Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2019

Supplementary Information for:

One-Pot Fluorosulfurylation of Grignard Reagents Using Sulfuryl Fluoride

Cayo Lee,^a Nicholas D. Ball *^b and Glenn M. Sammis *^a

^a Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

^b Department of Chemistry, Pomona College, 645 North College Avenue, Claremont, California 91711, United States

Table of Contents

General methods and instrumentation	\$3
Synthesis of Grignard reagents	\$3
Titration of Grignard reagents	S 4
Optimization of sulfonyl fluoride A: addition of SO_2F_2 to the Grignard reagent	S 5
General procedure A: addition of SO_2F_2 to the Grignard reagent (Entry 7 in Table S1)	S6
Determination of conversion in the optimization of sulfonyl fluoride synthesis	S7
Optimization of sulfonyl fluoride formation B: addition of the Grignard reagent to a SO_2F_2 solution in THF	58
General procedure B: addition of the Grignard reagent to a SO_2F_2 solution in THF (Entry 5 in Table 2)	S 8
General procedure C: for sulfonyl fluoride formation using Grignard reagent and sulfuryl fluoride on a larger scale	S 9
General procedure D: for one-pot reaction of sulfonyl derivatives using sulfonyl fluoride intermediate	S10
Experimental data	S10
References	S22
¹ H, ¹³ C and ¹⁹ F NMR Spectra	S23

General methods and instrumentation

All chemicals were from commercial sources Sigma-Aldrich, TCI, AK Scientific and Alfa Aesar. All reactions were performed in flame-dried disposable scintillation 3.70 mL (15 x 45 mm), 20 mL (28 x 61 mm), or 30 mL (25 x 95 mm) glass vials under nitrogen atmosphere. 1,1'-sulfonyldiimidazole (SDI) was prepared to synthesize sulfuryl fluoride (SO_2F_2) following the procedure reported by De Borggraeve.¹ Screw caps and PTFE/Silicone septa (13 mm x 0.060" and 22 mm x 0.060") were from Chemglass Life Sciences. Polyethylene tubing (I.D. 1.57 mm) was from Becton Dickinson. KDS 100 Legacy Single Syringe Infusion Pump was from KD Scientific. Disposable 1 mL syringes (I.D. 4.69 mm) and 3 mL Syringes (I.D. 9.65 mm) were from Norm-Ject. Disposable needles used in adding trifluoroacetic acid (TFA) were from Air-Tite.

Tetrahydrofuran (THF) was obtained from Sigma-Aldrich, dried by a solvent purification system (SPS), or distilled over sodium and benzophenone. Diethyl ether (Et₂O) was obtained from Sigma-Aldrich or dried by a solvent purification system (SPS).

Column chromatography was performed using SiliaFlash F60 (40-63 μ m) silica from Silicycle. Thin-layer chromatography (TLC) was run on TLC Silica gel 60 F₂₅₄ aluminium sheets from Merck.

Infrared (IR) spectra were obtained using a Thermo Nicolet 4700 FT-IR spectrometer or a Perkin Elmer Frontier FT-IR. The spectra are reported in cm^{-1} .

High resolution mass spectra (HRMS) were recorded on either a Waters or Micromass LCT spectrometer.

NMR spectra were obtained on a Bruker AV-300 or AV-400 spectrometer. ¹H, ²H, ¹³C, and ¹⁹F NMR chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak (CDCl₃: ¹H: δ = 7.26 ppm, ¹³C: δ = 77.16 ppm). ¹⁹F NMR chemical shifts were referenced to CFCl₃. NMR yields were determined by ¹⁹F NMR using a relaxation time of 40 seconds to complete relaxation of all fluorine nuclei. α, α, α -Trifluorotoluene (PhCF₃) was used as an internal standard. ¹H and ¹⁹F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), triplet of doublets (td), and doublet of doublets (dd). Coupling constants (J) are reported in Hz.

Synthesis of Grignard reagents

Procedure for the generation of Grignard reagents from liquid aryl halides:

An oven-dried 25 mL three-necked round-bottom flask equipped with a reflux condenser, an addition funnel, a septum, and a stir bar, was sealed and flame-dried under vacuum. After cooling to room temperature, the round-bottom flask was placed under N₂ atmosphere. Mg turnings (15 mmol, 1.5 equiv) and iodine (0.01 equiv) were added under a positive pressure of N₂. The round-bottom flask was then sealed, evacuated and back-filled with N₂ three times. The round-bottom flask was heated by a heat gun to generate purple I₂ gas, followed by the addition of THF (10 mL). A small amount of aryl halide (10 mmol, 1.0 equiv) was added at room temperature, while the reaction was initiated by gently heating the flask with a heat gun. Once the reaction had initiated, the remaining aryl bromide was added dropwise.

Procedure for the generation of Grignard reagents from solid aryl halides:

An oven-dried 25 mL three-necked round-bottom flask equipped with a reflux condenser, two septa, and a stir bar, was sealed and flame-dried under vacuum. After cooling to room temperature, the roundbottom flask was placed under N₂ atmosphere. Mg turnings (15 mmol, 1.5 equiv) and iodine (0.01 equiv) were added under a positive pressure of N₂. The round-bottom flask was then sealed, evacuated and backfilled with N₂ three times. The round-bottom flask was heated by a heat gun to generate purple I₂ gas, followed by the addition of THF (5 mL). A flame-dried 20 mL vial was charged with a stir bar, aryl bromide (10 mmol, 1.0 equiv), and THF (5 mL). A small amount of aryl halide solution was added at room temperature, while the reaction was initiated by gently heating the flask with a heat gun. Once the reaction had initiated, the remaining aryl bromide was added dropwise.

Procedure for the generation of Grignard reagents using Br/Mg-exchange²:

An oven-dried 10 mL round-bottom flask equipped with a stir bar, was sealed and flame-dried under vacuum. After cooling to room temperature, the round-bottom flask was placed under N₂ atmosphere and charged with *i*-PrMgCl·LiCl (2.35 mL, 1.30 M in THF, 3.05 mmol). After aryl bromide (3 mmol, 1 equiv) was added at 0 °C, the reaction was stirring for 2 hours.

Titration of Grignard reagents

Titration method using diphenylacetic acid as the indicator:

A 3.70 mL vial with a stir bar was flame-dried under high vacuum, and then cooled to room temperature and filled with argon. To the vial was added 100 mg of diphenylacetic acid. Under argon, THF (2 mL) was added to the vial and stirred until the diphenylacetic acid was dissolved. A 1 mL syringe was flushed with argon gas three times. The Grignard reagent solution was taken up into the syringe followed by a cushion of inert gas and inserted into the vial. The solution of the Grignard reagent was added dropwise until a light blue color appeared and the total volume of solution used was recorded.

$$Molarity (M) = \frac{Mass_{diphenylacetic acid}}{\left(\frac{MW_{diphenylacetic acid}}{Volume_{Grignard reagent}}\right)}$$

 $MW_{diphenylacetic \ acid} = 212.24 \text{ g/mol}$

Titration method using iodine as the indicator:

A 3.70 mL vial with a stir bar was flame-dried under high vacuum, and then cooled to room temperature and filled with argon. To the vial was quickly added 100 mg of iodine. Under argon, a 0.5 M solution of LiCl in THF (2 mL) was added to the vial and stirred until the iodine was dissolved. A 1 mL syringe was flushed with argon gas three times. The Grignard reagent solution was taken up into the syringe followed by a cushion of inert gas and inserted into the vial. The solution of the Grignard reagent was added dropwise until a colorless or pale-yellow color appeared and the total volume of solution used was recorded.

 $Molarity (M) = \frac{Mass_{iodine}}{\left(\frac{MW_{iodine}}{Volume_{Grignard\ reagent}}\right)}$

$$MW_{iodine} = 253.81 \text{ g/mol}$$

Optimization of sulfonyl fluoride A: addition of SO₂F₂ to the Grignard reagent Table S1. Optimization of sulfonyl fluoride formation using 1a^a

	F 1a	Br (SDI, KF, TFA) solvent conc. (M), T (°C) 0.5 hr	0 2a	O S F	
entry	solvent	rate of TFA addition ^b	conc. (M)	Т (°С)	yield (%)
1	Et ₂ O regular ^c	one portion	0.1	23	28
2	Et ₂ O SPS ^d	one portion	0.1	23	33
3	THF regular ^e	one portion	0.1	23	32
4	THF SPS ^d	one portion	0.1	23	36
5	THF solvent still	one portion	0.1	23	39
6	THF solvent still	12 mL/hr	0.1	23	36
7	THF solvent still	9 mL/hr	0.1	23	45
8	THF SPS ^d	9 mL/hr	0.1	23	40
9	THF solvent still	6 mL/hr	0.1	23	30
10	THF solvent still	3 mL/hr	0.1	23	30
11	THF solvent still	9 mL/hr	0.5	23	<5
12	THF solvent still	9 mL/hr	0.25	23	42
13	THF solvent still	9 mL/hr	0.05	23	23
14	THF solvent still	9 mL/hr	0.025	23	18
15	THF solvent still	9 mL/hr	0.1	40	30
16	THF solvent still	9 mL/hr	0.1	0	25
17	THF solvent still	9 mL/hr	0.1	-25	<5

^{*a*} Reaction conditions: The reactions were run on 0.29 mmol scale of Grignard reagent **1a** in 3.70 mL vials following the general procedure A. The yield was determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard. ^{*b*} Rate of TFA addition by a syringe pump. ^{*c*} Diethyl ether was from Sigma-Aldrich (anhydrous, ACS reagent, ≥99.0%). ^{*d*} The solvents were obtained from a solvent purification system. ^{*e*} The 1 L THF can was from OmniSolv (For HPLC, Spectrophotometry and Gas Chromatography).

General procedure A: addition of SO₂F₂ to the Grignard reagent (Entry 7 in Table S1)

Two 3.70 mL vials equipped with magnetic stir bars were capped with septum-fitted screw caps connected by a 15 - 20 cm polyethylene tube. Vial A was charged with 1,1'-sulfonyldiimidazole (SDI) (0.875 mmol, 3.07 equiv) and anhydrous KF (2.31 mmol, 8.18 equiv). The system was evacuated and filled with nitrogen three times. To vial B was added anhydrous THF (2.36 mL) and 4-fluorophenylmagnesium bromide (0.49 mL, 0.285 mmol, 1.0 equiv, 0.58 M in THF) dropwise by a syringe at room temperature. A 1 mL syringe filled with excess of trifluoroacetic acid (TFA) (0.5 mL, 6.53 mmol, 22.9 equiv) was inserted into vial A. The nitrogen gas inlet was then removed. The tip of the cannula in vial B was lowed through the headspace until it touched the top of the solution in vial B. The addition of TFA into vial A was initiated at a rate of 9 mL/hr by a syringe pump. The polyethylene tube in vial B was fully immersed into the solution after the first bubbles of SO₂F₂ appeared in vial B. Bubbling of SO₂F₂ continued in vial B for a few minutes. Once bubbling almost stopped, the tube was removed and the mixture in vial B was stirred at room temperature for 30 minutes. An excess of deuterium oxide (D₂O) was used to quench the reaction mixture. Trifluorotoluene (1.0 equiv) and dichloromethane-d₂ (1.0 equiv) were added into vial B as internal standards. An aliquot was taken for quantitative ²H NMR and ¹⁹F NMR analyses.



Figure S1. Setup for the optimization of sulfonyl fluoride used in Table S1.

Determination of conversion in the optimization of sulfonyl fluoride synthesis

The conversion of 4-fluorophenylmagensium bromide (**1a**) was determined using ²H NMR spectroscopy after the D_2O reaction quench. For a representative example, see the protocol below:





4-Fluorophenylmagnesium bromide **1a** was used as the substrate in condition optimization with reactions run at 0.29 mmol scale. After running under the designated conditions, the reactions were quenched with excess deuterium oxide to give deuterated fluorobenzene. Dichloromethane-d₂ was used as an internal standard. Analysis of the deuterated fluorobenzene and dichloromethane-d₂ via ²H NMR spectroscopy gives the conversion of substrate.

For example, ²H NMR of deuterated fluorobenzene is shown below:

0.0276 g of dichloromethane-d₂ were added as an internal standard. The ratio of deuterated fluorobenzene and deuterium oxide integration is 0.04/2.



Figure S2. ²H NMR spectrum of deuterated fluorobenzene of **1a** and conversion determination for entry 7 (Table S1).

Optimization of sulfonyl fluoride formation B: addition of the Grignard reagent to a SO₂F₂ solution in THF

	F MgBr SO ₂ F ₂ THF (0.1 M 23 (°C) 1 hr	0,0 5 F 2a	
entry	solvent/	SO_2F_2	yield
	reaction vessel	(equiv)	(%)
	(v/v; mL)		
1	3/4	3.1	53
2	3/20	3.1	59
3	3/20	4.6	78
4	3/20	6.1	77
5	3/20	7.7	81

Table S2. Headspace and SO_2F_2 optimization for the formation of 2a.

Reaction conditions: The reactions were run on 0.29 mmol scale of Grignard reagent following the General procedure B: for sulfonyl fluoride formation using Grignard reagent and sulfuryl fluoride on a smaller scale. The yield was determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard.

<u>General procedure B: addition of the Grignard reagent to a SO₂F₂ solution in THF (Entry 5 in Table 2)</u>

A 3.70 mL vial A and a 20 mL vial B were equipped with magnetic stir bars and capped with septum-fitted screw caps. The vials were connected by a cannula and a vacuum/nitrogen gas inlet was inserted into vial B. The system was evacuated and filled with nitrogen three times. Vial A was charged with 1,1'sulfonyldiimidazole (SDI) (1.31 mmol, 4.61 equiv) and anhydrous KF (3.50 mmol, 12.3 equiv) and then the system was flushed with nitrogen for a few minutes. To vial B was added anhydrous THF (2.70 mL) from a solvent still. A 3 mL syringe filled with excess of trifluoroacetic acid (TFA) (0.75 mL, 9.80 mmol) was inserted into the vial A. The nitrogen gas inlet was then removed. The tip of the cannula in vial B was lowed through the headspace until it touched the top of the solution in vial B. The addition of TFA into vial A was initiated at a rate of 9 mL/hr by a syringe pump. The cannula in vial B was fully immersed into the solution after the first bubbles of SO_2F_2 appeared in vial B. Bubbling of SO_2F_2 continued in vial B for a few minutes. Once bubbling of SO₂F₂ subsided, into vial B was inserted an empty balloon to increase the bubbling rate. When the bubbling had almost stopped, the cannula was removed. Trifluorotoluene (1.0 equiv) was added into vial B as an internal standard. An aliquot was taken for quantitative ¹⁹F NMR analysis to confirm no TFA contaminant and quantify the amount of SO_2F_2 . 4-Fluorophenylmagnesium bromide (0.143 mL, 0.285 mmol, 1.0 equiv, 2.0 M in THF) was added dropwise into vial B by a syringe over a few minutes. The reaction mixture was stirred at room temperature for 1 hour. An aliquot was taken for quantitative ¹⁹F NMR analysis.



Figure S3. Setup for the optimization of sulfonyl fluoride (Table S2).

<u>General procedure C: for sulfonyl fluoride formation using Grignard reagent and</u> <u>sulfuryl fluoride on a larger scale</u>

A 3.70 mL vial A and a 30 mL vial B were equipped with magnetic stir bars and capped with septum-fitted screw caps. The vials were connected by a cannula and a vacuum/nitrogen gas inlet was inserted into vial B. The system was evacuated and filled with nitrogen three times. Vial A was charged with 1,1'sulfonyldiimidazole (SDI) (2.77 mmol, 4.61 equiv) and anhydrous KF (7.36 mmol, 12.3 equiv) and then the system was flushed with nitrogen for a few minutes. To Vial B was charged anhydrous THF (5.70 mL) from solvent still. A 3 mL syringe filled with excess of trifluoroacetic acid (TFA) (1.50 mL, 19.6 mmol) was inserted into the vial A. The nitrogen gas inlet was then removed. The tip of the cannula in vial B was lowed through the headspace until it touched the top of the solution in vial B. The addition of TFA into vial A was initiated at a rate of 9 mL/hr by a syringe pump. The cannula in vial B was fully immersed into the solution after the first bubbles of SO_2F_2 appeared in vial B. Bubbling of SO_2F_2 continued in vial B for a few minutes. Once bubbling of SO₂F₂ subsided, into vial B was inserted an empty balloon to increase the bubbling rate. When the bubbling almost stopped, the cannula was removed. Trifluorotoluene (1.0 equiv) was added into vial B as an internal standard. An aliquot was taken for guantitative ¹⁹F NMR analysis to check no containment of TFA and quantify the amount of SO₂F₂. 4-Fluorophenylmagnesium bromide (0.3 mL, 0.6 mmol, 1.0 equiv, 2.0 M in THF) was added dropwise into vial B by a syringe over a few minutes. The reaction mixture was stirred at room temperature for 1 hour. An aliquot was taken for quantitative ¹⁹F NMR analysis.

Workup and purification:

The reaction mixture was diluted with petroleum ether (20 mL), then washed with sat. aq. NH_4Cl (2 x 20 mL) and brine (20 mL). The organic layers were dried over Na_2SO_4 , filtered and concentrated in vacuo to afford the crude product, which was purified by silica gel column chromatography (10% dichloromethane in petroleum ether as eluent). Fractions containing the desired product were combined and concentrated in vacuo to dryness.

General procedure D: for one-pot reaction of sulfonyl derivatives using sulfonyl fluoride intermediate

General procedure for the synthesis of intermediate 2a:

4-Fluorophenylsulfonyl fluoride **2a** was prepared on 0.6 mmol scale according to general procedure C. The reaction mixture (vial B) was inserted a vent needle and purged with nitrogen gas for 3 minutes to remove residual SO_2F_2 .

Procedure for sulfone 7a:

After the formation of 4-fluorophenylsulfonyl fluoride intermediate **2a** and subsequent purging, phenylmagnesium bromide (0.24 mL, 0.6 mmol, 1.0 equiv, 2.5 M in diethyl ether) was added dropwise by a 1 mL syringe into vial B over a few minutes under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. An aliquot was taken for ¹⁹F NMR analysis.

Procedure sulfonate ester 8a:

After the formation of 4-fluorophenylsulfonyl fluoride intermediate **2a** and subsequent purging, trimethyl(phenoxy)silane (0.11 mL, 0.6 mmol, 1.0 equiv) and a 1 M THF solution of TBAF (0.6 mL, 0.6 mmol, 1 equiv) were added into vial B by 1 mL syringes under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 hour. An aliquot was taken for ¹⁹F NMR analysis.

Procedure sulfonamide 9a:

After the formation of 4-fluorophenylsulfonyl fluoride intermediate **2a** and subsequent purging, imidazole (0.0817g, 1.2 mmol, 2 equiv) were quickly added into vial B by open-to-air, then capped the vial. DBU (0.27 mL, 1.8 mmol, 3 equiv) and anhydrous THF (6 mL) were added into the vial B by syringes and stirred at 40 °C. (Note: a larger headspace may be required for a larger scale synthesis to avoid solvent explosion.) The reaction mixture was stirred at room temperature for 20 hours. An aliquot was taken for ¹⁹F NMR analysis.

Workup and purification:

The reaction mixture was diluted with petroleum ether (40 mL), then washed with sat. aq. NH_4Cl (2 x 40 mL) and brine (40 mL). The organic layers were dried by Na_2SO_4 , filtered and concentrated in vacuo to afford the crude product, which was purified by silica gel column chromatography (10% ethyl acetate in petroleum ether as eluent). Fractions containing the desired product were combined and concentrated in vacuo to dryness.

Experimental data

4-Fluorobenzenesulfonyl fluoride (2a)



Compound **2a** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-fluorobenzenesulfonyl fluoride as a colourless liquid (83.5 mg, 78% and 82.0 mg, 77%). The spectroscopic data were consistent with those previously published.³

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.01 (m, 2H), 7.37 – 7.28 (m, 2H).

¹³C {1H} NMR (101 MHz, Chloroform-*d*) δ 166.9 (d, *J* = 259.8 Hz), 131.6 (d, *J* = 10.0 Hz), 129.0 (dd, *J* = 25.7, 3.3 Hz), 117.3 (d, *J* = 23.1 Hz).

¹⁹**F NMR** (377 MHz, Chloroform-*d*) δ 67.1, -99.0.

4-Chlorobenzenesulfonyl fluoride (2b)



Compound **2b** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-chlorobenzenesulfonyl fluoride as a white solid (67.8 mg, 58% and 70.1 mg, 60%). The spectroscopic data were consistent with those previously published.⁴

¹H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.66 – 7.57 (m, 2H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 142.8, 131.5 (d, *J* = 25.7 Hz), 130.3, 130.0.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 66.2.

3,5-Bis(trifluoromethyl)benzenesulfonyl fluoride (2c)



Compound **2c** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 3,5-bis(trifluoromethyl)benzenesulfonyl fluoride as a colorless oil (28.6 mg, 16% and 32.9 mg, 19%). The spectroscopic data were consistent with those previously published.^{5, 6}

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 1.6 Hz, 2H), 8.28 (s, 1H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 135.8 (q, *J* = 28.7 Hz), 134.1 (q, *J* = 35.3 Hz), 129.3 (dt, *J* = 7.2, 3.4 Hz), 129.2 – 128.7 (m), 122.1 (d, *J* = 273.9 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 66.4, -63.4.

5,5'-sulfonylbis(1,3-bis(trifluoromethyl)benzene) (3c)



Compound **3c** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 5,5'-sulfonylbis(1,3-bis(trifluoromethyl)benzene) as a white solid (111.9 mg, 76% and 74.0 mg, 50%).

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.42 (s, 4H), 8.16 (s, 2H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 142.7, 133.9 (q, *J* = 34.9 Hz), 128.5 – 128.2 (m), 128.2 – 128.0 (m), 122.1 (d).¹⁹F NMR (282 MHz, Chloroform-*d*) δ -63.3.

HRMS-EI (m/z) calculated for $C_{16}H_6F_{12}O_2S_1$: 489.98969. Found: 489.98982.

IR (cm⁻¹): 3088, 1628, 1695, 1348, 1275, 1168, 1124, 1109.

Benzenesulfonyl fluoride (2d)



Compound **2d** was prepared on 0.6 mmol and 1.0 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave benzenesulfonyl fluoride as a colorless liquid (73.8 mg, 77% and 73.7 mg, 77% for 0.6 mmol scale and 120.0 mg, 75% for 1.0 mmol scale). The spectroscopic data were consistent with those previously published.⁴

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 8.5, 7.3 Hz, 2H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 135.7, 133.1 (d, *J* = 24.3 Hz), 129.8, 128.4.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 65.5.

4-Methylbenzenesulfonyl fluoride (2e)



Compound **2e** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-methylbenzenesulfonyl fluoride as a white solid (59.7 mg, 57% and 56.1 mg, 54%). The spectroscopic data were consistent with those previously published.⁴

¹H NMR (300 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 2.52 (s, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 147.0, 130.2, 130.1, 128.5, 21.8.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 66.3.

3,5-Dimethylbenzenesulfonyl fluoride (2f)



Compound **2f** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 3,5-dimethylbenzenesulfonyl fluoride as a white solid (86.4 mg, 77% and 79.4 mg, 70%). The spectroscopic data were consistent with those previously published.⁷

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.62 (s, 2H), 7.37 (s, 1H), 2.43 (s, 6H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 140.0, 137.3, 132.7 (d, *J* = 23.2 Hz), 125.8, 21.1.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 65.3.

2-Methylbenzenesulfonyl fluoride (2g)



Compound **2g** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 2-methylbenzenesulfonyl fluoride as a colorless liquid (54.1 mg, 52% and 52.0 mg, 50%). The spectroscopic data were consistent with those previously published.⁸

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 2.70 (d, *J* = 1.3 Hz, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 139.2, 135.4, 133.0, 130.2, 130.2, 126.8, 20.4.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 59.9.

2,4,6-Trimethyl-benzenesulfonyl fluoride (2h)



Compound **2h** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 2,4,6-trimethyl-benzenesulfonyl fluoride as a white solid (69.1 mg, 57% and 57.0 mg, 47%). The spectroscopic data were consistent with those previously published.³

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.03 (s, 2H), 2.64 (d, *J* = 1.9 Hz, 6H), 2.35 (s, 3H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 145.2, 140.2, 132.0 (d, *J* = 1.4 Hz), 129.2 (d, *J* = 20.3 Hz), 22.5 (d, *J* = 1.9 Hz), 21.3.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 68.2.

4-Methoxybenzenesulfonyl fluoride (2i)



Compound **2i** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-methoxybenzenesulfonyl fluoride as a colourless liquid (68.3 mg, 60% and 85.5 mg, 75%). The spectroscopic data were consistent with those previously published.⁷

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 165.2, 130.9, 124.1 (d, *J* = 24.6 Hz), 114.8, 55.9.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 67.0.

4-Methoxy-2-methylbenzenesulfonyl fluoride (2j)



Compound **2j** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-methoxy-2-methylbenzenesulfonyl fluoride as a colorless liquid (92.4 mg, 75% and 78.0 mg, 64%).

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.7 Hz, 1H), 6.92 – 6.81 (m, 2H), 3.89 (s, 3H), 2.65 (s, 3H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 164.8, 141.7, 132.9, 123.8 (d, *J* = 23.1 Hz), 118.4, 111.4, 55.9, 20.7.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 61.5.

HRMS-EI (m/z) calculated for C₈H₉F₁O₃S₁: 204.02564. Found: 204.02618.

IR (cm⁻¹): 2945, 2849, 1597, 1568, 1488, 1388, 1326, 1251, 1202, 1177, 1061, 757, 668.

4-(Methylthio)benzenesulfonyl fluoride (2k)



Compound **2k** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-(methylthio)benzenesulfonyl fluoride as a white solid (69.6 mg, 56% and 87.4 mg, 71%). The spectroscopic data were consistent with those previously published.⁹

¹H NMR (300 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 150.3, 128.6, 128.0 (d, *J* = 24.8 Hz), 125.4, 14.6.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 66.4.

4-Phenylbenzenesulfonyl fluoride (2l)



Compound **2I** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 4-phenylbenzenesulfonyl fluoride as a white solid (96.3 mg, 68% and 83.2 mg, 59%). The spectroscopic data were consistent with those previously published.⁹

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.13 – 8.03 (m, 2H), 7.87 – 7.77 (m, 2H), 7.67 – 7.57 (m, 2H), 7.57 – 7.40 (m, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 148.8, 138.7, 131.5 (d, *J* = 25.0 Hz), 129.4, 129.3, 129.1, 128.3, 127.6.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 66.1.

1-Naphthylenesulfonyl fluoride (2m)



Compound **2m** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 1-naphthylenesulfonyl fluoride as a white solid (72.7 mg, 58% and 94.9 mg, 75%). The spectroscopic data were consistent with those previously published.⁷

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 8.3, 2.3 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.78 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.5, 1.5 Hz, 1H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 136.9, 134.1, 131.1 (d, J = 2.1 Hz), 129.5, 129.1 (d, J = 23.4 Hz), 129.1, 128.3 (d, J = 0.7 Hz), 127.7, 124.2 (d, J = 1.3 Hz), 124.1 (d, J = 1.0 Hz).¹⁹F NMR (282 MHz, Chloroform-*d*) δ 62.2.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 62.2.

Methanesulfonyl fluoride (2n)



Compound **2n** was prepared on 0.6 mmol scale following the general procedure C. The crude product was obtained (48% and 48%) based on quantitative ¹⁹F NMR using trifluorotoluene as the internal standard. The spectroscopic data were consistent with those previously published.¹⁰

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 60.6.

1-Octanesulfonyl fluoride (2o)



Compound **2o** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 1-octanesulfonyl fluoride as a colorless liquid (69.3 mg, 59% and 81.1 mg, 69%). The spectroscopic data were consistent with those previously published.^{3, 11}

¹**H NMR** (400 MHz, Chloroform-*d*) δ 3.42 – 3.33 (m, 2H), 2.03 – 1.91 (m, 2H), 1.49 (q, *J* = 7.2 Hz, 2H), 1.41 – 1.23 (m, 8H), 0.91 (dq, *J* = 7.3, 3.3 Hz, 3H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 50.9 (d, *J* = 16.0 Hz), 31.6, 29.7 (d, *J* = 8.6 Hz), 28.8 (d, *J* = 4.9 Hz), 27.9, 23.4, 22.6, 14.0.

¹⁹**F NMR** (377 MHz, Chloroform-*d*) δ 53.5 (t, *J* = 4.3 Hz).

Thiophene-2-sulfonyl fluoride (6a)



Compound **6a** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave thiophene-2-sulfonyl fluoride as a yellow liquid (60.5 mg, 61% and 56.2 mg, 56%). The spectroscopic data were consistent with those previously published.⁴

¹H NMR (300 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 3.9 Hz, 1H), 7.88 (d, *J* = 5.0 Hz, 1H), 7.24 (t, *J* = 4.1 Hz, 1H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 137.0, 136.6 (d, *J* = 2.1 Hz), 131.7 (d, *J* = 31.2 Hz), 128.3.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 71.3.

5-Methylthiophene-2-sulfonyl fluoride (6b)



Compound **6b** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 5-methylthiophene-2-sulfonyl fluoride as a yellow liquid (65.8 mg, 61% and 64.8 mg, 60%).

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 2.6 Hz, 1H), 6.90 (d, *J* = 3.9 Hz, 1H), 2.62 (s, 3H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 153.1, 137.5, 128.1 (d, *J* = 30.5 Hz), 126.8, 16.0.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 71.2.

HRMS-EI (m/z) calculated for C₅H₅F₁O₂S₂: 179.97150. Found: 179.97089.

IR (cm⁻¹): 3103, 2928, 2856, 1407, 1202.

3-Methylthiophene-2-sulfonyl fluoride (6c)



Compound **6c** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 3-methylthiophene-2-sulfonyl fluoride as a yellow liquid (54.7 mg, 51% and 47.3 mg, 44%).

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 5.1 Hz, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 2.57 (s, 3H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 148.2, 134.0 (d, *J* = 2.1 Hz), 132.2, 125.8 (d, *J* = 29.2 Hz), 15.2.

¹⁹**F NMR** (377 MHz, Chloroform-*d*) δ 70.5.

HRMS-EI (m/z) calculated for C₅H₅F₁O₂S₂: 179.97150. Found: 179.97177.

IR (cm⁻¹): 3114, 2965, 2928, 2853, 1527,1406, 1376, 1201, 1108.

3-Octylthiophene-2-sulfonyl fluoride (6d)



Compound **6d** was prepared on 0.6 mmol scale following the general procedure. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 3-octylthiophene-2-sulfonyl fluoride as a yellow liquid (51.4 mg, 31% and 54.2mg, 32%).

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 5.1 Hz, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 3.00 – 2.89 (m, 2H), 1.66 (p, *J* = 7.4 Hz, 2H), 1.42 – 1.20 (m, 10H), 0.93 – 0.83 (m, 3H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 153.4, 134.2 (d, *J* = 2.0 Hz), 131.1, 125.4 (d, *J* = 28.9 Hz), 31.9, 30.3, 29.4, 29.3, 29.2, 22.8, 14.2.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 71.0.

HRMS-EI (m/z) calculated for C₁₂H₁₉F₁O₂S₂: 278.08105. Found: 278.08174.

IR (cm⁻¹): 3116, 2927, 2856, 1408, 1203, 764, 674.

5-Chlorothiophene-2-sulfonyl fluoride (6e)



Compound **6e** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave 5-chlorothiophene-2-sulfonyl fluoride as a yellow liquid (55.3 mg, 46% and 58.9 mg, 49%).

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 4.2, 1.2 Hz, 1H), 7.08 (dd, *J* = 4.2, 0.9 Hz, 1H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 142.7 (d, *J* = 2.4 Hz), 136.7, 129.2 (d, *J* = 31.9 Hz), 127.7.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 71.1.

HRMS-EI (m/z) calculated for C₄H₂Cl₁F₁O₂S₂: 199.91688. Found: 199.91786.

IR (cm⁻¹): 3110, 3099, 1516, 1417, 1401, 1318, 1214, 1203.

Benzo[b]thiophene-3-sulfonyl fluoride (6f)



Compound **6f** was prepared on 0.6 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% dichloromethane in petroleum ether as eluent) to leave benzo[b]thiophene-3-sulfonyl fluoride as a yellow liquid (70.1 mg, 54% and 58.0 mg, 45%).

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 1.4 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.02 – 7.86 (m, 1H), 7.66 – 7.45 (m, 2H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 140.0, 139.2 (d, *J* = 2.7 Hz), 133.2, 129.7, 126.8 (d, *J* = 8.1 Hz), 125.3 (d, *J* = 8.6 Hz), 123.1 (d, *J* = 8.7 Hz), 122.8 (d, *J* = 30.0 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 63.6.

HRMS-EI (m/z) calculated for $C_8H_5F_1O_2S_2$: 215.97150. Found: 215.97143.

IR (cm⁻¹): 3106, 3068, 1458, 1405, 1376, 1263, 1200.

3-Pyridinesulfonyl fluoride (6g)



Compound **6g** was prepared on 0.6 mmol following the general procedure C. The crude product was purified by column chromatography on silica (100% dichloromethane as eluent) to leave 3-pyridinesulfonyl fluoride as a yellow liquid (43.0 mg, 45% and 40.6 mg, 42%). The spectroscopic data were consistent with those previously published.⁶

¹**H NMR** (300 MHz, Chloroform-*d*) δ 9.25 – 9.20 (m, 4H), 9.00 (dd, *J* = 4.9, 1.6 Hz, 4H), 8.30 (ddd, *J* = 8.2, 2.4, 1.6 Hz, 4H), 7.61 (ddt, *J* = 8.2, 4.9, 0.8 Hz, 4H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 156.1, 149.1, 136.2, 130.4 (d, *J* = 25.6 Hz), 124.3.

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 67.6.

Thiazole-2-sulfonyl fluoride (6h)



Compound **6h** was prepared on 0.6 mmol and 1.0 mmol scale following the general procedure C. The crude product was purified by column chromatography on silica (10% ethyl acetate in petroleum ether

as eluent) to leave thiazole-2-sulfonyl fluoride as a yellow liquid (51.7 mg, 52% and 62.6 mg, 62% for 0.6 mmol scale and 88.2 mg, 53% for 1.0 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (d, J = 3.0 Hz, 2H), 7.94 (d, J = 3.0 Hz, 2H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.0 (d, J = 38.5 Hz), 145.8 (d, J = 2.3 Hz), 128.3 (d, J = 0.9 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ 63.9.

HRMS-EI (m/z) calculated for C₃H₂F₁N₁O₂S₂: 166.95110. Found: 166.95087.

IR (cm⁻¹): 3123, 1422, 1352, 1317, 1219.

1-Fluoro-4-(phenylsulfonyl)benzene (7a)



Compound **7a** was prepared on 0.6 mmol scale following the general procedure D. The crude product was purified by column chromatography on silica (10% ethyl acetate in petroleum ether as eluent) to leave 1-fluoro-4-(phenylsulfonyl)benzene as a white solid (110.7 mg, 78% and 101.0 mg, 71%). The spectroscopic data were consistent with those previously published.¹²

¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 4H), 7.61 – 7.46 (m, 3H), 7.22 – 7.10 (m, 2H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 165.6 (d, *J* = 255.9 Hz), 141.6, 137.8, 133.5, 130.6 (d, *J* = 9.6 Hz), 129.5, 127.7, 116.7 (d, *J* = 22.7 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ -104.6.

Phenyl *p*-fluorobenzenesulfonate (8a)



Compound **8a** was prepared on 0.6 mmol scale following the general procedure D. The crude product was purified by column chromatography on silica (10% ethyl acetate in petroleum ether as eluent) to leave 2-methylphenyl phenyl *p*-fluorobenzenesulfonate as a colorless liquid (90.5 mg, 60% and 88.8 mg, 59%). The spectroscopic data were consistent with those previously published.^{13, 14}

¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.19 (dd, *J* = 8.9, 8.2 Hz, 2H), 6.98 (dd, *J* = 8.2, 1.7 Hz, 2H).

¹³C{1H} NMR (75 MHz, Chloroform-*d*) δ 165.8 (d, *J* = 257.4 Hz), 149.3, 131.2 (d, *J* = 9.7 Hz), 129.6, 127.2, 123.9, 122.2, 116.4 (d, *J* = 22.7 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ -102.5.

1-((4-Fluorophenyl)sulfonyl)-1H-imidazole (9a)



Compound **9a** was prepared on 0.6 mmol scale following the general procedure D. The crude product was purified by column chromatography on silica (50% ethyl acetate in petroleum ether as eluent) to leave 1- ((4-fluorophenyl)sulfonyl)-1H-imidazole as a white solid (84.5 mg, 62% and 82.4 mg, 61%). The spectroscopic data were consistent with those previously published.¹⁵

¹**H NMR** (300 MHz, Chloroform-*d*) δ 8.07 – 7.93 (m, 3H), 7.31 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 7.11 (dd, *J* = 1.6, 0.8 Hz, 1H).

¹³C{1H} NMR (101 MHz, Chloroform-*d*) δ 166.4 (d, *J* = 259.3 Hz), 136.8, 134.1 (d, *J* = 3.4 Hz), 131.9, 130.5 (d, *J* = 9.9 Hz), 117.5, 117.5 (d, *J* = 23.0 Hz).

¹⁹**F NMR** (282 MHz, Chloroform-*d*) δ -100.6.

REFERENCES

1. C. Veryser, J. Demaerel, V. Bieliūnas, P. Gilles and W. M. De Borggraeve, *Org. Lett.* 2017, **19**, 5244-5247.

2. A. Krasovskiy and P. Knochel, Angew. Chem. Int. Ed. 2004, 25, 3333-3336.

3. L. Tang, Y. Yang, L. Wen, X. Yang and Z. Wang, Green Chem. 2016, 5, 1224-1228.

4. L. Matesic, N. A. Wyatt, B. H. Fraser, M. P. Roberts, T. Q. Pham and I. Greguric, *J. Org. Chem.* 2013, 22, 11262-11270.

5. J. T. Gerig and D. C. Roe, J. Am. Chem. Soc. 1974, 1, 233-238.

6. M. K. Nielsen, C. R. Ugaz, W. Li and A. G. Doyle, J. Am. Chem. Soc. 2015, 30, 9571-9574.

7. A. L. Tribby, I. Rodríguez, S. Shariffudin and N. D. Ball, J. Org. Chem. 2017, 4, 2294-2299.

8. J. Dong, L. Krasnova, M. G. Finn and K. B. Sharpless, Angew. Chem. Int. Ed. 2014, 36, 9430-9448.

9. A. T. Davies, J. M. Curto, S. W. Bagley and M. C. Willis, Chem. Sci. 2017, 2, 1233-1237.

10. P. Švec, A. Eisner, L. Kolářová, T. Weidlich, V. Pejchal and A. Růžička, *Tetrahedron Lett.* 2008, **44**, 6320-6323.

11. C. Comninellis, P. Javet and E. Plattner, 1974, 887.

12. N. Liu, K. Hofman, A. Herbert and G. Manolikakes, Org. Lett. 2018, 3, 760-763.

13. V. Percec, J. Bae, M. Zhao and D. H. Hill, J. Org. Chem. 1995, 1, 176-185.

14. T. Ogata and J. F. Hartwig, J. Am. Chem. Soc. 2008, 42, 13848-13849.

15. Y. Shi, S. Chen, F. Zhang and B. Chen, *ChemistrySelect* 2018, 4, 997-999.






















































2i








































































6f































