Differential Dihydrofunctionalization of Terminal Alkynes: Synthesis of Benzylic Alkyl Boronates Through Reductive Three-Component Coupling

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1. General Information

All reactions were performed under a nitrogen atmosphere with flame-dried or oven-dried (120 °C) glassware, using standard Schlenk techniques, or in a glovebox (Nexus II from Vacuum Atmospheres). Column chromatography was performed using a Biotage Iso-1SV flash purification system with silica gel from Agela Technologies Inc. (60Å, 40-60 μm, 230-400 mesh). High Pressure Liquid Chromatography was performed using a Agilent LC column (Zorbax CN PrepHT, 21.2 x 250mm, 7μm). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer. IR peak absorbencies are represented as follows: s = strong, m = medium, w = weak, br = broad. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual solvent peak ($CDCl_3$: δ 7.26 ppm). ^{13}C NMR chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.2 ppm). ^{19}F NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to the internal standard, hexafluorobenzene (C_6F_6: δ -164.9 ppm). ^{11}B NMR chemical shifts (δ) are reported in part per million (ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet), coupling constants in Hertz (Hz), intergration. Mass spectra were collected on a JEOL HX-110 mass spectrometer. GC analysis was performed on a Shimadzu GC-2010 instrument with a flame ionization detector and a SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 μm film thickness). The following temperature program was used: 2 min @ 60 °C, 13 °C/min to 160 °C, 30 °C/min to 250 °C, 5.5 min @ 250 °C.

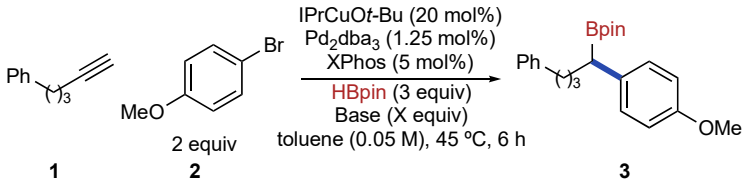
Materials: THF, CH_2Cl_2, ether, benzene, and toluene were degassed and dried by passing through columns of neutral alumina. Anhydrous isooctane was purchased from Millipore Sigma, and was subsequently degassed and stored over 4Å molecular sieves. Pinacolborane was purchase from TCI America and distilled over calcium hydride under reduced pressure before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were stored over 4Å molecular sieves prior to use. Commercial reagents were purchased from Millipore Sigma, TCI America, GFS-Chemicals, Ark-Pharm, Combi-Blocks, Oakwood Chemicals, Strem Chemicals and Alfa Aesar.

2. Reaction Development (Table 1)

All reactions were performed on a 0.05 mmol scale with the stoichiometry shown in Tables S1-S9. In a nitrogen-filled glovebox a dram vial was charged with a stir bar, alkoxide additive (Table S1), 5-phenyl-1-pentyne, 1,3,5-trimethoxybenzene (TMB, used as an internal standard for GC), palladium (Table S2 and S7), IPrCuX (Table S3 an S6), ligand (Table S4), 4-bromoanisole, HBpin (Table S5) and toluene (Table S8 and S9). The reaction mixture was stirred at 45 ºC. 30 μL aliquots were taken at 6 h, and 24 h time points, pushed through a plug of silica with 1.5 mL of EtOAc and monitored by Gas Chromatography.

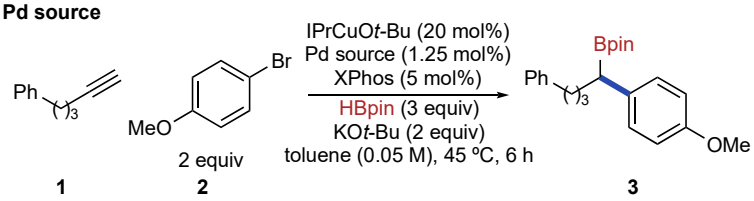
During preliminary reaction optimization both aryl chlorides and aryl bromides were explored. Aryl bromides were found to be competent coupling partners, while aryl chlorides did not provide product and were not used in further reaction development.

Table S1: Alkoxide Additive Screen



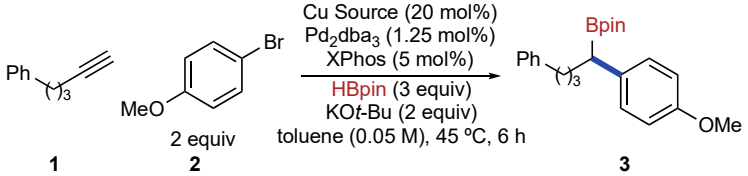
Entry	Alkoxide	Stoichiometry	%Yield 6 h	%Yield 24 h
1	NaO*t*-Bu	2 equiv	52	53
2	NaO*t*-Bu	3 equiv	54	56
3	LiO*t*-Bu	2 equiv	18	20
4	LiO*t*-Bu	3 equiv	34	36
5	KO*t*-Bu	1 equiv	5	4
6	KO*t*-Bu	2 equiv	38	40
7	KO*t*-Bu	2.5 equiv	82	85
8	KO*t*-Bu	3 equiv	86	87
9	KO*t*-Bu	4 equiv	73	75
10	KO*t*-Bu	5 equiv	60	62

Table S2: Palladium Catalyst Screen



Entry	Pd Source	%Yield 6 h	%Yield 24 h
1	$Pd(OAc)_2$	54	56
2	Pd_2dba_3	86	87
3	$Pddba_2$	39	42
4	$Pd(t\text{-}Bu_3)_2$	20	30
5	$Pd(PPh_3)_2Cl_2$	3	4
6	$Pd(TFA)_2$	35	34
7	Peppsi Pd	32	33
8	$Pd(cinnamyl)Cl_2$	15	16
9	$Pd(COD)_2Cl_2$	21	31

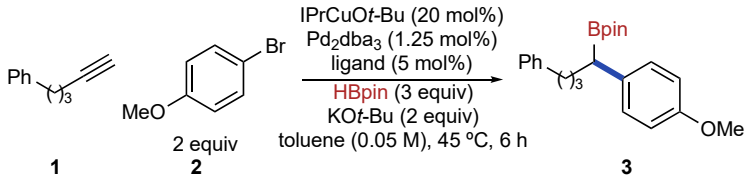
Table S3: Copper Catalyst Screen



Entry	Copper Catalyst	%Yield 6 h	%Yield 24 h

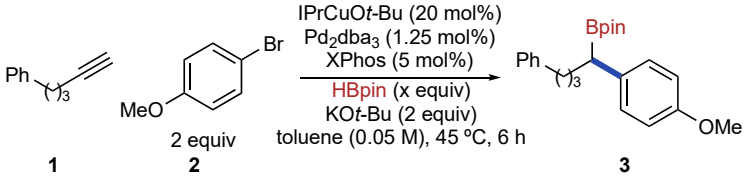
1	IPrCuO*t*-Bu	86	87
2	IPrCuCl	67	70
3	SIPrCuCl	58	60
4	SIPrCuO*t*-Bu	54	58
5	IMesCuCl	8	10
6	SIMesCuCl	10	11
7	ICyCuCl	0	0
8	I*t*-BuCuCl	0	1
9	IBoxCuCl	0	0
10	IPr*CuCl	4	7
11	(6DIPP)CuO*t*-Bu	3	3
12	CyIMesCuCl	0	0
13	CyIPrCuCl	3	4
14	CyIBoxCuCl	1	2
15	IPrCuO(2-*t*-Bu-C_6H_4)	43	47

Table S4: Ligand Screen



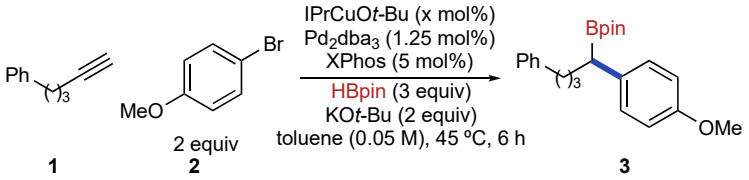
Entry	Ligand	%Yield 6 h	%Yield 24 h
1	XPhos	86	87
2	RuPhos	18	18
3	SPhos	6	8
4	BrettPhos	20	22
5	DavePhos	13	16
6	CPhos	8	15
7	Di-BIME	3	5
8	JosiPhos	4	4
9	Me-DuPhos	2	2
10	PCy_3	5	17
11	(*R*)-DTBM-SEGPhos	8	8
12	QuinoxP	2	5
13	XantPhos	0	0
14	chiraphos	5	6
15	*rac*-BINAP	5	5
16	NMDPP	2	3
17	DPPF	7	7

Table S5: HBpin Stoichiometry Screen



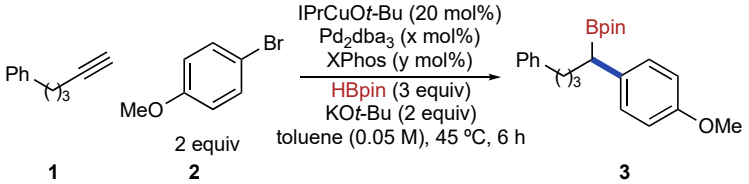
Entry	Equivalents of HBpin	%Yield 6 h	%Yield 24 h
1	2.0	49	50
2	2.5	61	60
3	2.8	71	74
4	3.0	86	87
5	4.0	55	55
6	5.0	52	53

Table S6: Copper Catalyst Loading Screen



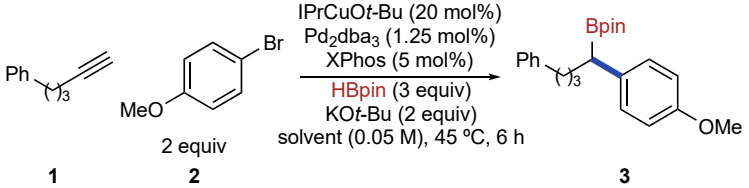
Entry	Cu catalyst loading	%Yield 6 h	%Yield 24 h
1	10 mol%	31	30
2	15 mol%	62	65
3	20 mol%	86	87

Table S7: Palladium Catalyst Loading Screen



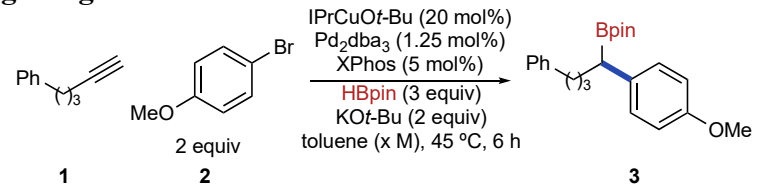
Entry	Pd catalyst loading	XPhos Loading	%Yield 6 h	%Yield 24 h
1	1.25 mol%	5 mol%	86	87
2	2.5 mol%	10 mol%	59	60
3	5 mol%	20 mol%	32	32

Table S8: Solvent Screen



Entry	Solvent	%Yield 6 h	%Yield 24 h
1	toluene	86	87
2	benzene	65	68
3	isooctane	24	24
4	dioxane	5	6
5	THF	0	0
6	ether	0	0
7	DCM	0	0
8	DME	0	0

Table S9: Limiting Reagent Concentration Screen



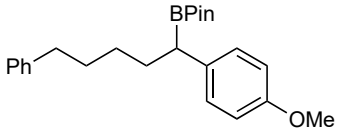
Entry	Concentration (M) (w.r.t alkyne)	%Yield 6 h	%Yield 24 h
1	0.1	74	73
2	0.075	80	81
3	0.05	86	87
4	0.033	69	68
5	0.025	59	59
6	0.01	55	56

3. General Procedure for the Differential Dihydrofunctionalization of Alkynes (Table 2)

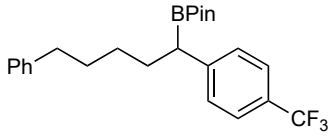
In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, KO*t*-Bu (122.3 mg, 1.00 mmol, 2.0 equiv), IPrCuO*t*-Bu (52.6 mg, 0.1 mmol, 0.20 equiv), HBpin (192.0 mg, 1.50 mmol, 3.0 equiv), toluene (10 mL, 0.05M) and alkyne (0.5 mmol, 1.0 equiv). The reaction mixture was stirred at 45 °C until the yellow color disappeared. To this reaction mixture was added Pd_2dba_3 (5.7 mg, 0.00625 mmol, 0.0125 equiv), XPhos (11.9 mg, 0.025 equiv) and aryl bromide (1.0 mmol, 2.0 equiv) and the reaction mixture was vigorously stirred at 45 °C. After 6 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC. Upon consumption of the alkyne, the reaction mixture was diluted with Et_2O, washed with 1 M HCl and brine, dried over Na_2SO_4, filtered through a pad a silica gel and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography.

A variety of aryl chlorides were also surveyed under the optimized reaction conditions using 5-phenyl-1-pentyne as a coupling partner, but did not produce the desired product and were not further optimized.

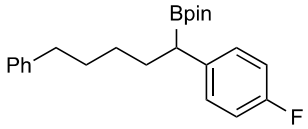
4. Characterization of Differential Dihydrofunctionalization Products



2-[1-(4-methoxyphenyl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3), compound was prepared according to reported procedure and was purified by silica gel column chromatography, 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (162 mg, 85% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 – 7.23 (m, 3H), 7.21 – 7.06 (m, 5H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 1H), 1.95 – 1.73 (m, 1H), 1.72 – 1.51 (m, 4H), 1.38 – 1.24 (m, 3H), 1.18 (d, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4, 142.9, 135.5, 129.3, 128.5, 128.3, 125.6, 113.9, 83.3, 55.2, 35.9, 32.9, 31.5, 29.0, 25.0, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.7. GCMS (EI) calculated for [M]+ 380.25, found 380.3. FTIR (neat, cm^{-1}): 3053(m), 2980(s), 2929(s), 2858(m), 1604(m), 1510(s), 1456(m), 1371(m), 1325(m), 1246(m), 1145(s), 1030(m), 851(m), 755(s).

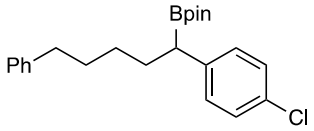


4,4,5,5-tetramethyl-2-{5-phenyl-1-[4-(trifluoromethyl)phenyl]pentyl}-1,3,2-dioxaborolane (8), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography, 0-100% DCM in hexanes and was isolated as a clear colorless liquid (171 mg, 82% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.19 (m, 6H), 7.21 – 7.09 (m, 3H), 2.65 – 2.51 (m, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.97 – 1.79 (m, 1H), 1.76 – 1.51 (m, 3H), 1.39 – 1.22 (m, 2H), 1.18 (d, *J* = 5.7 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.9, 142.7, 128.7, 128.5, 128.3, 127.3 (q, *J* = 34.2 Hz), 125.7, 125.3 (q, *J* = 3.7 Hz), 124.8 (q, *J* = 266.7 Hz), 83.6, 35.8, 32.4, 31.4, 28.9, 24.7, 24.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.1. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5. GCMS (EI) calculated for [M]+ 418.23, found 418.4. FTIR (neat, cm^{-1}): 3027(m), 2979(s), 2931(s), 2858(m), 1617(s), 1454(m), 1371(s), 1325(s), 1164(m), 1123(s), 1068(s), 1018(s), 966(m), 851(m), 734(m), 699(m).

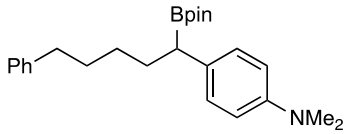


2-[1-(4-fluorophenyl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes and was isolated as a clear colorless liquid (172 mg, 93% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 – 7.10 (m, 8H), 6.93 (t, *J* = 8.8 Hz, 2H), 2.65 – 2.50 (m, 1H), 2.27 (t, *J* = 7.9 Hz, 1H), 1.93 – 1.76 (m, 1H), 1.73 – 1.46 (m, 3H), 1.38 – 1.10 (m, 14H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.1 (d, *J* = 242.3 Hz), 142.8, 139.1, 129.7 (d, *J* = 7.9 Hz), 128.4 (d, *J* = 24.0 Hz), 125.7, 115.0 (d, *J* = 20.9 Hz), 83.4, 35.9, 32.7, 31.4, 28.9, 24.9, 24.7, 24.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -121.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ

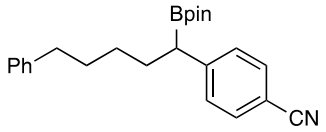
32.4. GCMS (EI) calculated for [M]+ 368.23, found 368.3. FTIR (neat, cm^{-1}): 3058(m), 2978(s), 2930(s), 2857(m), 1603(s), 1506(s), 1370(s), 1324(s), 1219(s), 1142(s), 967(m), 852(m), 699(m).



2-[1-(4-chlorophenyl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10), compound was prepared according to reported procedure and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (126 mg, 65% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.06 (m,11H), 2.65 – 2.50 (m, 2H), 2.26 (t, *J* = 7.9 Hz, 1H), 1.94 – 1.75 (m, 1H), 1.60 (m, 3H), 1.31 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.8, 142.1, 130.9, 129.8, 128.5, 128.3, 125.7, 120.1, 83.5, 35.9, 32.5, 31.4, 28.9, 24.8, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3. GCMS (EI) calculated for [M]+ 384.20, found 384.3. FTIR (neat, cm^{-1}): 3059(m), 2979(s), 2931(s), 2858(m), 1604(s), 1490(s), 1366(s), 1322(s), 1143(s), 1091(s), 1015(s), 967(m), 851(m), 699(m).

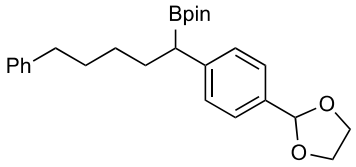


***N,N*-dimethyl-4-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]aniline (11)**, compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu, NaO*t*-Bu instead of KO*t*-Bu and a 1:1 mixture of toluene isooctane, and was purified by prep TLC, 2% TEA, 20% EtOAc in hexanes, and was isolated as a clear colorless liquid (156 mg, 79% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 9.0 Hz, 2H), 7.27 – 7.19 (m, 6H), 6.61 (d, *J* = 9.0 Hz, 2H), 3.01 (s, 6H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.88 - 1.83 (m, 1H), 1.70 - 1.55 (m, 3H), 1.35 - 1.16 (m, 14H) .^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.4, 142.6, 130.4, 130.4, 128.5, 128.4, 125.8, 125.2, 110.8, 83.5, 40.1, 37.8, 36.0, 31.4, 24.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8. GCMS (EI) calculated for [M]+ 393.28, found 393.3. FTIR (neat, cm^{-1}): 2052(m), 2980(s), 2940(s), 2858(m), 1606(m), 1511(s), 1456(m), 1415(m), 1340(m), 1248(m), 1152(s), 1035(m), 850(m), 755(s), 699(m).

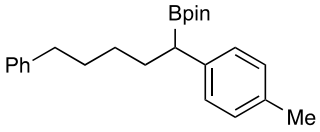


4-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]benzonitrile (12), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel column chromatography, 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (120 mg, 64% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.21 (m, 5H), 7.15 (m, 3H), 2.57 (td, *J* = 7.4, 3.4 Hz, 2H), 2.37 (t, *J* = 7.9 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.75 – 1.55 (m, 3H), 1.39 – 1.24 (m, 4H), 1.17 (d, *J* = 5.0 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.6, 142.6, 132.2, 129.1, 128.5, 128.3, 125.7, 119.5, 109.0, 83.8, 35.8, 32.0, 31.3, 28.8, 25.0, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3. GCMS (EI) calculated for [M]+ 375.23, found 375.2. FTIR (neat,

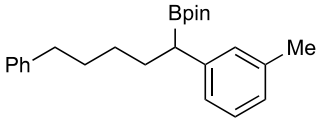
cm^{-1}): 3049(m), 2978(s), 2931(s), 2857(m), 2226(s), 1605(s), 1455(m), 1370(s), 1327(s), 1142(s), 967(m), 851(m), 699(m).



2-{1-[4-(1,3-dioxolan-2-yl)phenyl]-5-phenylpentyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13), compound was prepared according to reported procedure and was purified by silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (187 mg, 89% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.17 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 5.77 (s, 1H), 4.29 – 3.88 (m,4H), 2.67 – 2.45 (m, 2H), 2.30 (t, *J* = 7.9 Hz, 1H), 2.00 – 1.74 (m, 1H), 1.74 – 1.46 (m, 3H), 1.46 – 1.20 (m, 2H), 1.16 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.7, 142.8, 134.5, 128.4, 128.4, 128.2, 126.5, 125.6, 104.0, 83.3, 65.4, 35.9, 32.5, 31.5, 28.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.6. GCMS (EI) calculated for [M]+ 422.26, found 422.3. FTIR (neat, cm^{-1}): 3048(m), 2978(s), 2930(s), 2857(s), 1615(s), 1454(m), 1370(m), 1325(s), 1217(m), 1217(m), 1142(m), 1020(m), 966(m), 911(w), 851(m), 699(m).

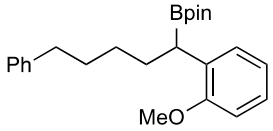


4,4,5,5-tetramethyl-2-[1-(4-methylphenyl)-5-phenylpentyl]-1,3,2-dioxaborolane (14), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (142 mg, 78% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.01 (m,10H), 2.57 (t, *J* = 9.0 Hz, 1H), 2.43 – 2.20 (m, 5H), 1.95 – 1.74 (m, 1H), 1.64 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.41 – 1.29 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.8, 140.3, 134.4, 129.3, 129.0, 128.4, 128.3, 125.6, 83.2, 35.9, 32.7, 31.5, 29.0, 24.7, 24.6, 24.6, 21.1. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3. GCMS (EI) calculated for [M]+ 364.26, found 364.3. FTIR (neat, cm^{-1}): 3059(m), 2977(m), 2857(m), 1604(s), 1512(m), 1453(m), 1370(m), 1325(m), 1142(s), 1030(m), 982(m), 851(m), 734(m).

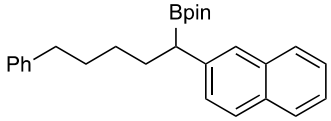


4,4,5,5-tetramethyl-2-[1-(3-methylphenyl)-5-phenylpentyl]-1,3,2-dioxaborolane (15), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (134 mg, 74% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.20 (m,3H), 7.21 – 7.08 (m,42H), 7.05 – 6.90 (m, 3H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.29 (d, *J* = 17.0 Hz,4H), 1.97 – 1.76 (m, 1H), 1.64 (m, 7.8 Hz, 3H), 1.35 (t, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 7.5 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.4, 142.9, 129.3, 128.5, 128.3, 128.2, 126.0, 125.6, 125.4, 83.3, 35.9, 32.7, 31.6, 29.1, 24.9, 24.7, 21.6. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4. GCMS (EI) calculated for [M]+ 364.26, found 364.3. FTIR (neat, cm^{-1}): 3061(m), 3026(m), 2978(s), 2929(s), 2857(m), 1604(s),

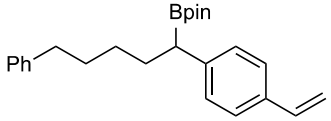
1496(m), 1496(m), 1454(m), 1370(s), 1322(s), 1142(s), 1109(m), 967(m), 864(m), 750(m), 698(m).



2-[1-(2-methoxyphenyl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (158 mg, 83% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.05 (m, 10H), 6.97 – 6.71 (m, 2H), 3.78 (s, 3H), 2.57 (m, 2H), 2.42 (t, *J* = 7.7 Hz, 1H), 1.95 – 1.75 (m, 1H), 1.75 - 1.55 (m, 3H), 1.42 – 1.14 (m, 14H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.1, 143.1, 132.4, 129.7, 128.5, 128.2, 126.3, 125.5, 120.6, 110.0, 83.1, 55.1, 36.0, 31.6, 30.6, 29.0, 24.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.1. GCMS (EI) calculated for [M]+ 380.25, found 380.3. FTIR (neat, cm^{-1}): 3063(s), 2979(m), 2932(s), 2858(m), 1600(m), 1490(m), 1454(m), 1370(s), 1319(s), 1241(m), 1144(m), 1030(m), 967(m), 851(m), 752(s).

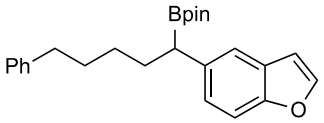


4,4,5,5-tetramethyl-2-[1-(naphthalen-2-yl)-5-phenylpentyl]-1,3,2-dioxaborolane (17), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (174 mg, 87% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 – 7.68 (m, 3H), 7.63 (s, 1H), 7.55 – 7.30 (m, 3H), 7.26 (s, 3H), 7.14 (d, *J* = 7.7 Hz, 3H), 2.57 (m, 2H), 2.47 (t, *J* = 7.9 Hz, 1H), 1.97 (m, 1H), 1.79 (m, 1H), 1.63 (m, 2H), 1.45 – 1.28 (m, 2H), 1.18 (d, *J* = 8.2 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.9, 141.1, 133.9, 131.9, 128.5, 128.3, 127.8, 127.8, 127.6, 127.6, 126.3, 125.7, 125.6, 124.9, 83.4, 35.9, 32.4, 31.6, 29.1, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8. GCMS (EI) calculated for [M]+ 400.26, found 400.3. FTIR (neat, cm^{-1}): 3059(s), 2978(s), 2930(s), 2857(s), 1632(m), 1601(s), 1506(m), 1454(s), 1370(s), 1329(s), 1269(m), 1210(m), 1135(m), 968(m), 856(s), 748(s), 699(s).

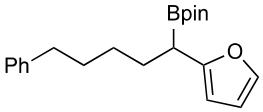


2-[1-(4-ethenylphenyl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (188 mg, 86% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 4H), 7.15 (dd, *J* = 15.3, 8.7 Hz, 6H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.30 (t, *J* = 7.9 Hz, 1H), 1.87 (dt, *J* = 13.2, 7.9 Hz, 1H), 1.77 – 1.55 (m, 2H), 1.43 – 1.27 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.9, 137.0, 134.7, 128.6, 128.5, 128.3, 126.3, 125.6, 112.6, 111.0, 83.4, 35.9, 32.5, 31.5, 29.0, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ

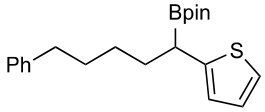
33.4. GCMS (EI) calculated for [M]+ 376.26, found 376.3. FTIR (neat, cm^{-1}): 3059(m), 2978(s), 2930(s), 2857(m), 1605(m), 1509(s), 1454(s), 1371(s), 1326(s), 1143(s), 851(m), 699(m).



2-[1-(1-benzofuran-5-yl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19), compound was prepared according to reported procedure and was purified by silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (180 mg, 92% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.26 (s, 2H), 7.21 – 7.07 (m, 4H), 6.77 – 6.68 (m, 1H), 2.68 – 2.50 (m, 2H), 2.43 (t, *J* = 7.9 Hz, 1H), 2.03 – 1.85 (m, 1H), 1.84 – 1.57 (m, 3H), 1.49 – 1.30 (m, 2H), 1.20 (d, *J* = 8.1 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6, 144.3, 142.9, 140.3, 128.5, 128.3, 125.6, 124.8, 123.8, 120.7, 111.0, 106.5, 83.4, 35.9, 33.0, 31.6, 29.0, 24.8, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.1. GCMS (EI) calculated for [M]+ 390.24, found 390.2. FTIR (neat, cm^{-1}): 3027(m), 2977(m), 2927(s), 1621(m), 1531(m), 1454(s), 1370(m), 1323(m), 1266(m), 1142(s), 1028(m), 860(m), 733(m).

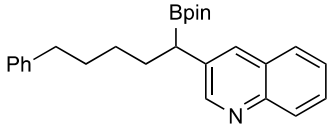


2-[1-(furan-2-yl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by HPLC, 100% hexanes after, silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid. GC yield (82% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.33 – 7.22 (m, 8H), 6.26 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.00 (d, *J* = 3.4 Hz, 1H), 2.45 (t, *J* = 7.5 Hz, 1H), 2.20 (q, *J* = 7.5 Hz, 2H), 1.77 (q, *J* = 7.8 Hz, 3H), 1.69 – 1.57 (m, 2H), 1.36 (q, *J* = 8.2 Hz, 1H), 1.22 (d, *J* = 2.7 Hz, 13H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.7, 141.8, 128.5, 128.4, 125.8, 125.7, 109.2, 106.2, 83.0, 35.8, 34.9, 31.3, 29.8, 24.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 GCMS (EI) calculated for [M]+ 340.27, found 340.3. FTIR (neat, cm^{-1}): 3024(m), 2976(m), 2927(s), 1616(m), 1530(m), 1454(s), 1372(m), 1319(m), 1265(m), 1140(s), 1036(m), 861(m), 733(m).

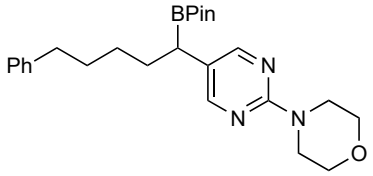


4,4,5,5-tetramethyl-2-[5-phenyl-1-(thiophen-2-yl)pentyl]-1,3,2-dioxaborolane (21), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (139 mg, 78% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.1 Hz, 4H), 7.19 – 7.11 (m, 3H), 7.07 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.90 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 2.61 (m, 3H), 1.97 – 1.55 (m, 4H), 1.39 (m, 2H), 1.21 (d, *J* = 4.8 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.6, 142.8, 128.5, 128.3, 126.8, 125.7, 123.8, 122.5, 83.7, 35.9, 33.8, 31.4, 28.8, 24.9, 24.8, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.1. GCMS (EI) calculated for [M]+ 356.26, found 356.3. FTIR (neat,

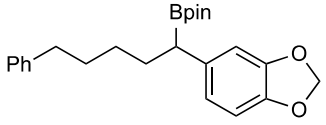
cm^{-1}): 3064(m), 3064(m), 3026(m), 2978(s), 2931(s), 2857(s), 1604(s), 1496(s), 1454(m), 1370(s), 1327(s), 1143(s), 1030(m), 966(m), 849(m), 750(m), 697(m).



3-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]quinoline (22), compound was prepared according to reported procedure and was purified by prep TLC, 2% Triethylamine, 20% EtOAc in hexanes and was isolated as a clear colorless liquid (148 mg, 74% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.88 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.06 (dd, *J* = 17.9, 7.6 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.19 – 7.12 (m, 3H), 2.58 (m, 2H), 2.49 (t, *J* = 7.8 Hz, 1H), 1.99 (m, 1H), 1.80 (m, 1H), 1.65 (m, 2H), 1.39 – 1.35 (m, 2H), 1.19 (d, *J* = 7.9 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.1, 146.1, 136.9, 129.5, 129.3, 128.8, 127.3, 126.7, 117.0 , 83.6, 35.9, 32.9, 31.5, 29.0, 25.0, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.1. GCMS (EI) calculated for [M]+ 401.25, found 400.3. FTIR (neat, cm^{-1}): 3095 (m), 3062(s), 2978(s), 2924(s), 2860(s), 1630(m), 1604(s), 1509(m), 1450(s), 1372(s), 1322(s), 1269(m), 1210(m), 1134(m), 968(m), 856(s), 748(s), 699(s).

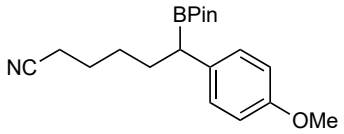


4-{5-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]pyrimidin-2-yl}morpholine (**23**), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu, KOTMS instead of KO*t*-Bu and a 1:1 mixture of toluene and THF. Compound was purified by prep TLC, 2% Triethylamine, 20% EtOAc in hexanes and was isolated as a clear colorless liquid (178 mg, 81% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.37 (s, 2H), 7.43 – 7.13 (m, 7H), 3.84 (qq, *J* = 4.8, 2.3 Hz, 10H), 2.30 (t, *J* = 7.9 Hz, 1H), 2.00 - 1.79 (m, 1H), 1.74 - 1.46 (m, 3H), 1.46 - 1.20 (m, 2H), 1.16 (d, *J* = 6.7Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.2, 129.3, 128.6, 128.4, 125.9, 123.9, 120.8, 83.7, 66.9, 44.6, 35.5, 32.8, 31.1, 29.8, 25.1, 24.8, 24.8. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.7. GCMS (EI) calculated for [M]+ 437.28, found 437.4. FTIR (neat, cm^{-1}): 3104(m), 3095 (m), 3062(s), 2978(s), 2924(s), 2860(s), 1630(m), 1604(s), 1509(m), 1449(s), 1401(s), 1375(s), 1319(s), 1299(m), 1269(m), 1209(m), 1132(m), 1101(m), 966(m), 856(s), 748(s), 699(s).

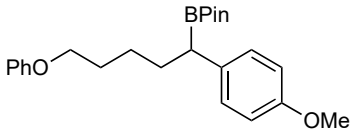


2-[1-(2H-1,3-benzodioxol-5-yl)-5-phenylpentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24), compound was prepared according to reported procedure and was purified by silica gel column chromatography, 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (184 mg, 93% yield). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.33 – 7.07 (m,7H), 6.77 – 6.56 (m, 3H), 5.90 (s, 2H), 2.63 – 2.48 (m, 2H), 2.21 (t, *J* = 7.9 Hz, 1H), 1.92 – 1.71 (m, 1H), 1.70 – 1.52 (m, 3H), 1.30 (d, J = 16.1 Hz, 4H), 1.18 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.5,

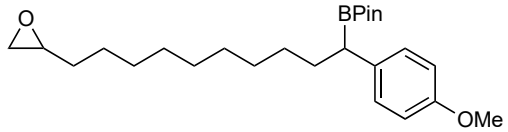
145.1, 142.8, 137.2, 128.4, 128.2, 125.6, 121.2, 108.9, 108.2, 100.6, 83.4, 35.9, 32.8, 31.5, 28.8, 25.5, 24.7, 24.6. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.0. GCMS (EI) calculated for [M]+ 394.32, found 394.3. FTIR (neat, cm^{-1}): 3062(w), 3021(m), 2984(m), 2934(m), 1672(w), 1604(m), 1489(s), 1444(s), 1246(s), 1142(s), 1040(m), 933(m), 851(m), 755(m).



6-(4-methoxyphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanenitrile (25), compound was prepared according to reported procedure and was purified by HPLC, 0-1% IPA in hexanes, after silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid. GC yield (76% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 3H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.68 – 2.43 (m, 2H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.94 – 1.71 (m, 1H), 1.71 – 1.58 (m, 3H), 1.38 – 1.24 (m, 2H), 1.18 (d, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.6, 127.4, 125.5, 119.8, 114.1, 83.5, 58.9, 31.8, 29.8, 29.5, 25.3, 24.7, 16.5. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.2. GCMS (EI) calculated for [M]+ 375.24, found 375.2. FTIR (neat, cm^{-1}): 3057(m), 2926(s), 2849(s), 2247(s), 2606(s), 1515(s), 1371(s), 1243(s), 1143(s), 1032(s), 967(s), 833(m), 751(m).

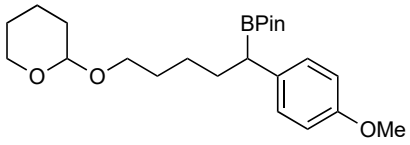


2-[1-(4-methoxyphenyl)-5-phenoxypentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26), compound was prepared according to reported procedure and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (185 mg, 93% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 (s, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.77 (s, 3H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 1H), 1.71 – 1.51 (m, 2H), 1.43 – 1.23 (m, 2H), 1.19 (d, *J* = 6.0 Hz, 13H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4, 138.9, 135.4, 129.3, 128.4, 127.6, 127.4, 113.8, 83.3, 72.8, 70.5, 55.2, 32.7, 29.8, 25.8, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.9. GCMS (EI) calculated for [M]+ 396.25, found 396.3. FTIR (neat, cm^{-1}):3051(m), 2978(s), 2932(s), 2858(m), 1601(m), 1510(s), 1454(m), 1370(m), 1325(m), 1247(m), 1143(s), 1031(m), 851(m), 755(s).

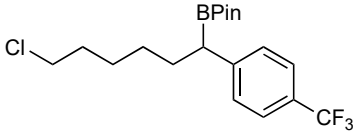


2-[1-(4-methoxyphenyl)-10-(oxiran-2-yl)decyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27), compound was prepared according to reported procedure and was purified by silica gel column chromatography, 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (193 mg, 93% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.94 – 2.84 (m, 1H), 2.79 – 2.69 (m, 1H), 2.46 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.89 – 1.69 (m, 1H), 1.67 – 1.36 (m, 6H), 1.37 – 1.13 (m, 26H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.3, 135.5, 129.3, 113.8, 83.3, 55.2, 52.5, 47.2, 33.0, 32.6, 29.7, 29.6, 29.6, 29.5, 29.3, 26.1, 24.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.9. GCMS (EI)

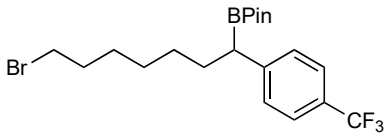
calculated for [M]+ 416.31, found 416.3. FTIR (neat, cm^{-1}): 3045(m), 2976(s), 2926(s), 2855(m), 1611(m), 1512(s), 1454(m), 1370(s), 1323(s), 1246(m), 1142(s), 1112(m), 1037(m), 967(m), 851(m), 754(m).



2-[1-(4-methoxyphenyl)-5-(oxan-2-yloxy)pentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28), compound was prepared according to reported procedure and was purified by prep TLC, 2% Triethylamine in DCM, and was isolated as a clear colorless liquid (176 mg, 78% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95, (d, *J* = 8.8 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.59 (t, *J* = 3.5 Hz, 1H), 3.94 – 3.71 (m, 5H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.77 (m, 3H), 1.78 – 1.45 (m, 10H), 1.25 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.2, 136.4, 130.5, 113.8, 99.0, 83.5, 67.4, 62.5, 55.6, 38.1, 30.9, 29.9, 25.7, 24.9, 24.8, 24.7, 22.8, 21.6, 19.8. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.0. GCMS (EI) calculated for [M]+ 404.27, found 404.3. FTIR (neat, cm^{-1}): 3035(m), 2972(s), 2929(s), 2849(m), 1609(s), 1510(s), 1455(m), 1373(s), 1323(s), 1241(m), 1139(s), 1111(m), 1040(m), 966(m), 851(m), 755(m), 699(m).

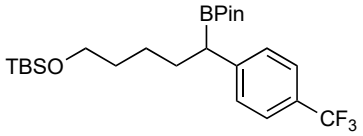


2-{6-chloro-1-[4-(trifluoromethyl)phenyl]hexyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (163 mg, 83% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.99 – 1.58 (m, 5H), 1.46 – 1.38 (m, 2H), 1.30 - 1.25 (m, 4H), 1.20 (d, *J* = 4.4 Hz, 11H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.6, 128.4, 127.6 (q, *J* = 34.7 Hz), 125.1 (q, *J* = 5.5 Hz), 124.7 (q, *J* = 265.3 Hz), 83.4, 33.7, 32.6, 32.0, 28.5, 27.9, 24.6, 24.5, 24.5. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.0. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3. GCMS (EI) calculated for [M]+ 390.17, found 390.2. FTIR (neat, cm^{-1}): 3029(m), 2985(s), 2931(s), 2861(s), 1617(s), 1368(m), 1325(s), 1318(m), 1172(m), 1120(s), 1054(m), 1018(s), 967(m), 852(m), 699(m).

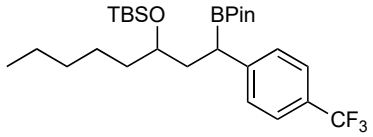


2-{7-bromo-1-[4-(trifluoromethyl)phenyl]heptyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography, 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (182 mg, 81% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 6.9 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 3H), 1.74 – 1.54 (m, 1H), 1.49 – 1.35 (m, 2H), 1.35 – 1.20 (m, 6H), 1.19 (d, *J* = 4.3 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.9, 127.9 (q, *J* = 34.7

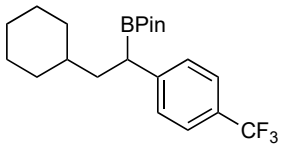
Hz), 125.3 (q, *J* = 5.5 Hz), 124.9 (q, *J* = 265.3 Hz), 83.7, 34.0, 32.9, 32.3, 29.1, 28.8, 28.1, 24.9, 24.7, 24.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.1. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.6. GCMS (EI) calculated for [M]+ 448.14, found 448.2. FTIR (neat, cm^{-1}):2984(m), 2931(s), 2858(s), 1617(s), 1465(m), 1371(s), 1164(m), 1123(s), 1018(s), 967(m), 852(m).



tert-butyldimethyl{[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-[4-(trifluoromethyl)phenyl]pentyl]oxy}silane (31), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (185 mg, 82% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.98 – 1.77 (m, 1H), 1.74 – 1.59 (m, 1H), 1.59 – 1.42 (m, 2H), 1.41 – 1.13 (m, 19H), 0.88 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.0, 128.7, 127.3 (q, *J* = 31.1 Hz), 125.3 (q, *J* = 2.5 Hz), 124.7 (q, *J* = 279.3 Hz), 83.6, 63.3, 32.8, 32.4, 26.1, 25.9, 24.9, 24.9, 24.7, 24.7, 18.5, -5.1. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.1. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.4. GCMS (EI) calculated for [M]+ 486.29, found 486.3. FTIR (neat, cm^{-1}): 3057(m), 2930(s), 2858(s), 1617(s), 1473(m), 1372(m), 1325(s), 1257(m), 1164(s), 1124(s), 1068(s), 835(m), 699(m).

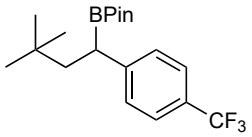


tert-butyl({[1-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-3-yl]oxy})dimethylsilane (**32**), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by prep TLC, 2% Triethylamine in DCM and was isolated as a clear colorless liquid (199 mg, 76% yield). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.49 (d, J = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.57 (dt, *J* = 12.1, 5.9 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 1H), 1.93 – 1.64 (m, 2H), 1.32 - 1.26 (m, 11H), 1.17 (d, *J* = 3.2 Hz, 12H), 0.88 (s, 9H), -0.01 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.2, 129.8 (q, *J* = 32.7 Hz), 127.0 (q, *J* = 3.4 Hz), 126.6, 125.1 (q, *J* = 272.2 Hz), 85.9, 83.4, 38.7, 31.6, 25.9, 25.0, 24.3, 24.0, 23.9, 22.7, 18.4, 14.2, -4.4, -5.0. ^{19}F NMR (470 MHz, Chloroform-*d*) -62.3. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.3. GCMS (EI) calculated for [M]+ 514.33, found 499.3. FTIR (neat, cm^{-1}): 3058(m), 2929(s), 2860(s), 1617(s), 1474(m), 1376(m), 1326(s), 1254(m), 1160(s), 1122(s), 1069(s), 835(m), 699(m).

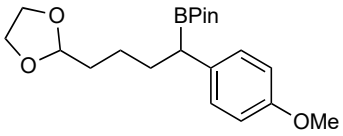


2-{2-cyclohexyl-1-[4-(trifluoromethyl)phenyl]ethyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**33**), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (133 mg, 77% yield). ^{1}H NMR (300 MHz,

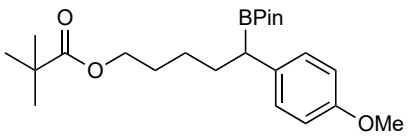
Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.1 Hz, 1H), 1.86 – 1.57 (m, 7H), 1.18 (d, *J* = 2.8 Hz, 16H), 0.99 – 0.76 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.2, 128.7, 127.5 (q, *J* = 32.7 Hz), 125.3 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 277.2, Hz), 83.6, 39.9, 36.7, 33.8, 33.0, 26.8, 26.4, 26.4, 24.7, 24.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.2. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5. GCMS (EI) calculated for [M]+ 344.25, found 344.2. FTIR (neat, cm^{-1}): 3051(m), 2980(m), 2924(s), 1617(s), 1448(m), 1381(m), 1324(s), 1163(m), 1123(s), 1068(s), 1018(m), 968(m), 853(m).



2-[1-(4-methoxyphenyl)-3,3-dimethylbutyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**34**), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by prep TLC, 2% Triethylamine in DCM and was isolated as a clear colorless liquid (134 mg, 75% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.46 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.03 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.49 (dd, *J* = 13.3, 4.0 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 128.5, 127.7 (q, *J* = 266.7 Hz), 127.5 (q, *J* = 34.0 Hz), 125.3 (q, *J* = 3.4 Hz), 120.4, 83.6, 46.5, 31.6, 29.8, 24.7, 24.6, 24.2. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.1. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4. GCMS (EI) calculated for [M]+ 356.21, found 356.2. FTIR (neat, cm^{-1}): 3052(m), 2979(m), 2924(s), 1615(s), 1450(m), 1382(m), 1322(s), 1159(m), 1124(s), 1070(s), 967(m), 853(m).

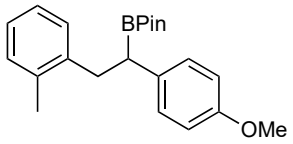


2-[4-(1,3-dioxolan-2-yl)-1-(4-methoxyphenyl)butyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35), compound was prepared according to reported procedure and was purified by silica gel column chromatography, 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (158 mg, 87% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.79 (t, *J* = 4.9 Hz, 1H), 3.92 – 3.79 (m, 4H), 3.76 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.83 (m, 1H), 1.70 – 1.59 (m, 3H), 1.39 (q, *J* = 7.7 Hz, 2H), 1.19 (d, *J* = 5.9 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4, 135.2, 129.3, 113.8, 104.7, 83.3, 64.9, 55.3, 34.1, 32.9, 24.8, 24.7, 23.9. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.6. GCMS (EI) calculated for [M]+ 362.23, found 361.2. FTIR (neat, cm^{-1}): 3050(m), 2974(s), 2930(s), 2851(s), 1617(s), 1452(m), 1369(m), 1326(s), 1218(m), 1202(m), 1142(m), 1019(m), 911(w), 851(m), 699(m).

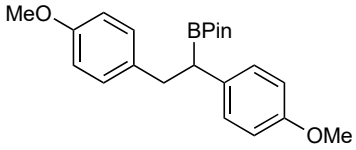


5-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl-2,2-dimethylpropanoate (36), compound was prepared according to reported procedure and was purified by silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (159 mg, 79% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz,

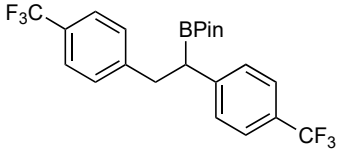
2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.81 (m, 1H), 1.62 (m, 3H), 1.45 – 1.00 (m, 27H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.5, 157.4, 135.0, 129.2, 113.7, 83.2, 64.3, 55.1, 38.7, 32.4, 28.6, 27.2, 25.5, 24.8, 24.6, 24.6. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5. GCMS (EI) calculated for [M]+ 404.27, found 404.3. FTIR (neat, cm^{-1}): 3059(m), 2976(s), 2946(s), 2834(m), 1725(s), 1609(s), 1511(m), 1462(m), 1369(s), 1320(s), 1245(s), 1142(s), 1036(m), 967(m), 851(s), 830(m), 756(m).



2-[1-(4-methoxyphenyl)-2-(2-methylphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37), compound was prepared according to reported procedure and was isolated as a clear colorless liquid (147 mg, 83% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H), 3.12 (dd, *J* = 13.8, 9.9 Hz, 1H), 2.87 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.60 (dd, *J* = 9.9, 6.4 Hz, 1H), 2.28 (s, 3H), 1.13 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1, 136.4, 135.0, 133.6, 130.1, 129.5, 128.0, 126.0, 125.6, 114.3, 83.5, 70.7, 55.9, 29.8, 24.8, 24.7, 19.5. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8. GCMS (EI) calculated for [M]+ 352.25, found 352.3. FTIR (neat, cm^{-1}): 2980(s), 2924(s), 2832(m), 1612(s), 1360(m), 1242(s), 1178(m), 1141(m), 1301(s), 970(m), 841(m), 699(m).

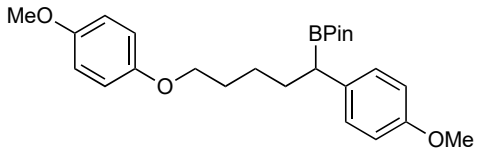


2-[1,2-bis(4-methoxyphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38), compound was prepared according to reported procedure and was purified by silica gel column chromatography 0-10% EtOAc in hexanes and was isolated as a clear colorless liquid (153 mg, 81% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.12 (dd, *J* = 17.3, 8.6 Hz, 4H), 6.79 (dd, *J* = 11.0, 8.5 Hz, 4H), 3.77 (d, *J* = 3.7 Hz, 6H), 3.07 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.87 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 9.5, 7.0 Hz, 1H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.8, 157.5, 134.7, 134.1, 129.9, 129.4, 113.8, 113.5, 83.4, 55.3, 55.2, 38.3, 24.9, 24.7, 24.7. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5. GCMS (EI) calculated for [M]+ 368.22, found 368.2. FTIR (neat, cm^{-1}): 2979(s), 2924(s), 2834(m), 1737(m), 1612(s), 1362(m), 1326(m), 1246(s), 1177(m), 1142(m), 1307(s), 968(m), 841(m), 756(m).

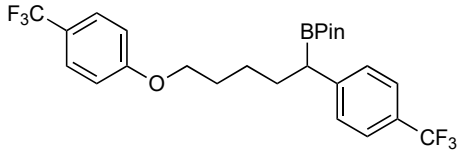


2-{1,2-bis[4-(trifluoromethyl)phenyl]ethyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (147 mg, 83% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 1H), 7.39 (m, 4H), 7.23 – 7.11 (m, 4H), 3.12 (dd, *J* = 13.7, 8.9

Hz, 1H), 2.93 (dd, *J* = 20.6, 13.1 Hz, 1H), 2.63 (t, *J* = 8.2 Hz, 1H), 1.03 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.3, 145.4, 129.2, 128.7, 128.6 (q, *J* = 311.2), 128.3 (q, *J* = 32.3 Hz), 128.1 (q, *J* = 31.0 Hz), 125.5 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 349.3 Hz), 84.0, 38.3, 34.5, 24.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.2, -65.3. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5. GCMS (EI) calculated for [M]+ 444.28, found 444.3. FTIR (neat, cm^{-1}): 2984(m), 2939(m), 1616(s), 2372(w), 1325(s), 1164(m), 1121(s), 1067(s), 1017(m), 848(m).

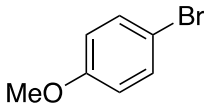


2-[5-(4-methoxyphenoxy)-1-(4-methoxyphenyl)pentyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40), compound was prepared according to reported procedure and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (179 mg, 84% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 4H), 3.96 (t, *J* = 5.9 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 1H), 1.71 – 1.51 (m, 2H), 1.43 – 1.23 (m, 2H), 1.19 (d, *J* = 6.0 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.5, 153.9, 153.3, 130.4, 120.1, 115.6, 114.8, 113.8, 83.4, 68.4, 55.8, 55.6, 37.9, 29.1, 24.6, 24.2, 24.0, 21.3. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4. GCMS (EI) calculated for [M]+ 426.26, found 426.3. FTIR (neat, cm^{-1}): 3055(m), 2924(s), 2918(s), 2874(m), 1617(s), 1364(m), 1322(m), 1244(s), 1177(m), 1142(m), 1303(s), 966(m), 841(m), 756(m). 699(m).

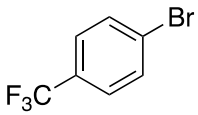


4,4,5,5-tetramethyl-2-{5-[4-(trifluoromethyl)phenoxy]-1-[4-(trifluoromethyl)phenyl]pentyl}-1,3,2-dioxaborolane (41), compound was prepared according to reported procedure using IPrCuCl instead of IPrCuO*t*-Bu and NaO*t*-Bu instead of KO*t*-Bu, and was purified by silica gel chromatography 0-100% DCM in hexanes, and was isolated as a clear colorless liquid (171 mg, 82% yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.6, 3.7 Hz, 45H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.95 (t, *J* = 6.3 Hz, 3H), 2.40 (t, *J* = 7.9 Hz, 1H), 2.03 – 1.84 (m, 1H), 1.77 (m, 3H), 1.44 (q, *J* = 7.7 Hz, 2H), 1.20 (d, J = 5.2 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.5, 147.5, 128.6, 127.6 (q, J = 32.8), 126.8 (q, J = 3.8 Hz), 125.9 (q, J = 277.1 Hz), 125.2 (q, J = 3.8 Hz), 124.5 (q, J = 272.2 Hz), 122.6 (q, J = 32.8 Hz), 114.4, 83.6, 67.9, 32.0, 29.0, 25.5, 24.6, 24.5. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.3, -65.0. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.7. GCMS (EI) calculated for [M]+ 502.21, found 502.2. FTIR (neat, cm^{-1}): 3054(m), 2980(s), 2937(s), 2872(m), 1617(s), 1372(m), 1326(s), 1259(m), 1162(m), 1111(s), 1068(m), 836(m).

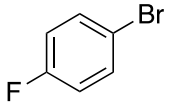
5. Aryl Bromide Starting Materials



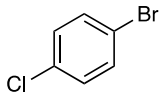
4-bromoanisole (2) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



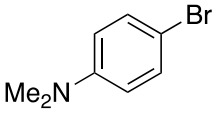
4-bromobenzotrifluoride (S1) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



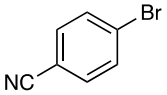
1-bromo-4-fluorobenzene (S2) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



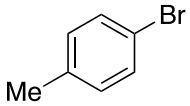
1-bromo-4-chlorobenzene (S3) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



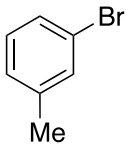
4-bromo-N,N-dimethylaniline (S4) was purchased from Oakwood Chemicals and used without purification.



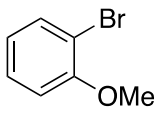
4-bromobenzonitrile (S5) was purchased from Millipore Sigma and used without purification.



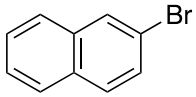
4-bromotoluene (S6) was purchased form Alfa Aesar and using without purification.



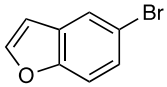
3-bromotoluene (S7) was purchased form TCI America and distilled over calcium hydride under reduced pressure before use.



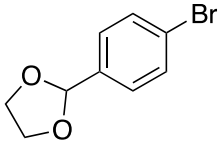
2-bromoanisole (S8) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



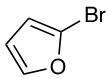
2-bromonaphthalene (S9) was purchased from Ark-Pharm and used without purification.



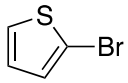
2-bromobenzofuran (S10) was purchased from Ark-Pharm and used without further purification



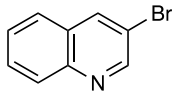
1-bromo-4-phenyl-1,3-dioxolane (S11) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.



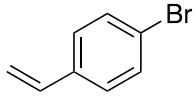
2-bromofuran (S12) was purchased from TCI chemicals and distilled over calcium hydride under reduced pressure before used.



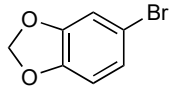
2-bromothiophene (S13) was purchased from Combi-Blocks and distilled over calcium hydride under reduced pressure before use.



3-bromoquinoline (S14) was purchased form Millipore Sigma and distilled over calcium hydride under reduced pressure before use.

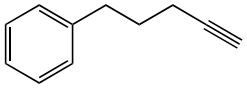


4-bromostyrene (S15) was purchased from TCI America and degassed before use.

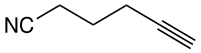


4-Bromo-1,2-(methylenedioxy)benzene (S16) was purchased from Millipore Sigma and distill over calcium hydride under reduced pressure before use.

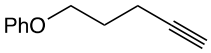
6. Alkyne Starting Materials



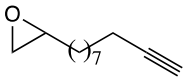
5-phenyl-1-pentyne (1) was purchased from GFS Chemical and distilled over calcium hydride under reduced pressure before use.



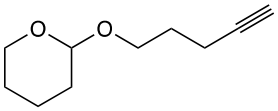
hex-5-ynenitrile (S17) was purchased from Oakwood Chemical and distilled over calcium hydride under reduced pressure before use.



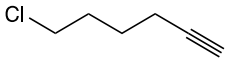
(pent-4-yn-1-yloxy)benzene (S18) was prepared according to a known procedure and has been previously characterized.[1]



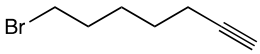
2-(dec-9-yn-1-yl)oxirane (S19) was prepared according to a known procedure and has been previously characterized.[2]



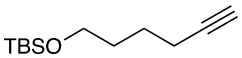
2-(pent-4-yn-1-yloxy)tetrahydra-2*H*-pyran (S20) has been previously characterized and spectral data match literature values.[3]



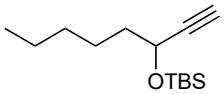
6-chlorohex-1-yne (S21) was purchased from TCI America and distilled over calcium hydride under reduced pressure before use.



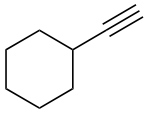
7-bromohept-1-yne (S22) was prepared according to a known procedure and has been previously characterized.[4]



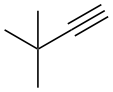
tert-butyldimethyl(pent-4-yn-1-yloxy)silane (S23) was prepared according to a known procedure and has been previously characterized.[5]



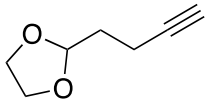
tert-butyldimethyl(oct-1-yn-3-yloxy)silane (S24) was prepared according to a known literature procedure and has been previously characterized.[6]



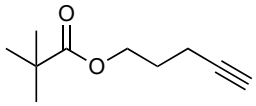
ethynylcyclohexane (S25) was purchased from Milipore Sigma and distilled over calcium hydride under reduced pressure before use.



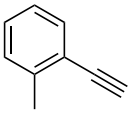
3,3-dimethylbut-1-yne (S26) was purchased from Milipore Sigma and distilled over calcium hydride under reduced pressure before use.



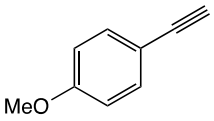
2-(but-3-yn-1-yl)-1,3-dioxolane (S27) was synthesized according to a known literature procedure and has been previously characterized.[7]



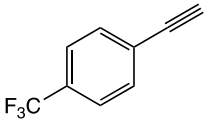
pent-4-yn-1-yl 2,2-dimethylpropanoate (S28) was synthesized according to a known literature procedure and has been previously characterized.[8]



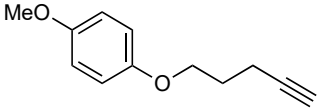
1-ethynyl-2-methylbenzene (S29) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



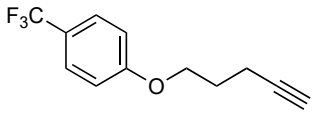
1-ethynyl-4-methoxybenzene (S30) was purchase from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



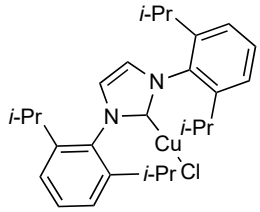
1-ethynyl-4-(trifluoromethyl)benzene (S31) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



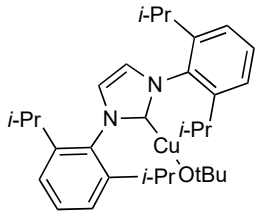
1-methoxy-4-(pent-4-yn-1-yloxy)benzene (S32) was synthesized according to a known literature procedure and has been previously characterized.[9]



1-(pent-4-yn-1-yloxy)-4-(trifluoromethyl)benzene (**S33**) was synthesized according to a modified procedure.[9] ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 – 7.44 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.12 (t, *J* = 6.1 Hz, 2H), 2.42 (td, *J* = 6.9, 2.7 Hz, 2H), 2.10 – 1.92 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 127.0 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 270.9 Hz), 123.0 (q, *J* = 32.6 Hz), 114.6, 83.2, 69.2, 66.5, 28.1, 15.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.4.



{1-[2,6-bis(propan-2-yl)phenyl]-3-[2-methyl-6-(propan-2-yl)phenyl]-2,3-dihydro-1H-imidazol-2-yl}(chloro)copper (**S34**), was synthesized according to a known literature procedure and has been previously characterized.[10]

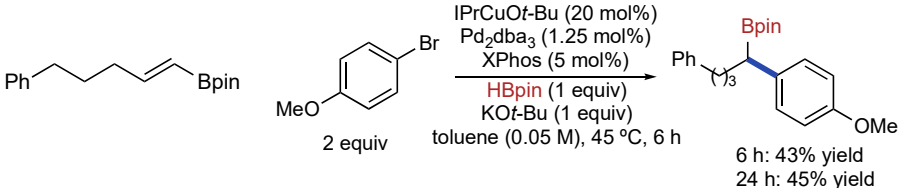


{1-[2,6-bis(propan-2-yl)phenyl]-3-[2-methyl-6-(propan-2-yl)phenyl]-2,3-dihydro-1H-imidazol-2-yl}(tert-butoxy)copper (**S35**), was synthesized according to a known literature procedure and has been previously characterized.[11]

7. Mechanistic Experiments (Scheme 3)

Analysis of Potential Catalytic Intermediates

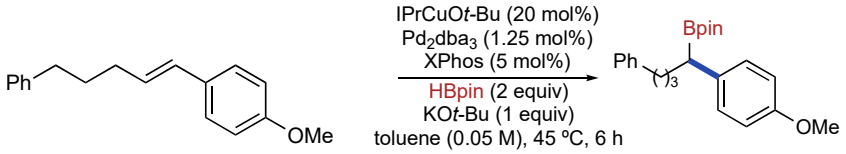
Alkenyl Bpin (**5**)



5 **2** **3**

In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, KO*t*-Bu (6.1 mg, 0.050 mmol, 1 equiv), IPrCuO*t*-Bu (5.3 mg, 0.01 mmol, 0.20 equiv), HBpin (6.4 mg, 0.05 mmol, 1.0 equiv), toluene (1 mL) and alkenyl Bpin (**5**) (13.6 mg, 0.05 mmol, 1.0 equiv). The reaction mixture was stirred at 45 °C for 1 min. To this reaction mixture was added Pd_2dba_3 (0.6 mg, 0.001 mmol, 0.0125 equiv), XPhos (1.2 mg, 0.0025 equiv) and 4-bromoanisole (**2**) (18.7 mg, 0.1 mmol, 2.0 equiv) and the reaction mixture was vigorously stirred at 45 °C. After both 6 h and 24 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC.

E-styrene (**6**)

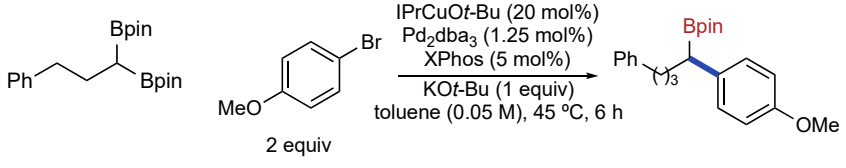


6 **3**

6 h: <5% yield
24 h: <5% yield

In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, KO*t*-Bu (12.2 mg, 0.10 mmol, 2 equiv), IPrCuO*t*-Bu (5.3 mg, 0.01 mmol, 0.20 equiv), HBpin (12.8 mg, 0.10 mmol, 2.0 equiv), toluene (1 mL) and *E*-styrene (**6**) (12.6 mg, 0.05 mmol, 1.0 equiv). The reaction mixture was stirred at 45 °C for 1 min. To this reaction mixture was added Pd_2dba_3 (0.6 mg, 0.001 mmol, 0.0125 equiv) and XPhos (1.2 mg, 0.0025 equiv) and the reaction mixture was vigorously stirred at 45 °C. After both 6 h and 24 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC.

Alkyl diboronate (**7**)

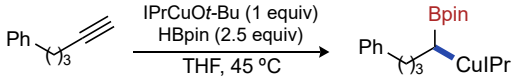


7 **2** **3**

6 h: <5% yield
24 h: <5% yield

In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, KO*t*-Bu (6.1 mg, 0.05 mmol, 1 equiv), IPrCuO*t*-Bu (5.3 mg, 0.01 mmol, 0.20 equiv), toluene (1 mL) and alkyl diboronate (**7**) (18.6 mg, 0.05 mmol, 1.0 equiv). The reaction mixture was stirred at 45 °C for 1 min. To this reaction mixture was added Pd_2dba_3 (0.6 mg, 0.001 mmol, 0.0125 equiv), XPhos (1.2 mg, 0.0025 mmol, 0.05 equiv) and 4-bromoanisole (**2**) (18.7 mg, 0.1 mmol, 2.0 equiv) and the reaction mixture was vigorously stirred at 45 °C. After 6 h and 24 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC.

Synthesis of Heterobimetallic Intermediate (42)

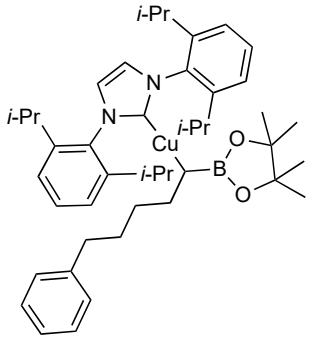


1 **42**

quantitative yield

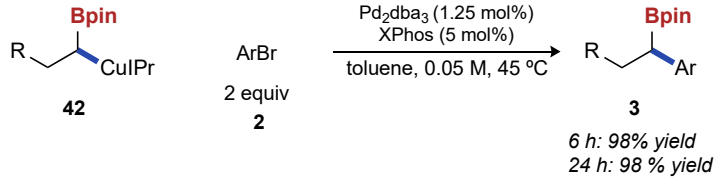
In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, IPrCuO*t*-Bu (131.6 mg, 0.250 mmol, 1.0 equiv) and THF (1 mL). To this reaction mixture was added HBpin (80.0 mg, 0.625 mmol, 2.50 equiv) and 5-phenyl-1-pentyne (**1**) (37.9 mg, 0.263 mmol, 1.05 equiv) and the reaction mixture was vigorously stirred at 45 °C until the orange color had disappeared. The reaction was removed from hot plate and pentane was carefully layered over the reaction mixture

and then placed in a -35 °C freezer overnight. Filtration with cold pentane yielded the desired product as a white solid (180.3 mg, 99% yield).



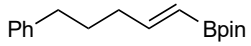
{1,3-bis[2,6-bis(propan-2-yl)phenyl]-2,3-dihydro-1H-imidazol-2-yl}[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl]copper (**42**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 - 7.14 (m, 15H), 6.30 (s, 2H), 2.71 – 2.60 (m, 6H), 2.20 – 2.11 (m, 1H), 1.90 - 1.86 (m, 1H), 1.69 (p, *J* = 7.7 Hz, 2H), 1.52 (t, *J* = 6.0 Hz, 12H), 1.16 (m, 12H), 1.12 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.9, 145.9, 135.5, 130.4, 128.9, 125.4, 124.2, 124.2, 122.2, 120.3, 117.6, 79.7, 37.7, 36.7, 32.7, 29.1, 29.0, 28.8, 25.5, 25.3, 25.1, 23.8. ^{11}B NMR (96 MHz, Chloroform-*d*) δ 28.4. LCMS (ESI) calculated for [M+]: 726.3, found: 726.7.

Palladium-catalyzed Cross Coupling of Bimetallic Intermediate (42) and ArBr (2)

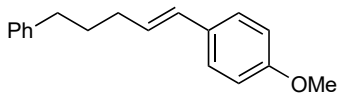


In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, hetereobimetallic complex (**38**) (36.3 mg, 0.05 mmol, 1.0 equiv), XPhos (1.2 mg, 0.0025 mmol, 0.05 equiv) and 4-bromoanisole (18.7 mg, 0.1 mmol, 2.0 equiv) and the reaction mixture was vigorously stirred at 45 °C. After 6 h and 24 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC.

Characterization of Mechanistic Compounds

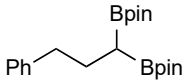


4,4,5,5-tetramethyl-2-[(1E)-5-phenylpent-1-en-1-yl]-1,3,2-dioxaborolane (**5**), compound was synthesized according to known literature procedure and has been previously characterized.[12] ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 3H), 7.21 – 7.12 (m, 3H), 6.65 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.46 (d, *J* = 18.0 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.28 – 2.12 (m, 2H), 1.76 (m, 2H), 1.27 (s, 12H).



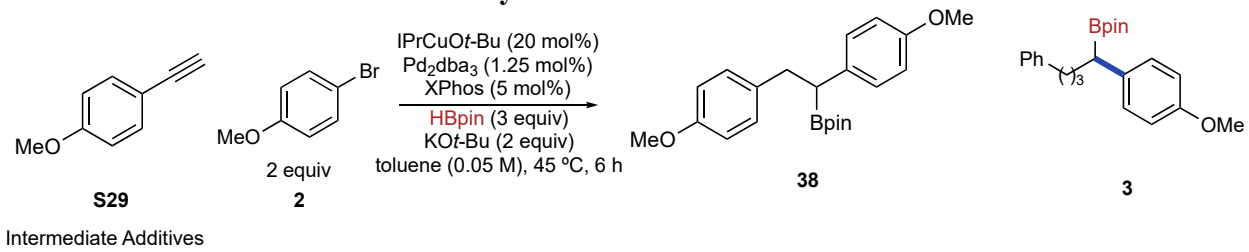
1-methoxy-4-[(1E)-5-phenylpent-1-en-1-yl]benzene (**6**), compound was synthesized according to known literature procedure and has been previously characterized.[13] ^{1}H NMR (300 MHz,

Chloroform-*d*) δ 7.37 – 7.12 (m, 8H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.80 (p, *J* = 7.5 Hz, 2H).

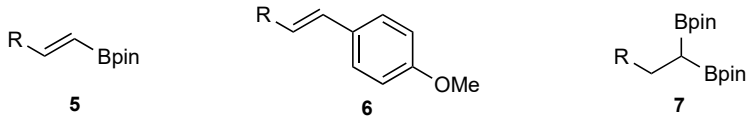


4,4,5,5-tetramethyl-2-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-1,3,2-dioxaborolane (**7**), compound was synthesized according to known literature procedure and has been previously characterized.[14] ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.05 (m, 7H), 2.70 – 2.53 (m, 2H), 1.85 (q, *J* = 7.8 Hz, 2H), 1.23 (s, 25H), 0.81 (t, *J* = 7.9 Hz, 1H).

Evaluation of Intermediates in Catalytic Reaction



Intermediate Additives



In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, KO*t*-Bu (12.2 mg, 0.10 mmol, 2.0 equiv), IPrCuO*t*-Bu (5.3 mg, 0.01 mmol, 0.20 equiv), HBpin (19.2 mg, 0.15 mmol, 3.0 equiv), toluene (1 mL) and 4-ethynylanisole (**S29**) (6.6 mg, 0.05 mmol, 1.0 equiv). The reaction mixture was stirred at 45 °C for 1 min. To this reaction mixture was added Pd_2dba_3 (0.6 mg, 0.001 mmol, 0.0125 equiv), XPhos (1.2 mg, 0.0025 equiv) and 4-bromoanisole (**2**) (18.7 mg, 0.1 mmol, 2.0 equiv) and either alkenyl Bpin (**5**), *E*-styrene (**6**) or alkyl diboronate (**7**) (0.05 mmol, 1.0 equiv). The reaction mixture was vigorously stirred at 45 °C. After 6 h a 60 µL was taken and pushed through a plug of silica with 1.5 mL EtOAc and analyzed by GC.

Entry	Additive	Yield **38**	Yield **3**
1	Alkenyl Bpin (**5**)	28	33
2	*E*-styrene (**6**)	31	0
3	Alkyl diboronate (**7**)	42	0

8. References

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(2) Uehling, M. R., Rucker, R. P. & Lalic, G. Catalytic Anti-Markovnikov Hydrobromination of Alkynes. *J. Am. Chem. Soc.* **136**, 8799–8803 (2014).

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(12) Pereira, S. & Srebnik, M. Hydroboration of Alkynes with Pinacolborane Catalyzed by HZrCp2Cl. *Organometallics* **14**, 3127–3128 (1995).
(13) Armstrong, M. K., Goodstein, M. B. & Lalic, G. Diastereodivergent Reductive Cross Coupling of Alkynes through Tandem Catalysis: *Z* - and *E* -Selective Hydroarylation of Terminal Alkynes. *J. Am. Chem. Soc.* **140**, 10233–10241 (2018).
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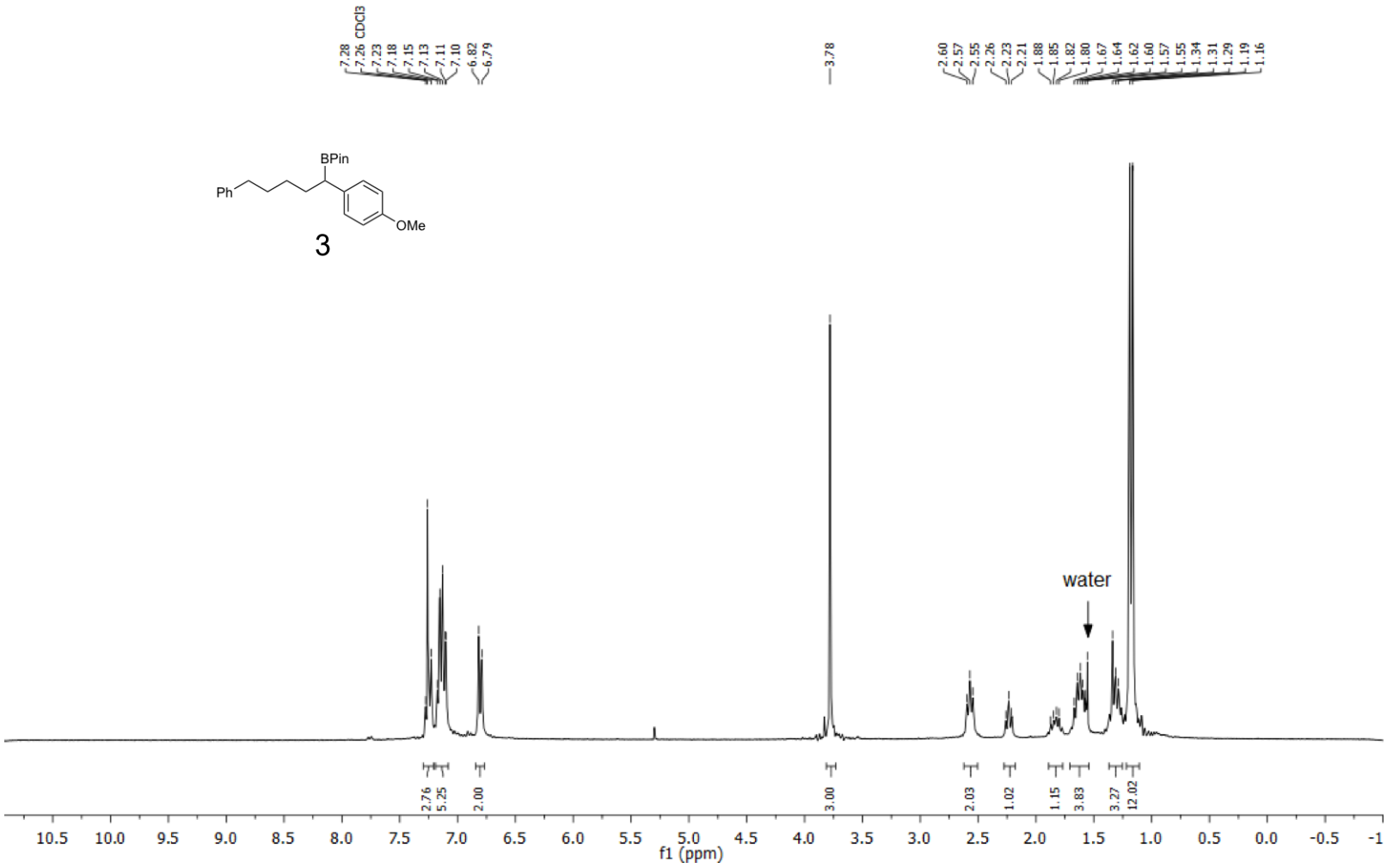
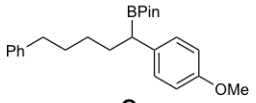
9. Spectral Data

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 - 7.23 (m, 3H), 7.21 – 7.06 (m, 5H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 1H), 1.95 – 1.73 (m, 1H), 1.72 – 1.51 (m, 4H), 1.38 – 1.24 (m, 3H), 1.18 (d, *J* = 7.3 Hz, 12H).

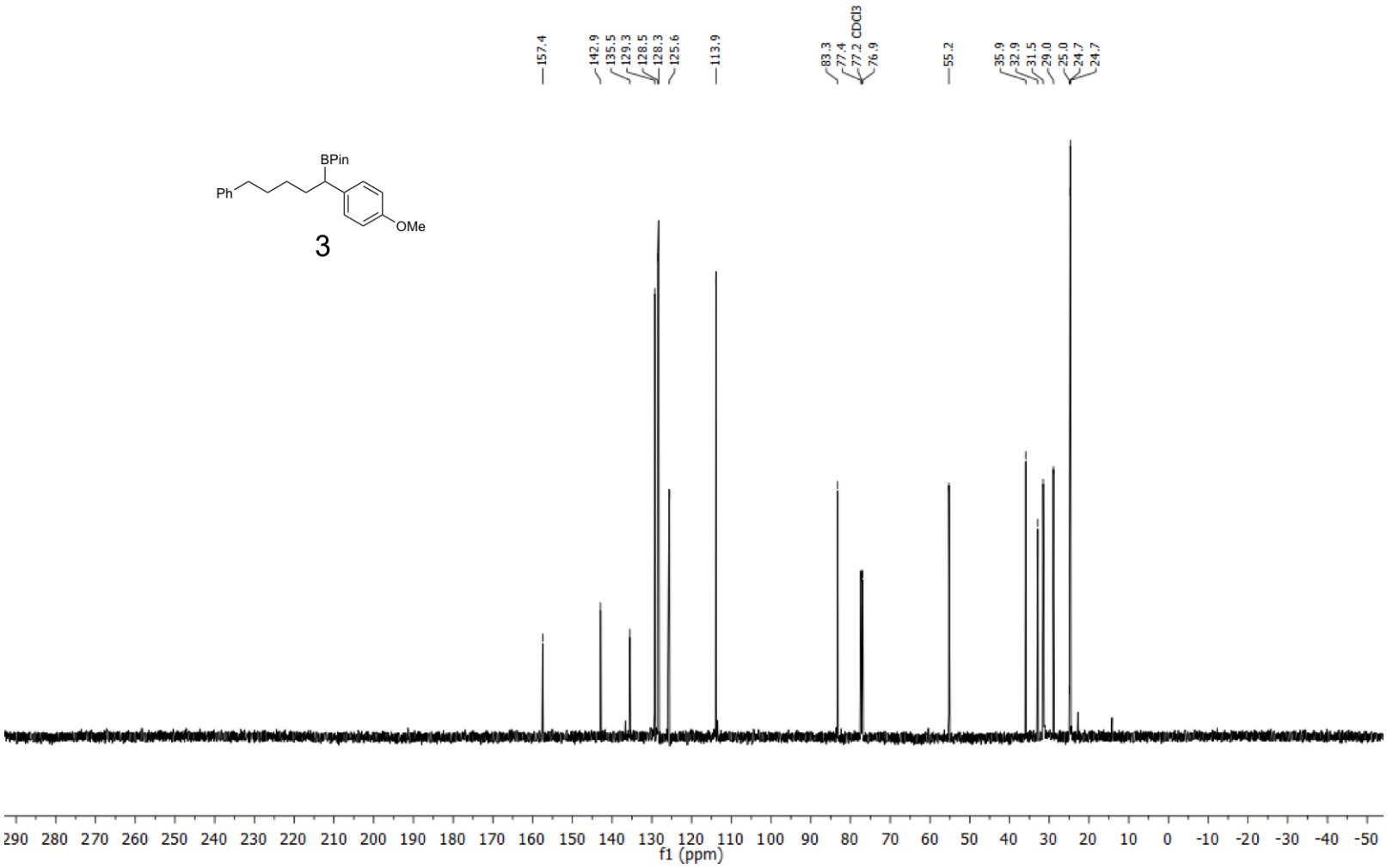


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.7 .

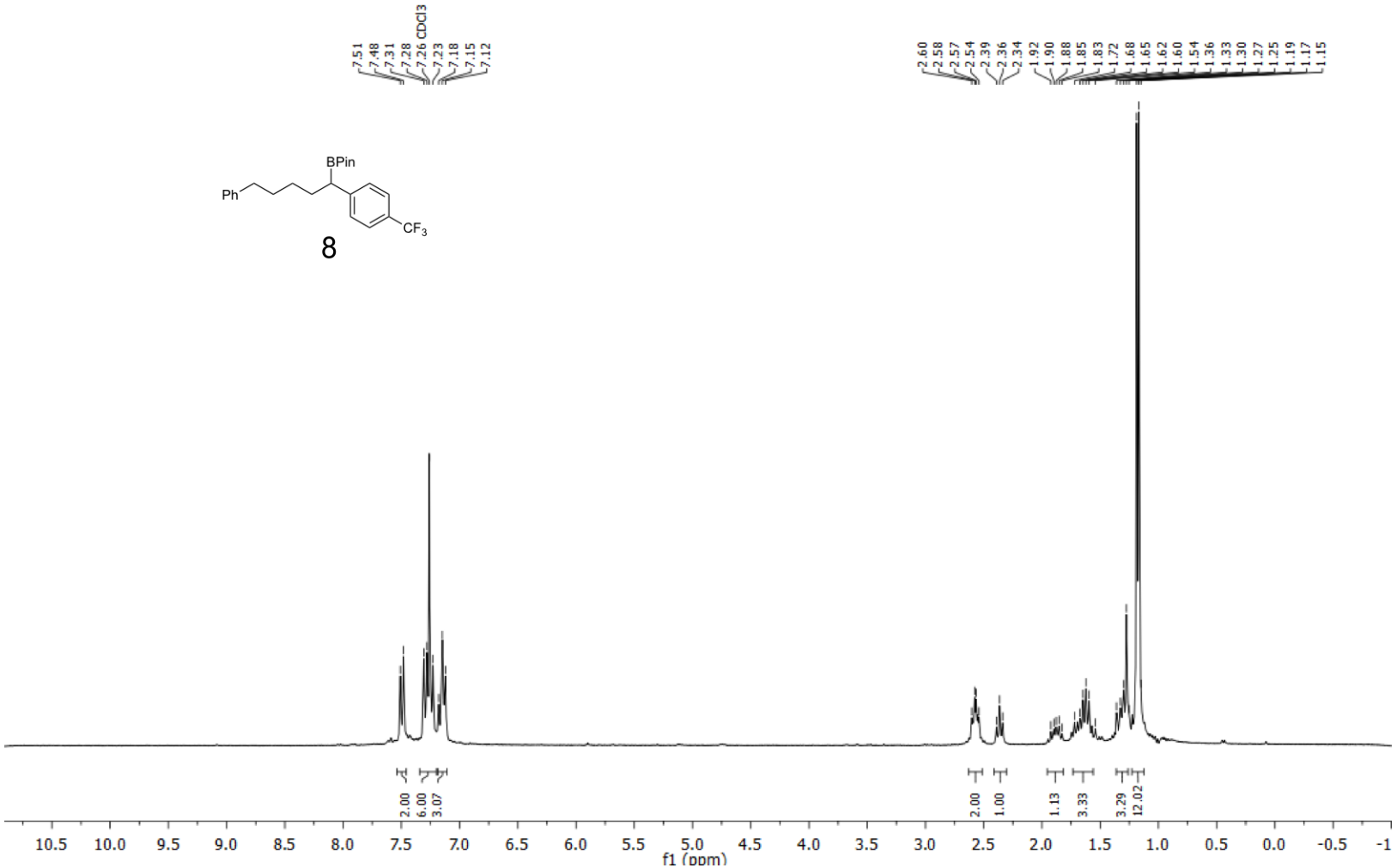


3

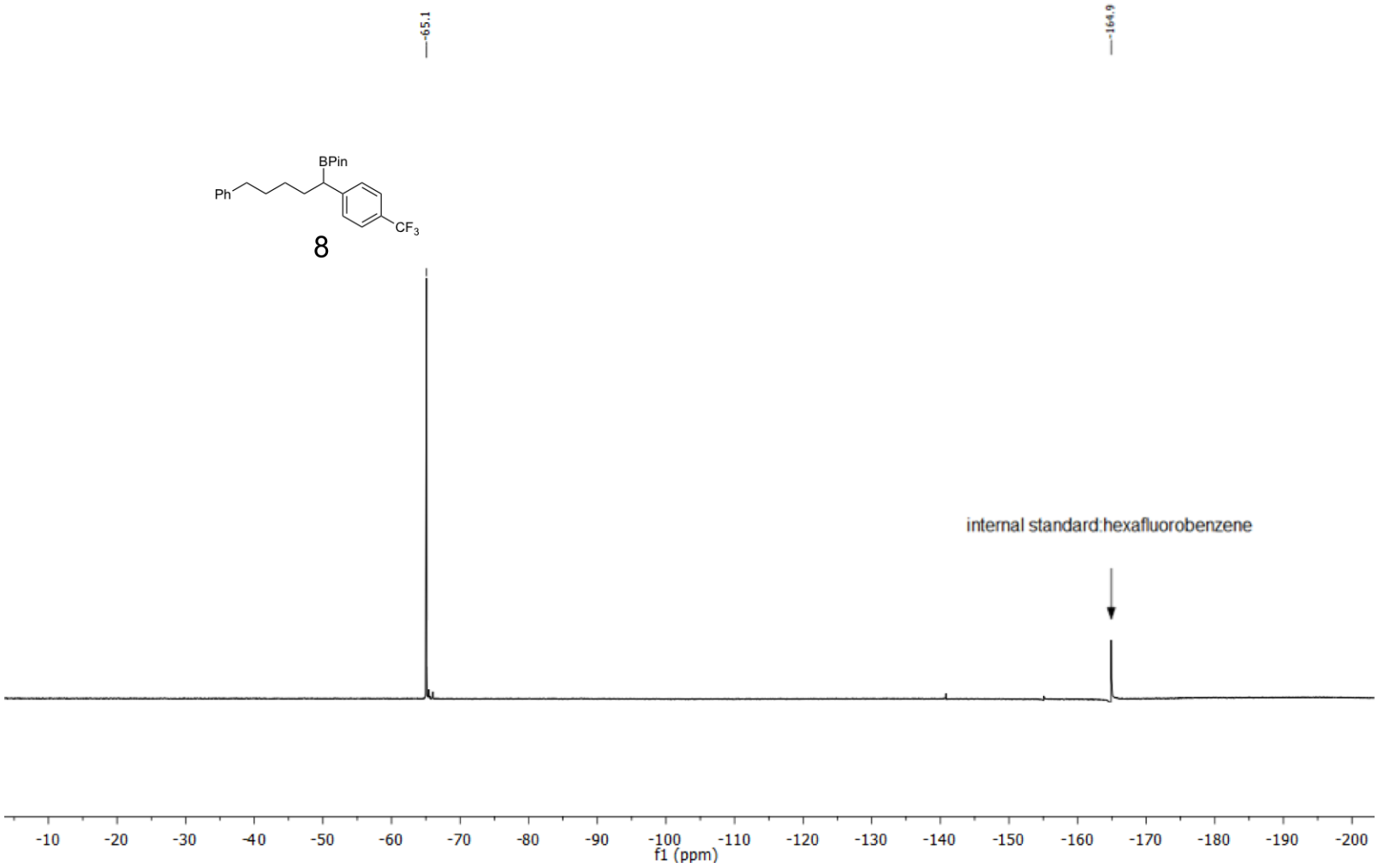
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4 , 142.9 , 135.5 , 129.3 , 128.5 , 128.3 , 125.6 , 113.9 , 83.3 , 55.2 , 35.9 , 32.9 , 31.5 , 29.0 , 25.0 , 24.7 , 24.7 .



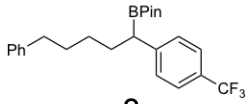
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.19 (m, 6H), 7.21 – 7.09 (m, 3H), 2.65 – 2.51 (m, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.97 – 1.79 (m, 1H), 1.76 – 1.51 (m,3H), 1.39 – 1.22 (m, 2H), 1.18 (d, *J* = 5.7 Hz, 12H).



^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.1 .

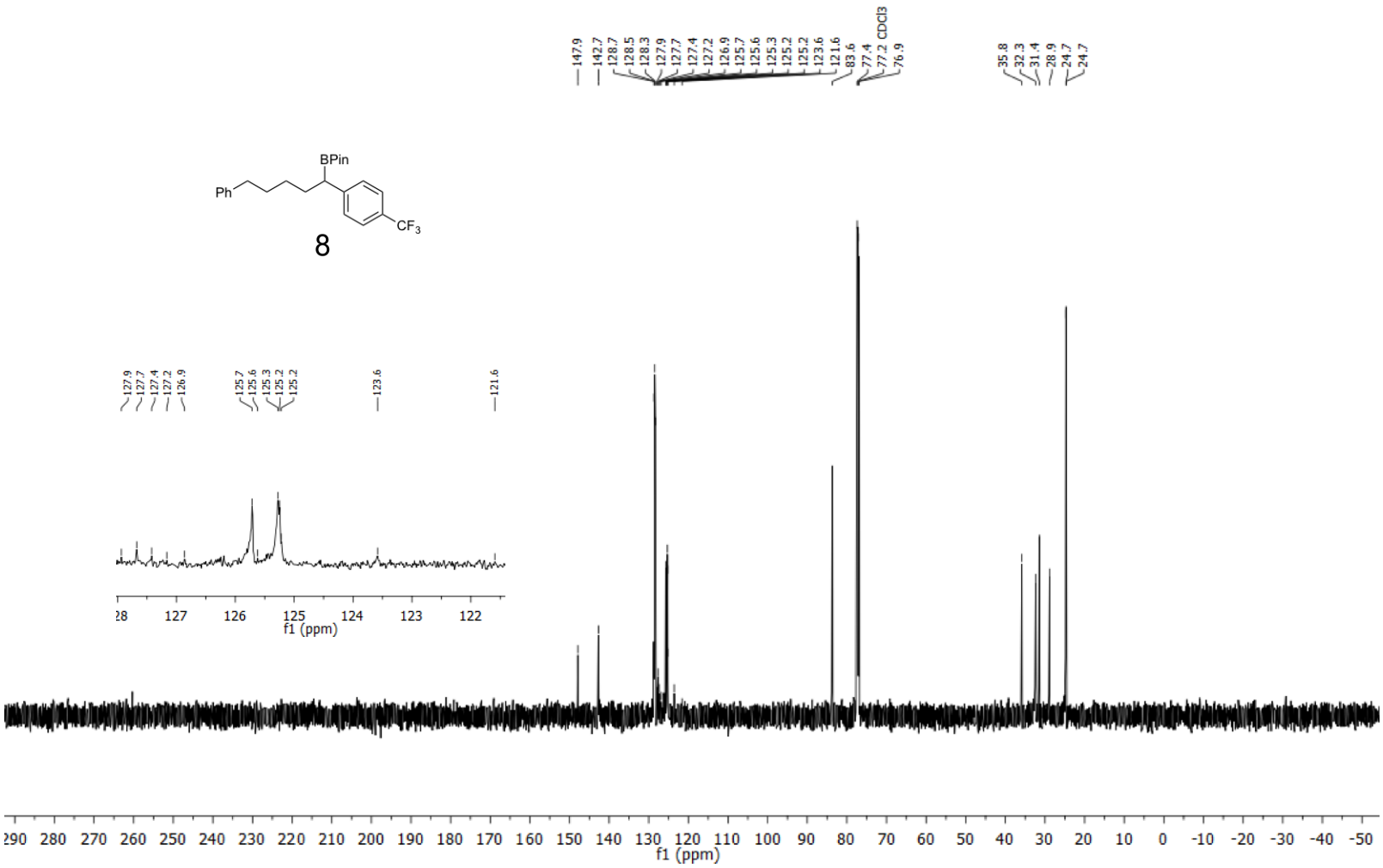


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5 .

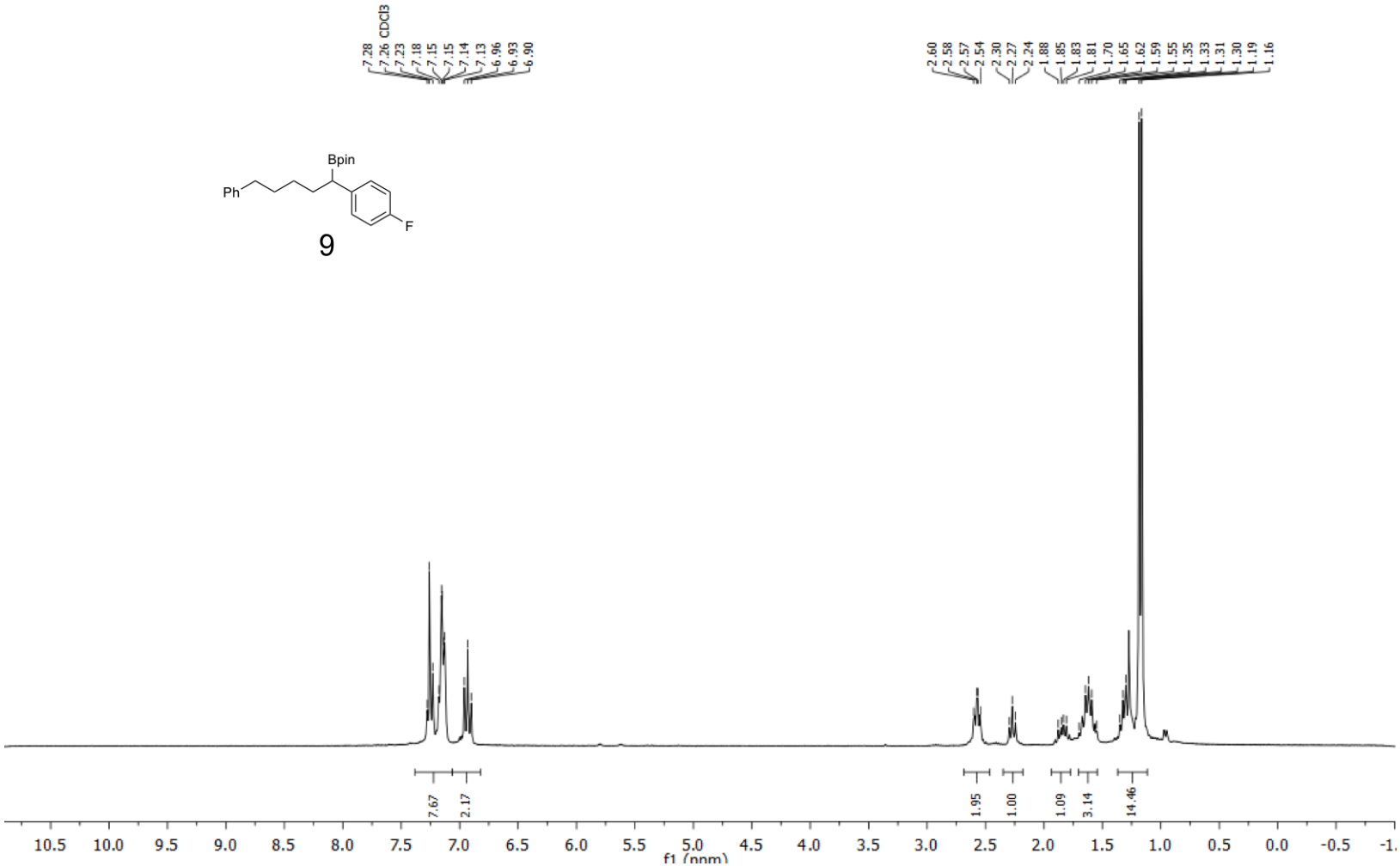


8

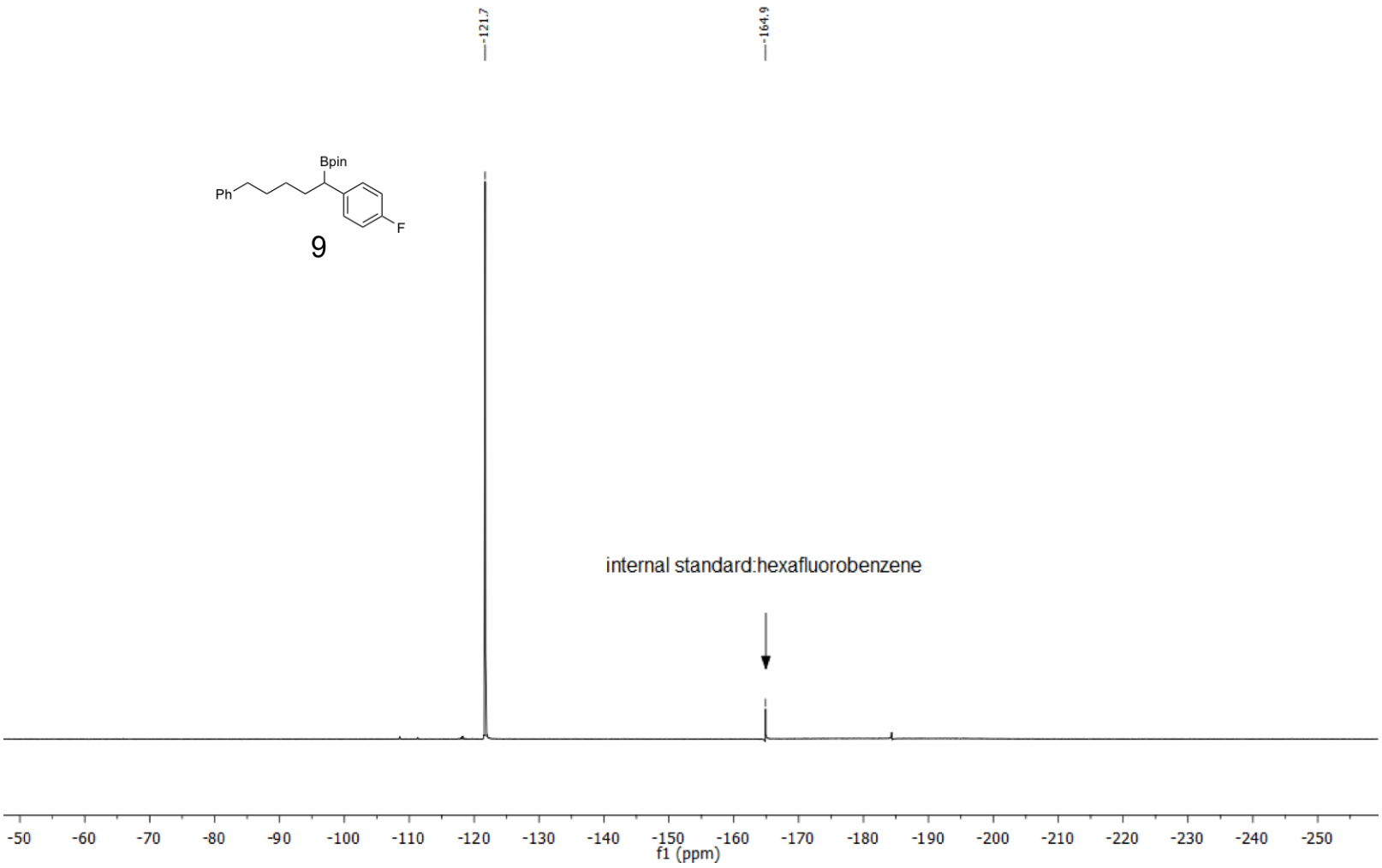
^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.9 , 142.7 , 128.7 , 128.5 , 128.3 , 127.3(q, *J* = 34.2 Hz), 125.7 , 125.3 (q, *J* = 3.7 Hz), 124.8 (q, *J* = 266.7 Hz), 83.6 , 35.8 , 32.4 , 31.4 , 28.9 , 24.7 , 24.7 .



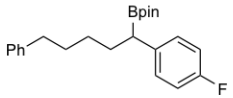
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 – 7.10 (m, 8H), 6.93 (t, *J* = 8.8 Hz, 2H), 2.65 – 2.50 (m, 1H), 2.27 (t, *J* = 7.9 Hz, 1H), 1.93 – 1.76 (m, 1H), 1.73 – 1.46 (m, 3H), 1.38 – 1.10 (m, 14H).



^{19}F NMR (470 MHz, Chloroform-*d*) δ -121.7 .

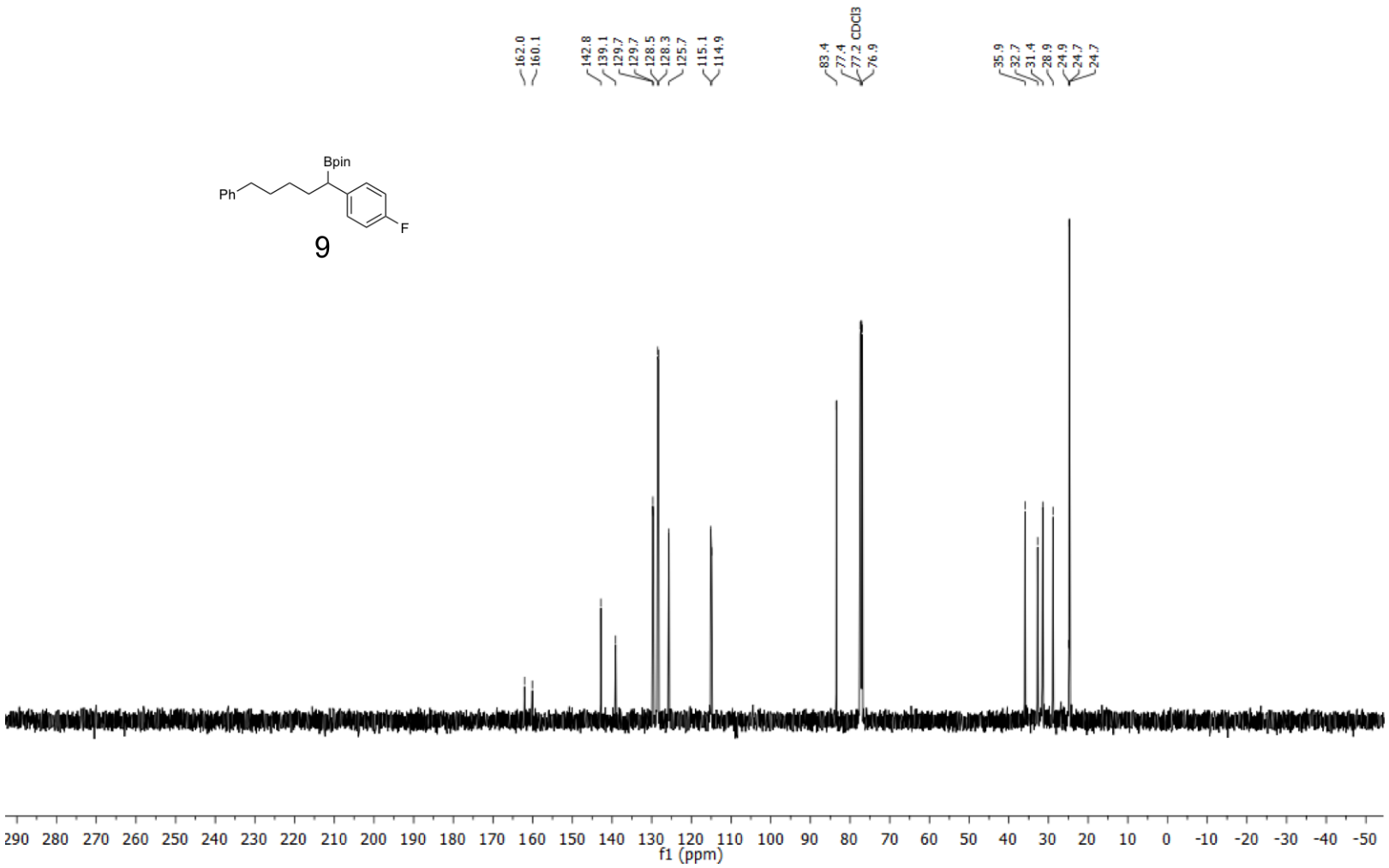


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 .

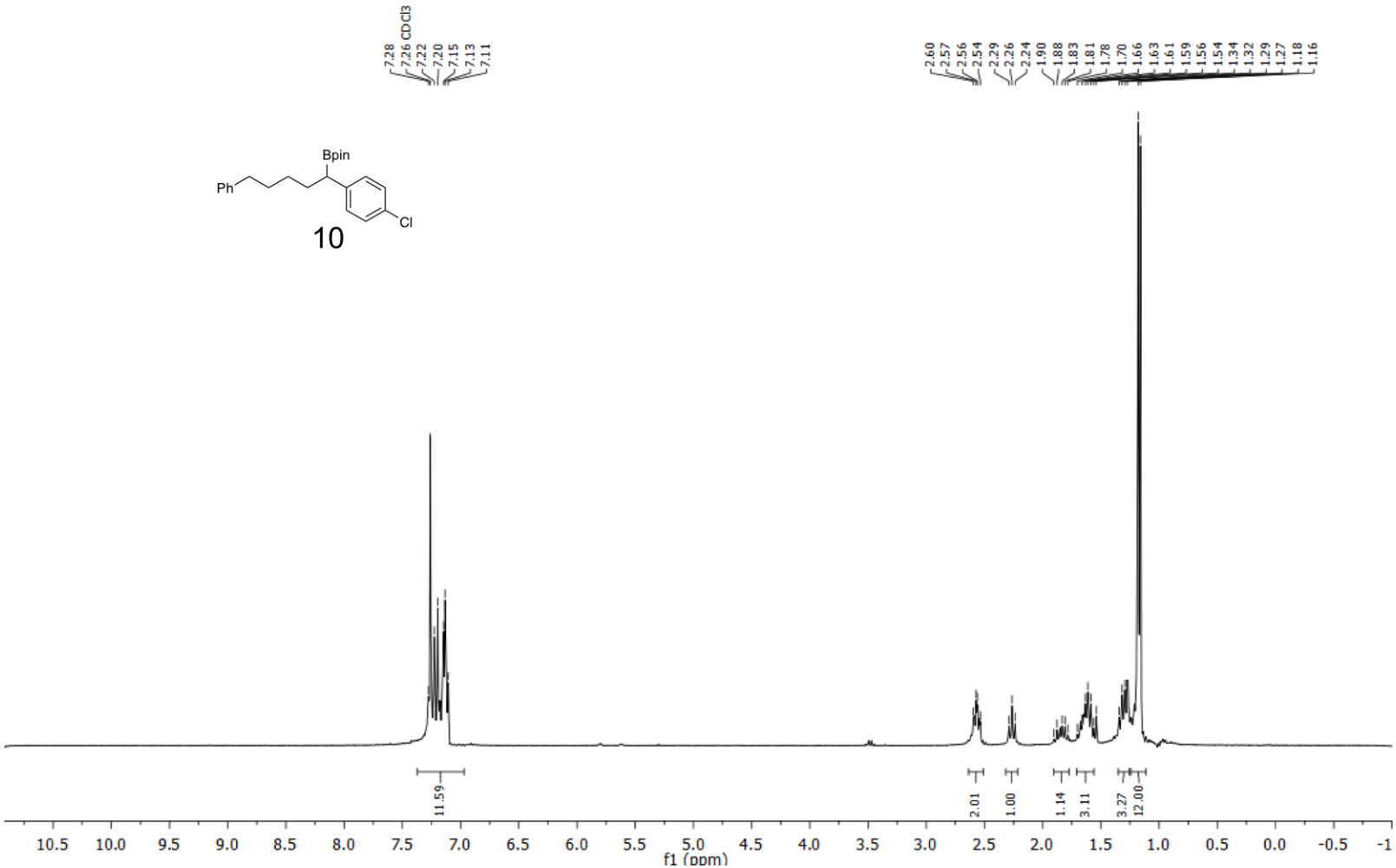


9

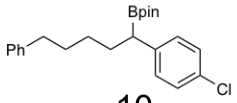
^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.1 (d, *J* = 242.3 Hz), 142.8 , 139.1 , 129.7 (d, *J* = 7.9 Hz), 128.4 (d, *J* = 24.0 Hz), 125.7 , 115.0 (d, *J* = 20.9 Hz), 83.4 , 35.9 , 32.7 , 31.4 , 28.9 , 24.9 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.06 (m,11H), 2.65 – 2.50 (m, 2H), 2.26 (t, *J* = 7.9 Hz, 1H), 1.94 – 1.75 (m, 1H), 1.60 (m, 3H), 1.31 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 12H).

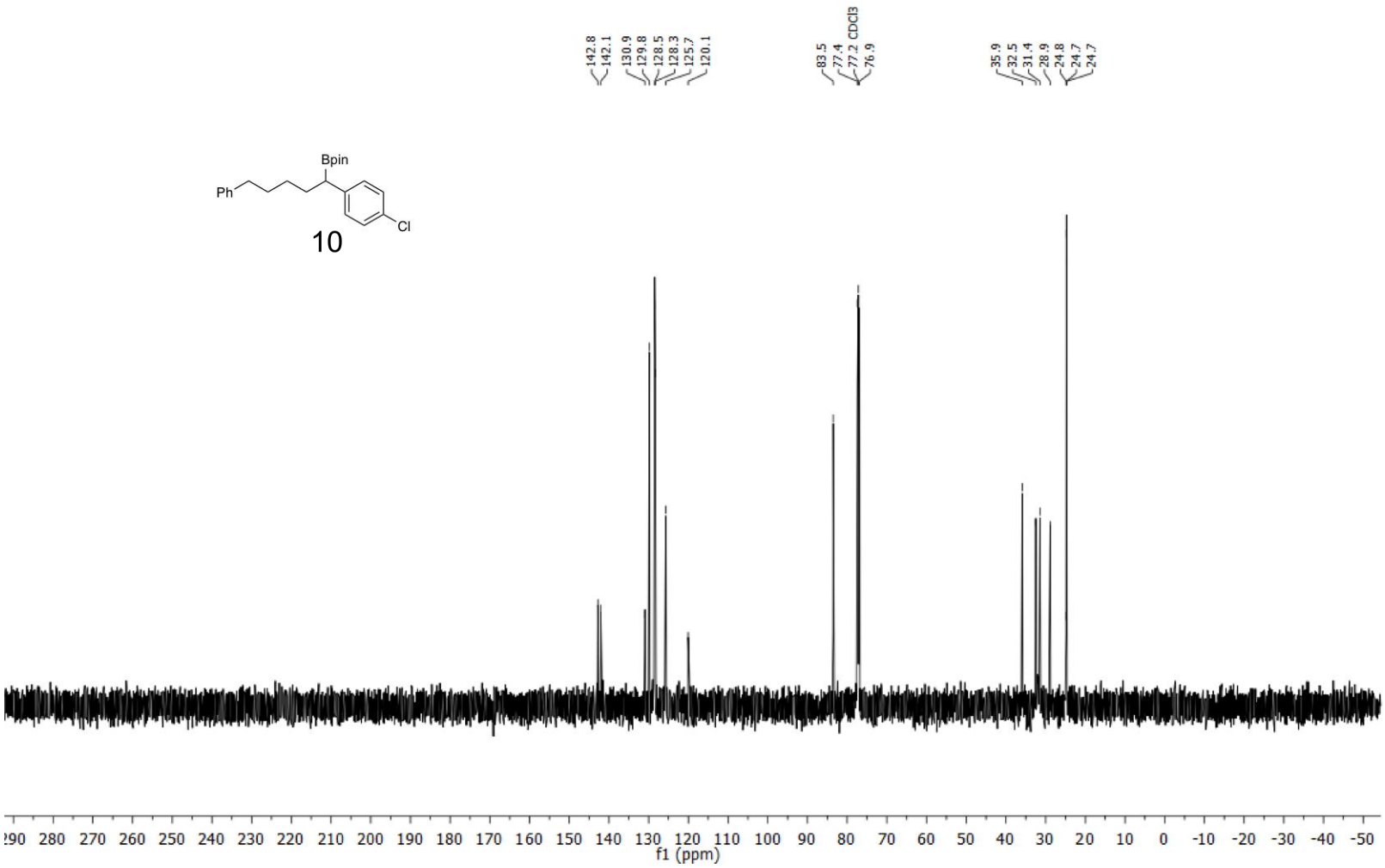


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3 .

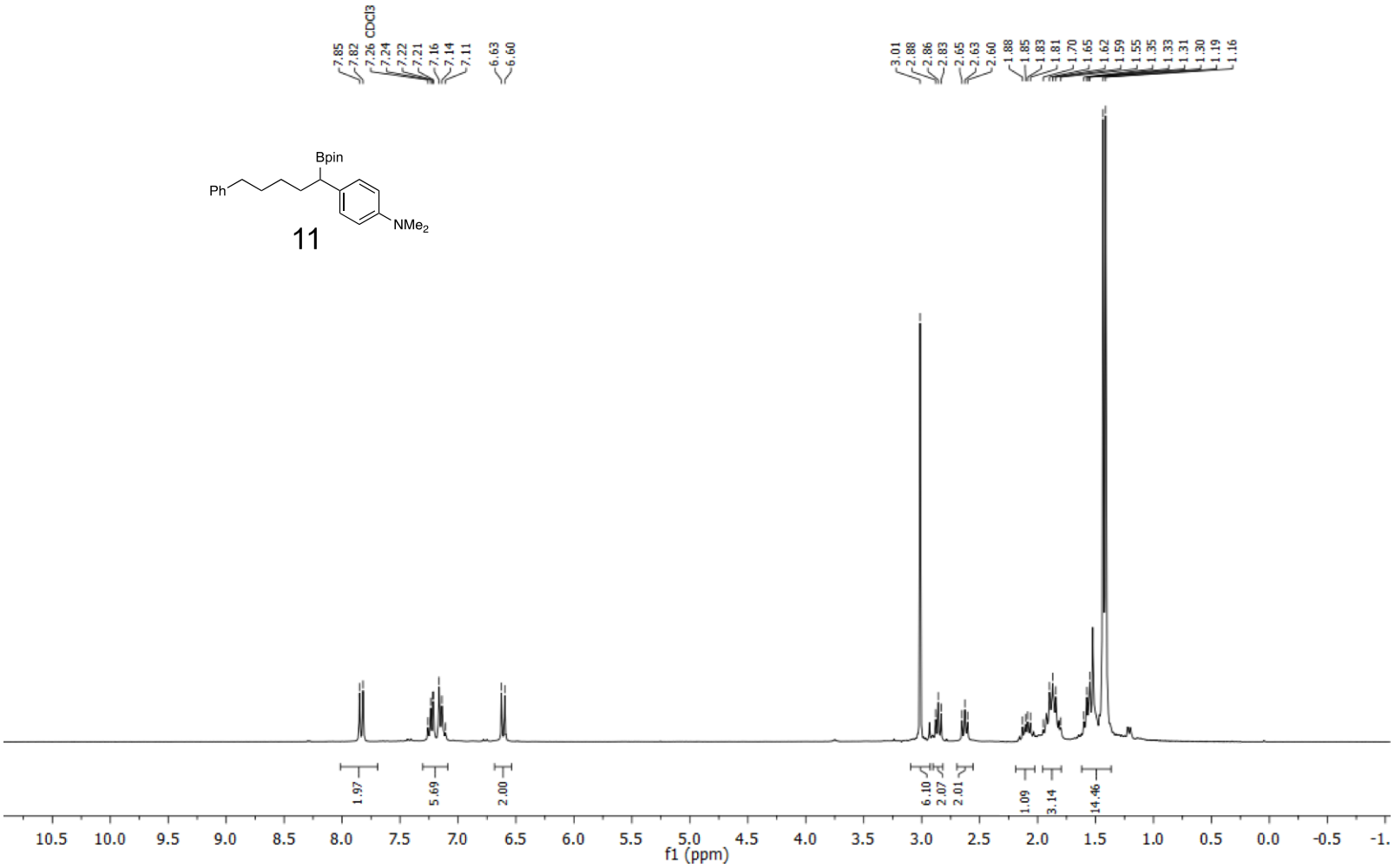


10

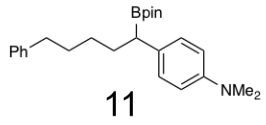
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.8 , 142.1 , 130.9 , 129.8 , 128.5 , 128.3 , 125.7 , 120.1 , 83.5 , 35.9 , 32.5 , 31.4 , 28.9 , 24.8 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 9.0 Hz, 2H), 7.27 – 7.19 (m, 6H), 6.61 (d, *J* = 9.0 Hz, 2H), 3.01 (s, 6H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.88 - 1.83 (m, 1H), 1.70 - 1.55 (m, 3H), 1.35 - 1.16 (m, 14H) .

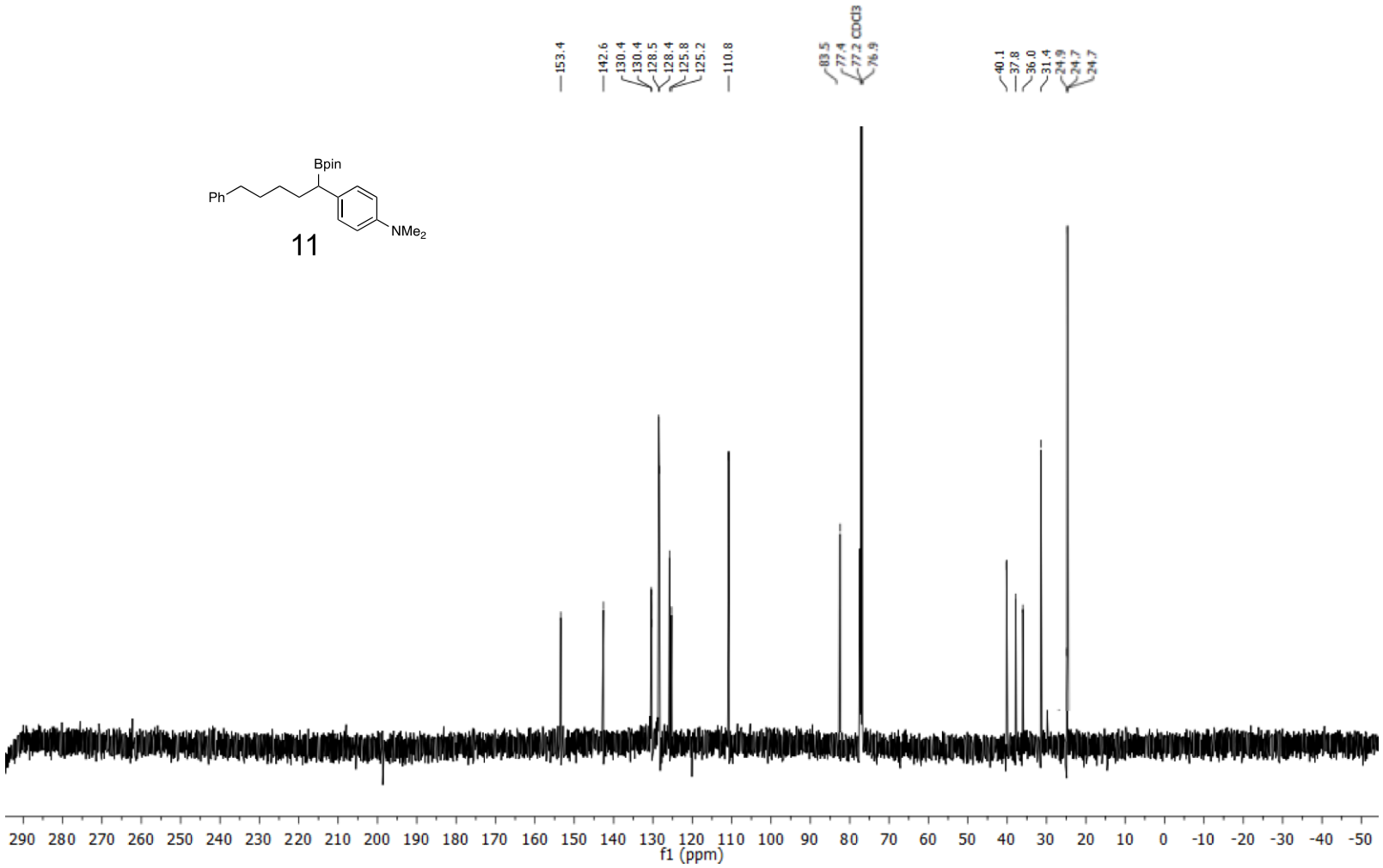


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8 .

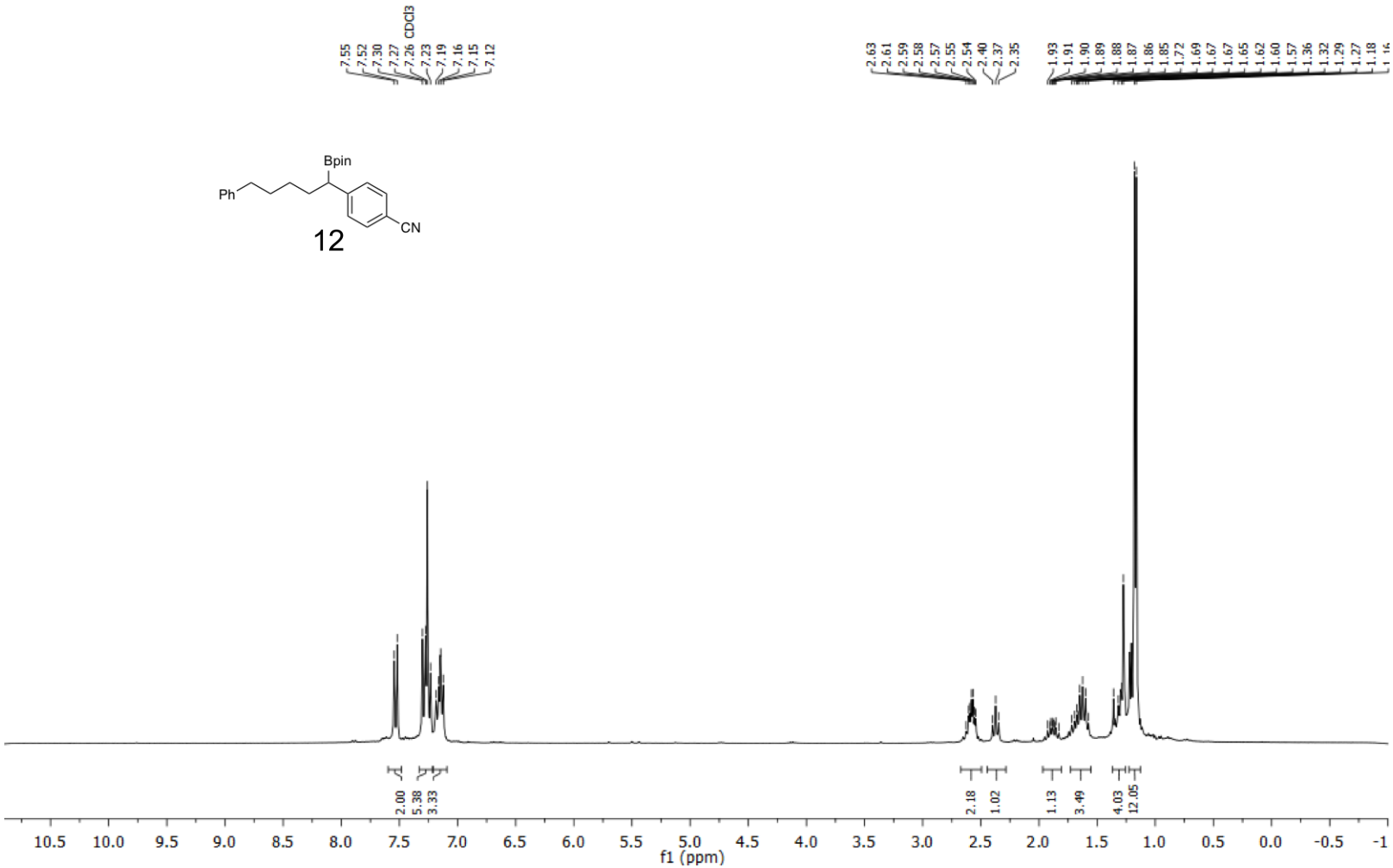


11

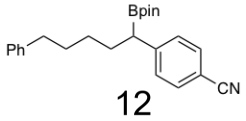
^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.4 , 142.6 , 130.4 , 130.4 , 128.5 , 128.4 , 125.8 , 125.2 , 110.8 , 83.5 , 40.1 , 37.8 , 36.0 , 31.4 .24.9 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.21 (m, 5H), 7.15 (m, 3H), 2.57 (td, *J* = 7.4, 3.4 Hz, 2H), 2.37 (t, *J* = 7.9 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.75 – 1.55 (m, 3H), 1.39 – 1.24 (m, 4H), 1.17 (d, *J* = 5.0 Hz, 12H).

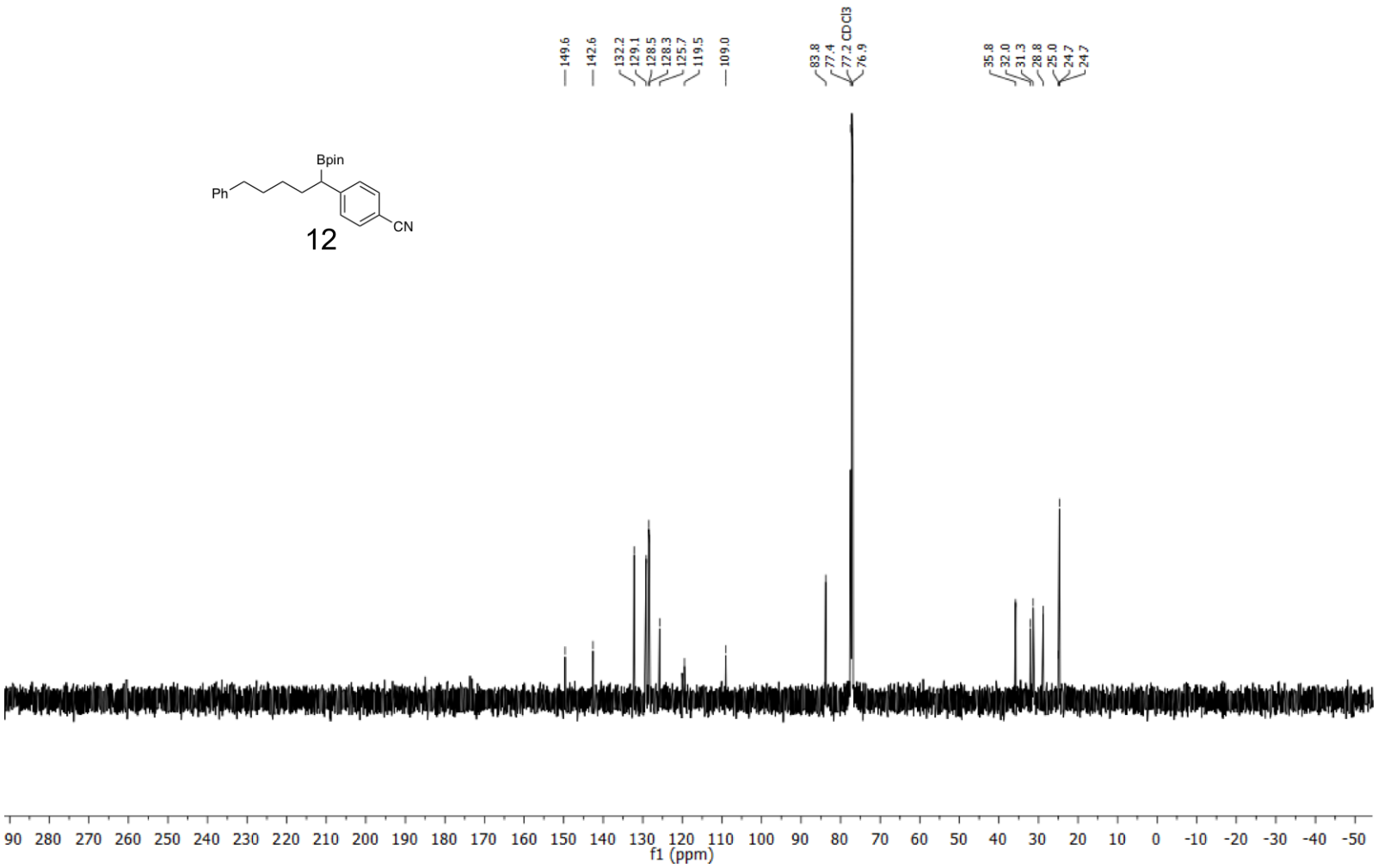


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.2 .

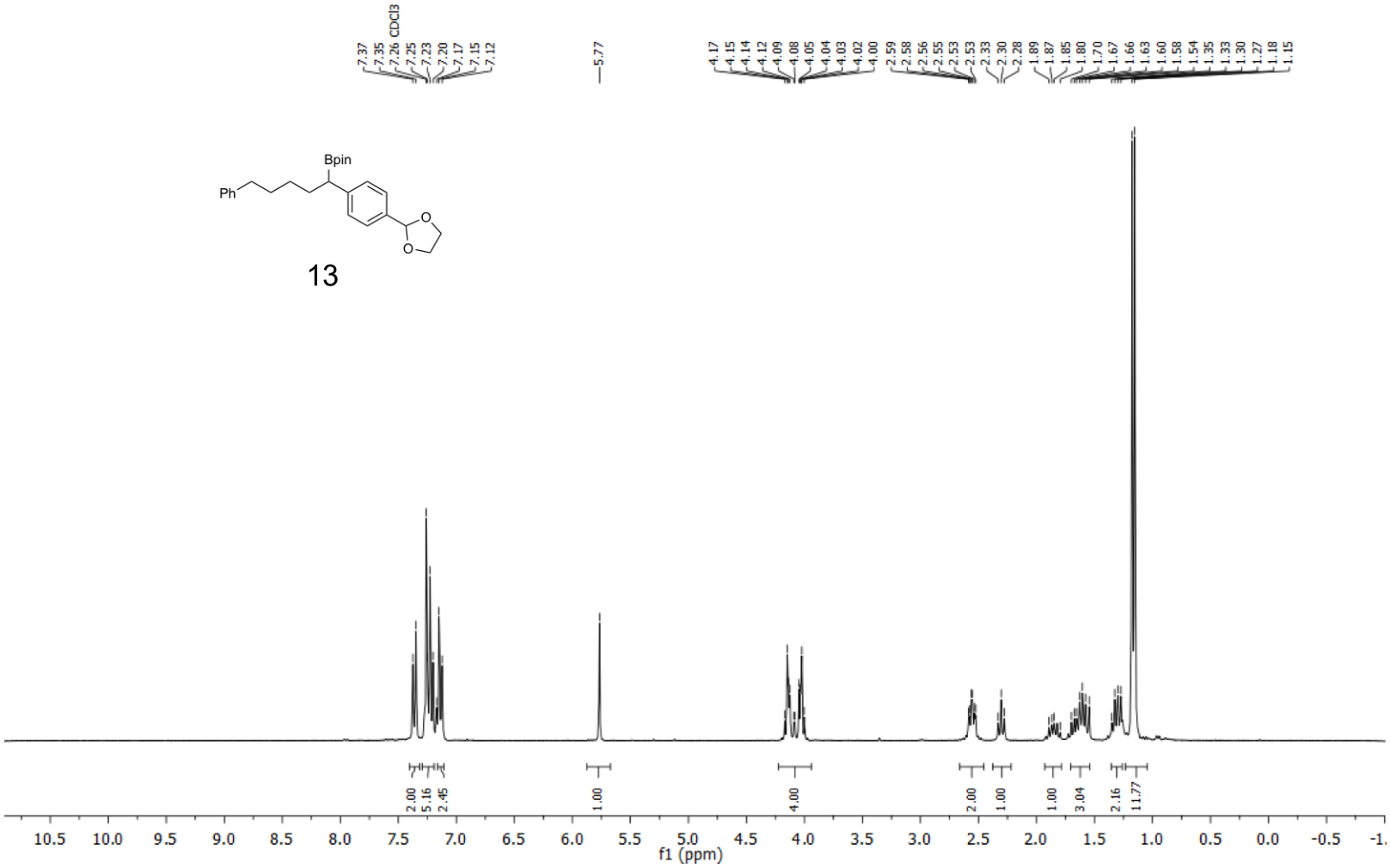


12

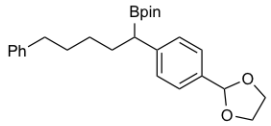
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.6 , 142.6 , 132.2 , 129.1 , 128.5 , 128.3 , 125.7 , 119.5 , 109.0 , 83.8 , 35.8 , 32.0 , 31.3 , 28.8 , 25.0 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.17 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 5.77 (s, 1H), 4.29 – 3.88 (m,4H), 2.67 – 2.45 (m, 2H), 2.30 (t, *J* = 7.9 Hz, 1H), 2.00 – 1.74 (m, 1H), 1.74 – 1.46 (m, 3H), 1.46 – 1.20 (m, 2H), 1.16 (d, *J* = 6.7 Hz, 12H).

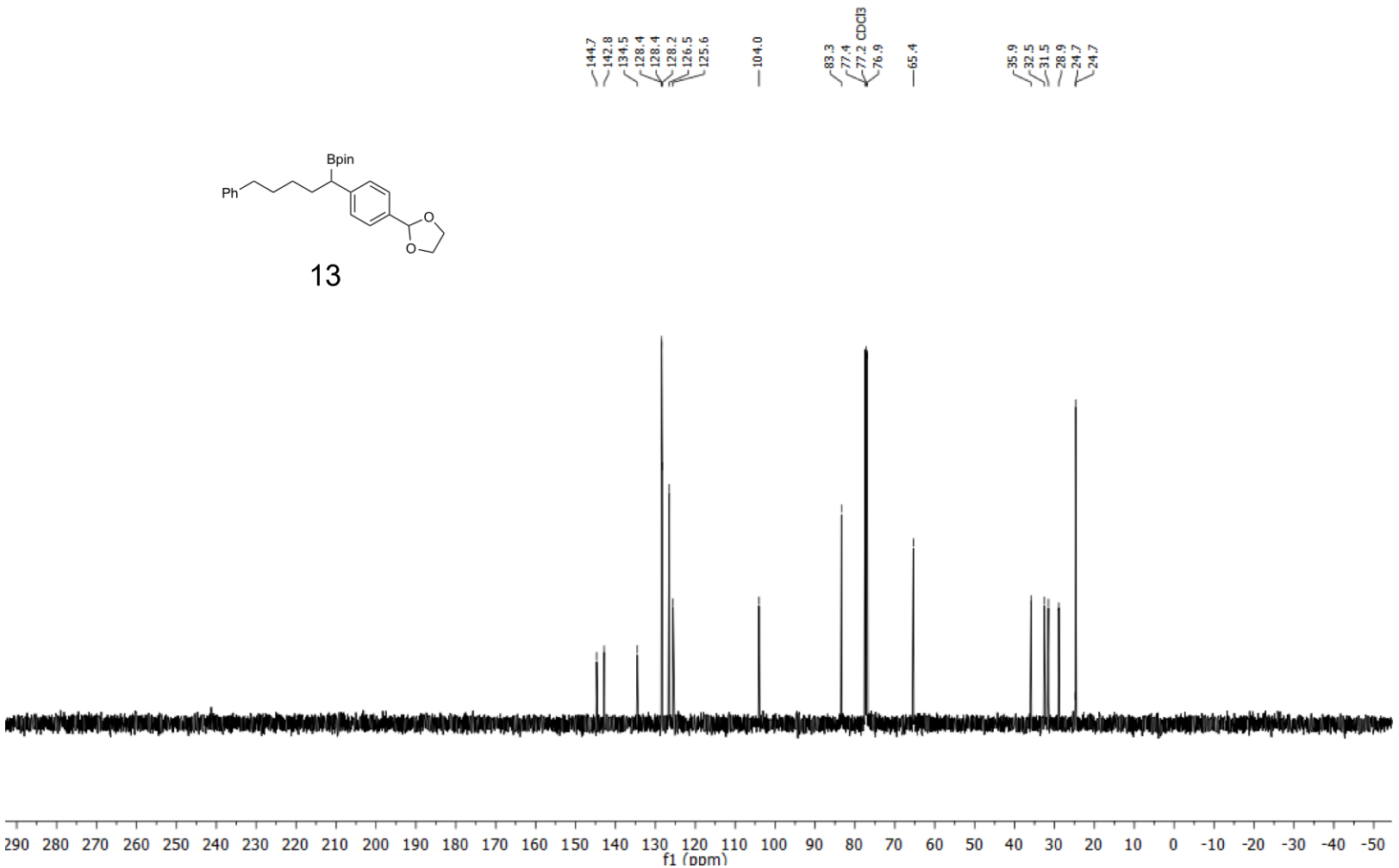


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.6 .



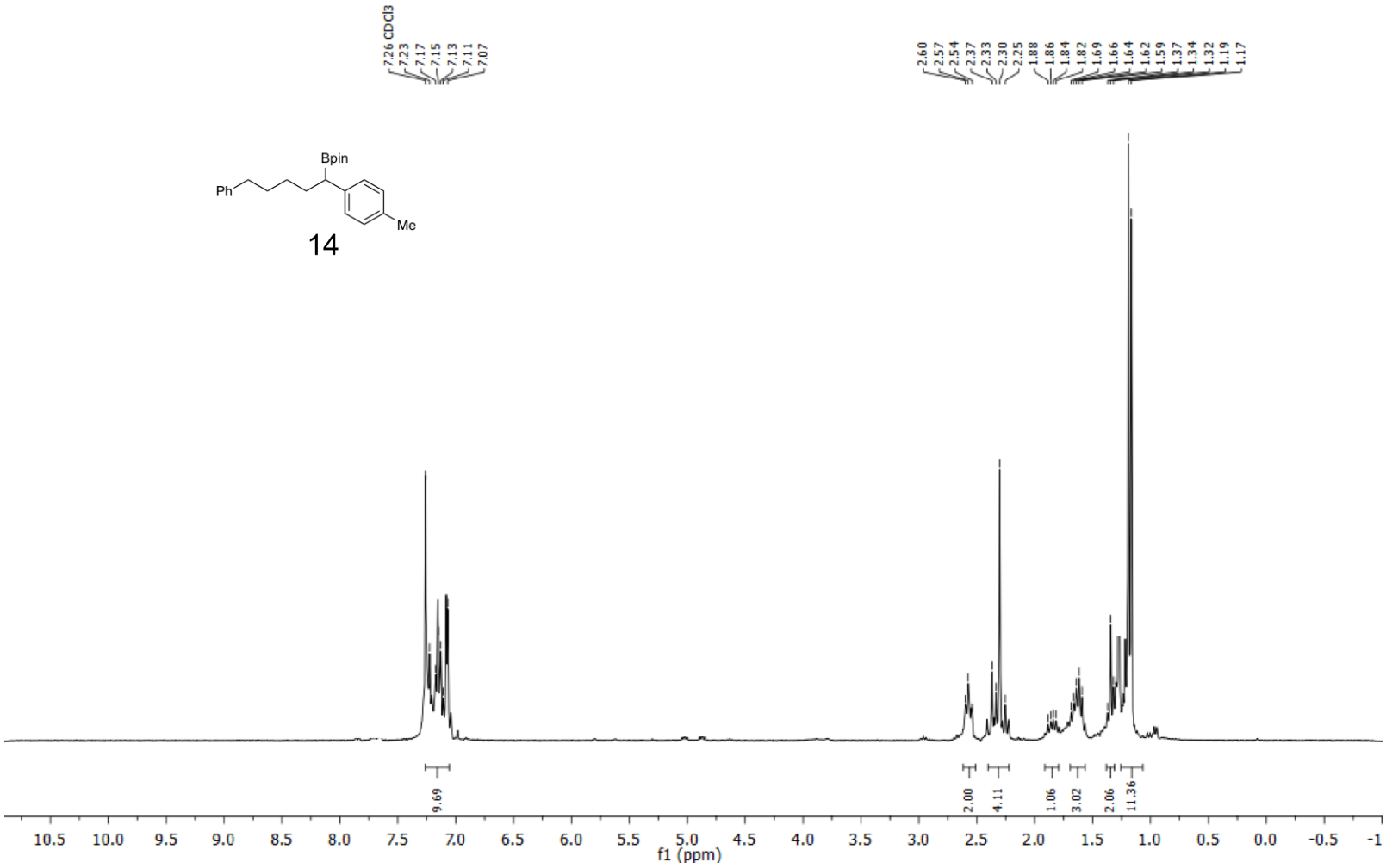
13

^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.7 , 142.8 , 134.5 , 128.4, 128.4, 128.2 , 126.5 , 125.6 , 104.0 , 83.3 , 65.4 , 35.9 , 32.5 , 31.5 , 28.9 , 24.7 , 24.7 .

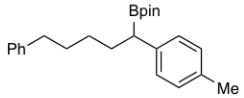


13

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.01 (m,10H), 2.57 (t, *J* = 9.0 Hz, 1H), 2.43 – 2.20 (m, 5H), 1.95 – 1.74 (m, 1H), 1.64 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.41 – 1.29 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 12H).

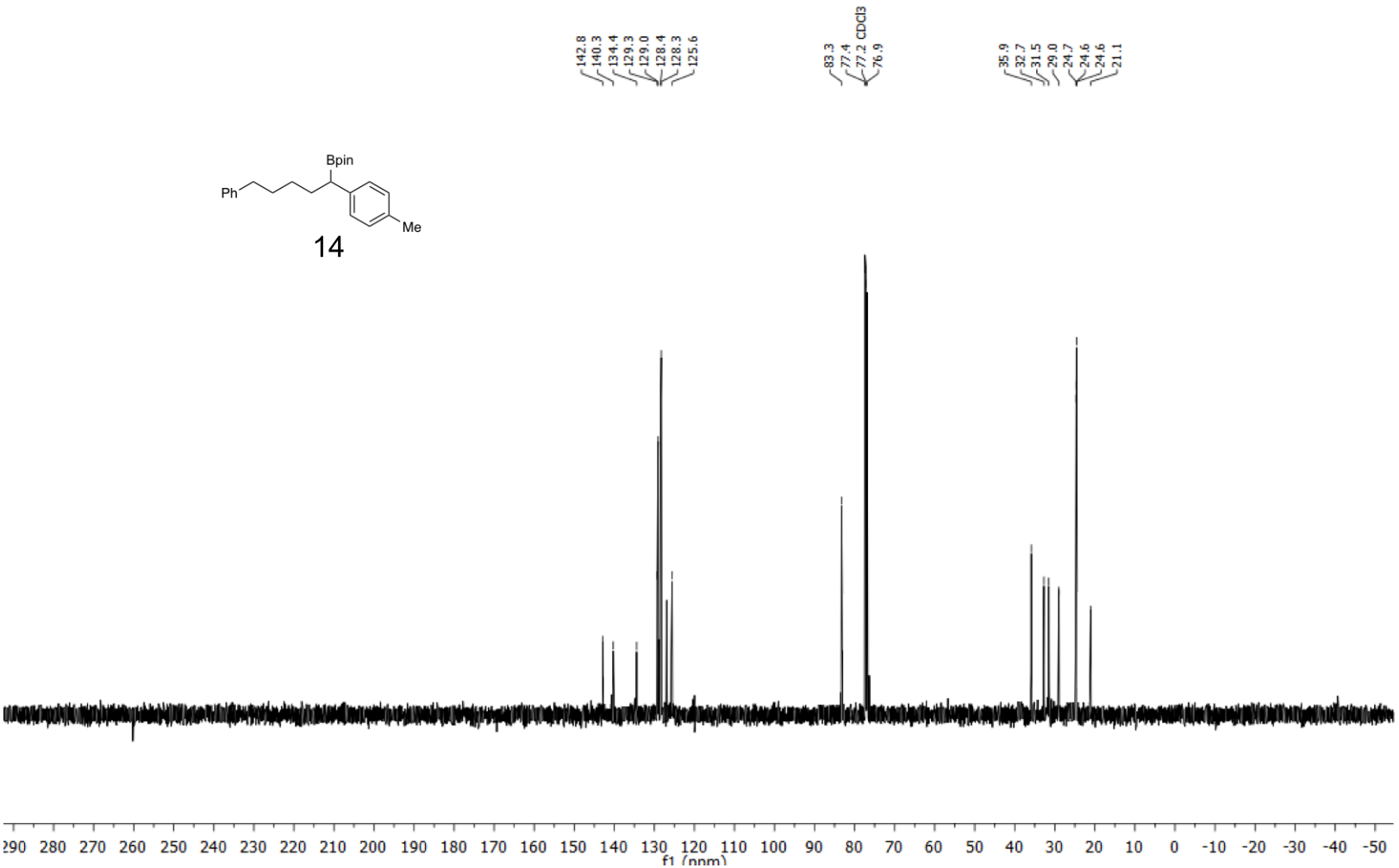


^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.3 .

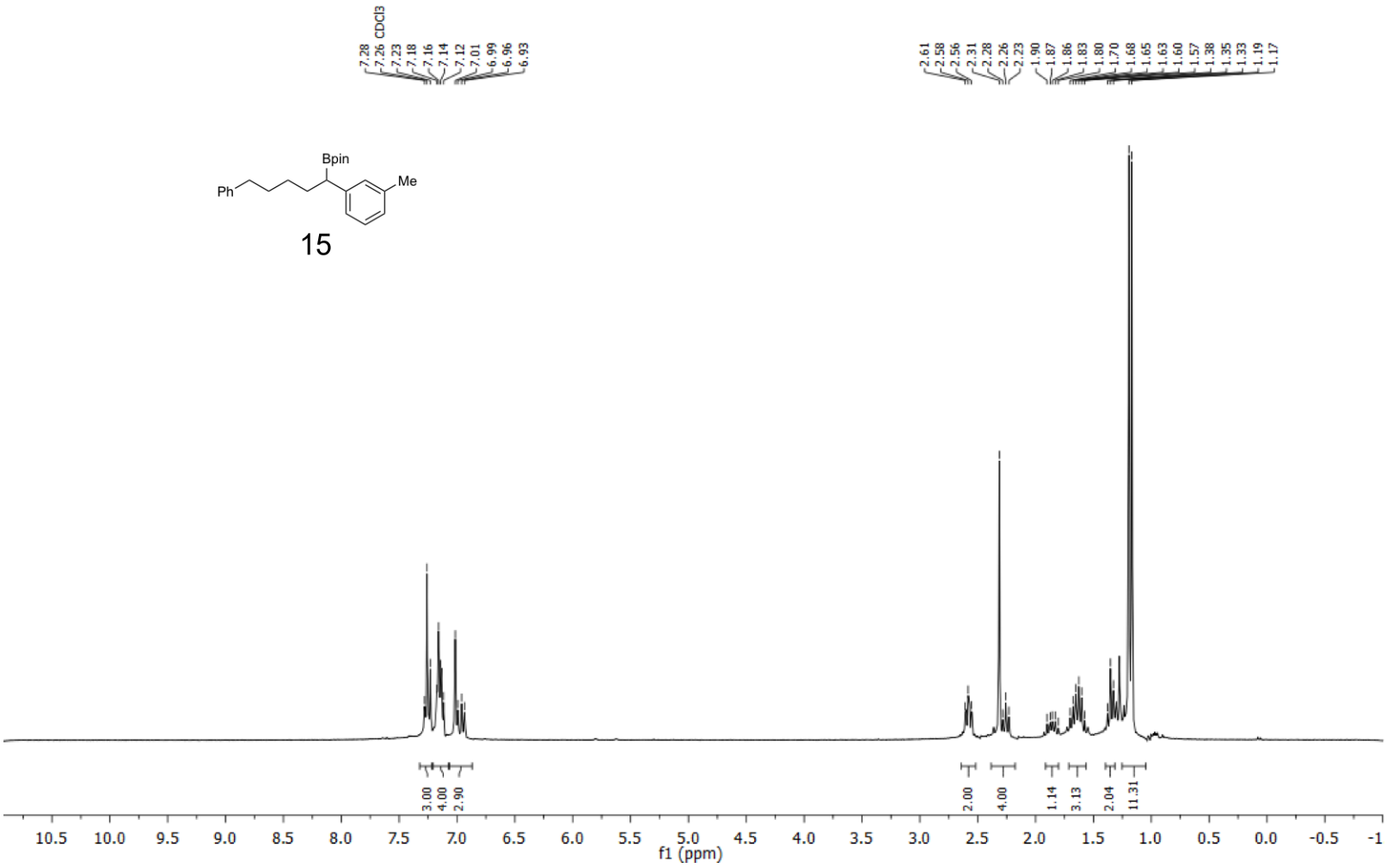


14

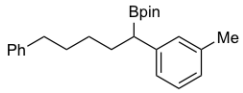
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.8 , 140.3 , 134.4 , 129.3 , 129.0 , 128.4 , 128.3 , 125.6 , 83.2 , 35.9 , 32.7 , 31.5 , 29.0 , 24.7 , 24.6 , 24.6 , 21.1 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.20 (m,3H), 7.21 – 7.08 (m,42H), 7.05 – 6.90 (m, 3H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.29 (d, *J* = 17.0 Hz,4H), 1.97 – 1.76 (m, 1H), 1.64 (m, 7.8 Hz, 3H), 1.35 (t, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 7.5 Hz, 12H).

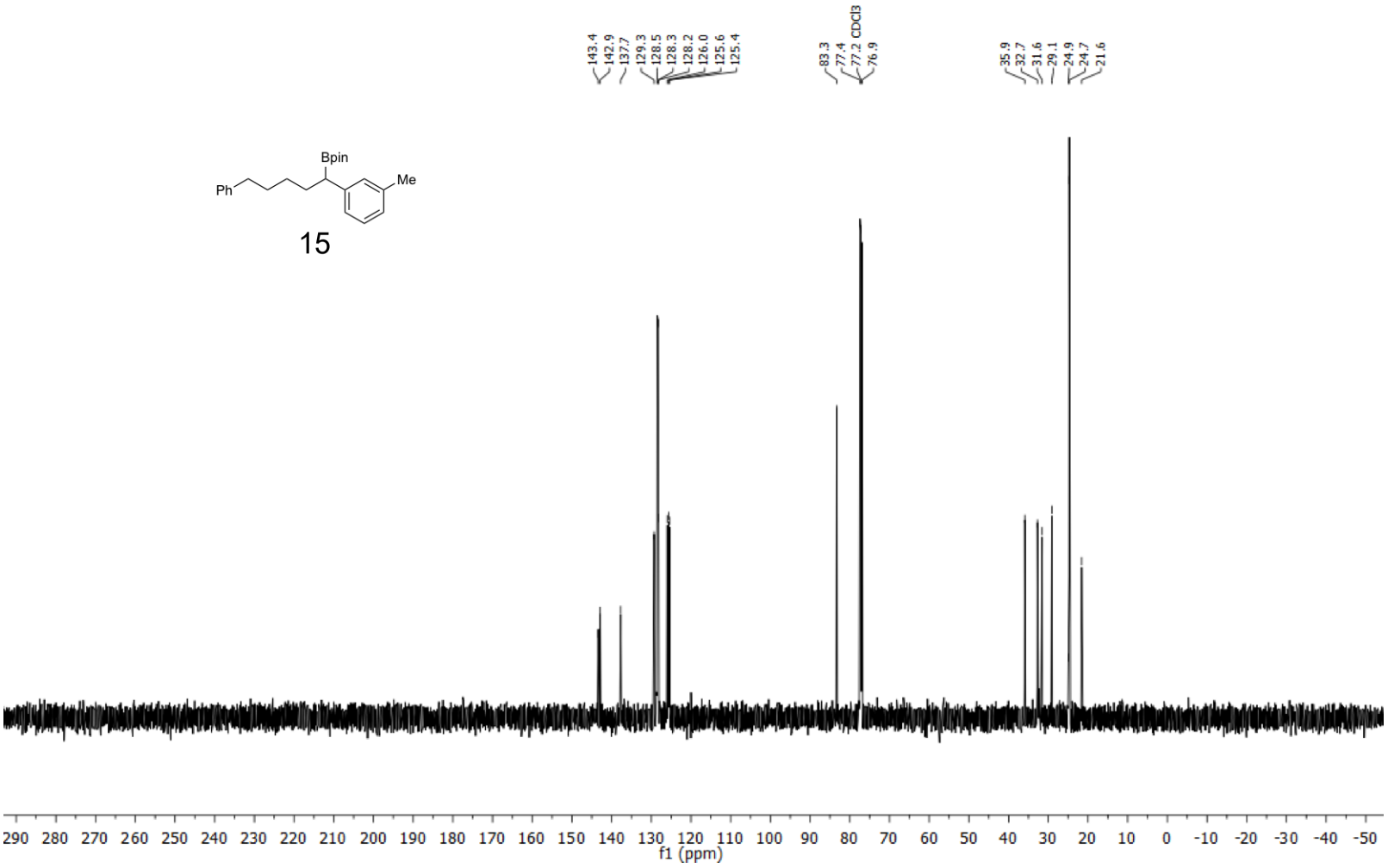


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 .

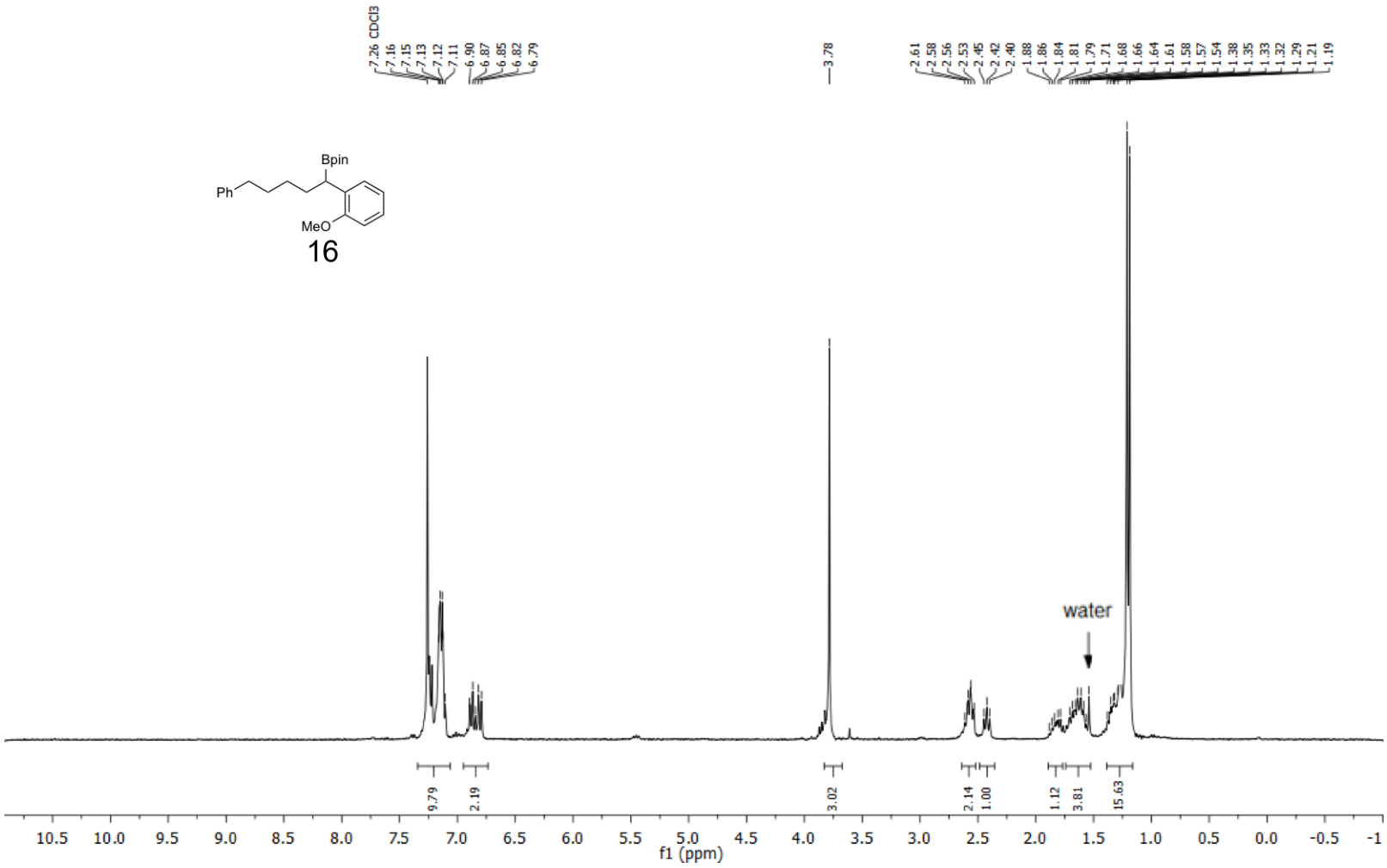


15

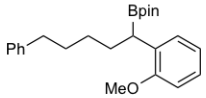
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.4 , 142.9 , 129.3 , 128.5 , 128.3 , 128.2 , 126.0 , 125.6 , 125.4 , 83.3 , 35.9 , 32.7 , 31.6 , 29.1 , 24.9 , 24.7 , 21.6 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.05 (m, 10H), 6.97 – 6.71 (m, 2H), 3.78 (s, 3H), 2.57 (m, 2H), 2.42 (t, *J* = 7.7 Hz, 1H), 1.95 – 1.75 (m, 1H), 1.75 - 1.55 (m, 3H), 1.42 – 1.14 (m, 14H).

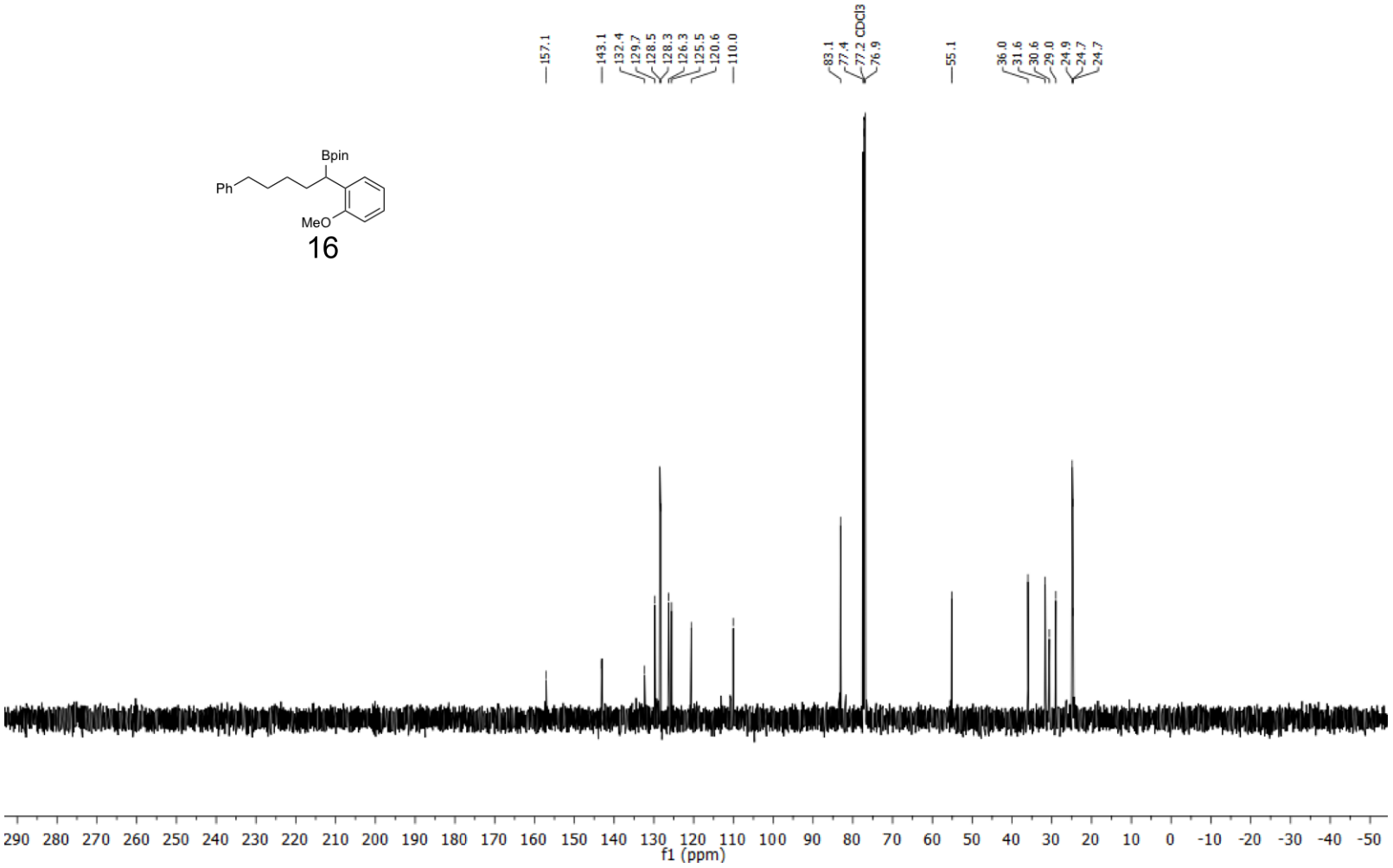


^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.1 .

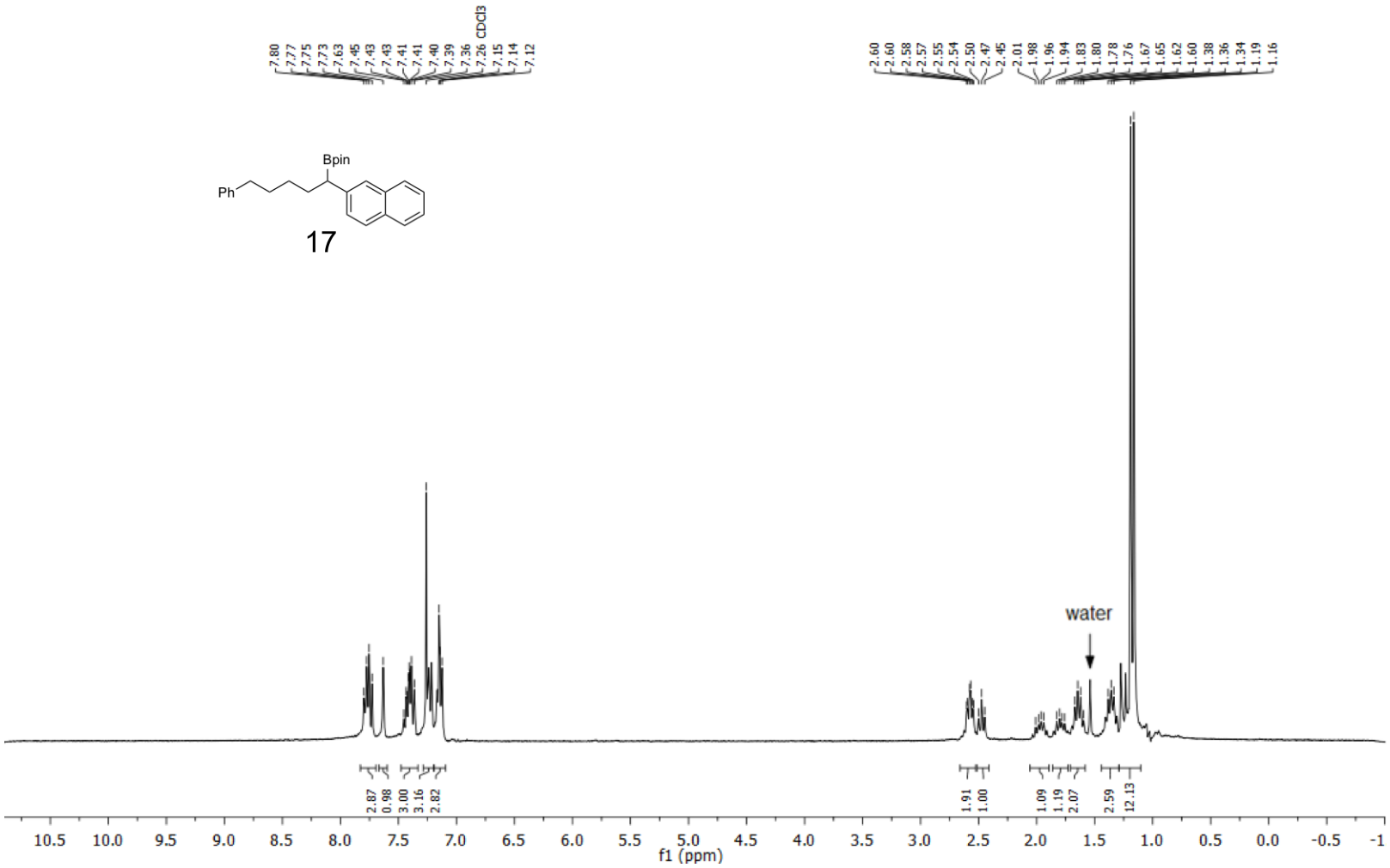


16

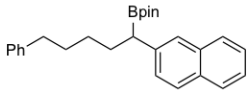
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.1 , 143.1 , 132.4 , 129.7 , 128.5 , 128.2 , 126.3 , 125.5 , 120.6 , 110.0 , 83.1 , 55.1 , 36.0 , 31.6 , 30.6 , 29.0 , 24.9 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 – 7.68 (m, 3H), 7.63 (s, 1H), 7.55 – 7.30 (m, 3H), 7.26 (s, 3H), 7.14 (d, *J* = 7.7 Hz, 3H), 2.57 (m, 2H), 2.47 (t, *J* = 7.9 Hz, 1H), 1.97 (m, 1H), 1.79 (m, 1H), 1.63 (m, 2H), 1.45 – 1.28 (m, 2H), 1.18 (d, *J* = 8.2 Hz, 12H).

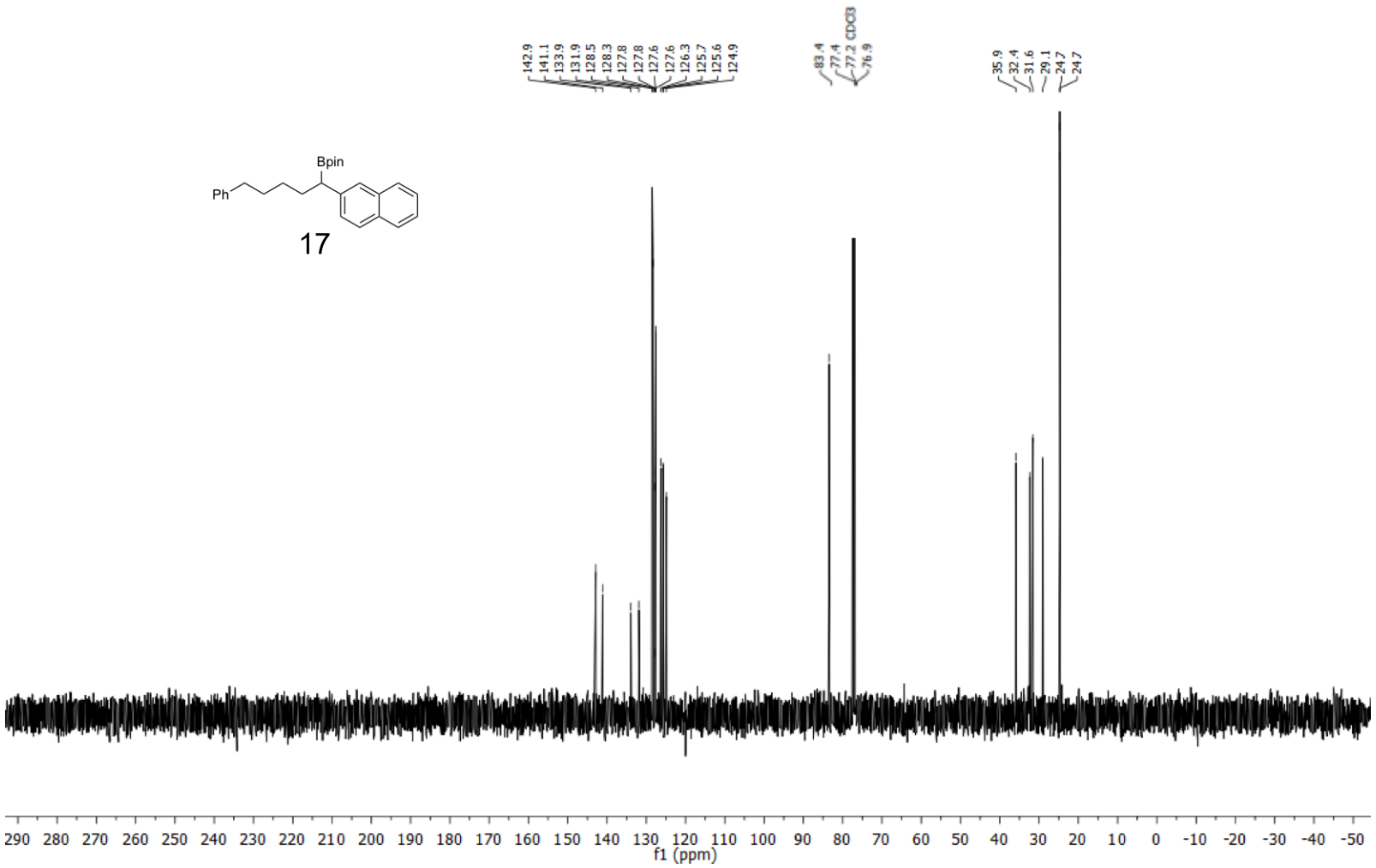


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8 .

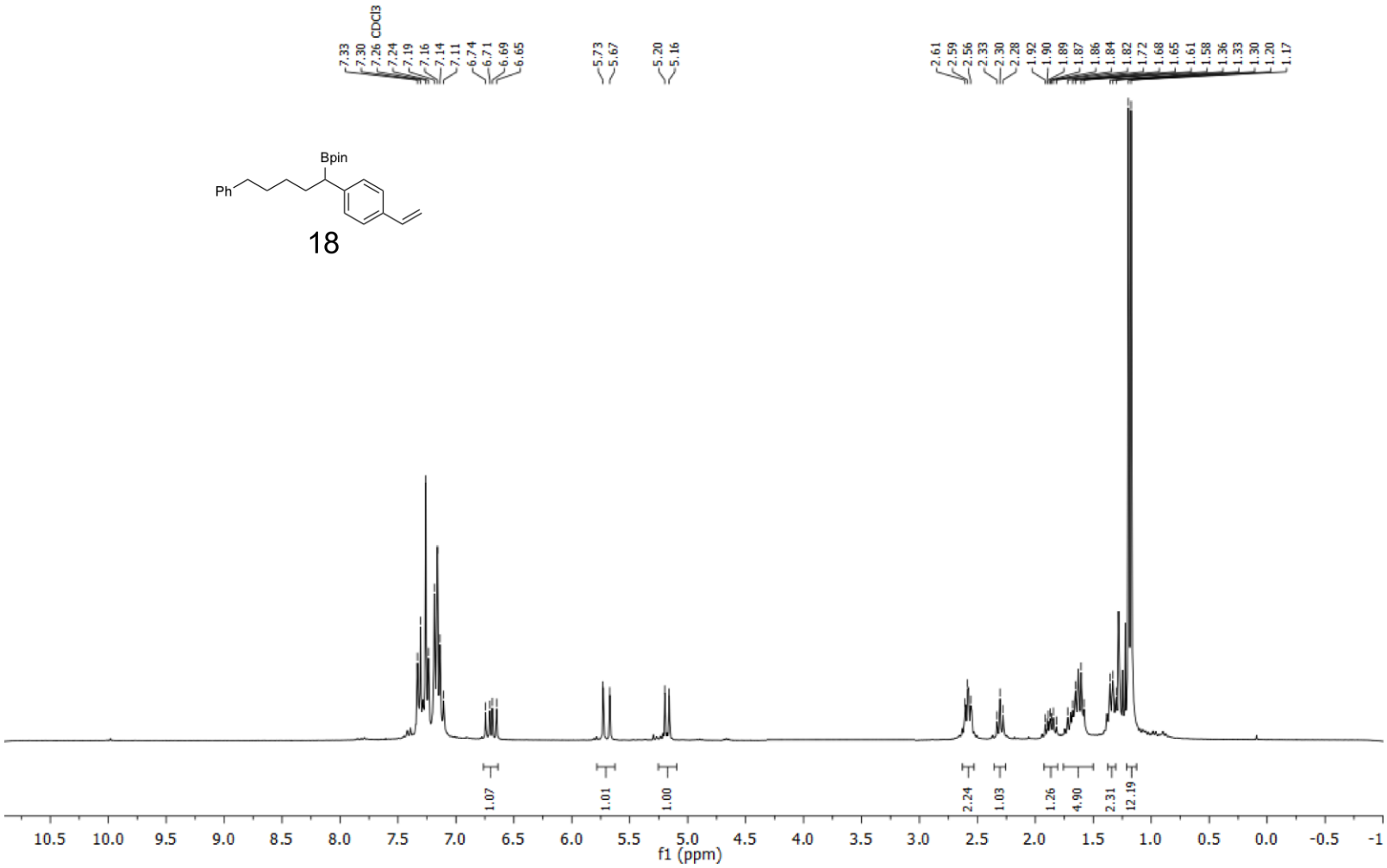


17

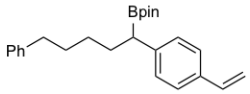
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.9 , 141.1 , 133.9 , 131.9 , 128.5 , 128.3 , 127.8 , 127.8 , 127.6 , 127.6 , 126.3 , 125.7 , 125.6 , 124.9 , 83.4 , 35.9 , 32.4 , 31.6 , 29.1 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 4H), 7.15 (dd, *J* = 15.3, 8.7 Hz, 6H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.30 (t, *J* = 7.9 Hz, 1H), 1.87 (dt, *J* = 13.2, 7.9 Hz, 1H), 1.77 – 1.55 (m, 2H), 1.43 – 1.27 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 12H).

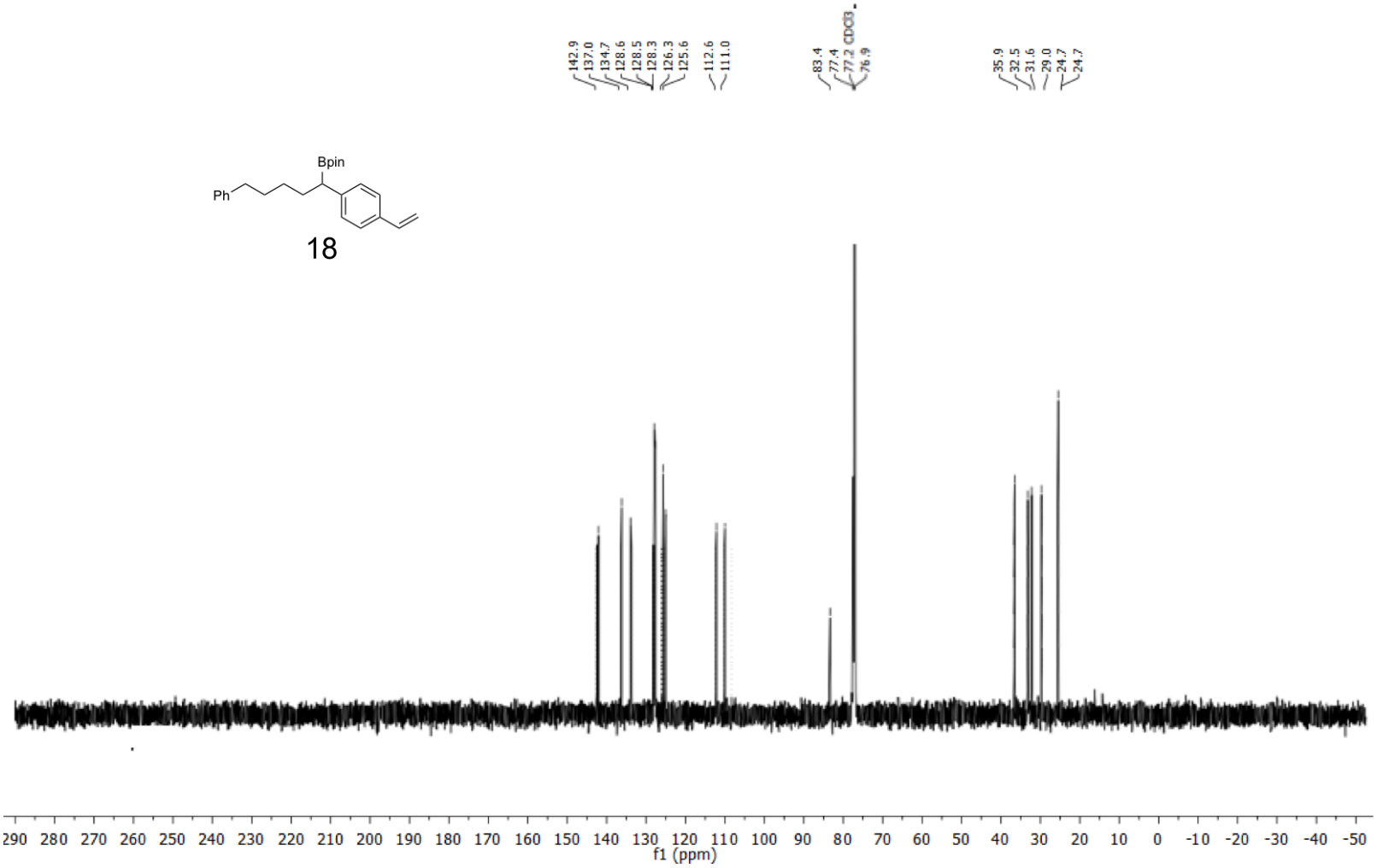


^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.4 .

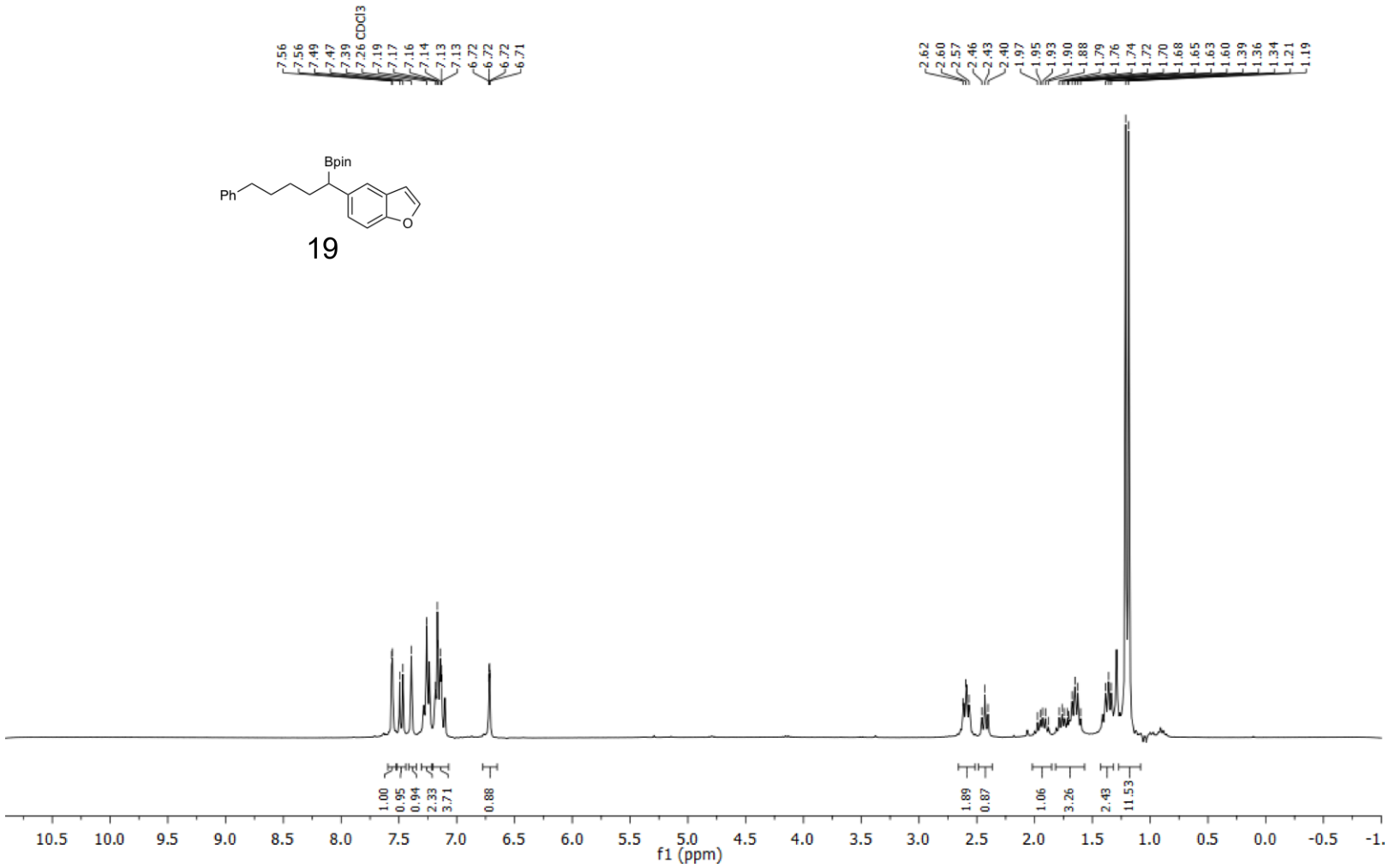


18

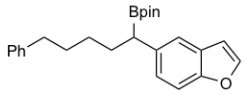
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.9 , 137.0 , 134.7 , 128.6 , 128.5 , 128.3 , 126.3 , 125.6 , 112.6 , 111.0 , 83.4 , 35.9 , 32.5 , 31.5 , 29.0 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.26 (s, 2H), 7.21 – 7.07 (m, 4H), 6.77 – 6.68 (m, 1H), 2.68 – 2.50 (m, 2H), 2.43 (t, *J* = 7.9 Hz, 1H), 2.03 – 1.85 (m, 1H), 1.84 – 1.57 (m, 3H), 1.49 – 1.30 (m, 2H), 1.20 (d, *J* = 8.1 Hz, 12H).



^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.1 .



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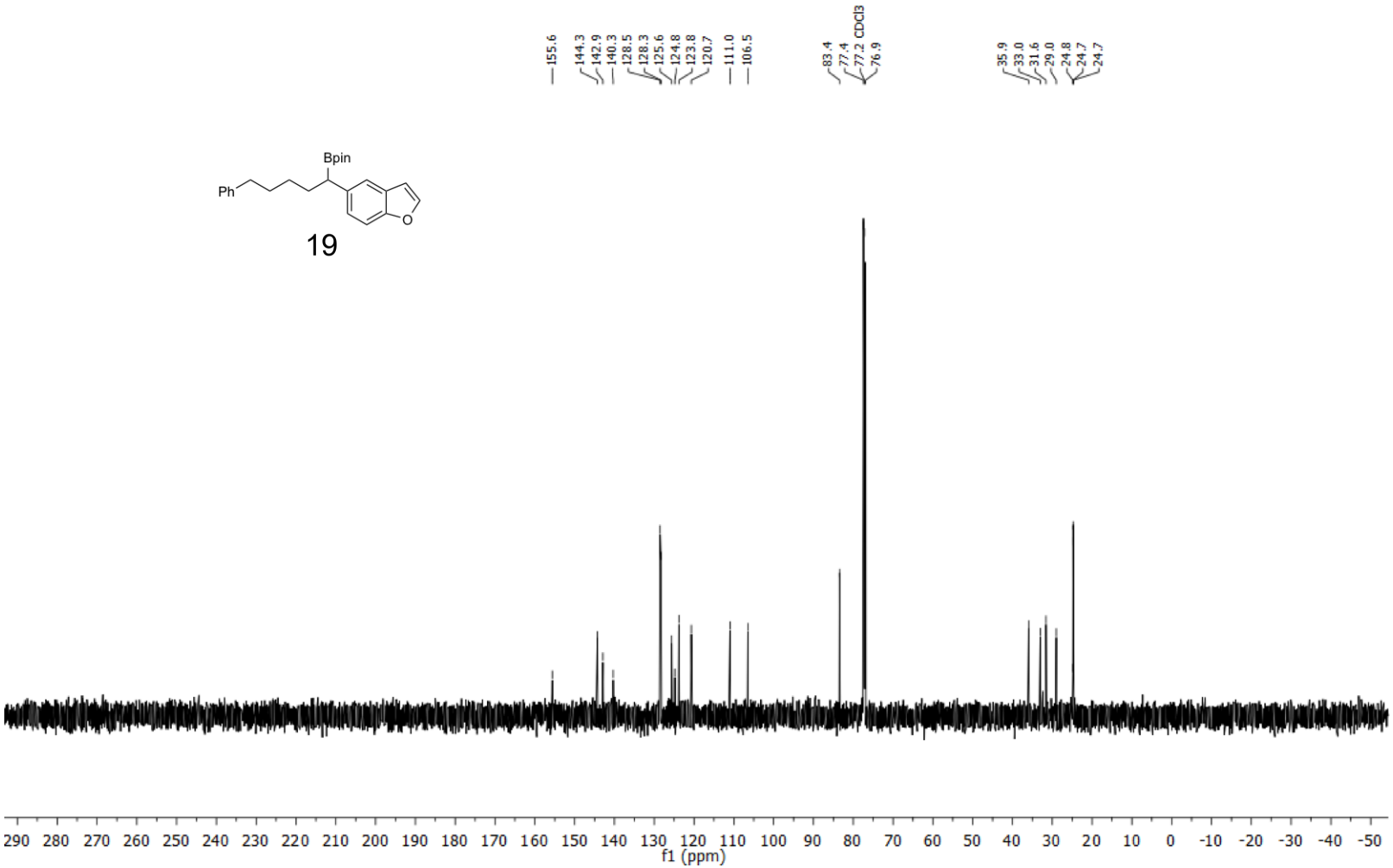
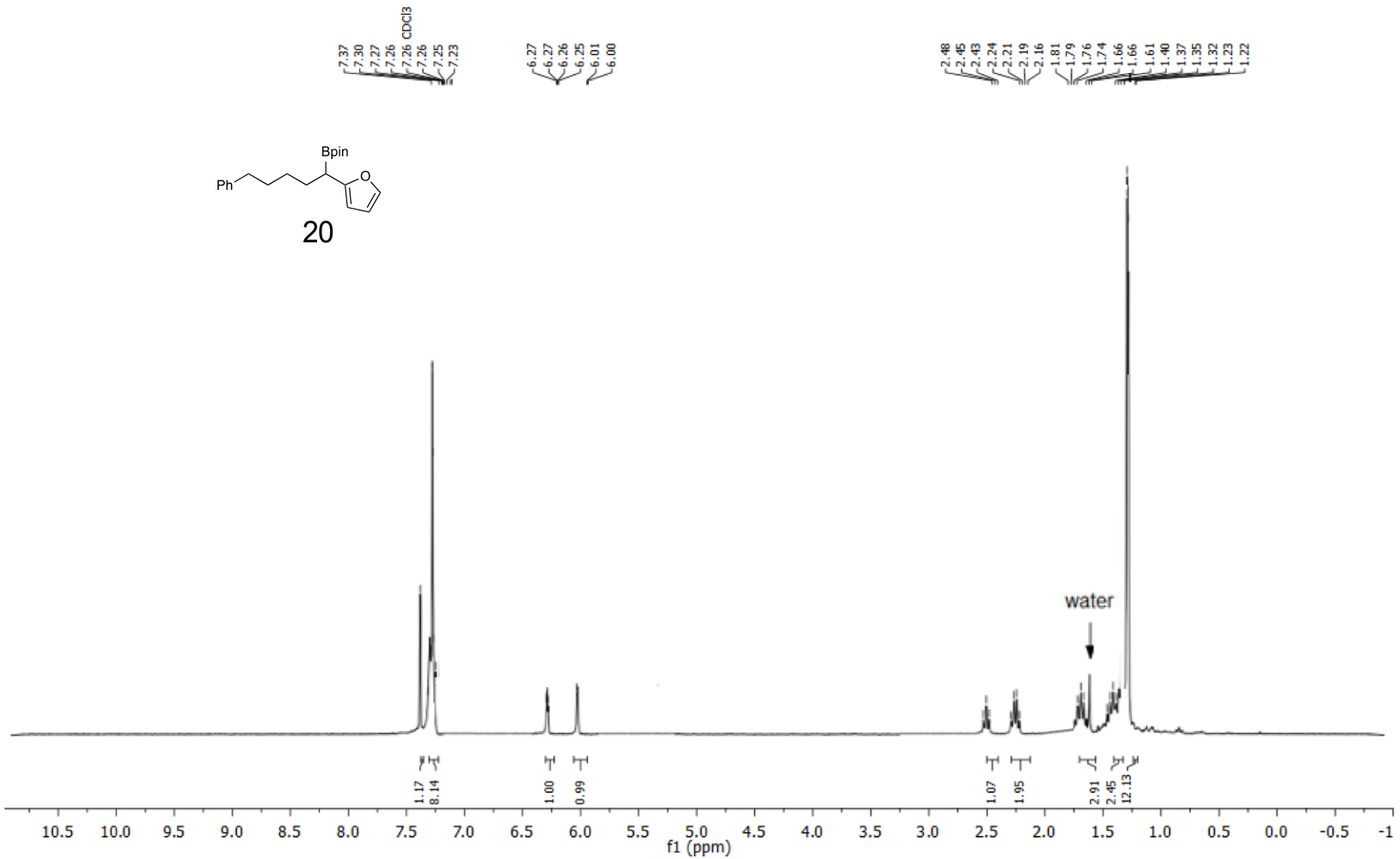
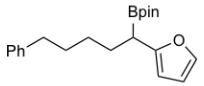
^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.6 , 144.3 , 142.9 , 140.3 , 128.5 , 128.3 , 125.6 , 124.8 , 123.8 , 120.7 , 111.0, 106.5 , 83.4 , 35.9 , 33.0 , 31.6 , 29.0 , 24.8 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.33 – 7.22 (m, 8H), 6.26 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.00 (d, *J* = 3.4 Hz, 1H), 2.45 (t, *J* = 7.5 Hz, 1H), 2.20 (q, *J* = 7.5 Hz, 2H), 1.77 (q, *J* = 7.8 Hz, 3H), 1.69 – 1.57 (m, 2H), 1.36 (q, *J* = 8.2 Hz, 1H), 1.22 (d, *J* = 2.7 Hz, 13H).

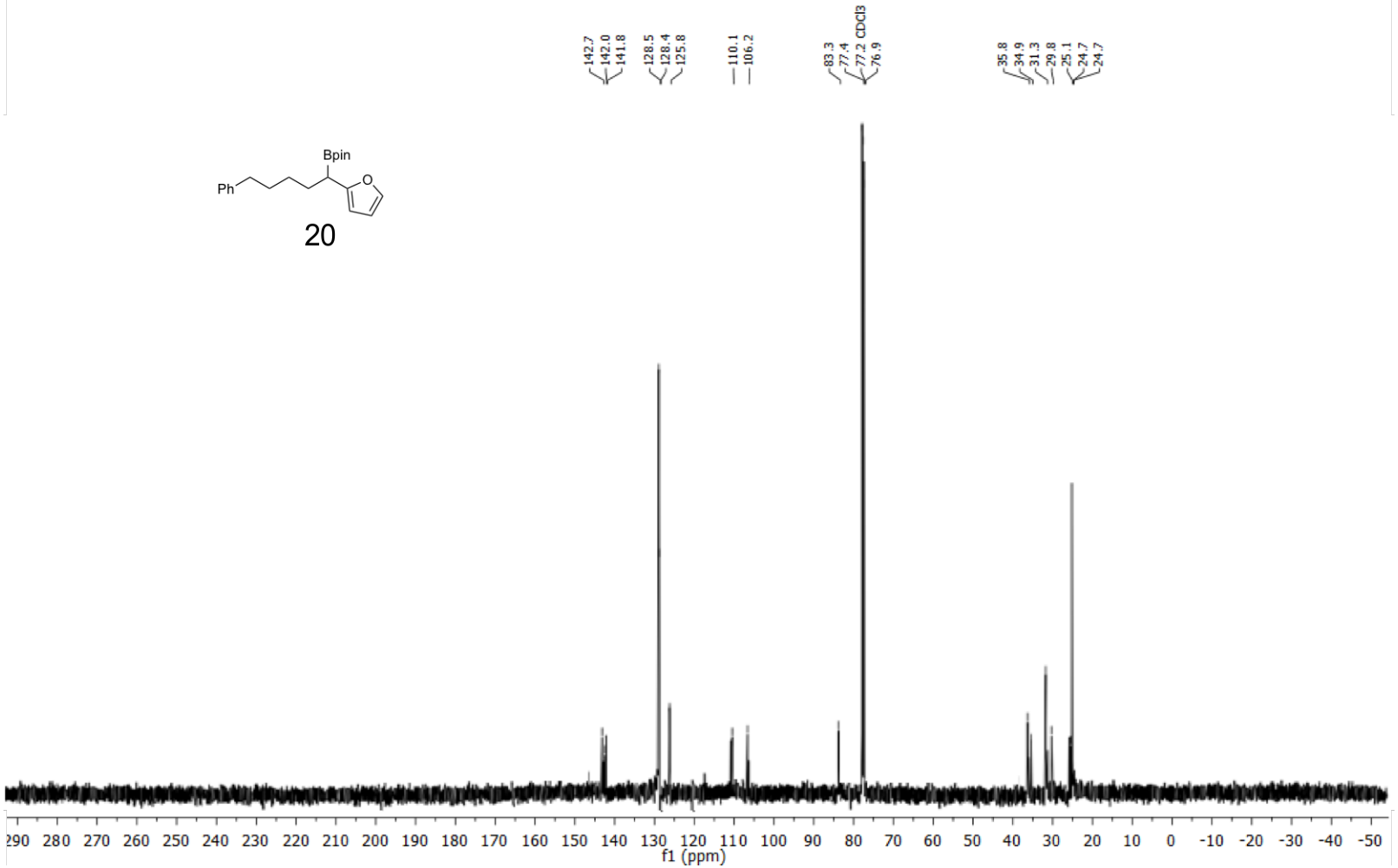


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 .

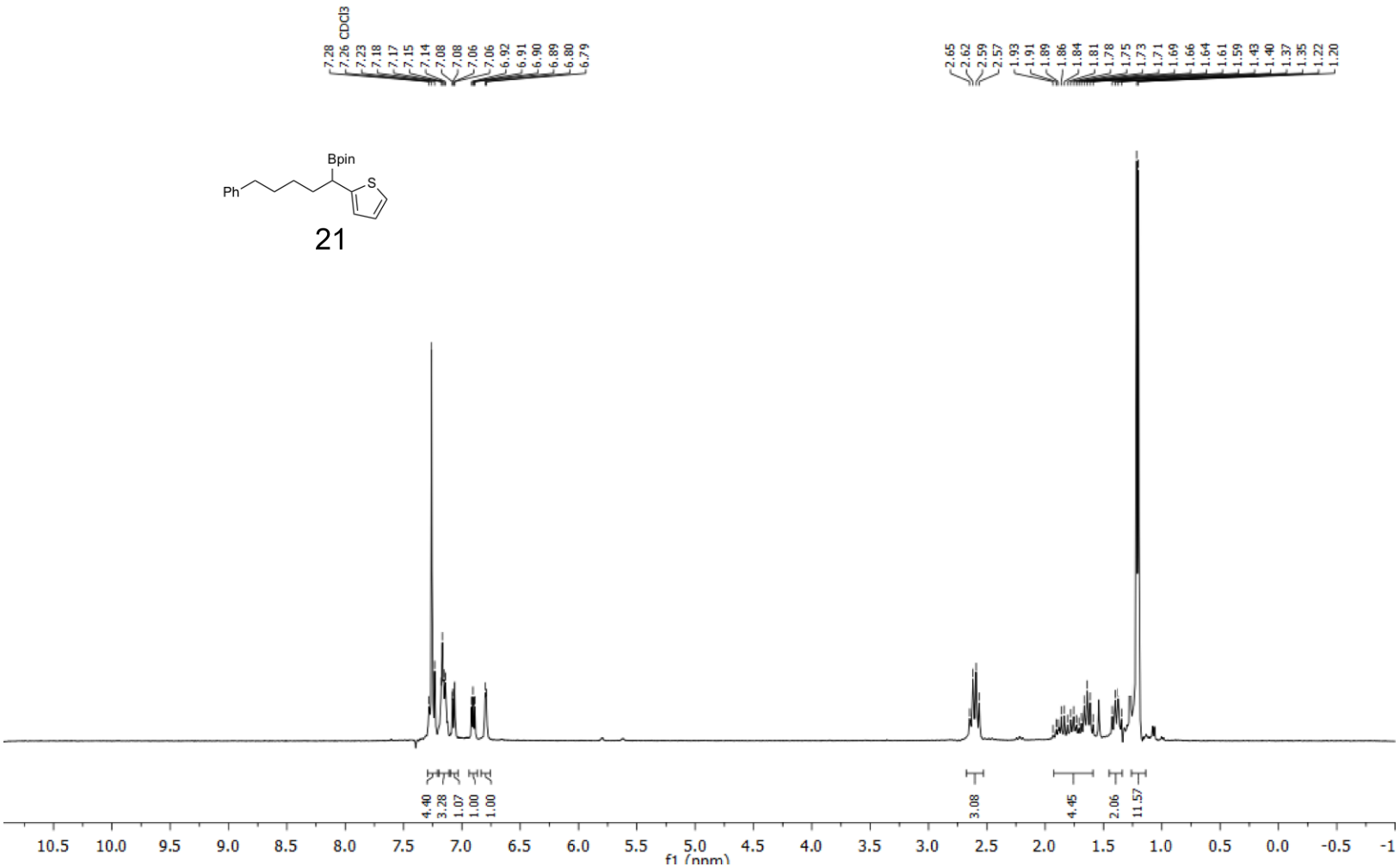


20

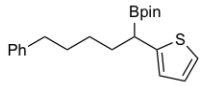
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.7 , 142.0 , 141.8 , 128.5 , 128.4 , 125.8 , 110.1 , 106.2 , 83.3 , 35.8 , 34.9 , 31.3 , 29.8 , 25.1 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.1 Hz, 4H), 7.19 – 7.11 (m, 3H), 7.07 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.90 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 2.61 (m, 3H), 1.97 – 1.55 (m, 4H), 1.39 (m, 2H), 1.21 (d, *J* = 4.8 Hz, 12H).



^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.12 .



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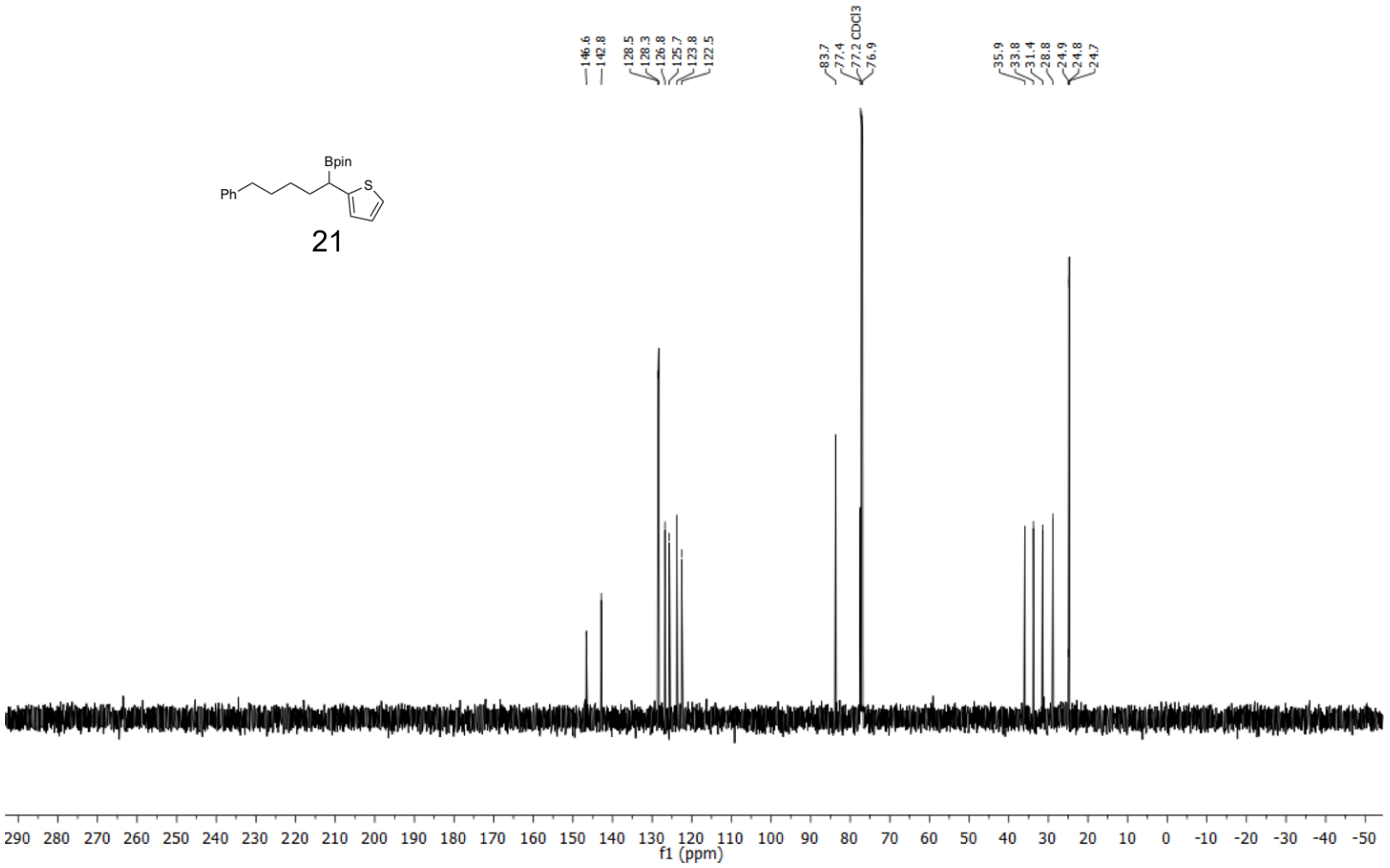
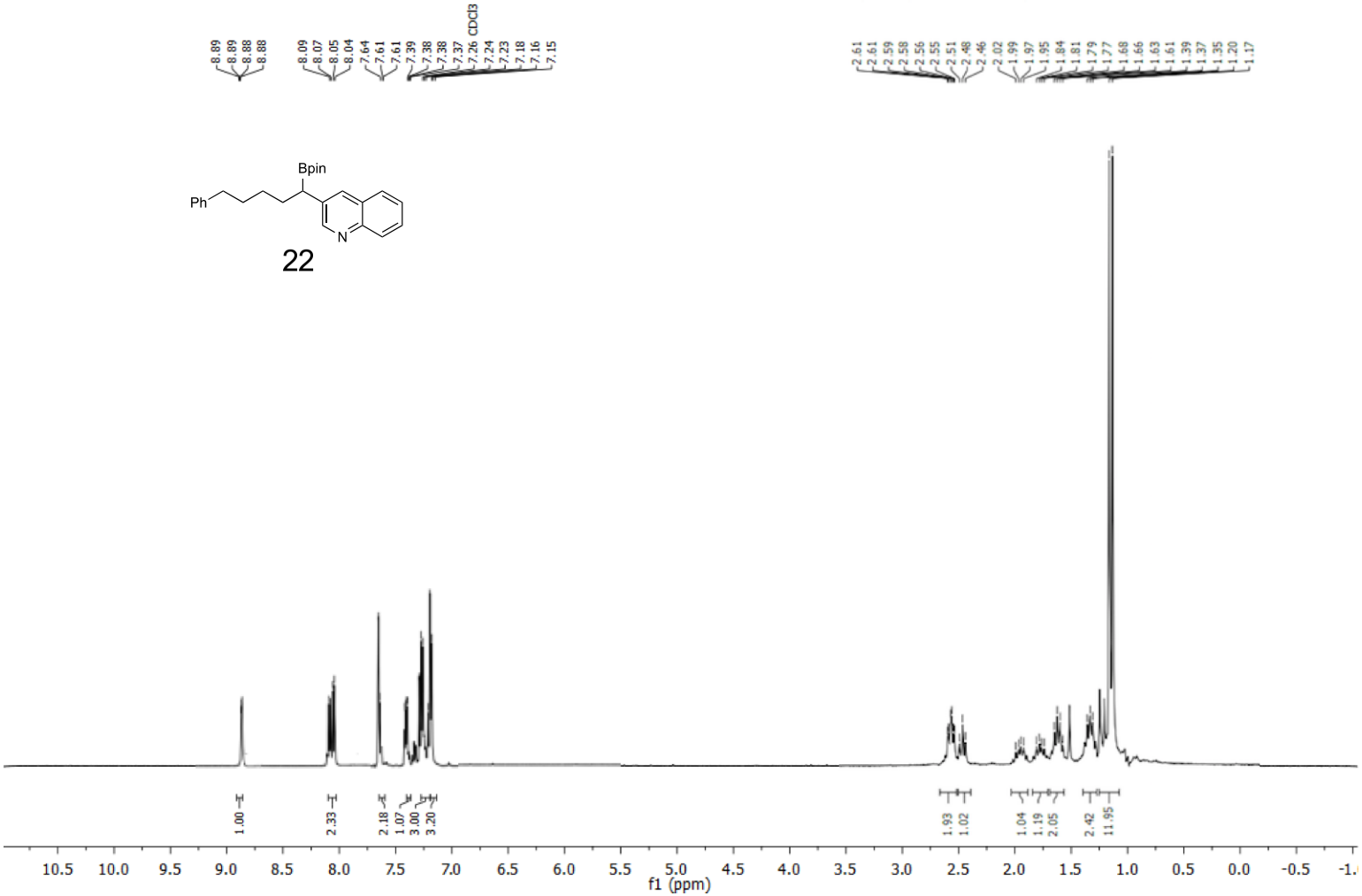
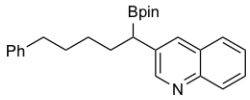
^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.6 , 142.8 , 128.5 , 128.3 , 126.8 , 125.7 , 123.8 , 122.5 , 83.7 , 35.9 , 33.8 , 31.4 , 28.8 , 24.9 , 24.8 , 24.7 .



^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.88 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.06 (dd, *J* = 17.9, 7.6 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 – 7.19 (m, 2H), 7.19 – 7.12 (m, 3H), 2.58 (m, 2H), 2.49 (t, *J* = 7.8 Hz, 1H), 1.99 (m, 1H), 1.80 (m, 1H), 1.65 (m, 2H), 1.39 – 1.35 (m, 2H), 1.19 (d, *J* = 7.9 Hz, 12H).

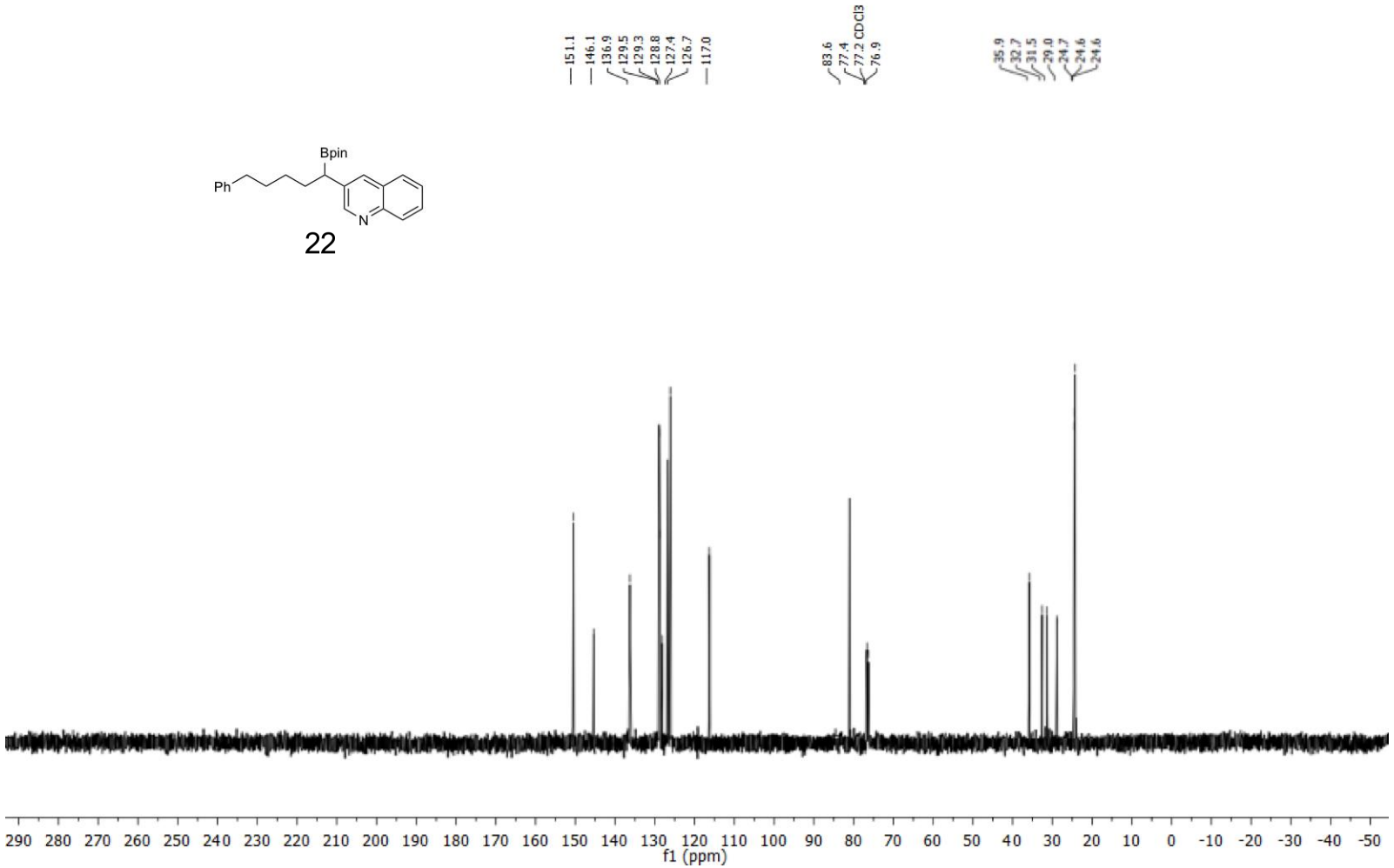


^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.1 .

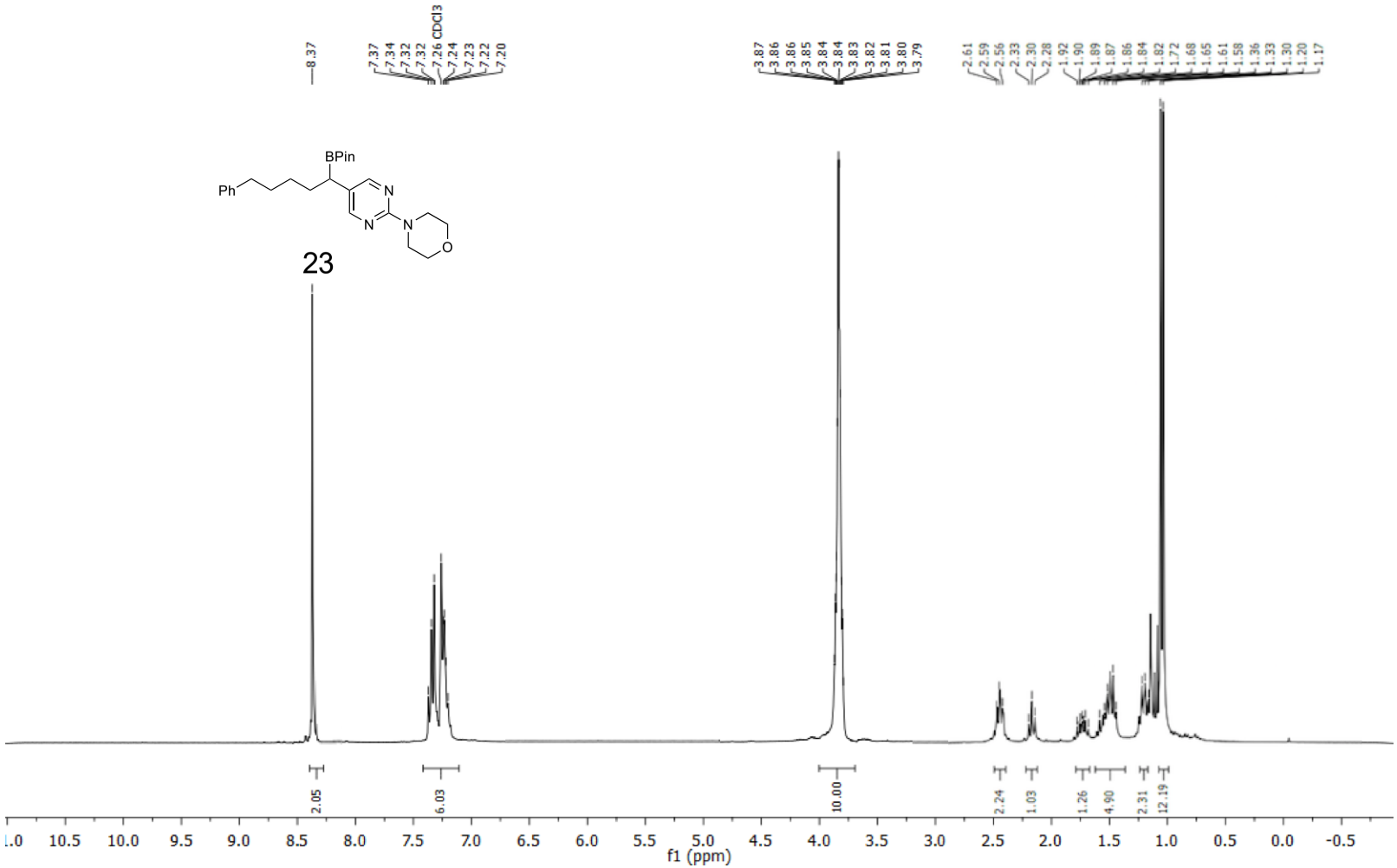


22

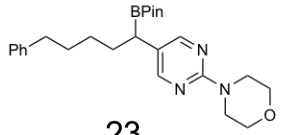
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.1 , 146.1 , 136.9 , 129.5 , 129.3 , 128.8 , 127.3 , 126.7 , 117.0 , 83.6 , 35.9 , 32.9 , 31.5 , 29.0 , 25.0 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.37 (s, 2H), 7.43 – 7.13 (m, 7H), 3.84 (qq, *J* = 4.8, 2.3 Hz, 10H), 2.30 (t, *J* = 7.9 Hz, 1H), 2.00 - 1.79 (m, 1H), 1.74 - 1.46 (m, 3H), 1.46 - 1.20 (m, 2H), 1.16 (d, *J* = 6.7Hz, 12H).

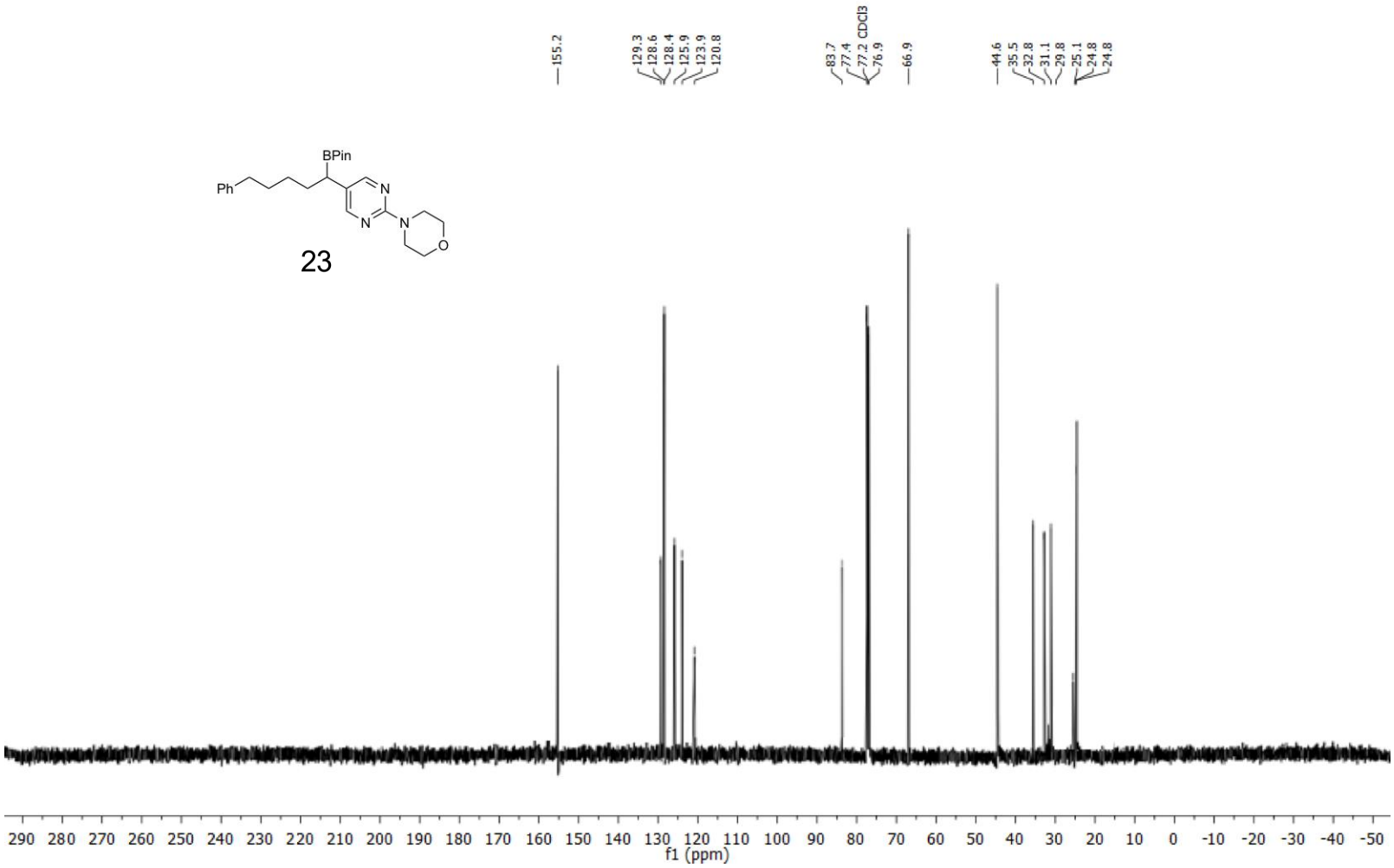


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.7 .

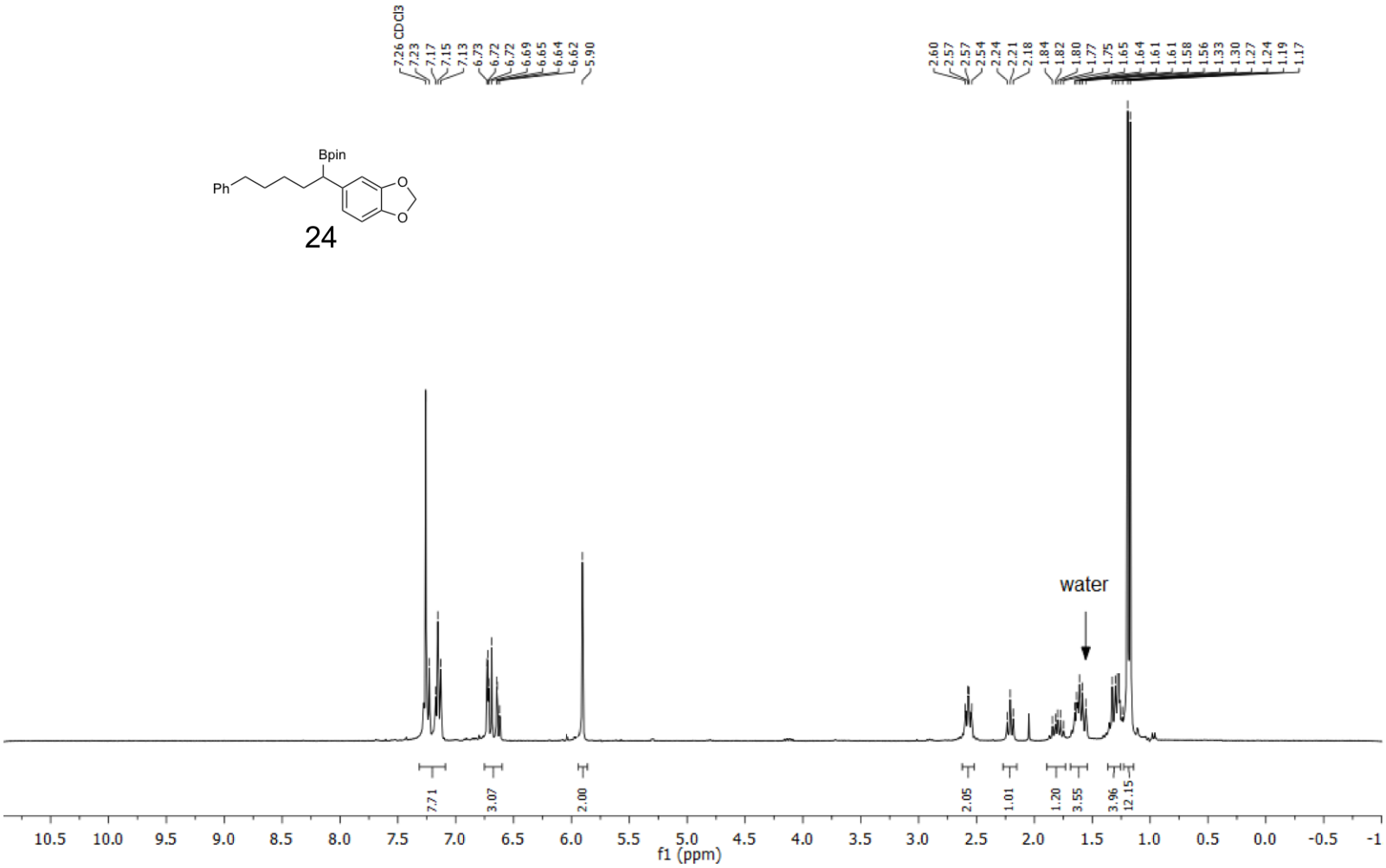


23

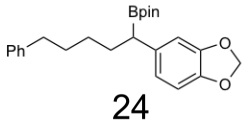
^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.2 , 129.3 , 128.6 , 128.4 , 125.9 , 123.9 , 120.8 , 83.7 , 66.9 , 44.6 , 35.5 , 32.8 , 31.1 , 29.8 , 25.1 , 24.8 , 24.8 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.07 (m,7H), 6.77 – 6.56 (m, 3H), 5.90 (s, 2H), 2.63 – 2.48 (m, 2H), 2.21 (t, *J* = 7.9 Hz, 1H), 1.92 – 1.71 (m, 1H), 1.70 – 1.52 (m, 3H), 1.30 (d, *J* = 16.1 Hz, 4H), 1.18 (d, *J* = 6.8 Hz, 12H).

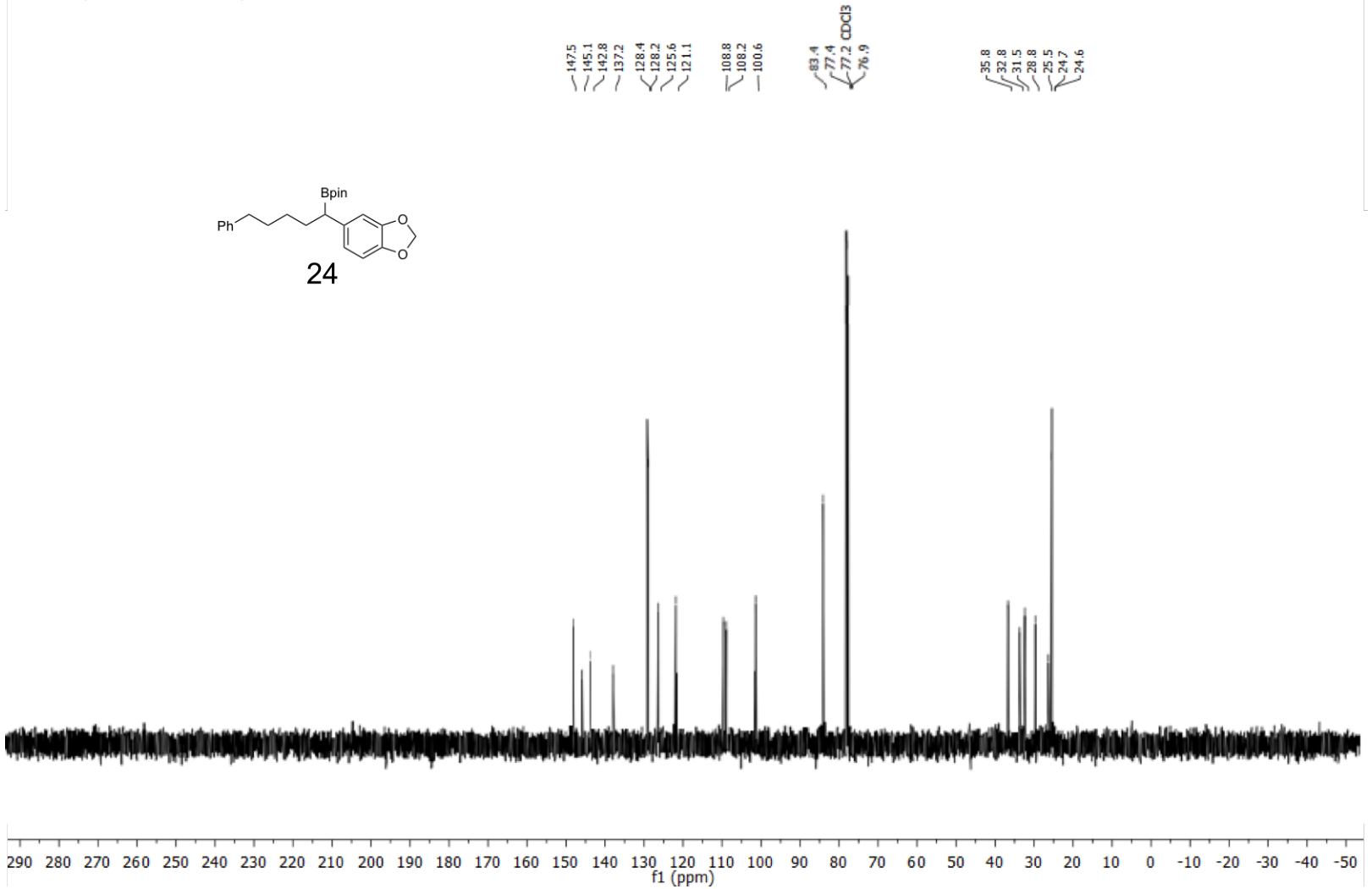


^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.0 .

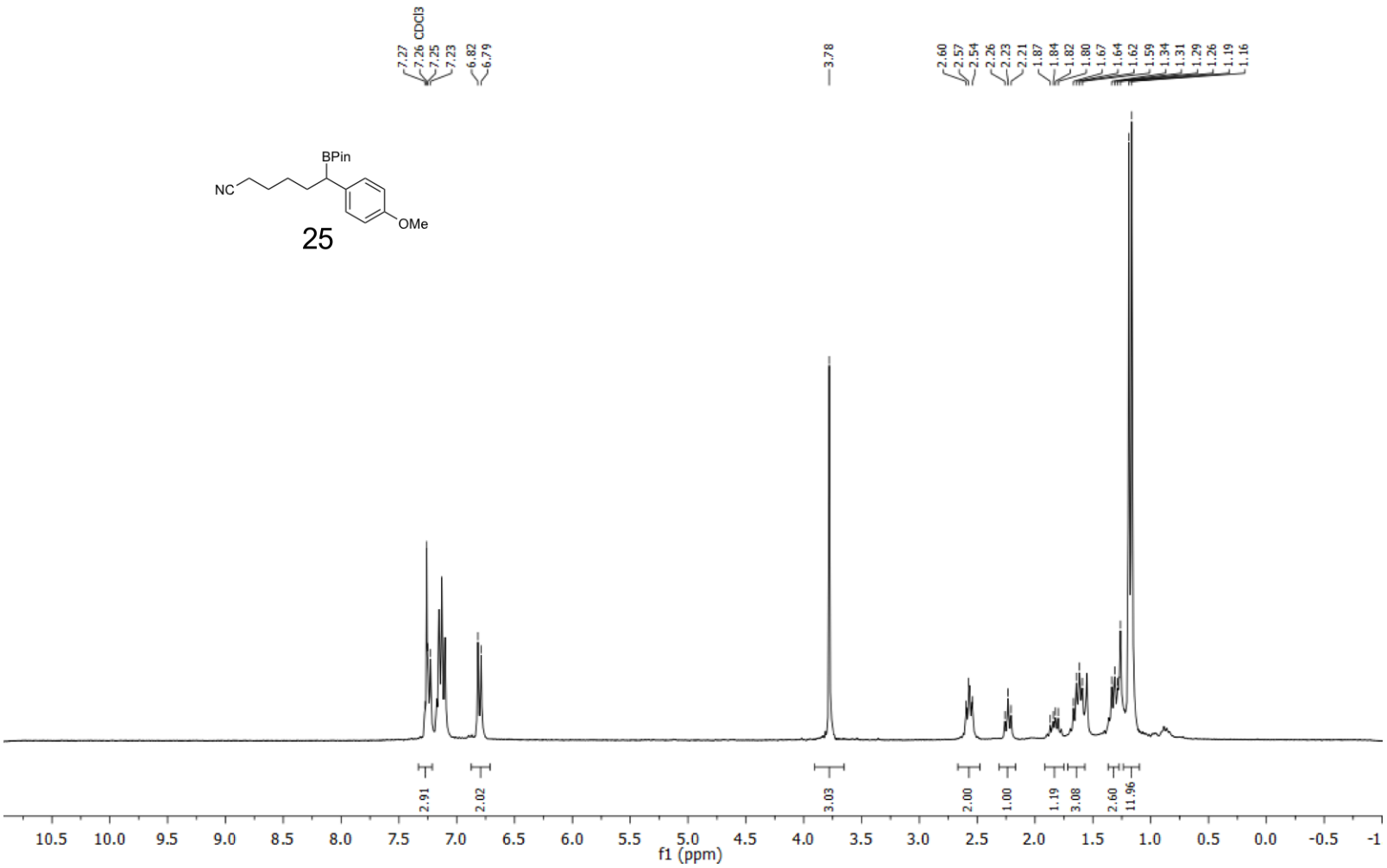


24

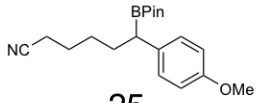
^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.5 , 145.1 , 142.8 , 137.2 , 128.4 , 128.2 , 125.6 , 121.2 , 108.9 , 108.2 , 100.6 , 83.4 , 35.9 . 32.8 . 31.5 , 28.8 , 25.5 , 24.7 , 24.6 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 3H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.68 – 2.43 (m, 2H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.94 – 1.71 (m, 1H), 1.71 – 1.58 (m, 3H), 1.38 – 1.24 (m, 2H), 1.18 (d, *J* = 7.3 Hz, 12H).

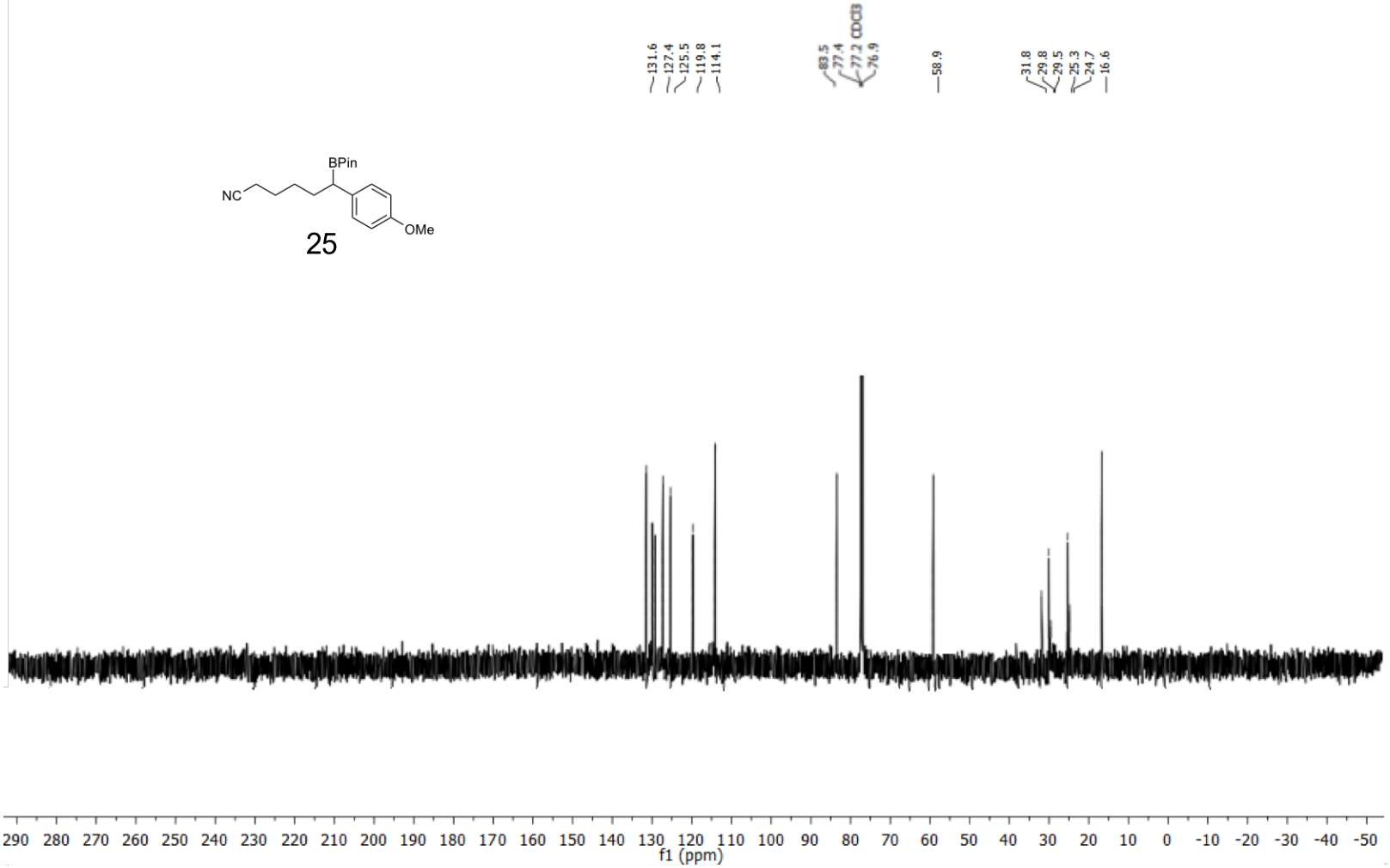


^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.2 .

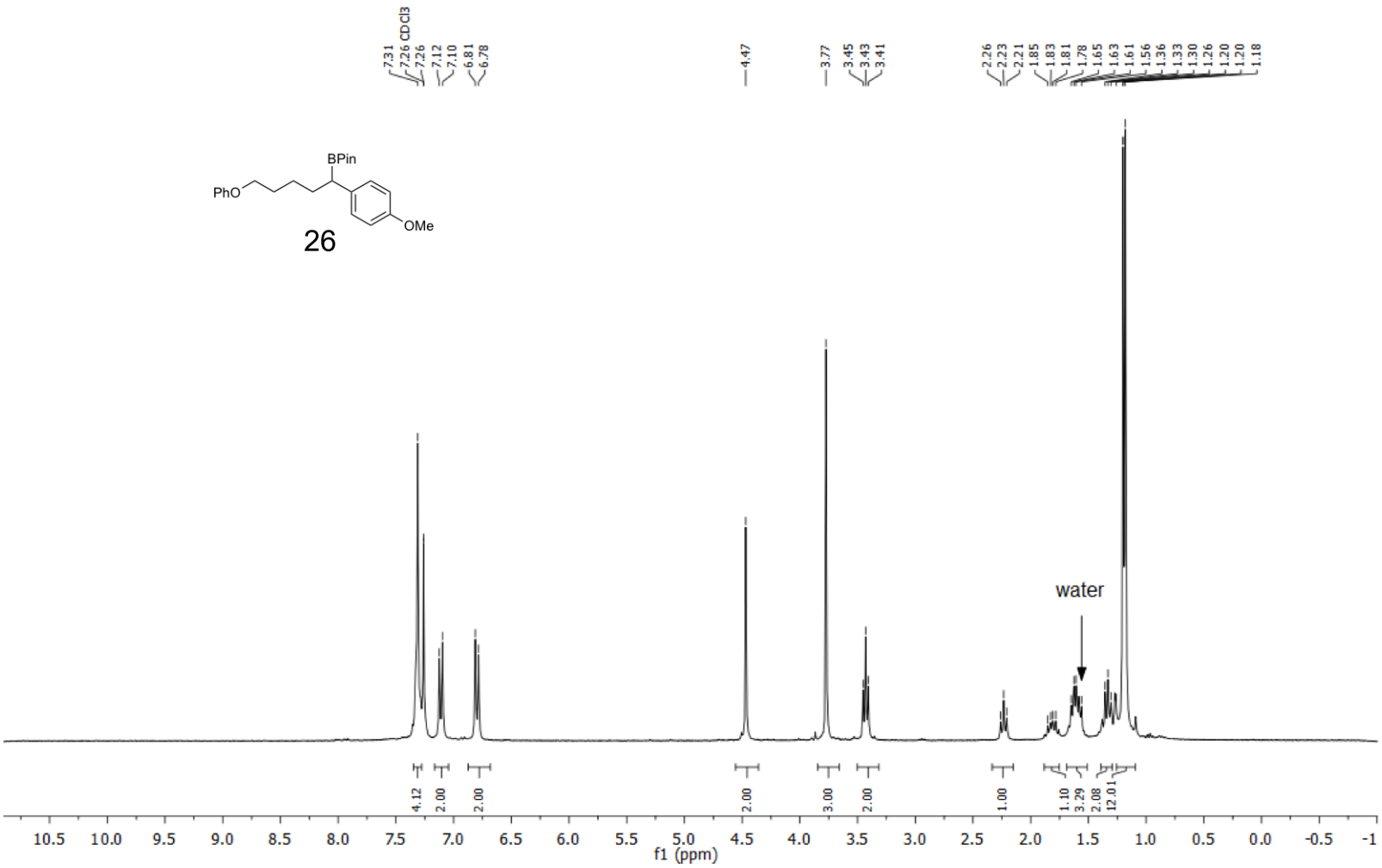


25

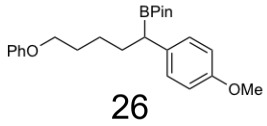
^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.57 , 127.35 , 125.48 , 119.75 , 114.13 , 83.51 , 58.93 , 31.79 , 29.83 , 29.50 , 25.27 , 24.73 , 16.55 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 (s, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.77 (s, 3H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 1H), 1.71 – 1.51 (m, 2H), 1.43 – 1.23 (m, 2H), 1.19 (d, *J* = 6.0 Hz, 13H).

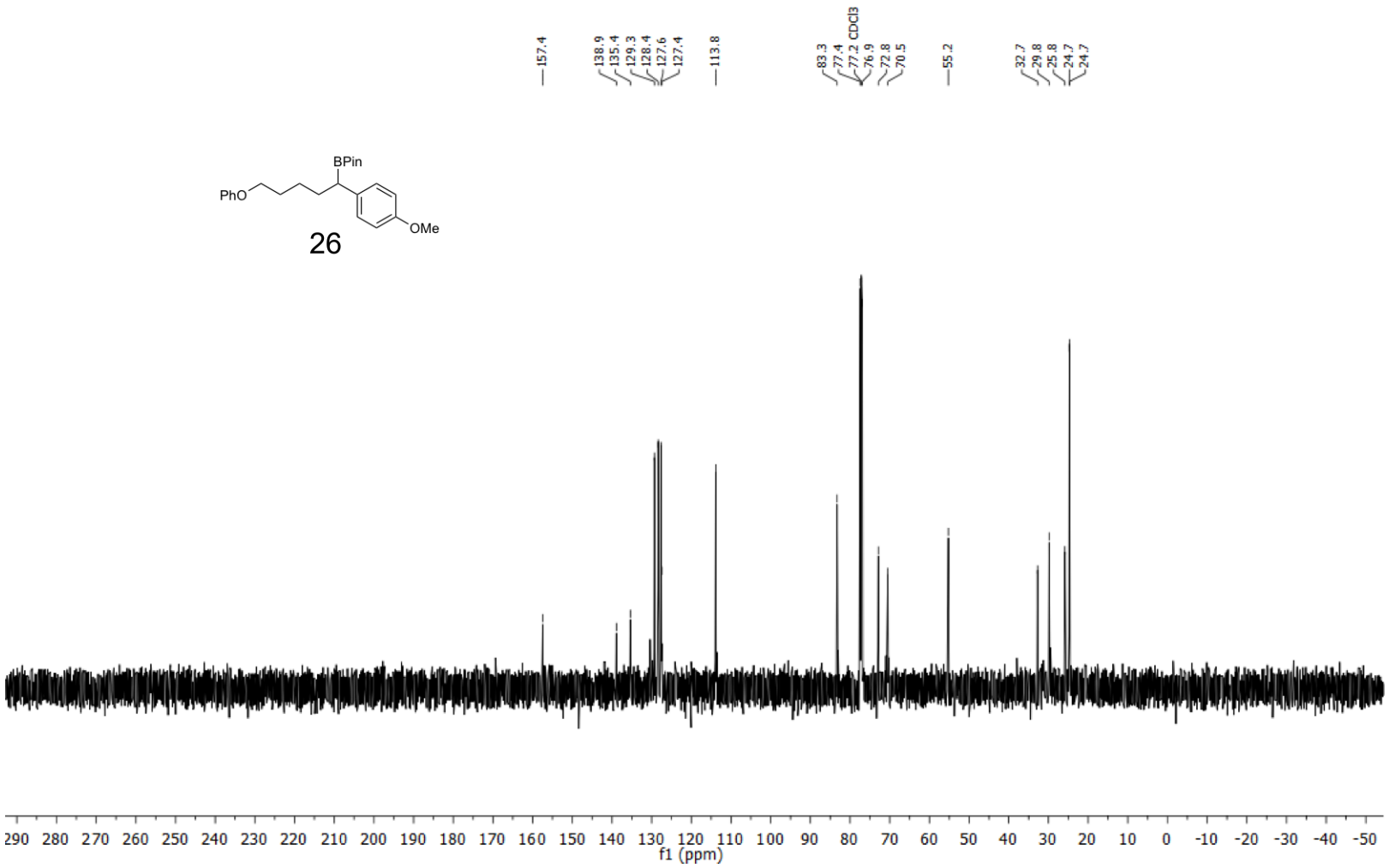


^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.9 .

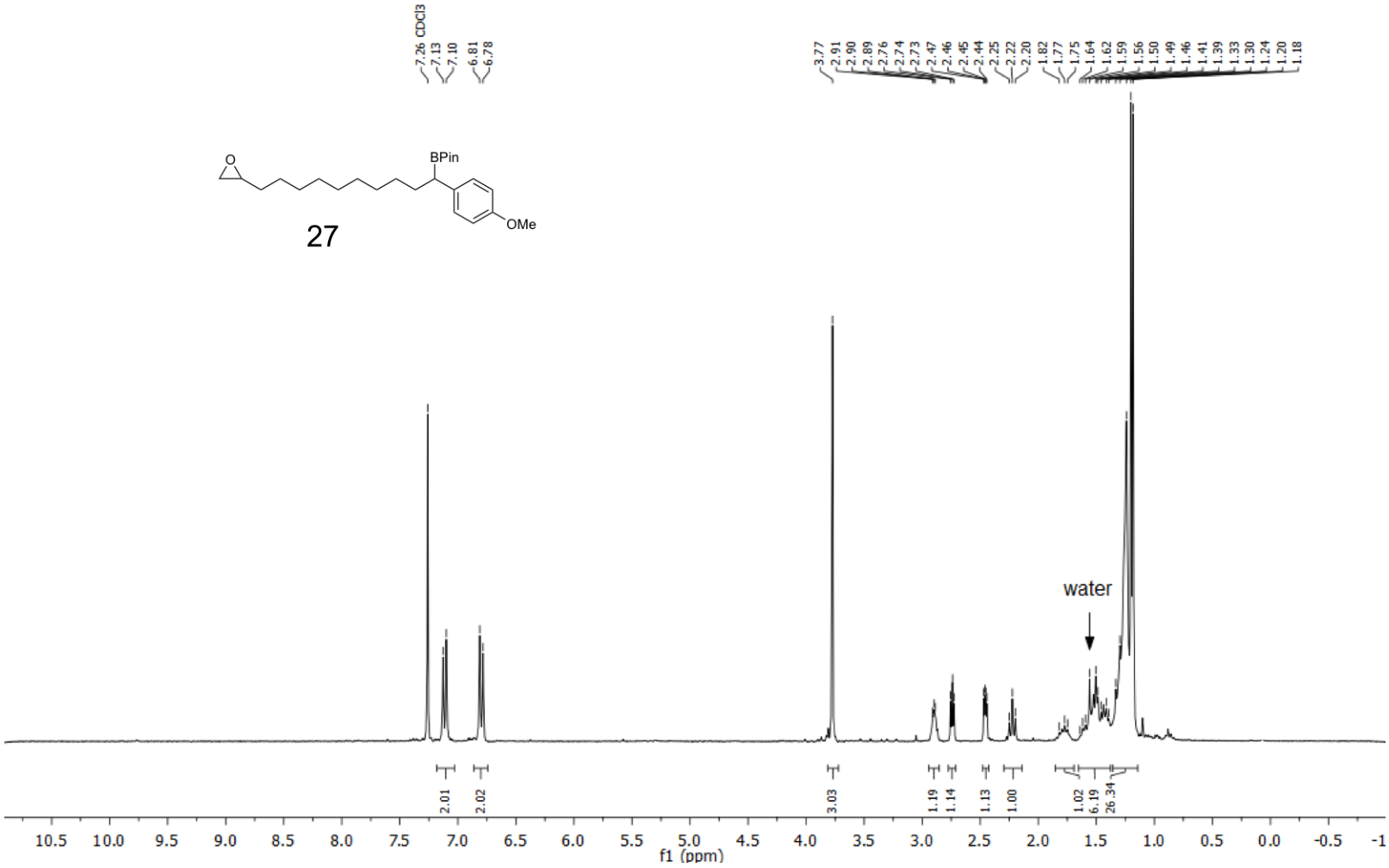


26

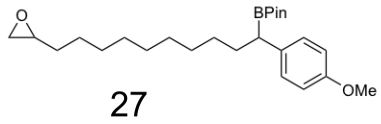
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4 , 138.9 , 135.4 , 129.3 , 128.4 , 127.6 , 127.4 , 113.8 , 83.3 , 72.8 , 70.5 , 55.2 , 32.7 , 29.8 , 25.8 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.94 – 2.84 (m, 1H), 2.79 – 2.69 (m, 1H), 2.46 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.89 – 1.69 (m, 1H), 1.67 – 1.36 (m, 6H), 1.37 – 1.13 (m, 26H).

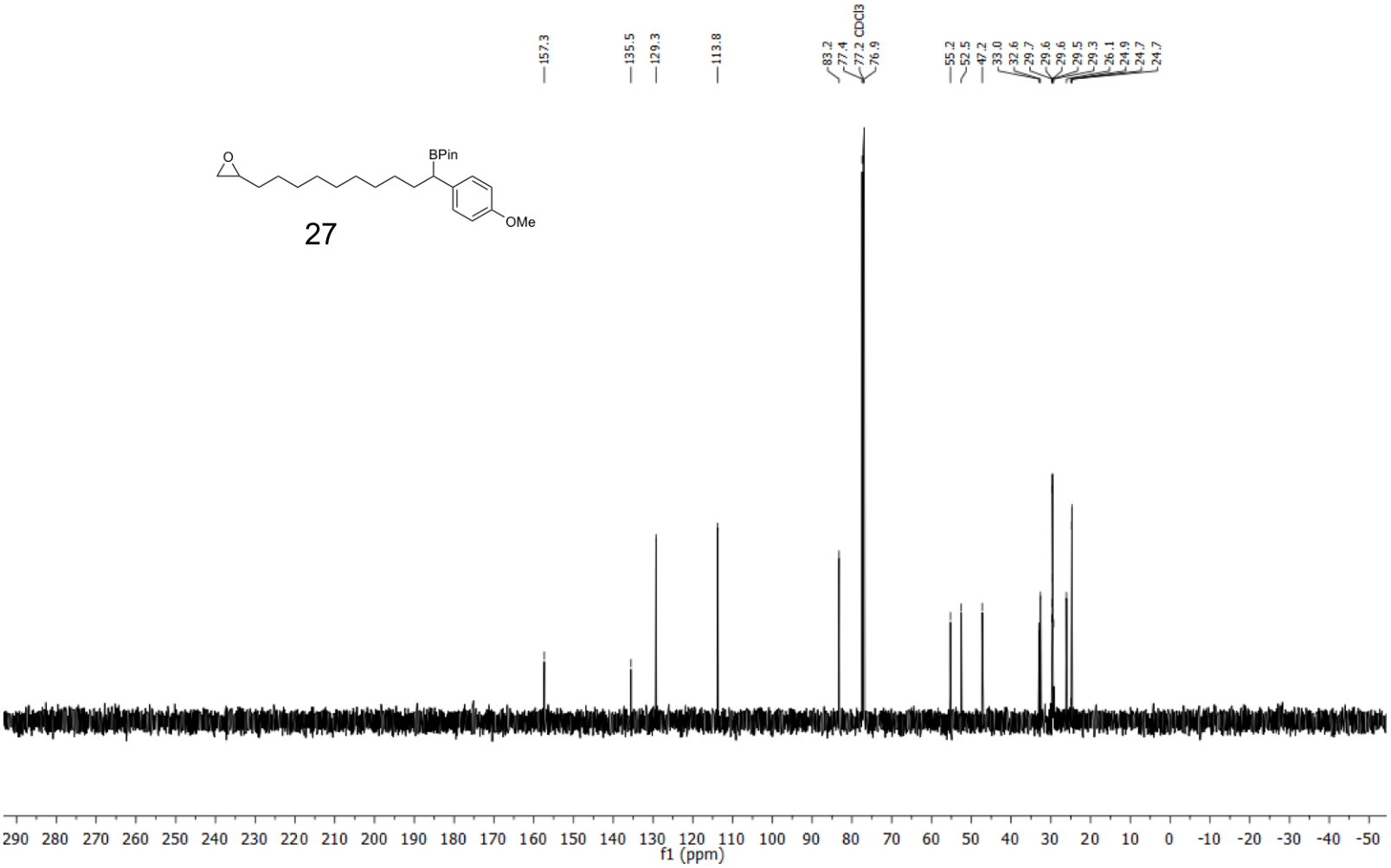


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.9 .

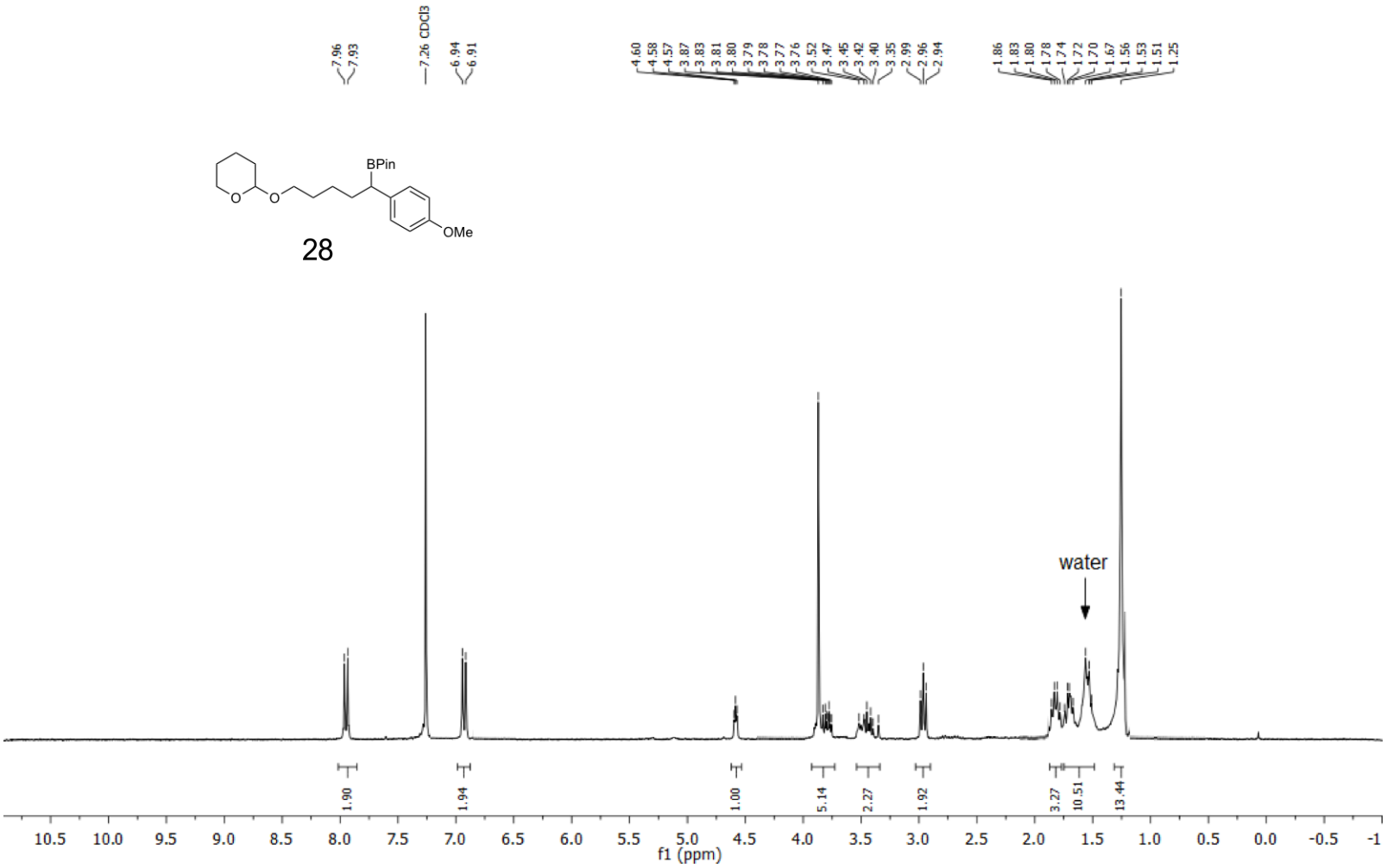


27

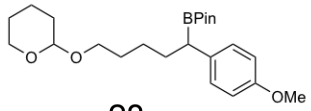
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.3 , 135.5 , 129.3 , 113.8 , 83.3 , 55.2 , 52.5 , 47.2 , 33.0 , 32.6 , 29.7 , 29.6 , 29.6 , 29.5 , 29.3 , 26.1 , 24.9 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.58 (t, *J* = 3.5 Hz, 1H), 3.94 – 3.71 (m, 5H), 3.57 – 3.32 (m, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.77 (m, 3H), 1.78 – 1.45 (m, 10H), 1.25 (s, 12H).

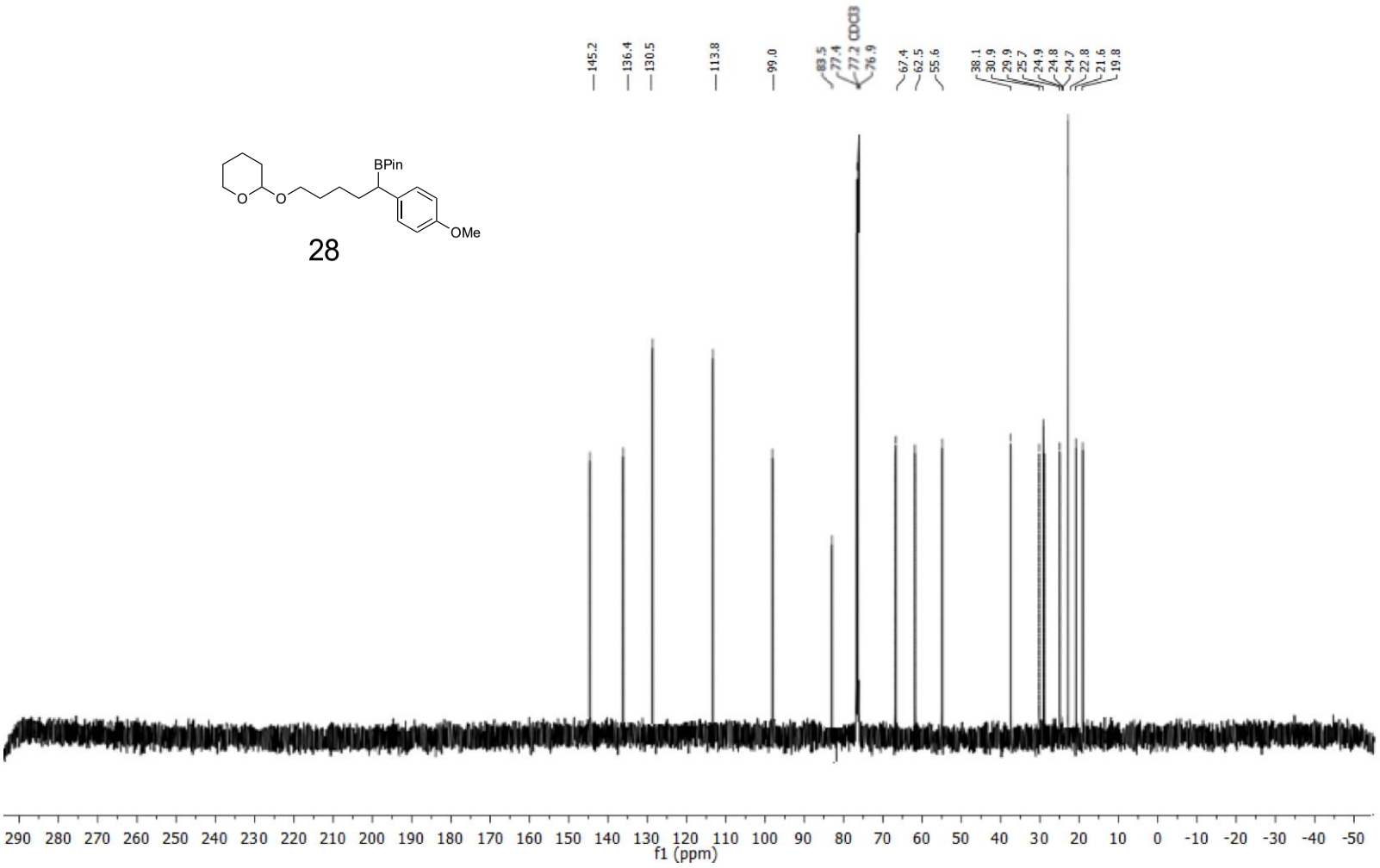


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.0 .

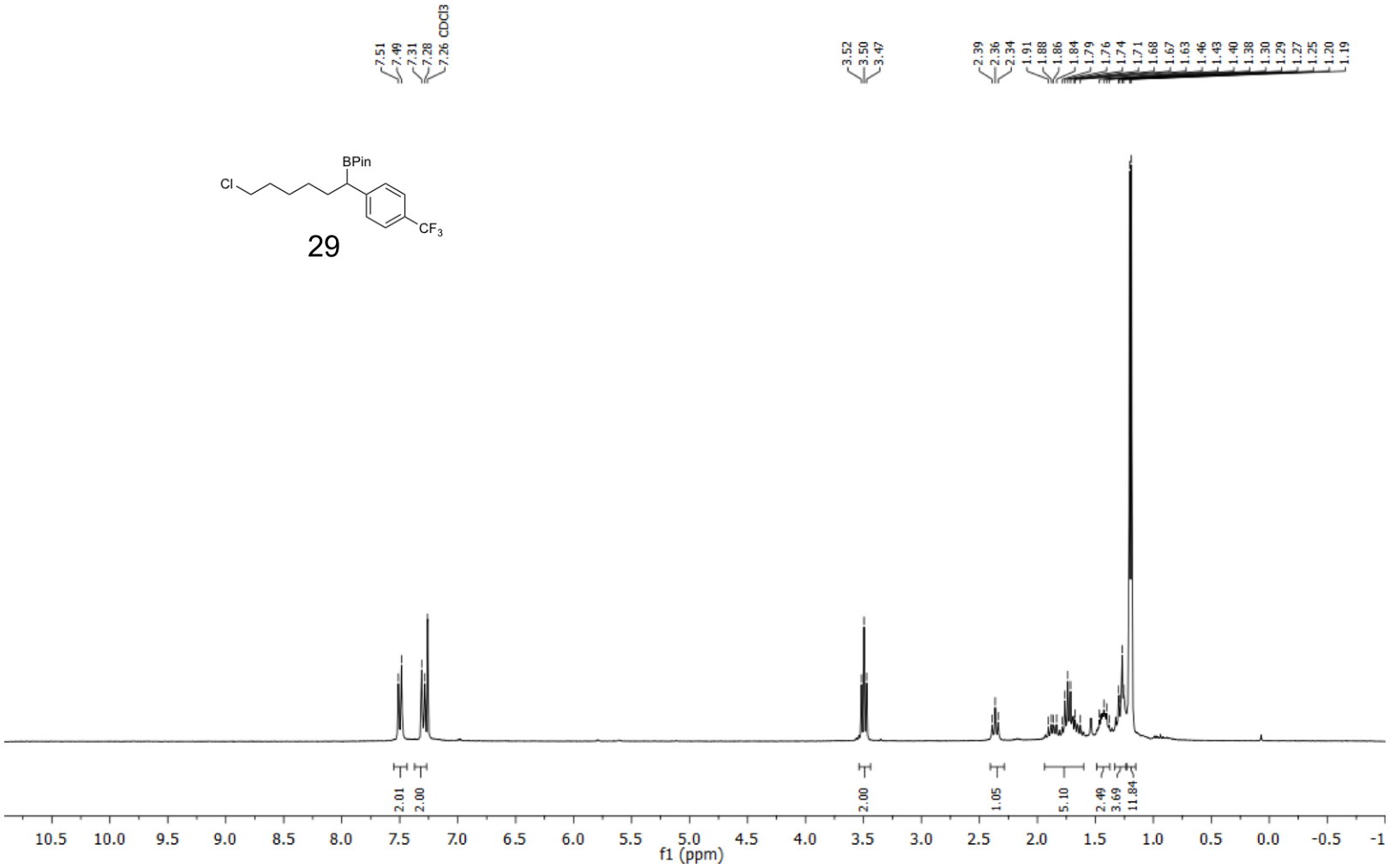


28

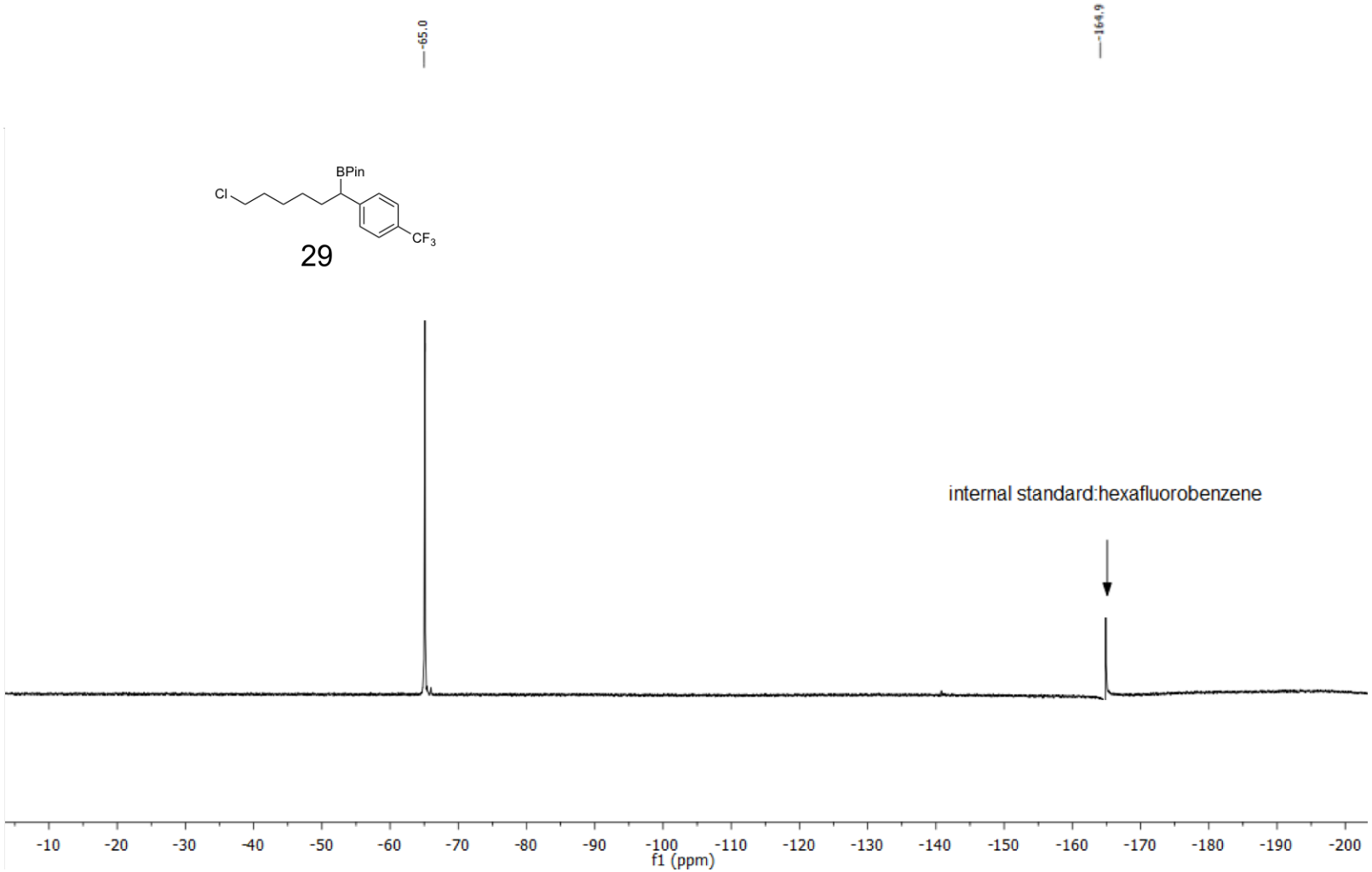
^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.2 , 136.4 , 130.5 , 113.8 , 99.0 , 83.5 , 67.4 , 62.5 , 55.6 , 38.1 , 30.9 , 29.9 , 25.7 , 24.9 , 24.8 , 24.7 , 22.8 , 21.6 , 19.8 .



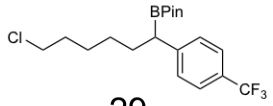
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.99 – 1.58 (m, 5H), 1.46 – 1.38 (m, 2H), 1.30 - 1.25 (m, 4H), 1.20 (d, *J* = 4.4 Hz, 11H).



^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.0 .

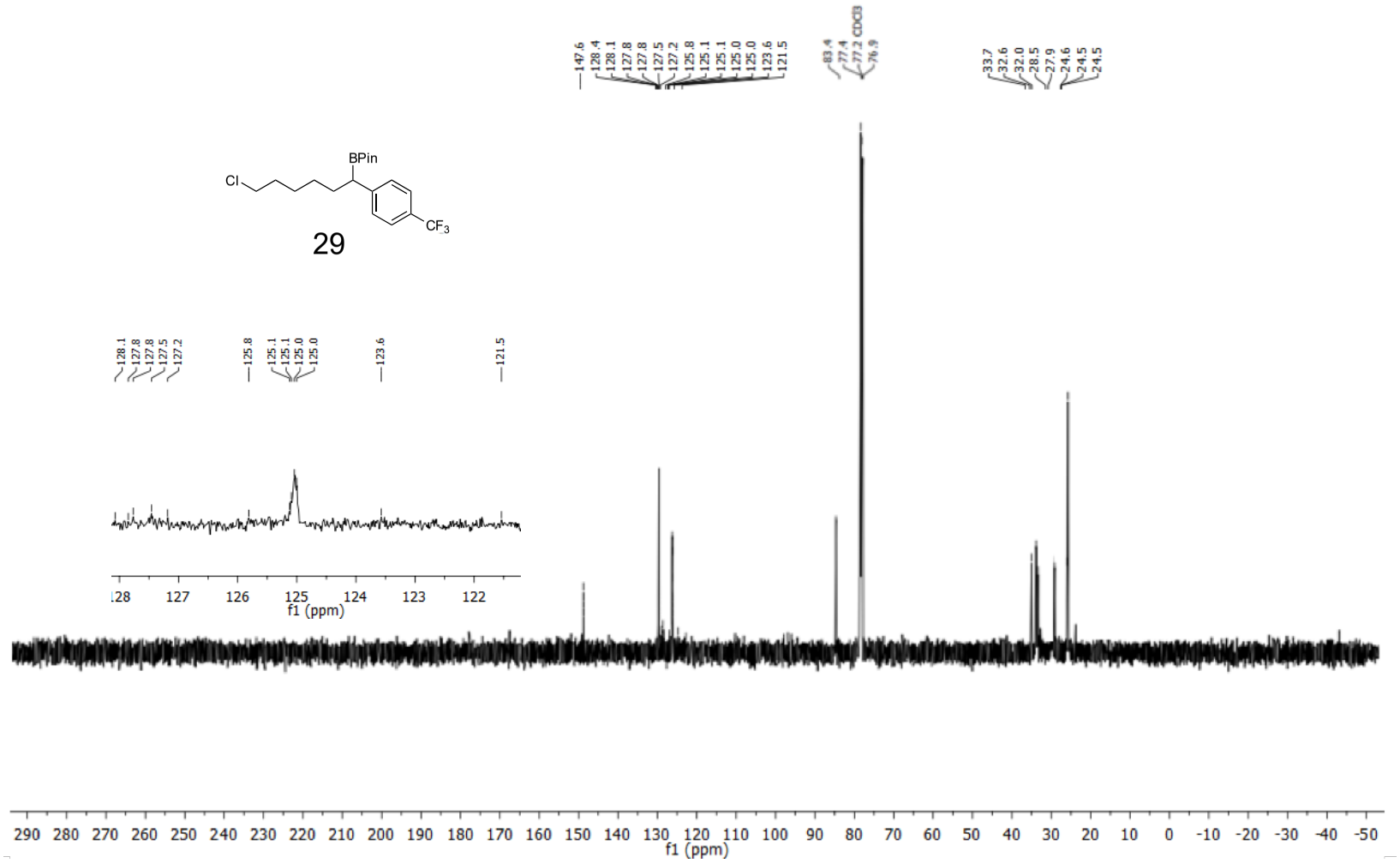


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.3 .

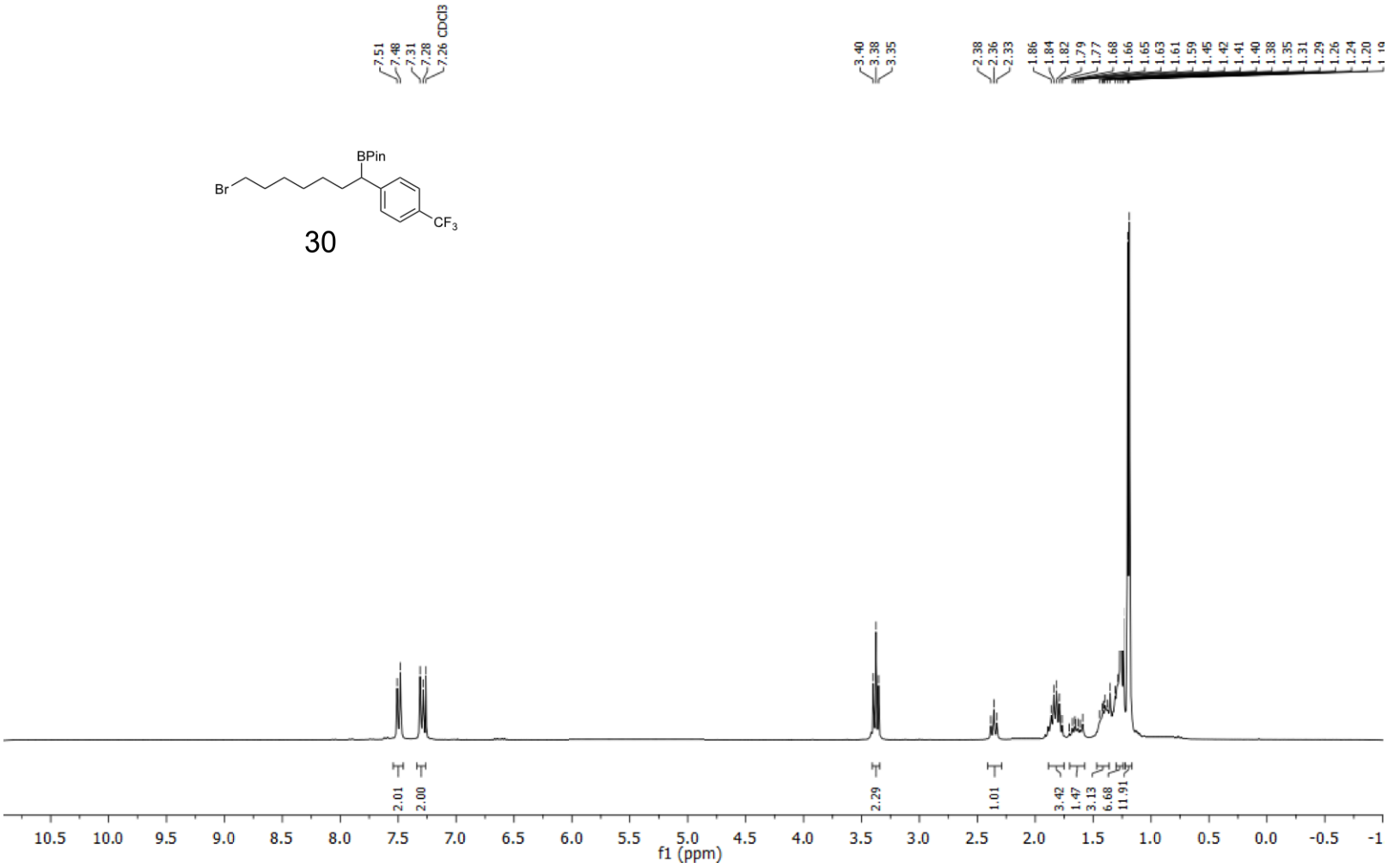


29

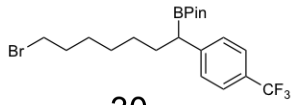
^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.6 , 128.4 , 127.6 (q, *J* = 34.7 Hz) , 125.1 (q, *J* = 5.5 Hz), 124.7 (q, *J* = 265.3 Hz), 83.4 , 33.7 , 32.6 , 32.0 , 28.5 , 27.9 , 24.6 , 24.5 , 24.5 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 6.9 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 3H), 1.74 – 1.54 (m, 1H), 1.49 – 1.35 (m, 2H), 1.35 – 1.20 (m, 6H), 1.19 (d, *J* = 4.3 Hz, 12H).

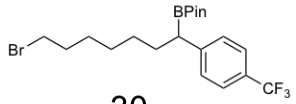


^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.1 .



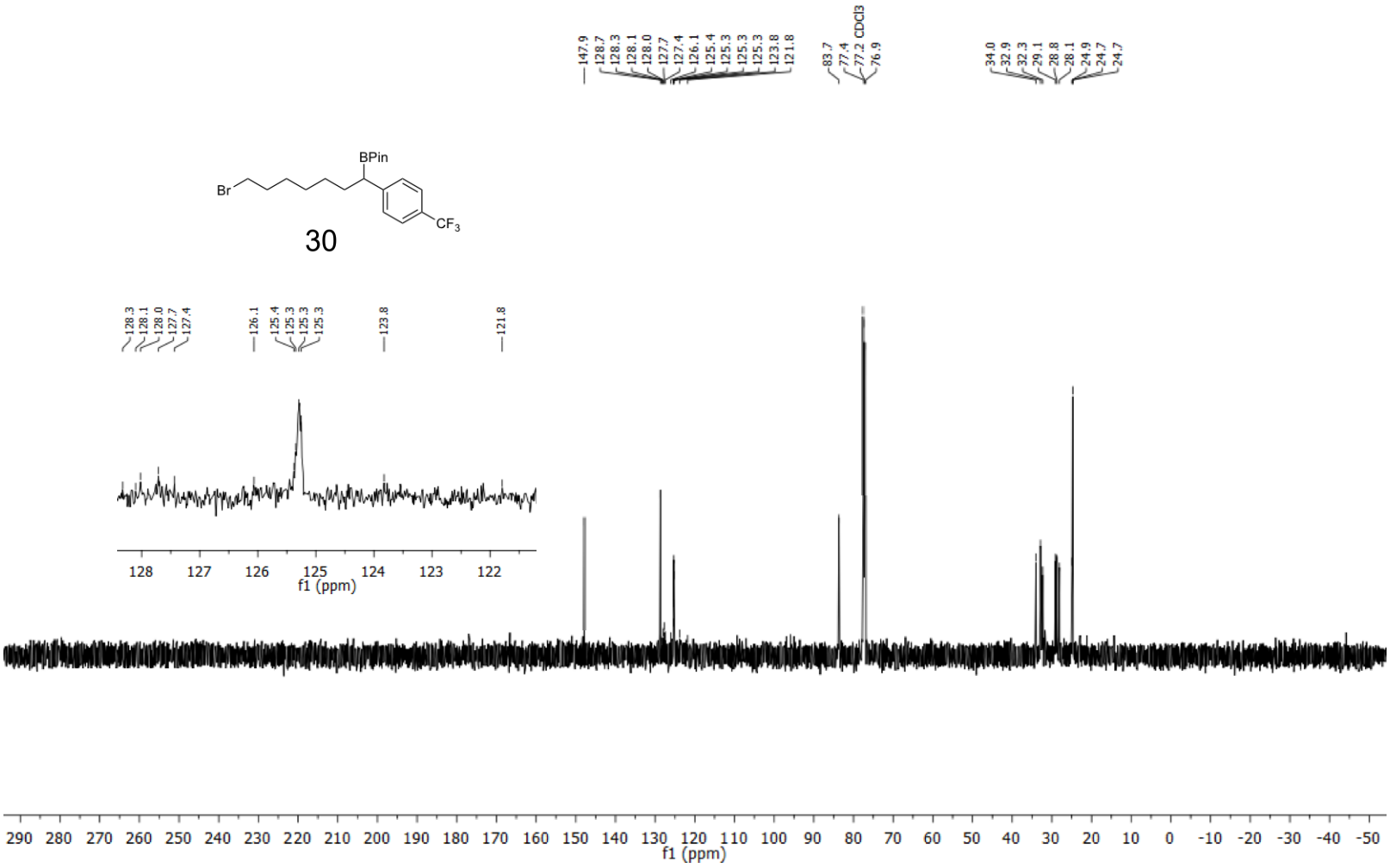
30

^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.6 .

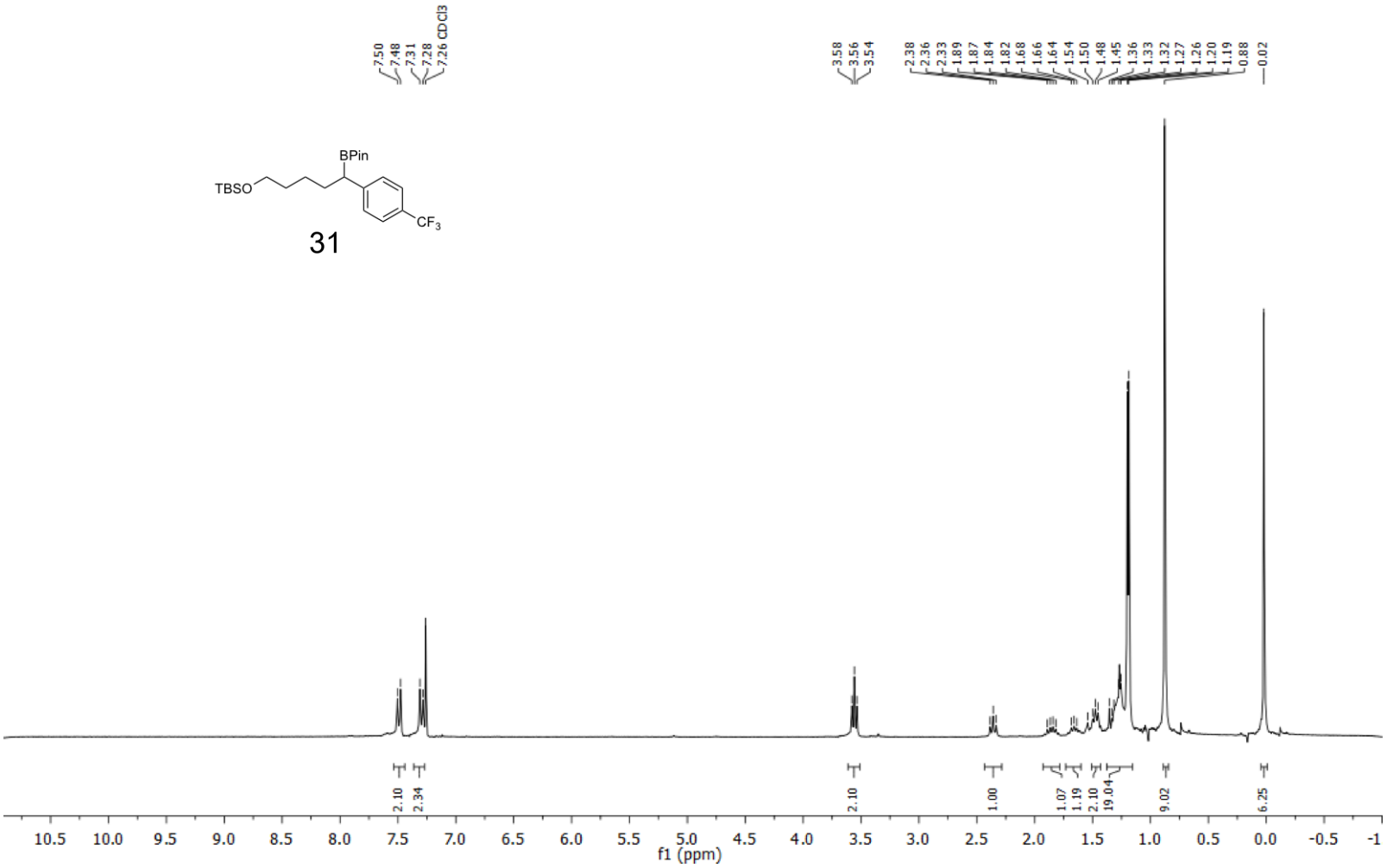


30

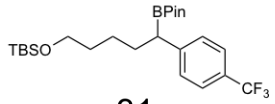
^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.9 , 128.7 , 127.9 (q, *J* = 34.7 Hz), 125.3 (q, *J* = 5.5 Hz), 124.9 (q, *J* = 265.3 Hz), 83.7 , 34.0 , 32.9 , 32.3 , 29.1 , 28.8 , 28.1 , 24.9 , 24.7 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 1H), 1.98 – 1.77 (m, 1H), 1.74 – 1.59 (m, 1H), 1.59 – 1.42 (m, 2H), 1.41 – 1.13 (m, 19H), 0.88 (s, 9H), 0.02 (s, 6H).

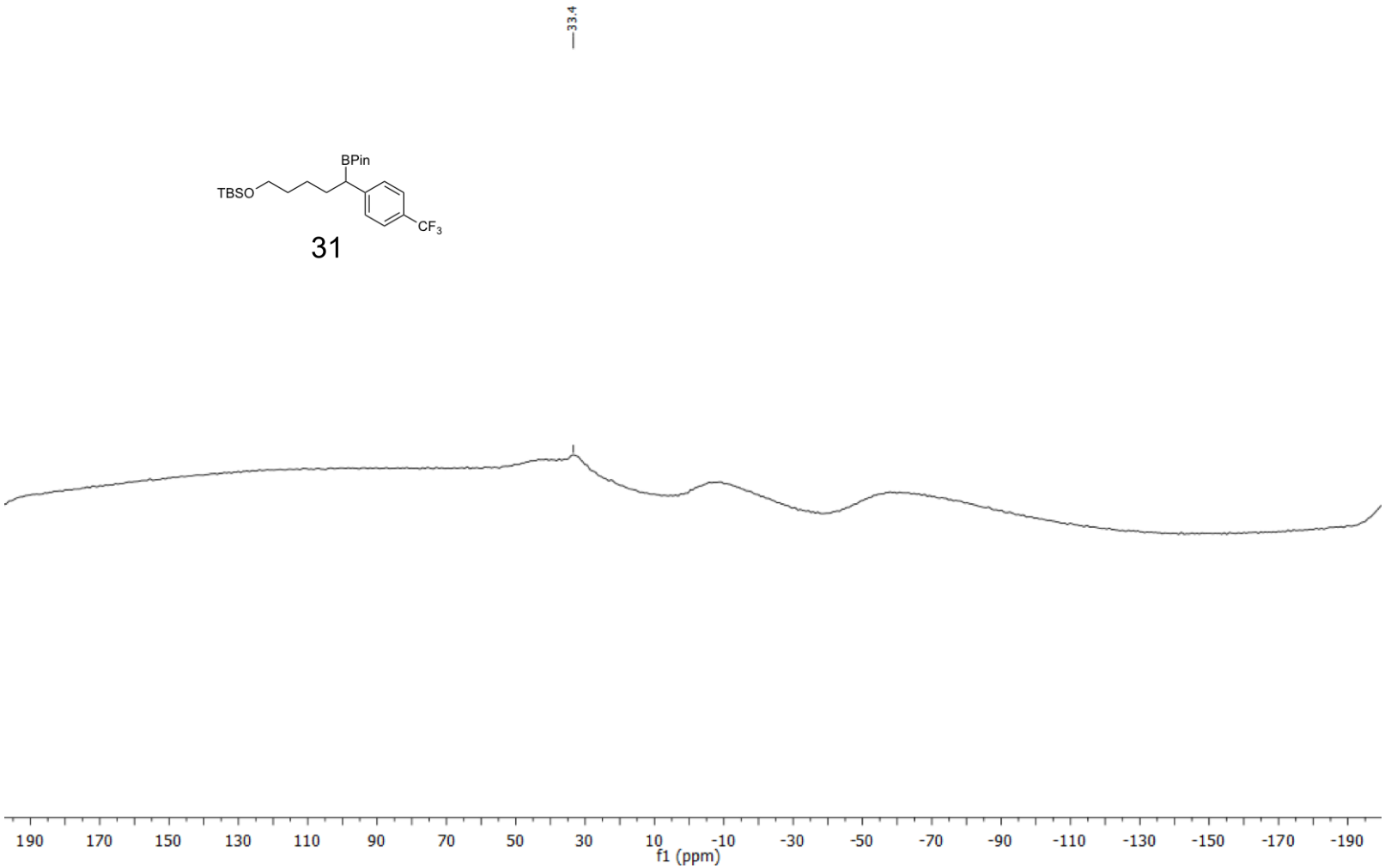


^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.1 .

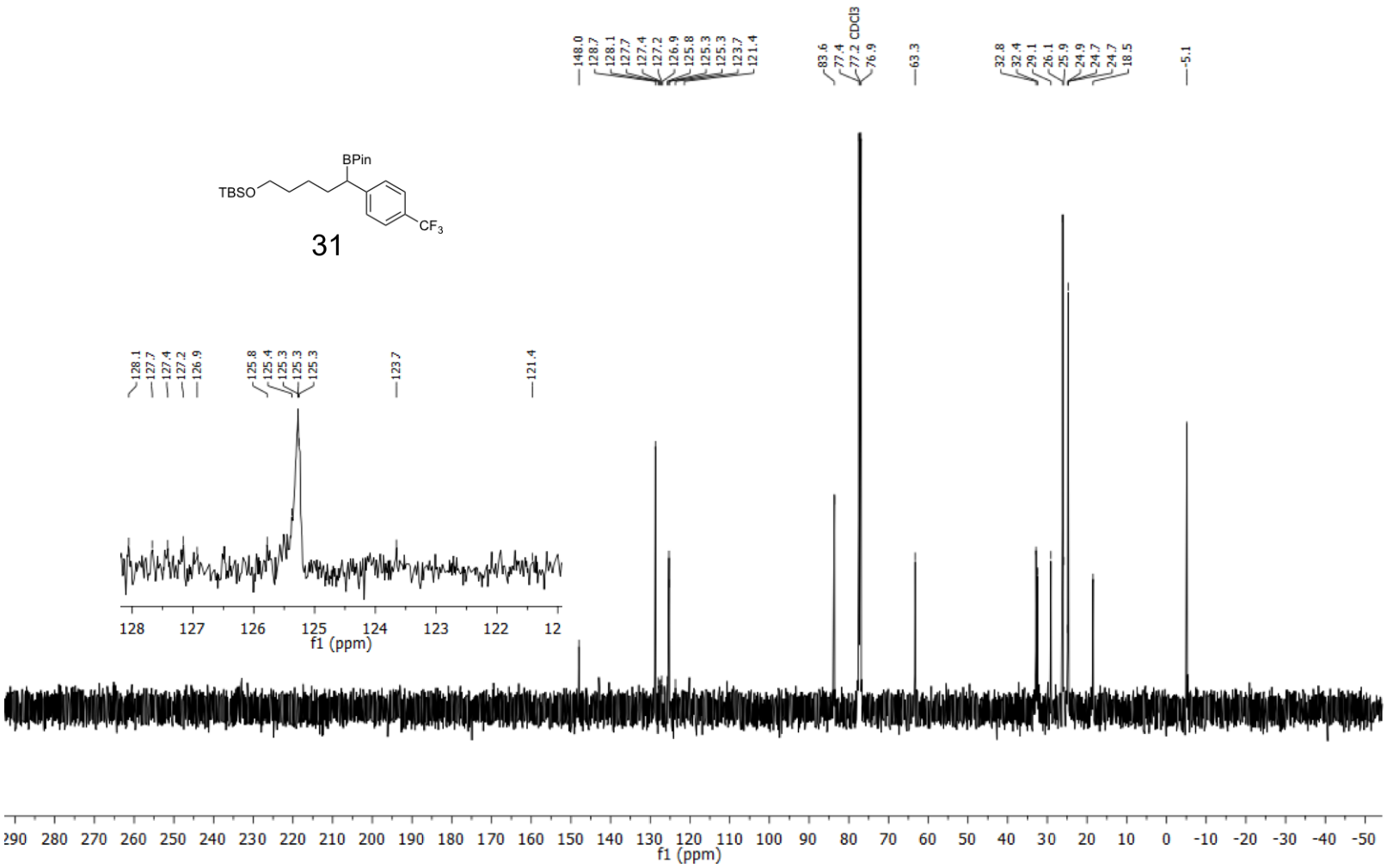


31

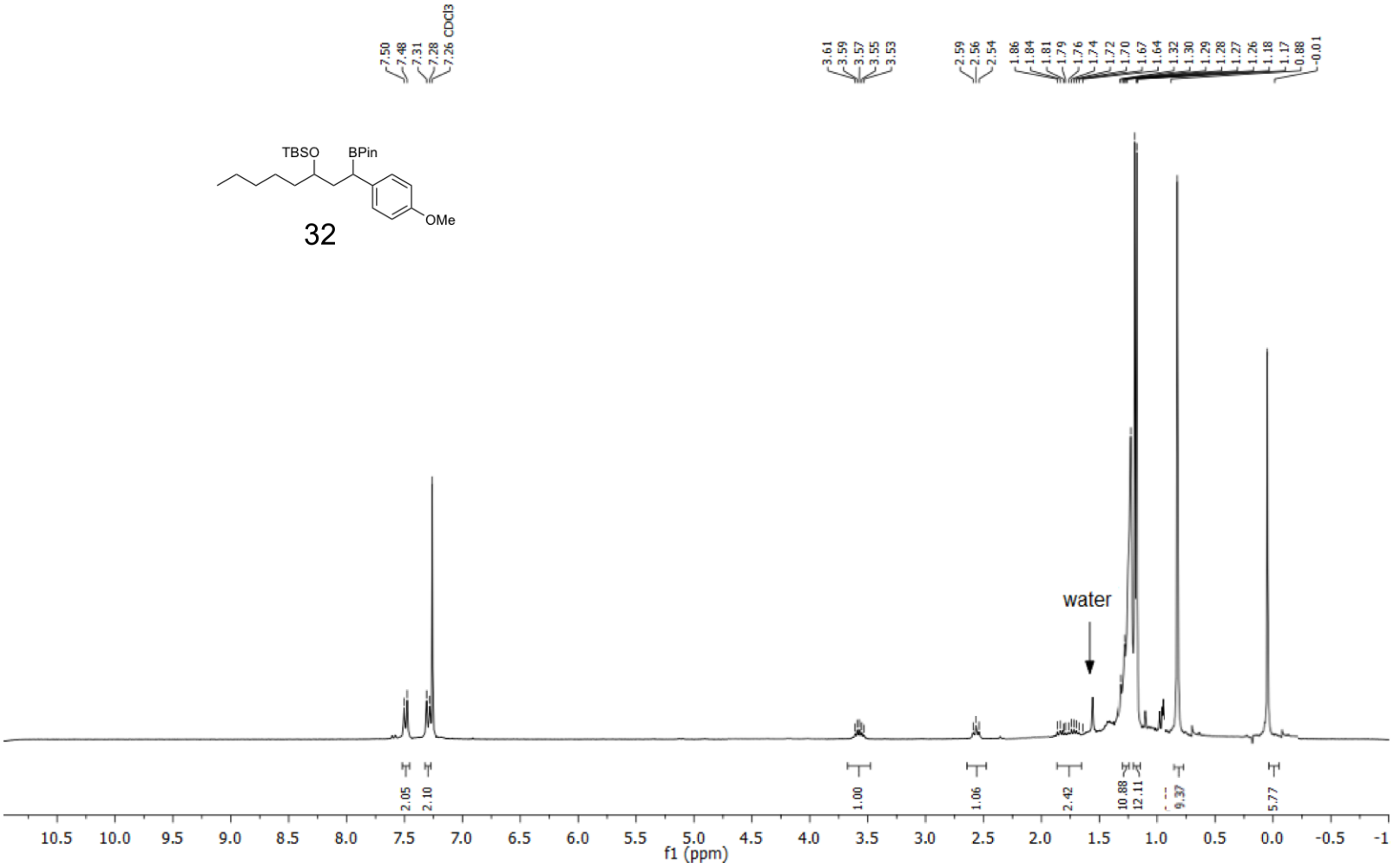
^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.4 .



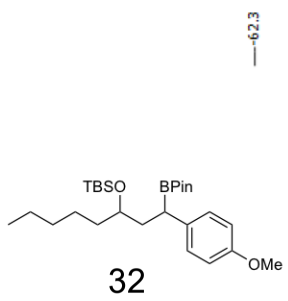
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.0 , 128.7 , 127.3 (q, *J* = 31.1 Hz), 125.3 (q, *J* = 2.5 Hz), 124.7 (q, *J* = 279.3 Hz), 83.6 , 63.3 , 32.8 , 32.4 , 29.1 , 26.1 , 25.9 , 24.9 , 24.7 , 24.7 , 18.5 , -5.1 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.57 (dt, *J* = 12.1, 5.9 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 1H), 1.93 – 1.64 (m, 2H), 1.32 - 1.26 (m, 11H), 1.17 (d, *J* = 3.2 Hz, 12H), 0.88 (s, 9H), -0.01 (s, 6H).

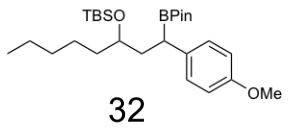


^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.3 .



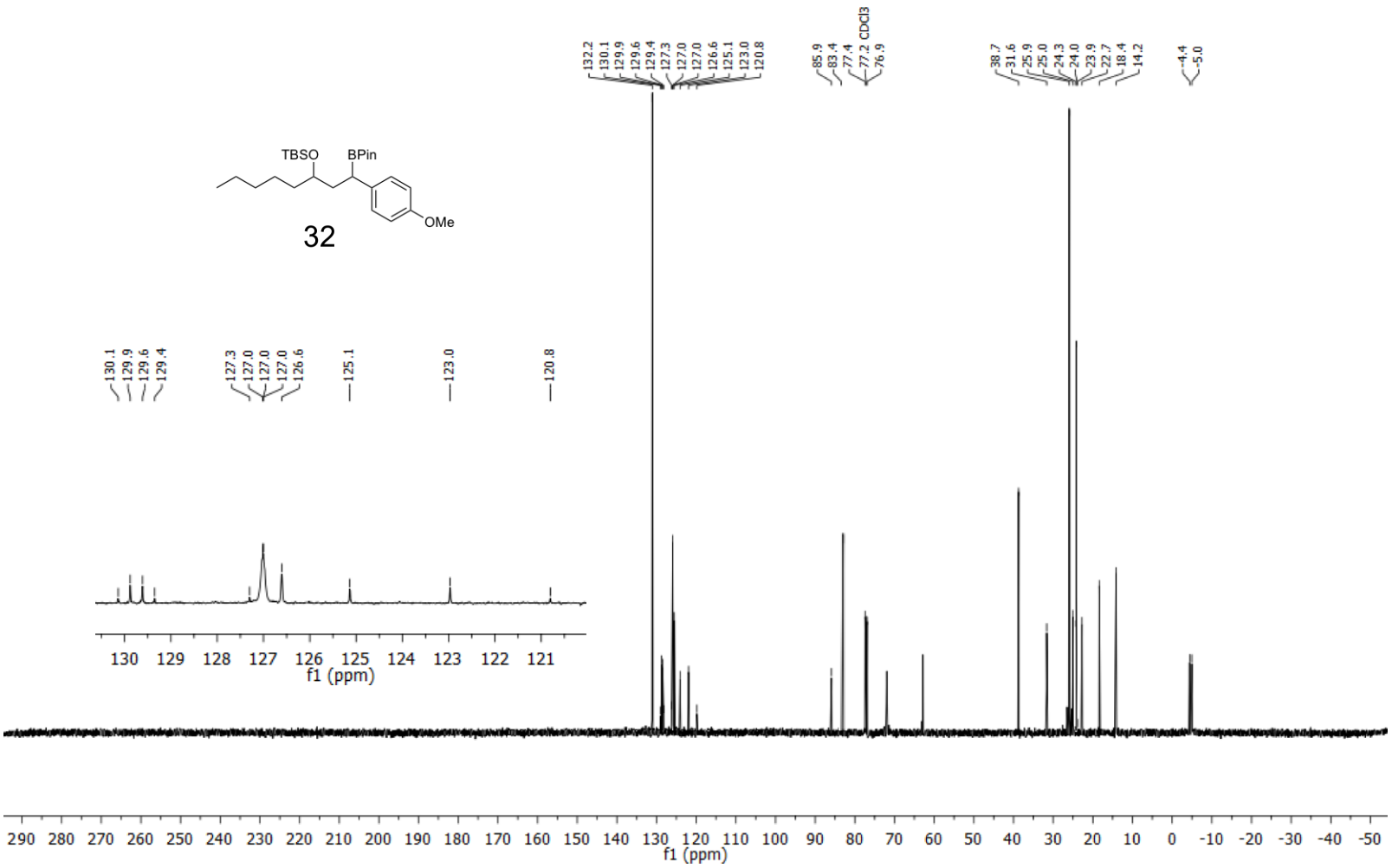
32

^{11}B NMR (96 MHz, Chloroform-*d*) δ 33.3 .

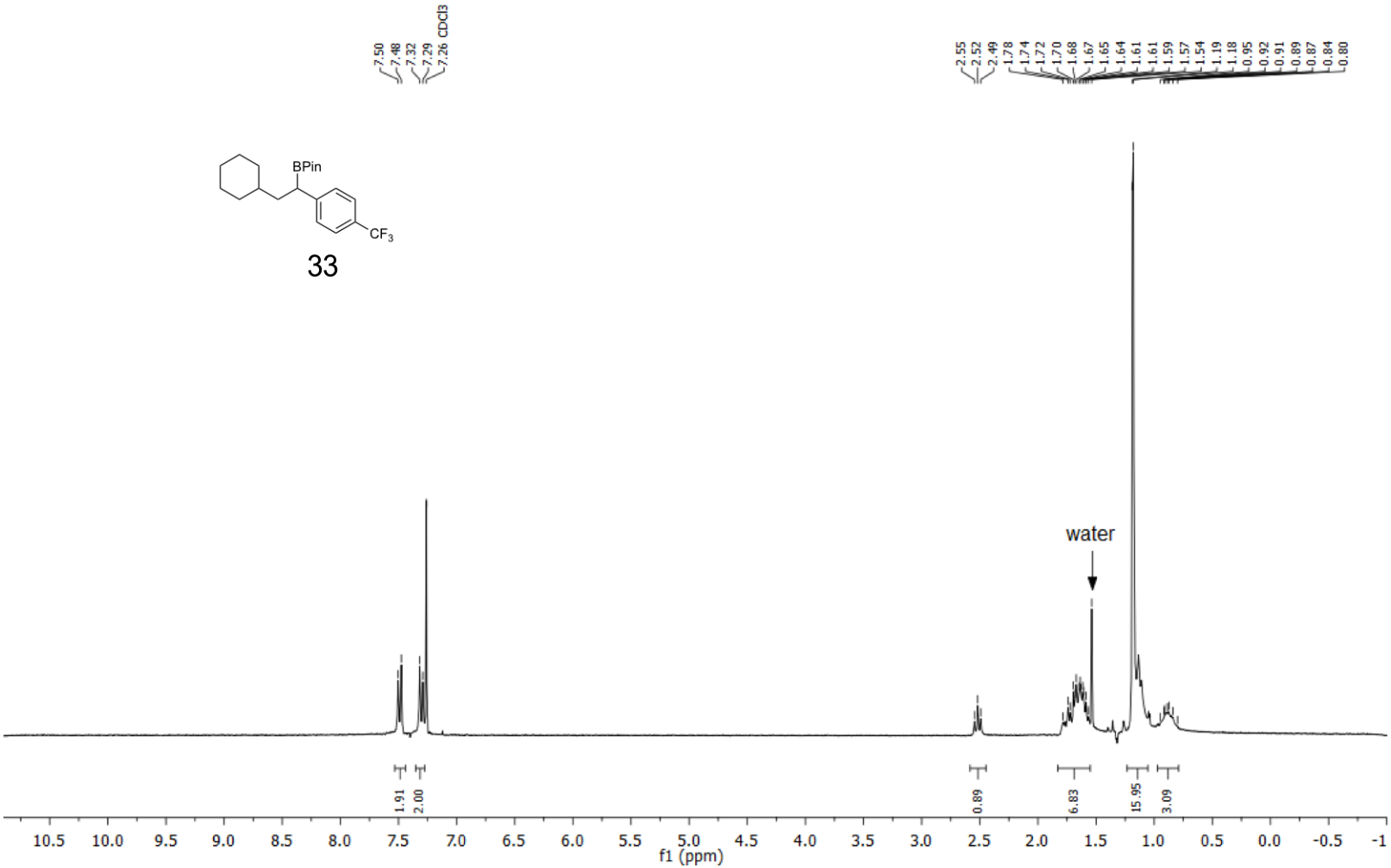


32

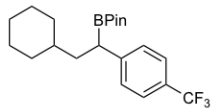
^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.2 , 129.8 (q, *J* = 32.7 Hz), 127.0 (q, *J* = 3.4 Hz), 126.6 , 125.1 (q, *J* = 272.2 Hz), 85.9 , 83.4 , 38.7 , 31.6 , 25.9 , 25.0 , 24.3 , 24.0 , 23.9 , 22.7 , 18.4 , 14.2 , -4.4 , -5.0 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.1 Hz, 1H), 1.86 – 1.57 (m, 7H), 1.18 (d, *J* = 2.8 Hz, 16H), 0.99 – 0.76 (m, 3H).

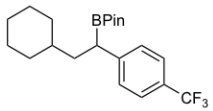


^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.2 .



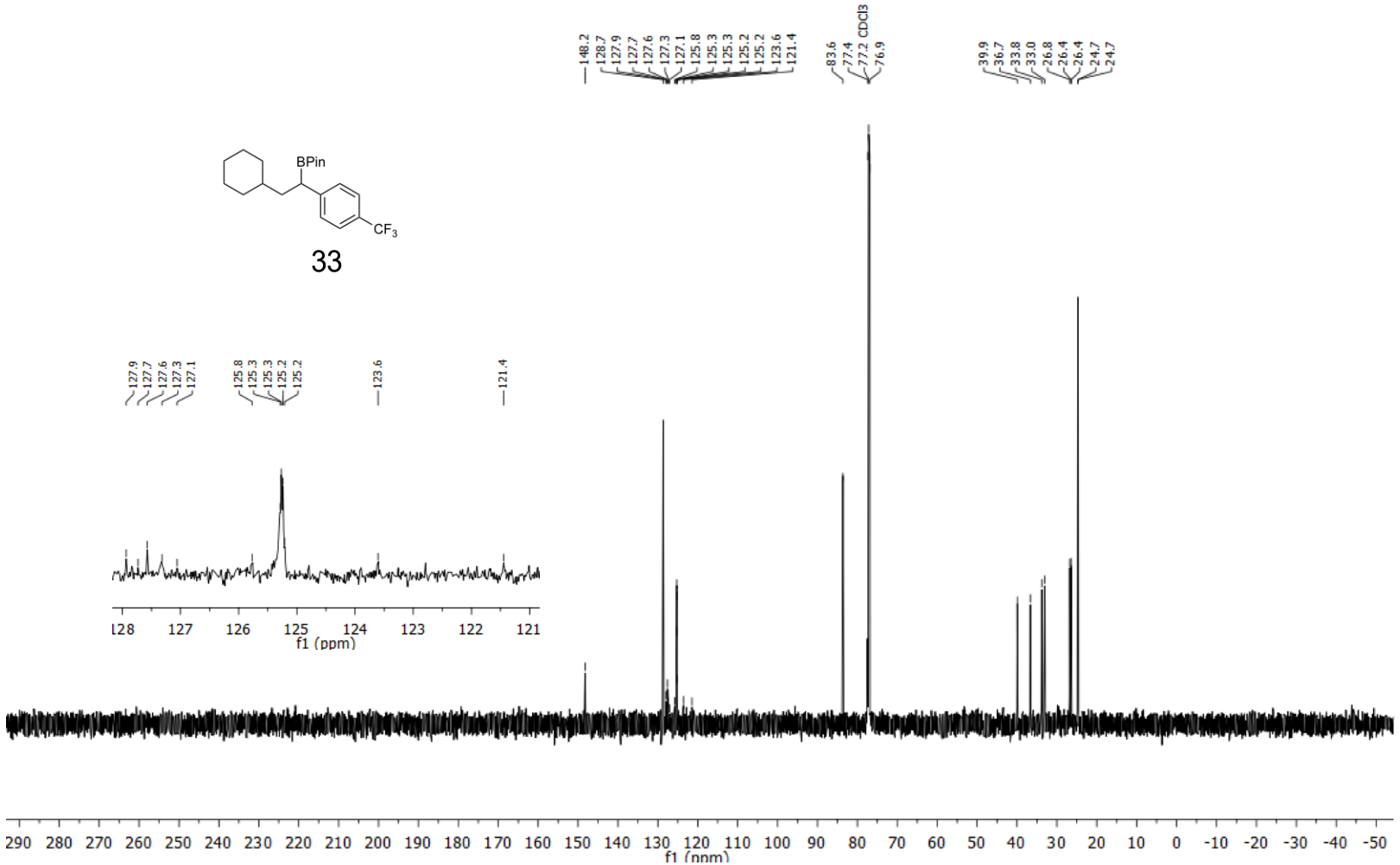
33

^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5 .

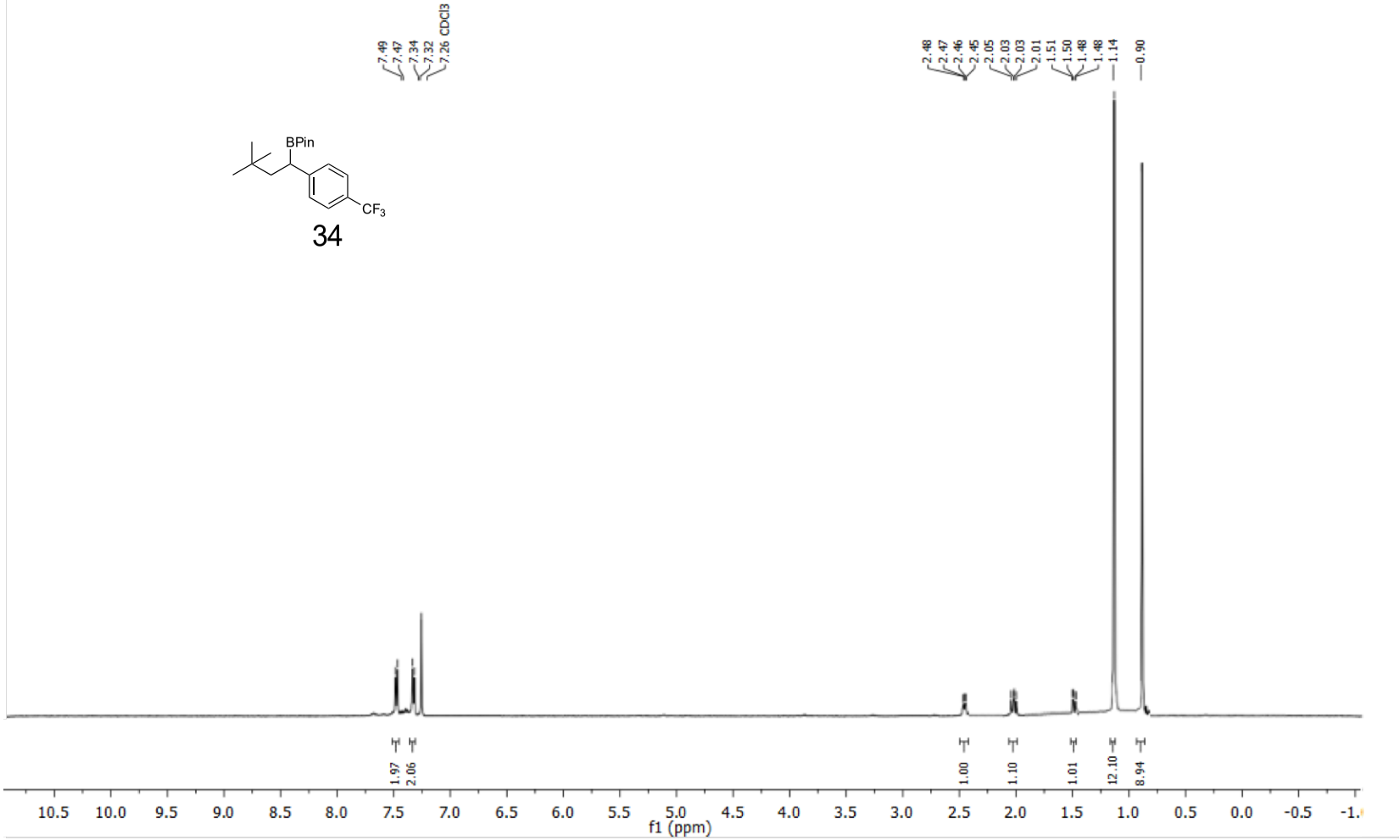


33

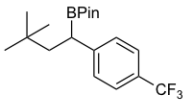
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.2 , 128.7 , 127.5 (q, *J* = 32.7 Hz), 125.3 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 277.2, Hz), 83.6 , 39.9 , 36.7 , 33.8 , 33.0 , 26.8 , 26.4 , 26.4 , 24.7 , 24.7



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.46 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.03 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.49 (dd, *J* = 13.3, 4.0 Hz, 1H), 1.14 (s, 12H), 0.90 (s, 9H).

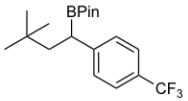


^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.1 .



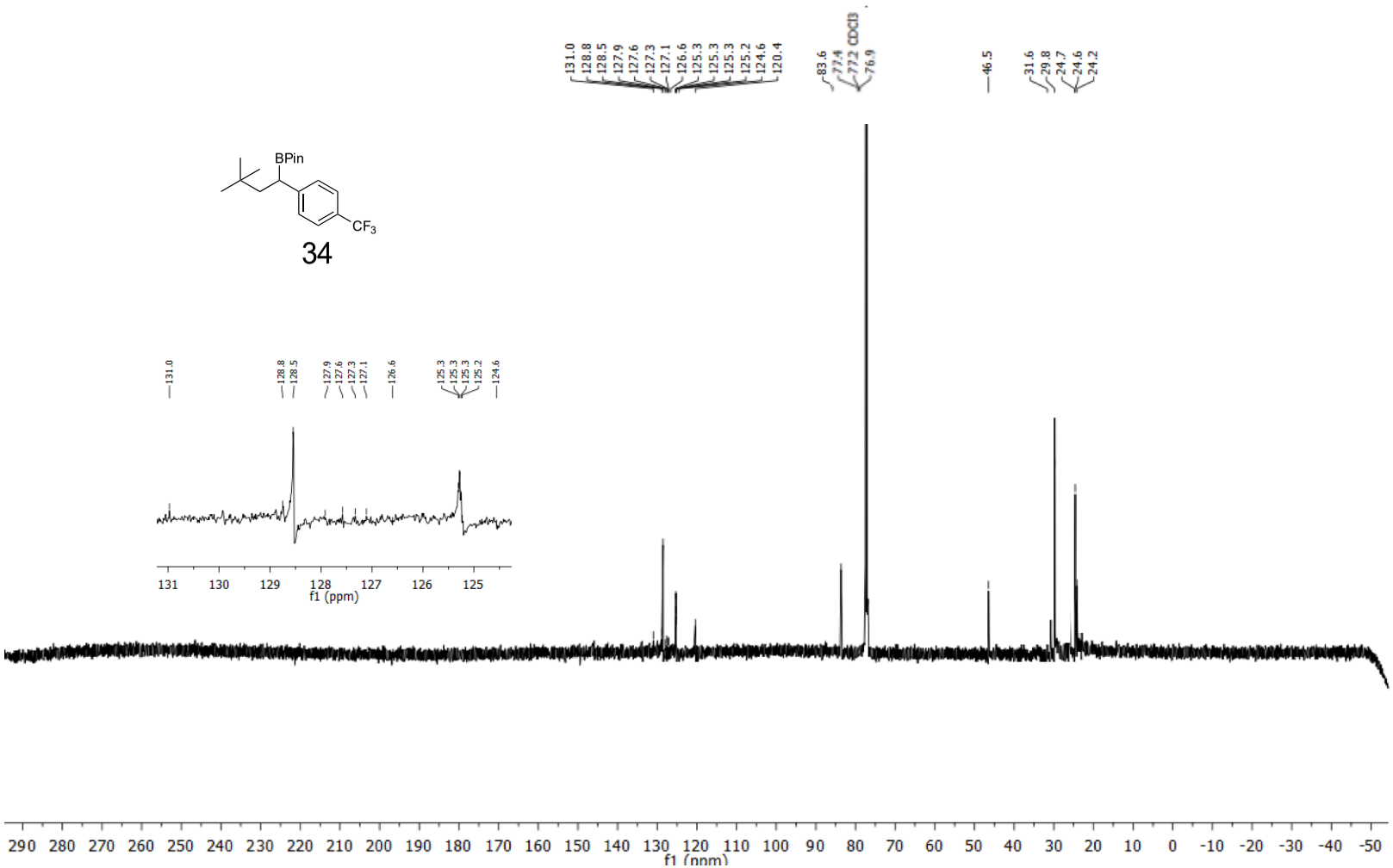
34

^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 .

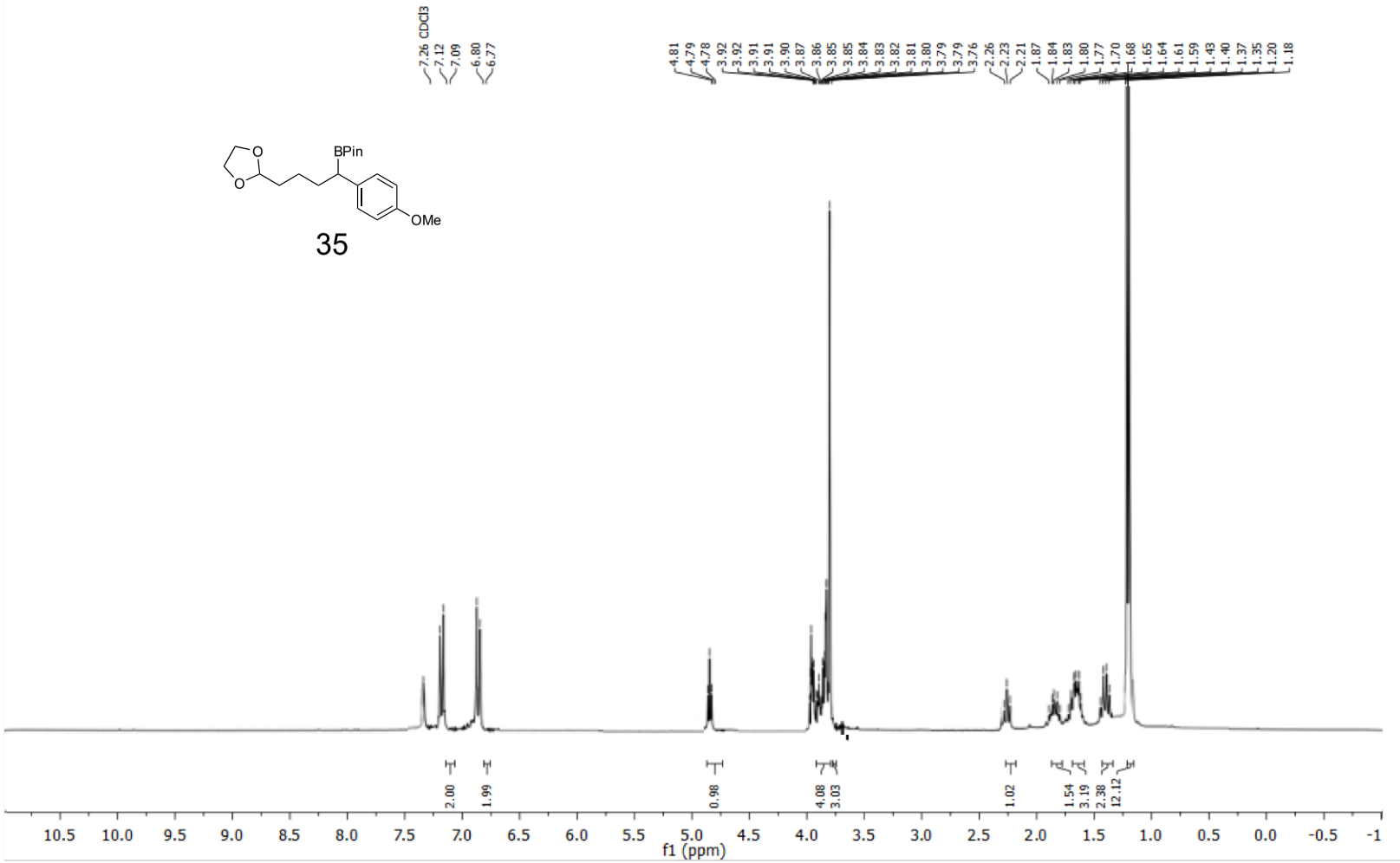


34

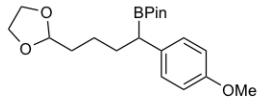
^{13}C NMR (126 MHz, Chloroform-*d*) δ 128.5, 127.7 (q, *J* = 266.7 Hz), 127.5 (q, *J* = 34.0 Hz), 125.3 (q, *J* = 3.4 Hz), 120.4 , 83.6 , 46.5 , 31.6 , 29.8 , 24.7 , 24.6 , 24.2 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.79 (t, *J* = 4.9 Hz, 1H), 3.92 – 3.79 (m, 4H), 3.76 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.83 (m, 1H), 1.70 – 1.59 (m, 3H), 1.39 (q, *J* = 7.7 Hz, 2H), 1.19 (d, *J* = 5.9 Hz, 12H).

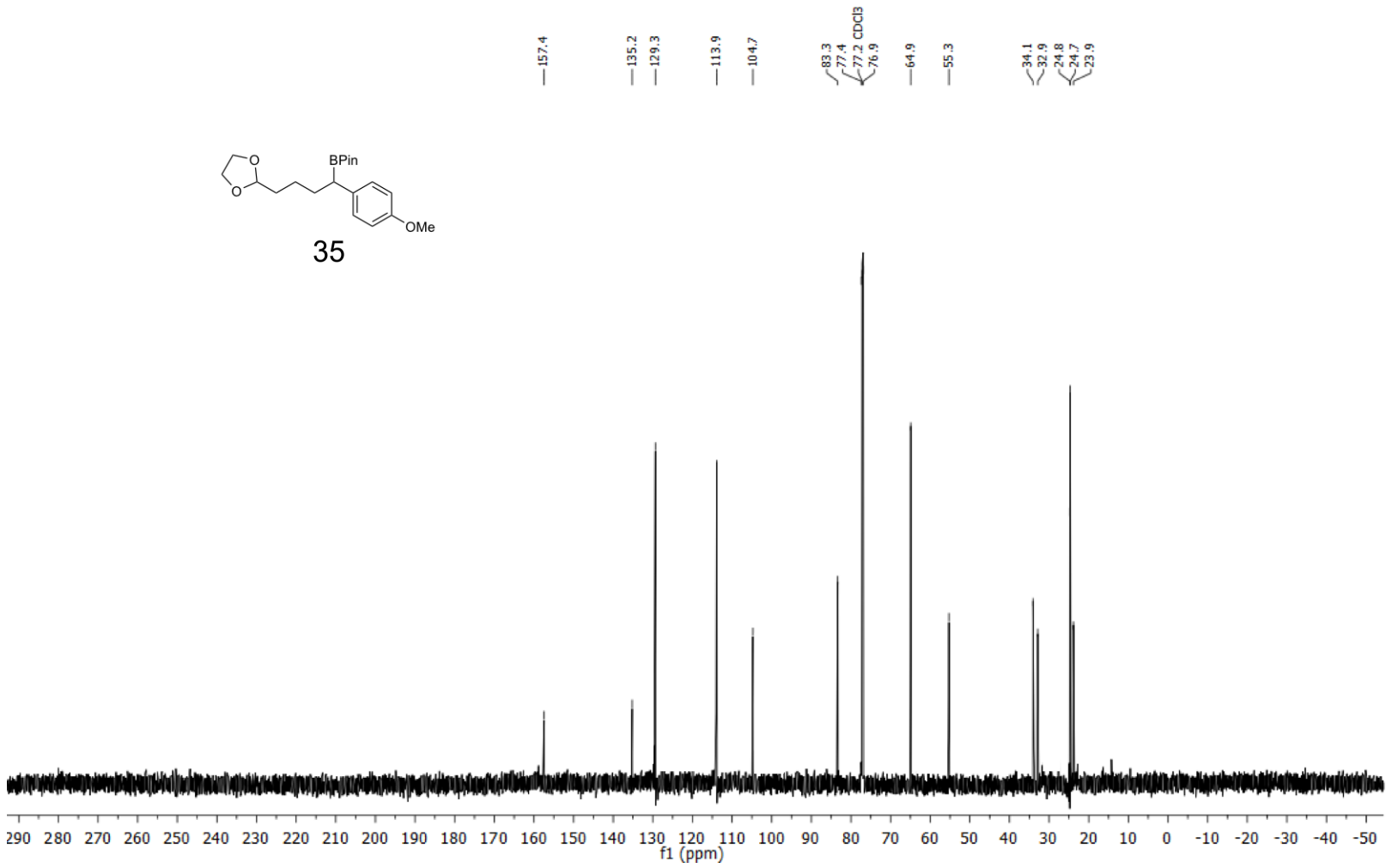


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.6 .

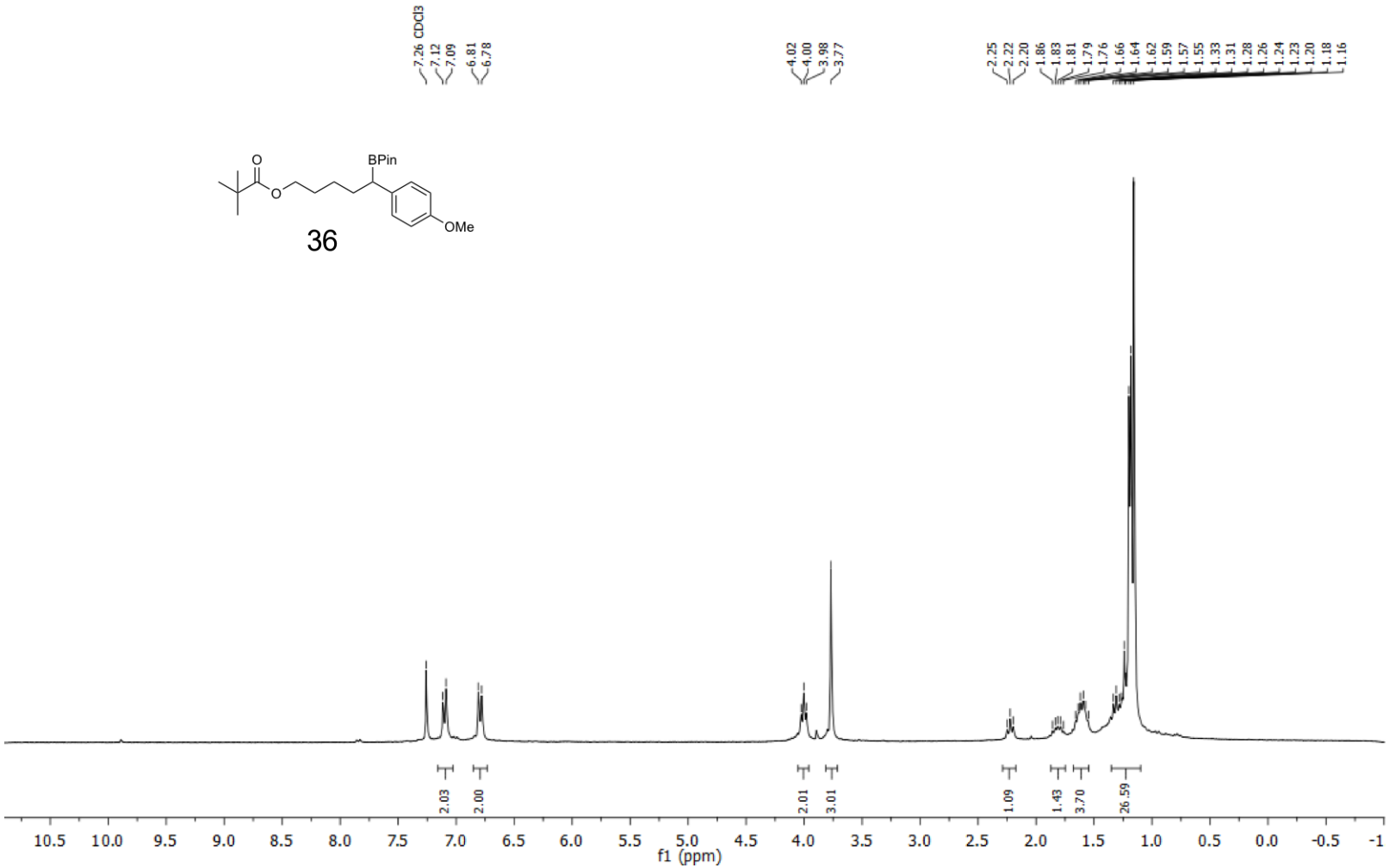


35

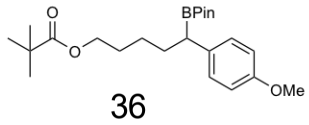
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4 , 135.2 , 129.3 , 113.8 , 104.7 , 83.3 , 64.9 , 55.3 , 34.1 , 32.9 , 24.8 , 24.7 , 23.9 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.81 (m, 1H), 1.62 (m, 3H), 1.45 – 1.00 (m, 27H).

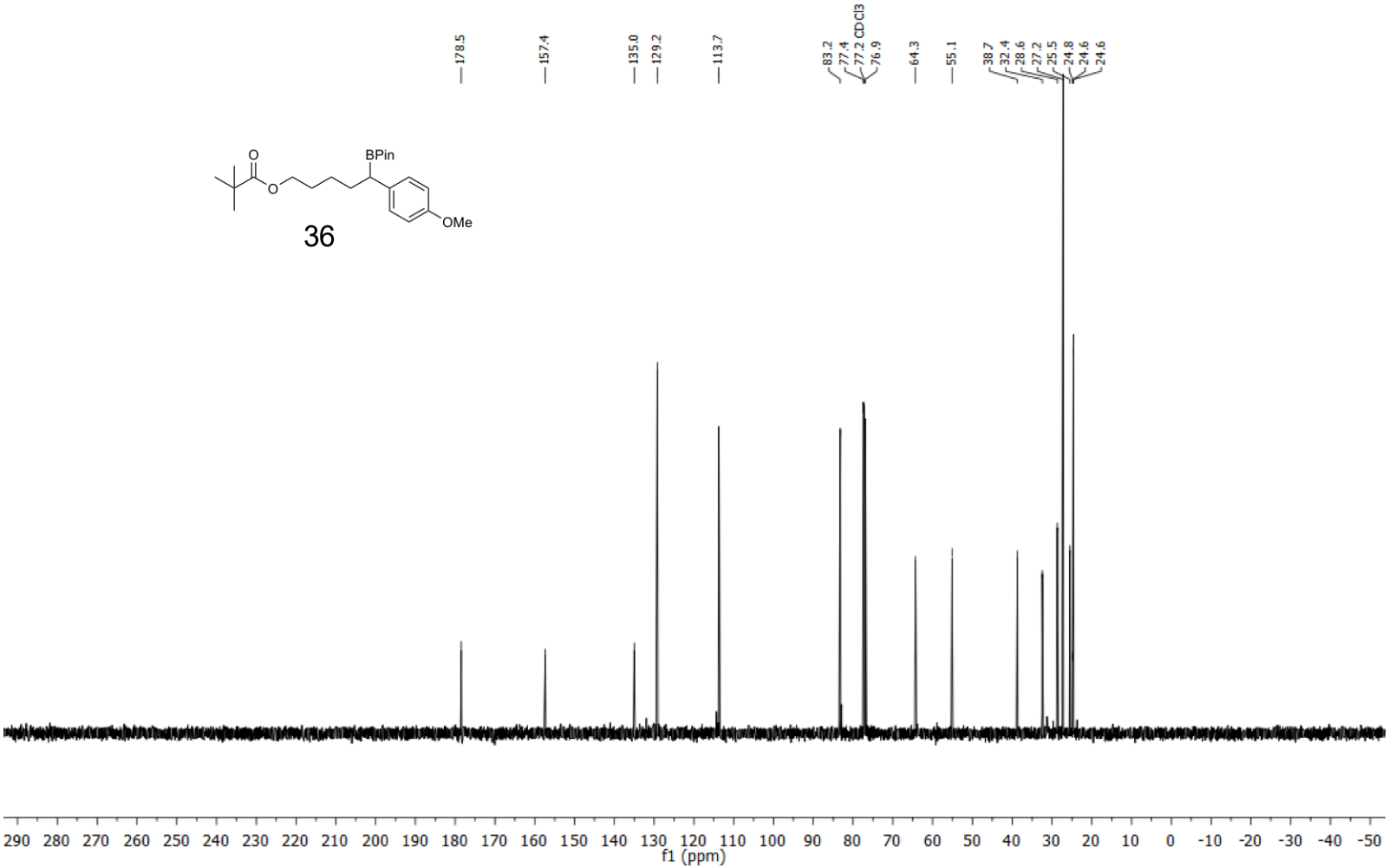


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5 .

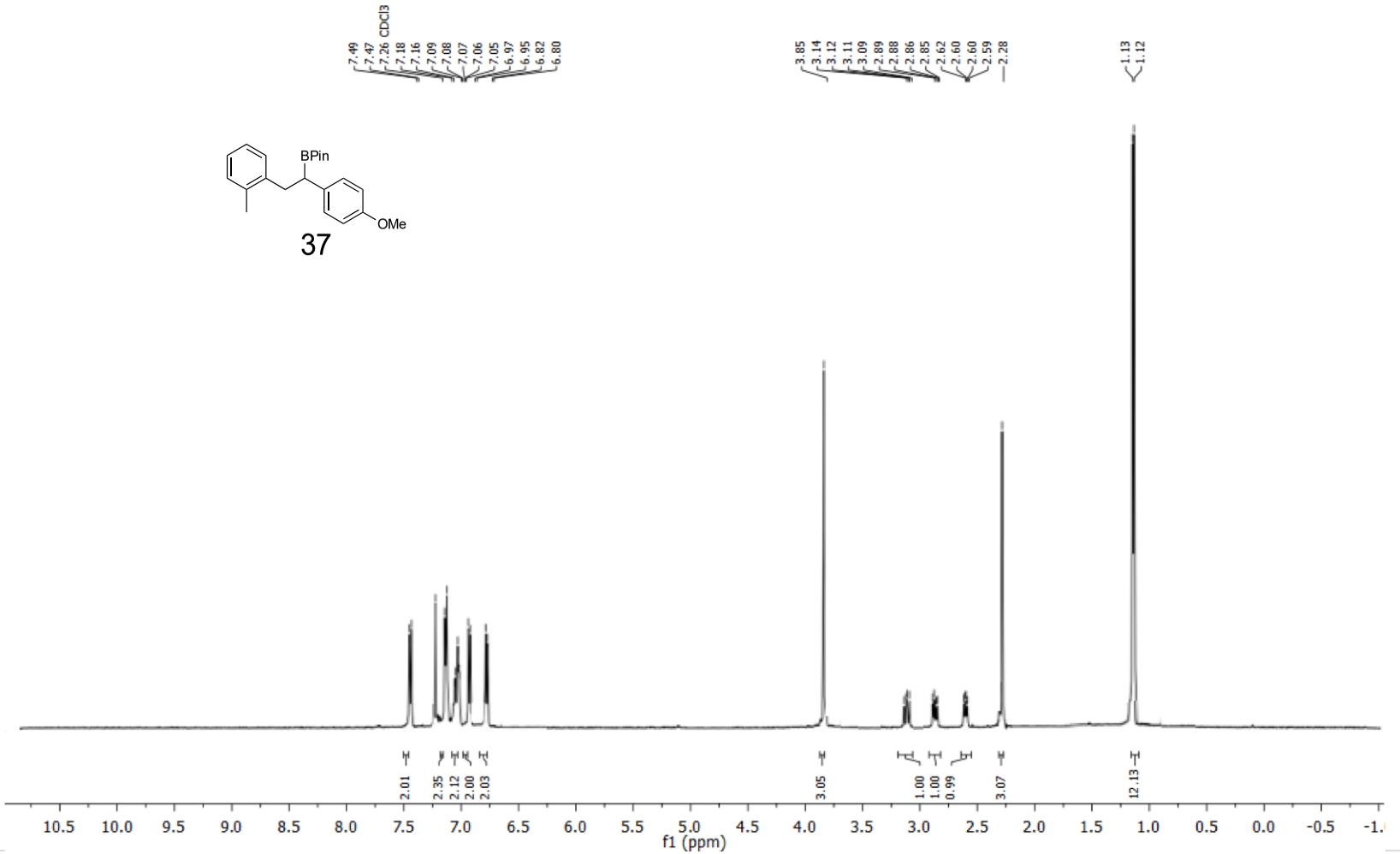


36

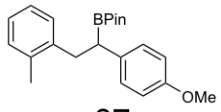
^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.5 , 157.3 , 135.0 , 129.2 , 113.7 , 83.2 , 64.3 , 55.1 , 38.7 , 32.4 , 28.6 , 27.2 , 25.5 , 24.8 , 24.6 , 24.6 .



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.85 (s, 3H), 3.12 (dd, *J* = 13.8, 9.9 Hz, 1H), 2.87 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.60 (dd, *J* = 9.9, 6.4 Hz, 1H), 2.28 (s, 3H), 1.13 (d, *J* = 6.7 Hz, 12H).

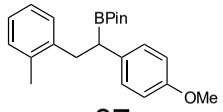


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.8 .



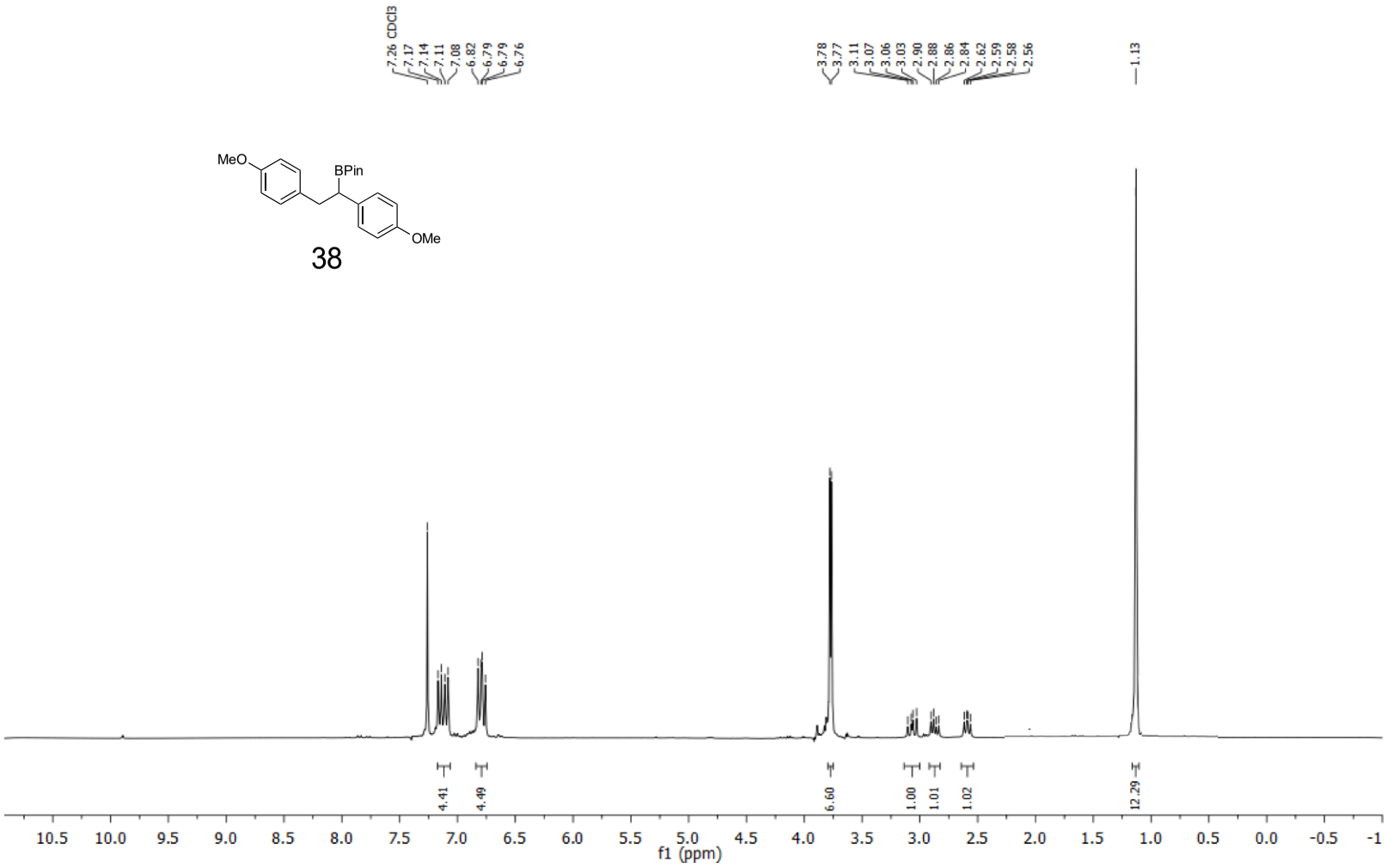
37

^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1 , 136.4 , 135.0 , 133.6 , 130.1 , 129.5 , 128.0 , 126.0 , 125.6 , 114.3 , 83.5 , 70.7 , 55.9 , 29.8 , 24.8 , 24.7 , 19.5 .

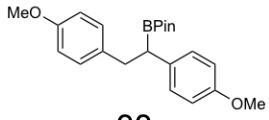


37

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.12 (dd, *J* = 17.3, 8.6 Hz, 4H), 6.79 (dd, *J* = 11.0, 8.5 Hz, 4H), 3.77 (d, *J* = 3.7 Hz, 6H), 3.07 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.87 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 9.5, 7.0 Hz, 1H), 1.13 (s, 12H).

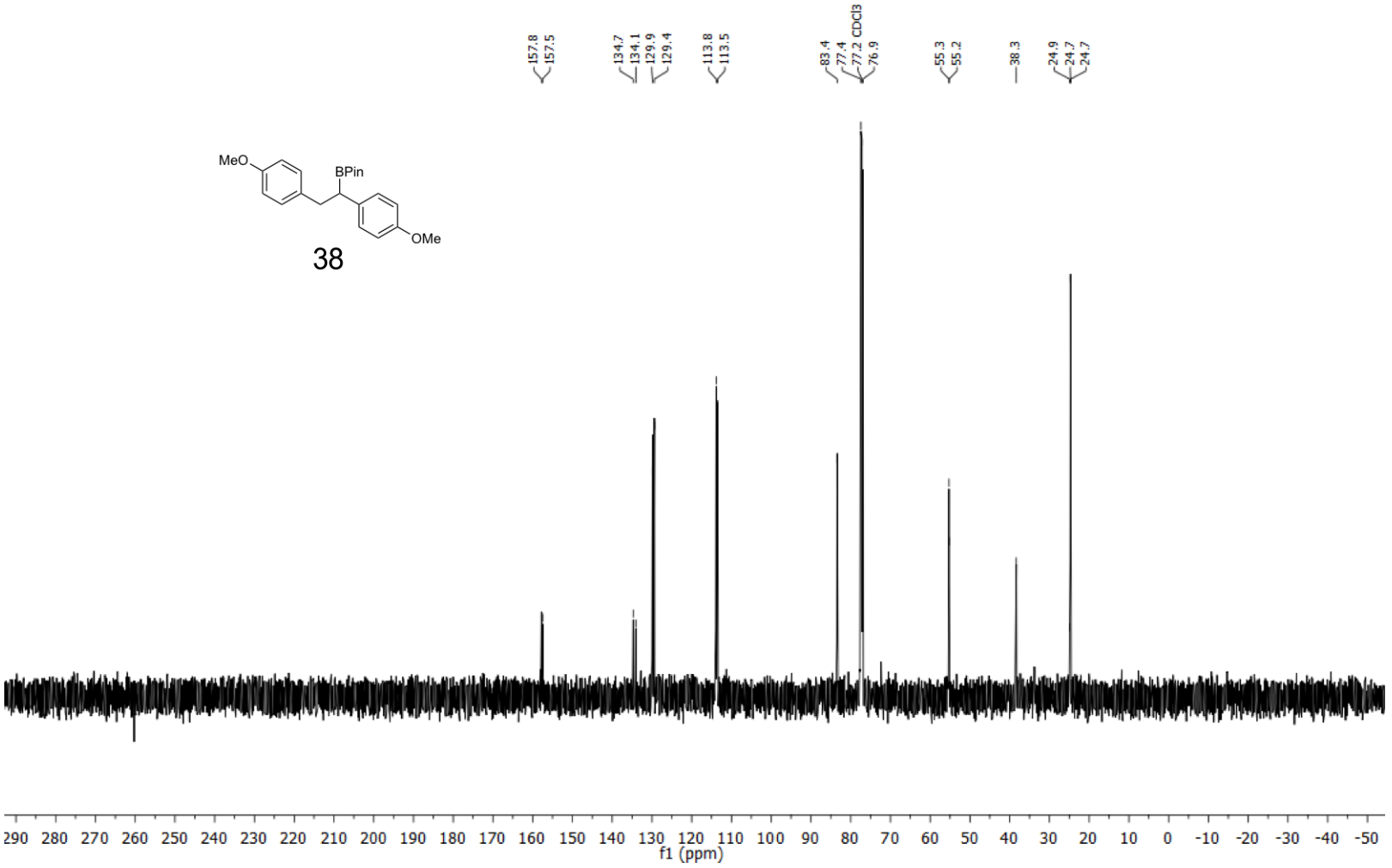


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5 .

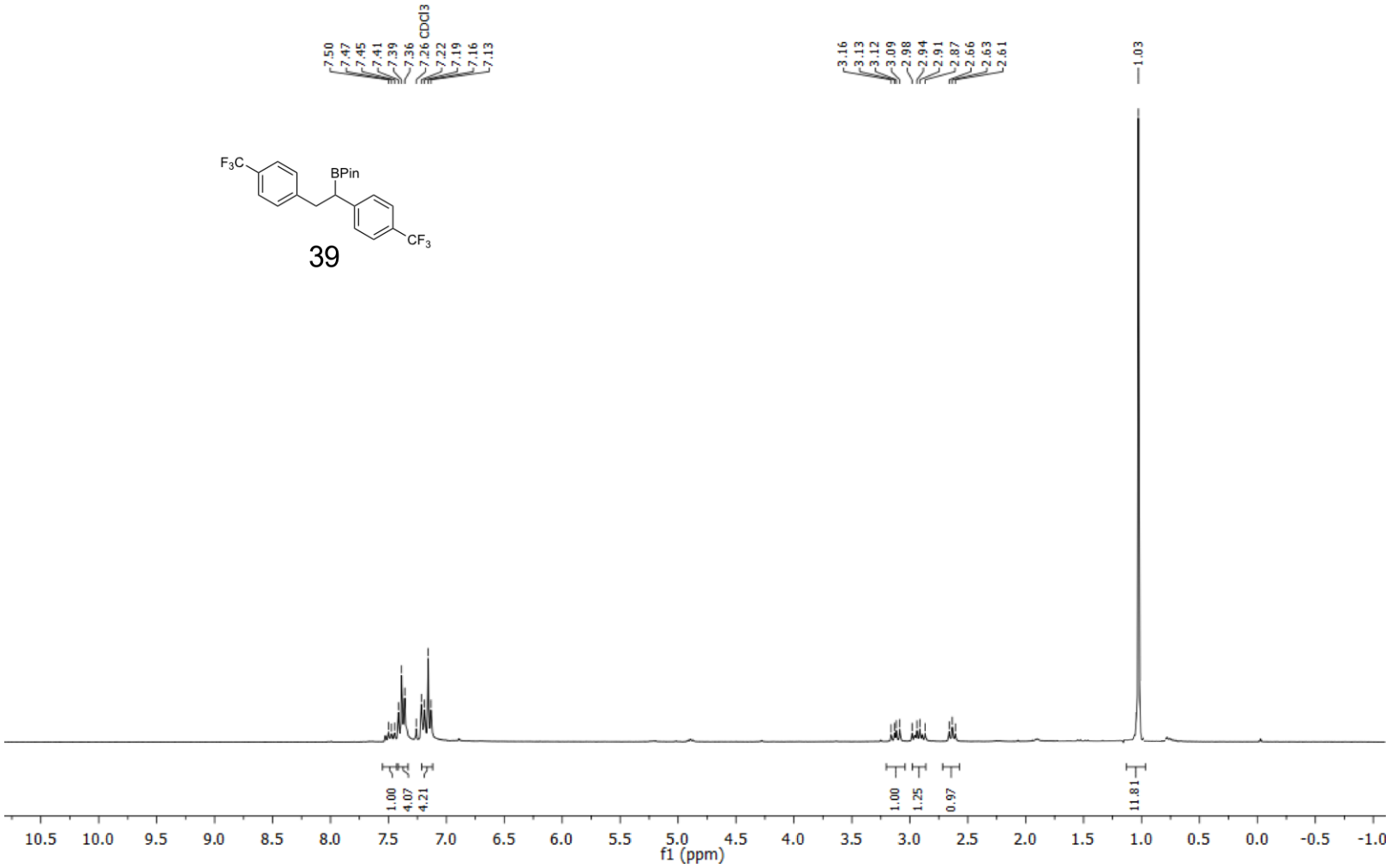


38

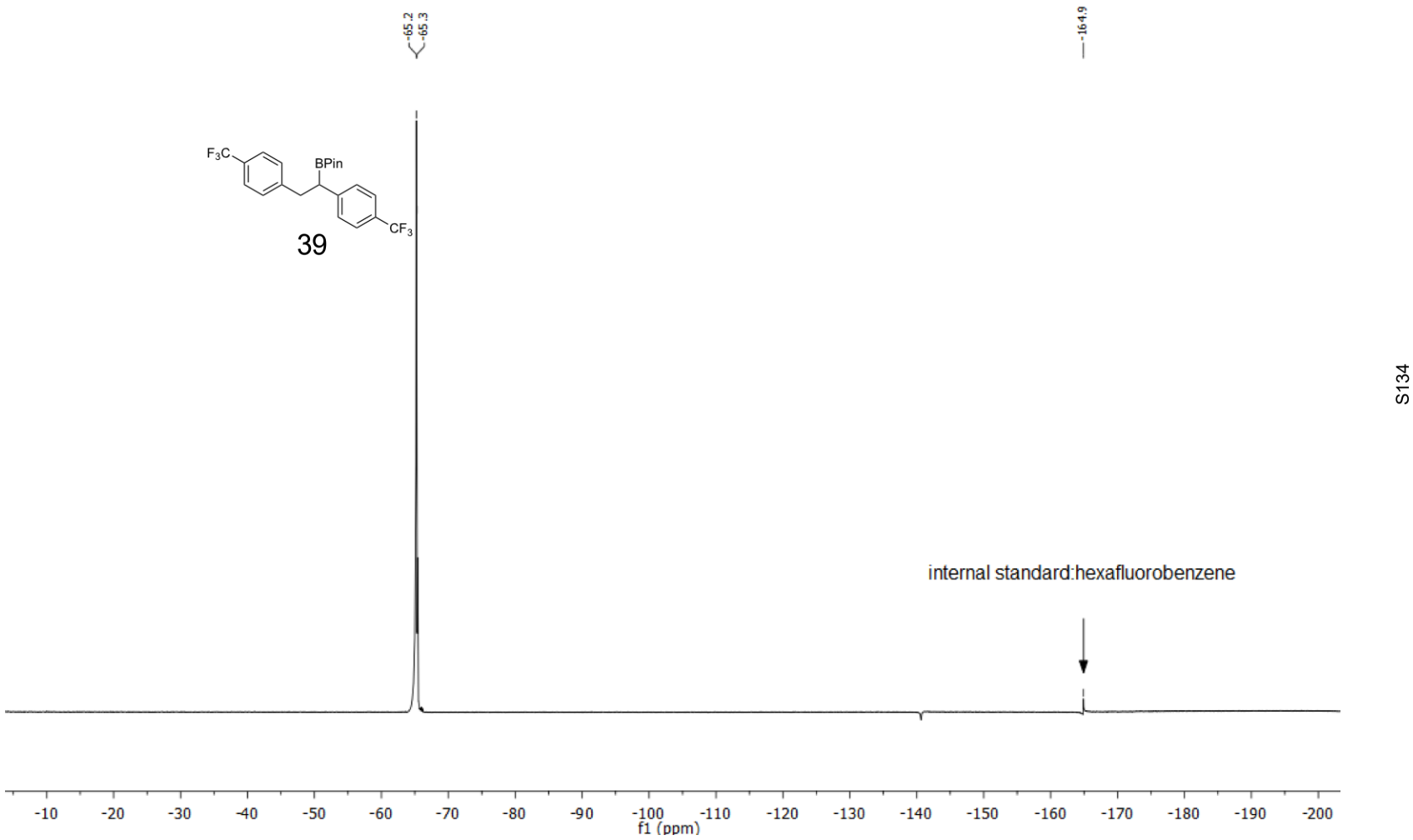
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.8 , 157.5 , 134.7 , 134.1 , 129.9 , 129.4 , 113.8 , 113.5 , 83.4 , 55.3 , 55.2 , 38.3 , 24.9 , 24.7 , 24.7 .



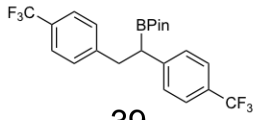
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 1H), 7.39 (m, 4H), 7.23 – 7.11 (m, 4H), 3.12 (**dd**, *J* = 13.7, 8.9 Hz, 1H), 2.93 (**dd**, *J* = 20.6, 13.1 Hz, 1H), 2.63 (t, *J* = 8.2 Hz, 1H), 1.03 (s, 12H).



^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.2 , -62.3 .



^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.5 .



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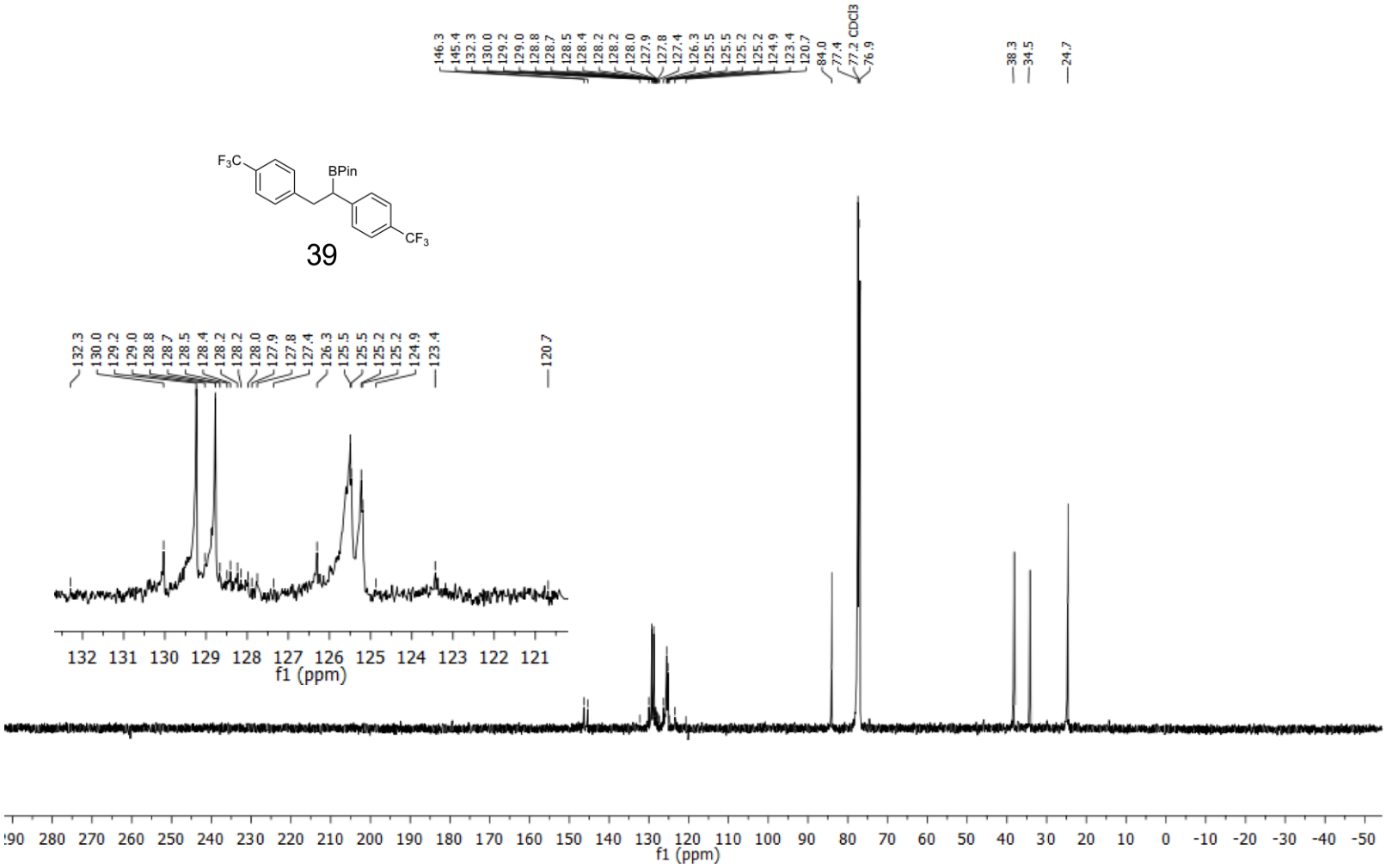
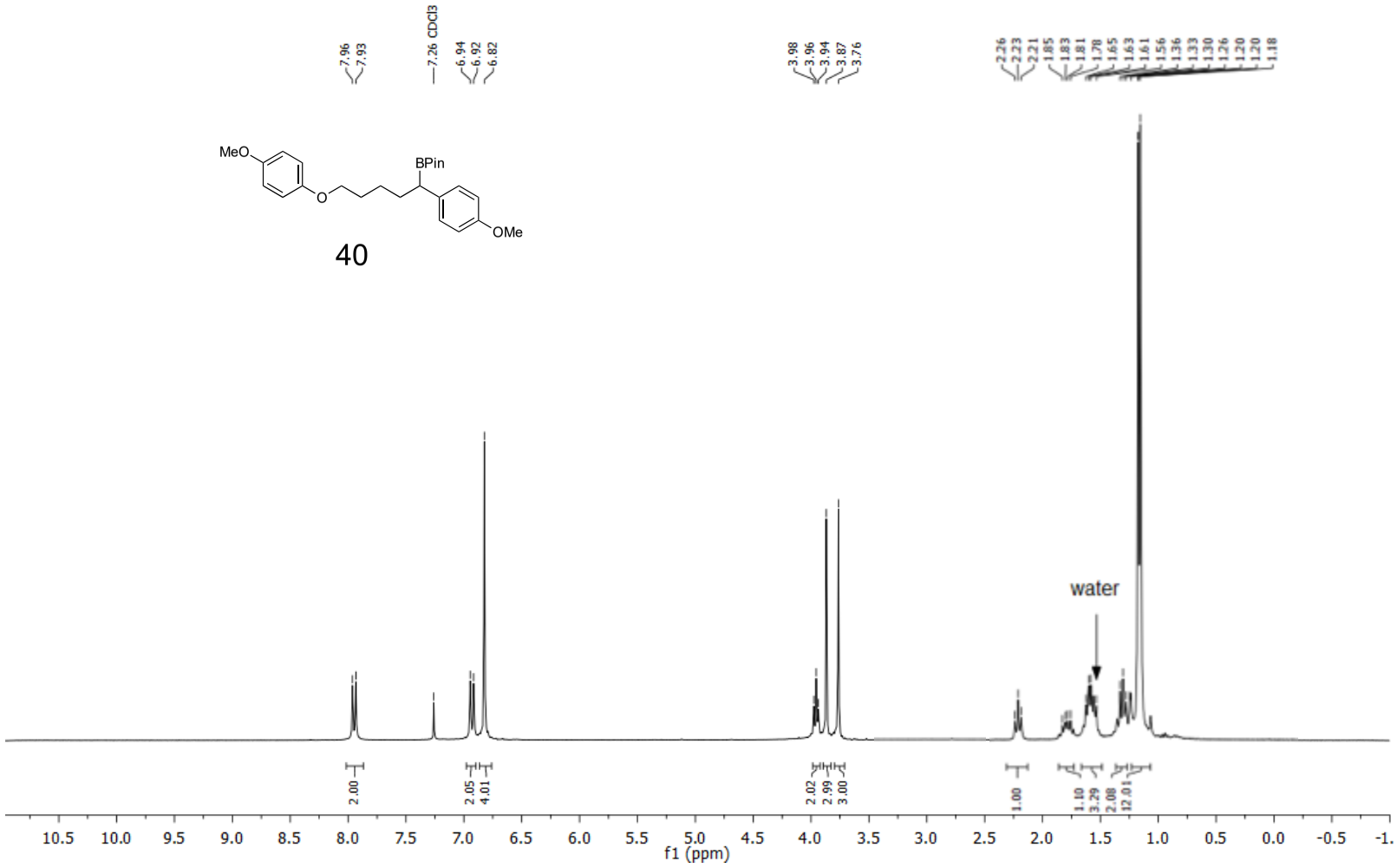
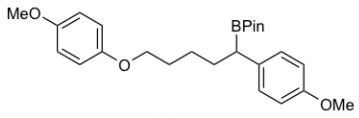
^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.3 , 145.4 , 129.2 , 128.7,128.6 (q, *J* = 311.2 Hz), 128.3 (q, *J* = 32.3 Hz), 128.1 (q, *J* = 31.0 Hz), 125.5 (q, *J* = 3.8 Hz), 125.2 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 349.3 Hz), 84.0 , 38.3 , 34.5 , 24.7 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 4H), 3.96 (t, *J* = 5.9 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.91 – 1.73 (m, 1H), 1.71 – 1.51 (m, 2H), 1.43 – 1.23 (m, 2H), 1.19 (d, *J* = 6.0 Hz, 12H).

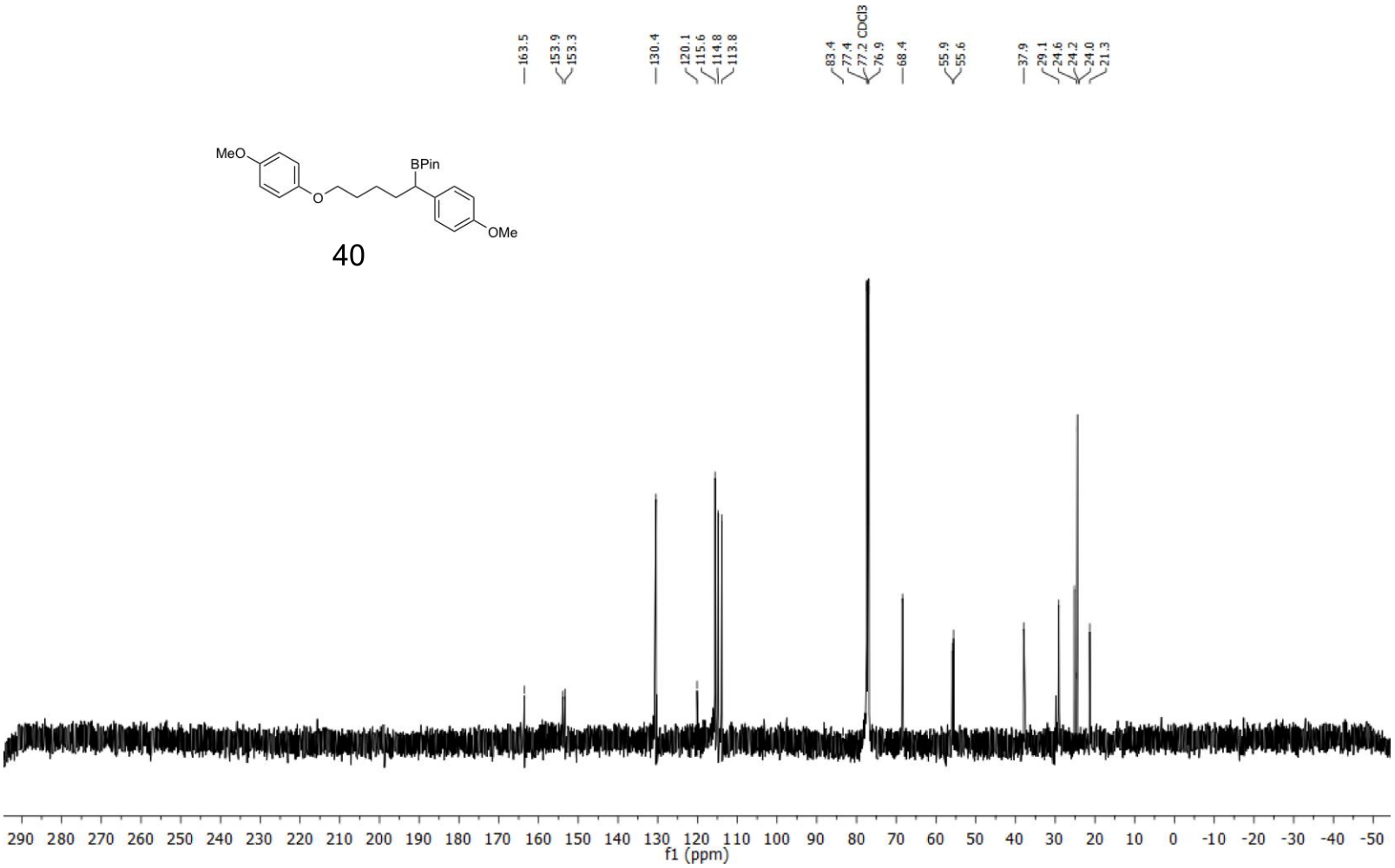


^{11}B NMR (96 MHz, Chloroform-*d*) δ 32.4 .

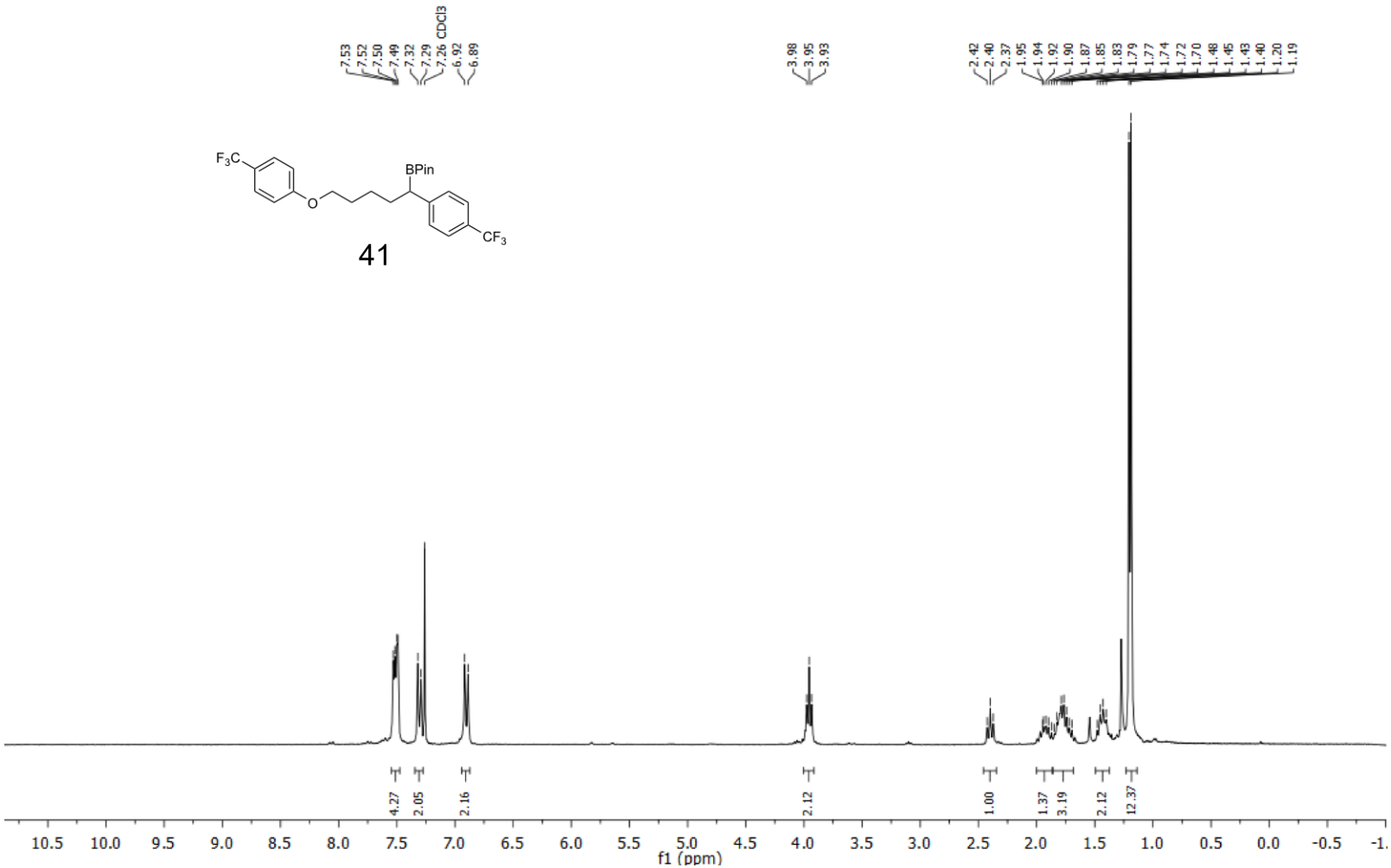


40

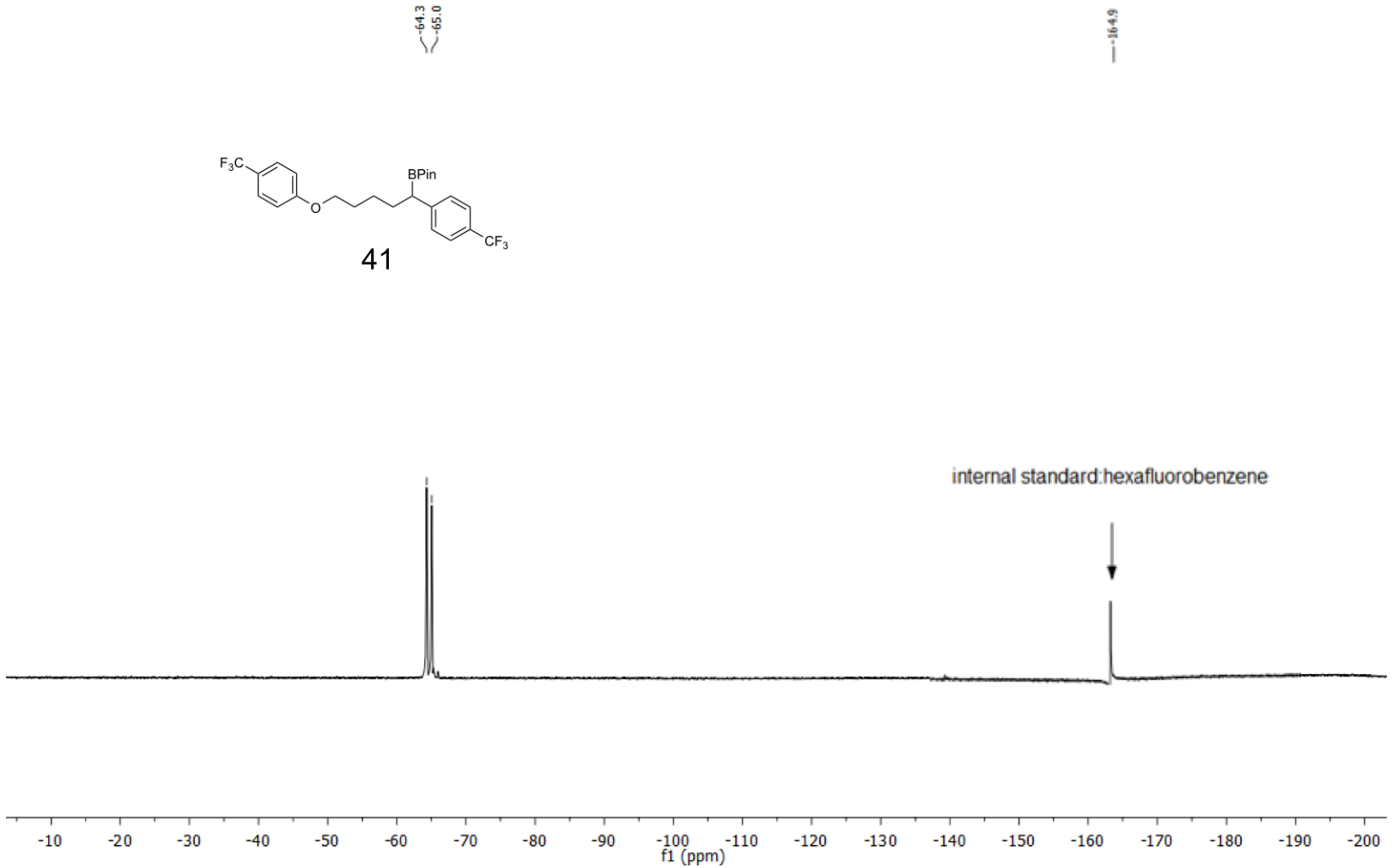
^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.5 , 153.9 , 153.3 , 130.4 , 120.1 , 115.6 , 114.8 , 113.8 , 83.4 , 68.4 , 55.8 , 55.6 , 37.9 , 29.1 , 24.6 , 24.2 , 24.0 , 21.3 .



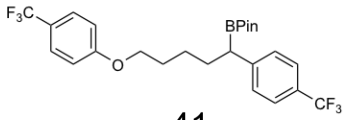
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.6, 3.7 Hz, 45H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.95 (t, *J* = 6.3 Hz, 3H), 2.40 (t, *J* = 7.9 Hz, 1H), 2.03 – 1.84 (m, 1H), 1.77 (m, 3H), 1.44 (q, *J* = 7.7 Hz, 2H), 1.20 (d, *J* = 5.2 Hz, 12H).



^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.3 , -65.0 .



^{11}B NMR (96 MHz, Chloroform-*d*) δ 31.7 .



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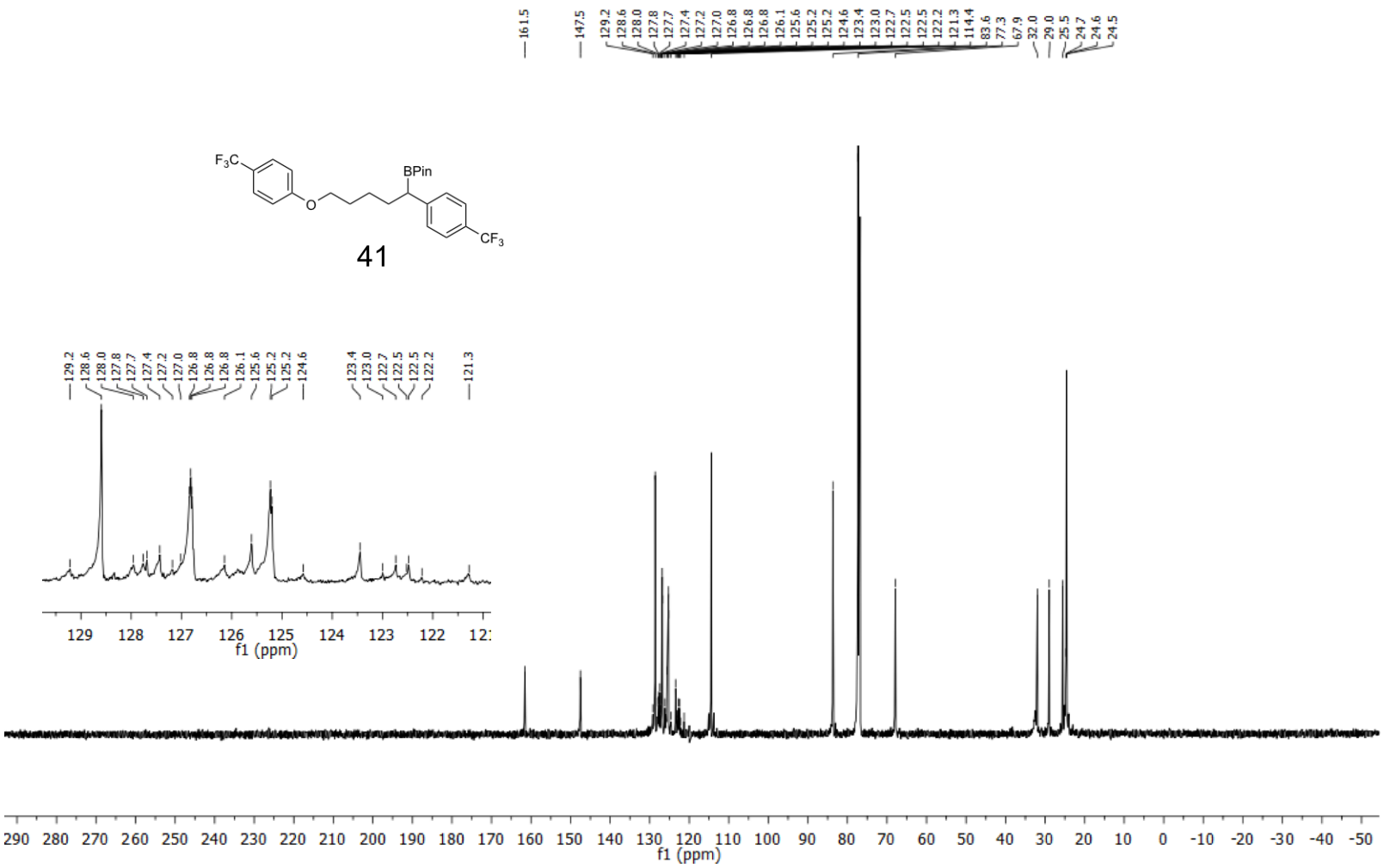
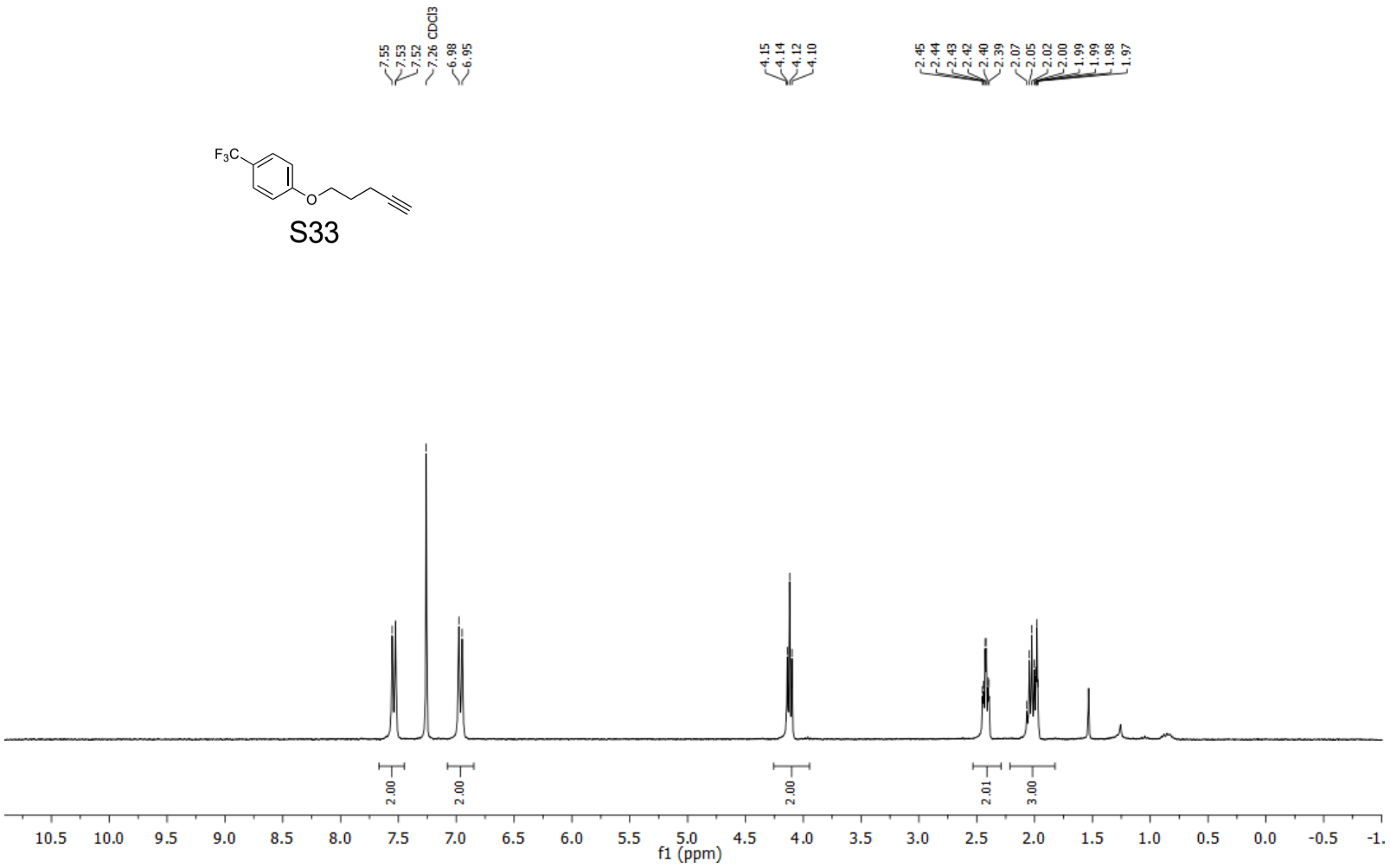
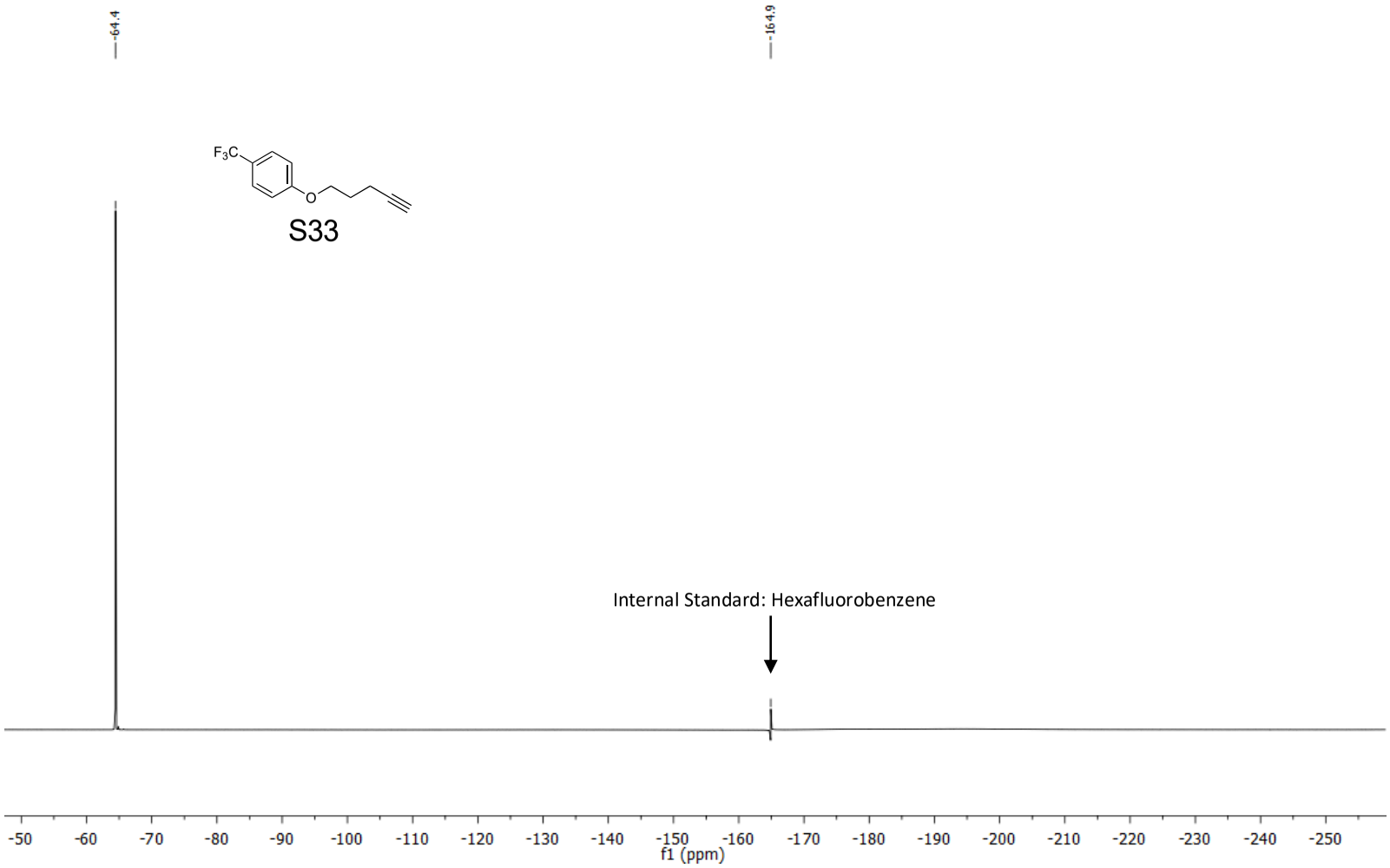
^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.5 , 147.5 , 128.59 , 127.6 (q, J = 32.8), 126.8 (q, J = 3.8 Hz), 125.9 (q, J = 277.1 Hz), 125.2 (q, J = 3.8 Hz),124.5 (q, J = 272.2 Hz), 122.6 (q, J = 32.8 Hz), 114.4 , 83.6 , 67.9 , 32.0 , 29.0, 25.5 , 24.6 , 24.5 .



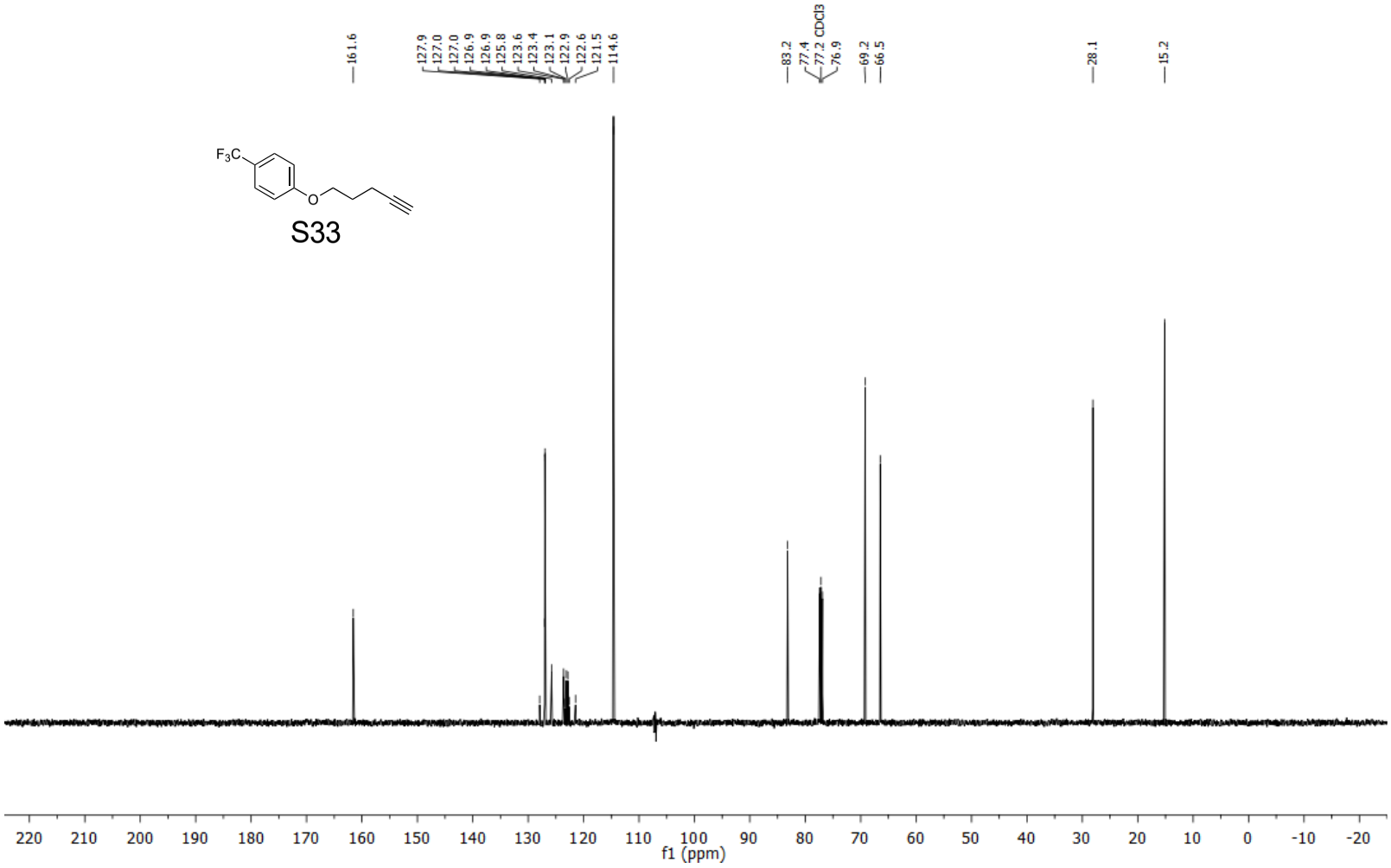
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 – 7.44 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.12 (t, *J* = 6.1 Hz, 2H), 2.42 (td, *J* = 6.9, 2.7 Hz, 2H), 2.10 – 1.92 (m, 3H).



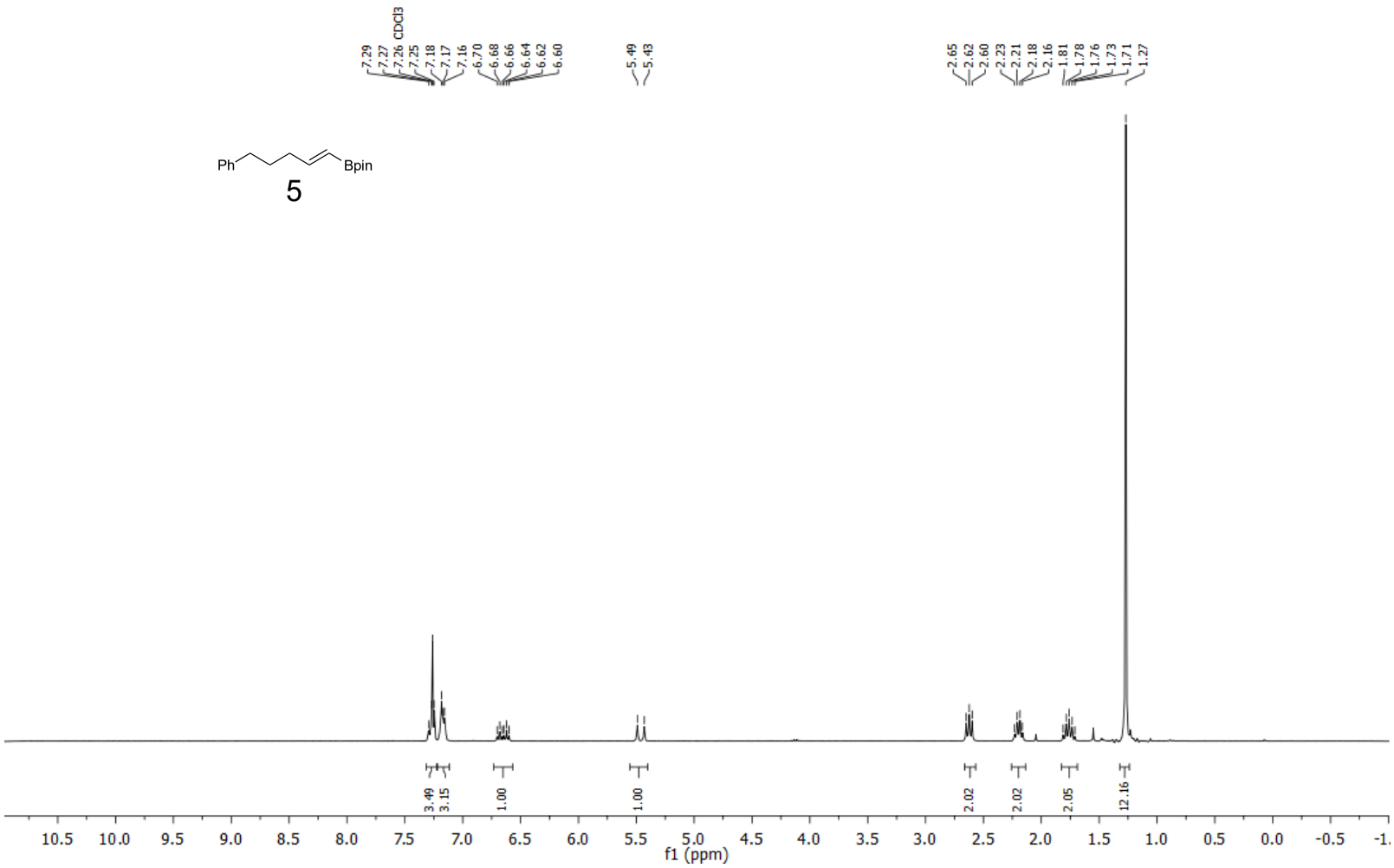
^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.4 .



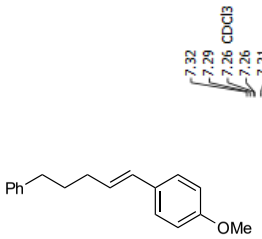
^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.6 , 127.0 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 270.9 Hz), 123.0 (q, *J* = 32.6 Hz), 114.6 , 83.2 , 69.2 , 66.5 , 28.1 , 15.2 .



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 3H), 7.21 – 7.12 (m, 3H), 6.65 (**dt**, *J* = 18.0, 6.4 Hz, 1H), 5.46 (**d**, *J* = 18.0 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.28 – 2.12 (m, 2H), 1.76 (**ddd**, *J* = 15.0, 8.4, 6.9 Hz, 2H), 1.27 (s, 12H).



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.12 (m, 8H), 6.84 (d, *J* = 8.7 Hz,2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.80 (p, *J* = 7.5 Hz, 2H).



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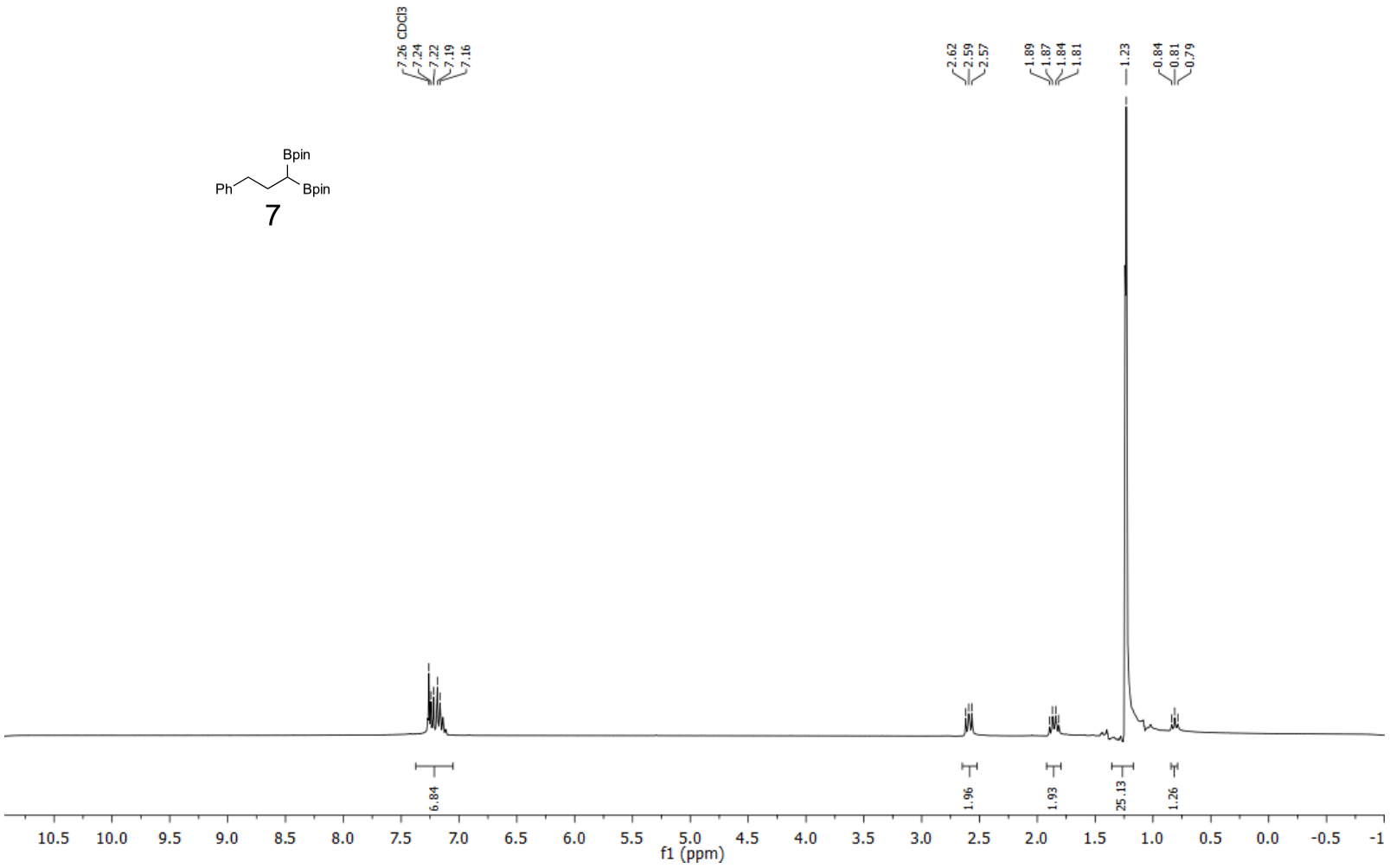
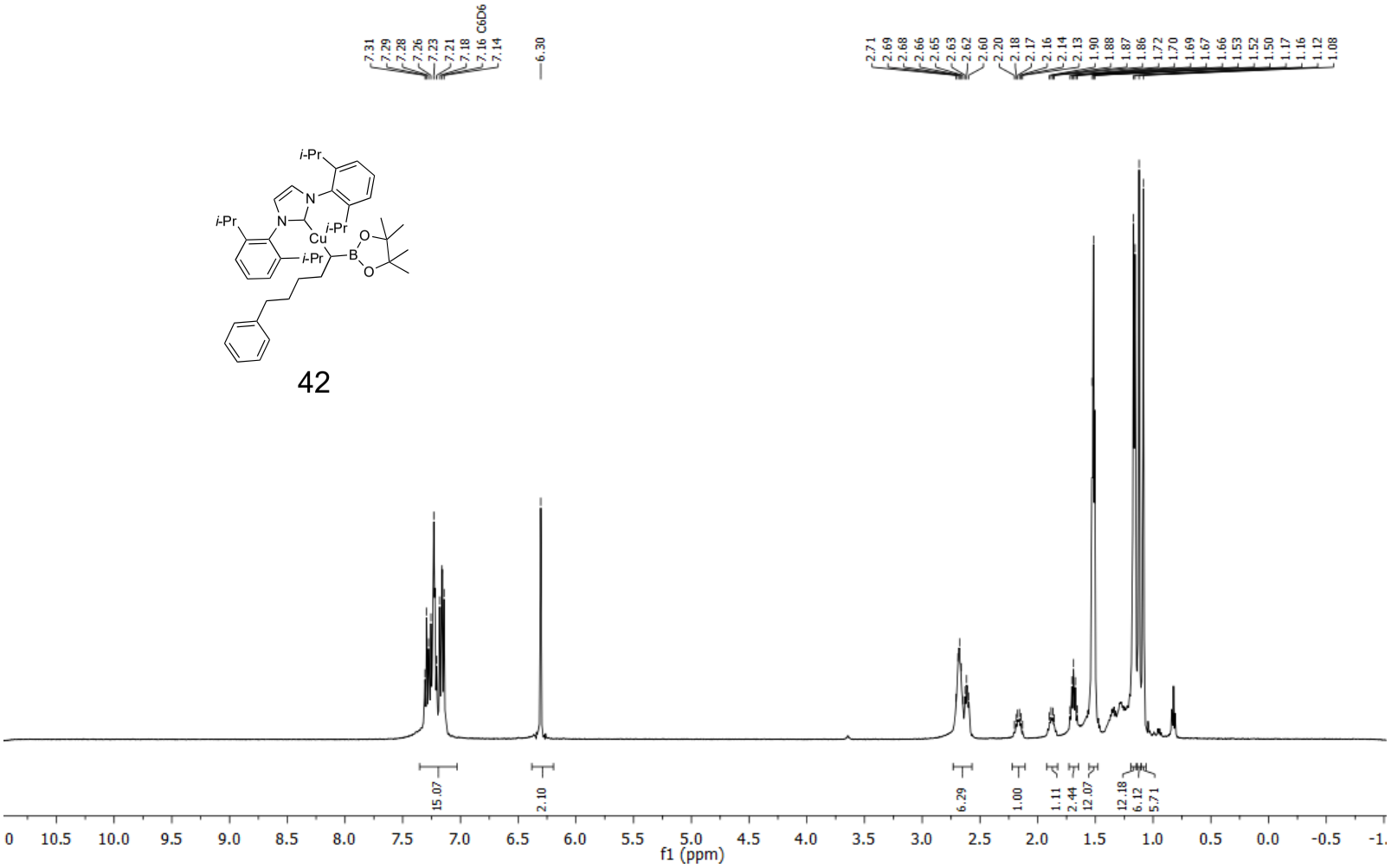
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.05 (m, 7H), 2.70 – 2.53 (m, 2H), 2.54 - 2.48 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.85 (q, *J* = 7.8 Hz, 2H), 1.23 (s, 25H), 0.81 (t, *J* = 7.9 Hz, 1H).



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 - 7.14 (m, 15H), 6.30 (s, 2H), 2.71 – 2.60 (m, 6H), 2.20 – 2.11 (m, 1H), 1.90 - 1.86 (m, 1H), 1.69 (p, *J* = 7.7 Hz, 2H), 1.52 (t, *J* = 6.0 Hz, 12H), 1.16 (m, 12H), 1.12 (s, 6H), 1.08 (s, 6H).



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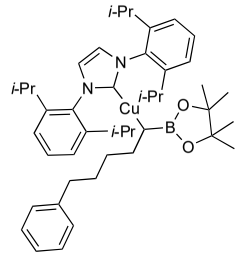
^{11}B NMR (96 MHz, Chloroform-*d*) δ 28.4 .



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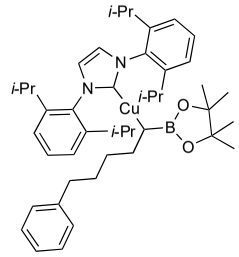
^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.9 , 145.9 , 135.5 , 130.4 , 128.9 , 125.4 , 124.2 , 124.2 , 122.2 , 120.3 , 117.6 , 79.7 , 37.7 , 36.7 , 32.7 , 29.1 , 29.0 , 28.8 , 25.5 , 25.3 , 25.1 , 23.8 .



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