Supporting information

Copper Catalysed Synthesis of Trifluoromethyl(hetero)arenes from Di(hetero)aryl-\(\lambda^3\)-iodanes

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1. General Comments:

All reactions were carried out under an atmosphere of dry nitrogen using reaction tubes and round bottom flask. Dry DCM and DMF was prepared by distilling over CaH₂ and stored over molecular sieves 4Å under N₂ atmosphere. The other dry solvent was also prepared by employing standard distillation procedure and stored over molecular sieves 4Å under N₂ atmosphere.

(Trifluoromethyl)trimethylsilane, KF, CuI, PPh₃, substituted arenes, iodoarenes, arylboronic acid, trifluoromethanesulfonic acid, m-CPBA and other reagents were obtained from commercially available sources and they were used as received. All the iododiacetate⁴ and diaryliodonium² derivatives were synthesized from corresponding iodoarenes and arenes employing literature procedure.

Column chromatography was performed using Rankem Silica gel (100-200 mesh) and ethyl acetate-hexanes was used as solvent system, unless otherwise specified, with various percentage of polarity depending on the nature of the substrate.

2. Analytical Methods:

NMR data were recorded on Bruker DPX 400 and AVC 500 MHz spectrometers.¹³C and¹H NMR spectra were referenced to signals of deuterio solvents and residual protiated solvents, respectively.¹⁹F NMR spectra were recorded on AVC 470 MHZ spectrometers using hexafluorobenzene as standard. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spry ionization (ESI) method on a Q-TOF Micro with lock spray source. Melting points are corrected. The GCMS analysis was performed on Agilent Technologies Inc. 7890A gas chromatography mass spectrometer.

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¹ Bielawski, M.; Olofsson, B. Chem. Commun. 2007, 2521–2523;
3. Copper(I) catalyzed trifluoromethylation of diphenyliodonium salt: Optimization:

![Chemical structure](image)

**Table S1: Copper (I) mediated trifluoromethylation of 1a:**

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<th>Ligand (equiv)</th>
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</table>

[a] reaction condition: substrate (0.11 mmol), CF3TMS (2.0 equiv) and 1.5 mL solvent were used, reaction time 12 h.
[b] yield was determined by 19F NMR using hexafluorobenzene as internal standard.
[c] (1.0 equiv) of tBuOK and TBAF were used.
4. Standard procedure for copper(I) catalyzed trifluoromethylation of diaryliodonium salt:

![Chemical structure](image)

In an oven dried reaction tube KF (6.7 mg, 0.11 mmol) was taken, then evacuated with flame heating and refilled with argon three times. CuI (2.2 mg, 0.01 mmol), PPh₃ (3.0 mg, 0.01 mmol), and a solution of diaryliodonium salt 1/6 (50 mg, 0.11 mmol) in 1.5 mL DMF were added under argon atmosphere and the reaction mixture was stirred at room temperature until a homogeneous solution was obtained. Next, CF₃TMS (33.0 mg, 0.23 mmol, 34 µl) was added, sealed with stopper and kept at 65 ºC on preheated oil bath. The reaction mixture was stirred for 12 h, then cooled to room temperature. Hexafluorobenzene was added as internal standard (17.0 mg, 0.09 mmol). The crude mixture was analyzed by ¹⁹F NMR.

5. ¹⁹F NMR and GCMS diagram for synthesized product:

**Trifluoromethylbenzene 2a:**

![Chemical structure](image)

The product trifluoromethylbenzene was synthesized from diphenyliodoniumtriflate in 85% yield. Yield was determined by ¹⁹F NMR spectroscopy using hexafluorobenzene (17.0 mg, 0.09 mmol) as the internal standard. The product peak was observed at (-65.4 ppm) in ¹⁹F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 2.07 min
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C)

Mass spectrum of product peak (2.07 min) from GCMS analysis:

Abundance
1,4-dimethyl-2-(trifluoromethyl)benzene 2b:

![Chemical Structure](image)

The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(2,5-dimethylphenyl)iodoniumtriflate to achieve 1,4-dimethyl-2-(trifluoromethyl)benzene in 85% yield using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (20 mg, 0.10 mmol) as internal standard. The product peak was observed at (-64.55 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 4.30 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):
1-(Trifluoromethyl)naphthalene 2c:

The reaction was performed on a (50 mg, 0.09 mmol) scale of di(naphthalen-1-yl)iodoniumtriflate to achieve 1-(trifluoromethyl)naphthalene in 68% yield using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (21.3 mg, 0.11 mmol) as the internal standard. The product peak was observed at (-62.15 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 18.60 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

Mass spectrum of product peak (18.60 min) from GCMS analysis:
1-Bromo-4-(trifluoromethyl)benzene 2d. ³a

The reaction was performed on a (50 mg, 0.08 mmol) scale of bis(4-bromophenyl)iodoniumtriflate to achieve 1-bromo-4-(trifluoromethyl)benzene 59% yield, along with 8% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by ¹⁹F NMR spectroscopy using hexafluorobenzene (19.4 mg, 0.10 mmol) as internal standard. The product peak was observed at (-65.73 ppm) in ¹⁹F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 5.25 min.

¹⁹F NMR (470 MHz, CDCl₃/C₆F₆, 24°C):

Mass spectrum of product peak (5.25 min) from GCMS analysis:

1-Chloro-4-(trifluoromethyl)benzene 2e:

The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(4-chlorophenyl)iodoniumtriflate to achieve 1-chloro-4-(trifluoromethyl)benzene in 42% yield using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (15.5 mg, 0.08 mmol) as internal standard. The product peak was observed at (-65.50 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 3.46 min.
\[19^F\text{NMR (470 MHz, CDCl}_3/C_6\text{F}_6, 24^\circ\text{C}):\]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{19F_NMR_spectrum.png}
\caption{19F NMR spectrum of the product.}
\end{figure}

Mass spectrum of product peak (3.46 min) from GCMS analysis:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Mass_spectrometry.png}
\caption{Mass spectrum of the product peak.}
\end{figure}
1-Methoxy-4-(trifluoromethyl)benzene 2f \(^{3a}\)

The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(4-methoxyphenyl)iodoniumtriflate to achieve 1-methoxy-4-(trifluoromethyl)benzene in 97% yield using standard procedure. The yield was determined by \(^{19}\)F NMR spectroscopy using hexafluorobenzene (17.0 mg, 0.09 mmol) as internal standard. The product peak was observed at (-64.41 ppm) in \(^{19}\)F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 4.88 min.

\(^{19}\)F NMR (470 MHz, CDCl\(_3\)/C\(_6\)F\(_6\), 24\(^{\circ}\)C):
Mass spectrum of product peak (4.88 min) from GCMS analysis:

1-nitro-4-(trifluoromethyl)benzene 2g:

The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(4-nitrophenyl)iodoniumtriflate to achieve 1-nitro-4-(trifluoromethyl)benzene in 60% yield, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (18.9 mg, 0.10 mmol) as internal standard. The product peak was observed at (-66.03 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 6.09 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

Mass spectrum of product peak (6.09 min) from GCMS analysis:
1-Methyl-4-(trifluoromethyl)benzene 2i:

The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(p-tolyl)iodoniumtriflate to achieve 1-methyl-4-(trifluoromethyl)benzene in 56% yield along with 22% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (21.8 mg, 0.11 mmol) as internal standard. The product peak was observed at (-65.13 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 3.07 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):
Mass spectrum of product peak (3.07 min) from GCMS analysis:

1-(tert-butyl)-4-(trifluoromethyl)benzene 2j:

The reaction was performed on a (50 mg, 0.09 mmol) scale of (4-(tert-butyl)phenyl)(mesityl)iodoniumtriflate to achieve 1-(tert-butyl)-4-(trifluoromethyl)benzene in 69% yield along with 18% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (17.4 mg, 0.09 mmol) as internal standard. The product peak was observed at (~65.1 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 5.86 min.
\[ 19^F \text{NMR (470 MHz, CDCl}_3/C_6\text{F}_6, 24^\circ\text{C}) : } \]

\[
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\text{Td} & : 13872 \\
\text{Solvent} & : CDCl3 \\
\text{Ns} & : 16 \\
\text{Ds} & : 4 \\
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\text{Fidres} & : 0.9899777 \text{Hz} \\
\text{Rg} & : 205.34 \\
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\text{Te} & : 298.0 \text{K} \\
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\[
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\text{Gb} & : 0.30 \text{Hz} \\
\text{Pc} & : 1.00 \\
\end{align*}
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\[ \text{Mass spectrum of product peak (5.86 min) from GCMS analysis:} \]
4-(trifluoromethyl)-1,1'-biphenyl 2k.\textsuperscript{3a}

The reaction was performed on a (50 mg, 0.09 mmol) scale of [1,1'-biphenyl]-4-yl(mesityl)iodoniumtriflate to achieve 4-(trifluoromethyl)-1,1'-biphenyl in 81% yield along with 17% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. Yield was determined by \textsuperscript{19}F NMR spectroscopy using hexafluorobenzene (19.0 mg, 0.10 mmol) as the internal standard. The product peak was observed at (-65.4 ppm) in \textsuperscript{19}F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 11.06 min.

\textbf{\textsuperscript{19}F NMR (470 MHz, CDCl\textsubscript{3}/C\textsubscript{6}F\textsubscript{6}, 24°C):}

![\textsuperscript{19}F NMR spectrum]
Mass spectrum of product peak (11.06 min) from GCMS analysis:

1-Methyl-2-(trifluoromethyl)benzene 2l:

The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(o-tolyl)iodoniumtriflate to achieve 1-methyl-2-(trifluoromethyl)benzene in 65% yield, along with 14% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (19.6 mg, 0.10 mmol) as internal standard. The product peak was observed at (-64.22 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 3.05 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

\[
\begin{align*}
&\text{Mass spectrum of product peak (3.05 min) from GCMS analysis:}
\end{align*}
\]
1-(trifluoromethyl)naphthalene 2m:

![Chemical Structure]

The reaction was performed on a (40 mg, 0.07 mmol) scale of 2-(naphthalenyl)(mesityl)iodoniumtriflate to achieve 2-(trifluoromethyl)naphthalene in 78% yield, along with 16% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (18.8 mg, 0.10 mmol) as internal standard. The product peak was observed at (-65.2 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 8.36 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

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F2 - Processing parameters
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GB              1.00
PC                 1.00
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Mass spectrum of product peak (8.36 min) from GCMS analysis:

1,3-dimethyl-5-(trifluoromethyl)benzene 2n:

The reaction was performed on a (50 mg, 0.10 mmol) scale of 3,5-dimethylphenyl)(mesityl)iodoniumtriflate to achieve 1,3-dimethyl-5-(trifluoromethyl)benzene in 84% yield along with 9% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (17.4 mg, 0.09 mmol) as internal standard. The product peak was observed at (-65.26 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 4.17 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

Mass spectrum of product peak (4.17 min) from GCMS analysis:

Abundance

Scan 407 (4.177 min): VKP-1147-xylene D.D\_data.ms

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1-Fluoro-4-(trifluoromethyl)benzene 2o:

The reaction was performed on a (50 mg, 0.10 mmol) scale of 4-(fluorophenyl)(mesityl)iodoniumtriflate to achieve 1-fluoro-4-(trifluoromethyl)benzene in 72% yield, along with 23% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (18.0 mg, 0.09 mmol) as internal standard. The product peak was observed at (-64.98 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 8.94 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

![19F NMR spectrum](image)
Mass spectrum of product peak (8.94 min) from GCMS analysis:

1-iodo-4-(trifluoromethyl)benzene 2p:

The reaction was performed on a (50 mg, 0.08 mmol) scale of (4-iodophenyl)(mesityl)iodoniumtriflate to achieve 1-iodo-4-(trifluoromethyl)benzene in 61% yield, along with 10% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (16.10 mg, 0.08 mmol) as internal standard. The product peak was observed at (-65.69 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 6.03 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

Mass spectrum of product peak (6.03 min) from GCMS analysis:
1,4-bis(trifluoromethyl)benzene 2q:

The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(4-(trifluoromethyl)phenyl)iodoniumtriflateto achieve 1,4-bis(trifluoromethyl)benzene in 71% yield along with trace amount of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (19.1 mg, 0.10 mmol) as internal standard. The product peak was observed at (-65.87 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 15.10 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):
Mass spectrum of product peak (15.10 min) from GCMS analysis:

4-(trifluoromethyl)benzonitrile 2r:

[Chemical structure image]

The reaction was performed on a (50 mg, 0.10 mmol) scale of 4-(cyanophenyl)(mesityl)iodoniumtriflate to achieve 4-(trifluoromethyl)benzonitrile in 57% yield, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (19.6 mg, 0.10 mmol) as internal standard. The product peak was observed at (-66.54 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 4.92 min.
**19F NMR (470 MHz, CDCl₃/C₆F₆, 24°C):**

![Chemical Structure]

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- **DS:** 4
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- **FIDRES:** 0.866977 Hz
- **AQ:** 0.5767168 sec
- **RG:** 202.34
- **DW:** 4.400 usec
- **DE:** 6.50 usec
- **TE:** 295.8 K
- **D1:** 1.00000000 sec
- **D11:** 0.03000000 sec
- **D12:** 0.00002000 sec
- **TD0:** 1

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- **PLW1:** 46.00000000 W

**======== CHANNEL f2 ========**
- **SFO2:** 500.1520006 MHz
- **NUC2:** 1H
- **CPDPRG[2:** waltz16
- **PCPD2:** 80.00 usec
- **PLW2:** 15.30000019 W

**F2 - Processing parameters**
- **SI:** 65536
- **SF:** 470.6124403 MHz
- **WDW:** EM
- **SSB:** 0
- **LB:** 0.30 Hz
- **GB:** 0
- **PC:** 1.00

---

**Mass spectrum of product peak (4.92 min) from GCMS analysis:**

![Mass Spectrum]
Ethyl 4-(trifluoromethyl)benzoate 2s :³a

The reaction was performed on a (50 mg, 0.09 mmol) scale of (4-ethoxycarbonyl)phenyl)(mesityl)iodonium triflate to achieve ethyl 4-(trifluoromethyl)benzoate in 72% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by ¹⁹F NMR spectroscopy using hexafluorobenzene (19.7 mg, 0.10 mmol) as internal standard. The product peak was observed at (-66.01 ppm) in ¹⁹F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 7.67 min.

¹⁹F NMR (470 MHz, CDCl₃/C₆F₆, 24°C):
Mass spectrum of product peak (7.67 min) from GCMS analysis:

Phenyl(4-(trifluoromethyl)phenyl)methanone 2t:3b

The reaction was performed on a (50 mg, 0.08 mmol) scale of (4-benzoylphenyl)(mesityl)iodoniumtriflate to achieve phenyl(4-(trifluoromethyl)phenyl)methanone in 93% yield along with 6% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (13.8 mg, 0.07 mmol) as internal standard. The product peak was observed at (-65.78 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 13.48 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

![Chemical Structure](image)

Current Data Parameters
- **NAME**: all product spectra
- **EXPNO**: 146
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20150529
- **Time**: 15.19
- **INSTRUM**: spect
- **PROBHD**: 5 mm PABBO BB/
- **PULPROG**: zgfhigqn.2
- **TD**: 1310.72
- **SOLVENT**: CDCl3
- **NS**: 16
- **DS**: 4
- **SWH**: 113636.367 Hz
- **FIDRES**: 0.986977 Hz
- **RG**: 202.34
- **DE**: 6.50 usec
- **TE**: 294.4 K
- **D1**: 1.02000000 sec
- **D11**: 0.03000000 sec
- **D12**: 0.00000000 sec
- **TD0**: 1

**====== CHANNEL f1 ========**
- **SFO1**: 470.5641349 MHz
- **NUC1**: 19F
- **P1**: 15.00 usec
- **PLW1**: 46.00000000 W

**====== CHANNEL f2 ========**
- **SFO2**: 500.1520006 MHz
- **NUC2**: 1H
- **CPDPRG**: waltz16
- **PCPD2**: 80.00 usec
- **PLW2**: 15.30000019 W
- **PLW12**: 0.33006001 W

**F2 - Processing parameters**
- **SI**: 65536
- **SF**: 470.6124958 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 0.30 Hz
- **QB**: 0
- **PC**: 1.00

Mass spectrum of product peak (13.48 min) from GCMS analysis:

![Mass Spectrum](image)
1-(4-(trifluoromethyl)phenyl)ethanone 2u:

The reaction was performed on a (50 mg, 0.09 mmol) scale of (4-acetylphenyl)(mesityl)iodonium to achieve 1-(4-(trifluoromethyl)phenyl)ethanone in 94% yield along with 4% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (20.0 mg, 0.10 mmol) as internal standard. The product peak was observed at (-65.70 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 6.03 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

![19F NMR spectrum](image)
Mass spectrum of product peak (6.03 min) from GCMS analysis:

1-nitro-2-(trifluoromethyl)benzene 2v:

![Chemical structure of 1-nitro-2-(trifluoromethyl)benzene 2v]

The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(2-nitrophenyl)iodoniumtriflate to achieve 1-nitro-2-(trifluoromethyl)benzene in 54% yield, using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (18.5 mg, 0.09 mmol) as internal standard. The product peak was observed at (-63.02 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 7.0 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C)

Mass spectrum of product peak (7.0 min) from GCMS analysis:
2-Trifluoromethylthiophene 2w:

![Chemical structure of 2-Trifluoromethylthiophene 2w](image)

The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(thiophen-2-yl)iodoniumtriflate to achieve 2-(trifluoromethyl)thiophene in 49% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (19.60 mg, 0.10 mmol) as internal standard. The product peak was observed at (-57.92 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 15.34 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):
Mass spectrum of product peak (15.34 min) from GCMS analysis:

2-Chloro-5-(trifluoromethyl)pyridine 2x:

The reaction was performed on a (50 mg, 0.09 mmol) scale of 6-chloropyridin-3-yl)(mesityl)iodoniumtriflate to achieve 2-chloro-5-(trifluoromethyl)pyridine in 72% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (17.30 mg, 0.09mmol) as internal standard. The product peak was observed at (-65.11 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 3.76 min.
$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

![Chemical Structure]

Current Data Parameters
- NAME: all product spectra
- EXPNO: 70
- PROCNO: 1

F2 - Acquisition Parameters
- Date: 20150518
- Time: 14.12
- INSTRUM: spect
- PROBHD: 5 mm PABBO BB/
- PULPROG: zgfhigqn.2
- TD: 131072
- SOLVENT: CDCl3
- NS: 16
- DS: 4
- SWH: 113636.367 Hz
- FIDRES: 0.866977 Hz
- AQ: 0.5767168 sec
- RG: 202.34
- DW: 4.400 usec
- DE: 6.50 usec
- TE: 296.2 K
- D1: 1.0000000 sec
- D11: 0.000000 sec
- D12: 0.0000200 sec
- D10: 1

-------- CHANNEL f1 --------
- SFO1: 470.5641349 MHz
- NUC1: 19F
- P1: 15.00 usec
- PLW1: 46.0000000 W

-------- CHANNEL f2 --------
- SFO2: 500.1520006 MHz
- NUC2: 1H
- CPDPRG[2: waltz16
- PCPD2: 80.00 usec
- PLW2: 15.30000019 W
- PLW12: 0.3300600 W

F2 - Processing parameters
- SI: 65536
- SF: 470.6123900 MHz
- WDW: EM
- SSB: 0
- LB: 0.30 Hz
- GB: 1.00
- PC: 1.00

Mass spectrum of product peak (16.76 min) from GCMS analysis:
6-Trifluoromethylquinoline 2y:3c

The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(quinolin-6-yl)iodonium triflate to achieve 6-(trifluoromethyl)quinoline in 88% yield along with 2% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by $^{19}$F NMR spectroscopy using hexafluorobenzene (19.7 mg, 0.10 mmol) as internal standard. The product peak was observed at (-65.22 ppm) in $^{19}$F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 8.73 min.

$^{19}$F NMR (470 MHz, CDCl$_3$/C$_6$F$_6$, 24°C):

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Current Data Parameters
NAME: all product spectra
EXPNO: 61
PROCNO: 1

F2 - Acquisition Parameters
Date: 20150512
Time: 21:57
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zgfhigqn.2
TD: 131072
SOLVENT: CDCl3
NS: 16
DS: 4
SWH: 113636.367 Hz
FIDRES: 0.866977 Hz
AQ: 0.5757168 sec
RG: 203.34
DW: 4.400 usec
DE: 6.50 usec
TE: 298.0 K
D1: 1.00000000 sec
D11: 0.03000000 sec
D12: 0.00002000 sec

F2 - Processing parameters
SI: 65536
SF: 470.6122651 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
PC: 1.00
Mass spectrum of product peak (8.73 min) from GCMS analysis:
6. Electronic and steric factor (Effect of substituent):

In order to understand the effect of substituent like, electron withdrawing electron releasing and neutral substrate has been subjected under standard reaction condition. The result is given in the scheme.

7. Mechanistic study:

7a. Radical scavenger experiment:

Copper(I) catalyzed trifluoromethylation of diphenyliodonium salt 1a with 2 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was performed, employing standard conditions, which the formation of trifluoromethylbenzene in 89% yield.
Without diaryliodonium salt under the standard reaction condition with (1 equiv.) of TEMPO, we did not observe TEMPO-CF$_3$ substituted product.

7b. Radical clock probe experiment:

Radical clock probe experiment was performed with (2-(allyloxy)phenyl)(mesityl)iodoniumtrifluoromethanesulfonate, which was synthesized according to literature procedure. (2-allyloxy)phenyl)(mesityl)iodonium trifluoromethanesulfonate was subjected under standard conditions and we observed 1-(allyloxy)-2-(trifluoromethyl)benzene in 36% yield, along with 50% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product. There is no formation any cyclized product. The yield was determined by $^{19}$F NMR using hexafluorobenzene as internal standard. The formation of product was further confirmed by GCMS.

The above experiment suggests that, formation of trifluoromethyl radical or aryl radical is less likely.
7c. \(^{31}\text{P}\) and \(^{19}\text{F}\) NMR studies:

To identify the possible intermediate species formation, \(^{31}\text{P}\) and \(^{19}\text{F}\) NMR studies were performed at various temperatures (\(-50^\circ\text{C}\) to \(+50^\circ\text{C}\)).

**Equimolar mixture of CuI and PPh\(_3\)**

\(^{31}\text{P}\) NMR (202 MHz, DMF, 24°C):

---

**Equimolar mixture of CuI, PPh\(_3\), CF\(_3\)TMS and KF at variable temperature**

\(^{31}\text{P}\) NMR (202 MHz, DMF, 24°C):
**$^{19}$F NMR (470 MHz, DMF, 24°C):**

-50 °C
-30 °C
0 °C
+30 °C
+50 °C

**Equimolar mixture of CuI, PPh₃, CF₃TMS, KF and mesityl(4-methylphenyl)iodonium triflate at variable temperature**

**$^{31}$P NMR (202 MHz, DMF, 24°C):**

-50 °C
-30 °C
0 °C
+30 °C
+50 °C

**$^{19}$F NMR (470 MHz, DMF, 24°C):**

-50 °C
-30 °C
0 °C
+30 °C
+50 °C
8. NMR spectra of isolated compound

1-Bromo-4-(trifluoromethyl)benzene 2d:

\[ ^1H \text{NMR (500 MHz, CDCl}_3, 24^\circ C) : \]

\[
\text{Br} \quad \text{CF}_3
\]

\[
\begin{array}{c}
\end{array}
\]

\[ ^19F \text{NMR (470 MHz, CDCl}_3, 24^\circ C) : \]

\[
\begin{array}{c}
-62.650
\end{array}
\]
1-Methoxy-4-(trifluoromethyl)benzene 2f:

$^1$H NMR (400 MHz, CDCl$_3$, 24°C):

```
H NMR (400 MHz, CDCl$_3$, 24°C):
```

```
Current Data Parameters
NAME           spa41015
EXPNO                190
PROCNO                1
F2 - Acquisition Parameters
Date_          20151009
Time              17.07
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH          8012.820 Hz
FIDRES     0.122266 Hz
AQ            4.0894465 sec
RG                25
DW               2.500 usec
DE                 6.50 usec
TE                293.1 K
D1           0.50000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                15.70 usec
PLW1         7.75000000 W
SFO1        400.1320007 MHz
F2 - Processing parameters
SI                65536
SF          400.1300095 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):

```
$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):
```

```
Current Data Parameters
NAME           spa41015
EXPNO                72
PROCNO                1
F2 - Acquisition Parameters
Date_          20151011
Time              16.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH          113636.367 Hz
FIDRES     0.866977 Hz
AQ            0.5767168 sec
RG               202.34
DW                4.400 usec
DE                 6.50 usec
TE                295.9 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00000000 sec
TD0                   1
======== CHANNEL f1 ========
SFO1        470.5641349 MHz
NUC1                1H
P1                15.00 usec
PLW1        46.00000000 W
======== CHANNEL f2 ========
SFO2        500.1520006 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        15.30000019 W
PLW12        0.33006001 W
F2 - Processing parameters
SI           65536
SF         470.6111960 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                 1.00
```

```
``
4-(trifluoromethyl)-1,1'-biphenyl 2k:

$^1$H NMR (500 MHz, CDCl$_3$, 24°C):

![Chemical Structure Image]

$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):

![Chemical Structure Image]
Ethyl 4-(trifluoromethyl)benzoate 2s:

$^1$H NMR (400 MHz, CDCl$_3$, 24°C):

![NMR spectrum for ethyl 4-(trifluoromethyl)benzoate 2s](image)

$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):

![NMR spectrum for ethyl 4-(trifluoromethyl)benzoate 2s](image)
Phenyl(4-(trifluoromethyl)phenyl)methanone 2t:

$^1$H NMR (400 MHz, CDCl$_3$, 24°C):

$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):
6-Trifluoromethylquinoline 2y:

$^1$H NMR (400 MHz, CDCl$_3$, 24°C):

$^{19}$F NMR (470 MHz, CDCl$_3$, 24°C):