# Catalytic Defluorinative [3+2] Cycloaddition of Trifluoromethylalkenes with Alkynes via Reduction of Nickel(II) Fluoride Species

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## *— Supporting Information —*

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**General Statements**

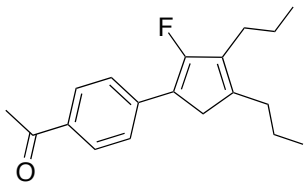
IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz ($^{1}$H NMR), at 126 MHz ($^{13}$C NMR), and at 470 MHz ($^{19}$F NMR). Chemical shifts were given in ppm relative to internal $Me_4Si$ (for $^{1}$H NMR: $\delta$ = 0.00), $CDCl_3$ (for $^{13}$C NMR: $\delta$ = 77.0), and $C_6F_6$ (for $^{19}$F NMR: $\delta$ = 0.0). Mass spectra were measured on a JEOL JMS-T100GCV spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory, Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba. X-ray diffraction study was performed on a Bruker APEXII ULTRA instrument equipped with a CCD diffractometer using Mo K$\alpha$ (graphite monochromated, $\lambda$ = 0.71069 Å) radiation. The structure was solved by direct methods (SIR97).[1] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on $F^2$ by the full-matrix least-squares method using SHELXS-97.[2] Hydrogen atoms were placed at calculated positions and refined with the riding mode on their corresponding carbon atoms. The CCDC deposition number of compound **9** is 1402817.

Column chromatography and preparative thin-layer chromatography (PTLC) were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries for PTLC, respectively). All the reactions were conducted under argon. Toluene was dried by a solvent-purification system (GlassContour) equipped with a columns of activated alumina followed by a column of Q-5 scavenger (Engelhard). 1,4-Dioxane was distilled from sodium, and stored over activated molecular sieves 4A.

$Ni(cod)_2$ and $PCy_3$ were purchased from Sigma-Aldrich Co. and stored in a globe box under an argon atmosphere. 4-Octyne (**2a**), 4-methylpent-2-yne (**2b**), bis(neopentylglycolato)diboron ($B_2(nep)_2$), *t*-BuOK, and $MgF_2$ were purchased from Sigma-Aldrich Co., Tokyo Chemical Industry Co., Ltd., or Wako Pure Chemical Industries, Ltd. These compounds were used without further purification. Other liquid reagents were purified by distillation and solid reagents were purified by recrystallization. 2-Trifluoromethyl-1-alkenes **1a**–**g**[3] and 7-bromohept-1-yne[4] were prepared according to the literature procedures.

**Synthesis of 2-Fluoro-1,3-cyclopentadienes 3 via Nickel-Catalyzed [3+2] Cycloaddition**

**1-[4-(2-Fluoro-3,4-dipropylcyclopenta-1,3-dien-1-yl)phenyl]ethan-1-one (3aa) < *Typical procedure*>**

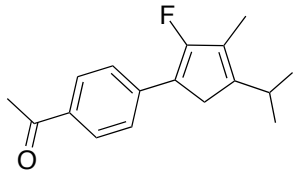



In a 30-mL Schlenk tube were placed $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL). After stirring for 10 min at room temperature, 2-trifluoromethyl-1-alkene **1a** (53 mg, 0.25 mmol) and 4-octyne (**2a**, 30 mg, 0.28 mmol) were added to the mixture. After stirring for 3 h at 80 °C, the reaction was quenched with aqueous HCl (1 M). Organic materials were extracted with $Et_2O$ two times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane:EtOAc = 50:1) to give 2-fluoro-1,3-cyclopentadiene **3aa** (38 mg, 53%) as a yellow solid.

**3aa**: IR (neat): $\tilde{\nu}$ = 2960, 2870, 1670, 1585, 1273, 912, 742 $cm^{-1}$. $^1H$ NMR: δ 0.95 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 1.48–1.63 (m, 4H), 2.29 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.7 Hz, 2H), 2.58 (s, 3H), 3.20 (d, $J_{HF}$ = 6.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H). $^{13}C$ NMR: δ 13.9, 14.1, 22.3, 23.1, 26.0, 26.4, 30.8, 37.8 (d, $J_{CF}$ = 8 Hz), 112.8 (d, $J_{CF}$ = 2 Hz), 125.1 (d, $J_{CF}$ = 7 Hz), 128.8, 133.8, 134.6 (d, $J_{CF}$ = 25 Hz), 138.6 (d, $J_{CF}$ = 5 Hz), 143.2 (d, $J_{CF}$ = 6 Hz), 161.2 (d, $J_{CF}$ = 285 Hz), 197.4. $^{19}F$ NMR: δ 43.9 (t, $J_{FH}$ = 7 Hz). HRMS (EI+): Calcd for $C_{19}H_{23}FO$ $[M]^+$ 286.1733, Found 286.1730.

Spectral data for this compound showed good agreement with the literature data.[5]

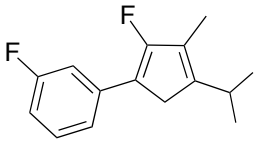
**1-{4-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]phenyl}ethan-1-one (3ab)**




Fluorocyclopentadiene **3ab** was synthesized according to the typical procedure using 2-trifluoromethyl-1-alkene **1a** (53 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **3ab** (45 mg, 70%) as a yellow solid.

Spectral data for this compound showed good agreement with the literature data.[5]

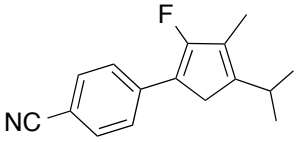
**1-Fluoro-3-[2-fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]benzene (3bb)**




Fluorocyclopentadiene **3bb** was synthesized according to the typical procedure using 2-trifluoromethyl-1-alkene **1b** (48 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane) gave **3bb** (29 mg, 50%) as a white solid.

**3bb**: IR (neat): $\tilde{\nu}$ = 2962, 2922, 1651, 1610, 1595, 1385, 1365, 1269, 1176, 858, 781, 686 $cm^{-1}$. $^1H$ NMR: δ 1.05 (d, $J$ = 7.0 Hz, 6H), 1.80 (s, 3H), 2.84 (septet, 1H), 3.04 (dd, $J_{HF}$ = 6.5 Hz, $J$ = 1.5 Hz, 2H), 6.72–6.76 (m, 1H), 7.13–7.21 (m, 3H). $^{13}C$ NMR: δ 8.6, 22.5, 27.4 (d, $J_{CF}$ = 2 Hz), 34.1 (d, $J_{CF}$ = 8 Hz), 112.0 (d, $J_{CF}$ = 19 Hz), 112.1 (dd, $J_{CF}$ = 22, 7 Hz), 112.2 (dd, $J_{CF}$ = 22, 2 Hz), 121.0 (dd, $J_{CF}$ = 7, 3 Hz), 128.0 (d, $J_{CF}$ = 26 Hz), 129.8 (d, $J_{CF}$ = 8 Hz), 136.0 (dd, $J_{CF}$ = 8, 5 Hz), 147.1 (d, $J_{CF}$ = 4 Hz), 159.6 (d, $J_{CF}$ = 281 Hz). 163.1 (d, $J_{CF}$ = 245 Hz), $^{19}F$ NMR: δ 38.9 (t, $J_{FH}$ = 6 Hz, 1F), 48.80–48.85 (m, 1F). HRMS (EI+): Calcd for $C_{15}H_{16}F_2$ $[M]^+$ 234.1220, Found 234.1209.

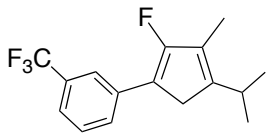
**4-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]benzonitrile (3cb)**




Fluorocyclopentadiene **3cb** was synthesized according to the typical procedure using 2-trifluoromethyl-1-alkene **1c** (50 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **3cb** (27 mg, 45%) as a white solid.

**3cb**: IR (neat): $\tilde{\nu}$ = 2958, 2868, 2222, 1585, 912, 742 $cm^{-1}$. $^1H$ NMR: δ 1.14 (d, $J$ = 6.9 Hz, 6H), 1.89 (s, 3H), 2.94 (septet, $J$ = 6.9 Hz, 1H), 3.15 (dd, $J_{HF}$ = 6.8 Hz, $J$ = 1.5 Hz, 2H), 7.57 (s, 4H). $^{13}C$ NMR: δ 8.5, 22.4, 27.5 (d, $J_{CF}$ = 2 Hz), 33.9 (d, $J_{CF}$ = 7 Hz), 108.0 (d, $J_{CF}$ = 3 Hz), 111.6 (d, $J_{CF}$ = 2 Hz), 119.4, 125.4 (d, $J_{CF}$ = 7 Hz), 128.3 (d, $J_{CF}$ = 26 Hz), 132.2, 138.1 (d, $J_{CF}$ = 5 Hz), 149.3 (d, $J_{CF}$ = 4 Hz), 161.4 (d, $J_{CF}$ = 285 Hz). $^{19}F$ NMR: δ 43.4 (t, $J_{FH}$ = 7 Hz). HRMS (EI+): Calcd for $C_{16}H_{16}FN$ $[M]^+$ 241.1267, Found 241.1270.

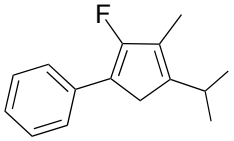
**1-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]-3-(trifluoromethyl)benzene (3db)**




Fluorocyclopentadiene **3db** was synthesized according to the typical procedure using 2-trifluoromethyl-1-alkene **1d** (60 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and toluene (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane) gave **3db** (29 mg, 40%) as a colorless liquid.

**3db**: IR (neat): $\tilde{\nu}$ = 2964, 1593, 1327, 1122, 1072, 796, 696 $cm^{-1}$. $^1H$ NMR: δ 1.14 (d, $J$ = 6.9 Hz, 6H), 1.88 (s, 3H), 2.93 (septet, $J$ = 6.9 Hz, 1H), 3.16 (dd, $J_{HF}$ = 6.6 Hz, $J$ = 1.6 Hz, 2H), 7.36 (d, $J$ = 7.8 Hz, 1H), 7.41 (dd, $J$ = 7.8, 7.8 Hz, 1H), 7.69–7.70 (m, 2H). $^{13}C$ NMR: δ 8.6, 22.5, 27.5, 34.0 (d, $J_{CF}$ = 8 Hz), 111.6 (d, $J_{CF}$ = 2 Hz), 121.7–121.8 (m), 121.8–121.9 (m), 124.3 (q, $J_{CF}$ = 270 Hz), 128.0 (d, $J_{CF}$ = 26 Hz), 128.5 (d, $J_{CF}$ = 7 Hz), 128.9, 130.8 (q, $J_{CF}$ = 32 Hz), 134.6 (d, $J_{CF}$ = 5 Hz), 147.5 (d, $J_{CF}$ = 4 Hz), 160.0 (d, $J_{CF}$ = 279 Hz). $^{19}F$ NMR: δ 39.3 (t, $J_{FH}$ = 7 Hz, 1F), 98.9 (s, 3F). HRMS (EI+): Calcd for $C_{16}H_{16}F_4$ $[M]^+$ 284.1188, Found: 284.1186.

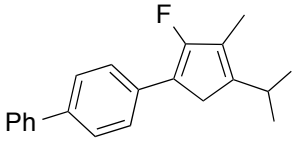
**[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]benzene (3eb)**




Fluorocyclopentadiene **3eb** was synthesized according to the typical procedure using α-(trifluoromethyl)styrene (**1e**, 43 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane) gave **3eb** (29 mg, 54%) as a white solid.

Spectral data for this compound showed good agreement with the literature data.[5]

**4-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]-1,1'-biphenyl (3fb)**

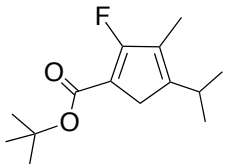



Fluorocyclopentadiene **3fb** was synthesized according to the typical procedure using

4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1f**, 63 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (hexane) gave **3fb** (33 mg, 45%) as a pale yellow solid.

**3fb**: IR (neat): $\tilde{\nu}$ = 3030, 2960, 1591, 1489, 1365, 1192, 1109, 912, 853, 764, 742, 696 $cm^{-1}$. $^1H$ NMR: δ 1.14 (d, $J$ = 7.0 Hz, 6H), 1.89 (s, 3H), 2.93 (septet, $J$ = 6.9 Hz, 1H), 3.17 (d, $J_{HF}$ = 6.1 Hz, 2H), 7.32 (t, $J$ = 7.5 Hz, 1H), 7.43 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.55–7.62 (m, 6H). $^{13}C$ NMR: δ 8.7, 22.6, 27.4 (d, $J_{CF}$ = 2 Hz), 34.1 (d, $J_{CF}$ = 8 Hz), 112.5 (d, $J_{CF}$ = 3 Hz), 125.8 (d, $J_{CF}$ = 7 Hz), 126.8, 127.0, 127.1, 128.1(d, $J_{CF}$ = 26 Hz), 128.7, 133.0, 138.0, 140.9, 146.6 (d, $J_{CF}$ = 4 Hz), 159.0 (d, $J_{CF}$ = 278 Hz). $^{19}F$ NMR: δ 37.3 (t, $J_{FH}$ = 6 Hz). HRMS (EI+): Calcd for $C_{21}H_{21}F$ $[M]^+$ 292.1627, Found: 292.1634.

***tert*-Butyl 2-fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-diene-1-carboxylate (3gb)**



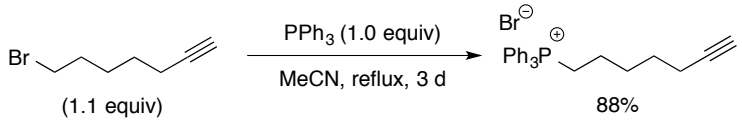

Fluorocyclopentadiene **3gb** was synthesized according to the typical procedure using *tert*-butyl 2-(trifluoromethyl)acrylate (**1g**, 49 mg, 0.25 mmol), 4-methylpent-2-yne (**2b**, 23 mg, 0.28 mmol), $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and toluene (3 mL) for 3 h at 80 ºC. Purification by silica gel column chromatography (pentane/$Et_2O$ = 10:1) gave **3gb** (25 mg, 42%) as a colorless liquid.

Spectral data for this compound showed good agreement with the literature data.[5]

**Synthesis of 5,6,7,7a-Tetrahydro-4*H*-indene 9**

**Preparation of 1-Trifluoromethyl-1-en-7-yne 5**

**(i) Hept-6-yn-1-yltriphenylphosphonium bromide**

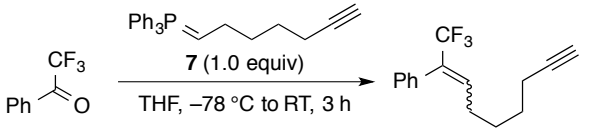



To an acetonitrile solution (15 mL) of triphenylphosphine (3.93 g, 15.0 mmol) was added 7-bromohept-1-yne (2.89 g, 16.5 mmol). After refluxed for 3 d, the reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. Toluene was added and the resulting heterogeneous mixture, and

the title compound (5.76 g, 88%) was obtained as a white solid.

**Hept-6-yn-1-yltriphenylphosphonium bromide**: IR (neat): $\tilde{\nu}$ = 2937, 2866, 1439, 1113, 914, 723, 530 $cm^{-1}$. $^1H$ NMR: δ 1.54 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.65–1.69 (m, 2H), 1.80 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.86 (t, *J* = 2.6 Hz, 1H), 2.15 (td, *J* = 7.2, 2.6 Hz, 2H), 3.87–3.93 (m, 2H), 7.69–7.72 (m, 6H), 7.78–7.82 (m, 3H), 7.85–7.89 (m, 6H). $^{13}C$ NMR: δ 18.0, 22.2 (d, $J_{CP}$ = 4 Hz), 22.7 (d, $J_{CP}$ = 49 Hz), 27.8, 29.3 (d, $J_{CP}$ = 16 Hz), 68.4, 84.2, 118.4 (d, $J_{CP}$ = 85 Hz), 130.4 (d, $J_{CP}$ = 12 Hz), 133.7 (d, $J_{CP}$ = 10 Hz), 134.9 (d, $J_{CP}$ = 3 Hz). HRMS (APCI+): Calcd for $C_{25}H_{27}BrP$ $[M + H]^+$ 437.1034, Found 437.1029.

**(ii) 1,1,1-Trifluoro-2-phenylnon-2-en-8-yne (8)**




**6** **8** 87% (*E*/*Z* = 64:36)

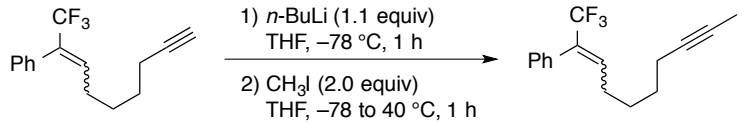
To a tetrahydrofuran solution (5 mL) of hept-6-yn-1-yltriphenylphosphonium bromide (481 mg, 1.10 mmol) was added *n*-BuLi (1.60 M in hexane, 0.76 mL, 1.2 mmol) at –78 ºC. After stirring for 5 min at –78 ºC, the reaction mixture was warmed to 0 ºC. After stirring for another 1 h at 0 ºC, the reaction mixture was then cooled to –78 ºC. To the mixture was added a tetrahydrofuran solution (4 mL) of 2,2,2-trifluoroacetophenone (**6**, 174 mg, 1.0 mmol) via cannula over 3 min at –78 °C. After being stirred for 1 h at –78 ºC, for 1 h at 0 ºC, and for 1 h at room temperature, the reaction was quenched with saturated aqueous $NH_4Cl$. Organic materials were extracted with $Et_2O$ two times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give enyne **8** (220 mg, 87%, *E*/*Z* = 64:36) as a colorless liquid.

**8**: IR (neat): $\tilde{\nu}$ = 3309, 2941, 2864, 1302, 1169, 1113, 758, 700, 633 $cm^{-1}$.

***E*-8**: $^1H$ NMR: δ 1.35–1.47 (m, 4H), 1.84 (t, *J* = 2.5 Hz, 1H), 1.91–1.97 (m, 2H), 2.04 (td, *J* = 6.5, 2.5 Hz, 2H), 6.33 (tq, *J* = 6.8 Hz, $J_{HF}$ = 1.6 Hz, 1H), 7.14–7.16 (m, 2H), 7.28–7.33 (m, 3H). $^{13}C$ NMR: δ 18.1, 27.70, 27.70, 27.72, 68.5, 83.9, 123.5 (q, $J_{CF}$ = 273 Hz), 128.2, 128.4, 129.7, 131.5 (q, $J_{CF}$ = 29 Hz), 132.3, 136.2 (q, $J_{CF}$ = 5 Hz). $^{19}F$ NMR: δ 96.0 (s). HRMS (EI+): Calcd for $C_{15}H_{15}F_3$ $[M]^+$ 252.1126, Found: 252.1112.

***Z*-8**: $^1H$ NMR: δ 1.49–1.58 (m, 4H), 1.88 (t, *J* = 3.0 Hz, 1H), 2.15 (td, *J* = 6.0, 3.0 Hz, 2H), 2.36–2.41 (m, 2H), 5.93 (t, *J* = 7.8 Hz, 1H), 7.20–7.22 (m, 2H), 7.25–7.28 (m, 3H). $^{13}C$ NMR: δ 18.2, 27.7, 27.9, 28.2, 68.5, 84.0, 123.9 (q, $J_{CF}$ = 276 Hz), 128.0, 128.2, 128.4, 131.9 (q, $J_{CF}$ = 30 Hz), 136.6 (q, $J_{CF}$ = 2 Hz), 141.6 (q, $J_{CF}$ = 3 Hz). $^{19}F$ NMR: δ 104.6 (s). HRMS (EI+): Calcd for $C_{15}H_{15}F_3$ $[M]^+$ 252.1126, Found: 252.1122.

**(iii) 1,1,1-Trifluoro-2-phenyldec-2-en-8-yne (5)**




**8** (*E*/*Z* = 64:36) **5** quant (*E*/*Z* = 60:40)

To a tetrahydrofuran solution (10 mL) of enyne **8** (251 mg, 0.994 mmol) was added *n*-BuLi (1.60 M in hexane, 0.68 mL, 1.1 mmol) at –78 ºC. After stirring for 1 h at –78 ºC, iodomethane (0.12 mL, 2.0 mmol) was added to the reaction mixture. The mixture was then warmed to 40 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous $NH_4Cl$. Organic materials were extracted with $Et_2O$ two times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give 1,1,1-trifluorodec-2-en-8-yne **5** (265 mg, quant, *E*/*Z* = 60:40) as a colorless liquid.

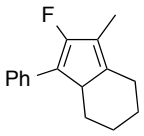
**5**: IR (neat): $\tilde{\nu}$ = 2935, 2862, 1302, 1169, 1117, 912, 737, 702 $cm^{-1}$.

***E*-5**: $^1H$ NMR: δ 1.31–1.37 (m, 2H), 1.39–1.45 (m, 2H), 1.69 (t, *J* = 2.5 Hz, 3H), 1.91–2.01 (m, 4H), 6.35 (tq, *J* = 7.5 Hz, $J_{HF}$ = 1.6 Hz, 1H), 7.15–7.16 (m, 2H), 7.29–7.33 (m, 3H). $^{13}C$ NMR: δ 3.4, 18.4, 27.8, 27.9, 28.3, 75.7, 78.6, 123.5 (q, $J_{CF}$ = 273 Hz), 128.33, 128.34, 129.7, 131.3 (q, $J_{CF}$ = 29 Hz), 132.4, 136.4 (q, $J_{CF}$ = 6 Hz). $^{19}F$ NMR: δ 96.0 (s). HRMS (EI+): Calcd for $C_{15}H_{14}F_3$ $[M–CH_3]^+$ 251.1048, Found: 251.1059.

***Z*-5**: $^1H$ NMR: δ 1.46–1.56 (m, 4H), 1.71 (t, *J* = 2.5 Hz, 3H), 2.08–2.12 (m, 2H), 2.35–2.41 (m, 2H), 5.95 (t, *J* = 7.8 Hz, 1H), 7.21–7.23 (m, 2H), 7.25–7.29 (m, 3H). $^{13}C$ NMR: δ 3.4, 18.5, 28.3, 28.4, 28.5, 75.8, 78.7, 124.0 (q, $J_{CF}$ = 276 Hz), 127.9, 128.15, 128.18, 131.7 (q, $J_{CF}$ = 30 Hz), 136.6, 141.9 (q, $J_{CF}$ = 3 Hz). $^{19}F$ NMR: δ 104.6 (s). HRMS (EI+): Calcd for $C_{15}H_{14}F_3$ $[M–CH_3]^+$ 251.1048, Found: 251.1053.

**Nickel-Catalyzed Intermolecular [3+2] Cycloaddition of 1-Trifluoromethyl-1-en-7-yne 5**

**2-Fluoro-3-methyl-1-phenyl-5,6,7,7a-tetrahydro-4*H*-indene (9)**




In a 30-mL Schlenk tube were placed $Ni(cod)_2$ (14 mg, 0.051 mmol), $PCy_3$ (29 mg, 0.10 mmol), $B_2(nep)_2$ (62 mg, 0.27 mmol), *t*-BuOK (30 mg, 0.27 mmol), $MgF_2$ (16 mg, 0.26 mmol), and 1,4-dioxane (3 mL). After stirring for 10 min at room temperature, 1-trifluoromethyl-1-en-7-yne **5** (67 mg, 0.25 mmol) was added to the mixture. After stirring for 3 h at 80 °C, the reaction was quenched with saturated aqueous $NH_4Cl$. Organic materials were extracted with $CH_2Cl_2$ two times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give 2-fluoro-5,6,7,7a-tetrahydro-4*H*-indene **9** (29 mg, 51%) as a white solid.

**9**: IR (neat): $\tilde{\nu}$ = 2933, 2856, 906, 731, 650 $cm^{-1}$. $^{1}H$ NMR: δ 0.84 (dddd, $J$ = 13.2, 13.2, 13.2, 3.3 Hz, 1H), 1.16–1.25 (m, 1H), 1.45–1.54 (m, 1H), 1.77–1.83 (m, 1H), 1.87 (t, $J_{HF}$ = 1.5 Hz, 3H), 1.97–2.03 (m, 1H), 2.09–2.16 (m, 1H), 2.37–2.42 (m, 1H), 2.69–2.73 (m, 1H), 2.96–3.01 (m, 1H), 7.14 (tt, $J$ = 7.5, 1.0 Hz, 1H), 7.33 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.46 (dd, $J$ = 7.5, 1.0 Hz, 2H). $^{13}C$ NMR: δ 8.5, 25.5, 26.2 (d, $J_{CF}$ = 2 Hz), 29.1, 33.4 (d, $J_{CF}$ = 3 Hz), 47.1 (d, $J_{CF}$ = 8 Hz), 118.3, 124.6 (d, $J_{CF}$ = 28 Hz), 125.4 (d, $J_{CF}$ = 2 Hz), 126.3 (d, $J_{CF}$ = 6 Hz), 128.5, 133.1 (d, $J_{CF}$ = 5 Hz), 144.5 (d, $J_{CF}$ = 6 Hz), 159.0 (d, $J_{CF}$ = 281 Hz). $^{19}F$ NMR: δ 33.8 (d, $J_{FH}$ = 6 Hz). HRMS (EI+): Calcd for $C_{16}H_{17}F$ $[M]^{+}$ 228.1314, Found: 228.1323.

**References**


(1) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.

(2) G. M. Sheldrick, *Programs for Crystal Structure Analysis (Release 972)*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

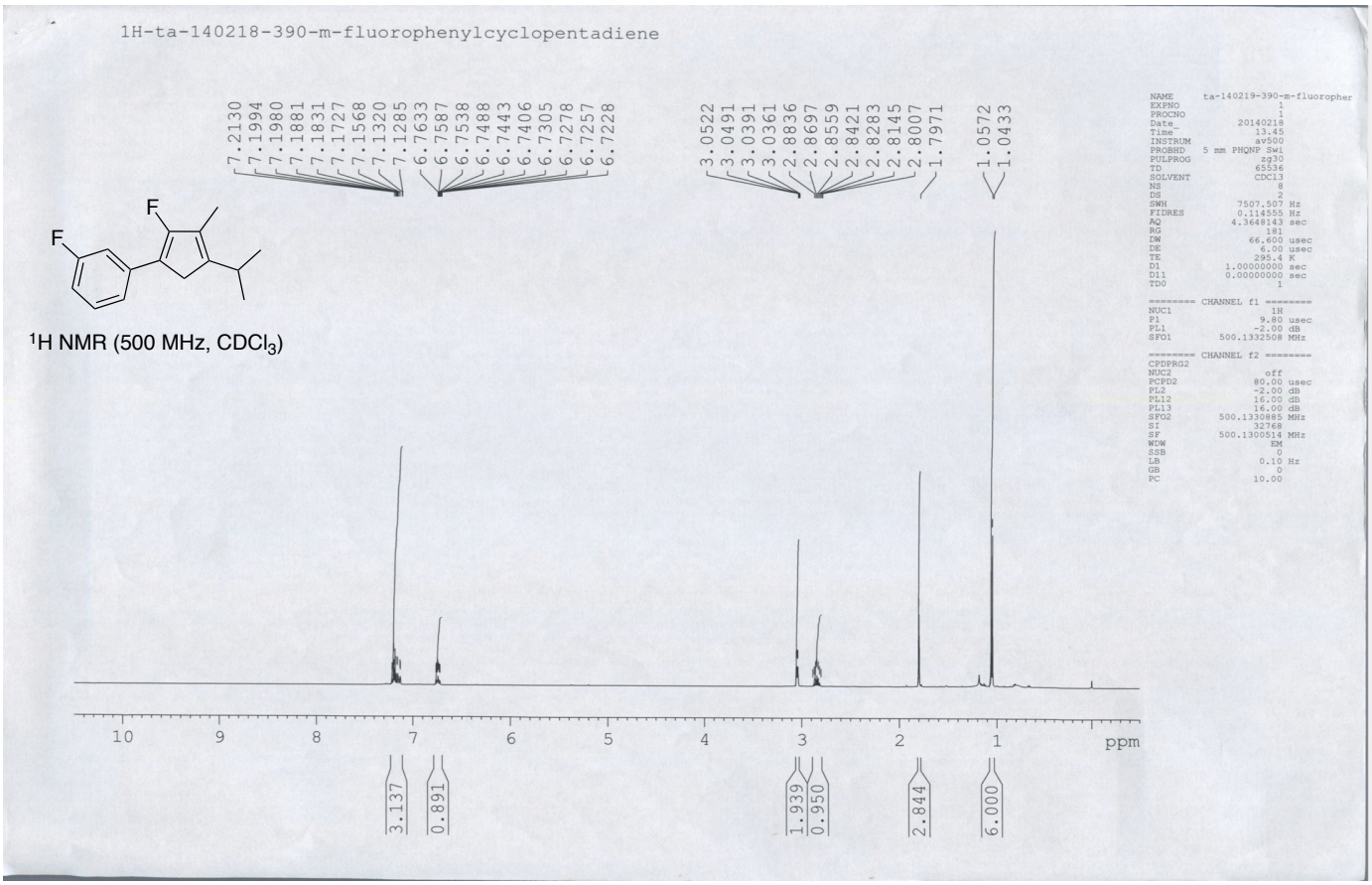
(3) (a) B. Jiang, Q.-F. Wang, C.-G. Yang and M. Xu, *Tetrahedron Lett.*, 2001, **42**, 4083–4085; (b) J. Walkowiak, T. M. del Campo, B. Ameduri and V. Gouverneur, *Synthesis*, 2010, **11**, 1883–1890.

(4) J. R. Coombs, L. Zhang and J. P. Morken, *J. Am. Chem. Soc.*, 2014, **136**, 16140–16143.

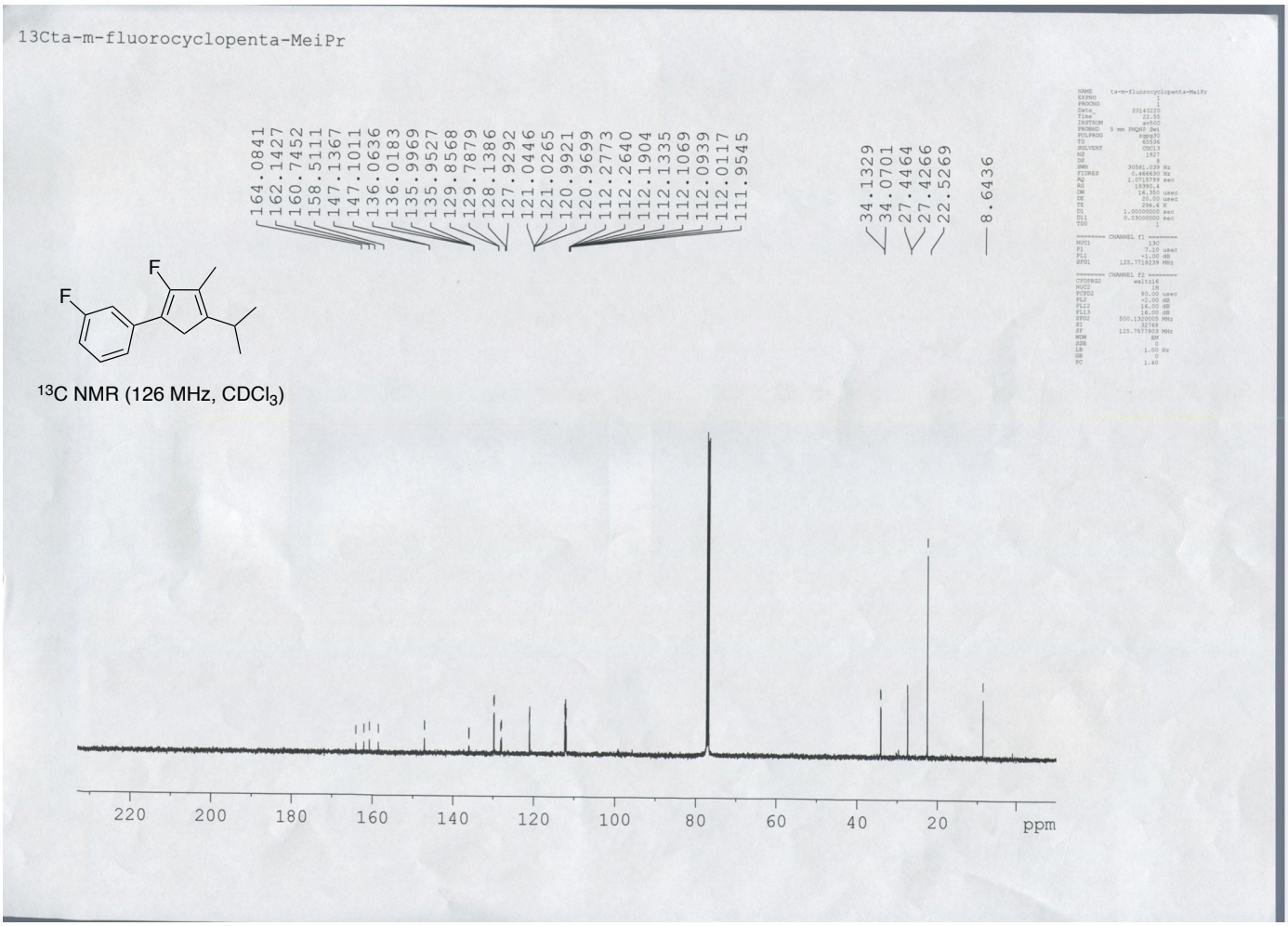
(5) T. Ichitsuka, T. Fujita, T. Arita and J. Ichikawa, *Angew. Chem., Int. Ed.*, 2014, **53**, 7564–7568.

## $^{1}$H, $^{13}$C, and $^{19}$F NMR Spectra

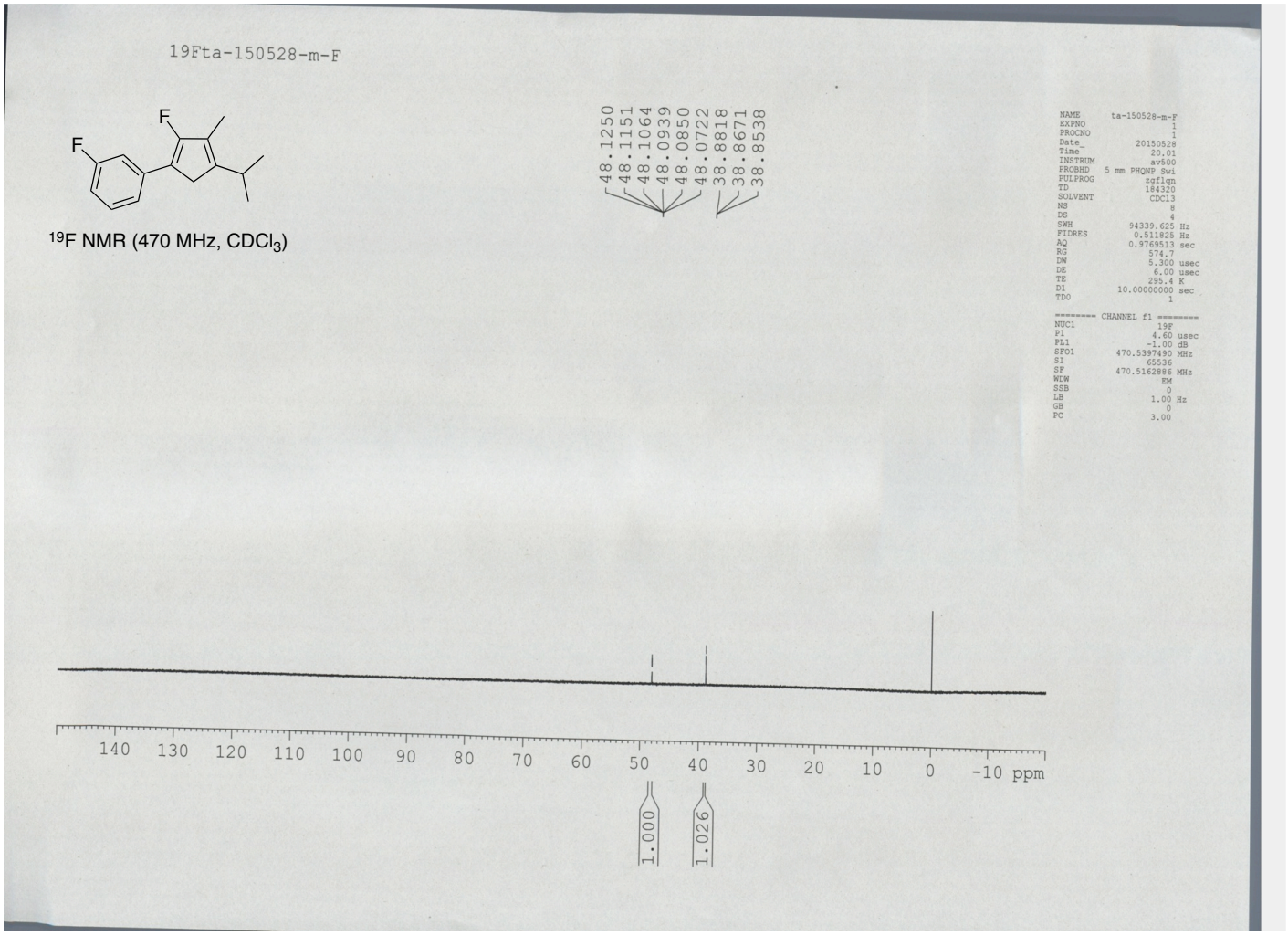
### 1-Fluoro-3-[2-fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]benzene (3bb)



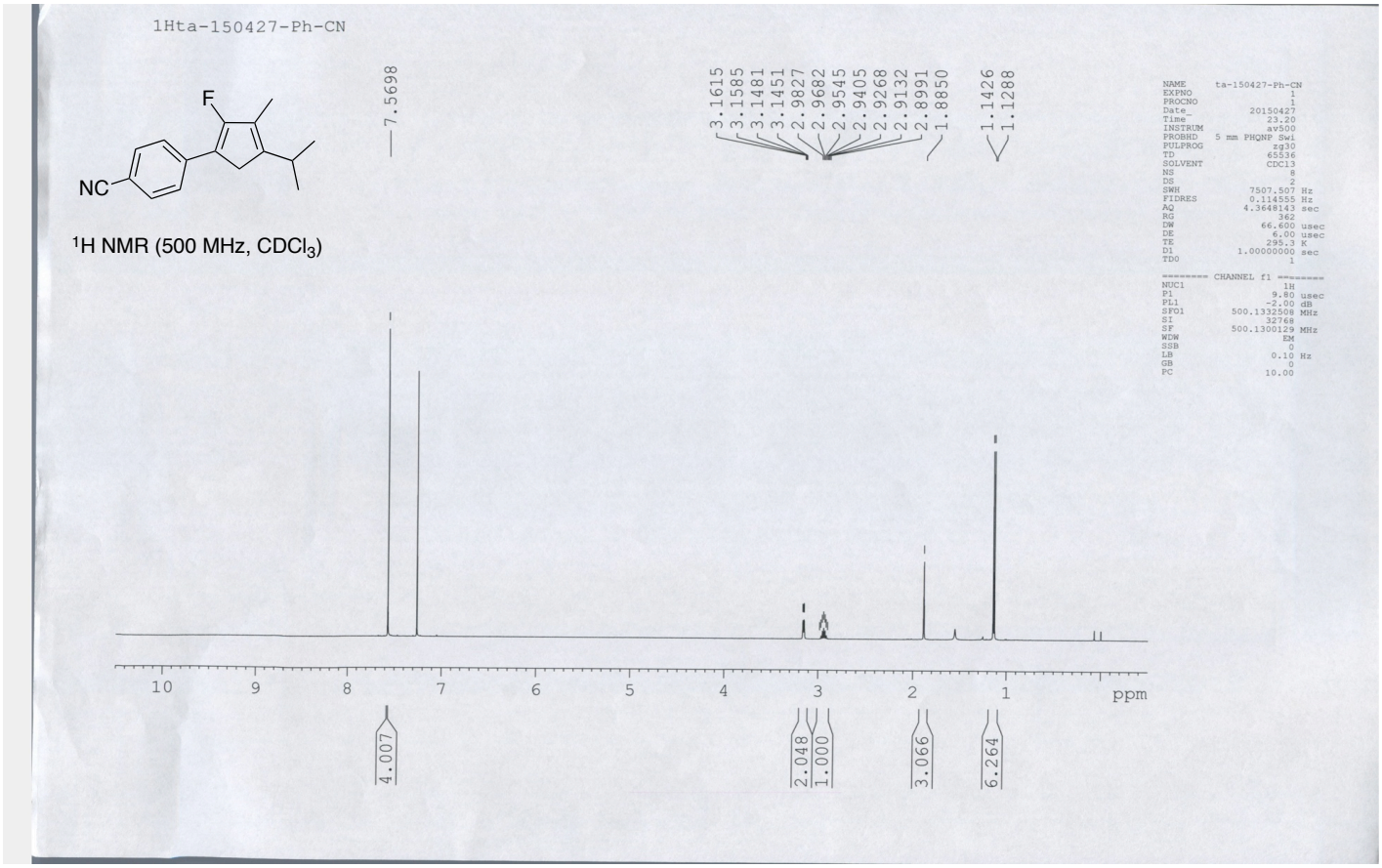

$^{1}$H NMR (500 MHz, $CDCl_3$)

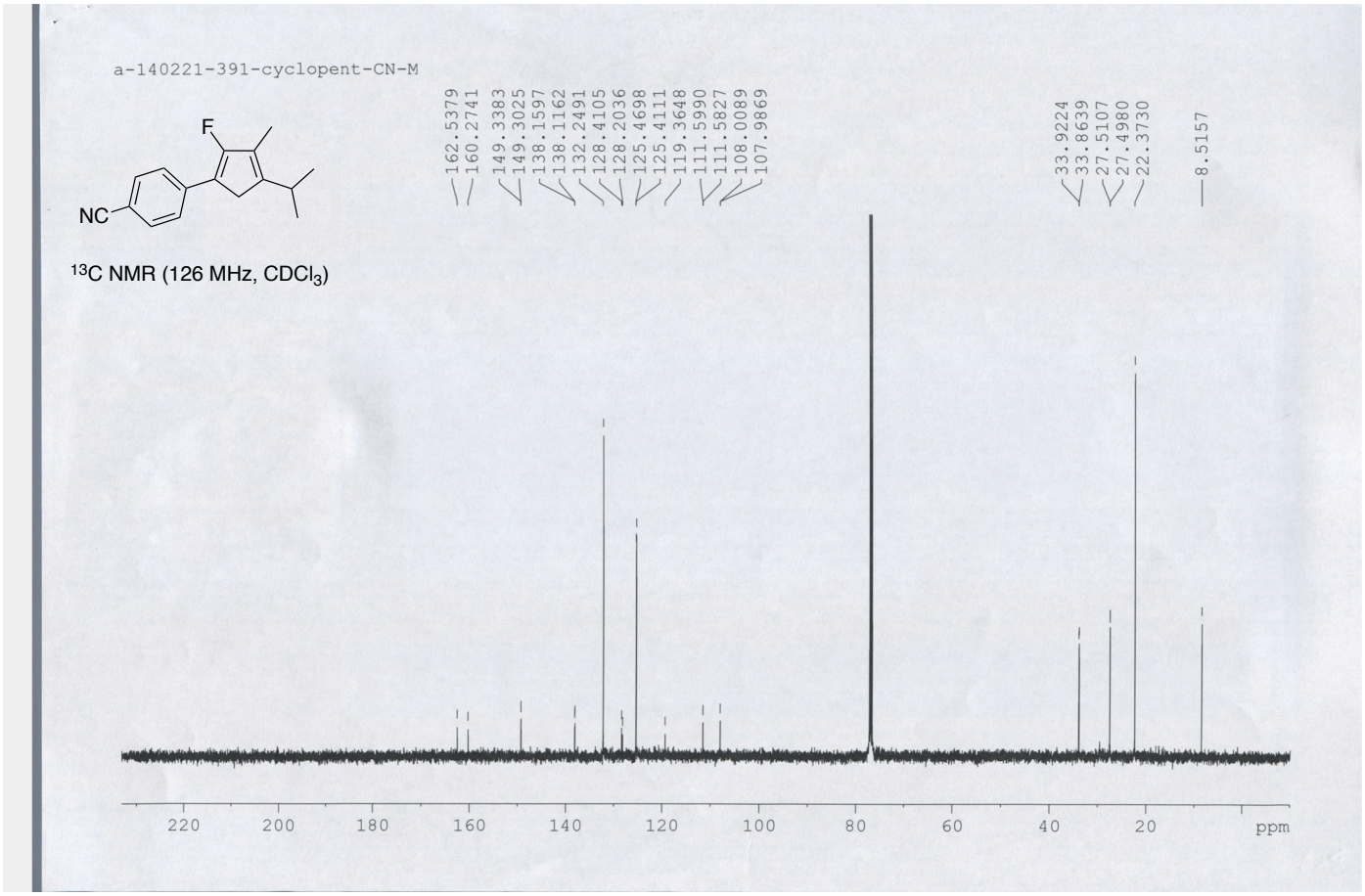



$^{13}$C NMR (126 MHz, $CDCl_3$)

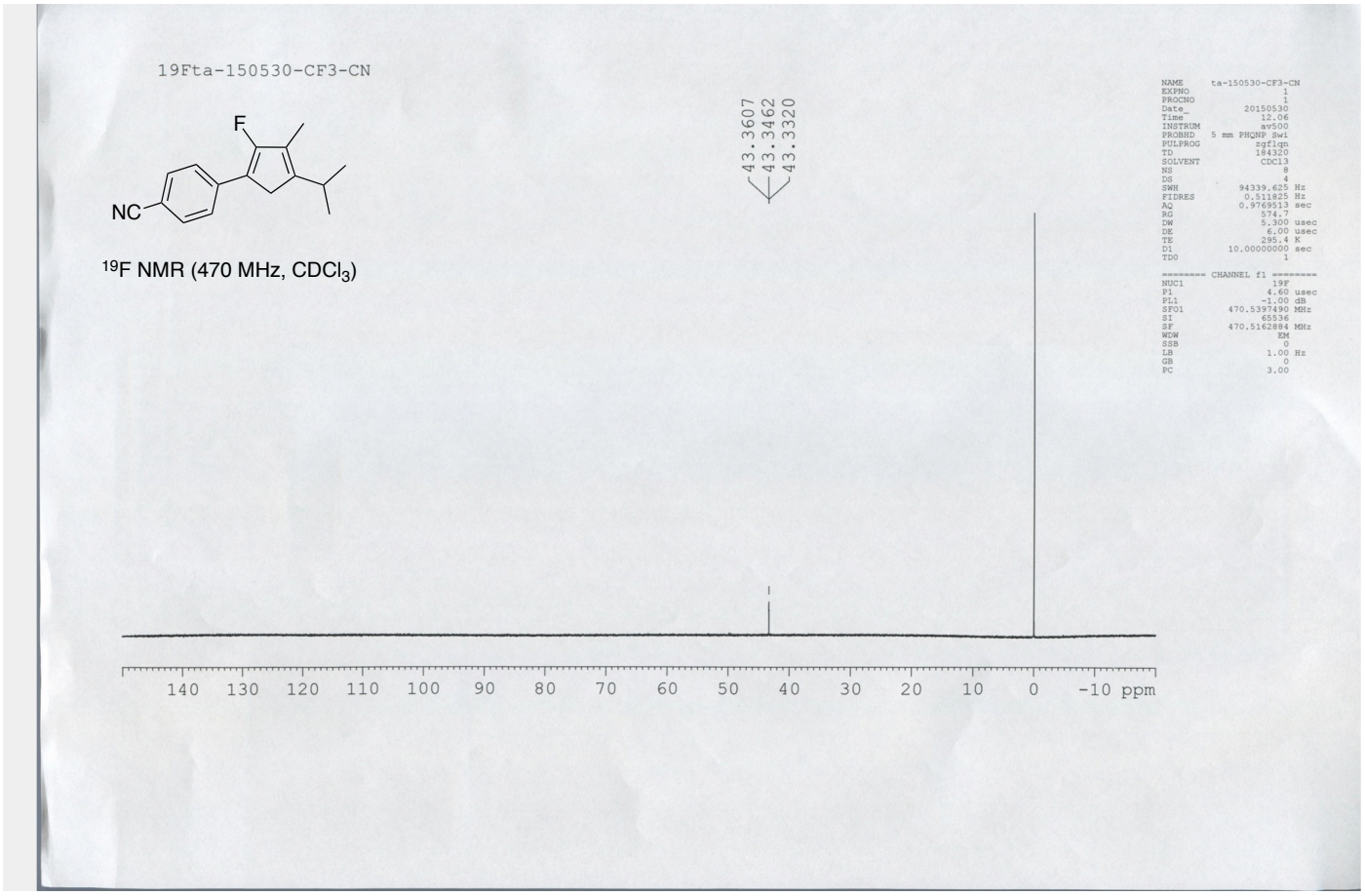



**4-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]benzonitrile (3cb)**



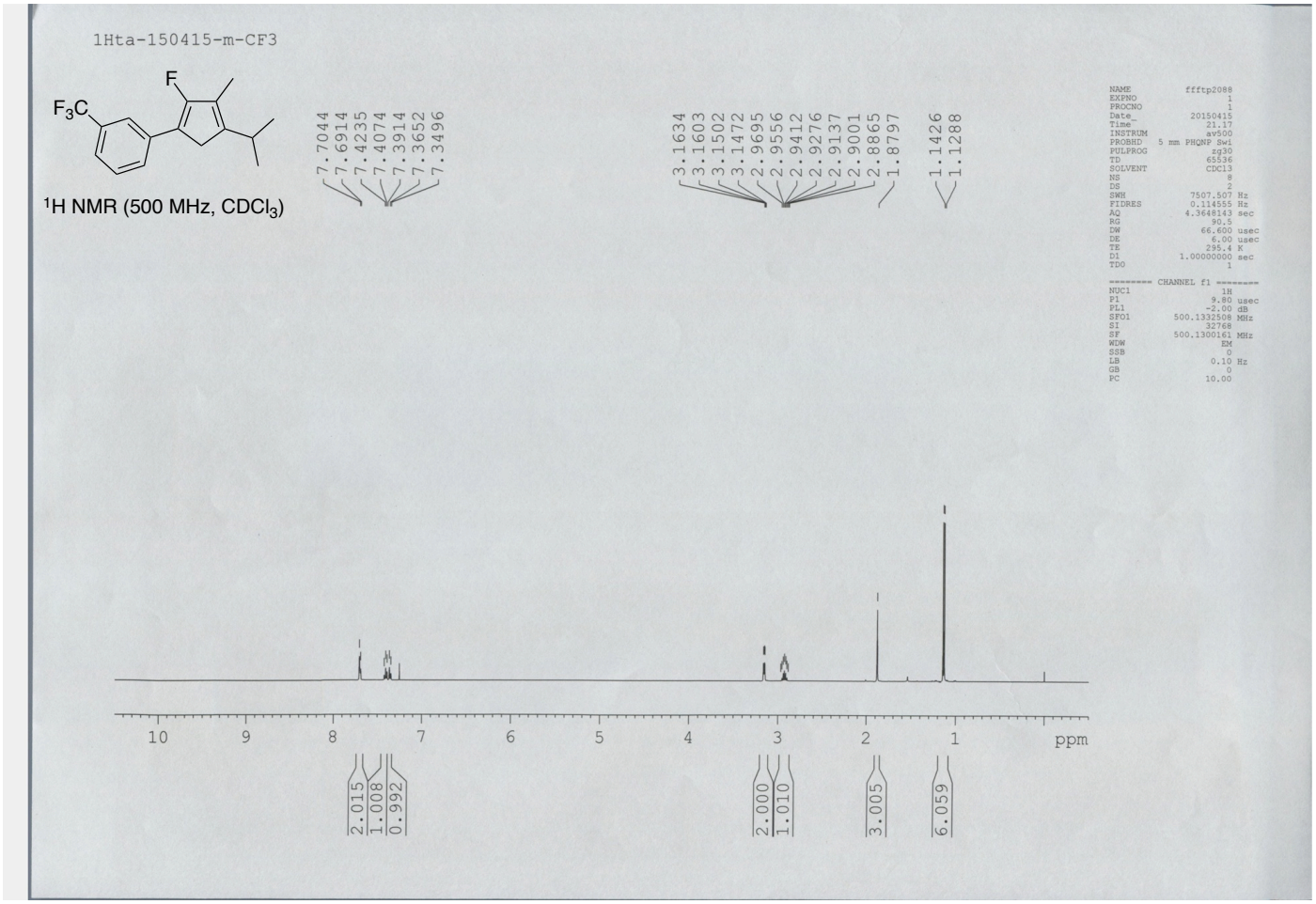


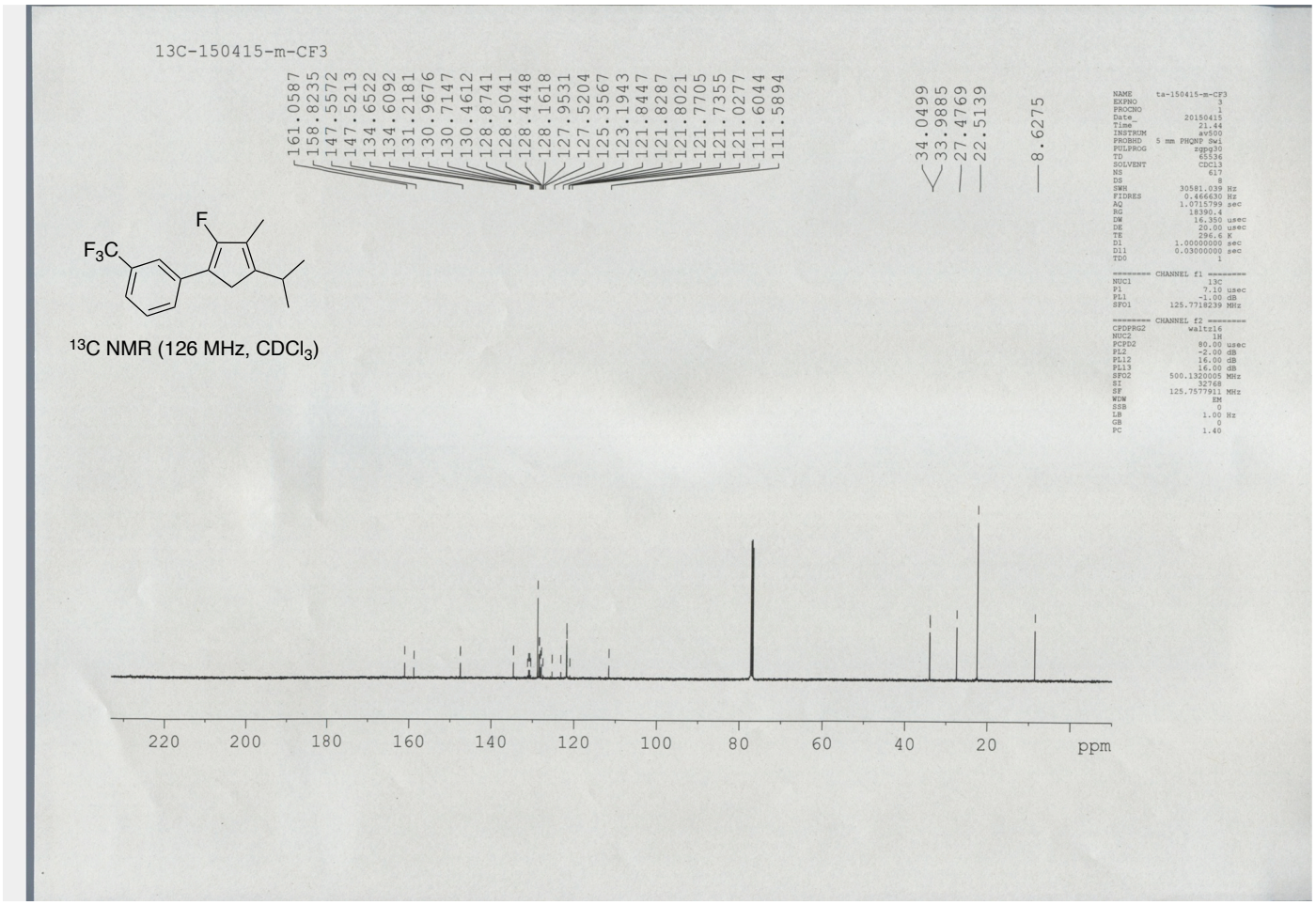

$^{13}C$ NMR (126 MHz, $CDCl_3$)

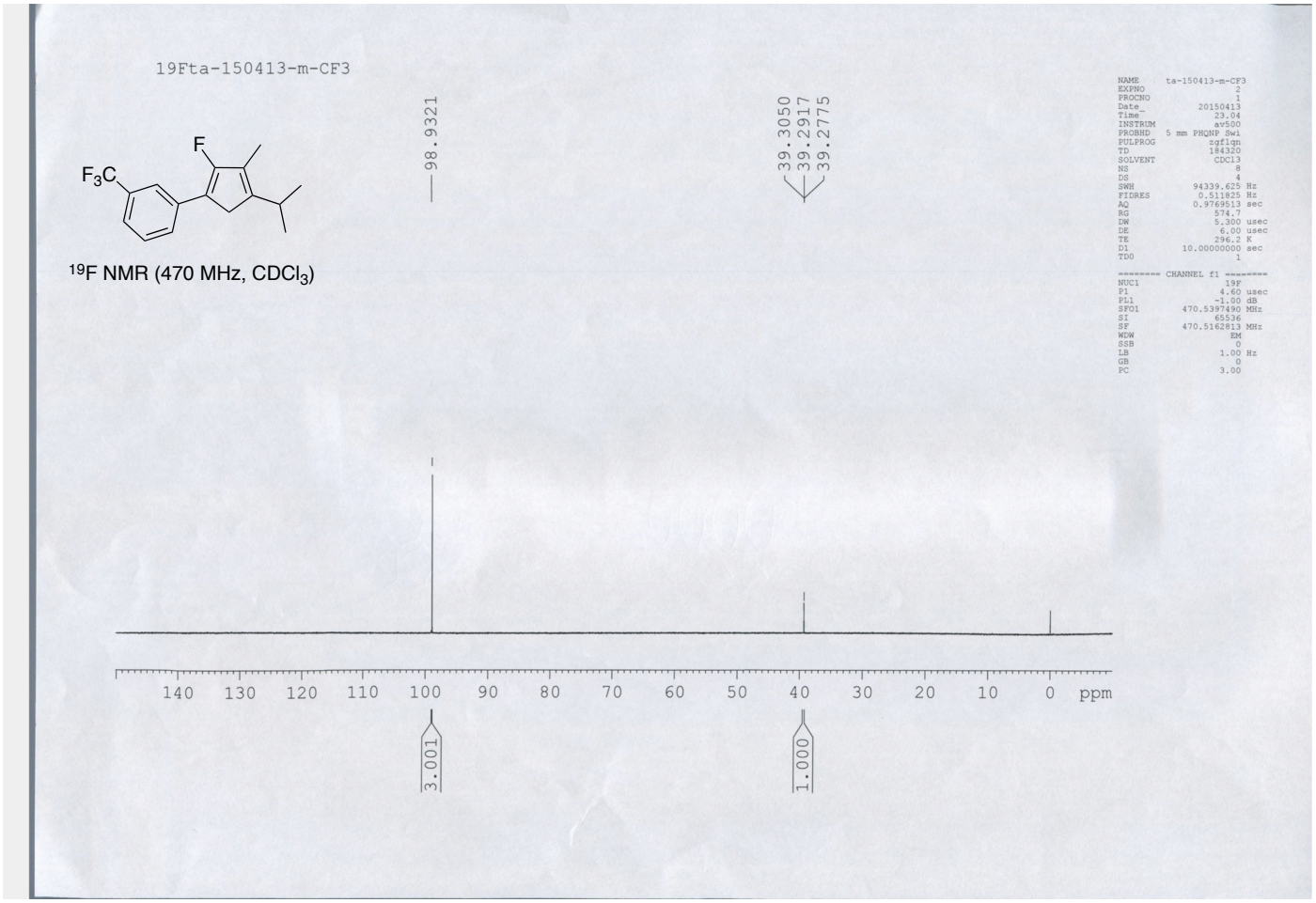



$^{19}F$ NMR (470 MHz, $CDCl_3$)

**1-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]-3-(trifluoromethyl)benzene (3db)**

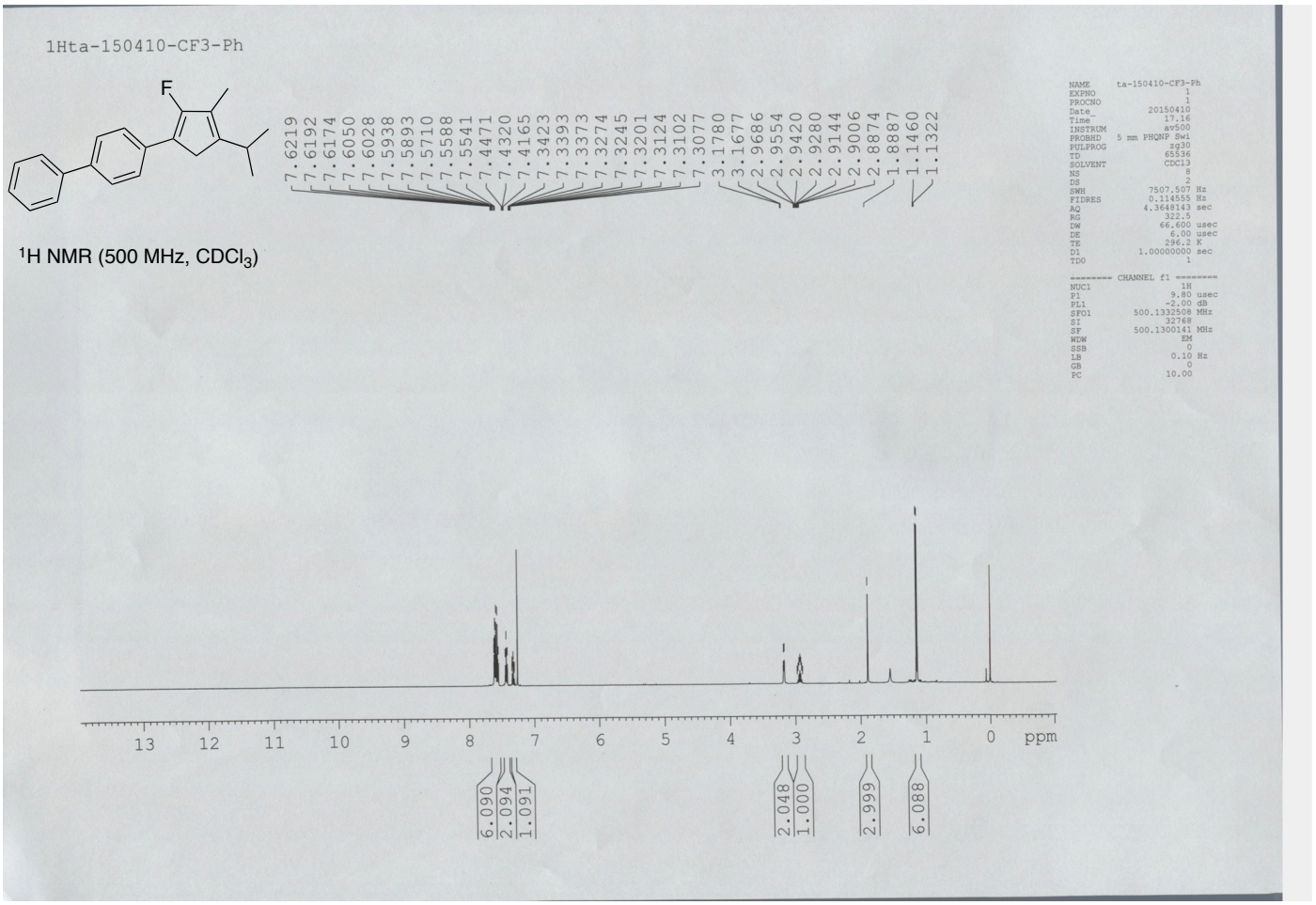





$^{19}$F NMR (470 MHz, $CDCl_3$)

**4-[2-Fluoro-3-methyl-4-(propan-2-yl)cyclopenta-1,3-dien-1-yl]-1,1'-biphenyl (3fb)**




$^{1}$H NMR (500 MHz, $CDCl_3$)

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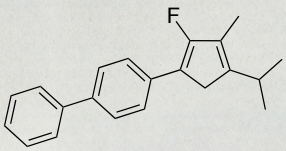


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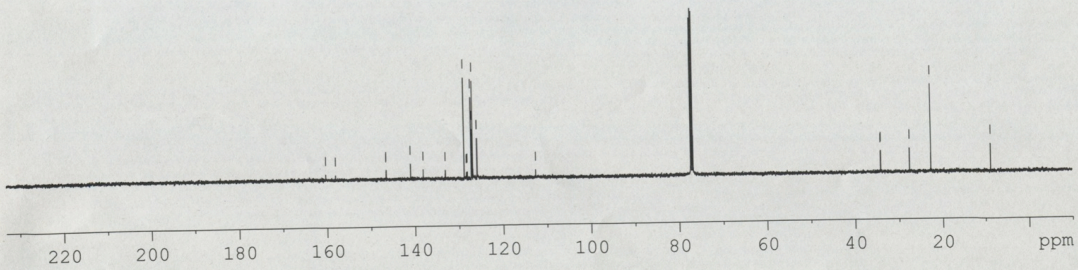
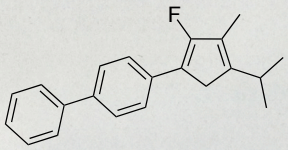
8.7134

$^{13}C$ NMR (126 MHz, $CDCl_3$)

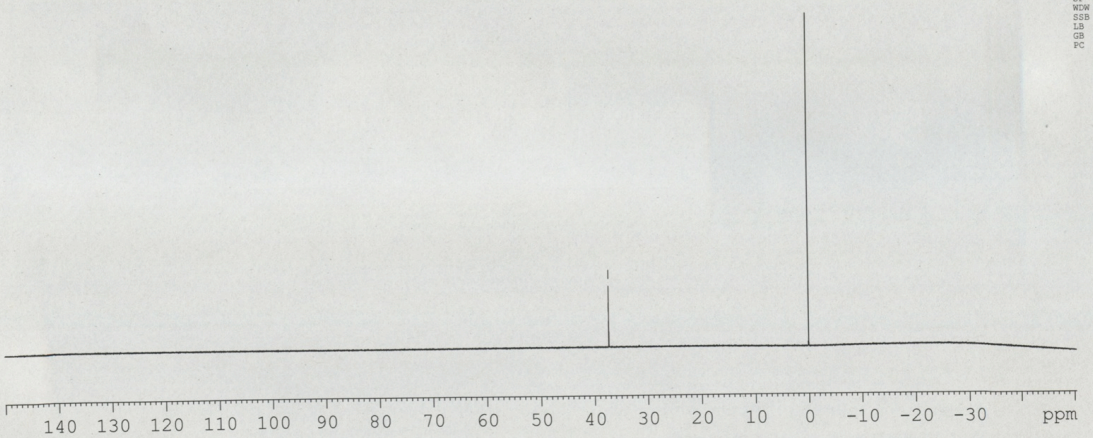



19Fta-1550406-CF3-Ph

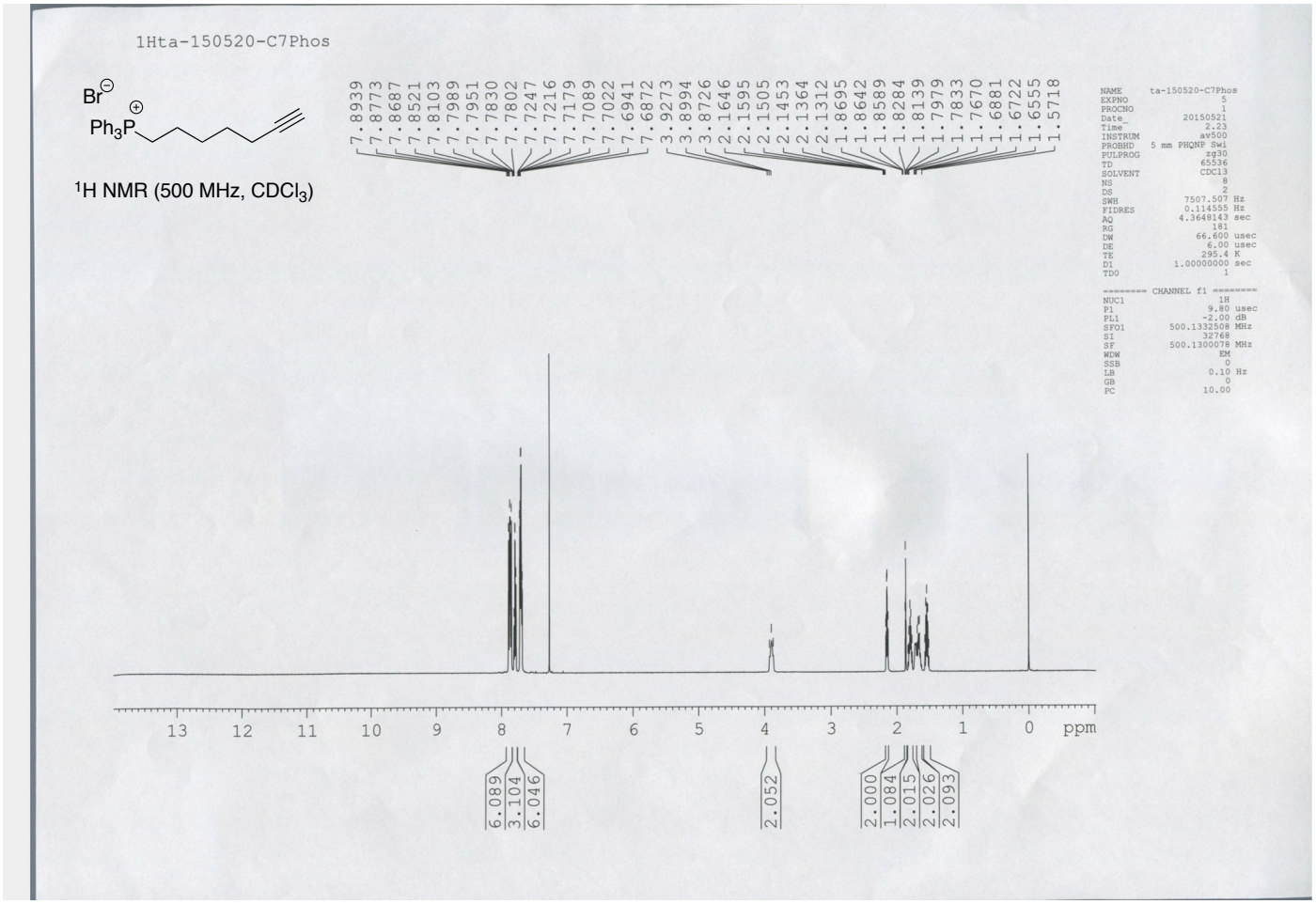


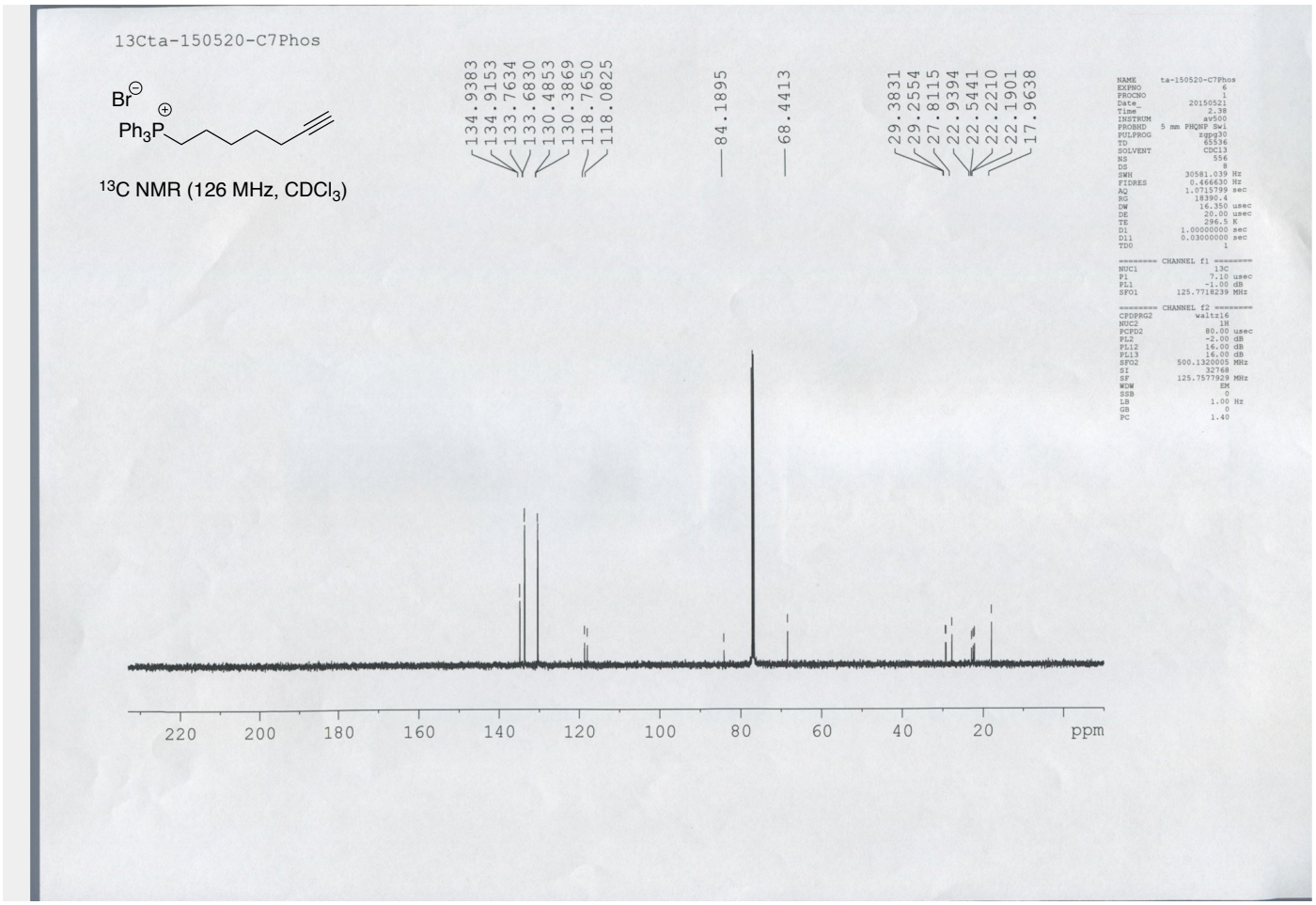

37.2900
37.2763
37.2636

$^{19}F$ NMR (470 MHz, $CDCl_3$)



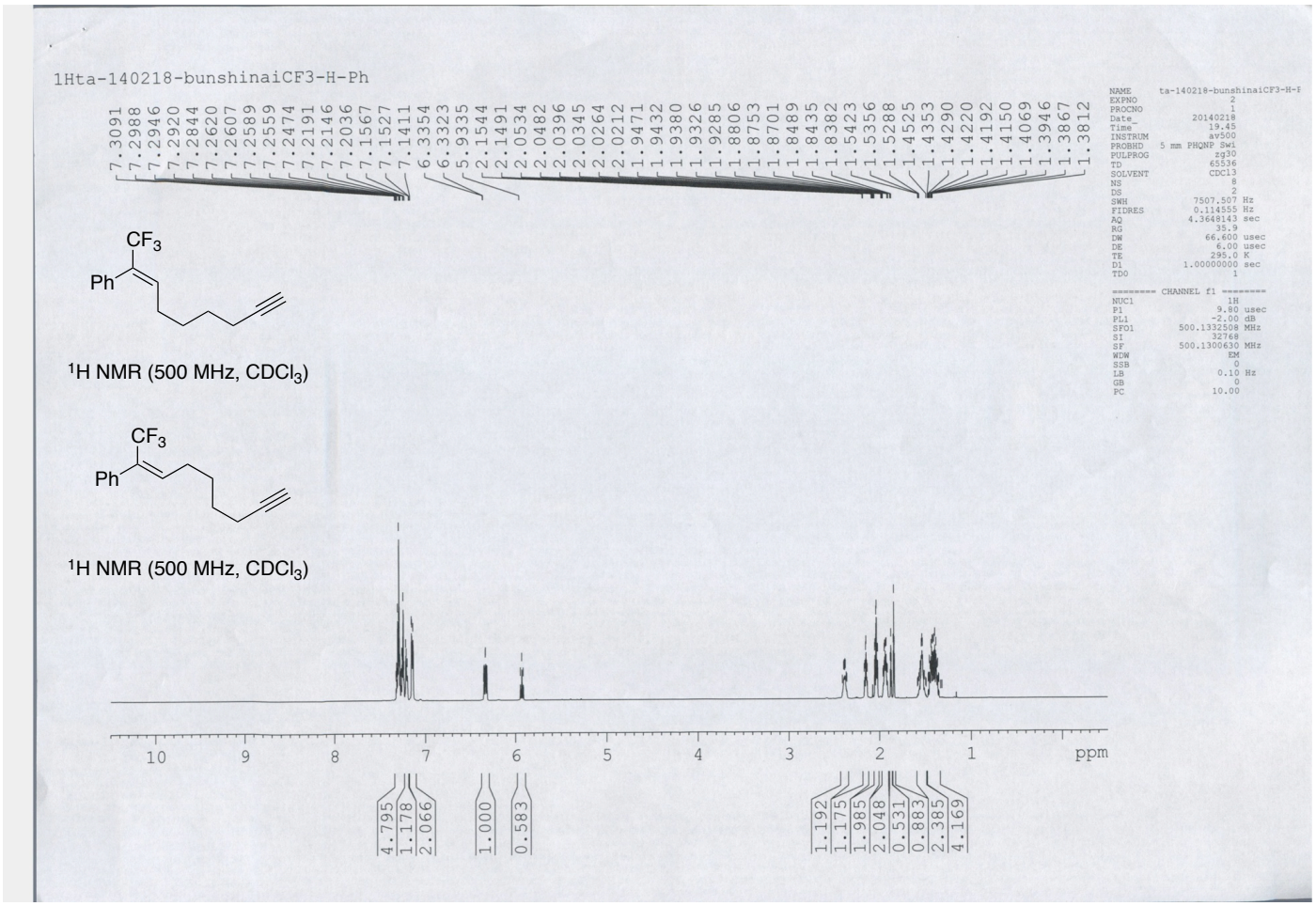
**Hept-6-yn-1-yltriphenylphosphonium bromide**

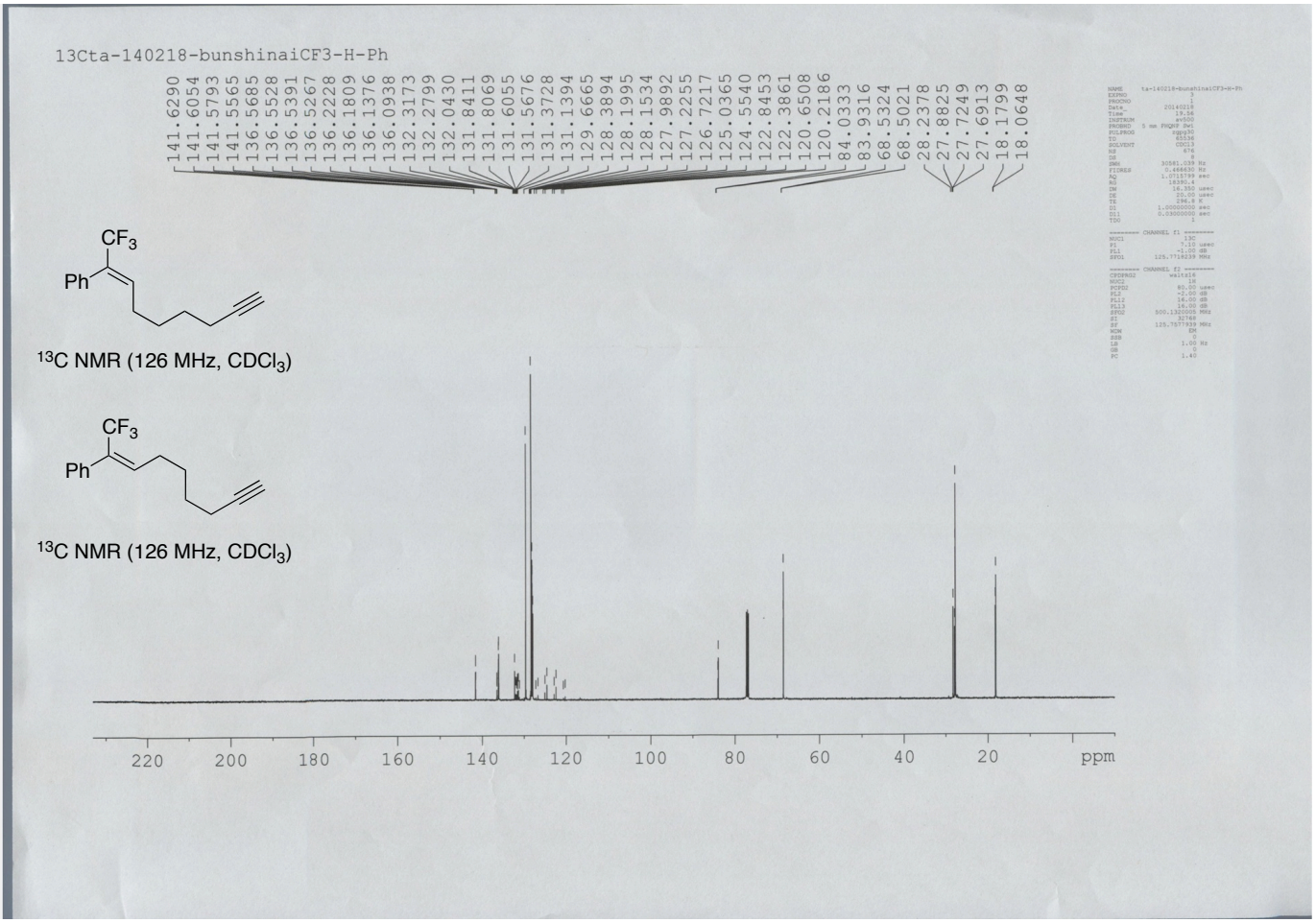


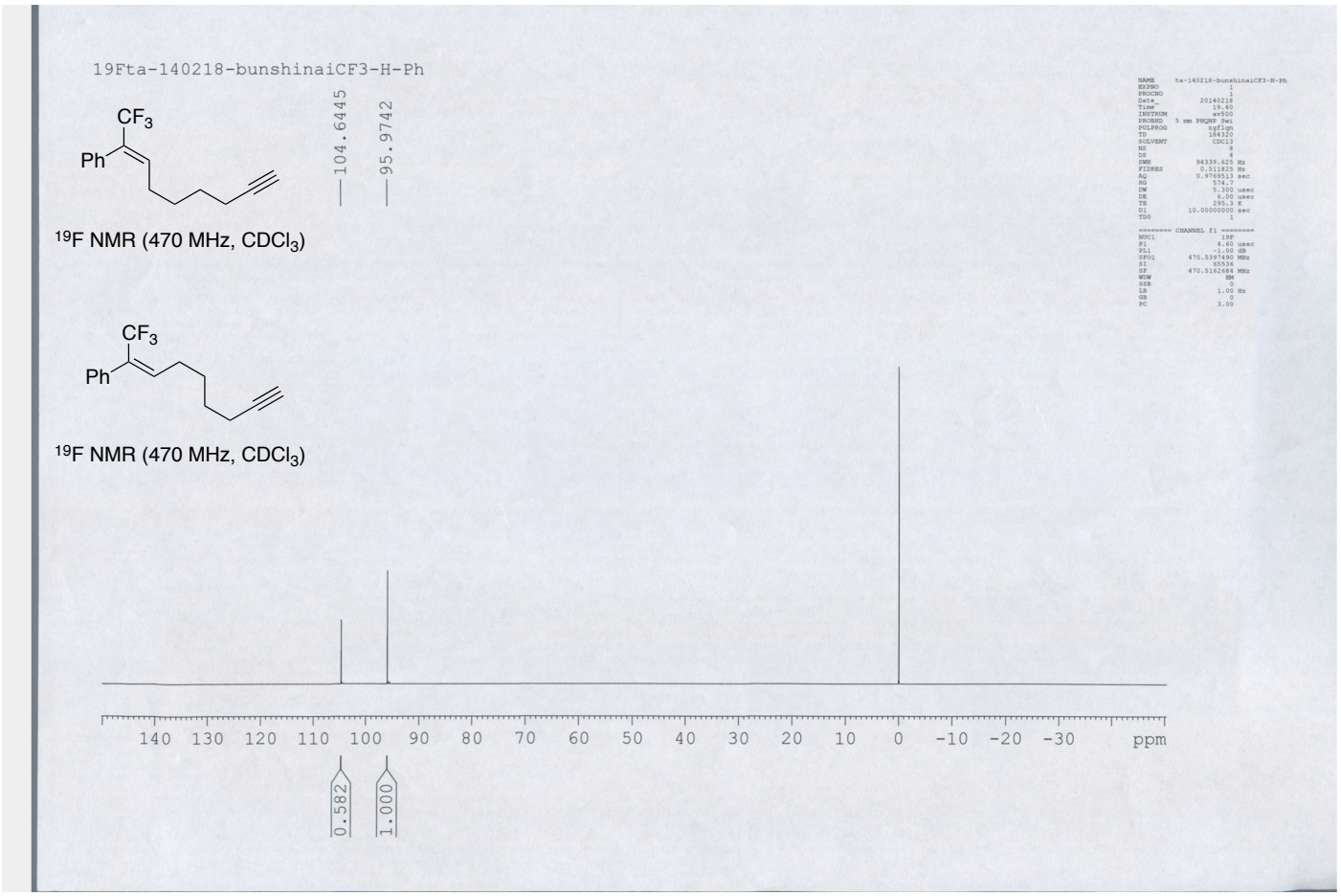



**(*E*)-1,1,1-Trifluoro-2-phenylnon-2-en-8-yne (8)**

**(*Z*)-1,1,1-Trifluoro-2-phenylnon-2-en-8-yne (8)**

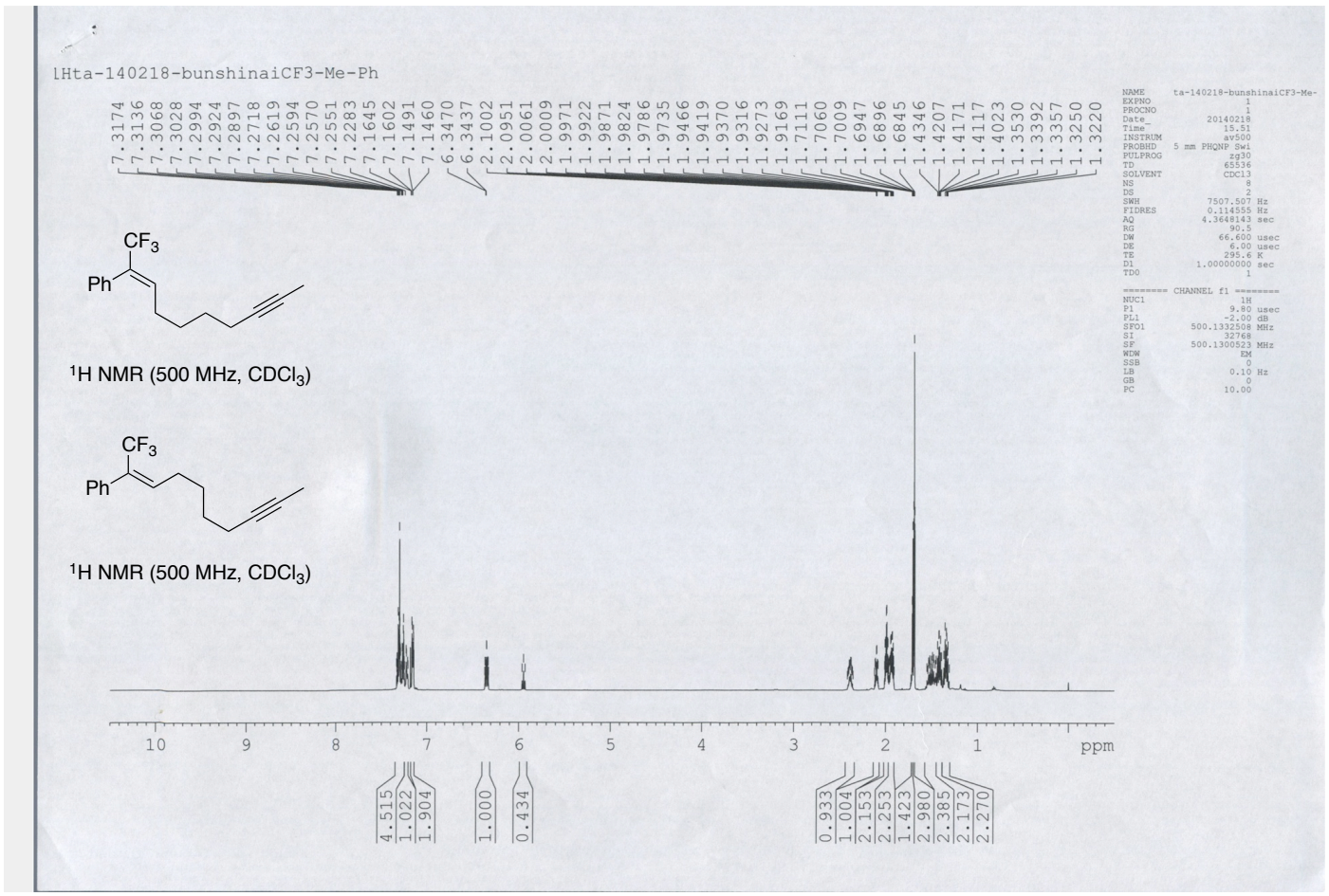





**(*E*)-1,1,1-Trifluoro-2-phenyldec-2-en-8-yne (5)**

**(*Z*)-1,1,1-Trifluoro-2-phenyldec-2-en-8-yne (5)**



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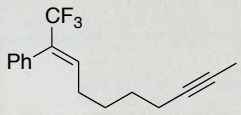
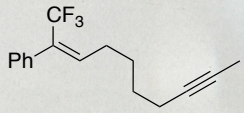



$^{13}$C NMR (126 MHz, $CDCl_3$)

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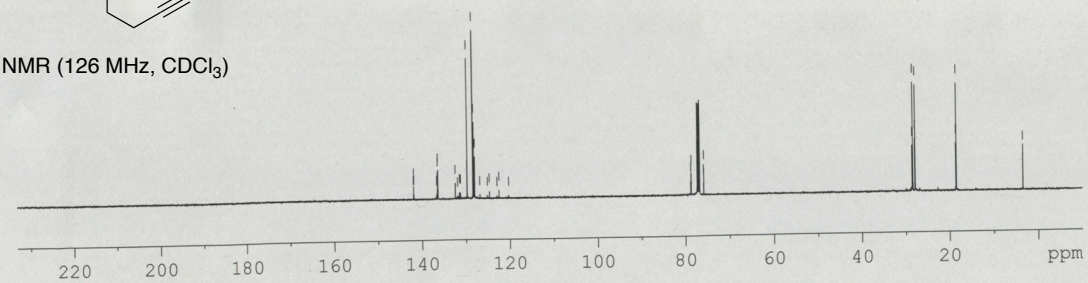


19Fta-140218-bunsinaiCF3-Me-Ph

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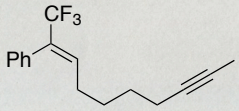


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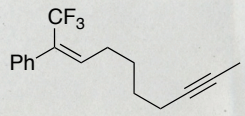
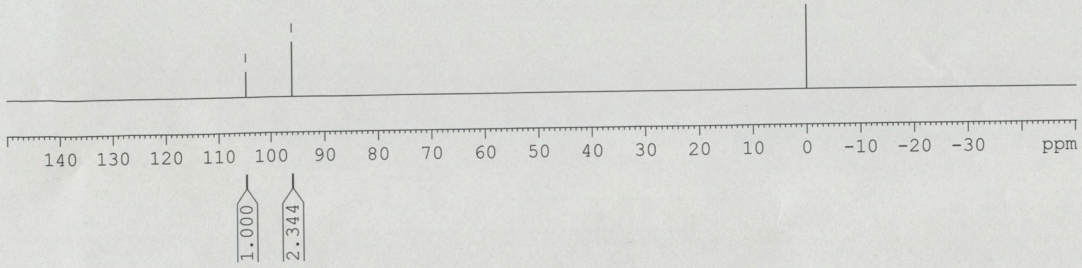
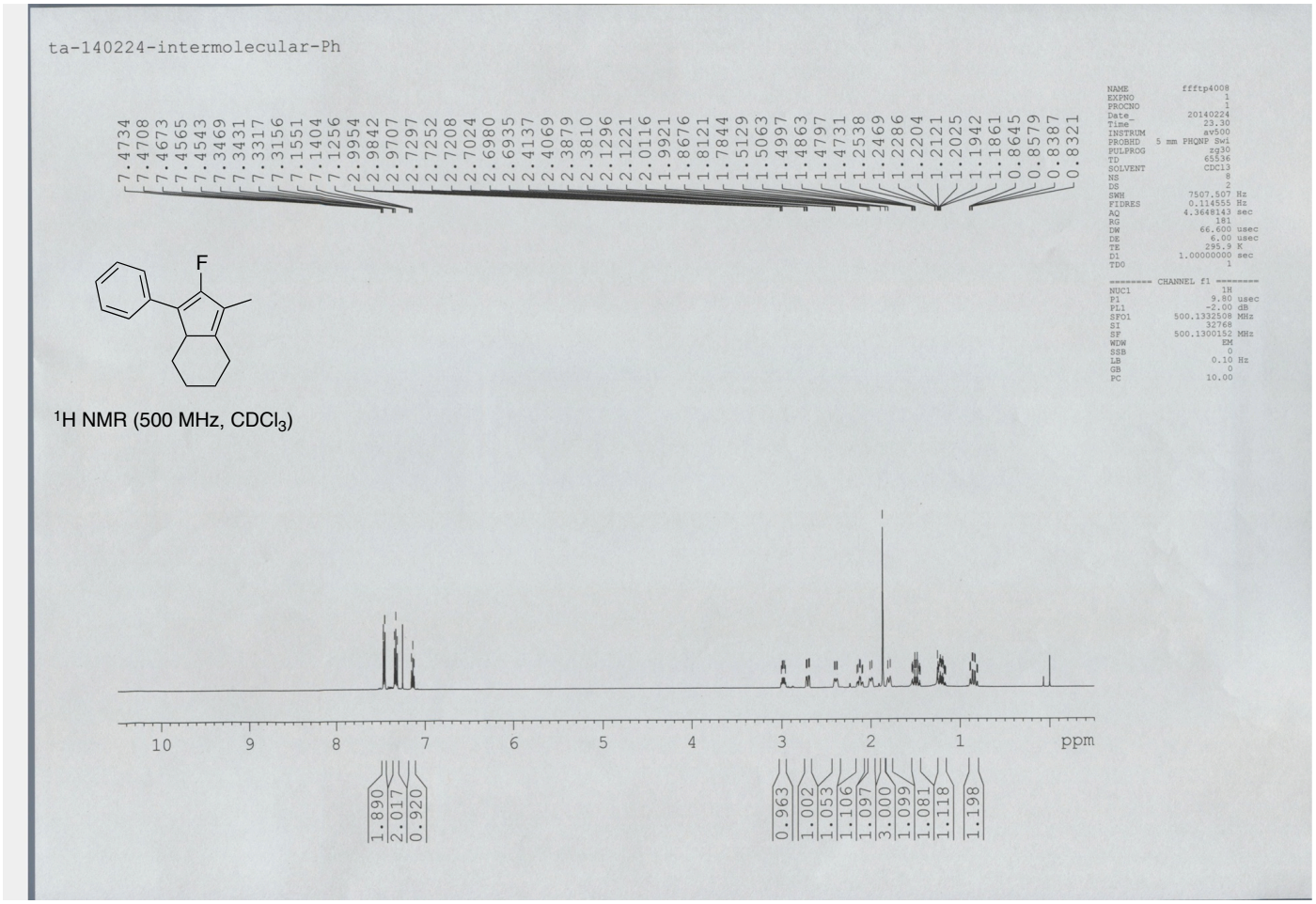


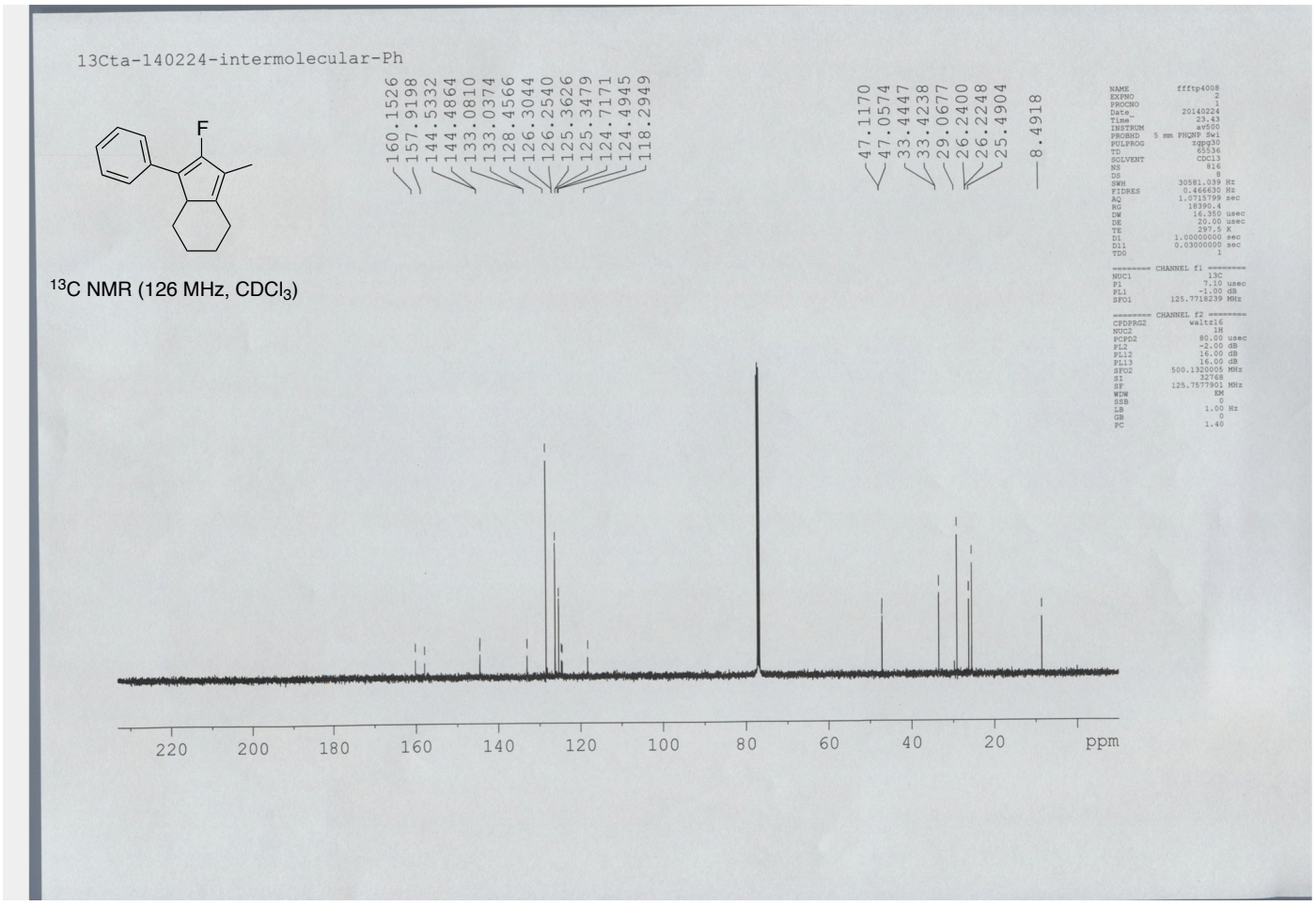

$^{19}$F NMR (470 MHz, $CDCl_3$)



**2-Fluoro-3-methyl-1-phenyl-5,6,7,7a-tetrahydro-4*H*-indene (9)**

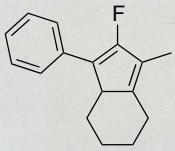


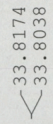

$^{1}$H NMR (500 MHz, $CDCl_3$)




$^{13}$C NMR (126 MHz, $CDCl_3$)

19Fta-140224-intermolecular-Ph





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RG 574.7
DW 5.300 usec
DE 6.00 usec
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D1 10.00000000 sec
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PL1 -1.00 dB
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00


$^{19}$F NMR (470 MHz, $CDCl_3$)