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Stille cross-coupling of secondary and tertiary α-(trifluoromethyl)-benzyl chlorides with allylstannanes

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A Stille cross-coupling reaction was developed that delivers for the first time trifluoromethyl-substituted homoallyl compounds from α-(trifluoromethyl)benzyl chlorides and allylstannanes. This reaction proceeds even with low catalyst loadings (1 mol %) *via* a rare CF_3-Pd-π-benzyl intermediate.

The introduction of fluorine or fluorine-containing functional groups into organic molecules represents a powerful tool in medicinal and pharmaceutical chemistry, as the high electronegativity of fluorine modulates the *p*Ka value and the electronic density of the products, which in turn affects their molecular properties such as the lipophilicity, solubility, permeability, and protein binding.[1] In this context, the introduction of the trifluoromethyl group is particularly noteworthy, as it increases the bio-efficacy and metabolic stability of the products, which is desirable for the identification of new drug leads.[2] The development of new methods to introduce trifluoromethyl groups at strategic positions of organic molecules is hence highly desirable.[1,2] Herein, we report the synthesis of α-(trifluoromethyl)-substituted homoallyl compounds using Stille cross-coupling reaction between α-(trifluoromethyl)benzyl chlorides and allylstannanes, which exhibits a broad substrate scope.

Transition-metal-catalyzed cross-coupling reactions have become an indispensable tool in synthetic organic chemistry for the formation of C (sp^3)–C (sp^3) bonds, and these reactions could potentially be used for the construction of new trifluoromethyl-substituted molecular architectures with specific physical and biological properties.[3] However, previously reported methods for the synthesis of α-(trifluoromethyl)-substituted homoallyl compounds suffer from a very limited substrate scope.[4] Kato et al. have reported on the reaction between chloro-trifluoroethylphenols with Grignard reagents, which requires the hydroxy group of the phenols while the substrate scope is narrow (Figure 1a).[4a] A Pd-catalyzed nucleophilic-addition-induced allylic alkylation was reported by Loh,[4b] albeit that this method is limited to difluoro-substrates that are substituted with electron-withdrawing groups, the synthesis of which is usually very tedious (Figure 1b).

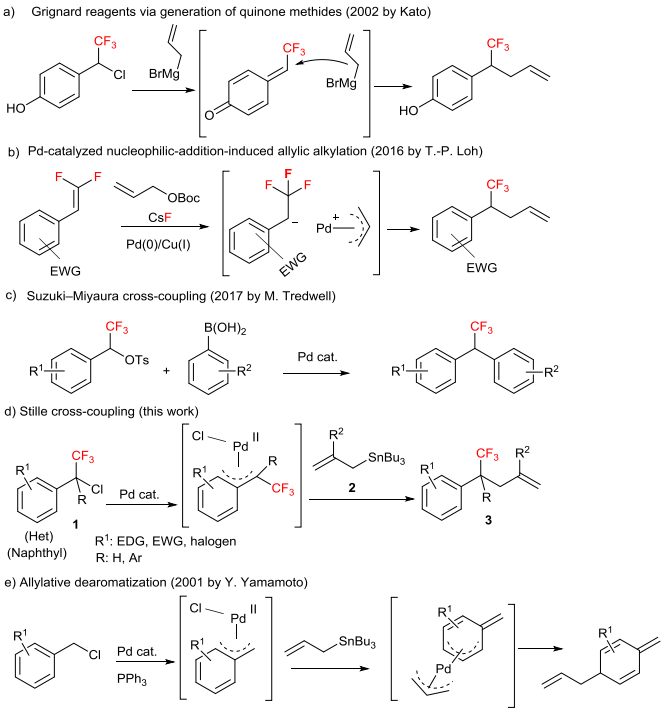

Fig. 1 Previously reported methods (a–c, e) and the method used in this study (d) for the introduction of the trifluoromethyl groups in organic molecules.

Even though transition-metal-catalyzed cross-coupling reactions are meanwhile well established and a variety of simple pseudohalide and secondary alkyl halide electrophiles is accessible, examples for the formation of α-(trifluoromethyl)-substituted compounds via this route remain extremely rare.[5] Recently, Tredwell and co-worker have reported the Suzuki-

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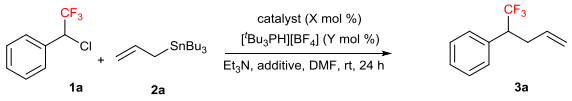
†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

Miyaura cross-coupling reaction between secondary α-(trifluoromethyl)benzyl tosylates (Figure 1c).[6] Herein, we disclose a method that is able to use allyl-substituted substrates, *i.e.*, a Pd-catalyzed Stille cross-coupling reaction between α-(trifluoromethyl)benzyl chlorides and allylstannanes, which delivers a broad variety of trifluoromethyl-substituted homoallylic compounds in high yield (Figure 1d). Stille cross-coupling reactions generally require alkenyl, aryl, or acyl halides, while the reaction with benzyl halides is not common.[7] More precisely, the reaction with benzyl chlorides proceeds very differently:[8] the Pd-catalyzed coupling reactions between benzyl chlorides and allyltributylstannane afford π-benzylpalladium chloride intermediates that furnish allylative-dearomatization products rather than Stille cross-coupling products (Figure 1e).[8] Naphthylmethyl and heteroarylmethyl chlorides also afford similar allylative-dearomatization products under such Pd-catalysis.[8c,d] The method presented herein thus represents not only an efficient method for the preparation of trifluoromethyl-substituted homoallyl compounds, but also the first examples for the formation of Stille cross-coupling products from benzyl, naphthylmethyl, and heteroarylmethyl chlorides with allyltributylstannanes using Pd-based catalysts.

Table 1 Optimization of the reaction conditions[a]

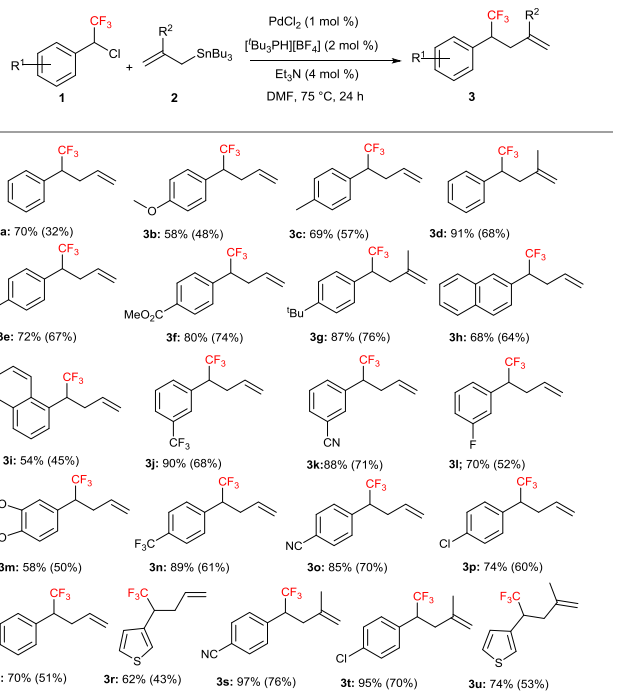


Entry	Catalyst	Additive/*T* °C	Yield[c] [%]
1[b]	$PdCl_2$ (5 mol %)	CsF, CuI/rt	31
2[b]	$Pd(PPh_3)_4$ (5 mol %)	CsF, CuI/rt	5
3[b]	$Pd(OAc)_2$ (5 mol %)	CsF, CuI/rt	13
4	$PdCl_2$ (5 mol %)	CsF, CuI/rt	35
5	$PdCl_2$ (5 mol %)	CsF/rt	45
6	$PdCl_2$ (5 mol %)	TBAF/rt	9
7	$PdCl_2$ (5 mol %)	KF/rt	49
8	$PdCl_2$ (5 mol %)	CsF, LiCl [d]/rt	40
9	$PdCl_2$ (2.5 mol %)	CsF/rt	53
10	$PdCl_2$ (2.5 mol %)	rt	57
11	$PdCl_2$ (1 mol %)	rt	27
12	$PdCl_2$ (1 mol %)	50 °C	55
13	$PdCl_2$ (2.5 mol %)	KF/rt	59
14	$PdCl_2$ (1 mol %)	75 °C	70
15	–	75 °C	–

[a] Experiments were performed with **1a** (0.5 mmol), **2a** (1.25 mmol), $PdCl_2$/[^{t}Bu$_3$PH][BF_4]/Et_3N (ratio: 1/2/4 mol %), F^- source (1.0 mmol), and CuI (4 mol %) in DMF (1.25 mL). [b] For entries 1–3, **2a** (0.65 mmol) was used. [c] Yields refer to ^{19}F NMR yields, for which $PhCF_3$ was used as an internal standard. [d] 3 equiv of LiCl was used.

We started our optimization studies by exposing the α-(trifluoromethyl) pseudohalides/secondary alkyl halides and allylstannanes (1.3 equiv) for 24 h at room temperature to $PdCl_2$ (5 mol %), [^{t}Bu$_3$PH][BF_4] (10 mol %), CuI (4 mol %), and CsF (2 equiv) in DMF. When α-(trifluoromethyl)benzyl chloride **1a** was used under these conditions, the desired cross-coupled product (**3a**) was obtained in 31% yield (entry 1, Table 1 and Table S1 in Supporting Information). Then, we screened a variety of solvents and phosphine ligands (Tables S2 and S3 in SI). Unfortunately, we did not observe any improvements of the yield, but found the formation of the β-fluoro-eliminated compound as a by-product. To improve the reaction efficiency, we examined various palladium sources and additives (Table 1 and Table S4 in SI), which improved the yield to 49% in the presence of KF (Table 1, entry 7). Surprisingly, upon decreasing the catalyst loading to 2.5 mol %, the yield increased to 57% (Table 1, entry 10). However, when the catalyst loading was further reduced to 1 mol %, the conversion was low and the product yield decreased to 27% (Table 1, entry 11). Nevertheless, the β-fluoro-eliminated compound was not formed. Encouraged by these results, we raised the reaction temperature to 75 °C and obtained the desire homoallyltrifluoromethylated compound **3a** in 70% yield (Table 1, entry 14). Thereafter, we conducted a control experiment in the absence of a palladium source, which did not proceed (Table 1, entry 15). However, the aforementioned results demonstrate that both the catalyst loading and the temperature play a crucial role for this cross-coupling reaction.

Table 2 Examining the substrate scope of **1**[a]



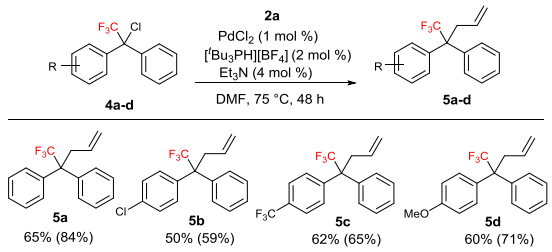
[a] Experiments were performed with **1** (0.5 mmol), **2** (1.25 mmol), and $PdCl_2$/[^{t}Bu$_3$PH][BF_4]/Et_3N (ratio: 1/2/4 mol %) in DMF (1.25 mL). [b] Percentage values refer to ^{19}F NMR yields, for which $PhCF_3$ or fluorobenzene were used as internal standards; isolated yields are given in parenthesis (all products are volatile liquids).

With the optimized reaction conditions in hand, we screened the scope of this cross-coupling reaction with respect to the substituents on the α-(trifluoromethyl)benzyl chloride substrate **1**. Substrates with electron-donating groups underwent the cross-coupling reaction smoothly to afford the desired products in up to 87% yield (Table 2). This stands in sharp contrast to the method reported by Loh, which is limited to electron-withdrawing groups.[4b] The electron-donating groups in **1b** (MeO), **1c** (Me), and **1e** (^{t}Bu) were tolerated under

the applied conditions to afford the desired products in moderate to good yields (**3b**: 58%; **3c**: 69%; **3e**: 72%). Substrates with electron-withdrawing substituents also produced the required products in up to 97% yield. CF_3 and CN groups at the *para*-position of the phenyl ring in the α-(trifluoromethyl)benzyl chloride (**1n** and **1o**) provided the homoallyltrifluoromethylated products in very good yields (**3n**: 89%; **3o**: 85%). Switching the location of the substituent from *para* to *meta* did not affect the reaction efficiency, and these *meta*-substituted substrates **1j** (3-CF_3) and **1k** (3-CN) afforded the corresponding products in excellent yields (**3j**: 90%; **3k**: 88%). Moreover, in the presence of halogen substituents at various positions of the phenyl ring, the reaction proceeded smoothly to furnish the desired products in moderate to good yields (**3l**: 70%; **3p**: 74%; **3q**: 70%). Extended π-conjugated naphthalene-derived α-(trifluoromethyl)benzyl chloride substrates **1h** (2-naphthyl) and **1i** (1-naphthyl) also generated the corresponding products in moderate to good yields (**3h**: 68%; **3i**: 54%). Importantly, heteroaryl-containing substrates such as thiophene **1r** also underwent the reaction smoothly and afforded the corresponding product in 62% yield. Subsequently, we turned our attention to variations on the tin substrates for this Stille cross-coupling reaction. When a methyl-substituted allylstannane was treated with electronically dissimilar α-(trifluoromethyl)benzyl chlorides, the corresponding homoallyltrifluoromethylated products were obtained in good to excellent yields (**3d**: 91%; **3g**: 87%; **3t**: 95%; **3u**: 74%). A wide variety of substituted allylstannanes is suitable for this cross coupling with α-(trifluoromethyl)benzyl chlorides and produced consistently good yields under low catalyst loadings.

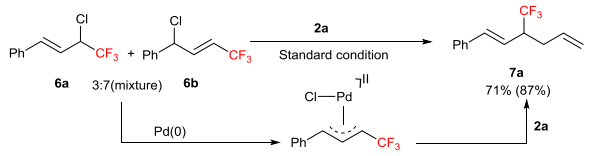
Moreover, trifluoromethyl-substituted tertiary alkyl chlorides substrates **4** could be used under the standard conditions, which provided the desired products in moderate to good yields after 48 h (Table 3). The unsubstituted substrate **4a** furnished the corresponding product in good yield (**5a**; 65%), while substrates with halogen (**4b**), electron-withdrawing (**4c**), and electron-donating groups (**4d**) afforded the desired products in moderate yields (**5b**: 50%; **5c**: 62%; **5d**: 60%).

Table 3 Substrate scope of tertiary chlorides **4**[a]



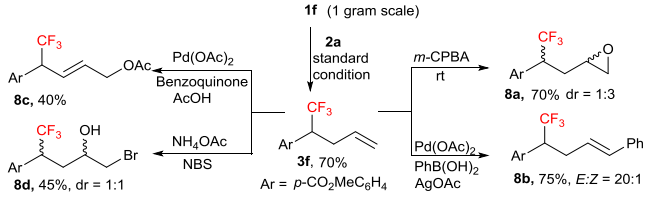
[a] Unless otherwise noted, the reactions were carried out as described in Table 2 for 48 h. Yields and ^{19}F NMR yields with internal standard PhCF3 also shown in parenthesis.

In order to elucidate the mechanism underlying this cross-coupling reaction, we wanted to examine the reactivity of α-(trifluoromethyl)allyl chloride (**6a**). However, the synthesis of **6a** delivered a non-separable mixture of allyl chlorides (**6a:6b** = 3:7). The subsequent cross-coupling reaction with this mixture of allyl chlorides produced the corresponding product (**7a**) as a single isomer in 71% yield, which supports our hypothesis that this reaction proceeds via a Pd-π-allyl intermediate that should be identical for **6a** and **6b** (Scheme 1).



Scheme 1 Stille cross coupling reaction of α-(trifluoromethyl)allyl chloride.

To demonstrate the synthetic utility of this method, we performed the cross-coupling reaction using **1f** on the gram scale, which provided **3f** in 70% isolated yield (Scheme 4). Furthermore, we subjected **3f** to several subsequent transformations, including an epoxidation with *m*-CPBA (**8a**; 70% yield) and a reaction with phenyl boronic acid in the presence of a palladium catalyst (**8b**; 75% yield; *E:Z* = 20:1). Moreover, a C–H oxidation using White's catalytic system produced the linear allylic acetate (**8c**) in 40% yield, while halohydrins such as **8d** were formed in the presence of ammonium acetate and NBS, albeit that the yield and the diastereoselectivity of **8d** were low (45%; dr = 1:1).



Scheme 2 Derivatization of **3f.**

A plausible mechanism for this cross-coupling reaction proceeds via the oxidative addition of the Pd(0) catalyst to **1a**, which results in the formation of trifluoromethyl-substituted Pd-π-benzyl intermediate **I** (Figure 2). In 1974, Stille disclosed the synthesis of an α-(trifluoromethyl) substituted π-benzyl complex like **I** using Pd- and Rh-based catalysts.[9] In the present study, the electrophilic Pd-π-benzyl intermediate **I** should coordinate to the allylstannane to form cyclic intermediate **II**, which should afford intermediate **III** following a transmetalation. Intermediate **III** should then undergo a reductive elimination to form the desired product **3a** under concomitant regeneration of the Pd(0) species. The detection of trace amounts of by-products **9** and **10** by ^{19}F NMR (**9**: -64.05 ppm (t, *J*=11.4 Hz); **10**: -82.43 ppm (dd, *J* = 34.9, 28.2 Hz), -84.31 ppm (d, *J* = 35.6 Hz), see Figure S1 in ESI) supports the generation of the Pd-π-benzyl intermediates. We did not observe clear evidence for the formation of the allylative dearomatization products **11a**,**b** via **IV**,[8,10] which is presumably due to the high reactivity of the highly electrophilic CF_3-Pd-π-benzyl intermediates in **I**, **II** and **III** induced by the high electronegativity of the CF_3 group. While we could not detect the intermediates **I**, **II** and **III** by ^{19}F-NMR analysis (see Figure S1 in ESI), finally the generation of Pd-π-benzyl intermediate **III** was confirmed by LC mass spectrometry (ESI). The intermediate **III**

with ligands ($^tBu_3P$, HBF_4) shows a prominent peak at *m/z* 597.15 ($[M + H]^+$ = 597.15) and the isotopic profile is compared with the calculated isotopic pattern for **III**, which shows a nearly similar match (see Figure S2 in ESI).

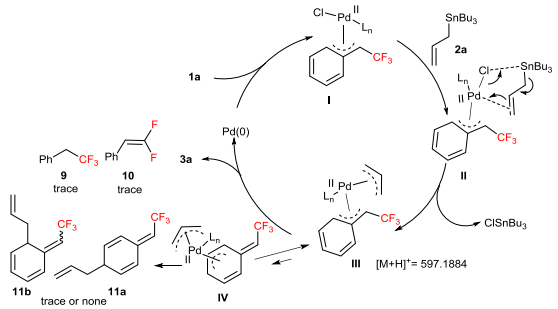


Fig. 2 Plausible mechanism for the Stille cross-coupling reaction of secondary α-(trifluoromethyl)benzyl chlorides with allylstannanes.

Conclusions

In summary, we have reported a Stille cross-coupling reaction for the preparation of trifluoromethyl-substituted homoallyl compounds **3** and **5**, which were obtained in very good yields from the reaction of readily available α-(trifluoromethyl)benzyl chlorides, naphthylmethyl chlorides and heteroarylmethyl chlorides with allylstannanes. This transformation proceeds via a crucial trifluoromethyl-substituted Pd-π-benzyl intermediate. The reaction proceeds with low catalyst loadings (1 mol %) and a broad substrate scope. Despite the use of benzyl chlorides, the alternative allylative dearomatization[8] is completely suppressed in this reaction. Although a CF_3-substituted Pd-π-benzyl intermediate was postulated by Stille in 1974,[9] such intermediates have rarely been discussed over the last 40 years. Our report thus demonstrates the potential of the aforementioned trifluoromethyl-substituted Pd-π-benzyl intermediates, which could be applied to a wide variety of transition-metal-mediated coupling reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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10 It cannot be ruled out that the trace amount of the peak at –61.24 ppm (d, *J* = 6.7 Hz) and/or others peaks around –63 — –64 ppm might be the signal of **11**. See Figures S1 in ESI.

Electronic Supplementary Information

Stille cross-coupling of secondary and tertiary α-(trifluoromethyl)benzyl chlorides with allylstannanes

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Table of contents

1. General information……..... ……S3
2. Optimization studies of Stille coupling reaction……S4
a) Screening of pseudohalide and secondary alkyl halide (**Table S1**)……S4
b) Screening of solvents (**Table S2**)…….. ……S4
c) Ligand screening (**Table S3**)…….. ……S5
d) Catalyst screening (**Table S4**)…….. ……S5
3. ^{19}F NMR studies to observe the progress of the Stille coupling reaction……S6
4. LC-MS analysis of CF_3-Pd-π-benzyl complex IV……S8
5. General experimental procedure for the synthesis of compound **1** & **4**..... ……S9
6. Typical procedure for the preparation of Stille-coupling products **3, 5** & **7** ……S11
7. Application of compound **3f**…….. ……S25
8. References……..……. ……S27
9. NMR Data……S28

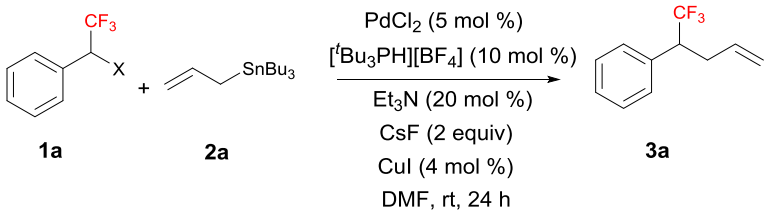
1. General information:

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen or argon. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All solvents were dried by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F_{254}). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat or *p*-anisaldehyde solution/heat. All of the reaction products were purified by column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 50-63 mm. The ^1H NMR (300 MHz and 500 MHz) and ^{19}F NMR (282 MHz) spectra (with hexafluorobenzene (δ ppm −162.2) as an internal standard) as for solution in $CDCl_3$ and DMSO were recorded on a Varian Mercury 300 and BRUKER 500 Ultra Shield TR. ^{13}C NMR (125.8 MHz) spectra for solution in $CDCl_3$ was recorded on a BRUKER 500 Ultra Shield TR. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or C_6F_6. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMADZU LCMS-2020 (ESI-MS).

Commercially available chemicals were obtained from Aldrich Chemical Co., Alfa Aesar, TCI, Ark Farm and used as received unless otherwise stated. The residual solvent signals were used as references (TMS: δ H = 0.00 ppm, δ C =77.16 ppm; and C_6F_6: δ F = −162.2 ppm). High resolution mass spectrometry (HRMS) was carried out on an electron impact ionization mass spectrometer with a micro-TOF analyzer.

2. Optimization studies of Stille coupling reaction

a) Table S1. Screening of pseudohalide and secondary alkyl halide[a]

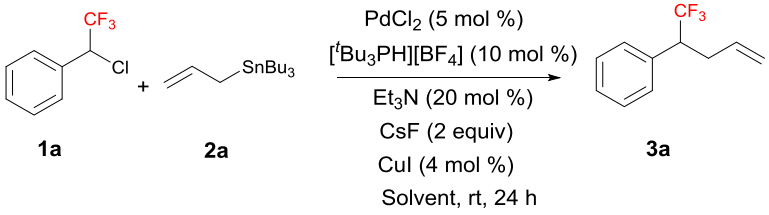


1a 2a 3a

Entry	X	Yield[b] [%]
1	OTs	-
2	OBoc	-
3	OC(O)OMe	-
4	Cl	31

[a] Experiments were performed with **1a** (0.5 mmol), **2a** (0.65 mmol) and $PdCl_2$/[^{t}Bu$_3$PH][BF_4]/Et_3N (ratio: 1/2/4 mol %) in DMF (1.25 mL). [b] Yields refer to ^{19}F NMR yields, for which $PhCF_3$ was used as internal standard.

b) Table S2. Screening of solvents[a]

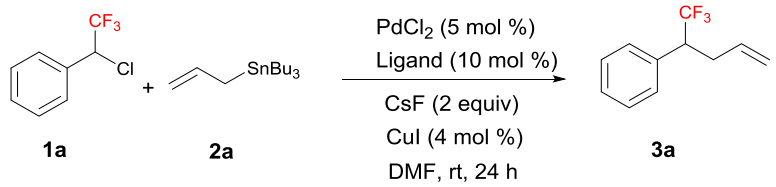


1a 2a 3a

Entry	Solvent	Yield[b] [%]
1	DMF	31
2	THF	NR
3	DCM	trace
4	Toluene	trace
5	DMSO	11
6	CH_3CN	25

[a] Experiments were performed with **1** (0.5 mmol), **2** (0.65 mmol) and $PdCl_2$/[^{t}Bu$_3$PH][BF_4]/Et_3N (ratio: 1/2/4 mol %) in solvent (1.25 mL). [b] Yields refer to ^{19}F NMR yields, for which $PhCF_3$ was used as internal standard.

c) Table S3. Ligand screening[a]

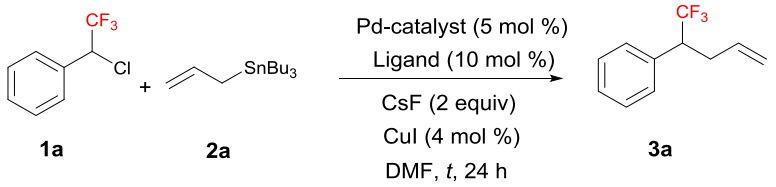


1a **2a** **3a**

Entry	Ligand	Yield[b] [%]
1[c]	$[^tBu_3PH][BF_4]$	31
2	Dppf	trace
3	Dppe	3
4	Dppp	4
5	PCy_3	4
6	DPEphos	3
7	Xanthphos	2

[a] Experiments were performed with **1** (0.5 mmol), **2** (0.65 mmol) and $PdCl_2$/$[^tBu_3PH][BF_4]$/Et_3N (ratio: 1/2/4 mol %) in DMF (1.25 mL). [b] Yields refer to ^{19}F NMR yields, for which $PhCF_3$ was used as internal standard. [c] Et_3N (20 mol %) was used.

d) Table S4. Catalyst screening[a]



1a **2a** **3a**

Entry	Catalyst	Ligand	*T* (°C)	Yield[b] [%]
1	-	-	75	-
2	$Pd(PPh_3)_4$	-	rt	5
3	$Pd(OAc)_2$	$[^tBu_3PH][BF_4]$/Et_3N	rt	13
4	$Pd_2(dba)_3$•$CHCl_3$	$[^tBu_3PH][BF_4]$ /Et_3N	rt	33
5	$PdCl_2$	$[^tBu_3PH][BF_4]$ /Et_3N	rt	31

[a] Experiments were performed with **1** (0.5 mmol), **2** (0.65 mmol) and $PdCl_2$/$[^tBu_3PH][BF_4]$/Et_3N (ratio: 1/2/4 mol %) in DMF (1.25 mL). [b] Yields refer to ^{19}F NMR yields, for which $PhCF_3$ was used as internal standard. Et_3N (20 mol %) was used.

3. ^{19}F NMR studies to observe the progress of the Stille coupling reaction

In a glove box, a flame dried NMR tube was charged with $PdCl_2$ (0.05 equiv, 5 mol %), tri-*tert*-butylphosphine tetrafluoroborate (0.1 equiv, 10 mol %), triethylamine (0.2 equiv, 20 mol %) and 0.7 mL DMF-d_7 then stirred the mixture for 5 min at room temperature. After that added the (1-chloro-2,2,2-trifluoroethyl)benzene substrate **1a** (0.3 mmol, 1 equiv) and stirred at room temperature. Separately, recorded the ^{19}F NMR of only (1-chloro-2,2,2-trifluoroethyl)benzene substrate **1a** [Figure S1 a)]. ^{19}F NMR spectra of the crude were recorded after 2h [Figure S1 b)]. Then, added allyltributylstannane (0.75 mmol, 2.5 equiv) and recorded ^{19}F NMR spectra after 2h and 4h respectively [Figure S1 c)-d)]. After that, the reaction mixture was warmed up to 75 °C and recorded ^{19}F NMR spectra after 10 min and 40 min respectively [Figure S1 e)-f)]. Reaction completed within 40 min.

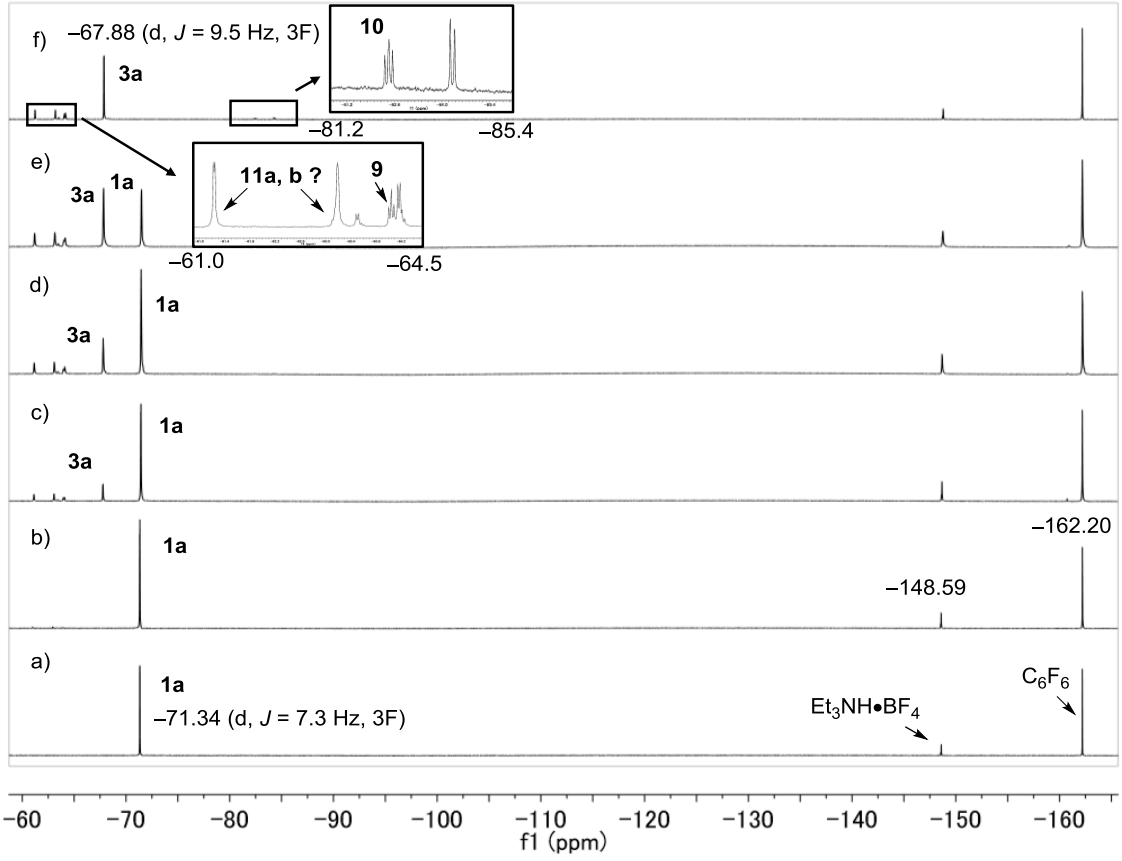


Figure S1a. ^{19}F NMR investigation in between the reaction of **1a** and **2a** in DMF-d_7. a) **1a** b) $PdCl_2$/[^{t}Bu$_3$PH][BF_4]/Et_3N was added, at rt for 2h. c) **2a** was added, at rt for 2h. d) at rt for 4h. e) at 75 °C for 10 min. f) at 75 °C for 40 min.

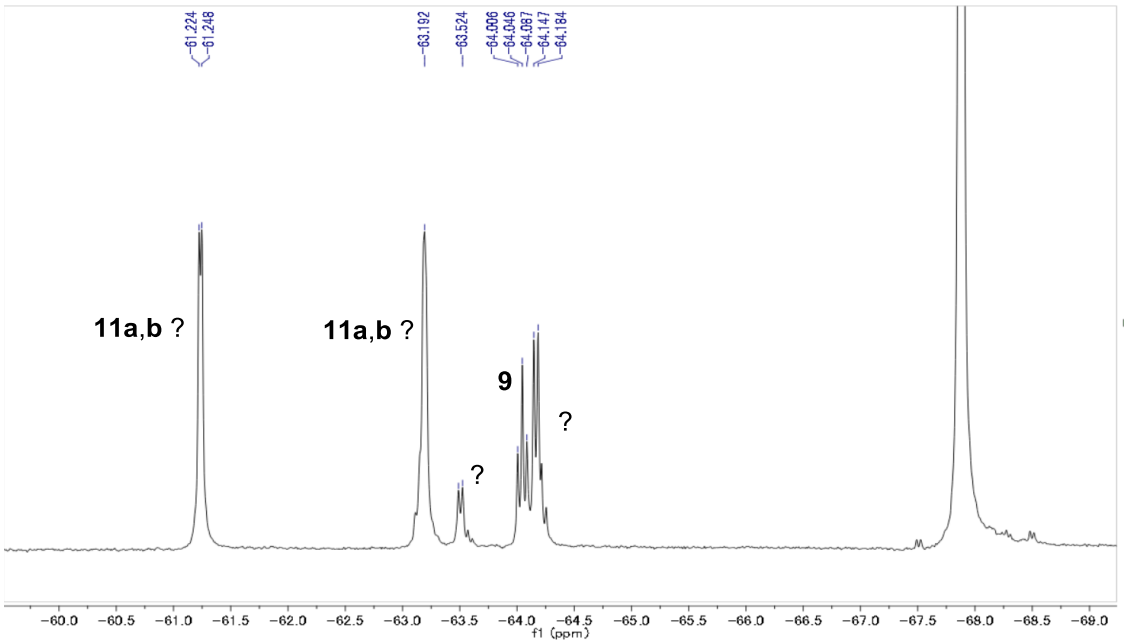


Figure S1b. Expanded ^{19}F NMR Spectra.

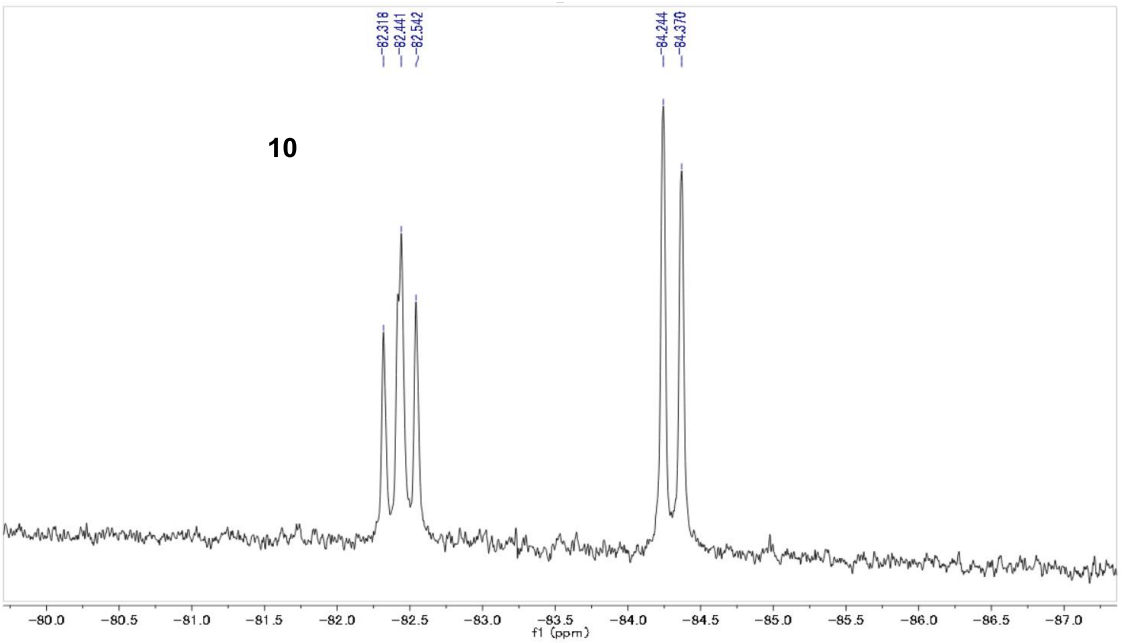


Figure S1c. Expanded ^{19}F NMR Spectra.

4. LC-MS analysis of CF_3-Pd-π-benzyl complex III

LC-MS analysis confirmed that CF_3-Pd-π-benzyl complex **III** was confirmed during the progress of the reaction. LC-MS (ESI, *m*/*z*): $[M+H]^+$ 597.15 (isotopic pattern) (Figure S2)

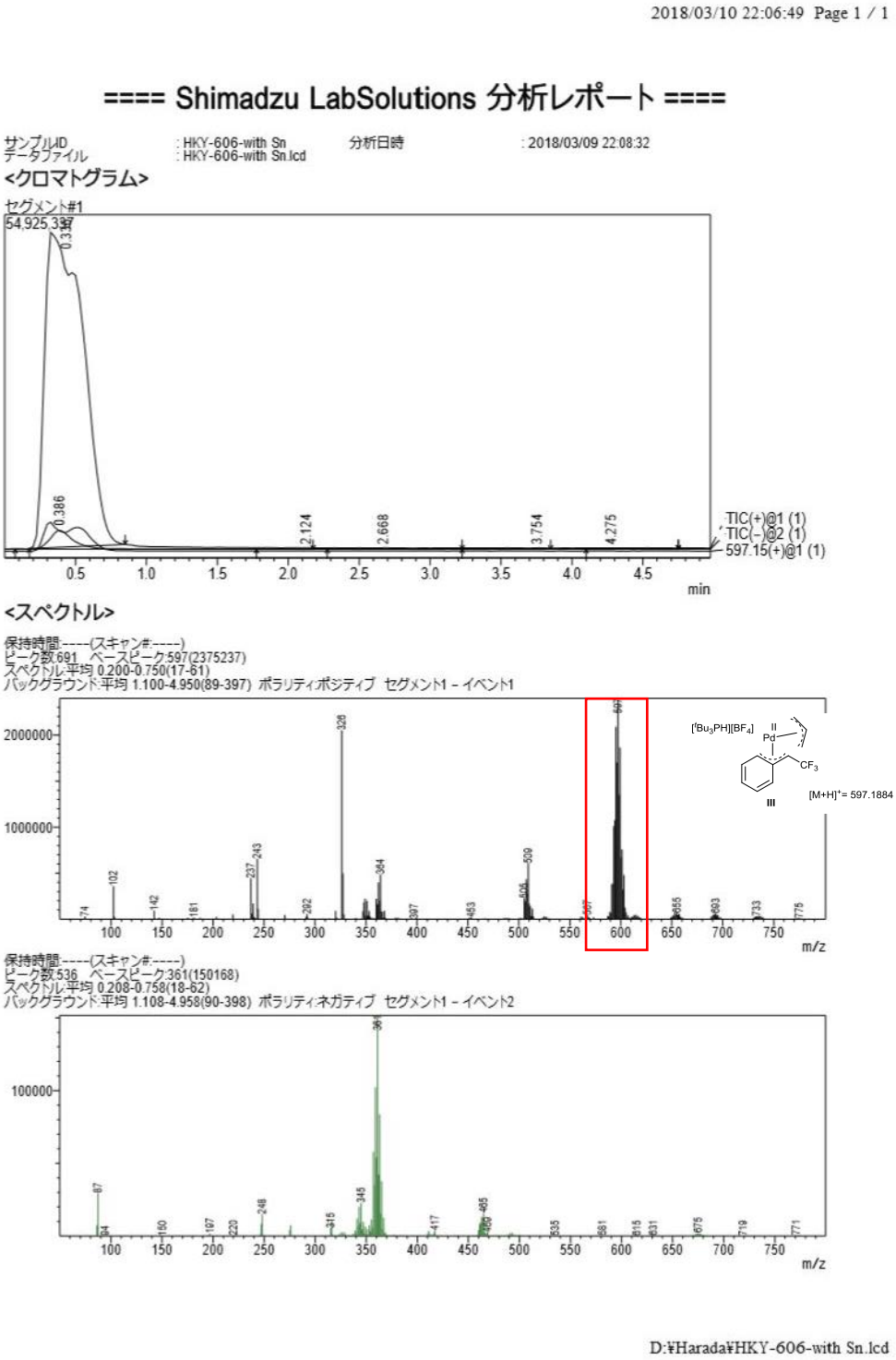


Figure S2. LC-MS spectra of Pd-intermediate **III.**

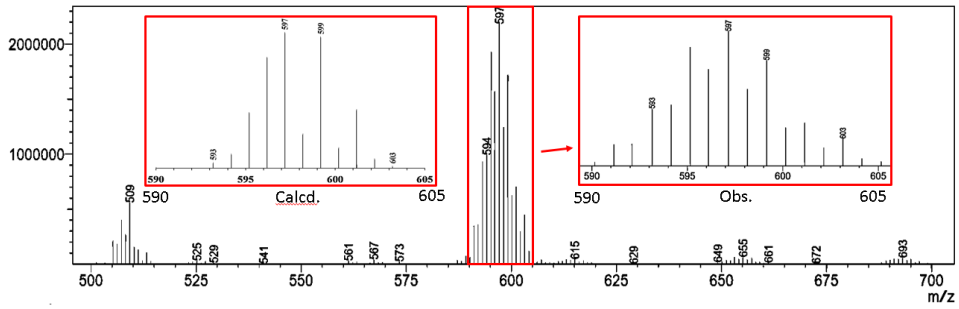
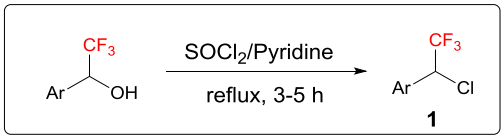


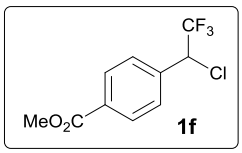
Figure S2a LC-MS spectra of III: Isotopic resolution of the calculated and observed LC-MS main peaks of the intermediate. Obs.: $[M + H]^+$ = 597.15, Calcd.: $[M + H]^+$ = 597.1884.

5. General experimental procedure for the synthesis of (1-chloro-2,2,2-trifluoroethyl)benzene substrates 1a–u & 4a–d

Followed by the general procedure from *J. Fluorine Chem.* 2005, **126**, 1174-1184. To a mixture of fluorinated alcohol (5.0 mmol) and pyridine (5.5 mmol) was slowly added thionyl chloride (5.5 mmol) and catalytic amount of DMF (0.1 mol %). The mixture was refluxed for 3–5 h and poured into cold water (5 mL). The organic layer was separated and the aqueous layer extracted with diethylether (3 × 10 mL). The combined organics extracts were washed with diluted HCl (4 × 3 mL), water (2 × 5 mL), saturated sodium bicarbonate (2 × 5 mL) and brine. Evaporation of the solvent yielded the crude product which was purified by column chromatography (by using 9:1 hexane/ethyl acetate as an eluents). All the starting materials was almost reported.[1]



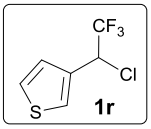
Methyl 4-(1-chloro-2,2,2-trifluoroethyl)benzoate (1f)



Following the general procedure, **1f** was obtained as a yellow oil (Yield: 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 5.17 (q, *J* = 6.7 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.32, 136.73, 131.96, 130.13, 128.99, 123.28 (q, *J* = 279.4 Hz), 58.24 (q, *J* = 34.5 Hz), 52.55. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –73.52 (d, *J*

= 6.4 Hz, 3F). **HRMS（EI）**calculated for $C_{10}H_8O_2F_3Cl$ [M]$^+$: 252.0165, found:252.0180.

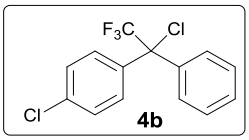
3-(1-Chloro-2,2,2-trifluoroethyl)thiophene (1r)



1r

Following the general procedure, **1r** was obtained as a yellow oil (Yield: 38%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.46 (m, 1H), 7.40–7.36 (m, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 5.25 (q, *J* = 6.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.65, 127.20, 126.99, 126.66. 123.30 (d, *J* = 278.9 Hz), 54.25 (q, *J* = 35.4 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ –73.96 (d, *J* = 6.7 Hz, 3F). **HRMS (EI)** calculated for $C_6H_4F_3SCl$ [M]$^+$: 199.9674, found:199.9699.

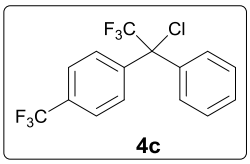
1-Chloro-4-(1-chloro-2,2,2-trifluoro-1-phenylethyl)benzene (4b)



4b

Following the general procedure, **4b** was obtained as a colorless oil (Yield: 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.30 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.77, 136.82, 135.43, 130.60, 129.36, 129.01, 128.49, 128.40. 124.33 (q, *J* = 283.2 Hz), 74.62 (q, *J* = 29.7 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.90 (s, 3F). **HRMS（EI）**calculated for $C_{14}H_9F_3Cl_2$ [M]$^+$: 304.0033, found: 304.0030.

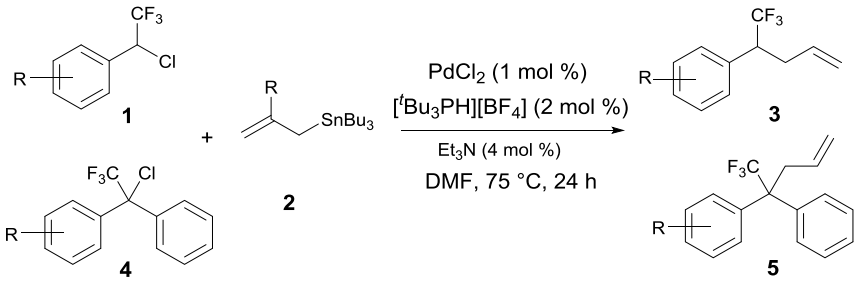
1-(1-Chloro-2,2,2-trifluoro-1-phenylethyl)-4-(trifluoromethyl)benzene (5c)



4c

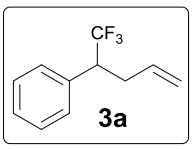
Following the general procedure, **4c** was obtained as a colorless oil (Yield: 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65–7.61 (m, 4H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.42–7.35 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.10, 137.45, 131.32 (q, *J* = 32.9 Hz), 129.69, 129.51, 129.00, 128.51, 125.31. 124.25 (q, *J* = 283.2 Hz), 123.80 (q, *J* = 272.3 Hz), 74.48 (d, *J* = 29.8 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ –63.44 (s, 3F), –69.75 (s, 3F). **HRMS（EI）**calculated for $C_{15}H_9F_6Cl$ [M]$^+$: 338.0297, found: 338.0311.

6.General experimental procedure for the synthesis of trifluoromethyl substituted homoallyl compounds 3a–u & 5a–d



In a glove box, a flame dried test tube was charged with $PdCl_2$ (0.01 equiv, 1 mol %), tri-*tert*-butylphosphine tetrafluoroborate (0.02 equiv, 2 mol %), triethylamine (0.04 equiv, 4 mol %) and 1.25 mL DMF then stirred the mixture for 5 min at room temperature. After that added the (1-chloro-2,2,2-trifluoroethyl)benzene substrate **1** (0.5 mmol, 1 equiv) and allyltributylstannane (1.25 mmol, 2.5 equiv) respectively at room temperature. The reaction mixture was warmed up to 7 and stirred for 24 hours, upon completion of the reaction, excess of allyltributylstannane was quenched with TBAF (2 mL, 1 M solution in THF) followed by the water then aqueous layer was extracted with diethyl ether (3 × 10 mL) and combined the organic layers, dried over Na_2SO_4 and concentrated on the reduced pressure, dried over sodium sulfate. The crude reaction mixture was purified by column chromatography (by using 9:1 hexane/ethyl acetate as an eluents) and all the products **3** are isolated as volatile liquids.

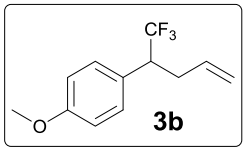
(1,1,1-Trifluoropent-4-en-2-yl)benzene (3a)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1a** (0.5 mmol, 97.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3a.**

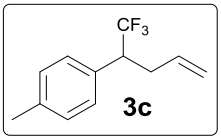
Volatile colorless oil (32.0 mg, yield: 32%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 5.62–5.51 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.97 (d, J_{cis} = 10.1 Hz, 1H), 3.38–3.26 (m, 1H), 2.83–2.72 (m, 1H), 2.70– 2.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.43, 134.03, 129.26, 128.75, 128.32, 126.84 (q, *J* = 280.0 Hz), 117.89, 50.20 (q, *J* = 26.3 Hz), 33.35. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.21 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{11}H_{11}F_3$ $[M]^+$: 200.0813, found: 200.0826.

1-Methoxy-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3b)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1b** (0.5 mmol, 112.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3b**. Volatile colorless oil (55.3 mg, yield: 48%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.63–5.51 (m, 1H), 5.04 (d, J_{trans} = 17.1 Hz, 1H), 4.97 (d, J_{cis} = 10.2 Hz, 1H), 3.81 (s, 3H), 3.33–3.21 (m, 1H), 2.80–2.70 (m, 1H), 2.66–2.55 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.50, 134.18, 130.30, 126.91 (q, *J* = 280.4 Hz), 126.32, 117.79, 114.12, 55.36, 49.33 (q, *J* = 26.3 Hz), 33.30. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.67 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{13}F_3O$ $[M]^+$: 230.0918, found: 230.0931.

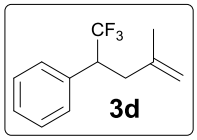
1-Methyl-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3c)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1c** (0.5 mmol, 104.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3c**.

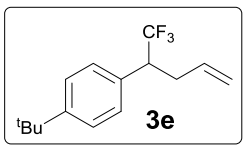
Volatile colorless oil (61.1 mg, yield: 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19–7.14 (m, 4H), 5.63–5.51 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.96 (d, J_{cis} = 10.1 Hz, 1H), 3.34–3.22 (m, 1H), 2.81–2.71 (m, 1H), 2.67–2.57 (m, 1H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.07, 134.17, 131.32, 129.47, 129.10, 126.90 (q, *J* = 280.3 Hz), 117.77, 49.77 (q, *J* = 26.3 Hz), 33.30, 21.25. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.40 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{13}F_3$ $[M]^+$: 214.0969, found: 214.0983.

(1,1,1-Trifluoro-4-methylpent-4-en-2-yl)benzene (3d)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1a** (0.5 mmol, 97.3 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3d**. Volatile colorless oil (72.8 mg, yield: 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37–7.31 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 4.69 (s, 1H), 4.60 (s, 1H), 3.54–3.40 (m, 1H), 2.73 (dd, *J* = 14.4, 3.9 Hz, 1H), 2.63 (dd, *J* = 14.3, 11.2 Hz, 1H), 1.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.77, 134.51, 129.25, 128.63, 128.25, 127.00 (q, *J* = 280.3 Hz), 113.98, 48.57 (q, *J* = 26.2 Hz), 36.94, 22.20. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.29 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{13}F_3$ $[M]^+$: 214.0969, found: 214.0989.

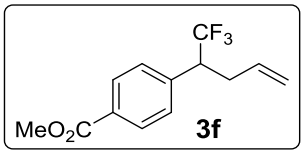
1-(*tert*-Butyl)-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3e)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1e** (0.5 mmol, 125.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3e**. Volatile colorless oil (85.9 mg, yield: 67%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2

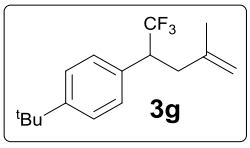
Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.66–5.53 (m, 1H), 5.06 (d, J_{trans} = 17.0 Hz, 1H), 4.97 (d, J_{cis} = 10.1 Hz, 1H), 3.36–3.23 (m, 1H), 2.81–2.71 (m, 1H), 2.69–2.58 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.14, 134.32, 131.31, 128.83, 126.95 (q, *J* = 280.1 Hz), 125.64, 117.68, 49.70 (q, *J* = 26.3 Hz), 34.65, 33.37, 31.43. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.24 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{15}H_{19}F_3$ $[M]^+$: 256.1439, found: 256.1464.

Methyl 4-(1,1,1-trifluoropent-4-en-2-yl)benzoate (3f)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1f** (0.5 mmol, 126.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3f**. Volatile colorless oil (95.5 mg, yield: 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.59–5.48 (m, 1H), 5.02 (d, J_{trans} = 17.0 Hz, 1H), 4.97 (d, J_{cis} = 10.2 Hz, 1H), 3.92 (s, 3H), 3.46–3.35 (m, 1H), 2.85–2.76 (m, 1H), 2.70–2.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.80, 139.46, 133.40, 130.24, 130.01, 129.36, 126.48 (q, *J* = 280.2 Hz), 118.40, 52.35, 50.17 (q, *J* = 26.6 Hz), 33.28. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.91 (d, *J* = 9.0 Hz, 3F). **GC-MS (*m/z*)**: 258 $[M]^+$. Compound is already known. (*J. Am. Chem. Soc.* **2016**, *138,* 15869−15872)

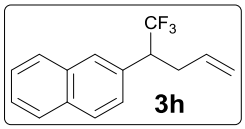
1-(*tert*-Butyl)-4-(1,1,1-trifluoro-4-methylpent-4-en-2-yl)benzene (3g)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1e** (0.5 mmol, 125.3 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash

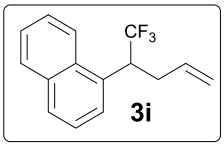
column chromatography (using hexane as an eluent) to obtain the pure product **3g**. Volatile colorless oil (102.7 mg, yield: 76%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.70 (s, 1H), 4.62 (s, 1H), 3.51–3.39 (m, 1H), 2.71 (dd, *J* = 14.5, 4.3 Hz, 1H), 2.60 (dd, *J* = 14.5, 10.8 Hz, 1H), 1.63 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.03, 141.00, 131.42, 128.80, 127.11 (q, *J* = 280.4 Hz), 125.52, 113.75, 48.03 (q, *J* = 26.2 Hz), 36.92, 34.63, 31.43, 22.29. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.29 (d, *J* = 9.3 Hz, 3F). **HRMS (EI)** calculated for $C_{16}H_{21}F_3$ $[M]^+$: 270.1595, found: 270.1620.

2-(1,1,1-Trifluoropent-4-en-2-yl)naphthalene (3h)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1h** (0.5 mmol, 122.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3h**. Volatile colorless oil (80.1 mg, yield: 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88–7.80 (m, 3H), 7.74 (s, 1H), 7.54–7.46 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 5.64–5.52 (m, 1H), 5.06 (d, J_{trans} = 17.0 Hz, 1H), 4.95 (d, J_{cis} = 10.1 Hz, 1H), 3.56–3.44 (m, 1H), 2.90–2.82 (m, 1H), 2.81–2.71 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.97, 133.33, 133.17, 131.84, 128.92, 128.54, 128.06, 127.80, 126.48, 126.46, 126.40, 124.68 (q, *J* = 280.4 Hz), 118.00, 50.36 (q, *J* = 26.4 Hz), 33.35. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.95 (d, *J* = 9.2 Hz, 3F). **HRMS (EI)** calculated for $C_{15}H_{13}F_3$ $[M]^+$: 250.0969, found: 250.0995.

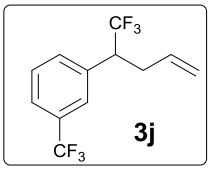
1-(1,1,1-Trifluoropent-4-en-2-yl)naphthalene (3i)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1i** (0.5 mmol, 122.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then

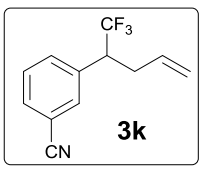
extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3i**. Volatile colorless oil (56.3 mg, yield: 45%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.64–7.47 (m, 4H), 5.64–5.51 (m, 1H), 5.05 (d, J_{trans} = 17.0 Hz, 1H), 4.90 (d, J_{cis} = 10.1 Hz, 1H), 4.44–4.27 (m, 1H), 3.02–2.91 (m, 1H), 2.90–2.77 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.02, 133.96, 132.76, 130.61, 129.26, 128.86, 127.11 (q, *J* = 280.6 Hz), 126.76, 125.84, 125.79, 125.41, 122.71, 117.91, 43.08 (q, *J* = 25.9 Hz), 33.98. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.34 (d, *J* = 7.7 Hz, 3F). **HRMS (EI)** calculated for $C_{15}H_{13}F_3$ $[M]^+$: 250.0969, found: 250.0996.

1-(Trifluoromethyl)-3-(1,1,1-trifluoropent-4-en-2-yl)benzene (3j)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1j** (0.5 mmol, 131.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3j**. Volatile colorless oil (91.2 mg, yield: 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64–7.57 (m, 1H), 7.55–7.46 (m, 3H), 5.61–5.48 (m, 1H), 5.04 (d, J_{trans} = 17.1 Hz, 1H), 5.00 (d, J_{cis} = 10.1 Hz, 1H), 3.48–3.34 (m, 1H), 2.88–2.76 (m, 1H), 2.71–2.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.43, 133.26, 132.63, 131.23 (q, *J* = 32.3 Hz), 129.32, 126.41 (q, *J* = 286.4 Hz), 126.12, 125.33, 124.03 (q, *J* = 272.4 Hz), 118.60, 50.04 (q, *J* = 26.9 Hz), 33.20. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –63.17 (s, 3F), –70.16 (d, *J* = 8.9 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{10}F_6$ $[M]^+$: 268.0687, found: 268.0711.

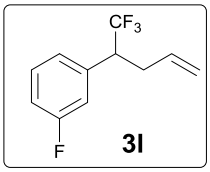
3-(1,1,1-Trifluoropent-4-en-2-yl)benzonitrile (3k)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1k** (0.5 mmol, 109.8 mg,

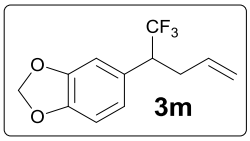
1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3k**. Volatile colorless oil (79.9 mg, yield: 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ7.64 (d, *J* = 7.4 Hz, 1H), 7.58 (s, 1H), 7.56–7.46 (m, 2H), 5.58–5.47 (m, 1H), 5.07–4.98 (m, 2H), 3.45–3.33 (m, 1H), 2.87–2.78 (m, 1H), 2.67–2.56 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.99, 133.75, 132.87, 132.90, 132.11, 129.71, 126.23 (q, *J* = 280.5 Hz), 118.93, 118.53, 113.14, 49.83 (q, *J* = 27.0 Hz), 33.09. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.14 (d, *J* = 8.9 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{10}F_3N$ $[M]^+$: 225.0765, found: 225.0745.

1-Fluoro-3-(1,1,1-trifluoropent-4-en-2-yl)benzene (3l)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1l** (0.5 mmol, 106.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3l**. Volatile colorless oil (56.7 mg, yield: 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 1H), 7.10–6.98 (m, 3H), 5.62–5.49 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.99 (d, J_{cis} = 10.1 Hz, 1H), 3.39–3.27 (m, 1H), 2.82–2.73 (m, 1H), 2.65–2.55 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ162.94 (d, *J* = 246.5 Hz), 136.84, 133.52, 130.25 (d, *J* = 8.2 Hz), 126.52 (q, *J* = 280.3 Hz), 125.12 (d, *J* = 2.5 Hz), 118.29, 116.18 (d, *J* = 22.3 Hz), 115.38 (d, *J* = 21.2 Hz), 49.95 (q, *J* = 26.3 Hz), 33.33. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.19 (d, *J* = 9.0 Hz, 3F), –113.04– –113.17 (m, 1F). **HRMS (EI)** calculated for $C_{11}H_{10}F_4$ $[M]^+$: 218.0719, found: 218.0728.

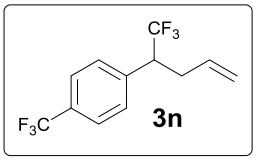
5-(1,1,1-Trifluoropent-4-en-2-yl)benzo[*d*][1,3]dioxole (3m)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2

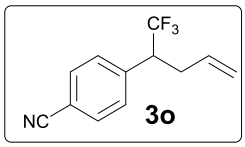
mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1m** (0.5 mmol, 119.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3m**. Volatile colorless oil (61.1 mg, yield: 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.81–6.76 (m, 2H), 6.75–6.70 (m, 1H), 5.97 (s, 2H), 5.64–5.51 (m, 1H), 5.05 (d, J_{trans} = 17.0 Hz, 1H), 4.99 (d, J_{cis} = 10.1 Hz, 1H), 3.30–3.18 (m, 1H), 2.77–2.69 (m, 1H), 2.62–2.51 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.06, 147.60, 133.97, 127.94, 126.76 (q, *J* = 280.2 Hz), 123.08, 117.93, 109.09, 108.43, 101.37, 49.83 (q, *J* = 26.4 Hz), 33.40. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.60 (d, *J* = 9.1 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{11}F_3O_2$ $[M]^+$: 244.0711, found: 244.0719.

1-(Trifluoromethyl)-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3n)



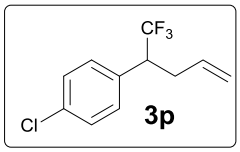
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1n** (0.5 mmol, 131.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3n**. Volatile colorless oil (81.8 mg, yield: 61%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 5.60–5.48 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.99 (d, J_{cis} = 10.1 Hz, 1H), 3.47–3.35 (m, 1H), 2.86–2.76 (m, 1H), 2.70–2.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.42, 133.26, 130.67 (q, *J* = 32.6 Hz), 129.72, 126.45 (q, *J* = 280.2 Hz), 125.76 (q, *J* = 3.8 Hz), 124.09 (q, *J* = 271.9 Hz), 118.55, 50.08 (q, *J* = 26.6 Hz), 33.25. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –63.21 (s, 3F), –70.03 (d, *J* = 9.0 Hz, 3F). **GC-MS (*m/z*)**: 268 $[M]^+$. Compound is already known. (*J. Am. Chem. Soc.* **2016**, *138,* 15869−15872)

4-(1,1,1-Trifluoropent-4-en-2-yl)benzonitrile (3o)



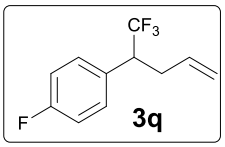
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1o** (0.5 mmol, 109.8 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3o**. Volatile colorless oil (78.8 mg, yield: 70 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.58–5.47 (m, 1H), 5.07–4.97 (m, 2H), 3.47–3.36 (m, 1H), 2.87–2.76 (m, 1H), 2.68–2.57 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.70, 132.90, 132.56, 130.11, 126.21 (q, *J* = 280.3 Hz), 118.84, 118.50, 112.50, 50.22 (q, *J* = 26.9 Hz), 33.14. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.87 (d, *J* = 8.9 Hz, 3F). **GC-MS (*m/z*)**: 225 $[M]^+$. Compound is already known. (*J. Am. Chem. Soc.* **2016**, *138,* 15869−15872)

1-Chloro-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3p)



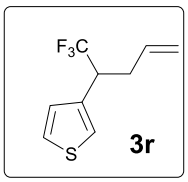
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1p** (0.5 mmol, 114.5 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3p**. Volatile colorless oil (70.4 mg, yield: 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.60–5.48 (m, 1H), 5.03 (d, J_{trans} = 17.0 Hz, 1H), 4.98 (d, J_{cis} = 10.1 Hz, 1H), 3.37–3.25 (m, 1H), 2.83–2.72 (m, 1H), 2.66–2.53 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.32, 133.55, 132.85, 130.59, 129.01, 126.55 (q, *J* = 280.4 Hz), 118.30, 49.61 (q, *J* = 26.6 Hz), 33.22. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.36 (d, *J* = 9.1 Hz, 3F). **HRMS (ESI)** calculated for $C_{11}H_{10}ClF_3$ $[M + H]^+$: 235.0501, found:235.0512.

1-Fluoro-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3q)



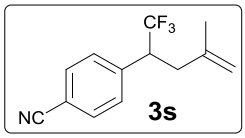
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1q** (0.5 mmol, 106.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3q**. Volatile colorless oil (55.6 mg, yield: 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 5.61–5.49 (m, 1H), 5.03 (d, J_{trans} = 17.0 Hz, 1H), 4.98 (d, J_{cis} = 10.1 Hz, 1H), 3.38–3.26 (m, 1H), 2.83–2.72 (m, 1H), 2.65–2.54 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.69 (d, *J* = 247.0 Hz), 133.71, 130.87 (d, *J* = 8.2 Hz), 130.13, 126.66 (q, *J* = 279.7 Hz), 118.17, 115.75 (d, *J* = 21.3 Hz), 49.45 (q, *J* = 26.5 Hz), 33.34. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.55 (d, *J* = 9.1 Hz, 3F), –114.44– –114.57 (m, 1F). **HRMS (EI)** calculated for $C_{11}H_{10}F_4$ $[M]^+$: 218.0719, found: 218.0740.

3-(1,1,1-Trifluoropent-4-en-2-yl)thiophene (3r)



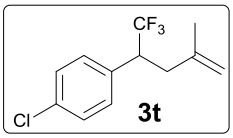
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1r** (0.5 mmol, 100.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3r**. Volatile colorless oil (44.3 mg, yield: 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35–7.30 (m, 1H), 7.19 (s, 1H), 7.04 (d, *J* = 4.4 Hz, 1H), 5.66–5.54 (m, 1H), 5.05 (d, J_{trans} = 17.0 Hz, 1H), 5.00 (d, J_{cis} = 10.1 Hz, 1H), 3.56–3.42 (m, 1H), 2.78–2.68 (m, 1H), 2.63–2.52 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.78, 133.98, 127.55, 126.49 (q, *J* = 279.9 Hz), 126.11, 124.36, 117.93, 45.57 (q, *J* = 27.2 Hz), 33.65. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.75 (d, *J* = 9.0 Hz, 3F). **HRMS (EI)** calculated for $C_9H_9F_3S$ $[M]^+$: 206.0377, found: 206.0391.

4-(1,1,1-Trifluoro-4-methylpent-4-en-2-yl)benzonitrile (3s)



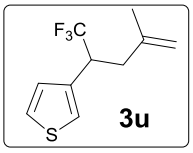
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1o** (0.5 mmol, 109.8 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3s**. Volatile colorless oil (90.9 mg, yield: 76%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 1H), 4.56 (s, 1H), 3.62–3.49 (m, 1H), 2.76 (dd, *J* = 14.5, 3.4 Hz, 1H), 2.61 (dd, *J* = 14.4, 11.5 Hz, 1H), 1.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.75, 132.47, 130.08, 126.37 (q, *J* = 280.2 Hz), 118.54, 114.72, 112.43, 48.56 (q, *J* = 26.7 Hz), 36.73, 22.08. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.96 (d, *J* = 8.9 Hz, 3F). **GC-MS (*m/z*)**: 239 $[M]^+$. Compound is already known. (*J. Am. Chem. Soc.* **2016**, *138,* 15869−15872)

1-Chloro-4-(1,1,1-trifluoro-4-methylpent-4-en-2-yl)benzene (3t)



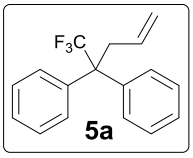
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1p** (0.5 mmol, 114.5 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3t**. Volatile colorless oil (87.0 mg, yield: 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.70 (s, 1H), 4.58 (s, 1H), 3.51–3.40 (m, 1H), 2.72 (dd, *J* = 14.5, 3.7 Hz, 1H), 2.58 (dd, *J* = 14.4, 11.4 Hz, 1H), 1.62 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.32, 134.24, 132.91, 130.58, 128.90, 126.72 (q, *J* = 279.9 Hz), 114.32, 47.96 (q, *J* = 26.5 Hz), 36.81, 22.13. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.44 (d, *J* = 9.1 Hz, 3F). **HRMS (EI)** calculated for $C_{12}H_{12}ClF_3$ $[M]^+$: 248.0580, found: 248.0599.

3-(1,1,1-Trifluoro-4-methylpent-4-en-2-yl)thiophene (3u)



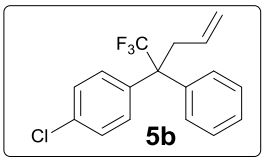
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1r** (0.5 mmol, 100.3 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **3u**. Volatile colorless oil (58.4 mg, yield: 53%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.28 (m, 1H), 7.18 (d-like, *J* = 1.9 Hz, 1H), 7.04 (d, *J* = 4.9 Hz, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 3.69–3.57 (m, 1H), 2.69 (dd, *J* = 14.3, 3.8 Hz, 1H), 2.54 (dd, *J* = 14.2, 11.1 Hz, 1H), 1.64 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.83, 134.88, 127.55, 126.64 (q, *J* = 279.9 Hz), 125.86, 124.30, 113.83, 44.04 (q, *J* = 27.1 Hz), 37.36, 22.15. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.86 (d, *J* = 9.1 Hz, 3F). **HRMS（EI）**calculated for $C_{10}H_{11}F_3S$ $[M]^+$: 220.0534, found: 220.0526.

(1,1,1-Trifluoropent-4-ene-2,2-diyl)dibenzene (5a)



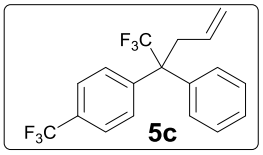
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu$_3$PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **4a** (0.5 mmol, 135.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **5a**. Volatile colorless oil (89.8 mg, yield: 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 10H), 5.62–5.50 (m, 1H), 5.02 (d, J_{trans} = 17.0 Hz, 1H), 4.94 (d, J_{cis} = 10.2 Hz, 1H), 3.21 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.02, 133.20, 129.47, 128.09, 127.63 (q, *J* = 285.3 Hz), 127.55, 118.47, 57.69 (q, *J* = 23.3 Hz), 40.82. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –66.49 (s, 3F). **HRMS（EI）**calculated for $C_{17}H_{15}F_3$ $[M]^+$: 276.1126, found: 276.1130.

1-Chloro-4-(1,1,1-trifluoro-2-phenylpent-4-en-2-yl)benzene (5b)



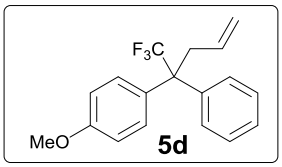
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **4b** (0.5 mmol, 152.6 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **5b**. Volatile colorless oil (77.7 mg, yield: 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 9H), 5.59–5.49 (m, 1H), 5.01 (d, J_{trans} = 17.0 Hz, 1H), 4.96 (d, J_{cis} = 10.2 Hz, 1H), 3.18 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.45, 138.54, 133.63, 132.72, 130.92, 129.37, 128.28, 128.24, 127.79, 127.41 (q, *J* = 285.2 Hz), 118.94, 57.40 (q, *J* = 23.2 Hz), 40.71. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –66.76 (s, 3F). **HRMS（EI）**calculated for $C_{17}H_{14}F_3Cl$ $[M]^+$: 310.0736, found: 310.0753.

1-(1,1,1-Trifluoro-2-phenylpent-4-en-2-yl)-4-(trifluoromethyl)benzene (5c)



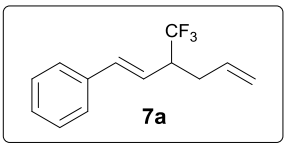
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **4c** (0.5 mmol, 169.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **5c**. Volatile colorless oil (106.7 mg, yield: 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36–7.30 (m, 3H), 7.28–7.22 (m, 2H), 5.60–5.49 (m, 1H), 5.02 (d, J_{trans} = 17.0, 1H), 4.97 (d, J_{cis} = 10.2 Hz, 1H), 3.22 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.05, 139.15, 132.44, 129.92, 129.42, 128.34, 127.97, 127.31 (q, *J* = 285.3 Hz), 125.04 (q, *J* = 3.6 Hz), 124.09 (q, *J* = 272.2 Hz), 119.16, 57.81 (q, *J* = 23.4 Hz), 40.68. One carbon of (CF_3-*C* (Ar)) is not observed. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –63.21 (s, 3F), –66.61 (s, 3F). **HRMS（EI）**calculated for $C_{18}H_{14}F_6$ $[M]^+$: 344.1000, found: 344.0993.

1-Methoxy-4-(1,1,1-trifluoro-2-phenylpent-4-en-2-yl)benzene (5d)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 μL) in 1.25 mL DMF. To it **4d** (0.5 mmol, 150.4 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **5d**. Volatile colorless oil (91.9mg, yield: 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.25 (m, 5H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.62–5.51 (m, 1H), 5.02 (d, J_{trans} = 17.0 Hz, 1H), 4.94 (d, J_{cis} = 10.2 Hz, 1H), 3.81 (s, 3H), 3.18 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.77, 140.15, 133.30, 131.95, 130.68, 129.36, 128.08, 127.72 (q, *J* = 285.2 Hz), 127.45, 118.39, 113.36, 57.09 (q, *J* = 23.0 Hz), 55.34, 40.86. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –66.77 (s, 3F). **HRMS（EI）**calculated for $C_{18}H_{17}OF_3$ $[M]^+$: 306.1232, found: 306.1239.

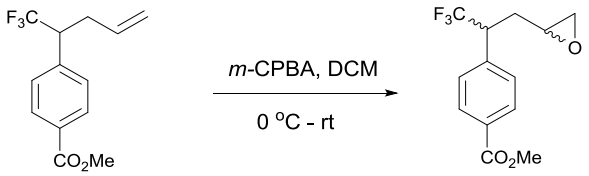
(*E*)-(3-(Trifluoromethyl)hexa-1,5-dien-1-yl)benzene (7a)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 μL) in 1.25 mL DMF. To it mixture of **6a** and **6b** (0.5 mmol, 110.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75°C for 24 h, the mixture was quenched with TBAF (2 mL, 1 M solution in THF) then extracted with diethyl ether and dried *in vacuo*. The crude product was purified by flash column chromatography (using hexane as an eluent) to obtain the pure product **7a.** Volatile colorless oil (80.3 mg, yield: 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29–7.26 (m, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 5.98 (dd, *J* = 15.9, 9.1 Hz, 1H), 5.80–5.69 (m, 1H), 5.13 (d, J_{trans} = 17.0 Hz, 1H), 5.08 (d, J_{cis} = 10.1 Hz, 1H), 3.00–2.88 (m, 1H), 2.63–2.55 (m, 1H), 2.41–2.31 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.33, 136.07, 134.00, 128.77, 128.22, 126.84 (q, *J* = 280.1 Hz), 126.64, 122.40, 118.00, 47.85 (q, *J* = 26.5 Hz), 32.84. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –71.18 (d, *J* = 8.8 Hz, 3F). **HRMS（EI）**calculated for $C_{13}H_{13}F_3$ $[M]^+$: 226.0969, found: 226.0974.

7. Applications

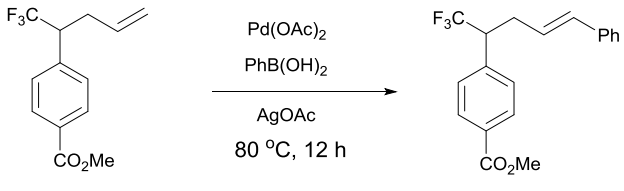
a) General procedure for the synthesis of methyl 4-(1,1,1-trifluoro-3-(oxiran-2-yl)propan-2-yl)benzoate (8a)



3f **8a;** dr = 1:3;

A flame dried test tube was charged with *m*-CPBA (0.3 mmol, 51.77 mg, 70% wt/wt in water) and dry DCM (3 mL) then cooled to 0 °C. Next added the compound **3f** (0.2 mmol, 51.6 mg) and increase the temperature gradually to room temperature and stirred for 24 h. After completion of reaction, mixture was quenched with saturated $NaHCO_3$ (3 mL). The organic layer was separated and the aqueous layer was extracted with additional DCM (2 × 10 mL). The organic layers were combined and washed with brine (10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated over rotary evaporator. The dr was calculated from the crude reaction mixture by using the ^{19}F NMR. The crude product was purified by silica gel column chromatography (by using 9:1 hexane/ethyl acetate as eluents) to obtain pure epoxide **8a**. Yield 70%, white solid, mp 64–65 °C, dr = 1:3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 3.69–3.57 (m, 1H), 2.72–2.62 (m, 2H), 2.48–2.44 (m, 1H), 2.33–2.24 (m, 1H), 2.04–1.96 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.68, 138.97, 130.59, 130.26, 129.29, 126.37 (q, *J* = 279.8 Hz), 52.42, 49.25, 48.01, 47.81 (q, *J* = 27.7 Hz), 32.64. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –70.18 (d, *J* = 9.1 Hz, 3F). **HRMS（ESI）**calculated for $C_{13}H_{14}O_3F_3$ $[M + H]^+$: 275.0895, found: 275.0901.

b) General procedure for the synthesis of methyl *(E)*-4-(1,1,1-trifluoro-5-phenylpent-4-en-2-yl)benzoate (8b)

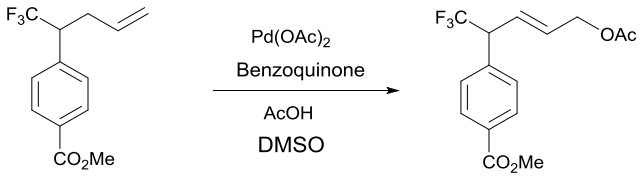


3f **8b;** *E/Z* = 20/1;

In a flame dried test tube compound **3f** (0.2 mmol, 51.6 mg, 1 equiv) was dissolved in 2 mL DMF then test tube was charged with $Pd(OAc)_2$ (0.01 mmol, 2.24 mg, 5 mol %), phenylboronic acid (0.22 mmol, 26.82 mg, 1.1 equiv) and AgOAc (0.3 mmol, 50.07 mg,

1.5 equiv). Next, the reaction mixture was stirred at 80 °C for 12 h. After completion of starting material, reaction mixture was quenched with water then extracted with ether (2 × 10 mL), dried over Na_2SO_4 and concentrated on reduced pressure. The crude product was purified by column chromatography (by using 9:1 hexane/ethyl acetate as eluents) to obtain pure product **8b**. Yield 75%, *E/Z* = 20/1, colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.27–7.15 (m, 5H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.93–5.85 (m, 1H), 3.91 (s, 3H), 3.52–3.42 (m, 1H), 2.99–2.91 (m, 1H), 2.84–2.75 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.76, 139.46, 136.86, 133.40, 130.29, 130.08, 129.31, 128.64, 127.63, 126.48 (d, *J* = 280.4 Hz), 126.23, 124.81, 50.55 (q, *J* = 26.5 Hz), 52.32, 32.66. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.73 (d, *J* = 9.0 Hz, 3F). **HRMS（ESI）**calculated for $C_{19}H_{17}O_2F_3$ $[M]^+$: 334.1181, found: 334.1204.

c) General procedure for the synthesis of methyl (*E*)-4-(5-acetoxy-1,1,1-trifluoropent-4-en-2-yl)benzoate (8c)

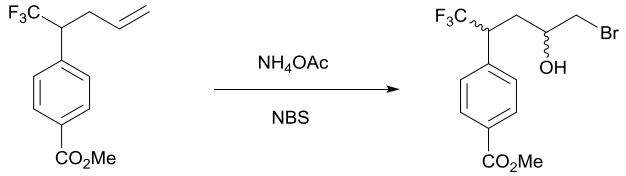


3f **8c**

To a flame dried test tube was charged with $Pd(OAc)_2$ (0.02 mmol, 4.5 mg, 10 mol %), benzoquinone (0.4 mmol, 43.2 mg, 2 equiv), and 4Å MS (21.7 mg). To the solids test tube was sequentially added the following: DMSO (0.3 mL), compound **3f** (0.2 mmol, 51.6 mg, 1 equiv), AcOH (0.3 mL). The vial was charged with a stir bar, capped and allowed to heat at 40 °C for 72 h. After that, the reaction was quenched with saturated NH_4Cl (1 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with H_2O (2 × 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified column chromatography (by using 9:1 hexane/ethyl acetate as eluents) to obtain pure product **8c**. Yield 40%, oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.05 (dd, *J* = 15.5, 7.8 Hz, 1H), 5.80 (dt, *J* = 15.5, 5.7 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 2H), 4.08 (p, *J* = 8.8 Hz, 1H), 3.93 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.72, 166.68, 139.09, 131.15, 130.37, 130.22, 129.21, 126.61, 125.59 (q, *J* = 280.4 Hz), 63.91, 52.87 (q, *J* = 28.1 Hz), 52.40, 21.00. **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.28 (d, *J* = 9.1 Hz, 3F). **HRMS（EI）**calculated for $C_{15}H_{15}O_4F_3Na$ $[M + Na]^+$: 339.0820, found: 339.0820.

d) General procedure for the synthesis of methyl 4-(5-bromo-1,1,1-trifluoro-4-

hydroxypentan-2-yl)benzoate (8d)



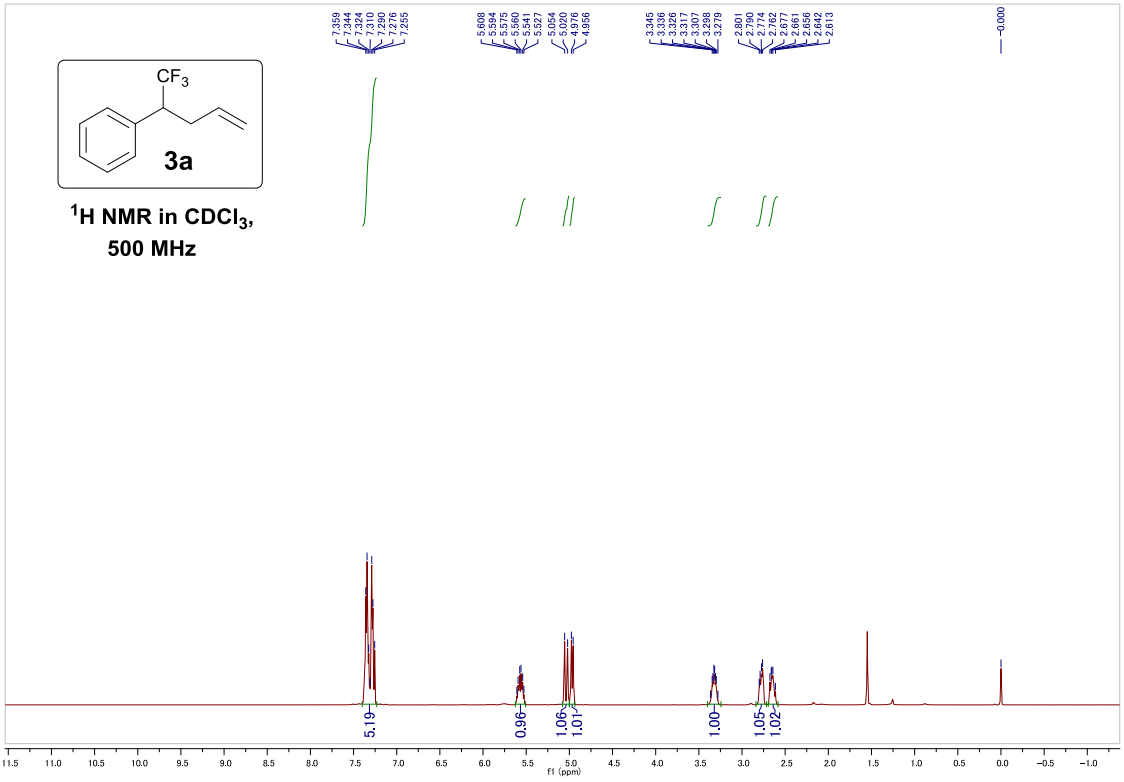
3f **8d**, 45%, dr = 1:1

To a suspension of compound **1f** (0.2 mmol, 51.6 mg, 1 equiv) and NH_4OAc (0.02 mmol, 1.54 mg, 10 mol%) in acetone (0.8 mL), NBS (0.22 mmol, 39.15 mg, 1.1 equiv) and water (0.2 mL) were added and the mixture was stirred at room temperature. After completion of the reaction as indicated by TLC the mixture was concentrated *in vacuum* and extracted with ethyl acetate and water (1:1) (3 × 5 ml). The organic portion was concentrated and the residue was subjected to silica gel column chromatography (by using 8:2 hexane/ethyl acetate as an eluents) to obtain pure product **8d**. Yield 45%, oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 3.83–3.68 (m, 3H), 3.60–3.50 (m, 1H), 2.51–2.35 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, major + minor isomers) δ 166.64, 139.42 (minor), 137.96 (major), 130.81(major), 130.62 (minor), 130.40 (major), 130.34 (minor), 129.39 (major), 129.15 (minor), 126.45 (q, *J* = 279.9 Hz, major), 126.35 (d, *J* = 280.5 Hz, minor), 67.38 (major), 66.49 (minor), 54.69 (major), 54.40 (minor), 52.45, 48.59 (q, *J* = 27.5 Hz, major), 47.99 (q, *J* = 27.2 Hz, minor), 35.12 (minor), 33.98 (major). **^{19}F NMR** (282 MHz, $CDCl_3$) δ –69.36 (d, *J* = 8.2 Hz, 3F, minor), –69.70 (d, *J* = 8.8 Hz, 3F, major). **HRMS（ESI）**calculated for $C_{13}H_{14}BrO_3F_3Na$ $[M + Na]^+$: 376.9976, found: 376.9977.

8. References:

1) (a) R. Anilkumar and D. J. Burton, *J. Fluorine Chem.* 2005, **126**, 1174-1184. (b) T. Okano, K. Ito, T. Ueda and H. Muramatsu, *J. Fluorine Chem.* 1986, **32**, 377-388. (c) Y. Gonga and K. Katob, *J. Fluorine Chem.* 2003, **121**, 141–146.

9. NMR Data
(^{1}H NMR , ^{13}C NMR and ^{19}F-NMR)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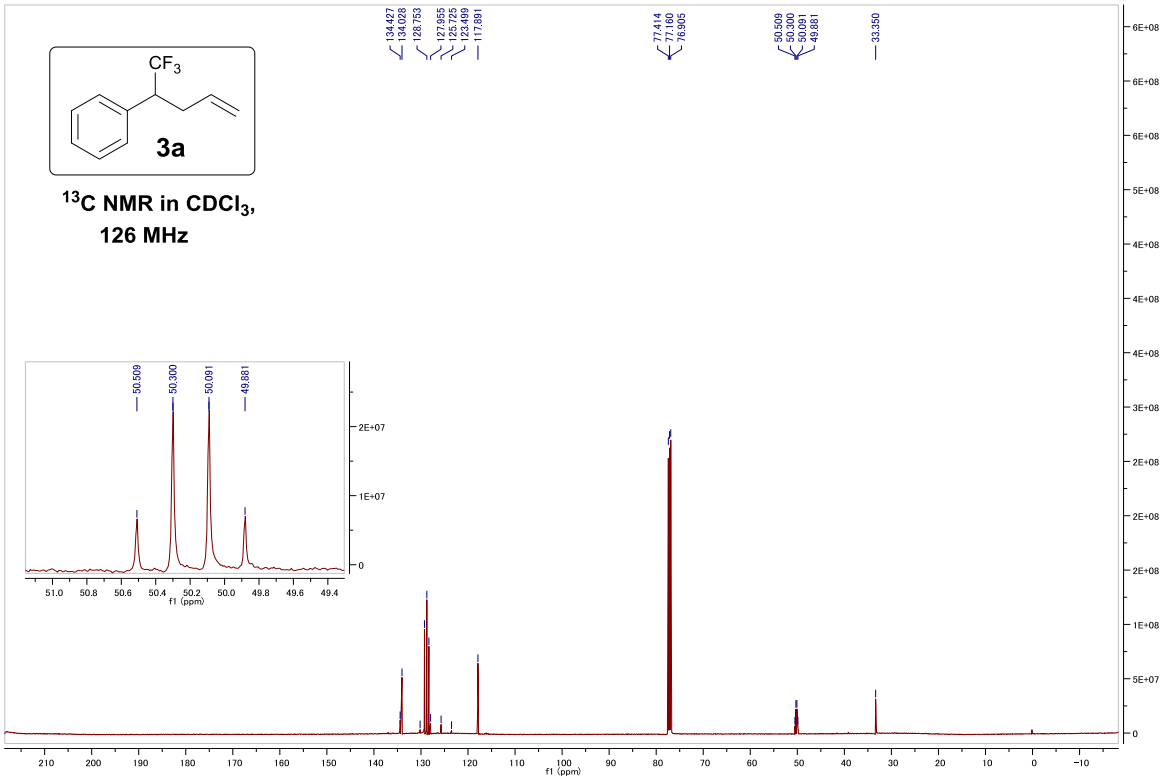
7.344
7.324
7.310
7.290
7.276
7.255
5.608
5.594
5.575
5.560
5.541
5.527
5.054
5.020
4.976
4.956
3.345
3.336
3.326
3.317
3.307
3.298
3.279
2.801
2.790
2.774
2.762
2.677
2.661
2.656
2.642
2.613
-0.000
5.19
0.96
1.06
1.01
1.00
1.05
1.02
f1 (ppm)


CF3
3a
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126 MHz
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134.028
128.753
127.955
125.575
123.499
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77.414
77.160
76.905
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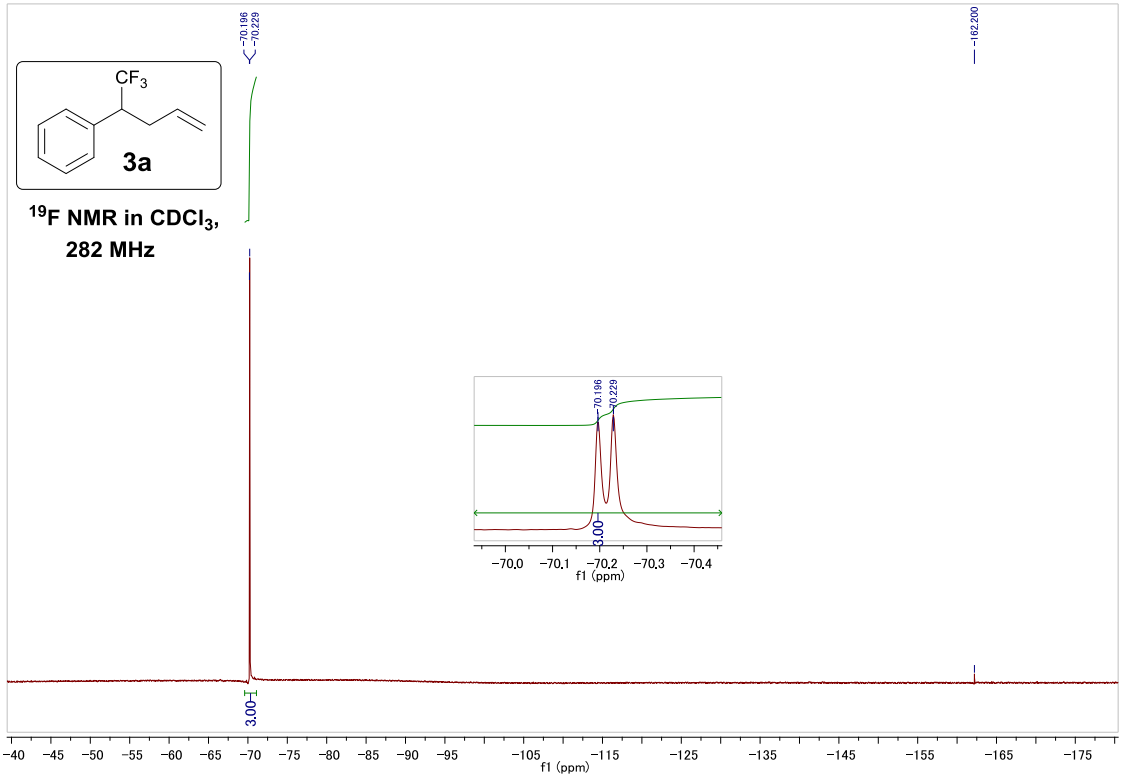
50.300
50.091
49.881
33.350
f1 (ppm)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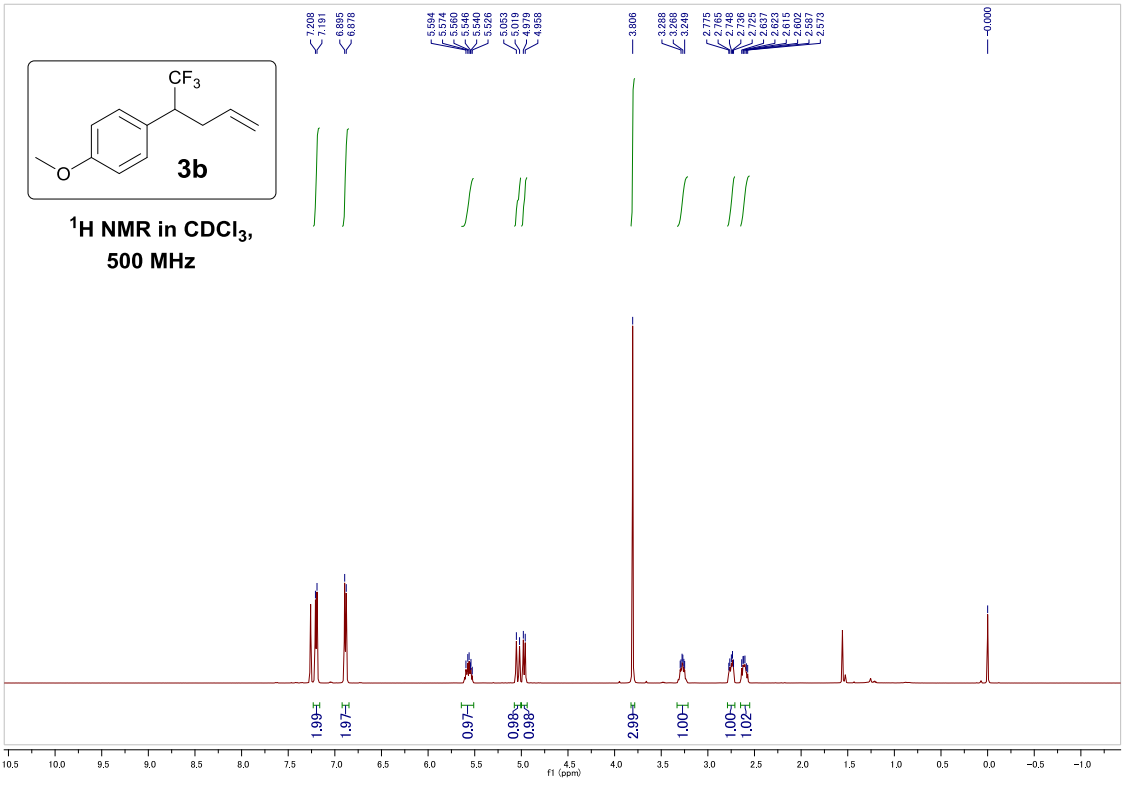
3.00
f1 (ppm)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O
3b
1H NMR in CDCl3,
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7.191
6.895
6.878
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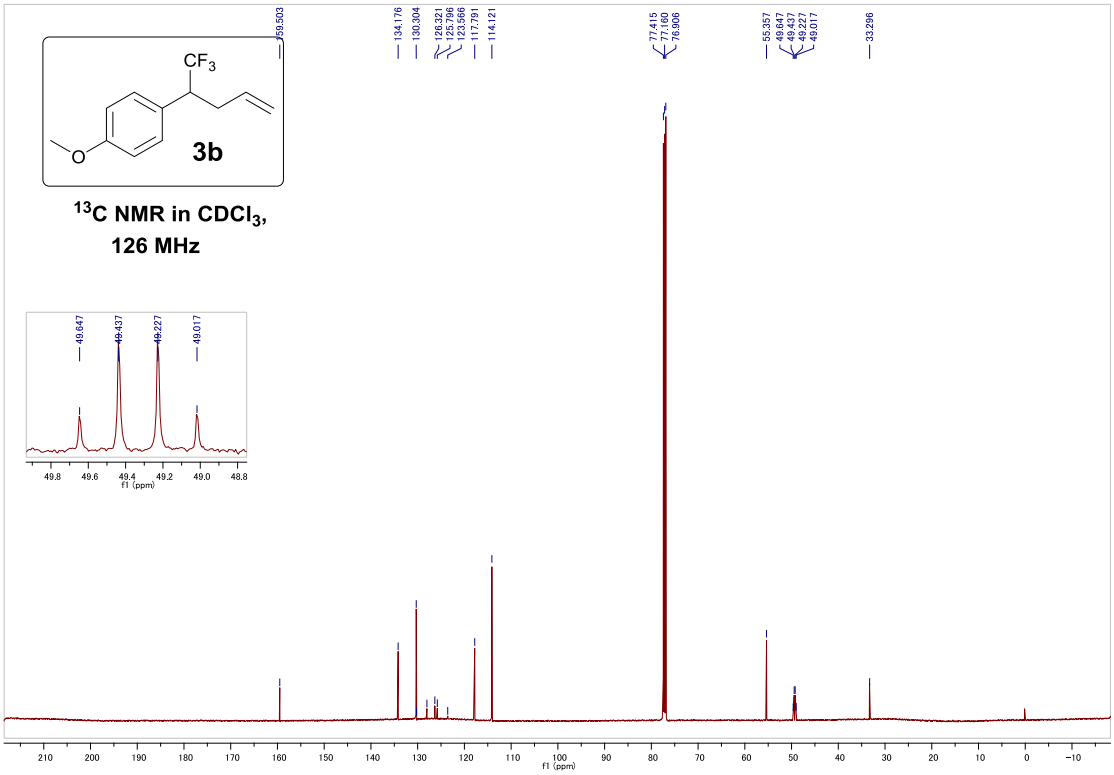
1.97
0.97
0.98
0.98
2.99
1.00
1.00
1.02
f1 (ppm)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126.321
125.796
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114.121
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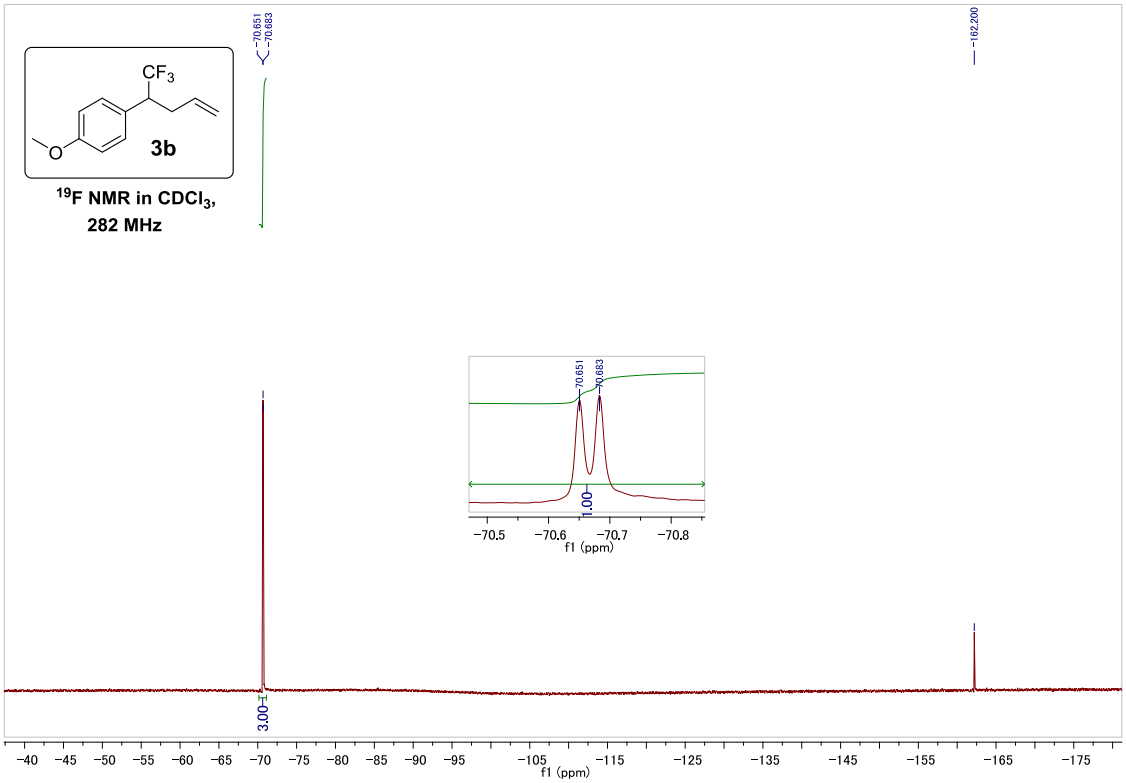
49.227
49.017
33.296
13C NMR in CDCl3,
126 MHz
f1 (ppm)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O
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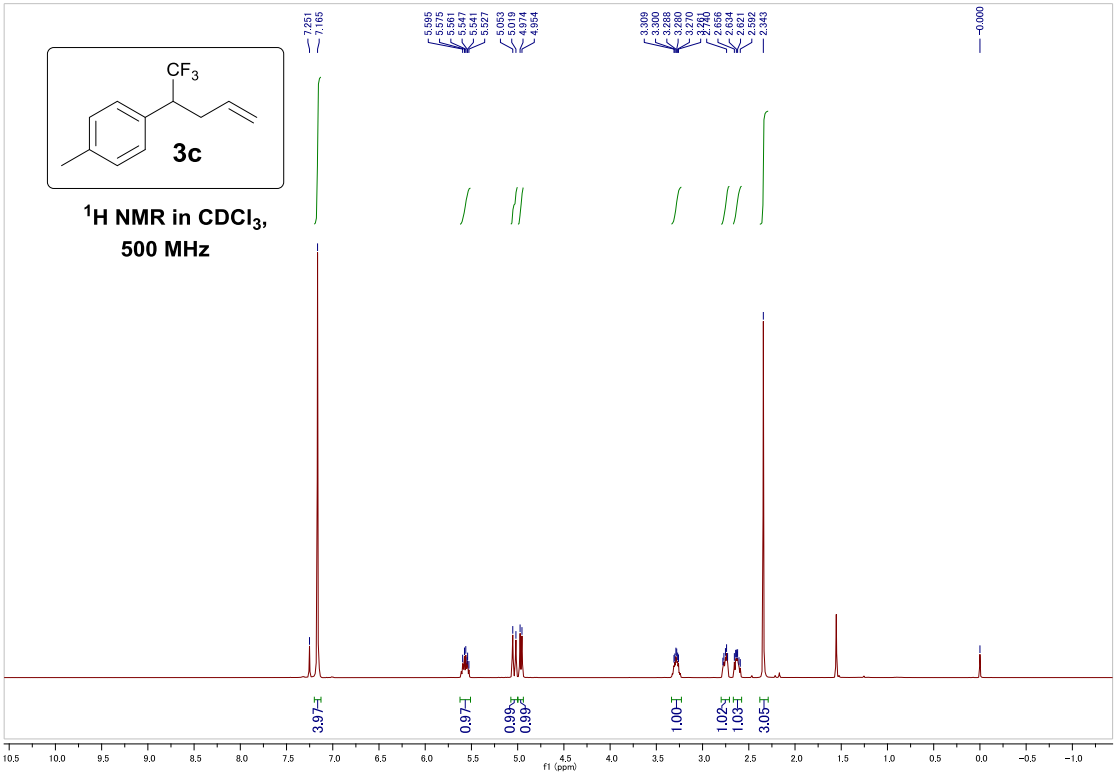
3.00
1.00
f1 (ppm)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5.527
5.053
5.019
4.974
4.954
3.309
3.300
3.288
3.280
3.270
2.781
2.686
2.634
2.621
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0.99
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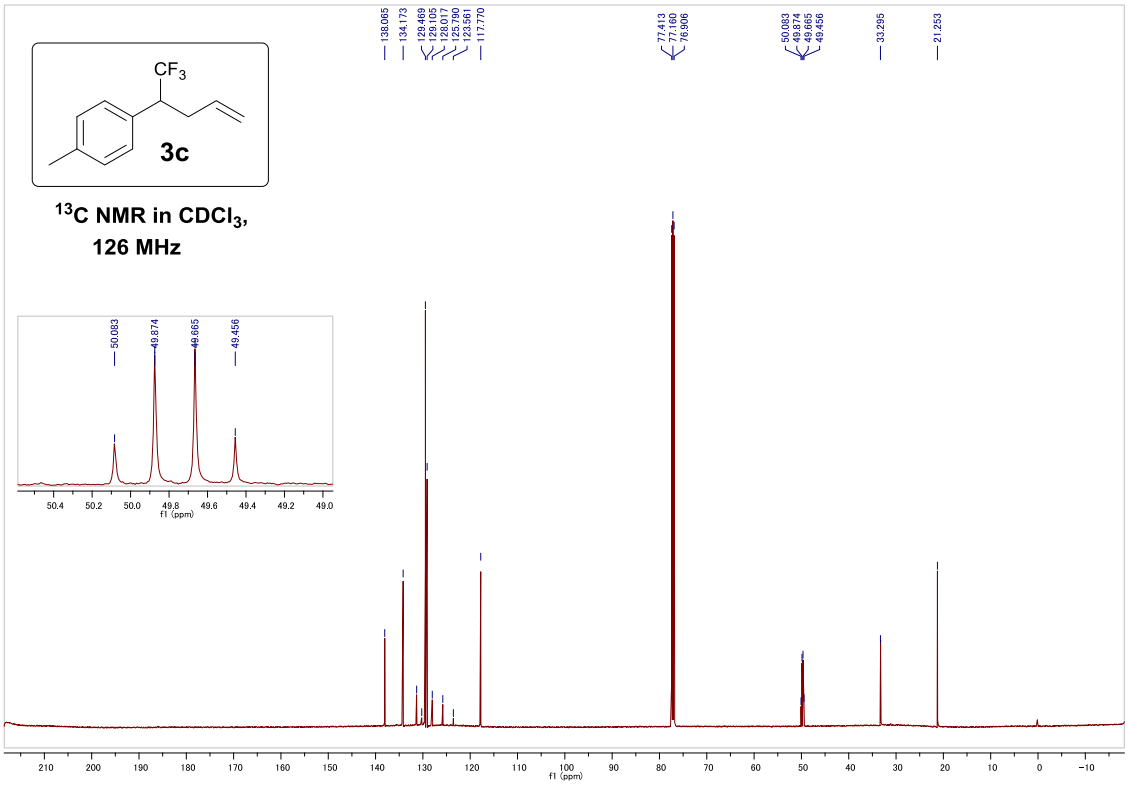
3.05
f1 (ppm)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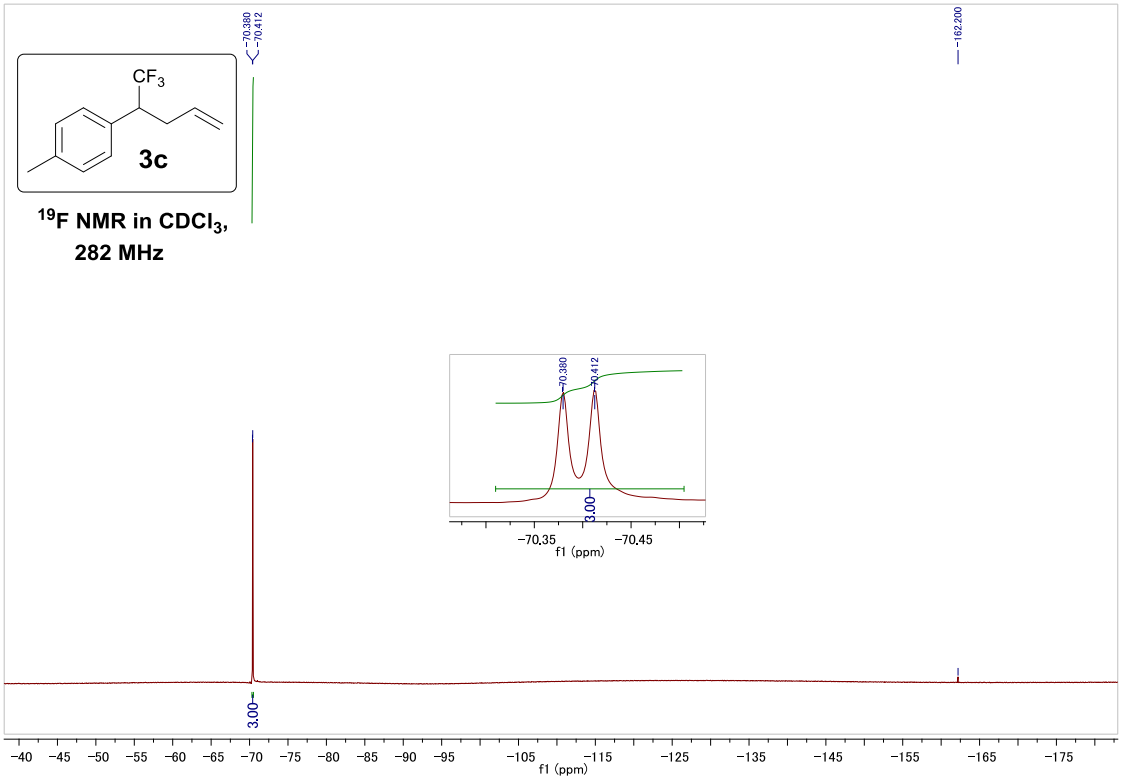
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3.00
-70.35
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f1 (ppm)
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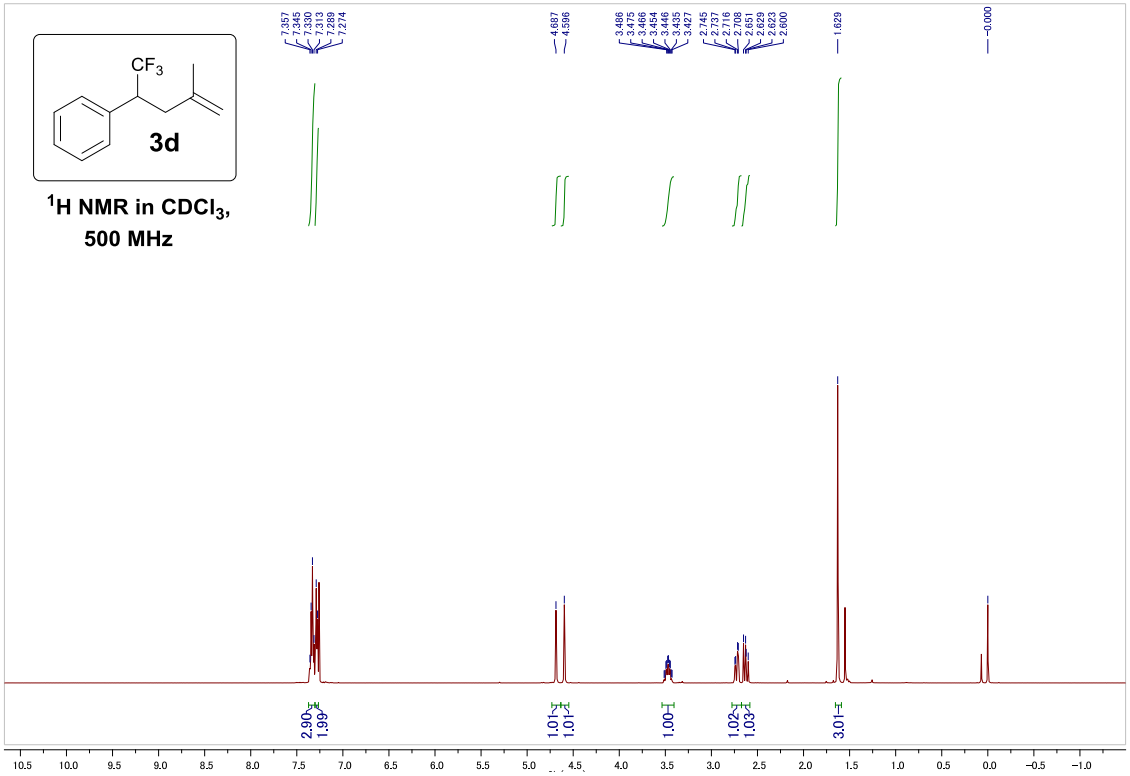
f1 (ppm)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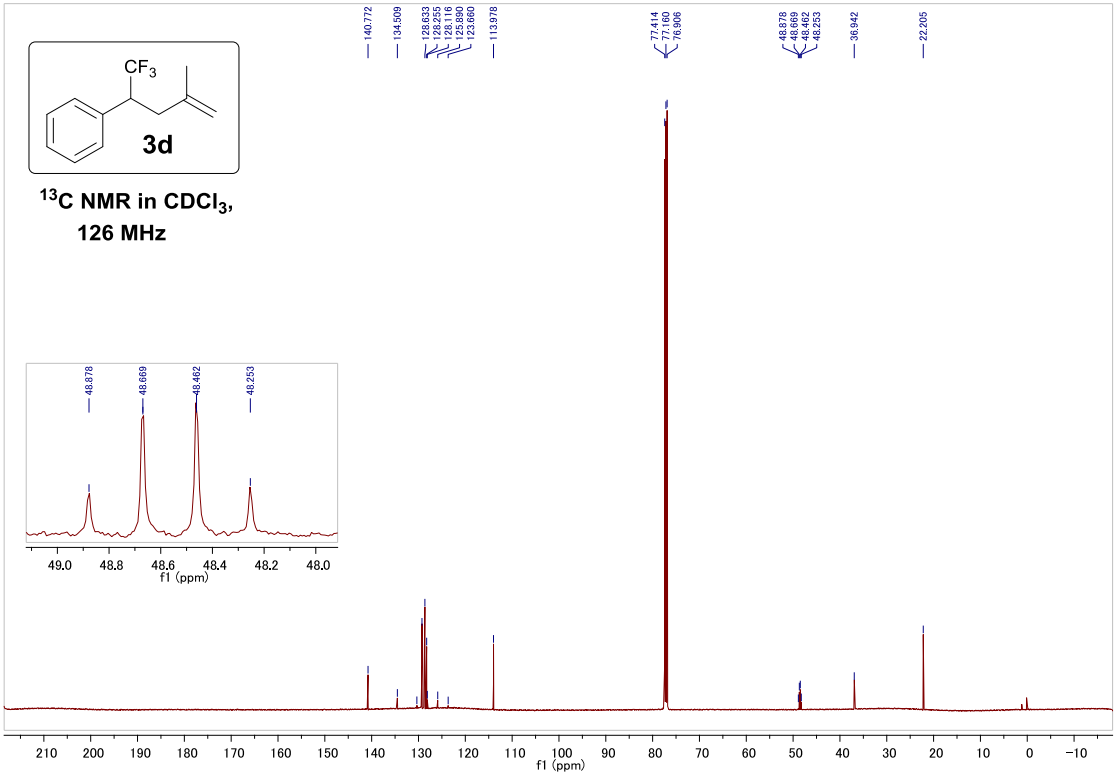
3.435
3.427
2.745
2.737
2.716
2.708
2.651
2.639
2.623
2.600
1.629
-0.000
2.90
1.99
1.01
1.01
1.00
1.02
1.03
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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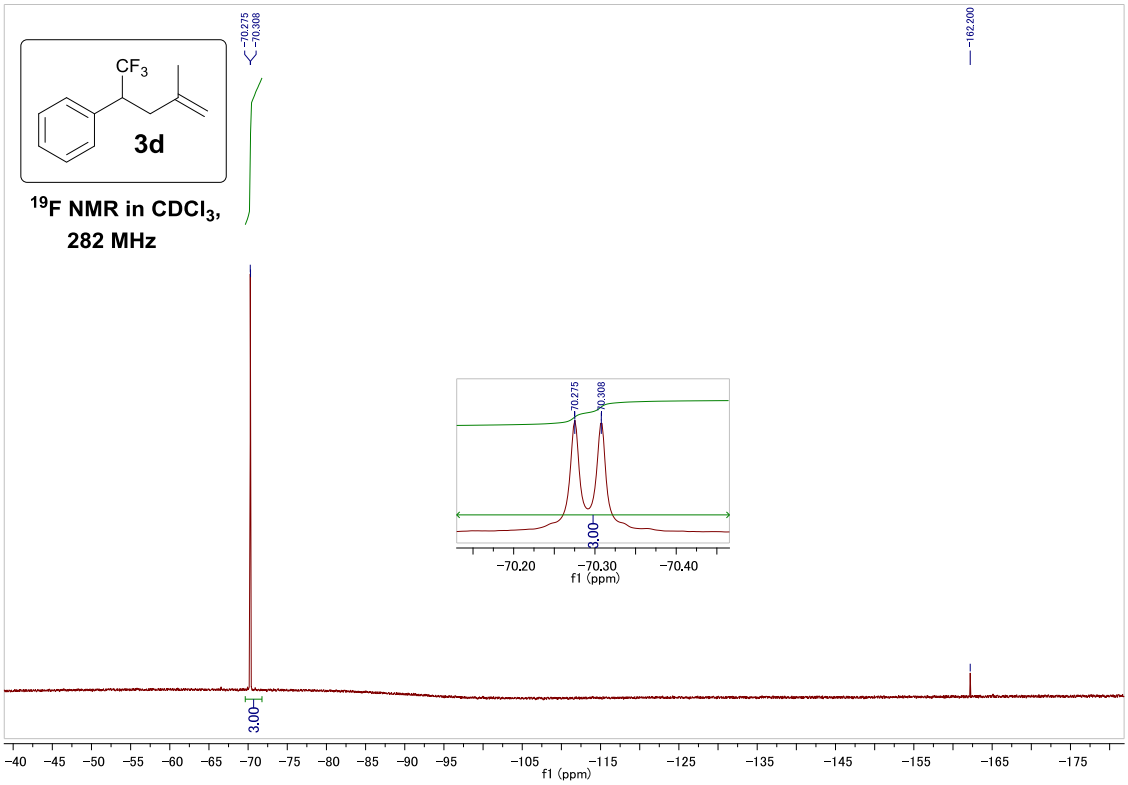
f1 (ppm)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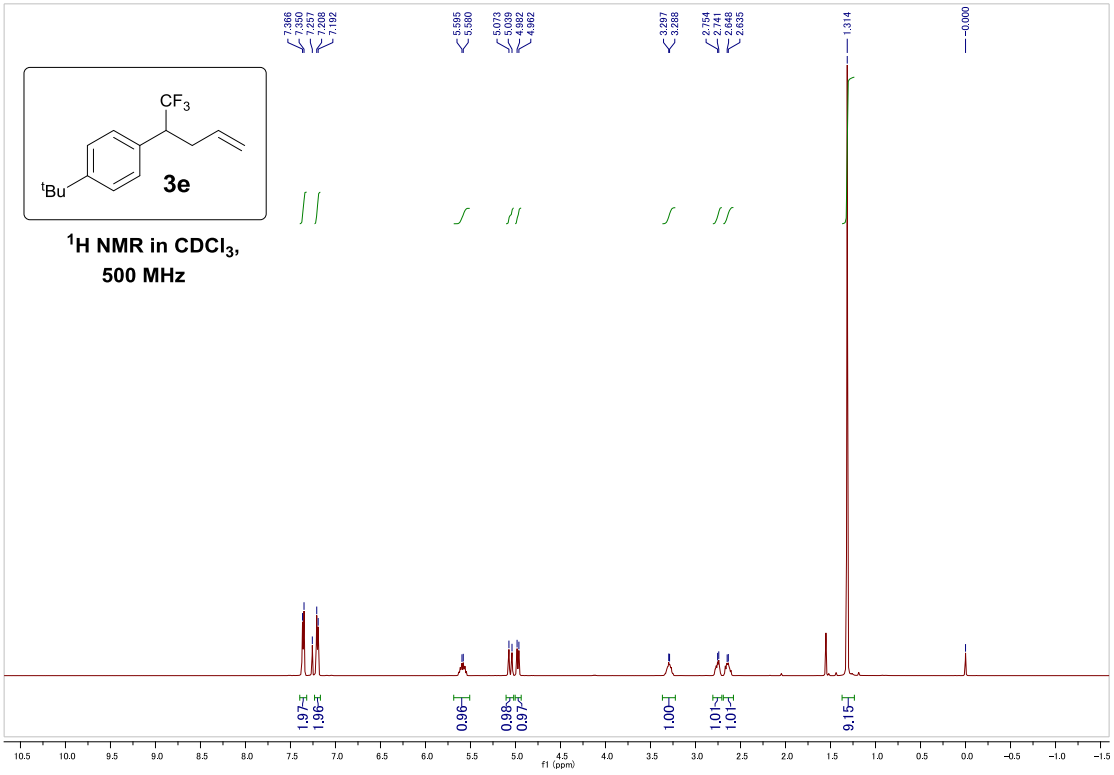
f1 (ppm)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3.297
3.288
2.754
2.741
2.648
2.635
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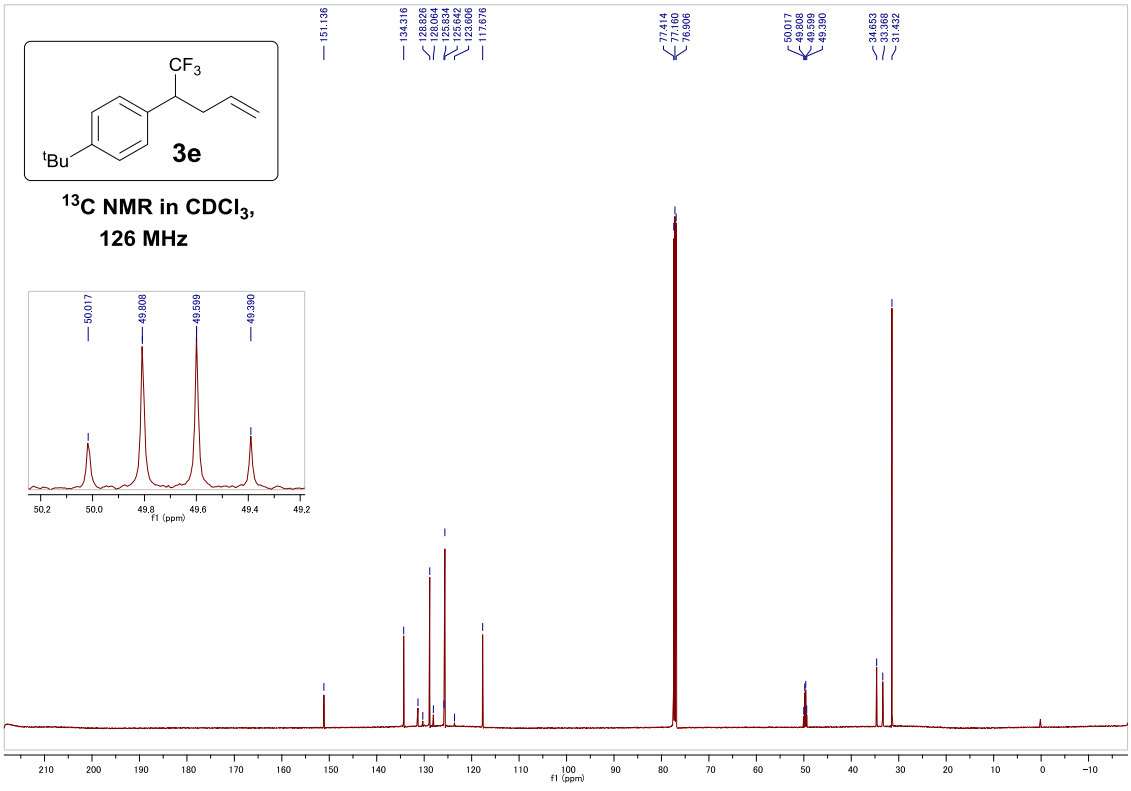
1.01
9.15
f1 (ppm)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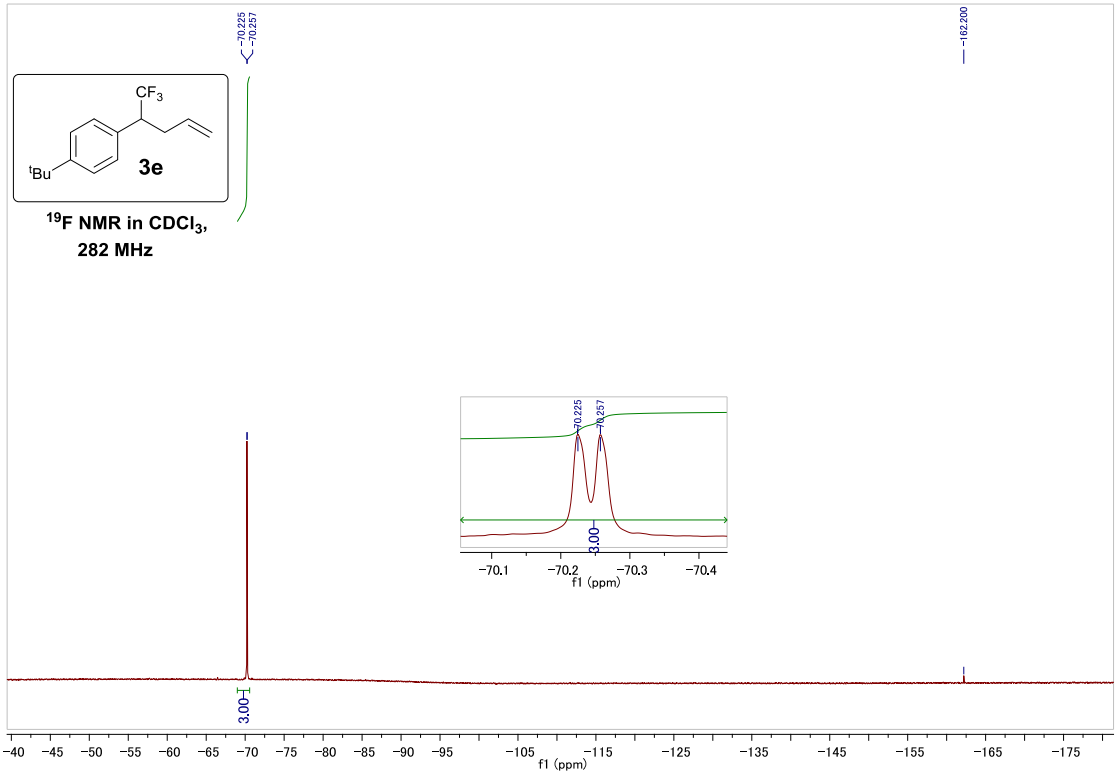
f1 (ppm)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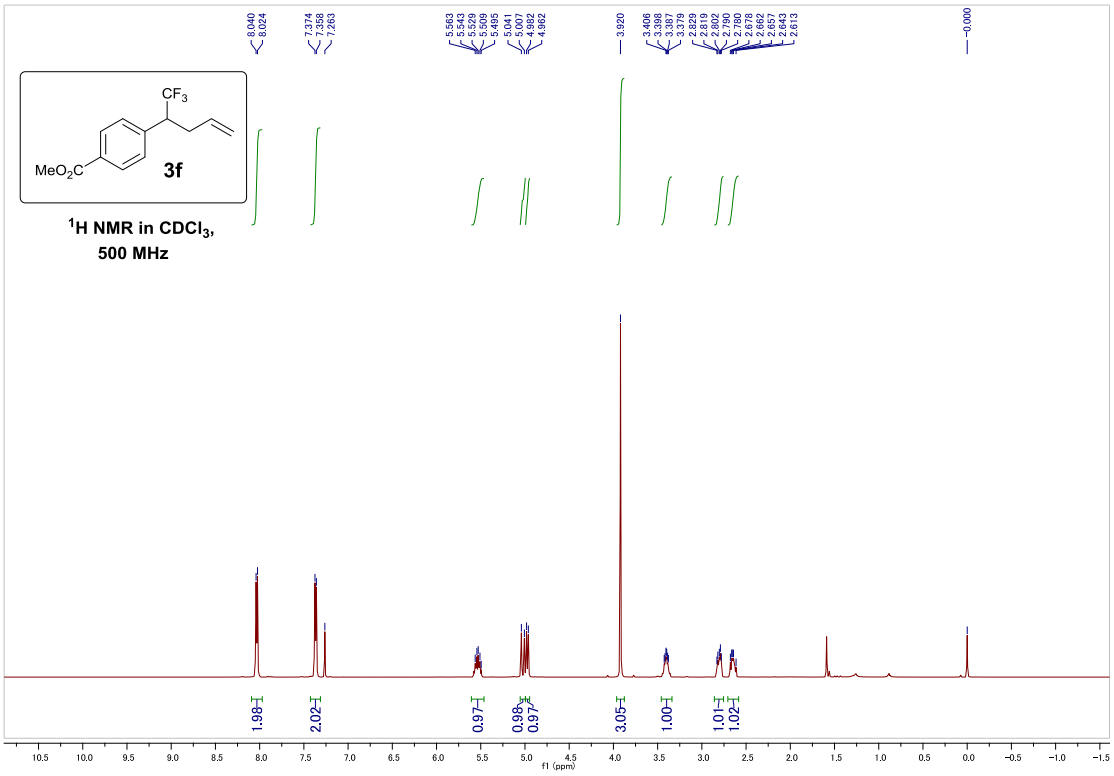
3.00
f1 (ppm)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3f
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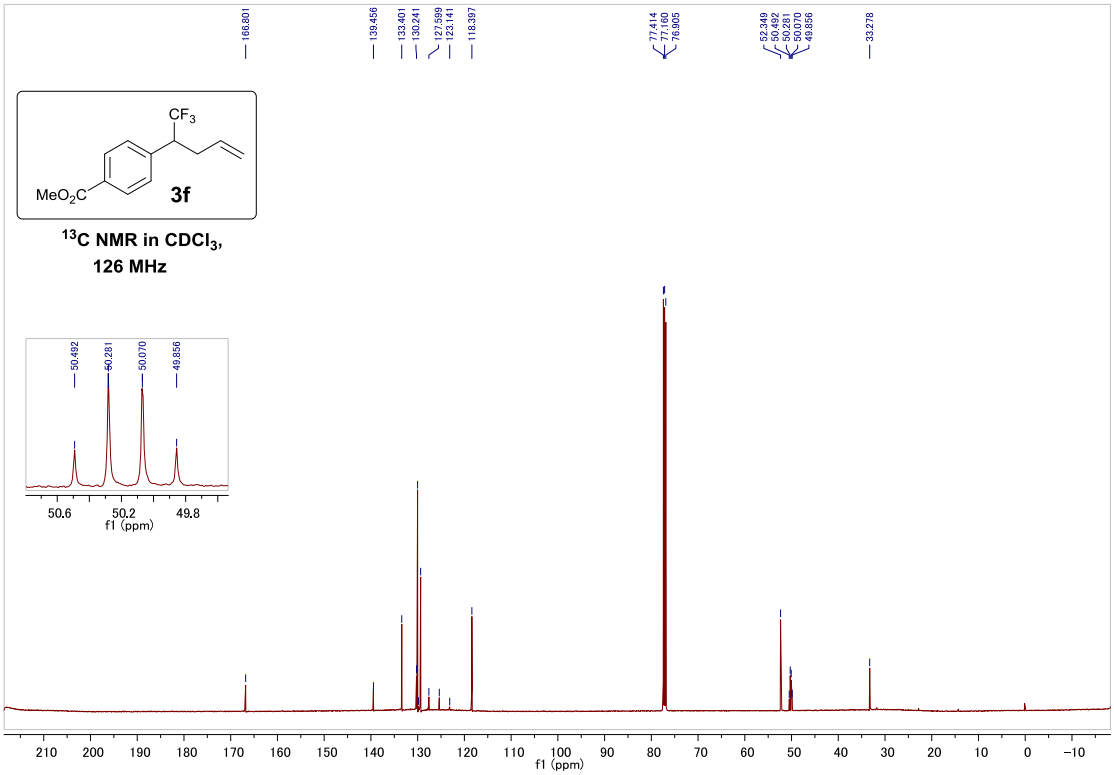
5.529
5.509
5.495
5.041
5.007
4.982
4.962
3.920
3.406
3.398
3.387
3.379
2.829
2.819
2.802
2.790
2.780
2.678
2.667
2.657
2.643
2.613
0.000
1.98
2.02
0.97
0.98
0.97
3.05
1.00
1.01
1.02
f1 (ppm)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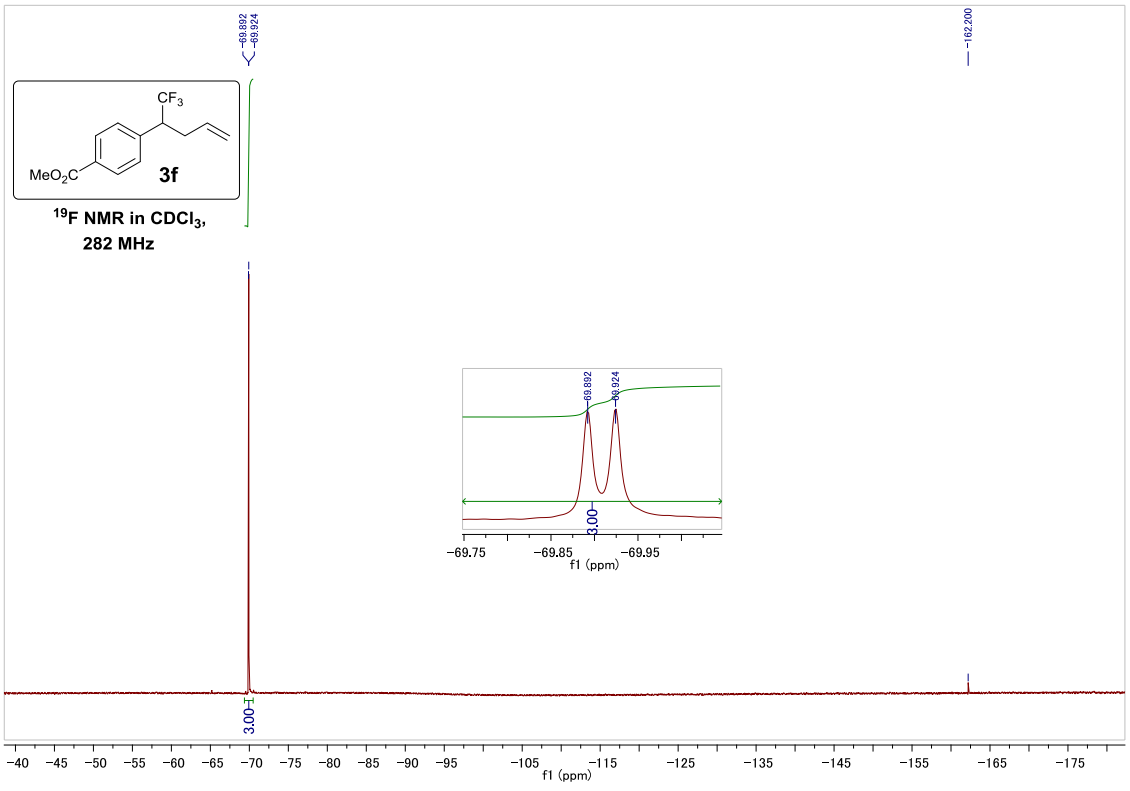
130.241
127.599
123.141
118.397
77.414
77.160
76.905
52.349
50.492
50.281
50.070
49.856
33.278
CF3
MeO2C
3f
13C NMR in CDCl3,
126 MHz
50.492
50.281
50.070
49.856
50.6
50.2
49.8
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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−162.200
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MeO2C
3f
19F NMR in CDCl3,
282 MHz
−69.892
−69.924
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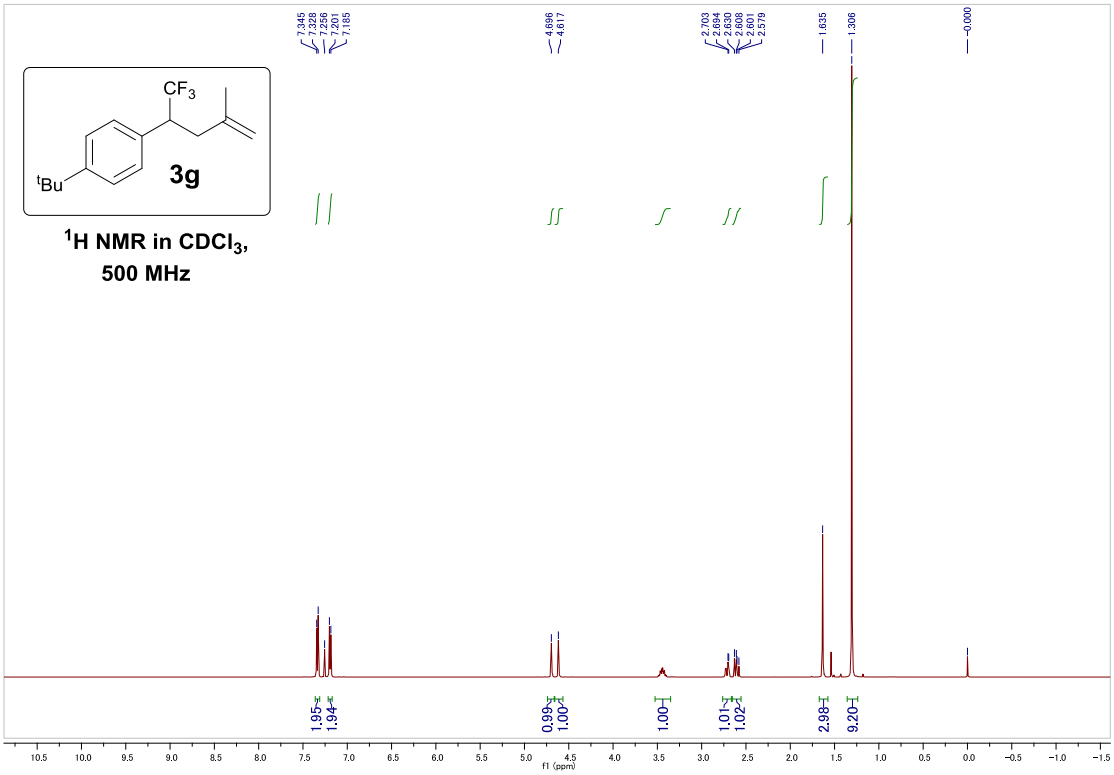
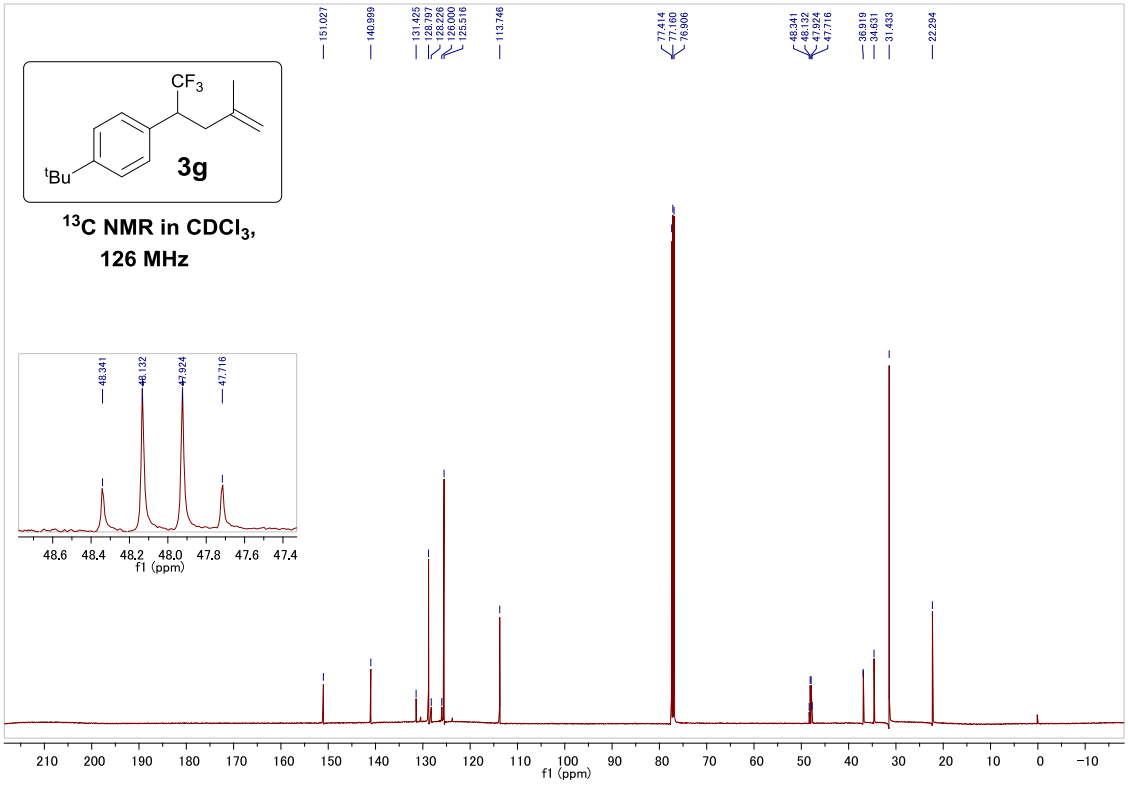
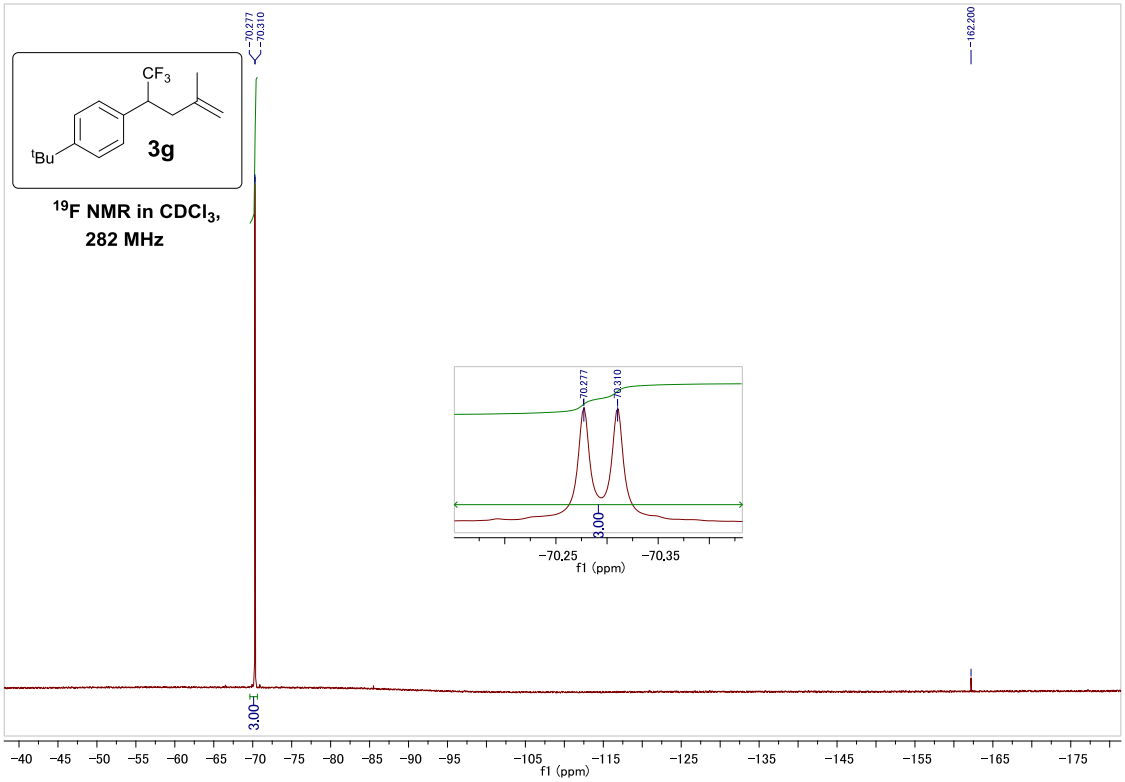
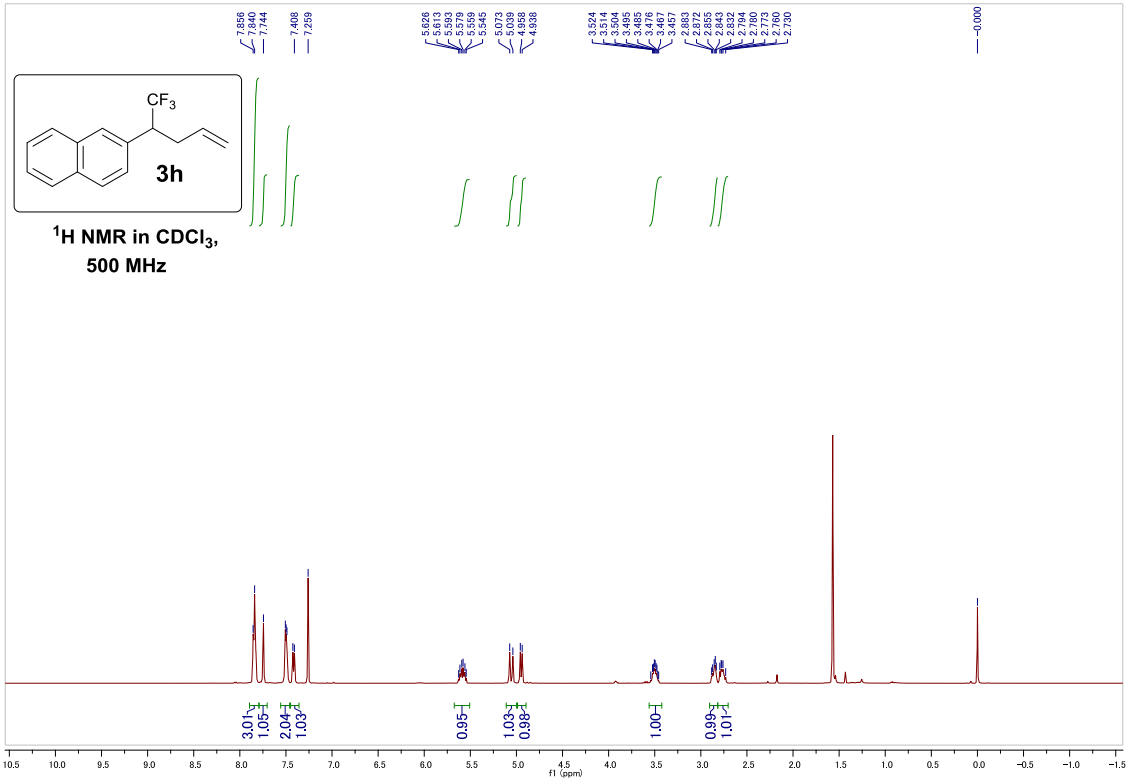
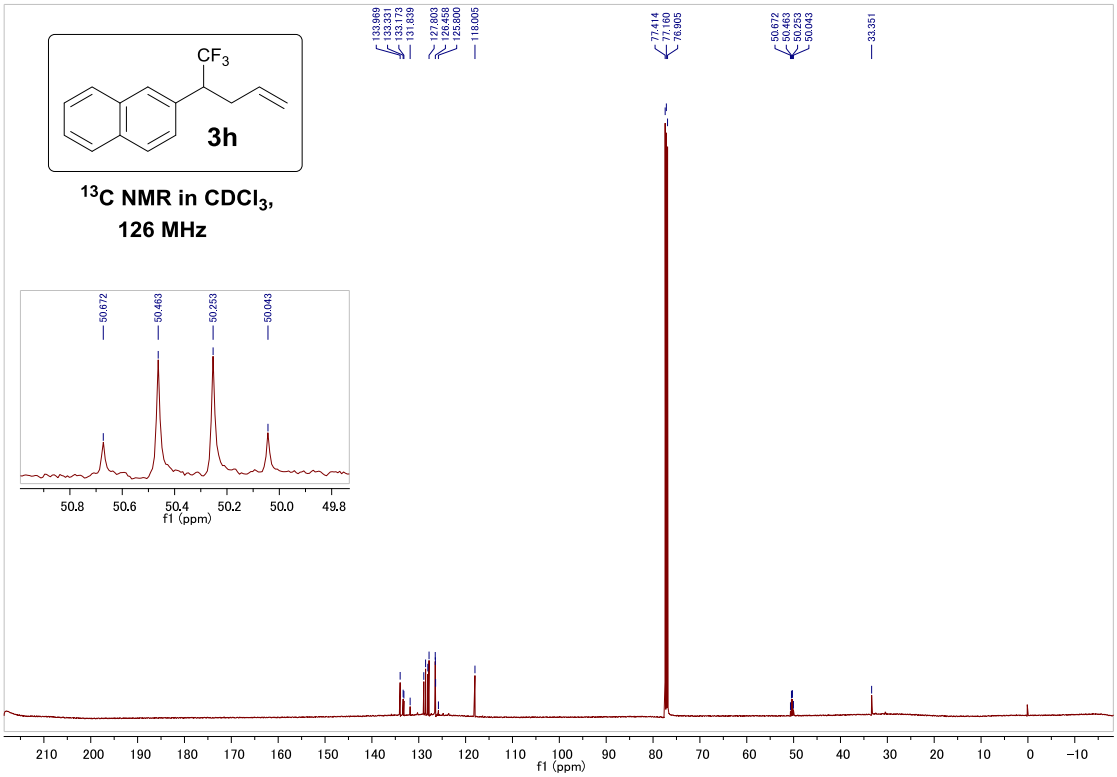
−69.75
−69.85
−69.95
f1 (ppm)
3.00
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

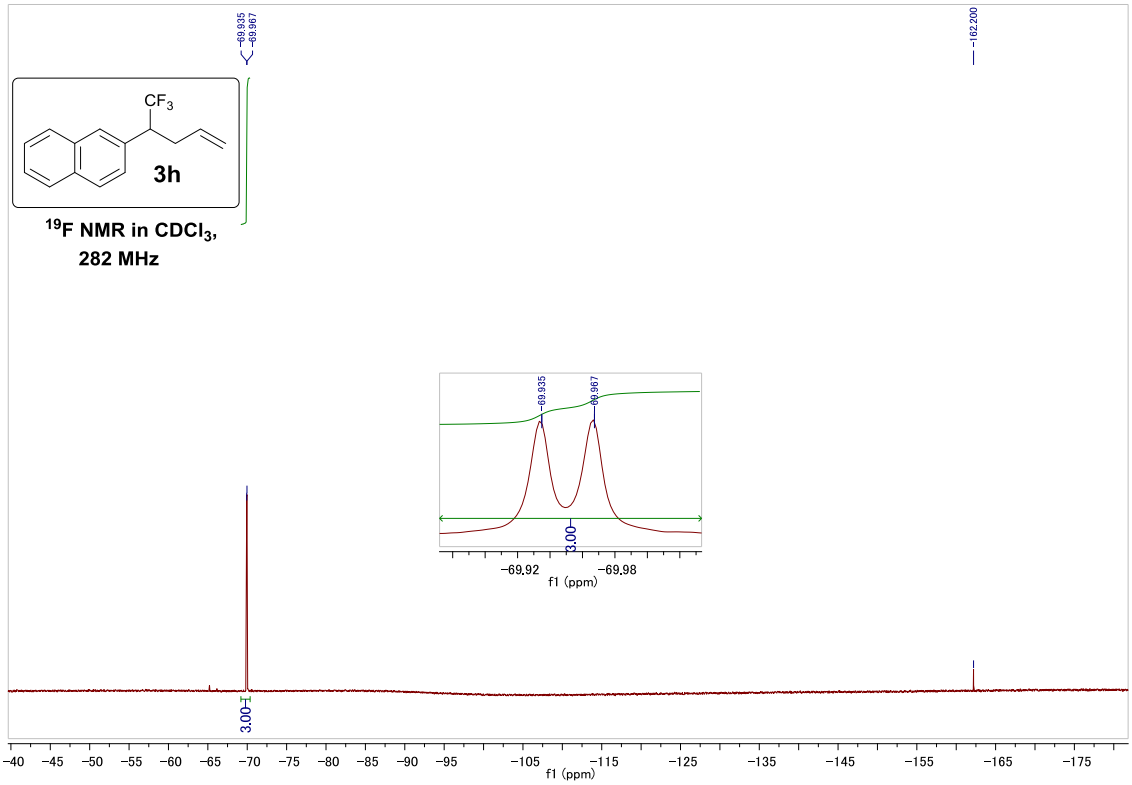

CF3
tBu
3g
1H NMR in CDCl3,
500 MHz
f1 (ppm)

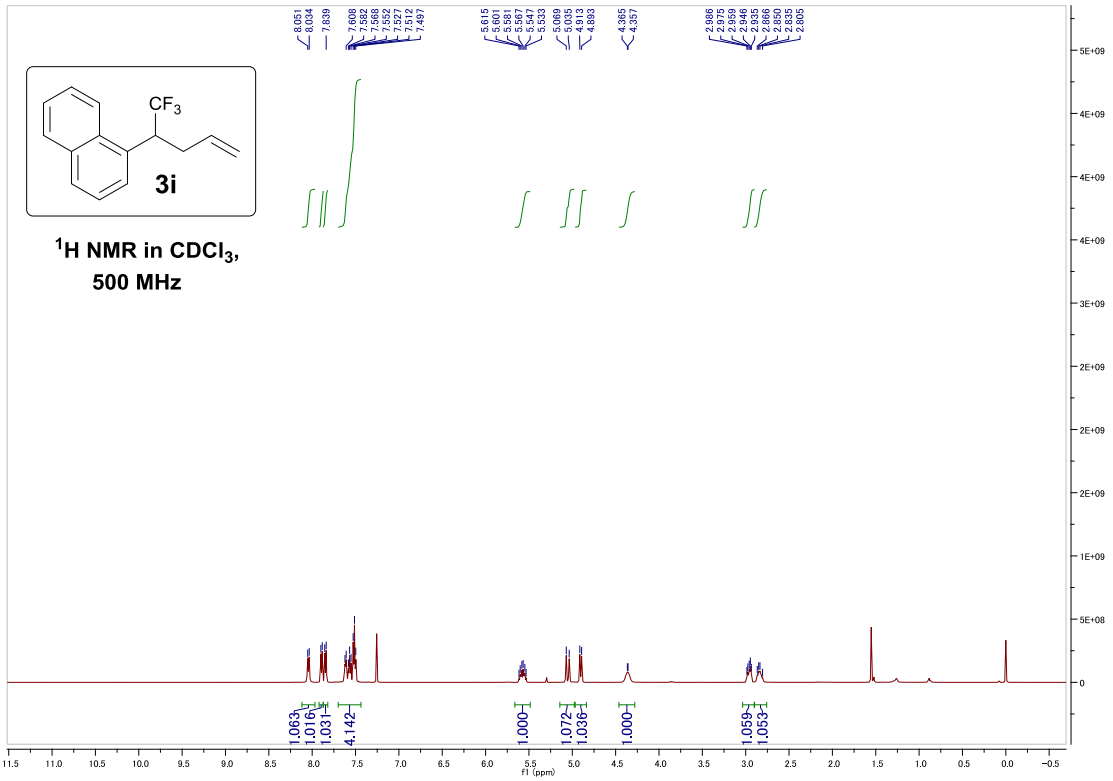

CF3
tBu
3g
13C NMR in CDCl3,
126 MHz
f1 (ppm)

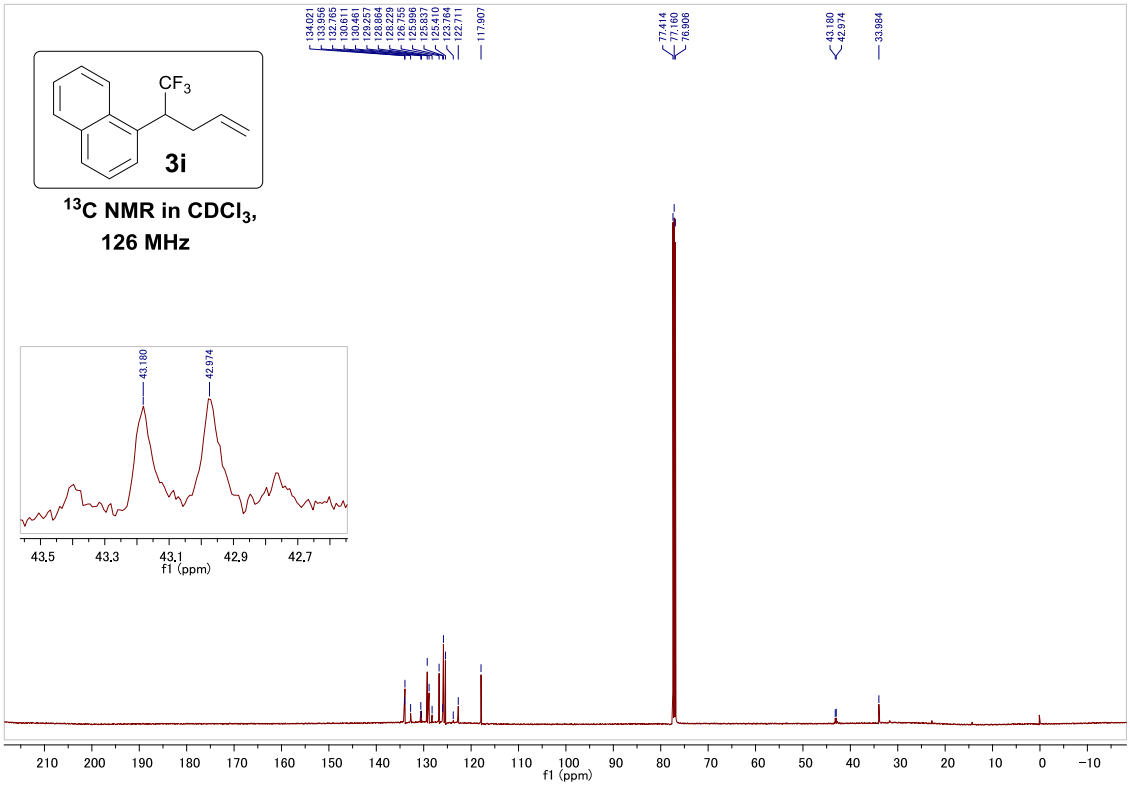

CF3
tBu
3g
19F NMR in CDCl3,
282 MHz
-70.277
-70.310
-162.200
3.00
-70.25
-70.35
f1 (ppm)

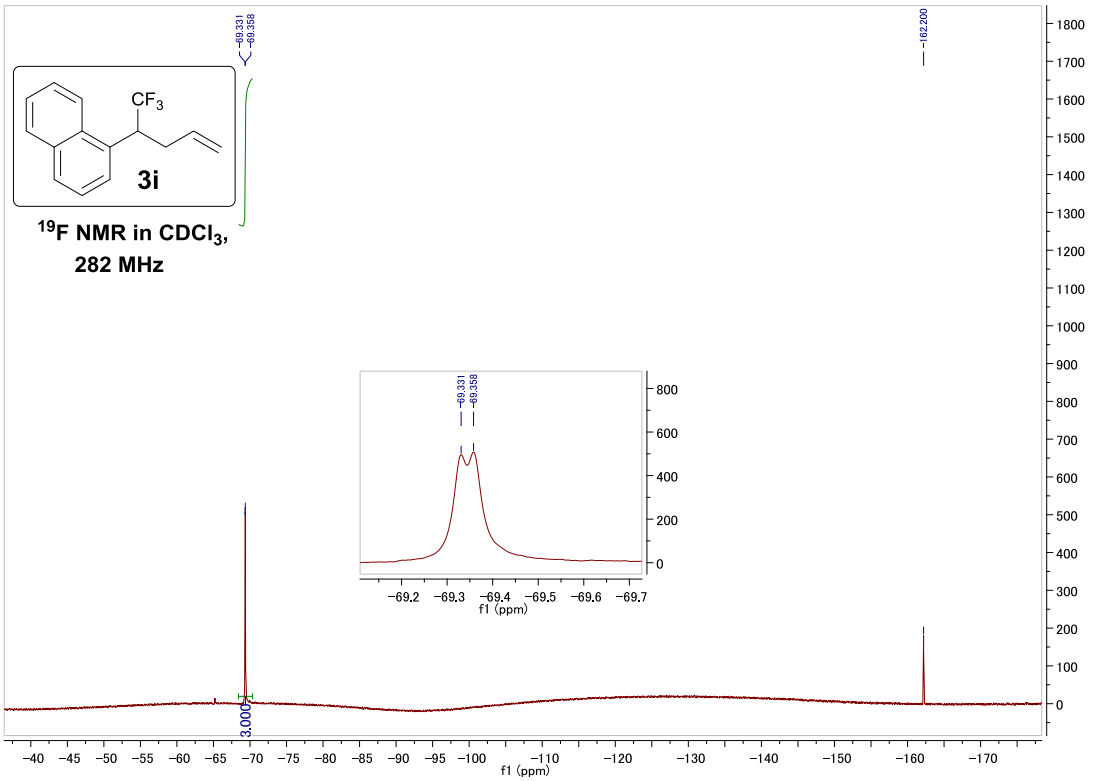

CF3
3h
1H NMR in CDCl3,
500 MHz
3.01
1.05
2.04
1.03
0.95
1.03
0.98
1.00
0.99
1.01
f1 (ppm)

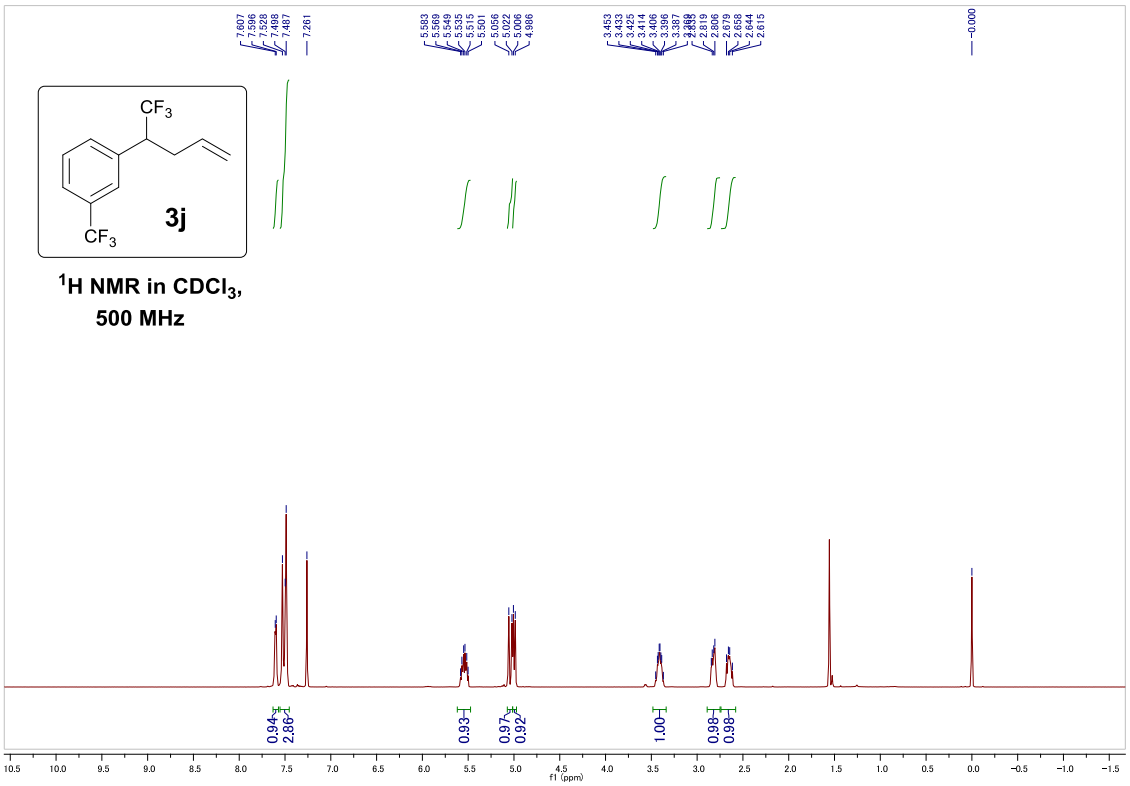

CF3
3h
13C NMR in CDCl3,
126 MHz
133.969
133.331
133.173
131.559
127.803
126.458
125.800
118.005
77.414
77.160
76.905
50.672
50.463
50.253
50.043
33.351
f1 (ppm)

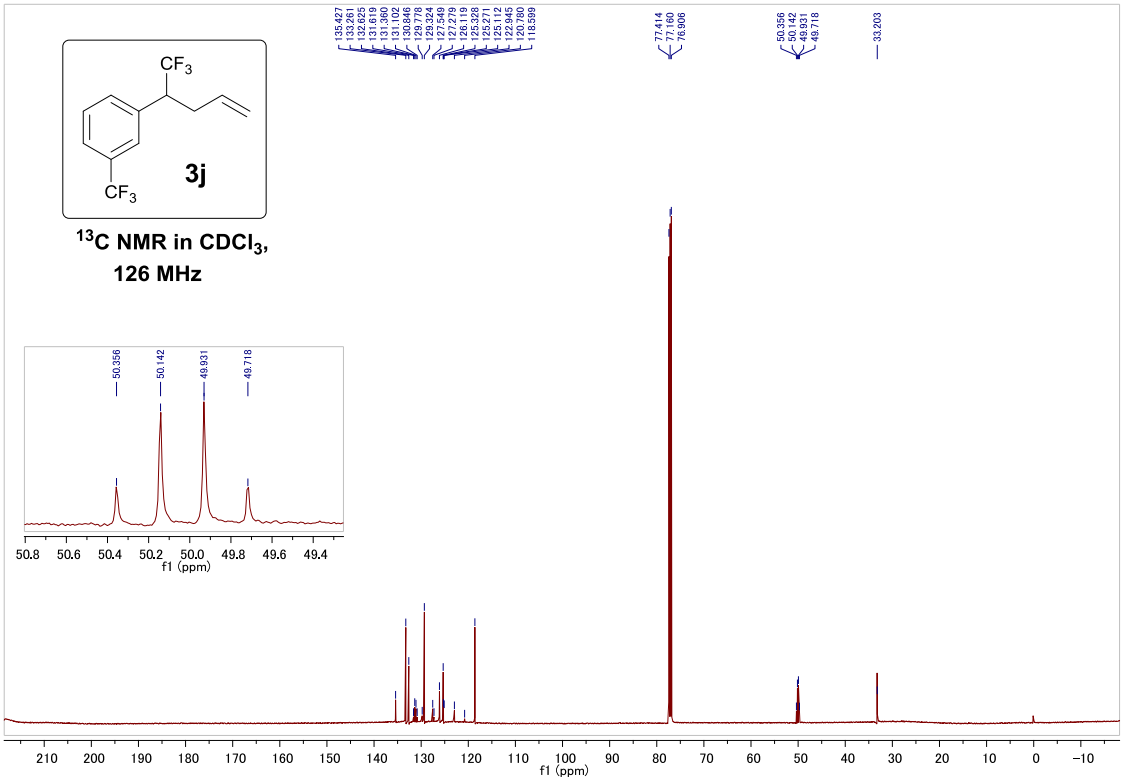

CF3
3h
19F NMR in CDCl3,
282 MHz
-69.935
-69.967
-162.200
3.00
f1 (ppm)

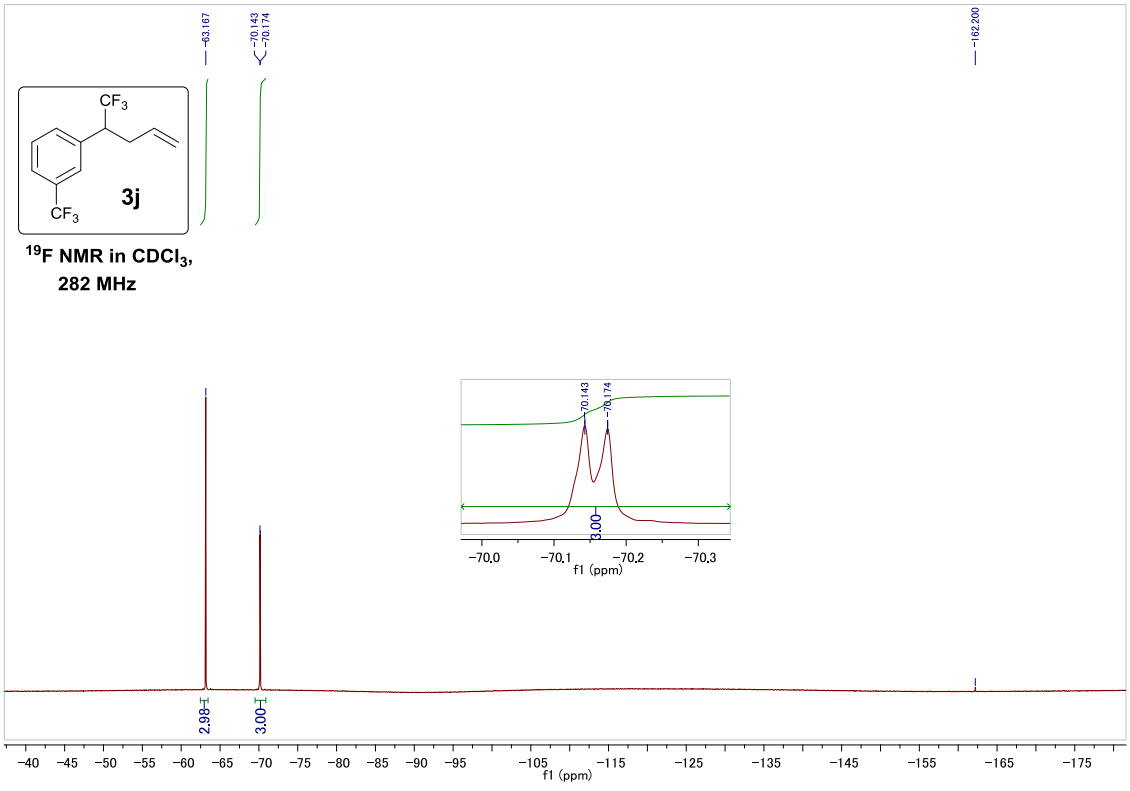

CF3
3i
1H NMR in CDCl3,
500 MHz
f1 (ppm)

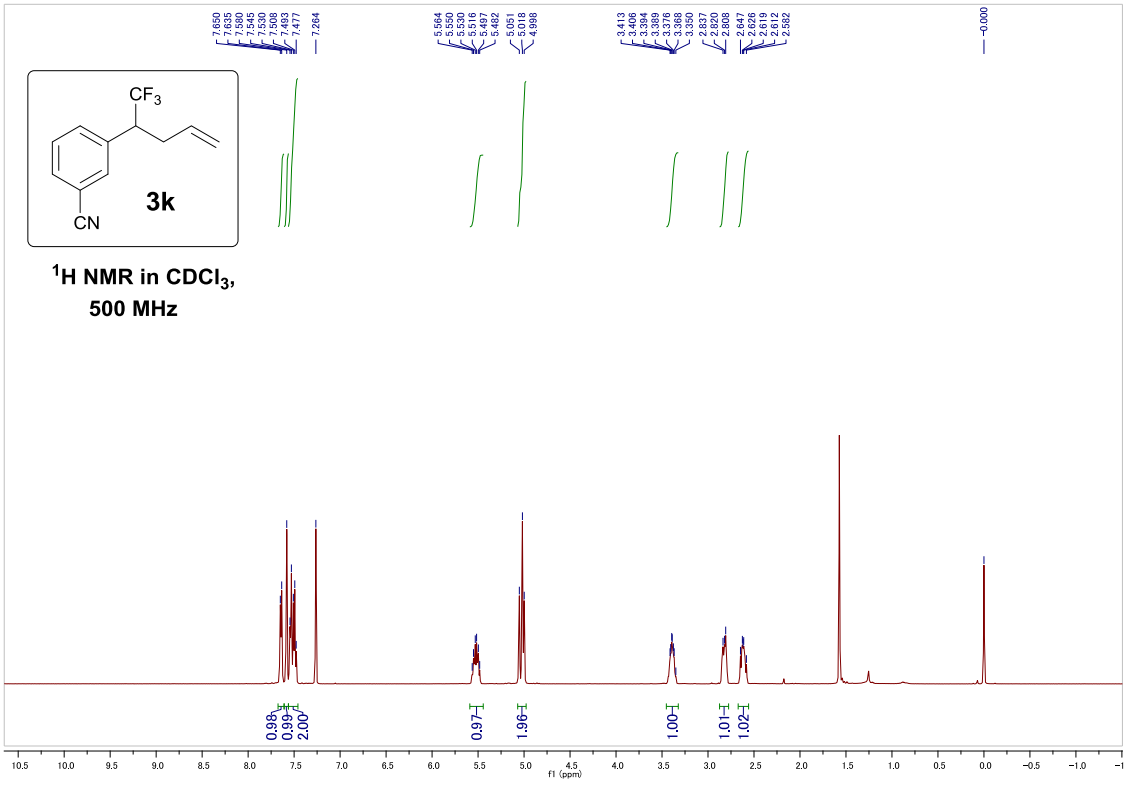

CF3
3i
13C NMR in CDCl3,
126 MHz
f1 (ppm)

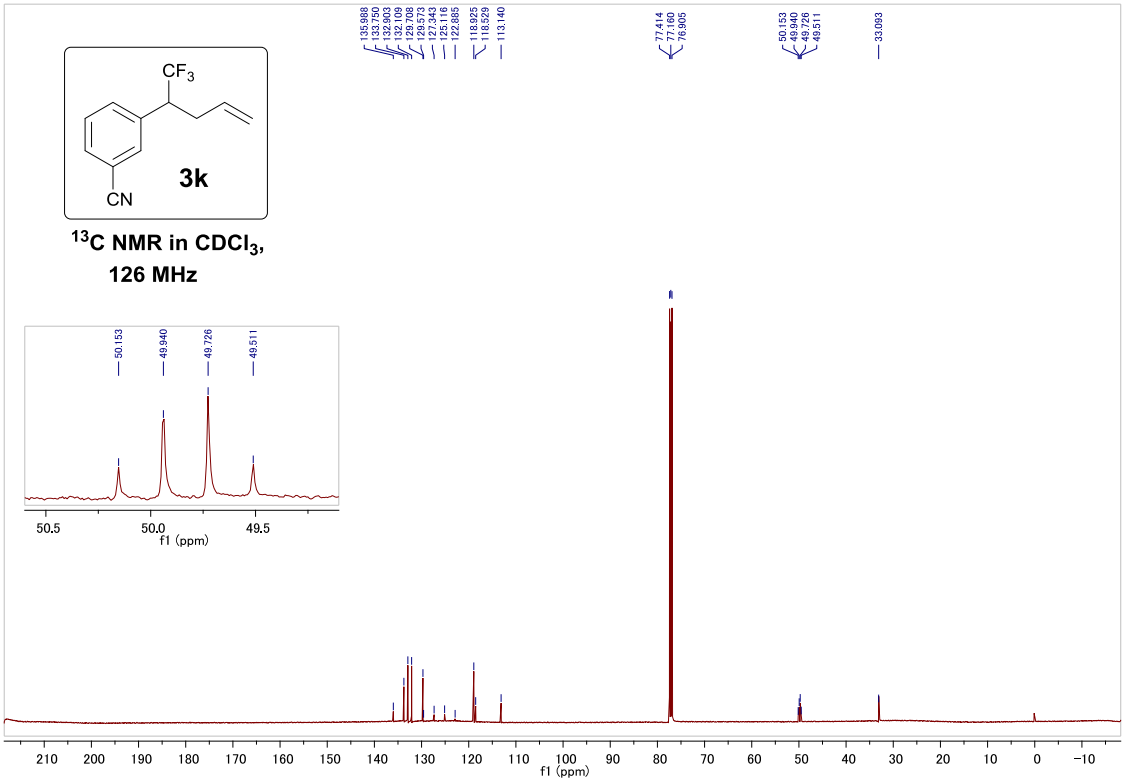

CF3
3i
19F NMR in CDCl3,
282 MHz
-69.331
-69.358
-162.200
3.000
f1 (ppm)

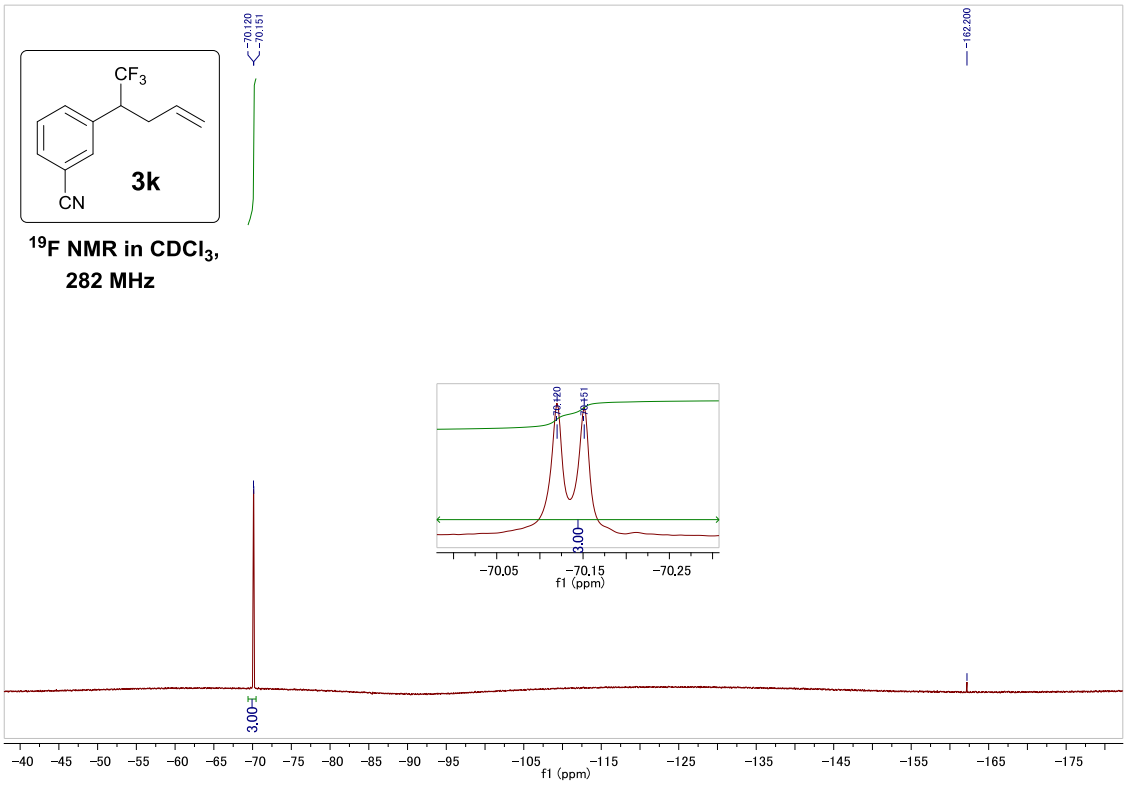

CF3
CF3
3j
1H NMR in CDCl3,
500 MHz
7.607
7.596
7.528
7.498
7.487
7.261
5.583
5.569
5.549
5.535
5.515
5.501
5.485
5.022
5.006
4.986
3.453
3.433
3.425
3.414
3.406
3.396
3.387
2.819
2.806
2.679
2.658
2.644
2.615
0.000
0.94
2.86
0.93
0.97
0.92
1.00
0.98
0.98
f1 (ppm)

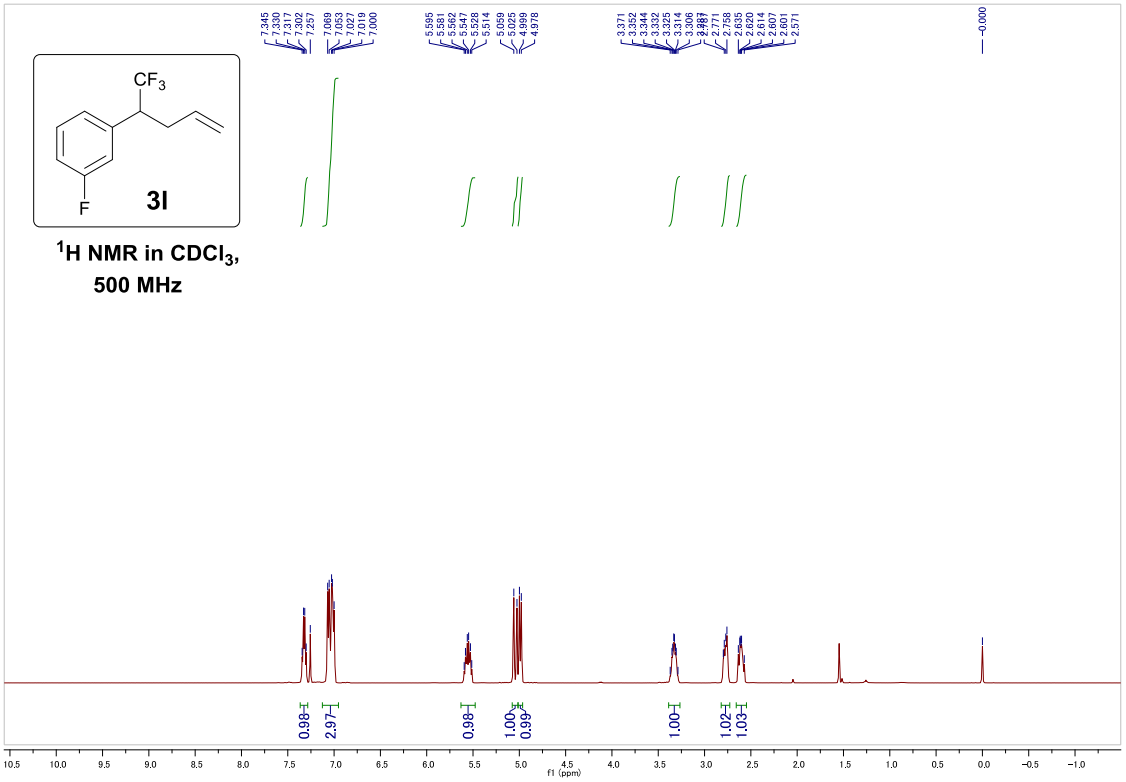

CF3
CF3
3j
13C NMR in CDCl3,
126 MHz
135.427
133.261
132.625
131.619
131.380
131.102
130.846
129.778
129.324
127.549
127.239
126.119
125.328
125.271
125.112
123.946
120.780
118.599
77.414
77.160
76.906
50.356
50.142
49.931
49.718
33.203
f1 (ppm)

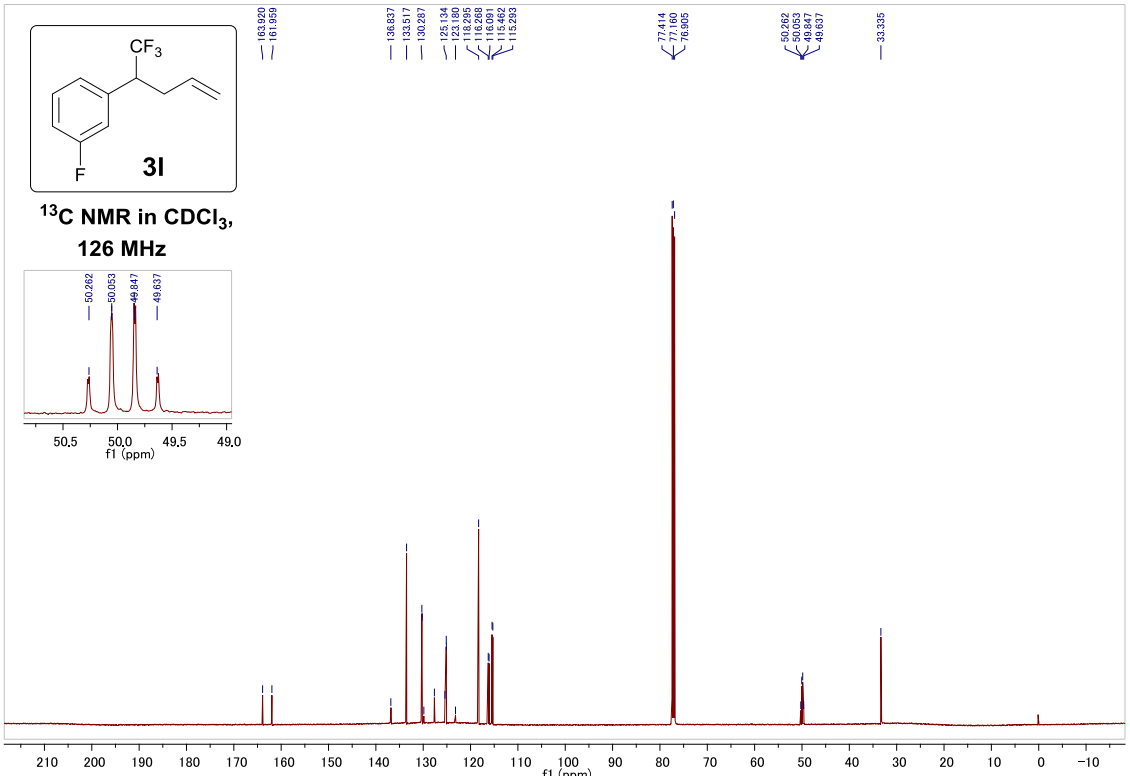

CF3
CF3
3j
19F NMR in CDCl3,
282 MHz
-63.167
-70.143
-70.174
-162.200
2.98
3.00
f1 (ppm)

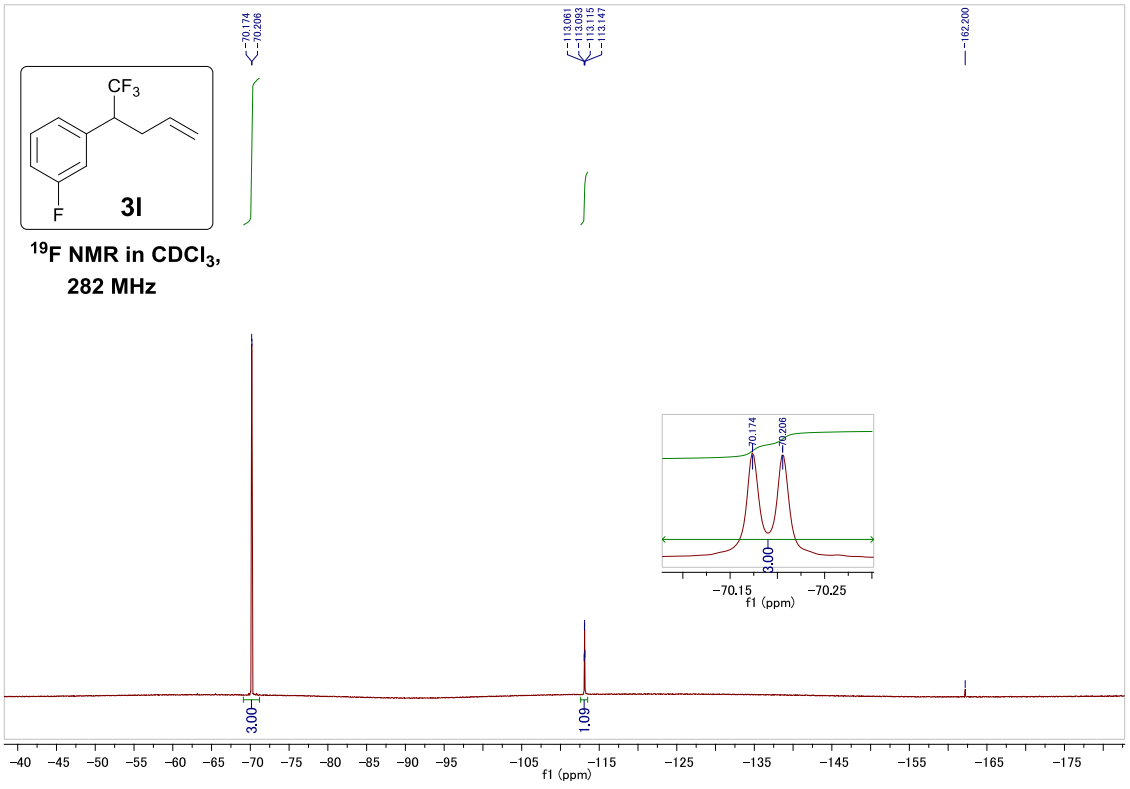

CF3
CN
3k
1H NMR in CDCl3,
500 MHz
f1 (ppm)

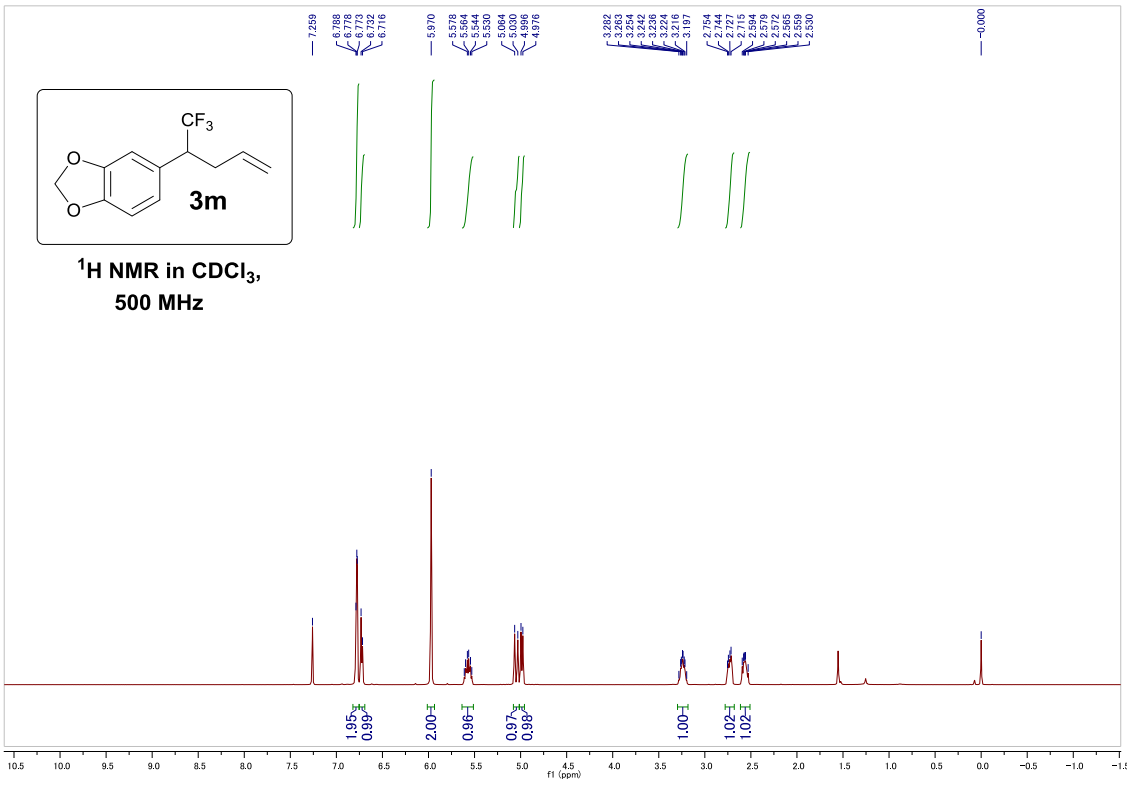

CF3
CN
3k
13C NMR in CDCl3,
126 MHz
f1 (ppm)

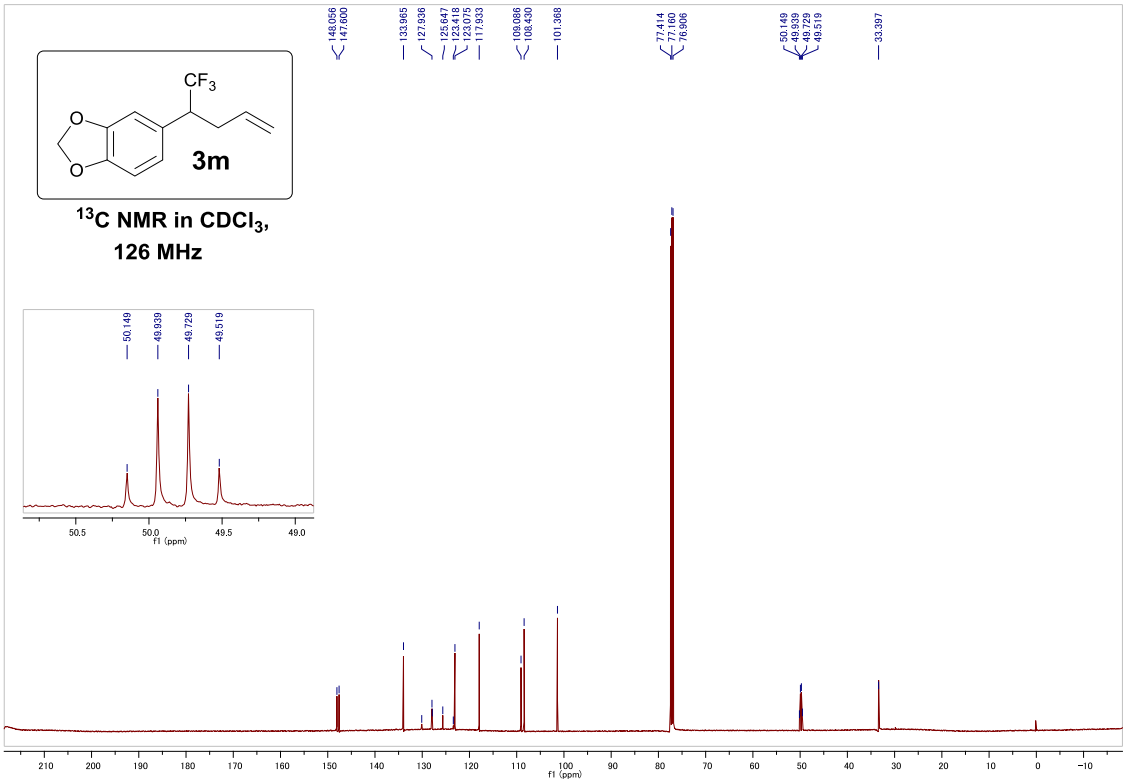

CF3
CN
3k
19F NMR in CDCl3,
282 MHz
-70.120
-70.151
-162.200
3.00
-70.05
-70.15
-70.25
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

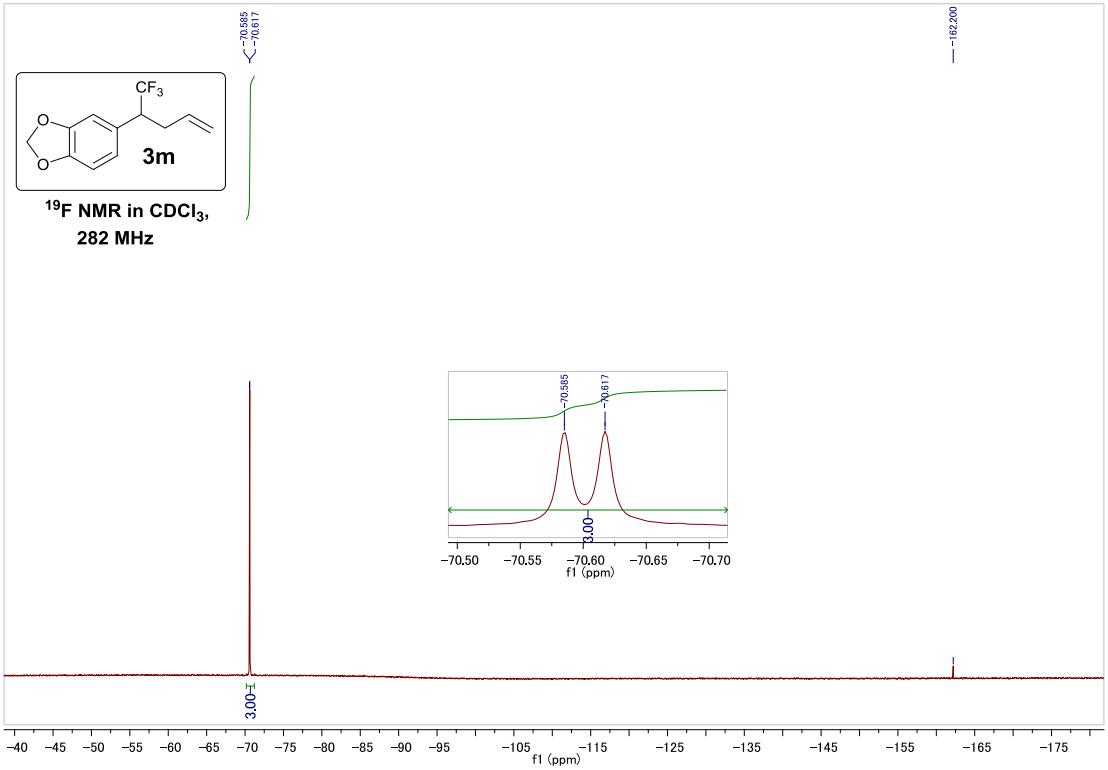

CF3
F
3l
1H NMR in CDCl3,
500 MHz
0.98
2.97
0.98
1.00
0.99
1.00
1.02
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

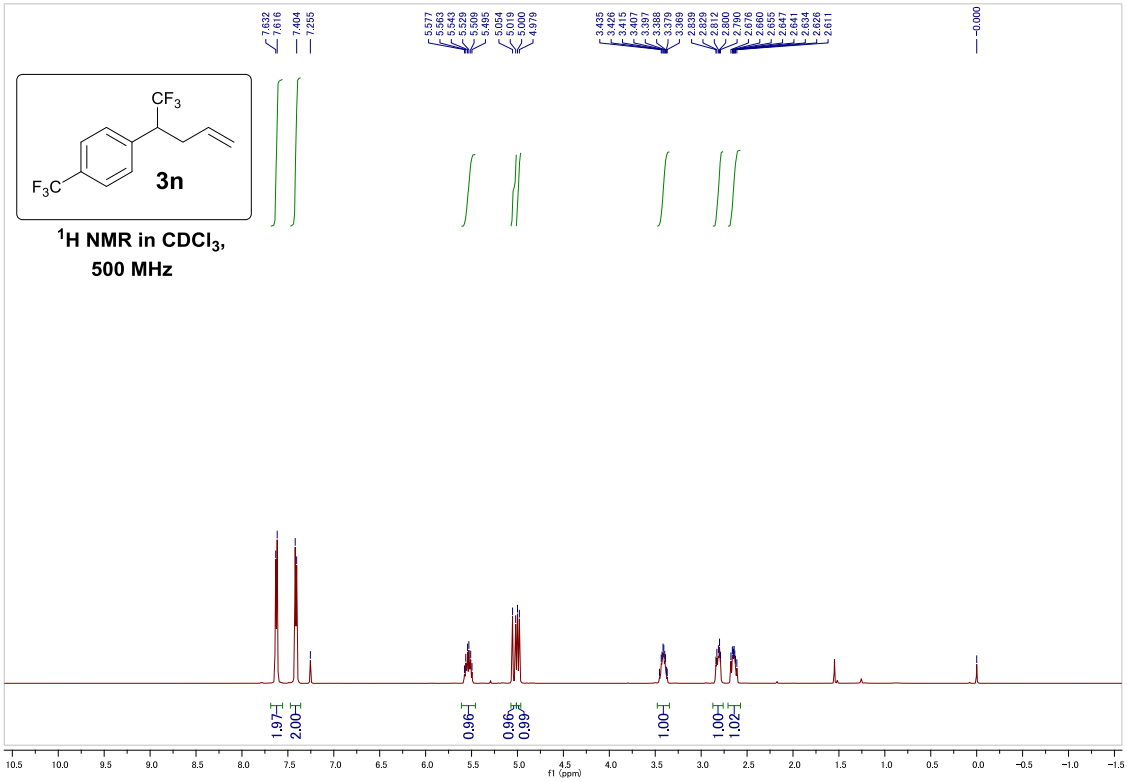

CF3
F
3l
13C NMR in CDCl3,
126 MHz
163.920
161.959
136.837
133.517
130.287
125.134
123.180
123.095
116.268
116.091
115.462
115.293
77.414
77.160
76.905
50.262
50.053
49.847
49.637
33.335
f1 (ppm)

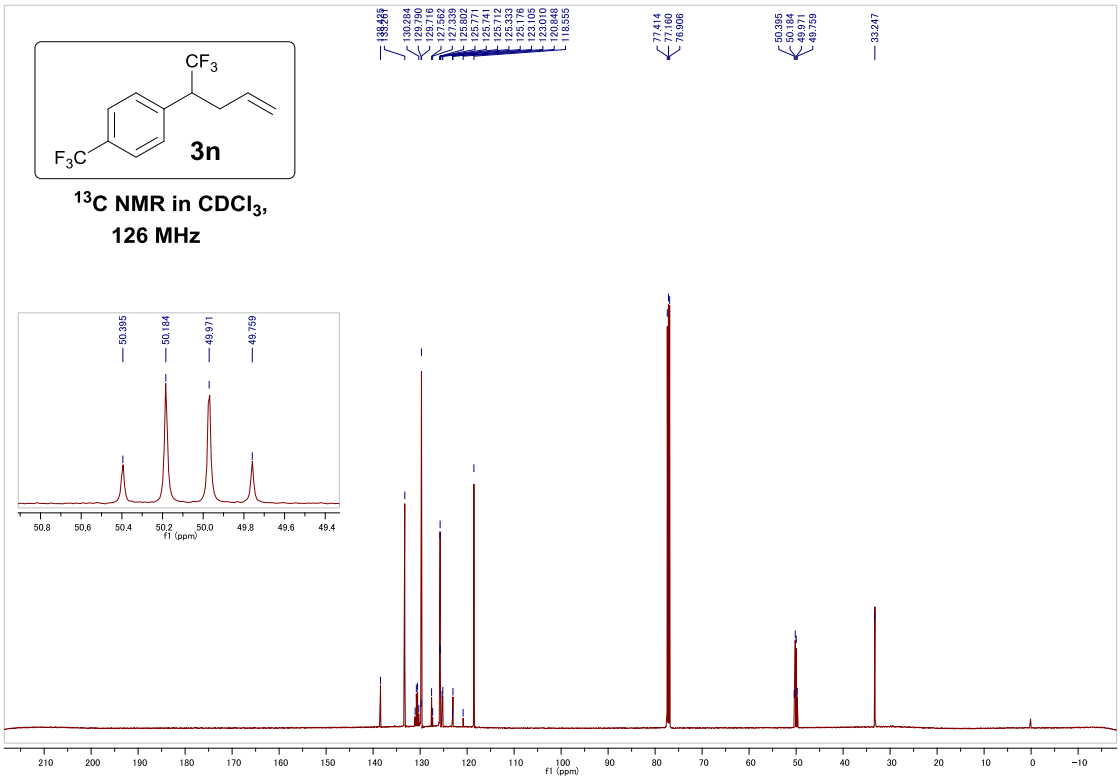

CF3
F
3l
19F NMR in CDCl3,
282 MHz
-70.174
-70.206
-113.061
-113.098
-113.115
-113.147
-162.200
3.00
1.09
f1 (ppm)

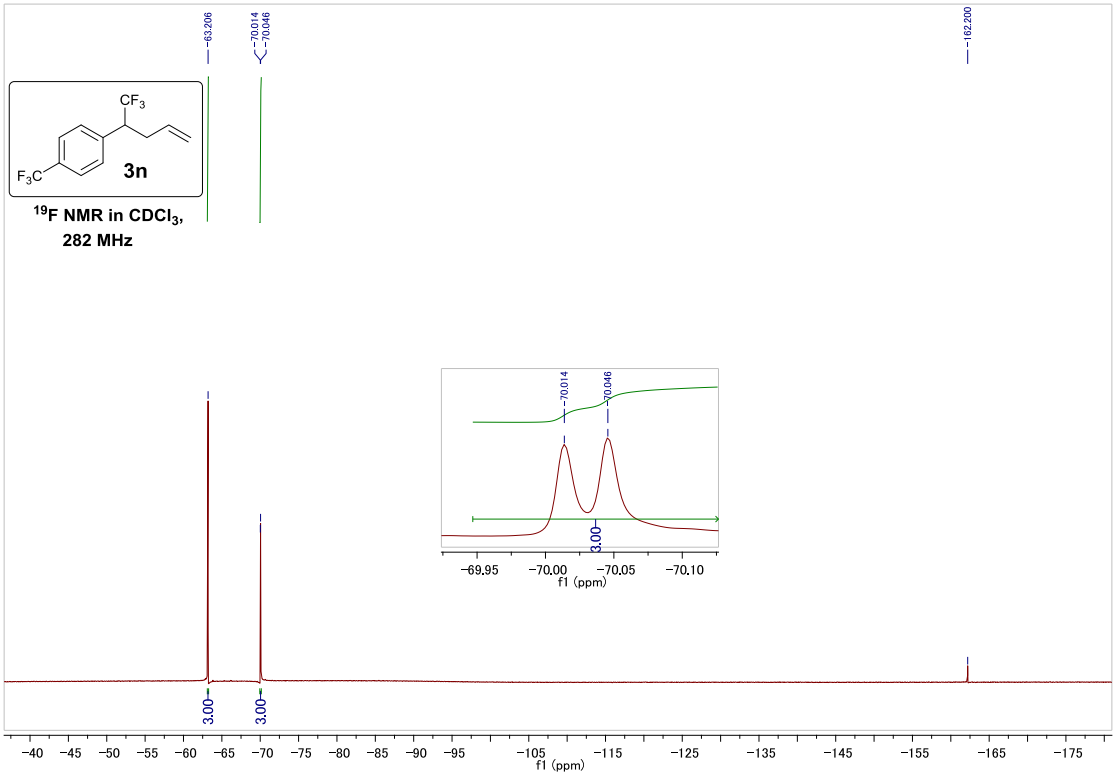

CF3
O
O
3m
1H NMR in CDCl3,
500 MHz
7.259
6.788
6.778
6.773
6.732
6.716
5.970
5.578
5.564
5.544
5.530
5.064
5.000
4.996
4.976
3.282
3.263
3.254
3.242
3.236
3.224
3.215
3.197
2.754
2.744
2.727
2.715
2.594
2.579
2.572
2.565
2.559
2.530
0.000
1.95
0.99
2.00
0.96
0.97
0.98
1.00
1.02
1.02
f1 (ppm)

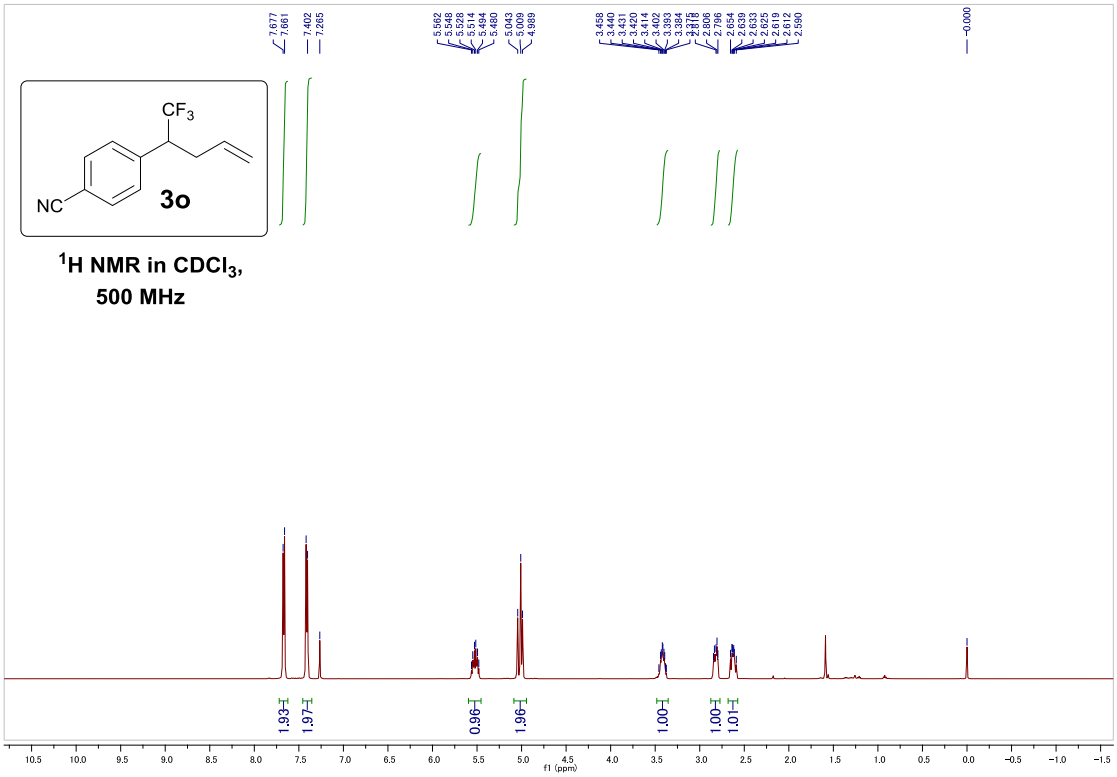

CF3
O
O
3m
13C NMR in CDCl3,
126 MHz
148.056
147.600
133.965
127.936
125.647
123.418
120.705
117.933
109.088
108.430
101.368
77.414
77.160
76.906
50.149
49.939
49.729
49.519
33.397
f1 (ppm)

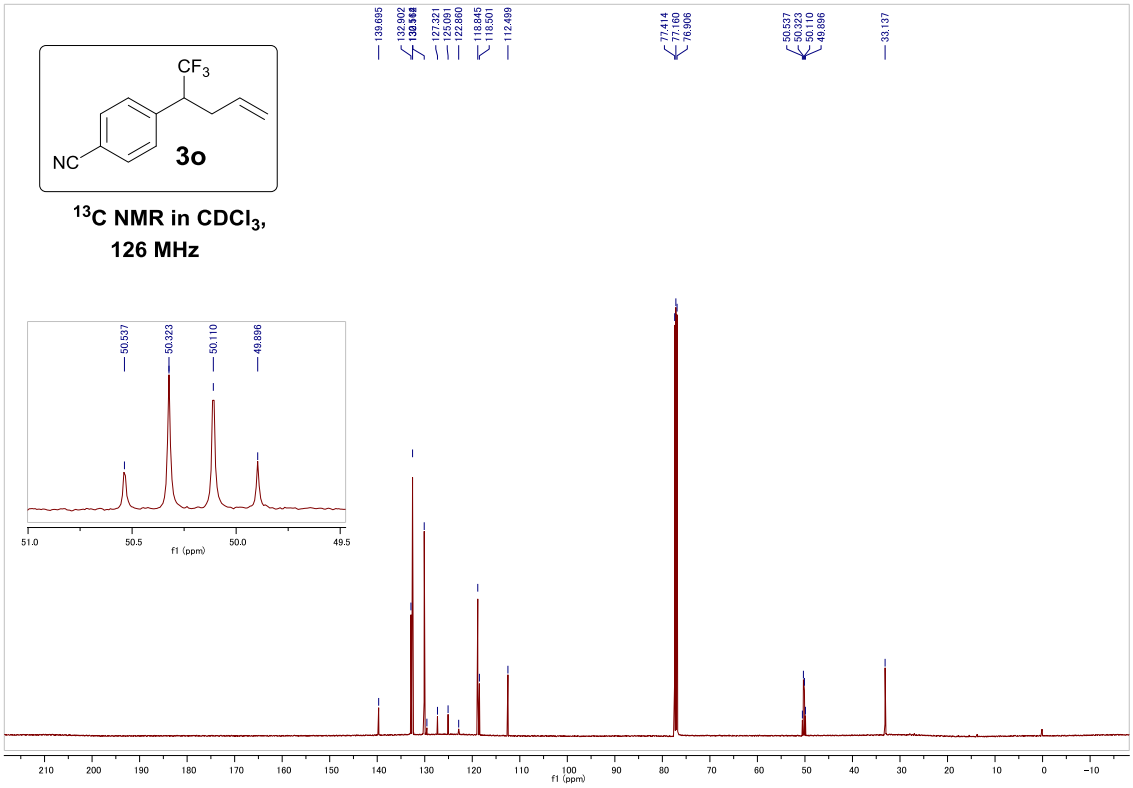

CF3
O
O
3m
19F NMR in CDCl3,
282 MHz
-70.585
-70.617
-162.200
3.00
-70.50
-70.55
-70.60
-70.65
-70.70
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

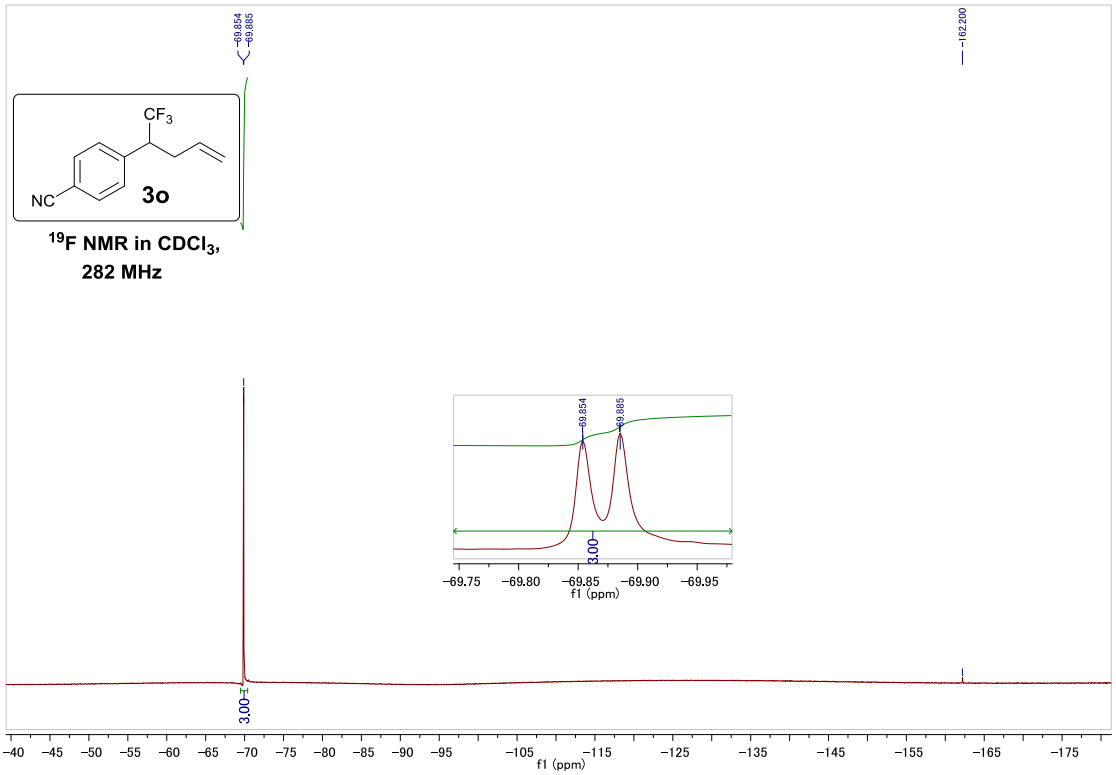

CF3
F3C
3n
1H NMR in CDCl3,
500 MHz
7.632
7.616
7.404
7.255
5.577
5.563
5.543
5.529
5.509
5.495
5.054
5.019
5.000
4.979
3.435
3.426
3.415
3.407
3.397
3.388
3.379
3.369
2.839
2.829
2.812
2.800
2.790
2.676
2.660
2.655
2.647
2.641
2.634
2.626
2.611
-0.000
1.97
2.00
0.96
0.96
0.99
1.00
1.00
1.02
f1 (ppm)

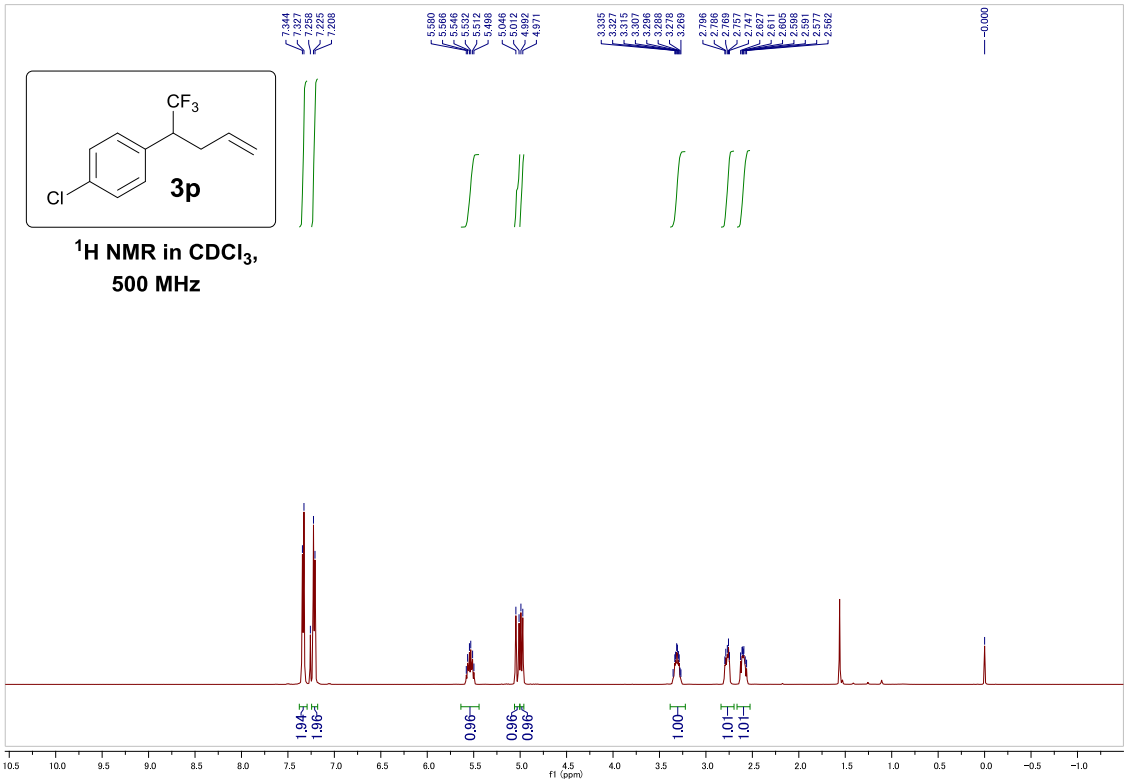

CF3
F3C
3n
13C NMR in CDCl3,
126 MHz
f1 (ppm)

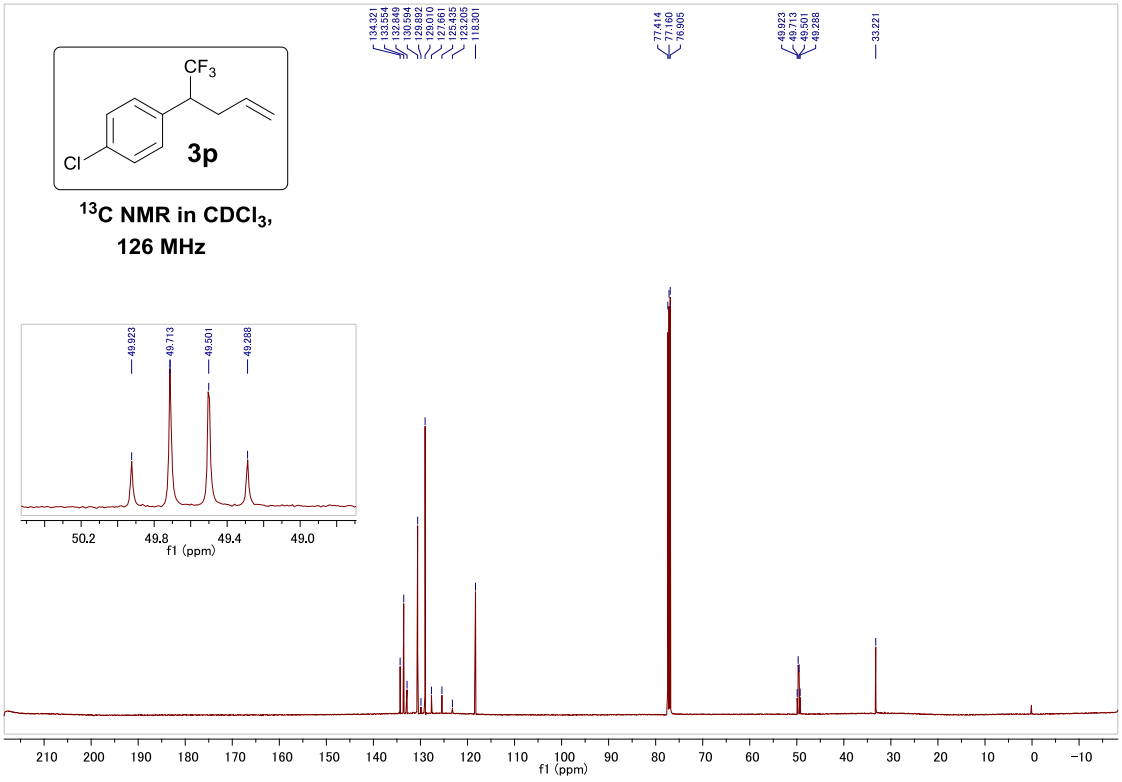

CF3
F3C
3n
19F NMR in CDCl3,
282 MHz
3.00
3.00
f1 (ppm)

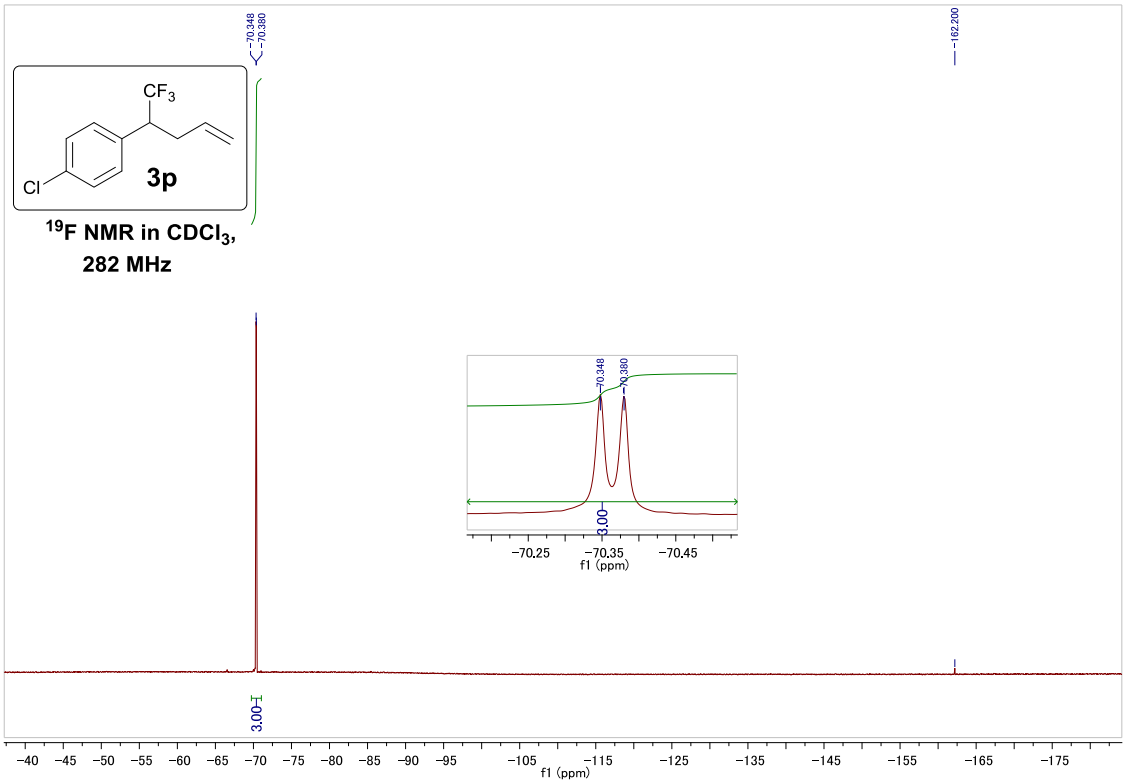

CF3
NC
3o
1H NMR in CDCl3,
500 MHz
1.93
1.97
0.96
1.96
1.00
1.00
1.01
f1 (ppm)

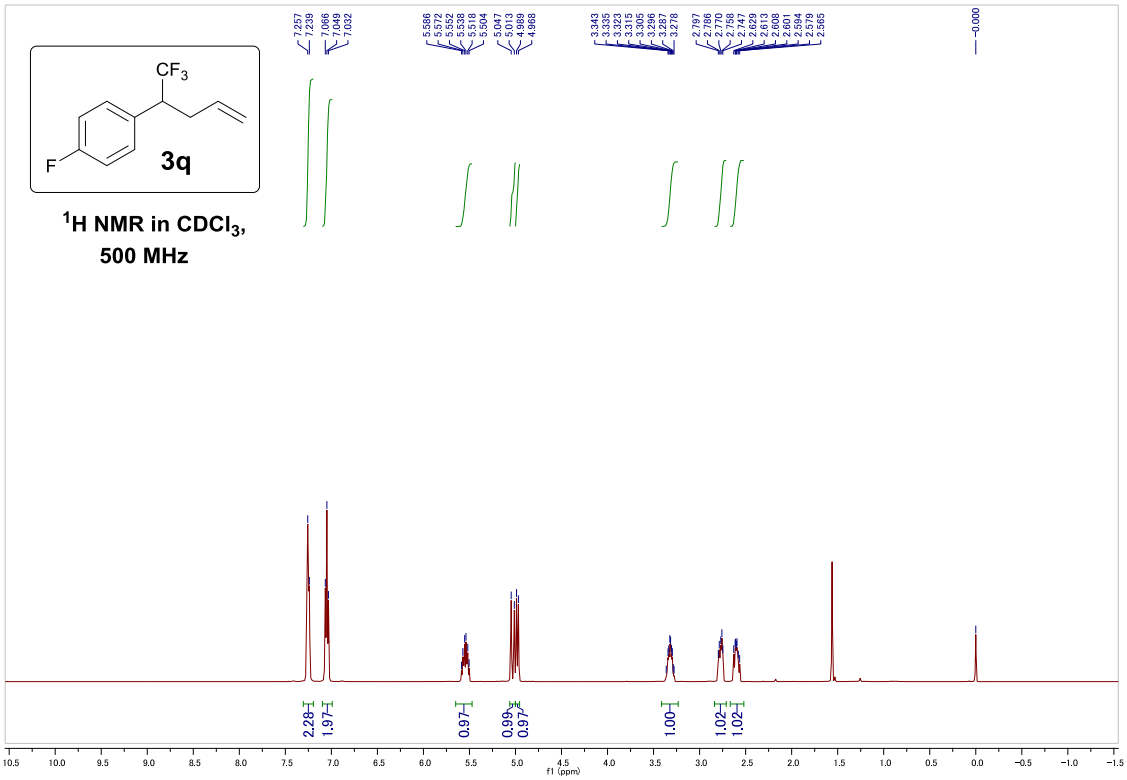

CF3
NC
3o
13C NMR in CDCl3,
126 MHz
50.537
50.323
50.110
49.896
f1 (ppm)

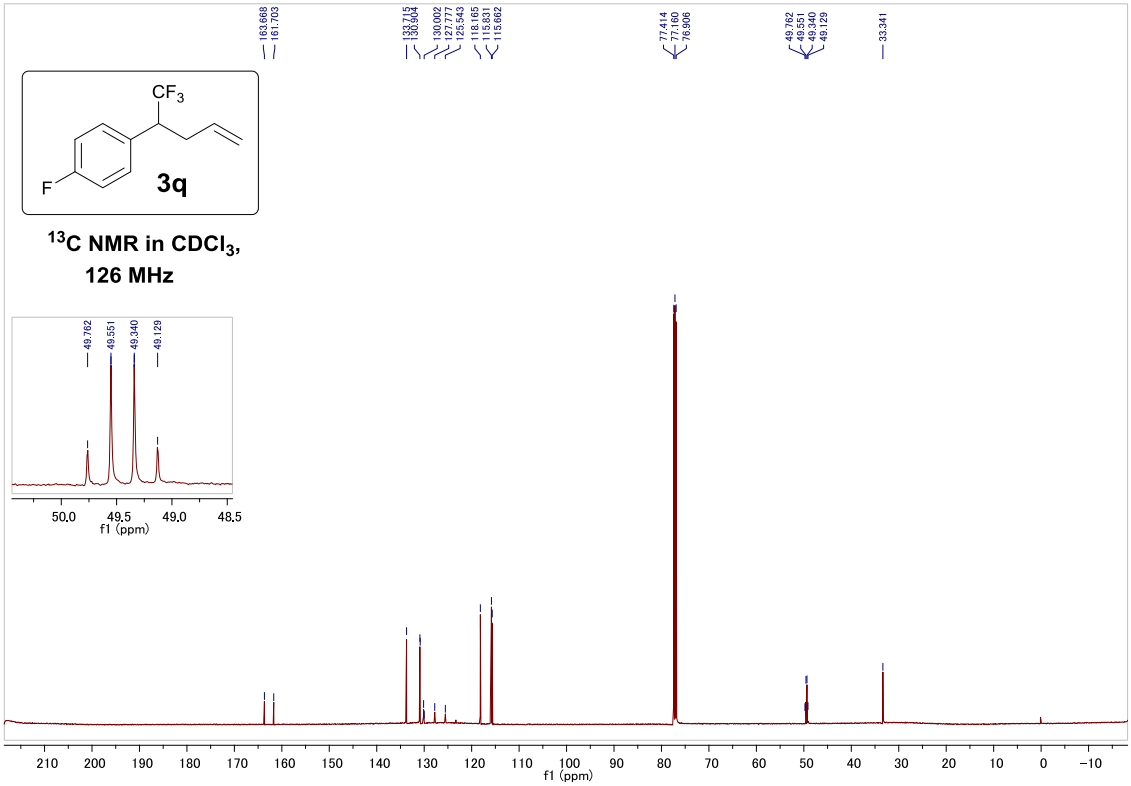

CF3
NC
3o
19F NMR in CDCl3,
282 MHz
-69.854
-69.885
-162.200
3.00
f1 (ppm)

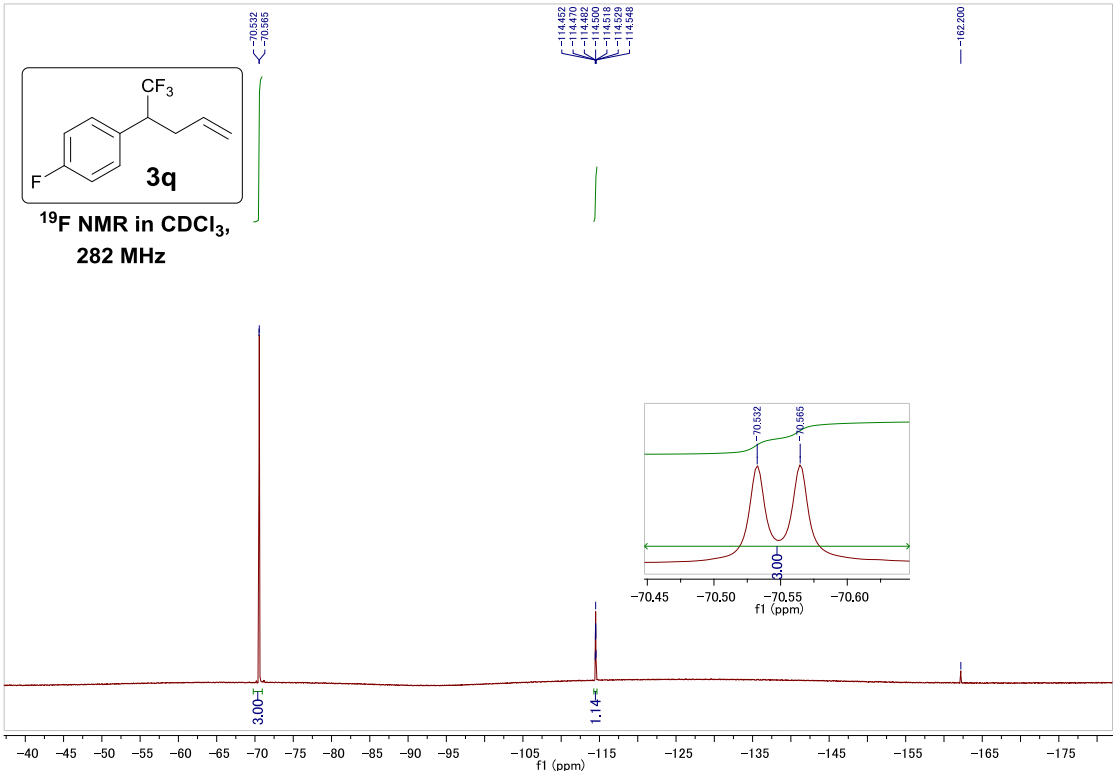

CF3
Cl
3p
1H NMR in CDCl3,
500 MHz
f1 (ppm)

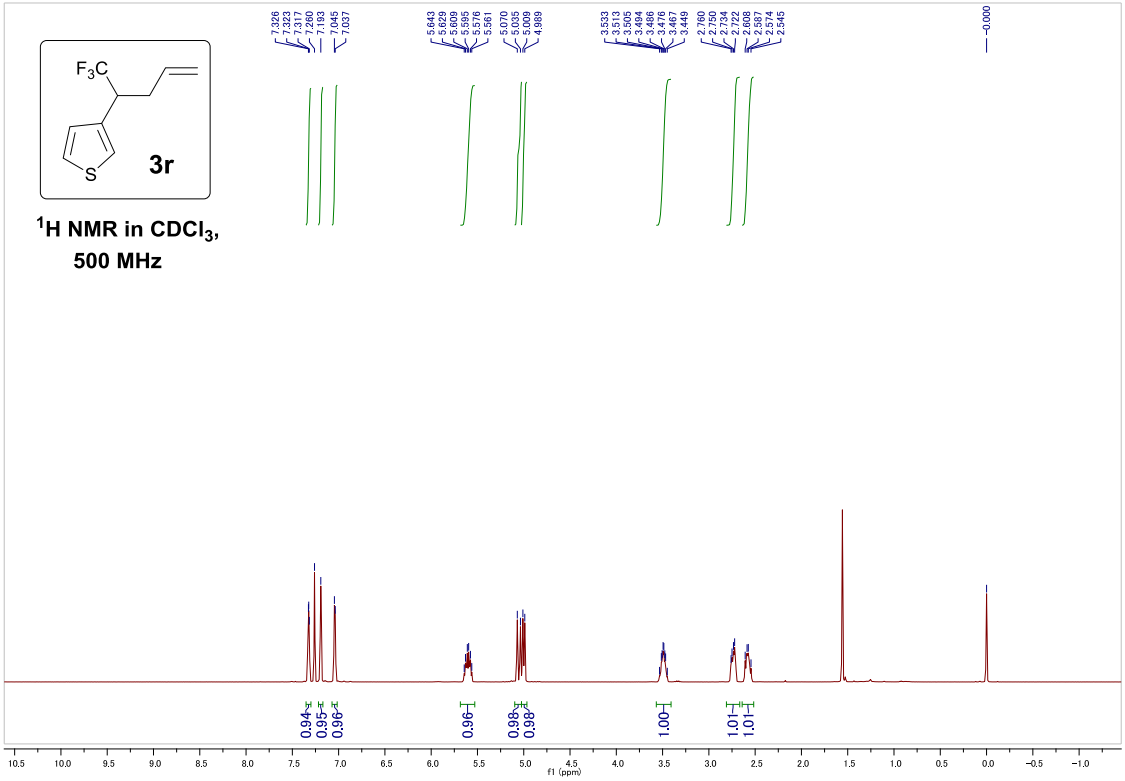

CF3
Cl
3p
13C NMR in CDCl3,
126 MHz
134.321
133.554
130.594
129.892
128.010
127.661
123.205
118.301
77.414
77.160
76.905
49.923
49.713
49.501
49.288
33.221
f1 (ppm)

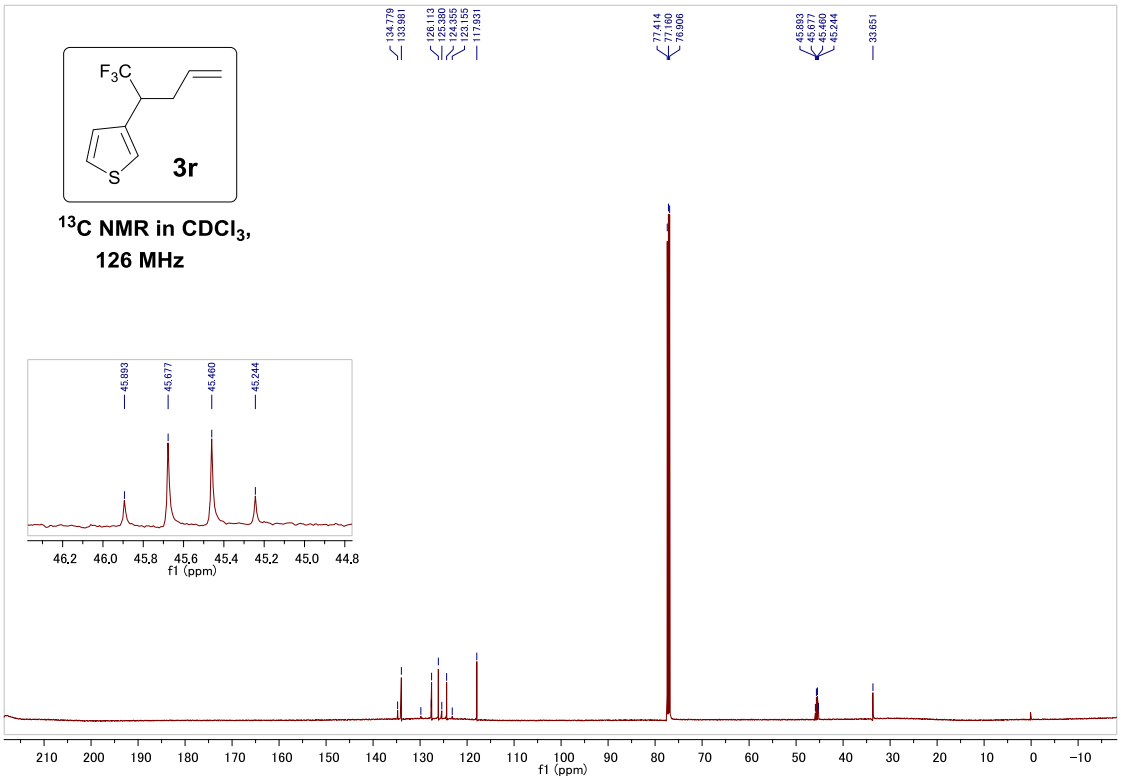

CF3
Cl
3p
19F NMR in CDCl3,
282 MHz
-70.348
-70.380
-162.200
3.00
f1 (ppm)

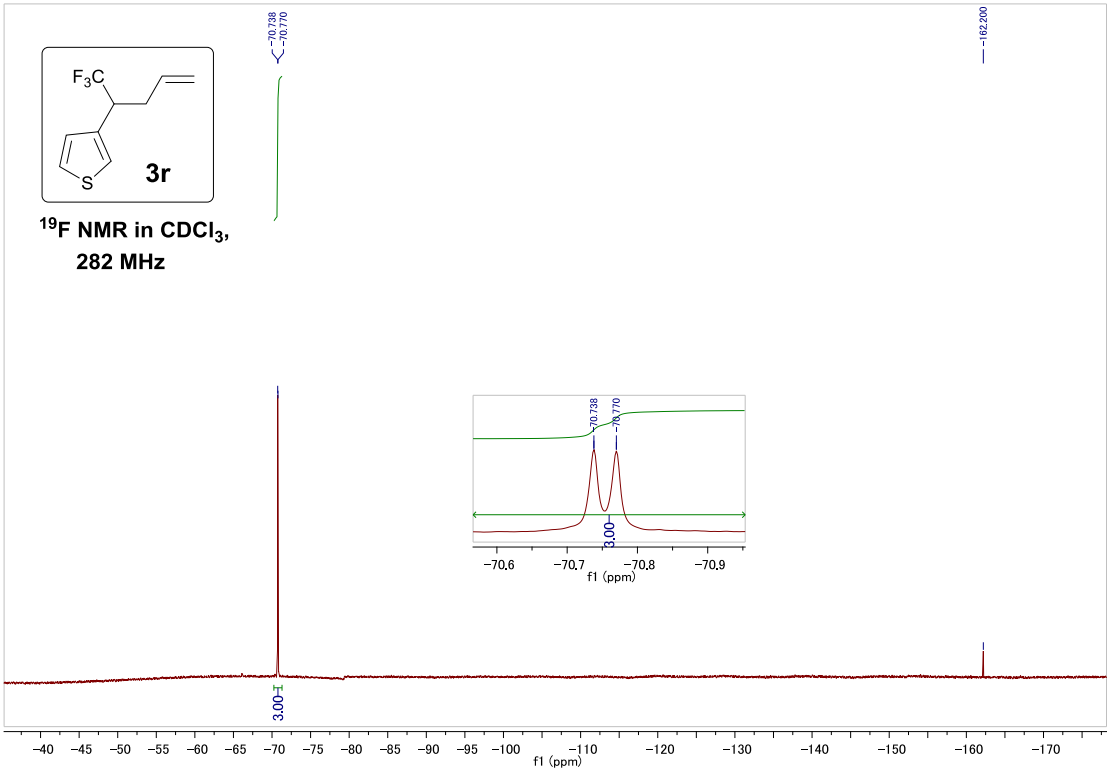

CF3
F
3q
1H NMR in CDCl3,
500 MHz
f1 (ppm)

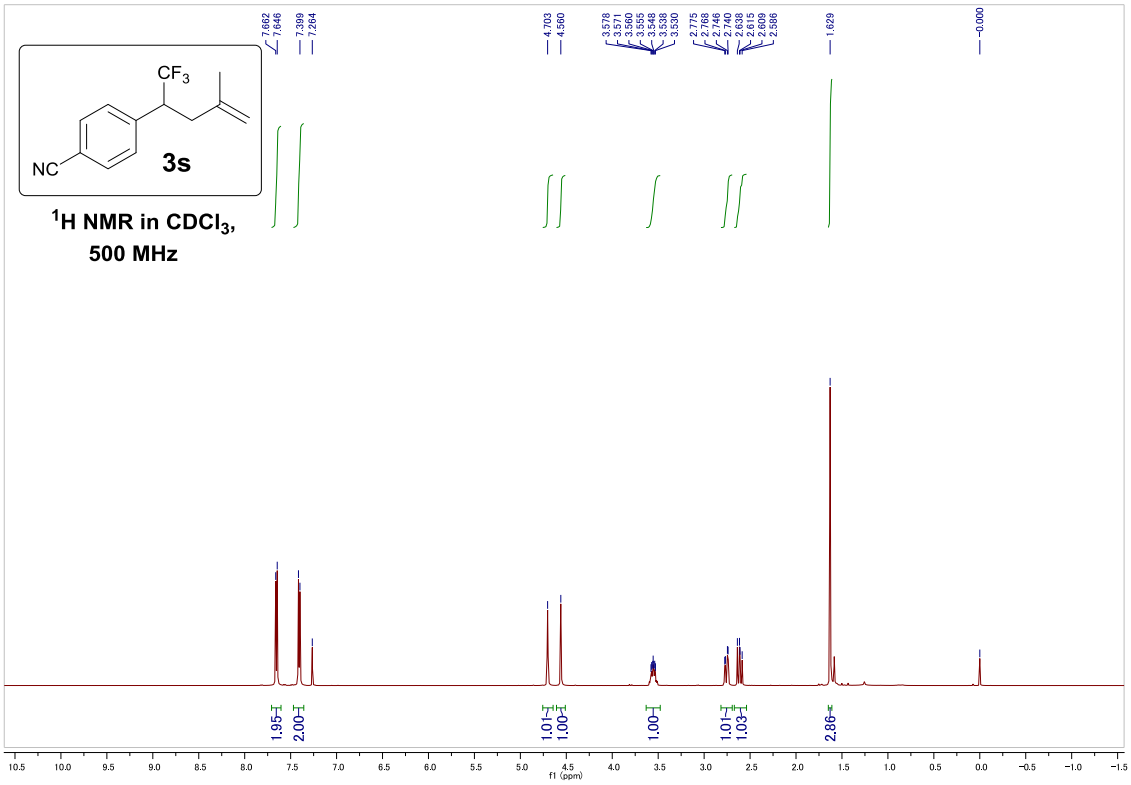

CF3
F
3q
13C NMR in CDCl3,
126 MHz
f1 (ppm)

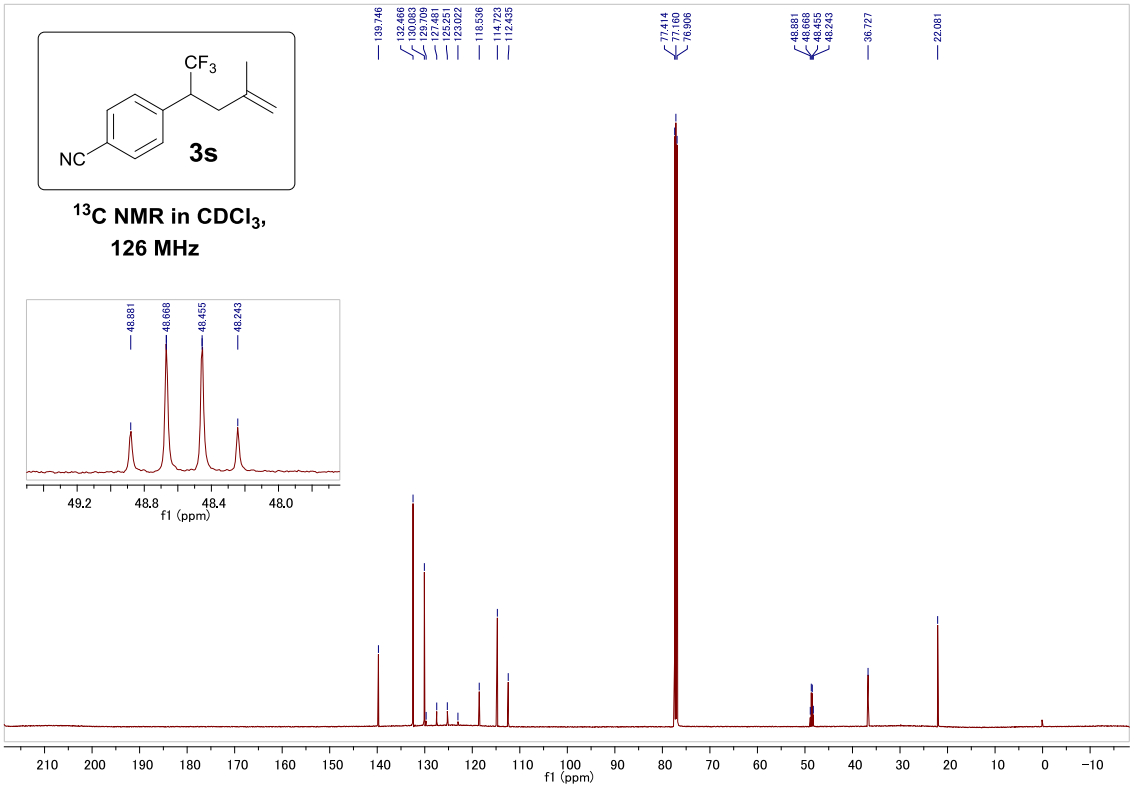

CF3
F
3q
19F NMR in CDCl3,
282 MHz
−70.532
−70.565
−114.452
−114.470
−114.482
−114.500
−114.518
−114.529
−114.548
−162.200
3.00
1.14
f1 (ppm)

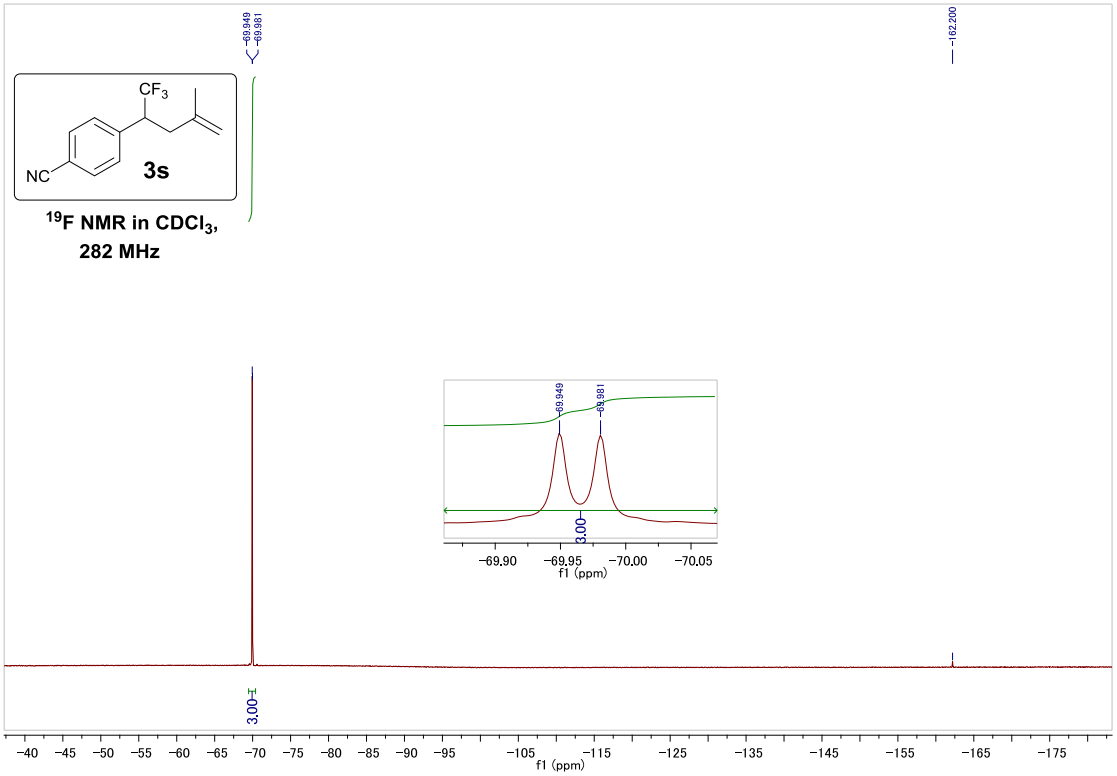

F3C
S
3r
1H NMR in CDCl3,
500 MHz
0.94
0.95
0.96
0.96
0.98
0.98
1.00
1.01
1.01
f1 (ppm)

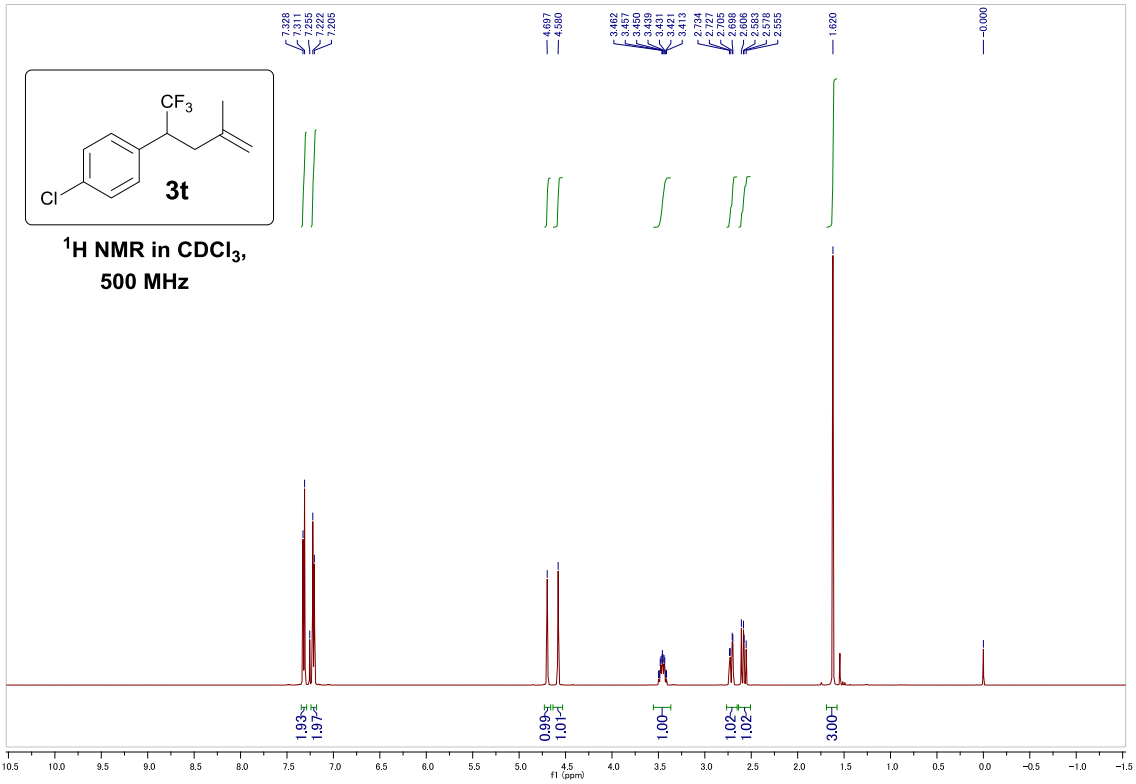

3r
^{13}C NMR in CDCl$_3$,
126 MHz
f1 (ppm)

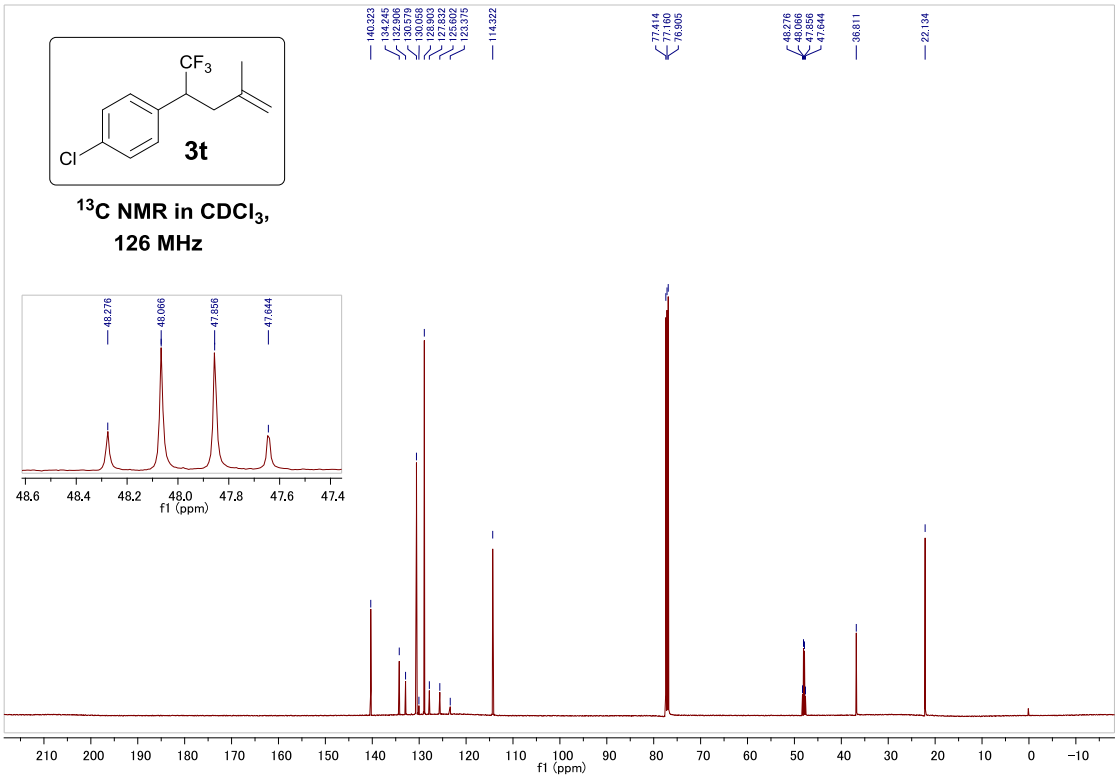

3r
^{19}F NMR in CDCl$_3$,
282 MHz
f1 (ppm)

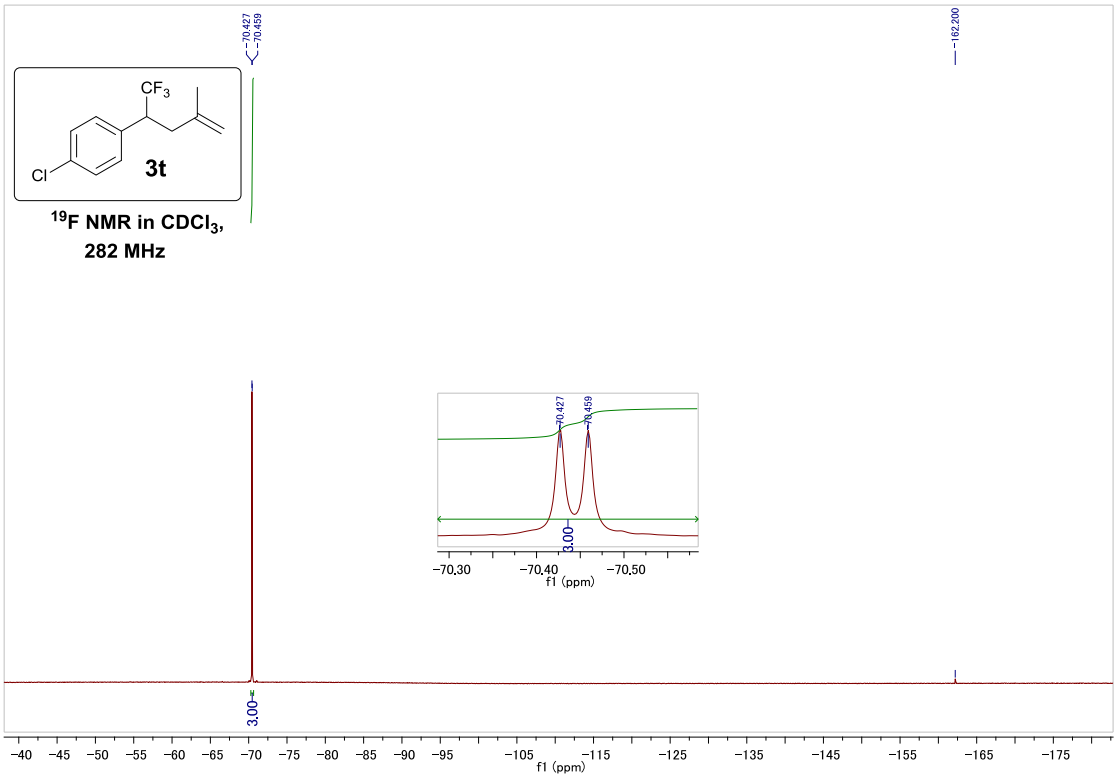

CF3
NC
3s
1H NMR in CDCl3,
500 MHz
f1 (ppm)

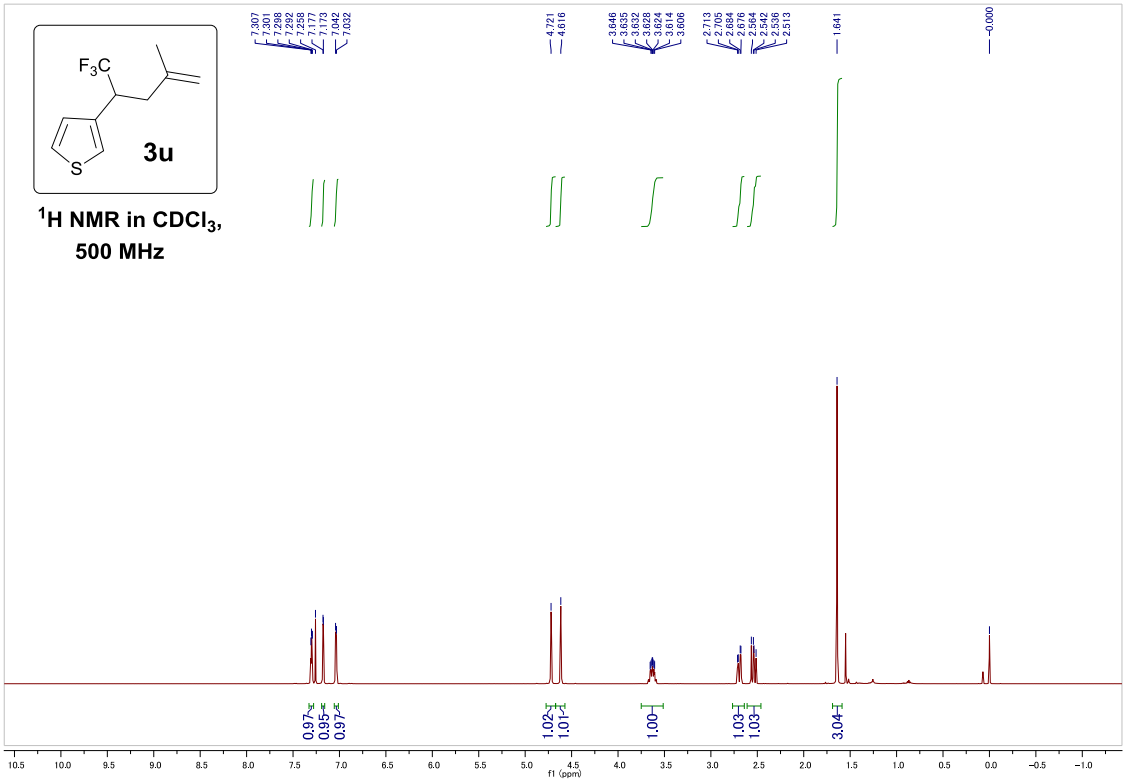

CF3
NC
3s
13C NMR in CDCl3,
126 MHz
f1 (ppm)

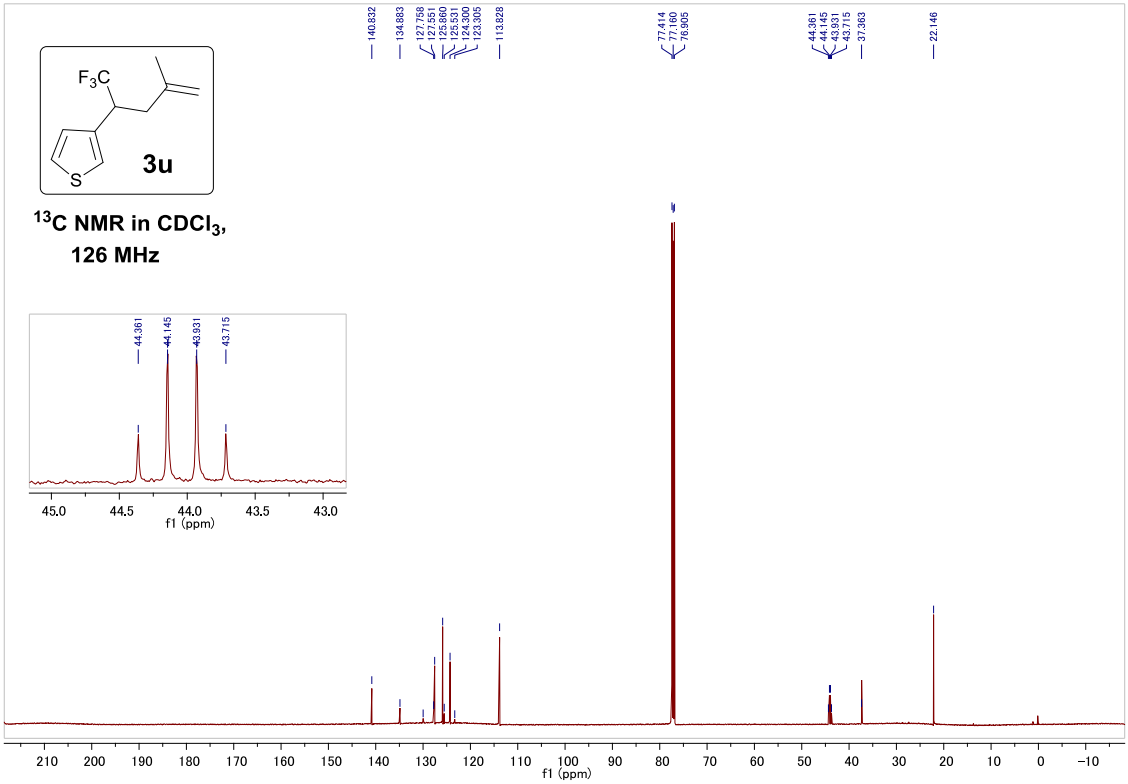

CF3
NC
3s
19F NMR in CDCl3,
282 MHz
-69.949
-69.981
-162.200
3.00
f1 (ppm)

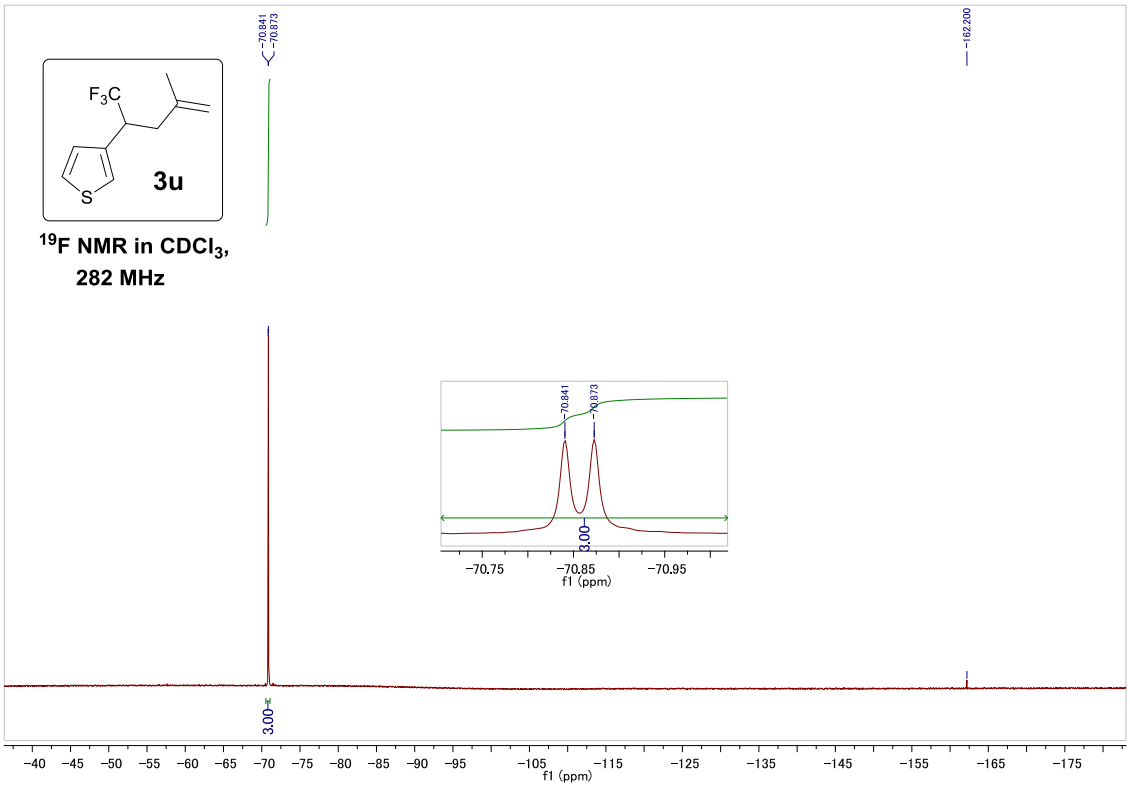

CF3
Cl
3t
1H NMR in CDCl3,
500 MHz
7.328
7.311
7.255
7.222
7.205
4.697
4.580
3.462
3.457
3.450
3.439
3.431
3.421
3.413
2.734
2.727
2.705
2.698
2.606
2.583
2.578
2.555
1.620
0.000
1.93
1.97
0.99
1.01
1.00
1.02
1.02
3.00
f1 (ppm)

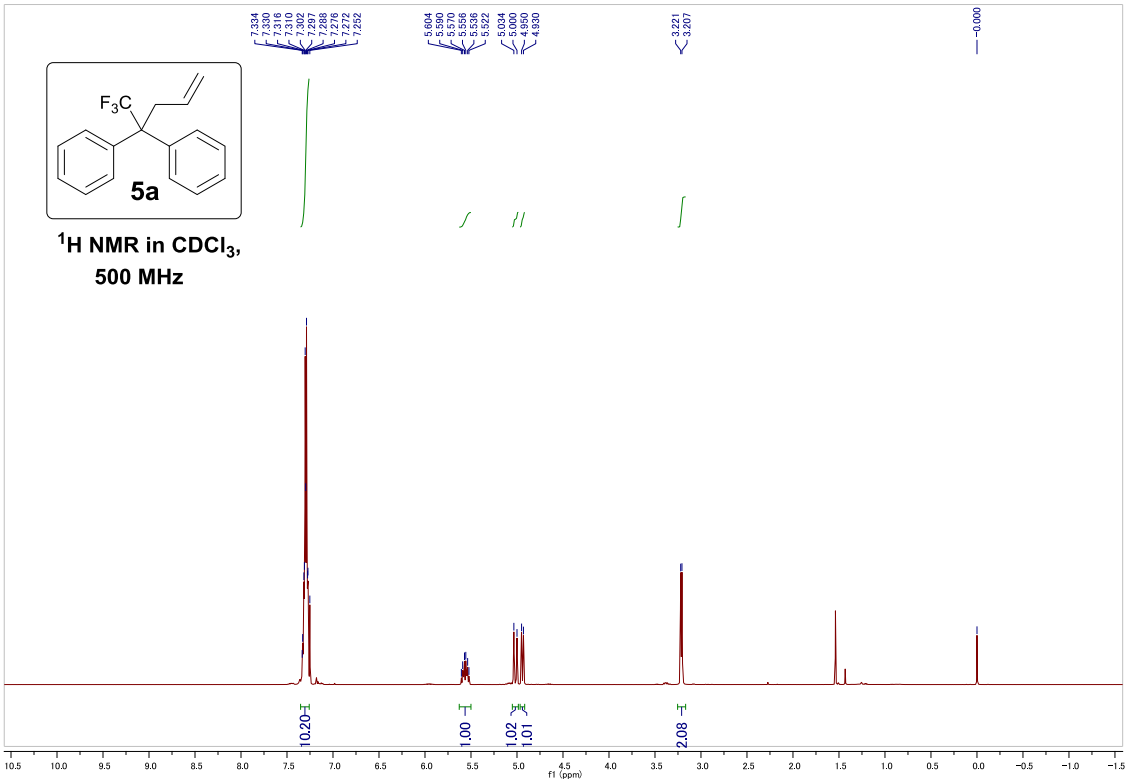

CF3
Cl
3t
13C NMR in CDCl3,
126 MHz
140.323
134.245
132.696
130.579
130.058
128.903
127.832
125.602
123.375
114.322
77.414
77.160
76.905
48.276
48.066
47.856
47.644
36.811
22.134
f1 (ppm)

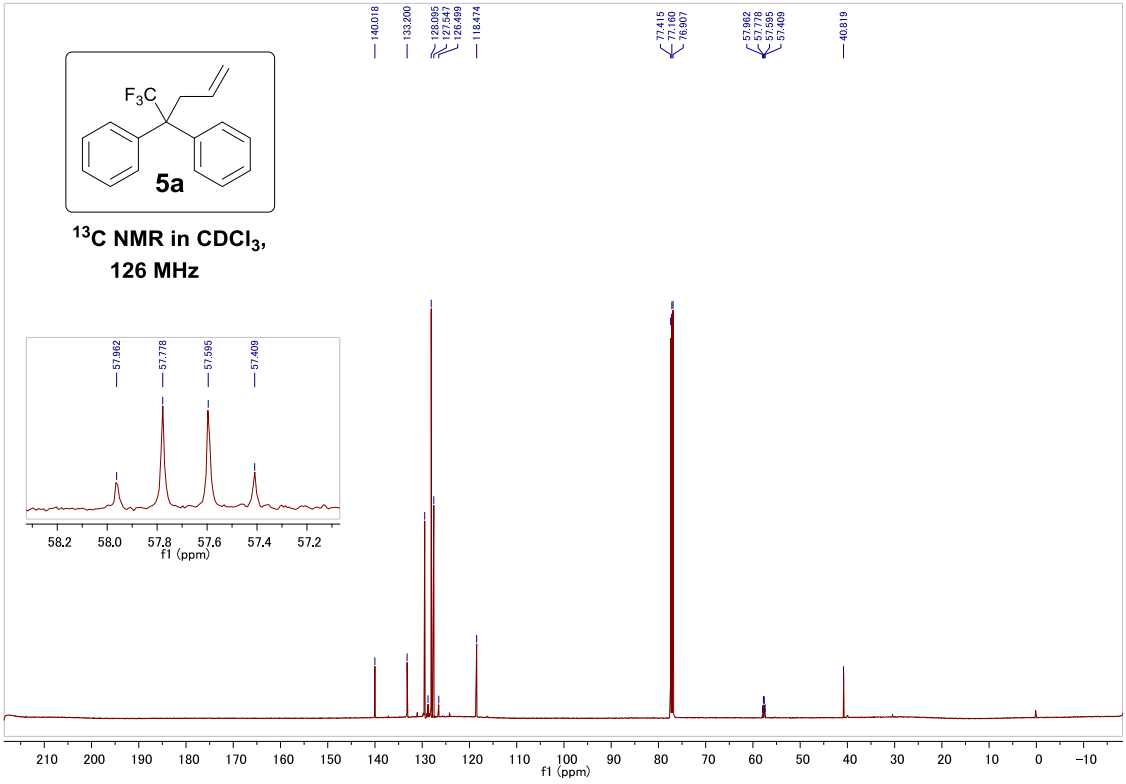

CF3
Cl
3t
19F NMR in CDCl3,
282 MHz
-70.427
-70.459
-162.200
3.00
f1 (ppm)

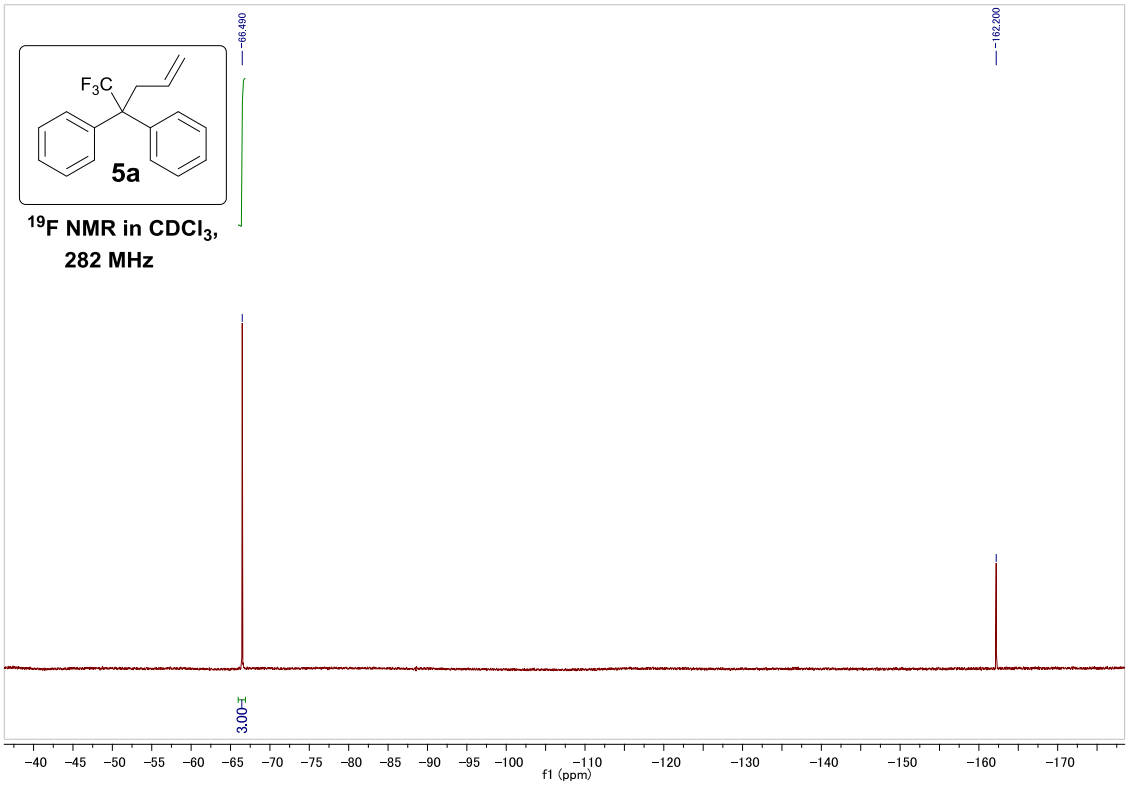

3u
^{1}H NMR in CDCl$_3$,
500 MHz

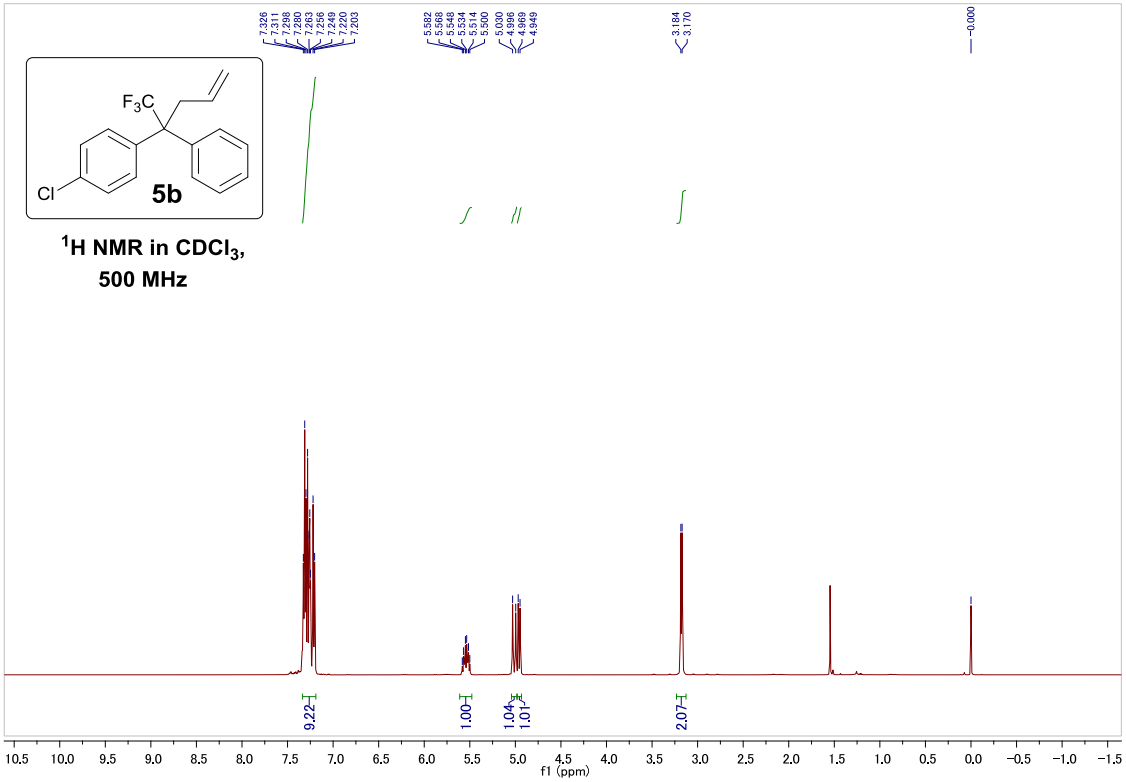

3u
^{13}C NMR in CDCl$_3$,
126 MHz

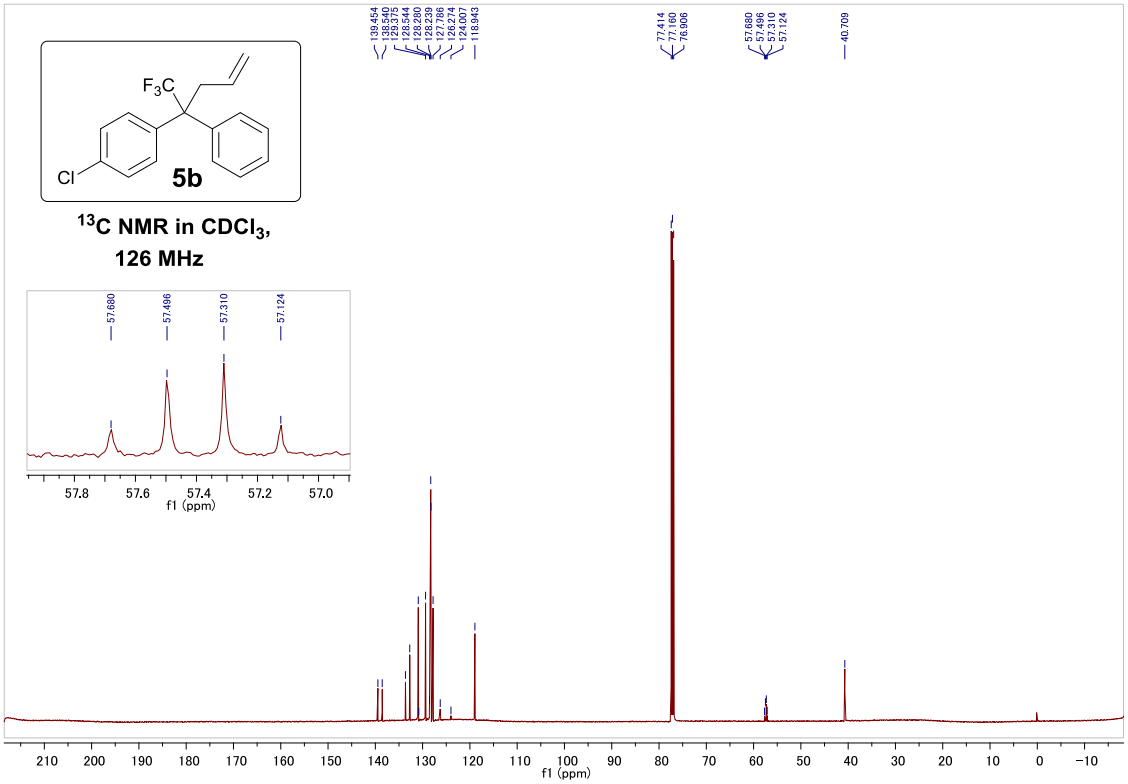

F3C
S
3u
19F NMR in CDCl3,
282 MHz
-70.841
-70.873
-162.200
3.00
-70.75
-70.85
-70.95
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

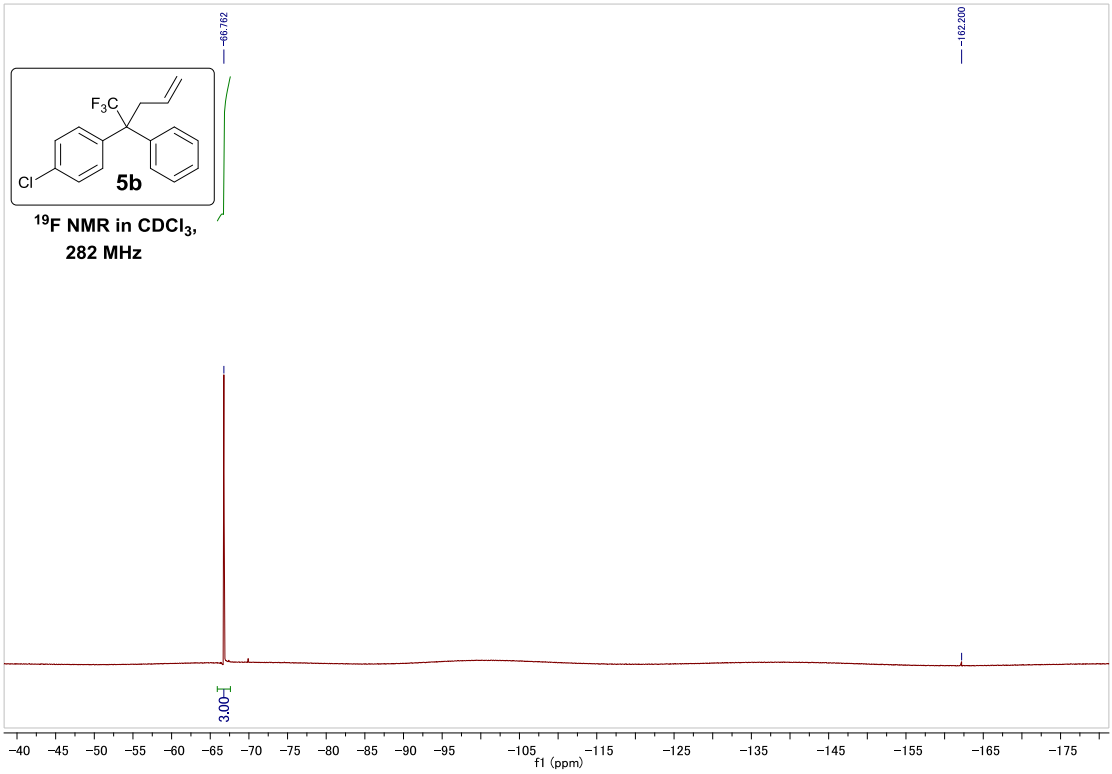

F3C
5a
1H NMR in CDCl3,
500 MHz
7.334
7.330
7.316
7.310
7.302
7.297
7.288
7.276
7.272
7.252
5.604
5.590
5.570
5.556
5.536
5.522
5.034
5.000
4.950
4.930
3.221
3.207
-0.000
10.20
1.00
1.02
1.01
2.08
f1 (ppm)

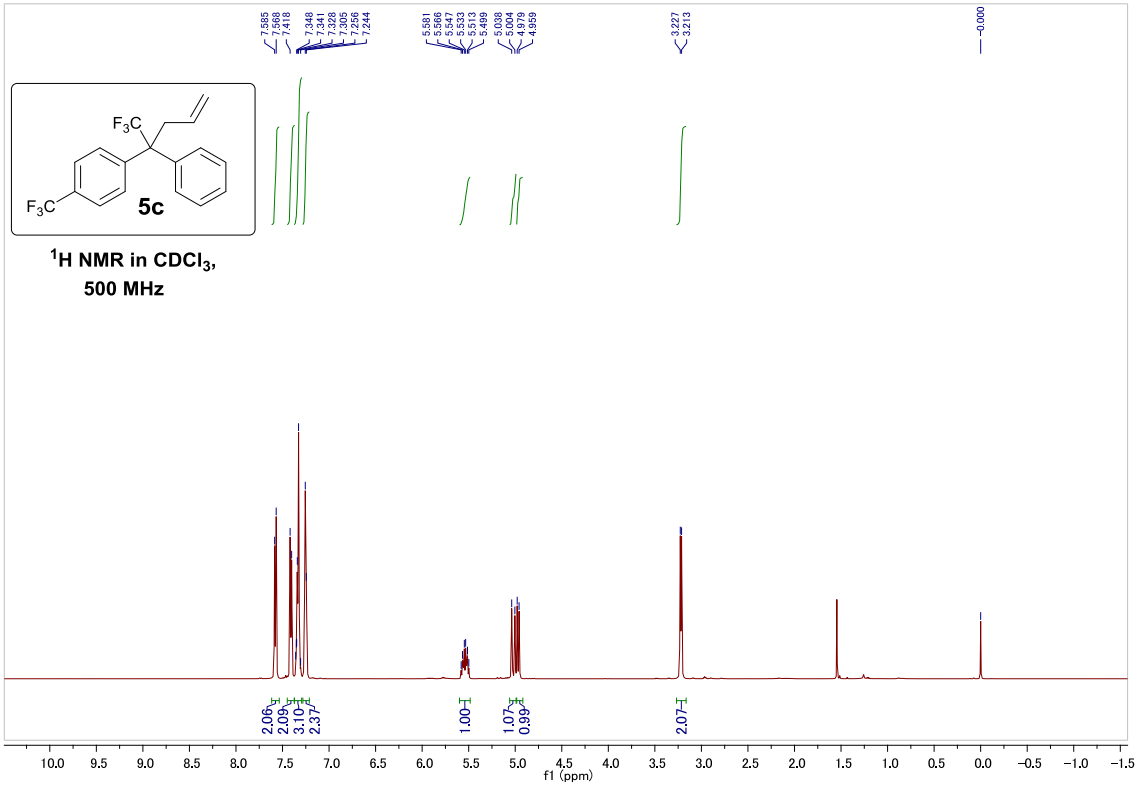

140.018
133.200
128.095
127.547
126.499
118.474
77.415
77.160
76.907
57.962
57.778
57.595
57.409
40.819
F3C
5a
13C NMR in CDCl3,
126 MHz
f1 (ppm)

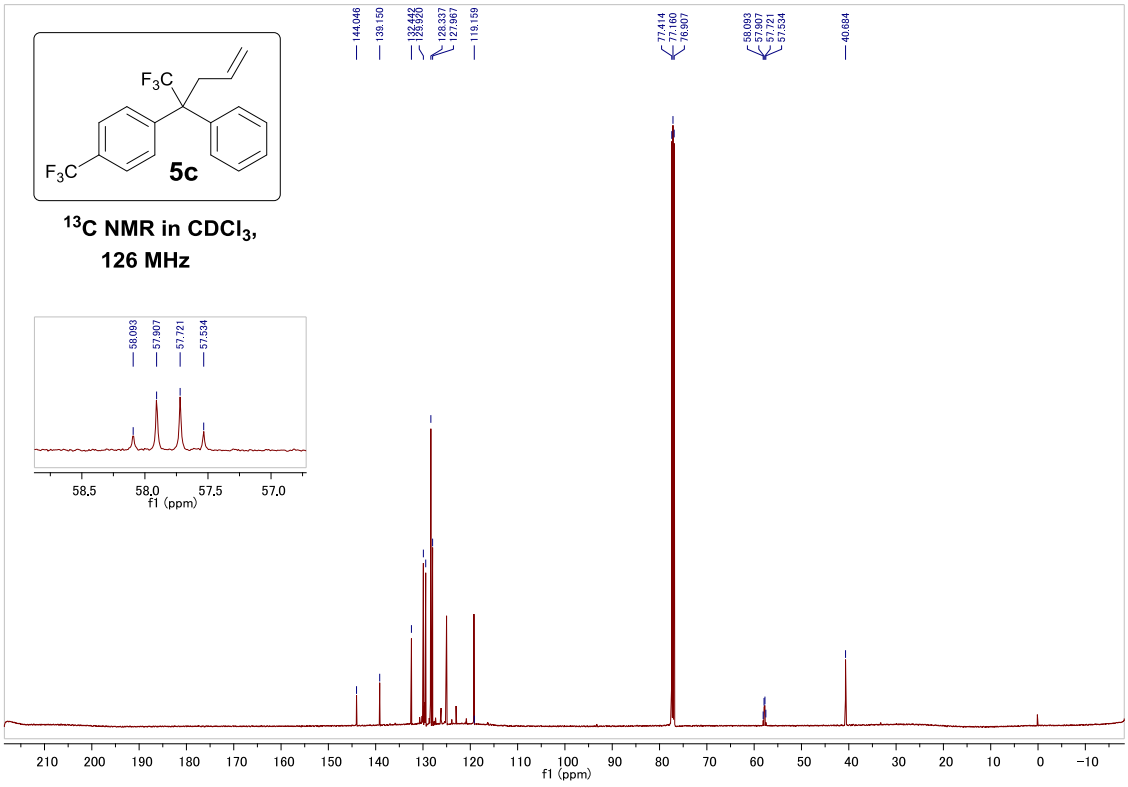

-66.490
-162.200
F3C
5a
19F NMR in CDCl3,
282 MHz
3.00
f1 (ppm)

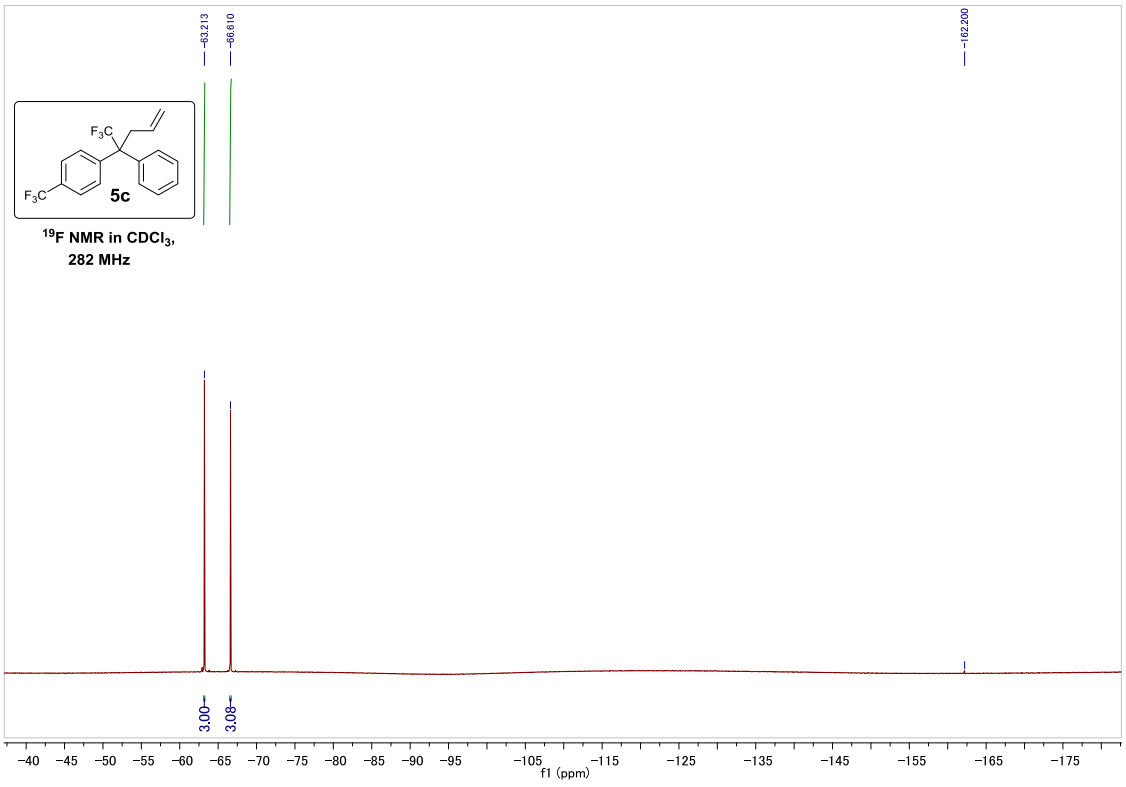

F3C
Cl
5b
1H NMR in CDCl3,
500 MHz
f1 (ppm)

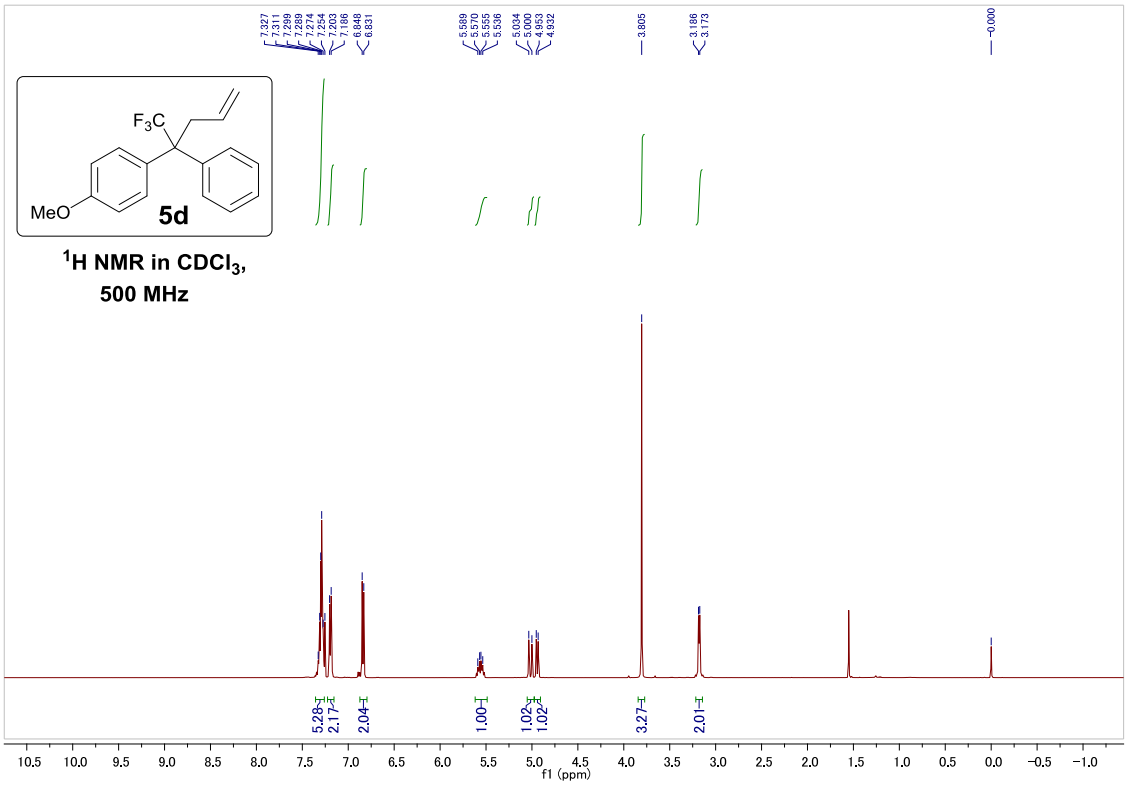

F3C
Cl
5b
13C NMR in CDCl3,
126 MHz
f1 (ppm)

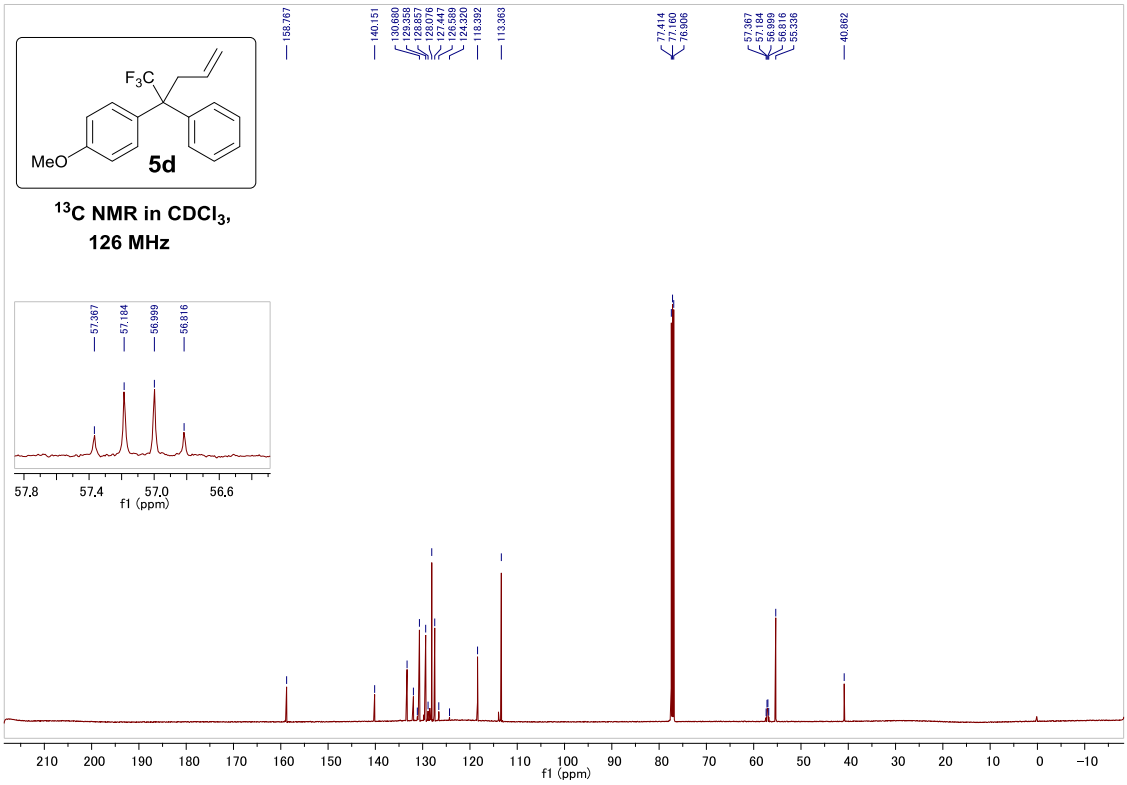

-66.762
-162.200
F3C
Cl
5b
19F NMR in CDCl3,
282 MHz
3.00
f1 (ppm)

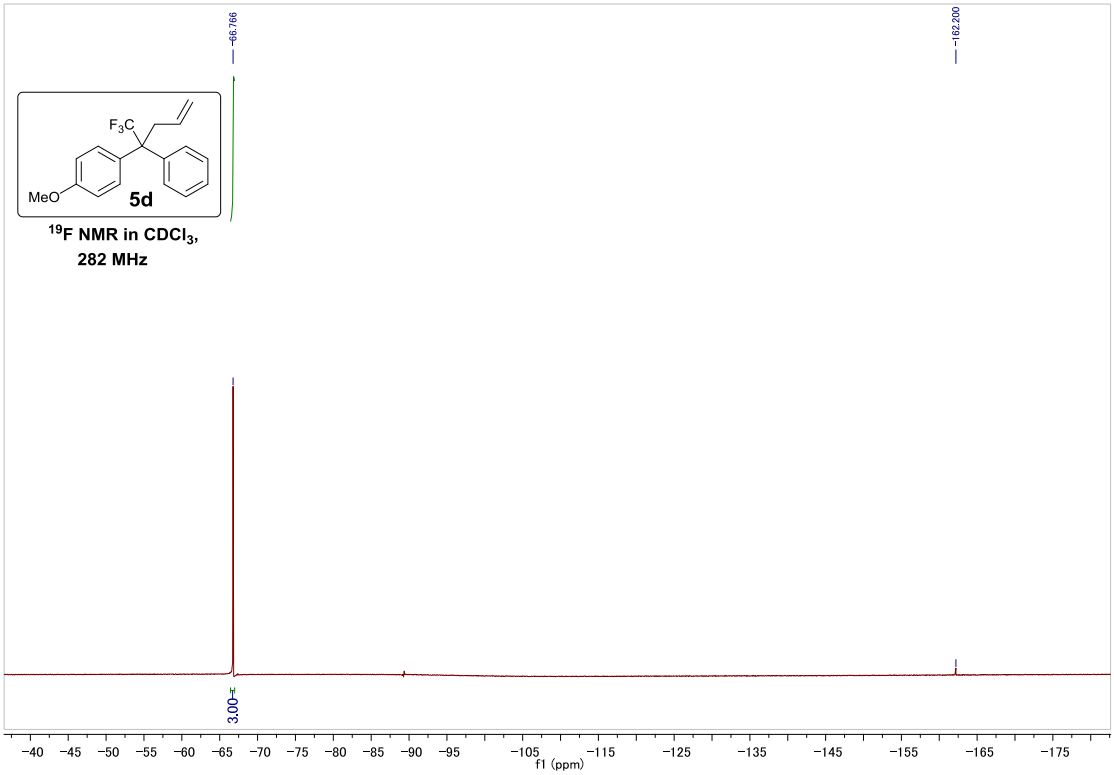

7.585
7.568
7.418
7.348
7.341
7.328
7.305
7.256
7.244
5.581
5.566
5.547
5.533
5.513
5.499
5.038
5.034
4.979
4.959
3.227
3.213
0.000
F3C
F3C
5c
1H NMR in CDCl3,
500 MHz
2.06
2.09
3.10
2.37
1.00
1.07
0.99
2.07
f1 (ppm)


144.046
139.150
132.442
129.926
128.337
127.967
119.159
77.414
77.160
76.907
58.093
57.907
57.721
57.534
40.684
F3C
F3C
5c
13C NMR in CDCl3,
126 MHz
f1 (ppm)

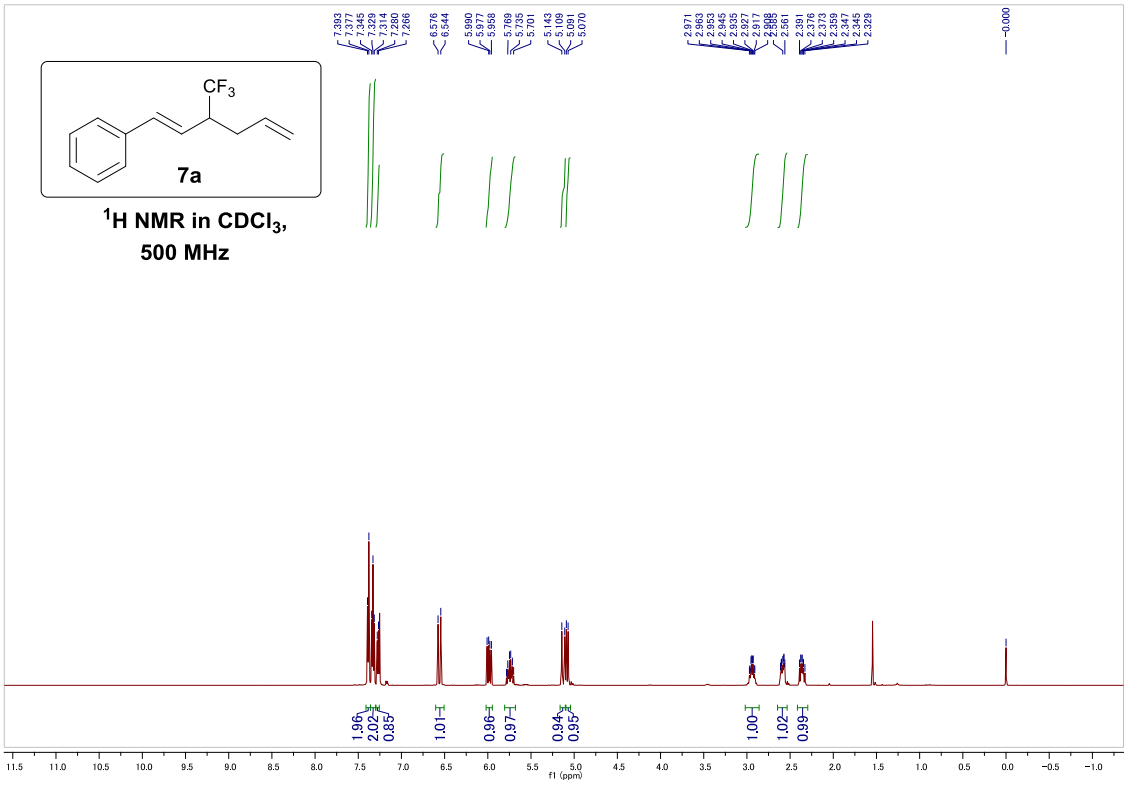

-63.213
-66.610
-162.200
F3C
F3C
5c
19F NMR in CDCl3,
282 MHz
3.00
3.08
f1 (ppm)


F3C
MeO
5d
1H NMR in CDCl3,
500 MHz
f1 (ppm)

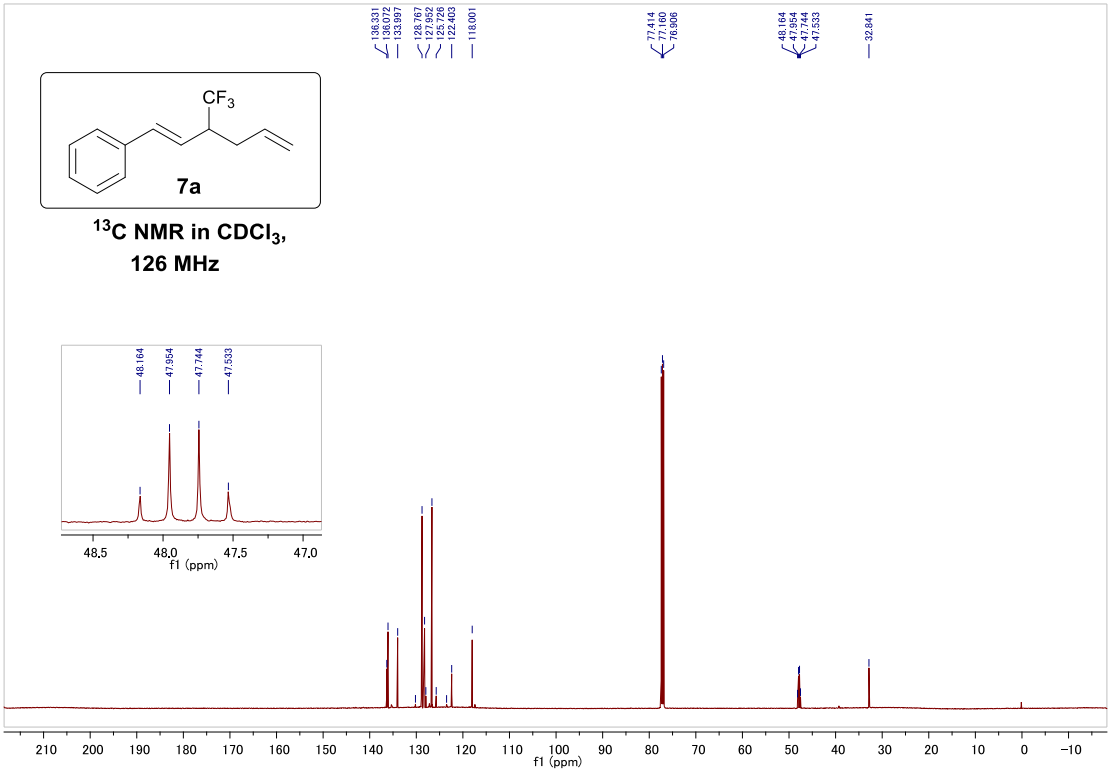

F3C
MeO
5d
13C NMR in CDCl3,
126 MHz
f1 (ppm)

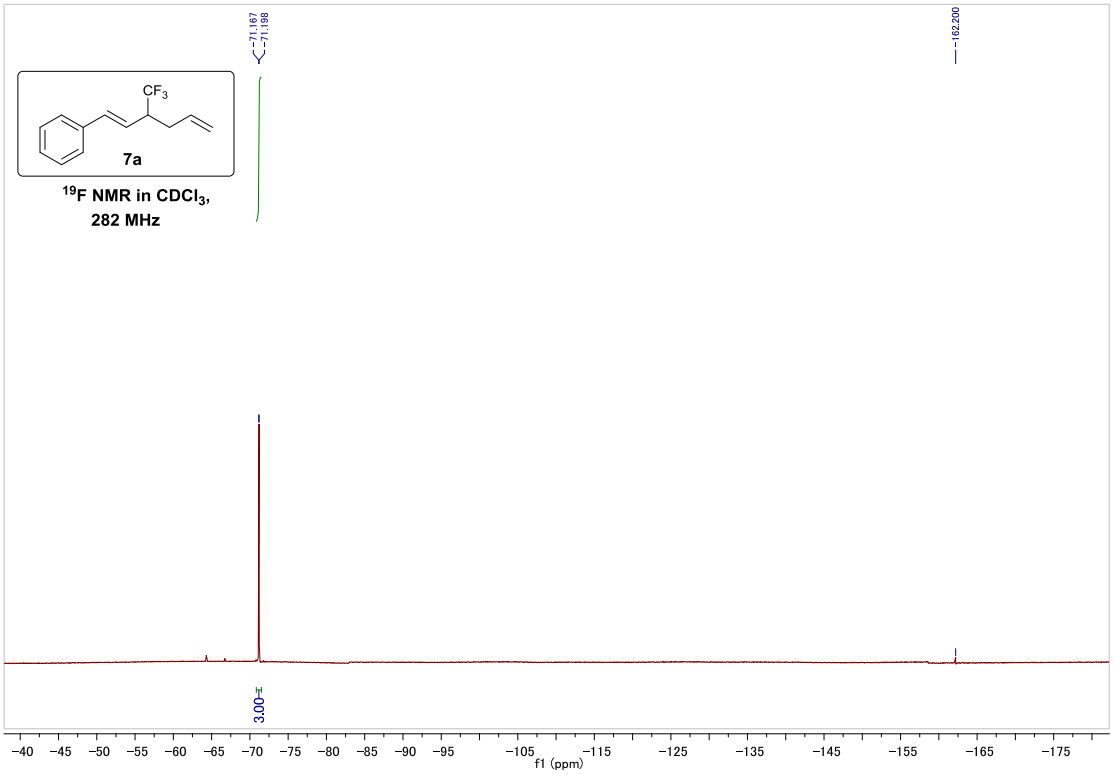


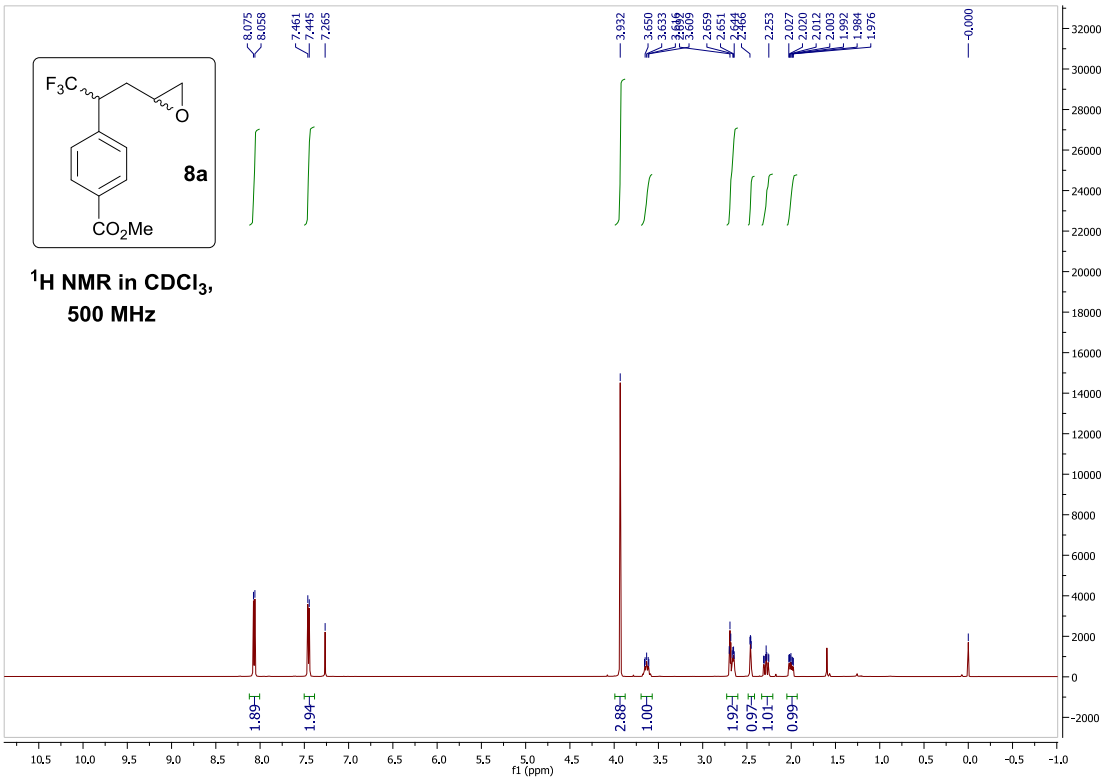
^{19}F NMR in $CDCl_3$, 282 MHz

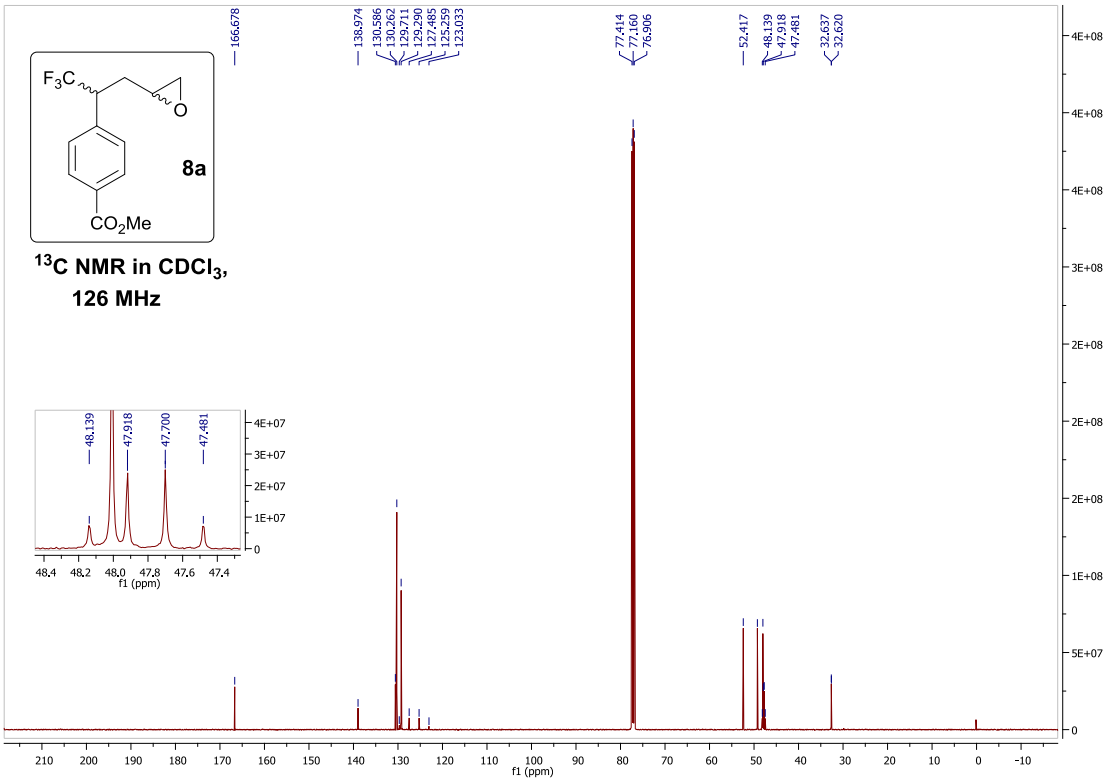


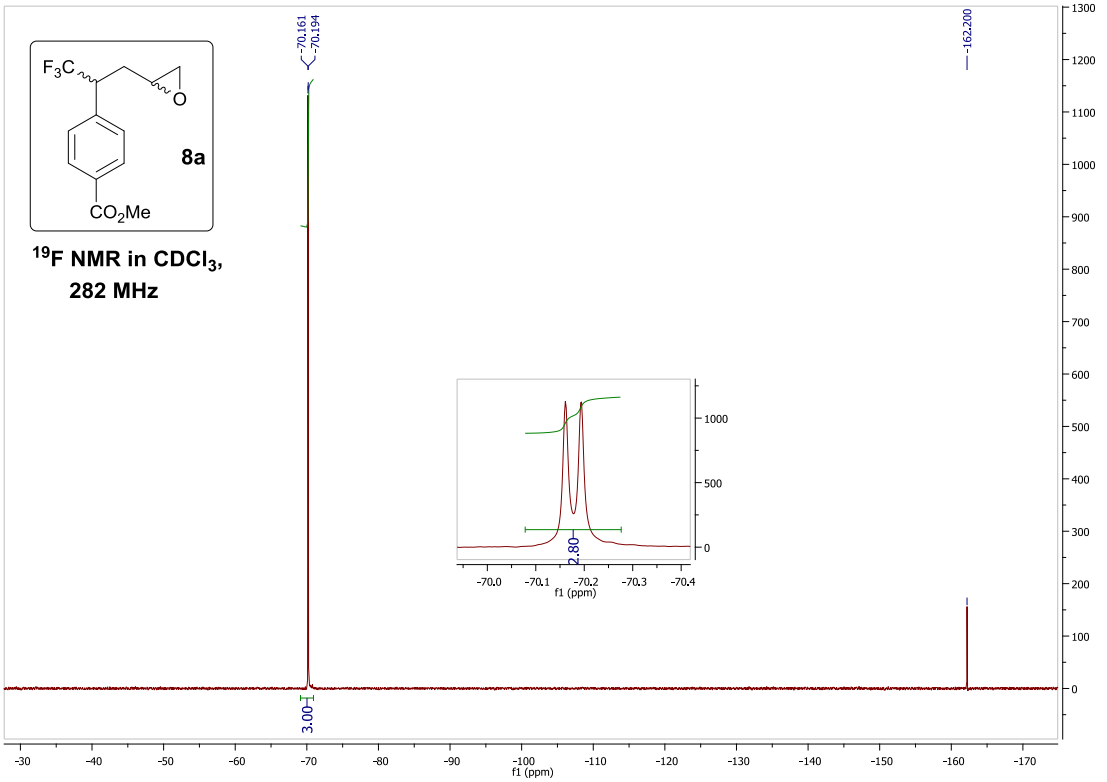
^{1}H NMR in $CDCl_3$, 500 MHz

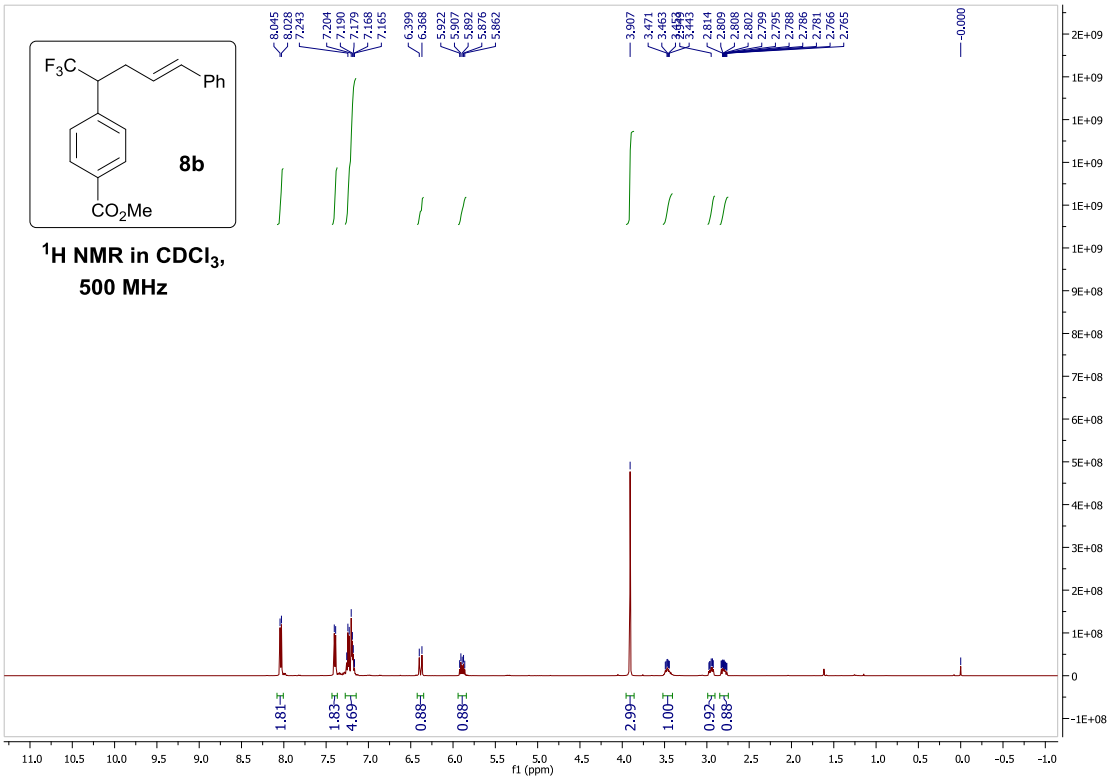

CF3
7a
13C NMR in CDCl3,
126 MHz
f1 (ppm)

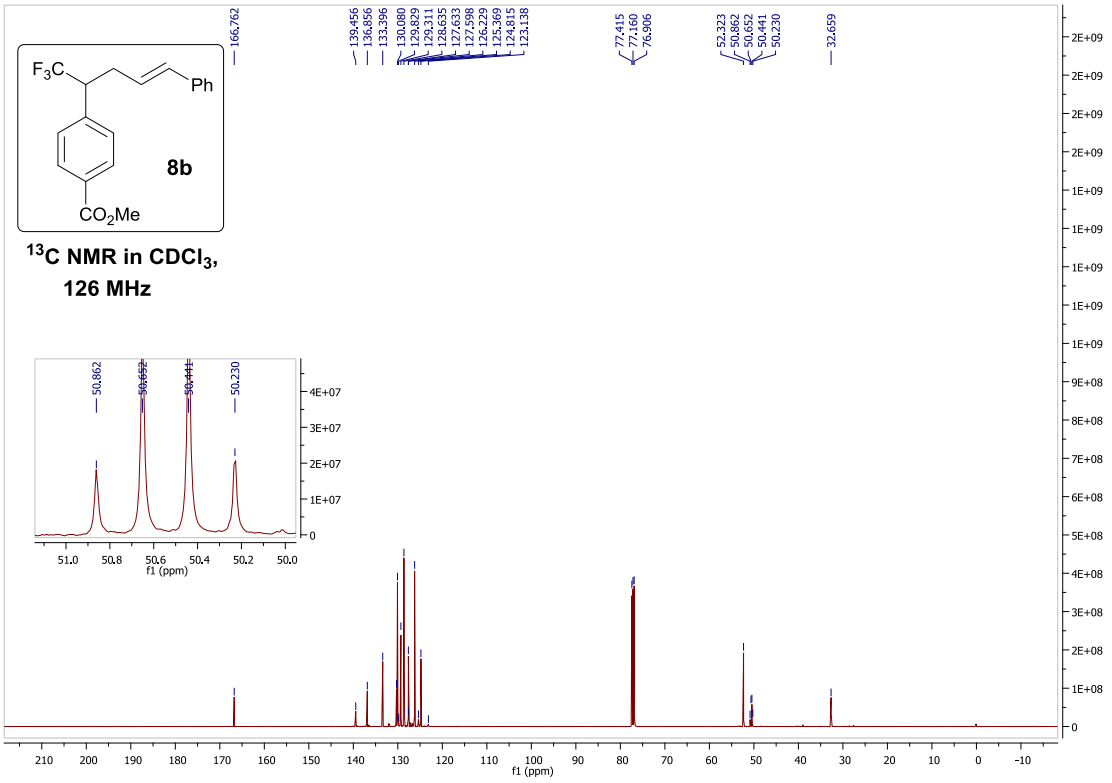

CF3
7a
19F NMR in CDCl3,
282 MHz
3.00
f1 (ppm)

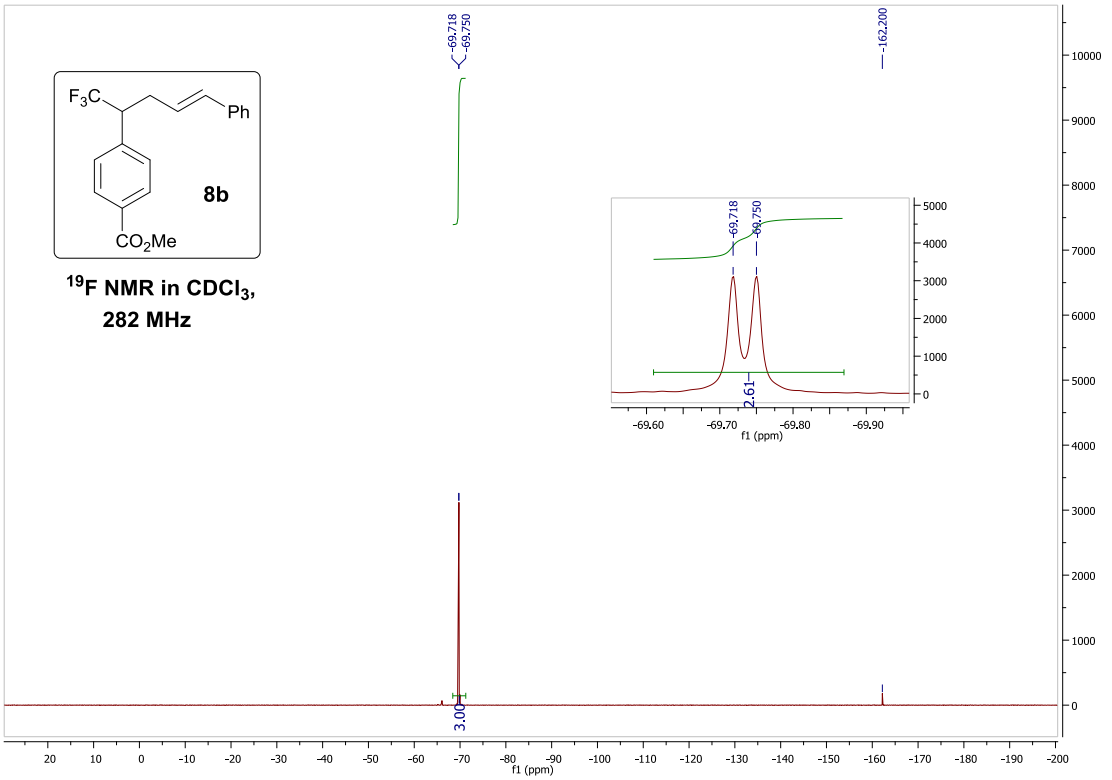

8a
^{1}H NMR in CDCl$_3$,
500 MHz
f1 (ppm)

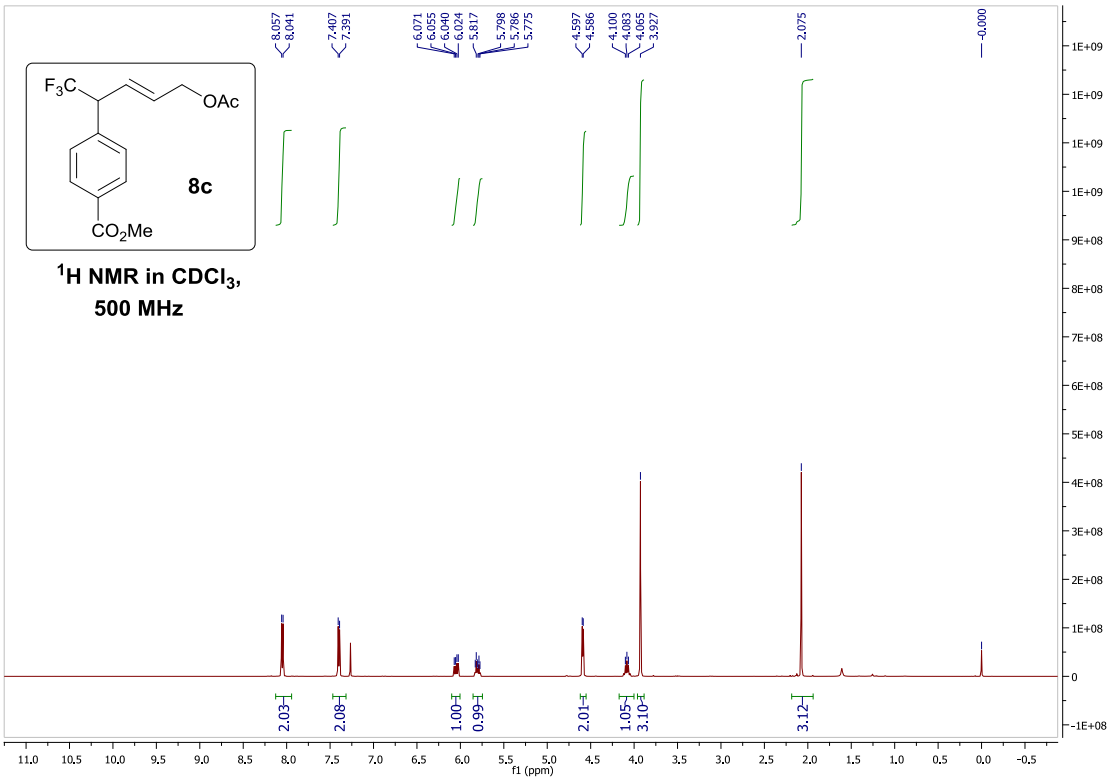

8a
^{13}C NMR in CDCl$_3$,
126 MHz
f1 (ppm)

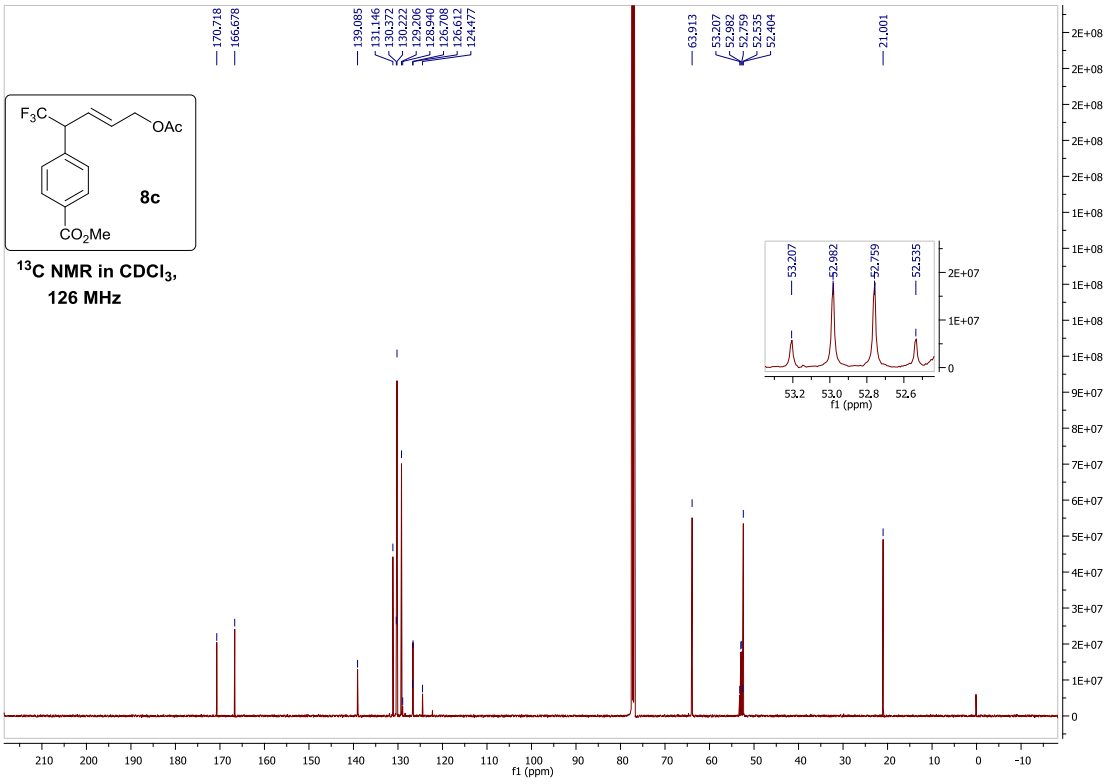

F3C
O
8a
CO2Me
19F NMR in CDCl3,
282 MHz
-70.161
-70.194
-162.200
2.80
3.00
f1 (ppm)

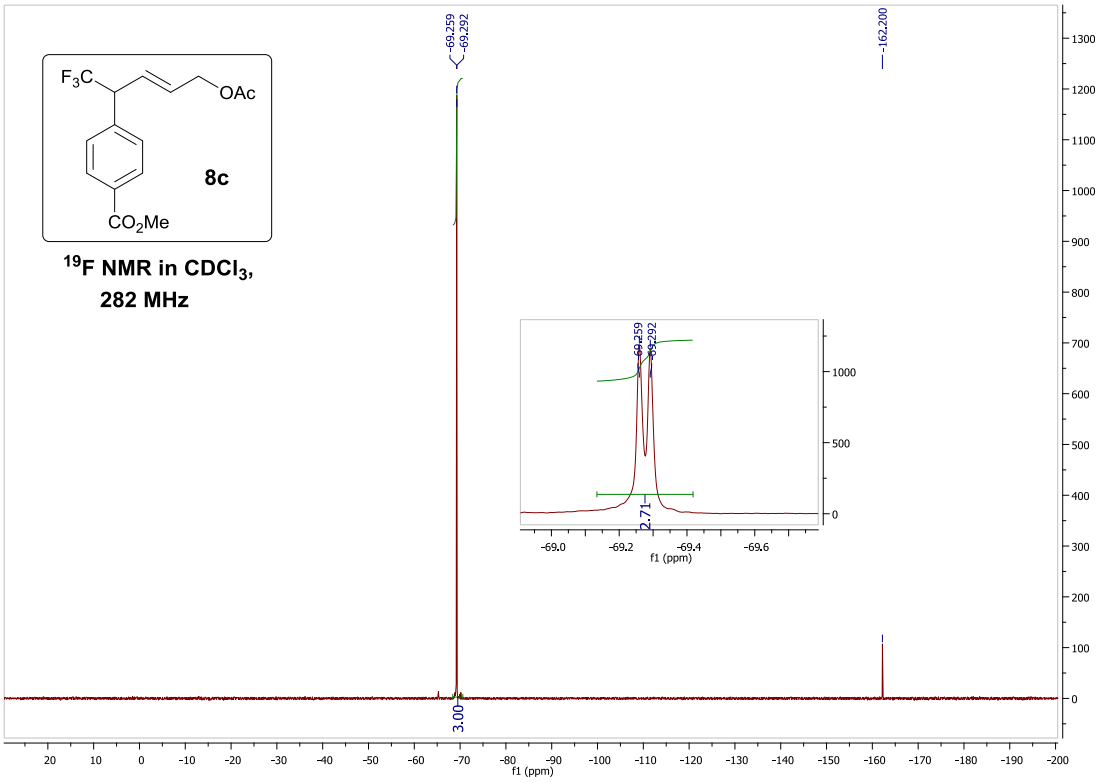

F3C
Ph
8b
CO2Me
1H NMR in CDCl3,
500 MHz
8.045
8.028
7.243
7.204
7.190
7.179
7.168
7.165
6.399
6.368
5.922
5.907
5.892
5.875
5.862
3.907
3.471
3.463
3.443
2.814
2.809
2.808
2.802
2.799
2.795
2.788
2.786
2.781
2.766
2.765
-0.000
1.81
1.83
4.69
0.88
0.88
2.99
1.00
0.92
0.88
f1 (ppm)


166.762
139.456
136.856
133.396
130.080
129.829
129.311
128.635
127.633
127.598
126.229
125.369
124.815
123.138
77.415
77.160
76.906
52.323
50.862
50.652
50.441
50.230
32.659
F3C
Ph
CO2Me
8b
13C NMR in CDCl3,
126 MHz
f1 (ppm)

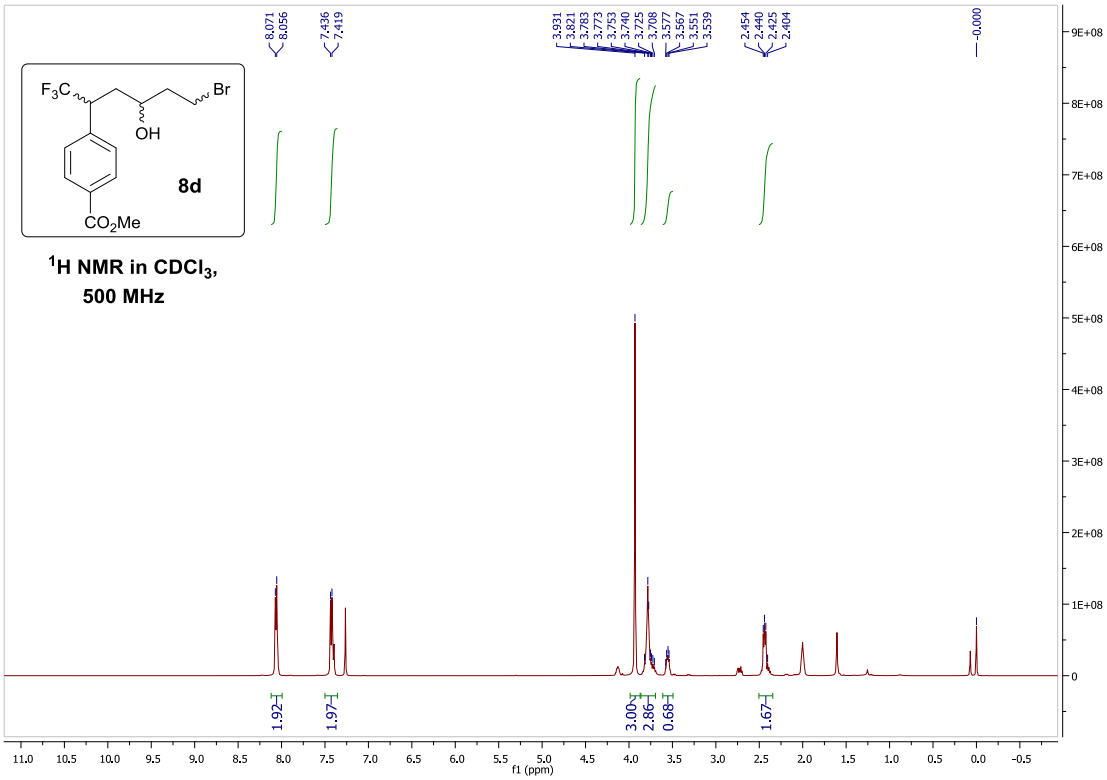

-69.718
-69.750
-162.200
F3C
Ph
CO2Me
8b
19F NMR in CDCl3,
282 MHz
2.61
3.00
f1 (ppm)


F3C
OAc
8c
CO2Me
1H NMR in CDCl3,
500 MHz
8.057
8.041
7.407
7.391
6.071
6.055
6.040
6.024
5.817
5.798
5.786
5.775
4.597
4.586
4.100
4.083
4.065
3.927
2.075
-0.000
2.03
2.08
1.00
0.99
2.01
1.05
3.10
3.12
f1 (ppm)

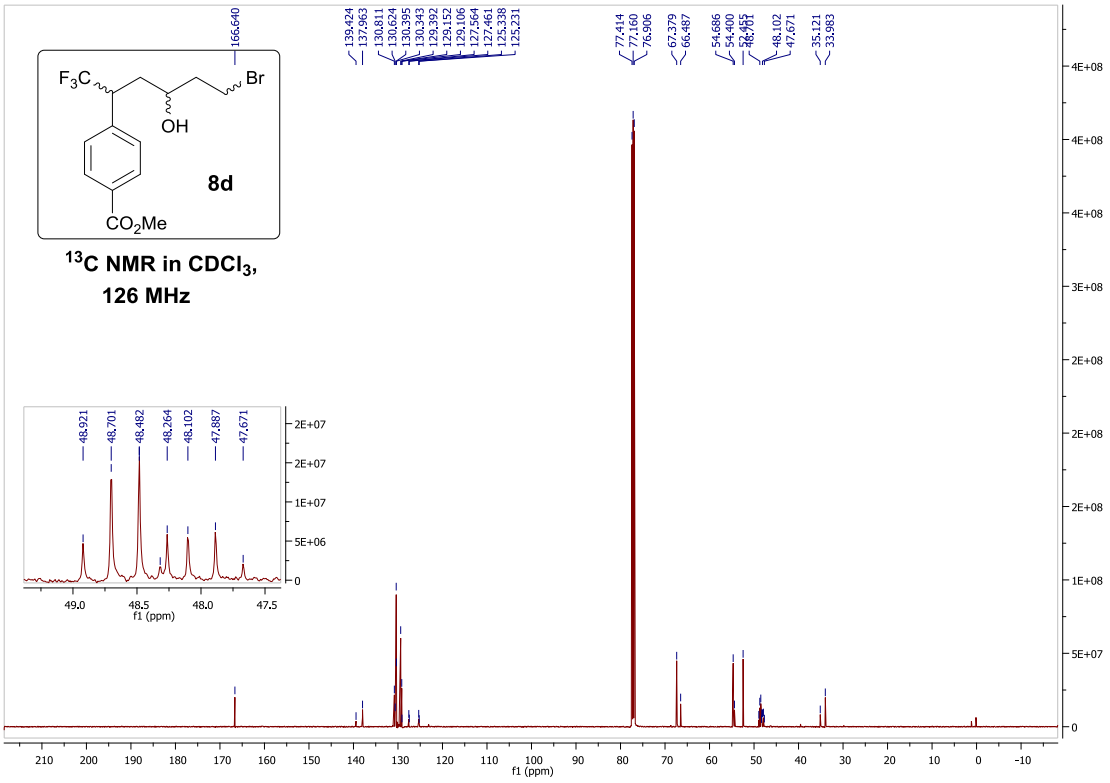

F3C
OAc
8c
CO2Me
13C NMR in CDCl3,
126 MHz
170.718
166.678
139.085
131.146
130.372
130.222
129.206
128.940
126.708
126.612
124.477
63.913
53.207
52.982
52.759
52.535
52.404
21.001
f1 (ppm)

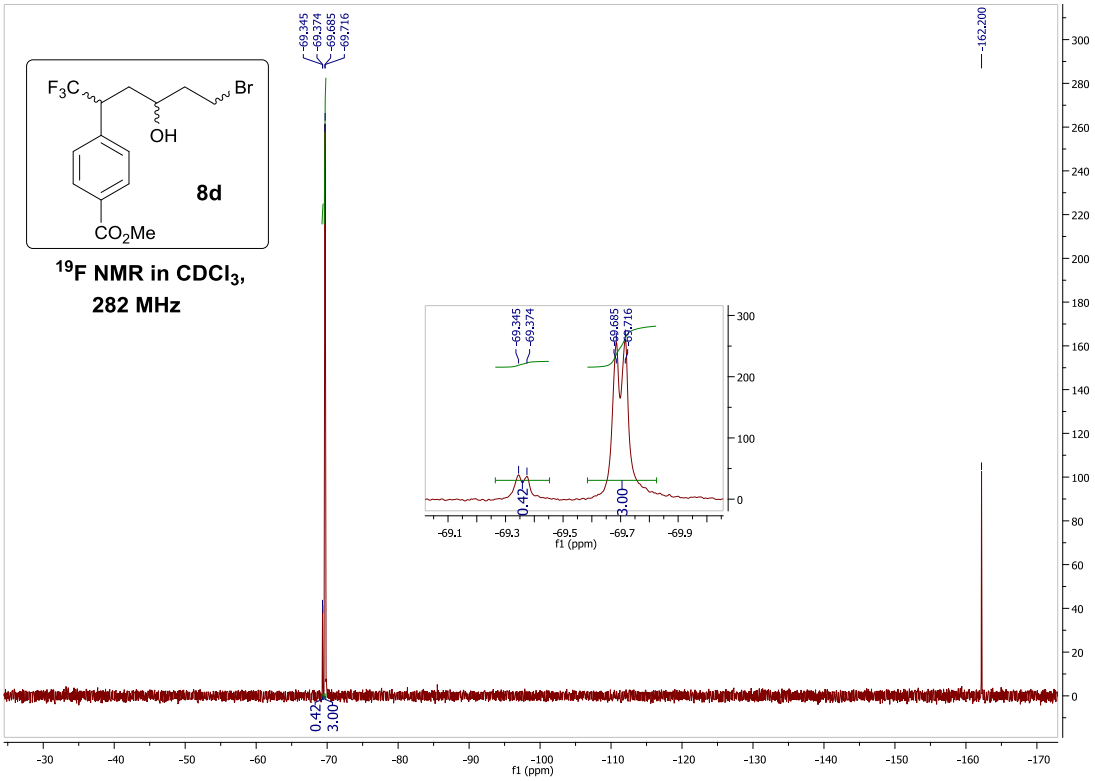


^{19}F NMR in $CDCl_3$, 282 MHz



^{1}H NMR in $CDCl_3$, 500 MHz


166.640
139.424
137.963
130.811
130.624
130.395
130.343
129.392
129.152
129.106
127.564
127.461
125.338
125.231
77.414
77.160
76.906
67.379
66.487
54.686
54.400
48.701
48.102
47.671
35.121
33.983
F3C
Br
OH
8d
CO2Me
13C NMR in CDCl3,
126 MHz
48.921
48.701
48.482
48.264
48.102
47.887
47.671
f1 (ppm)


-69.345
-69.374
-69.685
-69.716
-162.200
F3C
Br
OH
8d
CO2Me
19F NMR in CDCl3,
282 MHz
0.42
3.00
f1 (ppm)