Supplementary Information for

Synthesis, structural characterization, reactivity and catalytic activity of mixed halo/triflate ArI(OTf)(X) species

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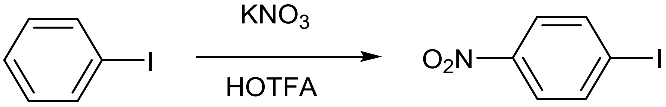
Table of Contents.

General Experimental Details:

All reagents were purchased from Sigma Aldrich and used as received. 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. Dry 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. **I1** and **I2** were synthesised according to literature procedure,[1] all other reagents were purchased from Sigma Aldrich and used as received. Experiments concerning **I1**, **I3** and **I5** were completed under inert conditions utilising Schlenck line and glovebox techniques unless stated otherwise. Procedures for catalytic chlorination reactions or utilising HOTf were performed under atmospheric conditions unless described otherwise, $CDCl_3$ for these reactions were distilled from CaH_2 and stored at atmospheric conditions over 3 Å molecular sieves. HOTf was stored in a Teflon tapped sealed flask under N_2. 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 Bruker Ultrashield Plus 500 MHz and Ascend 400 MHz spectrometers.

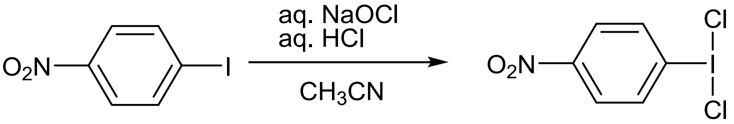
Synthetic Details:

Synthesis of NO_2-PhI



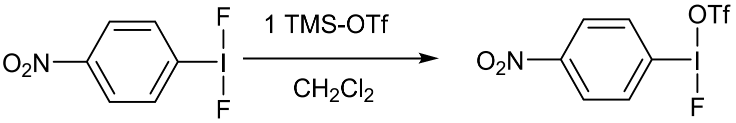
Following the procedure described by Kalid and Munawar.[2] To a solution of iodobenzene (9.3g, 45.6 mmol) in HOTFA (150 mL) was steadily added KNO_3 (4.6g, 45.6 mmol) which was allowed to stir for 10 minutes to receive a light brown solution. The solution was then heated to reflux for 4 hours until the brown colour dissipated. The resulting solution was poured into 350 mL of ice water to receive a yellow solid which was collected *via* filtration, washed with water (2 × 50 mL) and recrystallised from EtOH to receive NO_2PhI as a pale-yellow powder (7.1g, 63% yield).

Synthesis of I4



In adaptation of the procedure described by Zhang and Zhao.[3] A solution of NO_2PhI (4.98g, 20 mmol) in MeCN (100 mL) was added 6-14% NaOCl solution (100 mL) followed by the dropwise addition of concentrated aq. HCl (40 mL). All solids were observed to dissolve to receive a homogenous solution, subsequently the separation of an orange organic layer was observed. The reaction was subsequently treated with water to receive a yellow precipitate until precipitation ceased. The yellow solid was collected *via* filtration and washed with water (2 x 20 mL) and a cold 1:1 (CH_2Cl_2:hexanes) solution (2 x 20 mL) to receive **I4** as a light yellow solid (5.8g, 90% yield)

Synthesis of I3



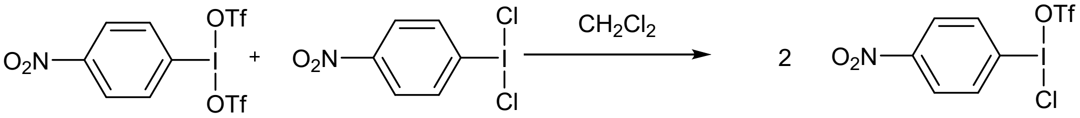
To a suspension of **I2** (152 mg, 0.53 mmol) in CH_2Cl_2 (2 mL) was added TMS-OTf (118 mg, 0.53 mmol) to receive a clear solution. This solution was subsequently treated with hexanes and stored at –35 °C for 2 hours to receive a white solid which was collected *via* filtration and washed hexanes (2 × 5 mL) to receive **I3** as a clear crystalline solid (173 mg, 78 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (d, 2H, *J*=9.0 Hz), 8.34(d, 2H, *J*=9.0 Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.7, 137.6, 134.7, 129.5 (d, J_F= 16 Hz), 127.1, 118.4 (q, J_F= 319 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -76.4, -190.6

Synthesis of I5



A rapidly stirring solution of **I4** (86 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) was subject to the dropwise addition of **I1** (146 mg, 0.27 mmol) in CH_2Cl_2 (1 mL). The resulting solution was stirred for 5 minutes and subsequently treated with n-hexane (7 mL). The resulting solution was concentrated in vacuo to ~7.5 mL to precipitate a pale yellow solid. The concentrated solution was then treated with n-hexane (3 mL), where the precipitate was then collected *via* filtration and washed with n-hexane to receive **I5** as a pale yellow solid (211 mg, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.43 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.8, 138.8, 136.4, 127.2, 126.6, 118.9 (q, J_F= 319 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -77.0

General procedure for reaction of I3 with aryl substrates

To a solution of I3 (~15 mg, 0.04 mmol) in $CDCl_3$ (0.6 mL) was added the respective aryl substrate in mild excess. The reaction was subsequently taken for ^1H NMR analysis prior to having an aliquot taken for ESI-MS analysis.

General Procedures for Chlorination of Deactivated Substrates:

(GP1) Chlorination using I5:

To a solution of **I5** (~25-30 mg, 0.06-0.07 mmol) in $CDCl_3$ (0.6 mL) was added ~1.05 eq. of respective aryl substrate. The reaction was then taken for ^1H NMR analysis.*

**Reactions with benzotrifluoride and nitrobenzene were subject to 2 hours of heating at 70 °C in a sealed vessel prior to being taken for analysis.*

(GP2) Catalytic chlorination using NO_2PhI, HOTf and exogenous Cl_2:

A 50 mL 3-necked flask was charged with a corresponding amount of TCICA with a stirrer bar and placed under a positive N_2 stream *via* side arm. To the other side arm was attached a drying tube attached to an oven dried gas bubbler which was subject to the positive N_2 stream. A reaction vial was then charged with NO_2-PhI (20 mg), $CDCl_3$ (5 mL) and HOTf (20 μL). This solution was subsequently transferred to the gas bubbler. A dropping funnel containing 25 mL of concentrated aq. HCl was then added to the vertical arm of the 3-necked flask. The nitrogen stream was then closed off from the apparatus and HCl slowly delivered to the flask dropwise whilst stirring to steadily deliver dry Cl_2 to the bubbler over the course of 1-2 hours (apparatus observable in Figure **GP2**). Aliquots were taken during reaction for *in situ* ^1H NMR analysis, where delivery of Cl_2 was ceased when substrates were consumed.

Cl_2 generation should be performed in a well-ventilated fume hood and exhaust of reaction bubbler delivered to an aq. NaOH solution to quench gaseous HCl and Cl_2.

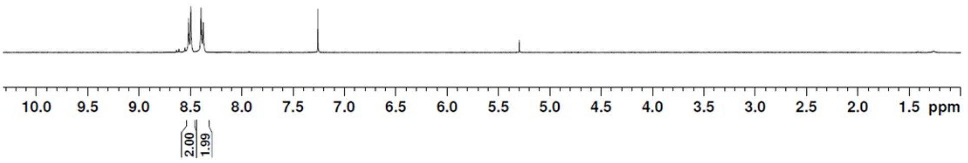
Table S1. Reaction scale for gram scale chlorination *via* GP2.

Substrate	**Amount (mmol)**	**TCICA**	**HOTf**	**NO_2-PhI**
o-Dichlorobenzene	1.5 mL (13.3 mmol)	~14 g (52 mmol)	20 µL (0.23 mmol)	20 mg
1,3-Dibromobenzene	800 µL (6.09 mmol)	~8 g (~23 mmol)	20 µL (0.23 mmol)	20 mg
Chlorobenzene	850 µL (8.38 mmol)	~8 g (~23 mmol)	20 µL (0.23 mmol)	20 mg
2,6-dichlorotoluene	2.0 mL (9.4 mmol)	~9 g (~39 mmol)	25 µL (0.23 mmol)	30 mg

Figure **GP2**. General apparatus for dry Cl_2 gas delivery to reaction.

(GP3) Chlorination using I4 and catalytic HOTf:

To a solution of **I4** (~50 mg, 15.6 mmol) in $CDCl_3$ (0.6 mL) was added ~1.1 eq. of the respective aryl substrate. 1.5 µL of HOTf was then added and the reaction was stirred under indicated conditions (Scheme 11) prior to being taken for ^{1}H NMR analysis.



Spectral Data:

Figure S1. ^{1}H NMR of **I3** in $CDCl_3$.

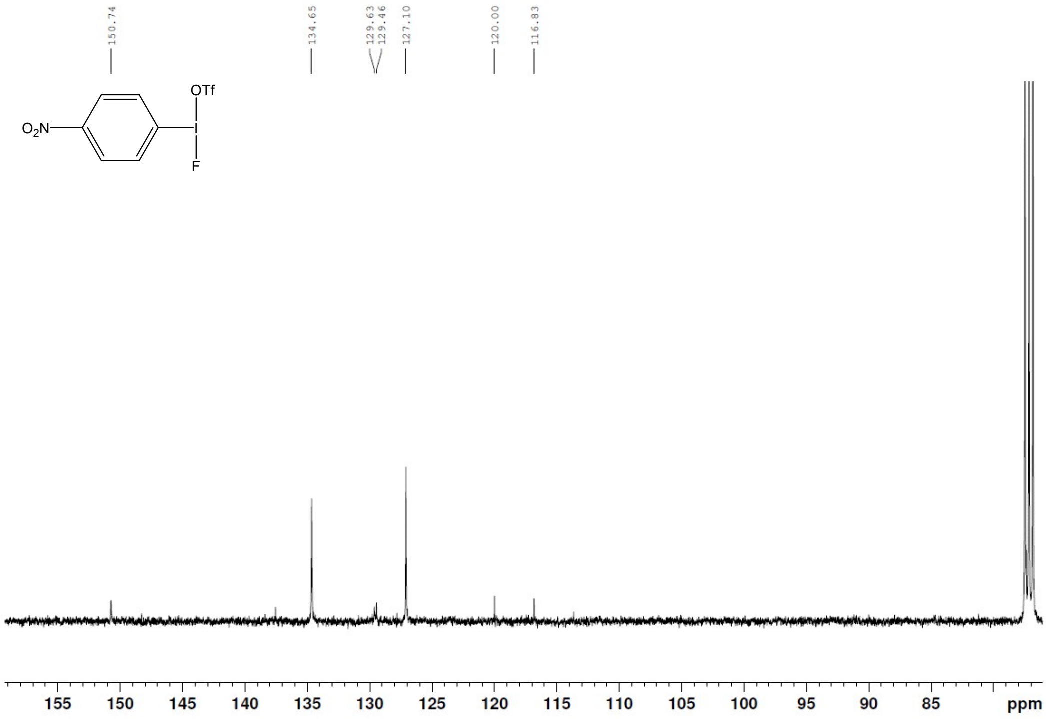


Figure S2. ^{13}C NMR of **I3** in CDCl$_3$.

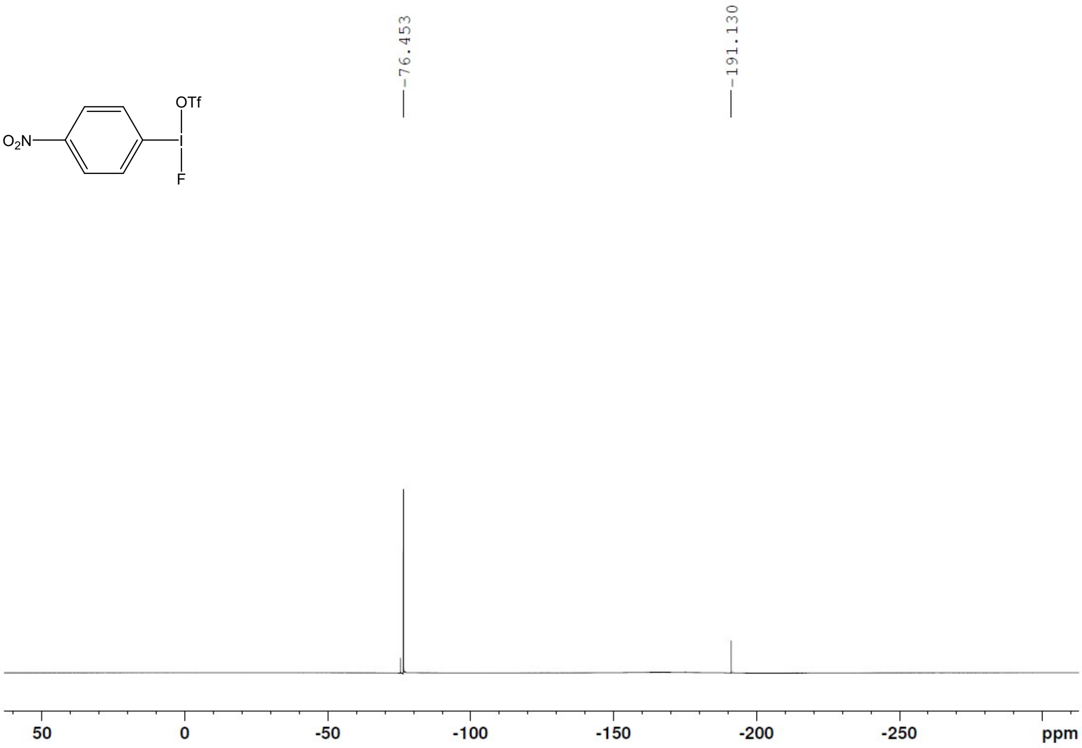


Figure S3. ^{19}F NMR of **I3** in CDCl$_3$.

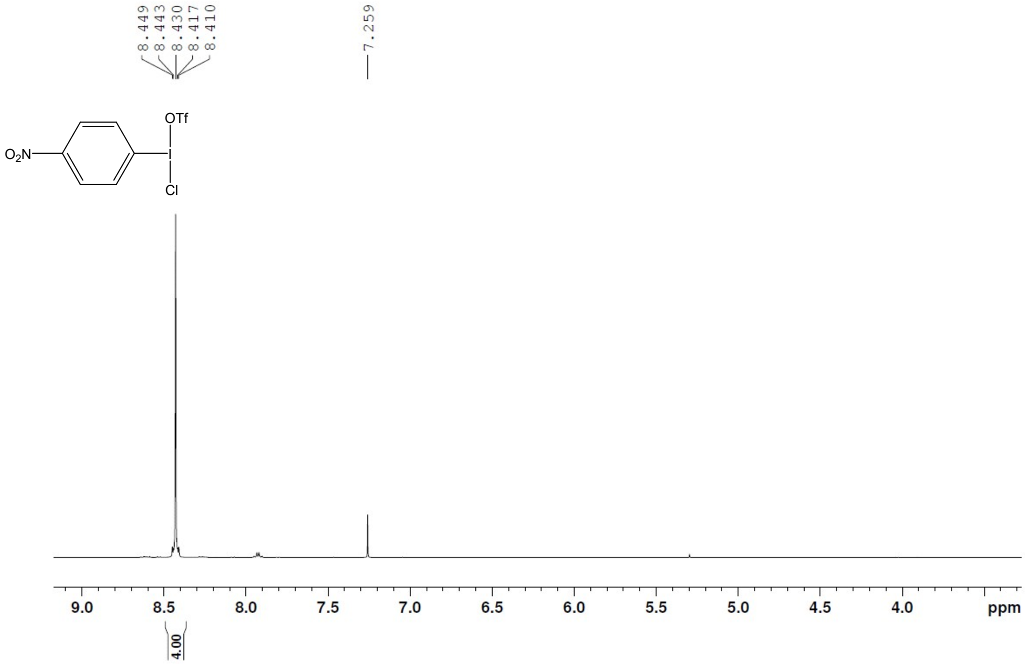


Figure S4. ^{1}H NMR of **I5** in $CDCl_3$.

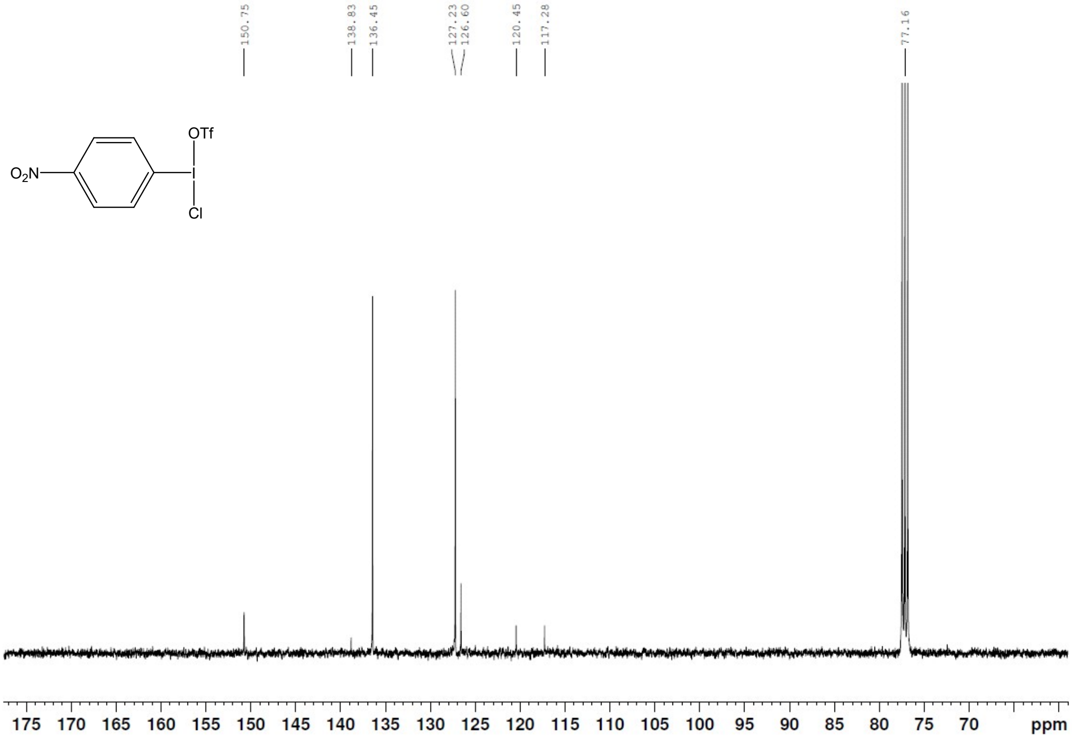


Figure S5. ^{13}C NMR of **I5** in $CDCl_3$.

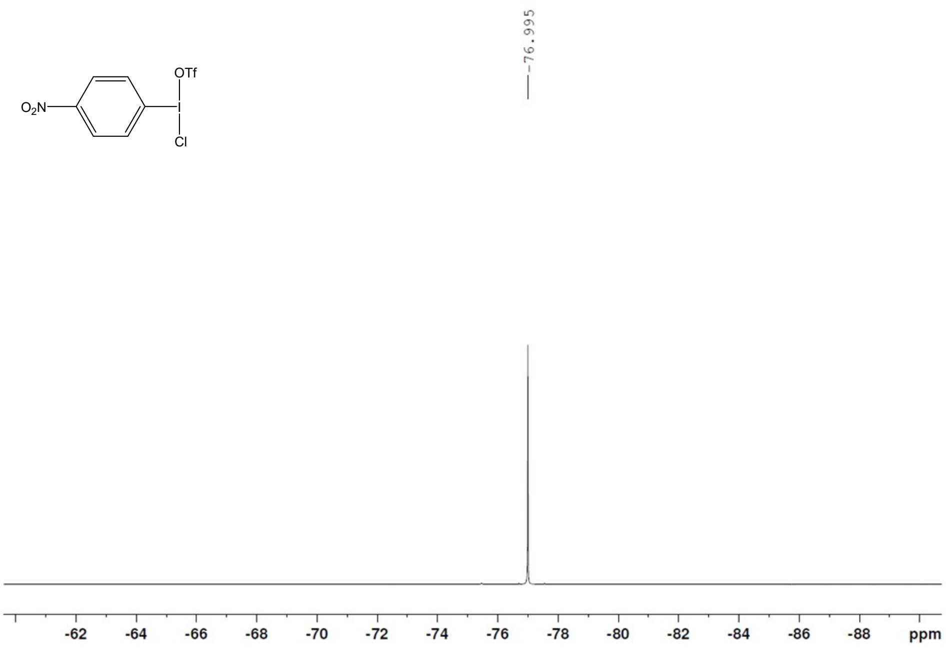


Figure S6. ^{19}F NMR of **I5** in $CDCl_3$.

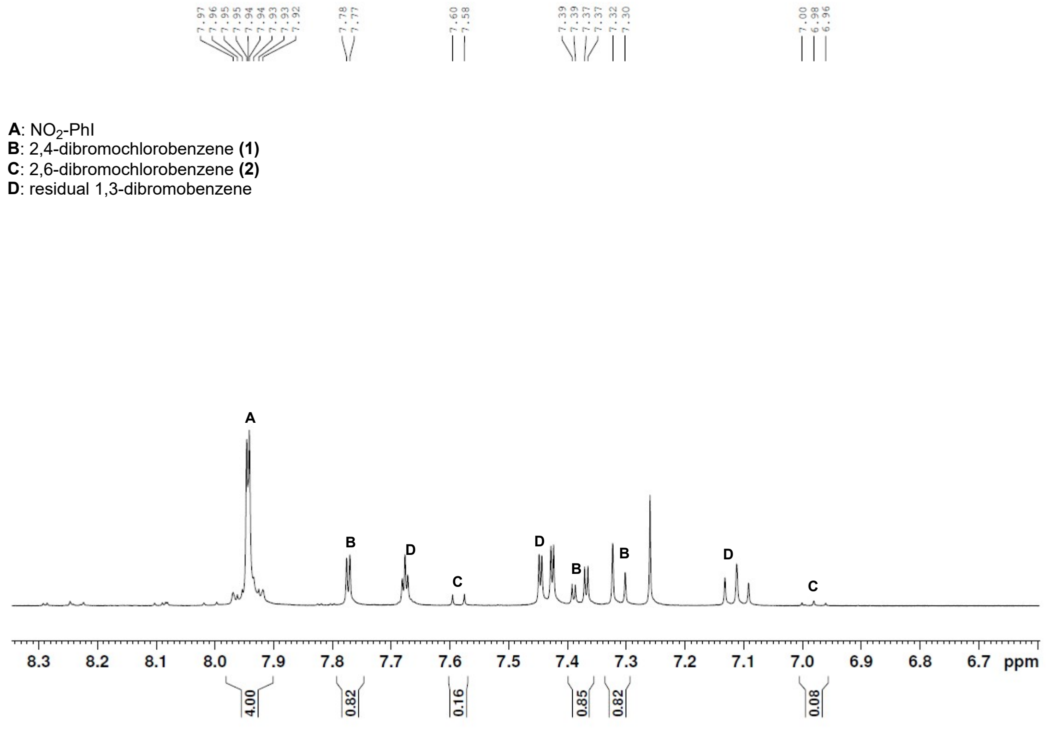


Figure S7. ^{1}H NMR for chlorination of 1,3-dibromobenzene with **GP1**.

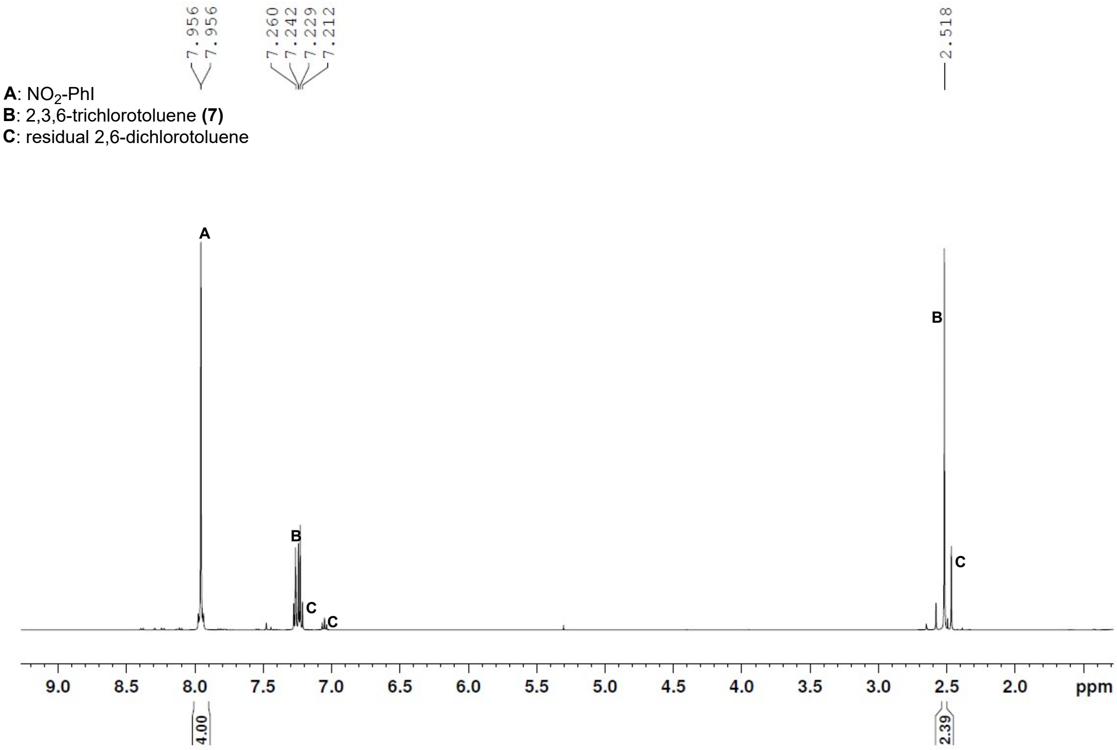


Figure S8. ^{1}H NMR for chlorination of 2,6-dichlorotoluene with **GP1**.

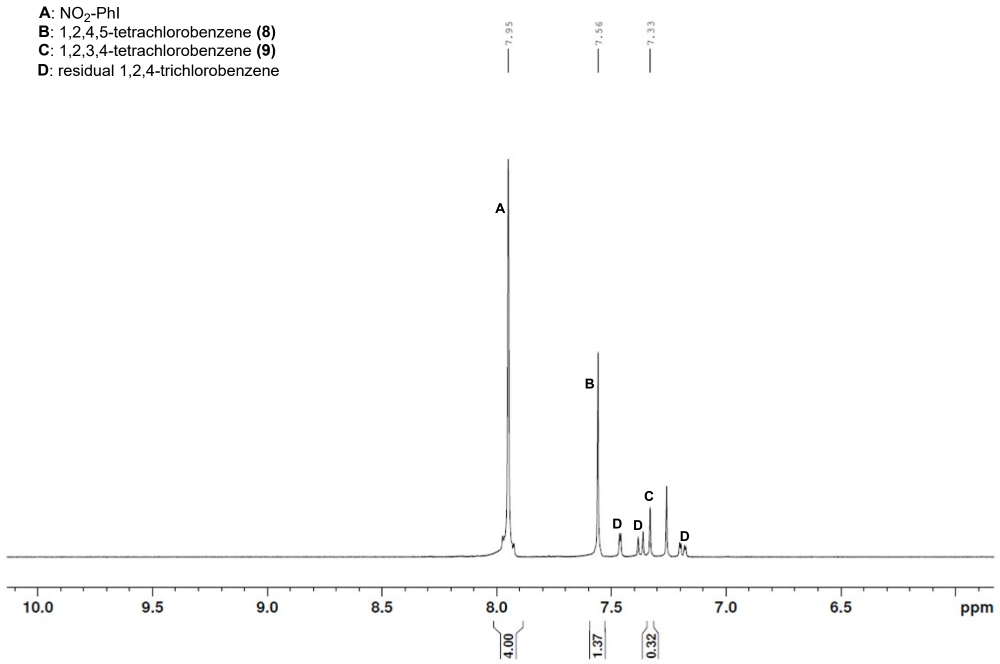


Figure S9. ^{1}H NMR for chlorination of 1,2,4-trichlorobenzene with **GP1**.

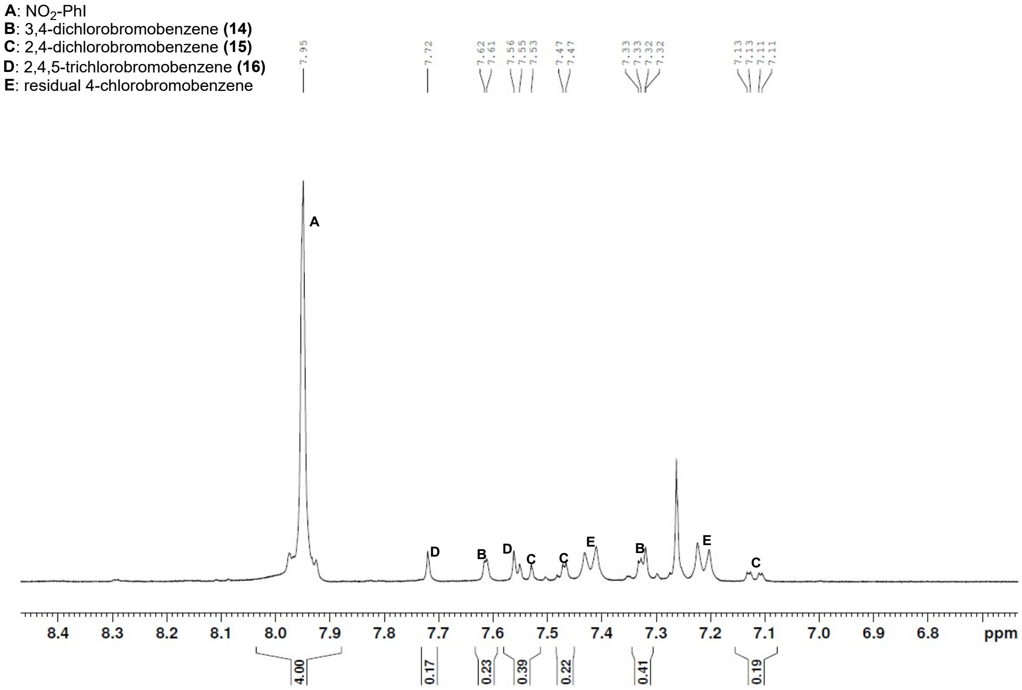


Figure S10. ^{1}H NMR for chlorination of 4-chlorobromobenzene with **GP1**.

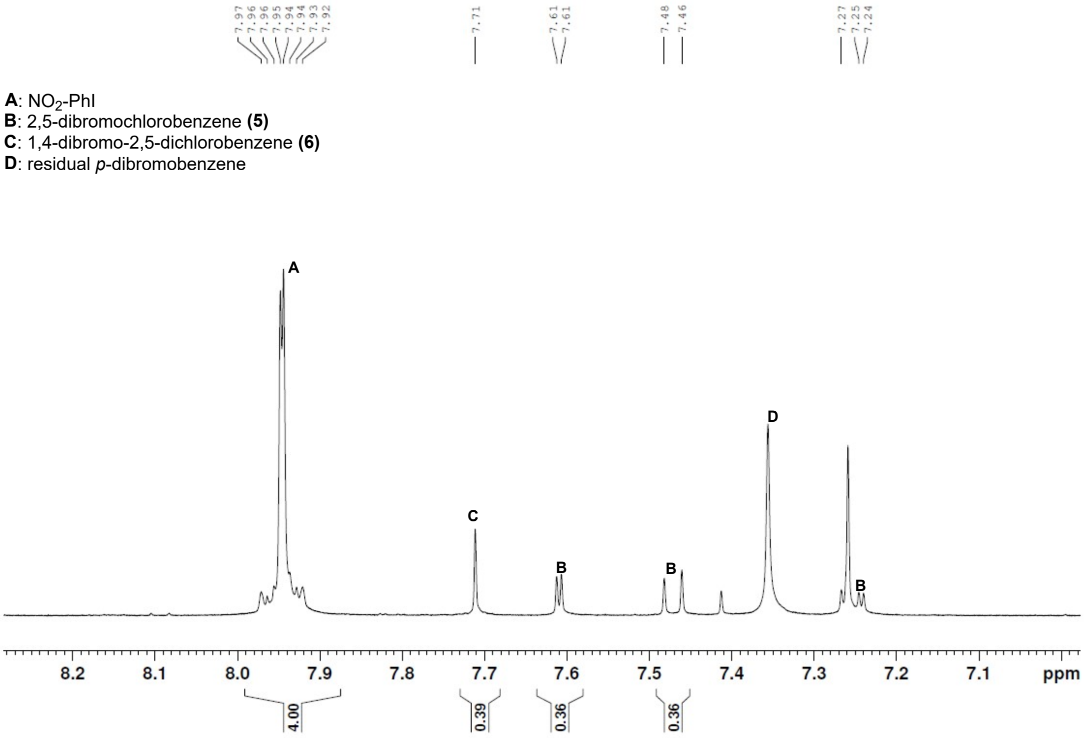


Figure S11. ^{1}H NMR for chlorination of *p*-dibromobenzene with **GP1**.

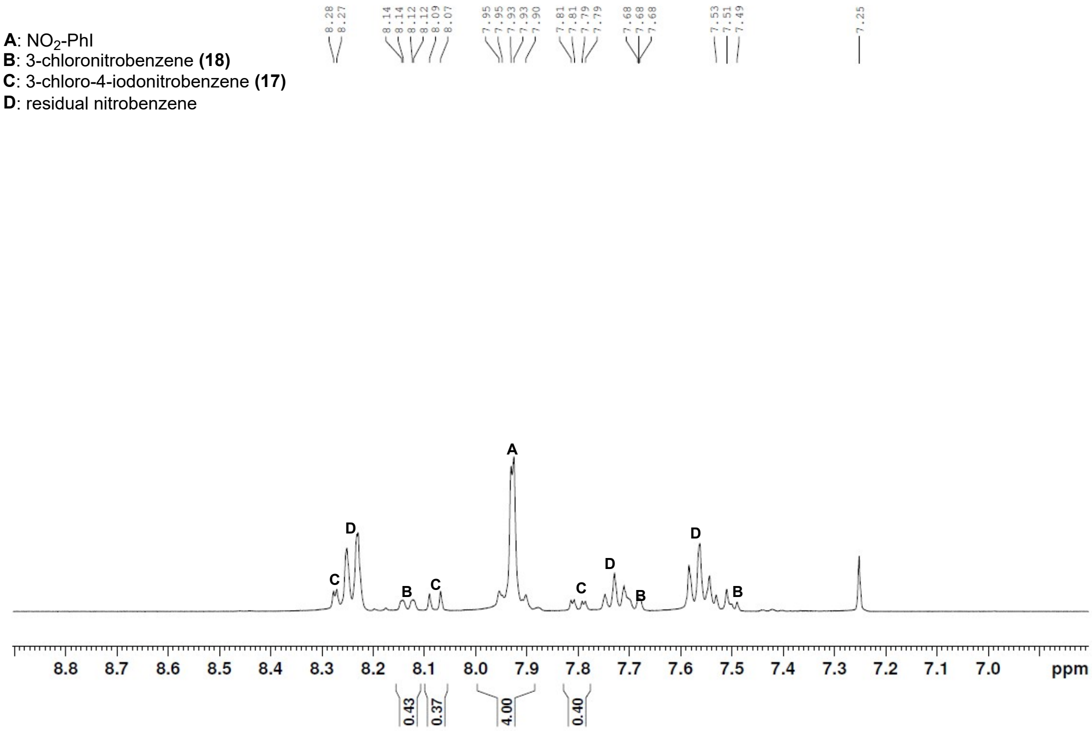


Figure S12. ^{1}H NMR for chlorination of nitrobenzene with **GP1**.

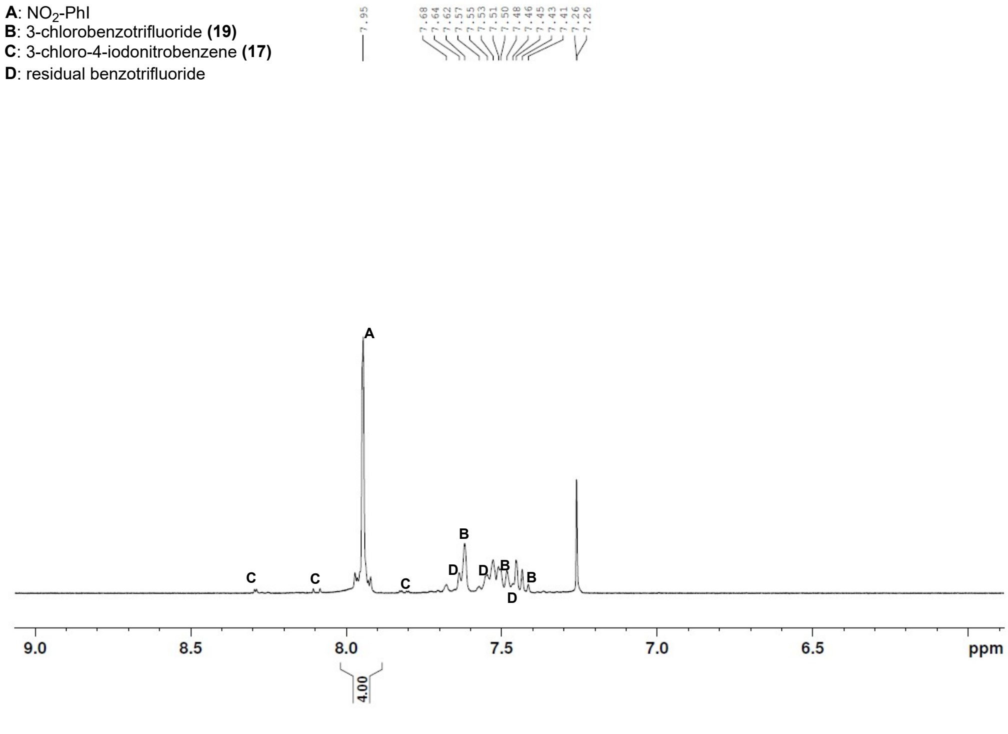


Figure S13. ^{1}H NMR for chlorination of benzotrifluoride with **GP1**. Product peaks obscured for CF_3 containing species.

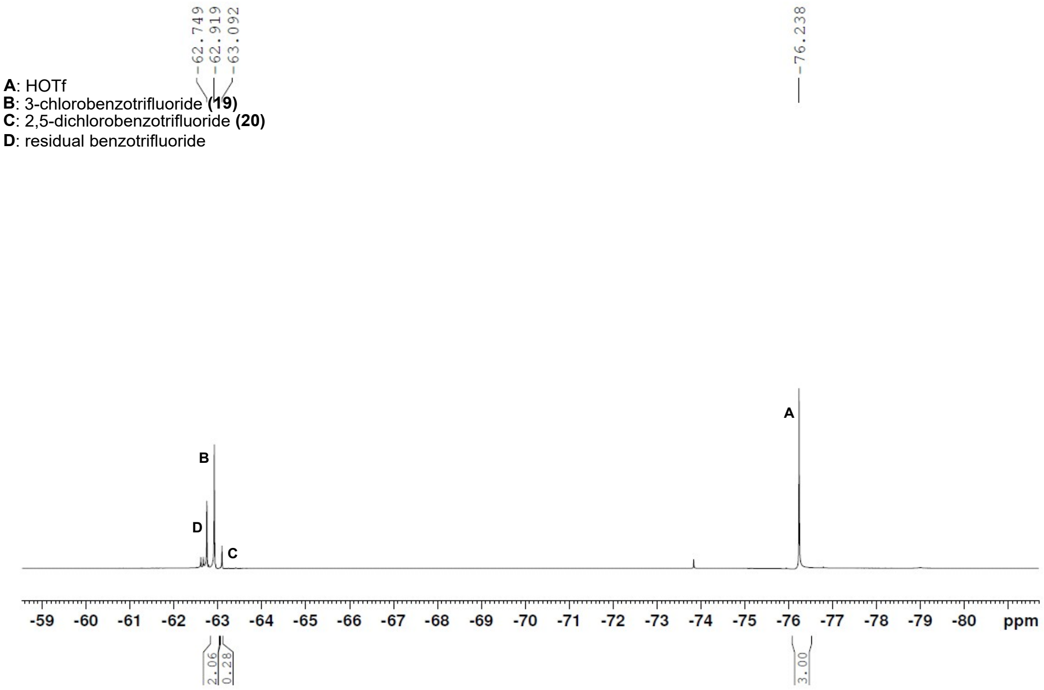


Figure S14. ^{19}F NMR for chlorination of benzotrifluoride with **GP1**.

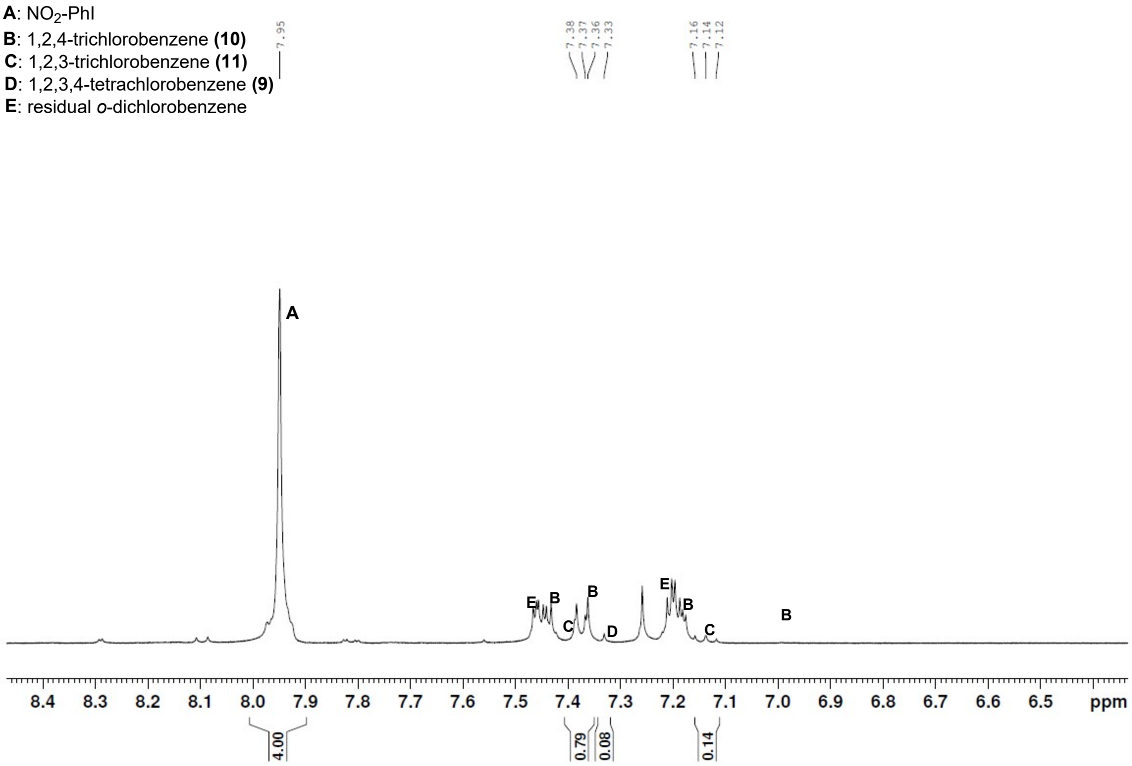


Figure S15. ^{1}H NMR for chlorination of *o*-dichlorobenzene with **GP1**.

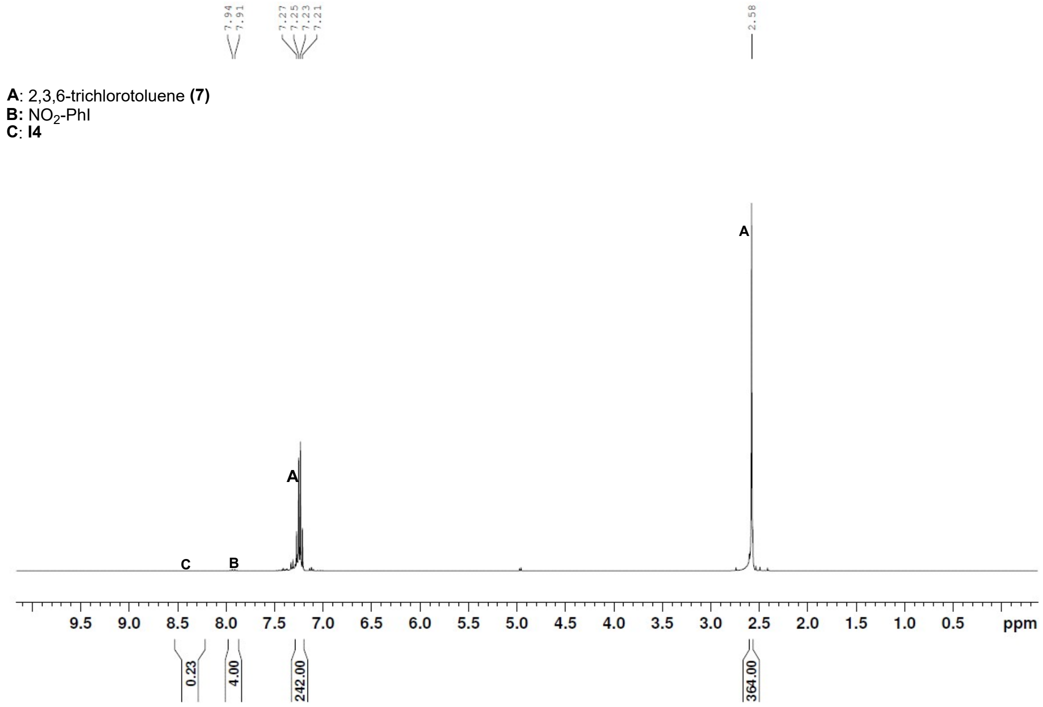


Figure S16. ^{1}H NMR for catalytic chlorination of 2,6-dichlorotoluene with **GP2**.

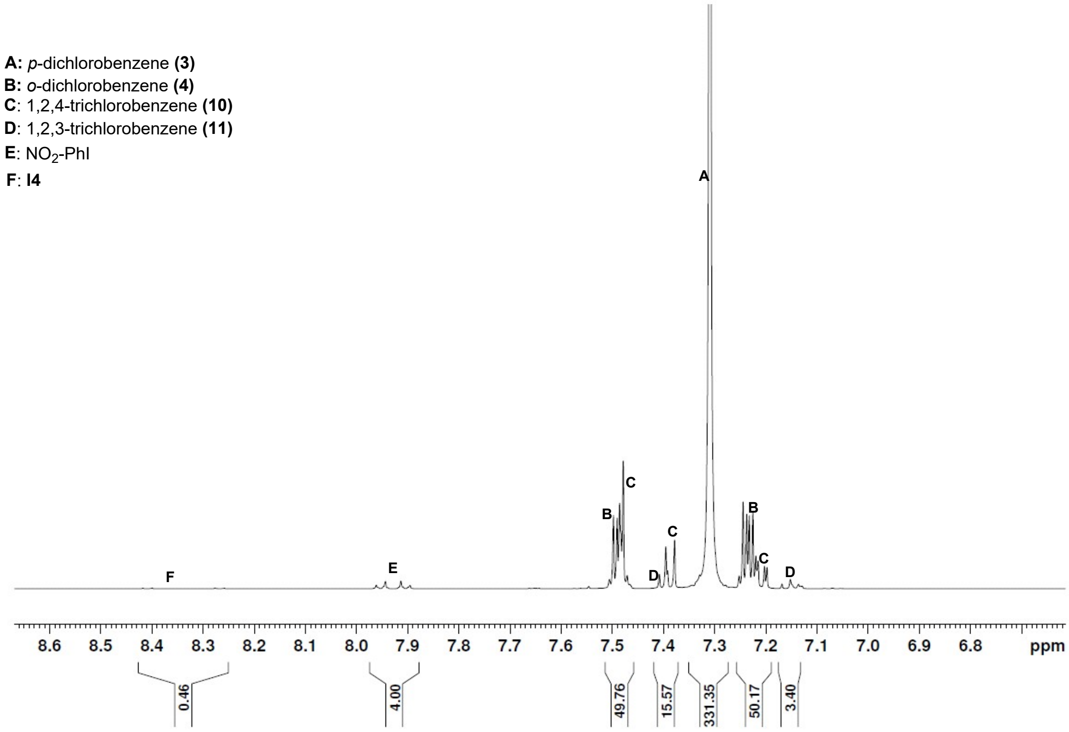


Figure S17. ^{1}H NMR for catalytic chlorination of chlorobenzene with **GP2**.

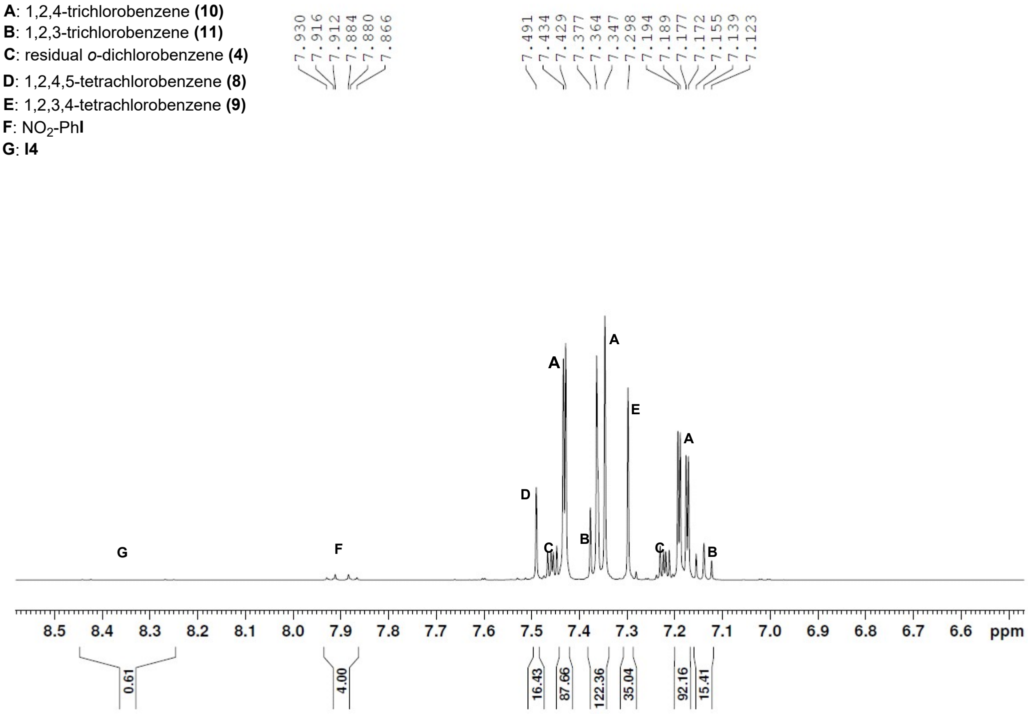


Figure S18. ^{1}H NMR for catalytic chlorination of *o*-dichlorobenzene with **GP2**.

C

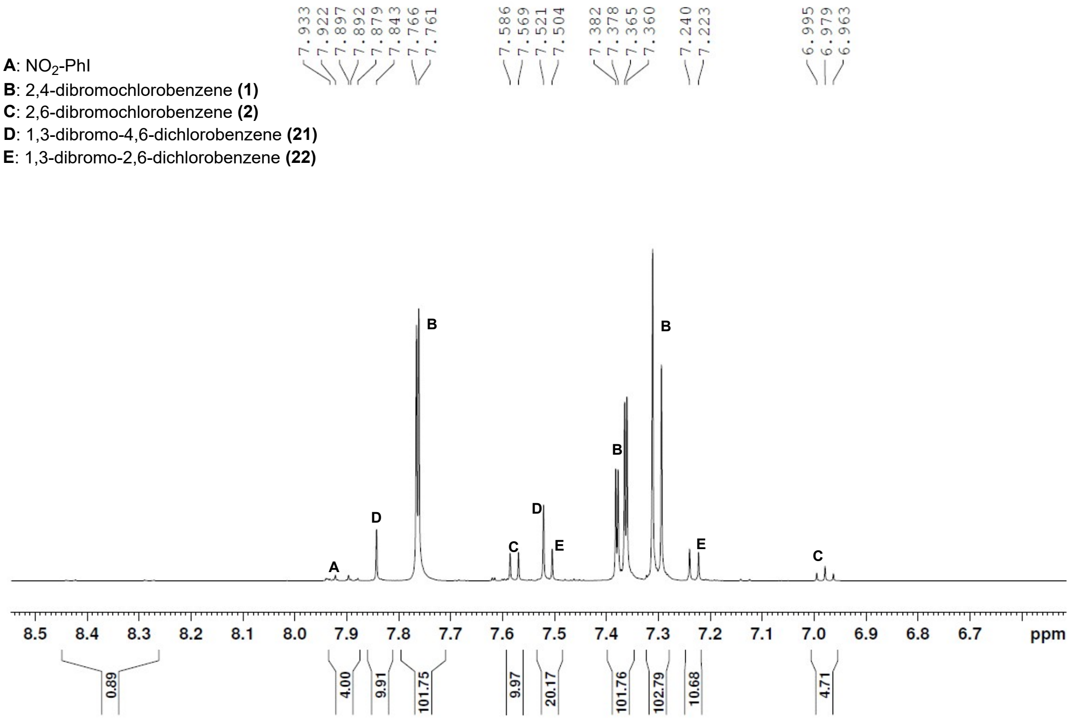


Figure S19. ^{1}H NMR for catalytic chlorination of 1,3-dibromobenzene with **GP2**.

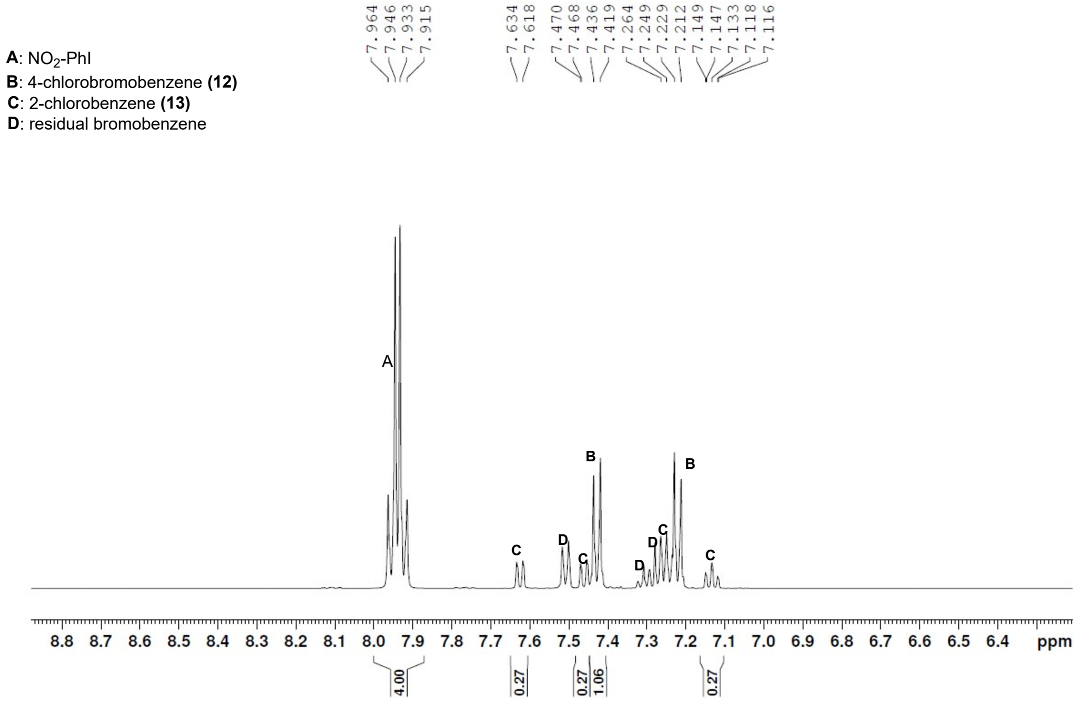


Figure S20. ^{1}H NMR for catalytic chlorination of bromobenzene using **GP3**.

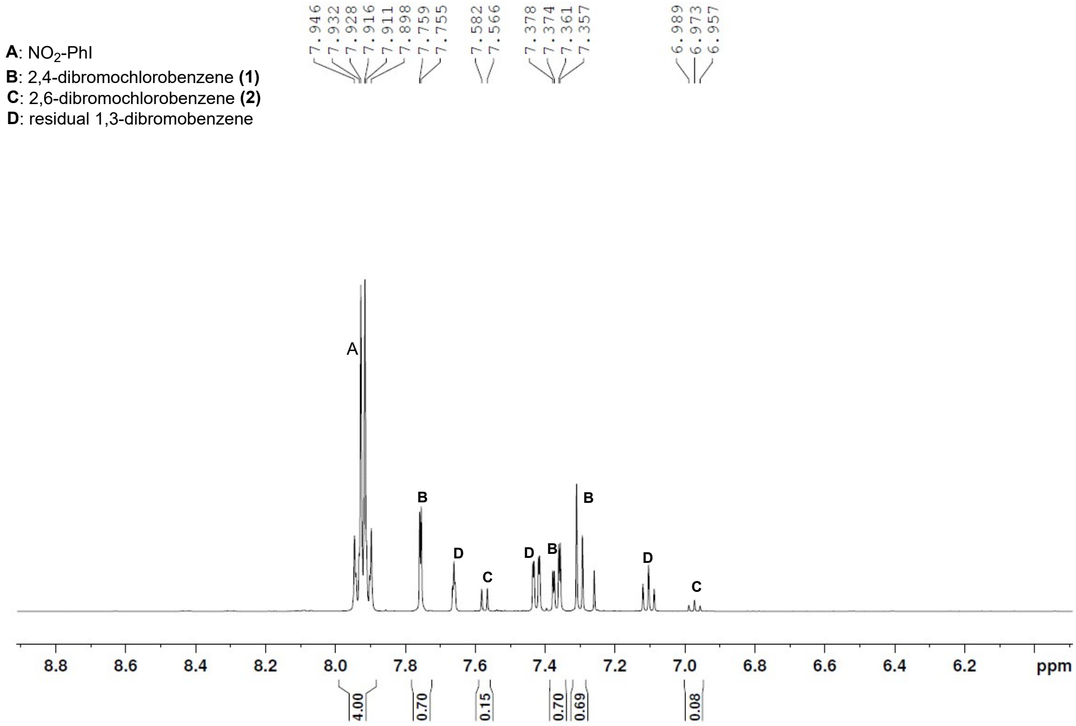


Figure S21. ^{1}H NMR for catalytic chlorination of 1,3-dibromobenzene using **GP3**.

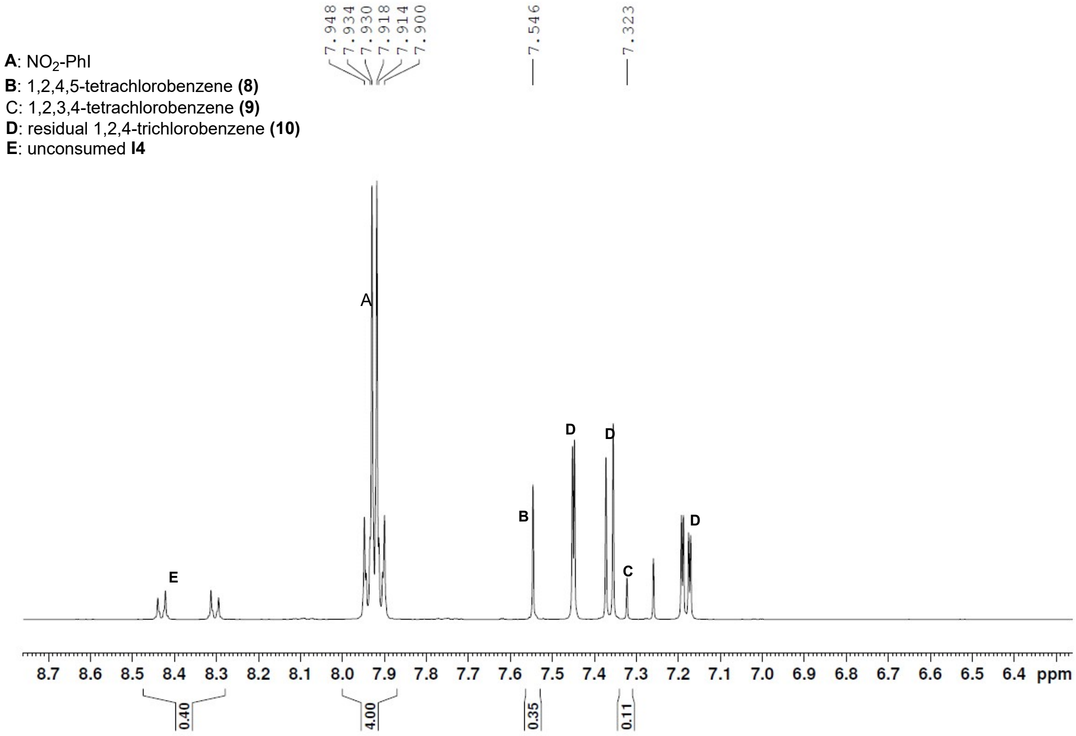


Figure S22. ^{1}H NMR for catalytic chlorination of 1,2,4-trichlorobenzene using **GP3**.

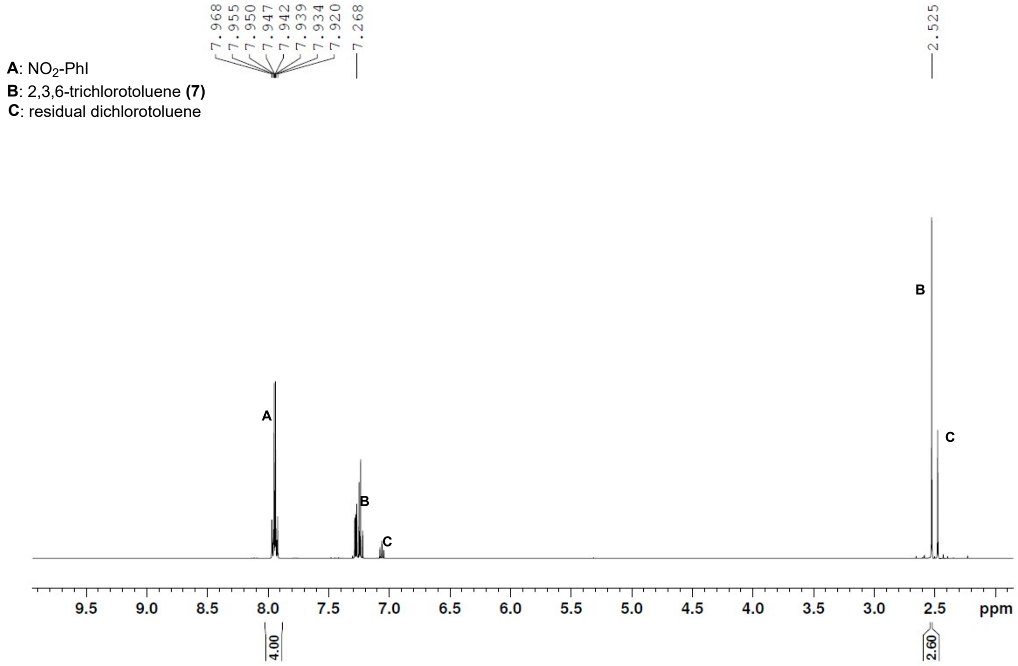


Figure S23. ^{1}H NMR for catalytic chlorination of 2,6-dichlorotoluene using **GP3**.

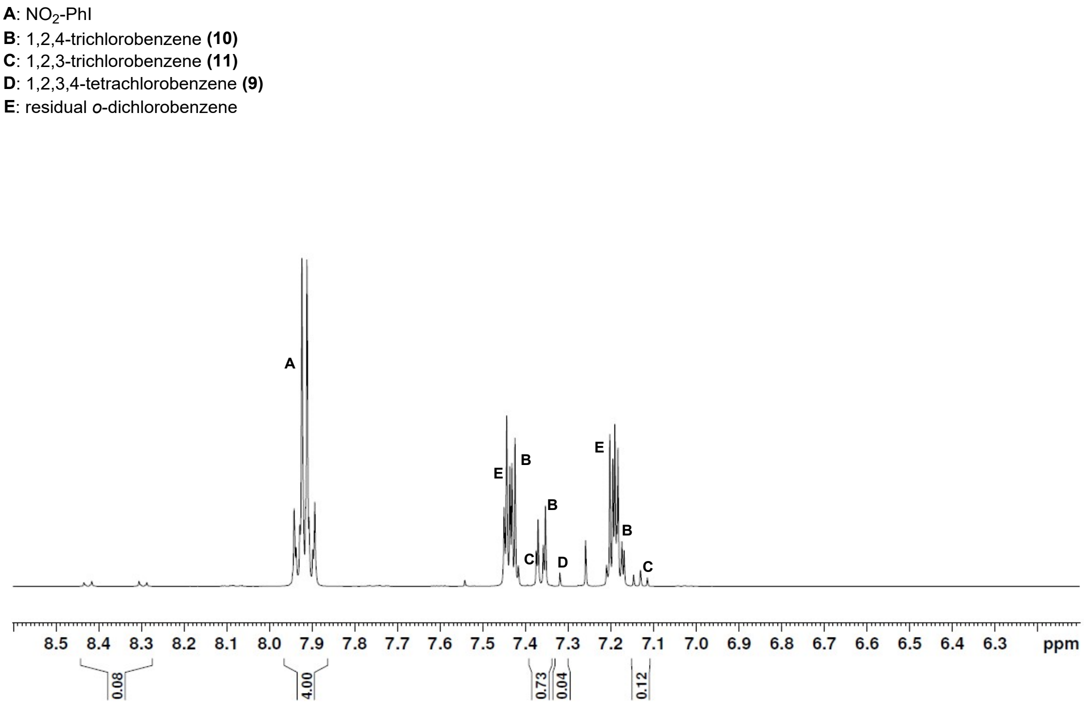


Figure S24. ^{1}H NMR for catalytic chlorination of *o*-dichlorobenzene using **GP3**.

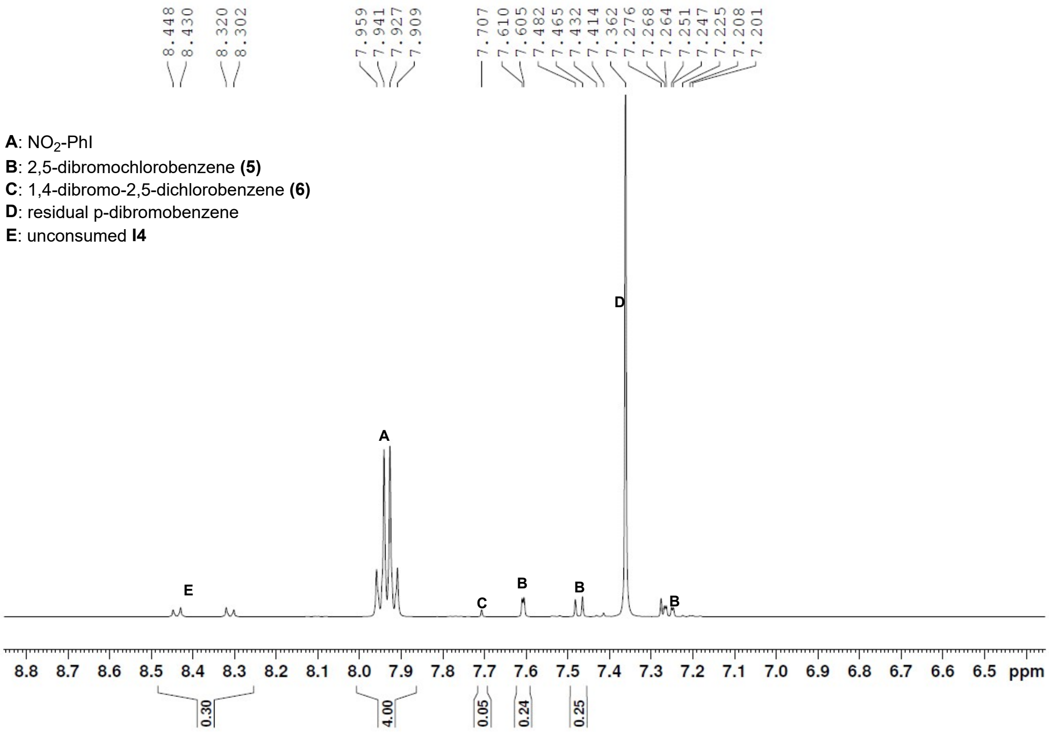


Figure S25. ^{1}H NMR for catalytic chlorination of *p*-dibromobenzene using **GP3**.

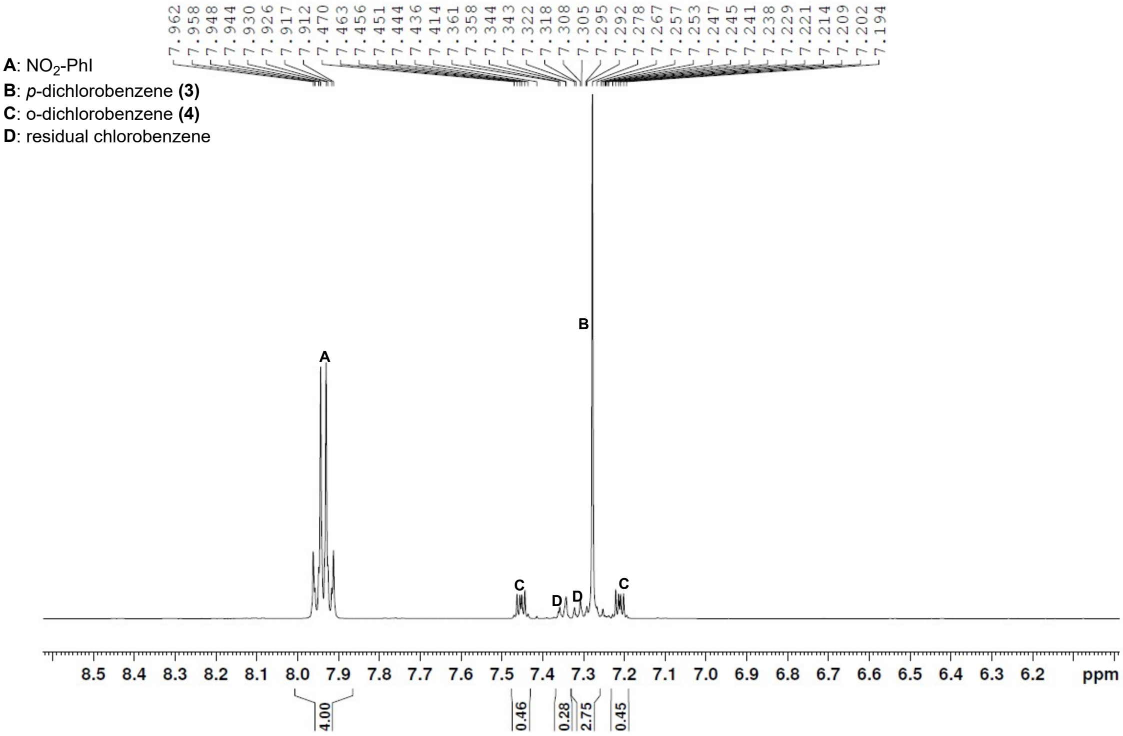


Figure S26. ^{1}H NMR for catalytic chlorination of chlorobenzene using **GP3**.

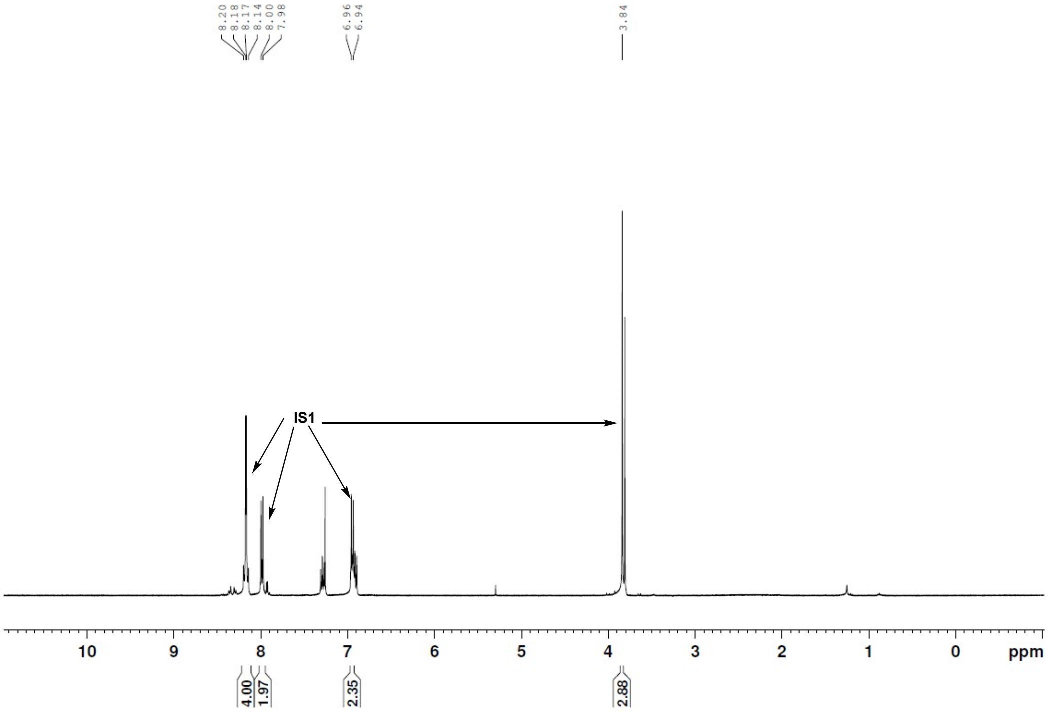


Figure S27. *In situ* ^{1}H NMR of reaction between **I3** and anisole displaying **IS1** in CDCl$_3$.

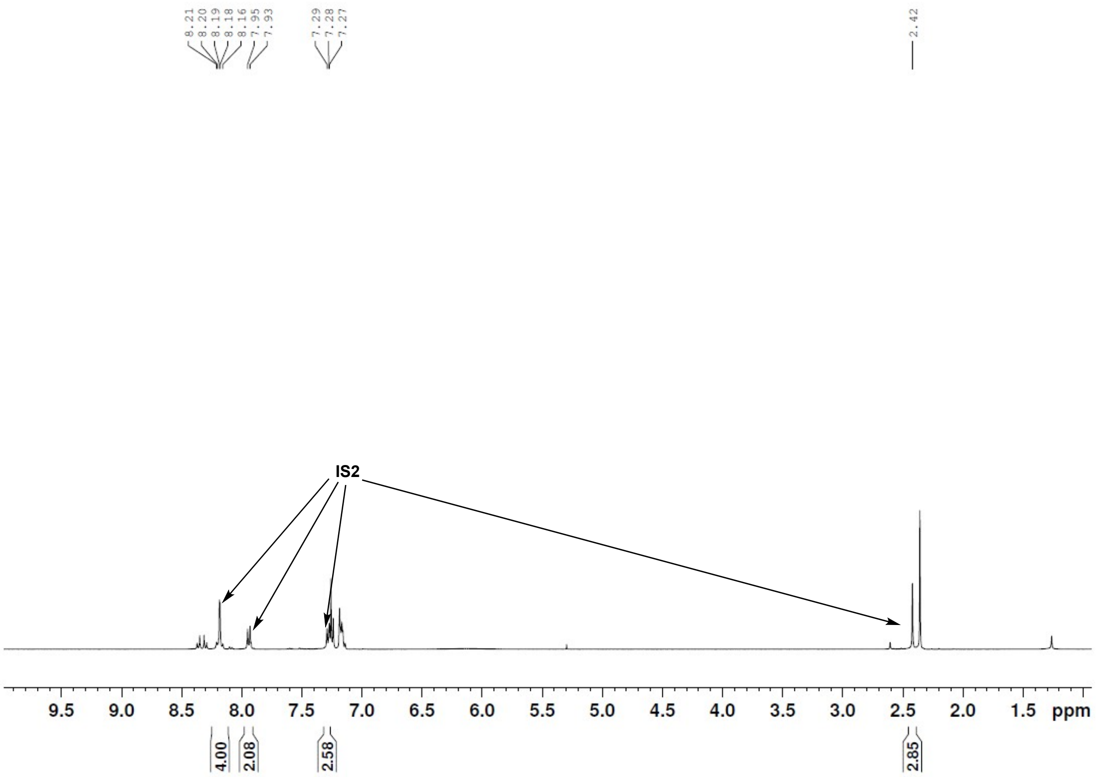


Figure S28. *In situ* ^{1}H NMR of reaction between **I3** and toluene displaying **IS2** in $CDCl_3$.

Mass Spectral Data for IS1 and IS2.

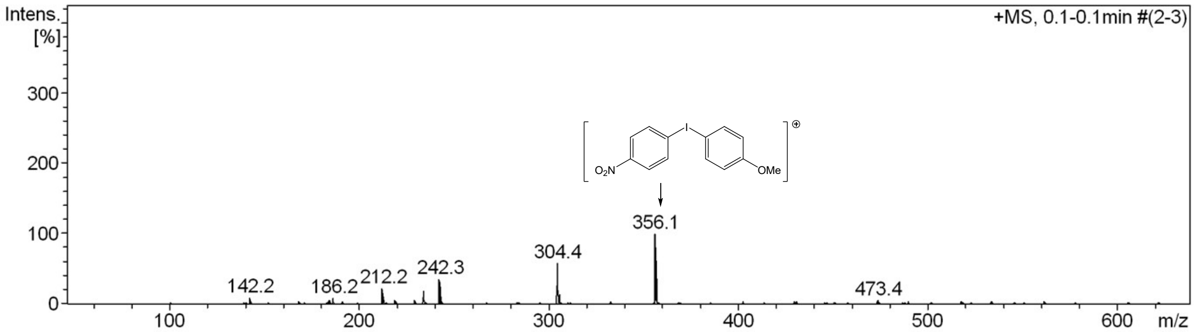


Figure S29. Positive ESI-MS of reaction between **I3** and anisole displaying **IS1**.

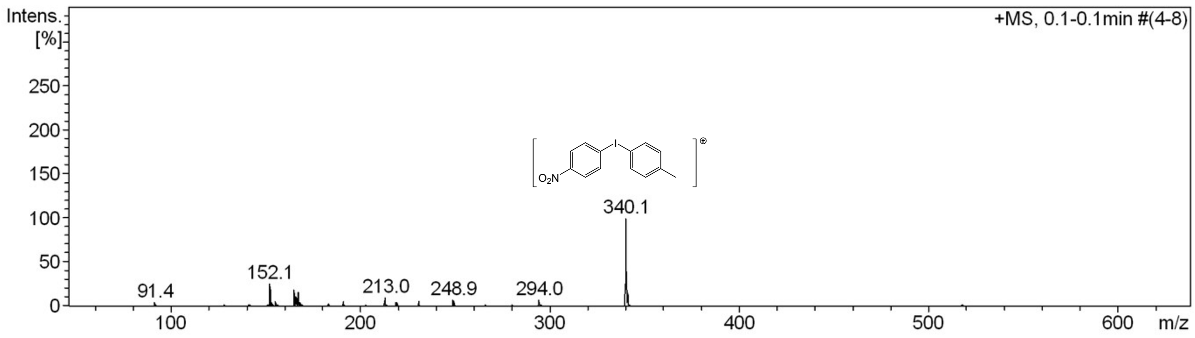
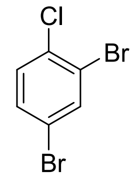


Figure S30. Positive ESI-MS of reaction between **I3** and toluene displaying **IS2**.

Reference NMR Spectral Data for Products Identified in Chlorination Reactions:

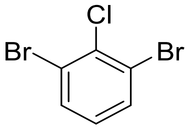
2,4-dibromochlorobenzene (1):

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.76 (d, 1H, *J*= 2.2 Hz), 7.37 (dd, 1H, J_1= 8.5 Hz, J_2= 2.2 Hz), 7.31, (d, 1H, *J*= 8.5 Hz)



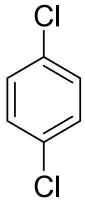
2,6-dibromochlorobenzene (2):

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.58 (d, 2H, *J*= 8.1 Hz), 6.98 (t, 1H, *J*= 8.1 Hz)



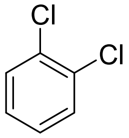
***p*-Dichlorobenzene (3):** Commercial sample

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26 (s, 4H)



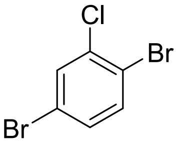
***o*-Dichlorobenzene (4):** Commercial sample

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 (dd, 2H, J_1= 6.0 Hz, J_2= 3.6 Hz), 7.20 (dd, 2H, J_1= 6.0 Hz, J_2= 3.6 Hz)



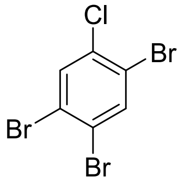
2,5-dibromochlorobenzene (5): Commercial sample

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, 1H, *J*= 2.2 Hz), 7.47 (d, 1H, *J*= 8.6 Hz), 7.25 (dd, 1H, J_1= 8.56 Hz, J_2= 2.2 Hz)



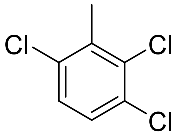
1,4-dibromo-2,5-chlorobenzene (6):[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (2H)



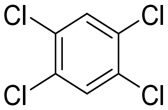
2,3,6-trichlorotoluene (7):

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22-7.13 (m, 2H), 2.52 (s, 3H)



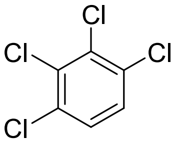
1,2,4,5-tetrachlorobenzene (8):[5] SDBS 1114

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (s, 2H)



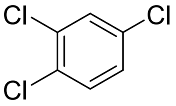
1,2,3,4-tetrachlorobenzene (9):[5] SDBS 1546

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (s, 2H)

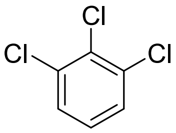


1,2,4-trichlorobenzene (10): Commercial sample

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (d, 2H, *J*=2.4 Hz), 7.37 (d, *J*= 8.6 Hz), 7.19 (dd, J_1= 8.6 Hz, J_2= 2.4 Hz)



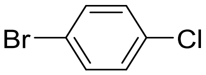
1,2,3-trichlorobenzene (11):[5] **SDBS 546**



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36 (d, 2H, *J*=8.1 Hz), 7.14 (t, 1H, *J*= 8.1 Hz)

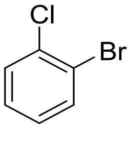
4-Chlorobromobenzene (12): Commercial sample

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, 2H, *J*= 8.5 Hz), 7.20 (d, 2H, *J*= 8.5 Hz)



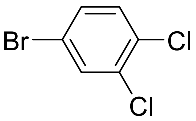
2-Chlorobromobenzene (13):[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm):7.61 (d, 1H, *J*= 8.0 Hz), 7.45 (d, 1H, *J*= 8.0 Hz), 7.25 (t, 7.8 Hz), 7.12 (t, 1H, *J*= 7.8 Hz)



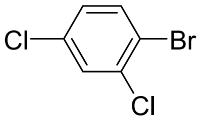
3,4-Dichlorobromobenzene (14):[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm):7.60 (d, 1H, J= 1.5 Hz), 7.33 (dd, 1H, J_1= 8.5 Hz, J_2= 1.5 Hz), 7.30 (d,1H, J= 8.5 Hz)



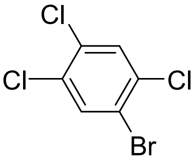
2,4-Dichlorobromobenzene (15):[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm):7.53 (d, 1H, J= 8.5 Hz), 7.45 (d, 1H, J= 2.2 Hz, J_2= 1.5 Hz), 7.11 (dd, 1H, J_1= 8.5 Hz, J_2= 2.2 Hz)



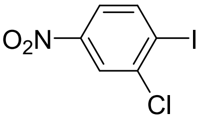
2,4,5-Trichlorobromobenzene (16):[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (s, 1H), 7.70 (s, 1H)



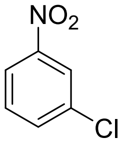
3-Chloro-4-iodonitronbenzene (17):

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, 1H, J= 2.6 Hz), 8.08 (d, 1H, J= 8.7 Hz), 7.81 (dd, 1H, J_1=8.7 Hz, J_2= 2.6 Hz)



3-chloronitronbenzene (18):[5]

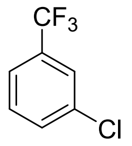
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (s, 1H), 8.13 (d, 1H, J= 8.1 Hz), 7.68 (d, 1H, J_1=8. Hz), 7.53 (t, 1H, J=8.2 Hz)



3-Chlorobenzotrifluoride (19):[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (s, 1H), 7.59-7.52 (m 2H), 7.46 (t, 1H)

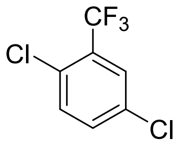
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.9



2,5-Dichlorobenzotrifluoride (20):[11]

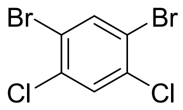
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65-7.55 (m, 1H), 7.40-7.30 (m, 2H)

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



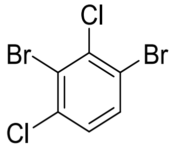
1,3-Dibromo-4,6-dichlorobenzene (21):

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (s, 1H), 7.52 (s, 1H)



1,3-Dibromo-2,6-dichlorobenzene (22):

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.51 (d, 1H, *J*=8.6 Hz), 7.24 (d, 1H, 8.6 Hz)



Computational Details:

Cartesian Coordinates for optimised compound geometries:

All geometry optimisation, vibrational frequency and molecular orbital calculations were performed using ωPBE/def2-TZVP within Gaussian 16 using the WebMO platform.[12-14] The structures obtained are minima with no negative frequencies. Cartesian coordinates are in Å and energies are given in Hartree.

NO$_2$-PhIF(OTf) **(I3)**

Electronic Energy: -1794.83916486 Hartree

S	0.00000000	0.00000000	0.00000000
O	-1.06648200	0.53263200	0.94945800
I	-2.01917000	2.41019300	0.60554000
F	-3.11494500	3.99681700	0.39936200
C	-3.78404800	1.30347300	0.64183300
C	-4.89665600	1.91867700	1.17893400
C	-6.08838400	1.22258900	1.19707400
C	-6.11762600	-0.05256300	0.67970800
C	-5.00728000	-0.66235200	0.14127400
C	-3.81102300	0.02728100	0.11889400
H	-2.92866200	-0.44202300	-0.29477400
H	-5.08163800	-1.66406300	-0.25868500
N	-7.39313200	-0.79497000	0.70193500
O	-8.34735700	-0.23869500	1.18494500
O	-7.39404900	-1.90615600	0.23606700
H	-6.98759700	1.65806200	1.60999100
H	-4.84844100	2.92758200	1.56459800
O	-0.45376200	-1.16601200	-0.67295800

C	1.23774400	-0.55683900	1.23466300
F	2.28234300	-1.06100400	0.59523500
F	1.63446900	0.47177400	1.97531200
F	0.71826000	-1.48454400	2.02548900
O	0.59857000	1.06834000	-0.72917600

NO_2-PhICl(OTf) **(I5)**

Electronic Energy: -2155.10534185 Hartree

S	0.00000000	0.00000000	0.00000000
O	-1.49700500	0.14912600	0.15302600
I	-2.19276900	2.21157800	0.57196700
Cl	-3.25685200	4.26348400	1.02285400
C	-4.01722800	1.21920000	0.64669300
C	-4.81205300	1.38412200	1.76168300
C	-6.02654800	0.73028500	1.80723900
C	-6.38986400	-0.06010800	0.73992400
C	-5.59439000	-0.22860800	-0.37100000
C	-4.37988200	0.42577700	-0.42183800
H	-3.72742600	0.30092800	-1.27534200
H	-5.92737900	-0.86204000	-1.18138300
N	-7.69052300	-0.75802400	0.78989500
O	-8.36194200	-0.60309700	1.77862600
O	-7.99136900	-1.43337900	-0.16138400

H	-6.68696400	0.82384000	2.65801800
H	-4.50416600	2.01805200	2.58292800
O	0.34359500	-0.93696800	-1.00487800
C	0.43010400	-0.78643600	1.59970600
F	1.74211400	-0.94540600	1.68252800
F	0.02525100	-0.00846900	2.60587900
F	-0.16141400	-1.96764500	1.71338000
O	0.61190900	1.29520700	0.03314700

ADDITIONAL CRYSTALLOGRAPHIC DETAILS

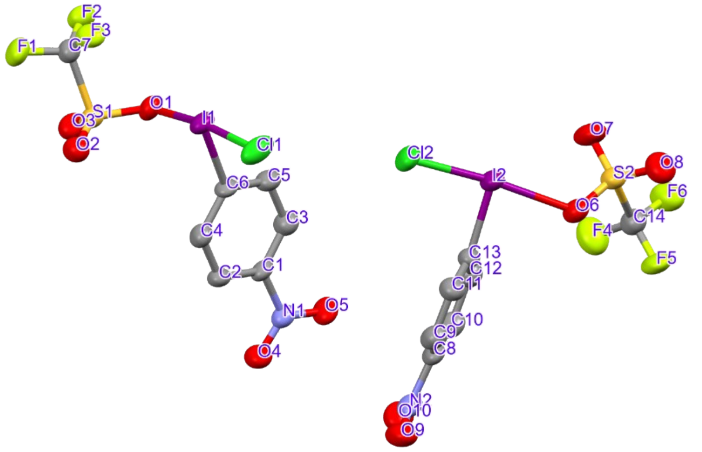


Figure 1: The asymmetric unit of **I5**, showing both NO_2-PhICl(OTf) units.

Selected Bond lengths [Å] for **I5**

I(1)-O(1)	2.332(5)
I(2)-O(6)	2.348(5)
I(1)-Cl(1)	2.359(2)
I(2)-Cl(2)	2.356(1)
S(1)-O(1)	1.486(5)
S(2)-O(6)	1.471(6)
S(1)-O(2)	1.428(6)
S(2)-O(7)	1.419(7)

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