Supporting Information

Niobium(V)-Catalyzed Defluorinative Triallylation of α,α,α-Trifluorotoluene Derivatives by Triple C-F Bond Activation

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General. NMR spectra were recorded on Unity Inova-400 instrument (Varian Inc., 400 MHz for 1H, 100 MHz for 13C, 376 MHz for 19F) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for 1H, 100 MHz for 13C) using CDCl3 as a solvent. Tetramethylsilane (TMS) (δ = 0) or CHCl3 (δ = 7.26) served as an internal standard for 1H NMR, CDCl3 was used as an internal standard (δ = 77.0) for 13C NMR and hexafluorobenzene (C6F6) was used as an external standard (δ = -164.9) for 19F NMR. Melting point (mp) determinations were performed by using AS ONE ATM-01 instrument and are uncorrected. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). EI mass spectra were recorded on JEOL GCmate™ II GC/MS Double-Focusing Mass Spectrometer. ESI mass spectra were recorded on Bruker Daltonics microTOF_15 focus. Elemental analyses were performed by Flash2000 instrument (Amco Inc). Purification of the products was performed by column chromatography on silica gel (Fuji sylisia PSQ-60B) or preparative TLC on silica gel (Wako gel B-5F). All solvents were purified according to the standard procedures.
1. Representative procedure for the defluorinative triallylation of \( \alpha,\alpha,\alpha \)-trifluorotoluene derivatives

The preparation of 2a is described below as a representative procedure. The reaction time and the amount of NbCl\(_5\) were optimized for each substrate (See Table 2). The reactions were carried out in 0.16-0.39 mmol scale.

![Chemical Reaction Diagram]

To a dried 20 mL two-necked flask, 1a (44.8 mg, 0.201 mmol) and 1,2-dichloroethane (0.2 mL) were added. Then, allyltrimethylsilane (0.16 mL, 1.01 mmol) and NbCl\(_5\) (5.4 mg, 0.020 mmol) were added in this manner, and the mixture was stirred for 0.5 h at room temperature. The resulting mixture was treated with aqueous 1M HCl and extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layer was filtered and concentrated. Purification by preparative TLC (hexane) afforded 2a in 61% yield (35.6 mg, 0.123 mmol).

2. Preparation and analytical data of substrates and products

2-1. Substrates

Substrate 1c, 1i, 1j were purchased from Sigma-Aldrich Co. Llc., Tokyo Chemical Industry Co., Ltd. and Wako Pure Chemical Industries Ltd., respectively.

Trifluorotoluene 1a

![Chemical Structure of 1a]

Trifluorotoluene 1a was prepared according to the reported procedure.\(^1\)

![Chemical Reaction Diagram for Preparation of 1a]

In a 110 mL test tube, 4-bromobenzotrifluoride (0.50 mL, 3.6 mmol), phenylboronic acid (0.57 g, 4.6 mmol), Pd(PPh\(_3\))\(_4\) (0.21 g, 0.18 mmol), Na\(_2\)CO\(_3\) (1.13 g, 10.7 mmol) were dissolved to a mixture of 1,2-dimethoxyethane (9 mL) and water (3 mL). The mixture was stirred at 80 °C for 13.5 h. After
being cooled to room temperature, the resulting mixture was filtered through Celite with AcOEt, and the filtrate was extracted by AcOEt three times. The organic layer was dried over MgSO$_4$, filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded 1a in 94% yield (0.75 g, 3.4 mmol).

White solid
Mp = 79-80 °C

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.43 (m, 1H), 7.48 (t, $J$ = 7.4 Hz, 2H), 7.58-7.62 (m, 2H), 7.70 (s, 4H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 124.3 (q, $J_{C,F}$ = 273.7 Hz), 125.7 (q, $J_{C,F}$ = 3.5 Hz), 127.3, 127.4, 128.2, 129.0, 129.3 (q, $J_{C,F}$ = 32.4 Hz), 139.8, 144.7

$^{19}$F NMR (376 Hz, CDCl$_3$) δ -65.0 (s, 3F)

IR (KBr) 3446, 3084, 2359, 1614, 1329, 1169, 1113, 1074, 843, 768, 727, 690 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.$^2$

**Trifluorotoluene 1b**

![Trifluorotoluene 1b](image)

Trifluorotoluene 1b was prepared according to the reported procedure.$^1$

\[
\text{Br} \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{B(OH)}_2
\]

\[
\text{Et} \quad \text{Et} \quad \text{Pd(PPh$_3$)$_4$ (5 mol\%)} \quad \text{Na$_2$CO$_3$ (3 equiv)} \quad \text{DME / H$_2$O (3/1), 80 °C}
\]

In a 110 mL test tube, 4-bromobenzotrifluoride (0.32 mL, 2.3 mmol), phenylboronic acid (0.44 g, 3.0 mmol), Pd(PPh$_3$)$_4$ (0.13 g, 0.11 mmol), Na$_2$CO$_3$ (0.73 g, 6.8 mmol) were dissolved to a mixture of 1,2-dimethoxyethane (9 mL) and water (3 mL). The mixture was stirred at 80 °C for 12 h. After being cooled to room temperature, the resulting mixture was filtered through Celite with AcOEt, and the filtrate was extracted with AcOEt three times. The organic layer was dried over MgSO$_4$, filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded 1b in 96% yield (0.55 g, 2.2 mmol).

White solid
Mp=143-144 °C
$^1$H NMR (400 MHz, CDCl$_3$) δ 1.28 (t, $J = 7.6$ Hz, 3H), 2.71 (q, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.68 (s, 4H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.5, 28.5, 124.3 (q, $J_{C-F} = 273.7$ Hz), 125.6 (q, $J_{C-F} = 3.6$ Hz), 126.9, 127.2, 128.5, 129.0 (q, $J_{C-F} = 32.4$ Hz), 137.1, 144.5, 144.6

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -65.0 (s, 3F)

IR (KBr) 3435, 2976, 2937, 2883, 1616, 1398, 1329, 1171, 1126, 1072, 823, 596 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.$^1$

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Trifluorotoluene 1d

![Diagram of reaction](image)

To a 30 mL two-neck flask equipped with a dropping funnel, Mg turnings (0.12 g, 4.9 mmol) was added and it was heated to dryness in vacuo. After cooling, Et$_2$O (1 mL) and a small piece of iodine were added under nitrogen. Then, Et$_2$O (3 mL) solution of 1-bromopentane (0.55 mL, 4.5 mmol) was slowly added through a dropping funnel. The mixture was stirred for 12 h at 40 ºC to afford a solution of pentylmagnesium bromide.

To another 30 mL two-neck flask, 4-bromobenzotrifluoride (0.12 mL, 0.89 mmol), NiCl$_2$(dppp) (dppp = 1,2-bis(diphenylphosphino)propane) (48 mg, 0.089 mmol) and Et$_2$O (3 mL) were added. Pentyl magnesium bromide was added dropwise via cannula and the mixture was stirred for 32 h at room temperature. The resulting mixture was treated with 1M aqueous HCl, and extracted with Et$_2$O three times. The combined organic layer was filtered through a short pad of Celite on silica gel with AcOEt. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford 1d in 42% yield (80 mg, 0.37 mmol).

Colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.85-0.93 (m, 3H), 1.26-1.40 (m, 4H), 1.58-1.67 (m, 2H), 2.65 (t, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.9, 22.5, 30.9, 31.4, 35.8, 124.5 (q, $J_{C-F} = 272.9$ Hz), 125.1 (q, $J_{C-F} = 3.6$ Hz), 128.0 (q, $J_{C-F} = 31.2$ Hz), 128.7, 147.0

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -65.1 (s, 3F)
IR (neat) 2960, 2933, 2860, 1618, 1466, 1417, 1327, 1165, 1126, 1068, 1018, 843 cm⁻¹
HRMS (EI) m/z calcd for C₁₂H₁₅F₃ (M)⁺ 216.1120, found 216.1126.

**Trifluorotoluene 1e**

![Diagram of trifluorotoluene 1e]

To a 30 mL two-neck flask equipped with a dropping funnel, Mg turning (0.44 g, 18 mmol) was added and it was heated to dryness in vacuo. After cooling, Et₂O (3 mL) and a small piece of iodine were added under nitrogen. Then, Et₂O (11 mL) solution of 1-bromooctane (2.9 mL, 17 mmol) was slowly added through a dropping funnel. The mixture was stirred for 5 h at 40 °C to afford a solution of octylimagnesium bromide.

To a dried 100 mL two-neck flask, 4-bromobenzotrifluoride (0.47 mL, 3.3 mmol), NiCl₂(dppp) (0.18 g, 0.33 mmol) and Et₂O (5 mL) were added. Octylimagnesium bromide was added dropwise via cannula at 0 °C, and the mixture was stirred for 13 h at room temperature. The resulting mixture was treated with 1M aqueous HCl, and extracted with CH₂Cl₂ three times. The combined organic layer was filtered through a pad of Celite on silica gel with CH₂Cl₂. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford 1e in 97% yield (0.839 g, 0.325 mmol).

Colorless oil

¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.38 (m, 10H), 1.57-1.67 (m, 2H), 2.65 (t, J = 8.0 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H)

¹³C NMR (100 MHz, CDCl₃) δ 14.1, 22.6, 29.2, 29.4, 29.7, 31.2, 31.9, 35.8, 124.4 (q, J_C-F = 272.9 Hz), 125.1 (q, J_C-F = 3.8 Hz), 127.9 (q, J_C-F = 32.5 Hz), 128.7, 147.0

¹⁹F NMR (376 MHz, CDCl₃) δ -64.8 (s, 3F)

IR (neat) 2956, 2925, 2856, 2360, 1618, 1466, 1327, 1165, 1126, 1068, 1018, 843 cm⁻¹
HRMS (EI) m/z calcd for C₁₃H₁₂F₃ (M)⁺ 258.1587, found 258.1595.

The analytical data were in accordance with those reported in the literature.³
Trifluorotoluene 1f

![Chemical structure of 1f]

To a dried 110 mL test tube, 4-bromobenzotrifluoride (0.62 mL, 4.4 mmol), styrene (0.60 g, 5.8 mmol), Pd(OAc)$_2$ (0.10 g, 0.44 mmol) and DMF (5 mL) were added, and the mixture was stirred at 120 ºC for 8 h. The resulting mixture was filtered through a short pad of Celite on silica gel with AcOEt. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford 1f in 33% yield (0.37 g, 1.5 mmol).

White solid
Mp = 169-170 °C

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (d, $J = 16.2$ Hz, 1H), 7.20 (d, $J = 16.2$ Hz, 1H), 7.28-7.33 (m, 1H), 7.36-7.41 (m, 2H), 7.51-7.56 (m, 2H), 7.61 (s, 4H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 124.2 (q, $J_{C-F} = 280.8$ Hz), 125.6 (q, $J_{C-F} = 3.8$ Hz), 126.6, 126.8, 127.1, 128.3, 128.8, 129.3 (q, $J_{C-F} = 32.6$ Hz), 131.2, 136.6, 140.8

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -65.0 (s, 3F)

IR (KBr) 3446, 3028, 2360, 1612, 1325, 1167, 1155, 1111, 1068, 827, 758, 694 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.

Trifluorotoluene 1g

![Chemical structure of 1g]

To a dried 30mL two-necked flask, CuCl (21 mg, 0.11 mmol), Pd(PPh$_3$)$_4$ (0.13 g, 0.11 mmol),
4-bromobenzotri fluoride (0.31 mL, 2.2 mmol) and NEt$_3$ (7.4 mL) were added. Then, phenylacetylene (0.37 mL, 3.3 mmol) was added to the mixture and it was stirred for 20.5 h at room temperature. The resulting mixture was filtered through Celite with CH$_2$Cl$_2$ and concentrated. Purification by silica gel column chromatography (hexane) afforded $1g$ in 50% yield (0.28 g, 1.1 mmol).

White solid

Mp = 129-130°C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.40 (m, 3H), 7.53-7.58 (m, 2H), 7.59-7.66 (m, 4H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 88.0, 91.8, 122.6, 123.9 (q, $J_{\text{C,F}} = 273.0$ Hz), 125.3 (q, $J_{\text{C,F}} = 3.7$ Hz), 127.1 (d, $J_{\text{C,F}} = 1.2$ Hz), 128.5, 128.9, 129.9 (q, $J_{\text{C,F}} = 32.8$ Hz), 131.8, 131.8

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -65.4 (s, 3F)

IR (KBr) 3444, 2220, 1608, 1325, 1167, 1155, 1105, 1066, 843, 760, 690 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.

Trifluorotoluene $1h$

![Trifluorotoluene structure](image)

$1h$ was prepared according to the reported procedure.$^6,^7$

Colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.84 (s, 3H), 6.96 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 9.0$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.4, 113.9, 122.8 (q, $J_{\text{C,F}} = 32.7$ Hz), 124.5 (q, $J_{\text{C,F}} = 272.4$ Hz), 126.9 (q, $J_{\text{C,F}} = 3.8$ Hz), 162.0

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -64.1 (s, 3F)

IR (neat) 2844, 2362, 1618, 1522, 1331, 1261, 1180, 1163, 1109, 1068, 1032, 837 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.$^6$

Trifluorotoluene $1k$

![Trifluorotoluene structure](image)
To a 100 mL two-necked flask, 4-(trifluoromethyl)benzonitrile (0.765 g, 4.47 mmol), ethanol (23 mL) and aqueous 5M KOH (23 mL) were added. After the mixture was stirred at 110 ºC for 16 h, it was cooled to room temperature and acidified by aqueous 6 M HCl. The mixture was extracted with CH$_2$Cl$_2$ 3 times and the combined organic layer was dried over MgSO$_4$, filtered and concentrated. Recrystallization from hexane/AcOEt afforded carboxylic acid s1 in 60% yield (508 mg, 2.67 mmol).

To a dried 30 mL two-neck flask, carboxylic acid s1 (0.400 g, 2.10 mmol), methanol (12 mL), conc. sulfuric acid (1.2 mL) were added, and the mixture was stirred at 80 ºC for 22 h. The resulting mixture was cooled to 0 ºC and diluted with water, then the most part of organic solvent was removed in vacuo. After the addition of AcOEt, the mixture was extracted with AcOEt twice and the combined organic layer was concentrated. Purification by silica gel column chromatography (hexane : AcOEt = 5 : 1) afforded 1k in 52% yield (0.222 g, 1.09 mmol).

Trifluorotoluene 3b

3b was prepared according to the reported procedure.$^8$

Colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30-7.36 (m, 3H), 7.37-7.42 (m, 3H), 7.46 (dd, $J = 7.6, 7.8$ Hz, 1H), 7.56 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.75 (d, $J = 7.6$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 124.1 (q, $J_{C-F} = 275.2$ Hz), 126.0 (q, $J_{C-F} = 5.4$ Hz), 127.3, 127.6, 127.7, 128.4 (q, $J_{C-F} = 29.9$ Hz), 128.9 (d, $J_{C-F} = 1.5$ Hz), 131.2, 132.0, 139.8, 141.4

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -59.5 (s, 3F)

IR (neat) 3066, 1483, 1315, 1261, 1173, 1128, 1110, 1072, 1036, 768, 748, 702 cm$^{-1}$.

The analytical data were in accordance with those reported in the literature.$^8$

Trichlorotoluene 6

To a dried 30 mL two-necked flask, AlCl$_3$ (832 mg, 8.17 mmol) and CH$_2$Cl$_2$ were added. CH$_2$Cl$_2$ (3 mL) solution of 4-methylbenzotrifluoride (0.114 mL, 0.817 mmol) was added at −78 °C, and the mixture was stirred overnight. The resulting mixture was treated with 1 M aqueous HCl and extracted with CH$_2$Cl$_2$ three times. The organic layer was filtered through Celite with CH$_2$Cl$_2$, and the filtrate was concentrated to afford analytically pure 6 in 96% yield (0.164 g, 0.781 mmol).

Brown solid

Mp = 54-55 ºC

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.40 (s, 3H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.2, 97.9, 125.5, 129.0, 140.7, 141.7

IR (KBr) 2925, 1914, 1715, 1506, 1276, 1179, 1017, 874, 804, 742, 695, 514 cm$^{-1}$

HRMS (EI) m/z calcd for C$_8$H$_7$Cl$_3$ (M$^+$) 207.9610, found 207.9614.

Monofluorotoluene 7

To a dried 100 mL two-necked flask, 4-phenylbenzaldehyde (0.500 g, 2.74 mmol) and methanol (15 mL) were added. NaBH$_4$ (0.125 g, 3.29 mmol) was added in one portion at 0 ºC, and the mixture was stirred at room temperature for 15.5 h. The resulting mixture was cooled to 0 ºC and diluted with water, then the most part of organic solvent was removed in vacuo. The mixture was extracted with AcOEt three times. Concentration of the combined organic layer afforded alcohol s2 in 95% yield (478 mg, 2.59 mmol). This material was used in the next step without further purification.

To a dried 100 mL one-necked flask, alcohol s2 (0.477 g, 2.59 mmol), CH$_2$Cl$_2$ (12 mL), and (N,N-diethylamino)sulfur trifluoride (DAST) (1.2 mL, 9.1 mmol) were added. The mixture was stirred for 24 h at room temperature. The resulting mixture was treated with ice and stirred at room temperature. The organic layer was extracted with CH$_2$Cl$_2$ three times and concentrated. Purification by silica gel column chromatography (hexane : AcOEt = 5 : 1) and further purification by...
preparative TLC (hexane : AcOEt = 5 : 1) afforded 7 in 36% yield (0.173 g, 0.931 mmol).

White solid
Mp = 84-85 °C

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 5.43\) (d, \(J_{HF} = 48.1\) Hz, 2H), 7.34-7.39 (m, 1H), 7.42-7.49 (m, 4H), 7.57-7.65 (m, 4H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 84.3\) (d, \(J_{CF} = 165.5\) Hz), 127.1, 127.4, 127.5, 128.0 (d, \(J_{CF} = 5.4\) Hz), 128.8, 135.1 (d, \(J_{CF} = 16.9\) Hz), 140.6, 141.7 (d, \(J_{CF} = 3.0\) Hz)

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -208.8\) (t, \(J_{FH} = 48.1\) Hz, 1F)

IR (KBr) 3438, 2962, 1614, 1487, 1408, 1225, 968, 849, 822, 762, 733, 696 cm\(^{-1}\).

The analytical data were in accordance with those reported in the literature.

Difluorotoluene 8

To a dried 30 mL two-necked flask, 4-phenylbenzaldehyde (0.500 g, 2.24 mmol), CH\(_2\)Cl\(_2\) (12 mL), and (N,N-diethylamino)sulfur trifluoride (DAST) (1.3 mL, 9.6 mmol) were added. The mixture was stirred for 20.5 h at room temperature. The resulting mixture was treated with water at 0 °C, and was extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layer was dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded 8 in 79% yield (0.442 g, 2.16 mmol).

White solid
Mp= 88-89 °C

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(6.70\) (t, \(J_{HF} = 56.0\) Hz, 1H), 7.39 (t, \(J = 7.4\) Hz, 1H), 7.47 (t, \(J = 7.8\) Hz, 2H), 7.57-7.62 (m, 4H), 7.68 (d, \(J = 8.0\) Hz, 2H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 114.7\) (t, \(J_{CF} = 237.2\) Hz), 126.0 (t, \(J_{CF} = 6.1\) Hz), 127.2, 127.4, 127.9, 128.9, 133.2 (t, \(J_{CF} = 22.3\) Hz), 140.2, 143.7

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -112.9\) (d, \(J_{FH} = 56.0\) Hz, 2F)

IR(KBr) 3440, 2970, 2359, 1925, 1614, 1381, 1227, 1078, 1022, 839, 766, 690 cm\(^{-1}\)

HRMS (EI) m/z calcd for C\(_{13}\)H\(_9\)F\(_2\) (M)\(^+\) 204.0769, found 204.0751.
The analytical data were in accordance with those reported in the literature.\textsuperscript{10}

2-2. Products

Product 2a

\[ \text{Product 2a} \]

35.6 mg, 61\% from 0.201 mmol 1a, colorless oil

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 2.52 \) (d, \( J = 7.2 \) Hz, 6H), 5.02-5.12 (m, 6H), 5.63 (ddt, \( J = 17.2, 10.0, 7.2 \) Hz, 3H), 7.32-7.37 (m, 1H), 7.39-7.48 (m, 4H), 7.57-7.66 (m, 4H)

$^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta 41.9, 43.2, 117.7, 126.6, 126.9, 127.1, 127.1, 128.7, 134.5, 138.3, 140.8, 144.9 \)

IR (neat) 3074, 2978, 2925, 1638, 1487, 1447, 997, 913, 835, 768, 737, 696 cm\textsuperscript{-1}

HRMS (EI) m/z calcd for C\textsubscript{22}H\textsubscript{24} (M)$^+$ 288.1886, found 288.1878.

Product 2b

\[ \text{Product 2b} \]

45.5 mg, 78\% from 0.184 mmol 1b, colorless oil

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta 1.30 \) (t, \( J = 7.6 \) Hz, 3H), 2.51 (d, \( J = 7.1 \) Hz, 6H), 2.71 (q, \( J = 7.6 \) Hz, 2H), 5.01-5.10 (m, 6H), 5.63 (ddt, \( J = 17.2, 10.4 \) Hz, 7.1 Hz, 3H), 7.26-7.30 (m, 2H), 7.36-7.40 (m, 2H), 7.51-7.59 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta 15.6, 28.5, 41.9, 43.1, 117.6, 126.4, 126.8, 127.0, 128.2, 134.5, 138.1, 138.3, 143.1, 144.5 \)

IR (neat) 3074, 2965, 2928, 1638, 1497, 1449, 1331, 1119, 1003, 913, 820, 626 cm\textsuperscript{-1}

HRMS (EI) m/z calcd for C\textsubscript{24}H\textsubscript{28} (M)$^+$ 317.2183, found 317.2191.
Product 2c

47.8 mg, 71% from 0.296 mmol 1c, 7.9 mg, 21% from 0.20 mmol 6, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 3H), 2.47 (d, $J = 7.2$ Hz, 6H), 4.98-5.08 (m, 6H), 5.59 (ddt, $J = 17.2$, 10.0 Hz, 7.2 Hz, 3H), 7.12-7.17 (m, 2H), 7.19-7.25 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.9, 41.9, 42.9, 117.5, 126.5, 128.7, 134.7, 135.1 142.6

IR (neat) 3074, 3008, 2978, 2923, 1638, 1515, 1448, 1248, 998, 912, 816, 731 cm$^{-1}$

HRMS (EI) m/z calcd for C$_{17}$H$_{22}$ (M)$^+$ 226.1723, found 226.1722.

Product 2d

33.0 mg, 71% from 0.164 mmol 1d, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.26-1.40 (m, 4H), 1.56-1.66 (m, 2H), 2.44 (d, $J = 6.8$ Hz, 6H), 2.57 (t, $J = 7.5$ Hz, 2H), 4.96-5.06 (m, 6H), 5.56 (ddt, $J = 16.0$, 10.0 Hz, 7.5 Hz, 3H), 6.99-7.14 (m, 2H), 7.18-7.23 (m, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.0, 22.6, 31.0, 31.6, 35.4, 41.9, 42.9, 117.4, 126.5, 128.0, 134.7, 140.1, 142.8

IR (neat) 3075, 3005, 2956, 2927, 2857, 1638, 1515, 1448, 1415, 998, 912, 835 cm$^{-1}$

HRMS (ESI) m/z calcd for C$_{21}$H$_{30}$(M+Na)$^+$ 305.2240, found 305.2259.

Product 2e

28.2 mg, 53%, from 0.164 mmol 1e, colorless oil
\textbf{Product 2f}

\begin{center}
\begin{tikzpicture}
\draw[thick] (0,0) -- (0.5,0.5) -- (1,0) -- (1.5,0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,-0.5) -- (1,0) -- (1.5,-0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,-0.5) -- (0.5,0.5) -- (1,0) -- (1,0.5) -- (1.5,0) -- (1.5,-0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,0.5) -- (0.5,-0.5) -- (1,-0.5) -- (1,-0.5) -- (1.5,-0.5) -- (2,0);
\end{tikzpicture}
\end{center}

20.9 mg, 35\%, from 0.191 mmol 1f, colorless oil

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 1.20-1.38 (m, 10H), 1.55-1.65 (m, 2H), 2.44 (d, \(J = 7.2\) Hz, 6H), 2.57 (t, \(J = 7.8\) Hz, 2H), 4.95-5.05 (m, 6H), 5.56 (ddt, \(J = 17.2, 10.0, 7.2\) Hz, 3H) 7.12 (d, \(J = 8.4\) Hz, 2H)

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 14.1, 22.7, 29.3, 29.4, 29.5, 31.3, 31.9, 35.4, 41.9, 42.9, 117.4, 126.5, 128.0, 134.7, 140.2, 142.8

IR (neat) 3583, 3075, 2854, 1638, 1515, 1449, 1326, 1126, 998, 912, 836 cm\textsuperscript{-1}

Anal. Calcd for C\textsubscript{24}H\textsubscript{36}: C, 88.82; H, 11.18; Found C, 88.76; H, 11.26.

\textbf{Product 2g}

\begin{center}
\begin{tikzpicture}
\draw[thick] (0,0) -- (0.5,0.5) -- (1,0) -- (1.5,0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,-0.5) -- (1,0) -- (1.5,-0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,-0.5) -- (0.5,0.5) -- (1,0) -- (1,0.5) -- (1.5,0) -- (1.5,-0.5) -- (2,0);
\draw[thick] (0,0) -- (0.5,0.5) -- (0.5,-0.5) -- (1,-0.5) -- (1,-0.5) -- (1.5,-0.5) -- (2,0);
\end{tikzpicture}
\end{center}

18.9 mg, 42\% from 0.182 mmol 1g, colorless oil

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.47 (d, \(J = 7.3\) Hz, 6H), 4.99-5.06 (m, 6H), 5.56 (ddt, \(J = 16.8, 10.4, 7.3\) Hz, 3H), 7.27-7.38 (m, 5H), 7.47-7.56 (m, 4H)

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 41.7, 43.5, 89.1, 89.3, 117.9, 120.5, 123.4, 126.8, 128.1, 128.3, 131.3, 131.6, 134.2, 146.3

HRMS (EI) m/z calcd for C\textsubscript{24}H\textsubscript{30}(M)\textsuperscript{+} 314.2037, found 314.2035.
IR (neat) 3074, 2978, 2926, 1638, 1515, 1444, 1415, 997, 913, 832, 755, 689 cm\(^{-1}\)

HRMS (EI) m/z calcd for C\(_{24}\)H\(_{24}\)(M)\(^+\) 312.1894, found 312.1878.

**Product 2h**

![Chemical Structure](image)

30 mg, 44%, from 0.281 mmol 1h, colorless oil

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.43 (d, \(J = 7.2\) Hz, 6H), 3.80 (s, 3H), 4.97-5.05 (m, 6H), 5.56 (ddt, \(J = 17.2, 10.0, 7.2\) Hz, 3H), 6.80-6.89 (m, 2H), 7.20-7.25 (m, 2H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 41.9, 42.7, 55.1, 113.3, 117.4, 127.6, 134.6, 137.7, 157.4

IR (neat) 3074, 2978, 2926, 1638, 1515, 1444, 1415, 997, 913, 832, 755, 689 cm\(^{-1}\)

HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{22}\)O (M+Na)\(^+\) 265.1563, found 265.1542.

**Product 2i**

![Chemical Structure](image)

15.8 mg, 34% from 0.276 mmol 1i, colorless oil

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.43 (d, \(J = 7.6\) Hz, 6H), 4.97-5.05 (m, 6H), 5.48-5.60 (m, 3H), 7.21-7.31 (m, 4H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 41.7, 43.2, 118.0, 128.1, 128.2, 131.5, 134.0, 144.3

IR (neat) 3075, 2979, 2925, 1638, 1496, 1449, 1096, 1012, 997, 914, 824, 622 cm\(^{-1}\)

HRMS (EI) m/z calcd for C\(_{18}\)H\(_{19}\)Cl (M)\(^+\) 246.1183, found 246.1175.
**Product 2j**

36.1 mg, 40% from 0.39 mmol 1j, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.44 (d, $J = 7.2$ Hz, 6H), 4.97-5.04 (m, 6H), 5.49-5.60 (m, 3H), 6.97-7.03 (m, 2H), 7.23-7.30 (m, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 41.9, 43.0, 114.7 (d, $J_{C-F} = 21.2$ Hz), 117.8, 128.2 (d, $J_{C-F} = 7.1$ Hz), 134.2, 141.3 (d, $J_{C-F} = 3.0$ Hz), 160.9 (d, $J_{C-F} = 242.0$ Hz)

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -120.5 (s, 1F)

IR (neat) 3076, 2979, 2926, 1638, 1603, 1512, 1449, 1235, 1165, 998, 914, 831 cm$^{-1}$

Anal. Calcd for C$_{16}$H$_{19}$F: C, 83.44; H, 8.32; Found C, 83.28; H, 8.46.

**Product 5**

20.3 mg, 40% 0.206 mmol from 3b, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.70 (d, $J = 7.2$ Hz, 4H), 4.74 (d, $J = 10.0$ Hz, 2H), 4.82 (d, $J = 17.2$ Hz, 2H), 5.19-5.31 (m, 2H), 7.25-7.36 (m, 4H), 7.40 (d, $J = 6.8$ Hz, 2H), 7.69 (d, $J = 7.2$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 43.5, 54.1, 117.5, 119.7, 123.6, 126.9, 127.1, 133.7, 140.7, 149.3

IR (neat) 3072, 3013, 2978, 2920, 2342, 1637, 1475, 1447, 1221, 994, 915, 736 cm$^{-1}$

HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$(M+Na)$^+$ 269.1301, found 269.1298.

**Product 9**

21.9 mg, 48% from 0.217 mmol 7, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.37-2.45 (m, 2H), 2.75 (t, $J = 7.8$ Hz, 2H), 4.97-5.11 (m, 2H), 5.89 (ddt, $J$
= 17.2, 10.4, 6.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.29-7.35 (m, 1H), 7.38-7.45 (m, 2H), 7.48-7.54 (m, 2H), 7.55-7.60 (m, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 35.0, 35.4, 115.0, 126.4, 126.8, 127.2, 128.5, 128.6, 129.0, 138.2, 138.8, 141.0

IR (neat) 3077, 3028, 2925, 2853, 1639, 1487, 1449, 1408, 911, 837, 761, 697 cm$^{-1}$

HRMS (EI) m/z calcd for C$_{16}$H$_{16}$ (M)$^+$ 208.1255, found 208.1252.

**Product 10**

![Product 10](image)

16.3 mg, 33%, from 0.199 mmol 8, colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.34-2.49 (m, 4H), 2.72-2.80 (m, 1H), 4.93-5.03 (m, 4H), 5.70 (ddt, $J = 16.8$ Hz, 10.2 Hz, 7.0 Hz, 2H), 7.20-7.25 (m, 2H), 7.29-7.34 (m, 1H), 7.39-7.45 (m, 2H), 7.50-7.55 (m, 2H), 7.57-7.61 (m, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 40.2, 45.2, 116.1, 126.9, 126.9, 127.0, 128.1, 128.7, 136.7, 138.9, 141.0, 143.8

IR (neat) 3075, 3028, 2977, 2921, 1639, 1486, 994, 912, 834, 765, 734, 697 cm$^{-1}$

HRMS (EI) m/z calcd for C$_{19}$H$_{20}$ (M)$^+$ 248.1572, found 248.1565.
3. Appendix

2-1. Detection and Quantification of Me₃SiF (Scheme 5)

Detection and quantification of Me₃SiF were carried out by ¹H and ¹⁹F NMR analyses of the reaction mixture.

In a dried 1.5 mL glass tube, trifluorotoluene 1a (44.4 mg, 0.200 mmol) was dissolved to dichloroethane (0.2 mL). Subsequently, allyltrimethylsilane (0.16 mL, 1.0 mmol) and NbCl₅ (5.4 mg, 0.020 mmol) were added in this manner. After the mixture was stirred for 30 minutes at room temperature, it was diluted with CDCl₃ at 0 °C (to prevent volatile compounds from evaporation) and rapidly transferred into NMR sample tube. The sample was analyzed by ¹H NMR, and then by ¹⁹F NMR using fluorobenzene (13.7 mg, 0.143 mmol) as an internal standard at room temperature. The ¹H NMR spectrum exhibited the formation of 2a (representatively δ 2.5) and Me₃SiF (δ 0.2) evidently in 1 : 3 ratio (Figure S1). The amount of Me₃SiF was estimated to 0.48 mmol (240% based on 1a) by ¹⁹F NMR analysis (Figure S2). No other fluorine-containing species were observed.

The mixture was treated with 1 M aqueous HCl, extracted with AcOEt three times, and the insoluble residue was filtered off. After removal of the solvent, the product was purified by preparative TLC (hexane) to afford 2a in 69% yield (39.6 mg, 0.14 mmol).

The NMR spectra of Me₃SiF were as follows;

¹H NMR (400 MHz, CDCl₃) δ 0.23 (d, J_H-F = 7.2 Hz, 9H)

¹⁹F NMR (376 MHz, CDCl₃) δ -160.3 (m, 1F).
Figure S1. $^1$H NMR spectrum of the reaction mixture (diluted with CDCl$_3$).

Figure S2. $^{19}$F NMR spectrum of the reaction mixture (diluted with CDCl$_3$).
2-2. Solvent Effect

The solvent effect was investigated by using substrate 1a (Table S1). The yield was found to be significantly dependent on the solvent. Not only coordinative MeCN, Et₂O and THF, but also non-coordinative CH₂Cl₂ were unsuitable to the reaction. Cyclohexane was not as effective as dichloroethane because of insolubility of NbCl₅.

![Chemical structure image]

Table S1. Solvent effect.

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4. References

5. $^1$H, $^{13}$C NMR and IR spectral data

$^1$H NMR spectrum of 1a.

$^1$H, $^{13}$C NMR and IR spectral data
$^{13}$C NMR spectrum of 1a.
$^{19}$F NMR spectrum of 1a.

Data file: /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CF3_19F.fid
Plot date: 2016-04-18
$^1$H NMR spectrum of 1b.
$^{13}$C NMR spectrum of 1b.
$^{19}$F NMR spectrum of 1b.
**1H NMR spectrum of 1d.**

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**Diagram:**

![1H NMR spectrum of 1d](image)
$^{13}$C NMR spectrum of 1d.
$^{13}$C NMR spectrum of 1d (magnified).
$^{19}$F NMR spectrum of 1d.
IR spectrum of **1d**.

![IR spectrum of 1d](image)

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$^1$H NMR spectrum of 1e.
$^{13}$C NMR spectrum of 1e.
$^{13}$C NMR spectrum of 1e (magnified).
$^{19}$F NMR spectrum of 1e.
$^1$H NMR spectrum of 1f.
$^{13}$C NMR spectrum of 1f.

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![13C NMR spectrum of 1f](image)
$^{19}$F NMR spectrum of 1f.
$^1$H NMR spectrum of 1g.
$^{13}$C NMR spectrum of 1g.
$^{19}$F NMR spectrum of 1g.

Data file /home/vnmr1/vnmrsy/data/Organic_Chemistry/Akiyama/Umi/p_phenyl_alkyne_CF3_19F.fid

Plot date 2016-04-21
$^1$H NMR spectrum of 1h.
$^{13}$C NMR spectrum of 1h.
$^{19}$F NMR spectrum of 1h.
$^1$H NMR spectrum of 3b.

Data file: `home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/o_phenyl_CF3_1H.fid`

Plot date: 2016-04-18
$^{13}$C NMR spectrum of 3b.

Data file: /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/phienyl_CF3_13C_overnight.fid

Plot date: 2016-07-15
$^{19}$F NMR spectrum of 3b.
\(^1\)H NMR spectrum of 6.
$^{13}$C NMR spectrum of 6.
IR spectrum of 6.
$^1$H NMR spectrum of 7.
$^{13}$C NMR spectrum of 7.
$^{19}$F NMR spectrum of 7.

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![19F NMR spectrum of 7.](image_url)
$^1$H NMR spectrum of 8.
$^{13}$C NMR spectrum of 8.
$^{19}$F NMR spectrum of 8.
$^1$H NMR spectrum of 2a.
\(^{13}\)C NMR spectrum of 2a.

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**Sample Name**: Pulse sequence

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**Study owner**: vnmr1

**Date collected**: 2014-12-03

**Solvent**: cdcl3

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**Operator**: vnmr1

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Plot date: 2015-10-10

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**Ph**
IR spectrum of 2a.
$^1$H NMR spectrum of 2b.
$^{13}$C NMR spectrum of 2b.
IR spectrum of 2b.

![IR spectrum of 2b](p.ethyl.allyl.jws)

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$^1$H NMR spectrum of 2c.
$^{13}$C NMR spectrum of 2c.
IR spectrum of 2c.

[pic]

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[pic]
**1H NMR spectrum of 2d.**

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Pulse sequence: PROTON  
Temperature: 25  
Solvent: cdcl3  
Spectrometer: Varian400-vnmrs400  
Operator: vnmr1
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![1H NMR spectrum of 2d.](image)

Data file: /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_pentyl_allyl_1H.fid

Plot date: 2016-04-20
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IR spectrum of 2d.
$^1$H NMR spectrum of 2e.
$^{13}$C NMR spectrum of 2e.

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![13C NMR spectrum of 2e.](image)
IR spectrum of 2e.
$^1$H NMR spectrum of 2f.
$^{13}$C NMR spectrum of 2f.
IR spectrum of 2f.

![IR spectrum](image)

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$^1$H NMR spectrum of 2g.
$^{13}$C NMR spectrum of 2g.
IR spectrum of 2g.
$^1$H NMR spectrum of 2h.
$^{13}$C NMR spectrum of $2h$. 

![NMR Spectrum Image]
$^{13}$C NMR spectrum of $2h$. 

![NMR spectrum of 2h](image)
\(^1\)H NMR spectrum of 2i.

---

**AM_49_hv_1h**

- **Sample Name**: AM_49_hv_1h
- **Pulse sequence**: PROTON
- **Temperature**: 50
- **Spectrometer**: Varian400-vnmrs400
- **Operator**: vnmr1

**Date collected**: 2016-06-16
**Solvent**: cdcl3

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Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_chloro_allyl_1H.fid
Plot date 2016-07-12
$^{13}$C NMR spectrum of 2i.
IR spectrum of 2i.

![IR spectrum image]

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$^1$H NMR spectrum of 2j.
$^{13}$C NMR spectrum of $2j$. 

![NMR Spectrum](image-url)
$^{19}$F NMR spectrum of 2j.
IR spectrum of $2j$. 

![IR spectrum graph]

**[Peak detection - Exp.280-umi.jws]**

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[ Comet Information]
Sample: fluorene, diallyl

[ Peak detection results ]

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IR spectrum of 9.

![IR Spectrum Image]
$^1$H NMR spectrum of 10.
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IR spectrum of 10.

![IR spectrum image]

[Comments on the IR spectrum: p_phenyl_diallyl]

[Peak detection results:]

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S95
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Solvent: cdcl3 Spectrometer: ---
Operator: vnmr1

Study owner: vnmr1

Plot date: 2015-10-10