

Iron-Catalyzed Ligand-Controlled Silylation and Borylation of Nitriles with Bpin-SiEt₃ via C-CN Bond Cleavage

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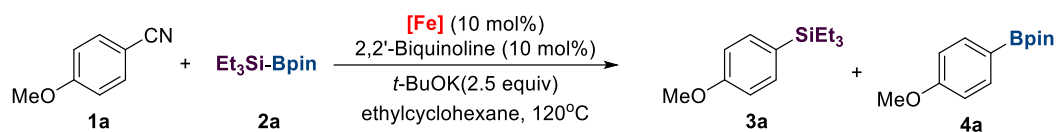
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General information: ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet. NMR yield was determined by ^1H NMR using mesitylene as an internal standard before working up the reaction.

Materials: All reagents that used were from commercial sources, unless otherwise specified. $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_3\text{Fe}$ (98%) was purchased from Adamas. FeCl_2 (>99.99%) was purchased from Alfa Aesar. LiOMe, *t*-BuONa, *t*-BuOK, KOMe, and NaOMe were purchased from Adamas, *t*-BuOLi was purchased from Accela. Triglyme was distilled under reduced pressure from CaH_2 . Ethylcyclohexane was distilled from CaH_2 . Hexane, THF, DME, MTBE, (*i*-Pr) $_2\text{O}$, 2-Me-THF and toluene were distilled from sodium and benzophenone before used. Diglyme and PhCF_3 were purchased from Energy Chemical.

Optimization of the Iron-Catalyzed Silylation of 4-methoxybenzonitrile **1a** (Tables S1-S9)

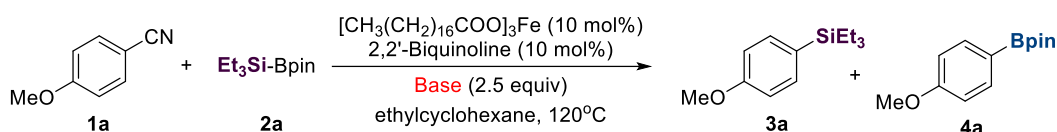


Entry	[Fe]	Yield ^b (3a/4a)
1	Fe(OAc) ₂	11%/3%
2	Fe(OTs) ₂	20%/11%
4	Fe(OTf) ₂	22%/11%
5	FeF ₂	15%/5%
6	[CH₃(CH₂)₁₆COO]₃Fe	14%/2%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (0.5 mmol, 2.5 equiv), ethylcyclohexane (1.0 mL), 120 °C, 15 h, under an nitrogen atmosphere.

^bDetermined by ¹H NMR using mesitylene as an internal standard.

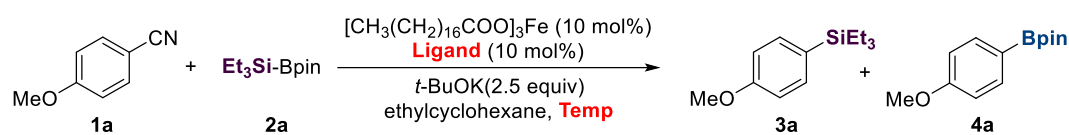
Table S2. Screening of Bases.^a



Entry	Base	Yield ^b (3a/4a)
1	<i>t</i>-BuOK	14%/2%
2	<i>t</i> -BuONa	10%/5%
3	<i>t</i> -BuOLi	0%
4	NaOEt	5%
5	LiOMe	0%
6	K ₃ PO ₄	0%
7	CsF	0%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), Base (2.5 equiv), ethylcyclohexane (1.0 mL), 120 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

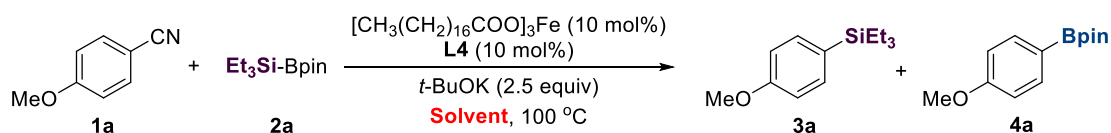
Table S3. Screening of Temperature and the Ligands.^a



Entry	[Ligand]	Temp (°C)	Yield ^b (3a/4a)
1	2,2'-Biquinoline	120	14%/2%
2	2,2'-Biquinoline	100	5%/16%
3	P(<i>t</i> -Bu) ₃ HBF ₄	100	21%/5%
4	TMEDA	100	18%/3%
5	1,10-Phen	100	24%/5%
6	<i>t</i> -BuDavePhos	100	29/14%
7	dppf	100	31%/15%
8	L1	100	15%/0%
9	L4	100	33%/1%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (2.5 equiv), ethylcyclohexane (1.0 mL), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

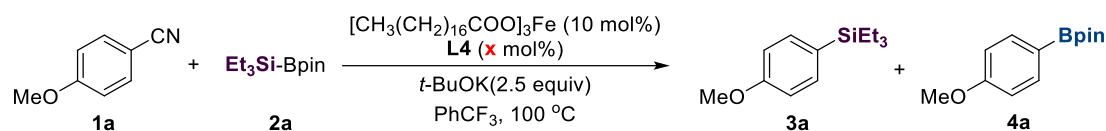
Table S4. Screening of Solvents.^a



Entry	Solvent	Yield ^b (3a/4a)
1	PhCF₃	60%/0%
2	toluene	36%
3	ethylcyclohexane	52%
4	hexane	55%
5	(<i>i</i> -Pr) ₂ O	48%
6	triglyme	0%
7	diglyme	0%
8	2-Me-THF	0%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (2.5 equiv), Solvent (1.0 mL), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

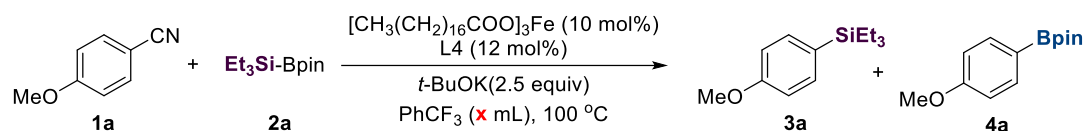
Table S5. Screening of the Amount of the Ligand and the Amount of **2a.^a**



Entry	2a (equiv)	L4 (mol%)	Yield ^b (3a/4a)
1	3.5	10	60%/0%
2	3.5	12	63%/0%
3	3.0	12	58%/0%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), *t*-BuOK (2.5 equiv), PhCF_3 (1.0 mL), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

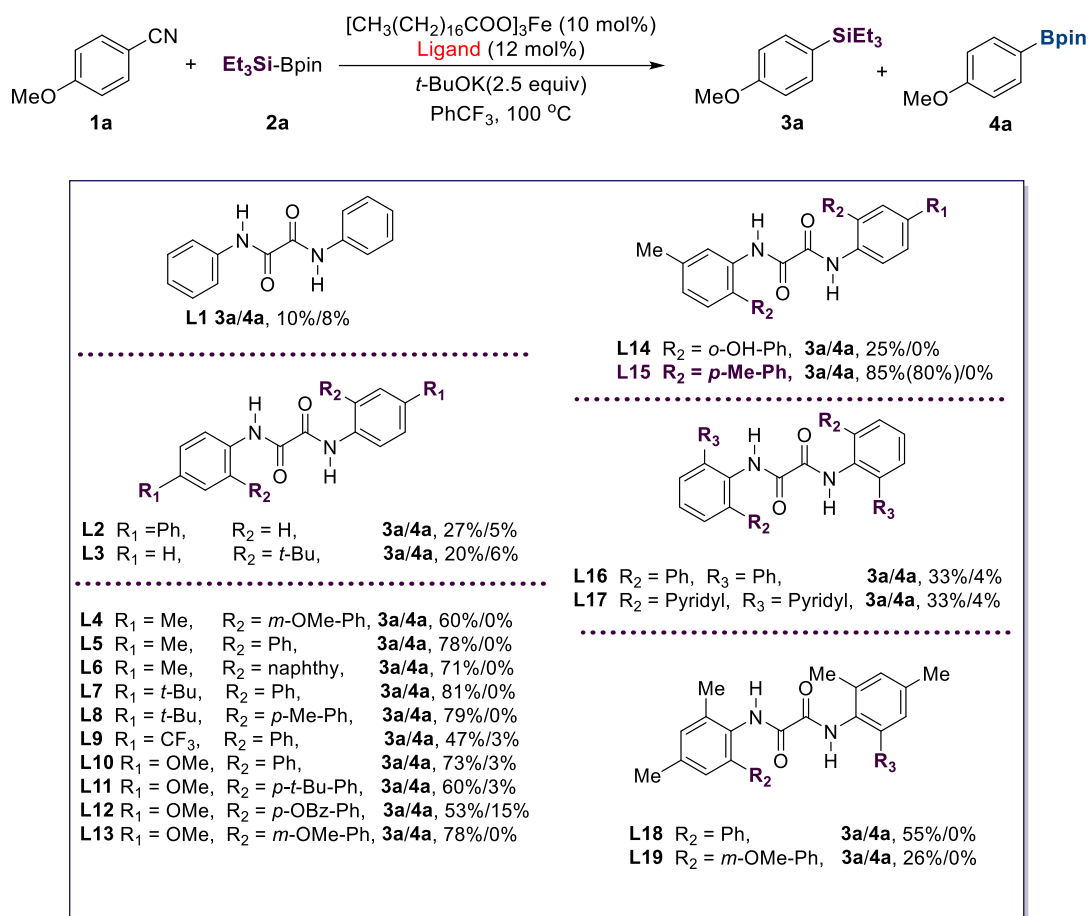
Table S6. Screening of the Concentration.^a



Entry	PhCF_3 (mL)	Yield ^b (3a/4a)
1	0.5	40%
2	1.0	63%/0%
3	1.5	51%
4	2.0	77%
5	2.5	66%/0%
6	3.0	72%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (2.5 equiv), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S7. Screening of the Ligands.^a



^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (2.5 equiv), PhCF₃ (2.5 mL), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.

Table S8. Control Experiments of Iron-Catalyzed Silylation of 1a.^a

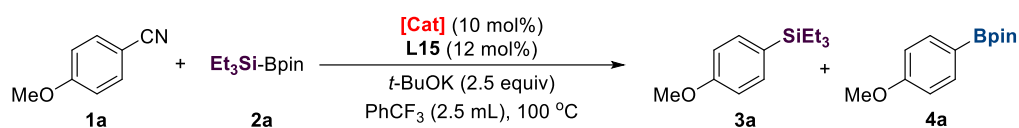
Reaction scheme showing the silylation of 1a (4-methoxybenzonitrile) with Et₃Si-Bpin (2a) catalyzed by [CH₃(CH₂)₁₆COO]₃Fe (10 mol%) and L15 (12 mol%) in PhCF₃ (2.5 mL) at 100 °C, using *t*-BuOK (2.5 equiv). The products are 3a (4-methoxyphenyltriethylsilane) and 4a (4-methoxyphenylboronic pinacol ester).

Entry	[Fe]	Base	Ligand	Yield ^b (3a/4a)
1	[CH ₃ (CH ₂) ₁₆ COO] ₃ Fe	<i>t</i> -BuOK	L15	85% (80%)/0%
2	[CH ₃ (CH ₂) ₁₆ COO] ₃ Fe	<i>t</i> -BuOK	-	37%/1%
5	-	<i>t</i> -BuOK	-	complex

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), *t*-BuOK (0.5 mmol, 2.5 equiv), PhCF₃ (2.5 mL), 100 °C, 15 h, under an nitrogen atmosphere.

^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S9. Evaluation of Other Transition-Metal Effect on the Silylation.^a

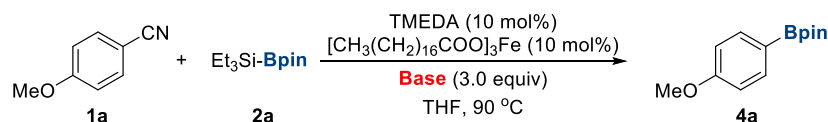


Entry	[Cat]	Yield ^b (3a/4a)
1	FeCl_2	69%/0%
2	FeCl_2 (99.99%)	68%/0%
3	$\text{Pd}(\text{OAc})_2$	4%
4	CuCl	0%
5	$\text{Cu}(\text{OTf})_2$	15%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.5 equiv), $t\text{-BuOLi}$ (0.5 mmol, 2.5 equiv), PhCF_3 (2.5 mL), 100 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ^1H NMR using mesitylene as an internal standard.

Optimization of the Iron-Catalyzed Boronylation of 4-methoxybenzonitrile **1a** (Tables S10-S16)

Table S10. Screening of Base.^a



Entry	[Base]	4a , Yield ^b
1	$t\text{-BuOK}$	2%
2	$t\text{-BuONa}$	8%
3	$t\text{-BuOLi}$	37%
4	KOMe	20%
5	NaOEt	18%
6	NaOMe	0%
7	LiOMe	0%
8	CsF	0%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), Base (x equiv), THF (1.0 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ^1H NMR using mesitylene as an internal standard.

Table S11. Screening the Loading of *t*-BuOLi.^a

Entry	[Base]	equiv	4a , Yield ^b
1	<i>t</i> -BuOLi	2.5	30%
2	<i>t</i>-BuOLi	2.75	39%
3	<i>t</i> -BuOLi	3.0	37%
4	<i>t</i> -BuOLi	3.5	28%
5	<i>t</i> -BuOLi	4.0	27%

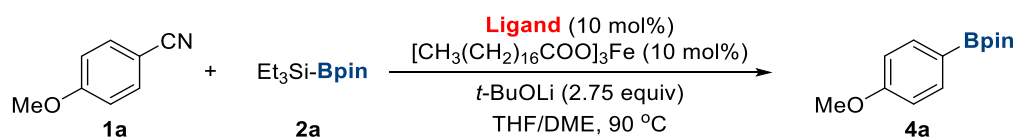
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), *t*-BuOLi (0.55 mmol, 2.75 equiv), THF (1.0 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S12. Screening of Solvents.^a

Entry	Solvent (1.0 mL)	4a , Yield ^b
1	THF	39%
2	DME	35%
3	diglyme	22%
4	Hexane	6%
5	MTBE	22%
6	THF/DME (0.5/0.5)	40%
7	THF/MTBE (0.5/0.5)	30%
8	MTBE/DME (0.5/0.5)	26%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), *t*-BuOLi (2.75 equiv), solvent (1 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

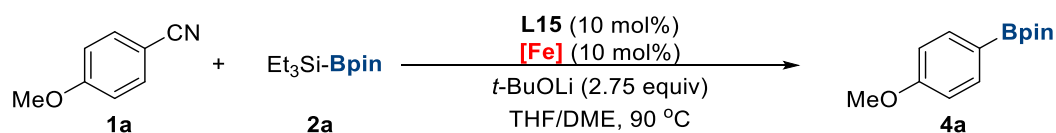
Table S13. Screening of the Ligands.^a



Entry	[Ligand]	4a , Yield ^b
1	TMEDA	40%
2	<i>IMes</i>	30%
3	bpy	34%
4	$\text{PPh}(\text{tri-}p\text{-Me})$	33%
5	Mephos	30%
6	Xphos	30%
7	PCy_3	0%
8	dppe	10%
9	L15	43%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), $t\text{-BuOLi}$ (2.75 equiv), THF/DME (0.5 mL/0.5 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ^1H NMR using mesitylene as an internal standard.

Table S14. Screening of the Iron Catalysts.^a



Entry	[Fe]	4a , Yield ^b
1	$[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_3\text{Fe}$	43%
2	$\text{Fe}(\text{OAc})_2$	10%
3	FeCl_2	15%
4	$\text{Fe}(\text{acac})_3$	23%
5	$\text{Fe}(\text{OTf})_2$	31%
6	$\text{Fe}(\text{OTf})_3$	26%
7	$\text{Fe}(\text{OTs})_3$	35%
8	FeI_2	30%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), $t\text{-BuOLi}$ (0.55 mmol, 2.75 equiv), THF/DME (0.5 mL/0.5 mL), 90 °C, 15 h, under an nitrogen atmosphere.

^bDetermined by ^1H NMR using mesitylene as an internal standard.

Table S15. Screening of the Ligands.^a

Entry	[Ligand]	4a , Yield ^b
1	(1S,2R)-(-)- <i>cis</i> -1-Amino-2-indanol	54%
2	bpy	47%
3	2,2'-Biquinoline	47%
4	(-)-Prolinol	52%
5	PCy ₃ HBF ₄	59%
6	P(<i>n</i> -Bu) ₃ HBF ₄	57%
7	P(<i>t</i>-Bu)₃HBF₄	63%

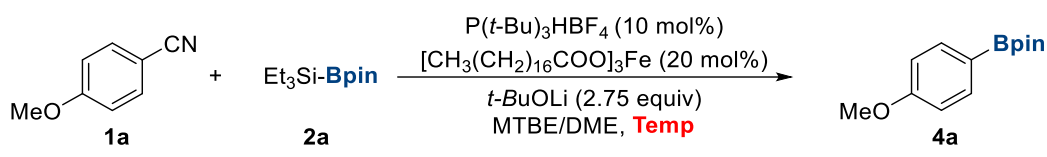
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), *t*-BuOLi (0.55 mmol, 2.75 equiv), THF/DME (0.5 mL/0.5 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S16. Screening of Solvents.^a

Entry	Solvent (1.0 mL)	4a , Yield ^b
1	THF/DME (0.5/0.5)	63%
2	THF/DME (0.4/0.6)	64%
3	THF/DME (0.3/0.7)	63%
4	THF/DME (0.2/0.8)	60%
5	THF/DME (0.1/0.9)	66%
6	MTBE/DME (0.1/0.9)	75%
7	MTBE/DME (0.2/0.8)	79% (78%)

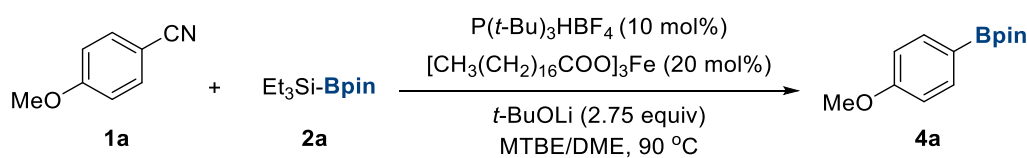
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), *t*-BuOLi (0.55 mmol, 2.75 equiv), Solvent (1.0 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard, the separation yield is shown in parentheses.

Table S17. Screening of Temperature.^a

		
Entry	Temp (°C)	4a, Yield ^b
1	120	55%
2	100	58%
3	90	79%
4	80	56%

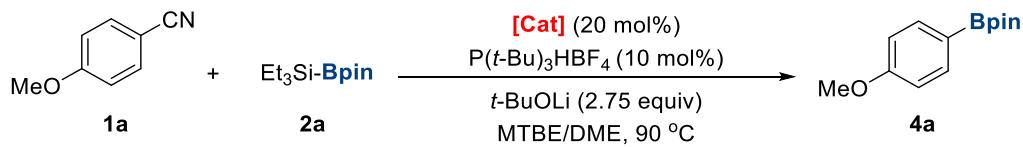
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), *t*-BuOLi (0.55 mmol, 2.75 equiv), MTBE/DME (0.2/0.8 mL), 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S18. Control Experiments of Iron-Catalyzed Borylation of 1a.^a

				
Entry	[Fe]	Base	Ligand	4a Yield ^b
1	[CH ₃ (CH ₂) ₁₆ COO] ₃ Fe	<i>t</i> -BuOLi	P(<i>t</i> -Bu) ₃ HBF ₄	79%
2	[CH ₃ (CH ₂) ₁₆ COO] ₃ Fe	<i>t</i> -BuOLi	-	47%
3	-	<i>t</i> -BuOLi	-	complex

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), *t*-BuOLi (0.55 mmol, 2.75 equiv), MTBE/DME (0.2/0.8 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Table S19. Evaluation of Other Transition-Metal Effect on the Borylation.^a

		
Entry	[Cat]	Yield ^b (4a)
1	FeCl ₂	21%
2	FeCl ₂ (99.99%)	17%
3	CuOAc	0%
4	Ni(OTf) ₃	0%
5	CoCl ₂	0%

^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (3.0 equiv), *t*-BuOLi (2.75 equiv), MTBE/DME (0.2/0.8 mL), 90 °C, 15 h, under an nitrogen atmosphere. ^bDetermined by ¹H NMR using mesitylene as an internal standard.

Mechanistic Studies

Radical Inhibition Experiments (Table S20-S21).

To gain some insights into the mechanism of this iron catalyzed C-CN bond activation reactions, radical inhibition experiments were conducted (Table S20-S21).

Table S20. Radical Inhibition Experiments of Iron-Catalyzed Borylation of **1a.^a**

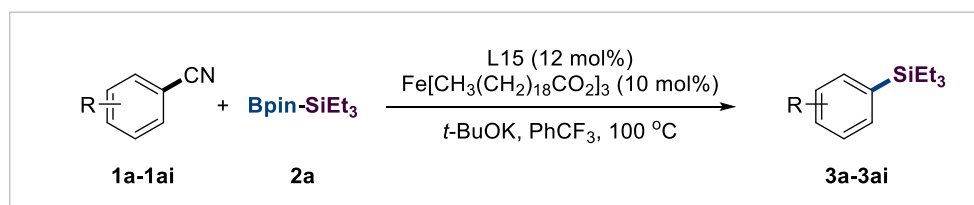
Entry	Additive	3a/4a Yield ^b
1	none	85% (80%)
2	TEMPO (1.0 equiv)	42%/0%
3	TEMPO (2.0 equiv)	19%/0%
4	BHT (1.0 equiv)	56%/0%
5	BHT (2.0 equiv)	0%/0%

Table S21. Radical Inhibition Experiments of Iron-Catalyzed Borylation of **1a.^a**

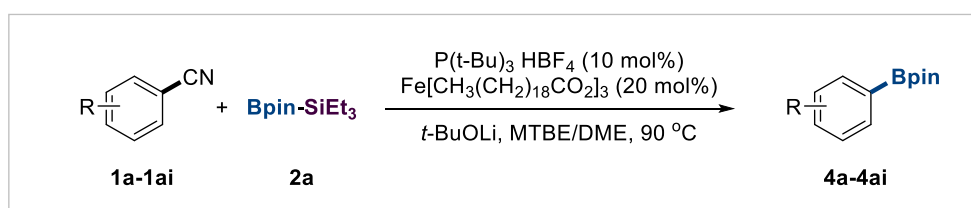
Entry	Additive	4a , Yield ^b
1	none	78%
2	TEMPO (0.5 equiv)	62%
3	TEMPO (1.5 equiv)	43%
4	TEMPO (2.5 equiv)	28%
5	TEMPO (3.0 equiv)	Trace
6	BHT (0.5 equiv)	33%
7	BHT (1.0 equiv)	0%

When the silylation and borylation reactions were conducted in the presence of a radical scavenger TEMPO or a radical inhibitor BHT, the efficiency of these transformations could be dramatically depressed, suggesting that organic radicals may be involved in these catalytic systems.

General Procedure of the Silylation and borylation of Nitriles:



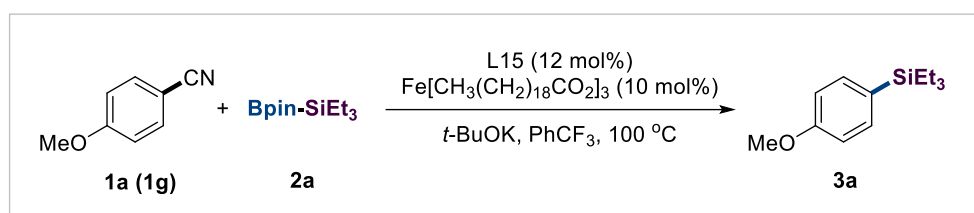
Decyanative Silylation of Nitriles: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with [CH₃(CH₂)₁₆COO]₃Fe (0.02 mmol, 18.1 mg, 0.1 equiv), **L15** (0.024 mmol, 10.8 mg, 0.12 equiv), *t*-BuOK (0.50 mmol, 56.1 mg, 2.5 equiv), **nitriles** (0.2 mmol, 26.6 mg, 1.0 equiv) in glove box, then moved it out of the glove box. The tube was evacuated and backfilled nitrogen three times, Et₃Si-Bpin (0.75 mmol, 3.75 equiv) and freshly distilled PhF₃ (2.5 mL) were then added under argon atmosphere. The reaction mixture stirred at 100 °C for 15 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound (**3a-3ai**).



Decyanative Borylation of Nitriles: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with [CH₃(CH₂)₁₆COO]₃Fe (0.04 mmol, 36.2 mg, 0.2 equiv), P(*t*-Bu)₃HBF₄ (0.02 mmol, 5.8 mg, 0.1 equiv), *t*-BuOLi (0.55 mmol, 44.0 mg, 2.75 equiv), **nitriles** (0.2 mmol, 26.6 mg, 1.0 equiv) in glove box, then moved it out of the glove box. The tube was evacuated and backfilled nitrogen three times, Et₃Si-Bpin

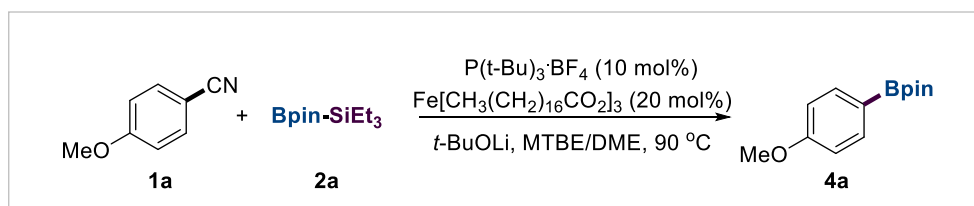
(0.6 mmol, 3.0 equiv) and freshly distilled MTBE (0.2 mL) and DME (0.8 mL) were then added under argon atmosphere. The reaction mixture stirred at 90 °C for 15 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound (**4a-4ai**).

Gram-Scale Synthesis of **3a**.



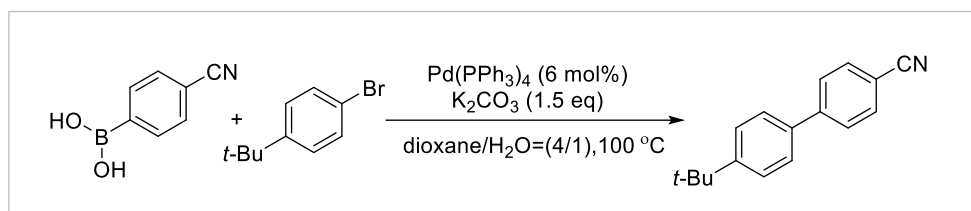
A 100 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with [CH₃(CH₂)₁₆COO]₃Fe (0.762 mmol, 0.690 g, 0.1 equiv), **L15** (0.914 mmol, 411.5 mg, 0.12 equiv), *t*-BuOK (19.05 mmol, 2.137 g, 2.5 equiv), **1a** (7.62 mmol, 1.015 g, 1.0 equiv) in glove box, then moved it out of the glove box. The tube was evacuated and backfilled nitrogen three times, Et₃Si-Bpin (28.58 mmol, 3.75 equiv) and freshly distilled PhF₃ (95.3 mL) were then added under argon atmosphere. The reaction mixture stirred at 100 °C for 15 h. The cooled solution was quenched with saturated NH₄Cl aqueous solution, then diluted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound **3a** (0.989 g, 53%).

Gram-Scale Synthesis of **4a**.



A 100 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_3\text{Fe}$ (1.50 mmol, 1.359 g, 0.2 equiv), $\text{P}(t\text{-Bu})_3\text{HBF}_4$ (0.75 mmol, 218 mg, 0.1 equiv), $t\text{-BuOLi}$ (20.65 mmol, 1.653 g, 2.75 equiv), **1a** (7.51 mmol, 1.008 g, 1.0 equiv) in glove box, then moved it out of the glove box. The tube was evacuated and backfilled nitrogen three times, **2a** (22.53 mmol, 3.0 equiv) and freshly distilled MTBE (7.51 mL) and DME (30.04 mL) were then added under argon atmosphere. The reaction mixture stirred at 90 °C for 16 h. The cooled solution was quenched with saturated NH_4Cl aqueous solution, then diluted with ethyl acetate and washed with saturated brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding compound **4a** (1.266 g, 72%).

General Procedure for the Synthesis of 4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-carbonitrile (**1z**)¹

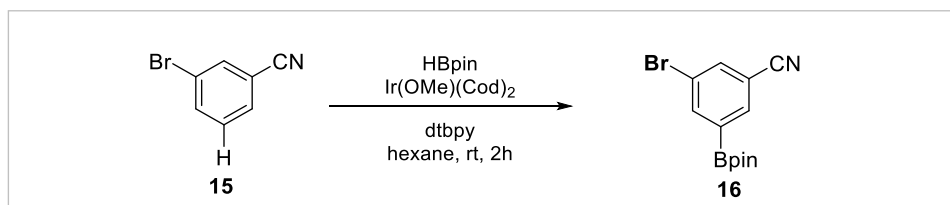


A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-Cyanophenylboronic acid (1.763 g, 12 mmol), 1-Bromo-4-(*tert*-butyl)benzene (2.131 g, 10 mmol), K_2CO_3 (2.07 g, 15 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.26 g, 3.8 mmol). The tube was evacuated and backfilled nitrogen three times, 1,4-Dioxane (20 mL) and water (6 mL) were then added under argon atmosphere. The mixture was heated to 100 °C for 24 h. The reaction mixture was cooled at room temperature and the solvent was removed under vacuum. The crude product thus obtained was portioned between water (20 mL) and ethyl acetate (30 mL). The organic layer was separated and the aqueous layer was further extracted with ethyl acetate (3 x 20 mL). The combined organics were dried over anhydrous sodium sulfate, filtered and evaporated under vacuum. The residue was purified by silica gel flash chromatography with (PE/EA = 10/1) to afford **1z** (1.788 g,

yield 76%). And compounds **1ab**, **1ac**, **1ad**, **1ae**, **1af**, **1ag**, **1ah** and **1ai** can be obtained in similar procedure.

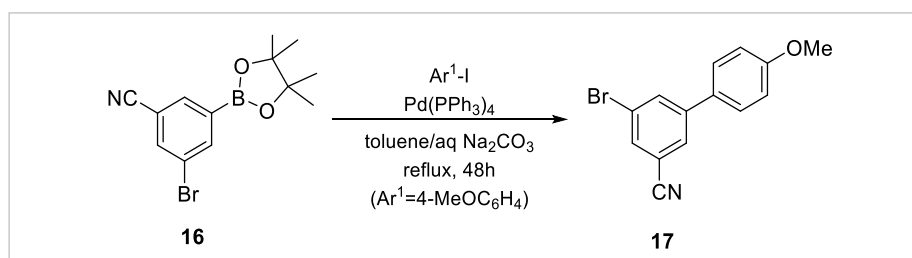
Downstream transformations

3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**16**)².



A procedure reported by Miyaura et al. was followed. A 100 mL flask was charged with [Ir(OMe)(cod)]₂ (198.8 mg, 0.3 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (161 mg, 0.6 mmol), and then flushed with nitrogen. Hexane (120 mL), pinacolborane (2.8 g, 22 mmol), and 3-bromobenzonitrile (3.6 g, 20 mmol) were added, and the mixture was stirred at 25 °C for 2 h. The reaction mixture was treated with water at room temperature, extracted with toluene, washed with brine, and dried over Na₂SO₄. Kugelrohr distillation in vacuo gave 3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile **16** (4.7 g, 76%).

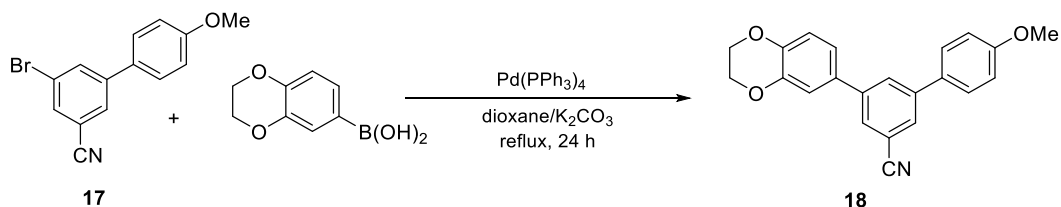
5-Bromo-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile (**17**).



1-Iodo-4-methoxybenzene (4.23 g, 18 mmol), 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- benzonitrile (4.7 g, 15 mmol), and Pd(PPh₃)₄ (261.5 mg, 0.23 mmol) were dissolved in a mixture of toluene (70 mL) and aq. 1 M Na₂CO₃ (70 mL), and the mixture was refluxed for 48 h. The contents were subjected to flash

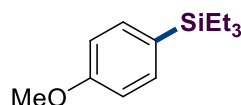
chromatography (hexane/CH₂Cl₂ = 1/1) to give 5-Bromo-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile **17** (2.749g, 53%) as a white solid.

5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile (18**).**



5-Bromo-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile (1.02 g, 3.56 mmol), K₂CO₃ (737.7 mg, 5.3 mmol), (2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)boronic acid (754 mg, 4.27 mmol), and Pd(PPh₃)₄ (24.7 mg, 0.0214 mmol). The tube was evacuated and backfilled nitrogen three times, 1,4-dioxane (8.57 mL) and water (2.14 mL) were then added under argon atmosphere. The mixture was heated to 100 °C for 24 h. The reaction mixture was extracted with ethyl acetate and dried over Na₂SO₄. The contents were subjected to flash chromatography (PE/EA = 10/1) to give 5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-carbonitrile **18** (1.026 g, 84%) as a white solid.

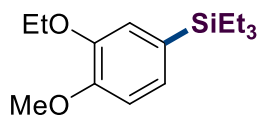
Experimental Procedures and Characterization Data for Silylated Products



Triethyl(4-methoxyphenyl)silane (3a**).** This compound is known.^[4] The product **3a** (35.5 mg, 80% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 3.83 (s, 3 H), 0.98 (t, *J* = 7.6 Hz, 9 H), 0.79 (q, *J* = 8.0 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 160.2, 135.6, 128.1, 113.5, 54.9, 7.4, 3.5.

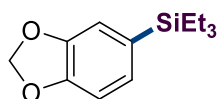


(4-Ethoxy-3-methoxyphenyl)triethylsilane (3b). The product **3b** (38.4 mg, 72% yield) was purified with silica gel chromatography (PE/EA = 100/1).

¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 8.0 Hz, 2 H), 6.98 (s, 1 H), 6.89 (d, *J* = 7.6 Hz, 2 H), 4.12 (q, *J* = 6.8 Hz, 2 H), 3.87 (s, 3 H), 1.46 (t, *J* = 7.2 Hz, 3 H), 0.96 (t, *J* = 8.0 Hz, 9 H), 0.77 (q, *J* = 8.0 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 137.2, 136.8, 131.9, 130.5, 21.4, 7.5, 3.4.

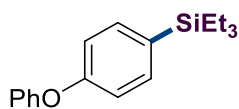
HRMS (ESI/Quadrupole): Calculated for C₁₅H₂₇O₂Si (M+H)⁺: 267.1780; Found: 267.1776.



Benzo[d][1,3]dioxol-4-yltriethylsilane (3c). This compound is known.^[4] The product **3c** (38.3 mg, 81% yield) was purified with silica gel chromatography (PE/EA = 100/1).

¹H NMR (400 MHz, CDCl₃) δ 6.97-6.95 (m, 2 H), 6.85 (d, *J* = 7.6 Hz, 2 H), 5.94 (s, 2 H), 0.95 (t, *J* = 8.0 Hz, 9 H), 0.75 (q, *J* = 7.6 Hz, 6 H).

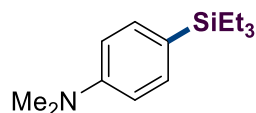
¹³C NMR (101 MHz, CDCl₃) δ 147.9, 147.1, 130.1, 127.9, 113.2, 108.3, 100.2, 7.2, 3.3.



Triethyl(4-phenoxyphenyl)silane (3d). This compound is known.^[5] The product **3d** (37.0 mg, 65% yield) was purified with silica gel chromatography (PE/EA = 100/1).

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 6.8 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.12 (t, *J* = 6.8 Hz, 1 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.00 (d, *J* = 6.4 Hz, 2 H), 0.98 (t, *J* = 8.0 Hz, 9 H), 0.80 (q, *J* = 7.6 Hz, 6 H).

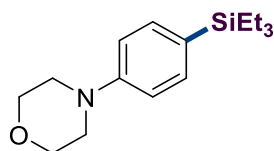
^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 156.8, 135.7, 131.3, 129.7, 123.4, 119.3, 117.8, 7.4, 3.5.



***N,N*-Dimethyl-4-(triethylsilyl)aniline (3e).** This compound is known.^[4] The product **3e** (32.5 mg, 69% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (600 MHz, CDCl_3) δ 7.39 (d, J = 7.2 Hz, 2 H), 7.76 (d, J = 7.6 Hz, 2 H), 2.98 (s, 6 H), 0.99 (t, J = 7.8 Hz, 9 H), 0.78 (q, J = 7.8 Hz, 6 H).

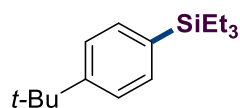
^{13}C NMR (101 MHz, CDCl_3) δ 150.8, 135.3, 122.4, 111.9, 40.2, 7.5, 3.6.



4-(4-(Triethylsilyl)phenyl)morpholine (3f). This compound is known.^[4] The product **3f** (41.1 mg, 74% yield) was purified with silica gel chromatography (PE/EA = 100/1).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 8.4 Hz, 2 H), 6.91 (t, J = 8.4 Hz, 2 H), 3.86 (t, J = 4.8 Hz, 4 H), 3.19 (t, J = 4.8 Hz, 4 H), 0.96 (t, J = 7.6 Hz, 9 H), 0.76 (q, J = 7.6 Hz, 6 H).

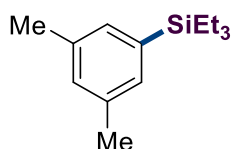
^{13}C NMR (101 MHz, CDCl_3) δ 151.4, 135.3, 126.9, 114.6, 66.9, 48.7, 7.4, 3.5.



4-(*tert*-Butyl)phenyltriethylsilane (3h). This compound is known.^[6] The product **3h** (32.3 mg, 65% yield) was purified with silica gel chromatography (Petroleum ether).

^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 1.33 (s, 9 H), 0.98 (t, J = 7.6 Hz, 9 H), 0.79 (q, J = 7.6 Hz, 6 H).

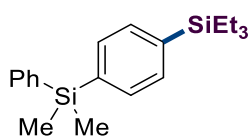
^{13}C NMR (101 MHz, CDCl_3) δ 151.5, 134.0, 124.6, 130.5, 34.6, 31.3, 7.5, 3.4.



(3,5-Dimethylphenyl)triethylsilane (3i). This compound is known.^[7] The product **3i** (22.0 mg, 50% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.10 (s, 2 H), 7.00 (s, 2 H), 2.33 (s, 6 H), 0.97 (t, *J* = 7.6 Hz, 9 H), 0.78 (q, *J* = 8.4 Hz, 6 H).

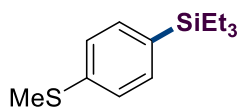
¹³C NMR (101 MHz, CDCl₃) δ 137.2, 136.8, 131.9, 130.5, 21.4, 7.5, 3.4.



(4-(Dimethyl(phenyl)silyl)phenyl)triethylsilane (3j). This compound is known.^[8] The product **3j** (26.8 mg, 41% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.55-7.52 (m, 2 H), 7.46 (dd, *J* = 8.0, 12.4 Hz, 4 H), 7.37-7.35 (m, 3 H), 0.96 (t, *J* = 7.6 Hz, 9 H), 0.78 (q, *J* = 8.0 Hz, 6 H), 0.55 (s, 6H).

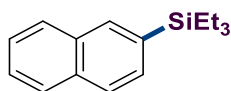
¹³C NMR (101 MHz, CDCl₃) δ 138.5, 138.4, 138.2, 134.2, 133.3, 129.1, 127.8, 7.4, 3.3, -2.5.



Triethyl(4-(methylthio)phenyl)silane (3l). This compound is known.^[9] The product **3l** (25.8 mg, 54% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.49 (s, 3 H), 0.96 (t, *J* = 7.6 Hz, 9 H), 0.78 (q, *J* = 8.4 Hz, 6 H).

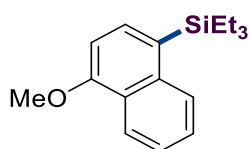
¹³C NMR (101 MHz, CDCl₃) δ 139.2 (2C), 134.6, 133.4, 125.5, 15.3, 7.4, 3.3.



Triethyl(naphthalen-2-yl)silane (3o). This compound is known.^[10] The product **3o** (24.2 mg, 50% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1 H), 7.86-7.81 (m, 3 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.49 (dd, *J* = 2.8 Hz, 6.0 Hz, 2 H), 1.02 (t, *J* = 7.6 Hz, 9 H), 0.90 (q, *J* = 7.6 Hz, 6 H).

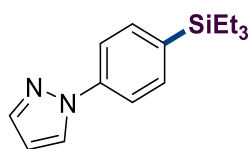
¹³C NMR (101 MHz, CDCl₃) δ 135.0, 134.8, 133.6, 132.9, 130.6, 128.0, 127.7, 126.7, 126.1, 125.7, 7.5, 3.4.



Triethyl(4-methoxynaphthalen-1-yl)silane (3r). This compound is known.^[6] The product **3r** (34.3 mg, 63% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.4 Hz, 1 H), 8.25 (d, *J* = 8.4 Hz, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 6.94 (s, 1 H), 4.07 (s, 3 H), 1.09 (t, *J* = 5.6 Hz, 6 H), 1.02 (q, *J* = 8.0 Hz, 9 H).

¹³C NMR (101 MHz, CDCl₃) δ 157.8, 145.2, 134.8, 128.9, 127.0, 125.4, 125.2, 122.6, 119.4, 108.9, 107.9, 55.9, 7.7, 3.3.

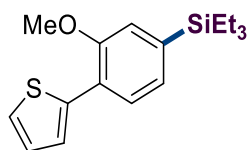


1-(4-(Triethylsilyl)phenyl)-1H-pyrazole (3s). This compound is unknown. The product **3s** (30.5 mg, 59% yield) was purified with silica gel chromatography (Petroleum ether).

^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1 H), 7.73 (s, 1 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H), 6.46 (t, J = 2.4 Hz, 1 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.81 (q, J = 8.4 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.1, 140.5, 135.6, 135.3, 126.6, 118.4, 107.6, 7.4, 3.3.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$: 259.1631; Found: 259.1628.

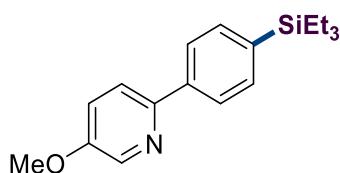


Triethyl(3-methoxy-4-(thiophen-2-yl)phenyl)silane (3u). This compound is unknown. The product **3u** (26.2 mg, 43% yield) was purified with silica gel chromatography (PE/EA=100/1).

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 7.6 Hz, 1 H), 7.52 (d, J = 3.2 Hz, 1 H), 7.32 (d, J = 4.8 Hz, 1 H), 7.12 (d, J = 7.2 Hz, 1 H), 7.10-7.08 (m, 2 H), 3.95 (s, 3 H), 1.00 (t, J = 8.0 Hz, 9 H), 0.82 (q, J = 8.0 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.9, 139.5, 138.1, 127.7, 126.9, 126.8, 125.4 (2C), 123.7, 116.9, 55.6, 7.4, 3.4.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{17}\text{H}_{25}\text{OSiS}$ ($\text{M}+\text{H}$) $^+$: 305.1935; Found: 305.1937.

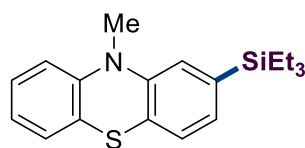


5-Methoxy-2-(4-(triethylsilyl)phenyl)pyridine (3v). This compound is unknown. The product **3v** (45.5 mg, 76% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1 H), 7.81 (dd, $J = 2.4, 8.4$ Hz, 1 H), 7.57 (d, $J = 8.0$ Hz, 2 H), 7.53 (d, $J = 8.0$ Hz, 2 H), 6.82 (d, $J = 8.4$ Hz, 1 H), 3.98 (s, 3 H), 0.99 (t, $J = 7.6$ Hz, 9 H), 0.82 (q, $J = 8.0$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.6, 145.0, 138.1, 137.5, 136.4, 134.9, 130.0, 125.9, 110.8, 53.6, 7.4, 3.3.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{18}\text{H}_{26}\text{NOSi}$ ($\text{M}+\text{H}$) $^+$: 300.1784; Found: 300.1786.

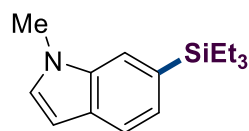


10-Methyl-2-(triethylsilyl)-10H-phenothiazine (3w). This compound is unknown. The product **3w** (40.0 mg, 61% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.20-7.18 (m, 1 H), 7.15-7.13 (m, 2 H), 7.05 (d, $J = 7.6$ Hz, 1 H), 6.94 (d, $J = 7.6$ Hz, 1 H), 6.90-6.89 (m, 2 H), 6.83 (d, $J = 8.0$ Hz, 1 H), 3.40 (s, 3 H), 0.97 (t, $J = 8.0$ Hz, 9 H), 0.78 (q, $J = 7.6$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.0, 145.0, 136.4, 128.4, 127.4, 127.1, 126.5, 124.4, 123.3, 122.3, 119.1, 114.1, 35.3, 7.4, 3.4.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{19}\text{H}_{26}\text{NOSi}$ ($\text{M}+\text{H}$) $^+$: 328.1555; Found: 300.1557.

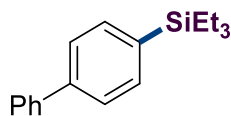


1-Methyl-6-(triethylsilyl)-1H-indole (3x). This compound is unknown. The product **3x** (39.3 mg, 80% yield) was purified with silica gel chromatography (PE/EA = 100/1).

^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 1 H), 7.22 (d, $J = 7.6$ Hz, 1 H), 7.03 (d, $J = 2.8$ Hz, 1 H), 6.46 (d, $J = 2.8$ Hz, 1 H), 3.80 (s, 3 H), 0.99 (t, $J = 7.2$ Hz, 9 H), 0.85 (q, $J = 8.0$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.6, 129.0 (3C), 124.7, 120.2, 114.9, 100.7, 32.8, 7.6, 3.7.

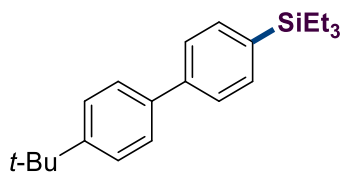
HRMS (ESI/Quadrupole): Calculated for $\text{C}_{15}\text{H}_{24}\text{NSi}$: $(\text{M}+\text{H})^+$: 246.1678; Found: 246.1678.



[1,1'-Biphenyl]-4-yltriethylsilane (3y). This compound is known.^[4] The product **3y** (34.9 mg, 65% yield) was purified with silica gel chromatography (Petroleum ether).

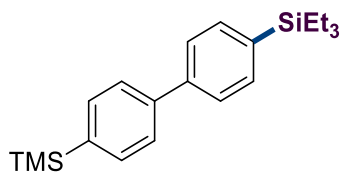
^1H NMR (400 MHz, CDCl_3) δ 7.63-7.59 (m, 5 H), 7.45 (t, J = 8.0 Hz, 2 H), 7.36 (t, J = 7.6 Hz, 1 H), 1.01 (t, J = 8.0 Hz, 9 H), 0.84 (q, J = 8.4 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.4, 141.2, 136.2, 134.4, 128.7, 127.3, 127.1, 126.4, 7.4, 3.4.



(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)triethylsilane (3z). This compound is known.^[4] The product **3z** (54.5 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.57 (m, 6 H), 7.50 (d, J = 7.6 Hz, 2 H), 1.40 (s, 9 H), 1.03 (t, J = 7.6 Hz, 9 H), 0.85 (q, J = 7.6 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.3, 141.3, 138.3, 135.8, 134.6, 126.8, 126.3, 125.7, 34.5, 31.4, 7.5, 3.4.

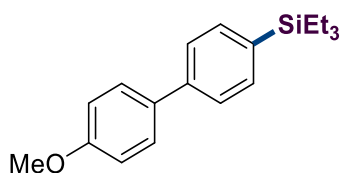


Triethyl(4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)silane (3ab). This compound is unknown. The product **3ab** (43.6 mg, 64% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 4 H), 7.58 (s, 4 H), 1.01 (t, *J* = 8.0 Hz, 9 H), 0.83 (q, *J* = 7.6 Hz, 6 H), 0.31 (s, 9 H) .

¹³C NMR (101 MHz, CDCl₃) δ 141.6, 141.4, 139.2, 136.3, 134.7, 133.8, 126.5, 126.4, 116.7, 7.4, 3.4, -1.1.

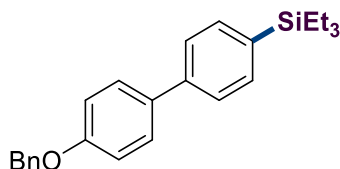
HRMS (ESI/Quadrupole): Calculated for C₂₁H₃₃Si₂ (M+H)⁺: 341.2121; Found: 341.2116.



Triethyl(4'-methoxy-[1,1'-biphenyl]-4-yl)silane (3ac). This compound is known.^[4] The product **3ac** (43.6 mg, 73% yield) was purified with silica gel chromatography (PE/EA = 100/1).

¹H NMR (400 MHz, CDCl₃) δ 7.56-7.54 (m, 8 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H), 1.00 (t, *J* = 7.6 Hz, 9 H), 0.82 (q, *J* = 8.4 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 159.4, 141.0, 135.4, 134.7, 128.1, 125.9, 114.2, 55.3, 7.5, 3.4.

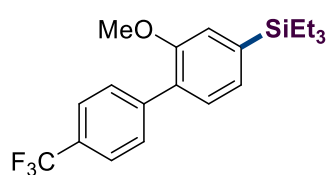


(4'-(Benzyloxy)-[1,1'-biphenyl]-4-yl)triethylsilane (3ad). This compound is unknown. The product **3ad** (53.2 mg, 71% yield) was purified with silica gel chromatography (PE/EA = 100/1).

^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (m, 6 H), 7.47 (d, $J = 7.2$ Hz, 2 H), 7.41 (t, $J = 7.6$ Hz, 2 H), 7.36 (d, $J = 7.2$ Hz, 1 H), 7.06 (d, $J = 8.8$ Hz, 2 H), 5.12 (s, 2 H), 1.00 (t, $J = 7.6$ Hz, 9 H), 0.83 (q, $J = 8.0$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 140.9, 137.0, 135.5, 134.7, 133.9, 128.6, 128.1, 128.0, 127.5, 126.0, 70.1, 7.4, 3.4.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{25}\text{H}_{31}\text{OSi}$ ($\text{M}+\text{H}$) $^+$: 375.2144; Found: 375.2140.

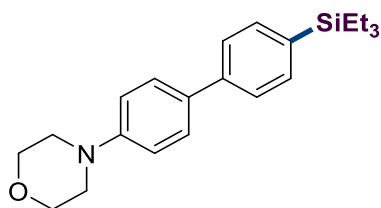


Triethyl(2-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)silane (3af). This compound is unknown. The product **3af** (30.05 mg, 41% yield) was purified with silica gel chromatography (PE/EA = 100/1).

^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 8.8, 12.0$ Hz, 4 H), 7.49 (d, $J = 8.0$ Hz, 1 H), 7.38 (s, 1 H), 7.01 (d, $J = 8.0$ Hz, 1 H), 3.82 (s, 3 H), 0.98 (t, $J = 8.0$ Hz, 9 H), 0.79 (q, $J = 7.6$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.0, 142.5, 136.6, 135.7, 128.8, 128.6, 124.9 (q, $J_{\text{CF}} = 3.7$ Hz), 124.8 (2C), 110.7, 55.4, 7.4, 3.5.

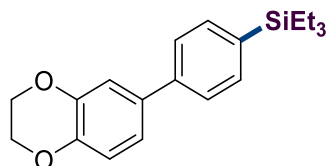
HRMS (ESI/Quadrupole): Calculated for $\text{C}_{20}\text{H}_{26}\text{OSiF}_3$ ($\text{M}+\text{H}$) $^+$: 367.1705; Found: 367.1696.



4-(4'-(Triethylsilyl)-[1,1'-biphenyl]-4-yl)morpholine (3ag). This compound is known.^[11] The product **3ag** (41.7 mg, 59% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.57-7.56 (m, 6 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.89 (t, *J* = 4.8 Hz, 4 H), 3.22 (t, *J* = 4.8 Hz, 4 H), 1.01 (t, *J* = 7.6 Hz, 9 H), 0.83 (q, *J* = 7.6 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 150.3, 141.0, 135.2, 134.7, 132.6, 127.8, 125.8, 115.7, 66.9, 49.1, 7.5, 3.4.

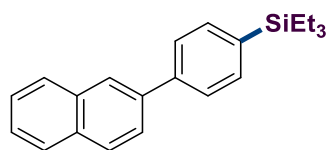


(4-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)phenyl)triethylsilane (3ah). This compound is unknown. The product **3ah** (42.4 mg, 65% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 4 H), 7.14 (d, *J* = 2.0 Hz, 1 H), 7.10 (dd, *J* = 2.4, 8.4 Hz, 1 H), 4.30 (s, 4 H), 0.99 (t, *J* = 7.2 Hz, 9 H), 0.81 (q, *J* = 8.8 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 143.6, 143.2, 140.7, 135.7, 134.6, 126.0, 120.1, 117.5, 115.8, 64.4, 7.4, 3.4.

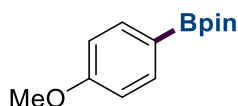
HRMS (ESI/Quadrupole): Calculated for C₂₀H₂₇O₂Si (M+H)⁺: 327.1780; Found: 327.1780.



Triethyl(4-(naphthalen-2-yl)phenyl)silane (3ai). This compound is known.^[4] The product **3ai** (33.1 mg, 52% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1 H), 7.91 (t, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.53-7.47 (m, 2 H), 1.02 (t, *J* = 7.6 Hz, 9 H), 0.85 (q, *J* = 7.6 Hz, 6 H).

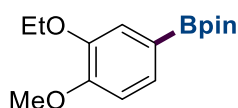
¹³C NMR (101 MHz, CDCl₃) δ 141.3, 138.5, 136.4, 134.8, 133.7, 132.6, 128.4, 128.2, 127.6, 126.6, 125.9, 125.8, 125.5, 7.5, 3.4.



2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a). This compound is known.^[12] The product **4a** (36.5 mg, 78% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 3.83 (s, 3 H), 1.33 (s, 12 H).

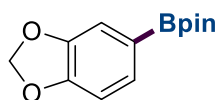
¹³C NMR (101 MHz, CDCl₃) δ 162.1, 136.5, 113.3, 83.5, 55.1, 24.8.



2-(3-Ethoxy-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b). This compound is known.^[12] The product **4b** (35.0 mg, 63% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 1 H), 7.28 (s, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 4.14 (q, *J* = 6.8 Hz, 2 H), 3.88 (s, 3 H), 1.46 (t, *J* = 6.8 Hz, 3 H), 1.33 (s, 12 H).

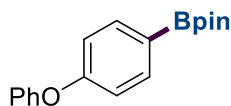
¹³C NMR (101 MHz, CDCl₃) δ 151.9, 147.7, 128.5, 118.1, 110.7, 83.6, 64.2, 55.8, 24.8, 14.8.



2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c). This compound is known.^[13] The product **4c** (25.8 mg, 52% yield) was purified with silica gel chromatography (PE/EA = 50/1).

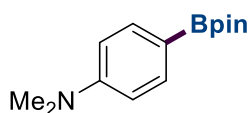
¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 1 H), 7.24 (s, 1 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 5.95 (s, 2 H), 1.33 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 150.1, 147.2, 129.7, 113.9, 108.3, 100.7, 83.7, 24.8.



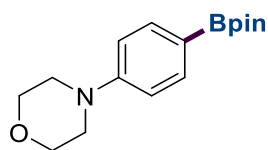
4,4,5,5-Tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (4d). This compound is known.^[14] The product **4d** (41.5 mg, 70% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 8.8 Hz, 2 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 7.03 (d, *J* = 8 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 1.34 (s, 12 H).
¹³C NMR (101 MHz, CDCl₃) δ 160.2, 156.5, 136.6, 129.8, 123.6, 119.4, 117.7, 83.7, 24.8.



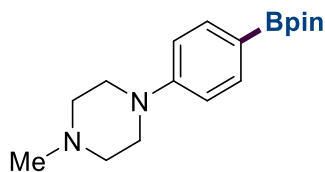
***N,N*-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4e).** This compound is known.^[15] The product **4e** (26.2 mg, 53 % yield) was purified with silica gel chromatography (PE/EA = 20/1).

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 2 H), 6.69 (d, *J* = 8.4 Hz, 2 H), 2.99 (s, 6 H), 1.33 (s, 12 H).
¹³C NMR (101 MHz, CDCl₃) δ 152.6, 136.1, 111.2, 83.1, 40.1, 24.8.



4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (4f). This compound is known.^[16] The product **4f** (42.8 mg, 74% yield) was purified with silica gel chromatography (PE/EA = 20/1).

¹H NMR (600 MHz, CDCl₃) δ 7.72 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 3.85 (t, *J* = 4.8 Hz, 4 H), 3.22 (t, *J* = 4.8 Hz, 4 H), 1.33 (s, 12 H).
¹³C NMR (101 MHz, CDCl₃) δ 153.3, 136.1, 114.0, 83.4, 66.8, 48.4, 24.8.

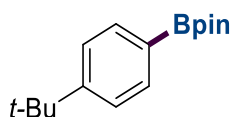


1-Methyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine

(4g). This compound is known.^[17] The product **4g** (45.3 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 3.28 (t, *J* = 4.8 Hz, 4 H), 2.56 (t, *J* = 4.8 Hz, 4 H), 2.34 (s, 3 H), 1.33 (s, 12 H).

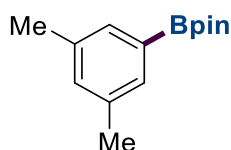
¹³C NMR (101 MHz, CDCl₃) δ 153.3, 136.1, 114.3, 83.4, 54.9, 48.0, 46.1, 24.8.



2-(4-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h). This compound is known.^[18] The product **4h** (30.2 mg, 58% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 8 Hz, 2 H), 1.33 (s, 12 H), 1.32 (s, 9 H).

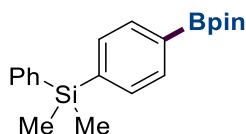
¹³C NMR (101 MHz, CDCl₃) δ 154.4, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8.



2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i). This compound is known.^[19] The product **4i** (26.5 mg, 57% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 2 H), 7.10 (s, 1 H), 2.32 (s, 6 H), 1.34 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 137.1, 133.0, 132.4, 83.7, 24.8, 21.1.

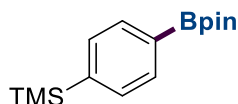


Dimethyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane

(4j). This compound is known.^[20] The product **4j** (35.2 mg, 52% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.51-7.49 (m, 3 H), 1.34 (s, 12 H), 0.55 (s, 6 H).

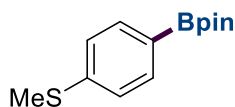
¹³C NMR (101 MHz, CDCl₃) δ 141.9, 138.0, 134.2, 133.9, 133.5, 129.1, 127.8, 83.8, 24.8, -2.5.



Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (4k). This compound is known.^[21] The product **4k** (33.2 mg, 60% yield) was purified with silica gel chromatography (PE/EA = 60/1).

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 1.34 (s, 12 H), 0.27 (s, 12 H).

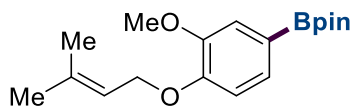
¹³C NMR (101 MHz, CDCl₃) δ 144.3, 133.8, 132.6, 83.7, 24.8, -1.26.



4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4l). This compound is known.^[22] The product **4l** (26.0 mg, 52% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 8 Hz, 2 H), 2.49 (s, 3H), 1.34 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 142.6, 135.1, 125.0, 83.7, 24.8, 15.0..

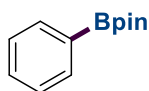


2-(3-Methoxy-4-((3-methylbut-2-en-1-yl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m). This compound is unknown. The product **4m** (35.5 mg, 43% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 8.0 Hz, 1 H), 7.30 (s, 1 H), 6.87 (d, J = 8.0 Hz, 1 H), 5.54 (t, J = 6.0 Hz, 1 H), 4.60 (d, J = 6.8 Hz, 2 H), 3.87 (s, 3H), 1.77 (s, 3 H), 1.74 (s, 3 H), 1.33 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 152.0, 147.7, 137.8, 128.5, 119.9, 118.1, 110.6, 83.6, 65.5, 55.7, 25.9, 24.9, 18.3.

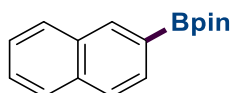
HRMS (ESI/Quadrupole): Calculated for $\text{C}_{18}\text{H}_{27}\text{BO}_4$ ($\text{M}+\text{H}$) $^+$: 341.1900; Found: 341.1907.



4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4n). This compound is known.^[12] The product **4n** (24.5 mg, 60% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 7.2 Hz, 2 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.37 (t, J = 7.2 Hz, 2 H), 1.35 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 134.8, 131.3, 127.7, 83.8, 24.9.

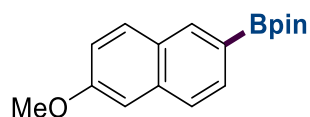


4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (4o). This compound is known.^[23] The product **4o** (25.4 mg, 50% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1 H), 7.89 (d, J = 7.6 Hz, 1 H), 7.84-7.83 (m, 3 H), 7.54-7.46 (m, 2 H), 1.40 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.3, 135.0, 132.8, 130.4, 128.7, 127.7, 127.0, 125.8,

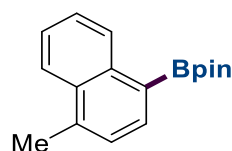
83.9, 24.9.



2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4p). This compound is known.^[24] The product **4p** (35.2 mg, 62% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1 H), 7.79 (dd, *J* = 5.6, 10.4 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.14-7.12 (m, 2 H), 7.12 (s, 1 H), 3.93 (s, 3 H), 1.39 (s, 12 H).

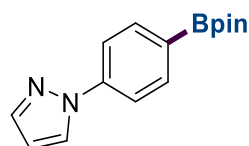
¹³C NMR (101 MHz, CDCl₃) δ 158.5, 136.4, 136.0, 131.1, 130.2, 128.4, 125.9, 118.6, 105.6, 83.8, 55.3, 24.9.



4,4,5,5-Tetramethyl-2-(4-methylnaphthalen-1-yl)-1,3,2-dioxaborolane (4q). This compound is known.^[25] The product **4q** (41.8 mg, 78% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 8.80 (d, *J* = 8.0 Hz, 2 H), 8.00 (dd, *J* = 9.2, 15.2 Hz, 2 H), 7.56-7.50 (m, 2 H), 7.33 (d, *J* = 6.8 Hz, 1 H), 2.72 (s, 3 H), 1.42 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 138.1, 137.0, 135.6, 132.4, 129.0, 126.0, 125.3, 124.2, 83.6, 24.9, 20.0.

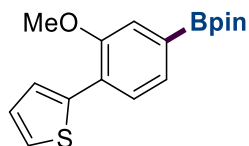


1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrazole (4s). This compound is known.^[12] The product **4s** (29.2 mg, 54% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1 H), 7.90 (d, *J* = 7.6 Hz, 2 H), 7.73 (d, *J* = 4.8

Hz, 2 H), 7.70 (s, 1 H), 6.47 (s, 1 H), 1.36 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.2, 141.3, 136.1, 126.7, 118.0, 107.8, 83.9, 24.9.



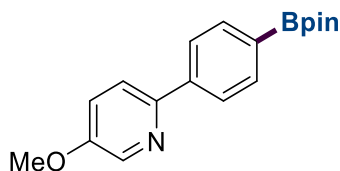
2-(3-Methoxy-4-(thiophen-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(4t). This compound is unknown. The product **4t** (32.25 mg, 51% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 7.6 Hz, 1 H), 7.58-7.57 (m, 1 H), 7.44 (d, J = 7.6 Hz, 1 H), 7.40 (s, 1 H), 7.35 (d, J = 4.8 Hz, 1H), 7.09 (dd, J = 4.0, 5.2 Hz, 1 H), 3.98 (s, 3 H), 1.36 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.9, 139.3, 127.6, 127.5, 126.8, 126.6, 125.9, 125.8, 117.3, 83.9, 55.6, 24.9.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{17}\text{H}_{22}\text{BO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 317.1383; Found: 317.1386.



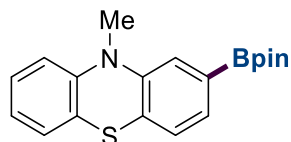
5-Methoxy-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine

(4v). This compound is unknown. The product **4v** (33.0 mg, 53% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, J = 2.4 Hz, 1 H), 7.88 (d, J = 1.6 Hz, 2 H), 7.81 (dd, J = 2.4 Hz, 8.8 Hz, 1 H), 6.82 (d, J = 8.4 Hz, 1 H), 3.98 (s, 3 H), 1.36 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.8, 145.1, 140.5, 137.4, 135.4, 129.9, 125.9, 110.8, 83.9, 53.5, 24.9.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{18}\text{H}_{23}\text{BNO}_3$ ($\text{M}+\text{H}$) $^+$: 312.1771; Found: 312.1778.



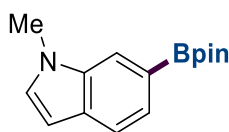
10-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine

(4w). This compound is unknown. The product **4w** (27.14 mg, 40% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 7.8 Hz, 1 H), 7.20 (s, 1 H), 7.17-7.11 (m, 3 H), 6.91 (t, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 7.8 Hz, 1 H), 3.42 (s, 3 H), 1.34 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 145.9, 145.1, 129.1, 127.5, 127.4, 127.0, 126.5, 123.0, 122.3, 119.5, 114.1, 83.8, 35.4, 24.8.

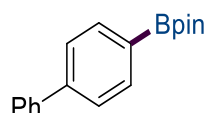
HRMS (ESI/Quadrupole): Calculated for C₁₉H₂₃BNO₂S (M+H)⁺: 340.1548; Found: 340.1543.



1-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (4x). This compound is known.^[26] The product **4x** (22.1 mg, 43% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 2.8 Hz, 1 H), 6.48 (d, *J* = 2.8 Hz, 1 H), 3.83 (s, 3 H), 1.38 (s, 12 H).

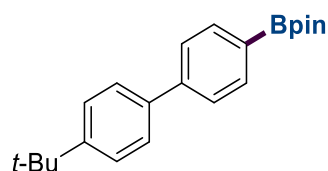
¹³C NMR (101 MHz, CDCl₃) δ 136.4, 131.0, 130.1, 125.1, 120.1, 116.1, 101.0, 83.5, 33.0, 24.9.



2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4y). This compound is known.^[12] The product **4y** (36.4 mg, 65% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2 H), 7.62 (d, J = 5.6 Hz, 4 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.35 (t, J = 7.2 Hz, 1 H), 1.36 (s, 12 H).

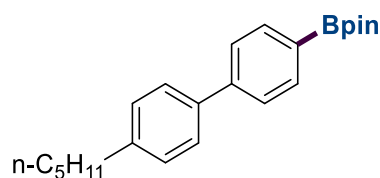
^{13}C NMR (101 MHz, CDCl_3) δ 143.9, 141.0, 135.3, 128.8, 127.5, 127.2, 126.4, 83.8, 24.9.



2-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4z). This compound is known.^[12] The product **4z** (27.6 mg, 41% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 3.6 Hz, 1 H), 7.59 (dd, J = 8.0, 14.4 Hz, 4 H), 7.48 (t, J = 8.0 Hz, 2 H), 1.36 (s, 12 H + 9 H, two signals overlapped).

^{13}C NMR (101 MHz, CDCl_3) δ 151.1, 144.2, 138.5, 135.7, 127.3, 126.8, 126.2, 84.2, 31.8, 25.3.

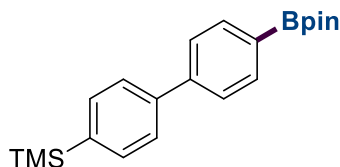


4,4,5,5-Tetramethyl-2-(4'-pentyl-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (4aa). This compound is unknown. The product **4aa** (41.3 mg, 59% yield) was purified with silica gel chromatography (PE/EA = 50/1).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.26 (d, J = 2.4 Hz, 1 H), 2.64 (t, J = 8.0 Hz, 2 H), 1.64 (t, J = 8.4 Hz, 2 H), 1.36 (s, 12 H), 0.90 (t, J = 6.4 Hz, 4 H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.8, 141.5, 137.2, 134.2, 127.8, 126.0, 125.2, 82.8, 30.5, 30.2, 28.7, 23.9, 13.0.

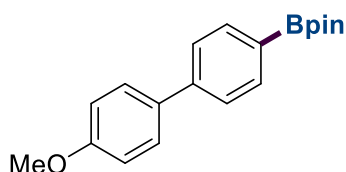
HRMS (ESI/Quadrupole): Calculated for $C_{23}H_{32}BO_2$ ($M+H$)⁺: 351.2495; Found: 351.2486.



Trimethyl(4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)silane (4ab). This compound is known.^[27] The product **4ab** (35.9 mg, 51% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 2 H), 7.64-7.62 (m, 6 H), 1.37 (s, 12 H), 0.31 (s, 9 H).

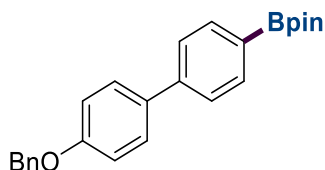
¹³C NMR (101 MHz, $CDCl_3$) δ 143.8, 141.4, 139.7, 135.3, 133.8, 126.5, 126.4, 83.8, 24.9, -1.1.



2-(4'-(4-Methoxyphenyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ac). This compound is known.^[12] The product **4ac** (34.7 mg, 56% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2 H), 7.56 (dd, J = 2.8 Hz, 8.8 Hz, 4 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.85 (s, 3 H), 1.36 (s, 12 H).

¹³C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.2, 143.5, 135.2, 128.2, 126.0, 114.2, 83.7, 77.3, 77.0, 55.3, 24.8.

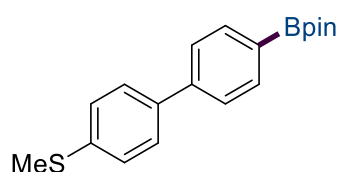


2-(4'-(Benzyloxy)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(4ad). This compound is known.^[12] The product **4ad** (50.2 mg, 65% yield) was purified with silica gel chromatography (PE/EA = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 1.2 Hz, 2 H), 7.57-7.55 (m, 1 H), 7.46 (d, J = 7.2 Hz, 2 H), 7.40 (t, J = 7.2 Hz, 2 H), 7.34 (d, J = 7.2 Hz, 1 H), 7.05 (d, J = 8.4 Hz, 2 H), 5.11 (s, 2 H), 1.36 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 158.6, 143.4, 137.0, 135.2, 133.7, 128.6, 128.3, 128.0, 127.5, 126.0, 115.2, 83.8, 70.1, 24.9.

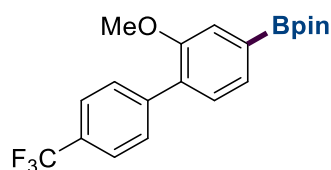


4,4,5,5-Tetramethyl-2-(4'-(methylthio)-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane

(4ae). This compound is known.^[28] The product **4ae** (36.5 mg, 56% yield) was purified with silica gel chromatography (PE/EA = 60/1).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 7.6 Hz, 2 H), 7.57 (dd, J = 8.0 Hz, 13.2 Hz, 4 H), 7.33 (d, J = 8.0 Hz, 2 H), 2.52 (s, 3 H), 1.36 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 143.1, 138.0, 137.7, 135.3, 127.5, 126.8, 126.1, 83.8, 24.9, 15.8.

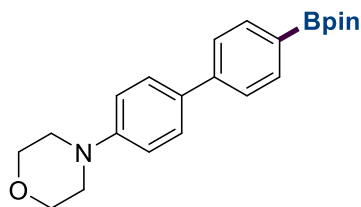


2-(2-Methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af). This compound is unknown. The product **4af** (40.1 mg, 53% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 1.6 Hz, 1 H), 7.76 (s, 1 H), 7.64 (s, 4 H), 7.00 (d, J = 8.0 Hz, 1 H), 3.85 (s, 3 H), 1.34 (s, 12 H).

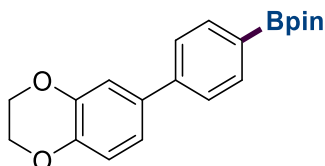
¹³C NMR (101 MHz, CDCl₃) δ 159.0, 154.6, 142.1, 137.5 (q, J = 32.4 Hz), 136.6, 130.0, 129.0, 125.8 (q, J = 3.7 Hz), 124.8, 110.6, 83.8, 55.5, 24.9.

HRMS (ESI/Quadrupole): Calculated for $C_{20}H_{23}BO_3F_3$ ($M+H$)⁺: 379.1692; Found: 379.1698.



4-(4'-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)morpholine (4ag). This compound is known.^[12] The product **4ag** (49.7 mg, 68% yield) was purified with silica gel chromatography (PE/EA = 10/1).

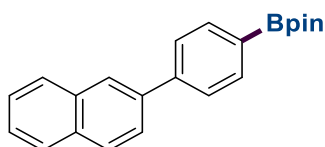
¹H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2 H), 7.57 (t, J = 5.2 Hz, 4 H), 6.98 (d, J = 8.0 Hz, 2 H), 3.89 (t, J = 4.8 Hz, 4 H), 3.22 (t, J = 4.4 Hz, 4 H), 1.36 (s, 12 H).
¹³C NMR (101 MHz, $CDCl_3$) δ 150.8, 143.4, 135.2, 132.3, 127.9, 125.7, 115.7, 83.7, 66.9, 49.1, 24.9.



2-(4-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ah). This compound is unknown. The product **4ah** (36.5 mg, 54% yield) was purified with silica gel chromatography (PE/EA = 20/1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2 H), 7.55 (d, J = 7.6 Hz, 2 H), 7.14-7.10 (m, 2 H), 6.93 (d, J = 8.4 Hz, 1 H), 4.30 (s, 4 H), 1.36 (s, 12 H).
¹³C NMR (101 MHz, $CDCl_3$) δ 143.7, 143.4, 143.2, 135.2, 126.0, 120.2, 117.6, 115.9, 83.8, 64.4, 24.9.

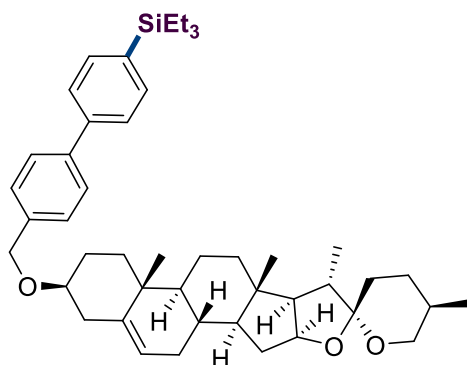
HRMS (ESI/Quadrupole): Calculated for $C_{20}H_{24}BO_4$ ($M+H$)⁺: 339.1768; Found: 339.1765.



4,4,5,5-Tetramethyl-2-(4-(naphthalen-2-yl)phenyl)-1,3,2-dioxaborolane (4ai). This compound is known.^[29] The product **4ai** (33.0 mg, 50% yield) was purified with silica gel chromatography (Petroleum ether).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1 H), 7.94-7.90 (m, 4 H), 7.87 (d, *J* = 6.8 Hz, 2 H), 7.79-7.73 (m, 3 H), 7.53-7.47 (m, 2 H), 1.34 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 143.7, 138.3, 135.3, 133.6, 132.8, 128.4, 127.6, 126.7, 126.3, 126.0, 125.9, 125.5, 83.8, 24.9.

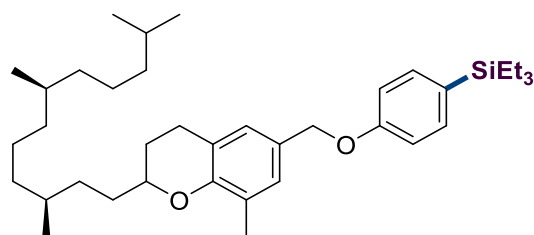


Triethyl(4'-((((4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)silane (5). The product **5** (58.4 mg, 42% yield) was purified with silica gel chromatography (PE/EA = 15/1).

¹H NMR (400 MHz, CDCl₃) δ 7.59-7.57 (m, 6 H), 7.42 (d, *J* = 7.2 Hz, 2 H), 5.36 (d, *J* = 2.0 Hz, 1 H), 4.60 (s, 2 H), 4.41 (q, *J* = 6.8 Hz, 2 H), 3.47 (d, *J* = 9.6 Hz, 2 H), 3.39 (d, *J* = 11.2 Hz, 1 H), 3.35-3.29 (m, 2 H), 2.46 (t, *J* = 11.2 Hz, 1 H), 2.00-1.98 (m, 4 H), 1.89-1.86 (m, 2 H), 1.79-1.72 (m, 3 H), 1.67-1.43 (m, 13 H), 1.04-0.97 (m, 13 H), 0.85-0.79 (m, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 141.0, 140.2, 137.9, 136.0, 134.5, 127.9, 127.0, 126.1, 121.2, 109.1, 80.7, 78.4 (2C), 69.5, 66.7, 61.9, 56.3, 49.9, 41.4, 40.1, 39.6, 39.0, 37.0, 36.9, 31.9, 31.7, 31.3, 30.1, 28.6, 28.3, 20.7, 19.3, 17.0, 16.1, 14.4, 7.3, 3.2.

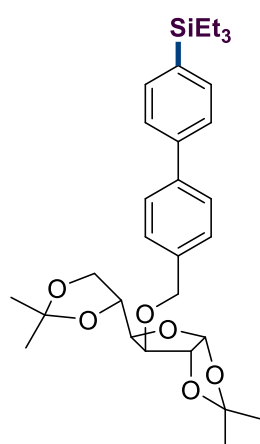
HRMS (ESI/Quadrupole): Calculated for $C_{46}H_{67}O_3Si$ ($M+H$)⁺: 695.48540; Found: 695.48782.



Triethyl(4-((8-methyl-2-((3S,7S)-3,7,11-trimethyldodecyl)chroman-6-yl)methoxy)phenyl)silane (6). The product **6** (52.1 mg, 45% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 2 H), 7.41 (d, J = 7.6 Hz, 2 H), 4.95 (s, 2 H), 2.71 (t, J = 5.6 Hz, 2 H), 2.15 (s, 3 H), 1.83-1.69 (m, 3 H), 1.56-1.49 (m, 5 H), 1.43-1.33 (m, 7 H), 1.16-1.05 (m, 9 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.87-0.78 (m, 18 H).
¹³C NMR (101 MHz, $CDCl_3$) δ 182.9, 151.4, 146.3, 138.0, 136.9, 134.4, 126.8, 120.9, 115.6, 112.1, 75.6, 70.6, 39.9, 39.4, 37.4, 37.3, 32.8, 32.7, 31.3, 27.9, 24.8, 24.4, 24.1, 22.7, 22.6, 21.0, 19.8, 19.7, 16.2, 7.4, 3.3.

HRMS (ESI/Quadrupole): Calculated for $C_{38}H_{63}O_2Si$ ($M+H$)⁺: 579.4597; Found: 579.4596.

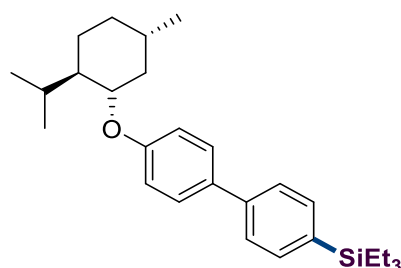


(4'-((((3aR,5R)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)triethylsilane (7). The product **7** (55.2 mg, 51% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.60-7.57 (m, 6 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 5.92 (d, *J* = 3.2 Hz, 1 H), 4.71 (dd, *J* = 11.6, 18.8 Hz, 2 H), 4.62 (d, *J* = 3.2 Hz, 1 H), 4.41 (dd, *J* = 6.4, 13.6 Hz, 1 H), 4.17-4.12 (m, 2 H), 4.06-4.00 (m, 2 H), 1.50 (s, 3 H), 1.44 (s, 3 H), 1.39 (s, 3 H), 1.32 (s, 3 H), 1.00 (t, *J* = 7.6 Hz, 9 H), 0.83 (q, *J* = 7.6 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 149.9, 140.8, 136.7, 136.4, 134.7, 128.1, 127.1, 126.3, 111.8, 109.0, 105.3, 82.7, 81.7, 81.3, 72.6, 72.1, 67.4, 26.8, 26.2, 25.5, 7.4, 3.4.

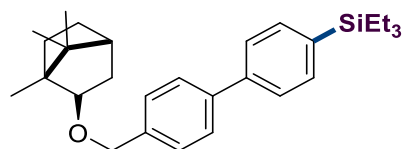
HRMS (ESI/Quadrupole): Calculated for C₃₁H₄₄O₆NaSi (M+Na)⁺: 563.2806; Found: 563.2808.



Triethyl(4'-((((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)-[1,1'-biphenyl]-4-yl)silane (8). The product **8** (36.4 mg, 43% yield) was purified with silica gel chromatography (PE/EA = 50/1). **¹H NMR** (400 MHz, CDCl₃) δ 7.59 -7.57 (m, 6 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 4.70 (d, *J* = 11.6 Hz, 1 H), 4.44 (d, *J* = 11.6 Hz, 1 H), 3.20 (td, *J* = 4.0, 10.4 Hz, 1 H), 2.38 -2.23 (m, 1 H), 2.22 (d, *J* = 12.0 Hz, 1 H), 1.68-1.61 (m, 2 H), 1.34-1.23 (m, 3 H), 1.17-1.12 (m, 1 H), 1.01-0.92 (m, 16 H), 0.82 (q, *J* = 8.0 Hz, 5 H), 0.73 (d, *J* = 6.8 Hz, 3 H).

¹³C NMR (101 MHz, CDCl₃) δ 141.0, 140.8, 136.7, 136.4, 134.7, 128.1, 127.1, 126.3, 111.8, 109.0, 105.3, 82.7, 81.7, 81.3, 72.5, 72.1, 67.4, 26.8, 26.2, 25.5, 7.4, 3.4.

HRMS (ESI/Quadrupole): Calculated for C₂₈H₄₃OSi (M+H)⁺: 423.3083; Found: 423.3081.

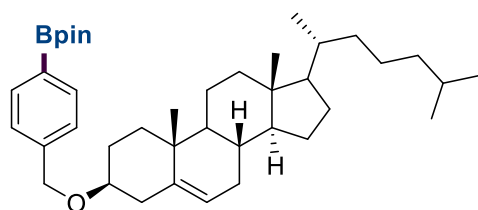


Triethyl(4'-((((1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)silane (9). The product **9** (39.1 mg, 45% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.57-7.56 (m, 6 H), 7.39 (d, *J* = 7.6 Hz, 2 H), 4.59 (d, *J* = 12.4 Hz, 1 H), 4.43 (d, *J* = 12.4 Hz, 1 H), 3.36 (dd, *J* = 2.8, 6.8 Hz, 1 H), 1.89-1.85 (m, 1 H), 1.72-1.60 (m, 4 H), 1.54-1.49 (m, 1 H), 1.01 (s, 3 H), 1.02-0.98 (m, 13 H), 0.86-0.82 (m, 9 H).

¹³C NMR (101 MHz, CDCl₃) δ 141.3, 139.9, 138.8, 136.1, 134.7, 128.7, 127.4, 126.9, 126.3, 86.7, 70.4, 49.4, 46.5, 45.1, 38.5, 34.5, 27.3, 10.4, 12.0, 7.4, 3.7.

HRMS (ESI/quadrupole): Calculated for C₂₉H₄₃OSi (M+H)⁺: 435.3083; Found: 435.3080.

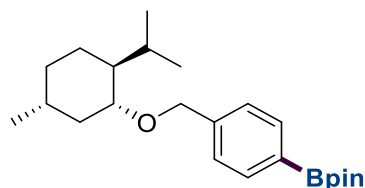


2-(4-((((3S,8S,10R,13R,14S)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10). The product **10** (62.7 mg, 52% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 7.6 Hz, 2 H), 5.33 (d, *J* = 4.8 Hz, 1 H), 4.58 (s, 1 H), 2.29-2.20 (m, 1 H), 2.42-2.38 (m, 1 H), 2.27 (t, *J* = 11.2 Hz, 1 H), 2.01-1.77 (m, 6 H), 1.54-1.42 (m, 10 H), 1.34 (s, 12 H), 1.17-0.97 (m, 14 H), 0.91 (d, *J* = 6.4 Hz, 4 H), 0.86 (dd, *J* = 1.6, 6.4 Hz, 6 H), 0.67 (s, 3 H).

¹³C NMR (101 MHz, CDCl₃) δ 142.4, 140.9, 134.8, 126.7, 121.6, 83.7, 78.5, 69.8, 56.7, 56.1, 50.1, 42.3, 39.8, 39.5, 39.1, 37.2, 36.9, 36.2, 35.8, 31.9, 31.8, 28.4, 28.2, 28.0, 24.8, 24.2, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.8.

HRMS (ESI/Quadrupole): Calculated for C₄₀H₆₄BO₃ (M+H)⁺: 603.4949; Found: 603.4946.

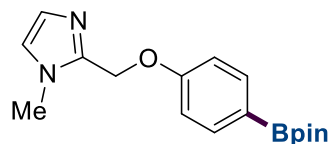


2-(4-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11). The product **11** (43.2 mg, 58% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 7.6 Hz, 2 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.43 (d, *J* = 12.0 Hz, 1 H), 3.16 (td, *J* = 4.0, 10.8 Hz, 1 H), 2.31-2.29 (m, 1 H), 2.17 (d, *J* = 12.4 Hz, 1 H), 1.66-1.59 (m, 3 H), 1.34 (s, 12 H), 0.91 (dd, *J* = 6.4, 7.2 Hz, 10 H), 0.70 (d, *J* = 6.8 Hz, 3 H).

¹³C NMR (101 MHz, CDCl₃) δ 142.4, 134.7, 126.9, 83.7, 78.7, 70.2, 48.3, 40.3, 34.6, 31.5, 25.5, 24.8, 23.2, 22.4, 21.0, 16.1.

HRMS (ESI/Quadrupole): Calculated for C₂₃H₃₈BO₃ (M+H)⁺: 373.2914; Found: 373.2918.



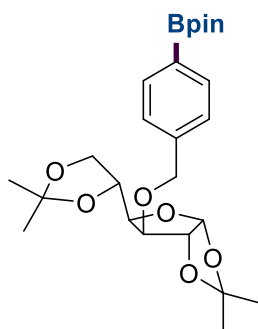
1-methyl-2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)methyl)-1H-imidazole (12). The product **12** (35.8 mg, 57% yield) was purified with silica gel chromatography (CH₂Cl₂/CH₃OH = 30/1).

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8 Hz, 2 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 7.01 (s, 1 H), 6.88 (s, 1 H), 5.17 (s, 2 H), 3.71 (s, 3 H), 1.32 (s, 12 H).

¹³C NMR (101 MHz, CDCl₃) δ 160.5, 143.4, 136.6, 127.5, 122.3, 114.8, 83.6, 62.3,

33.1, 24.8.

FTMS (ESI/Quadrupole): Calculated for $C_{17}H_{24}BN_2O_3$ ($M+H$)⁺: 315.18775; Found: 315.18750.

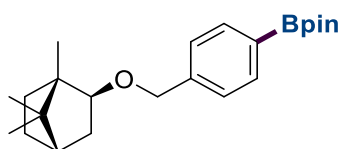


2-(4-(((3aR,5R)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). The product **13** (38.6 mg, 53% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2 H), 7.74 (d, J = 7.6 Hz, 2 H), 5.89 (d, J = 3.6 Hz, 1 H), 4.67 (q, J = 12.4 Hz, 1 H), 4.58 (d, J = 3.6 Hz, 1 H), 4.36 (dd, J = 6.4, 14.0 Hz, 1 H), 4.15-4.10 (m, 2 H), 4.01-3.99 (m, 2 H), 1.48 (s, 3 H), 1.43 (s, 3 H), 1.37 (s, 3 H), 1.34 (s, 12 H), 1.30 (s, 3 H).

¹³C NMR (101 MHz, $CDCl_3$) δ 140.8, 134.9, 126.7, 111.8, 109.0, 105.3, 83.8, 82.6, 81.8, 81.3, 72.5, 72.2, 67.4, 26.8, 26.7, 26.2, 25.4, 24.8.

HRMS (ESI/Quadrupole): Calculated for $C_{25}H_{37}BO_8Na$ ($M+Na$)⁺: 499.2479; Found: 499.2482.



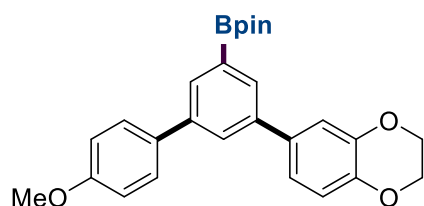
4,4,5,5-Tetramethyl-2-(4-(((1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)phenyl)-1,3,2-dioxaborolane (14). The product **14** (40.0 mg, 54% yield) was purified with silica gel chromatography (PE/EA = 50/1).

¹H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 7.6 Hz, 2 H), 4.55 (d, J = 12.8 Hz, 1 H), 4.40 (d, J = 12.8 Hz, 1 H), 3.29 (dd, J = 3.2, 7.6 Hz, 1 H), 1.85-

1.80 (m, 1 H), 1.66-1.63 (m, 2 H), 1.50-1.45 (m, 1 H), 1.34 (s, 12 H), 1.03 (s, 3 H), 0.97-0.94 (m, 6 H), 0.81 (s, 3 H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.9, 134.7, 126.4, 86.5, 83.7, 70.6, 49.3, 46.5, 45.1, 38.5, 34.4, 27.3, 24.8, 20.3, 11.9.

HRMS (ESI/Quadrupole): Calculated for $\text{C}_{23}\text{H}_{36}\text{BO}_3$ ($\text{M}+\text{H}$) $^+$: 371.2758; Found: 371.2761.

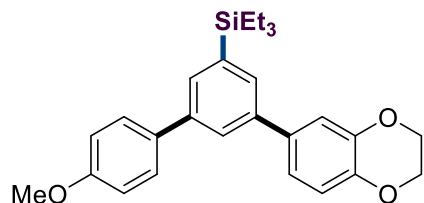


2-(5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19). This compound is unknown. The product **19** (44.4 mg, 50% yield) was purified with silica gel chromatography (PE/EA = 10/1).

^1H NMR (400 MHz, CDCl_3) δ 7.98 (s, 2 H), 7.84 (d, J = 1.6 Hz, 1 H), 7.36 (t, J = 8.0 Hz, 1 H), 7.26 (d, J = 2.4 Hz, 2 H), 7.22-7.17 (m, 3 H), 6.92 (dd, J = 8.4, 13.6 Hz, 2 H), 4.30 (s, 4 H), 3.88 (s, 3 H), 1.37 (s, 12 H)

^{13}C NMR (101 MHz, CDCl_3) δ 159.9, 143.6, 143.2, 142.7, 141.0, 140.4, 134.6, 132.3, 132.1, 129.7, 128.5, 120.4, 119.9, 117.5, 116.1, 113.0, 112.7, 83.9, 64.5, 55.4, 24.9.

FTMS (ESI/Quadrupole): Calculated for $\text{C}_{27}\text{H}_{30}\text{BO}_5$ ($\text{M}+\text{H}$) $^+$: 445.21855; Found: 445.21832.



(5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-yl)triethylsilane (20). This compound is unknown. The product **20** (55.5 mg, 65% yield) was purified with silica gel chromatography (PE/EA = 10/1).

¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1 H), 7.62 (s, 2 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 7.17-7.13 (m, 3 H), 6.94 (dd, *J* = 8.0, 16.8 Hz, 2 H), 4.32 (s, 4 H), 3.88 (s, 3 H), 1.02 (t, *J* = 7.6 Hz, 9 H), 0.87 (q, *J* = 7.6 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ 159.9, 143.7, 143.2, 140.7, 140.2, 138.6, 135.1, 131.8, 131.7, 129.8, 126.4, 120.4, 119.9, 117.6, 116.1, 113.2, 112.5, 55.3, 7.5, 3.4.

FTMS (ESI/quadrupole): Calculated for C₂₇H₃₂NaO₃Si (M+Na)⁺: 445.20129; Found: 445.20261.

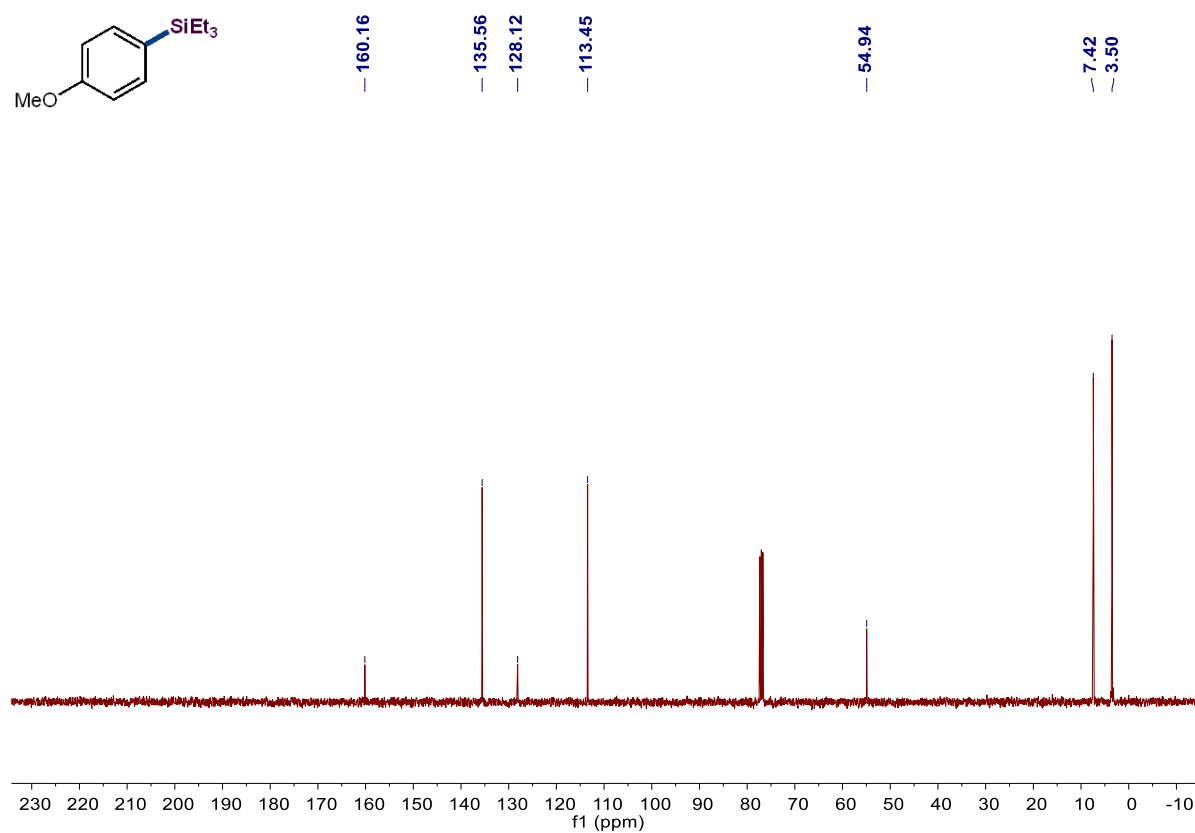
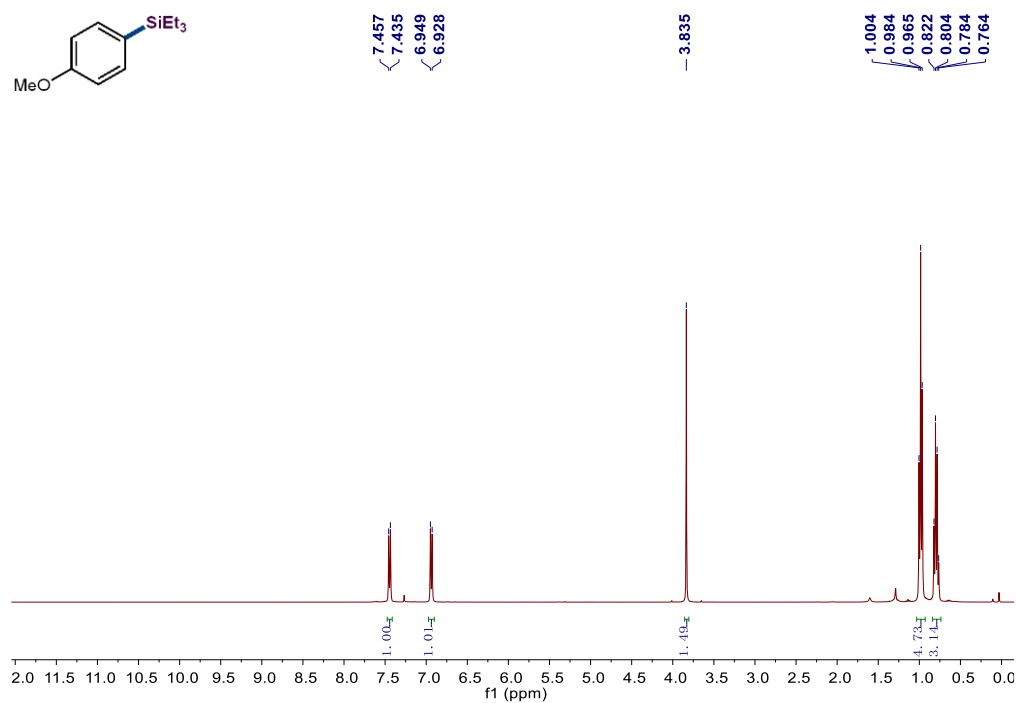
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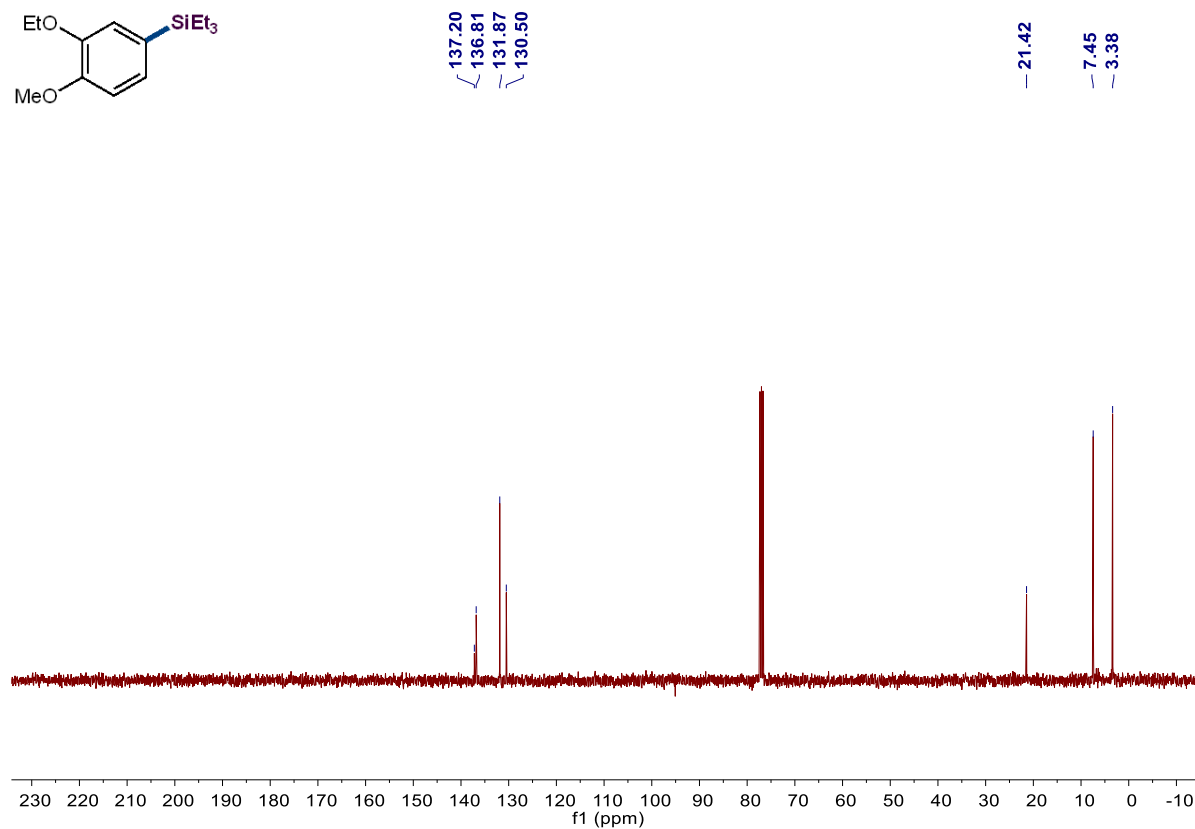
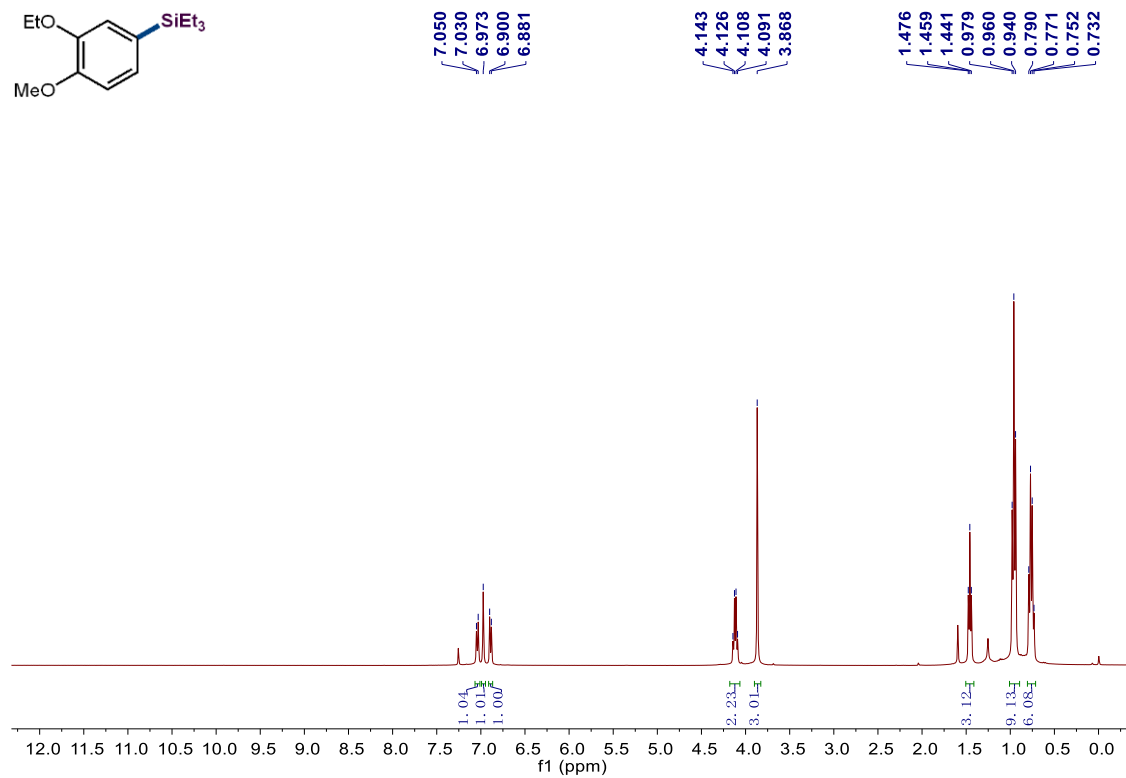
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^1H NMR and ^{13}C NMR of the Products

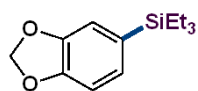
Triethyl(4-methoxyphenyl)silane (3a)



(4-Ethoxy-3-methoxyphenyl)triethylsilane (3b)

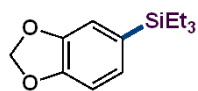
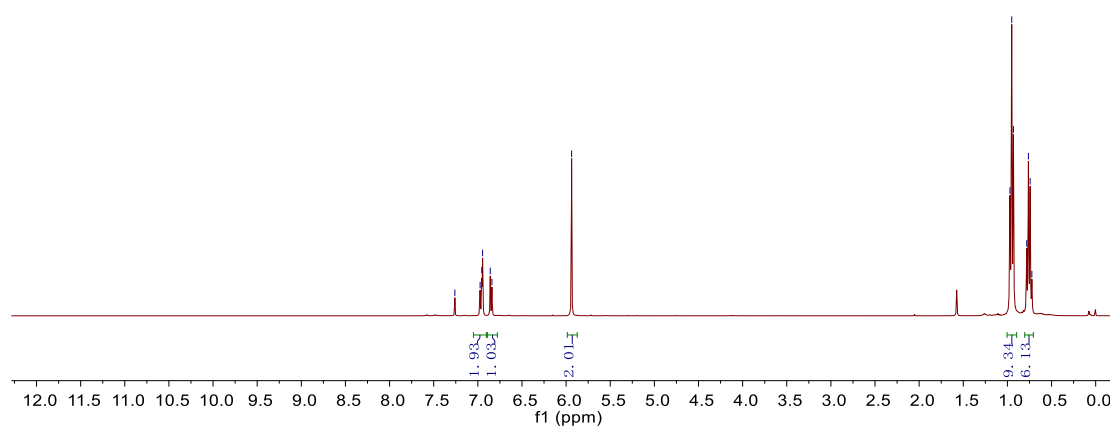


Benzo[d][1,3]dioxol-5-yltriethylsilane (3c)



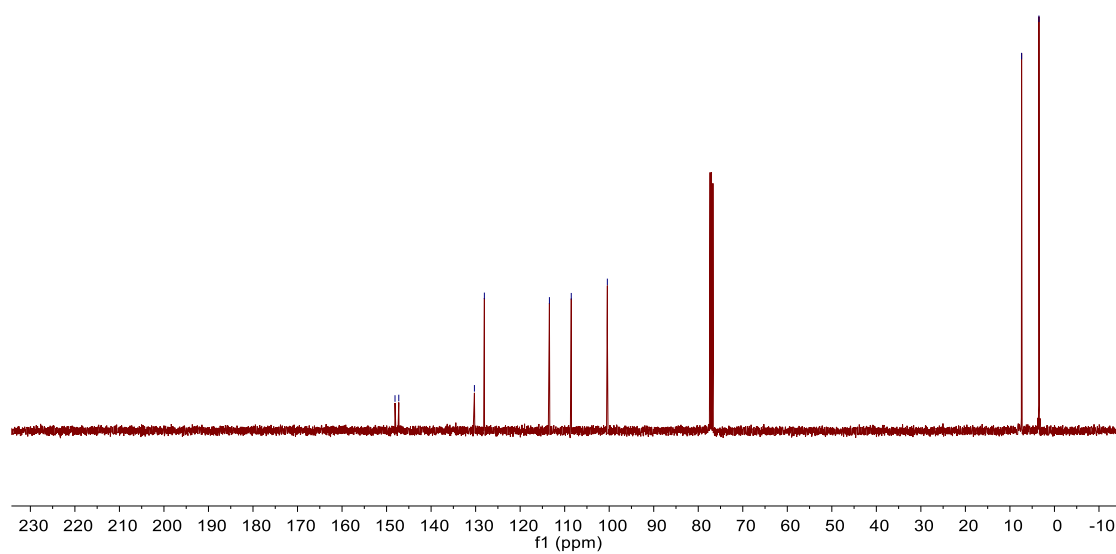
7.260
6.974
6.955
6.946
6.859
6.840
— 5.937

0.971
0.951
0.932
0.781
0.762
0.743
0.723

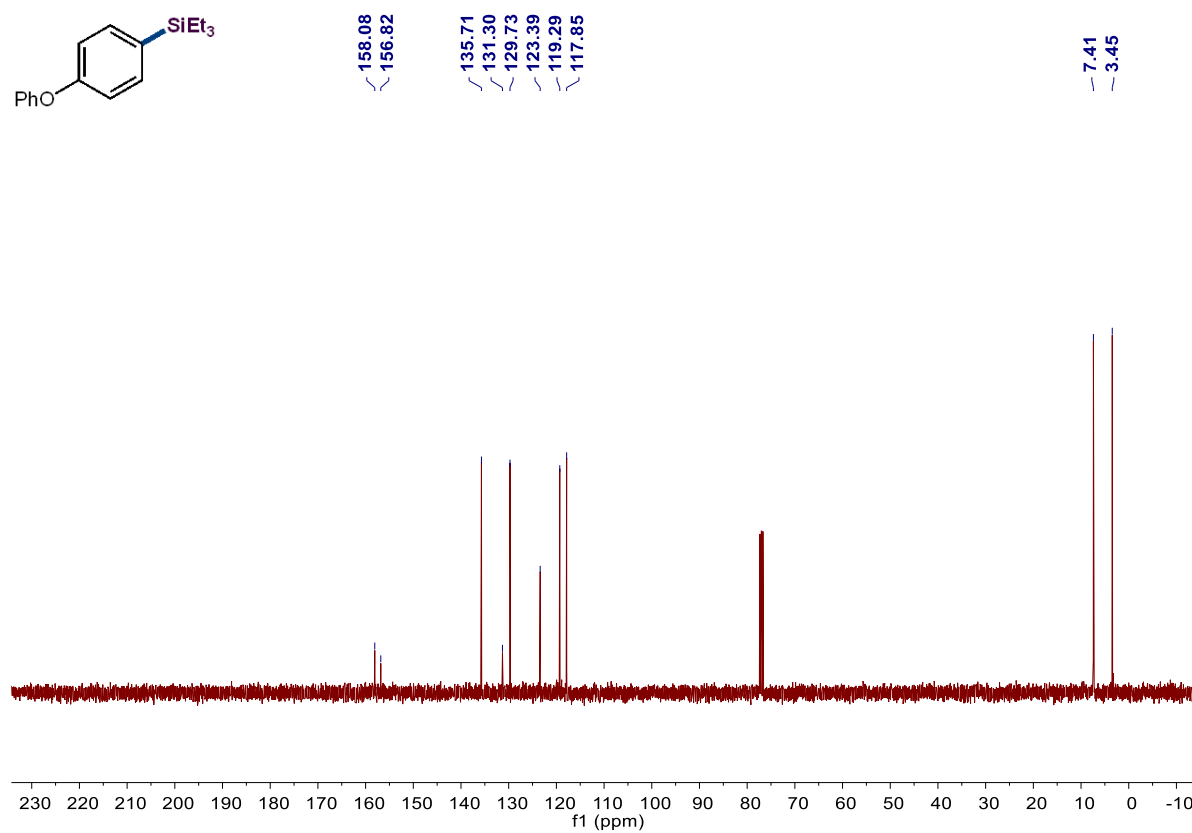
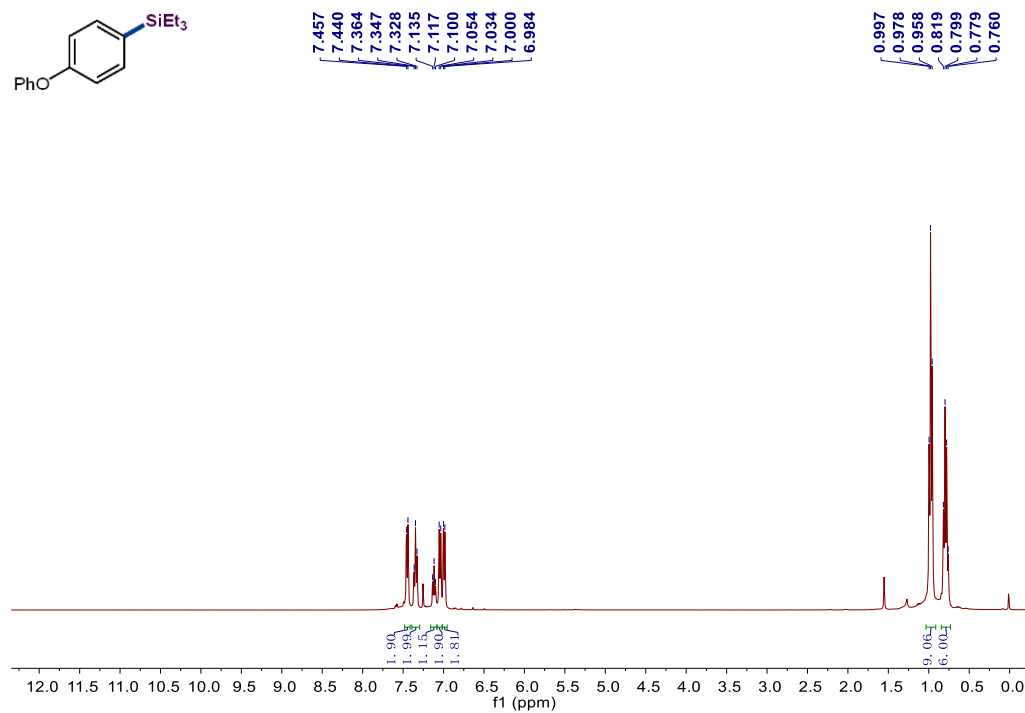


148.10
147.26
130.27
128.03
113.42
108.52
100.41

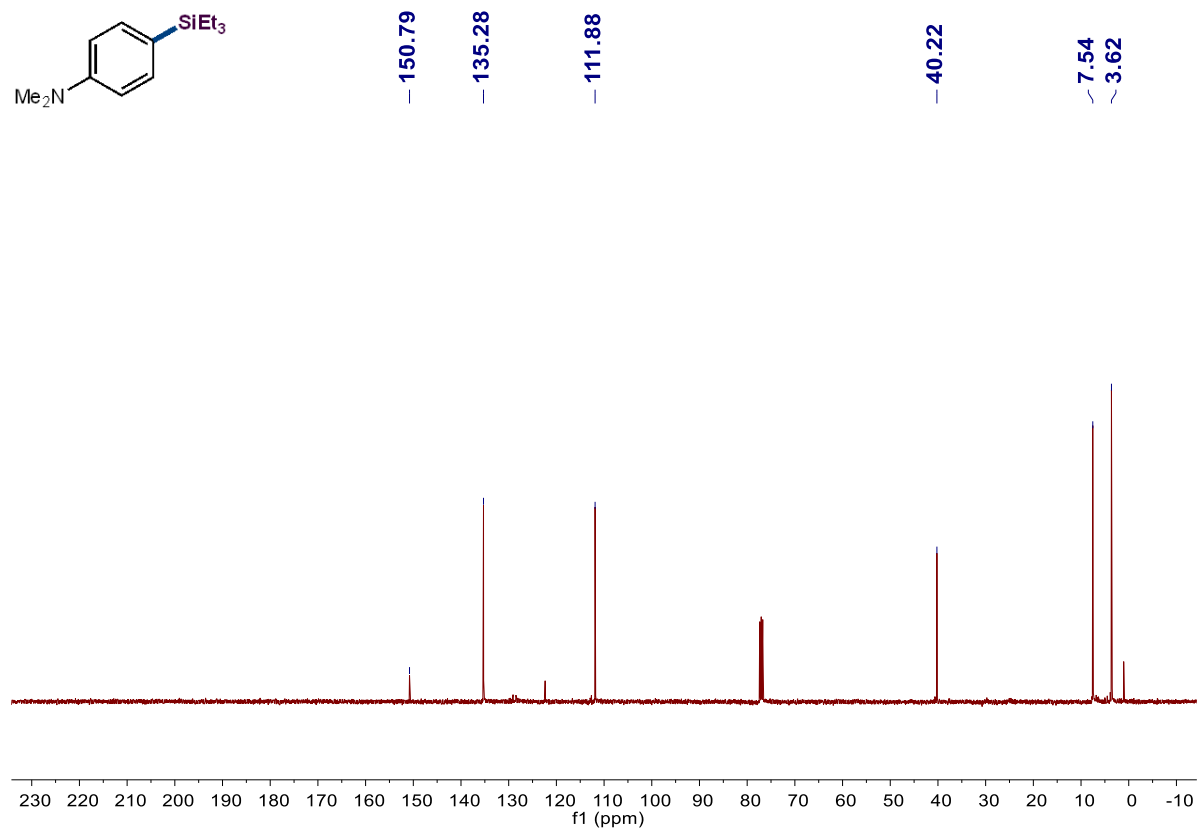
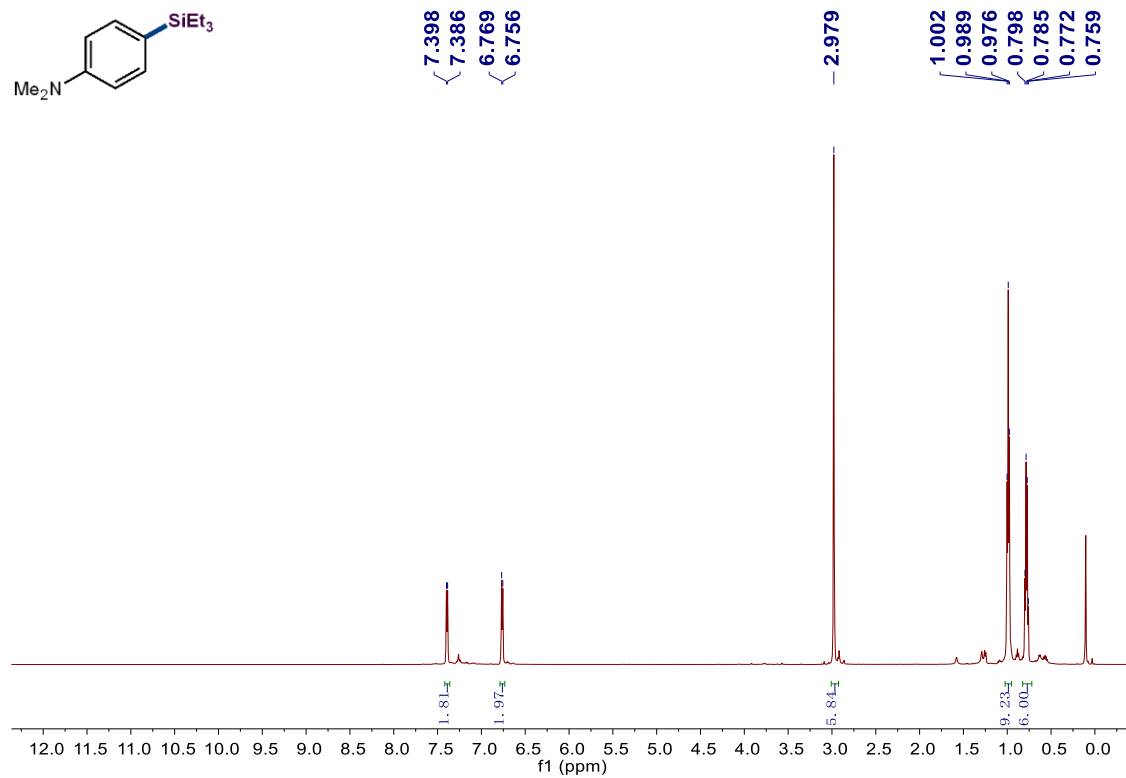
7.38
3.48



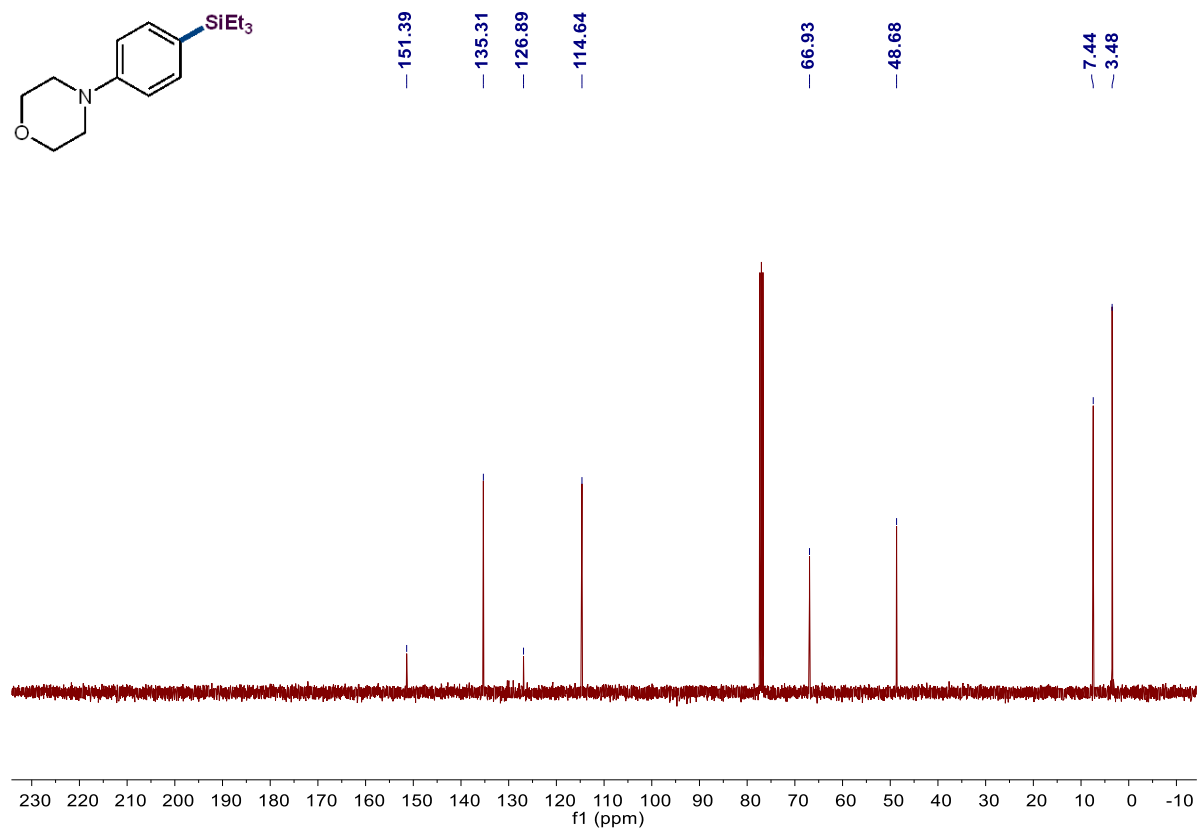
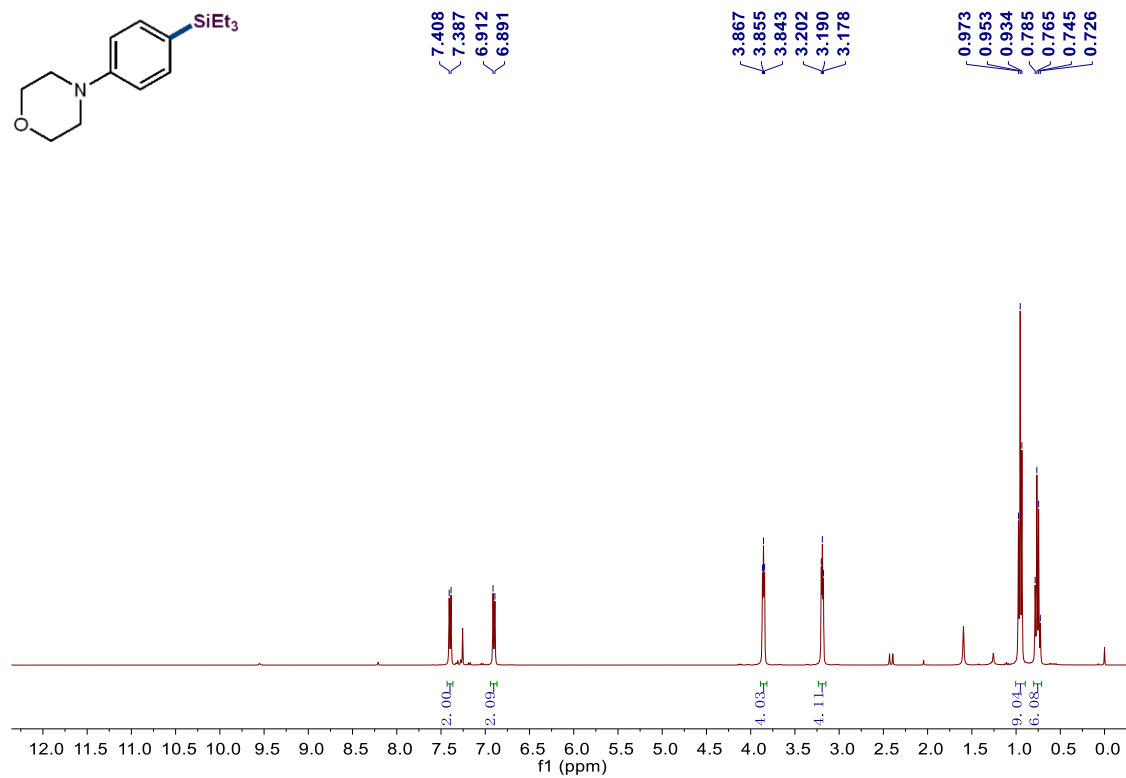
Triethyl(4-phenoxyphenyl)silane (3d).



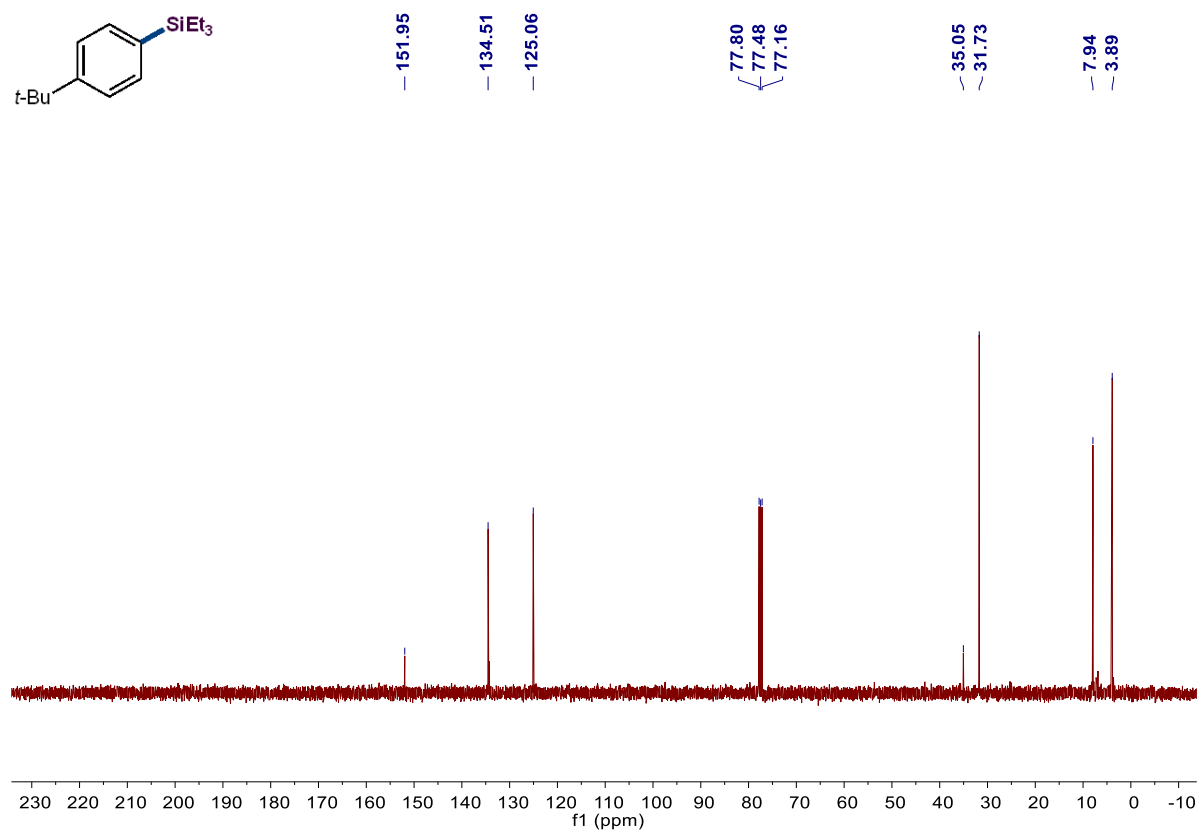
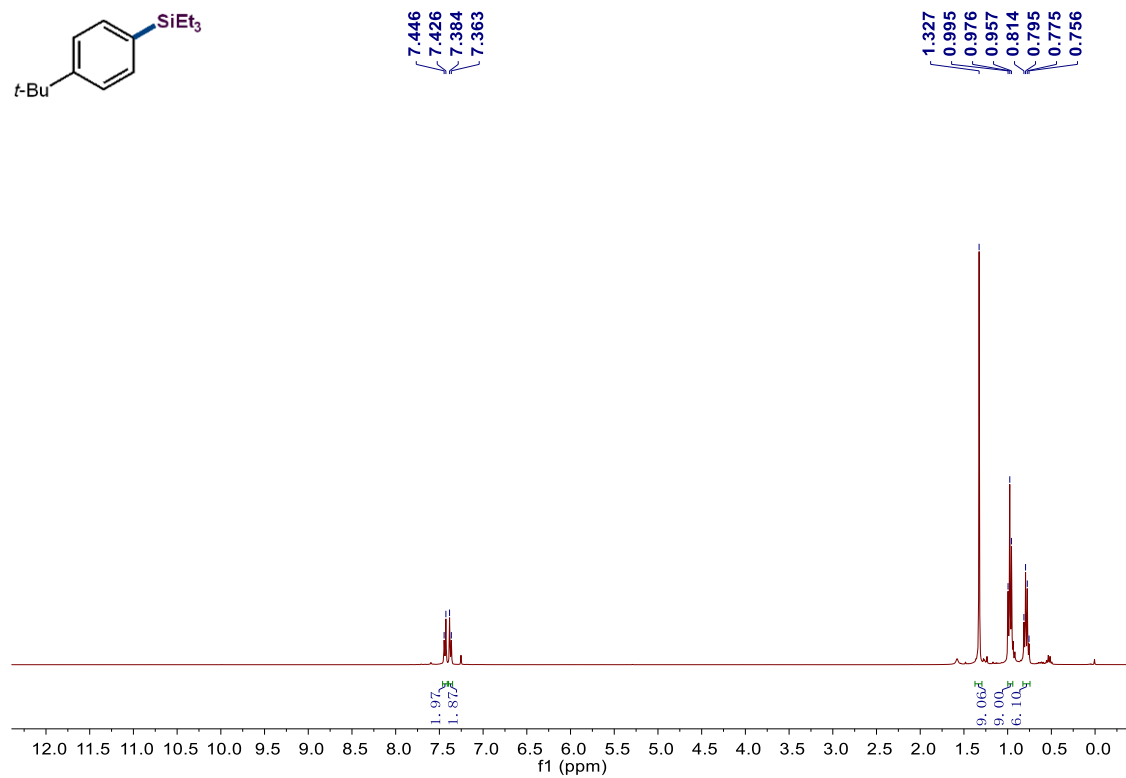
***N,N*-Dimethyl-4-(triethylsilyl)aniline (3e)**



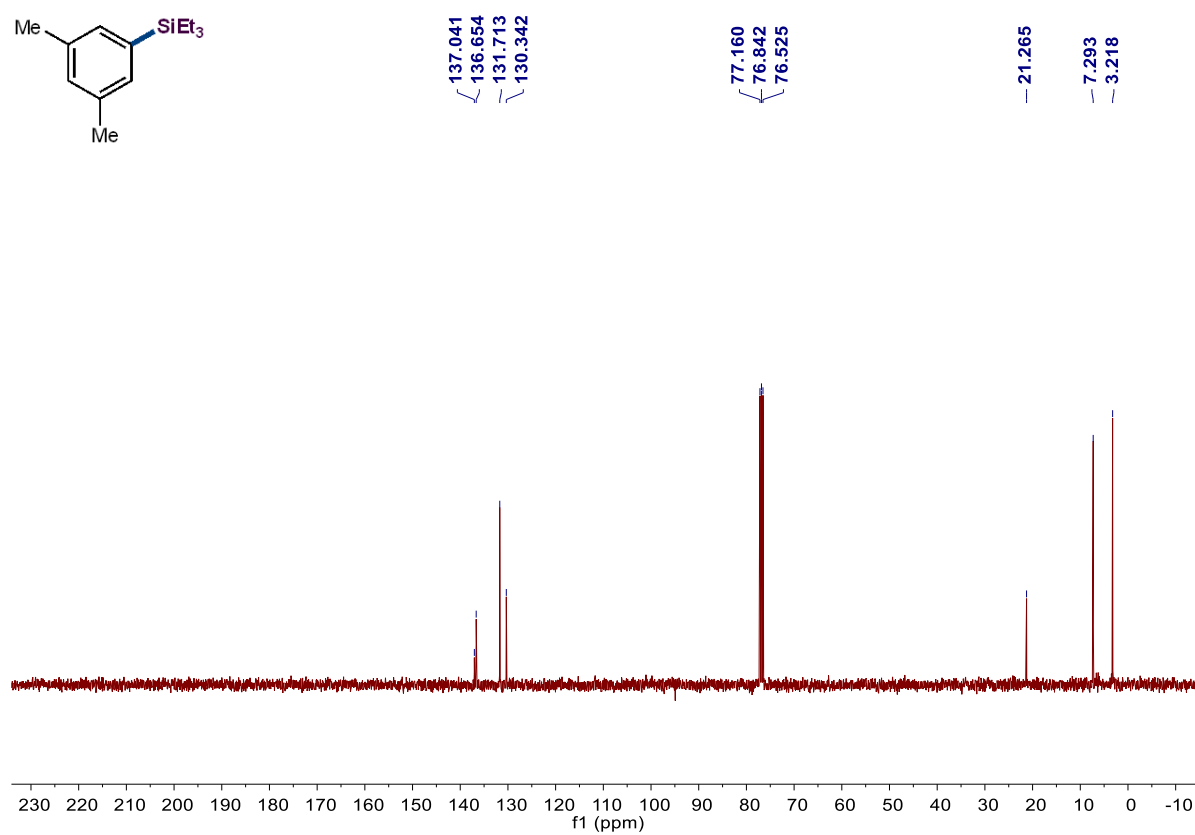
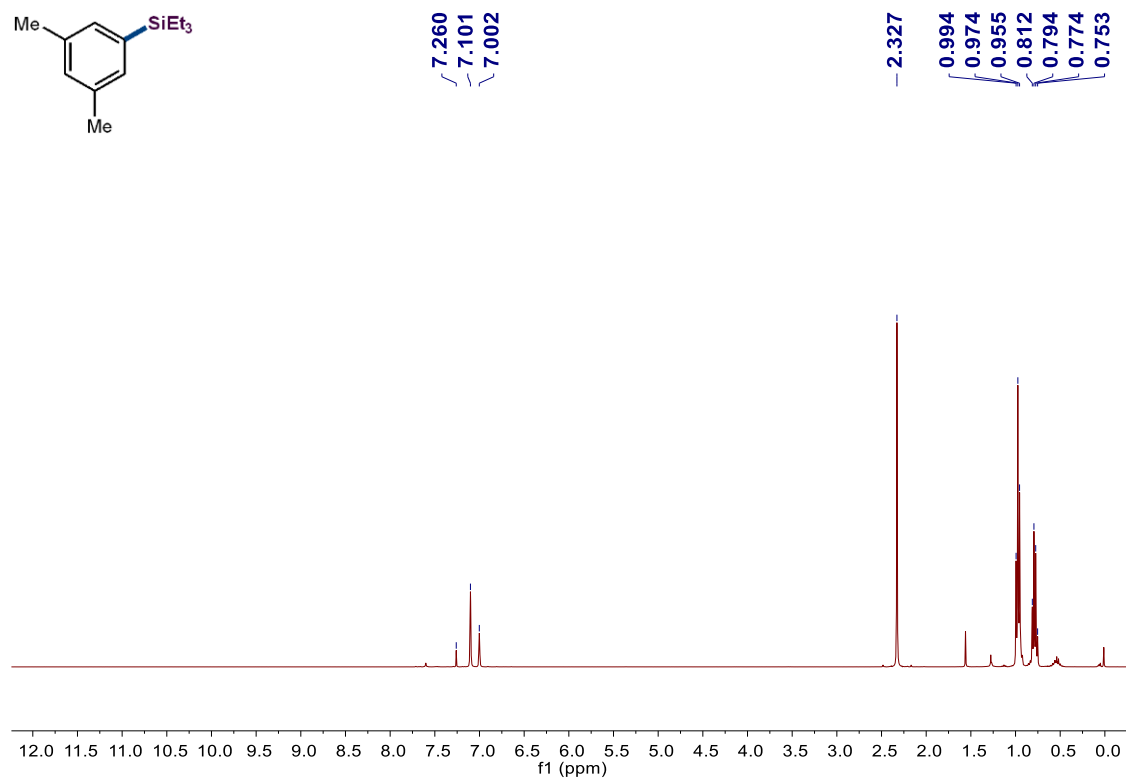
4-(4-(Triethylsilyl)phenyl)morpholine (3f)



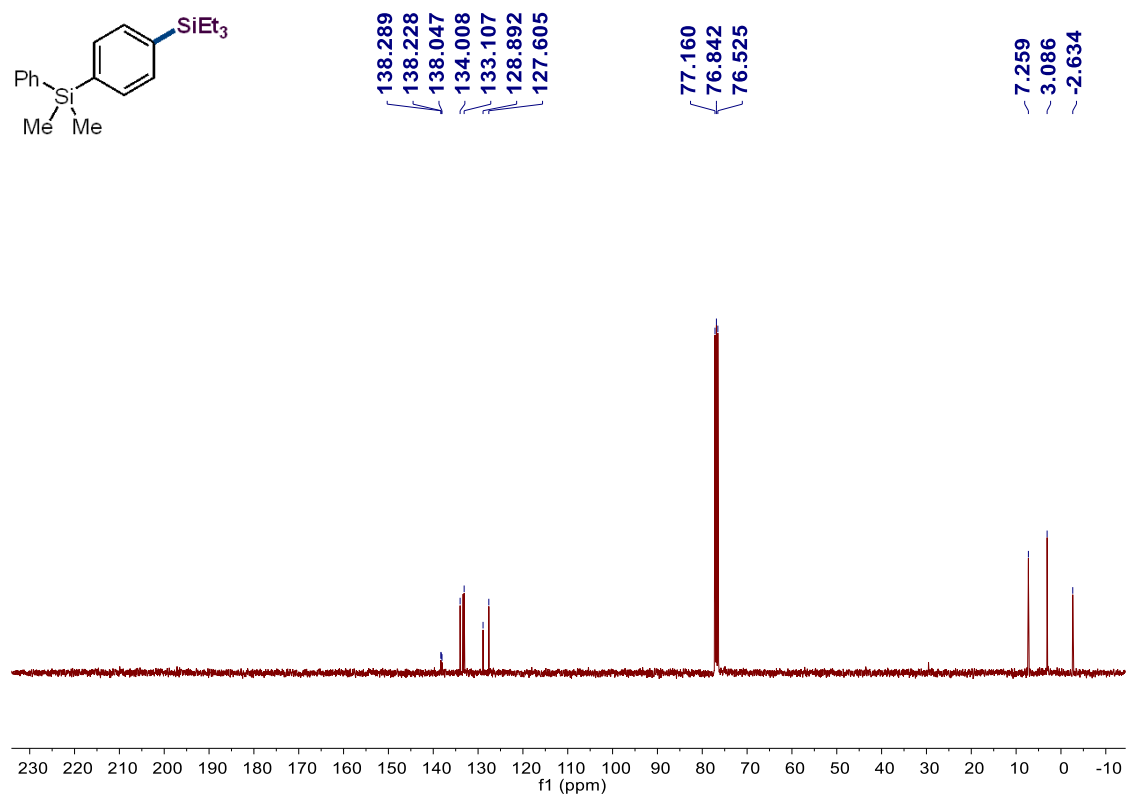
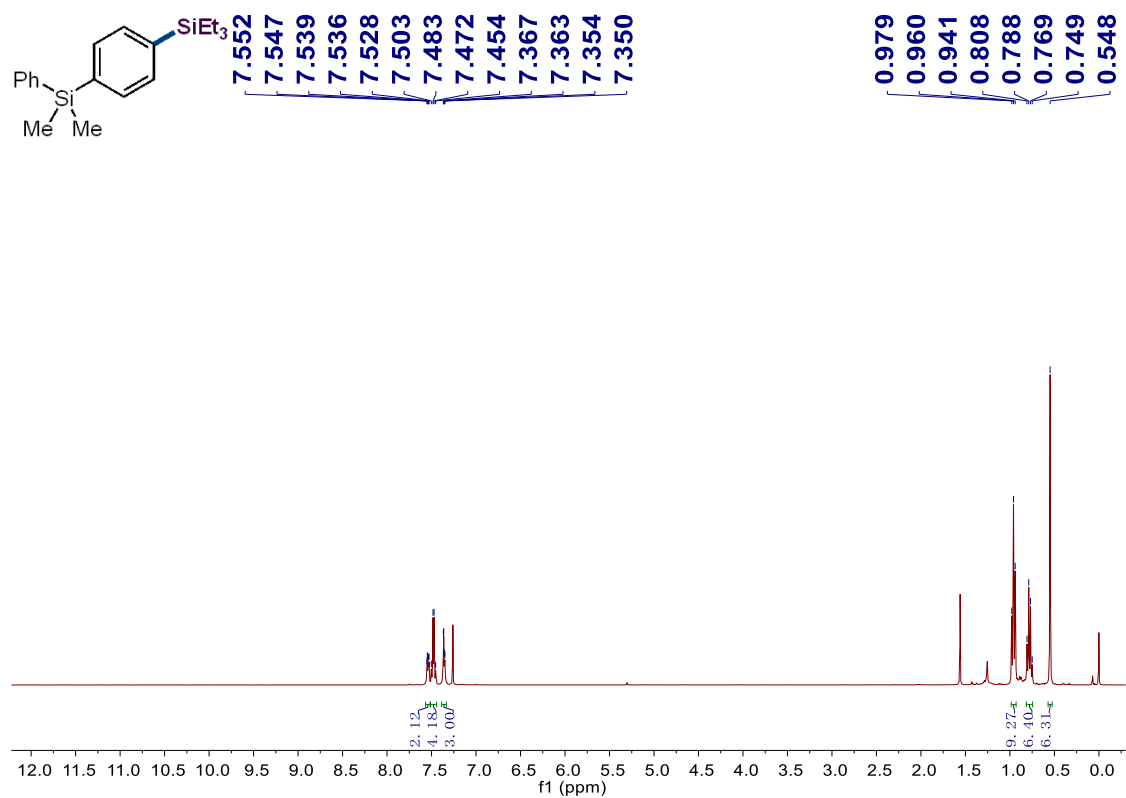
(4-(*tert*-Butyl)phenyl)triethylsilane (3h)



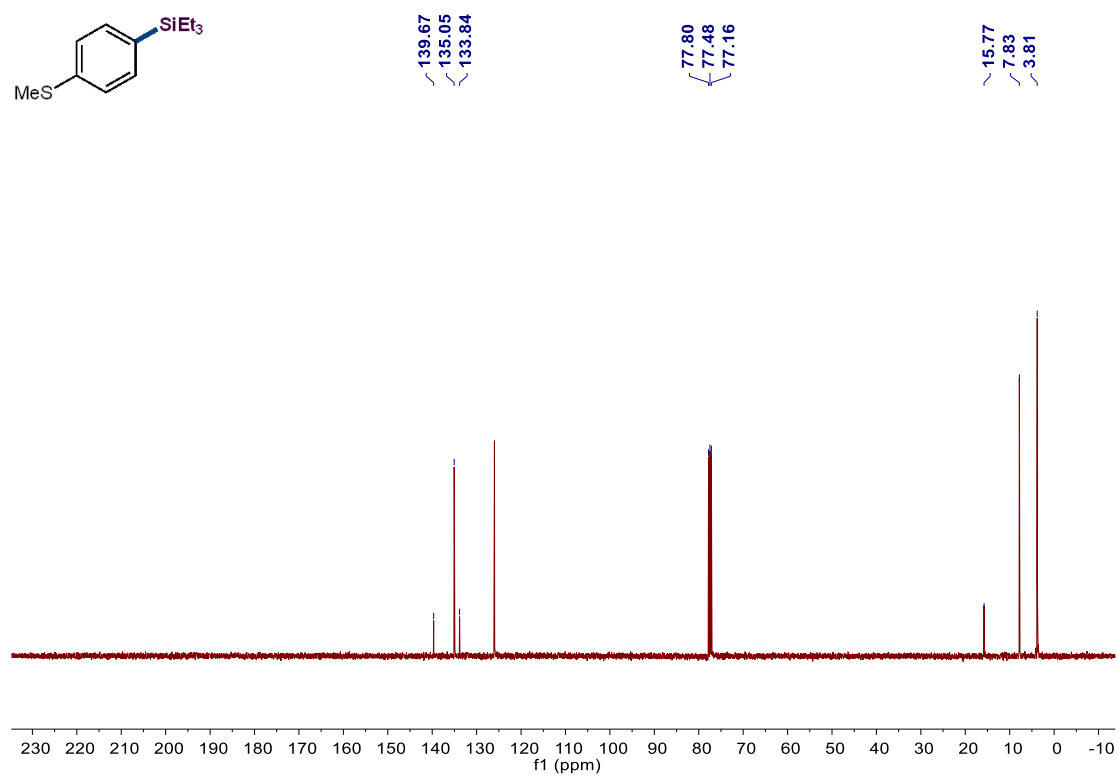
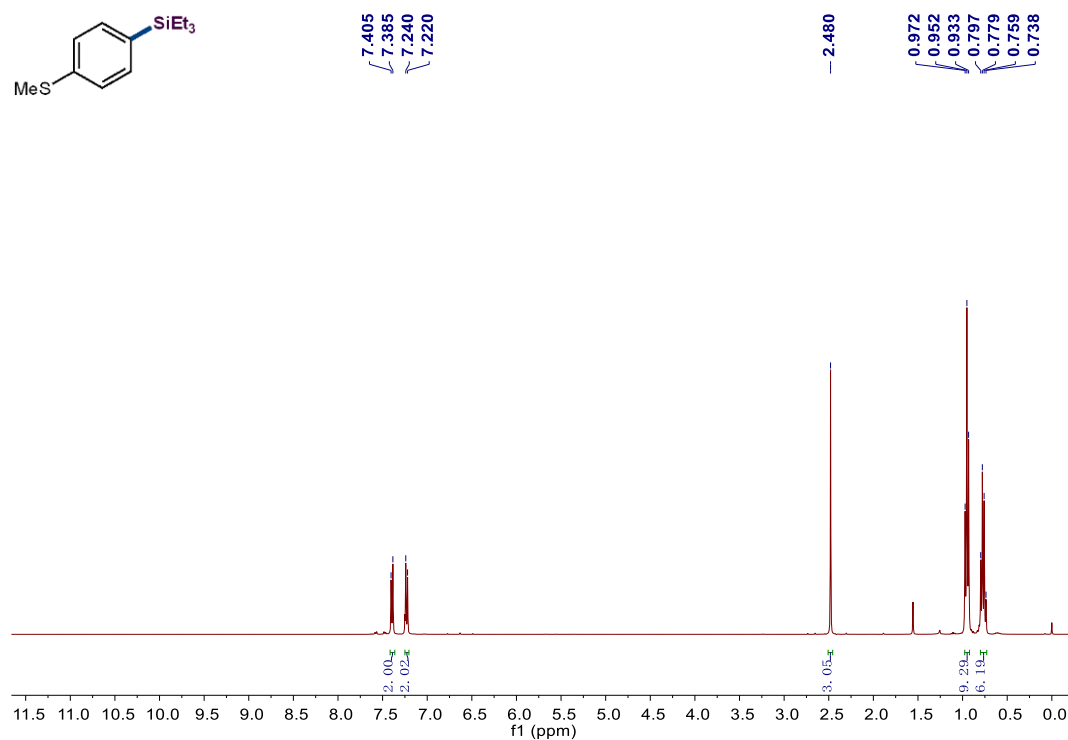
(3,5-Dimethylphenyl)triethylsilane (3i)



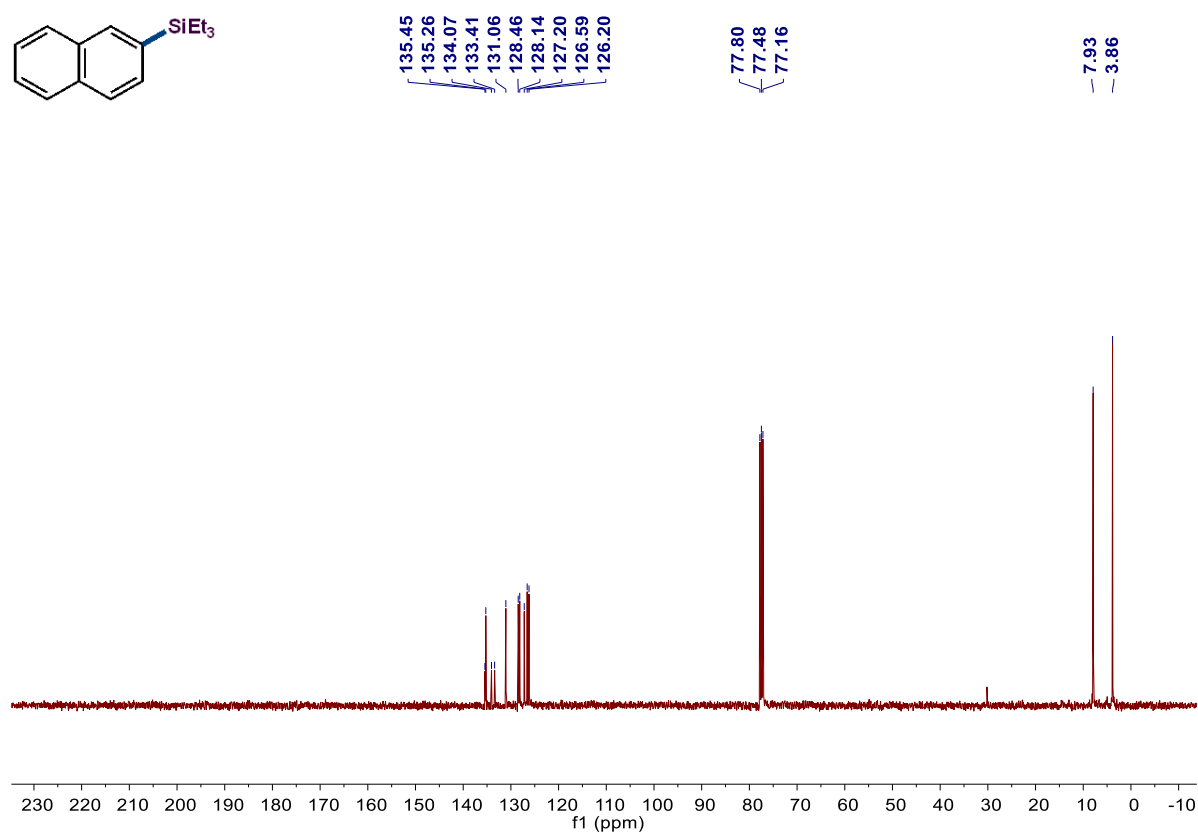
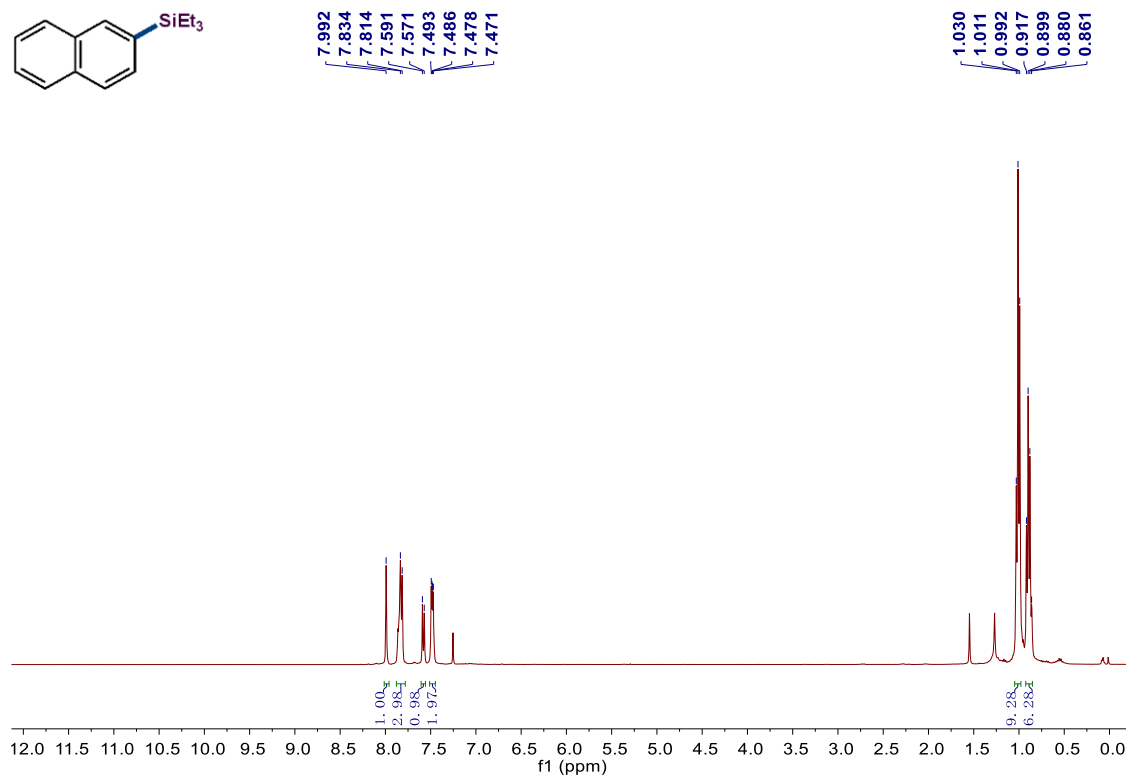
(4-(Dimethyl(phenyl)silyl)silyl)phenyl)triethylsilane (3j)



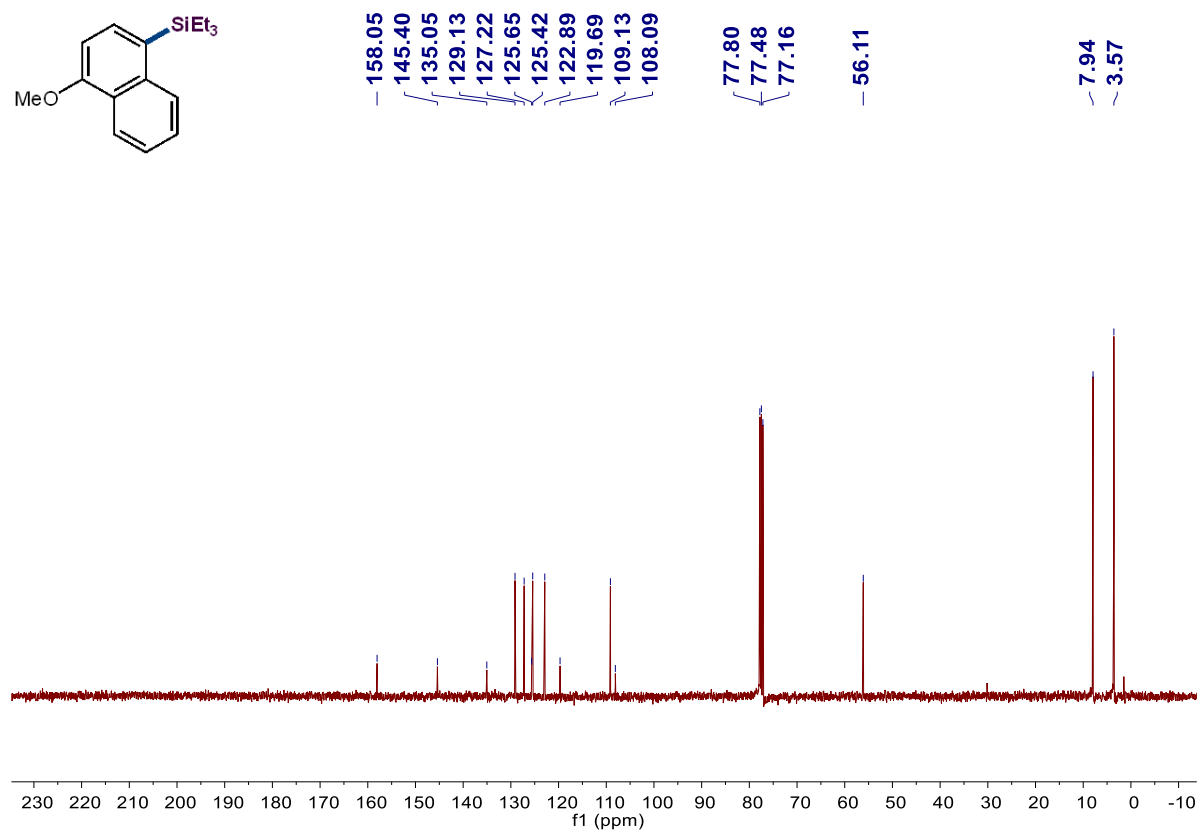
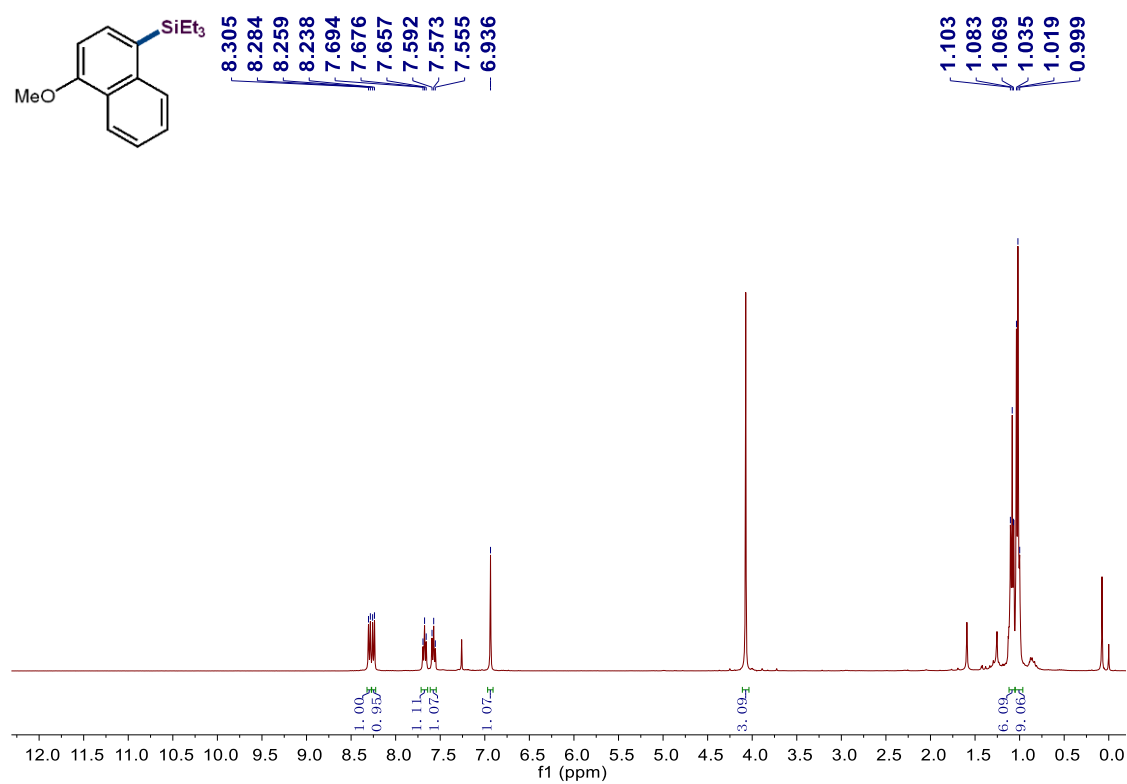
Triethyl(4-(methylthio)phenyl)silane (3l)



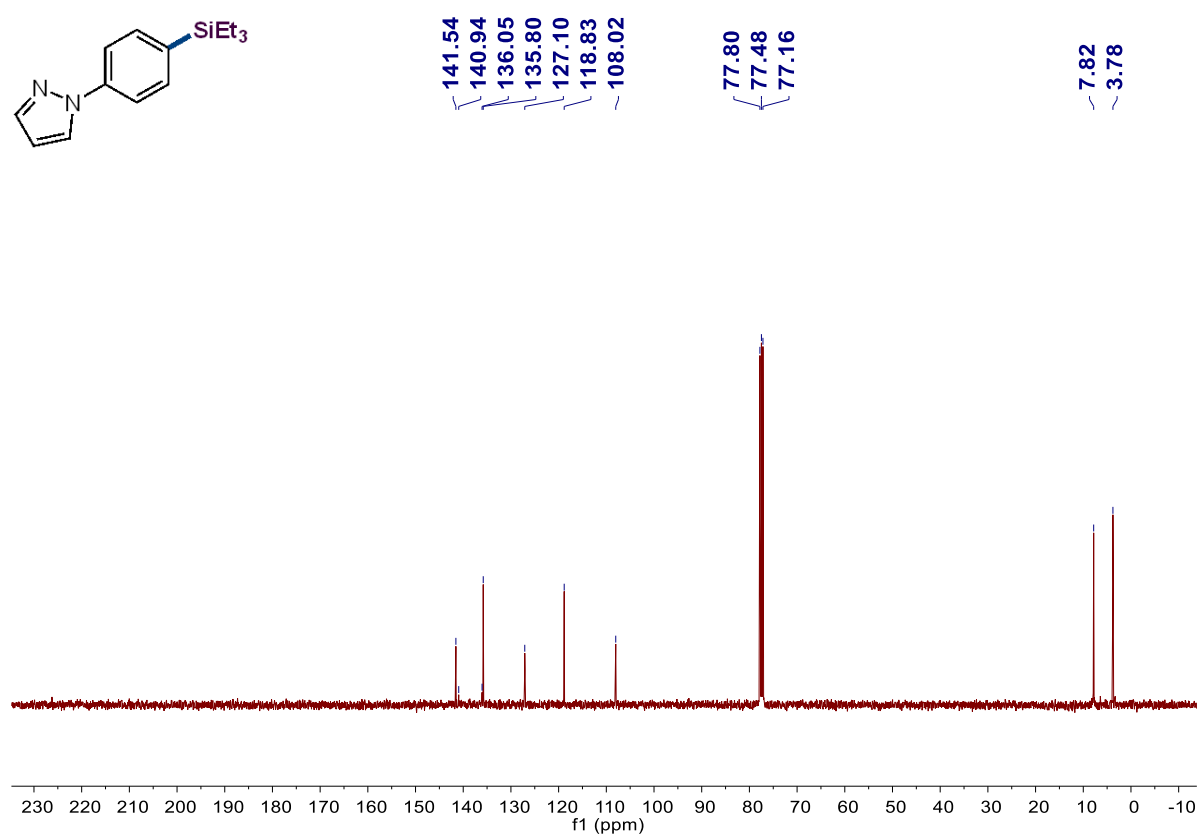
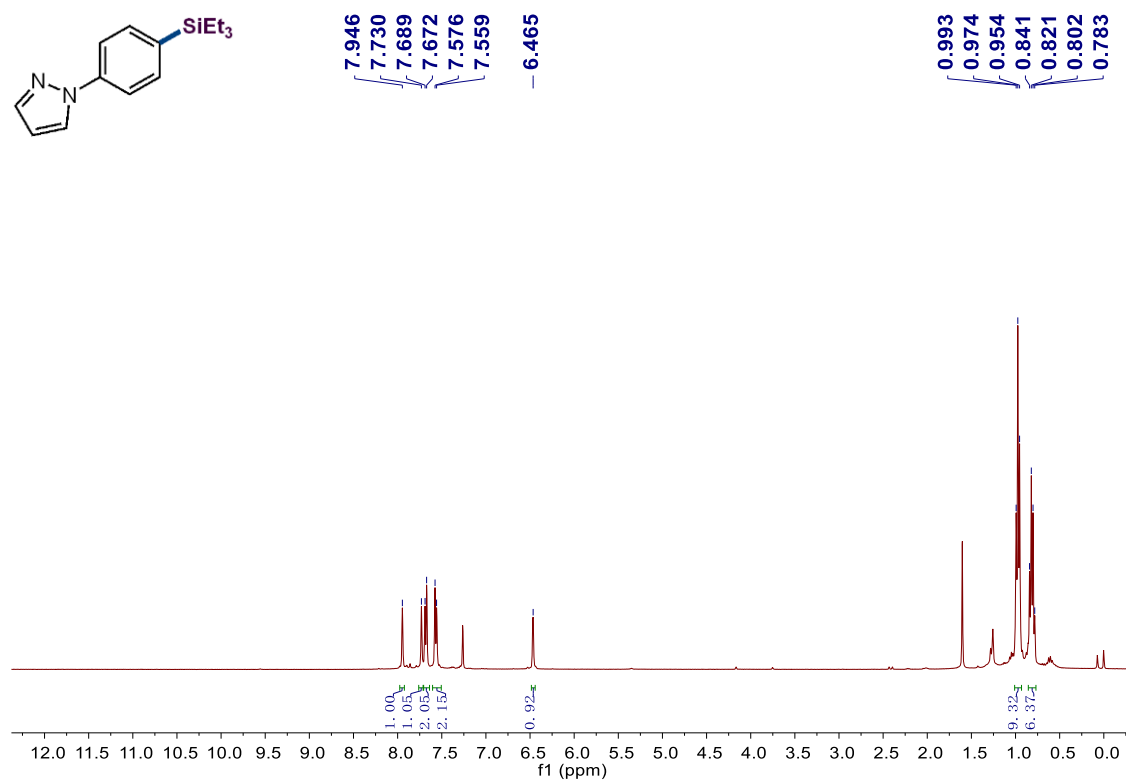
Triethyl(naphthalen-2-yl)silane (3o)



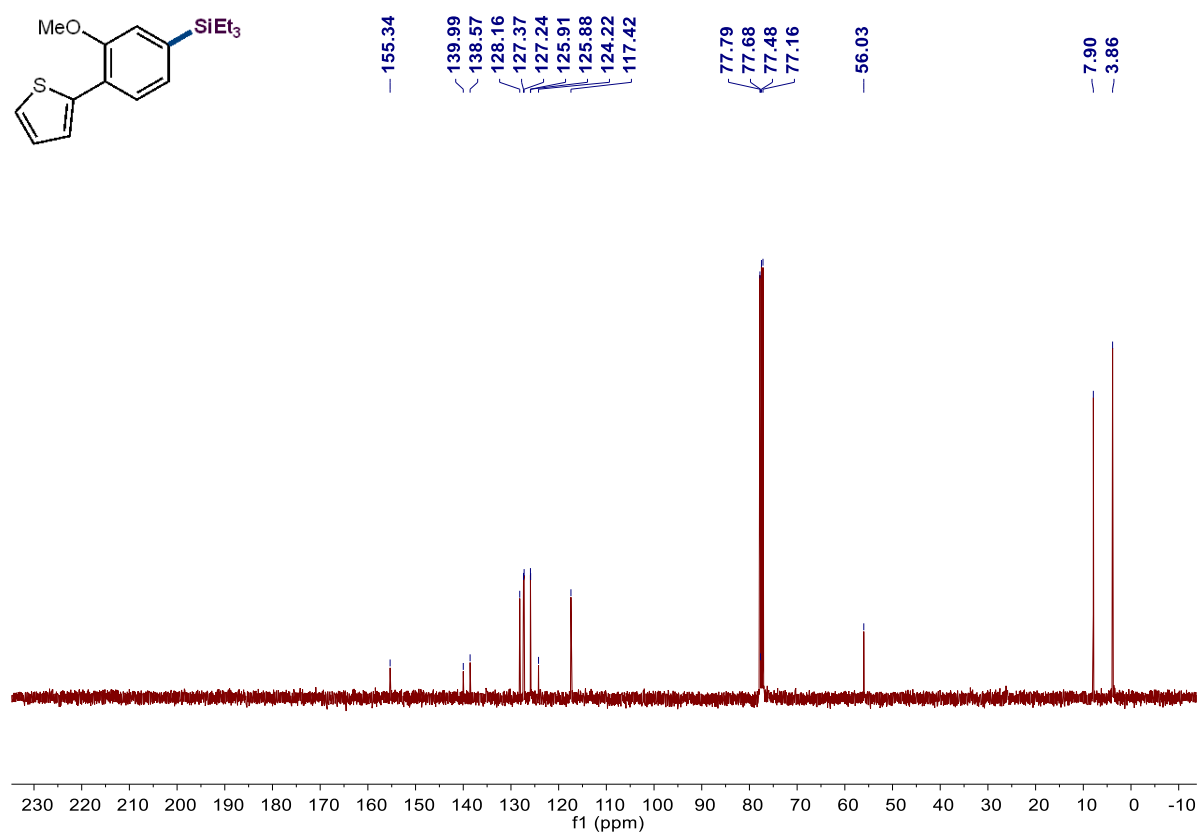
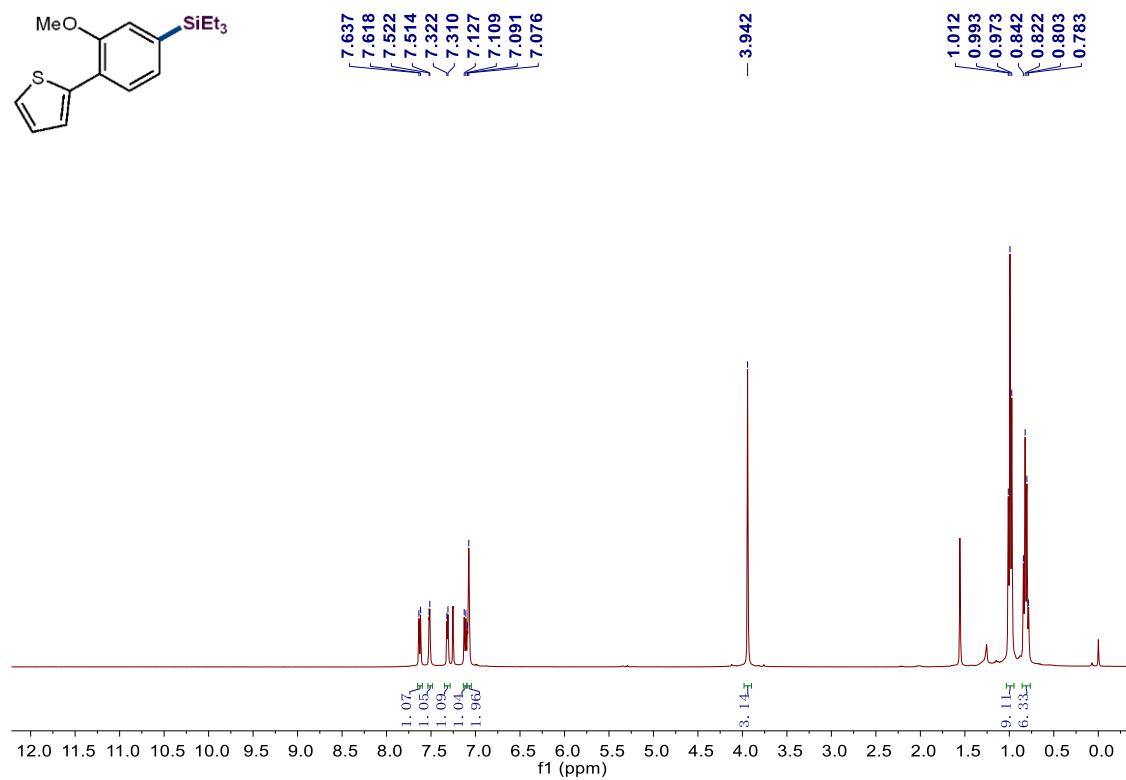
Triethyl(4-methoxynaphthalen-1-yl)silane (3r)



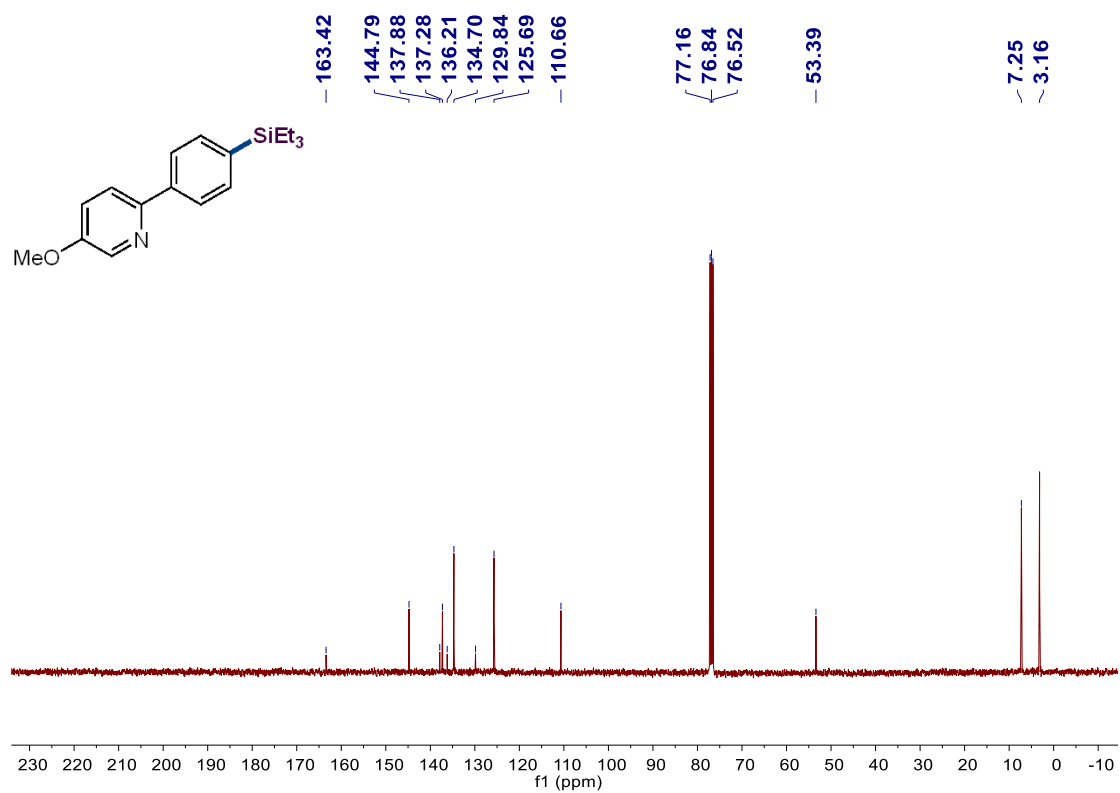
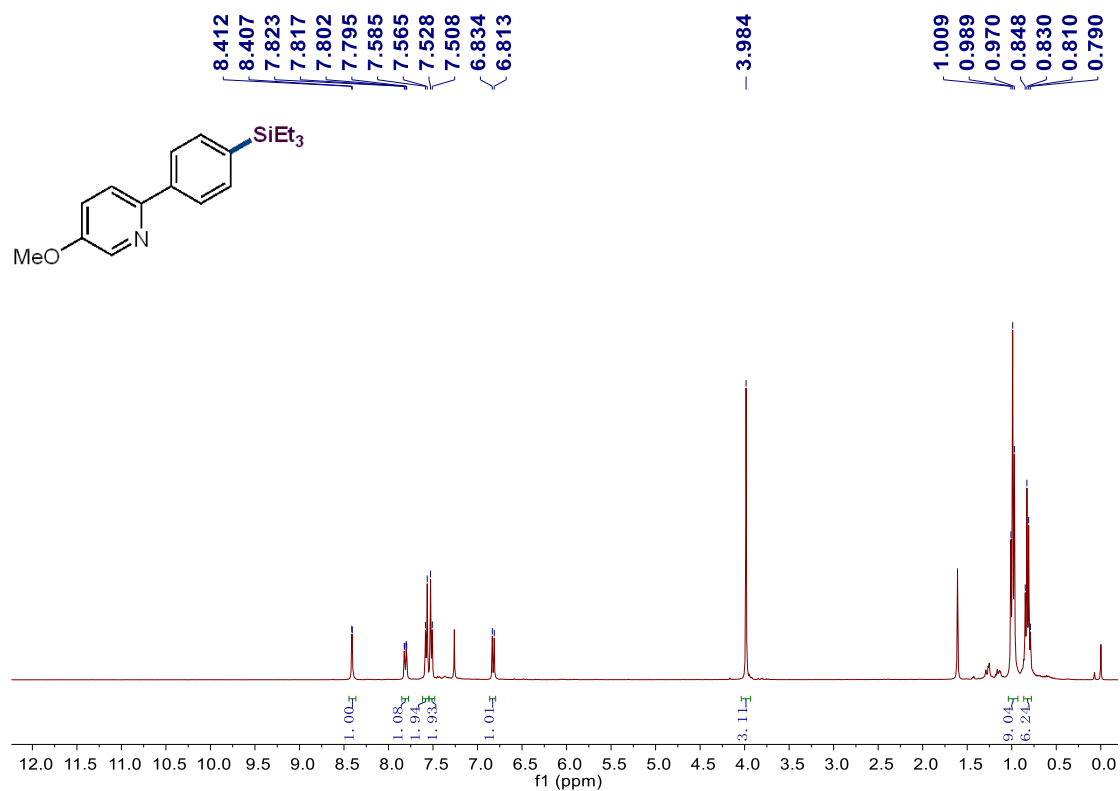
1-(4-(Triethylsilyl)phenyl)-1H-pyrazole (3s)



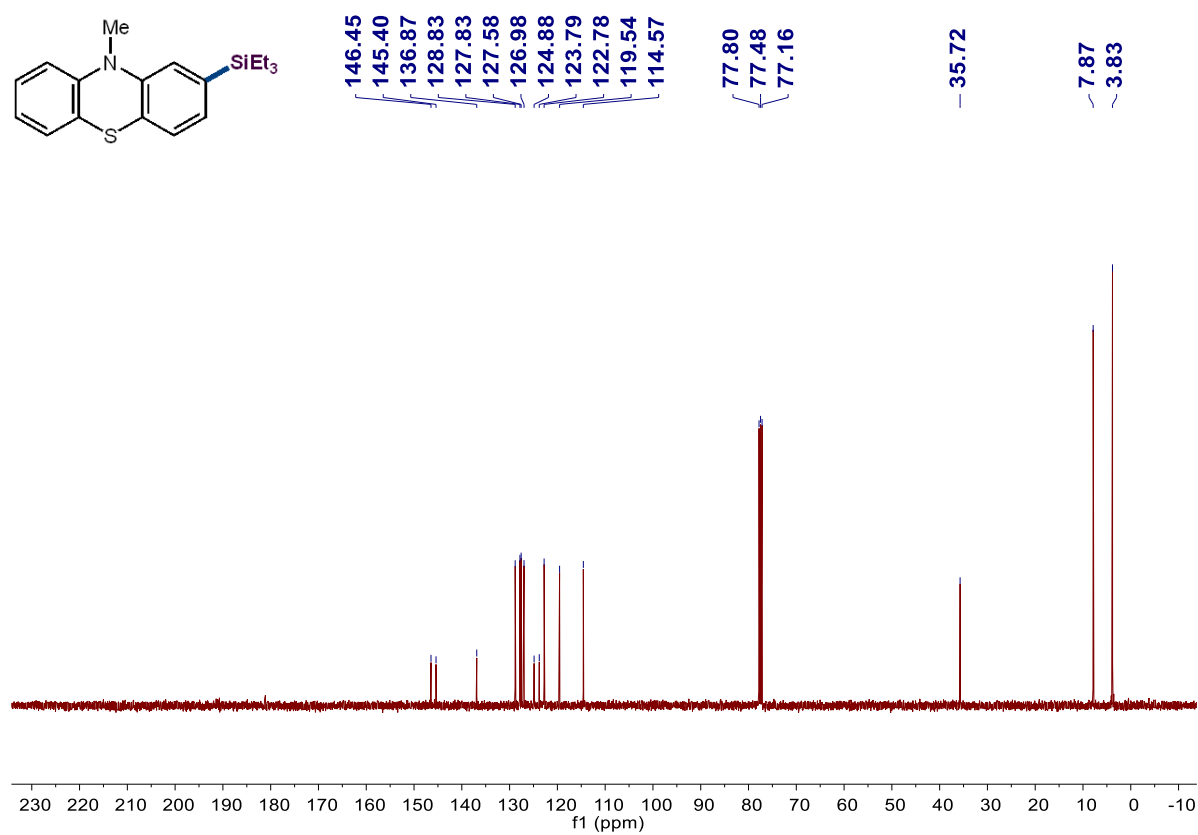
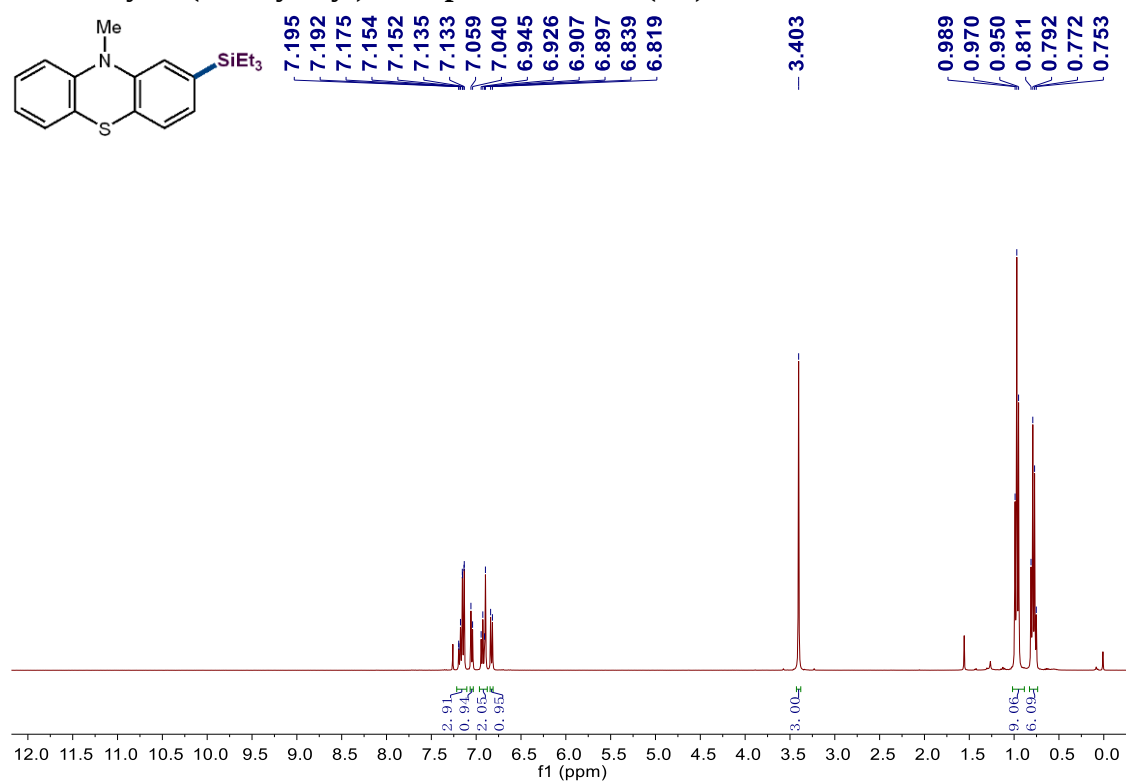
Triethyl(3-methoxy-4-(thiophen-2-yl)phenyl)silane (3u)



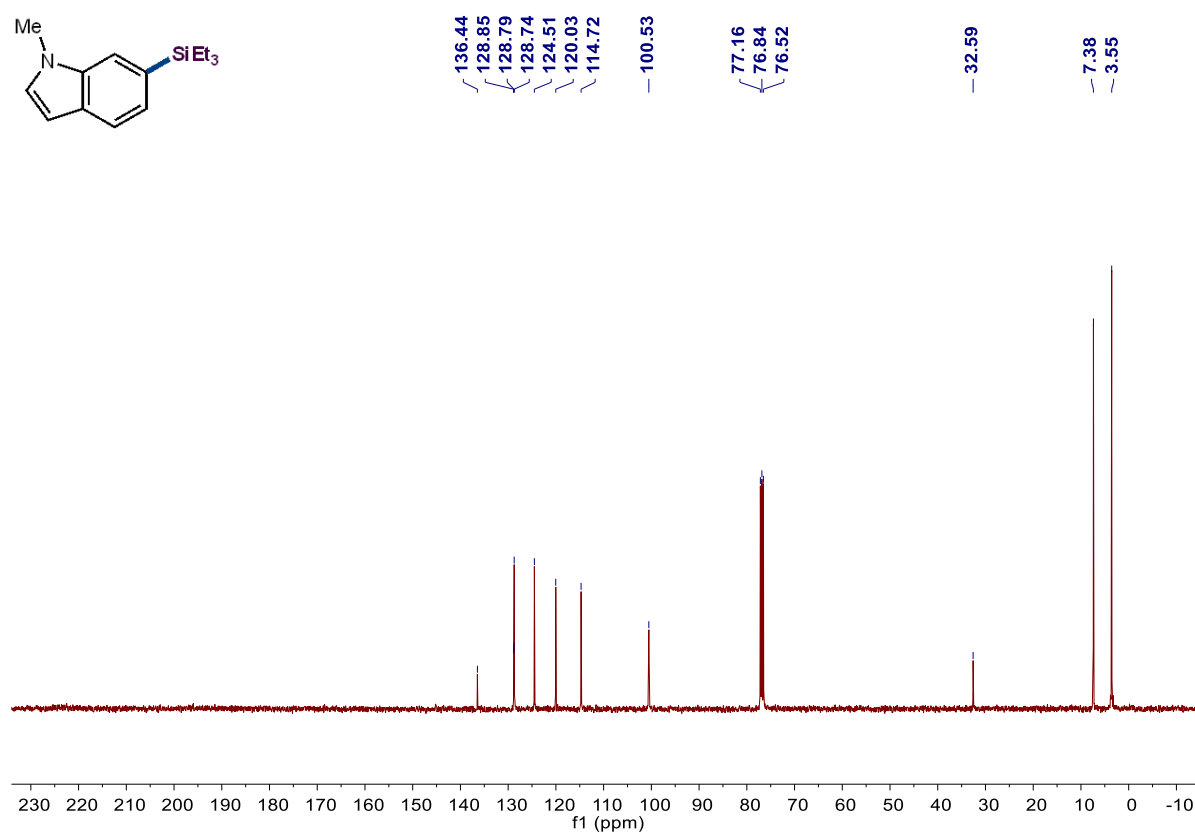
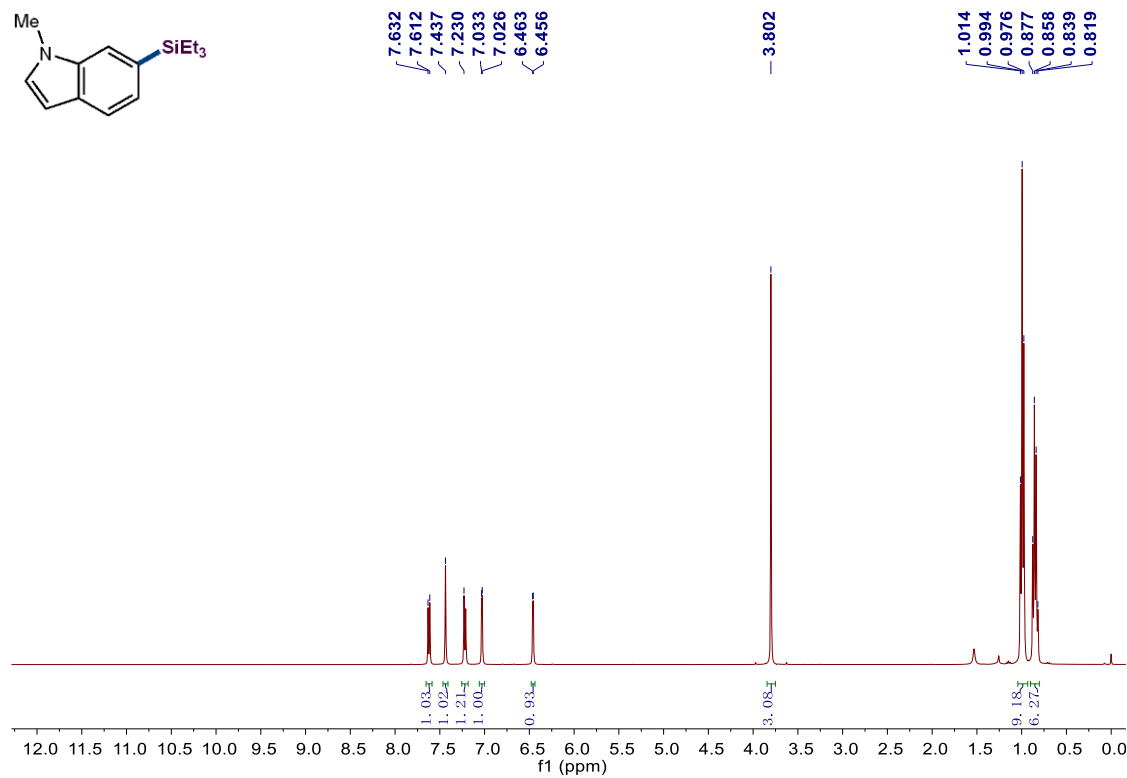
5-Methoxy-2-(4-(triethylsilyl)phenyl)pyridine (3v)



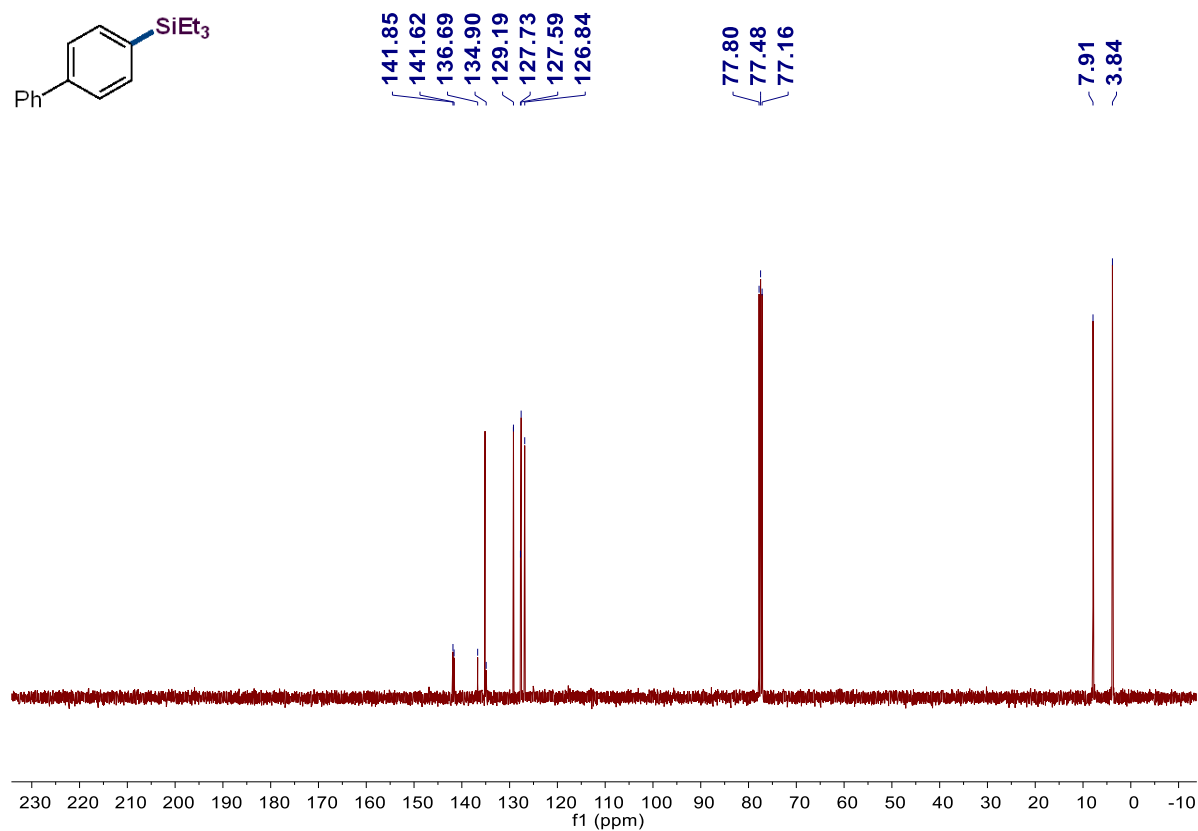
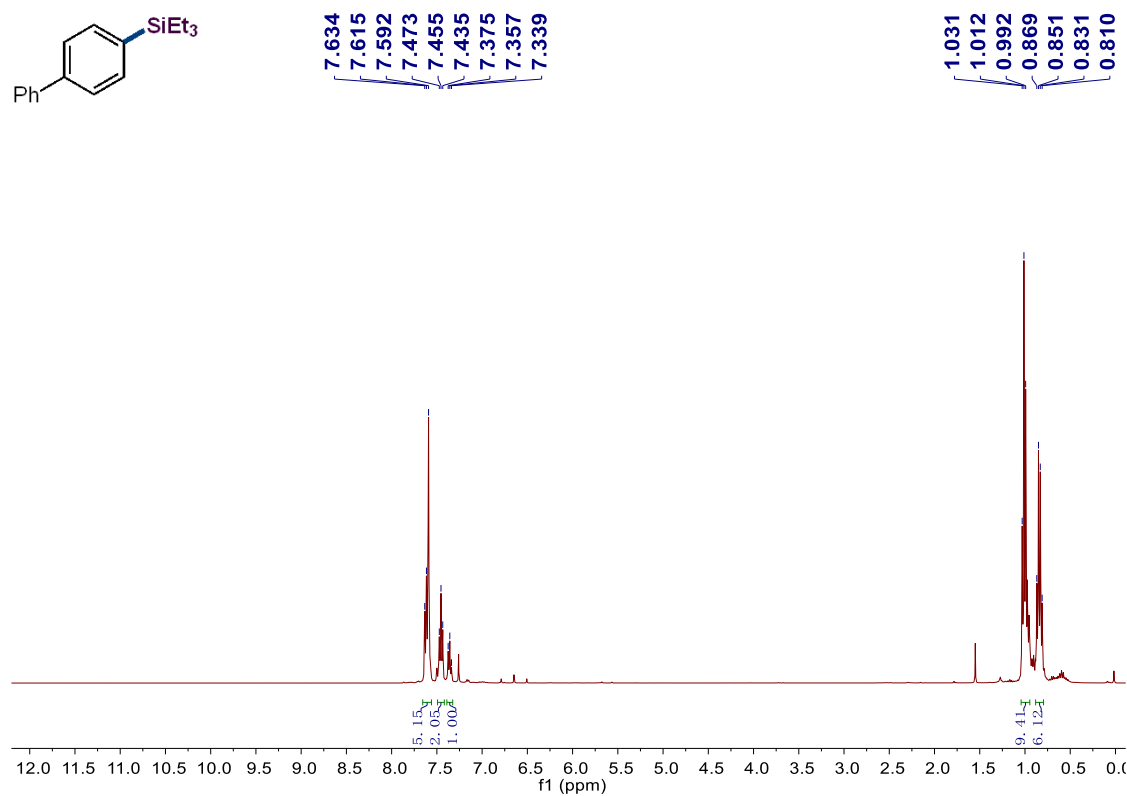
10-Methyl-2-(triethylsilyl)-10H-phenothiazine (3w).



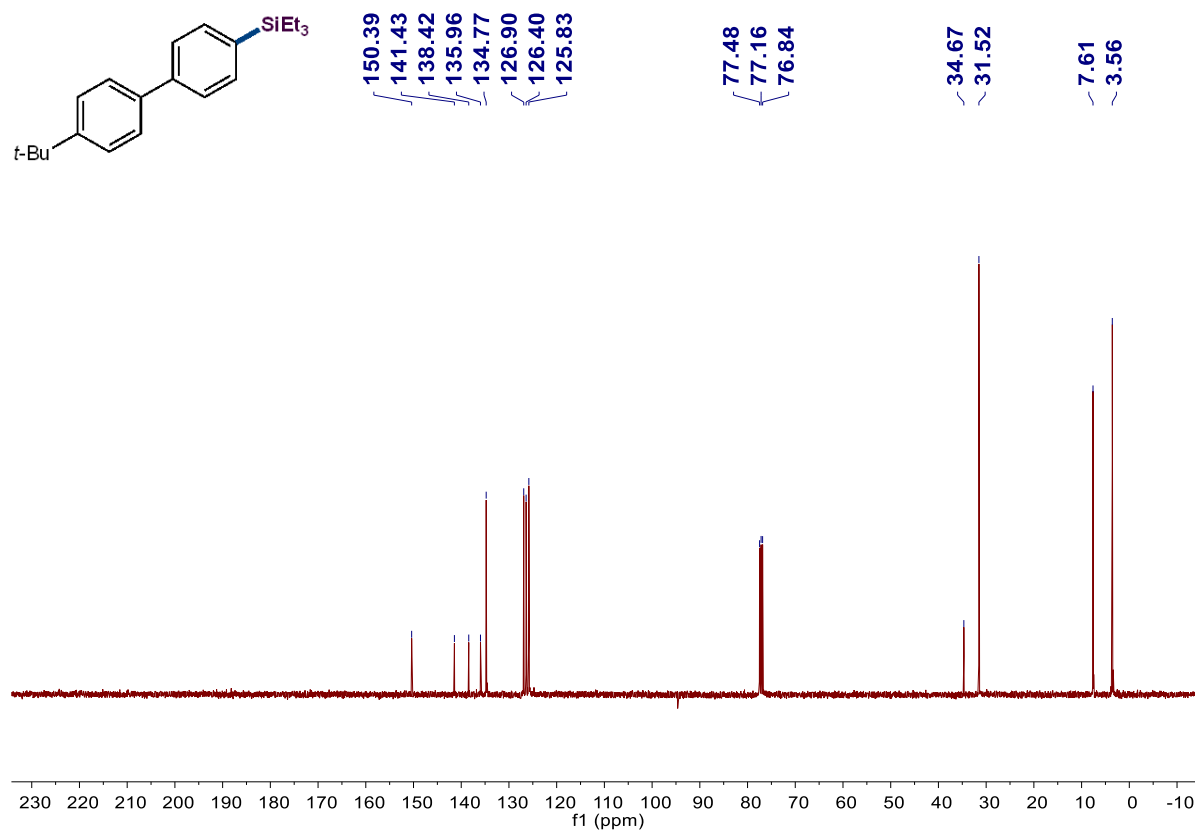
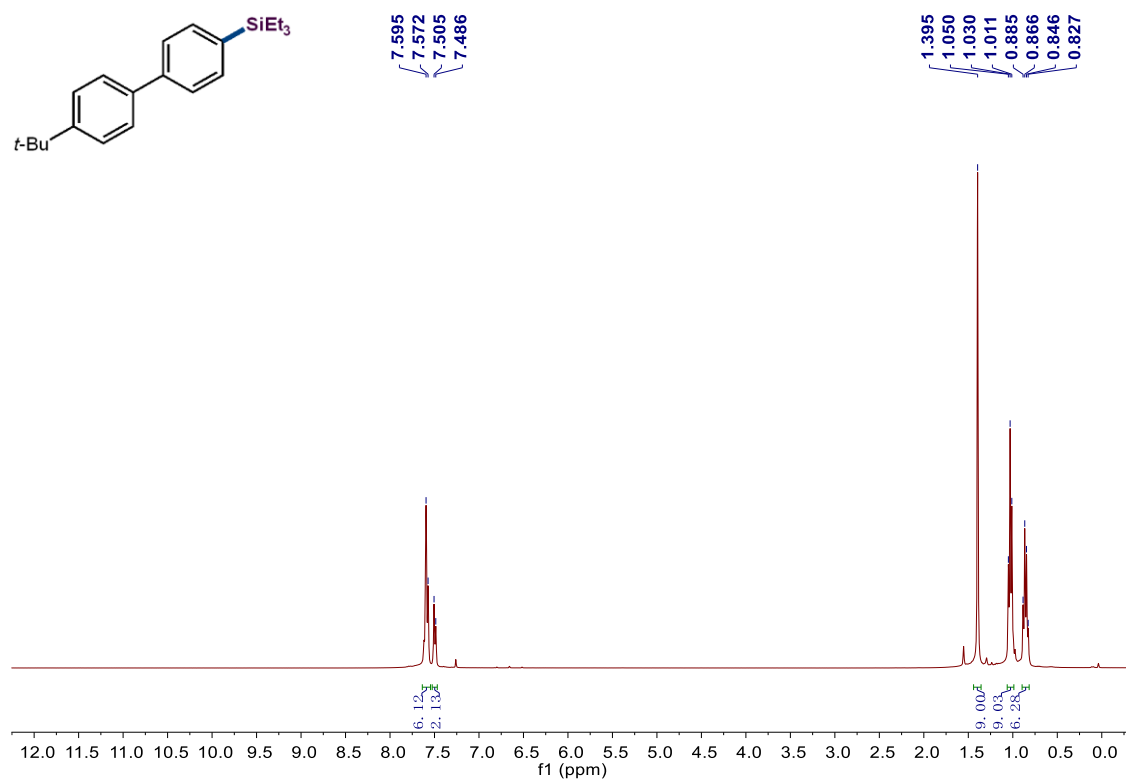
1-Methyl-6-(triethylsilyl)-1H-indole (3x)



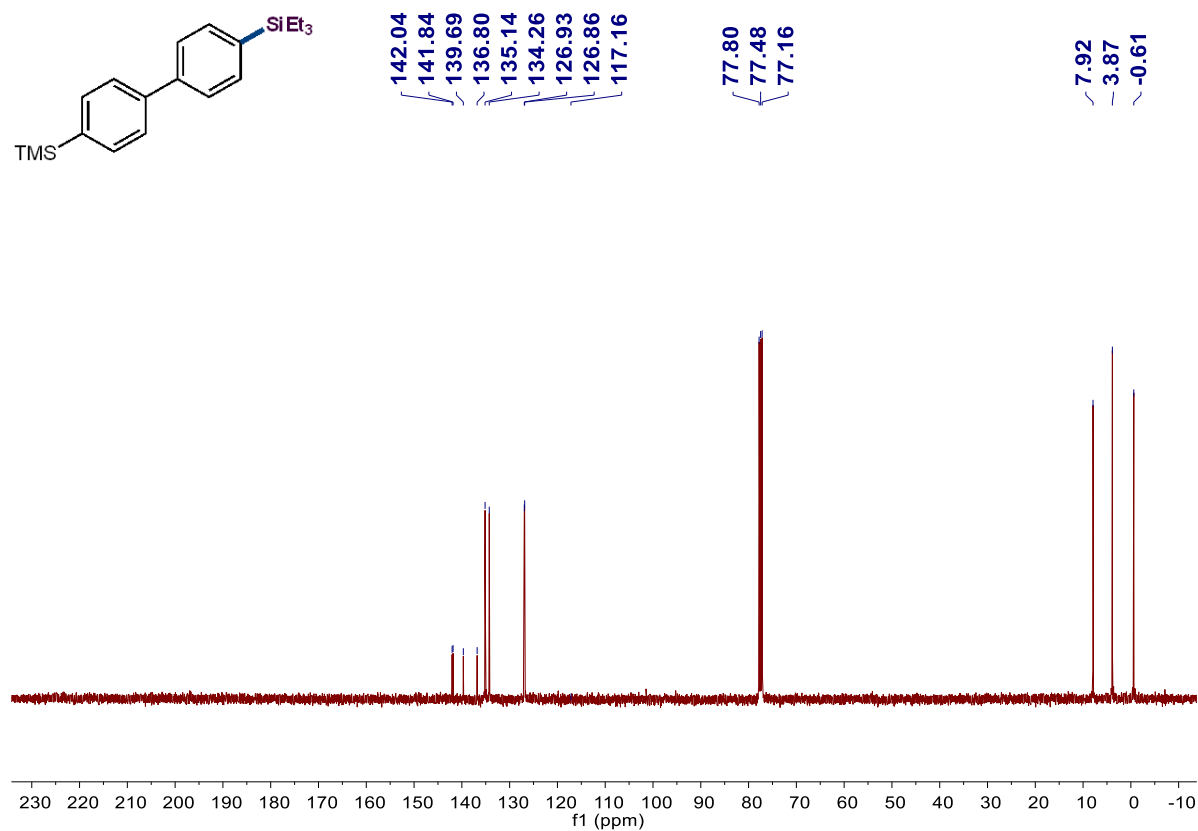
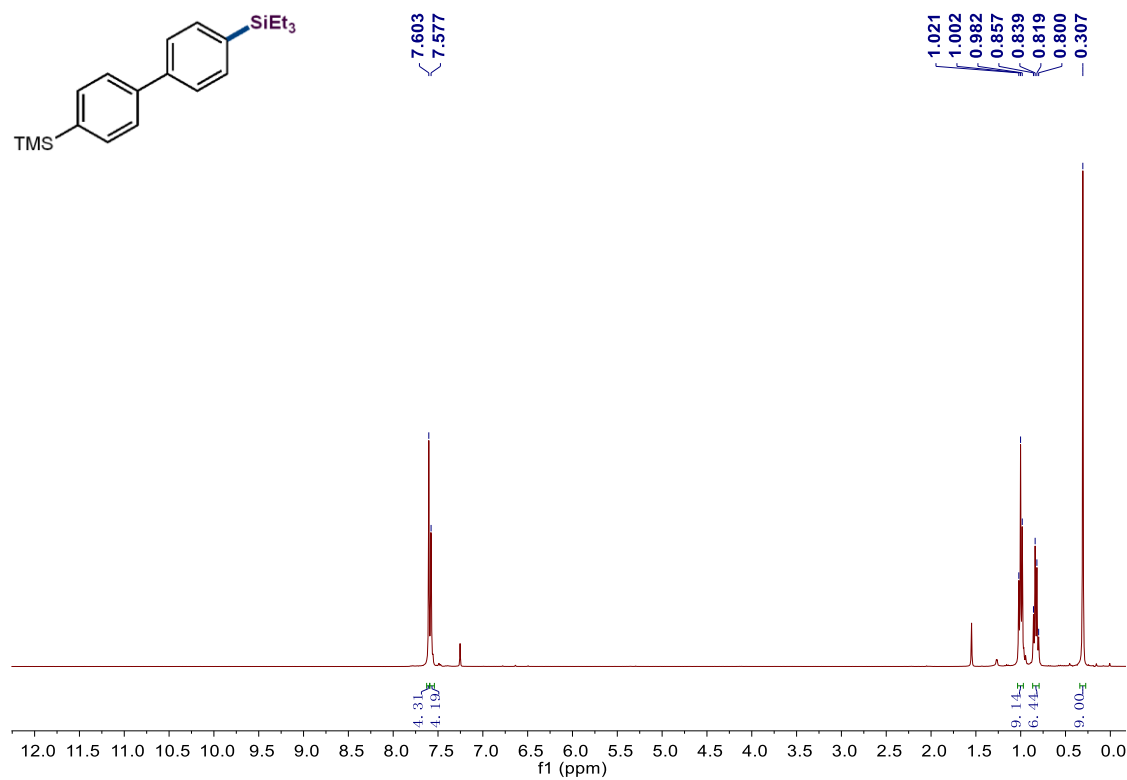
[1,1'-Biphenyl]-4-yltriethylsilane (3y)



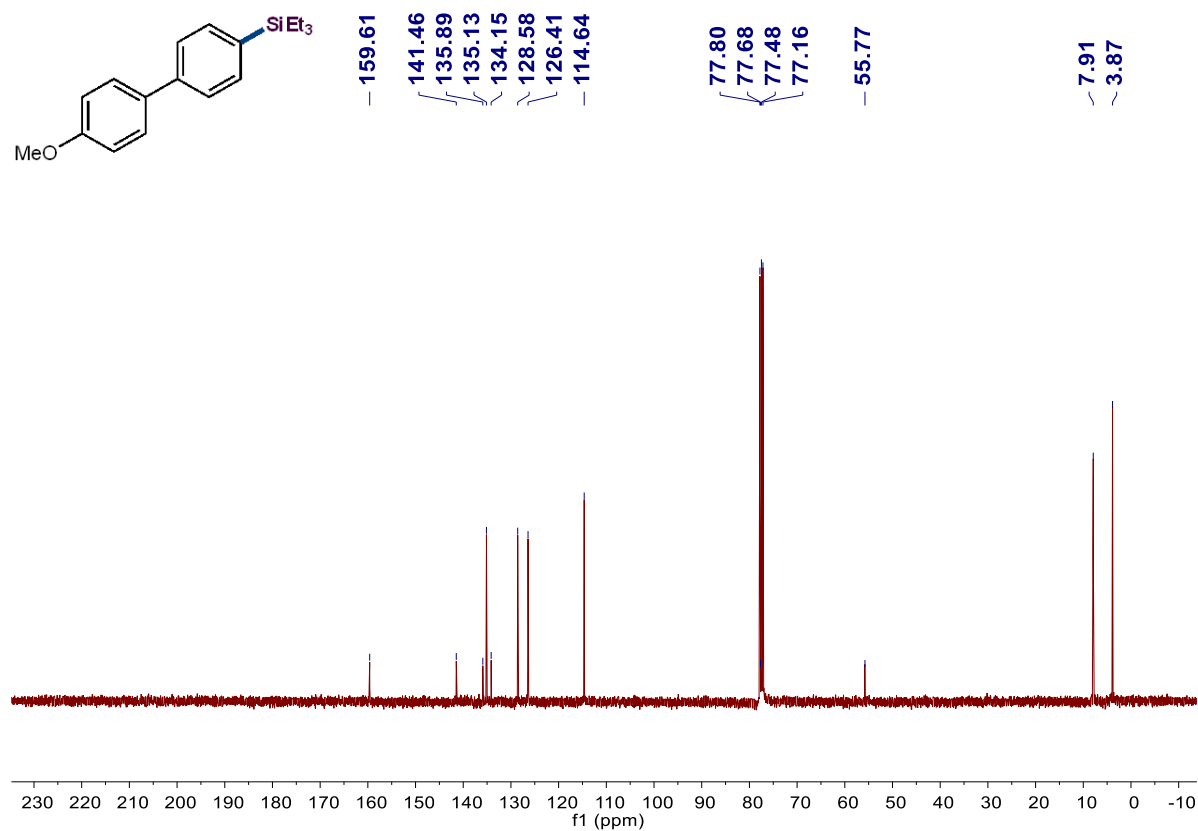
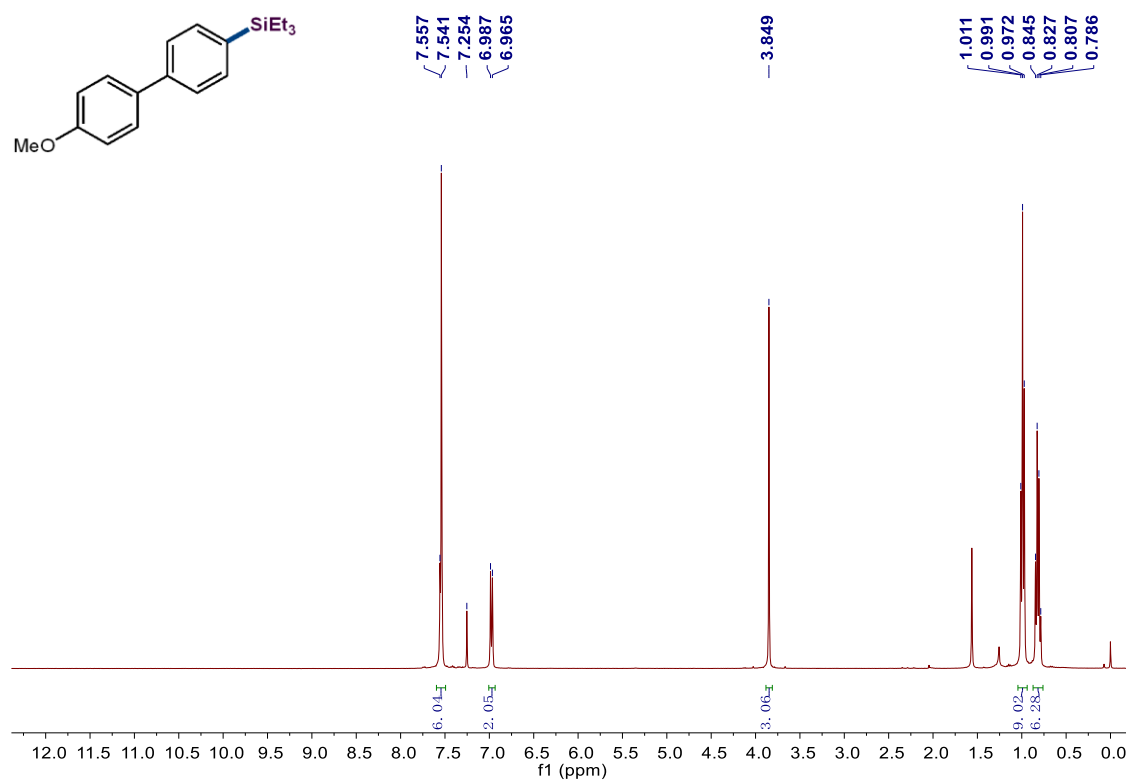
(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)triethylsilane (3z)



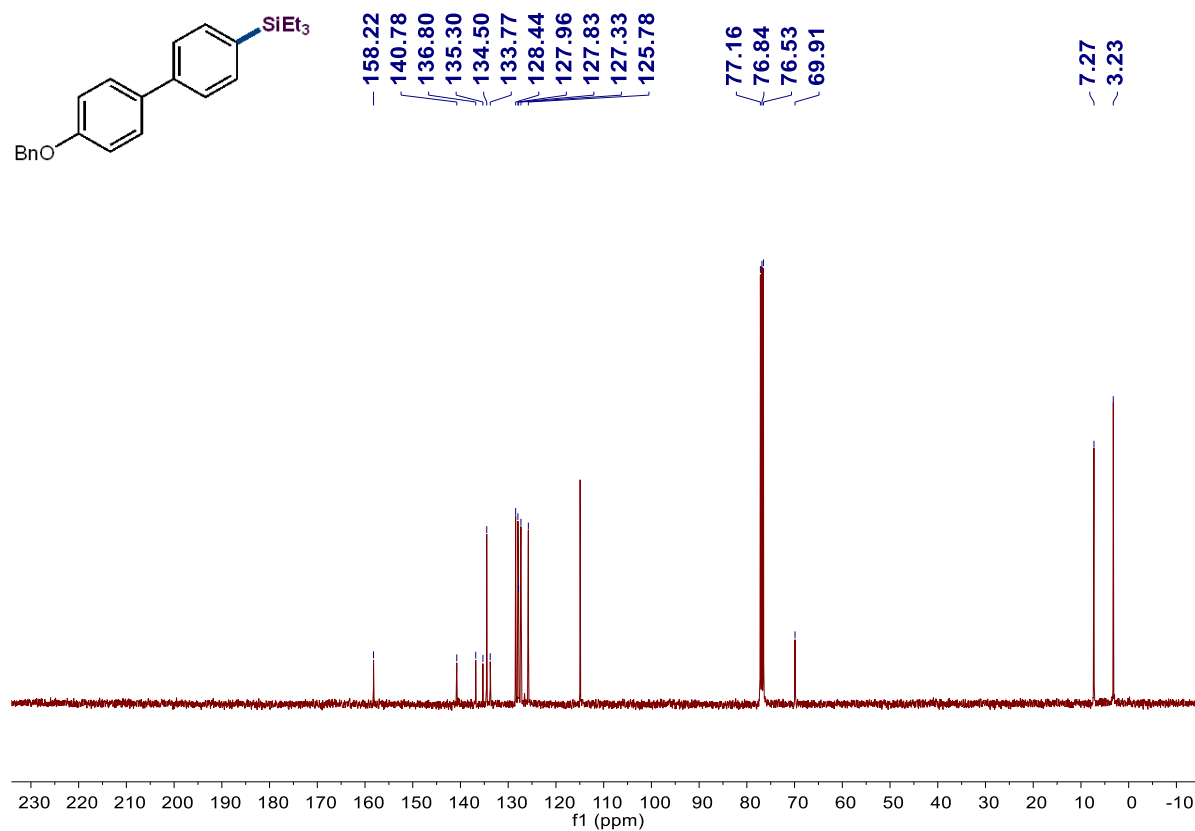
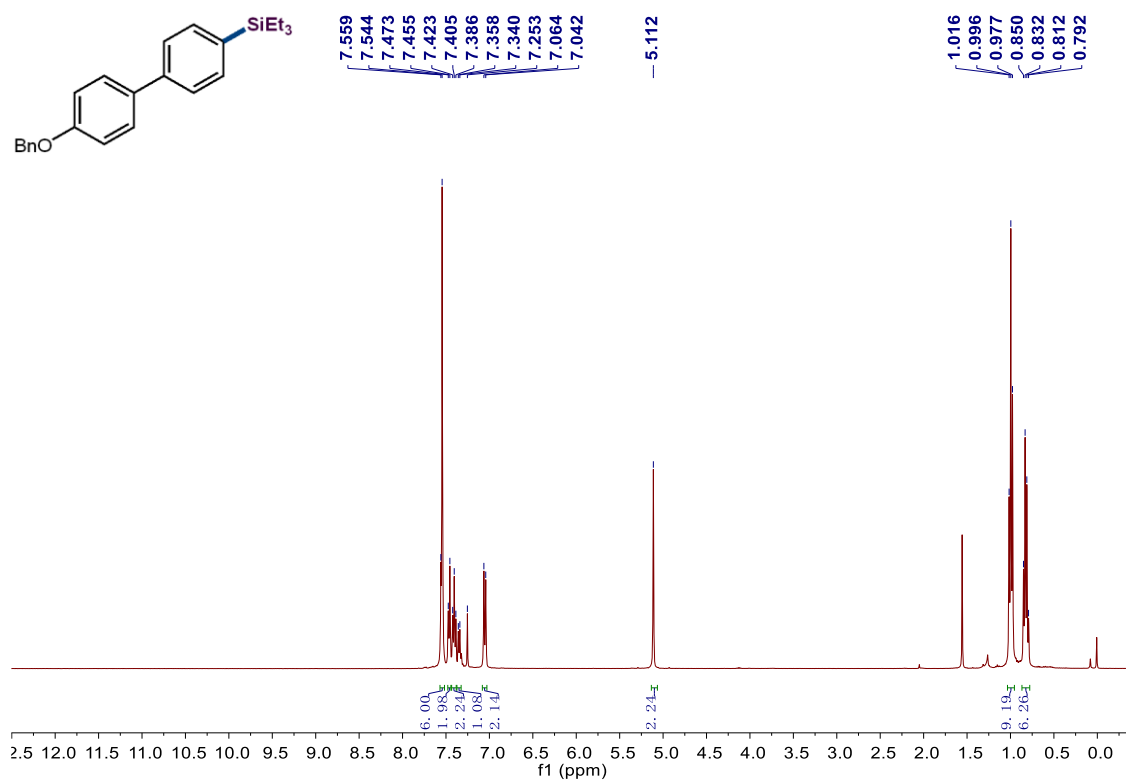
Triethyl(4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)silane (3ab)



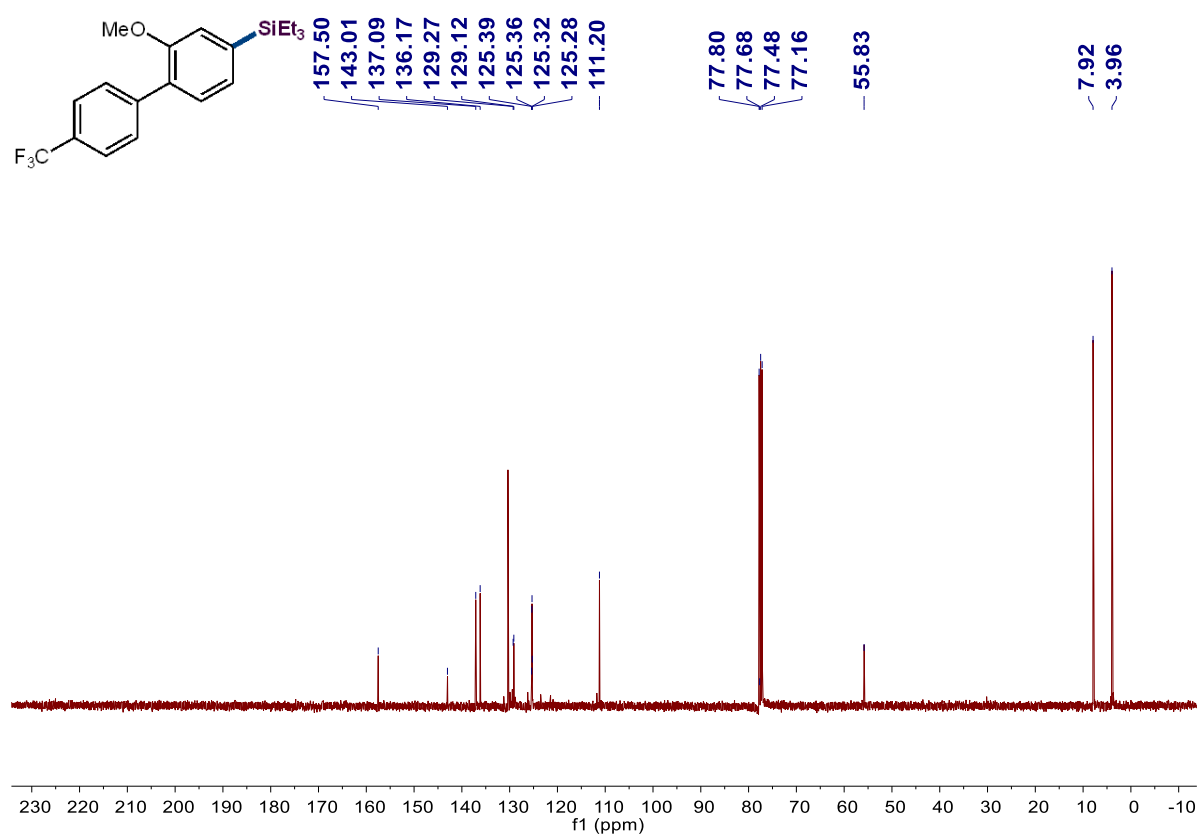
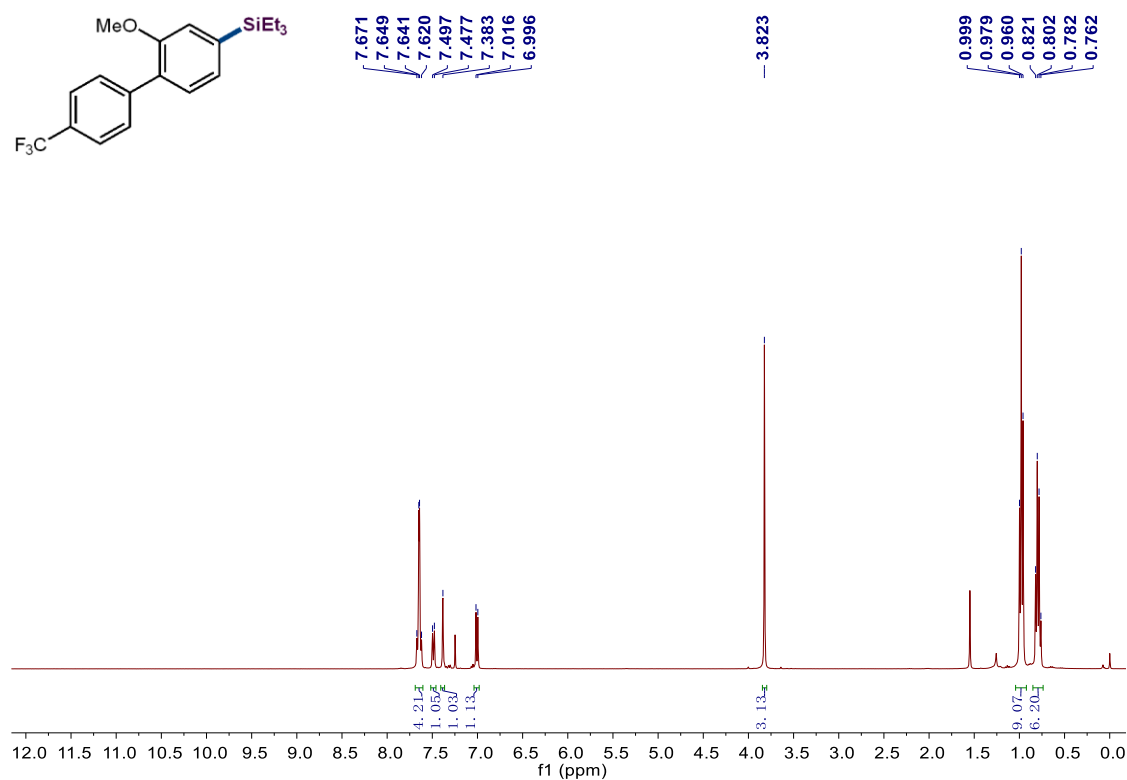
Triethyl(4'-methoxy-[1,1'-biphenyl]-4-yl)silane (3ac)



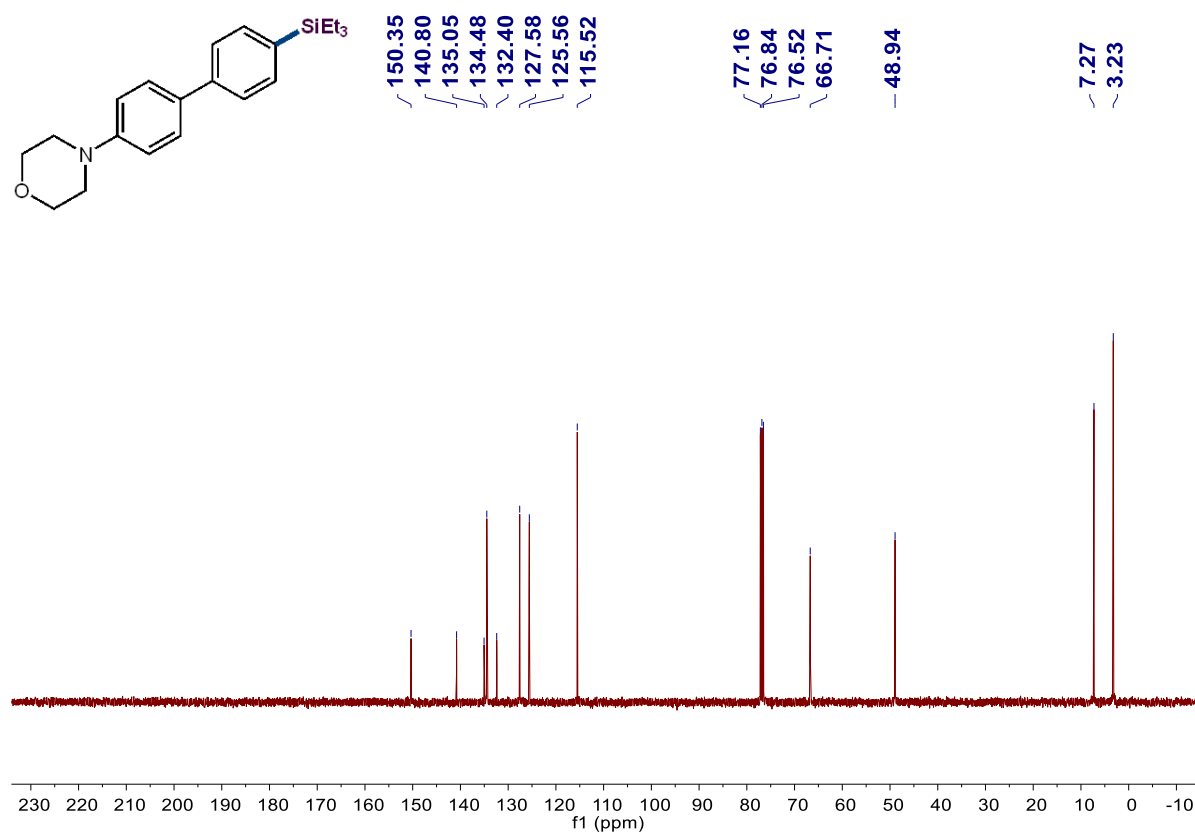
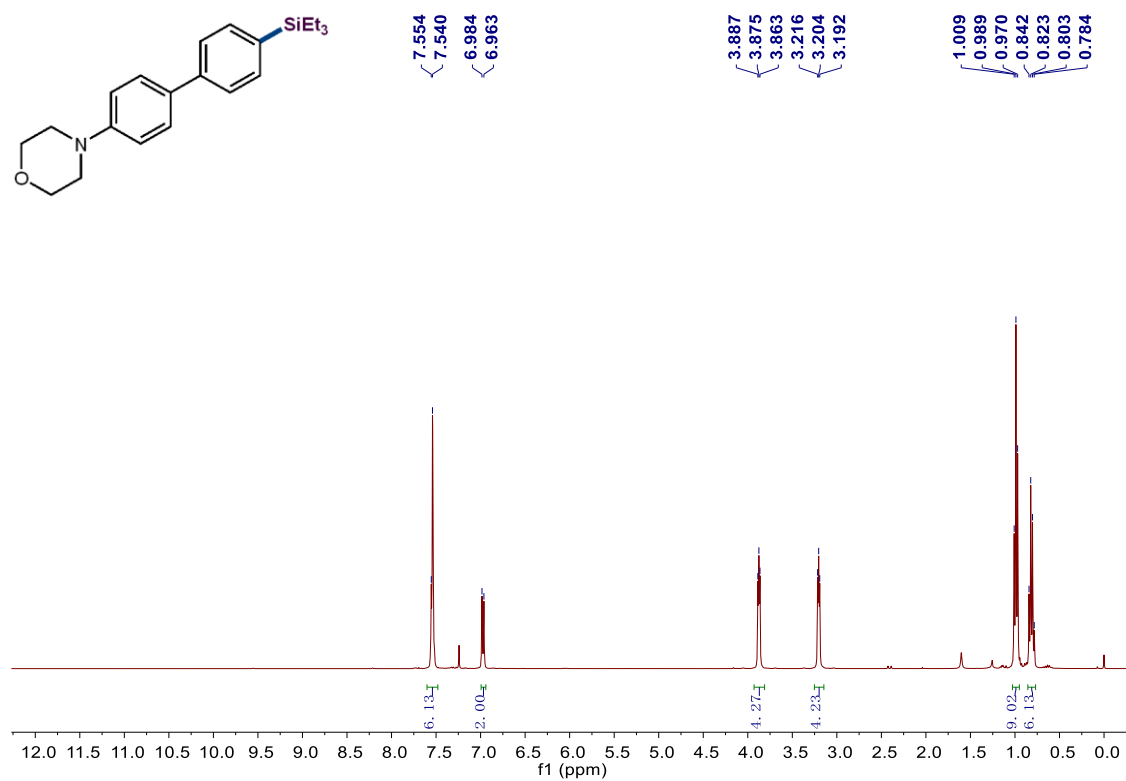
(4'-(Benzyloxy)-[1,1'-biphenyl]-4-yl)triethylsilane (3ad)



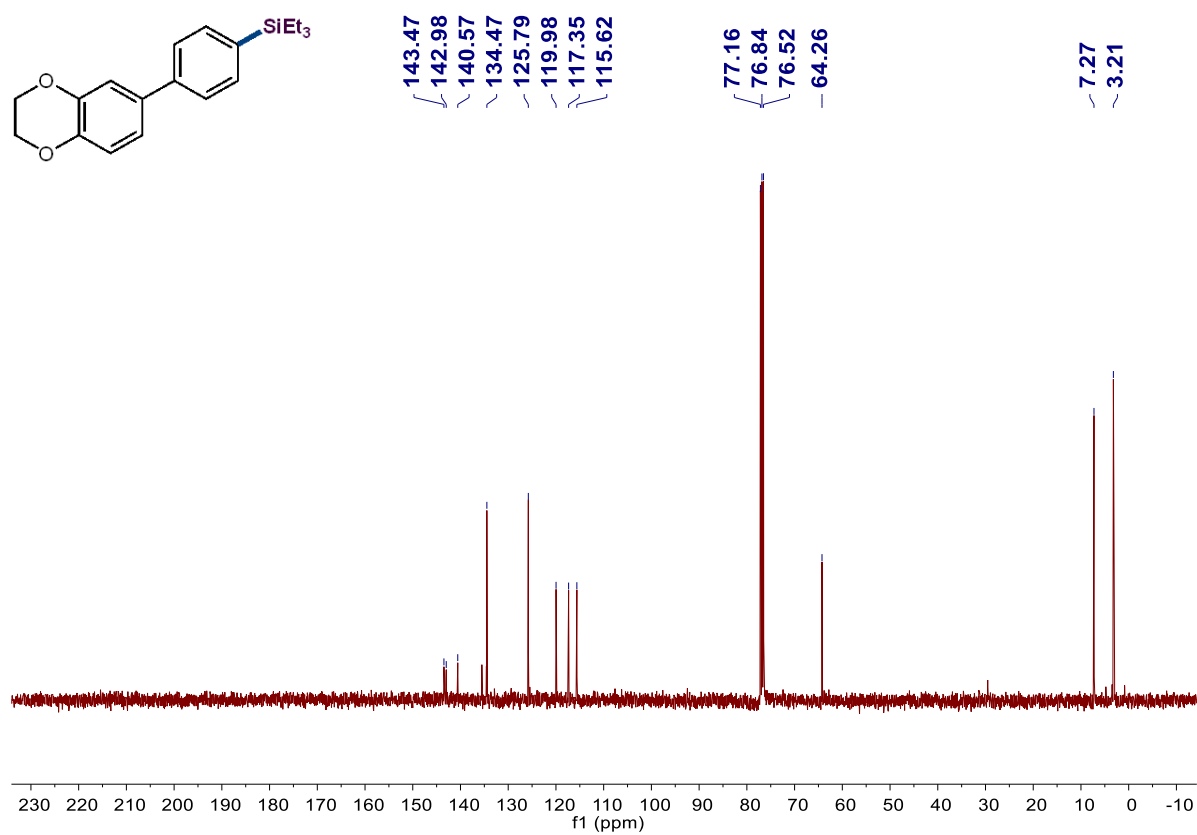
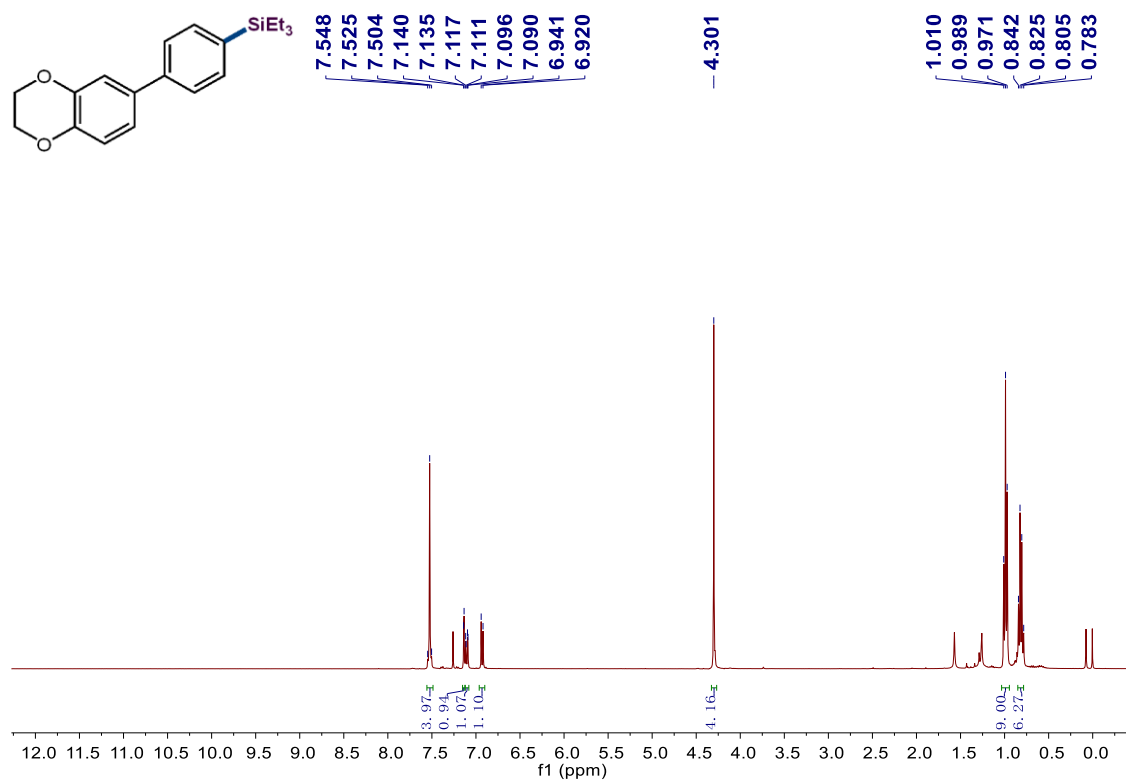
Triethyl(2-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)silane (3af)



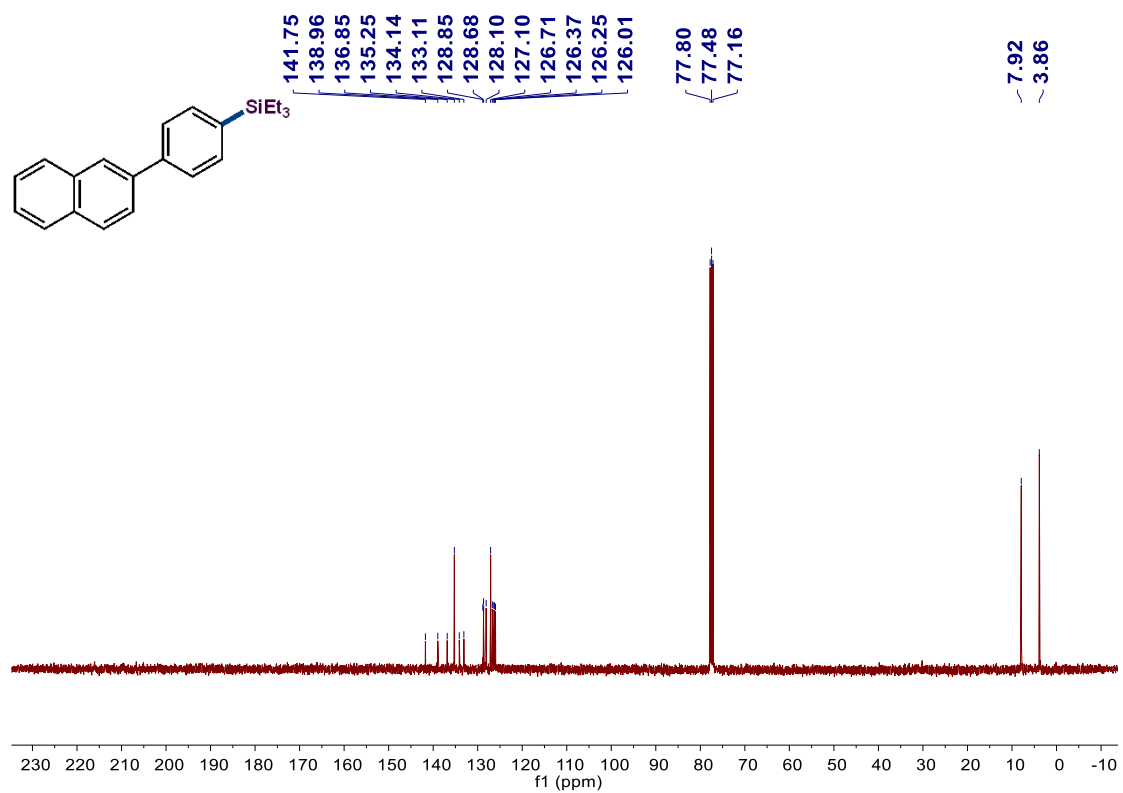
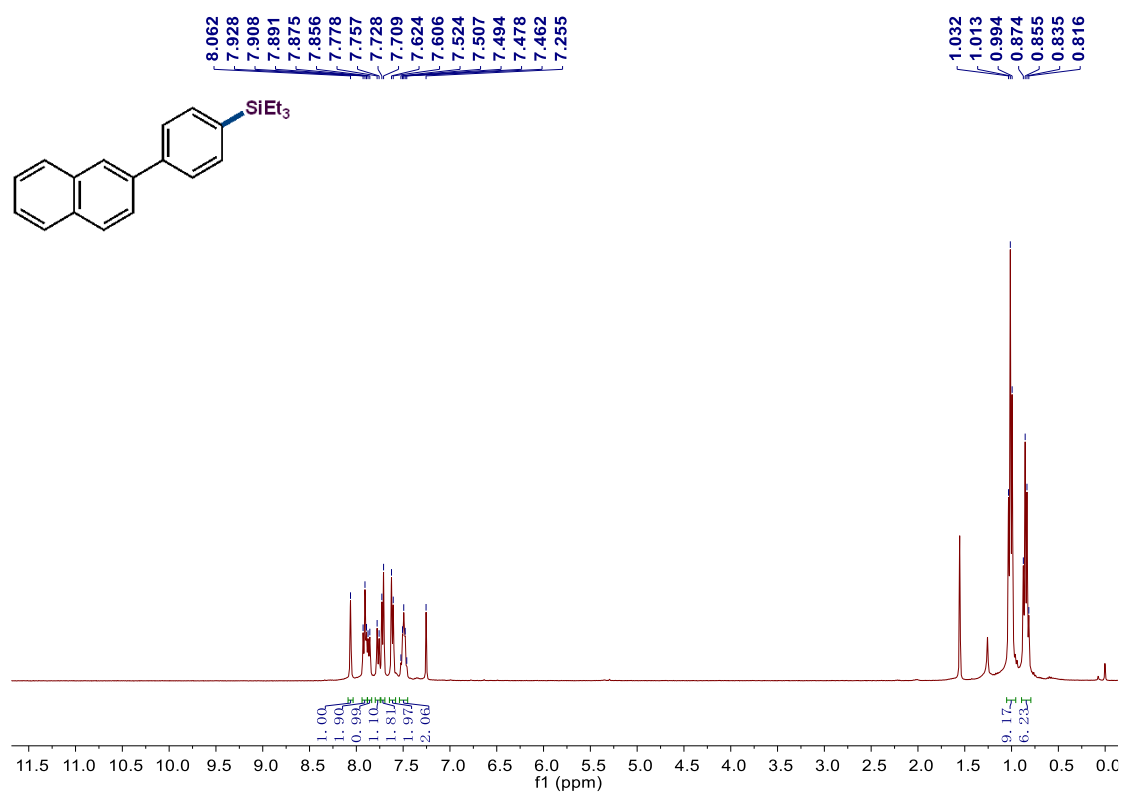
4-(4'-(Triethylsilyl)-[1,1'-biphenyl]-4-yl)morpholine (3ag)



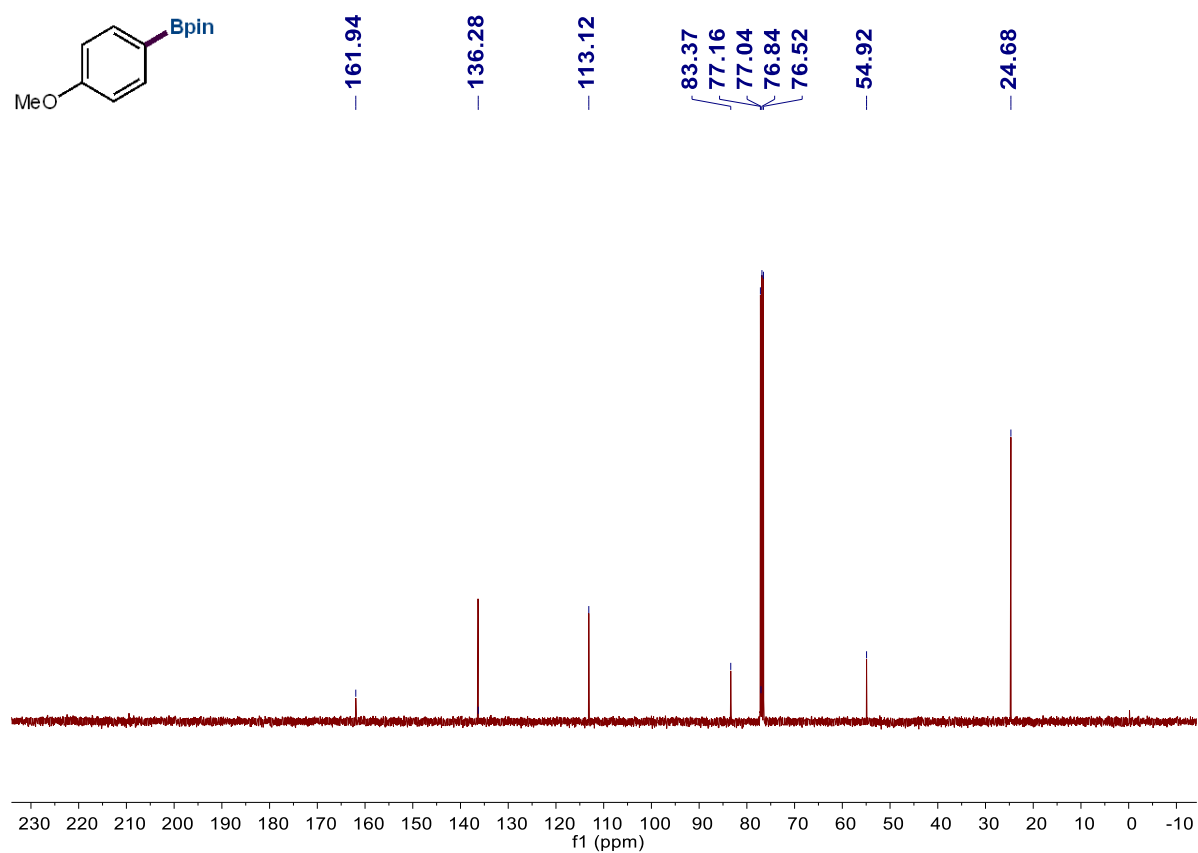
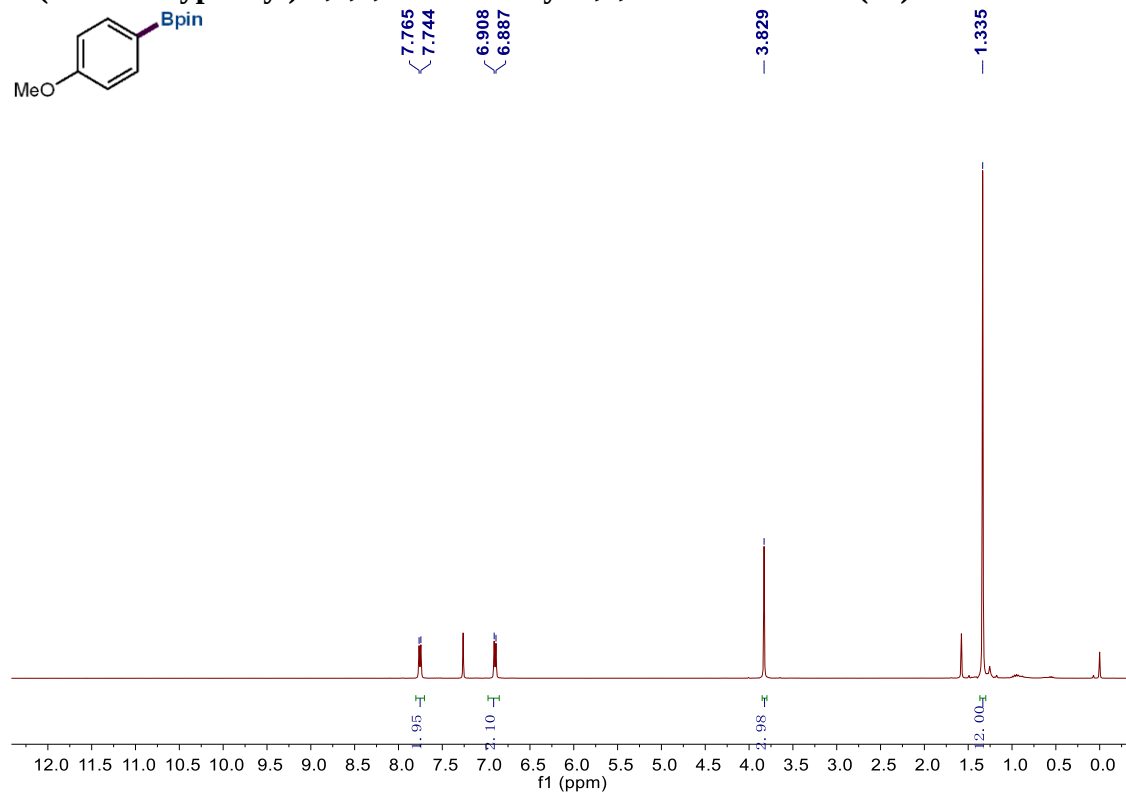
(4-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)phenyl)triethylsilane (3ah)



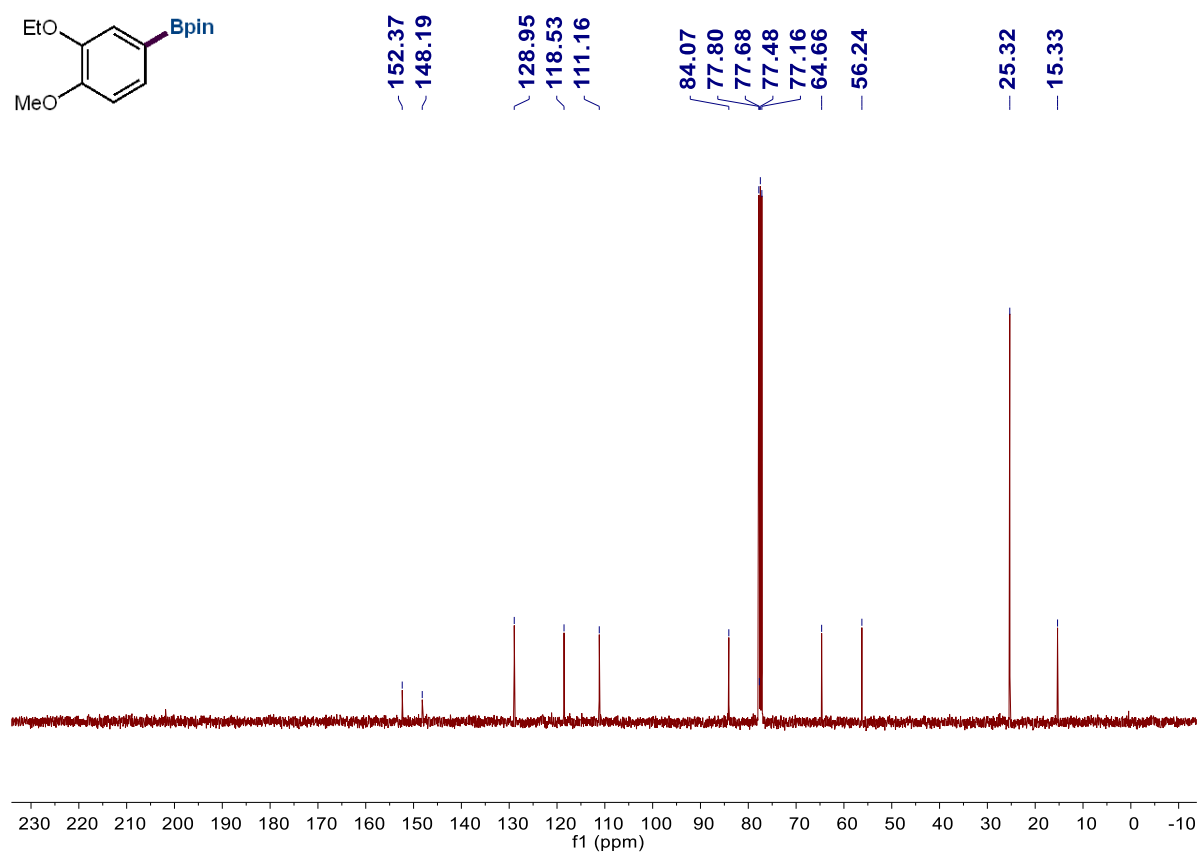
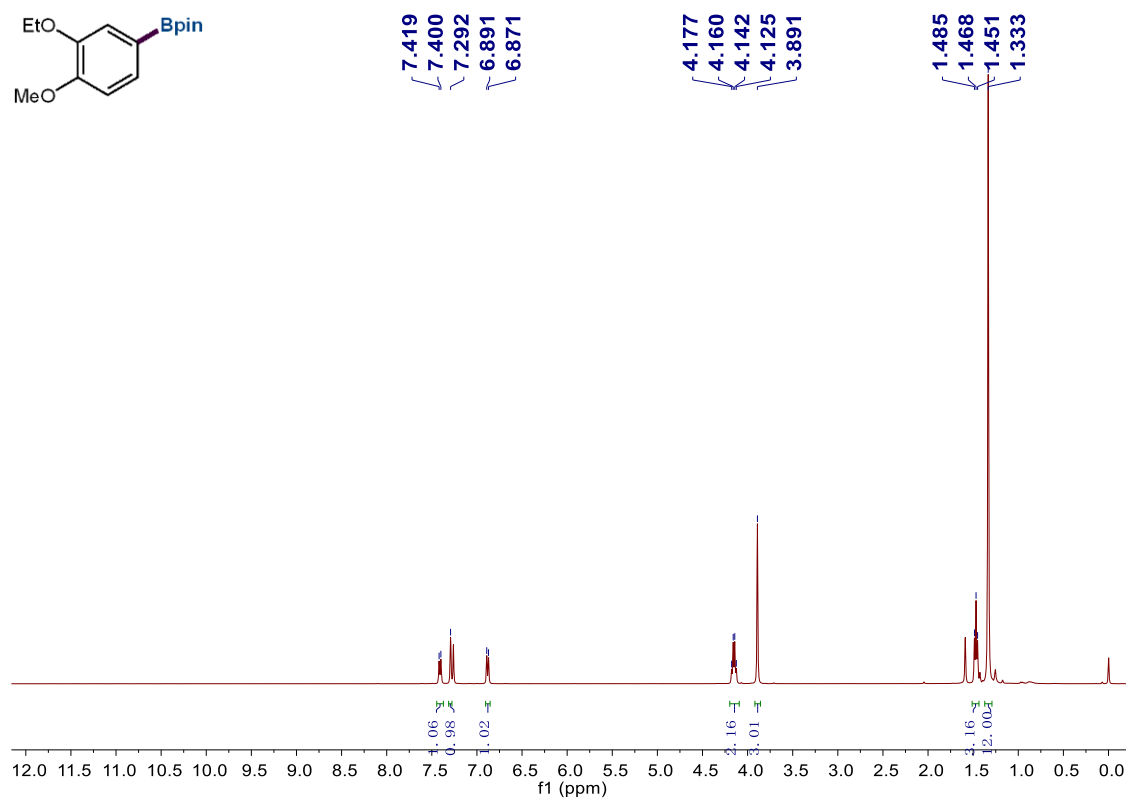
Triethyl(4-(naphthalen-2-yl)phenyl)silane (3ai)



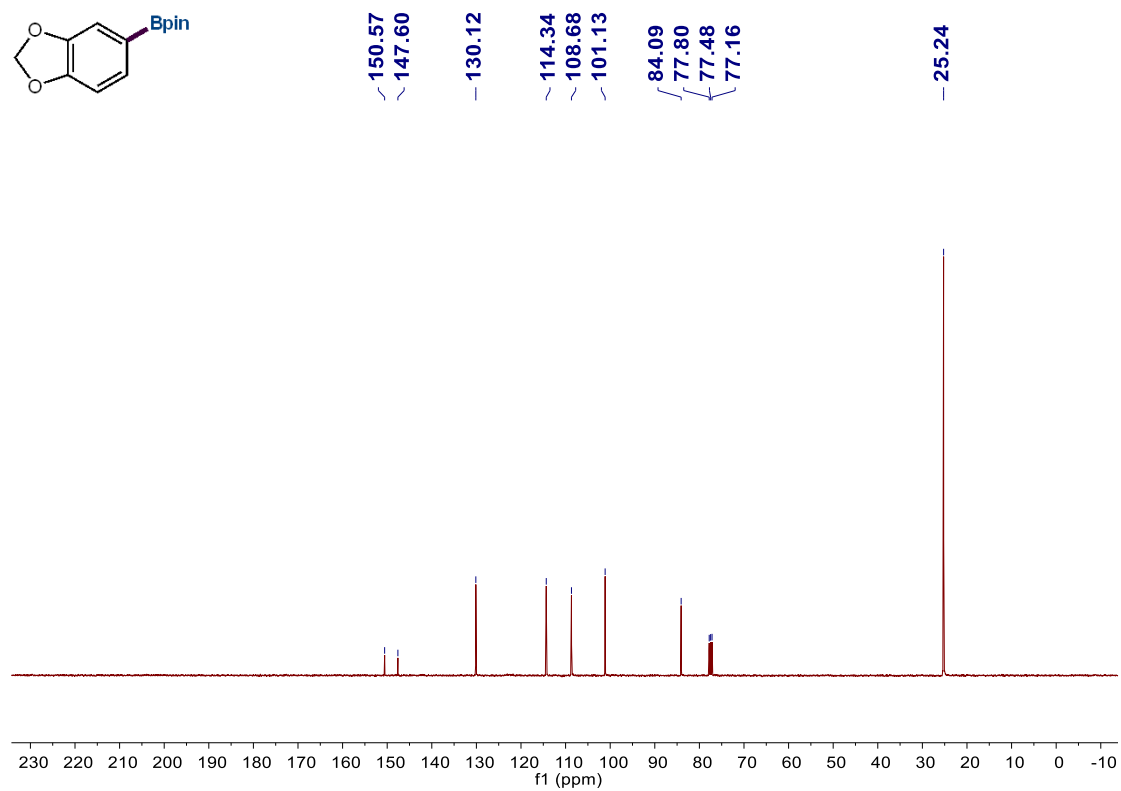
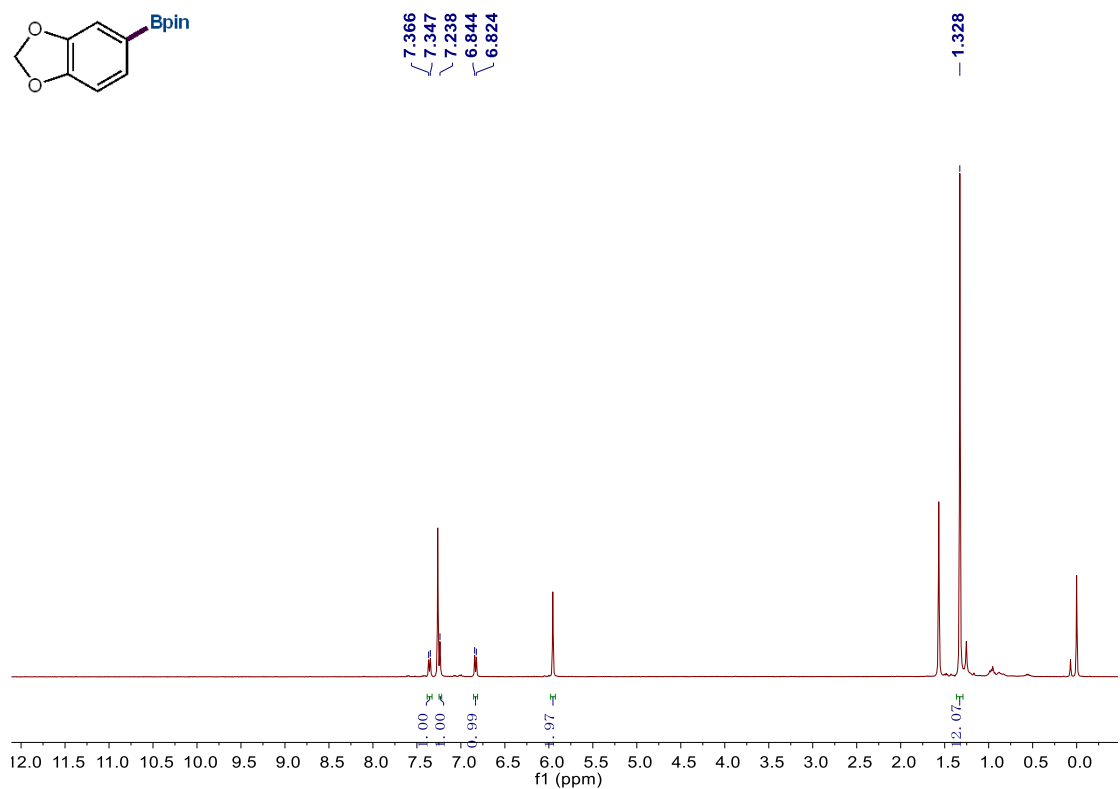
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)



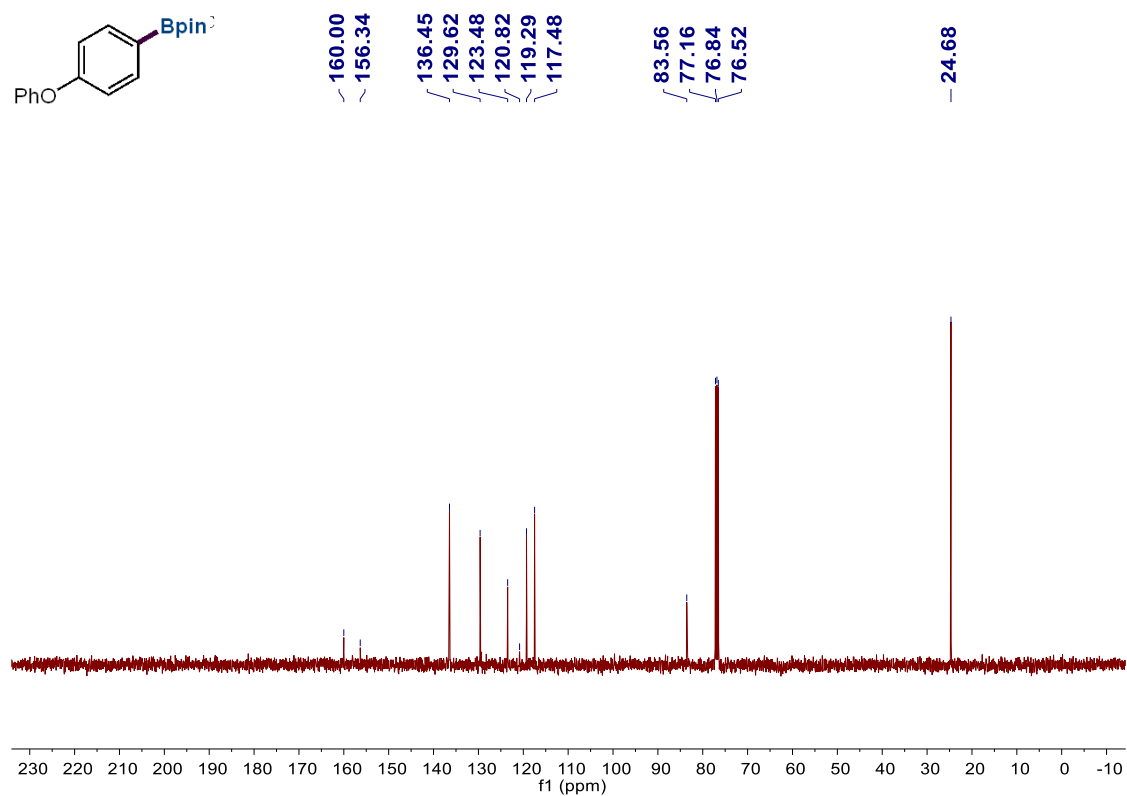
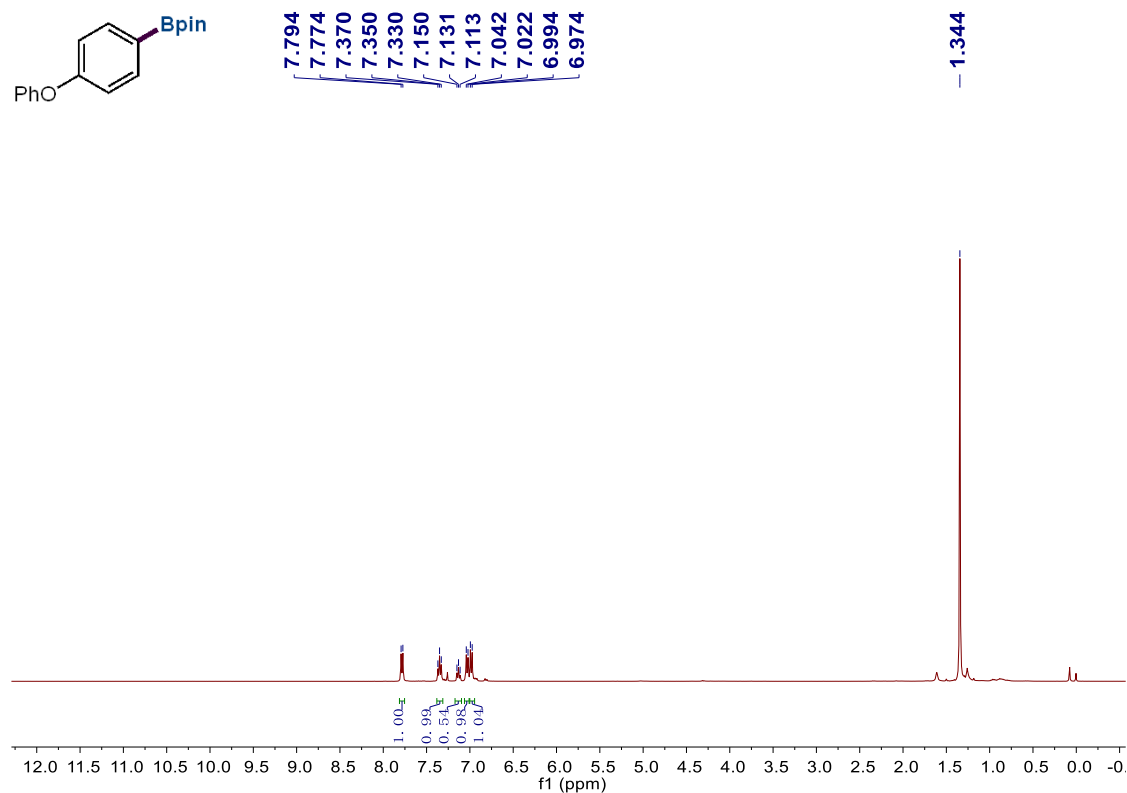
2-(3-Ethoxy-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)



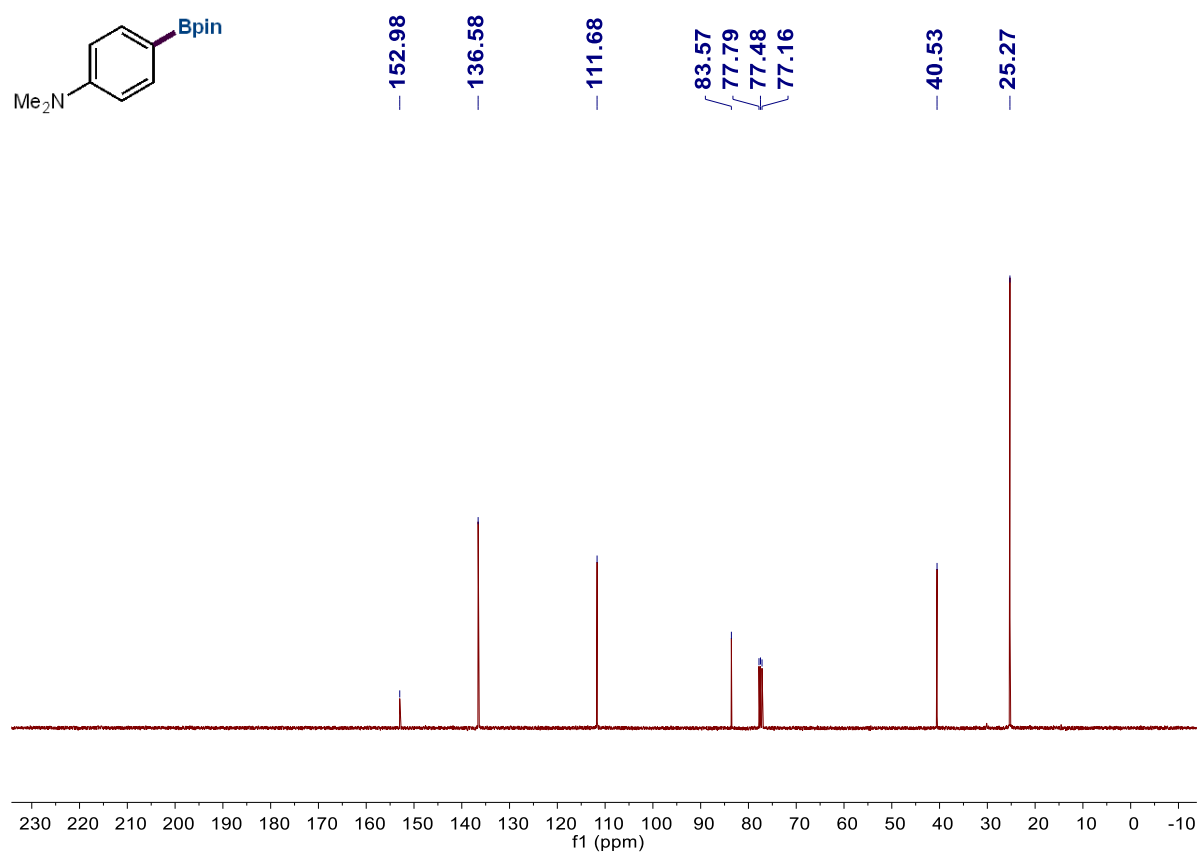
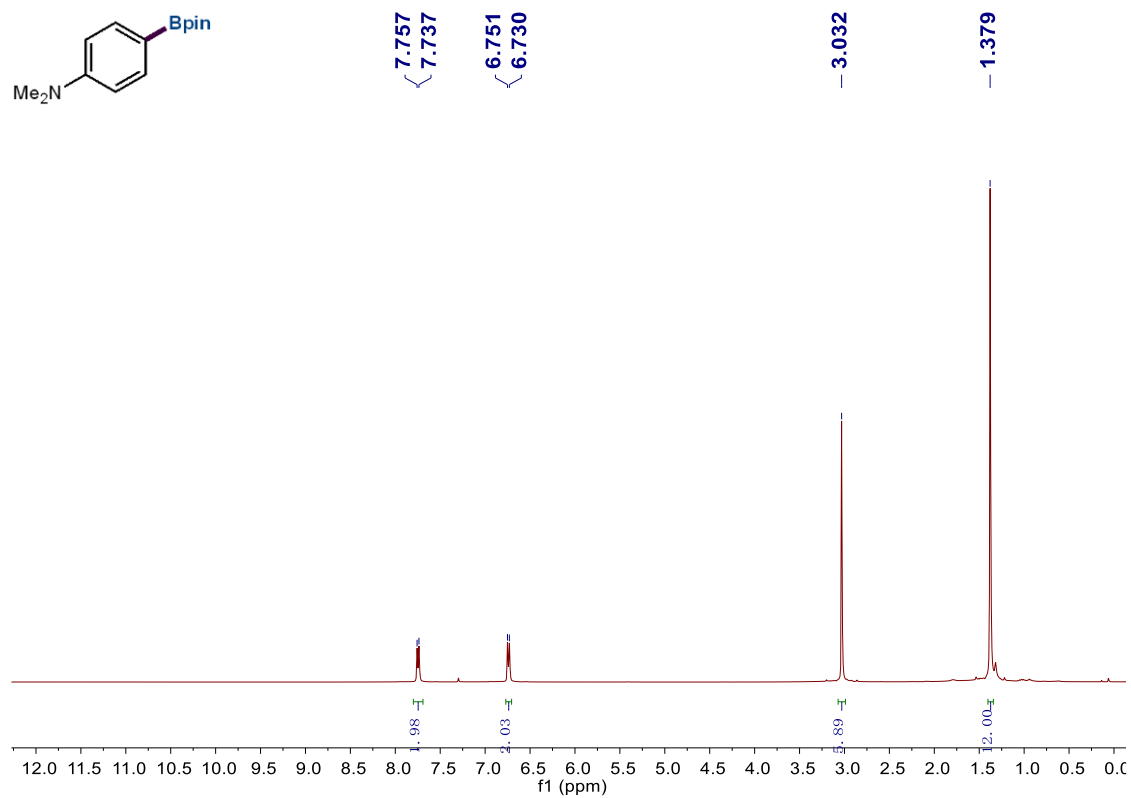
2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)



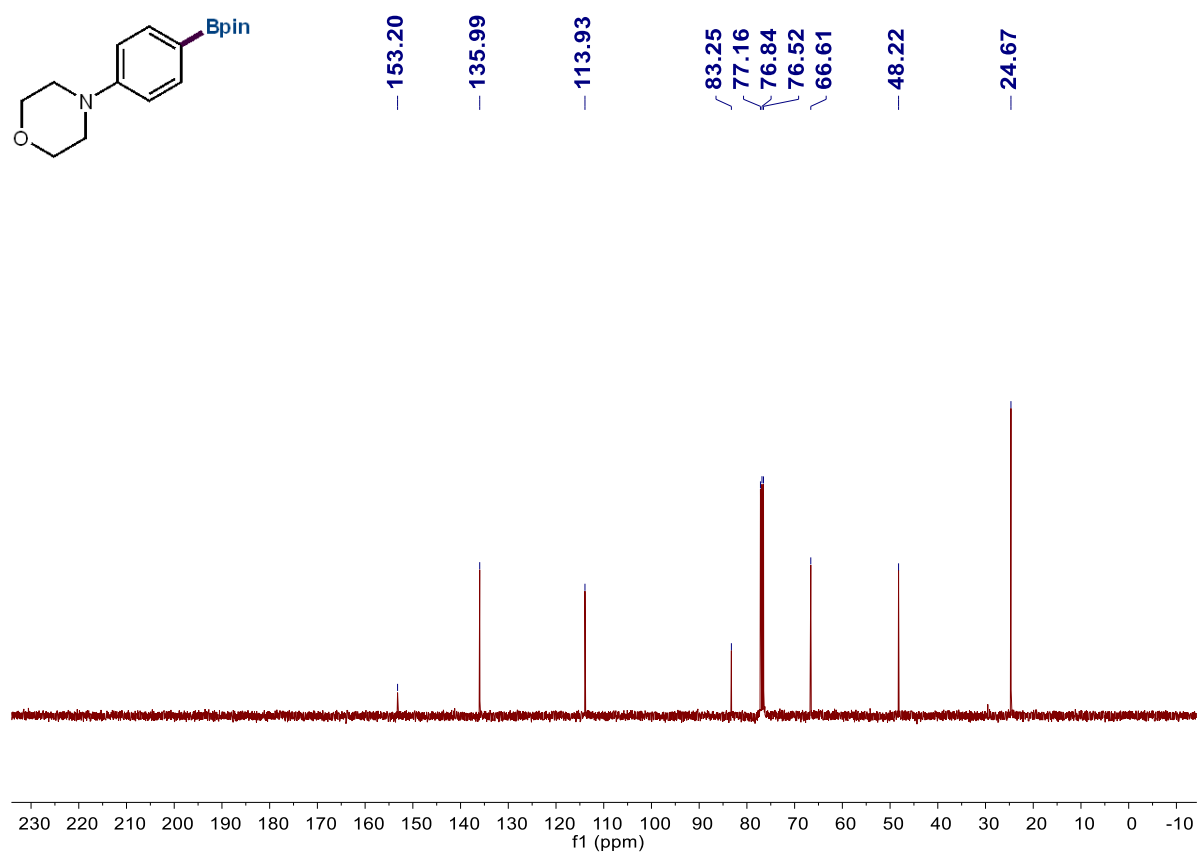
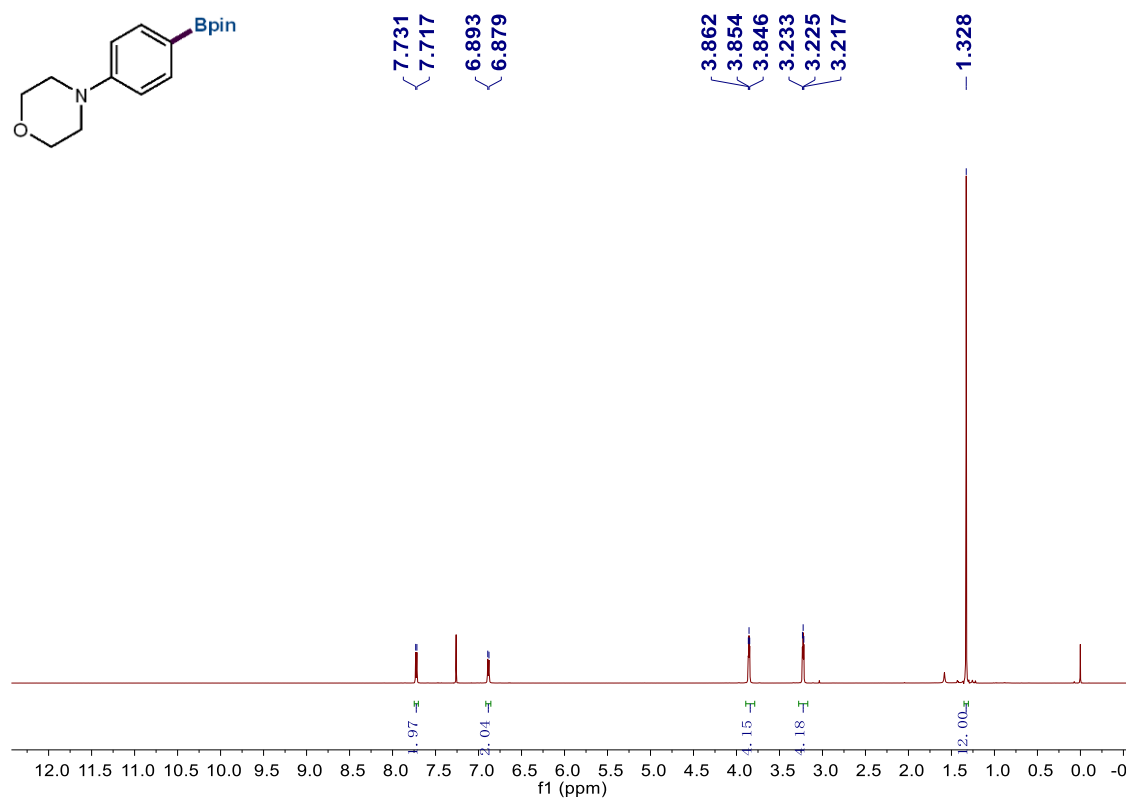
4,4,5,5-Tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (4d)



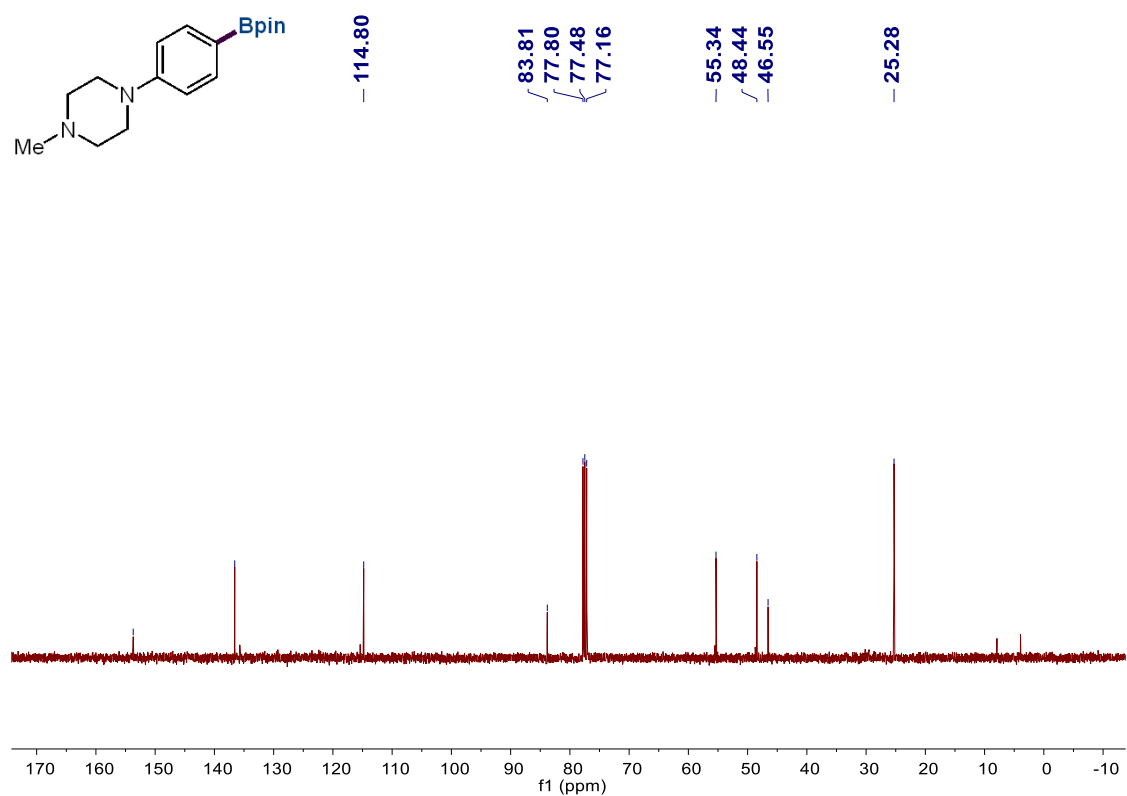
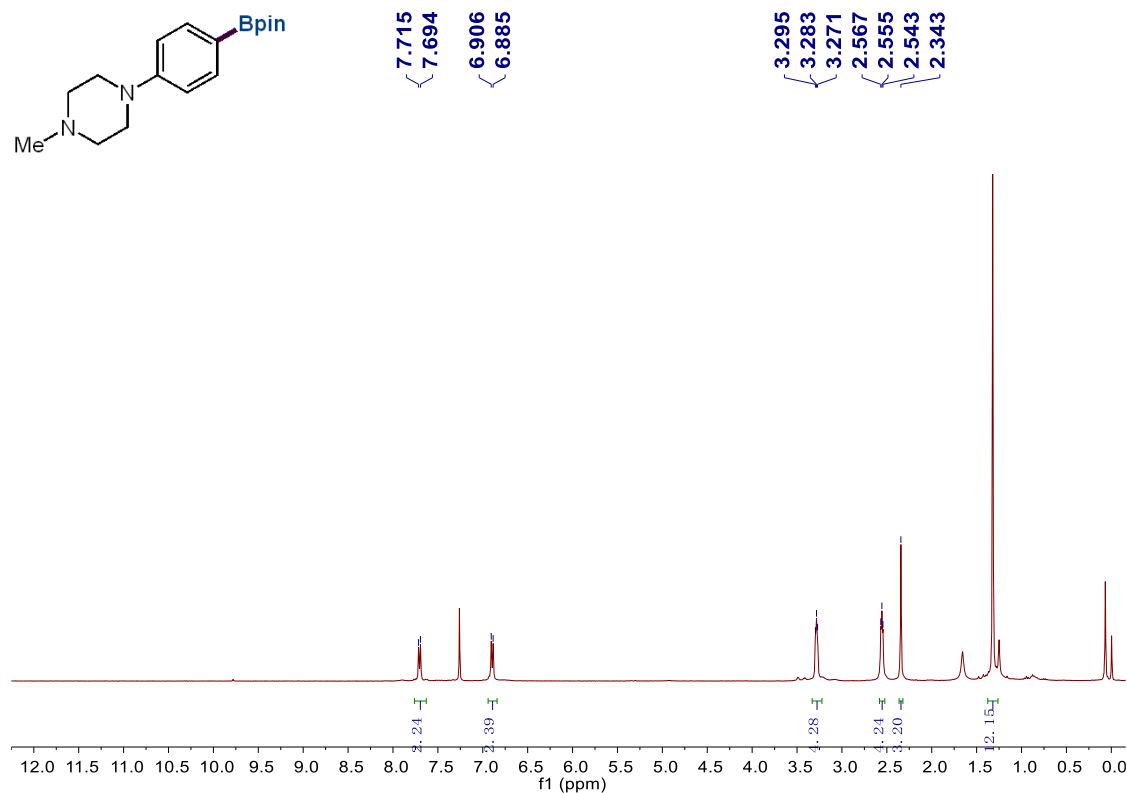
***N,N*-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4e)**



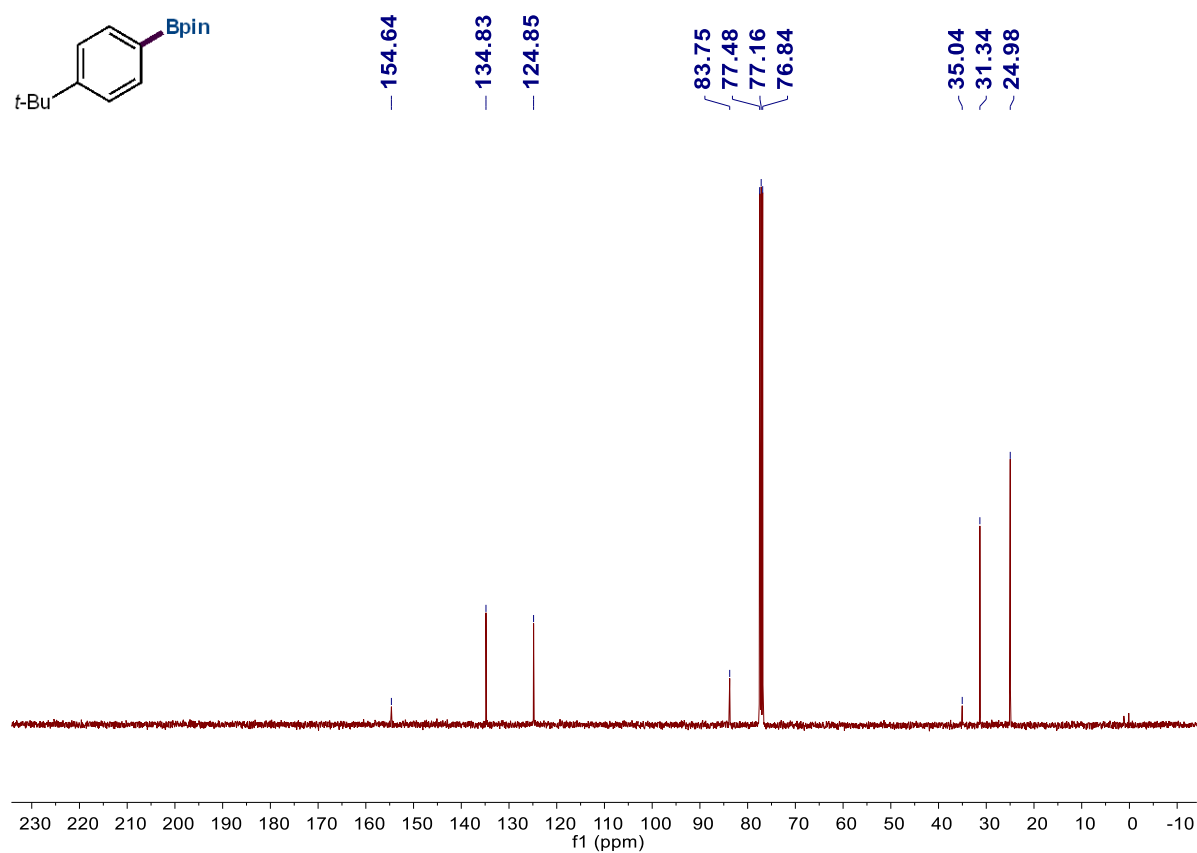
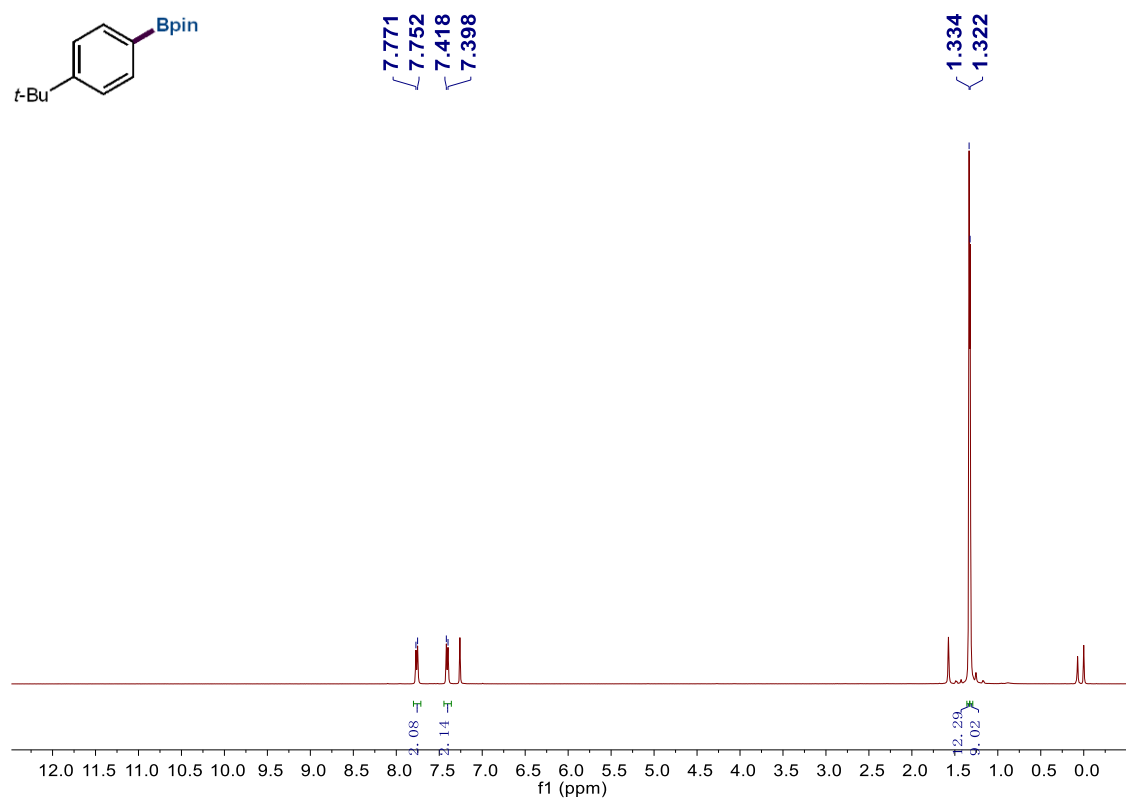
4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (4f)



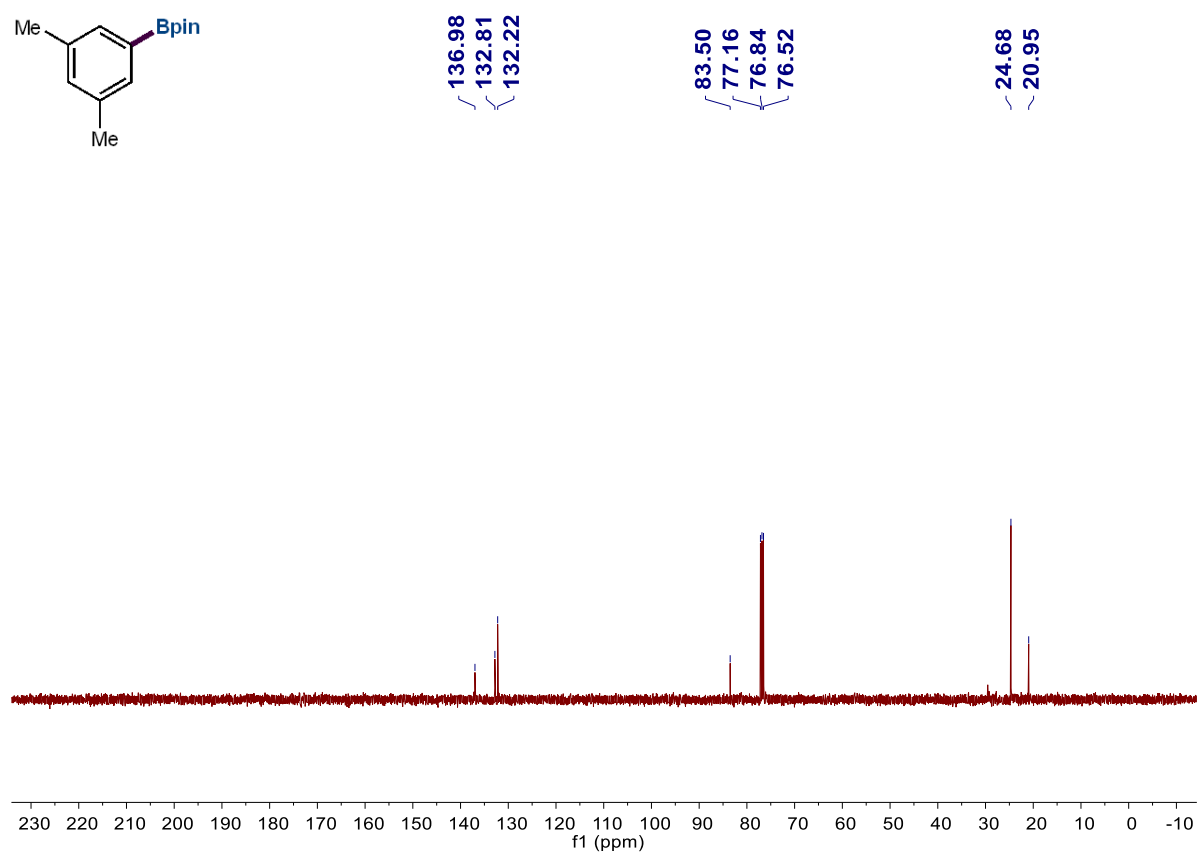
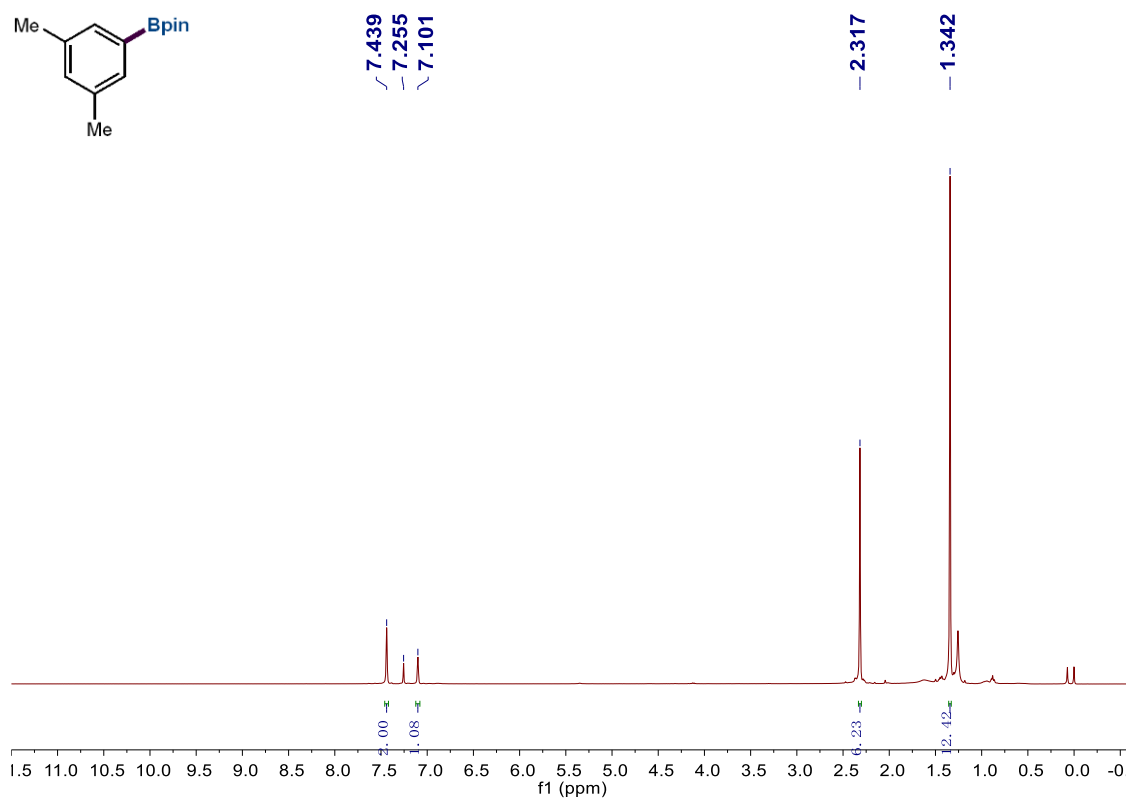
1-Methyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine (4g).



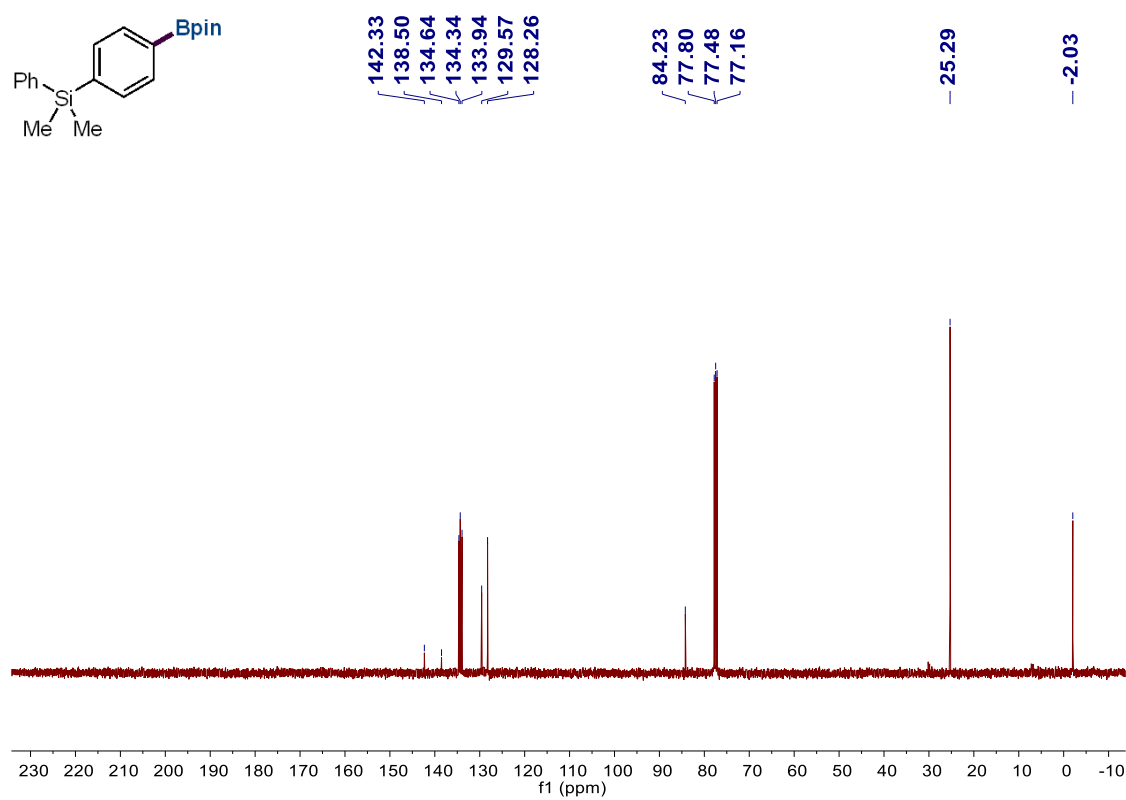
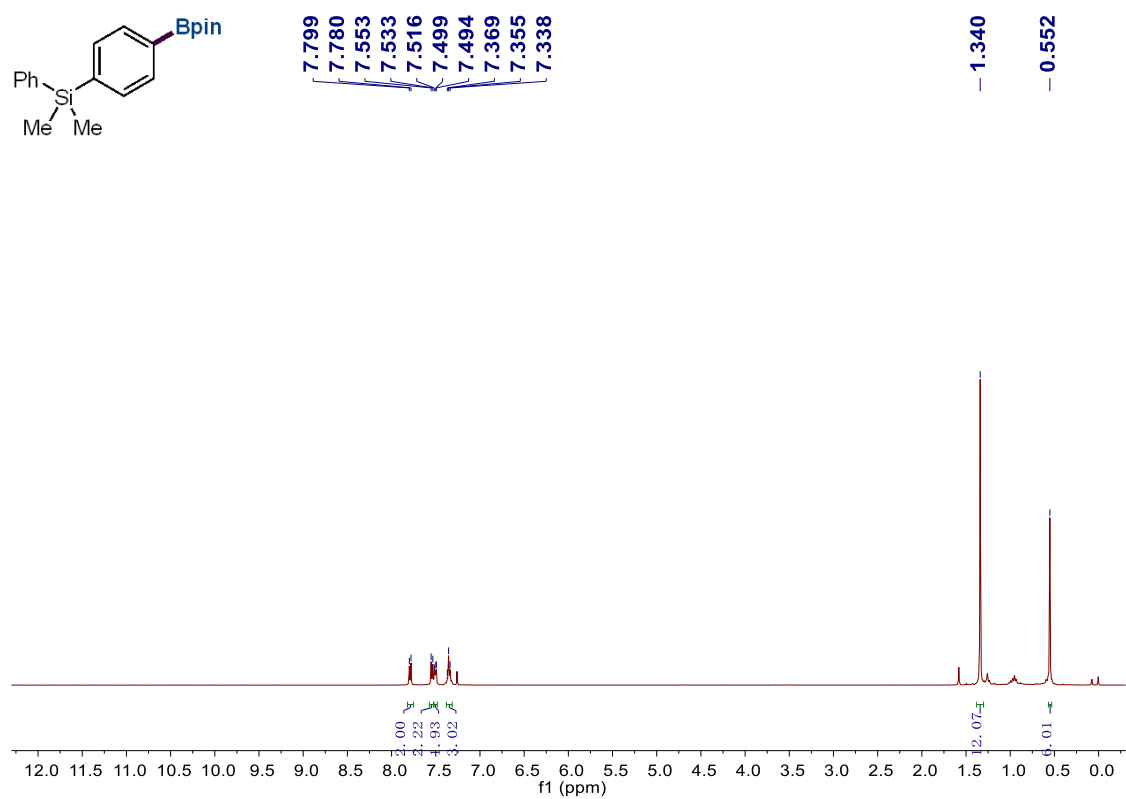
2-(4-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h).



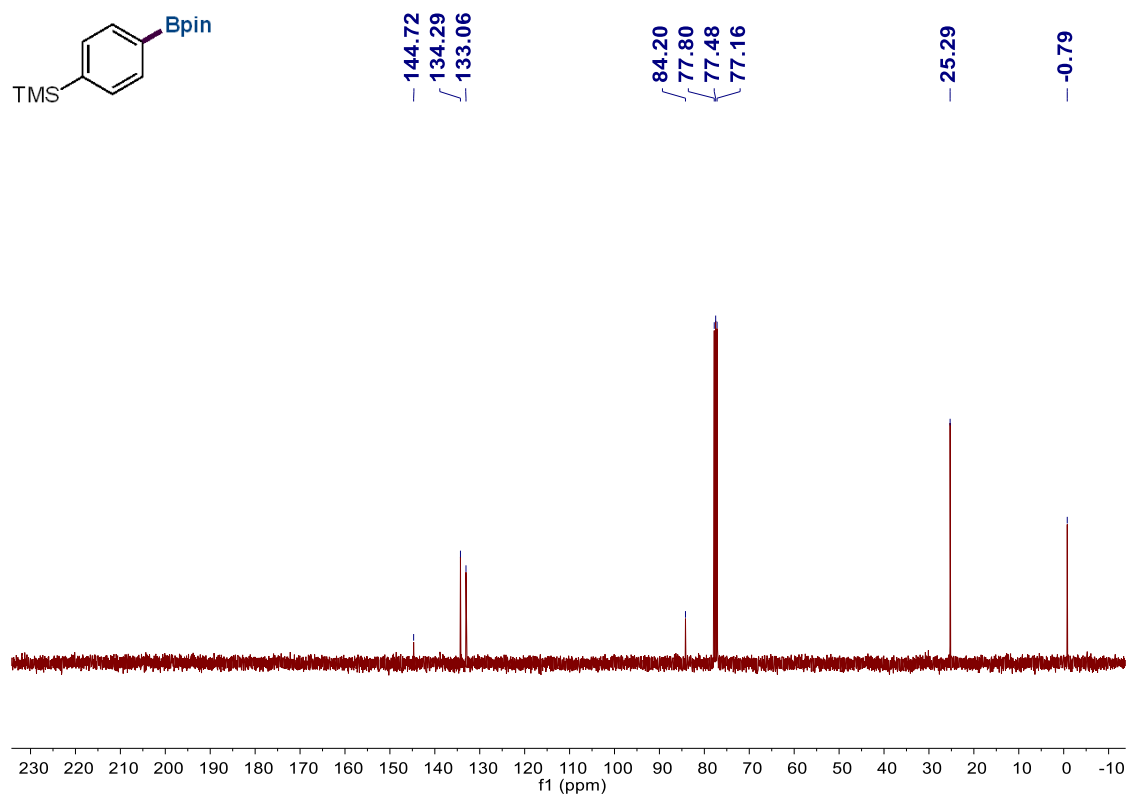
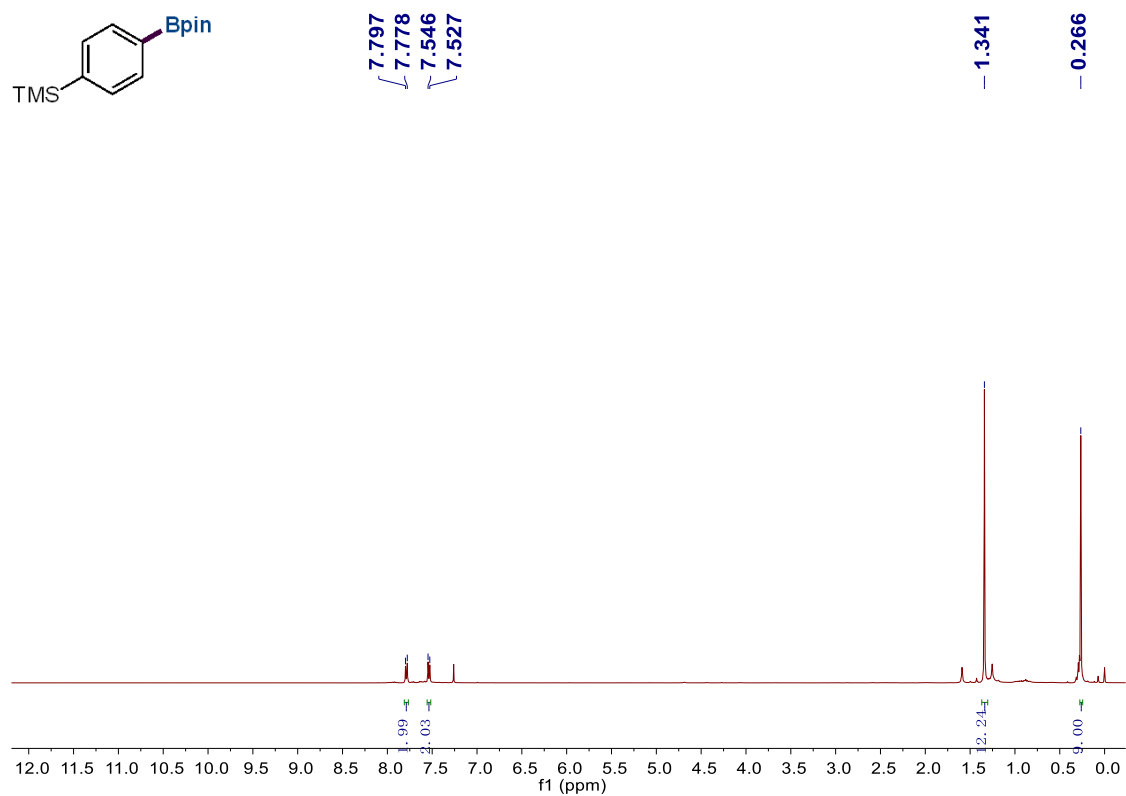
2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i).



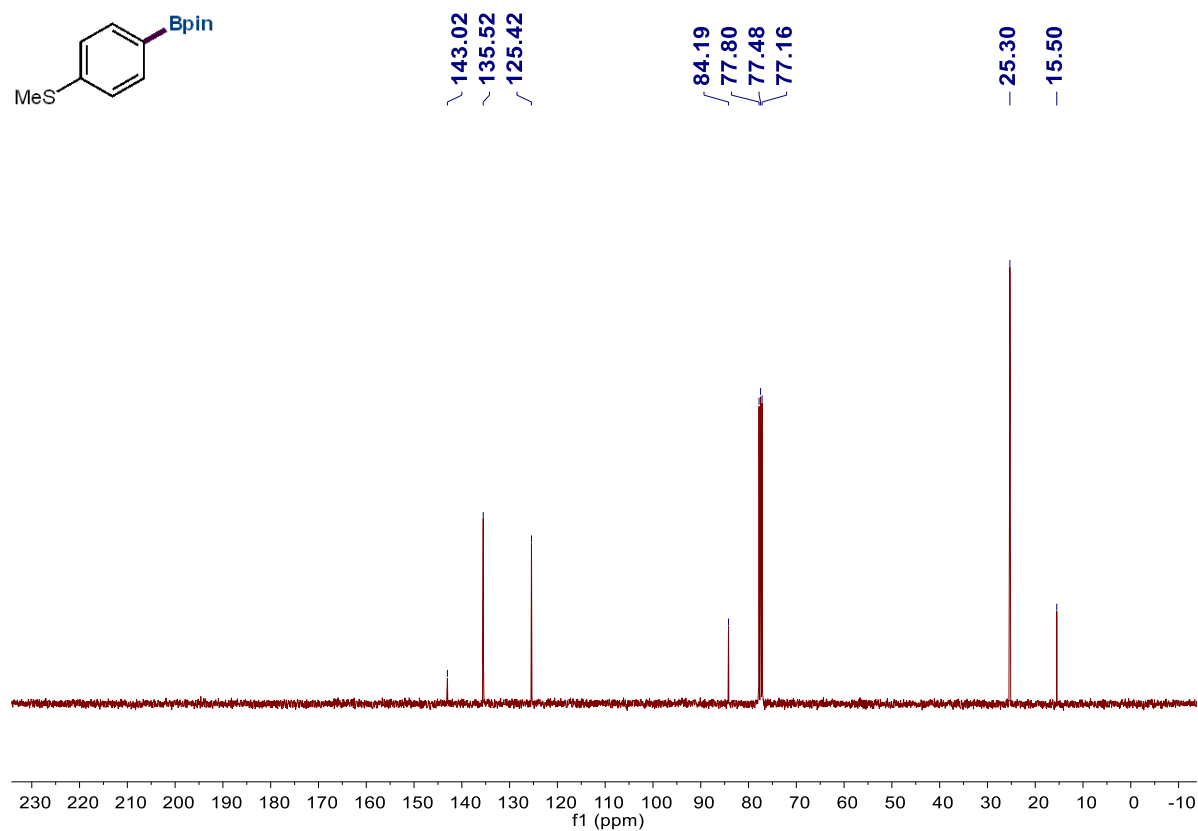
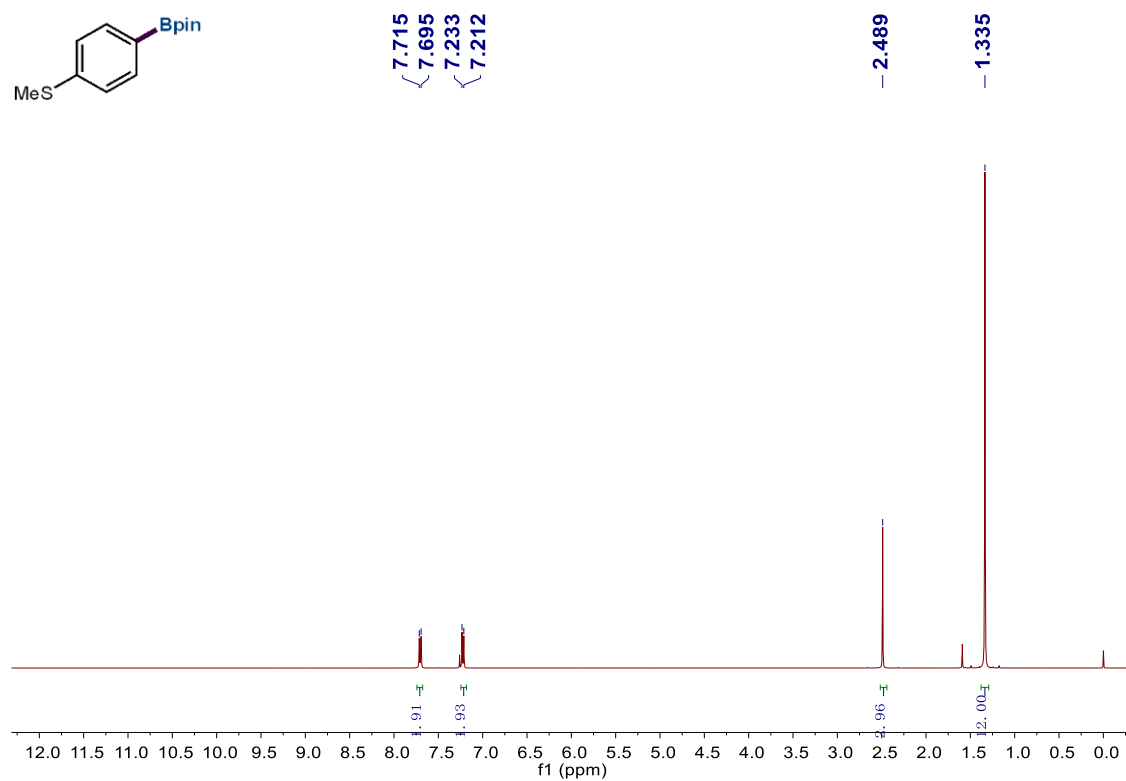
Dimethyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (4j).



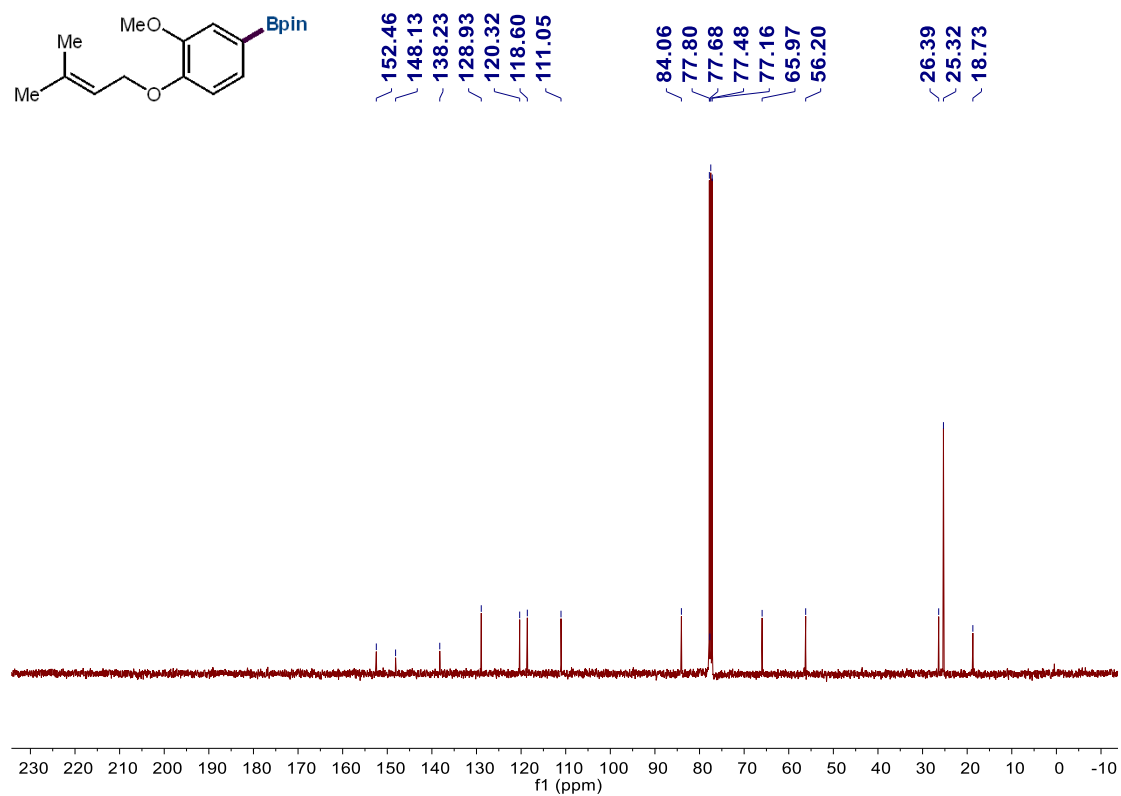
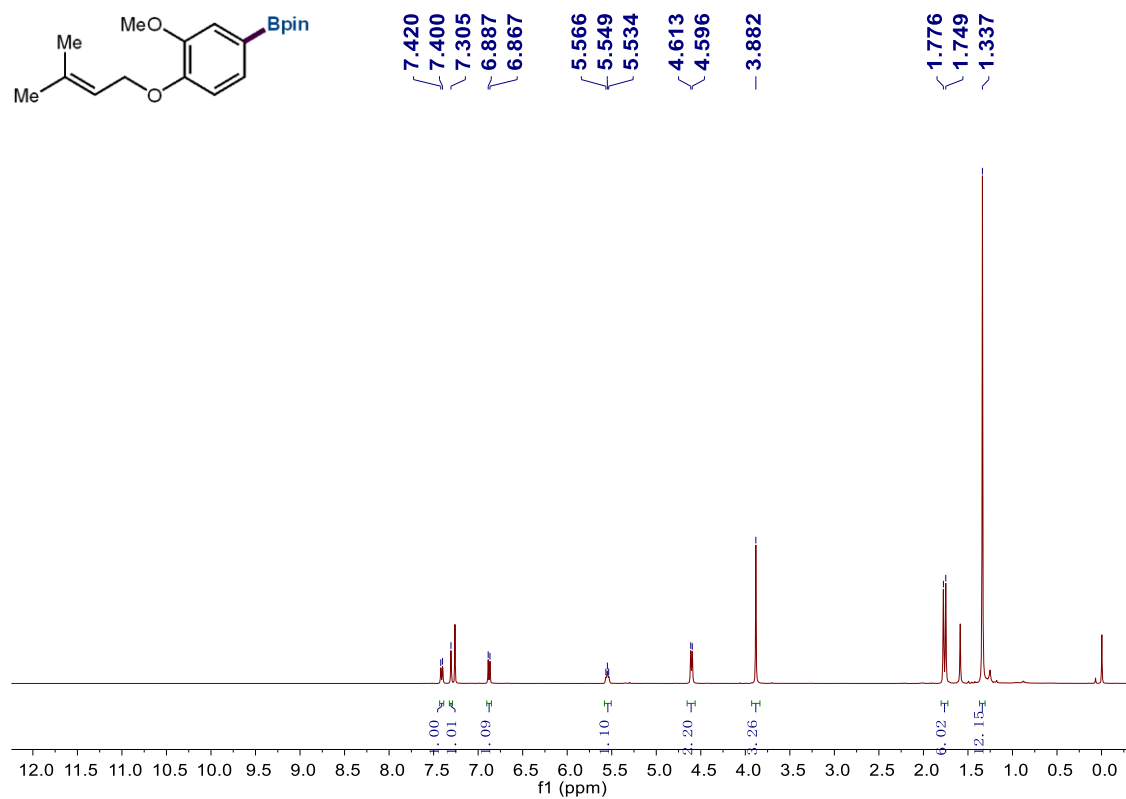
Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane(4k).



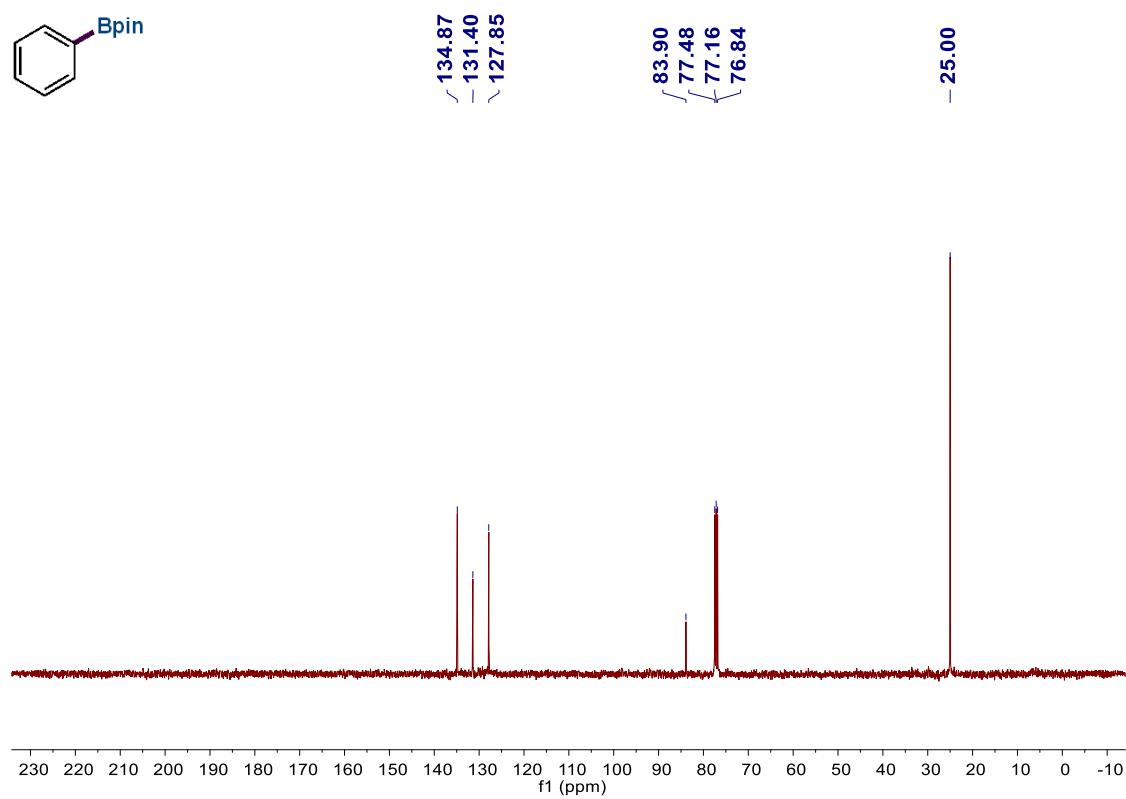
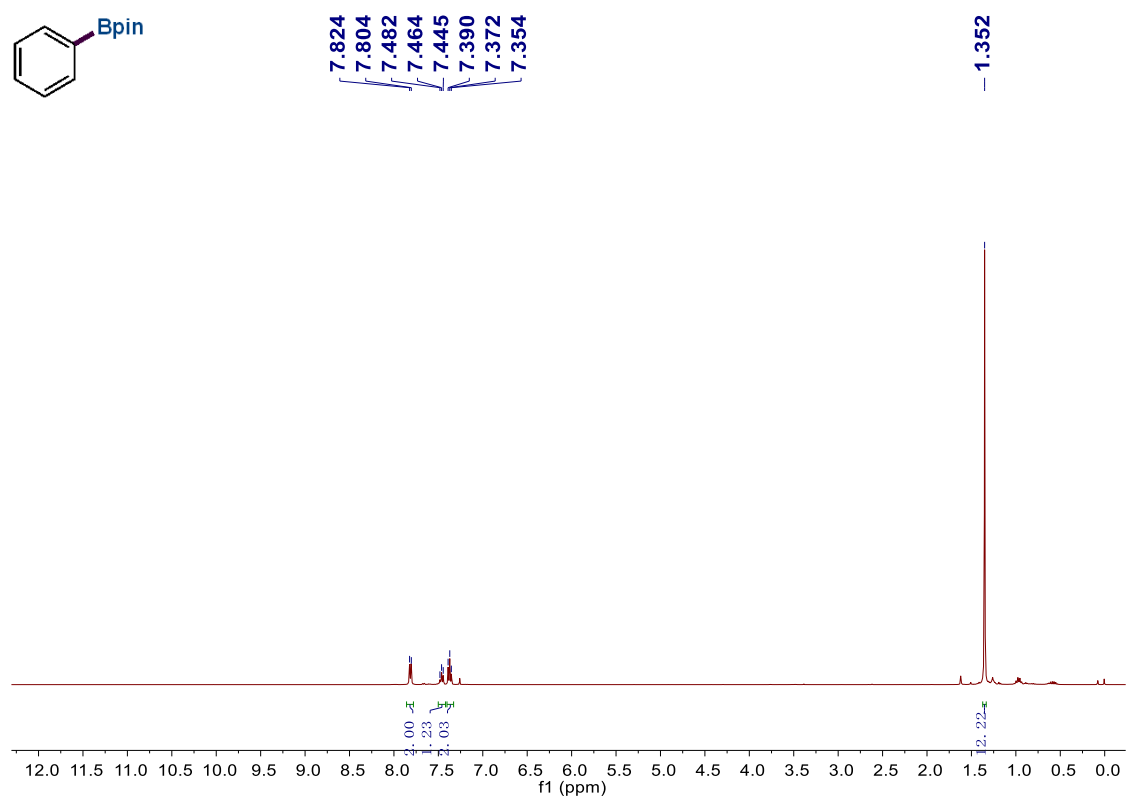
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4l)



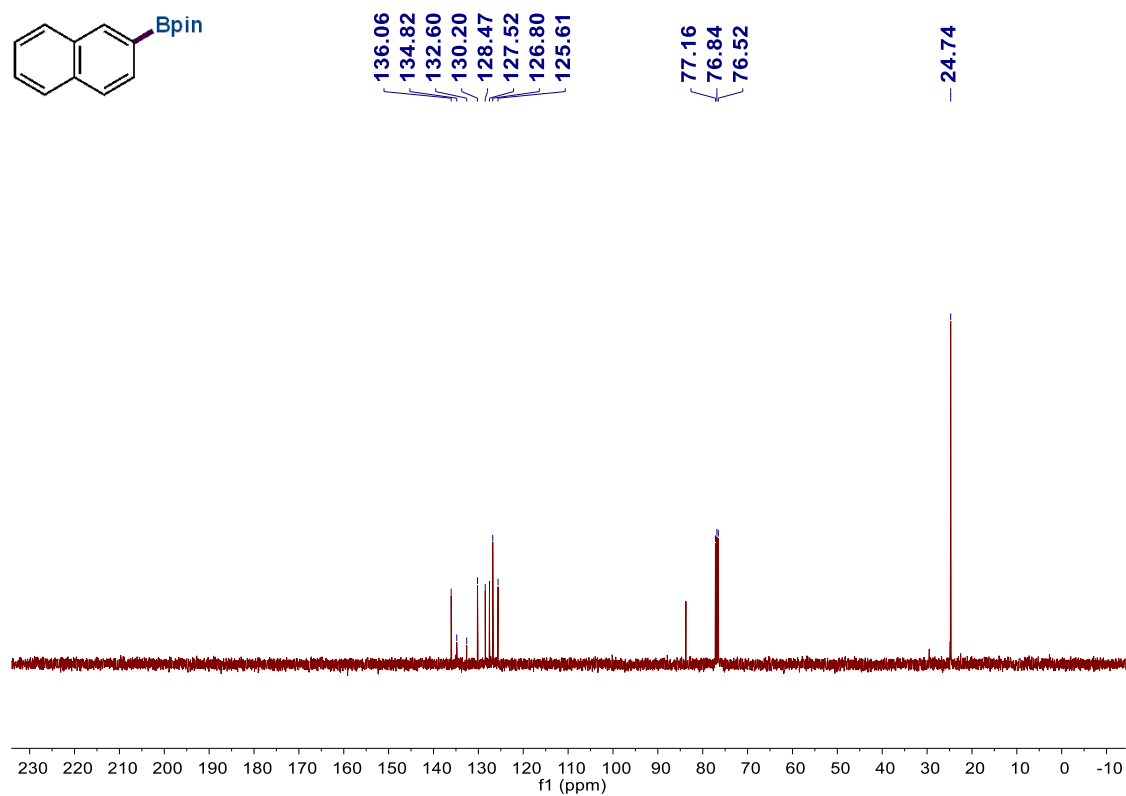
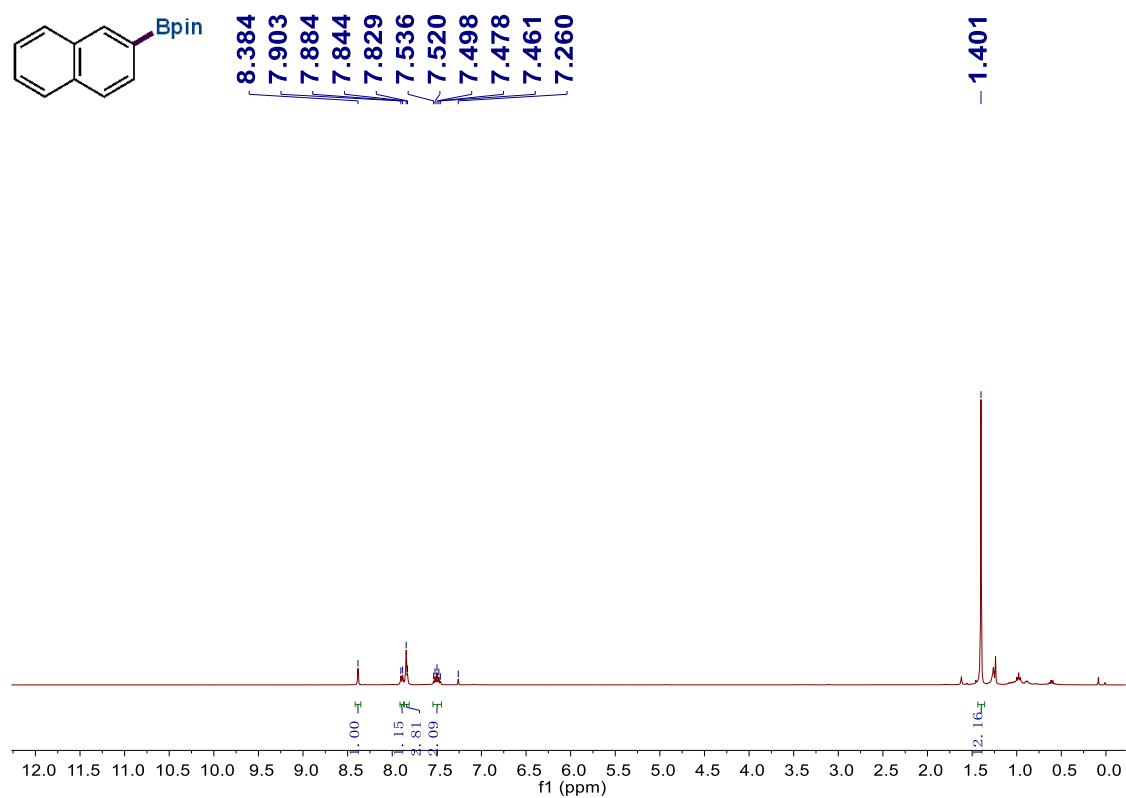
2-(3-Methoxy-4-((3-methylbut-2-en-1-yl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m).



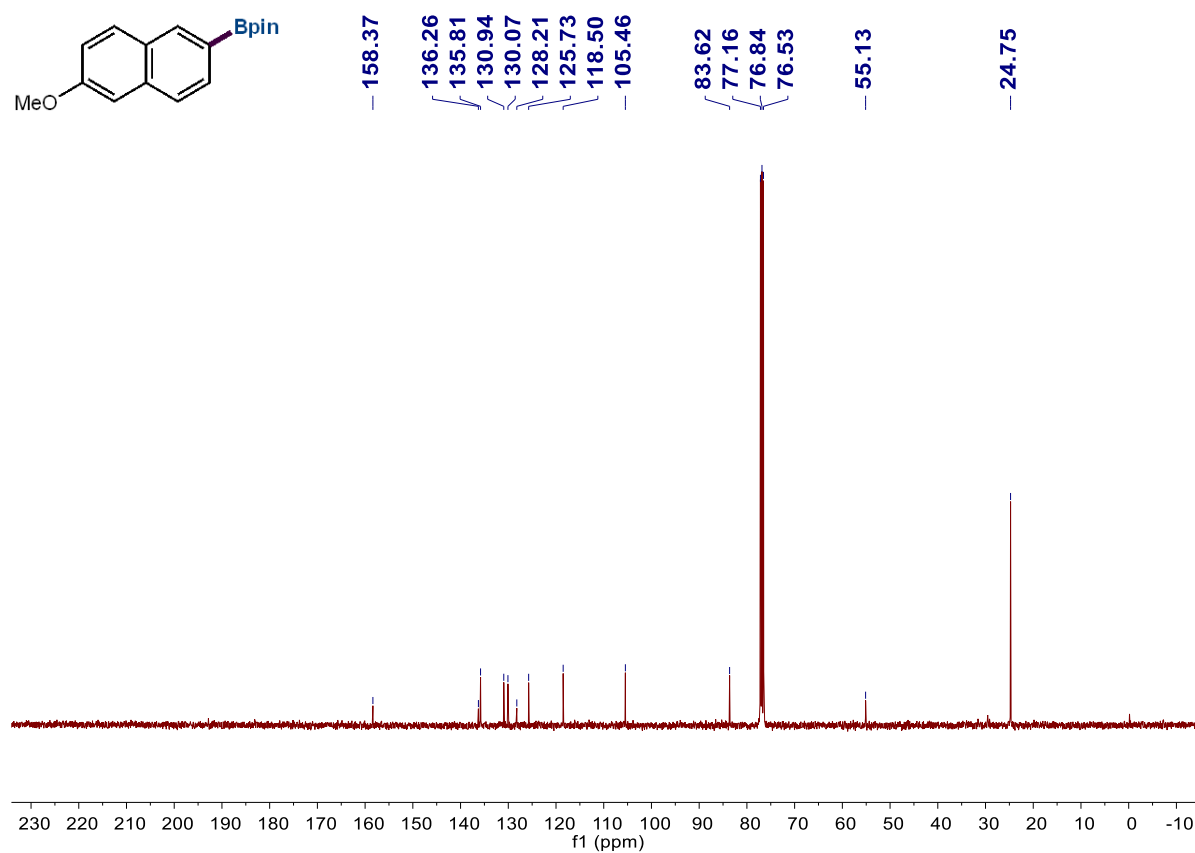
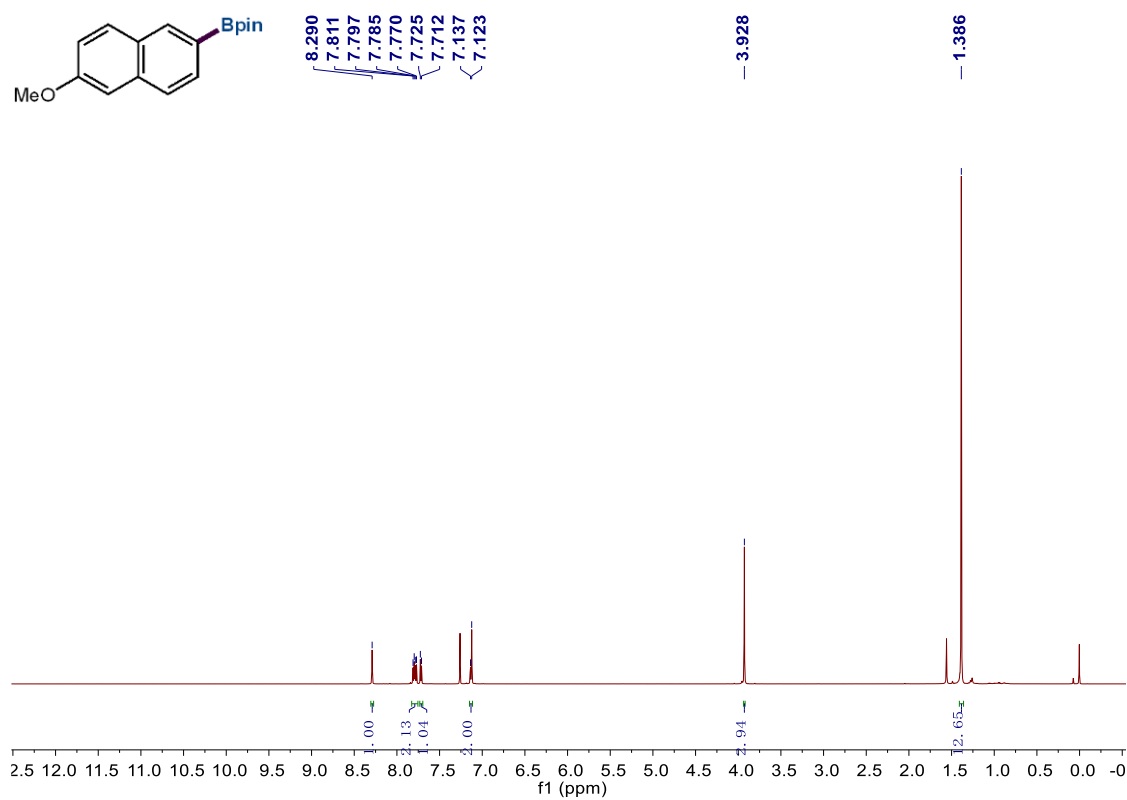
4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (4n).



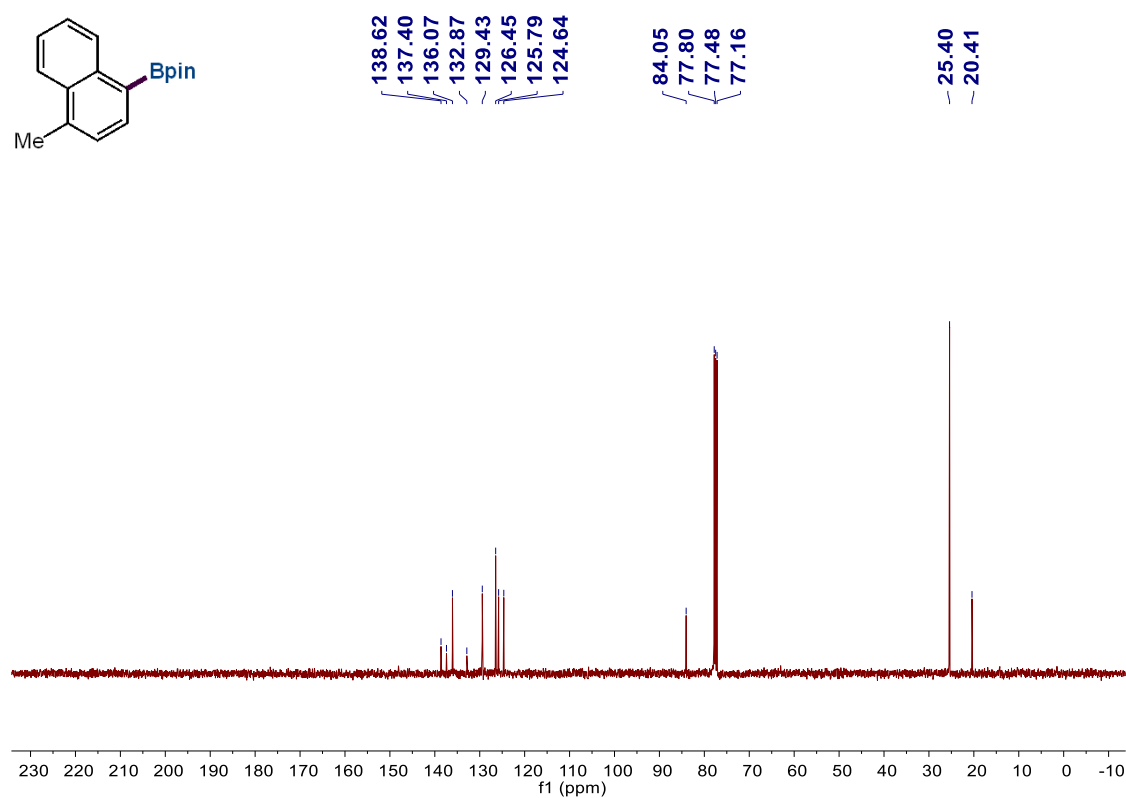
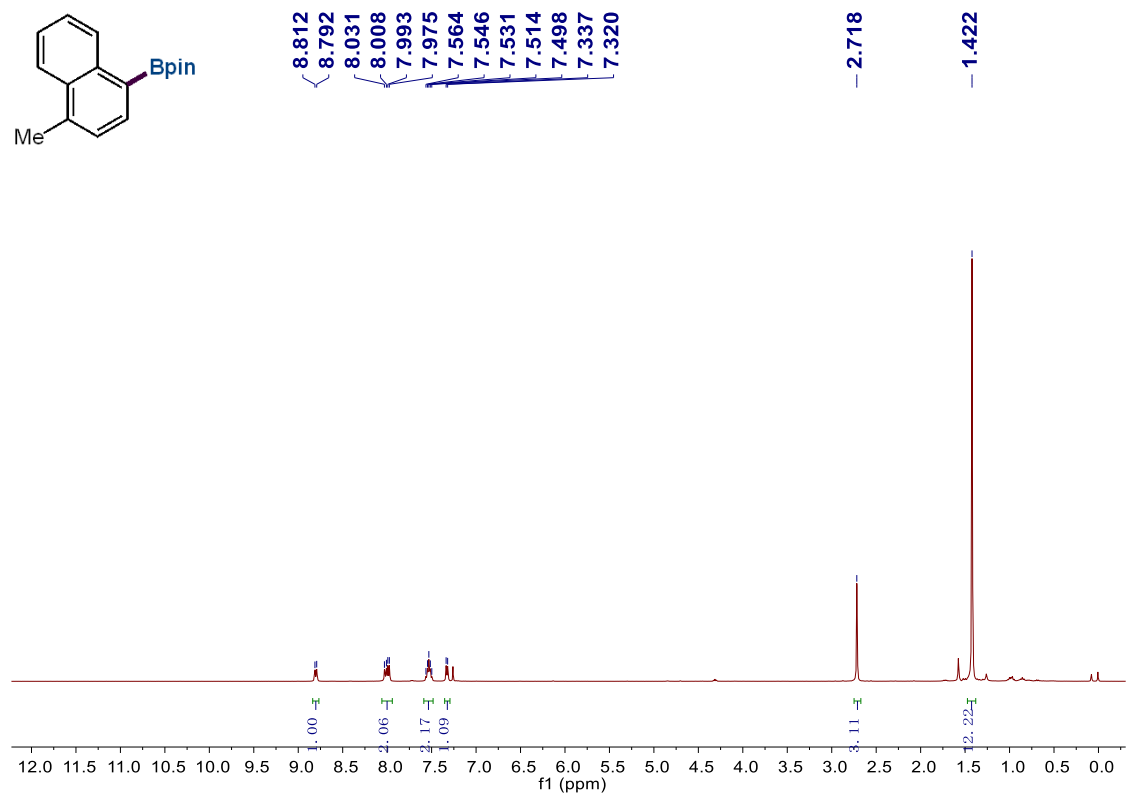
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (4o)



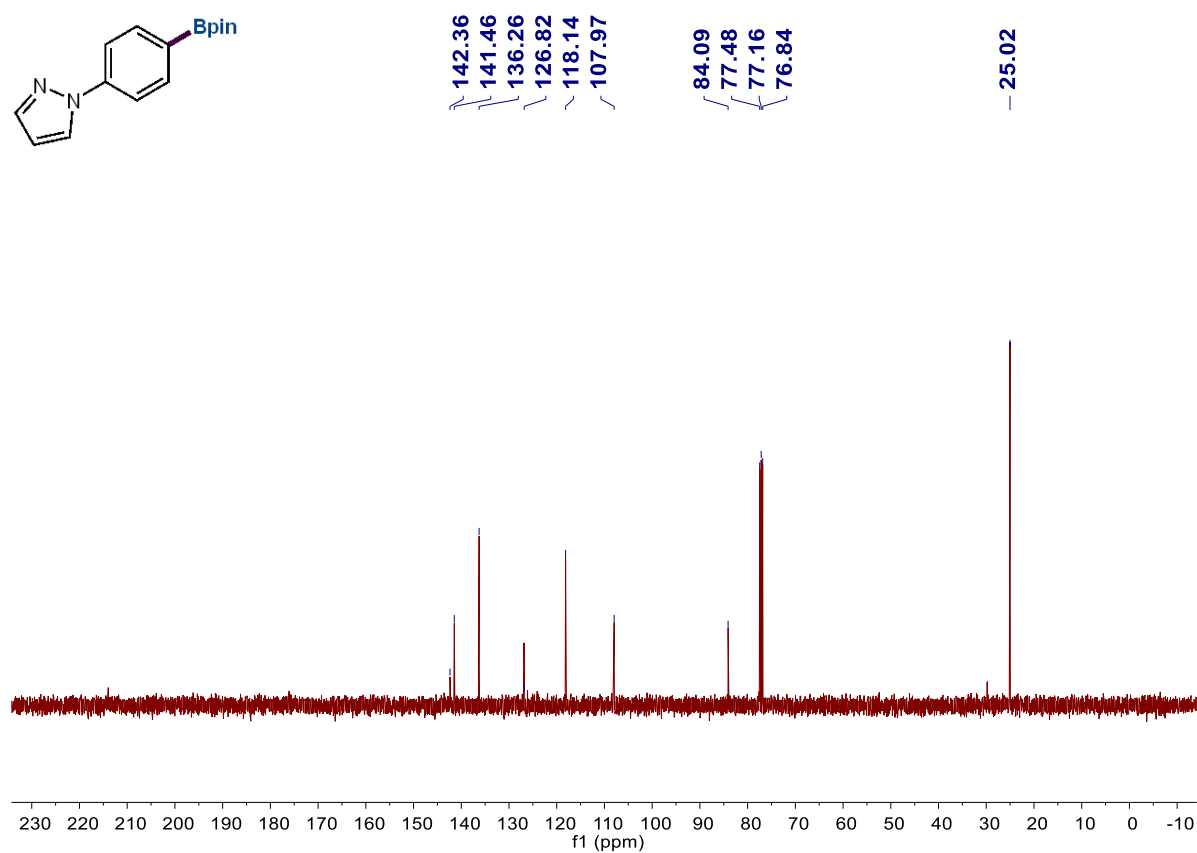
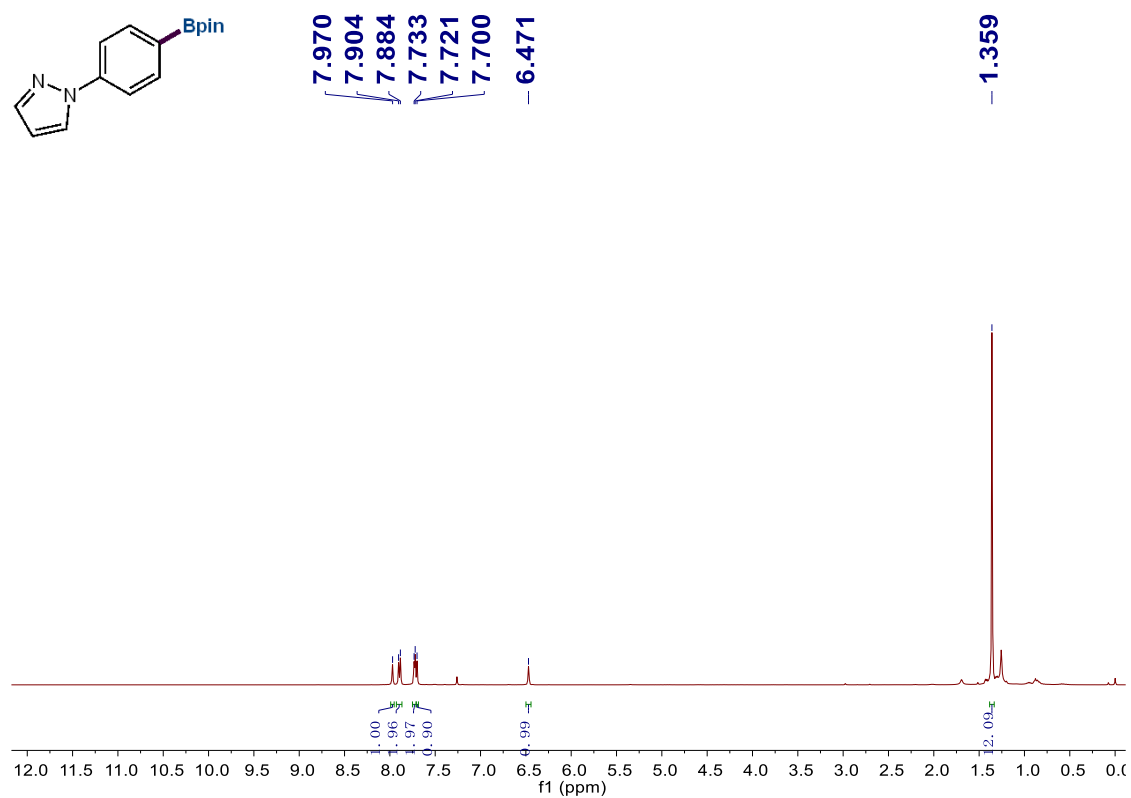
2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4p).



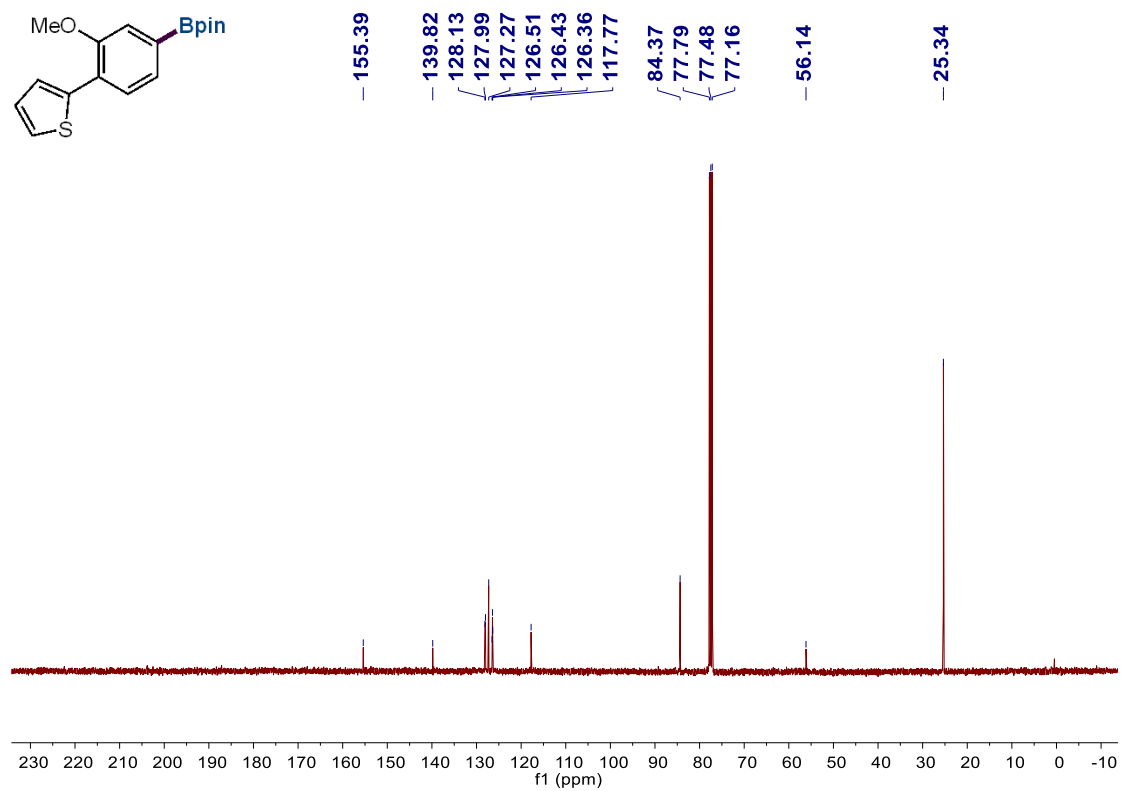
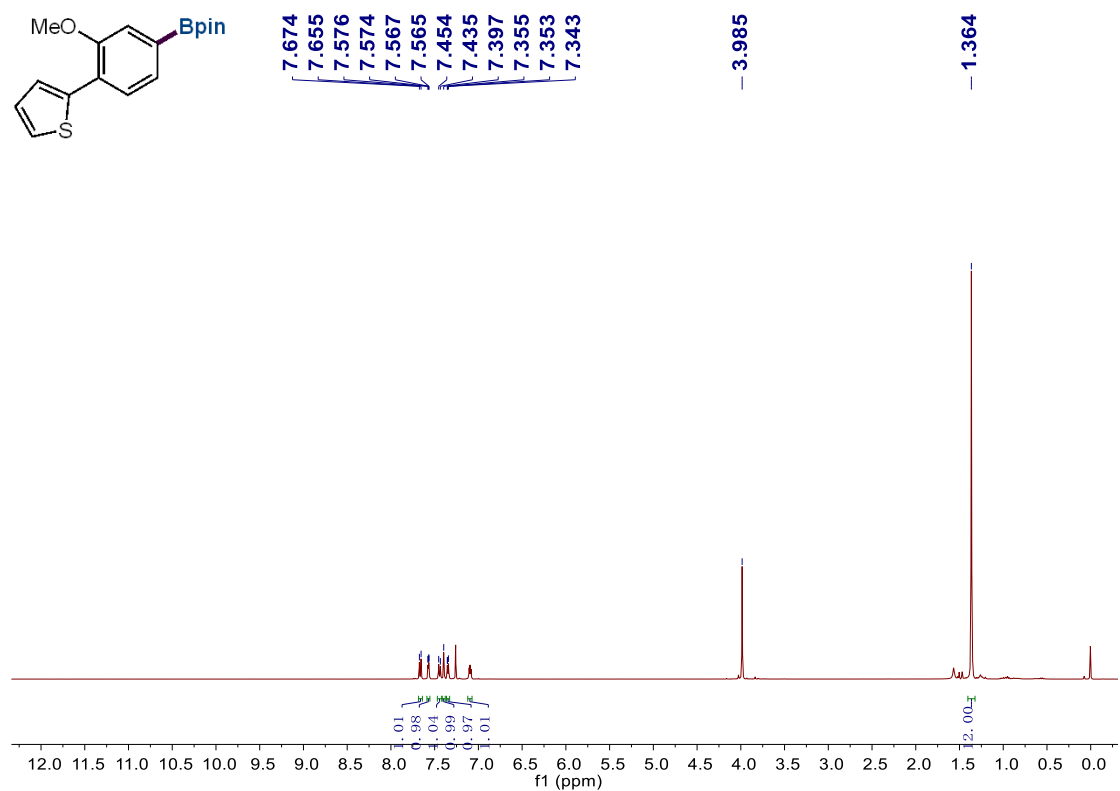
4,4,5,5-Tetramethyl-2-(4-methylnaphthalen-1-yl)-1,3,2-dioxaborolane (4q)



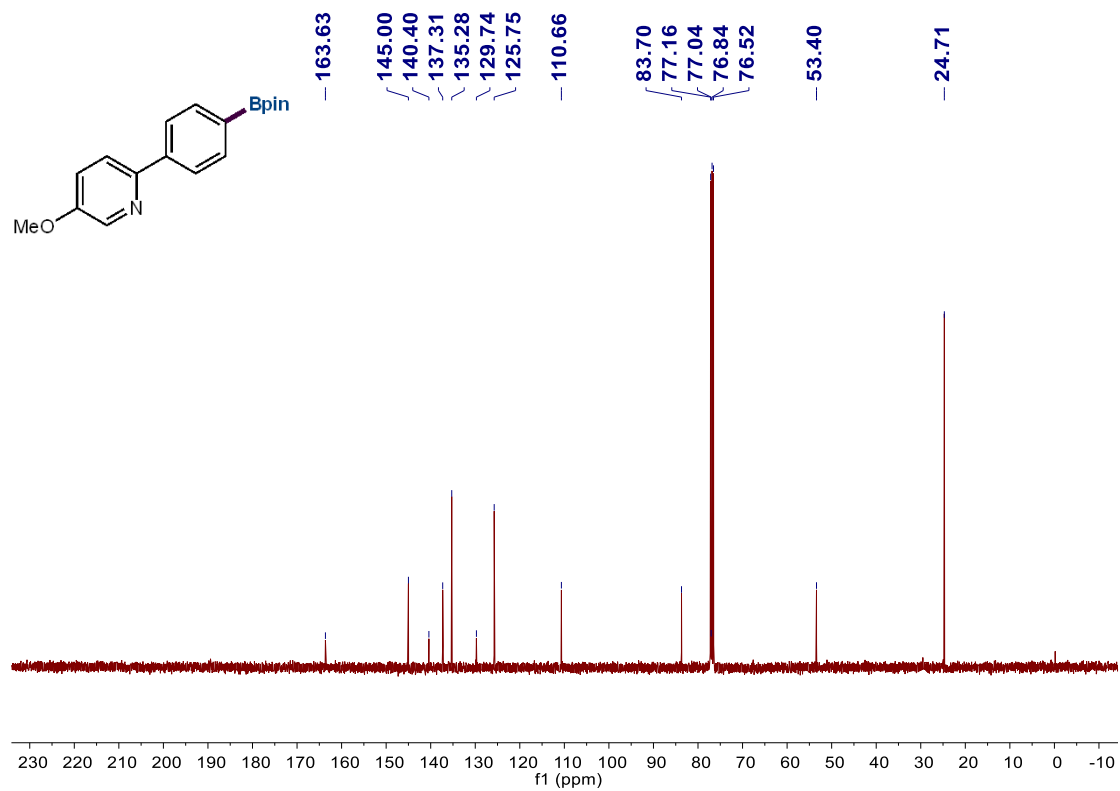
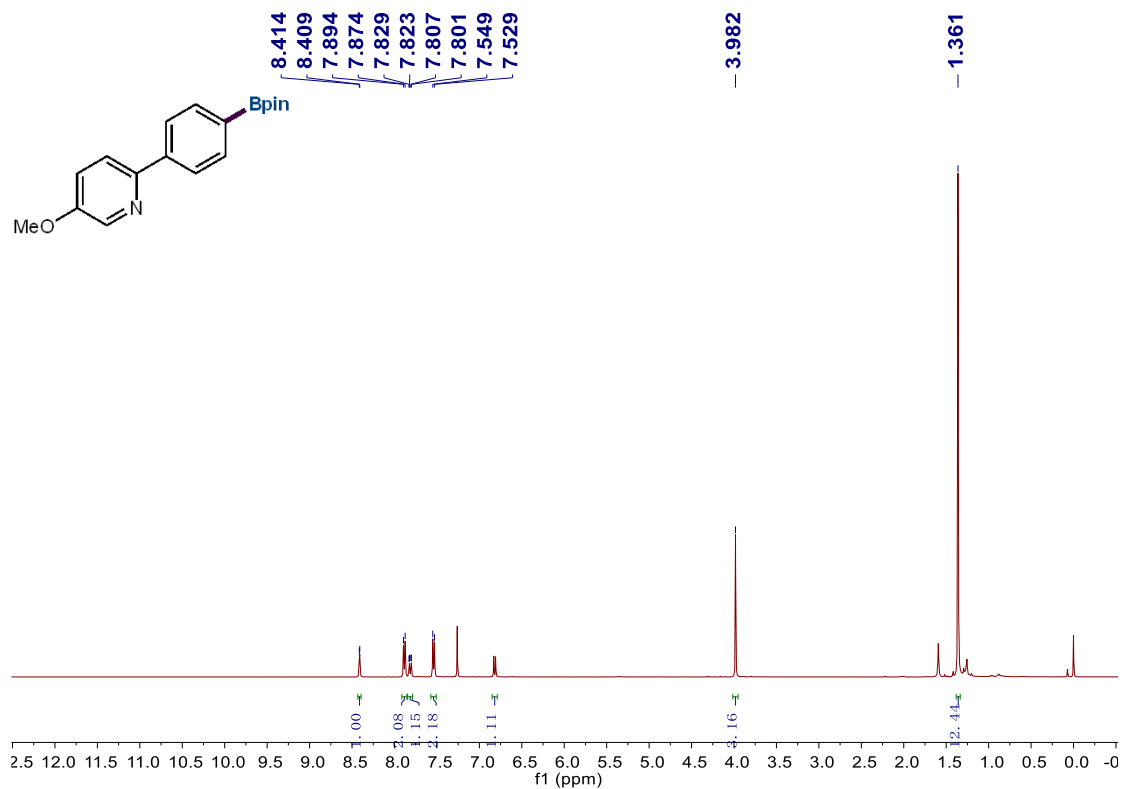
1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrazole (4s).



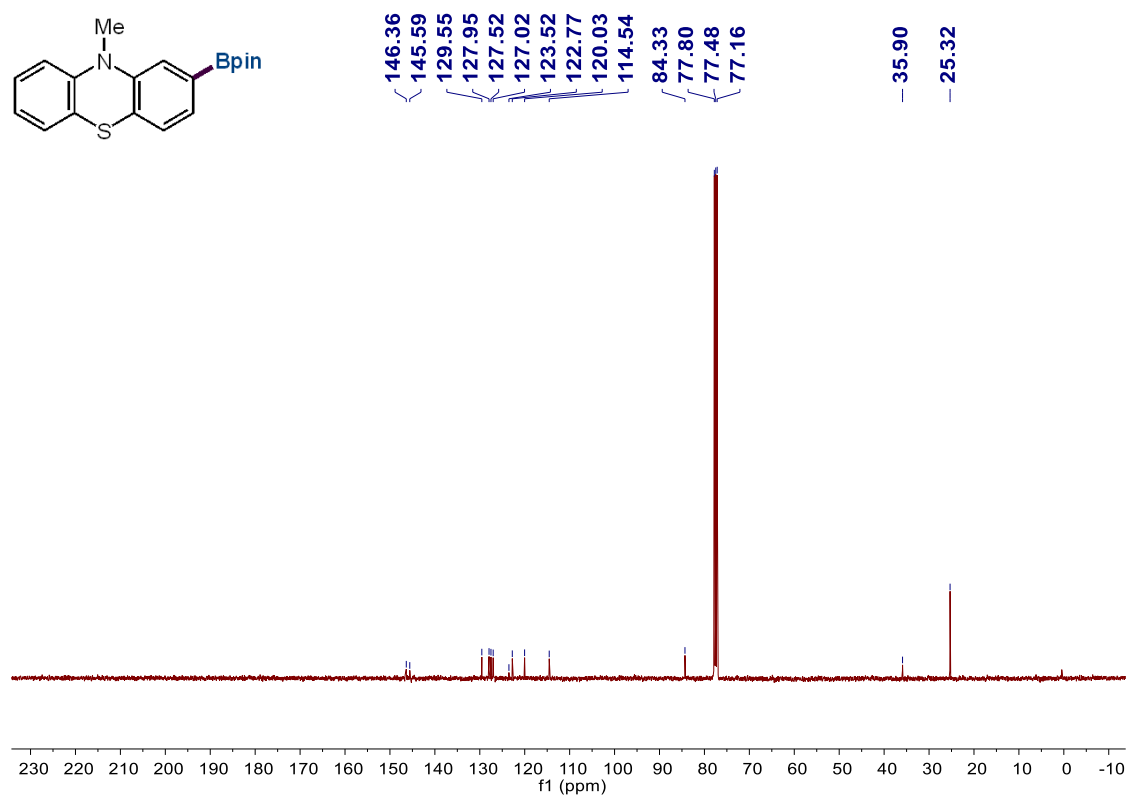
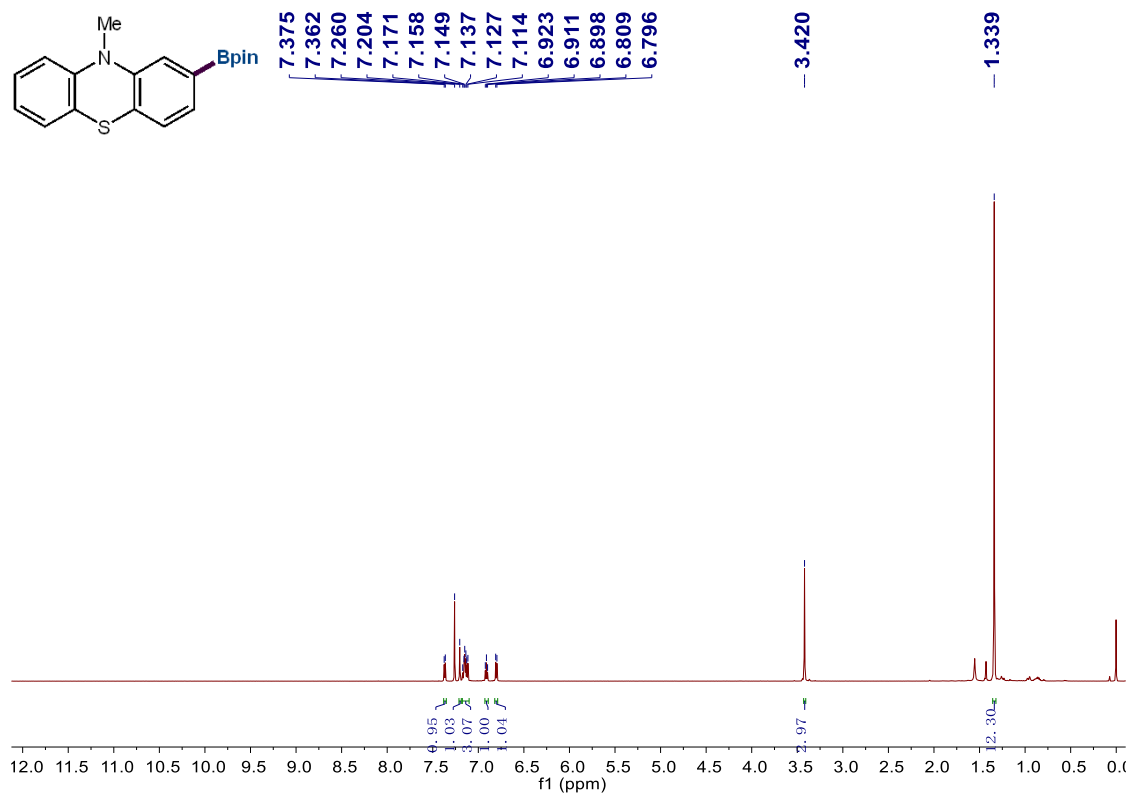
2-(3-Methoxy-4-(thiophen-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4t).



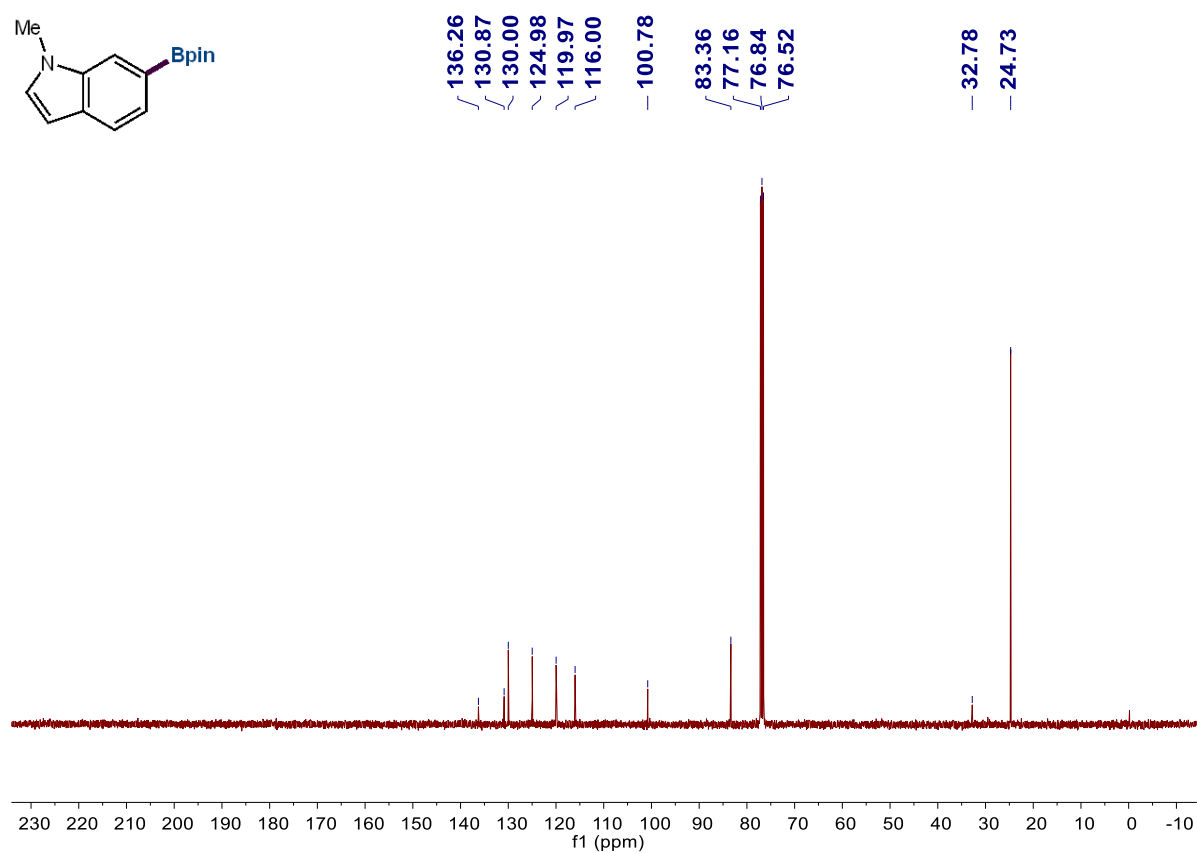
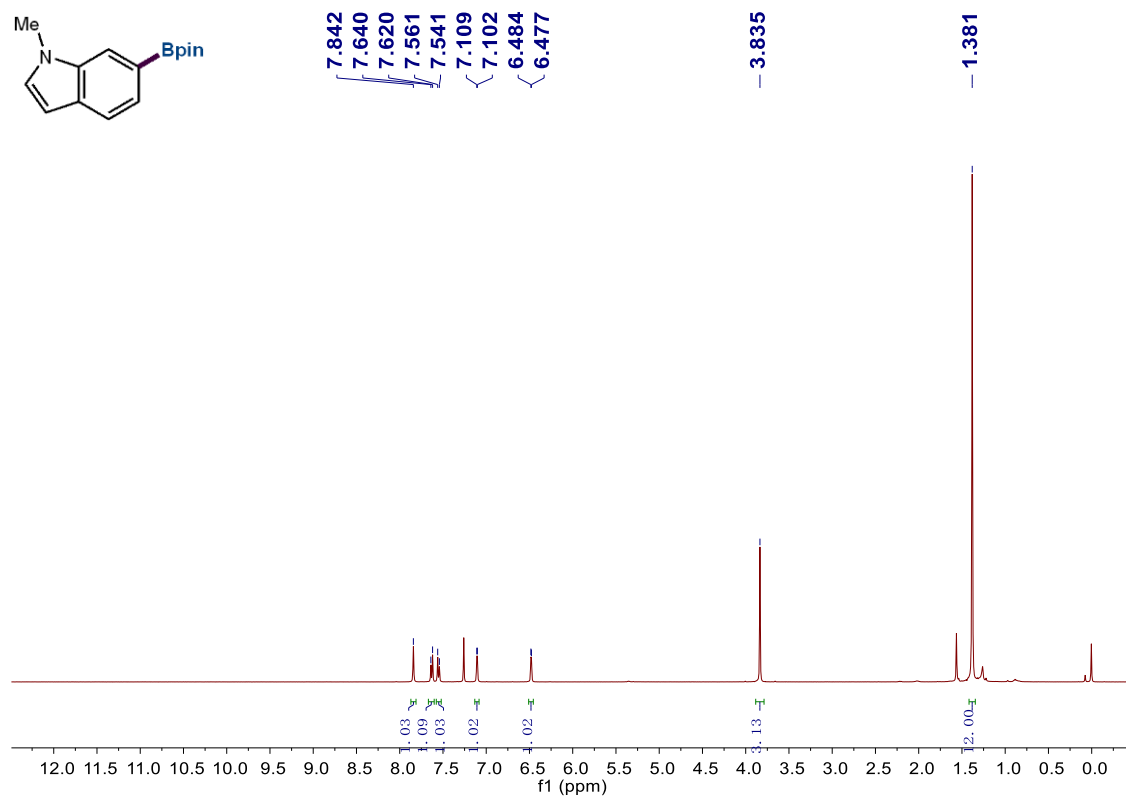
5-Methoxy-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (4v).



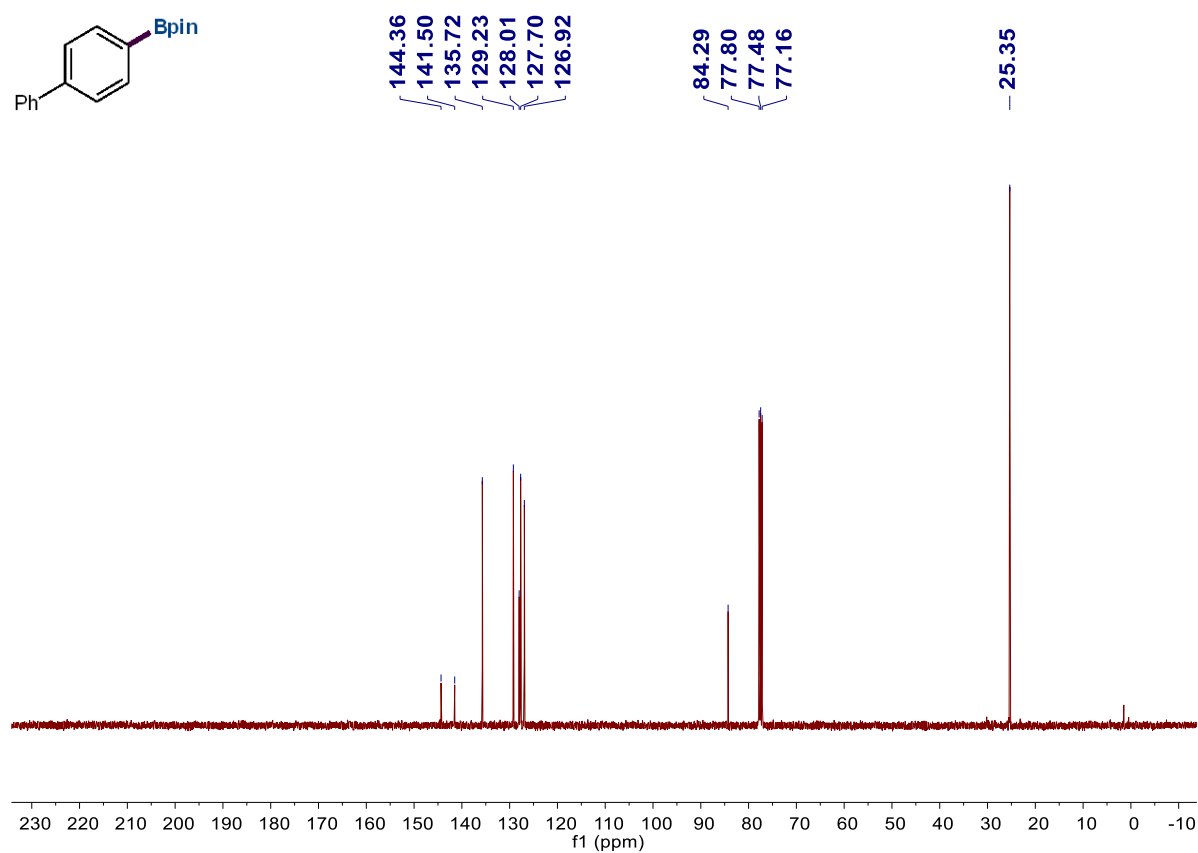
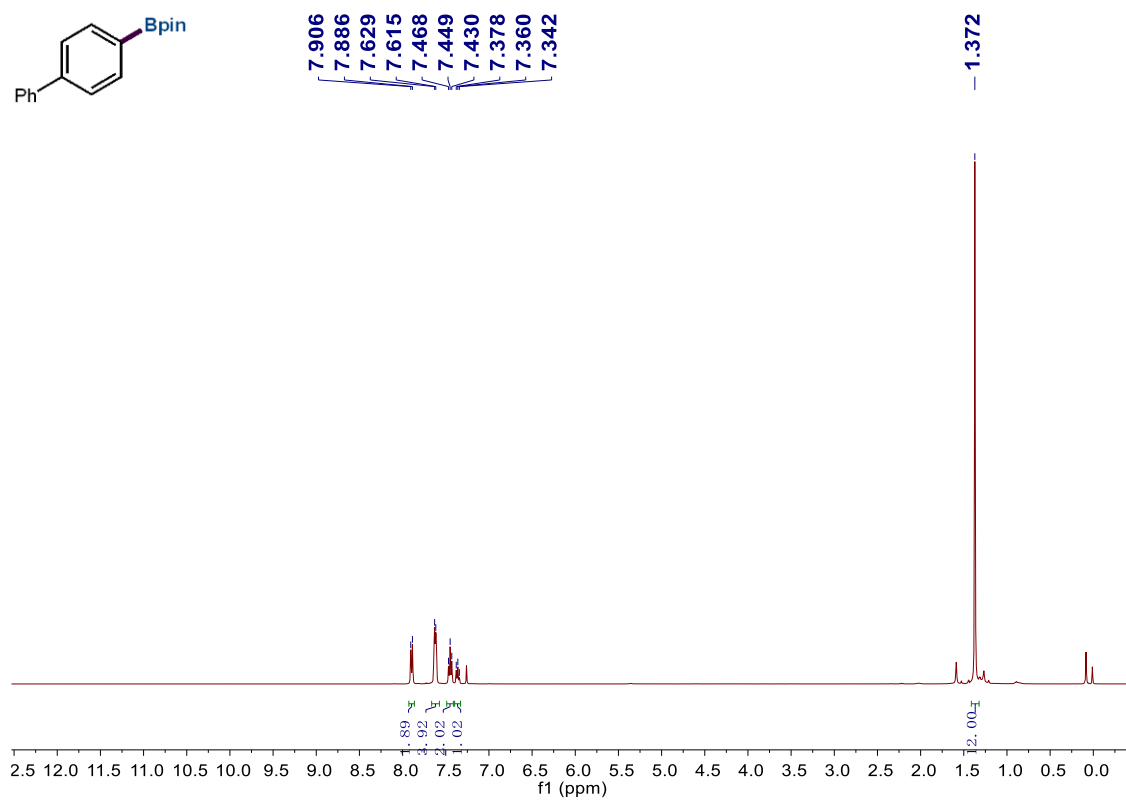
10-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (4w).



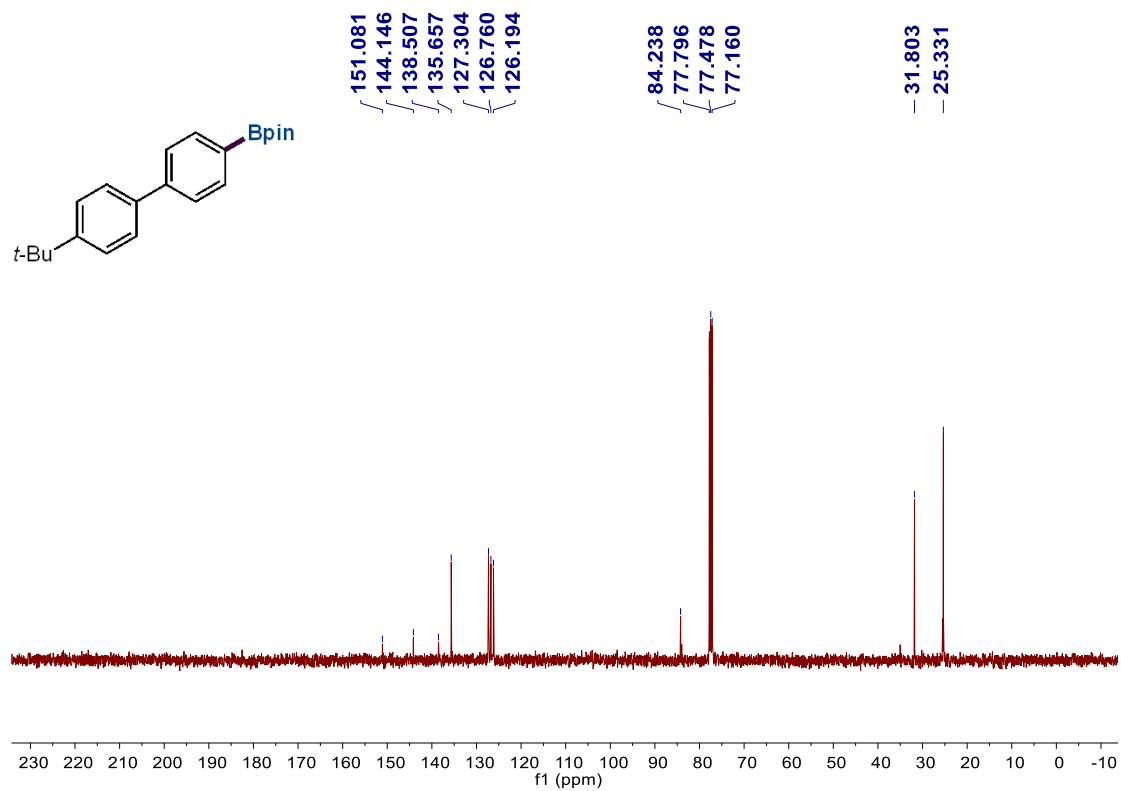
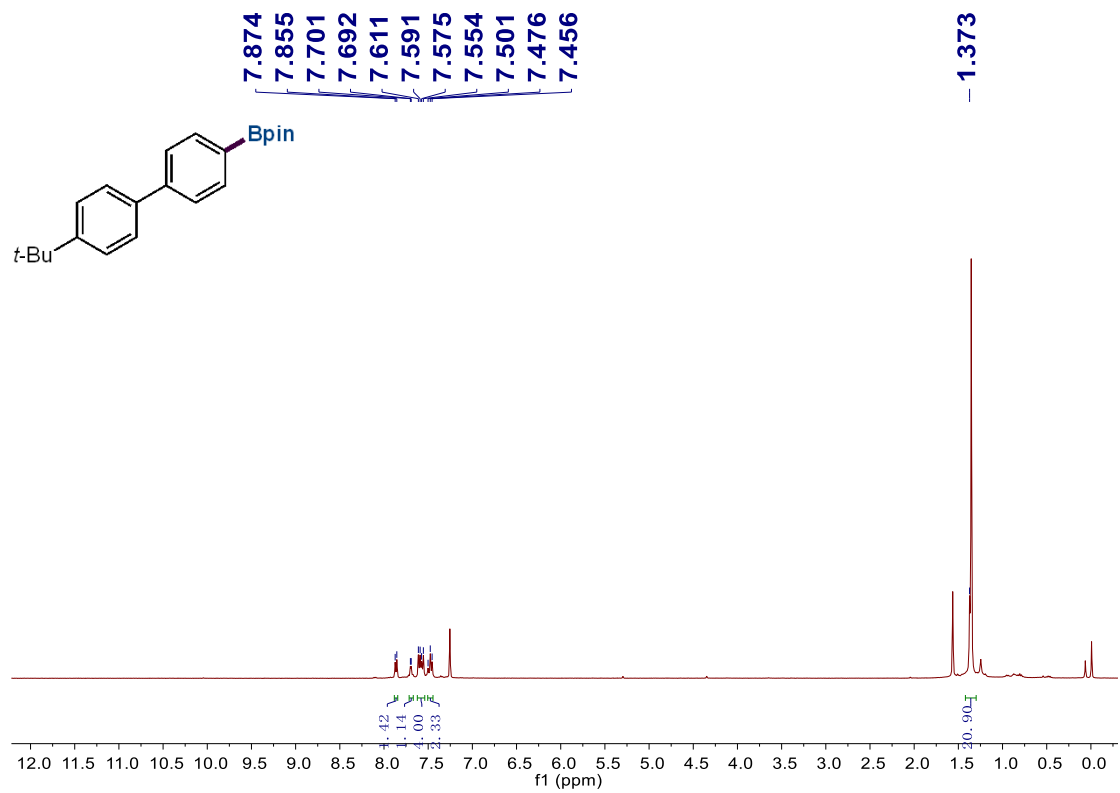
1-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (4x).



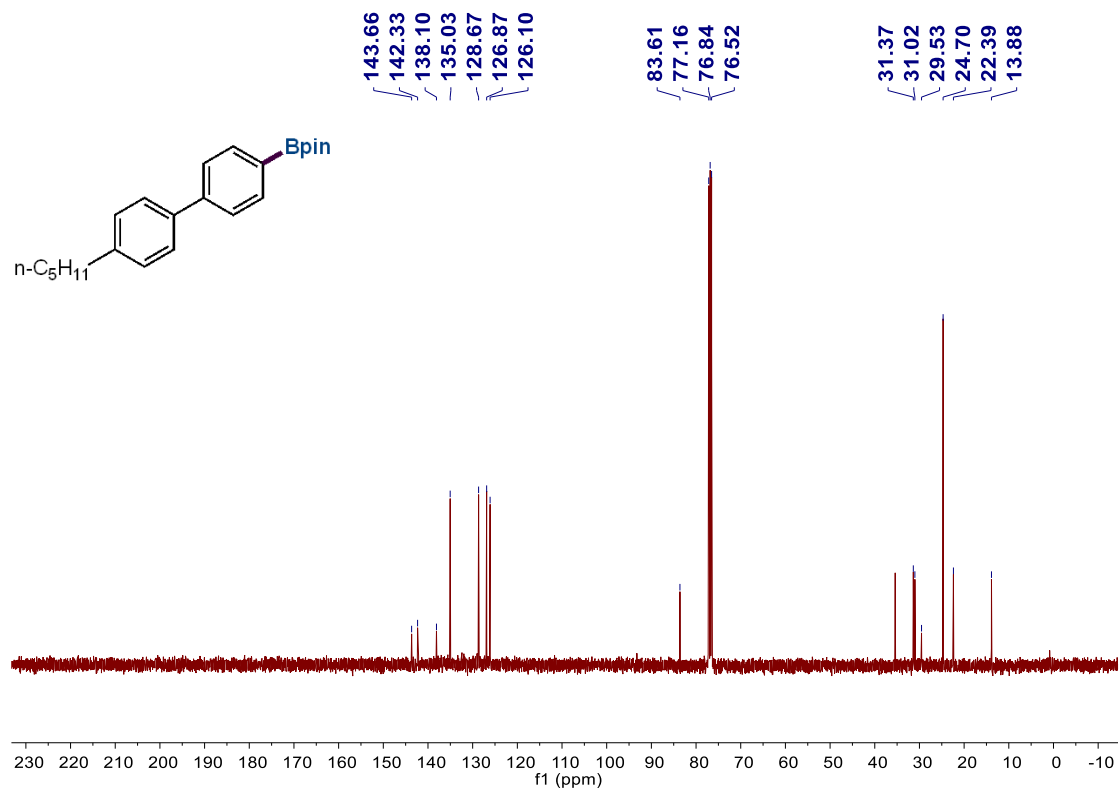
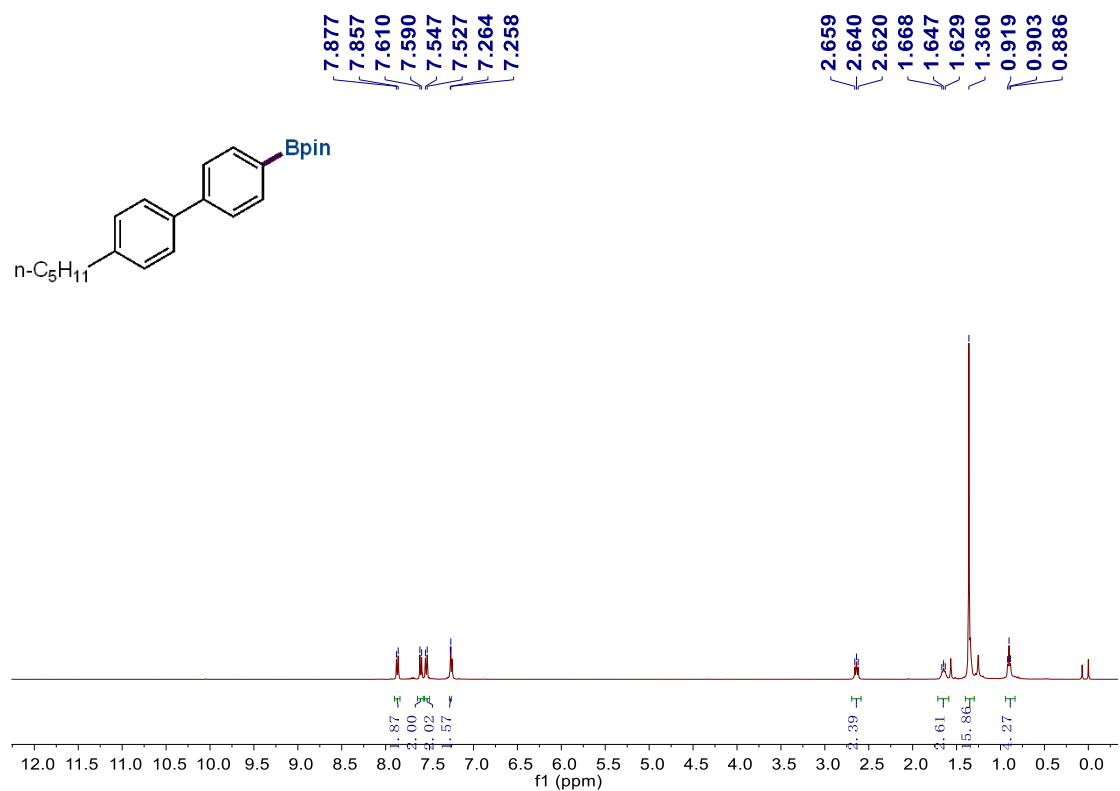
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4y)



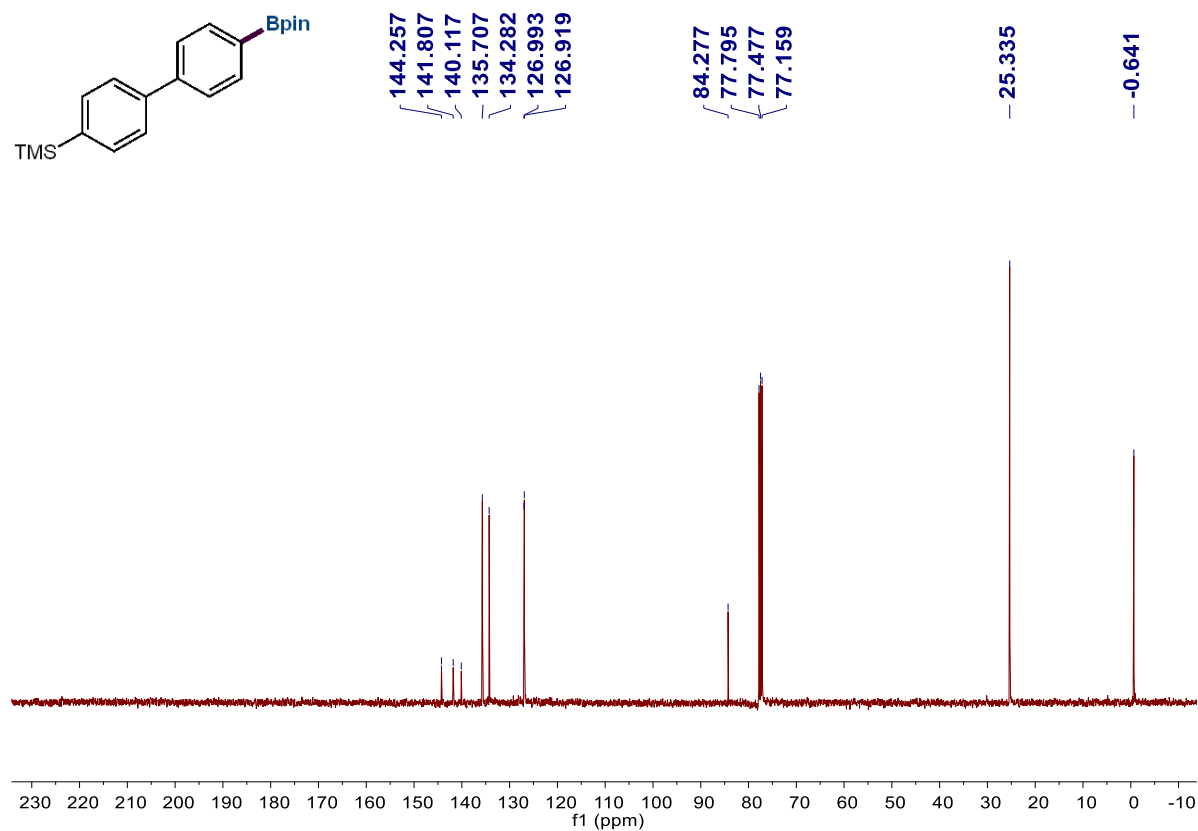
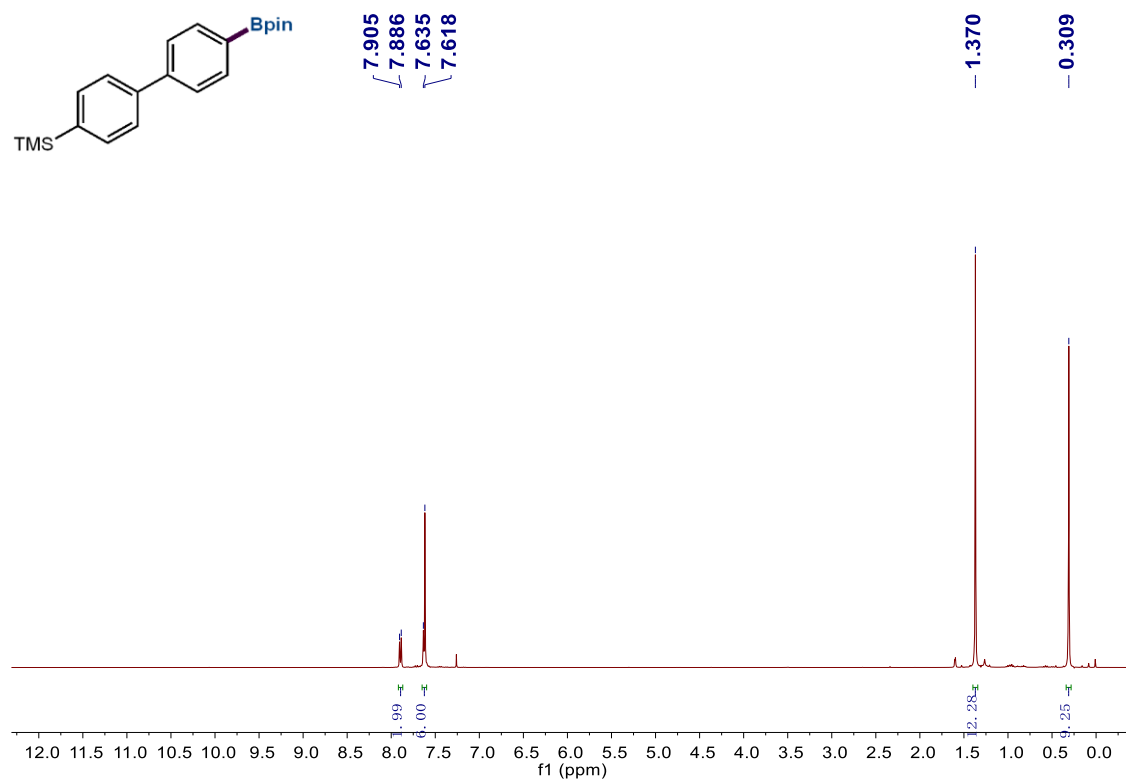
2-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(4z).



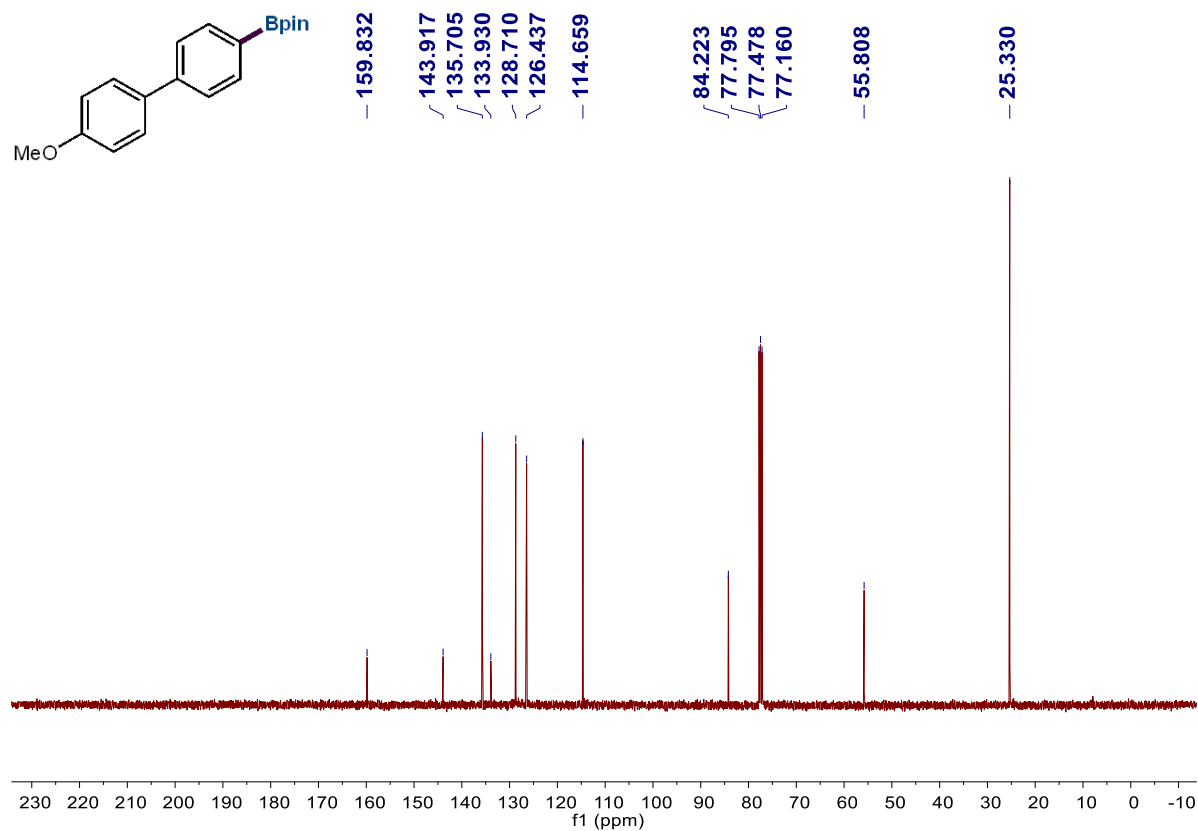
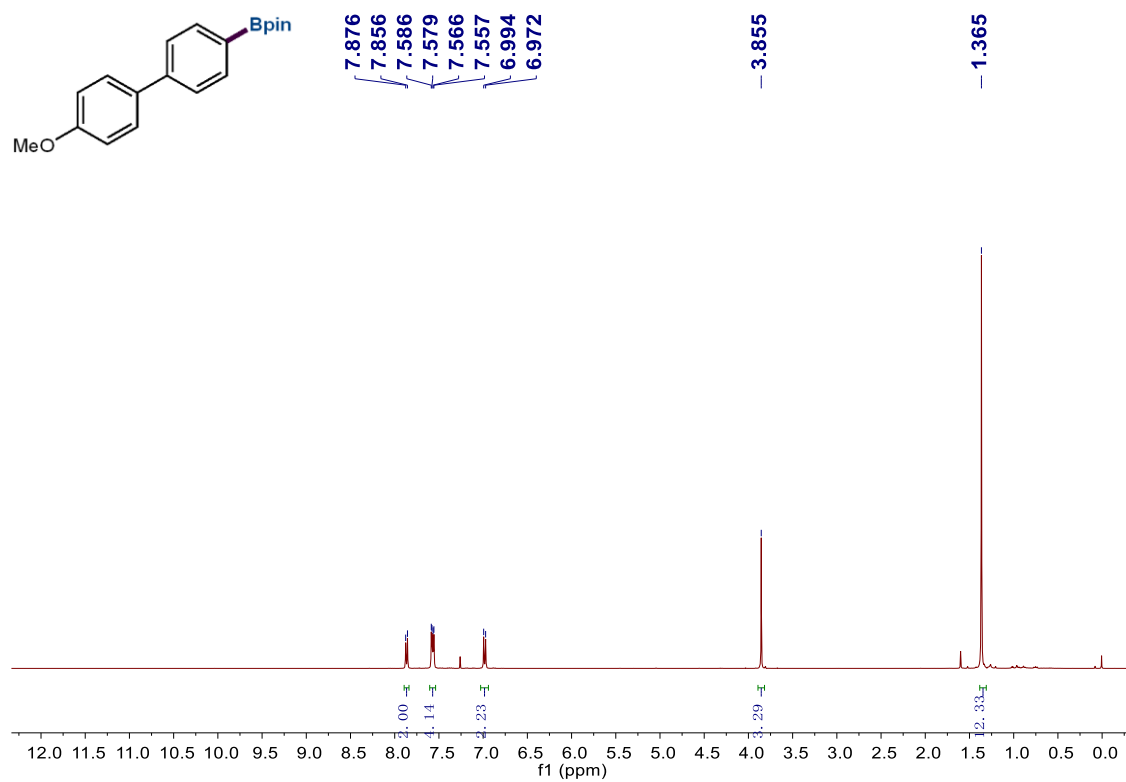
2-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa)



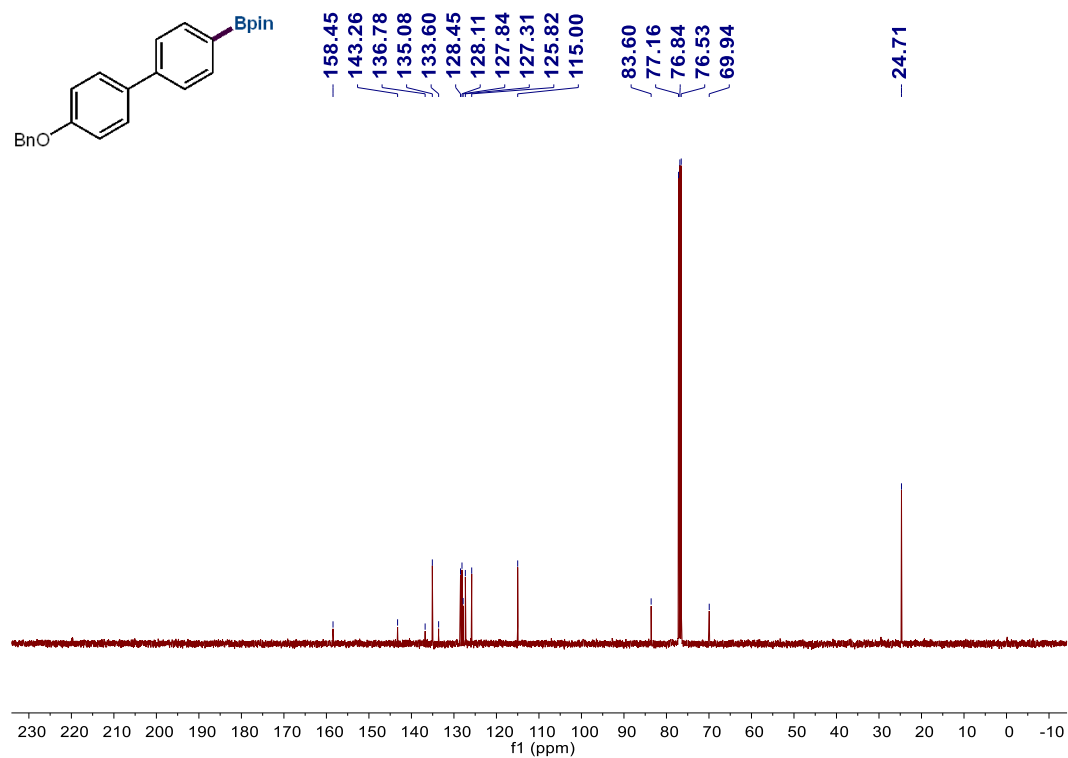
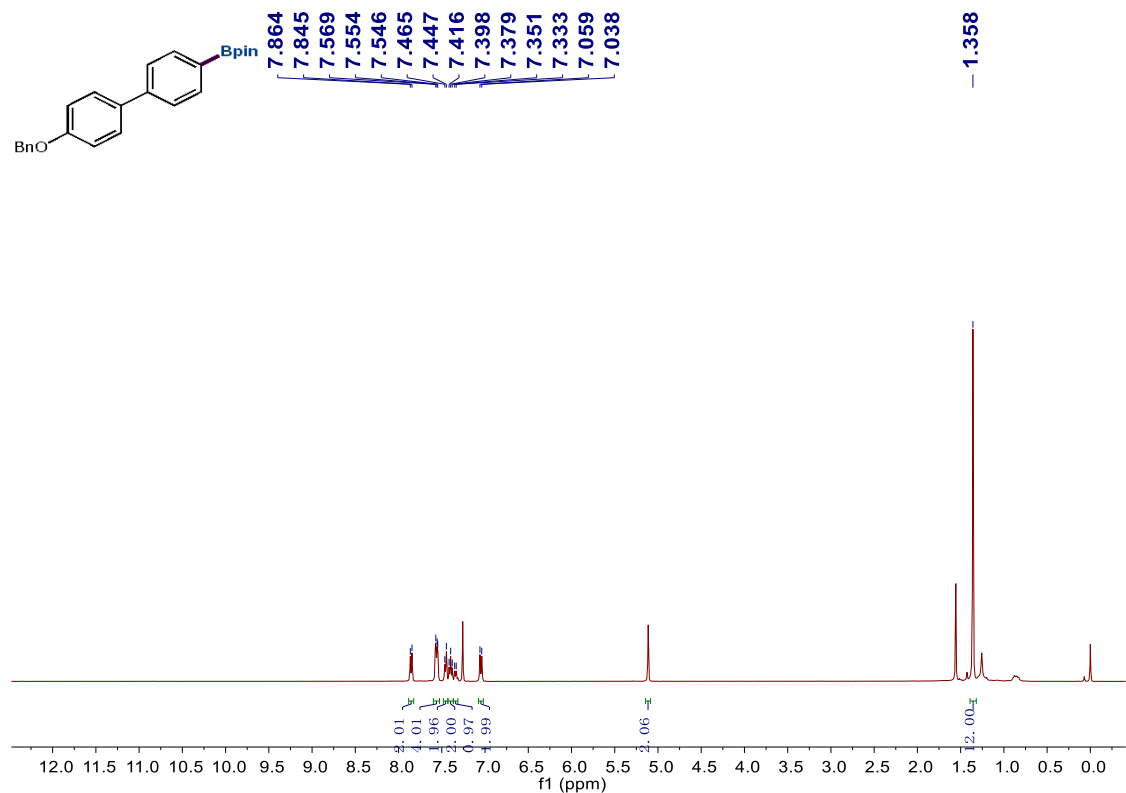
Trimethyl(4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)silane (4ab)



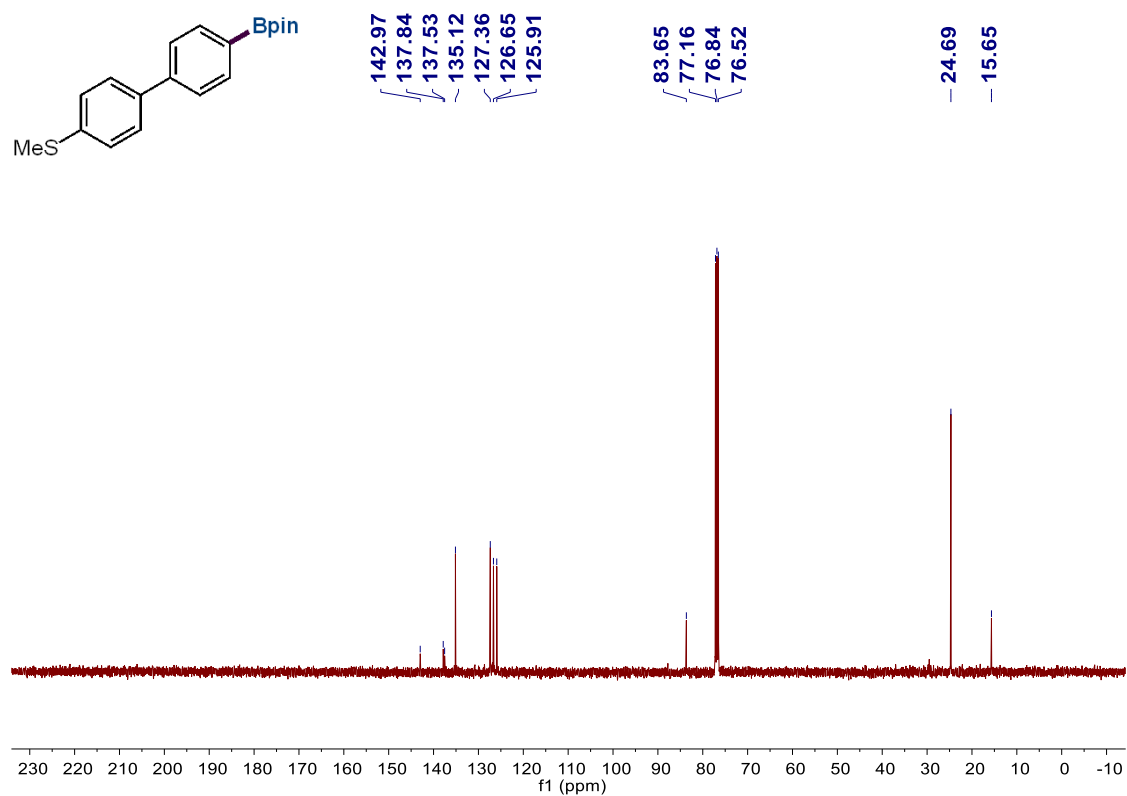
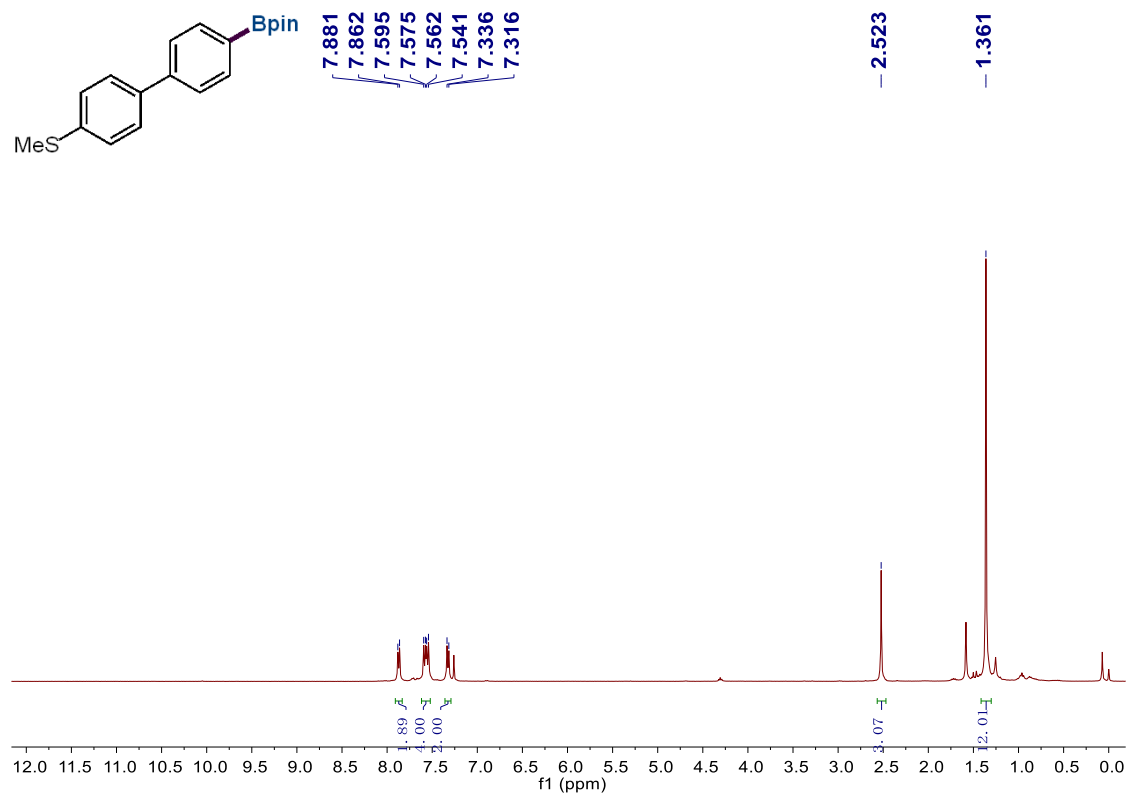
2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ac)



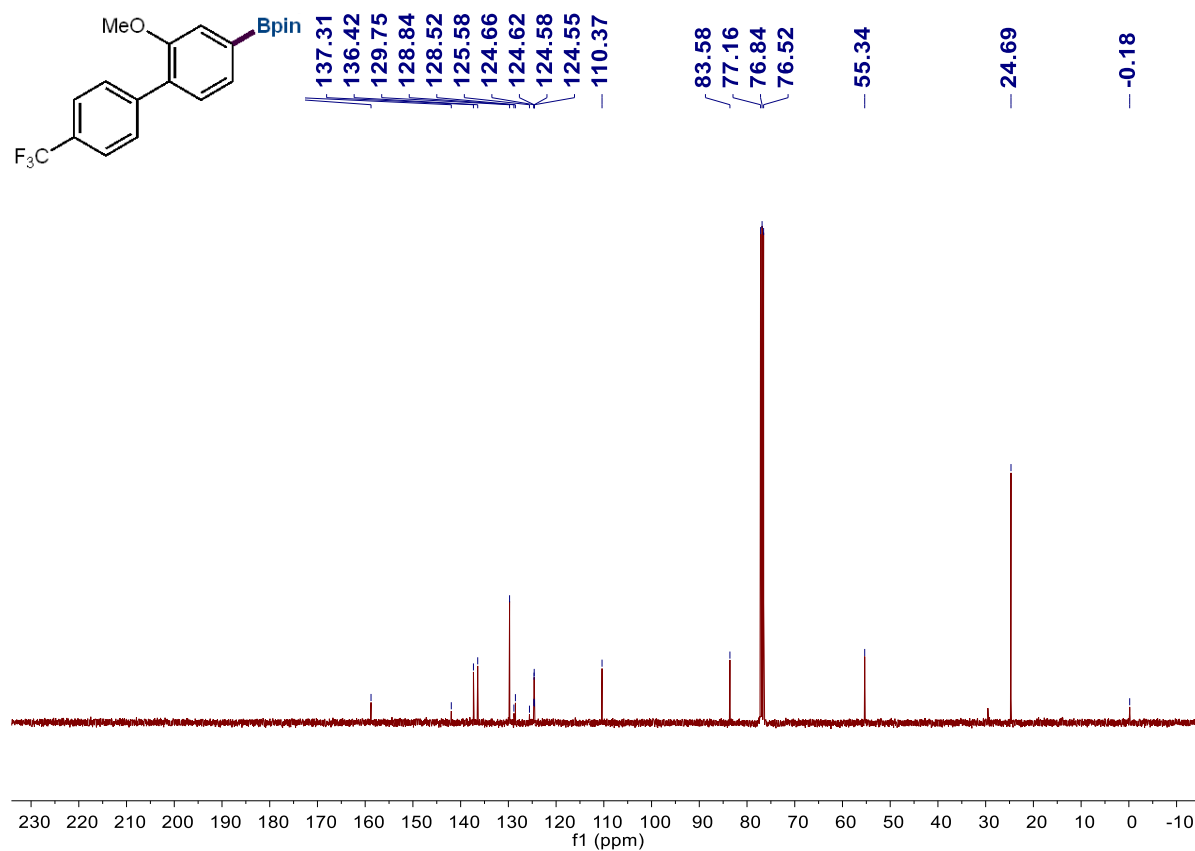
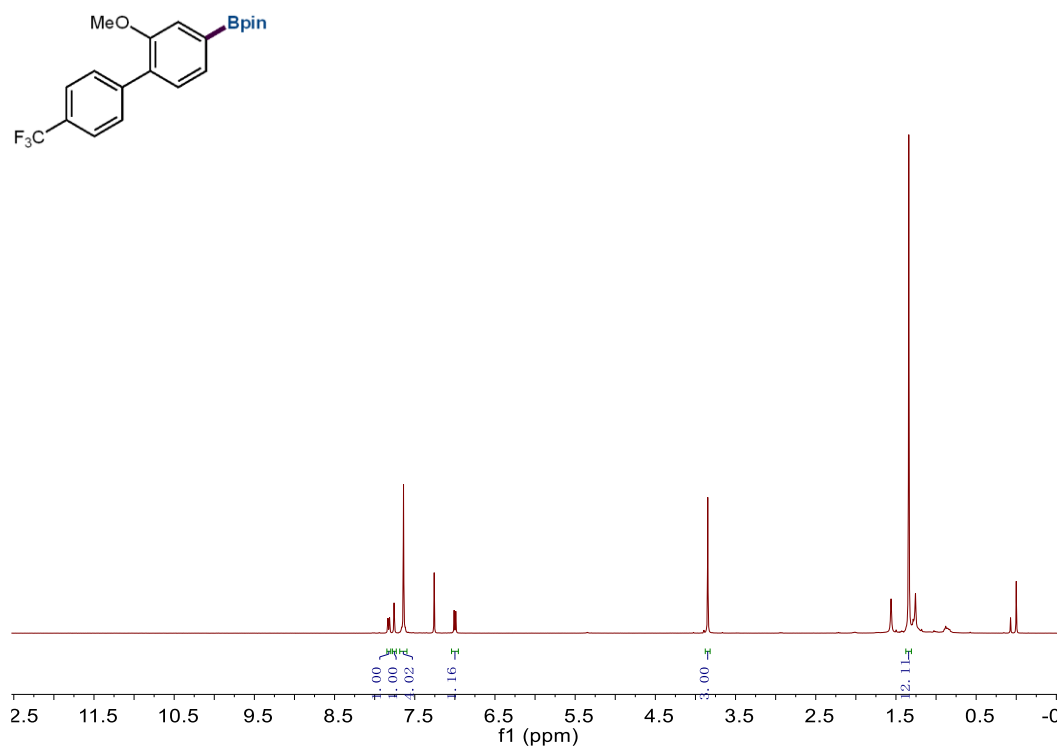
2-(4'-(Benzyloxy)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ad).



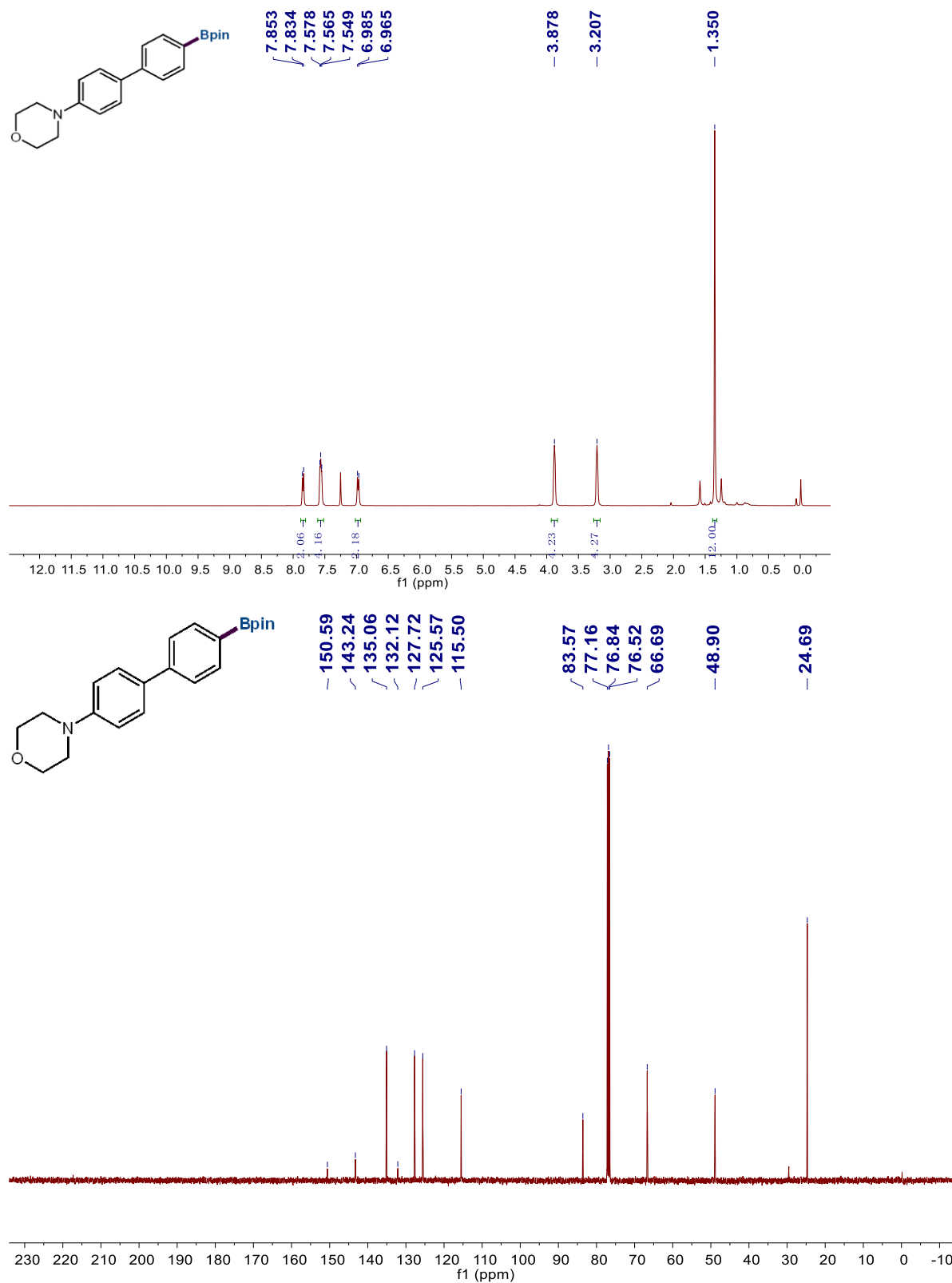
4,4,5,5-Tetramethyl-2-(4'-(methylthio)-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (4ae)



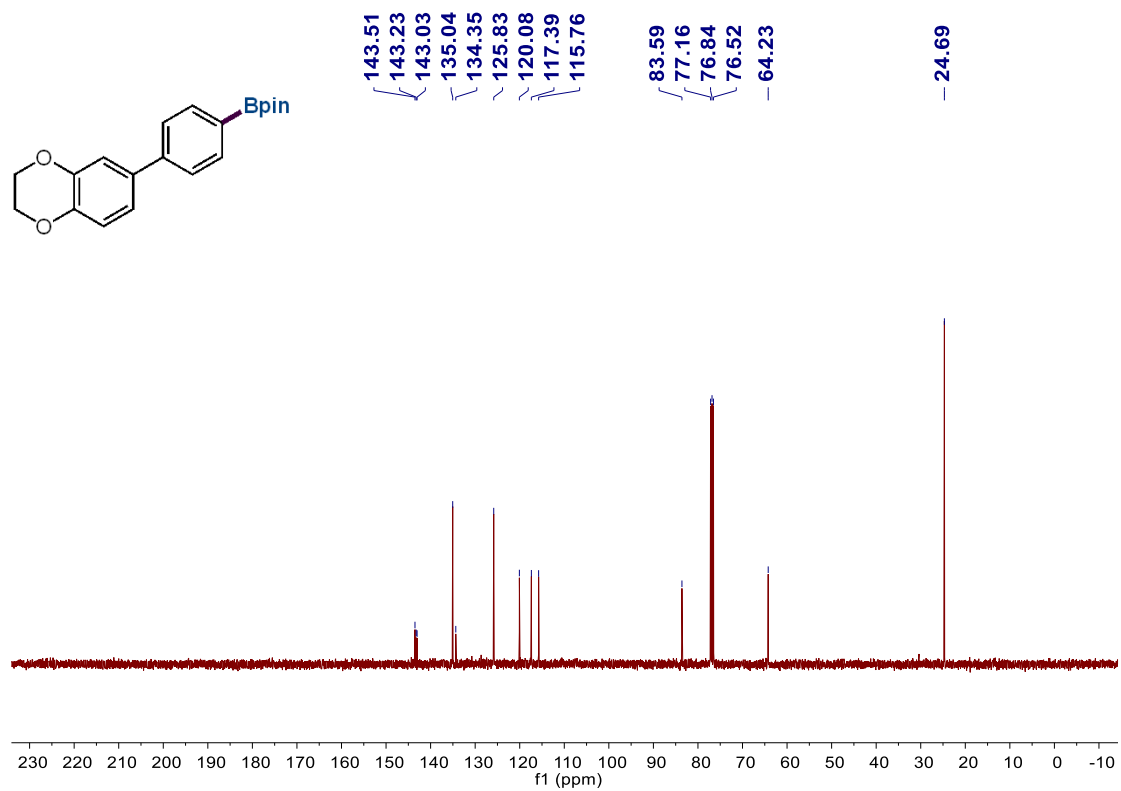
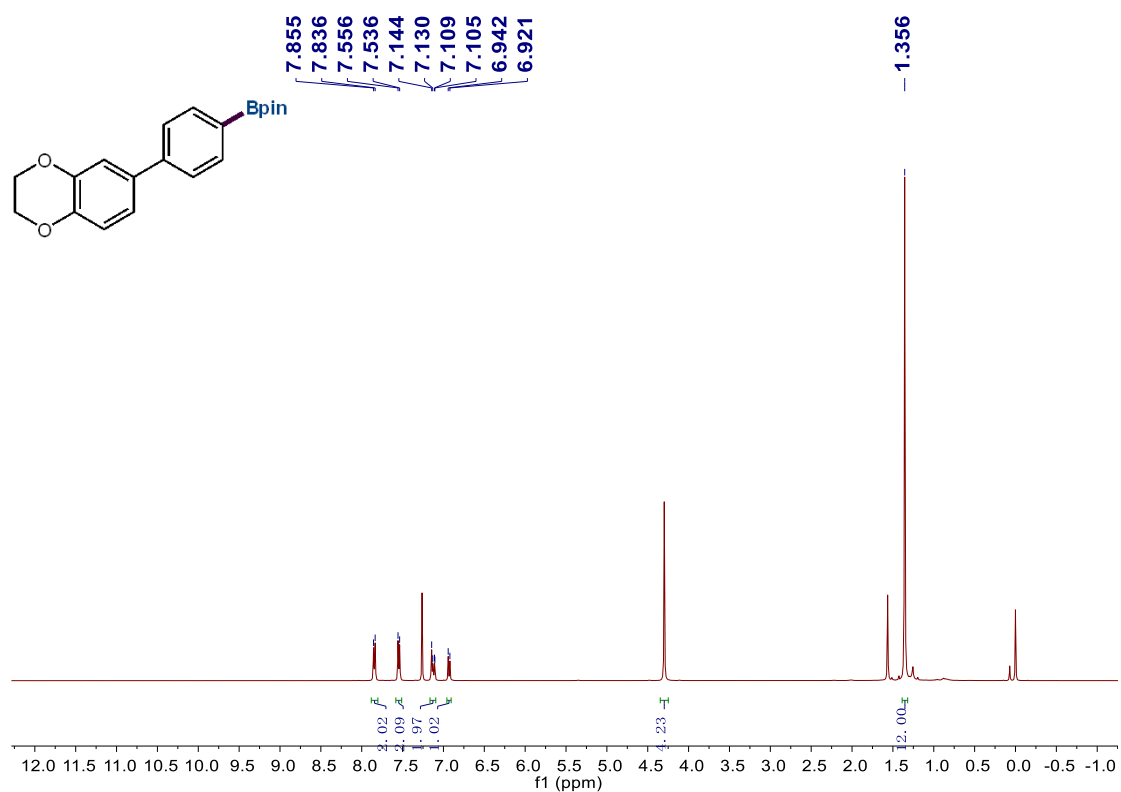
2-(2-Methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af).



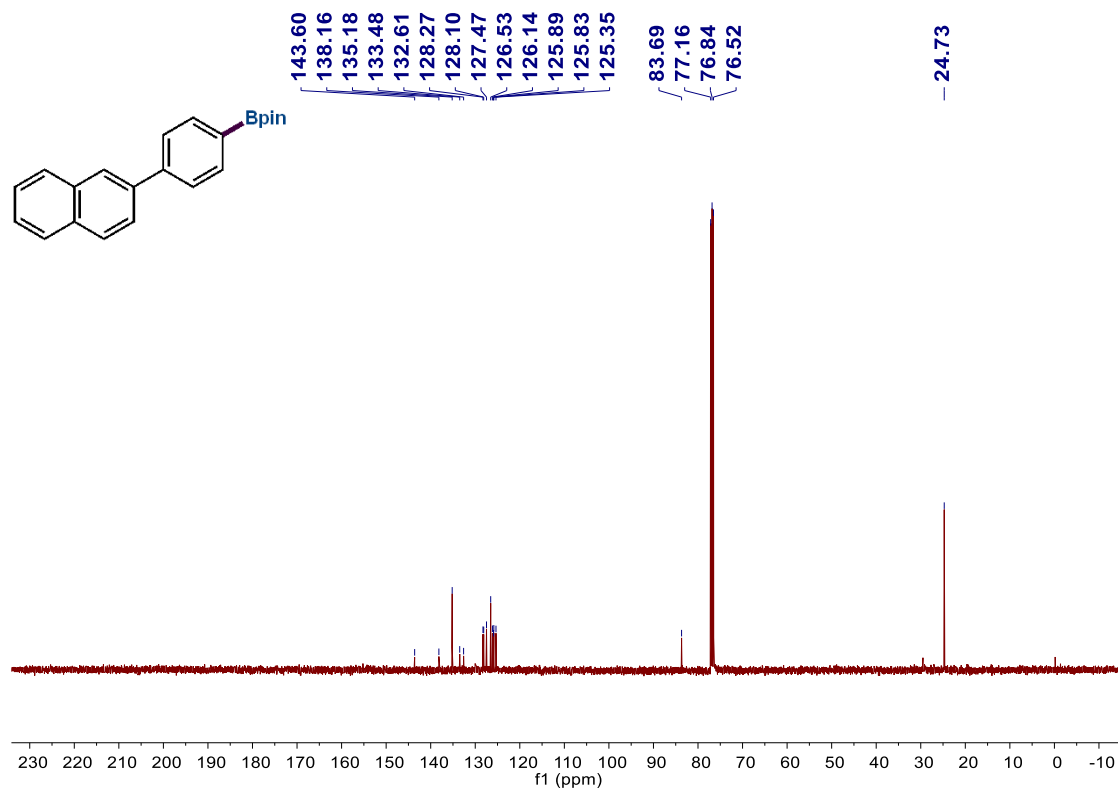
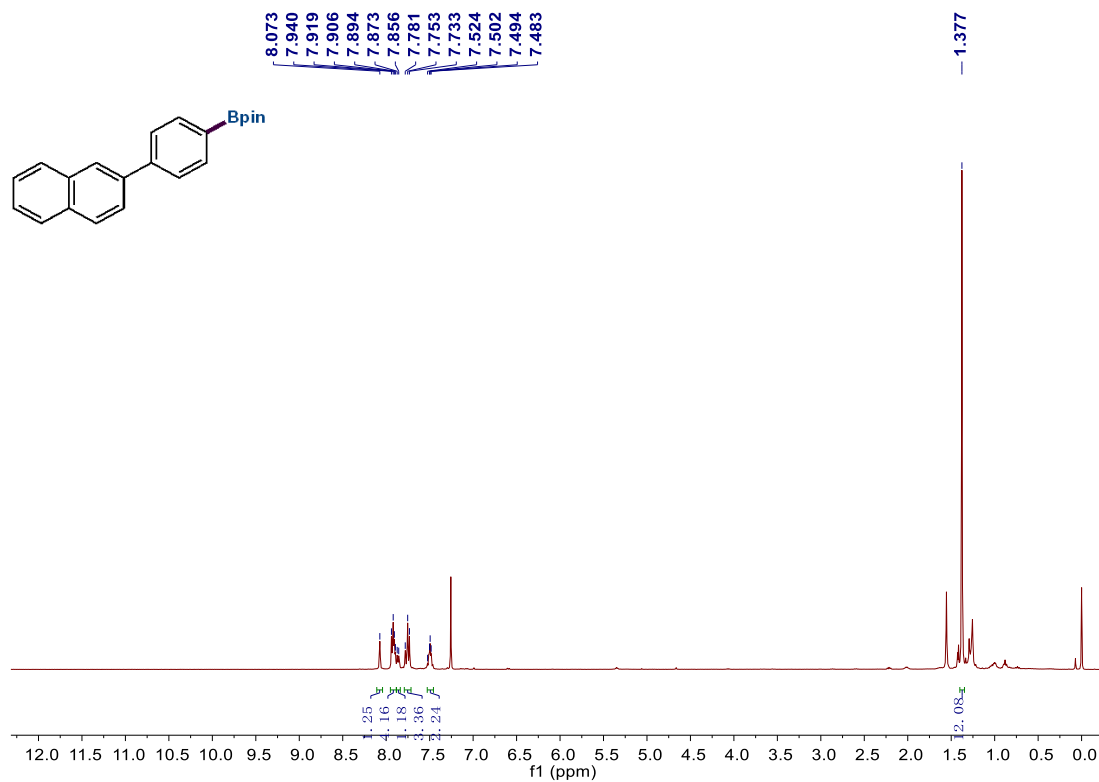
4-(4'-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)morpholine (4ag).



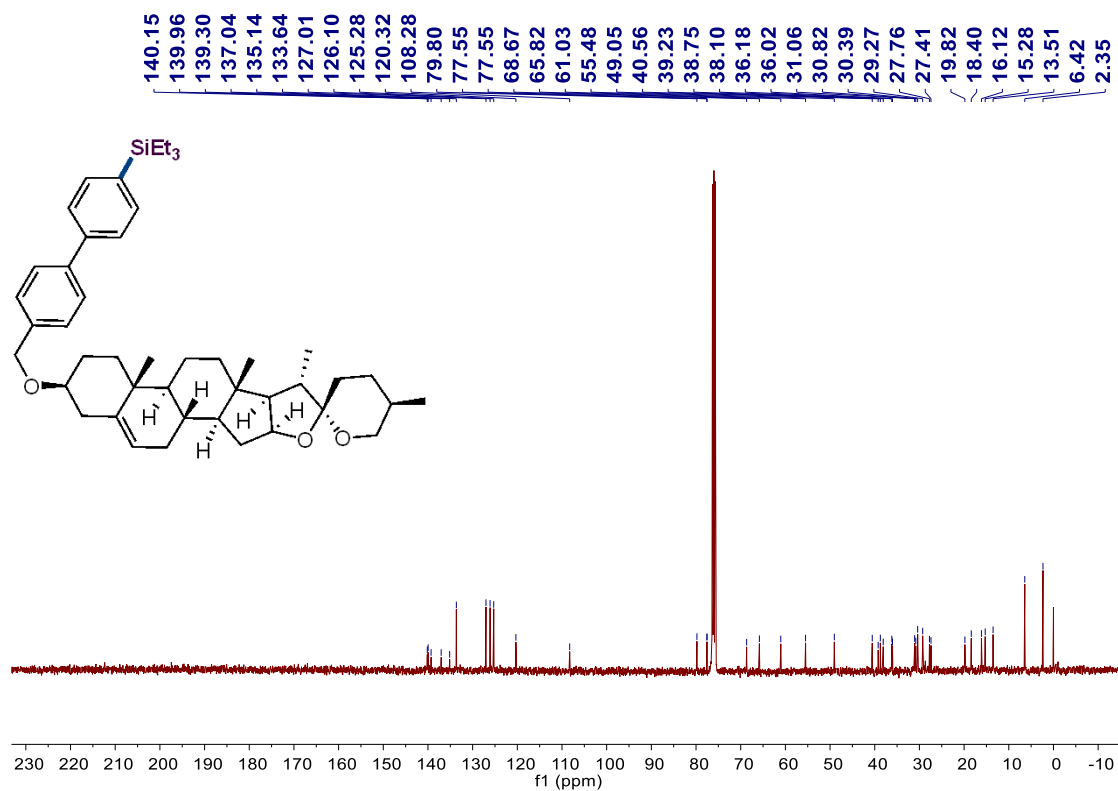
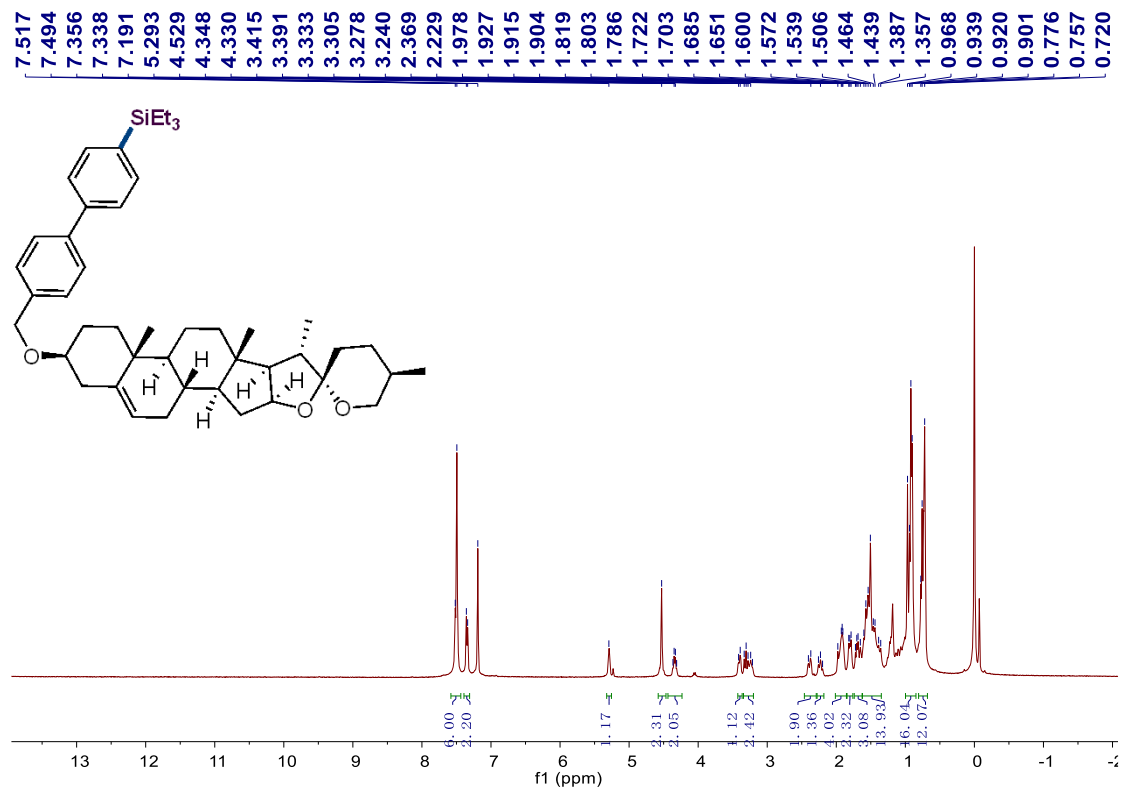
2-(4-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ah)



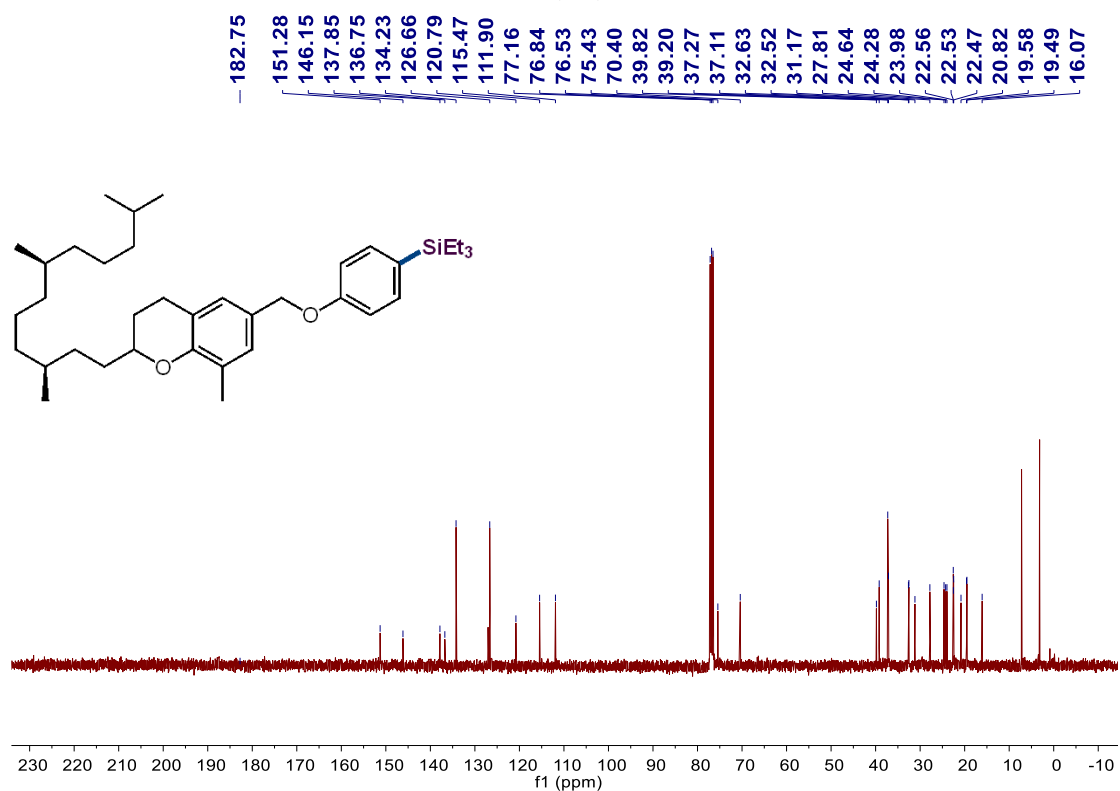
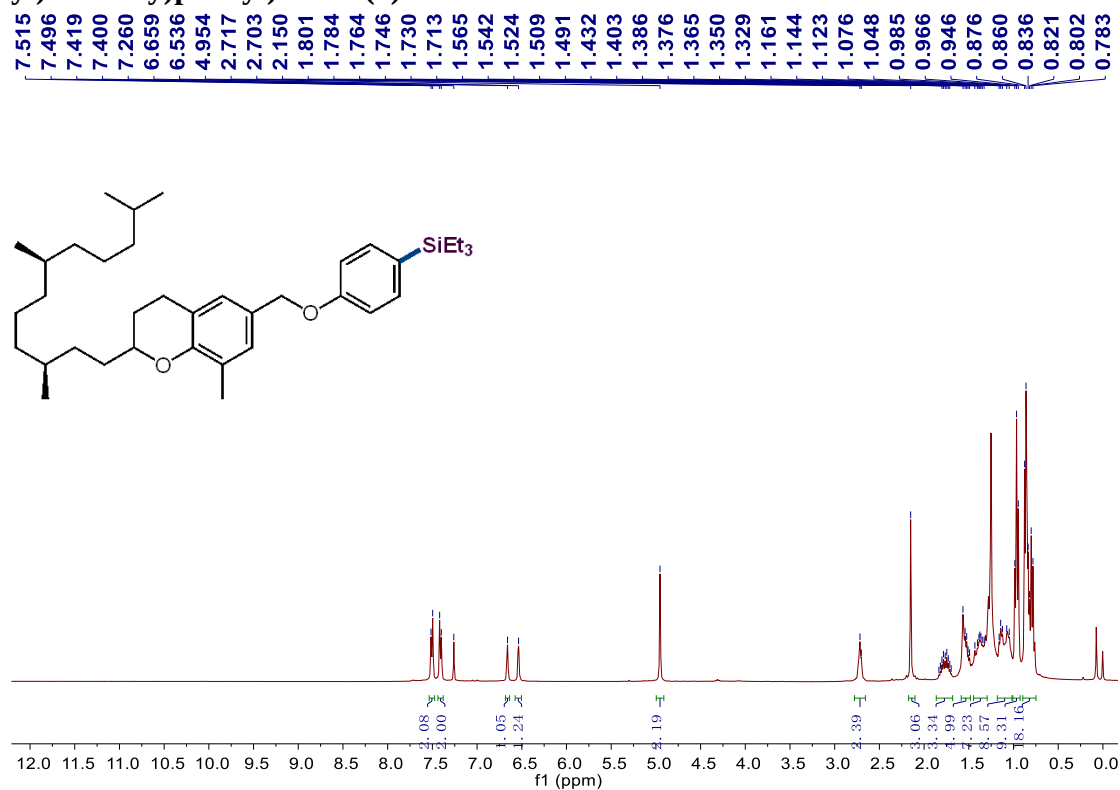
4,4,5,5-Tetramethyl-2-(4-(naphthalen-2-yl)phenyl)-1,3,2-dioxaborolane (4ai).



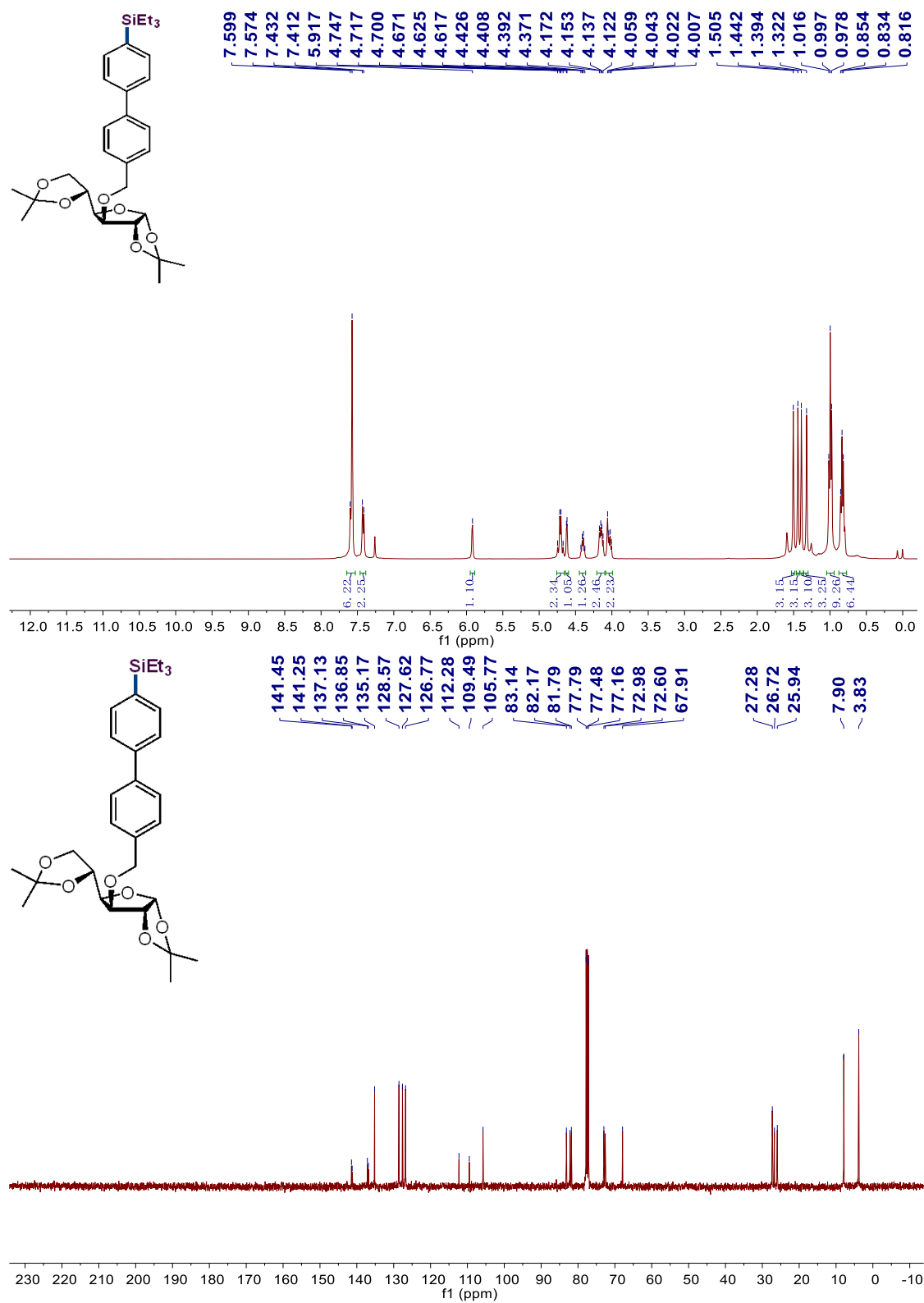
Triethyl(4'-((((4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)silane (5).



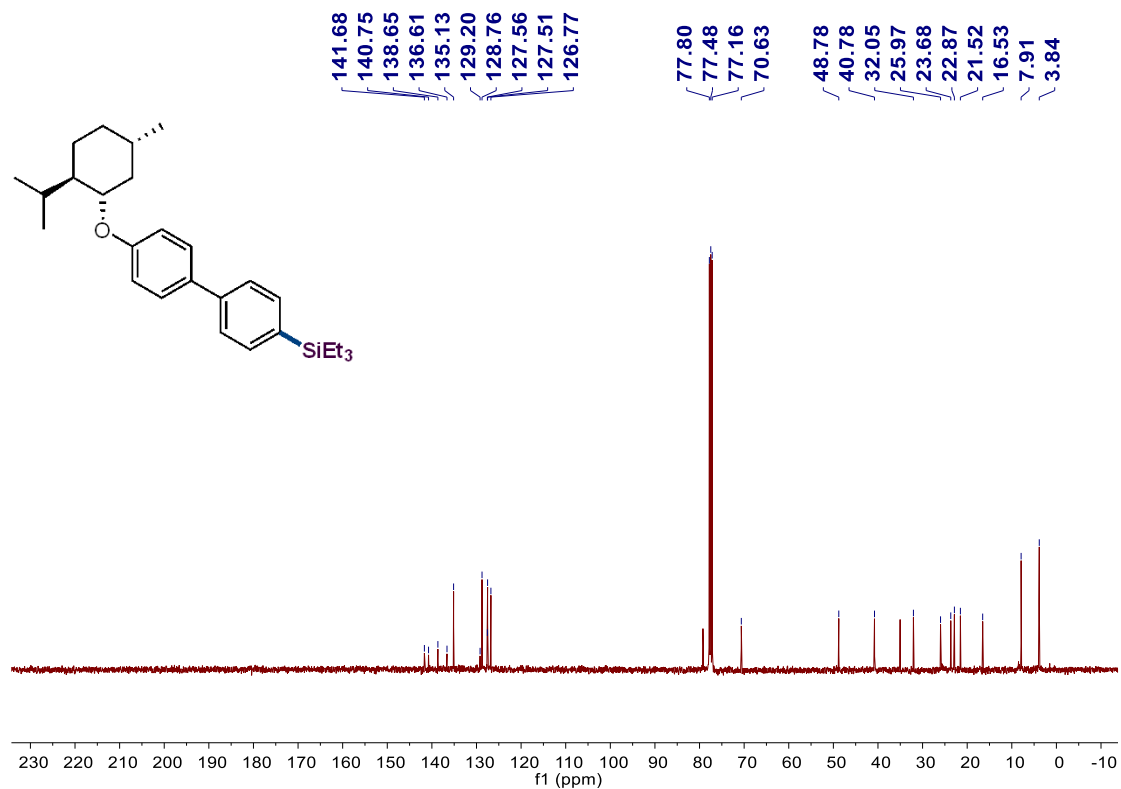
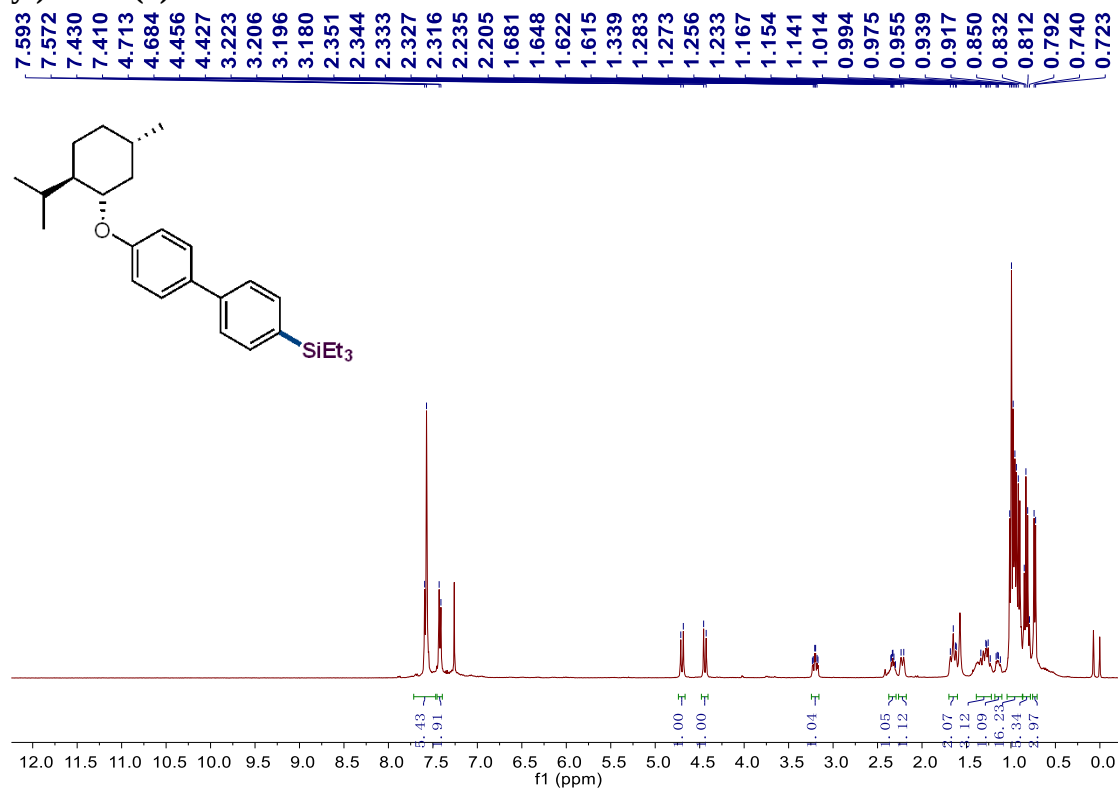
Triethyl(4-((8-methyl-2-((3S,7S)-3,7,11-trimethyldodecyl)chroman-6-yl)methoxy)phenyl)silane (6).



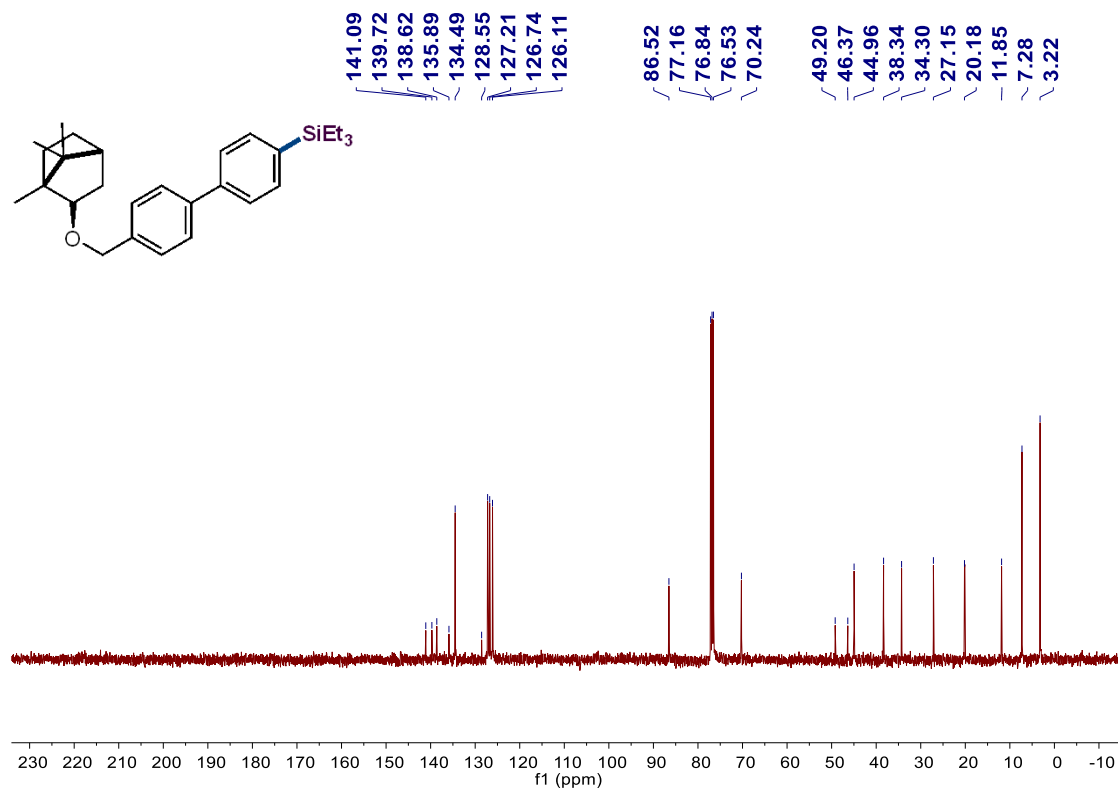
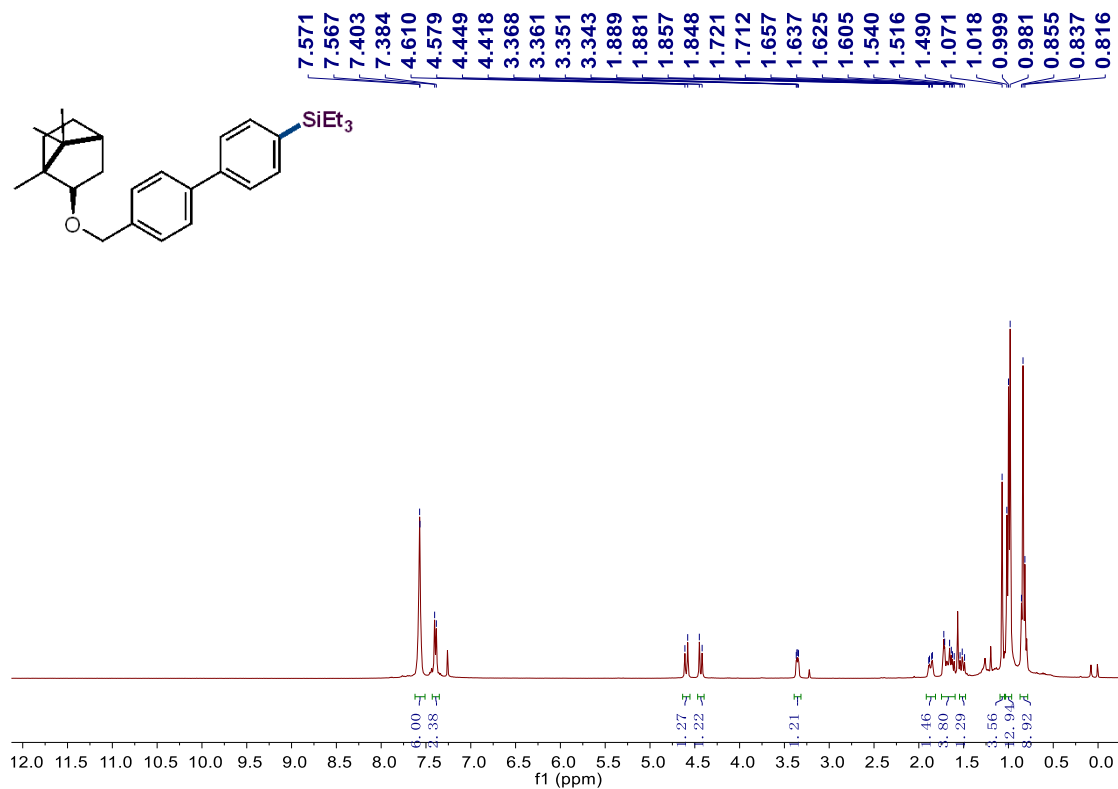
(4'-((((3aR,5R)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)triethylsilane (7).



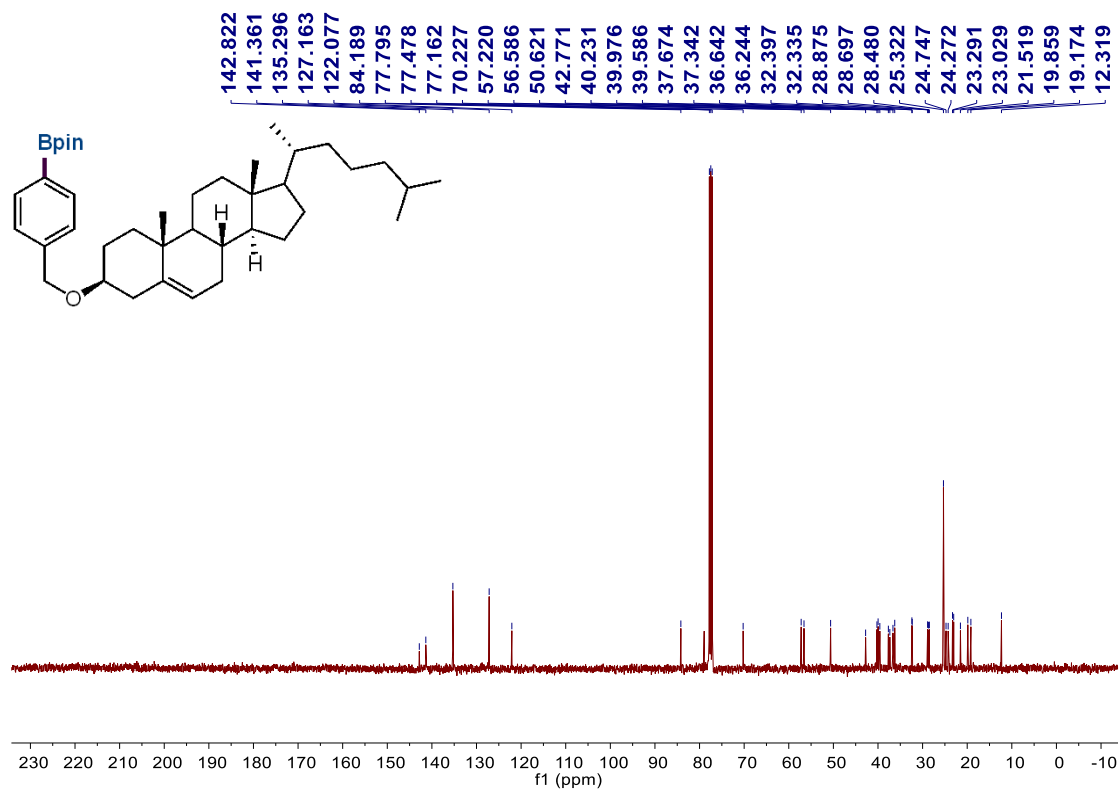
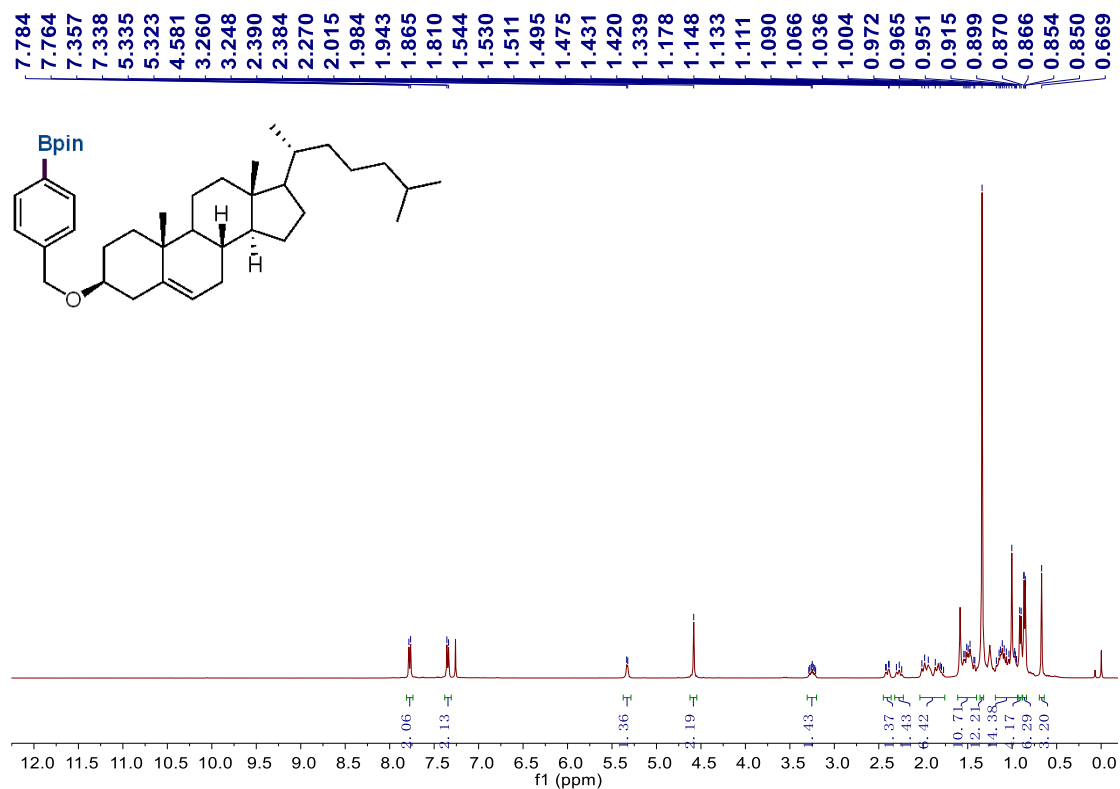
Triethyl(4'-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)-[1,1'-biphenyl]-4-yl)silane (8).



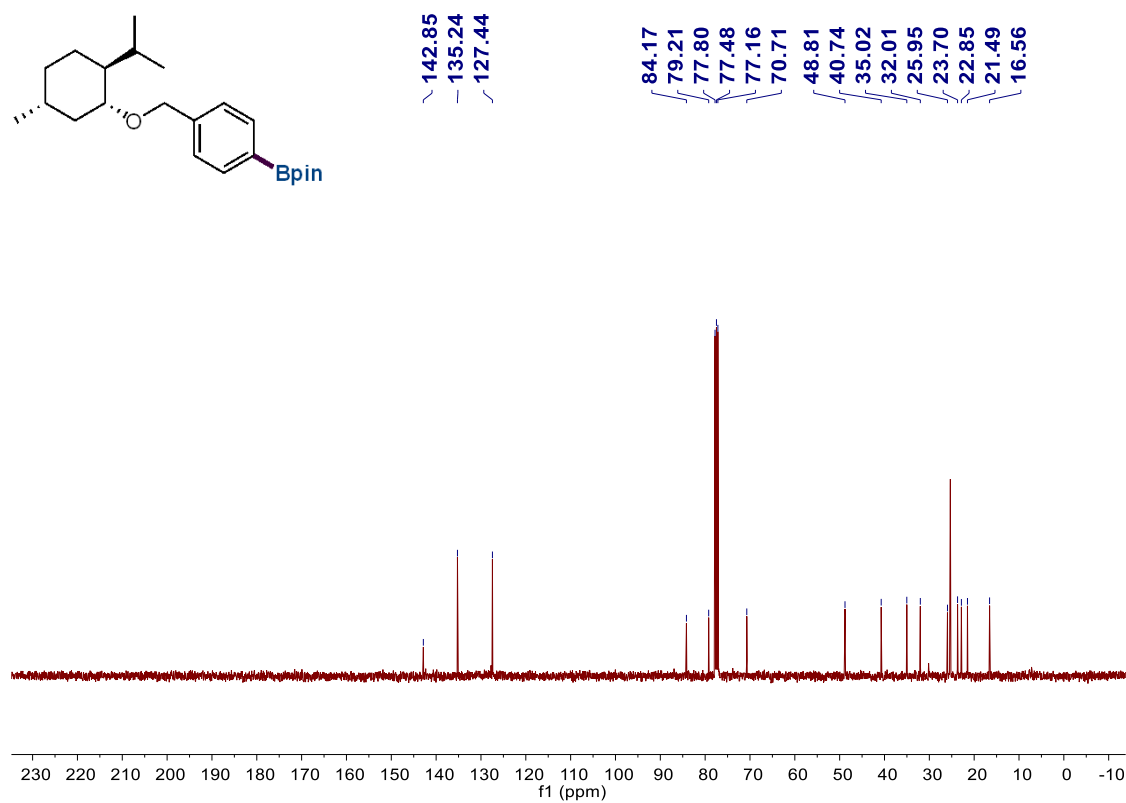
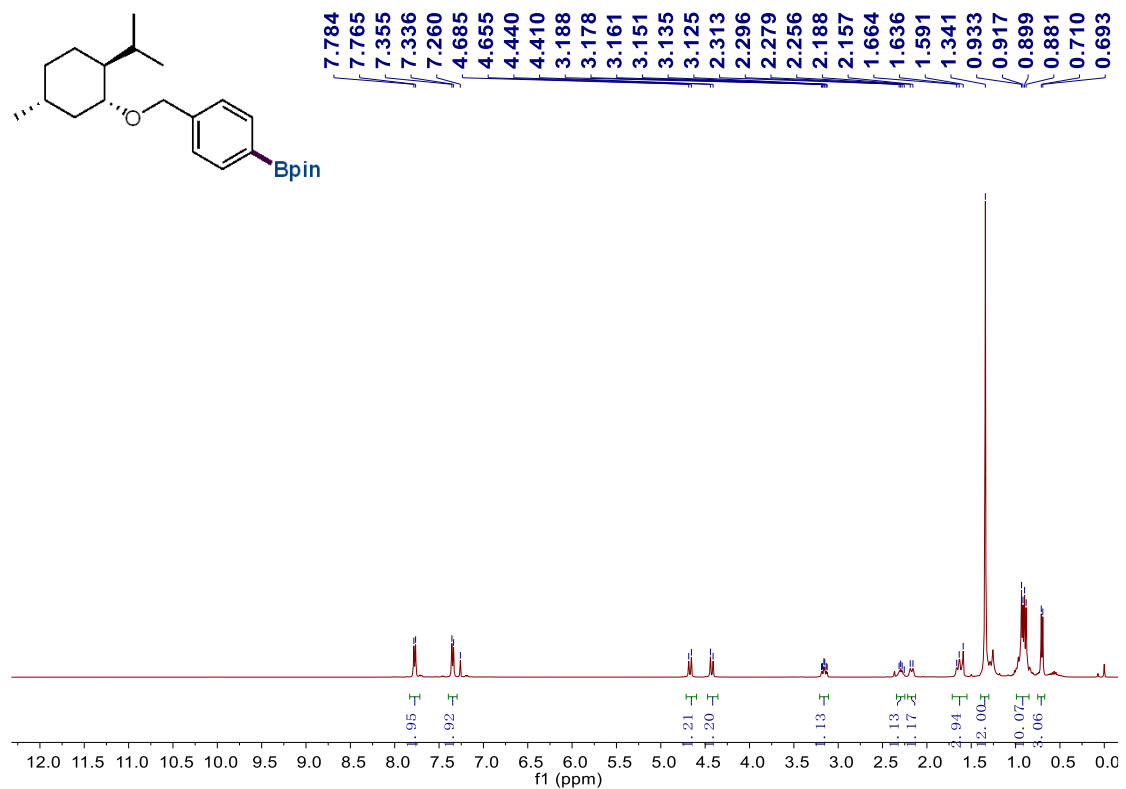
Triethyl(4'-((((1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl)silane (9).



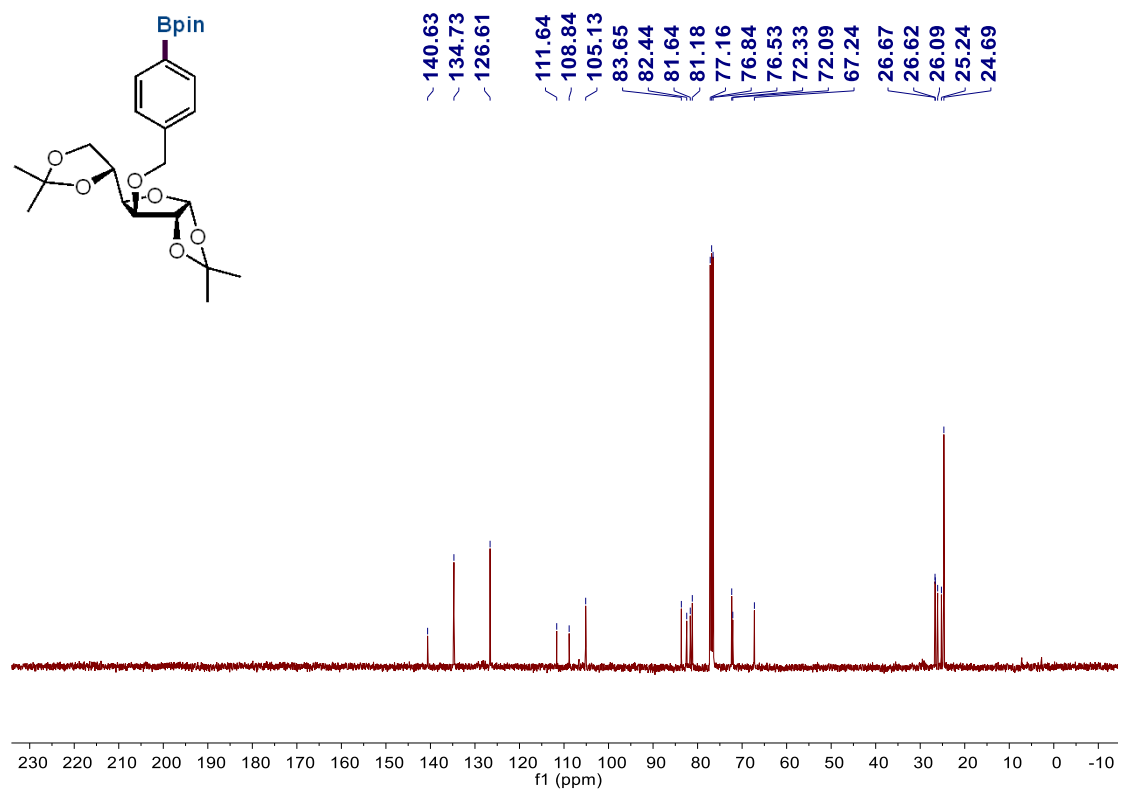
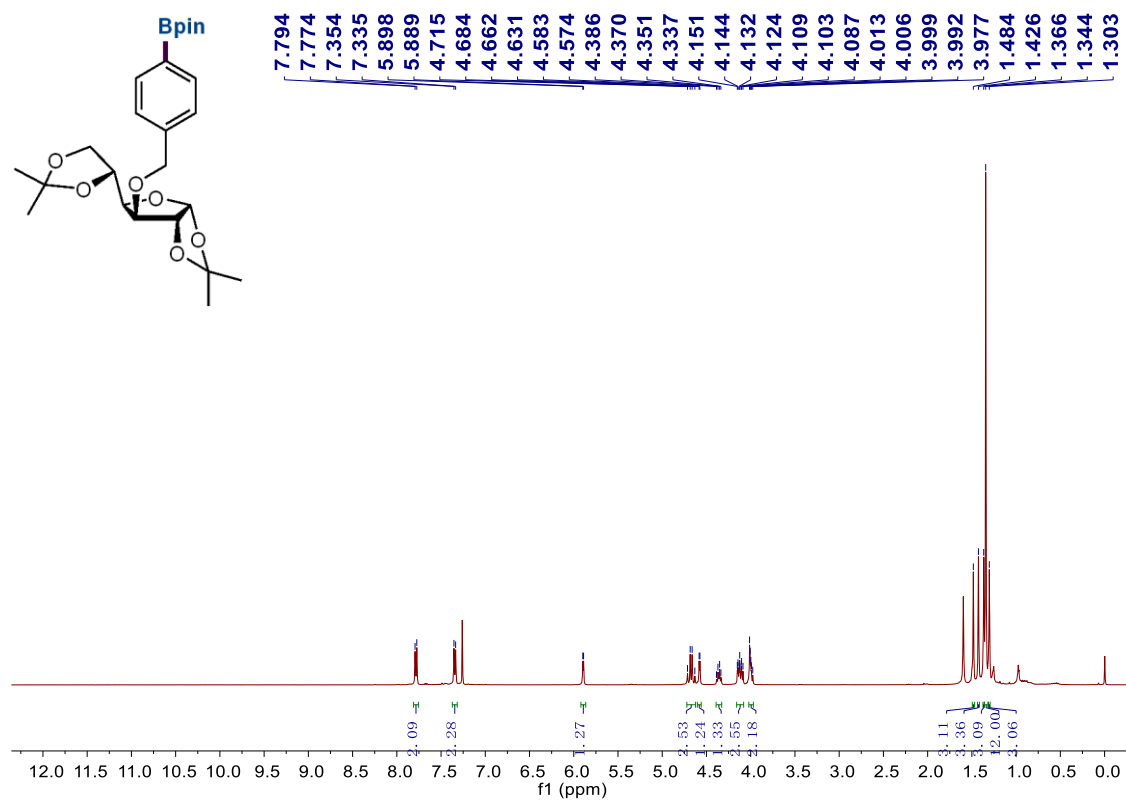
2-(4-(((3S,8S,10R,13R,14S)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



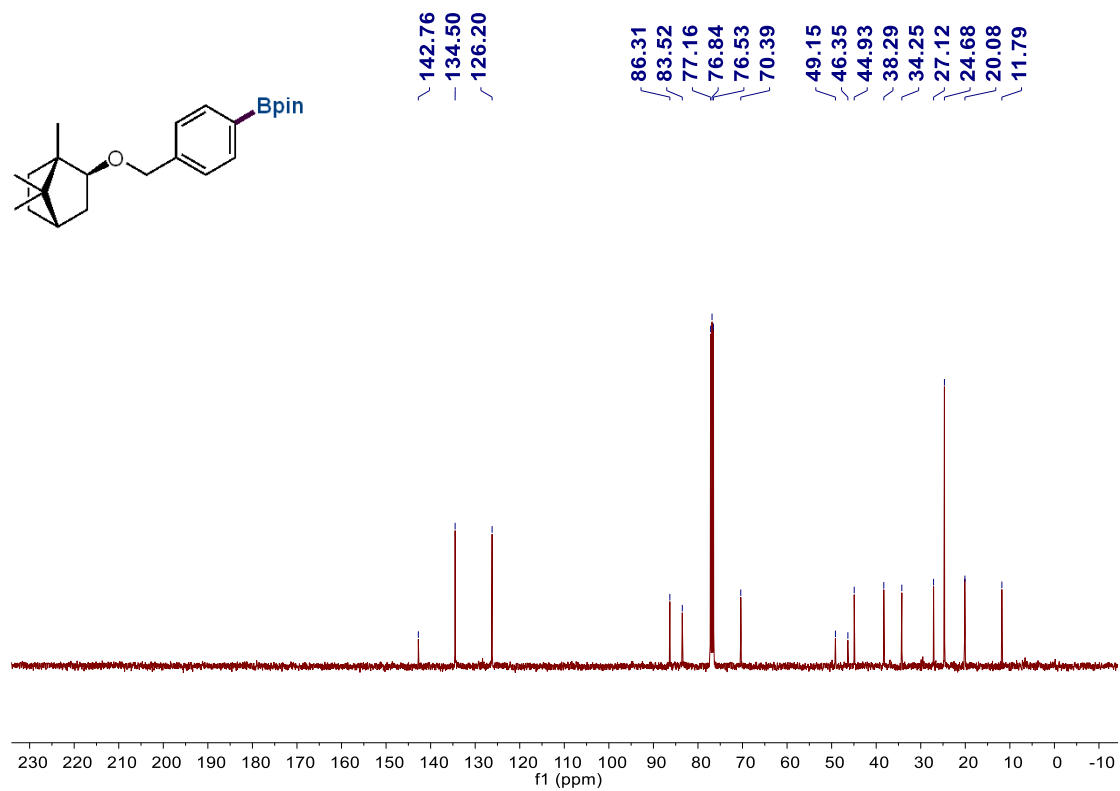
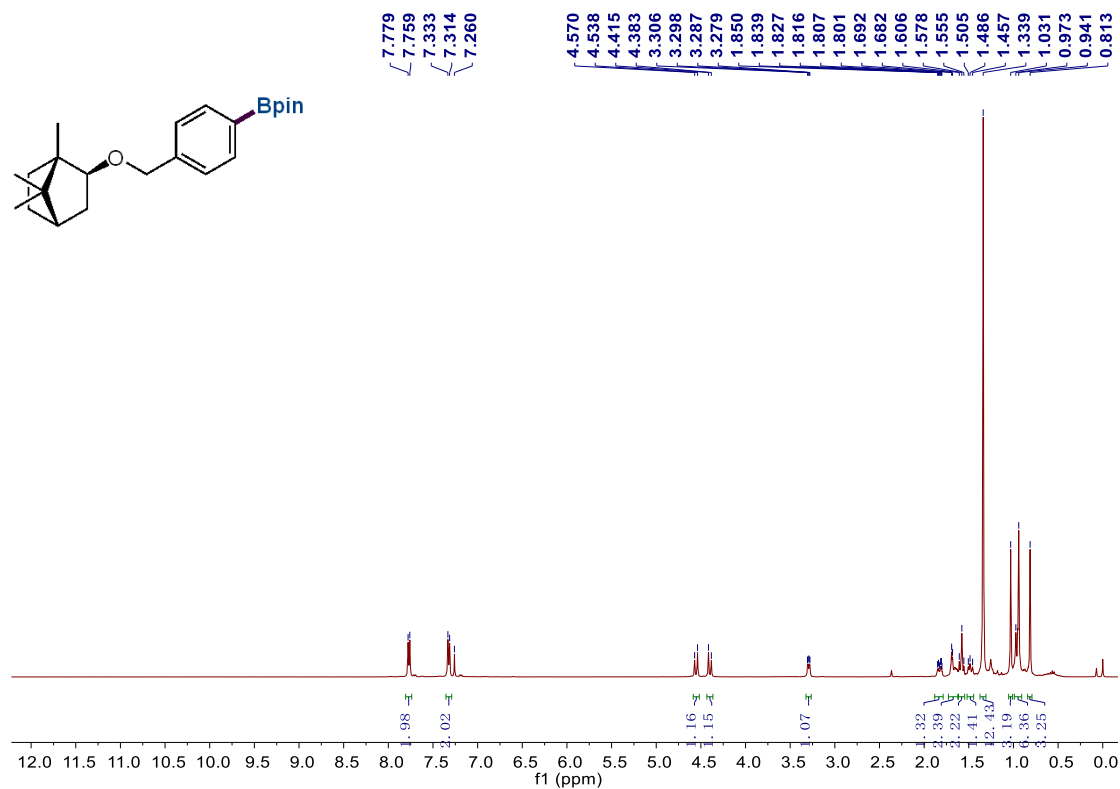
2-(4-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11).



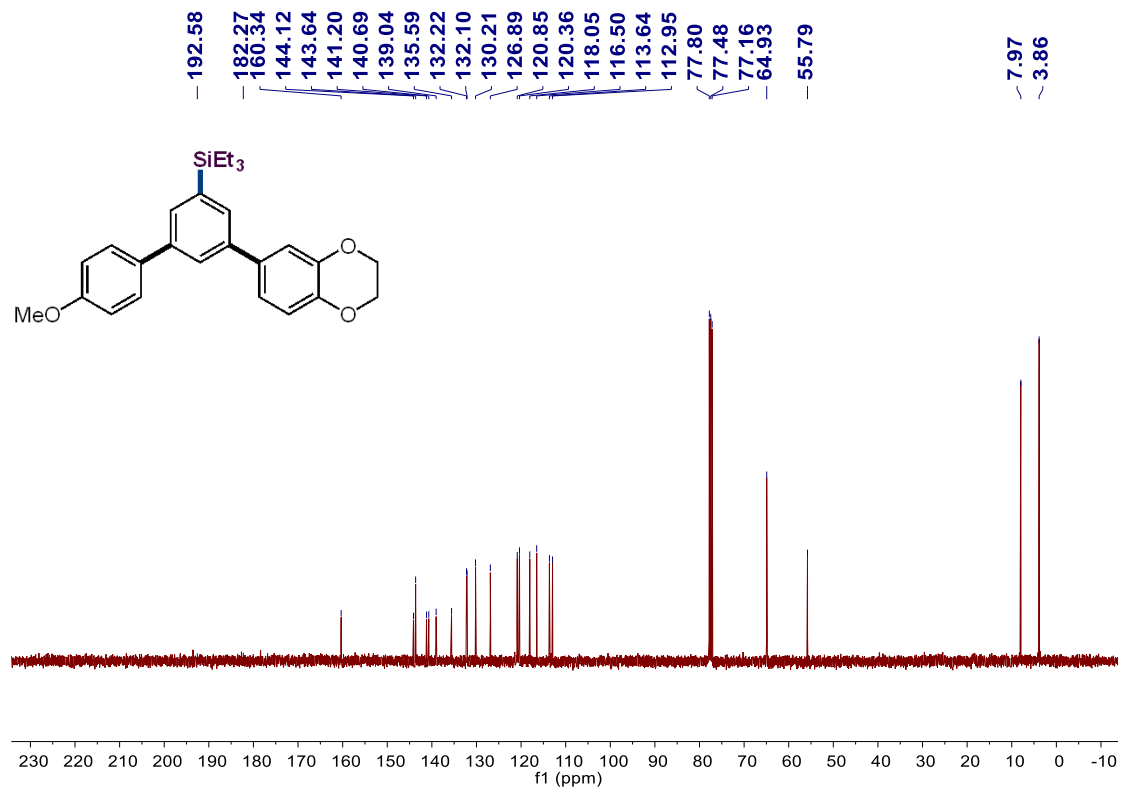
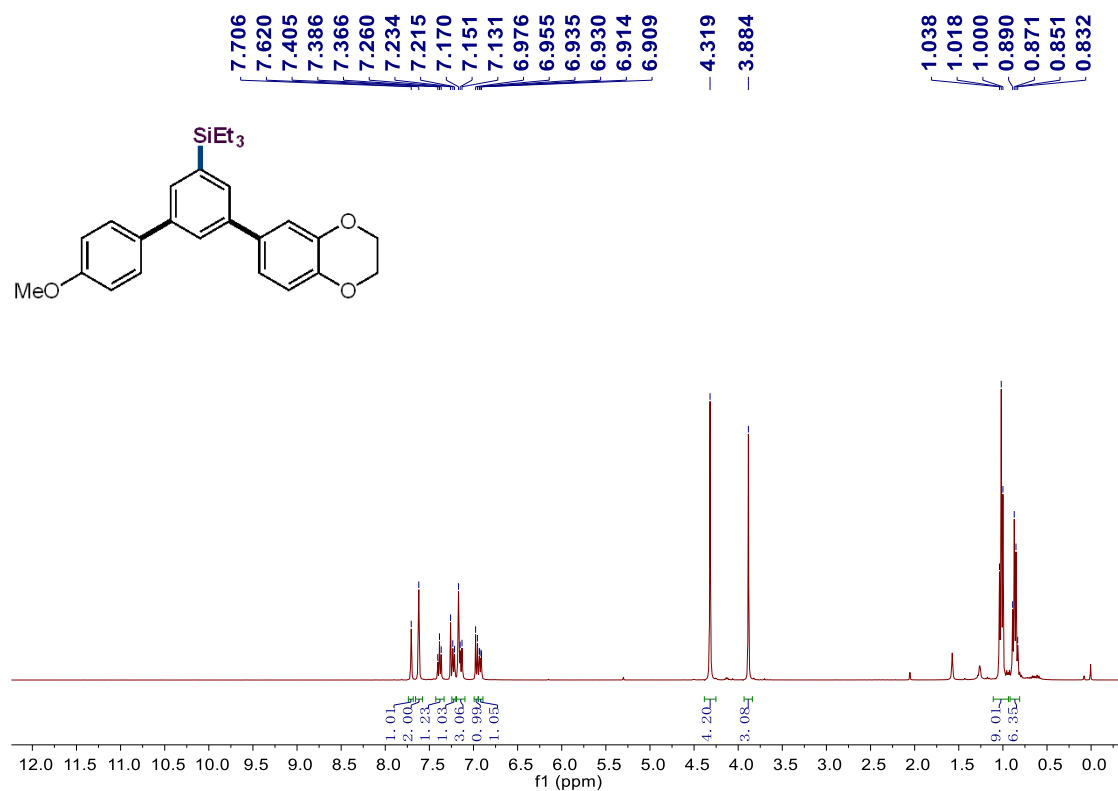
2-(4-(((3aR,5R)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13).



4,4,5,5-Tetramethyl-2-(4-(((1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)phenyl)-1,3,2-dioxaborolane (14).



(5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-yl)triethylsilane (16).



**2-(5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4'-methoxy-[1,1'-biphenyl]-3-yl)-
4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17).**

