Supplementary Information for

Electrophilic Activation of Molecular Bromine Mediated by I(III)

Lachlan Sharp-Bucknall, Tania, Marcus Sceney, Lachlan Barwise, and Jason L. Dutton *

Department of Biochemistry and Chemistry, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Victoria, Australia

j.dutton@latrobe.edu.au

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General Experimental

Glovebox solvents were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under N_2 atmosphere over 3 Å molecular sieves in the glovebox. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH_2, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. 4-NO_2-C_6H_4-I$(OAc)_2$ and 4-NO_2-C_6H_4-I$(OTFA)_2$ were synthesised by following literature procedure.[1] All other reagents were purchased from Sigma Aldrich and used as received. Glassware was dried in an oven at 120 °C overnight and transferred to the glovebox port or Schlenk line where it was subjected to three vacuum cycles over 30 minutes prior to use. NMR spectra for all experiments were recorded using Ascend 400 MHz spectrometer.

X-ray Crystallography Details

Single crystals were selected under n-paratone oil, mounted on nylon loops and placed into a cold stream (172 K) of N_2 on a Rigaku SuperNova CCD diffractometer using Cu Ka radiation. Structure solution and refinement were performed using the SHELXTL suite of software.

Experimental Procedures

Synthesis of 4-NO_2-C_6H_4-I(OAc)(OTf)

To a solution of 4-NO_2-C_6H_4-I$(OAc)_2$ (135 mg, 0.368 mmol) in CH_2Cl_2 (2 mL) was added TMS-OTf (75 mg, 0.337 mmol) which was stirred for 5 minutes at room temperature. This solution was then treated with hexanes (10 mL) to precipitate a white solid which was filtered and washed with hexanes (3 × 5 mL). Volatiles were then removed *in vacuo* to receive 4-NO_2-C_6H_4-I(OAc)(OTf) as a white crystalline solid (160 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.44 (m, 4H,), 2.24 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm): 150.6, 137.3, 126.8, 125.9, 18.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -77.13.

Synthesis of 4-NO_2-C_6H_4-I(OTFA)(OTf)

To a solution of 4-NO_2-C_6H_4-I$(OTFA)_2$ (208 mg, 0.438 mmol) in CH_2Cl_2 (2 mL) was added TMS-OTf (150 mg, 0.674 mmol) which was stirred for 5 minutes at room temperature. This solution was then treated with hexanes (10 mL) to precipitate a pale-yellow solid which was filtered and washed with hexanes (3 × 5 mL). Volatiles were then removed *in vacuo* to receive 4-NO_2-C_6H_4-I(OTFA)(OTf) as a pale-yellow solid (172 mg, 77 % yield). Single crystals suitable for X-ray crystallography were obtained *via* vapour diffusion ($CHCl_3$:pentane).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (m, 4H)

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm): 150.9, 136.9, 127.4, 119.5 (q, J_F = 319 Hz, $SO_3\underline{C}F_3$), *Carbon environments for trifluoroacetate not observed despite $SO_3\underline{C}F_3$ being clear. A quaternary carbon is overlapping the broad peak at 127.42 ppm*

DEPT-135 NMR (126 MHz, $CDCl_3$) δ (ppm): 136.9, 127.4

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -72.14 (OTFA), -76.37(OTf)

Reaction between PhI(OAc)(OTf) and TMS-Br

To a solution of $PhI(OAc)_2$ (23.6 mg, 0.0733 mmol) in $CDCl_3$ (0.5 mL) was added TMS-OTf (18.5 mg, 0.083 mmol) and stirred for 5 minutes to generate PhI(OAc)(OTf) This solution was then treated with TMS-Br (12.7 mg, 0.0830 mmol) immediately resulting in a colour change from colourless to orange which rapidly dissipated over the course of 15 minutes. The sample was taken for *in situ* ^1H NMR analysis to identify 4-bromoiodobenzene and 2-bromoiodobenzene as the major products.

Reaction between 4-NO_2-C_6H_4-I(OAc)(OTf) and TMS-Br

To a solution of 4-NO_2-C_6H_4-I(OAc)(OTf) (25 mg, 0.0547 mmol) in $CDCl_3$ (0.5 mL) was added TMS-Br (8.5 mg, 0.055 mmol) immediately resulting in a colour change from colourless to orange. The solution was stirred for 5 minutes at room temperature. The sample was then taken for *in situ* ^1H and ^{19}F NMR analysis.

General Procedure for bromination reactions using 4-NO_2-C_6H_4-I(OTFA)(OTf) (General Procedure A)

In a typical bromination reaction, 4-NO_2-C_6H_4-I(OTFA)(OTf) was generated *in situ* under glovebox conditions from 4-NO_2-C_6H_4-$I(OTFA)_2$ (30 mg, 0.0631 mmol) and TMS-OTf (15.4 mg, 0.07 mmol) in $CDCl_3$ (0.5 mL). This solution was then charged into an NMR tube with aryl substrate (0.0631 mmol, 1.0 eq.). The NMR tube was then removed from the glovebox and charged with Br_2 (3.4 µL, 0.0631 mmol) under a positive nitrogen stream, capped and inverted to reach homogeneity. The resulting solution was then immediately taken for ^1H NMR analysis.

General Procedure for bromination reactions using 4-NO_2-C_6H_4-I(OTFA)$_2$ and catalytic HOTf with aryl substrates (General procedure B)

In a typical bromination reaction, an NMR tube was charged with 4-NO_2-C_6H_4-I(OTFA)$_2$ (30 mg, 0.0631 mmol) and aryl substrate (0.0631 mmol, 1.0 eq.) in $CDCl_3$ (0.5 mL) under glovebox conditions. The NMR tube was removed from the glovebox and charged with Br_2 (3.4 µL, 0.0631 mmol) and 1 µL of HOTf (~0.15 eq) under a positive nitrogen stream, capped and inverted to reach homogeneity. The resulting solution was then immediately taken for ^{1}H NMR analysis.

General Procedure for bromination reactions using 4-NO_2-C_6H_4-I(OTFA)$_2$ and catalytic TMS-OTf with aryl substrates (General procedure C)

In a typical bromination reaction, an NMR tube was charged with 4-NO_2-C_6H_4-I(OTFA)$_2$ (30 mg, 0.0631 mmol), TMS-OTf (2 mg, 0.009 mmol) and aryl substrate (0.0631 mmol, 1.0 eq.) in $CDCl_3$ (0.5 mL) under glovebox conditions. The NMR tube was removed from the glovebox and charged with Br_2 (3.4 µL, 0.0631 mmol) under a positive nitrogen stream, capped and inverted to reach homogeneity. The resulting solution was then immediately taken for ^{1}H NMR analysis.

General Procedure for bromination reactions using 4-NO_2-C_6H_4-I(OTFA)$_2$ and catalytic HOTf with 2 equivalents of aryl substrate (General procedure D)

In a typical bromination reaction, a small vial was charged with 4-NO_2-C_6H_4-I(OTFA)$_2$ (60 mg, 0.126 mmol) and aryl substrate (0.252 mmol, 2.0 eq.) in $CDCl_3$ (0.5 mL) under glovebox conditions. The vial was then removed from the glovebox and charged with Br_2 (6.42 µL, 0.126 mmol) and 2.5 µL of HOTf (~0.2 eq) under a positive nitrogen stream. The reaction was stirred for an appropriate amount of time prior to being taken for ^{1}H NMR analysis.

General procedure for bromination of 2 equivalents aryl substrate via 4-NO_2-C_6H_4-I(OTFA)$_2$ and catalytic HOTf at low temperature (General procedure E)

4-NO_2-C_6H_4-I(OTFA)$_2$ (30 mg, 0.063 mmol) and two equivalents (0.126 mmol) of aryl substrate were combined in a solution of $CDCl_3$ (0.5 mL). The vessel was briefly purged with dry N_2, capped, and cooled to -45 °C. Br_2 (3.4 µL, 0.066 mmol) and HOTf (1.2 µL, 0.014 mmol, 0.20 eq) were added, and the solution was allowed to warm to room temperature over 2.5 h while stirring, before transfer to an NMR tube where further reaction progress was tracked.

General procedure for bromination of 3 equivalents aryl substrate via 4-NO_2-C_6H_4-I(OTFA)$_2$ and catalytic HOTf (General procedure F)

4-NO_2-C_6H_4-I(OTFA)$_2$ (30 mg, 0.063 mmol) and three equivalents (0.190 mmol) of aryl substrate were combined in a solution of $CDCl_3$ (0.5 mL). Br_2 (3.4 µL, 0.066 mmol) and HOTf (1.2 µL, 0.014 mmol, 0.20 eq) were added, and the solution was agitated for 10 minutes before transfer to an NMR tube for analysis.

General Procedure for bromination reactions using 4-NO_2-C_6H_4-I(OAc)(OTf) with aryl substrates

In a typical bromination reaction, an NMR tube was charged with 4-NO_2-C_6H_4-I(OAc)(OTf) (≈25 mg, 0.055 mmol) and aryl substrate (0.060 mmol, 1.1 eq.) in $CDCl_3$ (0.5 mL) under glovebox conditions. The NMR tube was then removed from the glovebox and charged with Br_2 (2.8 µL, 0.055 mmol) under a positive nitrogen stream, capped and inverted several times to reach homogeneity. The resulting solution was then immediately taken for ^{1}H NMR analysis.

Reaction between bromobenzene and HBr

To a solution of bromobenzene (6.1 mg, 0.039 mmol) in $CDCl_3$ (0.5 mL) was added 48% HBr (4.4 µL, 0.039 mmol). The solution was stirred for 5 minutes at room temperature. The sample was then taken for *in situ* ^1H NMR analysis.

Reaction between 4-NO_2-C_6H_4-I(OTFA)$_2$, catalytic HOTf and HBr with 2 equivalents of bromobenzene

In a typical bromination reaction, a small vial was charged with 4-NO_2-C_6H_4-I(OTFA)$_2$ (18.6 mg, 0.039 mmol) and bromobenzene (6.1 mg, 0.039 mmol) in $CDCl_3$ (0.5 mL). The vial was then charged with 48% HBr (4.4 µL, 0.039 mmol) and 1 µL of HOTf (~0.2 eq) immediately resulting in a colour change from colourless to orange. The solution was stirred for 5 minutes at room temperature prior to being taken for ^1H and ^{19}F NMR analysis.

Reaction between Br_2 with catalytic HOTf and aryl substrate

To a solution of Br_2 (2 µL, 0.039 mmol in $CDCl_3$ (0.5 mL)) aryl substrate (0.039 mmol) was added. The vial was then charged with 1 µL of HOTf (~0.2 eq). The solution was stirred for 5 minutes at room temperature. The sample was then taken for *in situ* ^1H NMR analysis.

NMR Spectra

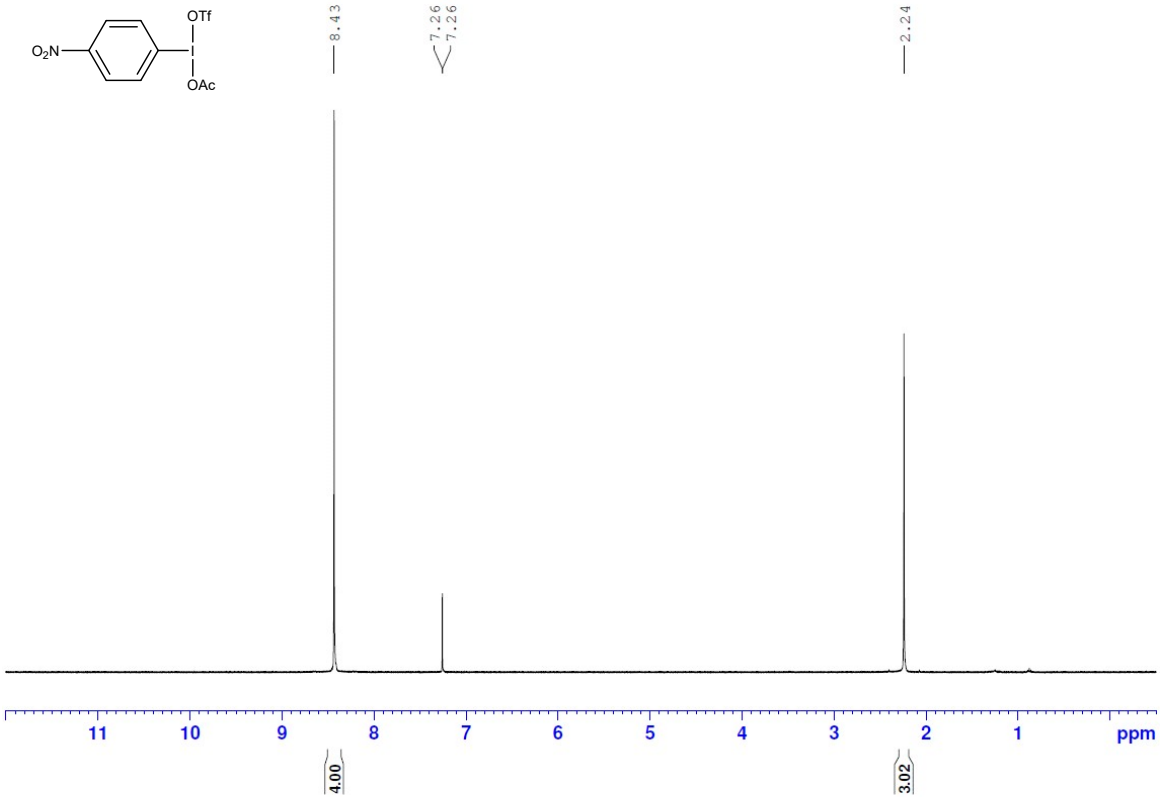


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OAc)(OTf).

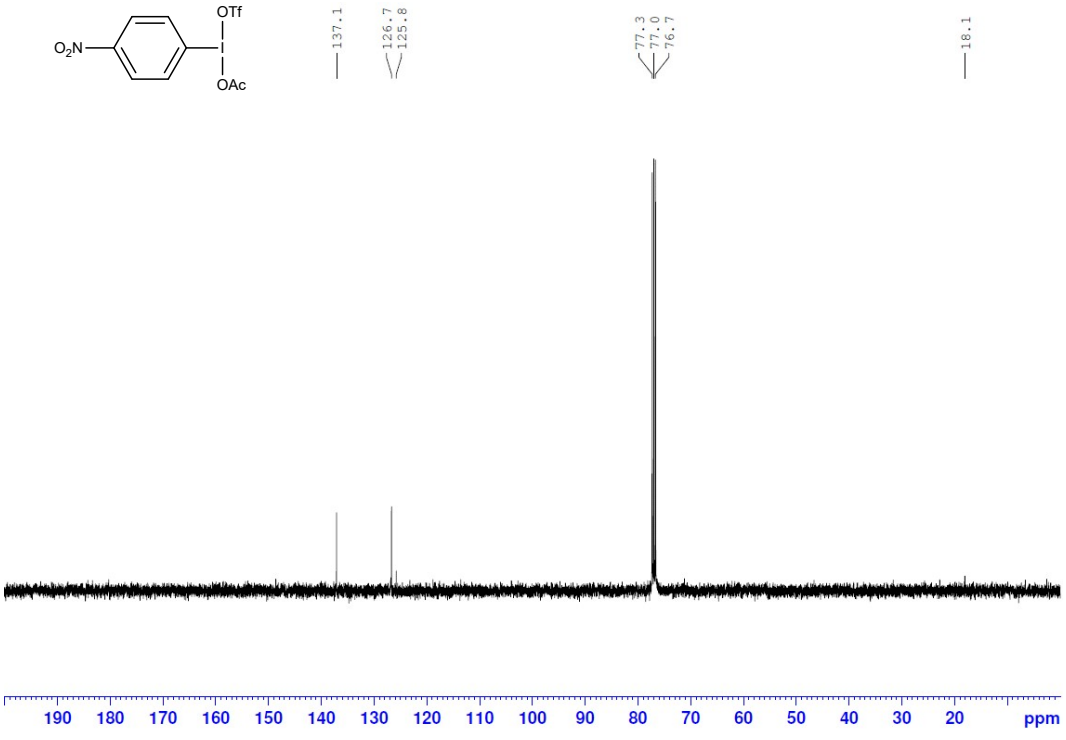


Figure S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OAc)(OTf).

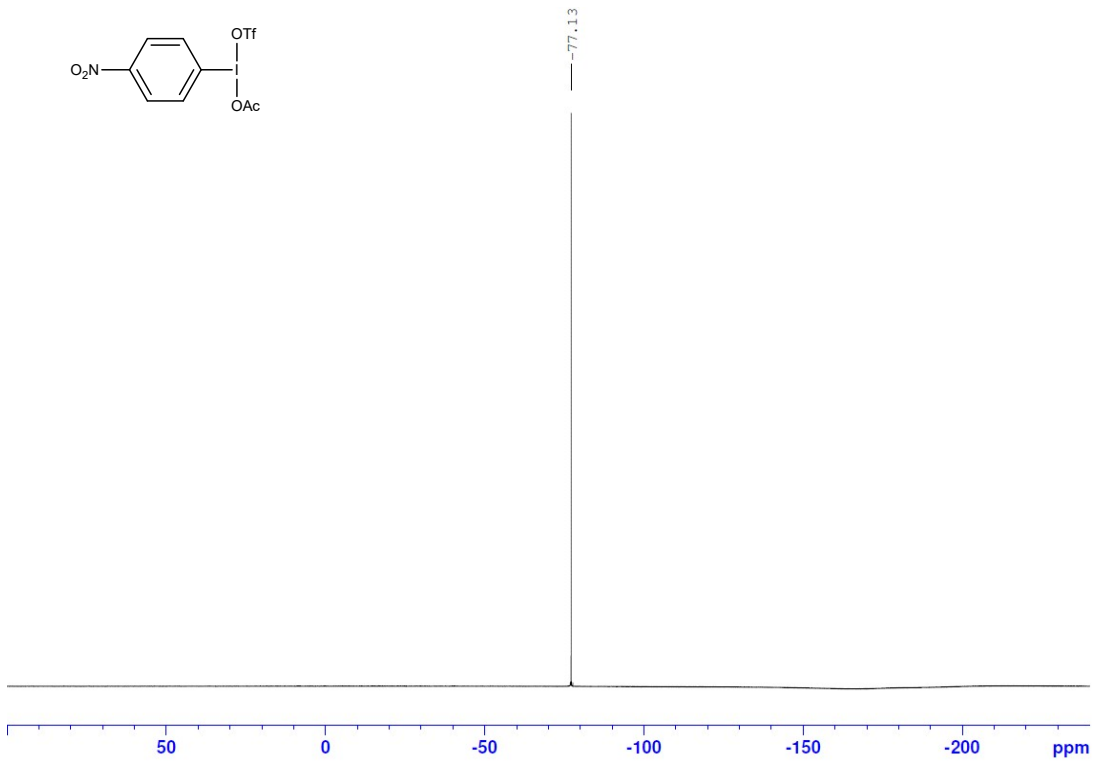


Figure S3. ^{19}F NMR (376 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OAc)(OTf).

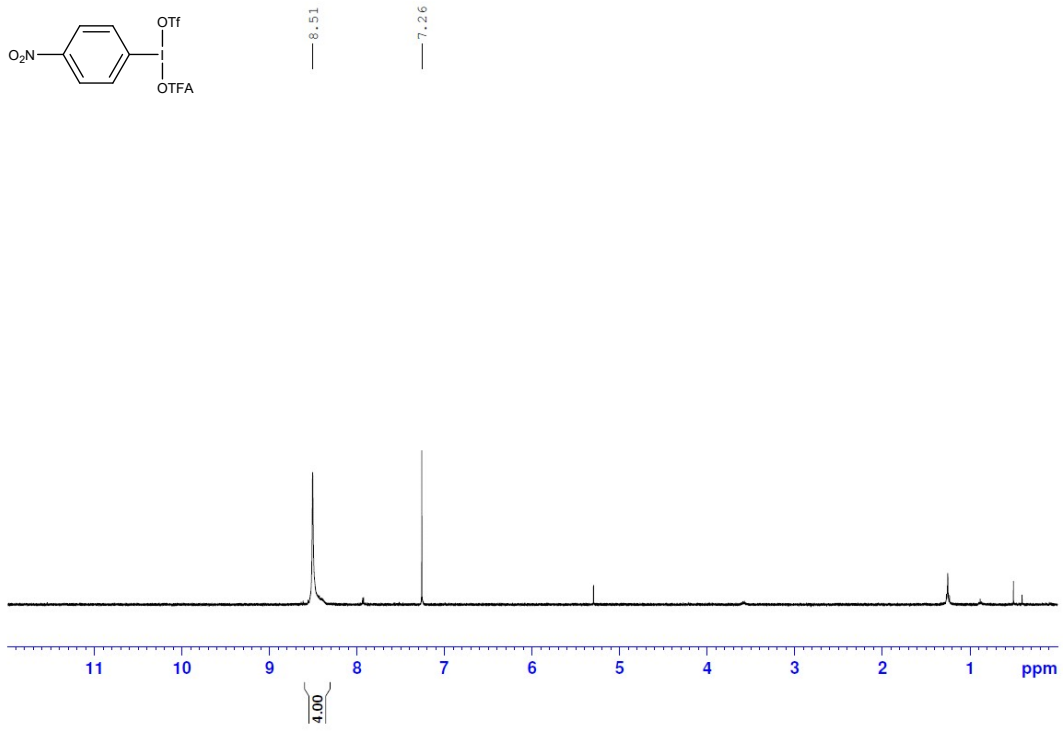


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)(OTf).

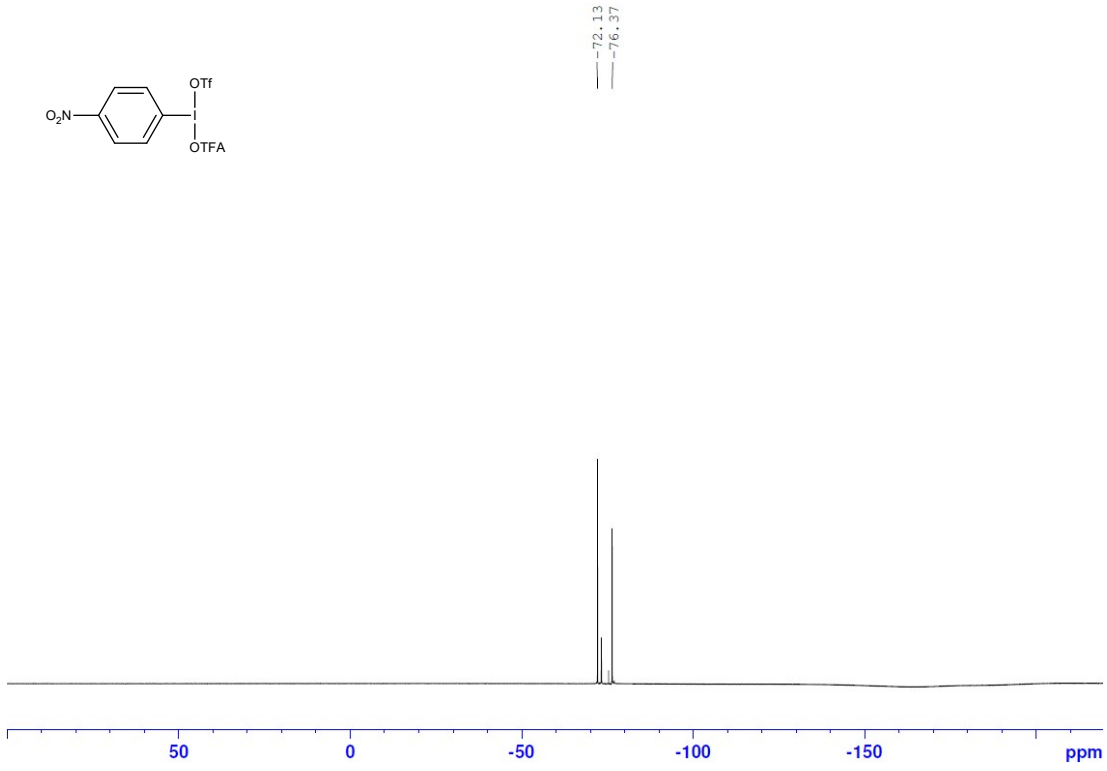


Figure S5. ^{19}F NMR (376 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)(OTf).

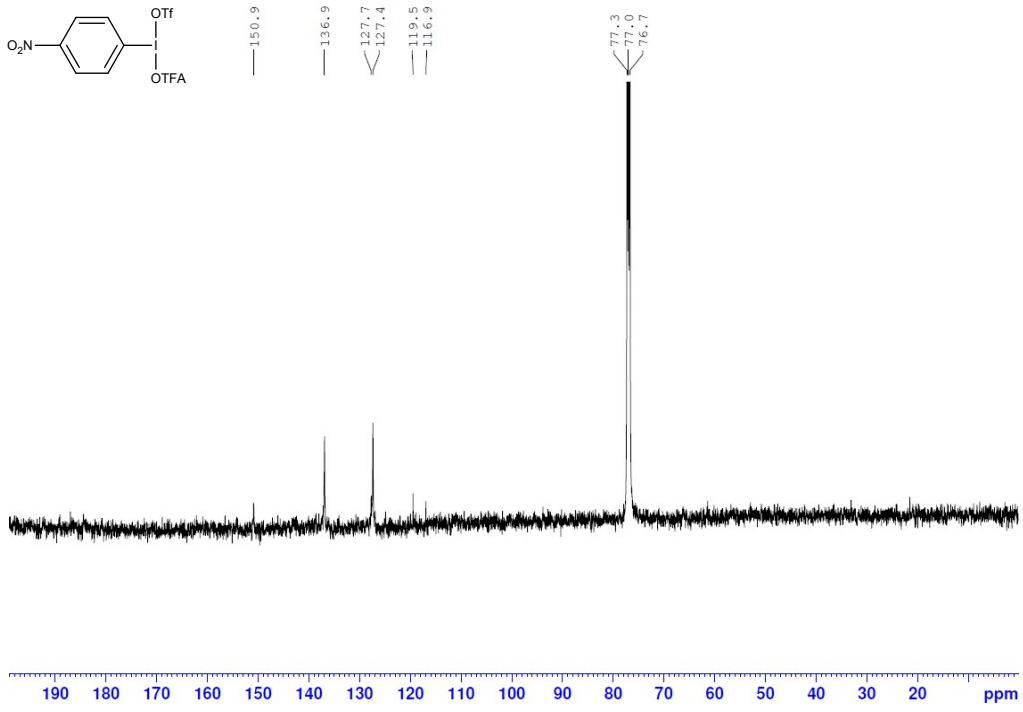


Figure S6. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)(OTf).

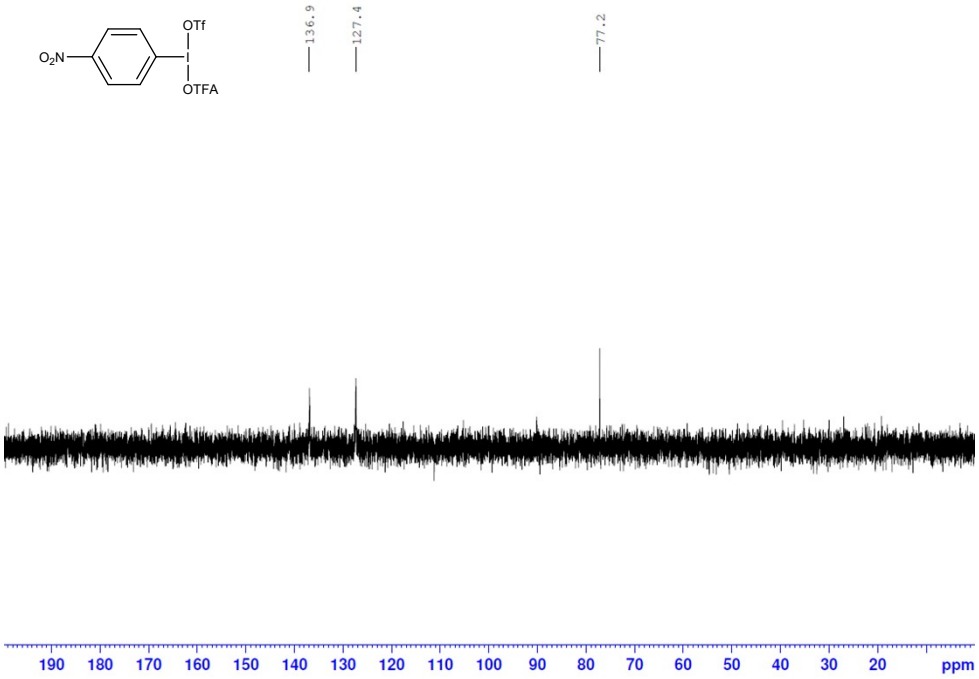


Figure S7. $^{13}C\{^{1}H\}$ 135DEPT NMR (126 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)(OTf).

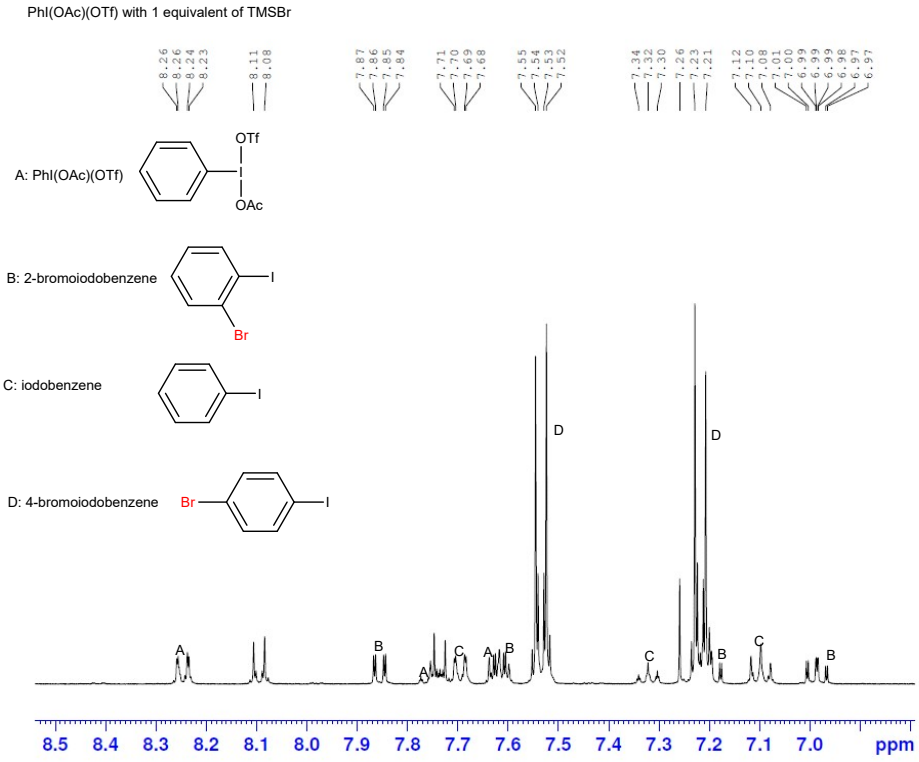


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of PhI(OAc)(OTf) with TMS-Br.

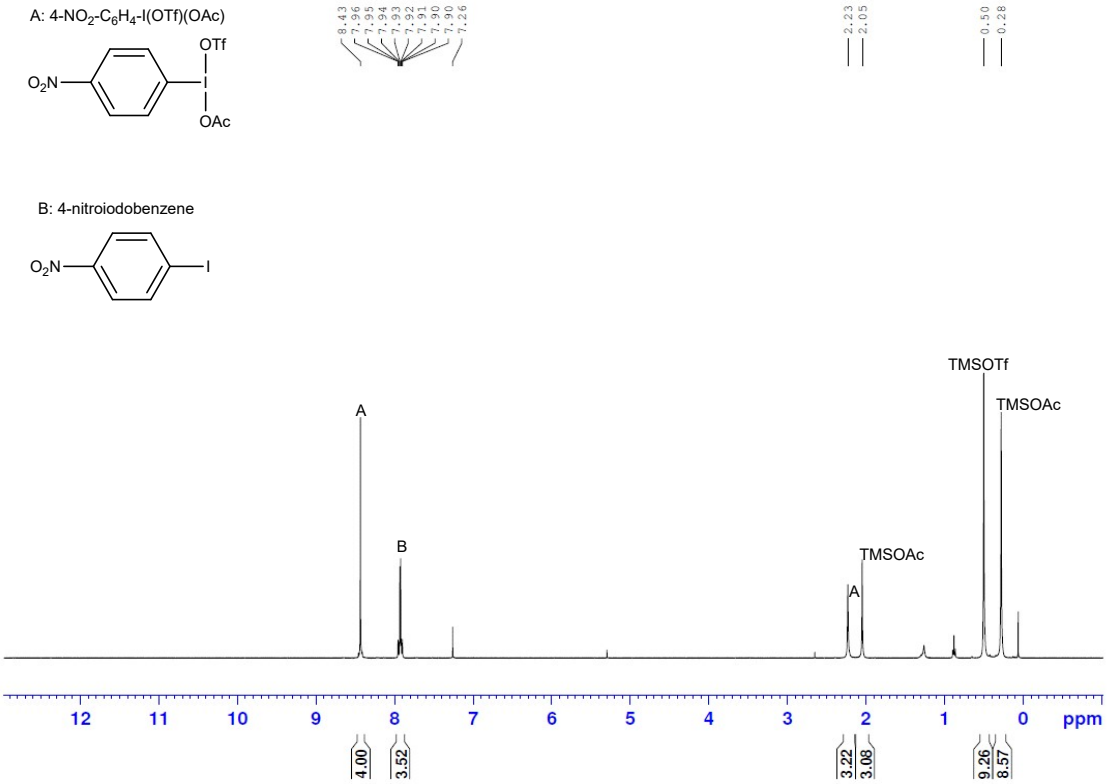


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OAc)(OTf) with TMS-Br.

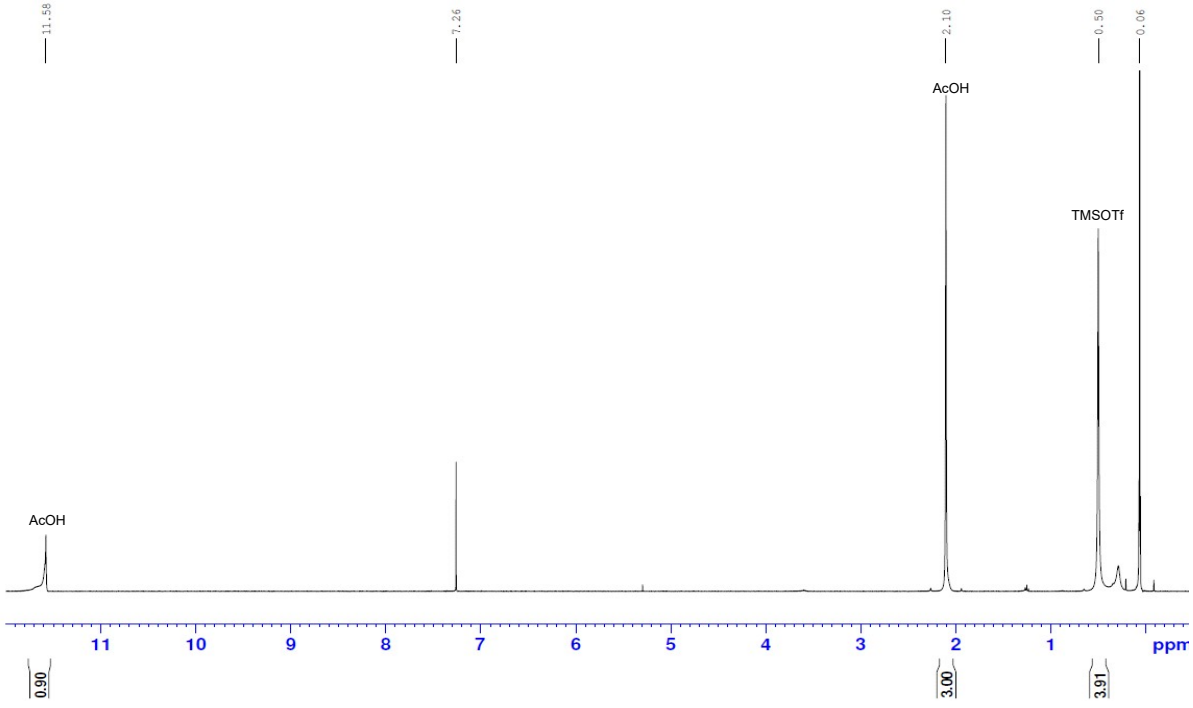


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of TMSOAc with HOTf.

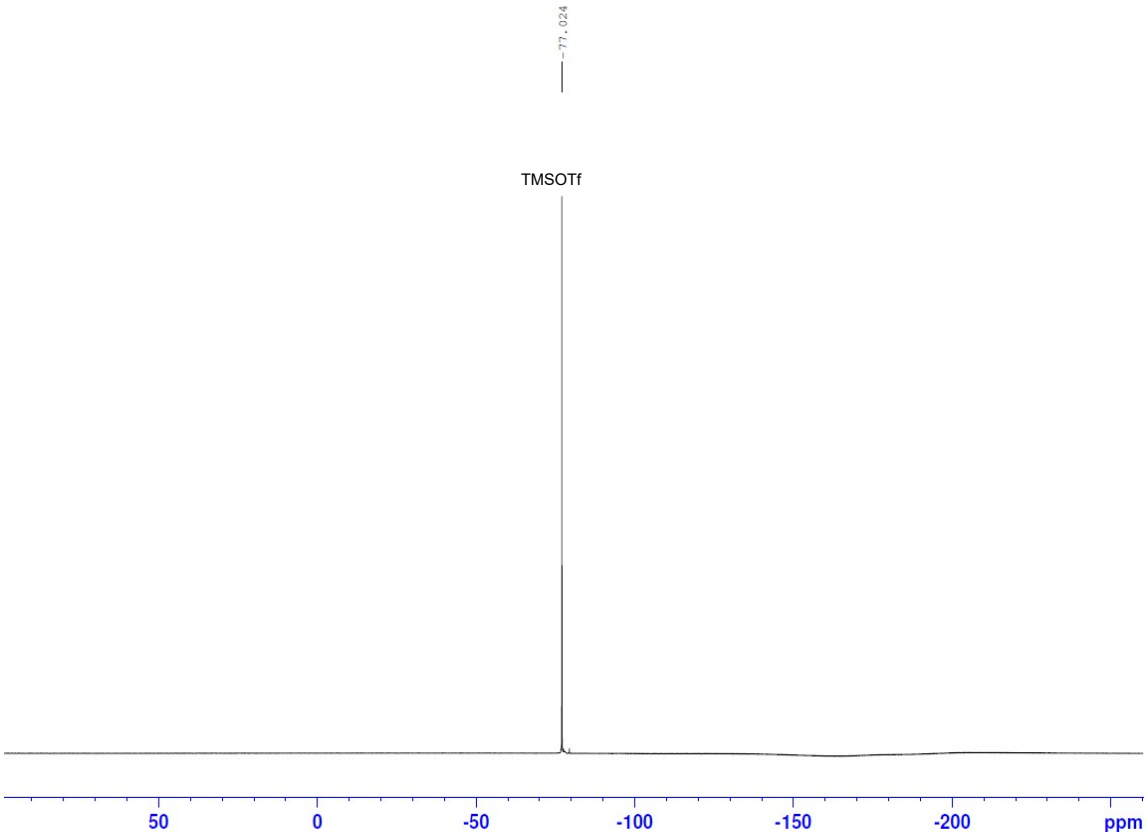


Figure S11. ^{19}F NMR (376 MHz, $CDCl_3$) of TMSOAc with HOTf.

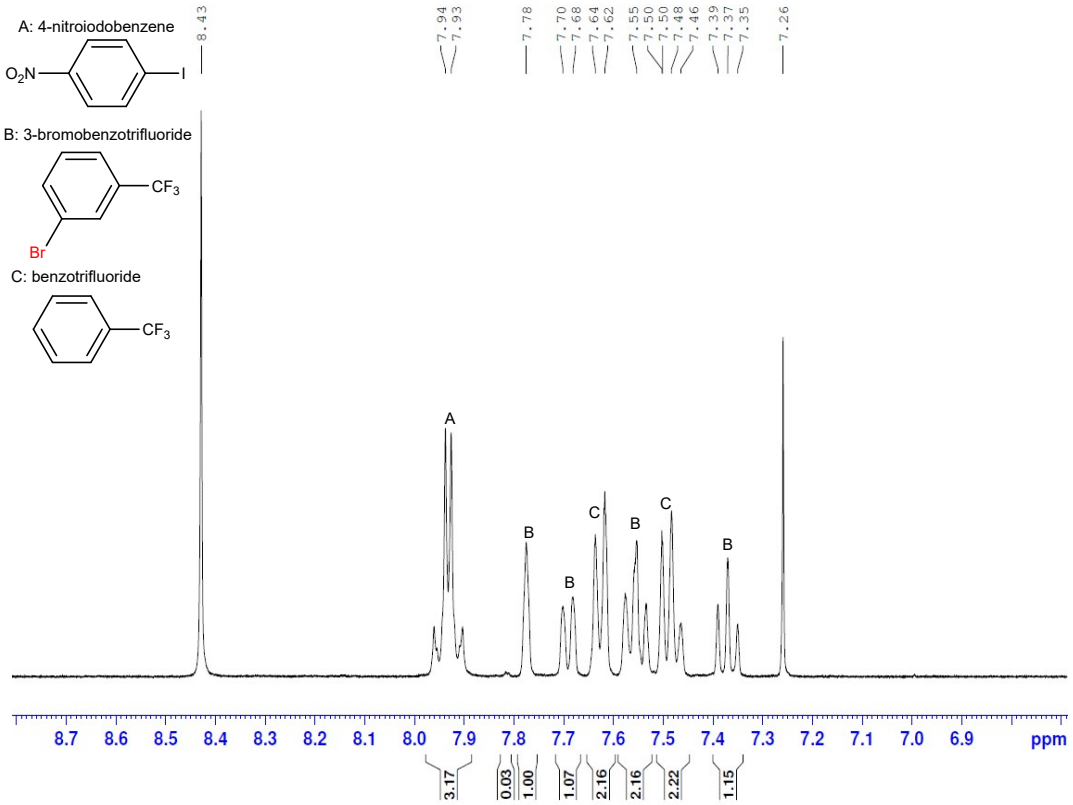


Figure S12. ^1H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OAc)(OTf) + Br_2 + benzotrifluoride.

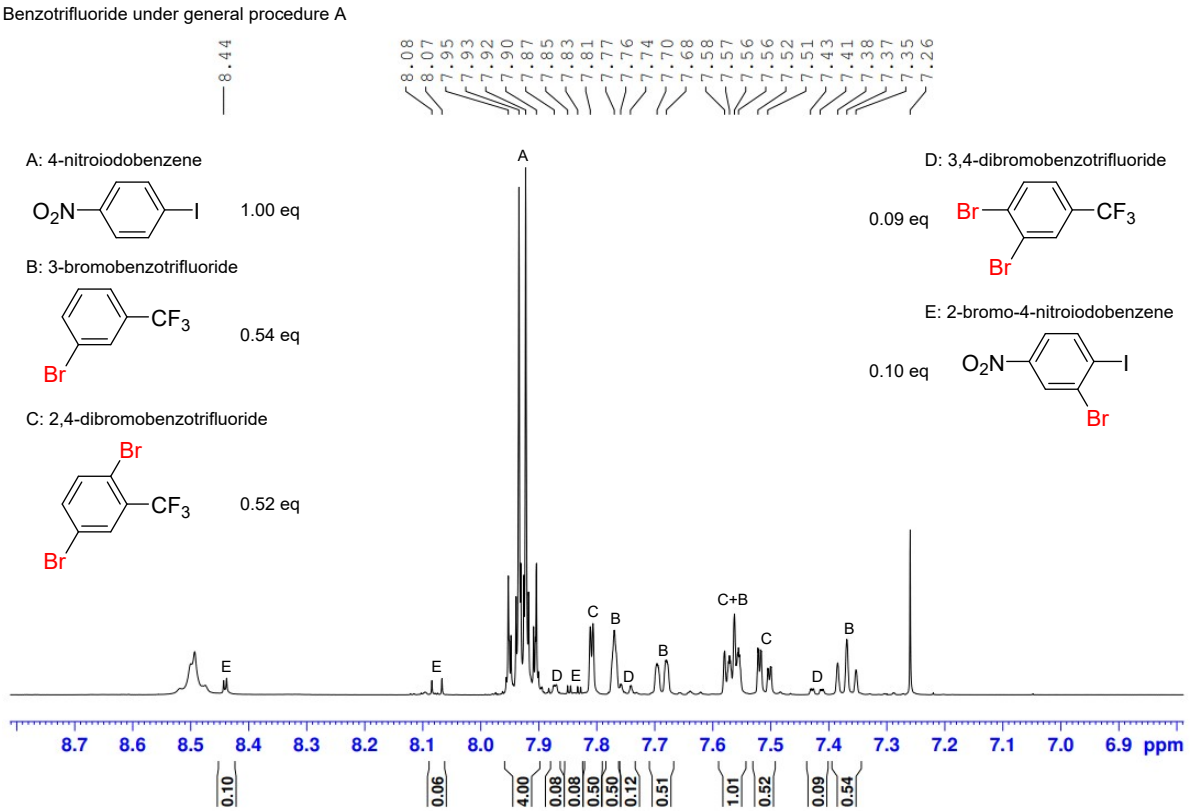


Figure S13. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of benzotrifluoride under general procedure A.

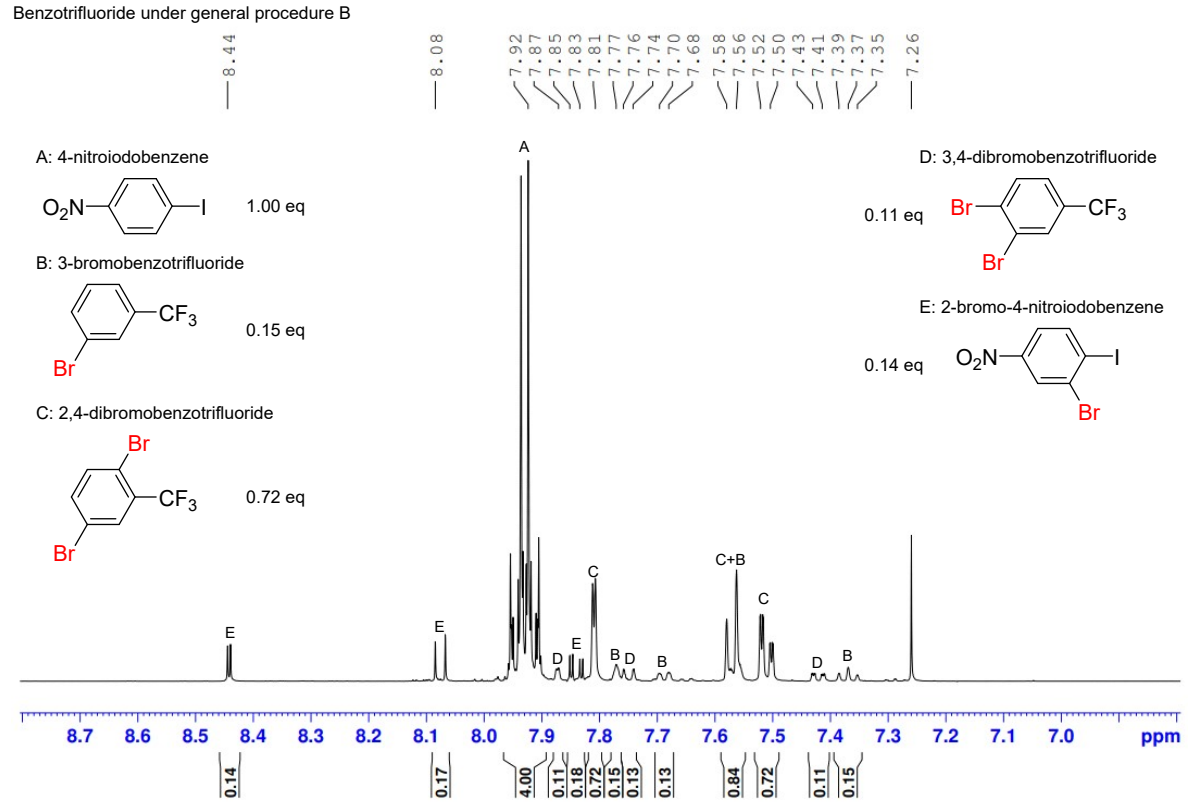


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)$_2$ + benzotrifluoride under general procedure B.

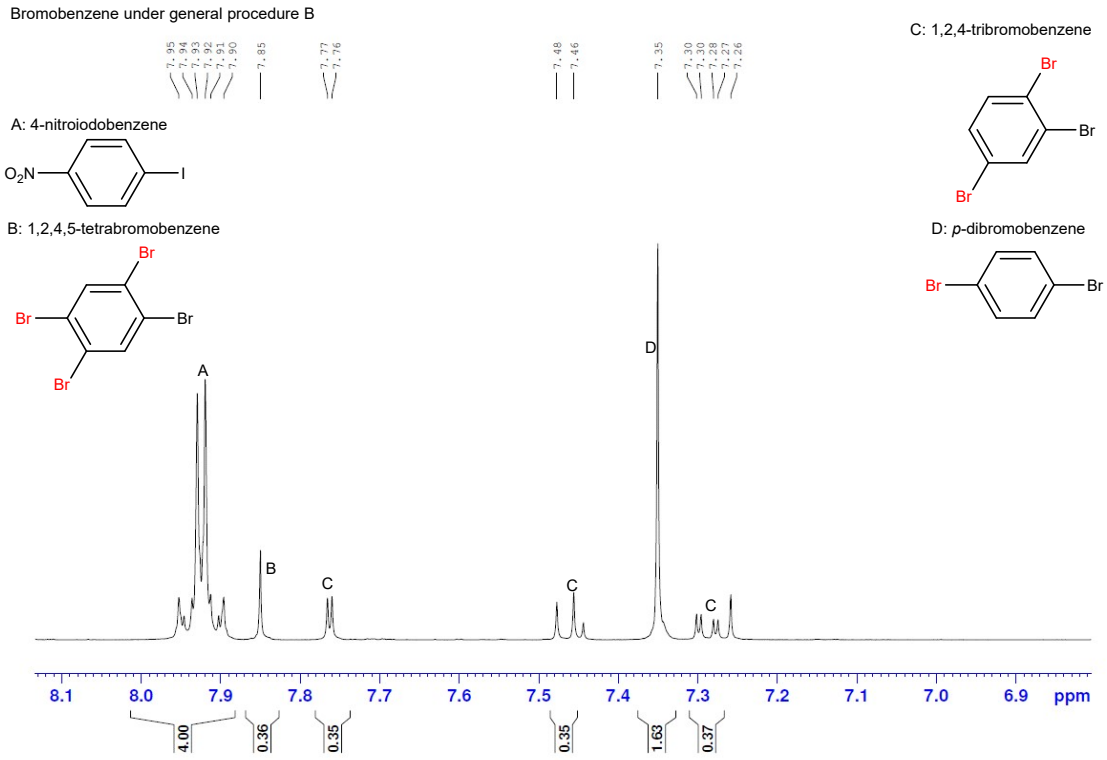


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)$_2$ + bromobenzene under general procedure B.

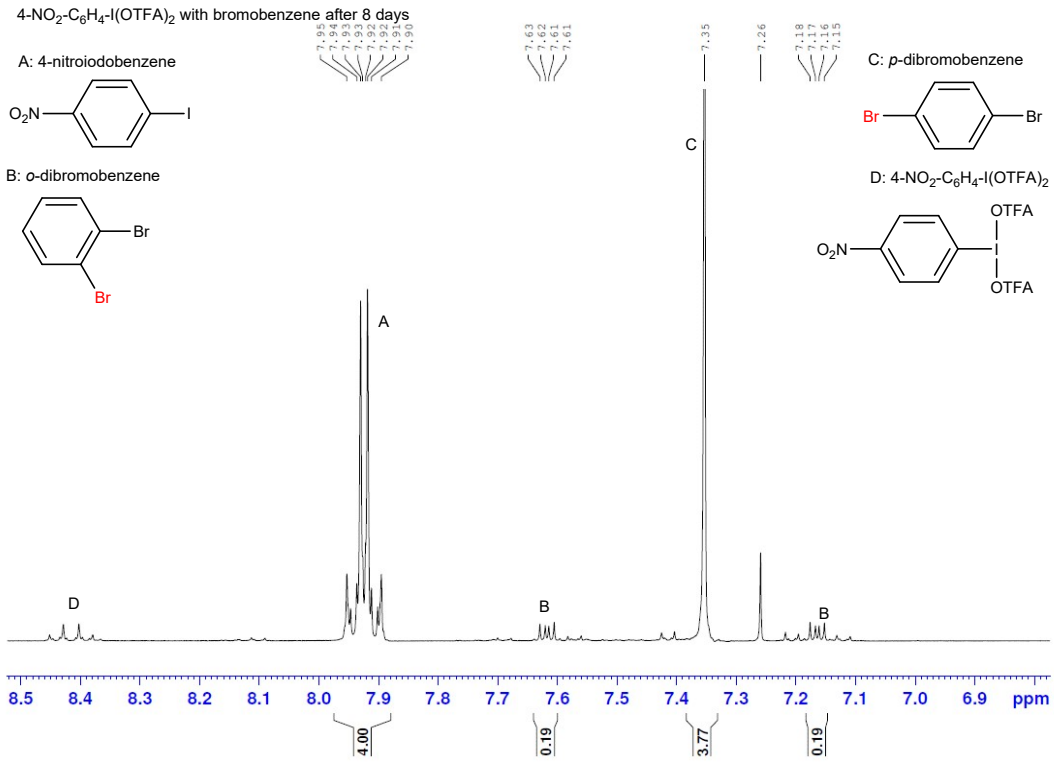


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-NO_2-C_6H_4-I(OTFA)$_2$ + Br_2 + bromobenzene after 8 days.

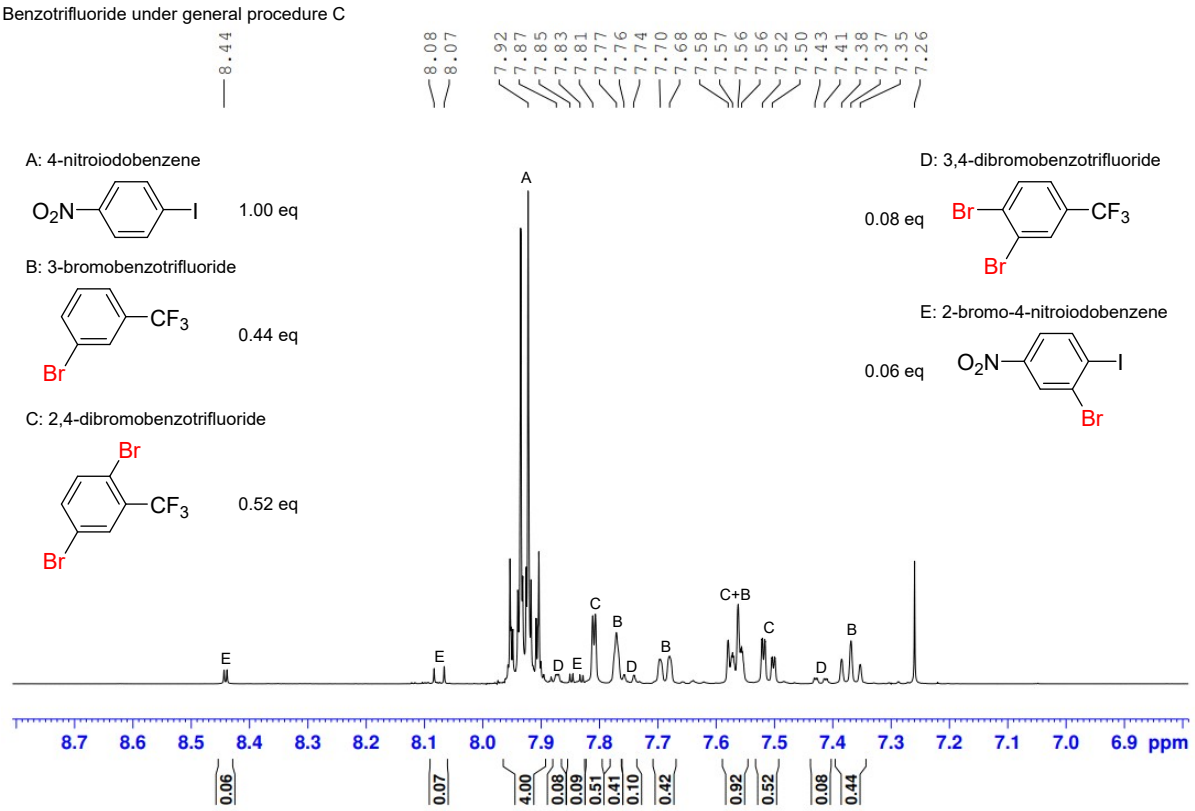


Figure S17. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of benzotrifluoride under general procedure C.

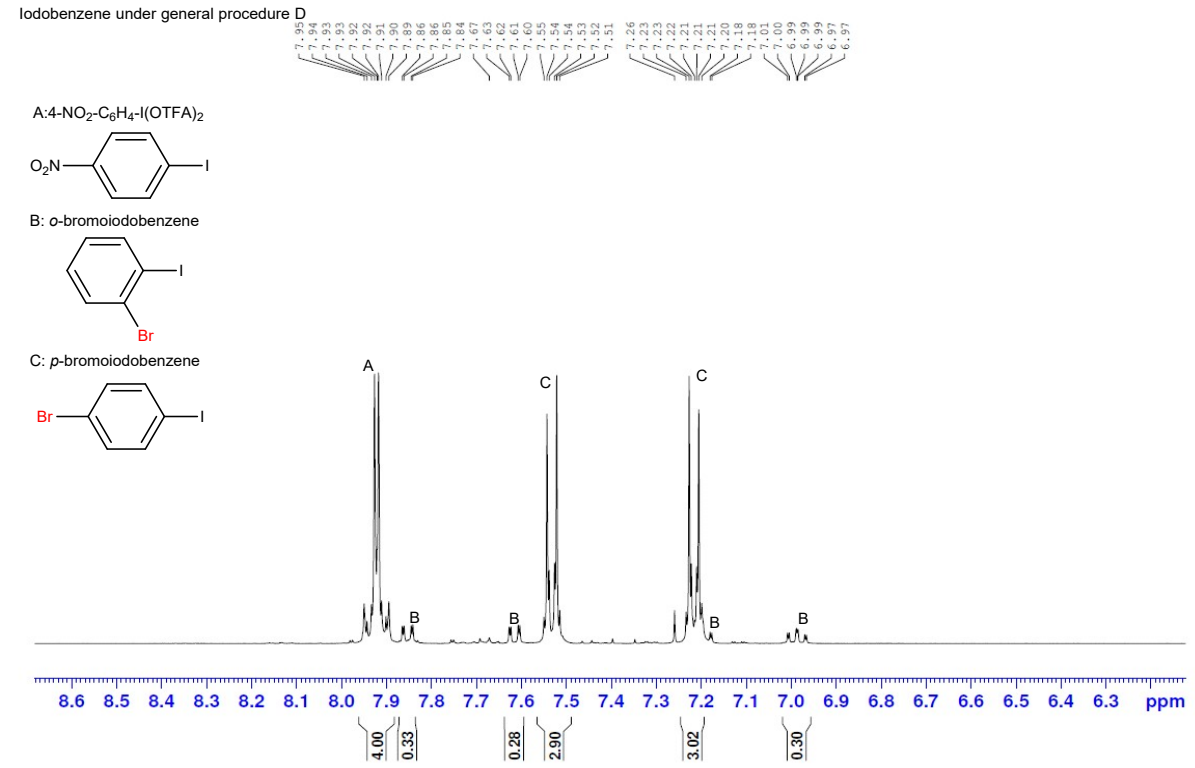


Figure S18. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of iodobenzene under general procedure D.

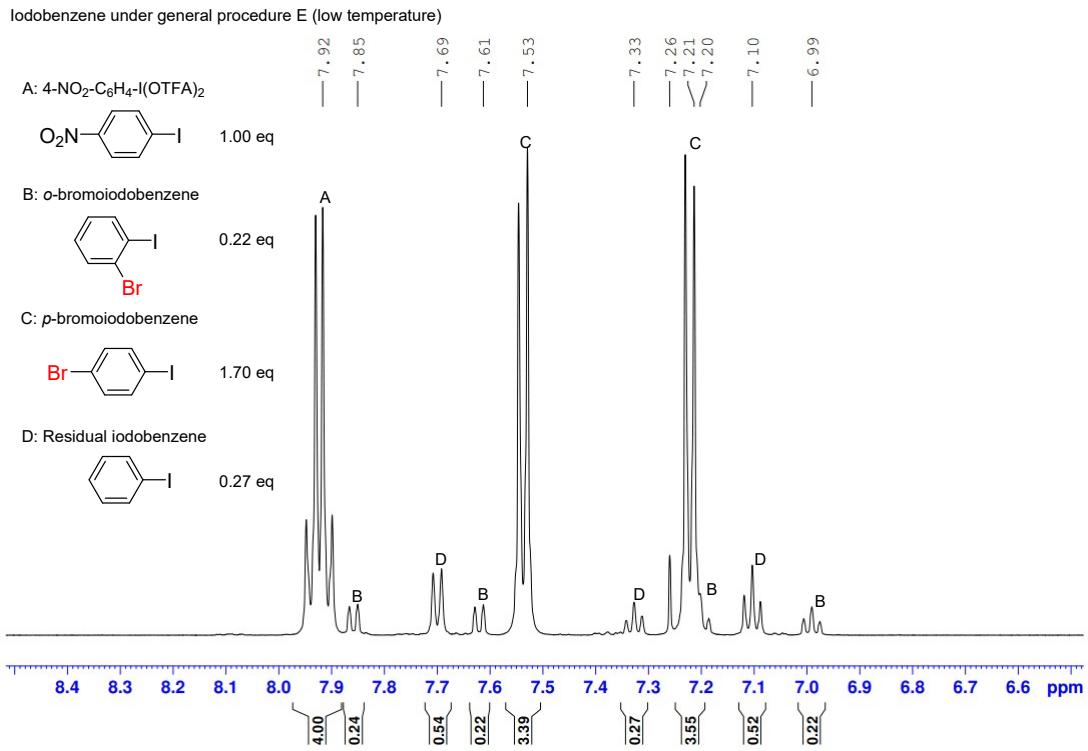


Figure S19. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of iodobenzene under general procedure E (low temperature). Reaction time = 2.5 h.

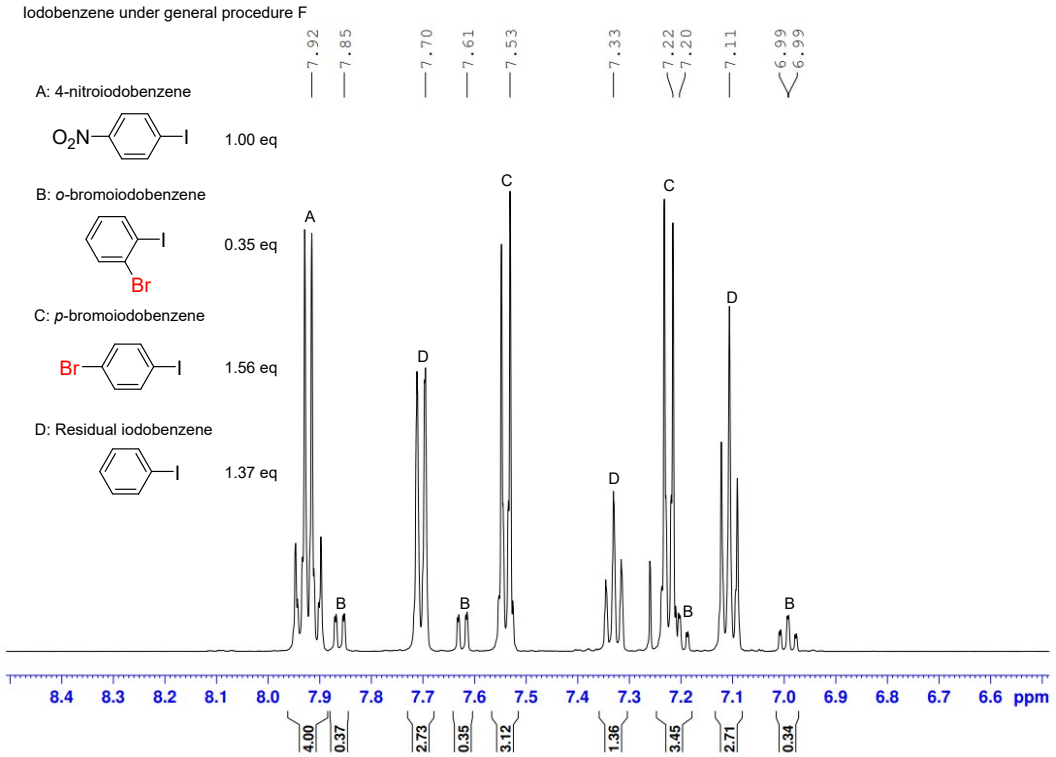


Figure S20. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of iodobenzene under general procedure F. Reaction time = 5 min.

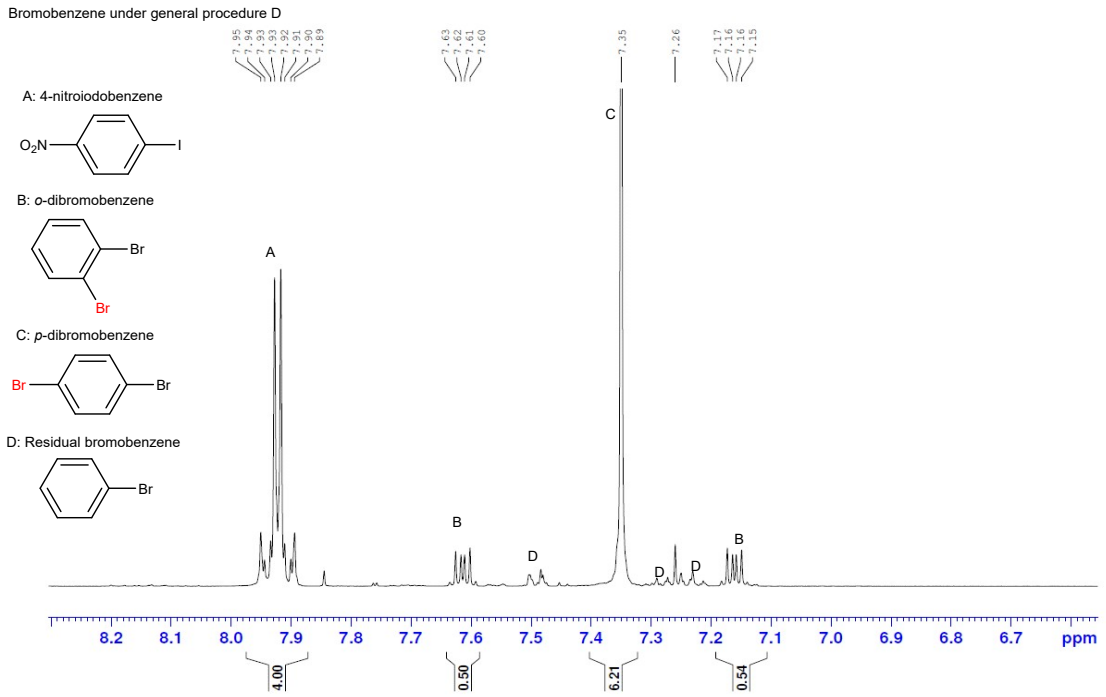


Figure S21. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of bromobenzene under general procedure D.

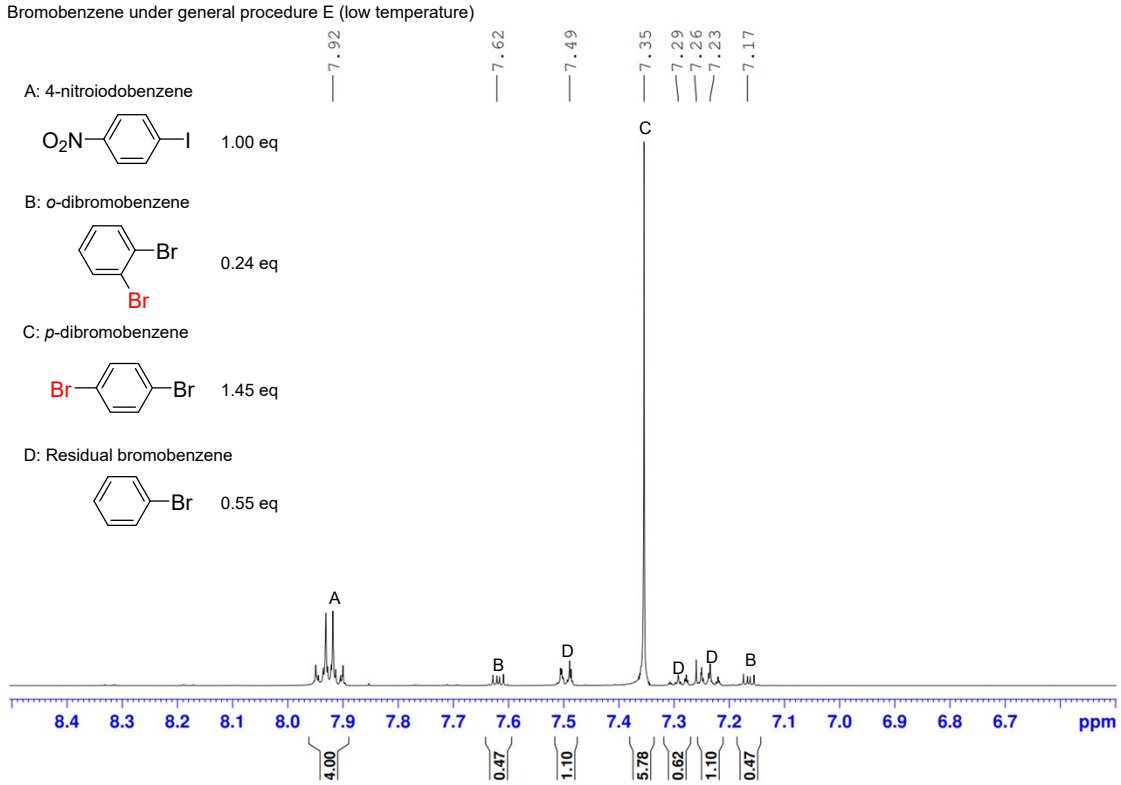


Figure S22. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of bromobenzene under general procedure E (low temperature). Reaction time = 9 h.

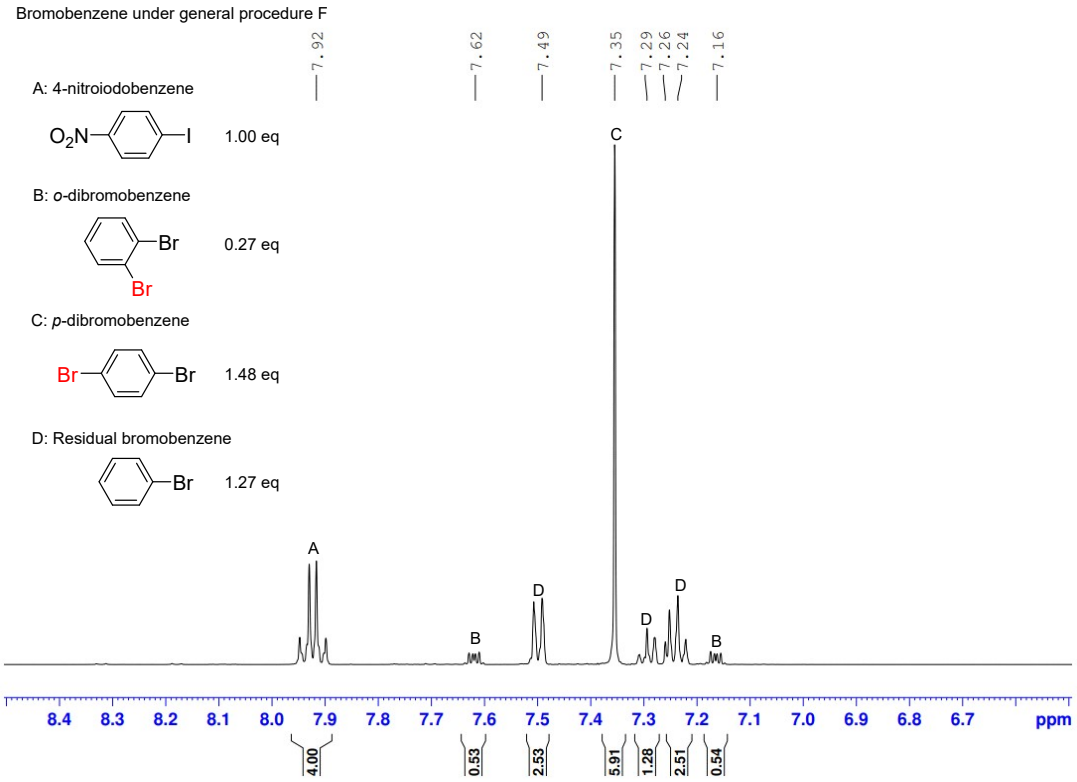


Figure S23. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of bromobenzene under general procedure F. Reaction time = 15 min.

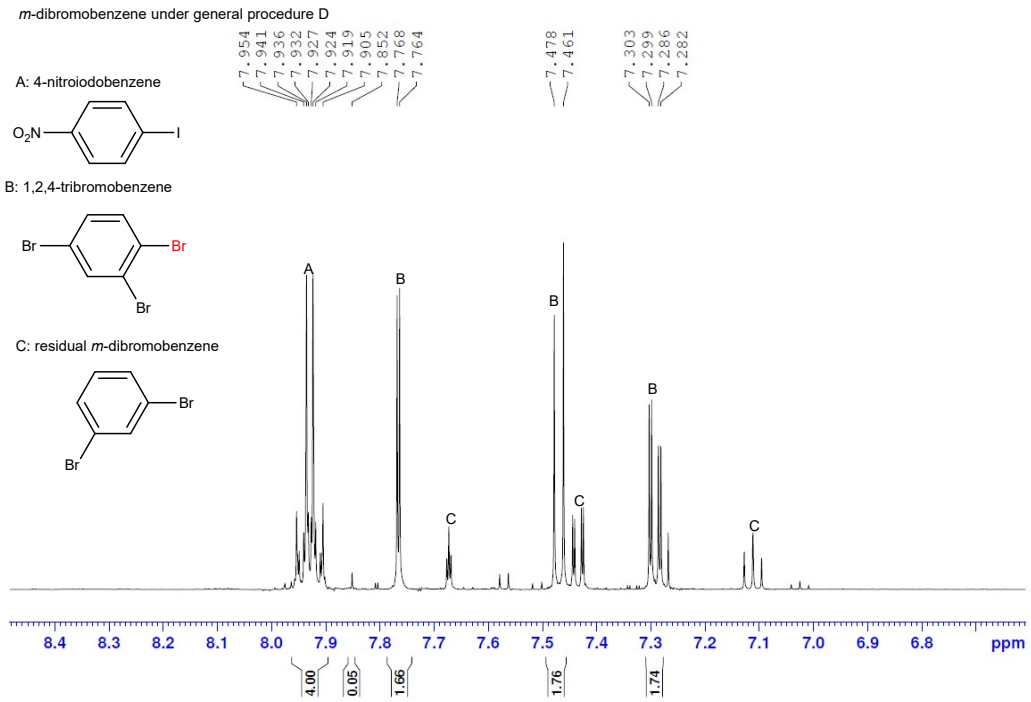


Figure S24. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of *m*-dibromobenzene under general procedure D.

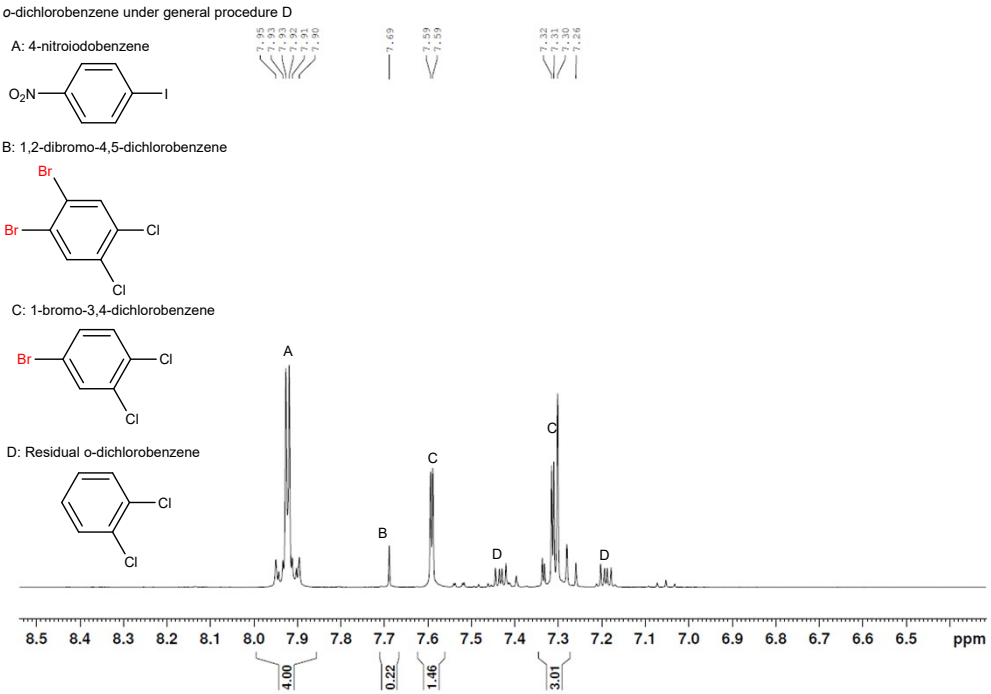


Figure S25. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of *o*-dichlorobenzene under general procedure D.

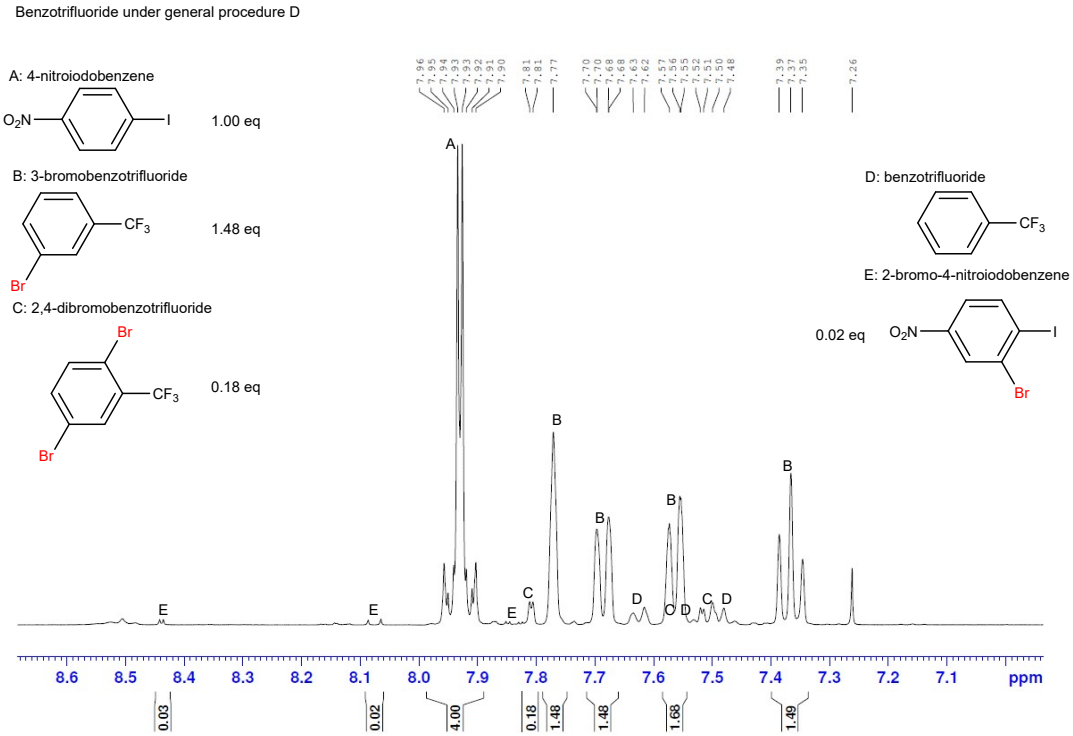


Figure S26. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of benzotrifluoride under general procedure D.

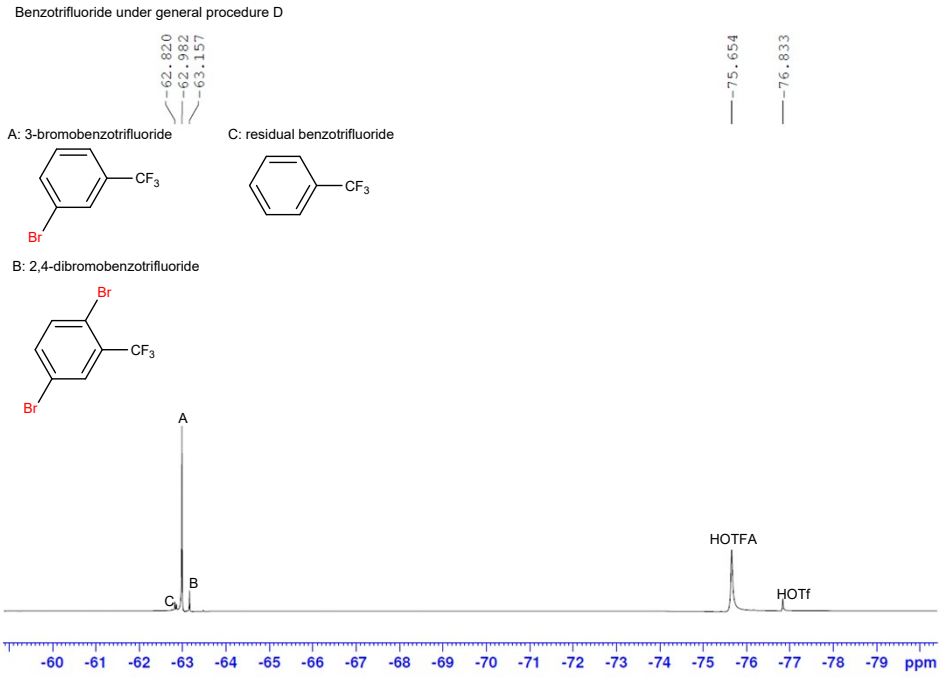


Figure S27. *In situ* ^{19}F NMR (376 MHz, $CDCl_3$) of benzotrifluoride under general procedure D.

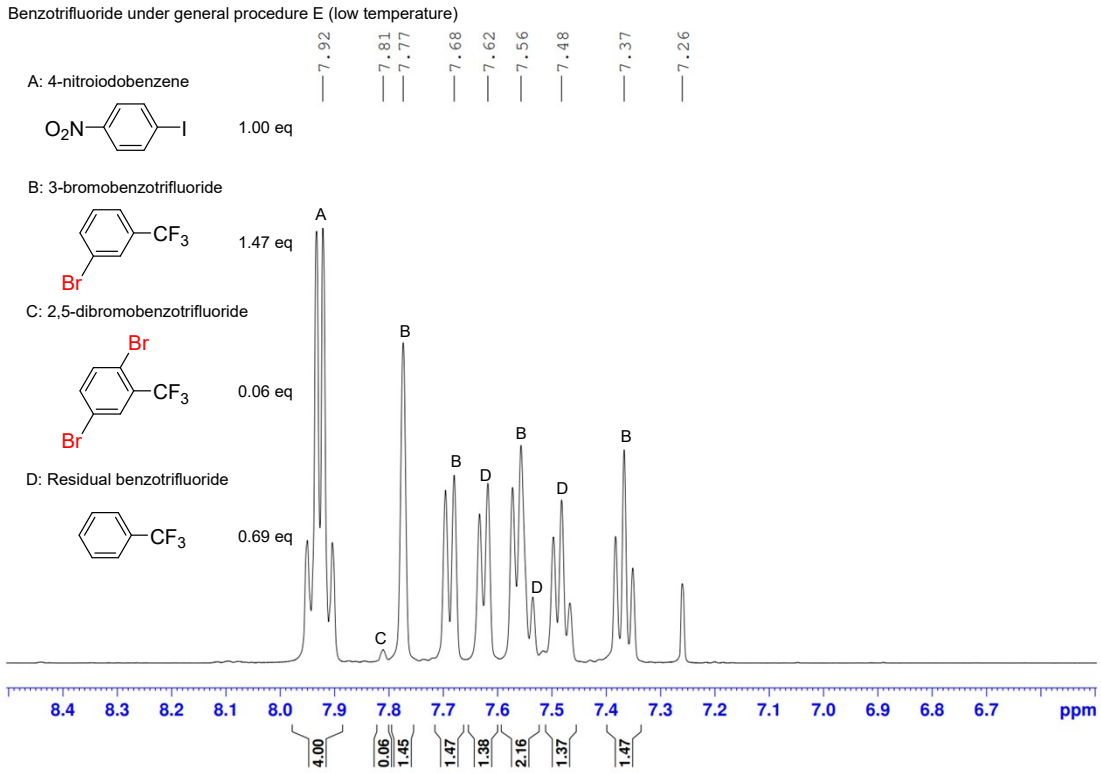


Figure S28. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of benzotrifluoride under general procedure E (low temperature). Reaction time = 40 h.

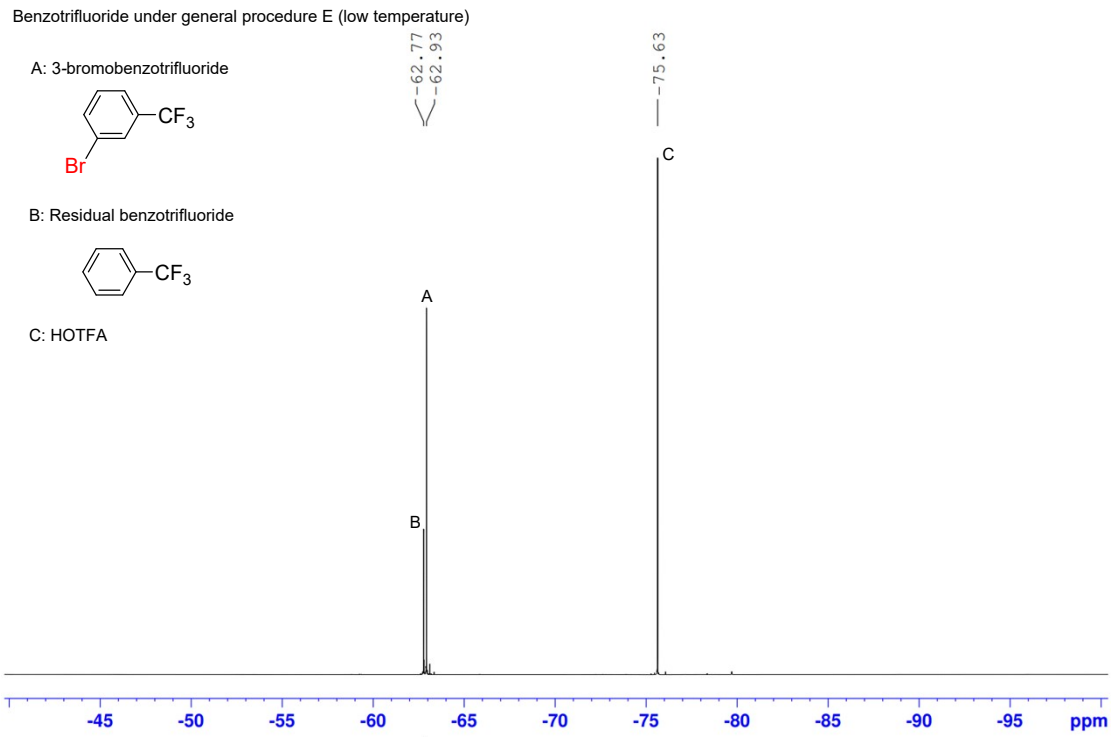


Figure S29. *In situ* ^{19}F NMR (376 MHz, $CDCl_3$) of benzotrifluoride under general procedure E (low temperature). Reaction time = 40 h.

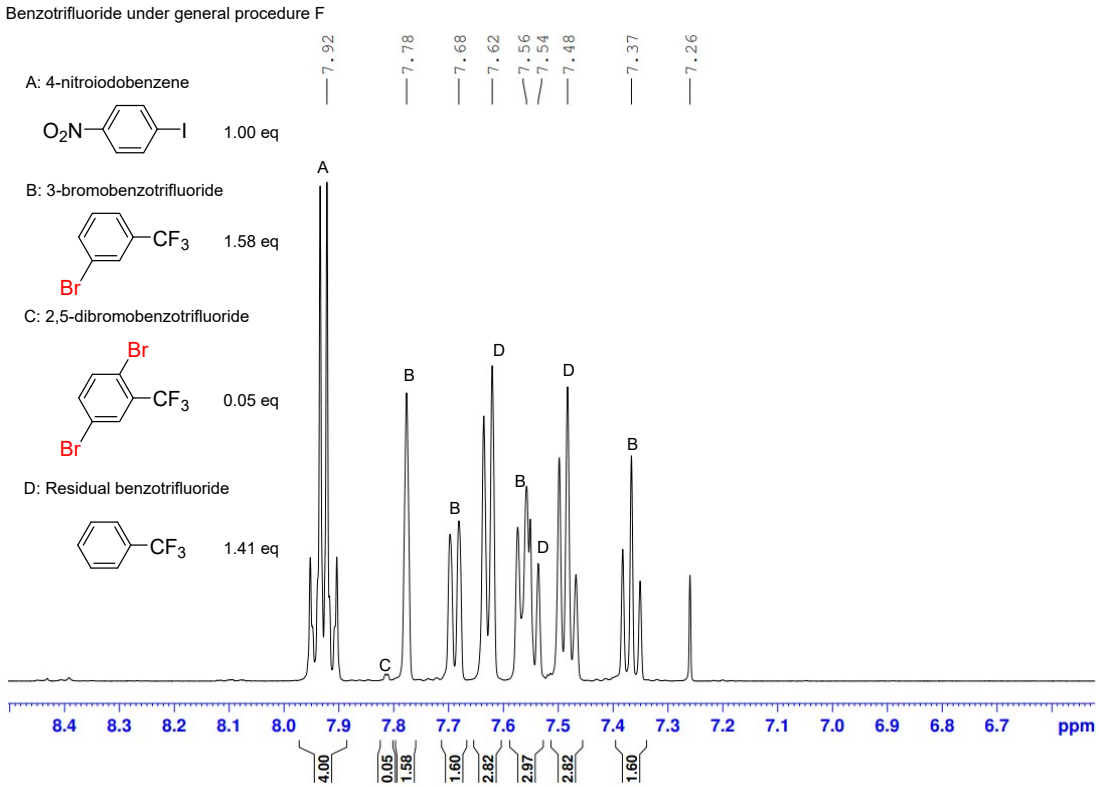


Figure S30. *In situ* ^{1}H NMR (500 MHz, $CDCl_3$) of benzotrifluoride under general procedure F. Reaction time = overnight.

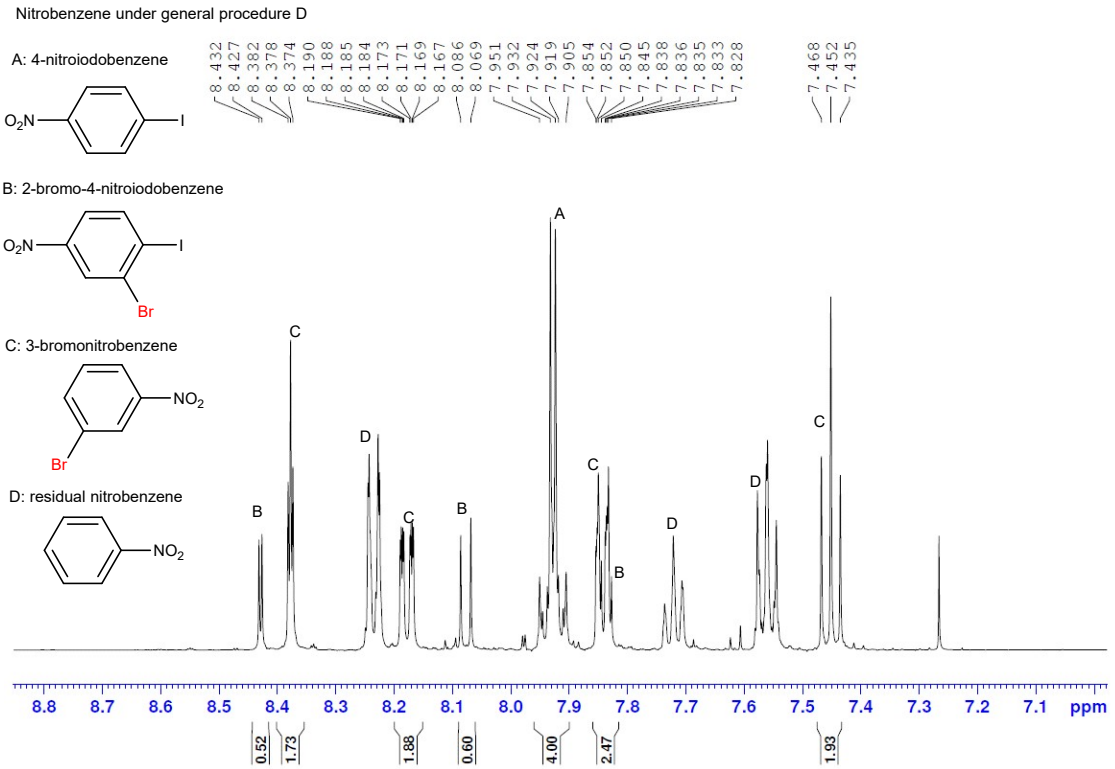


Figure S31. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of nitrobenzene under general procedure D.

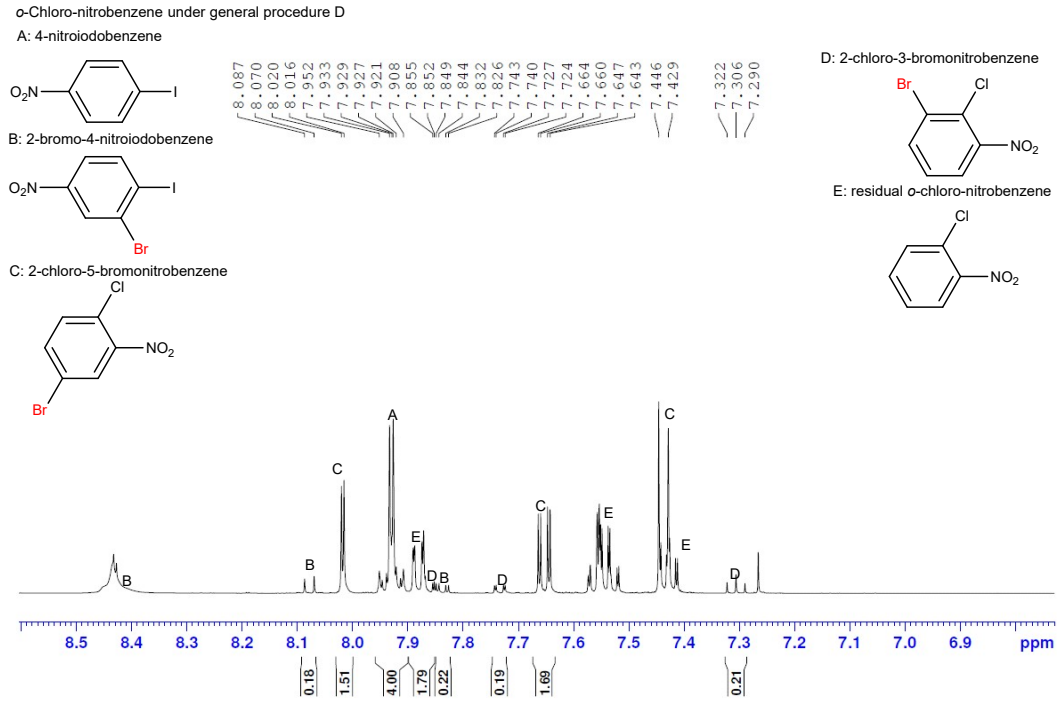


Figure S32. *In situ* ^{1}H NMR (400 MHz, $CDCl_3$) of *o*-chloronitrobenzene under general procedure D.

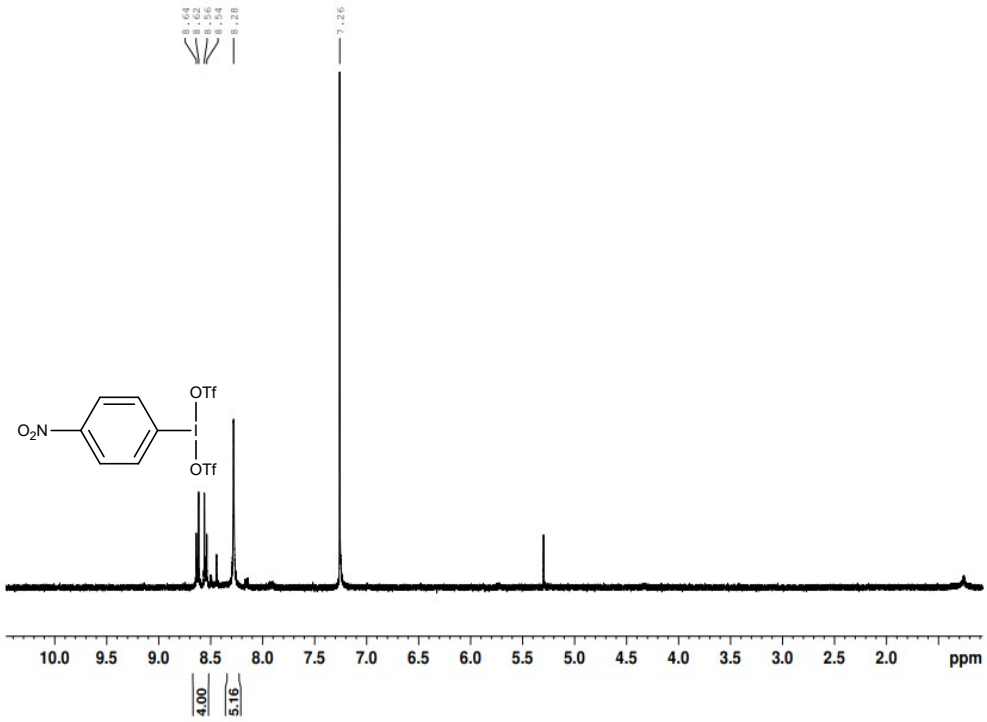


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of solution containing 4-NO_2-C_6H_4-I(OTf)$_2$ and Br_2.

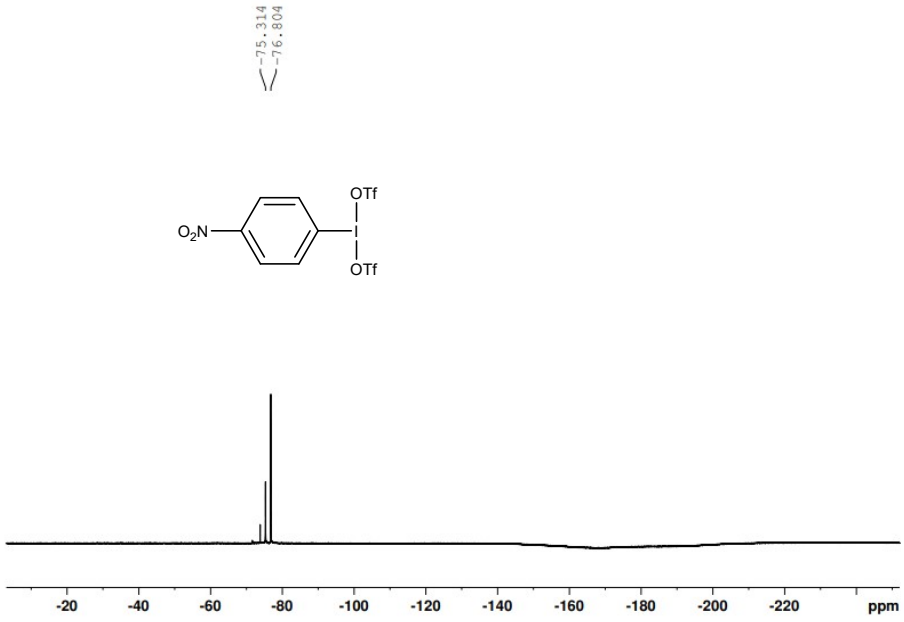


Figure S34. ^{19}F NMR (376 MHz, $CDCl_3$) of solution containing 4-NO_2-C_6H_4-I(OTf)$_2$ and Br_2.

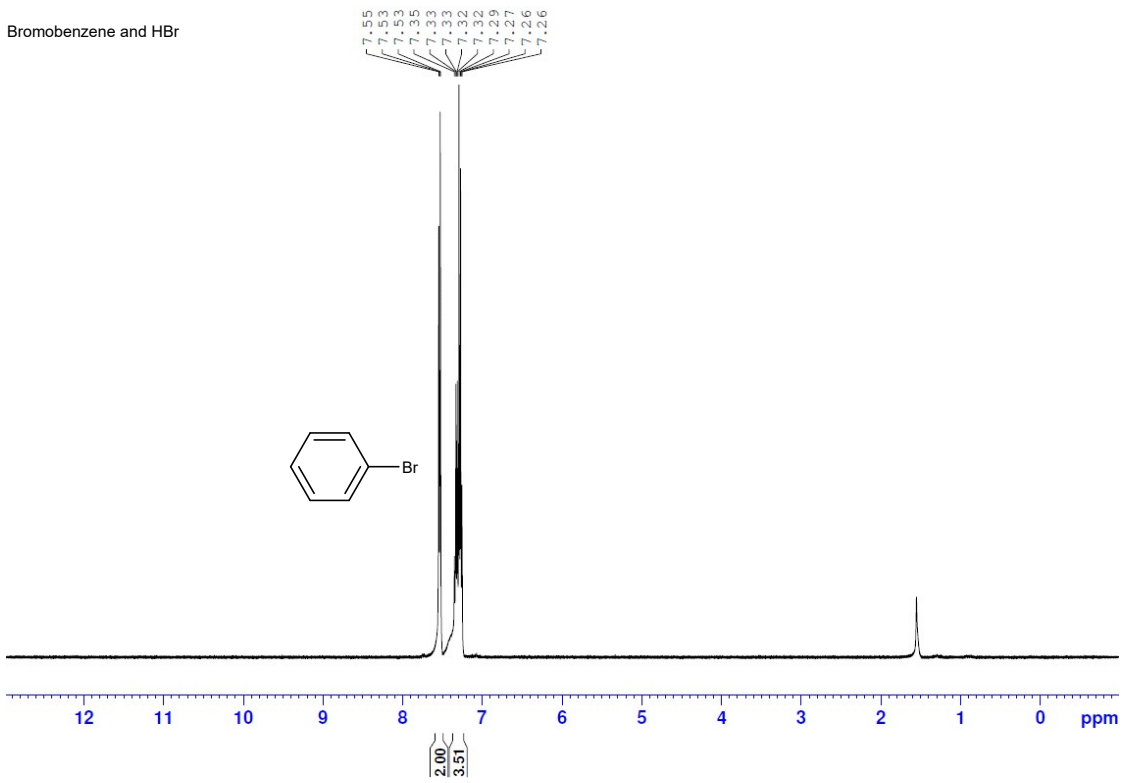


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of solution containing bromobenzene and HBr.

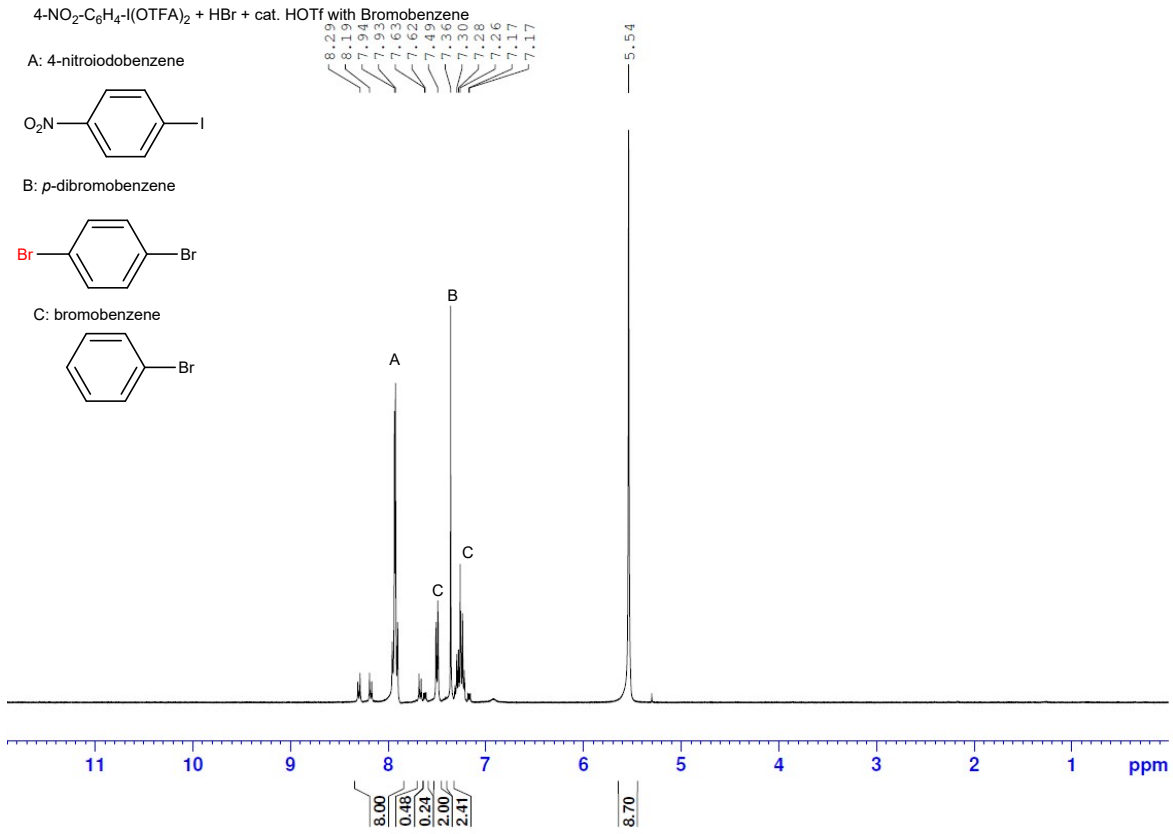


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of solution containing 4-NO_2-C_6H_4-I$(OTf)_2$, bromobenzene, HBr and catalytic HOTf.

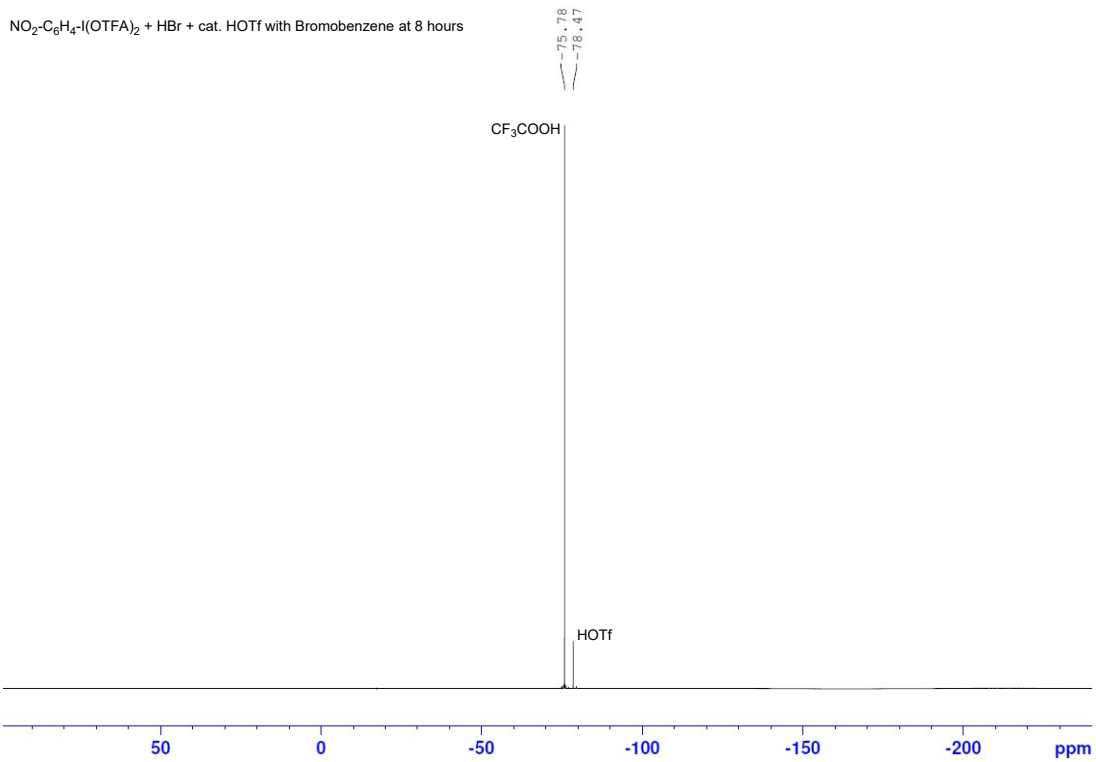


Figure S37. ^{19}F NMR (376 MHz, $CDCl_3$) of solution containing 4-NO_2-C_6H_4-I$(OTf)_2$, bromobenzene, HBr and catalytic HOTf.

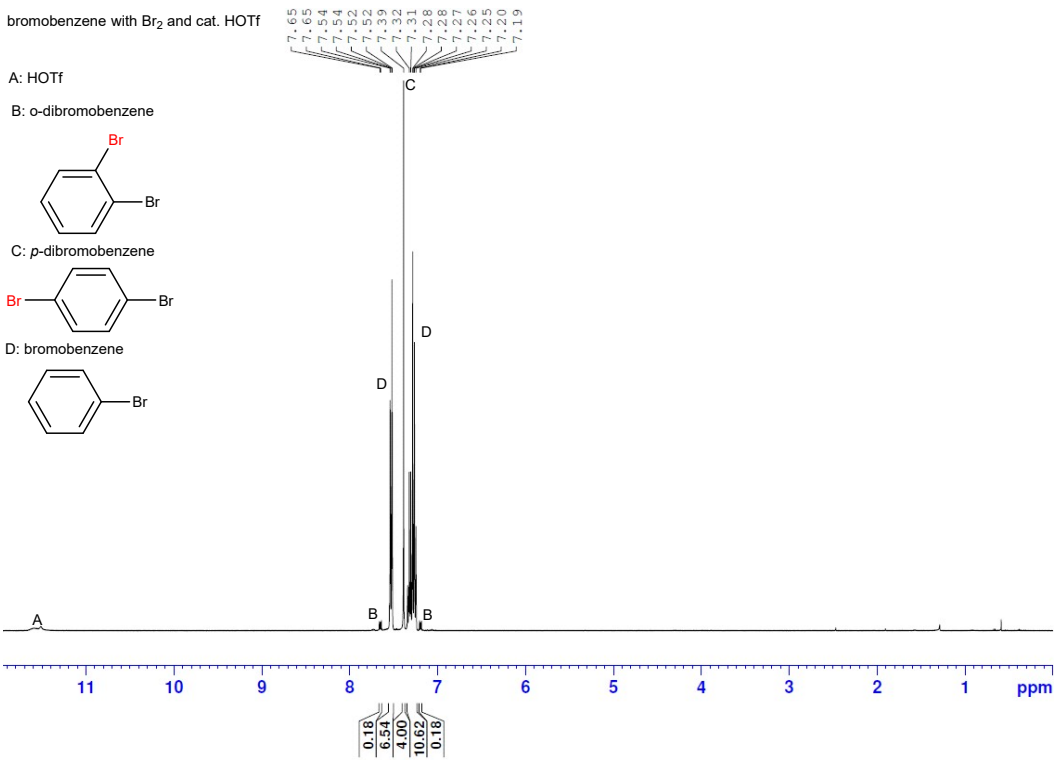


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of solution containing bromobenzene and Br_2 and catalytic HOTf after 48 hours.

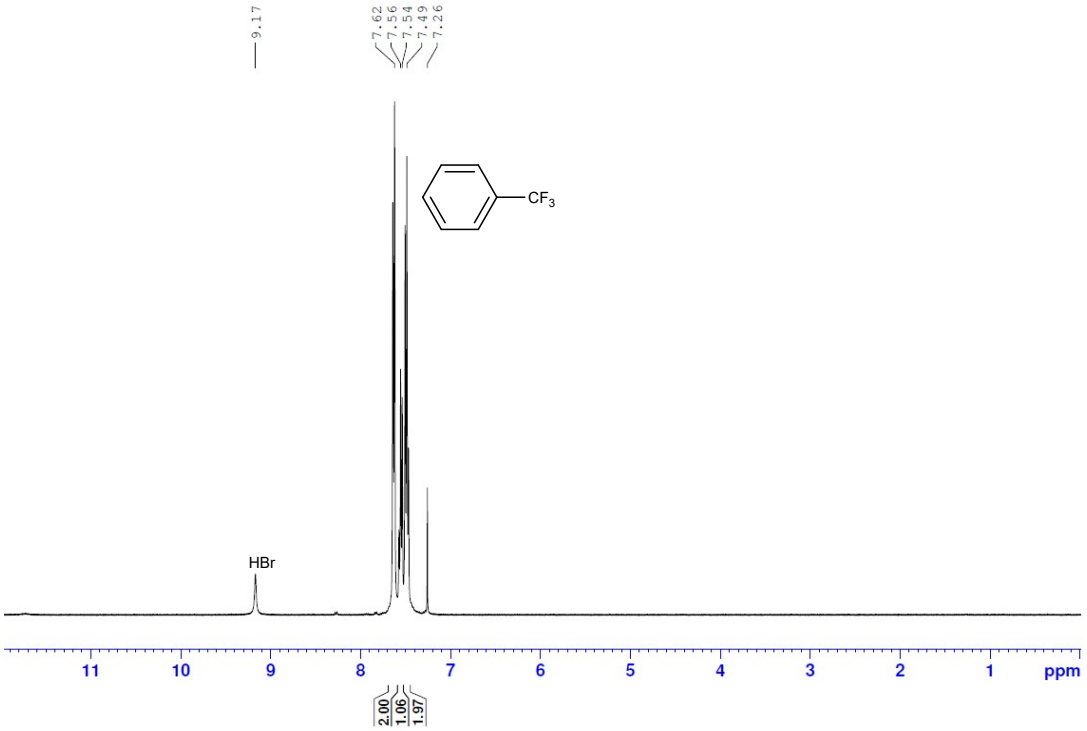


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of solution containing benzotrifluoride and Br_2 and catalytic HOTf after 20 hours .

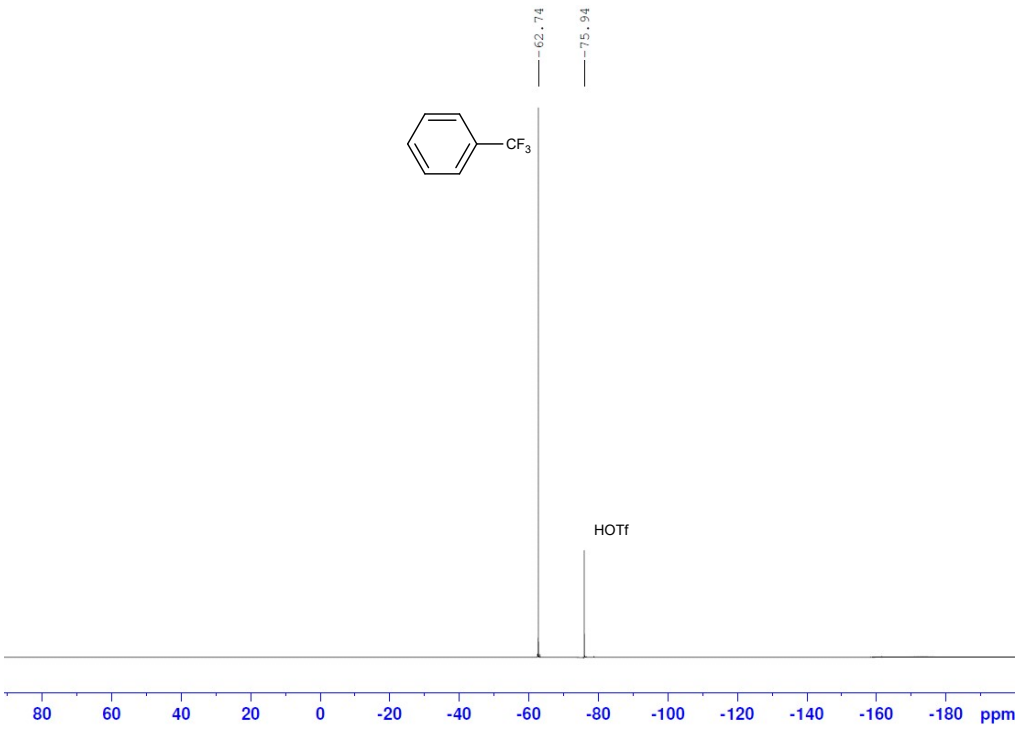


Figure S40. ^{19}F NMR (376 MHz, $CDCl_3$) of solution containing benzotrifluoride and Br_2 and catalytic HOTf after 20 hours .

Structural Data

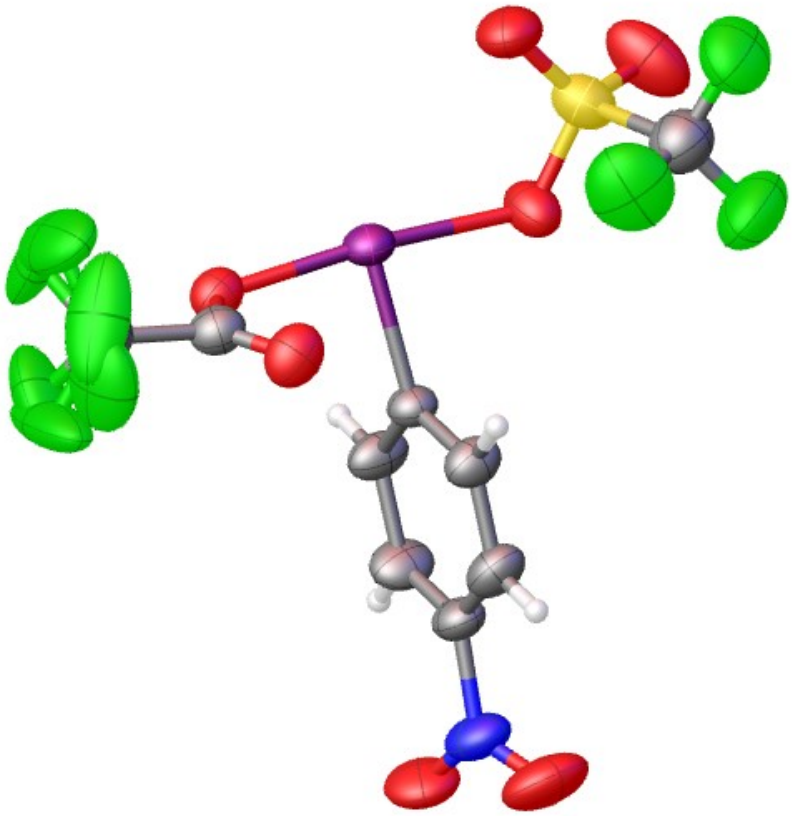


Figure S41. Thermal ellipsoid plot of 4-NO_2-C_6H_4-I(OTFA)OTf, thermal ellipsoids are drawn at the 50% probability level. Disorder of the -CF_3 moiety of the OTFA ligand has been modelled.

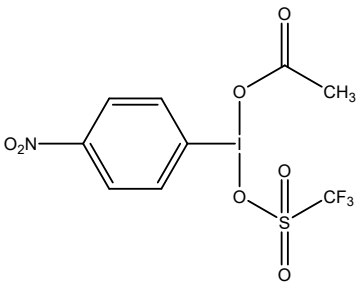
Table S1. X-ray crystallographic details

Compound	**4-NO_2-C_6H_4-I(OTFA)(OTf)**
Empirical Formula	$C_9H_4I_1N_1O_7F_6S_1$
FW (g/mol)	511.09
Crystal System	Monoclinic
Space Group	P(2)1/n
α (Å)	9.5843(1)
b (Å)	10.5374(2)
c (Å)	15.3990(2)
α (deg)	90
β (deg)	91.246(1)
γ (deg)	90
V (Å^3)	1554.83(4)
Z	4
R1[I>2σI]	0.0449
wR2(F^2)	0.1275
GOF (S)	1.096

Reference NMR values

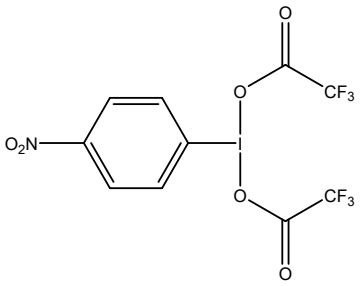
PhI(OAc)(OTf) (Compared with previously reported literature values)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.25 (d, 2H, *J* = 8.4 Hz), 7.76 (t, 1H, *J* = 7.6 Hz), 7.63 (t, 2H, *J* = 7.6 Hz), 2.21 (s, 3H)



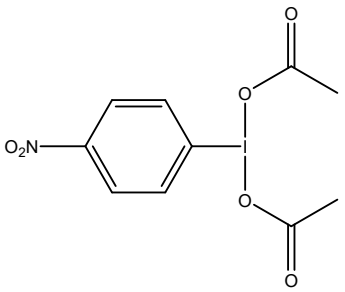
4-NO_2-C_6H_4-I(OTFA)$_2$ (Compared with previously reported literature values)[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.47-8.37 (m, 4H)



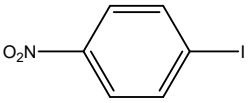
4-NO_2-C_6H_4-I(OAc)$_2$ (Compared with previously reported literature values)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, 2H, *J*= 9.3 Hz), 8.28 (d, 2H, *J*= 9.3 Hz), 2.03 (s, 6H)



4-nitroiodobenzene (Commercial sample)

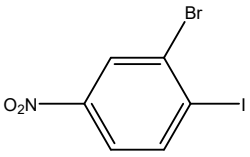
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97-7.89 (m, 4H)



2-bromo-4-nitroiodobenzene

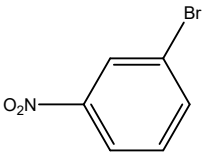
(Compared with previously reported literature values)[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.44 (d, 1H, J_1= 2.5 Hz), 8.07 (d, 1H, J_1= 8.7 Hz), 7.83 (dd, 1H, J_1= 8.7 Hz, J_2= 2.5 Hz)



3-bromonitrobenzene (Commercial sample)

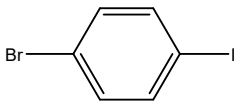
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (t, 1H, *J*= 2.0 Hz), 8.20-8.16 (m, 1H), 7.86-7.83 (m, 1H), 7.45 (t, 1H, *J*= 8.2 Hz)



4-Bromoiodobenzene

(Compared with previously reported literature values)[5]

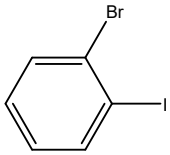
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 (d, 2H, *J*= 8.6 Hz), 7.23 (d, 2H, *J*= 8.6 Hz)



2-Bromoiodobenzene

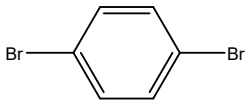
(Compared with previously reported literature values)[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (dd, 1H, J_1= 7.9Hz, J_2= 1.5 Hz), 7.62 (dd, 1H, J_1= 8.0 Hz, J_2= 1.5 Hz), 7.20 (td, 1H, J_1= 7.9 Hz, J_2= 1.7 Hz), 6.70 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.5 Hz),



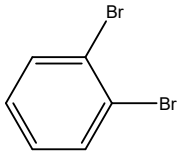
***p*-Dibromobenzene** (Commercial sample)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36 (s, 4H)



***o*-Dibromobenzene:** Commercial sample

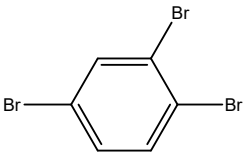
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64-7.61 (m, 2H), 7.19-7.15 (m, 2H)



1,2,4-tribromobenzene

(Compared with previously reported literature values)[6,7]

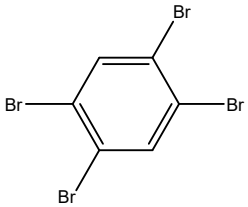
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (d, 1H, *J* = 2.3 Hz), 7.47 (d, 1H, *J* = 8.6 Hz), 7.29 (dd, 1H, J_1= 8.6 Hz, J_2= 2.3Hz)



1,2,4,5-tetrabromobenzene

(Compared with previously reported literature values)[6,8]

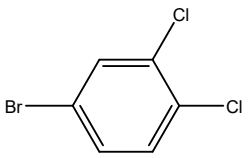
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (s, 2H)

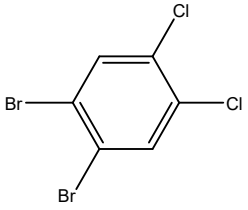


1-bromo-3,4-dichlorobenzene

(Compared with previously reported literature values)[6,8]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (d, 1H, *J* = 2.0 Hz), 7.31 (d, 1H, *J* = 2.0 Hz), 7.30 (s, 1H)





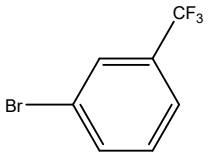
1,2-dibromo-3,4-dichlorobenzene

(Compared with previously reported literature values)[6,9]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (s, 2H)

3-bromobenzotrifluoride

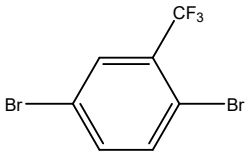
(Compared with previously reported literature values)[6,9]



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (s, 1H), 7.68 (d, 1H, *J* = 8.0 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.36 (t, 1H, *J* = 8.0 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.9

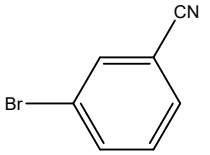
2,5-dibromobenzotrifluoride (Commercial sample)



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.81 (d, 1H, *J* = 2.2 Hz), 7.57 (d, 1H, J_1 = 8.4 Hz), 7.51 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.2 Hz)

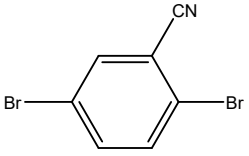
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.1

3-bromobenzonitrile (Commercial sample)



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.80 (t, 1H, *J* = 1.5 Hz), 7.78-7.74 (m, 1H), 7.64-7.59 (m, 1H), 7.39 (t, 1H, *J* = 7.8 Hz)

2,5-dibromobenzonitrile

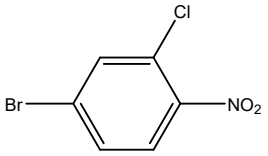


(Compared with previously reported literature values)[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (d, 1H, *J* = 2.1 Hz), 7.61-7.56 (m, 2H)

2-chloro-5-bromonitrobenzene

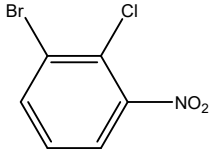
(Compared with previously reported literature values)[9]



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.01 (d, 1H, *J* = 2.3 Hz), 7.63 (m, 2H dd, 1H, J_1 = 8.6 Hz, J_2 = 2.3 Hz), 7.43 (d, 1H, *J* = 8.6 Hz)

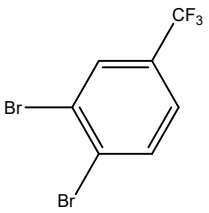
2-chloro-3-bromonitrobenzene

(Compared with previously reported literature values)[9]



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.87 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz), 7.73 (dd, ^{1}H, J_1 = 8.1 Hz, J_2 = 1.5 Hz), 7.31 (t, 1H, *J* = 8.1 Hz)

3,4-dibromobenzotrifluoride (Compared with previously reported spectra)[10]



^{1}H NMR (500 MHz, $CDCl_3$): 7.87 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.0 Hz, 1H)

References

(1) Zagulyaeva, A. A.; Yusubov, M. S.; Zhdankin, V. V. A General and Convenient Preparation of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes and [Bis(trifluoroacetoxy)iodo]arenes by Oxidation of Organic Iodides Using Oxone and Trifluoroacetic Acid *J. Org. Chem.* **2010**, *75*, 2119-2122.

(2) Aprile, A.; Iversen, K. J.; Wilson, D. J.; Dutton, J. L. Te(II)/Te(IV) Mediated C–N Bond Formation on 2,5-Diphenyltellurophene and a Reassignment of the Product from the Reaction of $PhI(OAc)_2$ with 2 TMS-OTf *Inorg. Chem.* **2015**, *54*, 4934-4939.

(3) Iinuma, M.; Moriyama, K.; Togo, H. Simple and Practical Method for Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and m-Chloroperoxybenzoic Acid *Synlett.* **2012**, *23*, 2663-2666.

(4) Shintani, R.; Misawa, N.; Takano, R.; Nozaki, K. Rhodium-Catalyzed Synthesis and Optical Properties of Silicon-Bridged Arylpyridines *Chem. Eur. J.* **2017**, *23*, 2660-2665.

(5) Moorthy, J. N.; Senapati, K.; Kumar, S. IBX–I_2 Redox Couple for Facile Generation of IOH and I^+: Expedient Protocol for Iodohydroxylation of Olefins and Iodination of Aromatics *J. Org. Chem.* **2009**, *74*, 6287-6290.

(6) https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2022).

(7) Du, B.; Jiang, X.; Sun, P. Palladium-Catalyzed Highly Selective ortho-Halogenation (I, Br, Cl) of Arylnitriles via sp^2 C–H Bond Activation Using Cyano as Directing Group *J. Org. Chem.* **2013**, *78*, 2786-2791.

(8) Luo, Y.; Pan, X.; Wu, J. Silver-Catalyzed Decarboxylative Halogenation of Carboxylic Acids *Tetrahedron Lett.* **2010**, *51*, 6646-6648.

(9) Wei, W.; Zhou, S.; Cheng, D.; Li, Y.; Liu, J.; Xie, Y.; Li, Y.; Li, Z. Design, Synthesis and Herbicidal Activity Study of Aryl 2, 6-Disubstituted Sulfonylureas as Potent Acetohydroxyacid Synthase Inhibitors *Bioorg. Med. Chem. Lett.* **2017**, *27*, 3365-3369.

(10) Menzel, K.; Fisher, EL.; DiMichele, L.; Frantz, DE.; Nelson, TD.; Kress, MH. An Improved Method for the Bromination of Metalated Haloarenes *via* Lithium, Zinc Transmetalation: A Convenient Synthesis of 1,2-dibromoarenes. *J. Org. Chem.* **2006**, *71,* 2188–91.