Supplementary Information

A Directive Ni Catalyst Overrides Conventional Site-Selectivity in Pyridine C–H Alkenylation

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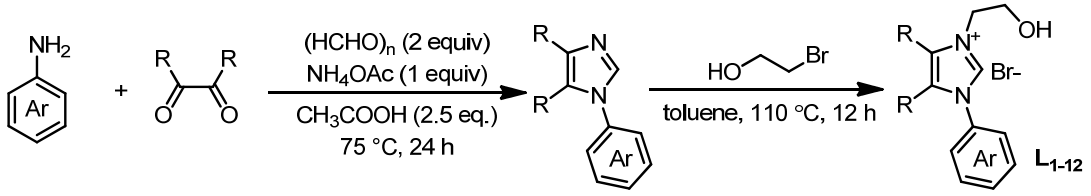
1. General Information

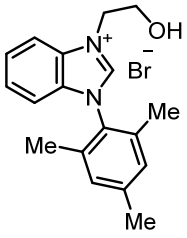
Unless stated otherwise, all reactions were conducted under N_2 atmosphere. All solvents were received from commercial sources without further purification. Commercially available reagents were used as received. Non-commercially available substrates were synthesized following reported protocols. Melting points were measured on X-4B microscope melting point apparatus and uncorrected. Thin-layer chromatography (TLC) was performed by UV absorbance (254 nm). 200–300 mesh silica gel was used for column chromatography separation. NMR spectra were recorded on Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR). Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.13 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). High resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF LC/MS with Electron Spray Ionization (ESI) resource. Single crystal X-ray diffraction data were collected on Rigaku Saturn70 diffract meter.

2. Synthesis of Ligands

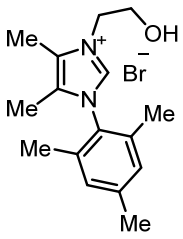


To a two-neck flask equipped with a magnetic stirring bar and a reflux condenser were added aniline (10 mmol), dione (10 mmol), $(CH_2O)_n$ (20 mmol, 600 mg), NH_4OAc (10 mmol, 770 mg) and 1.5 mL of CH_3COOH. The mixture was refluxed for 18 h and then cooled down to room temperature. The pH of the solution was adjusted to 9 by adding K_2CO_3. The resulting biphasic mixture was extracted with ether (4 × 50 mL). The combined organic extracts were washed with brine (30 mL) and dried over anhydrous sodium sulfate. All volatiles were removed under reduced pressure. The crude mixture was purified by column chromatography (EtOAc/*n*-hexane) to obtain imidazoles.

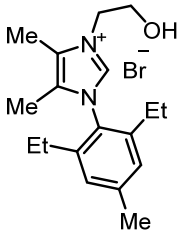
A solution of imidazole (5 mmol) and 2-bromoethanol (625 mg, 5 mmol) in toluene (15 mL) was refluxed for 18 h. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (DCM/EtOH) to obtain the corresponding ligands. Ligands **L_1-L_4** and **L_{12}** were synthesized according to the literature procedure.[1,2]



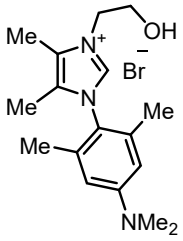
3-(2-Hydroxyethyl)-1-mesityl-1*H*-benzo[*d*]imidazol-3-ium bromide (L_5).
Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_5** as Brown solid(1.12 g, 3.25 mmol, 65% yield), m.p. 202-204 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.09 (s, 2H), 5.17 (t, J = 5.0 Hz, 2H), 4.95 (s, 1H), 4.15 (t, J = 4.6 Hz, 2H), 2.40 (s, 3H), 2.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 141.7, 135.4, 131.7, 131.4, 131.1, 130.2, 127.9, 127.7, 113.8, 113.3, 59.0, 49.5, 21.3, 17.7. **HRMS** (ESI) m/z: calcd. for $C_{18}H_{21}N_2O$ $[M–Br]^+$ 281.1648, found 281.1645.



3-(2-Hydroxyethyl)-1-mesityl-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_6)
Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_6** as White solid (0.95 g, 2.82 mmol, 56% yield), m.p. 201-203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.01 (s, 2H), 4.95 – 4.85 (m, 1H), 4.76 – 4.68 (m, 2H), 3.99 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.00 (s, 6H), 1.96 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 136.1, 135.0, 129.9, 128.9, 127.1, 59.1, 49.3, 21.2, 17.6, 9.1, 8.3. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{23}N_2O$ $[M–Br]^+$ 259.1805, found 259.1802.

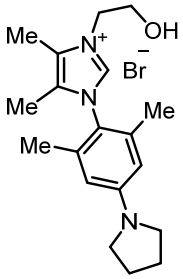


1-(2,6-Diethyl-4-methylphenyl)-3-(2-hydroxyethyl)-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_7)
Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_7** as Brown solid (1.24 g, 3.41 mmol, 68% yield), m.p. 212-214 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.04 (s, 2H), 4.87 (t, J = 6.8 Hz, 1H), 4.72 (t, J = 4.8 Hz, 2H), 4.02 – 3.90 (m, 2H), 2.38 (s, 6H), 2.18 (q, J = 7.6 Hz, 4H), 1.93 (s, 3H), 1.13 (t, J = 7.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 140.7, 136.7, 128.0, 127.7, 127.5, 126.8, 59.1, 49.2, 23.9, 21.5, 14.6, 9.0, 8.6. **HRMS** (ESI) m/z: calcd. for $C_{18}H_{27}N_2O$ $[M–Br]^+$ 287.2118, found 287.2114.



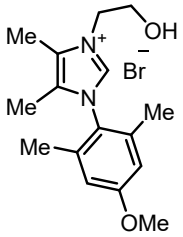
1-(4-(Dimethylamino)-2,6-dimethylphenyl)-3-(2-hydroxyethyl)-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_8)

Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_8** as Brown solid (1.36 g, 3.74 mmol, 74% yield), m.p. 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 6.42 (s, 2H), 4.94 (t, J = 7.0 Hz, 1H), 4.76 – 4.64 (m, 2H), 4.02 – 3.93 (m, 2H), 2.99 (s, 6H), 2.35 (s, 3H), 1.97 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 136.6, 135.6, 127.9, 126.6, 119.9, 111.7, 59.1, 49.1, 40.3, 18.2, 9.1, 8.3. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{26}N_3O$ $[M–Br]^+$ 288.2070, found 288.2067.



1-(2,6-Dimethyl-4-(pyrrolidin-1-yl)phenyl)-3-(2-hydroxyethyl)-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_9)

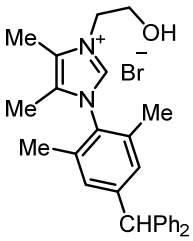
Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_9** as Brown solid (0.98 g, 2.52 mmol, 50% yield), m.p. 146-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 6.26 (s, 2H), 4.93 (t, J = 6.8 Hz, 1H), 4.76 – 4.55 (m, 2H), 3.96 (dd, J = 10.7, 5.9 Hz, 2H), 3.28 (t, J = 6.4 Hz, 4H), 2.36 (s, 3H), 2.05 – 1.99 (m, 4H), 1.94 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.9, 136.7, 135.6, 128.0, 126.4, 119.1, 111.2, 59.1, 49.1, 47.6, 25.5, 18.1, 9.0, 8.3. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{28}N_3O$ $[M–Br]^+$ 314.2227, found 314.2223.



3-(2-Hydroxyethyl)-1-(4-methoxy-2,6-dimethylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_{10})

Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_{10}** as Brown solid (1.22 g, 3.48 mmol, 69% yield), m.p. 157-158 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 6.72 (s, 2H), 4.92 (t, J = 7.0 Hz, 1H), 4.73 (t, J = 4.8 Hz, 2H), 4.05 – 3.93 (m, 2H), 3.84 (s, 3H), 2.37 (s, 3H), 2.02 (s, 6H),

1.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 136.8, 136.3, 127.4, 127.1, 124.1, 114.3, 59.1, 55.6, 49.3, 18.0, 9.1, 8.3. **HRMS** (ESI) m/z: calcd. for $C_{16}H_{23}N_2O_2$ $[M–Br]^+$ 275.1754, found 275.1749.

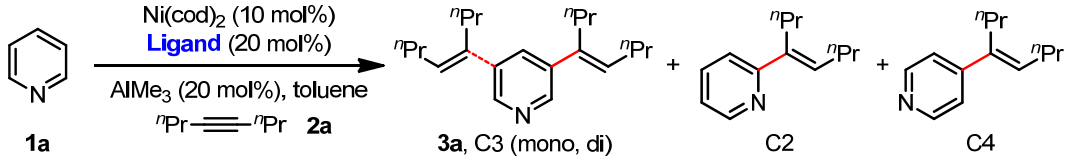


1-(4-Benzhydryl-2,6-dimethylphenyl)-3-(2-hydroxyethyl)-4,5-dimethyl-1*H*-imidazol-3-ium bromide (L_{11})

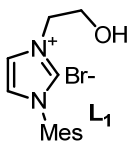
Purification via column chromatography on silica gel (DCM/EtOH = 15/1, v/v, R_f = 0.25) afforded **L_{11}** as Brown solid (1.74 g, 3.57 mmol, 71% yield), m.p. 216-218 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.33 (t, J = 7.3 Hz, 4H), 7.26 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 7.3 Hz, 4H), 6.96 (s, 2H), 5.53 (s, 1H), 4.89 (t, J = 6.3 Hz, 1H), 4.74 (t, J = 4.2 Hz, 2H), 3.97 (d, J = 4.2 Hz, 2H), 2.39 (s, 3H), 1.97 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 142.8, 136.2, 135.2, 130.3, 129.6, 129.5, 128.6, 127.1, 127.0, 126.8, 59.1, 56.5, 49.2, 17.8, 9.0, 8.4. **HRMS** (ESI) m/z: calcd. for $C_{28}H_{31}N_2O$ $[M–Br]^+$ 411.2431, found 411.2424.

3. Reaction Optimization

Table S1. Ligand Effects[a]

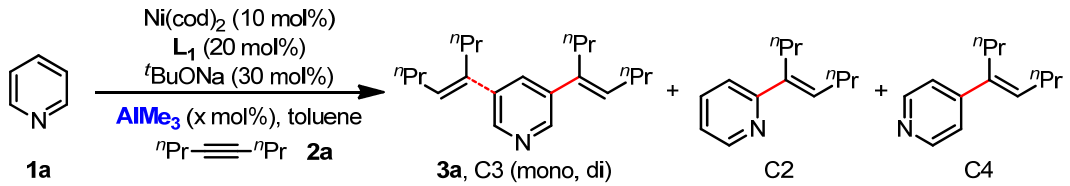


entry	Ligand (20 mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	Ph_3P	0	0	3	0
2	PCy_3	0	0	22	0
3	Cy_2POH	0	0	0	0
4	Ph_2POH	0	0	0	0
5[b]	IMes·HCl	1	0	0	2
6	IMes	1	0	0	16
7[b]	SIMes·HCl	0	0	0	0
8[b]	IPr·HCl	0	0	0	1
9	IPr	1	0	0	13
10[b]	SIPr·HCl	0	0	0	0
11[b]	L_1	33	5	5	8
12	—	0	0	0	0



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^{1}H NMR with CH_2Br_2 as the internal standard. [b]NaO^{t}Bu (30 mol%).

Table S2. $AlMe_3$ Loading Effects[a]

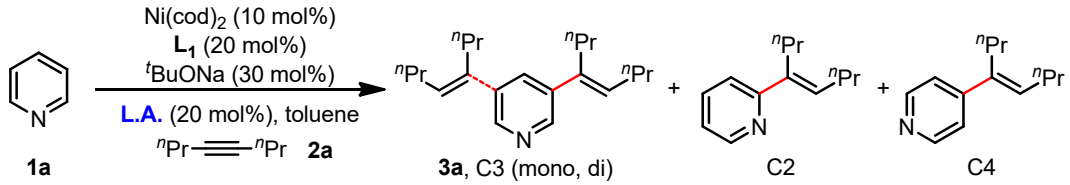


entry	$AlMe_3$ (mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	0	0	0	0	0
2	10	17	0	1	15
3	20	33	5	5	8
4	30	9	8	19	5
5	40	8	1	19	5

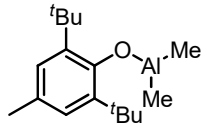
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^1H NMR with CH_2Br_2 as the internal standard.

More loadings of $AlMe_3$ favors C2 and C4-alkenylation without cooperative catalysis.

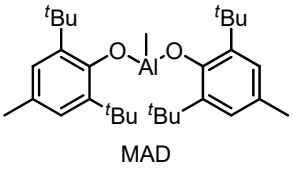
Table S3. Lewis Acid Effects[a]



entry	L.A. (20 mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	$AlMe_3$	33	5	5	8
2	$AlEt_3$	34	7	3	7
3	Al^iBu_3	36	12	5	7
4	$Al(Oct)_3$	17	12	0	8
5	$AlMe_2Cl$	0	0	0	0
6	$(BHT)AlMe_2$	0	0	0	0
7	MAD	0	0	0	0
8	$Al(O^tBu)_3$	1	0	0	1
9	$ZnEt_2$	0	0	0	0
10	BEt_3	0	0	0	0
11[b]	Al^iBu_3	31	19	1	14



$(BHT)AlMe_2$

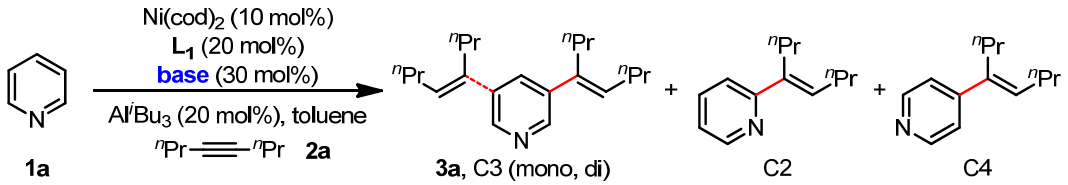


MAD

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^1H NMR with CH_2Br_2 as the internal standard. [b]18-crown-6 (10 mol%) added.

Strong Al-Lewis acids are required, and increasing the steric bulkiness of the substituent on the aluminum, the yields of the C3-mono and dialkenylation products slightly increased, which suggested a proper coordination between pyridine and Al^iBu_3 was critical to the reactivity and selectivity.

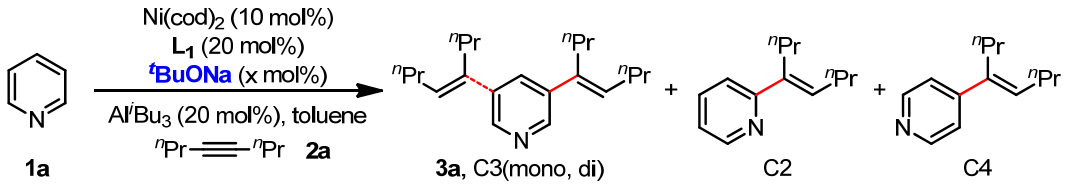
Table S4. Base Effects[a]



entry	base (30 mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	NaO^{t}Bu	36	12	5	7
2	KO^{t}Bu	24	12	5	7
3	NaHMDS	28	6	4	5
4	KHMDS	17	4	2	3
5	0	0	0	0	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^{1}H NMR with CH_2Br_2 as the internal standard.

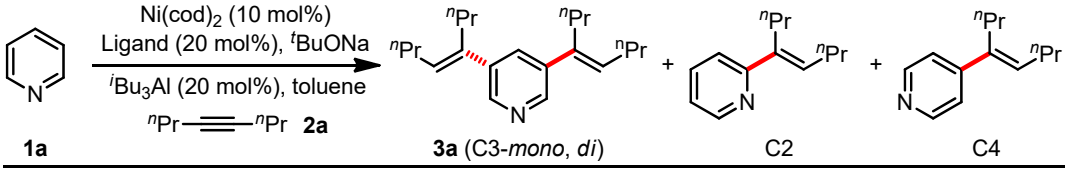
Table S5. Base Loading Effects[a]

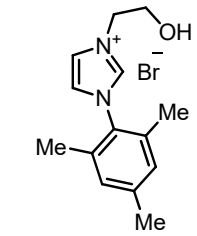


entry	^{t}BuONa (mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	20	25	12	5	5
2	25	39	14	5	5
3	30	36	12	5	7
4	35	19	8	8	8

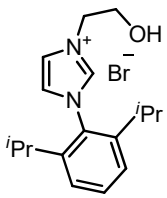
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^{1}H NMR with CH_2Br_2 as the internal standard.

Table S6. Ligand Effects[a]

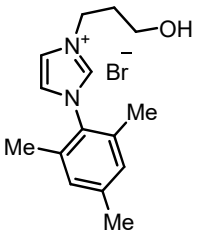




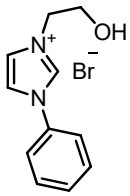
L_1, 39%/14%/ 5%/5%



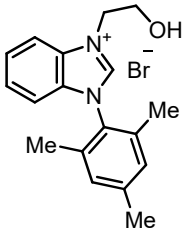
L_2, 11%/0/0/7%



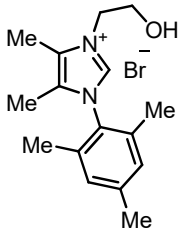
L_3, 28%/11%/7%/10%



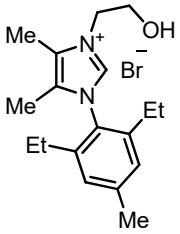
L_4, 0



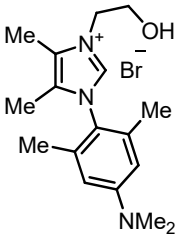
L_5, 0



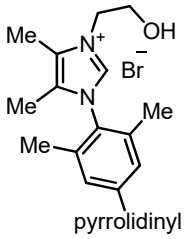
L_6, 45%/19%/4%/6%



L_7, 25%/8%/2%/7%

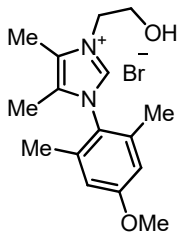


L_8, 37%/10%/6%/5%

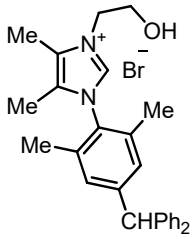


pyrrolidinyl

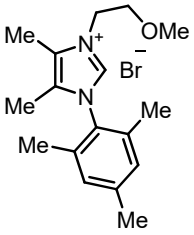
L_9, 34%/11%/4%/5%



L_{10}, 53%/19%/4%/5%
L_{10}, 59%/22%/5%/1%[b]



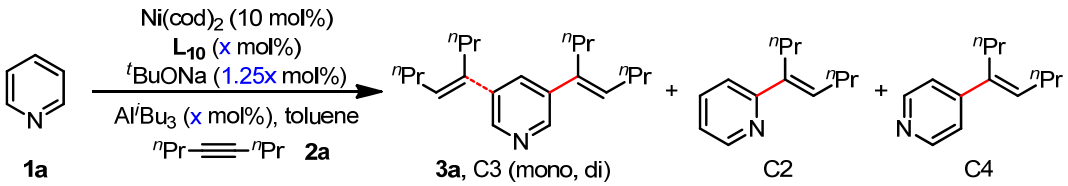
L_{11}, 20%/1%/0/3%



L_{12}, 0

[a]Reaction conditions:**1a** (0.2 mmol), **2a** (0.6 mmol), toluene (0.5 mL) under N_2 at 100 °C for 12h. Yield of isomers and regioselectivity (C3-mono/C3-di/C2/C4) were determined by ^{1}H-NMR with CH_2Br_2 as the internal standard. [b]L_{10} (10 mol%), Al^{i}Bu$_3$ (10 mol%), ^{t}BuONa (12.5 mol%)

Table S7. Ligand Loading Effects[a]



entry	loading (mol%)	C3-mono (%)	C3-di (%)	C2 (%)	C4 (%)
1	5	22	10	3	2
2	10	59	22	5	1
3	20	53	19	4	5

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) toluene (0.5 mL) at 100 °C under N_2 for 12h. Yield of isomers was determined by ^{1}H NMR with CH_2Br_2 as the internal standard.

Taking the results from Table S1 and Table S6, we can form the following conclusions with regards to the role of the bifunctional ligand in this reaction.

1) The native selectivity for the Lewis acid promoted Ni(0)-catalyzed C–H alkenylation favors the C2 and C4 positions. This is illustrated with control experiments using PCy_3, IMes and IPr as ligands, giving only C2 or C4 alkenylated products (Table S1, entry 2, 6 and 9). This native selectivity is also reinforced by Nakao and Ong's finding for their highly C4-selective processes.[3,4]

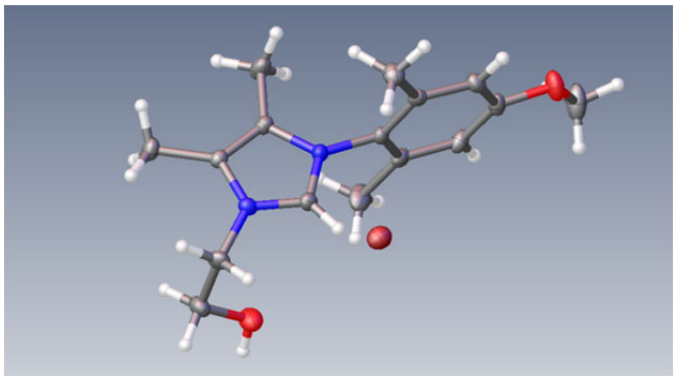
2) The incorporation of a hydroxyl directing handle in **L_1** (Table S1, entry 11) gives C3 product as the major product, indicating a switch in mechanism away from substrate-induced selectivity to ligand-induced selectivity.

3) Methylation of the free hydroxyl group (**L_{12}**, Table S6) completely shut down reactivity (from a ligand that otherwise gave 48% combined C3 yields: see **L_1**, Table S6), indicating that free OH group is crucial for both reactivity and selectivity of the reaction. This result reaffirms our mechanistic hypothesis that the free OH reacts with $^{t}Bu_3Al$ to form the active Al species, which is then able to recruit the pyridine substrate.

4) Structural deviations (in particular, alteration of linker chain length, see **L_1** vs **L_3** in Table S6) dramatically alter yield and selectivity distribution. These structural deviations from designed factors again point towards the crucial role the ligand plays in both the reactivity and the selectivity of the transformation
Altogether, these observations provide evidence for a critical ligand effect operative in this reaction. Crucially, these results provide overwhelming support that the ligand is enforcing both the reactivity and selectivity of the C3-selective process, overriding the intrinsic C2/C4 selectivity observed in our control studies (Table S1) and related works[3,4]

5) Notably, the use of the imidazolium halide precursor to **L_{12}** led to complete shut-down of the reaction in a manner similar to the use of IPr·HCl and IMes·HCl, where the formed $^{t}BuOH$ can deleteriously react with the Al Lewis acid. Unfortunately, our attempt at generating and employing the free carbene from **L_5** was unsuccessful due to the instability of the formed carbene species.

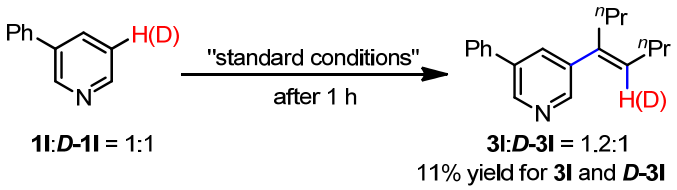
4. Crystal Structure Information of L_{10}



CCDC Deposition Number 2018614
Data Block Name: data_r20200517c; Unit Cell Parameters: a 10.4742(3) b 10.7125(3) c 15.1154(5) P21/c

5. Mechanistic Experiments

5.1 KIE Determination by Competitive Reaction.

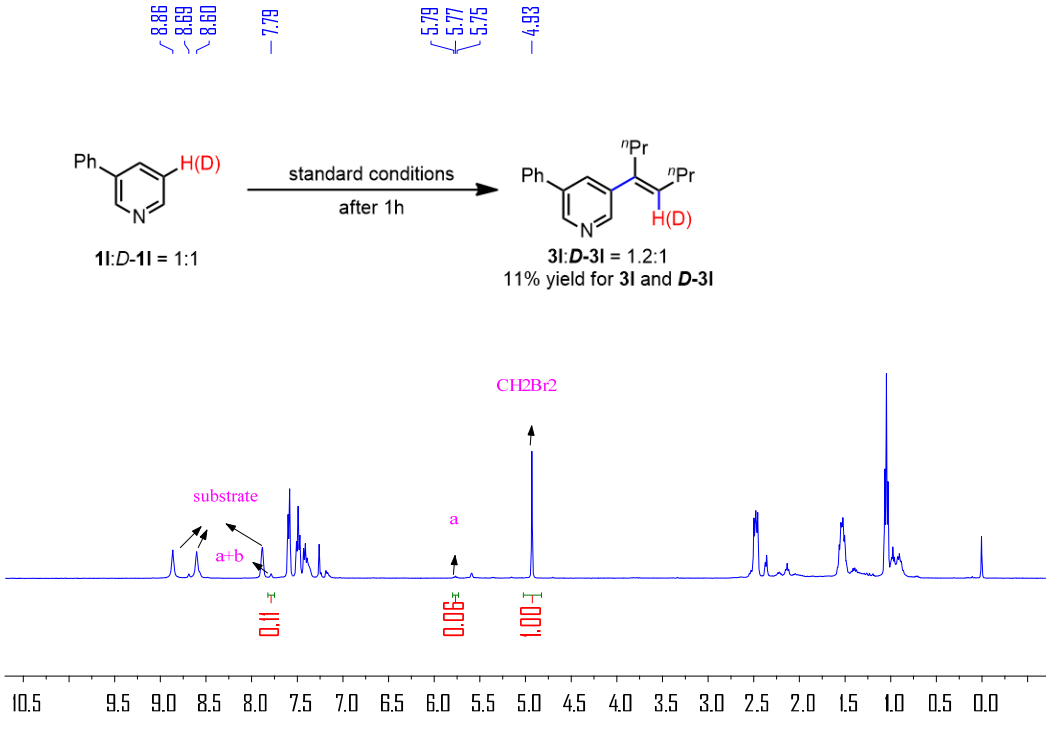


1l:***D*-1l** = 1:1

3l:***D*-3l** = 1.2:1
11% yield for **3l** and ***D*-3l**

$$KIE = k_H/k_D = 1.2$$

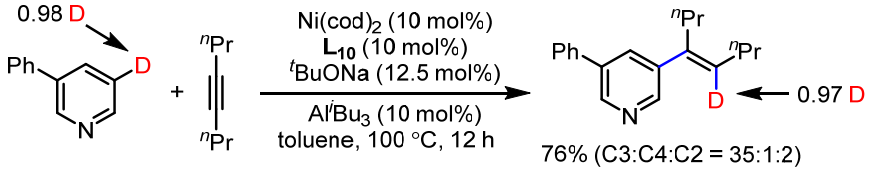
To a 15 mL oven dried tube were added ligand $\mathbf{L_{10}}$ (7.3 mg, 10 mol%), $Ni(cod)_2$ (5.5 mg, 10 mol%), ^{t}BuONa (2.3 mg, 12.5 mol%) and dry degassed toluene (0.5 mL) under N_2 atmosphere. The mixture solution was stirred at 80 °C for 30 mins and then cooled down to room temperature. To a solution of 3-phenylpyridine (15.5 mg, 0.1 mmol, 1equiv.) and deuterated 3-phenylpyridine (15.6 mg, 0.1 mmol, 1equiv.) in dry toluene (0.5 mL) were added Al^tBu_3 (1.1 M/toluene, 18.1 μL, 10 mol%) and alkyne (1.2 mmol, 3 equiv.). Then the tube was sealed and stirred at 100 °C for 1 h. After that, the mixture solution was cooled to r.t., quenched with 2 mL of 5% EDTA disodium salt solution, filtered through a short plug of silica gel (EtOAc as the eluent) and concentrated *in vacuo*. The residue was dissolved in 2.0 mL $CDCl_3$, and CH_2Br_2 (14 μL, 0.2 mmol) was added as the internal standard for ^{1}H NMR detection. KIE was obtained by calculating the NMR yields of mixed products. Low KIE (1.20) suggested that C–H cleavage was not involved in the rate-determining step.



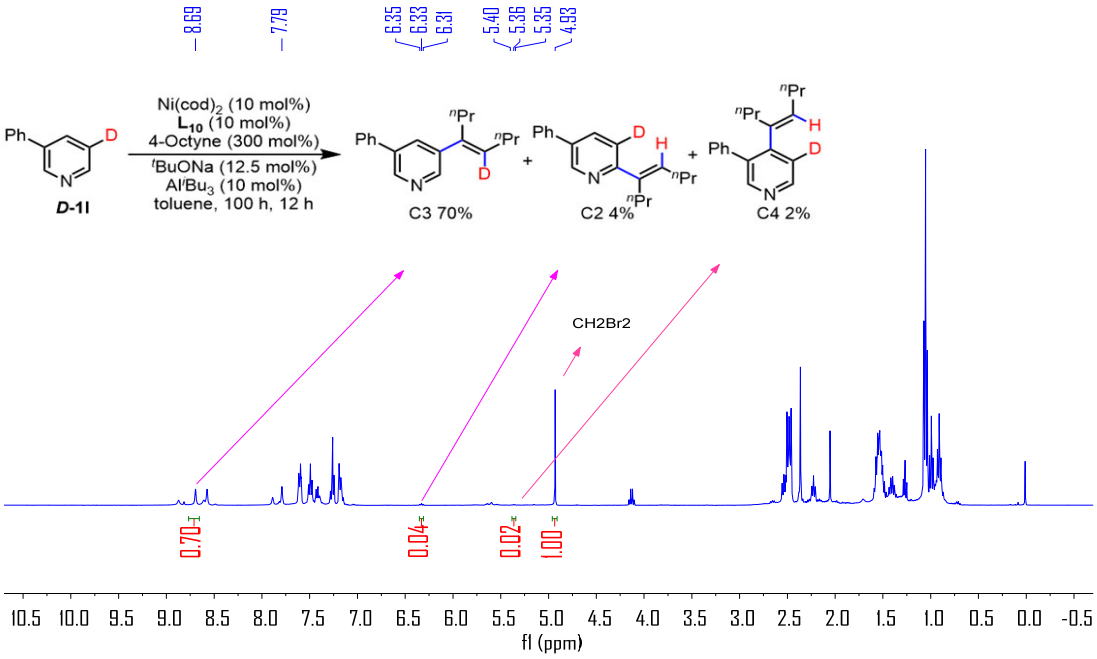
1l:***D*-1l** = 1:1

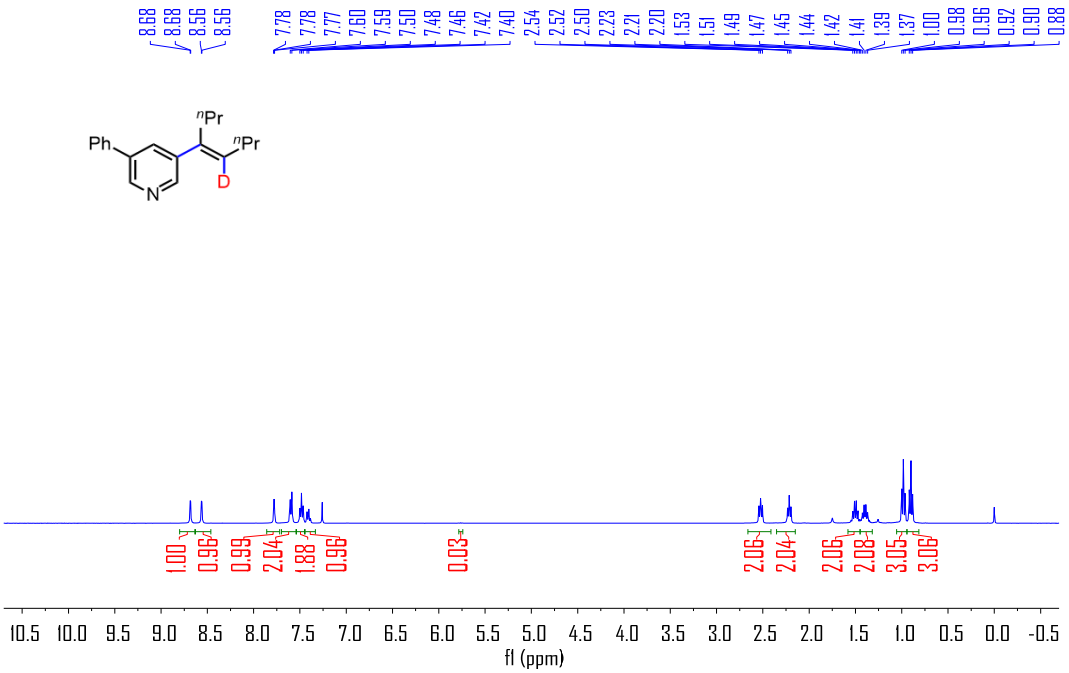
3l:***D*-3l** = 1.2:1
11% yield for **3l** and ***D*-3l**

5.2 Deuterium-Labeling Experiment

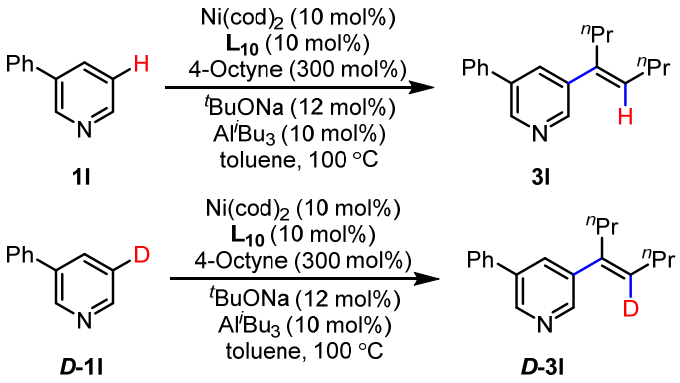


The experiment was carried out according to the typical procedure. And the ^{1}H NMR spectrum showed that complete deuterium-transfer occurred from the C3 position of pyridine to the olefinic position of the product.

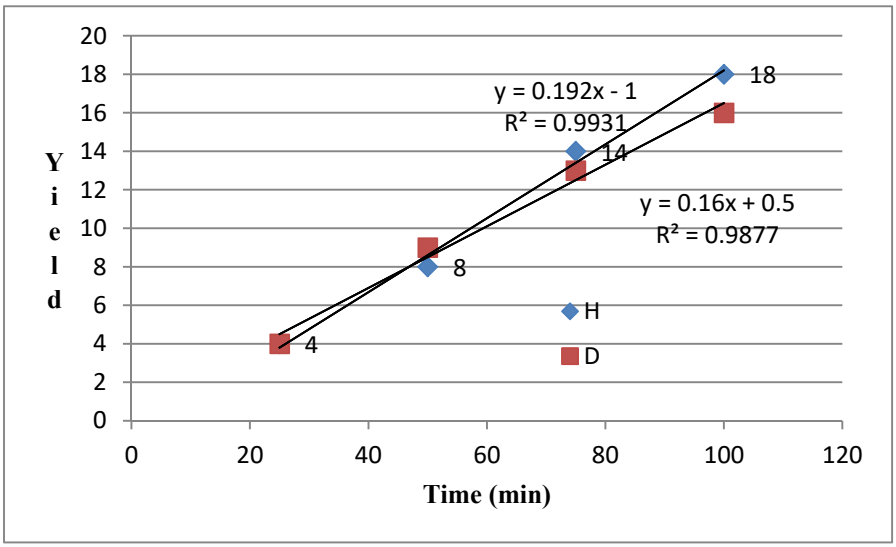




5.3 KIE Determined by Parallel Reactions



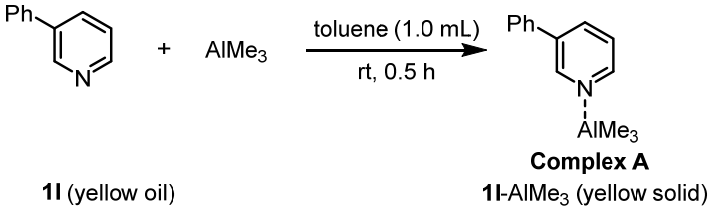
KIE = k_H/k_D = 0.19/0.16 = 1.2



Parallel reactions were set up following the typical procedure. Aliquots were taken at 25 minute intervals for the 100 minutes. Product yield was determined by ^{1}H MNR using CH_2Br_2 as an internal standard. Low KIE (1.2) suggested that C–H cleavage was not involved in the rate-determining step.

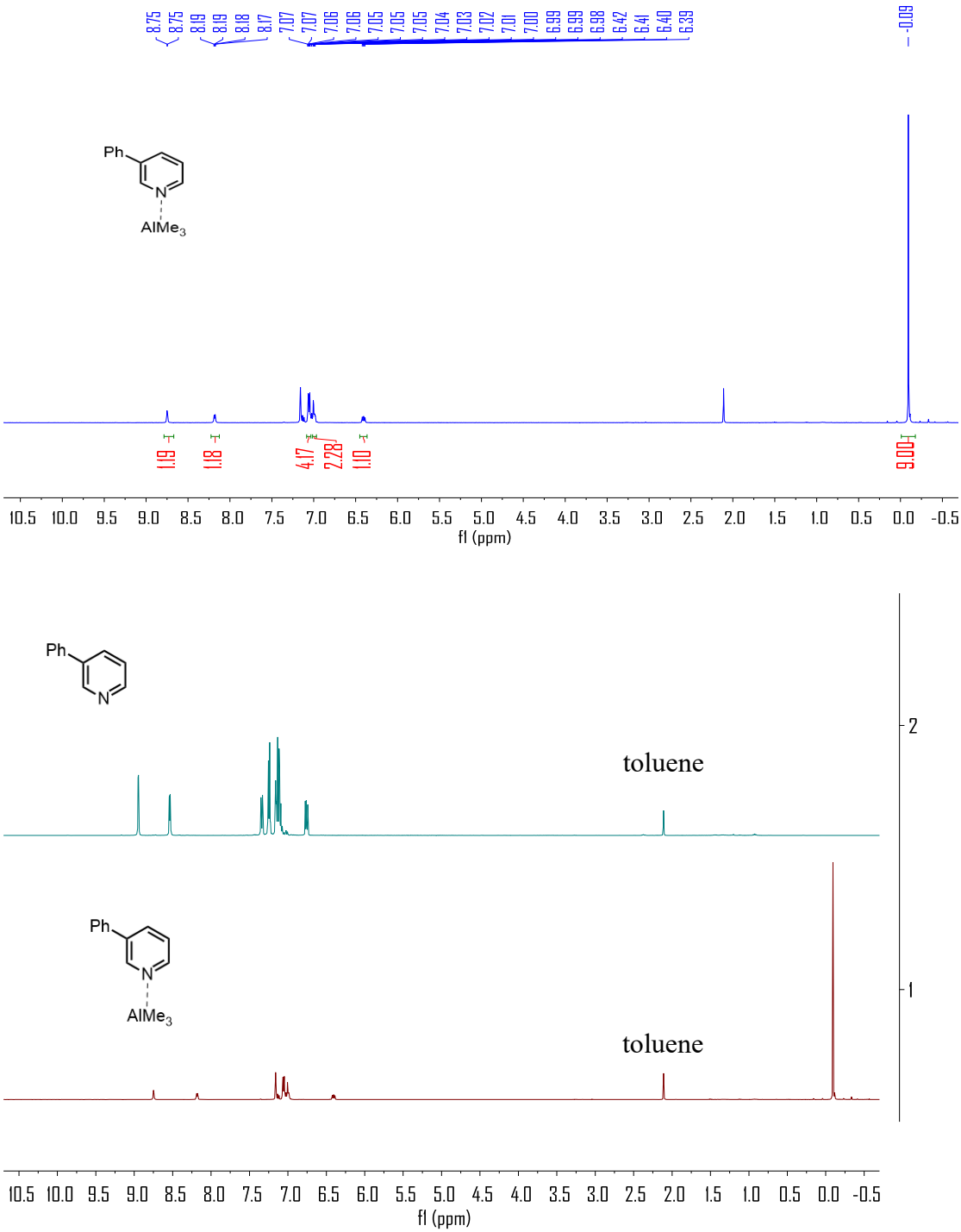
5.4 NMR Tracing Experiments

1) Synthesis of pyridine-Al **Complex A** (**1l**-$AlMe_3$)

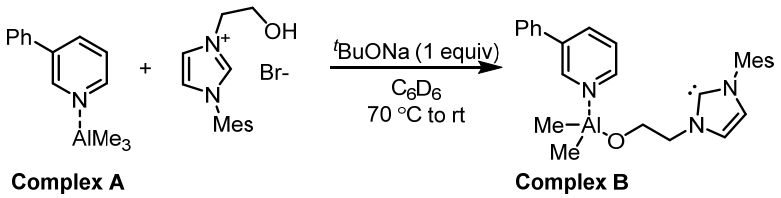


To a 15 mL oven dried Schlenk tube were added **1l** (310.4 mg, 2.0 mmol), toluene (1.0 mL) and $AlMe_3$ (1.0 mL, 2.0 M in toluene, 2.0 mmol) at room temperature under N_2 atmosphere. After stirring for 0.5 h, the solvent was removed *in vacuo* to afford a yellow solid (moisture-sensitive). **^{1}H NMR** (400 MHz, C_6D_6) δ 8.75 (d, J = 2.2 Hz,

1H), 8.18 (dd, *J* = 5.4, 1.4 Hz, 1H), 7.09 – 7.03 (m, 4H), 7.01– 6.97 (m, 2H), 6.41 (dd, *J* = 8.0, 5.4 Hz, 1H), -0.09 (s, 9H).

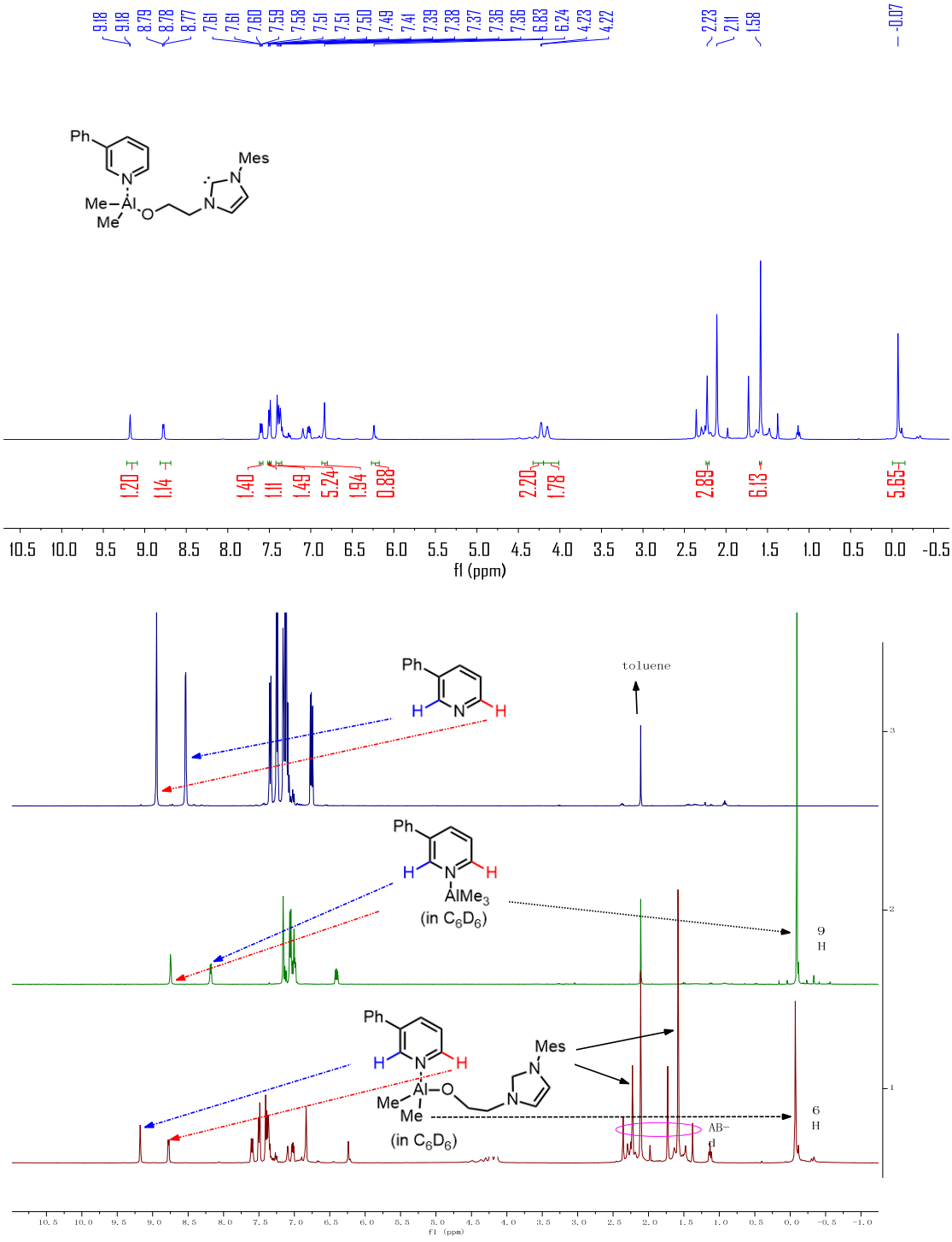


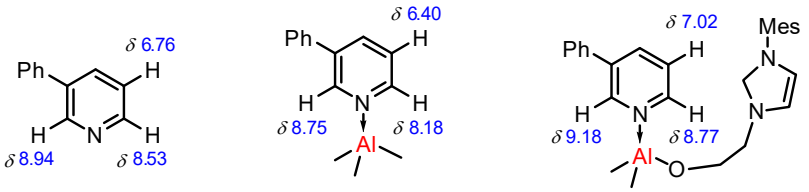
2) Synthesis of pyridine-Al-NHC **Complex B**



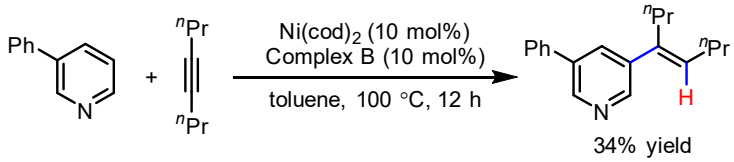
Complex A **Complex B**

To a 15 mL oven dried Schlenk tube were added **Complex A** (0.1 mmol), **L_1** (0.1 mmol), ^{t}BuONa (0.1 mmol) and C_6D_6 (1.0 mL) at room temperature under N_2 atmosphere. The solution was cooled to room temperature after stirring 0.5 h at 70 °C. The resulting solution was transferred into a NMR tube and sealed for **^{1}H NMR** detection. **^{1}H NMR** (400 MHz, C_6D_6) δ 9.18 (d, J = 2.2 Hz, 1H), 8.77 (d, J = 4.4 Hz, 1H), 7.62 –7.57 (m, 1H), 7.52 – 7.50 (m, 1H), 7.49 (s, 1H), 7.42 – 7.35 (m, 5H), 6.83 (s, 2H), 6.24 (s, 1H), 4.32 – 4.20 (m, 2H), 4.19 – 4.02 (m, 2H), 2.23 (s, 3H), 1.58 (s, 6H), -0.07 (s, 6H).



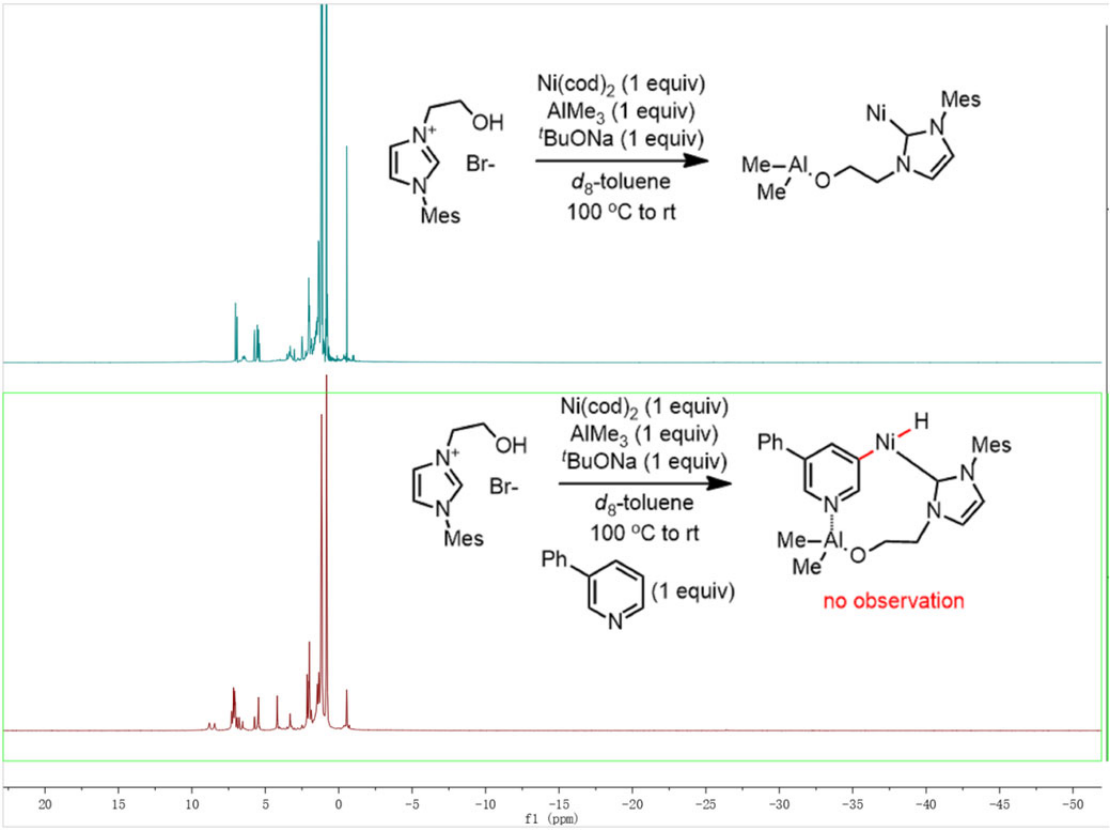


3) Catalytic reactivity of **Complex B**



To a 15 mL oven dried Schlenk with **Complex B** (0.01 mmol) in dry degassed toluene (0.5 mL) under N_2 atmosphere were added $Ni(cod)_2$ (5.5 mg, 0.02 mmol) and 3-phenylpyridine (29.5 mg, 0.19 mmol). The tube was then sealed with a Teflon-lined screw cap, removed from the glove box, and stirred at 100 °C for 12 h. After cooled to room temperature, the mixture was concentrated under reduce pressure and the crude product was examined by **^{1}H NMR** using CH_2Br_2 as the internal standard.

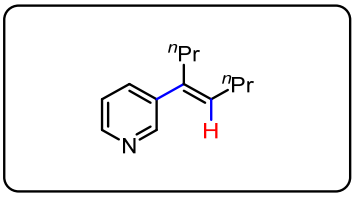
4) Attempted detection of Ni–H intermediates via ^{1}H NMR



6. Typical Procedure for Ni-Catalyzed C3-Alkenylation

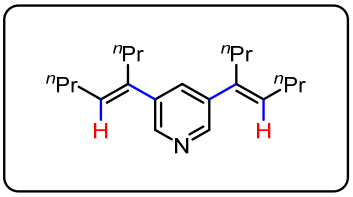
To a 15 mL oven dried tube were added ligand **L_{10}** (14.5 mg, 10 mol%), $Ni(cod)_2$ (11.0 mg, 10 mol%), and ^{t}BuONa (4.6 mg, 12.5 mol%) and dry degassed toluene (1.0

mL) under N_2 atmosphere. The mixture solution was stirred at 80 °C in a dry block heater for 30 mins and then cooled down to room temperature. The pyridine derivative **1** (0.4 mmol, 1 equiv.), Al^{i}Bu$_3$ (1.1 M/toluene, 36.3 μL, 10 mol%) and alkyne (1.2 mmol, 3 equiv.) were added, and the tube was sealed and stirred at 100 °C in a dry block heater for 12 h. After that, the mixture was cooled to r.t., quenched with 2 mL of 5% EDTA disodium salt solution, filtered through a short plug of silica gel (EtOAc as the eluent) and concentrated *in vacuo* to afford a crude product. Further purification by flash column chromatography on silica gel (eluting with EtOAc/hexanes) gave the pure product.



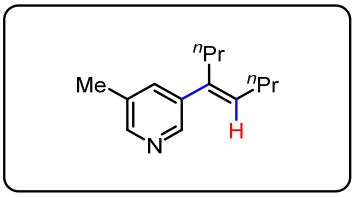
***(E)*-3-(Oct-4-en-4-yl)pyridine (3a, C3-*mono*)**[3]

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.3) afforded **3a (C3-*mono*)** as yellow oil (40.8 mg, 0.216 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 8.44 (d, J = 4.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 7.8, 4.8 Hz, 1H), 5.68 (t, J = 7.3 Hz, 1H), 2.55 – 2.39 (m, 2H), 2.18 (q, J = 7.3 Hz, 2H), 1.55 – 1.41 (m, 2H), 1.40 – 1.27 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.0, 147.7, 138.9, 137.2, 133.6, 131.2, 123.1, 31.5, 30.7, 23.0, 21.7, 14.0, 14.0.



3,5-Di((*E*)-oct-4-en-4-yl)pyridine (3a, C3-*di*)

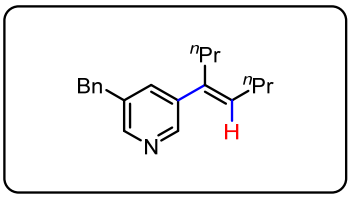
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.4) afforded **3a (C3-*di*)** as yellow oil (23.9 mg, 0.08 mmol, 20% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, J = 2.0 Hz, 2H), 7.51 (t, J = 2.2 Hz, 1H), 5.69 (t, J = 7.4 Hz, 2H), 2.53 – 2.42 (m, 4H), 2.19 (q, J = 7.4 Hz, 4H), 1.55 – 1.43 (m, 4H), 1.41 – 1.29 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H), 0.88 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.0, 138.2, 137.3, 131.2, 131.0, 31.6, 30.8, 23.1, 21.8, 14.1, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{21}H_{34}N$ $(M+H)^+$ 300.2686, found 300.2682.



(*E*)-3-Methyl-5-(oct-4-en-4-yl)pyridine (3b)[4]

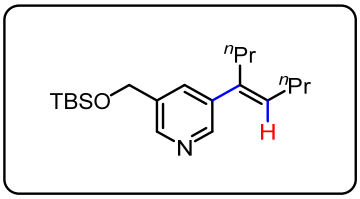
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.3) afforded **3b** as yellow oil (59.6 mg, 0.244 mmol, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, J = 1.6 Hz, 1H), 8.27 (s, 1H), 7.40 (s, 1H), 5.65 (t, J = 7.4 Hz,

1H), 2.50 – 2.40 (m, 2H), 2.31 (s, 3H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.46 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.33 (dd, *J* = 15.2, 7.6 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 145.2, 138.5, 137.2, 134.3, 132.4, 131.0, 31.6, 30.7, 23.0, 21.8, 18.5, 14.0, 13.9.



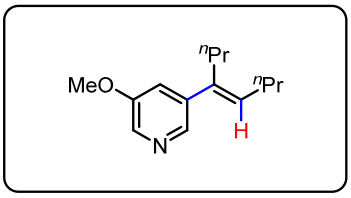
(*E*)-3-Benzyl-5-(oct-4-en-4-yl)pyridine (3c)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.3) afforded **3c** as yellow oil (64.8 mg, 0.232 mmol, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.2 Hz, 1H), 8.24 (d, *J* = 2.2 Hz, 1H), 7.31 (t, *J* = 2.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.15 – 7.06 (m, 3H), 5.57 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 2H), 2.38 – 2.29 (m, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.36 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.30 – 1.17 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 145.9, 140.0, 138.5, 137.0, 135.6, 133.9, 131.0, 128.8, 128.7, 126.4, 39.1, 31.4, 30.7, 23.0, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{20}H_{26}N$ $(M+H)^+$ 280.2060, found 280.2058.



(*E*)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-5-(oct-4-en-4-yl)pyridine (3d)

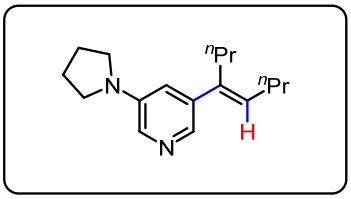
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3d** as yellow oil (71.9 mg, 0.216 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.0 Hz, 1H), 8.38 (d, *J* = 1.6 Hz, 1H), 7.58 (t, *J* = 2.0 Hz, 1H), 5.69 (t, *J* = 7.4 Hz, 1H), 4.75 (s, 2H), 2.51 – 2.43 (m, 2H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.40 – 1.28 (m, 2H), 0.96 (d, *J* = 7.3 Hz, 3H), 0.94 – 0.92 (m, 9H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.10 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 145.9, 138.4, 137.1, 136.0, 131.5, 131.1, 62.9, 31.6, 30.7, 26.0, 23.0, 21.8, 18.4, 14.0, 14.0, -5.2. **HRMS** (ESI) m/z: calcd. for $C_{20}H_{36}NOSi$ $(M+H)^+$ 334.2561, found 334.2557.



(*E*)-3-Methoxy-5-(oct-4-en-4-yl)pyridine (3e)

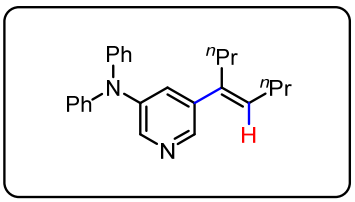
Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **3e** as yellow oil (54.3 mg, 0.248 mmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 8.16 (br s, 1H), 7.12 (s, 1H), 5.70 (t, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.35 (dt, *J*

= 14.6, 7.2 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 140.7, 139.7, 137.0, 135.0, 131.4, 118.7, 55.7, 31.7, 30.7, 23.0, 21.8, 14.1, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{14}H_{22}NO$ $(M+H)^+$ 220.1696, found 220.1694.



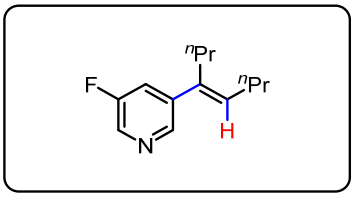
(*E*)-3-(Oct-4-en-4-yl)-5-(pyrrolidin-1-yl)pyridine (3f)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3f** as yellow oil (48.5 mg, 0.188 mmol, 47% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (br s, 1H), 7.86 (br s, 1H), 6.74 (s, 1H), 5.66 (t, J = 7.2 Hz, 1H), 3.32 (d, J = 6.0 Hz, 4H), 2.45 (t, J = 7.4 Hz, 2H), 2.17 (q, J = 7.2 Hz, 2H), 2.07 – 1.78 (m, 4H), 1.54 – 1.42 (m, 2H), 1.41 – 1.30 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 139.1, 138.0, 135.6, 132.5, 130.2, 115.8, 47.4, 31.8, 30.7, 25.5, 23.1, 21.8, 14.0, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{27}N_2$ $(M+H)^+$ 259.2169, found 259.2166.



(*E*)-5-(Oct-4-en-4-yl)-*N*,*N*-diphenylpyridin-3-amine (3g)

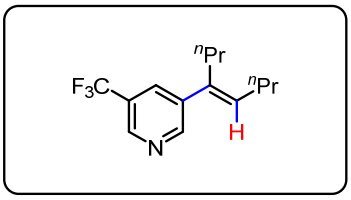
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3g** as yellow oil (88.3 mg, 0.248 mmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 1.6 Hz, 1H), 8.11 (d, J = 2.4 Hz, 1H), 7.32 – 7.15 (m, 5H), 7.07 – 6.94 (m, 6H), 5.57 (t, J = 7.2 Hz, 1H), 2.33 – 2.24 (m, 2H), 2.06 (q, J = 7.4 Hz, 2H), 1.36 (dt, J = 14.8, 7.4 Hz, 2H), 1.23 (dt, J = 14.8, 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 143.9, 143.3, 141.6, 139.1, 136.8, 131.1, 129.6, 127.7, 124.3, 123.6, 31.4, 30.7, 23.0, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{25}H_{29}N_2$ $(M+H)^+$ 357.2325, found 357.2322.



(*E*)-3-Fluoro-5-(oct-4-en-4-yl)pyridine (3h)

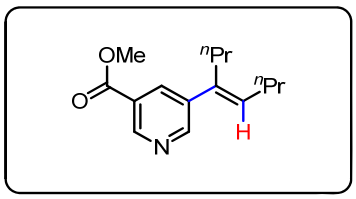
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **3h** as yellow oil (73.7 mg, 0.356 mmol, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (m, 1H), 8.30 (d, J = 4.8 Hz, 1H), 7.13 (t, J = 5.6 Hz, 1H), 5.68 (t, J = 7.2 Hz, 1H), 2.45 (t, J = 7.6 Hz, 2H), 2.19 (q, J = 7.2 Hz, 2H), 1.55 – 1.39 (m, 2H), 1.36 – 1.22 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J = 253.9 Hz), 145.7 (d, J = 4.6 Hz), 139.2 (d, J = 11.8

Hz), 138.4 (d, J = 26.1 Hz), 134.9, 134.0, 124.4, 31.8 (d, J = 2.6 Hz), 30.4, 22.8, 21.6, 13.9, 13.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.41. **HRMS** (ESI) m/z: calcd. for $C_{13}H_{19}FN$ $(M+H)^+$ 208.1496, found 208.1492.



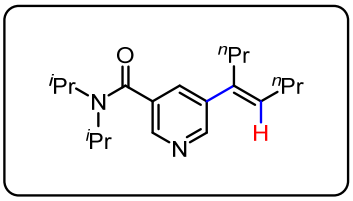
(*E*)-3-(Oct-4-en-4-yl)-5-(trifluoromethyl)pyridine (3i)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **3i** as yellow oil (82.3 mg, 0.320 mmol, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (br s, 1H), 8.71 (br s, 1H), 7.85 – 7.73 (m, 1H), 5.75 (t, J = 6.8 Hz, 1H), 2.57 – 2.40 (m, 2H), 2.21 (q, J = 6.6 Hz, 2H), 1.48 (dt, J = 14.0, 7.2 Hz, 2H), 1.41 – 1.27 (m, 2H), 1.04 – 0.93 (m, 3H), 0.92 – 0.81 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 144.4 (q, J = 3.8 Hz), 139.0, 136.0, 133.2, 130.4 (q, J = 3.4 Hz), 126.3 (q, J = 33.9 Hz), 123.7 (q, J = 270.8 Hz), 31.4, 30.8, 22.9, 21.7, 14.0, 13.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -62.36. **HRMS** (ESI) m/z: calcd. for $C_{14}H_{19}F_3N$ $(M+H)^+$ 258.1464, found 258.1459.



(*E*)-Methyl 5-(oct-4-en-4-yl)nicotinate (3j)

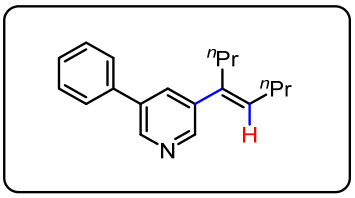
Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **3j** as yellow oil (60.3 mg, 0.244 mmol, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (d, J = 1.8 Hz, 1H), 8.72 (d, J = 2.2 Hz, 1H), 8.20 (t, J = 2.0 Hz, 1H), 5.75 (t, J = 7.4 Hz, 1H), 3.95 (s, 3H), 2.58 – 2.46 (m, 2H), 2.20 (q, J = 7.4 Hz, 2H), 1.48 (dt, J = 14.8, 7.4 Hz, 2H), 1.34 (dt, J = 14.8, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 151.6, 148.7, 138.7, 136.3, 134.5, 132.5, 125.6, 52.5, 31.4, 30.8, 22.9, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{15}H_{22}NO_2$ $(M+H)^+$ 248.1645, found 248.1641.



(*E*)-*N*,*N*-Diisopropyl-5-(oct-4-en-4-yl)nicotinamide (3k)[5]

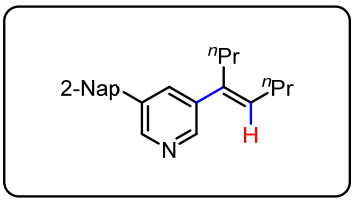
Purification via column chromatography on silica gel (*n*-hexane/EA = 2/1, v/v, R_f = 0.3) afforded **3k** as yellow oil (70.8 mg, 0.224 mmol, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (br s, 1H), 8.40 (br s, 1H), 7.61 – 7.51 (m, 1H), 5.71 (t, J = 7.4 Hz, 1H), 4.04 – 3.36 (m, 2H), 2.59 – 2.38 (m, 2H), 2.18 (q, J = 7.4 Hz, 2H), 1.75 – 1.40 (m, 7H), 1.40 – 1.28 (m, 4H), 1.28 – 1.06 (m, 5H), 0.95 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 148.1, 144.4, 138.8, 136.6, 133.9, 132.1,

131.2, 31.4, 30.8, 22.9, 21.7, 20.9, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{20}H_{33}N_2O$ $(M+H)^+$ 317.2587, found 317.2582.



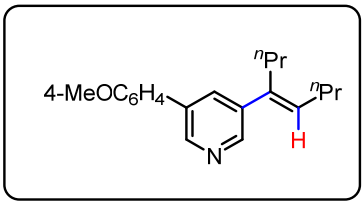
(*E*)-3-(Oct-4-en-4-yl)-5-phenylpyridine (3l)[4]

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3l** as yellow oil (75.3 mg, 0.284 mmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (br s, 1H), 8.57 (br s, 1H), 7.78 (d, J = 1.4 Hz, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.44 – 7.36 (m, 1H), 5.76 (t, J = 7.2 Hz, 1H), 2.53 (t, J = 7.6 Hz, 2H), 2.22 (q, J = 7.4 Hz, 2H), 1.56 – 1.45 (m, 2H), 1.45 – 1.34 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 146.3, 138.8, 138.3, 137.2, 136.1, 132.1, 131.5, 129.1, 128.1, 127.3, 31.6, 30.8, 23.0, 21.8, 14.0, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{24}N$ $(M+H)^+$ 266.1903, found 266.1899.



(*E*)-3-(Naphthalen-2-yl)-5-(oct-4-en-4-yl)pyridine (3m)

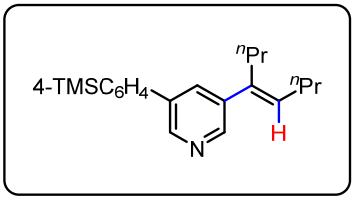
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3m** as yellow oil (107.1 mg, 0.340 mmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (d, J = 2.0 Hz, 1H), 8.63 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 1.8 Hz, 1H), 8.01 – 7.89 (m, 4H), 7.75 (dd, J = 8.6, 2.0 Hz, 1H), 7.60 – 7.50 (m, 2H), 5.83 (t, J = 7.2 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.27 (q, J = 7.2 Hz, 2H), 1.56 (dt, J = 14.8, 7.4 Hz, 2H), 1.45 (dt, J = 14.8, 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.4Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 146.6, 138.9, 137.2, 136.1, 135.5, 133.7, 132.9, 132.3, 131.6, 128.9, 128.3, 127.8, 126.7, 126.5, 126.3, 125.3, 31.6, 30.8, 23.0, 21.8, 14.1, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{23}H_{26}N$ $(M+H)^+$ 316.2060, found 316.2058.



(*E*)-3-(4-Methoxyphenyl)-5-(oct-4-en-4-yl)pyridine (3n)

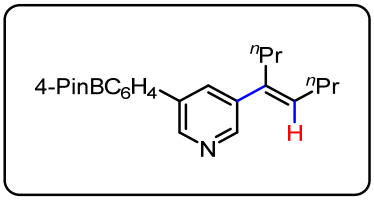
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3n** as yellow oil (97.9 mg, 0.332 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, J = 1.6 Hz, 1H), 8.51 (d, J = 2.1 Hz, 1H), 7.74 (t, J = 2.2 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 5.75 (t, J = 7.2 Hz, 1H), 3.86 (s, 3H), 2.59 – 2.44 (m, 2H), 2.21 (q, J = 7.2 Hz, 2H), 1.50 (dt, J = 14.8, 7.4 Hz, 2H), 1.39 (dt, J = 14.8, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 159.8, 146.2, 146.0, 138.8, 137.2, 135.7, 131.7, 131.4, 130.6, 128.4, 114.6, 55.5, 31.6, 30.8, 23.0, 21.8, 14.1, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{20}H_{26}NO$ $(M+H)^+$ 296.2009, found 296.2005.



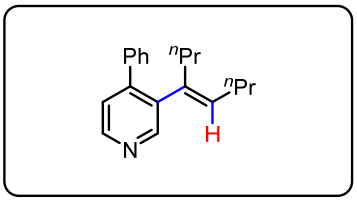
(*E*)-3-(Oct-4-en-4-yl)-5-(4-(trimethylsilyl)phenyl)pyridine (3o)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3o** as yellow oil (120.0 mg, 0.356 mmol, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, J = 2.0 Hz, 1H), 8.57 (d, J = 2.0 Hz, 1H), 7.79 (t, J = 2.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 5.77 (t, J = 7.2 Hz, 1H), 2.58 – 2.50 (m, 2H), 2.22 (q, J = 7.2 Hz, 2H), 1.51 (dt, J = 14.8, 7.4 Hz, 2H), 1.40 (dt, J = 14.8, 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H), 0.32 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 146.3, 140.4, 138.8, 138.6, 137.1, 136.1, 134.1, 132.1, 131.5, 126.7, 31.6, 30.8, 23.0, 21.8, 14.1, 14.0, -1.0. **HRMS** (ESI) m/z: calcd. for $C_{22}H_{32}NSi$ $(M+H)^+$ 338.2299, found 338.2294.



(*E*)-3-(Oct-4-en-4-yl)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (3p)

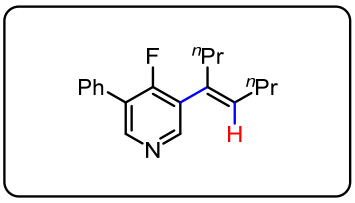
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3p** as light yellow solid (106.4 mg, 0.272 mmol, 68% yield), m.p. 73.0 - 73.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, J = 2.2 Hz, 1H), 8.57 (d, J = 2.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.79 (t, J = 2.2 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 5.76 (t, J = 7.2 Hz, 1H), 2.62 – 2.45 (m, 2H), 2.22 (q, J = 7.2 Hz, 2H), 1.58 – 1.44 (m, 2H), 1.44 – 1.38 (m, 2H), 1.37 (s, 12H), 0.98 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 146.4, 140.9, 138.9, 137.1, 136.0, 135.6, 132.2, 131.6, 126.6, 84.0, 31.6, 30.8, 25.0, 23.0, 21.8, 14.1, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{25}H_{35}BNO_2$ $(M+H)^+$ 392.2755, found 392.2758.



(*E*)-3-(Oct-4-en-4-yl)-4-phenylpyridine (3q)

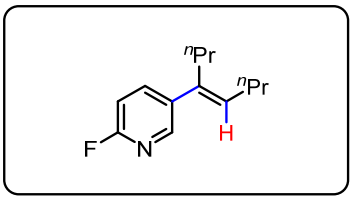
Purification via column chromatography on silica gel (*n*-hexane/EA = 15/1, v/v, R_f = 0.2) afforded **3q** as yellow oil (31.8 mg, 0.120 mmol, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 5.0 Hz, 1H), 8.42 (s, 1H), 7.46 – 7.35 (m, 5H), 7.18 (d, J = 5.0 Hz, 1H), 5.57 (t, J = 7.4 Hz, 1H), 2.12 (q, J = 7.4 Hz, 2H), 1.83 – 1.76 (m, 2H), 1.45 (dt, J =

14.8, 7.4 Hz, 2H), 1.07 (dt, J = 14.8, 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.68 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 148.2, 146.9, 139.6, 138.6, 138.3, 133.3, 128.6, 128.4, 128.1, 124.1, 32.3, 30.5, 22.9, 21.5, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{24}N$ $(M+H)^+$ 266.1903, found 266.1901.



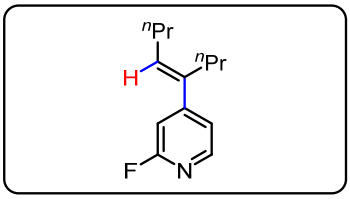
(*E*)-4-Fluoro-3-(oct-4-en-4-yl)-5-phenylpyridine (3r)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3r** as yellow oil (101.9 mg, 0.360 mmol, 90% yield). **^{1}H NMR** (400 MHz) δ 8.53 (d, J = 9.4 Hz, 1H), 8.39 (d, J = 9.2 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 5.61 (t, J = 7.2 Hz, 1H), 2.47 (t, J = 7.6 Hz, 2H), 2.27 – 2.16 (m, 2H), 1.55 – 1.45 (m, 2H), 1.38 – 1.31 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, J = 262.3 Hz), 151.0 (d, J = 4.9 Hz), 150.3 (d, J = 3.6 Hz), 134.1, 132.9, 132.5, 129.3, 129.3, 128.8, 128.5, 125.2 (d, J = 11.8 Hz), 32.4 (d, J = 2.0 Hz), 30.4, 22.9, 21.6, 13.9, 13.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -112.40. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{23}NF$ $(M+H)^+$ 284.1809, found 284.1804.



(*E*)-2-Fluoro-5-(oct-4-en-4-yl)pyridine (3t)

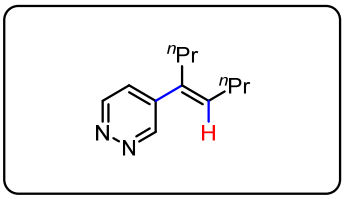
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3t** as yellow oil (24.9 mg, 0.120 mmol, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 5.4 Hz, 1H), 7.16 – 7.03 (m, 1H), 6.83 (s, 1H), 5.91 (t, J = 7.4 Hz, 1H), 2.43 (t, J = 7.8 Hz, 2H), 2.19 (q, J = 7.4 Hz, 2H), 1.54 – 1.42 (m, 2H), 1.40 – 1.30 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5 (d, J = 236.1 Hz), 156.6 (d, J = 7.7 Hz), 147.2 (d, J = 15.3 Hz), 137.3 (d, J = 2.1 Hz), 133.6, 118.9 (d, J = 3.4 Hz), 106.3 (d, J = 37.0 Hz), 31.0, 30.8, 22.8, 21.8, 14.0, 13.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -69.37. **HRMS** (ESI) m/z: calcd. for $C_{13}H_{19}FN$ $(M+H)^+$ 208.1496, found 208.1492.



(*E*)-2-Fluoro-4-(oct-4-en-4-yl)pyridine (3t′)

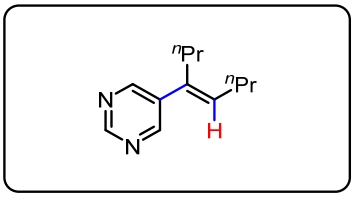
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3t′** as yellow oil (48.8 mg, 0.236 mmol, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 4.6 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.14 – 7.05 (m, 1H),

5.55 (t, J = 7.4 Hz, 1H), 2.43 (t, J = 7.6 Hz, 2H), 2.22 – 2.11 (m, 2H), 1.51 – 1.38 (m, 2H), 1.33 – 1.20 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7 (d, J = 238.2 Hz), 145.4 (d, J = 15.1 Hz), 140.6 (d, J = 5.6 Hz), 134.8 (d, J = 4.4 Hz), 133.7, 126.7 (d, J = 29.3 Hz), 121.3 (d, J = 4.3 Hz), 31.9 (d, J = 3.2 Hz), 30.4, 22.8, 21.6, 13.9, 13.8. **^{19}F NMR** (376 Hz, $CDCl_3$) -68.78. **HRMS** (ESI) m/z: calcd. for $C_{13}H_{19}FN$ $(M+H)^+$ 208.1496, found 208.1494.



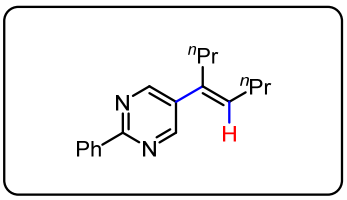
(*E*)-4-(Oct-4-en-4-yl)pyridazine (3u)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3u** as yellow oil (63.0 mg, 0.332 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.06 (d, J = 5.4 Hz, 1H), 7.42 – 7.32 (m, 1H), 6.04 (t, J = 7.2 Hz, 1H), 2.57 – 2.42 (m, 2H), 2.25 (q, J = 7.2 Hz, 2H), 1.59 –1.45 (m, 2H), 1.44 – 1.32 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 149.7, 140.5, 135.3, 134.9, 122.4, 30.9, 30.3, 22.6, 21.7, 13.9, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{12}H_{19}N_2$ $(M+H)^+$ 191.1543, found 191.1542.



(*E*)-5-(Oct-4-en-4-yl)pyrimidine (3v)

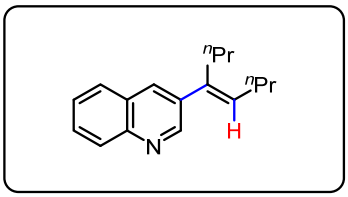
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3v** as yellow oil (38.0 mg, 0.200 mmol, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (br s, 1H), 8.66 (br s, 2H), 5.73 (t, J = 7.2 Hz, 1H), 2.45 (t, J = 7.6 Hz, 2H), 2.28 – 2.03 (m, 2H), 1.46 (dt, J = 14.4, 7.2 Hz, 2H), 1.35 (dq, J = 15.0, 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 154.4, 136.3, 134.1, 133.1, 31.1, 30.7, 22.8, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{12}H_{19}N_2$ $(M+H)^+$ 191.1543, found 191.1541.



(*E*)-5-(Oct-4-en-4-yl)-2-phenylpyrimidine (3w)

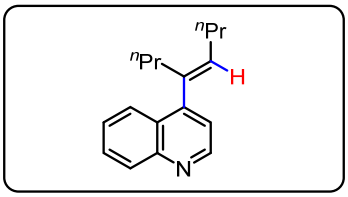
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3w** as yellow oil (69.2 mg, 0.260 mmol, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 2H), 8.50 – 8.38 (m, 2H), 7.55 – 7.42 (m, 3H), 5.82 (t, J = 7.2 Hz, 1H), 2.51 (t, J = 7.6 Hz, 2H), 2.23 (q, J = 7.34 Hz, 2H), 1.52 (dt, J = 14.6, 7.4 Hz, 2H), 1.41 (dt, J = 14.8, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8, 154.7, 137.6, 134.3, 133.7, 132.3, 130.5, 128.7, 128.0, 31.1,

30.8, 22.9, 21.8, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{18}H_{23}N_2$ $(M+H)^+$ 267.1856, found 267.1851.



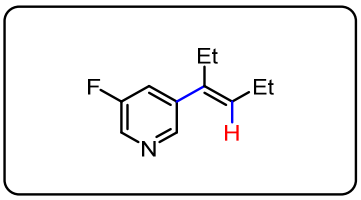
(*E*)-3-(Oct-4-en-4-yl)quinoline (3x)[4]

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3u** as yellow oil (34.2 mg, 0.144 mmol, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.00 (s, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 5.85 (t, J = 7.2 Hz, 1H), 2.59 (t, J = 7.5 Hz, 2H), 2.65 – 2.54 (m, 2H), 1.52 (dt, J = 14.8, 7.4 H, 2H), 1.41 (dt, J = 14.8, 7.4 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.1, 147.1, 137.3, 136.1, 132.0, 131.8, 129.2, 128.8, 128.1, 127.8, 126.7, 31.6, 30.9, 23.1, 21.8, 14.0, 14.0.



(*E*)-4-(Oct-4-en-4-yl)quinoline (3x′)[4]

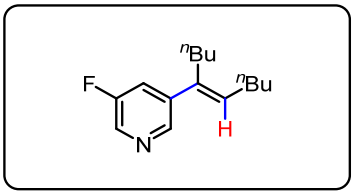
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **3x′** as yellow oil (34.0 mg, 0.142 mmol, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, J = 4.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.08 – 7.97 (m, 1H), 7.72 – 7.65 (m, 1H), 7.54 – 7.47 (m, 1H), 7.16 (d, J = 4.4 Hz, 1H), 5.52 (t, J = 7.4 Hz, 1H), 2.52 (q, J = 8.8, 2H), 2.32 – 2.24 (m, 2H), 1.58 – 1.48 (m, 2H), 1.35 – 1.26 (m, 2H), 1.01 (q, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 150.0, 148.7 137.3, 132.9, 129.8, 129.1, 127.4, 126.2, 126.0, 120.3, 34.2, 30.4, 23.0, 21.8, 14.1, 14.1.



(*E*)-3-Fluoro-5-(hex-3-en-3-yl)pyridine (4a)

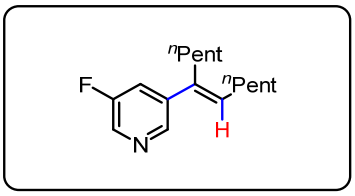
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4a** as yellow oil (65.9 mg, 0.368 mmol, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.2 Hz, 1H), 8.31 (d, J = 5.0 Hz, 1H), 7.18 – 7.10 (m, 1H), 5.65 (t, J = 7.2 Hz, 1H), 2.47 (q, J = 7.4 Hz, 2H), 2.22 (quint, J = 7.4 Hz, 2H), 1.06 (t, J = 7.6 Hz, 3H), 0.92 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1 (d, J = 254.0 Hz), 145.7 (d, J = 5.0 Hz), 138.8 (d, J = 26.1 Hz), 138.4 (d, J = 27.0 Hz), 135.7 (d, J = 2.0 Hz), 135.0, 124.4, 23.0 (d, J = 2.0 Hz), 21.6, 14.2, 13.3. **^{19}F NMR** (376 Hz,

$CDCl_3$) -130.28. **HRMS** (ESI) m/z: calcd. for $C_{11}H_{15}FN$ $(M+H)^+$ 180.1183, found 180.1180.



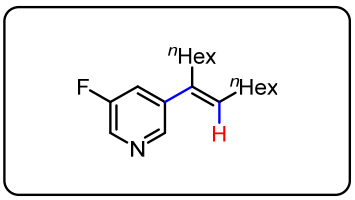
(*E*)-3-(Dec-5-en-5-yl)-5-fluoropyridine (4b)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4b** as yellow oil (78.0 mg, 0.332 mmol, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, J = 2.4 Hz, 1H), 8.29 (dd, J = 4.8, 0.8 Hz, 1H), 7.11 (dd, J = 6.6, 5.0 Hz, 1H), 5.65 (t, J = 7.2 Hz, 1H), 2.54 – 2.38 (m, 2H), 2.20 (q, J = 7.2 Hz, 2H), 1.50 – 1.32 (m, 4H), 1.30 – 1.20 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1 (d, J = 253.9 Hz), 145.6 (d, J = 4.9 Hz), 139.2 (d, J = 11.7 Hz), 138.4 (d, J = 26.1 Hz), 134.8 (d, J = 2.6 Hz), 134.0 (d, J = 0.9 Hz), 124.3, 31.7, 30.6, 29.5 (d, J = 2.6 Hz) 28.1, 22.5, 22.5, 14.1, 13.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.39. **HRMS** (ESI) m/z: calcd. for $C_{15}H_{23}FN$ $(M+H)^+$ 236.1809, found 236.1807.



(*E*)-3-(Dodec-6-en-6-yl)-5-fluoropyridine (4c)

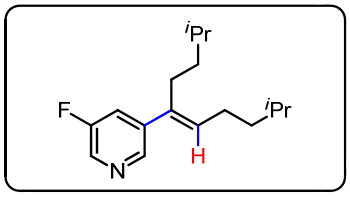
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4c** as yellow oil (86.2 mg, 0.328 mmol, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 2.6 Hz, 1H), 8.23 (d, J = 4.8 Hz, 1H), 7.06 (dd, J = 6.6, 5.0 Hz, 1H), 5.60 (t, J = 7.2 Hz, 1H), 2.50 – 2.32 (m, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.45 – 1.32 (m, 2H), 1.31 – 1.23 (m, 4H), 1.22 – 1.07 (m, 6H), 0.88 – 0.80 (m, 3H), 0.80 – 0.71 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J = 253.9 Hz), 145.6 (d, J = 4.9 Hz), 139.1 (d, J = 11.7 Hz), 138.3 (d, J = 26.1 Hz), 134.8 (d, J = 2.3 Hz), 134.0 (d, J = 1.0 Hz), 124.3 (d, J = 1.4 Hz), 31.6, 29.7 (d, J = 2.5 Hz), 29.2, 28.4, 28.1, 22.6, 22.5, 14.1, 14.0. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.37. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{27}FN$ $(M+H)^+$ 264.2122, found 264.2125.



(*E*)-3-Fluoro-5-(tetradec-7-en-7-yl)pyridine (4d)

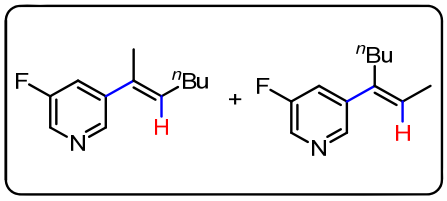
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4d** as yellow oil (105.9 mg, 0.364 mmol, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.4 Hz, 1H), 8.30 (d, J = 4.8 Hz, 1H), 7.12 (dd, J = 6.6, 5.0 Hz, 1H), 5.66 (t, J = 7.2 Hz, 1H), 2.54 – 2.39 (m, 2H), 2.20 (q, J = 7.2 Hz, 2H),

1.52 – 1.40 (m, 2H), 1.39 – 1.28 (m, 6H), 1.28 – 1.19 (m, 8H), 0.95 – 0.79 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7 (d, J = 250.0 Hz), 145.7 (d, J = 4.9 Hz), 139.1 (d, J = 11.7 Hz), 138.5 (d, J = 26.1 Hz), 134.9 (d, J = 2.2 Hz), 134.1 (d, J = 1.0 Hz), 124.3 (d, J = 1.6 Hz), 31.8, 31.7, 29.8 (d, J = 2.5 Hz), 29.5, 29.1, 28.4, 22.7, 22.7, 14.2, 14.1. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.38. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{31}FN$ $(M+H)^+$ 292.2435, found 292.2431.



(*E*)-3-(2,9-Dimethyldec-5-en-5-yl)-5-fluoropyridine (4e)

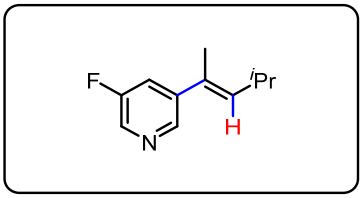
Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4e** as yellow oil (97.9 mg, 0.372 mmol, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, J = 2.2 Hz, 1H), 8.29 (d, J = 4.8 Hz, 1H), 7.16 – 7.04 (m, 1H), 5.64 (t, J = 7.2 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.20 (q, J = 7.6 Hz, 2H), 1.61 (dq, J = 13.4, 6.6 Hz, 1H), 1.49 (dq, J = 13.4, 6.6 Hz, 1H), 1.32 (q, J = 7.2 Hz, 2H), 1.19 – 1.10 (m, 2H), 0.91 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J = 254.1 Hz), 145.7 (d, J = 4.8 Hz), 139.2 (d, J = 11.6 Hz), 138.4 (d, J = 26.1 Hz), 134.7 (d, J = 2.4 Hz), 134.1, 124.3 (d, J = 0.5 Hz), 38.7, 37.7, 28.0, 27.8 , 27.8 (d, J = 2.5 Hz), 26.3, 22.6, 22.5. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.28. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{27}FN$ $(M+H)^+$ 264.2122, found 264.2119.



(*E*)-3-Fluoro-5-(hept-2-en-2-yl)pyridine (4f)

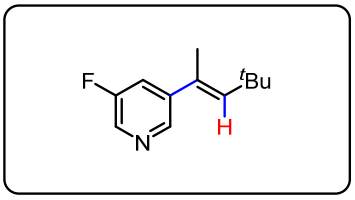
(*E*)-3-Fluoro-5-(hept-2-en-3-yl)pyridine (4f′)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4f + 4f′**as yellow oil (71.8 mg, 0.372 mmol, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, J = 2.4 Hz, 1H), 8.29 (d, J = 4.8 Hz, 1H), 7.20 – 7.06 (m, 1H), 5.85 – 5.71 (m, 1H), 2.46 (t, J = 7.0 Hz, 0.5 H), 2.20 (q, J = 7.2 Hz, 1.5H), 1.99 (s, 2.3H), 1.80 (d, J = 7.0 Hz, 0.7H), 1.48 – 1.31 (m, 3H), 1.30 – 1.18 (m, 1H), 0.92 (t, J = 7.1 Hz, 2.2H), 0.87 – 0.80 (m, 0.8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J = 253.7 Hz), 156.8 (d, J = 254.2 Hz), 145.6 (d, J = 4.8 Hz), 145.6 (d, J = 4.8 Hz), 139.6 (d, J = 10.9 Hz), 139.0 (d, J = 11.9 Hz), 138.4 (d, J = 26.1 Hz), 138.3 (d, J = 26.1 Hz), 135.2 (d, J = 3.1 Hz), 134.9 (d, J = 0.9 Hz), 128.7 (d, J = 0.9 Hz), 128.5 (d, J = 2.3 Hz), 124.1, 123.3, 31.2, 30.3, 29.1 (d, J = 2.4 Hz), 28.3, 22.4, 22.4, 16.0 (d, J = 3.3 Hz), 14.0, 13.9, 13.8. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.48, -130.16. **HRMS** (ESI) m/z: calcd. for $C_{12}H_{17}FN$ $(M+H)^+$ 194.1340, found 194.1340.



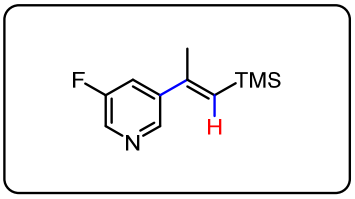
(*E*)-3-Fluoro-5-(4-methylpent-2-en-2-yl)pyridine (4g)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4g** as yellow oil (58.7 mg, 0.328 mmol, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.6 Hz, 1H), 8.30 (d, J = 4.8 Hz, 1H), 7.15 (dd, J = 6.8, 4.8 Hz, 1H), 5.63 (d, J = 12.0, 1H), 2.77 – 2.62 (m, 1H), 2.02 (s, 3H), 1.05 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J = 254.2 Hz), 145.7 (d, J = 4.9 Hz), 142.3 (d, J = 3.0 Hz), 139.7 (d, J = 10.9 Hz), 138.5 (d, J = 26.1 Hz), 126.9 (d, J = 0.8 Hz), 123.5 (d, J = 1.4 Hz), 27.9, 22.6, 16.1 (d, J = 3.5 Hz). **^{19}F NMR** (376 Hz, $CDCl_3$) -129.97. **HRMS** (ESI) m/z: calcd. for $C_{11}H_{15}FN$ $(M+H)^+$ 180.1183, found 180.1181.



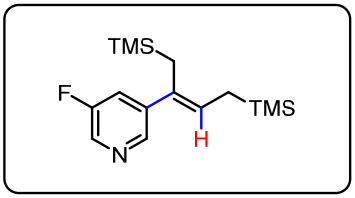
(*E*)-3-(4,4-Dimethylpent-2-en-2-yl)-5-fluoropyridine (4h)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4h** as yellow oil (67.9 mg, 0.352 mmol, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.6 Hz, 1H), 8.32 (d, J = 4.6 Hz, 1H), 7.24 – 7.05 (m, 1H), 5.86 (s, 1H), 2.17 (s, 3H), 0.20 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J = 254.1 Hz), 145.7 (d, J = 5.0 Hz), 144.5 (d, J = 1.5 Hz), 141.7 (d, J = 11.4 Hz), 138.4 (d, J = 25.9 Hz), 128.4, 123.9, 33.3, 30.7, 17.5 (d, J = 3.4 Hz). **^{19}F NMR** (376 Hz, $CDCl_3$) -130.30. **HRMS** (ESI) m/z: calcd. for $C_{12}H_{17}FN$ $(M+H)^+$ 194.1340, found 194.1339.



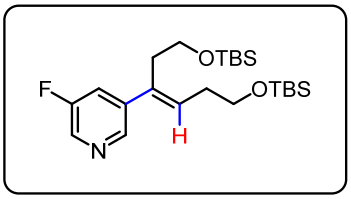
(*E*)-3-Fluoro-5-(1-(trimethylsilyl)prop-1-en-2-yl)pyridine (4i)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4i** as yellow oil (65.2 mg, 0.312 mmol, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.6 Hz, 1H), 8.32 (d, J = 4.6 Hz, 1H), 7.23 – 7.09 (m, 1H), 5.86 (s, 1H), 2.17 (s, 3H), 0.2 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6 (d, J = 255.6 Hz), 146.0, 145.7 (d, J = 4.7 Hz), 140.6 (d, J = 11.7 Hz), 138.6 (d, J = 25.9 Hz), 135.1 (d, J = 0.8 Hz), 123.21, 21.5 (d, J = 3.5 Hz), -0.2. **^{19}F NMR** (376 Hz, $CDCl_3$) -129.87. **HRMS** (ESI) m/z: calcd. for $C_{11}H_{17}FNSi$ $(M+H)^+$ 210.1109, found 210.1108.



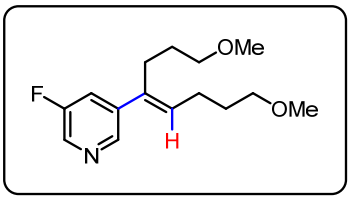
(*Z*)-3-(1,4-Bis(trimethylsilyl)but-2-en-2-yl)-5-fluoropyridine (4j)

Purification via column chromatography on silica gel (*n*-hexane/EA = 20/1, v/v, R_f = 0.2) afforded **4j** as yellow oil (112.1 mg, 0.380 mmol, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.6 Hz, 1H), 8.28 (d, J = 4.8 Hz, 1H), 7.13 (dd, J = 6.6, 5.0 Hz, 1H), 5.64 (t, J = 8.6 Hz, 1H), 1.93 (s, 2H), 1.59 (d, J = 8.6 Hz, 2H), 0.04 (s, 9H), -0.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (d, J = 253.4 Hz), 145.6 (d, J = 4.8 Hz), 140.8 (d, J = 11.2 Hz), 138.5 (d, J = 26.4 Hz), 128.7, 128.4 (d, J = 2.4 Hz), 124.1, 20.5, -0.9, -1.5. **^{19}F NMR** (376 Hz, $CDCl_3$) -119.77. **HRMS** (ESI) m/z: calcd. for $C_{15}H_{27}FNSi_2$ $(M+H)^+$ 296.1661, found 296.1660.



(*E*)-3-Fluoro-5-(2,2,3,3,12,12,13,13-octamethyl-4,11-dioxa-3,12-disilatetradec-7-en-7-yl)pyridine (4k)

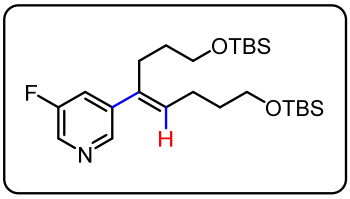
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **4k** as yellow oil (126.4 mg, 0.288 mmol, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.0 Hz, 1H), 8.30 (d, J = 4.7 Hz, 1H), 7.20 – 7.08 (m, 1H), 5.80 (t, J = 7.2 Hz, 1H), 3.70 (t, J = 6.6 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H), 2.72 (t, J = 6.8 Hz, 2H), 2.46 (q, J = 6.8 Hz, 2H), 0.88 (s, 9H), 0.81 (s, 9H), 0.05 (s, 6H), -0.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, J = 254.4 Hz), 145.6 (d, J = 4.7 Hz), 138.7 (d, J = 11.2 Hz), 138.3 (d, J = 26.0 Hz), 132.8 (d, J = 2.1 Hz), 132.5, 124.3, 62.4, 61.5, 33.5 (d, J = 2.2 Hz), 32.2, 25.9, 25.8, 18.3, 18.2, -5.3, -5.5. **^{19}F NMR** (376 Hz, $CDCl_3$) -129.87. **HRMS** (ESI) m/z: calcd. for $C_{23}H_{43}FNO_2Si_2$ $(M+H)^+$ 440.2811, found 440.2809.



(*E*)-3-(1,8-Dimethoxyoct-4-en-4-yl)-5-fluoropyridine (4l)

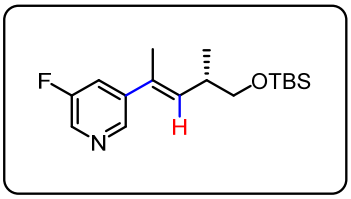
Purification via column chromatography on silica gel (*n*-hexane/EA = 1/1, v/v, R_f = 0.3) afforded **4l** as yellow oil (82.2 mg, 0.308 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 8.31 (d, J = 4.4 Hz, 1H), 7.13 (t, J = 5.6 Hz, 1H), 5.70 (t, J = 7.2 Hz, 1H), 3.40 (t, J = 6.4 Hz, 2H), 3.33 (s, 3H), 3.29 (t, J = 6.4 Hz, 2H), 3.26 (s, 3H), 2.55 (t, J = 7.6 Hz, 2H), 2.30 (q, J = 7.4 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.60 – 1.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J = 253.9 Hz), 145.6 (d, J = 4.7 Hz), 138.6 (d, J = 11.8 Hz), 138.3, 134.5 (d, J = 2.1 Hz), 133.7, 124.1, 71.9, 71.8,

58.6, 58.4, 29.3, 28.2, 26.2 (d, J = 2.1 Hz), 24.9. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.10. **HRMS** (ESI) m/z: calcd. for $C_{15}H_{23}FNO_2$ $(M+H)^+$ 268.1707, found 268.1704.



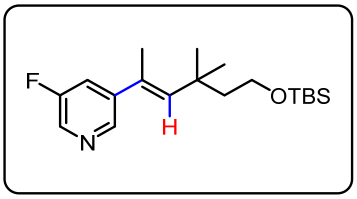
(*E*)-3-Fluoro-5-(2,2,3,3,14,14,15,15-octamethyl-4,13-dioxa-3,14-disilahexadec-8-en-8-yl)pyridine (4m)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **4m** as yellow oil (175.6 mg, 0.376 mmol, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 2.4 Hz, 1H), 8.25 (d, J = 4.6 Hz, 1H), 7.16 – 6.96 (m, 1H), 5.67 (t, J = 7.2 Hz, 1H), 3.60 (t, J = 6.2 Hz, 2H), 3.49 (t, J = 6.2 Hz, 2H), 2.56 – 2.42 (m, 2H), 2.24 (q, J = 7.4 Hz, 2H), 1.69 – 1.53 (m, 2H), 1.51 – 1.38 (m, 2H), 0.84 (s, 9H), 0.81 (s, 9H), -0.00 (s, 6H), -0.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9 (d, J = 254.1 Hz), 145.6 (d, J = 4.9 Hz), 138.7 (d, J = 11.2 Hz), 138.4 (d, J = 26.1 Hz), 134.6 (d, J = 2.5 Hz), 133.7 (d, J = 1.2 Hz), 124.1, 62.4, 62.3, 32.5, 31.5, 26.0 (d, J = 2.3 Hz), 25.9, 25.9, 24.7, 18.3, 18.2, -5.3, -5.4. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.19. **HRMS** (ESI) m/z: calcd. for $C_{25}H_{47}FNO_2Si_2$ $(M+H)^+$ 468.3124, found 468.3124.



(*S*,*E*)-3-(5-((*tert*-Butyldimethylsilyl)oxy)-4-methylpent-2-en-2-yl)-5-fluoropyridine (4n)

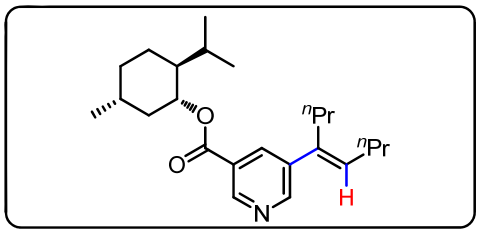
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **4n** as yellow oil (93.9 mg, 0.304 mmol, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 8.29 (br s, 1H), 7.23 – 7.01 (m, 1H), 5.58 (d, J = 9.4 Hz, 1H), 3.49 (d, J = 6.6 Hz, 2H), 2.81 – 2.66 (m, 1H), 2.02 (s, 3H), 1.01 (d, J = 6.6 Hz, 3H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, J = 256.8 Hz), 145.6 (d, J = 3.3 Hz), 139.5 (d, J = 10.8 Hz), 138.4 (d, J = 25.2 Hz), 137.8 (d, J = 2.8 Hz), 129.2, 123.3, 67.5, 36.0, 25.8, 18.3, 16.7, 16.4 (d, J = 3.2 Hz), -5.4. **^{19}F NMR** (376 Hz, $CDCl_3$) -129.79. **HRMS** (ESI) m/z: calcd. for $C_{17}H_{29}FNOSi$ $(M+H)^+$ 310.1997, found 310.1993.



(*E*)-3-(6-((*tert*-Butyldimethylsilyl)oxy)-4,4-dimethylpent-2-en-2-yl)-5-fluoropyridine (4o)

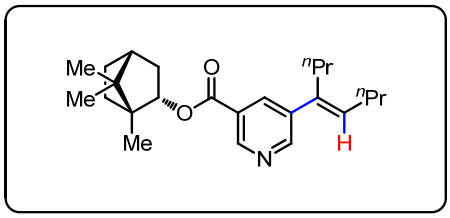
Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **4o** as yellow oil (71.4 mg, 0.212 mmol, 53% yield). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 8.36 (s, 1H), 8.30 (d, J = 4.8 Hz, 1H), 7.10 (t, J = 5.6 Hz, 1H), 5.62 (s, 1H), 3.70 (t, J = 7.6 Hz, 2H), 2.09 (s, 3H), 1.77 (t, J = 7.6 Hz, 2H), 1.22 (s, 6H), 0.88 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (d, J = 251.0 Hz), 145.7 (d, J = 5.2 Hz), 143.0, 141.6 (d, J = 11.8 Hz), 138.5 (d, J = 25.9Hz), 129.0, 123.8, 60.6, 46.1, 35.6, 29.2, 26.1, 18.4, 17.7 (d, J = 2.5 Hz), -5.2. **^{19}F NMR** (376 Hz, $CDCl_3$) -130.38. **HRMS** (ESI) m/z: calcd. for $C_{19}H_{33}FNOSi$ $(M+H)^+$ 338.2310, found 338.2305.



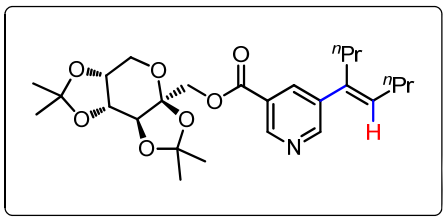
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 5-((*E*)-oct-4-en-4-yl)nicotinate (5a)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5a** as yellow oil (111.3 mg, 0.298 mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (d, J = 1.4 Hz, 1H), 8.71 (d, J = 2.0 Hz, 1H), 8.22 – 8.16 (m, 1H), 5.74 (t, J = 7.4 Hz, 1H), 5.02 – 4.90 (m, 1H), 2.50 (q, J = 7.6 Hz, 2H), 2.20 (q, J = 7.6 Hz, 2H), 2.16 – 2.08 (m, 1H), 1.98 – 1.88 (m, 1H), 1.78 – 1.68 (m, 2H), 1.63 – 1.52 (m, 2H), 1.52 – 1.42 (m, 2H), 1.40 – 1.28(m, 2H), 1.21 – 1.07 (m, 2H), 1.02 – 0.85 (m, 13H), 0.82 – 0.76 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 151.4, 148.7, 138.7, 136.4, 134.5, 132.3, 126.2, 75.6, 47.3, 41.0, 34.3, 31.6, 31.4, 30.8, 26.7, 23.8, 23.0, 22.1, 21.7, 20.8, 16.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{24}H_{38}NO_2$ $(M+H)^+$ 372.2897, found 372.2893.



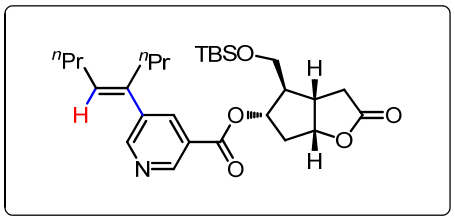
(1*S*,2*S*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl5-((*E*)-oct-4-en-4-yl)nicotinate (5b)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5b** as yellow oil (113.7 mg, 0.306 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.06 (d, J = 1.8 Hz, 1H), 8.72 (d, J = 2.2 Hz, 1H), 8.19 (t, J = 2.0 Hz, 1H), 5.74 (t, J = 7.4 Hz, 1H), 5.20 – 5.03 (m, 1H), 2.55 – 2.41 (m, 3H), 2.19 (q, J = 7.3 Hz, 2H), 2.14 – 2.02 (m, 1H), 1.86 – 1.75 (m, 1H), 1.75 – 1.70 (m, 1H), 1.53 – 1.43 (m, 2H), 1.38 – 1.26 (m, 3H), 1.11 (dd, J = 13.8, 3.4 Hz, 1H), 0.98 – 0.93 (m, 6H), 0.93 – 0.80 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 151.4, 148.6, 138.7, 136.3, 134.4, 132.3, 126.2, 81.2, 49.2, 48.0, 45.0, 37.0, 31.4, 30.8, 28.1, 27.4, 22.9, 21.7, 19.8, 19.0, 14.0, 13.9, 13.7. **HRMS** (ESI) m/z: calcd. for $C_{24}H_{36}NO_2$ $(M+H)^+$ 370.2741, found 370.2736.



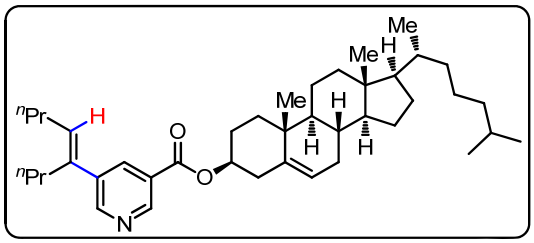
((3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 5-((*E*)-oct-4-en-4-yl)nicotinate (5c)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5c** as yellow oil (79.8 mg, 0.166 mmol, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.07 (d, J = 2.0 Hz, 1H), 8.72 (d, J = 2.2 Hz, 1H), 8.22 (t, J = 2.2 Hz, 1H), 5.72 (t, J = 7.4 Hz, 1H), 4.69 – 4.61 (m, 2H), 4.44 (d, J = 2.6 Hz, 1H), 4.37 (d, J = 11.8 Hz, 1H), 4.25 (dd, J = 8.0, 1.2 Hz, 1H), 3.95 (dd, J = 13.0, 1.8 Hz, 1H), 3.84 – 3.76 (m, 1H), 2.52 – 2.41 (m, 2H), 2.19 (q, J = 7.4 Hz, 2H), 1.54 (s, 3H), 1.51 – 1.41 (m, 5H), 1.37(s, 3H), 1.35 – 1.26 (m, 5H), 0.95 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 151.7, 148.7, 138.8, 136.2, 134.7, 132.6, 125.3, 109.3, 109.0, 101.6, 70.8, 70.6, 70.1, 65.6, 61.5, 31.3, 30.8, 26.6, 26.0, 25.6, 24.1, 22.9, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z: calcd. for $C_{26}H_{38}NO_7$ $(M+H)^+$ 476.2643, found 476.2639.



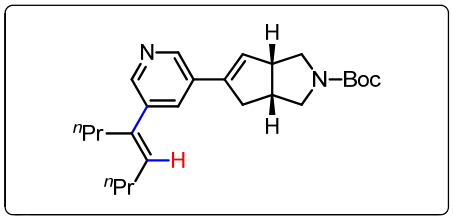
(3*aS*,4*R*,5*S*,6*aR*)-4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-oxohexahydro-2*H*-cyclopenta[b]furan-5-yl 5-((*E*)-oct-4-en-4-yl)nicotinate (5d)

Purification via column chromatography on silica gel (*n*-hexane/EA = 4/1, v/v, R_f = 0.2) afforded **5b** as yellow oil (122.2 mg, 0.242 mmol, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01 (d, J = 1.8 Hz, 1H), 8.72 (d, J = 2.2 Hz, 1H), 8.14 (t, J = 2.2 Hz, 1H), 5.76 (t, J = 7.4 Hz, 1H), 5.35 (dt, J = 6.2, 3.2 Hz, 1H), 5.06 (t, J = 5.8 Hz, 1H), 3.74 (dd, J = 10.2, 4.8 Hz, 1H), 3.68 (dd, J = 10.2, 4.6 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.59 – 2.44 (m, 4H), 2.40 – 2.25 (m, 2H), 2.20 (q, J = 7.43 Hz, 2H), 1.55 – 1.44 (m, 2H), 1.40 – 1.28 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.91 – 0.85 (m, 12H), 0.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 165.3, 151.9, 148.8, 138.8, 136.3, 134.4, 132.6, 125.2, 85.1, 79.1, 63.3, 54.9, 40.5, 39.0, 36.2, 31.2, 30.9, 25.9, 22.9, 21.7, 18.3, 14.1, 13.9, -5.5. **HRMS** (ESI) m/z: calcd. for $C_{28}H_{44}NO_5Si$ $(M+H)^+$ 502.2983, found 502.2982.



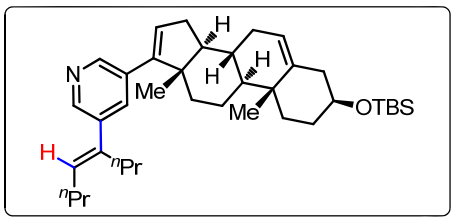
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 5-((*E*)-oct-4-en-4-yl)nicotinate (5e)

Purification via column chromatography on silica gel (*n*-hexane/EA = 10/1, v/v, R_f = 0.2) afforded **5f** as yellow oil (149.1 mg, 0.247 mmol, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (d, J = 1.6 Hz, 1H), 8.70 (d, J = 2.0 Hz, 1H), 8.25 – 8.15 (m, 1H), 5.74 (t, J = 7.4 Hz, 1H), 5.46 – 5.38 (m, 1H), 4.95 – 4.80 (m, 1H), 2.58 – 2.40 (m, 4H), 2.20 (q, J = 7.3 Hz, 2H), 2.04 – 1.92(m, 4H), 1.87 – 1.70 (m, 2H), 1.61 – 1.44 (m, 8H), 1.39 – 1.30 (m, 5H), 1.25 – 1.06 (m, 11H), 1.04 – 0.99 (m, 6H), 0.93 – 0.89 (m, 4H), 0.88 – 0.83 (m, 8H), 0.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 151.4, 148.7, 139.6, 138.7, 136.4, 134.5, 132.3, 126.1, 123.1, 75.3, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.3, 37.1, 36.7, 36.3, 35.9, 32.0, 32.0, 31.4, 30.8, 28.3, 28.1, 27.9, 24.4, 23.9, 23.0, 22.9, 22.7, 21.7, 21.2, 19.5, 18.8, 14.0, 13.9, 12.0. **HRMS** (ESI) m/z: calcd. for $C_{41}H_{64}NO_2$ $(M+H)^+$ 602.4932, found 602.4929.



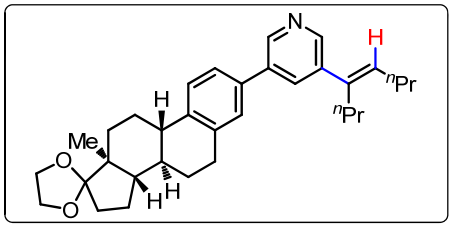
(3a*S*,6a*R*)-*tert*-Butyl 5-(5-((*E*)-oct-4-en-4-yl)pyridin-3-yl)-3,3a,6,6a-tetrahydrocyclopenta[c]pyrrole-2(1H)-carboxylate (5f)

Purification via column chromatography on silica gel (*n*-hexane/EA = 1/1, v/v, R_f = 0.2) afforded **5e** as yellow oil (91.9 mg, 0.231 mmol, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.44 (s, 1H), 7.60 (s, 1H), 6.12 (s, 1H), 5.68 (t, J = 7.2 Hz, 1H), 3.85 – 3.63 (m, 1H), 3.62 – 3.39 (m, 3H), 3.21 – 2.91 (m, 3H), 2.71 – 2.55 (m, 1H), 2.48 (t, J = 7.6 Hz, 2H), 2.20 (q, J = 7.4 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.44 (s, 9H), 1.35 (q, J = 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 148.4, 148.4, 146.9, 145.3, 138.6, 137.1, 131.4, 130.9, 130.6, 79.3, 31.6, 30.7, 28.6, 23.0, 21.7, 14.0, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{25}H_{37}N_2O_2$ $(M+H)^+$ 397.2850, found 397.2847.



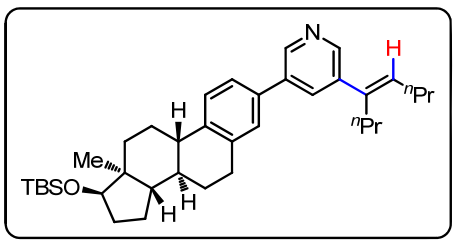
3-((3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-5-((*E*)-oct-4-en-4-yl)pyridine (5g)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5i** as yellow oil (144.5 mg, 0.253 mmol, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, J = 1.8 Hz, 1H), 8.43 (d, J = 1.8 Hz, 1H), 7.63 – 7.46 (t, J = 2.0 Hz, 1H), 6.03 – 5.95 (m, 1H), 5.68 (t, J = 7.2 Hz, 1H), 5.41 – 5.31 (m, 1H), 3.57 – 3.42 (m, 1H), 2.53 – 2.40 (m, 2H), 2.34 – 2.15 (m, 5H), 2.10 – 1.99 (m, 3H), 1.83 – 1.44 (m, 11H), 1.41 – 1.30 (m, 2H), 1.12 – 1.00 (m, 8H), 0.96 (t, J = 7.4 Hz, 3H), 0.89 (s, 12H), 0.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 146.2, 145.9, 142.0, 138.2, 137.2, 132.3, 131.4, 131.0, 129.1, 120.9, 72.7, 57.7, 50.6, 47.5, 43.0, 37.4, 36.9, 35.4, 32.2, 31.9, 31.7, 31.6, 30.8, 30.6, 26.0, 23.1, 21.8, 21.0, 19.5, 18.4, 16.7, 14.0, 14.0, -4.5. **HRMS** (ESI) m/z: calcd. for $C_{38}H_{60}NOSi$ $(M+H)^+$ 574.4439, found 574.4440.



3-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-5-((*E*)-oct-4-en-4-yl)pyridine (5h)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5g** as yellow oil (164.9 mg, 0.320 mmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 2.0 Hz, 1H), 8.53 (d, J = 2.0 Hz, 1H), 7.75 (t, J = 2.0 Hz, 1H), 7.48 – 7.33 (m, 2H), 7.31 (br s, 1H), 5.75 (t, J = 7.2 Hz, 1H), 4.01 – 3.86 (m, 4H), 3.02 – 2.90 (m, 2H), 2.57 – 2.48 (m, 2H), 2.44 – 2.29 (m, 2H), 2.21 (q, J = 7.4 Hz, 2H), 2.10 – 2.01 (m, 1H), 2.00 – 1.92 (m, 1H), 1.89 – 1.76 (m, 3H), 1.72 – 1.63 (m, 1H), 1.62 – 1.55 (m, 2H), 1.53 – 1.44 (m, 4H), 1.44 – 1.35 (m, 3H), 0.98 (t, J = 7.4 Hz, 3H), 0.93 – 0.86 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 146.2, 140.6, 138.7, 137.7, 137.2, 136.1, 135.5, 132.0, 131.3, 127.9, 126.2, 124.6, 119.5, 65.4, 64.7, 49.5, 46.2, 44.1, 38.9, 34.3, 31.6, 30.8, 30.8, 29.7, 27.0, 26.1, 23.0, 22.5, 21.8, 14.4, 14.0, 14.0. **HRMS** (ESI) m/z: calcd. for $C_{33}H_{44}NO_2$ $(M+H)^+$ 486.3367, found 486.3363.



3-((8*R*,9*S*,13*S*,14*S*,17*R*)-17-((*tert*-Butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-5-((*E*)-oct-4-en-4-yl)pyridine (5i)

Purification via column chromatography on silica gel (*n*-hexane/EA = 8/1, v/v, R_f = 0.2) afforded **5h** as yellow oil (185.1 mg, 0.334 mmol, 83% yield). **^{1}H NMR** (400

MHz, $CDCl_3$) δ 8.66 (d, J = 2.0 Hz, 1H), 8.53 (d, J = 2.0 Hz, 1H), 7.75 (t, J = 2.0 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 5.75 (t, J = 7.4 Hz, 1H), 3.67 (t, J = 8.2 Hz, 1H), 2.96 (dd, J = 8.6, 3.8 Hz, 2H), 2.60 – 2.45 (m, 2H), 2.41 – 2.32 (m, 1H), 2.29 – 2.28 (m, 1H), 2.25 – 2.15 (m, 2H), 1.99 – 1.90 (m, 3H), 1.75 – 1.63 (m, 1H), 1.62 – 1.54 (m, 1H), 1.53 – 1.44 (dt, J = 7.1, 5.2 Hz, 4H), 1.43 – 1.33 (m, 4H), 1.29 – 1.14 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.93 – 0.88 (m, 12H), 0.77 (s, 3H), 0.08 – 0.01 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 146.2, 140.8, 138.8, 137.7, 137.2, 136.1, 135.5, 132.0, 131.4, 127.9, 126.3, 124.6, 81.8, 49.9, 44.6, 43.7, 38.8, 37.3, 31.6, 31.1, 30.8, 29.8, 27.3, 26.4, 26.0, 23.4, 23.1, 21.8, 18.2, 14.1, 14.0, 11.5, -4.5 (J = 33.8 Hz). **HRMS** (ESI) m/z: calcd. for $C_{37}H_{56}NOSi$ $(M+H)^+$ 558.4126, found 558.4117.

7. Reference

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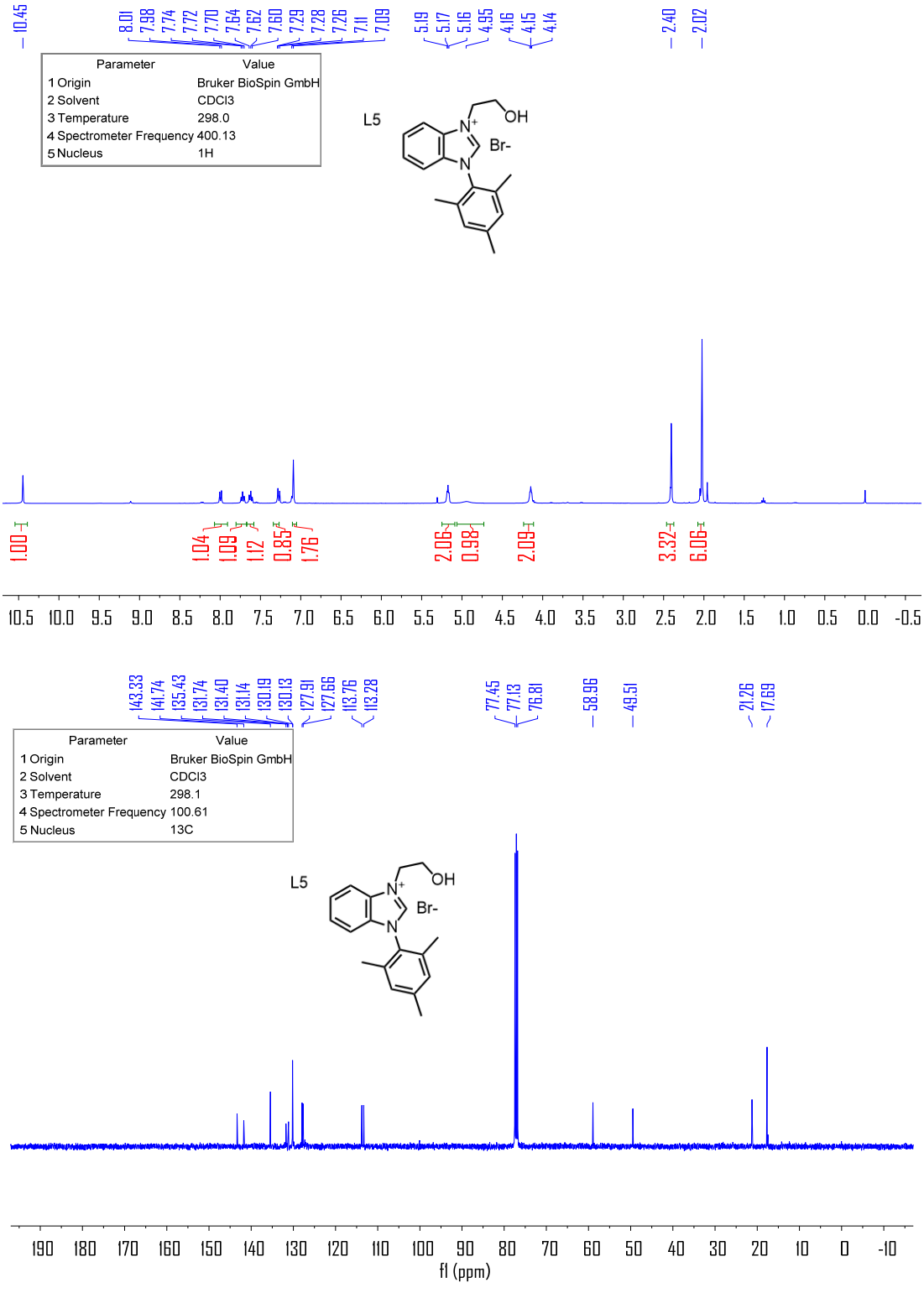
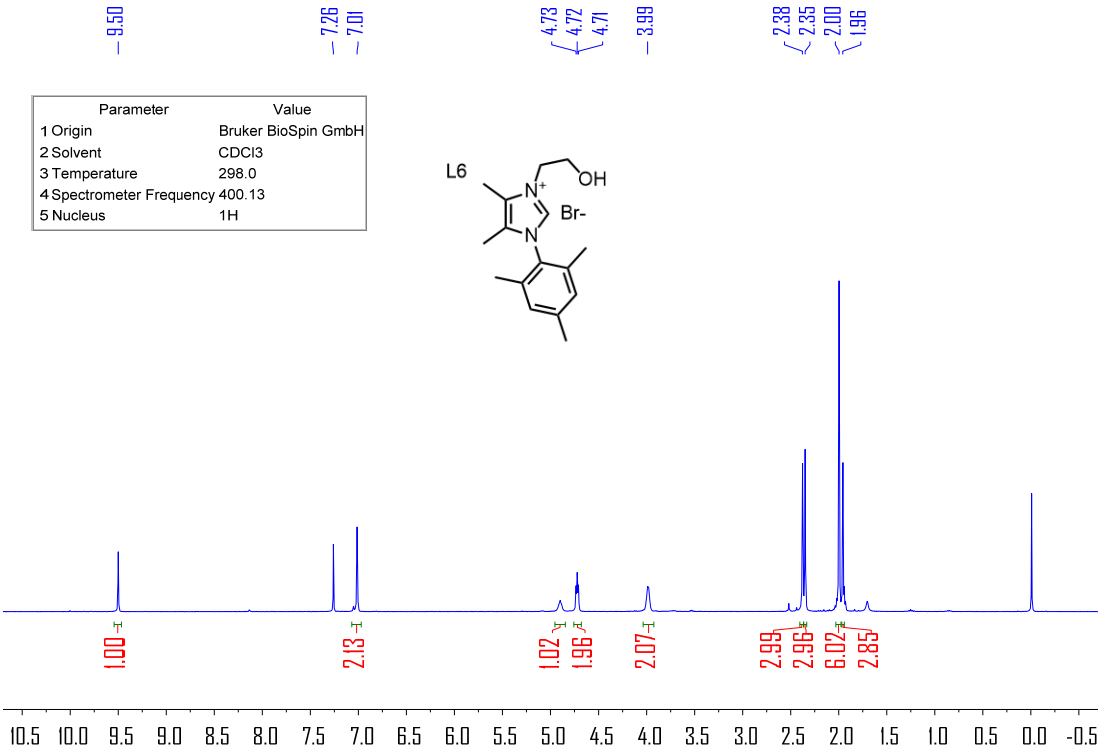
8. NMR Spectra

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4.73
4.72
4.71
3.99
2.38
2.35
2.00
1.96
Parameter Value
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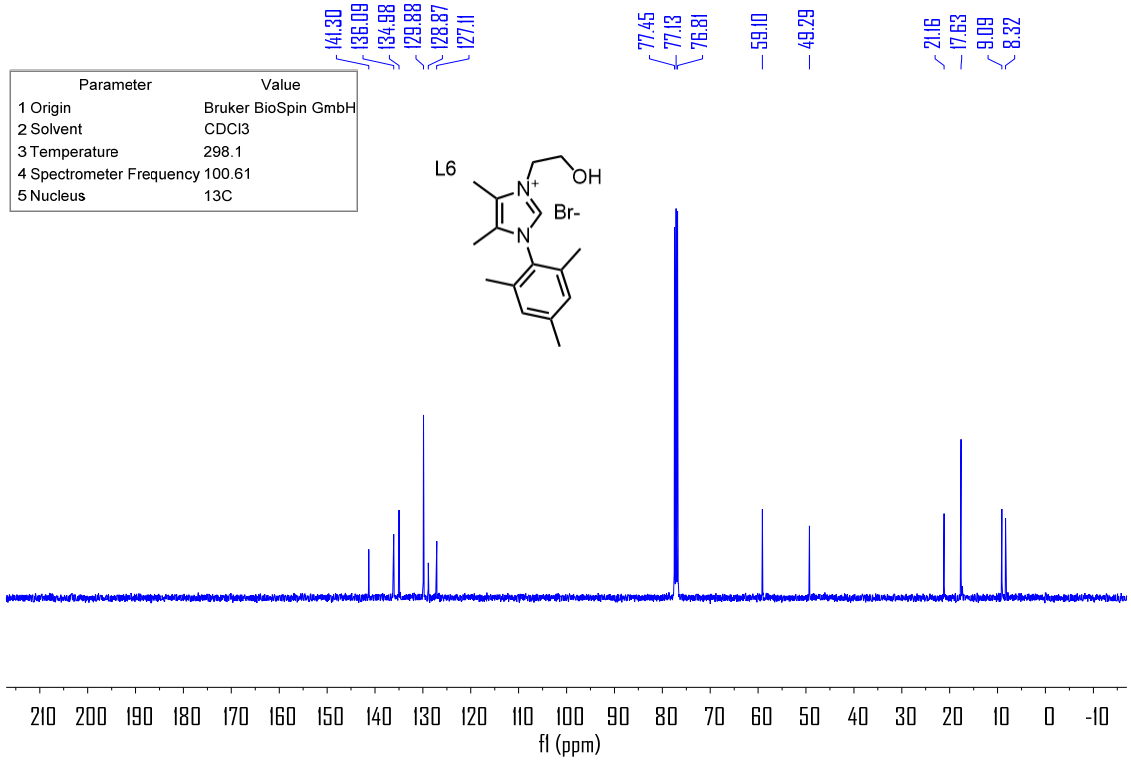
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
L6
OH
N+
Br-
N
1.00
2.13
1.02
1.96
2.07
2.99
2.96
6.02
2.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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134.98
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128.87
127.11
77.45
77.13
76.81
59.10
49.29
21.16
17.63
9.09
8.32
Parameter Value
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2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
L6
OH
N+
Br-
N
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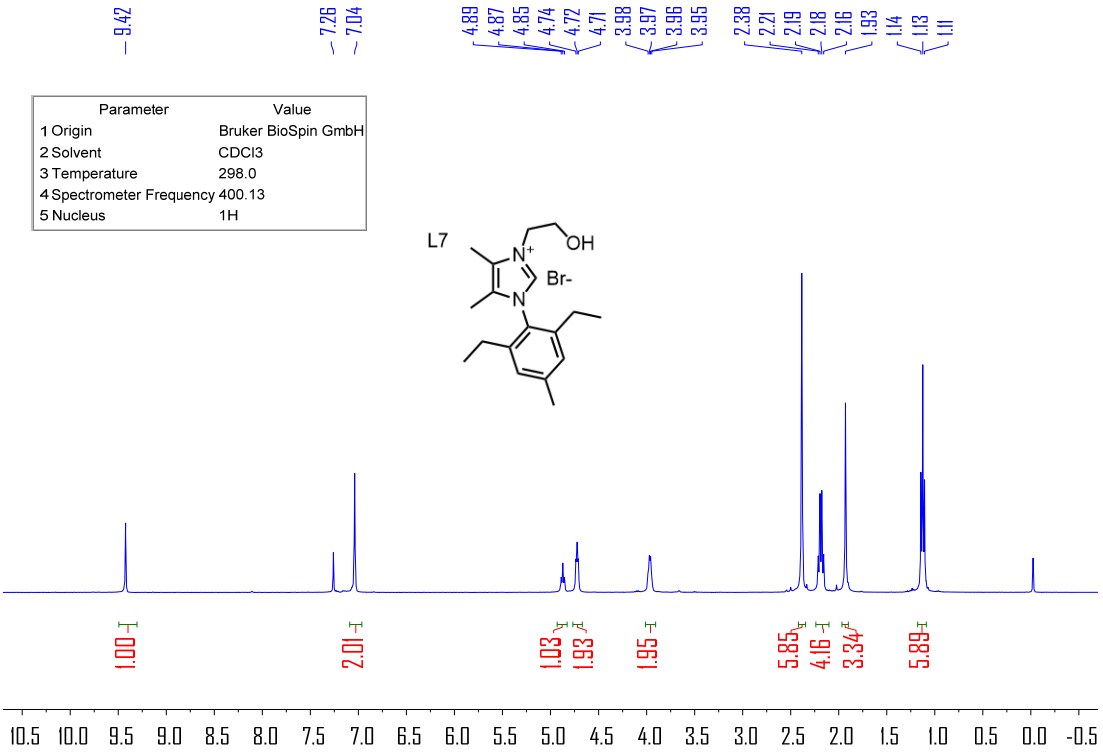
f1 (ppm)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3.97
3.96
3.95
2.38
2.21
2.19
2.18
2.16
1.93
1.14
1.13
1.11
Parameter Value
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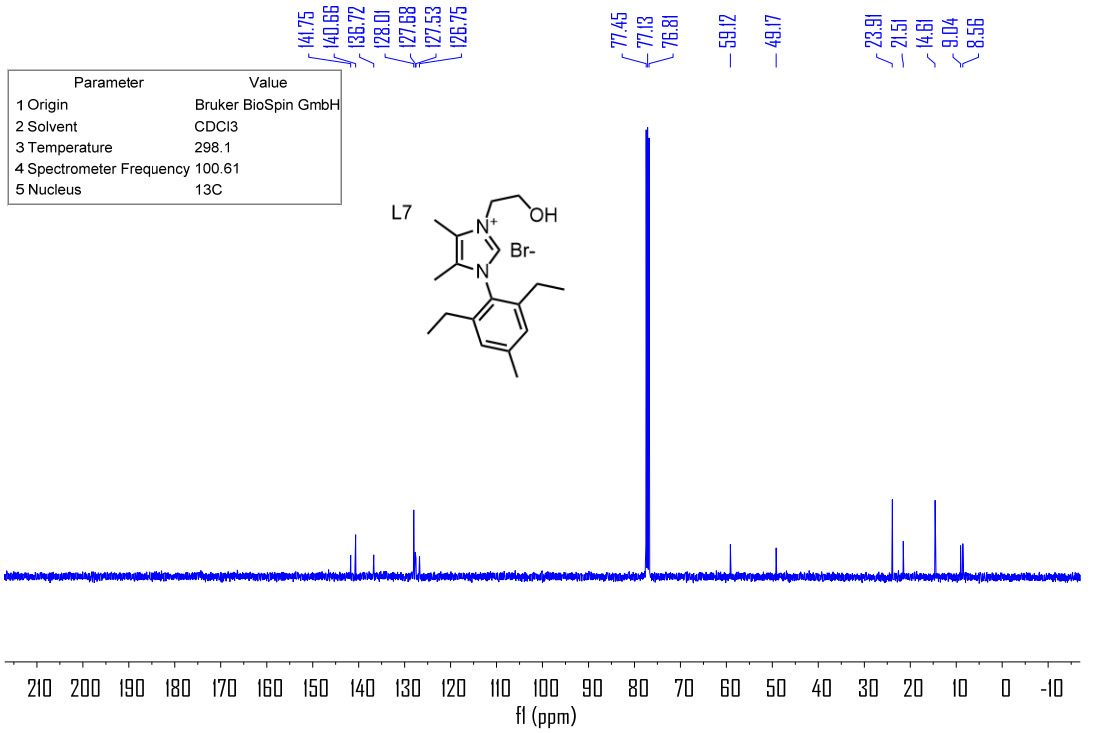
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
L7
OH
Br-
1.00
2.01
1.03
1.93
1.95
5.85
4.16
3.34
5.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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77.45
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76.81
59.12
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23.91
21.51
14.61
9.04
8.56
Parameter Value
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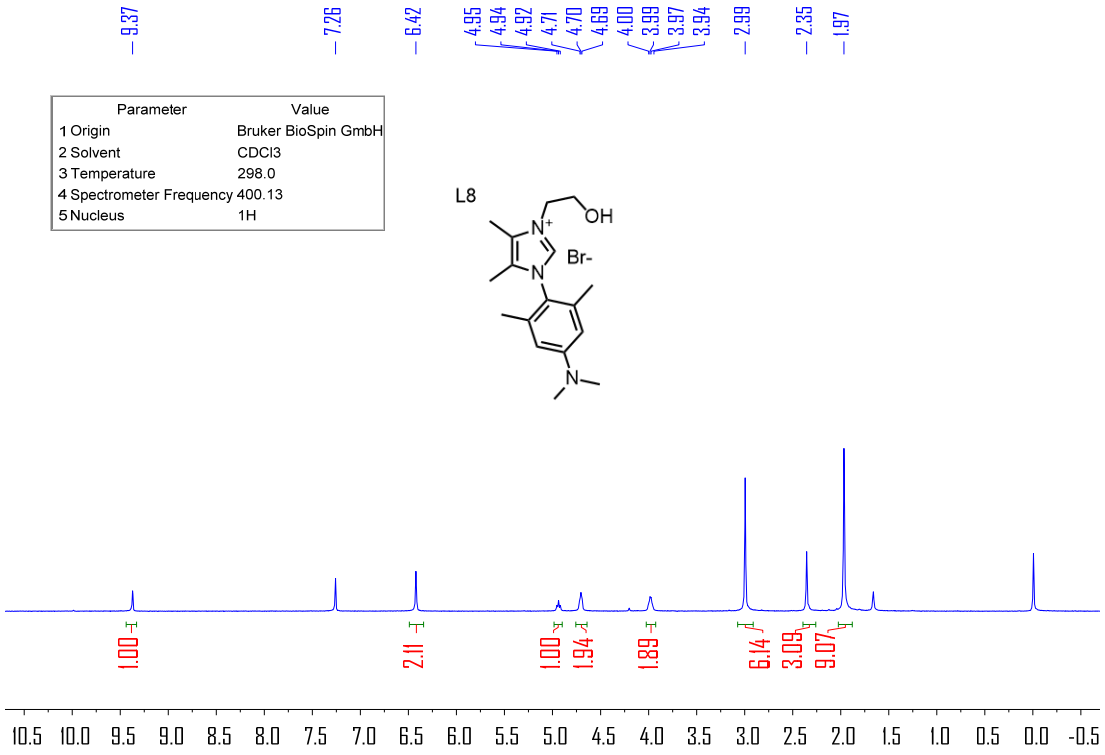
L7
OH
Br-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.94
2.99
2.35
1.97
Parameter Value
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2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
L8
OH
Br-
N
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2.11
1.00
1.94
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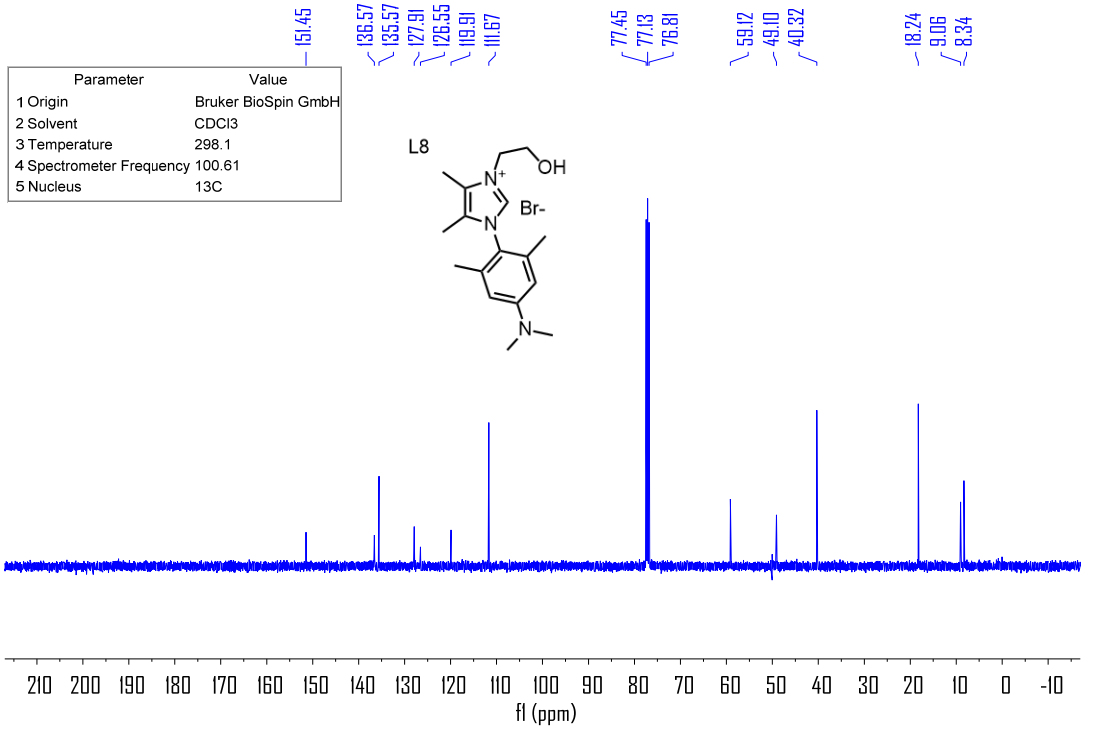
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40.32
18.24
9.06
8.34
Parameter Value
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2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
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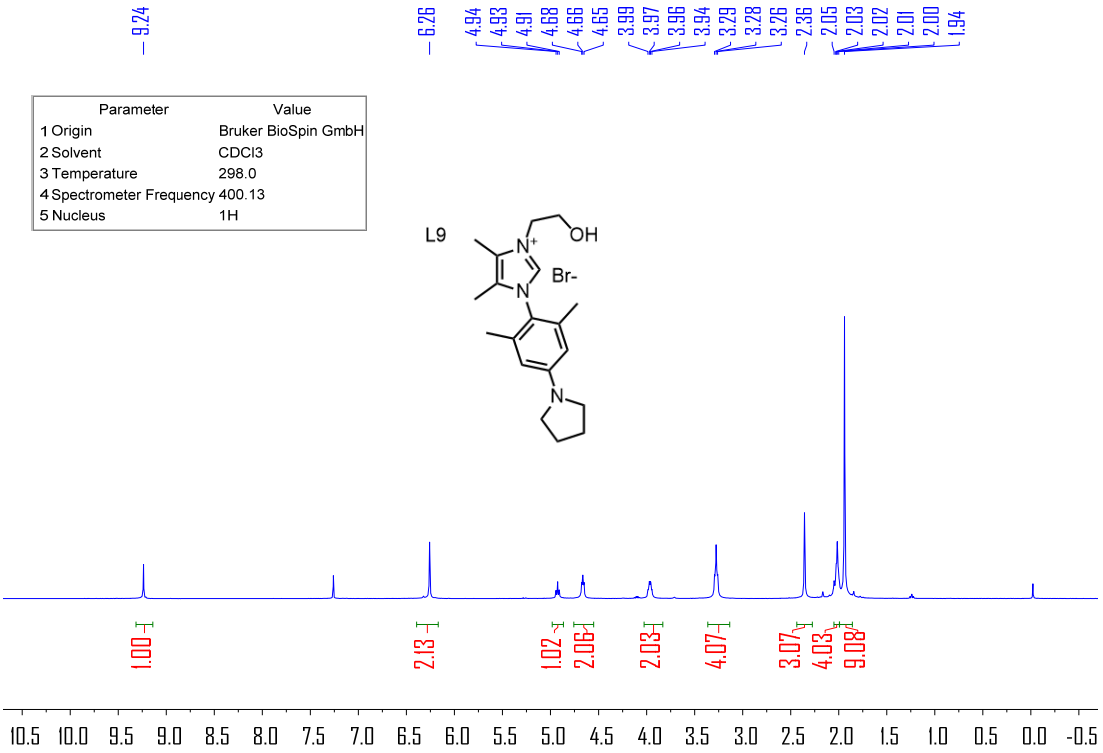
L8
OH
Br-
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.26
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4.93
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4.65
3.99
3.97
3.96
3.94
3.29
3.28
3.26
2.36
2.05
2.03
2.02
2.01
2.00
1.94
Parameter Value
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2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
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L9
OH
Br-
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2.13
1.02
2.06
2.03
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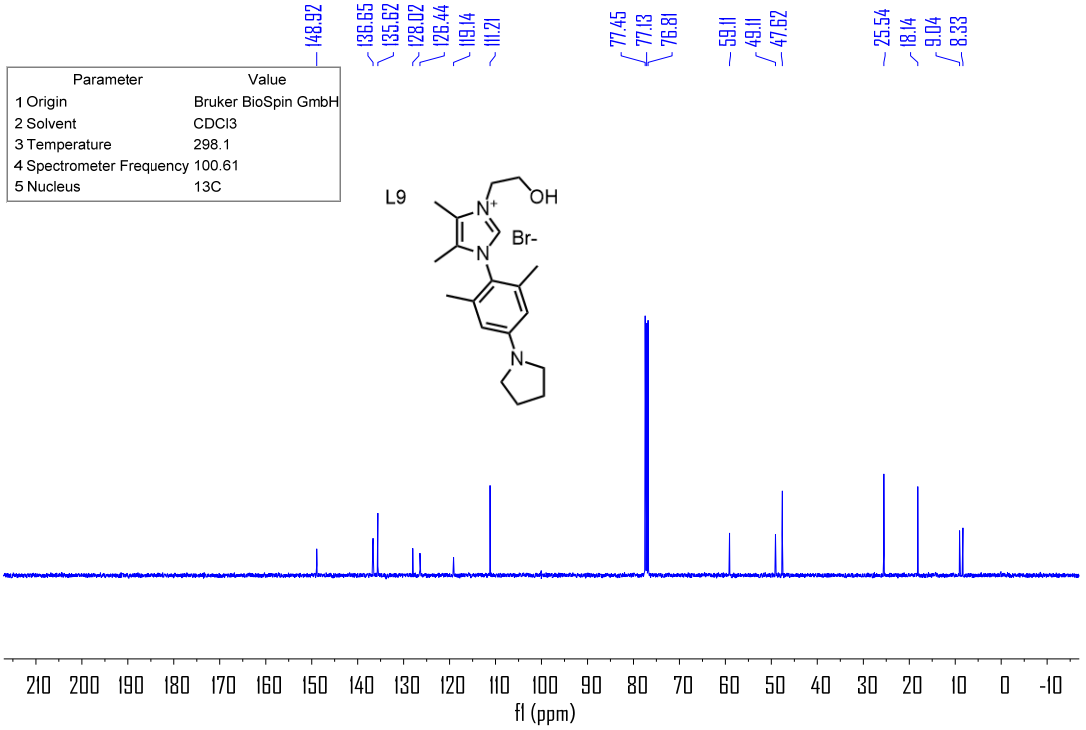
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76.81
59.11
49.11
47.62
25.54
18.14
9.04
8.33
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
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L9
OH
Br-
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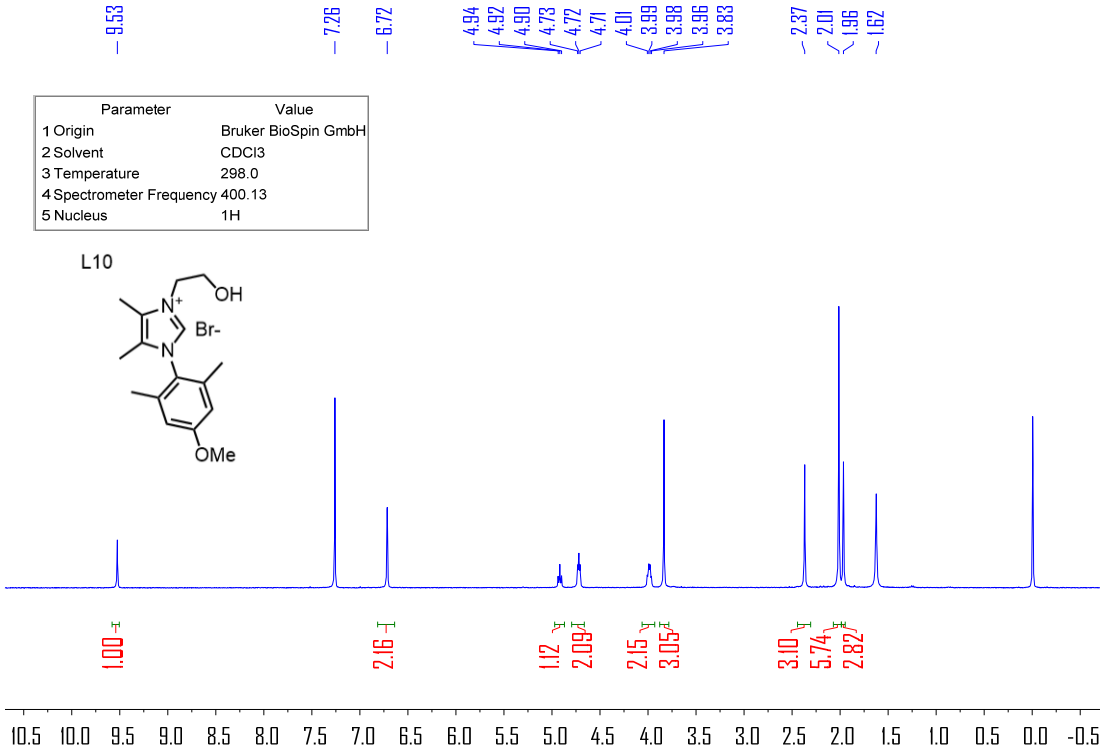
f1 (ppm)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4.71
4.01
3.99
3.98
3.96
3.83
2.37
2.01
1.96
1.62
Parameter Value
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L10
OH
N+
Br-
N
OMe
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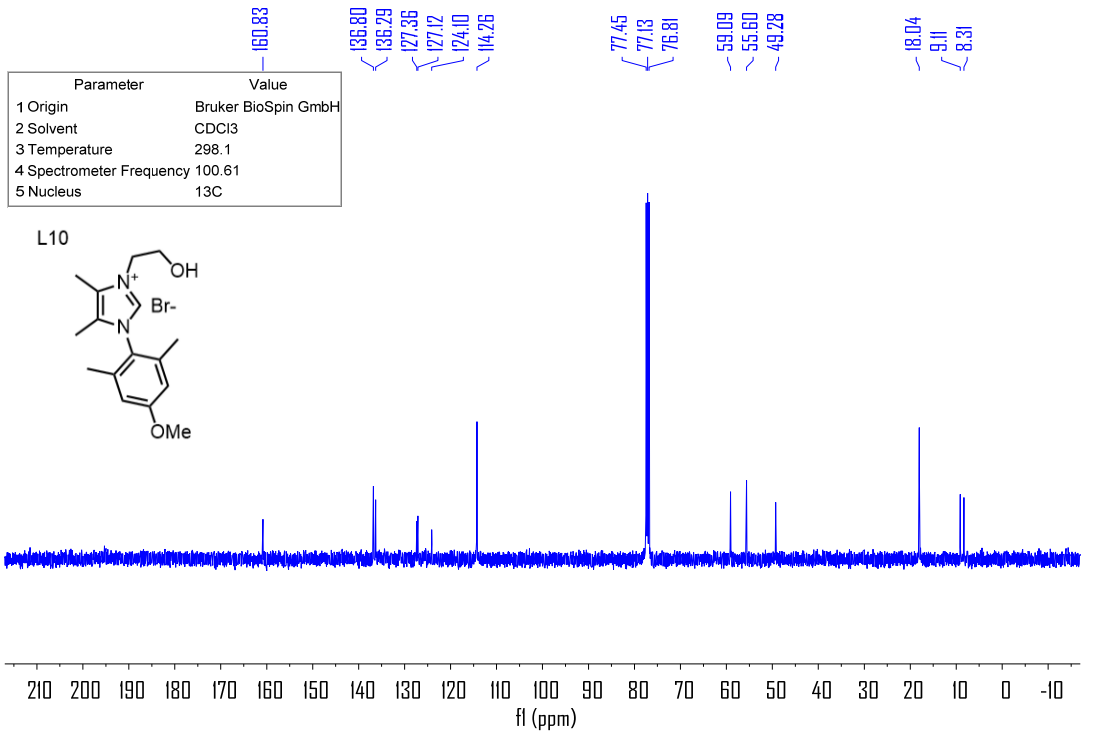
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55.60
49.28
18.04
9.11
8.31
Parameter Value
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2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
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OH
N+
Br-
N
OMe
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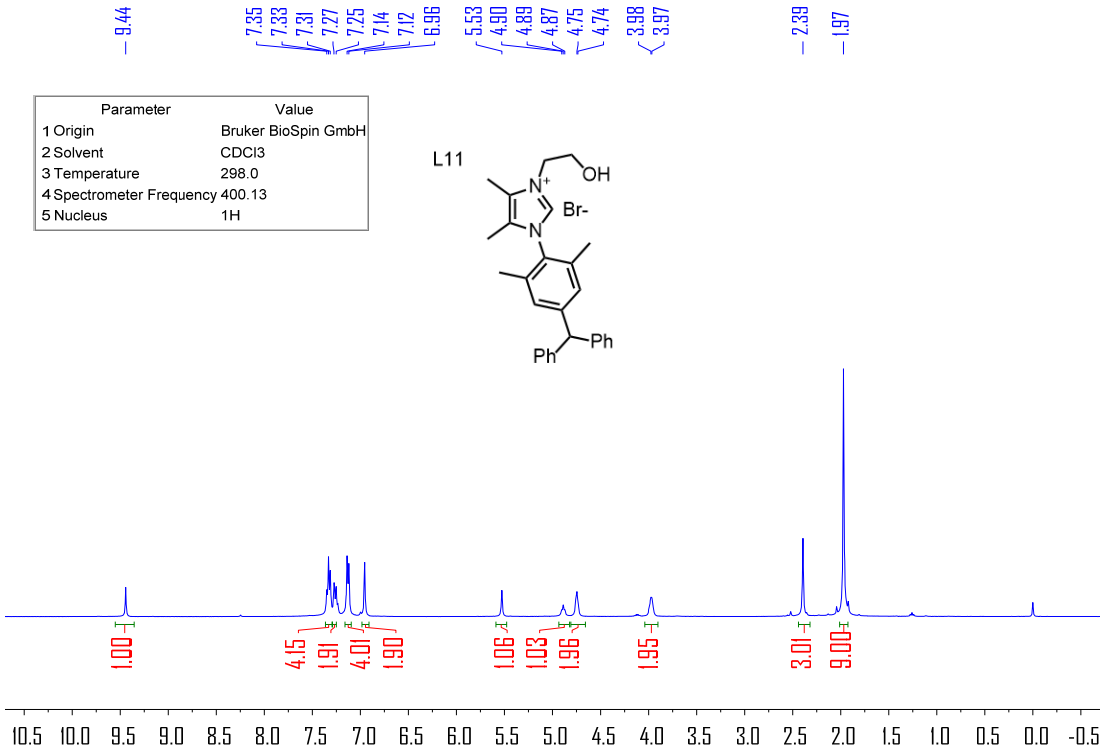
f1 (ppm)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4.87
4.75
4.74
3.98
3.97
2.39
1.97
Parameter Value
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L11
OH
N+
Br-
N
Ph
Ph
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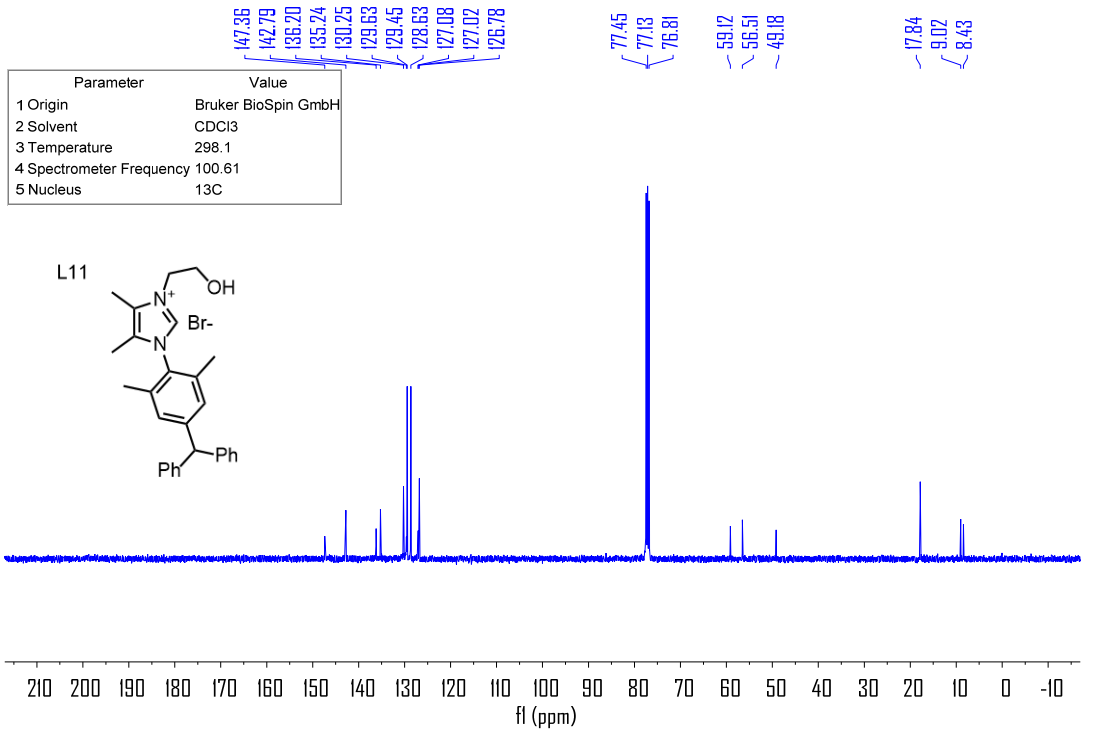
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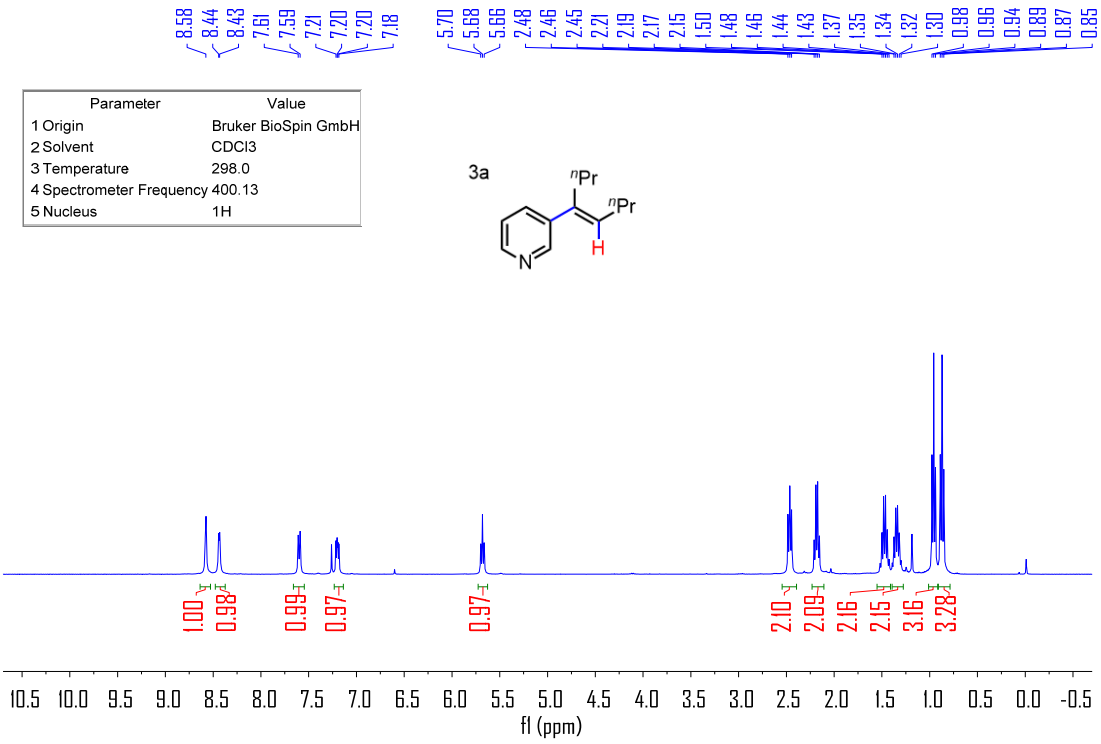
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
L11
OH
N+
Br-
N
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.20
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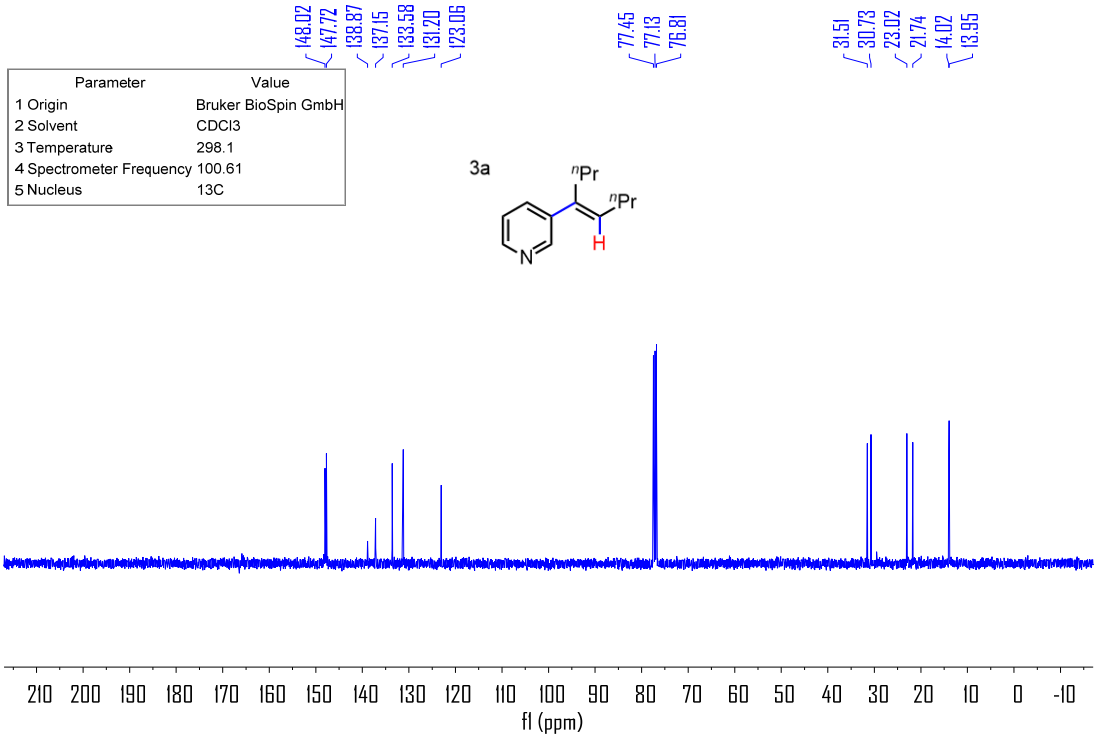
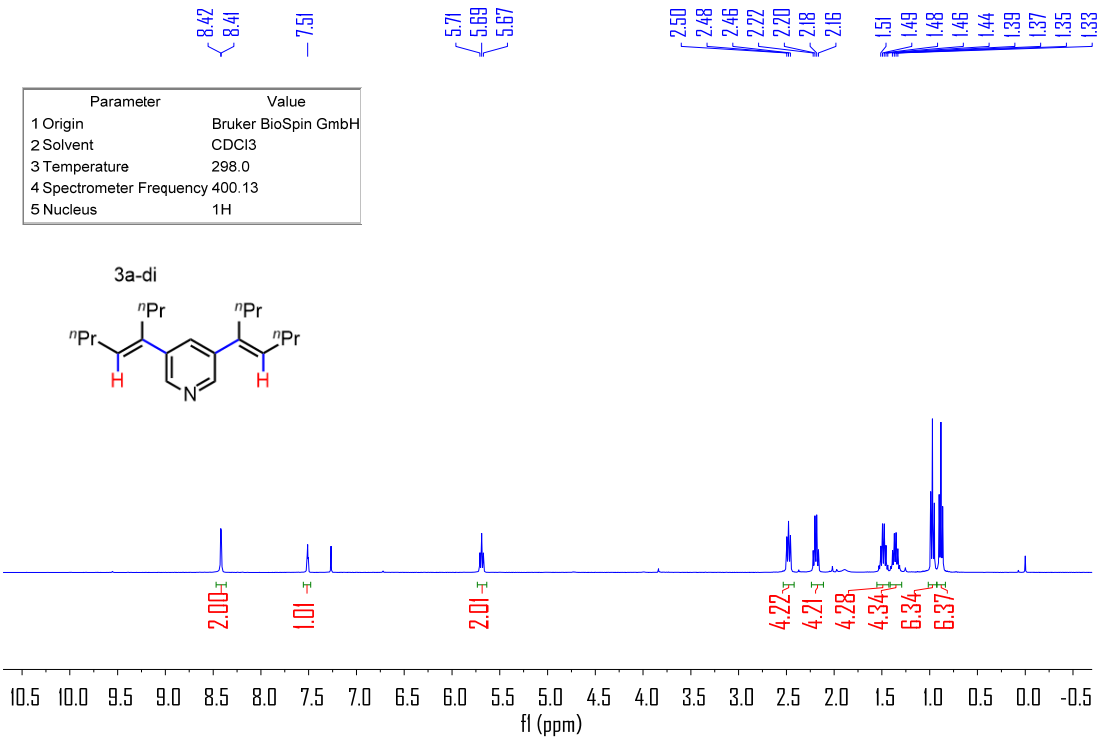
5.68
5.66
2.48
2.46
2.45
2.21
2.19
2.17
2.15
1.50
1.48
1.46
1.44
1.43
1.37
1.35
1.34
1.32
1.30
0.98
0.96
0.94
0.89
0.87
0.85
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3a
nPr
nPr
H
N
1.00
0.98
0.99
0.97
0.97
2.10
2.09
2.16
2.15
3.16
3.28
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


148.02
147.72
138.87
137.15
133.58
131.20
123.06
77.45
77.13
76.81
31.51
30.73
23.02
21.74
14.02
13.95
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3a
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.51
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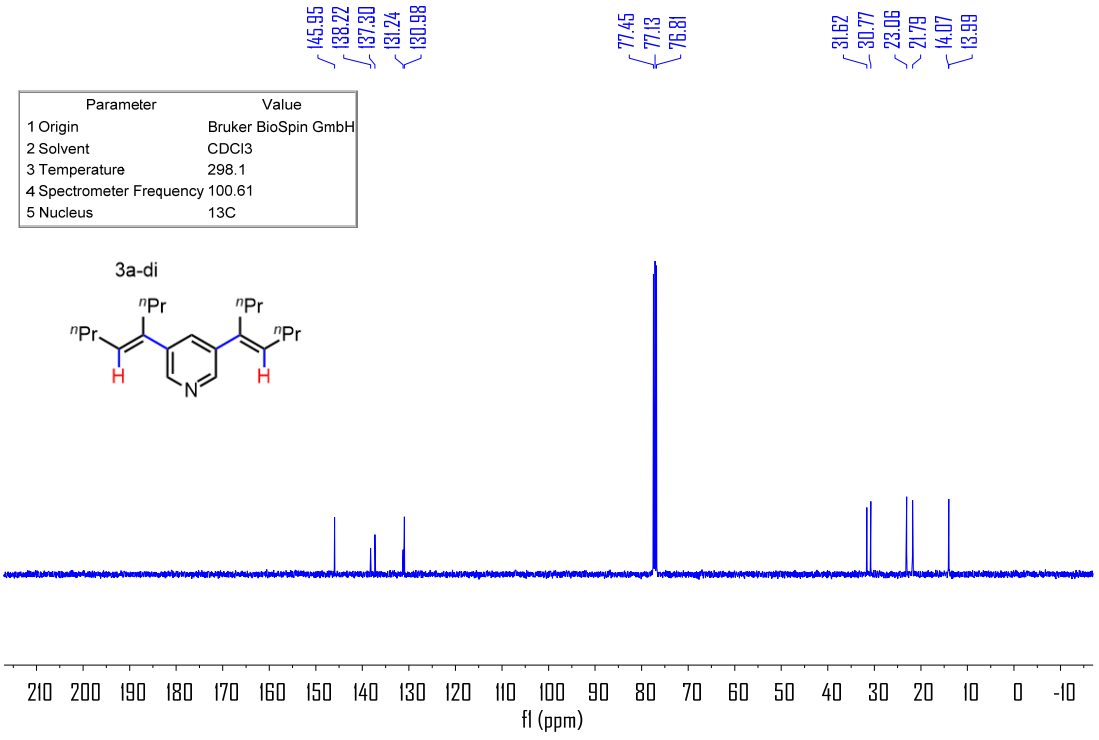
5.67
2.50
2.48
2.46
2.22
2.20
2.18
2.16
1.51
1.49
1.48
1.46
1.44
1.39
1.37
1.35
1.33
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3a-di
nPr
nPr
nPr
nPr
H
H
N
2.00
1.01
2.01
4.22
4.21
4.28
4.34
6.34
6.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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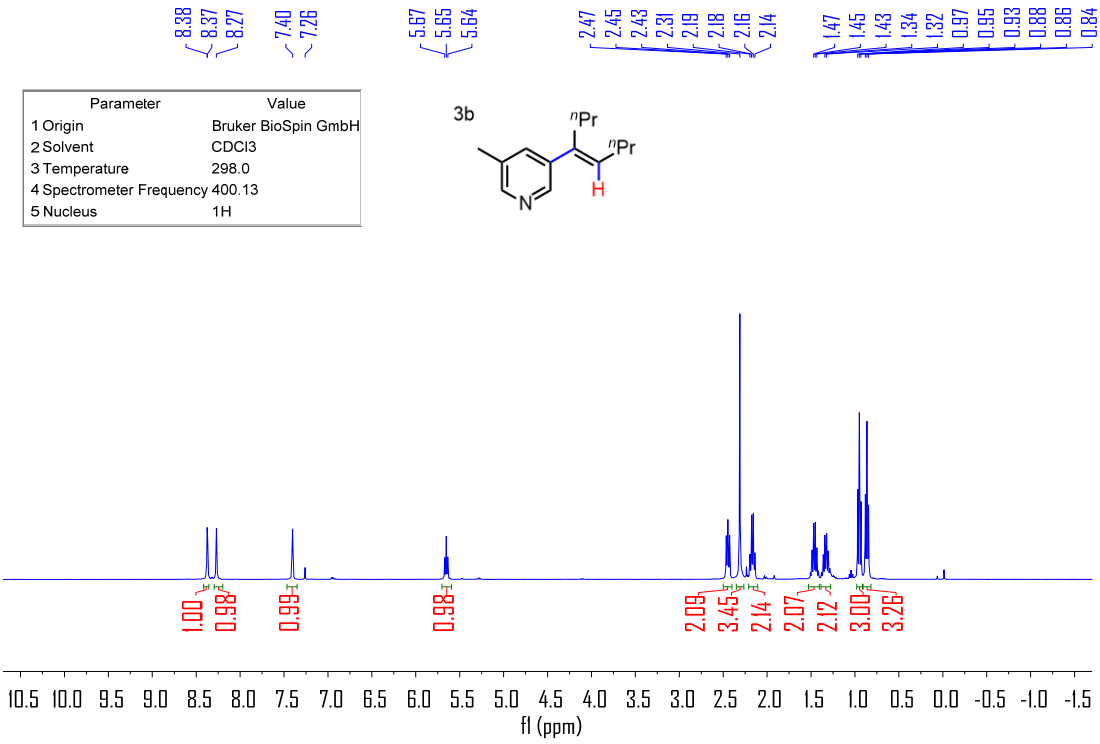
138.22
137.30
131.24
130.98
77.45
77.13
76.81
31.62
30.77
23.06
21.79
14.07
13.99
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3a-di
nPr
nPr
nPr
nPr
H
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.27
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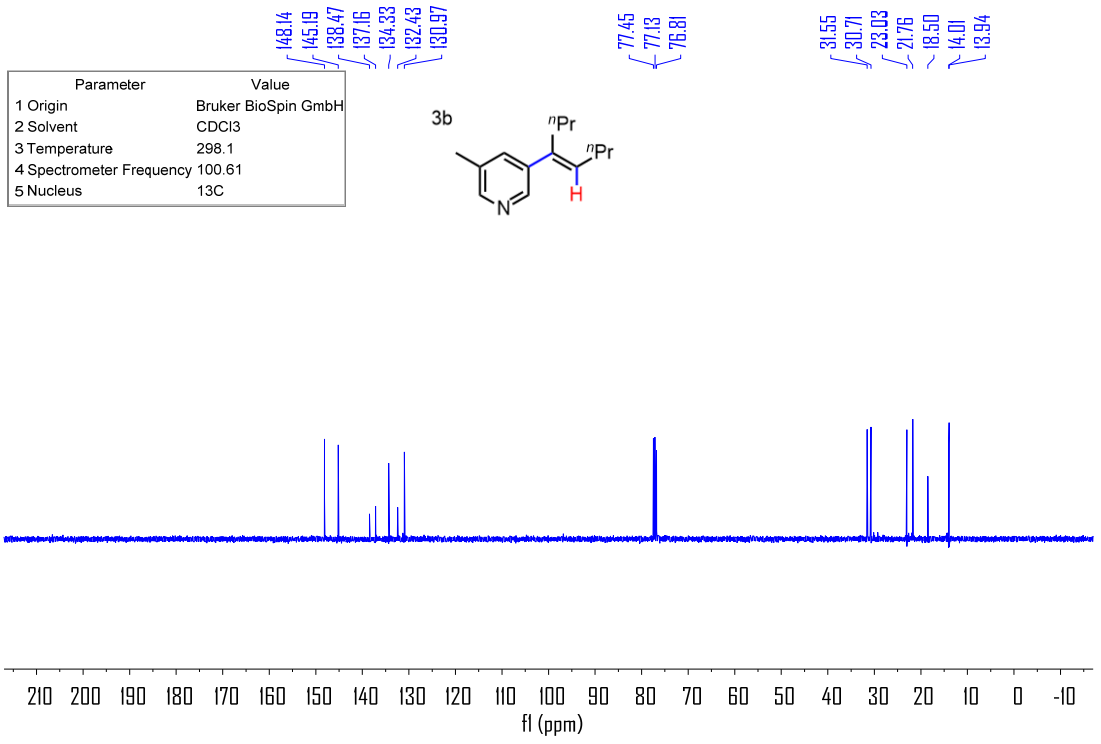
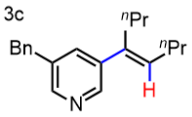
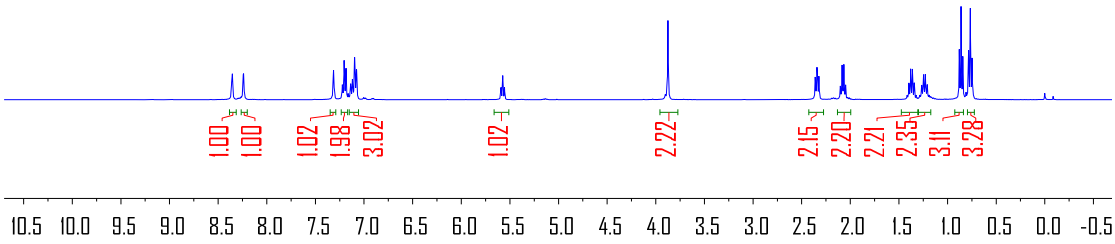
5.67
5.65
5.64
2.47
2.45
2.43
2.31
2.19
2.18
2.16
2.14
1.47
1.45
1.43
1.34
1.32
0.97
0.95
0.93
0.88
0.86
0.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3b
nPr
nPr
H
N
1.00
0.98
0.99
0.98
2.09
3.45
2.14
2.07
2.12
3.00
3.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

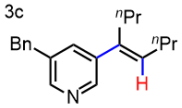

148.14
145.19
138.47
137.16
134.33
132.43
130.97
77.45
77.13
76.81
31.55
30.71
23.03
21.76
18.50
14.01
13.94
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3b
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

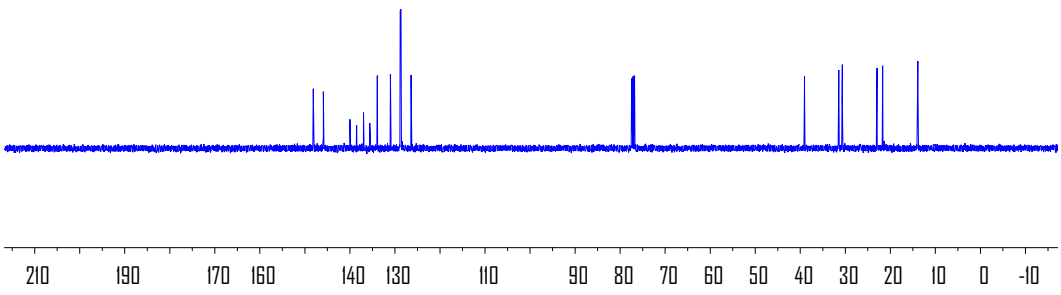
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

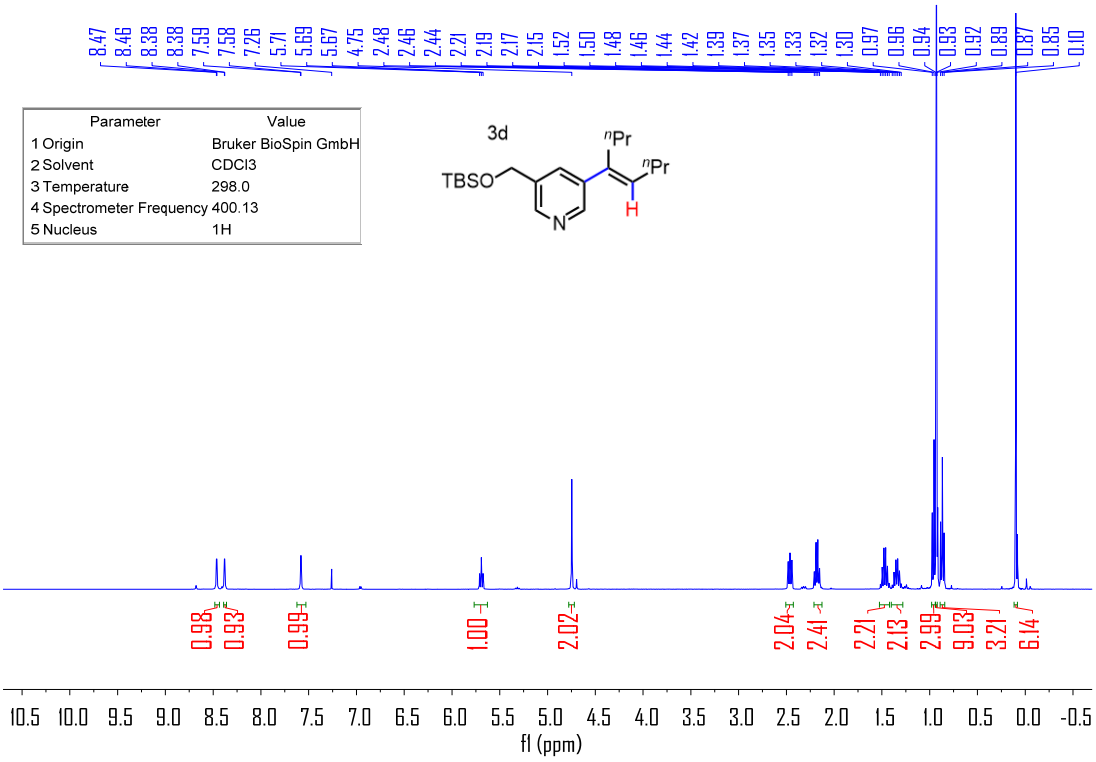


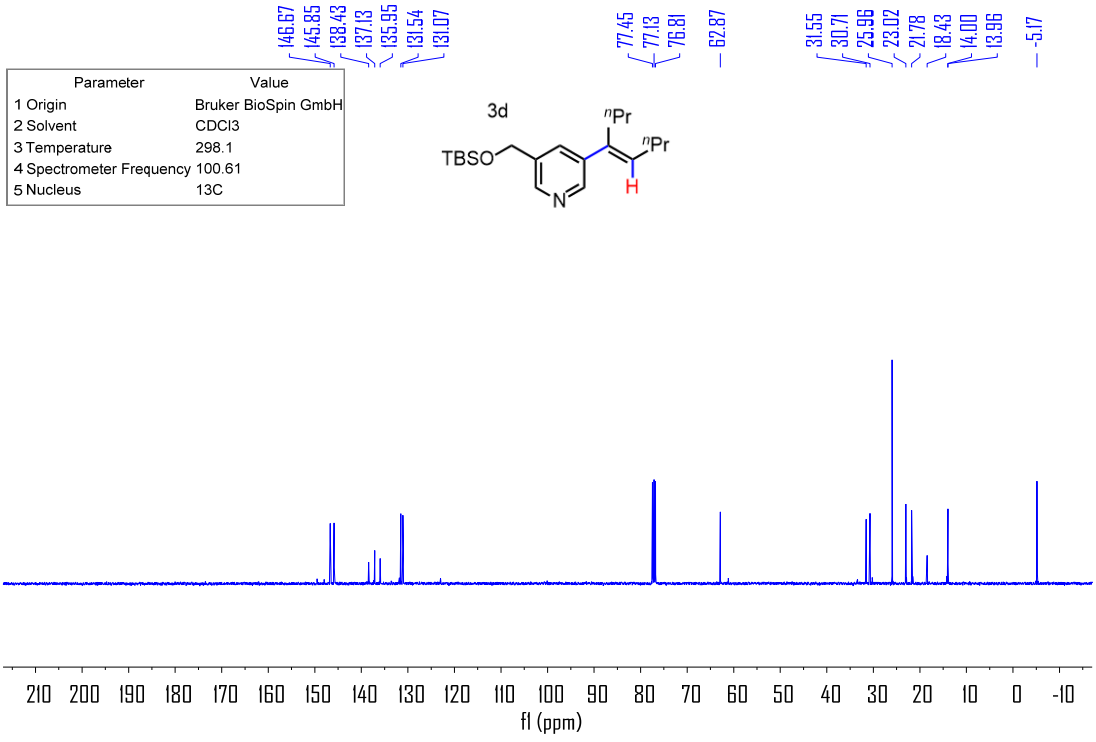


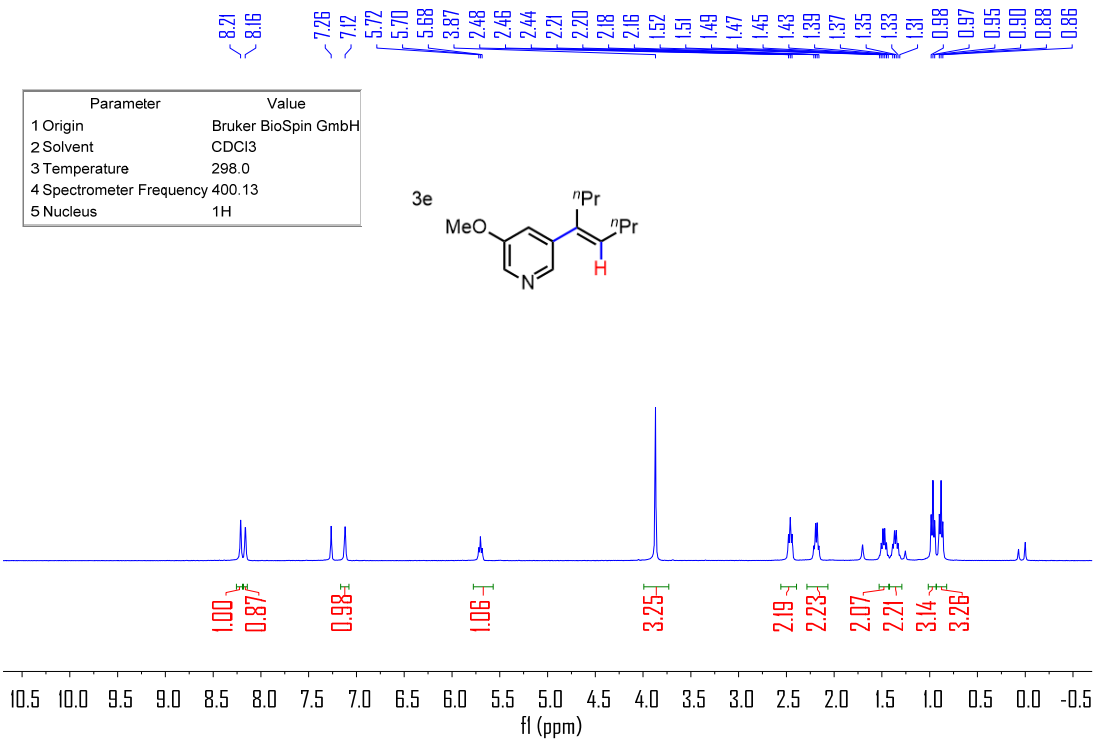
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Spectrometer Frequency	100.61
5 Nucleus	13C

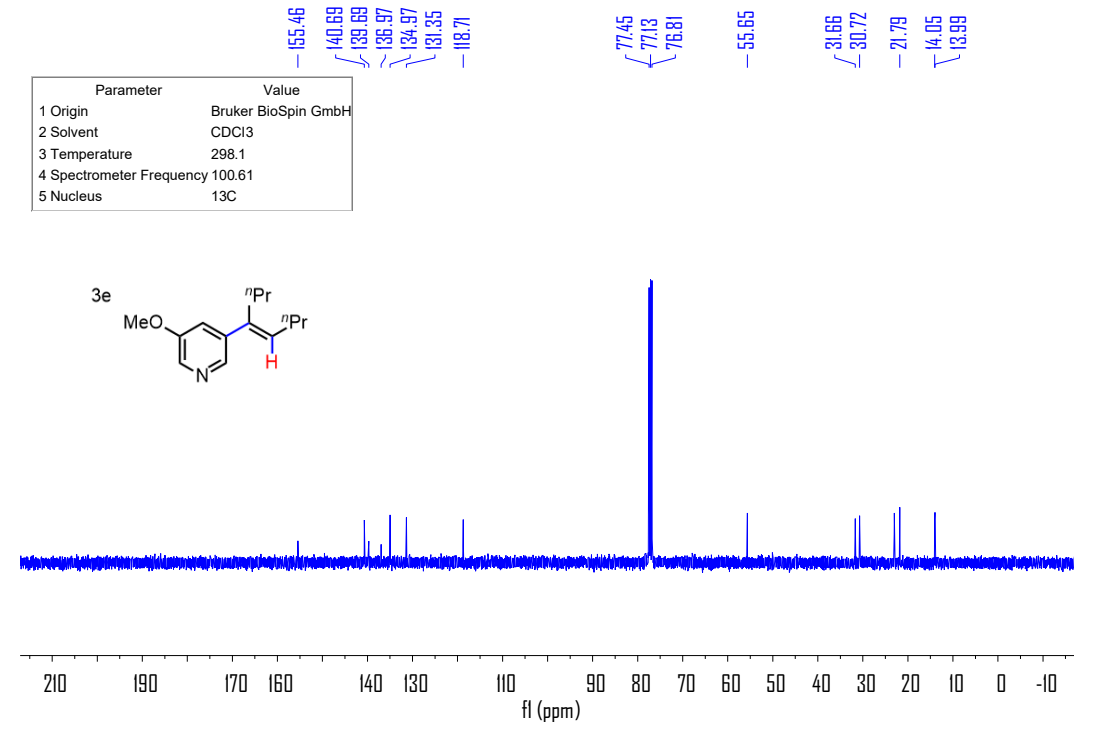





8.47 8.46 8.38 8.38 7.59 7.58 7.26 5.71 5.69 5.67 4.75 2.48 2.46 2.44 2.21 2.19 2.17 2.15 1.52 1.50 1.48 1.46 1.44 1.42 1.39 1.37 1.35 1.33 1.32 1.30 0.97 0.96 0.94 0.93 0.92 0.89 0.87 0.85 0.10
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3d
TBSO
nPr
nPr
H
N
0.98 0.93 0.99 1.00 2.02 2.04 2.41 2.21 2.13 2.99 9.03 3.21 6.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

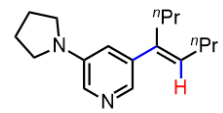

146.67 145.85 138.43 137.13 135.95 131.54 131.07 77.45 77.13 76.81 62.87 31.55 30.71 25.96 23.02 21.78 18.43 14.00 13.96 -5.17
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3d
TBSO
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

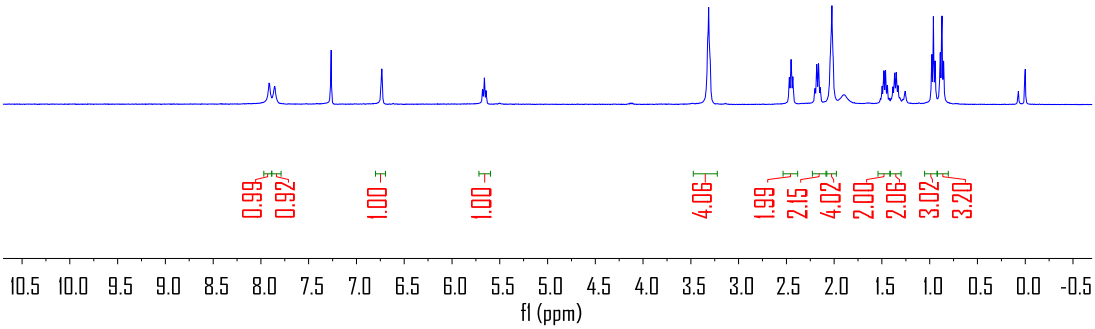

8.21
8.16
7.26
7.12
5.72
5.70
5.68
3.87
2.48
2.46
2.44
2.21
2.20
2.18
2.16
1.52
1.51
1.49
1.47
1.45
1.43
1.39
1.37
1.35
1.33
1.31
0.98
0.97
0.95
0.90
0.88
0.86
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3e
MeO
nPr
nPr
H
N
1.00
0.87
0.98
1.06
3.25
2.19
2.23
2.07
2.21
3.14
3.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

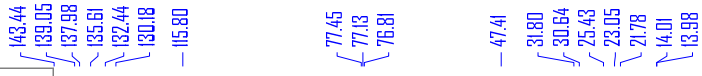

155.46
140.69
139.69
136.97
134.97
131.35
118.71
77.45
77.13
76.81
55.65
31.66
30.72
21.79
14.05
13.99
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3e
MeO
nPr
nPr
H
N
210 190 170 160 140 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

3f

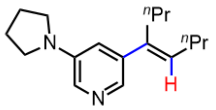


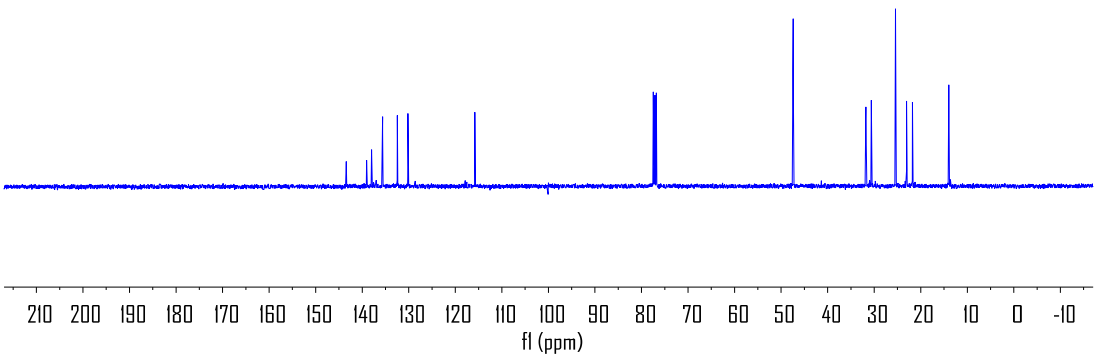




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Spectrometer Frequency	100.61
5 Nucleus	13C

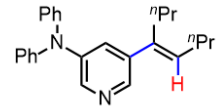
3f

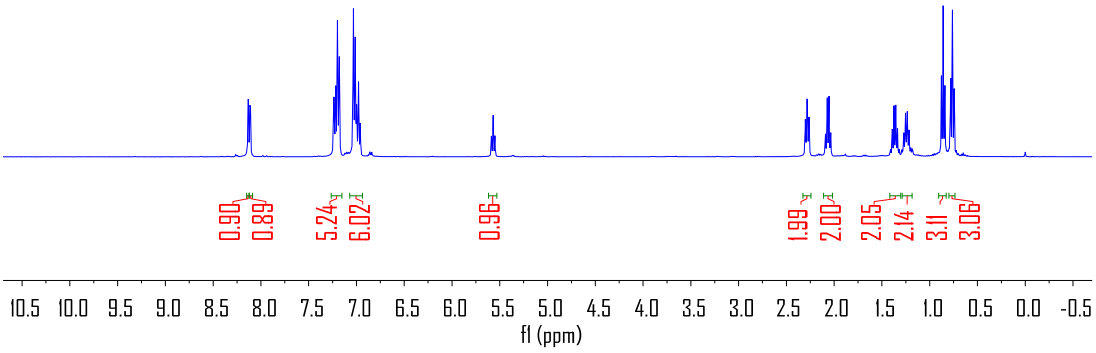


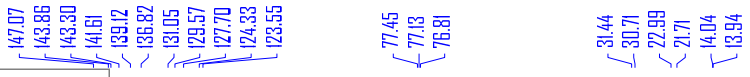


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

3g

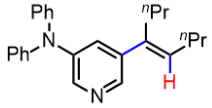


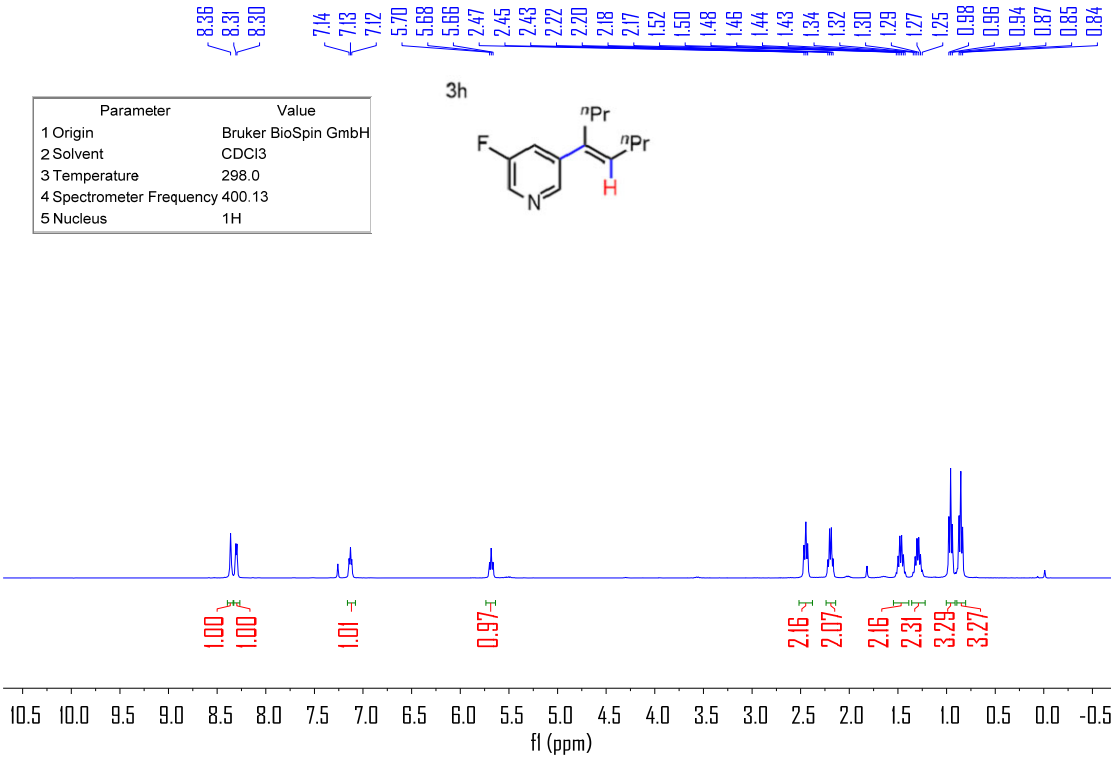


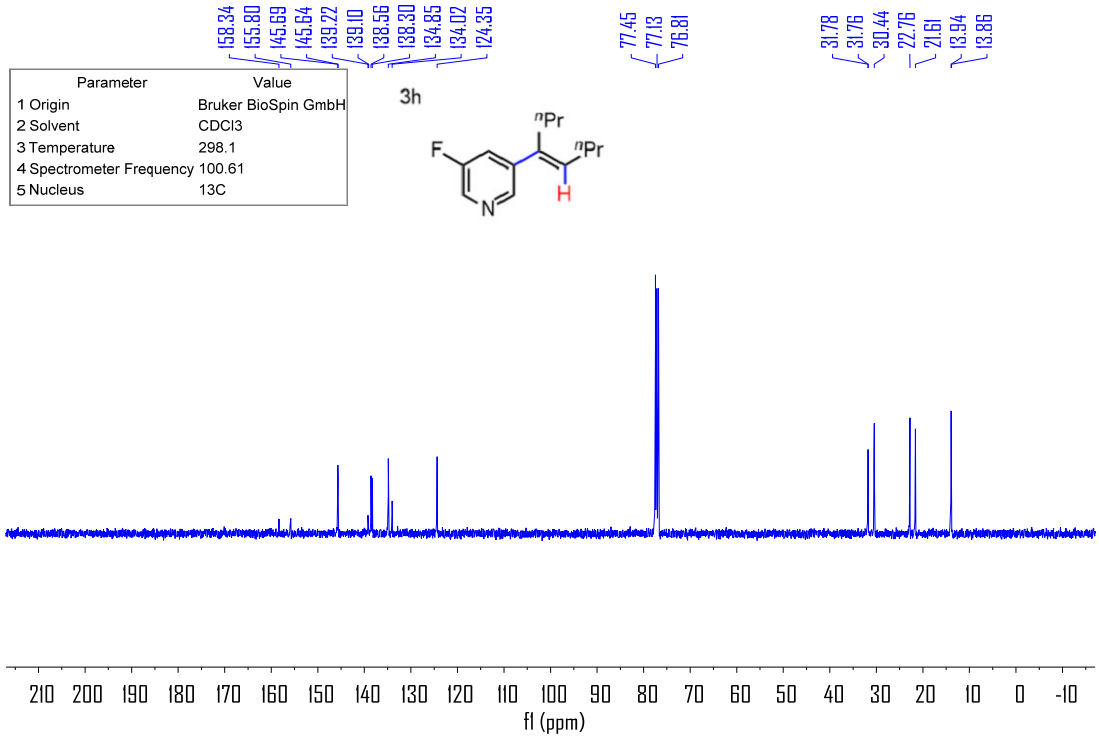


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Spectrometer Frequency	100.61
5 Nucleus	13C

3g




8.35
8.31
8.30
7.14
7.13
7.12
5.70
5.68
5.66
2.47
2.45
2.43
2.22
2.20
2.18
2.17
1.52
1.50
1.48
1.46
1.44
1.43
1.34
1.32
1.30
1.29
1.27
1.25
0.98
0.96
0.94
0.87
0.85
0.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3h
nPr
nPr
F
N
H
1.00
1.00
1.01
0.97
2.16
2.07
2.16
2.31
3.29
3.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.34
155.80
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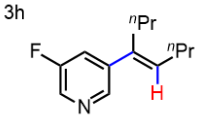
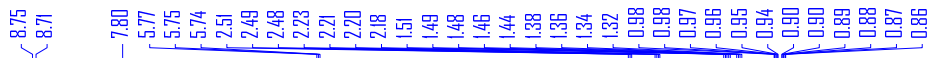
145.64
139.22
139.10
138.56
138.30
134.85
134.02
124.35
77.45
77.13
76.81
31.78
31.76
30.44
22.76
21.61
13.94
13.86
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3h
nPr
nPr
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

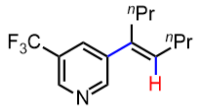
3h

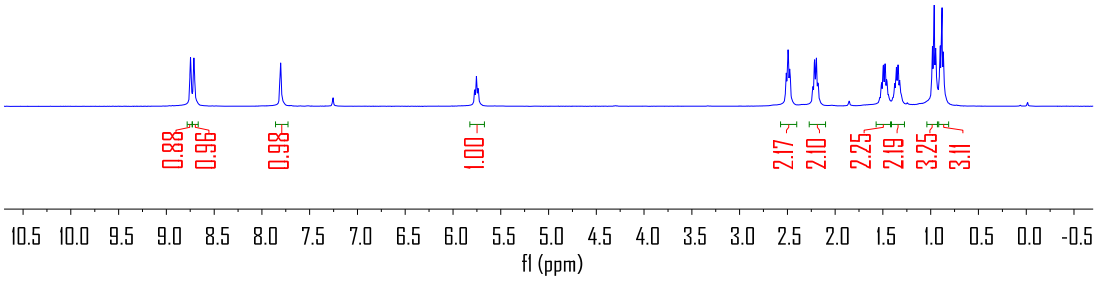


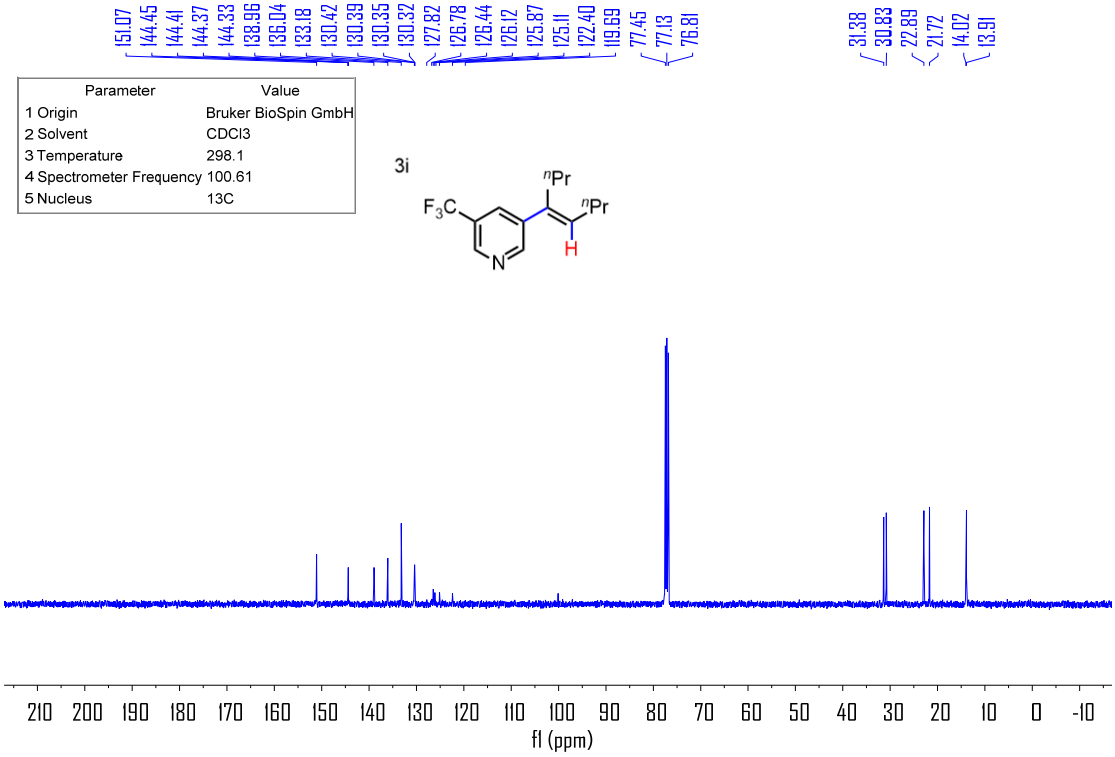


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

3i






151.07
144.45
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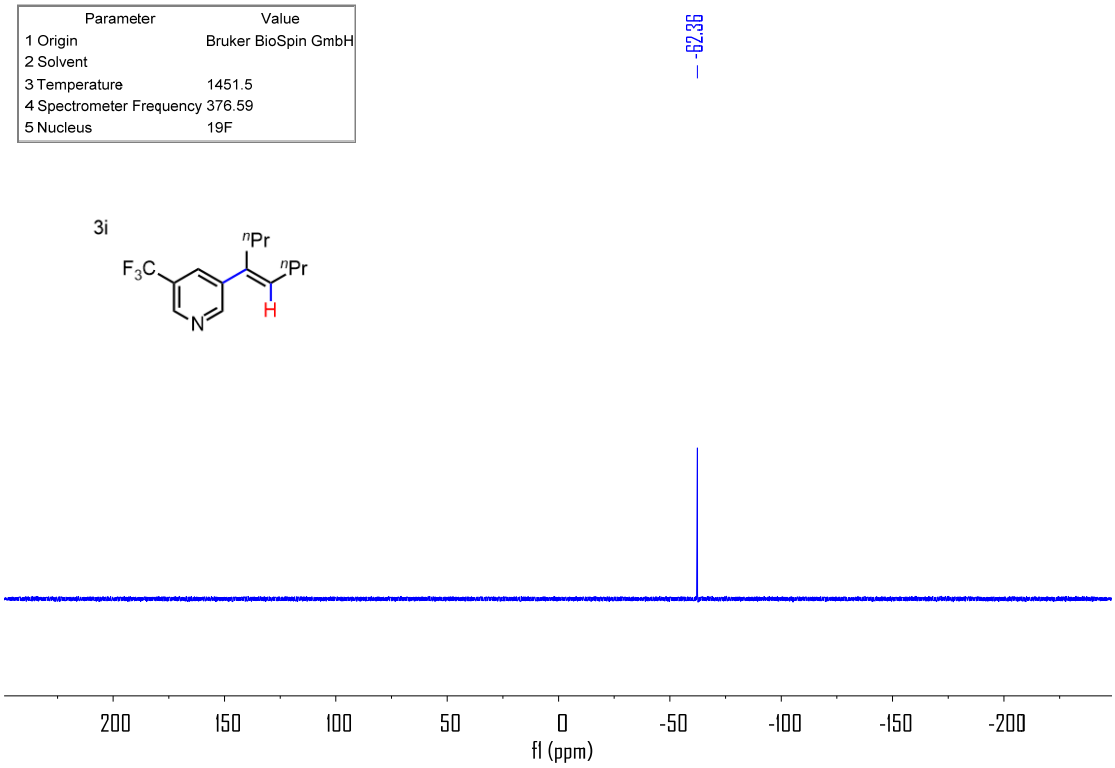
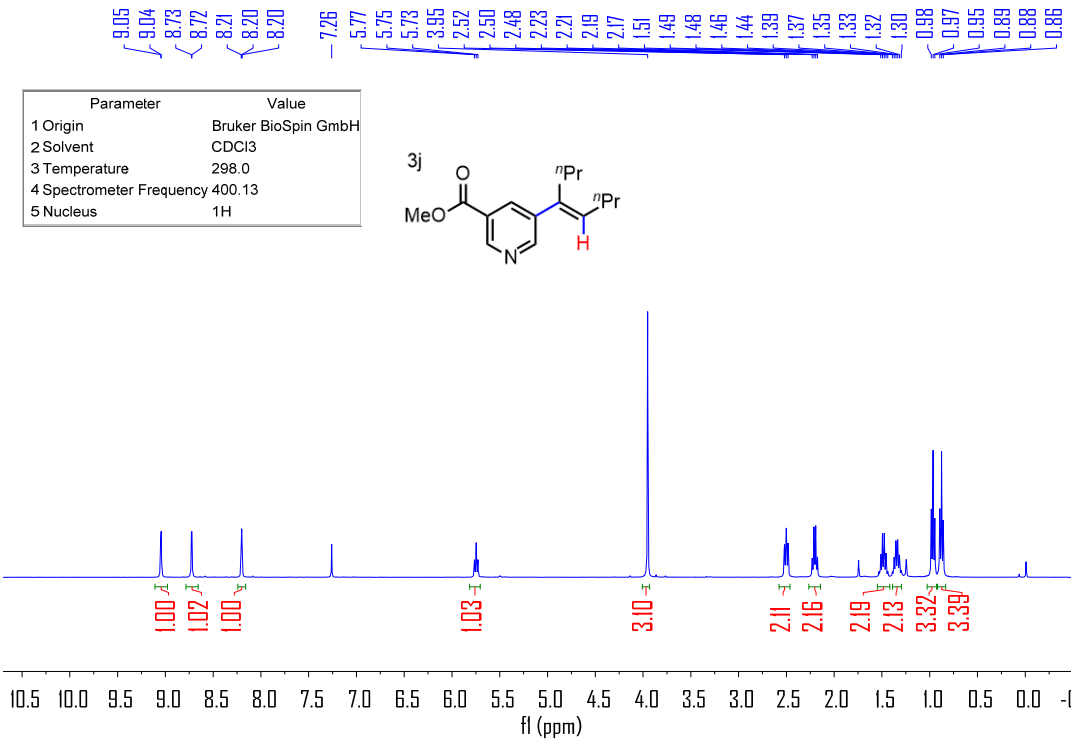
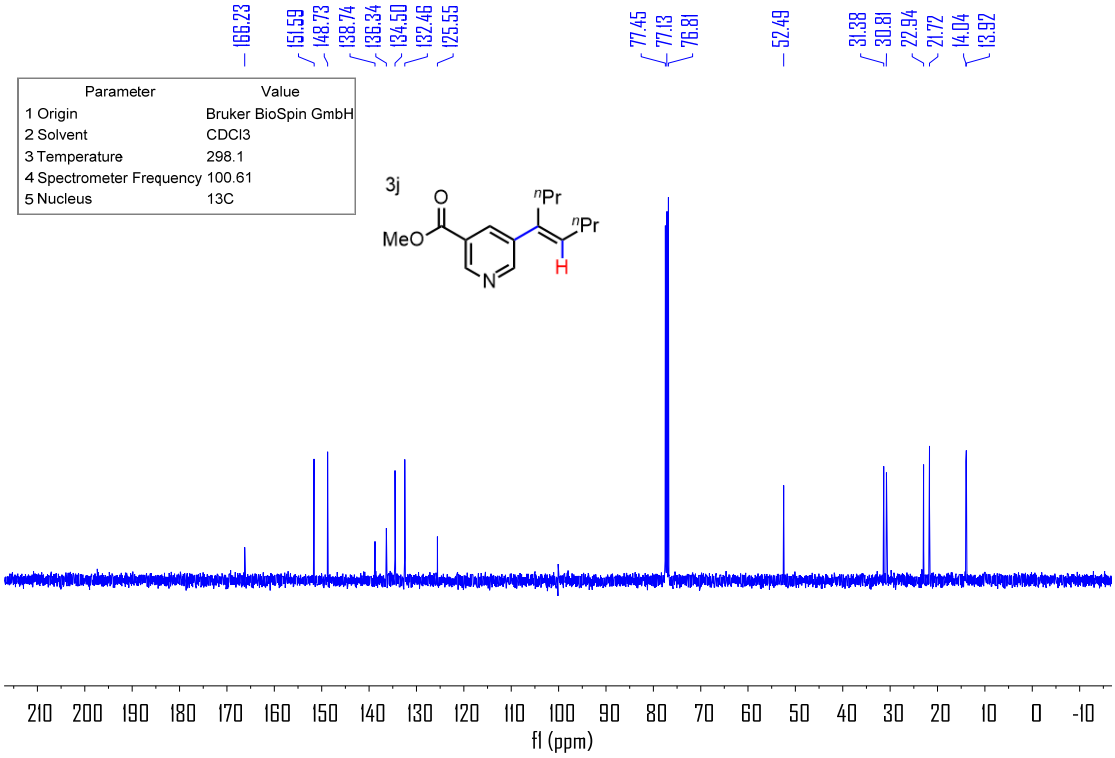
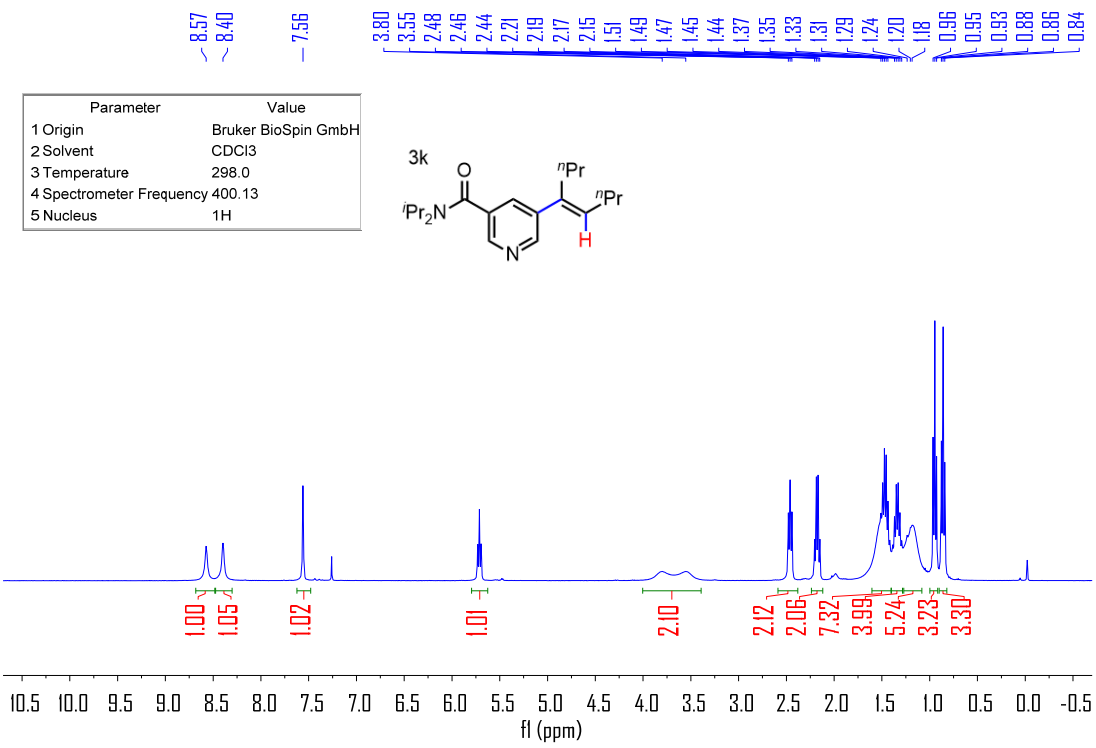
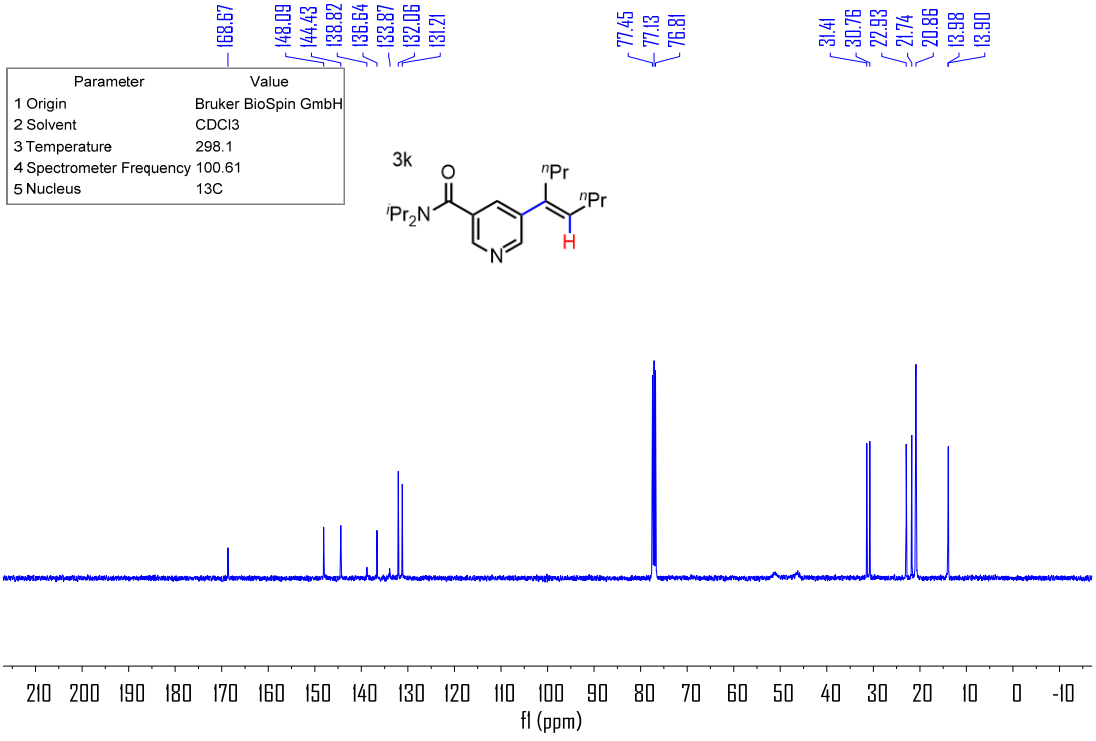
144.33
138.96
136.04
133.18
130.42
130.39
130.35
130.32
127.82
126.78
126.44
126.12
125.87
125.11
122.40
119.69
77.45
77.13
76.81
31.38
30.83
22.89
21.72
14.02
13.91
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3i
nPr
F3C
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.36
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1451.5
4 Spectrometer Frequency 376.59
5 Nucleus 19F
3i
nPr
F3C
nPr
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)


9.05 9.04 8.73 8.72 8.21 8.20 8.20 7.26 5.77 5.75 5.73 3.95 2.52 2.50 2.48 2.23 2.21 2.19 2.17 1.51 1.49 1.48 1.46 1.44 1.39 1.37 1.35 1.33 1.32 1.30 0.98 0.97 0.95 0.89 0.88 0.86
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3j
MeO
O
N
nPr
nPr
H
1.00 1.02 1.00 1.03 3.10 2.11 2.16 2.19 2.13 3.32 3.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

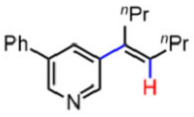

166.23 151.59 148.73 138.74 136.34 134.50 132.46 125.55 77.45 77.13 76.81 52.49 31.38 30.81 22.94 21.72 14.04 13.92
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3j
MeO
O
N
nPr
nPr
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

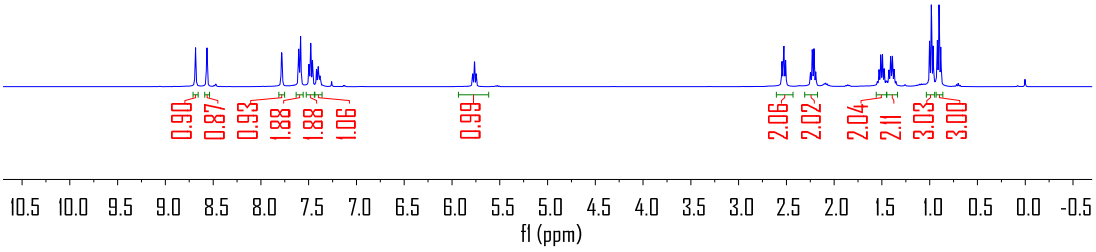

8.57
8.40
7.56
3.80
3.55
2.48
2.46
2.44
2.21
2.19
2.17
2.15
1.51
1.49
1.47
1.45
1.44
1.37
1.35
1.33
1.31
1.29
1.24
1.20
1.18
0.96
0.95
0.93
0.88
0.86
0.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3k
1.00
1.05
1.02
1.01
2.10
2.12
2.06
7.32
3.99
5.24
3.23
3.30
f1 (ppm)


168.67
148.09
144.43
138.82
136.64
133.87
132.06
131.21
77.45
77.13
76.81
31.41
30.76
22.93
21.74
20.86
13.98
13.90
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3k
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

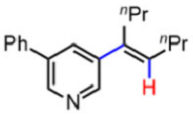
3l

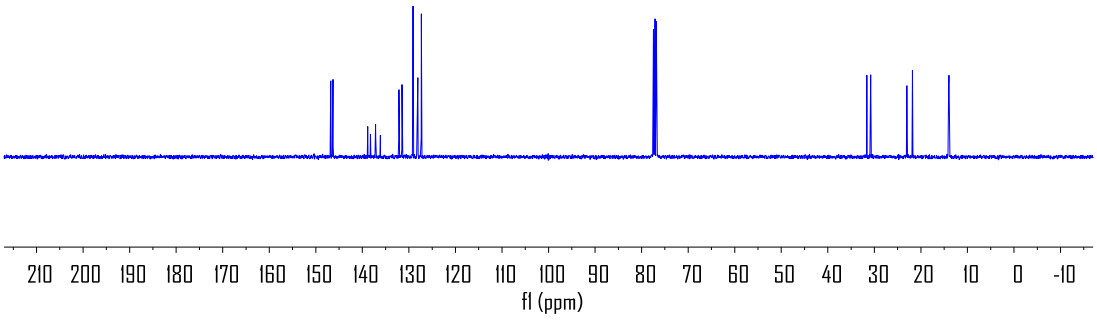


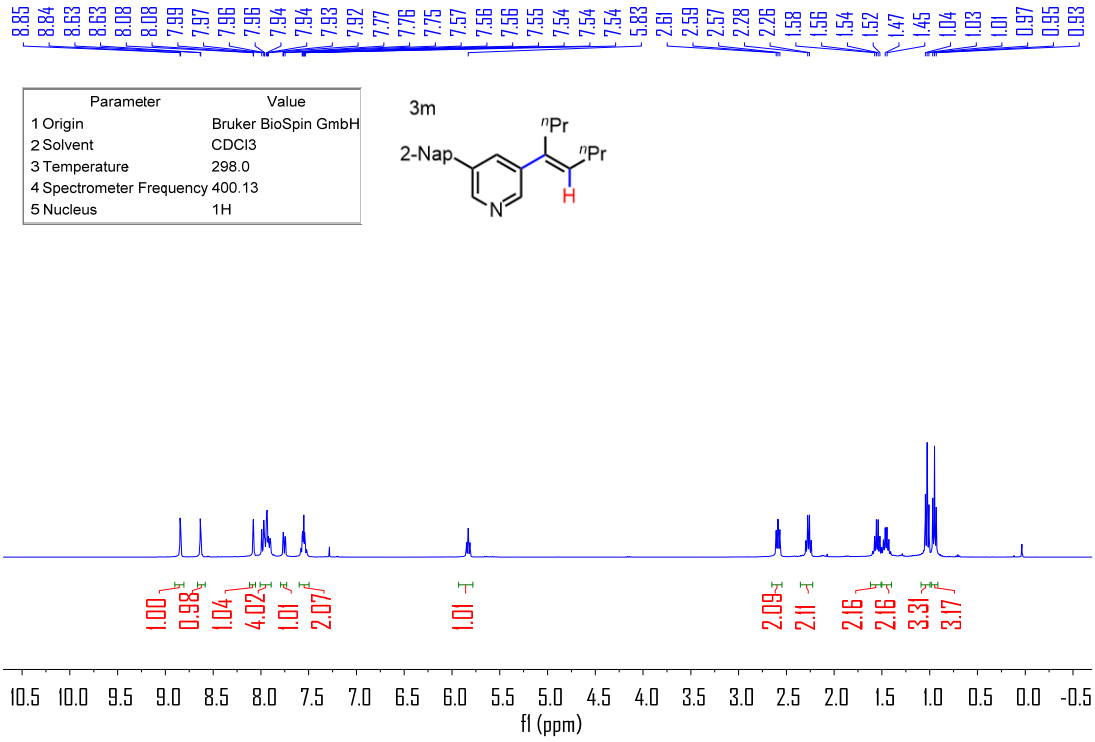


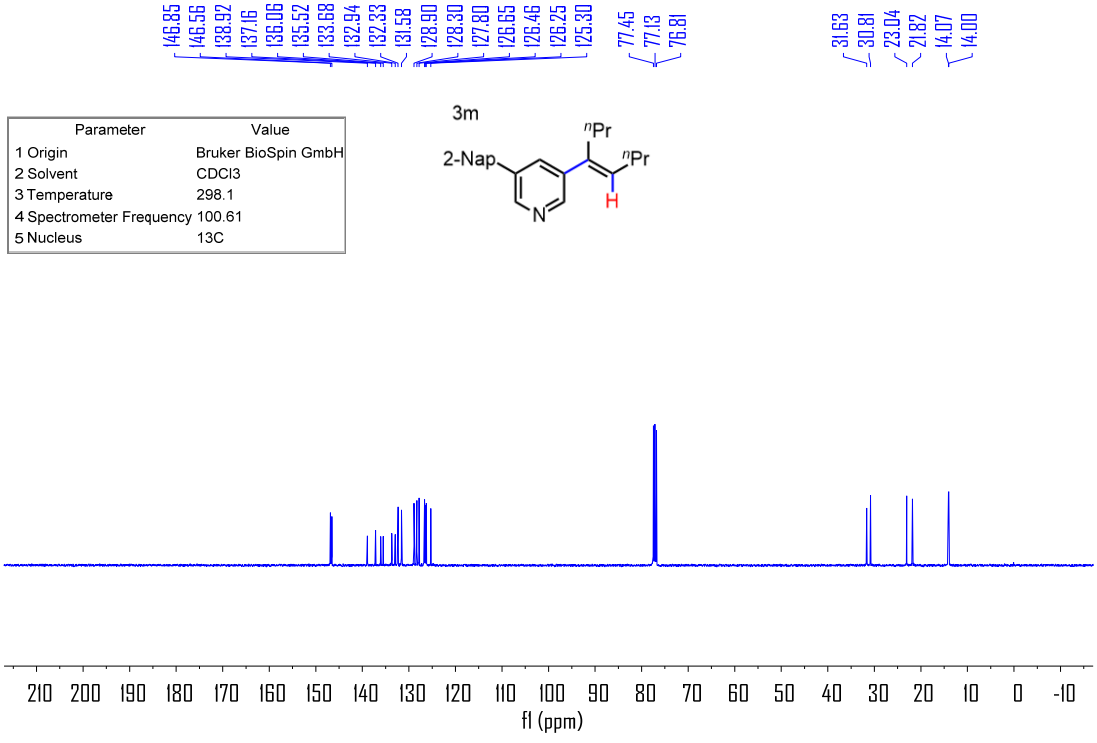
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Spectrometer Frequency	100.61
5 Nucleus	13C

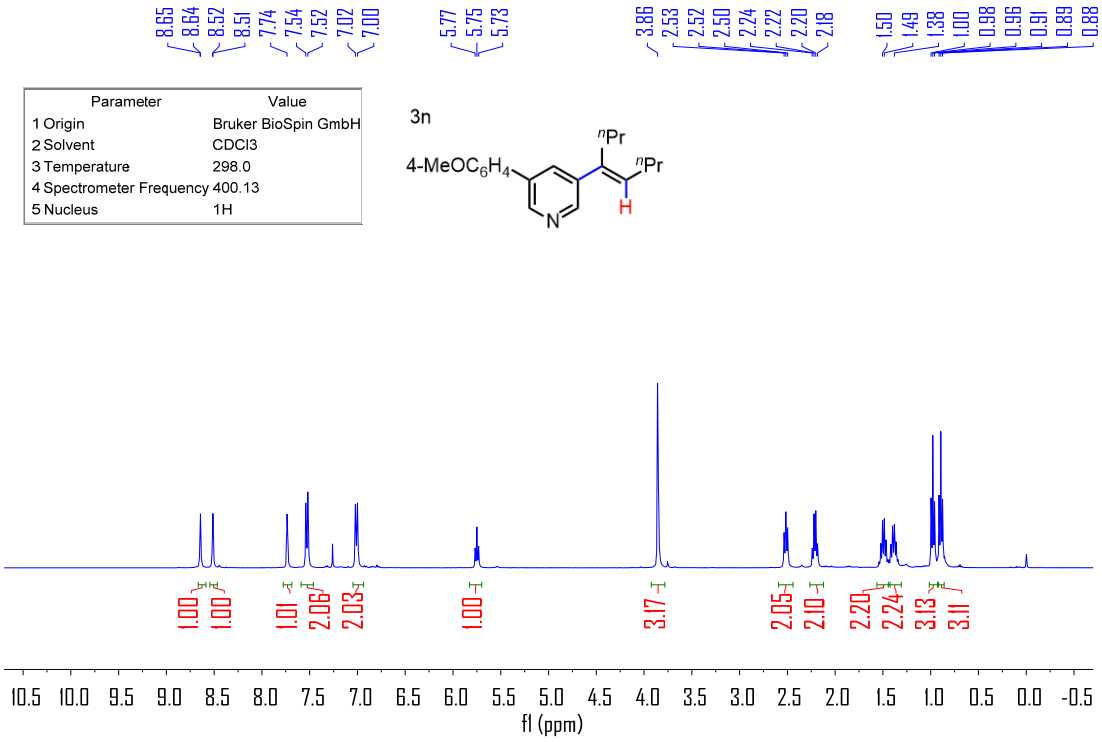
3l

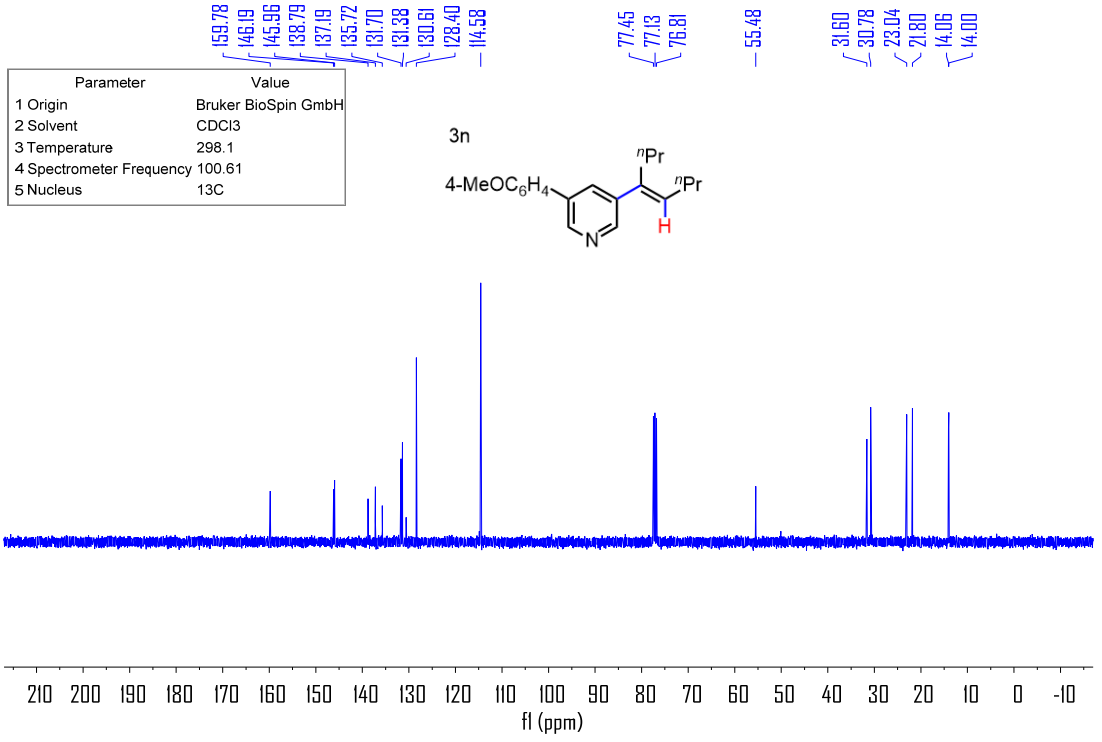


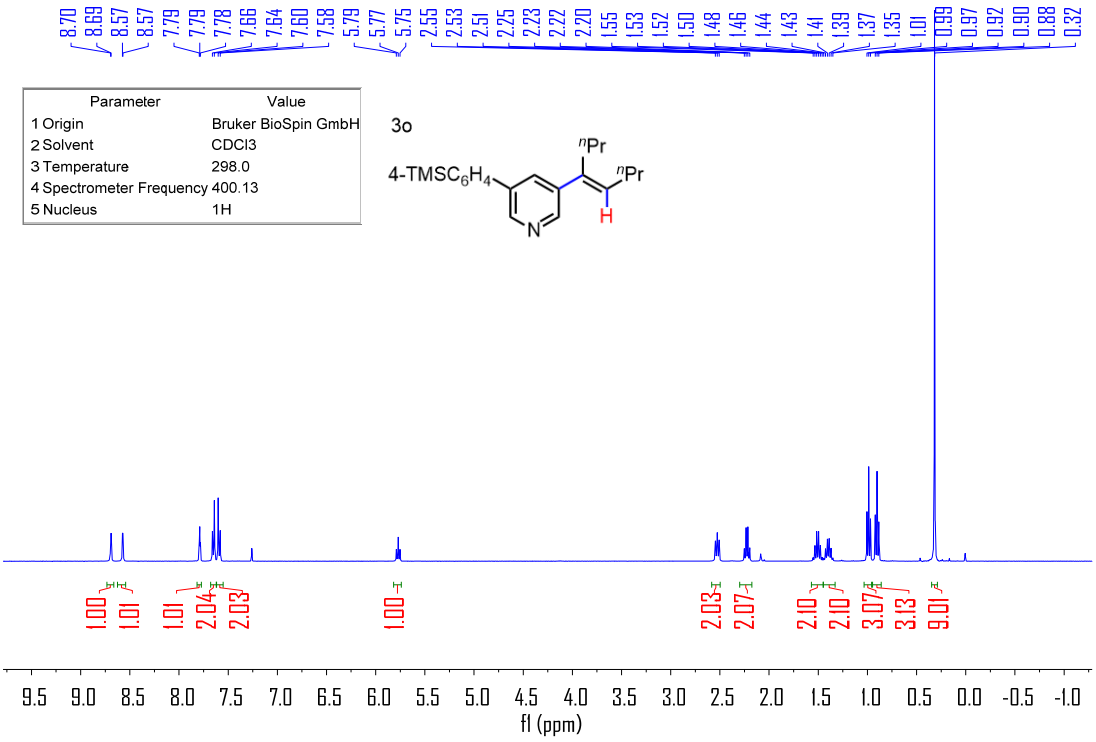


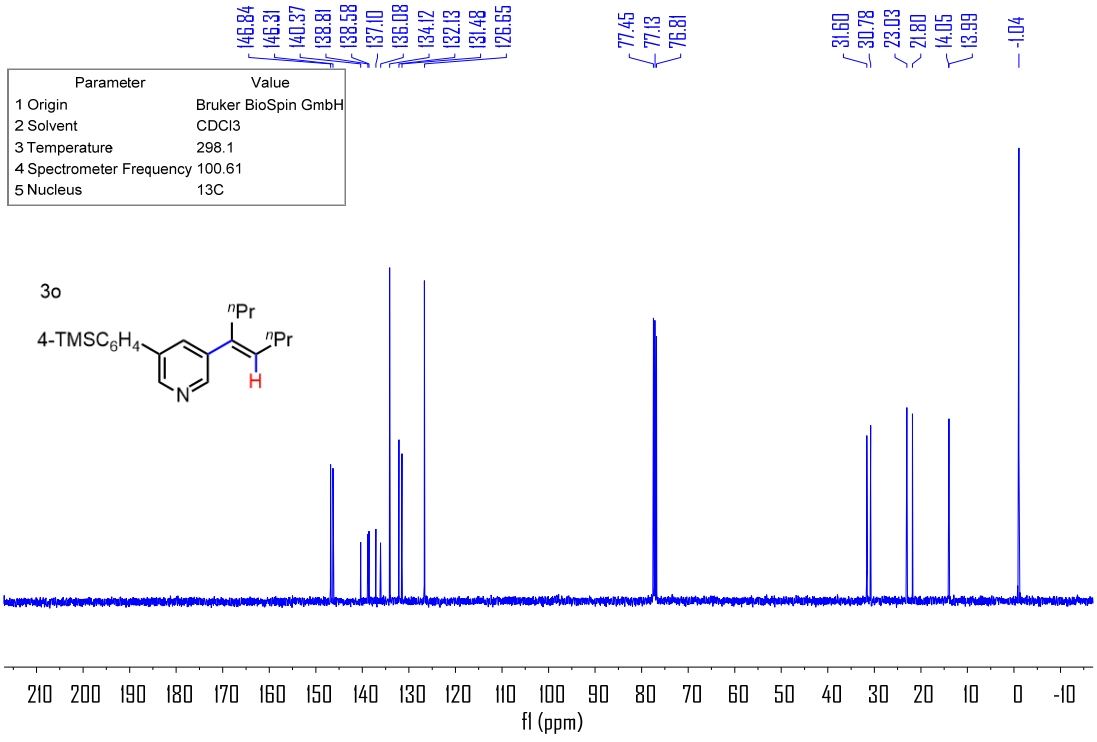

8.85 8.84 8.63 8.63 8.08 8.08 7.99 7.97 7.96 7.96 7.94 7.94 7.93 7.92 7.77 7.76 7.75 7.57 7.56 7.56 7.55 7.54 7.54 7.54 5.83 2.61 2.59 2.57 2.28 2.26 1.58 1.56 1.54 1.52 1.47 1.45 1.04 1.03 1.01 0.97 0.95 0.93
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3m
2-Nap
nPr
nPr
H
N
1.00 0.98 1.04 4.02 1.01 2.07 1.01 2.09 2.11 2.16 2.16 3.31 3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

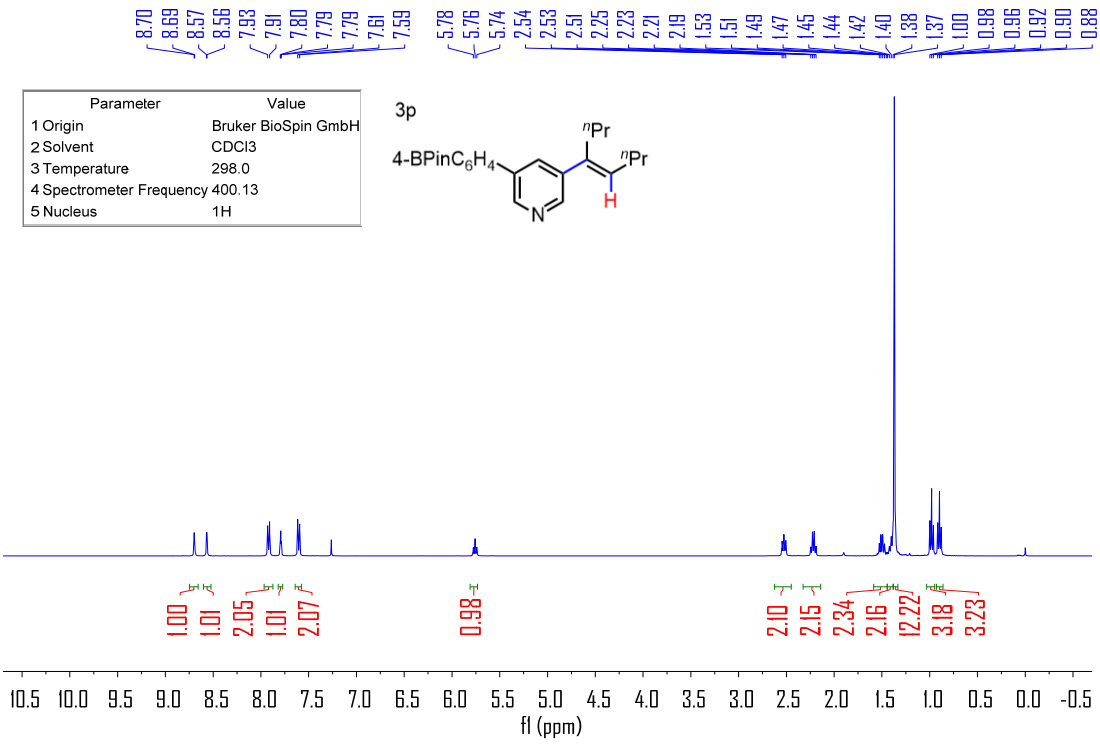

146.85 146.56 138.92 137.16 136.06 135.52 133.68 132.94 132.33 131.58 128.90 128.30 127.80 126.65 126.46 126.25 125.30 77.45 77.13 76.81 31.63 30.81 23.04 21.82 14.07 14.00
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3m
2-Nap
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

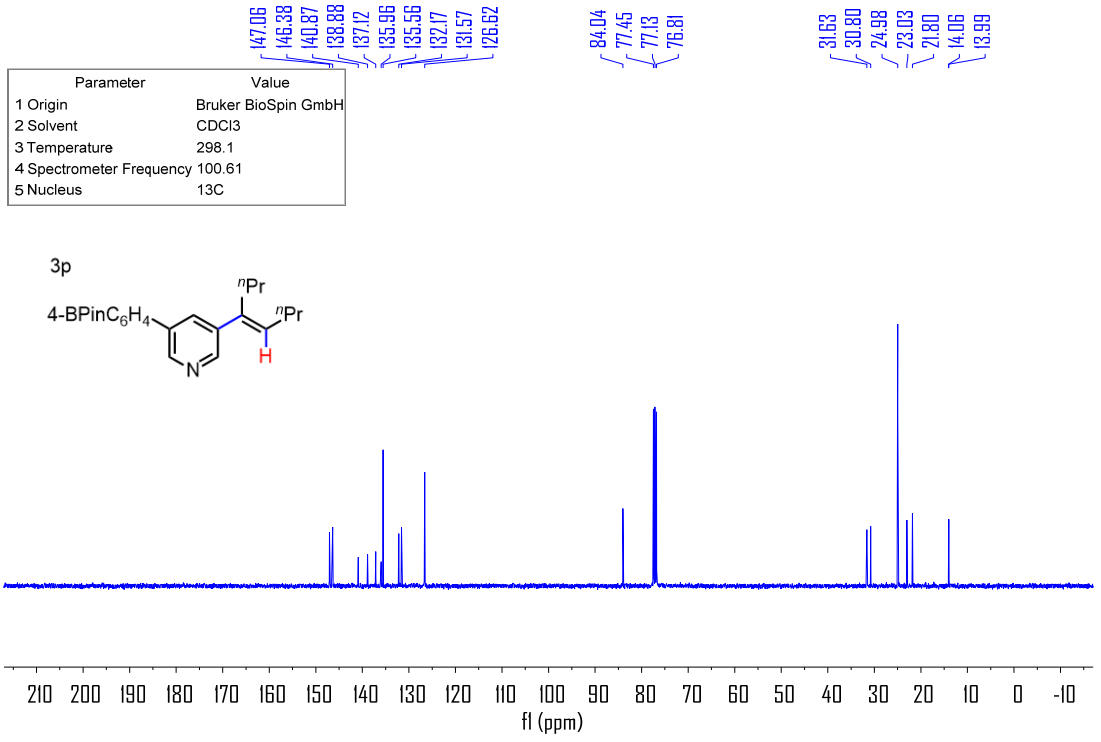

8.65
8.64
8.52
8.51
7.74
7.54
7.52
7.02
7.00
5.77
5.75
5.73
3.86
2.53
2.52
2.50
2.24
2.22
2.20
2.18
1.50
1.49
1.38
1.00
0.98
0.96
0.91
0.89
0.88
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3n
4-MeOC6H4
nPr
nPr
H
N
1.00
1.00
1.01
2.06
2.03
1.00
3.17
2.05
2.10
2.20
2.24
3.13
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

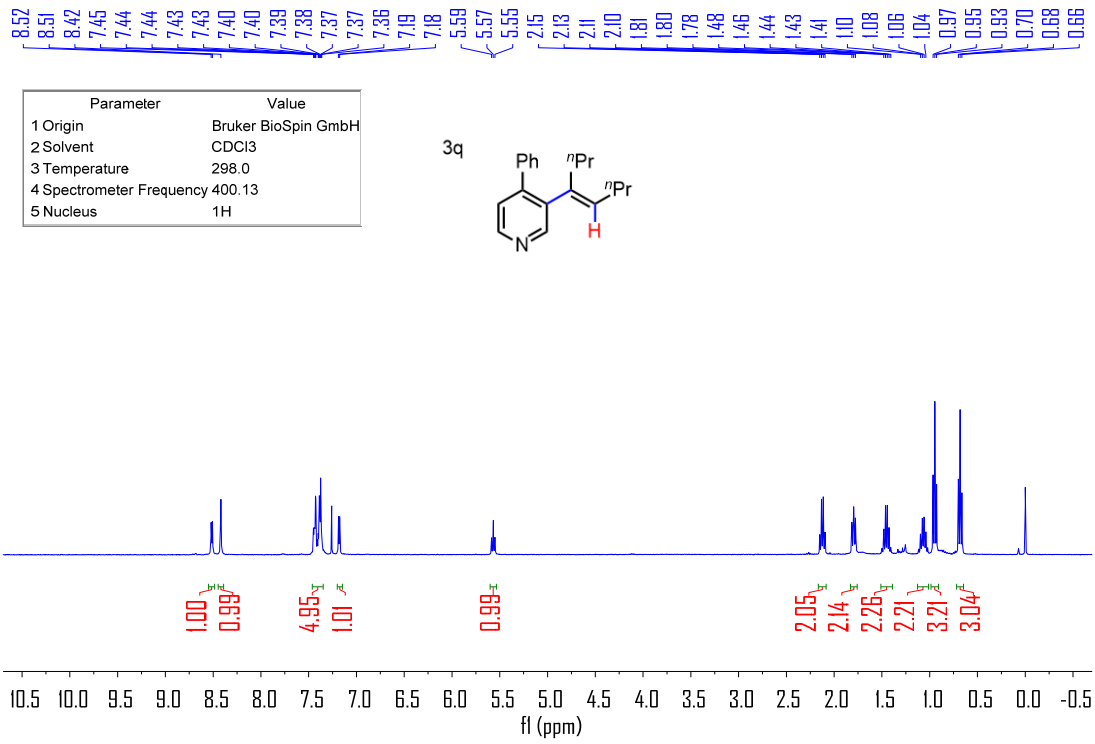

159.78
146.19
145.96
138.79
137.19
135.72
131.70
131.38
130.61
128.40
114.58
77.45
77.13
76.81
55.48
31.60
30.78
23.04
21.80
14.06
14.00
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3n
4-MeOC6H4
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

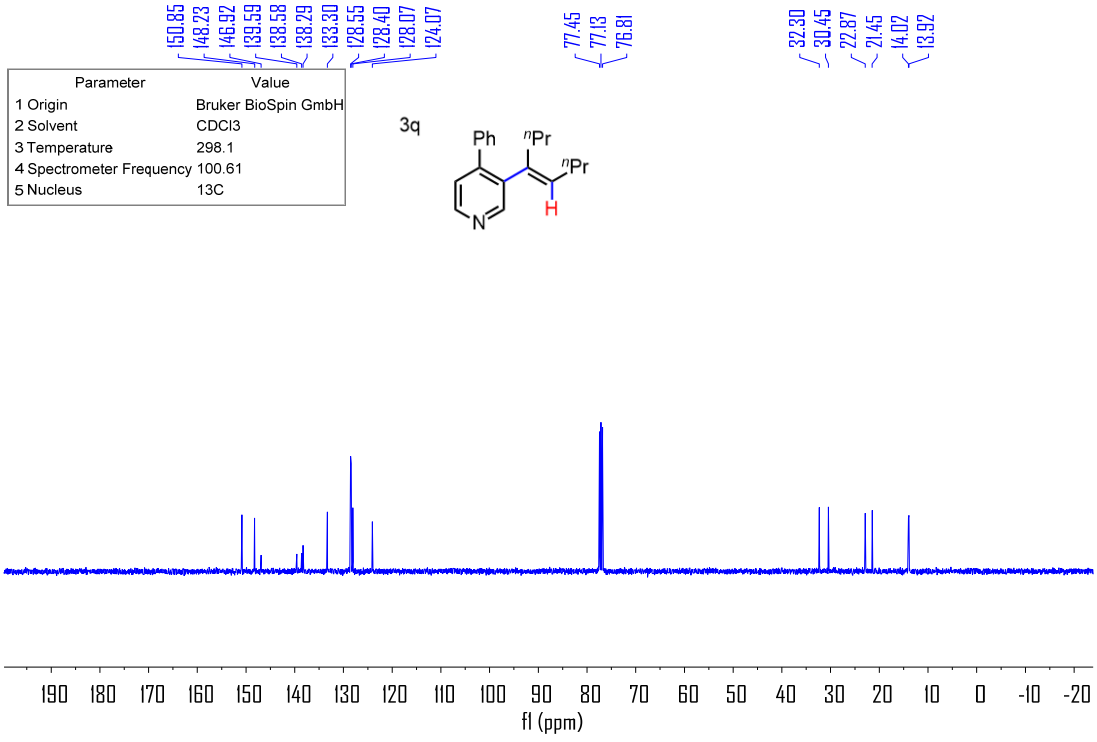

8.70 8.69 8.57 8.57 7.79 7.79 7.78 7.66 7.64 7.60 7.58 5.79 5.77 5.75 2.55 2.53 2.51 2.25 2.23 2.22 2.20 1.55 1.53 1.52 1.50 1.48 1.46 1.44 1.43 1.41 1.39 1.37 1.35 1.01 0.99 0.97 0.92 0.90 0.88 0.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3o
4-TMSC6H4
nPr
nPr
H
N
1.00 1.01 1.01 2.04 2.03 1.00 2.03 2.07 2.10 2.10 3.07 3.13 9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


146.84 146.31 140.37 138.81 138.58 137.10 136.08 134.12 132.13 131.48 126.65 77.45 77.13 76.81 31.60 30.78 23.03 21.80 14.05 13.99 -1.04
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3o
4-TMSC6H4
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.70 8.69 8.57 8.56 7.93 7.91 7.80 7.79 7.79 7.61 7.59
5.78 5.76 5.74 2.54 2.53 2.51 2.25 2.23 2.21 2.19 1.53 1.51 1.49 1.47 1.45 1.44 1.42 1.40 1.38 1.37 1.00 0.98 0.96 0.92 0.90 0.88
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3p
4-BPinC6H4
nPr
nPr
H
N
1.00 1.01 2.05 1.01 2.07 0.98 2.10 2.15 2.34 2.16 12.22 3.18 3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

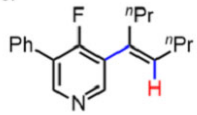

147.06 146.38 140.87 138.88 137.12 135.96 135.56 132.17 131.57 126.62
84.04 77.45 77.13 76.81
31.63 30.80 24.98 23.03 21.80 14.06 13.99
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3p
4-BPinC6H4
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

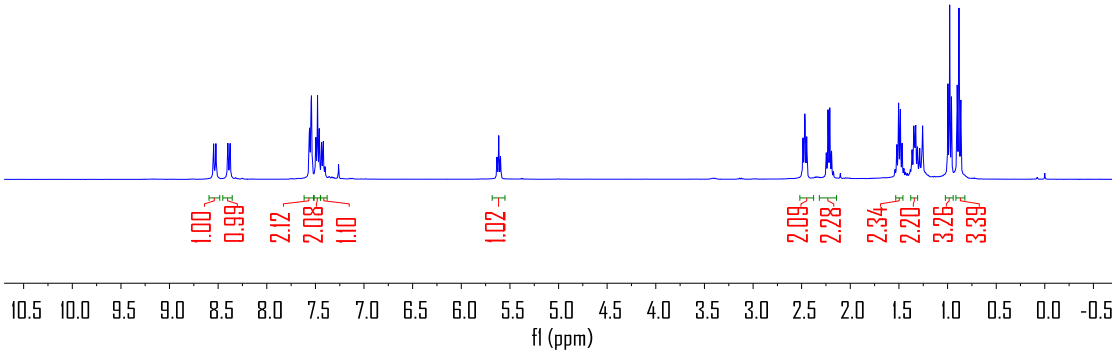

8.52 8.51 8.42 7.45 7.44 7.44 7.43 7.43 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.19 7.18 5.59 5.57 5.55 2.15 2.13 2.11 2.10 1.81 1.80 1.78 1.48 1.46 1.44 1.43 1.41 1.10 1.08 1.06 1.04 0.97 0.95 0.93 0.70 0.68 0.66
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3q
Ph
nPr
nPr
H
N
1.00 0.99 4.95 1.01 0.99 2.05 2.14 2.26 2.21 3.21 3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


150.85 148.23 146.92 139.59 138.58 138.29 133.30 128.55 128.40 128.07 124.07 77.45 77.13 76.81 32.30 30.45 22.87 21.45 14.02 13.92
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3q
Ph
nPr
nPr
H
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

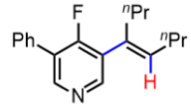
3r

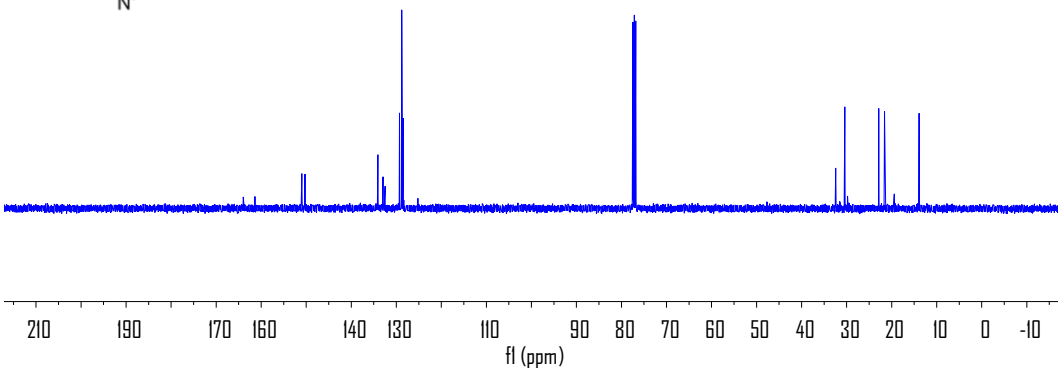




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Spectrometer Frequency	100.61
5 Nucleus	13C

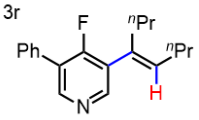
3r



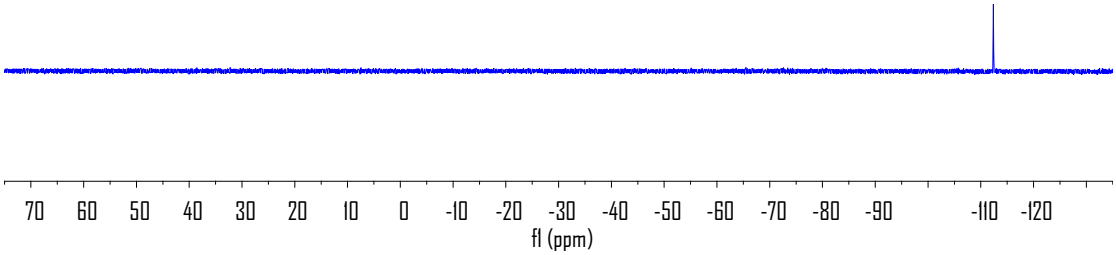


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

3r

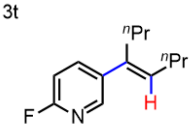


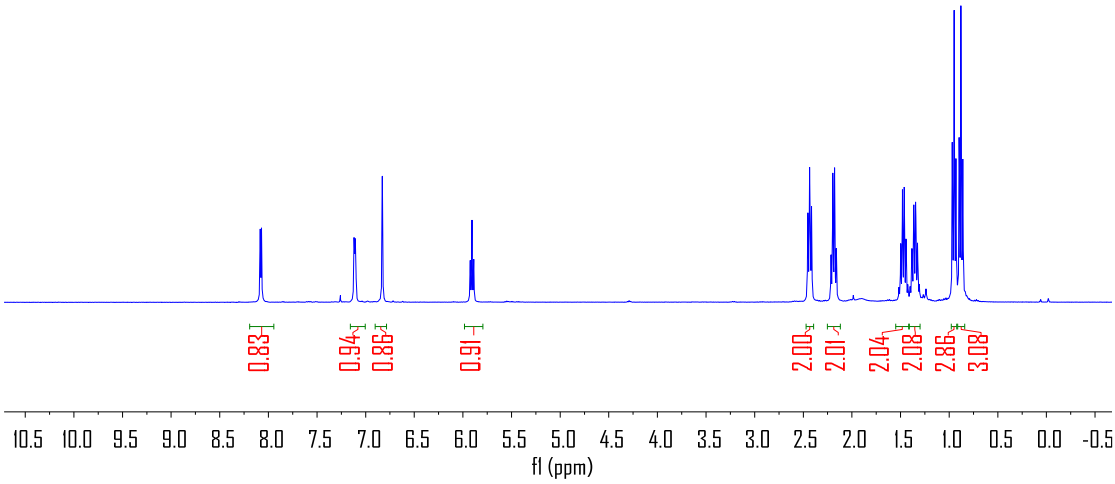
-112.40

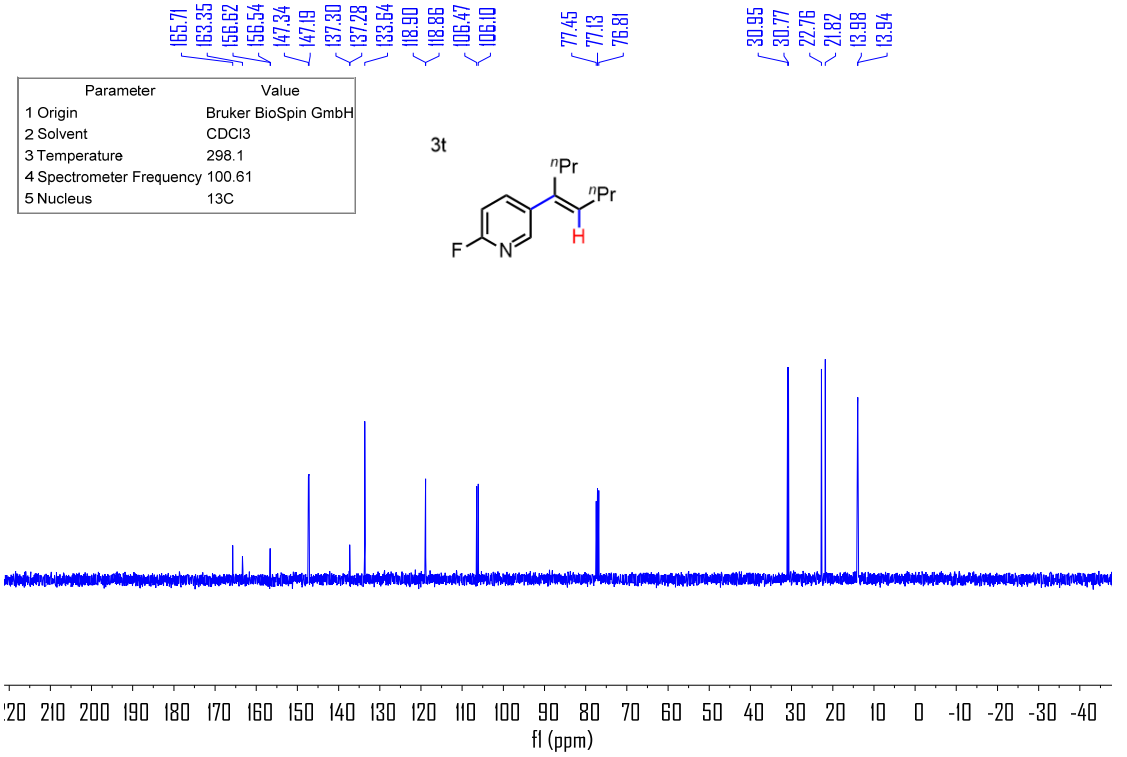


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

3t






165.71
163.35
156.62
156.54
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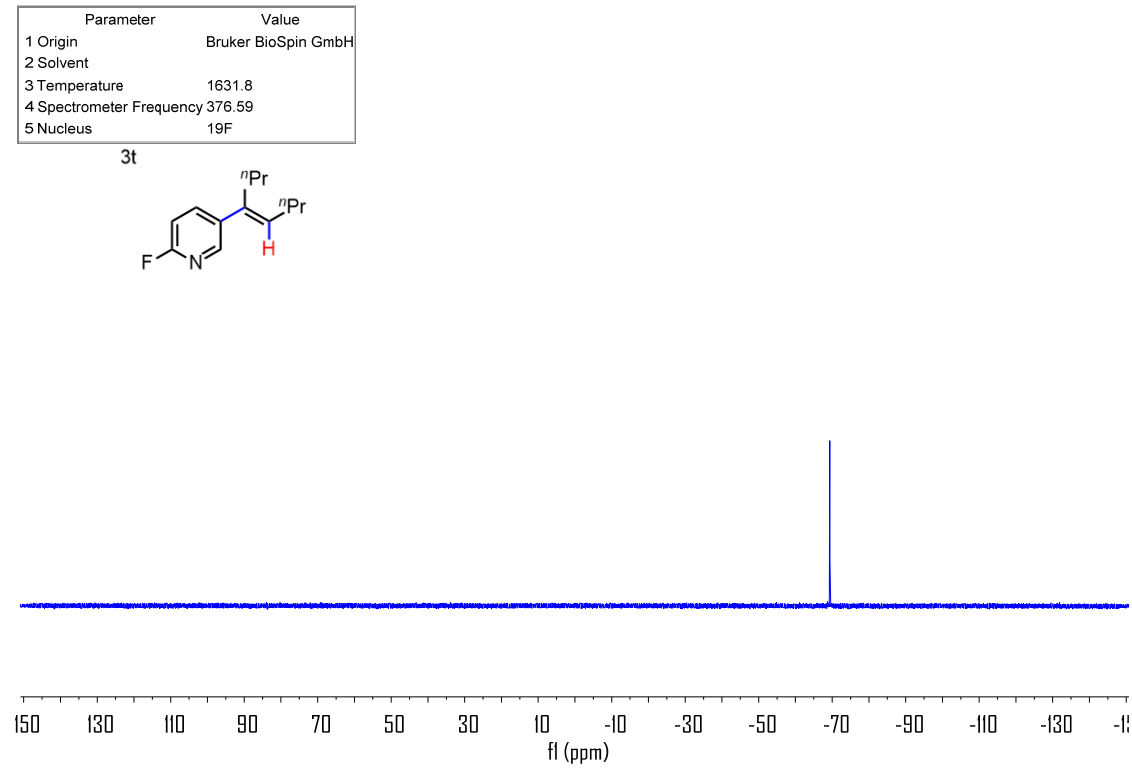
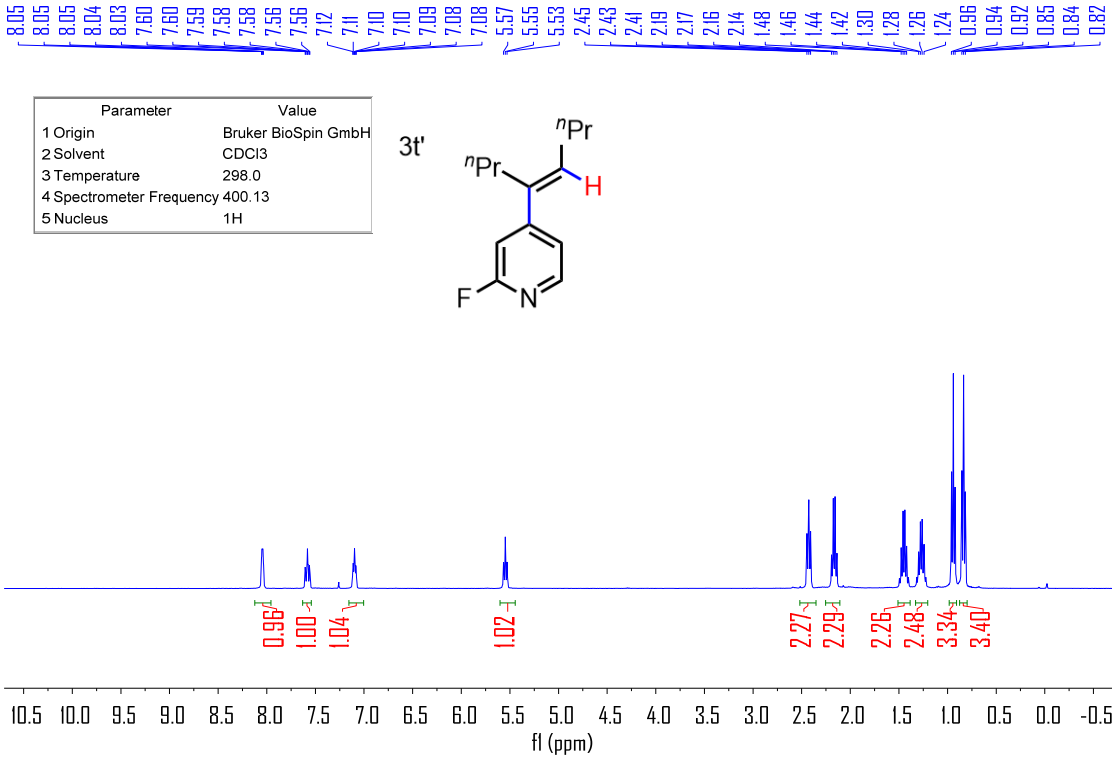
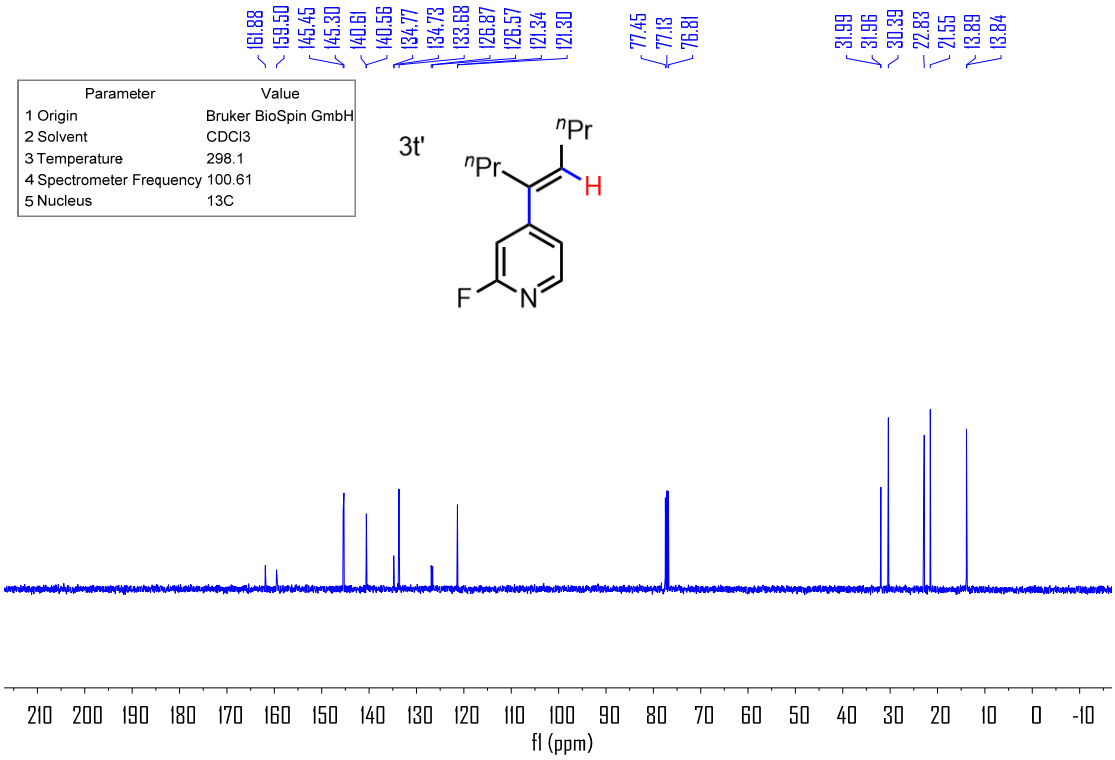
147.19
137.30
137.28
133.64
118.90
118.86
106.47
106.10
77.45
77.13
76.81
30.95
30.77
22.76
21.82
13.98
13.94
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3t
nPr
nPr
F
N
H
f1 (ppm)

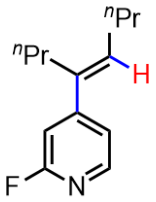

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
3t
nPr
nPr
F
N
H
f1 (ppm)


8.05 8.05 8.05 8.04 8.03 7.60 7.60 7.59 7.58 7.58 7.56 7.56 7.12 7.11 7.10 7.10 7.09 7.08 7.08 5.57 5.55 5.53 2.45 2.43 2.41 2.19 2.17 2.16 2.14 1.48 1.46 1.44 1.42 1.30 1.28 1.26 1.24 0.96 0.94 0.92 0.85 0.84 0.82
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3t'
nPr
nPr
H
F
N
0.96 1.00 1.04 1.02 2.27 2.29 2.26 2.48 3.34 3.40
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.88 159.50 145.45 145.30 140.61 140.56 134.77 134.73 133.68 126.87 126.57 121.34 121.30 77.45 77.13 76.81 31.99 31.96 30.39 22.83 21.55 13.89 13.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3t'
nPr
nPr
H
F
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

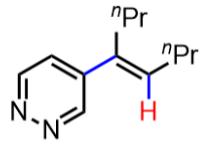
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

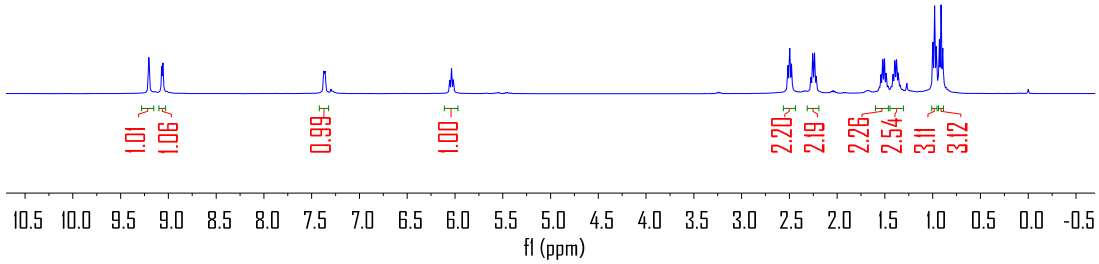
3t'

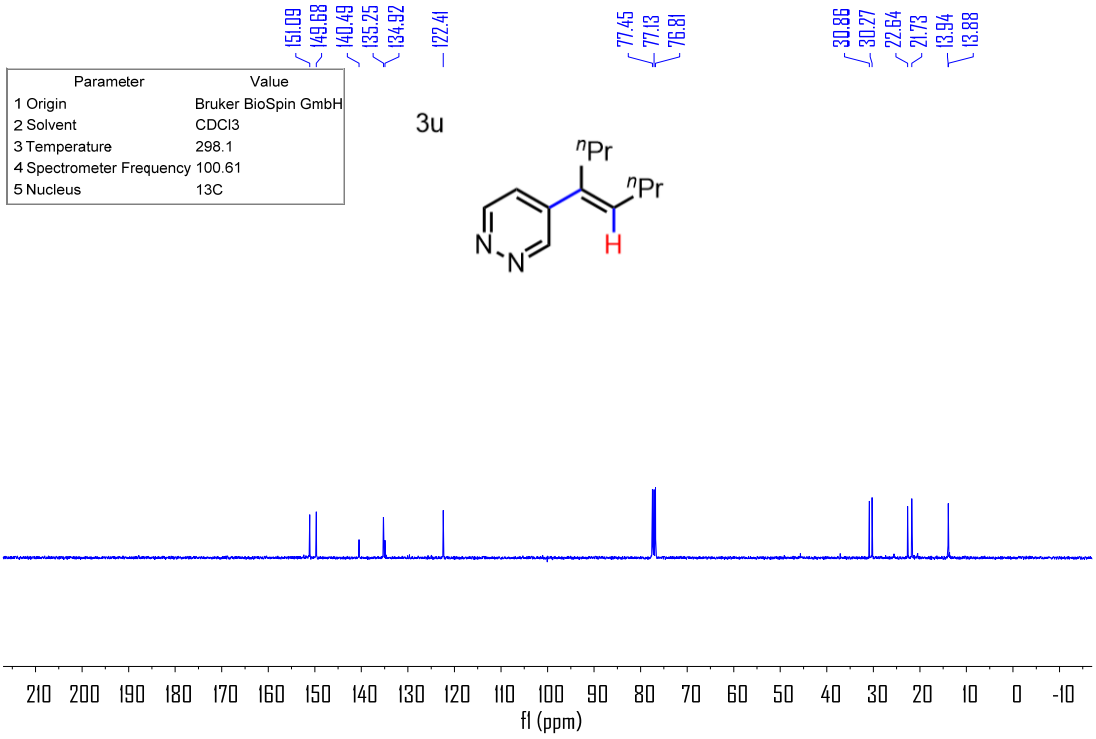


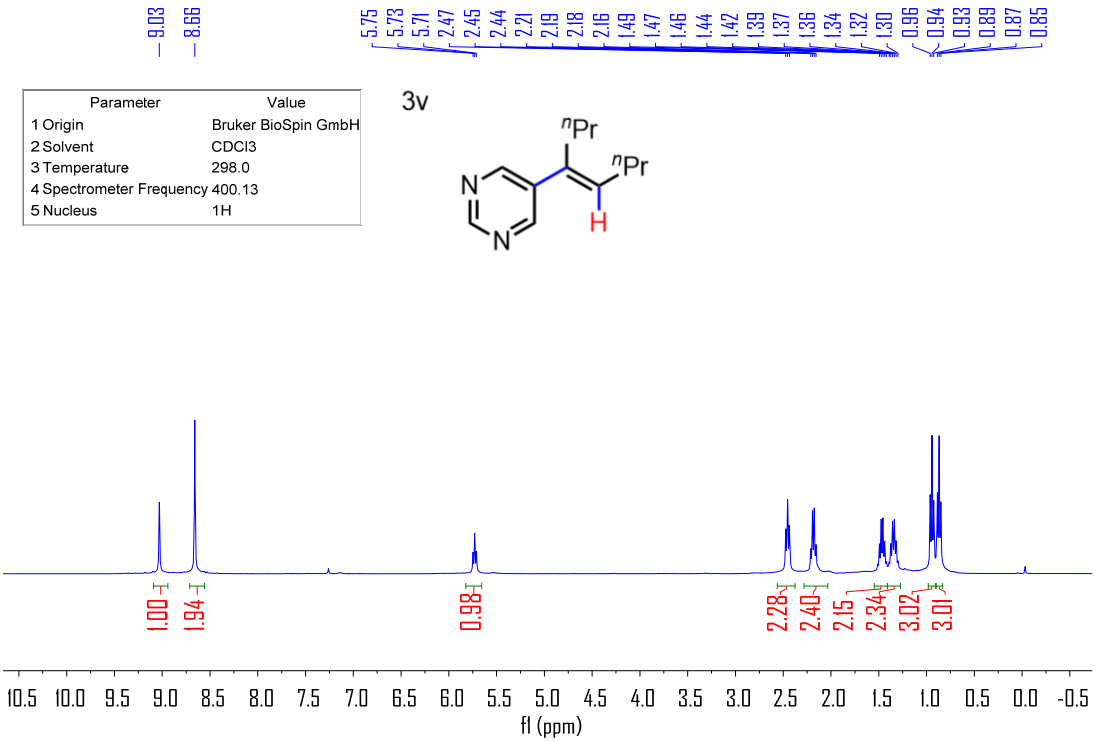
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

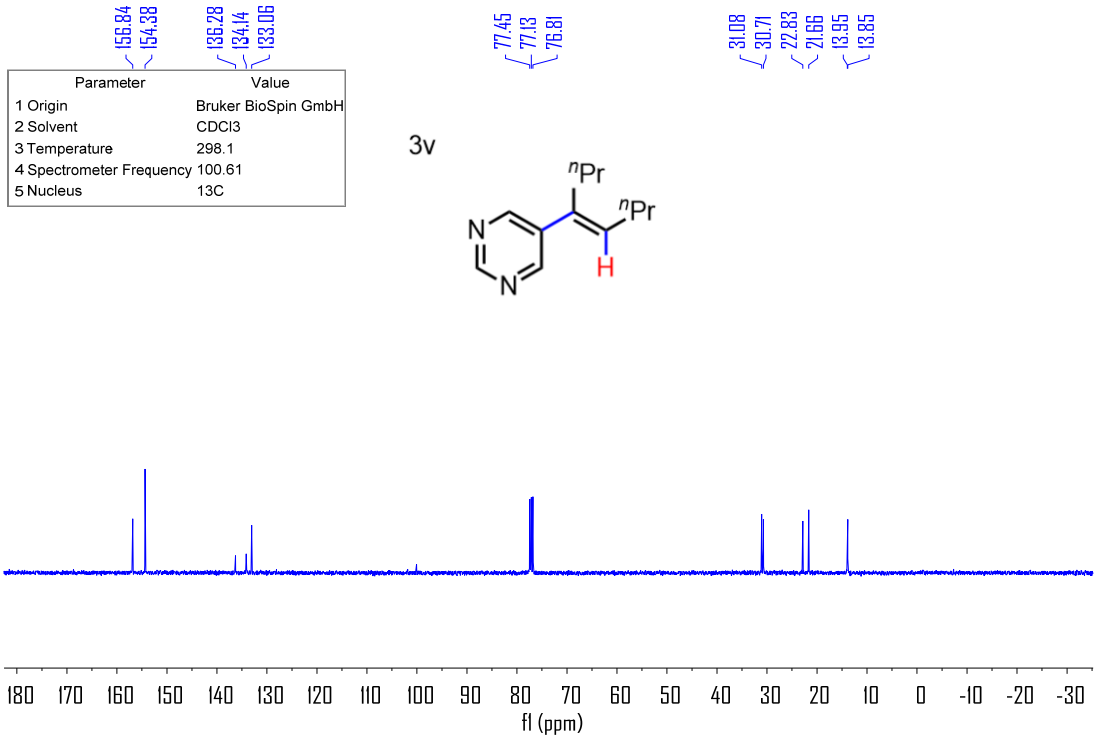
3u

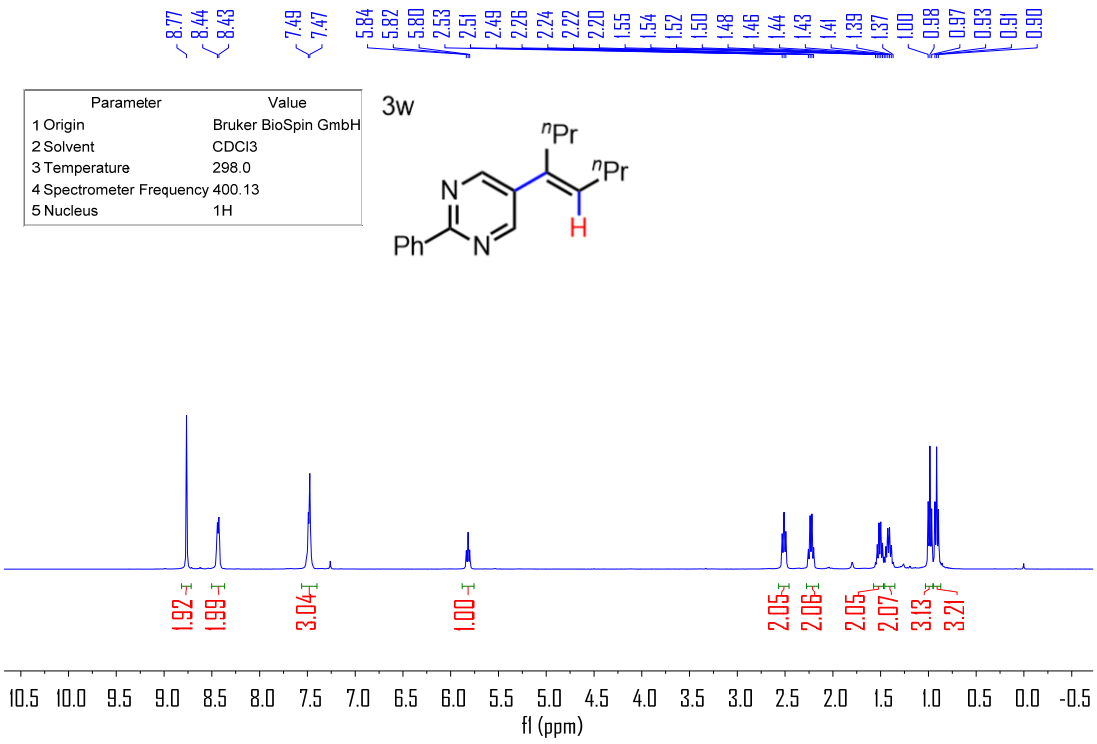


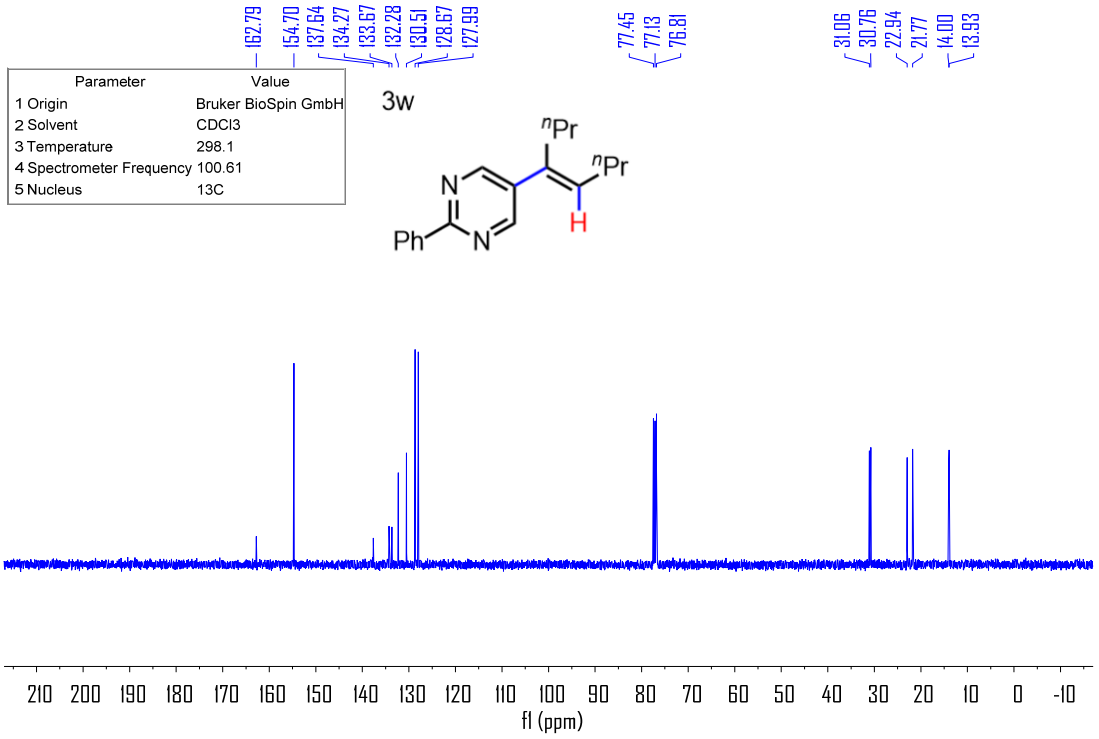


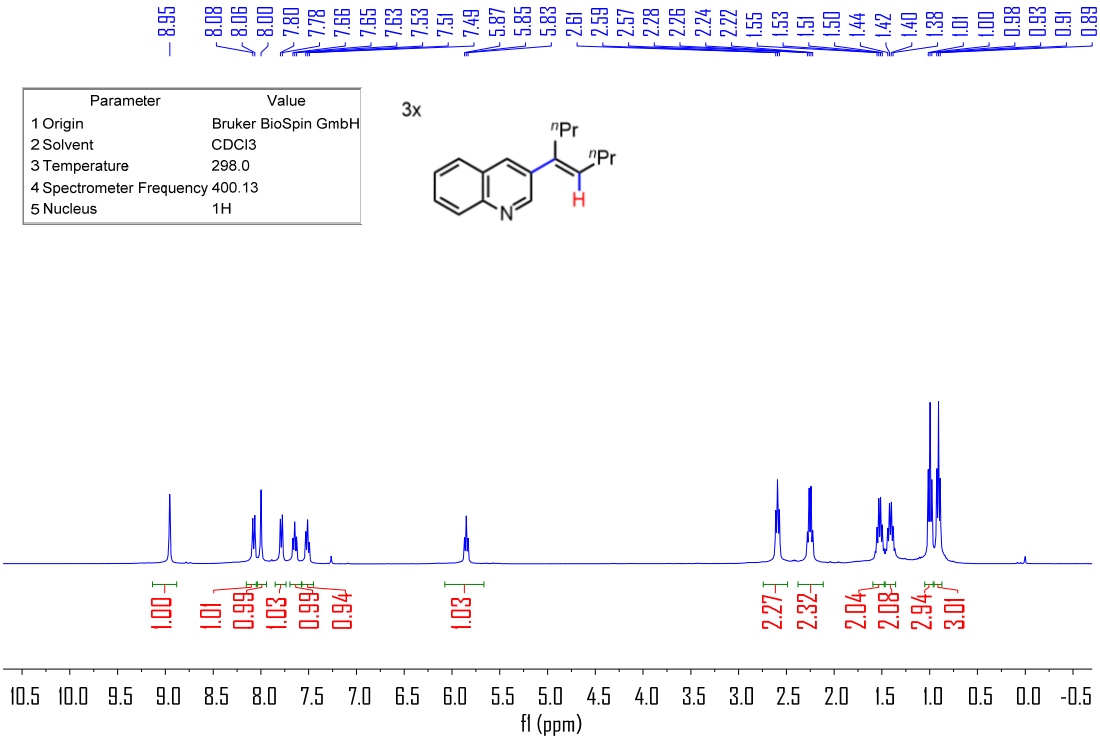

151.09
149.68
140.49
135.25
134.92
122.41
77.45
77.13
76.81
30.86
30.27
22.64
21.73
13.94
13.88
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3u
nPr
nPr
N
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

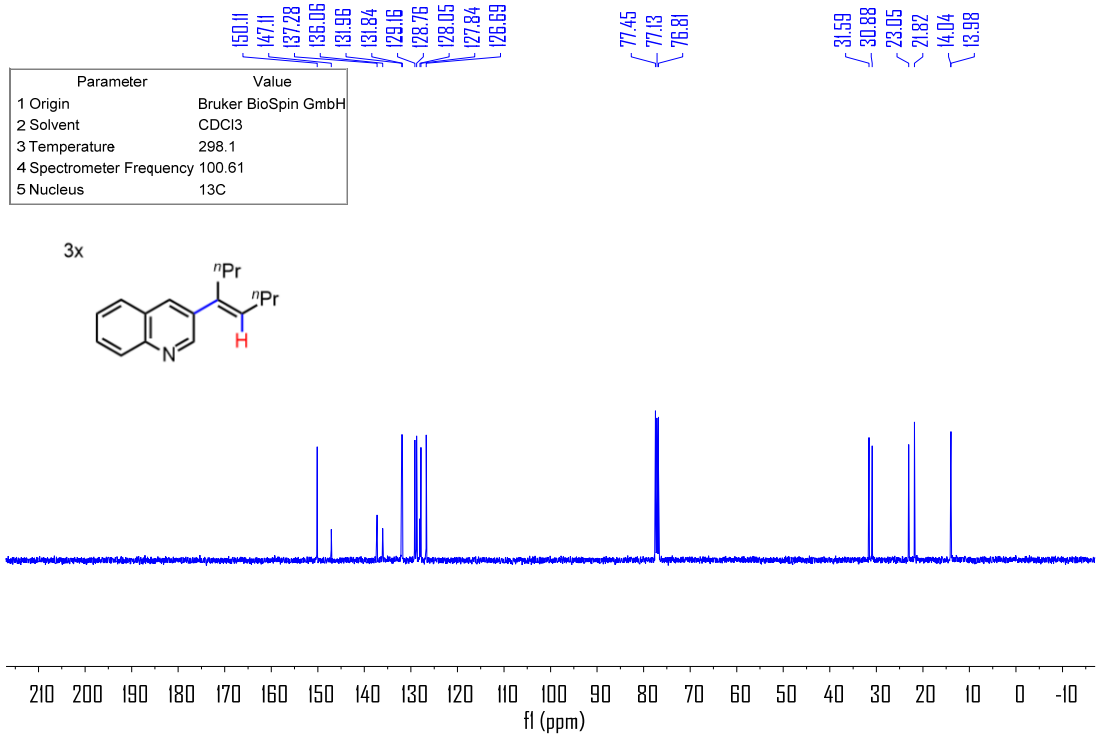

9.03
8.86
5.75
5.73
5.71
2.47
2.45
2.44
2.21
2.19
2.18
2.16
1.49
1.47
1.46
1.44
1.42
1.39
1.37
1.36
1.34
1.32
1.30
0.96
0.94
0.93
0.89
0.87
0.85
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3v
nPr
nPr
N
N
H
1.00
1.94
0.98
2.28
2.40
2.15
2.34
3.02
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

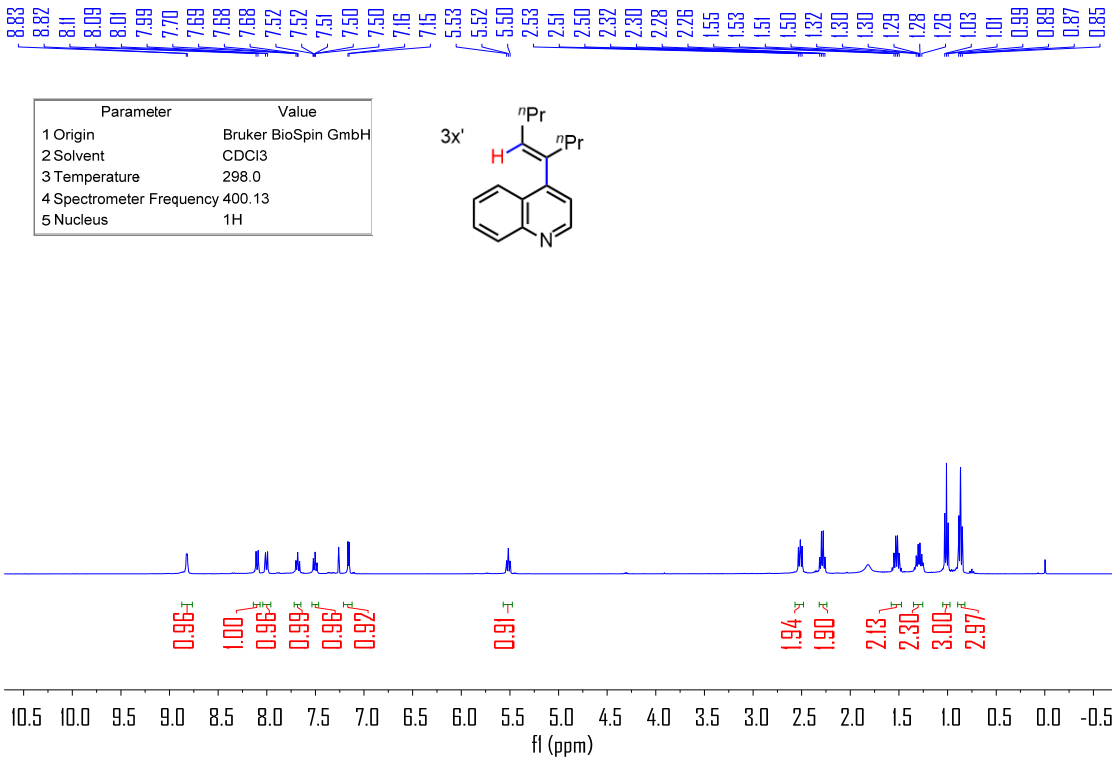

156.84
154.38
136.28
134.14
133.06
77.45
77.13
76.81
31.08
30.71
22.83
21.66
13.95
13.85
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3v
nPr
nPr
N
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

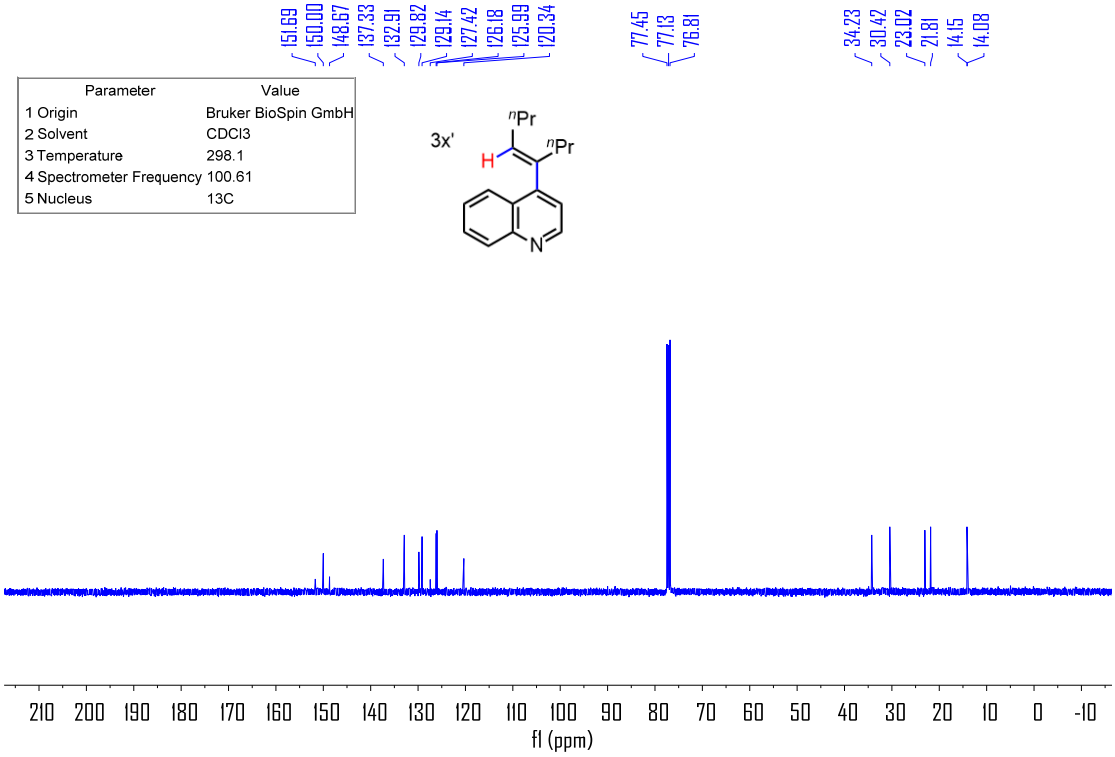

8.77
8.44
8.43
7.49
7.47
5.84
5.82
5.80
2.53
2.51
2.49
2.26
2.24
2.22
2.20
1.55
1.54
1.52
1.50
1.48
1.46
1.44
1.43
1.41
1.39
1.37
1.00
0.98
0.97
0.93
0.91
0.90
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3w
nPr
nPr
N
Ph
N
H
1.92
1.99
3.04
1.00
2.05
2.06
2.05
2.07
3.13
3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

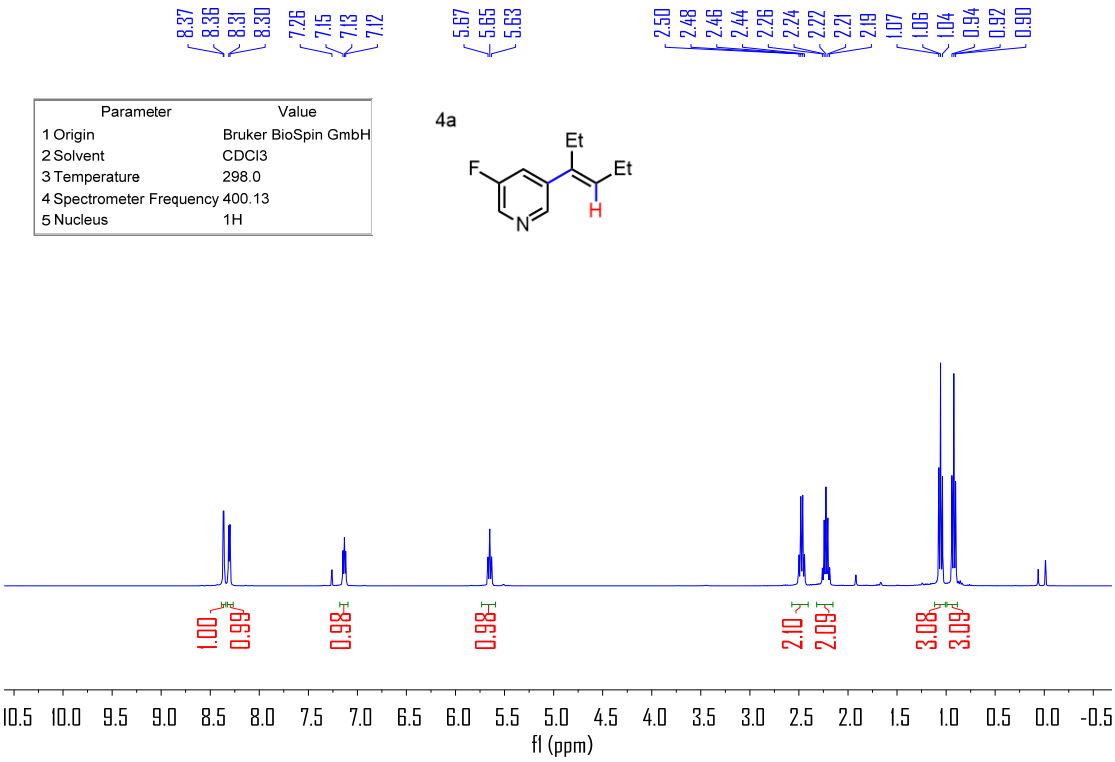

162.79
154.70
137.64
134.27
133.67
132.28
130.51
128.67
127.99
77.45
77.13
76.81
31.06
30.76
22.94
21.77
14.00
13.93
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3w
nPr
nPr
N
Ph
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

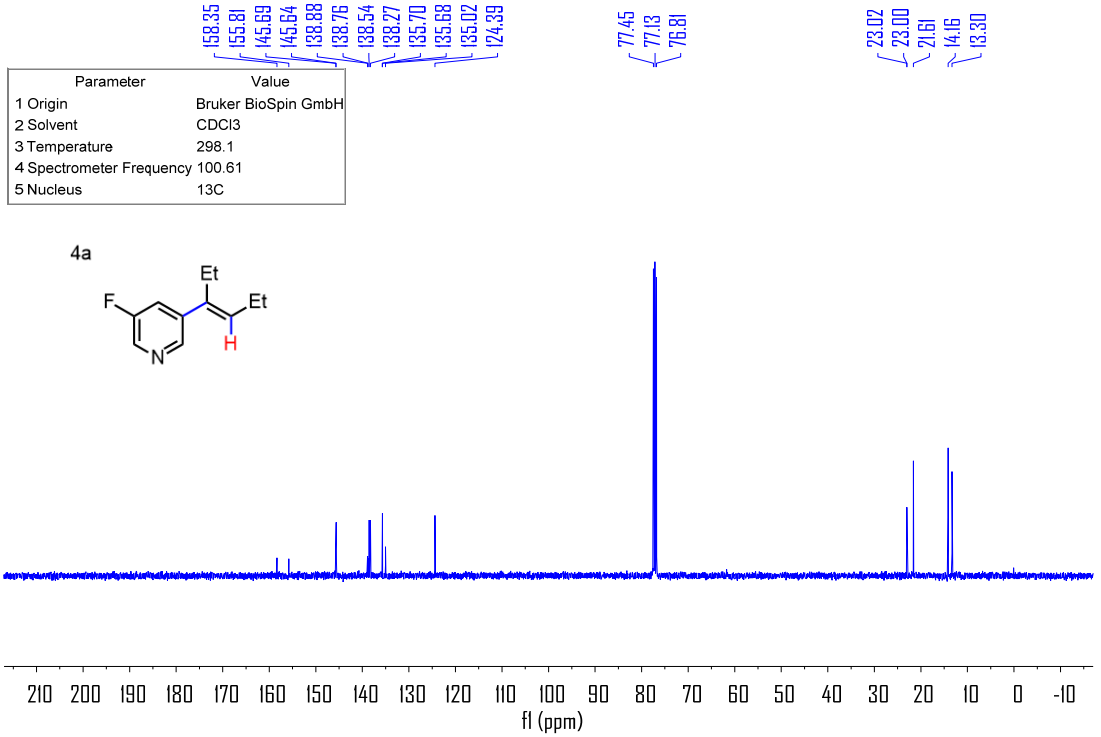

8.95
8.08
8.06
8.00
7.80
7.78
7.66
7.65
7.63
7.53
7.51
7.49
5.87
5.85
5.83
2.61
2.59
2.57
2.28
2.26
2.24
2.22
1.55
1.53
1.51
1.50
1.44
1.42
1.40
1.38
1.01
1.00
0.98
0.93
0.91
0.89
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3x
nPr
nPr
N
H
1.00
1.01
0.99
1.03
0.99
0.94
1.03
2.27
2.32
2.04
2.08
2.94
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

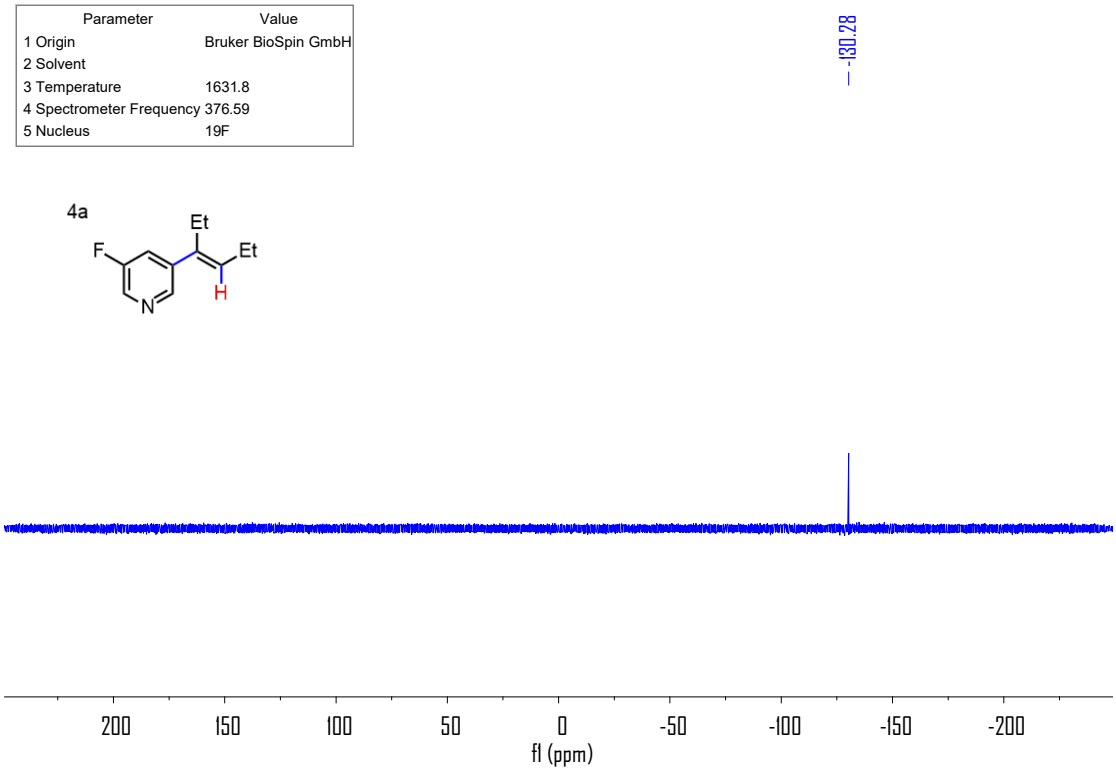

150.11
147.11
137.28
136.06
131.96
131.84
129.16
128.76
128.05
127.84
126.69
77.45
77.13
76.81
31.59
30.88
23.05
21.82
14.04
13.98
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3x
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

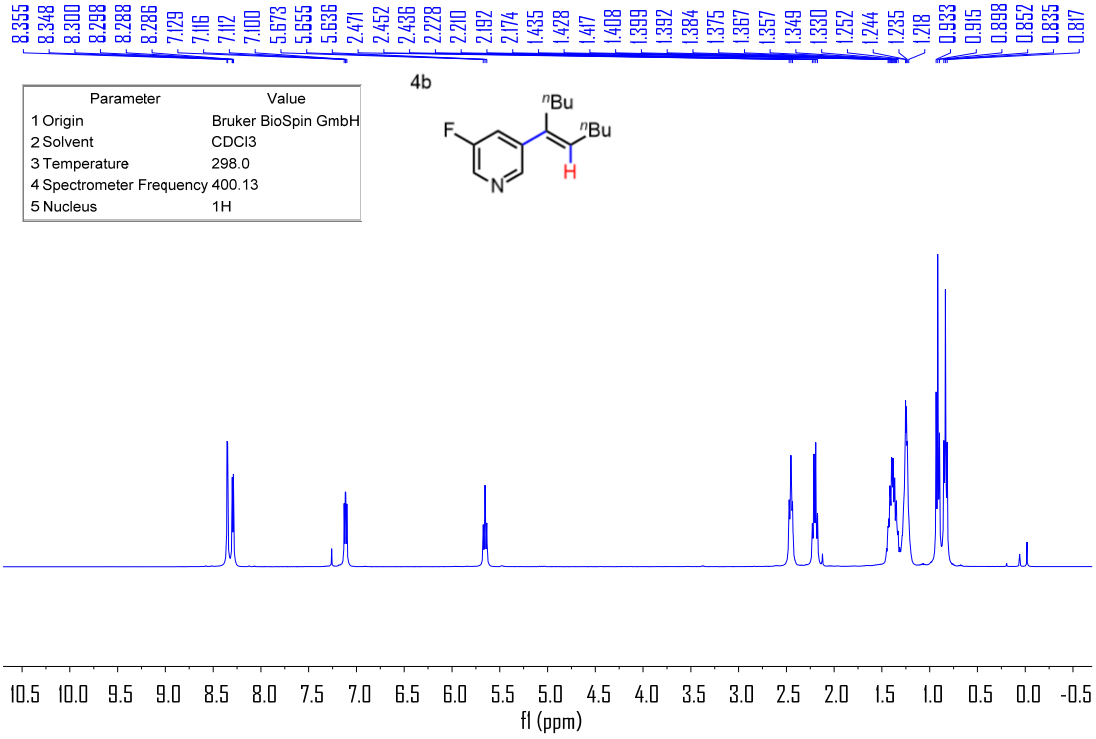

8.83
8.82
8.11
8.09
8.01
7.99
7.70
7.69
7.68
7.68
7.52
7.52
7.51
7.50
7.50
7.16
7.15
5.53
5.52
5.50
2.53
2.51
2.50
2.32
2.30
2.28
2.26
1.55
1.53
1.51
1.50
1.32
1.30
1.30
1.29
1.28
1.26
1.03
1.01
0.99
0.89
0.87
0.85
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
3x'
nPr
H
nPr
N
0.96
1.00
0.96
0.99
0.96
0.92
0.91
1.94
1.90
2.13
2.30
3.00
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151.69
150.00
148.67
137.33
132.91
129.82
129.14
127.42
126.18
125.99
120.34
77.45
77.13
76.81
34.23
30.42
23.02
21.81
14.15
14.08
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
3x'
nPr
H
nPr
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.37
8.36
8.31
8.30
7.26
7.15
7.13
7.12
5.67
5.65
5.63
2.50
2.48
2.46
2.44
2.26
2.24
2.22
2.21
2.19
1.07
1.06
1.04
0.94
0.92
0.90
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4a
Et
F
Et
H
N
1.00
0.99
0.98
0.98
2.10
2.09
3.08
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.35
155.81
145.69
145.64
138.88
138.76
138.54
138.27
135.70
135.68
135.02
124.39
77.45
77.13
76.81
23.02
23.00
21.61
14.16
13.30
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4a
Et
F
Et
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
-130.28
4a
Et
F
Et
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)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8.348
8.300
8.298
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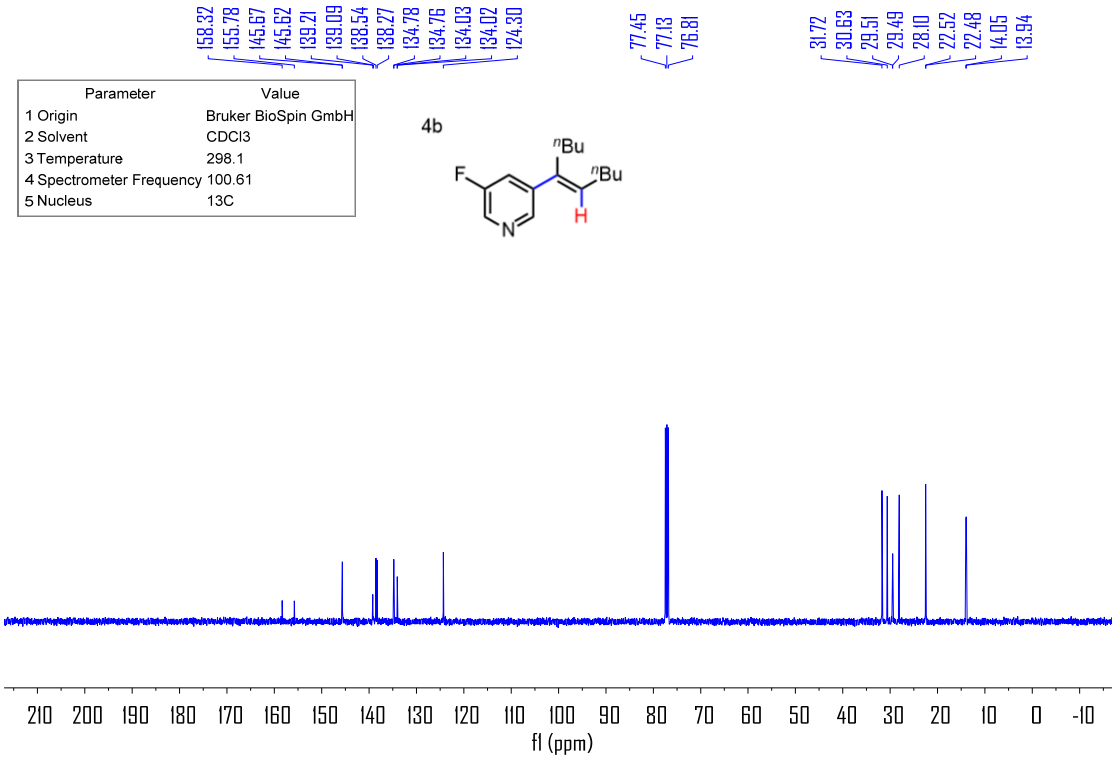
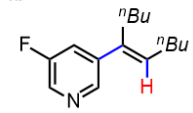
8.286
7.129
7.116
7.112
7.100
5.673
5.655
5.636
2.471
2.452
2.436
2.228
2.210
2.192
2.174
1.435
1.428
1.417
1.408
1.399
1.392
1.384
1.375
1.367
1.357
1.349
1.330
1.252
1.244
1.235
1.218
0.933
0.915
0.898
0.852
0.835
0.817
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4b
nBu
nBu
F
N
H
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.32
155.78
145.67
145.62
139.21
139.09
138.54
138.27
134.78
134.76
134.03
134.02
124.30
77.45
77.13
76.81
31.72
30.63
29.51
29.49
28.10
22.52
22.48
14.05
13.94
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4b
nBu
nBu
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

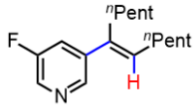
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

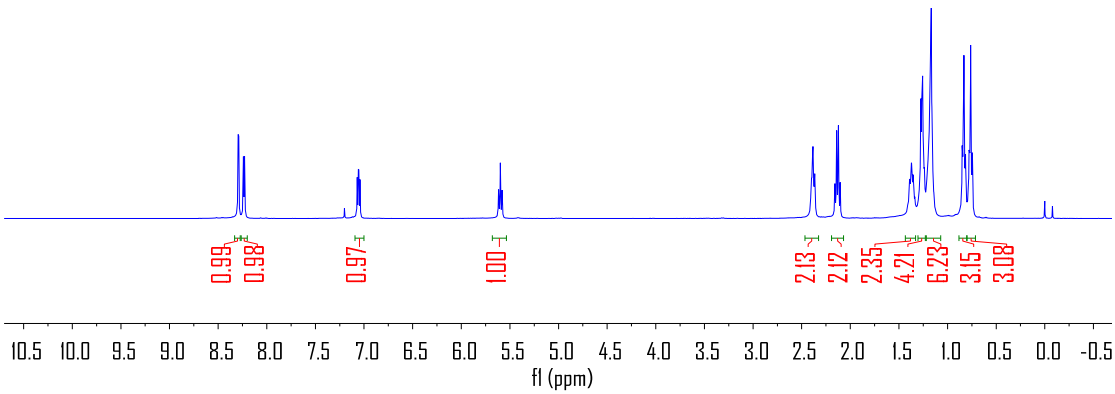
4b

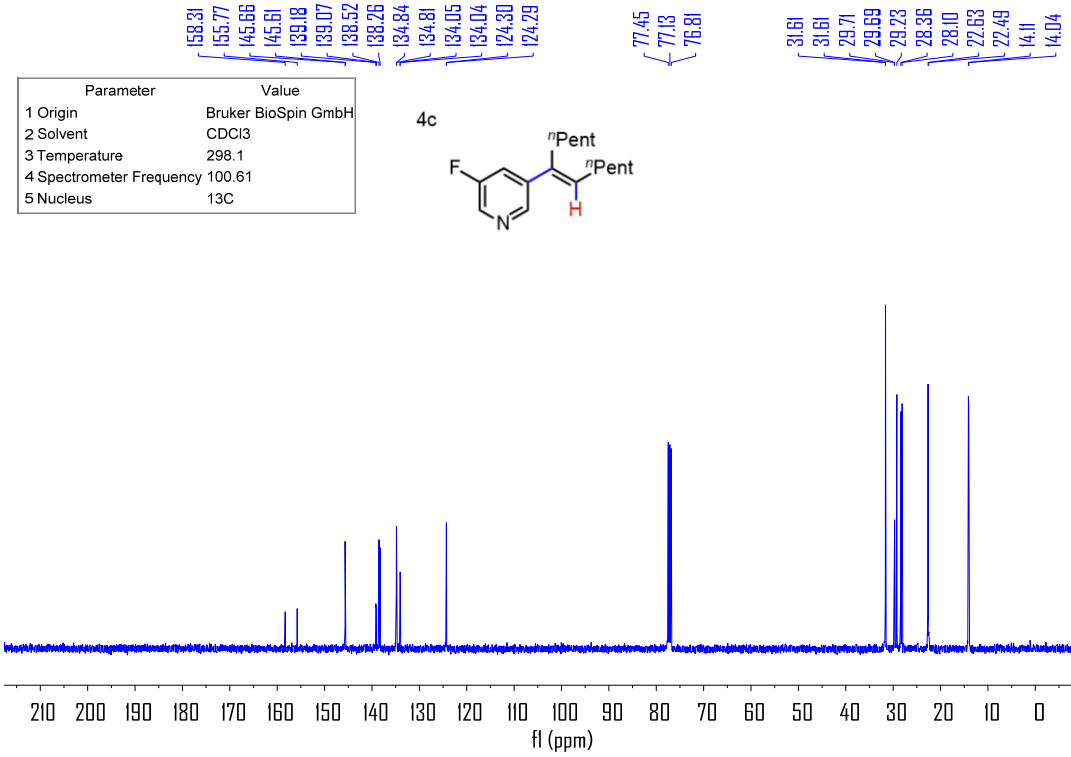


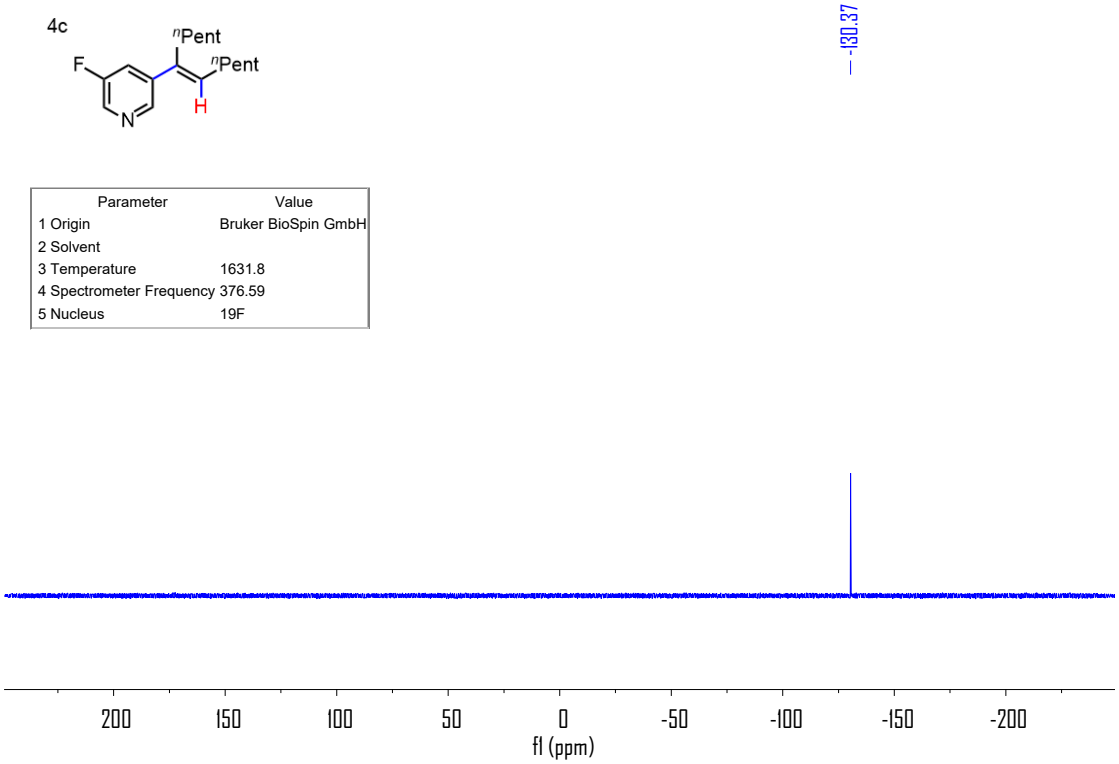
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

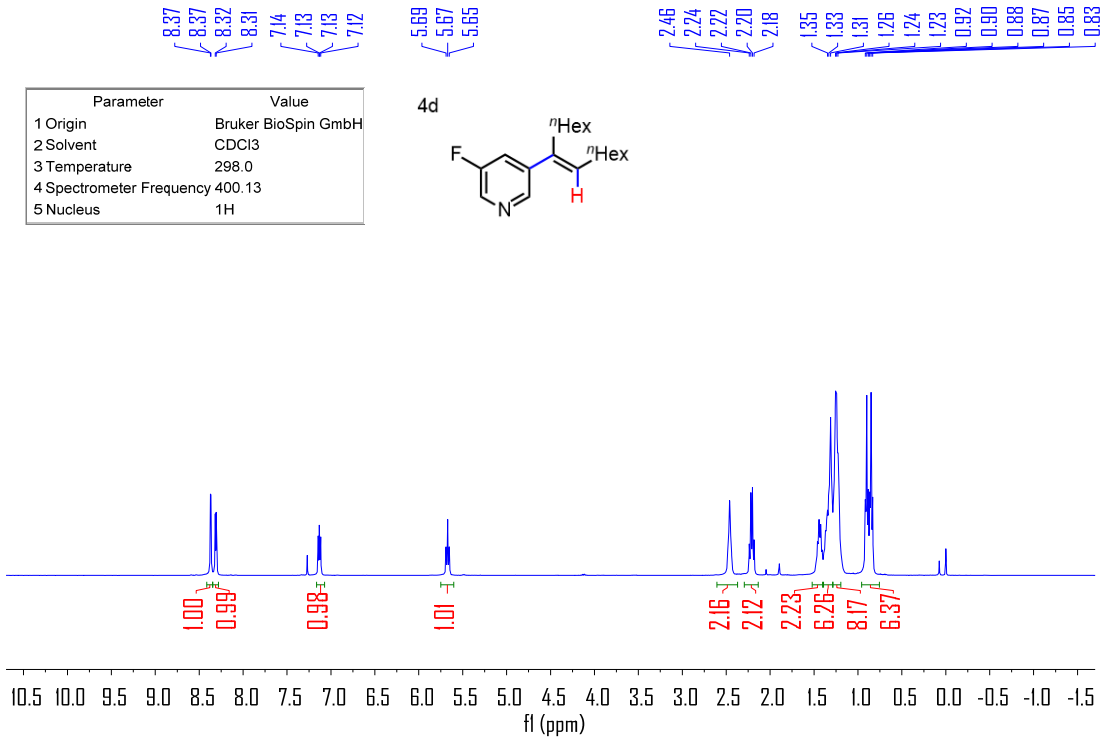
4c

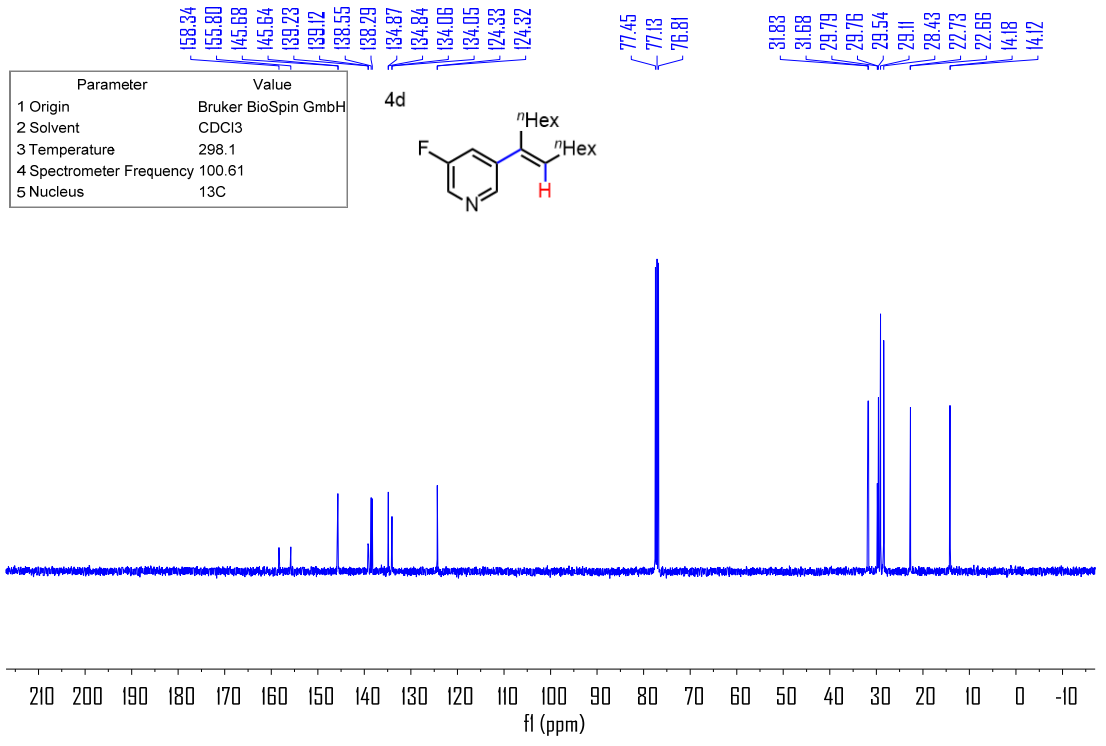





158.31
155.77
145.66
145.61
139.18
139.07
138.52
138.28
134.84
134.81
134.05
134.04
124.30
124.29
77.45
77.13
76.81
31.61
31.61
29.71
29.69
29.23
28.36
28.10
22.63
22.49
14.11
14.04
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4c
nPent
nPent
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

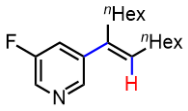

4c
nPent
nPent
F
N
H
-130.37
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)


8.37
8.37
8.32
8.31
7.14
7.13
7.13
7.12
5.69
5.67
5.65
2.46
2.24
2.22
2.20
2.18
1.35
1.33
1.31
1.26
1.24
1.23
0.92
0.90
0.88
0.87
0.85
0.83
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4d
nHex
nHex
F
N
H
1.00
0.99
0.98
1.01
2.16
2.12
2.23
6.26
8.17
6.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

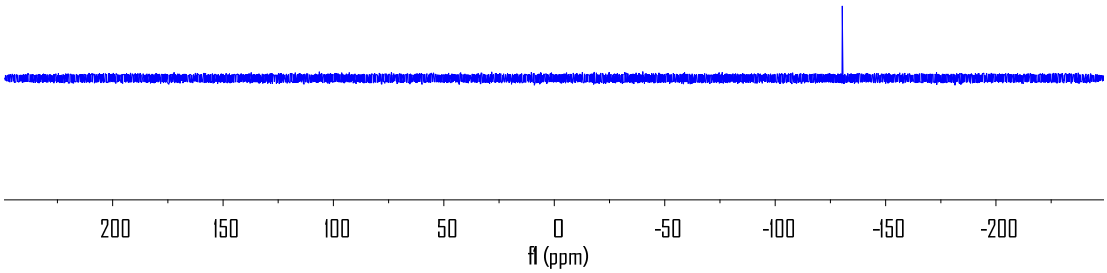

158.34
155.80
145.68
145.64
139.23
139.12
138.55
138.29
134.87
134.84
134.06
134.05
124.33
124.32
77.45
77.13
76.81
31.83
31.68
29.79
29.76
29.54
29.11
28.43
22.73
22.66
14.18
14.12
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4d
nHex
nHex
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1451.5
4 Spectrometer Frequency	376.59
5 Nucleus	19F

4d



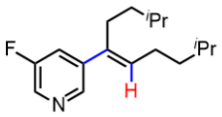
-130.38

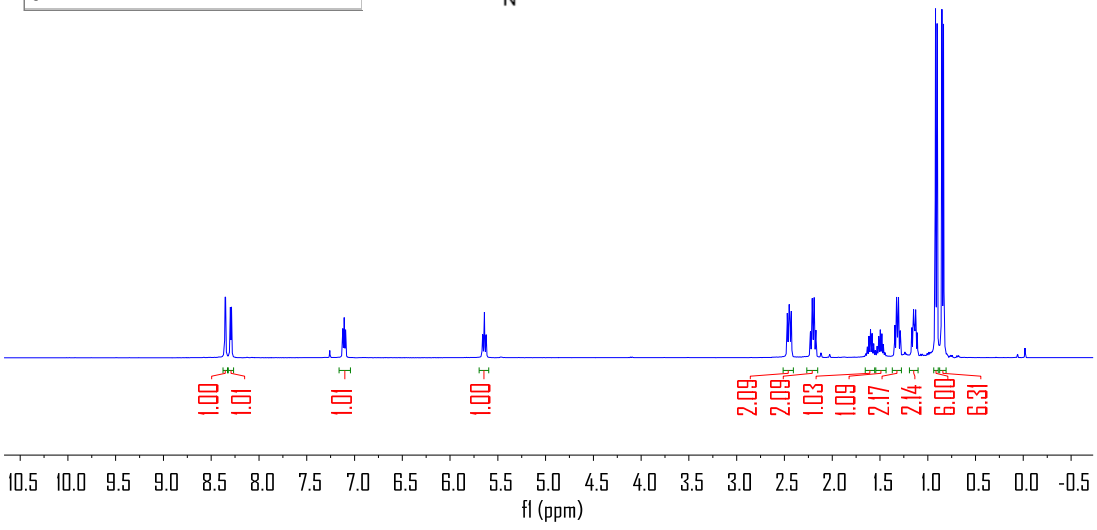


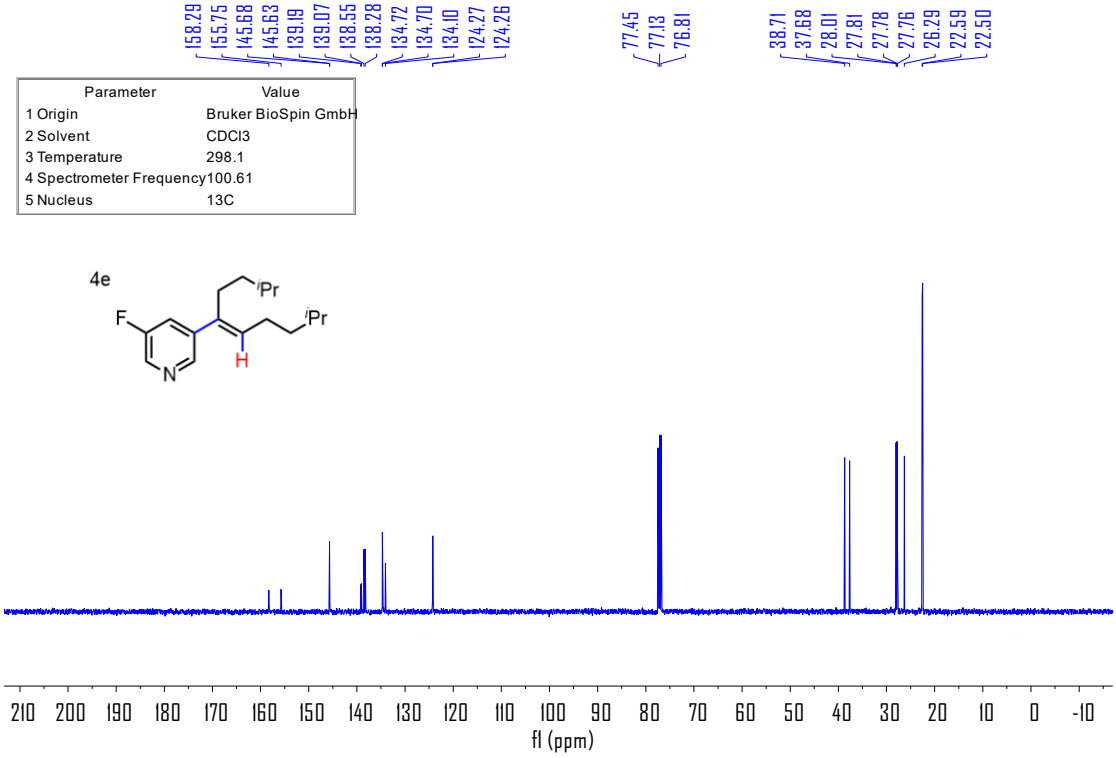
8.36 8.35 8.30 8.29 7.12 7.11 7.09 5.66 5.64 5.62 2.47 2.45 2.43 2.23 2.21 2.19 2.17 1.63 1.62 1.60 1.58 1.57 1.55 1.53 1.51 1.50 1.48 1.46 1.45 1.34 1.33 1.31 1.29 1.17 1.15 1.14 1.13 1.11 0.92 0.90 0.85 0.84

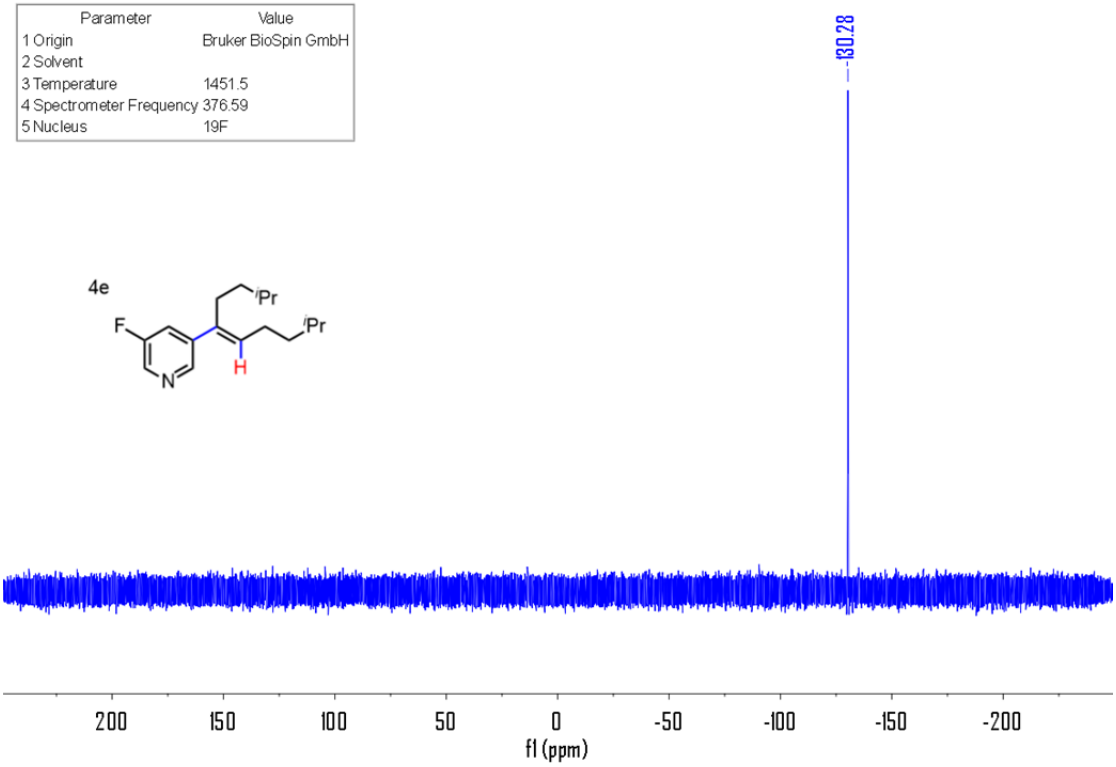
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

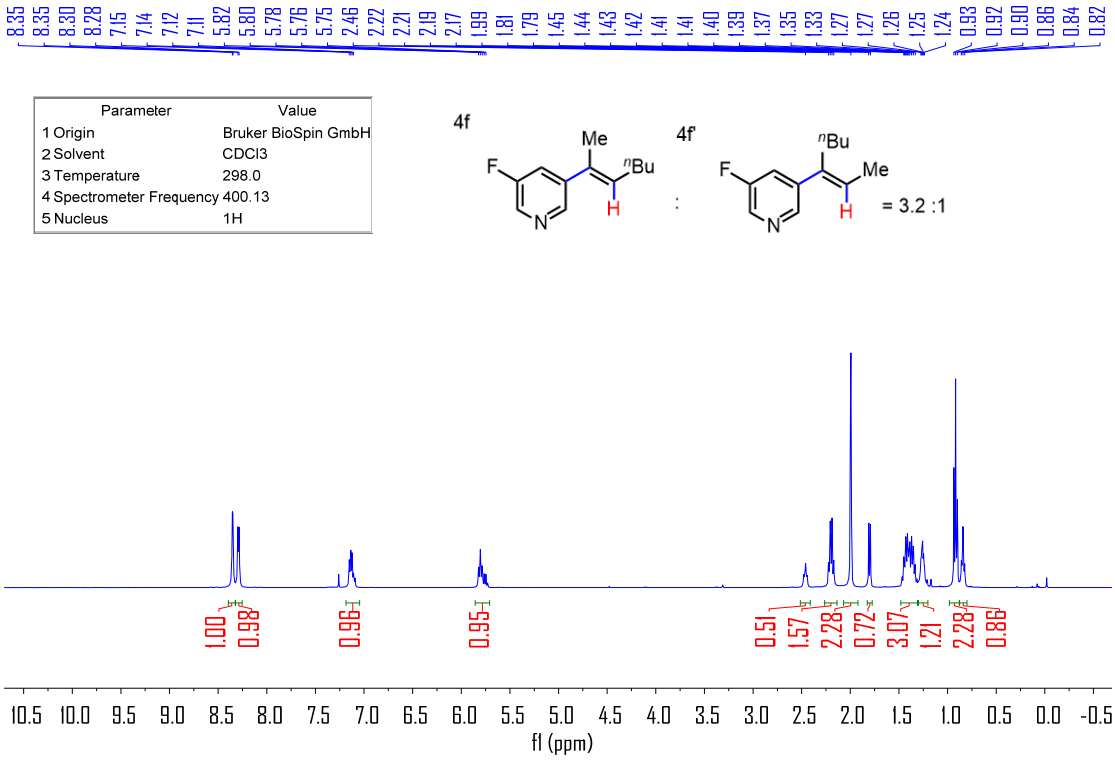
4e

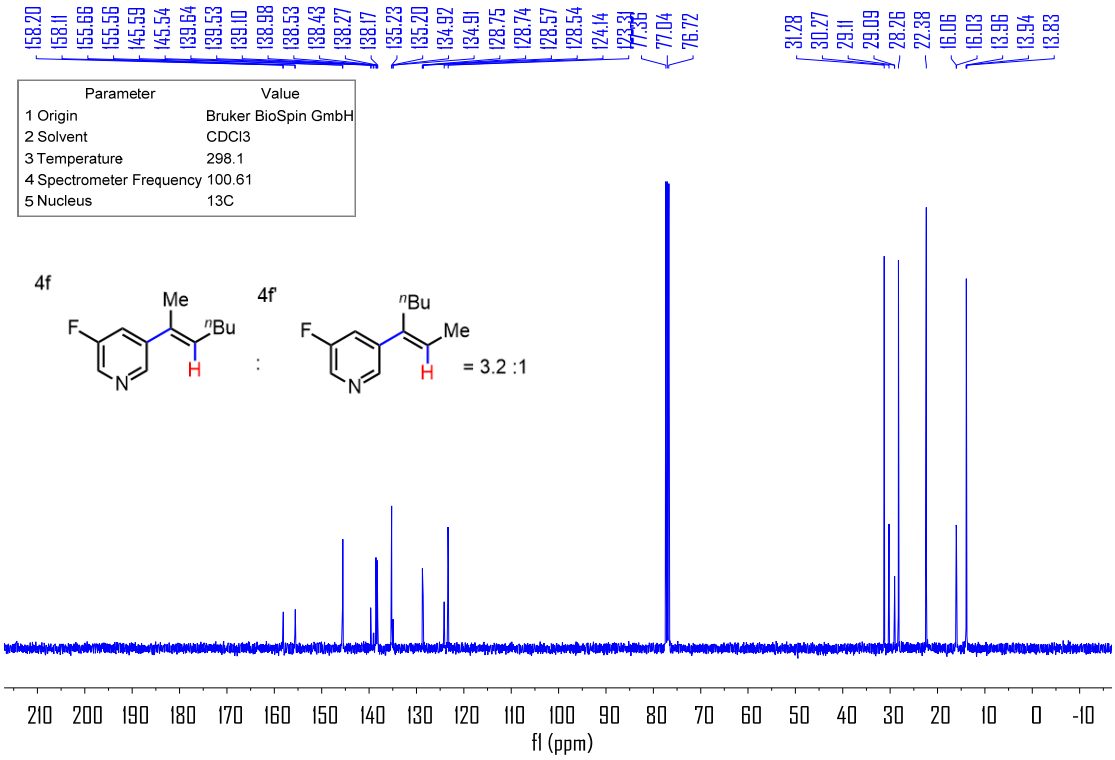


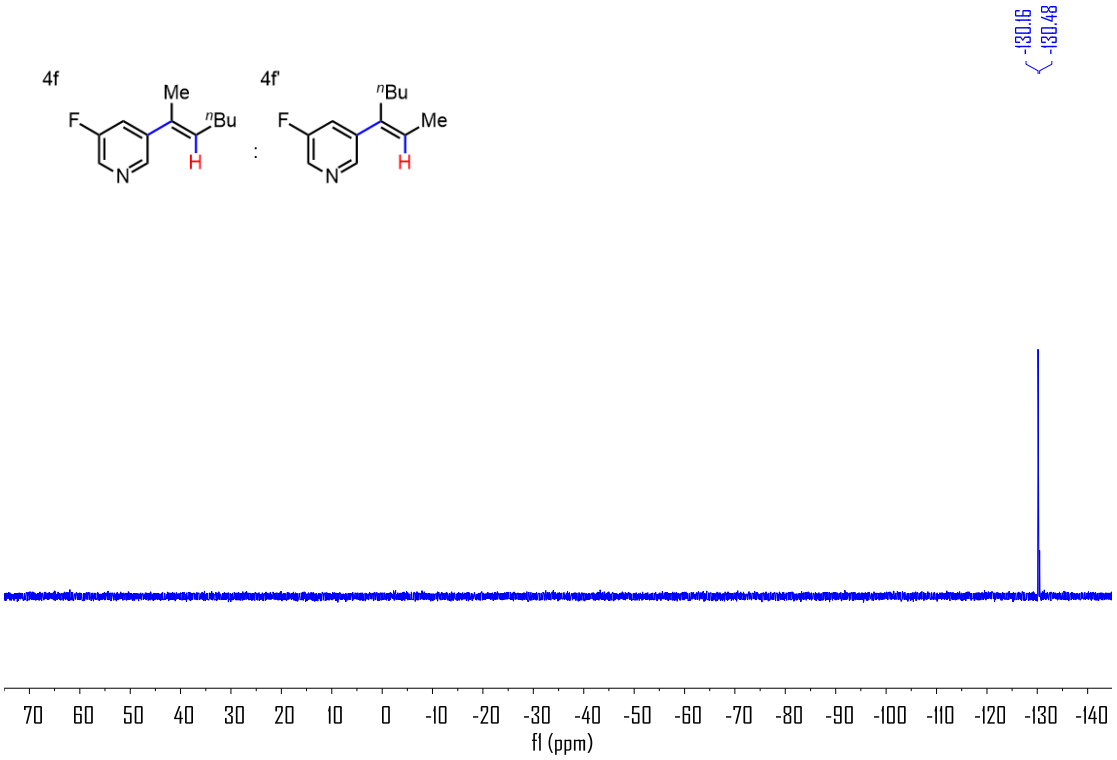


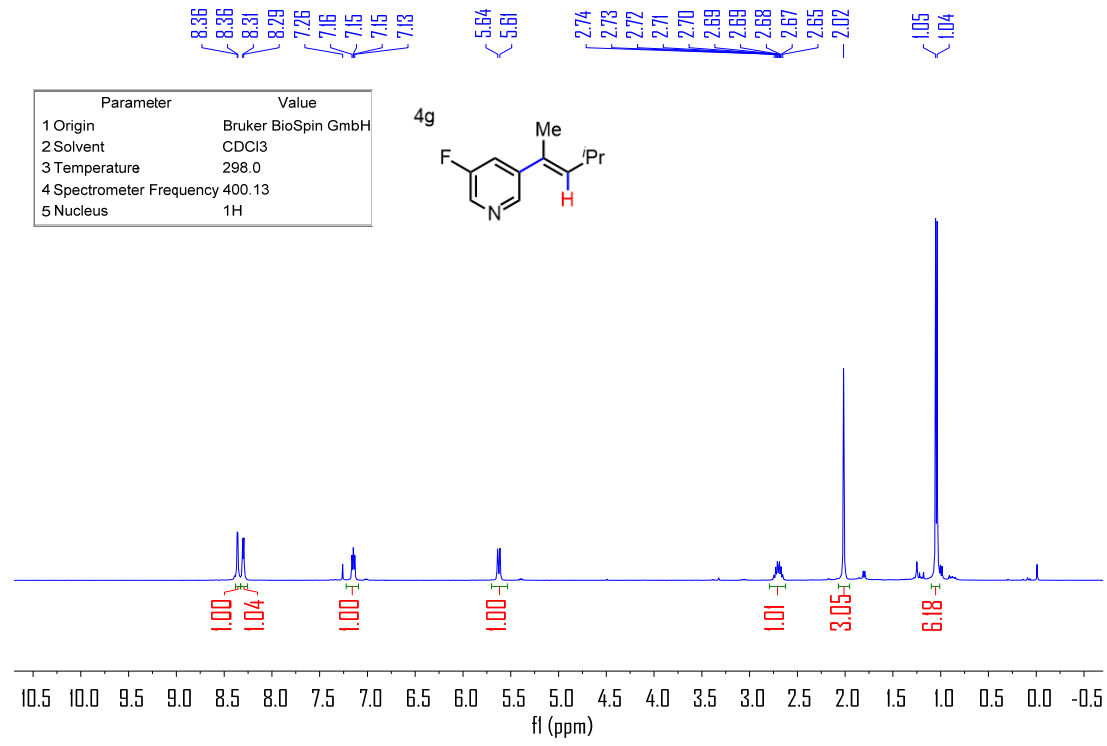

158.29
155.75
145.68
145.63
139.19
139.07
138.55
138.28
134.72
134.70
134.10
124.27
124.26
77.45
77.13
76.81
38.71
37.68
28.01
27.81
27.78
27.76
26.29
22.59
22.50
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4e
F
N
H
iPr
iPr
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

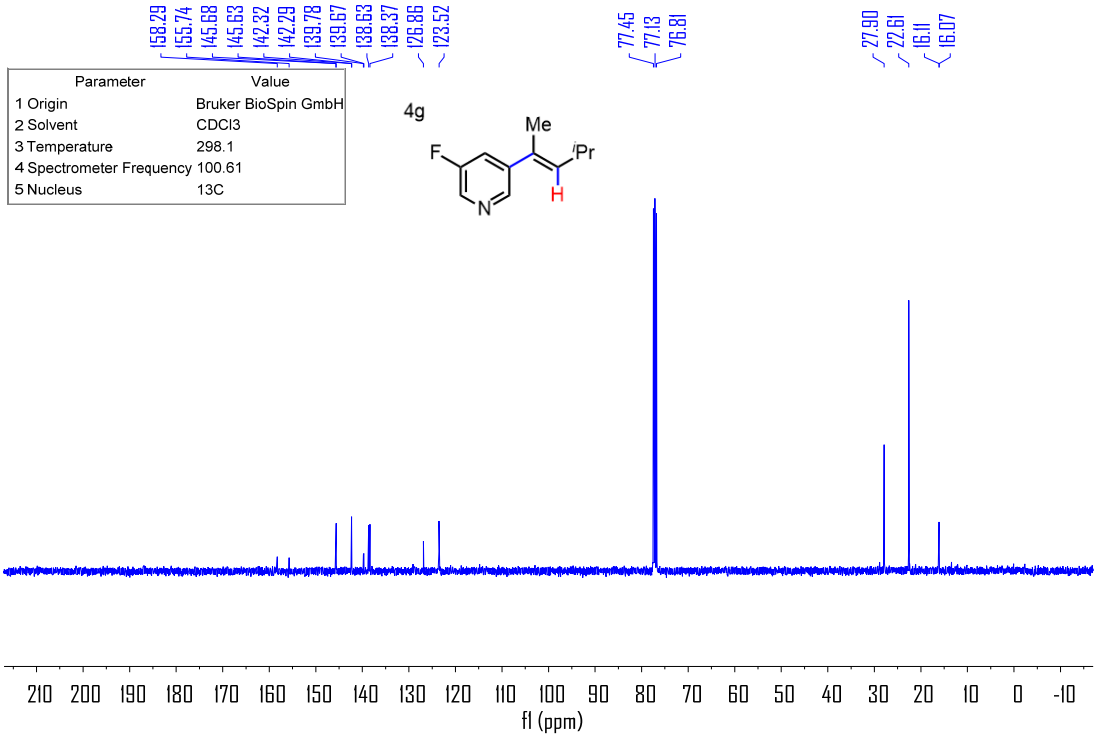

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1451.5
4 Spectrometer Frequency 376.59
5 Nucleus 19F
-130.28
4e
F
N
H
iPr
iPr
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

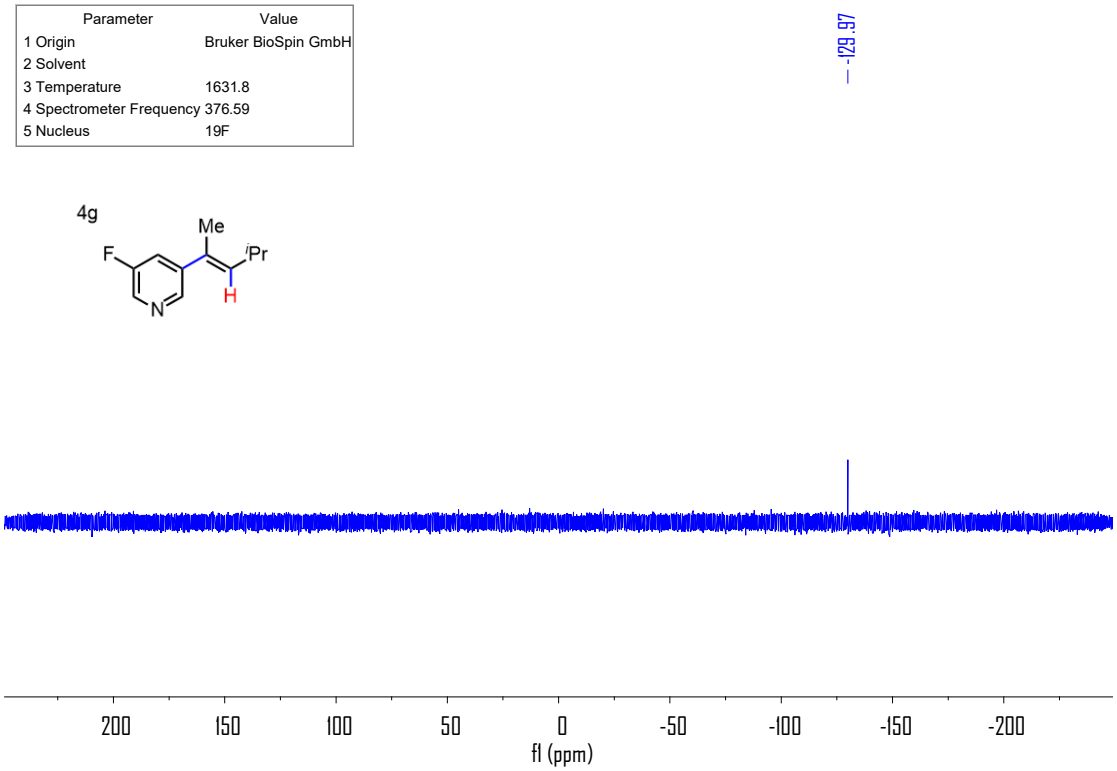

8.35 8.35 8.30 8.28 7.15 7.14 7.12 7.11 5.82 5.80 5.78 5.76 5.75 2.46 2.22 2.21 2.19 2.17 1.99 1.81 1.79 1.45 1.44 1.43 1.42 1.41 1.41 1.40 1.39 1.37 1.35 1.33 1.27 1.27 1.26 1.25 1.24 0.93 0.92 0.90 0.86 0.84 0.82
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4f
4f'
= 3.2 :1
1.00 0.98 0.96 0.95 0.51 1.57 2.28 0.72 3.07 1.21 2.28 0.86
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

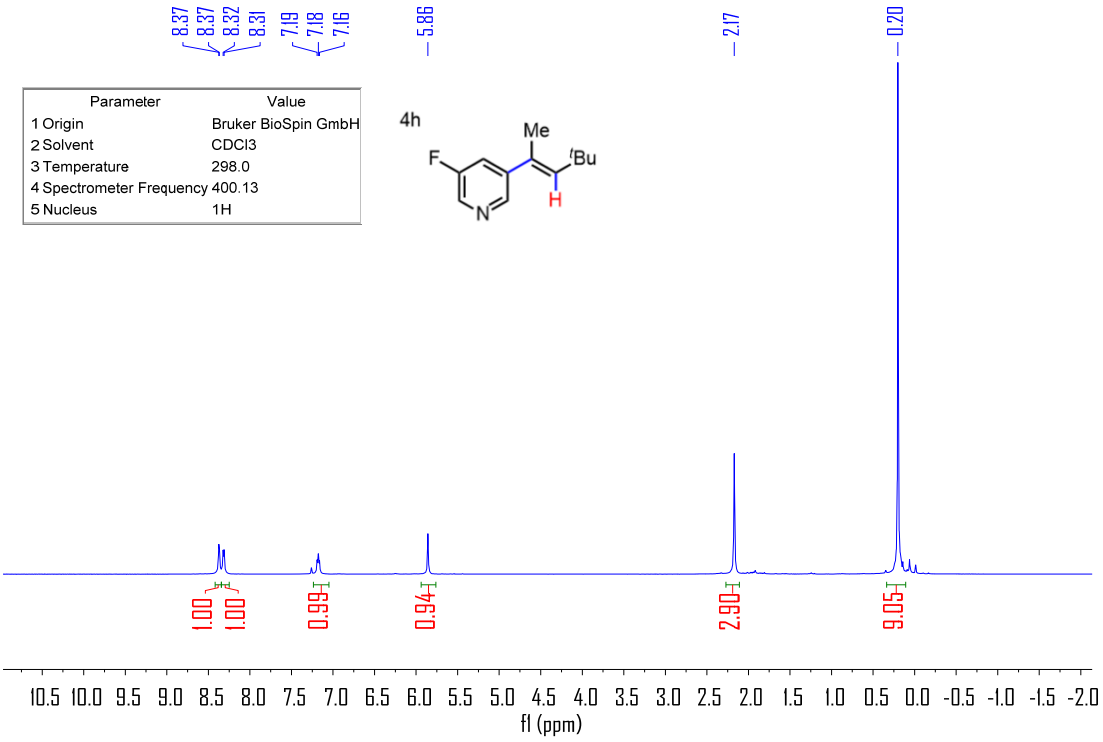

158.20 158.11 155.66 155.56 145.59 145.54 139.64 139.53 139.10 138.98 138.53 138.43 138.27 138.17 135.23 135.20 134.92 134.91 128.75 128.74 128.57 128.54 124.14 123.31 77.36 77.04 76.72 31.28 30.27 29.11 29.09 28.26 22.38 16.06 16.03 13.96 13.94 13.83
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4f
4f'
= 3.2 :1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

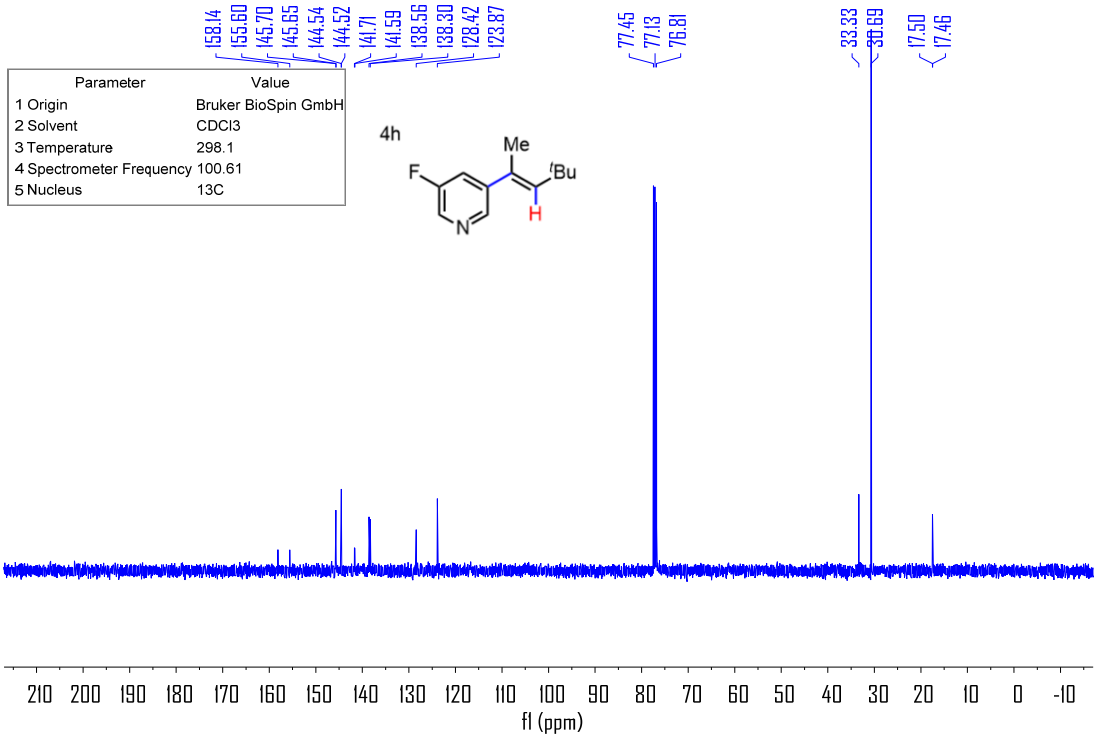

4f
Me
F
nBu
H
N
:
4f'
nBu
F
Me
H
N
-130.16
-130.48
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


8.36
8.36
8.31
8.29
7.26
7.16
7.15
7.15
7.13
5.64
5.61
2.74
2.73
2.72
2.71
2.70
2.69
2.69
2.68
2.67
2.65
2.02
1.05
1.04
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4g
Me
F
iPr
H
N
1.00
1.04
1.00
1.00
1.01
3.05
6.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.29
155.74
145.68
145.63
142.32
142.29
139.78
139.67
138.63
138.37
126.86
123.52
77.45
77.13
76.81
27.90
22.61
16.11
16.07
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4g
Me
F
iPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

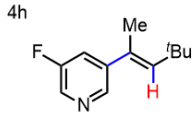

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
-129.97
4g
Me
F
iPr
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)


8.37
8.37
8.32
8.31
7.19
7.18
7.16
5.86
2.17
0.20
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4h
Me
F
tBu
H
N
1.00
1.00
0.99
0.94
2.90
9.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


158.14
155.60
145.70
145.65
144.54
144.52
141.71
141.59
138.56
138.30
128.42
123.87
77.45
77.13
76.81
33.33
30.69
17.50
17.46
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4h
Me
F
tBu
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

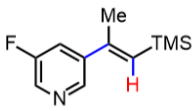
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

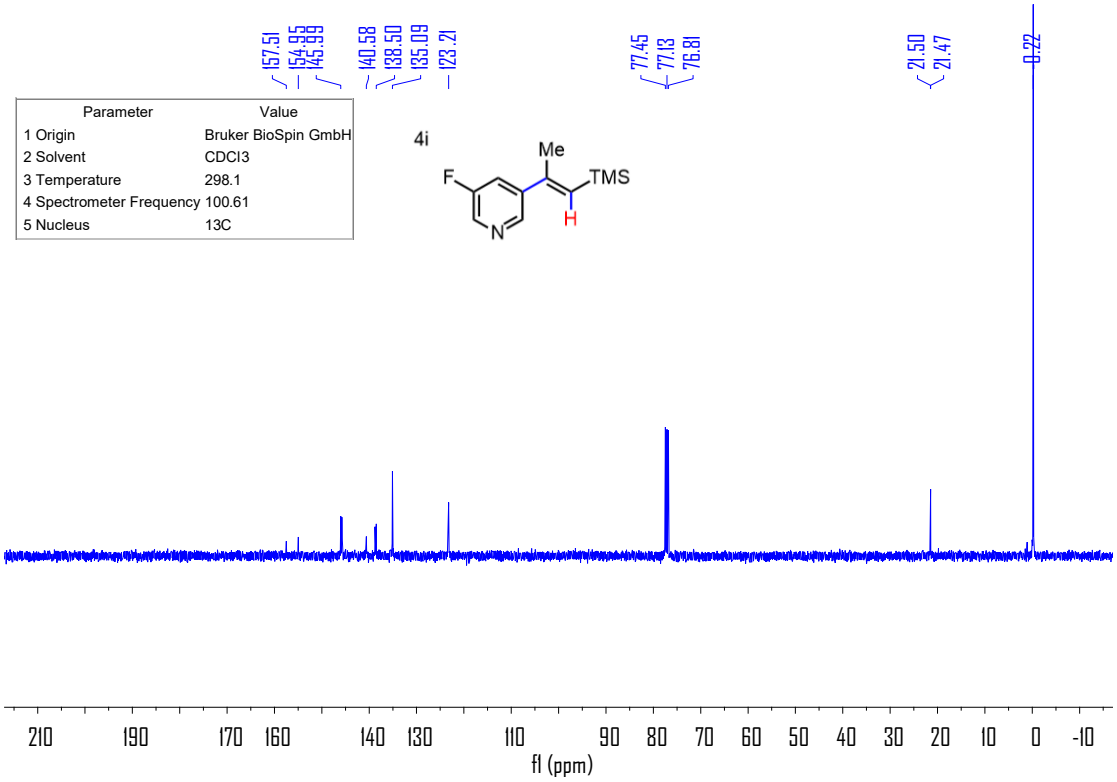
4h

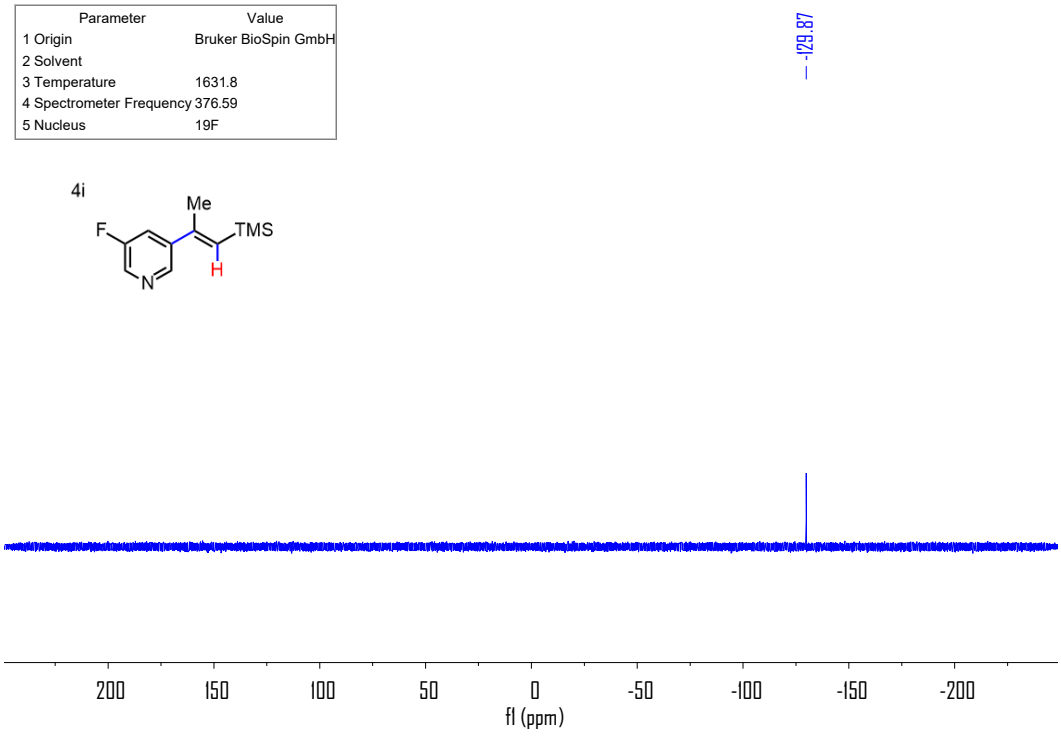


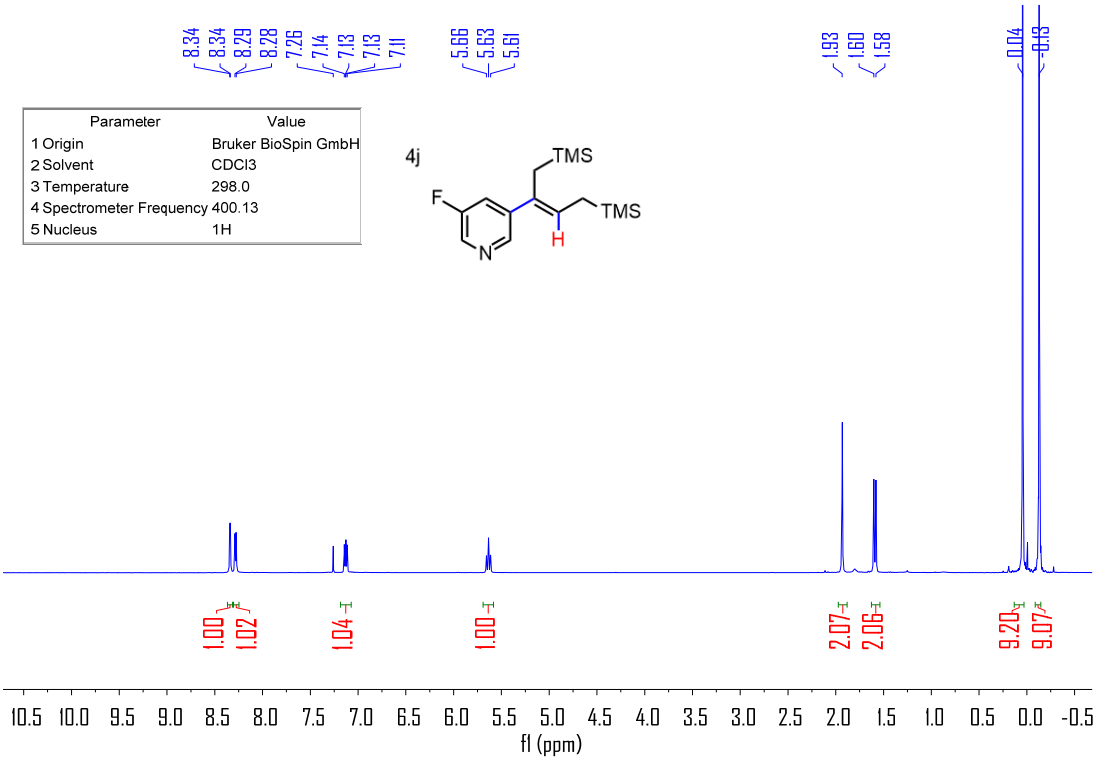
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

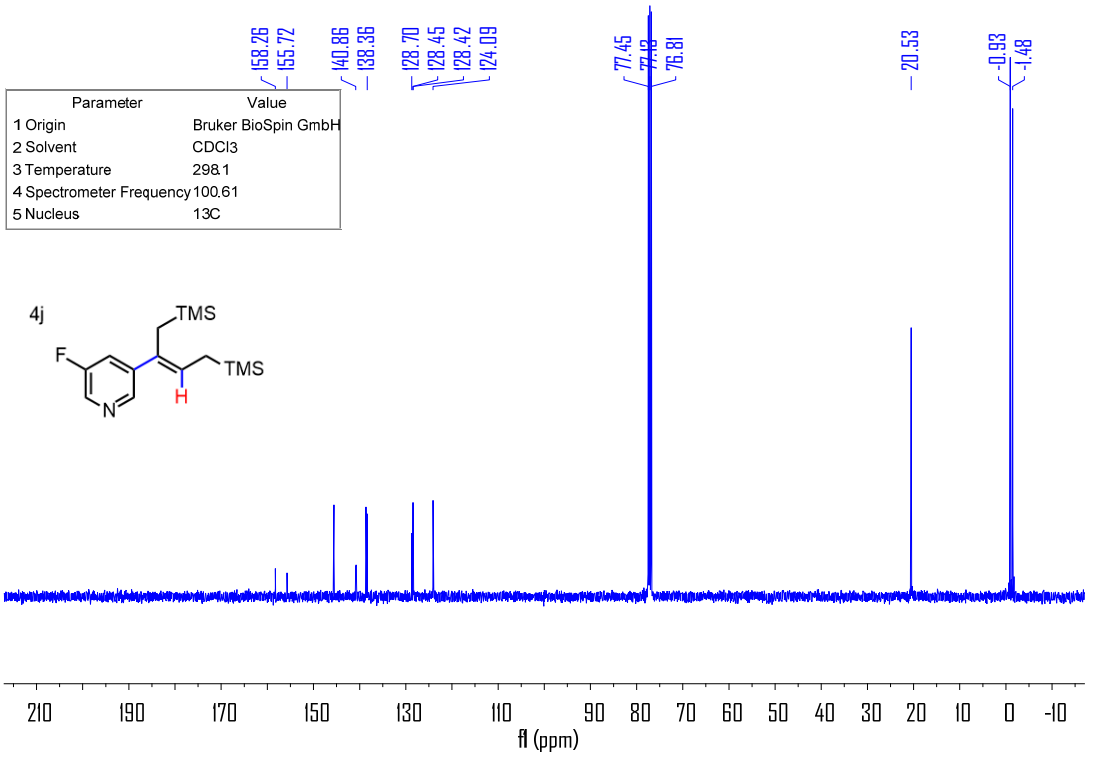
4i




157.51
154.95
145.99
140.58
138.50
135.09
123.21
77.45
77.13
76.81
21.50
21.47
0.22
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4i
Me
F
TMS
H
N
210 190 170 160 140 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

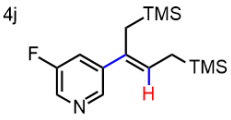

-129.87
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
4i
Me
F
TMS
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)


8.34
8.34
8.29
8.28
7.26
7.14
7.13
7.13
7.11
5.66
5.63
5.61
1.93
1.60
1.58
0.04
-0.13
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4j
TMS
TMS
F
N
H
1.00
1.02
1.04
1.00
2.07
2.06
9.20
9.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.26
155.72
140.86
138.36
128.70
128.45
128.42
124.09
77.45
77.19
76.81
20.53
-0.93
-1.48
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4j
TMS
TMS
F
N
H
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

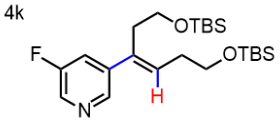
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

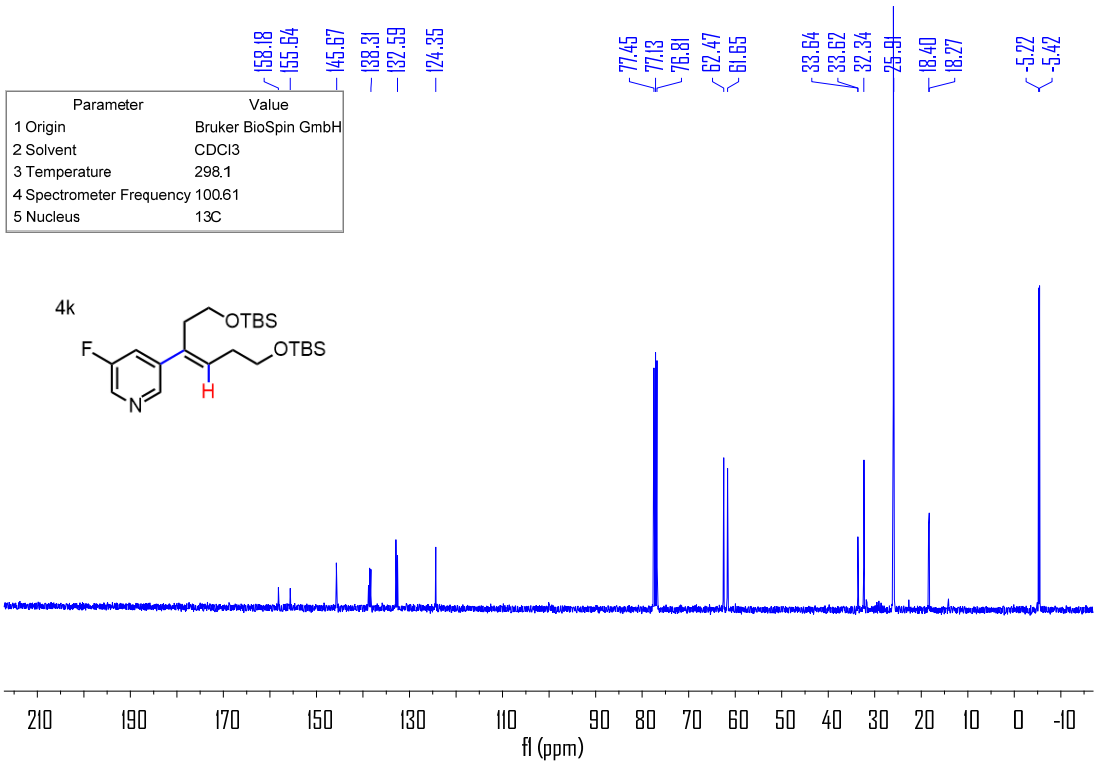
4j

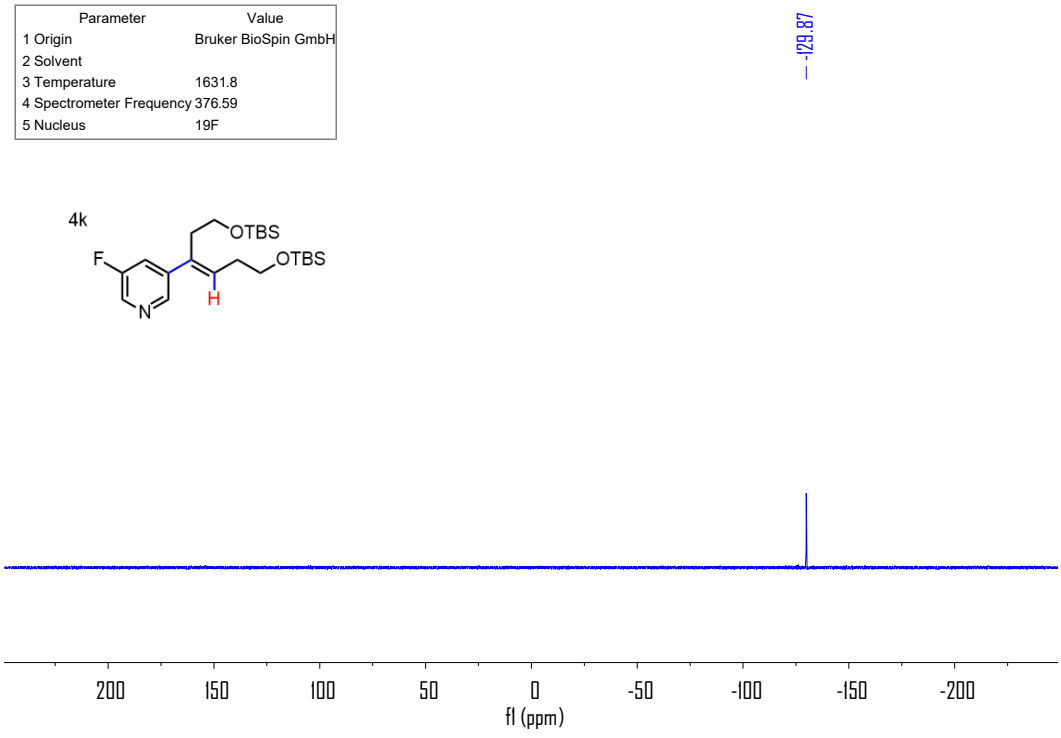


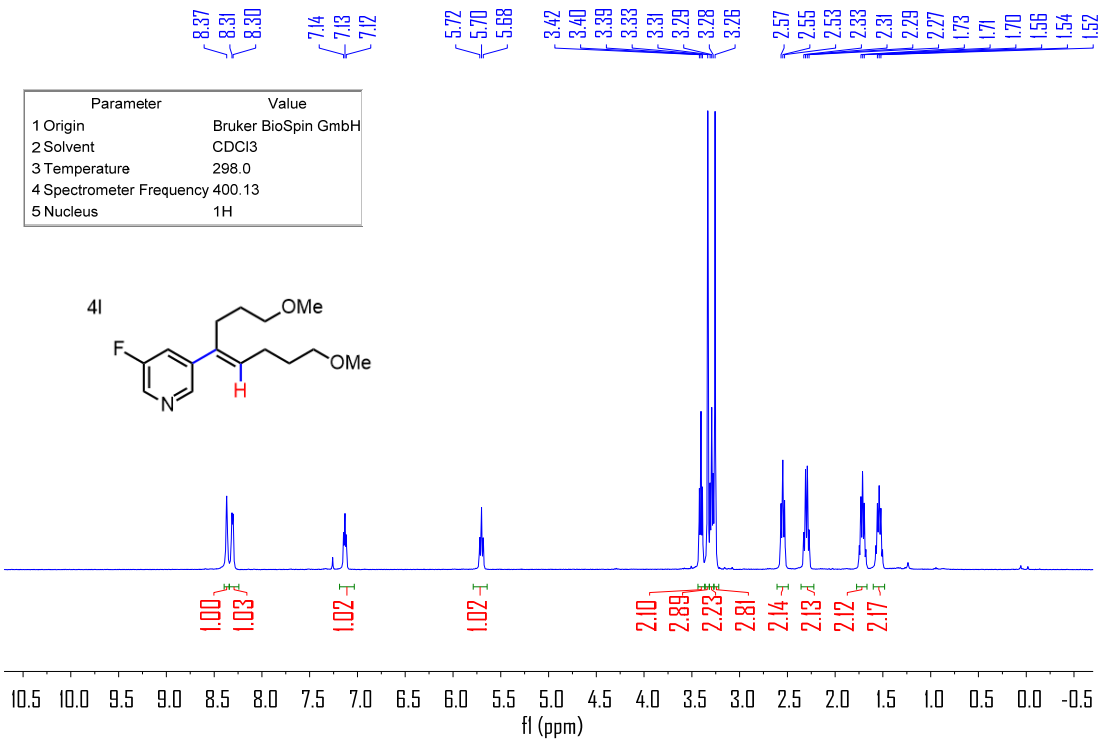
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

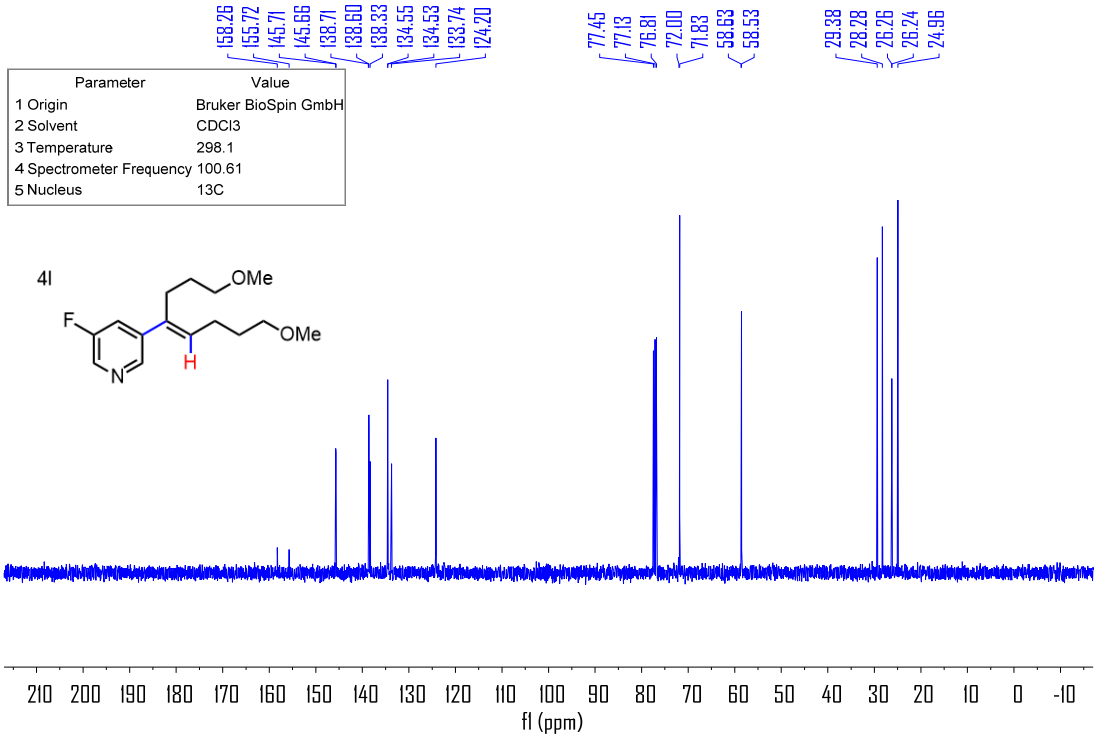
4k




158.18
155.64
145.67
138.31
132.59
124.35
77.45
77.13
76.81
62.47
61.65
33.64
33.62
32.34
25.91
18.40
18.27
-5.22
-5.42
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4k
OTBS
OTBS
F
N
H
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

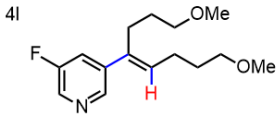

-129.87
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
4k
OTBS
OTBS
F
N
H
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)


8.37
8.31
8.30
7.14
7.13
7.12
5.72
5.70
5.68
3.42
3.40
3.39
3.33
3.31
3.29
3.28
3.26
2.57
2.55
2.53
2.33
2.31
2.29
2.27
1.73
1.71
1.70
1.56
1.54
1.52
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4l
OMe
OMe
F
N
H
1.00
1.03
1.02
1.02
2.10
2.89
2.23
2.81
2.14
2.13
2.12
2.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

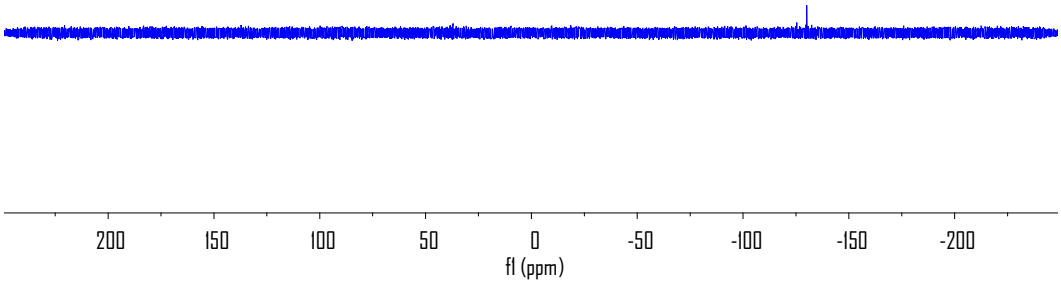

158.26
155.72
145.71
145.66
138.71
138.60
138.33
134.55
134.53
133.74
124.20
77.45
77.13
76.81
72.00
71.83
58.63
58.53
29.38
28.28
26.26
26.24
24.96
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4l
OMe
OMe
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

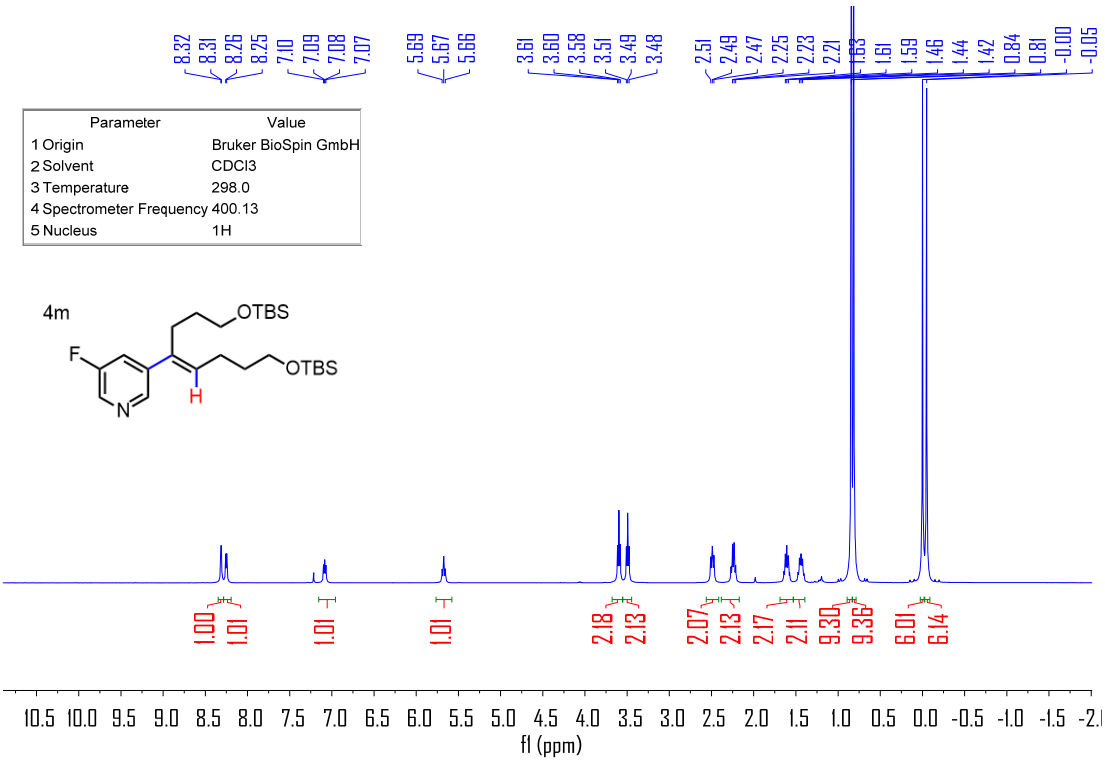
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F

4l



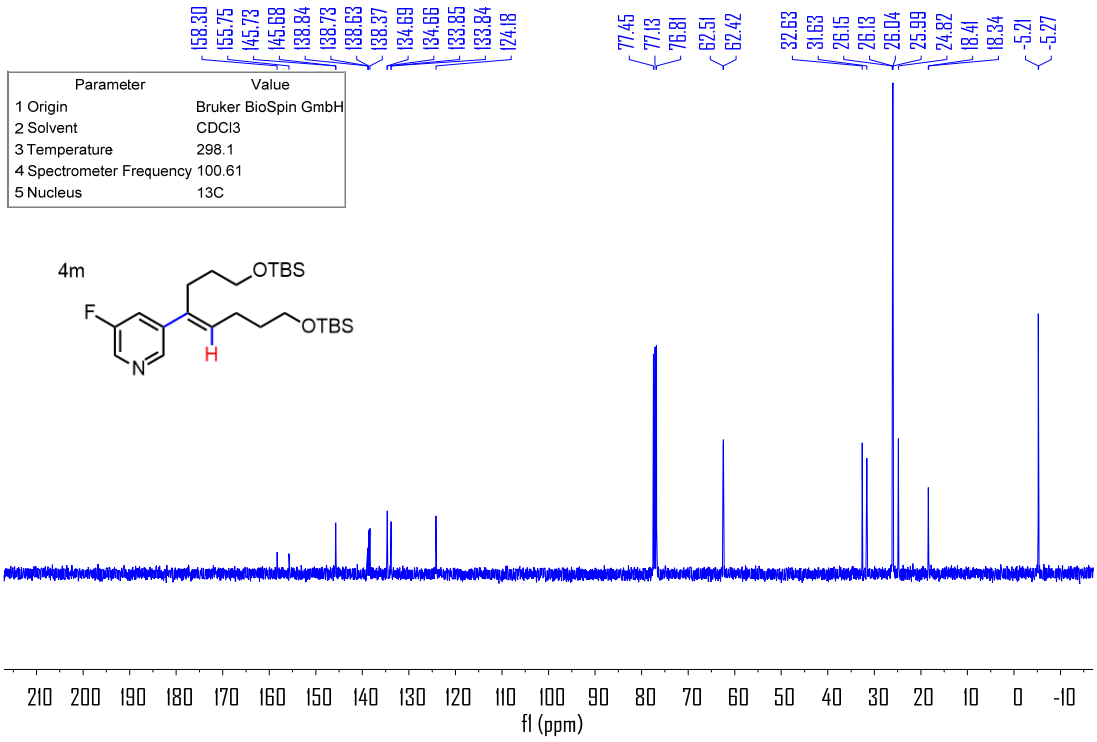
-180.10

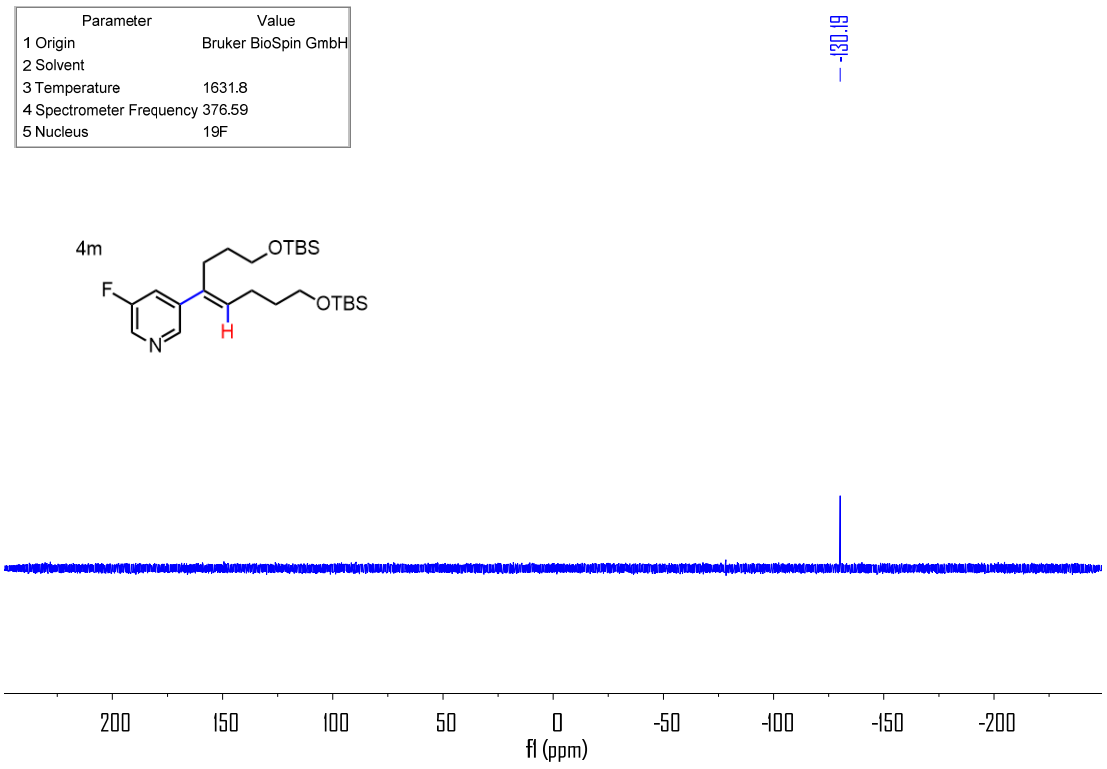


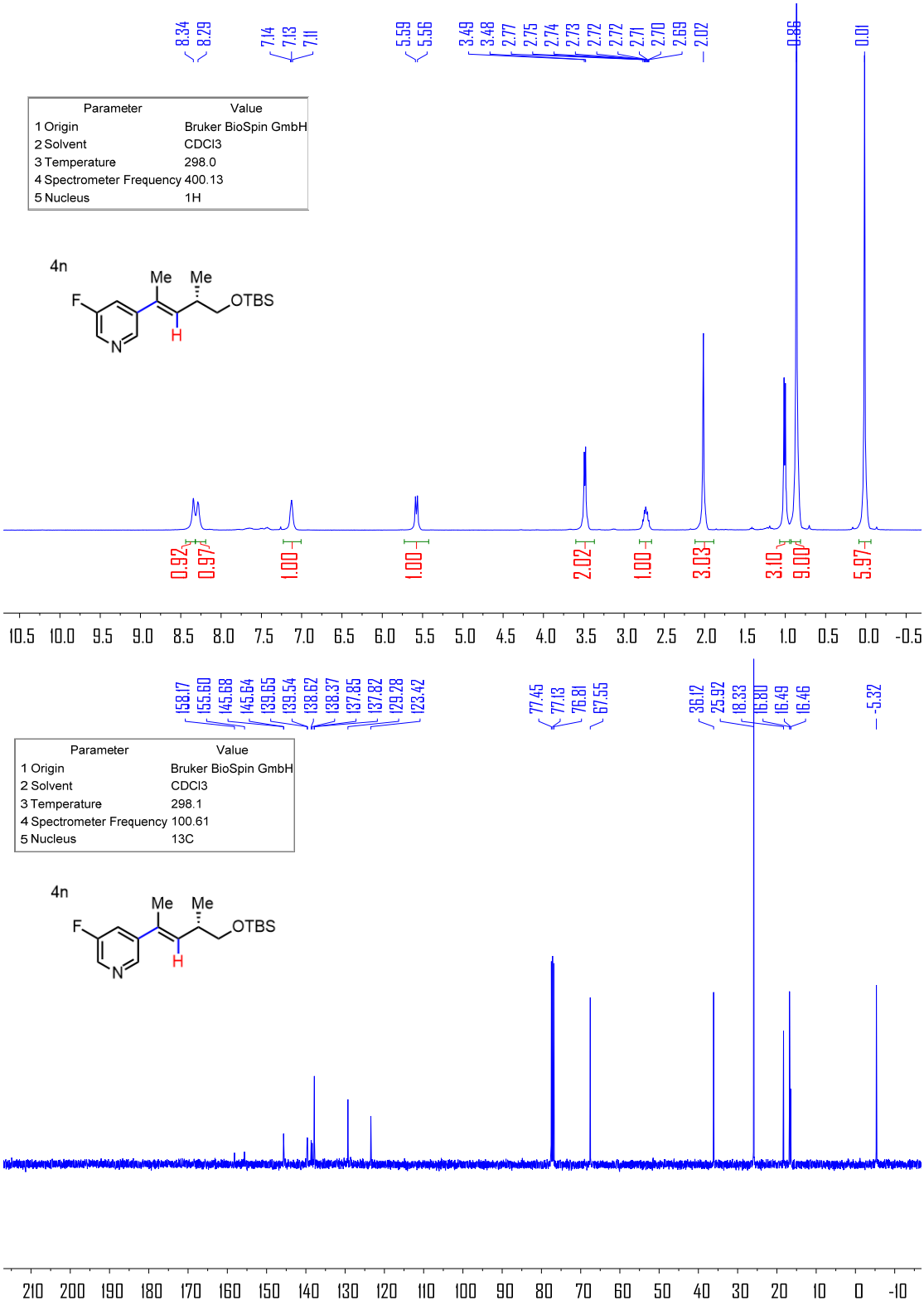


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H

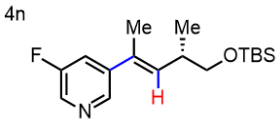
4m


158.30
155.75
145.73
145.68
138.84
138.73
138.63
138.37
134.69
134.66
133.85
133.84
124.18
77.45
77.13
76.81
62.51
62.42
32.63
31.63
26.15
26.13
26.04
25.99
24.82
18.41
18.34
-5.21
-5.27
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4m
OTBS
F
OTBS
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

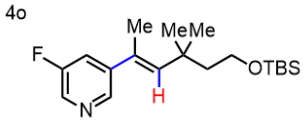

Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
-130.19
4m
OTBS
F
OTBS
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

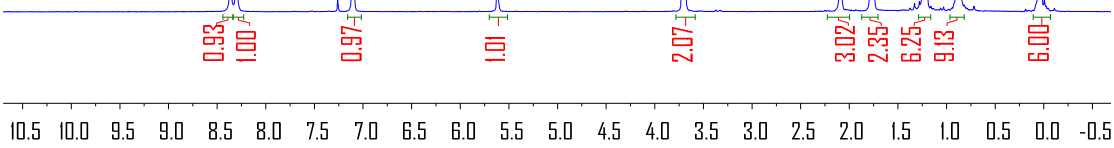

8.34
8.29
7.14
7.13
7.11
5.59
5.56
3.49
3.48
2.77
2.75
2.74
2.73
2.72
2.72
2.72
2.71
2.70
2.69
2.02
0.86
0.01
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
4n
Me
Me
F
OTBS
H
N
0.92
0.97
1.00
1.00
2.02
1.00
3.03
3.10
9.00
5.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
158.17
155.60
145.68
145.64
139.65
139.54
138.62
138.37
137.85
137.82
129.28
123.42
77.45
77.13
76.81
67.55
36.12
25.92
18.33
16.80
16.49
16.46
-5.32
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4n
Me
Me
F
OTBS
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

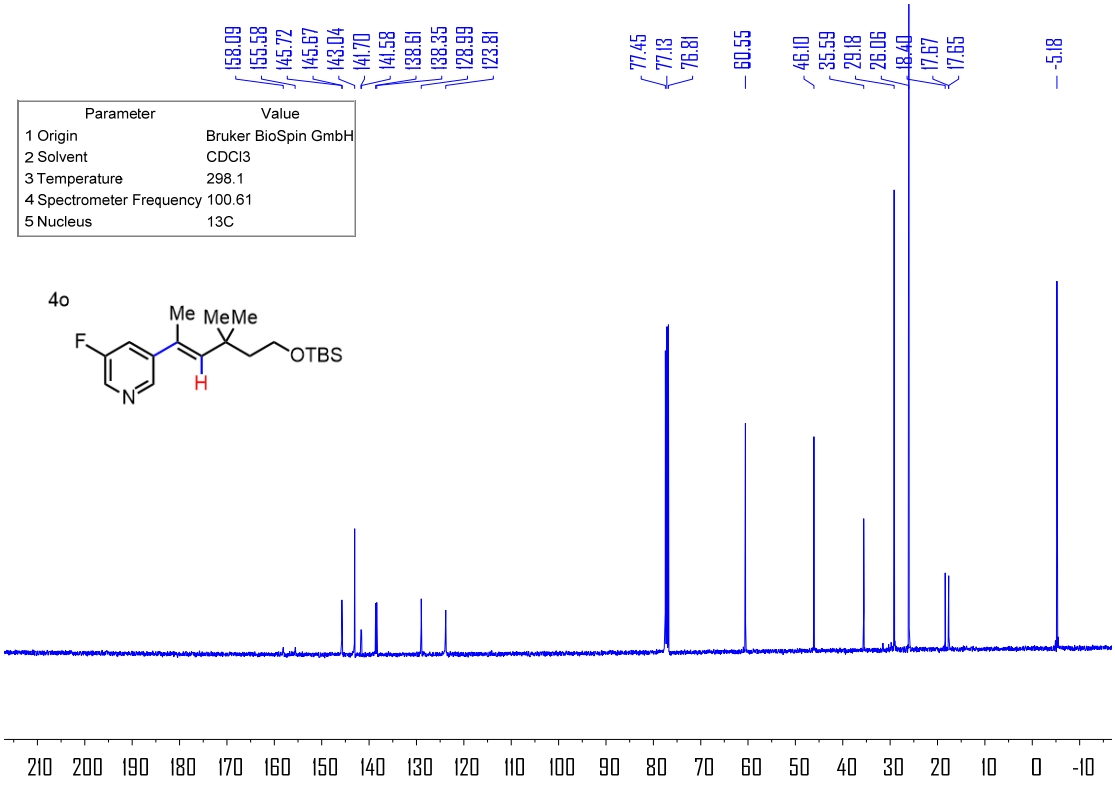
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	
3 Temperature	1631.8
4 Spectrometer Frequency	376.59
5 Nucleus	19F



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.0
4 Spectrometer Frequency	400.13
5 Nucleus	1H



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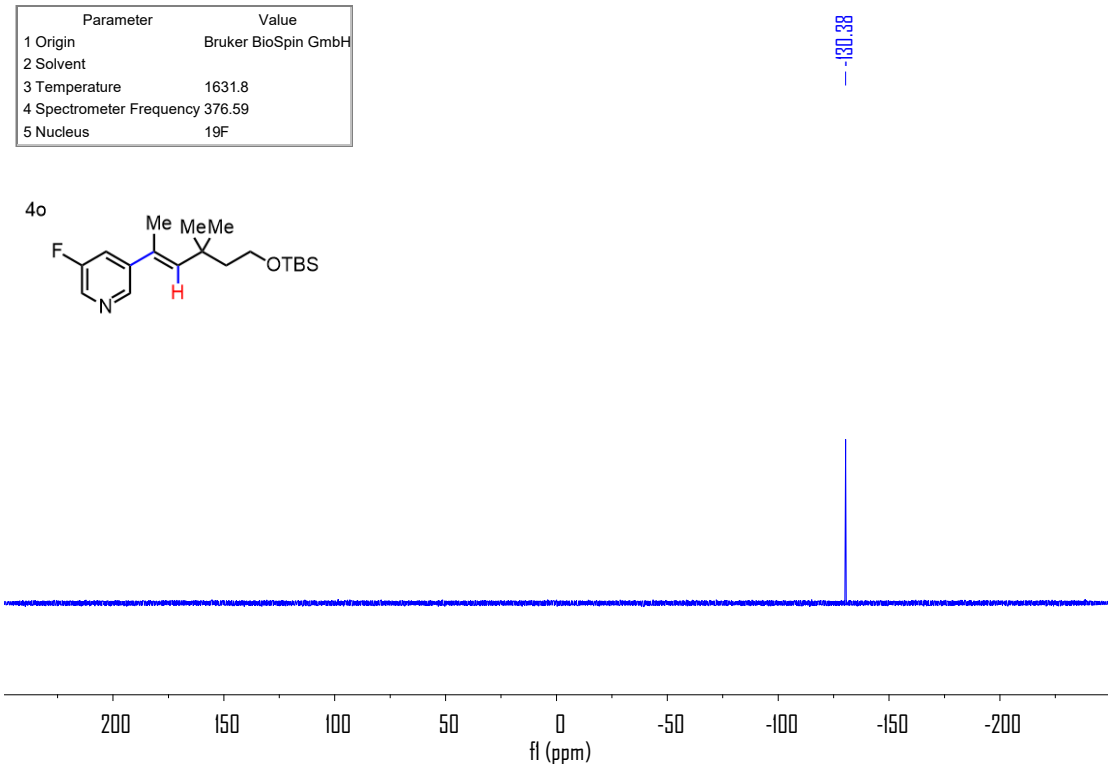
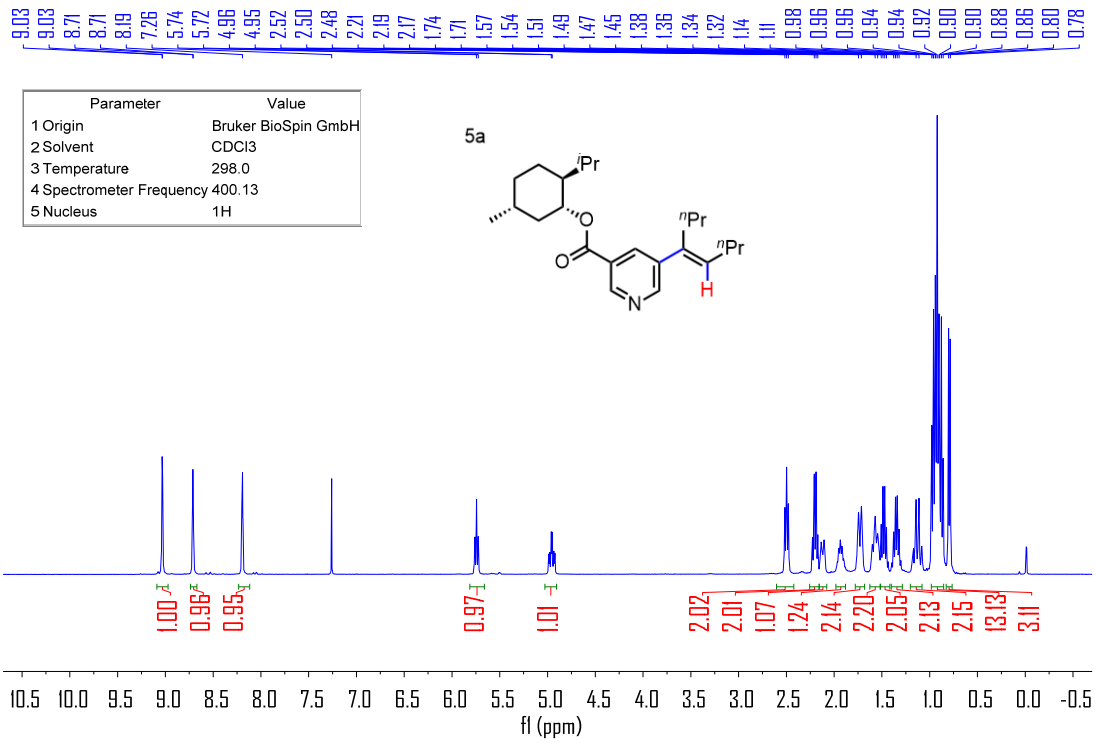
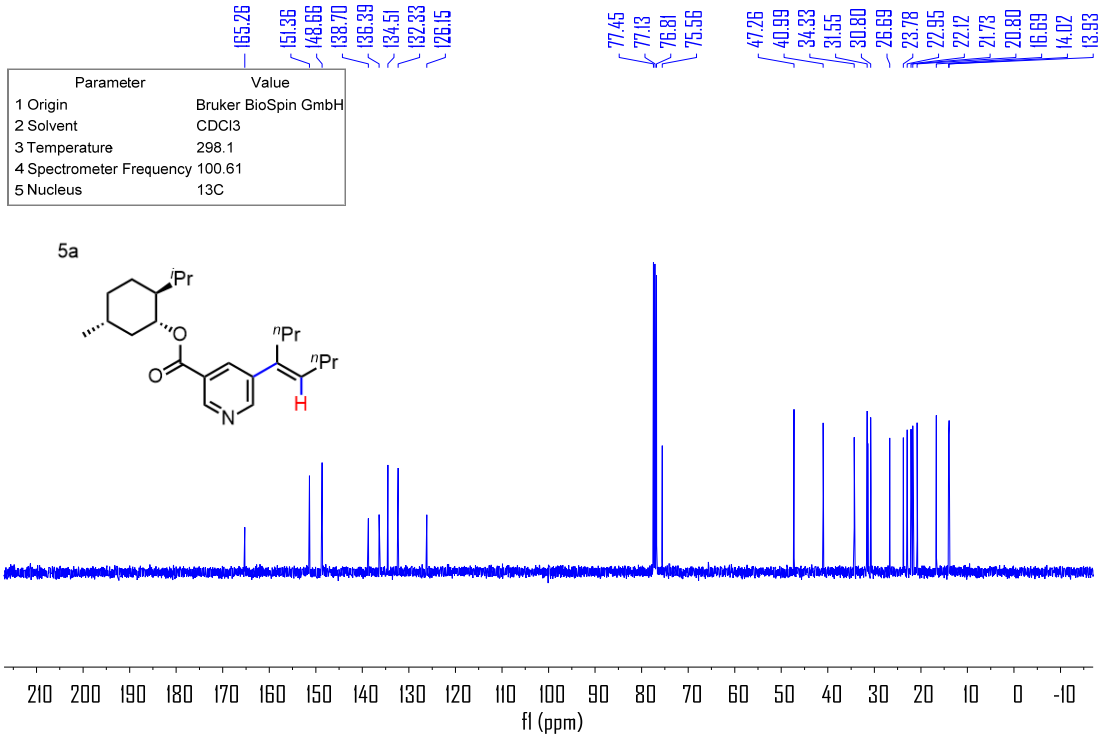
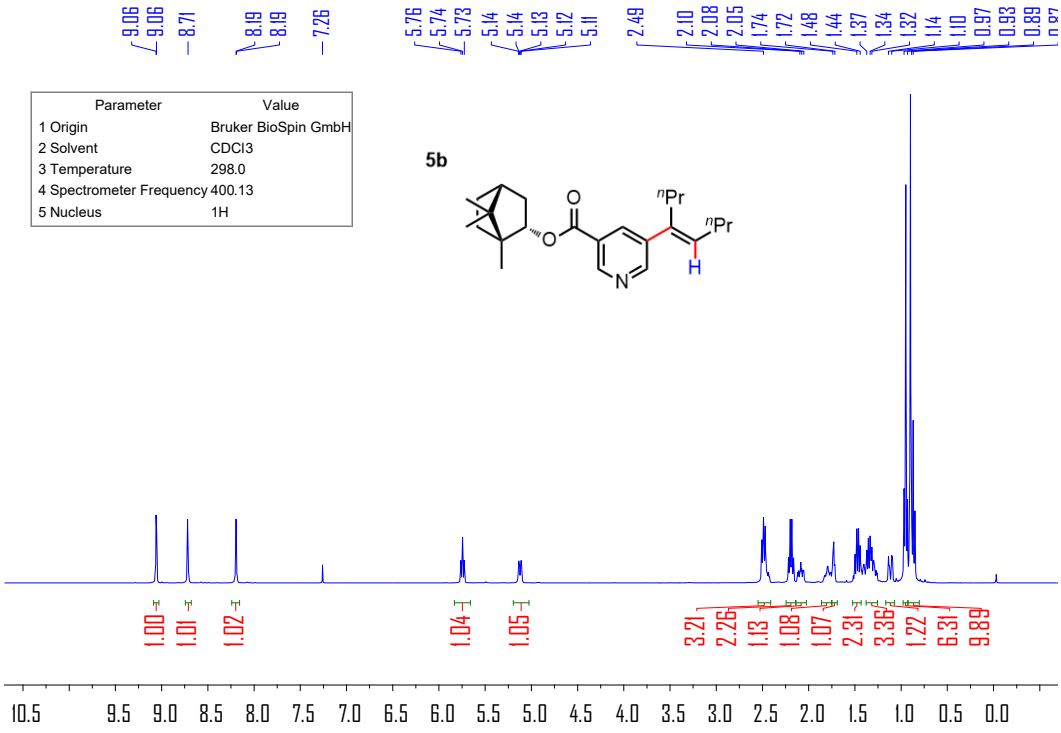
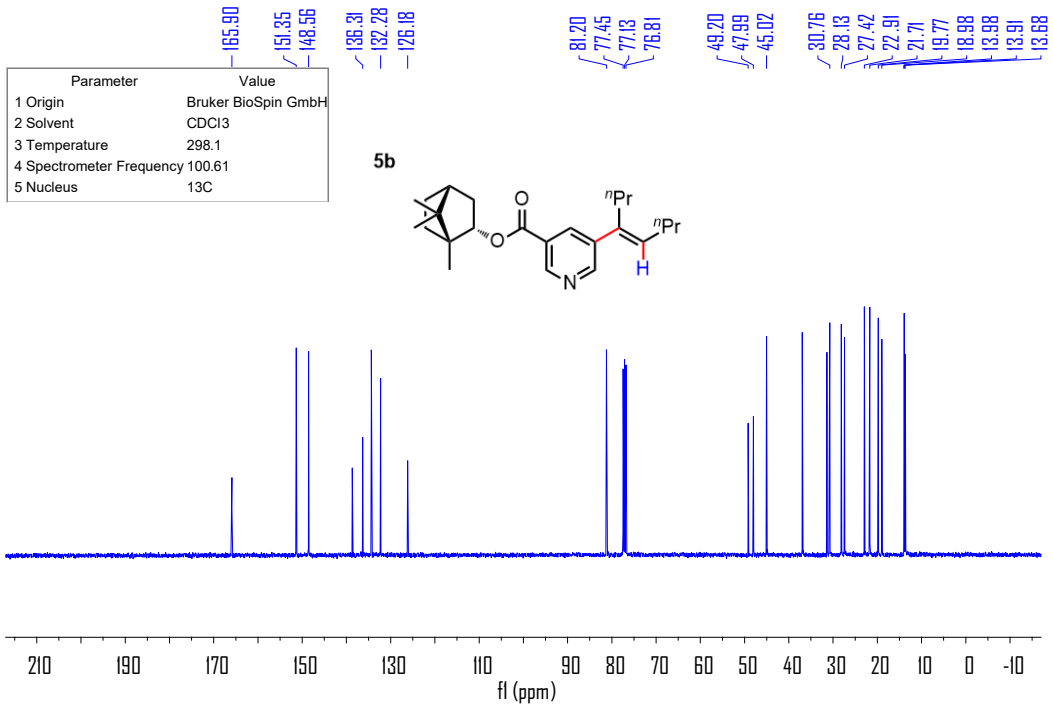
155.58
145.72
145.67
143.04
141.70
141.58
138.61
138.35
128.99
123.81
77.45
77.13
76.81
60.55
46.10
35.59
29.18
26.06
18.40
17.67
17.65
-5.18
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
4o
Me
MeMe
F
OTBS
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

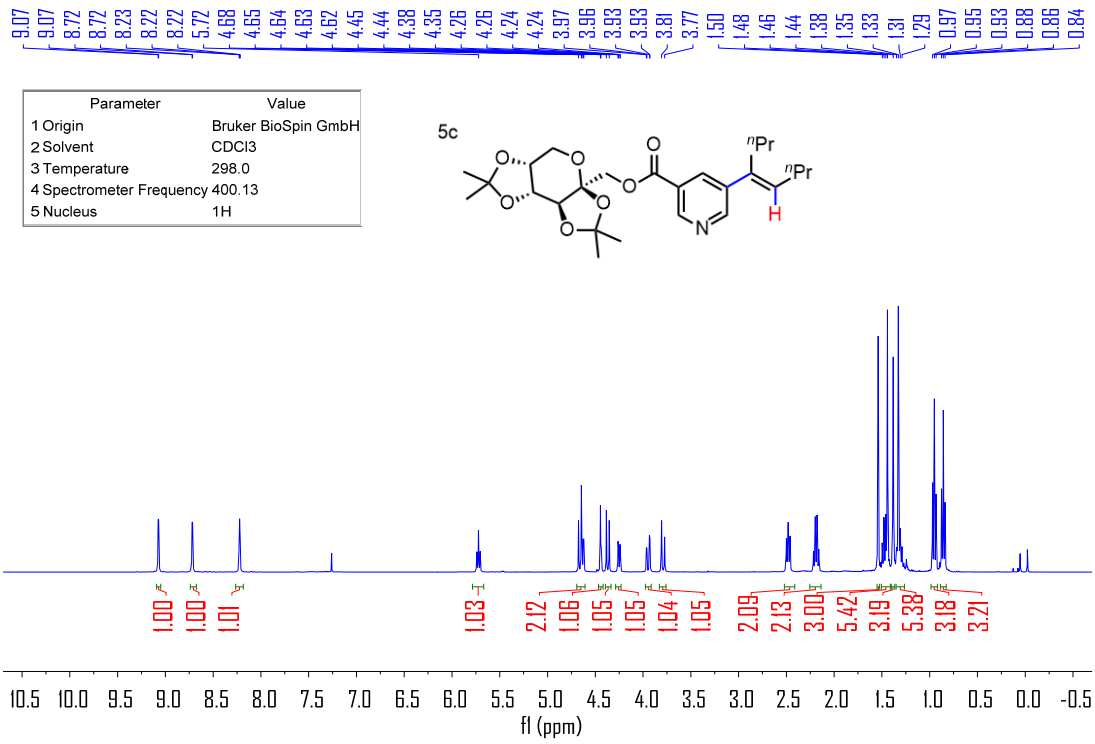

-130.38
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent
3 Temperature 1631.8
4 Spectrometer Frequency 376.59
5 Nucleus 19F
4o
Me
MeMe
F
OTBS
H
N
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

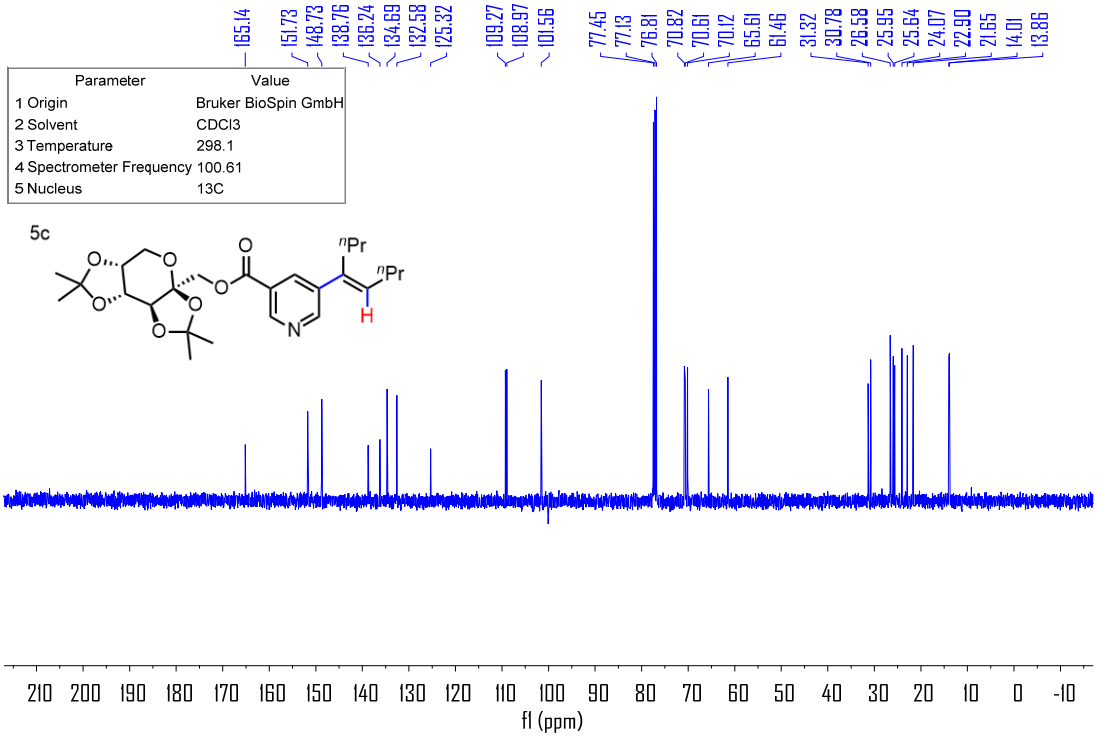

9.03 9.03 8.71 8.71 8.19 7.26 5.74 5.72 4.96 4.95 2.52 2.50 2.48 2.21 2.19 2.17 1.74 1.71 1.57 1.54 1.51 1.49 1.47 1.45 1.38 1.36 1.34 1.32 1.14 1.11 0.98 0.96 0.96 0.94 0.94 0.92 0.90 0.90 0.88 0.86 0.80 0.78
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5a
iPr
nPr
nPr
O
O
N
H
1.00 0.96 0.95 0.97 1.01 2.02 2.01 1.07 1.24 2.14 2.20 2.05 2.13 2.15 13.13 3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

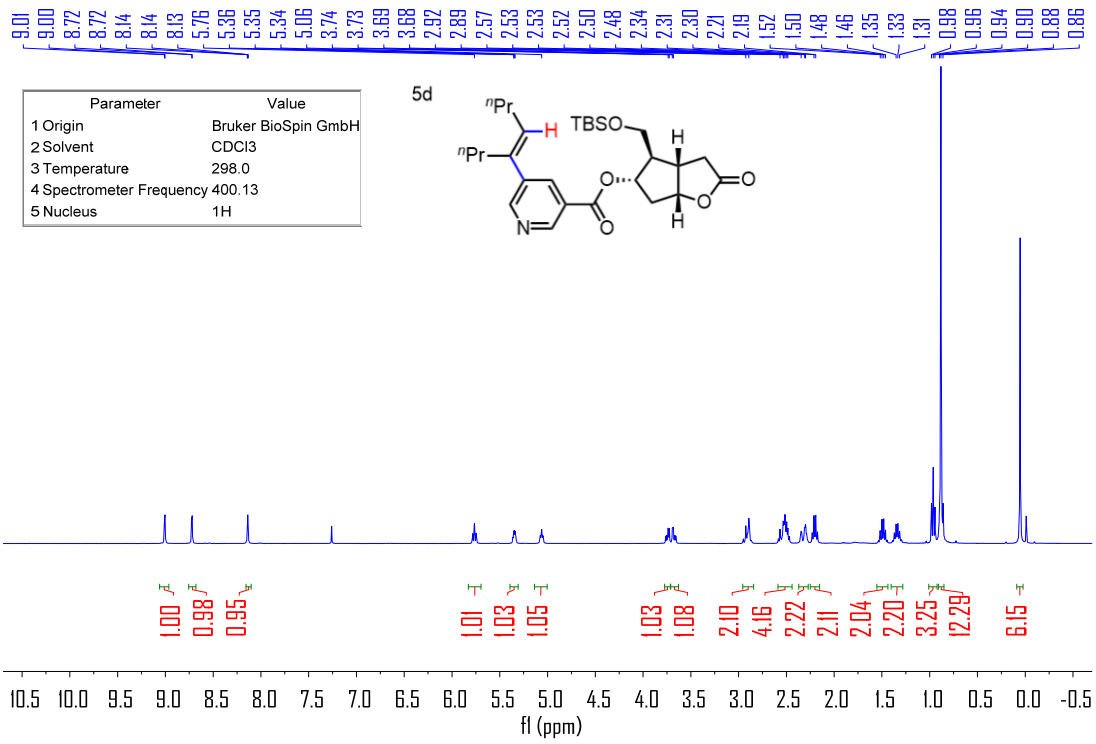

165.26 151.36 148.66 138.70 136.39 134.51 132.33 126.15 77.45 77.13 76.81 75.56 47.26 40.99 34.33 31.55 30.80 26.69 23.78 22.95 22.12 21.73 20.80 16.69 14.07 13.93
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5a
iPr
nPr
nPr
O
O
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

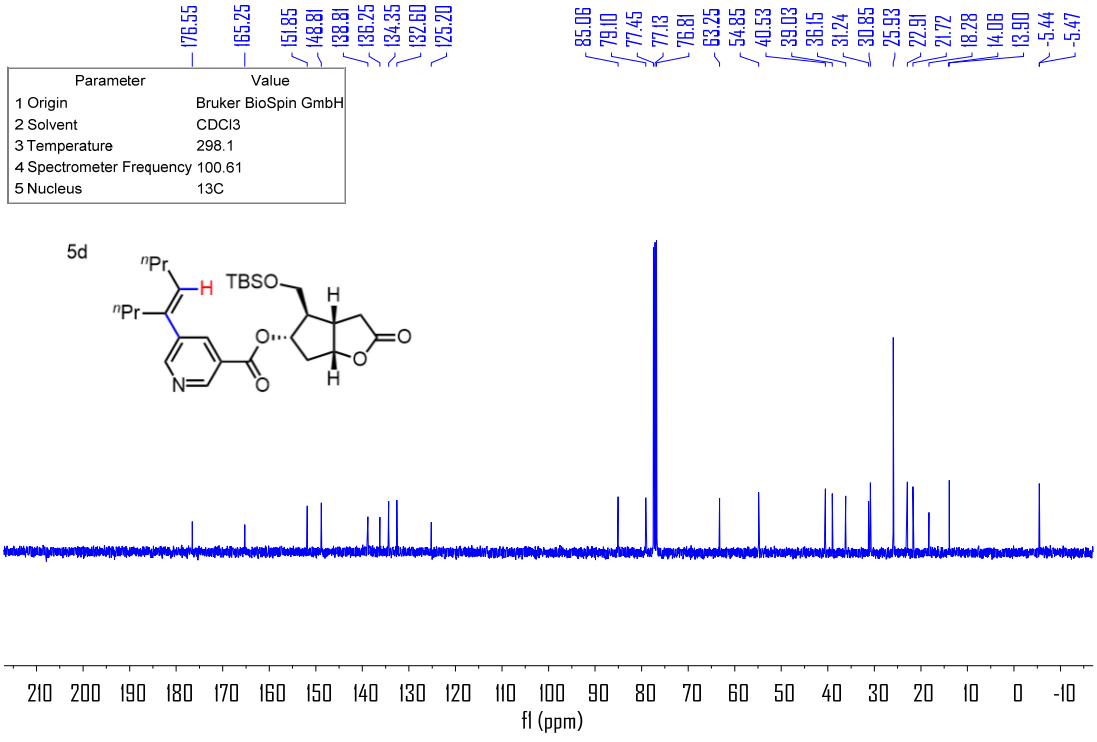

9.06
9.06
8.71
8.19
8.19
7.26
5.76
5.74
5.73
5.14
5.14
5.13
5.12
5.11
2.49
2.10
2.08
2.05
1.74
1.72
1.48
1.44
1.37
1.34
1.32
1.14
1.10
0.97
0.93
0.89
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5b
O
O
N
nPr
nPr
H
1.00
1.01
1.02
1.04
1.05
3.21
2.26
1.13
1.08
1.07
2.31
3.35
1.22
6.31
9.89
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.90
151.35
148.56
136.31
132.28
126.18
81.20
77.45
77.13
76.81
49.20
47.99
45.02
30.76
28.13
27.42
22.91
21.71
19.77
18.98
13.98
13.91
13.68
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5b
O
O
N
nPr
nPr
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.07 9.07 8.72 8.72 8.23 8.22 8.22 5.72 4.68 4.65 4.64 4.63 4.62 4.45 4.44 4.38 4.35 4.26 4.26 4.24 4.24 3.97 3.96 3.93 3.93 3.81 3.77 1.50 1.48 1.46 1.44 1.38 1.35 1.33 1.31 1.29 0.97 0.95 0.93 0.88 0.86 0.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5c
nPr
nPr
H
N
1.00 1.00 1.01 1.03 2.12 1.06 1.05 1.05 1.04 1.05 2.09 2.13 3.00 5.42 3.19 5.38 3.18 3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.14 151.73 148.73 138.76 136.24 134.69 132.58 125.32 109.27 108.97 101.56 77.45 77.13 76.81 70.82 70.61 70.12 65.61 61.46 31.32 30.78 26.58 25.95 25.64 24.07 22.90 21.65 14.01 13.86
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5c
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.01 9.00 8.72 8.72 8.14 8.14 8.13 5.76 5.36 5.35 5.34 5.06 3.74 3.73 3.69 3.68 2.92 2.89 2.57 2.53 2.53 2.52 2.50 2.48 2.34 2.31 2.30 2.21 2.19 1.52 1.50 1.48 1.46 1.35 1.33 1.31 0.98 0.96 0.94 0.90 0.88 0.86
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5d
nPr
nPr
H
TBSO
H
O
O
O
N
O
H
1.00 0.98 0.95 1.01 1.03 1.05 1.03 1.08 2.10 4.16 2.22 2.11 2.04 2.20 3.25 12.29 6.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.55 165.25 151.85 149.81 138.81 136.25 134.35 132.60 125.20
85.06 79.10 77.45 77.13 76.81 63.25 54.85 40.53 39.03 36.15 31.24 30.85 25.93 22.91 21.72 18.28 14.06 13.90 -5.44 -5.47
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5d
nPr
nPr
H
TBSO
H
O
O
O
N
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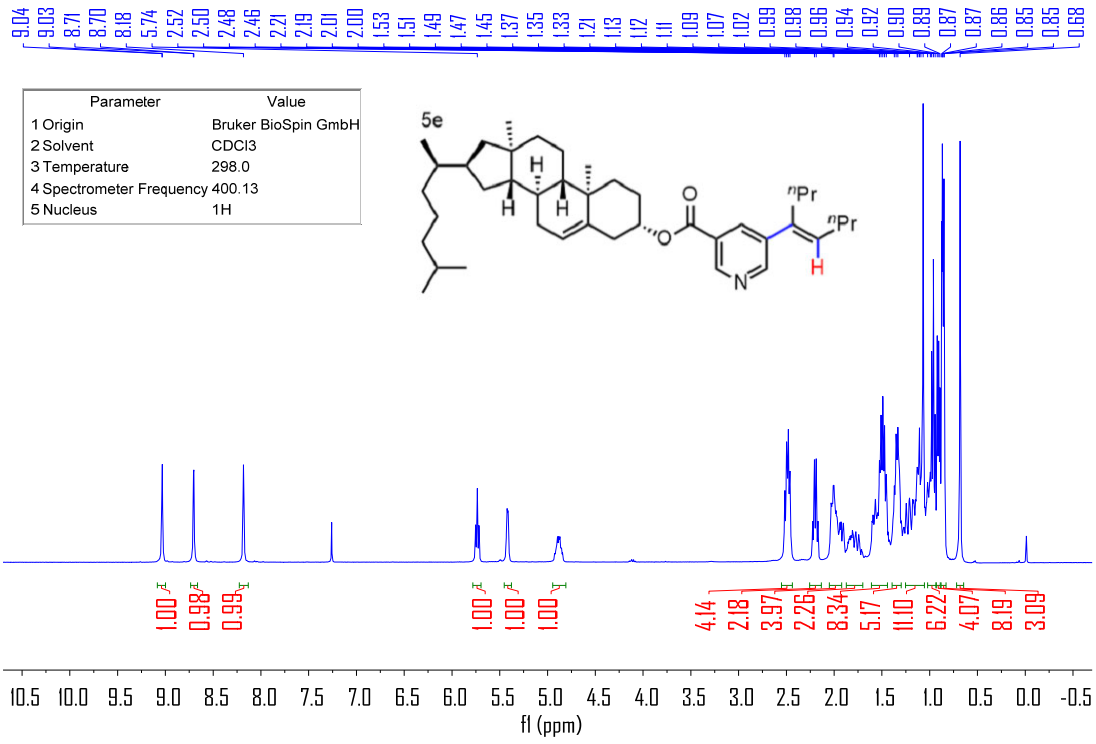
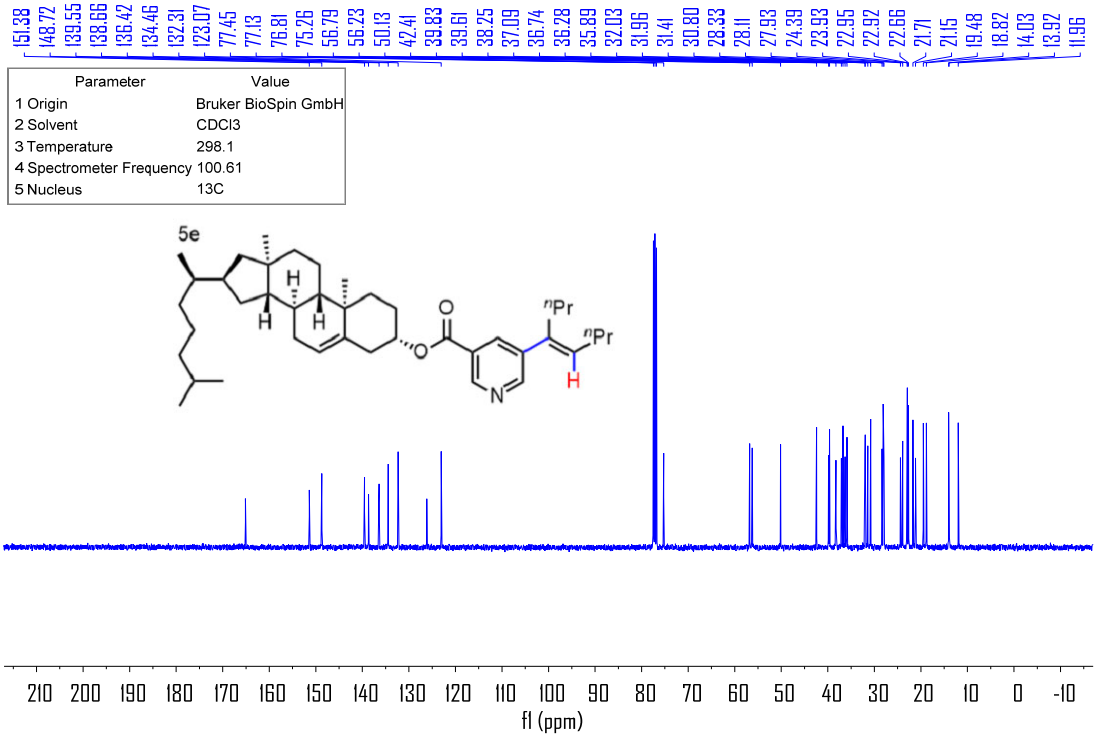
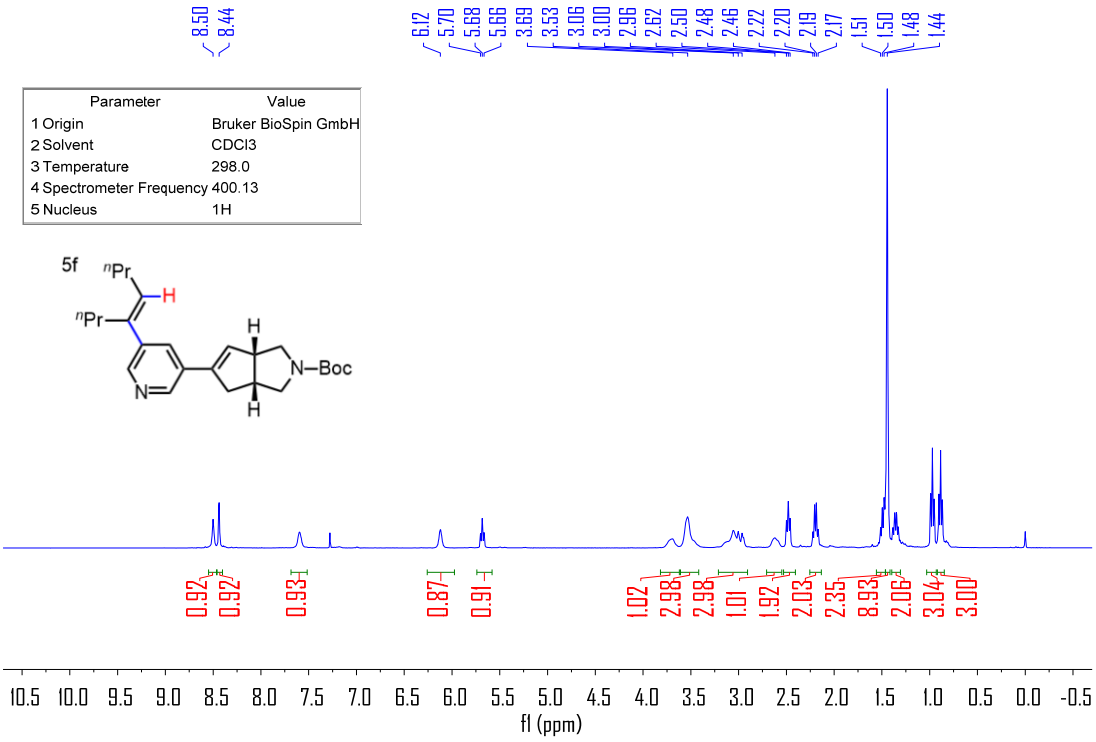
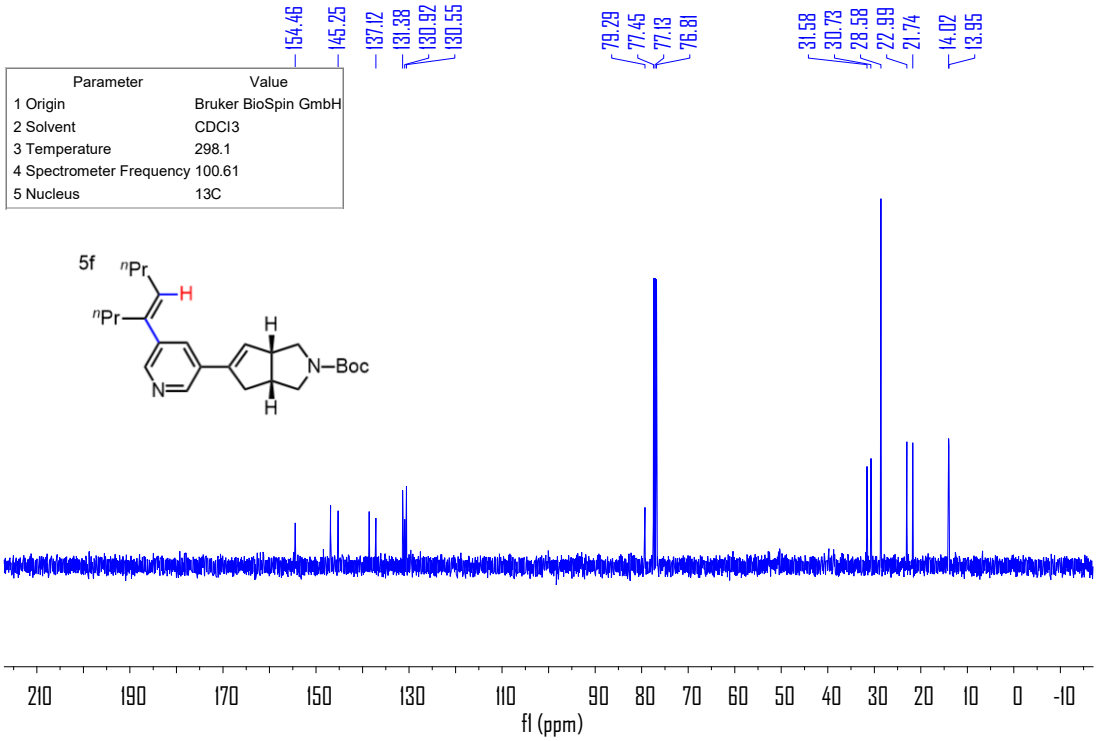
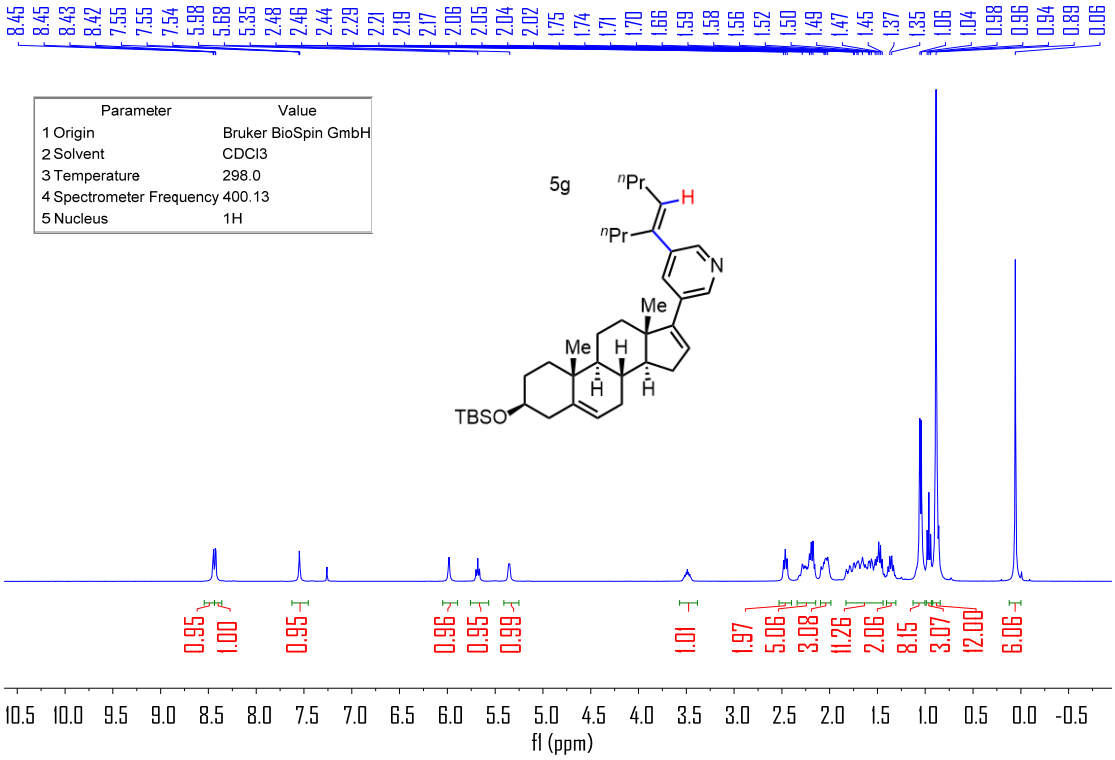
f1 (ppm)

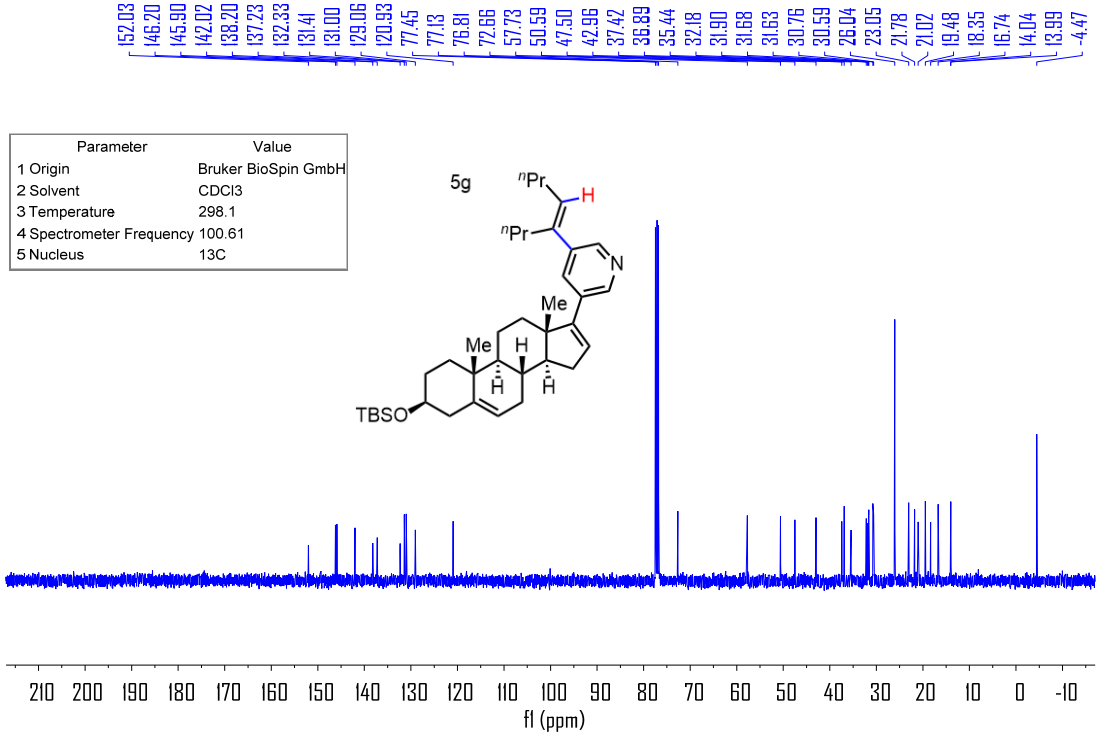

9.04 9.03 8.71 8.70 8.18 5.74 2.52 2.50 2.48 2.46 2.21 2.19 2.01 2.00 1.53 1.51 1.49 1.47 1.45 1.37 1.35 1.33 1.21 1.13 1.12 1.11 1.09 1.07 1.02 0.99 0.98 0.96 0.94 0.92 0.90 0.89 0.87 0.87 0.86 0.85 0.85 0.68
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5e
nPr
nPr
H
N
1.00 0.98 0.99 1.00 1.00 1.00 4.14 2.18 3.97 2.26 8.34 5.17 11.10 6.22 4.07 8.19 3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151.38 148.72 139.55 138.66 136.42 134.46 132.31 123.07 77.45 77.13 76.81 75.26 56.79 56.23 50.13 42.41 39.83 39.61 38.25 37.09 36.74 36.28 35.89 32.03 31.96 31.41 30.80 28.33 28.11 27.93 24.39 23.93 22.95 22.92 22.66 21.71 21.15 19.48 18.82 14.03 13.92 11.96
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5e
nPr
nPr
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.50
8.44
6.12
5.70
5.68
5.66
3.69
3.53
3.06
3.00
2.96
2.62
2.50
2.48
2.46
2.22
2.20
2.19
2.17
1.51
1.50
1.48
1.44
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5f
nPr
H
nPr
H
N
N—Boc
H
0.92
0.92
0.93
0.87
0.91
1.02
2.98
2.98
1.01
1.92
2.03
2.35
8.93
2.06
3.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


154.46
145.25
137.12
131.38
130.92
130.55
79.29
77.45
77.13
76.81
31.58
30.73
28.58
22.99
21.74
14.02
13.95
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5f
nPr
H
nPr
H
N
N—Boc
H
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.45 8.45 8.43 8.42 7.55 7.55 7.54 5.38 5.38 5.35 2.48 2.46 2.44 2.29 2.21 2.19 2.17 2.06 2.05 2.04 2.02 1.75 1.74 1.71 1.70 1.66 1.59 1.58 1.56 1.52 1.50 1.49 1.47 1.45 1.37 1.35 1.06 1.04 0.98 0.96 0.94 0.89 0.06
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5g
nPr
H
nPr
N
Me
Me
H
H
H
TBSO
0.95 1.00 0.95 0.96 0.95 0.99 1.01 1.97 5.06 3.08 11.26 2.06 8.15 3.07 12.00 6.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.03 146.20 145.90 142.02 138.20 137.23 132.33 131.41 131.00 129.06 120.93 77.45 77.13 76.81 72.66 57.73 50.59 47.50 42.96 37.42 36.89 35.44 32.18 31.90 31.68 31.63 30.76 30.59 26.04 23.05 21.78 21.02 19.48 18.35 16.74 14.04 13.99 -4.47
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5g
nPr
H
nPr
N
Me
Me
H
H
H
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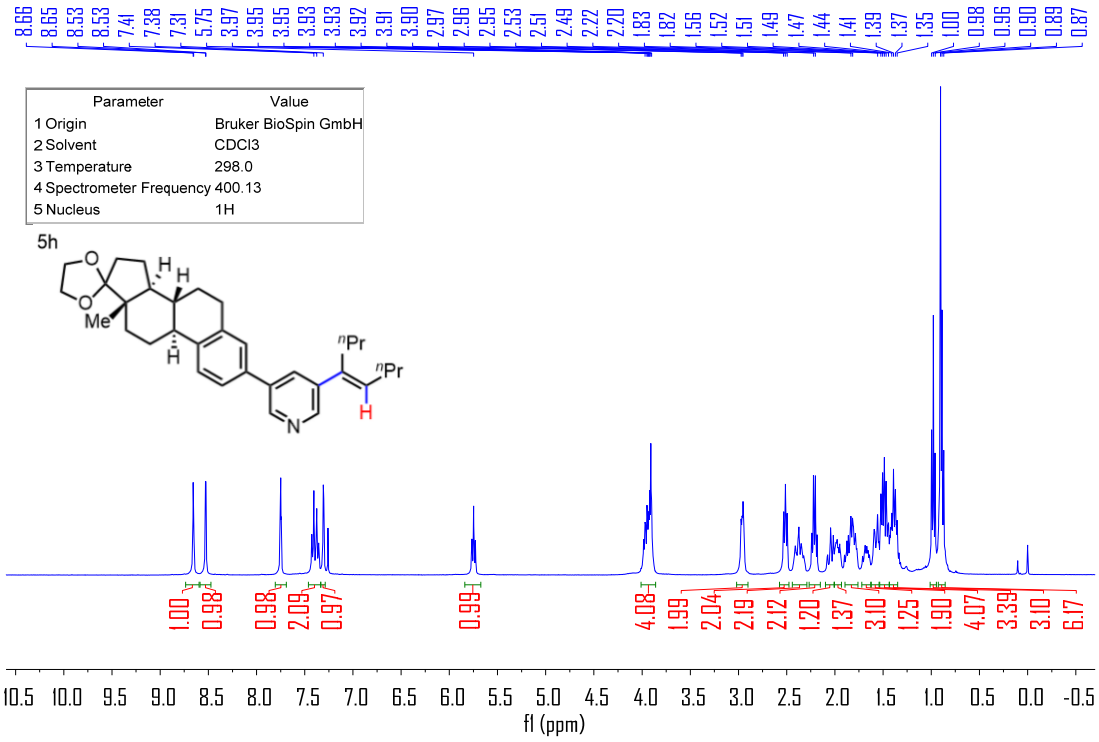
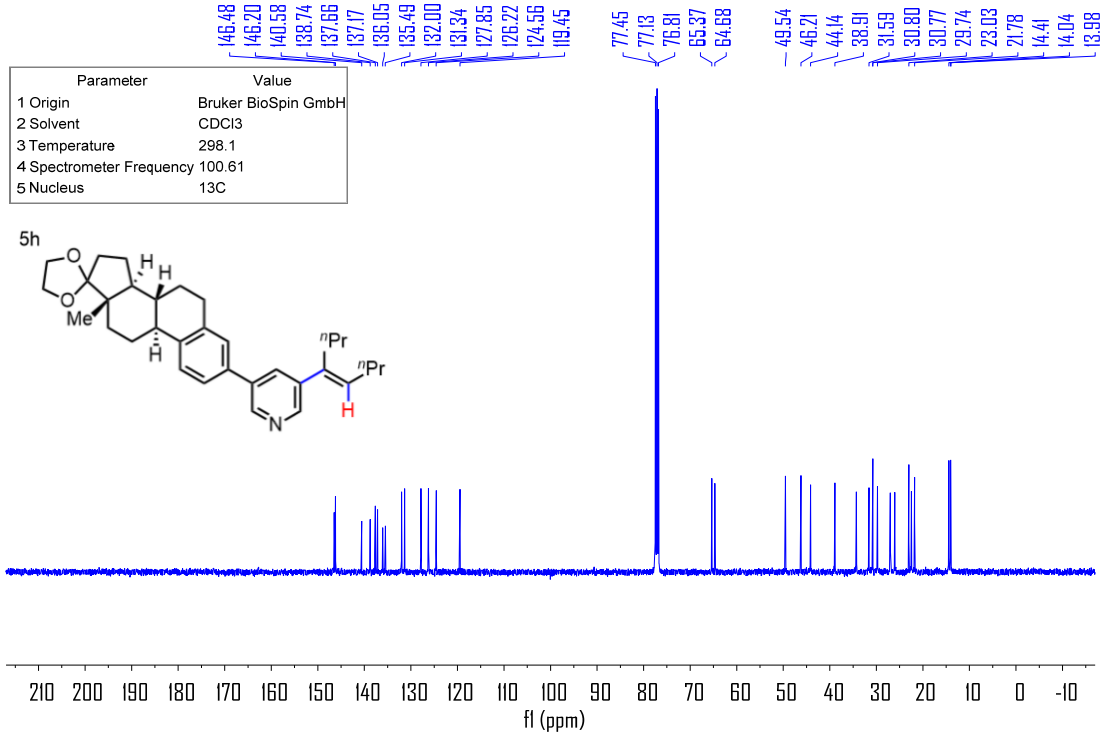
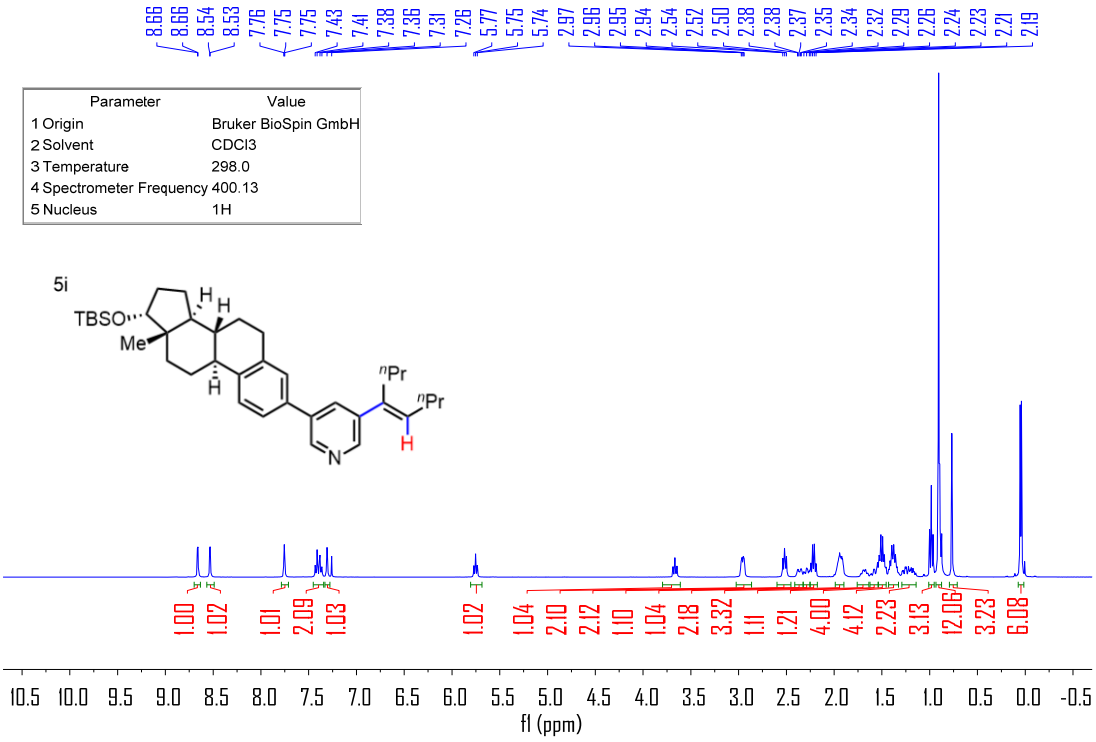
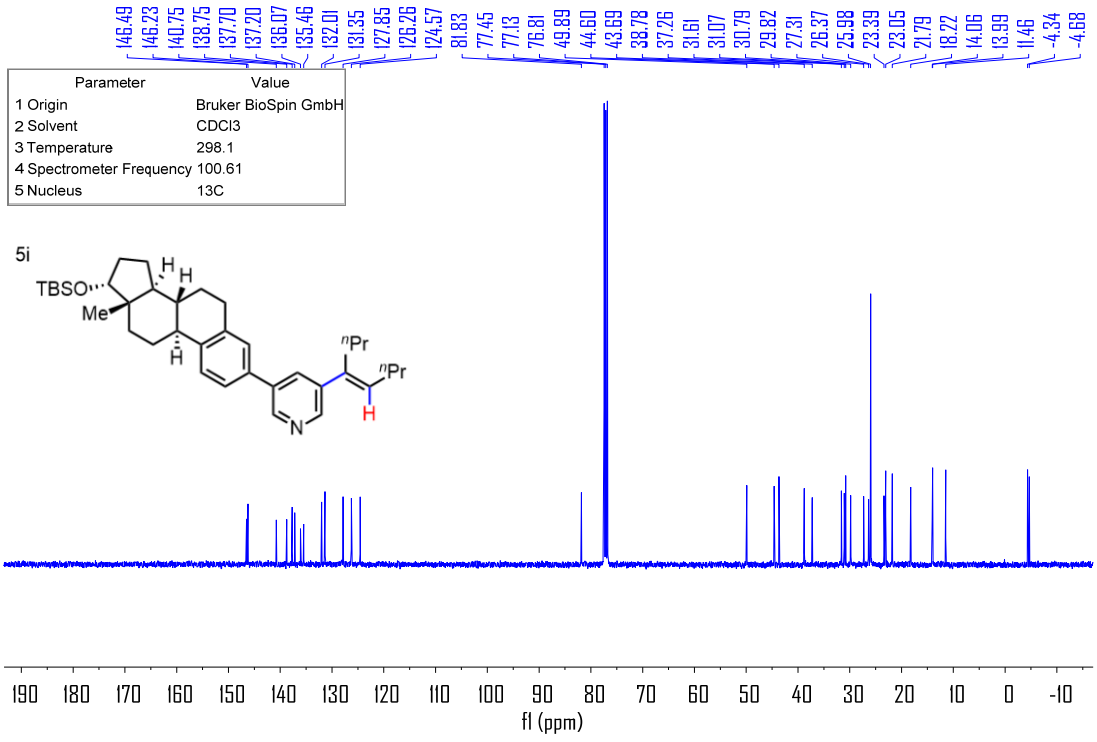
f1 (ppm)


8.66 8.65 8.53 8.53 7.41 7.38 7.31 5.75 3.97 3.95 3.95 3.93 3.93 3.92 3.91 3.90 2.97 2.96 2.95 2.53 2.51 2.49 2.22 2.20 1.83 1.82 1.56 1.52 1.51 1.49 1.47 1.44 1.41 1.39 1.37 1.35 1.00 0.98 0.96 0.90 0.89 0.87
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5h
1.00 0.98 0.98 2.09 0.97 0.99 4.08 1.99 2.04 2.19 2.12 1.20 1.37 3.10 1.25 1.90 4.07 3.39 3.10 6.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.48 146.20 140.58 138.74 137.66 137.17 136.05 135.49 132.00 131.34 127.85 126.22 124.56 119.45 77.45 77.13 76.81 65.37 64.68 49.54 46.21 44.14 38.91 31.59 30.80 30.77 29.74 23.03 21.78 14.41 14.04 13.98
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.66 8.66 8.54 8.53 7.76 7.75 7.75 7.43 7.41 7.38 7.36 7.31 7.26 5.77 5.75 5.74 2.97 2.96 2.95 2.94 2.54 2.52 2.50 2.38 2.38 2.37 2.35 2.34 2.32 2.29 2.26 2.24 2.23 2.21 2.19
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.0
4 Spectrometer Frequency 400.13
5 Nucleus 1H
5i
TBSO
Me
H
H
H
nPr
nPr
N
1.00 1.02 1.01 2.09 1.03 1.02 1.04 2.10 2.12 1.10 1.04 2.18 3.32 1.11 1.21 4.00 4.12 2.23 3.13 12.06 3.23 6.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.49 146.23 140.75 138.75 137.70 137.20 136.07 135.46 132.01 131.35 127.85 126.26 124.57 81.83 77.45 77.13 76.81 49.89 44.60 43.69 38.78 37.26 31.61 31.07 30.79 29.82 27.31 26.37 25.98 23.39 23.05 21.79 18.22 14.06 13.99 11.46 -4.34 -4.68
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Solvent CDCl3
3 Temperature 298.1
4 Spectrometer Frequency 100.61
5 Nucleus 13C
5i
TBSO
Me
H
H
H
nPr
nPr
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)