

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 CaH<sub>2</sub> and stored over molecular sieves 4Å under N<sub>2</sub> atmosphere. The other dry solvent was also prepared by employing standard distillation procedure and stored over molecular sieves 4Å under N<sub>2</sub> atmosphere.

(Trifluoromethyl)trimethylsilane, KF, CuI, PPh<sub>3</sub>, 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 iododiacetate<sup>1</sup> and diaryliodonium<sup>2</sup> 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:

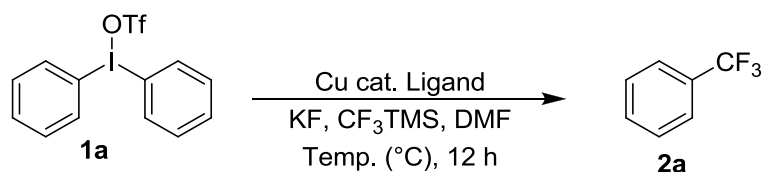
NMR data were recorded on Bruker DPX 400 and AVC 500 MHz spectrometers. <sup>13</sup>C and <sup>1</sup>H NMR spectra were referenced to signals of deuterio solvents and residual protiated solvents, respectively. <sup>19</sup>F NMR spectra were recorded on AVC 470 MHz spectrometers using hexafluorobenzene as standard. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spray 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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<sup>1</sup> Bielawski, M.; Olofsson, B. *Chem. Commun.* **2007**, 2521–2523;

<sup>2</sup>a) Bielawski, M.; Malmgren, J.; Pardo, L. M.; Wikmark, Y.; Olofsson, B. *ChemistryOpen* **2014**, 3, 19–22; b) Bielawski, M.; Aili, D.; Olofsson, B. *J. Org. Chem.* **2008**, 73, 4602–4607

### 3. Copper(I) catalyzed trifluoromethylation of diphenyliodonium salt: Optimization:

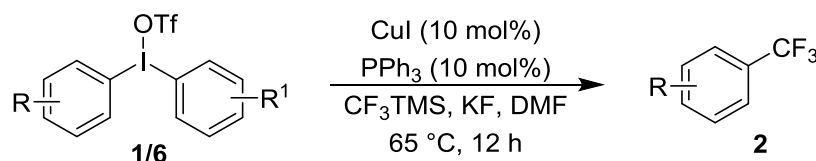


**Table S1: Copper (I) mediated trifluoromethylation of 1a:**

Entry	Cu Cat. (equiv)	Ligand (equiv)	F source (equiv)	Solvent (mL)	Temp. (°C)	Yield(%) <sup>b</sup>
1	CuI (0.2)	–	CsF (1)	DMF	65	50
2	CuI (0.2)	–	KF (1)	DMF	65	75
3	CuI (0.2)	–	<sup>t</sup> BuOK	DMF	65	7 <sup>c</sup>
4	CuI (0.2)	–	TBAF	DMF	65	15 <sup>c</sup>
5	CuI (0.1)	–	KF (1)	DMF	65	65
6	CuI (0.1)	X-Phos (0.1)	KF (1)	DMF	65	91
7	CuI (0.1)	Bipy (0.1)	KF (1)	CH <sub>3</sub> CN	65	48
8	CuI (0.1)	<i>o</i> -phen (0.1)	KF (1)	DMF	65	71
9	CuI (0.1)	P(tolyl) <sub>3</sub> (0.1)	KF (1)	DMF	65	88
10	CuI (0.1)	DPPE (0.1)	KF (1)	DMF	65	86
11	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DMF	65	85
12	Cu(OTf) <sub>2</sub> (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DMF	65	10
13	Cu(CH <sub>3</sub> CN)BF <sub>4</sub> (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DMF	65	6
14	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	CH <sub>3</sub> CN	65	23
15	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DCE	65	2
16	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	Dioxane	65	32
17	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	Toluene	65	3
18	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DMF	rt	20
19	CuI (0.1)	PPh <sub>3</sub> (0.1)	KF (1)	DMF	90	83
20	CuI (0.1)	PPh <sub>3</sub> (0.1)	–	DMF	65	0
21	–	–	KF (1)	DMF	65	0

[a] reaction condition: substrate ( 0.11 mmol), CF<sub>3</sub>TMS (2.0 equiv) and 1.5 mL solvent were used, reaction time 12 h.[b] yield was determine by <sup>19</sup>F NMR using hexafluorobenzene as internal standard.[c] (1.0 equiv) of <sup>t</sup>BuOK and TBAF were used.

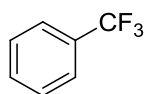
#### 4. Standard procedure for copper(I) catalyzed trifluoromethylation of diaryliodonium salt:



In an oven dried reaction tube KF (6.7 mg, 0.11mmol) was taken, then evacuated with flame heating and refilled with argon three times. CuI (2.2 mg, 0.01 mmol), PPh<sub>3</sub> (3.0 mg, 0.01mmol), 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, CF<sub>3</sub>TMS (33.0 mg, 0.23 mmol, 34  $\mu$ l) was added, sealed with stopper and kept at 65 °C 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, 0.09mmol). The crude mixture was analyzed by <sup>19</sup>F NMR.

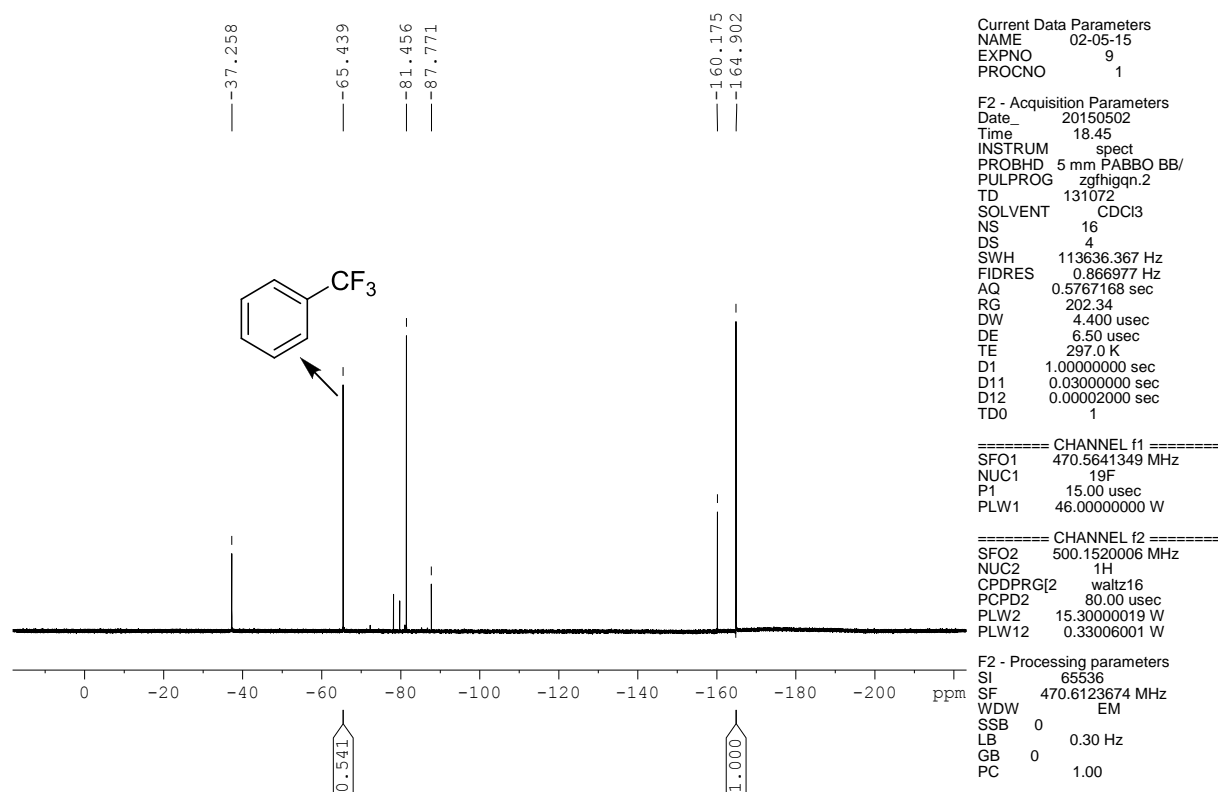
#### 5. <sup>19</sup>F NMR and GCMS diagram for synthesized product:

##### Trifluoromethylbenzene **2a**:



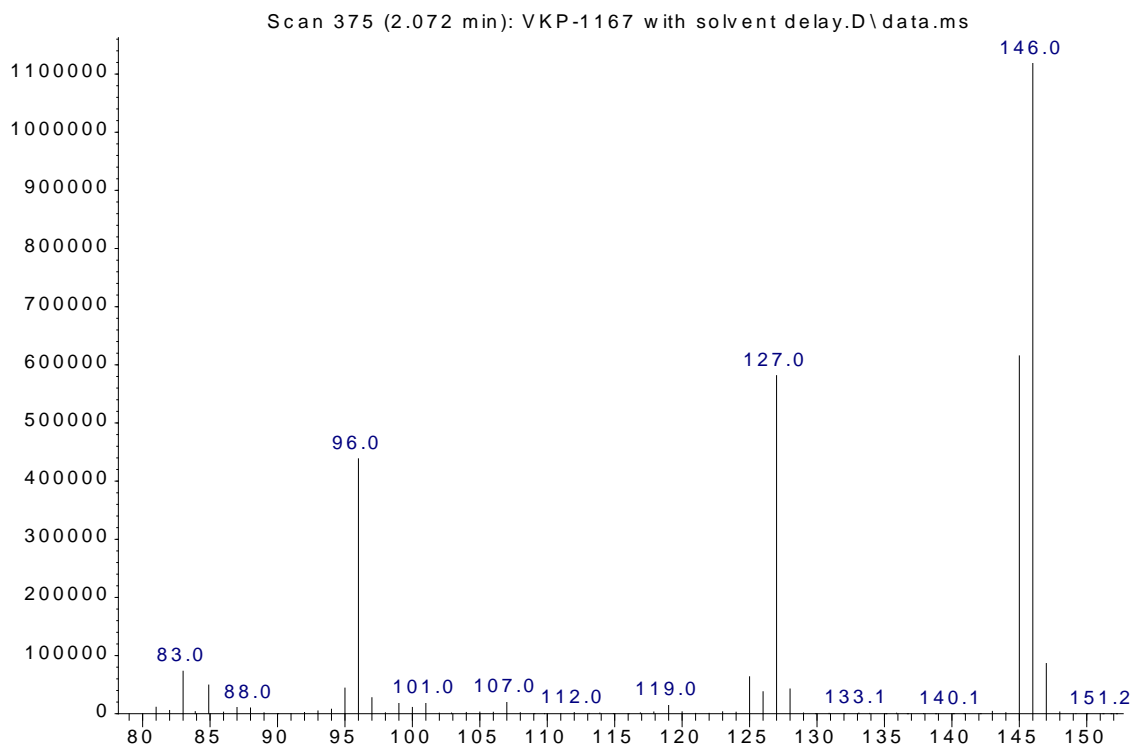
The product trifluoromethylbenzene was synthesized from diphenyliodoniumtriflate in 85% yield. Yield was determined by <sup>19</sup>F NMR spectroscopy using hexafluorobenzene (17.0 mg, 0.09mmol) as the internal standard. The product peak was observed at (-65.4 ppm) in <sup>19</sup>F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 2.07 min

# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C)



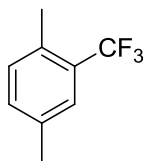
## Mass spectrum of product peak (2.07 min) from GCMS analysis:

Abundance



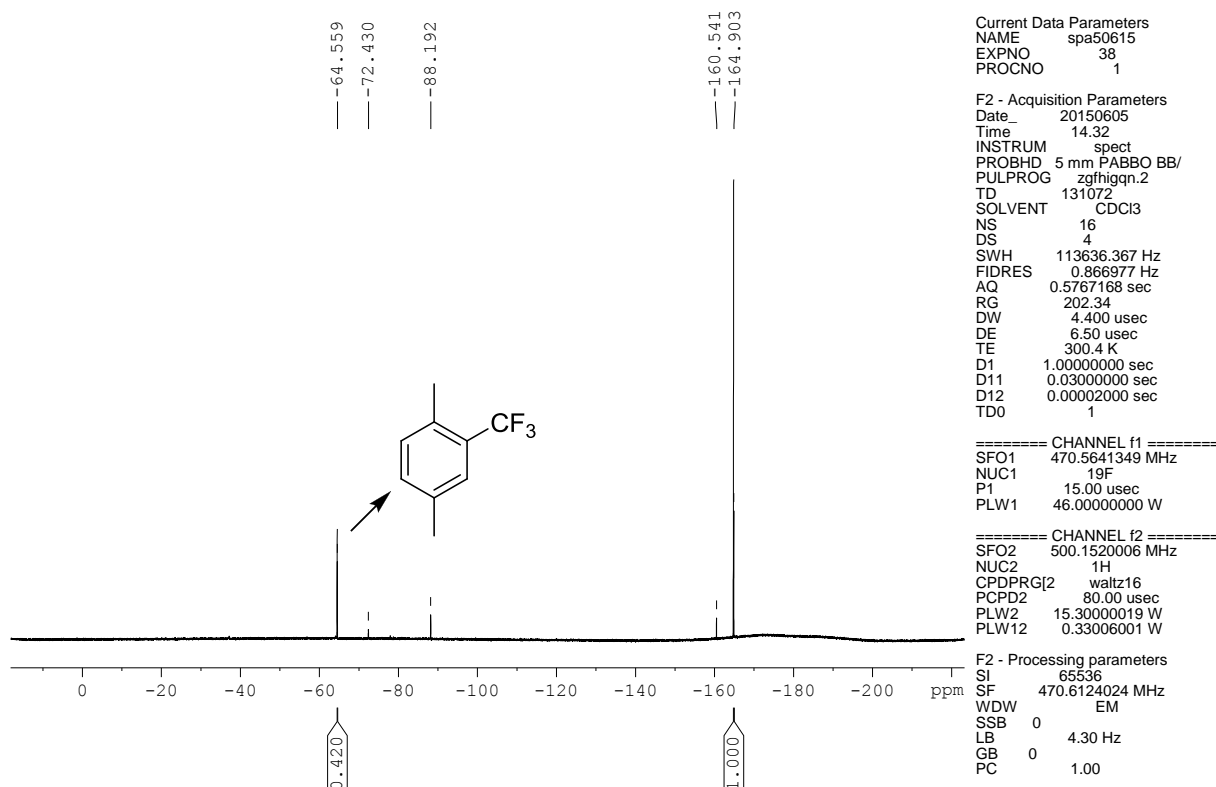
m/z-->

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

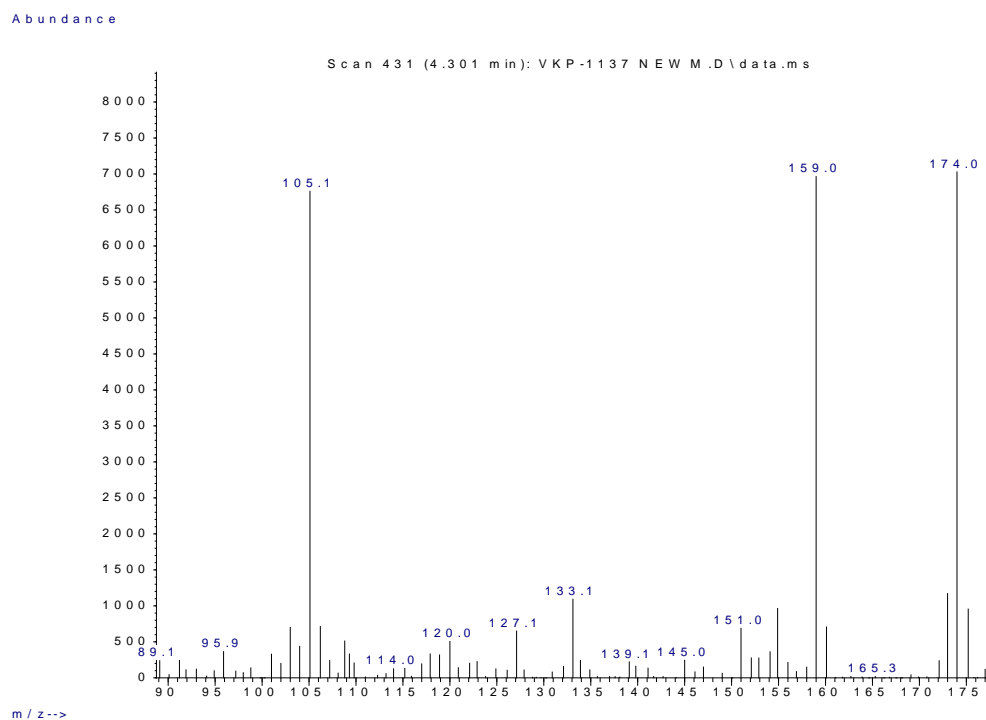


The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(2,5-dimethylphenyl)iodoniumtriflate to achieve 1,4-dimethyl-2-(trifluoromethyl)benzene in 85% yield using standard procedure. The yield was determined by  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (20 mg, 0.10 mmol) as internal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

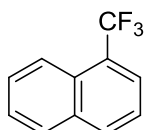
### $^{19}\text{F}$ NMR (470 MHz, $\text{CDCl}_3/\text{C}_6\text{F}_6$ , 24°C):



## Mass spectrum of product peak (4.30 min) from GCMS analysis:

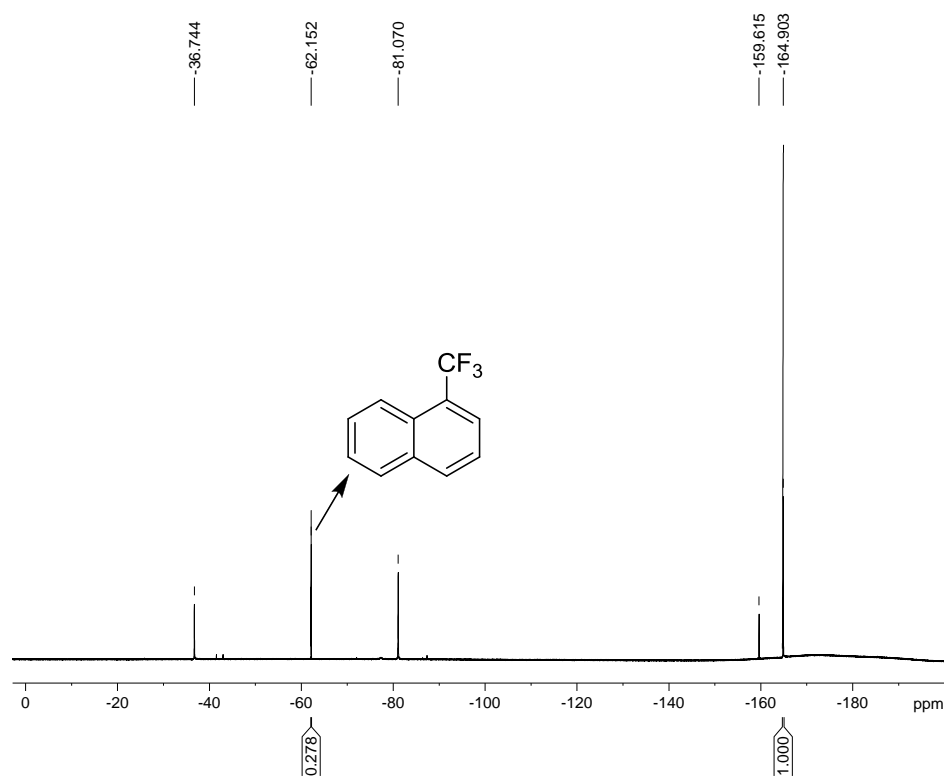


### 1-(Trifluoromethyl)naphthalene 2c:



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  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (21.3 mg, 0.11 mmol) as the internal standard. The product peak was observed at (-62.15 ppm) in  $^{19}\text{F}$  NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 18.60 min.

# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



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PROCNO 1

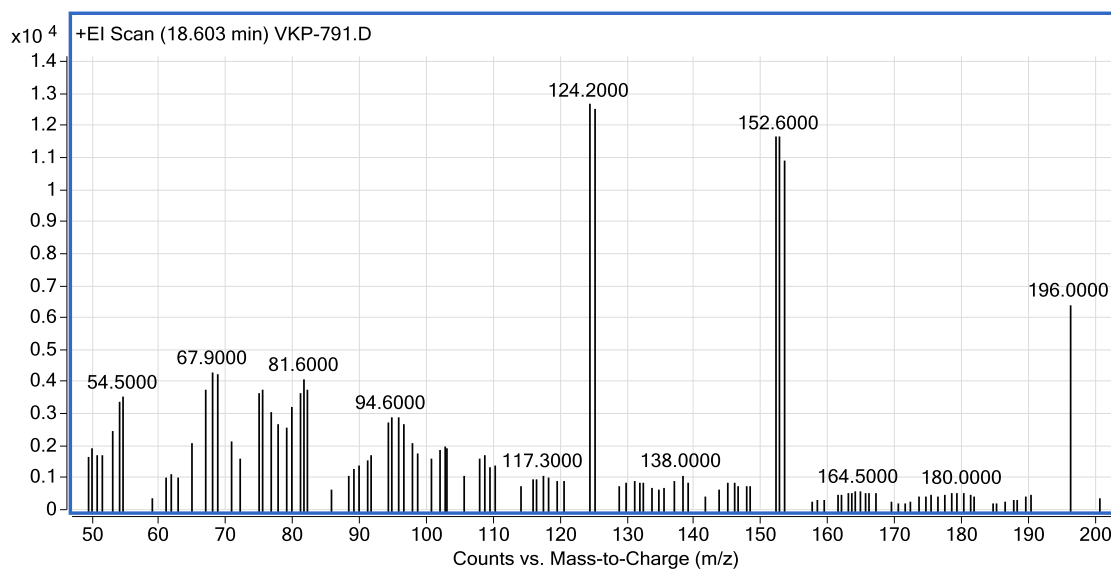
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SOLVENT CDCl3  
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DS 4  
SWH 113636.367 Hz  
FIDRES 0.866977 Hz  
AQ 0.5767168 sec  
RG 202.34  
DW 4.400 usec  
DE 6.50 usec  
TE 296.9 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
D12 0.00002000 sec  
TD0 1

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NUC1 19F  
P1 15.00 usec  
PLW1 46.00000000 W

==== CHANNEL f2 =====  
SFO2 500.1520006 MHz  
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PCPD2 80.00 usec  
PLW2 15.30000019 W  
PLW12 0.33006001 W

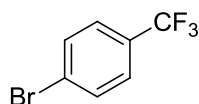
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## Mass spectrum of product peak (18.60 min) from GCMS analysis:



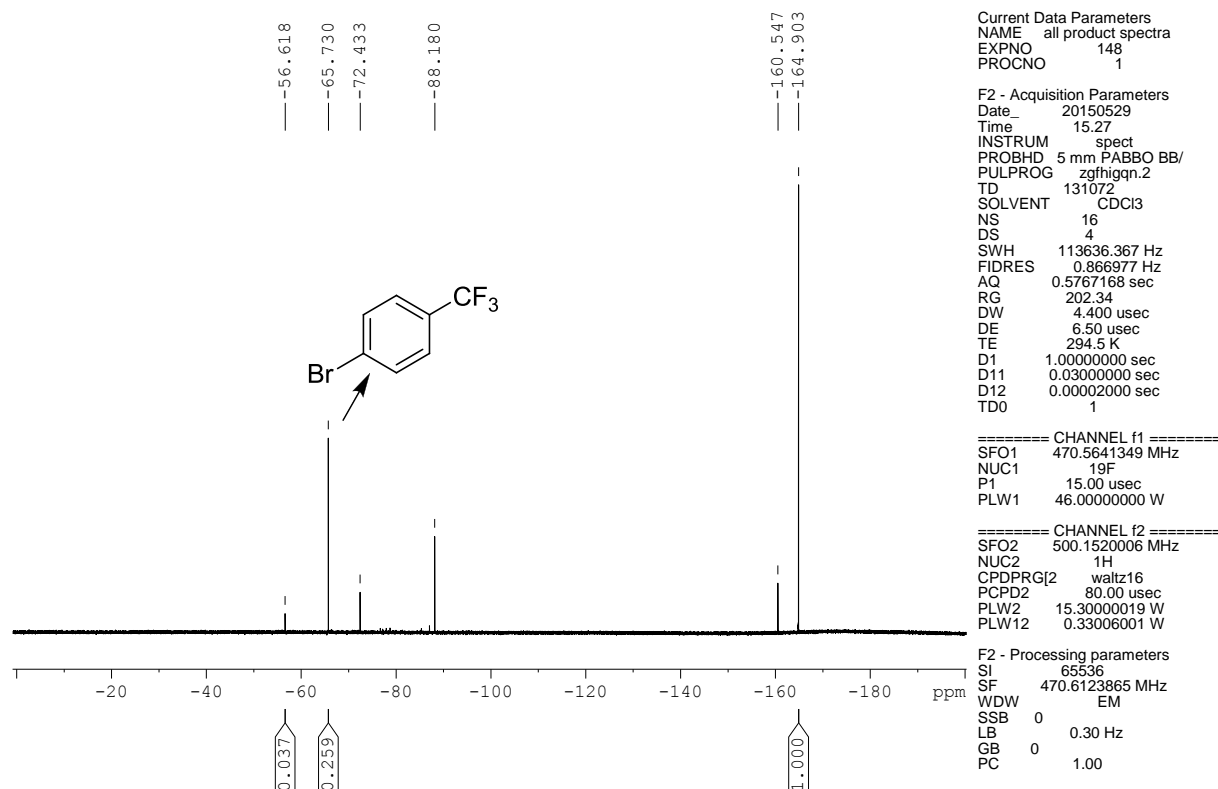


## 1-Bromo-4-(trifluoromethyl)benzene 2d:<sup>3a</sup>



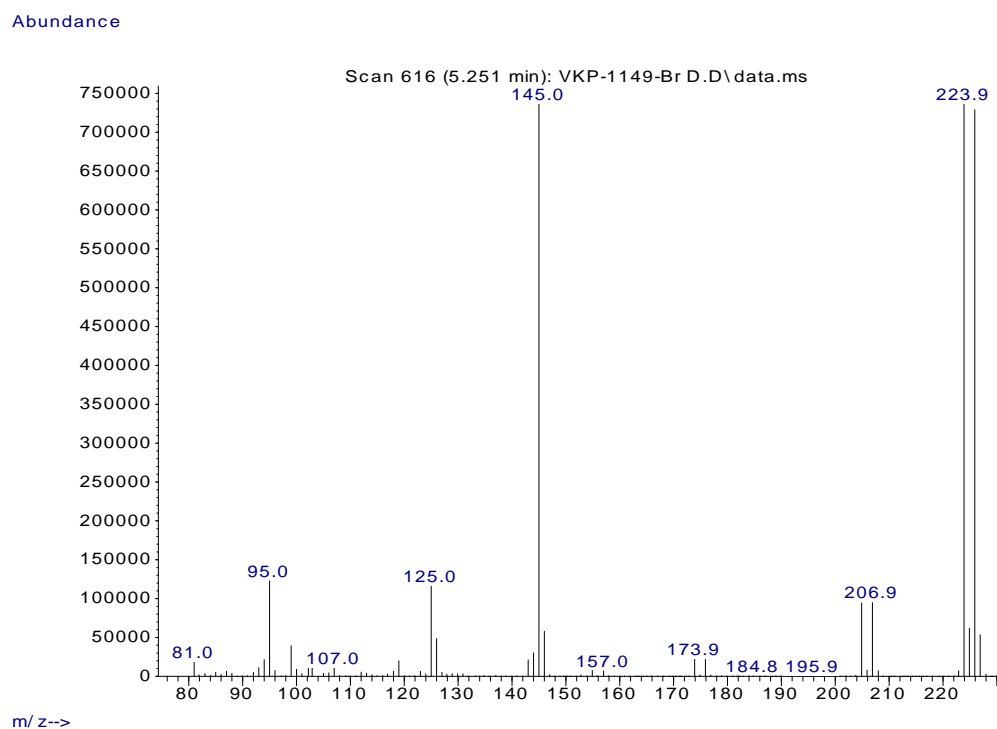
The reaction was performed on a (50 mg, 0.08 mmol) scale of bis(4-bromophenyl)iodoniumtriflate to achieve 1-bromo-4-(trifluoromethyl)benzene 59% yield, along with 8% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by <sup>19</sup>F NMR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

### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):

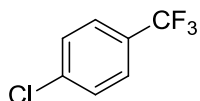


<sup>3a)</sup> Morimoto, H.; Tsubogo, T.; Litvinas, N. D.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 3793; b) Khan, B. A.; Buba, A. E.; Gooßen, L. J. *Chem. Eur. J.* **2012**, *18*, 1577; c) Zheng, J.; Lin, J-H.; Deng, X-Y.; Xiao, J-C. *Org. Lett.* **2015**, *17*, 532

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

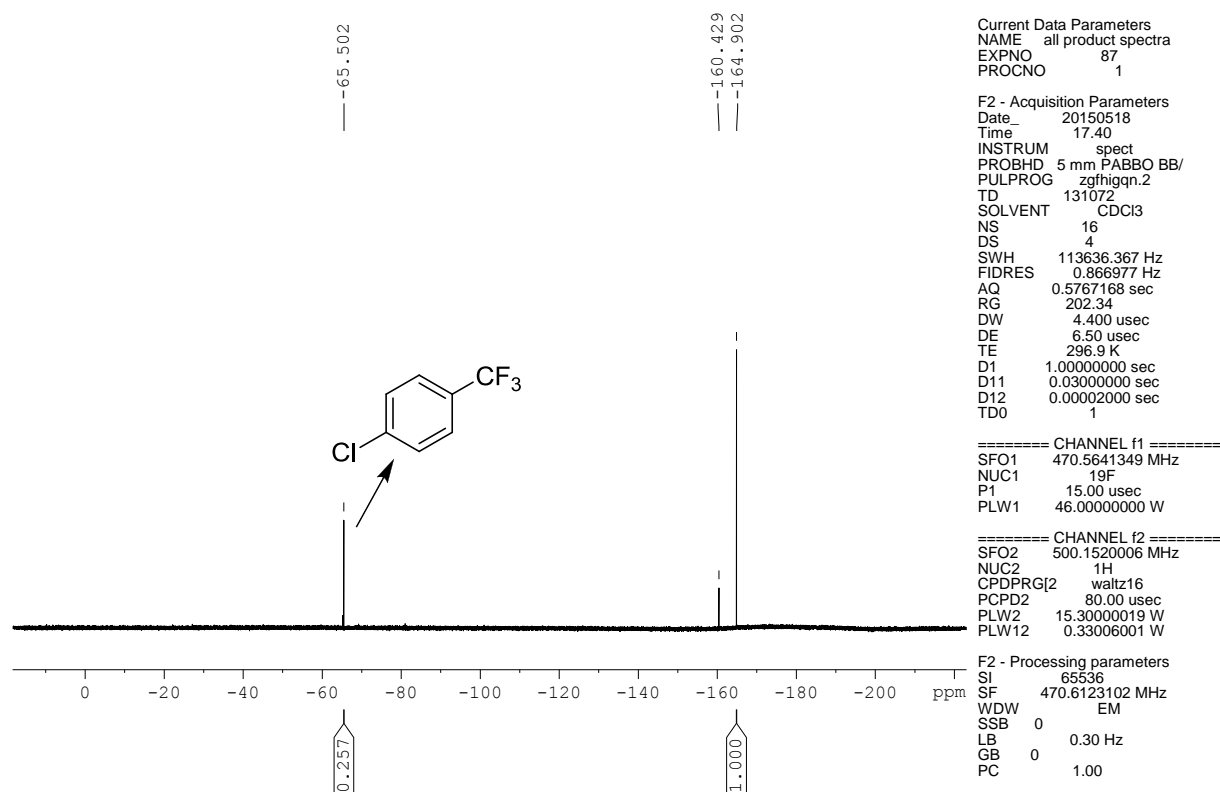


### 1-Chloro-4-(trifluoromethyl)benzene 2e:

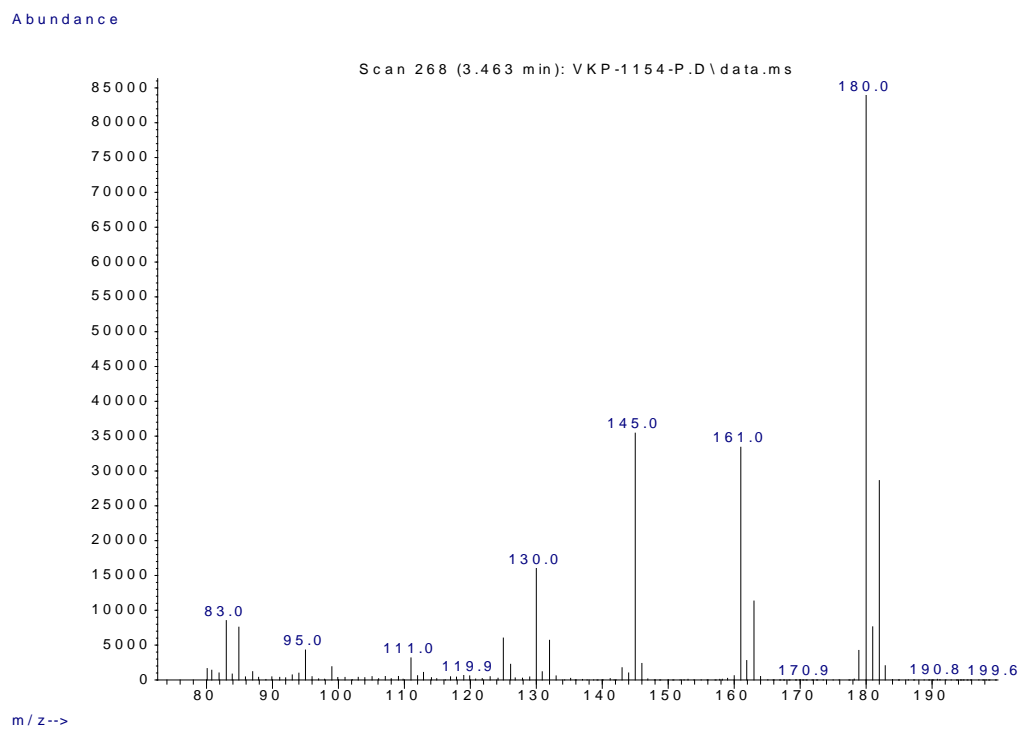


The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(4-chlorophenyl)iodoniumtriflate to achieve 1-chloro-4-(trifluoromethyl)benzene in 42% yield using standard procedure. The yield was determined by  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (15.5 mg, 0.08 mmol) as internal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

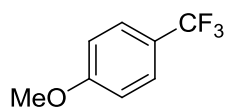
# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



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

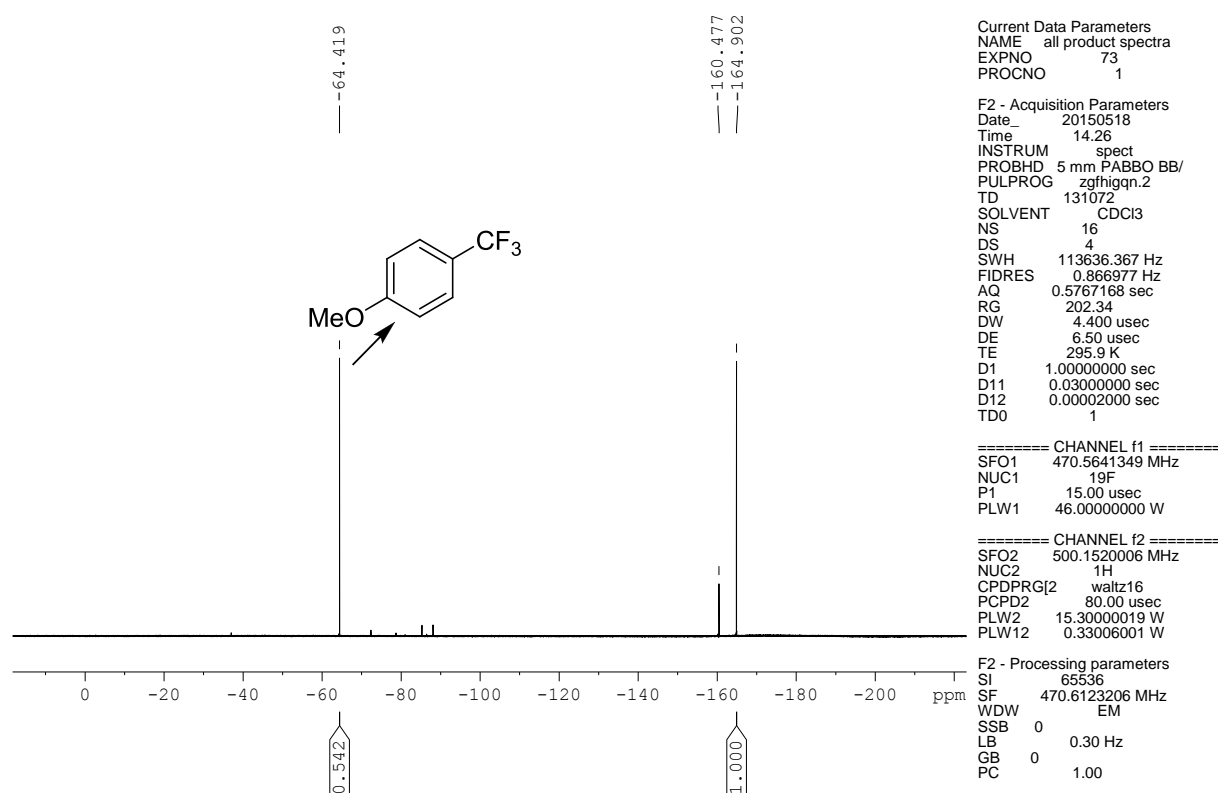


## 1-Methoxy-4-(trifluoromethyl)benzene 2f :<sup>3a</sup>

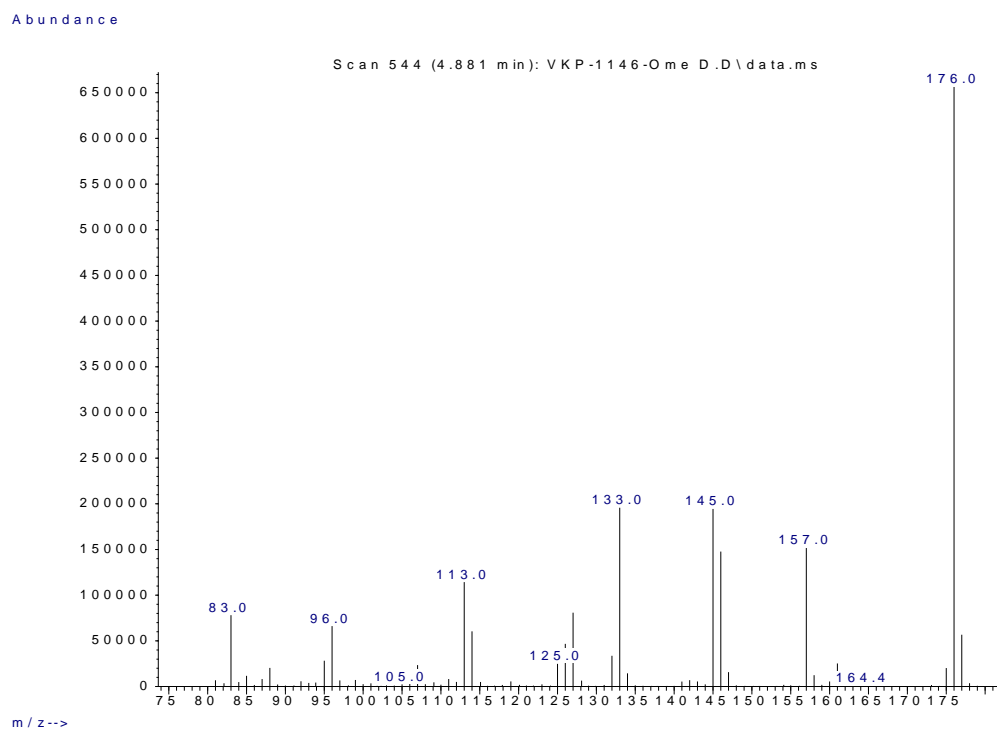


The reaction was performed on a (50 mg, 0.10 mmol) scale of bis(4-methoxyphenyl)iodoniumtriflate to achieve 1-methoxy-4-(trifluoromethyl)benzene in 97% yield using standard procedure. The yield was determined by <sup>19</sup>F NMR spectroscopy using hexafluorobenzene (17.0 mg, 0.09 mmol) as internal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

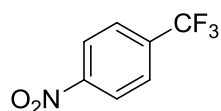
### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



## Mass spectrum of product peak (4.88 min) from GCMS analysis:

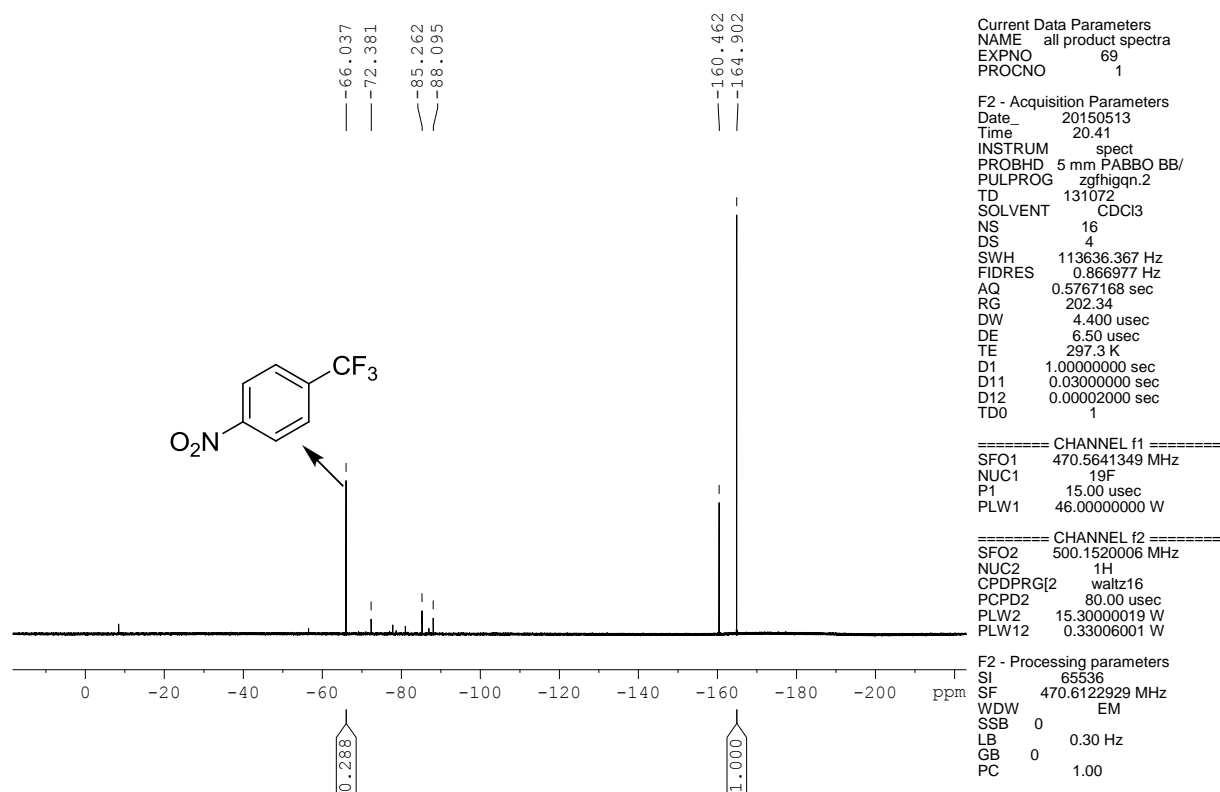


## 1-nitro-4-(trifluoromethyl)benzene 2g:



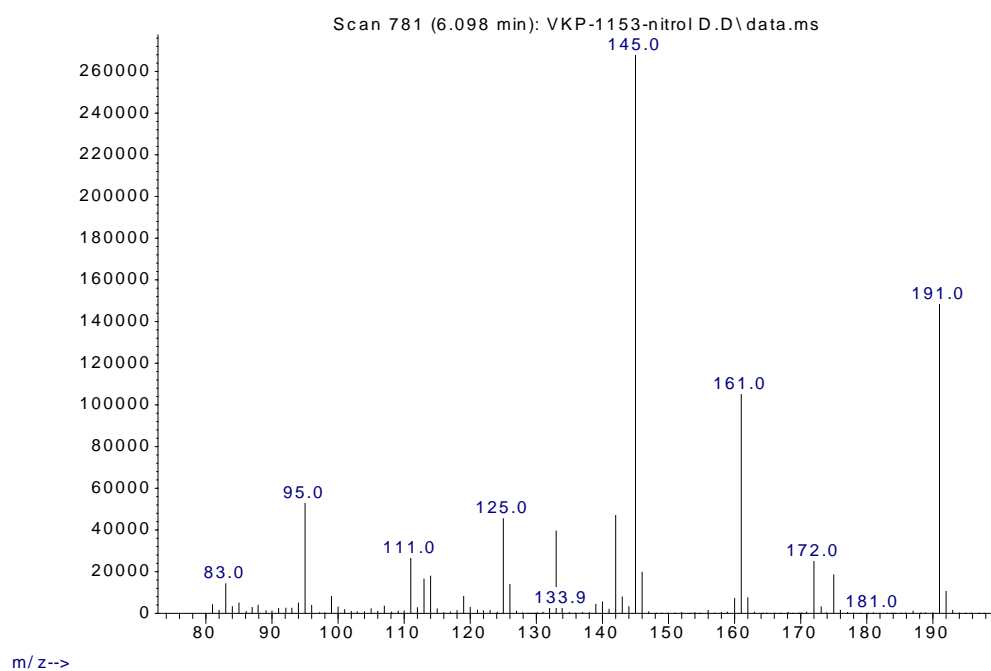
The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(4-nitrophenyl)iodoniumtriflate to achieve 1-nitro-4-(trifluoromethyl)benzene in 60% yield, using standard procedure. The yield was determined by  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (18.9 mg, 0.10 mmol) as internal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

### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):

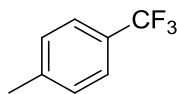


### Mass spectrum of product peak (6.09 min) from GCMS analysis:

Abundance

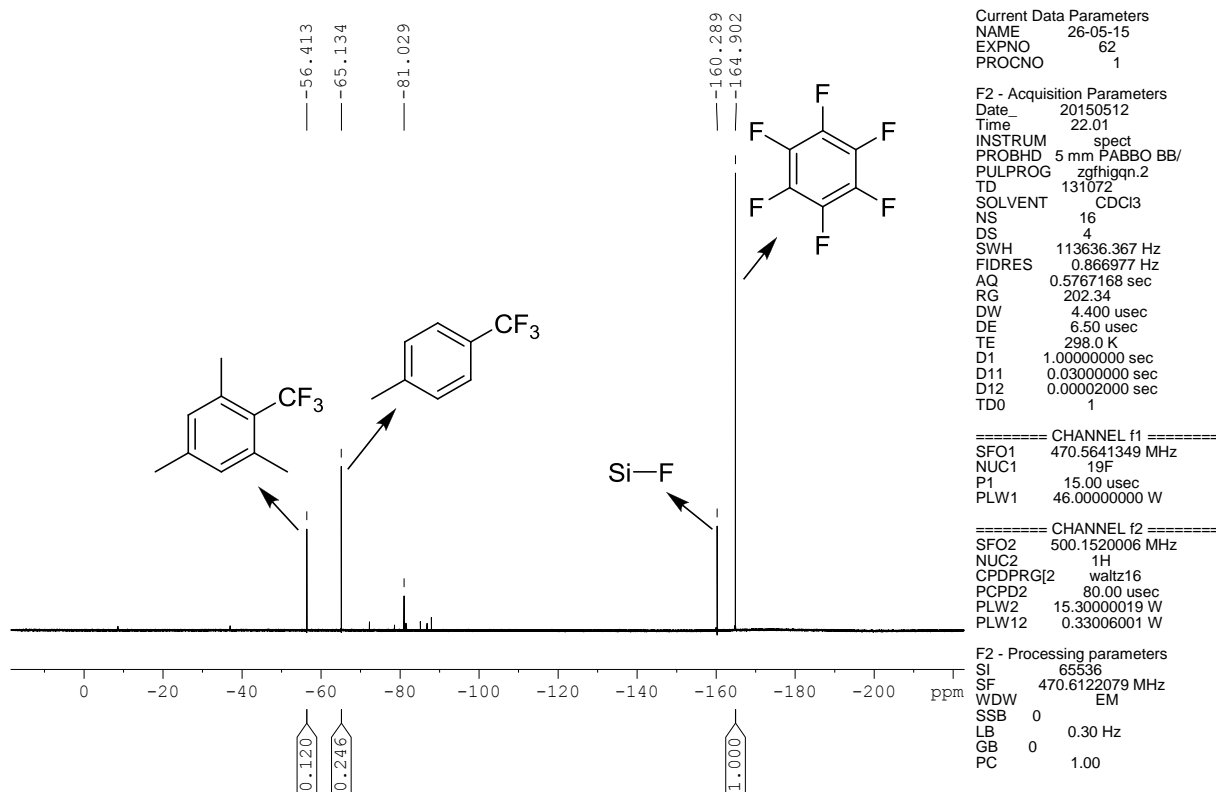


## 1-Methyl-4-(trifluoromethyl)benzene 2i:

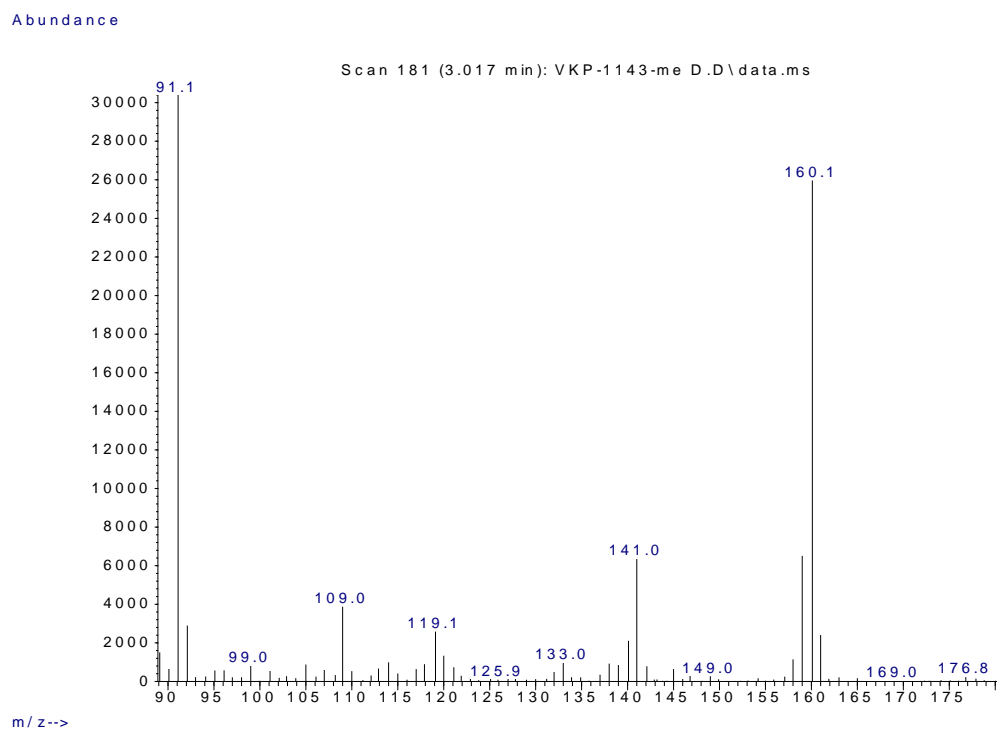


The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(p-tolyl)iodoniumtriflate to achieve 1-methyl-4-(trifluoromethyl)benzene in 56% yield along with 22% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by  $^{19}\text{F}$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

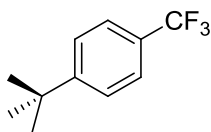
## $^{19}\text{F}$ NMR (470 MHz, $\text{CDCl}_3/\text{C}_6\text{F}_6$ , $24^\circ\text{C}$ ):



## Mass spectrum of product peak (3.07 min) from GCMS analysis:



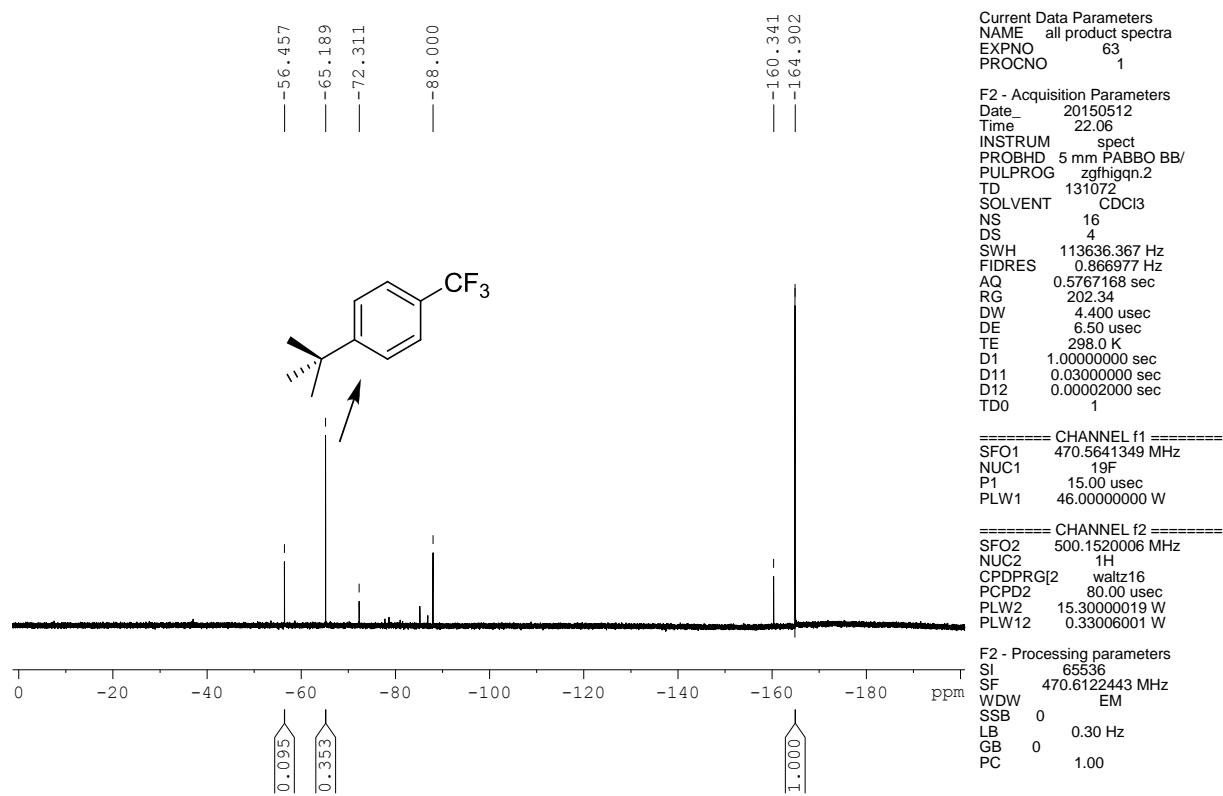
## 1-(tert-butyl)-4-(trifluoromethyl)benzene 2j:



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  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (17.4 mg, 0.09 mmol) as internal standard. The product peak was observed at (-65.1 ppm) in  $^{19}\text{F}$  NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 5.86 min.

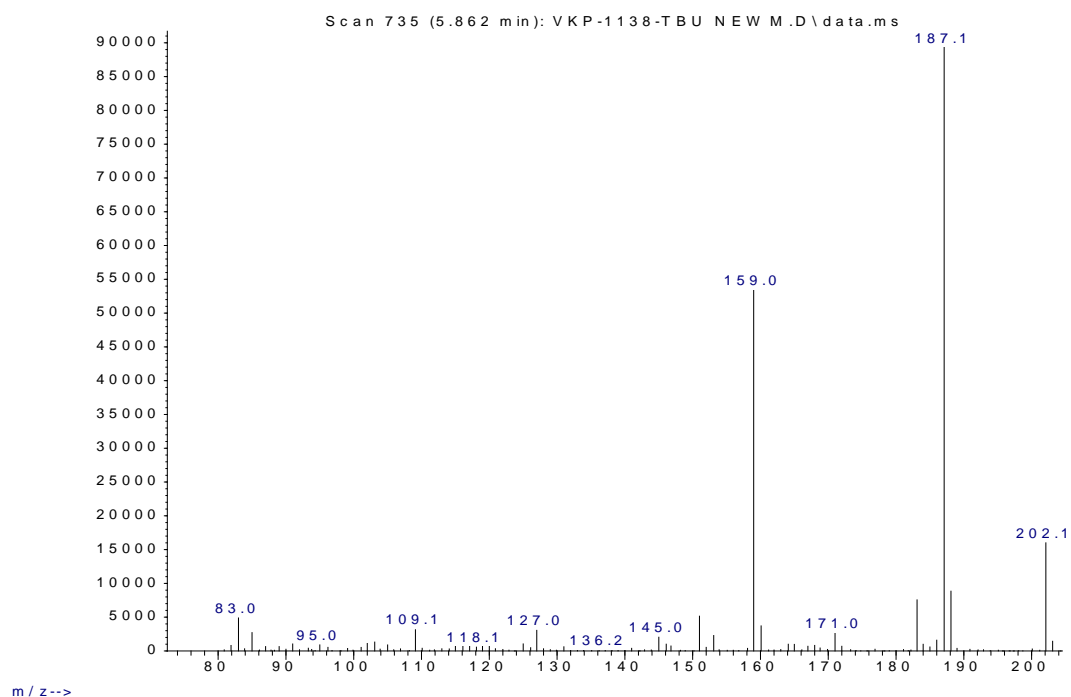


# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):

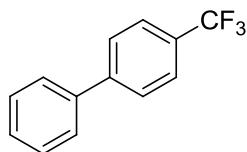


## Mass spectrum of product peak (5.86 min) from GCMS analysis:

Abundance

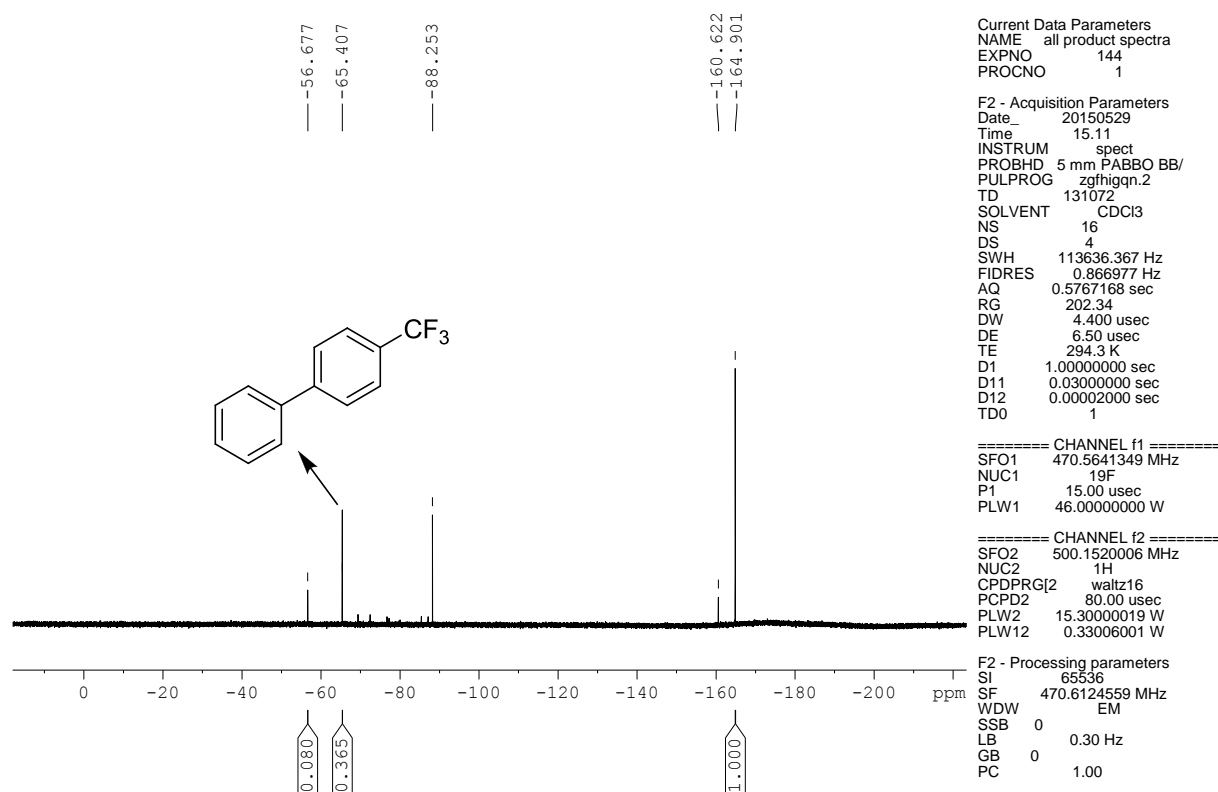


## 4-(trifluoromethyl)-1,1'-biphenyl 2k:<sup>3a</sup>



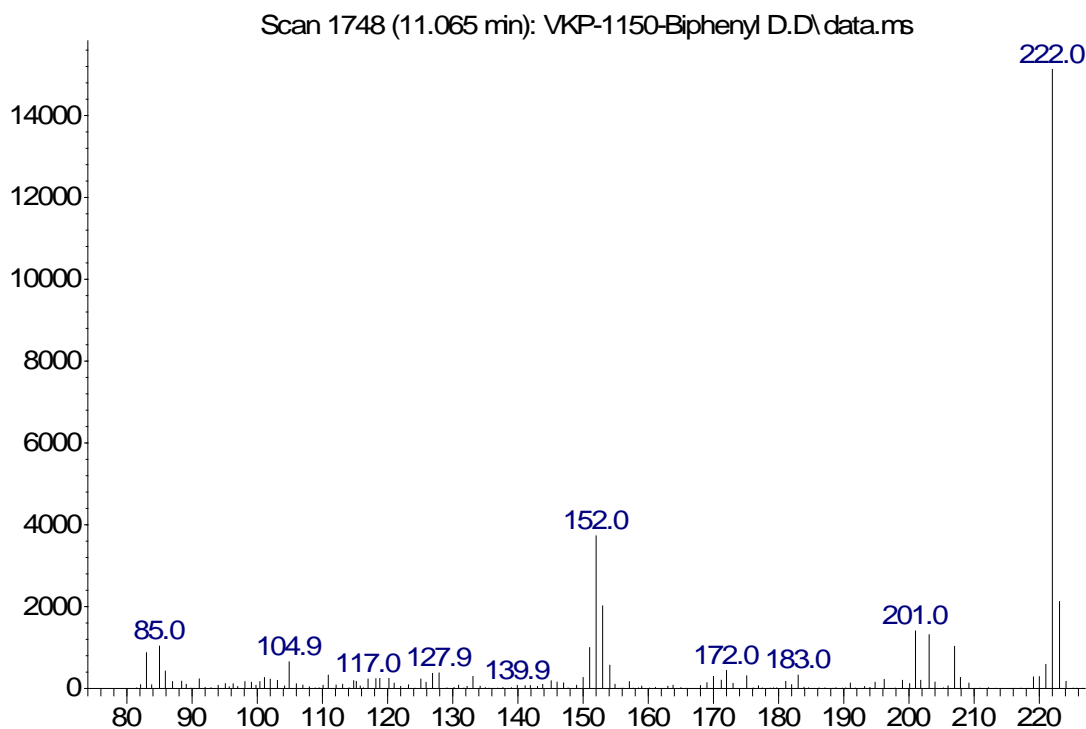
The reaction was performed on a (50 mg, 0.09 mmol) scale of [1,1'-biphenyl]-4-yl(mesityl)iodoniumtriflate to achieve 4-(trifluoromethyl)-1,1'-biphenyl in 81% yield along with 17% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. Yield was determined by <sup>19</sup>F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

### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



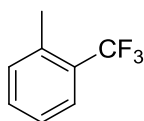
### Mass spectrum of product peak (11.06 min) from GCMS analysis:

Abundance



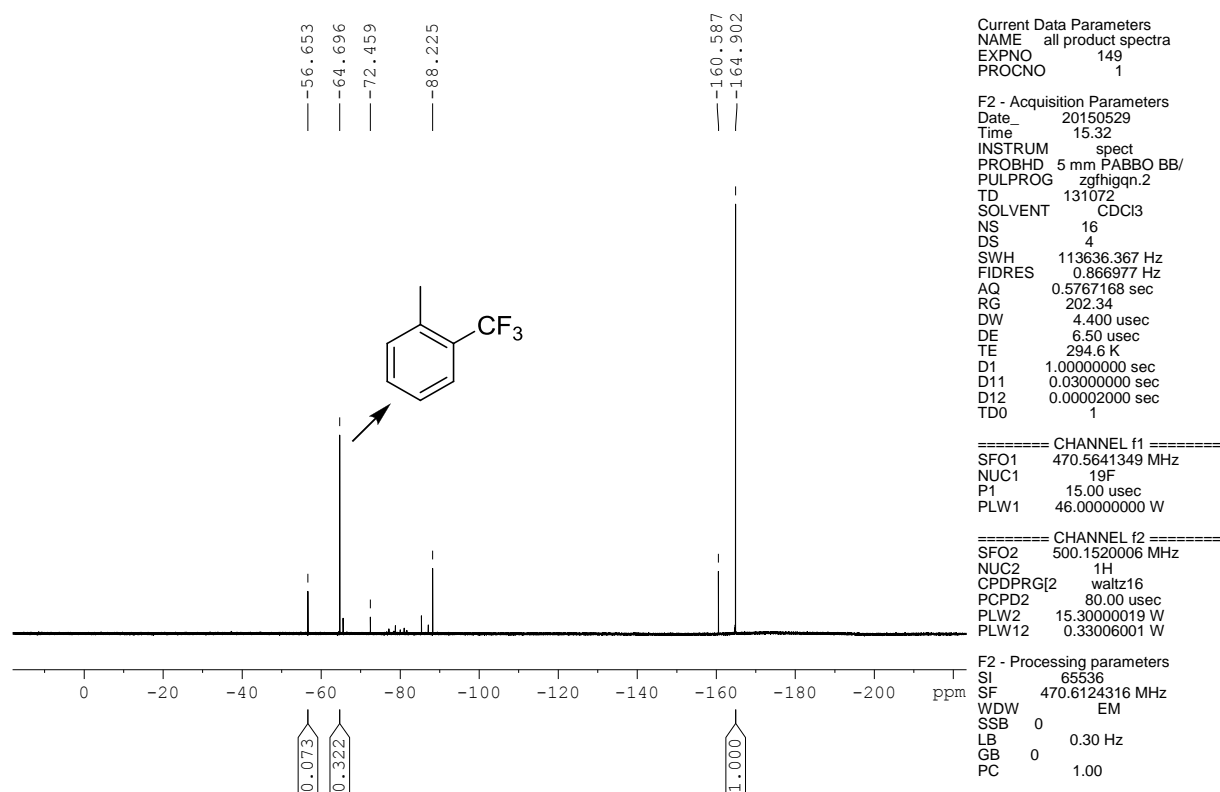
m/z->

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

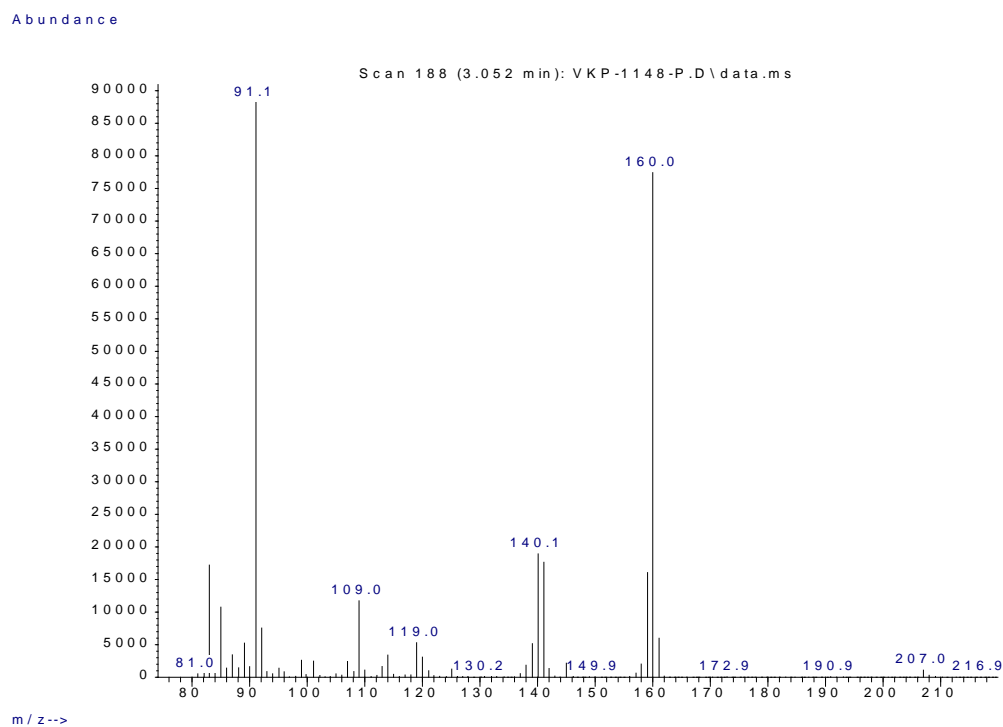


The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(o-tolyl)iodoniumtriflate to achieve 1-methyl-2-(trifluoromethyl)benzene in 65% yield, along with 14% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by  $^{19}\text{F}$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

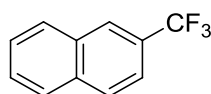
**<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):**



**Mass spectrum of product peak (3.05 min) from GCMS analysis:**

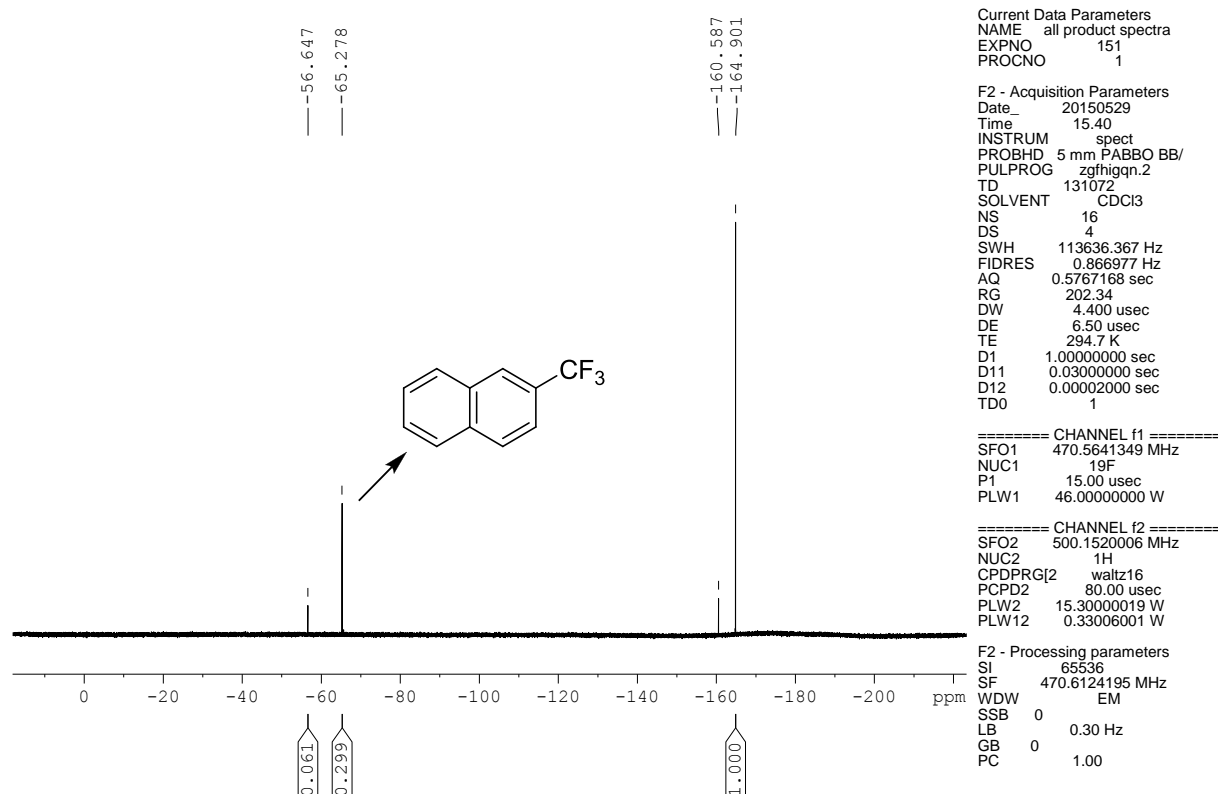


## 1-(trifluoromethyl)naphthalene 2m:

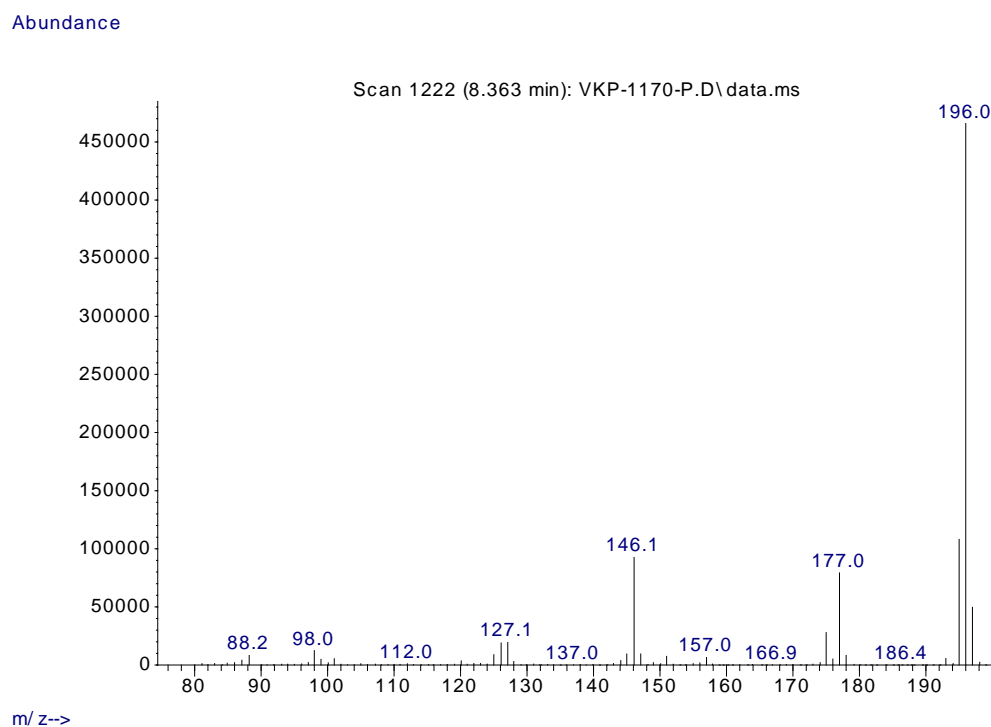


The reaction was performed on a (40 mg, 0.07mmol) scale of 2-(naphthaleny)(mesityl)iodoniumtriflate to achieve 2-(trifluoromethyl)naphthalene in 78% yield, along with 16% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

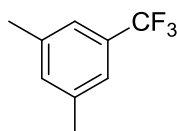
### $^{19}\text{F}$ NMR (470 MHz, $\text{CDCl}_3/\text{C}_6\text{F}_6$ , 24°C):



## Mass spectrum of product peak (8.36 min) from GCMS analysis:

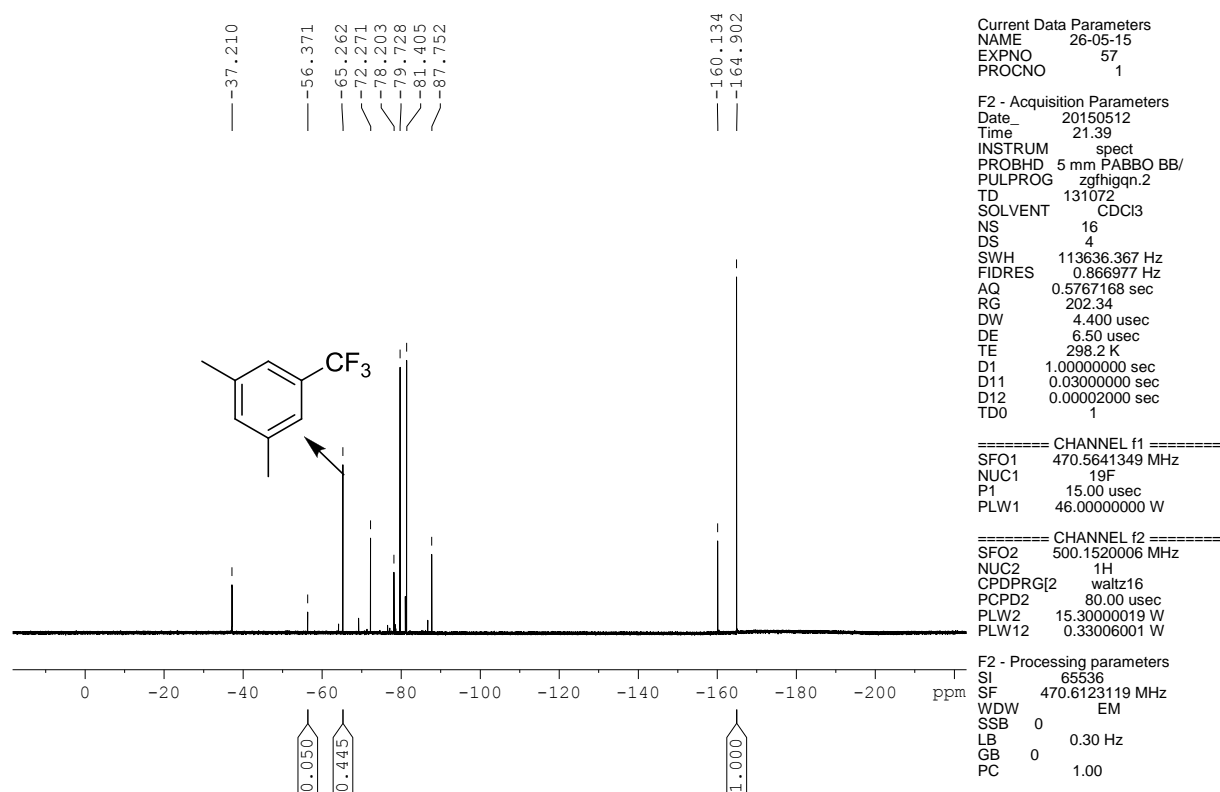


## 1,3-dimethyl-5-(trifluoromethyl)benzene 2n:



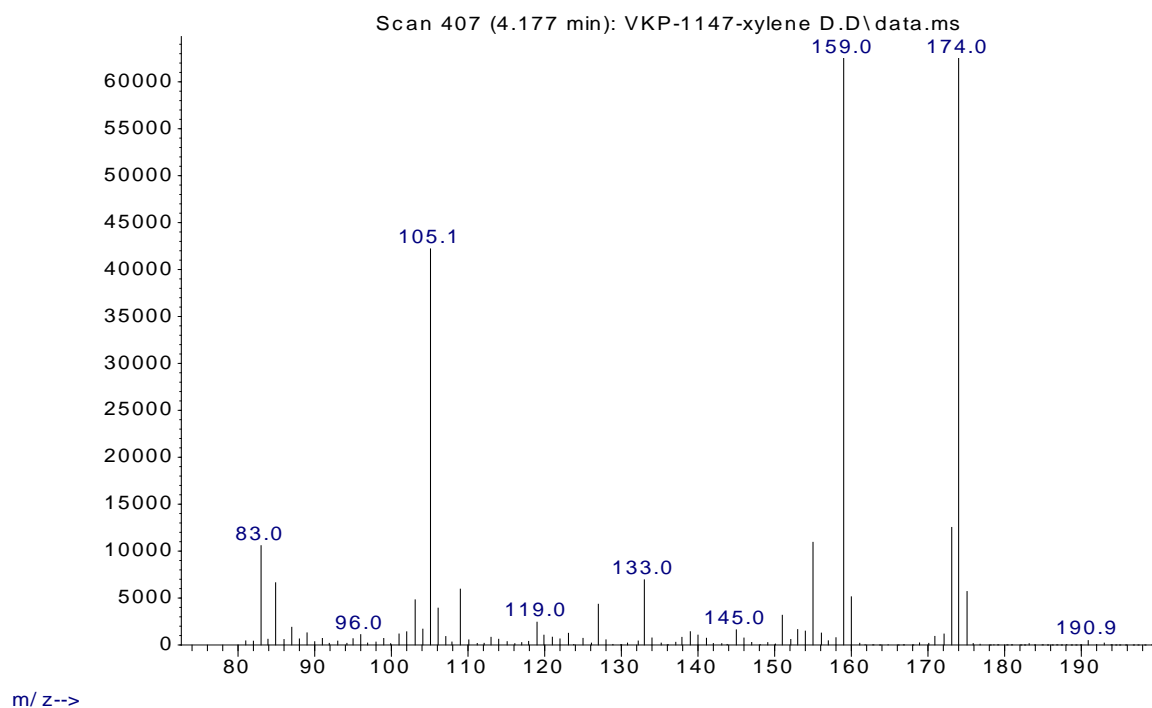
The reaction was performed on a (50 mg, 0.10 mmol) scale of 3,5-dimethylphenyl(mesityl)iodoniumtriflate to achieve 1,3-dimethyl-5-(trifluoromethyl)benzene in 84% yield along with 9% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

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

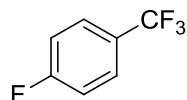


**Mass spectrum of product peak (4.17 min) from GCMS analysis:**

Abundance

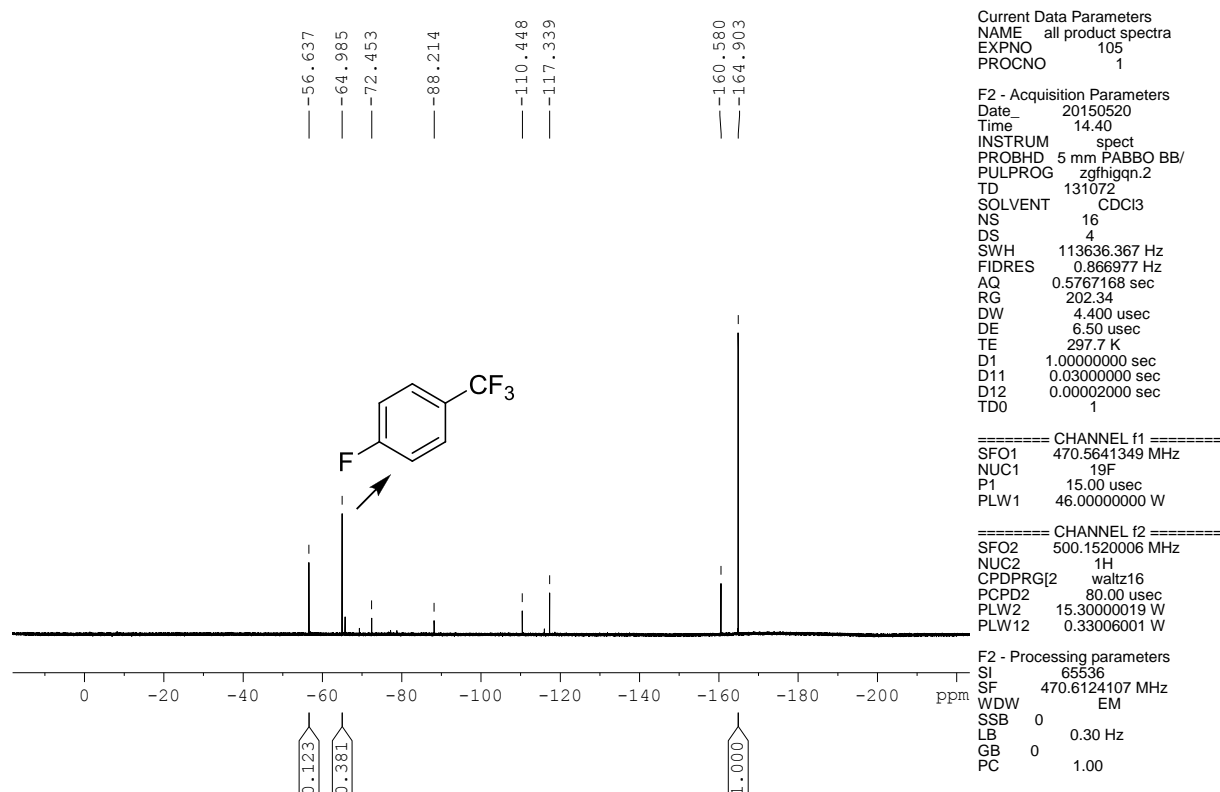


## 1-Fluoro-4-(trifluoromethyl)benzene 2o:



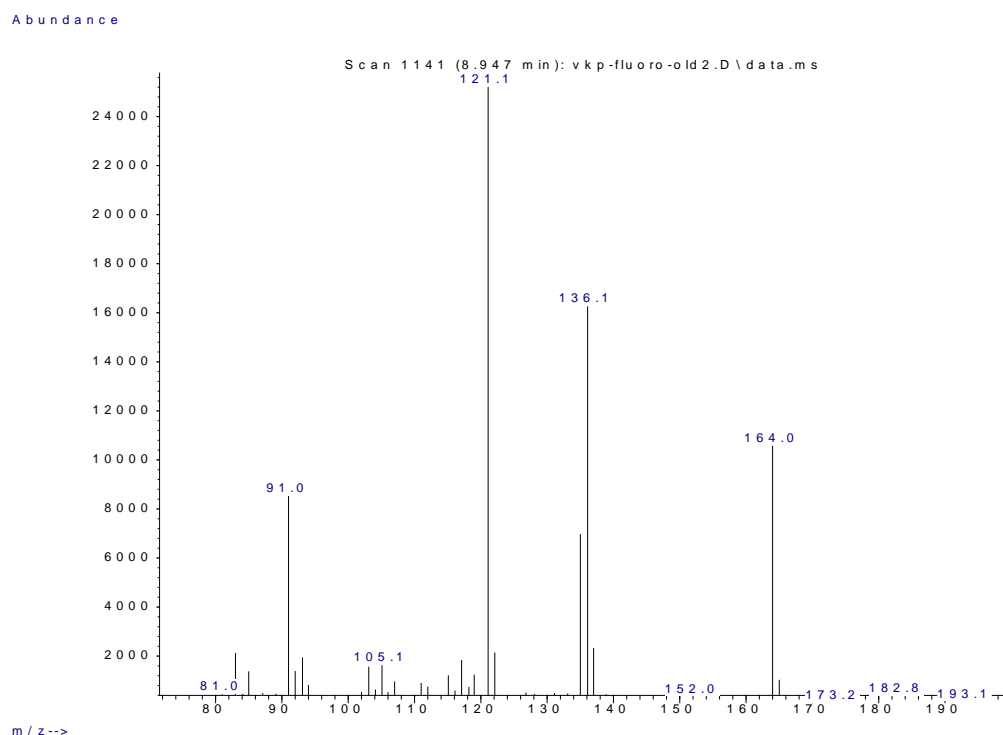
The reaction was performed on a (50 mg, 0.10 mmol) scale of 4-(fluorophenyl)(mesityl)iodoniumtriflate to achieve 1-fluoro-4-(trifluoromethyl)benzene in 72% yield, along with 23% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

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

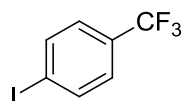




## Mass spectrum of product peak (8.94 min) from GCMS analysis:

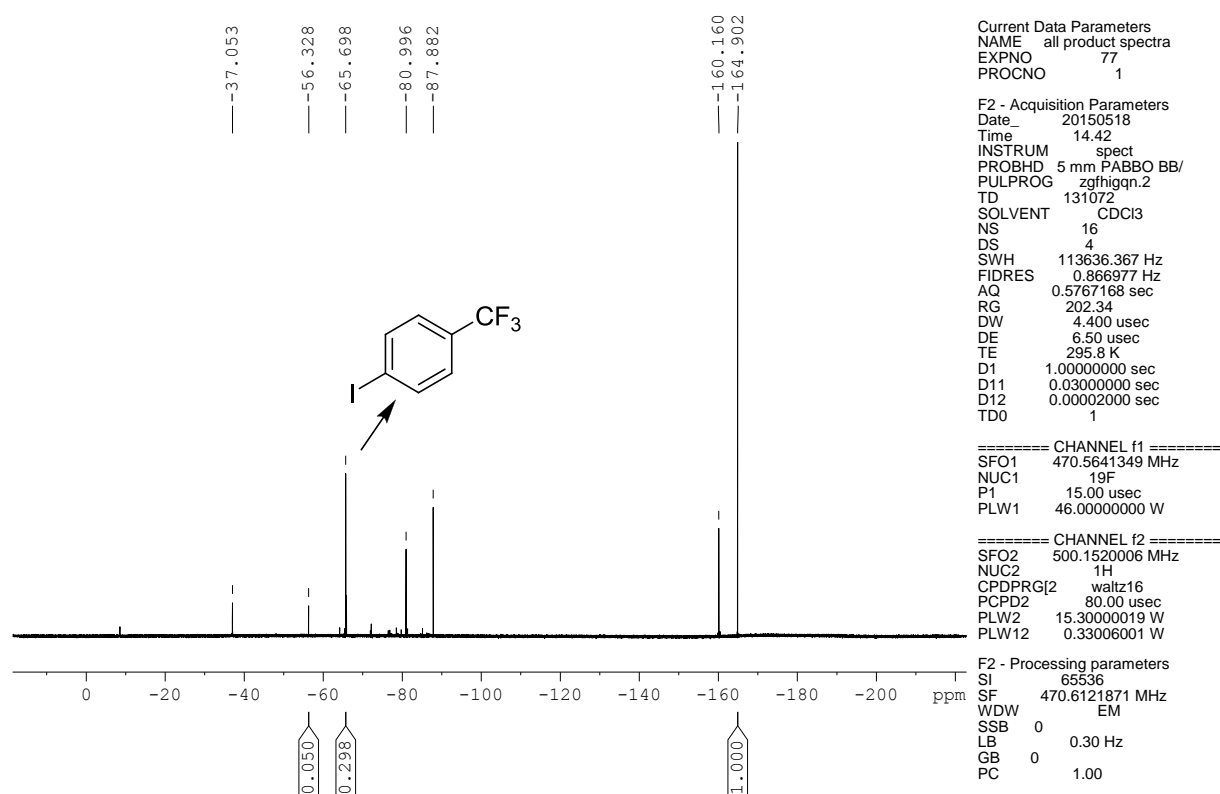


### 1-iodo-4-(trifluoromethyl)benzene 2p:

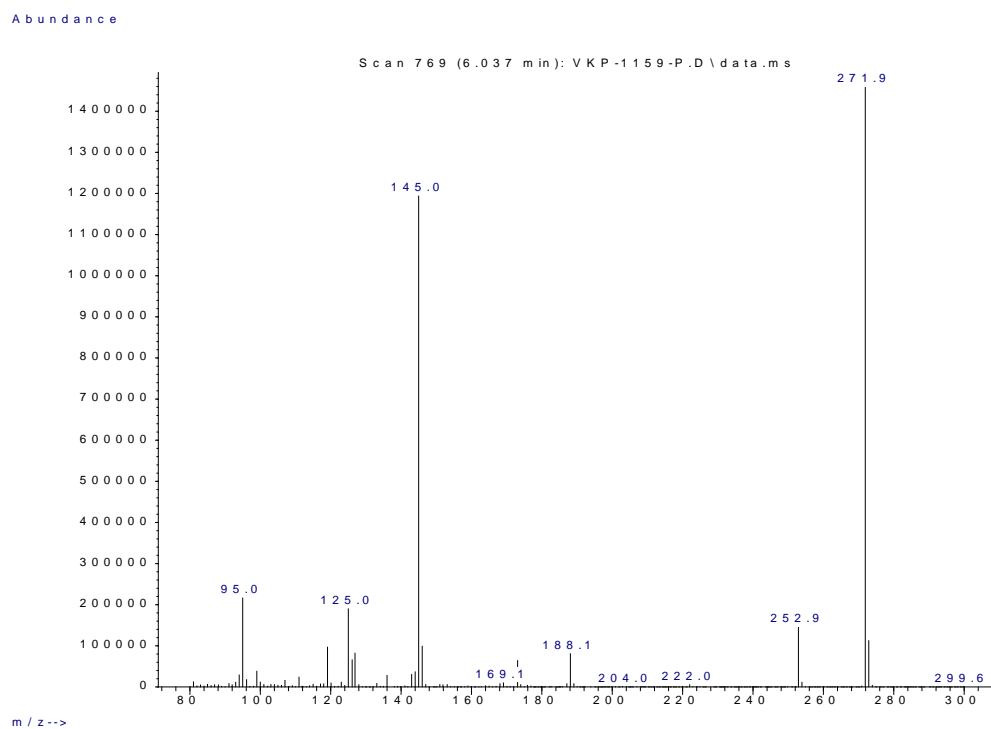


The reaction was performed on a (50 mg, 0.08 mmol) scale of (4-iodophenyl)(mesityl)iodoniumtriflate to achieve 1-iodo-4-(trifluoromethyl)benzene in 61% yield, along with 10% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

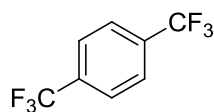
# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



# Mass spectrum of product peak (6.03 min) from GCMS analysis:

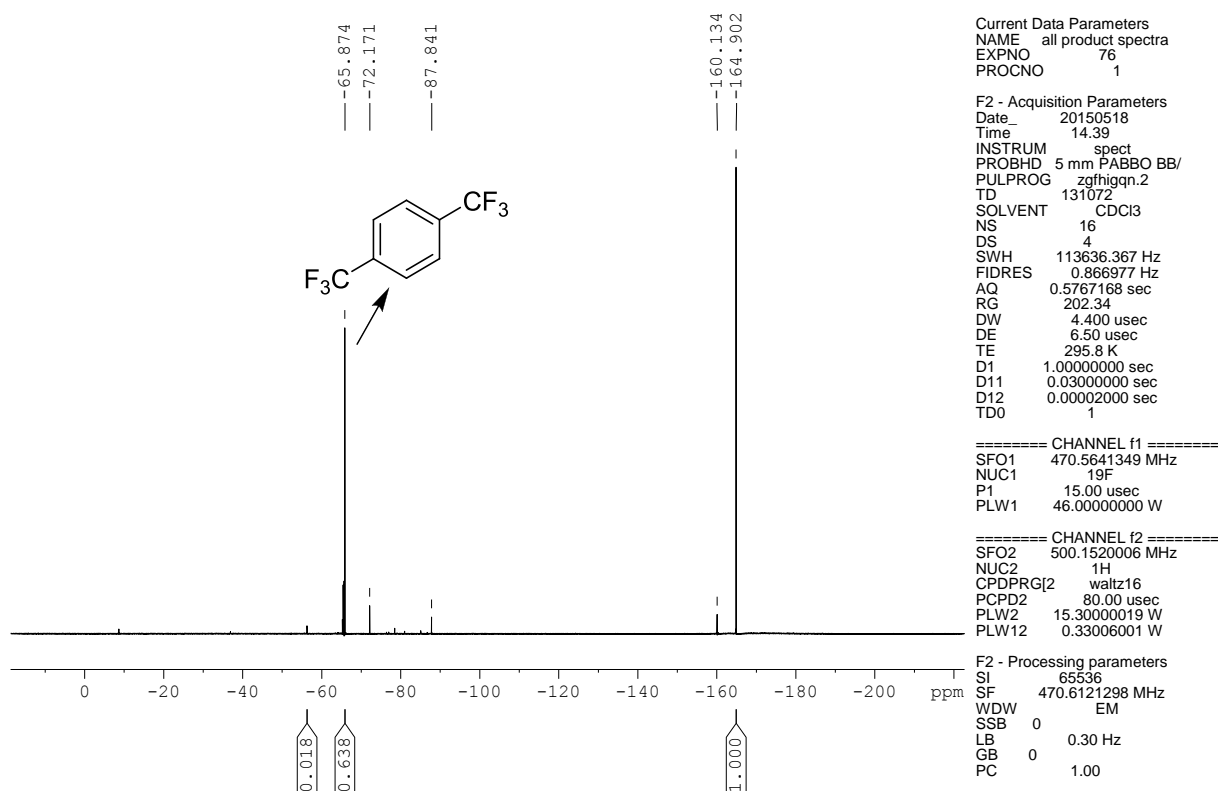


## 1,4-bis(trifluoromethyl)benzene 2q:

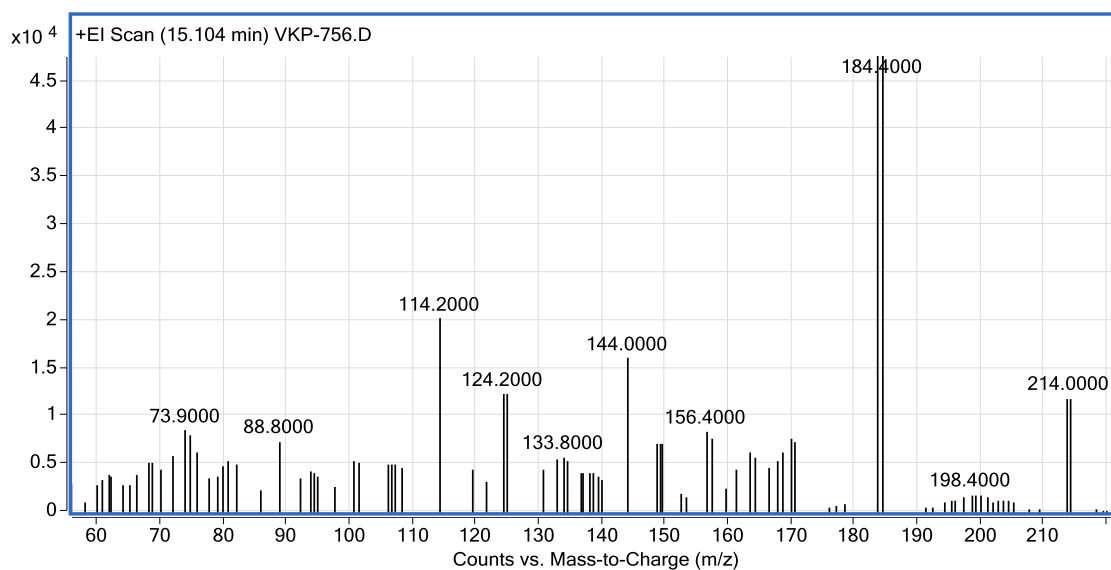


The reaction was performed on a (50 mg, 0.09mmol) scale of mesityl(4-(trifluoromethyl)phenyl)iodoniumtriflate to achieve 1,4-bis(trifluoromethyl)benzene in 71% yield along with trace amount of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined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

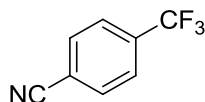
### $^{19}\text{F}$ NMR (470 MHz, $\text{CDCl}_3/\text{C}_6\text{F}_6$ , 24°C):



### Mass spectrum of product peak (15.10 min) from GCMS analysis:

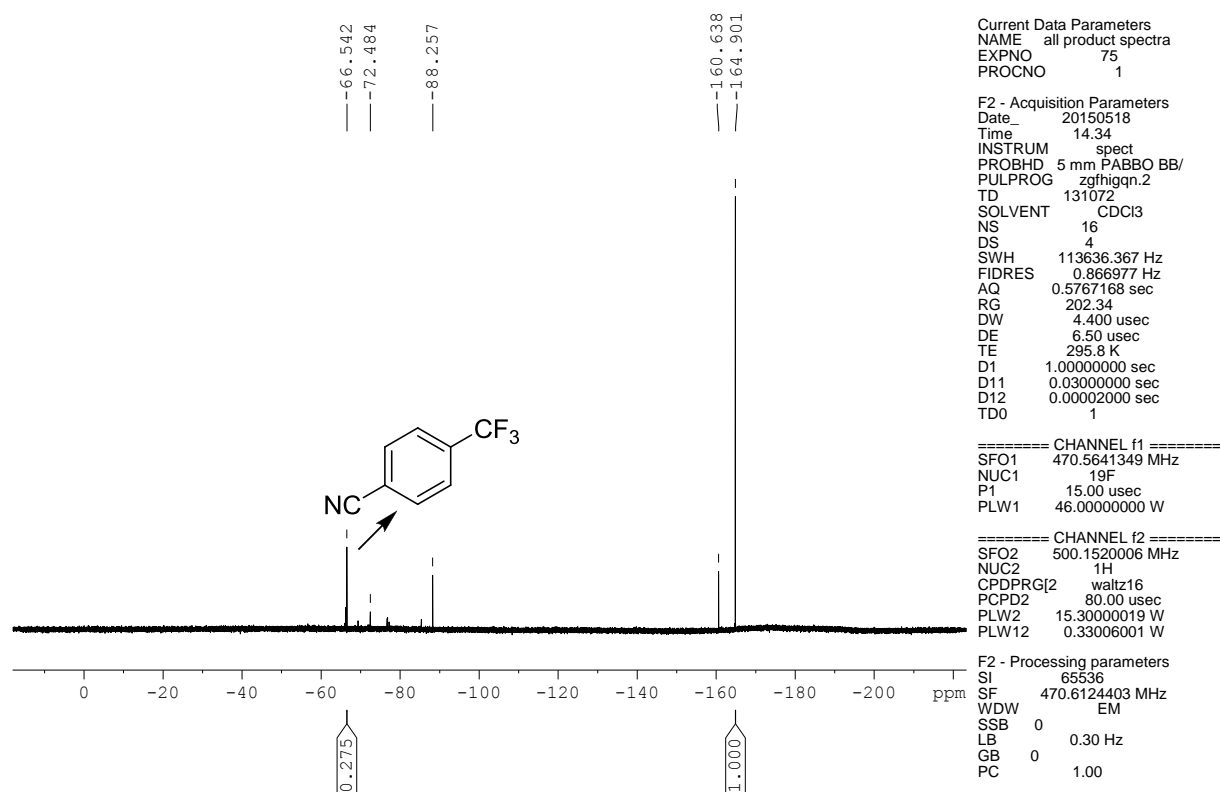


### 4-(trifluoromethyl)benzonitrile 2r:



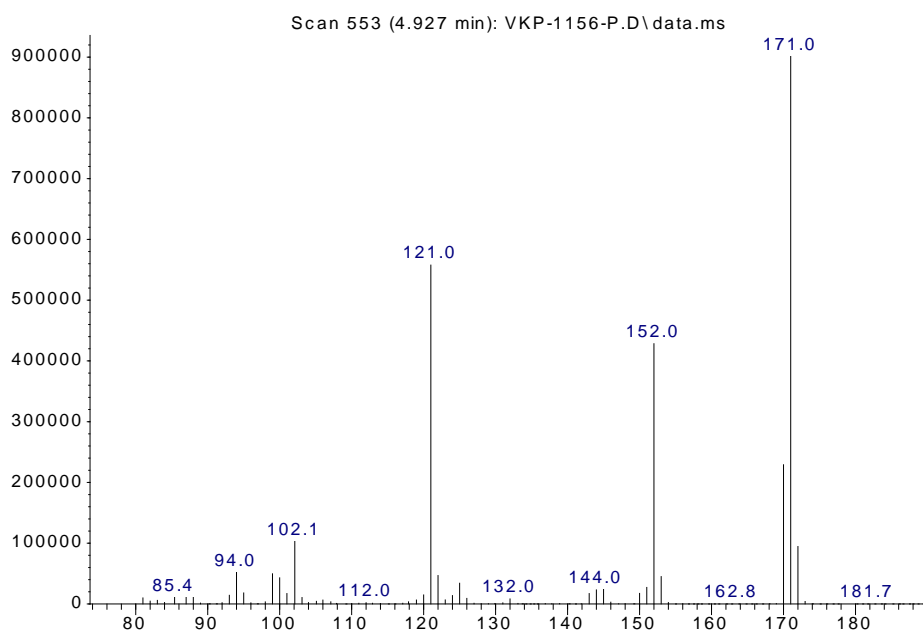
The reaction was performed on a (50 mg, 0.10 mmol) scale of 4-(cyanophenyl)(mesityl)iodoniumtriflate to achieve 4-(trifluoromethyl)benzonitrile in 57% yield, using standard procedure. The yield was determined by <sup>19</sup>F NMR spectroscopy using hexafluorobenzene (19.6 mg, 0.10 mmol) as internal standard. The product peak was observed at (-66.54 ppm) in <sup>19</sup>F NMR. The formation of product was further confirmed by GCMS analysis where, product peak found at 4.92 min.

# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



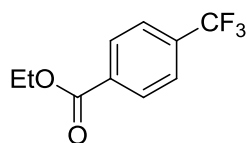
## Mass spectrum of product peak (4.92 min) from GCMS analysis:

Abundance



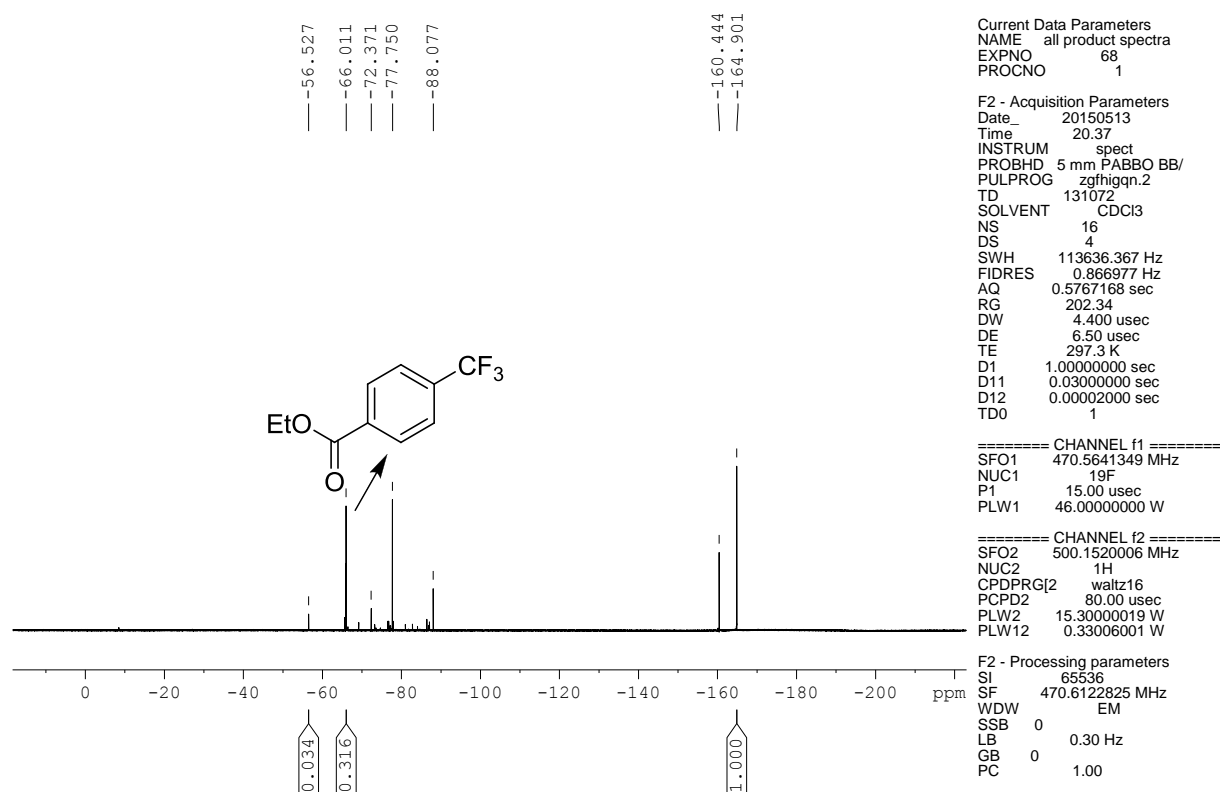
m/z-->

## Ethyl 4-(trifluoromethyl)benzoate 2s :<sup>3a</sup>

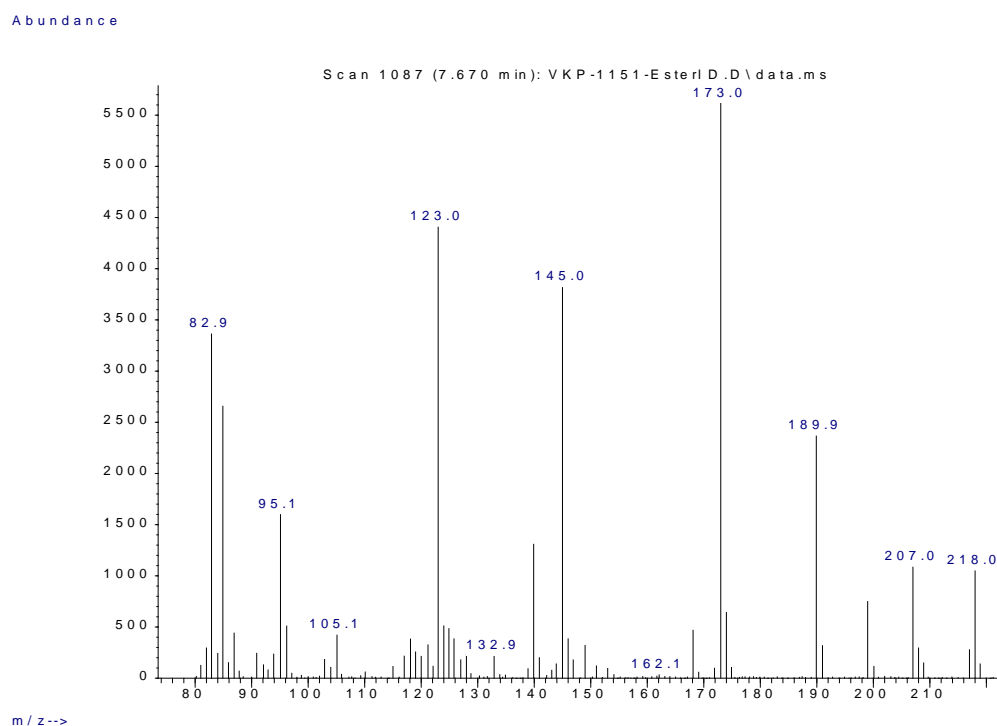


The reaction was performed on a (50 mg, 0.09 mmol) scale of (4-ethoxycarbonylphenyl)(mesityl)iodoniumtriflate to achieve ethyl 4-(trifluoromethyl)benzoate in 72% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product, using standard procedure. The yield was determined by 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

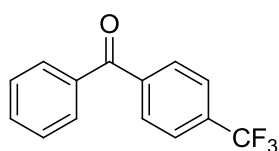
### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



## Mass spectrum of product peak (7.67 min) from GCMS analysis:

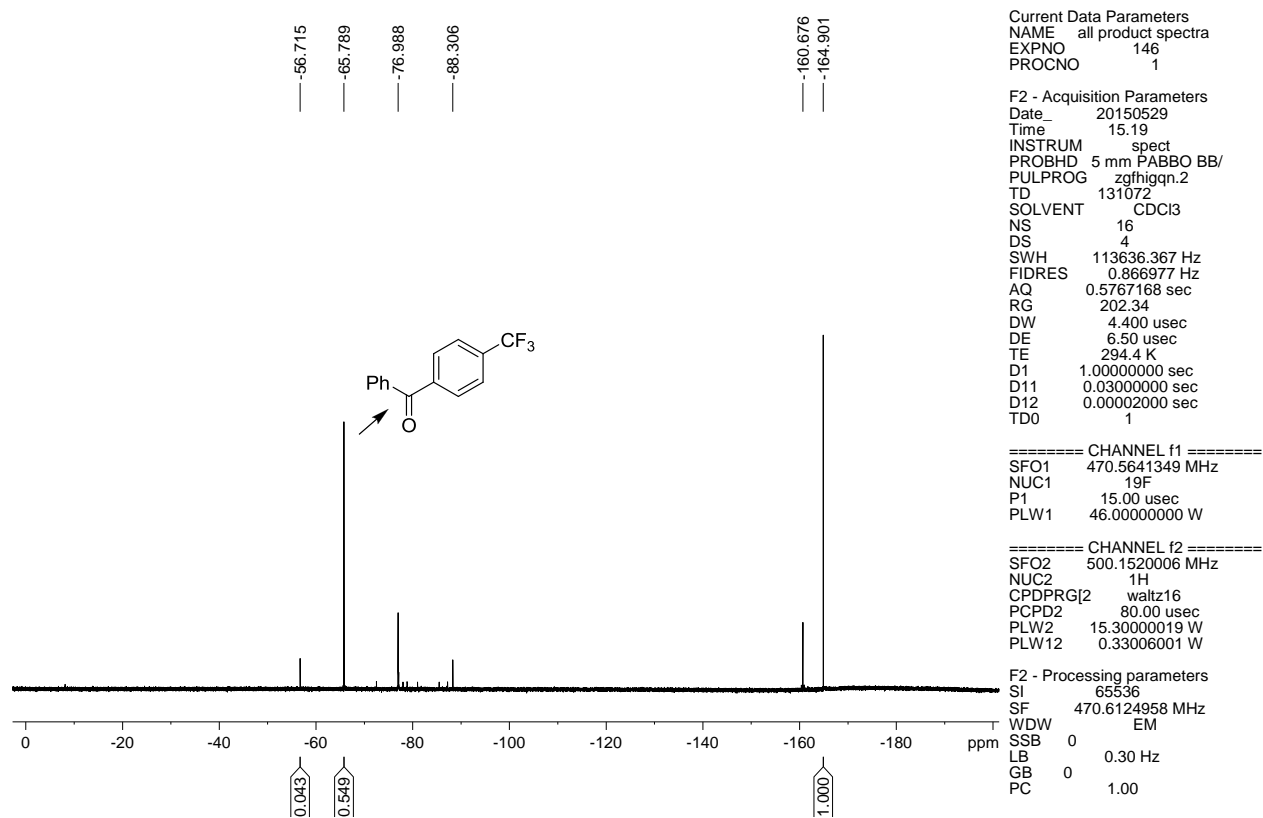


## Phenyl(4-(trifluoromethyl)phenyl)methanone 2t:<sup>3b</sup>

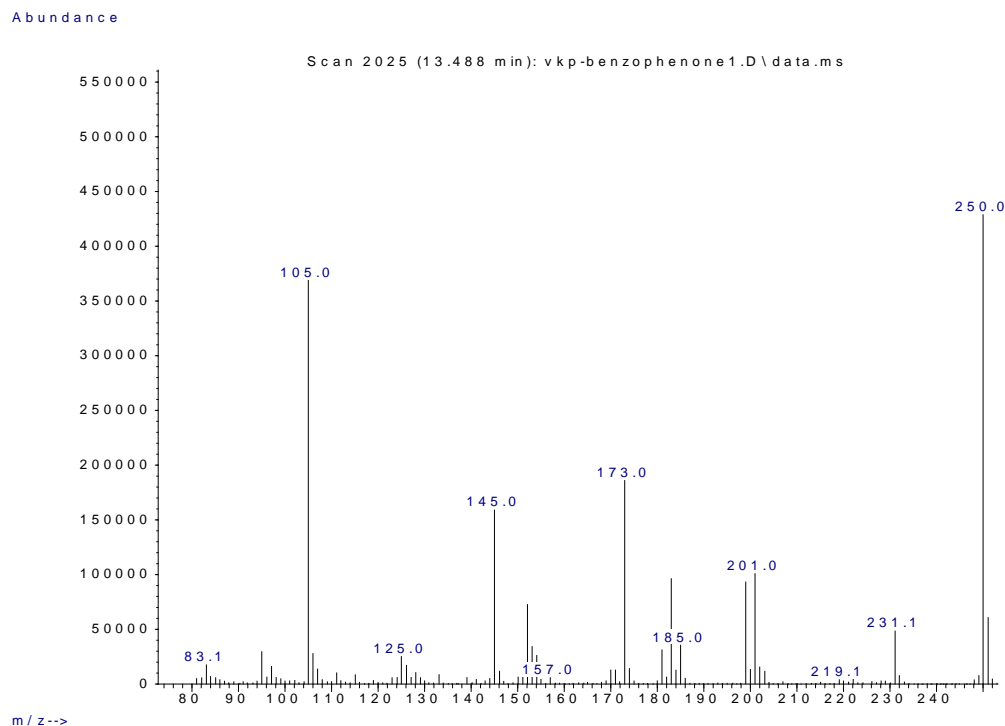


The reaction was performed on a (50 mg, 0.08 mmol) scale of (4-benzoylphenyl)(mesityl)iodoniumtriflate to achieve phenyl(4-(trifluoromethyl)phenyl)methanone in 93% yield along with 6% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by 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

# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):

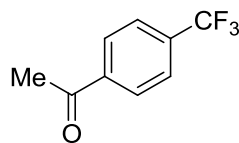


# Mass spectrum of product peak (13.48 min) from GCMS analysis:



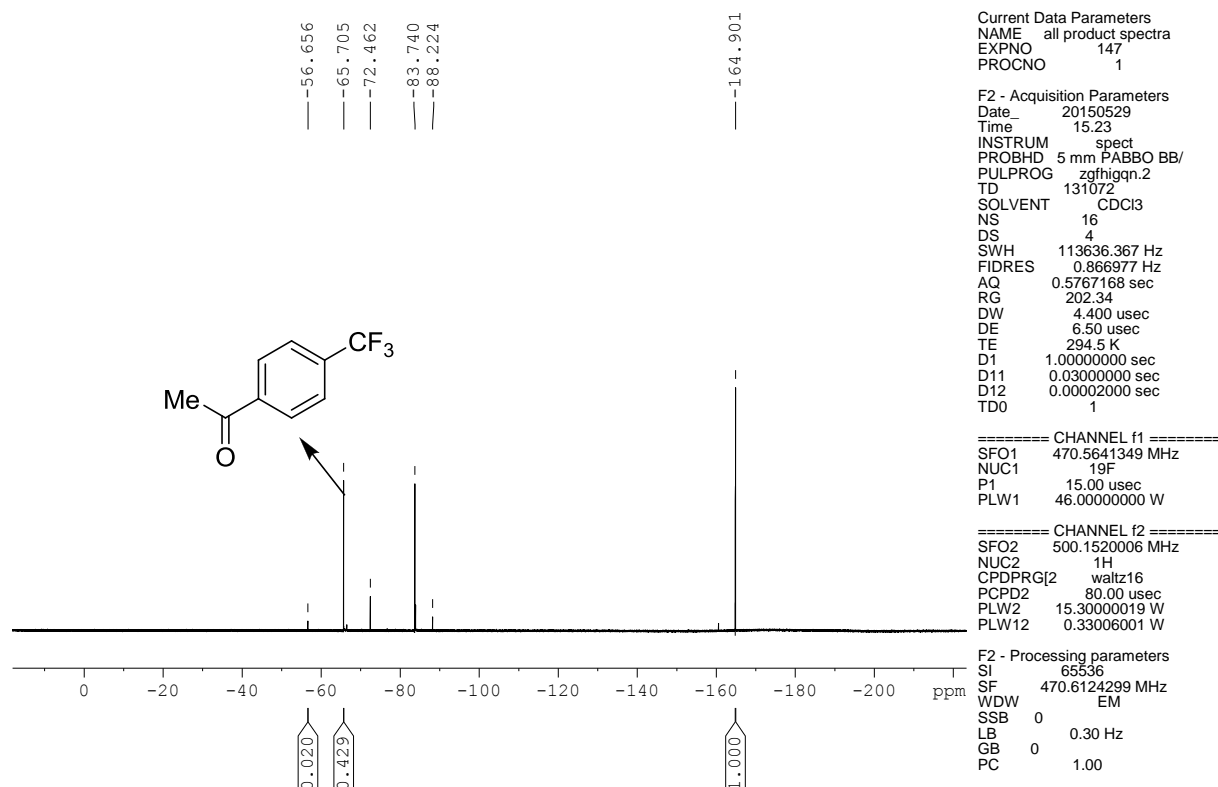


## 1-(4-(trifluoromethyl)phenyl)ethanone 2u:



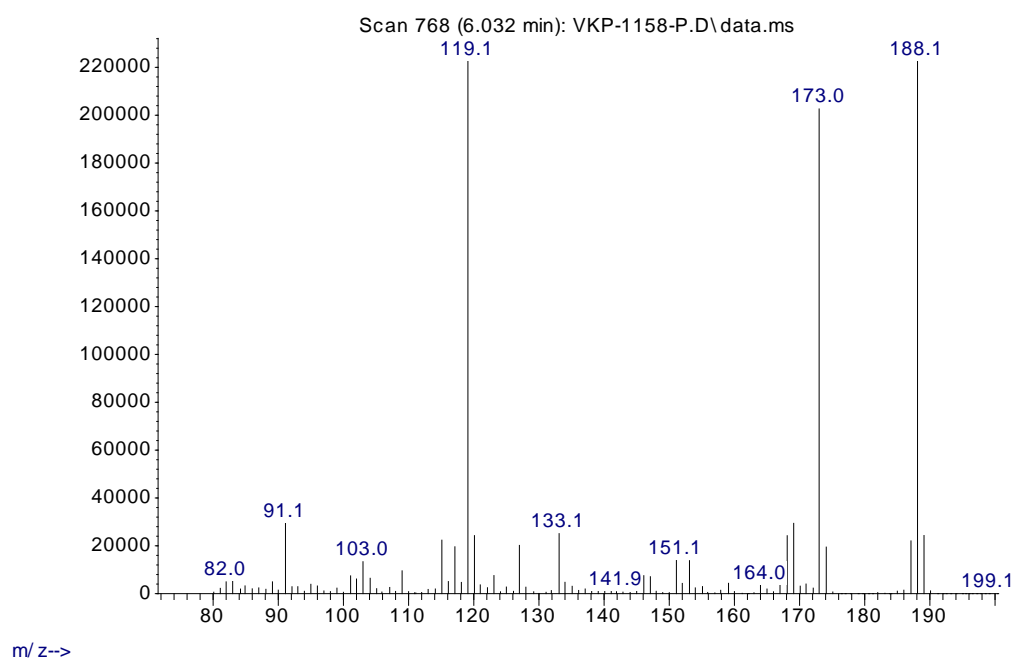
The reaction was performed on a (50 mg, 0.09mmol) scale of (4-acetylphenyl)(mesityl)iodonium to achieve 1-(4-(trifluoromethyl)phenyl)ethanone in 94% yield along with 4% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

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

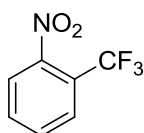


## Mass spectrum of product peak (6.03 min) from GCMS analysis:

Abundance

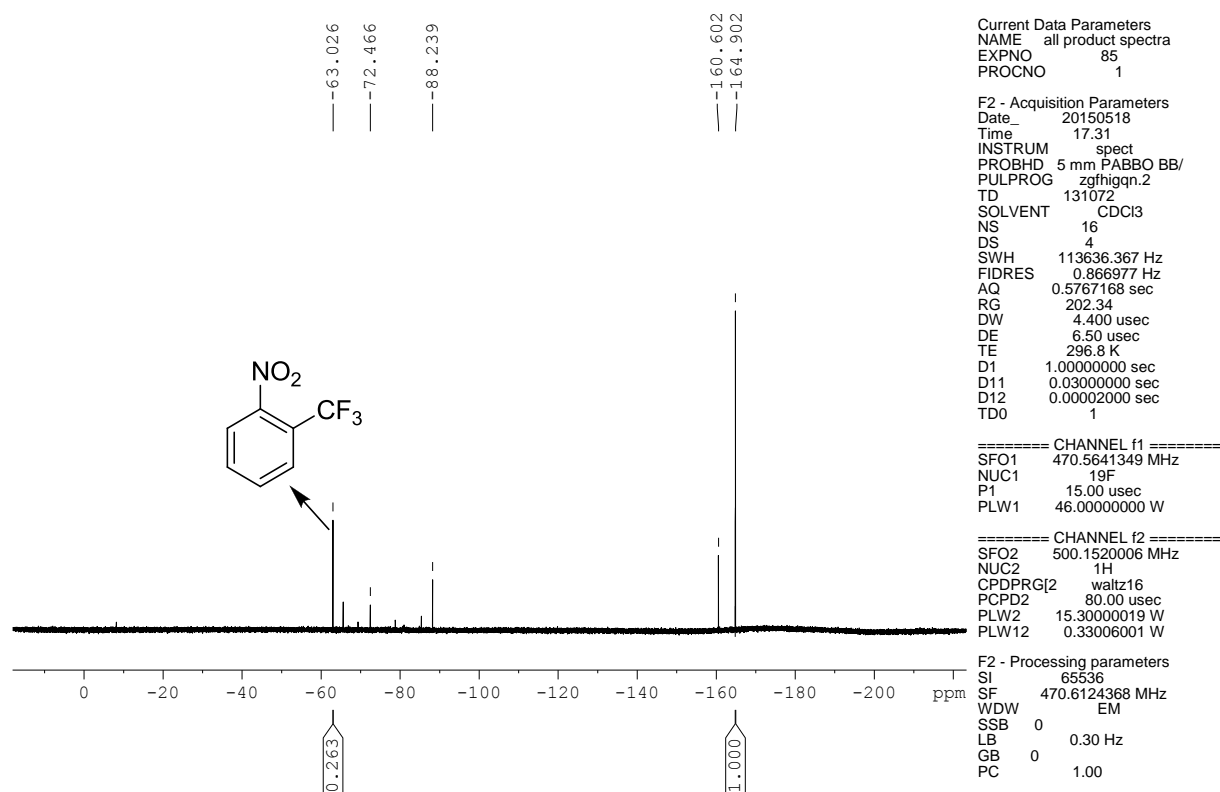


### 1-nitro-2-(trifluoromethyl)benzene 2v:

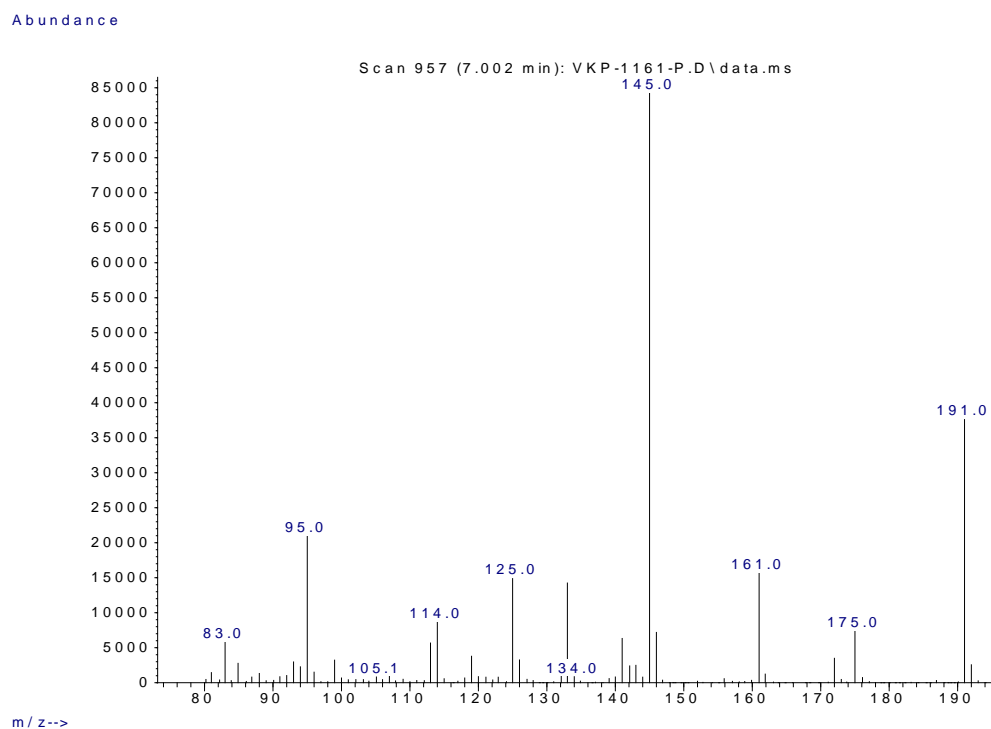


The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(2-nitrophenyl)iodoniumtriflate to achieve 1-nitro-2-(trifluoromethyl)benzene in 54% yield, using standard procedure. The yield was determined by  $^{19}\text{F}$  NMR spectroscopy using hexafluorobenzene (18.5 mg, 0.09 mmol) as internal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

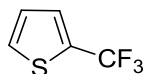
# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C)



## Mass spectrum of product peak (7.0 min) from GCMS analysis:

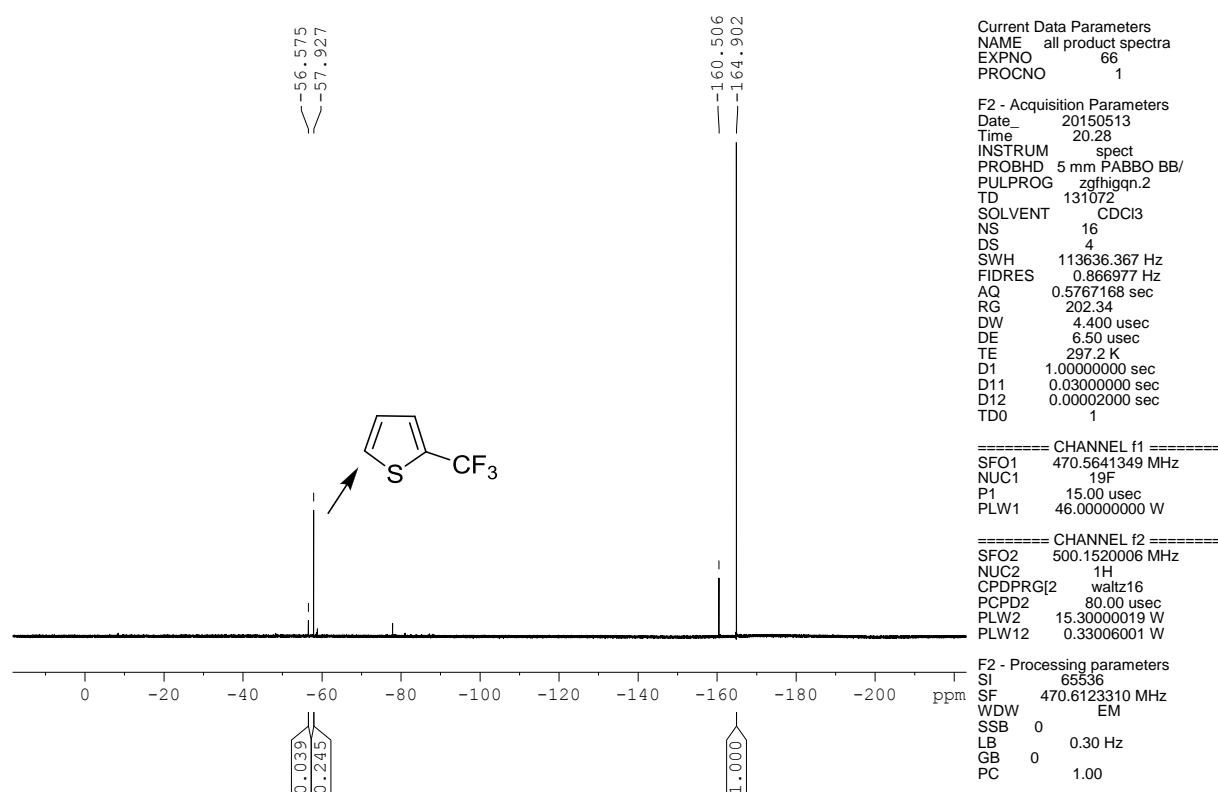


## 2-Trifluoromethylthiophene 2w:



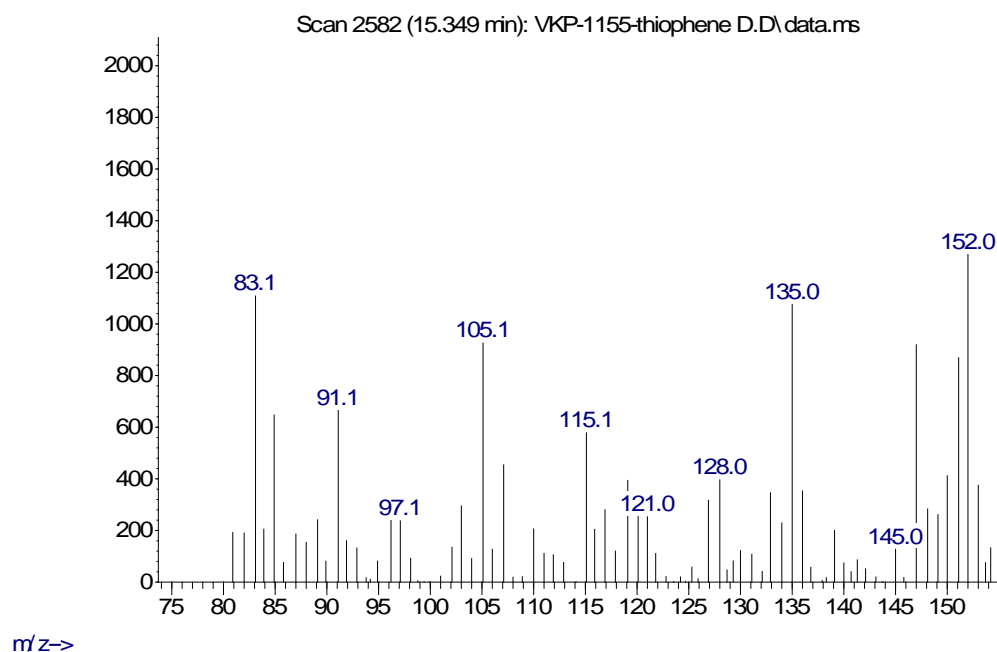
The reaction was performed on a (50 mg, 0.10 mmol) scale of mesityl(thiophen-2-yl)iodoniumtriflate to achieve 2-(trifluoromethyl)thiophene in 49% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$ 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

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

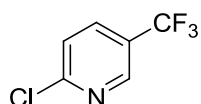


## Mass spectrum of product peak (15.34 min) from GCMS analysis:

Abundance

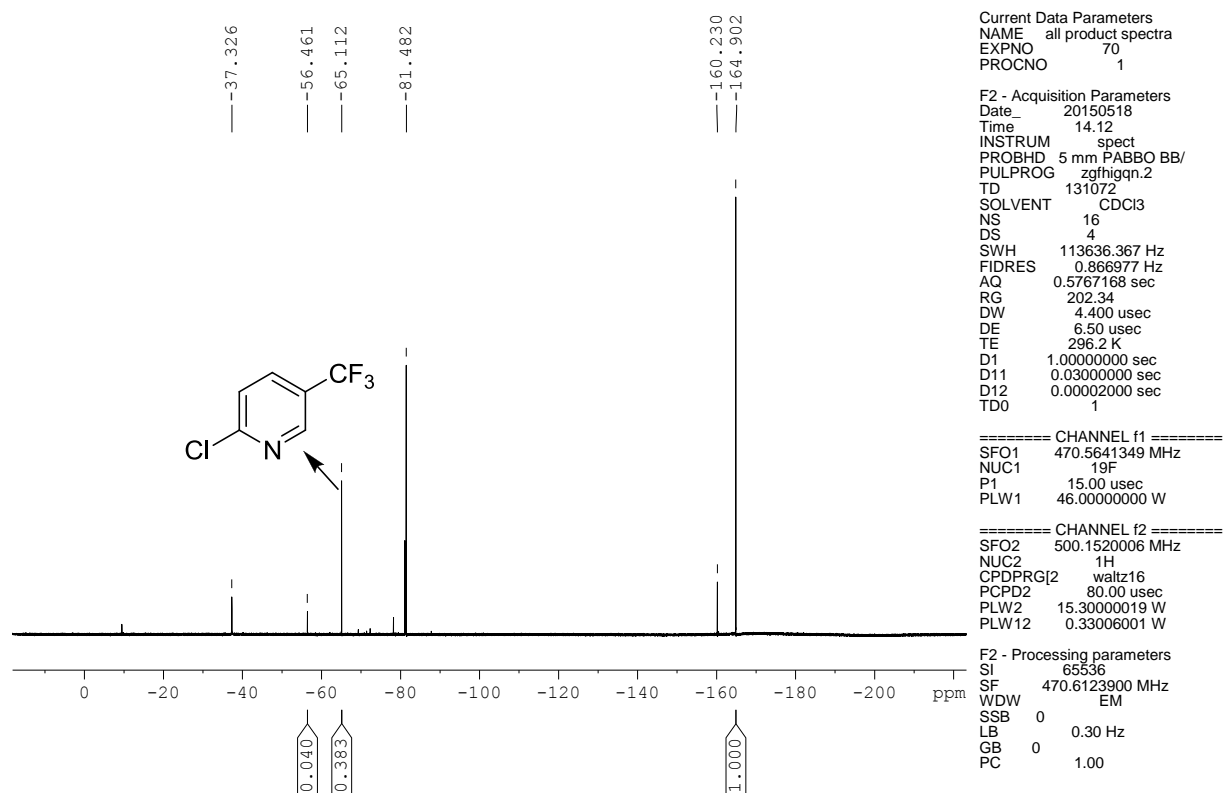


## 2-Chloro-5-(trifluoromethyl)pyridine 2x:

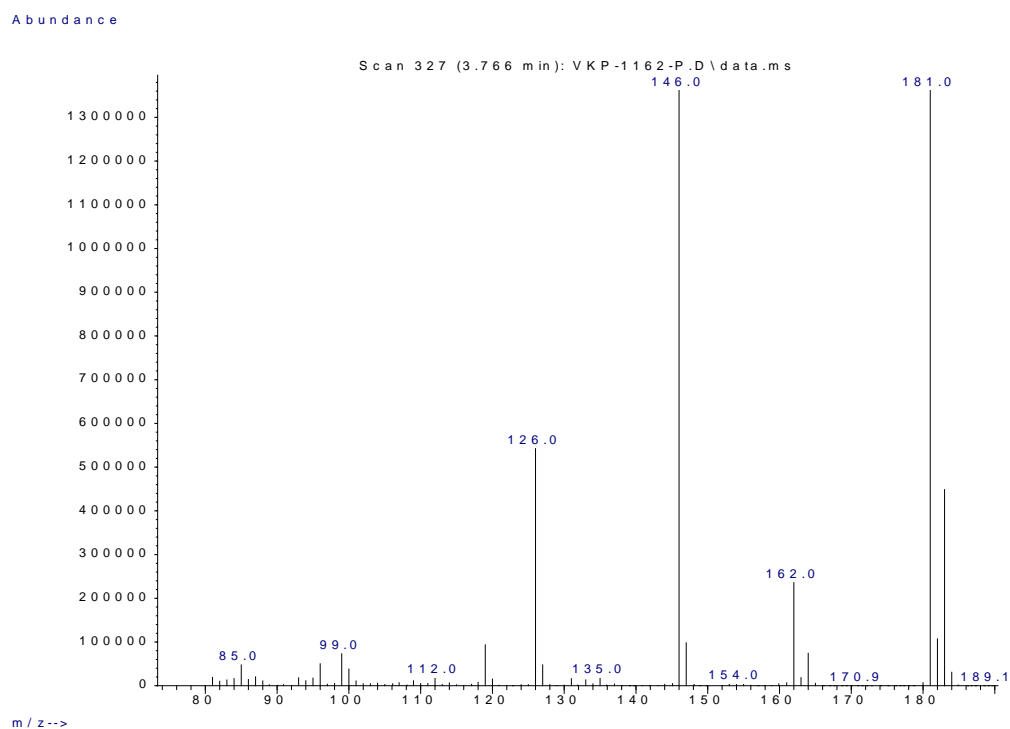


The reaction was performed on a (50 mg, 0.09 mmol) scale of 6-chloropyridin-3-yl(mesityl)iodoniumtriflate to achieve 2-chloro-5-(trifluoromethyl)pyridine in 72% yield, along with 7% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by  $^{19}\text{F}$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

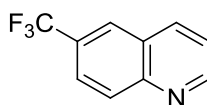
# <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



# Mass spectrum of product peak (16.76 min) from GCMS analysis:

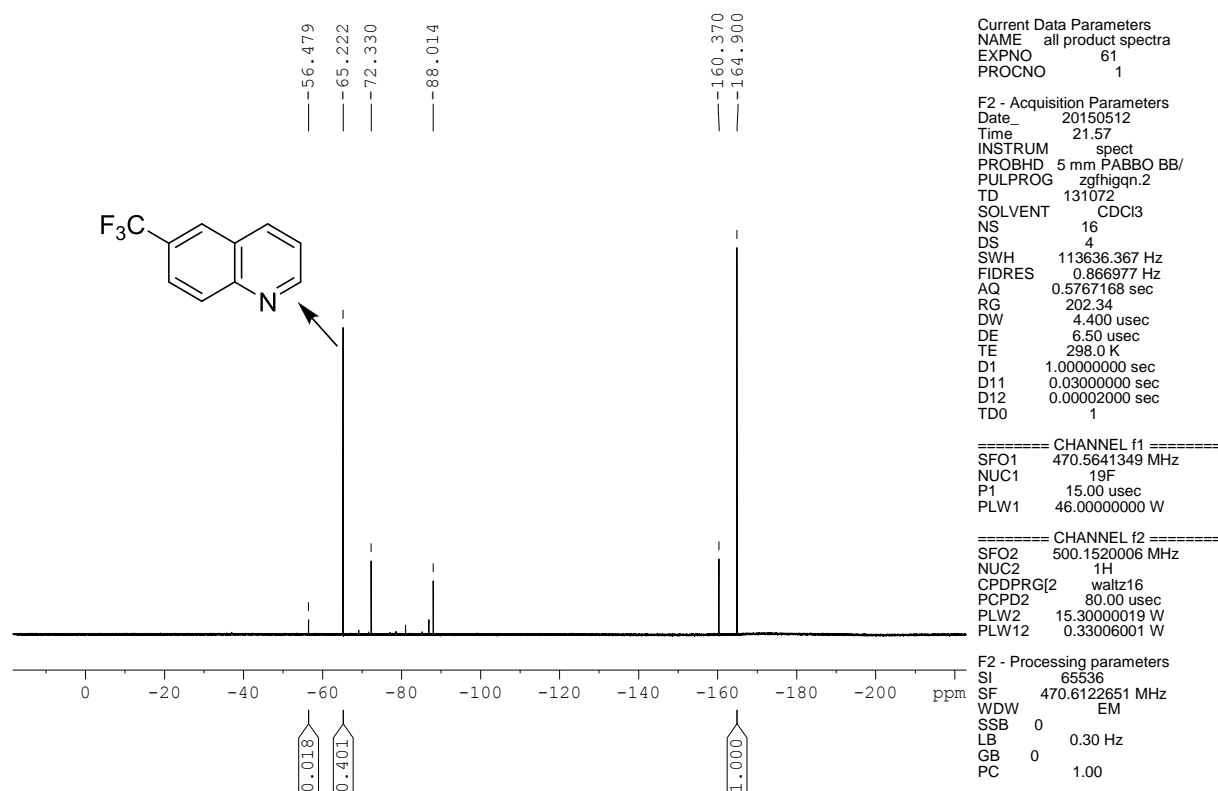


## 6-Trifluoromethylquinoline 2y:<sup>3c</sup>

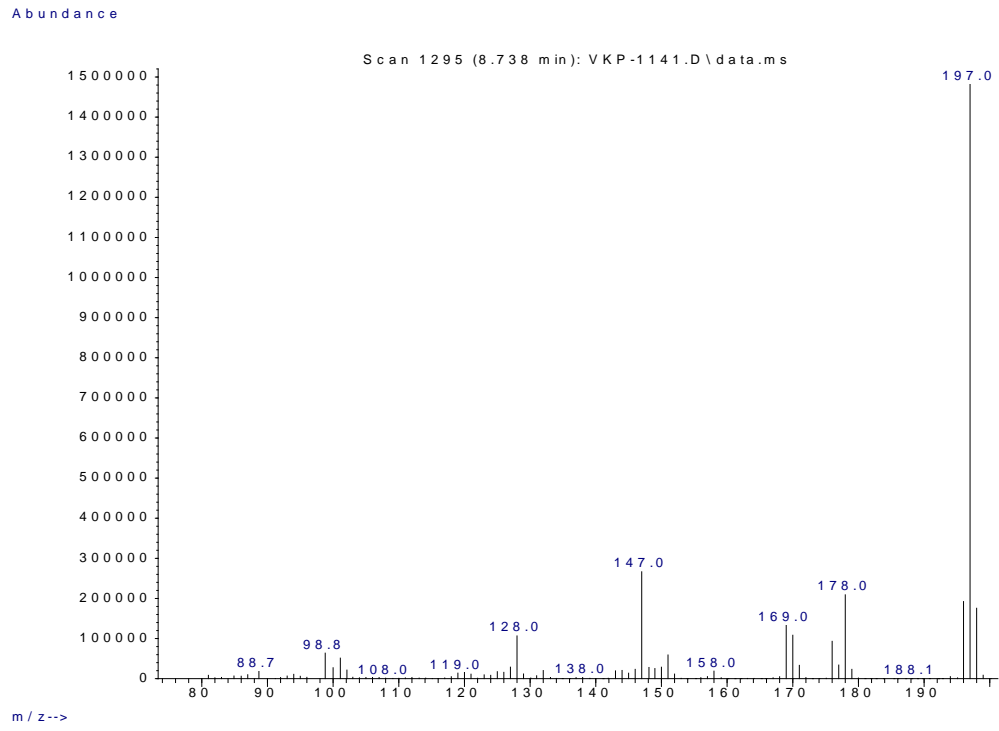


The reaction was performed on a (50 mg, 0.09 mmol) scale of mesityl(quinolin-6-yl)iodoniumtriflate to achieve 6-(trifluoromethyl)quinoline in 88% yield along with 2% of 1,3,5-trimethyl-2-(trifluoromethyl)benzene as side product using standard procedure. The yield was determined by <sup>19</sup>F NMR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

### <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, 24°C):



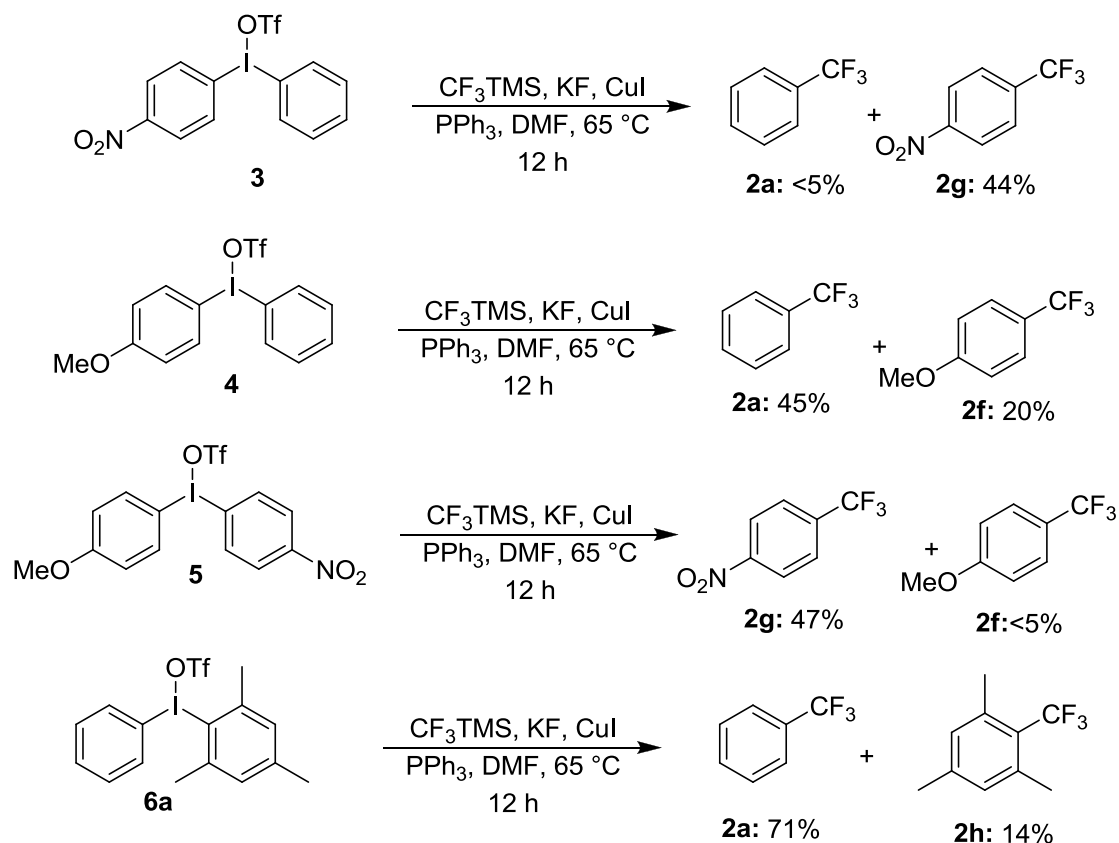
# Mass spectrum of product peak (8.73 min) from GCMS analysis:





## 6. Electronic and steric factor (Effect of substituent):

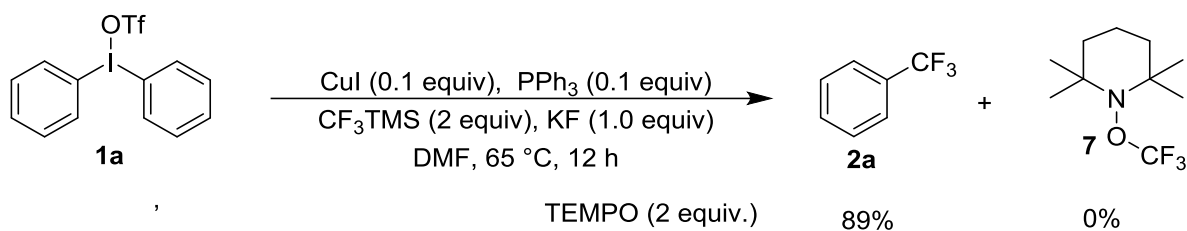
In order to understand the effect of substituent like, electron withdrawing electron releasing and neutral substrate has been subjected under standard reaction condition. The result is given in the scheme.



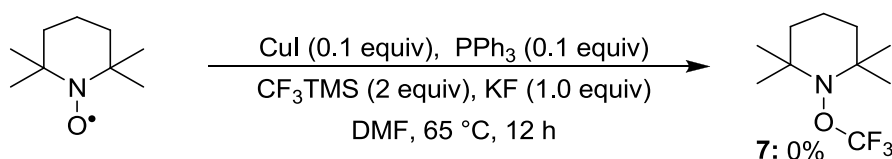
## 7. Mechanistic study:

### 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.

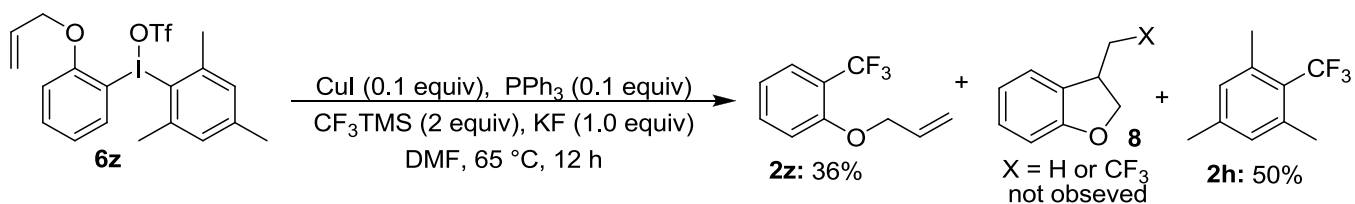


Without diaryliodonium salt under the standard reaction condition with (1 equiv.) of TEMPO, we did not observe TEMPO-CF<sub>3</sub> substituted product.



## 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 <sup>19</sup>F NMR using hexafluorobenzene as internal standard. The formation of product was further confirmed by GCMS.



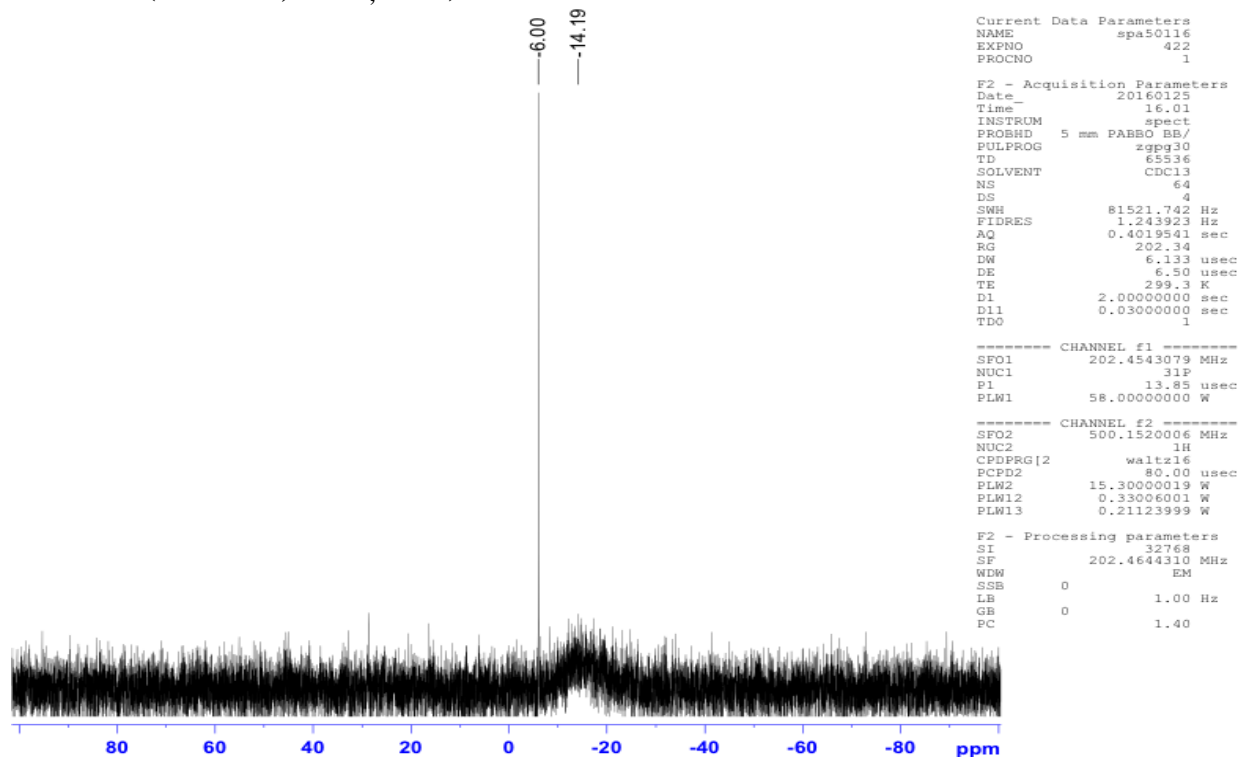
The above experiment suggests that, formation of trifluoromethyl radical or aryl radical is less likely.

## 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 ( $-50\text{ }^\circ\text{C}$  to  $+50\text{ }^\circ\text{C}$ ).

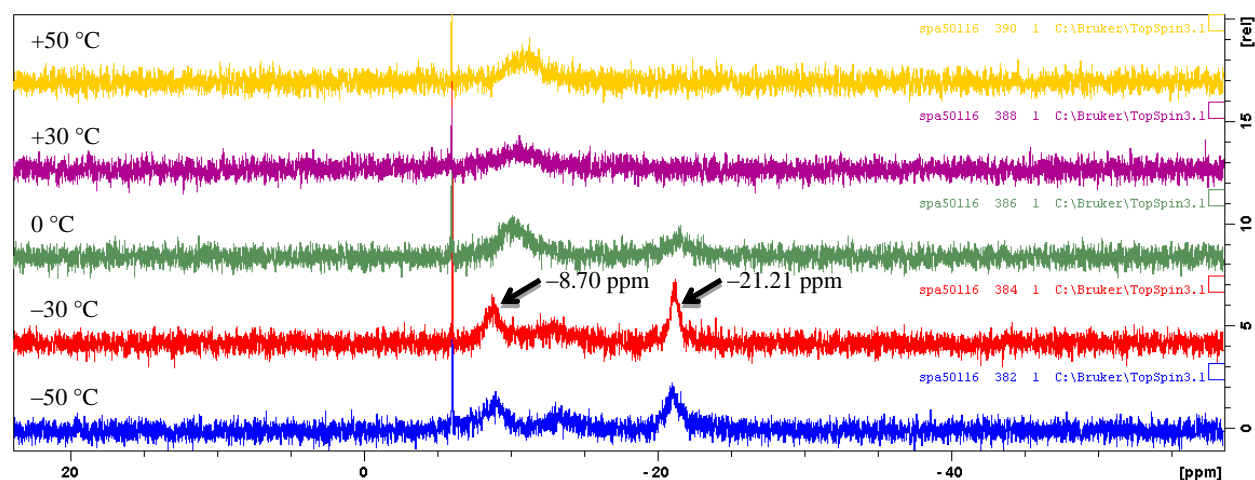
### Equimolar mixture of $\text{CuI}$ and $\text{PPh}_3$

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

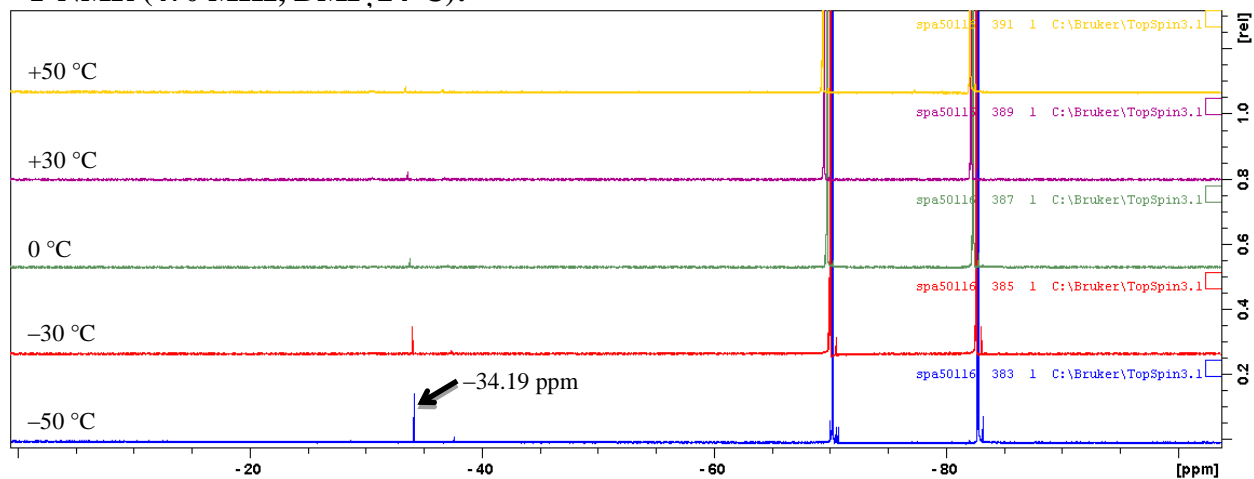


### Equimolar mixture of $\text{CuI}$ , $\text{PPh}_3$ , $\text{CF}_3\text{TMS}$ and $\text{KF}$ at variable temperature

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

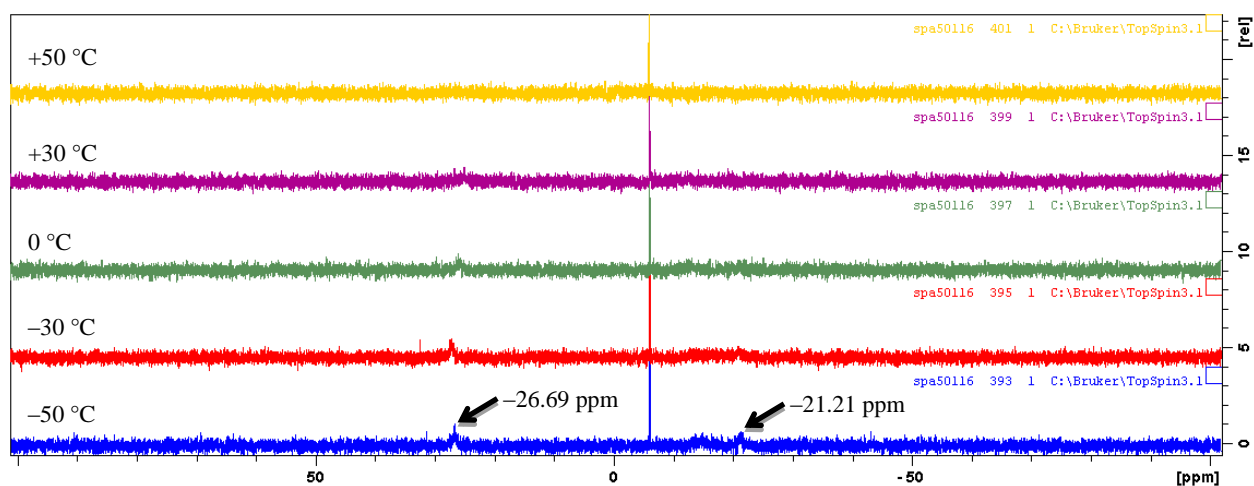


**$^{19}\text{F}$  NMR (470 MHz, DMF, 24°C):**

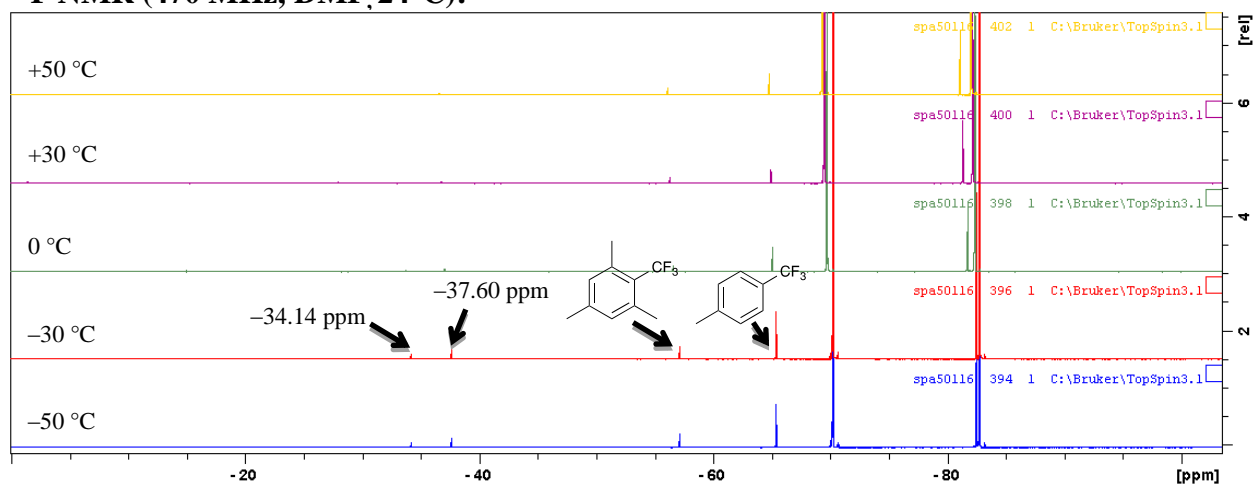


**Equimolar mixture of CuI,  $\text{PPh}_3$ ,  $\text{CF}_3\text{TMS}$ , KF and mesityl(4-methylphenyl)iodonium triflate at variable temperature**

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



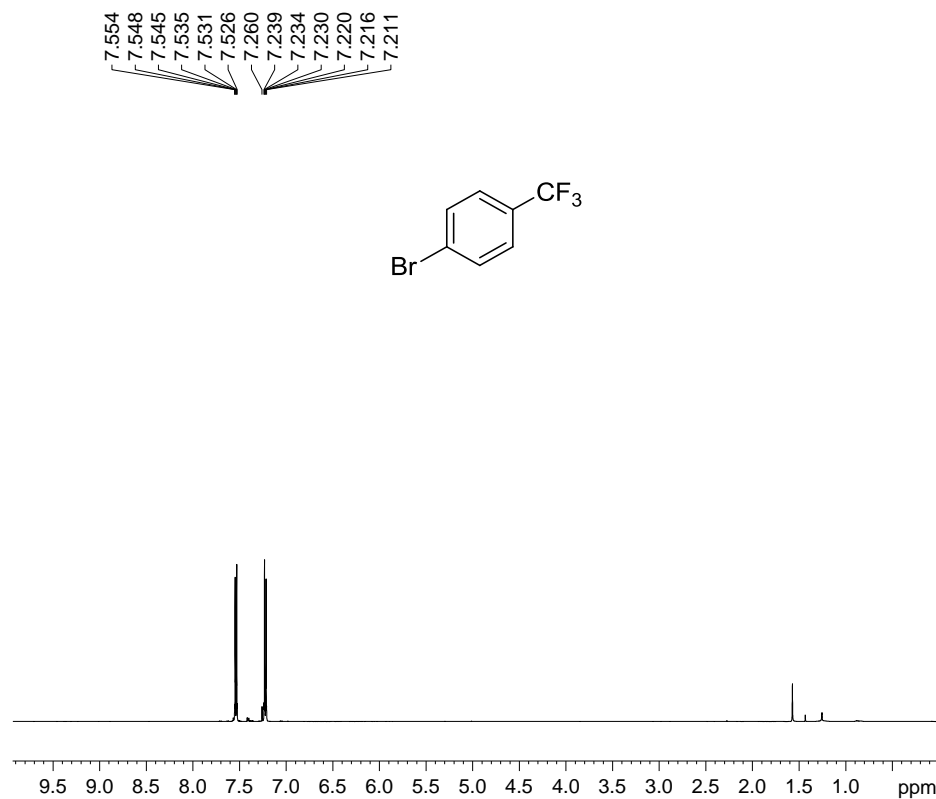
**$^{19}\text{F}$  NMR (470 MHz, DMF, 24°C):**



## 8. NMR spectra of isolated compound

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

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



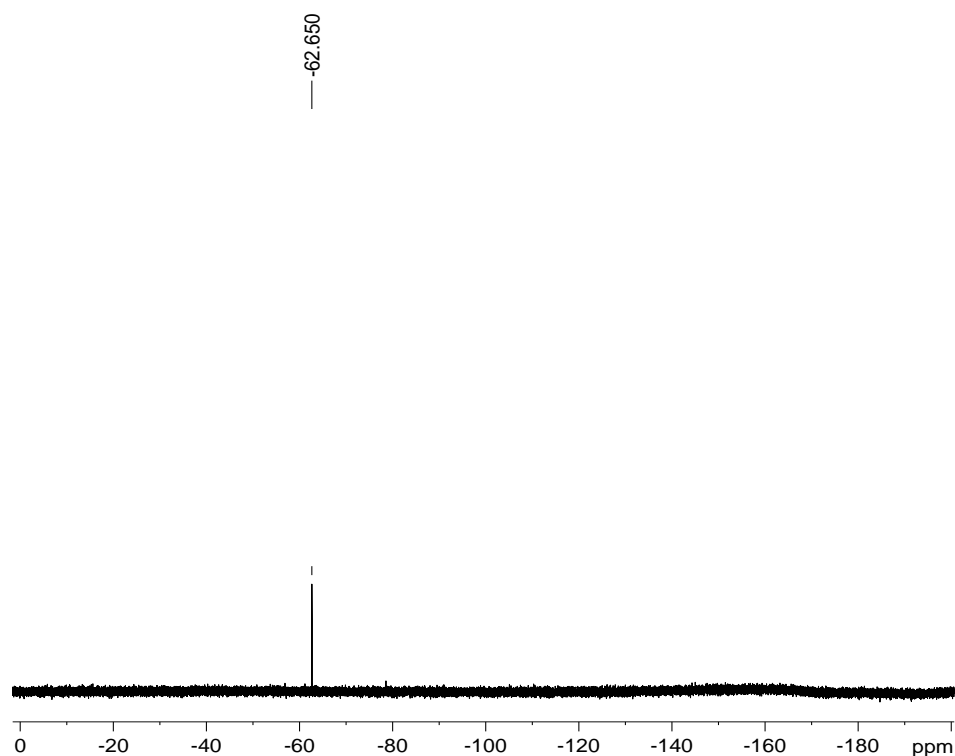
Current Data Parameters  
NAME spa51015  
EXPNO 71  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20151011  
Time 16.16  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 32768  
SOLVENT  $\text{CDCl}_3$   
NS 32  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.305176 Hz  
AQ 1.6384000 sec  
RG 124.08  
DW 50.000 usec  
DE 6.50 usec  
TE 295.2 K  
D1 0.50000000 sec  
TD0 1

===== CHANNEL f1 =====  
SFO1 500.1525008 MHz  
NUC1  $^1\text{H}$   
P1 11.75 usec  
PLW1 15.30000019 W

F2 - Processing parameters  
SI 65536  
SF 500.1500221 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

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



Current Data Parameters  
NAME spa51015  
EXPNO 67  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20151011  
Time 16.19  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpgqg.2  
TD 131072  
SOLVENT  $\text{CDCl}_3$   
NS 16  
DS 4  
SWH 113636.367 Hz  
FIDRES 0.868977 Hz  
AQ 0.5767168 sec  
RG 202.34  
DW 4.400 usec  
DE 6.50 usec  
TE 295.3 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
D12 0.00002000 sec  
TD0 1

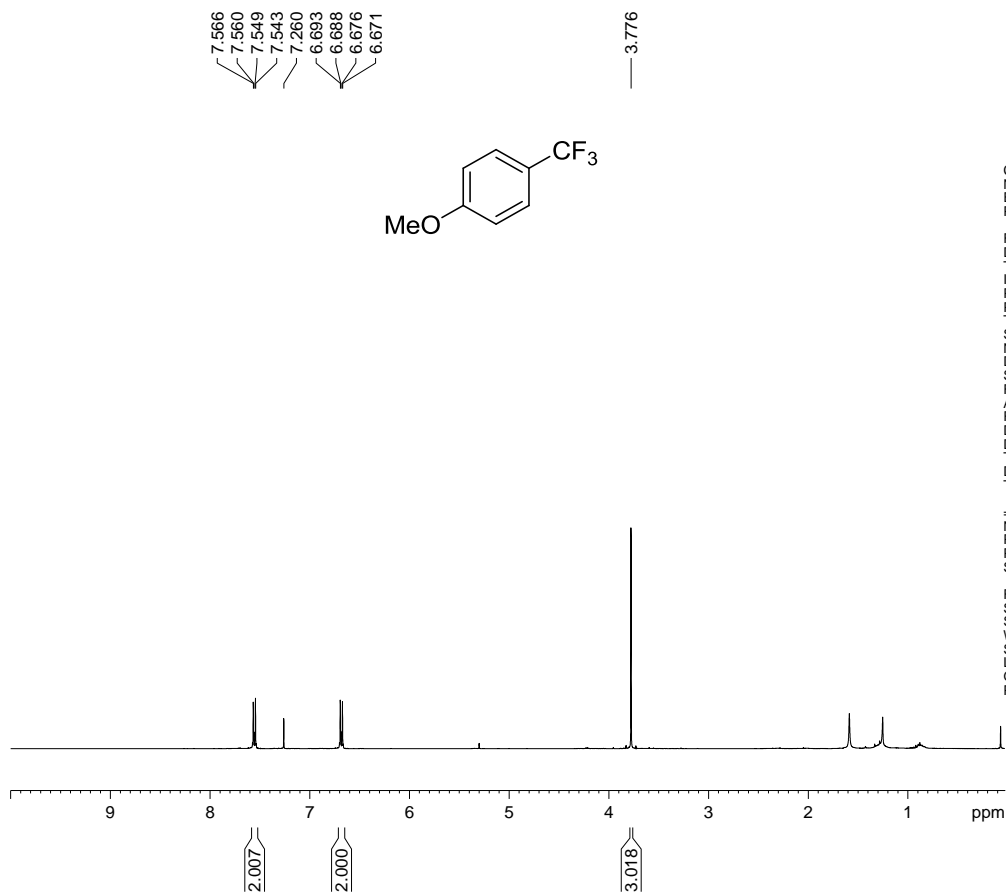
===== CHANNEL f1 =====  
SFO1 470.5641349 MHz  
NUC1  $^{19}\text{F}$   
P1 15.00 usec  
PLW1 46.00000000 W

===== CHANNEL f2 =====  
SFO2 500.1520006 MHz  
NUC2  $^1\text{H}$   
CPDPRG2 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

# 1-Methoxy-4-(trifluoromethyl)benzene 2f:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24°C):



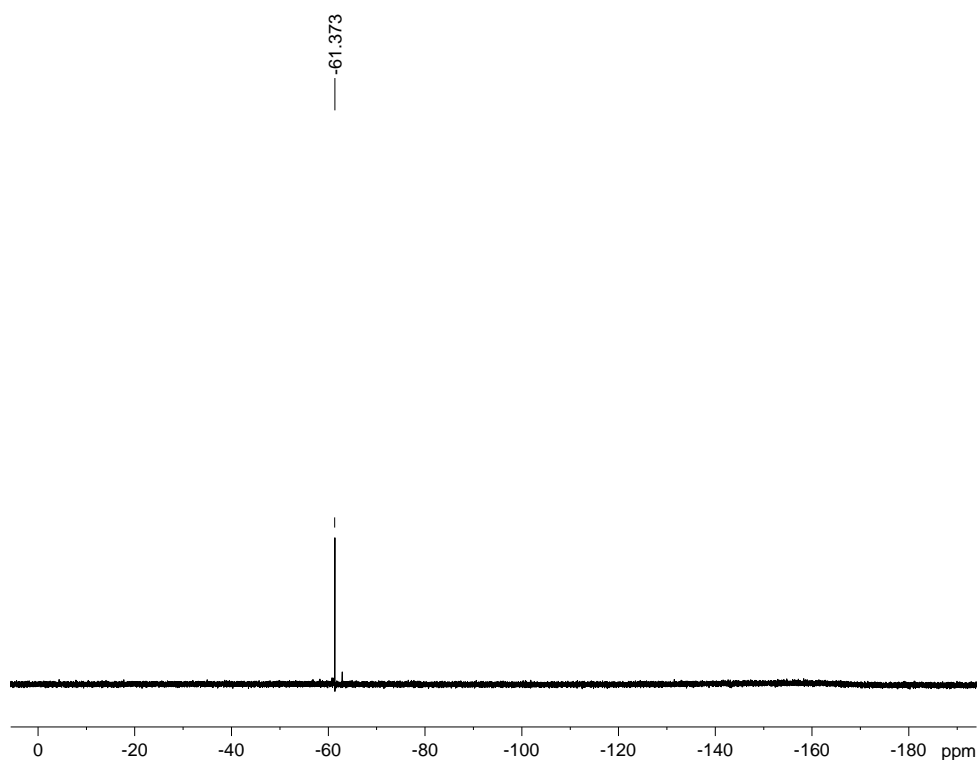
Current Data Parameters  
NAME spa41015  
EXPNO 190  
PROCNO 1

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 79.8  
DW 62.400 usec  
DE 6.50 usec  
TE 293.1 K  
D1 0.5000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.70 usec  
PLW1 7.7500000 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

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 24°C):



Current Data Parameters  
NAME spa51015  
EXPNO 72  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20151011  
Time 16.55  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
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 1.0000000 sec  
D11 0.0300000 sec  
D12 0.0000200 sec  
TD0 1

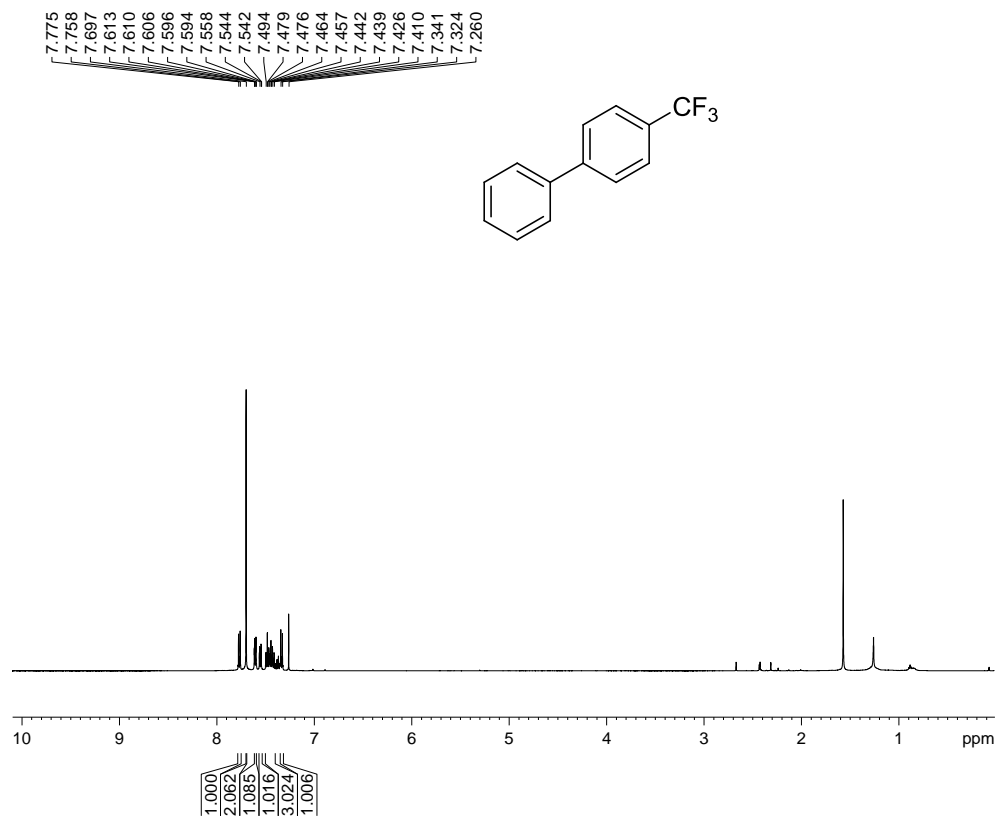
===== CHANNEL f1 =====  
SFO1 470.5641349 MHz  
NUC1 19F  
P1 15.00 usec  
PLW1 46.0000000 W

===== CHANNEL f2 =====  
SFO2 500.1520006 MHz  
NUC2 1H  
CPDPRG2 waltz16  
PCPD2 80.00 usec  
PLW2 15.3000019 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:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 24°C):



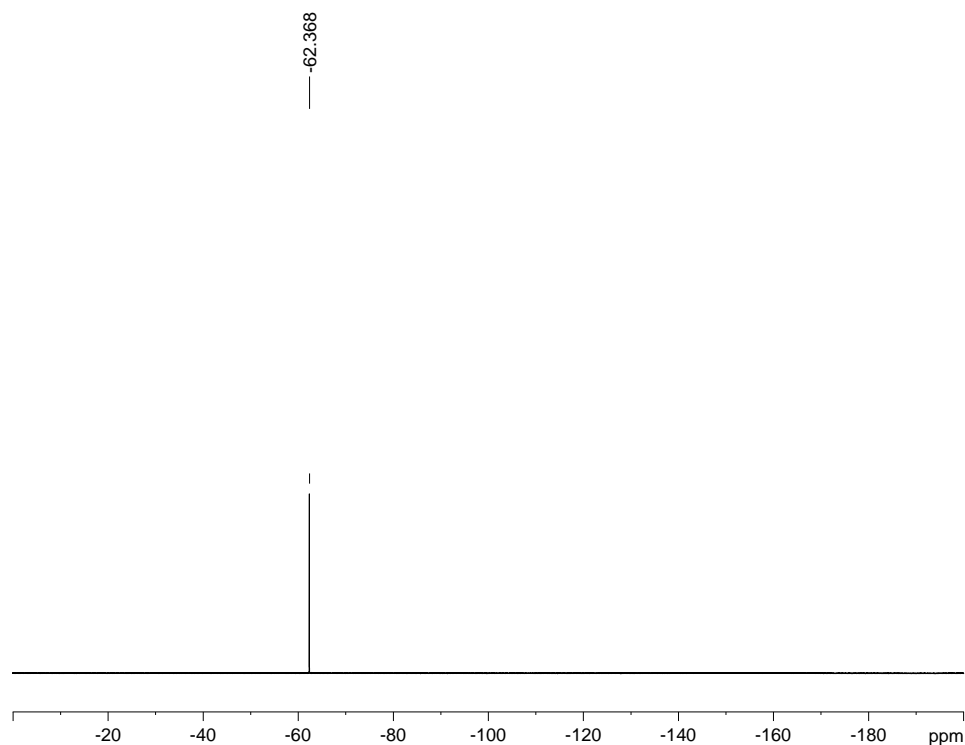
```
Current Data Parameters
NAME spa51015
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151011
Time 16.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32788
SOLVENT CDCl3
NS 32
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 180.86
DW 50.000 usec
DE 6.50 usec
TE 295.9 K
D1 0.5000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 500.1525008 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500221 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 24°C):



```
Current Data Parameters
NAME spa51015
EXPNO 33
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151005
Time 11.14
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 297.3 K
D1 1.0000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

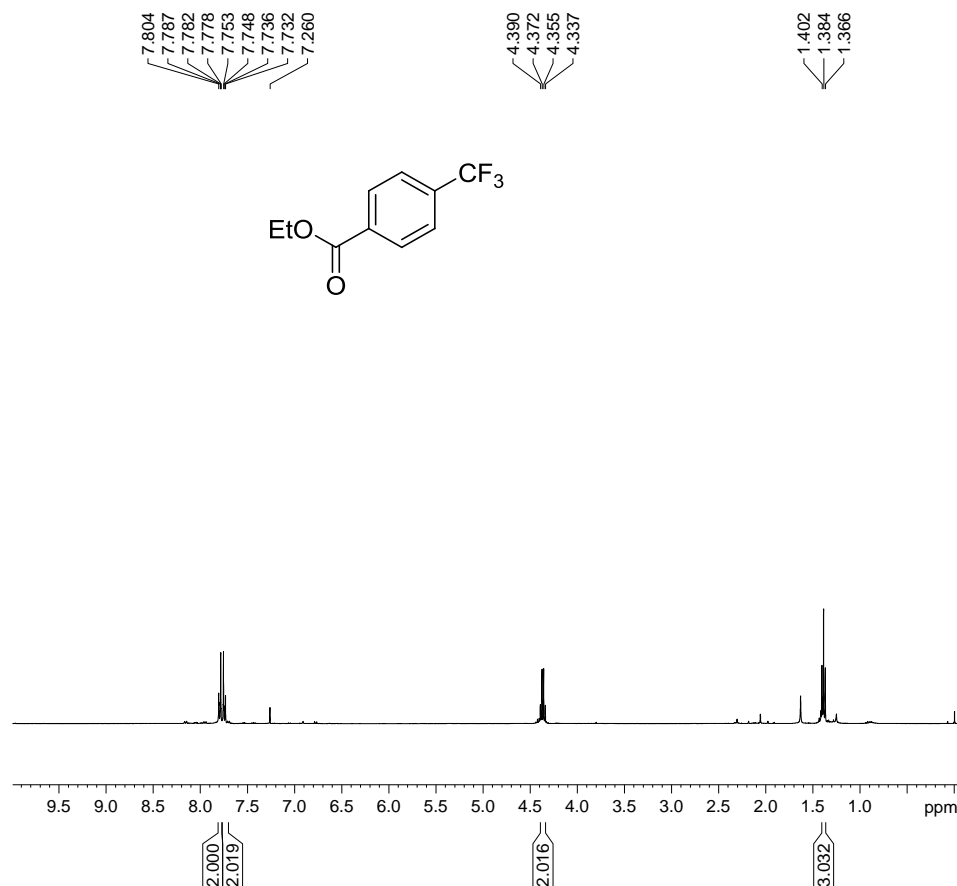
===== CHANNEL f1 =====
SFO1 470.5641349 MHz
NUC1 19F
P1 15.00 usec
PLW1 46.00000000 W

===== CHANNEL f2 =====
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG2 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
```

# Ethyl 4-(trifluoromethyl)benzoate 2s:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24°C):



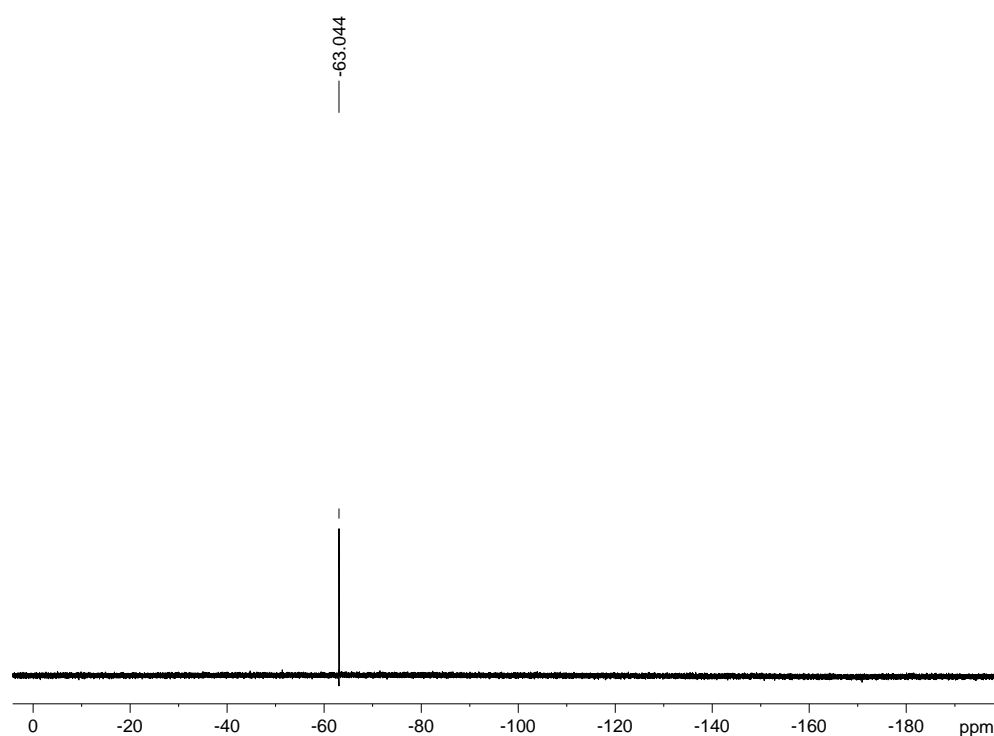
Current Data Parameters  
 NAME isolated nmr  
 EXPNO 172  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20151009  
 Time 4.04  
 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 169.77  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 293.0 K  
 D1 0.5000000 sec  
 TDO 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 15.70 usec  
 PLW1 7.7500000 W  
 SFO1 400.1320007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 400.1300093 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 24°C):



Current Data Parameters  
 NAME isolated nmr  
 EXPNO 52  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20151009  
 Time 13.18  
 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 295.4 K  
 D1 1.0000000 sec  
 D11 0.0300000 sec  
 D12 0.0002000 sec  
 TDO 1

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

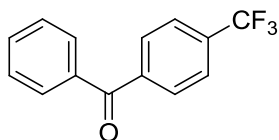
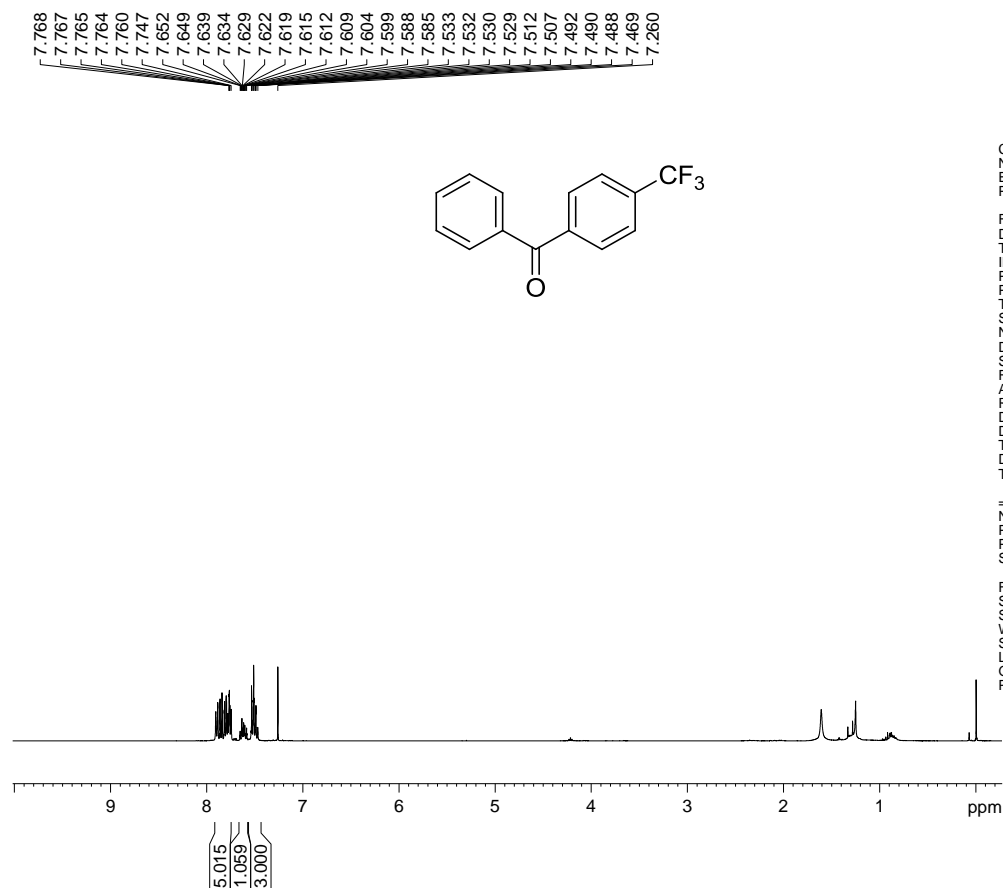
===== CHANNEL f2 =====  
 SFO2 500.1520006 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 15.3000019 W  
 PLW12 0.33006001 W

F2 - Processing parameters  
 SI 65536  
 SF 470.6111960 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



# Phenyl(4-(trifluoromethyl)phenyl)methanone 2t:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24°C):



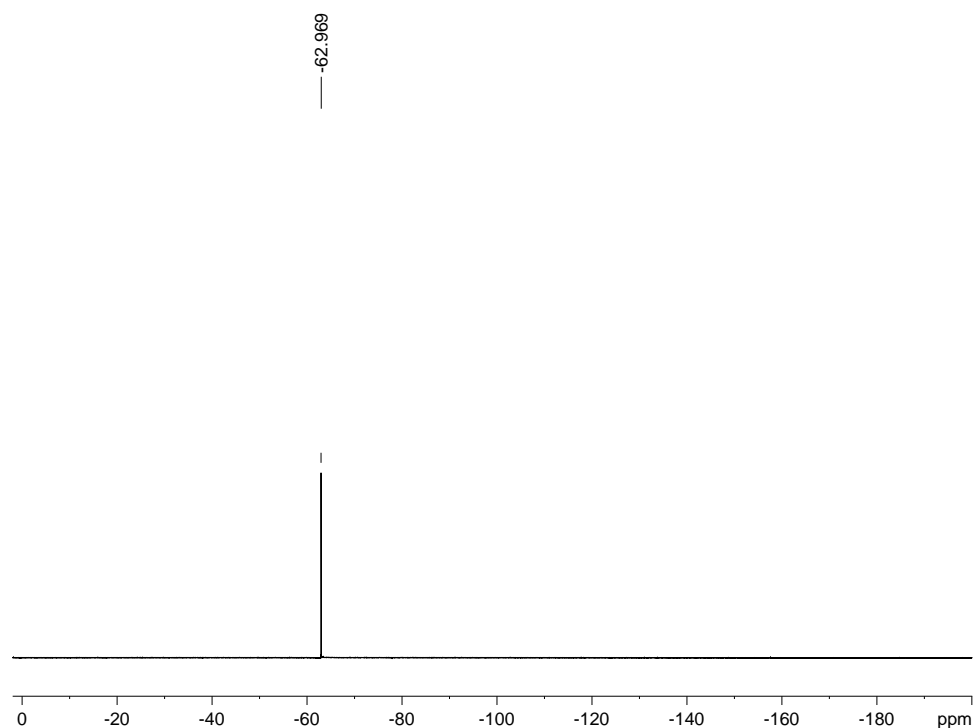
```
Current Data Parameters
NAME isolated nmr
EXPNO 168
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151009
Time 3.40
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 200.34
DW 62.400 usec
DE 6.50 usec
TE 293.0 K
D1 0.50000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 15.70 usec
PLW1 7.7500000 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
```

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 24°C):



```
Current Data Parameters
NAME isolated nmr
EXPNO 53
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151009
Time 13.22
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 0.5787168 sec
RG 202.34
DW 4.400 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

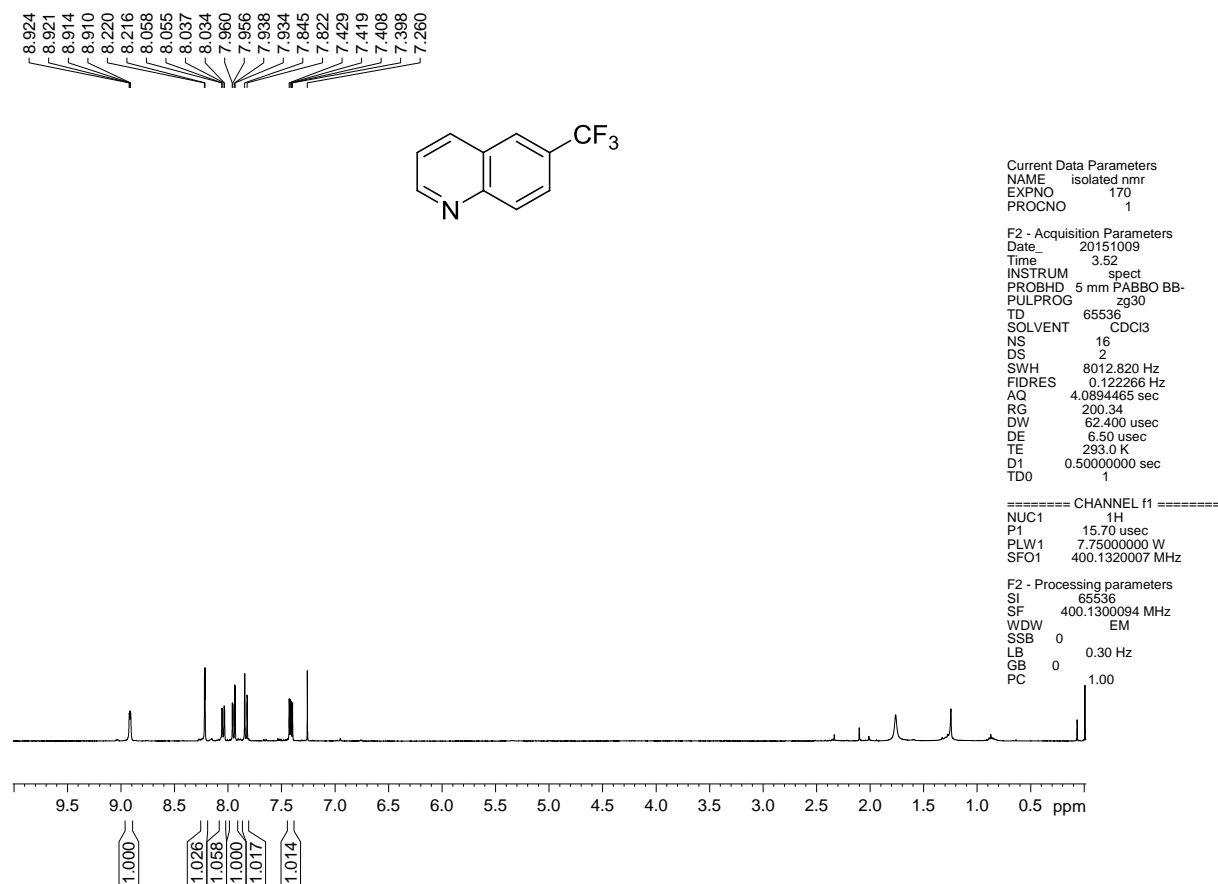
===== CHANNEL f1 =====
SFO1 470.5641349 MHz
NUC1 19F
P1 15.00 usec
PLW1 46.00000000 W

===== CHANNEL f2 =====
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG2 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
```

# 6-Trifluoromethylquinoline 2y:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24°C):



<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>, 24°C):

