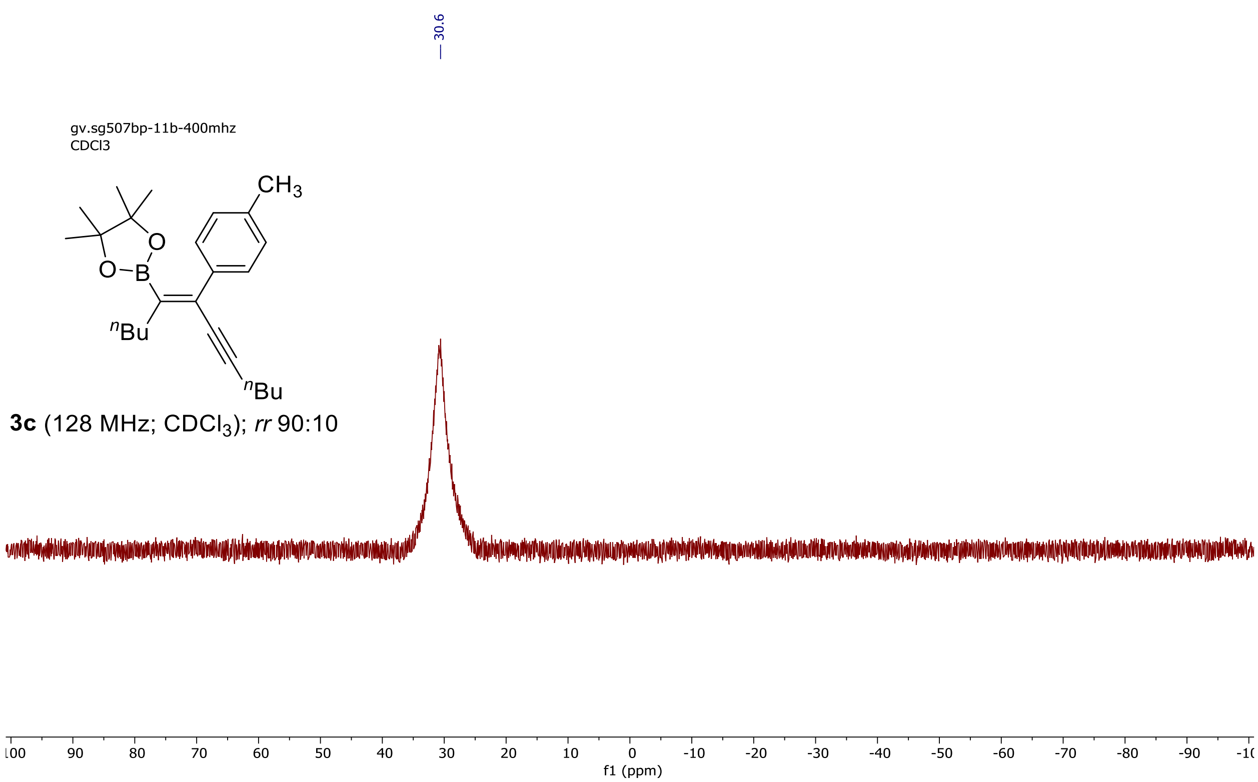

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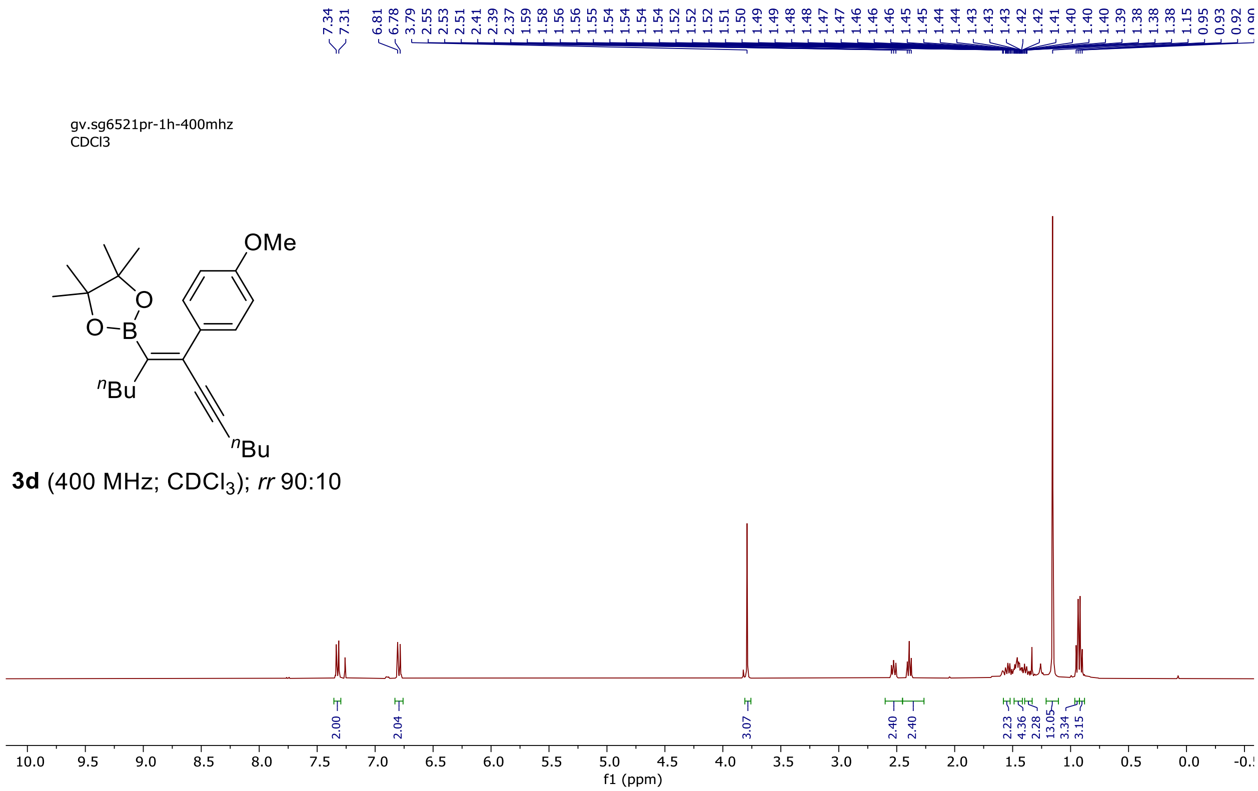
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OMe
O
O
B
nBu
nBu
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2.00
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2.40
2.40
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4.36
2.28
13.05
3.34
3.15
10.0
9.5
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8.5
8.0
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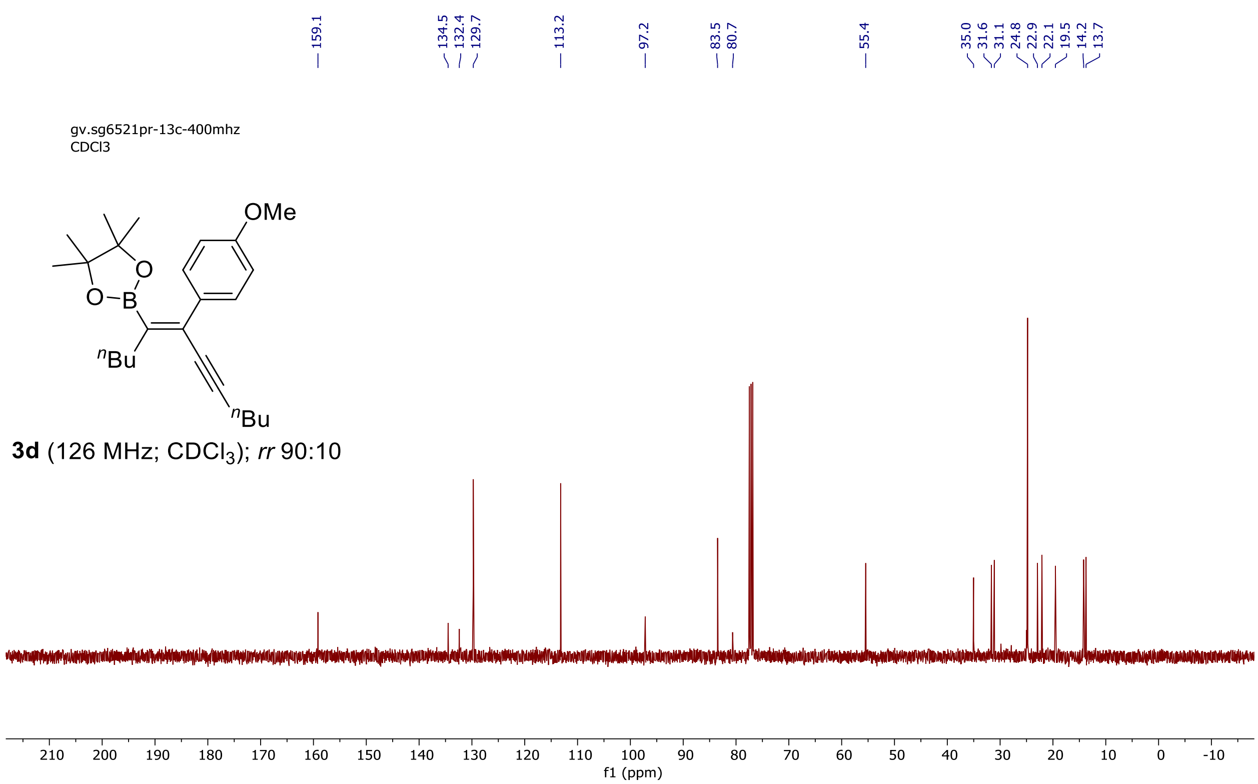
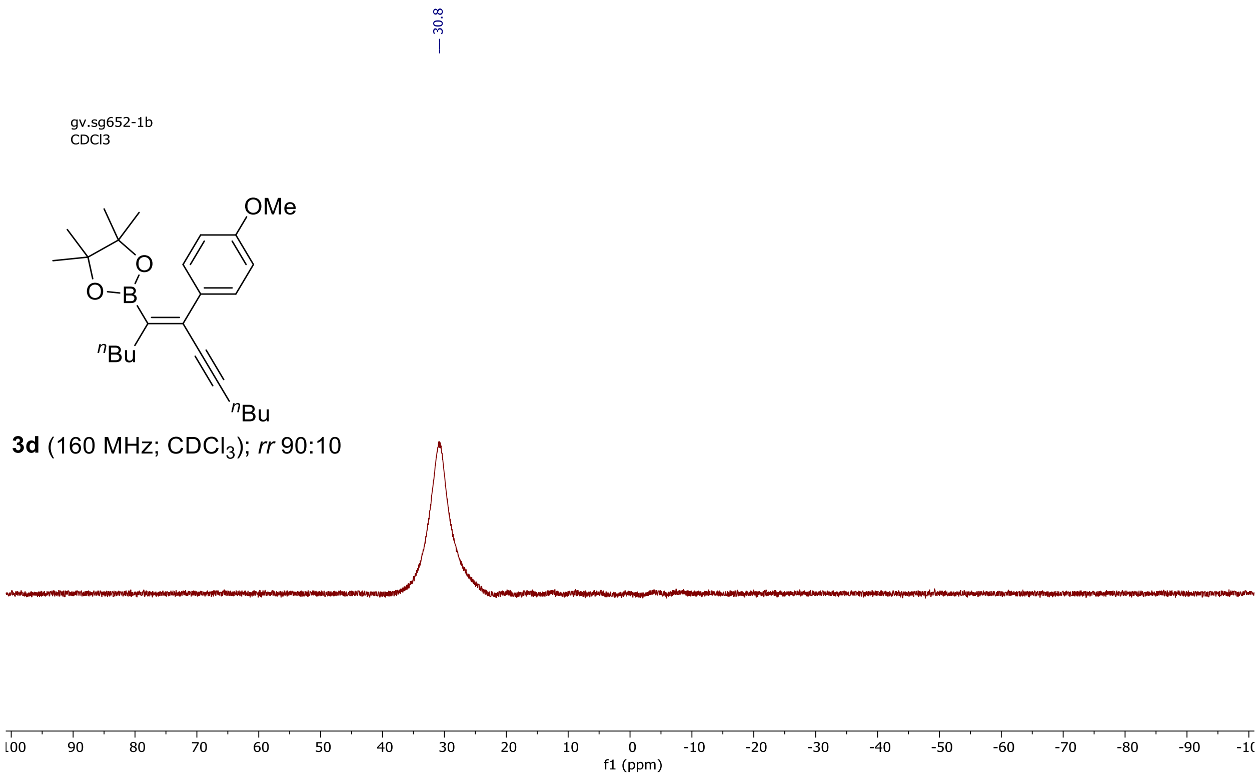
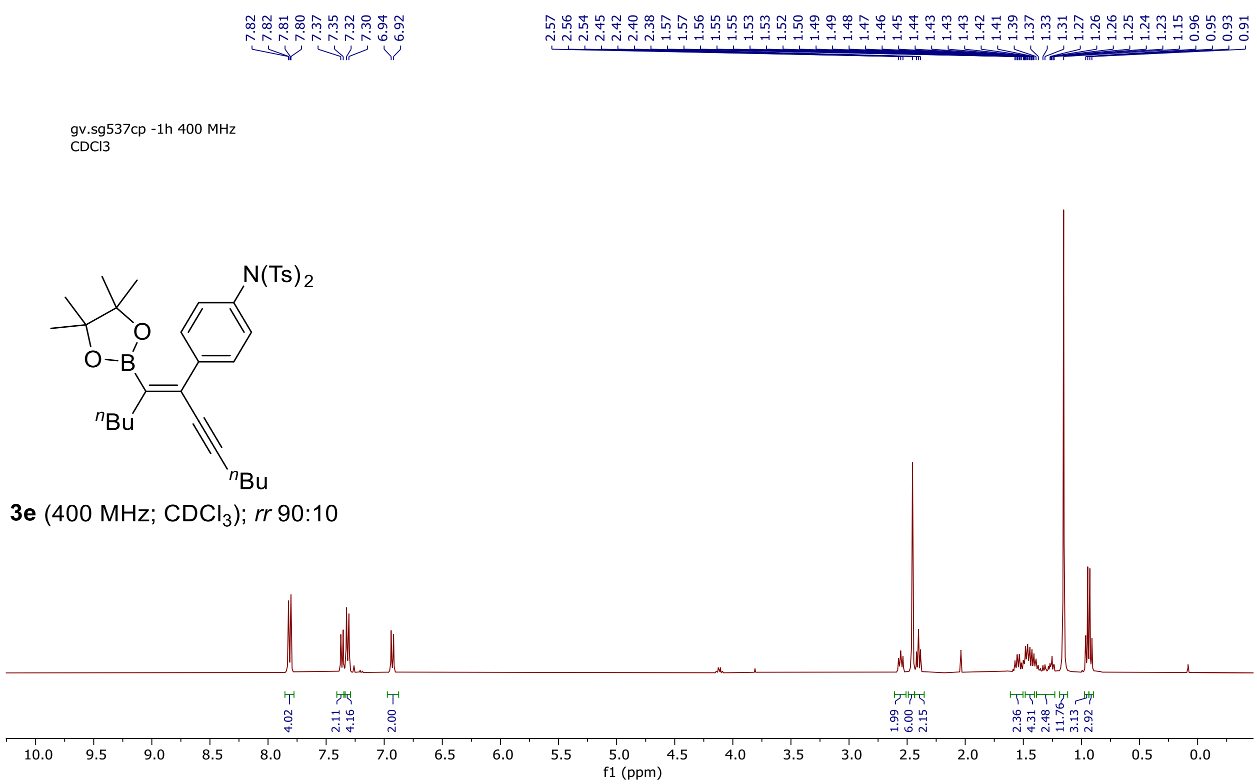
f1 (ppm)

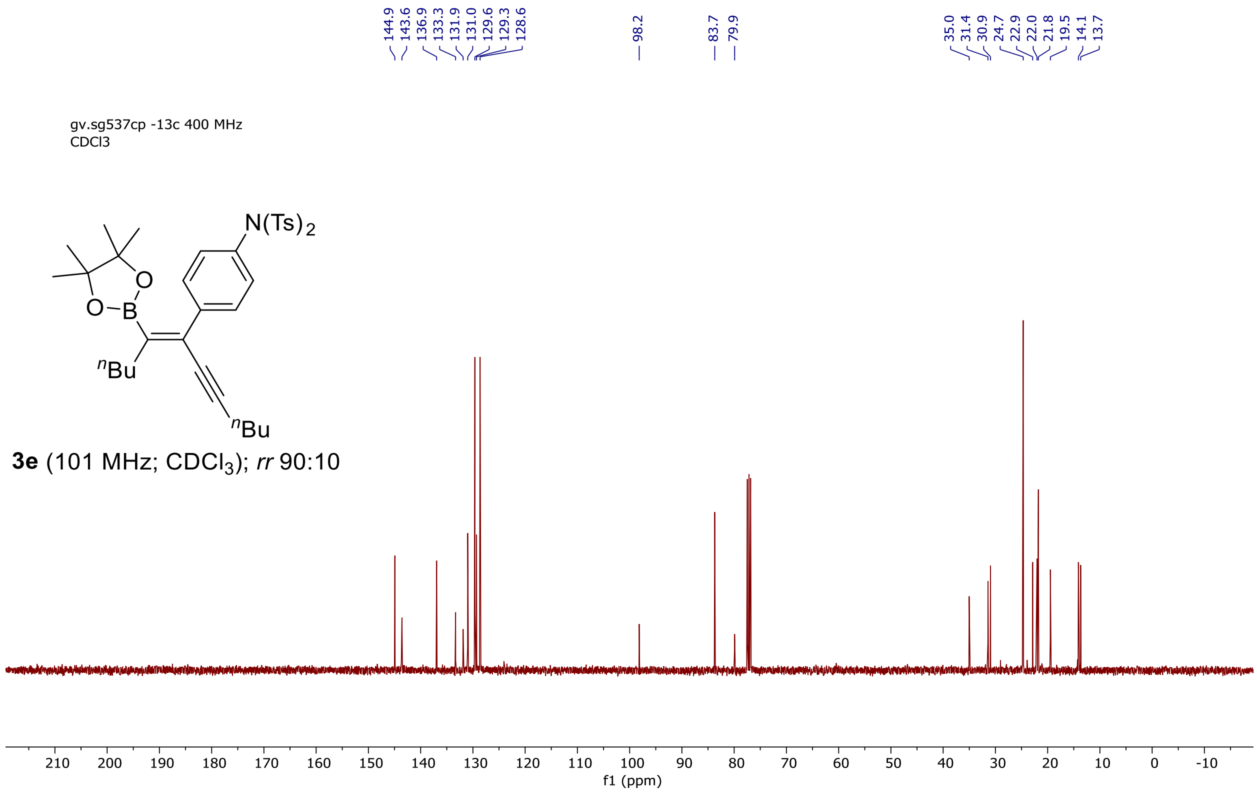

159.1
134.5
132.4
129.7
113.2
97.2
83.5
80.7
55.4
35.0
31.6
31.1
24.8
22.9
22.1
19.5
14.2
13.7
gv.sg6521pr-13c-400mhz
CDCl3
OMe
O
O
B
nBu
nBu
3d (126 MHz; CDCl3); rr 90:10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



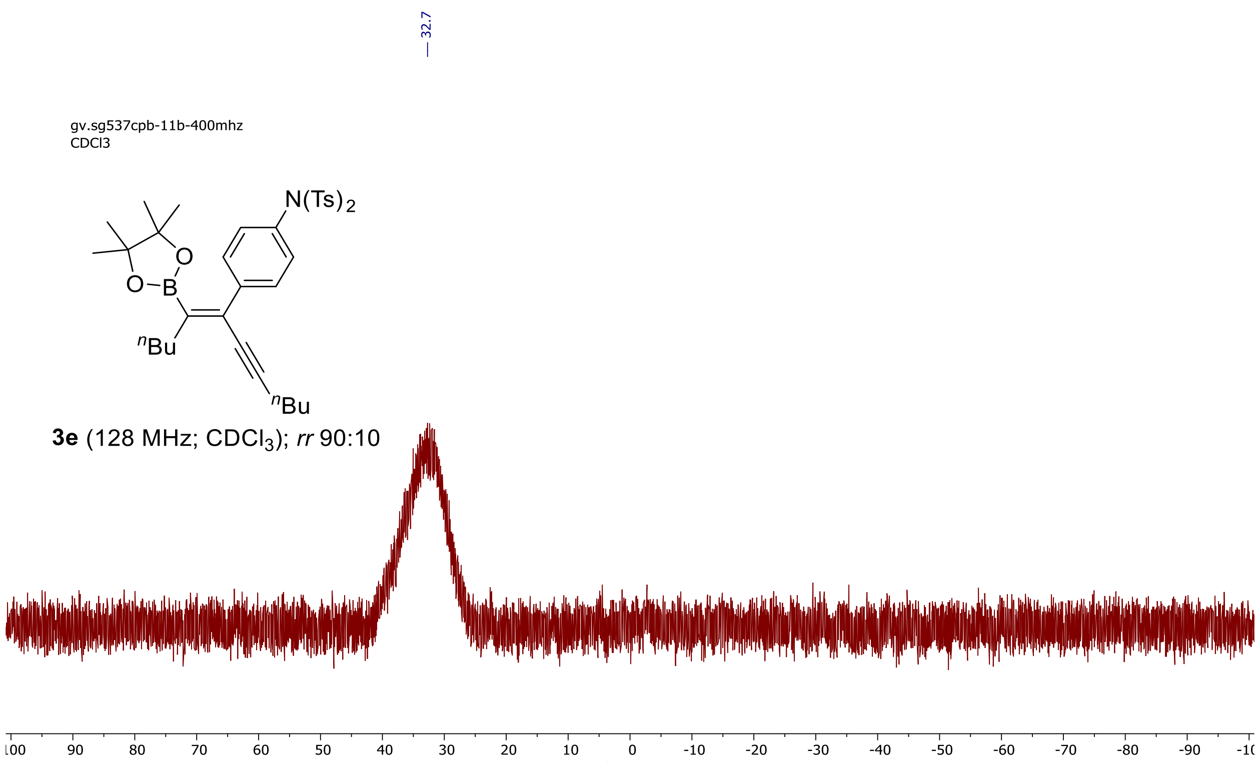
3d (160 MHz; $CDCl_3$); *rr* 90:10



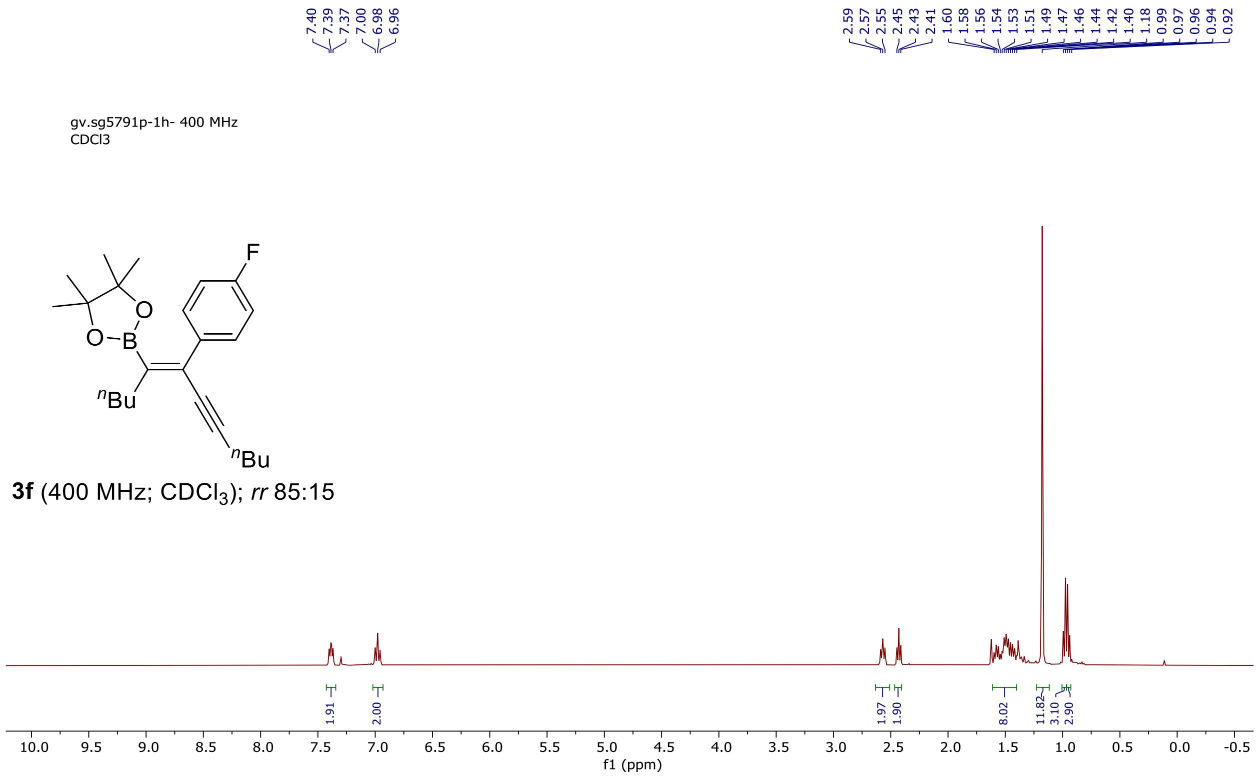
3e (400 MHz; $CDCl_3$); *rr* 90:10



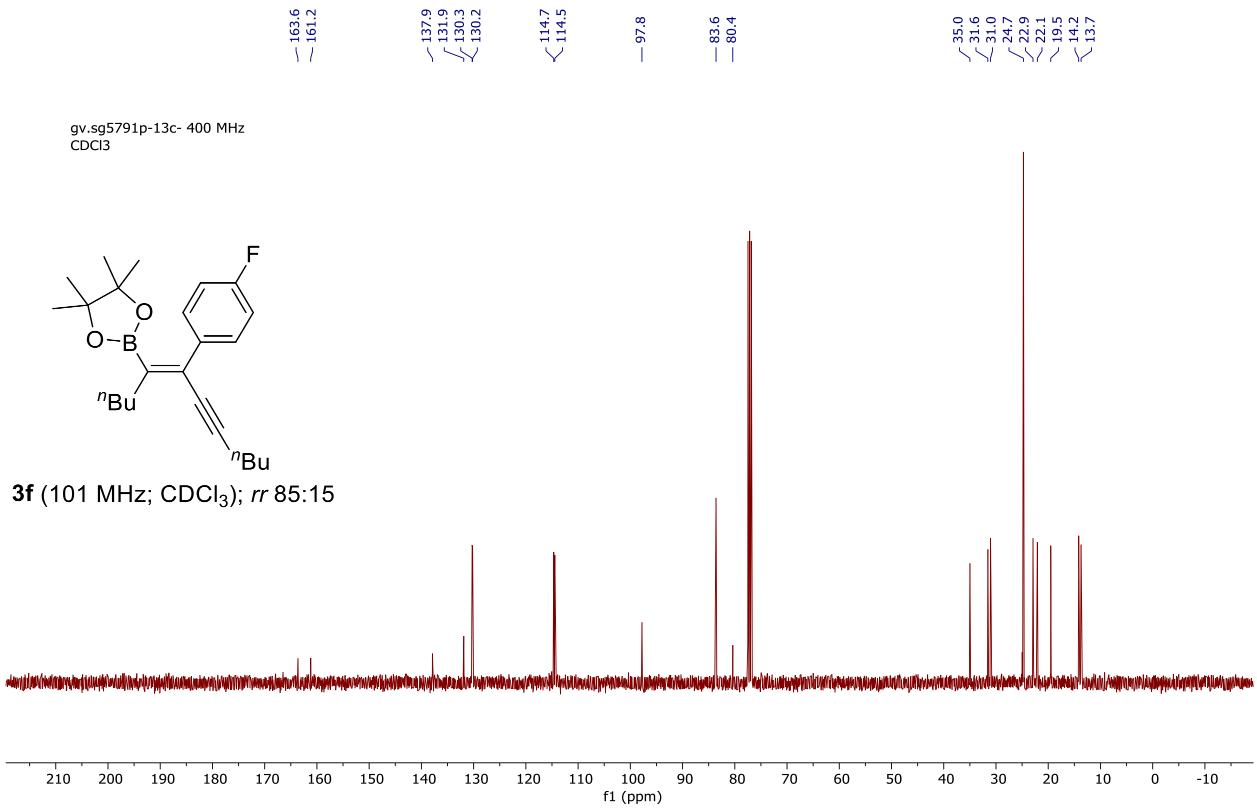
3e (101 MHz; $CDCl_3$); *rr* 90:10



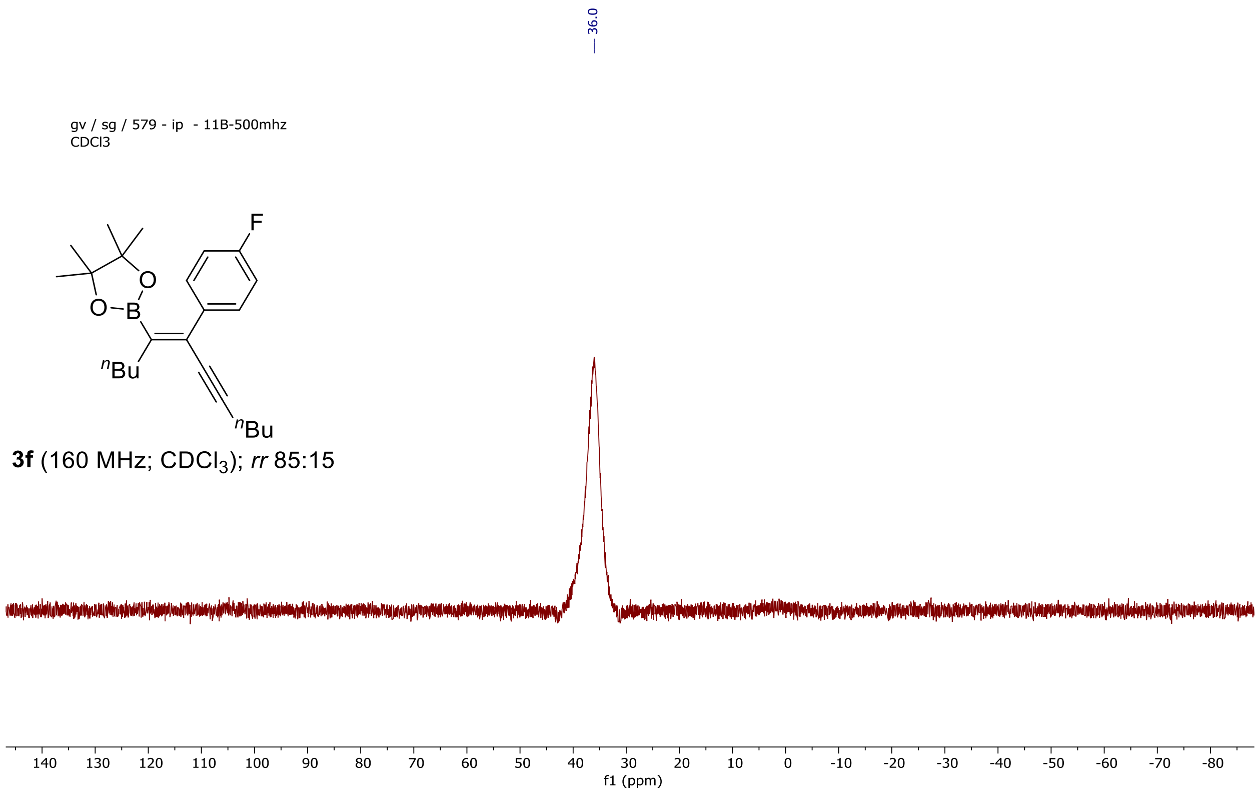
3e (128 MHz; $CDCl_3$); *rr* 90:10

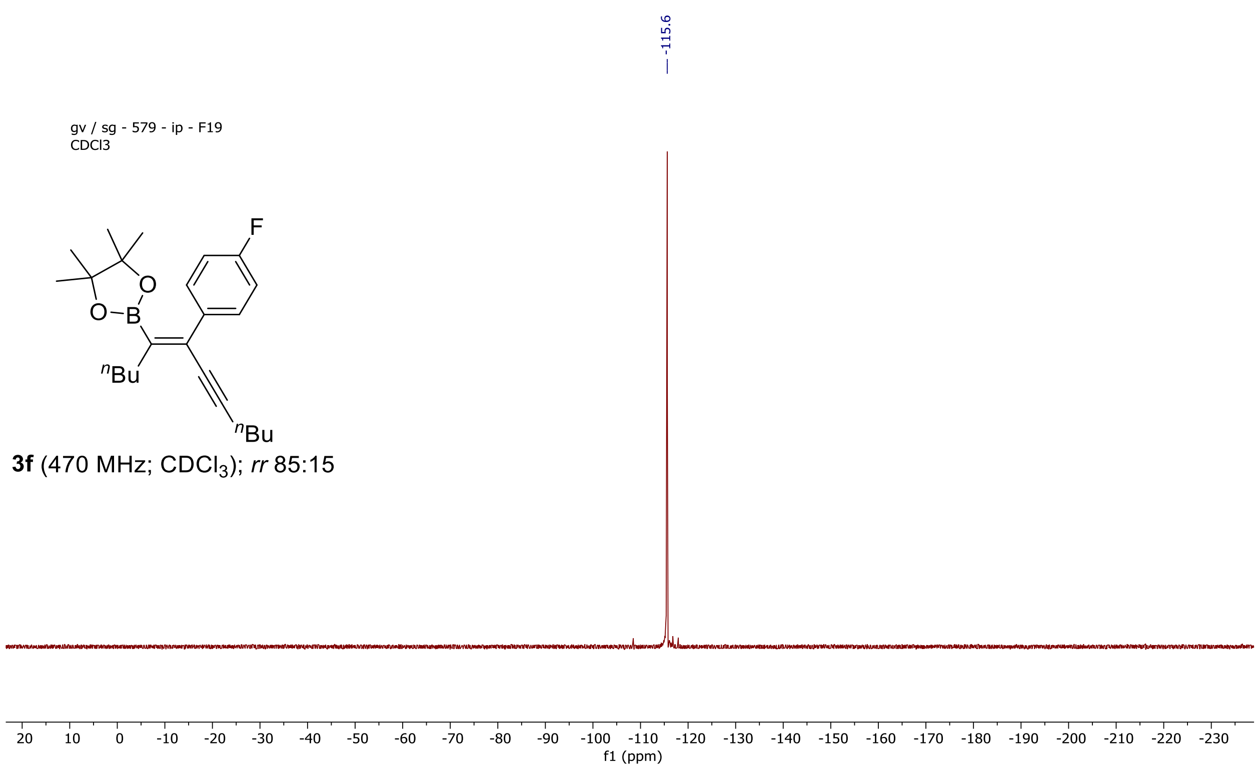


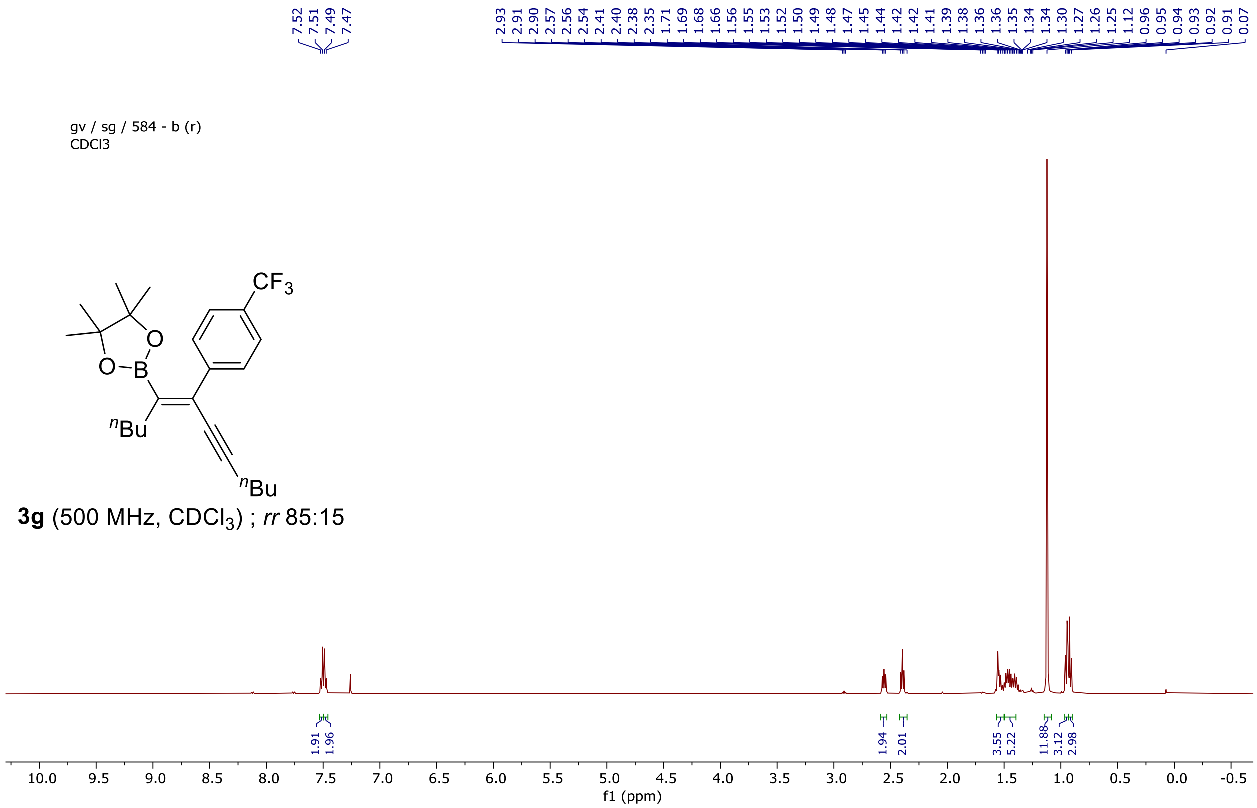
3f (400 MHz; $CDCl_3$); *rr* 85:15



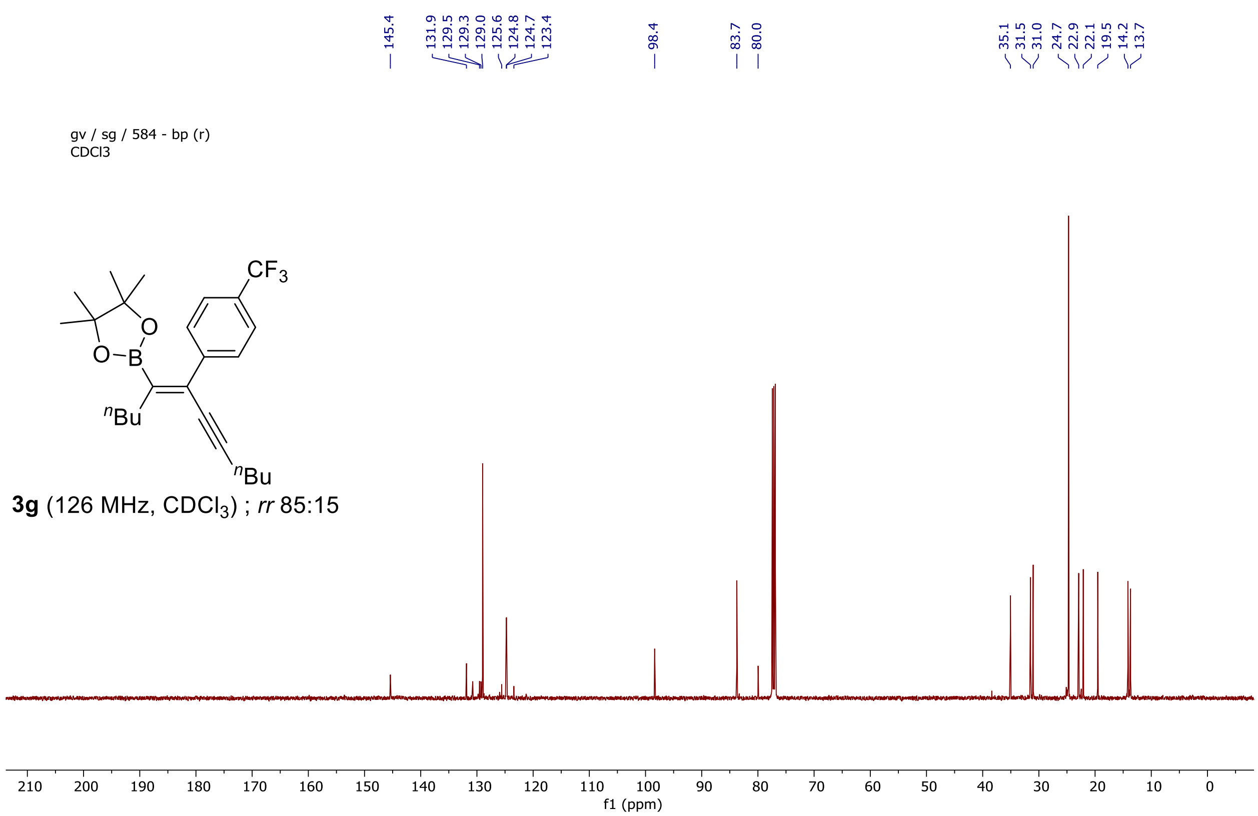
3f (101 MHz; $CDCl_3$); *rr* 85:15


36.0
gv / sg / 579 - ip - 11B-500mhz
CDCl3
F
O
O
B
nBu
nBu
3f (160 MHz; CDCl3); rr 85:15
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

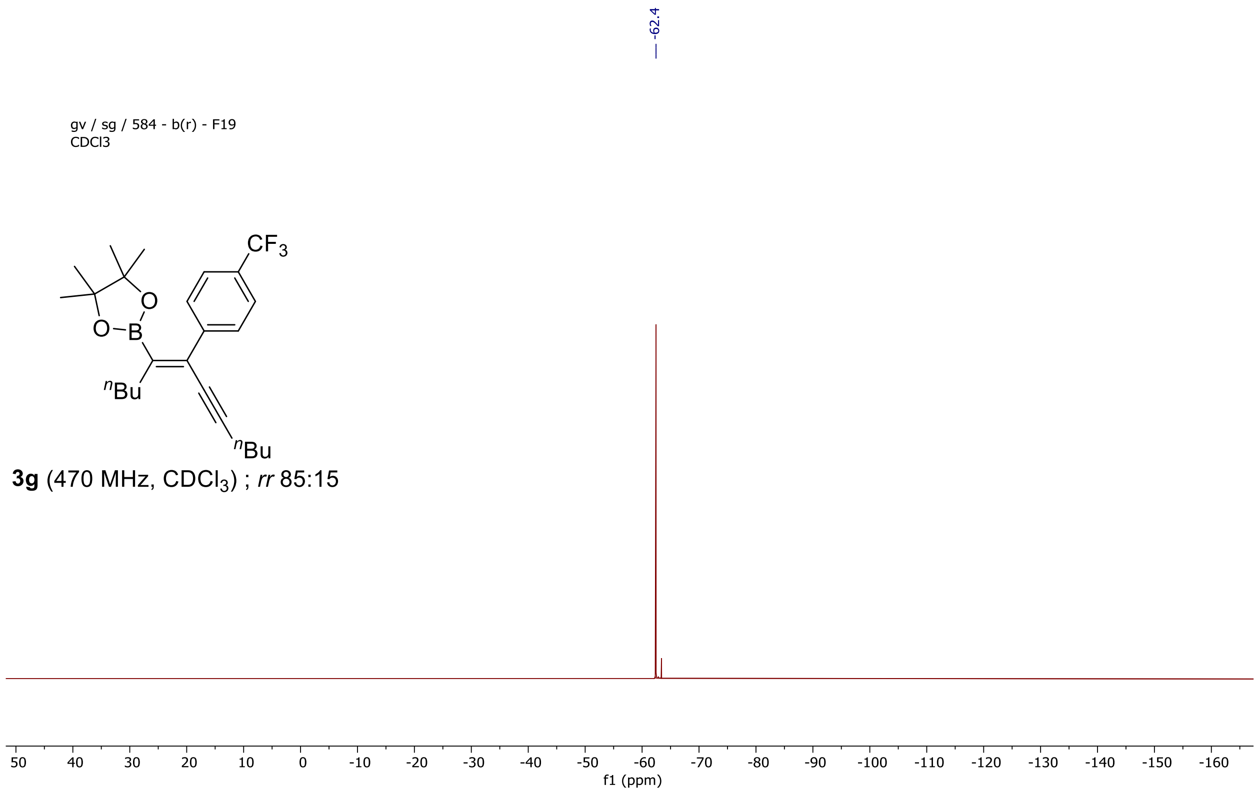

-115.6
gv / sg - 579 - ip - F19
CDCl3
F
O
O
B
nBu
nBu
3f (470 MHz; CDCl3); rr 85:15
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)



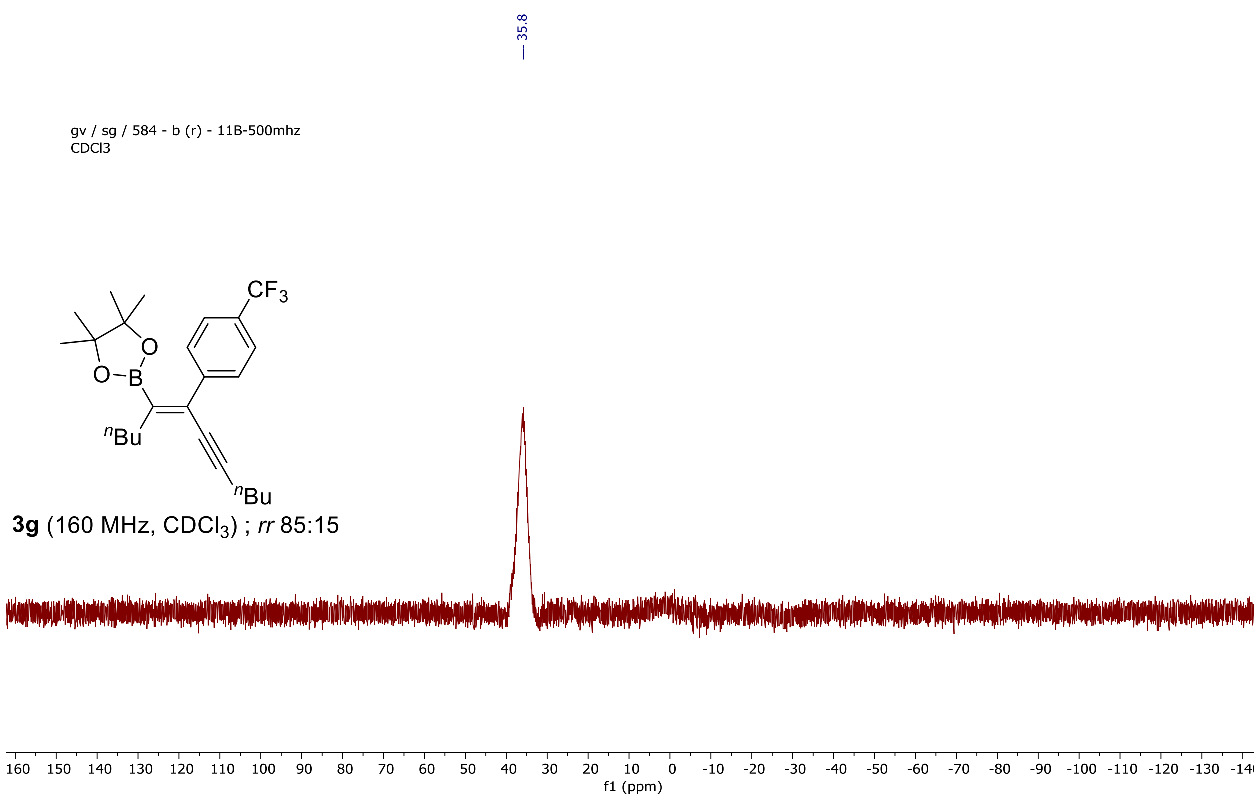
3g (500 MHz, $CDCl_3$) ; *rr* 85:15



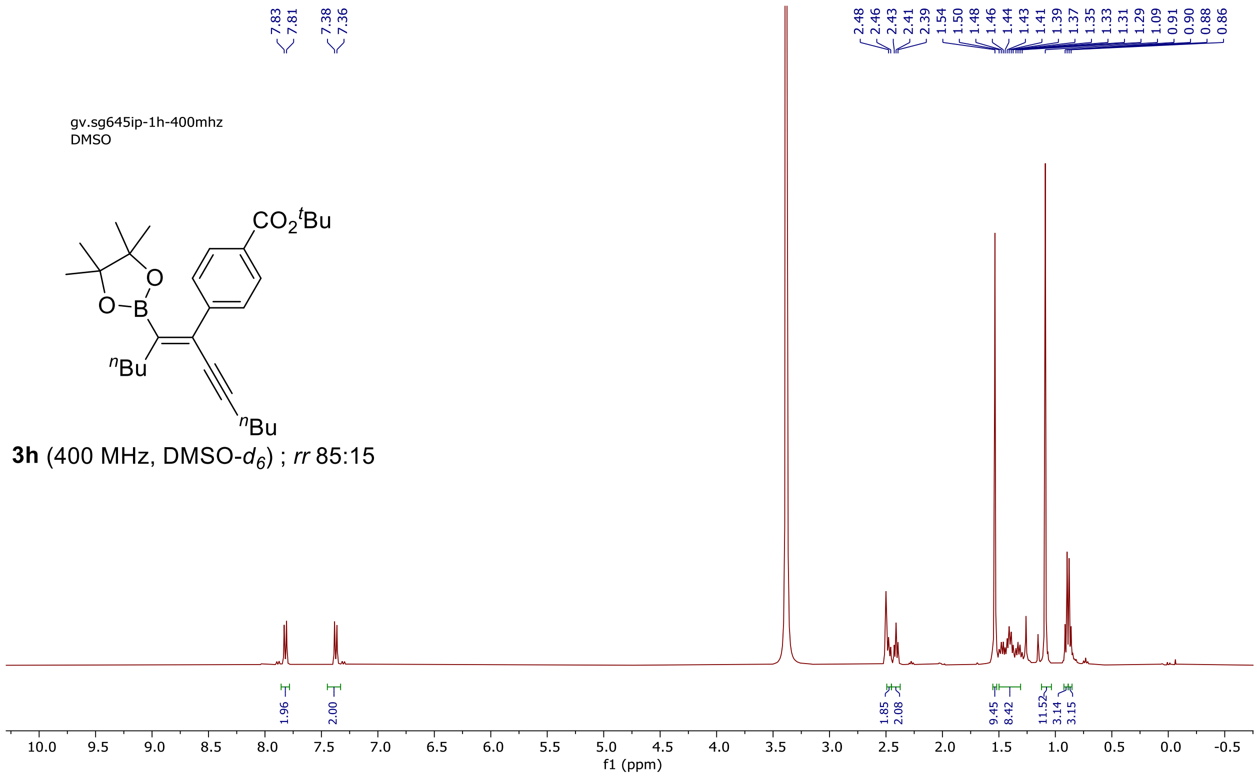
3g (126 MHz, $CDCl_3$) ; *rr* 85:15



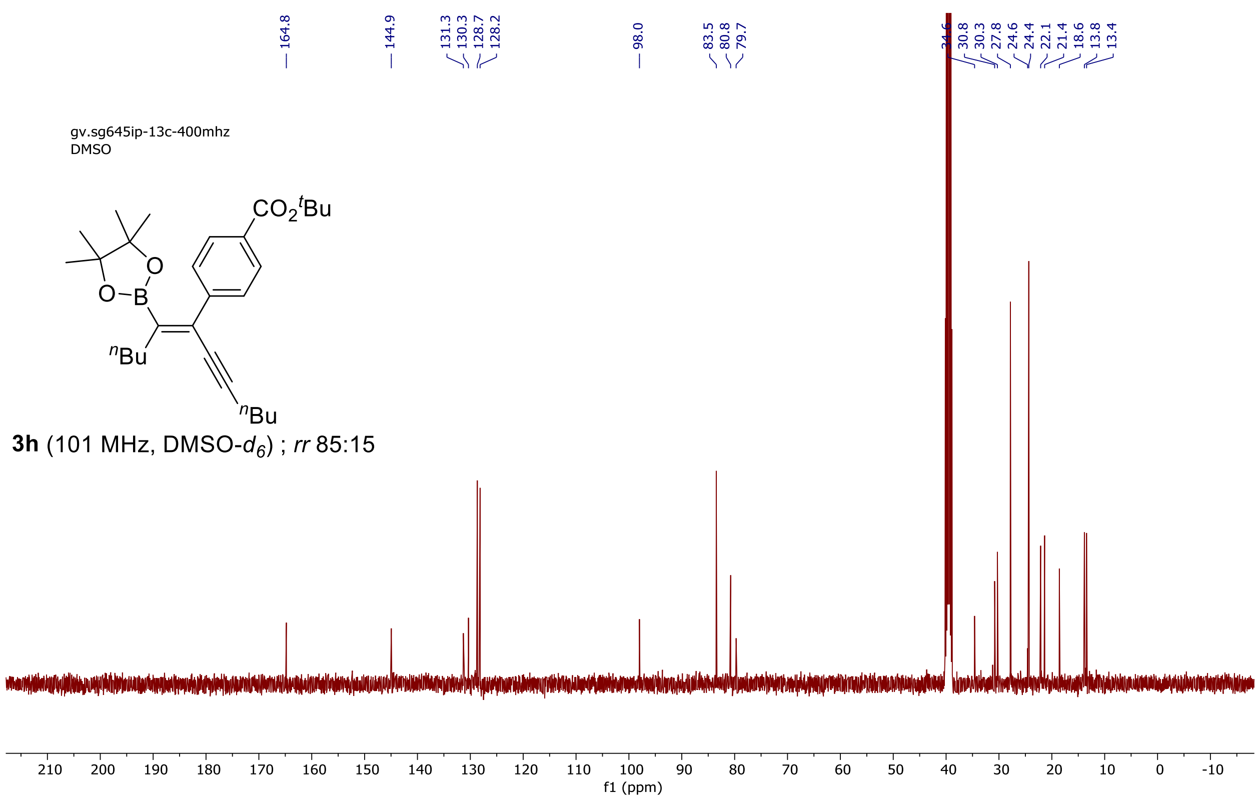
3g (470 MHz, $CDCl_3$) ; *rr* 85:15



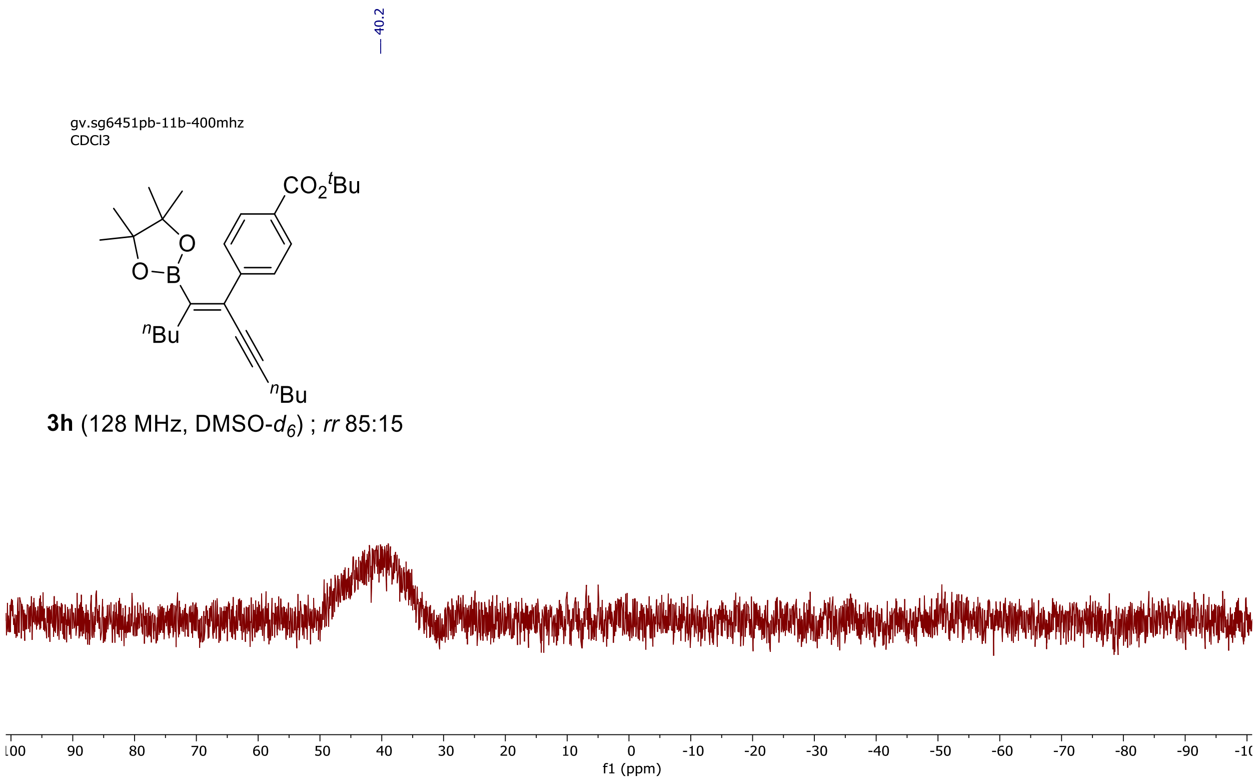
3g (160 MHz, $CDCl_3$) ; *rr* 85:15



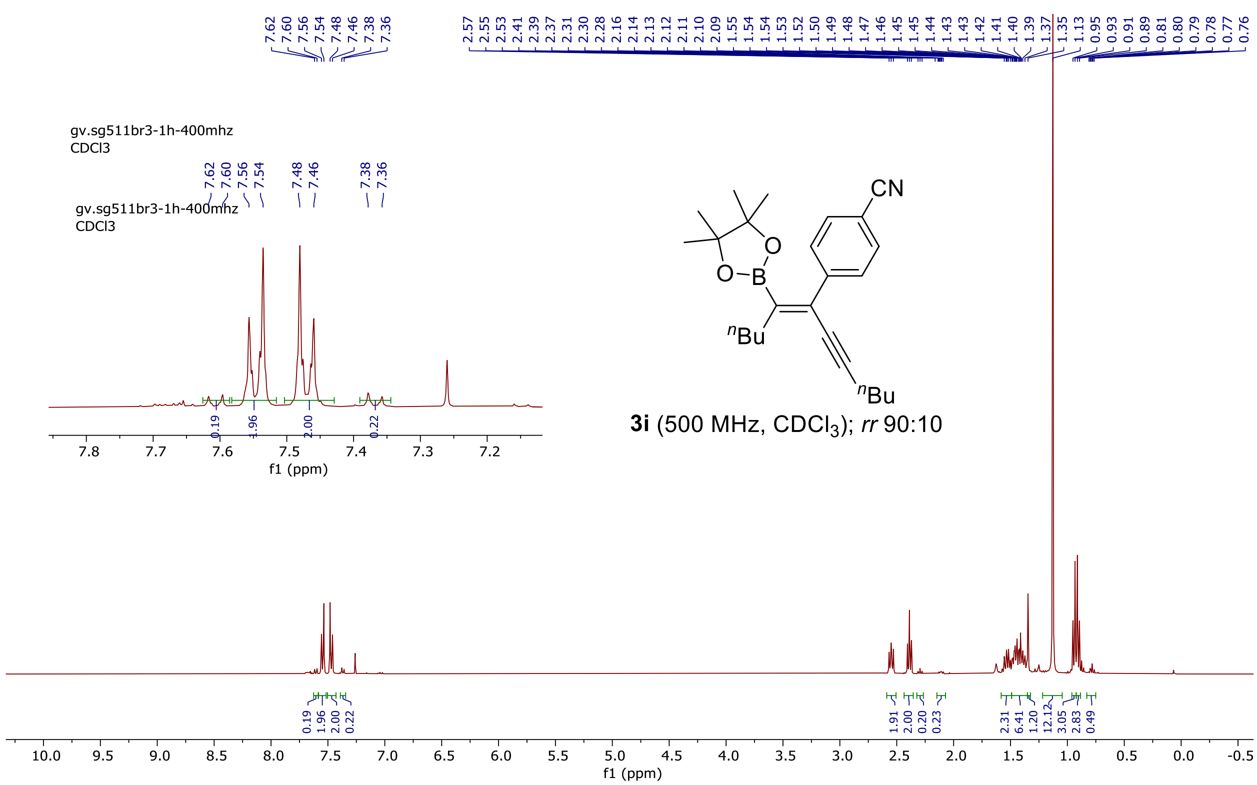
3h (400 MHz, DMSO-d_6) ; *rr* 85:15



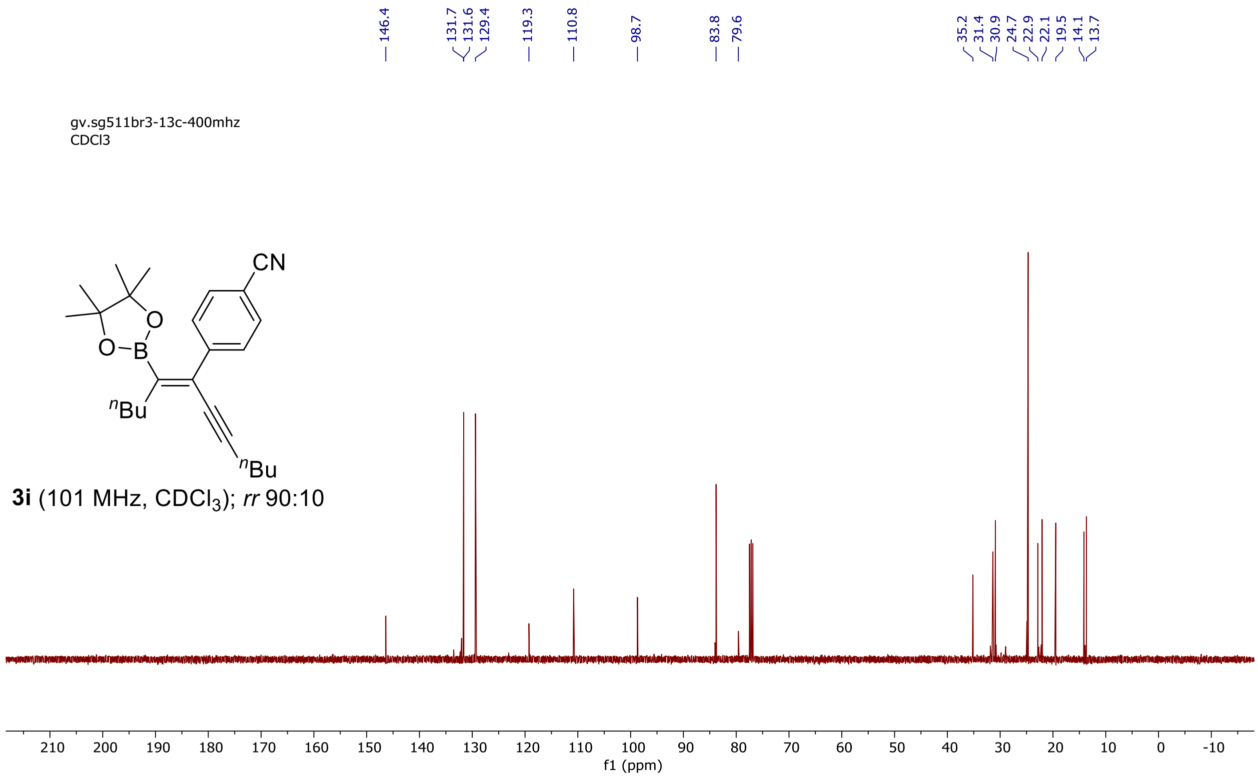
3h (101 MHz, DMSO-d_6) ; *rr* 85:15



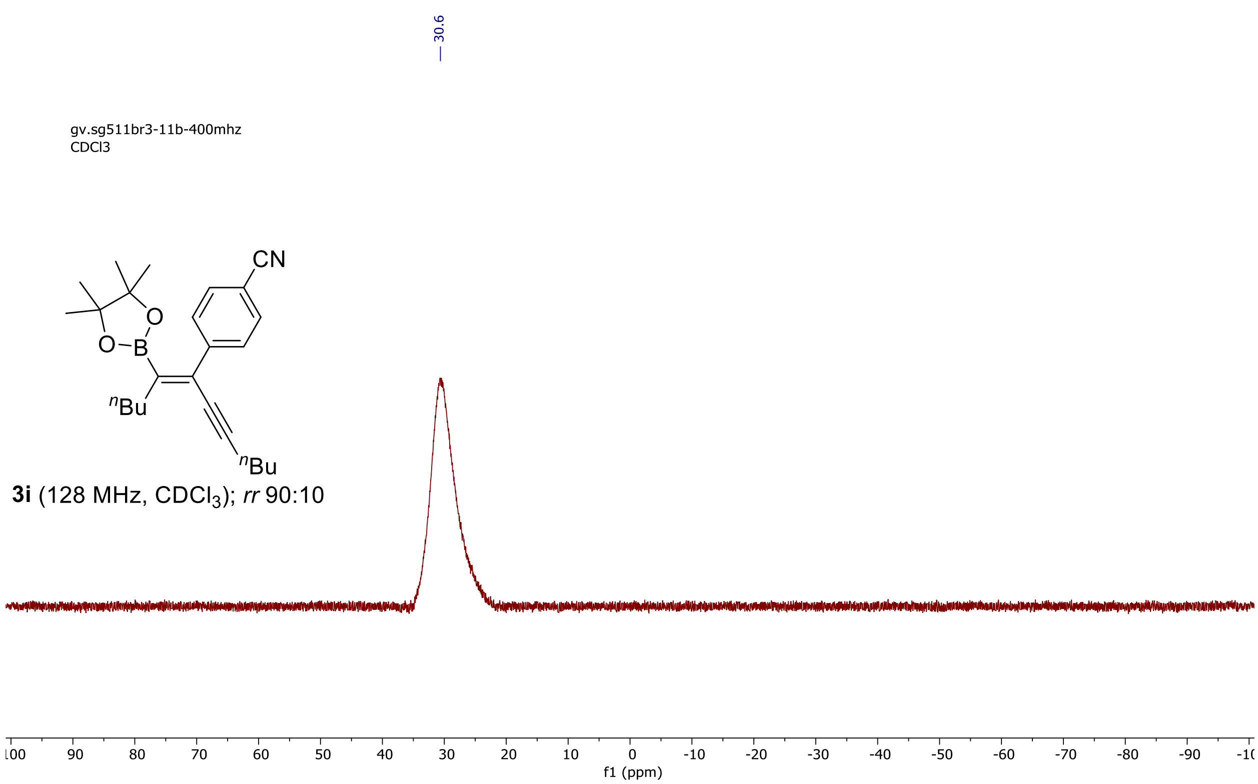
gv.sg6451pb-11b-400mhz
CDCl3
3h (128 MHz, DMSO-d6) ; rr 85:15
f1 (ppm)



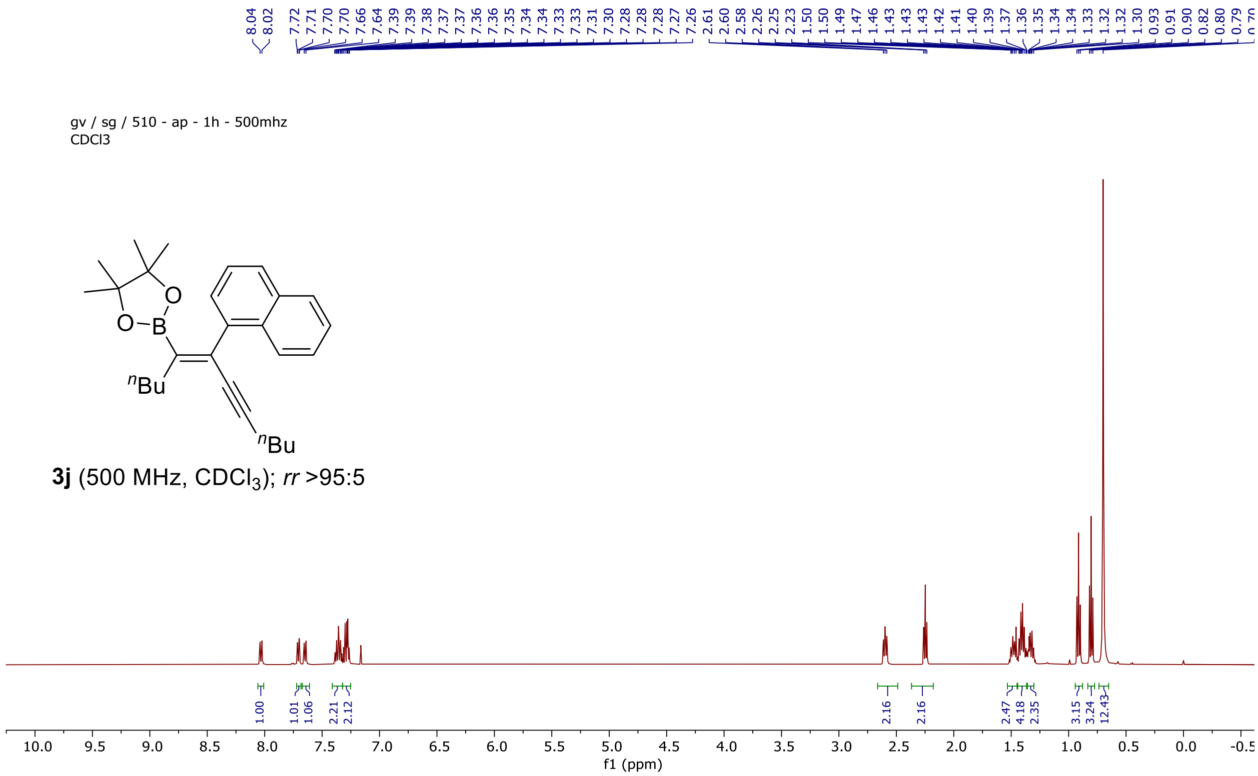
gv.sg511br3-1h-400mhz
CDCl3
3i (500 MHz, CDCl3); rr 90:10
f1 (ppm)

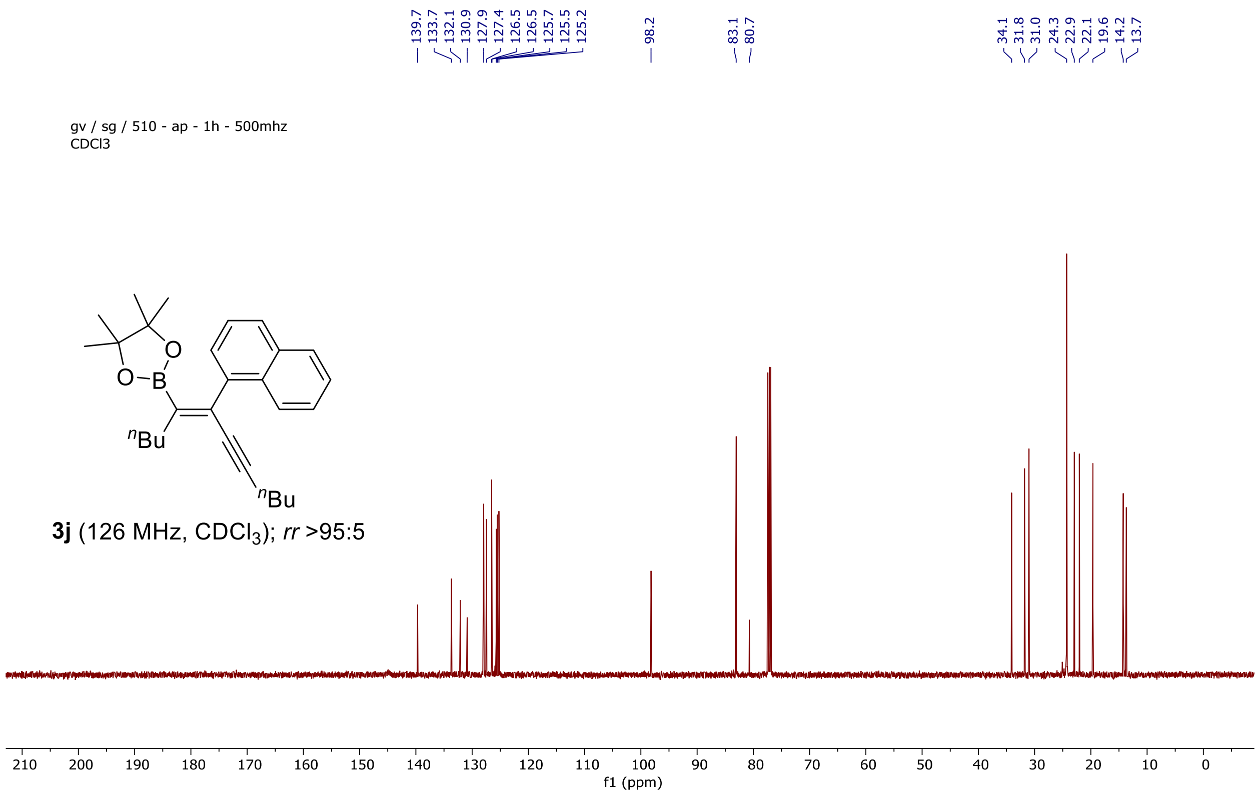


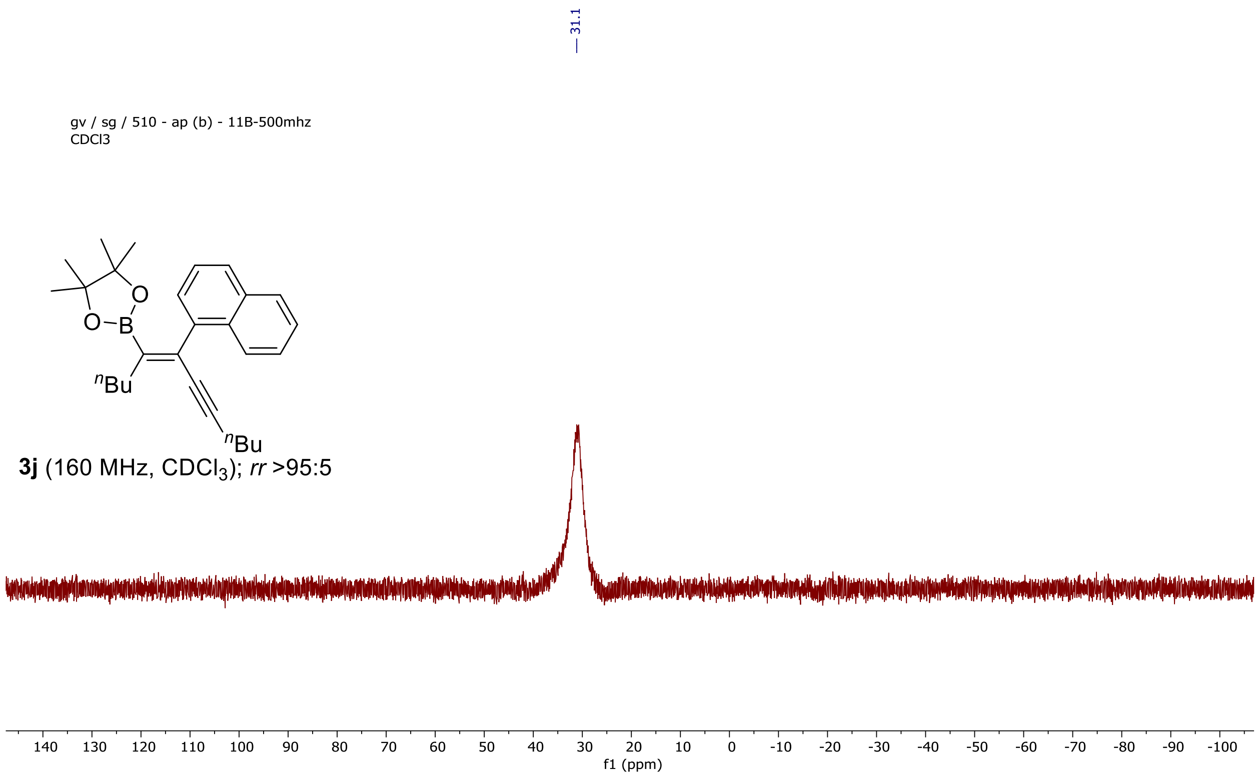
3i (101 MHz, $CDCl_3$); *rr* 90:10



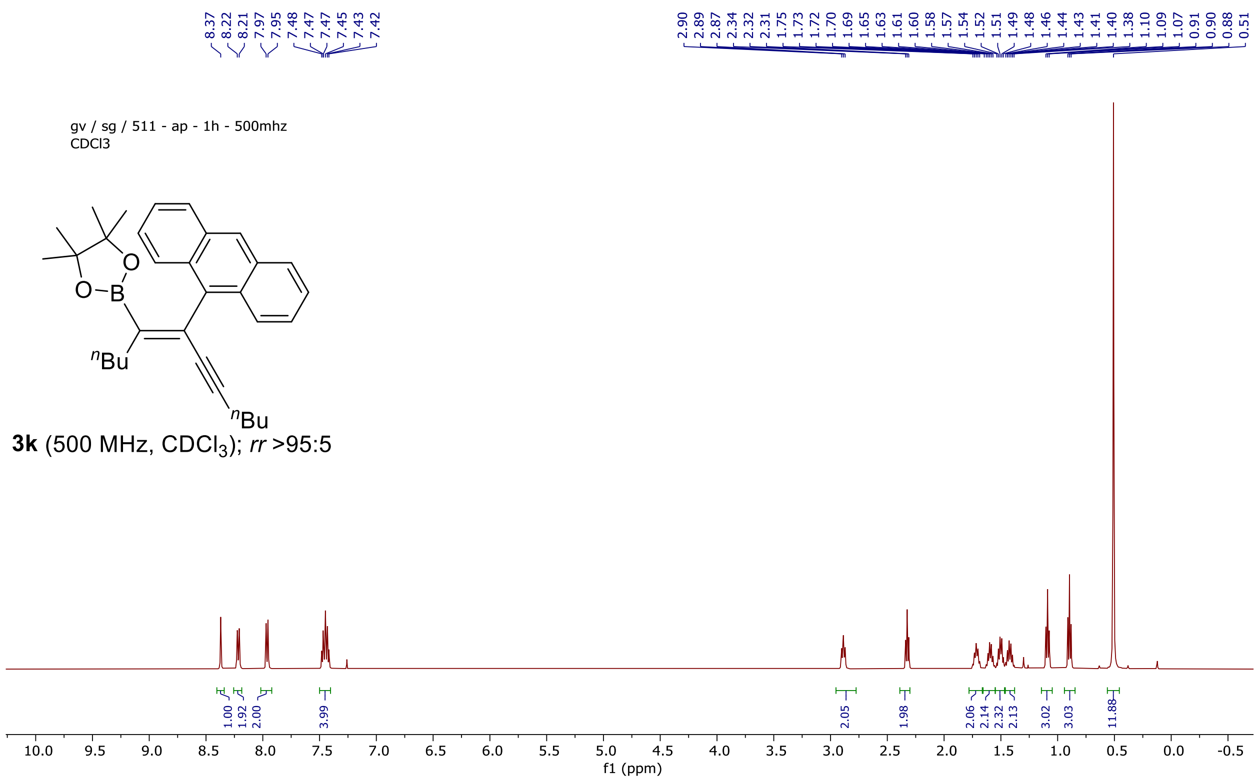
3i (128 MHz, $CDCl_3$); *rr* 90:10


gv / sg / 510 - ap - 1h - 500mhz
CDCl3
O
B
O
^{n}Bu
^{n}Bu
3j (500 MHz, CDCl$_3$); rr >95:5
f1 (ppm)

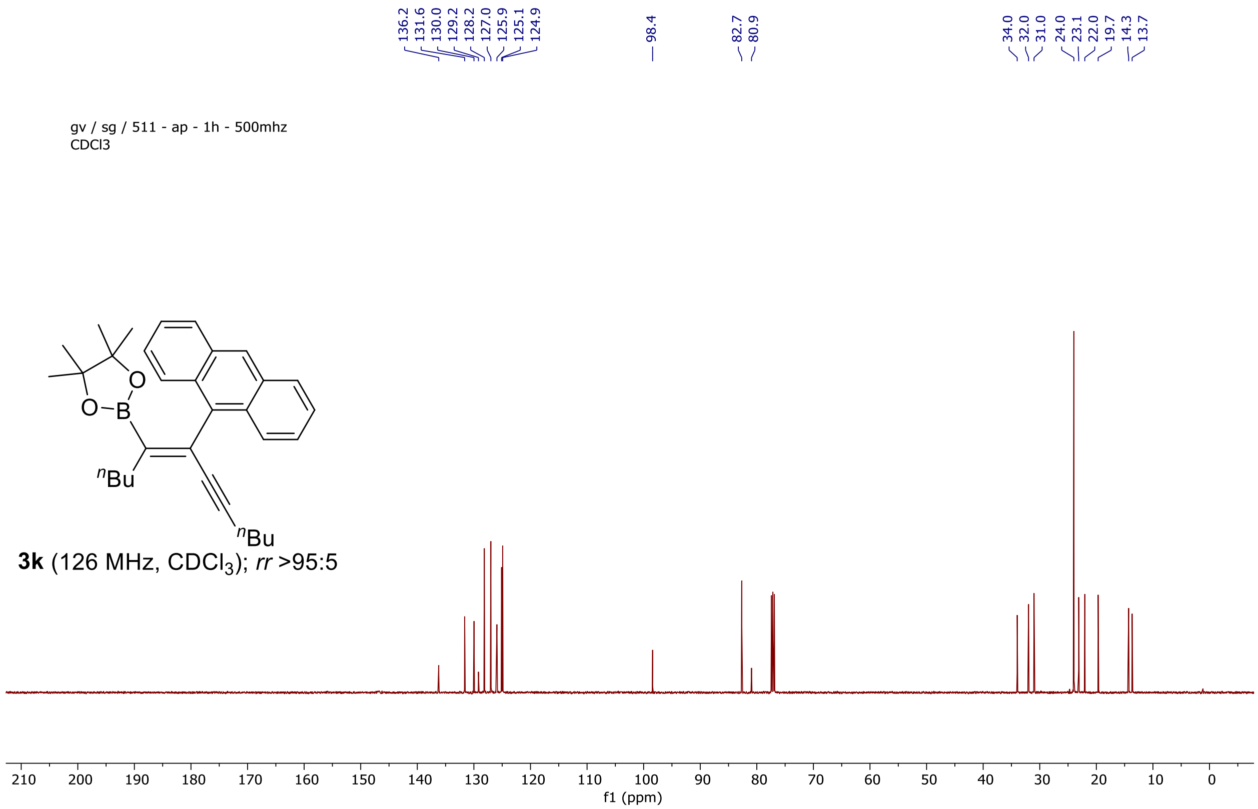

139.7
133.7
132.1
130.9
127.9
127.4
126.5
126.5
125.7
125.5
125.2
98.2
83.1
80.7
34.1
31.8
31.0
24.3
22.9
22.1
19.6
14.2
13.7
gv / sg / 510 - ap - 1h - 500mhz
CDCl3
O
B
O
^{n}Bu
^{n}Bu
3j (126 MHz, CDCl$_3$); rr >95:5
f1 (ppm)



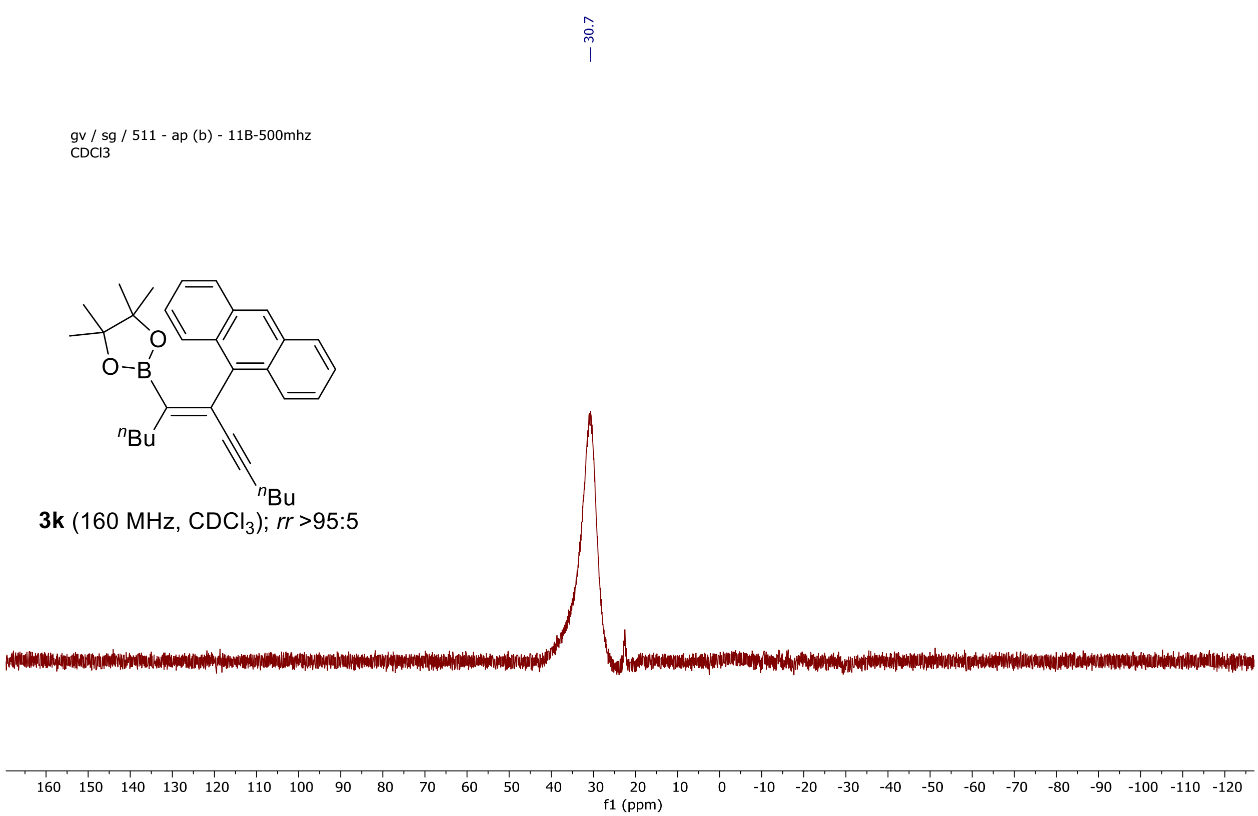
3j (160 MHz, $CDCl_3$); *rr* >95:5



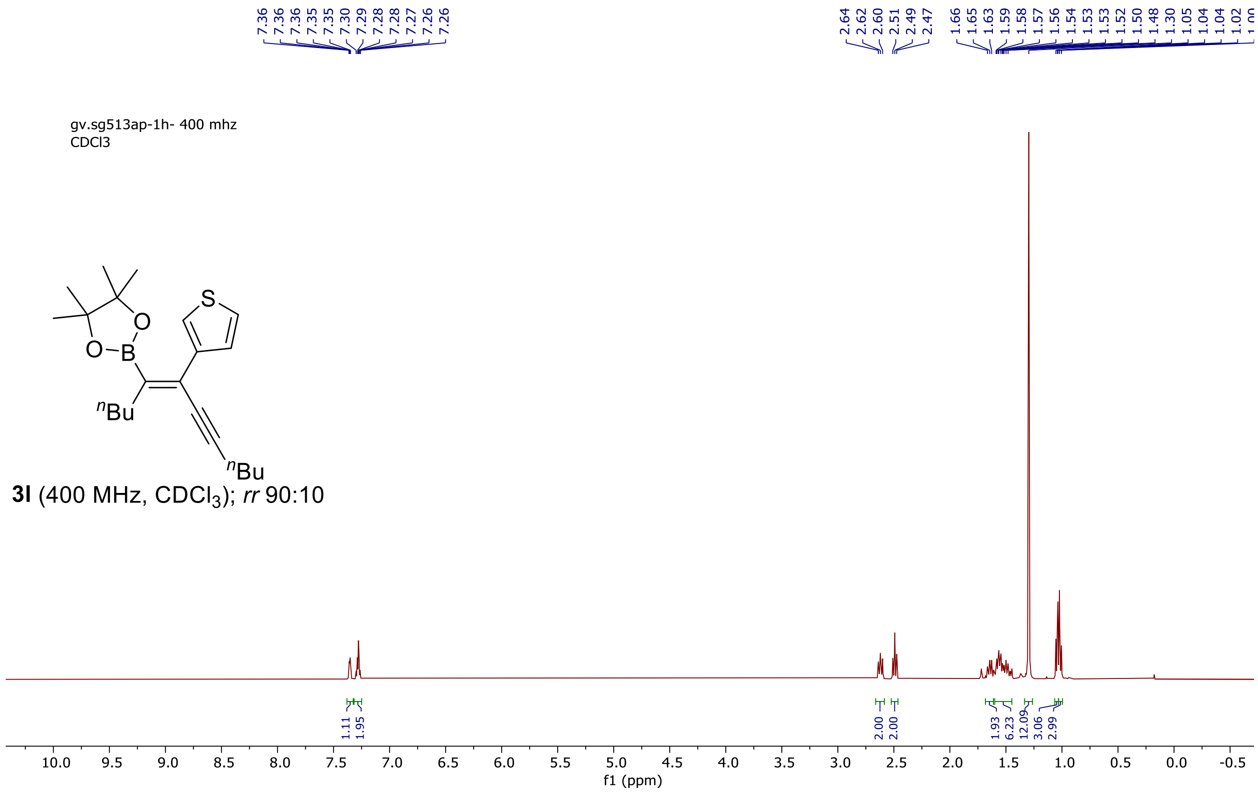
3k (500 MHz, $CDCl_3$); *rr* >95:5



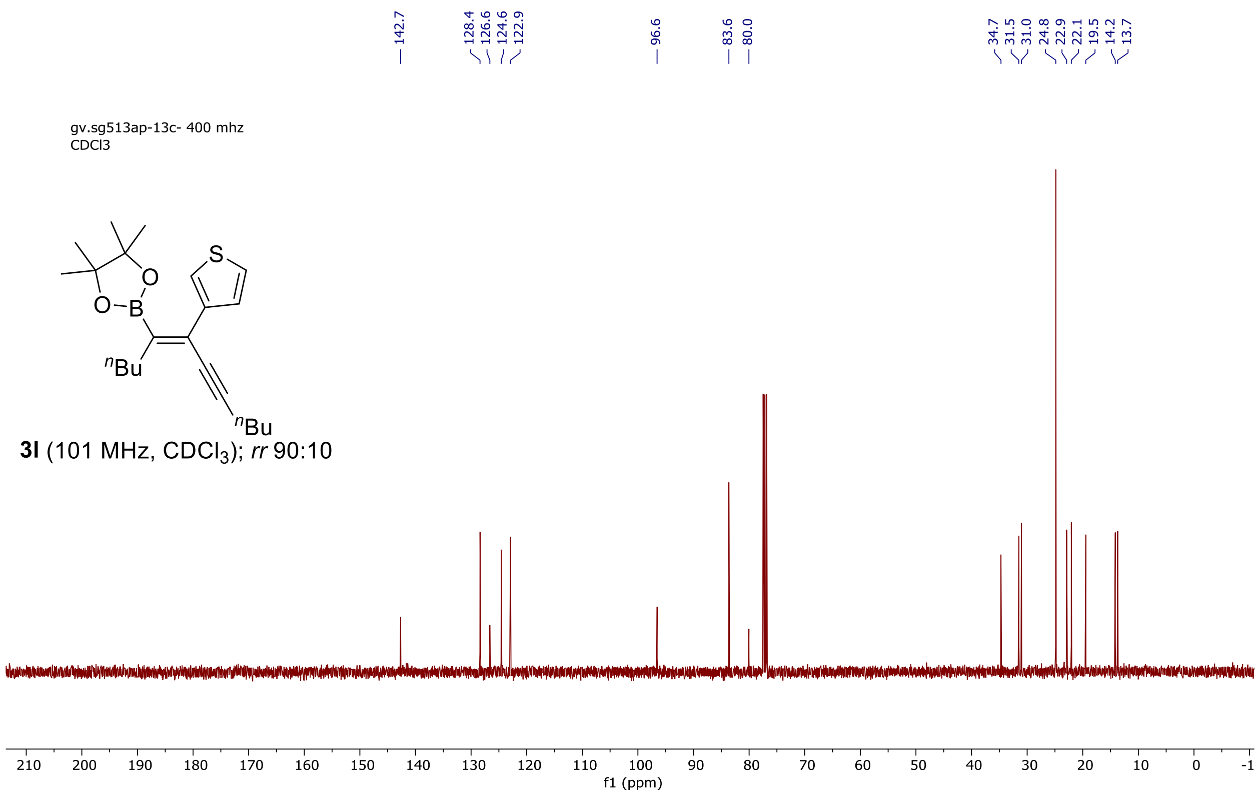
3k (126 MHz, $CDCl_3$); *rr* >95:5



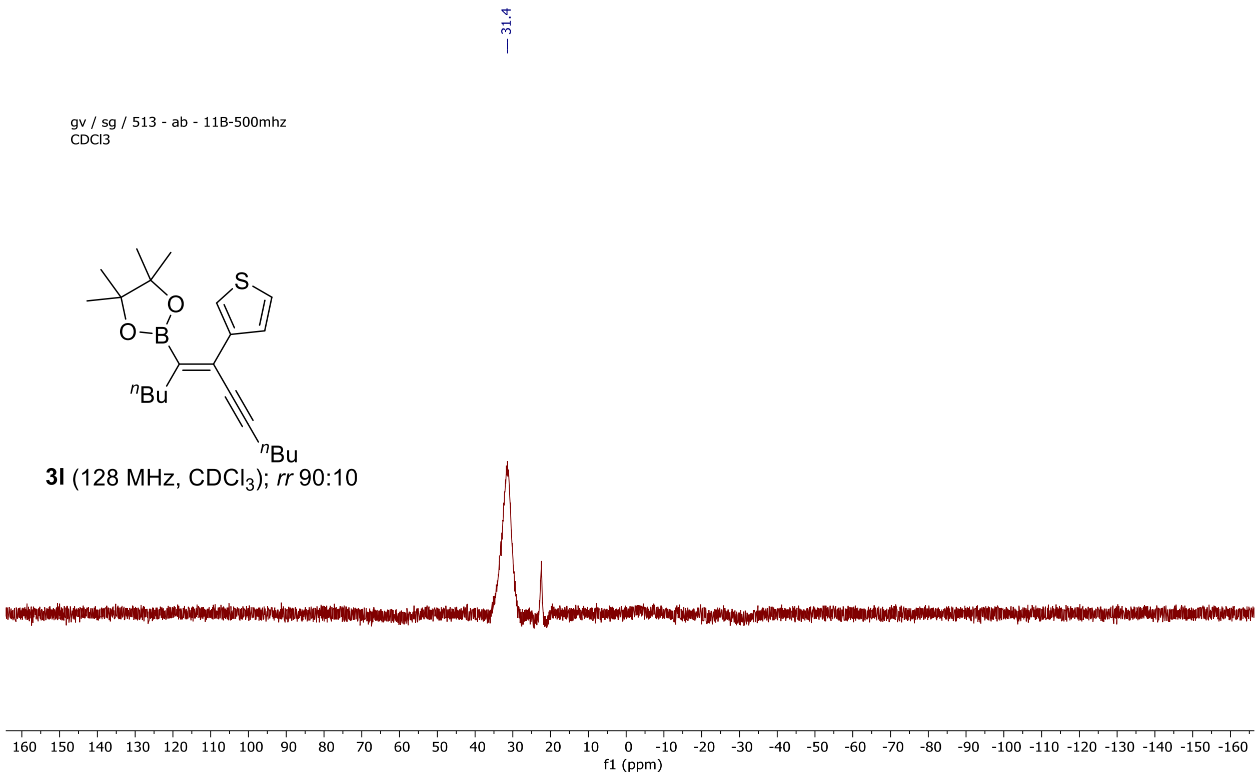
3k (160 MHz, $CDCl_3$); *rr* >95:5



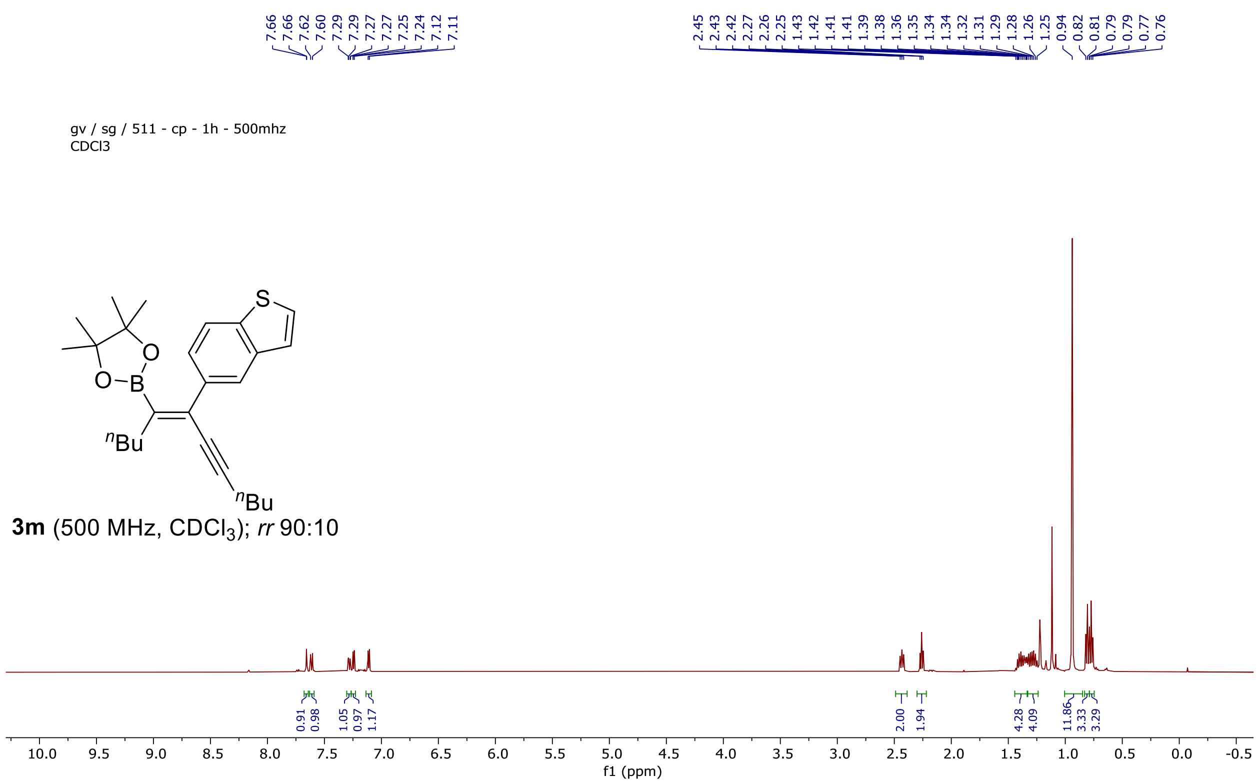
3l (400 MHz, $CDCl_3$); *rr* 90:10



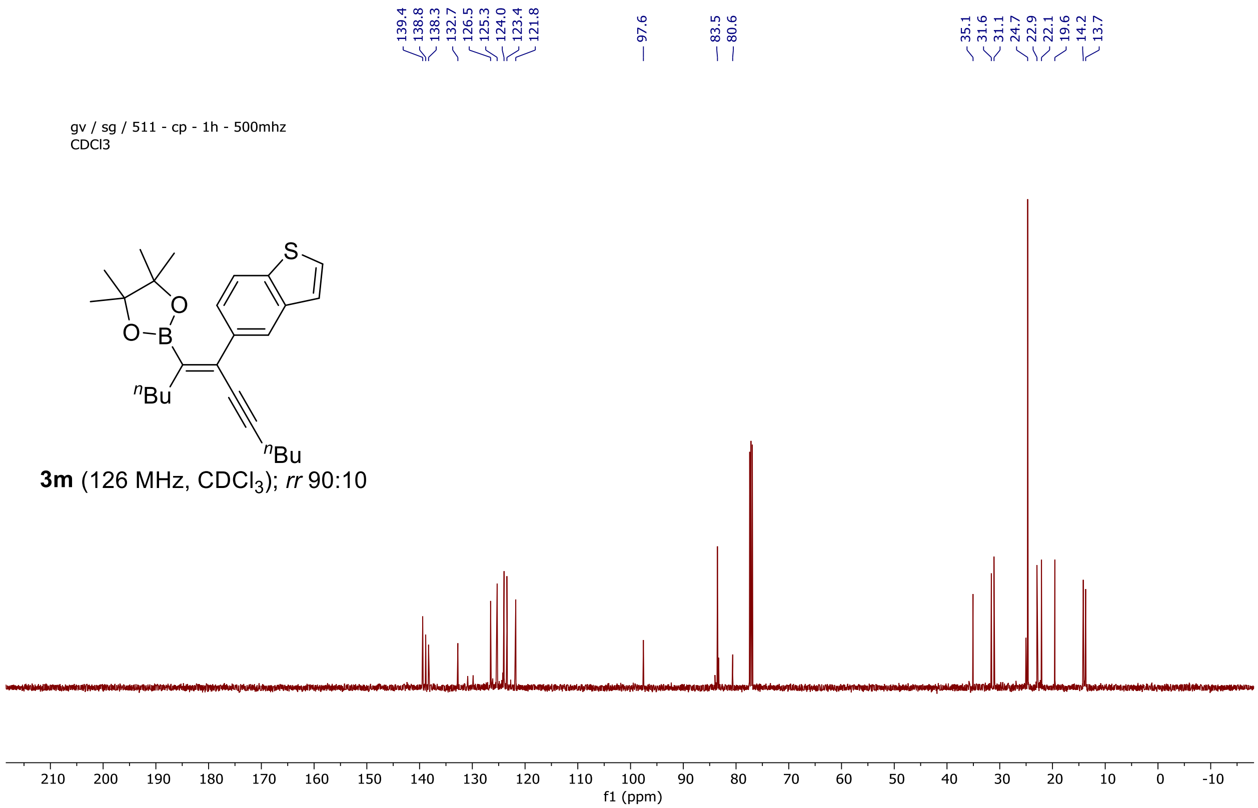
3l (101 MHz, $CDCl_3$); *rr* 90:10

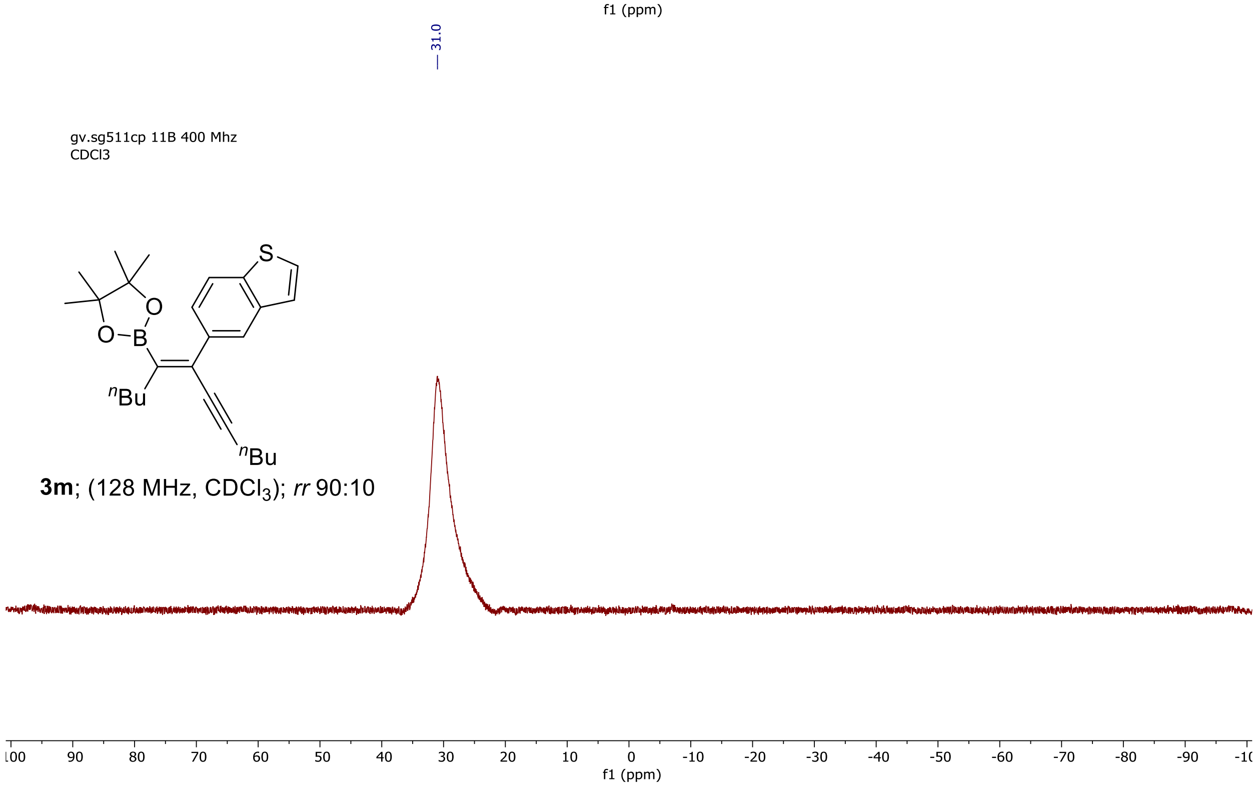


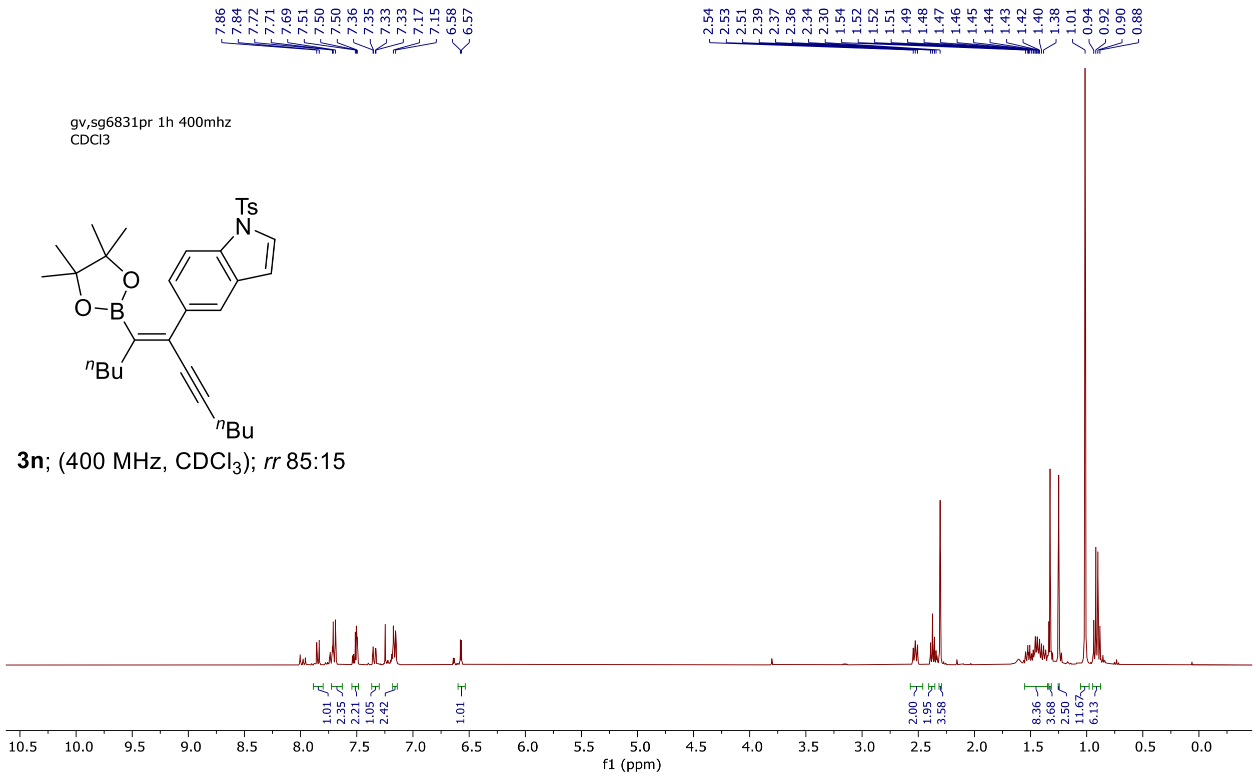
3l (128 MHz, $CDCl_3$); *rr* 90:10

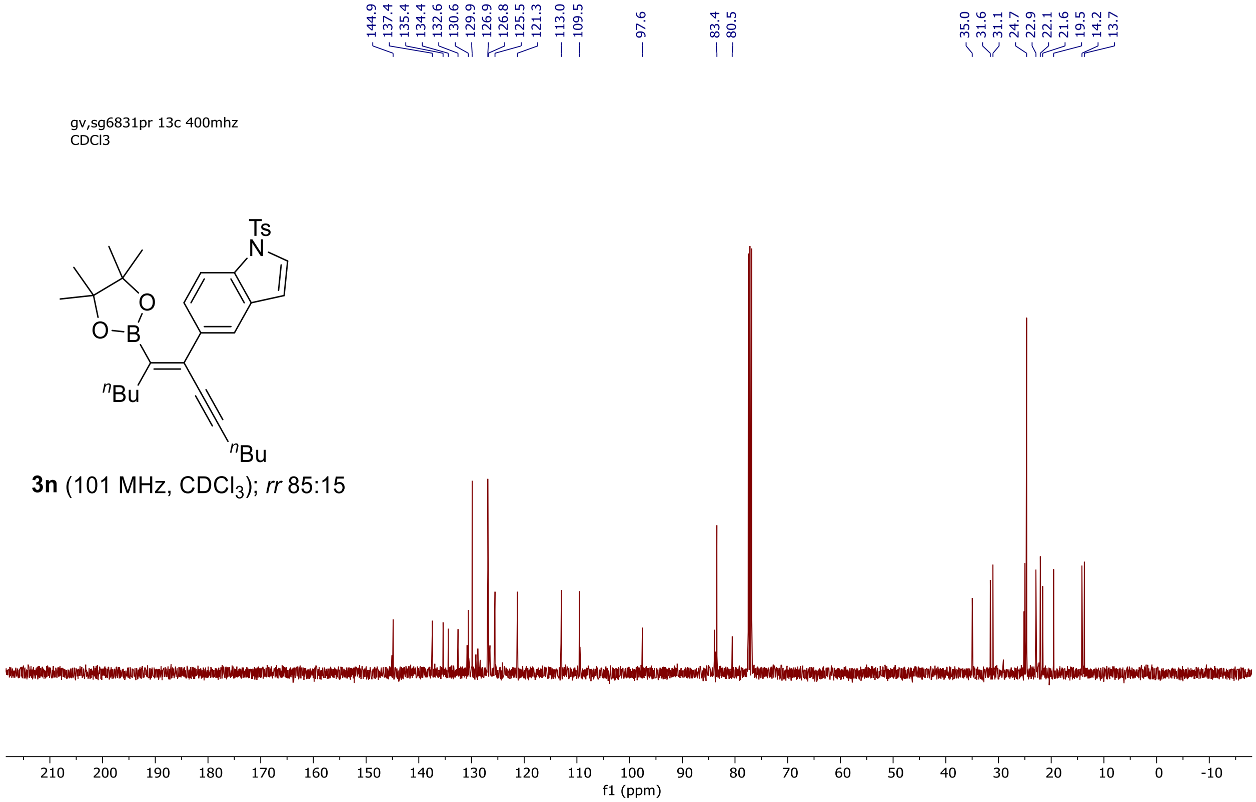


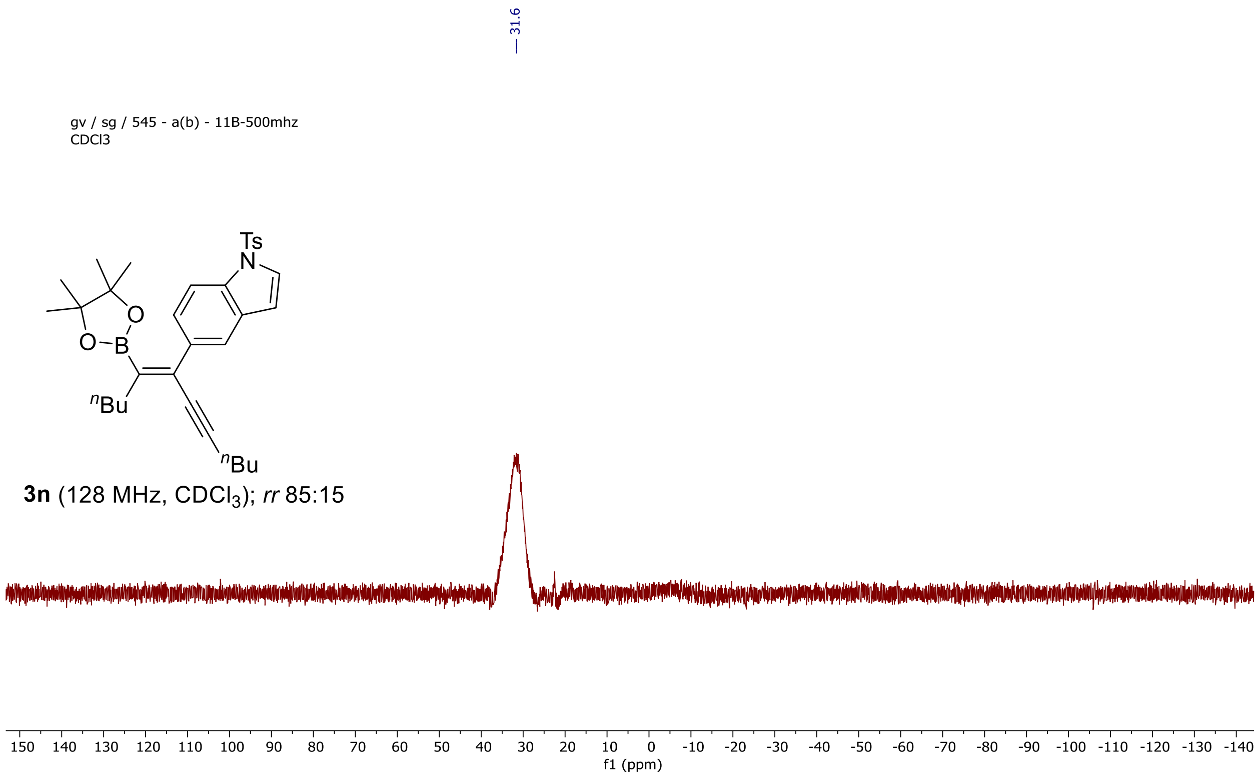
3m (500 MHz, $CDCl_3$); *rr* 90:10


139.4
138.8
138.3
132.7
126.5
125.3
124.0
123.4
121.8
97.6
83.5
80.6
35.1
31.6
31.1
24.7
22.9
22.1
19.6
14.2
13.7
gv / sg / 511 - cp - 1h - 500mhz
CDCl3
S
O
B
O
nBu
nBu
3m (126 MHz, CDCl3); rr 90:10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

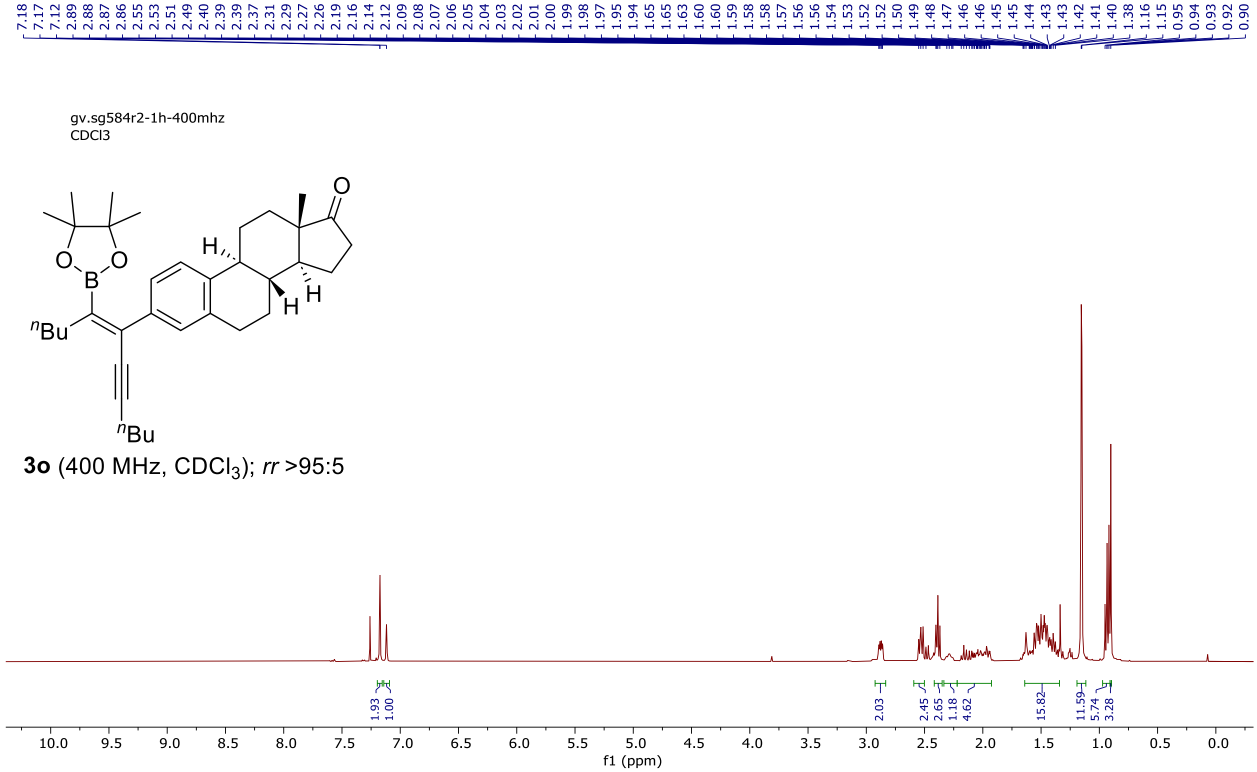

31.0
gv.sg511cp 11B 400 Mhz
CDCl3
S
O
B
O
nBu
nBu
3m; (128 MHz, CDCl3); rr 90:10
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


7.86 7.84 7.72 7.71 7.69 7.51 7.50 7.50 7.36 7.35 7.33 7.33 7.17 7.15 6.58 6.57
2.54 2.53 2.51 2.39 2.37 2.36 2.34 2.30 1.54 1.52 1.52 1.51 1.49 1.48 1.47 1.46 1.45 1.44 1.43 1.42 1.40 1.38 1.01 0.94 0.92 0.90 0.88
gv,sg6831pr 1h 400mhz
CDCl3
Ts
N
O
O
B
^{n}Bu
^{n}Bu
3n; (400 MHz, $CDCl_3$); *rr* 85:15
1.01 2.35 2.21 1.05 2.42 1.01 2.00 1.95 3.58 8.36 3.68 2.50 11.67 6.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

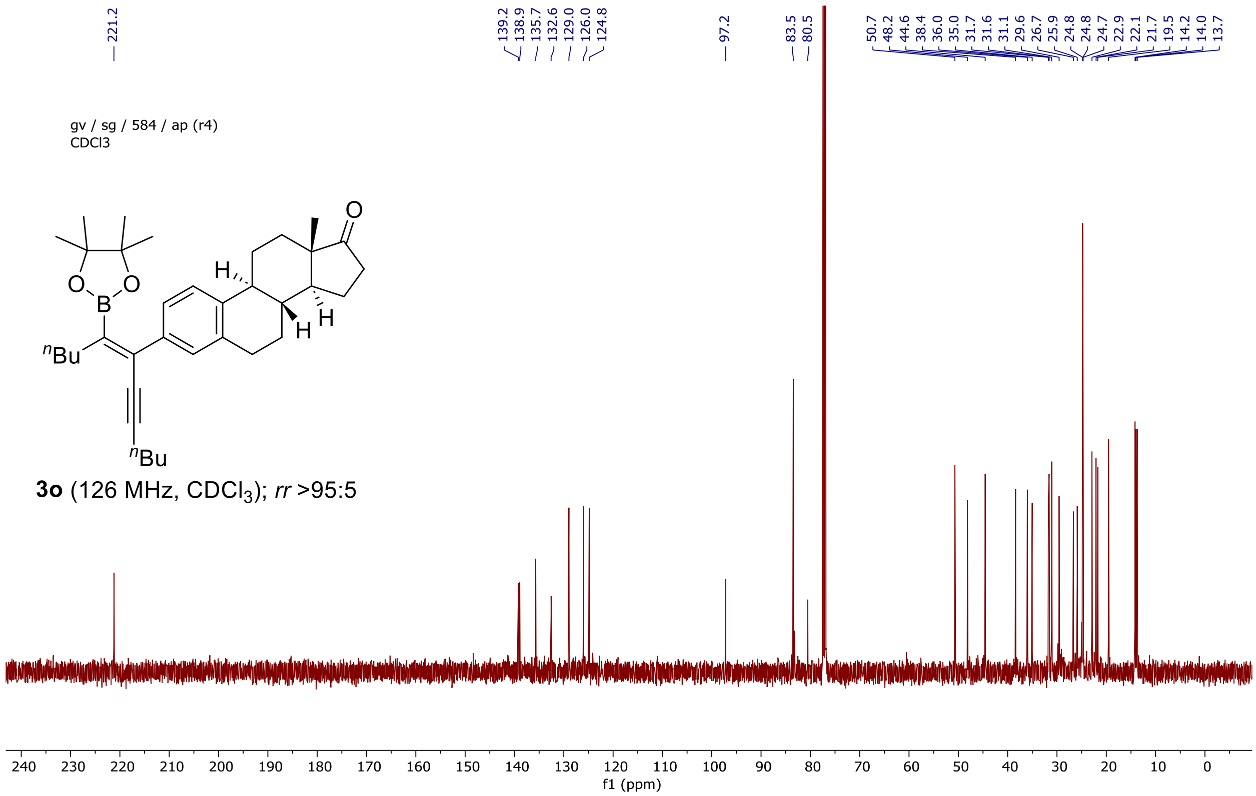

144.9 137.4 135.4 134.4 132.6 130.6 129.9 126.9 126.8 125.5 121.3 113.0 109.5 97.6 83.4 80.5 35.0 31.6 31.1 24.7 22.9 22.1 21.6 19.5 14.2 13.7
gv,sg6831pr 13c 400mhz
CDCl3
Ts
N
O
O
B
^{n}Bu
^{n}Bu
3n (101 MHz, $CDCl_3$); *rr* 85:15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



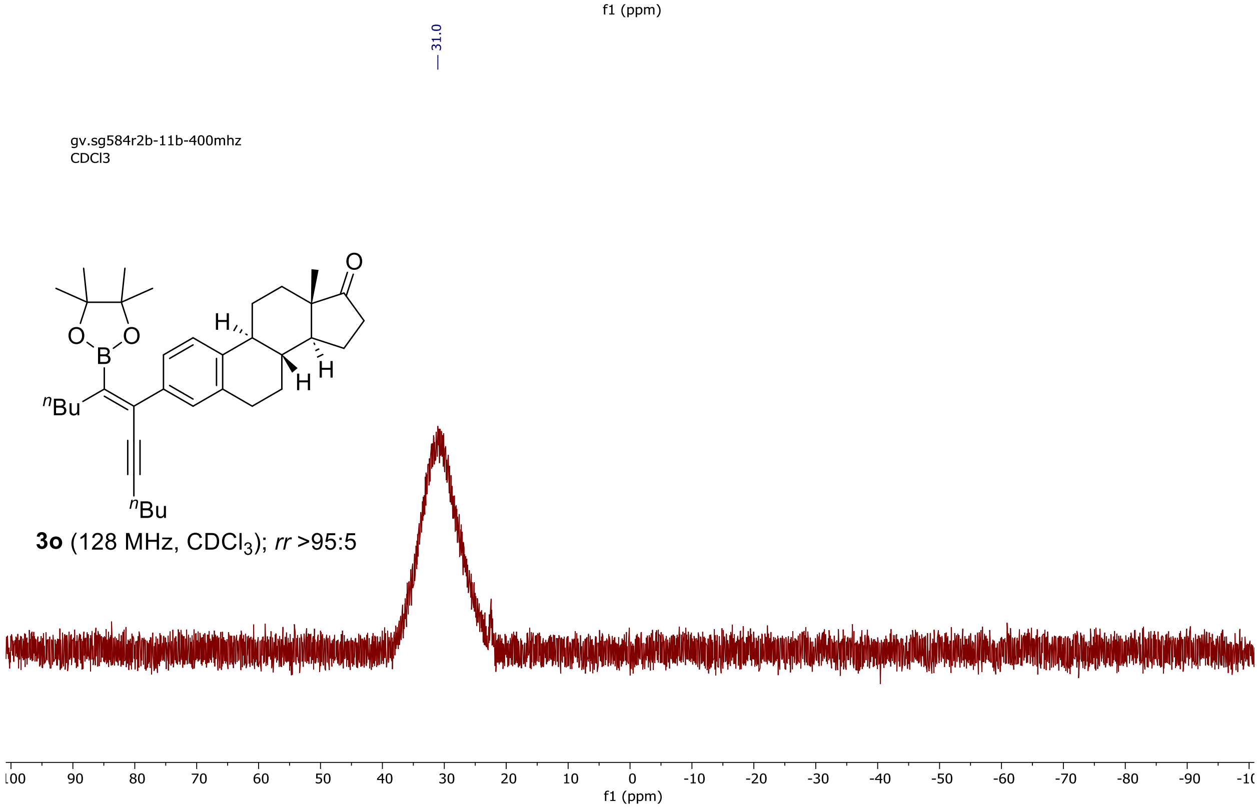
3n (128 MHz, $CDCl_3$); *rr* 85:15



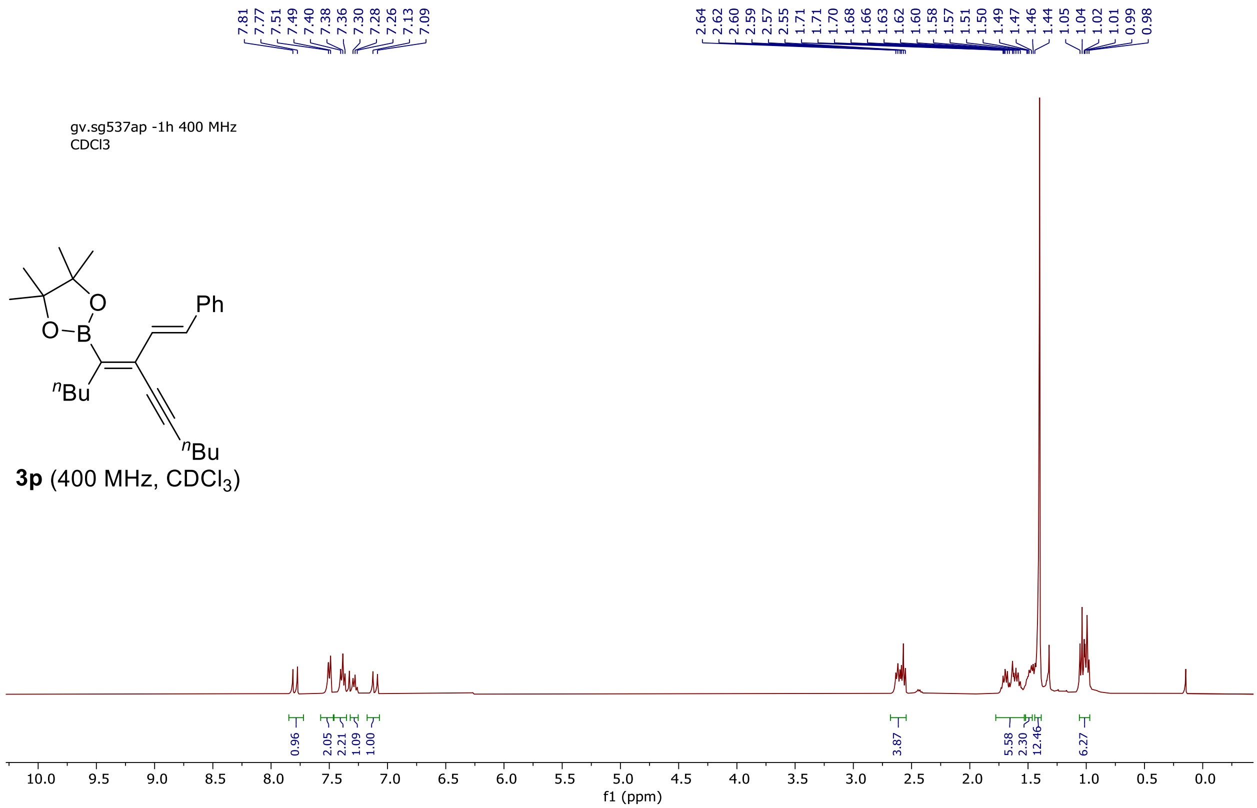
3o (400 MHz, $CDCl_3$); *rr* >95:5



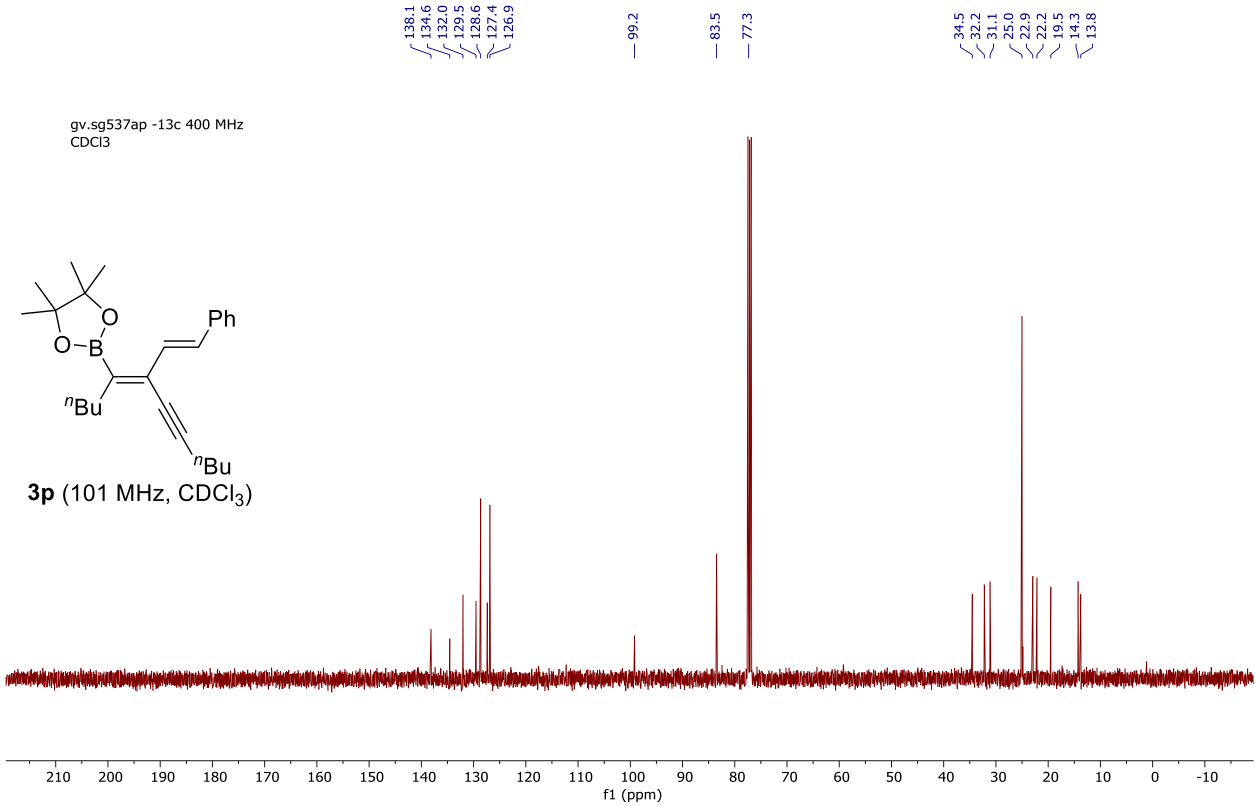
3o (126 MHz, $CDCl_3$); *rr* >95:5



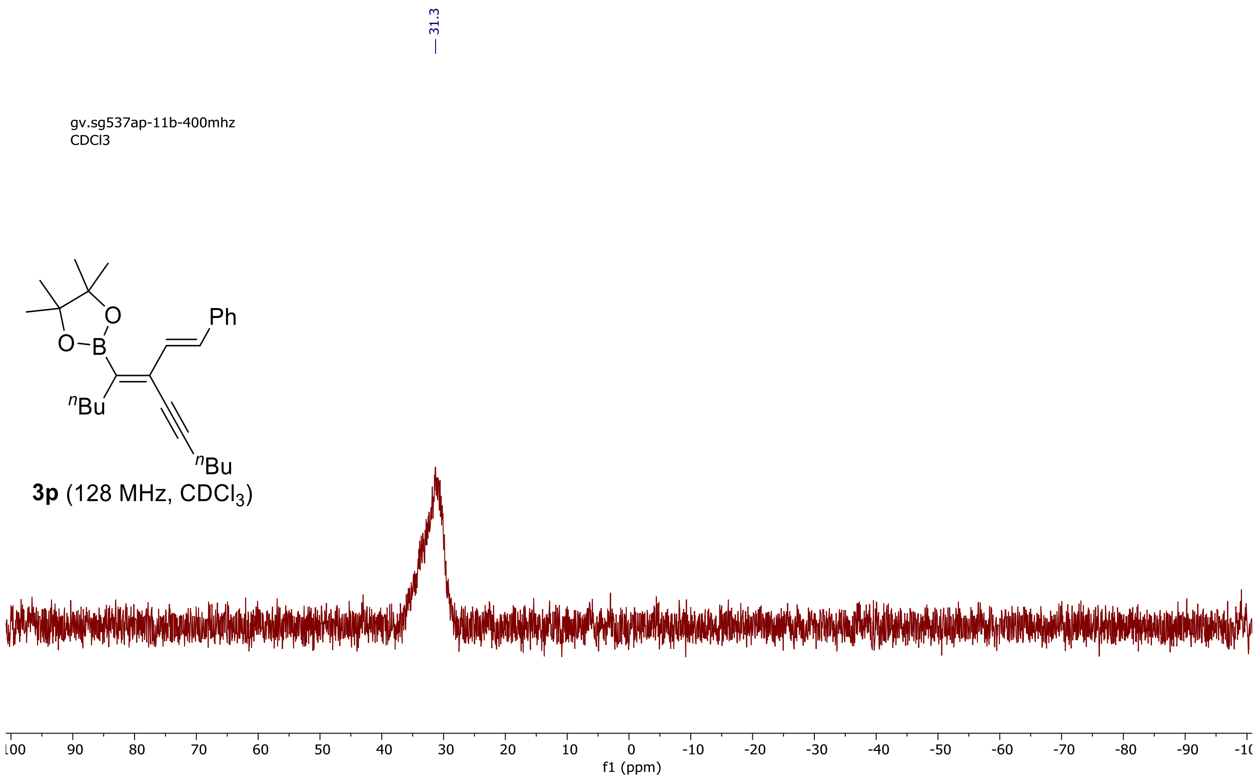
3o (128 MHz, $CDCl_3$); *rr* >95:5



3p (400 MHz, $CDCl_3$)

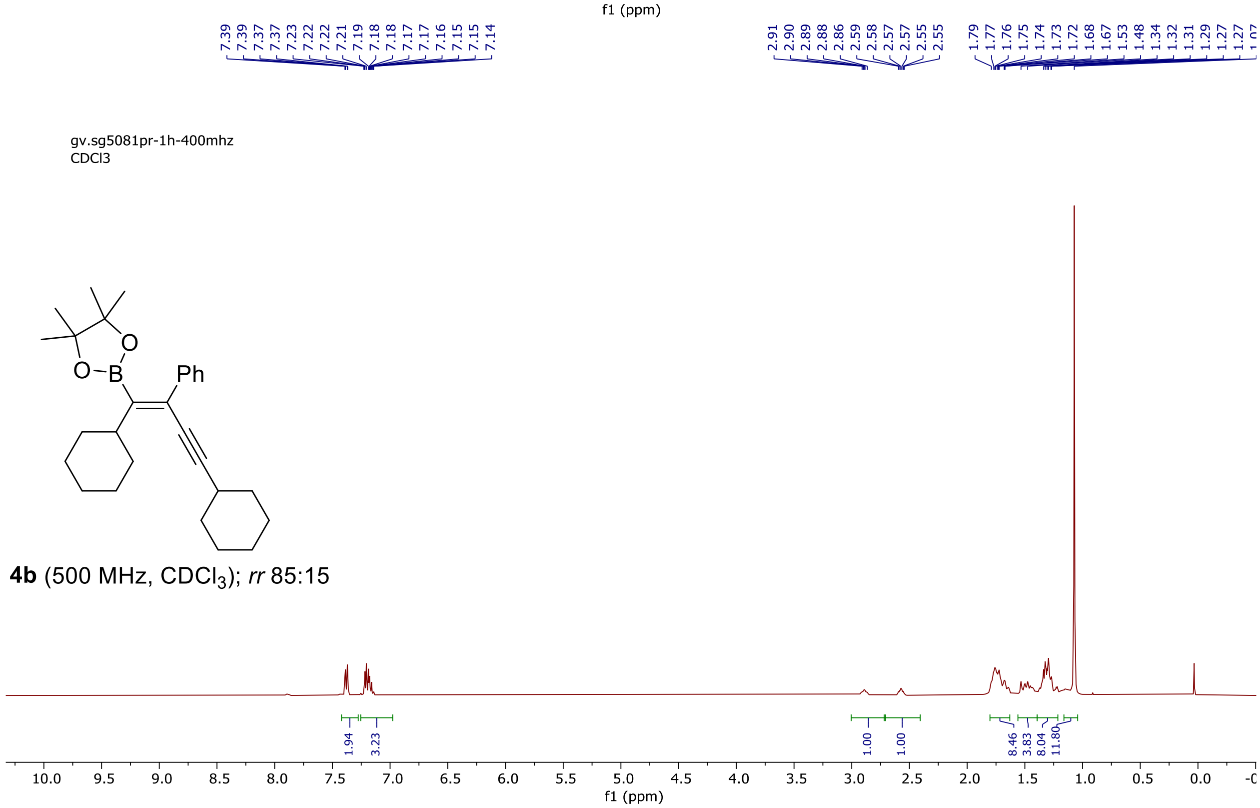


3p (101 MHz, $CDCl_3$)



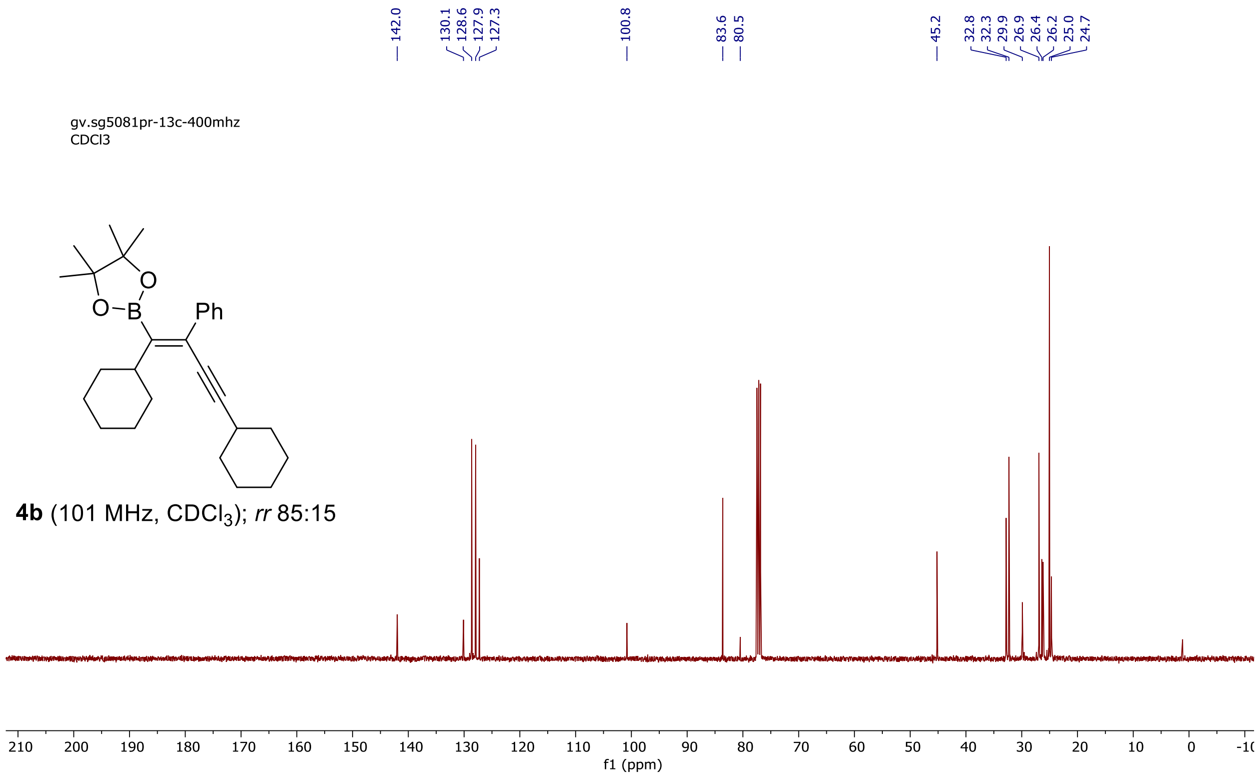
gv.sg537ap-11b-400mhz
CDCl3

3p (128 MHz, $CDCl_3$)

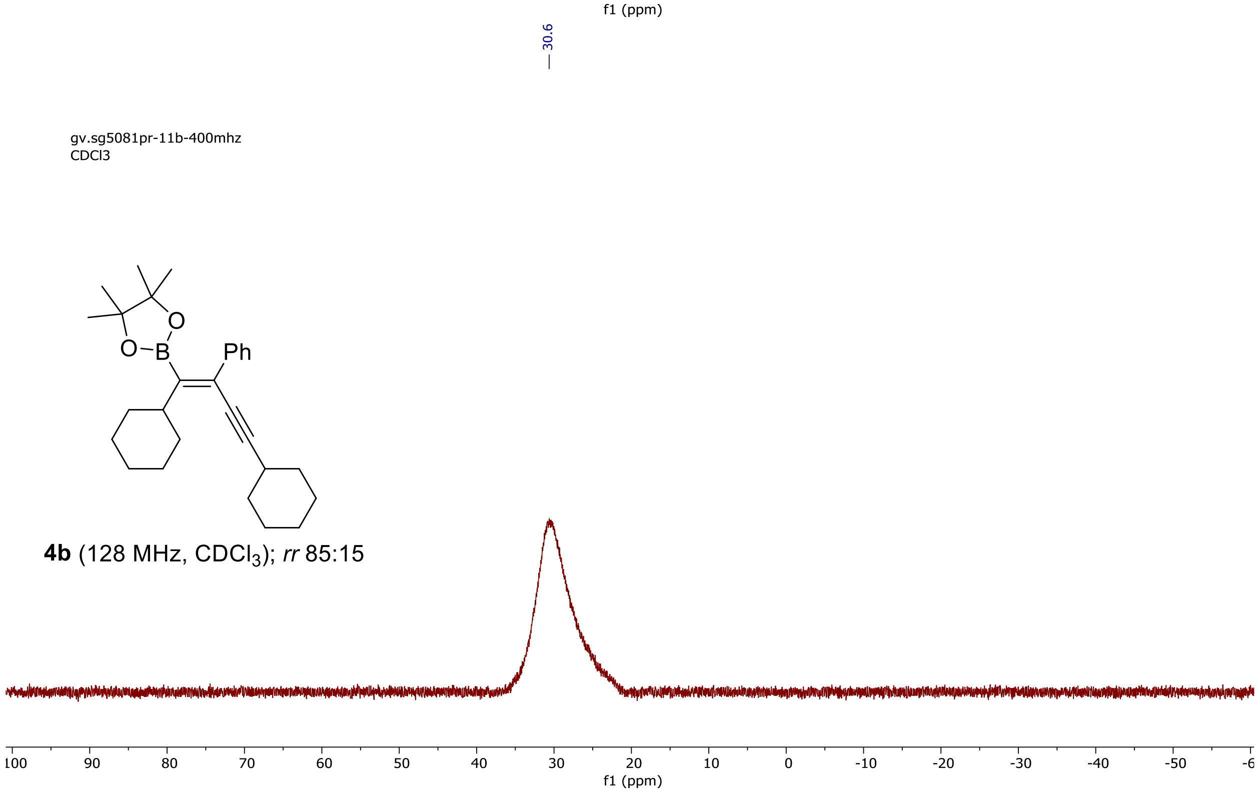


gv.sg5081pr-1h-400mhz
CDCl3

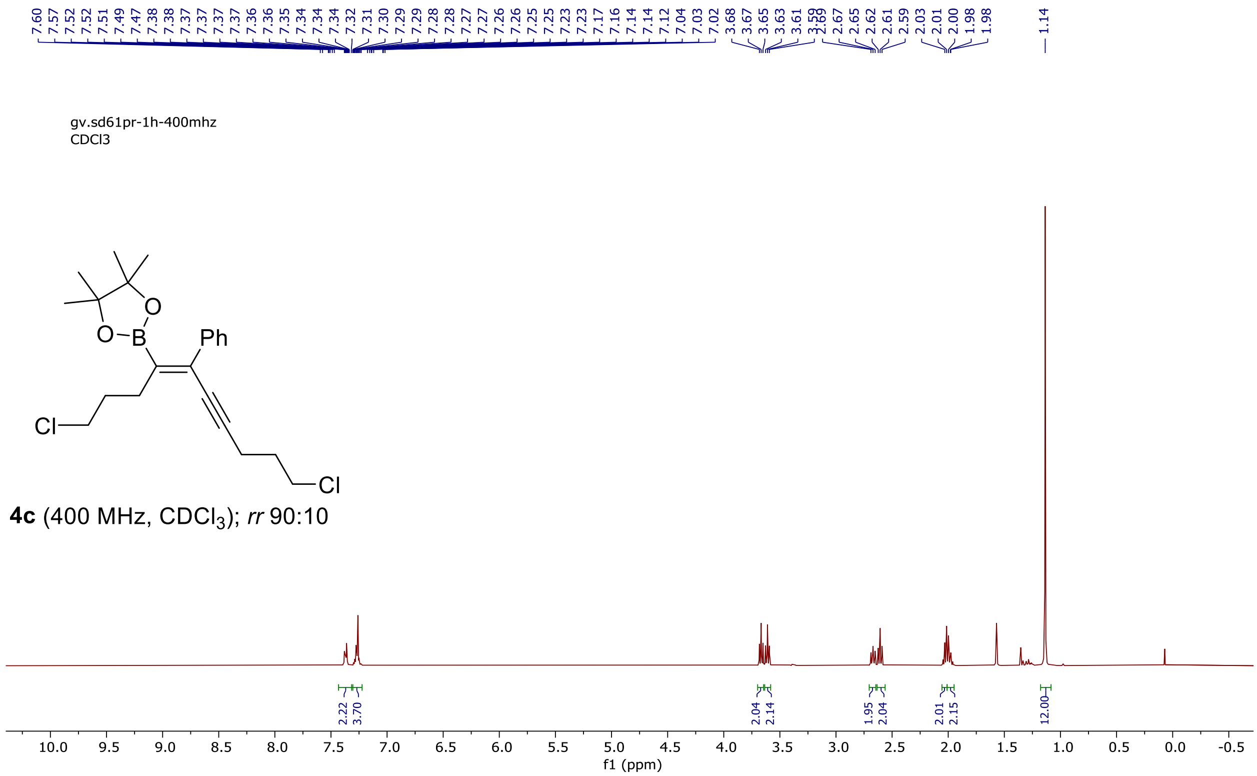
4b (500 MHz, $CDCl_3$); *rr* 85:15



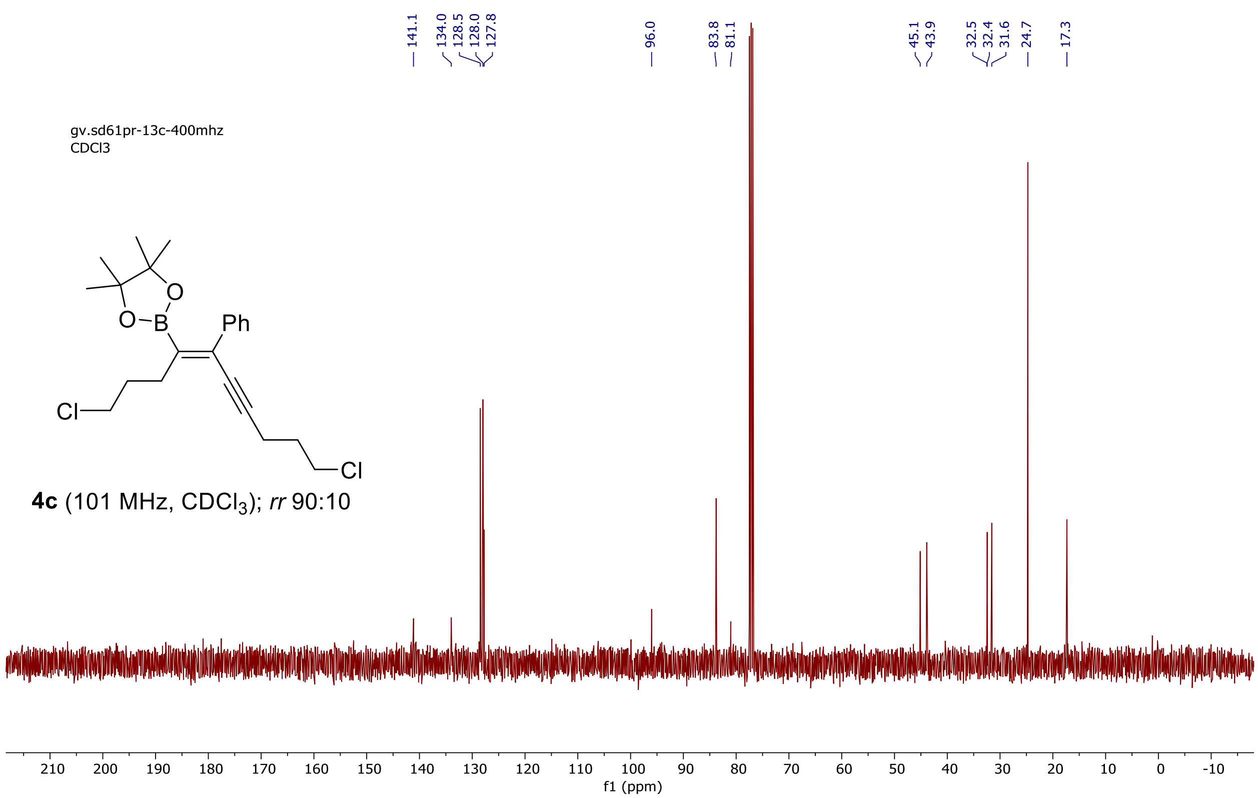
4b (101 MHz, $CDCl_3$); *rr* 85:15



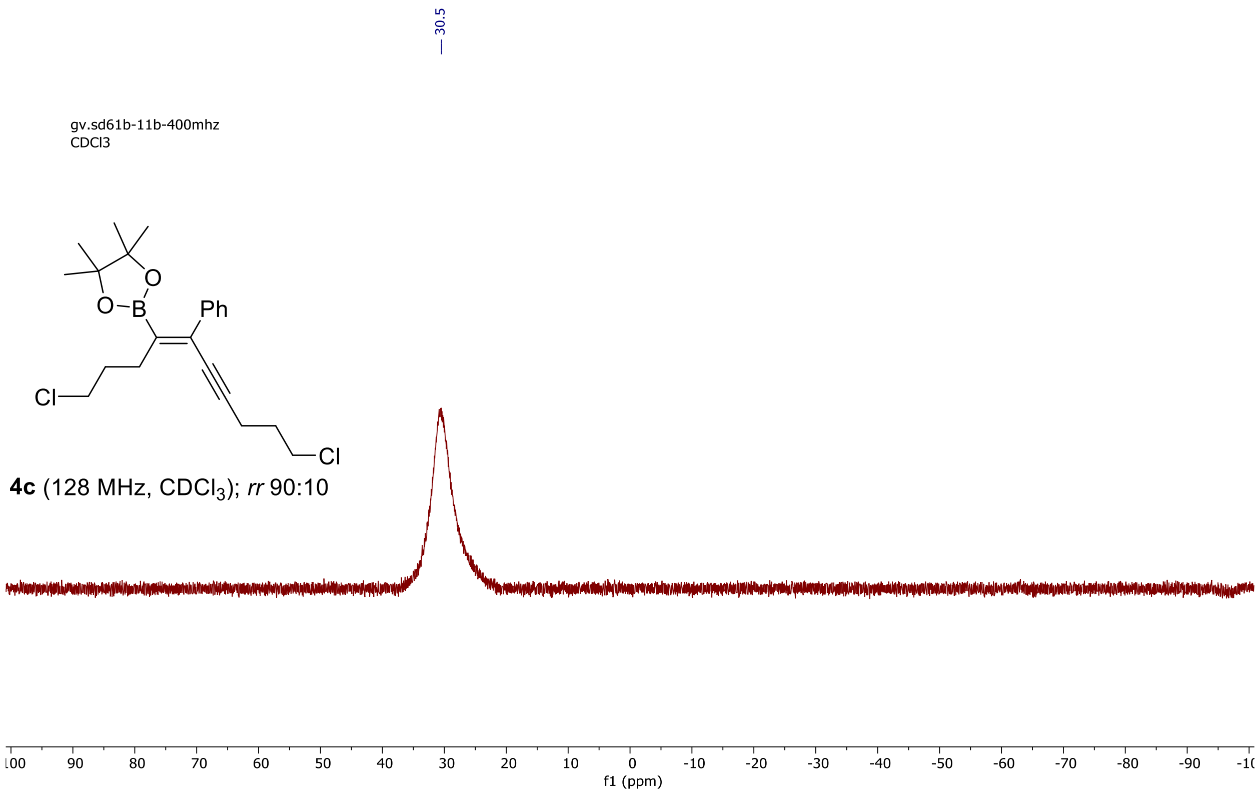
4b (128 MHz, $CDCl_3$); *rr* 85:15



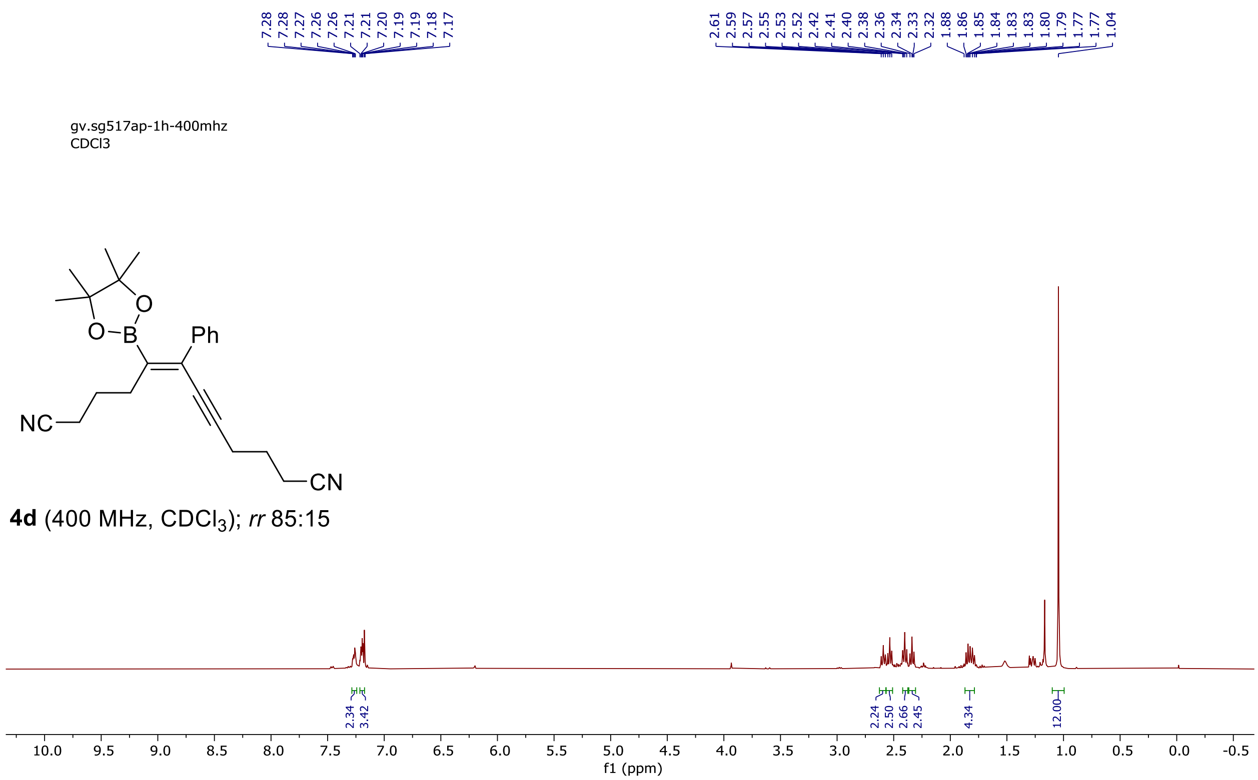
4c (400 MHz, $CDCl_3$); *rr* 90:10



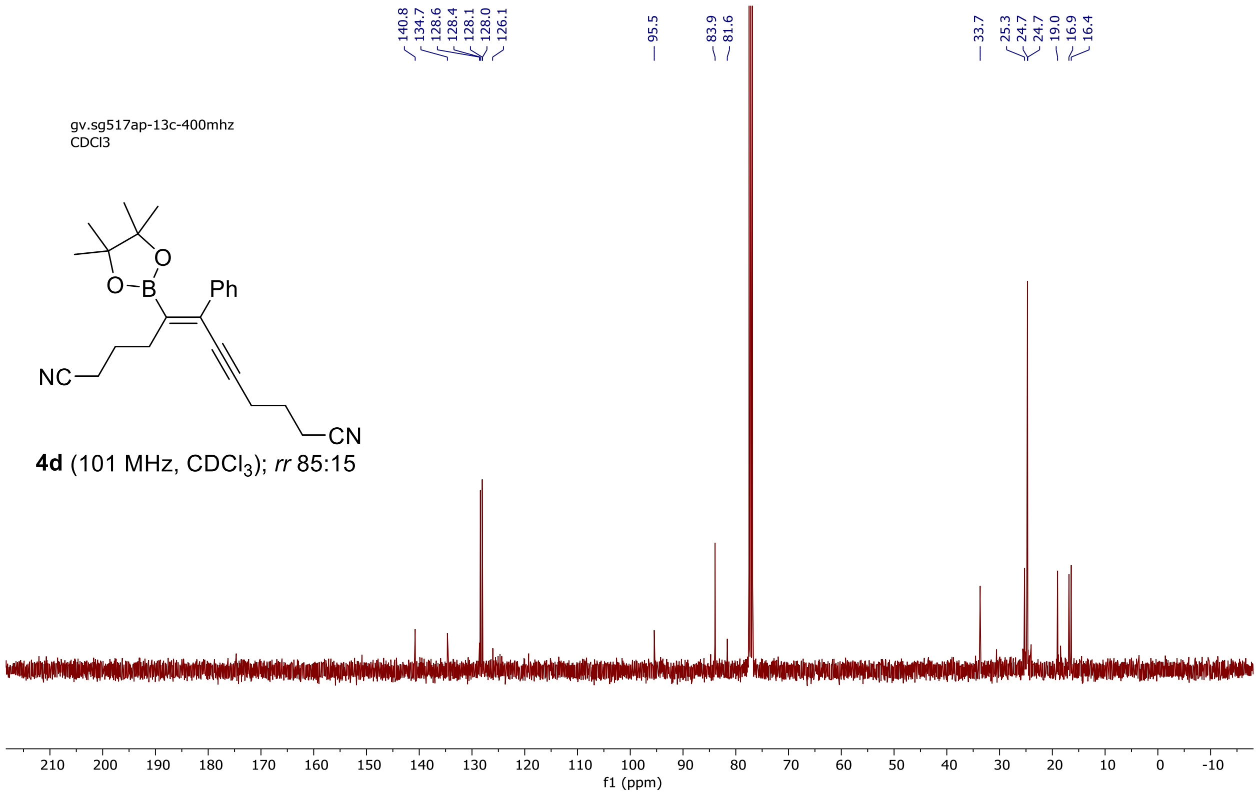
4c (101 MHz, $CDCl_3$); *rr* 90:10



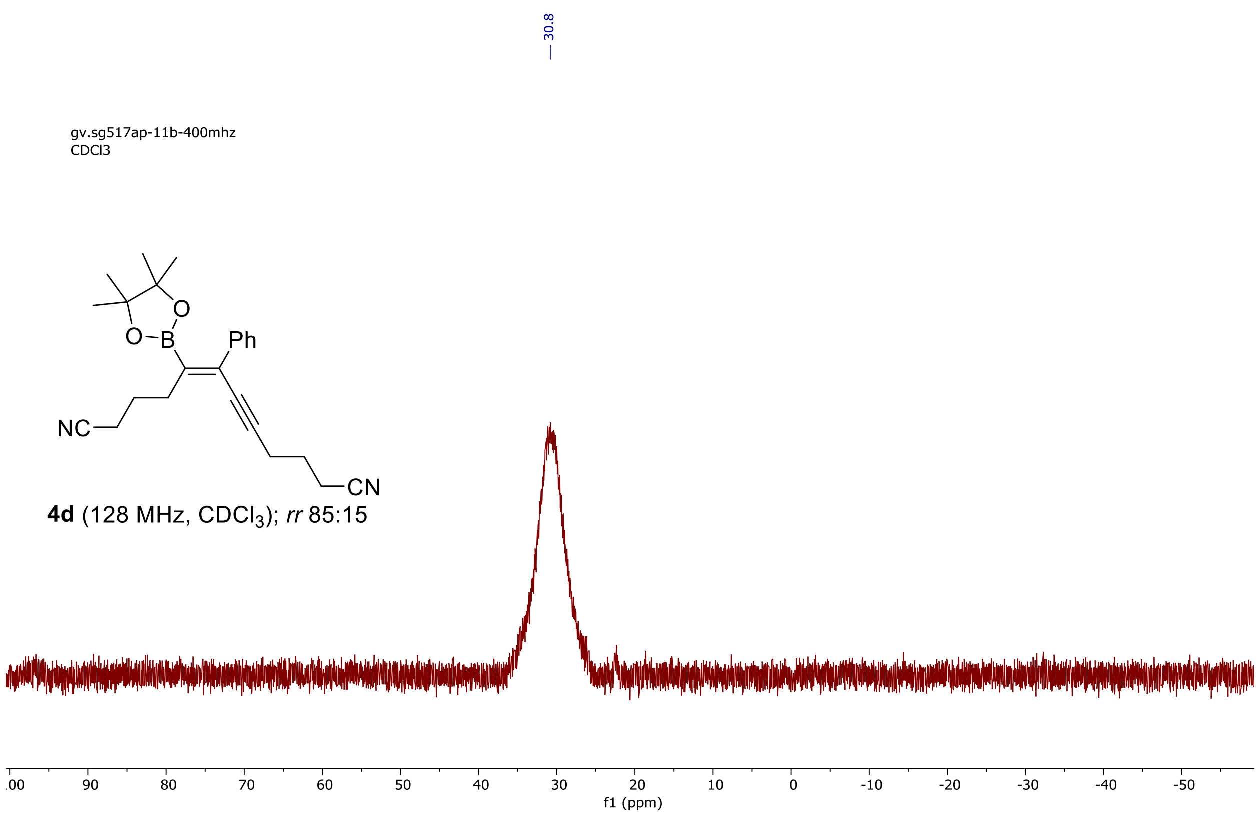
4c (128 MHz, $CDCl_3$); *rr* 90:10



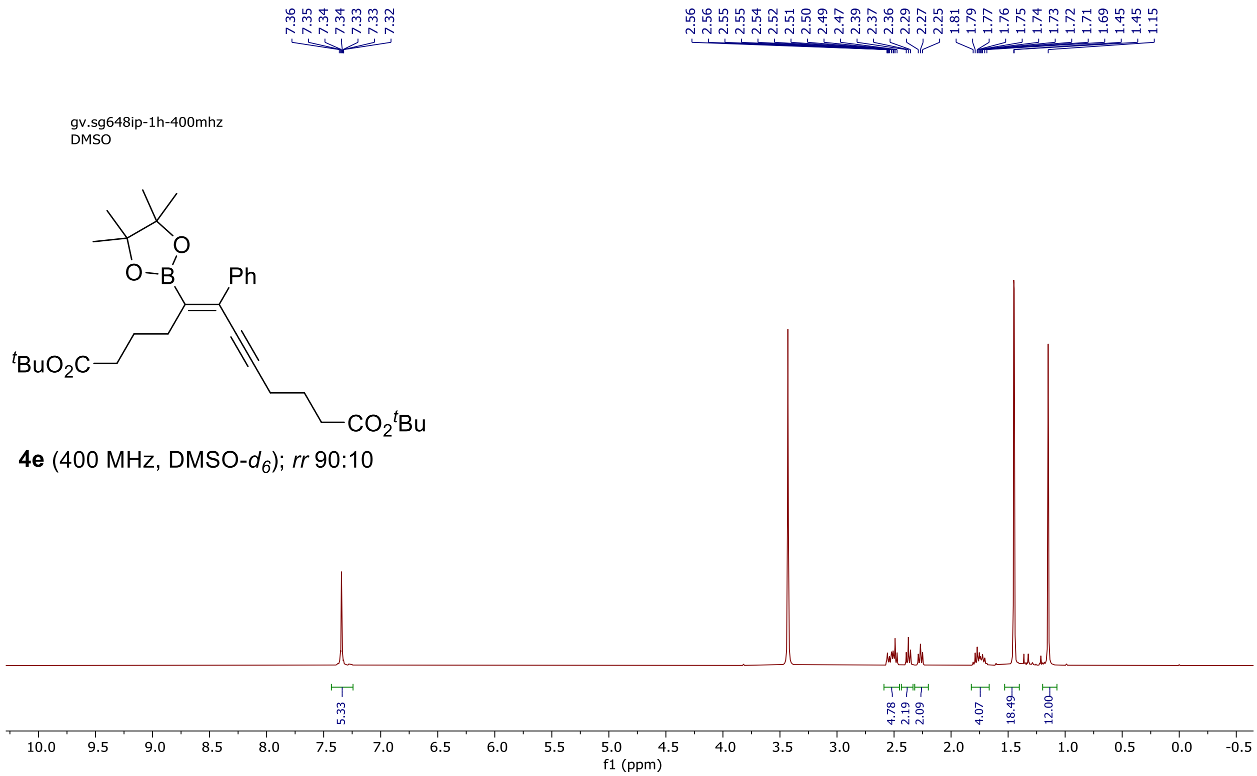
4d (400 MHz, $CDCl_3$); *rr* 85:15

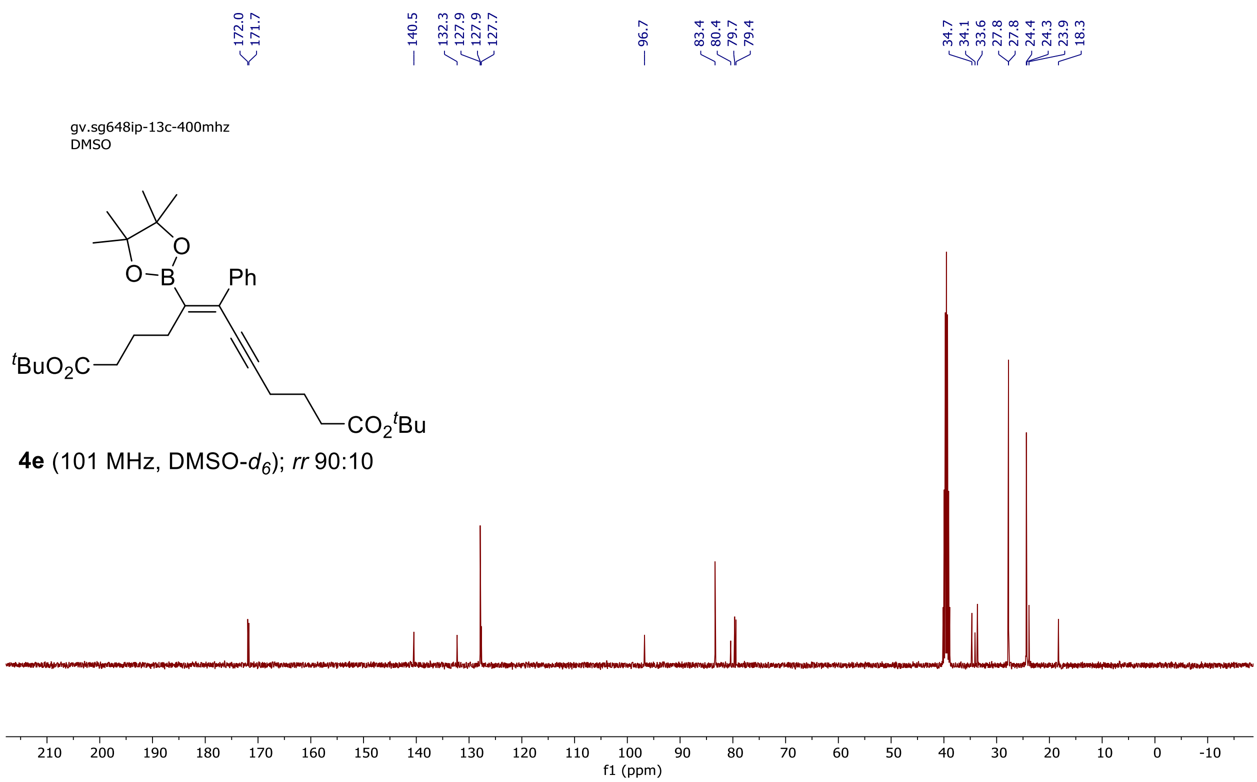


4d (101 MHz, $CDCl_3$); *rr* 85:15

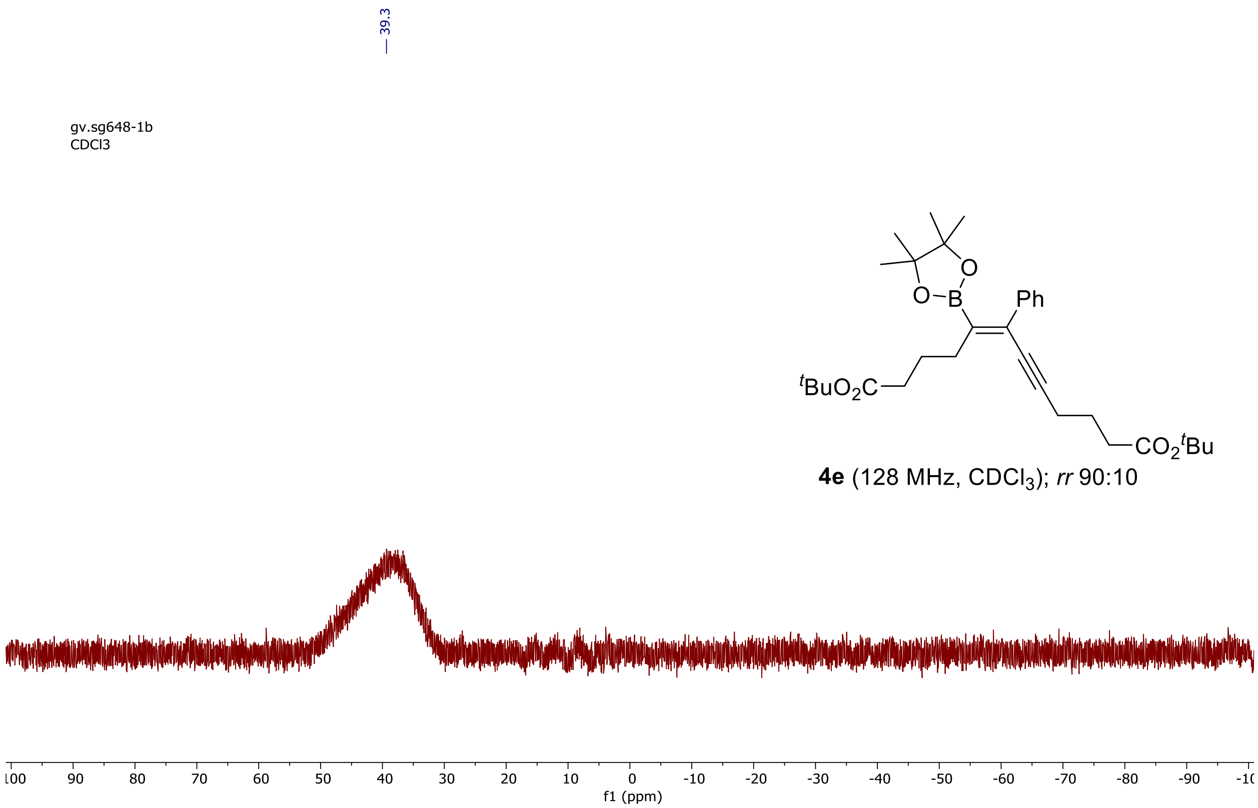


4d (128 MHz, $CDCl_3$); *rr* 85:15


7.36
7.35
7.34
7.34
7.33
7.33
7.32
2.56
2.56
2.55
2.55
2.54
2.52
2.51
2.50
2.49
2.47
2.39
2.37
2.36
2.29
2.27
2.25
1.81
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.69
1.45
1.45
1.15
gv.sg648ip-1h-400mhz
DMSO
O
O
B
Ph
^{t}BuO$_2$C
CO$_2$^{t}Bu
4e (400 MHz, DMSO-d_6); *rr* 90:10
5.33
4.78
2.19
2.09
4.07
18.49
12.00
f1 (ppm)

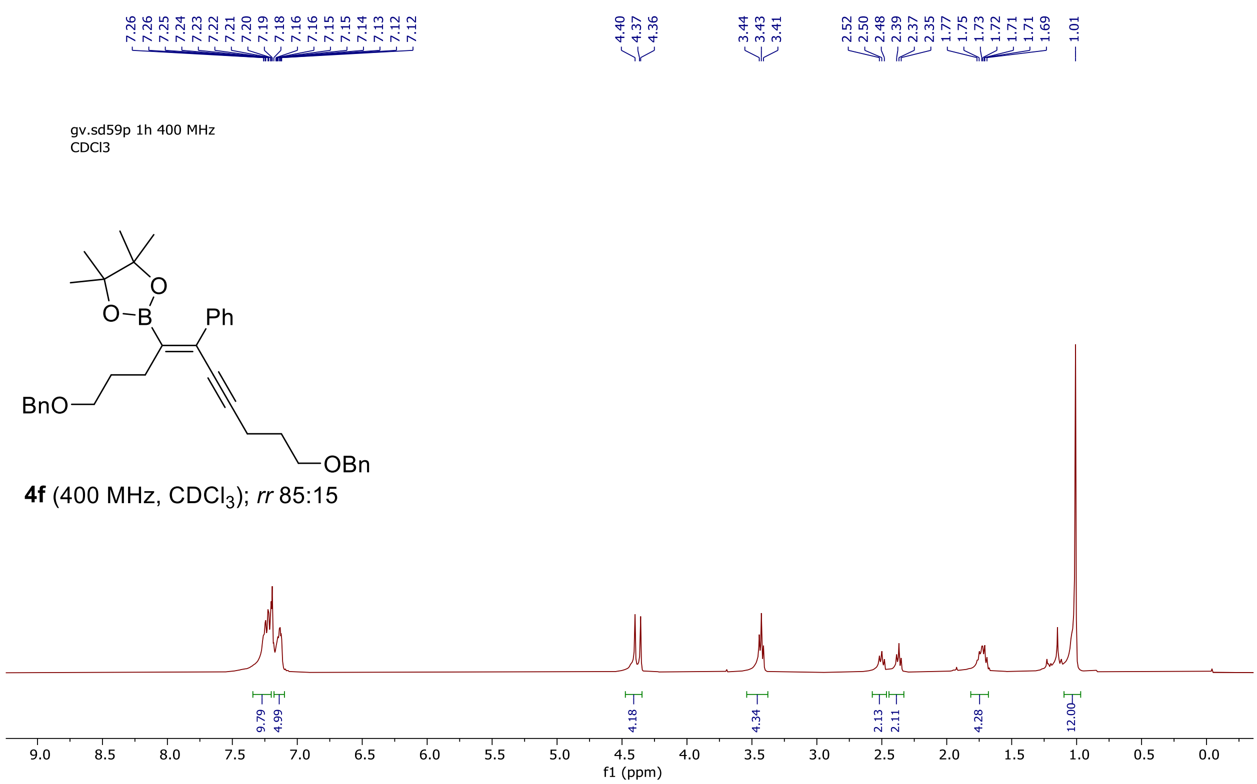

172.0
171.7
140.5
132.3
127.9
127.9
127.7
96.7
83.4
80.4
79.7
79.4
34.7
34.1
33.6
27.8
27.8
24.4
24.3
23.9
18.3
gv.sg648ip-13c-400mhz
DMSO
O
O
B
Ph
^{t}BuO$_2$C
CO$_2$^{t}Bu
4e (101 MHz, DMSO-d_6); *rr* 90:10
f1 (ppm)

gv.sg648-1b
CDCl3

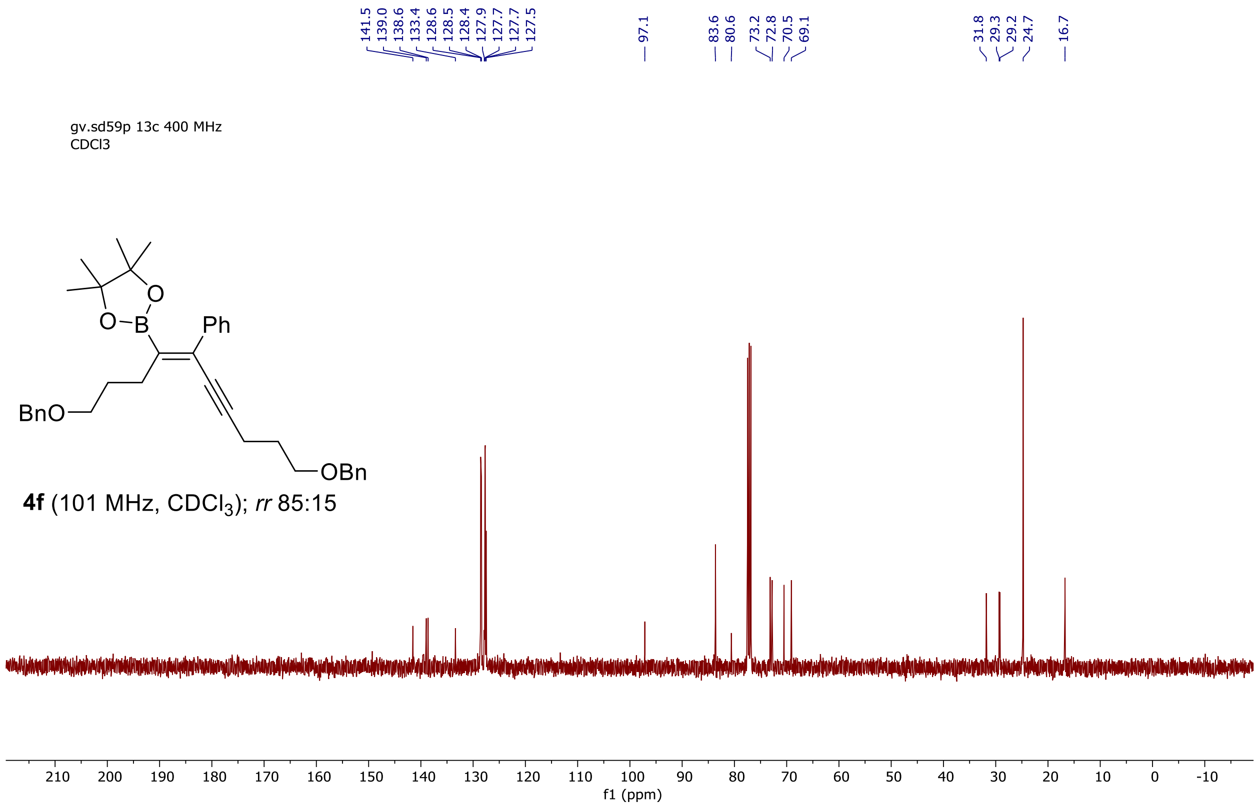


4e (128 MHz, $CDCl_3$); *rr* 90:10

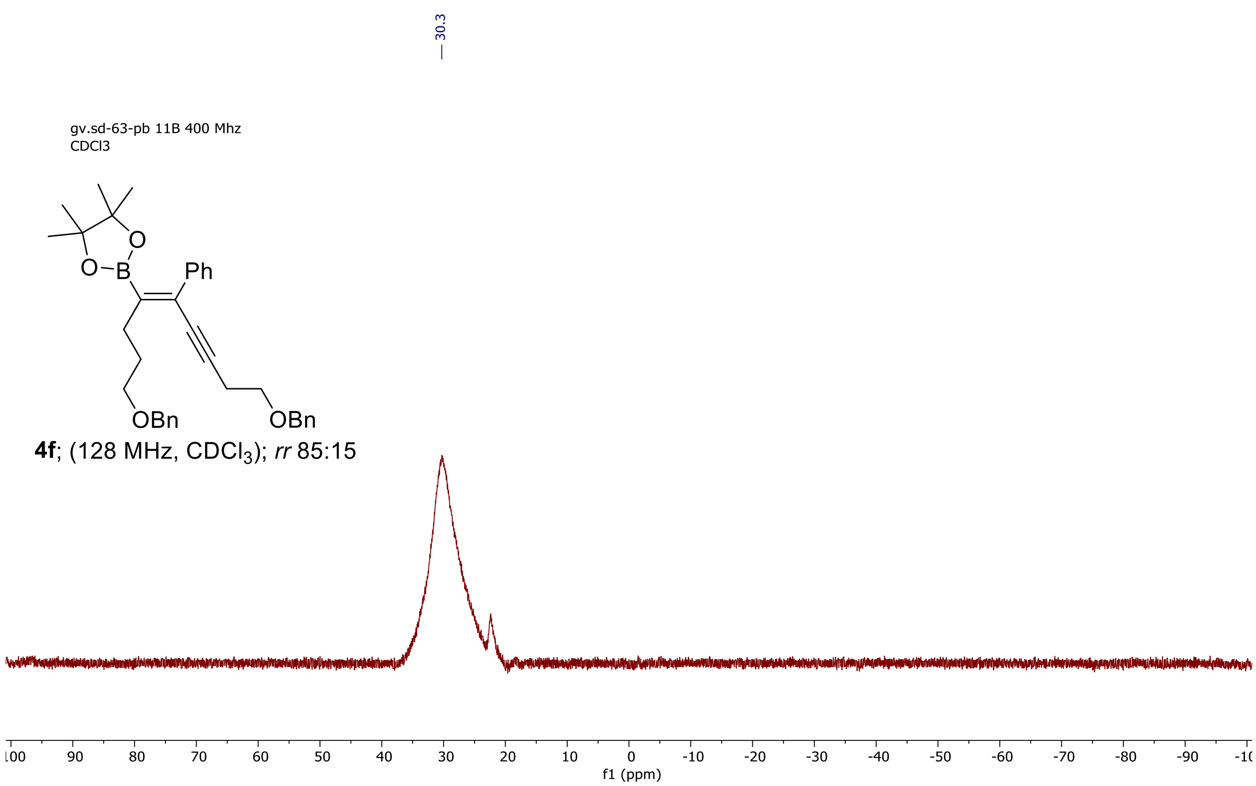
gv.sd59p 1h 400 MHz
CDCl3



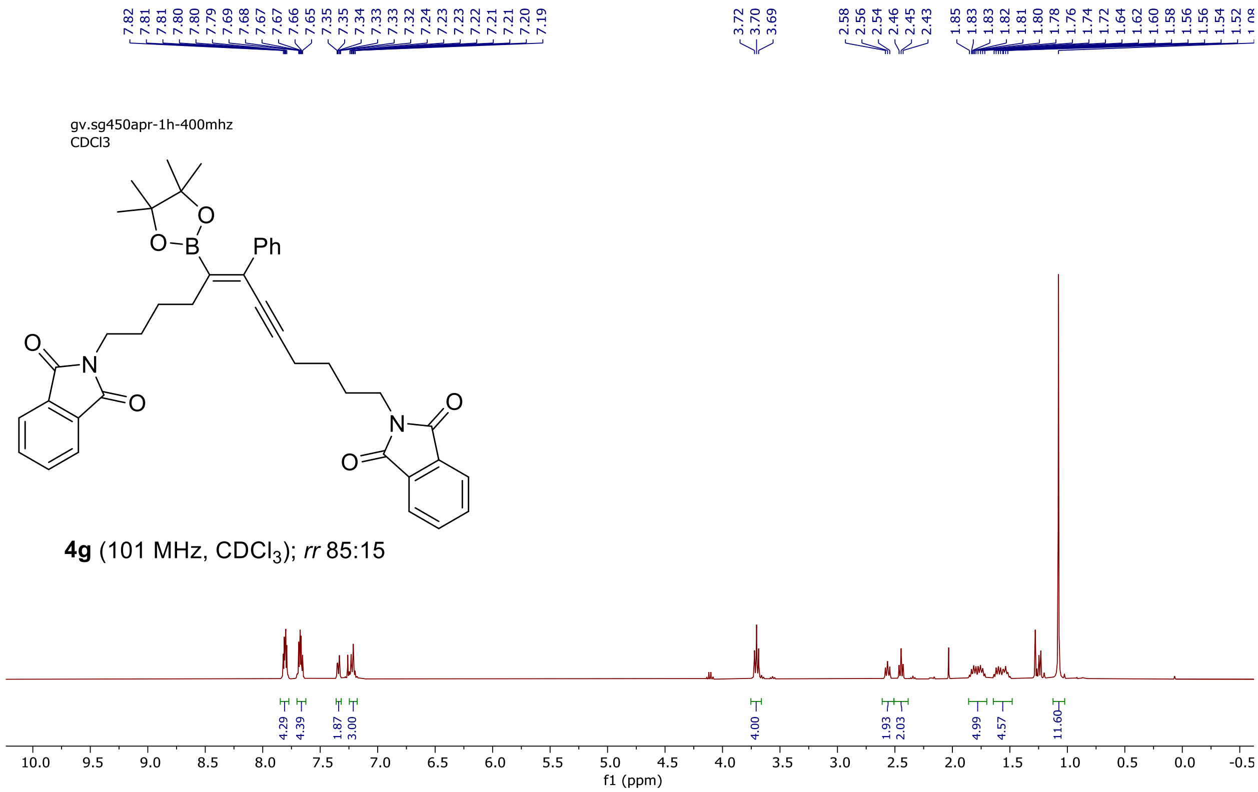
4f (400 MHz, $CDCl_3$); *rr* 85:15



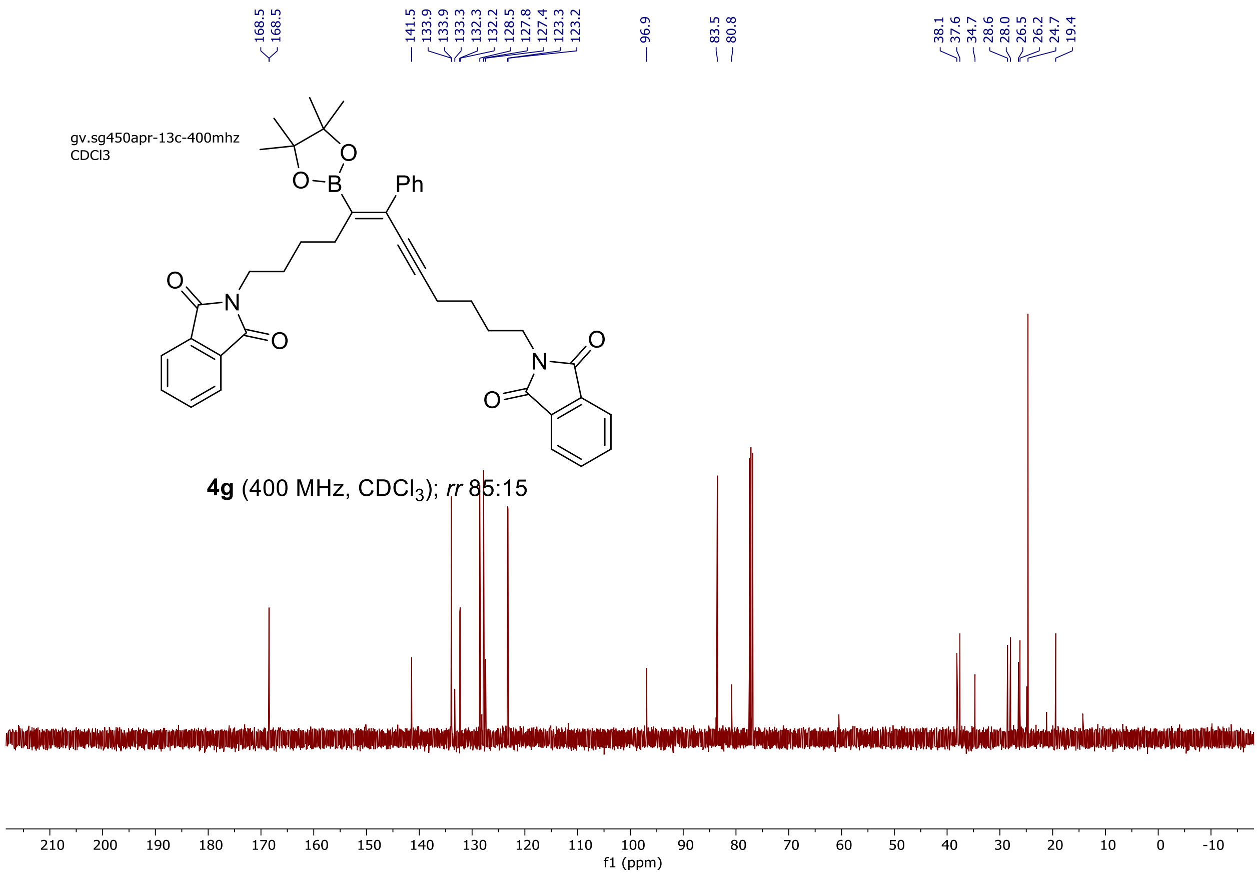
4f (101 MHz, $CDCl_3$); *rr* 85:15



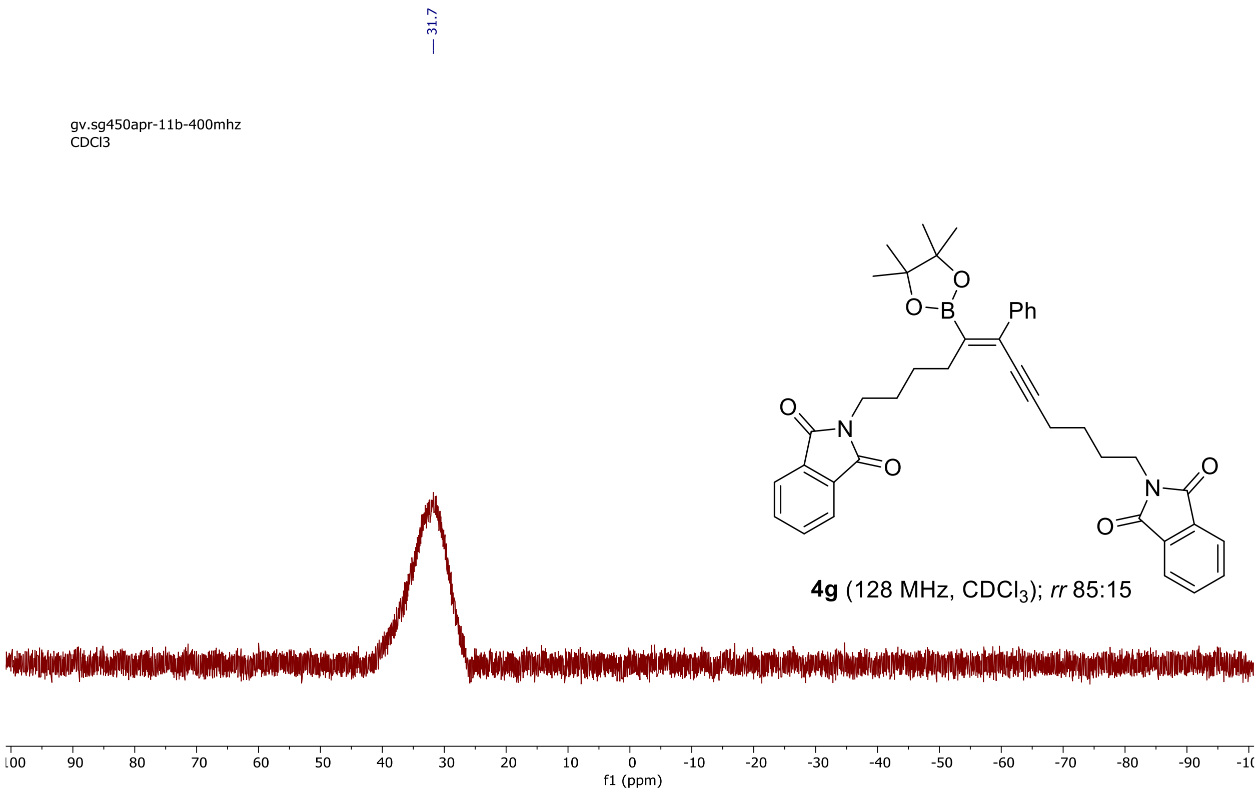
4f; (128 MHz, $CDCl_3$); *rr* 85:15



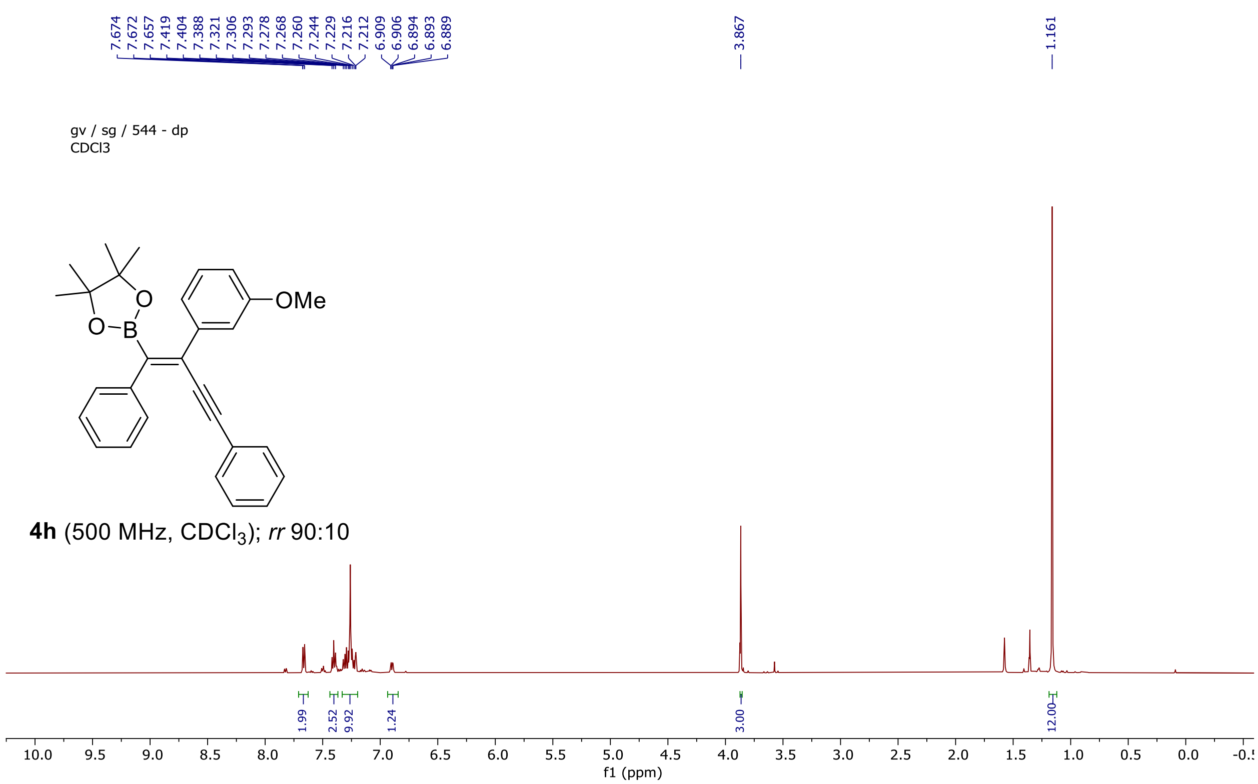
4g (101 MHz, $CDCl_3$); *rr* 85:15



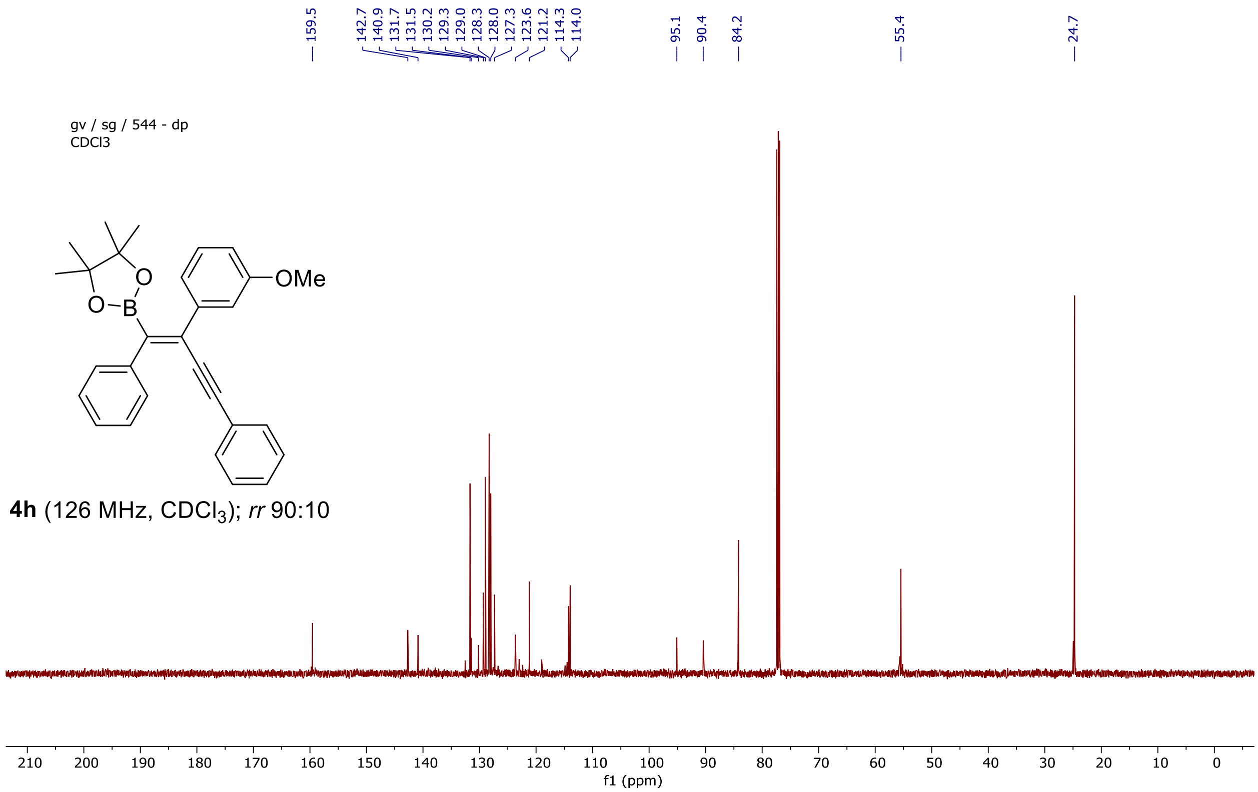
4g (400 MHz, $CDCl_3$); *rr* 85:15

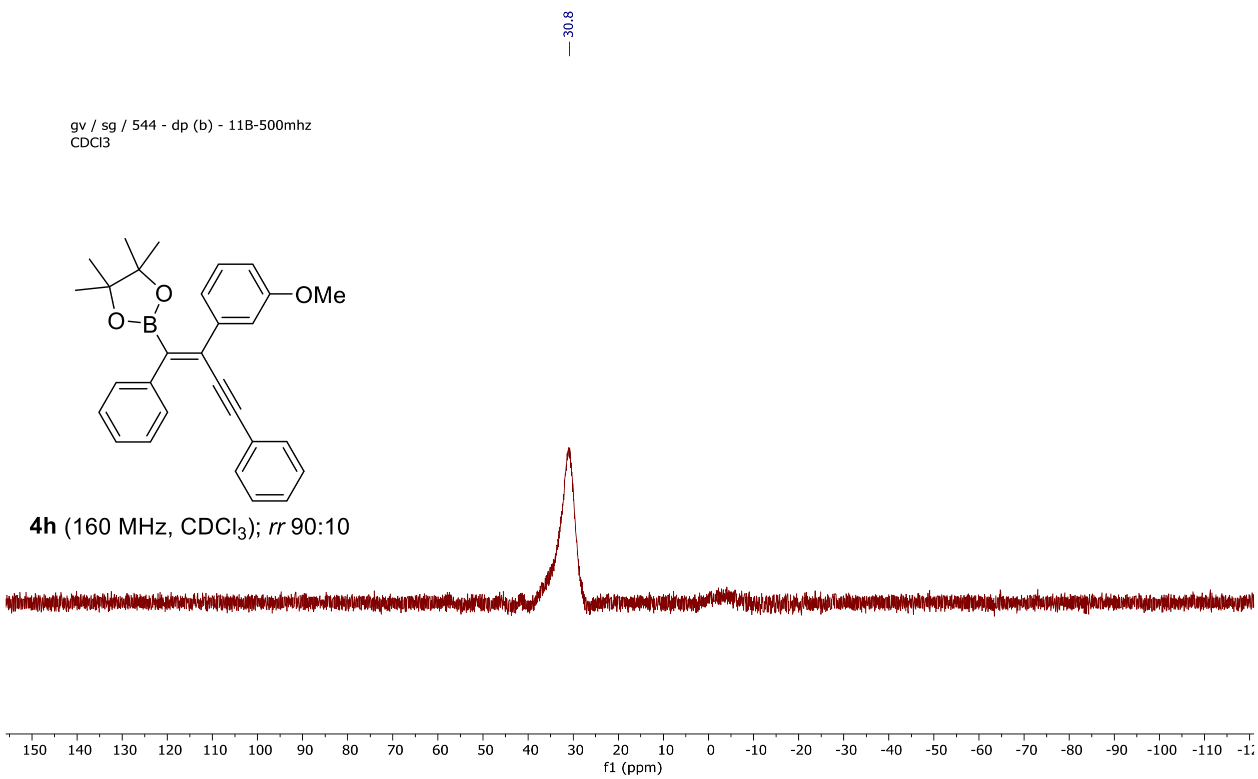


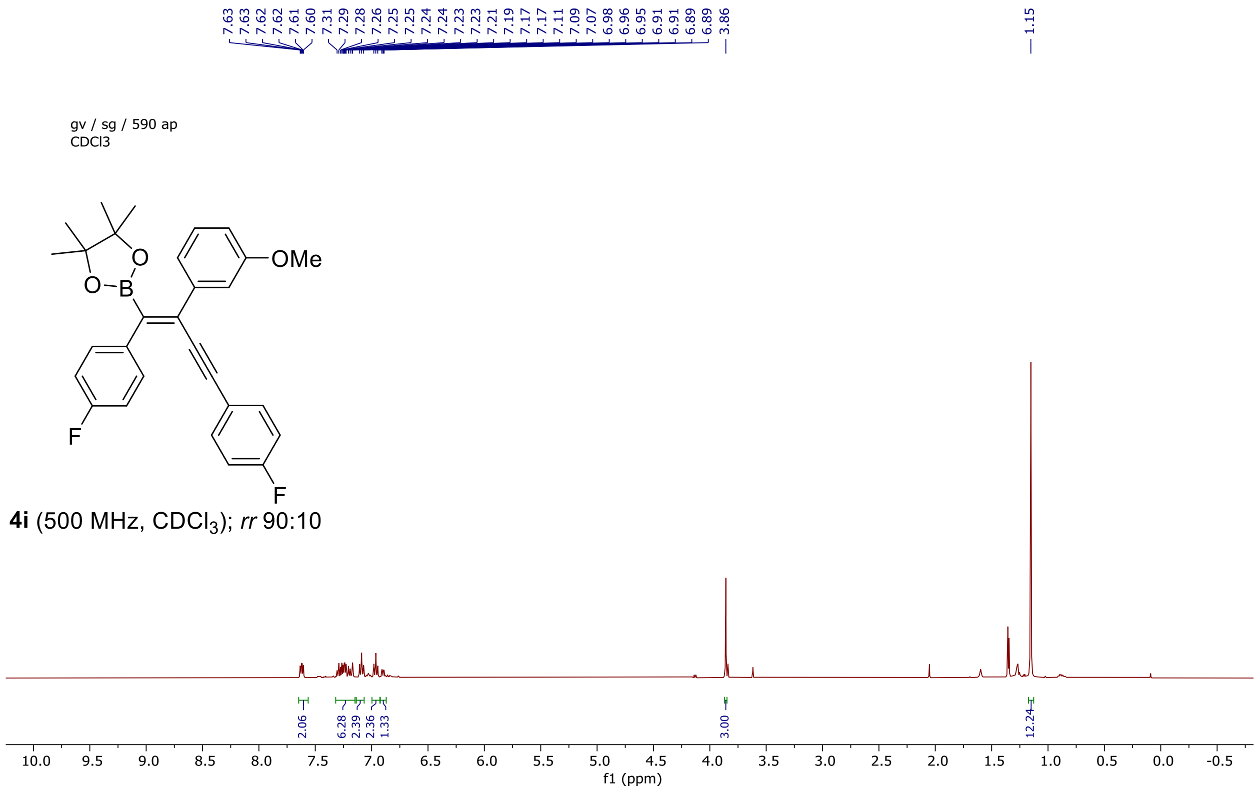
4g (128 MHz, $CDCl_3$); *rr* 85:15



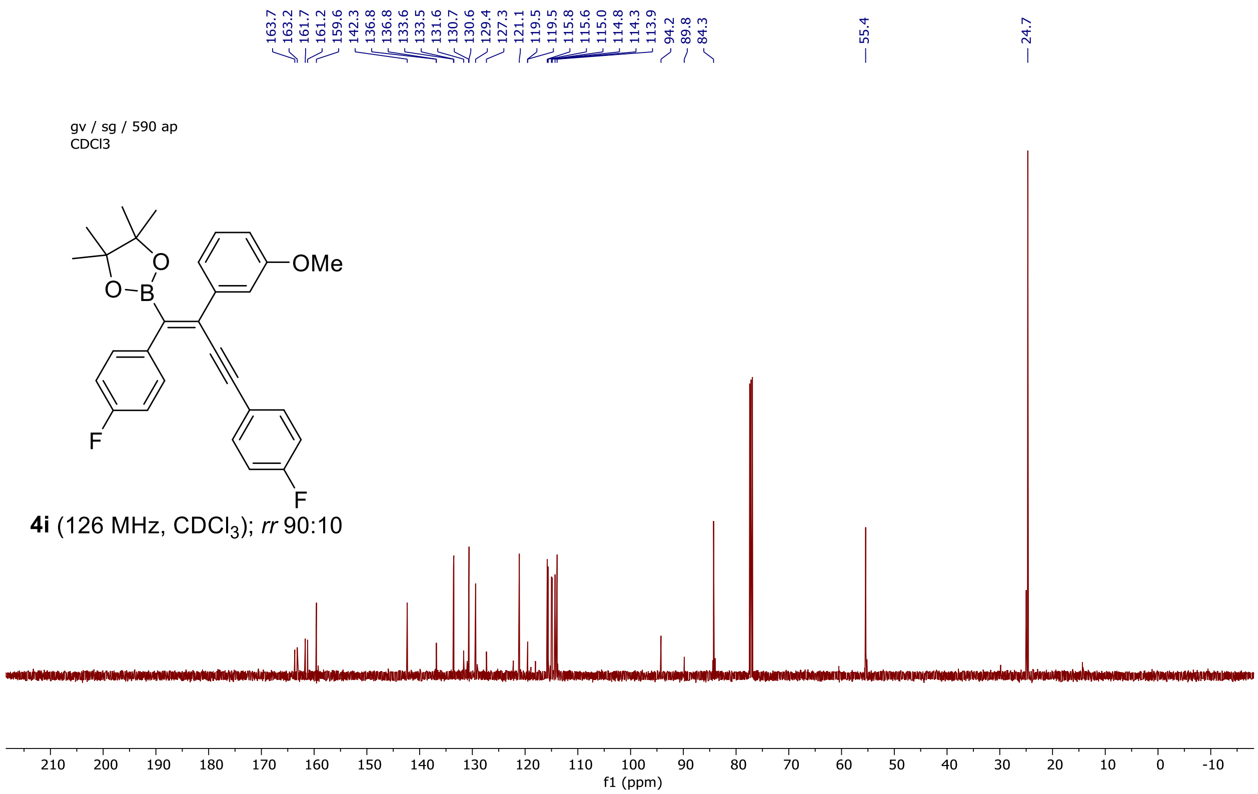
4h (500 MHz, $CDCl_3$); *rr* 90:10


159.5
142.7
140.9
131.7
131.5
130.2
129.3
129.0
128.3
128.0
127.3
123.6
121.2
114.3
114.0
95.1
90.4
84.2
55.4
24.7
gv / sg / 544 - dp
CDCl3
OMe
O
B
O
4h (126 MHz, $CDCl_3$); rr 90:10
f1 (ppm)

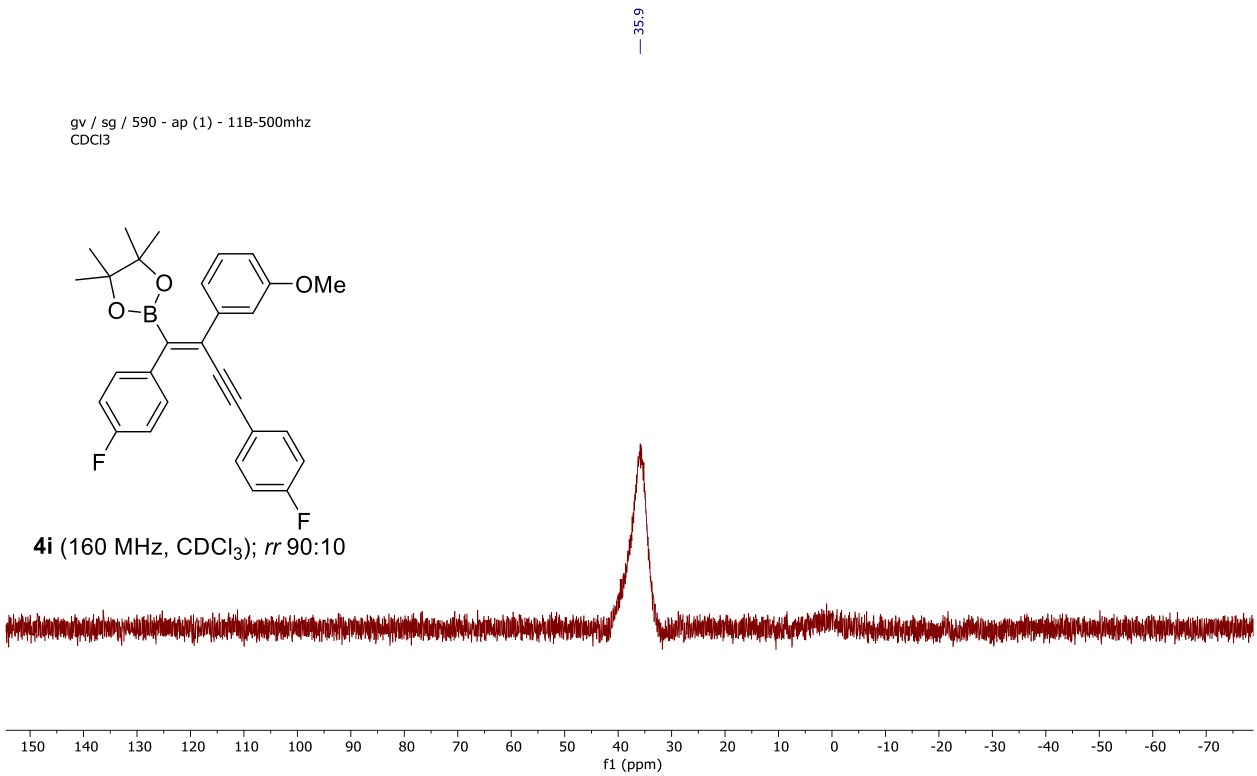

30.8
gv / sg / 544 - dp (b) - 11B-500mhz
CDCl3
OMe
O
B
O
4h (160 MHz, $CDCl_3$); rr 90:10
f1 (ppm)



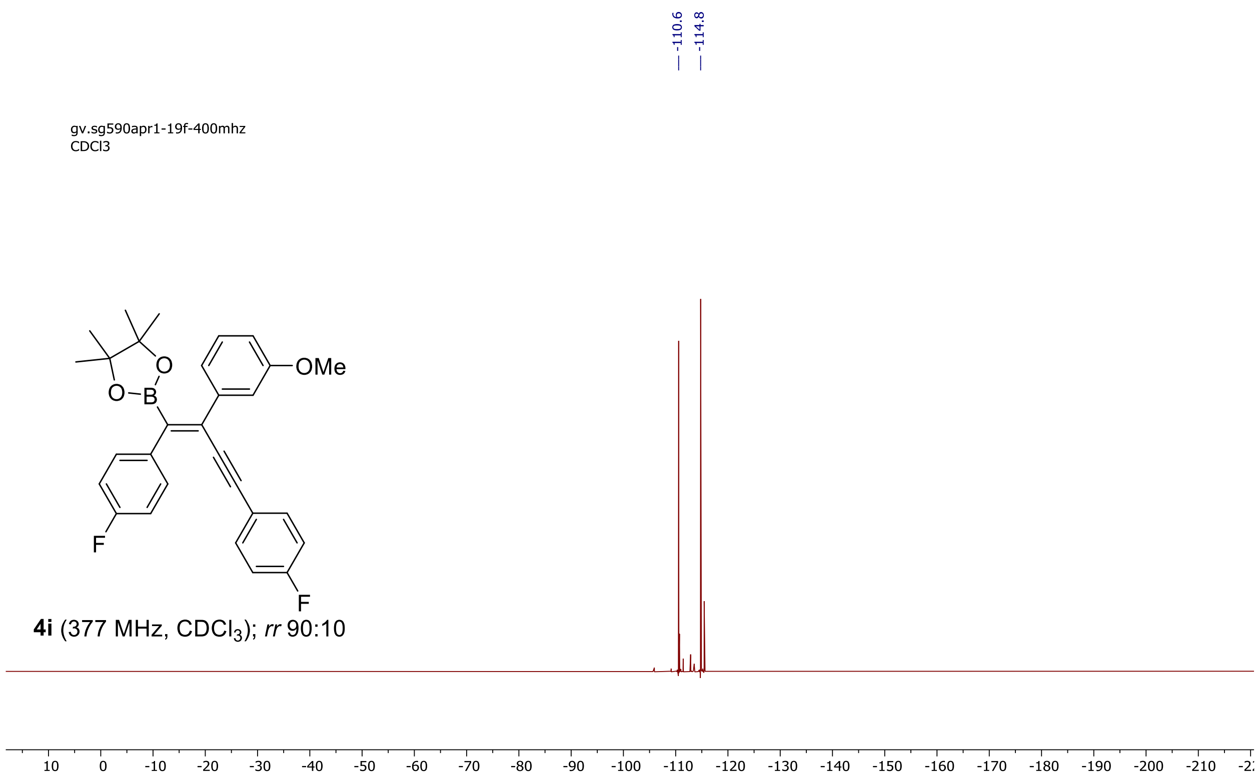
4i (500 MHz, $CDCl_3$); *rr* 90:10



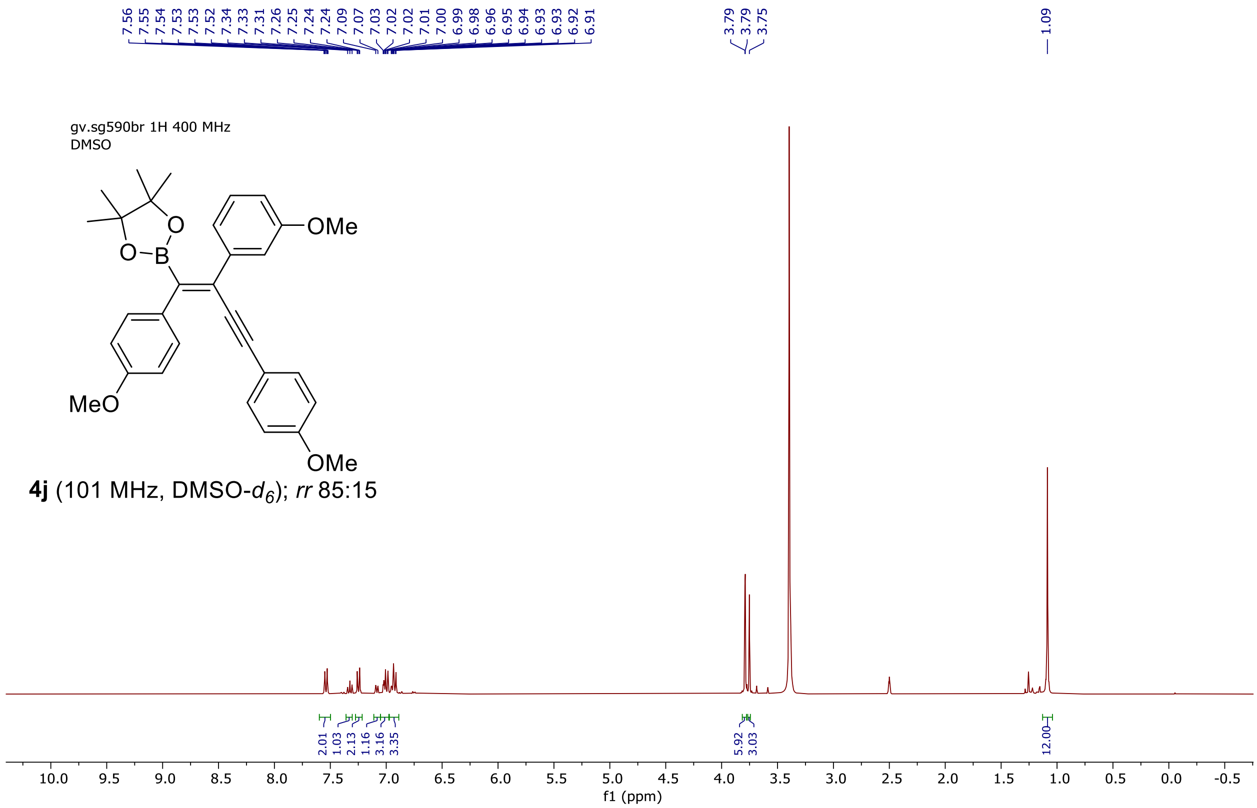
4i (126 MHz, $CDCl_3$); *rr* 90:10



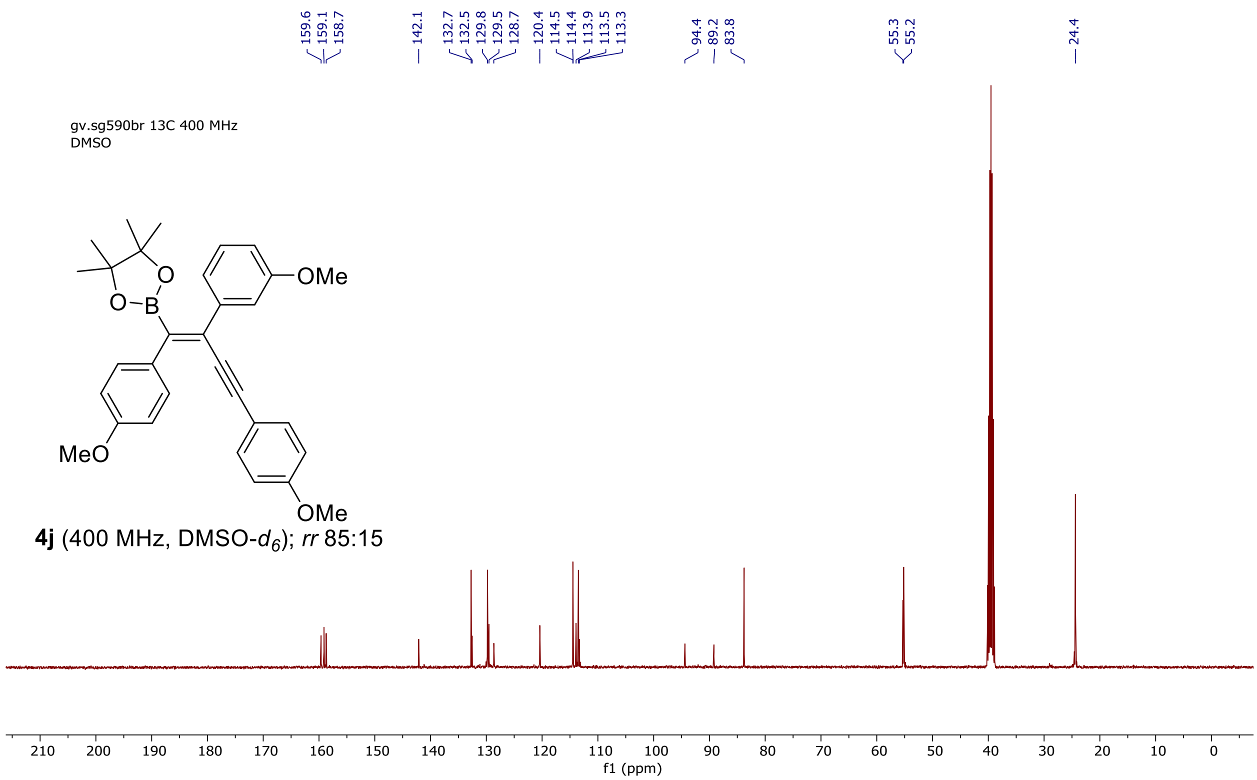
4i (160 MHz, $CDCl_3$); *rr* 90:10



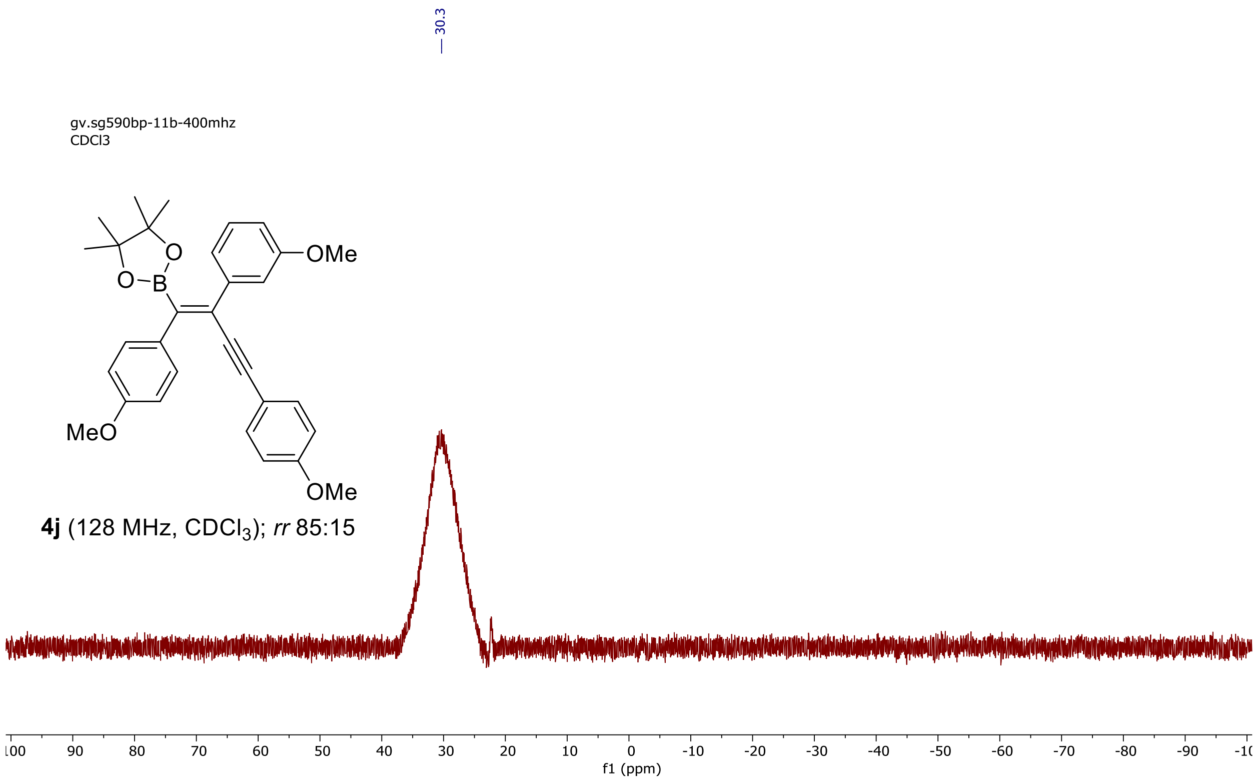
4i (377 MHz, $CDCl_3$); *rr* 90:10



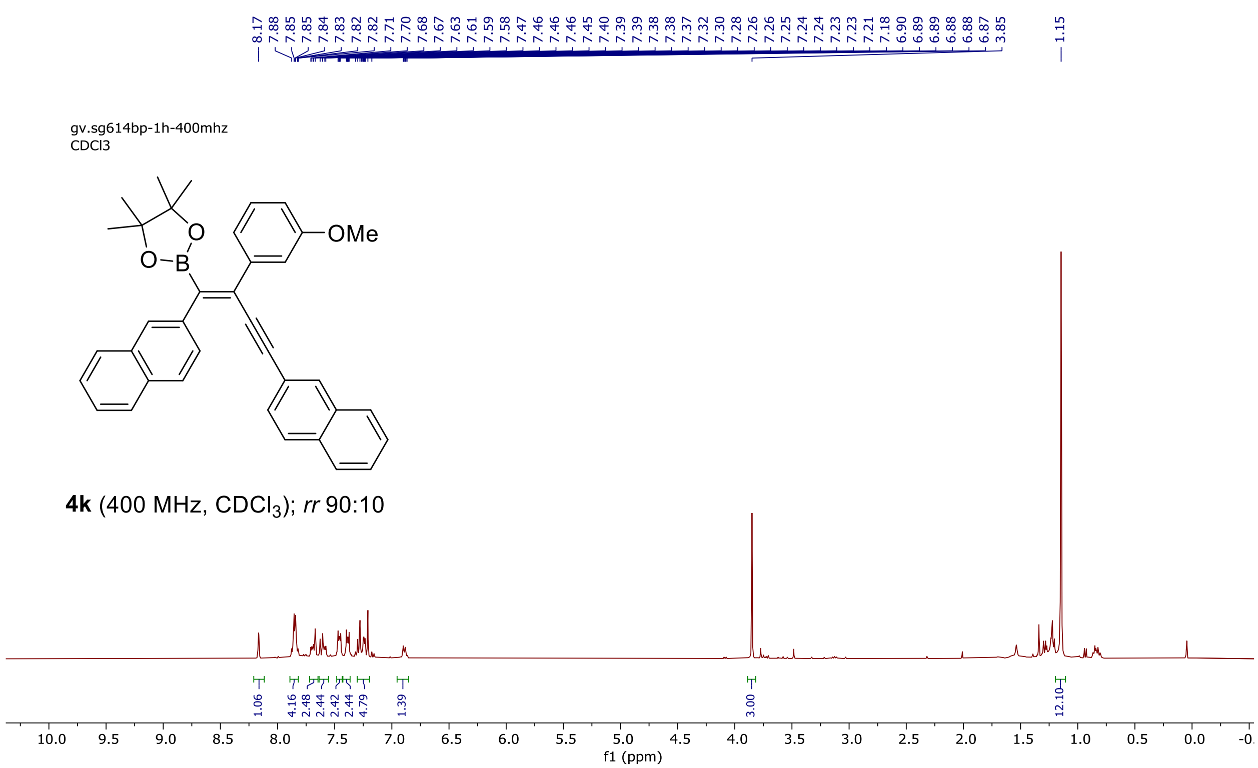
4j (101 MHz, DMSO-d_6); *rr* 85:15



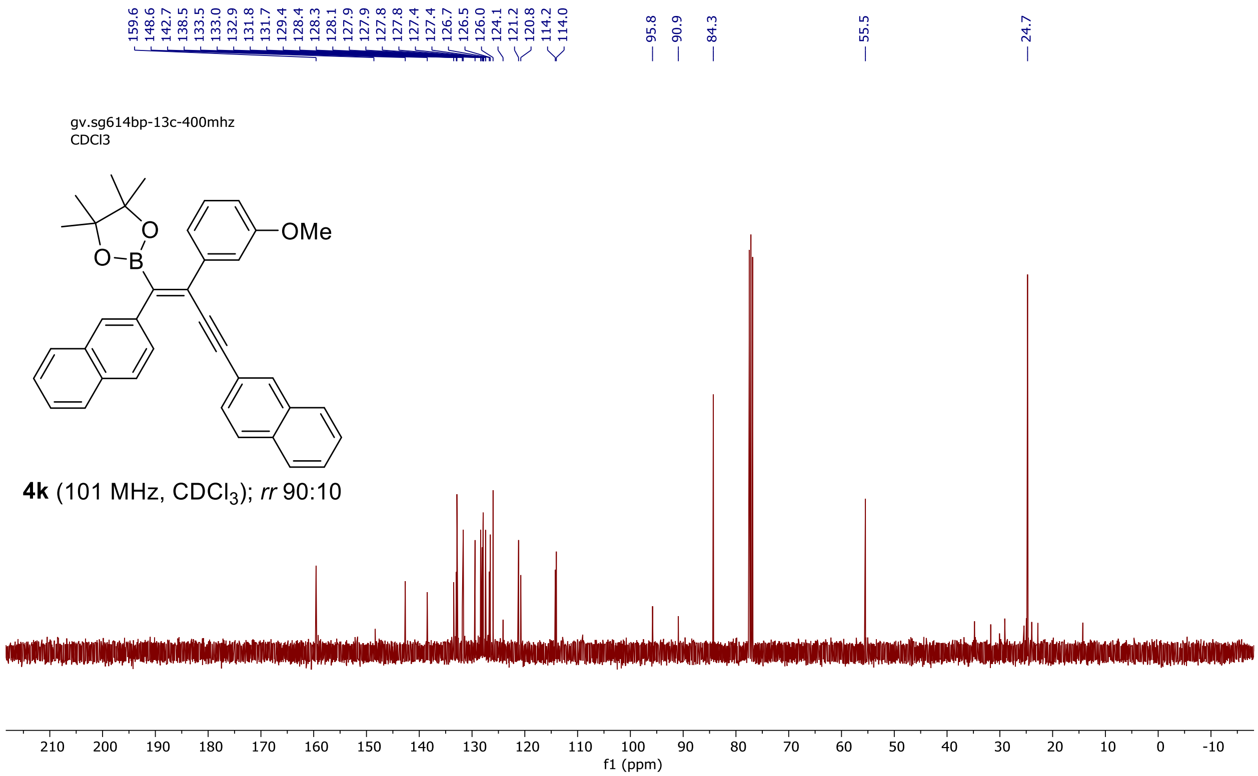
4j (400 MHz, DMSO-d_6); *rr* 85:15

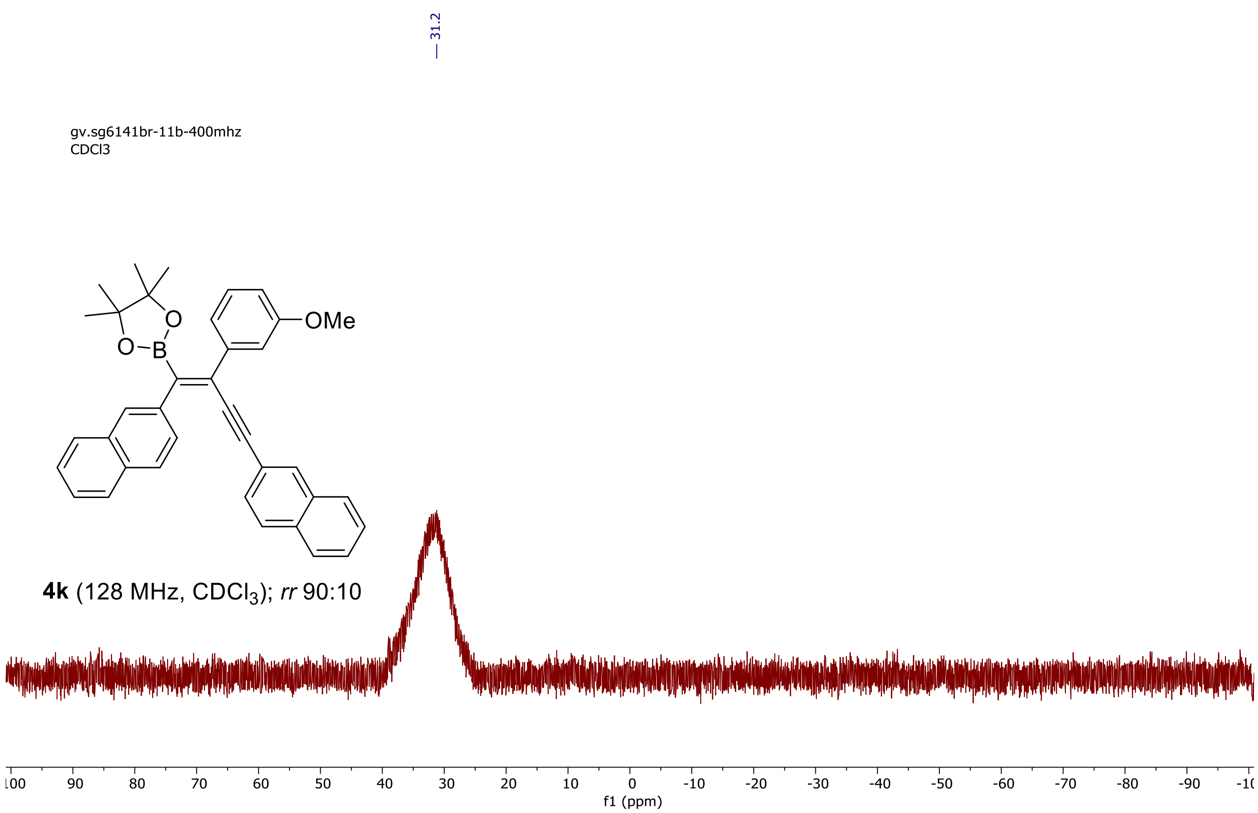


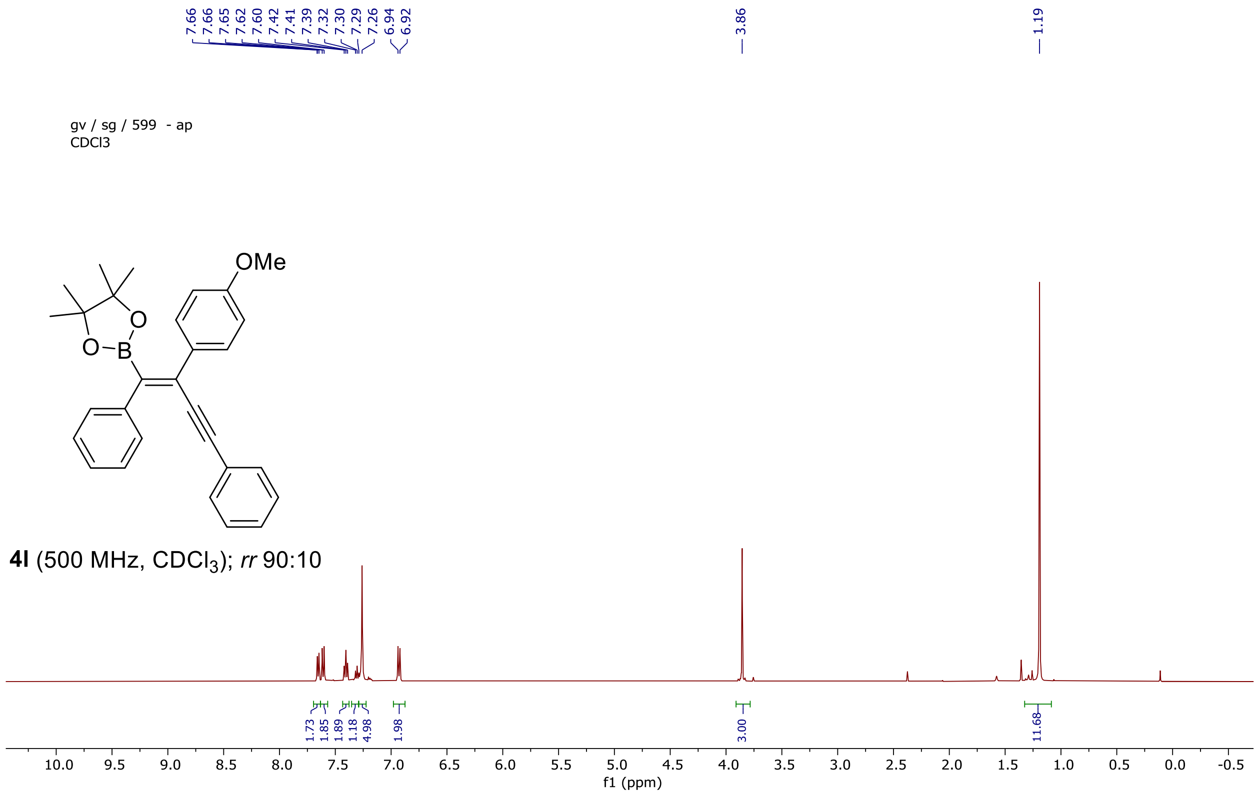
30.3
gv.sg590bp-11b-400mhz
CDCl3
OMe
O
B
O
MeO
OMe
4j (128 MHz, CDCl3); rr 85:15
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)



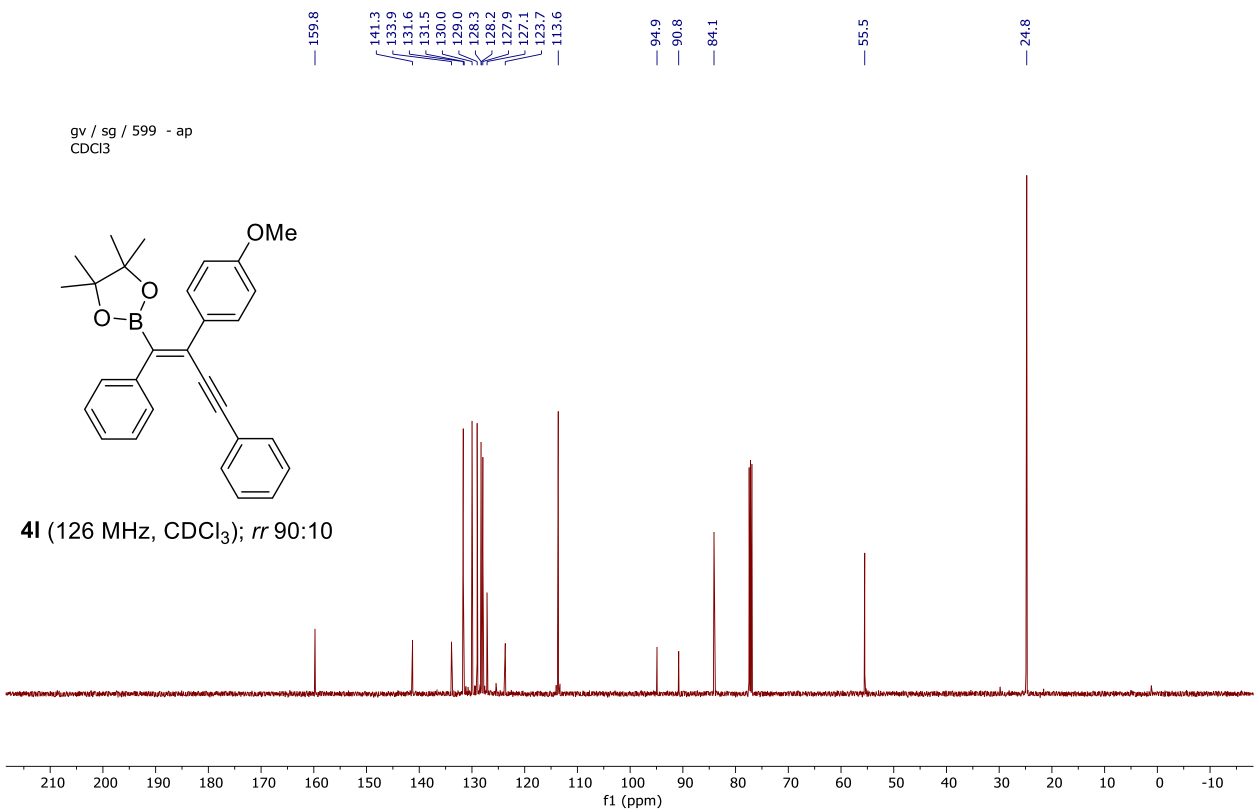
8.17 7.88 7.85 7.85 7.84 7.83 7.82 7.82 7.71 7.70 7.68 7.67 7.63 7.61 7.59 7.58 7.47 7.46 7.46 7.46 7.45 7.40 7.39 7.39 7.38 7.38 7.37 7.32 7.30 7.28 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.21 7.18 6.90 6.89 6.89 6.88 6.88 6.87 3.85
1.15
gv.sg614bp-1h-400mhz
CDCl3
OMe
O
B
O
4k (400 MHz, CDCl3); rr 90:10
1.06 4.16 2.48 2.44 2.42 2.44 4.79 1.39
3.00
12.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.6
148.6
142.7
138.5
133.5
133.0
132.9
131.8
131.7
129.4
128.4
128.3
128.1
127.9
127.9
127.8
127.8
127.4
127.4
126.7
126.5
126.0
124.1
121.2
120.8
114.2
114.0
95.8
90.9
84.3
55.5
24.7
gv.sg614bp-13c-400mhz
CDCl3
OMe
O
O
B
4k (101 MHz, $CDCl_3$); *rr* 90:10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

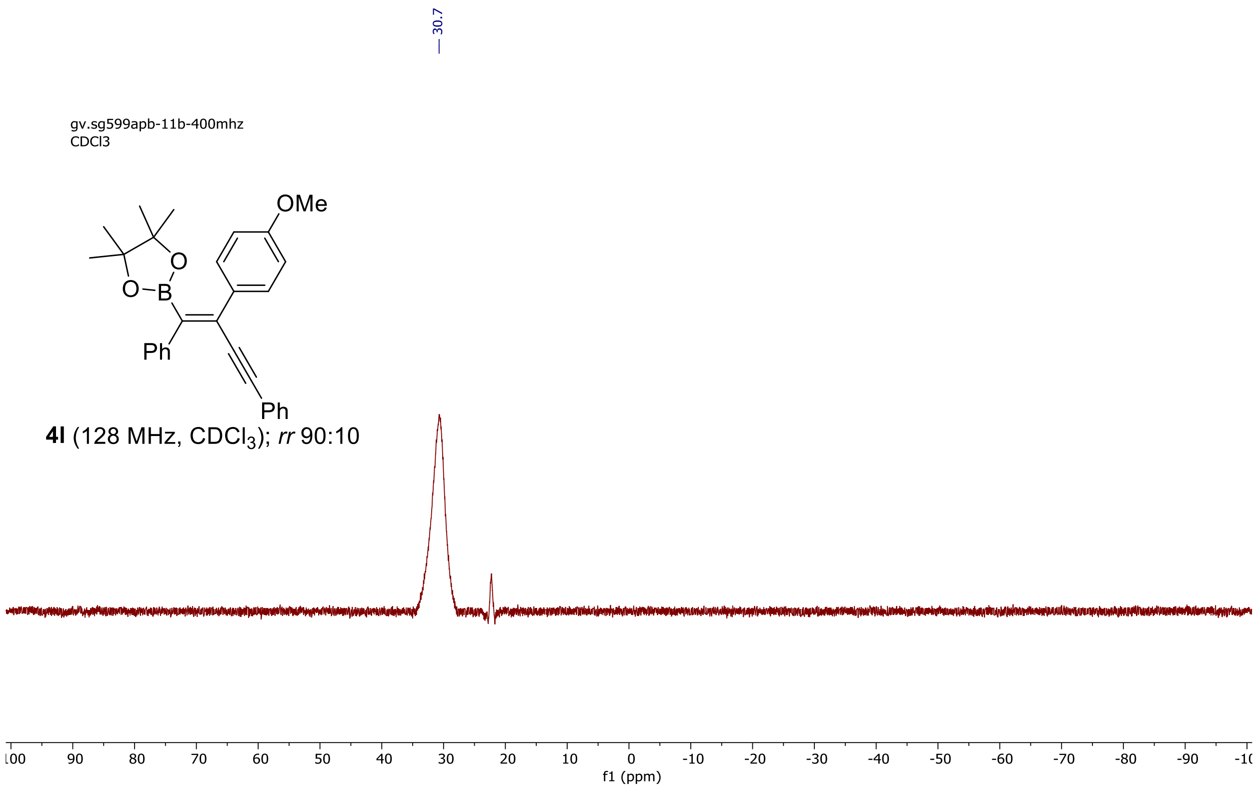

31.2
gv.sg6141br-11b-400mhz
CDCl3
OMe
O
O
B
4k (128 MHz, $CDCl_3$); *rr* 90:10
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)



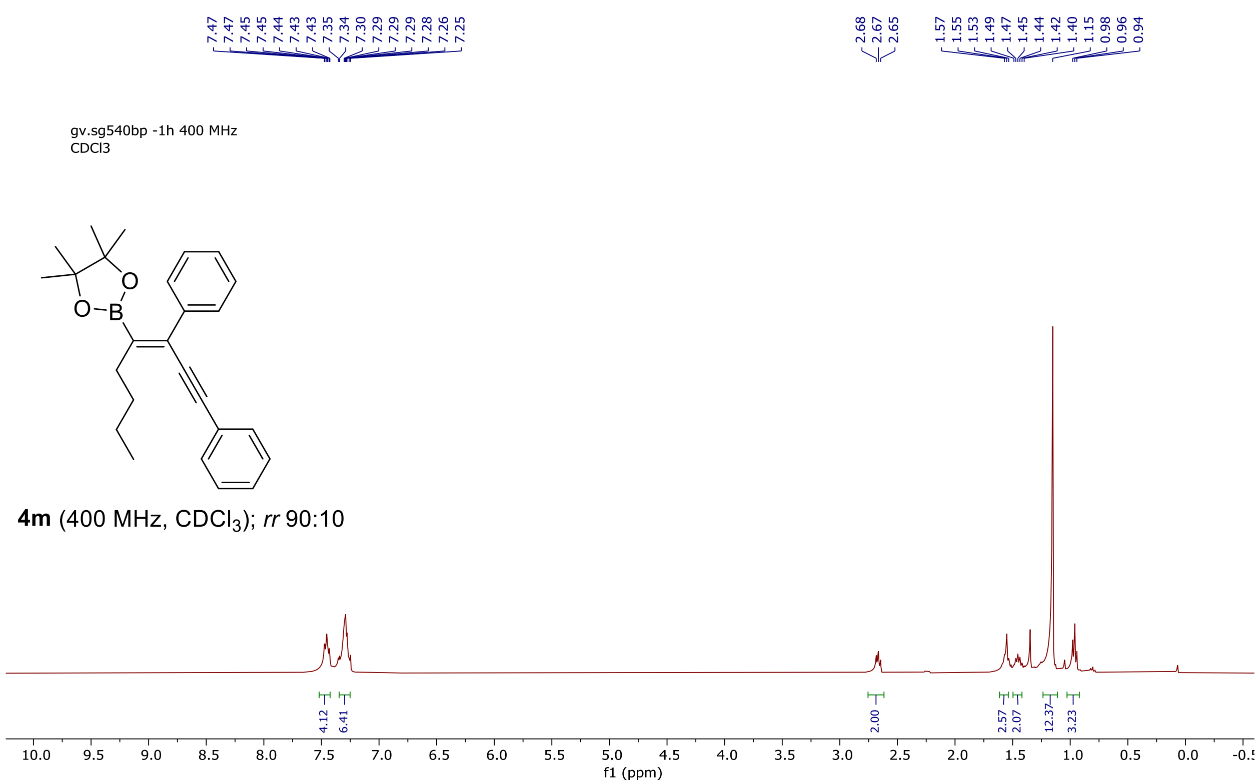
4l (500 MHz, $CDCl_3$); *rr* 90:10



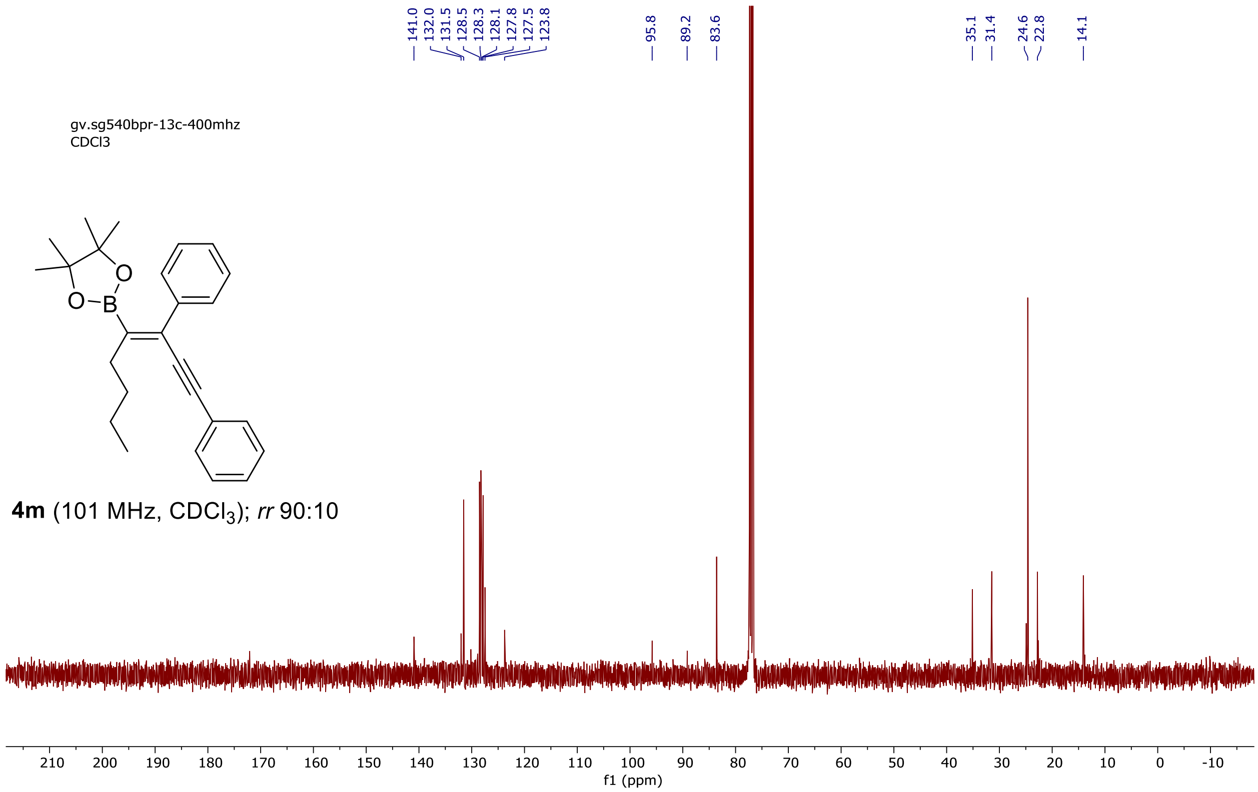
4l (126 MHz, $CDCl_3$); *rr* 90:10



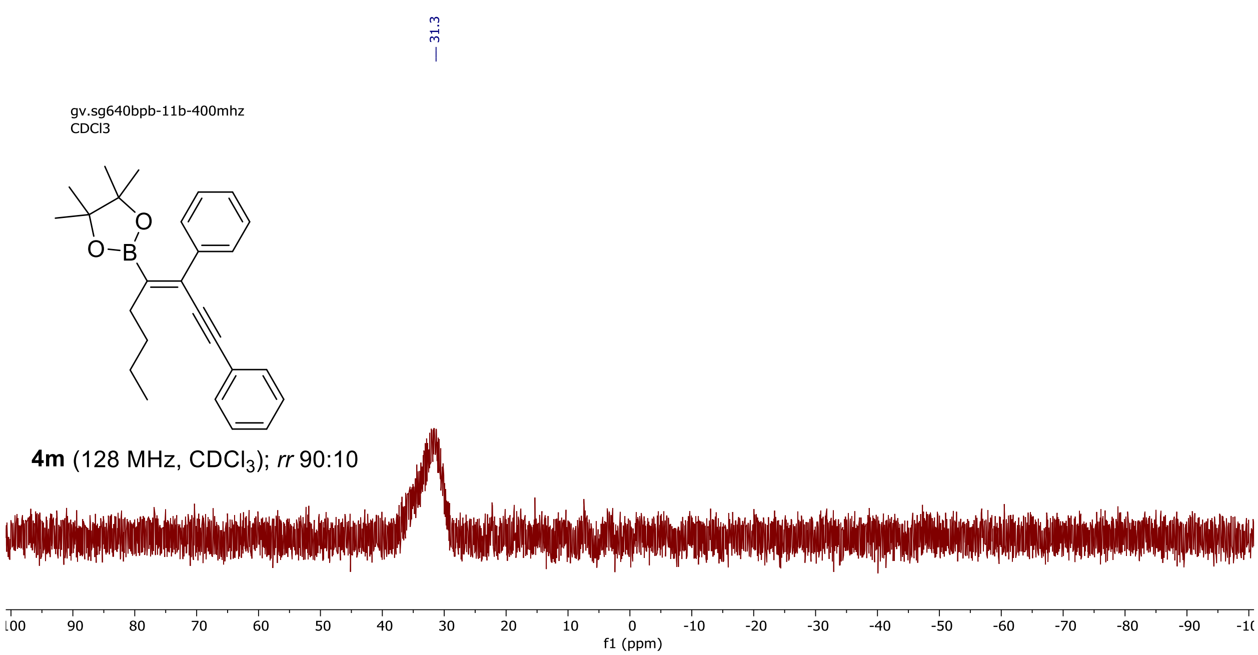
4l (128 MHz, $CDCl_3$); *rr* 90:10



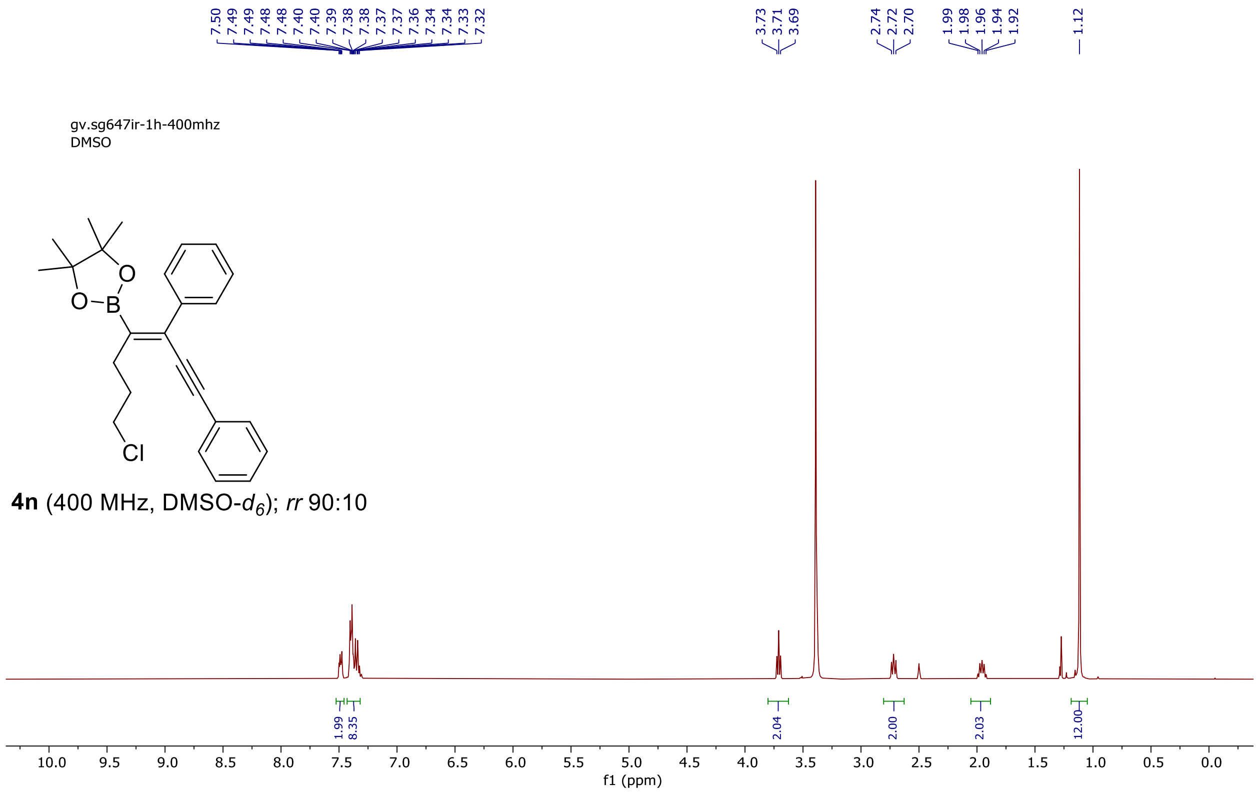
4m (400 MHz, $CDCl_3$); *rr* 90:10

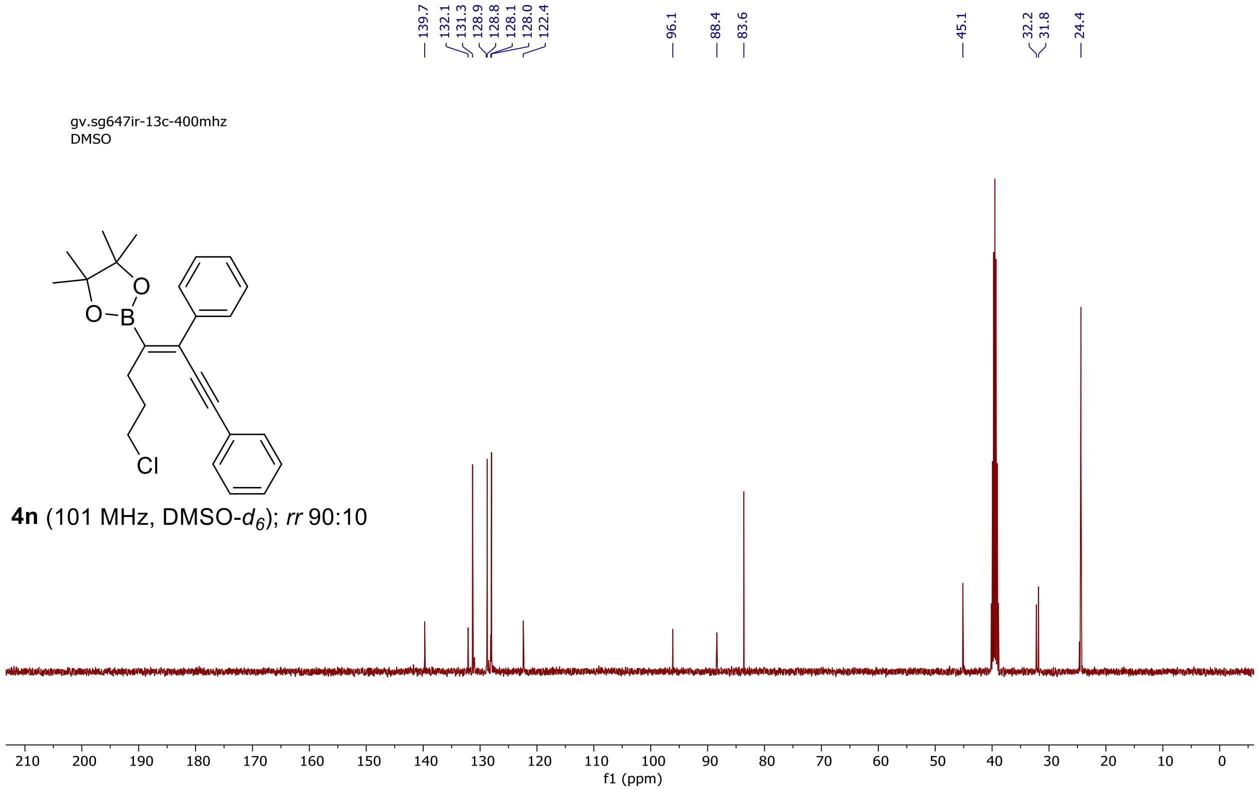


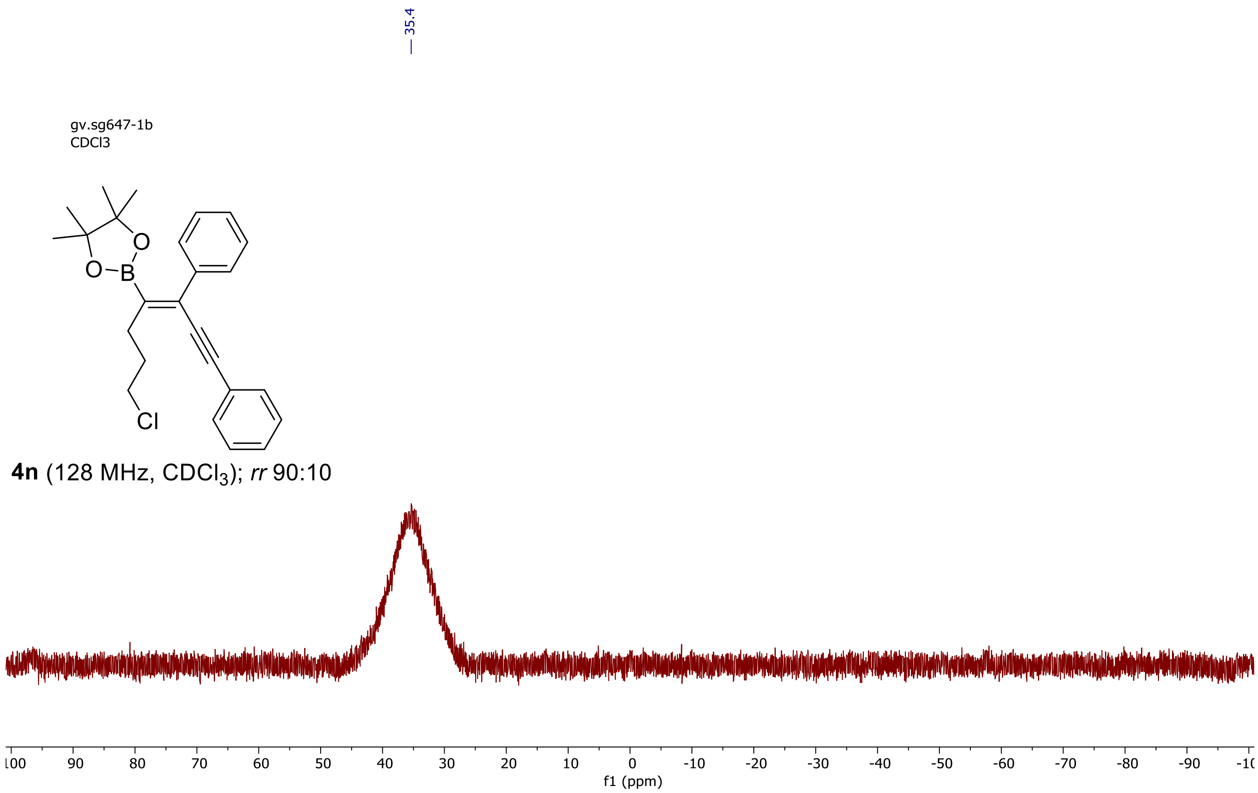
4m (101 MHz, $CDCl_3$); *rr* 90:10



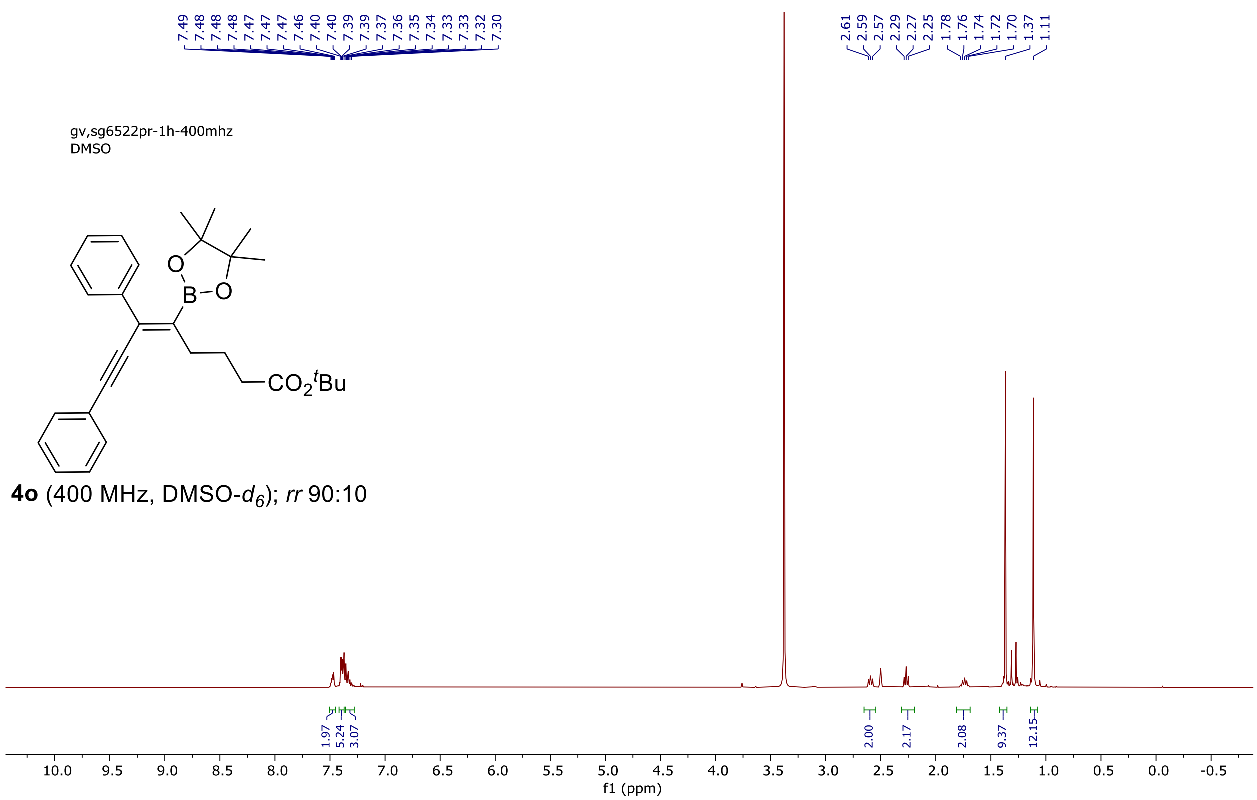
4m (128 MHz, $CDCl_3$); *rr* 90:10


7.50 7.49 7.49 7.48 7.48 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.34 7.34 7.33 7.32
3.73 3.71 3.69
2.74 2.72 2.70
1.99 1.98 1.96 1.94 1.92
1.12
gv.sg647ir-1h-400mhz
DMSO
O
O
B
Cl
4n (400 MHz, DMSO-d_6); *rr* 90:10
1.99
8.35
2.04
2.00
2.03
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

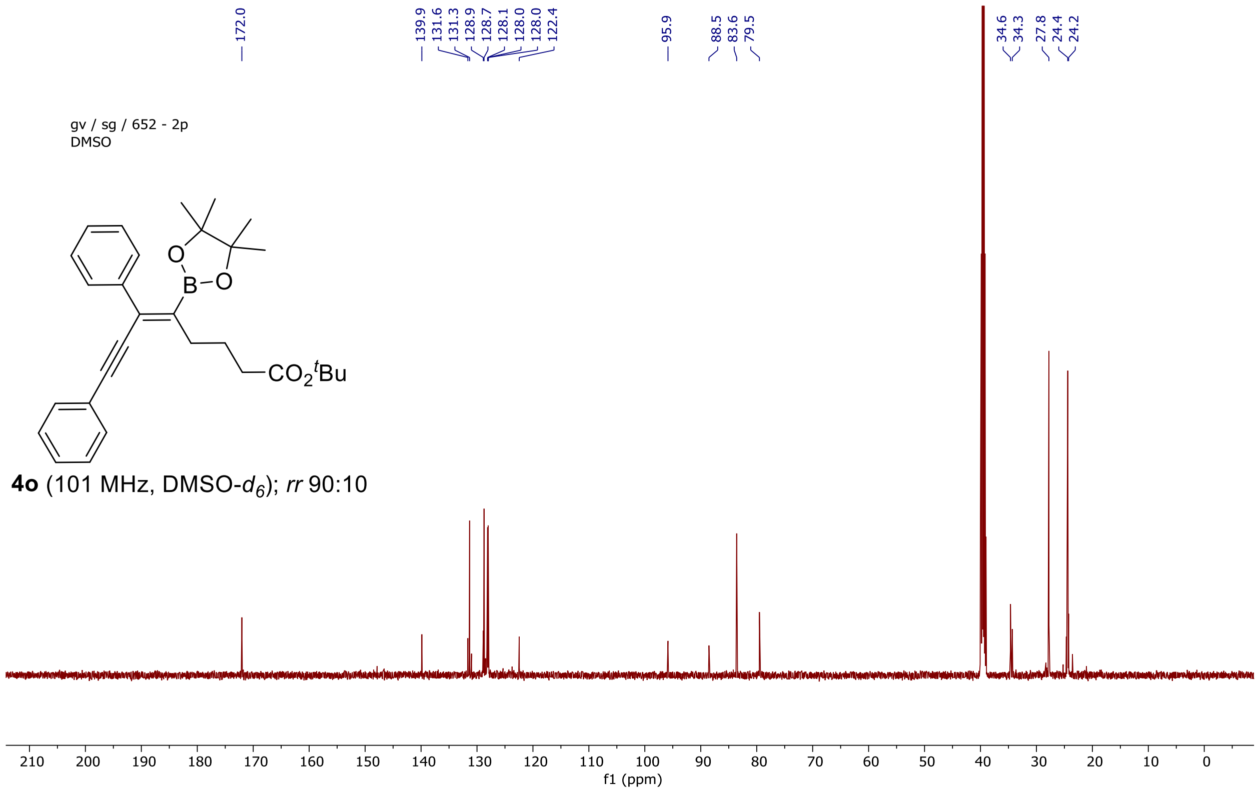

139.7
132.1 131.3 128.9 128.8 128.1 128.0 122.4
96.1
88.4
83.6
45.1
32.2 31.8
24.4
gv.sg647ir-13c-400mhz
DMSO
O
O
B
Cl
4n (101 MHz, DMSO-d_6); *rr* 90:10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



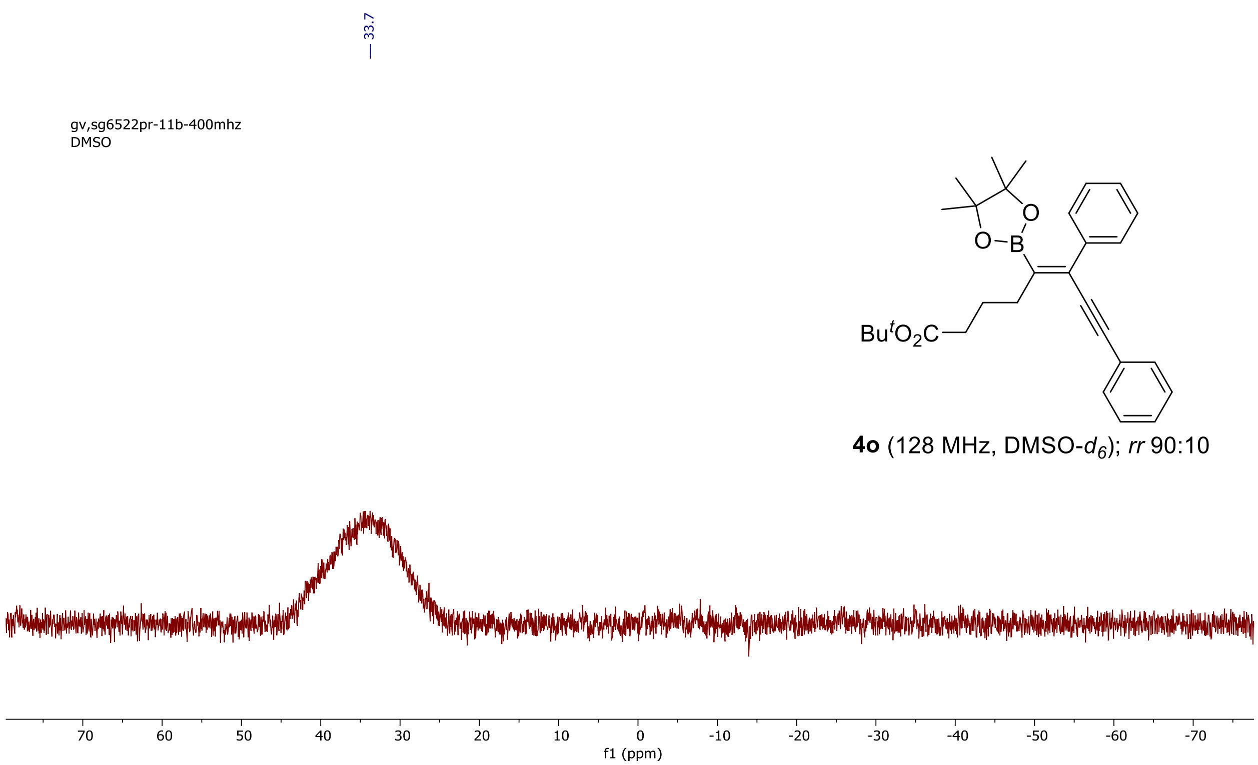
4n (128 MHz, $CDCl_3$); *rr* 90:10



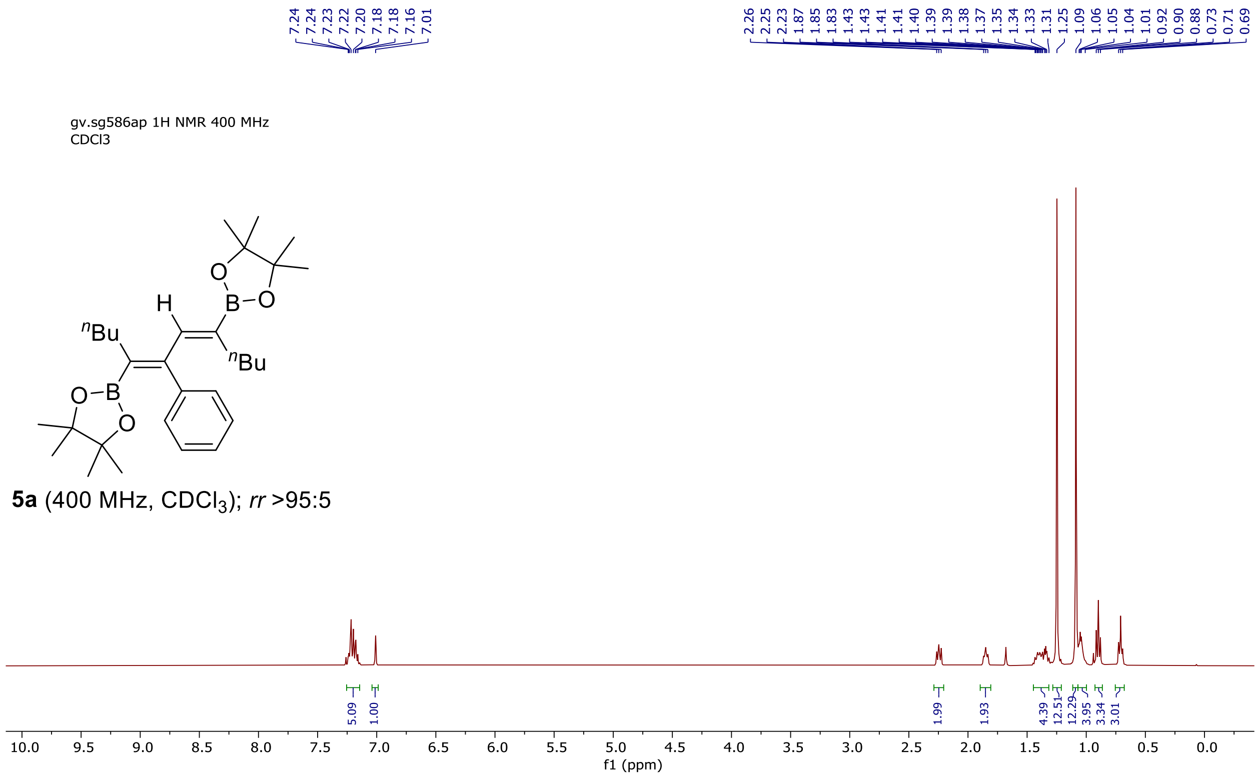
4o (400 MHz, DMSO-d_6); *rr* 90:10

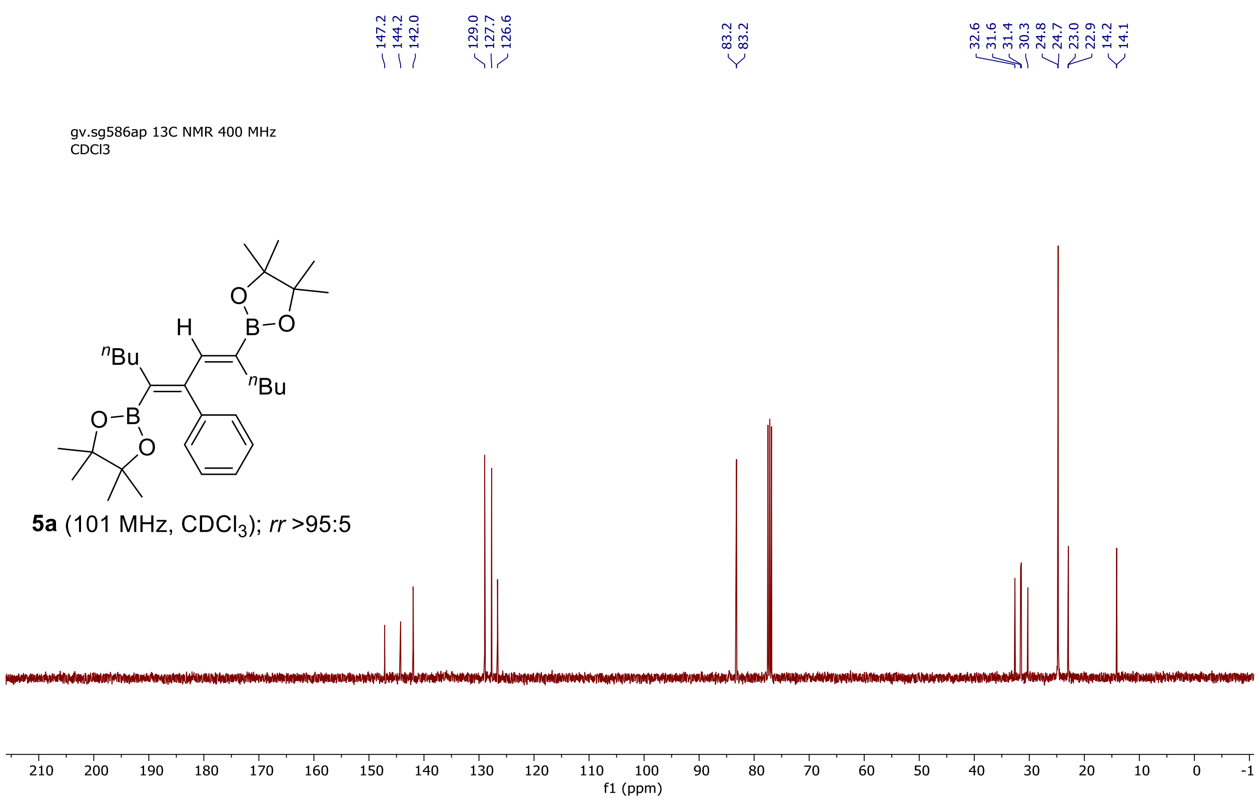


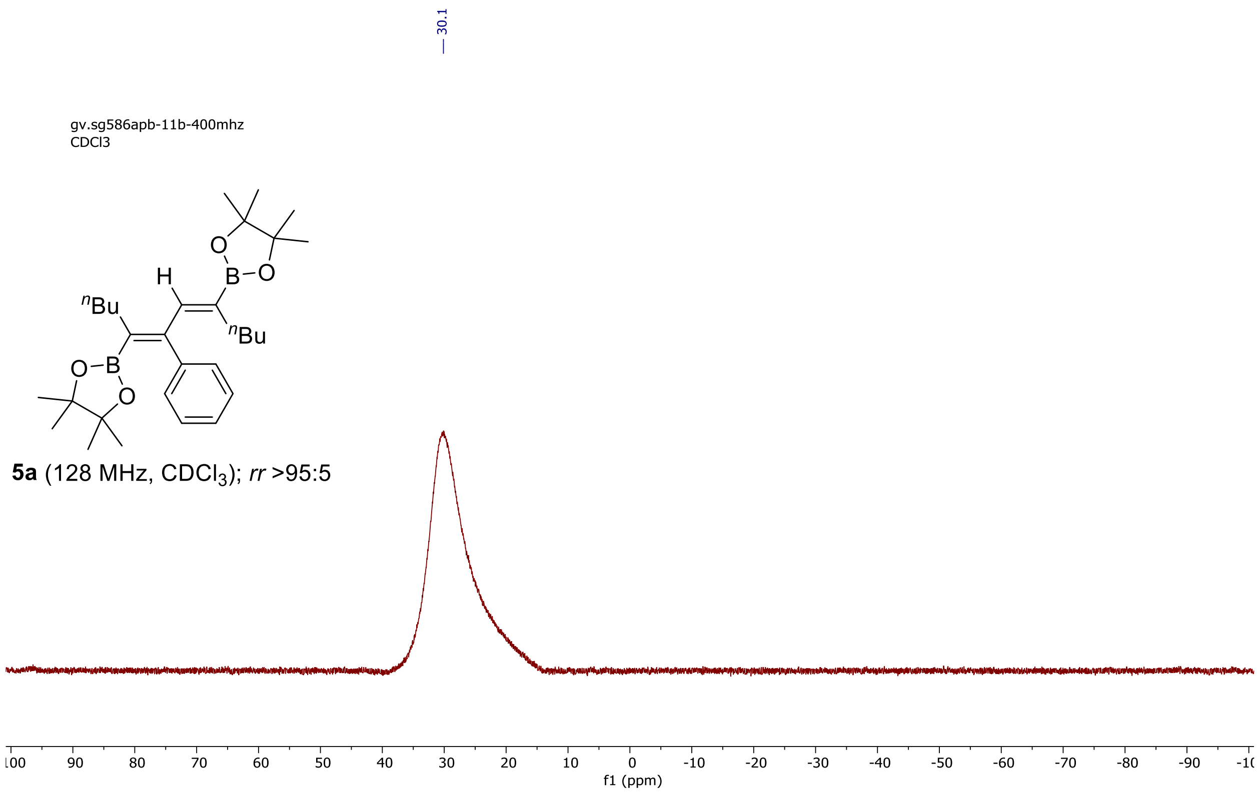
4o (101 MHz, DMSO-d_6); *rr* 90:10



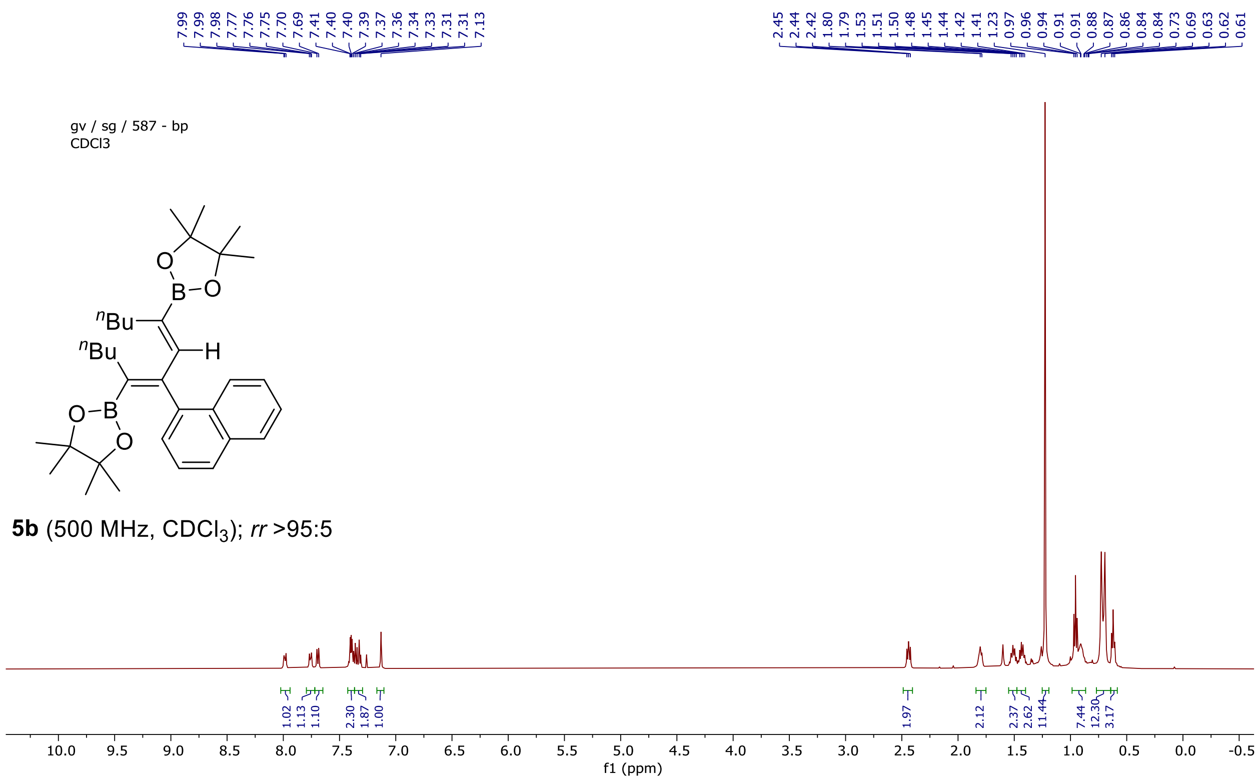
4o (128 MHz, DMSO-d_6); *rr* 90:10


7.24 7.24 7.23 7.22 7.20 7.18 7.18 7.16 7.01
2.26 2.25 2.23 1.87 1.85 1.83 1.43 1.43 1.41 1.41 1.40 1.39 1.39 1.38 1.37 1.35 1.34 1.33 1.31 1.25 1.09 1.06 1.05 1.04 1.01 0.92 0.90 0.88 0.73 0.71 0.69
gv.sg586ap 1H NMR 400 MHz
CDCl3
H
^{n}Bu
^{n}Bu
B
O
O
O
B
O
5a (400 MHz, $CDCl_3$); *rr* >95:5
5.09
1.00
1.99
1.93
4.39
12.51
12.29
3.95
3.34
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

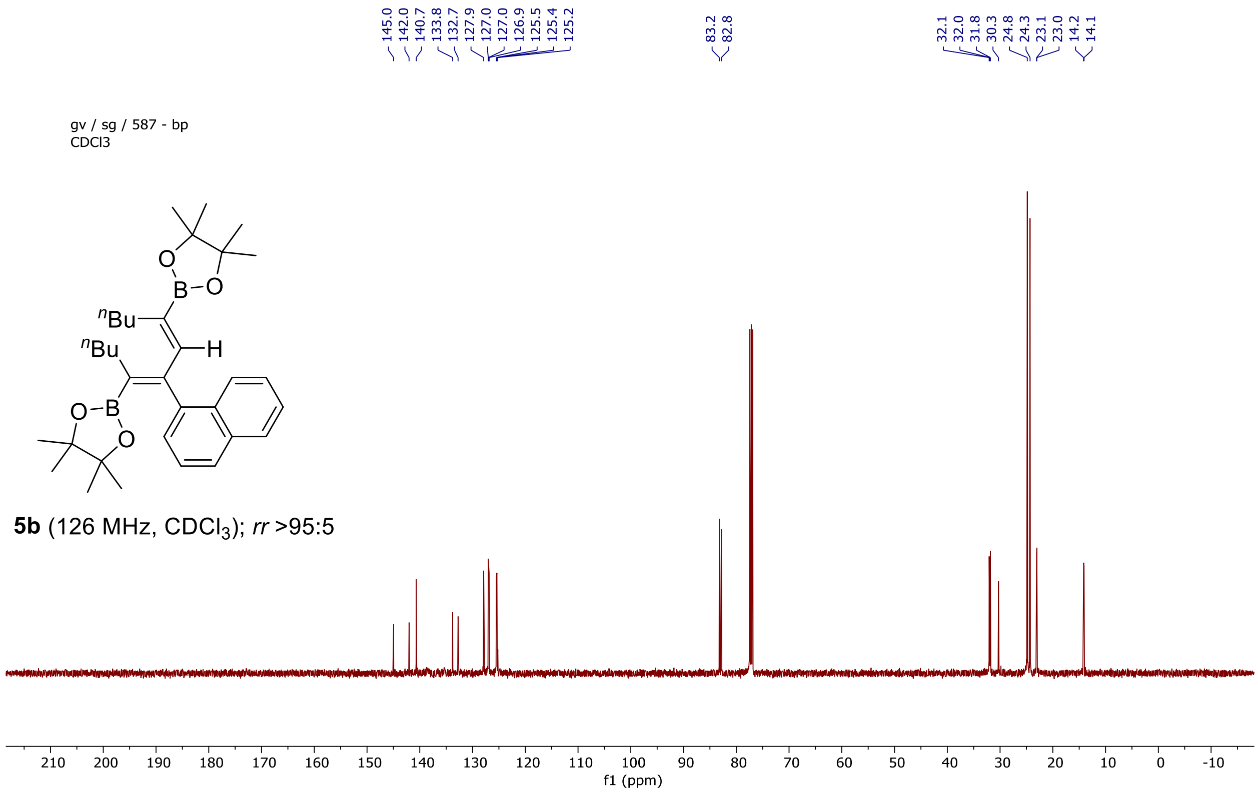

147.2 144.2 142.0
129.0 127.7 126.6
83.2 83.2
32.6 31.6 31.4 30.3 24.8 24.7 23.0 22.9 14.2 14.1
gv.sg586ap 13C NMR 400 MHz
CDCl3
H
^{n}Bu
^{n}Bu
B
O
O
O
B
O
5a (101 MHz, $CDCl_3$); *rr* >95:5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



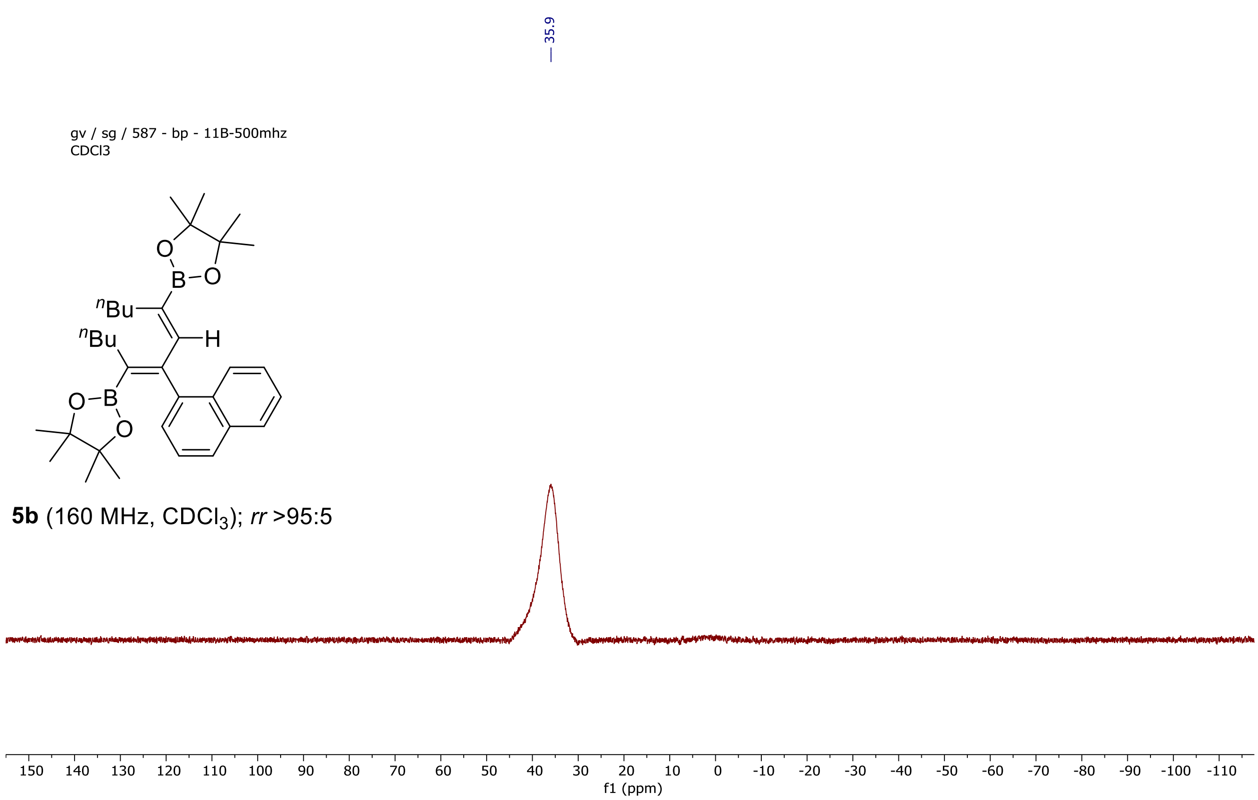
5a (128 MHz, $CDCl_3$); *rr* >95:5



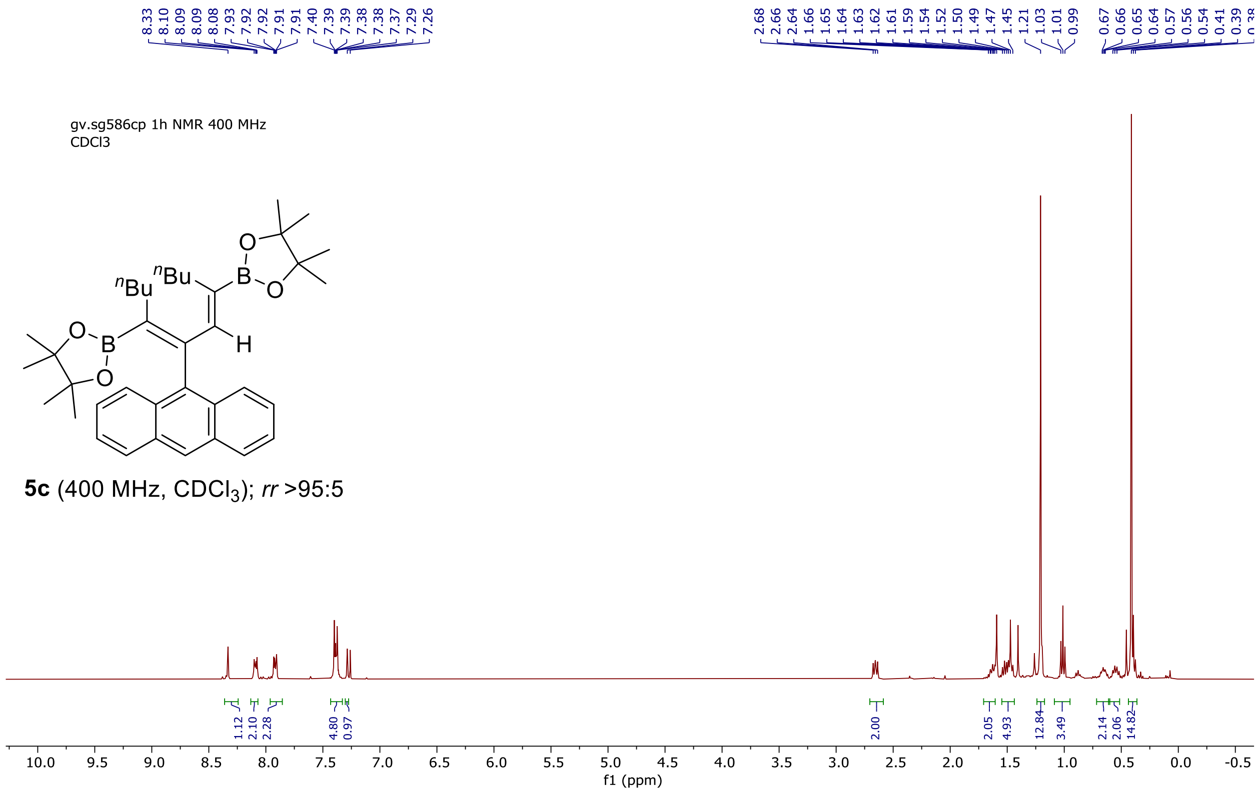
5b (500 MHz, $CDCl_3$); *rr* >95:5

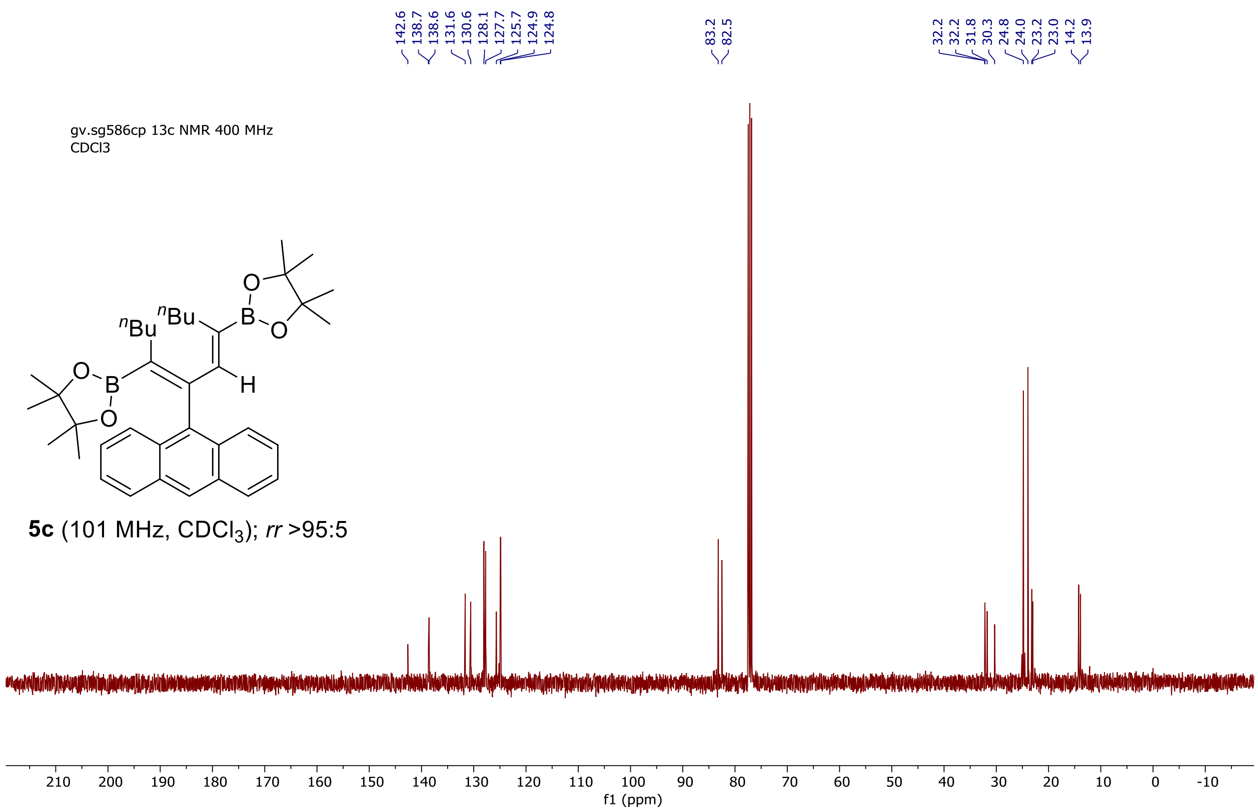


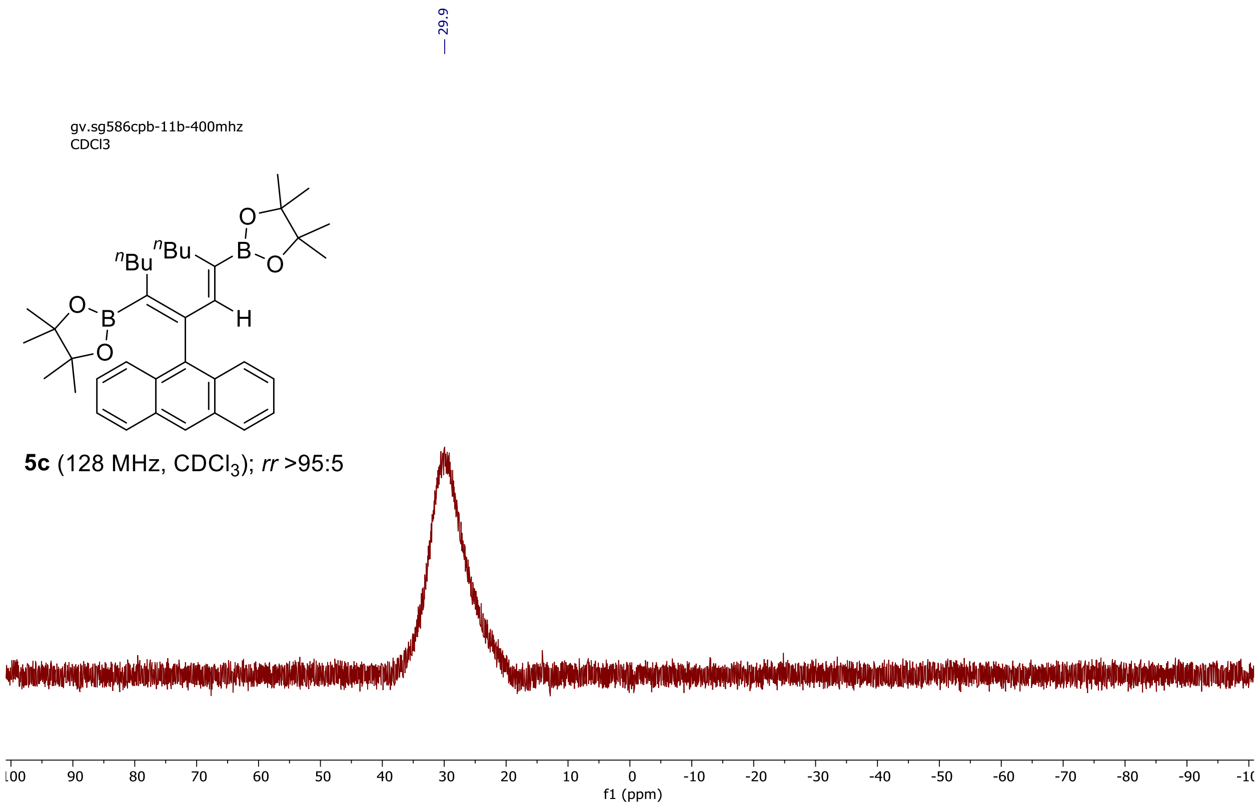
5b (126 MHz, $CDCl_3$); *rr* >95:5



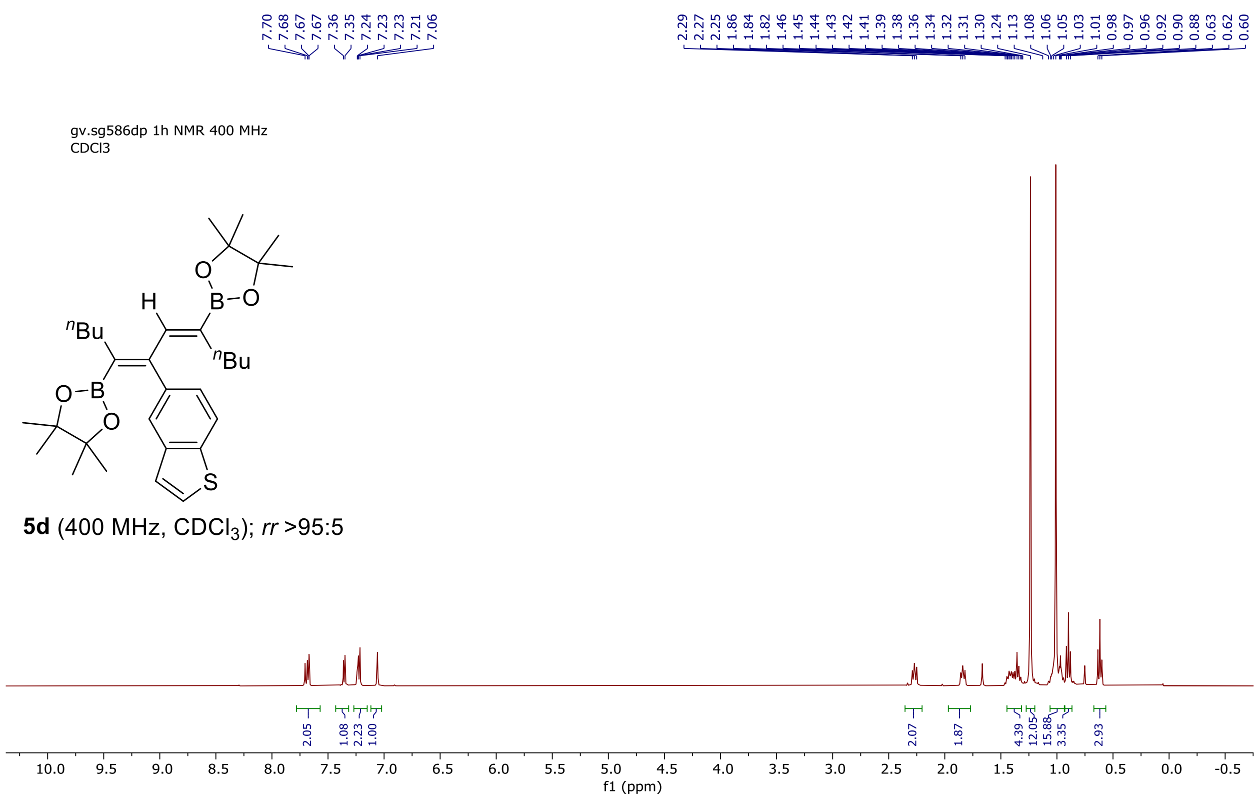
5b (160 MHz, $CDCl_3$); *rr* >95:5


8.33 8.10 8.09 8.09 8.08 7.93 7.92 7.92 7.91 7.91 7.40 7.39 7.39 7.38 7.38 7.37 7.29 7.26
2.68 2.66 2.64 1.66 1.65 1.64 1.63 1.62 1.61 1.59 1.54 1.52 1.50 1.49 1.47 1.45 1.21 1.03 1.01 0.99 0.67 0.66 0.65 0.64 0.57 0.56 0.54 0.41 0.39
gv.sg586cp 1h NMR 400 MHz
CDCl3
^{n}Bu ^{n}Bu
O B O H
5c (400 MHz, $CDCl_3$); *rr* >95:5
1.12 2.10 2.28 4.80 0.97 2.00 2.05 4.93 12.84 3.49 2.14 2.06 14.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

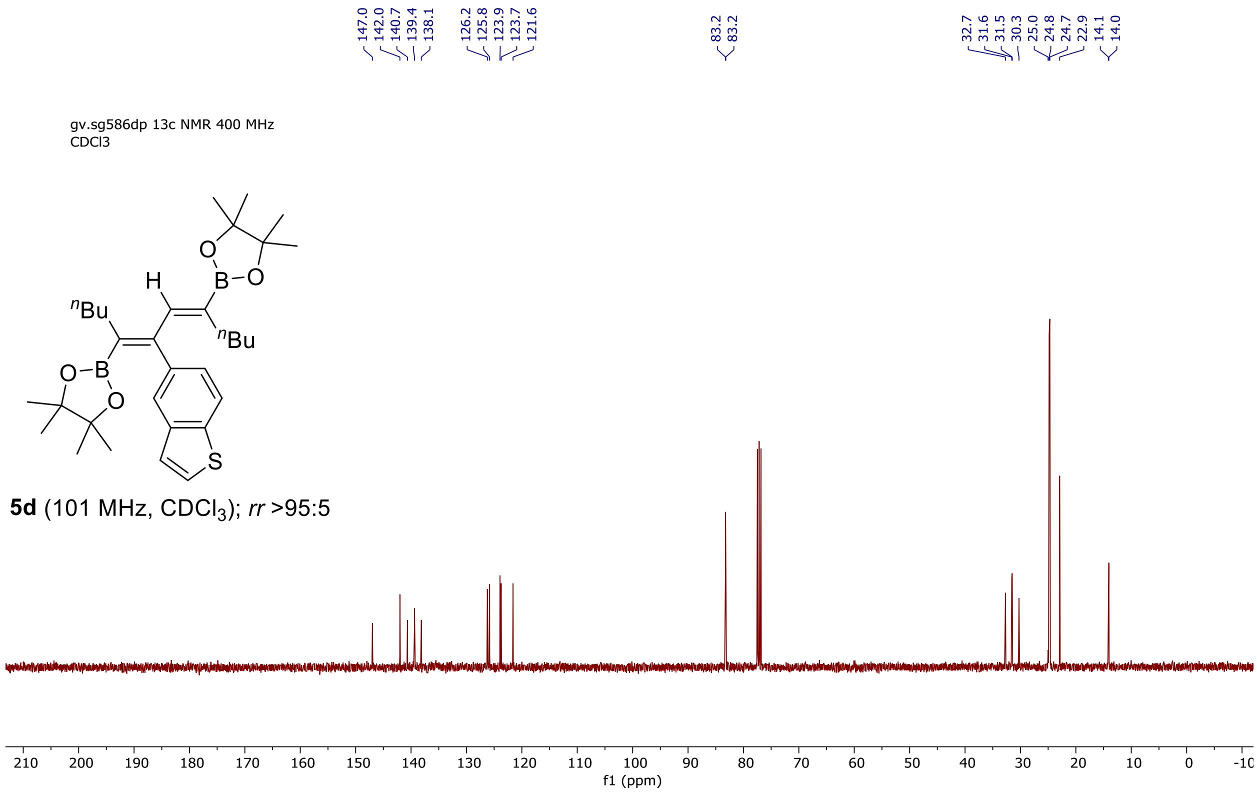

142.6 138.7 138.6 131.6 130.6 128.1 127.7 125.7 124.9 124.8
83.2 82.5
32.2 32.2 31.8 30.3 24.8 24.0 23.2 23.0 14.2 13.9
gv.sg586cp 13c NMR 400 MHz
CDCl3
^{n}Bu ^{n}Bu
O B O H
5c (101 MHz, $CDCl_3$); *rr* >95:5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



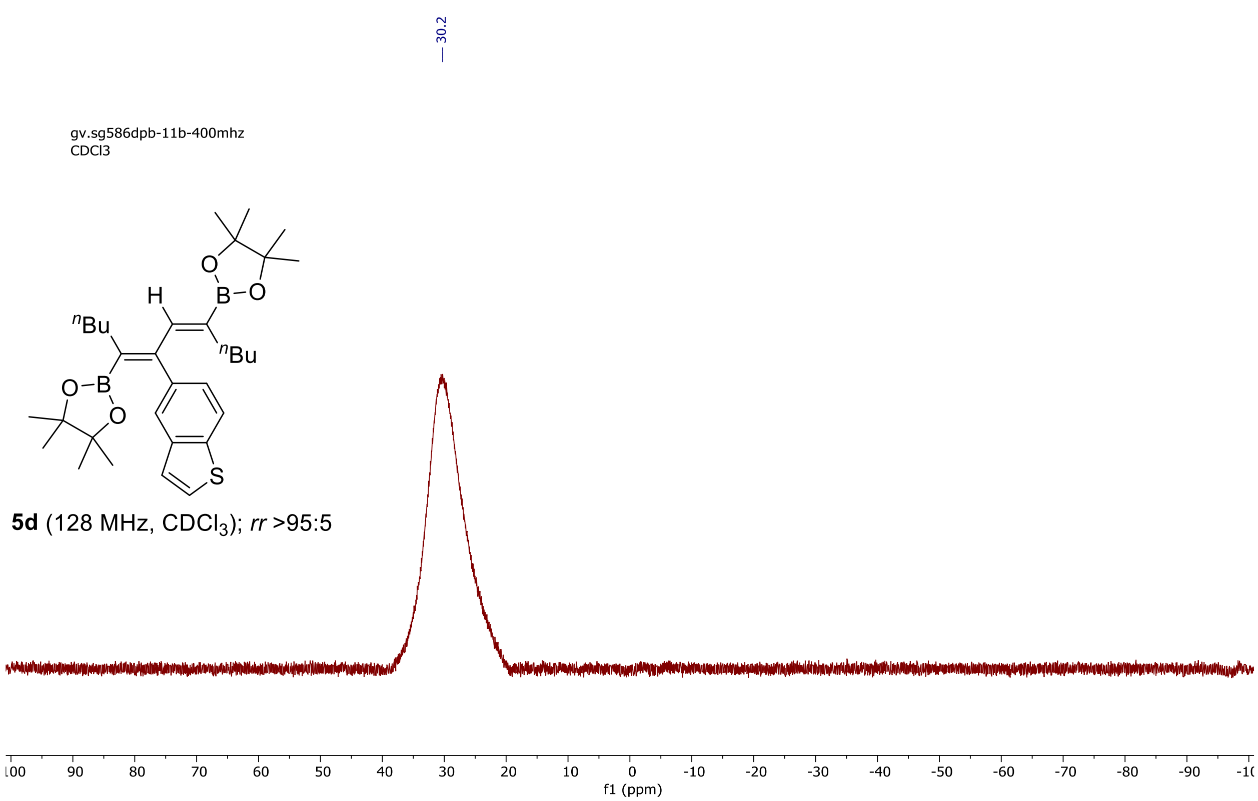
5c (128 MHz, $CDCl_3$); *rr* >95:5



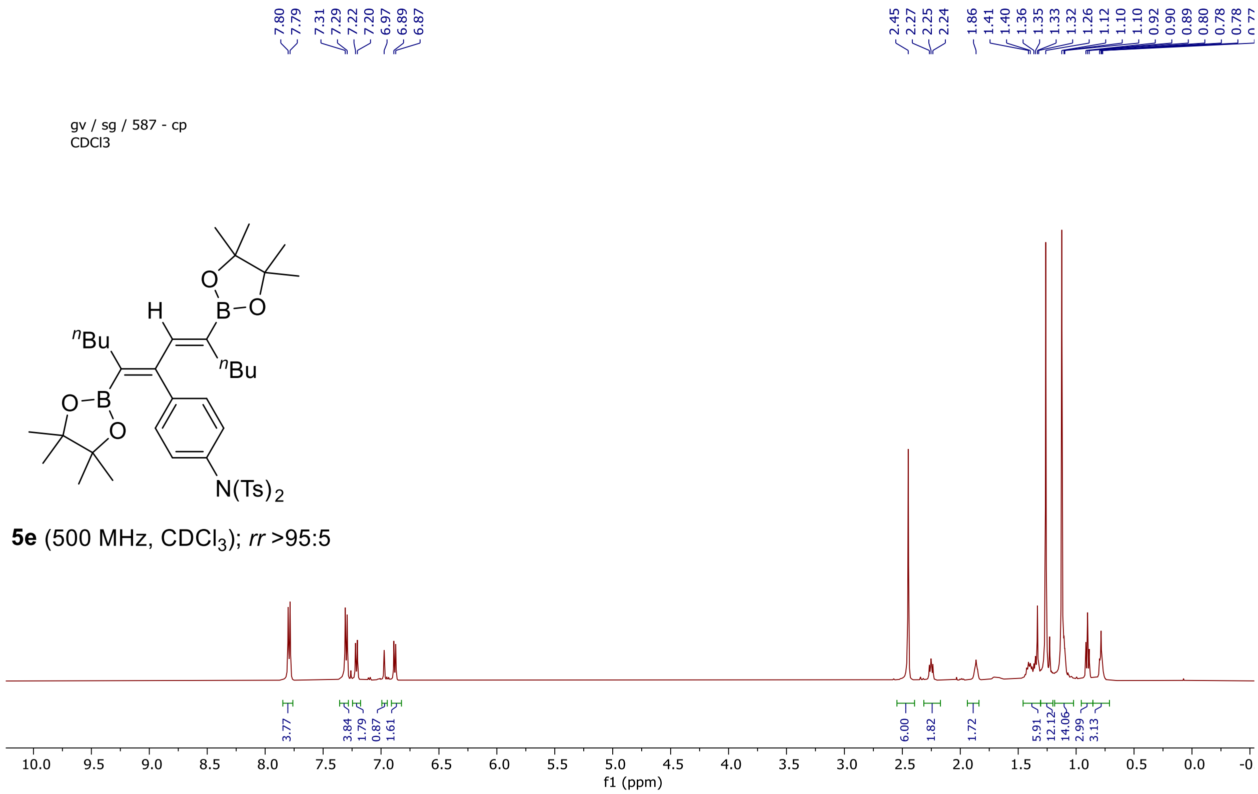
5d (400 MHz, $CDCl_3$); *rr* >95:5

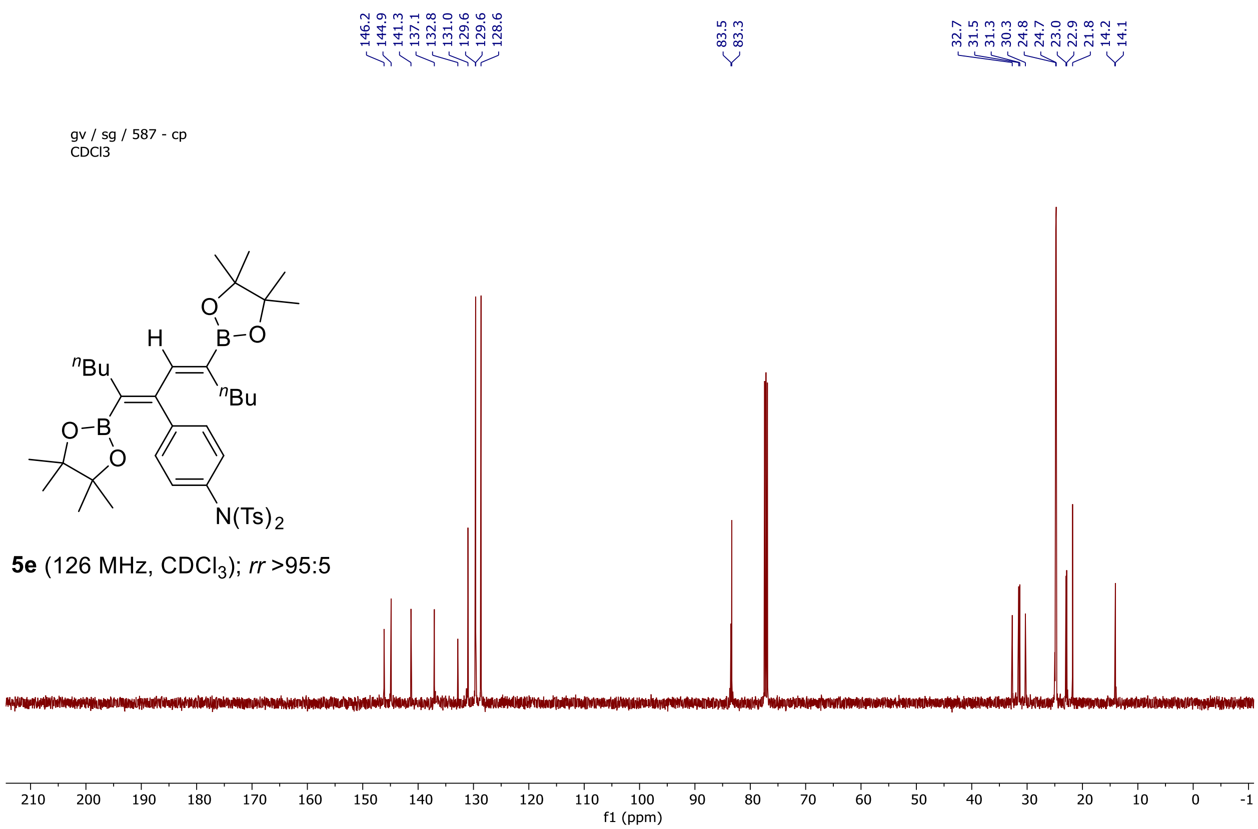


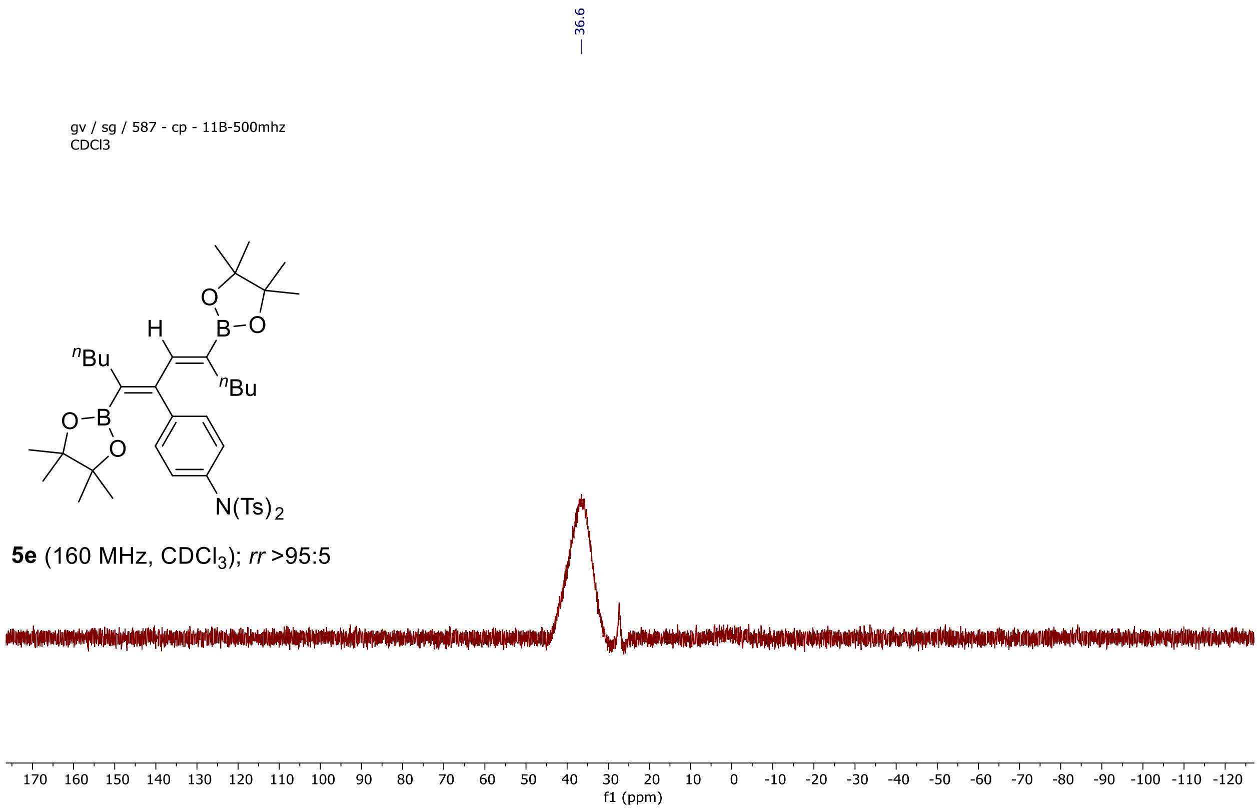
5d (101 MHz, $CDCl_3$); *rr* >95:5



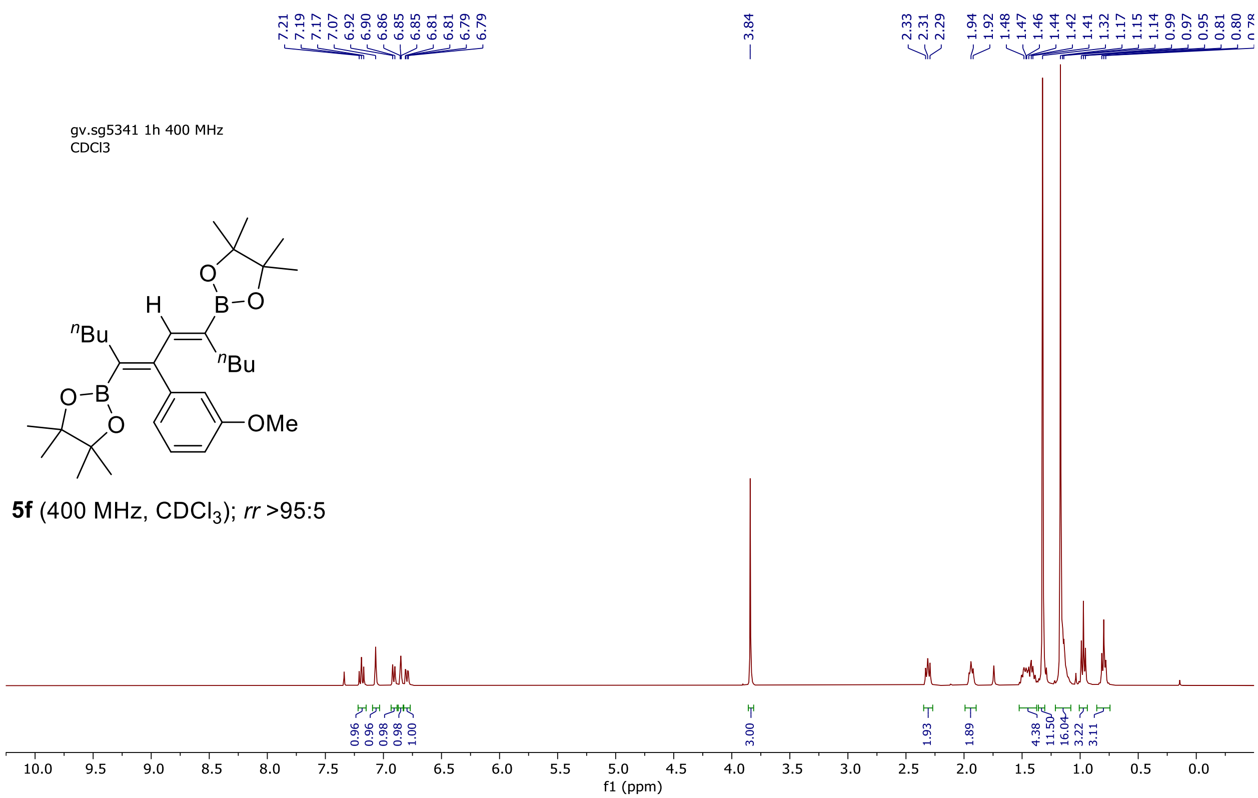
5d (128 MHz, $CDCl_3$); *rr* >95:5


7.80 7.79 7.31 7.29 7.22 7.20 6.97 6.89 6.87
2.45 2.27 2.25 2.24 1.86 1.41 1.40 1.36 1.35 1.33 1.32 1.26 1.12 1.10 0.92 0.90 0.89 0.80 0.78
gv / sg / 587 - cp
CDCl3
H
^{n}Bu
^{n}Bu
O
B
N(Ts)$_2$
5e (500 MHz, $CDCl_3$); rr >95:5
3.77 3.84 1.79 0.87 1.61 6.00 1.82 1.72 5.91 12.12 14.06 2.99 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

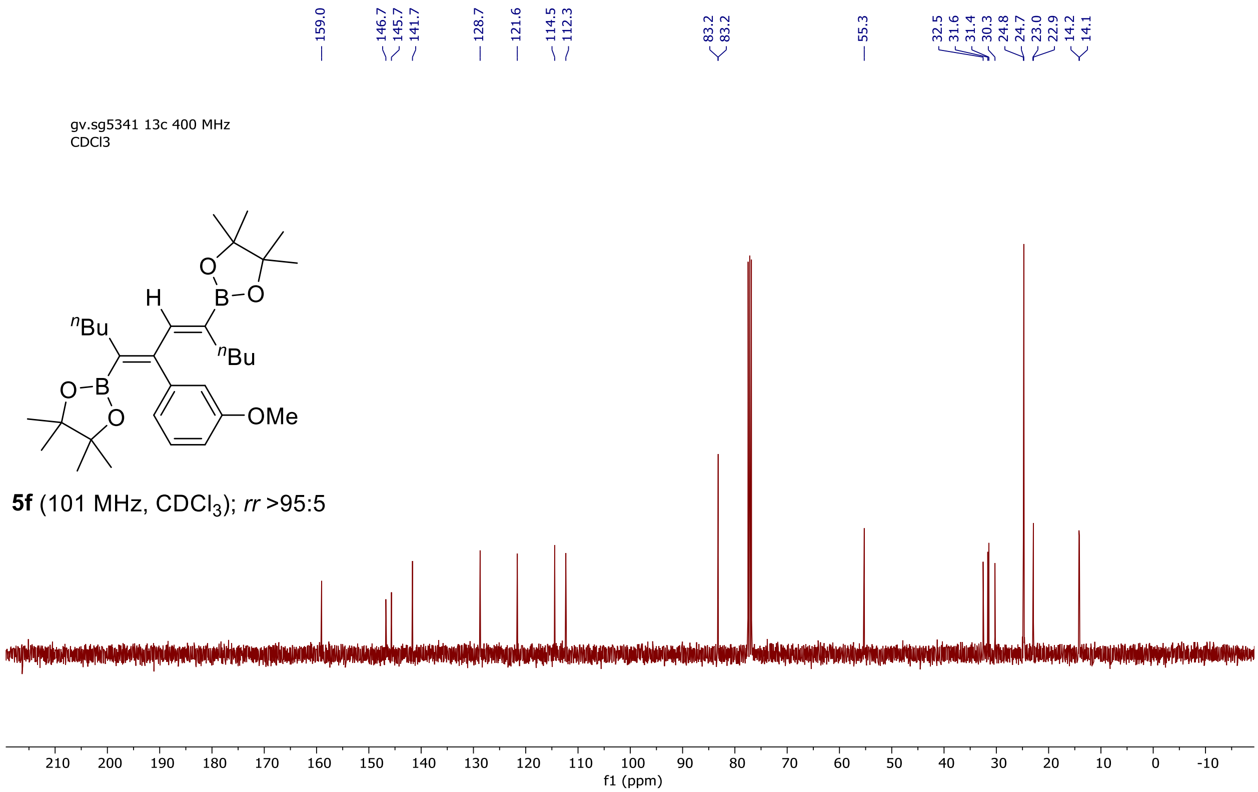

146.2 144.9 141.3 137.1 132.8 131.0 129.6 129.6 128.6
83.5 83.3
32.7 31.5 31.3 30.3 24.8 24.7 23.0 22.9 21.8 14.2 14.1
gv / sg / 587 - cp
CDCl3
H
^{n}Bu
^{n}Bu
O
B
N(Ts)$_2$
5e (126 MHz, $CDCl_3$); rr >95:5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



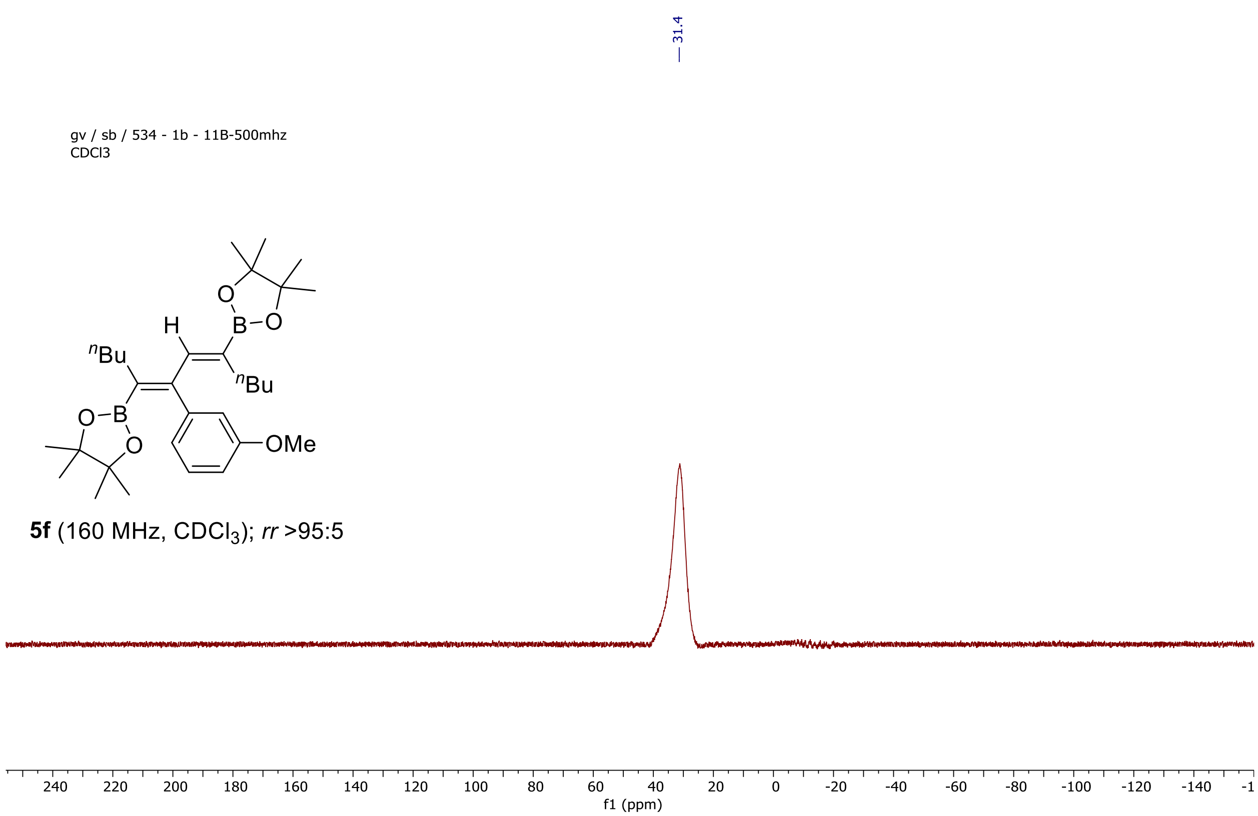
5e (160 MHz, $CDCl_3$); *rr* >95:5



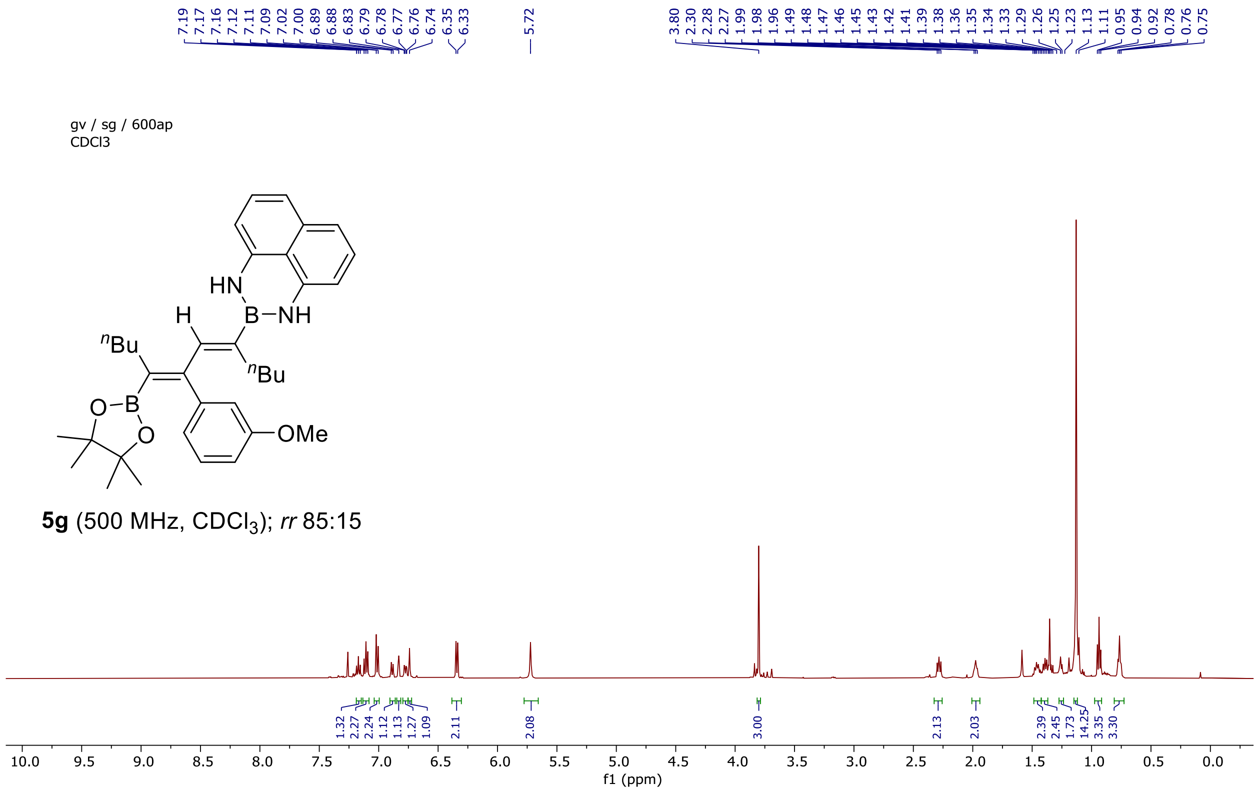
5f (400 MHz, $CDCl_3$); *rr* >95:5



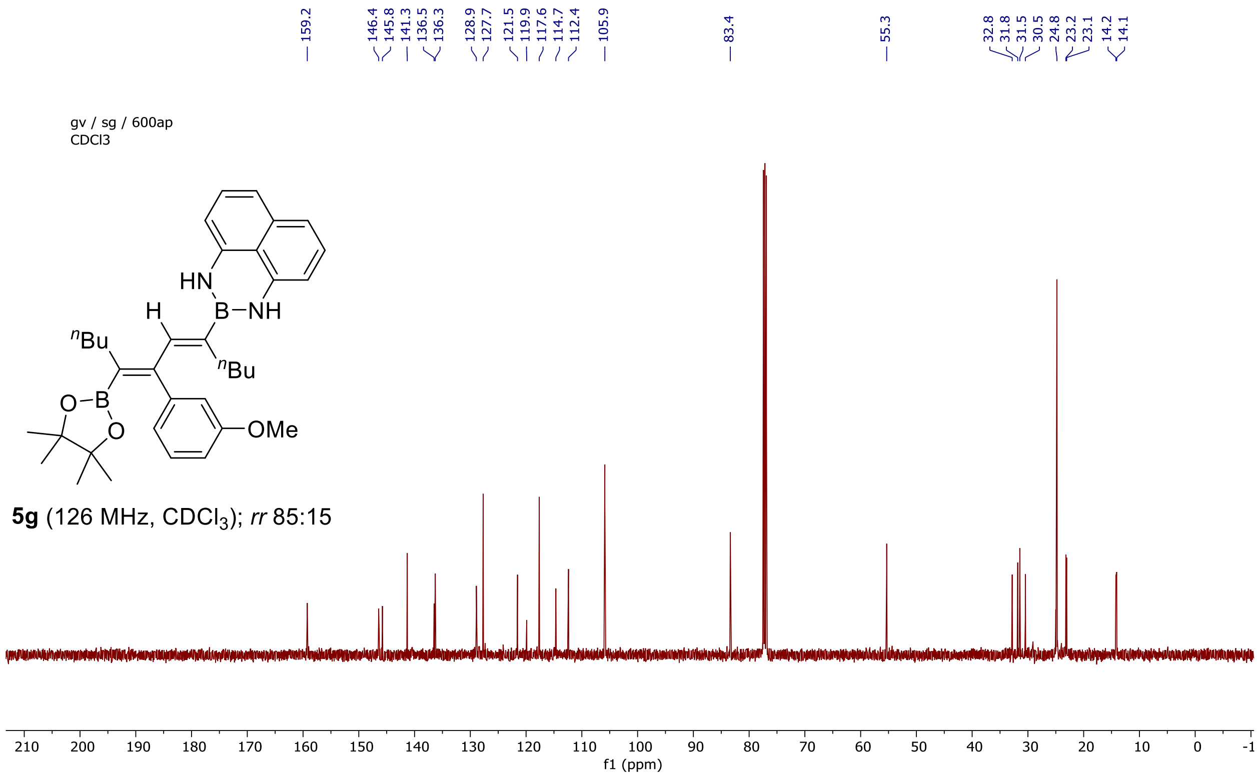
5f (101 MHz, $CDCl_3$); *rr* >95:5



5f (160 MHz, $CDCl_3$); *rr* >95:5

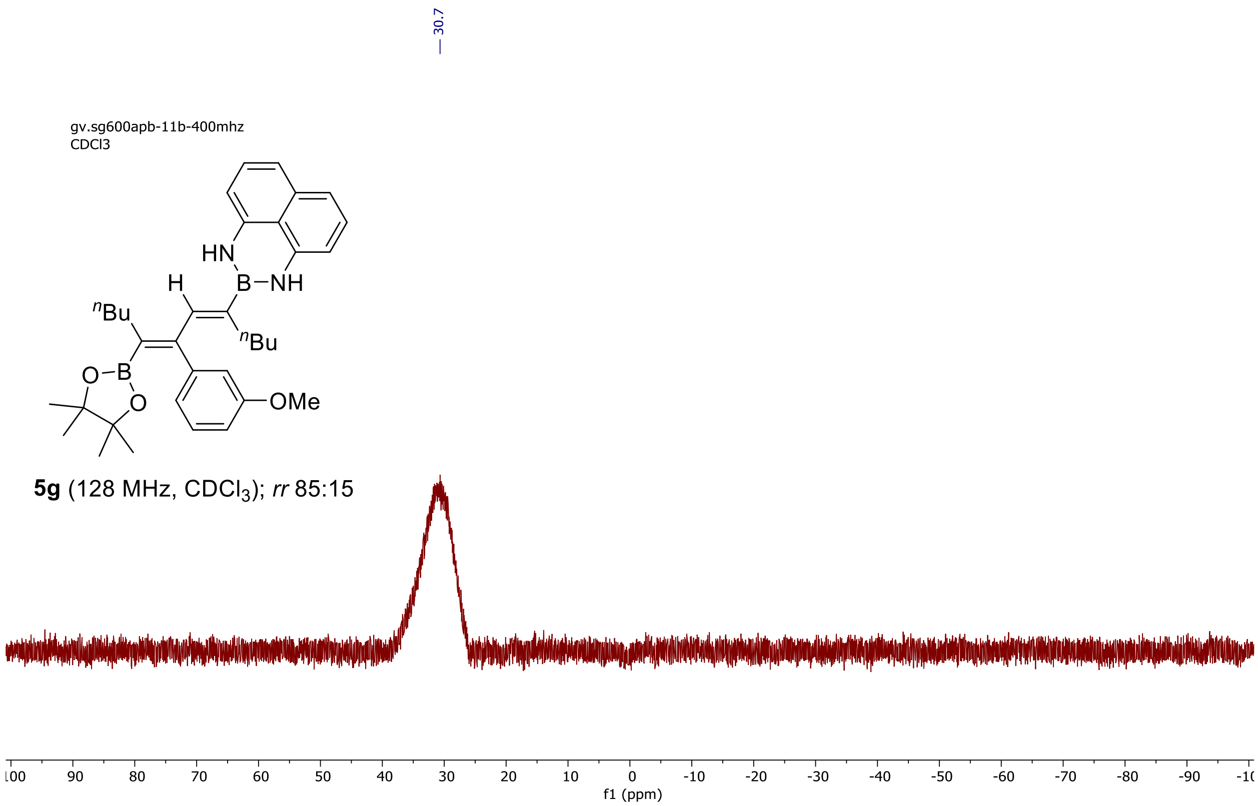


5g (500 MHz, $CDCl_3$); *rr* 85:15



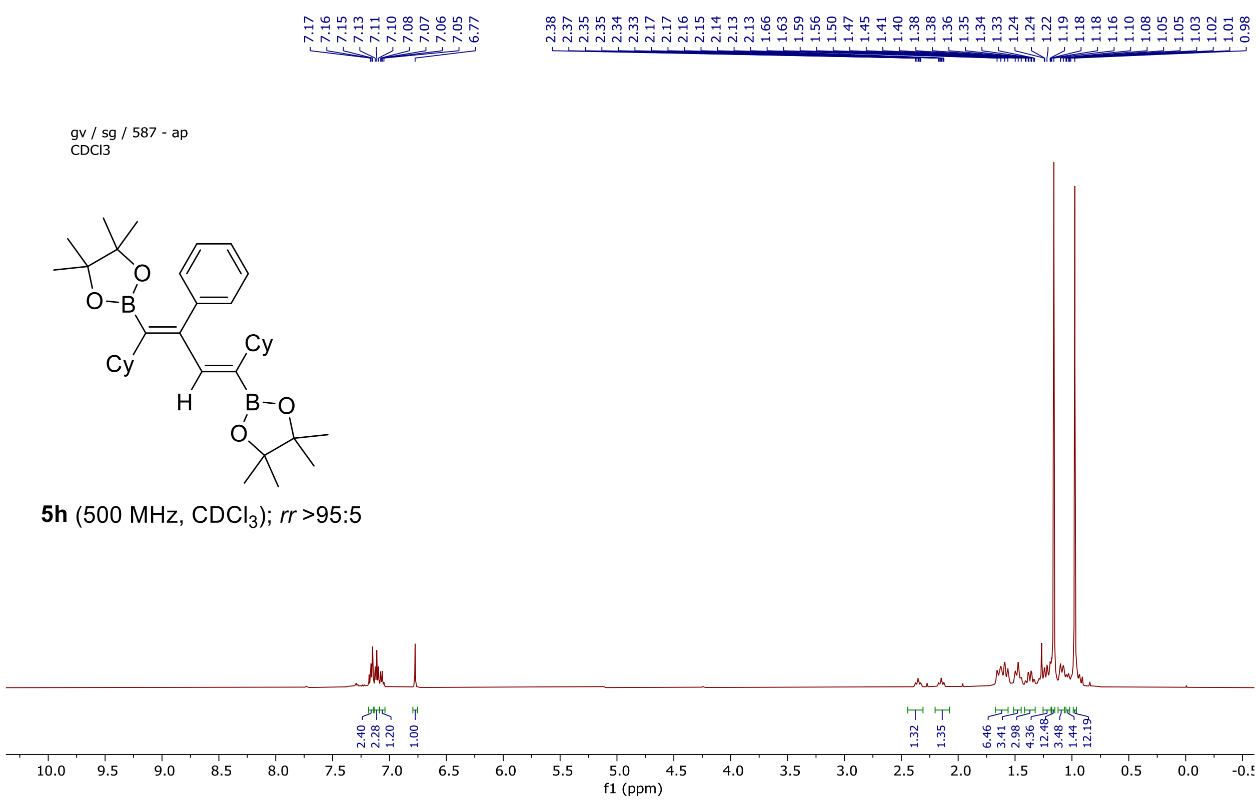
5g (126 MHz, $CDCl_3$); *rr* 85:15

gv.sg600apb-11b-400mhz
CDCl3

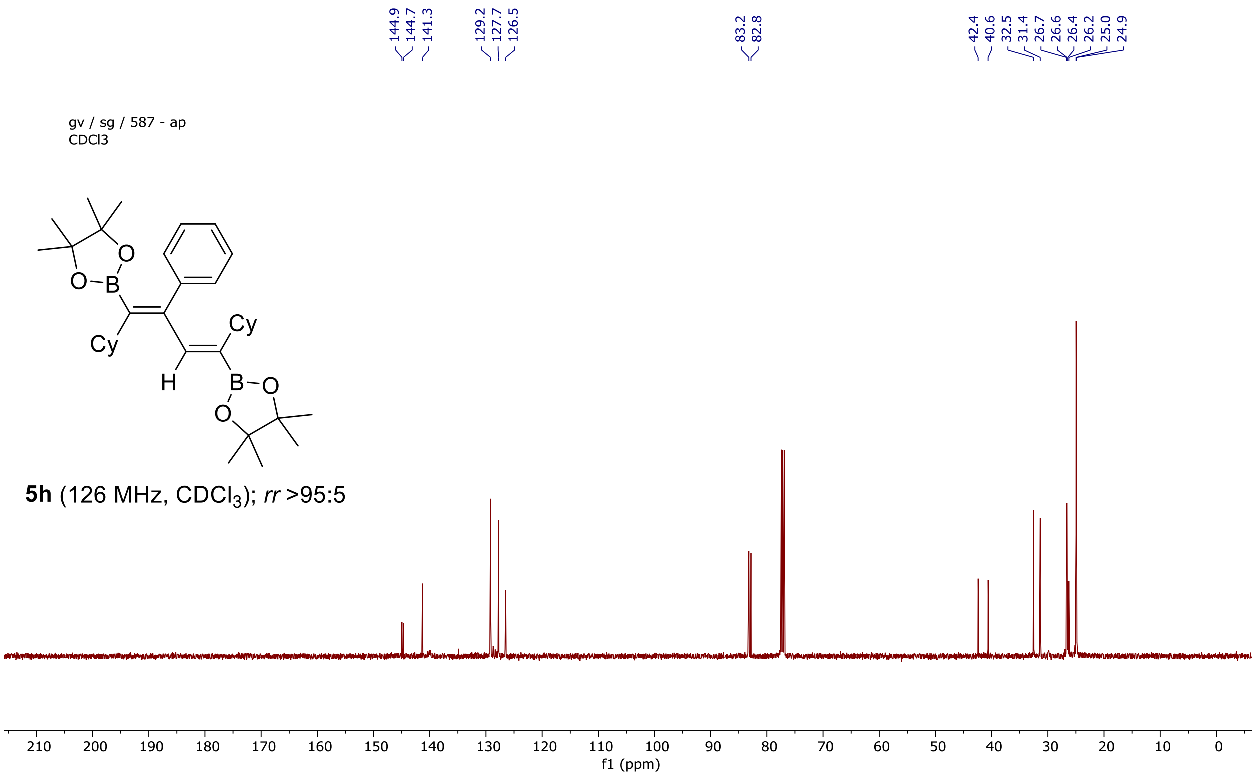


5g (128 MHz, $CDCl_3$); *rr* 85:15

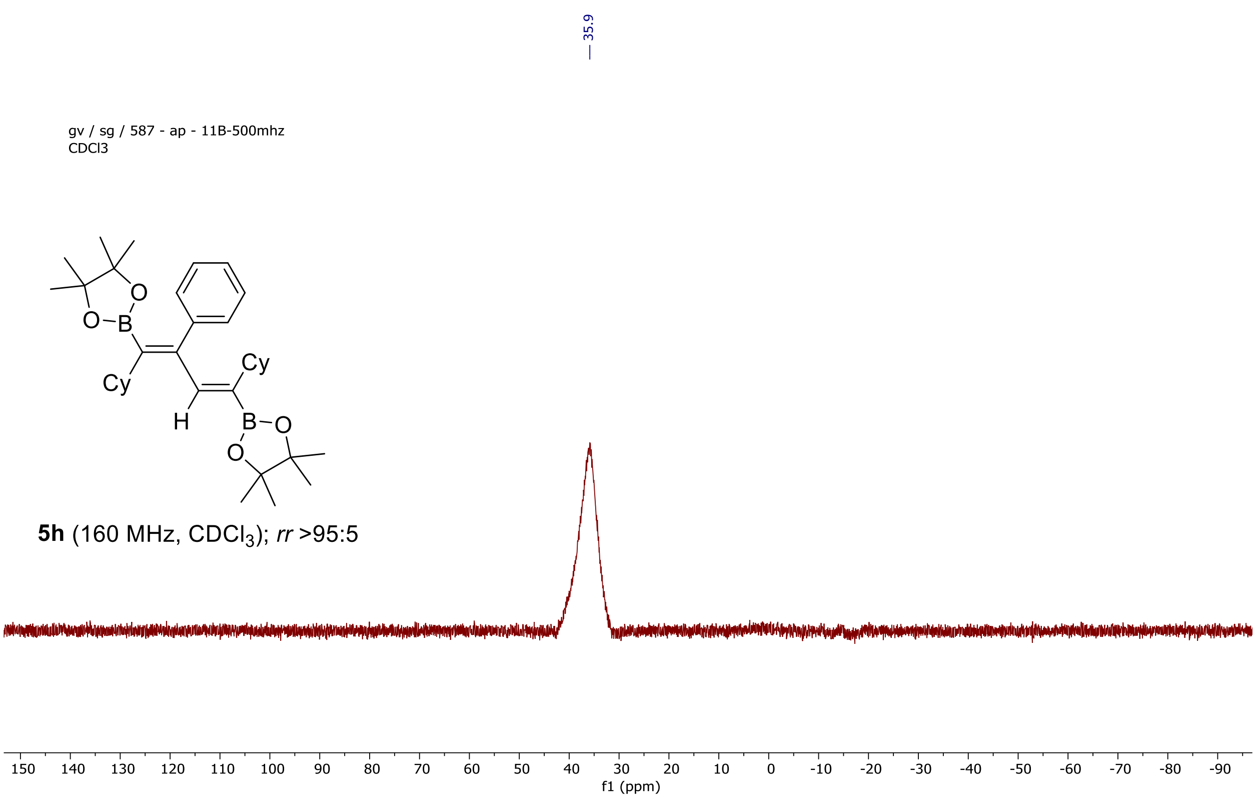
gv / sg / 587 - ap
CDCl3



5h (500 MHz, $CDCl_3$); *rr* >95:5

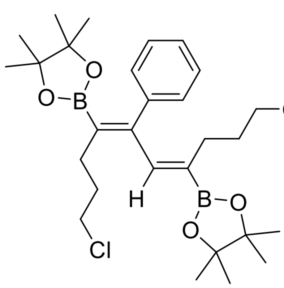


5h (126 MHz, $CDCl_3$); *rr* >95:5

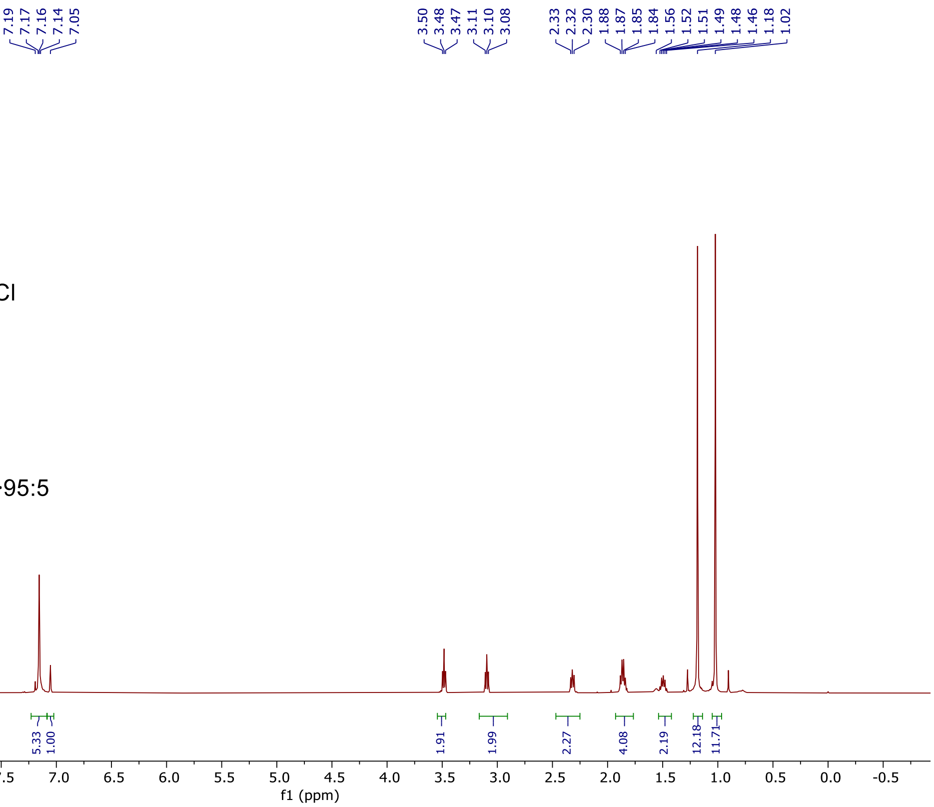


5h (160 MHz, $CDCl_3$); *rr* >95:5

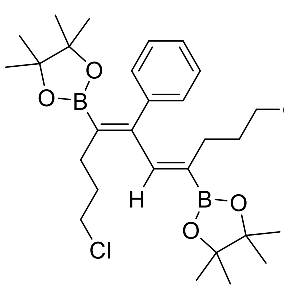
gv / sg / 587 - ep
CDCl3



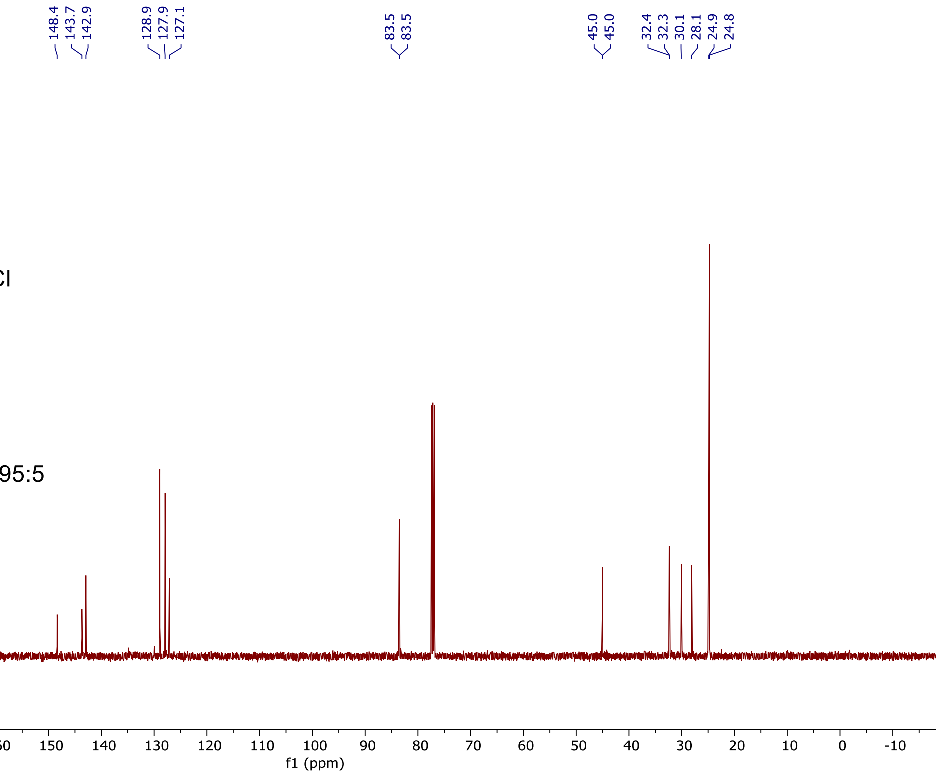
5i (500 MHz, $CDCl_3$); *rr* >95:5

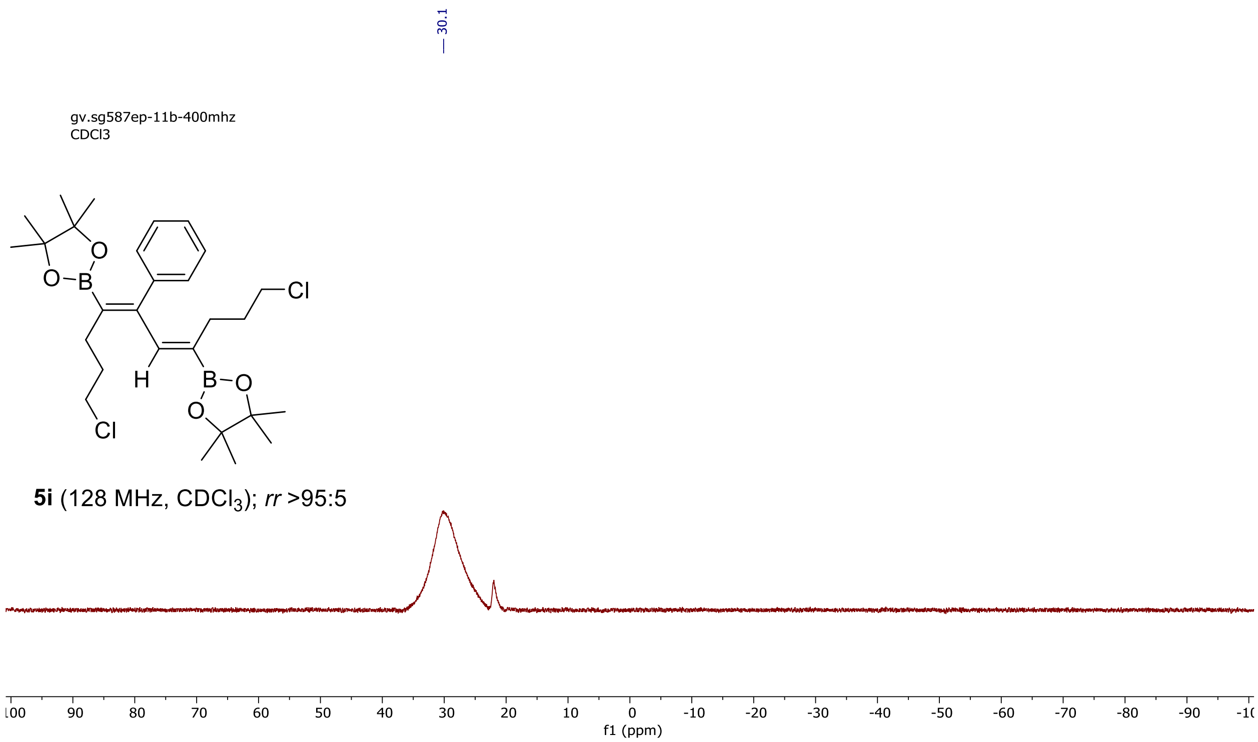


gv / sg / 587 - ep
CDCl3

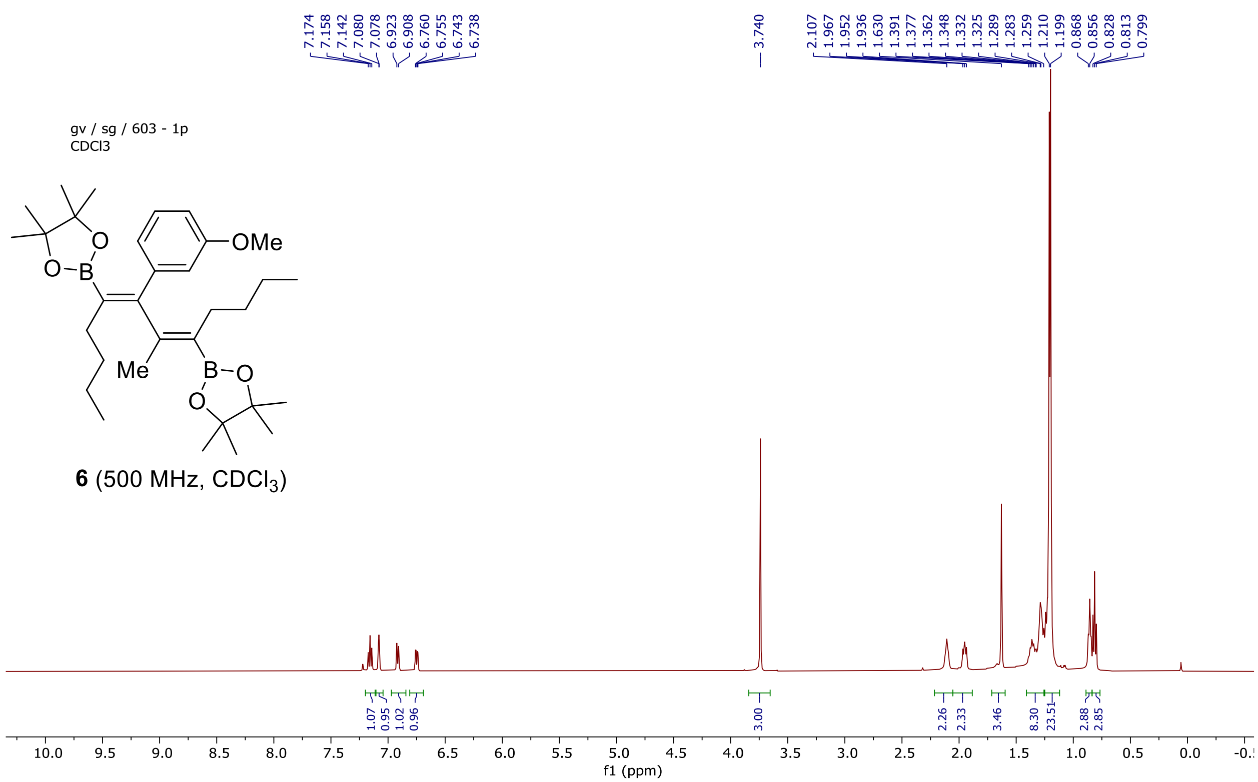


5i (126 MHz, $CDCl_3$); *rr* >95:5

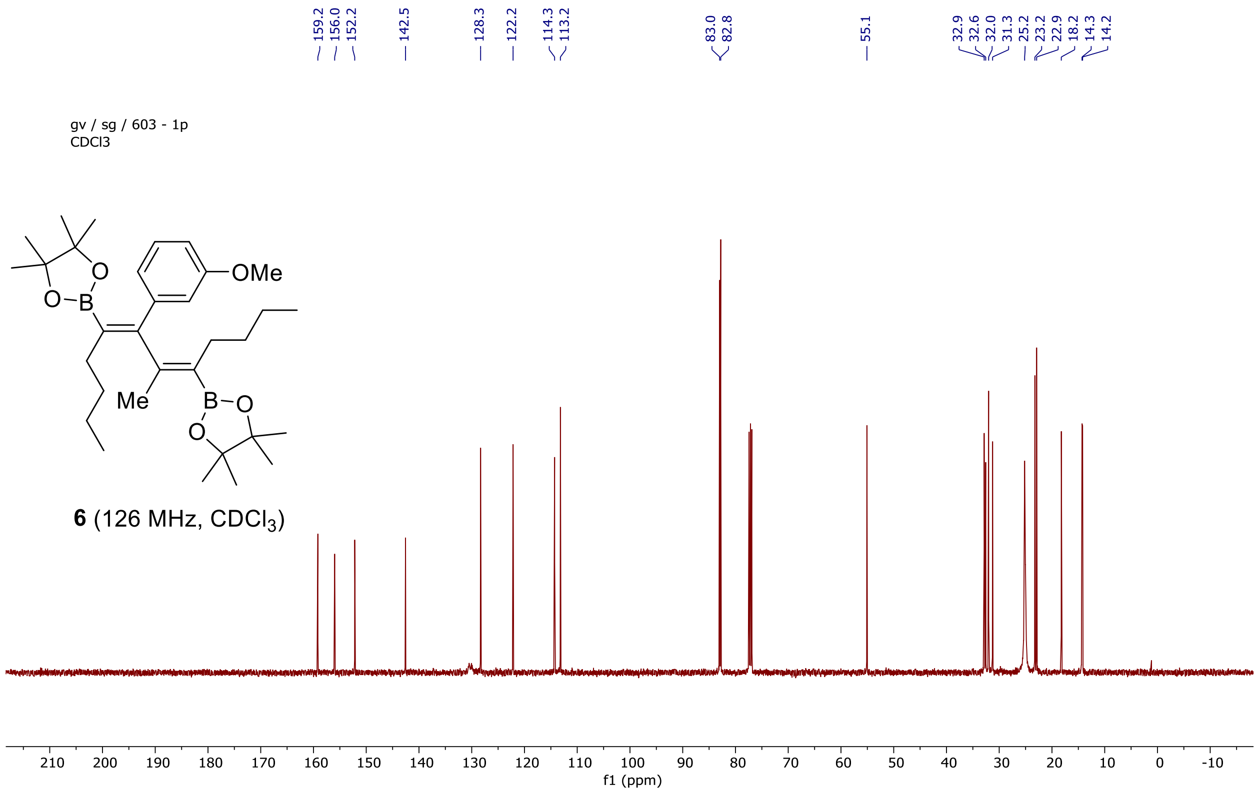


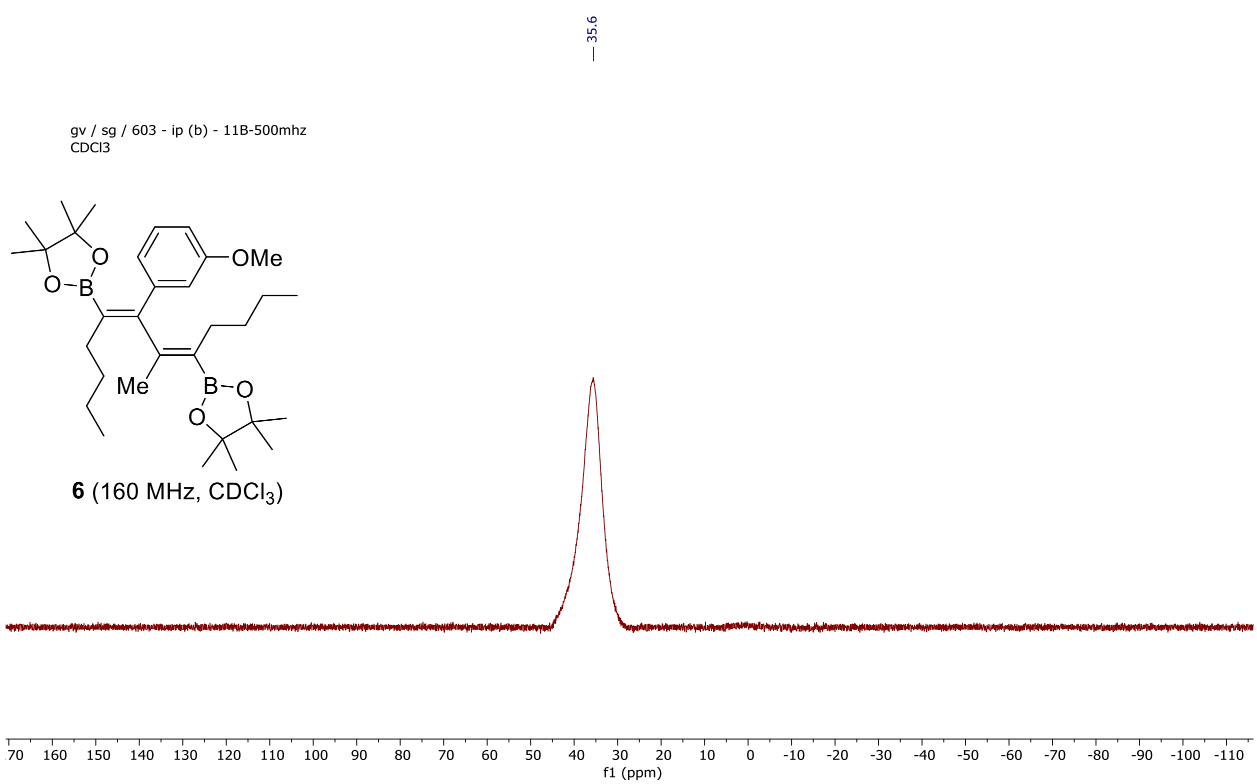


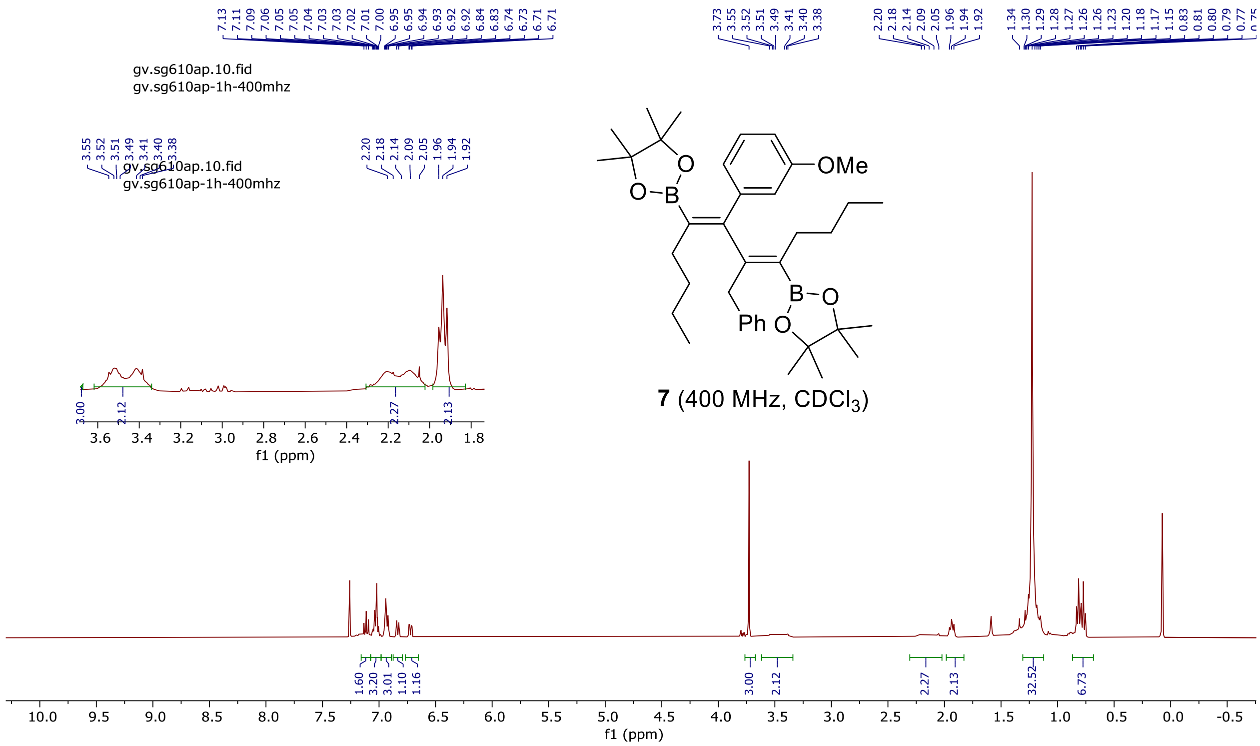
5i (128 MHz, $CDCl_3$); *rr* >95:5

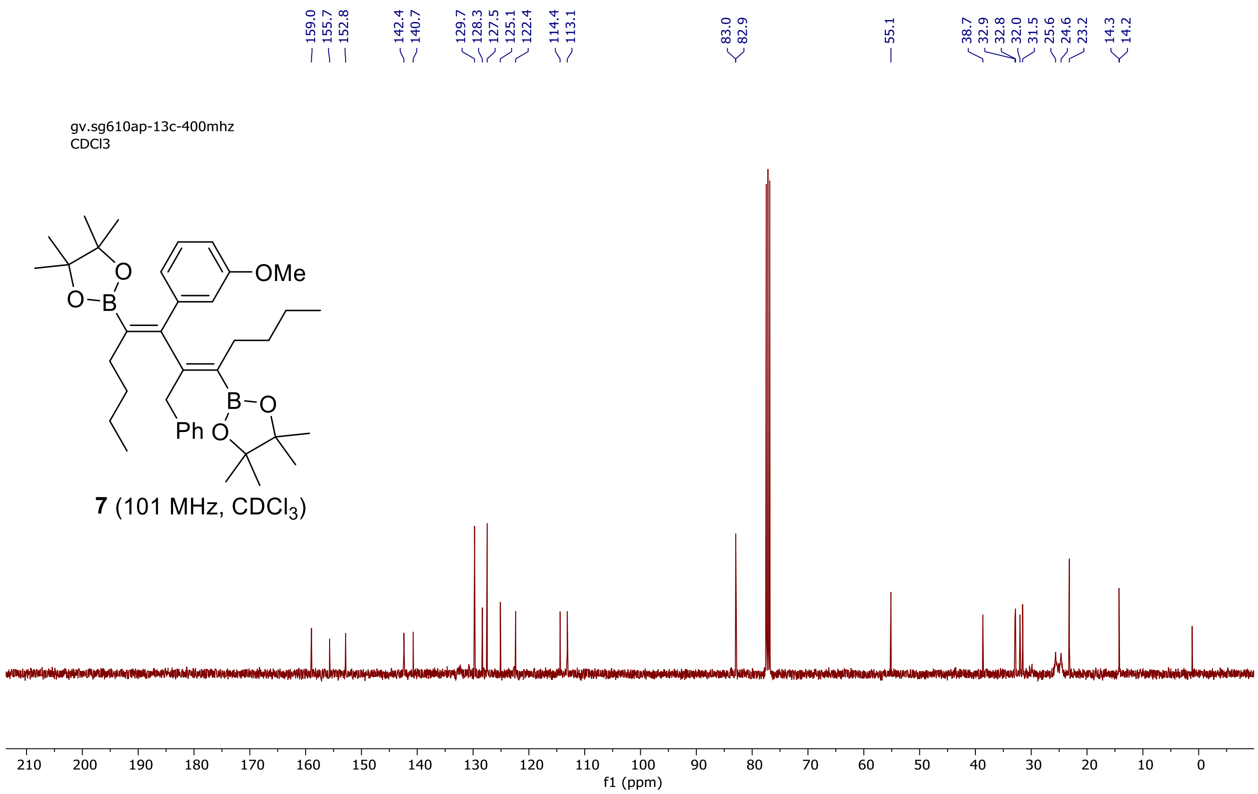


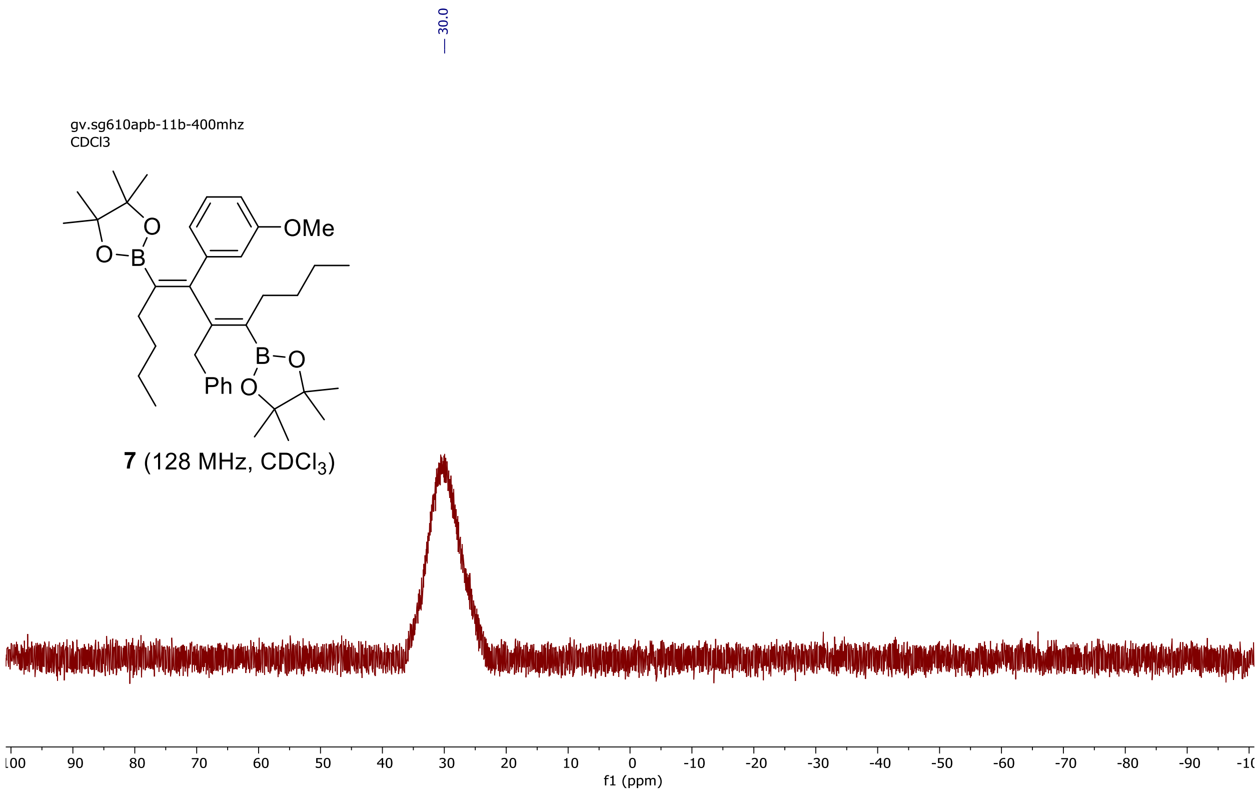
6 (500 MHz, $CDCl_3$)

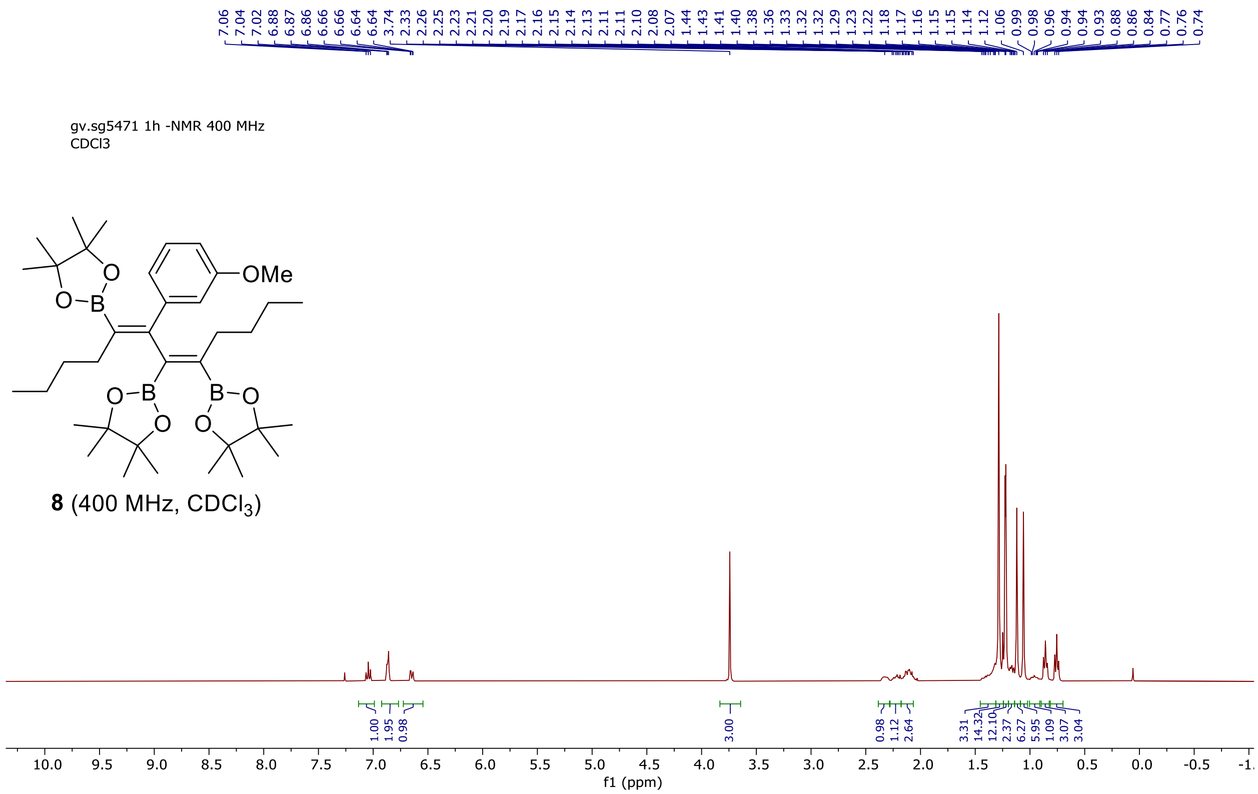

159.2
156.0
152.2
142.5
128.3
122.2
114.3
113.2
83.0
82.8
55.1
32.9
32.6
32.0
31.3
25.2
23.2
22.9
18.2
14.3
14.2
gv / sg / 603 - 1p
CDCl3
OMe
O
B
O
B
O
O
Me
6 (126 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

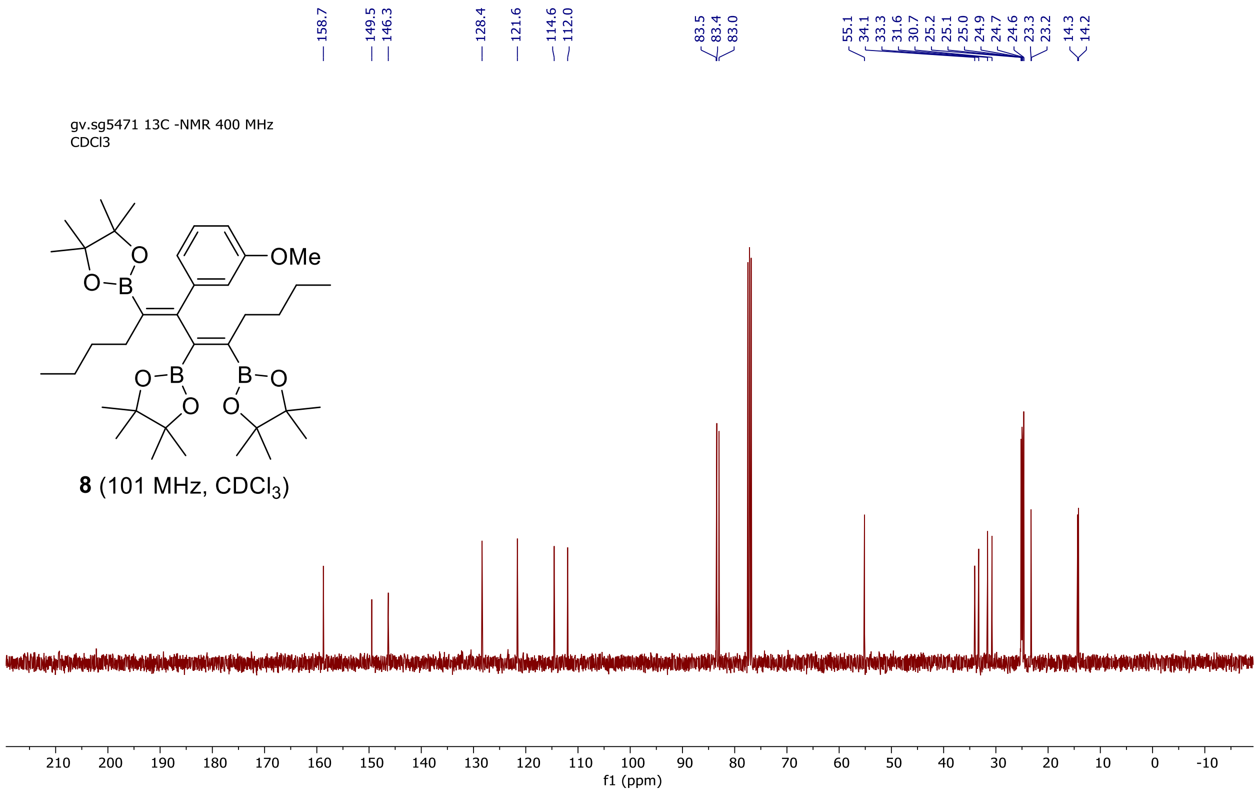

35.6
gv / sg / 603 - ip (b) - 11B-500mhz
CDCl3
OMe
O
B
O
B
O
O
Me
6 (160 MHz, $CDCl_3$)
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

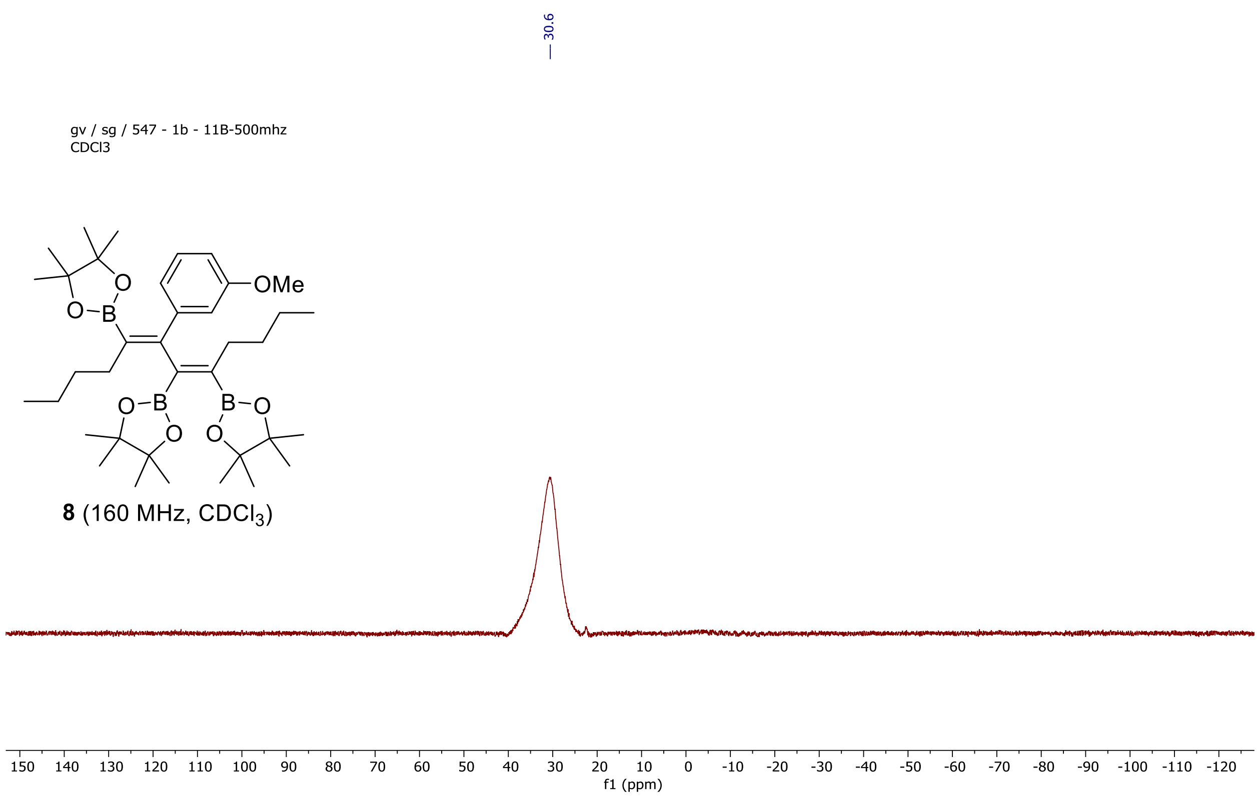

gv.sg610ap.10.fid
gv.sg610ap-1h-400mhz
OMe
Ph
7 (400 MHz, $CDCl_3$)
f1 (ppm)

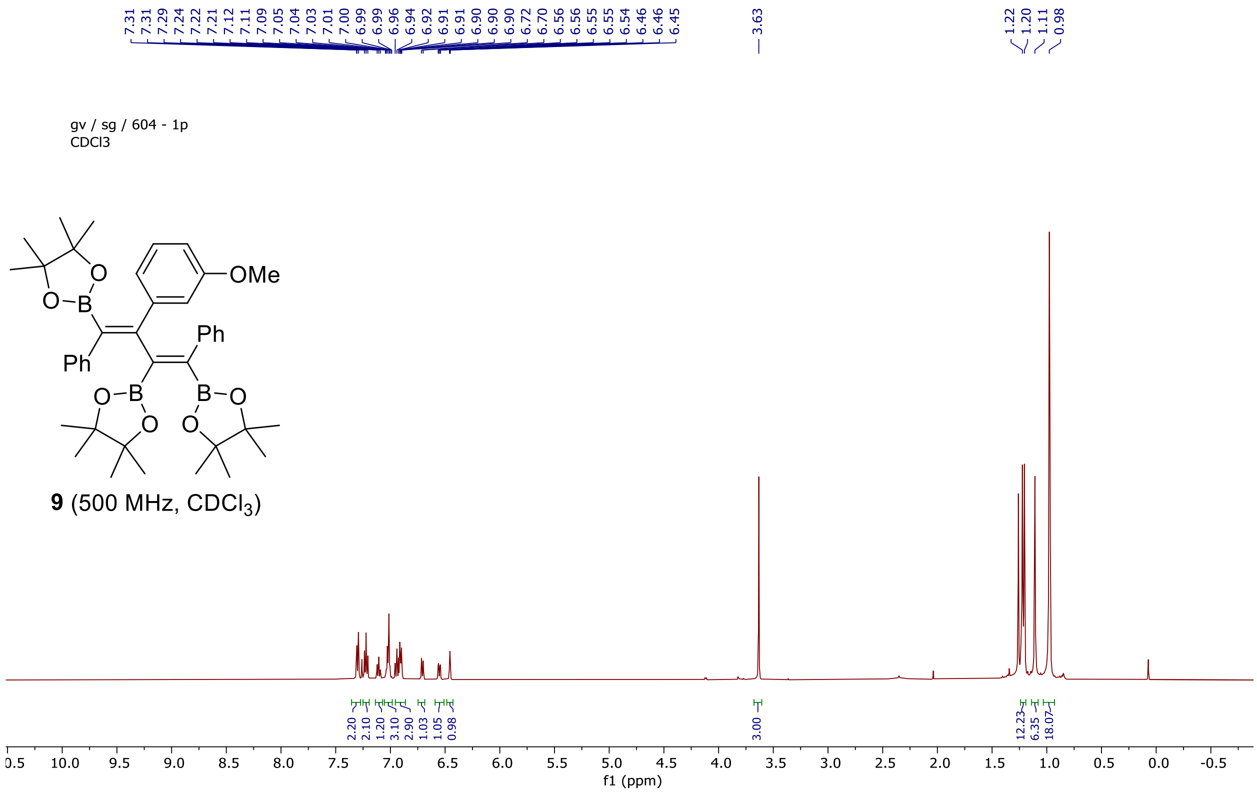

gv.sg610ap-13c-400mhz
CDCl3
OMe
Ph
7 (101 MHz, $CDCl_3$)
f1 (ppm)

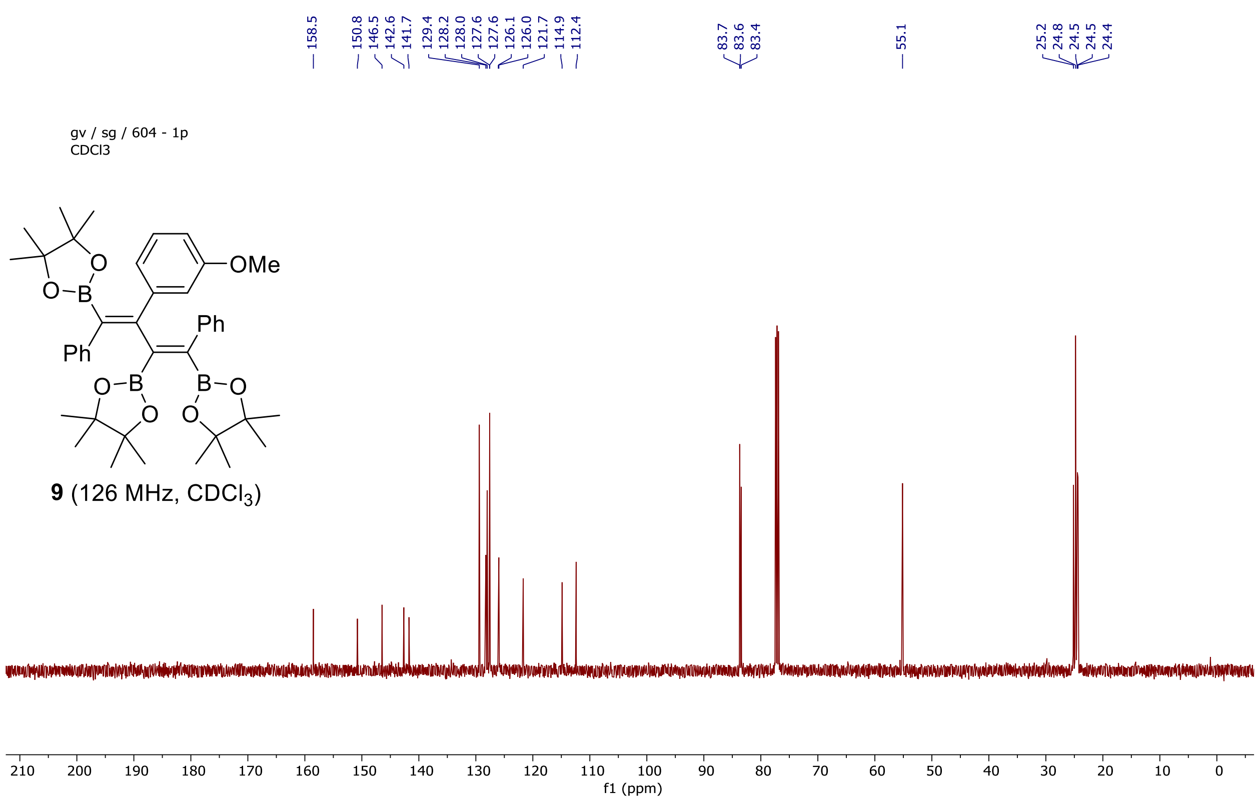

30.0
gv.sg610apb-11b-400mhz
CDCl3
OMe
Ph
7 (128 MHz, $CDCl_3$)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

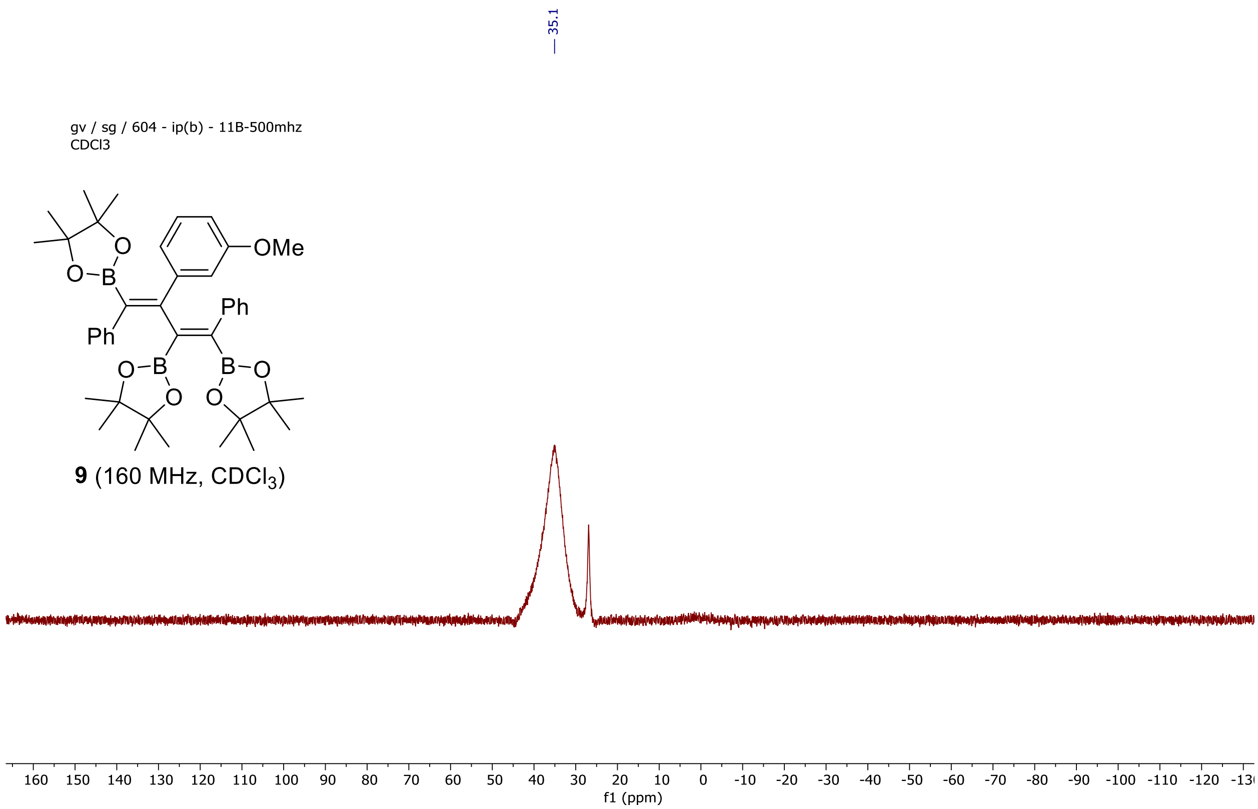

7.06 7.04 7.02 6.88 6.87 6.86 6.66 6.66 6.64 6.64 3.74 2.33 2.26 2.25 2.23 2.21 2.20 2.19 2.17 2.16 2.15 2.14 2.13 2.11 2.11 2.10 2.08 2.07 1.44 1.43 1.41 1.40 1.38 1.36 1.33 1.32 1.32 1.29 1.23 1.22 1.18 1.17 1.16 1.15 1.15 1.14 1.12 1.06 0.99 0.98 0.96 0.94 0.94 0.93 0.88 0.86 0.84 0.77 0.76 0.74
gv.sg5471 1h -NMR 400 MHz
CDCl3
OMe
8 (400 MHz, $CDCl_3$)
1.00 1.95 0.98 3.00 0.98 1.12 2.64 3.31 14.32 12.10 2.37 6.27 5.95 1.09 3.07 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.7
149.5
146.3
128.4
121.6
114.6
112.0
83.5
83.4
83.0
55.1
34.1
33.3
31.6
30.7
25.2
25.1
25.0
24.9
24.7
24.6
23.3
23.2
14.3
14.2
gv.sg5471 13C -NMR 400 MHz
CDCl3
OMe
8 (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

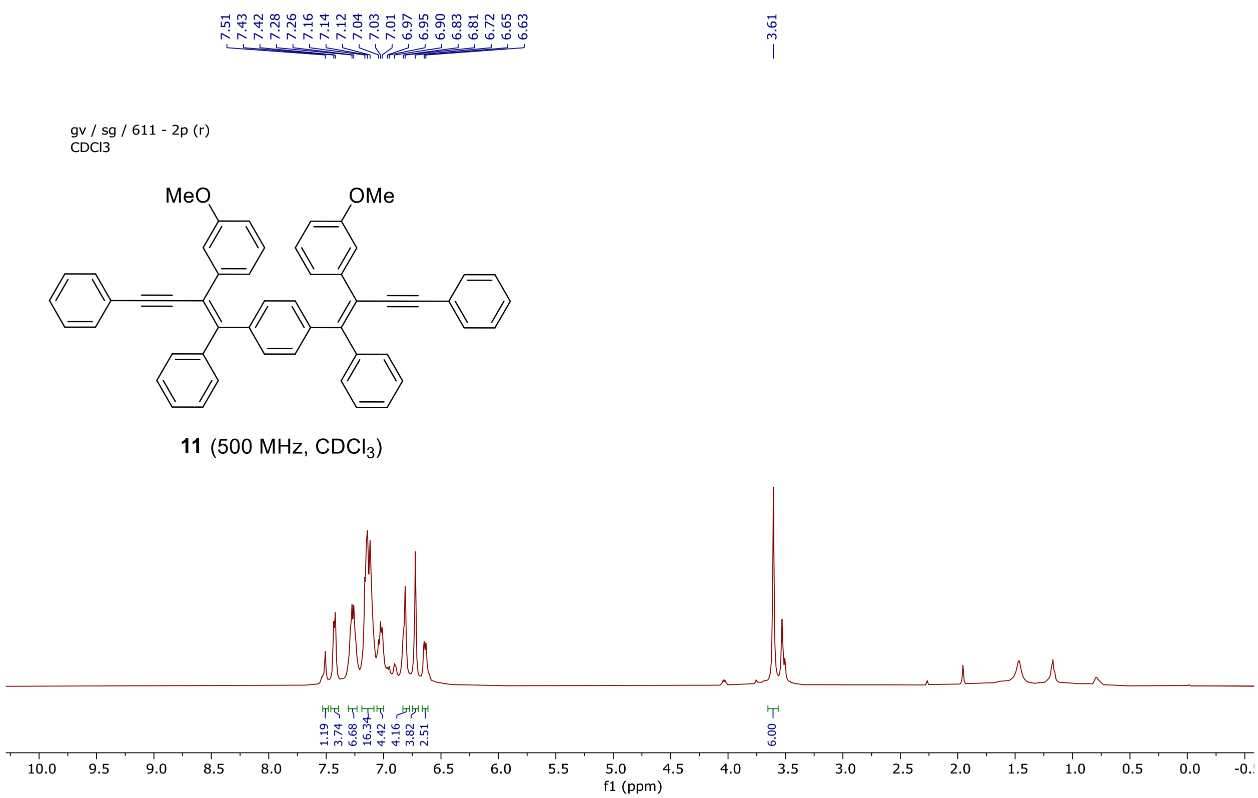

30.6
gv / sg / 547 - 1b - 11B-500mhz
CDCl3
OMe
8 (160 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)


7.31
7.31
7.29
7.24
7.22
7.21
7.12
7.11
7.09
7.05
7.04
7.03
7.01
7.00
6.99
6.99
6.96
6.94
6.92
6.91
6.91
6.90
6.90
6.90
6.72
6.70
6.56
6.56
6.55
6.55
6.54
6.46
6.45
3.63
1.22
1.20
1.11
0.98
gv / sg / 604 - 1p
CDCl3
OMe
Ph
Ph
9 (500 MHz, CDCl3)
2.20
2.10
1.20
3.10
2.90
1.03
1.05
0.98
3.00
12.23
6.35
18.07
f1 (ppm)

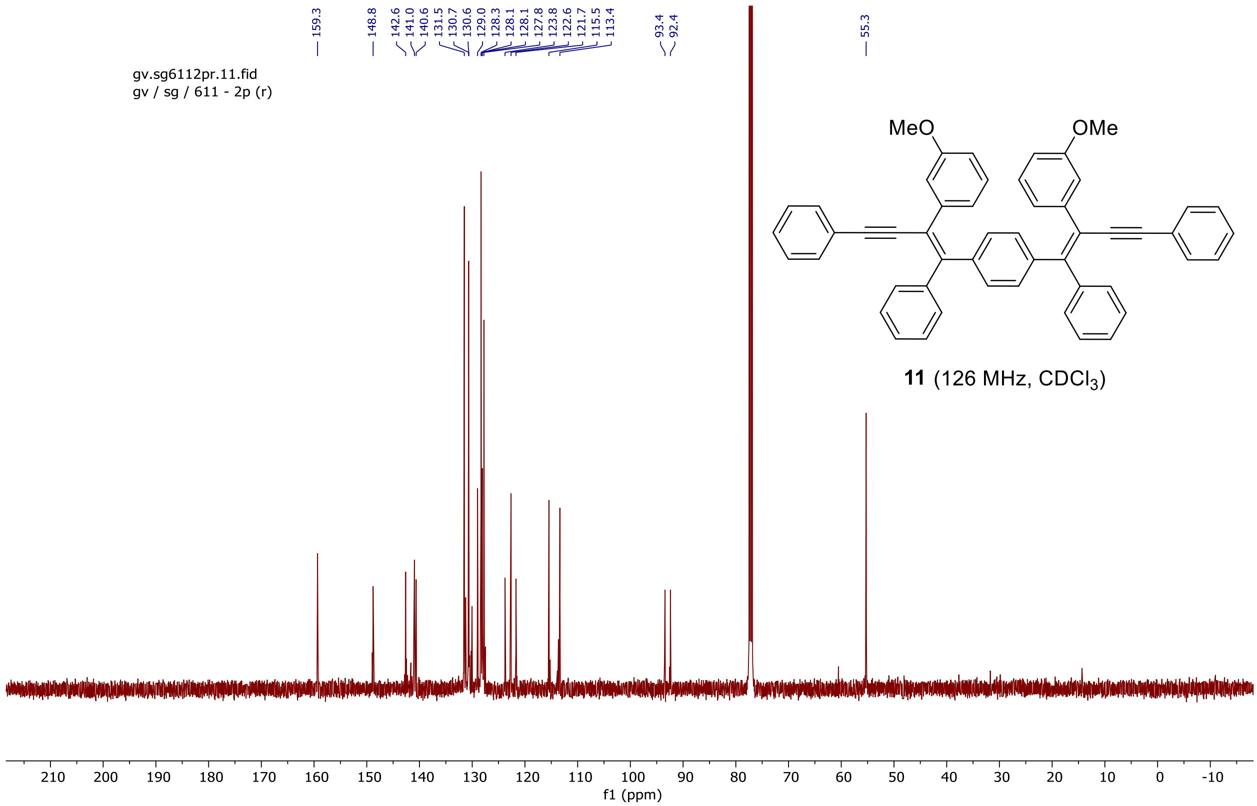

158.5
150.8
146.5
142.6
141.7
129.4
128.2
128.0
127.6
127.6
126.1
126.0
121.7
114.9
112.4
83.7
83.6
83.4
55.1
25.2
24.8
24.5
24.5
24.4
gv / sg / 604 - 1p
CDCl3
OMe
Ph
Ph
9 (126 MHz, CDCl3)
f1 (ppm)



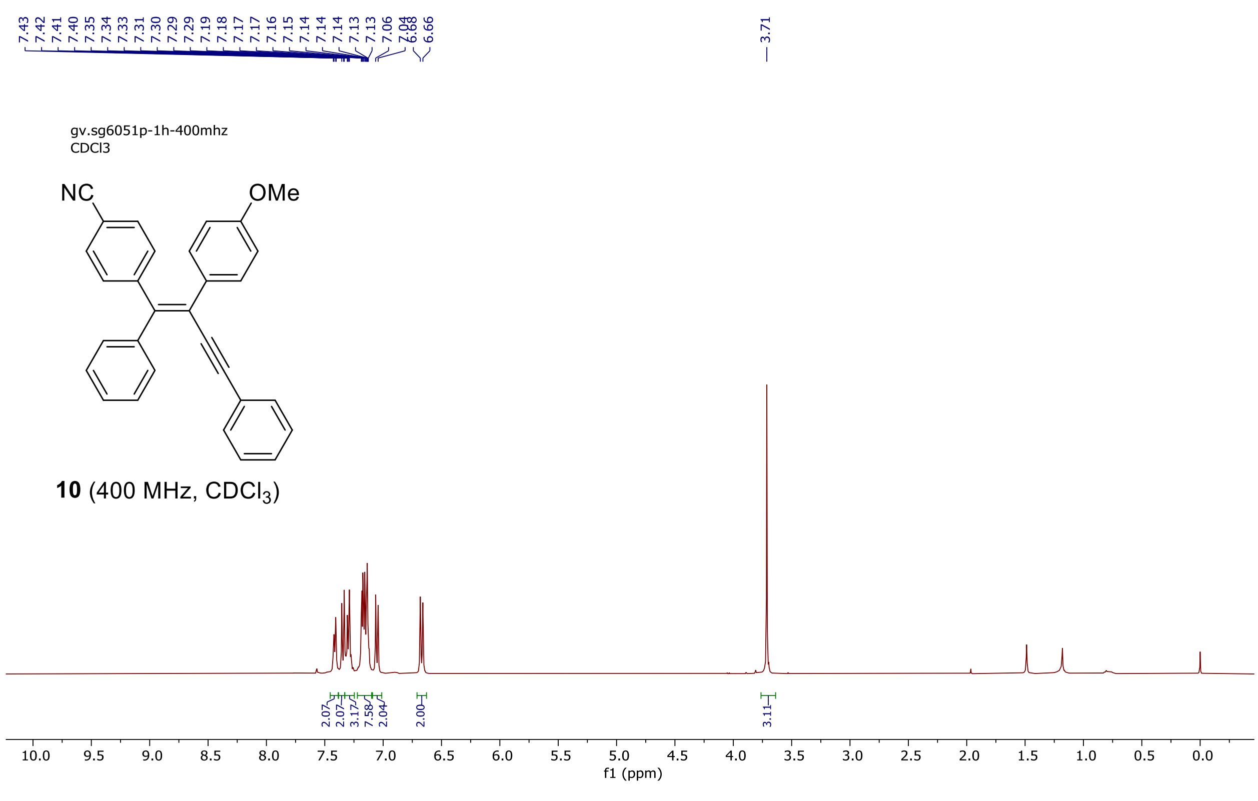
9 (160 MHz, $CDCl_3$)



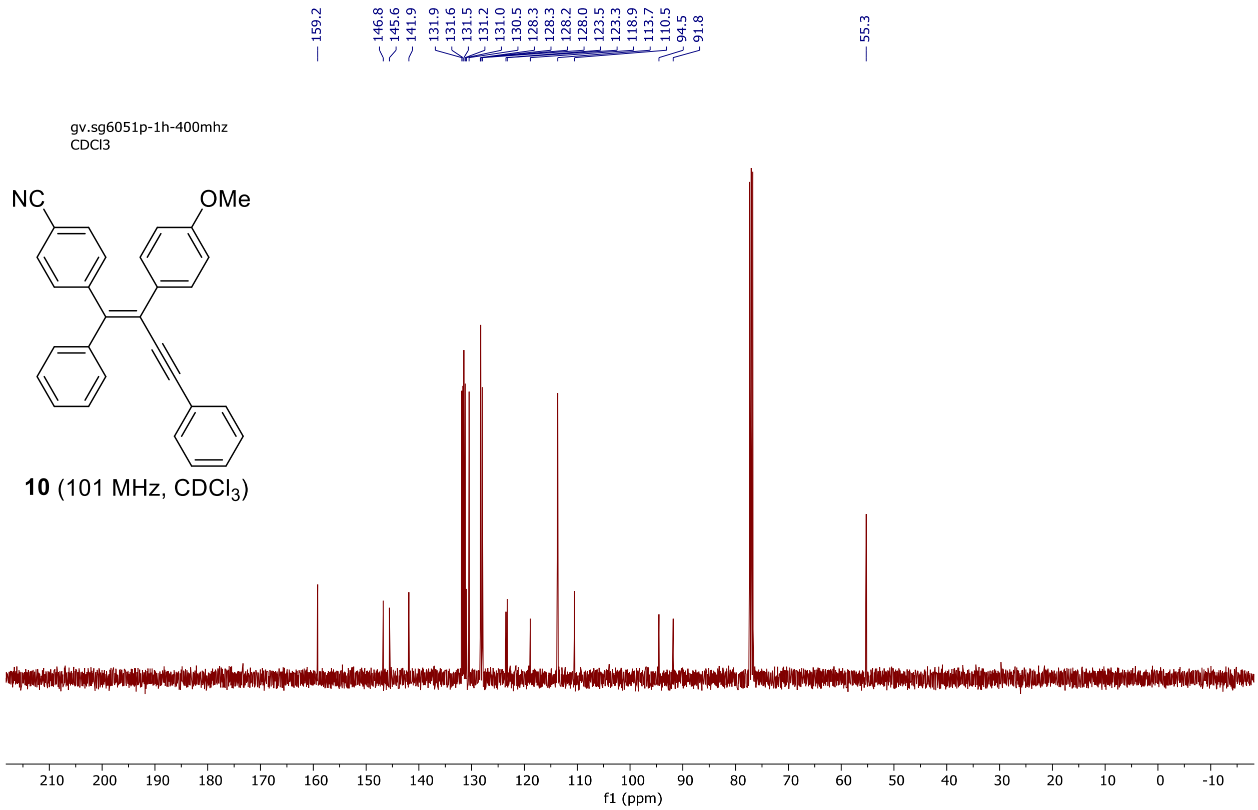
11 (500 MHz, $CDCl_3$)



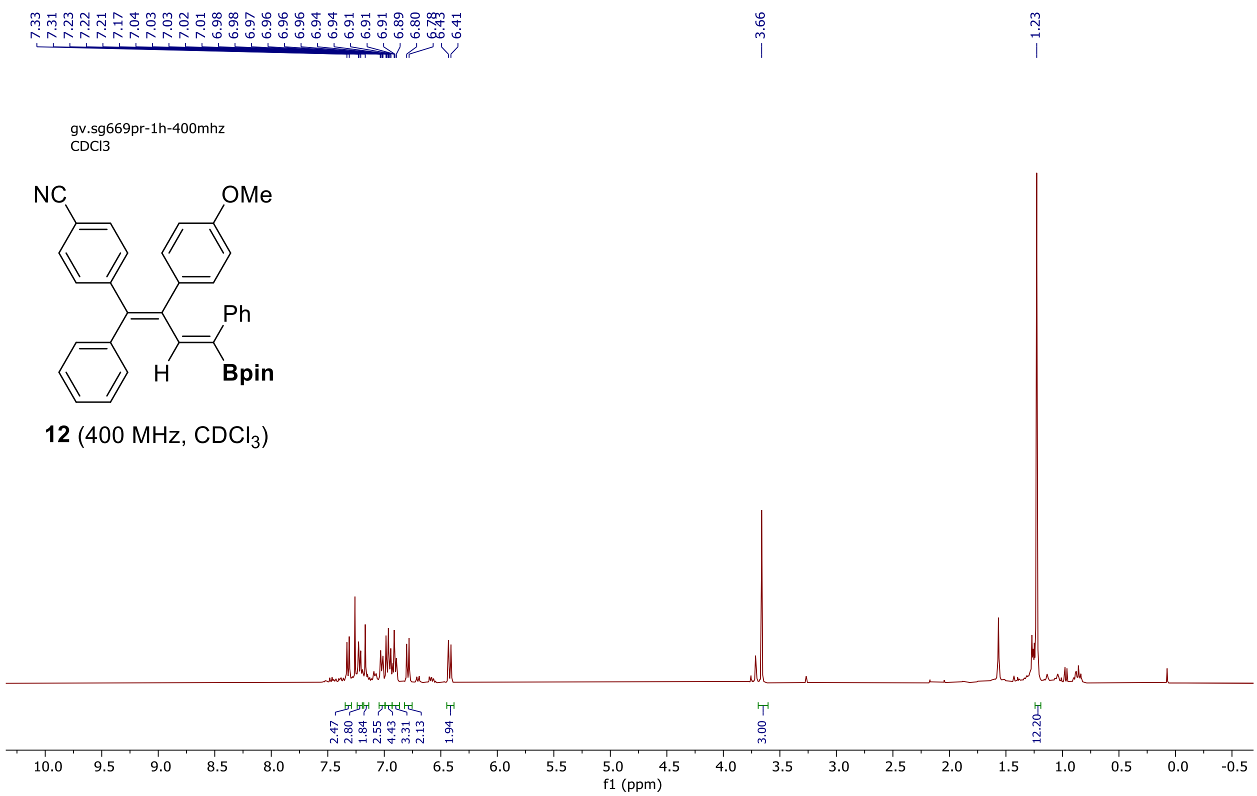
159.3
148.8
142.6
141.0
140.6
131.5
130.7
130.6
129.0
128.3
128.1
128.1
127.8
123.8
122.6
121.7
115.5
113.4
93.4
92.4
55.3
gv.sg6112pr.11.fid
gv / sg / 611 - 2p (r)
MeO
OMe
11 (126 MHz, CDCl3)
f1 (ppm)



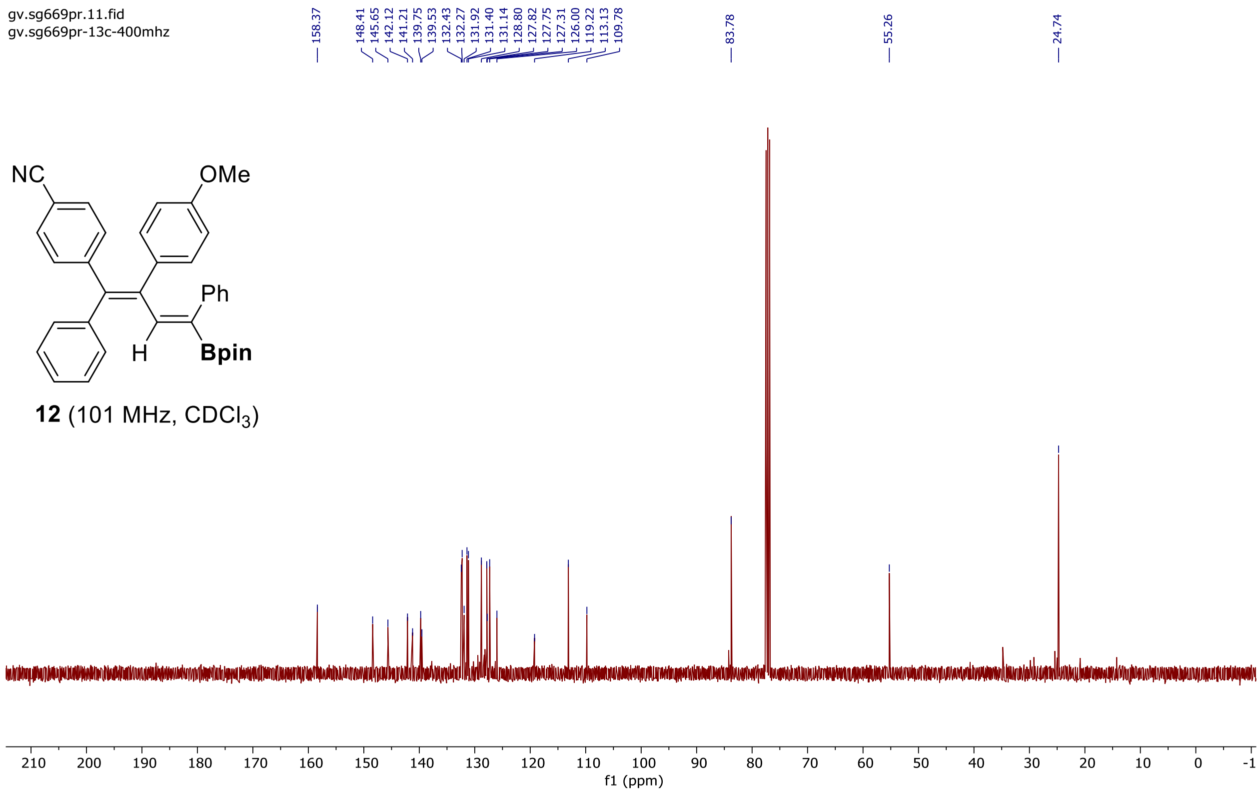
7.43
7.42
7.41
7.40
7.35
7.34
7.33
7.31
7.30
7.29
7.29
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.06
7.04
6.68
6.66
3.71
gv.sg6051p-1h-400mhz
CDCl3
NC
OMe
10 (400 MHz, CDCl3)
2.07
2.07
3.17
7.58
2.04
2.00
3.11
f1 (ppm)

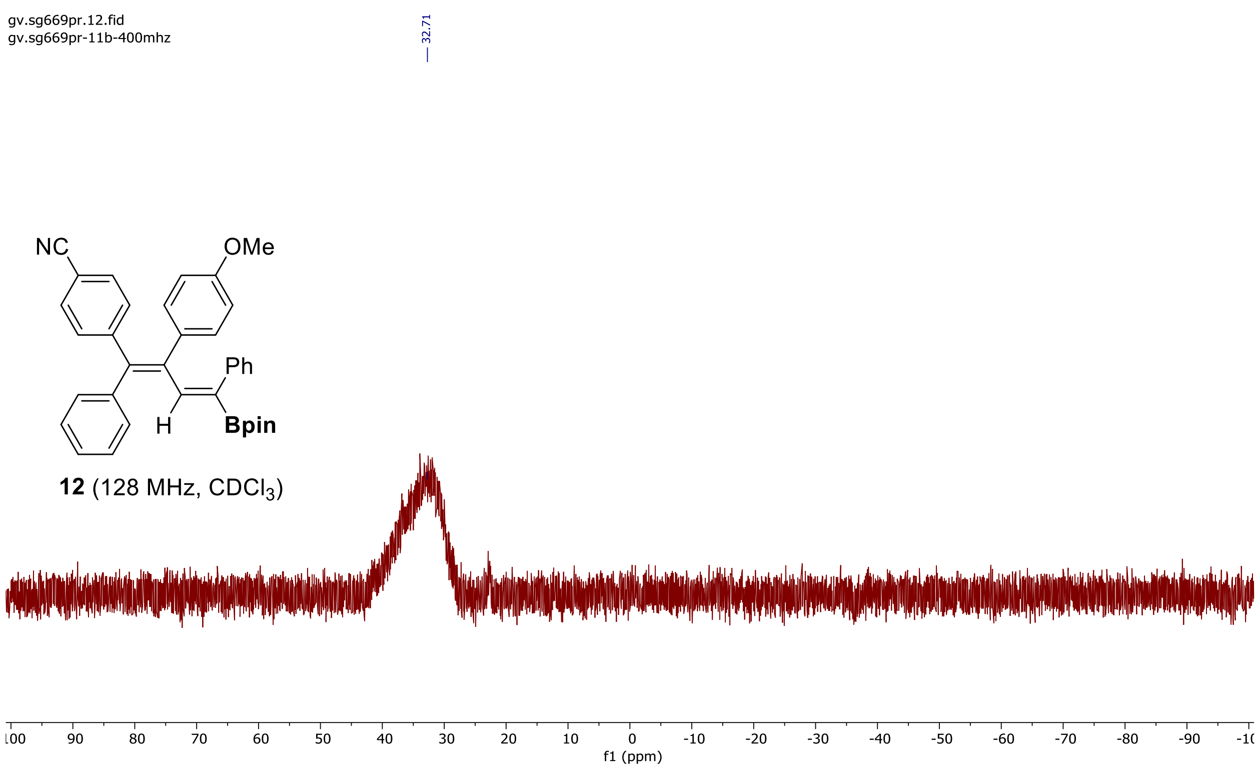


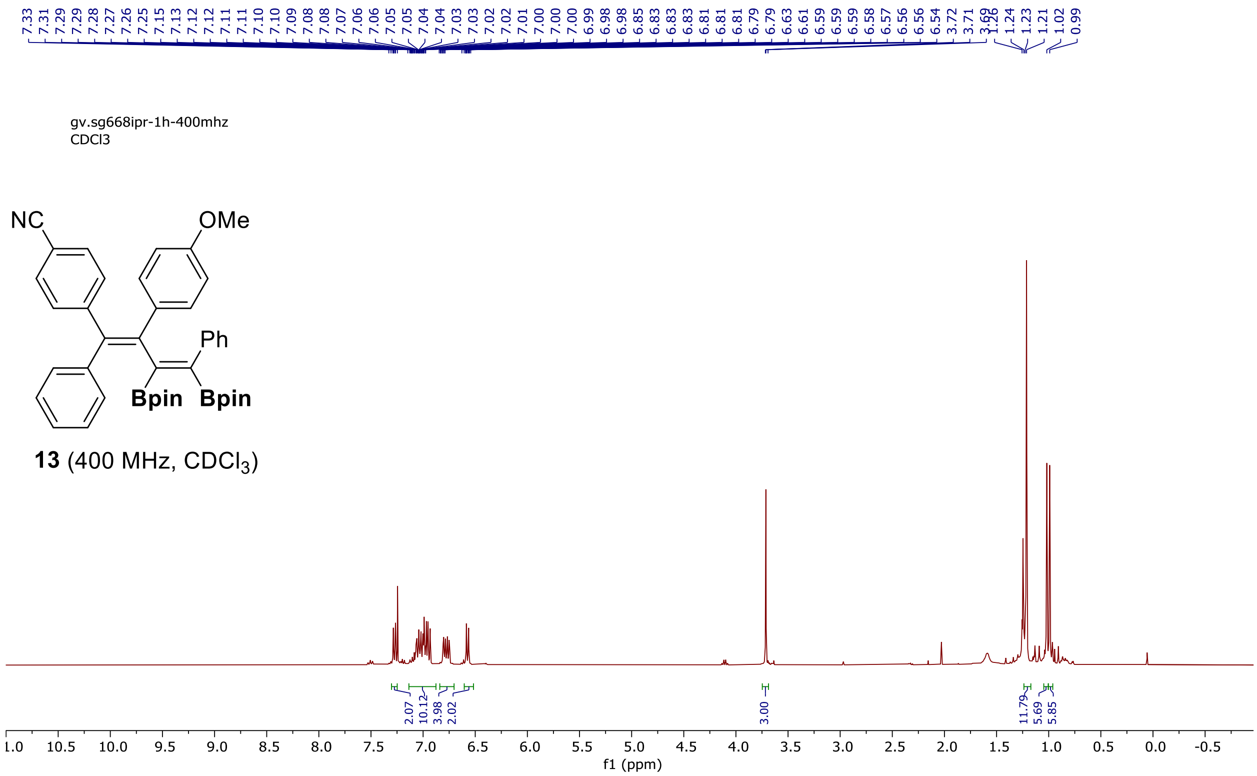
10 (101 MHz, $CDCl_3$)

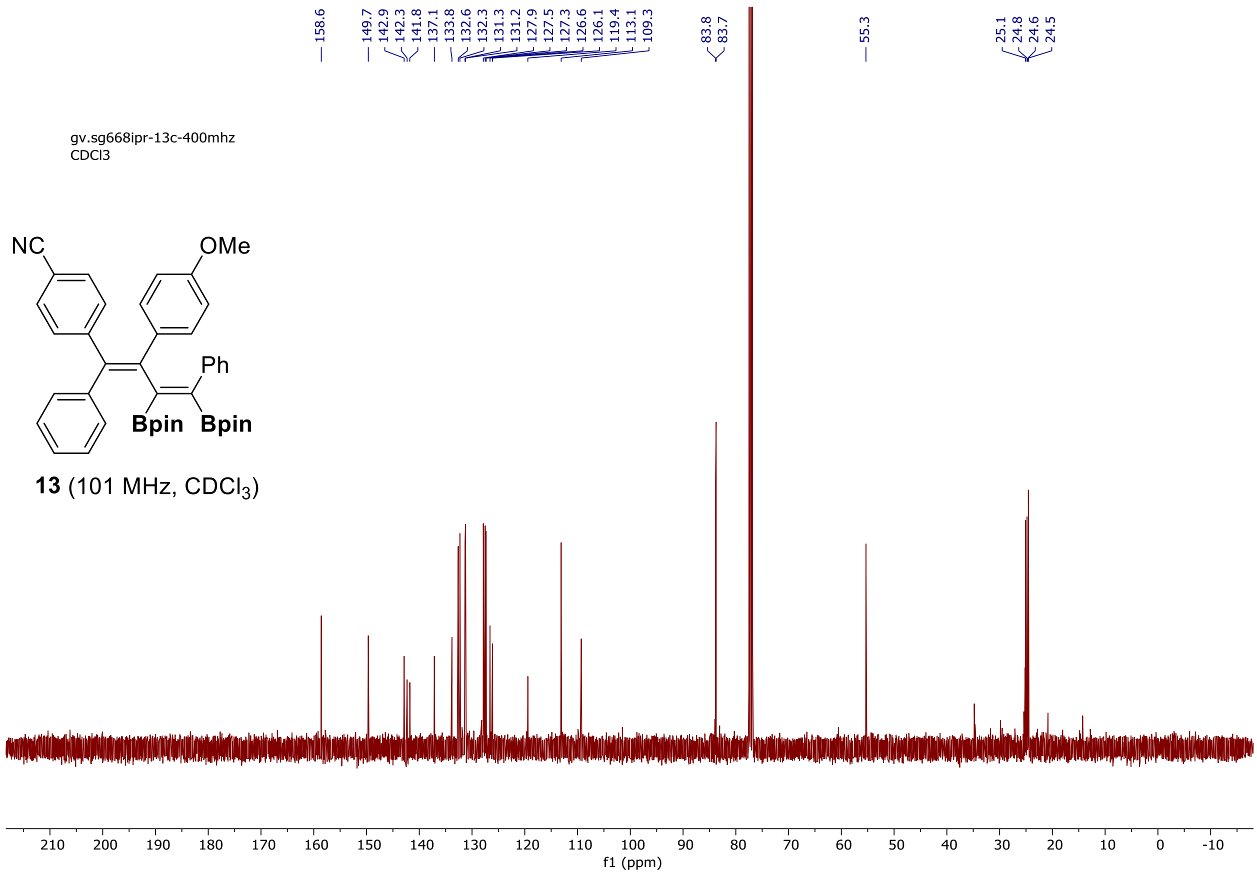


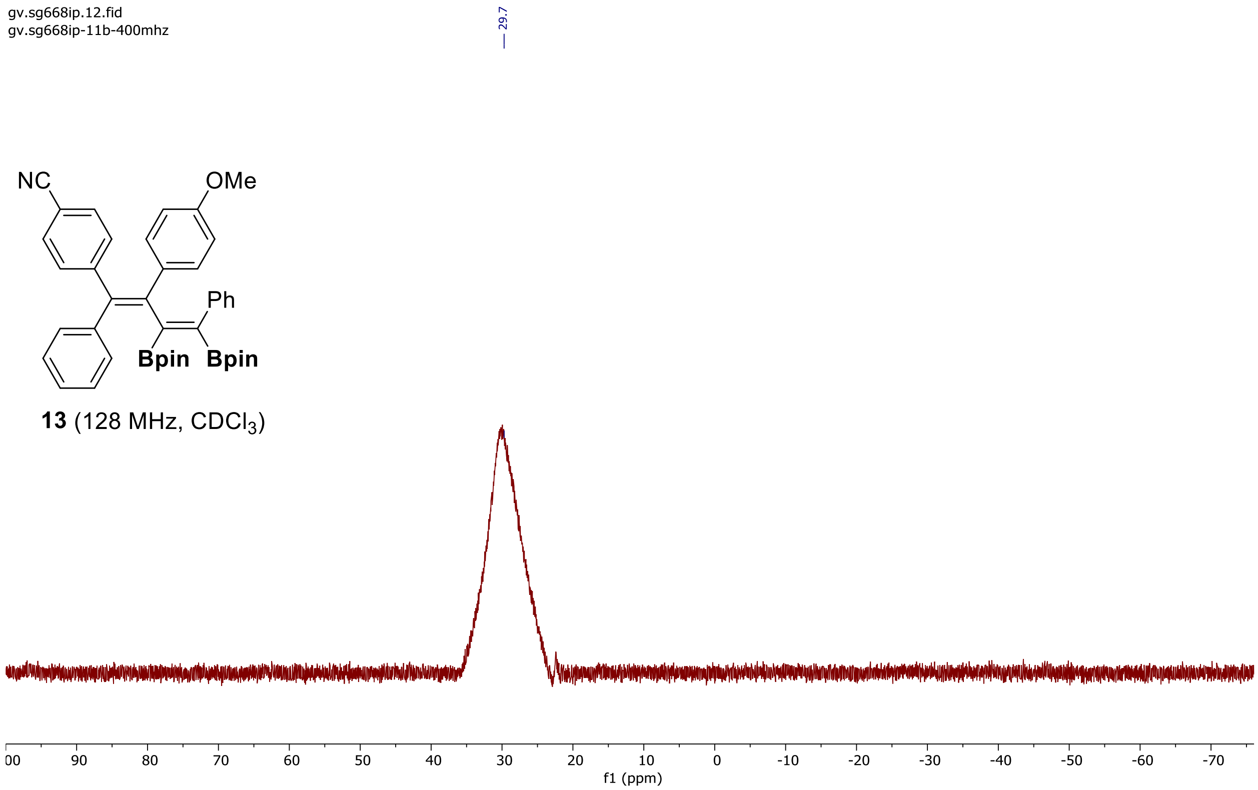
12 (400 MHz, $CDCl_3$)


gv.sg669pr.11.fid
gv.sg669pr-13c-400mhz
158.37
148.41
145.65
142.12
141.21
139.75
139.53
132.43
132.27
131.92
131.40
131.14
128.80
127.82
127.75
127.31
126.00
119.22
113.13
109.78
83.78
55.26
24.74
NC
OMe
Ph
H
Bpin
12 (101 MHz, CDCl3)
f1 (ppm)


gv.sg669pr.12.fid
gv.sg669pr-11b-400mhz
32.71
NC
OMe
Ph
H
Bpin
12 (128 MHz, CDCl3)
f1 (ppm)


7.33 7.31 7.29 7.29 7.28 7.27 7.26 7.25 7.15 7.13 7.12 7.12 7.11 7.11 7.10 7.10 7.09 7.08 7.08 7.07 7.06 7.05 7.05 7.04 7.04 7.03 7.03 7.02 7.02 7.01 7.00 7.00 6.99 6.98 6.98 6.85 6.83 6.83 6.83 6.81 6.81 6.81 6.79 6.79 6.63 6.61 6.59 6.59 6.59 6.58 6.57 6.56 6.54 3.72 3.71 3.69 1.26 1.24 1.23 1.21 1.02 0.99
gv.sg668ipr-1h-400mhz
CDCl3
NC
OMe
Ph
Bpin Bpin
13 (400 MHz, CDCl3)
2.07 10.12 3.98 2.02
3.00
11.79 5.69 5.85
f1 (ppm)


158.6 149.7 142.9 142.3 141.8 137.1 133.8 132.6 132.3 131.3 131.2 127.9 127.5 127.3 126.6 126.1 119.4 113.1 109.3
83.8 83.7
55.3
25.1 24.8 24.6 24.5
gv.sg668ipr-13c-400mhz
CDCl3
NC
OMe
Ph
Bpin Bpin
13 (101 MHz, CDCl3)
f1 (ppm)



14. References

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