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Supplementary Information

Nickel(0)-Catalyzed Intramolecular Reductive Coupling of Alkenes and Aldehydes or Ketones with Hydrosilanes

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1. General

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III 400, Bruker AVANCE III 600, and JEOL AL-400 spectrometers at 25 °C unless otherwise noted. The chemical shifts in the ^{1}H NMR spectra were recorded relative to Me_4Si or residual protonated solvent ($CHCl_3$ (δ 7.26)). The chemical shifts in the ^{13}C NMR spectra were recorded relative to Me_4Si or residual protonated solvent ($CHCl_3$ (δ 77.16)). The chemical shifts in ^{19}F NMR spectra were recorded relative to α,α,α-trifluorotoluene (δ –65.64). Assignment of the resonances in the ^{1}H and ^{13}C NMR spectra was based on ^{1}H-^{1}H COSY, HMQC and HMBC experiments. Mass spectra were obtained using a Shimadzu GCMS-QP 2010 instrument with an ionization voltage of 70 eV. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. Medium-pressure column chromatography was carried out on a Biotage Flash Purification System Isolera, equipped with a 254 nm UV detector. High resolution mass spectrometry (HRMS) was performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. Enantioselectivities were recorded by means of JASCO-Supercritical Fluid chromatography (SFC) equipped with PU-2080-CO_2 plus CO_2 delivery pump and MD-2018 plus as a photodiode array detector. Optical rotations were measured in JASCO-DIP 1000 polarimeter with a path length of 1 dm using the sodium D line, 589 nm.

2. Materials

Toluene and 1,4-dioxane were distilled from sodium benzophenone ketyl, and other solvents were distilled and degassed prior to use. All commercially available reagents were distilled over CaH_2 under reduced pressure prior to use. $Ni(cod)_2$ was recrystallized from toluene prior to use. All synthesized starting materials were purified either by distillation over CaH_2 or recrystallization prior to use for catalytic reactions. *N*-Heterocyclic carbenes (NHCs) shown in Figure S1 were prepared according to the reported procedures.[S1] (η^6-Toluene)Ni(SIPr) (**TNSI**) was prepared according to our previous report.[S2] The preparation procedures for chiral imidazolinium salts (**Ln**·HBF_4) are shown in Chapter 7. The preparation procedures for substrates depicted in Figure S2 are shown in Chapter 8.

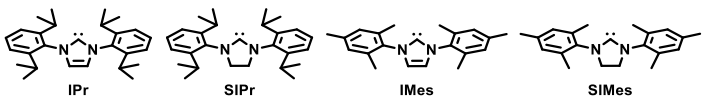


Figure S1. NHCs employing in this work

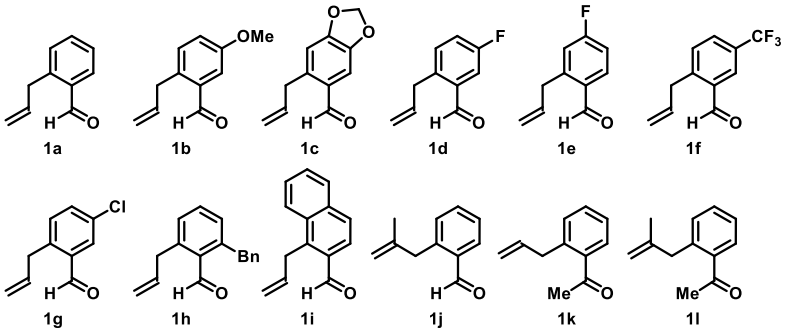
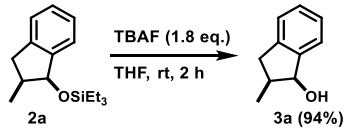


Figure S2. Substrates employing in this work

3. Optimization of reaction conditions (Table 1)

General procedures: A reaction tube was charged with **1a** (0.80 mmol) and triethylsilane (0.80 mmol) in the presence of catalyst (0.04 mmol) in solvent (3.0 mL). The reaction mixture was stirred at room temperature or 40 °C. The reaction was monitored by GC, and GC yield of **2a** was determined by using *n*-pentadecane as an internal standard.



Desilylation of 2a with TBAF: To a solution of **2a** (221.2 mg, 0.84 mmol) in THF (2.0 mL) was added TBAF (1M in THF, 2.0 mL, 2.0 mmol) at room temperature and stirred for 2 h to complete the reaction. Then, the reaction was quenched by sat. NH_4Cl aq., and the organic layer was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. After the filtration, the solvent was removed under reduced pressure followed by the purification by the silica gel column chromatography to give **3a** (117.0 mg, 0.80 mmol, 94%) as a white solid. Spectroscopic data of **3a** was identical to that previously reported.[S3]

4. Scope of hydrosilanes (Table 2)

General procedures: A reaction tube was charged with **1a** (0.40 mmol) and a hydrosilane (0.40–0.45 mmol) in the presence of **TNSI** (0.02 mmol) in toluene (1.5 mL). The reaction mixture was stirred at 40 °C. The reaction was monitored by GC, and GC yield of **2a** was detected by using *n*-pentadecane as an internal standard.

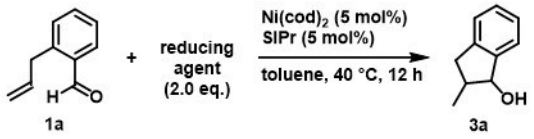
5. Scope of other reducing reagents (Table S1)

General procedures: A reaction tube was charged with **1a** (0.80 mmol) and a reducing reagent (1.6 mmol) in the presence of $Ni(cod)_2$ (0.04 mmol) and SIPr (0.04 mmol) in toluene (3.0 mL). The reaction mixture was stirred at 40 °C for 12 h and quenched with sat. NH_4Cl aq. followed by 1M HCl aq. The

organic layer was extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure.

Result and Discussions: The results of the scope of other reducing reagents are summarized in Table S1. The reaction was conducted with **1a** in the presence of 5 mol% $Ni(cod)_2$ and SIPr in toluene. In the case of triethylborane, **3a** was obtained in 91% isolated yield and >99:1 *dr* (entry 1). Whereas, in the case of diethylzinc, **1a** was fully consumed (entry 2), and **3a** was obtained in 63% GC yield; however, *o*-allylbenzyl alcohol was also generated as a by-product.

Table S1. Scope of reducing reagents



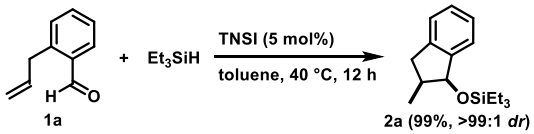
1a 3a

entry	reducing agent	conv. (%)[a]	yield (%)[a]	*dr*[a]
1	BEt_3 (1M in pentane)	>99	91[b]	>99:1
2	$ZnEt_2$ (1M in heptene)	>99	63	>99:1

[a] Determined by GC using *n*-pentadecane as an internal standard.
[b] Isolated yield.

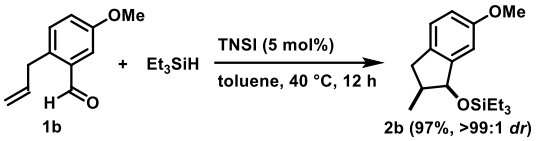
6. Scope of substrates (Table 3, Scheme 2)

General procedures: A reaction tube was charged with **1a–l** (0.80 mmol) and triethylsilane (0.80 mmol) in the presence of **TNSI** (0.04 mmol) in toluene (3.0 mL). The reaction mixture was stirred at 40 °C for 12 h. The reaction was monitored by GC. The products were isolated either by silica gel column chromatography or Kugelrohr distillation.

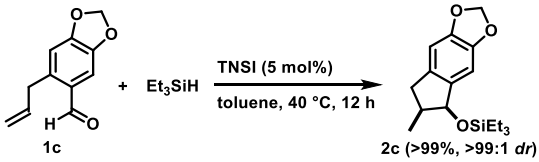


1a 2a (99%, >99:1 *dr*)

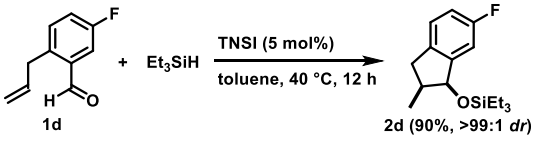
Reaction of 1a giving 2a: The general procedure was followed with **1a** (118.0 mg, 0.81 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 120 °C) gave **2a** (209.9 mg, 0.80 mmol, 99 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 3.2 Hz, 1H, Ar-*H*), 7.20–7.19 (m, 3H, Ar-*H*), 5.11 (d, *J* = 6.4 Hz, 1H, C*H*OSi), 2.91 (dd, *J* = 15.2, 6.4 Hz, 1H, ArCH_2CH), 2.64 (dd, *J* = 15.2, 4.8 Hz, 1H, ArCH_2CH), 2.56–2.50 (m, 1H, CH_2CHCH_3), 1.01 (t, *J* = 7.2 Hz, 12H, $CHCH_3$ and $Si(CH_2CH_3)_3$), 0.69 (apparent q, *J* = 7.2 Hz, 6H, $Si(CH_2CH_3)_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ145.2, 142.3, 127.6, 126.4, 125.0, 124.5, 77.8, 40.3, 38.0, 14.1, 7.1, 5.3. **HRMS** (EI): *m/z* Calcd for $C_{16}H_{26}OSi$: (M^+) 262.1753, found 262.1752.



Reaction of 1b giving 2b: The general procedure was followed with **1b** (142.4 mg, 0.81 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 150 °C) gave **2b** (229.5 mg, 0.79 mmol, 97 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.08 (d, J = 8.0 Hz, 1H, Ar-*H*), 6.86 (d, J = 2.0 Hz, 1H, Ar-*H*), 6.75 (dd, J = 8.0, 2.0 Hz, 1H, Ar-*H*), 5.08 (d, J = 5.6 Hz, 1H, C*H*OSi), 3.80 (s, 3H, OCH_3), 2.85 (dd, J = 15.6, 7.4 Hz, 1H, ArCH_2CH), 2.56–2.53 (m, 2H, ArCH_2CH and CH_2C*H*CH_3), 1.03–0.97 (m, 12H, CHCH_3 and Si(CH_2CH_3)$_3$), 0.70 (q, J = 7.4 Hz, 6H, Si(C$H_2$$CH_3$)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.9, 146.6, 134.0, 125.7, 113.7, 109.8, 78.0, 55.5, 40.7, 37.1, 14.2, 7.1, 5.3. **HRMS** (EI): *m/z* Calcd for $C_{17}H_{28}O_2Si$: (M^+) 292.1859, found 292.1865.

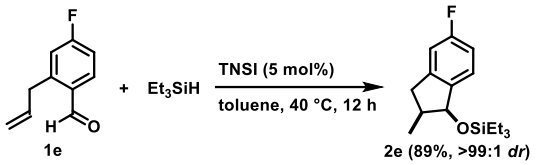


Reaction of 1c giving 2c: The general procedure was followed with **1c** (153.0 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 180 °C) gave **2c** (244.6 mg, 0.80 mmol, >99 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.75 (s, 1H, Ar-*H*), 6.65 (s, 1H, Ar-*H*), 5.91 (d, J = 2.8 Hz, 2H, OCH_2O), 5.00 (d, J = 6.0 Hz, 1H, C*H*OSi), 2.80 (dd, J = 16.4, 8.0 Hz, 1H, ArCH_2CH), 2.54–2.51 (m, 2H, ArCH_2CH and CH_2C*H*CH_3), 1.02–0.98 (m, 12H, CHCH_3 and Si(CH_2CH_3)$_3$), 0.68 (q, J = 7.6 Hz, 6H, Si(C$H_2$$CH_3$)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ147.5, 146.5, 138.3, 135.6, 105.6, 105.2, 101.0, 77.6, 40.7, 37.9, 14.3, 7.1, 5.3. **HRMS** (EI): *m/z* Calcd for $C_{17}H_{26}O_3Si$: (M^+) 306.1651, found 306.1650.

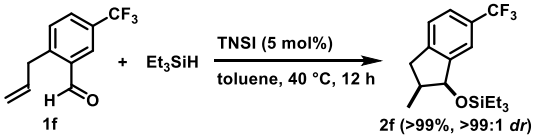


Reaction of 1d giving 2d: The general procedure was followed with **1d** (132.1 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 150 °C) gave **2d** (201.6 mg, 0.72 mmol, 90 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12–7.09 (m, 1H, Ar-*H*), 6.96 (d, J = 8.0 Hz, 1H, Ar-*H*), 6.90–6.85 (m, 1H, Ar-*H*), 5.08 (d, J = 5.6 Hz, 1H, C*H*OSi), 2.86 (dd, J = 16.0, 7.2 Hz, 1H, ArCH_2CH), 2.58–2.55 (m, 2H, ArCH_2CH and CH_2C*H*CH_3), 1.03–0.96 (m, 12H, CHCH_3 and Si(CH_2CH_3)$_3$), 0.70 (q, J = 8.0 Hz, 6H, Si(C$H_2$$CH_3$)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 162.3 (d, J_{CF} = 240.8 Hz), 147.3 (d, J_{CF} = 7.6 Hz), 137.3 (d, J_{CF} = 2.5 Hz), 126.0 (d, J_{CF} = 8.3 Hz), 114.4 (d, J_{CF} = 22.3 Hz), 111.4 (d, J_{CF} = 21.7 Hz), 77.7 (d, J_{CF} = 2.0 Hz), 40.9, 37.1, 14.0, 7.0, 5.2. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –117.2. **HRMS** (EI): *m/z* Calcd for $C_{16}H_{25}FOSi$: (M^+) 280.1659,

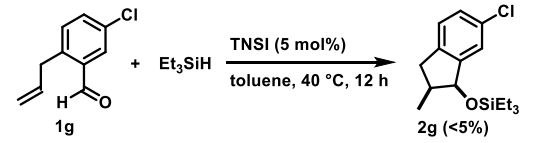
found 280.1659.



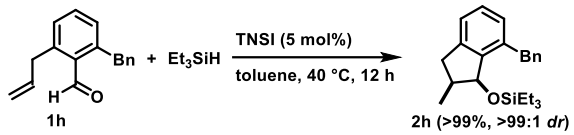
Reaction of 1e giving 2e: The general procedure was followed with **1e** (131.0 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 150 °C) gave **2e** (198.9 mg, 0.72 mmol, 89 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24–7.20 (m, 1H, Ar-*H*), 6.88–6.86 (m, *2*H, Ar-*H*), 5.04 (d, *J* = 6.0 Hz, 1H, C*H*OSi), 2.87 (dd, *J* = 15.6, 7.2 Hz, 1H, ArCH_2CH), 2.62 (dd, *J* = 15.6, 4.8 Hz, 1H, ArCH_2CH), 2.56–2.51 (m, 1H, CH_2CHCH_3), 1.01–0.97 (m, 12H, $CHCH_3$ and $Si(CH_2CH_3)_3$), 0.68 (q, *J* = 7.6 Hz, 6H, $Si(CH_2CH_3)_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 162.9 (d, J_{CF} = 242.2 Hz), 144.8 (d, J_{CF} = 8.7 Hz), 140.9 (d, J_{CF} = 2.0 Hz), 125.6 (d, J_{CF} = 8.7 Hz), 113.3 (d, J_{CF} = 22.1 Hz), 112.0 (d, J_{CF} = 21.4 Hz), 77.0, 40.8, 38.0 (d, J_{CF} = 2.0 Hz), 14.1, 7.1, 5.2. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –115.8. **HRMS** (EI): *m/z* Calcd for $C_{16}H_{25}FOSi$: (M^+) 280.1659, found 280.1657.



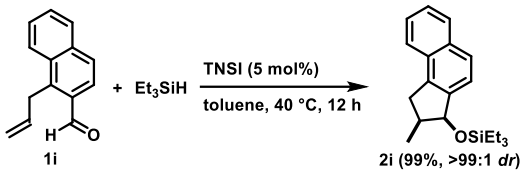
Reaction of 1f giving 2f: The general procedure was followed with **1f** (171.9 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 150 °C) gave **2f** (267.8 mg, 0.81 mmol, >99 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (s, 1H, Ar-*H*), 7.46 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.28 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 5.12 (d, *J* = 6.0 Hz, 1H, C*H*OSi), 2.94 (dd, *J* = 15.6, 6.8 Hz, 1H, ArCH_2CH), 2.67 (dd, *J* = 15.6, 4.0 Hz, 1H, ArCH_2CH), 2.61–2.55 (m, 1H, CH_2CHCH_3), 1.02–0.98 (m, 12H, $CHCH_3$ and $Si(CH_2CH_3)_3$), 0.70 (apparent q, *J* = 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). **^{13}C{^{1}H,^{19}F} NMR** (100 MHz, $CDCl_3$): δ 146.4, 146.0, 129.0, 125.4, 124.8, 124.7, 121.4, 77.3, 40.5, 37.8, 13.9, 7.0, 5.2. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –61.9. **HRMS** (CI): *m/z* Calcd for $C_{17}H_{26}F_3OSi$: $[M+H]^+$ 331.1705, found 331.1700.



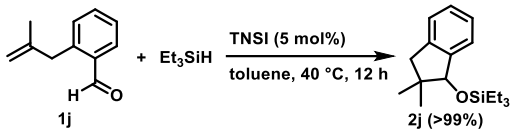
Reaction of 1g giving 2g: The general procedure was followed with **1g** (70.2 mg, 0.39 mmol), triethylsilane (70 μL, 0.44 mmol), and TNSI (10.8 mg, 0.02 mmol) in toluene (2.0 mL). The reaction was monitored by GC, and GC yield of **2g** was determined by using *n*-pentadecane as an internal standard.



Reaction of 1h giving 2h: The general procedure was followed with **1h** (189.4 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by silica gel column chromatography gave **2h** (285.4 mg, 0.81 mmol, >99 %) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.05 (m, 7H, Ar-*H* overlapped with residual $CHCl_3$), 6.81 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.23 (d, *J* = 5.6 Hz, 1H, C*H*OSi), 4.15 (s, 2H, ArCH_2Ph), 2.84 (dd, *J* = 15.2, 6.8 Hz, 1H, ArCH_2CH), 2.72 (dd, *J* = 15.2, 6.8 Hz, 1H, ArCH_2CH), 2.42–2.39 (m, 1H, CH_2CHCH_3), 1.10 (d, *J* = 6.8 Hz, 3H, CHCH_3), 0.95 (t, *J* = 8.0 Hz, 9H, Si(CH_2CH_3)$_3$), 0.65 (q, *J* = 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 143.7, 143.4, 141.3, 137.6, 129.2, 128.5, 128.2, 127.7, 126.0, 122.9, 77.9, 40.9, 38.1, 37.9, 14.6, 7.2, 5.7. **HRMS** (FAB): *m/z* Calcd for $C_{23}H_{32}OSiNa$: $[M+Na]^+$ 375.2120, found 375.2133.

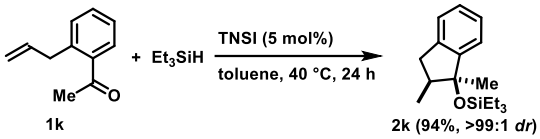


Reaction of 1i giving 2i: The general procedure was followed with **1i** (158.2 mg, 0.81 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by silica gel column chromatography gave **2i** (250.6 mg, 0.80 mmol, 99 %) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.81 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.51–7.43 (m, 3H, Ar-*H*), 5.30 (d, *J* = 6.4 Hz, 1H, C*H*OSi), 3.23 (dd, *J* = 15.8, 7.0 Hz, 1H, ArCH_2CH), 2.99 (dd, *J* = 15.8, 4.6 Hz, 1H, ArCH_2CH), 2.76–2.70 (m, 1H, CH_2CHCH_3), 1.10 (d, *J* = 7.2 Hz, 3H, CHCH_3), 1.03 (t, *J* = 8.0 Hz, 9H, Si(CH_2CH_3)$_3$), 0.84 (q, *J* = 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 141.8, 138.5, 133.6, 130.7, 128.6, 127.2, 125.9, 125.4, 124.5, 122.9, 78.5, 39.9, 36.3, 14.8, 7.1, 5.3. **HRMS** (EI): *m/z* Calcd for $C_{20}H_{28}OSi$: (M^+) 312.1909, found 312.1905.

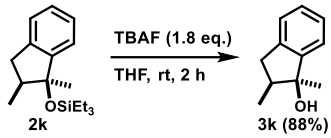


Reaction of 1j giving 2j: The general procedure was followed with **1j** (129.8 mg, 0.81 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 160 °C) gave **2j** (227.3 mg, 0.82 mmol, >99 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26–7.14 (m, 4H, Ar-*H* overlapped with residual $CHCl_3$), 4.76 (s, 1H, C*H*OSi), 2.71 (d, *J* = 15.2 Hz, 1H, ArCH_2C(CH_3)$_2$), 2.61 (d, *J* = 15.2 Hz, 1H, ArCH_2C(CH_3)$_2$), 1.17 (s, 3H, C(CH_3)), 1.02 (t, *J* = 8.0 Hz, 9H, Si(CH_2CH_3)$_3$), 0.94 (s, 3H, C(CH_3)), 0.71 (q, *J* = 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 145.6, 141.5, 127.4, 126.3, 125.0, 124.3, 83.7, 45.7, 45.0, 26.8, 21.8, 7.1, 5.4. **HRMS** (EI): *m/z* Calcd

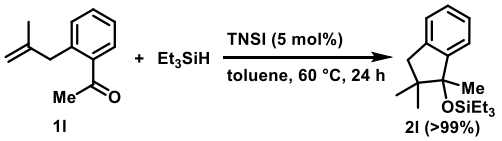
for $C_{17}H_{28}OSi$: (M^+) 276.1909, found 276.1911.



Reaction of 1k giving 2k: The general procedure was followed with **1k** (128.4 mg, 0.80 mmol) and triethylsilane (130 μL, 0.82 mmol). The reaction mixture was stirred at 40 °C for 24 h. Purification by Kugelrohr distillation (0.4 mmHg, 160 °C) gave **2k** (208.6 mg, 0.75 mmol, 94 %) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 7.22–7.17 (m, 3H, Ar-*H*), 2.79 (dd, *J* = 15.2, 7.2 Hz, 1H, ArCH_2CH), 2.67 (dd, *J* = 15.2, 9.6 Hz, 1H, ArCH_2CH), 2.10–2.04 (m, 1H, CH_2CHCH_3), 1.55 (s, 3H, C(CH_3)OSi), 1.12 (d, *J* = 6.8 Hz, 3H, CHCH_3), 0.79 (t, *J* = 8.0 Hz, 9H, Si(CH_2CH_3)$_3$), 0.32 (apparent q, *J* = 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.4, 144.3, 128.1, 125.9, 124.9, 123.2, 82.1, 47.8, 38.2, 25.2, 12.9, 7.1, 6.3. **HRMS** (EI): *m/z* Calcd for $C_{17}H_{28}OSi$: (M^+) 276.1909, found 276.1906.



Desilylation of 2k with TBAF: To a solution of **2k** (386.2 mg, 1.4 mmol) in THF (4.0 mL) was added TBAF (1M in THF, 3.0 mL, 3.0 mmol) at room temperature and stirred for 2 h to complete the reaction. Then, the reaction was quenched by sat. NH_4Cl aq., and the organic layer was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. After the filtration, the solvent was removed under reduced pressure followed by the purification by the silica gel column chromatography to give **3k** (198.9 mg, 1.2 mmol, 88%) as pale yellow oil. Spectroscopic data of **3k** was identical to that previously reported.[S4]



Reaction of 1l giving 2l: The general procedure was followed with **1l** (140.6 mg, 0.81 mmol) and triethylsilane (130 μL, 0.82 mmol). Purification by Kugelrohr distillation (0.4 mmHg, 180 °C) gave **2l** (233.6 mg, 0.80 mmol, >99%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28–7.26 (m, 1H, Ar-*H* overlapped with residual $CHCl_3$), 7.20–7.15 (m, 3H, Ar-*H*), 2.95 (d, *J* = 15.2 Hz, 1H, ArCH_2C(CH_3)$_2$), 2.42 (d, *J* = 15.2 Hz, 1H, ArCH_2C(CH_3)$_2$), 1.42 (s, 3H, C(CH_3)OSi), 1.13 (s, 3H, ArCH_2C(CH_3)$_2$), 0.83–0.79 (m, 12H, Si(CH_2CH_3)$_3$ and ArCH_2C(CH_3)$_2$), 0.38–0.32 (m, 6H, Si(CH_2CH_3)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.0, 143.6, 127.9, 125.8, 125.2, 123.5, 85.0, 48.6, 45.6, 25.0, 21.8, 21.1, 7.2, 6.4. **HRMS** (EI): *m/z* Calcd for $C_{18}H_{30}OSi$: (M^+) 290.2066, found 290.2066.

7. Enantioselective reductive coupling reaction (Scheme 3)

7-1. Preliminary optimization of reaction conditions

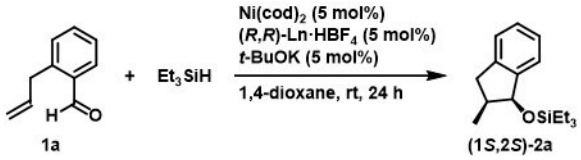
General procedures for the evaluation of chiral NHC ligands (Table S2): A reaction tube was charged with **Ln**·HBF_4 (0.04 mmol) and *t*-BuOK (0.04 mmol) in 1,4-dioxane (3.0 mL). After stirring for 5 minutes, the reaction mixture was added $Ni(cod)_2$ (0.04 mmol), **1a** (0.80 mmol), and triethylsilane (0.82 mmol). The reaction mixture was stirred at room temperature for 24 h. The reaction was monitored by GC, and GC yield of **2a** was determined by using *n*-pentadecane as an internal standard. **2a** was isolated by Kugelrohr distillation. The enantioselectivity of **2a** was determined by using SFC after converting it into desilylated product **3a**. Desilylation was conducted by the same procedure as mentioned above (see Chapter 3).

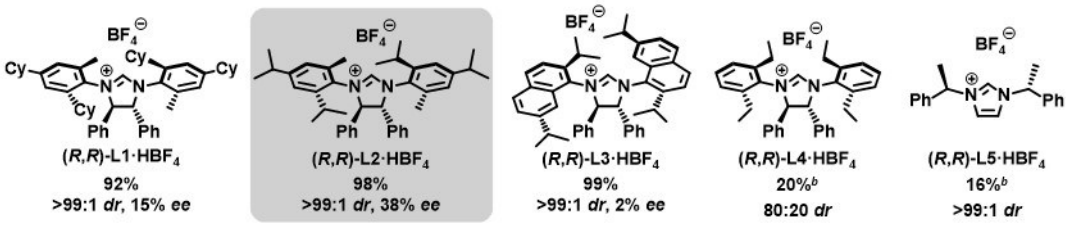
General procedures for the evaluation of solvents (Table S3): A reaction tube was charged with **L2**·HBF_4 (0.04 mmol) and *t*-BuOK (0.04 mmol) in solvent (3.0 mL). After stirring for 5 minutes, the reaction mixture was added $Ni(cod)_2$ (0.04 mmol), **1a** (0.80 mmol), and triethylsilane (0.82 mmol). The reaction mixture was stirred at room temperature for 24 h. The reaction was monitored by GC, and GC yield of **2a** was determined by using *n*-pentadecane as an internal standard. **2a** was isolated by Kugelrohr distillation. The enantioselectivity of **2a** was determined by using SFC after converting it into desilylated product **3a**. Desilylation was conducted by the same procedure as mentioned above (see Chapter 3).

Chiral separation (Figure S3): The enantioselectivity was measured by using SFC with Chiralpak IC (Back pressure = 15 MPa, Flow (CO_2) = 4.0 mL/min, Flow (isopropanol) = 0.3 mL/min, 25 °C, λ = 264 nm). Retention time: t_R = 2.3 min (1*S*,2*S*-enantiomer) and 2.5 min (1*R*,2*R*-enantiomer).

Result and Discussions: The reaction conditions were optimized with **1a** and triethylsilane. The results of the preliminary optimization of reaction conditions are summarized in Tables S2 and S3. In the case of employing **L1**, **L2**, and **L3** as a chiral ligand, **2a** was obtained in excellent yields and diastereoselectivities. Among them, **L2** gave **2a** in the highest enantioselectivity (38% *ee*). The result of the SFC analysis is shown in Figure S3. **L4** and **L5** gave **2a** in poor yields (16–20% GC yield). Next, the effect of solvent on the reaction was surveyed by employing **L2** as a ligand and we found that 1,4-dioxane gave **2a** in the highest enantioselectivity (entry 1). The use of THF, DME and toluene allowed the reaction to give **2a** in moderate to good yields, however enantioselectivities were relatively low (<24% *ee*, entries 2–4). The absolute configuration of **3a** was confirmed by the analogy to the literature data.[S3b]

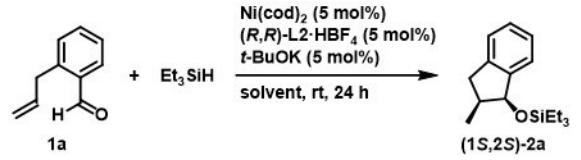
Table S2. Preliminary optimization of reaction conditions: chiral NHC ligands[a]





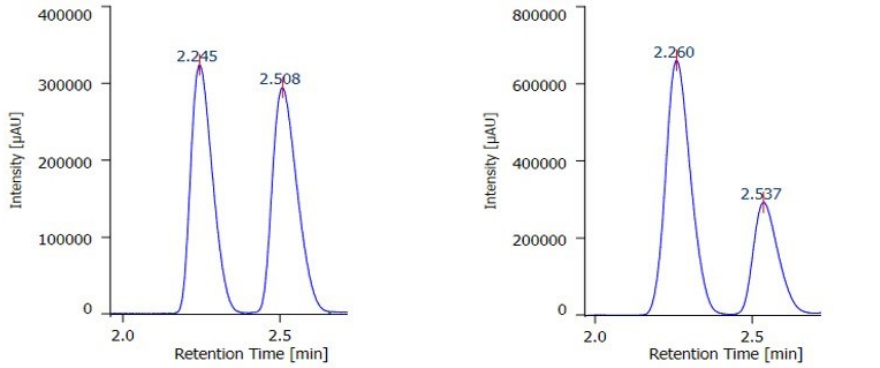
[a] Isolated yield of **2a** is presented. Diastereoselectivity was determined by GC, and enantioselectivity was determined by SFC after converting it into **3a** by desilylation.
[b] Determined by GC using *n*-pentadecane as an internal standard.

Table S3. Preliminary optimization of reaction conditions: solvents



entry	solvent	conv. (%)[a]	yield (%)[a]	*dr*[a]	*ee* (%)[b]
1	1,4-dioxane	>99	82 (98)[c]	>99:1	38
2	THF	>99	75	>99:1	10
3	DME	>99	91	>99:1	24
4	toluene	>99	86	>99:1	23

[a] Determined by GC using *n*-pentadecane as an internal standard.
[b] Determined by SFC after converting into **3a** by desilylation.
[c] Isolated yield.



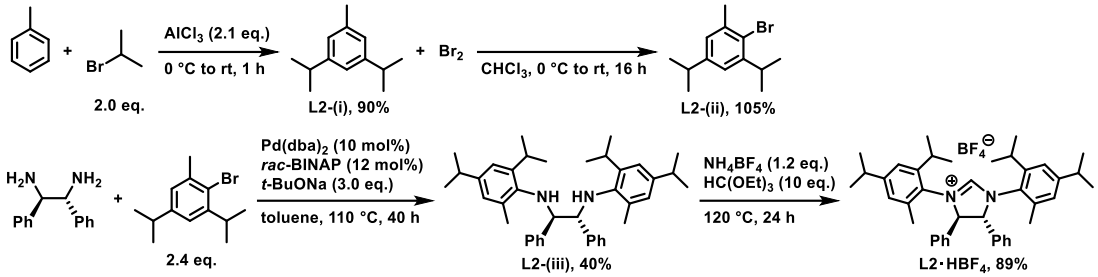
peak #	tR (min)	area (µV·sec)	hight (µV)	area (%)
1	2.245	1600938	325914	49.036
2	2.508	1663882	296433	50.964

peak #	tR (min)	area (µV·sec)	hight (µV)	area (%)
1	2.260	3683446	661107	69.005
2	2.537	1654482	293032	30.995

Figure S3. Chiral separation by using SFC

7-2. Preparation of Chiral imidazolinium salt (Ln•HBF_4)

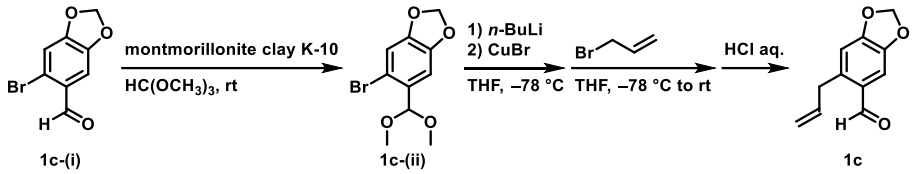
Chiral imidazolinium salt **Ln** · HBF_4 was prepared by literature procedures.[S5] A novel chiral imidazolinium salt **L2** · HBF_4 was prepared according to the procedures reported for **L1** · HBF_4 by Montgomery *et al*.[S5a]



Preparation of (4*R*,5*R*)-1,3-bis(2,4-diisopropyl-6-methylphenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-iumtetrafluoroborate (L2 · HBF_4): Synthesis of 3,5-diisopropyl toluene (**L2-(i)**),[S6] 2-bromo-3,5-diisopropyl toluene (**L2-(ii)**),[S7] and 1*R*,2*R*-N^1,N^2-bis(2,4-diisopropyl-6-methylphenyl)-1,2-diphenylethane-1,2-diamine (**L2-(iii)**)[S7] were previously reported. To a solution of **L2-(iii)** (4.5 g, 8.0 mmol) in triethyl orthoformate (12.0 g, 80.0 mmol) was added ammonium tetrafluoroborate (1.0 g, 9.6 mmol) and formic acid (3 drops). The reaction mixture was stirred at 120 °C for 24 h. The crude reaction mixture was purified by silica gel column chromatography (with 5% methanol/CH_2Cl_2) to give (4*R*,5*R*)-1,3-bis(2,4-diisopropyl-6-methylphenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-iumtetrafluoroborate (**L2** · HBF_4) (4.7 g, 7.1 mmol, 89%) as a pale yellow solid. The complicated spectroscopic data would suggest an existence of rotamers. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.80 (s, 0.13H), 8.58 (s, 0.60H), 8.31 (s, 0.29H) (correspond to the three rotamers of a single proton: NC*H*N), 7.39–7.26 (m, 10H, Ar-*H* overlapped with residual $CHCl_3$), 7.09 (bs, 2H, Ar-*H*), 6.86–6.80 (m, 2H, Ar-*H*), 6.09–6.06 (m, 1H), 5.85–5.77 (m, 1H) (correspond to three rotamers of two protons: NC*H*Ph), 3.30–3.18 (m, 1H, C*H*$(CH_3)_2$), 2.84–2.65 (m, 8H, C*H*$(CH_3)_2$ and CH_3), 1.90–1.08 (m, 21H), 0.57 (d, *J* = 6.4 Hz, 2H, CH(CH_3)$_2$), 0.47 (d, *J* = 6.4 Hz, 2H, CH(CH_3)$_2$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.5, 157.9, 152.1, 151.8, 151.7, 147.4, 146.4, 145.2, 137.6, 135.0, 134.6, 131.4, 131.3, 131.0, 130.9, 130.8, 130.4, 129.8, 129.8, 129.6, 129.4, 129.4, 129.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.2, 127.0, 123.2, 122.7, 122.7, 77.4, 74.8, 72.9, 72.7, 34.1, 34.0, 29.9, 29.3, 25.8,. 25.6, 25.2, 24.7, 23.8, 23.8, 22.6, 22.3, 19.4, 19.1, 18.8. **HRMS** (FAB^+): *m/z* Calcd for $C_{41}H_{51}BF_4N_2$: $[M–BF_4]^+$ 571.4047, found 571.4039.

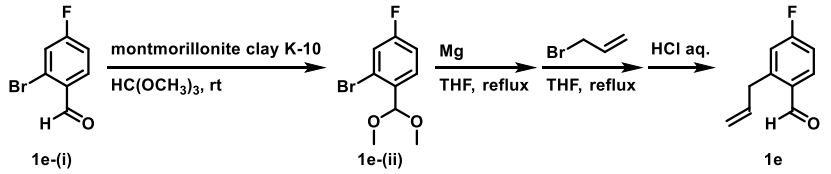
8. Preparation of substrates

1a–b, **1d**, and **1g–j** were prepared by following the procedure reported previously.[S8]



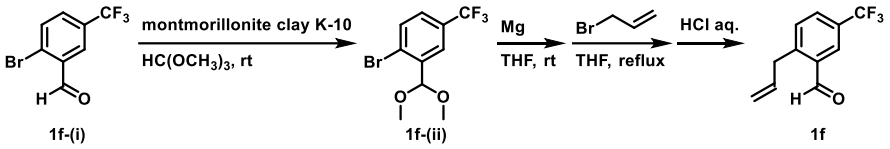
Preparation of 1c-(ii): A mixture of montmorillonite K-10 (20 g) and trimethyl orthoformate (30 mL) was stirred for 10 minutes at room temperature. Then, **1c-(i)** (10.0 g, 43.7 mmol) was added and the resultant mixture was stirred for 1 h. After filtration, all volatiles were removed under reduced pressure to give **1c-(ii)** (12.0 g, 43.6 mmol, >99%) as pale yellow oil, which was employed in the next step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.09 (s, 1H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 5.98 (s, 2H, OCH_2O), 5.46 (s, 1H, C*H*(OCH_3)$_2$), 3.37 (s, 6H, CH(OCH_3)$_2$).

Preparation of 1c: To a solution of **1c-(ii)** (12.0 g, 43.6 mmol) in THF (40 mL) was added dropwise a solution of *n*-BuLi (2.6 M in hexane, 20.0 mL, 56.0 mmol) in THF (40 mL) at –78 °C, and the reaction mixture was stirred at –78 °C for 1 h. CuBr (6.3 g, 43.7 mmol) was added portionwise and the reaction mixture was stirred at –78 °C for 4 h. To this reaction mixture was added dropwise a solution of allyl bromide (6.3 g, 52.0 mmol) in THF (30 mL), and then the resultant mixture was allowed to warm to room temperature with stirring overnight. 1 M HCl aq. was added to the reaction mixture, and stirred for 10 minutes. The organic layer was extracted with ether and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give **1c** (8.2 g, 43.1 mmol, 99%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.12 (s, 1H, C*H*O), 7.33 (s, 1H, Ar-*H*), 6.72 (s, 1H, Ar-*H*), 6.09–5.98 (m, 3H, OCH_2O and CH_2C*H*=CH_2), 5.11 (d, *J* = 10.4 Hz, 1H, CH_2CH=CH_2), 4.98 (d, *J* = 16.8 Hz, 1H, CH_2CH=CH_2), 3.72 (d, *J* = 6.0 Hz, 2H, CH_2CH=CH_2). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 189.6, 152.7, 147.1, 139.9, 137.1, 128.6, 116.7, 110.7, 108.6, 102.1, 36.1. **HRMS** (EI): *m/z* Calcd for $C_{11}H_{10}O_3$: (M^+) 190.0630, found 190.0628.

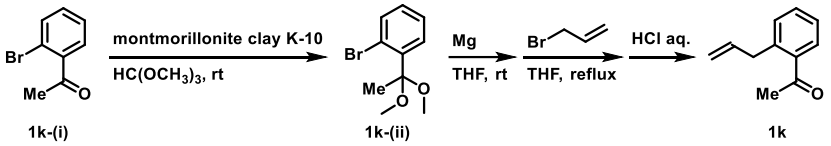


Preparation of 1e: Synthesis of **1e-(ii)** was conducted by the same procedure as mentioned above. To a suspension of Mg (3.8 g, 157.0 mmol), which had been activated by stirring under reduced pressure for 3 h, in THF (40 mL) was added slowly a solution of **1e-(ii)** (36.2 g, 145.3 mmol) in THF (100 mL) at 0 °C. The reaction mixture was stirred at 80 °C for 2 h. Then, to this solution was added dropwise a solution of allyl bromide (19.0 g, 157.0 mmol) in THF (80 mL) at 0 °C. The reaction mixture was

stirred at 80 °C for 16 h. After cooling to room temperature, 5 M HCl aq. was added to the reaction mixture, and stirred for 4 h. The organic layer was extracted with ether and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give **1e** (24.0 g, 146.2 mmol, >99%) as orange oil. Spectroscopic data of **1e** was identical to that previously reported.[S9]

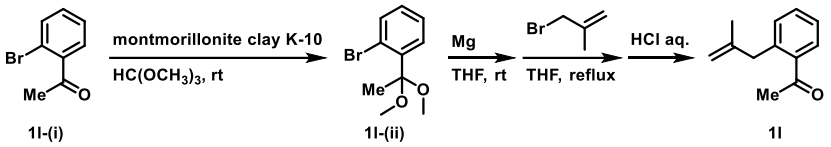


Preparation of 1f: Synthesis of **1f-(ii)** was conducted by the same procedure as mentioned above. To a suspension of Mg (0.6 g, 24.7 mmol), which had been activated by stirring under reduced pressure for 3 h, in THF (10 mL) was added slowly a solution of **1f-(ii)** (5.7 g, 19.1 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. Then, to the solution was added dropwise a solution of allyl bromide (3.4 g, 28.5 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at 80 °C for 6 h. After cooling to room temperature, 5 M HCl aq. was added to the reaction mixture, and stirred for 3 days. The organic layer was extracted with ether and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give **1f** (3.9 g, 18.0 mmol, 94%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.29 (s, 1H, C*H*O), 8.12 (s, 1H, Ar-*H*), 7.78 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.45 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.07–5.97 (m, 1H, CH_2CH=CH_2), 5.15 (d, *J* = 10.0 Hz, 1H, CH_2CH=CH_2), 5.00 (d, *J* = 16.8 Hz, 1H, CH_2CH=CH_2), 3.87 (d, *J* = 6.0 Hz, 2H, CH_2CH=CH_2). **^{13}C{^{1}H,^{19}F} NMR** (100 MHz, $CDCl_3$): δ 190.9, 146.1, 136.0, 134.2, 131.9, 130.3, 129.8, 128.2, 123.7, 117.5, 36.5. **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.8. **HRMS** (CI): *m/z* Calcd for $C_{11}H_{10}F_3O$: $[M+H]^+$ 215.0684, found 215.0682.



Preparation of 1k: Synthesis of **1k-(ii)** was conducted by the same procedure as mentioned above. To a suspension of Mg (3.0 g, 126.5 mmol), which had been activated by stirring under reduced pressure for 3 h, in THF (20 mL) was added slowly a solution of **1k-(ii)** (28.2 g, 115.1 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. Then, to the solution was added dropwise a solution of allyl bromide (16.7 g, 138.0 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at 80 °C for 2 h. After cooling to room temperature, 1 M HCl aq. was added to the reaction mixture, and stirred for 1 h. The organic layer was extracted with ether and dried

over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give **1k** (18.1 g, 113.0 mmol, 98%) as pale yellow oil. Spectroscopic data of **1k** was identical to that previously reported.[S10]



Preparation of 1l: Synthesis of **1l-(ii)** was conducted by the same procedure as mentioned above. To a suspension of Mg (1.0 g, 43.0 mmol), which had been activated by stirring under reduced pressure for 3 h, in THF (10 mL) was added slowly a solution of **1l-(ii)** (9.8 g, 40.0 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. To the solution was added dropwise a solution of methallyl bromide (6.5 g, 48.0 mmol) in THF (40 mL) at 0 °C. The reaction mixture was stirred at 80 °C for 2 h. After cooling to room temperature, 3 M HCl aq. was added to the reaction mixture, and stirred for overnight. The organic layer was extracted with ether and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure to give **1l** (6.9 g, 39.6 mmol, 99%) as pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 1H, Ar-*H*), 7.39 (dd, J = 7.6 Hz, 1H, Ar-*H*), 7.30–7.24 (m, 2H, Ar-*H* overlapped with residual $CHCl_3$), 4.77 (s, 1H, $CH_2C(CH_3)=CH_2$), 4.42 (s, 1H, $CH_2C(CH_3)=CH_2$), 3.59 (s, 2H, $CH_2CH=CH_2$), 2.54 (s, 3H, $ArCOCH_3$), 1.72 (s, 3H, $CH_2C(CH_3)=CH_2$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 202.6, 145.6, 139.1, 139.0, 131.8, 131.3, 128.8, 126.3, 111.7, 41.4, 30.0, 23.1. **HRMS** (EI): *m/z* Calcd for $C_{12}H_{14}O$: (M^+) 174.1045, found 174.1044.

9. References for the *Supplementary Information*

S1. (a) A. J. Arduengo III, R. Krafczyk and R. Schmutzler, *Tetrahedron*, 1999, **55**, 14523; (b) E. A. Mistryukov, *Mendeleev Commun.*, 2006, **16**, 258.

S2. Y. Hoshimoto, Y. Hayashi, H. Suzuki, M. Ohashi and S. Ogoshi, *Organometallics*, 2014, **33**, 1276.

S3. (a) P. A. Marshall and R. H. Prager, *Aust. J. Chem.*, 1979, **32**, 1251; (b) R. Fernández, A. Ros, A. Magriz, H. Dietrich and J. M. Lassaletta, *Tetrahedron*, 2007, **63**, 6755.

S4. N. M. Kablaoui and S. L. Buchwald, *J. Am. Chem. Soc.,* 1996, **118**, 3182.

S5. Preparation of **L1**·HBF_4, see: (a) M. R. Chaulagain, G. J. Sormunen and J. Montgomery, *J. Am. Chem. Soc.*, 2007, **129**, 9568; Preparation of **L3**·HBF_4, see: (b) X. Luan, R. Mariz, C. Robert, M. Gatti, S. Blumentritt, A. Linden, and R. Dorta, *Org. Lett.*, 2008, **10**, 5569; Preparation of **L4**·HBF_4, see: (c) L. Xu and Y. Shi, *J. Org. Chem.*, 2008, **73**, 749; Preparation of **L5**·HBF_4, see: (d) C. D. Campbell, C. Concellón and A. D. Smith, *Tetrahedron: Asymmetry*, 2011, **22**, 797.

S6. M. Ghiaci and J. Asghari, *Synth. Commun.*, 1998, **28**, 2213.

S7. G. J. Mercer, M. Sturdy, D. R. Jensen and M. S. Sigman, *Tetrahedron*, 2005, **61**, 6418.

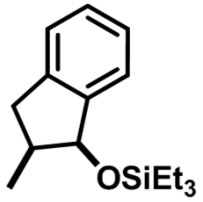
S8. Y. Hoshimoto, Y. Hayashi, H. Suzuki, M. Ohashi and S. Ogoshi, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 10812.

S9. S. Fustero, E. Rodríguez, R. Lázaro, L. Herrera, S. Catalán and P. Barrio, *Adv. Synth. Catal.*, 2013, **355**, 1058.

S10. K. T. Tarantino, P. Liu and R. R. Knowles, *J. Am. Chem. Soc.*, 2013, **135**, 10022.

10. NMR spectra

^{1}H NMR (400 MHz, $CDCl_3$)



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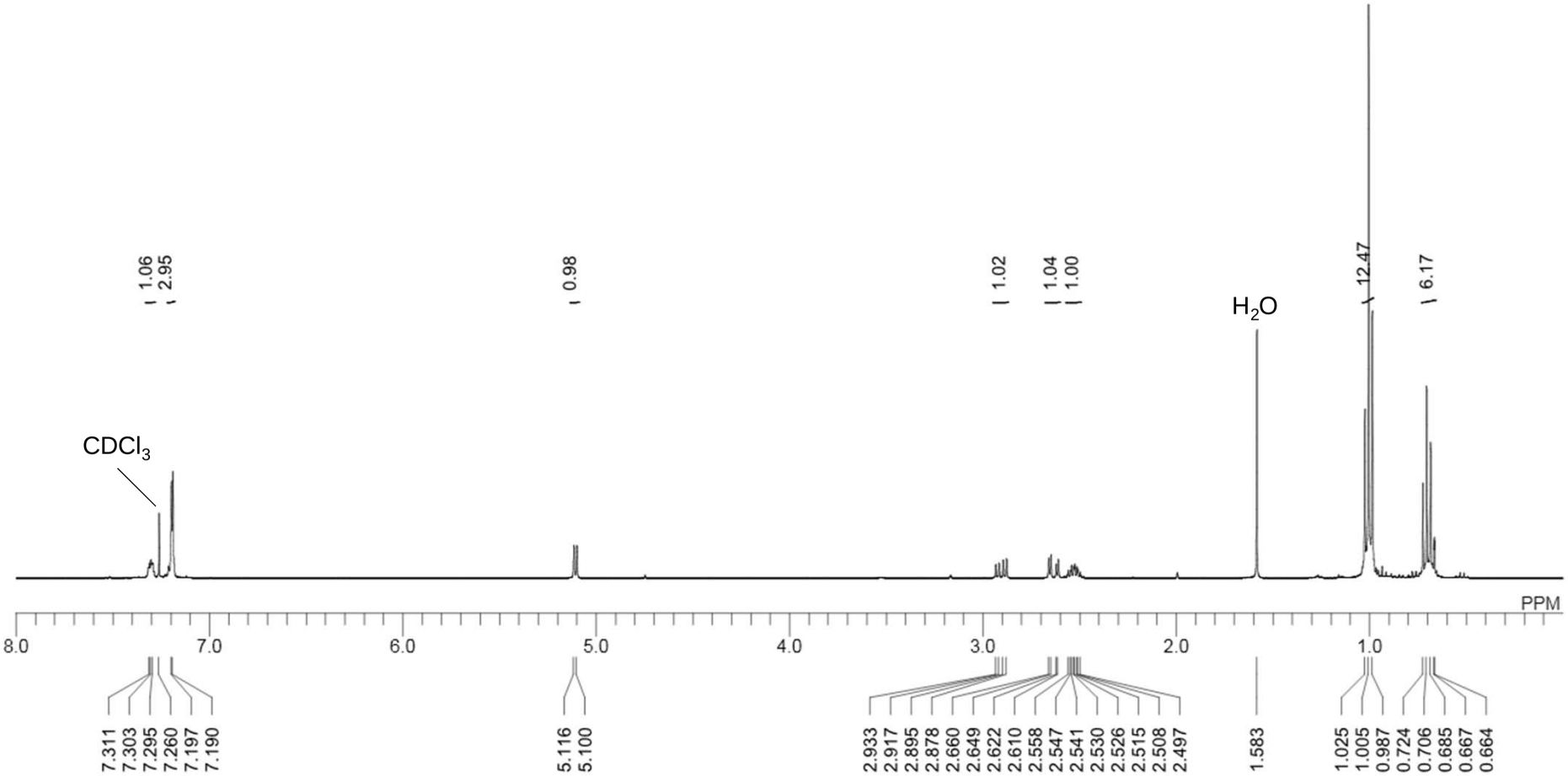
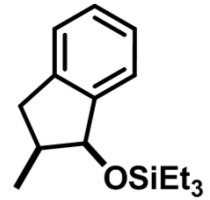


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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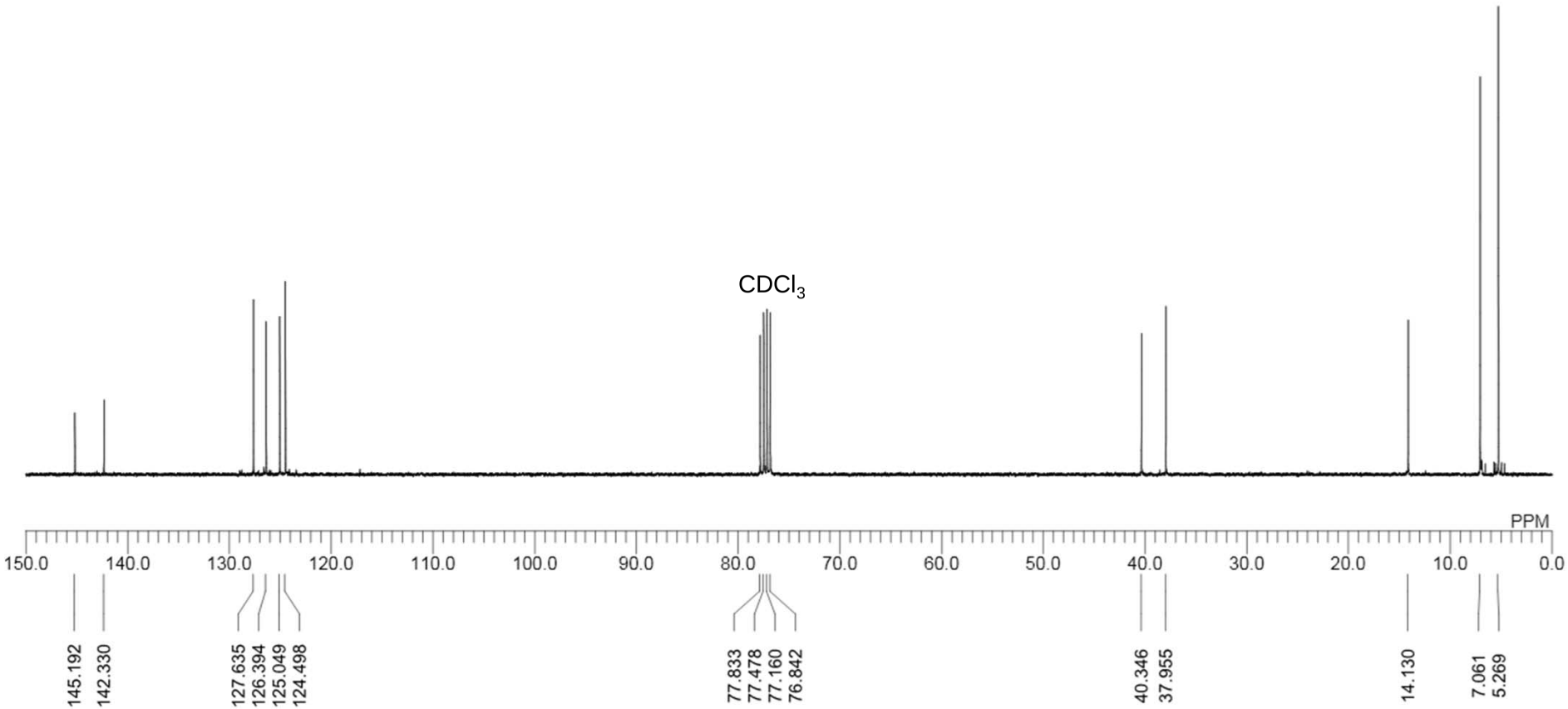
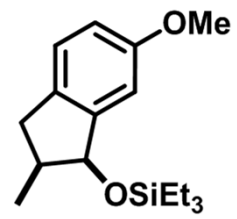


^{1}H NMR (400 MHz, $CDCl_3$)



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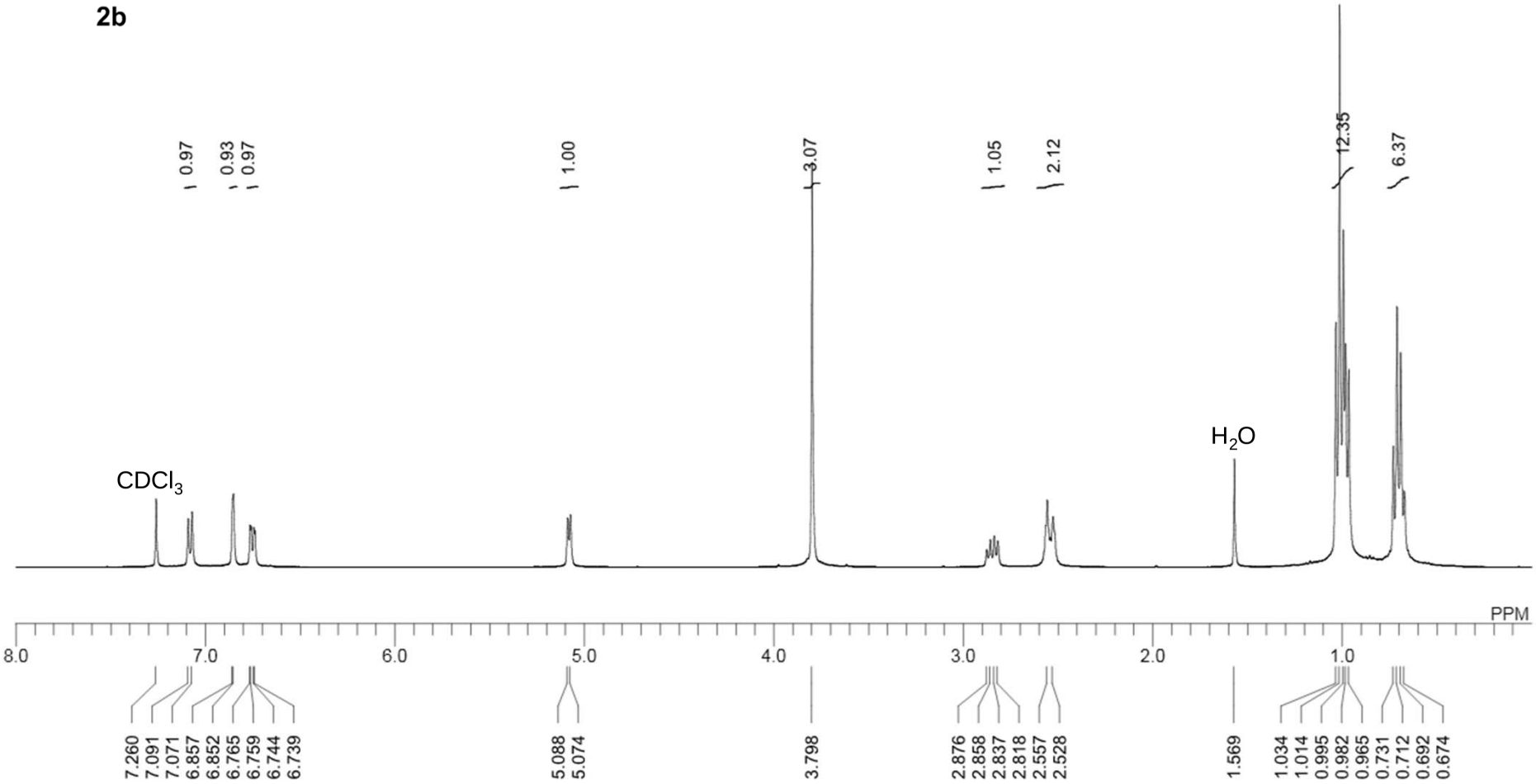
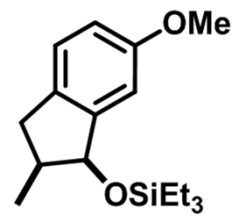


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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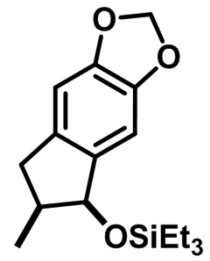
^{1}H NMR (400 MHz, $CDCl_3$)



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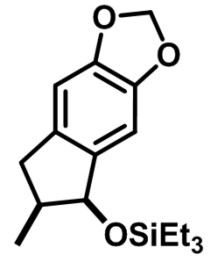
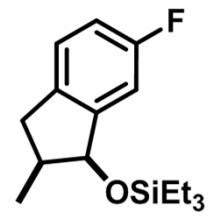
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



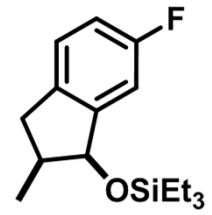
2c

^{1}H NMR (400 MHz, $CDCl_3$)



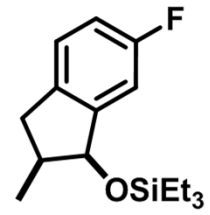
2d

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



2d

^{19}F NMR (376 MHz, $CDCl_3$)



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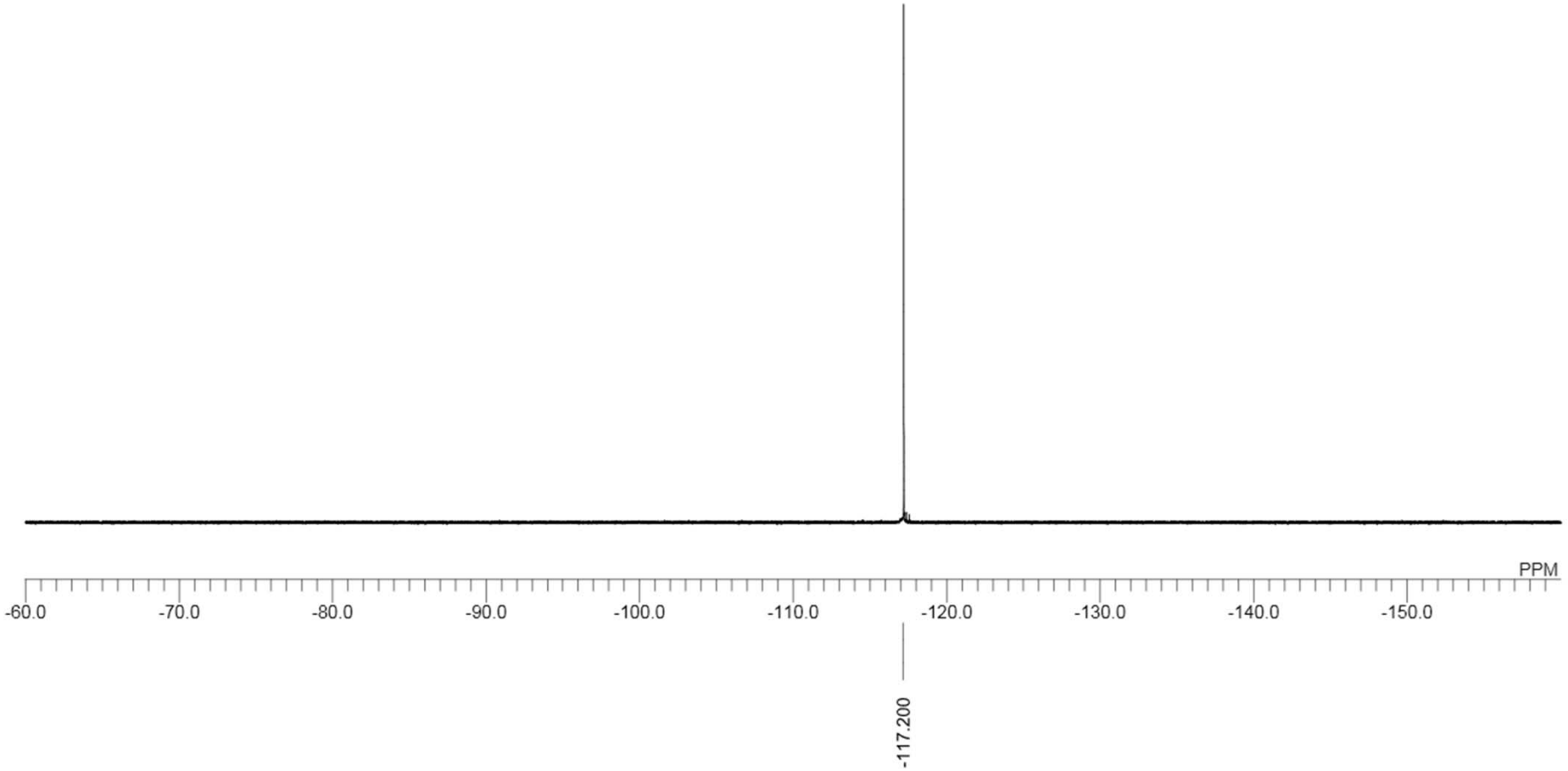
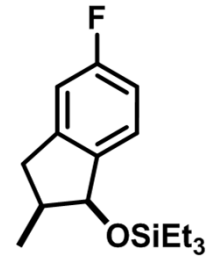


^{1}H NMR (400 MHz, $CDCl_3$)



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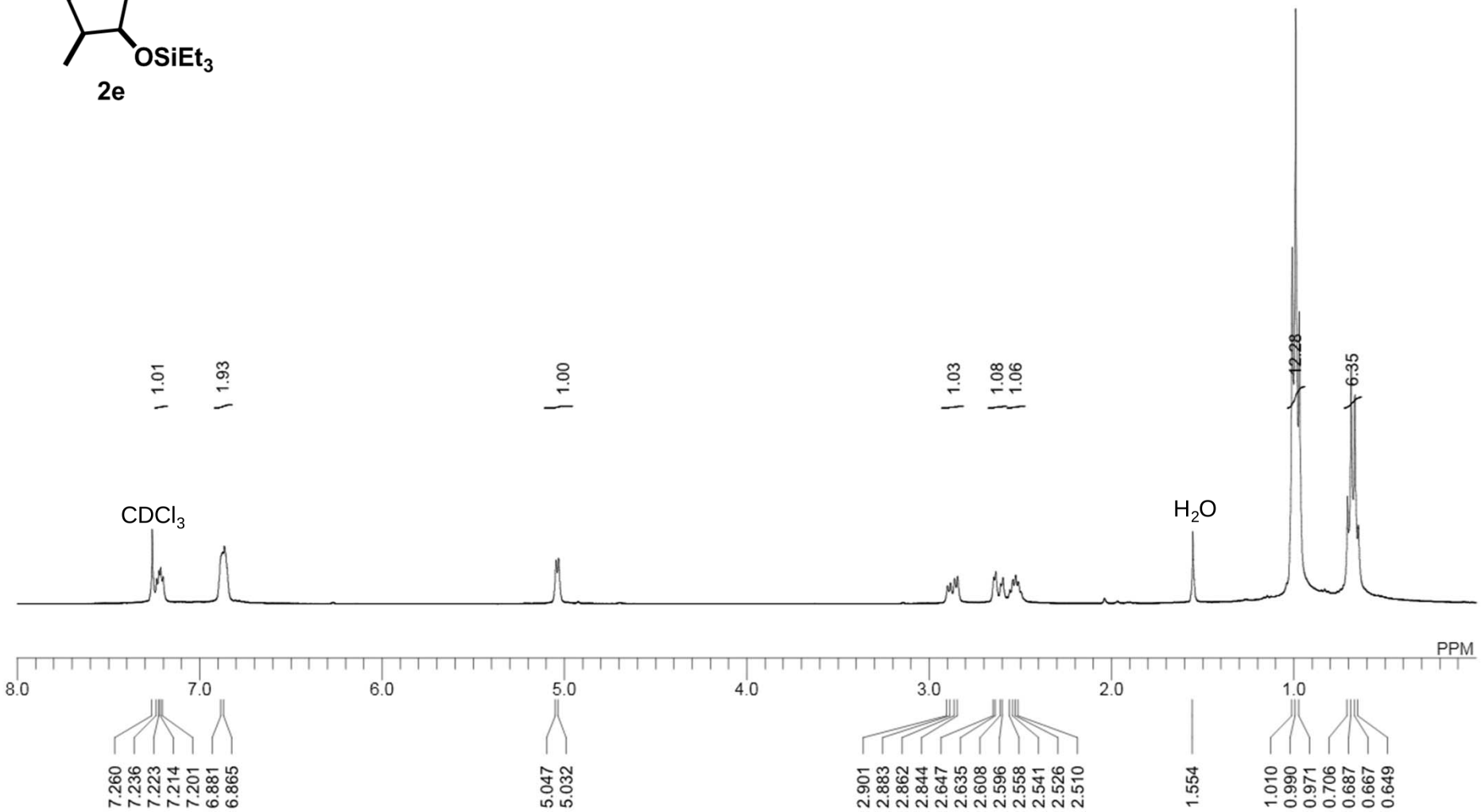
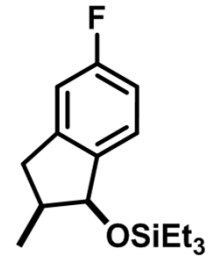
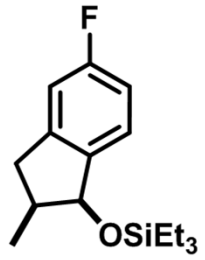


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



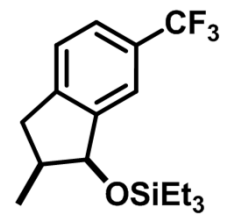
2e

^{19}F NMR (376 MHz, $CDCl_3$)



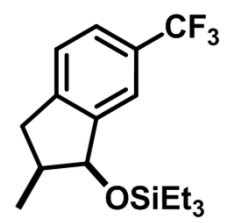
2e

^{1}H NMR (400 MHz, $CDCl_3$)



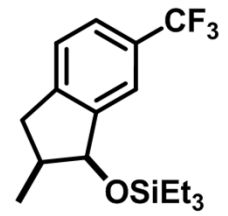
2f

$^{13}C\{^{1}H, ^{19}F\}$ NMR (100 MHz, $CDCl_3$)



2f

^{19}F NMR (376 MHz, $CDCl_3$)



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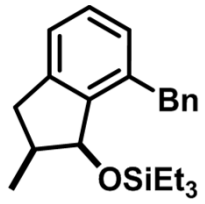
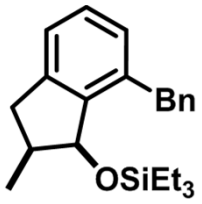
^{1}H NMR (400 MHz, $CDCl_3$)



2h

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



2h

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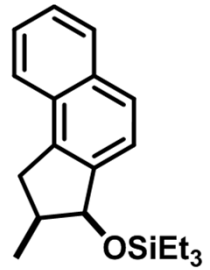

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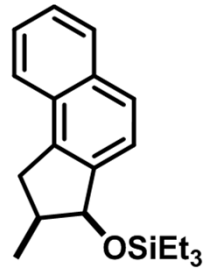
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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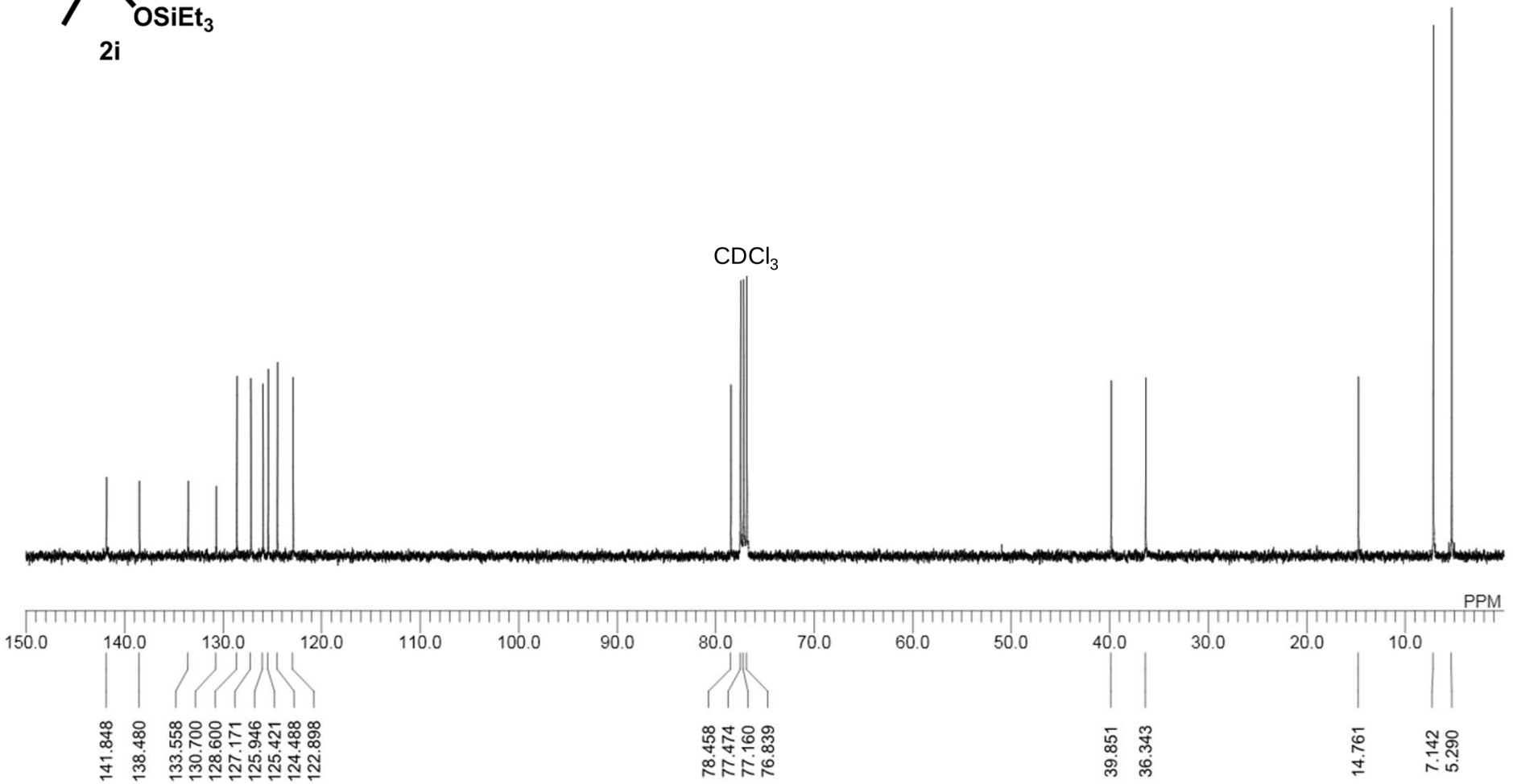
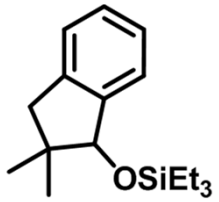


^{1}H NMR (400 MHz, $CDCl_3$)



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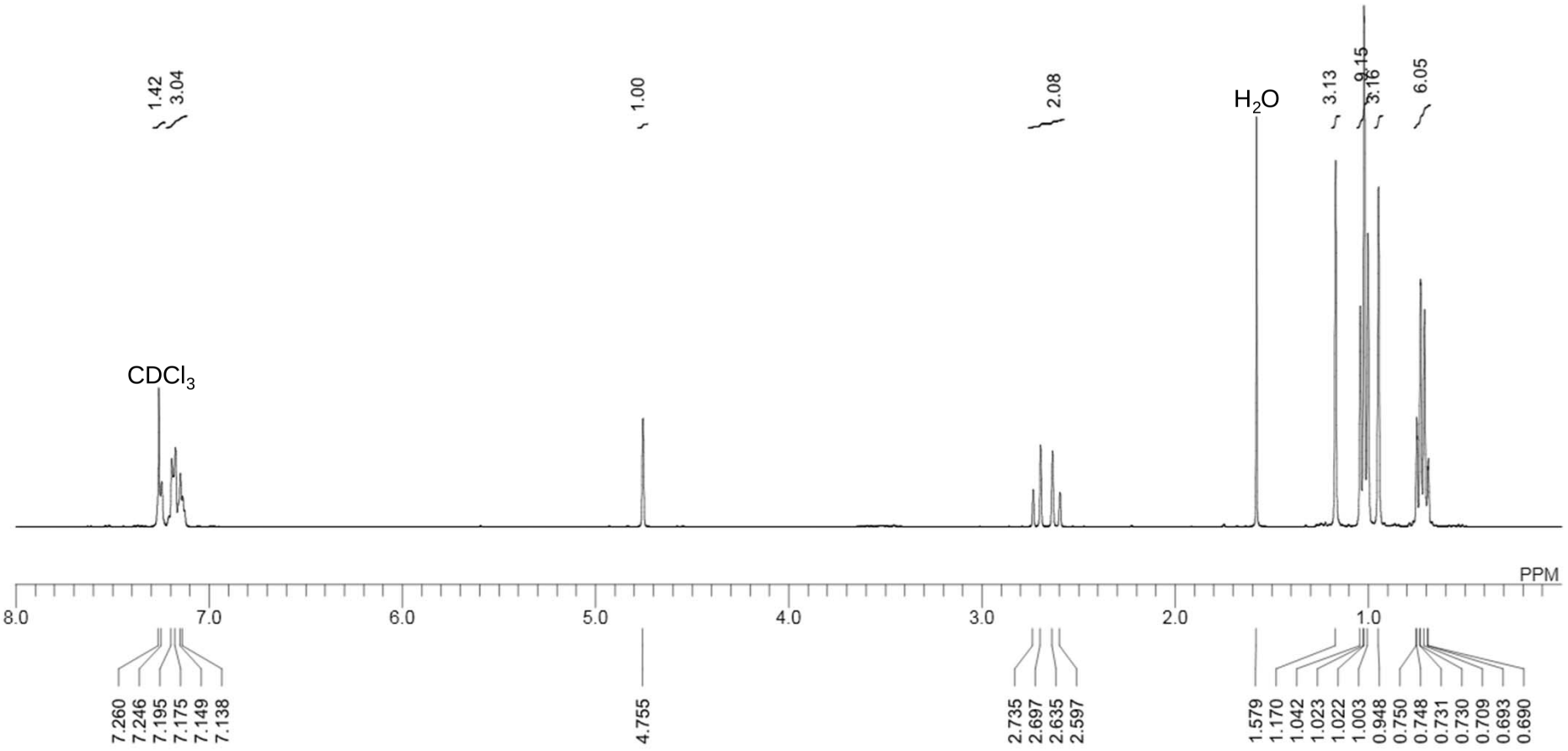
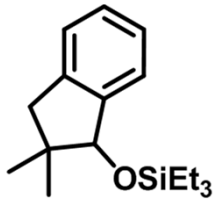


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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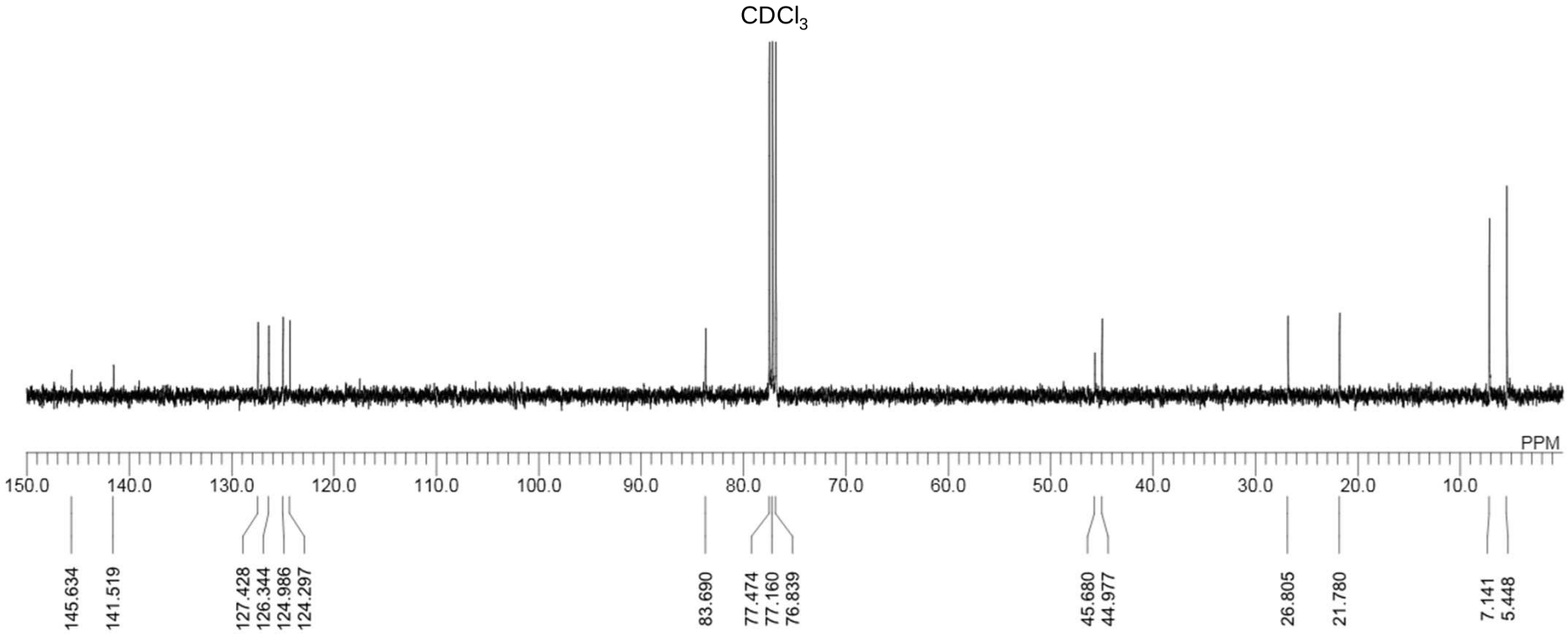

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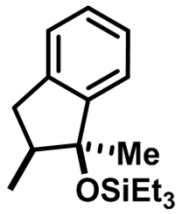

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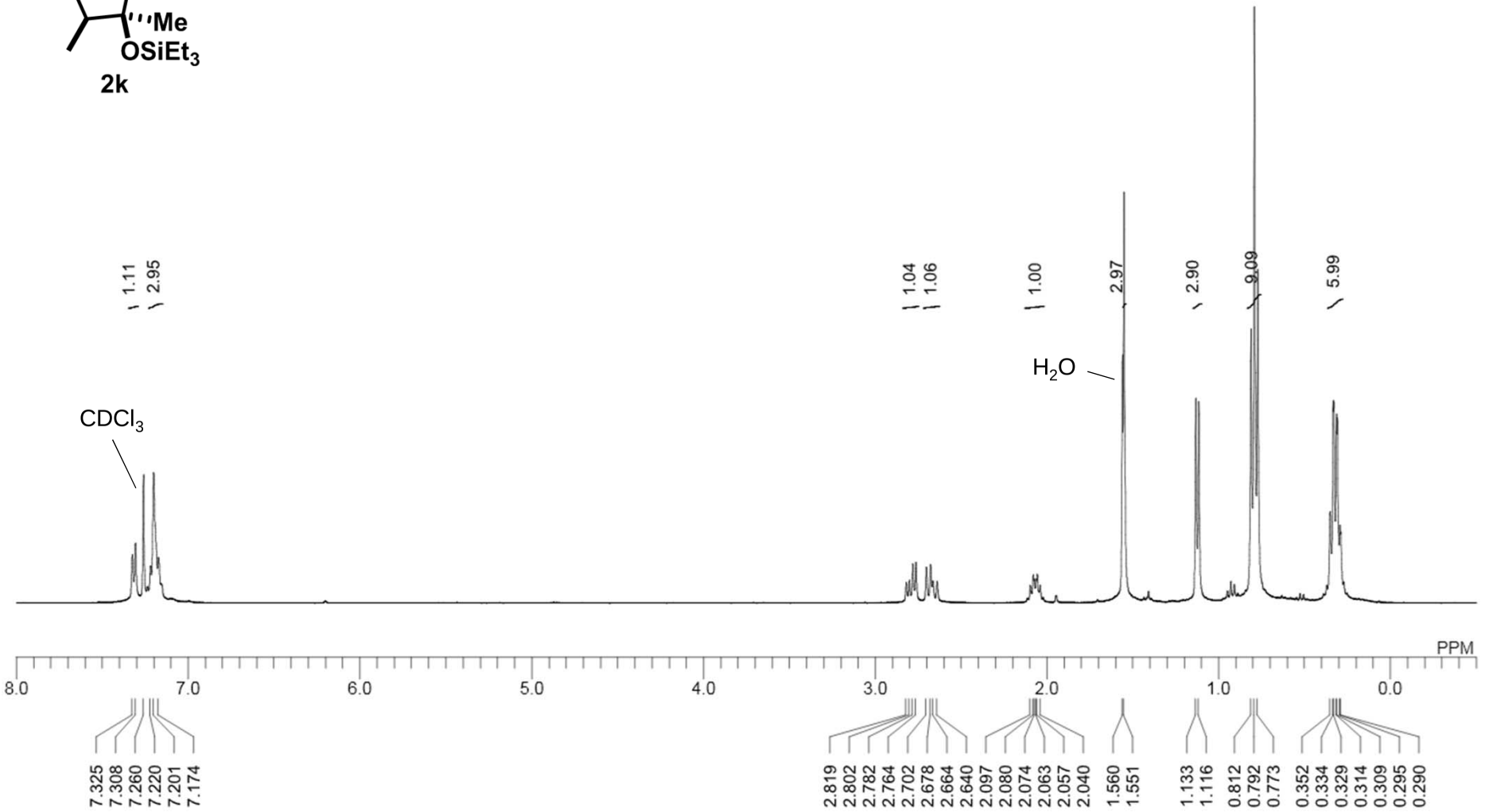

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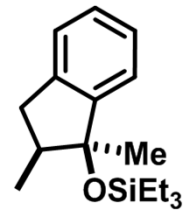

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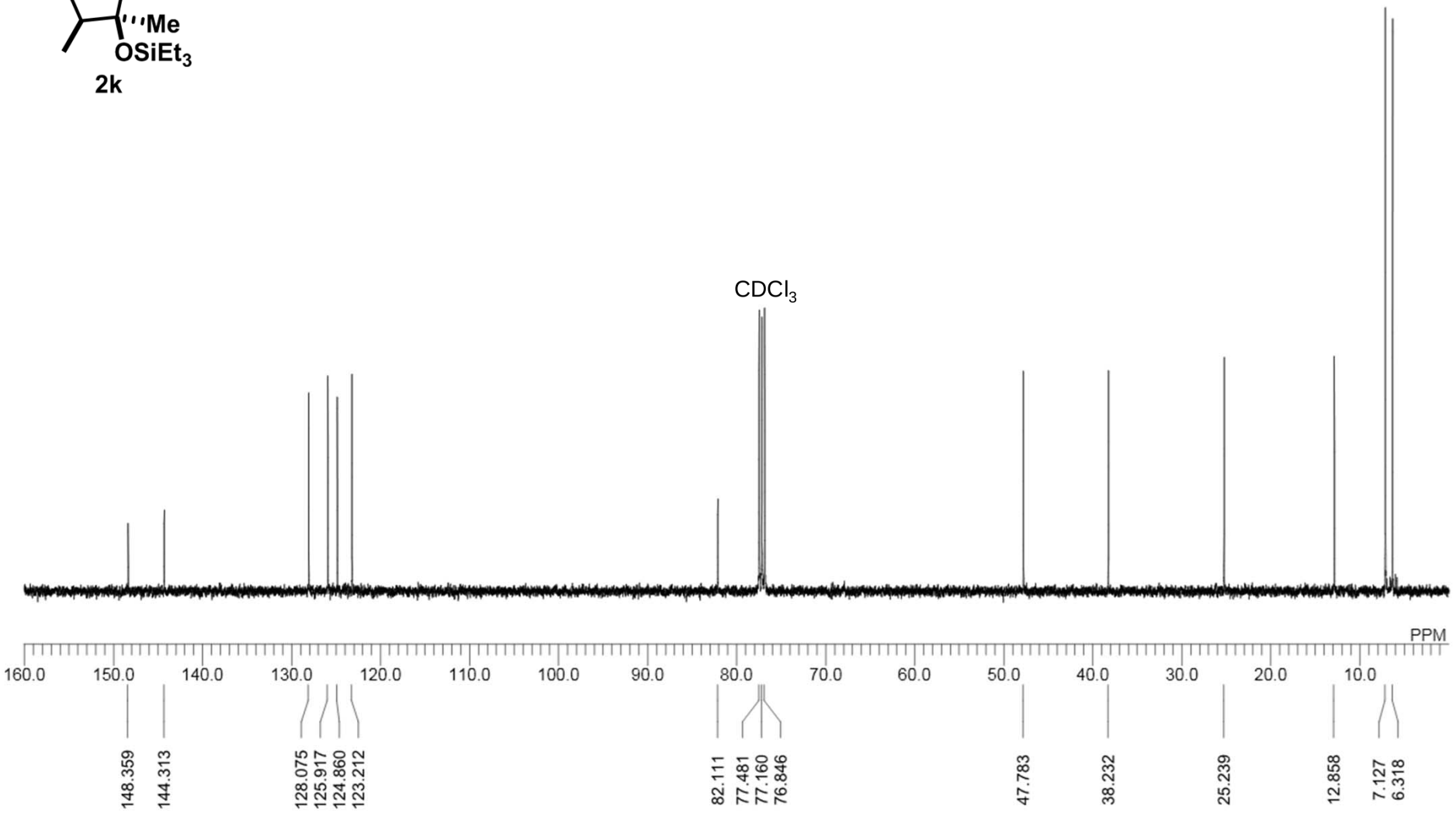

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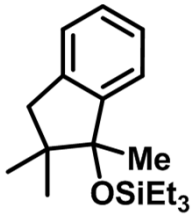

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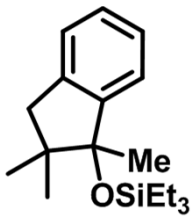

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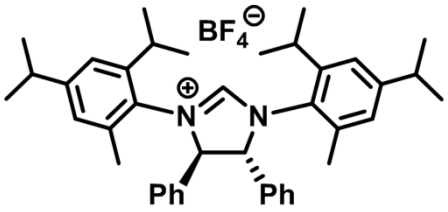

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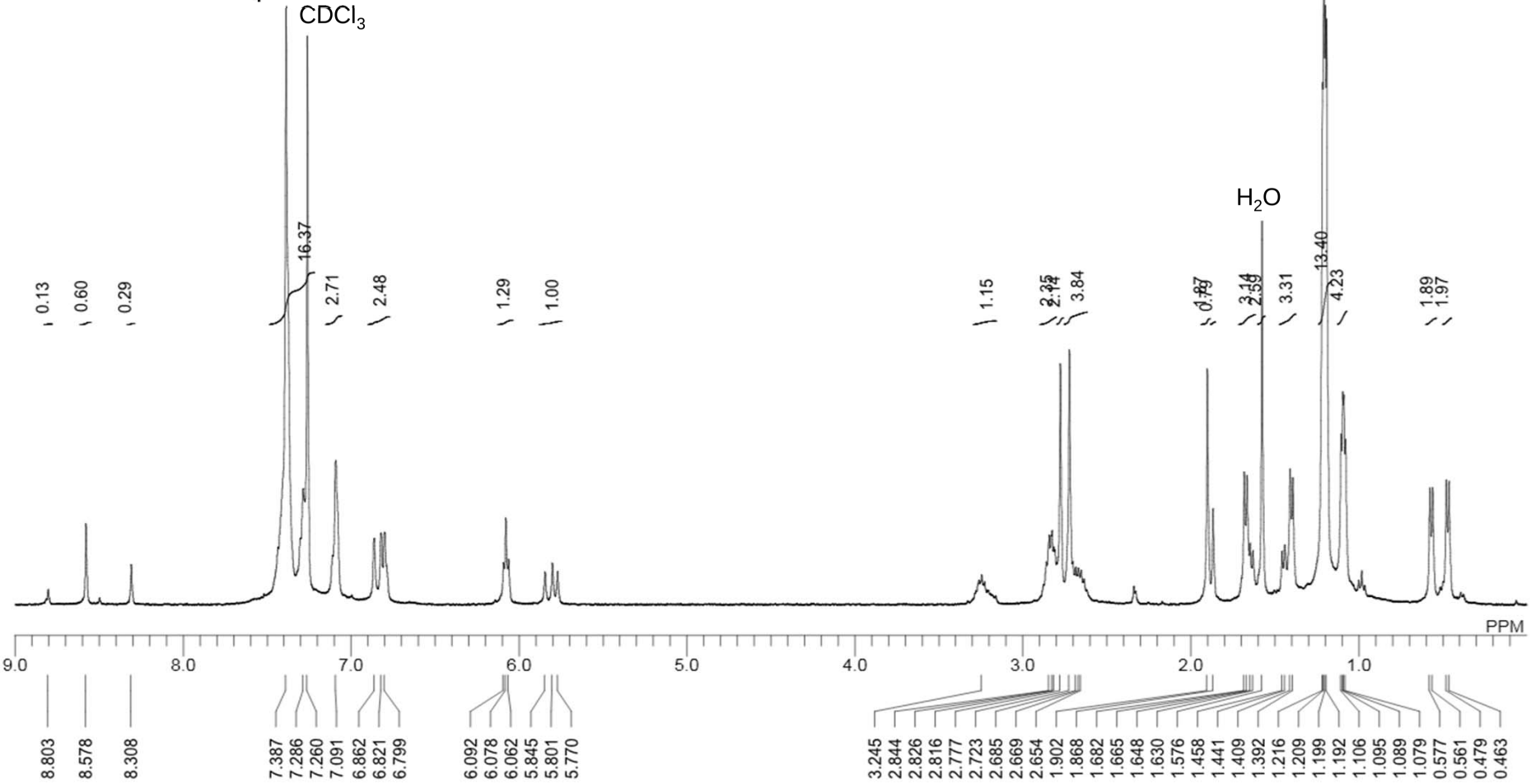
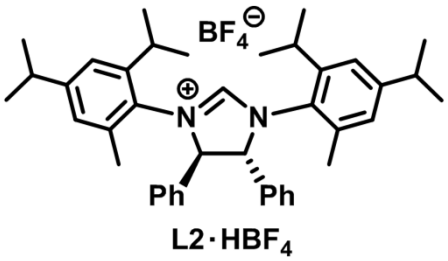


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



L2·HBF_4

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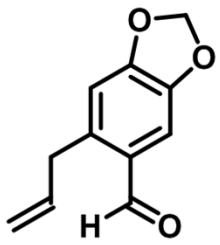

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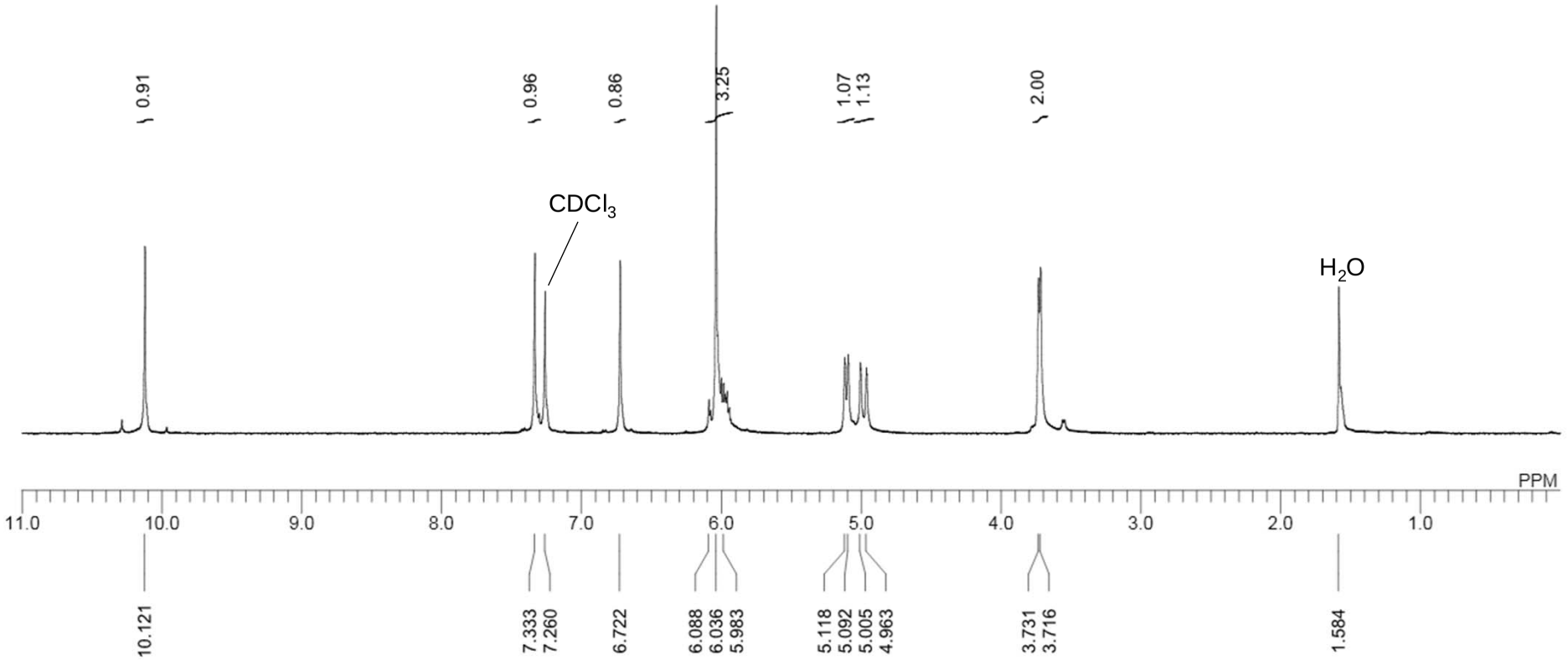
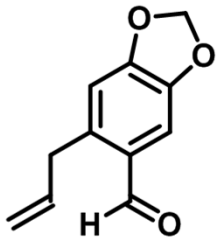


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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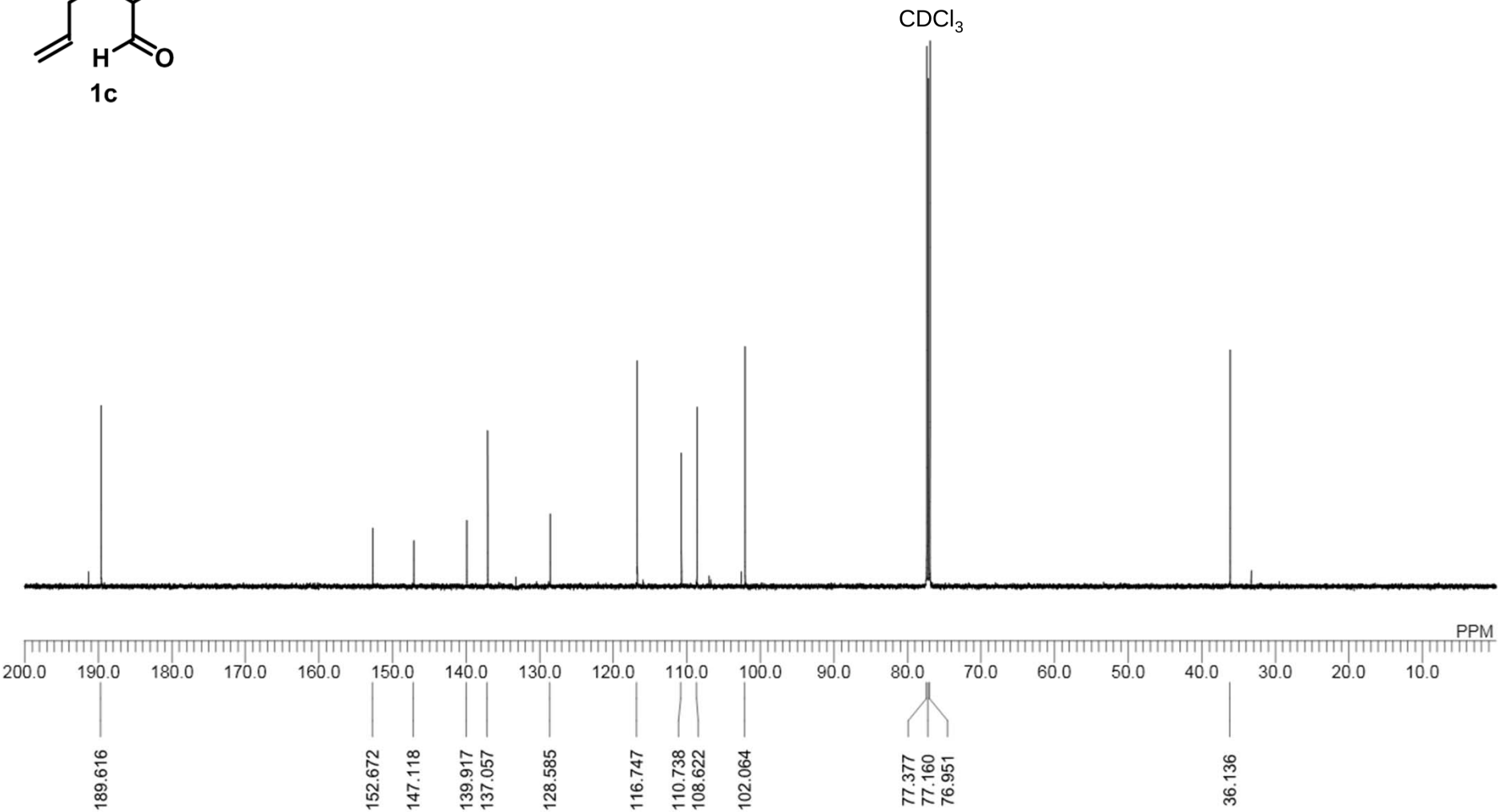
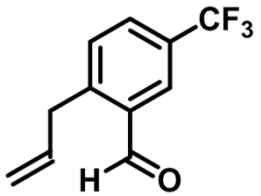


^{1}H NMR (400 MHz, $CDCl_3$)



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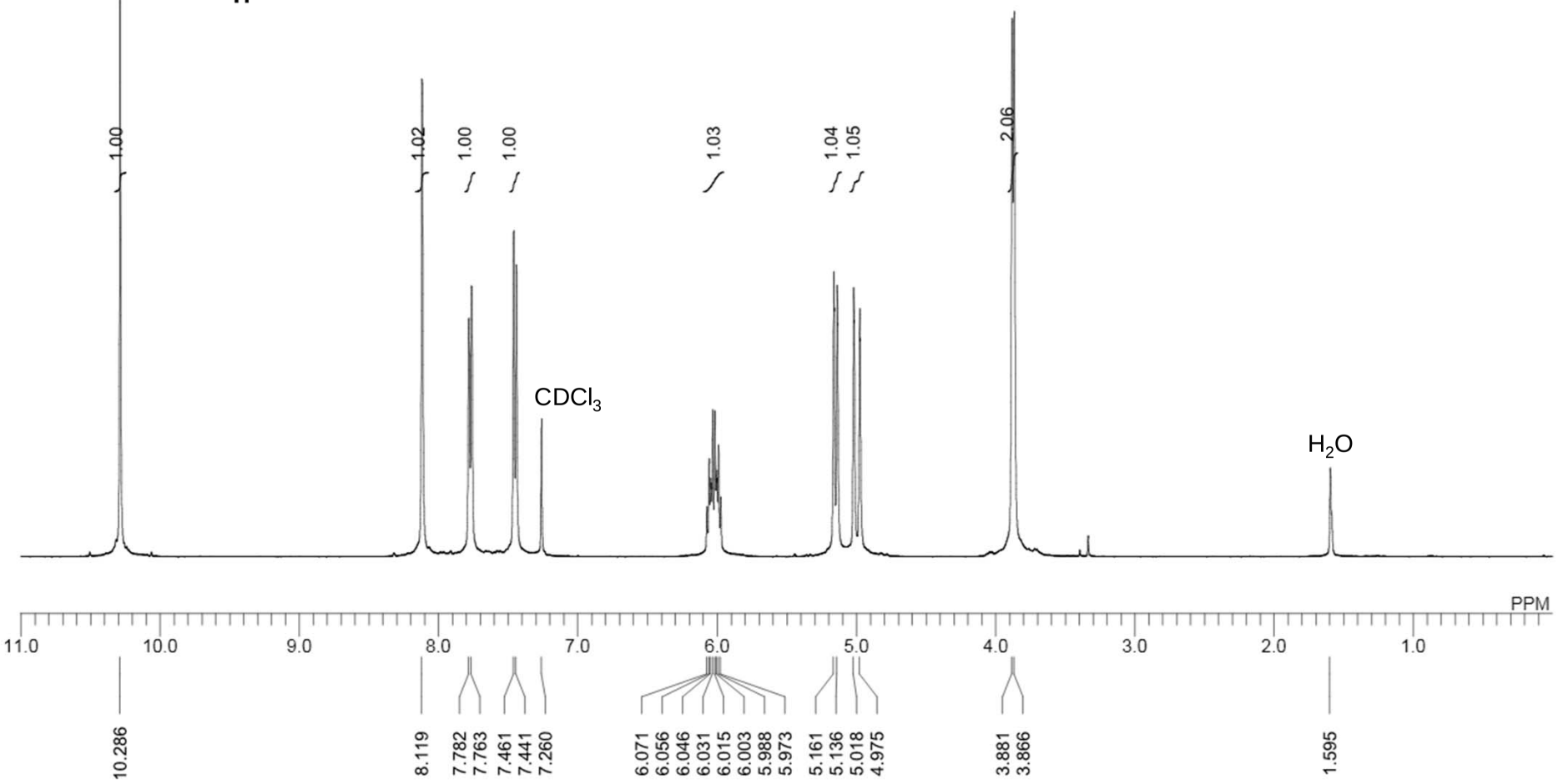

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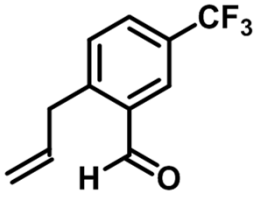

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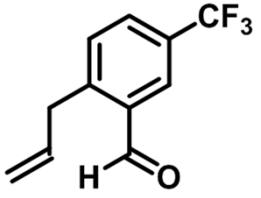
^{19}F NMR (376 MHz, $CDCl_3$)



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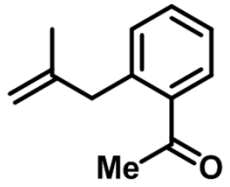

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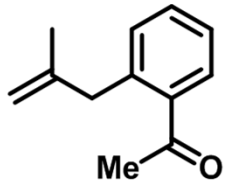
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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