Low Valent Niobium-mediated Double Activation of C–F/C–H Bonds: Fluorene Synthesis from *o*-Arylated α,α,α-Trifluorotoluenes

Supporting Information

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1. General Statement

1,4-Dioxane was distilled from $LiAlH_4$ after being refluxed for 3 hours. The distilled dioxane was stored over molecular sieves 4A under nitrogen atmosphere. Toluene was distilled after azeotoropic removal of water and stored over molecular sieves 4A under nitrogen atmosphere. $NbCl_5$ was used as purchased (Aldrich Co.) and handled under argon atmosphere. All the reactions were carried out under argon atmosphere.

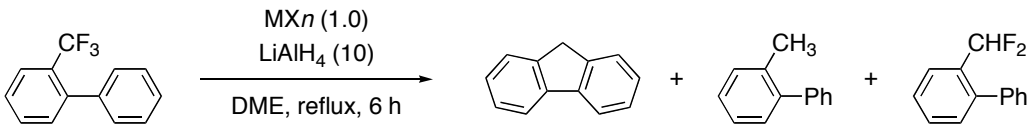
Column chromatography and preparative thin layer chromatography (preparative TLC) were conducted on silica gel (PSQ 60B, Fuji Silysia Chemical Ltd. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries for PTLC, respectively). Purification by preparative HPLC was performed by LC-918 instrument (Japan Analytical Industry Co., $CHCl_3$).

NMR spectra were recorded on Unity Inova-400 instrument (Varian Ltd., 400 MHz for ^1H, 100 MHz for ^{13}C) and JNM-Al300 instrument (JEOL, 300 MHz for ^1H, 75 MHz for ^{13}C) using $CDCl_3$ as a solvent. Chemical shifts (δ) for ^1H were referenced to tetramethylsilane (δ = 0.00 ppm) as an internal standard. Chemical shifts (δ) for ^{13}C were referenced to a solvent signal ($CDCl_3$, δ = 77.00 ppm). IR spectra were recorded on FTIR-8600PC instrument (Shimadzu Co.) using $CHCl_3$ as a solvent. Elemental analysis (EA) was carried out on EA1110 instrument (Amco Inc.). GC analysis was performed by Hitachi G-5000 instrument (Hitachi, Ltd.).

2. Supplementary Data

2-1. Reaction with Various Metal Salts

Amounts of the reagents are indicated in parenthesis(molar amounts).

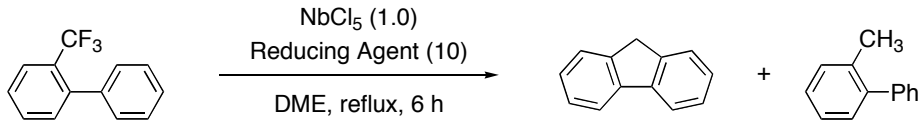


1a **2a** **3a** **4**

Entry	MX*n*	**2a** / %	**3a** / %	**4** / %	**1** / % (recovery)
1	$ZrCl_4$	40	29	–	–
2	VCl_3	36	29	–	–
3	$NbCl_5$	61	18	–	–
4	$NbBr_5$	43	33	–	–
5	NbF_5	21	34	–	–
6	Nb_2O_5	–	36	46	6
7	$NbBr_3$(dme)	55	26	–	–
8	$NbCl_4(thf)_2$	55	23	–	–
9	$TaCl_5$	57	27	–	–
10	$TaBr_5$	16	23	–	–
11	WCl_6	4	26	37	17
12	$FeCl_3$	28	70	–	–
13	$PdCl_2$	41	44	4	
14	None	–	11	52	33

2-2. Reaction with Various Reducing Agents

Amounts of the reagents are indicated in parenthesis(molar amounts).



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

Entry	Reducing Agent	**2a** / %	**3a** / %	**1** / % (recovery)
1	$LiAlH_4$	61	18	–
2	$LiAl(Oi\text{–}Pr)H_3$	40	33	–
3	Red-Al	16	64	–
4	$LiAl(t\text{–}Bu)_3H$	–	–	79
5	DIBAL	–	–	91
6	$NaBH_4$	–	–	90
7	Nb turnings (3.0 mol. amt.) [a]	–	–	80
8	Mg turnings	–	–	94
9	Zn powder	–	–	91
10	Al powder	–	–	Quant.
11	Sm turnings	–	–	84

[a] The reaction was carried out in the absence of $NbCl_5$.

3. Preparation of the Starting Materials

3-1. Preparation of **1a-1m**

Substrate **1a** was prepared from 2-bromo-α,α,α-trifluorotoluene and phenylboronic acid. Substrates **1b**-**1j** and **1m** were prepared from 2-(trifluoromethyl)phenylboronic acid and the corresponding aryl bromides. **1k** and **1l** were prepared from 4-dimethylamino-2-(trifluoromethyl)phenyl bromide and corresponding arylboronic acid.

Preparations of **1a** is described as a typical procedure.

***2*-Phenyl-α,α,α-trifluorotoluene (1a)**

To a solution of 2-bromo-α,α,α-trifluorotoluene (4.55 g, 17.8 mmol) in 1,4-dioxane/H_2O (3/1, 40 mL) were added phenylboronic acid ($PhB(OH)_2$, 2.39 g, 19.6 mmol), barium sulfate octahydrate (11.8 g, 37.4 mmol), and tetrakis(triphenylphospine)palladium (297 mg, 1 mol%) successively. The mixture was refluxed over 2.5 hours and then 30 mL of saturated aqueous sodium chloride was added. Products were extracted with ethyl acetate and the combined organic layers were dried over anhydrous sodium sulfate. Purification by column chromatography (SiO_2, hexane) gave **1a** (3.88 g, 98%). Spectra data: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31-7.36 (3H, m), 7.38-7.42 (3H, m), 7.46 (1H, t, J = 7.6 Hz), 7.56 (1H, dq, J = 7.6, 0.8 Hz), 7.75 (1H, dt, J =7.6, 0.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 124.18 (q, $^1J_{C-F}$ = 272 Hz), 126.02 (q, $^3J_{C-F}$ = 5.3 Hz), 127.30, 127.59, 127.72, 128.46 (q, $^2J_{C-F}$ = 29.7 Hz), 128.93, 131.26, 132.02, 139.85, 141.43. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3067, 1601, 1578, 1483, 1450, 1315, 1261, 1173, 1132, 1072, 1038, 702 cm^{-1}. **EA**: Found. C 70.03%, H 4.33%; Calcd. for $C_{13}H_9F_3$: C 70.27%, H 4.08%. Colorless liquid.

***2*-(*p*-Tolyl)-α,α,α-trifluorotoluene (1b)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (3H, s), 7.21-7.24 (4H, m), 7.32 (1H, d, J = 8.0 Hz), 7.45 (1H, t, J = 8.0 Hz), 7.54 (1H, t, J = 8.0 Hz), 7.74 (1H, d, J = 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.18, 124.21 (q, $^1J_{C-F}$ = 272 Hz), 126.60 (q, $^3J_{C-F}$ = 5.4 Hz), 127.11, 128.45, 128.47 (q,

$^{2}J_{C-F}$ = 29.4 Hz), 128.81, 131.23, 132.14, 136.97, 137.30, 141.49. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3011, 1489, 1448, 1315, 1171, 1132, 1113, 1036, 824 cm^{-1}. **EA**: Found. C 71.11%, H 4.47%; Calcd. for $C_{14}H_{11}F_3$: C 71.18%, H 4.69%. Colorless liquid.

***2*-(*p-Tert*-butylphenyl)-α,α,α-trifluorotoluene (1c)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (9H, s), 7.26 (2H, d, *J* = 8.0 Hz), 7.34 (1H, d, *J* = 7.6 Hz), 7.41 (2H, d, *J* = 8.0 Hz), 7.44 (1H, t, *J* = 7.6 Hz), 7.54 (1H, t, *J* = 7.6 Hz), 7.73 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 31.31, 34.56, 124.23 (q, $^{1}J_{C-F}$ = 272 Hz), 124.64, 126.03 (q, $^{3}J_{C-F}$ = 5.4 Hz), 127.07, 128.59, 131.21, 132.21, 136.88, 141.53, 150.44. **IR** ($CHCl_3$): $\tilde{\nu}$ = 2966, 1315, 1217, 1171, 1132, 1036, 839 cm^{-1}. **EA**: Found. C 73.41%, H 6.04%; Calcd. for $C_{17}H_{17}F_3$: C 73.36%, H 6.16%. Colorless liquid.

***2*-(*p*-Ethoxyphenyl)-α,α,α-trifluorotoluene (1d)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (3H, t, *J* = 6.8 Hz), 4.08 (2H, d, *J* = 6.8 Hz), 6.92 (2H, d, *J* = 8.8 Hz), 7.24 (2H, d, *J* = 8.8 Hz), 7.32 (1H, d, *J* = 7.2 Hz), 7.43 (1H, t, *J* = 7.2 Hz), 7.54 (1H, t, *J* = 7.2 Hz), 7.73 (1H, d, *J* = 7.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.86, 63.39, 113.67, 124.22 (q, $^{1}J_{C-F}$= 272 Hz), 126.03 (q, $^{3}J_{C-F}$ = 5.3 Hz), 127.00, 128.55 (q, $^{2}J_{C-F}$= 29.4 Hz), 130.05, 131.23, 132.05, 132.30, 141.25, 158.51. **IR** ($CHCl_3$): $\tilde{\nu}$ = 2984, 1612, 1518, 1477, 1315, 1244, 1171, 1130, 837 cm^{-1}. **EA**: Found. C 67.94%, H 4.82%; Calcd. for $C_{15}H_{13}F_3O$: C 67.66%, H 4.92%. Colorless crystal.

***2*-(*p*-Methylthiophenyl)-α,α,α-trifluorotoluene (1e)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (3H, s), 7.25 (2H, d, *J* = 8.8 Hz), 7.28 (2H, d, *J* = 8.8 Hz), 7.31 (1H, d, *J* = 7.6 Hz), 7.45 (1H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.74 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 15.55, 124.12 (q, $^{1}J_{C-F}$ = 3.0 Hz), 125.60, 126.09 (q, $^{3}J_{C-F}$= 5.4

Hz), 127.32, 128.45 (q, $^{2}J_{C-F}$ = 29.4 Hz), 129.34, 131.33, 132.05, 136.49, 138.08, 140.81. **IR** ($CHCl_3$): $\tilde{\nu}$ = 1481, 1315, 1213, 1171, 1132, 671 cm^{-1}. Colorless liquid.

***2*-(*p*-Dimethylaminophenyl)-α,α,α-trifluorotoluene (1f)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.00 (6H, s), 6.75 (2H, d, *J* = 9.0 Hz), 7.22 (2H, d, *J* = 9.0 Hz), 7.33 (1H, d, *J* = 7.2 Hz), 7.39 (1H, t, *J* = 7.2 Hz), 7.51 (1H, t, *J* = 7.2 Hz), 7.71 (1H, d, *J* = 7.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 40.30, 111.52, 124.41 (q, $^{1}J_{C-F}$ = 272 Hz), 126.03 (q, $^{3}J_{C-F}$ = 5.4 Hz), 126.51, 127.76, 128.41 (q, $^{2}J_{C-F}$ = 29.4 Hz), 126.68, 131.18, 132.43, 141.86, 149.83. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3020, 1614, 1528, 1489, 1315, 1217, 1169, 1132, 783 cm^{-1}. **EA**: Found. C 68.17%, H 5.32%, N 5.25%; Calcd. for $C_{15}H_{14}F_3N$: C 67.91%, H 5.32%, N 5.28%. Colorless liquid.

***2*-(*p*-Fluorophenyl)-α,α,α-trifluorotoluene (1g)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (2H, tt, *J* = 8.4, 2.8 Hz), 7.26-7.33 (3H, m), 7.47 (1H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.74 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =114.72 (d, $^{2}J_{C-ArF}$ = 21.3 Hz), 124.08 (q, $^{1}J_{C-F3C}$ = 272 Hz), 126.10 (q, $^{3}J_{C-F3C}$ = 5.4 Hz), 127.52, 128.60 (q, $^{2}J_{C-F3C}$ = 29.7 Hz), 130.62 (dq, $^{3}J_{C-ArF}$ = 8.0 Hz, $^{5}J_{C-F3C}$ = 1.5 Hz), 131.35, 132.07, 135.70, 140.35, 162.43 (d, $^{1}J_{C-ArF}$ = 245 Hz). **IR** ($CHCl_3$): $\tilde{\nu}$ = 1609, 1487, 1317, 1173, 1132, 669 cm^{-1}. **EA**: Found. C 64.77%, H 3.08%; Calcd. for $C_{13}H_8F_4$: C 65.00%, H 3.36%. Colorless liquid.

***2*-(*m*-Ethoxyphenyl)-α,α,α-trifluorotoluene (1h)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (3H, t, *J* = 7.2 Hz), 4.05 (2H, q, *J* = 7.2 Hz), 6.87 (1H, s), 6.90 (1H, d, *J* = 8.6 Hz), 6.93 (1H, d, *J* = 8.6 Hz), 7.30 (1H, t, *J* = 8.6 Hz), 7.34 (1H, d, *J* = 7.6 Hz), 7.46 (1H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.74 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.80, 63.42, 113.87, 115.21, 121.36, 124.13 (q, $^{1}J_{C-F}$ = 272 Hz), 126.02 (q, $^{3}J_{C-F}$ = 5.3 Hz), 127.32, 128.37 (q, $^{2}J_{C-F}$ = 29.8 Hz), 128.72, 131.23, 131.89, 141.09, 141.28, 158.24. **IR**

($CHCl_3$): $\tilde{\nu}$ = 1601, 1578, 1317, 1171, 1132, 1036 cm^{-1}. **EA**: Found. C 67.83%, H 4.88%; Calcd. for $C_{15}H_{13}F_3O$: C 67.66%, H 4.92%. Colorless liquid.

***2*-(*m*-Tolyl)-α,α,α-trifluorotoluene (1i)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (3H, s), 7.13 (1H, d, *J* = 7.6 Hz), 7.14 (1H, s), 7.19 (1H, d, *J* = 7.6 Hz), 7.28 (1H, t, *J* = 7.6 Hz), 7.32 (1H, d, *J* = 7.6 Hz), 7.43 (1H, t, *J* = 7.6 Hz), 7.53 (1H, t, *J* = 7.6 Hz), 7.73 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.38, 124.18 (q, $^1J_{C-F}$ = 272 Hz), 125.99 (q, $^3J_{C-F}$ = 5.4 Hz), 126.01, 127.18, 127.57, 128.31, 128.40 (q, $^2J_{C-F}$ = 29.1 Hz), 129.66, 131.19, 132.01, 137.29, 139.80, 141.57. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3018, 1605, 1315, 1173, 1132, 735 cm^{-1}. **EA**: Found. C 71.29%, H 4.43%; Calcd. for $C_{14}H_{11}F_3$: C 71.18%, H 4.69%. Colorless liquid.

***2*-(*o*-Ethoxyphenyl)-α,α,α-trifluorotoluene (1j)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (3H, t, *J* = 7.2 Hz), 3.88-4.01 (2H, m), 6.91 (1H, d, *J* = 8.4 Hz), 6.94 (1H, t, *J* = 8.4 Hz), 7.14 (1H, d, *J* = 8.4 Hz), 7.27 (1H, d, *J* = 8.0 Hz), 7.31 (1H, t, *J* = 8.4 Hz), 7.40 (1H, t, *J* = 8.0 Hz), 7.49 (1H, t, *J* = 8.0 Hz), 7.70 (1H, d, *J* = 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.40, 63.64, 111.60, 119.63, 124.23 (q, $^1J_{C-F}$ = 272 Hz), 125.88 (q, $^3J_{C-F}$ = 4.9 Hz), 127.12, 128.95, 129.17, 129.20 (q, $^2J_{C-F}$= 29.8 Hz), 130.65, 130.93, 132.27, 137.83, 156.08. **IR** ($CHCl_3$): $\tilde{\nu}$ = 2930, 1445, 1315, 1124, 1136 cm^{-1}. **EA**: Found. C 67.86%, H 4.75%; Calcd. for $C_{15}H_{13}F_3O$: C 67.66%, H 4.92%. Colorless liquid.

***5*-Dimethylamino-2-phenyl-α,α,α-trifluorotoluene (1k)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (6H, s), 6.85 (1H, dd, *J* = 8.8, 2.8 Hz), 7.02 (1H, d, *J* = 2.8 Hz), 7.18 (1H, d, *J* = 8.8 Hz), 7.29-7.39 (5H, m). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 40.38, 109.33 (q, $^3J_{C-F}$= 5.7 Hz), 114.51, 124.47 (q, $^1J_{C-F}$= 273 Hz), 126,89, 127.61, 128.65, 128.72 (q, $^2J_{C-F}$ = 30.9 Hz), 129.43, 132.85, 140.37, 149.32. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3020, 1618, 1489, 1364, 1217,

1178, 1126, 787 cm^{-1}. **EA**: Found. C 67.94%, H 5.08%, N 5.29%; Calcd. for $C_{15}H_{14}F_3N$: C 67.91%, H 5.32%, N 5.28%. Colorless crystal.

***5*-Dimethylamino-2-(*p*-ethoxyphenyl)-α,α,α-trifluorotoluene (1l)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (3H, t, *J* = 7.2 Hz), 3.01 (6H, s), 4.06 (2H, q, *J* = 7.2 Hz), 6.84 (1H, dd, *J* = 8.8, 2.8 Hz), 7.89 (2H, d, *J* = 8.8 Hz), 7.01 (1H, d, *J* =2.8 Hz), 7.16 (1H, d, *J* = 8.8 Hz), 7.21 (2H, d, *J* = 8.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.88, 40.40, 63.33, 109.37 (q, $^3J_{C-F}$ = 5.8 Hz), 113.57, 114.57, 124.52 (q, $^1J_{C-F}$ = 273 Hz), 128.49, 128.83 (q, $^2J_{C-F}$ = 28.6 Hz), 130.44, 132.55, 133.07, 149.15, 158.02. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3018, 1611, 1501, 1209, 1177, 789 cm^{-1}. **EA**: Found. C 66.31%, H 5.93%, N 4.53%; Calcd. for $C_{17}H_{18}F_3NO$: C 66.01%, H 5.87%, N 4.53%. Colorless liquid.

***2*-(*m,m*-Di*tert*-butyl-*p*-methoxyphenyl)-α,α,α-trifluorotoluene (1m)**

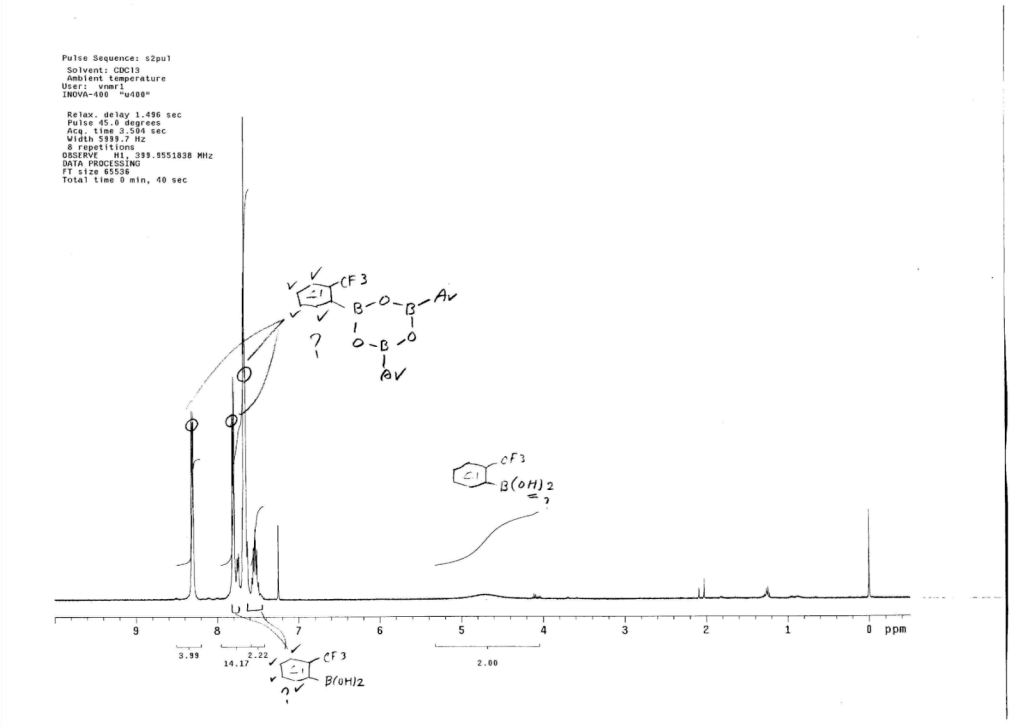
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (18H, s), 3.73 (3H, s), 7.19 (2H, s), 7.38 (1H, d, *J* = 7.6 Hz), 7.43 (1H, t, *J* = 7.6 Hz), 7.54 (1H, t, *J* = 7.6 Hz), 7.73 (1H, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 32.10, 35.77, 64.26, 124.25 (q, $^1J_{C-F}$ = 272 Hz), 126.09 (q, $^3J_{C-F}$ = 5.3 Hz), 126.87, 127.37, 128.54 (q, $^2J_{C-F}$ = 29.4 Hz), 131.18, 132.10, 133.96, 142.20, 142.72, 158.98. **IR** ($CHCl_3$): $\tilde{\nu}$ = 2966, 1414, 1315, 1225, 1132, 787 cm^{-1}. **EA**: Found. C 72.71%, H 7.23%; Calcd. for $C_{22}H_{27}F_3O$: C 72.50%, H 7.47%. Colorless crystal.

3-2. Preparation of Arylboronic Acid

2-(Trifluoromethyl)phenylboronic acid was prepared based on the literatural method (Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536).

2-(Trifluoromethyl)phenylboronic acid

To a THF solution (50 mL) of 2-bromo-α,α,α-trifluorotoluene (9.79 g, 43.5 mmol) was added hexane solution of butyllithium (30 mL, 1.58 M, 47 mmol) dropwise at –78 °C. After 3 hours stirring at the temperature, the resulting aryllithium was transferred into a THF solution (100 mL) of triethyl borate ($B(OEt)_3$, 30 mL, 176 mmol) via cannula (*The aryllithium is presumably unstable at higher temperature. We recommend that the transfer should be operated as quickly as possible*). The reaction mixture was warmed up to room temperature and stirred overnight. Hydrochloric acid (2 M, 80 mL) was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate and then evaporated under vacuum. The desired boronic acid was dissolved into hot toluene and separated from toluene-insoluble residues. The combined toluene solution was evaporated and the remaining solid was recrystallized from toluene to give the desired material (6.02 g, 73% yield as 2-(trifluoromethyl)phenylboronic acid). This material was a mixture of the boronic acid and (presumably) the corresponding triboroxane. This material was used for Suzuki coupling reaction without further purification. ^{1}H and ^{13}C NMR spectra are shown below.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User: vnmrl
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Pulse 45.0 degrees
Acq. time 3.504 sec
Width 5999.7 Hz
8 repetitions
OBSERVE H1, 399.8551838 MHz
DATA PROCESSING
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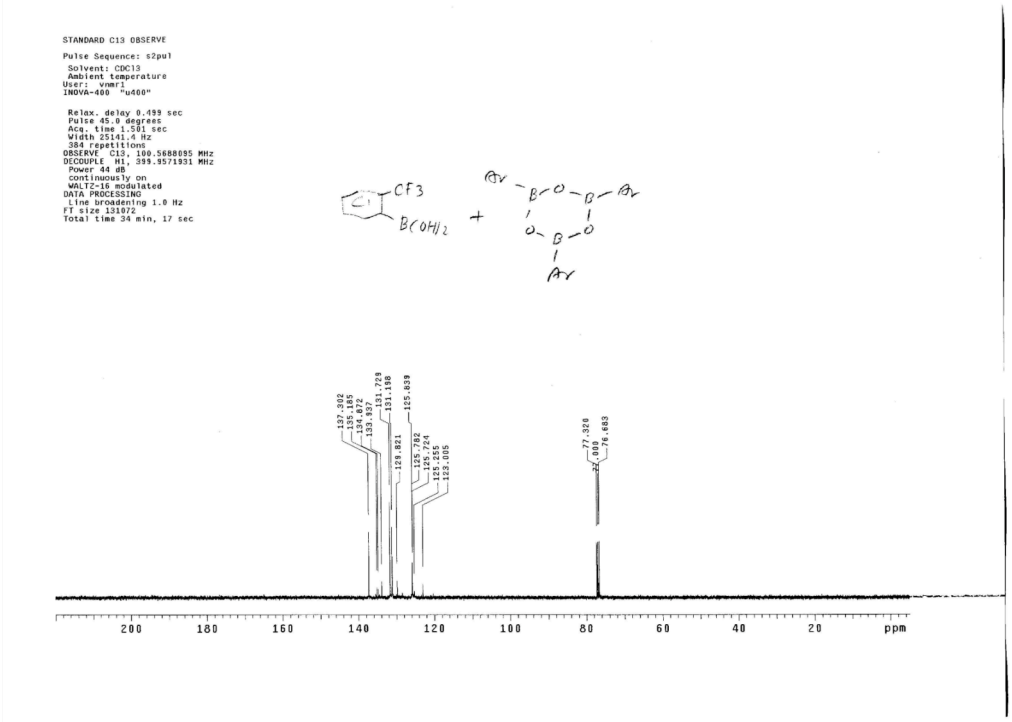
Total time 0 min, 40 sec
CF3
B(OH)2
Ar
9
8
7
6
5
4
3
2
1
0 ppm
3.99
14.17
2.22
2.00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Pulse Sequence: s2pul
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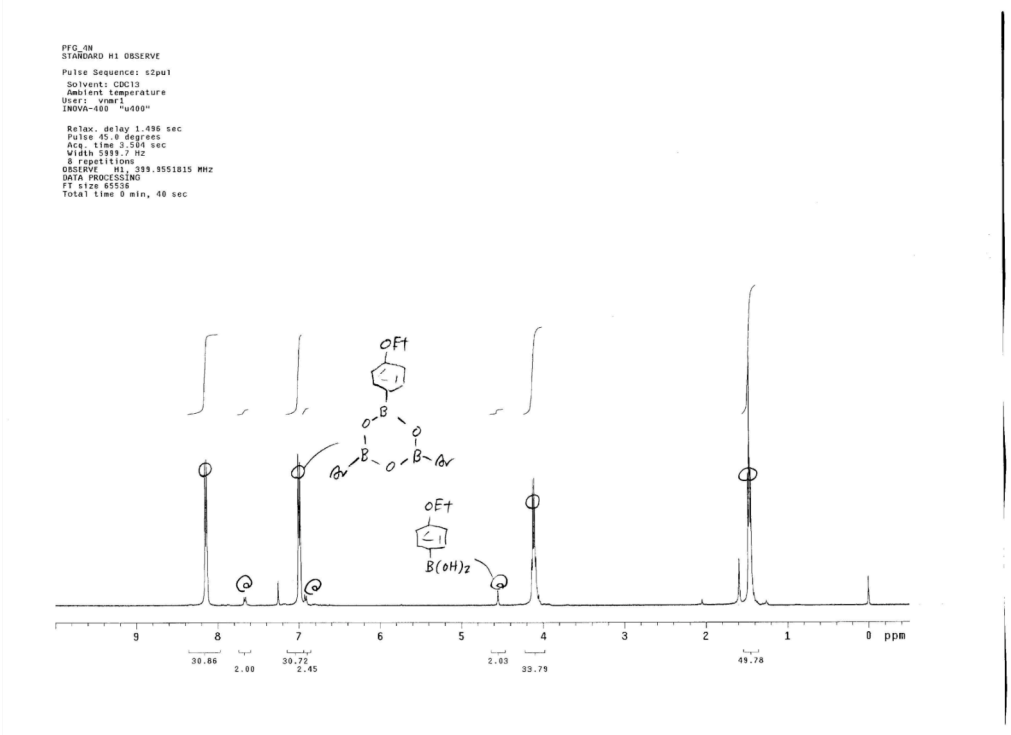
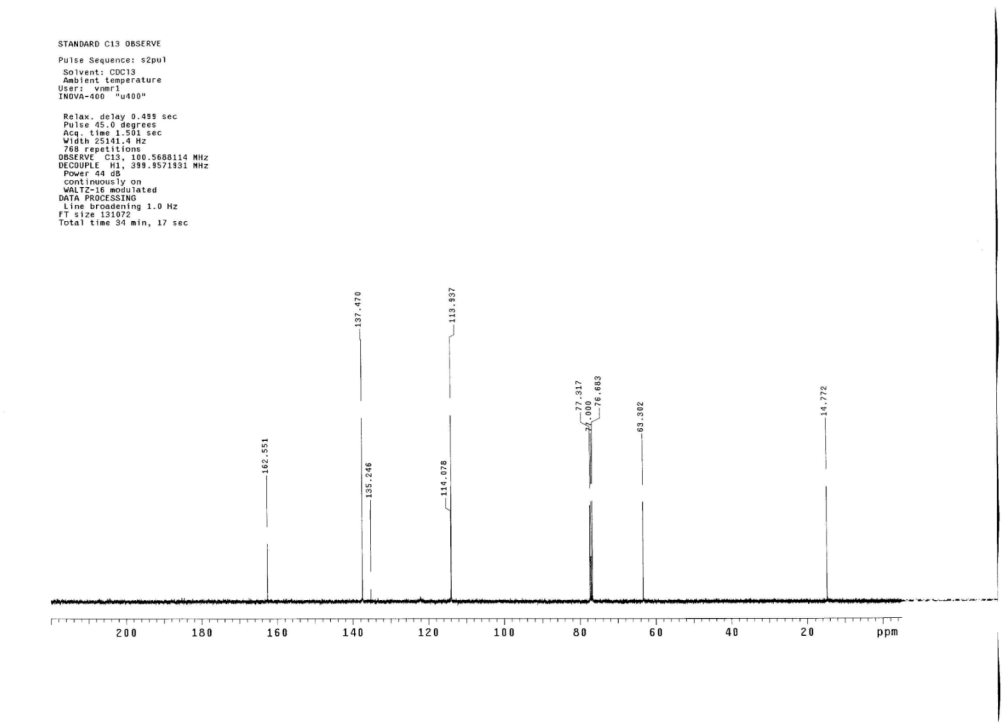
Ambient temperature
User: vnmrl
INOVA-400 "u400"
Relax. delay 0.499 sec
Pulse 45.0 degrees
Acq. time 1.581 sec
Width 25141.4 Hz
384 repetitions
OBSERVE C13, 100.5688095 MHz
DECOUPLE H1, 399.9571931 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 34 min, 17 sec
CF3
B(OH)2
Ar
137.302
135.185
134.672
133.921
131.729
131.198
129.821
125.839
125.782
125.724
125.625
123.005
77.320
77.000
76.683
200
180
160
140
120
100
80
60
40
20
ppm

4-Ethoxyphenylboronic acid

4-Ethoxyphenylboronic acid was prepared according to the method described above, but in 16% yield. This acid seemed to be obtained predominantly as its triboroxane form. ^{1}H and ^{13}C NMR spectra are shown below.





*3-3. Preparation of 9,9-difluorofluorene **7***

9,9-Difluorofluorene **7** was prepared according to the literature (Sondej, S. C.; Katzenellenbogen, J. A. *J. Org. Chem.* **1986**, *551*, 3508.) and purified by preparative HPLC. This material was readily decomposed at room temperature and used just after purification. Spectra data: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31 (2H, t, *J* = 7.6 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.53 (2H, d, *J* = 7.6 Hz), 7.61 (2H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 120.34, 123.23 (t, $^1J_{C-F}$= 241 Hz), 123.72, 128.73, 131.99, 137.91 (t, $^2J_{C-F}$= 25 Hz), 139.42 (t, $^3J_{C-F}$ = 5 Hz). **IR** ($CHCl_3$): $\tilde{\nu}$ = 3026, 1618, 1597, 1454, 1263, 1049 cm^{-1}. **MS**: *m*/*z* (intensity) = 202 (100), 183 (40, M^+–F). Colorless liquid at room temperature and colorless crystal at –10 °C.

4. Procedures

4-1. Typical procedure

Preparation of **2a** is described as a typical procedure (Table 2, entry 1). *A reaction vessel was equipped with a dropping funnel and one extra stirring bar was placed in the funnel. A second magnetic stirrer was placed on the side of the dropping funnel and a dioxane suspension of $LiAlH_4$ was stirred during operation.*

A dioxane solution (8 mL) of *o*-phenyl-α,α,α-trifluorotoluene **1a** (209 mg, 0.941 mmol) was added to $NbCl_5$ (77 mg, 0.28 mmol) placed in a reaction vessel. Immediately after the flask was immersed into an oil bath of 110 °C, addition of a dioxane suspension of $LiAlH_4$ (prepared from 214 mg of $LiAlH_4$ and 4 mL of 1,4-dioxane, 5.64 mmol) was started. The suspention of $LiAlH_4$ was added over 2 hours. The yellow solution of **1a** and $NbCl_5$ became colorless and then turned dark gray with gas evolution. The reaction mixture was refluxed for additional 2 hours and quenched with water at 0 °C. After 0.2 g of sodium tartrate was added, the mixture was extracted with ethyl acetate and the combined organic layers were dried over anhydrous sodium sulfate. Evaporation and purification by preparative TLC (SiO_2, hexane) gave **2a** (130 mg, 0.782 mmol, 83% yield, R_f=0.45).

4-2. Formation of **5** and **6** from **1a** (Scheme 2).

The reaction was carried out under the similar conditions described in (4-1), using **1a** (79 mg, 0.36 mmol), $LiAlH_4$ (132 mg, 3.47 mmol), and $NbCl_5$ (88 mg, 0.33 mmol) in toluene. The crude mixture was purified by column chromatography (SiO_2, hexane) to give **5** (88 mg, 0.25 mmol, 71% yield, R_f(hexane)=0.50) and **6** (13 mg, 0.05 mmol, 14% yield, R_f(hexane)=0.53). Regioisomer ratios of **5** and **6** were determined by GC analysis to be 13:51:36 (*m*-*m*:*m*-*p*:*p*-*p*) and 41:59 (*m*:*p*), respectively.

*4-3. Formation of **5** and **6** from **7** (Scheme 2).*

The reaction was carried out under the similar conditions described in (4-2), using **7** (53 mg, 0.26 mmol), $LiAlH_4$ (107 mg, 2.81 mmol), and $NbCl_5$ (71 mg, 0.26 mmol) in toluene. The crude mixture was purified by column chromatography (SiO_2, hexane) to give **5** (79 mg, 0.23 mmol, 87% yield). Regioisomer ratio of **5** was determined to be 22:78 (*m-p*:*p-p*) by GC analysis. Trace amount of **6** was detected by ^1H NMR and GC analysis.

5. Spectra Data of the Products

Spectra data of **2a** and **3a** are in complete agreement with those of commercially available fluorene and 2-phenyltoluene. See *the Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, Pouchert, C. P.; Behnke, J., Ed., Edition I, Vol. 2, 47A for **2a** and 31B for **3a**.

2-Methylfluorene (2b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (3H, s), 3.82 (2H, s), 7.16 (1H, dd, *J* = 8.0, 0.8 Hz), 7.25 (1H, dt, *J* = 7.5, 1.2 Hz), 7.30-7.36 (2H, m), 7.49 (1H, dd, *J* = 8.0, 0.8 Hz), 7.65 (1H, d, *J* = 8.0 Hz), 7.72 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.57, 36.76, 119.52, 119.56, 124.93, 125.72, 126.19, 126.64, 127.56, 136.52, 139.12, 141.82, 143.07, 143.50. **IR** ($CHCl_3$): $\tilde{\nu}$ = 573, 824, 955, 1134, 1298, 1404, 1456, 1472, 3011 cm^{-1}. **EA**: Found. C 93.57%, H 6.71%; Calcd. for $C_{14}H_{12}$: C 93.29%, H 6.71%. **M.p.**: 102.8-103.5 °C, colorless crystal.

2-*Tert*-butylfluorene (2c)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (9H, s), 3.87 (2H, s), 7.25 (1H, tt, *J* = 7.2, 1.2Hz), 7.34 (1H, t, *J* = 7.2 Hz), 7.41 (1H, d, *J* = 8.4 Hz), 7.51 (1H, dd, *J* = 7.6, 0.8 Hz), 7.58 (1H, s), 7.70 (1H, d, *J* = 8.4 Hz), 7.74 (1H, d, *J* = 7.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 31.61, 34.85, 37.02, 119.36, 119.61, 121.91, 123.92, 124.91, 126.21, 126.63, 139.14, 141.77, 143.20, 143.31, 150.06. **IR** ($CHCl_3$): $\tilde{\nu}$ = 831, 1269, 1364, 1466, 2964 cm^{-1}. **EA**: Found. C 91.62%, H 7.94%; Calcd. for $C_{17}H_{18}$: C 91.84%, H 8.16%. **M.p.**: 123.6-124.1 °C, colorless crystal.

2-Ethoxyfluorene (2d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (3H, t, *J* = 7.0 Hz), 3.83 (2H, s), 4.07 (2H, q, *J* = 7.0 Hz), 6.90 (1H, dd, *J* = 8.4, 1.6 Hz), 7.07 (1H, d, *J* = 1.6 Hz), 7.21 (1H, dt, *J* = 7.3, 1.2 Hz), 7.32 (1H, t, *J* = 7.6 Hz), 7.47 (1H, dd, *J* = 7.6, 0.8 Hz), 7.64 (1H, d, *J* = 8.4 Hz), 7.66 (1H, d, *J* = 7.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.91, 37.00, 63.74, 111.27, 113.60, 119.00, 120.48, 124.80, 125.51, 126.69, 134.68, 141.75, 142.68, 145.03, 158.65. **IR** ($CHCl_3$): $\tilde{\nu}$ = 826, 955, 1047, 1119, 1308, 1456, 1614, 3011 cm^{-1}. **EA**: Found. C 85.56%, H 6.44%; Calcd. for $C_{15}H_{14}O$: C 85.68%, H 6.71%. **M.p.**: 114.5-115.4 °C, colorless crystal.

2-(Methylthio)fluorene (2e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (3H, s), 3.88 (2H, s), 7.25-7.32 (2H, m), 7.36 (1H, t, *J* = 7.4 Hz), 7.46 (1H, d, *J* = 0.8 Hz), 7.52 (1H, d, *J* =7.2 Hz), 7.69 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 16.49, 36.73, 119.60, 120.08, 123.65, 124.95, 125.72, 126.51, 126.77, 136.65, 139.27, 141.27, 142.81, 144.03. **IR** ($CHCl_3$): $\tilde{\nu}$ = 741, 822, 1223, 1452, 1609, 3011 cm^{-1}. **EA**: Found. C 79.23%, H 5.80%, S 15.04%; Calcd. for $C_{14}H_{12}S$: C 79.20%, H 5.70%, S 15.10%. **M.p.**: 136.0-136.9 °C, colorless crystal.

2-(Dimethylamino)fluorene (2f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (6H, s), 3.82 (2H, s), 6.77 (1H, d, *J* = 8.4 Hz), 6.95 (1H, s), 7.16 (1H, t, *J* = 7.4 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 7.44 (1H, d, *J* = 7.6 Hz), 7.61 (2H, d, *J* = 8.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 37.09, 41.14, 109.52, 111.88, 118.52, 120.38, 124.65, 124.83, 126.59, 131.51, 142.31, 144.97, 150.07. **IR** ($CHCl_3$): $\tilde{\nu}$ = 962, 1119, 1213, 1358, 1501, 1614, 3009 cm^{-1}. **EA**: Found. C 86.07%, H 7.21%, N 6.56%; Calcd. for $C_{15}H_{15}N$: C 86.08%, H 7.22%, N 6.69%. **M.p.**: 173.0-174.0 °C, colorless crystal.

2-Fluorofluorene (2g)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (2H, s), 7.07 (1H, dt, *J* = 8.8, 2.4 Hz), 7.23 (1H, d, *J* = 9.2 Hz), 7.28 (1H, dt, *J* = 7.4, 1.2 Hz), 7.37 (1H, dt, *J* = 7.6, 0.8 Hz), 7.52 (1H, d, *J* = 7.6 Hz), 7.70 (1H, dd, *J* = 8.4, 5.2 Hz), 7.72 (1H, d, *J* = 6.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 36.97, 112.29 (d, $^2J_{C\text{-}F}$ = 23 Hz), 113.92 (d, $^2J_{C\text{-}F}$ = 23 Hz), 119.54, 120.68 (d, $^3J_{C\text{-}F}$ = 9 Hz), 124.98, 126.38, 126.90, 137.76, 140.89, 142.98, 145.29 (d, $^3J_{C\text{-}F}$ = 9 Hz), 162.41 (d, $^1J_{C\text{-}F}$ = 243 Hz). **IR** ($CHCl_3$): $\tilde{\nu}$ = 669, 729, 785, 1103, 1209, 1456, 1593, 3018 cm^{-1}. **EA**: Found. C 85.03%, H 5.08%; Calcd. for $C_{13}H_9F$: C 84.76%, H 4.92%. **M.p.**: 99.4-99.6 °C, colorless crystal.

1-Ethoxyfluorene (2h)

Regioisomer of 1-ethoxy- and 3-ethoxyfluorenes **2h** were separated by preparative HPLC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.47 (3H, t, *J* = 7.0 Hz), 3.85 (2H, s), 4.16 (2H, q, *J* = 7.0 Hz), 6.82 (1H, d, *J* = 8.4 Hz), 7.27-7.37 (3H, m), 7.40 (1H, t, *J* = 7.2 Hz), 7.56 (1H, d, *J* = 7.6 Hz), 7.77 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.99, 34.33, 63.48, 109.66, 112.55, 120.01, 125.00, 126.51, 126.63, 128.28, 130.90, 141.88, 143.37, 143.46, 155.74. **IR** ($CHCl_3$): $\tilde{\nu}$ = 696, 947, 1086, 1121, 1261, 1456, 1495, 1585, 1607, 3009 cm^{-1}. **EA**: Found. C 85.81%, H 6.80%; Calcd. for $C_{15}H_{14}O$: C 85.68%, H 6.71%. **M.p.**: 57.5-59.0 °C, colorless crystal.

3-Ethoxyfluorene (2h)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (3H, t, *J* = 7.2 Hz), 3.81 (2H, s), 4.11 (2H, q, *J* = 7.2 Hz), 6.86 (1H, dd, *J* =8.4, 2.4 Hz), 7.28 (1H, dt, *J* = 7.6, 1.2 Hz), 7.30 (1H, d, *J* = 2.4 Hz), 7.35 (1H, t, *J* = 7.2 Hz), 7.40 (1H, dd, *J* = 8.4, 0.4 Hz), 7.51 (1H, dt, *J* = 6.4, 1.2 Hz), 7.73 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =14.93, 36.17, 63.79, 105.74, 113.85, 119.74, 125.00, 125.49, 126.62, 126.69, 135.30, 141.74, 142.98, 144.29, 158.57. **IR** ($CHCl_3$): $\tilde{\nu}$ = 667, 739, 1047, 1188, 1204, 1286, 1452, 1493, 1582, 1614, 3013 cm^{-1}. **EA**: Found. C 85.69%, H 6.66%; Calcd. for $C_{15}H_{14}O$: C 85.68%, H 6.71%. **M.p.**: 61.5-62.0 °C, colorless crystal.

1-Methylfluorene (2i)

Regioisomer of 1-methyl- and 3-methylfluorenes **2i** were separated by preparative HPLC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.40 (3H, s), 3.76 (2H, s), 7.11 (1H, d, *J* = 7.6 Hz), 7.25-7.32 (2H, m), 7.35 (1H, t, *J* = 7.4 Hz), 7.54 (1H, d, *J* = 7.6 Hz), 7.62 (1H, d, *J* = 7.6 Hz), 7.76 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.83, 35.83, 117.38, 119.97, 124.97, 126.52, 126.65, 127.03, 127.69, 134.19, 141.34, 141.99, 142.07, 143.05. **IR** ($CHCl_3$): $\tilde{\nu}$ = 671, 727, 1020, 1213, 1456, 1589, 3013 cm^{-1}. **EA**: Found. C 93.50%, H 6.75%; Calcd. for $C_{14}H_{12}$: C 93.29%, H 6.71%. **M.p.**: 81.1-81.2 °C, colorless crystal.

3-Methylfluorene (2i)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (3H, s), 3.85 (2H, s), 7.12 (1H, d, *J* = 8.0 Hz), 7.28 (1H, t, *J* = 7.2 Hz), 7.36 (1H, t, *J* = 7.4 Hz), 7.42 (1H, d, *J* = 7.6 Hz), 7.52 (1H, dd, *J* = 7.6, 1.2 Hz), 7.60 (1H, s), 7.76 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 21.54, 36.52, 119.71, 120.44, 124.66, 124.99, 126.51, 126.61, 127.64, 136.32, 140.28, 141.72, 141.82, 143.64. **IR** ($CHCl_3$): $\tilde{\nu}$ = 731, 810, 1221, 1452, 1491, 1618, 3013 cm^{-1}. **EA**: Found. C 93.00%, H 6.66%; Calcd. for $C_{14}H_{12}$: C 93.29%, H 6.71%. **M.p.**: 84.2-85.2 °C, colorless crystal.

4-Ethoxyfluorene (2j)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (3H, t, *J* = 6.8 Hz), 3.87 (2H, s), 4.17 (2H, q, *J* = 6.8 Hz), 6.83 (1H, d, *J* = 8.0 Hz), 7.12 (1H, d, *J* = 7.2 Hz), 7.21 (1H, t, *J* = 8.4 Hz), 7.26 (1H, dd, *J* = 6.4, 1.2 Hz), 7.36 (1H, t, *J* = 7.6 Hz), 7.48 (1H, d, *J* = 7.2 Hz), 8.18 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =14.97, 37.24, 63.55, 109.50, 117.15, 123.73, 124.18, 125.69, 126.61, 127.57, 129.83, 141.12, 142.52, 145.21, 155.33. **IR** ($CHCl_3$): $\tilde{\nu}$ = 729, 772, 1067, 1115, 1213, 1271,

1456, 1583, 1607, 3011 cm^{-1}. **EA**: Found. C 85.53%, H 6.61%; Calcd. for $C_{15}H_{14}O$: C 85.68%, H 6.71%. **M.p.**: 63.0-64.0 °C, colorless crystal.

2-Ethoxy-7-dimethylaminofluorene (2l)

^{1}H NMR (400 MHz, $CDCl_3$): 1.43 (3H, t, *J* = 7.0 Hz), 2.99 (6H, s), 3.81 (2H, s), 4.07 (2H, q, *J* = 7.0 Hz), 6.75 (1H, dd, *J* = 8.4, 2.0 Hz), 6.86 (1H, dd, *J* = 8.4, 2.0 Hz), 6.93 (1H, s), 7.03 (1H, s), 7.52 (2H, t, *J* = 8.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): 14.97, 37.19, 41.15, 63.76, 109.68, 111.50, 111.82, 113.21, 118.97, 119.50, 131.39, 135.40, 144.04, 144.36, 149.65, 157.33. **IR** ($CHCl_3$): $\tilde{\nu}$ = 669, 752, 1123, 1209, 1472, 1612, 3011. **EA**: Found. C 80.52%, H 7.31%, N 5.57%; Calcd. for $C_{17}H_{19}NO$: C 80.60%, H 7.56%, N 5.53%. **M.p.**: 152.0-153.1 °C, colorless crystal.

1,3-Di-*tert*-butyl-2-methoxyfluorene (2m)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (9H, s), 1.61 (9H, s), 3.60 (3H, s), 4.12 (2H, broad s), 7.21 (1H, dt, *J* = 7.6, 0.8 Hz), 7.31 (1H, t, *J* = 7.6 Hz), 7.46 (1H, d, *J* = 7.6 Hz), 7.68 (1H, s), 7.69 (1H, d, *J* = 7.6 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 32.03, 32.28, 35.97, 37.42, 39.95, 64.74, 117.07, 118.68, 123.89, 125.64, 126.33, 137.25, 140.55, 140.64, 141.06, 142.92, 143.10, 159.50. **IR** ($CHCl_3$): $\tilde{\nu}$ = 621, 1020, 1042, 1234, 1385, 1398, 1479, 2964 cm^{-1}. **EA**: Found. C 85.63%, H 9.07%; Calcd. for $C_{22}H_{28}O$: C 85.66%, H 9.15%. **M.p.**: 84.0-84.9 °C, colorless crystal.

***o*-Phenyl-α,α-difluorotoluene (4)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 26.54 (1H, t, $^2J_{H-F}$ = 55 Hz), 7.30-7.40 (3H, m), 7.40-7.56 (5H, m), 7.79 (1H, d, *J* =6.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ =113.11 (t, $^1J_{C-F}$ = 235 Hz), 125.58 (t, $^3J_{C-F}$ = 5 Hz), 127.82, 127.85, 128.39, 129.43, 130.19, 130.43, 131.71 (t, $^2J_{C-F}$ = 43 Hz), 138.63,

141.37. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3034, 1601, 1483, 1383, 1221, 1128, 1063, 1026 cm^{-1}. **EA**: Found. C 76.33%, H 5.12%; Calcd. for $C_{13}H_{10}F_2$: C 76.46%, H 4.94%. Colorless liquid.

9,9-Ditolylfluorene (5)

Each regioisomer was separated by preparative HPLC.

meta-meta isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.23 (6H, s), 6.96-7.03 (6H, m), 7.11 (2 H, dd, *J* = 7.6 Hz), 7.26 (2H, dt, *J* = 7.4, 1.2 Hz), 7.35 (2H, dt, *J* = 6.8, 1.2 Hz), 7.41 (2H, d, *J* = 6.8 Hz), 7.76 (2H, dt, *J* = 7.6 0.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.57, 65.43, 120.05, 125.38, 126.24, 127.33, 127.35, 127.65, 127.98, 128.64, 137.65, 140.12, 145.96, 151.29. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3020, 1603, 1225, 1217 cm^{-1}. **EA**: Found. C 93.64%, H 6.17%; Calcd. for $C_{27}H_{22}$: C 93.60%, H 6.40%. **M.p.**: 88.1-88.9 °C, colorless crystal. Retention time (GC) = 17.87 min (200 °C).

meta-para isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.22 (3H, s), 2.28 (3H, s), 6.98-7.03 (5H, m), 7.07-7.11 (3H, m), 7.25 (2H, t, *J* = 7.4 Hz), 7.34 (2H, dt, *J* = 7.4, 1.2 Hz), 7.40 (2H, d, *J* = 7.6 Hz), 7.75 (2H, d, *J* = 7.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 20.92, 21.55, 65.11, 120.05, 125.34, 126.14, 127.30, 127.35, 127.64, 127.99, 128.65, 128.85, 136.09, 137.64, 140.08, 143.05, 145.92, 151.40. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3020, 3009, 1711, 1603, 1508, 1448, 1364 cm^{-1}. **EA**: Found. C 93.36%, H 6.15%; Calcd. for $C_{27}H_{22}$: C 93.60%, H 6.40%. **M.p.**: 138.8-139.6 °C, colorless crystal. Retention time (GC) = 21.52 min (200 °C).

para-para isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.28 (6H, s), 7.01 (4H, d, *J* = 8.2 Hz), 7.08 (4H, d, *J* = 8.2 Hz), 7.24 (2H, dt, *J* = 6.8, 1.2 Hz), 7.33 (2H, dt, *J* = 7.0, 1.2 Hz), 7.39 (2H, d, *J* = 7.6 Hz), 7.74 (2H, d, *J* = 8.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 20.92, 64.83, 120.06, 126.06, 127.28, 127.65, 128.00, 128.85, 136.10, 140.06, 143.02, 151.52. **IR** ($CHCl_3$): $\tilde{\nu}$ = 3067, 3007, 1510,

1448, 1022 cm^{-1}. **EA**: Found. C 93.48%, H 6.21%; Calcd. for $C_{27}H_{22}$: C 93.60%, H 6.40%. **M.p.**: 127.6-128.3 °C, colorless crystal. Retention time (GC) = 25.96 min (200 °C).

9-Tolylfluorene (6)

Each regioisomer was separated by preparative HPLC.

meta isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.27 (3H, s), 5.01 (1H, s), 6.87 (1H, s), 6.91 (1H, d, *J* =8.0 Hz), 7.04 (1H, d, *J* =8.0 Hz), 7.16 (1H, t, *J* =8.0 Hz), 7.25 (2H, t, *J* = 8.0 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 7.38 (2H, t, *J* = 8.0 Hz), 7.80 (2H, d, *J* = 8.0 Hz). The data is in agreement with the literature data (Siddall, T. H., III; Stewart, W. E. *J. Org. Chem.* **1969**, *34*, 233.). Retention time (GC) = 4.07 min (200 °C).

para isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.30 (3H, s), 5.00 (1H, s), 6.97 (2H, d, *J* = 8.0 Hz), 7.06 (2H, d, *J* = 8.0 Hz), 7.23 (2H, t, *J* =8.0 Hz), 7.30 (2H, d, *J* =8.0 Hz), 7.36 (2H, t, *J* =8.0 Hz), 7.78 (2H, d, *J* =8.0 Hz). The data is in agreement with the literature data (Nakamura, M.; Nakamura, N.; Oki, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1097.). Retention time (GC) = 4.43 min (200 °C).