Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

C-H, Si-H and C-F abstraction with an extremely electron poor I(III) reagent

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Experimental Details

General Experimental

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. All other reagents were purchased from Sigma-Aldrich and used as received. NO_2-C_6H_4-$I(OTf)_2$ was synthesised by following literature procedure.[1] 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 a Bruker Ultrashield Plus 500 MHz. Single crystals were selected under paratone-n oil, mounted on nylon loops and placed into a cold stream (150 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 Methods

Reactions of NO_2-C_6H_4-I(OTf)$_2$, PhI(TFA)$_2$, PhI(OAc)$_2$ with triethyl silane (Et_3SiH)

A reaction vial was charged with the respective I(III) species (0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, Et_3SiH (6.4 µL, 0.04 mmol) was added while stirring. The sample was analysed by ^1H and ^{19}F NMR spectroscopy.

NMR Conversion with respect to Et_3SiH: 100% (Et_3SiOTf), 76% (Et_3SiTFA), 27% (Et_3SiOAc)

Reaction of NO_2-C_6H_4-I(OTf)$_2$ and PhI(OAc)(OTf) with triphenylmethane (Ph_3CH)

A reaction vial was charged with NO_2-C_6H_4-I(OTf)$_2$ (22 mg, 0.04 mmol) in CH_2Cl_2 (3 mL). To this mixture, a solution of Ph_3CH (9.7 mg, 0.04 mmol) in CH_2Cl_2 (0.5 mL) was added while stirring. The clear mixture turned yellow immediately. The solution was treated with hexanes (8 mL) and stored at -35 °C for 2 hours resulting in formation of a yellow precipitate. The solid was washed with hexanes (3 x 5 mL) and dried *in vacuo* to afford [Ph_2CHPhI-C_6H_4-NO_2]OTf (yield 75%). Single crystals suitable for X-Ray crystallography were obtained via vapour diffusion ($CHCl_3$:Pentane) at -35 °C.

^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.25-8.23 (d, 2H), 8.18-8.16 (d, 2H), 7.95-7.93 (d, 2H), 7.31-7.27 (m, 4H), 7.26-7.24 (m, 3H), 7.05-7.03 (m, 4H), 5.56 (s, 1H)

^{19}F NMR (472 MHz, $CDCl_3$) δ (ppm): -78.29

ESI m/z: 492.0467

Reaction of NO_2-C_6H_4-I(OTf)$_2$ with cycloheptatriene

A reaction vial was charged with NO_2-C_6H_4-I(OTf)$_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, cycloheptatriene (3.6 mg, 0.04 mmol) was added while stirring. The clear mixture turned yellow immediately and then brown gradually. The sample was analysed by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

NMR Conversion with respect to NO_2-C_6H_4-I: 18% (tropylium)

Reactions of NO_2-C_6H_4-I(OTf)$_2$, PhI(TFA)$_2$ with adamantane

A reaction vial was charged with respective I(III) species (0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, adamantane (5.4 mg, 0.04 mmol) was added while stirring. The clear mixture turned yellow immediately. The sample was analysed by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

NMR Conversion with respect to adamantane: 17% (adamantyl triflate), 0% (adamantyl TFA)

Optimised reaction of NO_2-C_6H_4-I(OTf)$_2$ with adamantane

A reaction vial was charged with NO_2-C_6H_4-I(OTf)$_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (2 mL). To this solution, adamantane (5.4 mg, 0.04 mmol) was added while stirring. The reaction mixture was heated at 60 °C for 30 minutes. The clear mixture turned pale brown upon heating. The sample was analysed by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

NMR Conversion with respect to adamantane: 72% (adamantyl triflate)

Reactions of NO_2-C_6H_4-I(OTf)$_2$ with 1-fluoro adamantane

A reaction vial was charged with NO_2-C_6H_4-I(OTf)$_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, 1-fluoro adamantane (10 mg, 0.04 mmol) was added while stirring. The clear mixture turned pale yellow immediately. The sample was analysed by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

NMR Conversion with respect to NO_2-C_6H_4-I: 70% (NO_2-C_6H_4-I(OTf)F)

Reaction of NO_2-C_6H_4-I(OTf)$_2$ with cyclohexene

A reaction vial was charged with NO_2-C_6H_4-I(OTf)$_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, cyclohexene (4 µL, 0.04 mmol) was added while stirring. The clear mixture turned violet immediately. The sample was analysed by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

NMR Conversion with respect to NO_2-C_6H_4-I: 2% (benzene)

Optimised reaction of NO_2-C_6H_4-I(OTf)$_2$ with cyclohexene

A Schlenk flask was charged with NO_2-C_6H_4-I(OTf)$_2$ (38 mg, 0.07 mmol) in 3 mL CH_2Cl_2 and cooled to -94 °C. A solution of cyclohexene (14 µL, 0.14 mmol) in 3 mL CH_2Cl_2 was transferred *via* cannula into this mixture while stirring. The solution turned pale pink with white solid. Subsequently, the reaction was gradually warmed to room temperature and solid dissolved

along with a stark change of colour to clear violet. An aliquot was dissolved in $CDCl_3$ and taken for NMR analysis.

NMR Conversion with respect to NO_2-C_6H_4-I: 10% (benzene)

Reaction of NO_2-C_6H_4-I$(OTf)_2$ with limonene

A reaction vial was charged with NO_2-C_6H_4-I$(OTf)_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, limonene (6.5 µL, 0.04 mmol) was added while stirring. The clear mixture turned violet immediately. The sample was analysed by ^1H and ^{19}F NMR spectroscopy.

NMR Conversion with respect to NO_2-C_6H_4-I : 32% (*p*-cymene)

Reaction of NO_2-C_6H_4-I$(OTf)_2$ with α-pinene

A reaction vial was charged with NO_2-C_6H_4-I$(OTf)_2$ (22 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, α-pinene (6.4 µL, 0.04 mmol) was added while stirring. The clear mixture turned dark red immediately. The sample was analysed by ^1H and ^{19}F NMR spectroscopy.

NMR Conversion with respect to NO_2-C_6H_4-I : 10% (*p*-cymene), 13% ([NO_2-C_6H_4-I-(p-cymene)][OTf])

Optimised reaction of NO_2-C_6H_4-I$(OTf)_2$ with α-pinene

A Schlenk flask was charged with NO_2-C_6H_4-I$(OTf)_2$ (20 mg, 0.036 mmol) in 3 mL CH_2Cl_2 and cooled to -94 °C. A solution of α-pinene (7.0 µL, 0.04 mmol) in 3 mL CH_2Cl_2 was transferred *via* cannula into this mixture while stirring. The solution turned pale yellow. Subsequently, the reaction was gradually warmed to room temperature and the colour changed to clear brown. The excess solvent was removed *in vacuo* to obtain brown solid. The solid was dissolved in $CDCl_3$ and taken for NMR analysis.

NMR Conversion with respect to NO_2-C_6H_4-I : 20% (*p*-cymene)

Reactions of PhI(OAc)(OTf) with substrates

A reaction vial was charged with $PhI(OAc)_2$ (12 mg, 0.04 mmol) and TMSOTf (6.8 µL, 0.04 mmol) in $CDCl_3$ (0.5 mL). To this solution, respective substrate (0.04 mmol) was added while stirring. The reaction samples were analysed by ^1H and ^{19}F NMR spectroscopy.

NMR conversions with respect to NO_2-C_6H_4-I and residual I(III):

Et_3SiH (1.24 eq) → Et_3SiOAc (51%) + Et_3SiOTf (64%*). *Excess Et_3SiOTf is from the reaction of HOTf with Et_3SiH.

Ph_3CH → No reaction (17 h).

Cycloheptatriene → Tropylium (2%) + Benzaldehyde (3%) + Benzene (3%).

Adamantane → No reaction (17 h).

1-fluoro adamantane → No reaction (17 h).

Cyclohexene → Benzene (0.3%).

Limonene → *p*-cymene (19%).

α-pinene → *p*-cymene (37%).

Synthesis of 3-CF_3-C_6H_4-IF_2

A reaction vial was charged with 3-CF_3-C_6H_4-I (10.6 µL, 0.074 mmol) in 2 mL CH_2Cl_2. To this solution, XeF_2 (12.5 mg, 0.074 mmol) was added and then spiked with TMSOTf. The reaction slightly turned yellow and was left to stir for 30 minutes. The solvent was reduced *in vacuo* to yield a white solid. The solid was redissolved in CH_2Cl_2 and the solvent was removed *in vacuo* to ensure removal of any remaining 3-CF_3-C_6H_4-I. This process was repeated to yield 3-CF_3-C_6H_4-IF_2 (20.3 mg, 89% yield), with subsequent NMR analysis matching a previous report.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 1H), 8.12 (d, 1H), 7.81-7.73 (m, 2H)

^{19}F NMR (472 MHz, $CDCl_3$) δ (ppm): -62.79, -176.89

Synthesis of 3-CF_3-C_6H_4-IF(OTf)

A reaction vial was charged with 3-CF_3-C_6H_4-I (10.6 µL, 0.074 mmol) in 2 mL CH_2Cl_2. To this solution, XeF_2 (12.5 mg, 0.074 mmol) was added and then spiked with TMSOTf. The reaction slightly turned yellow, and then TMSOTf (13.5 µL, 0.074 mmol) was added two minutes later which turned darker yellow.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.47 (s, 1H), 8.42 (d, 1H, J = 8.58 Hz), 8.01 (d, 1H, J = 8.10 Hz), 7.85 (t, 1H, J = 8.10 Hz)

^{19}F NMR (472 MHz, $CDCl_3$) δ (ppm): -62.99, -76.74, -192.90

***In situ* synthesis of 3-CF_3-C_6H_4-I$(OTf)_2$**

A reaction vial was charged with 3-CF_3-C_6H_4-I (10.6 µL, 0.074 mmol) in 2 mL CH_2Cl_2. To this solution, XeF_2 (12.5 mg, 0.074 mmol) was added and then spiked with TMSOTf. The reaction slightly turned yellow. Then TMSOTf (27 µL, 0.15 mmol) was added two minutes later and the solution immediately turned a darker yellow. The reaction was left to stir for 5 minutes, and then the solvent was removed *in vacuo* to yield a beige solid. The solid was redissolved in CH_2Cl_2 and the solvent was removed *in vacuo* to ensure removal of any remaining 3-CF_3-C_6H_4-I. This process was repeated to yield 3-CF_3-C_6H_4-I$(OTf)_2$ as a beige solid (26.4 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.67 (s, 1H), 8.63 (d, 1H, J = 8.34 Hz), 8.15 (d, 1H, J = 8.10 Hz), 7.93 (t, 1H, J = 8.1 Hz)

^{19}F NMR (472 MHz, $CDCl_3$) δ (ppm): -63.03, -75.56

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 132.42, 135.37, 135.09, 133.58, 133.36, 132.69, 126.10, 123.20, 119.06, 116.54

Synthesis of 3-CF_3-C_6H_4-I$(OTf)_2$ from 3-CF_3-C_6H_4-IF_2

A reaction vial was charged with 3-CF_3-C_6H_4-IF_2 (20 mg, 0.065 mmol) in 2 mL CH_2Cl_2. To this solution, TMSOTf (23.5 µL, 0.13 mmol) was added and the solution turned dark yellow. The reaction was left to stir for 5 minutes. The solvent was removed *in vacuo* to yield a beige solid. The solid was redissolved in CH_2Cl_2 and the solvent removed in vacuo. This process was repeated to yield 3-CF_3-C_6H_4-I$(OTf)_2$ as a beige solid (24.8 mg, 67% yield). The acquired ^{1}H, ^{19}F and ^{13}C NMR spectra of the isolated product was identical to 3-CF_3-C_6H_4-I$(OTf)_2$ made using the *in situ* method reported above.

Reaction of 3-CF_3-C_6H_4-I$(OTf)_2$ with adamantane

A reaction vial was charged with 3-CF_3-C_6H_4-I (10.6 µL, 0.074 mmol) in 2 mL CH_2Cl_2. To this solution, XeF_2 (12.5 mg, 0.074 mmol) was added and then spiked with TMSOTf. The reaction slightly turned yellow, and then TMSOTf (27 µL, 0.15 mmol) was added two minutes later which turned darker yellow. After 5 minutes, adamantane (10 mg, 0.074 mmol) was added and the solution became lighter yellow. The reaction was left to stir for 5 minutes, and then

the solvent was removed *in vacuo* to produce a dark brown solid. The solid was redissolved in CH_2Cl_2 and the solvent was removed *in vacuo* to ensure removal of any remaining 3-CF_3-C_6H_4-I. This process was repeated, and the remaining dark brown solid was dried to yield adamantyl triflate (15.2 mg, 72% yield).

NMR Spectra

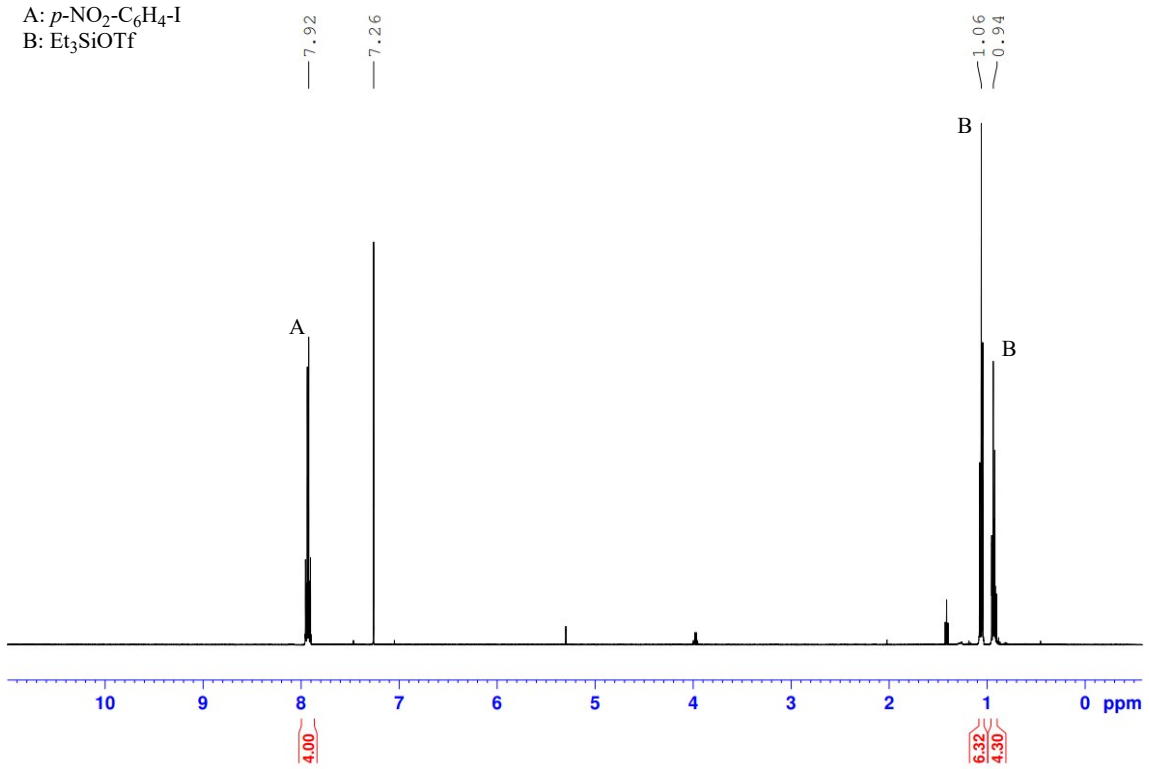


Figure S 1: ^{1}H NMR of NO_2-C_6H_4-I(OTf)$_2$ with Et_3SiH in $CDCl_3$

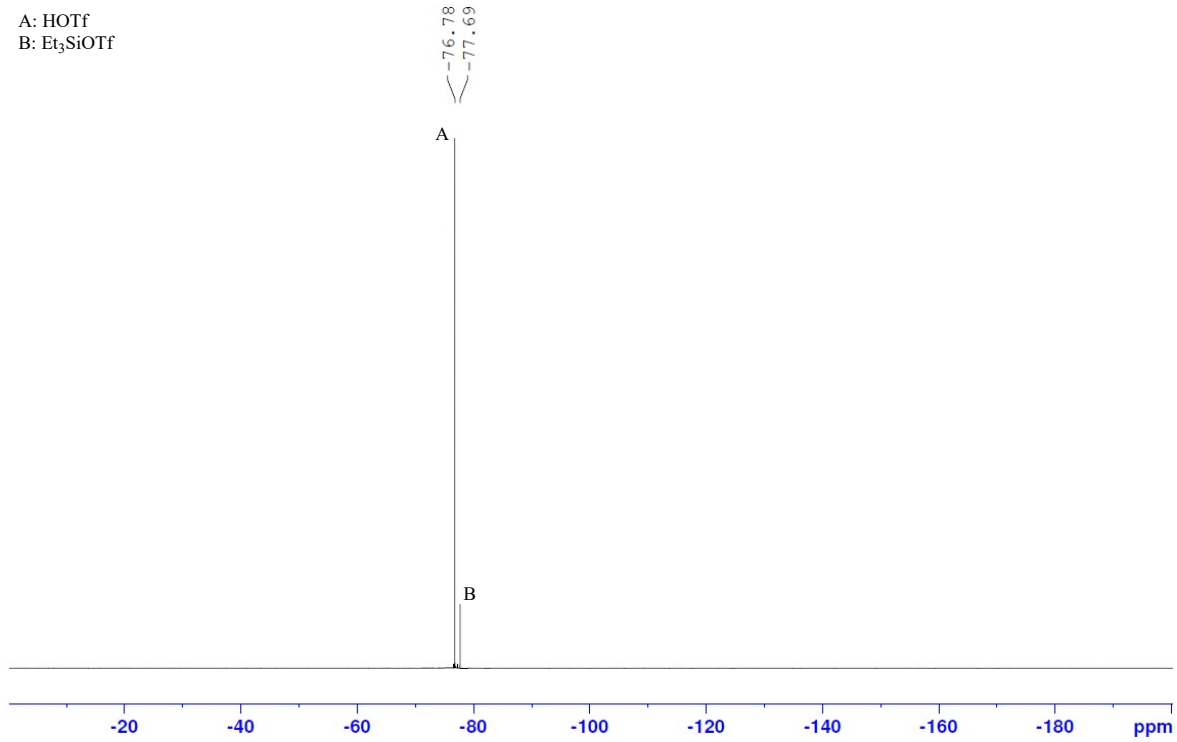


Figure S 2: ^{19}F NMR of NO_2-C_6H_4-I(OTf)$_2$ with Et_3SiH in $CDCl_3$

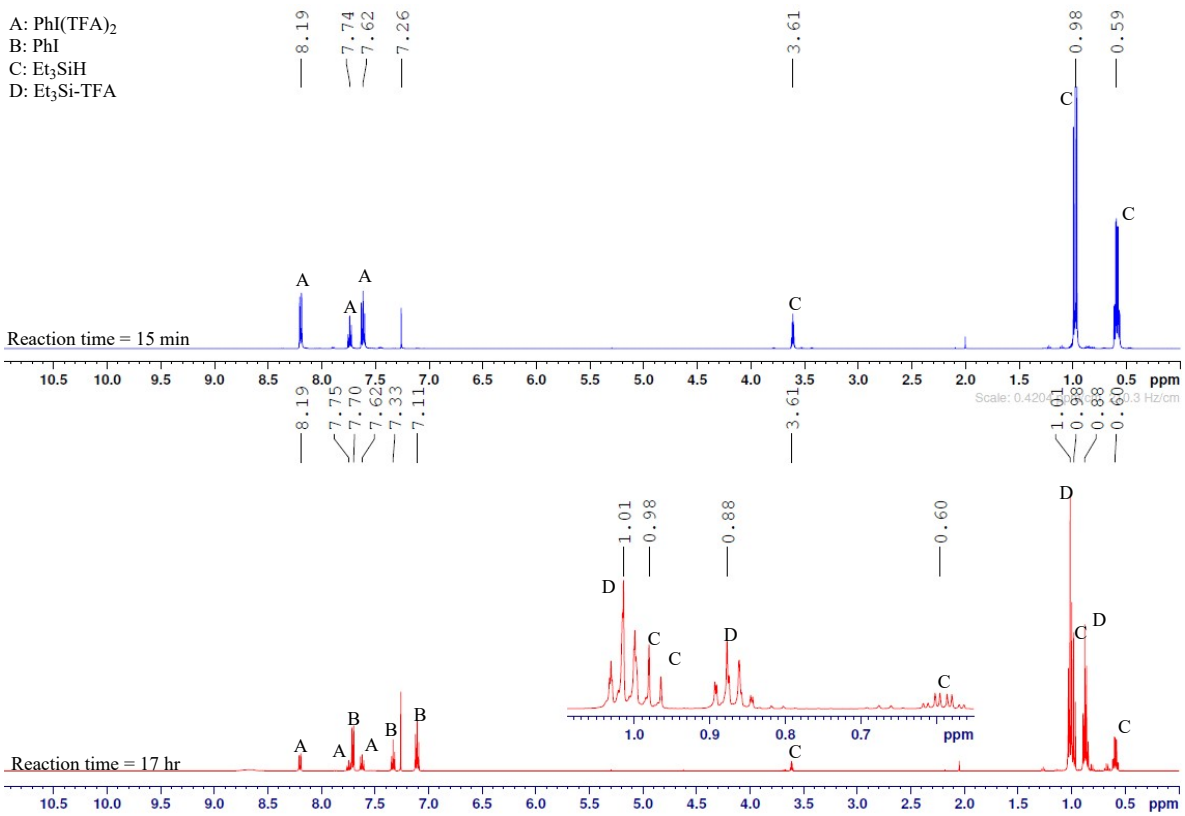


Figure S 3: ^{1}H NMR of $PhI(TFA)_2$ with Et_3SiH in $CDCl_3$ monitored over time

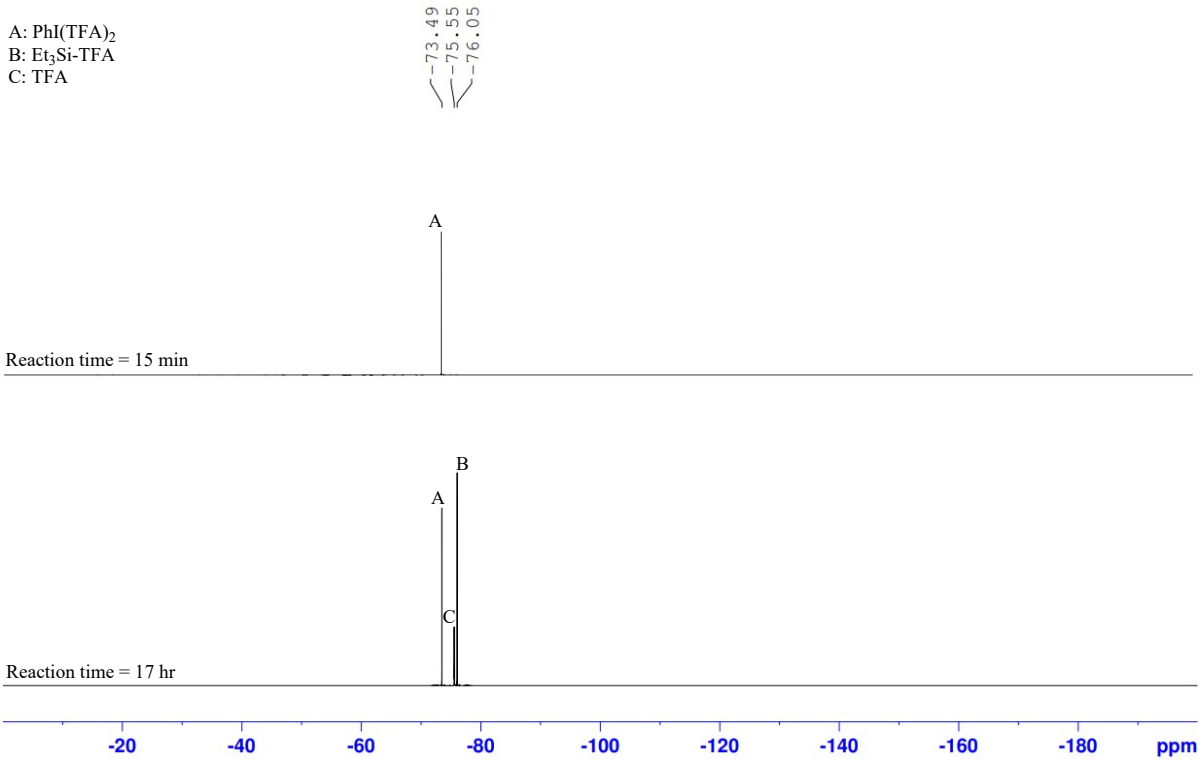


Figure S 4: ^{19}F NMR of $PhI(TFA)_2$ with Et_3SiH in $CDCl_3$ monitored over time

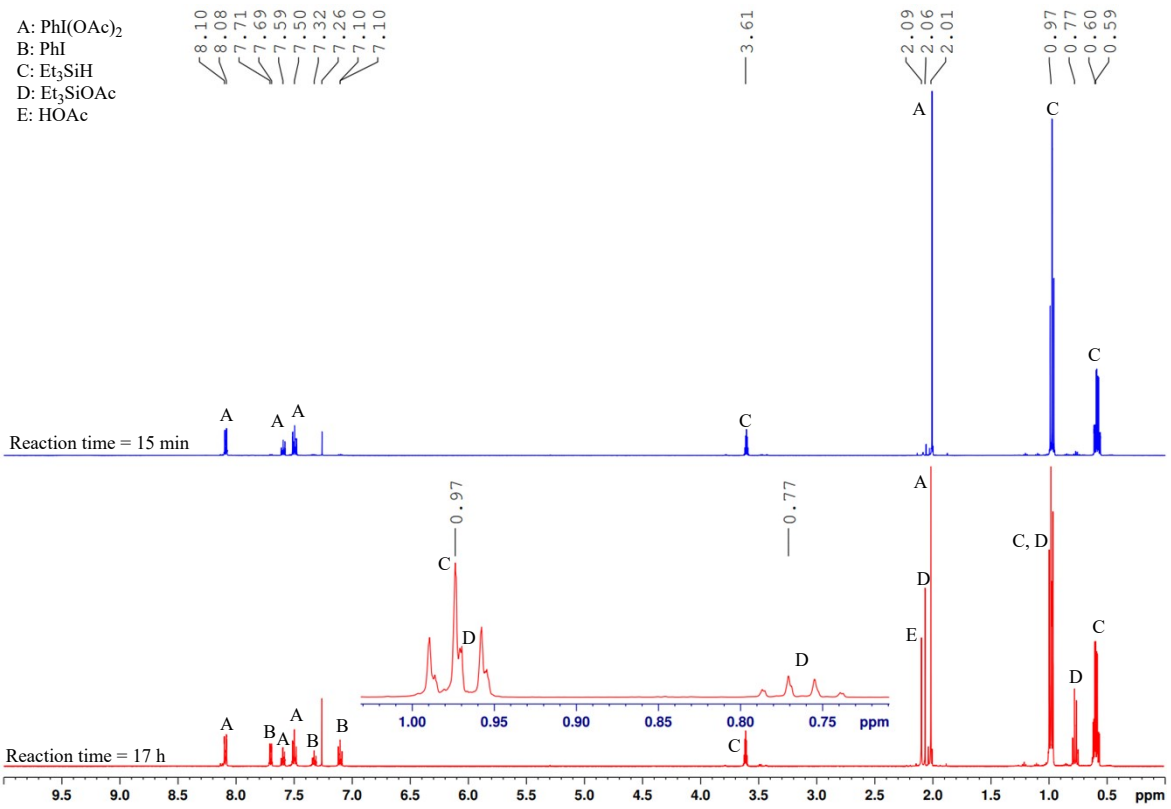


Figure S 5: ^{1}H NMR of $PhI(OAc)_2$ with Et_3SiH in $CDCl_3$ monitored over time

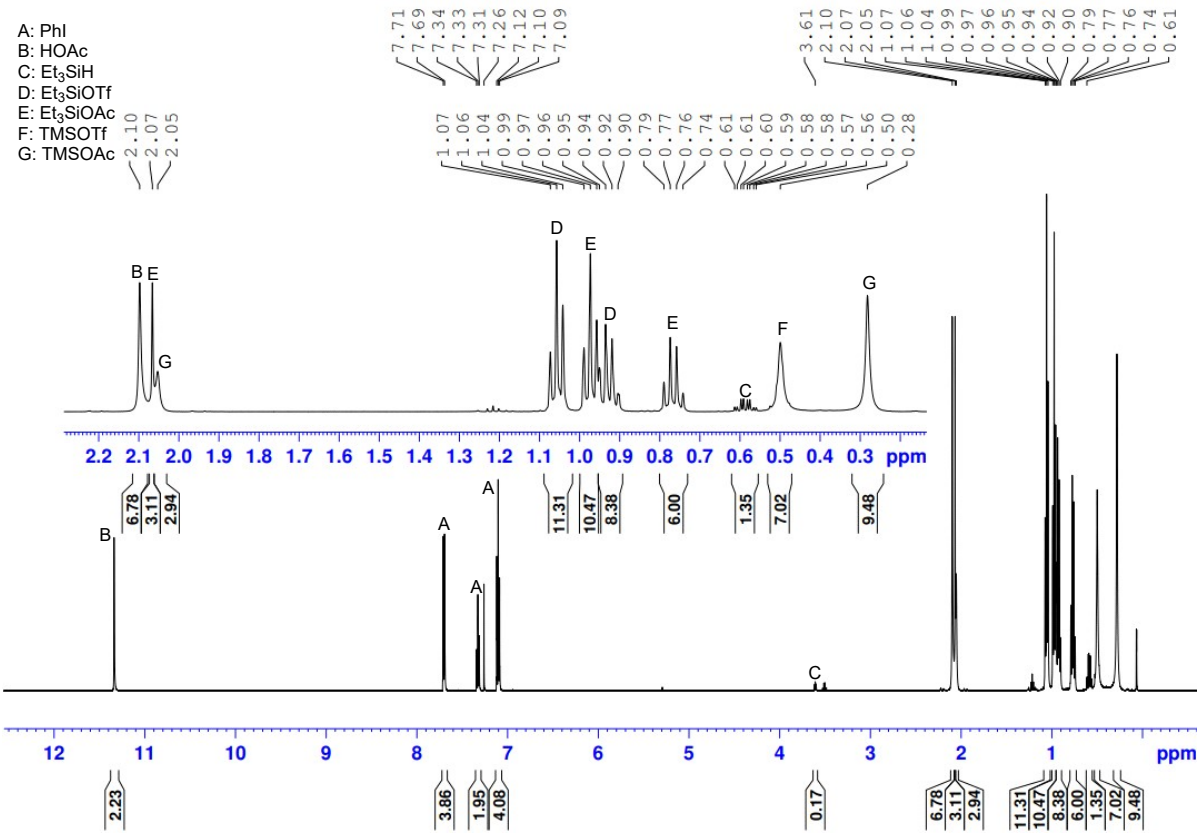


Figure S 6: ^{1}H NMR of PhI(OAc)(OTf) with Et_3SiH in $CDCl_3$ (reaction time ~ 15 min)

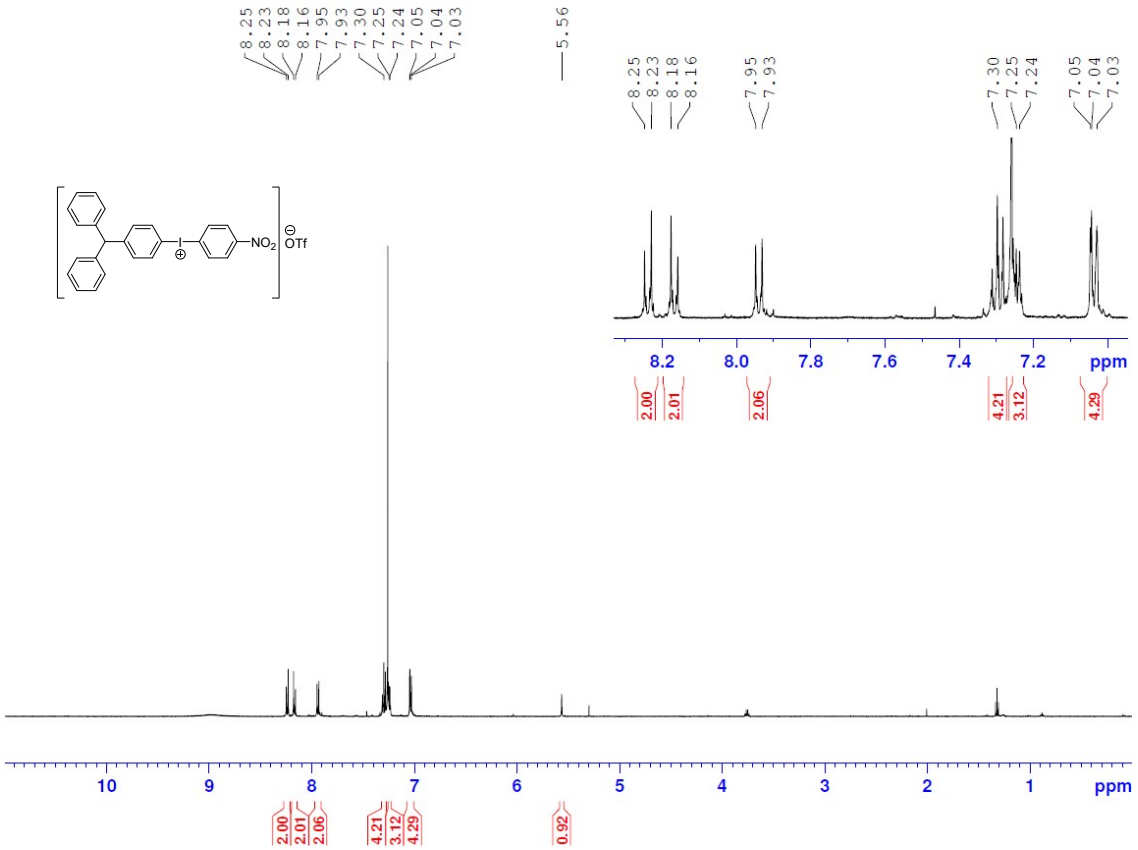


Figure S 7: ^{1}H NMR of NO_2-C_6H_4-$I(OTf)_2$ with Ph_3CH in $CDCl_3$

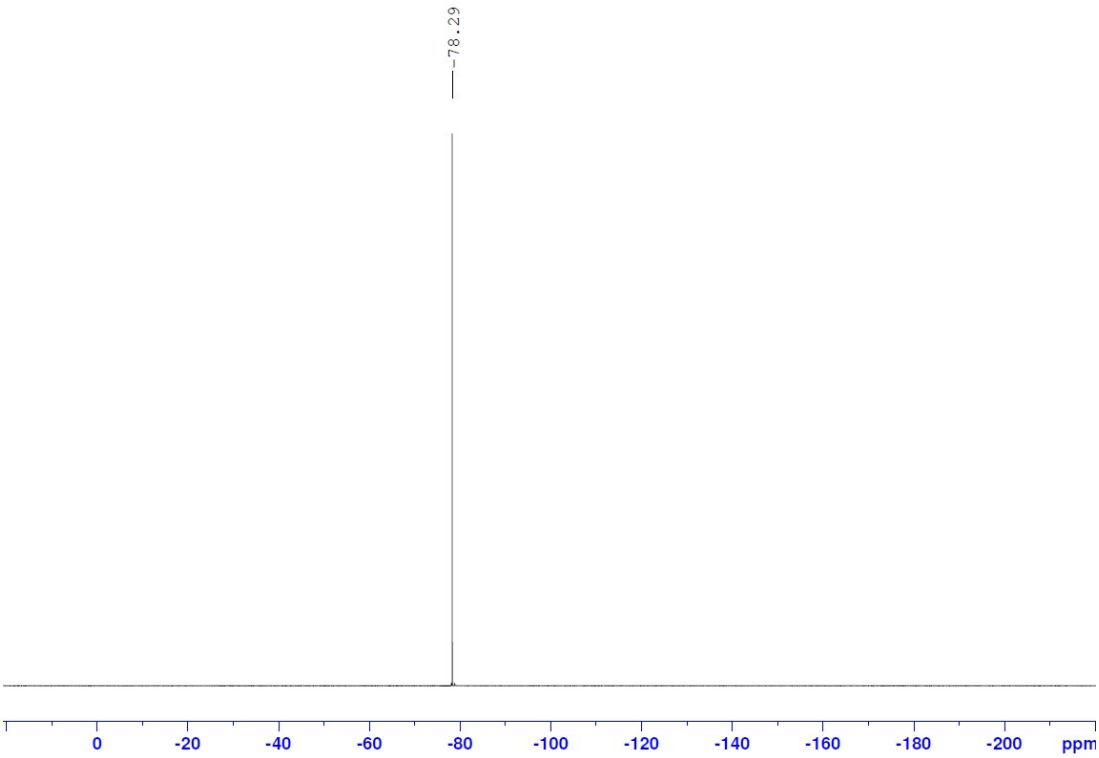


Figure S 8: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with Ph_3CH in $CDCl_3$

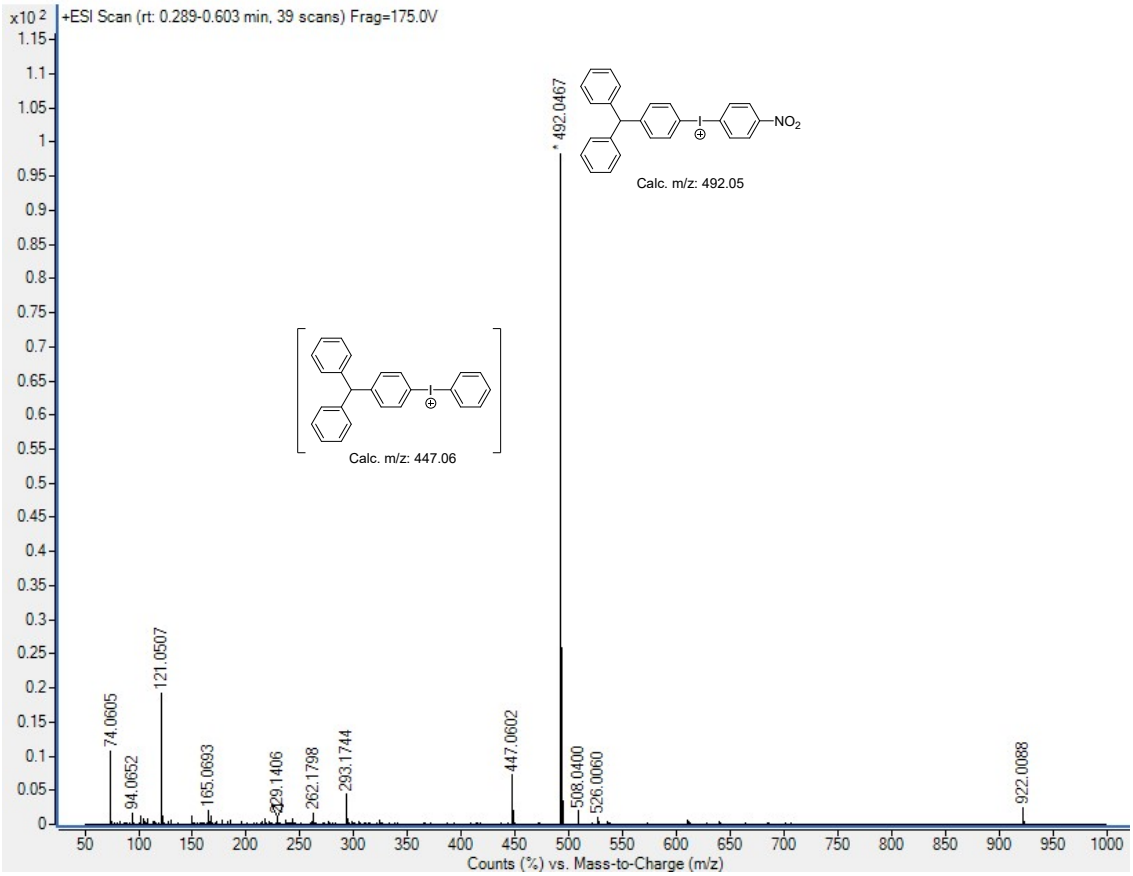


Figure S 9: HRMS of NO_2-C_6H_4-$I(OTf)_2$ with Ph_3CH

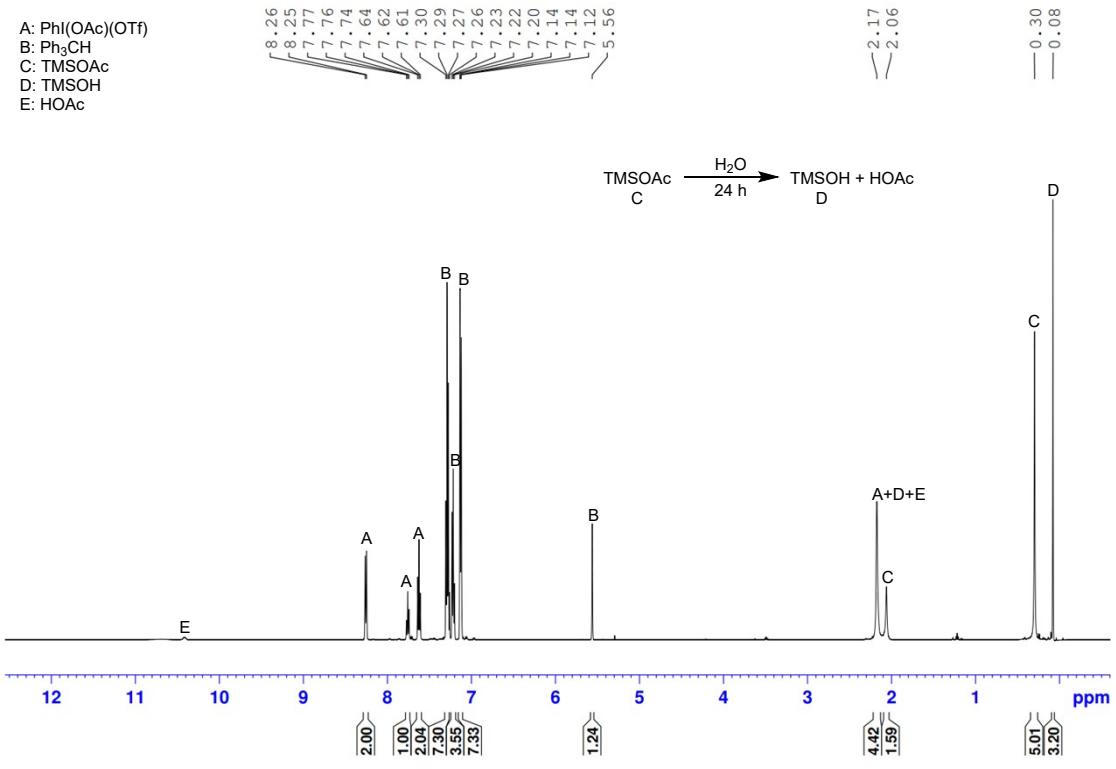


Figure S 10: ^1H NMR of PhI(OAc)(OTf) with Ph_3CH in $CDCl_3$ (reaction time ~ 17 h)

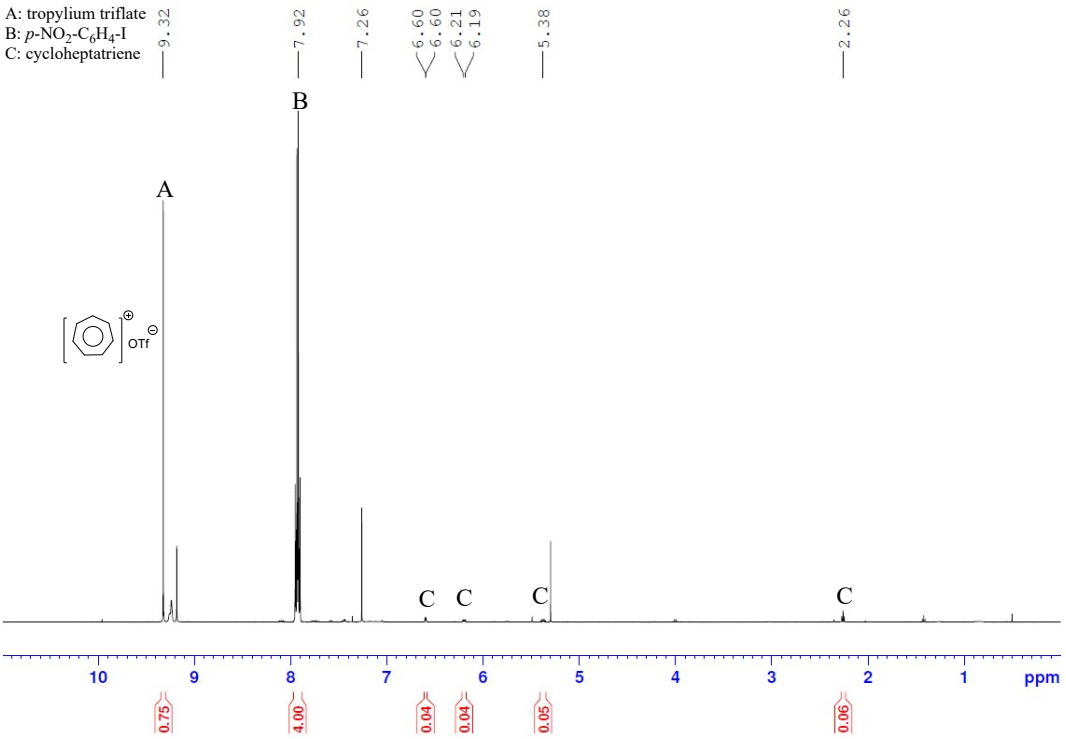


Figure S 11: ^{1}H NMR of NO_2-C_6H_4-I(OTf)$_2$ with cycloheptatriene in $CDCl_3$

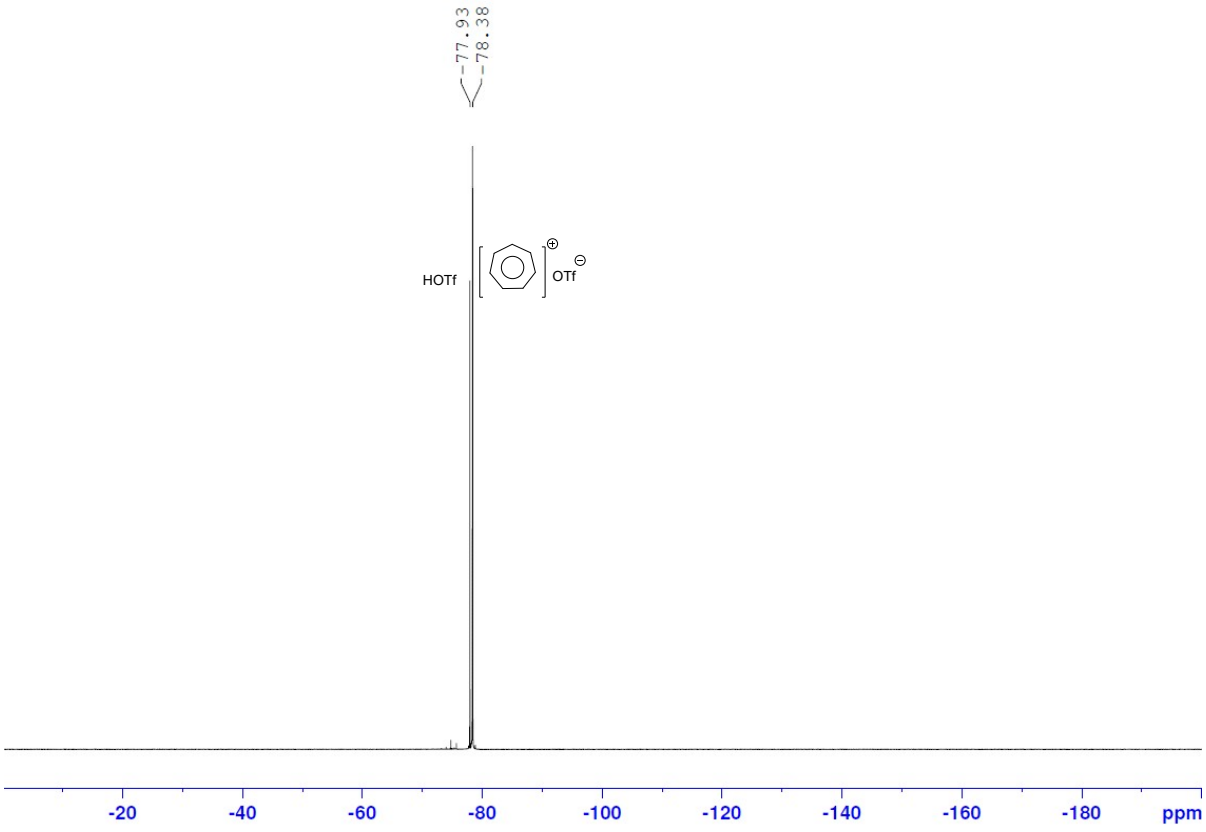


Figure S 12: ^{19}F NMR of NO_2-C_6H_4-I(OTf)$_2$ with cycloheptatriene in $CDCl_3$

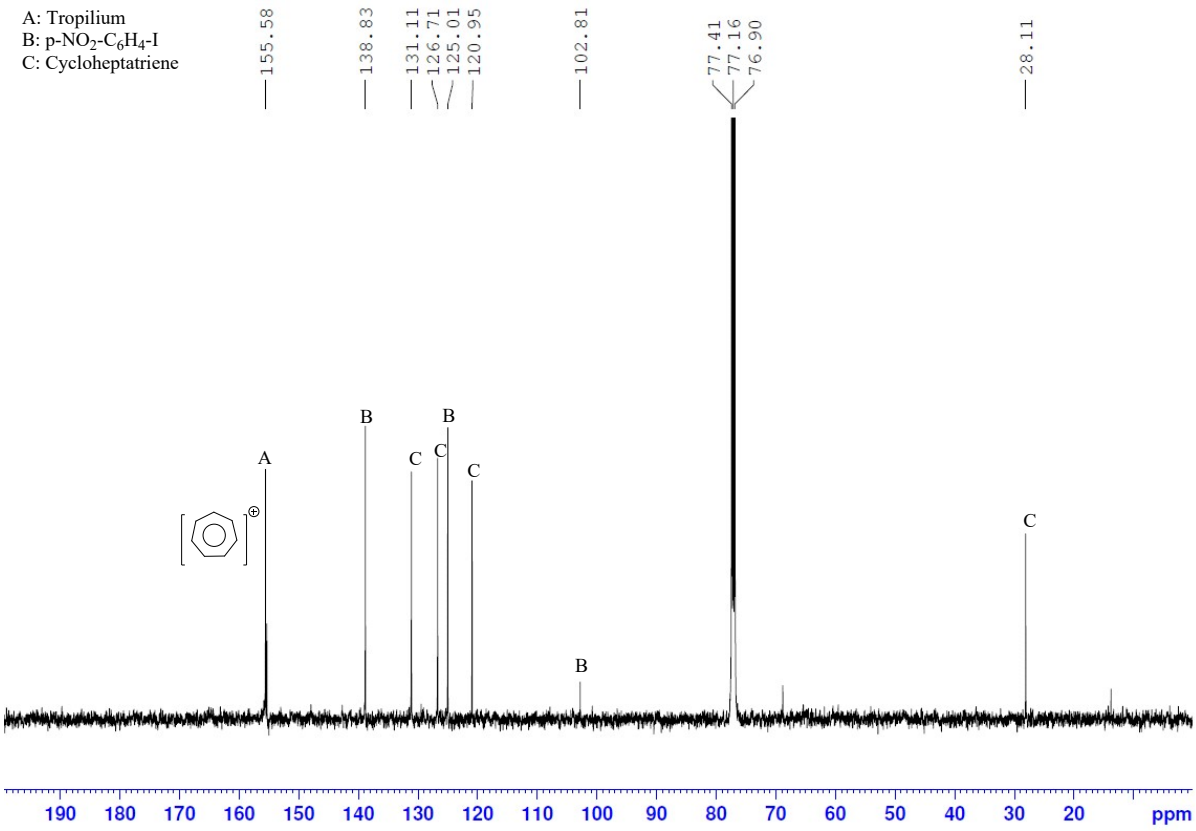


Figure S 13: ^{13}C NMR of NO_2-C_6H_4-$I(OTf)_2$ with cycloheptatriene in $CDCl_3$

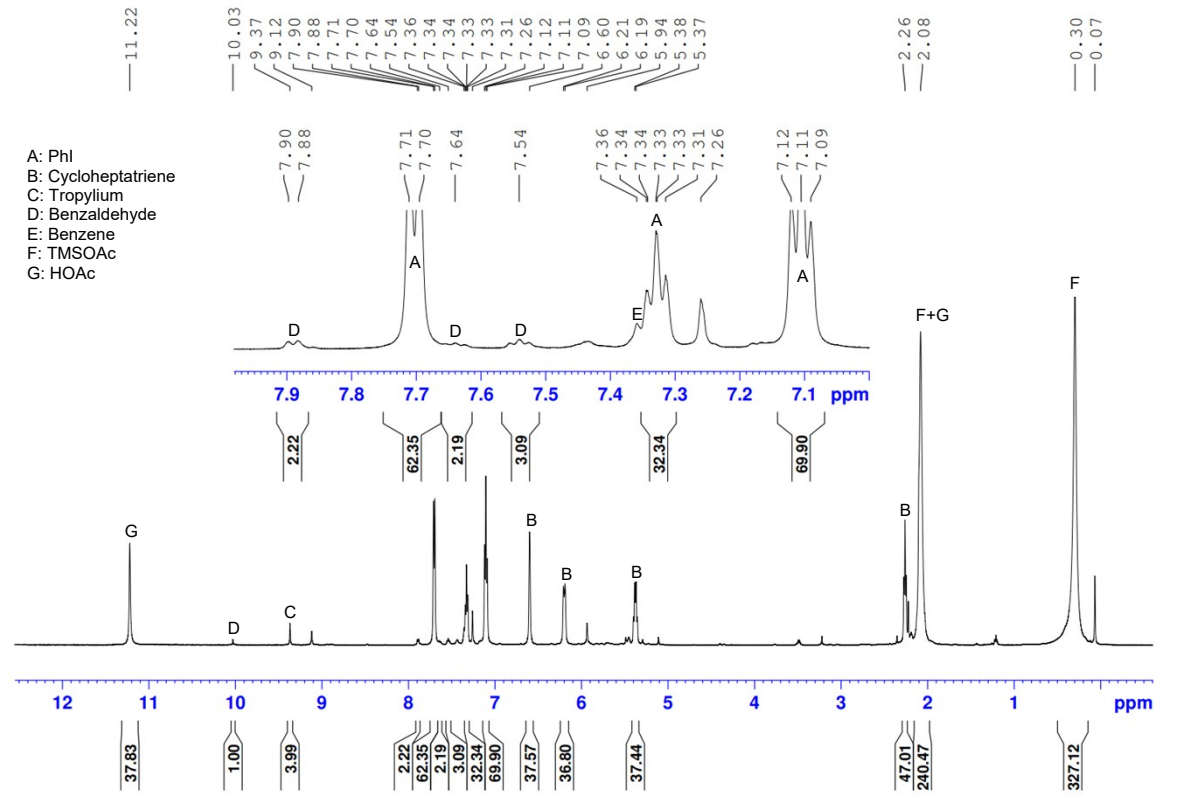


Figure S 14: ^{1}H NMR of PhI(OAc)(OTf) with cycloheptatriene in $CDCl_3$ (reaction time ~ 15 min)

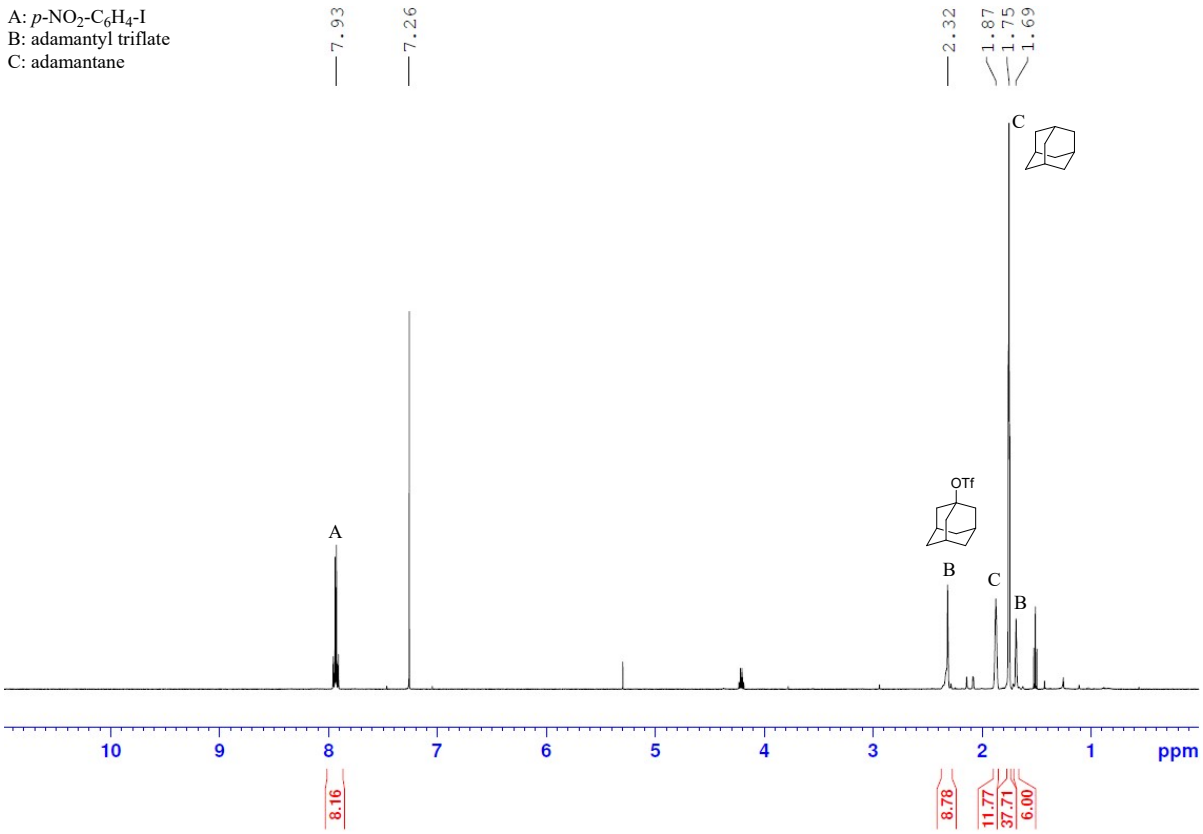


Figure S 15: ^{1}H NMR of NO_2-C_6H_4-$I(OTf)_2$ with adamantane in $CDCl_3$

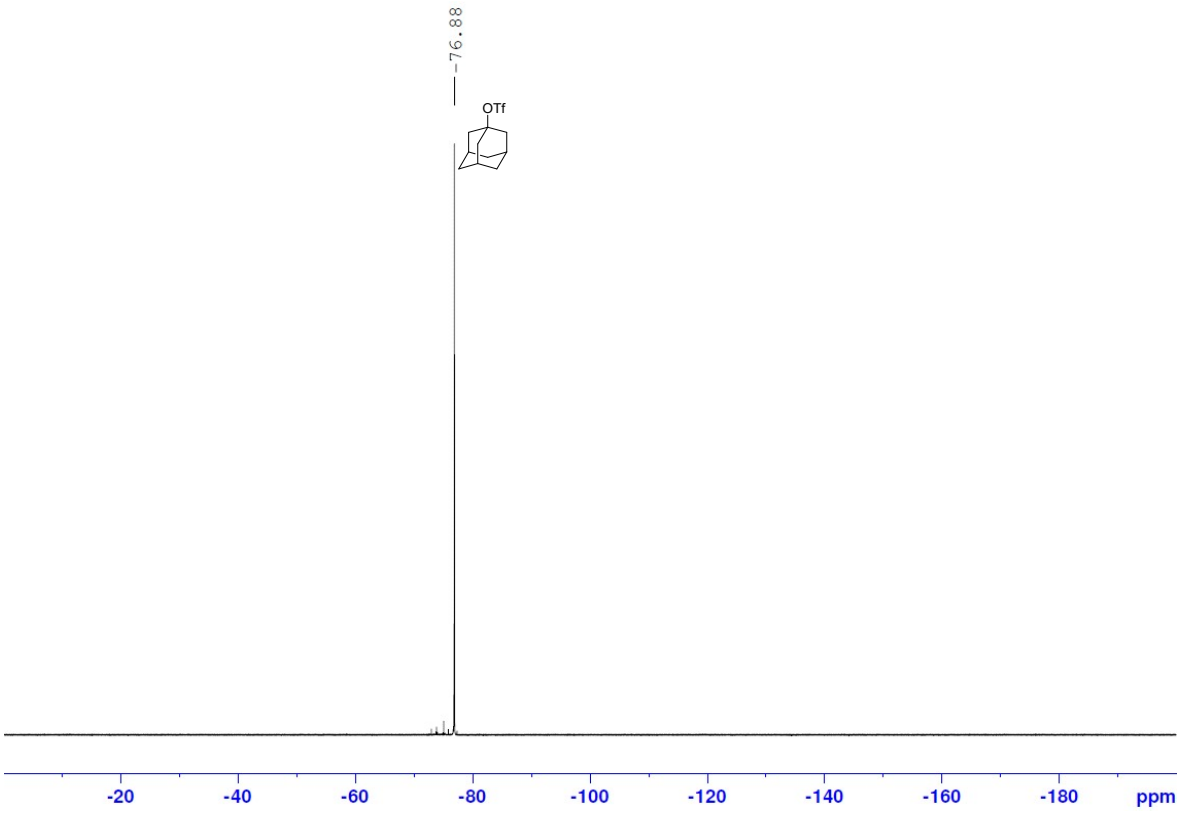


Figure S 16: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with adamantane in $CDCl_3$

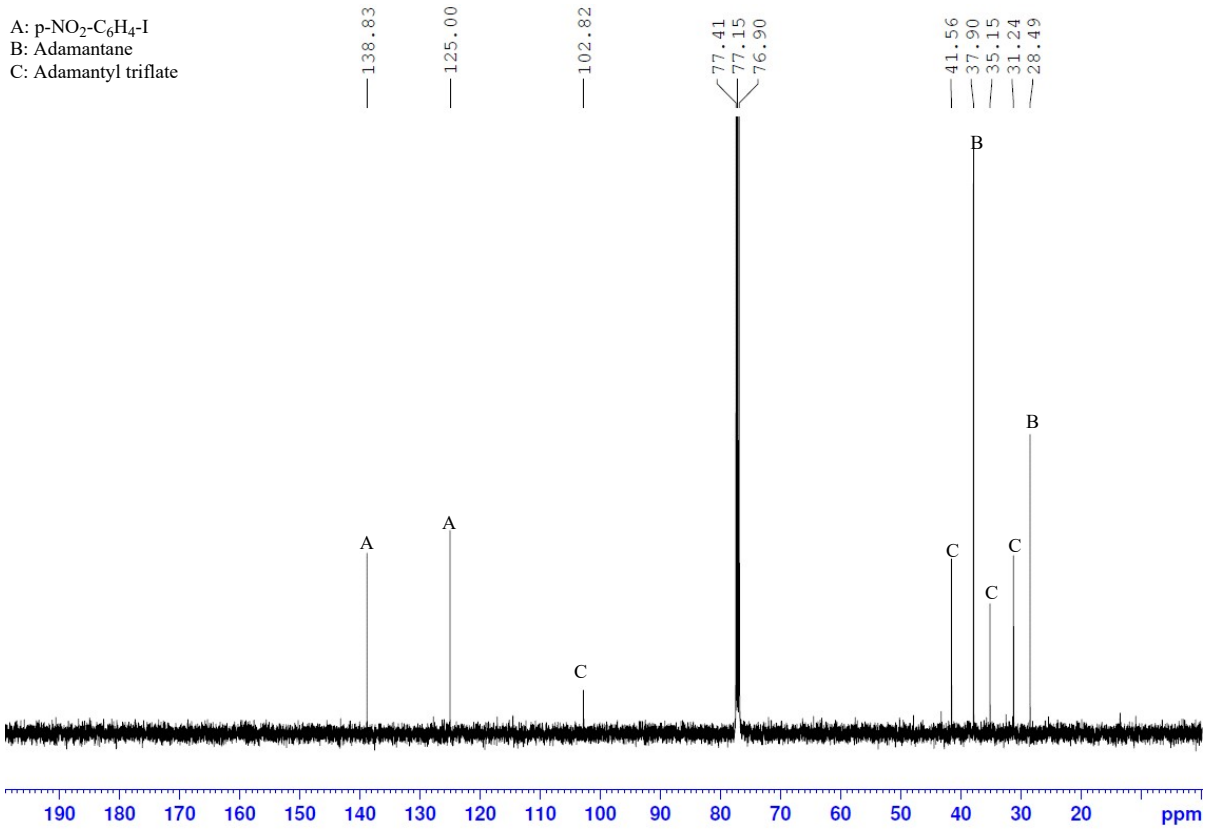


Figure S 17: ^{13}C NMR of NO_2-C_6H_4-I(OTf)$_2$ with adamantane in $CDCl_3$

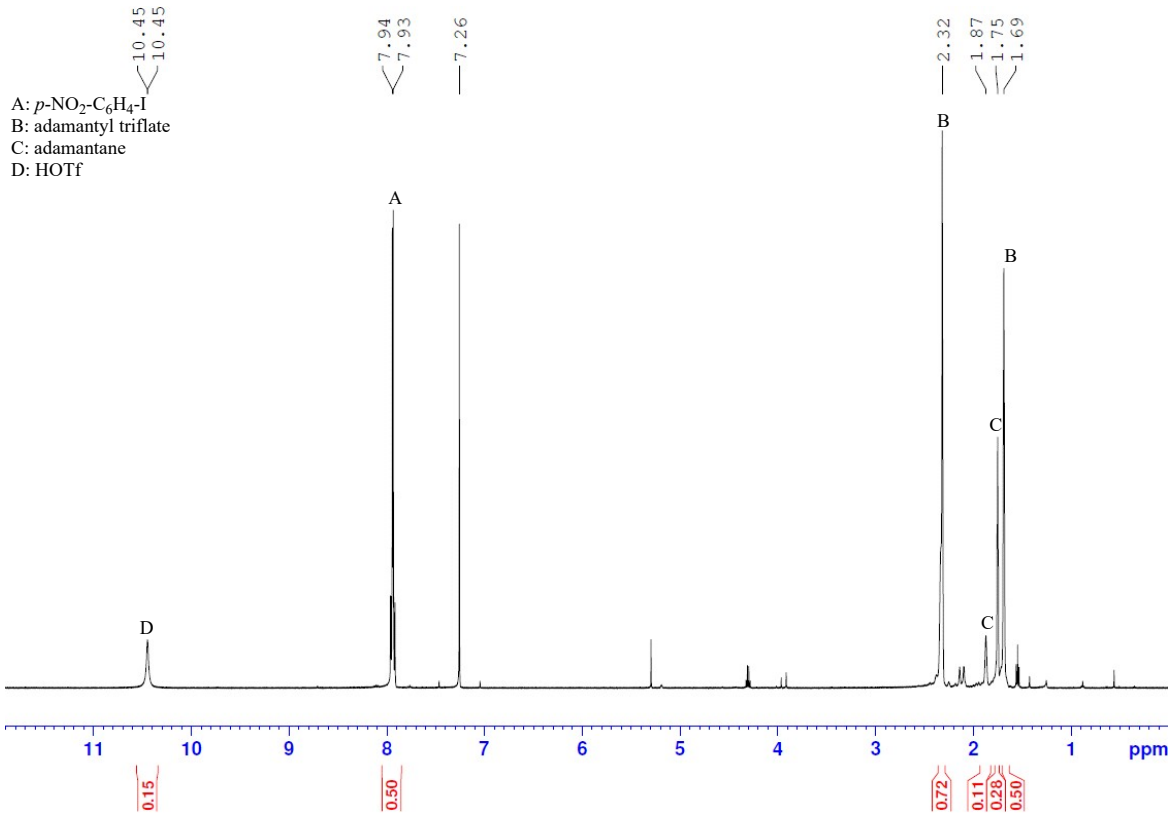


Figure S 18: ^{1}H NMR of NO_2-C_6H_4-I(OTf)$_2$ with adamantane at 60 °C in $CDCl_3$

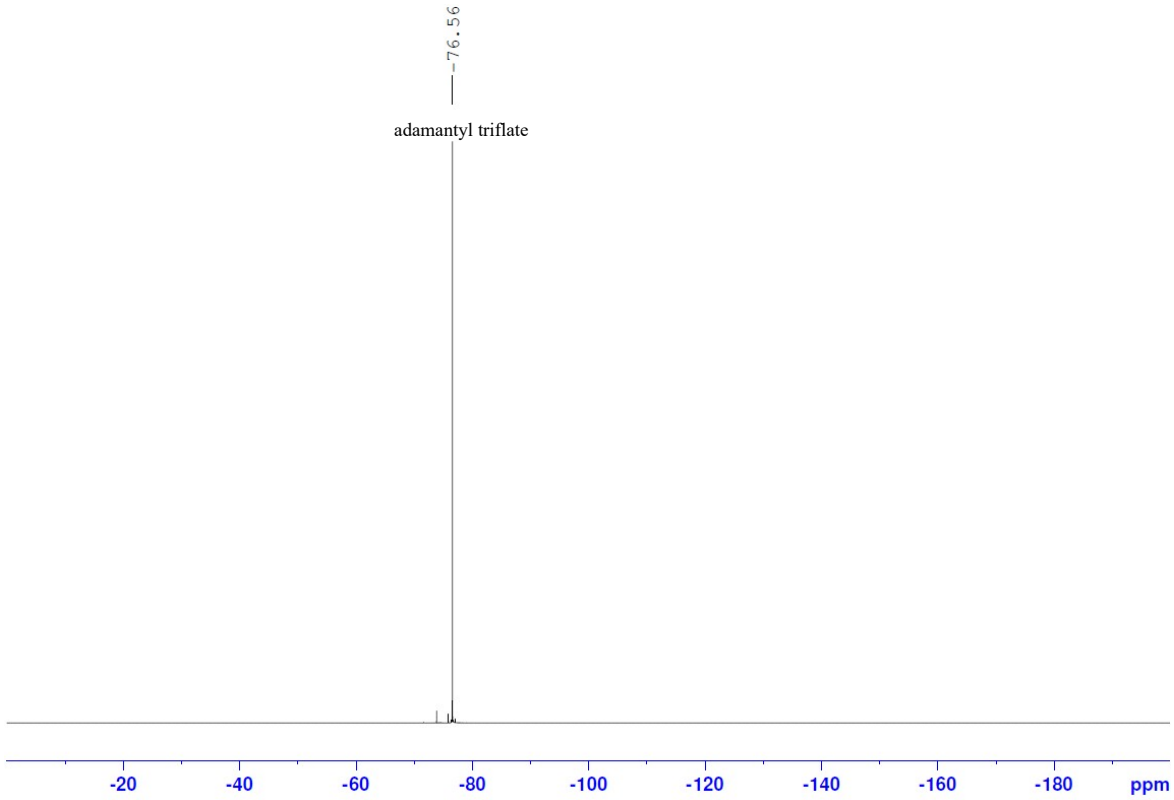


Figure S 19: ^{19}F NMR of NO_2-C_6H_4-I(OTf)$_2$ with adamantane at 60 °C in $CDCl_3$

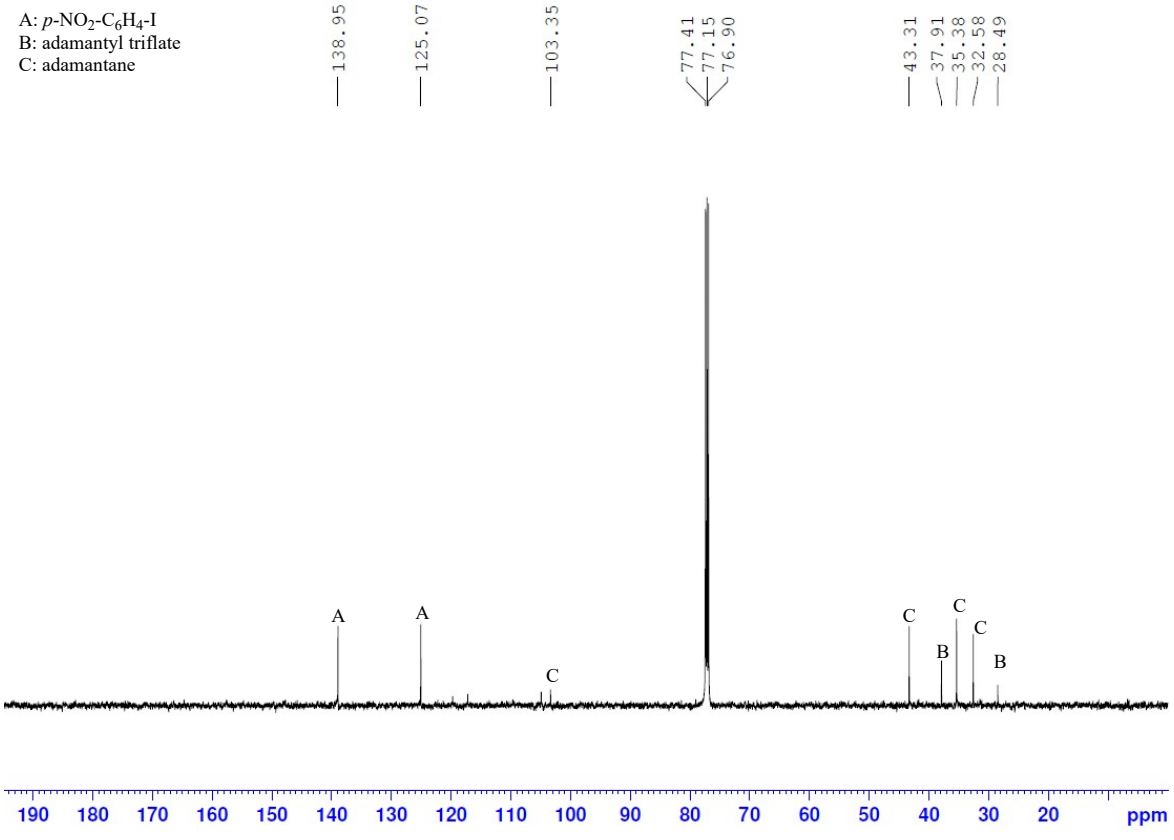


Figure S 20: ^{13}C NMR of NO_2-C_6H_4-I(OTf)$_2$ with adamantane at 60 °C in $CDCl_3$

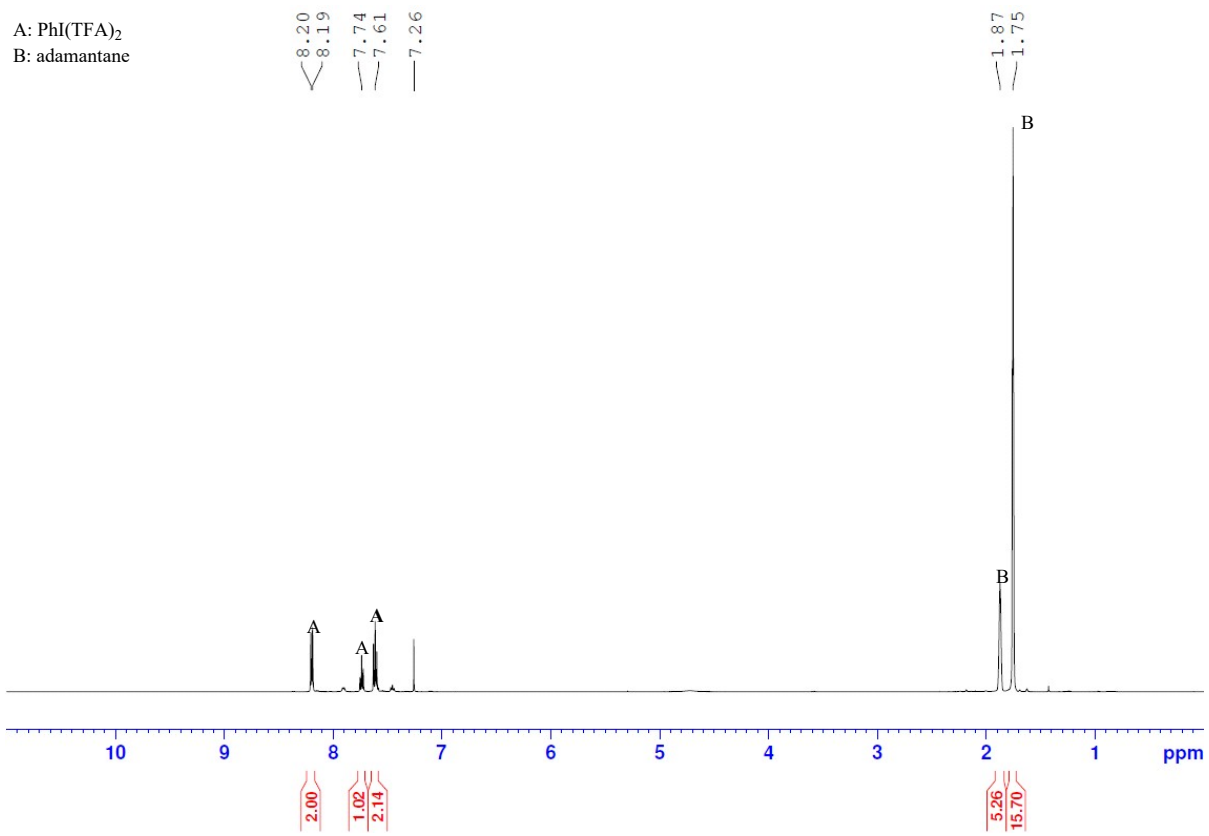


Figure S 21: ^{1}H NMR of $PhI(TFA)_2$ with adamantane in $CDCl_3$ (reaction time ~ 17 h)

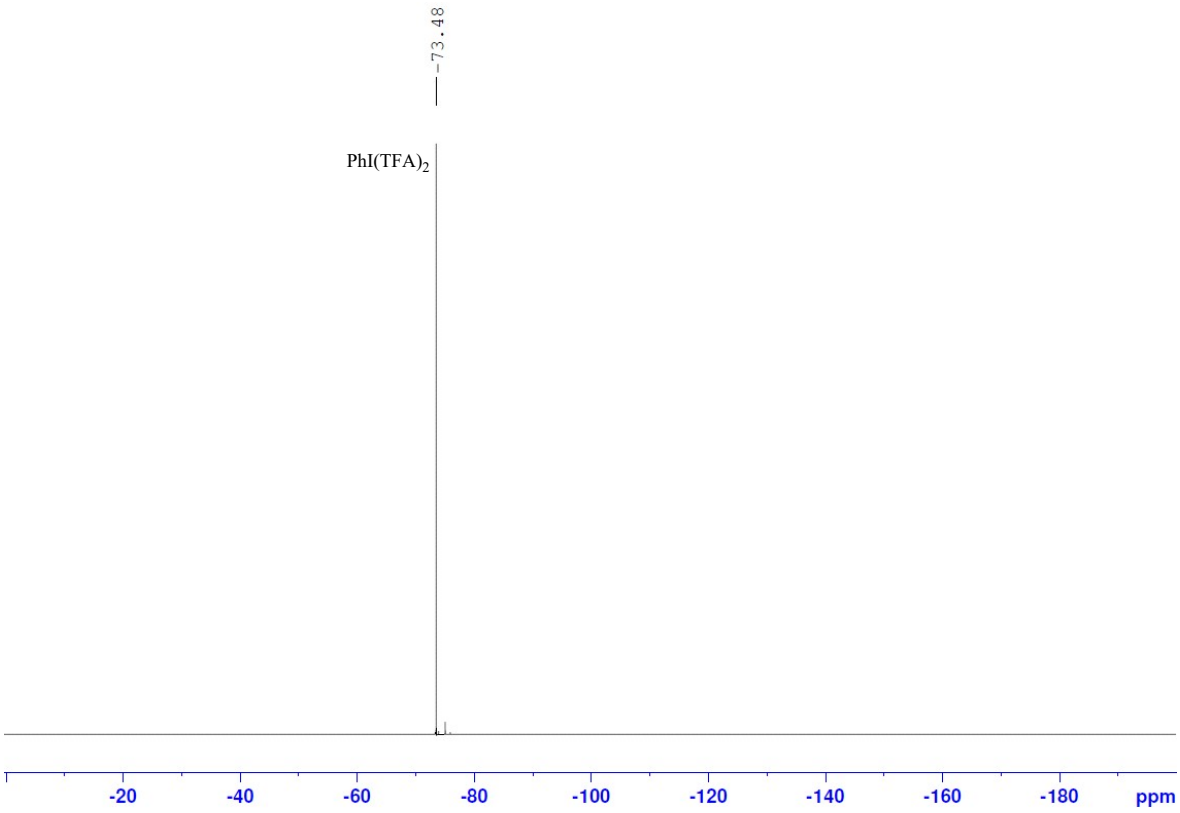


Figure S 22: ^{19}F NMR of $PhI(TFA)_2$ with adamantane in $CDCl_3$ (reaction time ~ 17 h)

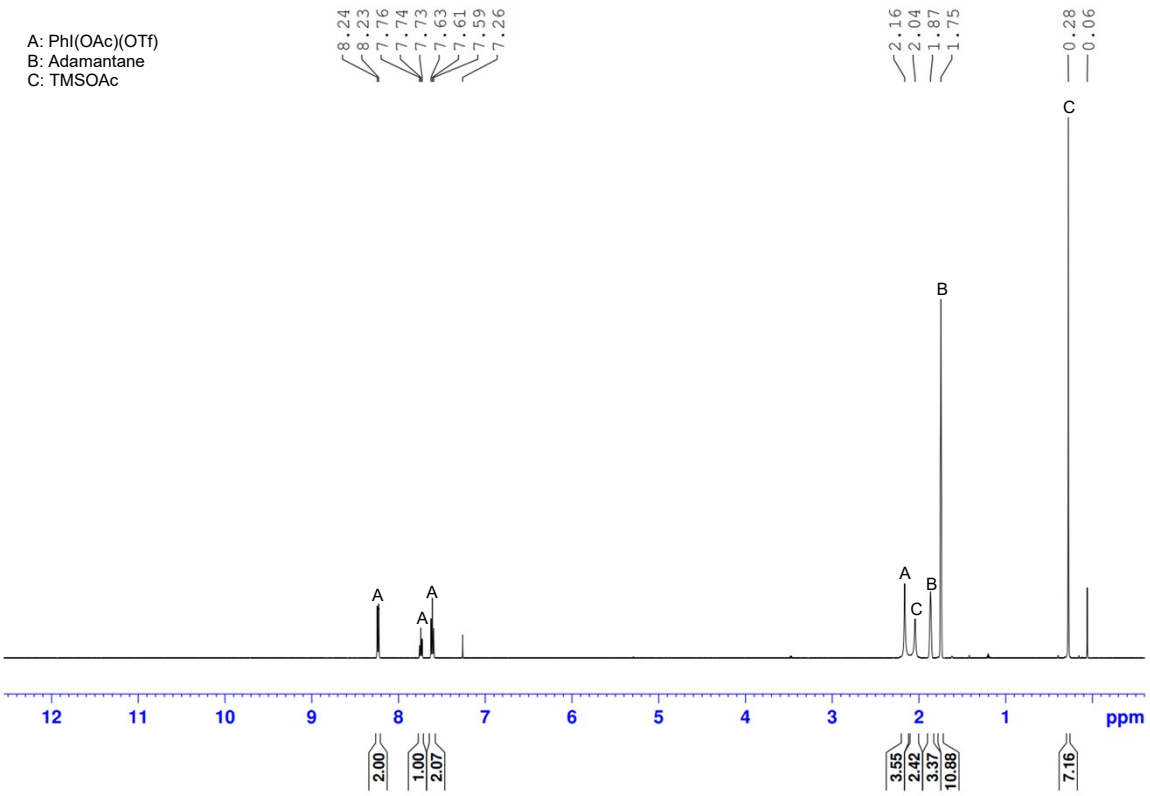


Figure S 23: ^{1}H NMR of PhI(OAc)(OTf) with adamantane in $CDCl_3$ (reaction time ~ 17 h)

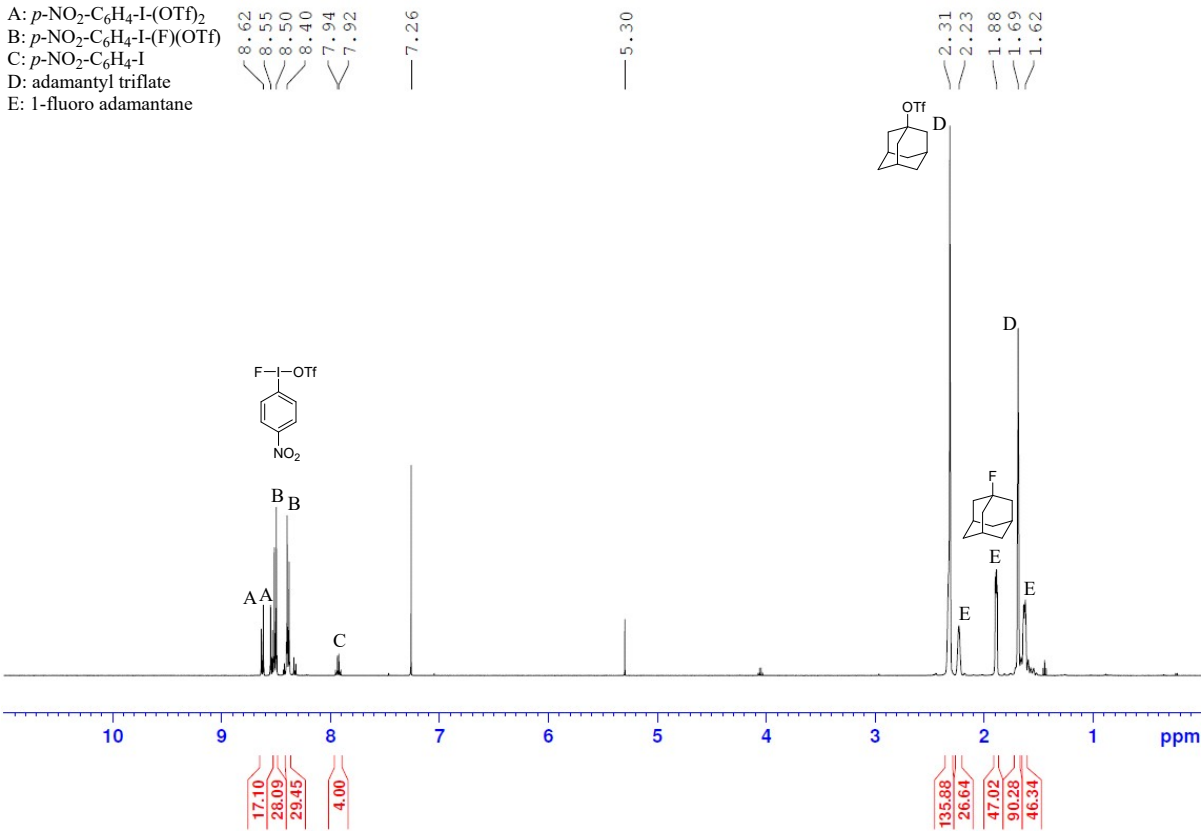


Figure S 24: ^{1}H NMR of NO_2-C_6H_4-I(OTf)$_2$ with 1-fluoro adamantane in $CDCl_3$

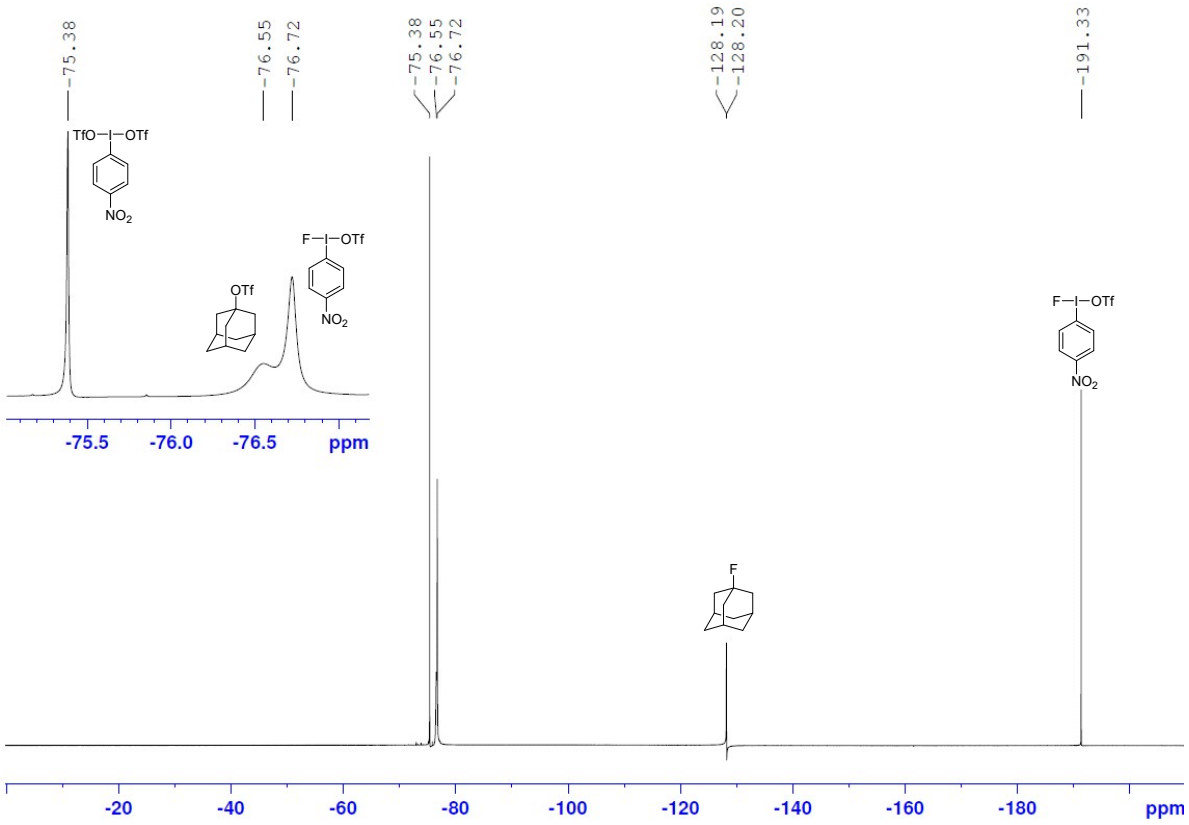


Figure S 25: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with 1-fluoro adamantane in $CDCl_3$

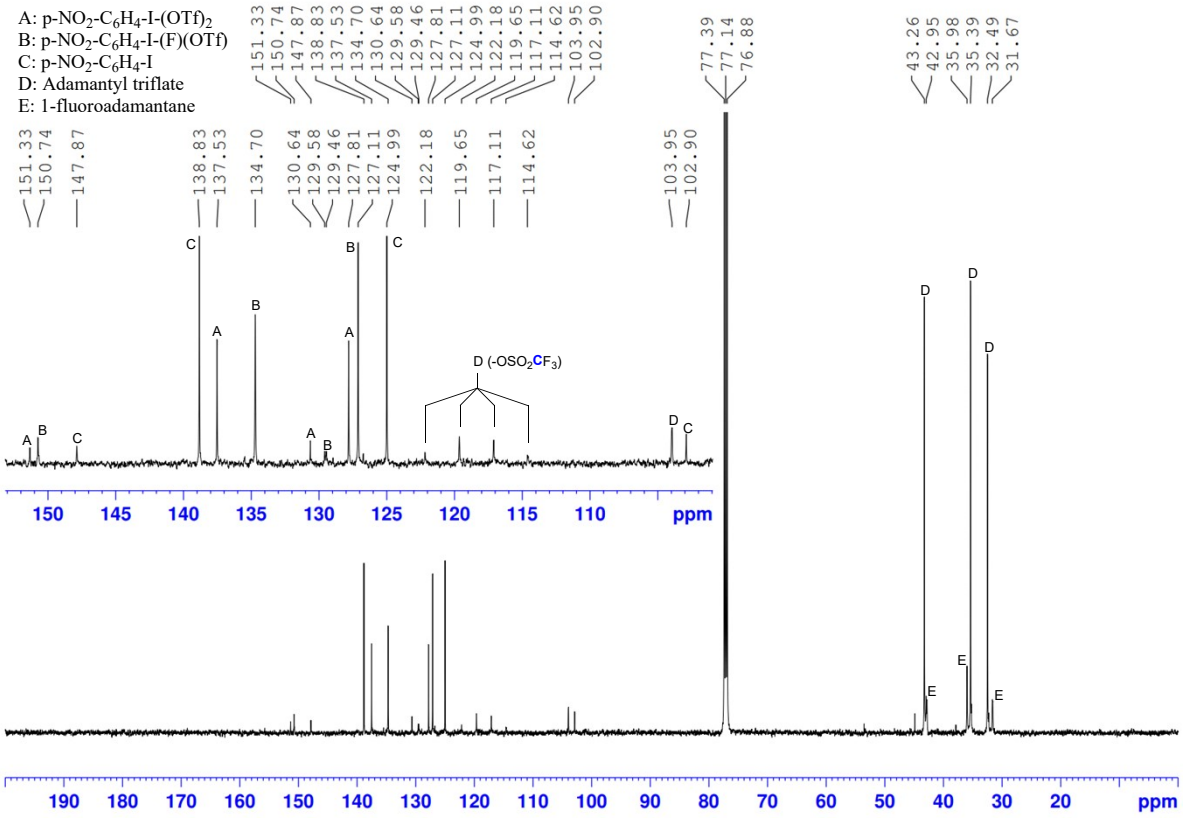


Figure S 26: ^{13}C NMR of NO_2-C_6H_4-$I(OTf)_2$ with 1-fluoro adamantane in $CDCl_3$

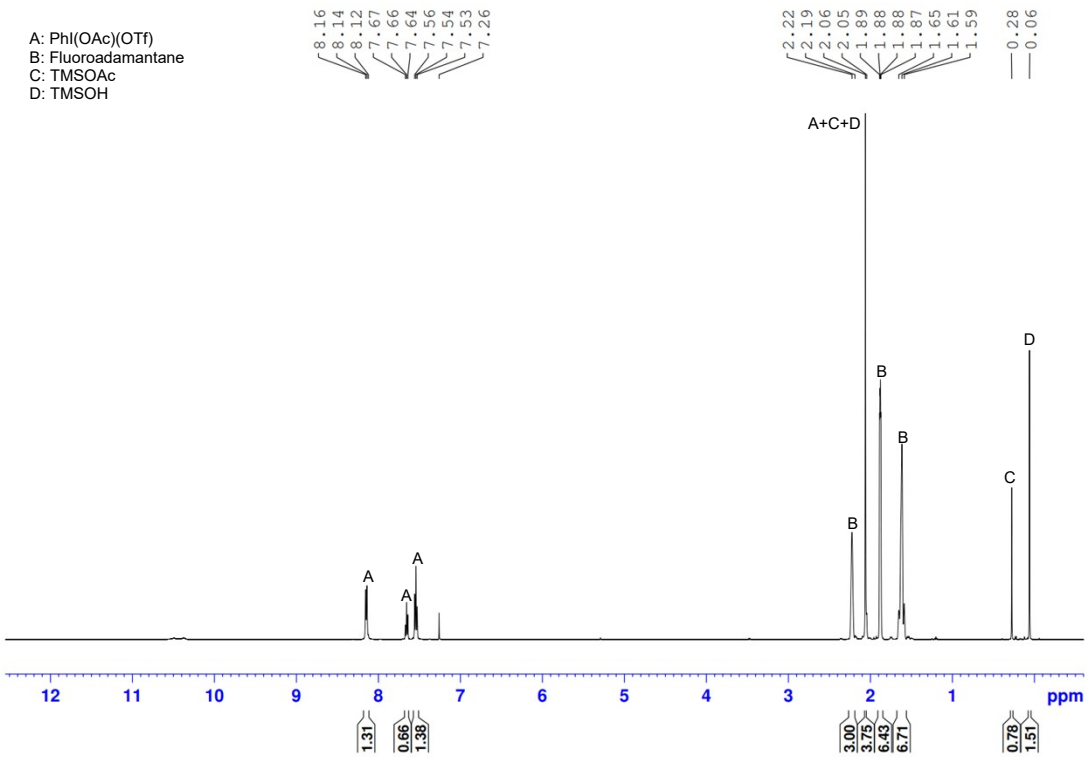


Figure S 27: ^{1}H NMR of PhI(OAc)(OTf) with 1-fluoro adamantane in $CDCl_3$ (reaction time ~ 17 h)

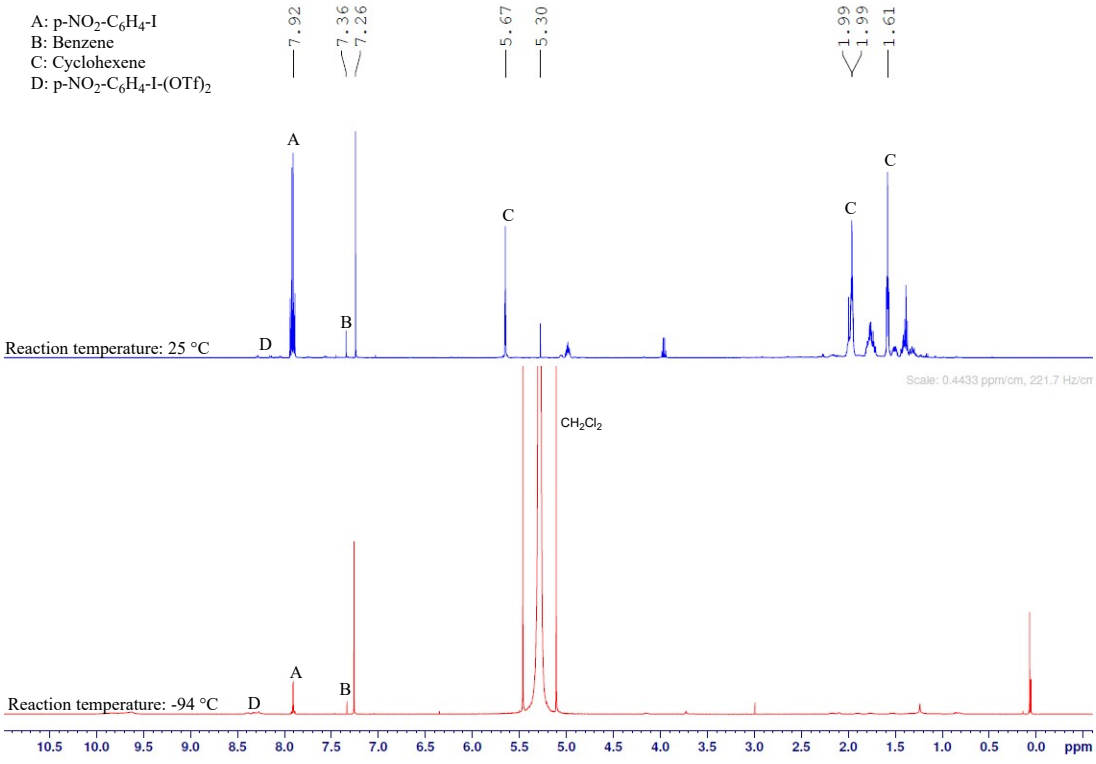


Figure S 28: ^{1}H NMR spectrum stack of reaction of NO_2-C_6H_4-I$(OTf)_2$ with cyclohexene at different temperatures in $CDCl_3$

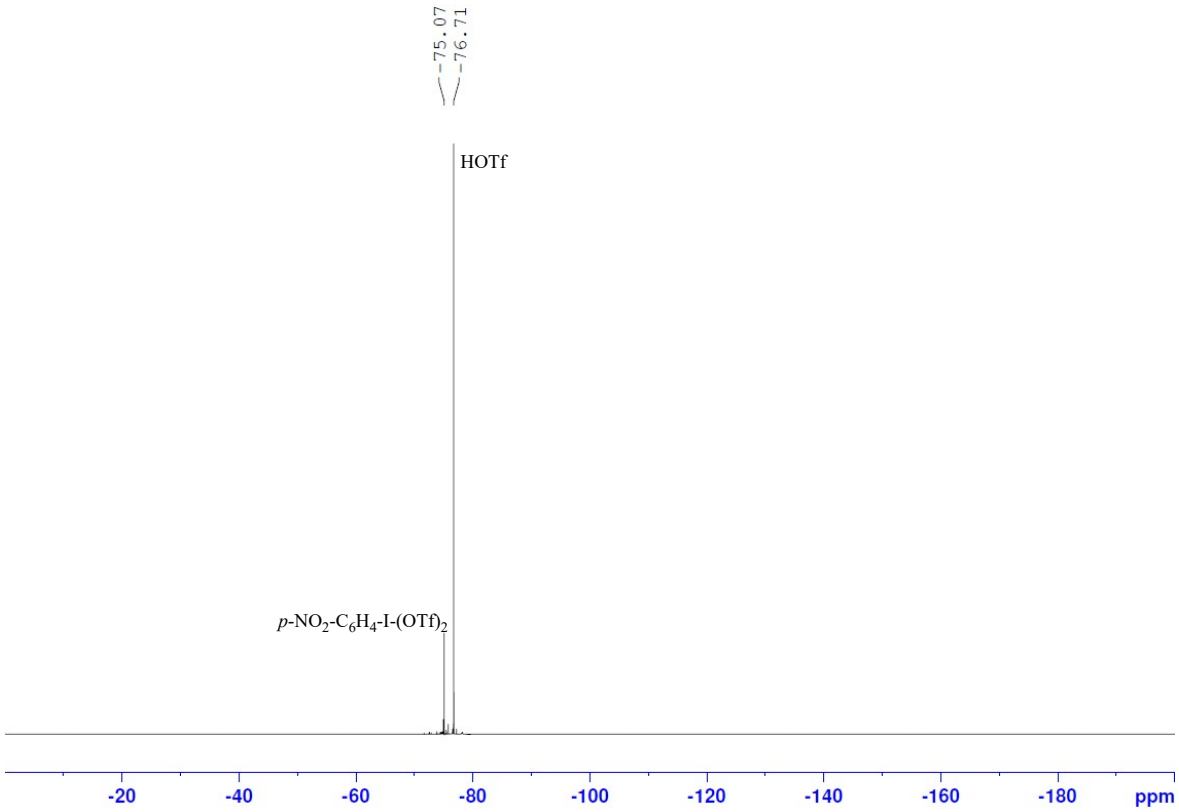


Figure S 29: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with cyclohexene in $CDCl_3$

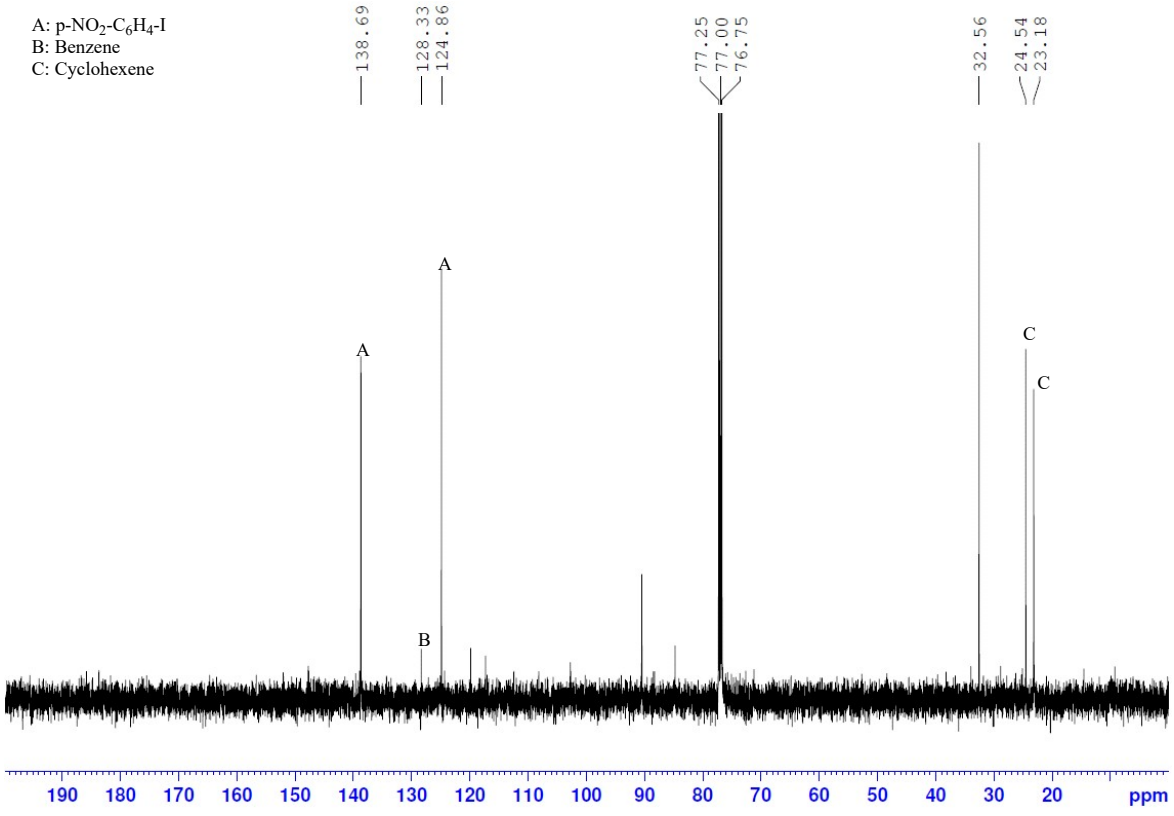


Figure S 30: ^{13}C NMR of NO_2-C_6H_4-$I(OTf)_2$ with cyclohexene in $CDCl_3$

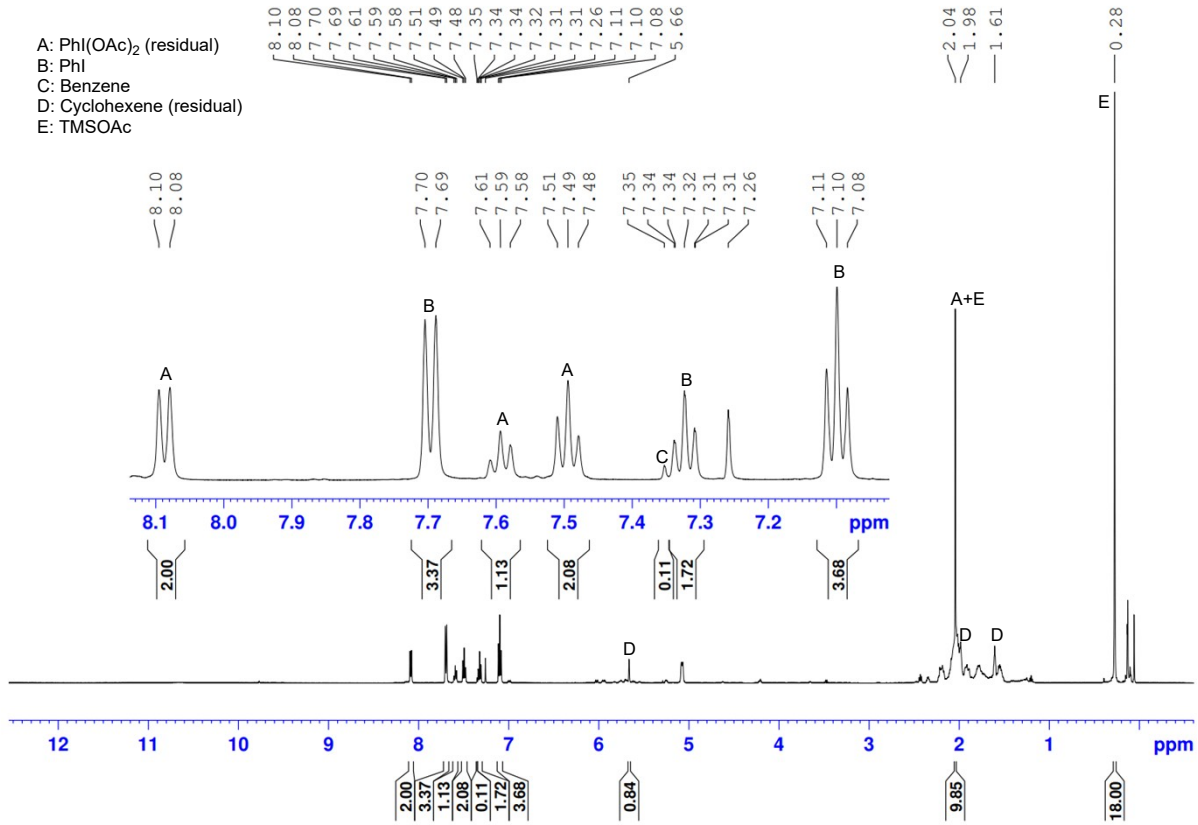


Figure S 31: ^{1}H NMR of PhI(OAc)(OTf) with cyclohexene in $CDCl_3$ (reaction time ~ 15 min)

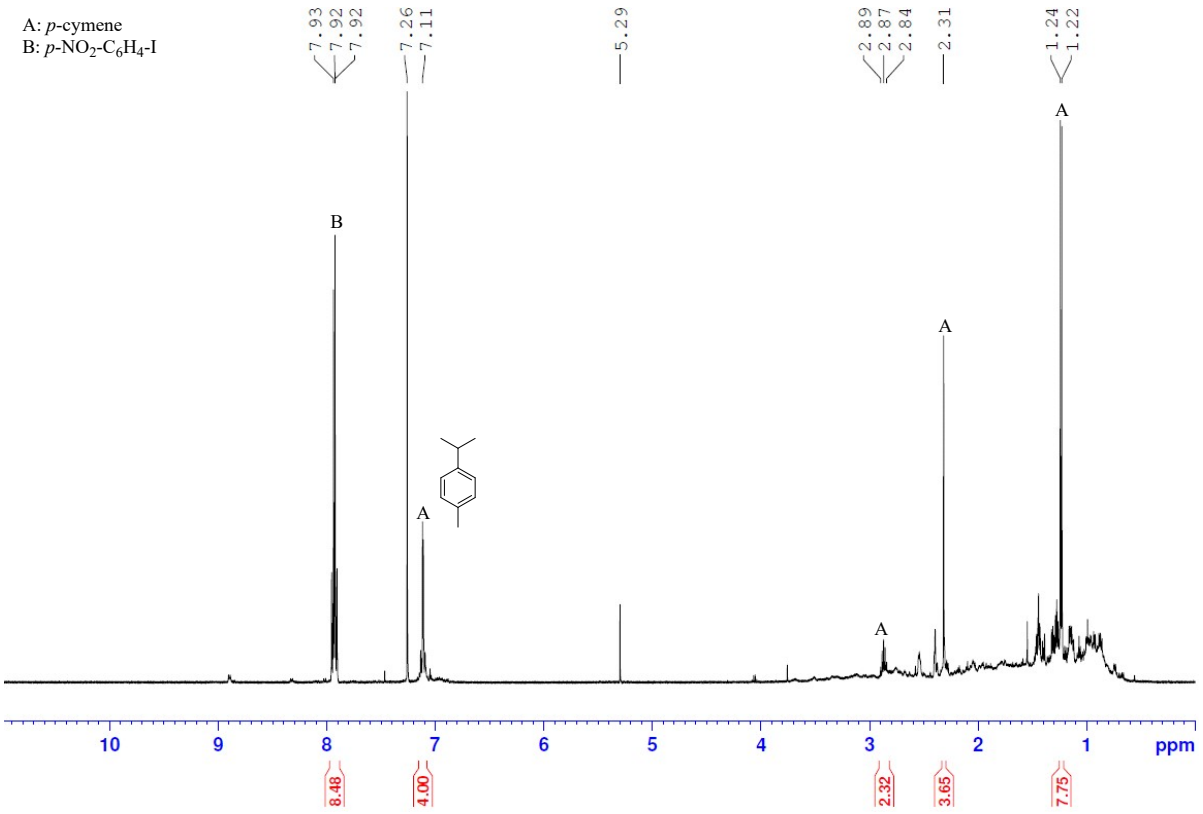


Figure S 32: ^{1}H NMR of NO_2-C_6H_4-$I(OTf)_2$ with limonene in $CDCl_3$

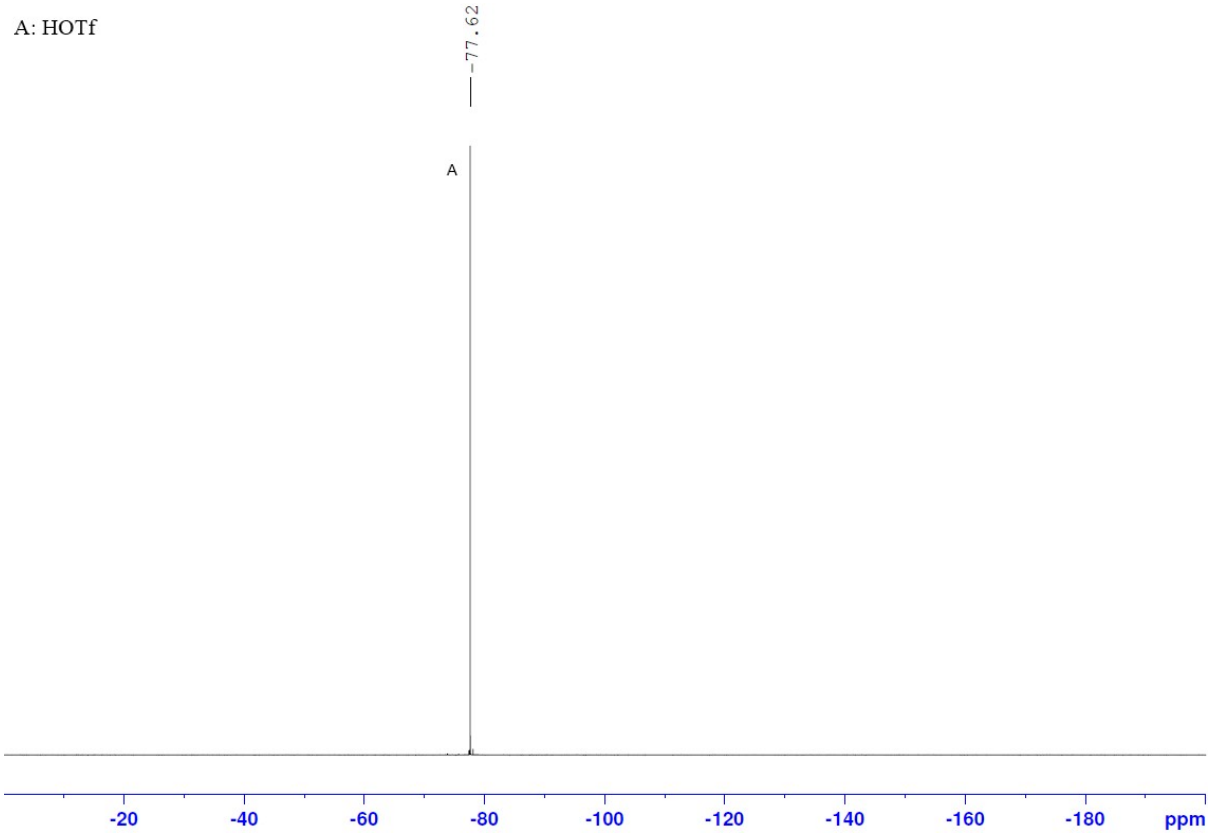


Figure S 33: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with limonene in $CDCl_3$

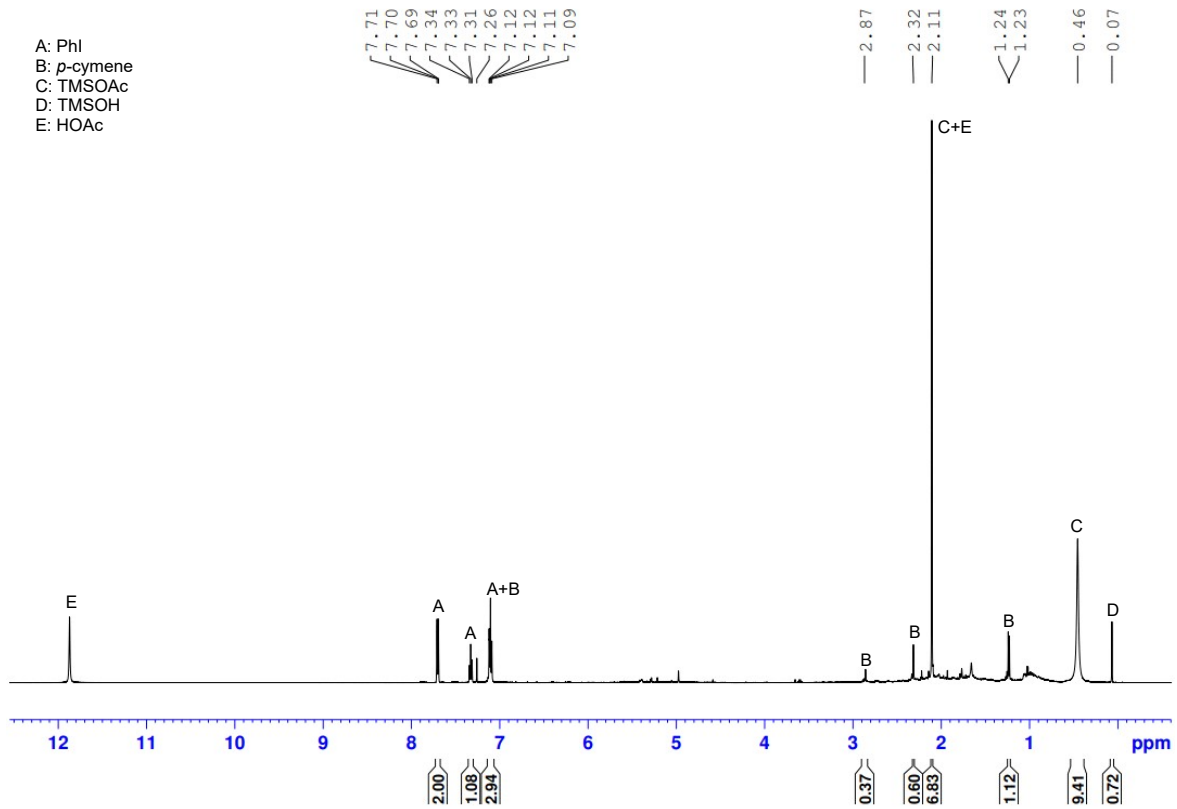


Figure S 34: ^{1}H NMR of PhI(OAc)(OTf) with limonene in $CDCl_3$ (reaction time ~ 15 min)

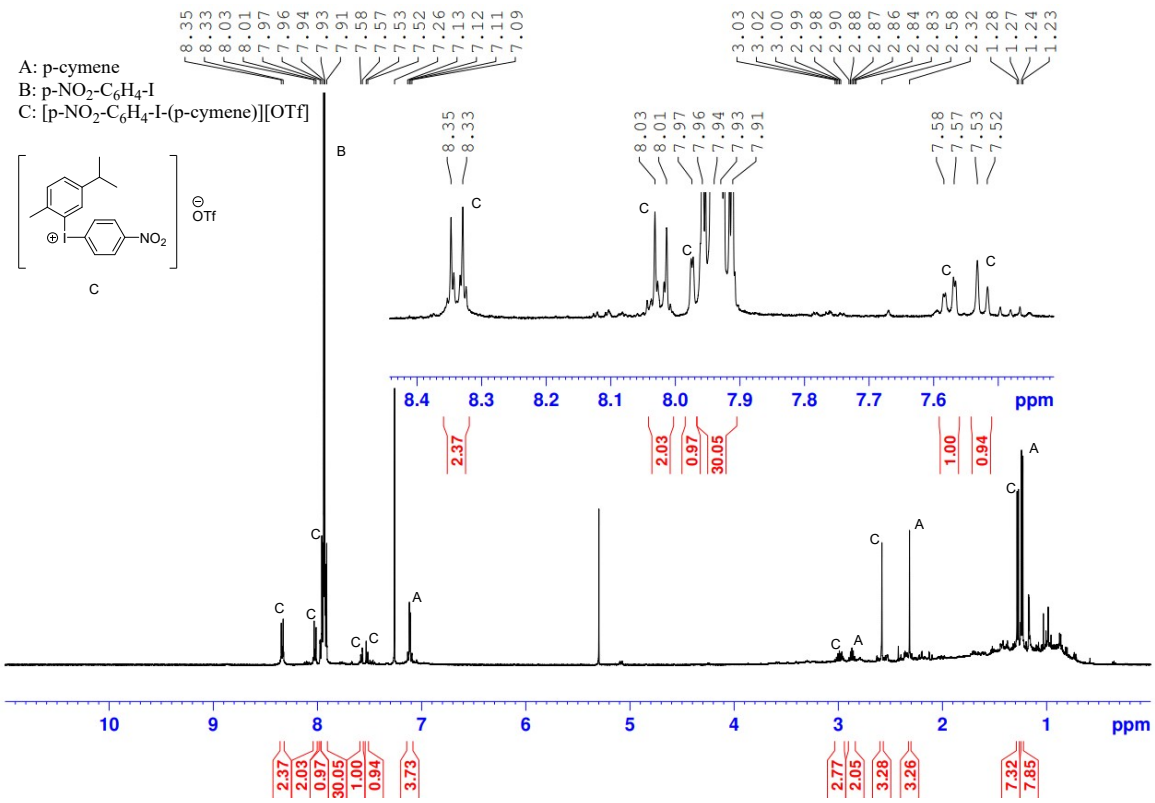


Figure S 35: ^{1}H NMR of NO_2-C_6H_4-I$(OTf)_2$ with α-pinene in $CDCl_3$

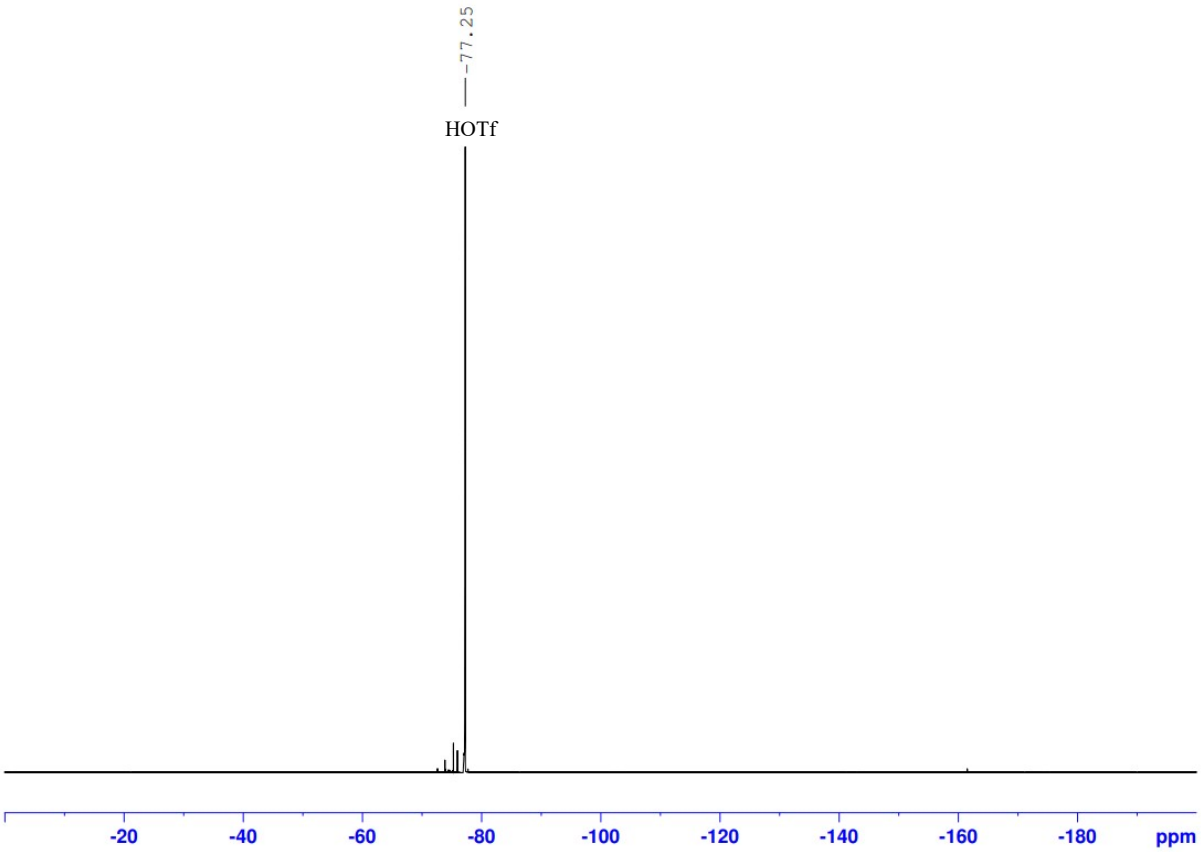


Figure S 36: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with α-pinene in $CDCl_3$

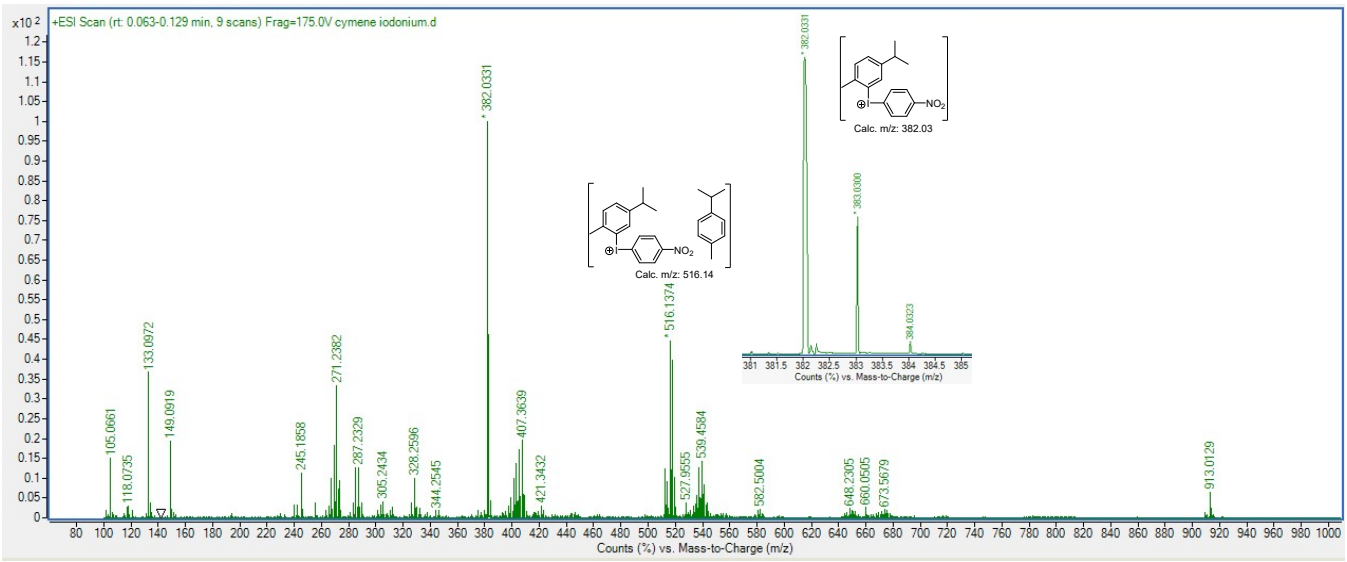


Figure S 37: HRMS of NO_2-C_6H_4-$I(OTf)_2$ with α-pinene

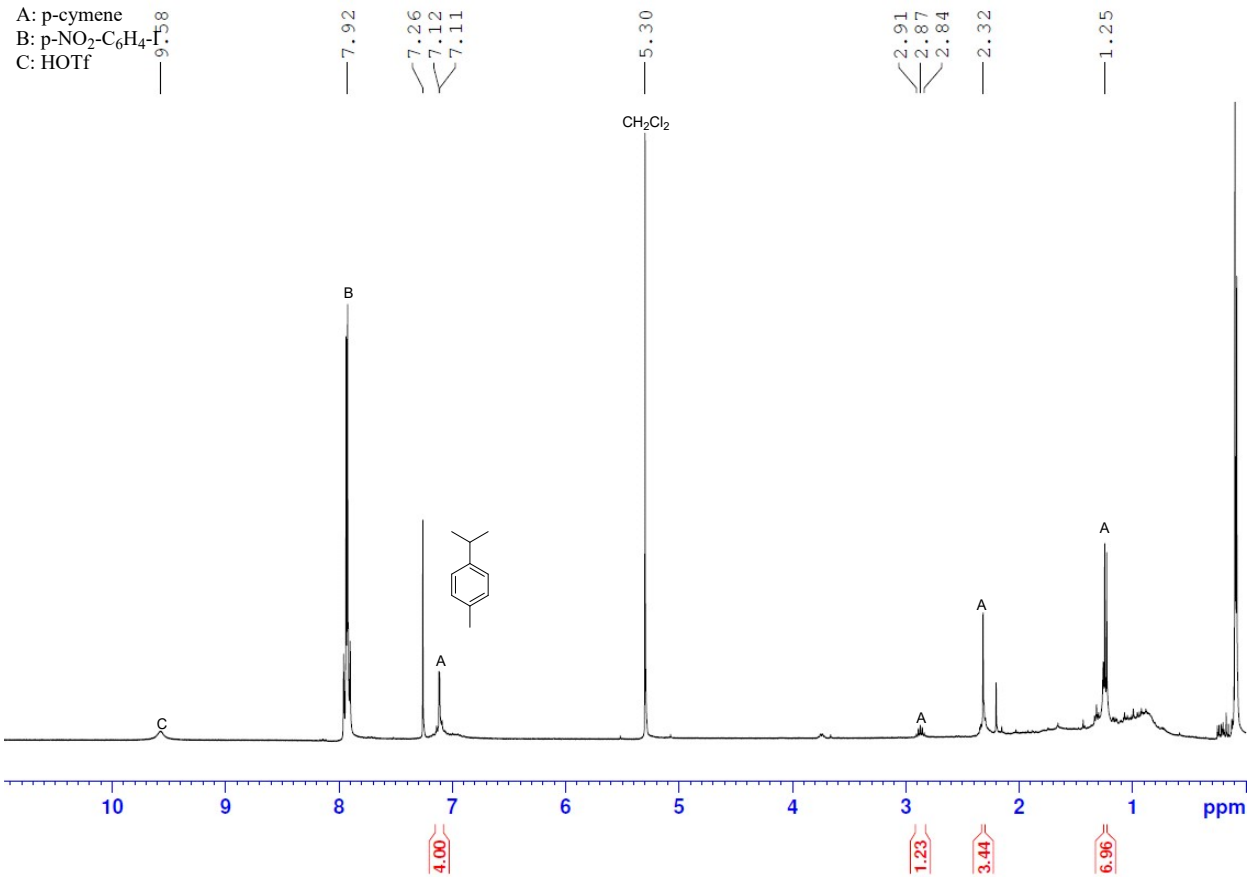


Figure S 38: ^{1}H NMR of NO_2-C_6H_4-$I(OTf)_2$ with α-pinene at -94 °C in $CDCl_3$

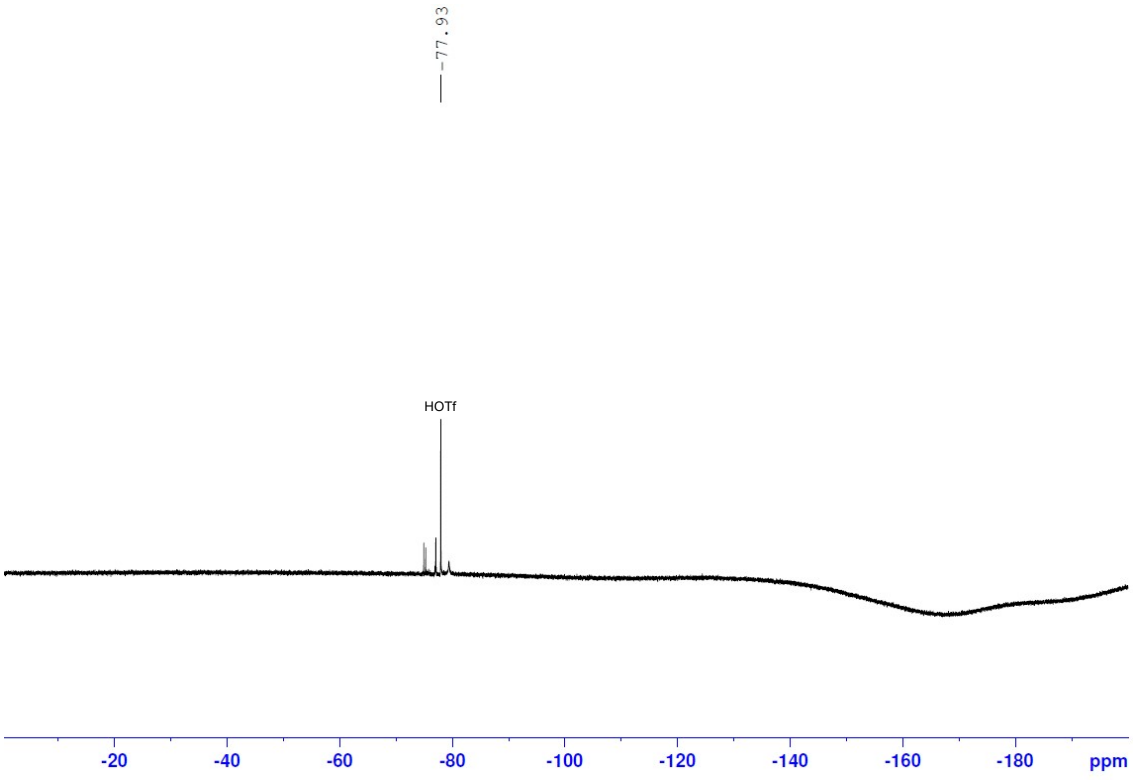


Figure S 39: ^{19}F NMR of NO_2-C_6H_4-$I(OTf)_2$ with α- pinene at -94 °C in $CDCl_3$

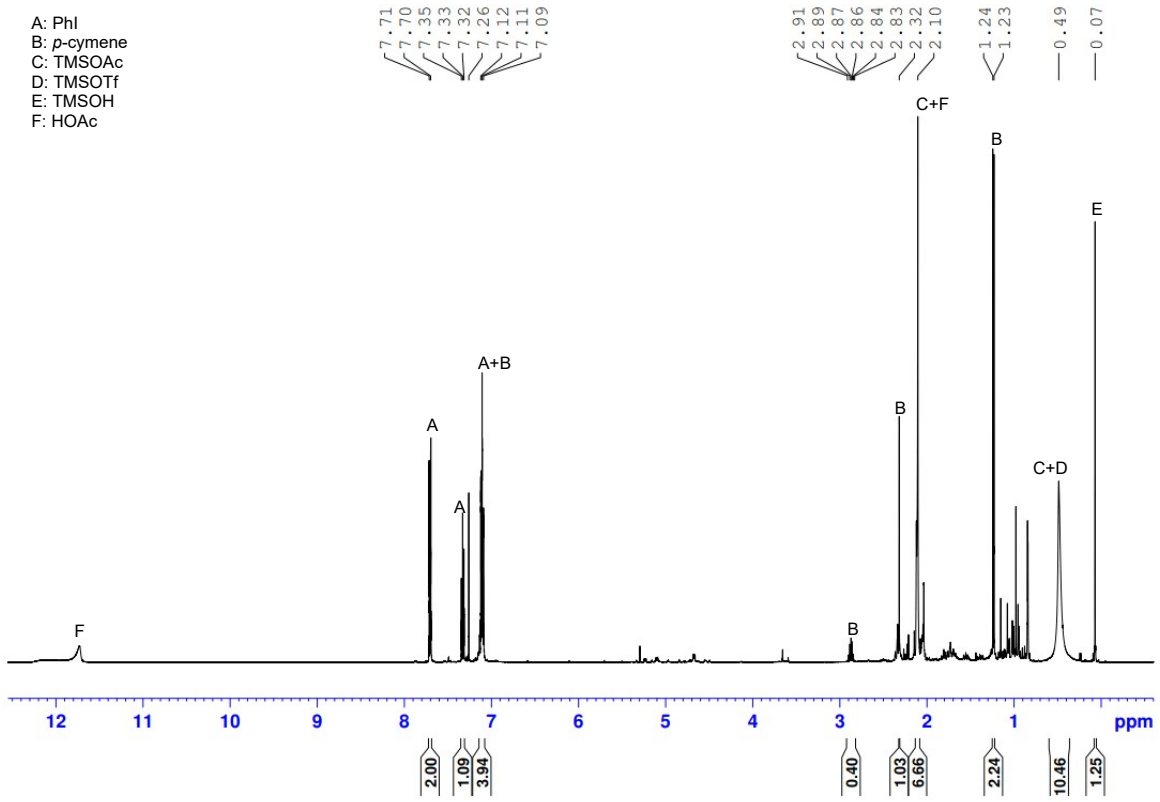


Figure S 40: ^{1}H NMR of PhI(OAc)(OTf) with α-pinene in $CDCl_3$ (reaction time ~ 17 h)

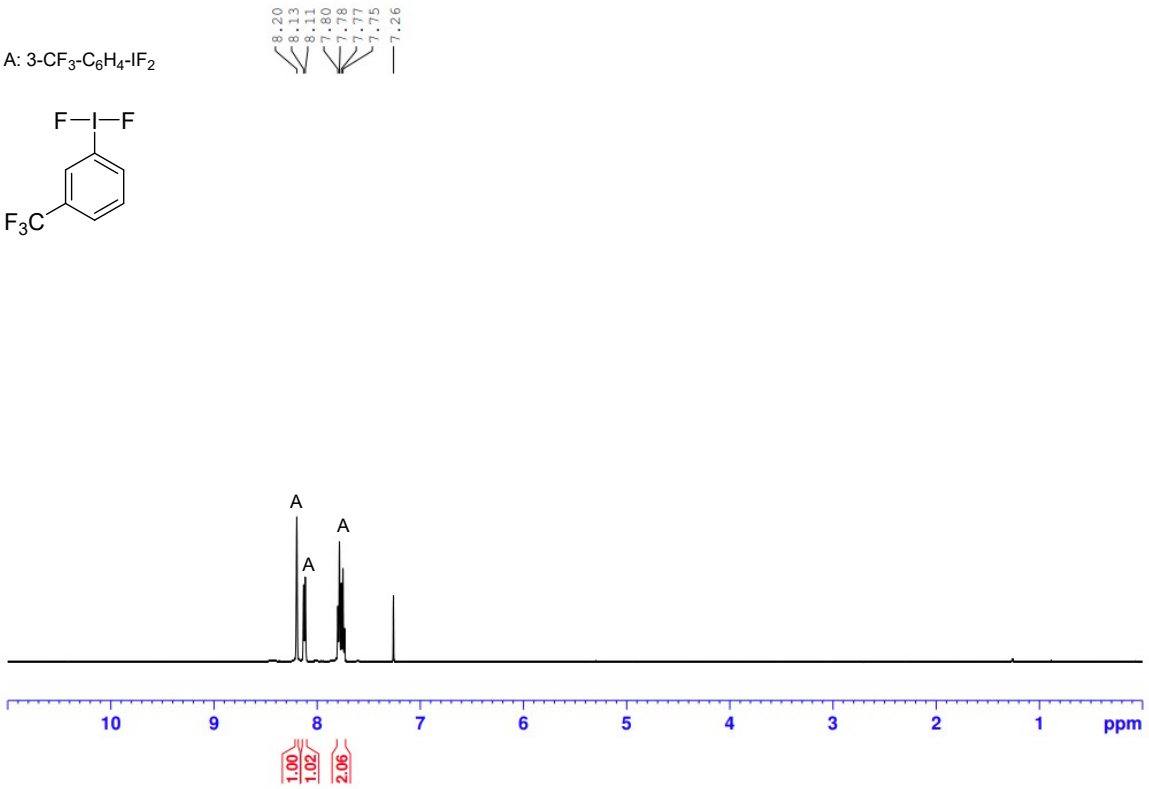


Figure S 41: ^{1}H NMR of 3-CF_3-C_6H_4-IF_2 synthesised via XeF_2 in $CDCl_3$

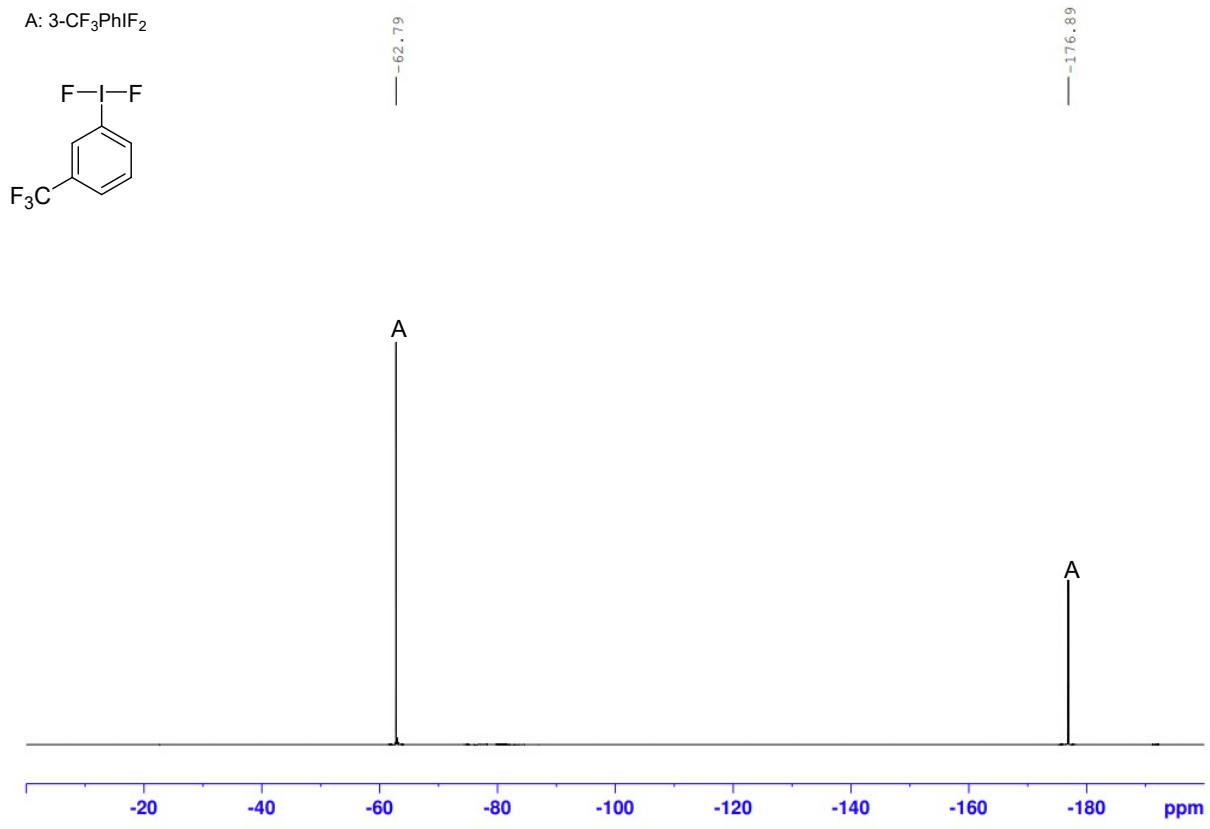


Figure S 42: ^{19}F NMR of 3-CF_3-C_6H_4-IF_2 via XeF_2 in $CDCl_3$

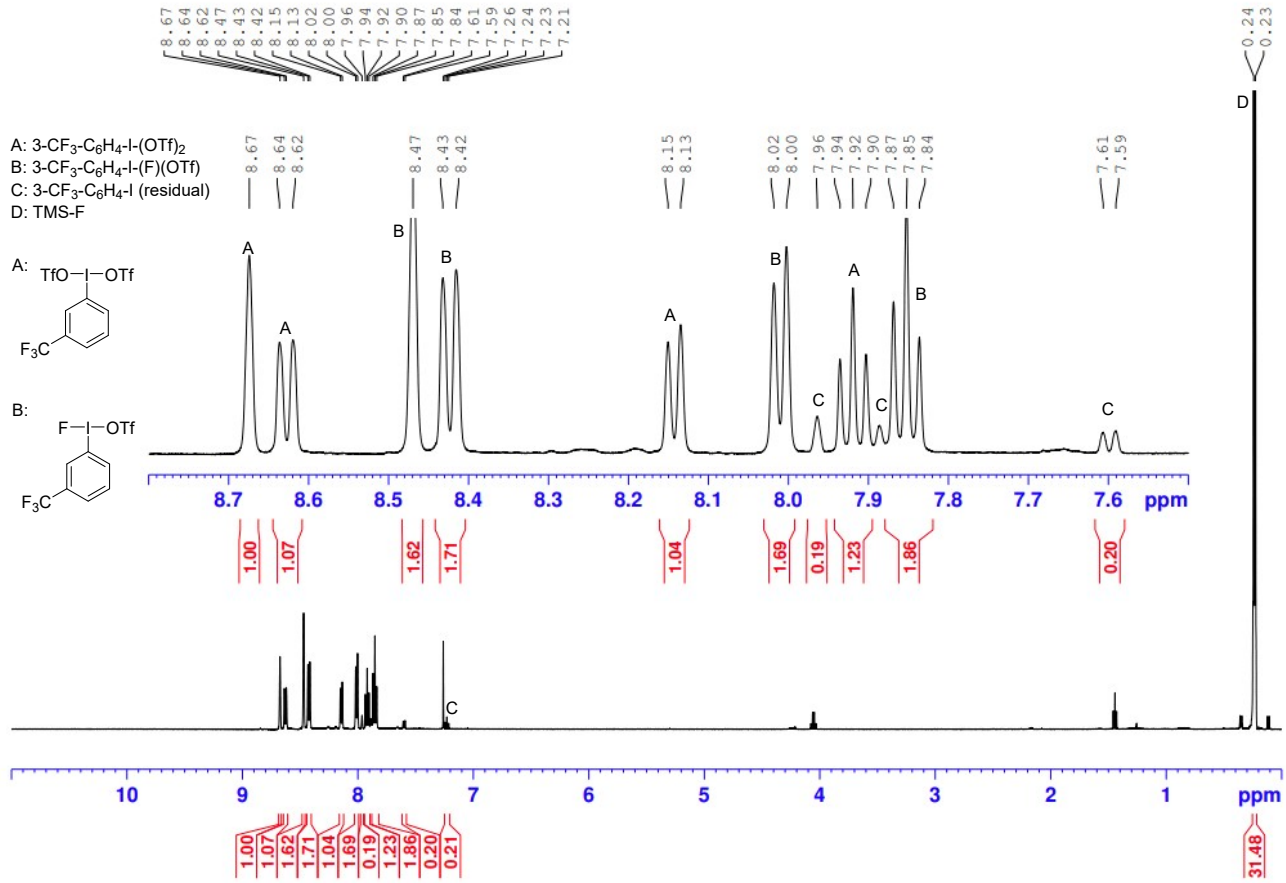


Figure S 43: ^{1}H NMR of crude reaction of 3-CF_3-C_6H_4-I with XeF_2 with TMSOTf spike and then added 1 equivalent of TMSOTf in $CDCl_3$. Spectrum shows the formation of 3-CF_3-C_6H_4-I$(OTf)_2$ even with 1 equivalent of TMSOTf

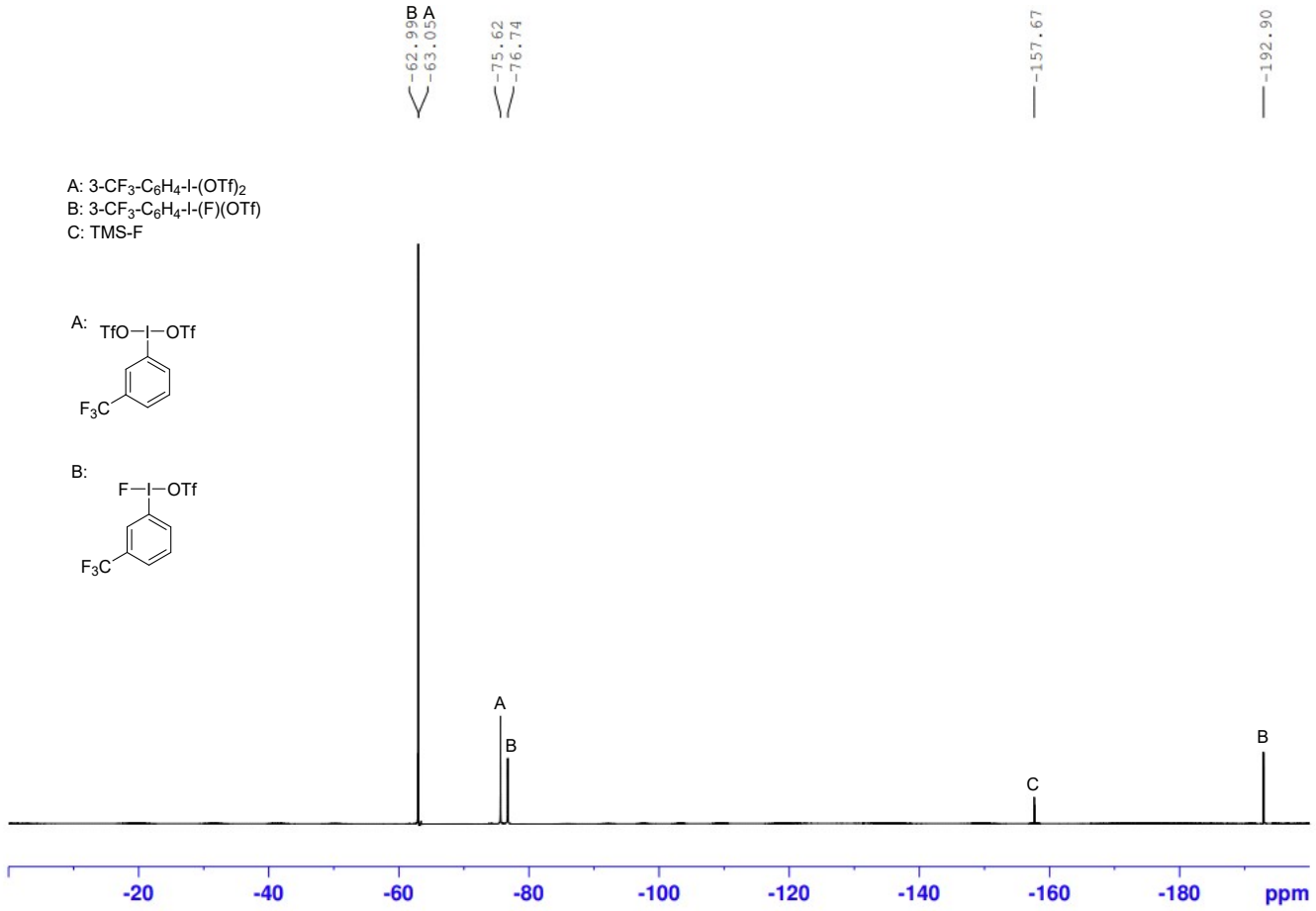


Figure S 44: ^{19}F NMR of crude reaction of 3-CF_3-C_6H_4-I with XeF_2 with TMSOTf spike and then added 1 equivalent of TMSOTf in $CDCl_3$. Spectrum shows the formation of 3-CF_3-C_6H_4-I$(OTf)_2$ with 1 equivalent of TMSOTf

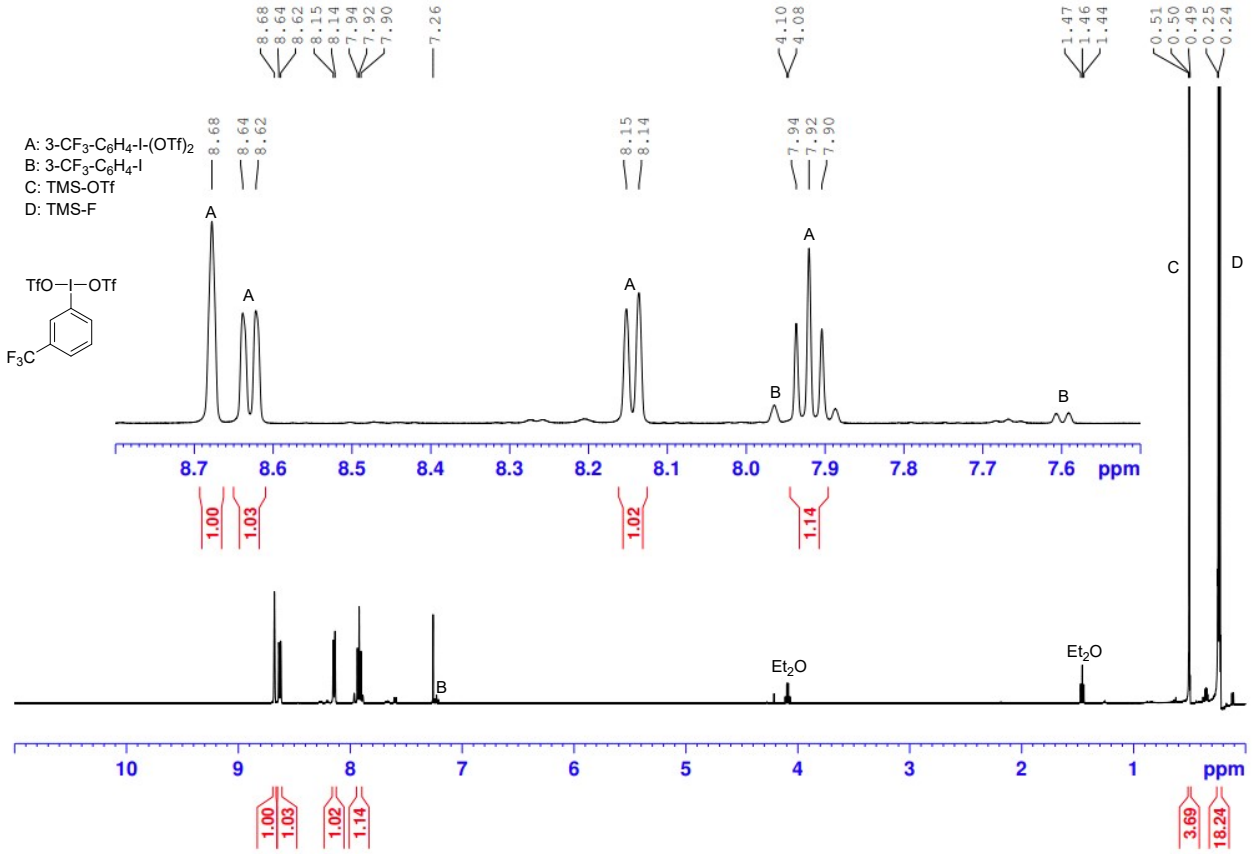


Figure S 45: ^{1}H NMR of crude reaction of 3-CF_3-C_6H_4-I with XeF_2 and two equivalents TMS-OTf in $CDCl_3$

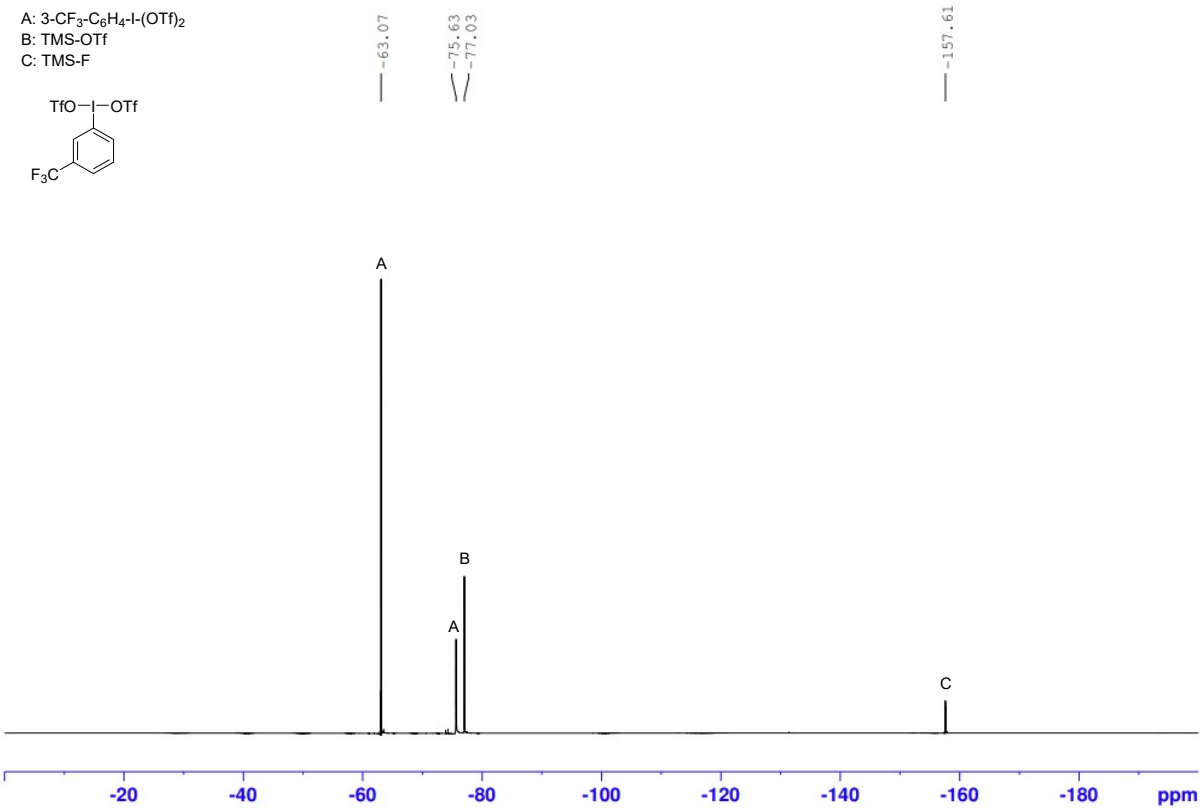


Figure S 46: ^{19}F NMR of crude reaction of 3-CF_3-C_6H_4-I with XeF_2 and two eq. of TMS-OTf in $CDCl_3$

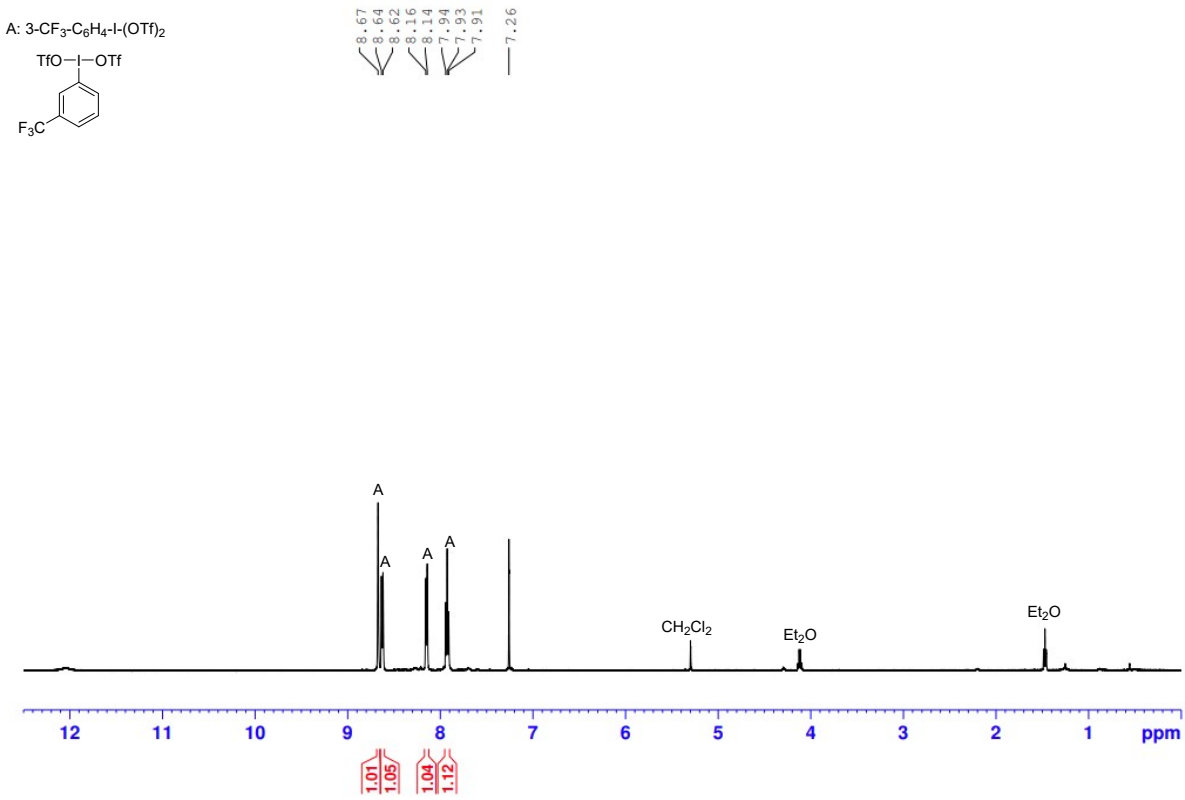


Figure S 47: ^{1}H NMR of 3-CF_3-C_6H_4-I$(OTf)_2$ in $CDCl_3$

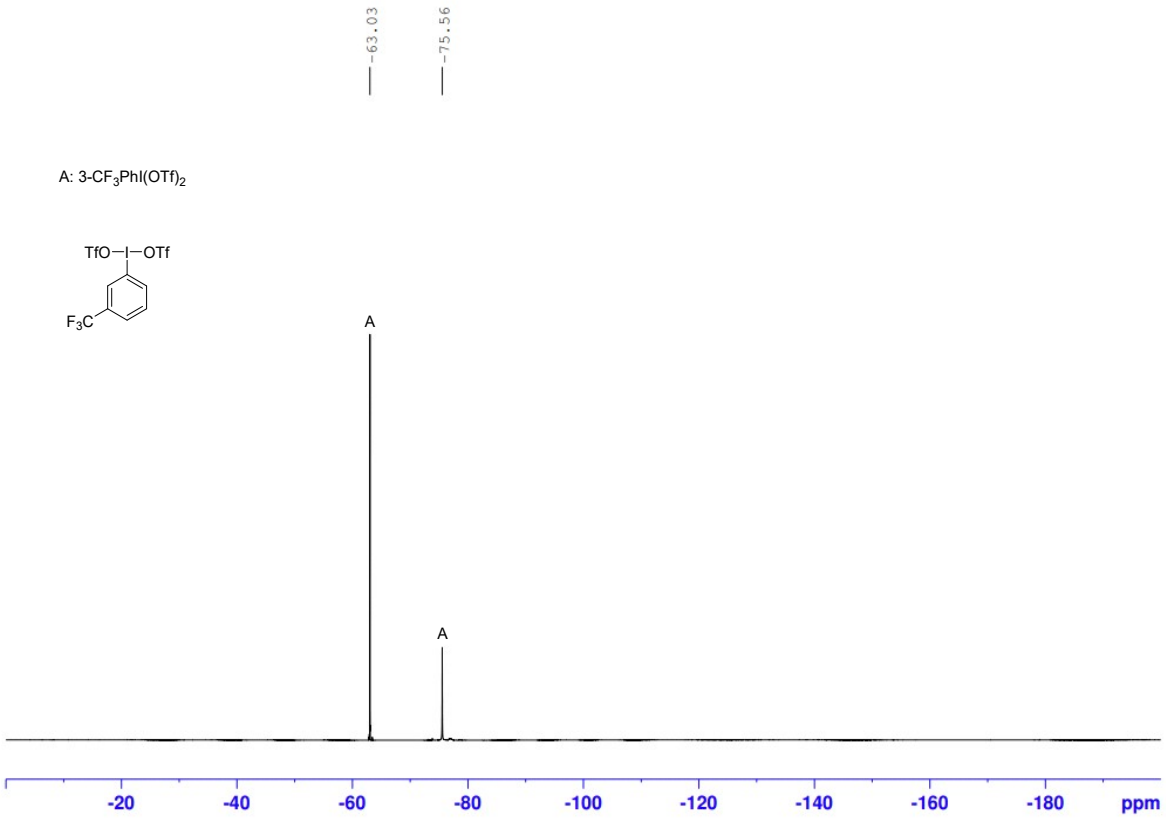


Figure S 48: ^{19}F NMR of 3-CF_3-C_6H_4-$I(OTf)_2$ in $CDCl_3$

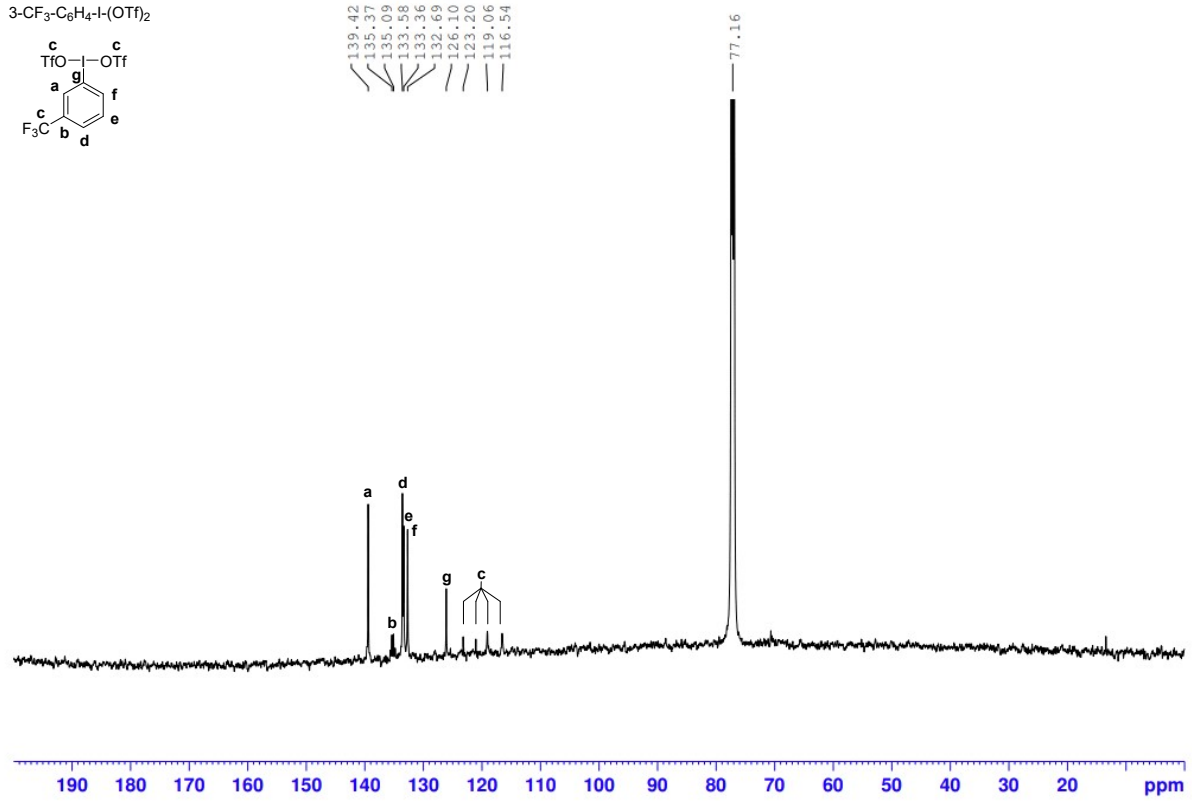


Figure S 49: ^{13}C NMR of 3-CF_3-C_6H_4-I$(OTf)_2$ in $CDCl_3$

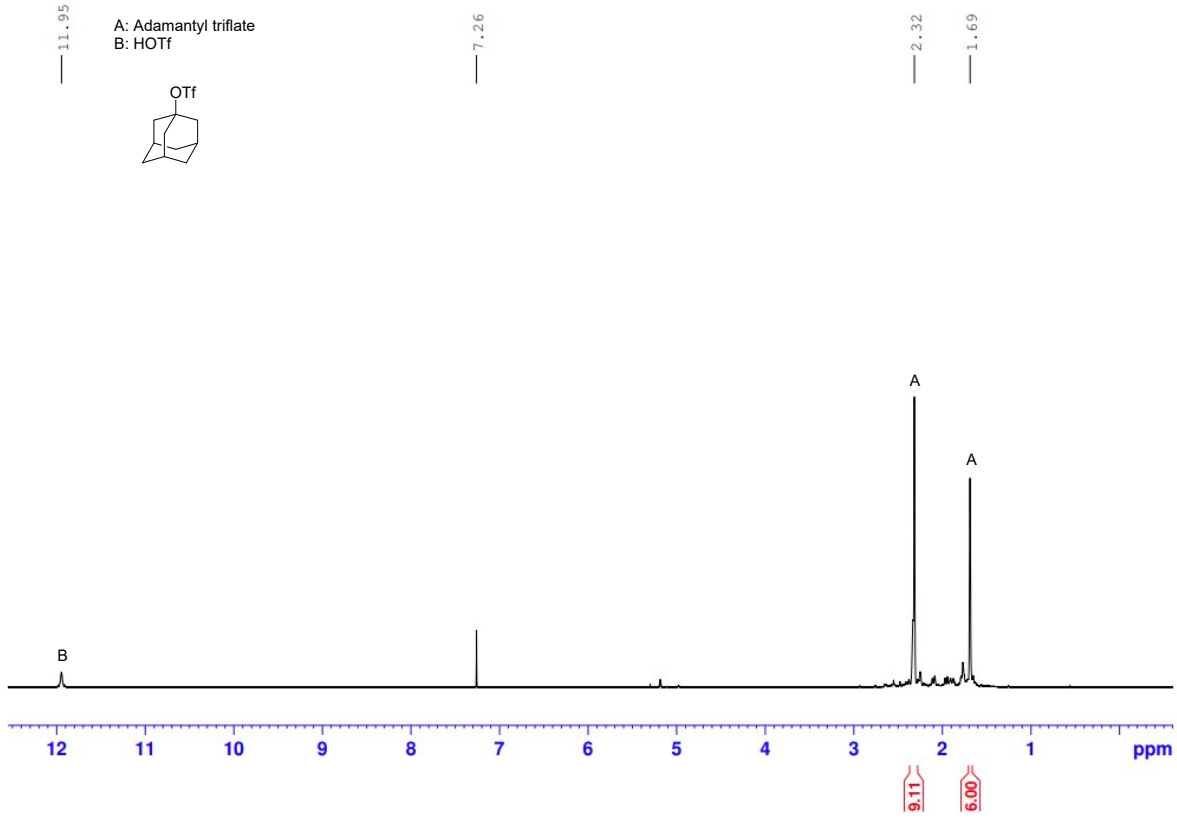


Figure S 50: ^{1}H NMR of adamantyl triflate generated via reaction of 3-CF_3-C_6H_4-$I(OTf)_2$ with adamantane in $CDCl_3$

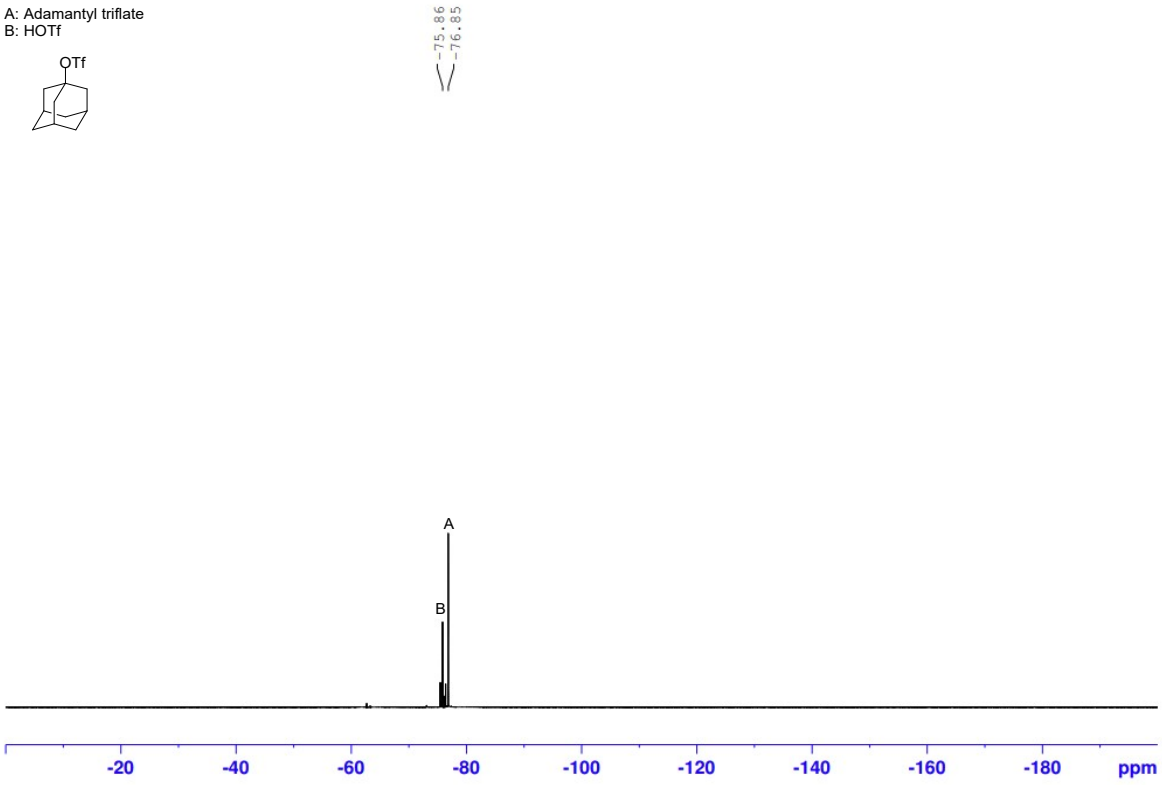


Figure S 51: ^{19}F NMR of adamantyl triflate generated via reaction of 3-CF_3-C_6H_4-$I(OTf)_2$ with adamantane in $CDCl_3$

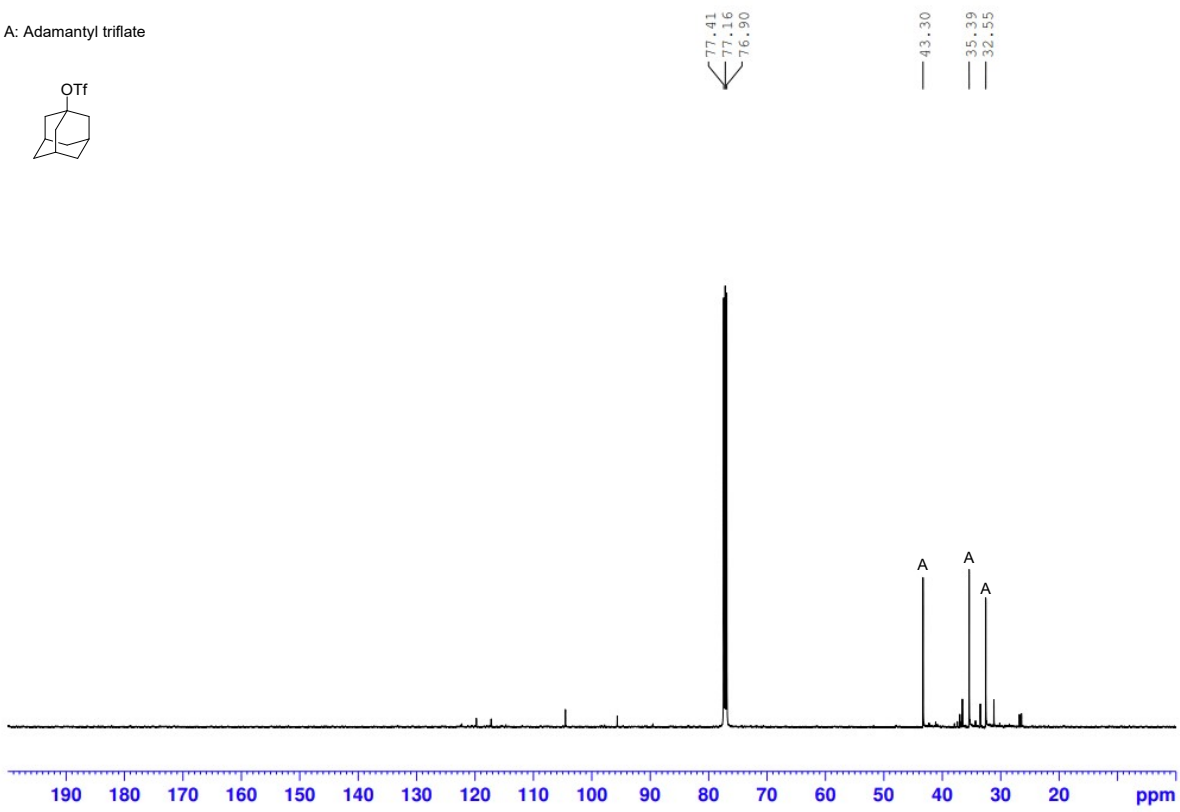


Figure S 52: ^{13}C NMR of adamantyl triflate generated via reaction of 3-CF_3-C_6H_4-I$(OTf)_2$ with adamantane in $CDCl_3$Structural Data

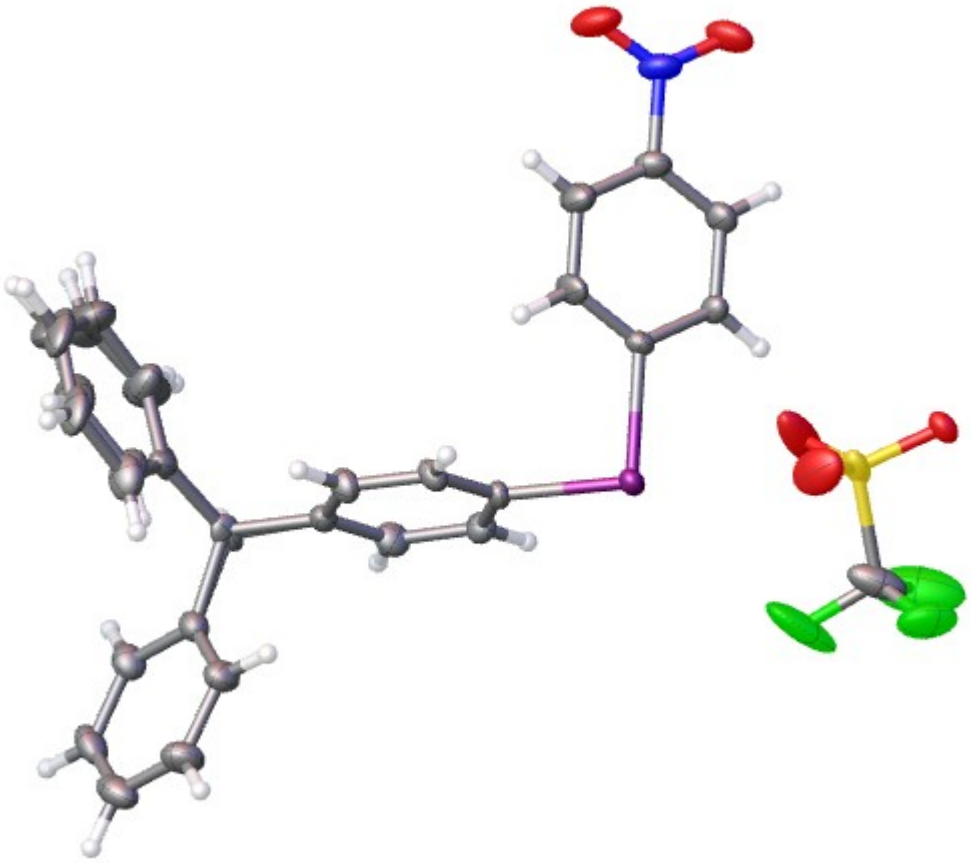
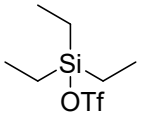


Figure S 53: Crystal structure of [Ph_2CHPhI-C_6H_4-NO_2][OTf]

Reference chemical shifts for NMR Spectra

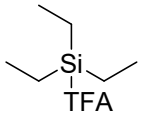
Et_3SiOTf (from the reaction of Et_3SiH with 1 eq HOTf in $CDCl_3$)



^1H NMR ($CDCl_3$) δ (ppm): 1.06 (t, 9H), 0.93 (q, 6H)

^{19}F NMR ($CDCl_3$) δ (ppm): -79.57 (s, 3F)

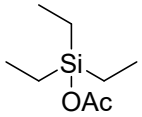
Et_3SiTFA (from the reaction of $PhI(TFA)_2$ with 1 eq Et_3SiH in $CDCl_3$)



^1H NMR ($CDCl_3$) δ (ppm): 1.01 (t, 9H), 0.87 (q, 6H)

^{19}F NMR ($CDCl_3$) δ (ppm): -76.04 (s, 3F)

Et_3SiOAc[3]



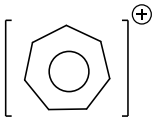
^1H NMR ($CDCl_3$) δ (ppm): 2.05 (s, 3H), 0.93 (t, 9H), 0.72 (q, 6H)

Cycloheptatriene (commercially available sample)

^1H NMR ($CDCl_3$) δ (ppm): 6.58 (t, 2H), 6.18 (t of d, 2H), 5.35 (t of d, 2H), 2.42 (t, 2H)

^{13}C NMR ($CDCl_3$) δ (ppm): 130.92, 126.55, 120.88, 27.97

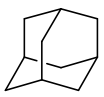
Tropylium (from the reaction of cycloheptatriene with 1 eq TMSOTf in $CDCl_3$)



^1H NMR ($CDCl_3$) δ (ppm): 9.33 (s, 7H)

^{13}C NMR ($CDCl_3$) δ (ppm): 155.58

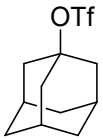
Adamantane (commercially available sample)



^1H NMR ($CDCl_3$) δ (ppm): 1.87 (br. s, 4H), 1.75 (t, 12H)

^{13}C NMR ($CDCl_3$) δ (ppm): 37.85, 28.46

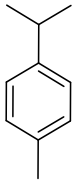
Adamantyl triflate[4]



^{1}H NMR ($CDCl_3$) δ (ppm): 2.27 (s, 9H), 1.68 (s,6H)

^{13}C NMR ($CDCl_3$) δ (ppm): 118.3, 103.7, 43.3, 35.4, 32.5

p-cymene[5]



^{1}H NMR ($CDCl_3$) δ (ppm): 7.14-7.10 (m, 4H), 2.89-2.85 (m, 1H), 2.31 (s, 3H),

1.24 (d, 6H)

Computational Details

All geometry optimisation, vibrational frequency and molecular orbital calculations were performed using ωPBE/def2-TZVP within Gaussian 16 using the WebMO platform.[6-8] The structures obtained are minima with no negative frequencies. Cartesian coordinates are in Å and energies are given in Hartree. The free energy is calculated at 1 atm and 298 K.

Cartesian Coordinates for optimised compound geometries

NO_2-C_6H_4-I$(OTf)_2$

Electronic Energy: -2656.30893914 Hartree

S	0.00000000	0.00000000	0.00000000
C	-1.13600600	-0.74388100	1.23589400
F	-2.09799600	-1.38300800	0.58996200
F	-0.47194600	-1.60180200	1.99828500
F	-1.66627000	0.19927300	1.99807800
O	1.00063100	0.65490100	0.96539800
I	3.05931700	0.47597300	0.65324800
C	3.05961100	2.55911400	0.65336800
C	2.09529800	3.21431900	-0.08375500

C	2.09827800	4.59484000	-0.07920100
C	3.05996900	5.25290300	0.65350500
C	4.02149000	4.59451000	1.38613300
C	4.02410400	3.21398500	1.39054600
H	4.77947600	2.67998700	1.95218300
H	4.75396100	5.15787900	1.94734600
N	3.06015200	6.73014100	0.65359600
O	2.21654200	7.28121400	-0.00681700
O	3.90387300	7.28092400	1.31410600
H	1.36596200	5.15846500	-0.64035900
H	1.33980300	2.68055700	-0.64545000
O	5.11804000	0.65419700	0.34104900
S	6.11860500	0.00001000	1.30699800
C	7.25448900	-0.74509300	0.07173000
F	8.21639200	-1.38380700	0.71820200
F	6.59029500	-1.60356900	-0.68991700
F	7.78489100	0.19733000	-0.69127400
O	6.85792300	0.98859000	2.00564000
O	5.49128600	-1.07196200	2.00344100
O	0.62722900	-1.07265900	-0.69547600
O	-0.73919500	0.98804200	-0.69952400

$HSiEt_3$

Electronic Energy: -527.64961327 Hartree

Si 0.00000000 0.00000000 0.00000000

C 1.35088000 -1.08996300 -0.72015700

C 2.65615500 -1.12078100 0.06906700

H 3.10892400 -0.13140700 0.14678600

H 2.49056400 -1.47764400 1.08703200

H 3.39126500 -1.78057500 -0.39592200

H 0.94660000 -2.10421000 -0.79479900

H 1.53881500 -0.77247000 -1.75094600

C -1.67998700 -0.64588200 -0.52670300

C -2.86503100 0.14898500 0.01036000

H -3.81695100 -0.29576400 -0.28558000

H -2.85069000 0.19550000 1.10132900

H -2.85836300 1.17622500 -0.35828100

H -1.71086900 -0.67496300 -1.62076300

H -1.75061000 -1.68801100 -0.20039100

C 0.17931000 1.79648300 -0.51084900

H -0.61600600 2.35919800 -0.01287500

C 1.52959700 2.43615800 -0.20769700

H 1.53868900 3.49670400 -0.46619300

H 1.78194900 2.35565600 0.85169200

H 2.33297600 1.95917600 -0.77145200

H -0.03489400 1.86612100 -1.58254000

H 0.08971700 -0.07165700 1.49007300

NO_2-C6H4-I

Electronic Energy: -733.753165289 Hartree

C 0.00000000 0.00000000 0.00000000

C 0.68406100 -1.20389400 -0.00085400

C 2.06383000 -1.20639200 -0.00067100

C 2.72849500 -0.00010300 0.00015100

C 2.06389500 1.20618800 0.00084400

C 0.68406500 1.20377300 0.00080400

H 0.14266000 2.14081100 0.00149400

H 2.62692700 2.12923400 0.00141700

N 4.20031100 -0.00005600 0.00025800

O 4.75794300 -1.07017500 0.00199600

O 4.75762100 1.07018200 -0.00207300

H 2.62686700 -2.12942900 -0.00108800

H 0.14249700 -2.14084400 -0.00156800

I -2.06699400 -0.00005300 0.00006400

HOTf

Electronic Energy: -961.91585154 Hartree

S 0.00000000 0.00000000 0.00000000

C 1.82881000 -0.14063700 -0.07717700

F 2.36030300 0.75447100 0.73820600

F 2.19421500 -1.35984800 0.30789800

F 2.25609700 0.07174000 -1.30998400

O -0.39210700 -1.16908700 -0.97099000

H -0.53854500 -1.98218600 -0.46570200

O -0.34822000 1.21454700 -0.62446400

O -0.38056200 -0.34594600 1.32045600

NO_2-C_6H_4-I(OTf)(H)

Electronic Energy: -1695.59888025 Hartree

S 0.00000000 0.00000000 0.00000000

O -1.47820500 0.05147100 0.11489000

I -2.19967600 2.31540900 0.71975500

H -3.00994500 3.69231500 1.10023500

C -4.03302100 1.32440200 0.74037900

C -4.90341000 1.57094300 1.78346800

C -6.12485400 0.92873900 1.79172400

C -6.42037000 0.06414500 0.76187100

C -5.54795400 -0.19026500 -0.27188700

C -4.32586100 0.45316500 -0.28726200

H -3.60961200 0.25459200 -1.07218200

H -5.82544100 -0.88499100 -1.05252400

N -7.72848800 -0.62067900 0.77079200

O -8.46786400 -0.38477500 1.69328000

O -7.96809500 -1.36548100 -0.14494800

H -6.84120500 1.08607100 2.58601200

H -4.64319000 2.24445800 2.59002900

O 0.47317600 -0.85675500 -1.03018100

C 0.45779400 -0.82388600 1.57199000

F 1.77702300 -0.90814500 1.68757400

F -0.01211500 -0.11887200 2.61000100

F -0.05743000 -2.04714000 1.63580000

O 0.55966100 1.32275900 0.11646300

Et_3SiOTf

Electronic Energy: -1488.42469982 Hartree

Si 0.00000000 0.00000000 0.00000000

C 1.07940000 -1.26185300 -0.83604700

C 0.61729400 -2.71449000 -0.76033000

H 0.49184100 -3.05195100 0.26849900

H -0.33778400 -2.85444200 -1.26840400

H 1.33823700 -3.37794000 -1.23970600

H 1.18421800 -0.95975400 -1.88236700

H 2.07875100 -1.15894800 -0.39850200

C 0.24237500 1.69202900 -0.72629800

C -0.62705500 2.78722800 -0.11722000

H -0.42974300 3.75421600 -0.58166000

H -1.68820400 2.57163800 -0.25007600

H -0.44672000 2.89652900 0.95359800

H 1.30283100 1.94229400 -0.61240500

H 0.06715300 1.62324600 -1.80373000

C 0.12917100 0.04186400 1.85707700

C 0.54938000 -1.23477900 2.57768500

H 0.67633300 -1.05182500 3.64566100

H -0.19815200 -2.01814000 2.46419100

H 1.49935000 -1.61621900 2.19886500

H -0.81984600 0.40829700 2.25828000

H 0.85634600 0.83592000 2.06506500

O -1.62816700 -0.35188800 -0.48266600

S -2.72798400 -1.31400000 -0.03711400

C -4.01815500 -0.08315800 0.39171100

F -4.32927200 0.65397200 -0.66550600

F -5.09855400 -0.72218400 0.81304300

F -3.58197100 0.71843800 1.36004300

O -3.22131800 -2.03955500 -1.14792500

O -2.37779100 -1.96751800 1.17479400

Cyclohexene

Electronic Energy: -234.576600754 Hartree

C 0.00000000 0.00000000 0.00000000

C -0.79633600 1.22033000 -0.43406100

C 0.02878000 2.46998600 -0.38146600

C 1.34648700 2.46996300 -0.26455900

C 2.17152600 1.22025500 -0.21184100

C 1.37515700 0.00000800 -0.64606000

H 1.91900200 -0.91407600 -0.39886500

H 1.25811500 0.01511900 -1.73421000

H 2.55031900 1.08129700 0.80705500

H 3.05596300 1.34078200 -0.84301400

H 1.87473000 3.41722100 -0.20710000

H -0.49942600 3.41726000 -0.43904000

H -1.17534200 1.08143900 -1.45288600

H -1.68064800 1.34091800 0.19728100

H 0.11704600 0.01495000 1.08815200

H -0.54388500 -0.91403000 -0.24731300

Benzene

Electronic Energy: -232.150999992 Hartree

C 0.00000000 0.00000000 0.00000000

C 1.31312500 -0.43457600 0.00000100

C 1.59330000 -1.78891500 -0.00000200

C 0.56037600 -2.70881100 -0.00000300

C -0.75259700 -2.27427500 0.00000200

C -1.03281300 -0.91978600 -0.00000300

H -2.06182400 -0.57933000 -0.00001100

H -1.56206200 -2.99506900 0.00000500

H 0.77997300 -3.77020400 0.00000300

H 2.62225200 -2.12956100 -0.00000700

H 2.12246800 0.28635000 0.00000300

H -0.21940800 1.06143600 0.00000100

$PhI(TFA)_2$

Electronic Energy: -1581.47924091 Hartree

C 0.00000000 0.00000000 0.00000000

C 1.45865500 0.31253900 -0.41008700

O 2.25661300 0.24561200 0.61765000

I 4.30438200 0.52843400 0.26194900

C 3.93203000 2.55030300 0.12633500

C 3.96172400 3.30423800 1.28335700

C 3.71754500 4.66020100 1.18960000

C 3.45250300 5.23283500 -0.04114200

C 3.42699600 4.45831500 -1.18601700

C 3.66786600 3.09959200 -1.11230300

H 3.63246000 2.48050200 -1.99868400

H 3.21515900 4.91059200 -2.14692500

H 3.26145600 6.29722800 -0.10816900

H 3.73571000 5.27040900 2.08410200

H 4.17184000 2.84741100 2.24205400

O 6.30979700 1.14974400 0.00453100

C 7.09956000 0.12273100 0.03090200

O 6.76336400 -1.02446800 0.17814500

C 8.58152000 0.52181400 -0.14931300

F 9.36691000 -0.54359600 -0.12332000

F 8.75448000 1.14799900 -1.31577300

F 8.95842600 1.34999500 0.82873800

O 1.74868900 0.58004500 -1.54263400

F -0.42234100 0.88001100 0.91253700

F -0.08386600 -1.22270400 0.52960700

F -0.81085800 0.06058300 -1.04569900

Et_3SiTFA

Electronic Energy: -1053.23514592 Hartree

Si 0.00000000 0.00000000 0.00000000

C 0.50615200 -1.24625900 -1.28870500

C -0.27416200 -2.55657500 -1.33489700

H -0.24211500 -3.08618100 -0.38320100

H -1.32449400 -2.38355200 -1.57270300

H 0.12583400 -3.22267900 -2.10082000

H 0.44721000 -0.74626800 -2.26035200

H 1.57129600 -1.44726300 -1.12809800

C 0.51408600 1.71450600 -0.50446400

C 0.12114000 2.81291300 0.47833800

H 0.44200900 3.79493300 0.12794300

H -0.96065000 2.85119500 0.61555200

H 0.57131100 2.65442400 1.46005300

H 1.59966400 1.70532400 -0.64964700

H 0.08308300 1.91736200 -1.48919000

C 0.58747100 -0.38000100 1.72941300

H -0.10926200 0.08325300 2.43443200

C 0.81718500 -1.84103100 2.10015900

H 1.22465000 -1.92748300 3.10866700

H -0.11264000 -2.40669400 2.06722200

H 1.52650400 -2.31946300 1.42218400

H 1.52392200 0.17891300 1.84158700

O -1.71832600 0.12950100 -0.04434500

C -2.59581300 -0.64101800 0.54431300

O -2.38664100 -1.60888200 1.21172900

C -4.03058300 -0.13709600 0.26982100

F -4.28089700 -0.14389300 -1.04320800

F -4.92767900 -0.90272100 0.87123000

F -4.17771900 1.11504300 0.71387200

Trifluoroacetic acid

Electronic Energy: -526.733471294 Hartree

C 0.00000000 0.00000000 0.00000000

C -1.53441600 -0.16077000 -0.00001100

O -2.08450100 -1.21496200 -0.00002600

O -2.11973400 1.02974500 0.00000300

H -3.07807800 0.89105200 0.00001200

F 0.39385200 0.67374200 -1.08187700

F 0.39389600 0.67380800 1.08176600

F 0.58694900 -1.18477400 0.00002500

Et_3SiOAc

Electronic Energy: -755.542608854 Hartree

Si 0.00000000 0.00000000 0.00000000

C -0.30030900 -1.33952100 -1.26476400

C -1.68519900 -1.97479900 -1.32708500

H -1.97292900 -2.41927400 -0.37526200

H -2.44865900 -1.23692700 -1.57536300

H -1.72336100 -2.75566600 -2.08889700

H -0.04643800 -0.91197900 -2.24016600

H	0.45785300	-2.10962600	-1.08120400
C	1.48846600	0.99945000	-0.51491600
C	1.85207500	2.13688700	0.43348900
H	2.72456800	2.69040600	0.08220000
H	1.02901900	2.84696400	0.52909500
H	2.08261900	1.76734500	1.43457700
H	2.33289700	0.30971500	-0.61900100
H	1.29898500	1.39297200	-1.51796500
C	0.23515300	-0.62231700	1.74722200
H	-0.08535200	0.16931700	2.43104800
C	-0.42919900	-1.94054400	2.12759500
H	-0.17387200	-2.22756100	3.14933800
H	-1.51323500	-1.86419200	2.06072600
H	-0.10823700	-2.75373600	1.47348500
H	1.31947600	-0.70439300	1.88558800
O	-1.24527000	1.16550200	-0.09496700
C	-2.45460900	1.03778600	0.44677400
O	-2.80578400	0.05315100	1.04247600
C	-3.31278300	2.24658100	0.23159000
H	-3.41614000	2.43408900	-0.83698900
H	-4.28876000	2.09290900	0.68238000
H	-2.82883200	3.11906100	0.67018300

Acetic Acid

Electronic Energy: -229.045788093 Hartree

C 0.00000000 0.00000000 0.00000000

C -1.05760900 1.05576500 0.00000000

O -2.29454700 0.52550700 0.00000000

H -2.91358700 1.26902900 0.00000000

O -0.87208300 2.24013500 0.00000000

H 0.98034300 0.46614400 0.00000000

H -0.11577500 -0.63330600 0.87915800

H -0.11577500 -0.63330600 -0.87915800

$PhI(OAc)_2$

Electronic Energy: -986.095129962 Hartree

C 0.00000000 0.00000000 0.00000000

C -1.23323700 0.79977300 -0.29440700

O -2.33932000 0.09594900 -0.30900500

I -3.96486900 1.37599900 -0.71896200

C -5.01511400 -0.39621300 -0.58156500

C -5.07713500 -1.21623500 -1.69147100

C -5.77183100 -2.40669900 -1.60014700

C -6.38886500 -2.75896900 -0.41355400

C -6.31644800 -1.92478300 0.68621100

C -5.62456200 -0.72997500 0.61111700

H -5.57946300 -0.05840000 1.45784300

H -6.80318900 -2.20132900 1.61358700

H -6.93341500 -3.69346900 -0.34645300

H -5.83004600 -3.06094500 -2.46155700

H -4.58924600 -0.93420200 -2.61595500

O -5.76244200 2.30897300 -1.23561000

C -6.59068600 2.61268500 -0.25235700

C -7.78726200 3.38836000 -0.72210300

H -7.45945000 4.30349700 -1.21414700

H -8.42915600 3.62419000 0.12193400

H -8.33490300 2.79920800 -1.45730400

O -6.40720300 2.29552400 0.90037200

O -1.22897200 1.99810000 -0.50269600

H 0.87307500 0.64576500 -0.02494400

H -0.09548300 -0.46377800 0.98141400

H 0.10083700 -0.79957300 -0.73315000

Adamantane

Electronic Energy: -390.625386723 Hartree

C 0.00000000 0.00000000 0.00000000

C 0.70231800 1.35350400 -0.06148700

C 1.13749800 1.63276600 -1.49734400

C 2.09383100 0.53998300 -1.96681100

C 1.38847300 -0.81171000 -1.90138500

C 0.95376000 -1.09631300 -0.46637300

C 2.18185900 -1.11713300 0.43941200

C 2.88905800 0.23388500 0.37879300

C 1.93117300 1.32749500 0.84310700

H 2.43344600 2.29949600 0.82052500

H 1.62953200 1.14598600 1.87926300

C 3.31961100 0.51539300 -1.05800700

H 4.02122500 -0.25335400 -1.39616000

H 3.84412000 1.47438100 -1.11070600

H 3.76872900 0.21684100 1.02847900

H 1.88407100 -1.33794900 1.46903700

H 2.86533600 -1.91197300 0.12535400

H 0.44854700 -2.06531400 -0.42153400

H 0.51726000 -0.81188600 -2.56361000

H 2.05926300 -1.60160800 -2.25305200

H 2.40444400 0.74185700 -2.99587400

H 0.26223800 1.67145500 -2.15307700

H 1.62692500 2.60972400 -1.55707500

H 0.01723500 2.13769300 0.27306600

H -0.33261300 -0.20306400 1.02259300

H -0.89348200 0.01267900 -0.63172800

Adamantyl triflate

Electronic Energy: -1351.33549852 Hartree

C	0.00000000	0.00000000	0.00000000
C	-0.46589700	1.43914500	-0.12853100
C	-0.16321300	1.98618400	-1.51068200
C	1.35040000	1.94705900	-1.72176600
C	1.83867600	0.50609000	-1.60568100
C	1.51330700	-0.03362900	-0.21609800
C	2.19993600	0.82570700	0.84024100
C	1.70790700	2.26464000	0.72213500
C	0.19617200	2.29789500	0.93194700
H	-0.18393600	3.31942100	0.85649900
H	-0.06763900	1.91621000	1.92086900
C	2.03774900	2.80587100	-0.66534200
H	3.11988200	2.79708500	-0.82187300
H	1.70796900	3.84509000	-0.75229500
H	2.18483700	2.88377800	1.48548900
H	1.98719200	0.43555800	1.83958600
H	3.28414000	0.78904000	0.70384000
H	1.85506600	-1.06765400	-0.13153300
H	1.36358700	-0.11432500	-2.37057200
H	2.91745700	0.46237700	-1.77848100
H	1.57620800	2.33413900	-2.71801800

H -0.67180700 1.38973800 -2.26845000

H -0.53680600 3.01069800 -1.58207700

O -1.90838000 1.56534300 0.16046300

S -3.00406700 0.60660500 -0.36028900

O -3.32367000 -0.37617100 0.60965600

O -2.79455900 0.24413300 -1.71817000

C -4.36598900 1.83834700 -0.33574600

F -5.47321500 1.23112900 -0.73989700

F -4.09657700 2.84378400 -1.15745400

F -4.54954200 2.31270200 0.88724200

H -0.25915100 -0.38334000 0.98968700

H -0.49622700 -0.62617400 -0.74476000

1-Fluoroadmantane

Electronic Energy: -489.864019142 Hartree

C 0.00000000 0.00000000 0.00000000

C -0.48547200 0.95602800 1.07059600

C -0.00021100 2.36134800 0.77832500

C 1.52753800 2.36607100 0.77739600

C 2.03473900 1.40639800 -0.29543800

C 1.52776900 -0.00316400 -0.00338600

C 2.03452500 -0.45253000 1.36418100

C 1.52719900 0.50524300 2.43863700

C -0.00049300 0.50666600 2.43392800

H -0.39182600 1.18482100 3.19647000

H -0.39173200 -0.49201300 2.64388000

C 2.03438700 1.91422100 2.14409600

H 3.12795600 1.92860400 2.16037600

H 1.69144500 2.60598400 2.91892400

H 1.88492200 0.18199200 3.41934700

H 1.69150200 -1.46942600 1.57583700

H 3.12808900 -0.47385400 1.36884600

H 1.88570500 -0.69082500 -0.77360600

H 1.69189000 1.73155900 -1.28197000

H 3.12830700 1.41321100 -0.31599200

H 1.88541400 3.37695700 0.56696900

H -0.39120500 2.68288100 -0.19028400

H -0.39139600 3.04248000 1.53828300

F -1.88447200 0.95600400 1.07052100

H -0.39112600 -0.99954100 0.20596200

H -0.39096700 0.31746800 -0.96995300

NO_2-C_6H_4-I(OTf)(F)

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

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