Electronic Supplementary Information

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

Nagender Punna,[a] Kyosuke Harada,[a] and Norio Shibata*[ab]

[a] Department of Nanopharmaceutical Sciences & Department of Life Science and Applied Chemistry,
Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan.

[b] Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, 688 Yingbin Avenue,
321004 Jinhua, China.

nozshiba@nitech.ac.jp

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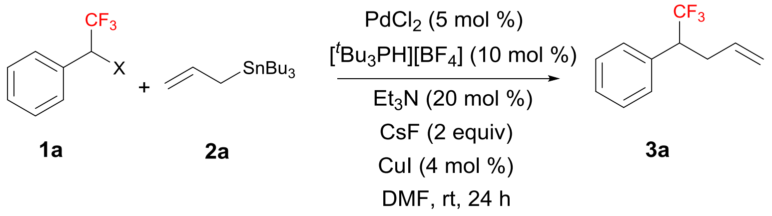
1. General information:

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 ^{1}H 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

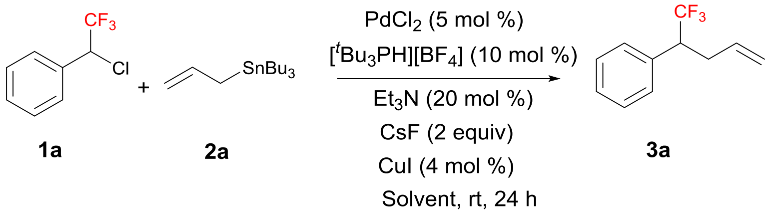
a) Table S1. Screening of pseudohalide and secondary alkyl halide[a]



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 $PdCl_2/[^tBu_3PH][BF_4]/Et_3N$ (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.

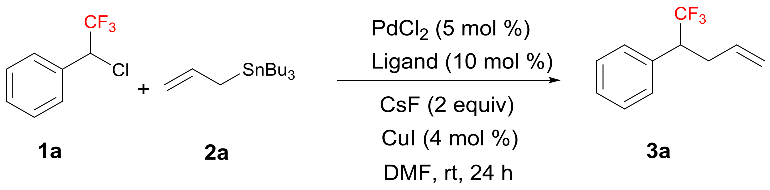
b) Table S2. Screening of solvents[a]



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 $PdCl_2/[^tBu_3PH][BF_4]/Et_3N$ (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.

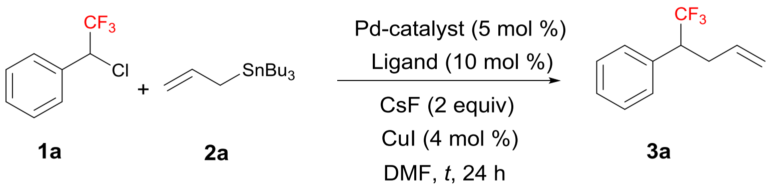
c) Table S3. Ligand screening[a]



Entry	Ligand	Yield[b] [%]
1[c]	[^{t}Bu$_3$PH][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$_2$/[^{t}Bu$_3$PH][BF$_4$]/Et$_3$N (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$_3$N (20 mol %) was used.

d) Table S4. Catalyst screening[a]



Entry	Catalyst	Ligand	*T* (°C)	Yield[b] [%]
1	-	-	75	-
2	Pd(PPh$_3$)$_4$	-	rt	5
3	Pd(OAc)$_2$	[^{t}Bu$_3$PH][BF$_4$]/Et$_3$N	rt	13
4	Pd$_2$(dba)$_3$•CHCl$_3$	[^{t}Bu$_3$PH][BF$_4$] /Et$_3$N	rt	33
5	PdCl$_2$	[^{t}Bu$_3$PH][BF$_4$] /Et$_3$N	rt	31

[a] Experiments were performed with **1** (0.5 mmol), **2** (0.65 mmol) and PdCl$_2$/[^{t}Bu$_3$PH][BF$_4$]/Et$_3$N (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$_3$N (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.

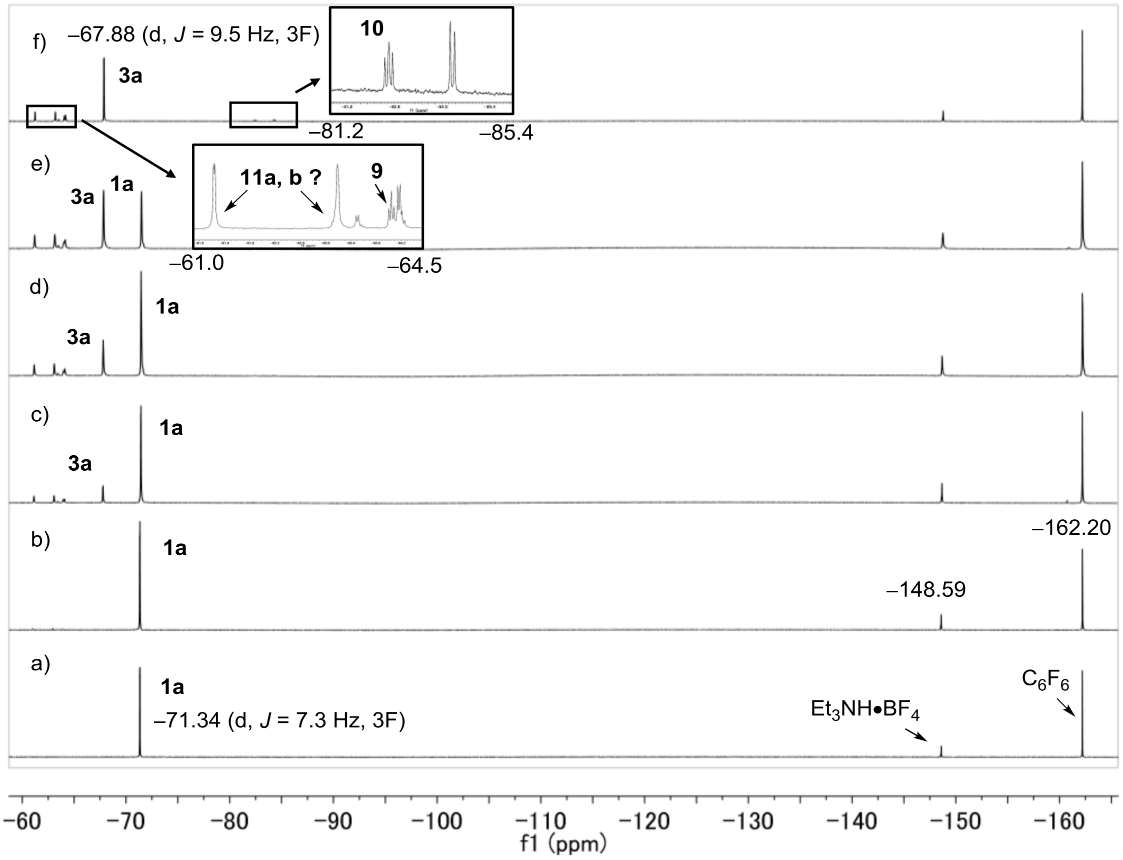


Figure S1a. ^{19}F NMR investigation in between the reaction of **1a** and **2a** in DMF-d_7. a) **1a** b) $PdCl_2$/[$^tBu_3PH$][BF_4]/Et_3N was added, at rt for 2h. c) **2a** was added, at rt for 2h. d) at rt for 4h. e) at 75 °C for 10 min. f) at 75 °C for 40 min.

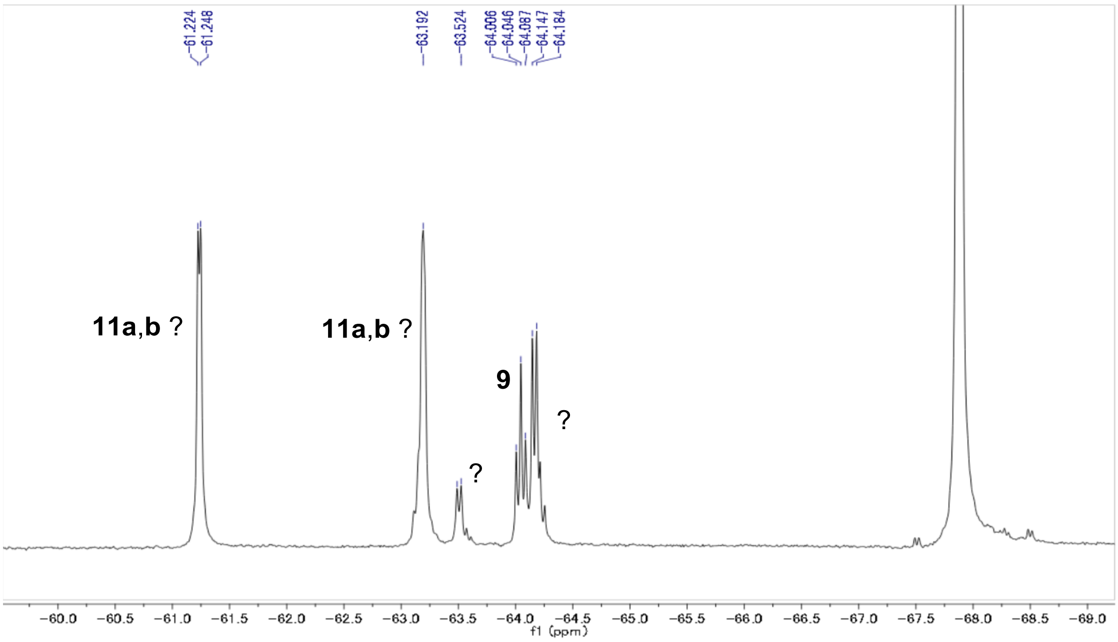


Figure S1b. Expanded ^{19}F NMR Spectra.

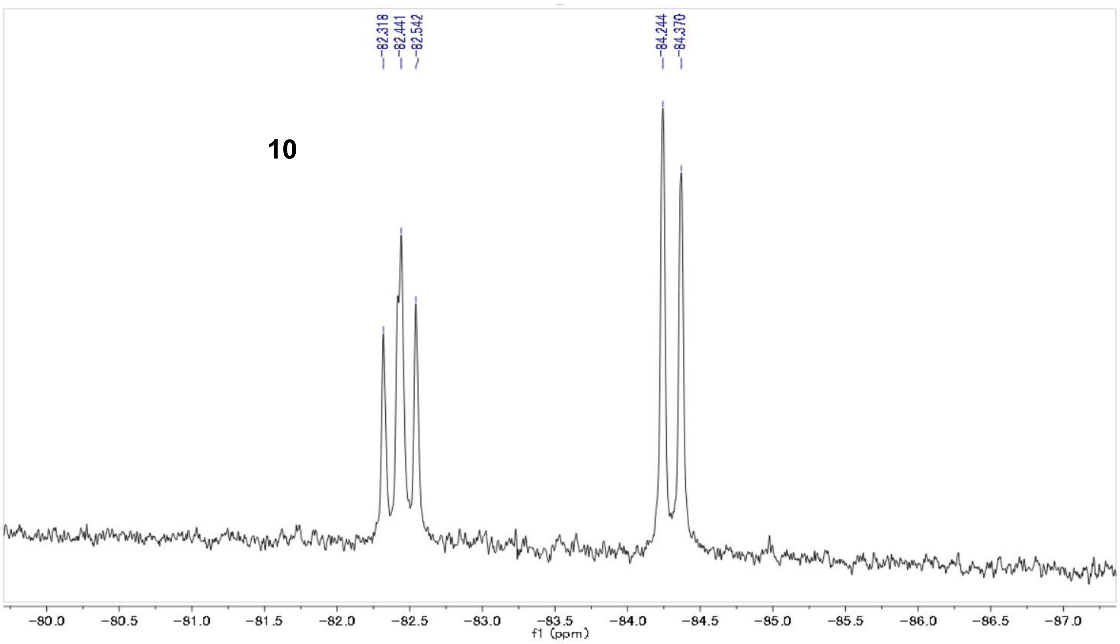
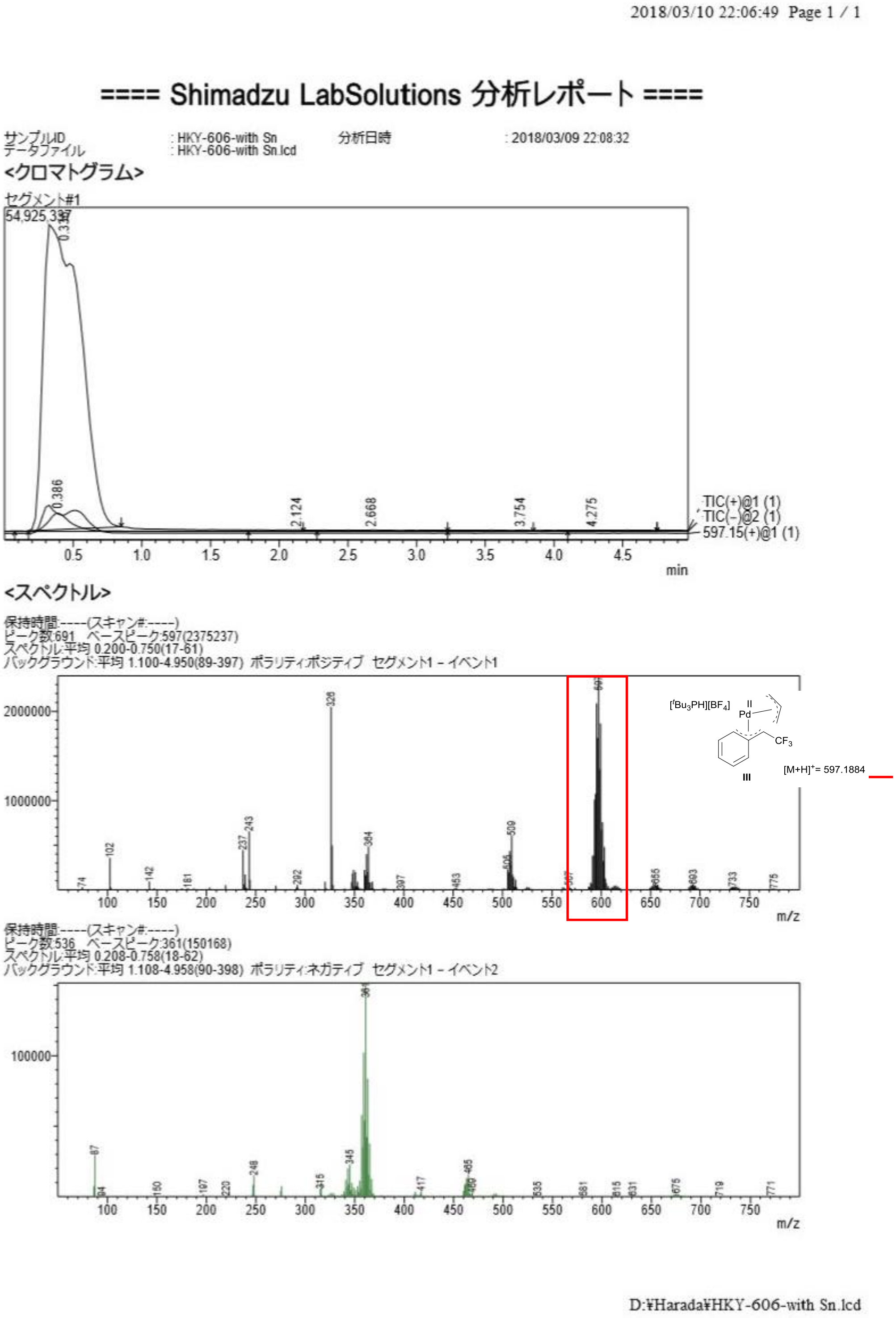


Figure S1c. Expanded ^{19}F NMR Spectra.

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)



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==== Shimadzu LabSolutions 分析レポート ====

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データファイル : HKY-606-with Sn.lcd

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セグメント#1

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D:¥Harada¥HKY-606-with Sn.lcd

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

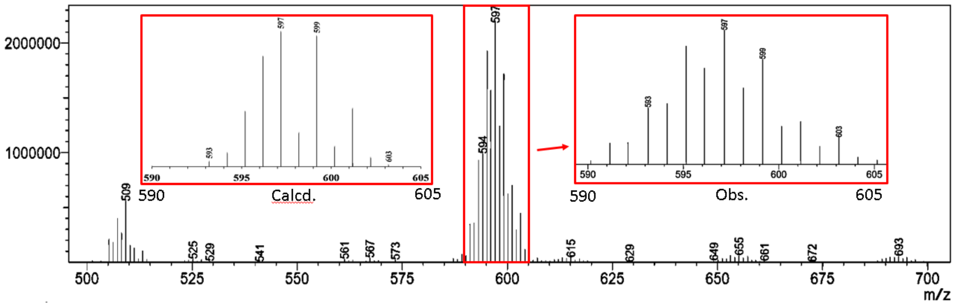
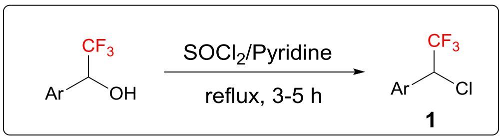


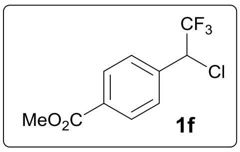
Figure S2a LC-MS spectra of III: Isotopic resolution of the calculated and observed LC-MS main peaks of the intermediate. Obs.: $[M + H]^+ = 597.15$, Calcd.: $[M + H]^+ = 597.1884$.

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]



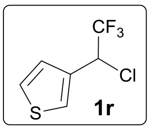
Methyl 4-(1-chloro-2,2,2-trifluoroethyl)benzoate (1f)



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.

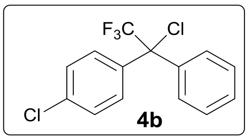
3-(1-Chloro-2,2,2-trifluoroethyl)thiophene (1r)



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.

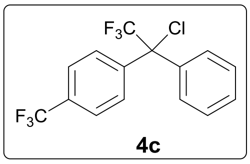
1-Chloro-4-(1-chloro-2,2,2-trifluoro-1-phenylethyl)benzene (4b)



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.

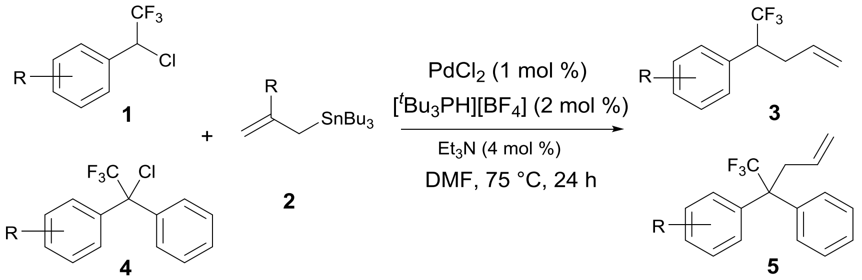
1-(1-Chloro-2,2,2-trifluoro-1-phenylethyl)-4-(trifluoromethyl)benzene (5c)



4c

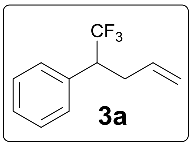
Following the general procedure, **4c** was obtained as a colorless oil (Yield: 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65–7.61 (m, 4H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.42–7.35 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.10, 137.45, 131.32 (q, *J* = 32.9 Hz), 129.69, 129.51, 129.00, 128.51, 125.31. 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.

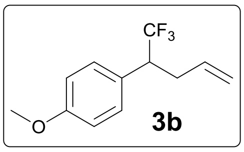
(1,1,1-Trifluoropent-4-en-2-yl)benzene (3a)



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

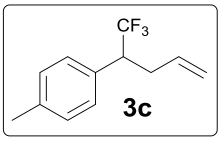
Volatile colorless oil (32.0 mg, yield: 32%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 5.62–5.51 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.97 (d, J_{cis} = 10.1 Hz, 1H), 3.38–3.26 (m, 1H), 2.83–2.72 (m, 1H), 2.70– 2.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.43, 134.03, 129.26, 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), [^{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 **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.

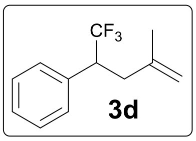
1-Methyl-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3c)



Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{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 **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**.

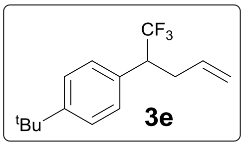
Volatile colorless oil (61.1 mg, yield: 57%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.19–7.14 (m, 4H), 5.63–5.51 (m, 1H), 5.04 (d, J_{trans} = 17.0 Hz, 1H), 4.96 (d, J_{cis} = 10.1 Hz, 1H), 3.34–3.22 (m, 1H), 2.81–2.71 (m, 1H), 2.67–2.57 (m, 1H), 2.34 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 138.07, 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), $[^tBu_3PH][BF_4]$ (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.

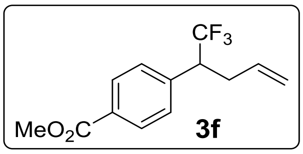
1-(*tert*-Butyl)-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3e)



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

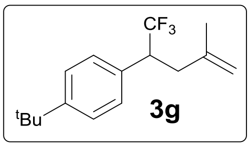
Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.66–5.53 (m, 1H), 5.06 (d, J_{trans} = 17.0 Hz, 1H), 4.97 (d, J_{cis} = 10.1 Hz, 1H), 3.36–3.23 (m, 1H), 2.81–2.71 (m, 1H), 2.69–2.58 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.14, 134.32, 131.31, 128.83, 126.95 (q, *J* = 280.1 Hz), 125.64, 117.68, 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)



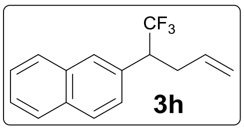
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1f** (0.5 mmol, 126.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



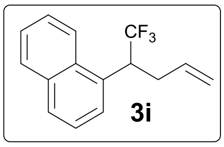
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1e** (0.5 mmol, 125.3 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



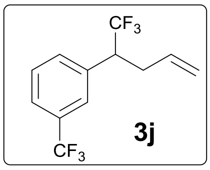
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1h** (0.5 mmol, 122.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture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

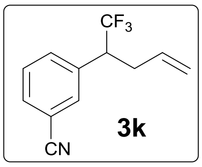
1-(Trifluoromethyl)-3-(1,1,1-trifluoropent-4-en-2-yl)benzene (3j)



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.

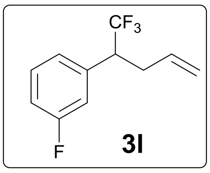
3-(1,1,1-Trifluoropent-4-en-2-yl)benzonitrile (3k)



3k

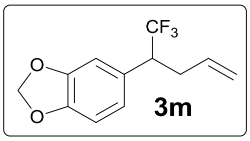
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1k** (0.5 mmol, 109.8 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



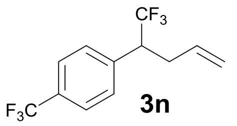
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [^{t}Bu_3PH][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1l** (0.5 mmol, 106.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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), [^{t}Bu_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.

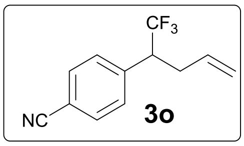
1-(Trifluoromethyl)-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3n)



3n

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 **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)

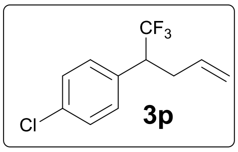
4-(1,1,1-Trifluoropent-4-en-2-yl)benzonitrile (3o)



3o

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 **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)

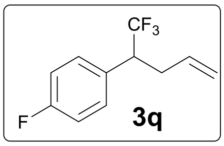
1-Chloro-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3p)



3p

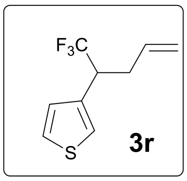
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1p** (0.5 mmol, 114.5 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



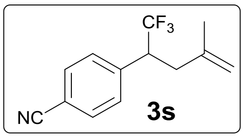
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1q** (0.5 mmol, 106.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



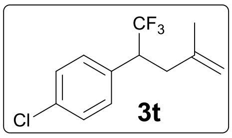
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1r** (0.5 mmol, 100.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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)



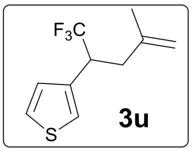
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), $[^tBu_3PH][BF_4]$ (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **1o** (0.5 mmol, 109.8 mg, 1.0 equiv) and **2b** (1.25 mmol, 431.4 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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.

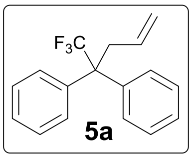
3-(1,1,1-Trifluoro-4-methylpent-4-en-2-yl)thiophene (3u)



3u

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 **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.

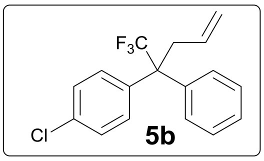
(1,1,1-Trifluoropent-4-ene-2,2-diyl)dibenzene (5a)



5a

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 **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.

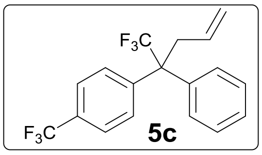
1-Chloro-4-(1,1,1-trifluoro-2-phenylpent-4-en-2-yl)benzene (5b)



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.

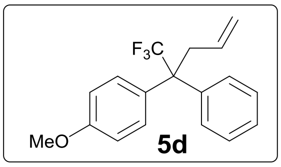
1-(1,1,1-Trifluoro-2-phenylpent-4-en-2-yl)-4-(trifluoromethyl)benzene (5c)



5c

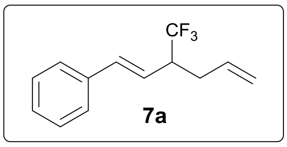
Followed by the general procedure, by using $PdCl_2$ (1 mol %; 0.9 mg), [$^tBu_3PH$][BF_4] (2 mol %; 2.9 mg) and Et_3N (4 mol %; 2.8 µL) in 1.25 mL DMF. To it **4c** (0.5 mmol, 169.3 mg, 1.0 equiv) and **2a** (1.25 mmol, 413.9 mg, 2.5 equiv) were added. After being stirred at 75 °C for 24 h, the mixture 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-$\underline{C}$ (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.

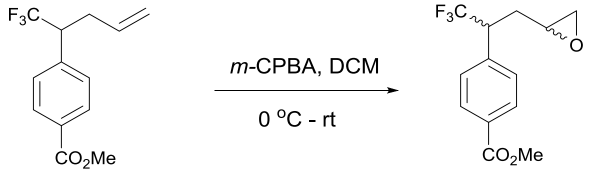
(*E*)-(3-(Trifluoromethyl)hexa-1,5-dien-1-yl)benzene (7a)



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

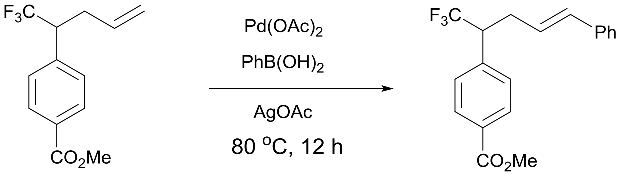
a) General procedure for the synthesis of methyl 4-(1,1,1-trifluoro-3-(oxiran-2-yl)propan-2-yl)benzoate (8a)



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.

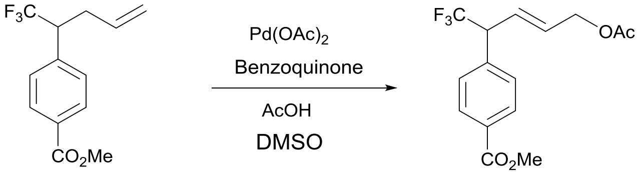
b) General procedure for the synthesis of methyl *(E)*-4-(1,1,1-trifluoro-5-phenylpent-4-en-2-yl)benzoate (8b)



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)

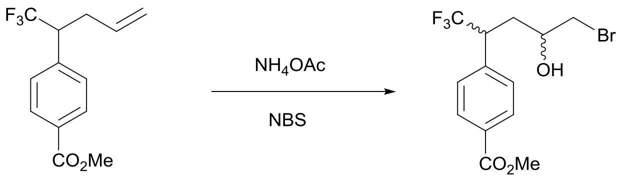


3f **8c**

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)



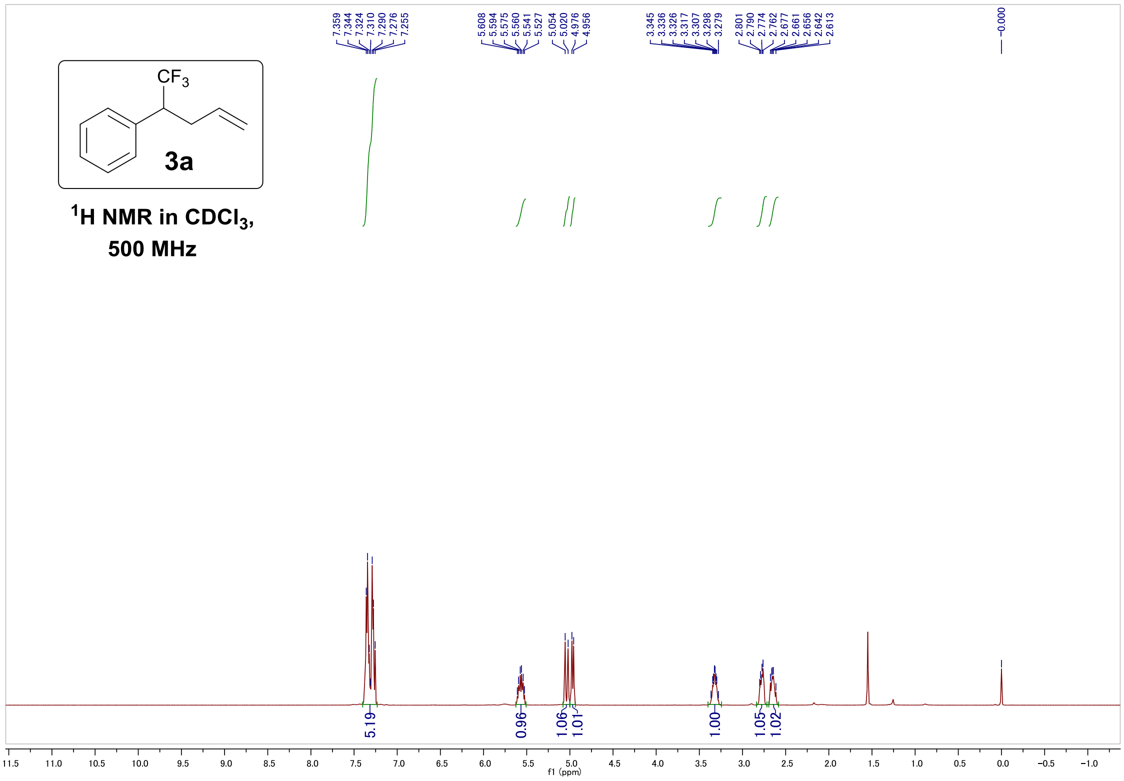
3f **8d**, 45%, dr = 1:1

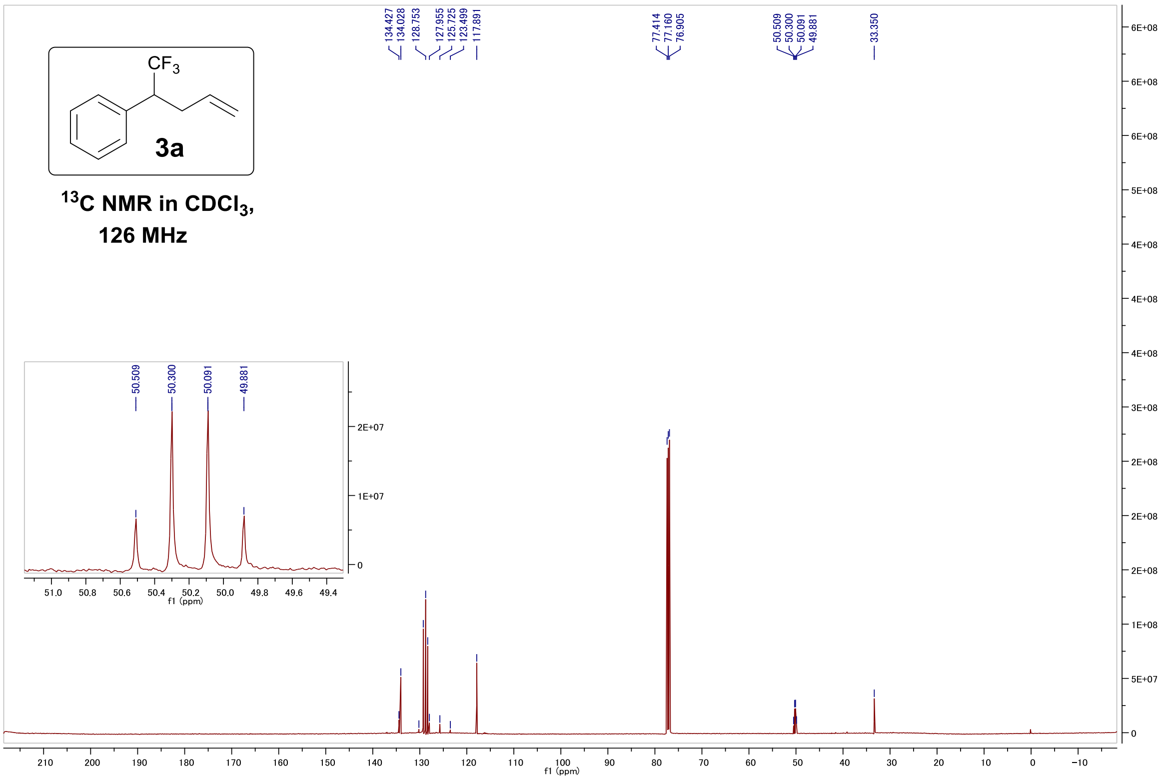
To a suspension of compound **1f** (0.2 mmol, 51.6 mg, 1 equiv) and NH_4OAc (0.02 mmol, 1.54 mg, 10 mol%) in acetone (0.8 mL), NBS (0.22 mmol, 39.15 mg, 1.1 equiv) and water (0.2 mL) were added and the mixture was stirred at room temperature. After completion of the reaction as indicated by TLC the mixture 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.

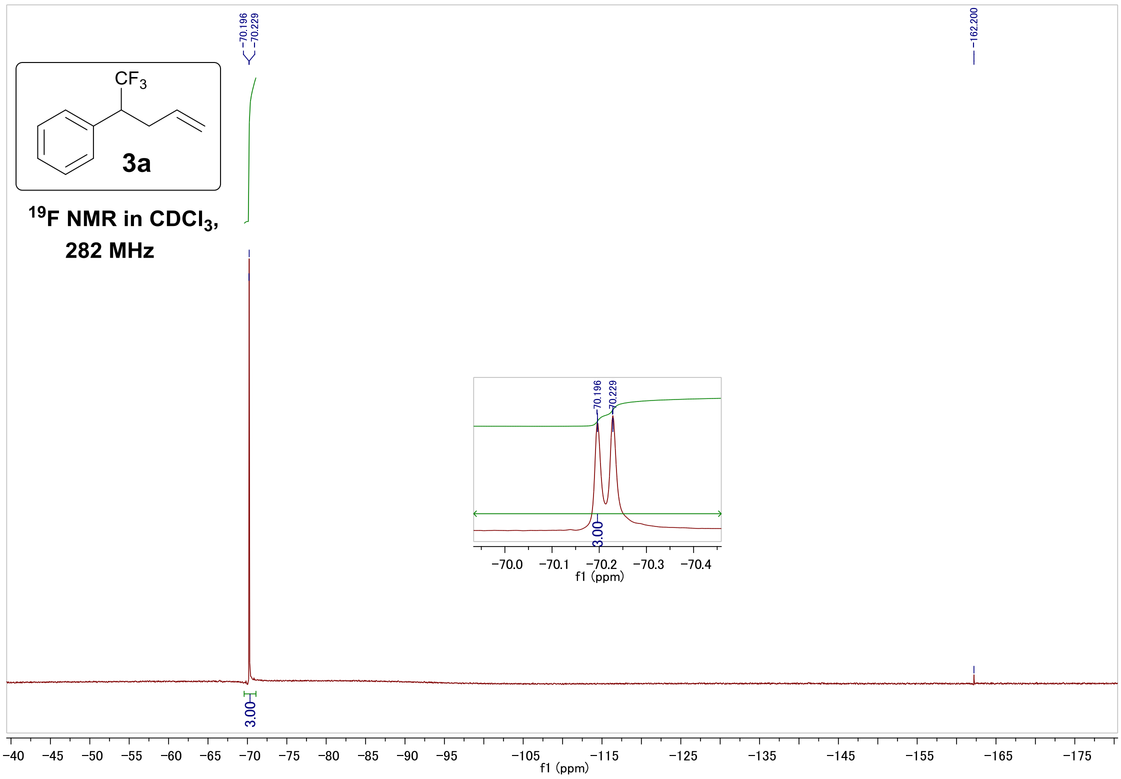
8. References:

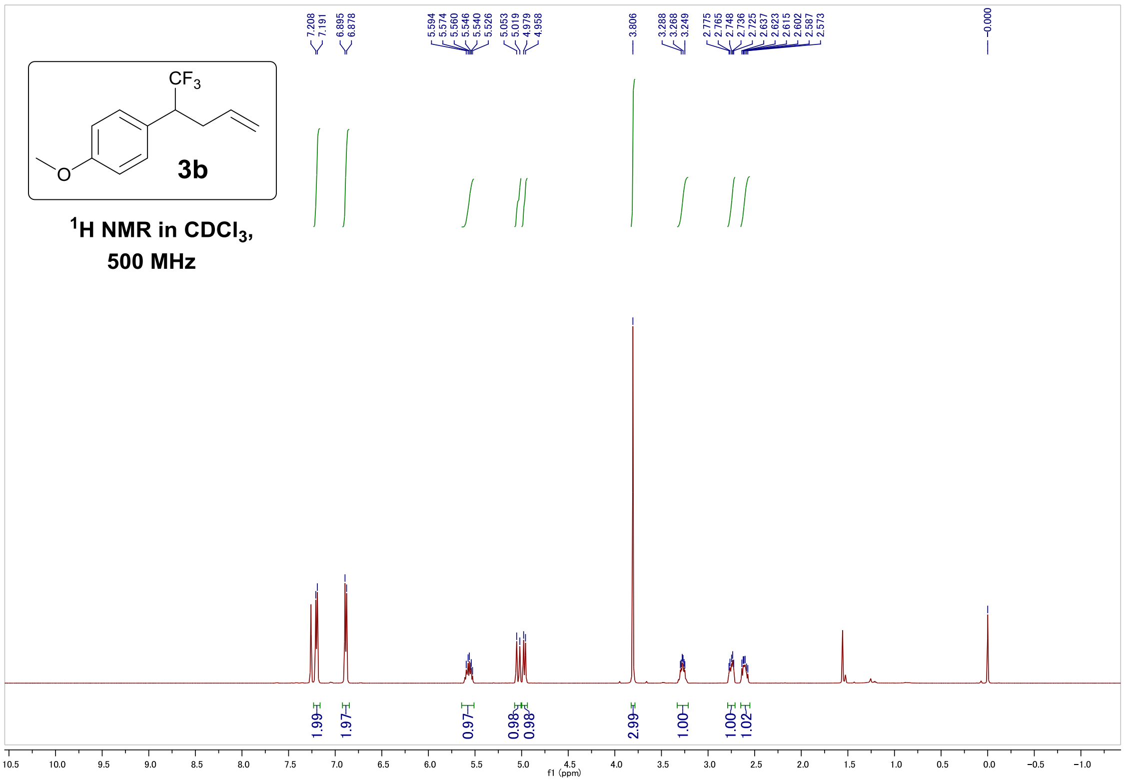
1) (a) R. Anilkumar and D. J. Burton, *J. Fluorine Chem.* 2005, **126**, 1174-1184. (b) T. Okano, K. Ito, T. Ueda and H. Muramatsu, *J. Fluorine Chem.* 1986, **32**, 377-388. (c) Y. Gonga and K. Katob, *J. Fluorine Chem.* 2003, **121**, 141–146.

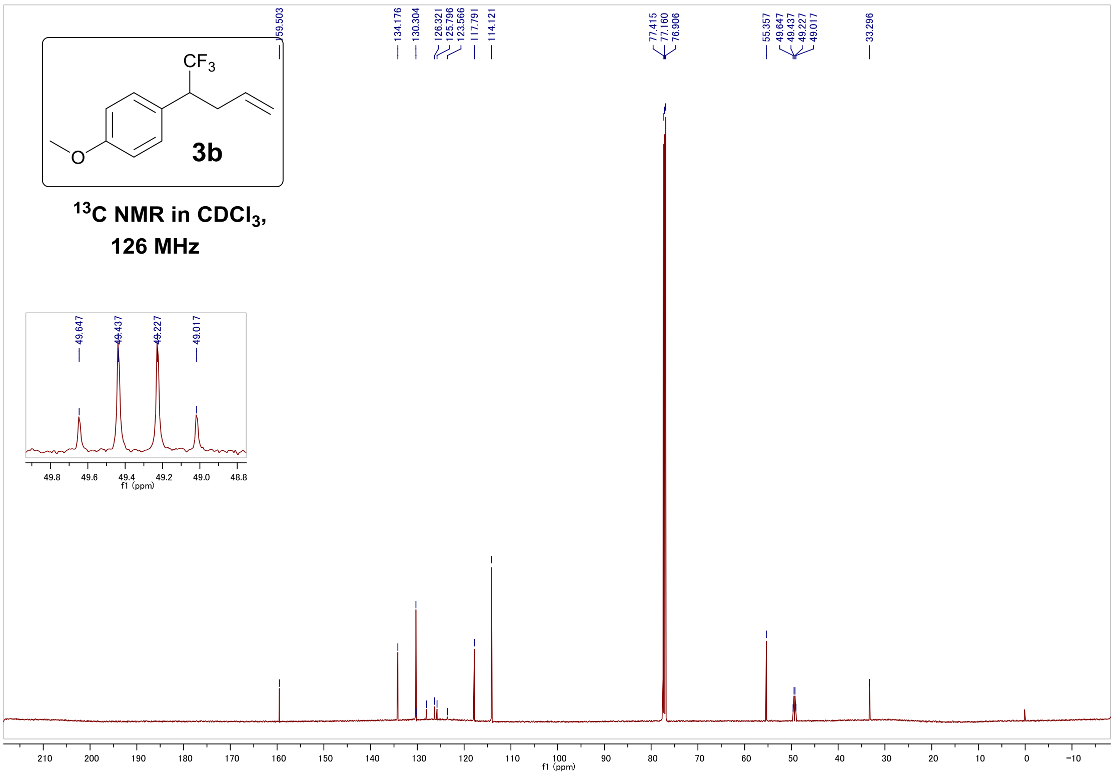
9. NMR Data
(^{1}H NMR , ^{13}C NMR and ^{19}F-NMR)

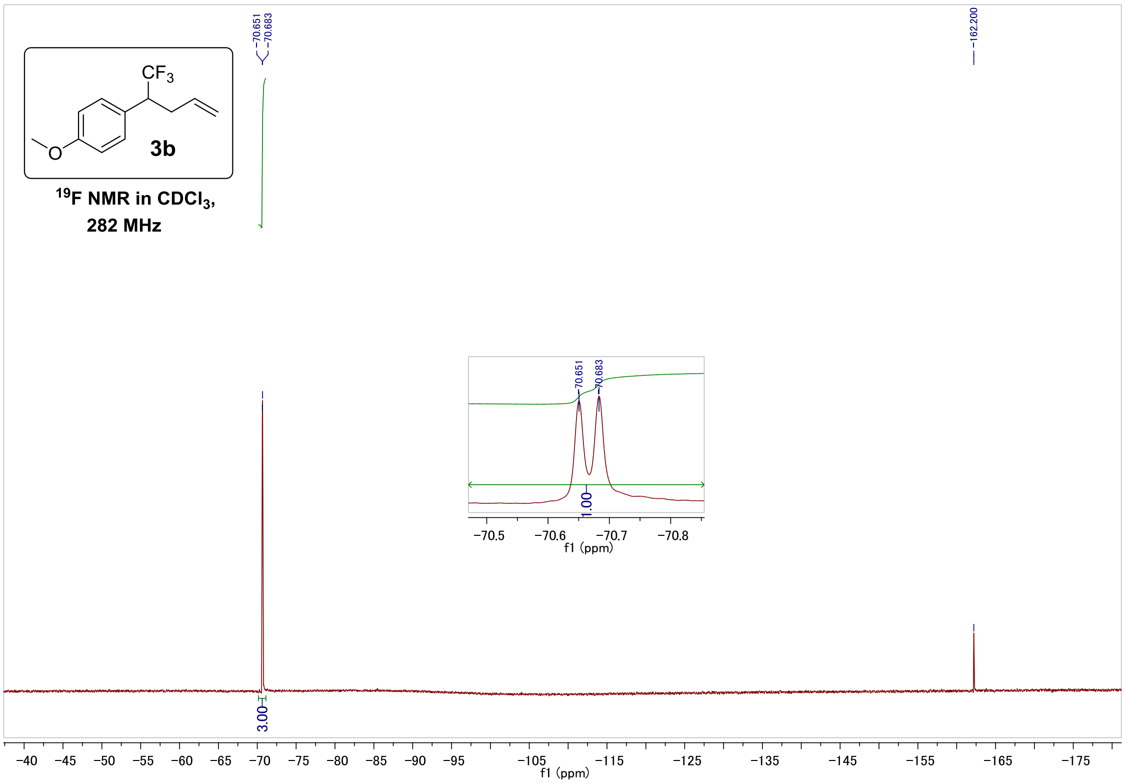

CF3
3a
1H NMR in CDCl3, 500 MHz
7.359
7.344
7.324
7.310
7.290
7.276
7.255
5.608
5.594
5.575
5.560
5.541
5.527
5.054
5.020
4.976
4.956
3.345
3.336
3.326
3.317
3.307
3.298
3.279
2.801
2.790
2.774
2.762
2.677
2.661
2.656
2.642
2.613
-0.000
5.19
0.96
1.06
1.01
1.00
1.05
1.02
f1 (ppm)

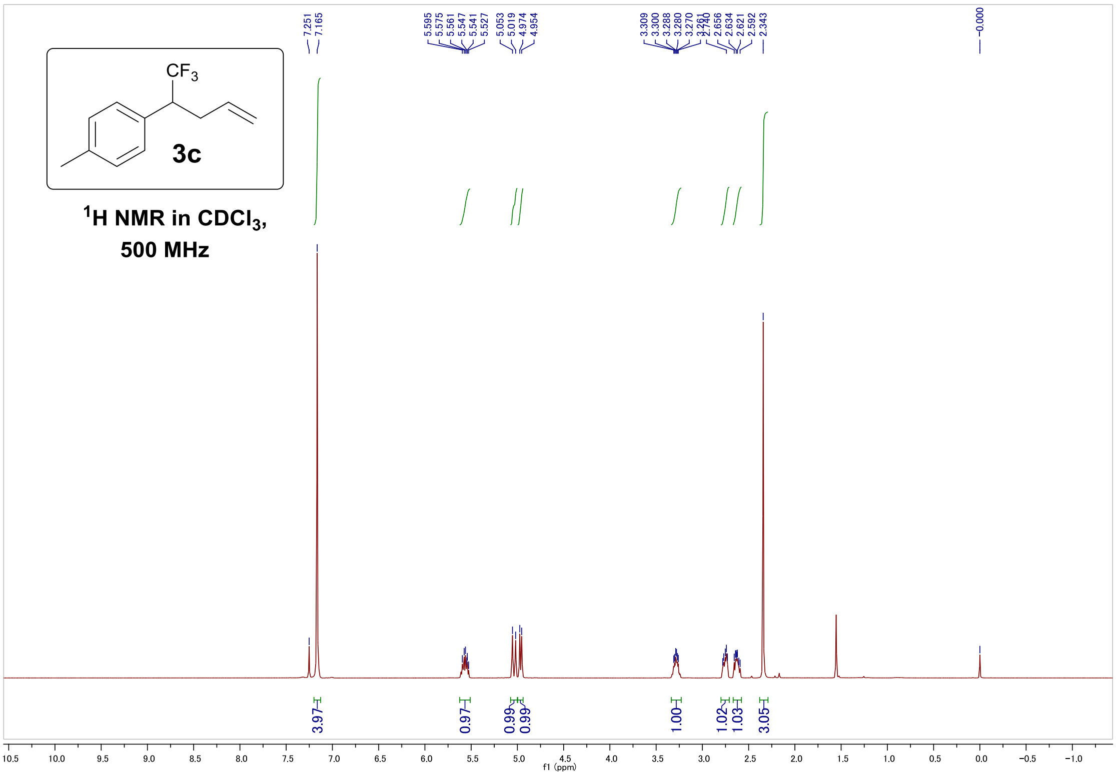

CF3
3a
13C NMR in CDCl3, 126 MHz
134.427
134.028
128.753
127.955
125.725
123.499
117.891
77.414
77.160
76.905
50.509
50.300
50.091
49.881
33.350
f1 (ppm)


CF$_3$
3a
^{19}F NMR in CDCl$_3$, 282 MHz
-70.196
-70.229
-162.200
3.00
-70.0 -70.1 -70.2 -70.3 -70.4
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175

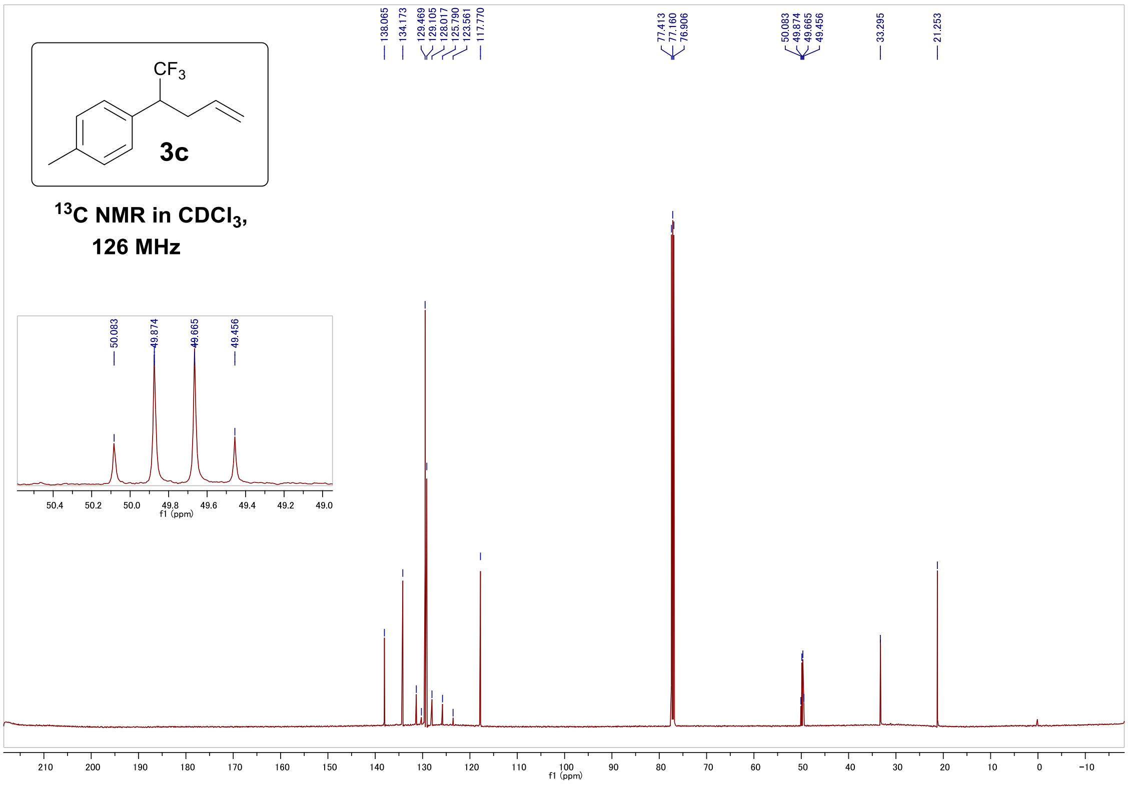

CF$_3$
O
3b
^{1}H NMR in CDCl$_3$, 500 MHz
7.208
7.191
6.895
6.878
5.594
5.574
5.560
5.546
5.540
5.526
5.053
5.019
4.979
4.958
3.806
3.288
3.268
3.249
2.775
2.765
2.748
2.736
2.725
2.637
2.623
2.615
2.602
2.587
2.573
-0.000
1.99
1.97
0.97
0.98
0.98
2.99
1.00
1.00
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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
3b
^{13}C NMR in CDCl$_3$,
126 MHz
159.503
134.176
130.304
126.321
125.766
123.566
117.791
114.121
77.415
77.160
76.906
55.357
49.647
49.437
49.227
49.017
33.296
49.647
49.437
49.227
49.017
49.8
49.6
49.4
49.2
49.0
48.8
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)

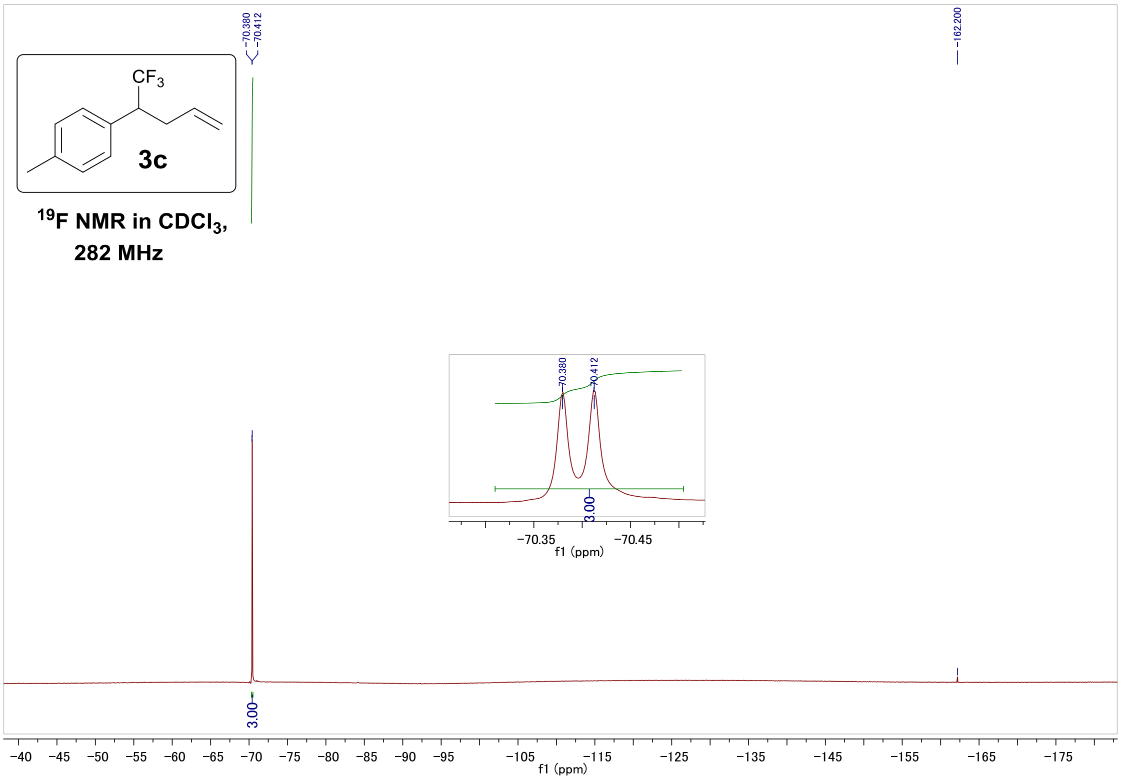

CF3
3b
^{19}F NMR in CDCl$_3$,
282 MHz
−70.651
−70.683
−162.200
3.00
−70.651
−70.683
1.00
−70.5
−70.6
−70.7
−70.8
f1 (ppm)
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

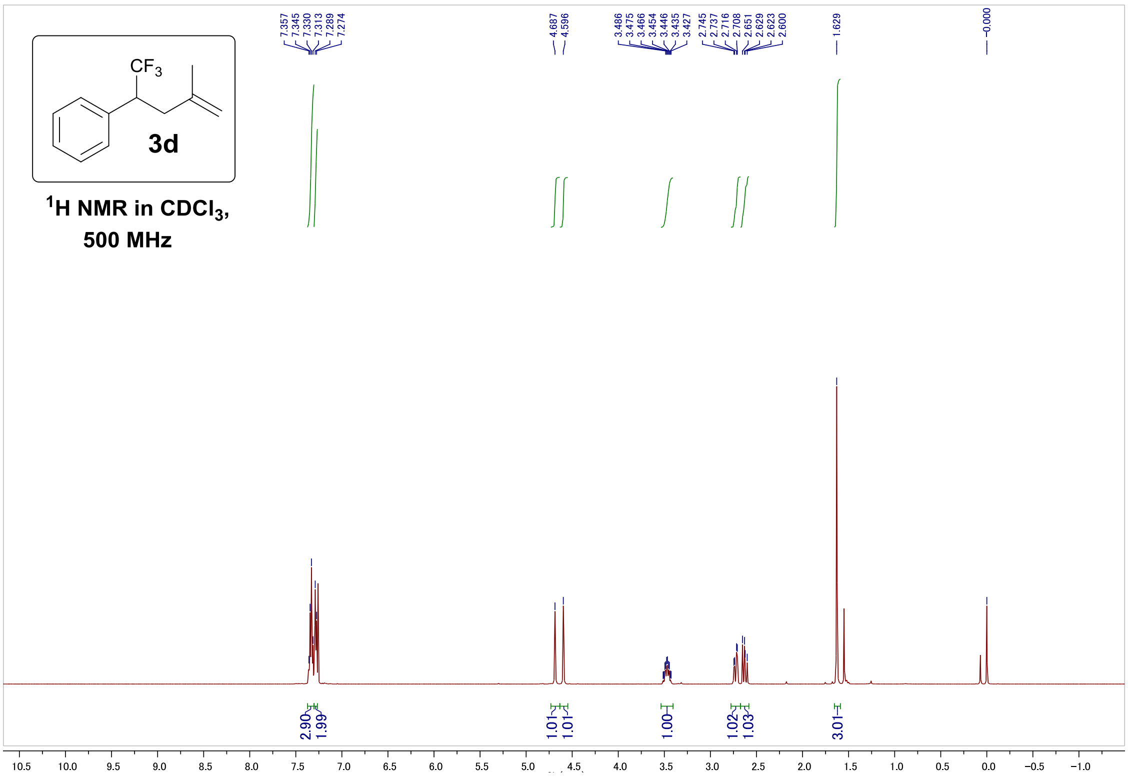


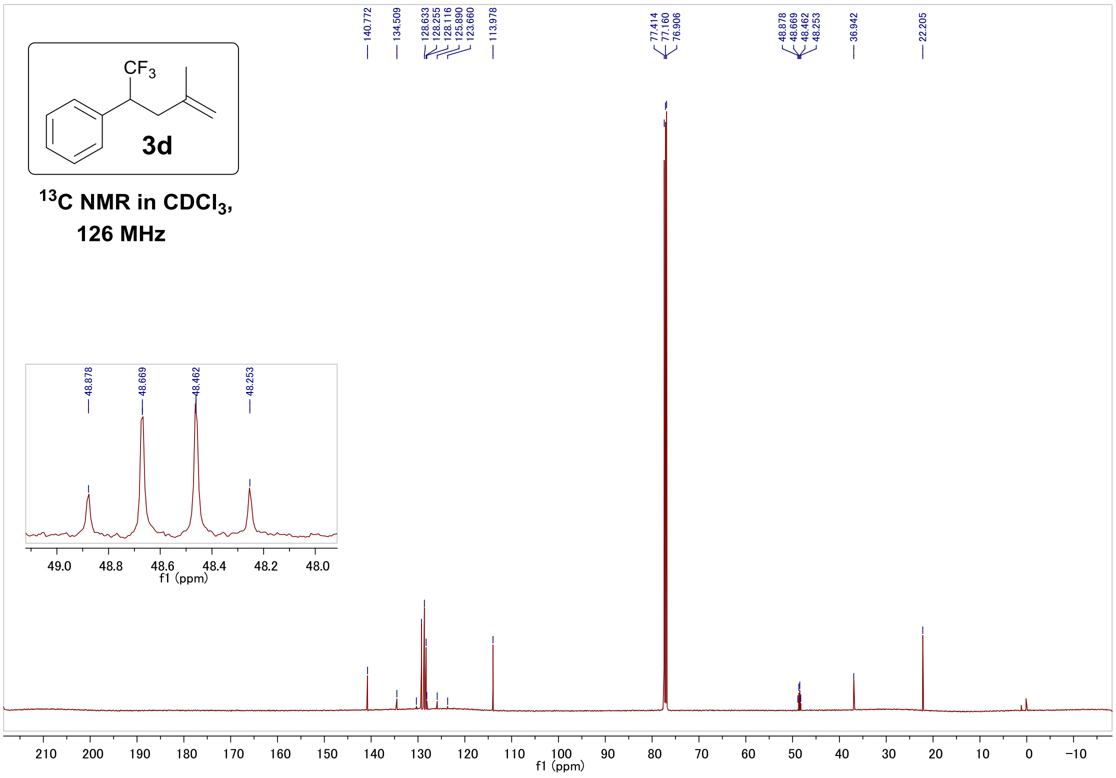
^{1}H NMR in CDCl$_3$,
500 MHz

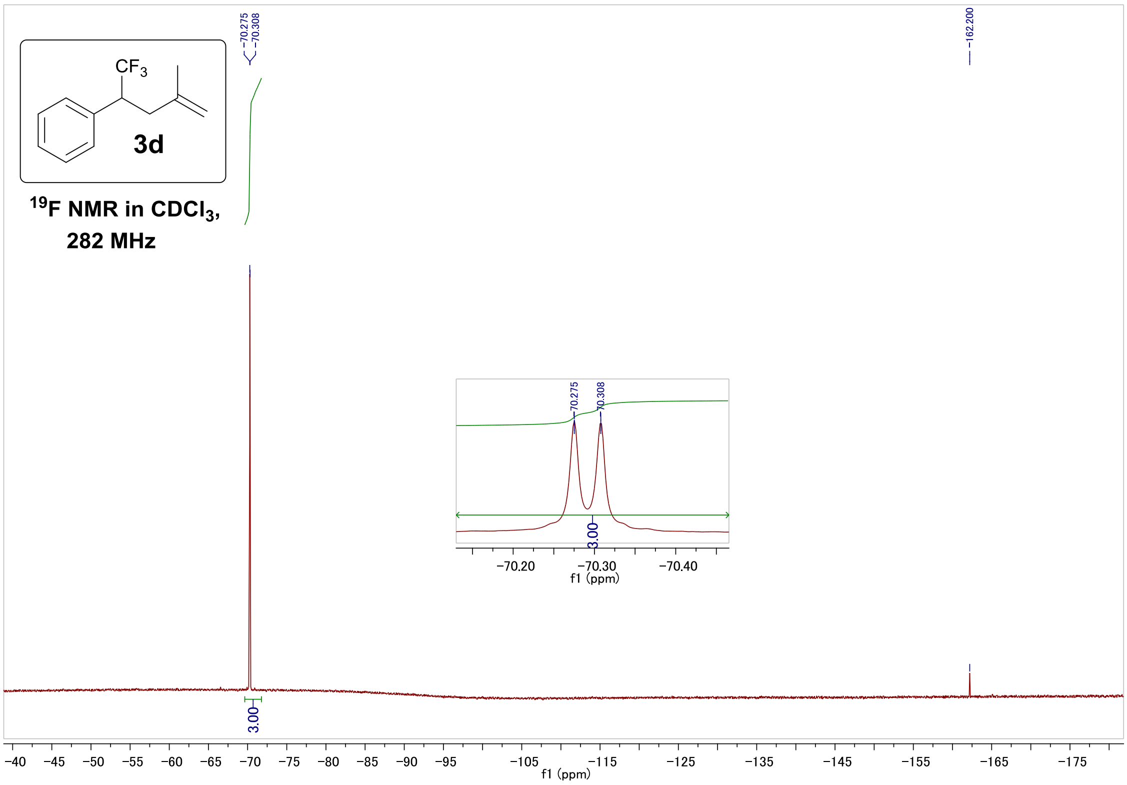


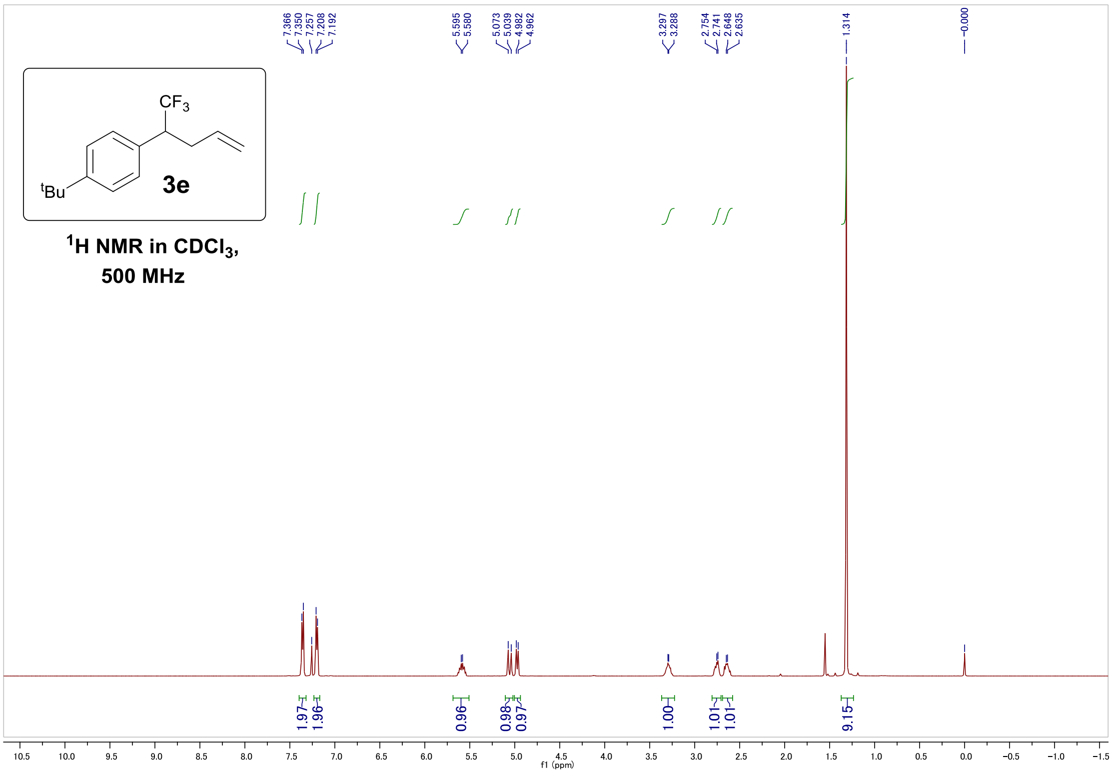
^{13}C NMR in CDCl$_3$,
126 MHz


CF3
3c
19F NMR in CDCl3, 282 MHz
-70.380
-70.412
-162.200
3.00
-70.35
-70.45
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

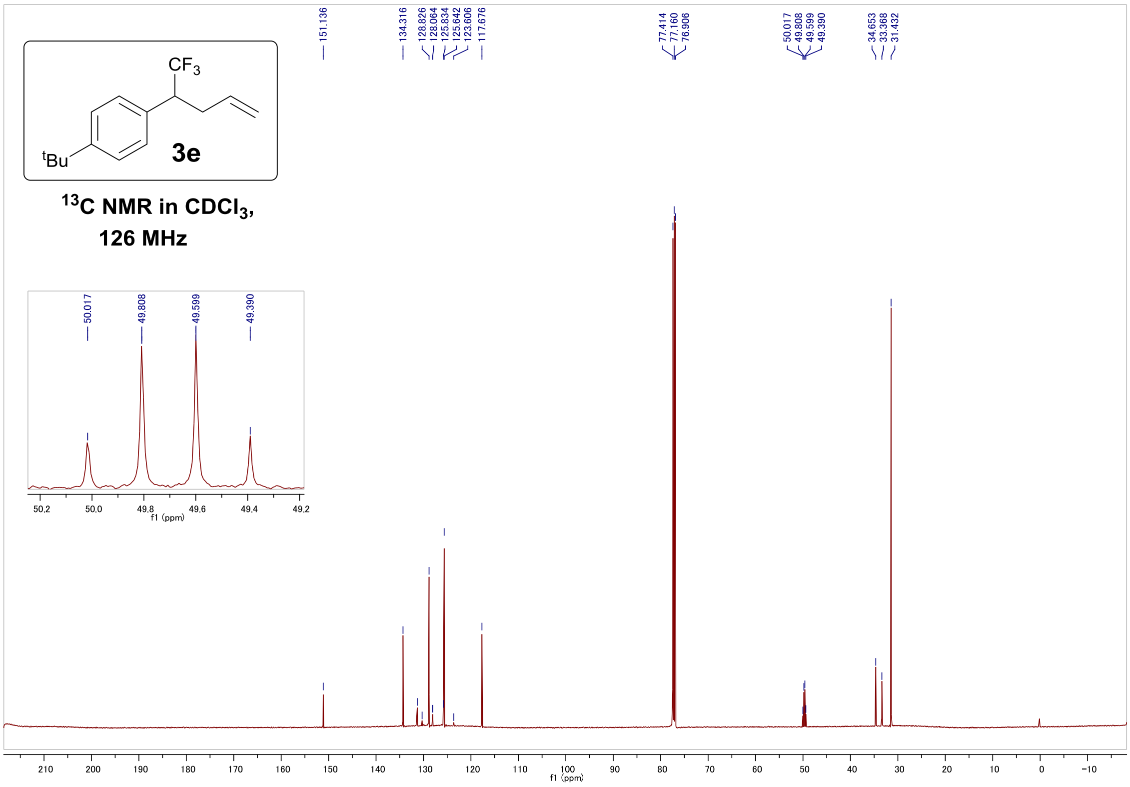

CF3
3d
1H NMR in CDCl3, 500 MHz
7.357
7.345
7.330
7.313
7.289
7.274
4.687
4.596
3.486
3.475
3.466
3.454
3.446
3.435
3.427
2.745
2.737
2.716
2.708
2.651
2.629
2.623
2.600
1.629
-0.000
2.90
1.99
1.01
1.01
1.00
1.02
1.03
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


CF3
3d
13C NMR in CDCl3,
126 MHz
140.772
134.509
128.633
128.255
128.116
125.890
123.660
113.978
77.414
77.160
76.906
48.878
48.669
48.462
48.253
36.942
22.205
49.0
48.8
48.6
48.4
48.2
48.0
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)

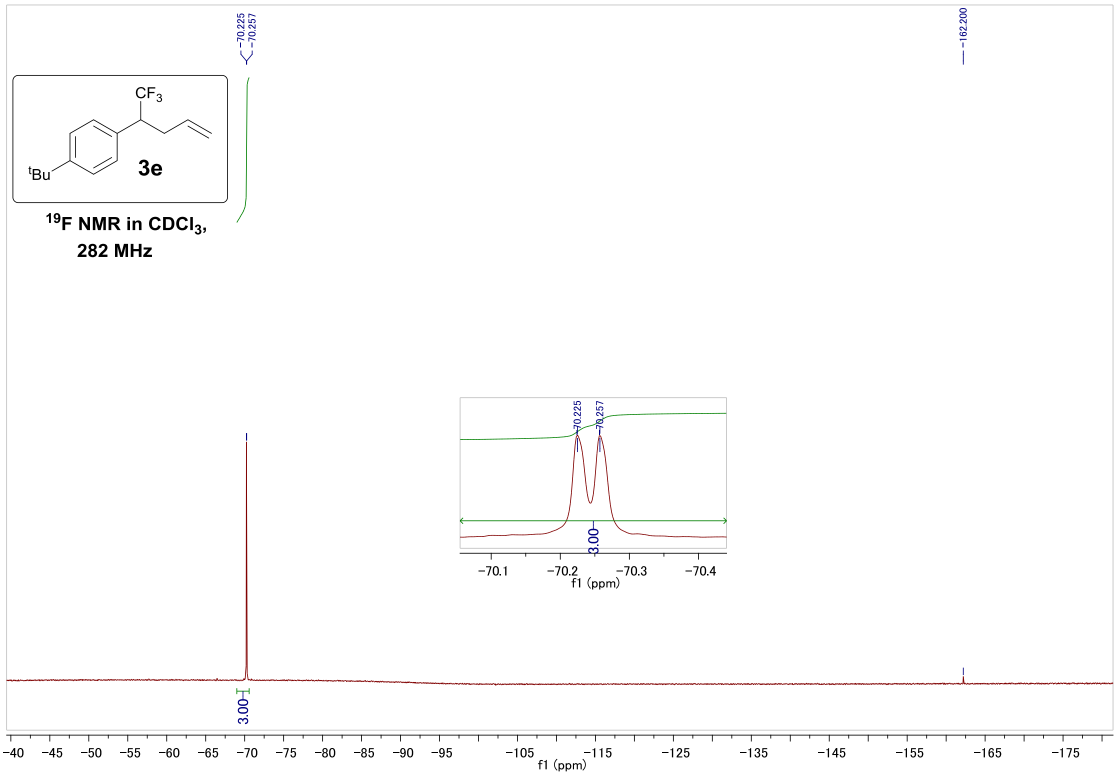

CF3
3d
19F NMR in CDCl3,
282 MHz
−70.275
−70.308
−162.200
3.00
−70.20
−70.30
−70.40
f1 (ppm)
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

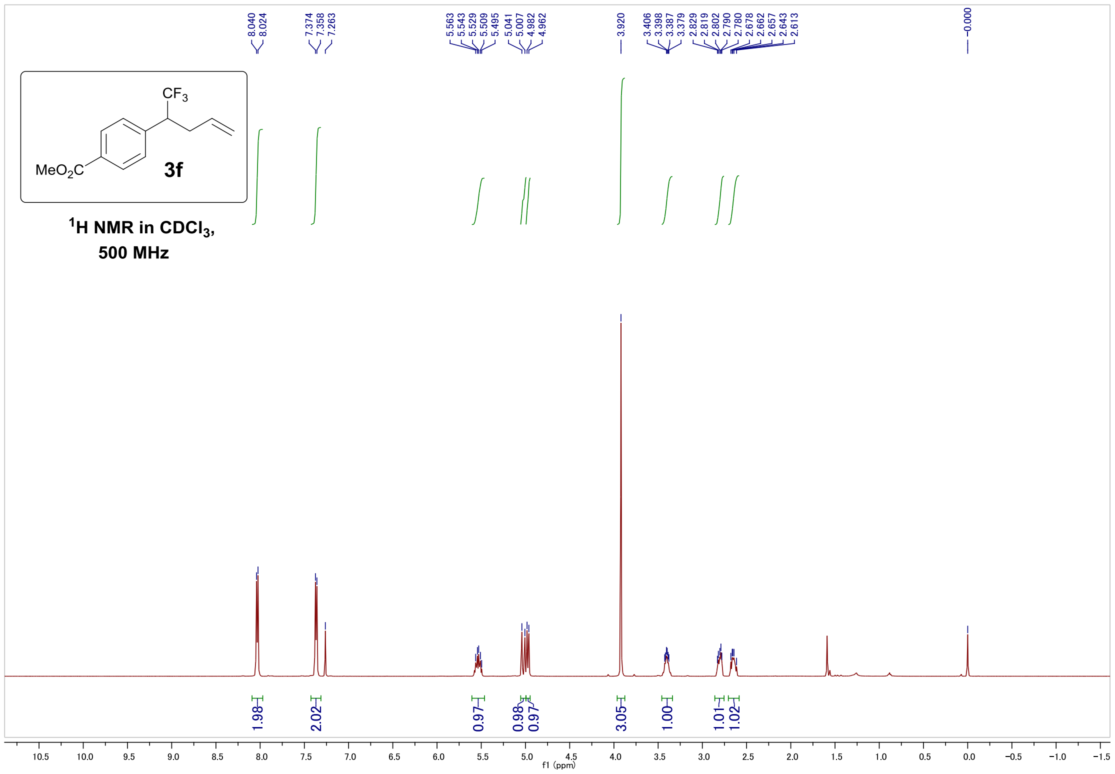


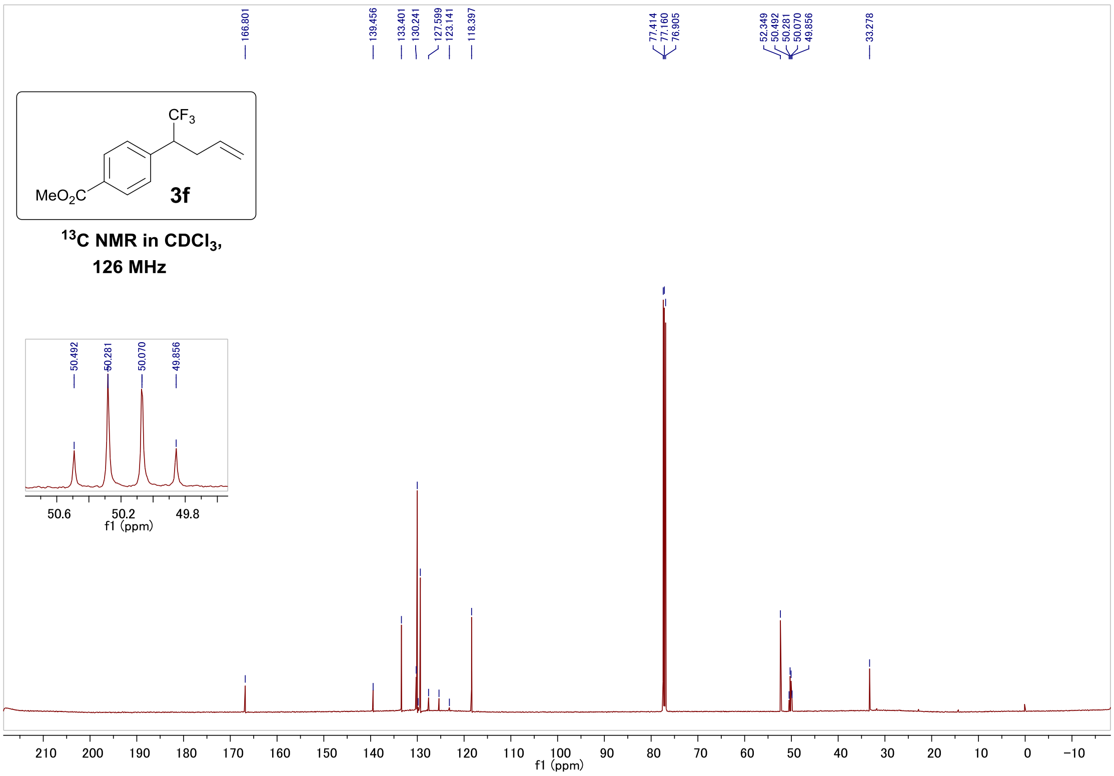
^{1}H NMR in CDCl$_3$, 500 MHz

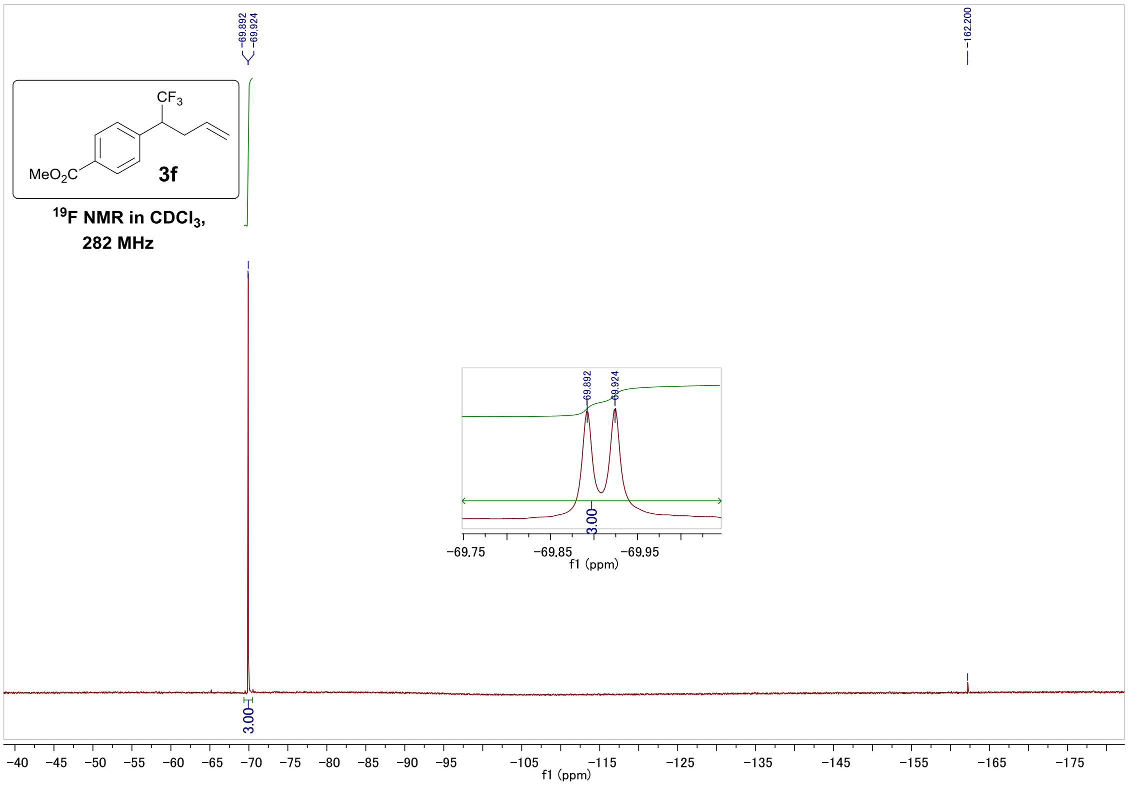


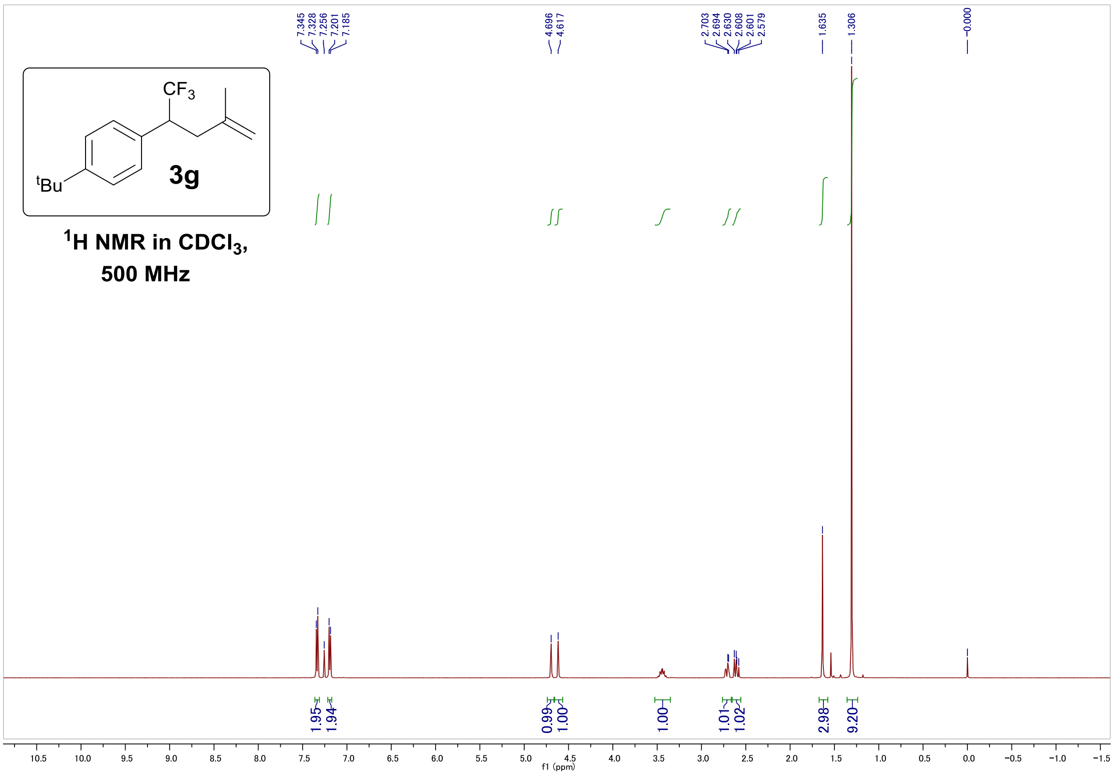
^{13}C NMR in CDCl$_3$, 126 MHz

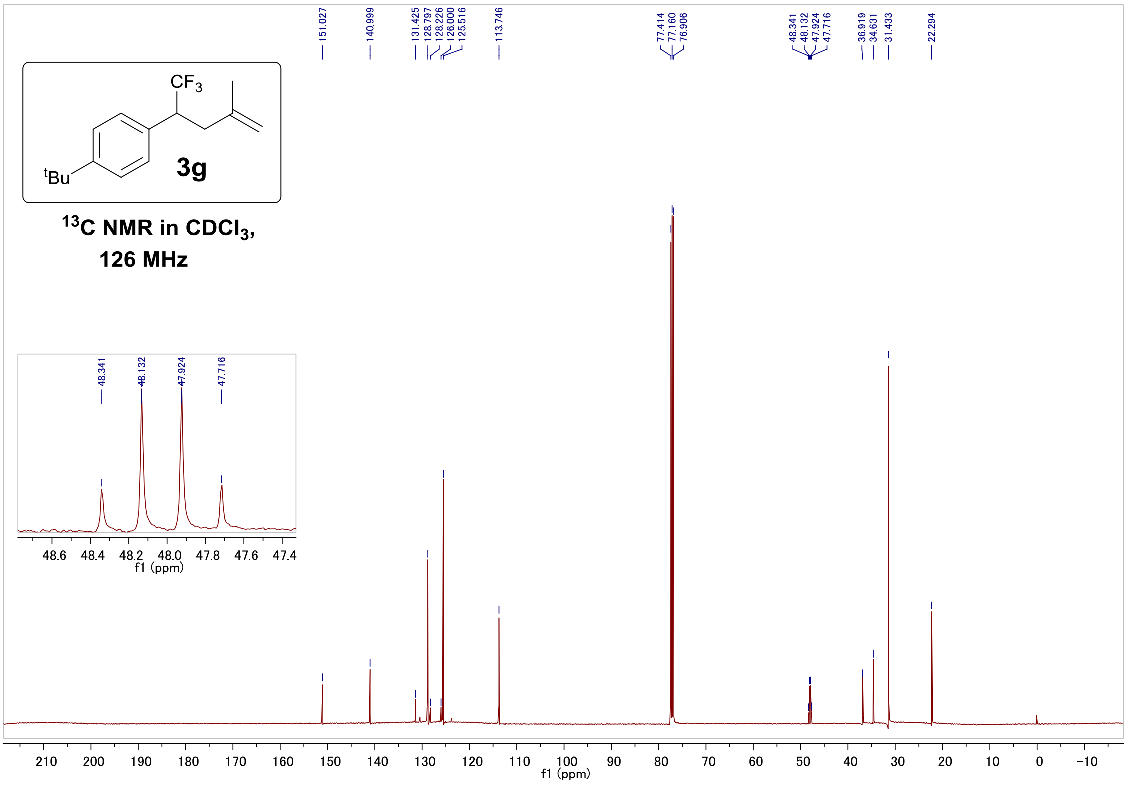

-70.225
-70.257
-162.200
CF3
tBu
3e
19F NMR in CDCl3, 282 MHz
3.00
-70.1
-70.2
-70.3
-70.4
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

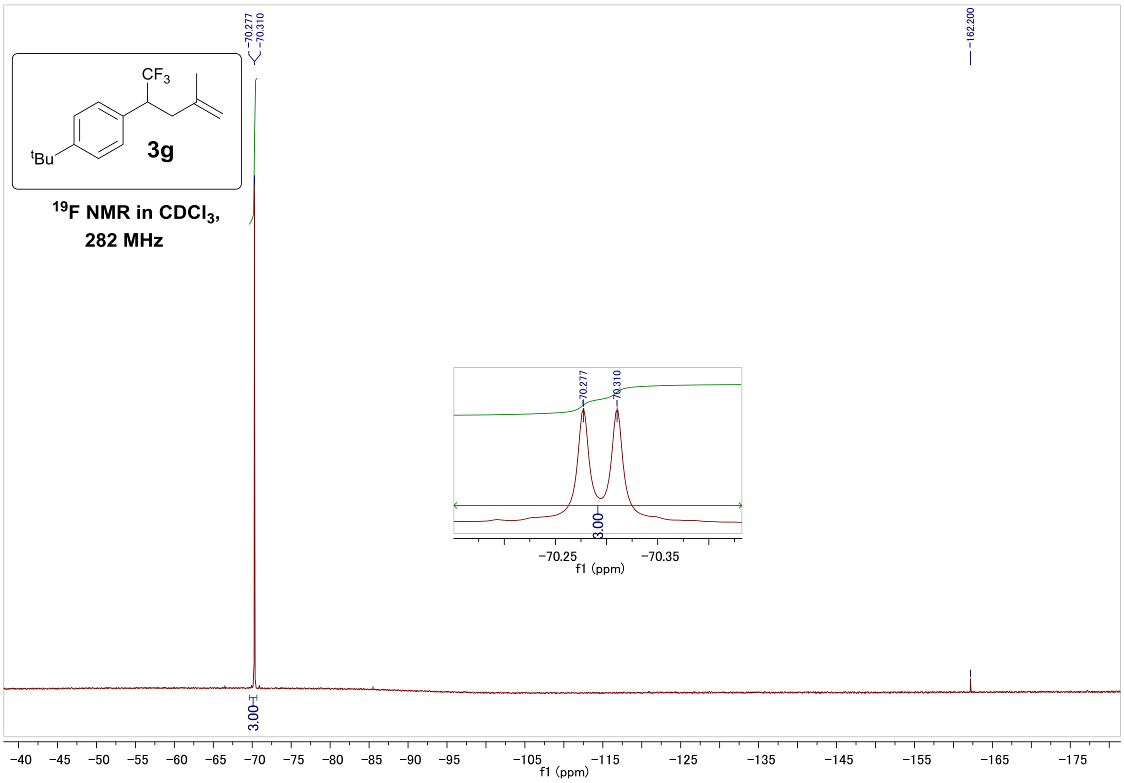

8.040
8.024
7.374
7.358
7.263
5.563
5.543
5.529
5.509
5.495
5.041
5.007
4.982
4.962
3.920
3.406
3.398
3.387
3.379
2.829
2.819
2.802
2.790
2.780
2.678
2.662
2.657
2.643
2.613
-0.000
CF3
MeO2C
3f
1H NMR in CDCl3, 500 MHz
1.98
2.02
0.97
0.98
0.97
3.05
1.00
1.01
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

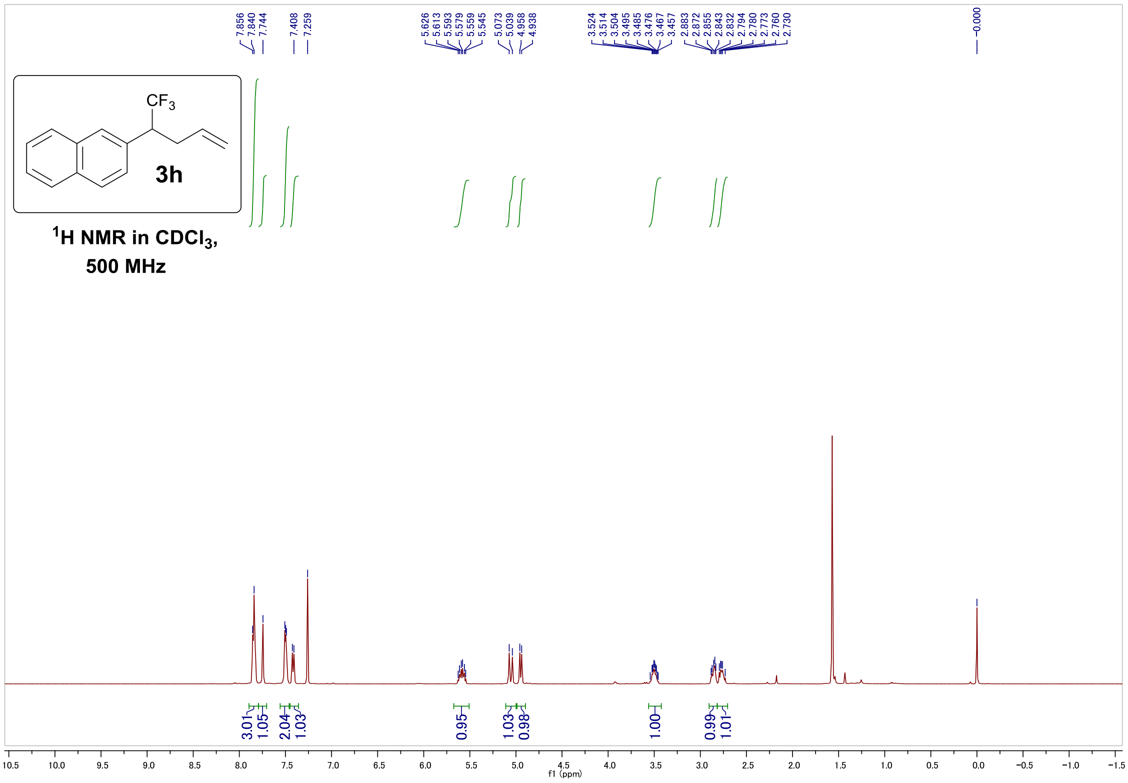

166.801
139.456
133.401
130.241
127.599
123.141
118.397
77.414
77.160
76.905
52.349
50.492
50.281
50.070
49.856
33.278
CF$_3$
MeO$_2$C
3f
^{13}C NMR in CDCl$_3$,
126 MHz
50.492
50.281
50.070
49.856
50.6
50.2
49.8
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

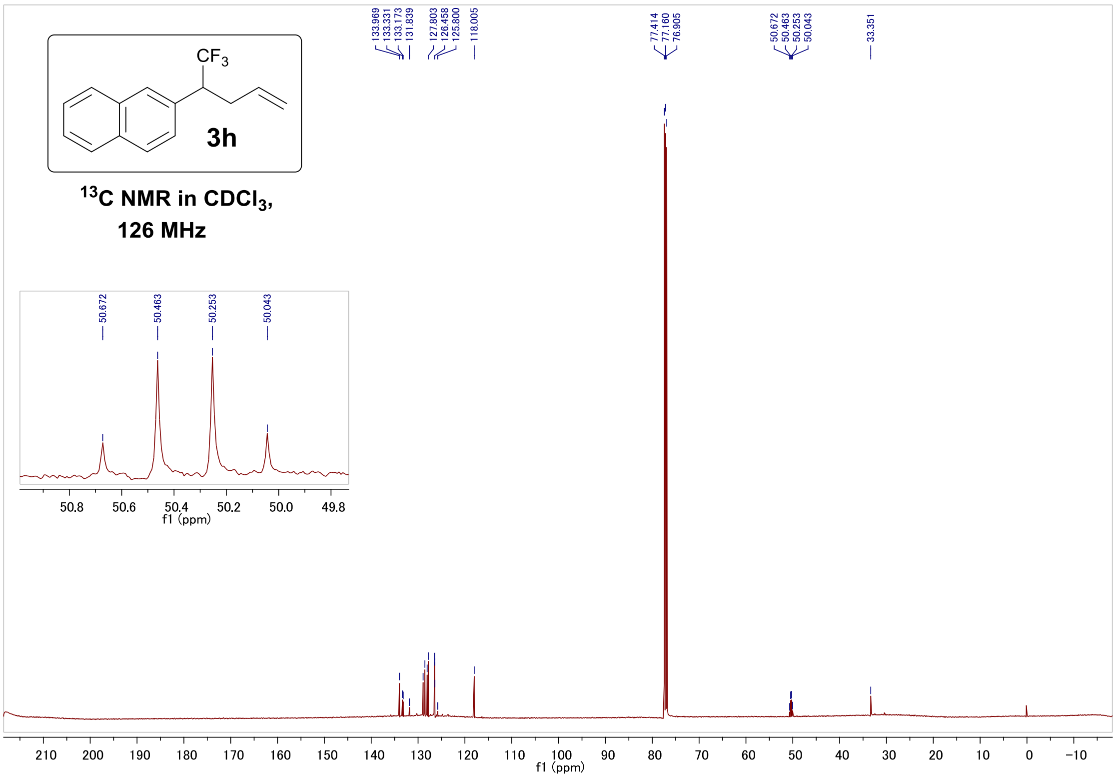

−69.892
−69.924
−162.200
CF$_3$
MeO$_2$C
3f
^{19}F NMR in CDCl$_3$,
282 MHz
−69.892
−69.924
3.00
−69.75
−69.85
−69.95
f1 (ppm)
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)


CF$_3$
^{t}Bu
3g
^{1}H NMR in CDCl$_3$, 500 MHz
7.345
7.328
7.256
7.201
7.185
4.696
4.617
2.703
2.694
2.630
2.608
2.601
2.579
1.635
1.306
-0.000
1.95
1.94
0.99
1.00
1.00
1.01
1.02
2.98
9.20
f1 (ppm)

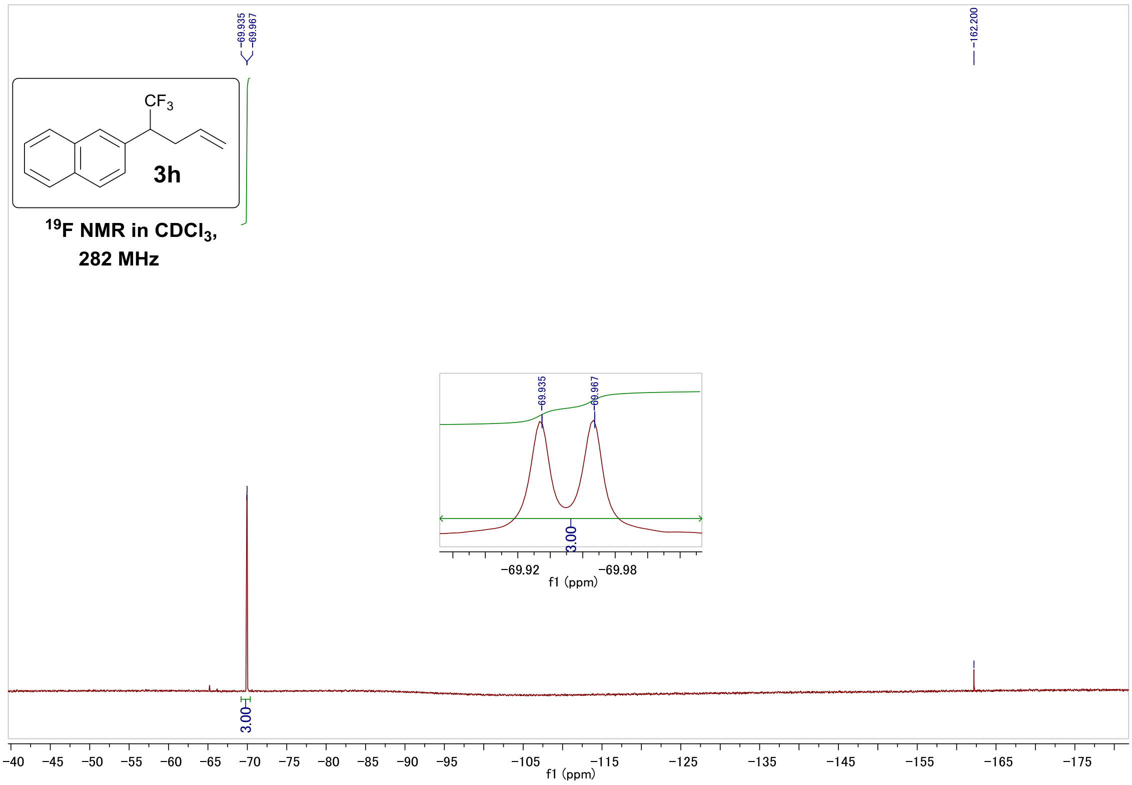

CF$_3$
^{t}Bu
3g
^{13}C NMR in CDCl$_3$, 126 MHz
151.027
140.999
131.425
128.797
128.226
126.000
125.516
113.746
77.414
77.160
76.906
48.341
48.132
47.924
47.716
36.919
34.631
31.433
22.294
f1 (ppm)


3g
^{19}F NMR in CDCl$_3$, 282 MHz
CF$_3$
^{t}Bu
−70.277
−70.310
−162.200
3.00
−70.25
−70.35
f1 (ppm)
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

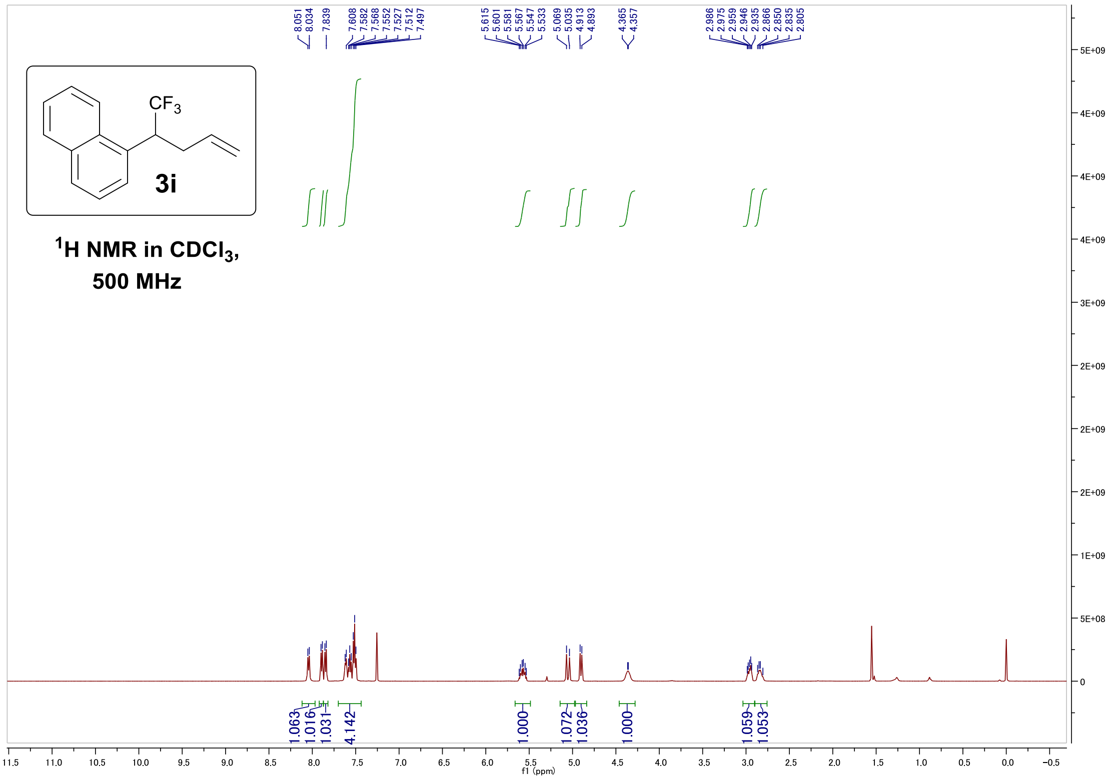

3h
^{1}H NMR in CDCl$_3$, 500 MHz
CF$_3$
7.856
7.840
7.744
7.408
7.259
5.626
5.613
5.593
5.579
5.559
5.545
5.073
5.039
4.958
4.938
3.524
3.514
3.504
3.495
3.485
3.476
3.467
3.457
2.883
2.872
2.855
2.843
2.832
2.794
2.780
2.773
2.760
2.730
−0.000
3.01
1.05
2.04
1.03
0.95
1.03
0.98
1.00
0.99
1.01
10.5 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 −1.5
f1 (ppm)

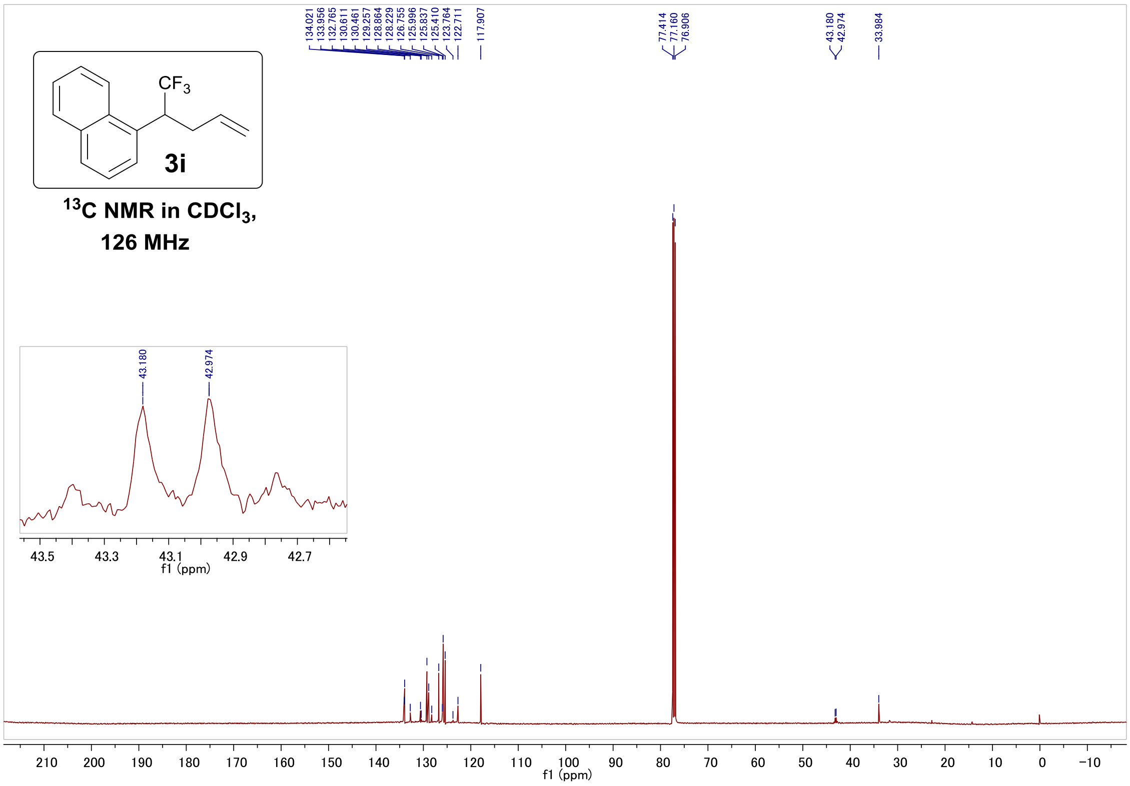


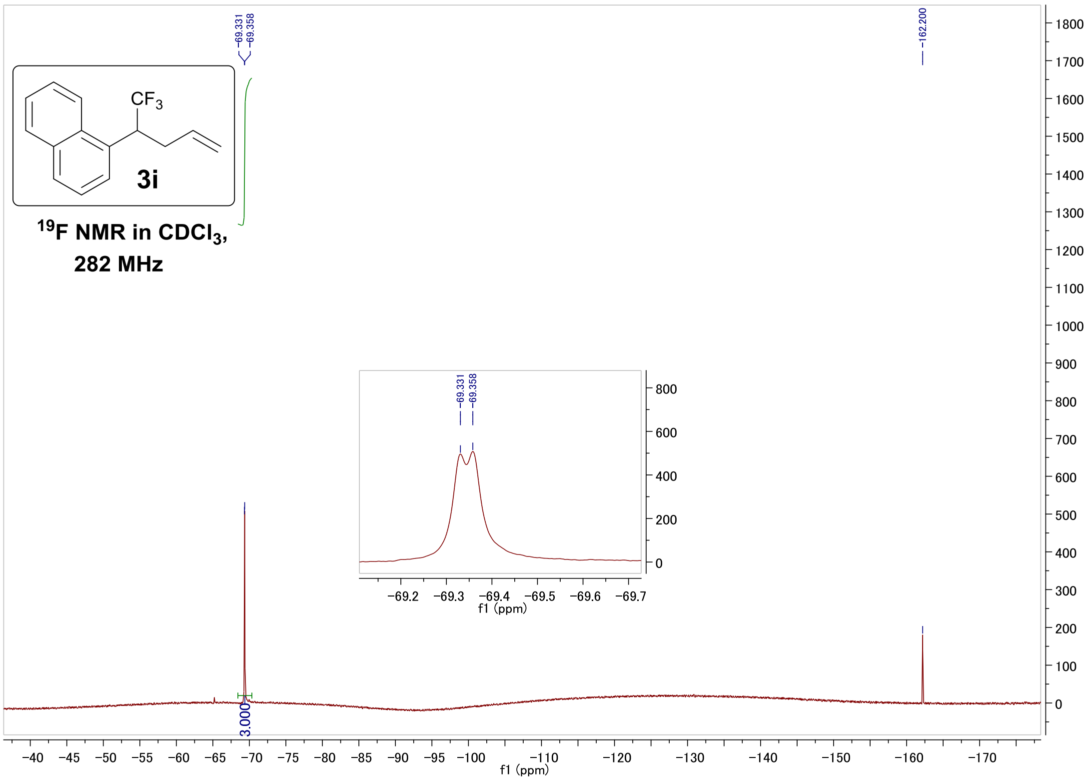
133.969
133.331
133.173
131.839
127.803
126.458
125.800
118.005
77.414
77.160
76.905
50.672
50.463
50.253
50.043
33.351
CF_3
3h
^{13}C NMR in $CDCl_3$,
126 MHz
50.8
50.6
50.4
50.2
50.0
49.8
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



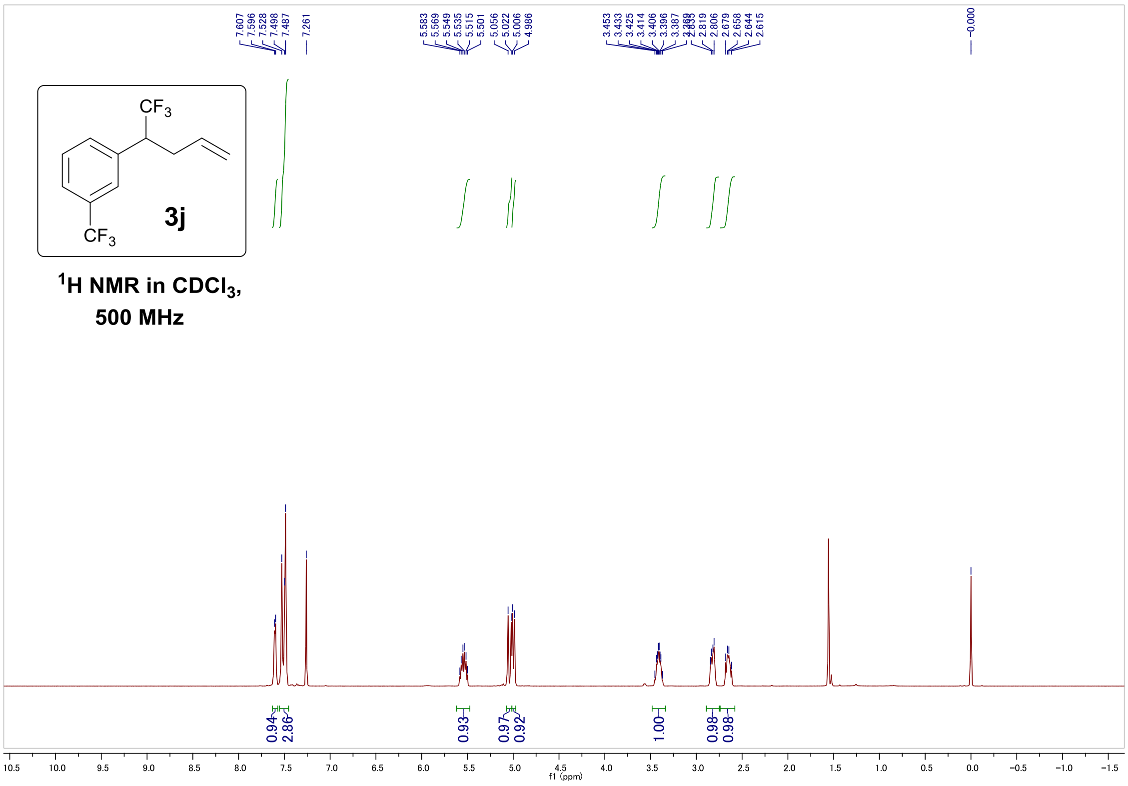
−69.935
−69.967
−162.200
CF_3
3h
^{19}F NMR in $CDCl_3$,
282 MHz
3.00
−69.92
−69.98
f1 (ppm)
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175


CF$_3$
3i
^{1}H NMR in CDCl$_3$, 500 MHz
8.051
8.034
7.839
7.608
7.582
7.568
7.552
7.527
7.512
7.497
5.615
5.601
5.581
5.567
5.547
5.533
5.069
5.035
4.913
4.893
4.365
4.357
2.986
2.975
2.959
2.946
2.935
2.866
2.850
2.835
2.805
1.063
1.016
1.031
4.142
1.000
1.072
1.036
1.000
1.059
1.053
5E+09
4E+09
4E+09
4E+09
3E+09
2E+09
2E+09
2E+09
1E+09
5E+08
0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

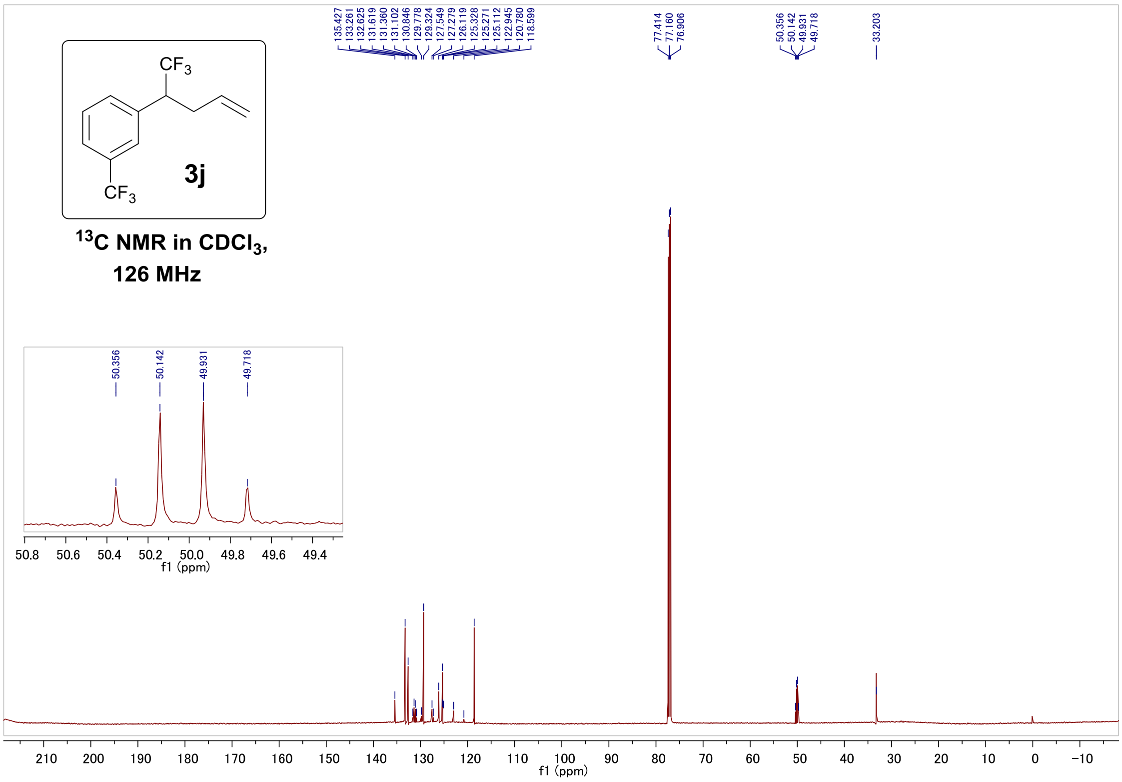

CF$_3$
3i
^{13}C NMR in CDCl$_3$, 126 MHz
134.021
133.956
132.765
130.611
130.461
129.257
128.864
128.229
126.755
125.996
125.837
125.410
123.764
122.711
117.907
77.414
77.160
76.906
43.180
42.974
33.984
43.180
42.974
43.5
43.3
43.1
42.9
42.7
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

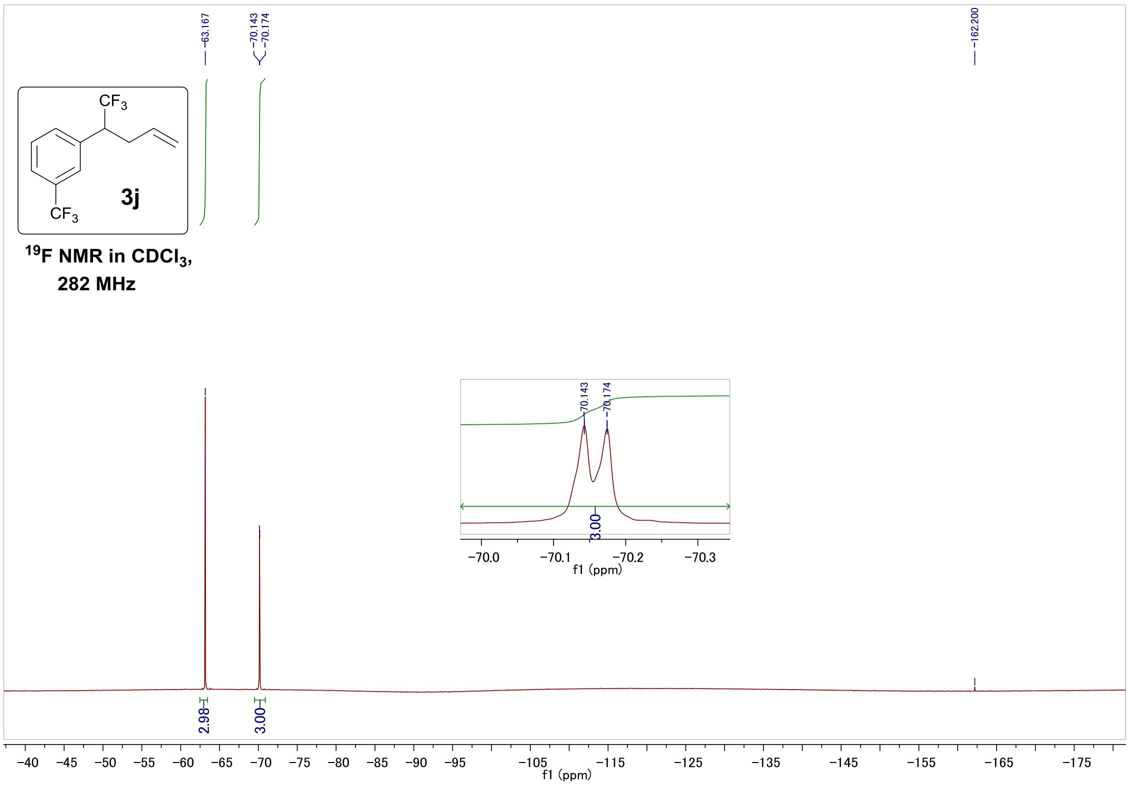


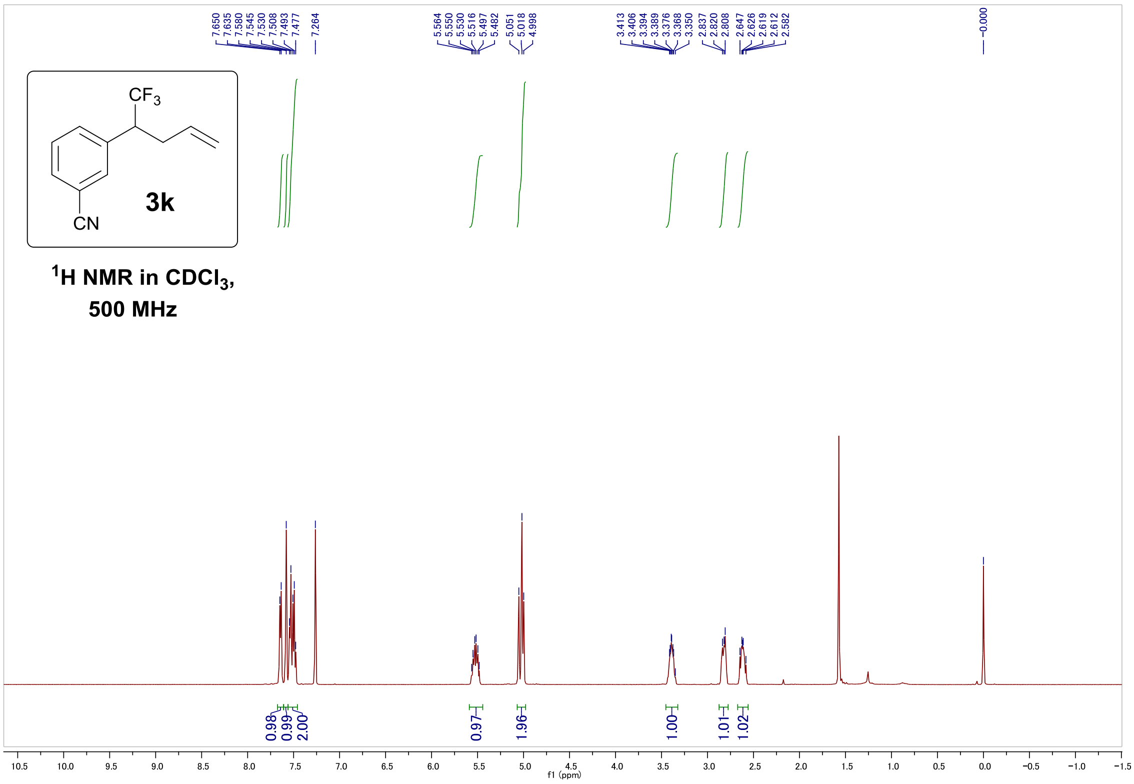
CF$_3$
3i
^{19}F NMR in CDCl$_3$, 282 MHz
−69.331
−69.358
−162.200
3.000
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −110 −120 −130 −140 −150 −160 −170
f1 (ppm)
−69.2 −69.3 −69.4 −69.5 −69.6 −69.7
800
600
400
200
0

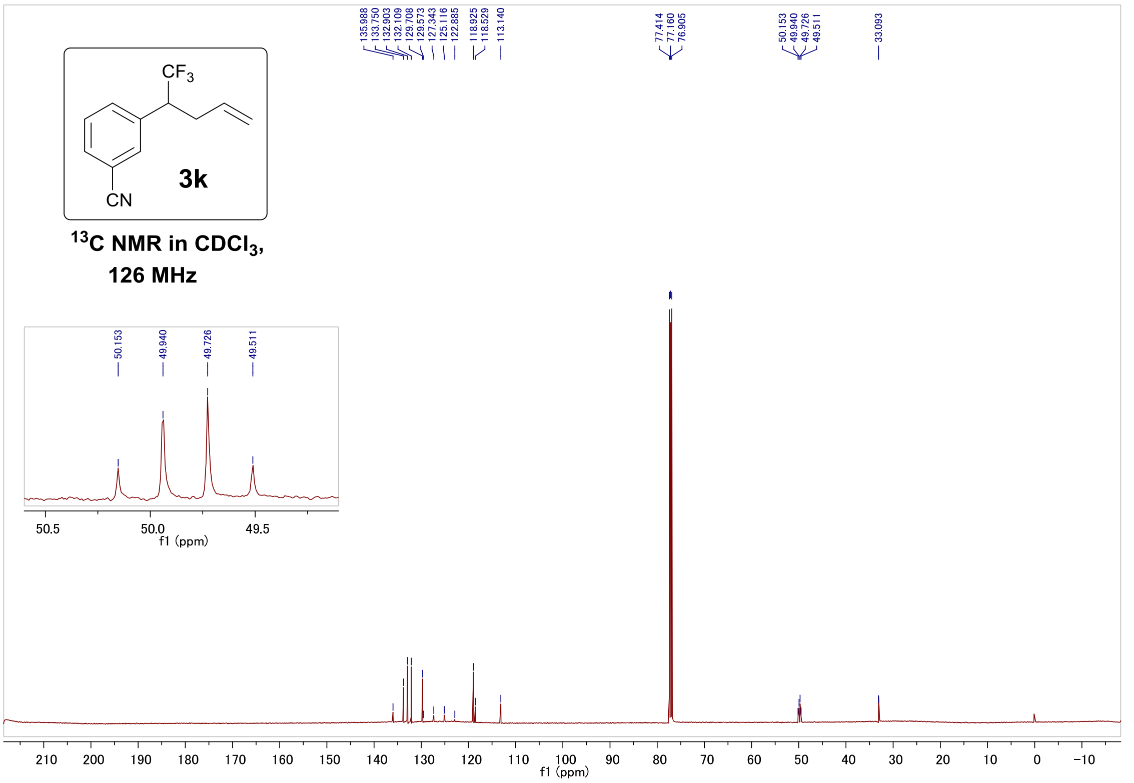


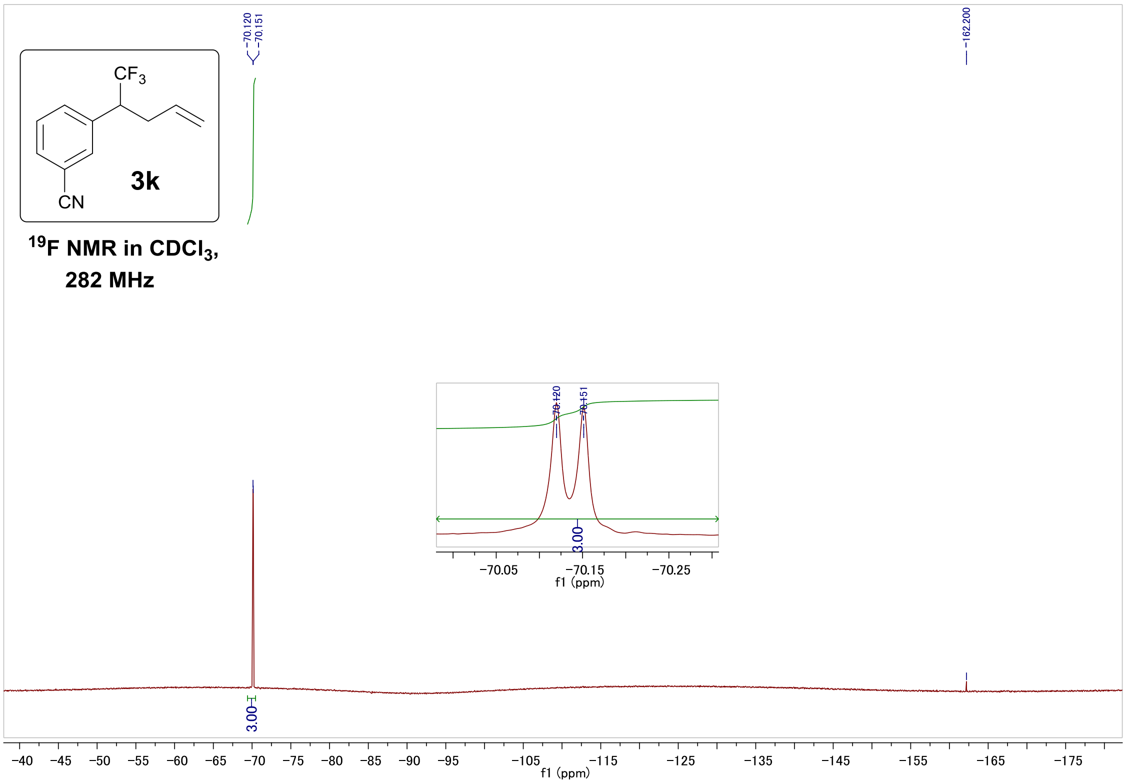
CF$_3$
CF$_3$
3j
^{1}H NMR in CDCl$_3$, 500 MHz
7.607
7.596
7.528
7.498
7.487
7.261
5.583
5.569
5.549
5.535
5.515
5.501
5.056
5.022
5.006
4.986
3.453
3.433
3.425
3.414
3.406
3.396
3.387
2.819
2.806
2.679
2.658
2.644
2.615
0.000
0.94
2.86
0.93
0.97
0.92
1.00
0.98
0.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)

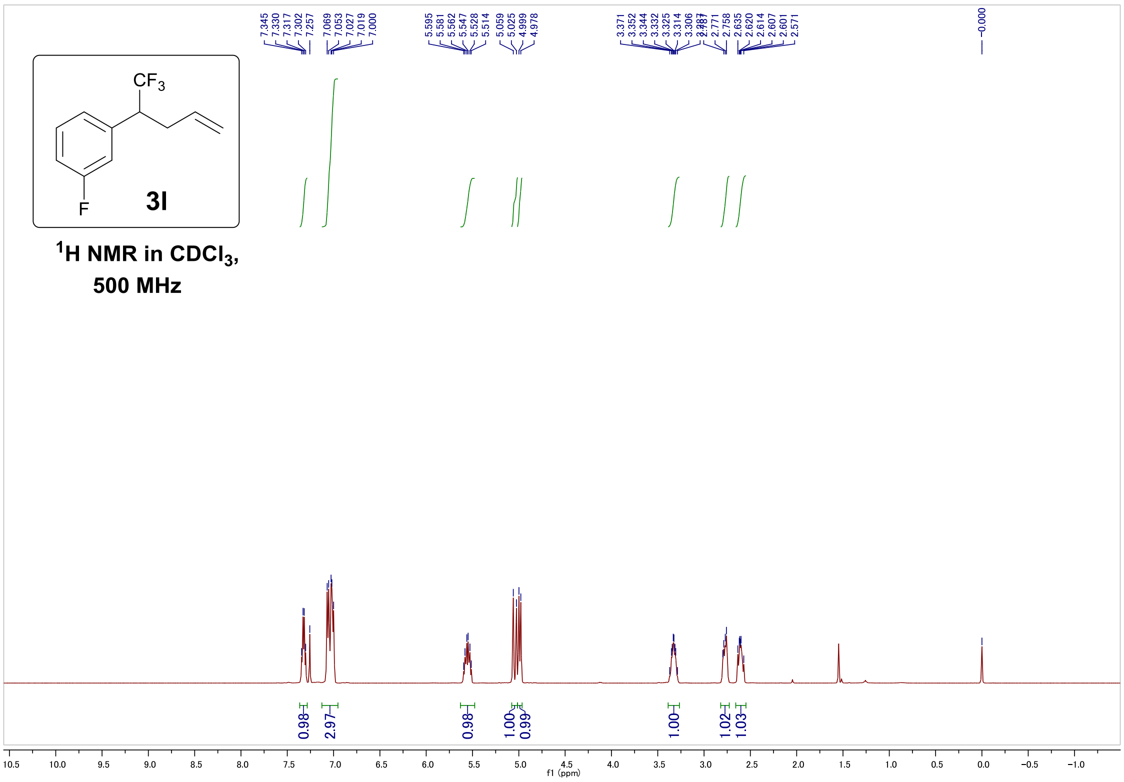

135.427
133.261
132.625
131.619
131.360
131.102
130.846
129.778
129.324
127.549
127.279
126.119
125.328
125.271
125.112
122.945
120.780
118.599
77.414
77.160
76.906
50.356
50.142
49.931
49.718
33.203
CF3
CF3
3j
13C NMR in CDCl3,
126 MHz
50.356
50.142
49.931
49.718
50.8 50.6 50.4 50.2 50.0 49.8 49.6 49.4
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)

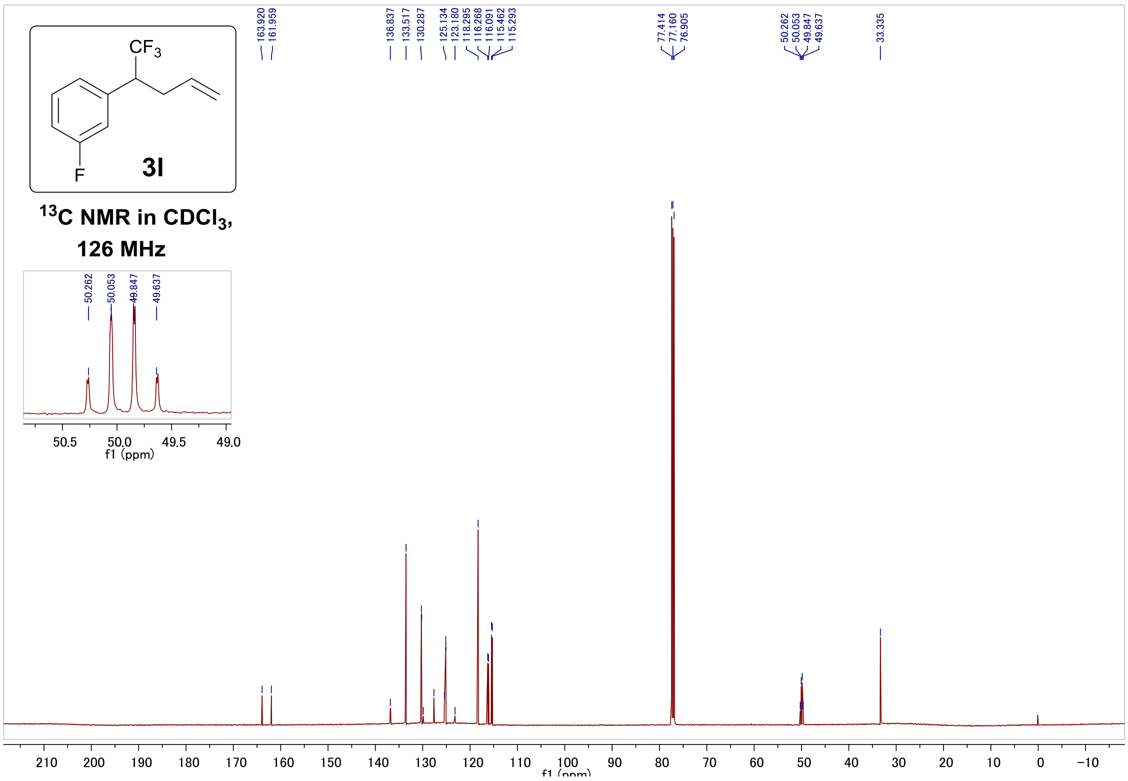

−63.167
−70.143
−70.174
−162.200
CF3
CF3
3j
19F NMR in CDCl3,
282 MHz
−70.143
−70.174
3.00
−70.0 −70.1 −70.2 −70.3
f1 (ppm)
2.98
3.00
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

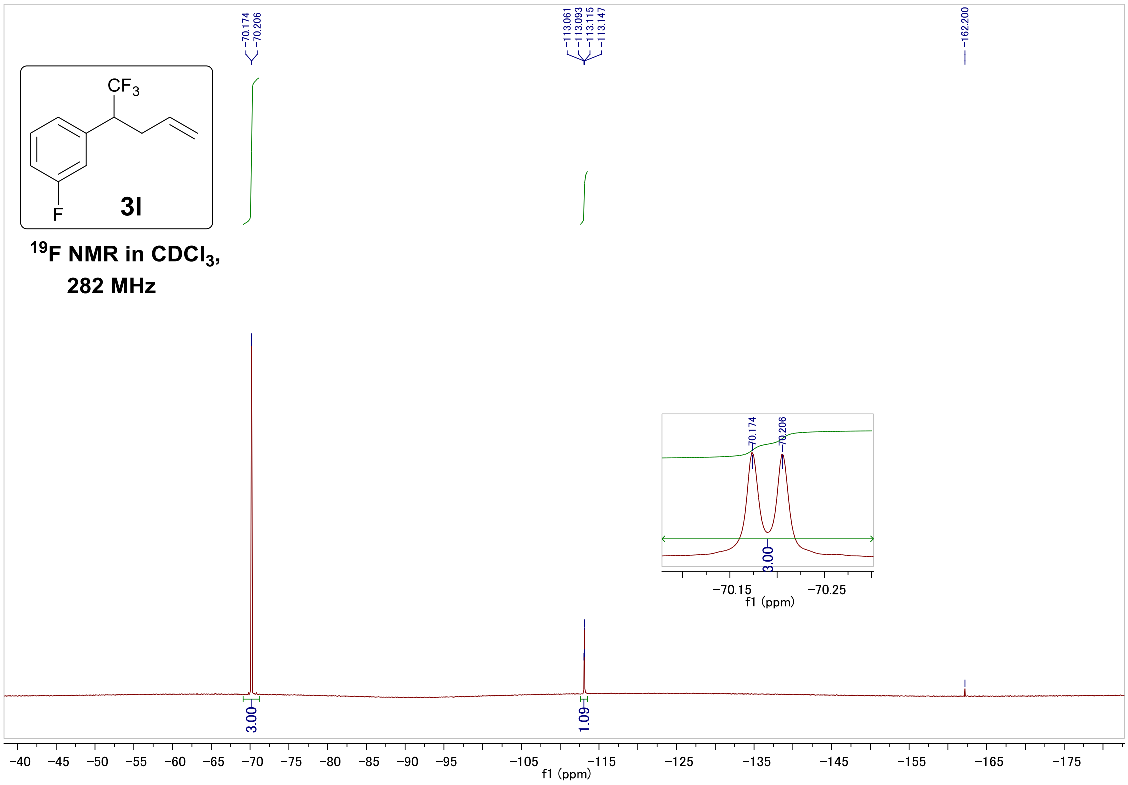

7.650
7.635
7.580
7.545
7.530
7.508
7.493
7.477
7.264
5.564
5.550
5.530
5.516
5.497
5.482
5.051
5.018
4.998
3.413
3.406
3.394
3.389
3.376
3.368
3.350
2.837
2.820
2.808
2.647
2.626
2.619
2.612
2.582
-0.000
CF3
CN
3k
1H NMR in CDCl3,
500 MHz
0.98
0.99
2.00
0.97
1.96
1.00
1.01
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
f1 (ppm)

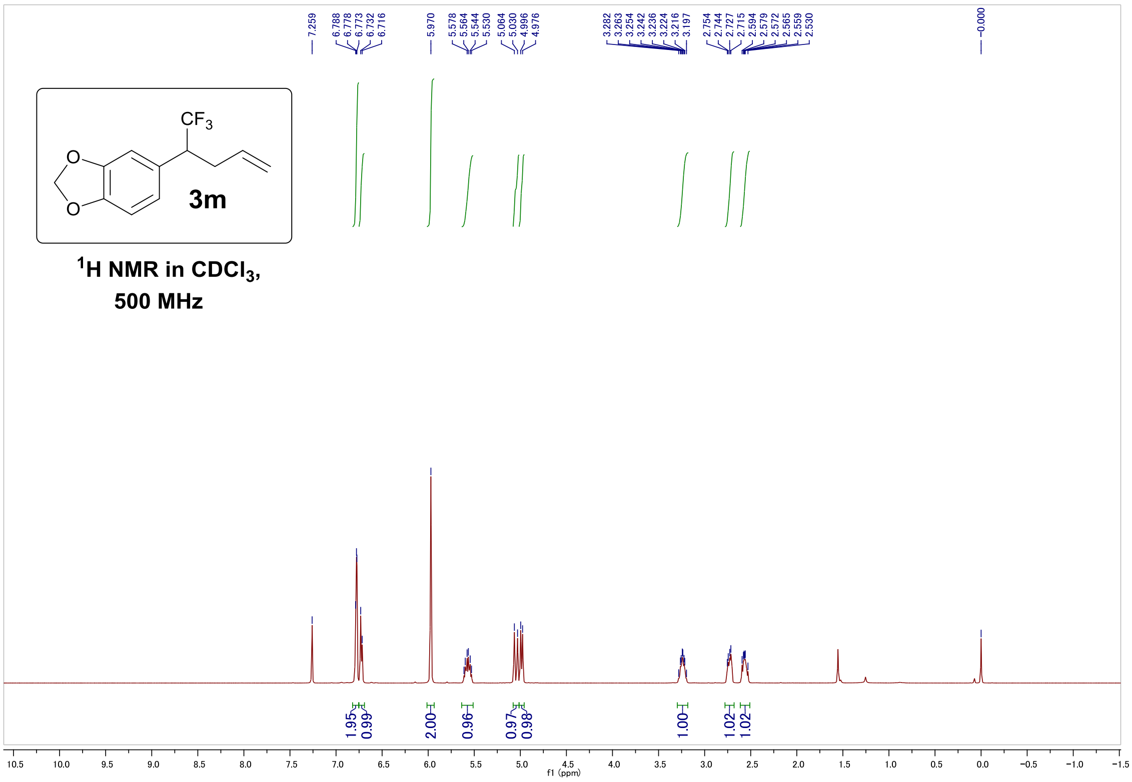

135.988
133.750
132.903
132.109
129.708
129.573
127.343
125.116
122.885
118.925
118.529
113.140
77.414
77.160
76.905
50.153
49.940
49.726
49.511
33.093
CF3
CN
3k
13C NMR in CDCl3,
126 MHz
50.153
49.940
49.726
49.511
50.5
50.0
49.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

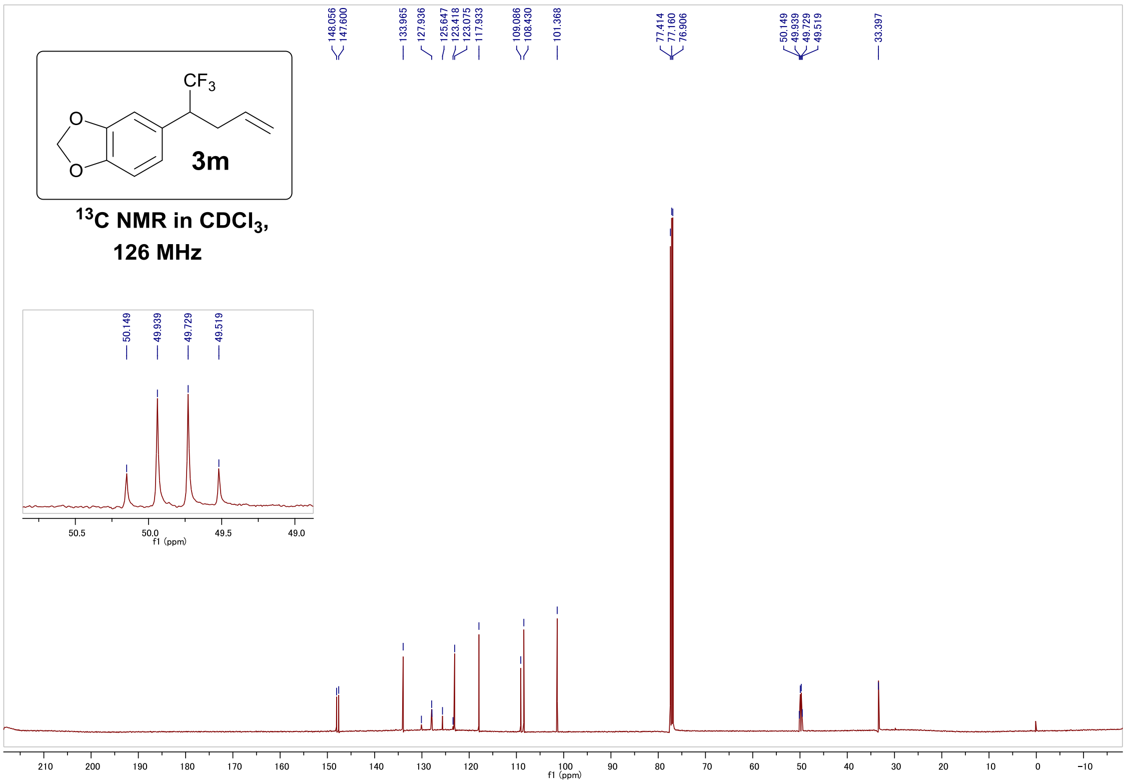

CF3
CN
3k
19F NMR in CDCl3,
282 MHz
−70.120
−70.151
−162.200
3.00
−70.05
−70.15
−70.25
f1 (ppm)
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175

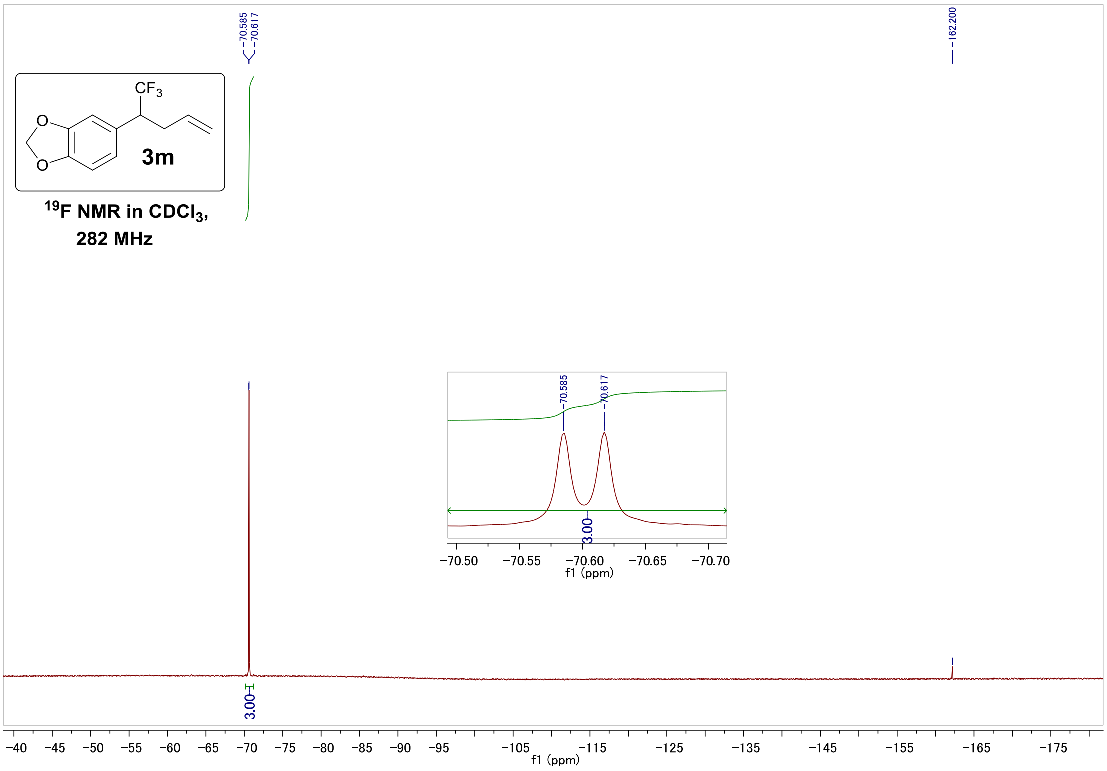

CF3
F
3l
1H NMR in CDCl3,
500 MHz
7.345
7.330
7.317
7.302
7.257
7.069
7.053
7.027
7.019
7.000
5.595
5.581
5.562
5.547
5.528
5.514
5.059
5.025
4.999
4.978
3.371
3.352
3.344
3.332
3.325
3.314
3.306
3.287
2.787
2.771
2.758
2.635
2.620
2.614
2.607
2.601
2.571
−0.000
0.98
2.97
0.98
1.00
0.99
1.00
1.02
1.03
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)

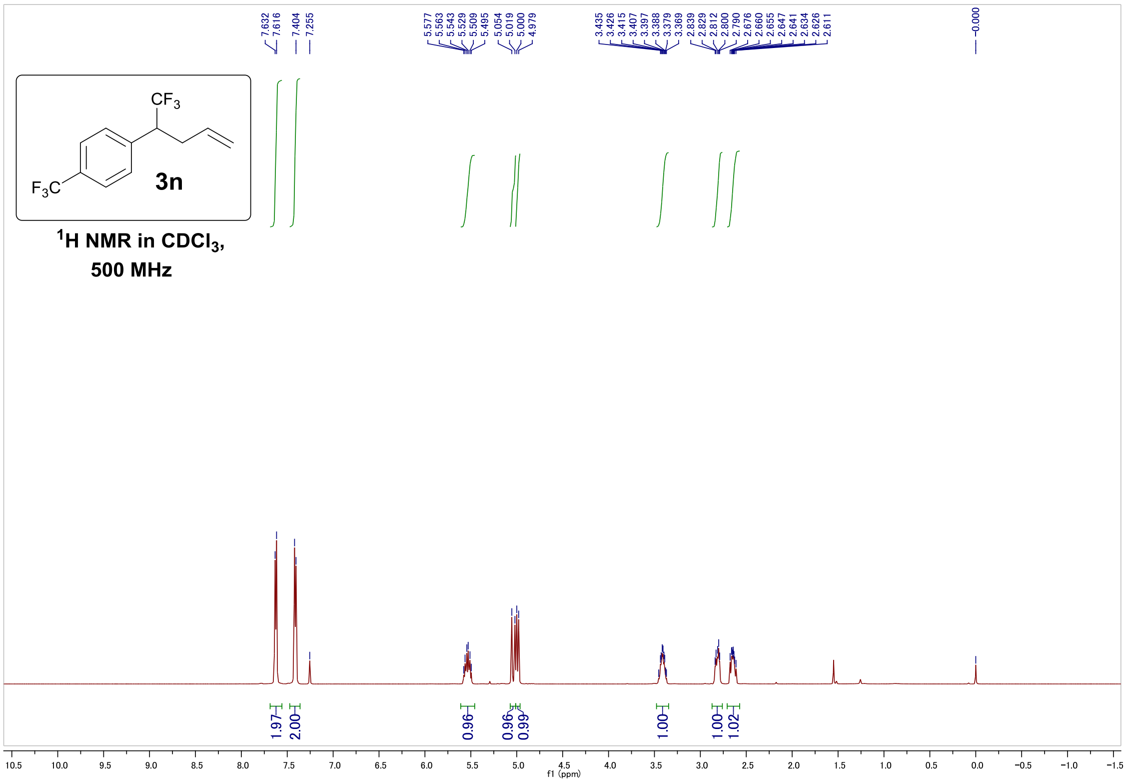

CF3
F
3l
13C NMR in CDCl3, 126 MHz
163.920
161.959
136.837
133.517
130.287
125.134
123.180
118.295
116.268
116.091
115.462
115.293
77.414
77.160
76.905
50.262
50.053
49.847
49.637
33.335
50.5
50.0
49.5
49.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

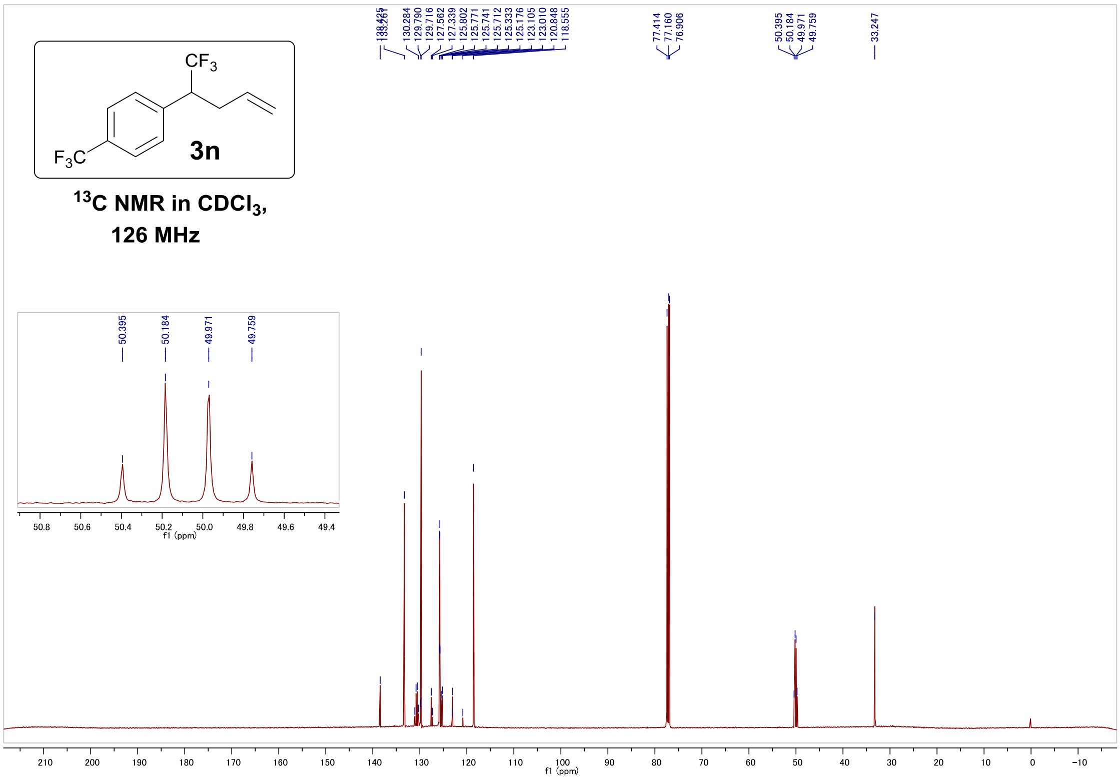

CF3
F
3l
19F NMR in CDCl3, 282 MHz
−70.174
−70.206
−113.061
−113.093
−113.115
−113.147
−162.200
3.00
1.09
−70.15
−70.25
f1 (ppm)
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

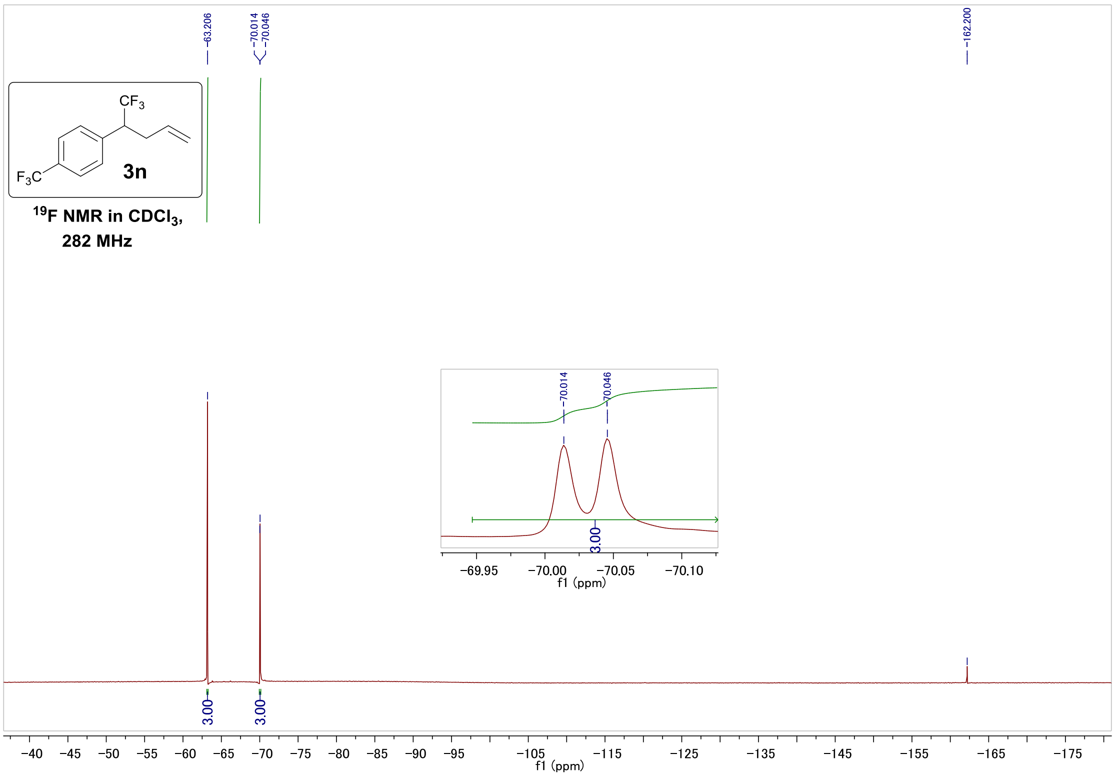

3m
^{1}H NMR in CDCl$_3$,
500 MHz
7.259
6.788
6.778
6.773
6.732
6.716
5.970
5.578
5.564
5.544
5.530
5.064
5.030
4.996
4.976
3.282
3.263
3.254
3.242
3.236
3.224
3.216
3.197
2.754
2.744
2.727
2.715
2.594
2.579
2.572
2.565
2.559
2.530
-0.000
1.95
0.99
2.00
0.96
0.97
0.98
1.00
1.02
1.02
f1 (ppm)

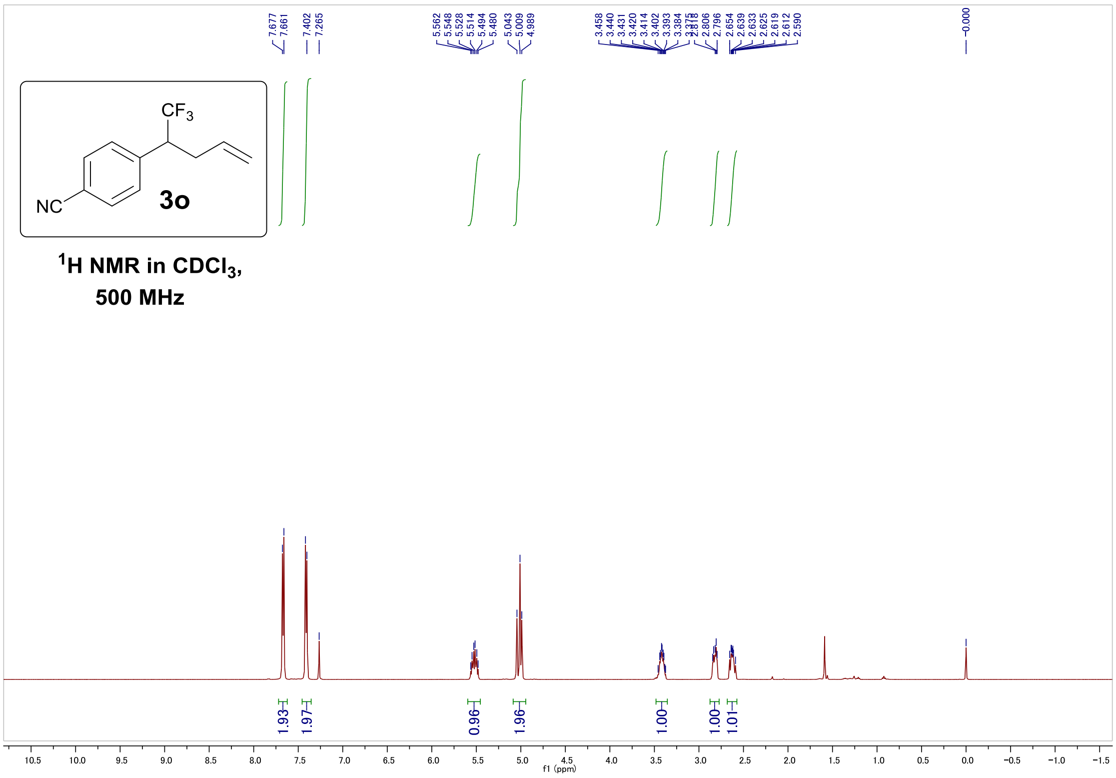

3m
^{13}C NMR in CDCl$_3$,
126 MHz
148.056
147.600
133.965
127.936
125.647
123.418
123.075
117.933
109.086
108.430
101.368
77.414
77.160
76.906
50.149
49.939
49.729
49.519
33.397
f1 (ppm)

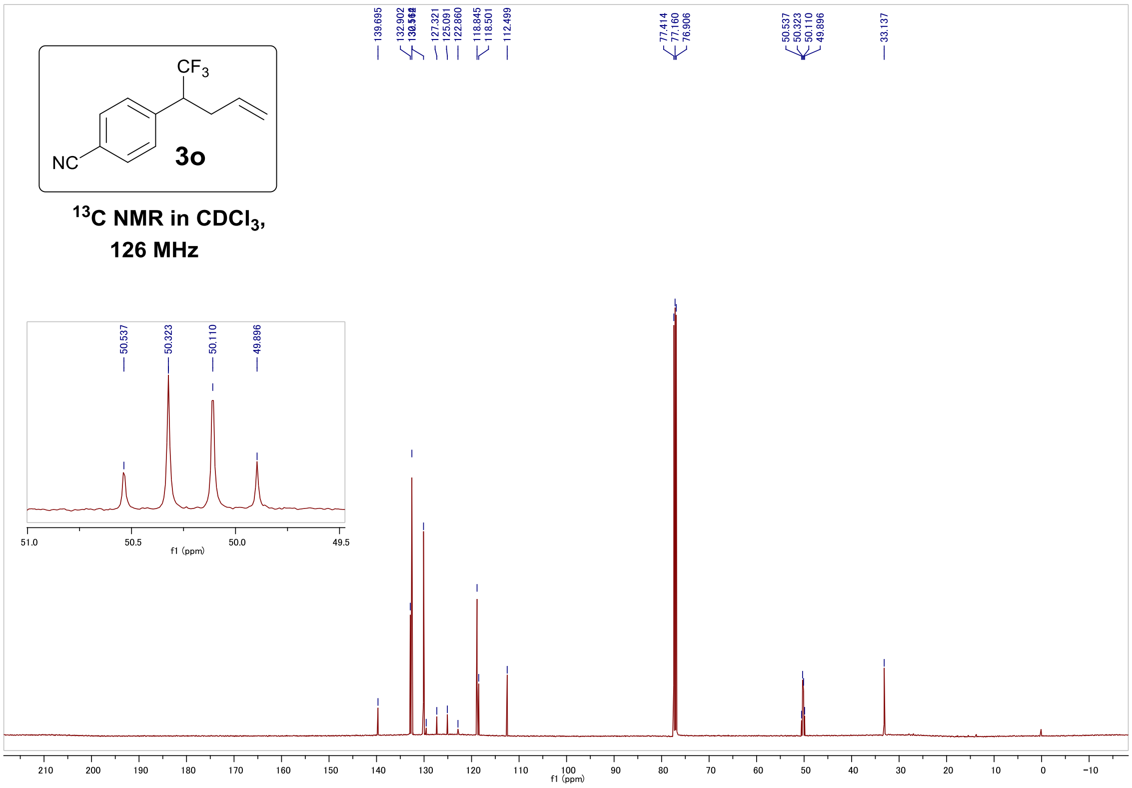

−70.585
−70.617
−162.200
CF3
O
O
3m
19F NMR in CDCl3,
282 MHz
3.00
−70.50
−70.55
−70.60
−70.65
−70.70
f1 (ppm)
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

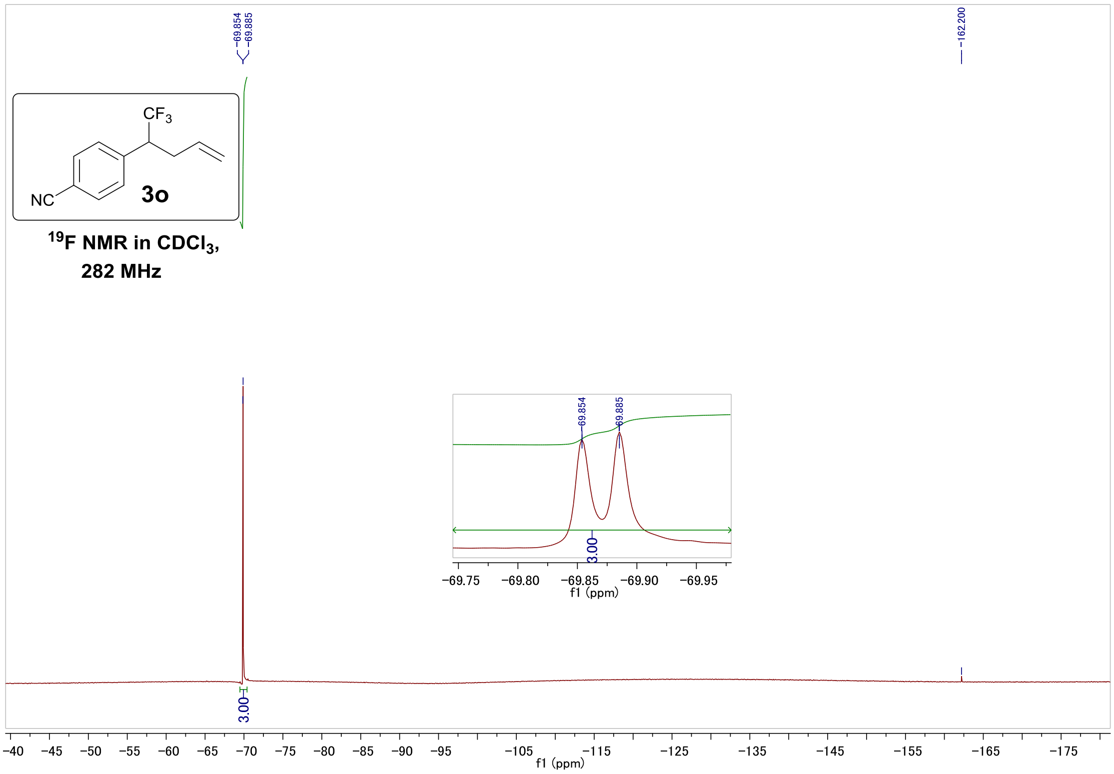

7.632
7.616
7.404
7.255
5.577
5.563
5.543
5.529
5.509
5.495
5.054
5.019
5.000
4.979
3.435
3.426
3.415
3.407
3.397
3.388
3.379
3.369
2.839
2.829
2.812
2.800
2.790
2.676
2.660
2.655
2.647
2.641
2.634
2.626
2.611
−0.000
CF3
F3C
3n
1H NMR in CDCl3,
500 MHz
1.97
2.00
0.96
0.96
0.99
1.00
1.00
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)

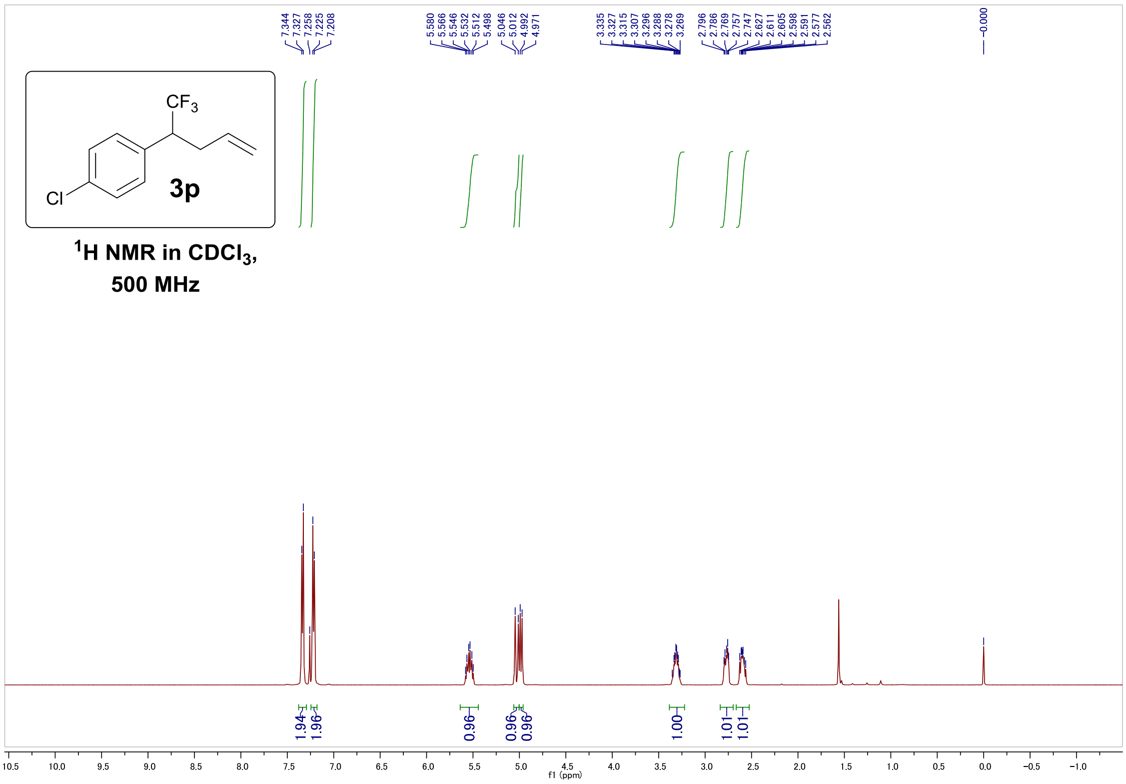

138.425
133.261
130.284
129.790
129.716
127.562
127.339
125.802
125.771
125.741
125.712
125.333
125.176
123.105
123.010
120.848
118.555
77.414
77.160
76.906
50.395
50.184
49.971
49.759
33.247
CF3
F3C
3n
13C NMR in CDCl3,
126 MHz
50.395
50.184
49.971
49.759
50.8
50.6
50.4
50.2
50.0
49.8
49.6
49.4
f1 (ppm)
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)

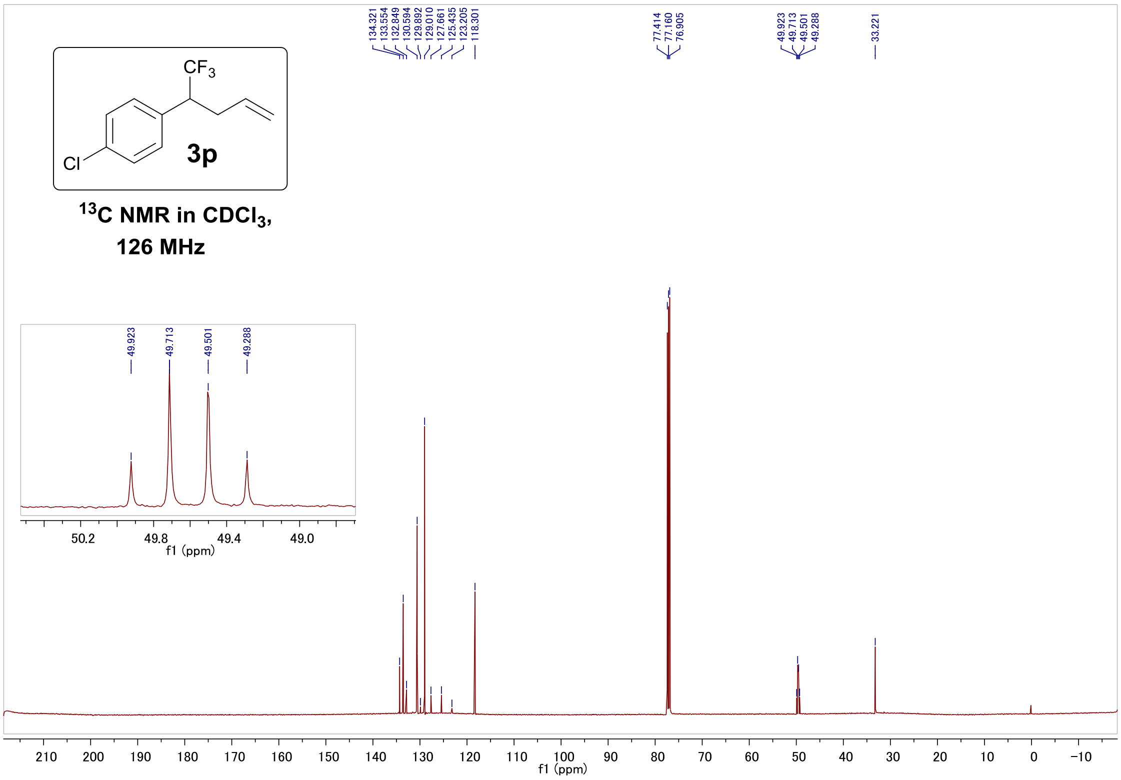

-63.206
-70.014
-70.046
-162.200
CF3
F3C
3n
19F NMR in CDCl3,
282 MHz
-70.014
-70.046
3.00
−69.95
−70.00
−70.05
−70.10
f1 (ppm)
3.00
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

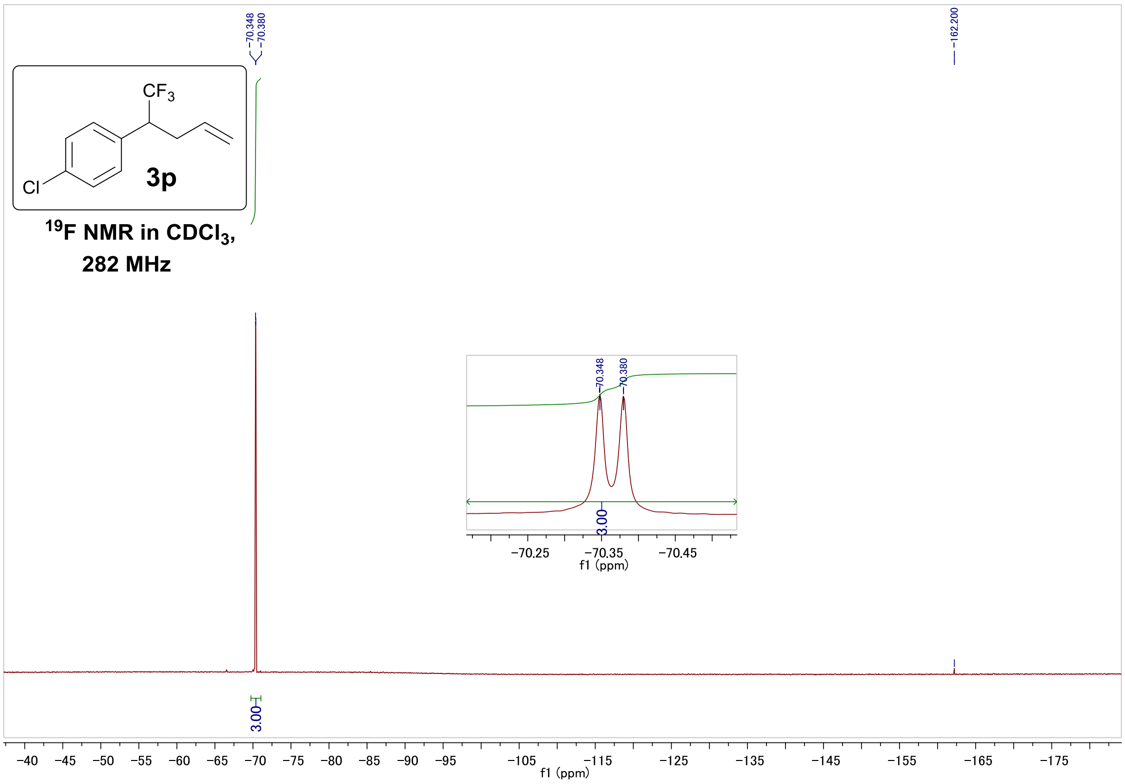

7.677
7.661
7.402
7.265
5.562
5.548
5.528
5.514
5.494
5.480
5.043
5.009
4.989
3.458
3.440
3.431
3.420
3.414
3.402
3.393
3.384
2.806
2.796
2.654
2.639
2.633
2.625
2.619
2.612
2.590
0.000
CF3
NC
3o
1H NMR in CDCl3, 500 MHz
1.93
1.97
0.96
1.96
1.00
1.00
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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
−1.5
f1 (ppm)

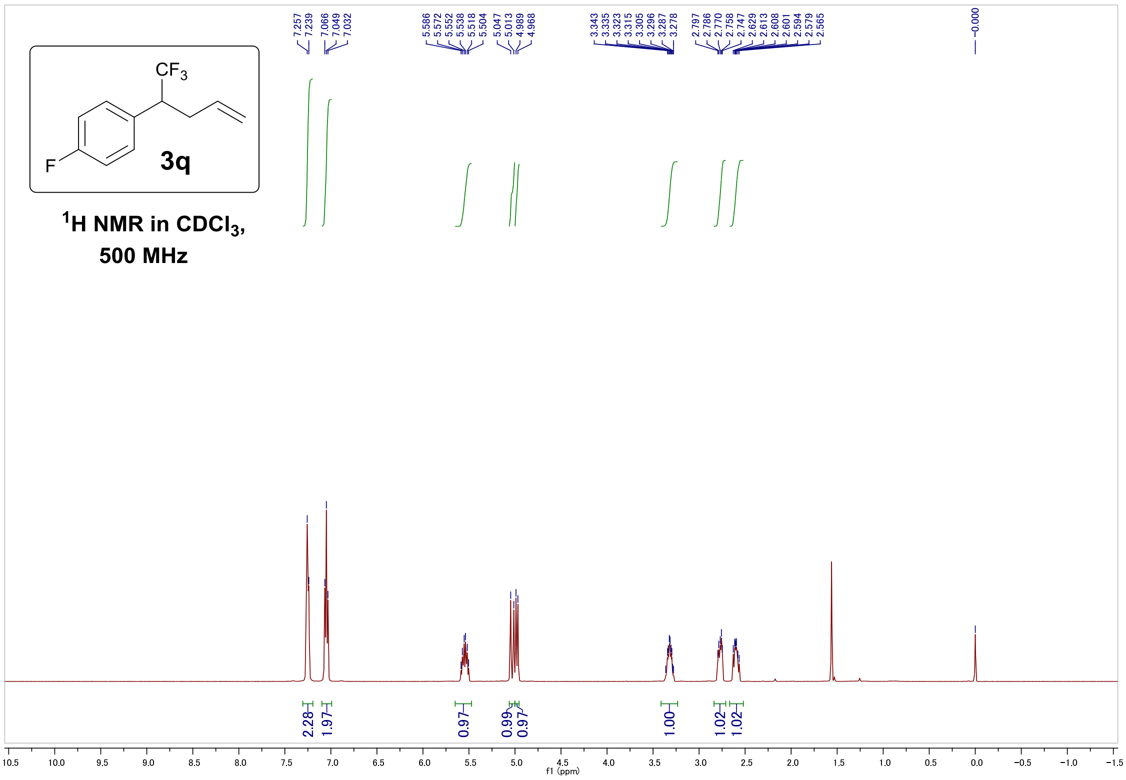

139.695
132.902
127.321
125.091
122.860
118.845
118.501
112.499
77.414
77.160
76.906
50.537
50.323
50.110
49.896
33.137
CF3
NC
3o
13C NMR in CDCl3, 126 MHz
50.537
50.323
50.110
49.896
51.0
50.5
50.0
49.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

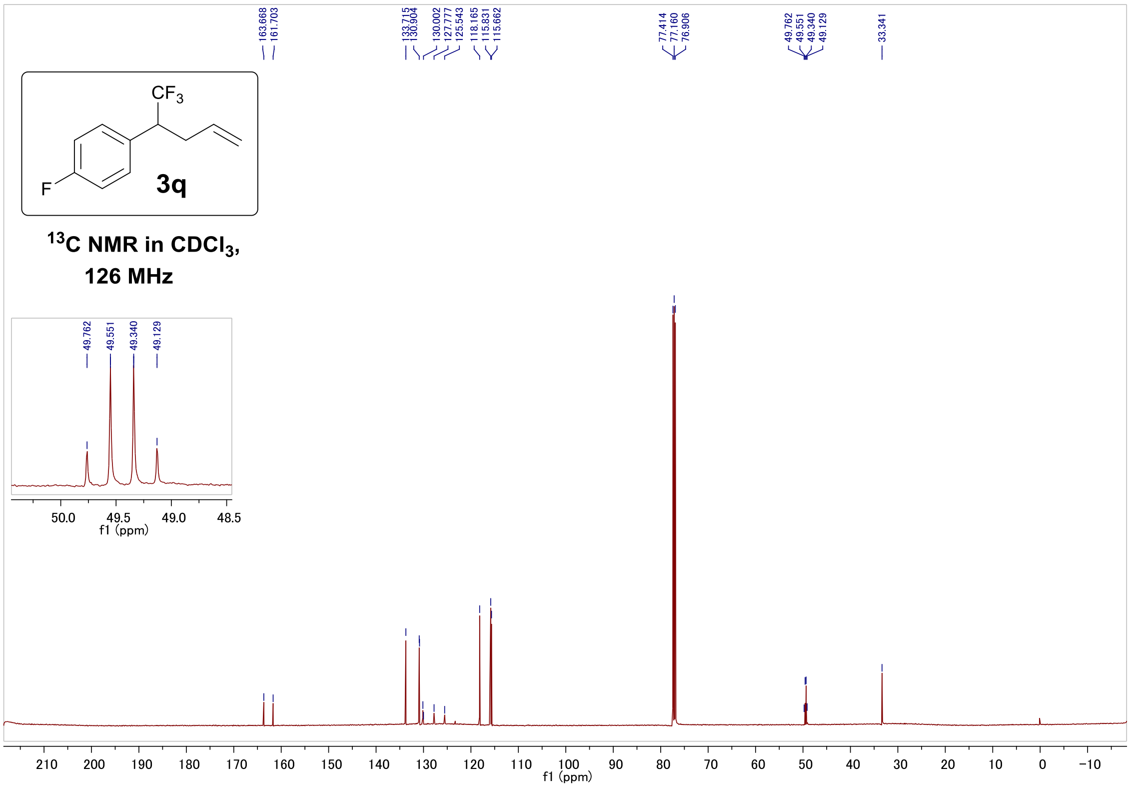

−69.854
−69.885
−162.200
CF$_3$
NC
3o
^{19}F NMR in CDCl$_3$,
282 MHz
69.854
69.885
3.00
−69.75
−69.80
−69.85
−69.90
−69.95
f1 (ppm)
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

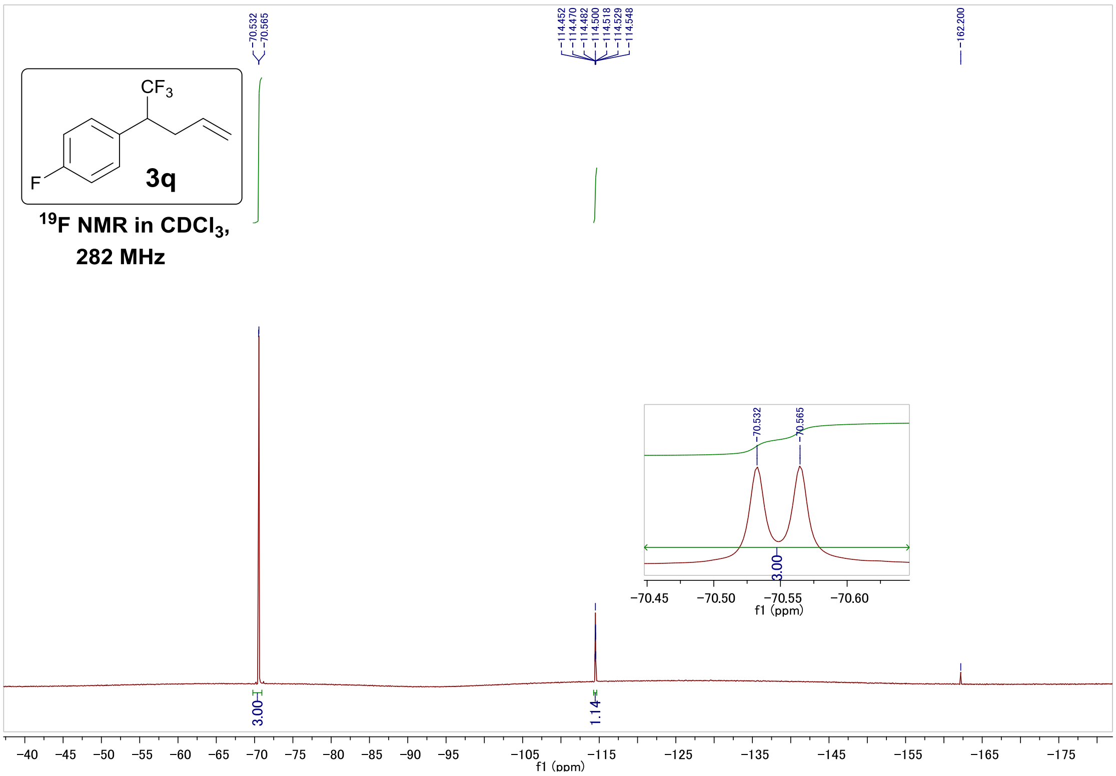

7.344
7.327
7.258
7.225
7.208
5.580
5.566
5.546
5.532
5.512
5.498
5.046
5.012
4.992
4.971
3.335
3.327
3.315
3.307
3.296
3.288
3.278
3.269
2.796
2.786
2.769
2.757
2.747
2.627
2.611
2.605
2.598
2.591
2.577
2.562
−0.000
CF$_3$
Cl
3p
^{1}H NMR in CDCl$_3$,
500 MHz
1.94
1.96
0.96
0.96
0.96
1.00
1.01
1.01
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
f1 (ppm)

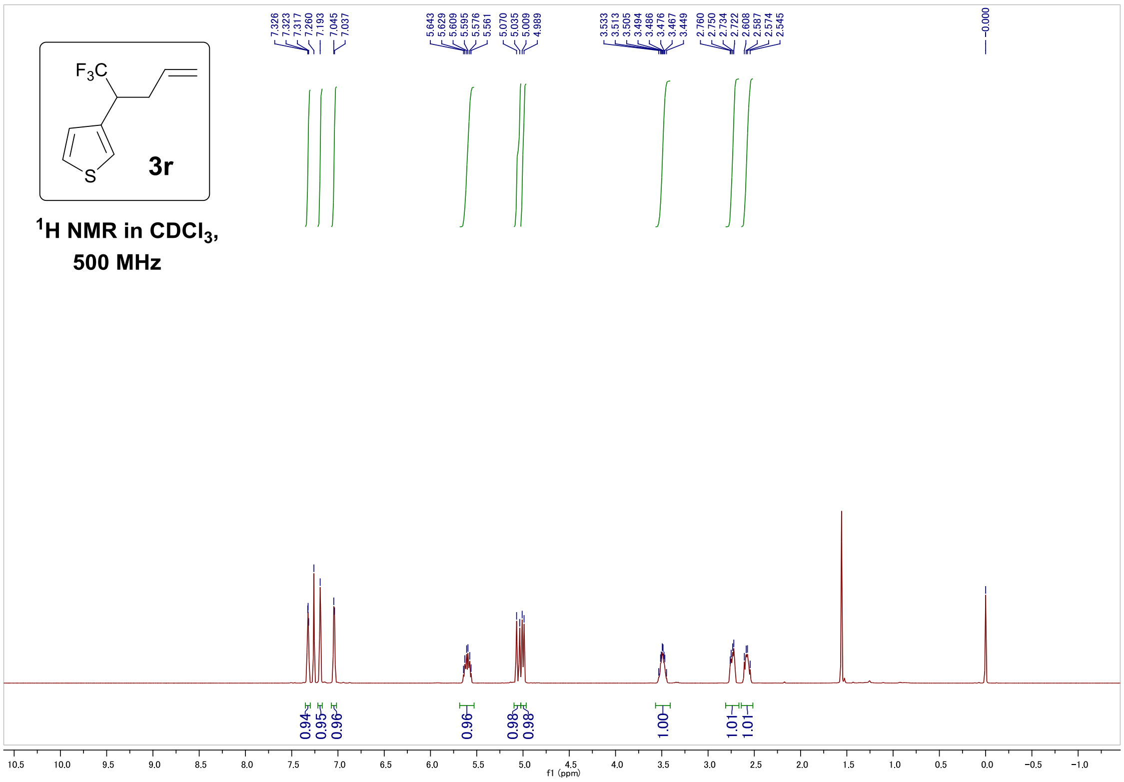

134.321
133.554
132.849
130.594
129.892
129.010
127.661
125.435
123.205
118.301
77.414
77.160
76.905
49.923
49.713
49.501
49.288
33.221
CF3
Cl
3p
13C NMR in CDCl3,
126 MHz
49.923
49.713
49.501
49.288
50.2
49.8
49.4
49.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

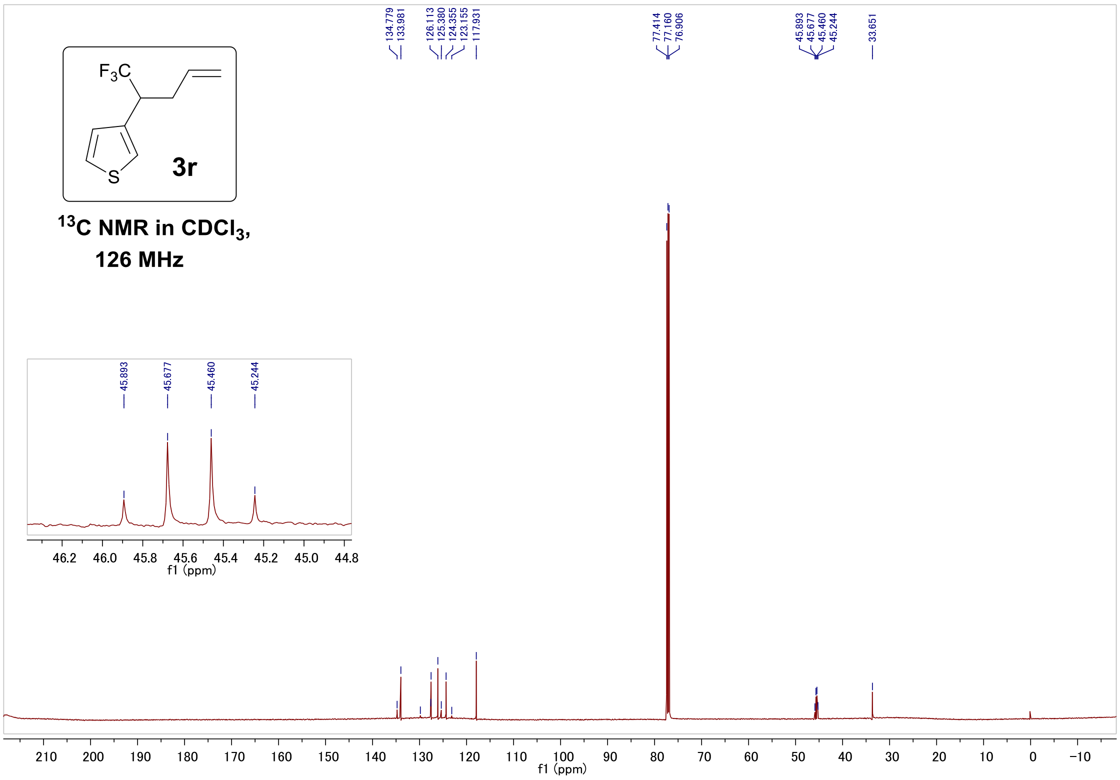

−70.348
−70.380
−162.200
CF3
Cl
3p
19F NMR in CDCl3,
282 MHz
−70.348
−70.380
3.00
−70.25
−70.35
−70.45
f1 (ppm)
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

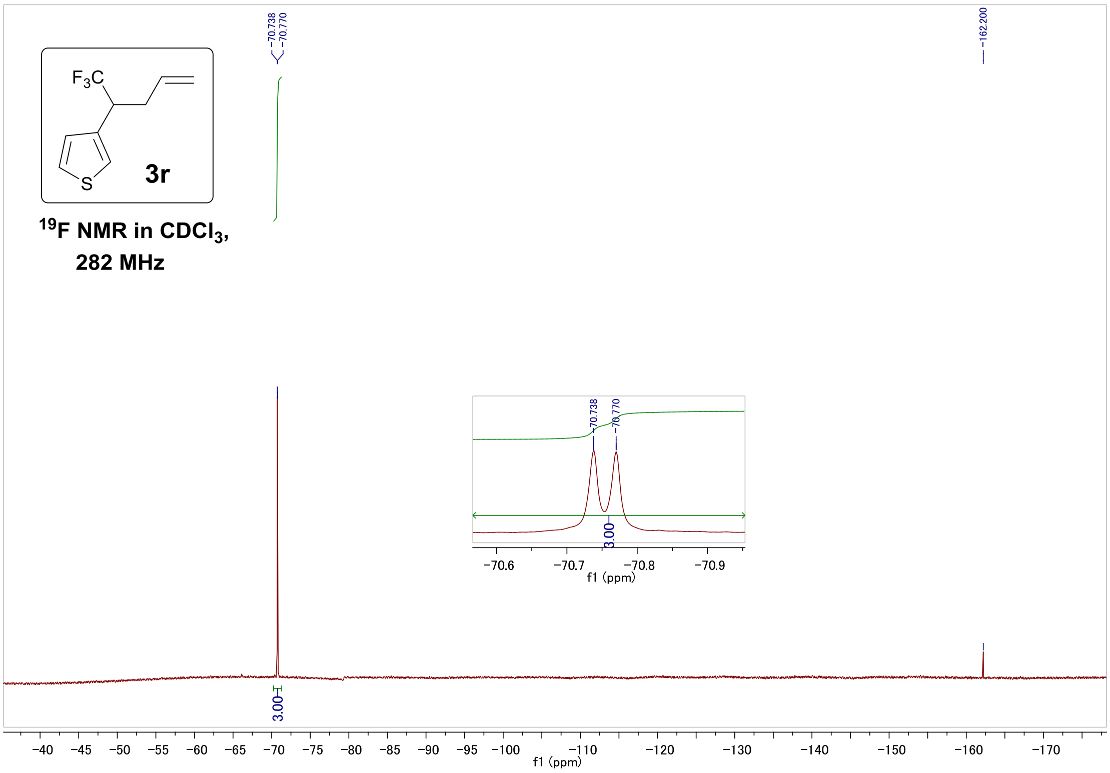

7.257
7.239
7.066
7.049
7.032
5.586
5.572
5.552
5.538
5.518
5.504
5.047
5.013
4.989
4.968
3.343
3.335
3.323
3.315
3.305
3.296
3.287
3.278
2.797
2.786
2.770
2.758
2.747
2.629
2.613
2.608
2.601
2.594
2.579
2.565
0.000
CF3
F
3q
1H NMR in CDCl3,
500 MHz
2.28
1.97
0.97
0.99
0.97
1.00
1.02
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
f1 (ppm)

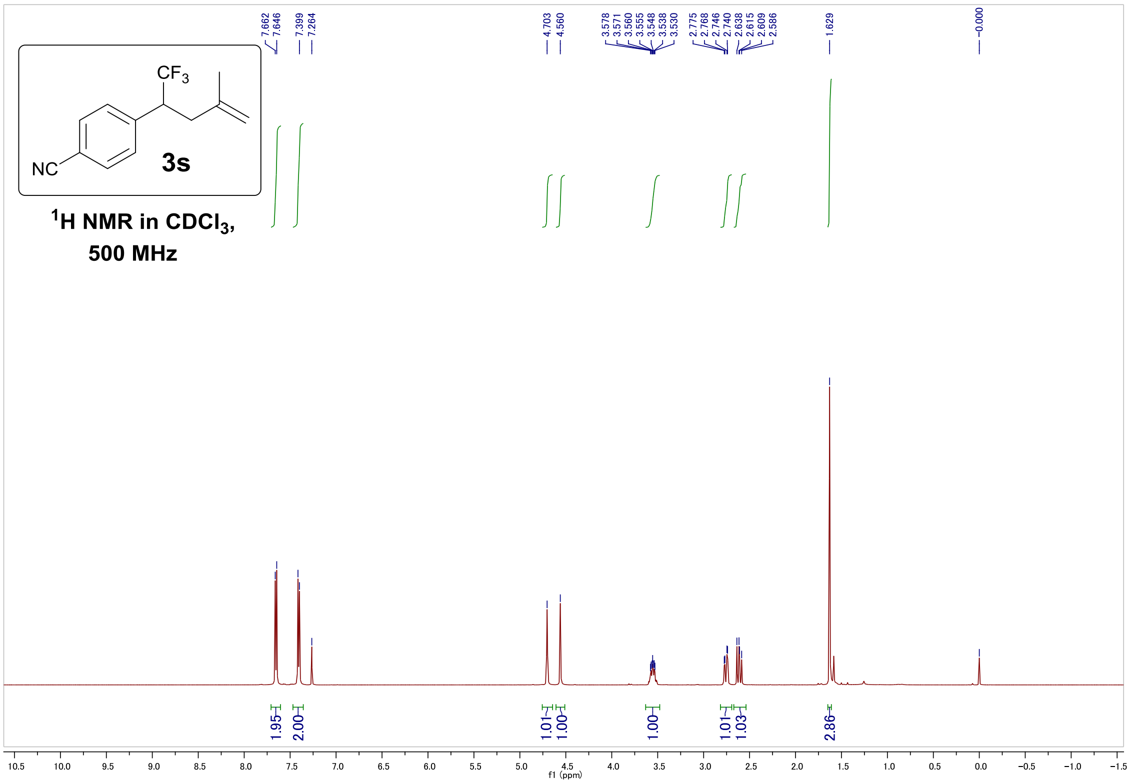

163.668
161.703
133.715
130.904
130.002
127.777
125.543
118.165
115.831
115.662
77.414
77.160
76.906
49.762
49.551
49.340
49.129
33.341
CF3
F
3q
13C NMR in CDCl3,
126 MHz
49.762
49.551
49.340
49.129
50.0
49.5
49.0
48.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

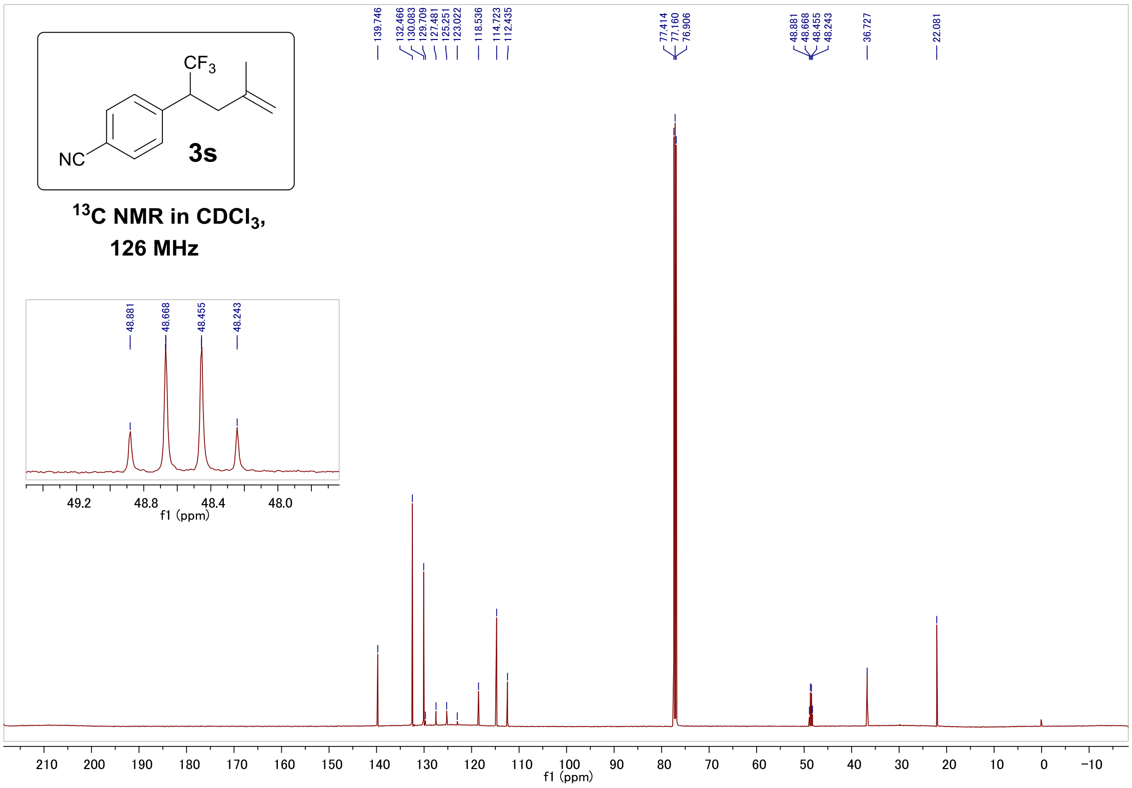

CF$_3$
F
3q
^{19}F NMR in CDCl$_3$,
282 MHz
-70.532
-70.565
-114.452
-114.470
-114.482
-114.500
-114.518
-114.529
-114.548
-162.200
3.00
1.14
-70.45
-70.50
-70.55
-70.60
f1 (ppm)
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165 -175
f1 (ppm)

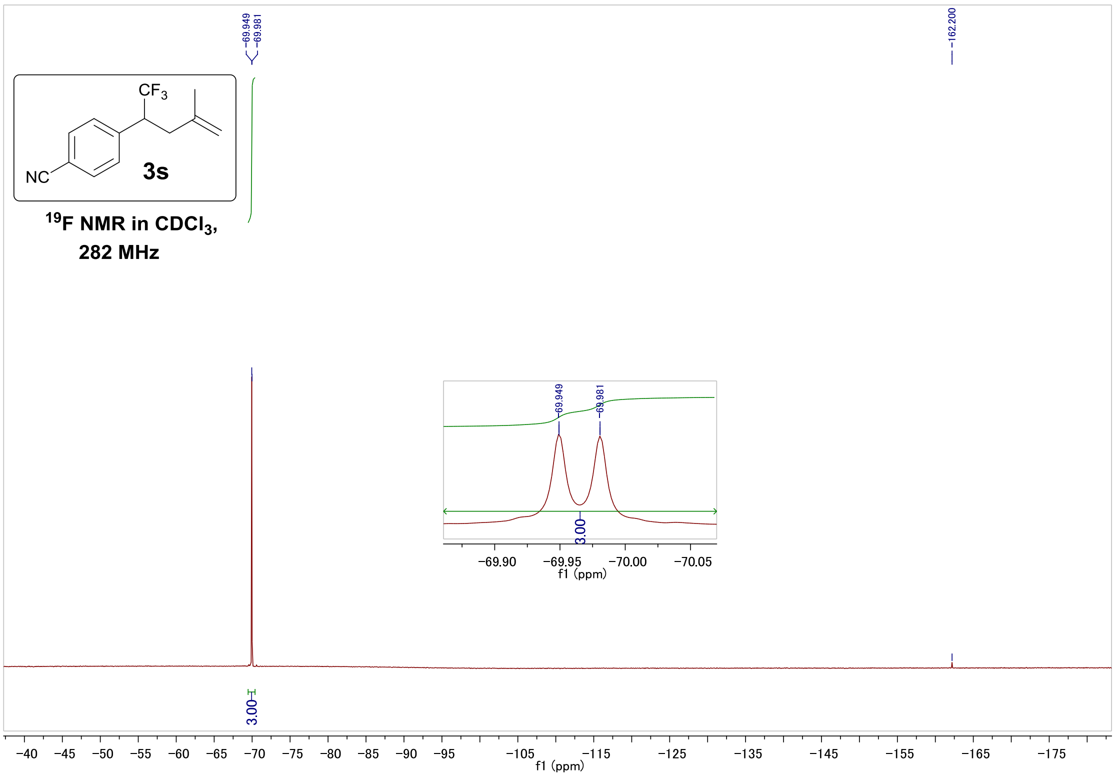

F$_3$C
S
3r
^{1}H NMR in CDCl$_3$,
500 MHz
7.326
7.323
7.317
7.260
7.193
7.045
7.037
5.643
5.629
5.609
5.595
5.576
5.561
5.070
5.035
5.009
4.989
3.533
3.513
3.505
3.494
3.486
3.476
3.467
3.449
2.760
2.750
2.734
2.722
2.608
2.587
2.574
2.545
-0.000
0.94
0.95
0.96
0.96
0.98
0.98
1.00
1.01
1.01
10.5 10.0 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
f1 (ppm)

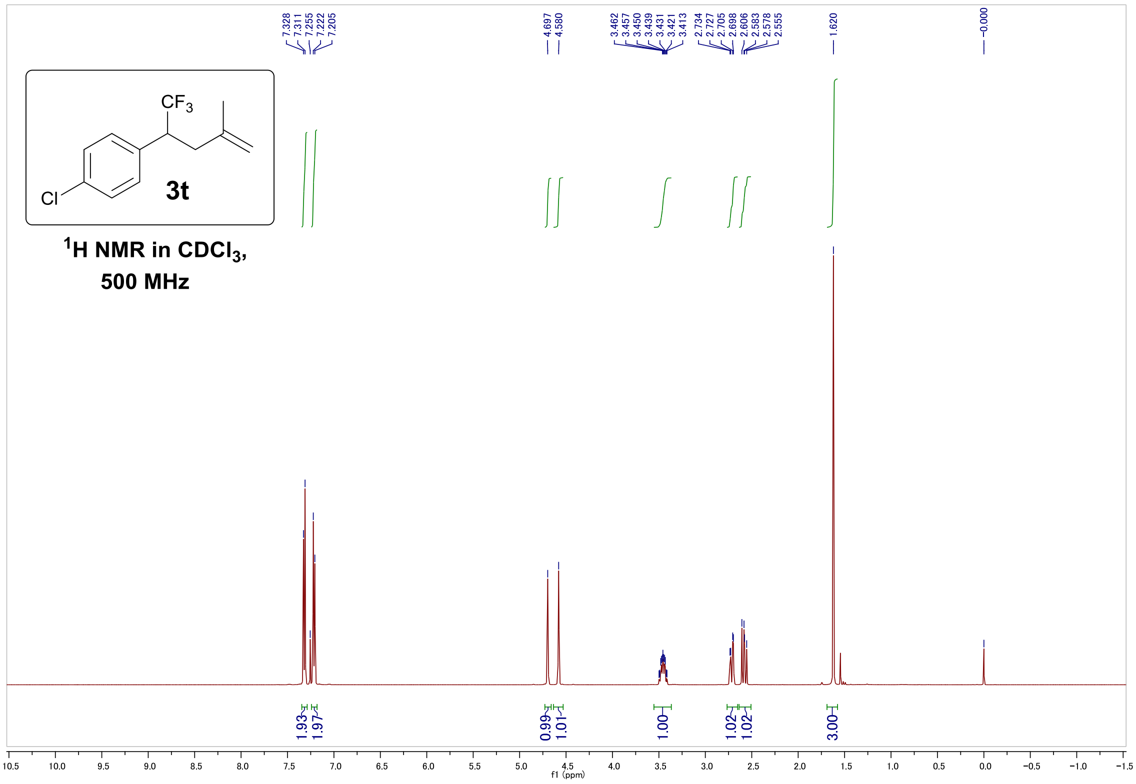

F_3C
S
3r
^{13}C NMR in $CDCl_3$,
126 MHz
134.779
133.981
126.113
125.380
124.355
123.155
117.931
77.414
77.160
76.906
45.893
45.677
45.460
45.244
33.651
46.2 46.0 45.8 45.6 45.4 45.2 45.0 44.8
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

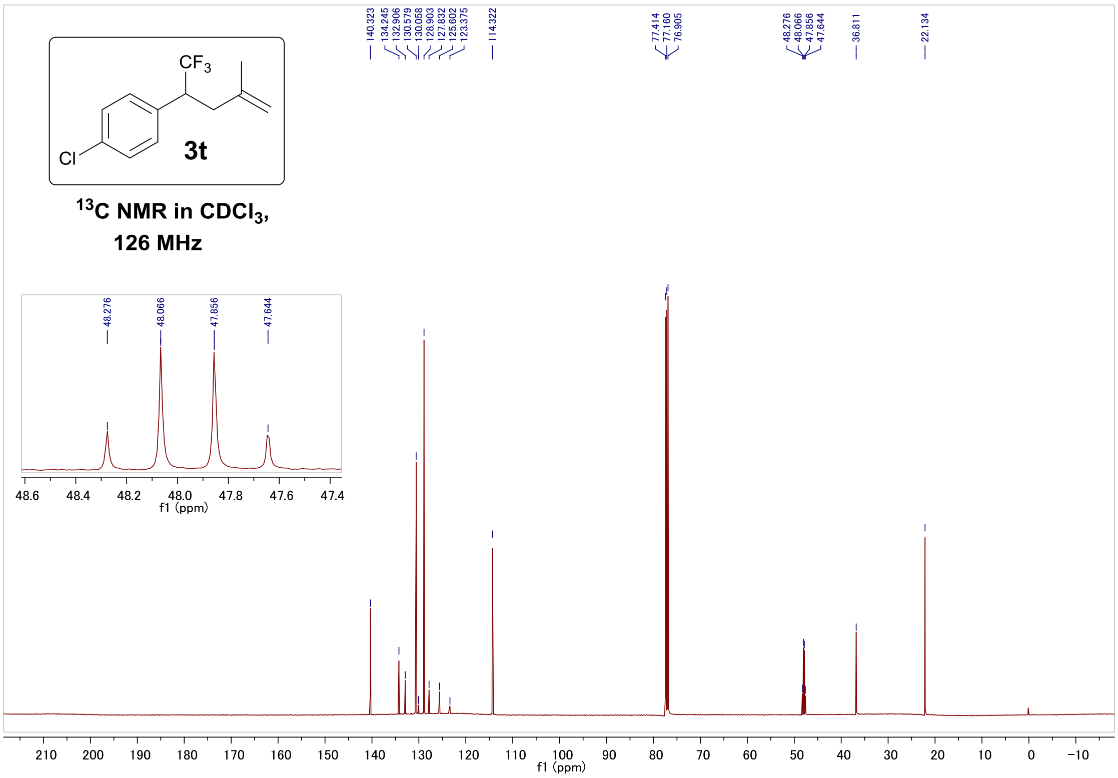

F_3C
S
3r
^{19}F NMR in $CDCl_3$,
282 MHz
−70.738
−70.770
−162.200
3.00
−70.6 −70.7 −70.8 −70.9
f1 (ppm)
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −110 −120 −130 −140 −150 −160 −170
f1 (ppm)


7.662
7.646
7.399
7.264
4.703
4.560
3.578
3.571
3.560
3.555
3.548
3.538
3.530
2.775
2.768
2.746
2.740
2.638
2.615
2.609
2.586
1.629
-0.000
CF3
NC
3s
1H NMR in CDCl3,
500 MHz
1.95
2.00
1.01
1.00
1.00
1.01
1.03
2.86
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

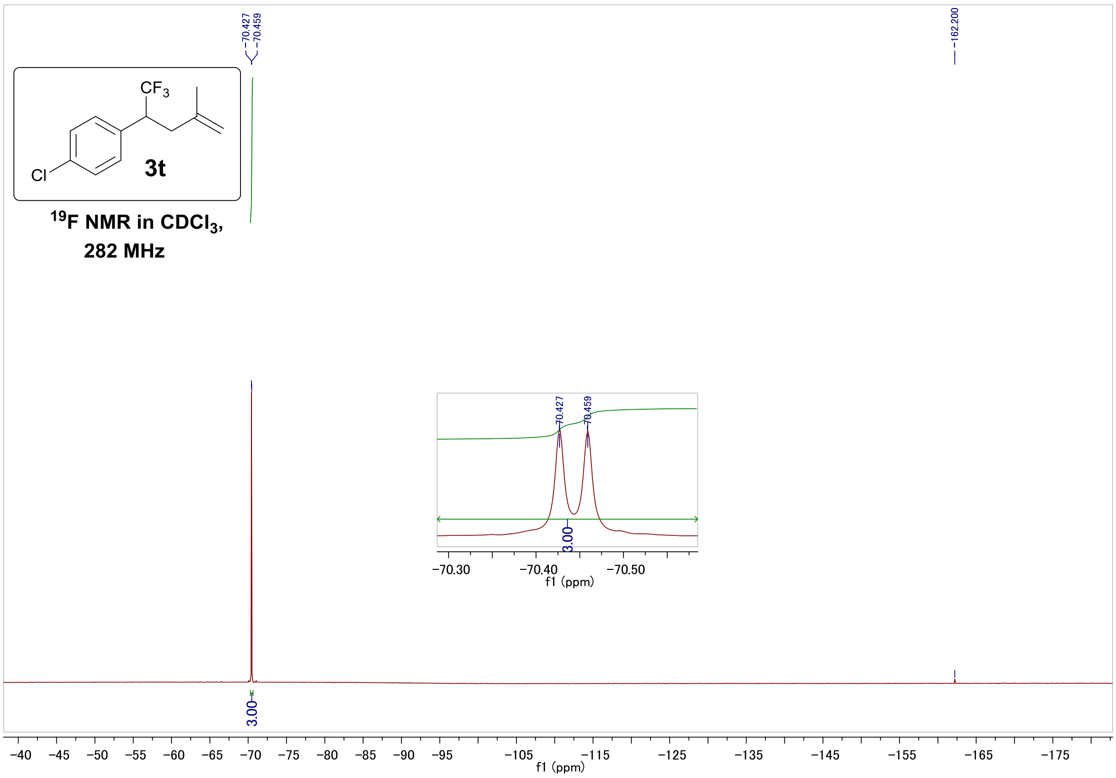

139.746
132.466
130.083
129.709
127.481
125.251
123.022
118.536
114.723
112.435
77.414
77.160
76.906
48.881
48.668
48.455
48.243
36.727
22.081
CF3
NC
3s
13C NMR in CDCl3,
126 MHz
48.881
48.668
48.455
48.243
49.2 48.8 48.4 48.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CF3
NC
3s
19F NMR in CDCl3,
282 MHz
-69.949
-69.981
-162.200
3.00
-69.90
-69.95
-70.00
-70.05
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)

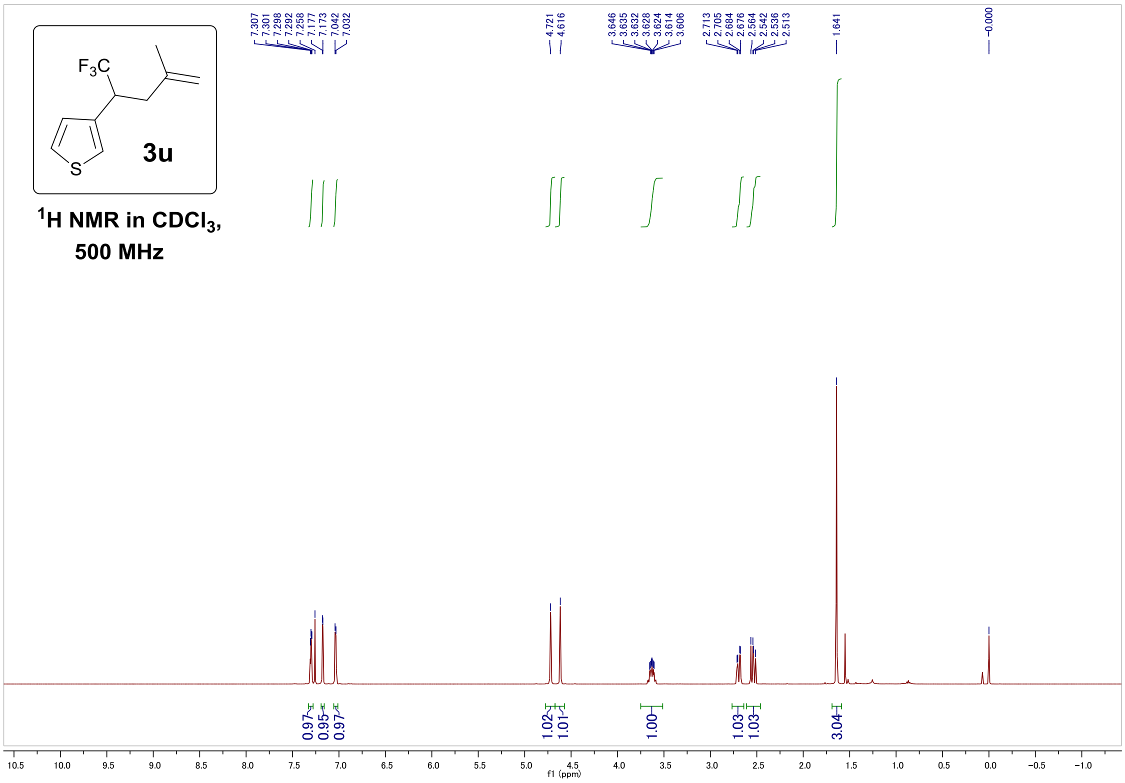

CF3
Cl
3t
1H NMR in CDCl3,
500 MHz
7.328
7.311
7.255
7.222
7.205
4.697
4.580
3.462
3.457
3.450
3.439
3.431
3.421
3.413
2.734
2.727
2.705
2.698
2.606
2.583
2.578
2.555
1.620
-0.000
1.93
1.97
0.99
1.01
1.00
1.02
1.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

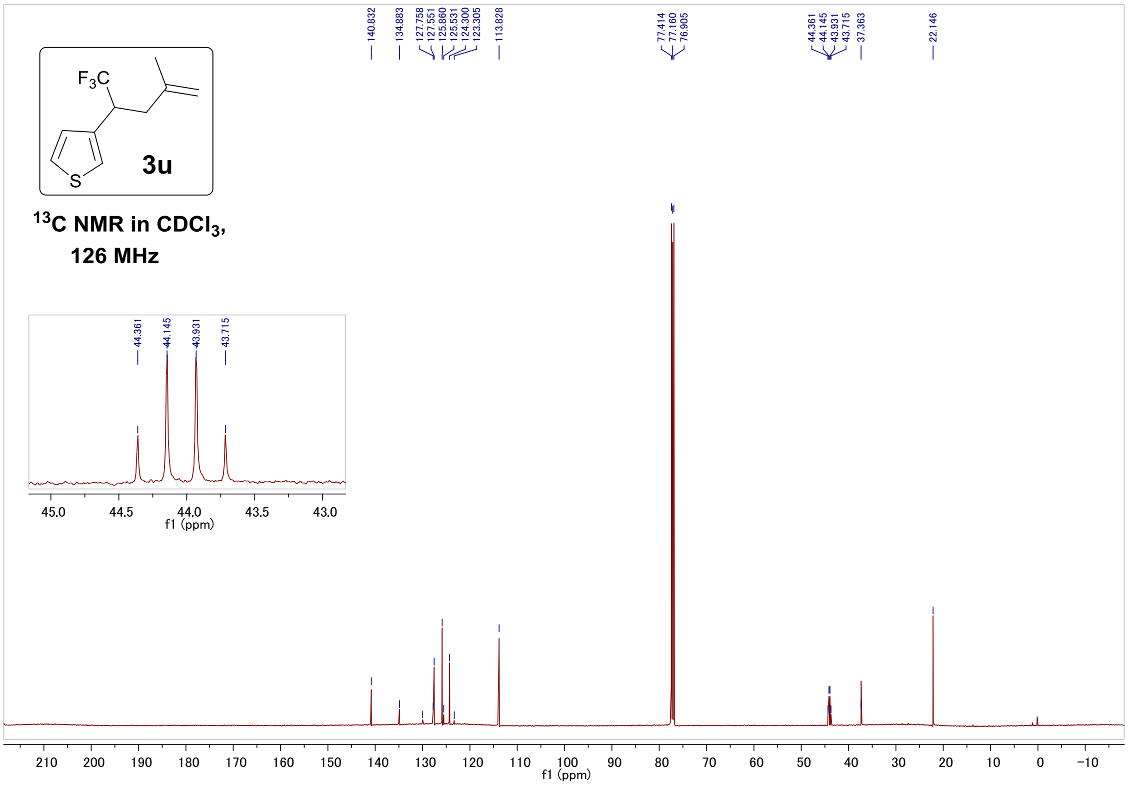


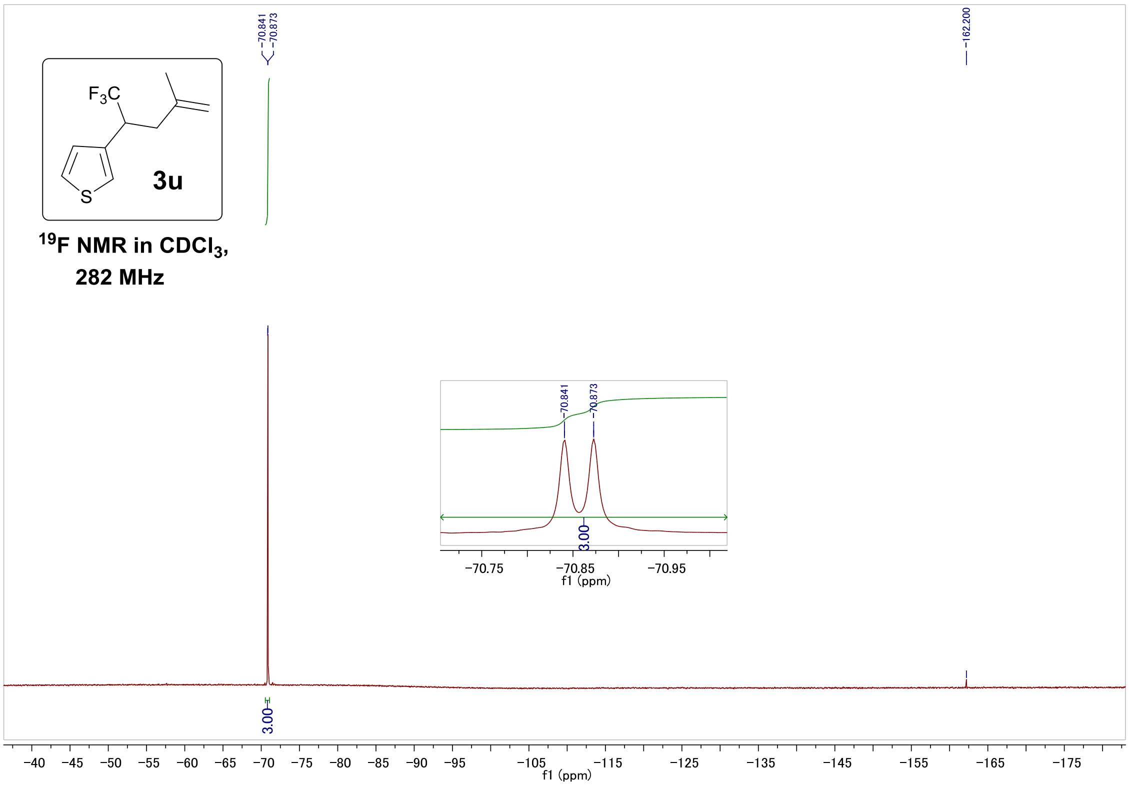
^{13}C NMR in $CDCl_3$, 126 MHz



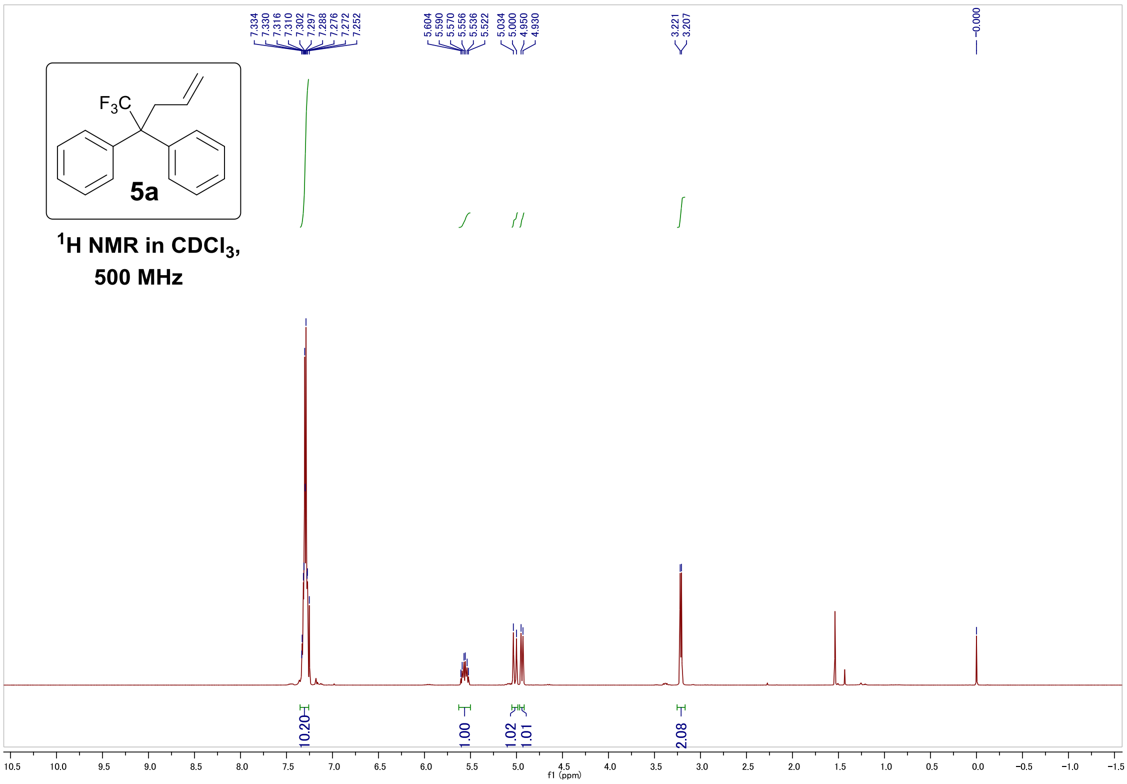
^{19}F NMR in $CDCl_3$, 282 MHz


F3C
S
3u
1H NMR in CDCl3,
500 MHz
7.307
7.301
7.298
7.292
7.258
7.177
7.173
7.042
7.032
4.721
4.616
3.646
3.635
3.632
3.628
3.624
3.614
3.606
2.713
2.705
2.684
2.676
2.564
2.542
2.536
2.513
1.641
-0.000
0.97
0.95
0.97
1.02
1.01
1.00
1.03
1.03
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

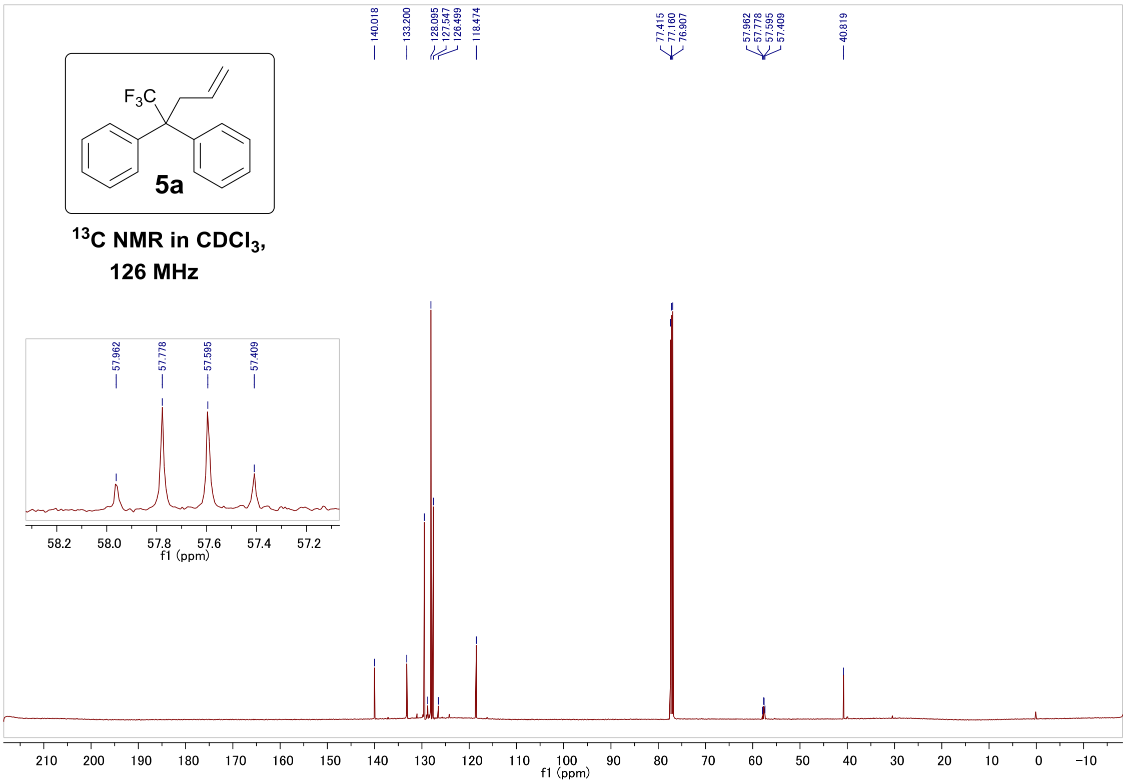

F3C
S
3u
13C NMR in CDCl3,
126 MHz
140.832
134.883
127.758
127.551
125.860
125.531
124.300
123.305
113.828
77.414
77.160
76.905
44.361
44.145
43.931
43.715
37.363
22.146
44.361
44.145
43.931
43.715
45.0
44.5
44.0
43.5
43.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

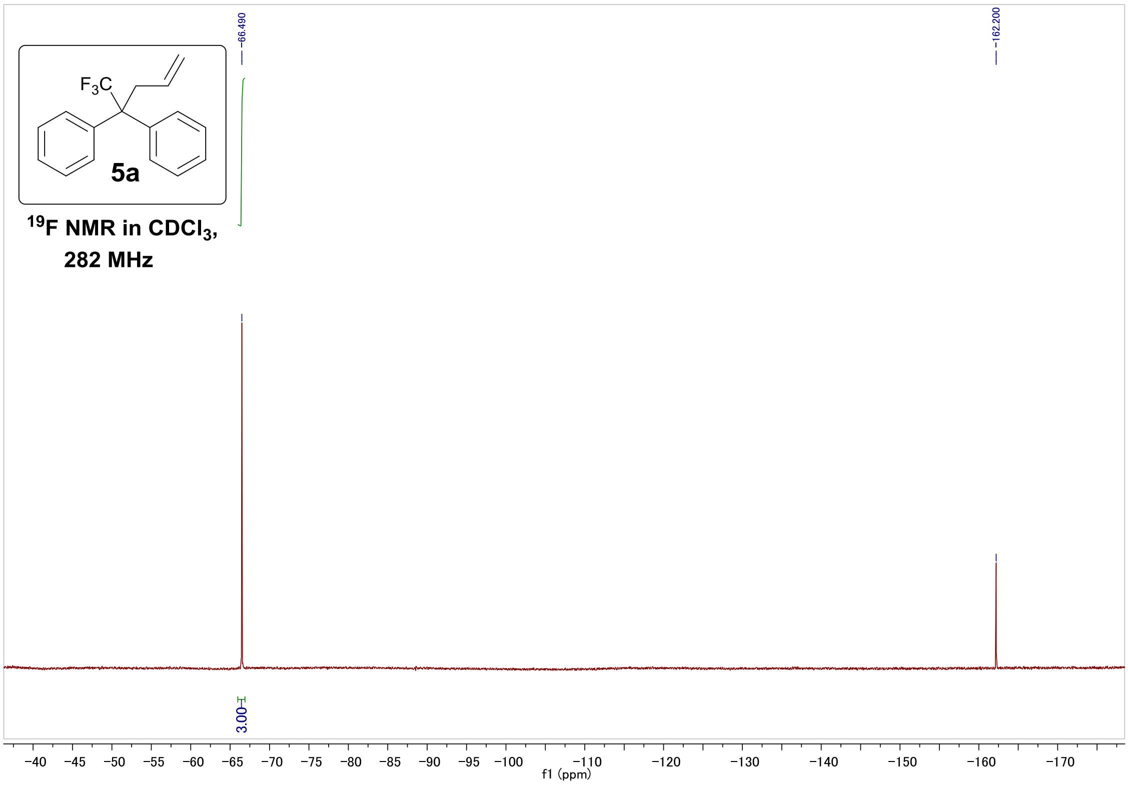


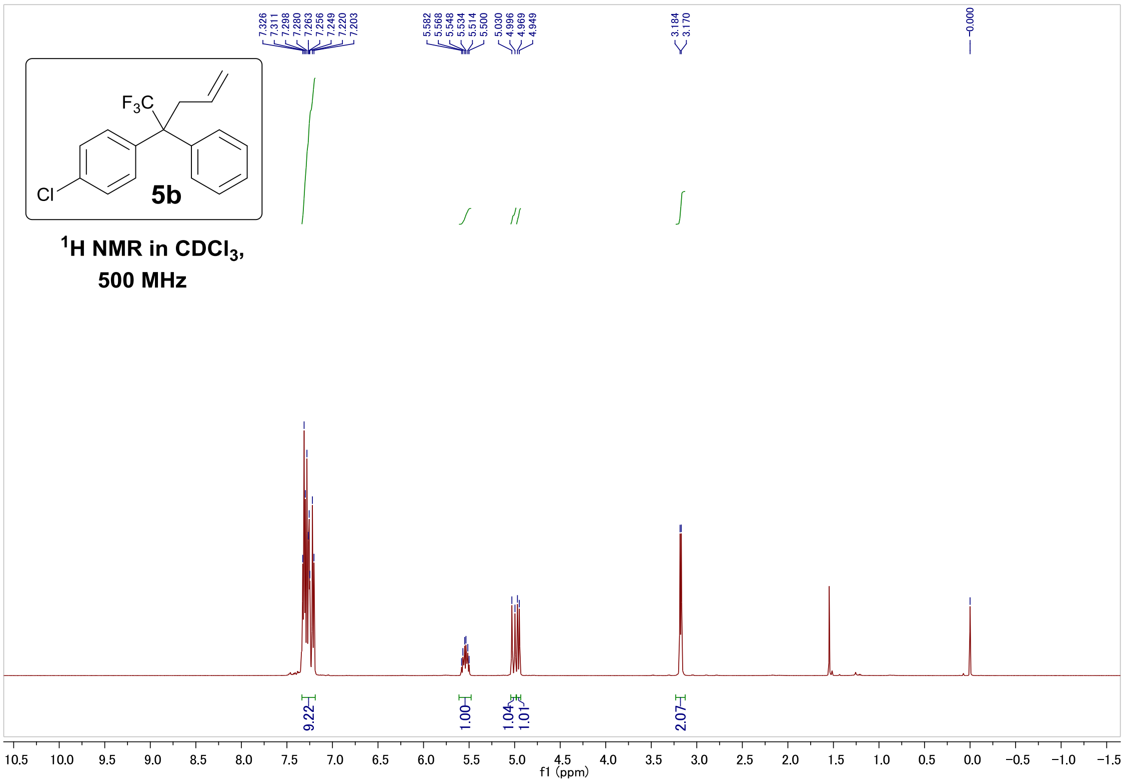
F_3C
S
3u
^{19}F NMR in CDCl$_3$,
282 MHz
−70.841
−70.873
−162.200
3.00
−70.75
−70.85
−70.95
f1 (ppm)
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

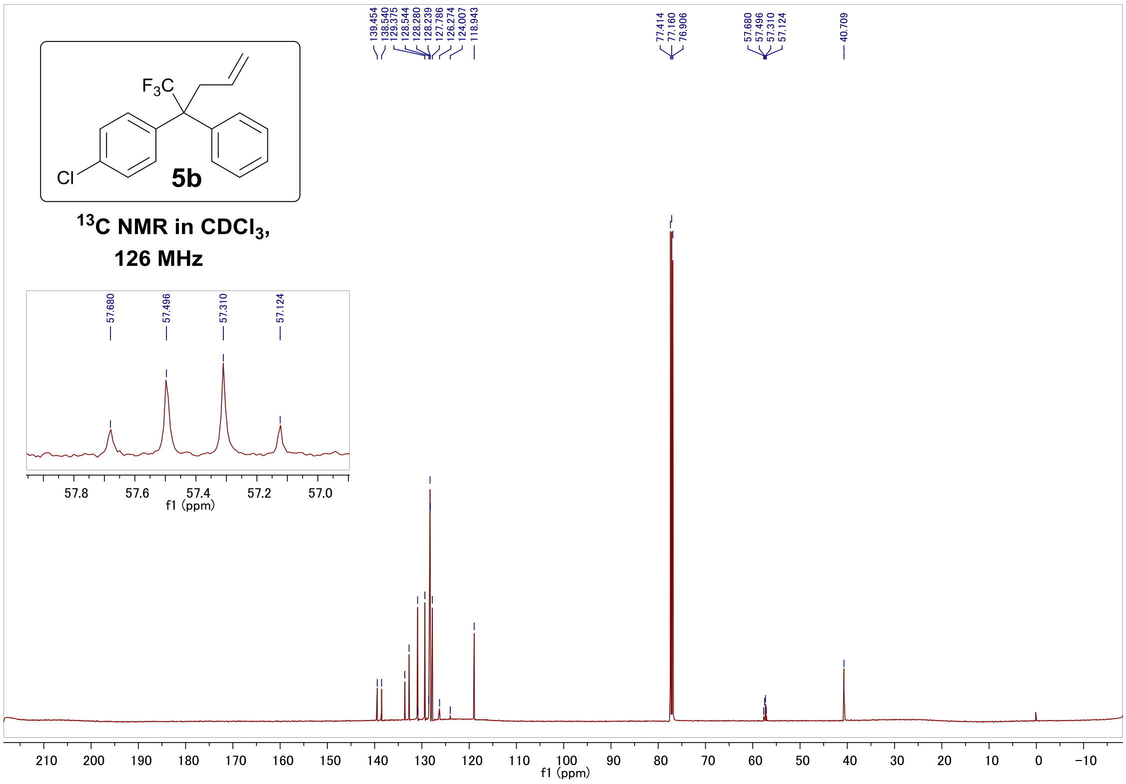


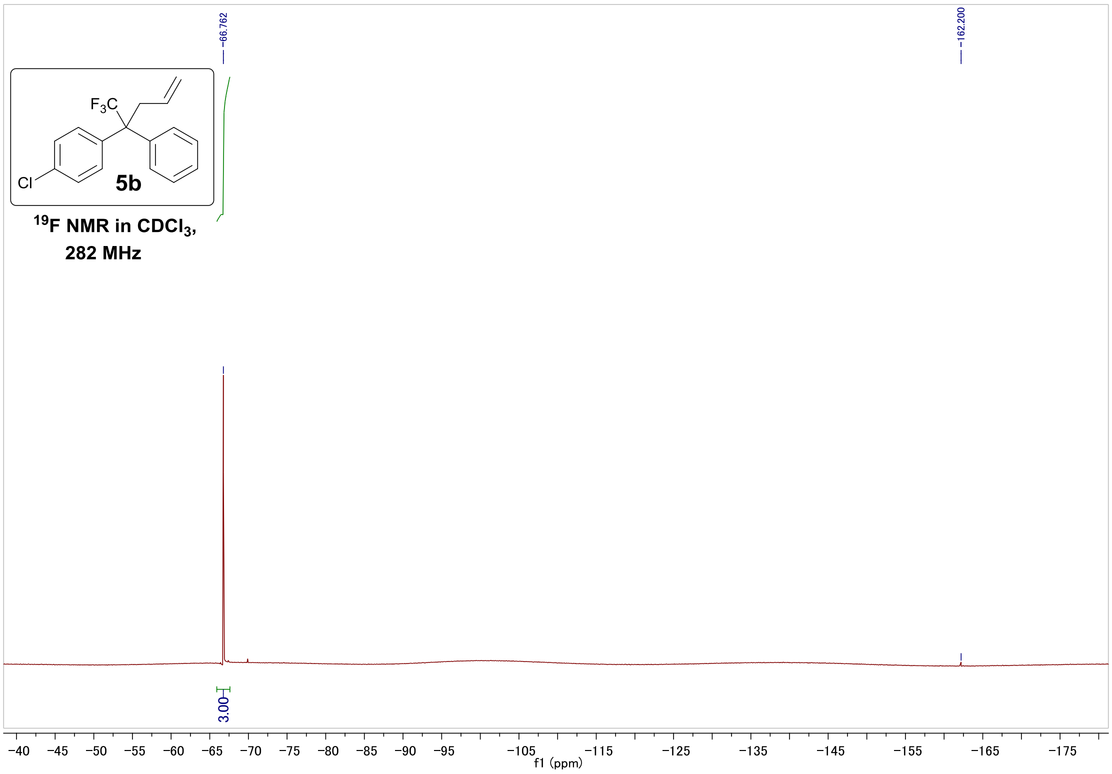
F_3C
5a
^{1}H NMR in CDCl$_3$,
500 MHz
7.334
7.330
7.316
7.310
7.302
7.297
7.288
7.276
7.272
7.252
5.604
5.590
5.570
5.556
5.536
5.522
5.034
5.000
4.950
4.930
3.221
3.207
−0.000
10.20
1.00
1.02
1.01
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)

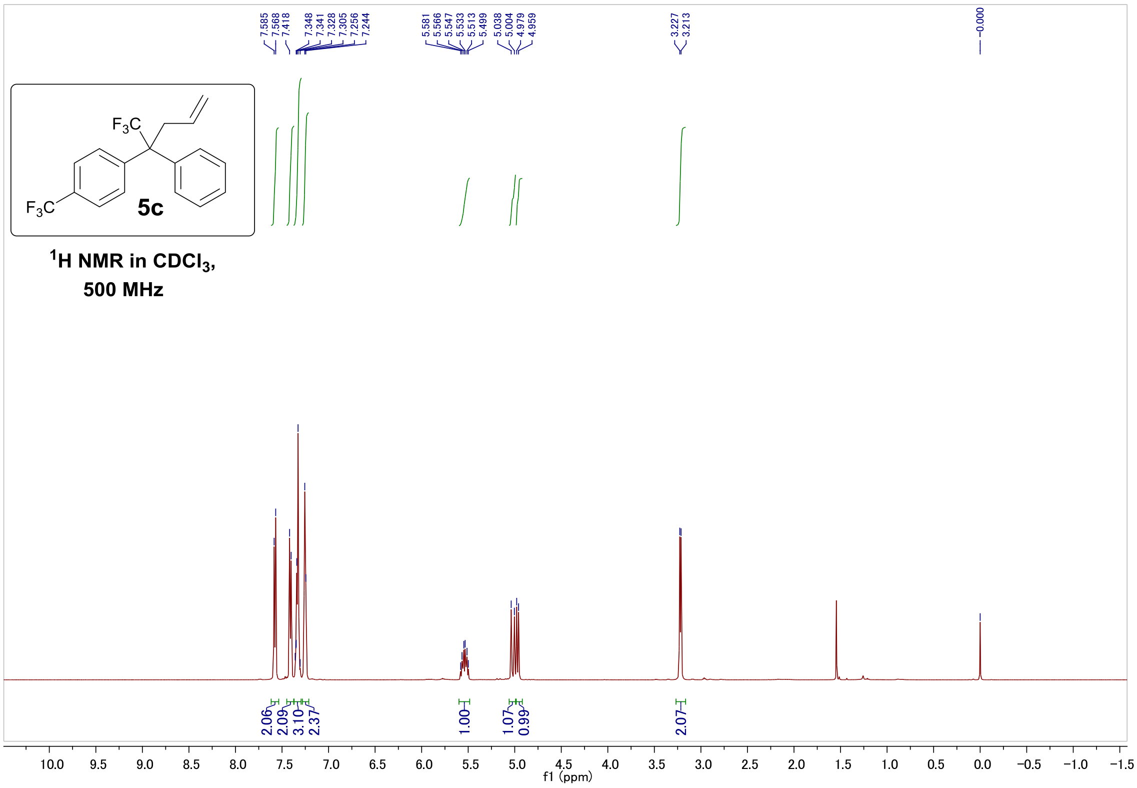

F3C
5a
13C NMR in CDCl3,
126 MHz
140.018
133.200
128.095
127.547
126.499
118.474
77.415
77.160
76.907
57.962
57.778
57.595
57.409
40.819
58.2
58.0
57.8
57.6
57.4
57.2
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

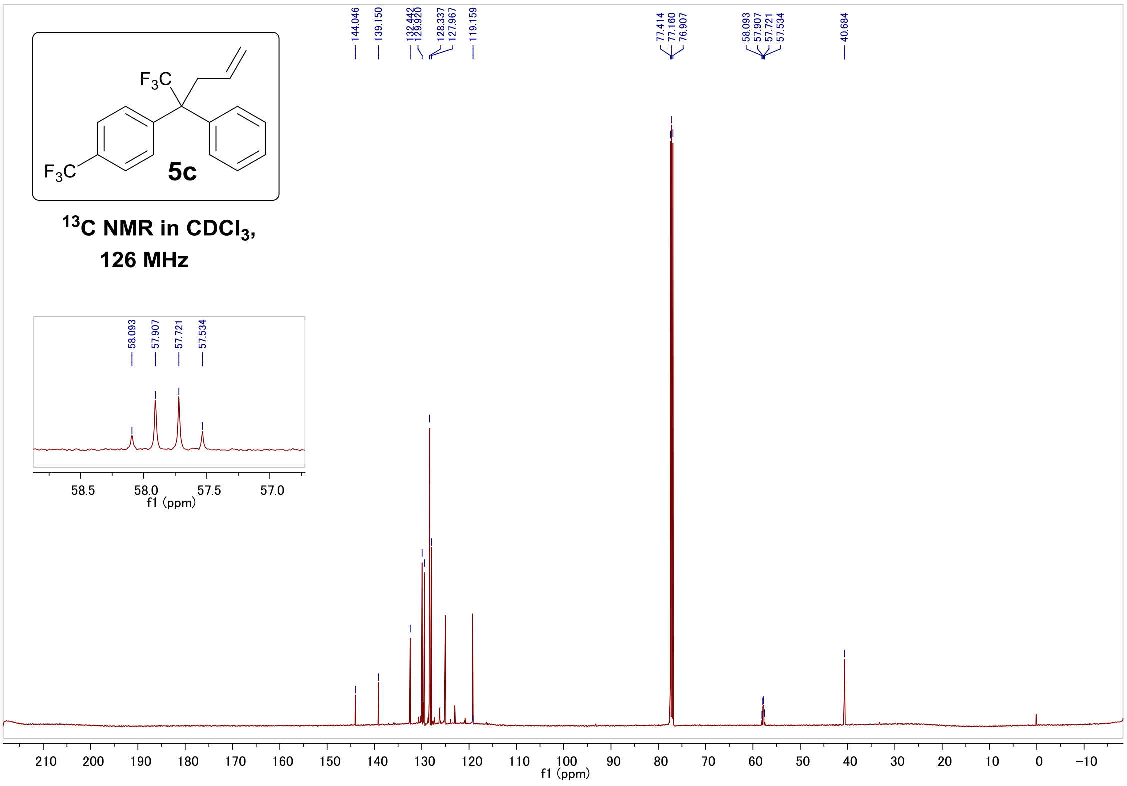

F3C
5a
19F NMR in CDCl3,
282 MHz
−66.490
−162.200
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−110
−120
−130
−140
−150
−160
−170
f1 (ppm)

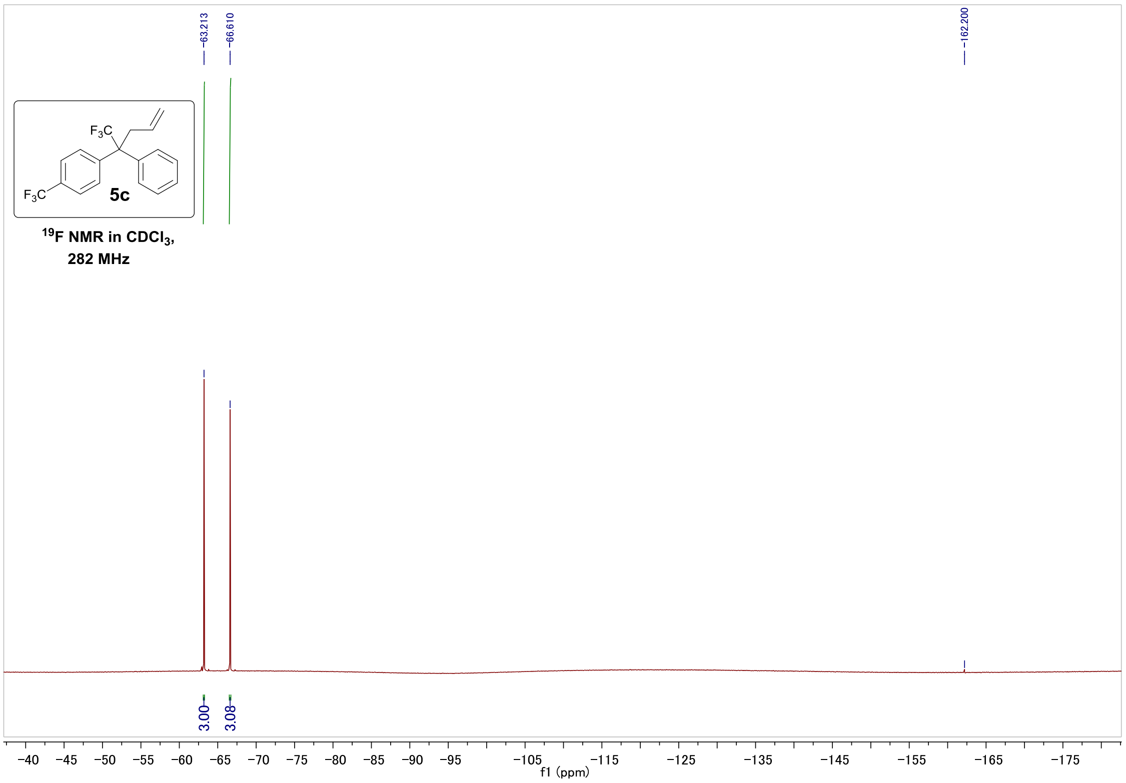

7.326
7.311
7.298
7.280
7.263
7.256
7.249
7.220
7.203
5.582
5.568
5.548
5.534
5.514
5.500
5.030
4.996
4.969
4.949
3.184
3.170
-0.000
F3C
Cl
5b
1H NMR in CDCl3,
500 MHz
9.22
1.00
1.04
1.01
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
f1 (ppm)

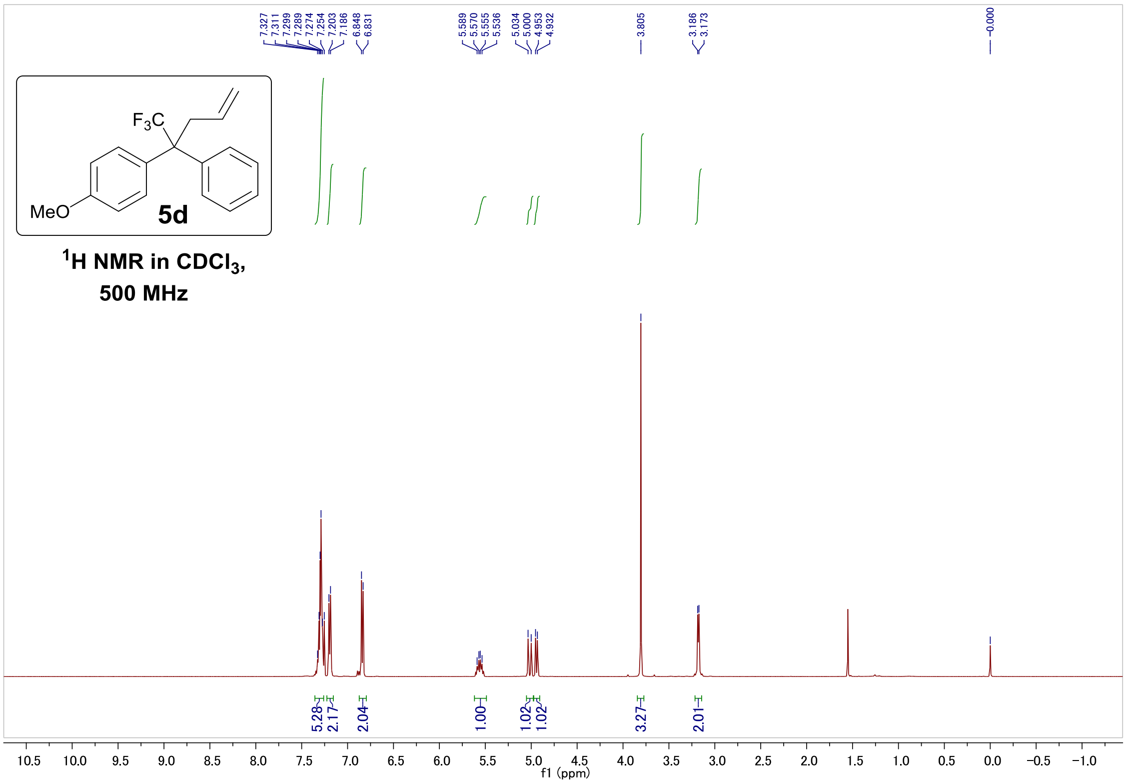

139.454
138.540
129.375
128.544
128.280
128.239
127.786
126.274
124.007
118.943
77.414
77.160
76.906
57.680
57.496
57.310
57.124
40.709
F3C
Cl
5b
13C NMR in CDCl3,
126 MHz
57.680
57.496
57.310
57.124
57.8
57.6
57.4
57.2
57.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

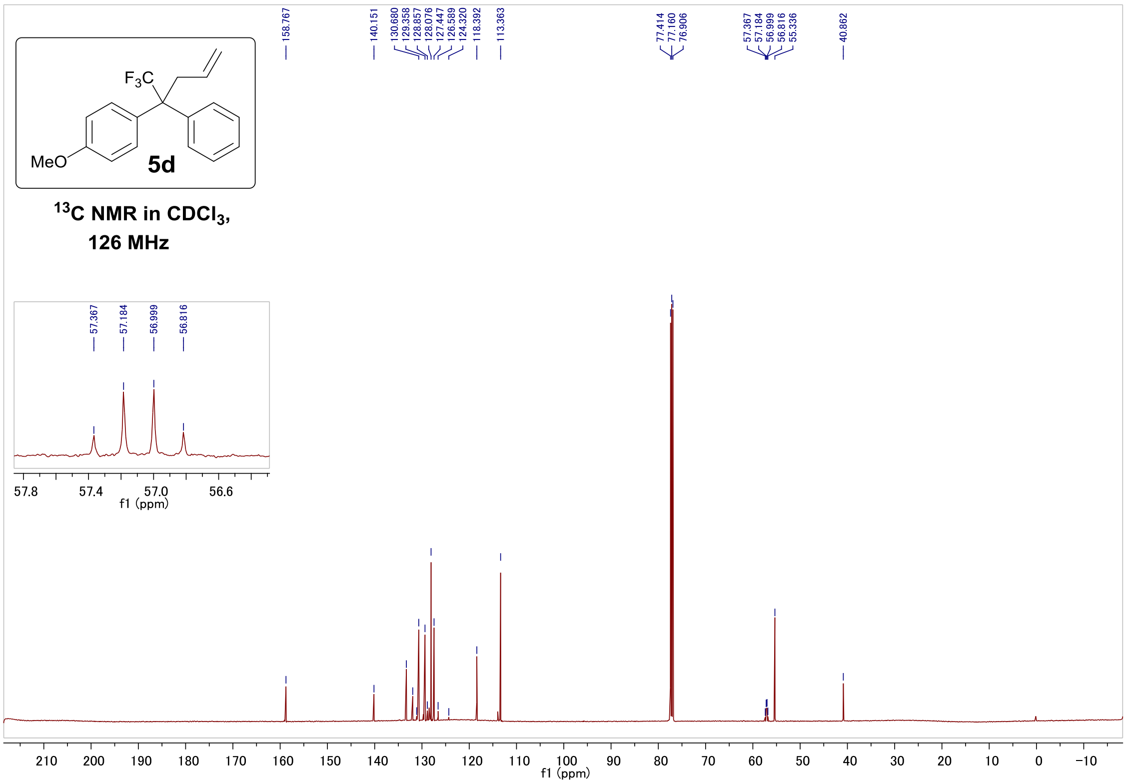

−66.762
−162.200
F3C
Cl
5b
19F NMR in CDCl3,
282 MHz
3.00
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

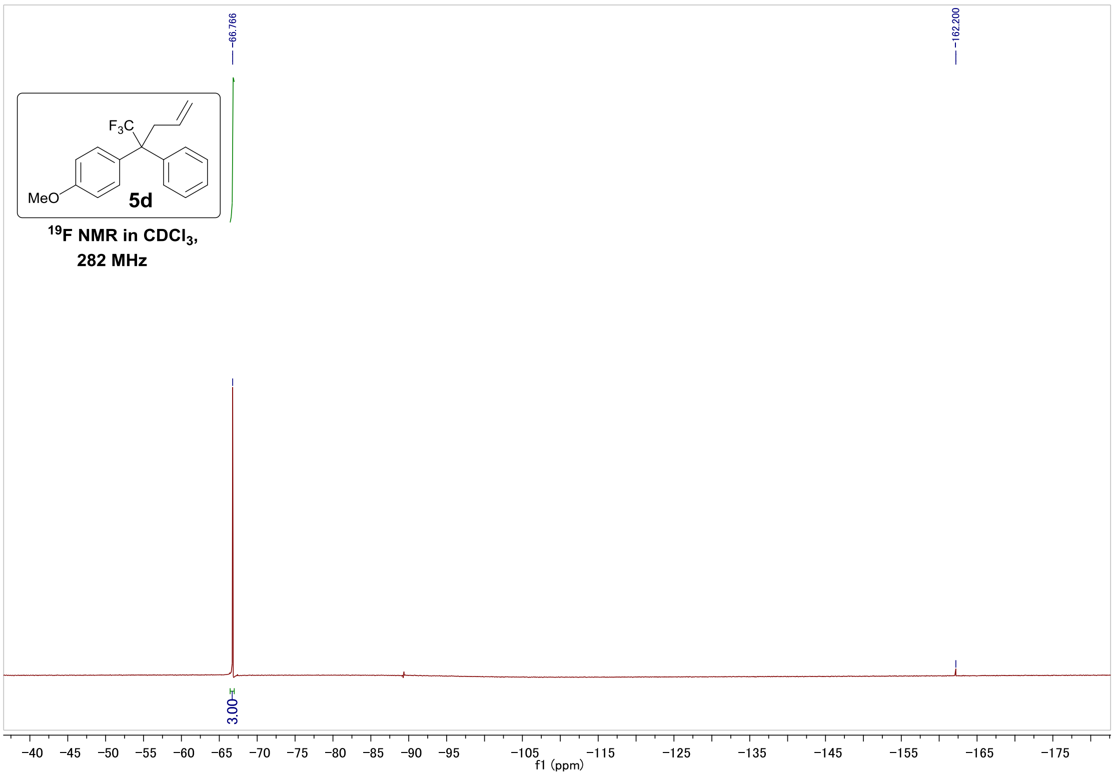

7.585
7.568
7.418
7.348
7.341
7.328
7.305
7.256
7.244
5.581
5.566
5.547
5.533
5.513
5.499
5.038
5.004
4.979
4.959
3.227
3.213
−0.000
F3C
F3C
5c
1H NMR in CDCl3,
500 MHz
2.06
2.09
3.10
2.37
1.00
1.07
0.99
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)


144.046
139.150
132.442
129.920
128.337
127.967
119.159
77.414
77.160
76.907
58.093
57.907
57.721
57.534
40.684
F_3C
F_3C
5c
^{13}C NMR in $CDCl_3$,
126 MHz
58.093
57.907
57.721
57.534
58.5
58.0
57.5
57.0
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)

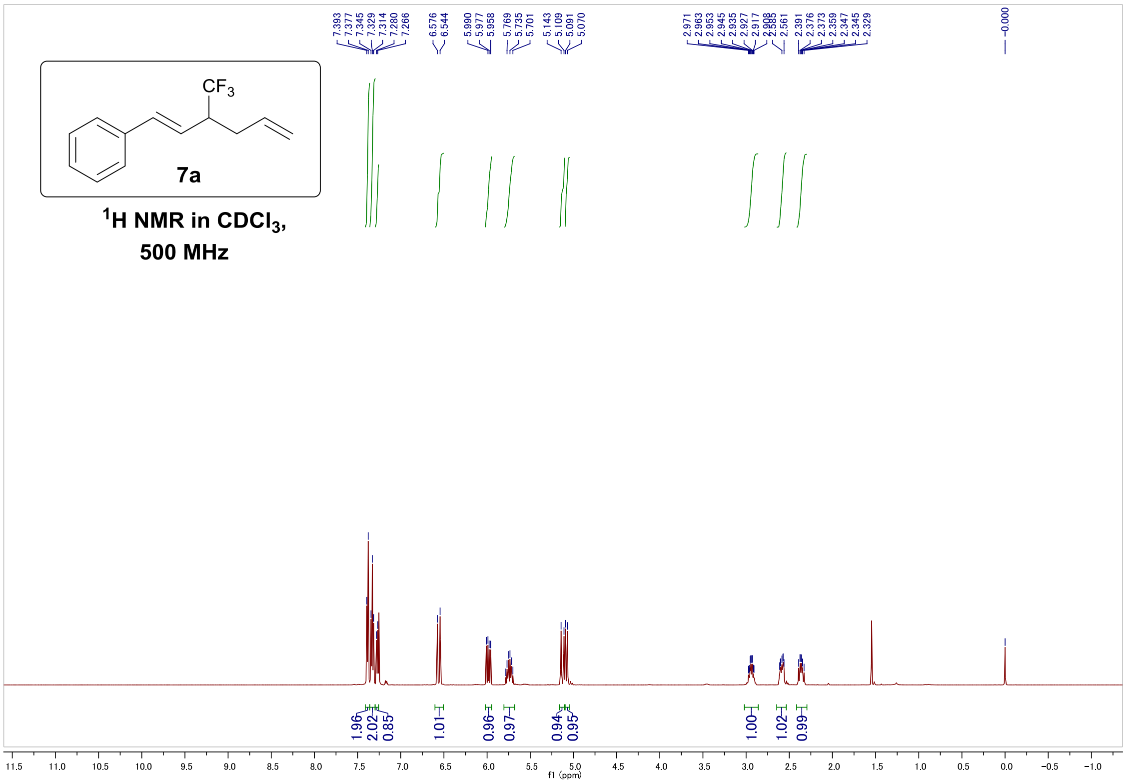

−63.213
−66.610
−162.200
F_3C
F_3C
5c
^{19}F NMR in $CDCl_3$,
282 MHz
3.00
3.08
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)


7.327
7.311
7.299
7.289
7.274
7.254
7.203
7.186
6.848
6.831
5.589
5.570
5.555
5.536
5.034
5.000
4.953
4.932
3.805
3.186
3.173
-0.000
F3C
MeO
5d
1H NMR in CDCl3,
500 MHz
5.28
2.17
2.04
1.00
1.02
1.02
3.27
2.01
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
f1 (ppm)

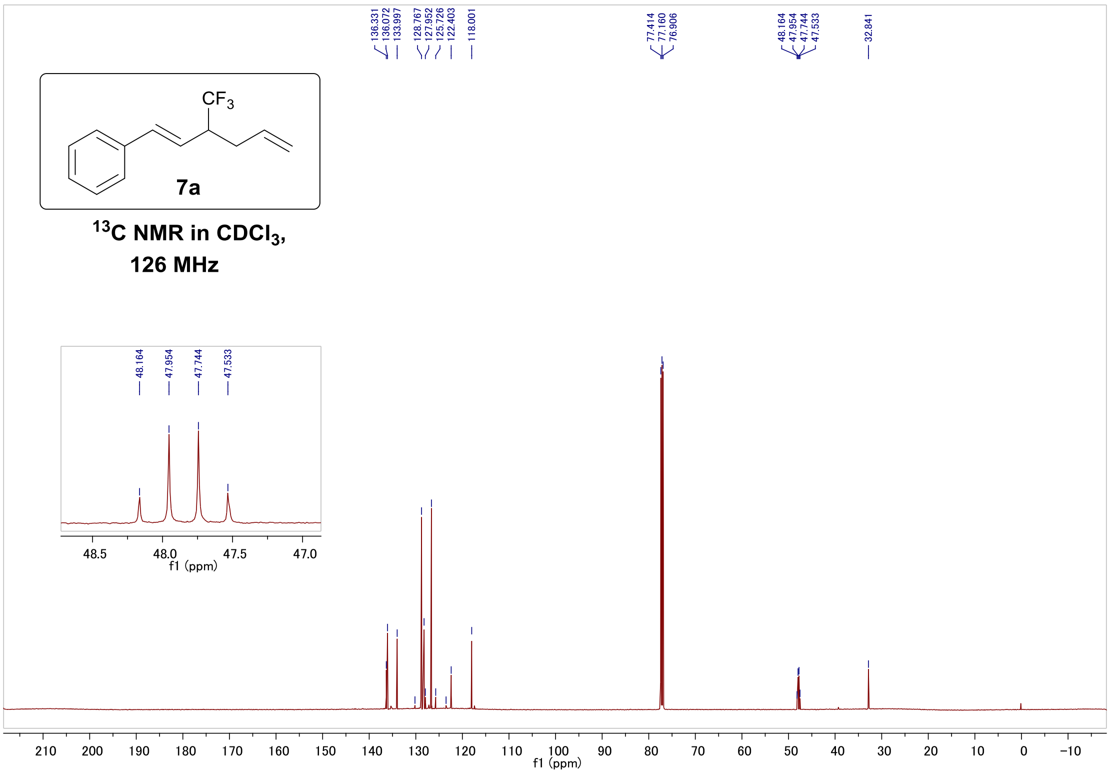

158.767
140.151
130.680
129.358
128.857
128.076
127.447
126.589
124.320
118.392
113.363
77.414
77.160
76.906
57.367
57.184
56.999
56.816
55.336
40.862
F3C
MeO
5d
13C NMR in CDCl3,
126 MHz
57.367
57.184
56.999
56.816
57.8
57.4
57.0
56.6
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

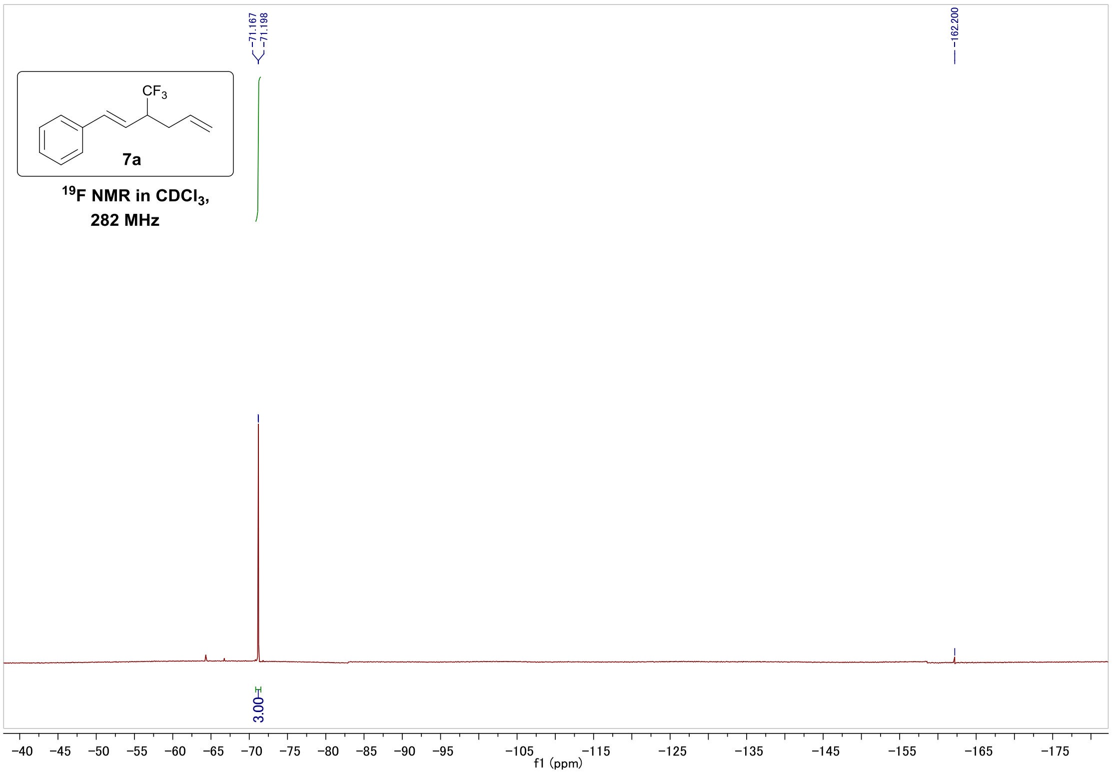


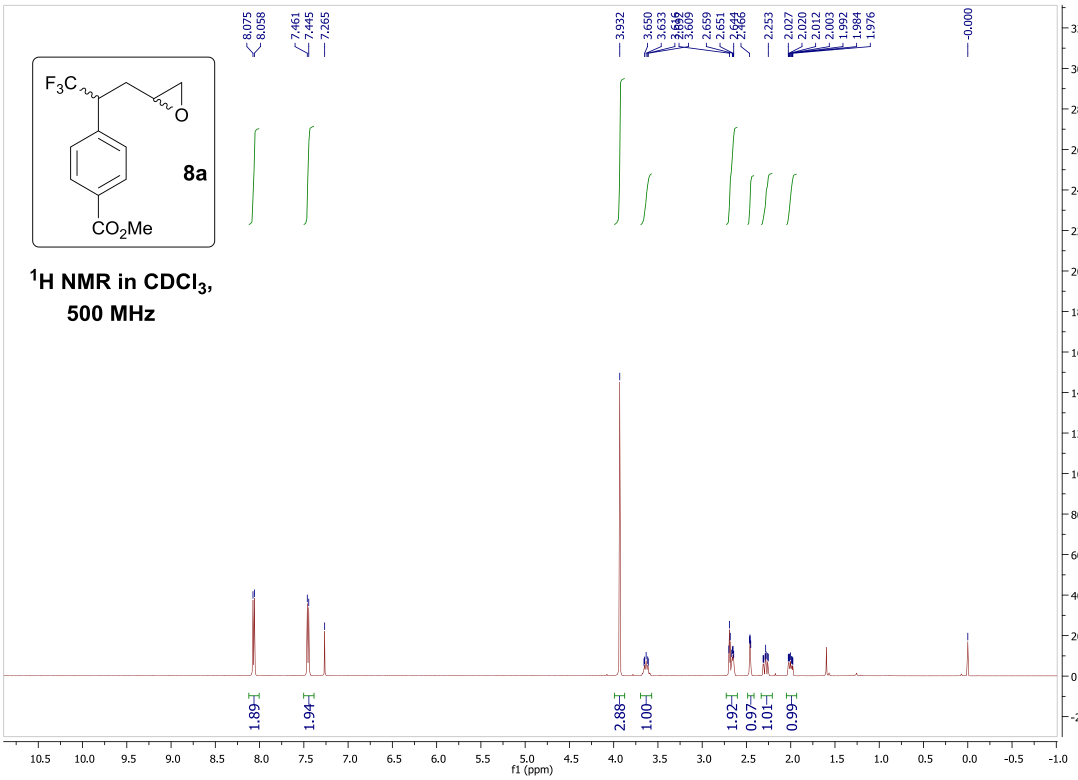
F3C
MeO
5d
19F NMR in CDCl3,
282 MHz
-66.766
-162.200
3.00
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −105 −115 −125 −135 −145 −155 −165 −175
f1 (ppm)

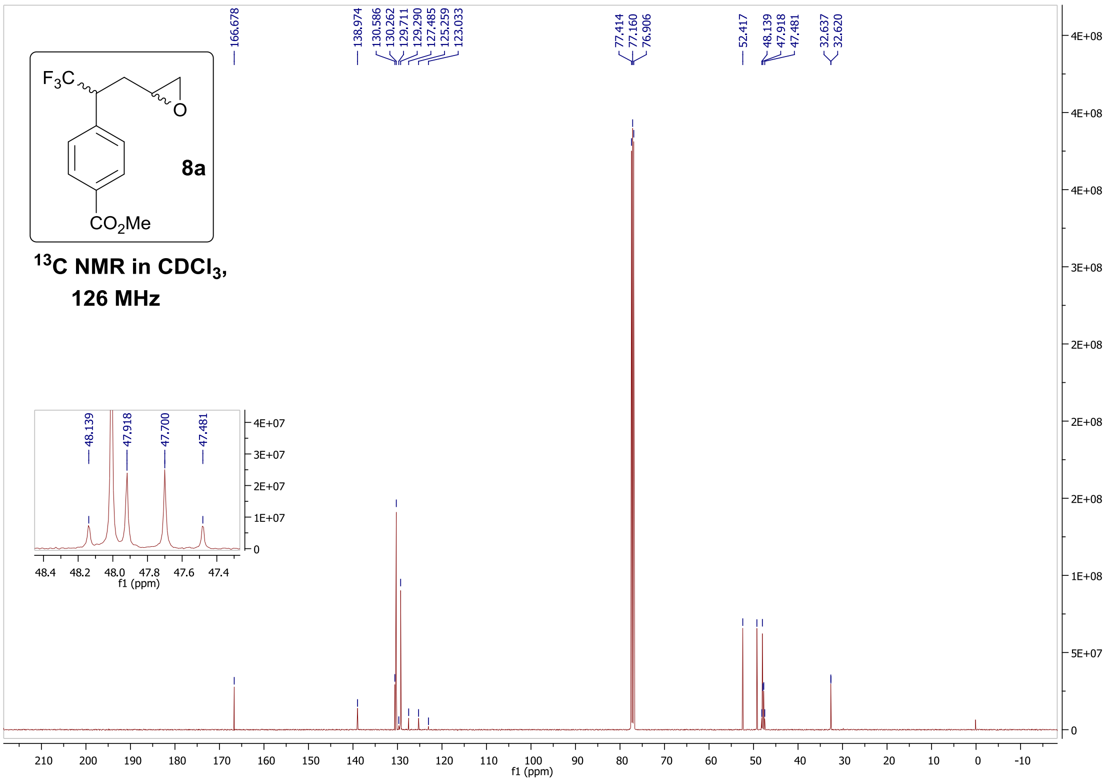


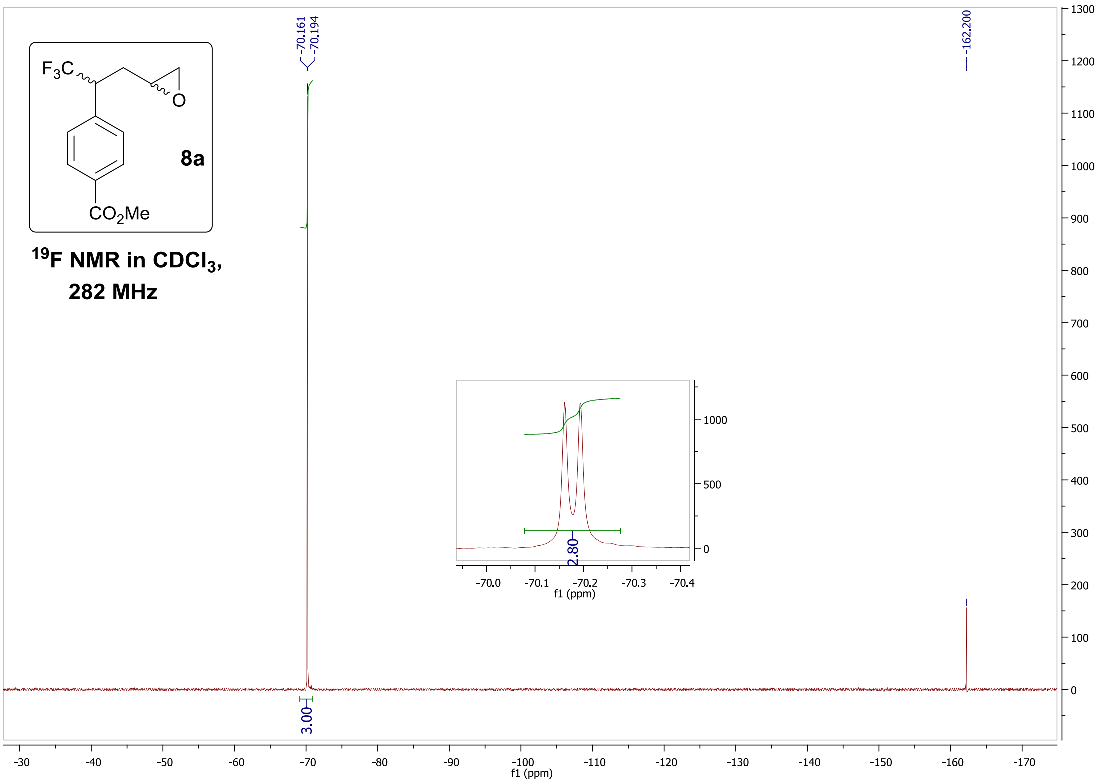
CF3
7a
1H NMR in CDCl3,
500 MHz
7.393 7.377 7.345 7.329 7.314 7.280 7.266
6.576 6.544
5.990 5.977 5.958
5.769 5.735 5.701
5.143 5.109 5.091 5.070
2.971 2.963 2.953 2.945 2.935 2.927 2.917 2.561
2.391 2.376 2.373 2.359 2.347 2.345 2.329
0.000
1.96 2.02 0.85 1.01 0.96 0.97 0.94 0.95 1.00 1.02 0.99
11.5 11.0 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)

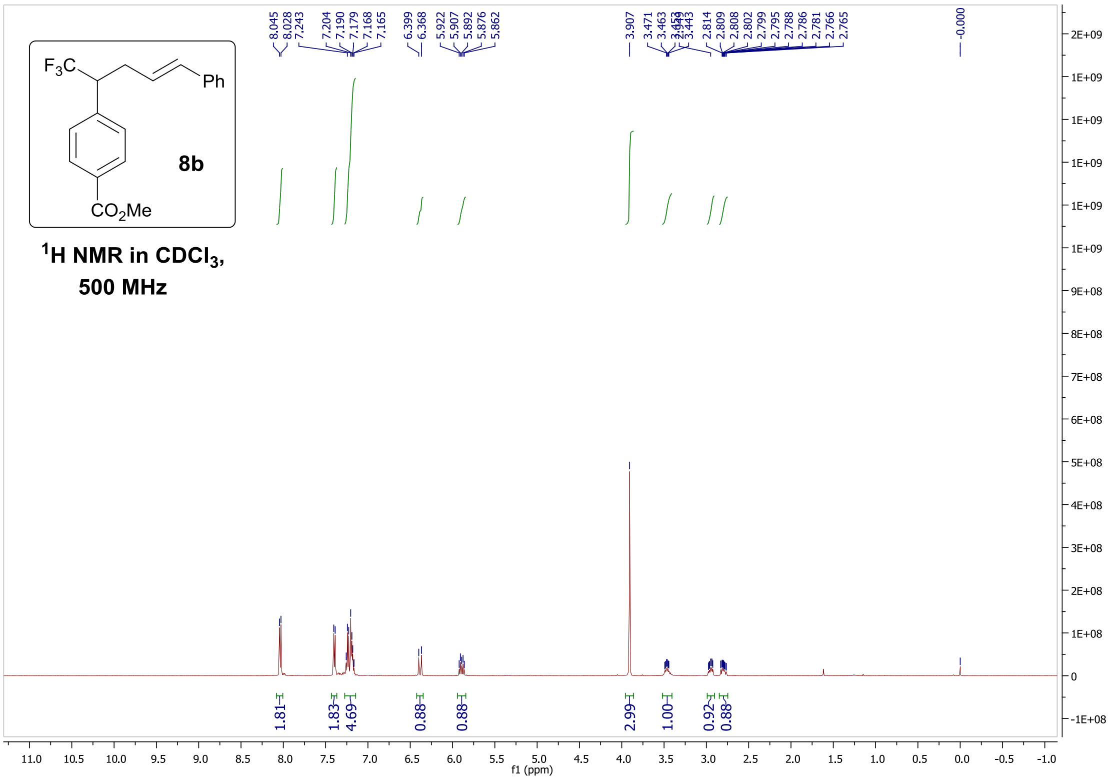

136.331
136.072
133.997
128.767
127.952
125.726
122.403
118.001
77.414
77.160
76.906
48.164
47.954
47.744
47.533
32.841
CF$_3$
7a
^{13}C NMR in CDCl$_3$,
126 MHz
48.164
47.954
47.744
47.533
48.5
48.0
47.5
47.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

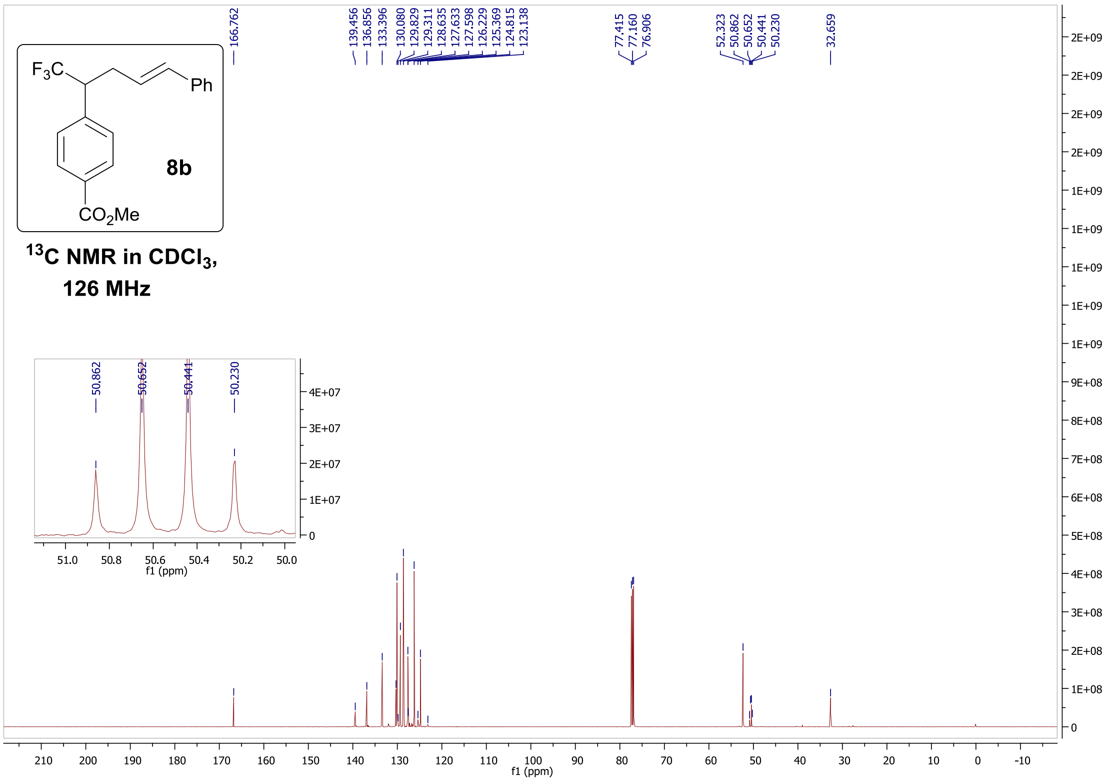

−71.167
−71.198
−162.200
CF$_3$
7a
^{19}F NMR in CDCl$_3$,
282 MHz
3.00
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
−175
f1 (ppm)

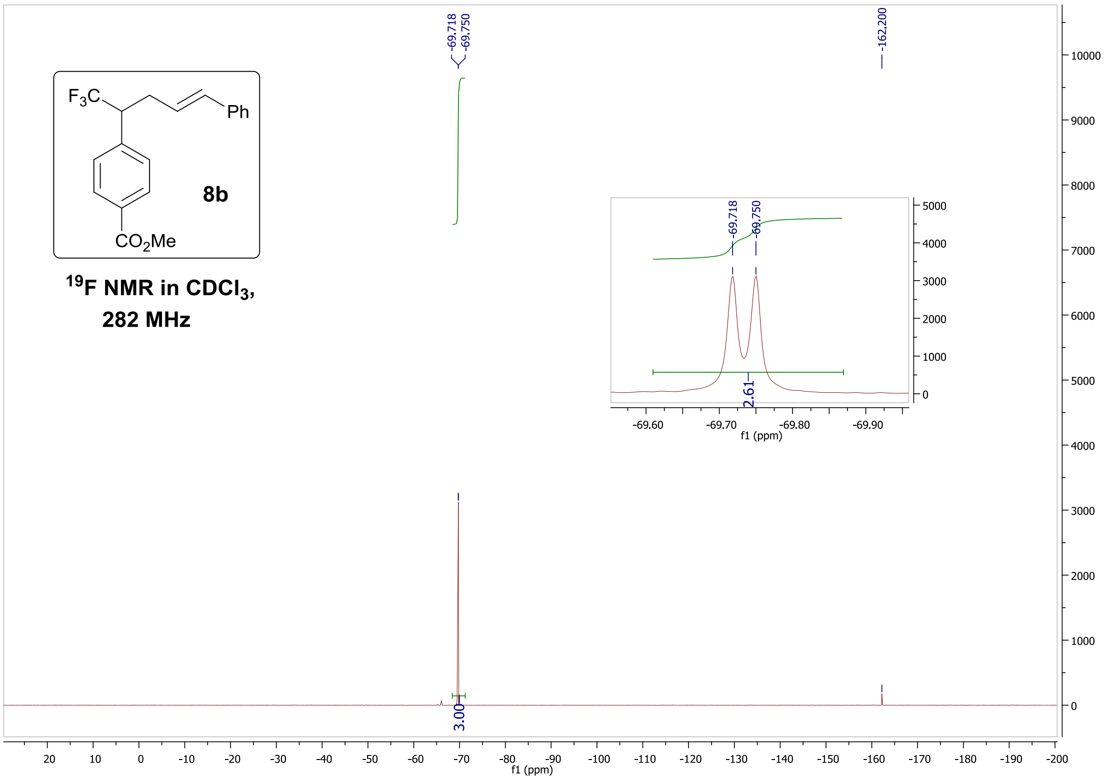

8.075
8.058
7.461
7.445
7.265
3.932
3.650
3.633
3.616
2.692
3.609
2.659
2.651
2.644
2.466
2.253
2.027
2.020
2.012
2.003
1.992
1.984
1.976
-0.000
F_3C
O
CO_2Me
8a
^{1}H NMR in $CDCl_3$,
500 MHz
1.89
1.94
2.88
1.00
1.92
0.97
1.01
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

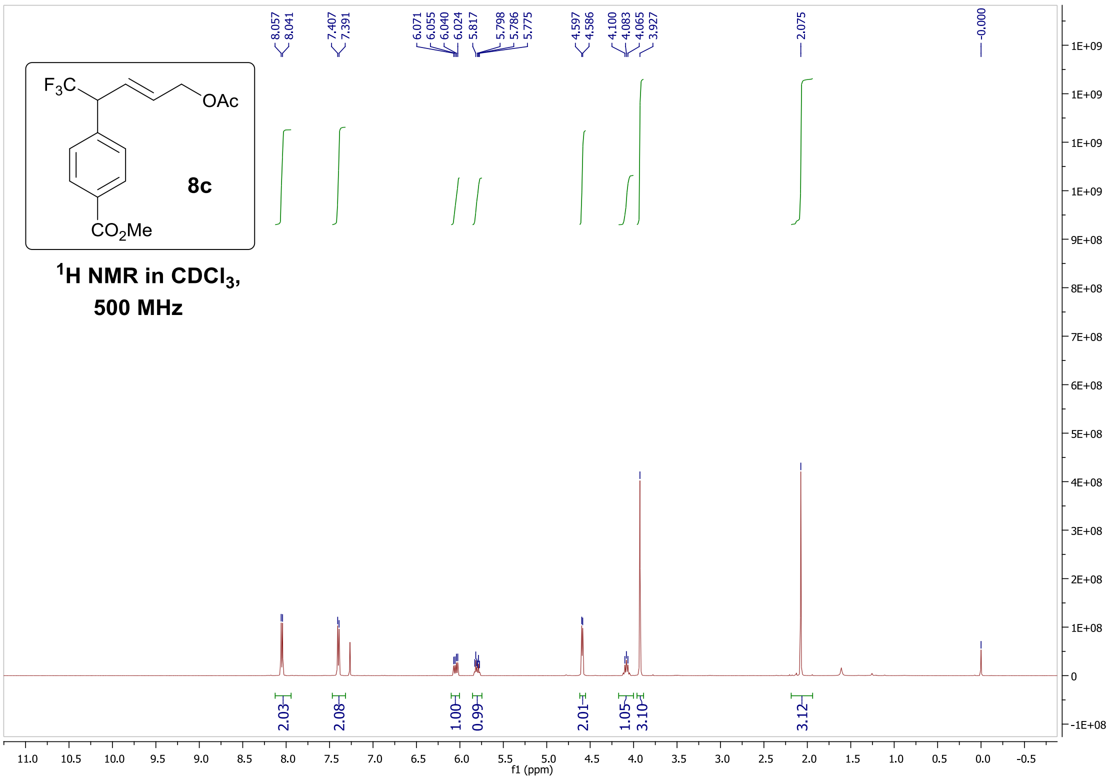

166.678
138.974
130.586
130.262
129.711
129.290
127.485
125.259
123.033
77.414
77.160
76.906
52.417
48.139
47.918
47.481
32.637
32.620
F_3C
O
CO_2Me
8a
^{13}C NMR in $CDCl_3$,
126 MHz
48.139
47.918
47.700
47.481
4E+07
3E+07
2E+07
1E+07
0
48.4
48.2
48.0
47.8
47.6
47.4
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0

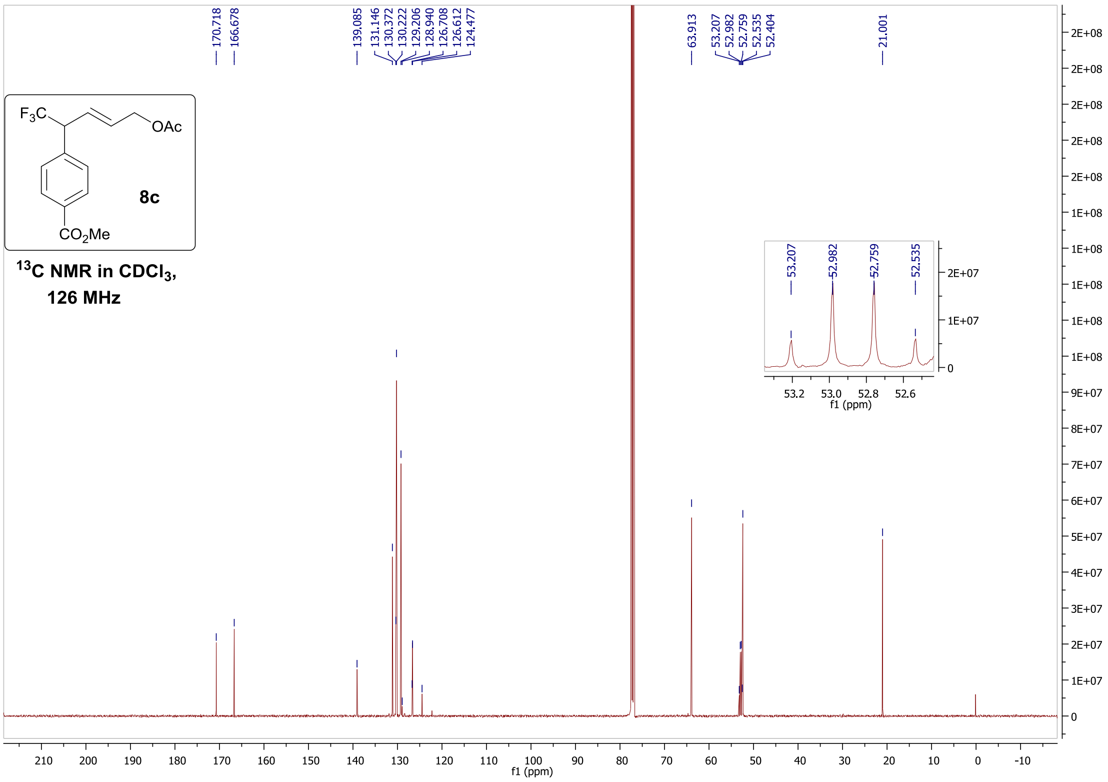

F3C
O
8a
CO2Me
19F NMR in CDCl3,
282 MHz
-70.161
-70.194
-162.200
3.00
2.80
f1 (ppm)

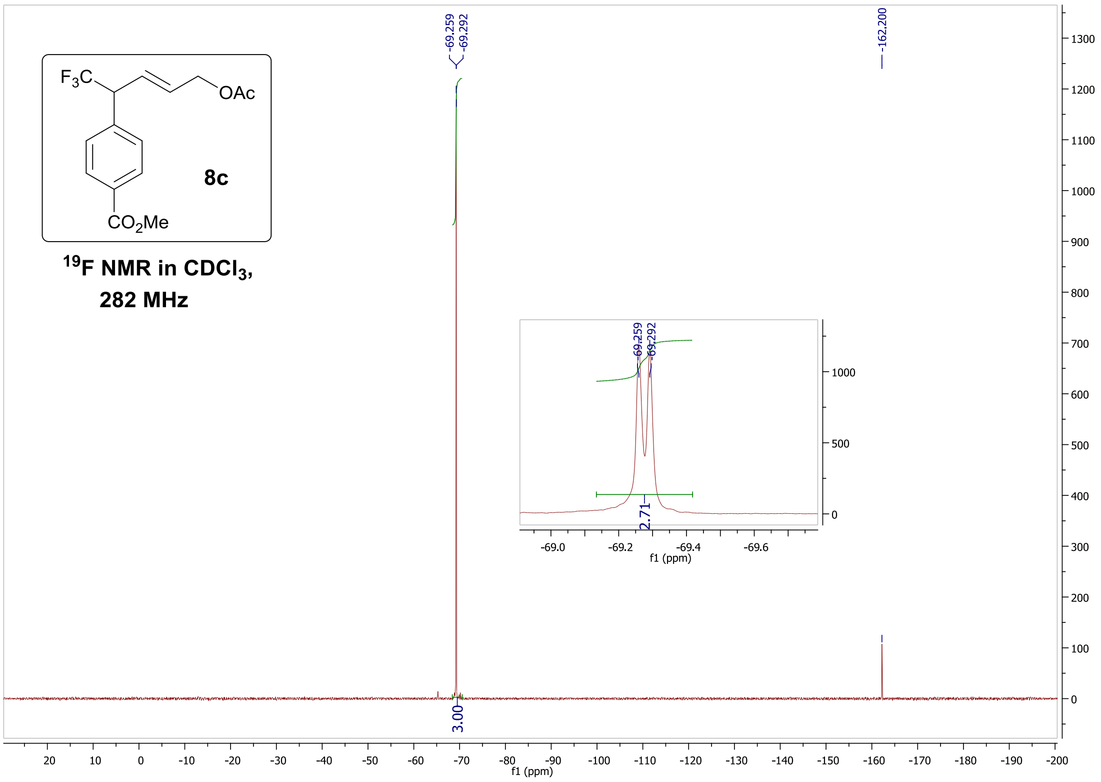

F3C
Ph
8b
CO2Me
1H NMR in CDCl3,
500 MHz
8.045
8.028
7.243
7.204
7.190
7.179
7.168
7.165
6.399
6.368
5.922
5.907
5.892
5.876
5.862
3.907
3.471
3.463
3.443
2.814
2.809
2.808
2.802
2.799
2.795
2.788
2.786
2.781
2.766
2.765
-0.000
1.81
1.83
4.69
0.88
0.88
2.99
1.00
0.92
0.88
f1 (ppm)

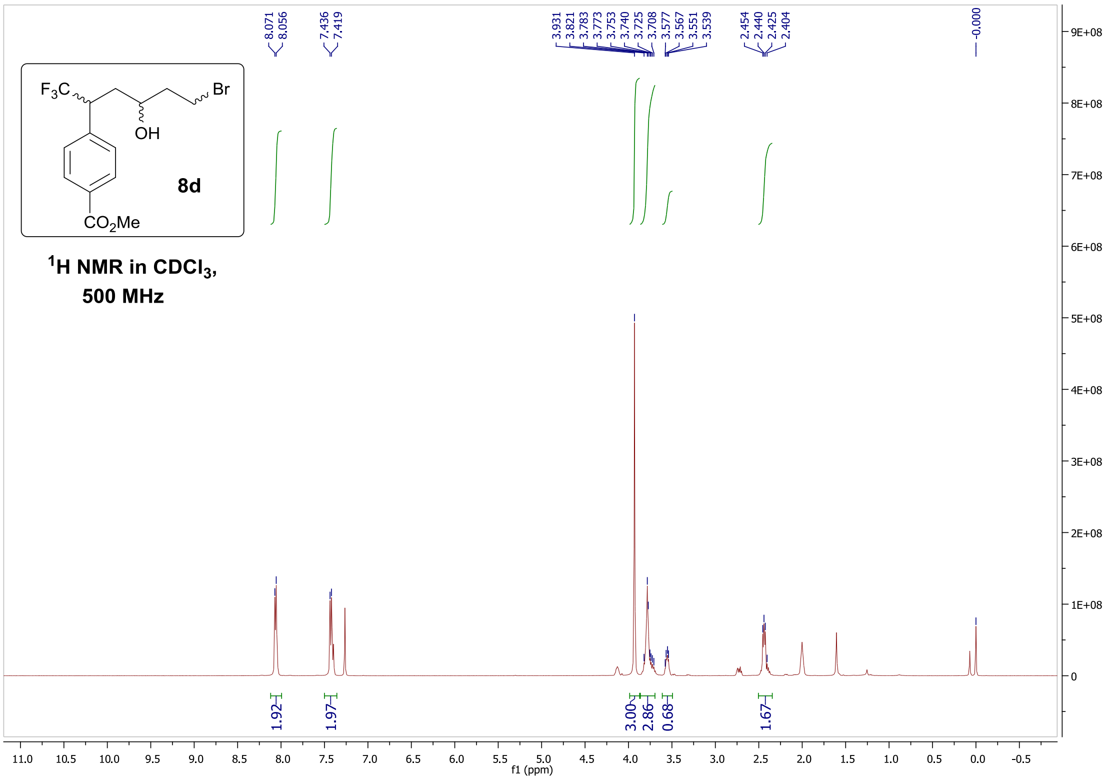

F$_3$C
Ph
8b
CO$_2$Me
^{13}C NMR in CDCl$_3$,
126 MHz
166.762
139.456
136.856
133.396
130.080
129.829
129.311
128.635
127.633
127.598
126.229
125.369
124.815
123.138
77.415
77.160
76.906
52.323
50.862
50.652
50.441
50.230
32.659
50.862
50.652
50.441
50.230
4E+07
3E+07
2E+07
1E+07
0
51.0
50.8
50.6
50.4
50.2
50.0
f1 (ppm)
2E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
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)

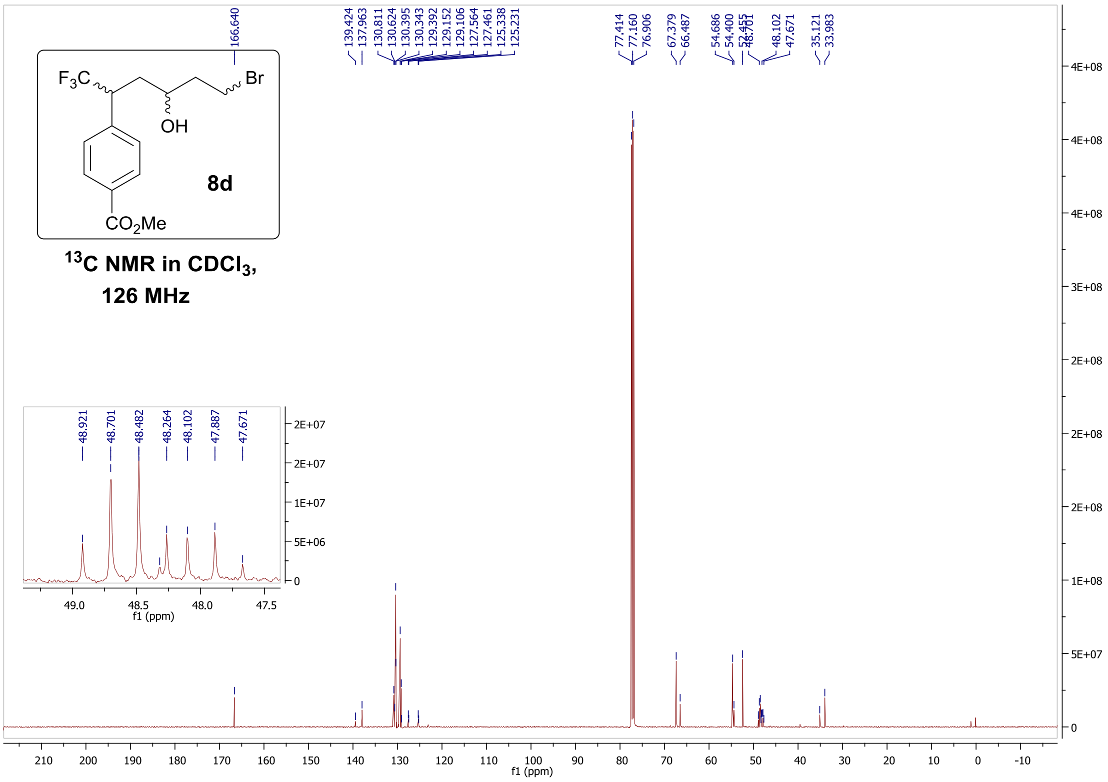

-69.718
-69.750
-162.200
F$_3$C
Ph
8b
CO$_2$Me
^{19}F NMR in CDCl$_3$,
282 MHz
-69.718
-69.750
2.61
5000
4000
3000
2000
1000
0
-69.60
-69.70
-69.80
-69.90
f1 (ppm)
3.00
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

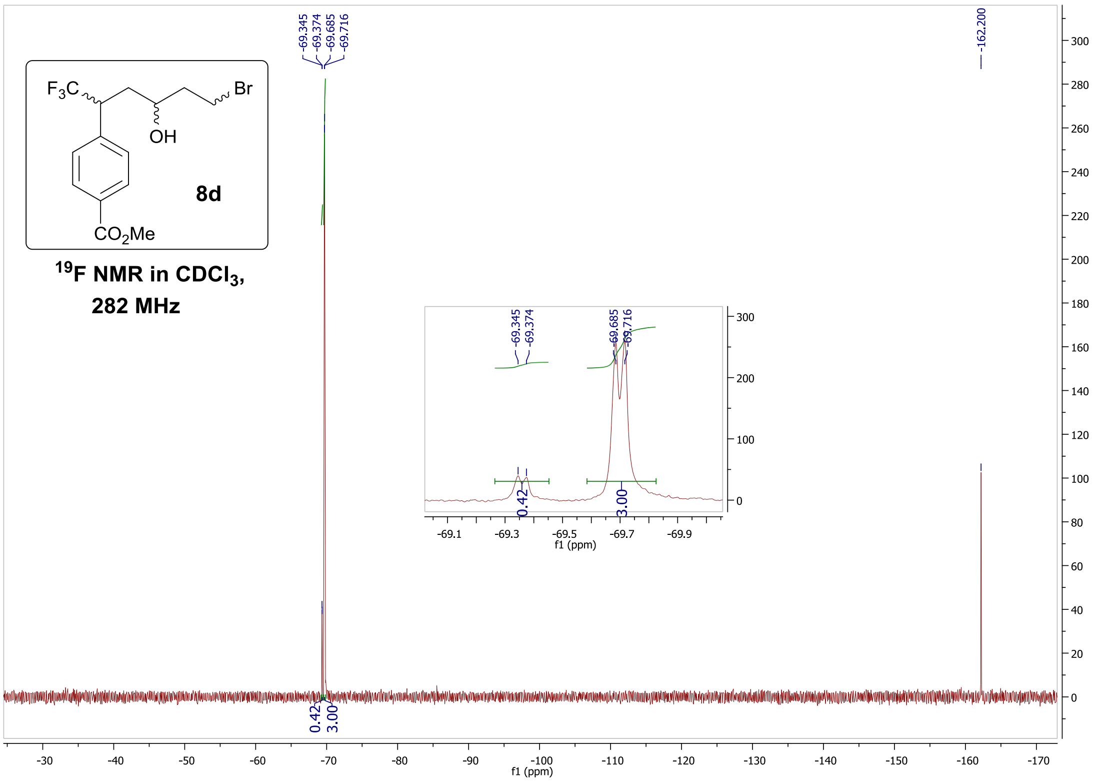

8.057
8.041
7.407
7.391
6.071
6.055
6.040
6.024
5.817
5.798
5.786
5.775
4.597
4.586
4.100
4.083
4.065
3.927
2.075
-0.000
F3C
OAc
CO2Me
8c
1H NMR in CDCl3,
500 MHz
2.03
2.08
1.00
0.99
2.01
1.05
3.10
3.12
f1 (ppm)


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
F3C
OAc
CO2Me
8c
13C NMR in CDCl3,
126 MHz
f1 (ppm)


F$_3$C
OAc
CO$_2$Me
8c
^{19}F NMR in CDCl$_3$,
282 MHz
-69.259
-69.292
-162.200
2.71
3.00
-69.0
-69.2
-69.4
-69.6
f1 (ppm)
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200


F$_3$C
Br
OH
CO$_2$Me
8d
^{1}H NMR in CDCl$_3$,
500 MHz
8.071
8.056
7.436
7.419
3.931
3.821
3.783
3.773
3.753
3.740
3.725
3.708
3.577
3.567
3.551
3.539
2.454
2.440
2.425
2.404
-0.000
1.92
1.97
3.00
2.86
0.68
1.67
f1 (ppm)
11.0 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


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
52.455
48.701
48.102
47.671
35.121
33.983
F3C
Br
OH
CO2Me
8d
13C NMR in CDCl3, 126 MHz
48.921
48.701
48.482
48.264
48.102
47.887
47.671
2E+07
2E+07
1E+07
5E+06
0
49.0
48.5
48.0
47.5
f1 (ppm)
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
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)


-69.345
-69.374
-69.685
-69.716
-162.200
F3C
Br
OH
CO2Me
8d
19F NMR in CDCl3, 282 MHz
-69.345
-69.374
-69.685
-69.716
300
200
100
0
0.42
3.00
-69.1
-69.3
-69.5
-69.7
-69.9
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0.42
3.00
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)