Supplementary Information

for

Direct multiple C-H bond arylation reaction of heteroarenes catalyzed by cationic palladium complex bearing 1,10–phenanthroline

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Experimental section

General Remarks. The IR spectra were obtained on a JASCO FT-IR spectrophotometer. The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a JEOL α-400 (400, 100, 376 MHz) in $CDCl_3$. Chemical shifts of ^{1}H and ^{13}C are reported in *d* values referred to tetramethylsilane and $CDCl_3$ as an internal standard, respectively. The ^{19}F chemical shifts are expressed in *d* value deshielded with respect to CF_3COOH as an external standard. The mass spectra (MS) and high resolution mass spectra (HRMS) were taken on a JEOL JNM 700 mass spectrometer. Melting points were determined using a Yanagimoto melting point apparatus and are uncorrected. Preparative recycling gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC equipped with JAIGEL-1H and -2H columns (chloroform as an eluent).

Materials. Unless otherwise noted, reagents were commercially available and were used without purification. DMA was distilled over CaH_2 under reduced pressure. $Pd(phen)(OAc)_2$,[9c] $Pd(phen)(OCOCF_3)_2$,[9c] $Pd(phen)_2(PF_6)_2$,[9c] $Pd(2,9\text{-dmphen})(OAc)_2$,[S1] $Pd(dpphen)(OAc)_2$,[S1] $Pd(dpphen)(OCOCF_3)_2$,[S1] $Pd(2,9\text{-dphphen})(OAc)_2$,[9b] $Pd(5,8\text{-dnbpy})(OAc)_2$,[S2] $Pd(bpy)(OAc)_2$,[S3] $Pd(5,8\text{-dpPhen})(OAc)_2$,[S4] 1-Methylindole[S5] and imidazo[1,5-a]pyridine derivatives[8d] were prepared according the literature. Silica gel 60N (Spherical, Neutral, 40-50 μm) used was from Kanto Chemical Co., Inc.

General procedure for the C-H arylation of heteroaromatics.

In a screw-capped test tube was placed Cs_2CO_3 (1.1 equiv.), which was then dried at 150 °C *in vacuo* for 3 h. Then, to the tube were added $Pd(phen)_2(PF_6)_2$ (5 mol%), azole (0.5 mmol), aryl iodide (1.1 equiv.) and DMA (1 mL). The resulting mixture was stirred under Ar atmosphere at 150 °C for 20 h. The resulting mixture was filtrated through celite pad and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give a title compound.

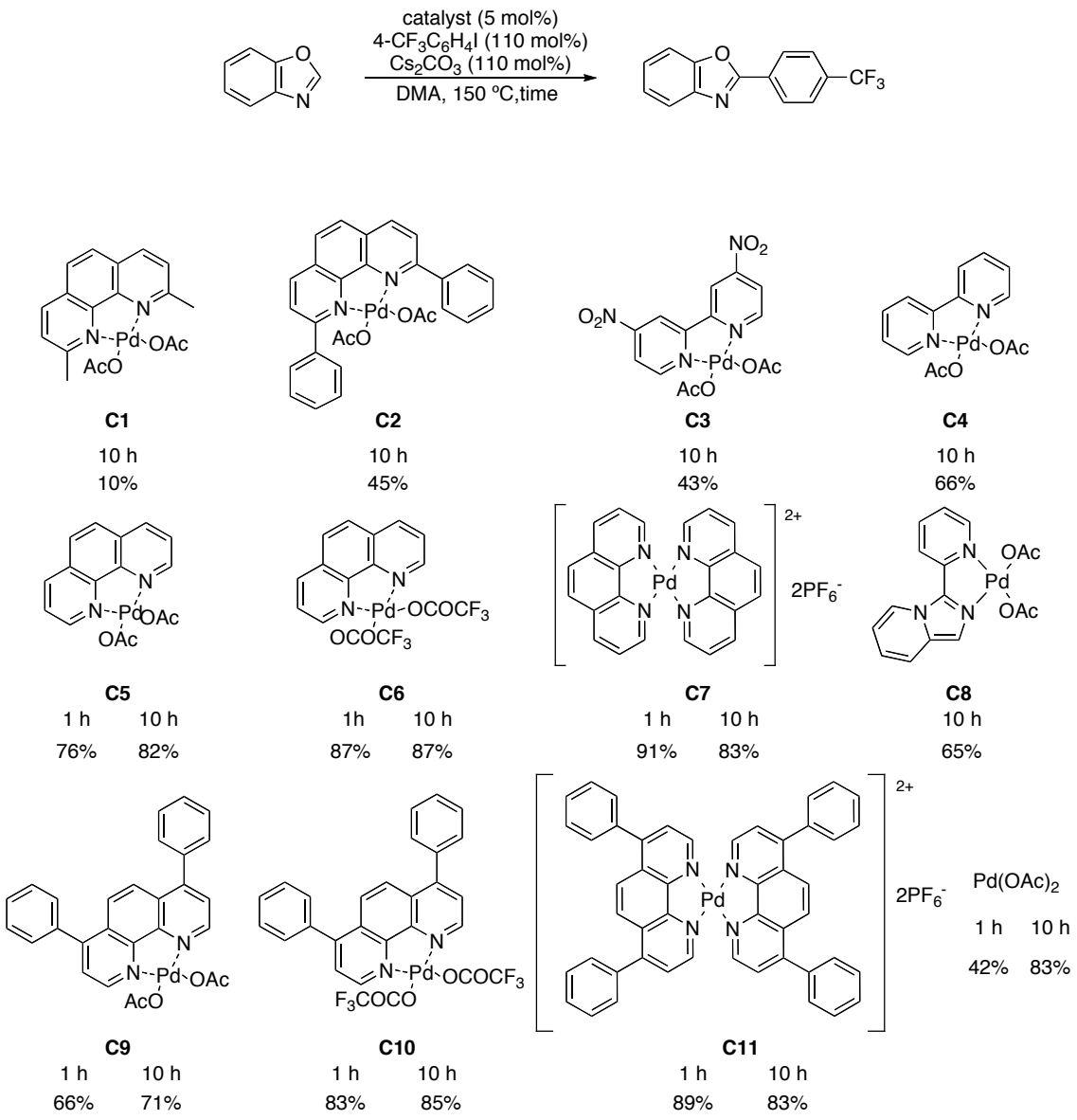


Figure S1. Results of reactions using a variety of Pd complex bearing diimine type ligands as a catalyst.

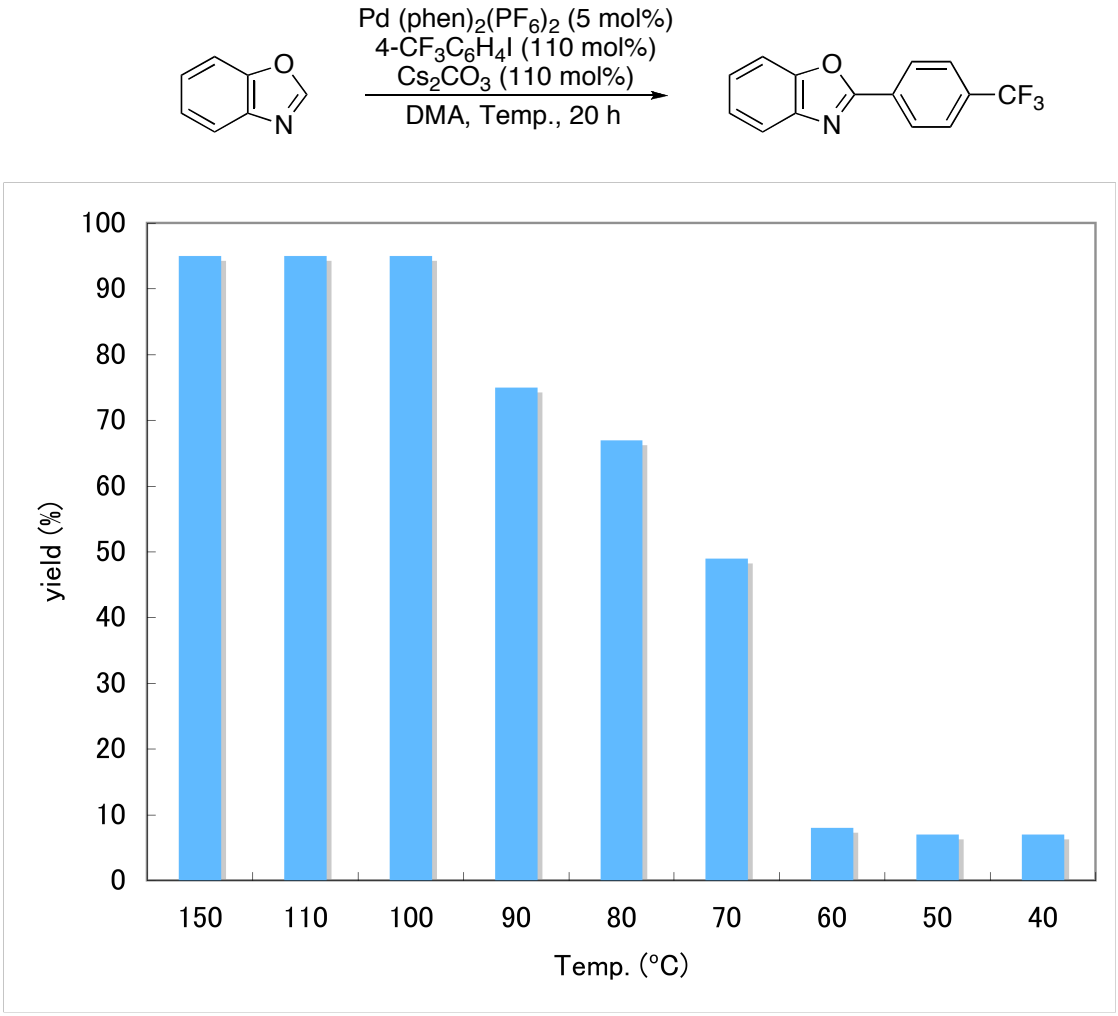


Figure S2. Temperature controlled experiments of direct arylation reaction of benzoxazole(**4**) and **2a**.

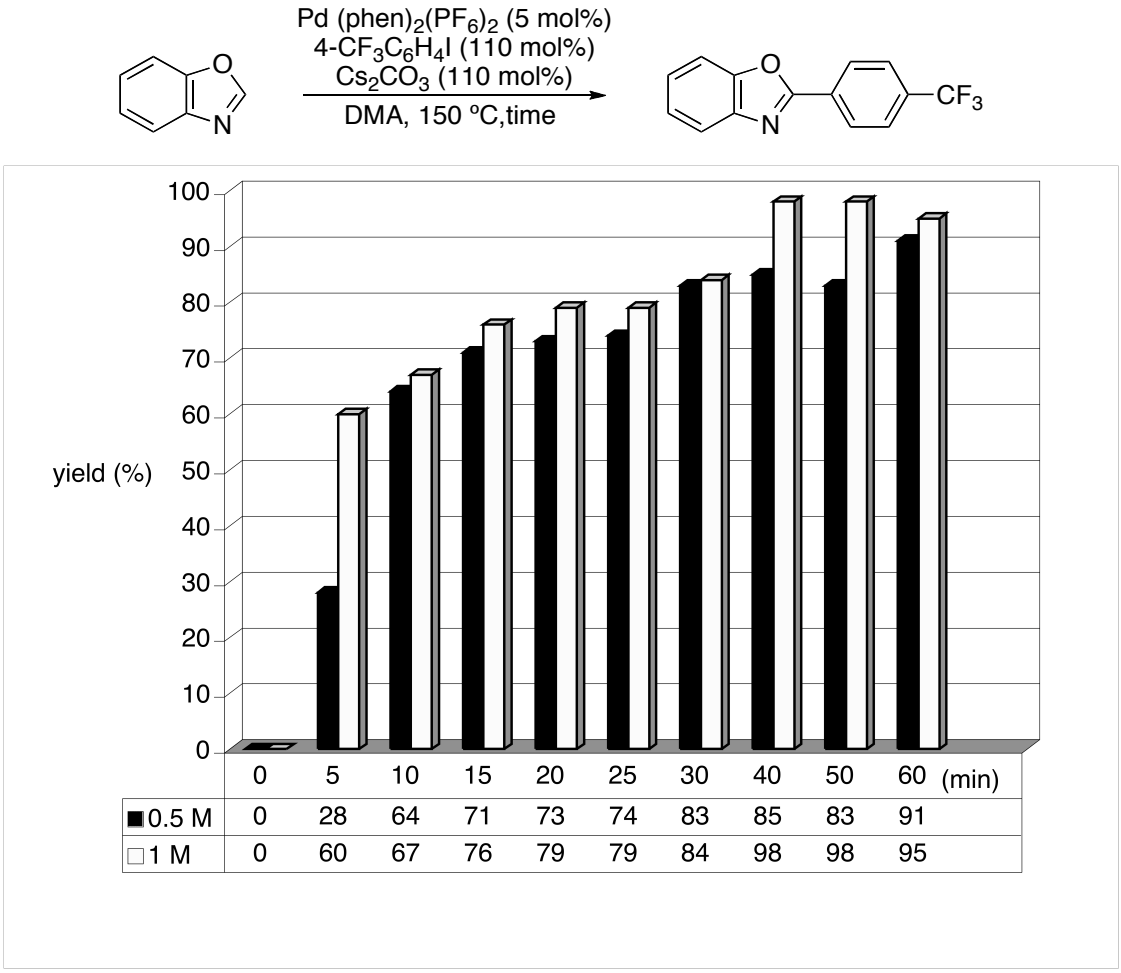
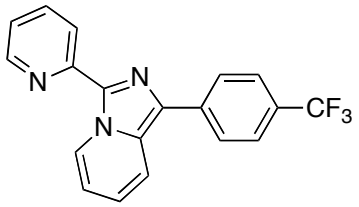


Figure S3. Kinetic plots of the reaction under two concentration.

Characterization of compounds

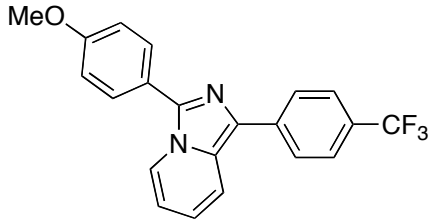
1-(4-Trifluoromethylphenyl)-3-(2-pyridyl)imidazo[1,5-a]pyridine (3a)



Chemical Formula: $C_{19}H_{12}F_3N_3$
Exact Mass: 339.0983
Molecular Weight: 339.3139

Yellow solid; Rf = 0.36 (hexane : AcOEt = 10 : 1); mp 128-129 °C; IR (KBr) 1615, 1589, 1324, 1124, 1067 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.60 (dd, *J* = 6.8, 6.3 Hz, 1H, Ar), 6.80 (dd, *J* = 8.8, 6.8 Hz, 1H, Ar), 7.07 (dd, *J*= 6.3, 4.4 Hz, 1H, Ar), 7.58 (d, *J* = 8.1 Hz, 2H, Ar), 7.62-7.70 (m, 2H, Ar), 7.92 (d, *J* = 8.1 Hz, 2H, Ar), 8.30 (d, *J* = 7.8 Hz, 1H, Ar), 8.49 (d, *J* = 4.4 Hz, 1H, Ar), 9.87 (d, *J* = 6.3 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ 113.7, 117.7, 121.8, 121.9, 122.2 (Ar), 124.8 (q, *J* = 272 Hz, $\underline{C}F_3$), 125.5 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 126.5, 126.6 (Ar), 128.0 (q, *J* = 32.3 Hz, CF_3-$\underline{C}$), 129.7, 130.2, 135.3, 136.4, 138.4, 148.0, 150.0 (Ar); ^{19}F NMR ($CDCl_3$) δ -58.7 (CF_3); MS (EI) *m/*z 339 (M^+); HRMS (EI) Calcd for $C_{19}H_{12}F_3N_3$: (M^+) 339.0983, Found: 339.0957.

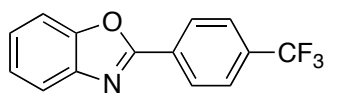
1-(4-Trifluoromethylphenyl)-3-(4-methoxyphenyl)imidazo[1,5-a]pyridine (3b)[8d]



$C_{21}H_{15}F_3N_2O$
Exact Mass: 368.1136
Mol. Wt.: 368.3518

Yellow Solid; Rf = 0.33 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 3.89 (s, 3H, OCH_3), 6.61 (dd, *J* = 7.4, 6.3 Hz, 1H, Ar), 6.86 (dd, *J* = 9.1, 6.3 Hz, 1H, Ar), 7.07 (d, *J* = 8.3 Hz, 2H, Ar), 7.69 (d, *J* = 8.5 Hz, 2H, Ar), 7.75 (d, *J* = 8.5 Hz, 2H, Ar), 7.83 (d, *J* = 9.1 Hz, 1H, Ar), 8.05 (d, *J* = 8.3 Hz, 2H, Ar), 8.19 (d, *J* = 7.4 Hz, 1H, Ar).

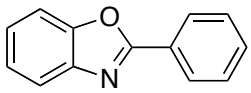
2-(4-Trifluoromethylphenyl)benzoxazole (5a)[S6]



Chemical Formula: $C_{14}H_8F_3NO$
Exact Mass: 263.0558
Molecular Weight: 263.2146

Colorless solid; Rf = 0.30 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 7.37-7.40 (m, 2H, Ar), 7.58-7.59 (m, 1H, Ar), 7.80 (d, *J* = 8.2 Hz, 2H, Ar), 7.80-7.81 (m, 1H, Ar), 8.36 (d, *J* = 8.2 Hz, 2H, Ar).

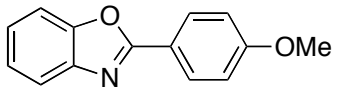
2-Phenylbenzoxazole (5b)[S6]



Chemical Formula: $C_{13}H_9NO$
Exact Mass: 195.0684
Molecular Weight: 195.2167

Colorless solid; Rf = 0.43 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 7.33-7.38 (m, 2H, Ar), 7.51-7.54 (m, 3H, Ar), 7.56-7.59 (m, 1H, Ar), 7.78-7.81 (m, 1H, Ar), 8.26-8.28 (m, 2H, Ar).

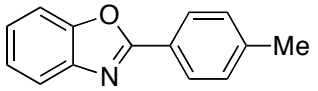
2-(4-Methoxyphenyl)benzoxazole (5c)[S6]



Chemical Formula: $C_{14}H_{11}NO_2$
Exact Mass: 225.0790
Molecular Weight: 225.2426

Colorless solid; Rf = 0.2 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 4.08 (s, 3H, OMe), 7.01 (d, *J* = 8.8 Hz, 2H, Ar), 7.24-7.32 (m, 2H, Ar), 7.74 (m, 1H, Ar), 7.72 (m, 1H, Ar), 8.18 (d, *J* = 8.8 Hz, 2H, Ar).

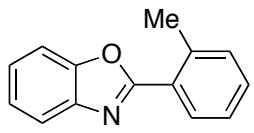
2-(4-Methylphenyl)benzoxazole (5d)[S6]



Chemical Formula: $C_{14}H_{11}NO$
Exact Mass: 209.0841
Molecular Weight: 209.2432

Colorless solid; Rf = 0.38 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H, Me), 7.32 (d, *J* = 8.3 Hz, 2H, Ar), 7.34-7.35 (m, 1H, Ar), 7.55-7.58 (m, 2H, Ar), 7.76-7.79 (m, 2H, Ar), 8.15 (d, *J* = 8.3 Hz, 2H, Ar).

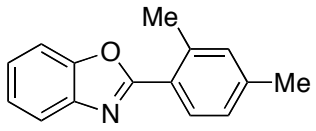
2-(2-Methylphenyl)benzoxazole (5e)[S6]



Chemical Formula: $C_{14}H_{11}NO$
Exact Mass: 209.0841
Molecular Weight: 209.2432

Colorless solid; Rf = 0.39 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 2.69 (s, 3H), 7.18-7.27 (m, 5H), 7.45 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.70 (dd, *J* = 6.6, 2.4 Hz, 1H), 8.05 (dd, *J* = 8.3, 2.0 Hz, 1H).

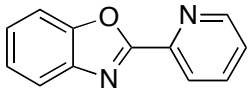
2-(2,4-Dimethylphenyl)benzoxazole (5f)



Chemical Formula: $C_{15}H_{13}NO$
Exact Mass: 223.0997
Molecular Weight: 223.2698

Colorless solid; Rf = 0.48 (hexane : AcOEt = 10 : 1); mp 87-88 °C; IR (KBr): 2921, 1546, 1490, 1455, 1247, 932 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H, Ar), 2.62 (s, 3H, Ar), 7.16-7.17 (m, 2H, Ar), 7.35-7.37 (m, 2H, Ar), 7.59 (dd, *J* = 5.8, 4.8 Hz, 1H, Ar), 7.83 (dd, *J* = 5.8, 4.8 Hz, 1H, Ar), 8.11 (d, *J* = 9.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ 21.3, 22.1 (Me), 110.3, 119.9, 123.4, 124.2, 124.7, 126.8, 129.8, 132.5, 138.7, 141.2, 142.2, 150.2, 163.6 (Ar); MS (EI) *m/*z 223 (M^+); HRMS (EI): Exact mass calcd for $C_{15}H_{13}NO_2$: 223.0997, Found: 223.0997.

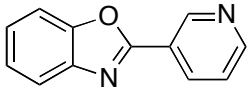
2-(2-Pyridyl)benzoxazole (5g)[S7]



Chemical Formula: $C_{12}H_8N_2O$
Exact Mass: 196.0637
Molecular Weight: 196.2047

Colorless solid; Rf = 0. 10 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.32-7.39 (m, Ar, 3H), 7.59-7.62 (m, 1H, Ar), 7.77-7.83 (m, 2H, Ar), 8.29 (d, *J* = 9.1 Hz, 1H, Ar), 8.76 (d, *J* = 4.6 Hz, 1H, Ar).

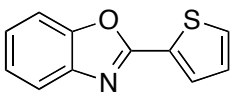
2-(3-Pyridyl)benzoxazole (5h)[S6]



Chemical Formula: $C_{12}H_8N_2O$
Exact Mass: 196.0637
Molecular Weight: 196.2047

Colorless solid; Rf = 0. 10 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.36-7.38 (m, 2H, Ar), 7.45 (dd, *J* = 7.9, 4.8 Hz, 1H, Ar), 7.58-7.60 (m, 1H, Ar), 7.77-7.79 (m, 1H, Ar), 8.48 (td, *J* = 8.0, 1.8 Hz, 1H, Ar), 8.75 (d, *J* = 4.8, 1.7 Hz, 1H, Ar), 9.46 (d, *J* = 1.7 Hz, 1H, Ar).

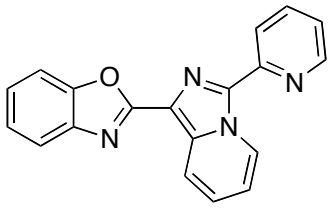
2-(2-Thienyl)benzoxazole (5i)[S6]



Chemical Formula: $C_{11}H_7NOS$
Exact Mass: 201.0248
Molecular Weight: 201.2444

Colorless solid; Rf = 0.27 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.17 (dd, *J* = 4.9, 3.4 Hz, 1H, Ar), 7.32-7.34 (m, 2H, Ar), 7.52-7.54 (m, 2H, Ar), 7.72-7.75 (m, 1H, Ar), 7.90 (dd, *J* = 3.9, 1.4 Hz).

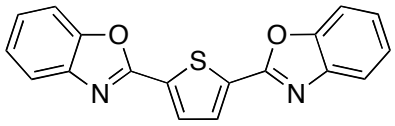
1-(2-Benzoxazolizyl)-3-(2-pyridyl)imidazo[1,5-a]pyridine (5j)



Chemical Formula: $C_{19}H_{12}N_4O$
Exact Mass: 312.1011
Molecular Weight: 312.3248

Yellow solid; Rf = 0.13 (hexane : AcOEt = 4 : 1); mp 218-220 °C; IR (KBr) 2360, 1618, 1580, 1505, 1454, 12456, 1018 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (dd, *J* = 7.3, 6.4 Hz, 1H, Ar), 7.14-7.28 (m, 4H, Ar), 7.55 (dd, *J* = 7.3, 1.2 Hz, 1H, Ar), 7.71 (dd, *J* = 7.3, 1.0 Hz, 1H, Ar), 7.74 (ddt, *J* = 7.8, 1.8, 0.8, 1H, Ar) 8.46 (dd, *J* = 9.3, 1.0 Hz, 1H, Ar), 8.50 (dd, *J* = 7.8, 0.8 Hz, 1H, Ar), 8.58 (dd, *J* = 4.9, 1.0 Hz, 1H, Ar), 10.01 (dd, *J* = 7.3, 1.0 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ 110.5, 114.9, 119.2, 119.3, 119.5, 122.5, 122.9, 124.2, 124.4, 124.5, 127.2, 134.0, 136.5, 136.6, 142.3, 148.1, 150.1, 150.2, 159.6 (Ar); MS (EI) *m/z* 312 (M^+); HRMS (EI): Exact mass calcd for $C_{19}H_{12}N_4O$:, 312.1011, Found: 312.1025.

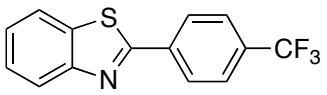
2,5-Bisbenzoxazolizylthiophene (5k)[S6]



Chemical Formula: $C_{18}H_{10}N_2O_2S$
Exact Mass: 318.0463
Molecular Weight: 318.3492

Yellow solid; Rf = 0.13 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.38-7.40 (m, 4H, Ar), 7.59 (dd, *J* = 5.3, 3.6, 2H, Ar), 7.79 (dd, *J* = 5.7, 3.6 Hz, 2H, Ar), 7.95 (s, 2H, Ar).

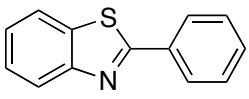
2-(4-Trifluoromethylphenyl)benzothiazole (7a)[S8]



Chemical Formula: $C_{14}H_8F_3NS$
Exact Mass: 279.0330
Molecular Weight: 279.2802

Colorless solid; Rf = 0.35 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.44 (ddd, *J* = 7.9, 7.3, 0.9 Hz, 1H, Ar), 7.54 (ddd, *J* = 8.3, 7.3, 0.9 Hz, 1H, Ar), 7.76 (d, *J* = 7.8 Hz, 2H, Ar), 7.94 (d, *J* = 8.3 Hz, 1H, Ar), 8.12 (d, *J* = 7.9 Hz, 1H, Ar), 8.22 (d, *J* = 7.8 Hz, 2H, Ar).

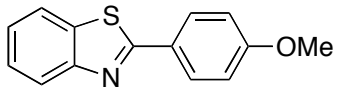
2-Phenylbenzothiazole (7b)[S8]



Chemical Formula: $C_{13}H_9NS$
Exact Mass: 211.0456
Molecular Weight: 211.2823

Colorless solid; Rf = 0.31 (hexane : AcOEt = 10 : 1); ^1H NMR ($CDCl_3$) δ 7.40 (t, *J* = 7.4 Hz, 1H, Ar), 7.50-7.53 (m, 4H, Ar), 7.91 (d, *J* = 7.47 Hz, 1H, Ar), 8.10-813 (m, 3H, Ar).

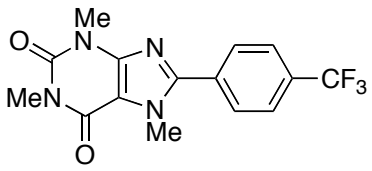
2-(4-Methoxyphenyl)benzothiazole (7c)[S9]



Chemical Formula: $C_{14}H_{11}NOS$
Exact Mass: 241.0561
Molecular Weight: 241.3082

Colorless solid; Rf = 0.22 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, OMe), 7.01 (d, *J* = 9.0 Hz, 2H, Ar), 7.36 (ddd, *J* = 7.8, 7.4, 1.3 Hz, 1H, Ar), 7.48 (ddd, *J* = 8.5, 7.4, 1.3 Hz, 1H, Ar), 7.88 (d, *J* = 8.5 Hz, 1H, Ar), 8.04-8.06 (m, 3H, Ar).

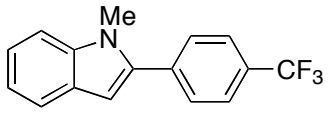
2-(4-Trifluoromethylphenyl)caffeine (9)



Chemical Formula: $C_{15}H_{13}F_3N_4O_2$
Exact Mass: 338.0991
Molecular Weight: 338.2845

Colorless solid; Rf = 0.05 (hexane : AcOEt = 10 : 1); mp 200-202 °C; IR (KBr) 3083, 1700, 1543, 1436, 1319, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.42 (s, 3H, Me), 3.61 (s, 3H, Me), 4.09 (s, 3H, Me), 7.79 (d, *J* = 8.5 Hz, 2H, Ar), 7.85 (d, *J* = 8.5 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 28.0, 29.7, 33.9 (Me), 108.8 (Ar), 123.5 (q, *J* = 273.8 Hz, <u>C</u>F_3), 125.8 (q, *J* = 3.3 Hz, CF_3-C=<u>C</u>), 129.5, 131.8 (Ar), 132.2 (q, *J* = 33.1 Hz, CF_3-<u>C</u>), 148.2, 150.2 (Ar), 151.5, 155.5 (C=O); ^{19}F NMR ($CDCl_3$) δ -63.3 (CF_3); MS (EI) *m/z* 338 (M^+); HRMS (EI): Exact mass calcd for $C_{15}H_{13}F_3N_4O_2$: 338.0991, Found: 338.0974.

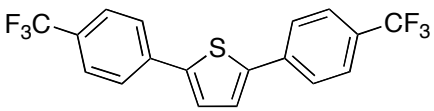
2-(4-Trifluoromethylphenyl)-*N*-methylindole (11)[S10]



Chemical Formula: $C_{16}H_{12}F_3N$
Exact Mass: 275.0922
Molecular Weight: 275.2684

Colorless solid; Rf = 0.05 (hexane : AcOEt = 10 : 1); ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H, Me), 6.75 (s, 1H, Ar), 7.30 (t, J = 7.5 Hz, 1H, Ar), 7.42 (t, J = 7.5 Hz, 1H, Ar), 7.51 (d, J = 7.5 Hz, 1H, Ar), 7.74 (d, J = 8.3 Hz, 2H, AR), 7.77 (d, J = 7.5 Hz, 1H, Ar) 7.84 (d, J = 8.3 Hz, 2H, Ar).

2,5-Bis(4-trifluoromethylphenyl)thiophene (12)

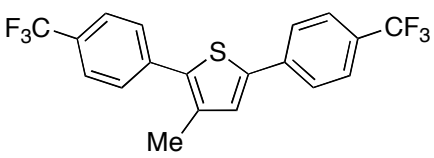


Chemical Formula: $C_{18}H_{10}F_6S$
Exact Mass: 372.0407
Molecular Weight: 372.3274

Yellow solid; Rf = 0.43 (hexane : AcOEt = 10 : 1); mp 148-150 °C; IR (KBr) 2925, 1612, 1321, 1164, 1129 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 2H, Ar), 7.63 (d, *J* = 8.3 Hz, 4H, Ar), 7.70 (d, *J* = 8.3 Hz, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 124.1 (q, *J* = 272 Hz, <u>C</u>F_3), 125.5, 125.7 (Ar), 126.0 (q, *J* = 4.1 Hz, CF_3-C=<u>C</u>), 129.6 (q, *J* = 32.3 Hz, CF_3-<u>C</u>),

137.2, 143.0 (Ar); ^{19}F NMR ($CDCl_3$) δ -62.9 (CF_3). MS (EI) *m/*z 372 (M^+); HRMS (EI) Calcd for $C_{18}H_{10}F_6S$: 372.0407, Found: 372.0402.

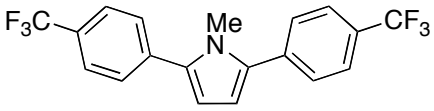
3-Methyl-2,5-bis(4-trifluoromethylphenyl)thiophene (**13**)



Chemical Formula: $C_{19}H_{12}F_6S$
Exact Mass: 386.0564
Molecular Weight: 386.3540

Colorless solid; Rf = 0.48 (hexane : AcOEt = 10 : 1); mp 59.5-60.5 °C; IR (KBr) 2924, 2360, 1409, 1068, 1015, 862 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, Me), 7.16 (s, 1H, Ar), 7.50-7.60 (m, 8H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.2 (Me), 124.1 (q, *J* = 271.3 Hz, $\underline{C}F_3$)*, 126.6 (Ar), 125.6 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 125.9 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 128.7, 128.9 (Ar), 129.4 (q, *J* = 33.2 Hz, F_3C-$\underline{C}$)*, 135.7, 137.0, 137.3, 137.8, 141.0 (Ar) (*two carbon peaks are overlapped.); ^{19}F NMR ($CDCl_3$) δ -62.9, -62.9 (CF_3). MS (EI) *m/*z 386 (M^+); HRMS (EI) Calcd for $C_{19}H_{12}F_6S$: 386.0564, Found: 386.0551.

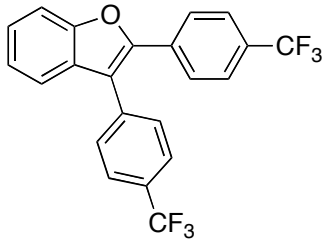
2,5-Bis(4-trifluoromethylphenyl)-*N*-methylpyrrole (**14**)



Chemical Formula: $C_{19}H_{13}F_6N$
Exact Mass: 369.0952
Molecular Weight: 369.3036

Colorless solid; Rf = 0.50 (hexane : AcOEt = 10 : 1); mp 155-157 °C; IR (KBr) 1610, 1456, 1416, 1321, 1179, 1132, 1109, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 3H, Me), 6.32 (s, 2H, Ar), 7.49 (d, *J* = 8.3 Hz, 4H, Ar), 7.59 (d, *J* = 8.3 Hz, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 34.6 (Me), 110.4 (Ar), 124.1 (q, *J* = 272 Hz, $\underline{C}F_3$), 125.5 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 128.6 (Ar), 128.9 (q, *J* = 32.6 Hz, CF_3-$\underline{C}$), 136.5, 136.6 (Ar); ^{19}F NMR ($CDCl_3$) δ -62.8 (CF_3); MS (EI) *m/*z 369 (M^+); HRMS (EI) Calcd for $C_{19}H_{13}F_6N$: 369.0952, Found: 369.0973.

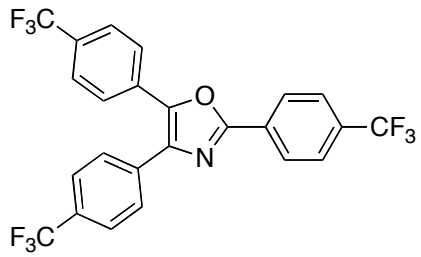
2,3-Bis(4-trifluoromethylphenyl)-2-benzofuran (15)



Chemical Formula: $C_{22}H_{12}F_6O$
Exact Mass: 406.0792
Molecular Weight: 406.3205

Colorless solid; Rf = 0.43 (hexane : AcOEt = 10 : 1); mp 118-120 °C; IR (KBr) 2360, 1930, 1475, 1258, 1210, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (dd, *J* = 7.8, 7.3 Hz, 1H, Ar), 7.44 (dd, *J* = 7.8, 7.4 Hz, 1H, Ar), 7.52 (d, *J* = 7.8 Hz, 1H, Ar), 7.61-7.66 (m, 1H, Ar), 7.63 (d, *J* = 7.8 Hz, 2H, Ar), 7.65 (d, *J* = 7.8 Hz, 2H, Ar), 7.76 (d, *J* = 7.8 Hz, 2H, Ar), 7.80 (d, *J* = 7.8 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 111.5, 118.0, 120.1, 123.7 (Ar), 124.0 (q, *J* = 272.3 Hz, $\underline{C}F_3$), 124.2 (q, *J* = 271.1 Hz, $\underline{C}F_3$), 125.6 (q, *J* = 3.5 Hz, CF_3-C=$\underline{C}$) , 125.8 (q, *J* = 3.5 Hz, CF_3-C=$\underline{C}$), 126.2, 127.2, 129.4, 130.1 (Ar), 130.4 (q, *J* = 33.1 Hz, CF_3-$\underline{C}$), 130.5 (q, *J* = 32.8 Hz, CF_3-$\underline{C}$), 133.6, 136.3, 149.5, 154.3 (Ar); ^{19}F NMR ($CDCl_3$) δ -62.9, -63.2 (CF_3); MS (EI) *m/z* 406 (M^+); HRMS (EI): Exact mass calcd for $C_{22}H_{12}F_6O$: 406.0792, Found: 406.0789.

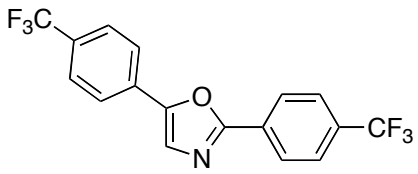
2,3,5-Tris(4-trifluoromethylphenyl)oxazole (18)



Chemical Formula: $C_{24}H_{12}F_9NO$
Exact Mass: 501.0775
Molecular Weight: 501.3438

Colorless solid; Rf = 0.34 (hexane : AcOEt = 10 : 1); mp 148-150 °C; IR (KBr) 2360, 1561, 1326, 1161, 1109, 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (m, 4H, Ar), 7.75-7.78 (m, 4H, Ar), 7.82 (d, *J* = 7.8 Hz, 2H, Ar), 8.25 (d, *J* = 8.3 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 123.8 (q, *J* = 272.9 Hz, $F_3\underline{C}$)*, 124.0 (q, *J* = 272.2 Hz, $F_3\underline{C}$), 125.9 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 126.1 (q, *J* = 3.4 Hz, CF_3-C=$\underline{C}$), 126.1 (q, *J* = 3.3 Hz, CF_3-C=$\underline{C}$), 126.8, 126.9, 128.4, 129.8 (Ar), 130.7 (q, *J* = 33.1 Hz, F_3C-$\underline{C}$), 131.1 (q, *J* = 33.0 Hz, F_3C-$\underline{C}$), 131.4 (Ar), 132.5 (q, *J* = 33.1 Hz, F_3C-$\underline{C}$), 135.3, 137.3, 145.7, 159.7 (Ar) (* two carbon peaks are overlapped.); ^{19}F NMR ($CDCl_3$) δ -63.1, -63.3, -63.3 (CF_3); MS (EI) *m/z* 501 (M^+); HRMS (EI): Exact mass calcd for $C_{24}H_{12}F_9NO$: 501.0775, Found: 501.0767.

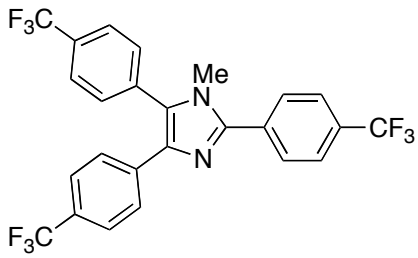
2,5-Bis(4-trifluoromethylphenyl)oxazole (19)



Chemical Formula: $C_{17}H_9F_6NO$
Exact Mass: 357.0588
Molecular Weight: 357.2499

Colorless solid; Rf = 0.23 (hexane : AcOEt = 10 : 1); mp 115-116 °C; IR (KBr) 3129, 1619, 1494, 1420, 1320, 1166, 1140, 1107, 1073, 1057, 1014, 952, 852, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (s, 1H, Ar), 7.63-7.69 (m, 4H, Ar), 7.76 (d, *J* = 8.3 Hz, 2H, Ar), 8.15 (d, *J* = 8.3 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 123.8 (q, *J* = 272.0 Hz, $F_3\underline{C}$), 123.9 (q, *J* = 272.0 Hz, $F_3\underline{C}$), 124.4, 125.5 (Ar), 125.9 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 126.1 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 126.7, 130.1 (Ar), 130.4 (q, *J* = 32.3 Hz, F_3C-$\underline{C}$), 130.9 (Ar) 132.2 (q, *J* = 33.1 Hz, F_3C-$\underline{C}$), 150.6, 160.5 (Ar); ^{19}F NMR ($CDCl_3$) δ -59.1, -59.2 (CF_3). MS (EI) *m/z* 357 (M^+); HRMS (EI): Exact mass calcd for $C_{17}H_9F_6NO$: 357.0588, Found: 357.0571.

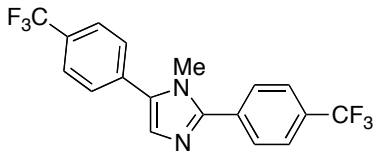
2,3,5-Tris(4-trifluoromethylphenyl)-1-methylimidazole (20)



Chemical Formula: $C_{25}H_{15}F_9N_2$
Exact Mass: 514.1092
Molecular Weight: 514.3856

Colorless solid; Rf = 0.52 (hexane : AcOEt = 4 : 1); mp 200-202 °C; IR (KBr) 2926, 2361, 1928, 1470, 1455, 1324, 1132, 1073, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.57 (s, 3H, Me), 7.51 (d, *J* = 8.8 Hz, 2H, Ar), 7.57 (d, *J* = 8.5 Hz, 2H, Ar), 7.62 (d, *J* = 8.5 Hz, 2H, Ar), 7.79-7.80 (m, 4H, Ar), 7.91 (d, *J* = 8.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 33.4 (Me), 123.7 (q, *J* = 272.1 Hz, $F_3\underline{C}$), 123.8 (q, *J* = 271.2 Hz, $F_3\underline{C}$), 124.1 (q, *J* = 272.1 Hz, $F_3\underline{C}$), 125.2 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 125.6 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 126.3 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 127.0 (Ar), 128.7 (q, *J* = 32.2 Hz, F_3C-$\underline{C}$), 129.2, 130.6 (Ar), 131.0 (q, *J* = 33.3 Hz, F_3C-$\underline{C}$), 131.2, (Ar), 131.2 (q, *J* = 33.1 Hz, F_3C-$\underline{C}$), 133.8, 134.0, 137.5, 137.7, 147.4 (Ar); ^{19}F NMR ($CDCl_3$) δ -62.9, -63.0, -63.0 (CF_3); MS (EI) *m/z* 514 (M^+); HRMS (EI): Exact mass calcd for $C_{25}H_{15}F_9N_2$: 514.1092, Found: 514.1090.

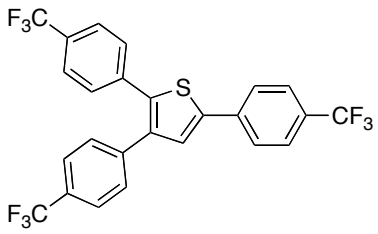
2,5-Bis(4-trifluoromethylphenyl)-1-methylimidazole (21)



Chemical Formula: $C_{18}H_{12}F_6N_2$
Exact Mass: 370.0905
Molecular Weight: 370.2917

Colorless solid; Rf = 0.23 (hexane : AcOEt = 4 : 1); mp 155-157 °C; IR (KBr) 2359, 1414, 1179, 1132, 1072, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3H, Me), 7.31 (s, 1H, Ar), 7.59 (d, *J* = 7.8 Hz, 2H, Ar), 7.74 (d, *J* = 7.8 Hz, 2H, Ar), 7.76 (d, *J* = 8.3 Hz, 2H, Ar), 7.85 (d, *J* = 8.3 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 33.9 (Me), 123.9 (q, *J* = 272.1 Hz, $F_3\underline{C}$), 124.0 (q, *J* = 271.2 Hz, $F_3\underline{C}$), 125.4 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 125.8 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 128.6, 128.9, 129.0 (Ar), 130.0 (q, *J* = 32.3 Hz, F_3C-$\underline{C}$), 130.6 (q, *J* = 33.1 Hz, F_3C-$\underline{C}$), 133.4, 133.9, 134.8, 148.7 (Ar); ^{19}F NMR ($CDCl_3$) δ -63.02, -63.09 (CF_3). MS (EI) *m/*z 370 (M^+); HRMS (EI): Exact mass calcd for $C_{18}H_{12}F_6N_2$: 370.0905, Found: 370.0893.

2,3,5-Tris(4-trifluoromethylphenyl)thiophene



Chemical Formula: $C_{25}H_{13}F_9S$
Exact Mass: 516.0594
Molecular Weight: 516.4213

Cs_2CO_3 (326 mg, 1 mmol, 2.0 equiv) was dried over *in vacuo* at 150 °C for 3 h and **12** (186 mg, 0.5 mmol), 4-trifluoromethylphenyl iodide (0.14 mL, 1 mmol, 2.0 equiv.) and DMA (1 mL) were added under Ar atmosphere. The mixture was degassed for 3 times, $Pd(phen)_2(PF_6)_2$ (19 mg, 0.025 mmol, 5 mol%) was added to the mixture, and this was heated at 150 °C for 20 h. The resulting mixture was filtrated through celite pad and concentrated *in vacuo*. The residue was purified by preparative recycling GPC to give the title compound (86 mg, 0.16 mmol, 33%) as a colorless solid. mp 182-184 °C; IR (KBr) 2928, 2360, 1417, 1240, 1193, 869 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H, Ar), 7.34 (d, *J* = 8.3 Hz, 2H, Ar), 7.35 (s, 1H, Ar), 7.47 (d, *J* = 8.3 Hz, 2H, Ar), 7.51 (d, *J* = 8.3 Hz, 2H, Ar), 7.85 (d, *J* = 8.3 Hz, 2H, Ar), 7.65 (d, *J* = 8.3 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 123.9 (q, *J* = 272.1 Hz, $F_3\underline{C}$), 124.0 (q, *J* = 271.2 Hz, $F_3\underline{C}$), 124.0 (q, *J* = 271.2 Hz, $F_3\underline{C}$), 125.6 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 125.7 (q, *J* = 3.8 Hz, F_3C-C=$\underline{C}$), 125.8 (Ar), 126.1 (q, *J* = 3.3 Hz, F_3C-C=$\underline{C}$), 127.4, 129.4, 129.4 (Ar), 129.5 (q, *J* = 30.8 Hz, F_3C-$\underline{C}$), 130.0 (q, *J* = 33.0 Hz, F_3C-$\underline{C}$), 130.1 (q, *J* = 32.8 Hz, F_3C-$\underline{C}$), 136.7, 137.0, 138.5, 138.9, 139.4, 142.5 (Ar); ^{19}F NMR ($CDCl_3$) δ -62.8, -63.1, -63.1 (CF_3); MS (EI) *m/*z 516 (M^+); HRMS (EI): Exact mass calcd for $C_{25}H_{13}F_9S$: 516.0594, Found: 516.0601.

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