# Supplementary information

# Synthesis of Biphenyl Iodonium Salts as (Radio)labelling Precursors for Fluoroarenes

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**Overview of synthesized diaryliodonium salts and their color**

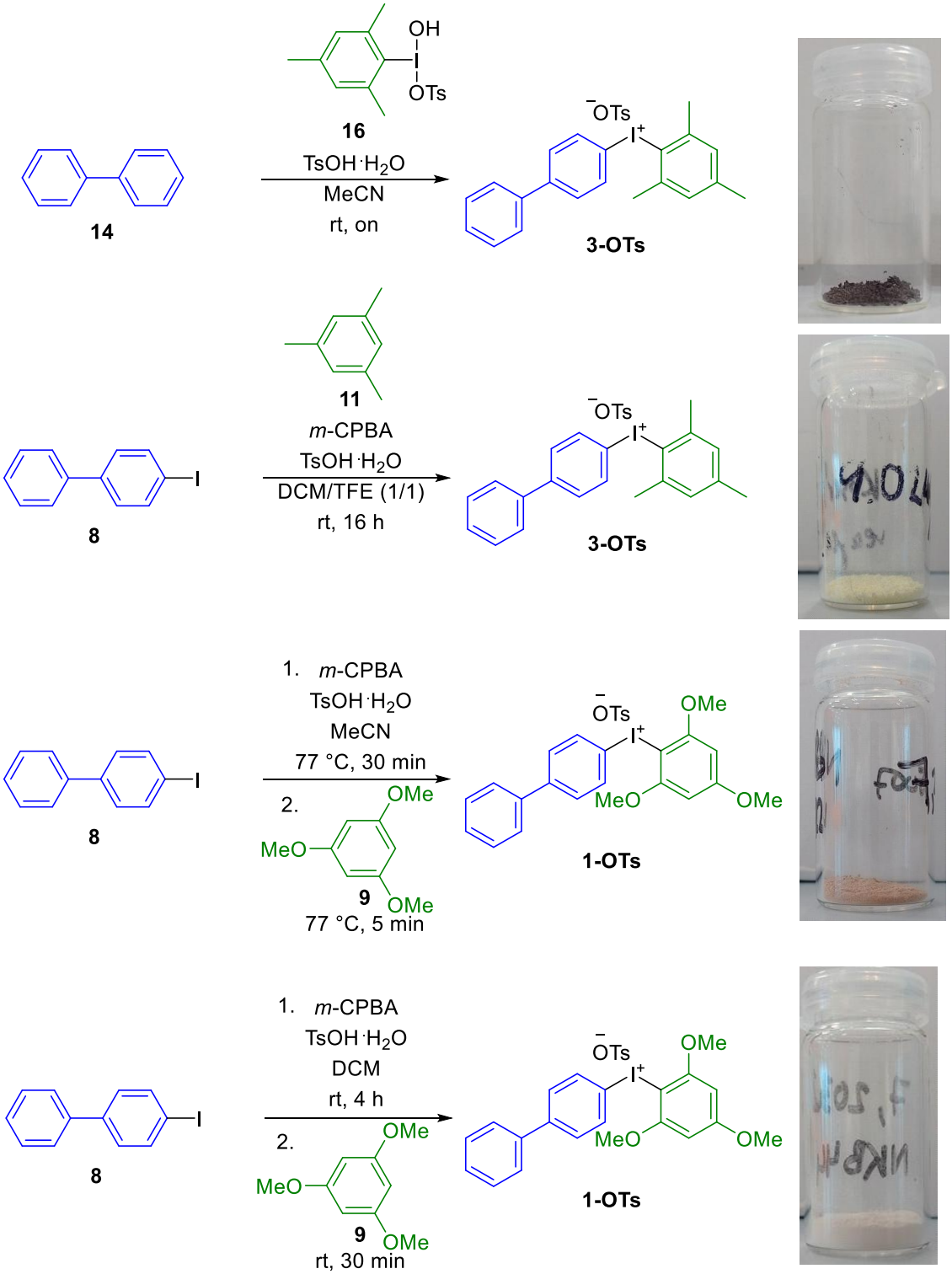


**Figure S1:** Overview of synthesized diaryliodonium salts and their color.

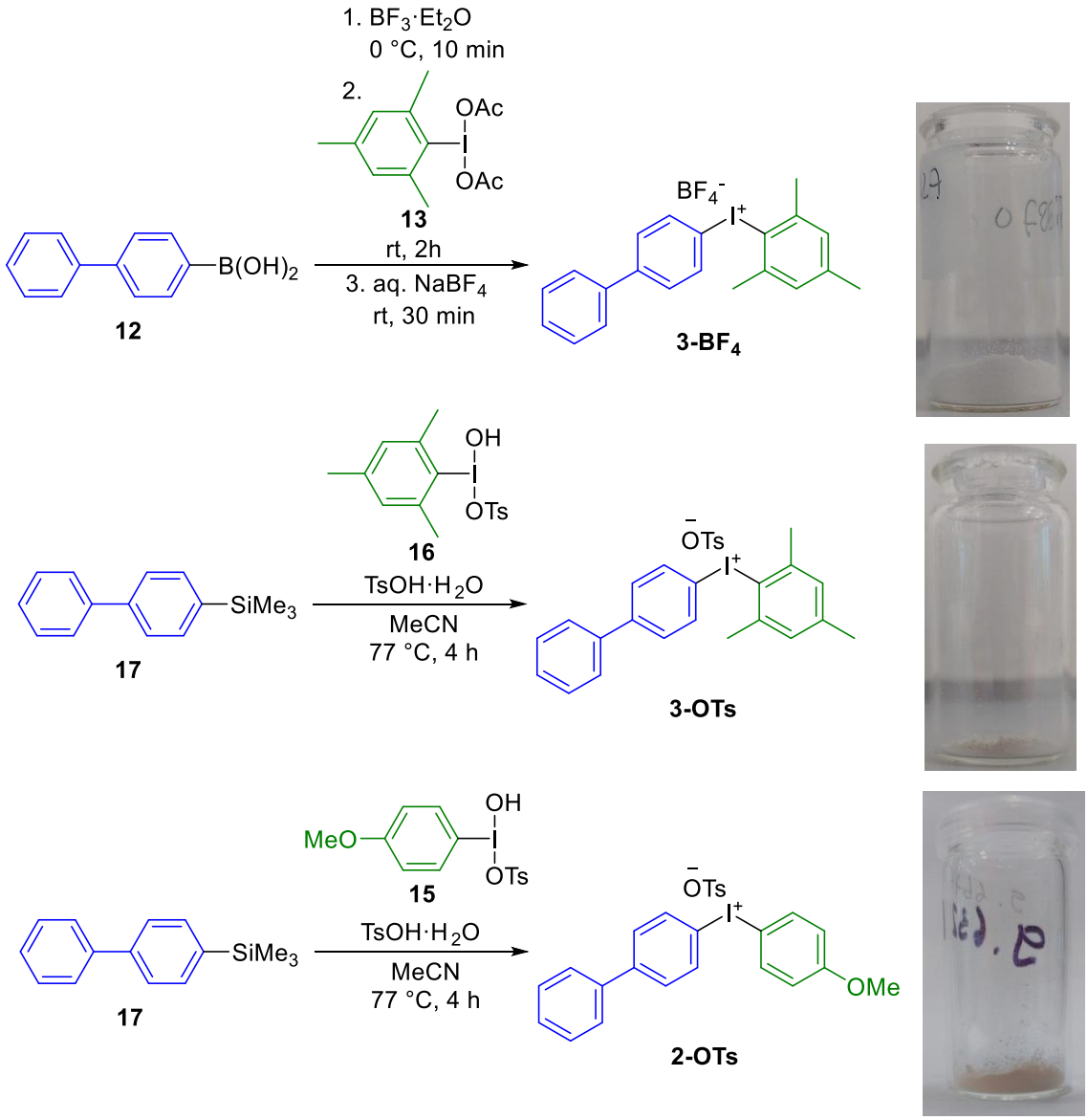


**Figure S1 (continued):** Overview of synthesized diaryliodonium salts and their color.

## Analytical spectra of synthesized compounds

Analytical spectra of compound **1-OTs**

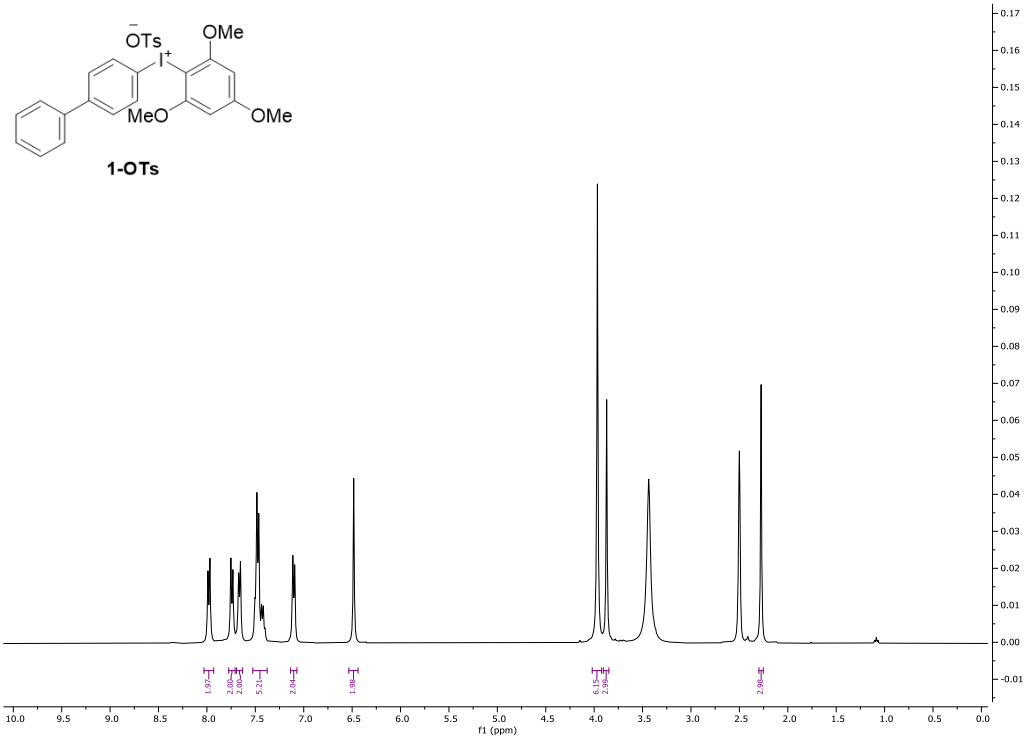


**Figure S2.** $^{1}$H NMR spectrum (DMSO-$d_6$, 400 MHz) of compound **1-OTs** (Method A).

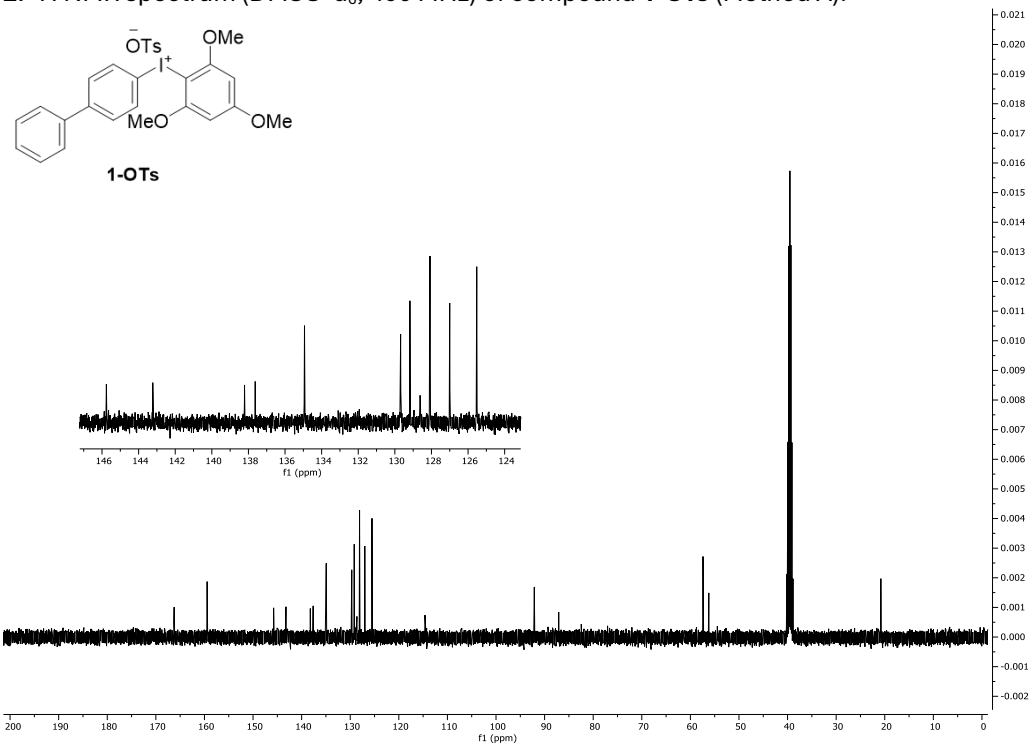


**Figure S3.** $^{13}$C NMR (DMSO-$d_6$, 101 MHz) of compound **1-OTs** (Method A).

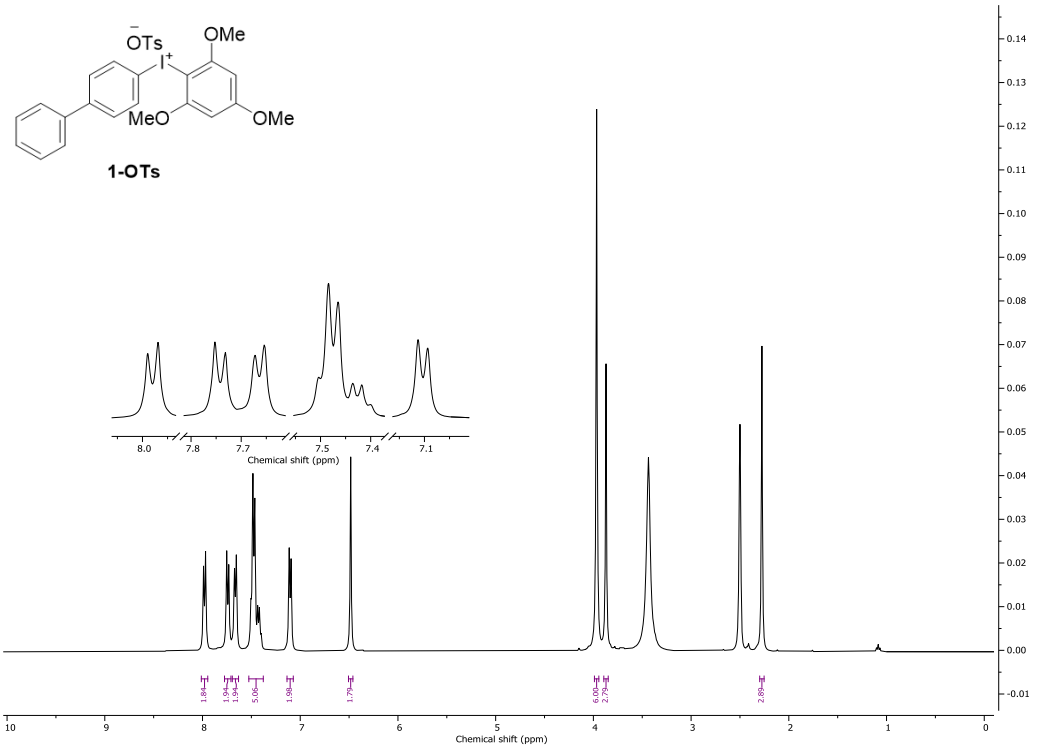


**Figure S4.** $^{1}$H NMR spectrum (DMSO-$d_6$, 400 MHz) of compound **1-OTs** (Method B).

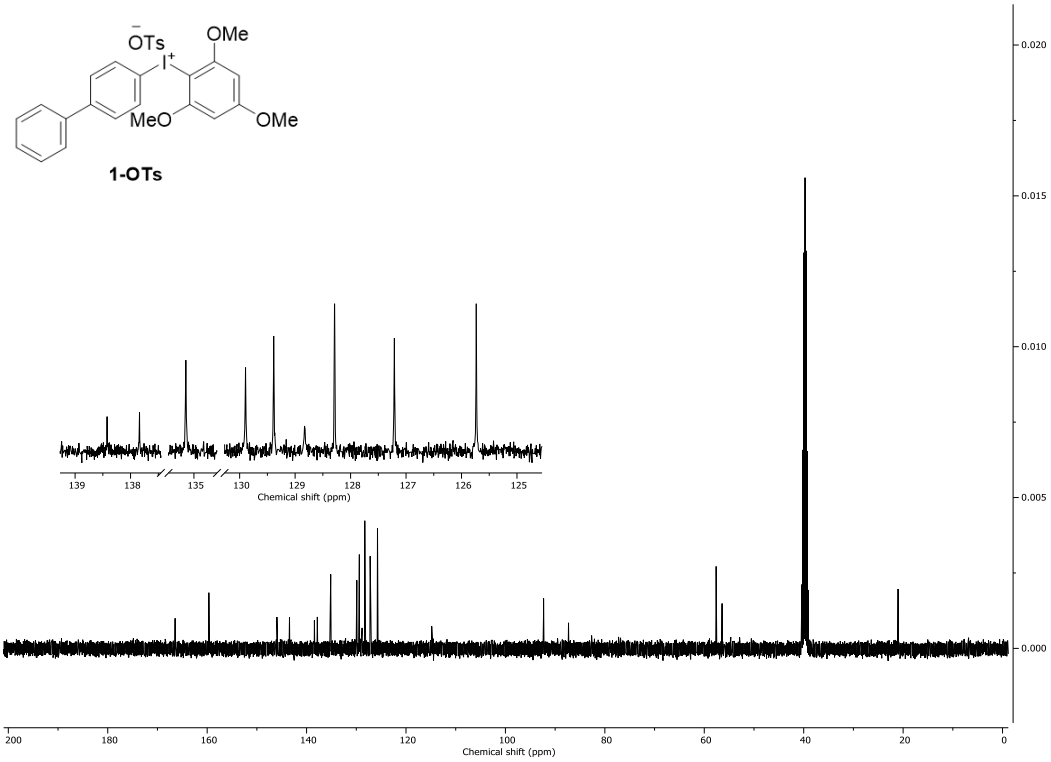


**Figure S5.** $^{13}$C NMR (DMSO-$d_6$, 101 MHz) of compound **1-OTs** (Method B).

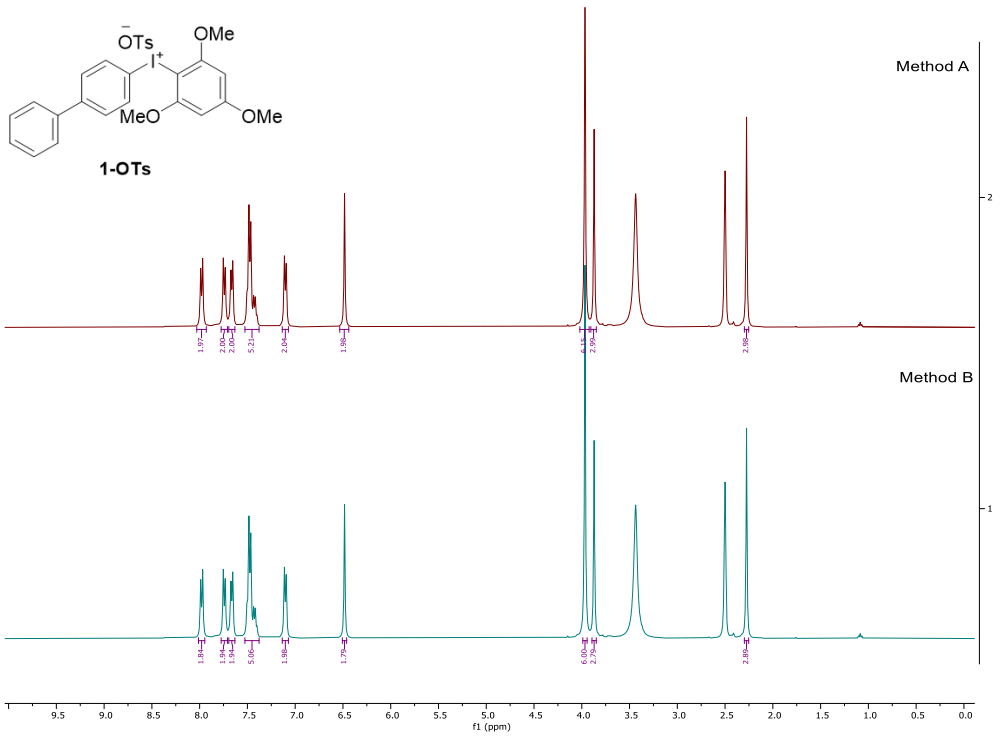


**Figure S6.** Overlay of $^{1}$H NMR spectra (DMSO-$d_6$, 400 MHz) of compound **1-OTs** prepared *via* different methods (Method A: red, top, red; Method B: blue, bottom).

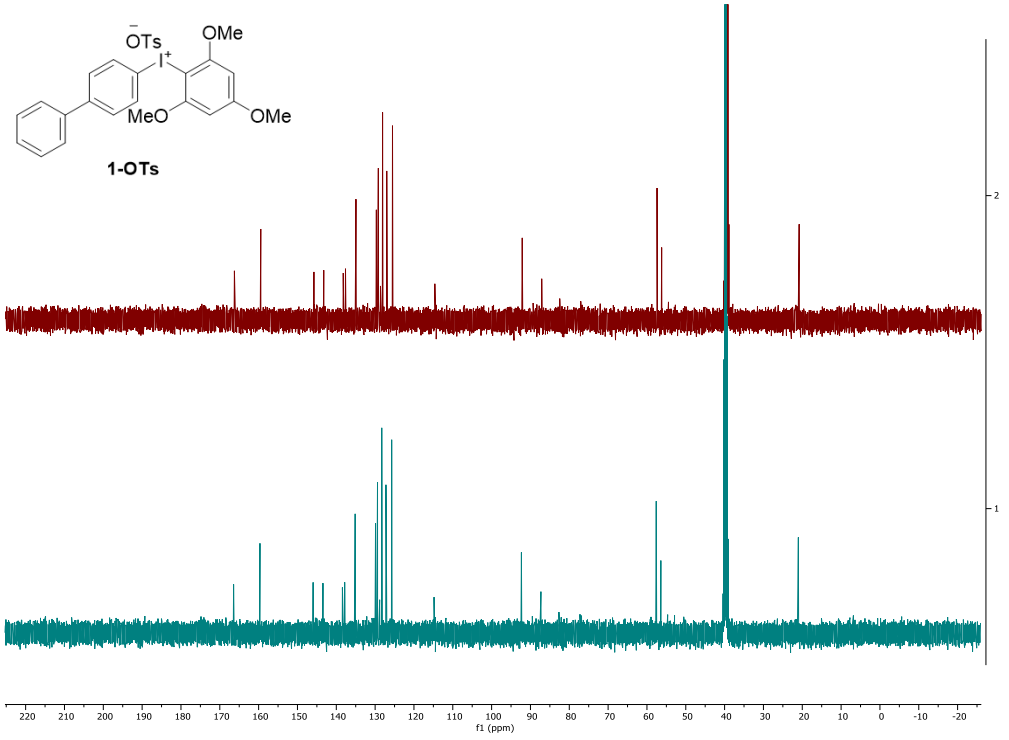


**Figure S7.** Overlay of $^{13}$C NMR spectra (DMSO-$d_6$, 101 MHz) of compound **1-OTs** prepared *via* different methods (Method A: red, top, red; Method B: blue, bottom).

Analytical spectra of compound **2-OTs**

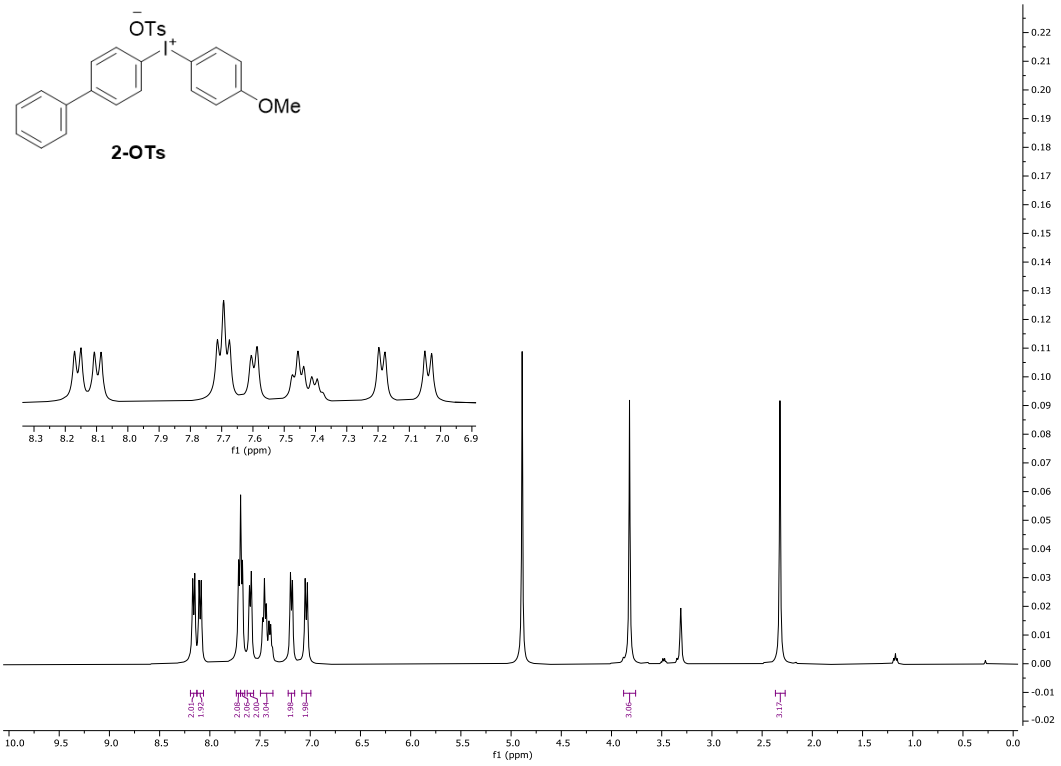


**Figure S8.** $^{1}$H NMR spectrum ($CD_3OD$, 400 MHz) of compound **2-OTs**.

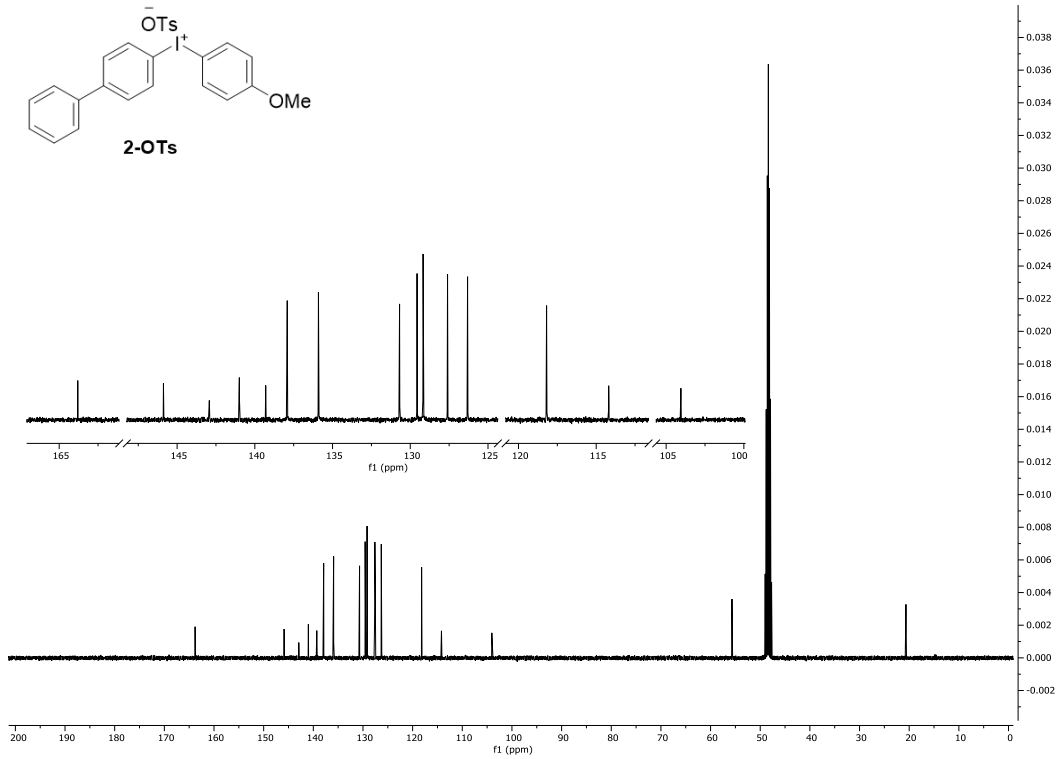


**Figure S9.** $^{13}$C NMR (DMSO-$d_6$, 101 MHz) of compound **2-OTs**.

Analytical spectra of compound **3-OTs**

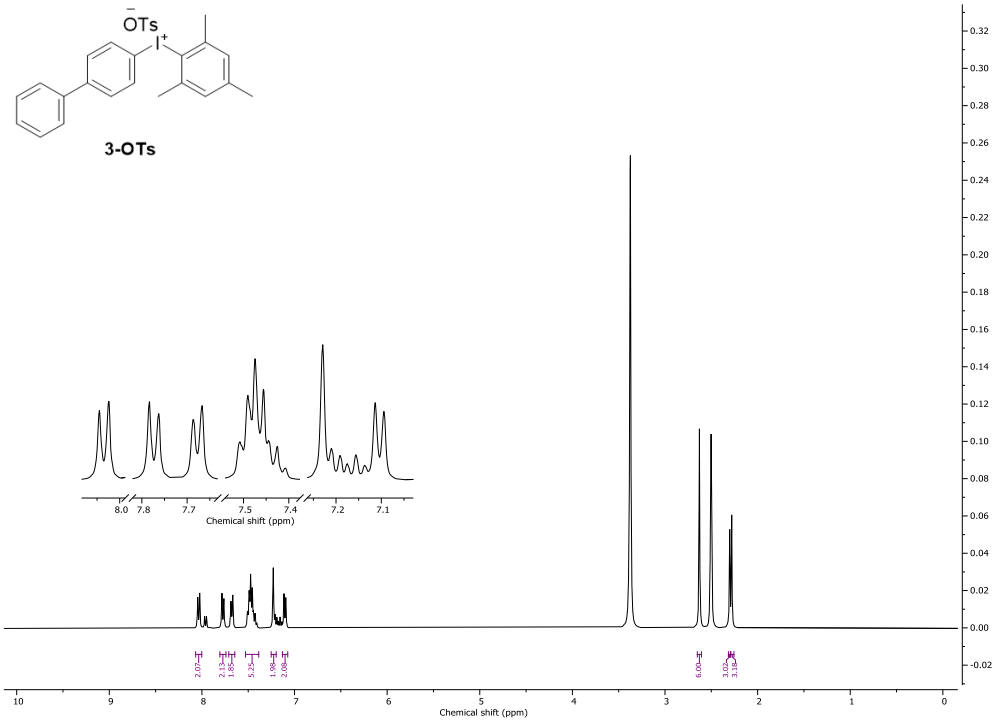


**Figure S10.** $^{1}$H NMR spectrum (DMSO-$d_6$, 400 MHz) of compound **3-OTs** (Method C).

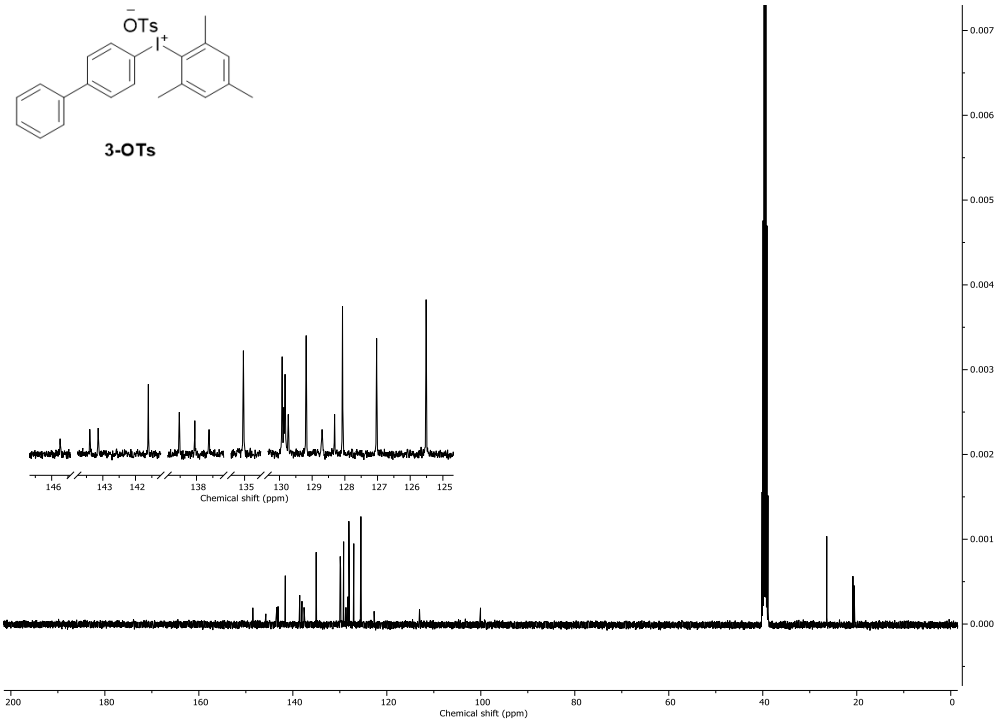


**Figure S11.** $^{13}$C NMR spectrum (DMSO-$d_6$, 101 MHz) of compound **3-OTs** (Method C).

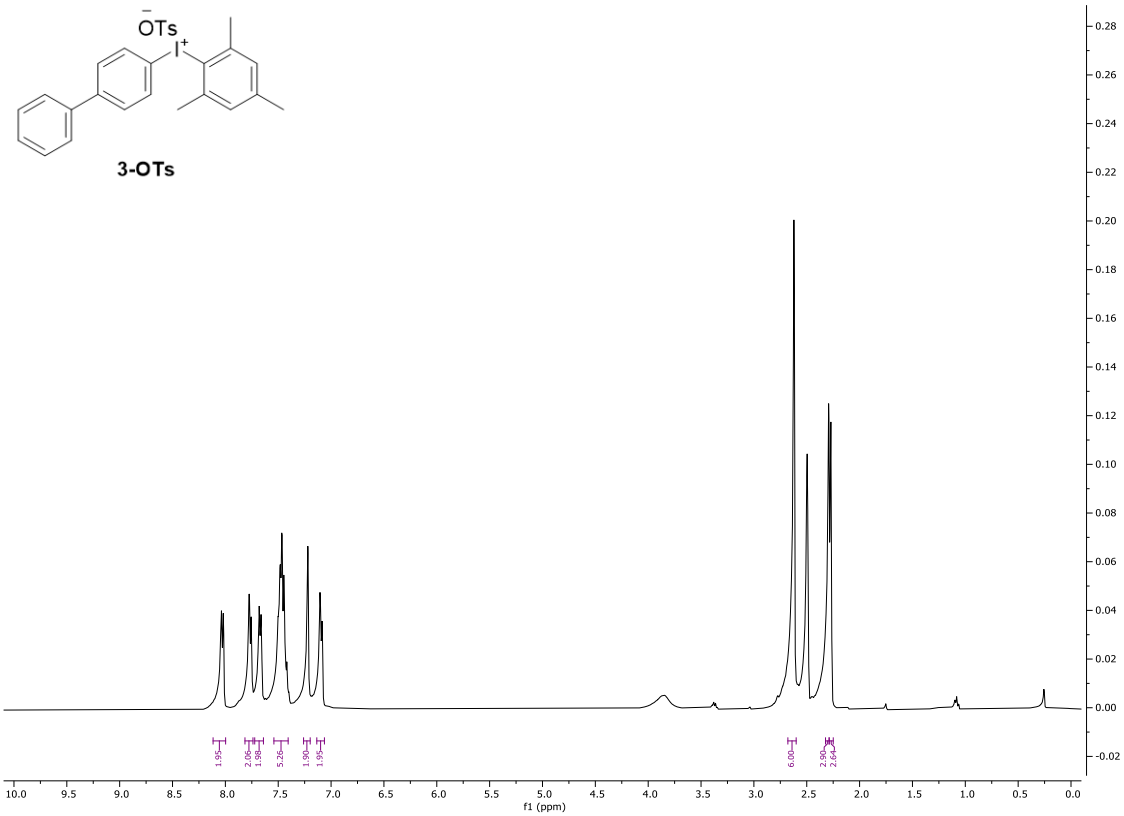


**Figure S12.** $^{1}$H NMR spectrum (DMSO-$d_6$, 400 MHz) of compound **3-OTs** (Method D).

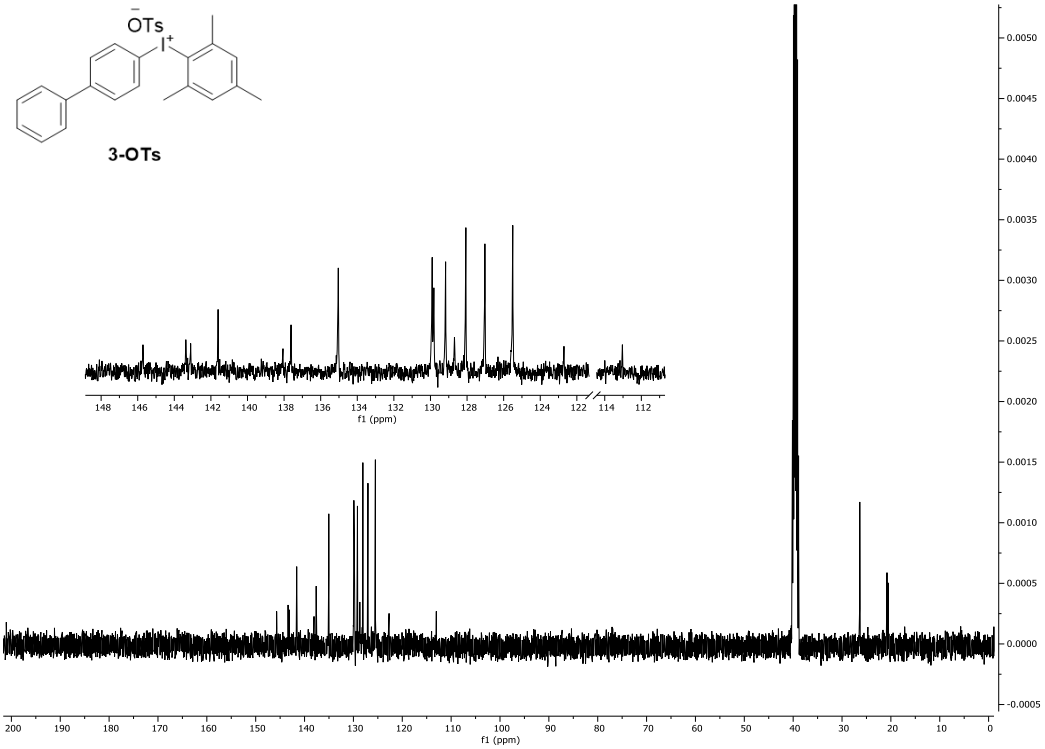


**Figure S13.** $^{13}$C NMR spectrum (DMSO-$d_6$, 101 MHz) of compound **3-OTs** (Method D).

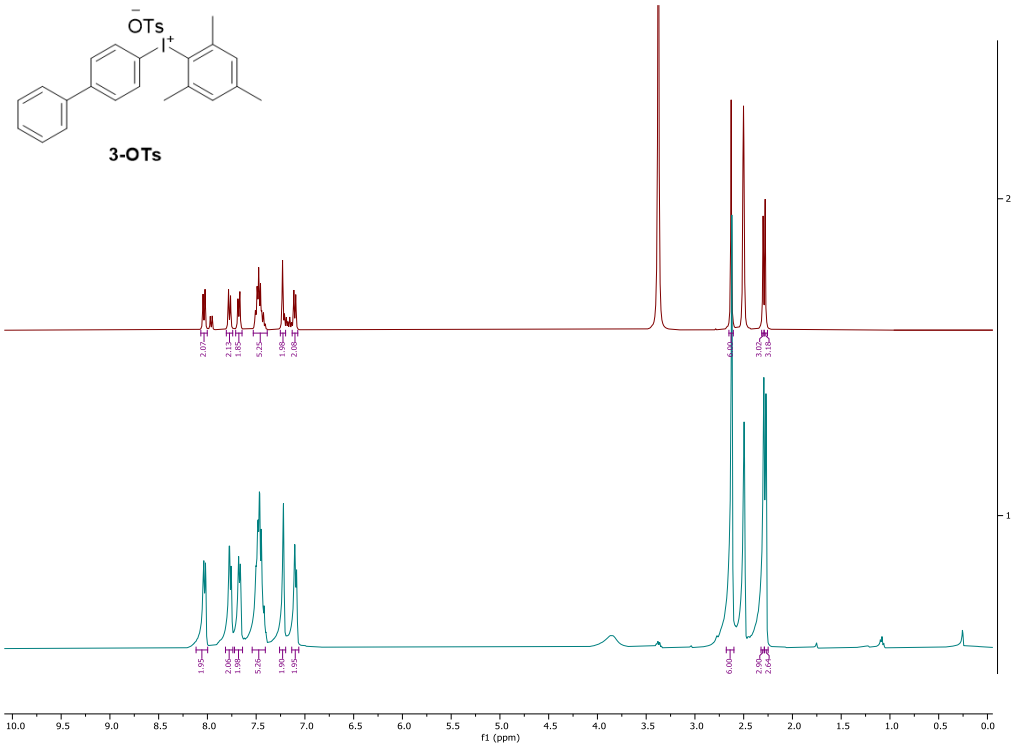


**Figure S14.** Overlay of $^{1}$H NMR spectra (DMSO-$d_6$, 400 MHz) of compound **3-OTs** prepared *via* different methods (Method C: red, top, red; Method D: blue, bottom).

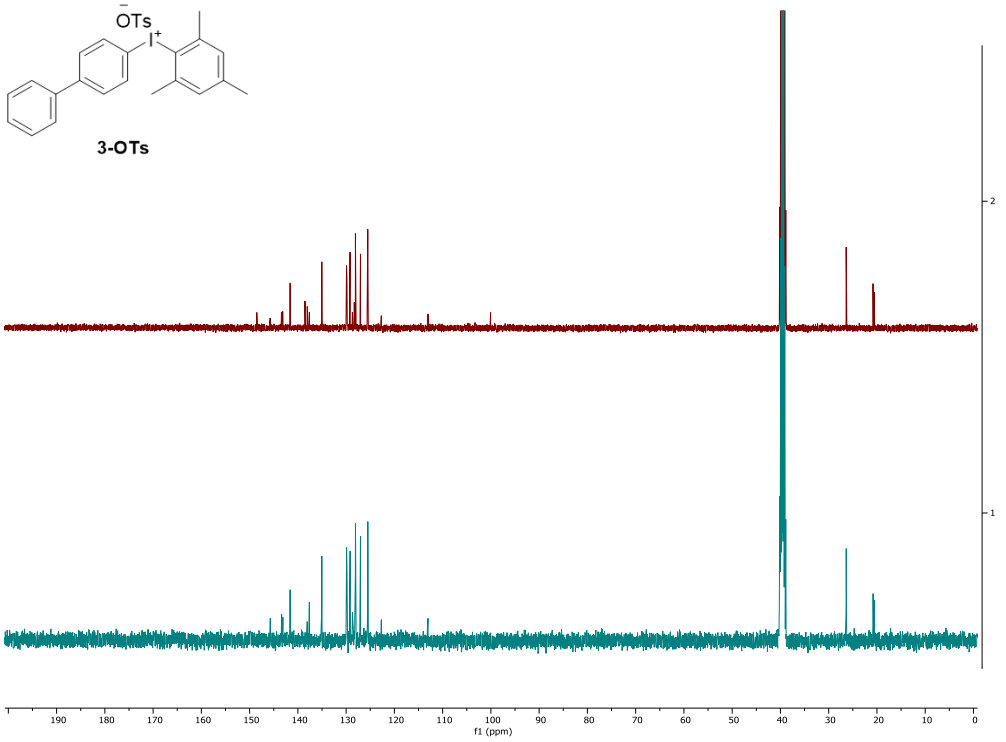


**Figure S15.** Overlay of $^{13}$C NMR spectra (DMSO-$d_6$, 101 MHz) of compound **3-OTs** prepared *via* different methods (Method C: red, top, red; Method D: blue, bottom).

Analytical spectra of compound **3-$BF_4$**

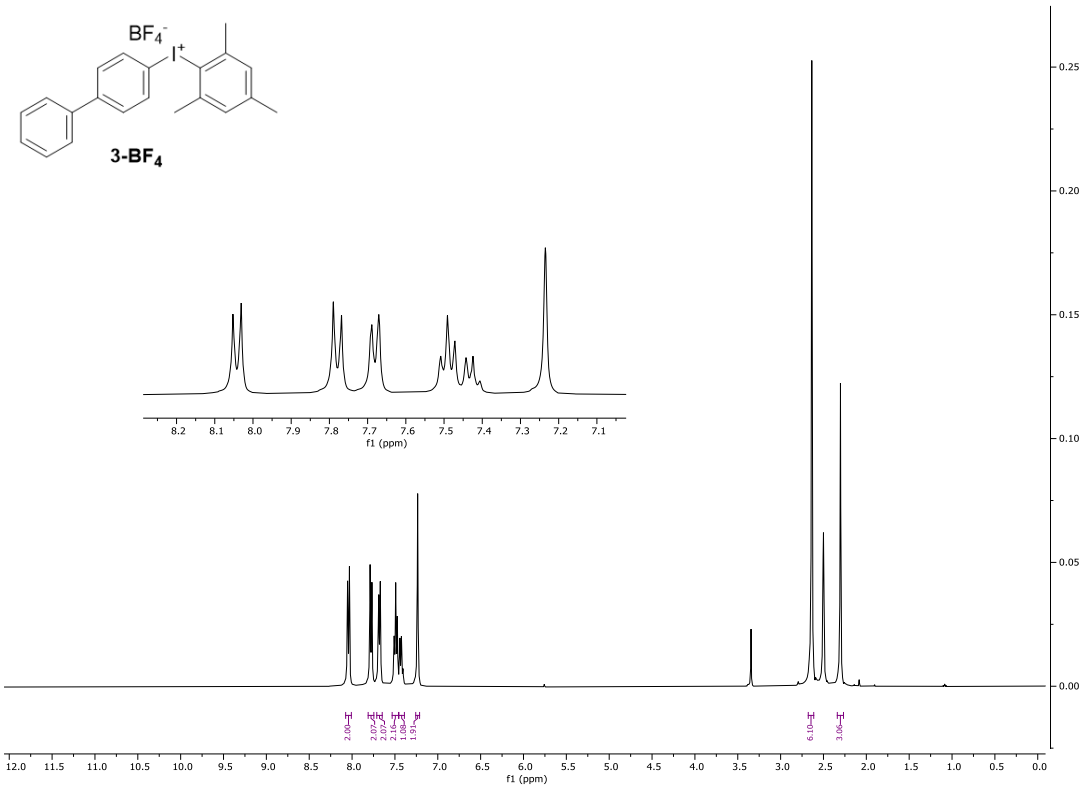


**Figure S16.** $^{1}$H NMR spectrum (DMSO-$d_6$, 400 MHz) of compound **3-$BF_4$**.

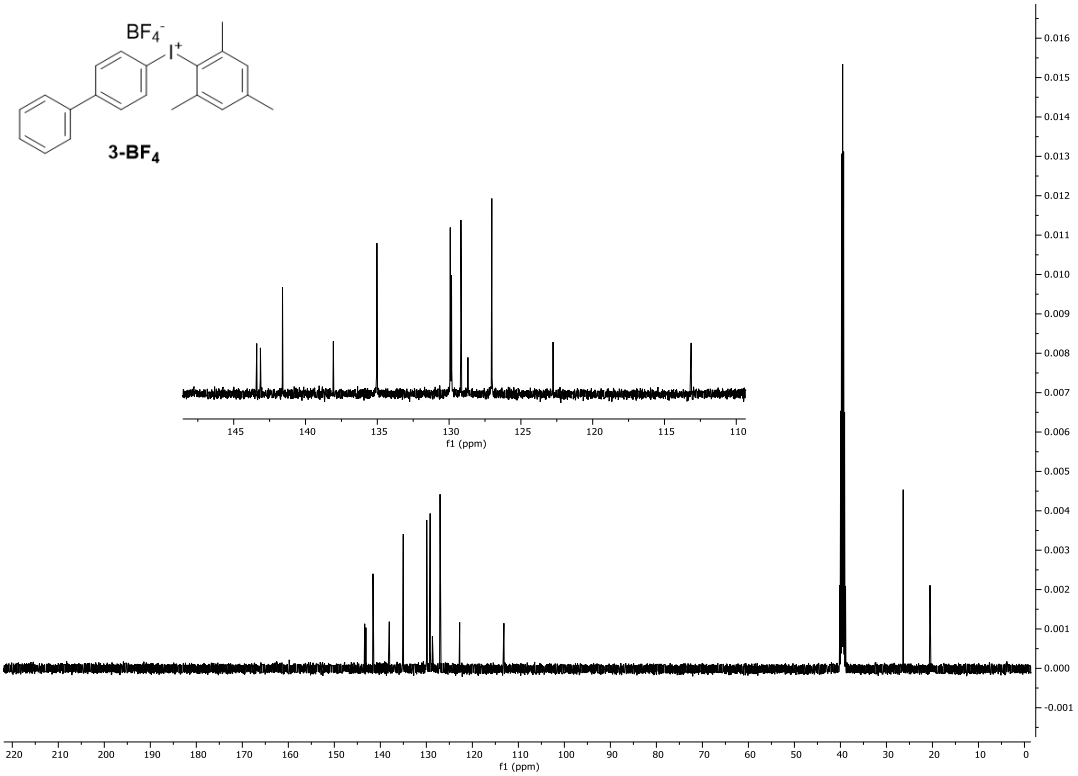


**Figure S17.** $^{13}$C NMR spectrum (DMSO-$d_6$, 101 MHz) of compound **3-$BF_4$**.


**Figure S18.** $^{19}F$ NMR spectrum (DMSO-$d_6$, 376 MHz) of compound **3-$BF_4$**. The observed splitting in $^{19}F$ NMR is due to the $^{11}B/^{10}B$ isotope effects.

Analytical spectra of compound **13**

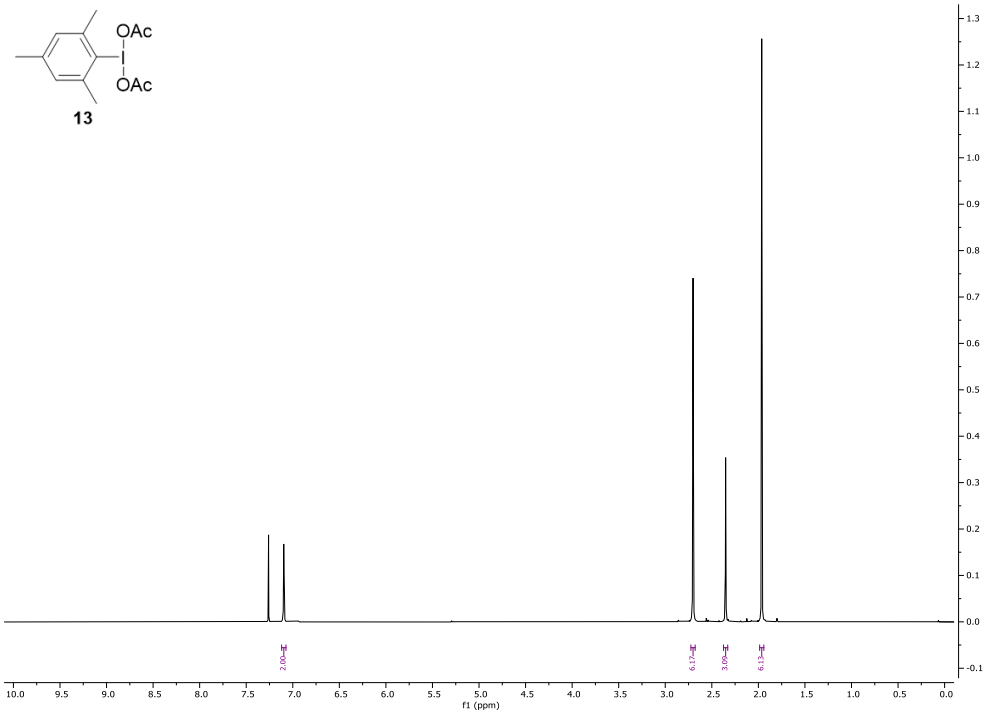


**Figure S19:** $^{1}H$ NMR spectrum ($CDCl_3$, 400 MHz) of compound **13**.

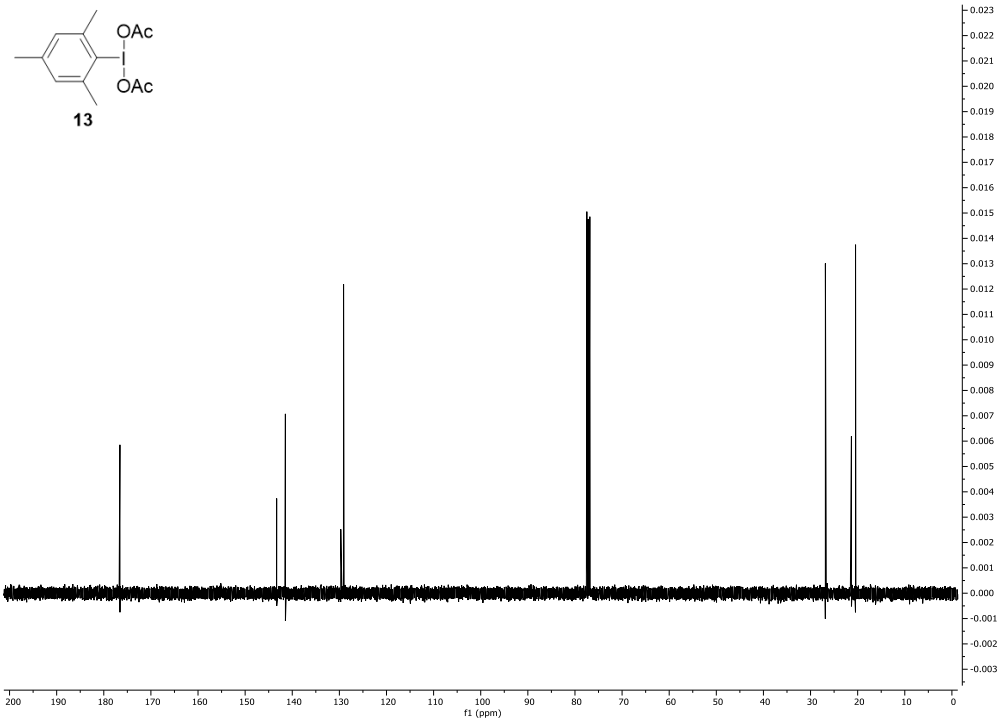


**Figure S20**: $^{13}C$ NMR spectrum ($CDCl_3$, 101 MHz) of compound **13**.

Analytical spectra of compound **15**

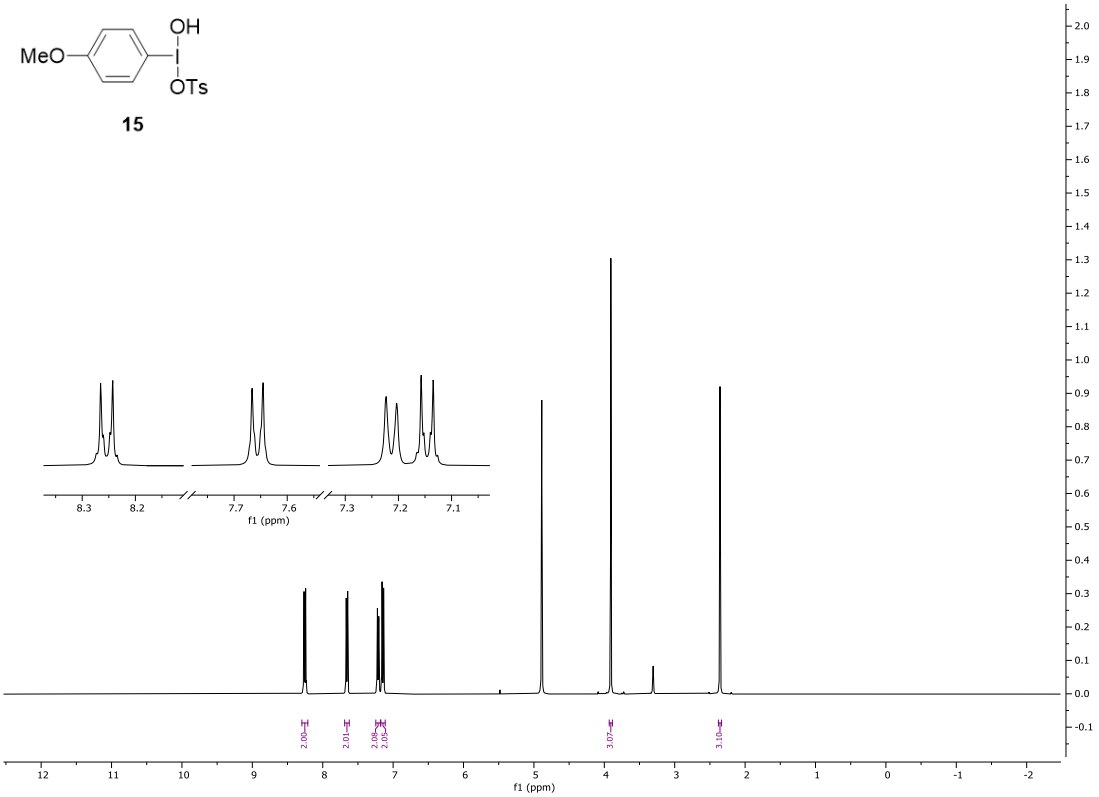


**Figure S21:** $^{1}H$ NMR spectrum ($CD_3OD$, 400 MHz) of compound **15**.

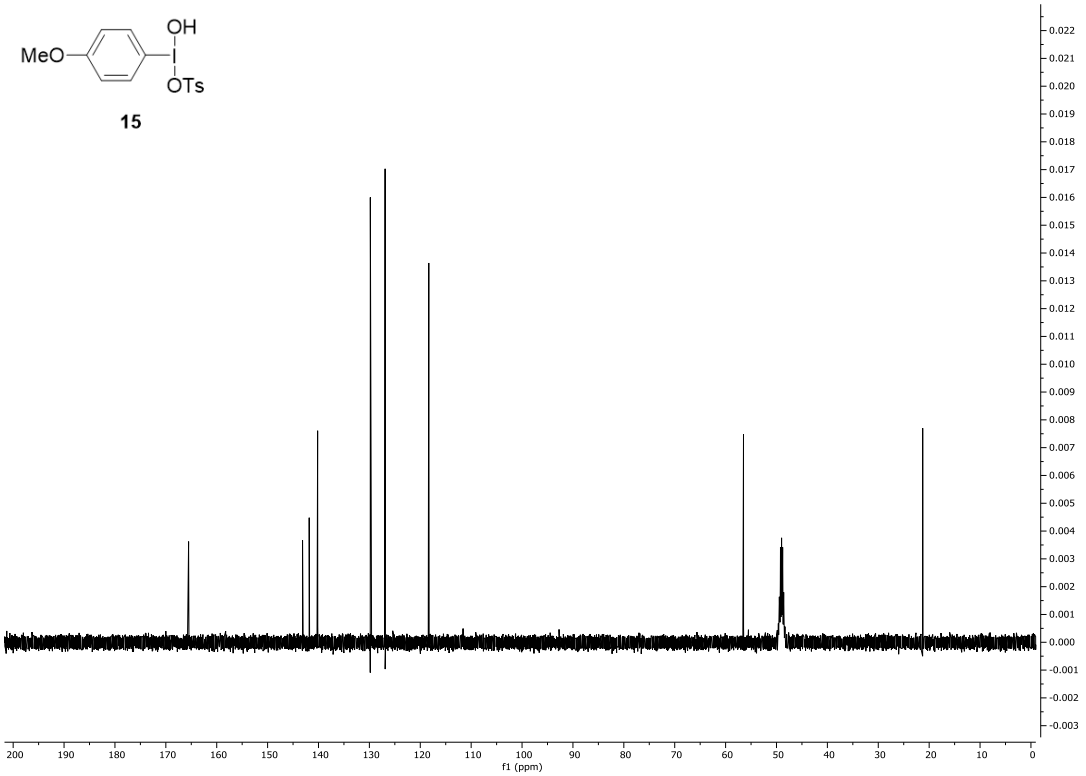


**Figure S22**: $^{13}C$ NMR spectrum ($CD_3OD$, 101 MHz) of compound **15**.

Analytical spectra of compound **16**

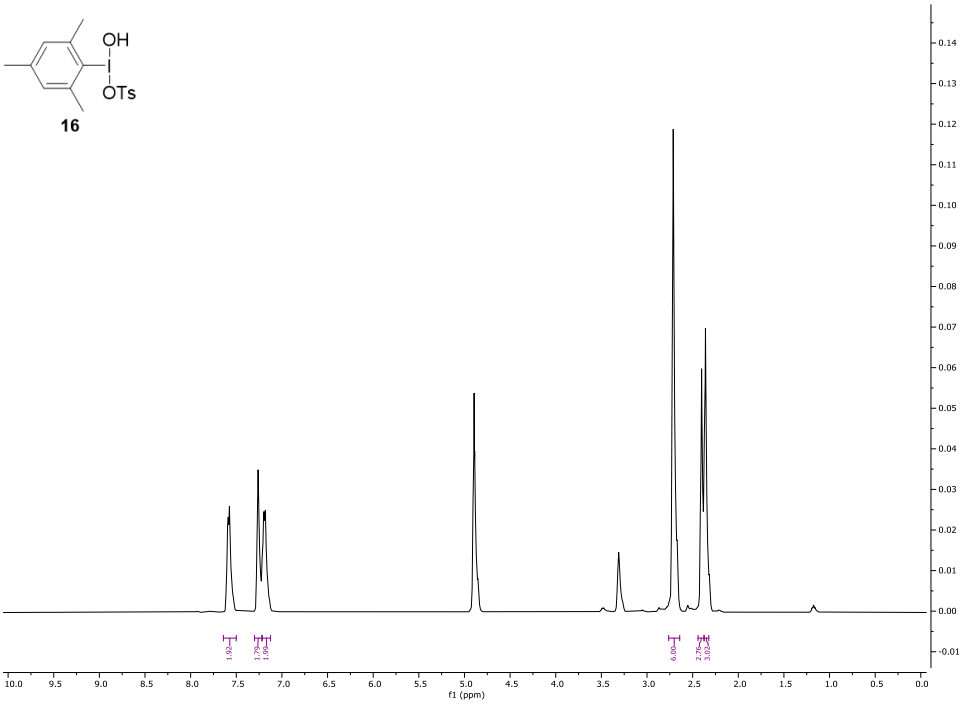


**Figure S23:** $^{1}H$ NMR spectrum ($CD_3OD$, 400 MHz) of compound **16**.

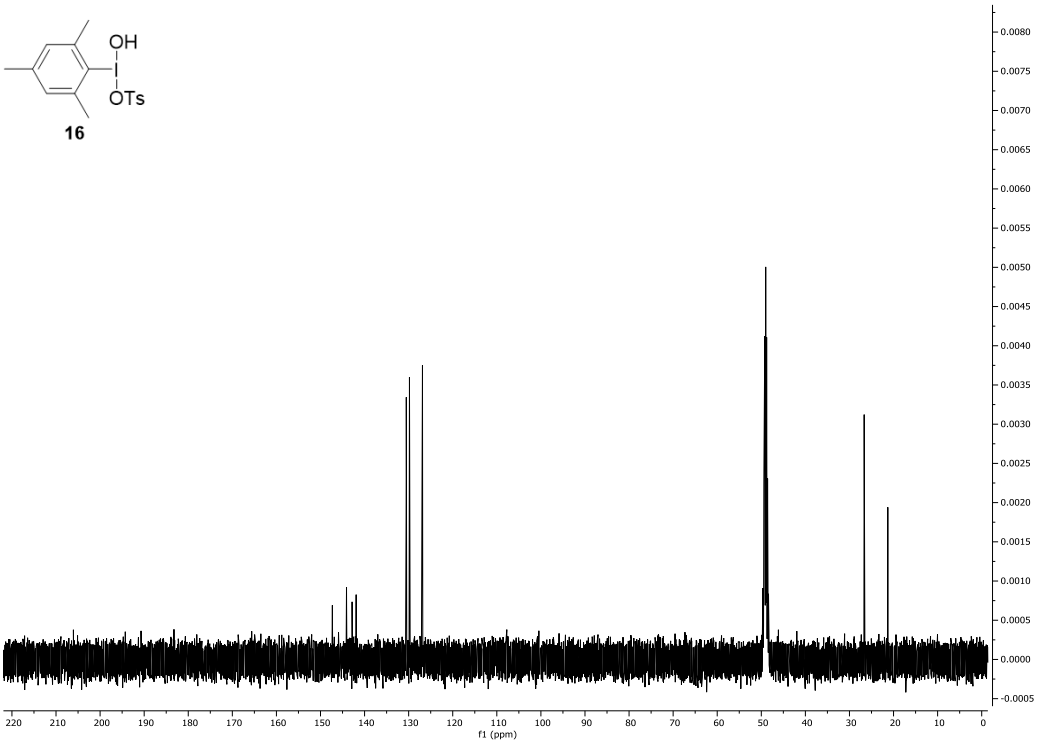


**Figure S24**: $^{13}C$ NMR spectrum ($CD_3OD$, 101 MHz) of compound **16**.

Analytical spectra of compound **17**

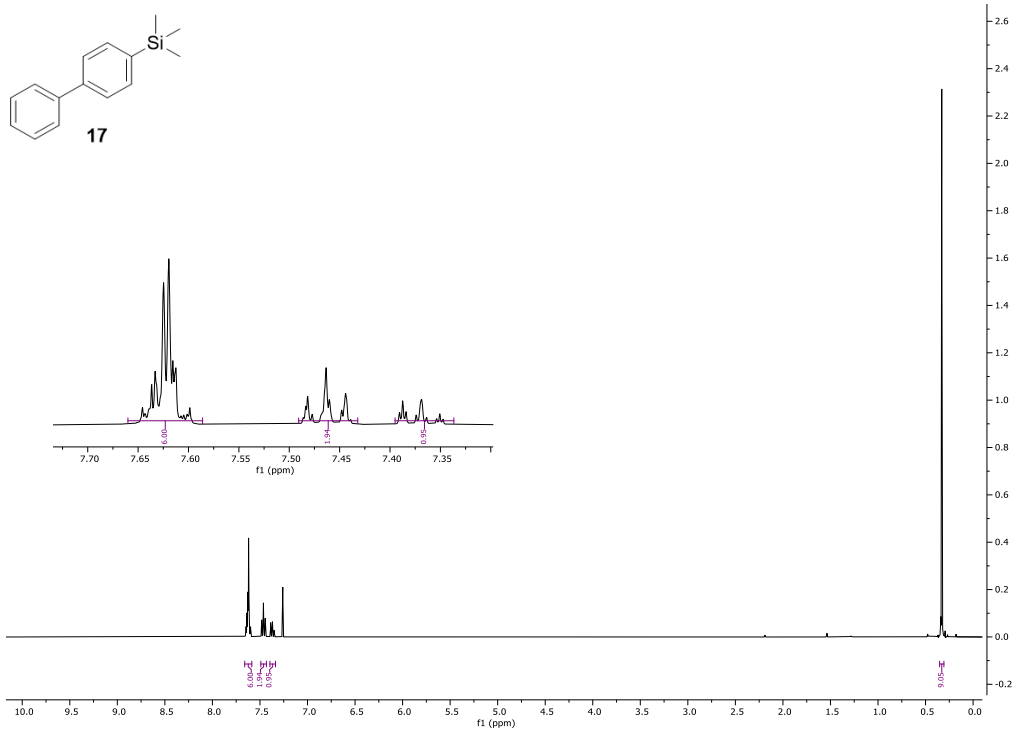


**Figure S25:** $^{1}H$ NMR spectrum ($CDCl_3$, 400 MHz) of compound **17**.

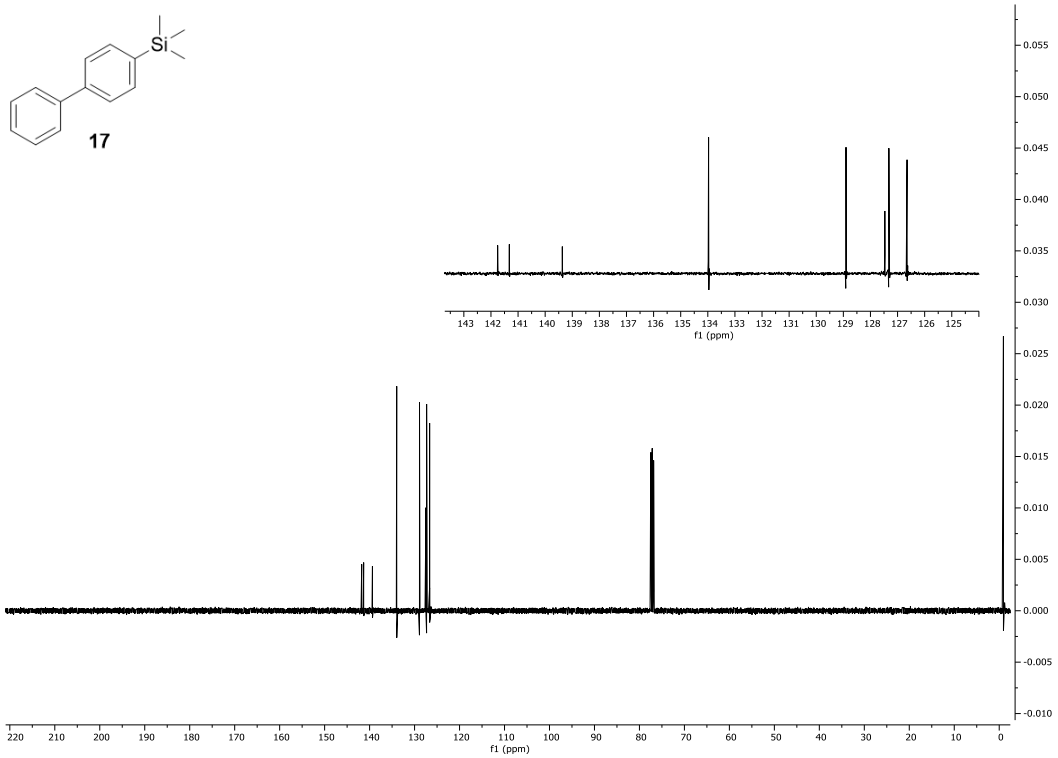


**Figure S26**: $^{13}C$ NMR spectrum ($CDCl_3$, 101 MHz) of compound **17**.

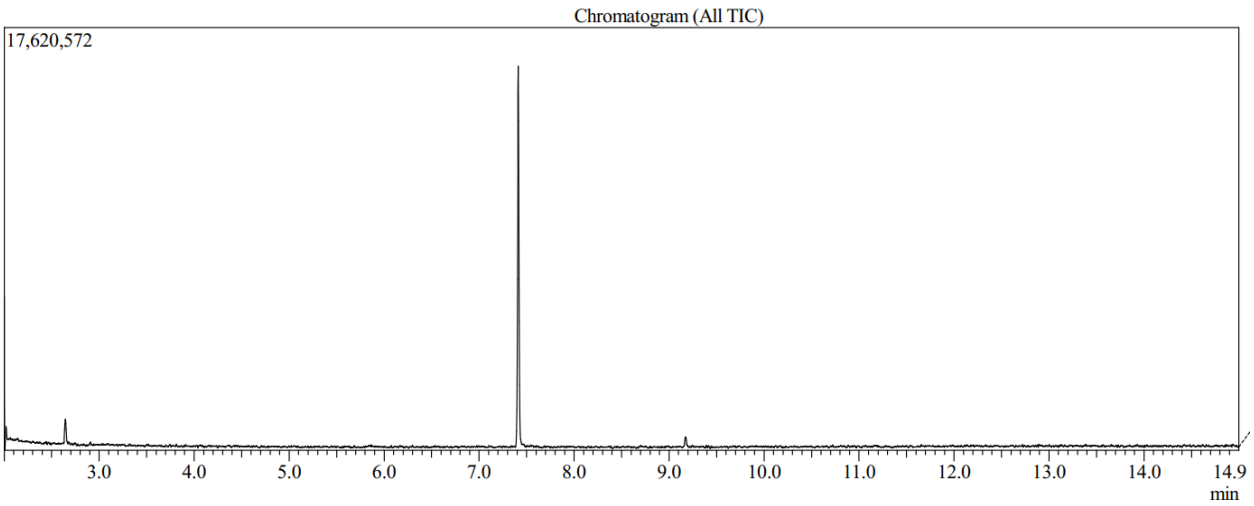


**Figure S27**: GC-MS chromatrogram of compound **17**.

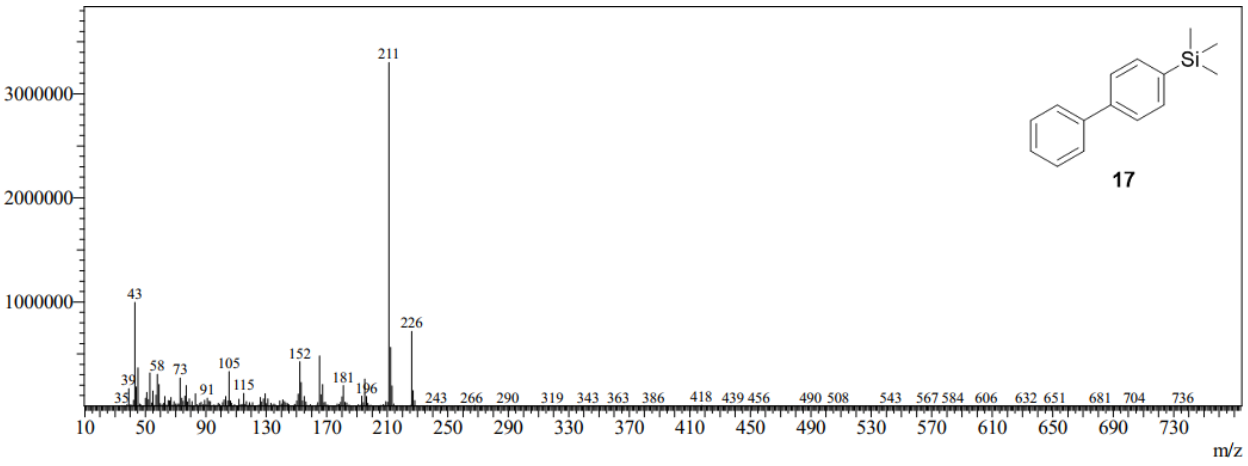


**Figure S28**: MS spectrum of compound **17** (7.4 min). Calculated mass for $C_{15}H_{18}Si^{+}$ = 226.

**Degradation studies of Koser intermediate 15**

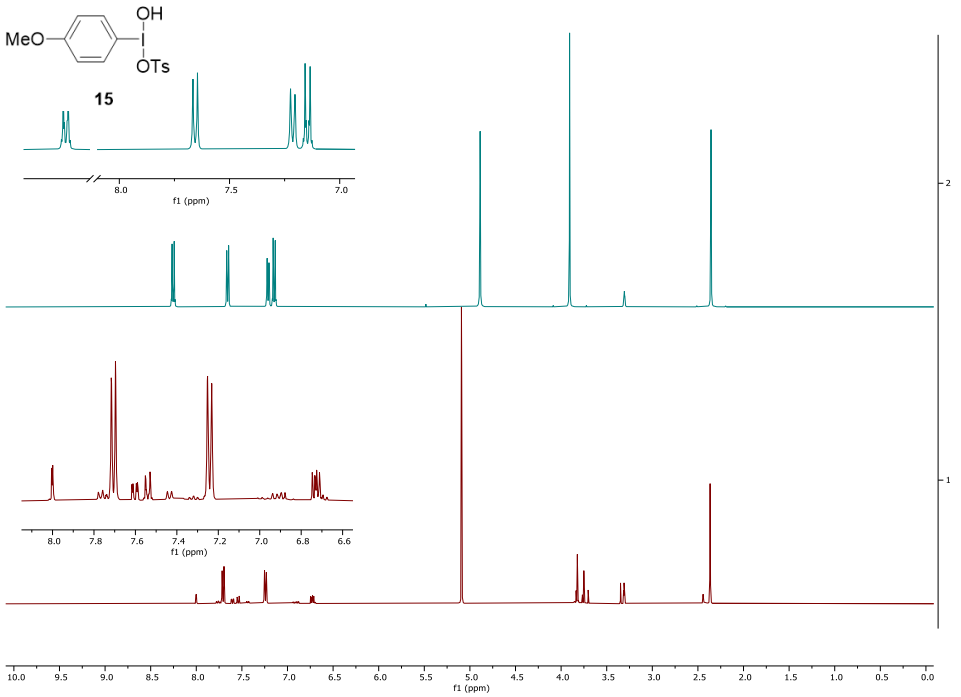


**Figure S29:** $^{1}$H NMR spectrum ($CD_3OD$, 400 MHz) of compound **15** directly after isolation (blue, top) and degraded after 20 minutes upon isolation as a solid (red, bottom).

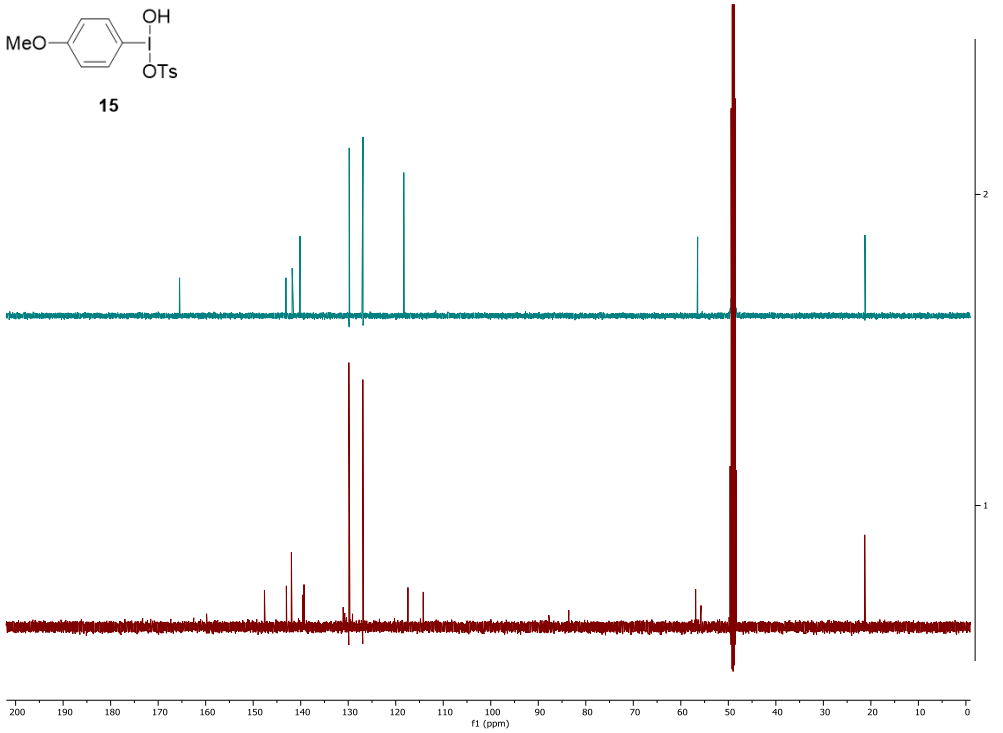


**Figure S30:** $^{13}$C NMR spectrum ($CD_3OD$, 101MHz) of compound **15** directly after isolation (blue, top) and degraded after 20 minutes upon isolation as a solid (red, bottom).

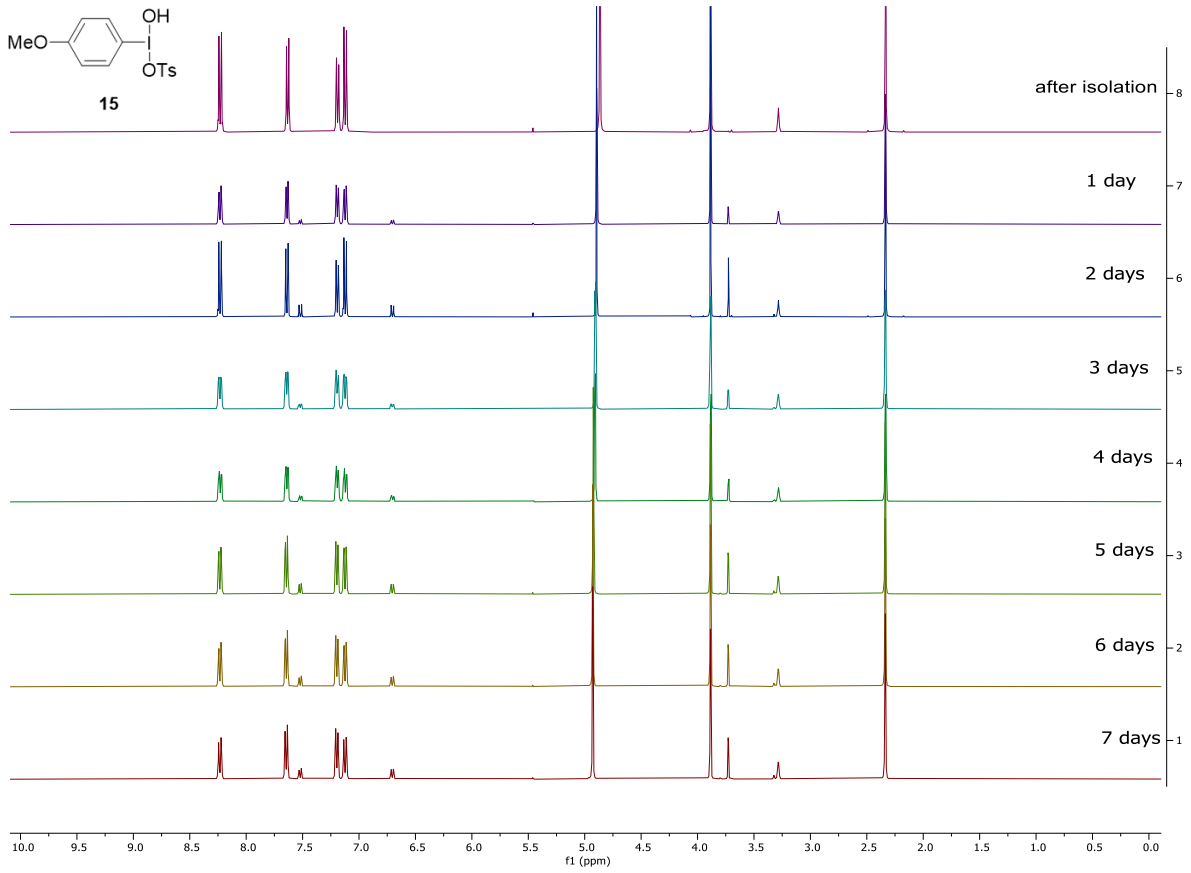


**Figure S31:** $^{1}$H NMR spectrum ($CD_3OD$, 400 MHz) of compound **15** directly after isolation (purple, top) and stored in $CD_3OD$ at room temperature over several days (1 day – 7 days, top to bottom). In solution degradation is slowed down with respect to storage as isolated solid (Figure S25).

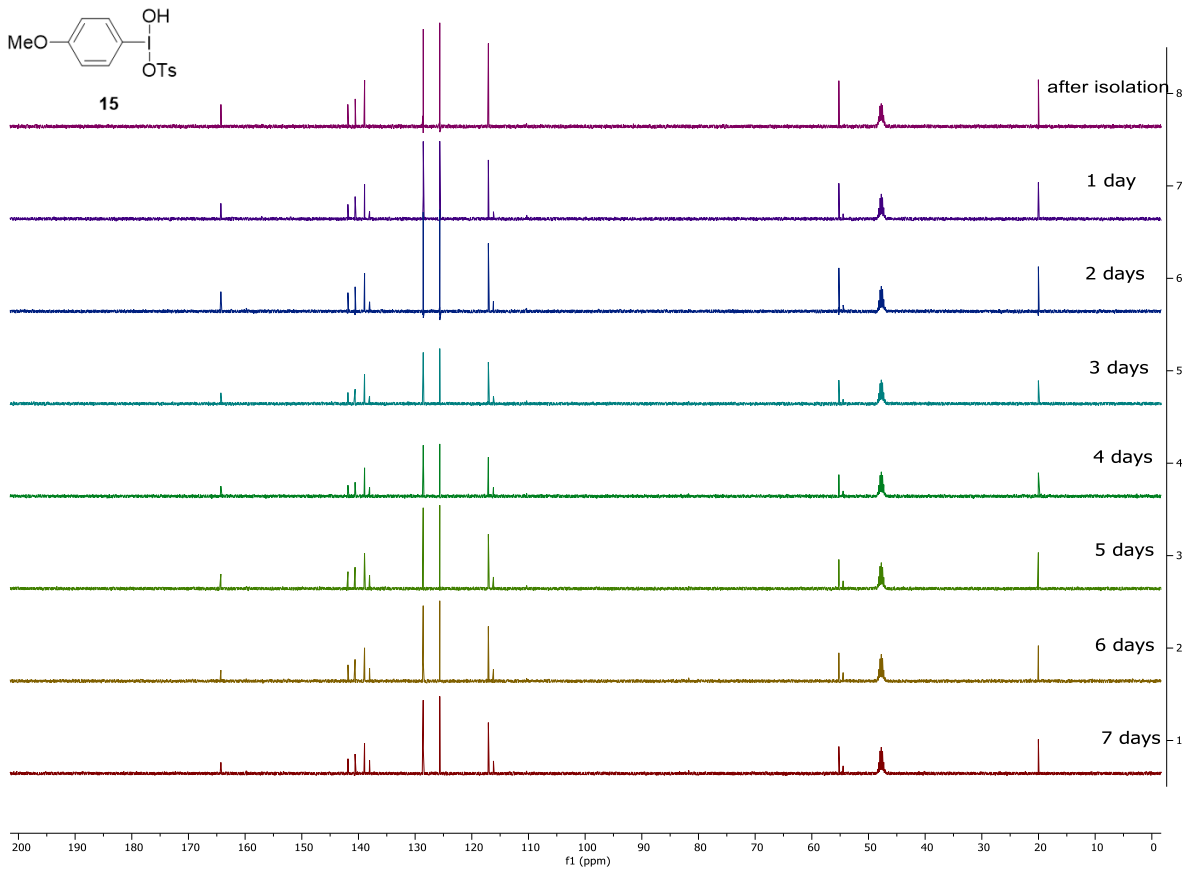


**Figure S32:** $^{13}C$ NMR spectrum ($CD_3OD$, 101 MHz) of compound **15** directly after isolation (purple, top) and stored in $CD_3OD$ at room temperature over several days (1 day – 7 days, top to bottom). In solution degradation is slowed down with respect to storage as isolated solid (Figure S26).

**Fluorination reactions using synthesized diaryliodonium salts 2-OTs and 3-OTs**

Method A (overnight fluorination of **3-OTs**)

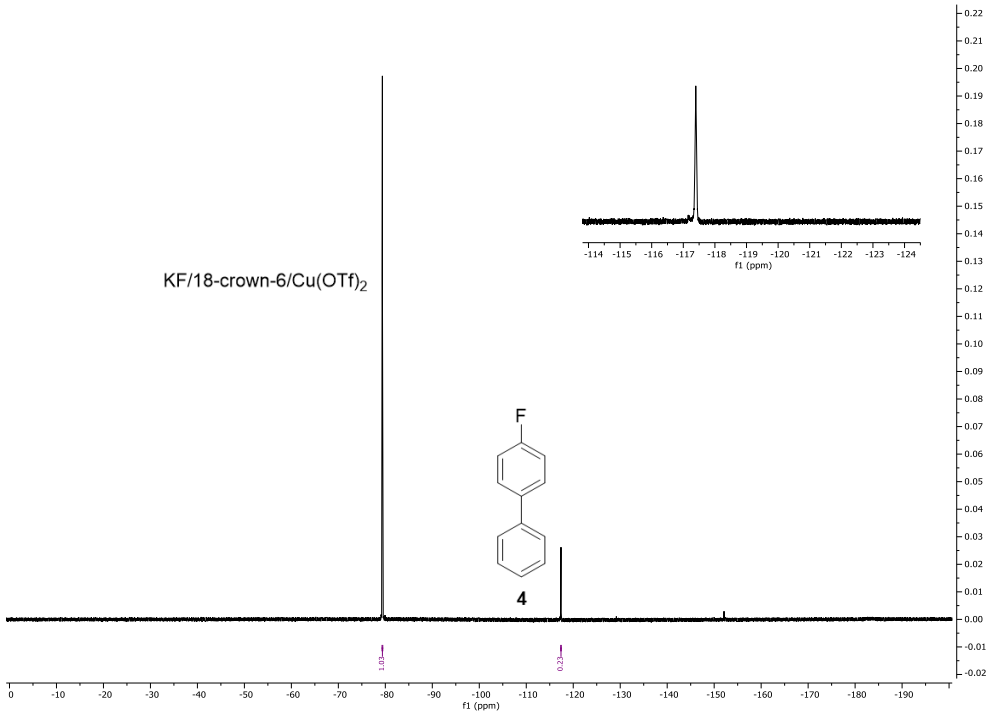


**Figure S33:** $^{19}$F NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude overnight fluorination reaction using diaryliodonium salt **3-OTs** (Method A).

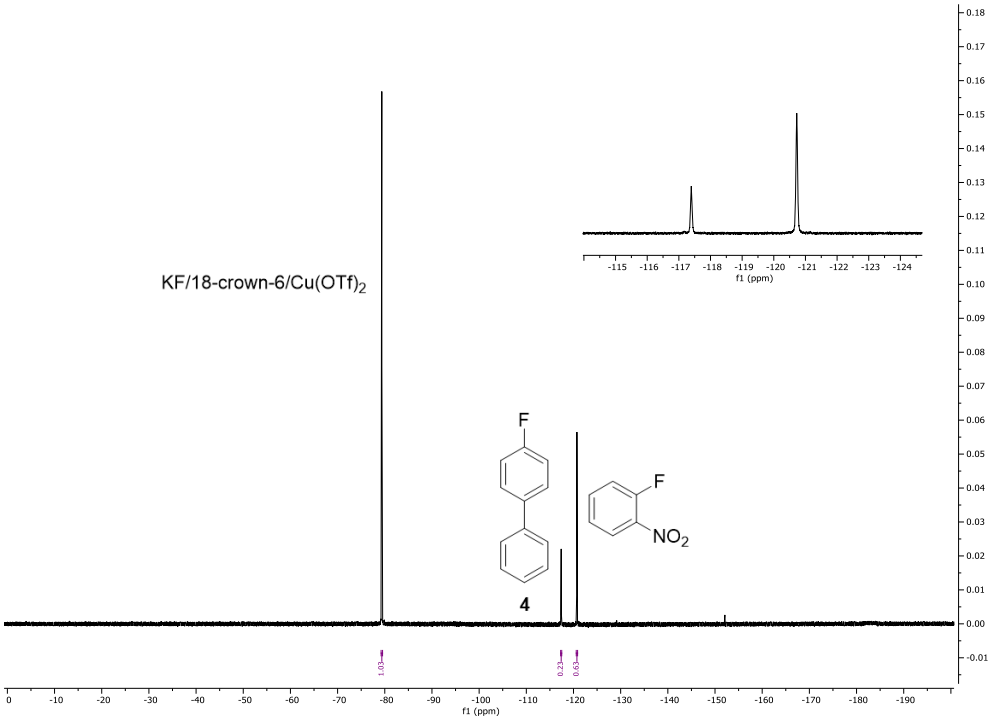


**Figure S34:** $^{19}$F NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude overnight fluorination reaction using diaryliodonium salt **3-OTs** (Method A) with added 1-fluoro-2-nitrobenzene (2.6 µL, 25 µmol, 0.5 equiv.) as internal standard.

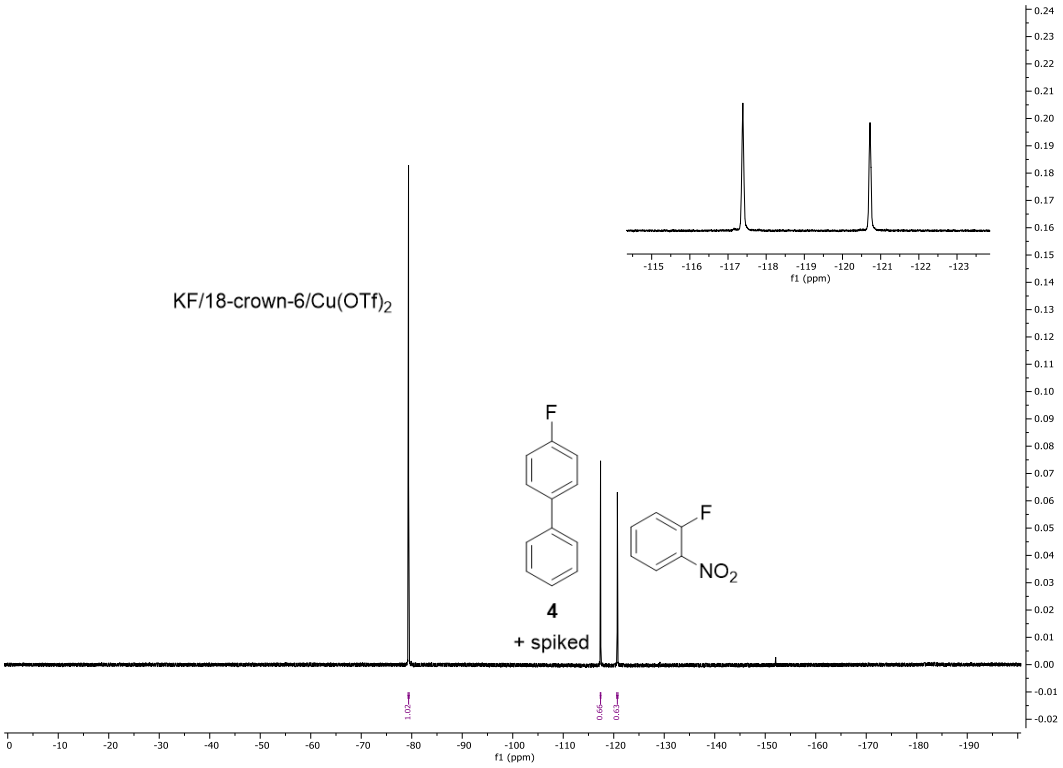


**Figure S35:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude overnight fluorination reaction using diaryliodonium salt **3-OTs** (Method A) with added 1-fluoro-2-nitrobenzene (2.6 µL, 25 µmol, 0.5 equiv.) as internal standard and spiked with commercial 4-fluorobiphenyl (approx. 3.0 mg).

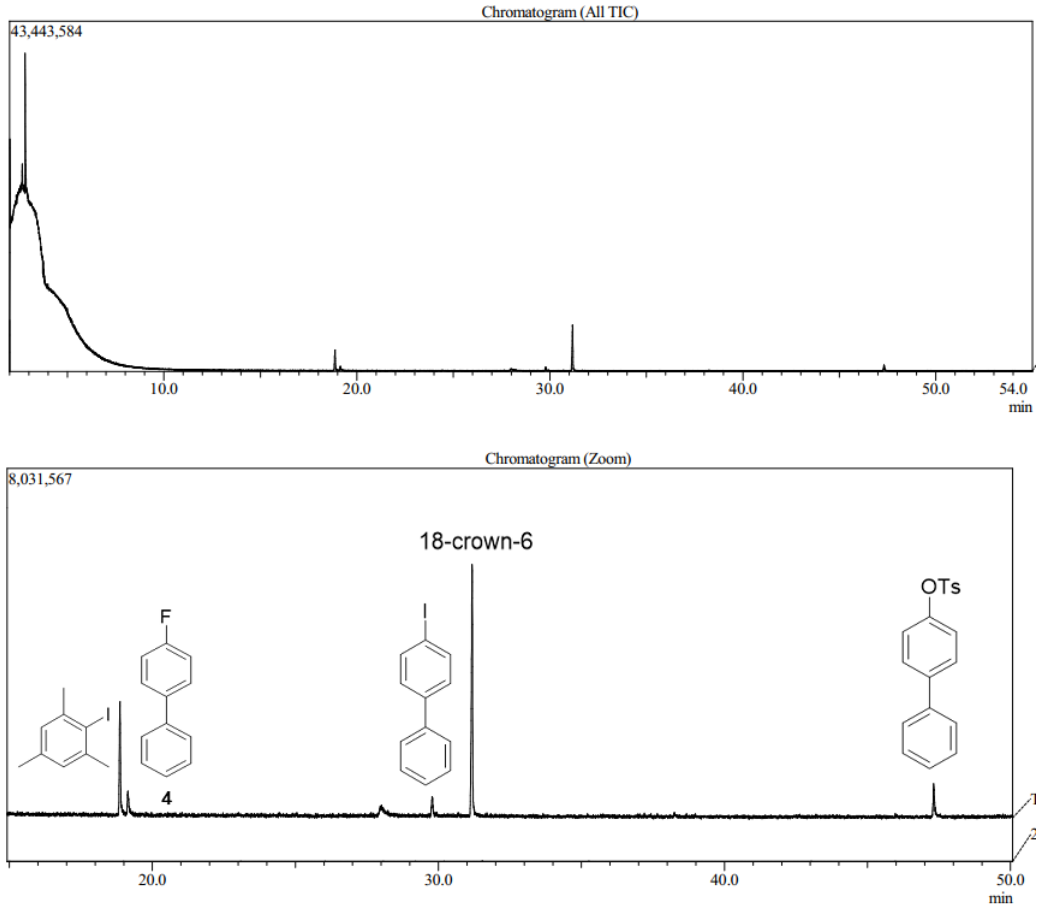


**Figure S36:** GC-MS chromatogram of the crude overnight fluorination reaction using diaryliodonium salt **3-OTs** (Method A).

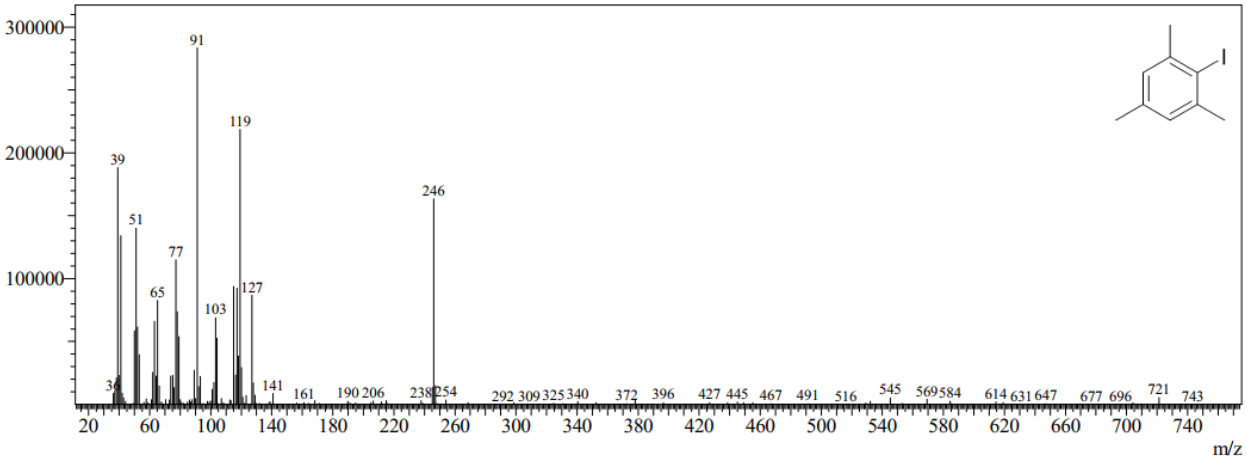


**Figure S37:** MS spectrum of 2-iodomesitylene (18.9 min). Calculated mass for $C_9H_{11}I^+$ = 246.

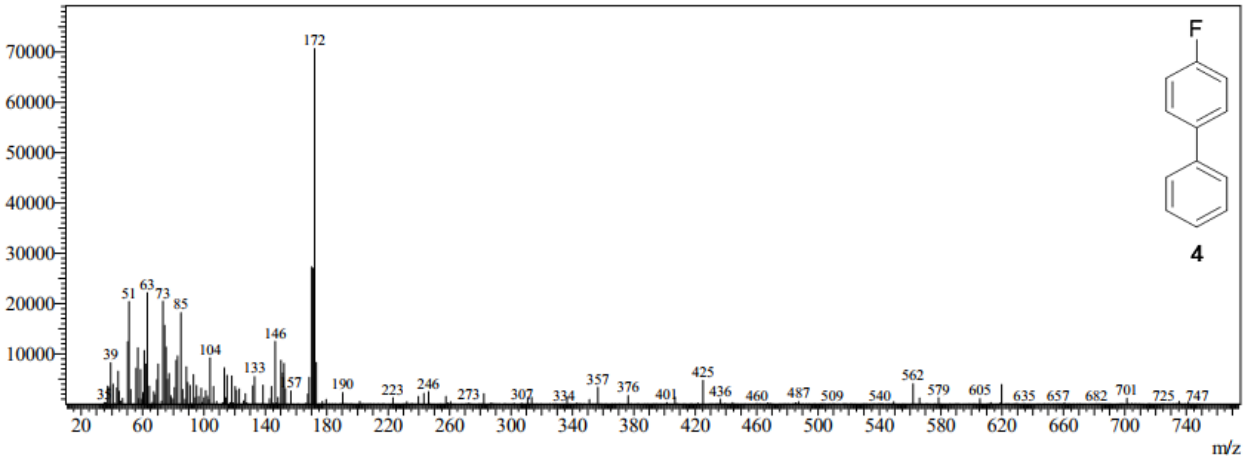


**Figure S38:** MS spectrum of 4-fluorobiphenyl (**4**) (19.1 min). Calculated mass for $C_{12}H_9F^+$ = 172.

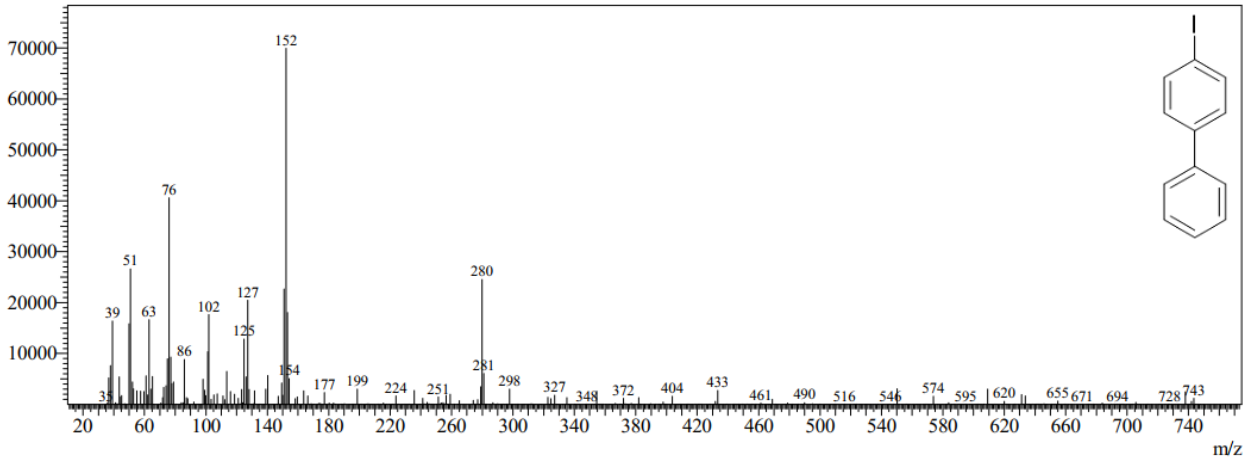


**Figure S39:** MS spectrum of 4-iodobiphenyl (29.8 min). Calculated mass for $C_{12}H_9I^+$ = 280.

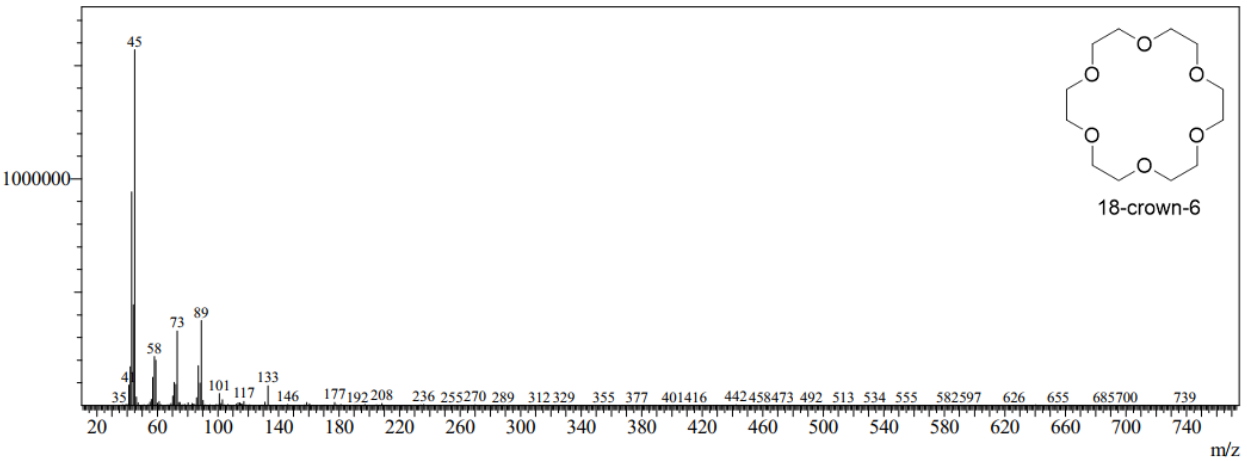


**Figure S40:** MS spectrum of 18-crown-6 (31.2 min). Calculated mass for $C_{12}H_{24}O_6^+$ = 264 ([$M^+$] not visible due to fragmentation).

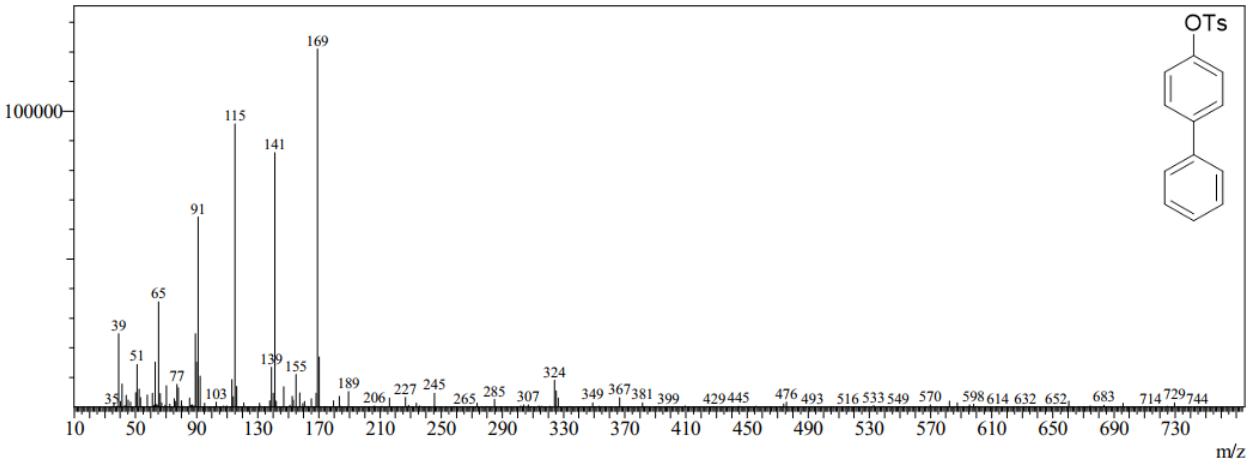


**Figure S41:** MS spectrum of biphenyl-4-yl tosylate (47.3 min). Calculated mass for $C_{19}H_{16}O_3S^+$ = 324.

Method B (20-minute fluorination of **3-OTs**)


**Figure S42:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **3-OTs** (Method B).


**Figure S43:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **3-OTs** (Method B) with added 1-fluoro-2-nitrobenzene (1.6 µL, 15 µmol, 0.5 equiv.) as internal standard.

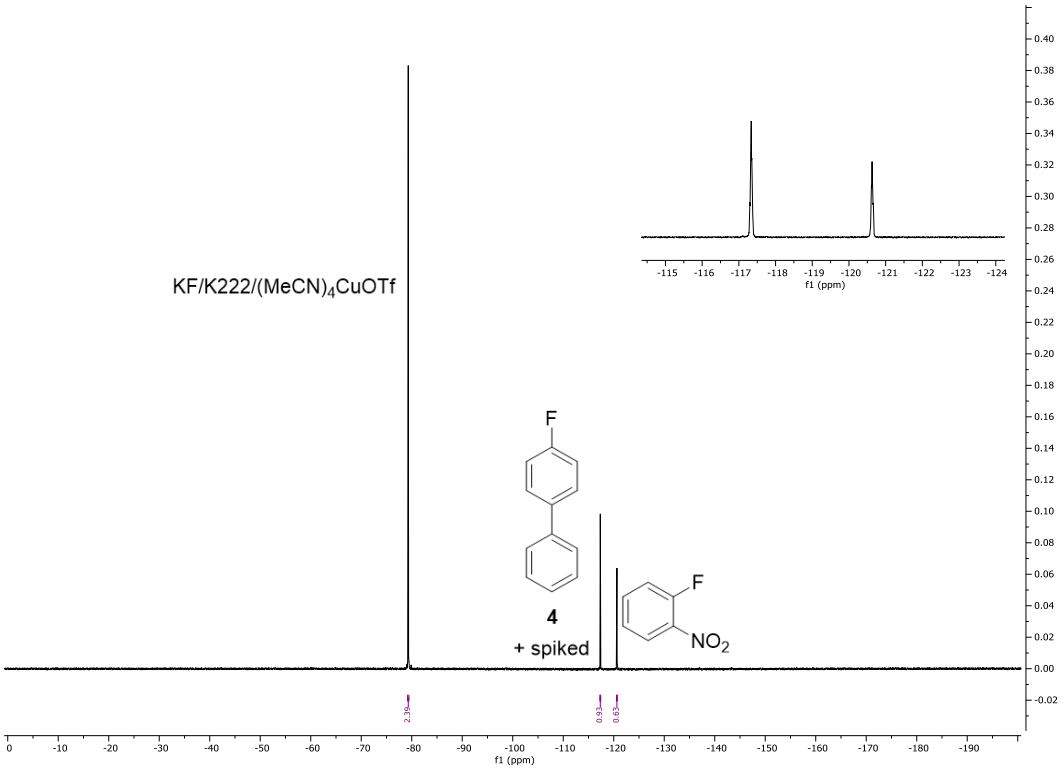


**Figure S44:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **3-OTs** (Method B) with added 1-fluoro-2-nitrobenzene (1.6 µL, 15 µmol, 0.5 equiv.) as internal standard and spiked with commercial 4-fluorobiphenyl (approx. 3.0 mg).

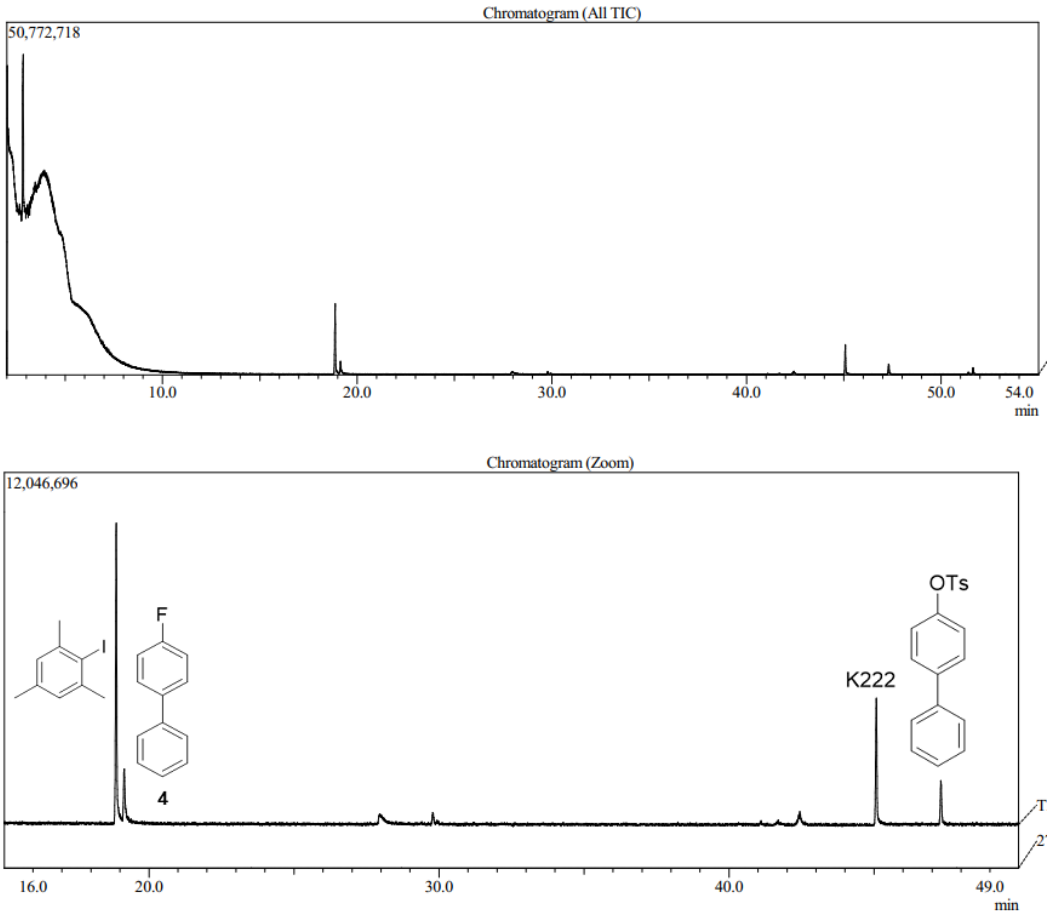


**Figure S45:** GC-MS chromatogram of the crude 20-minute fluorination reaction using diaryliodonium salt **3-OTs** (Method B).

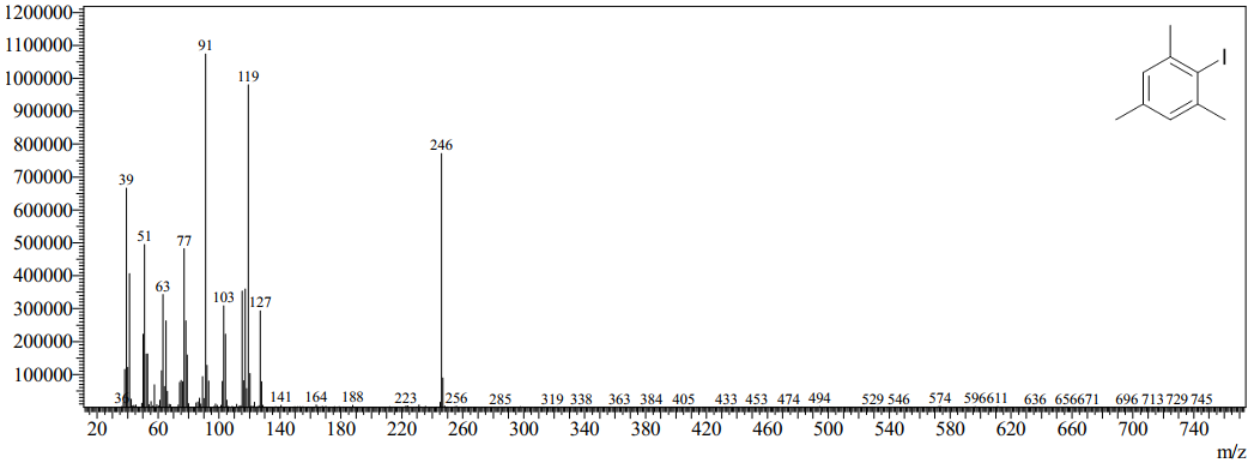


**Figure S46**: MS spectrum of 2-iodomesitylene (18.9 min). Calculated mass for $C_9H_{11}^+$ = 246.

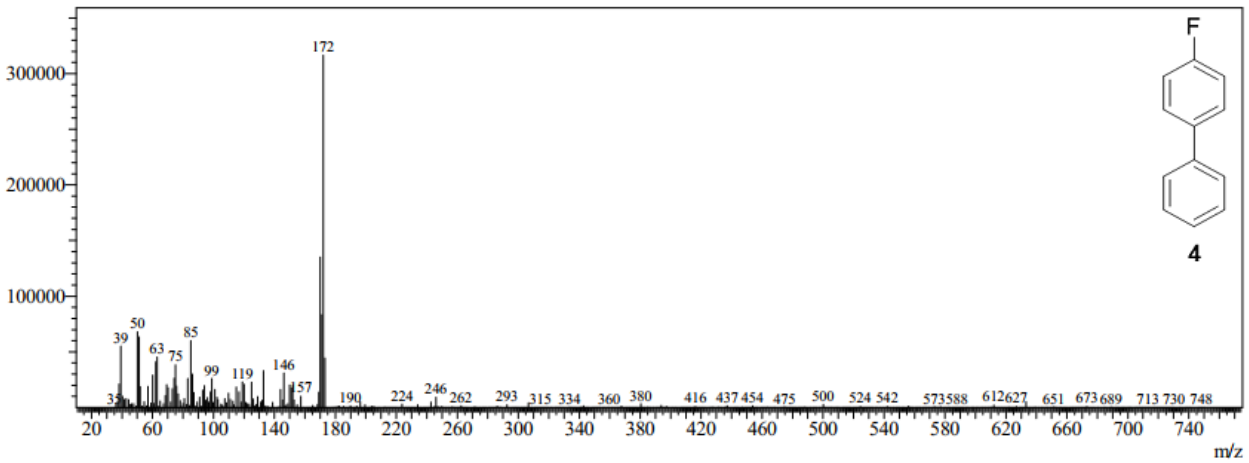


**Figure S47**: MS spectrum of 4-fluorobiphenyl (**4**) (19.1 min). Calculated mass for $C_{12}H_9F^+$ = 172.

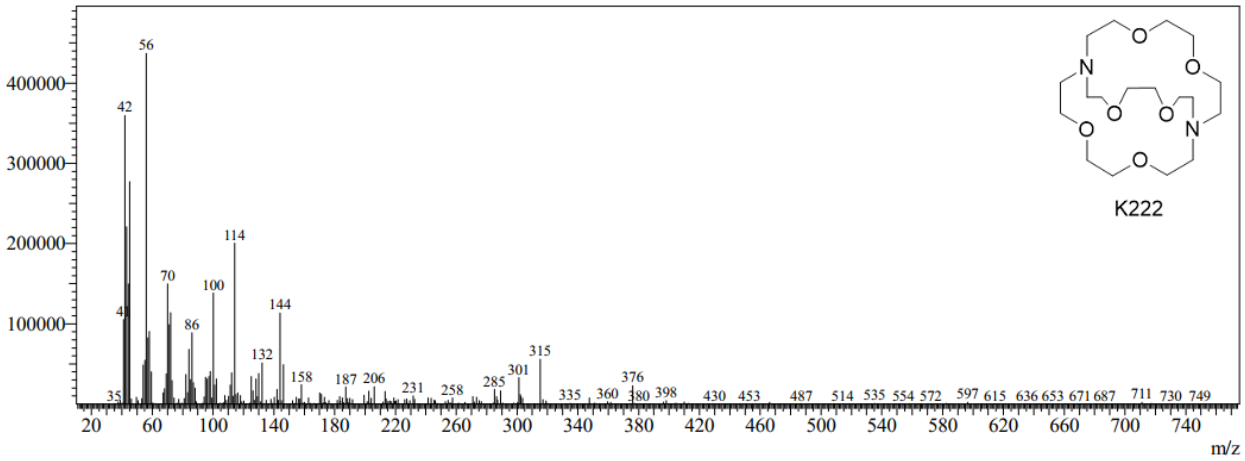


**Figure S48**: MS spectrum of K222 (45.1 min). Calculated mass for $C_{18}H_{36}N_2O_6^+$ = 376.

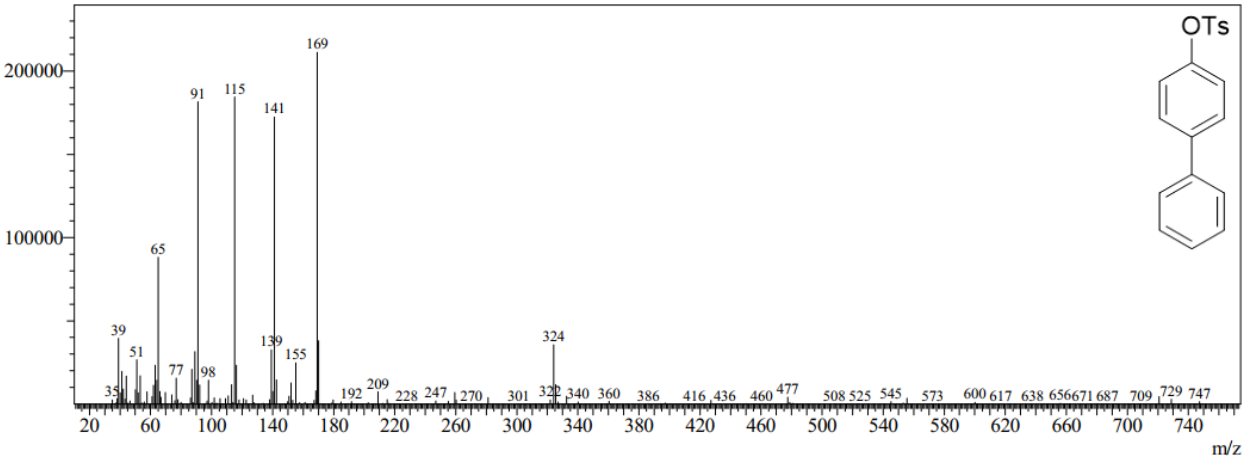


**Figure S49:** MS spectrum of biphenyl-4-yl tosylate (47.3 min). Calculated mass for $C_{19}H_{16}O_3S^+$ = 324.

Method C (20-minute fluorination of **2-OTs**)

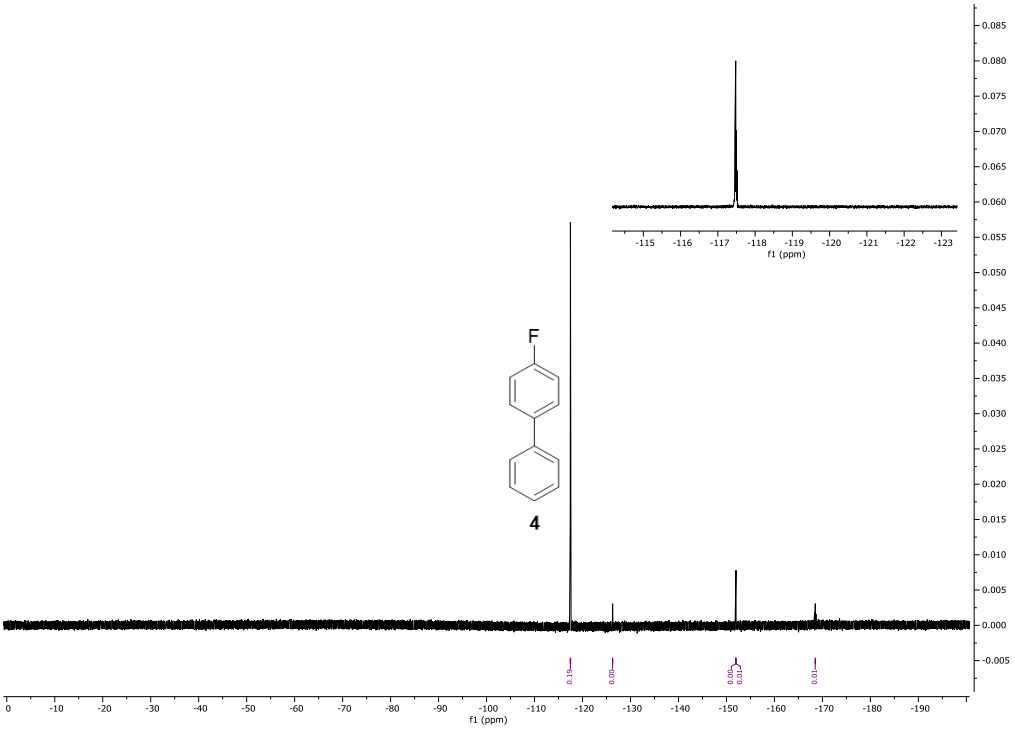


**Figure S50:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **2-OTs** (Method C).

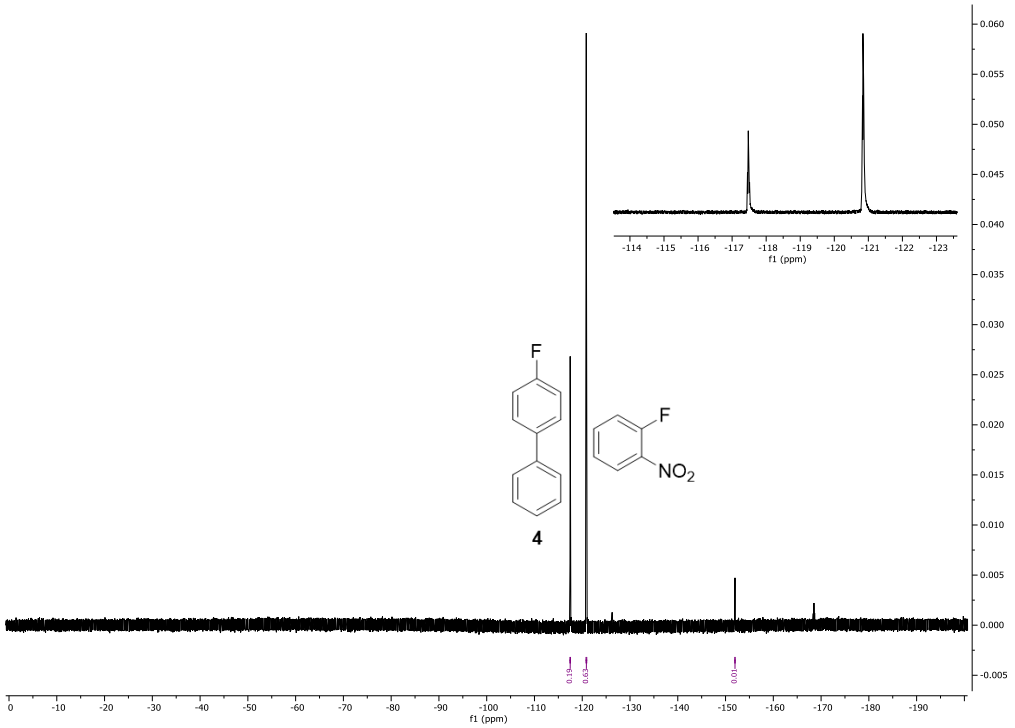


**Figure S51:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **2-OTs** (Method C) with added 1-fluoro-2-nitrobenzene (1.6 µL, 15 µmol, 0.5 equiv.) as internal standard.

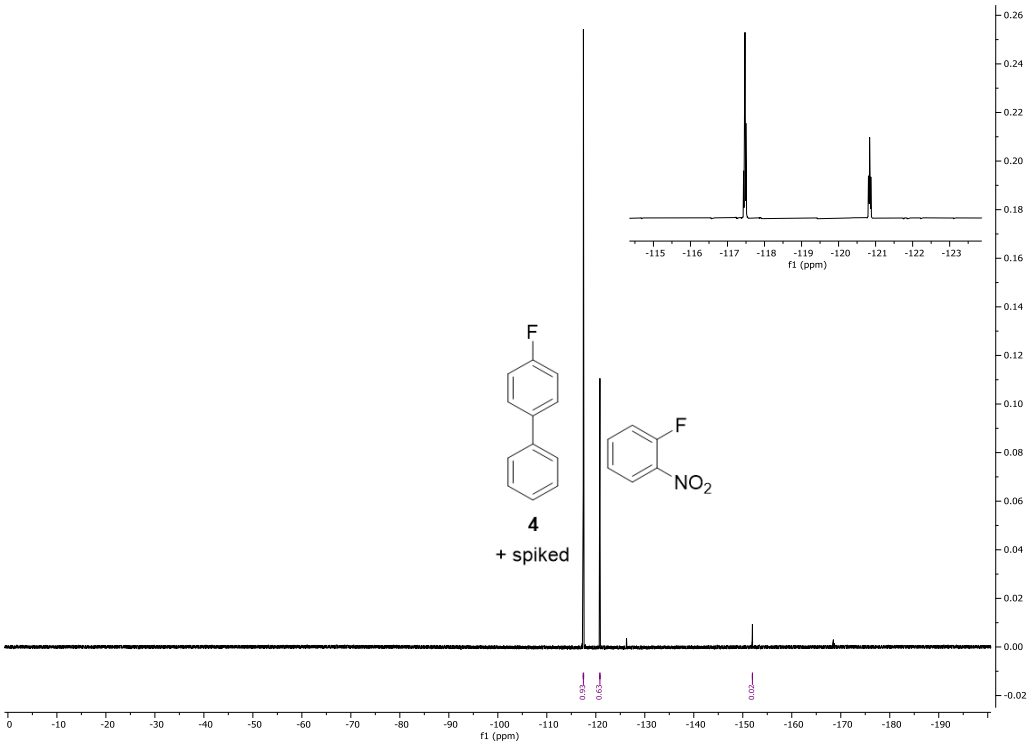


**Figure S52:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of the crude 20-minute fluorination reaction using diaryliodonium salt **2-OTs** (Method C) with added 1-fluoro-2-nitrobenzene (1.6 µL, 15 µmol, 0.5 equiv.) as internal standard and spiked with commercial 4-fluorobiphenyl (approx. 3.0 mg).

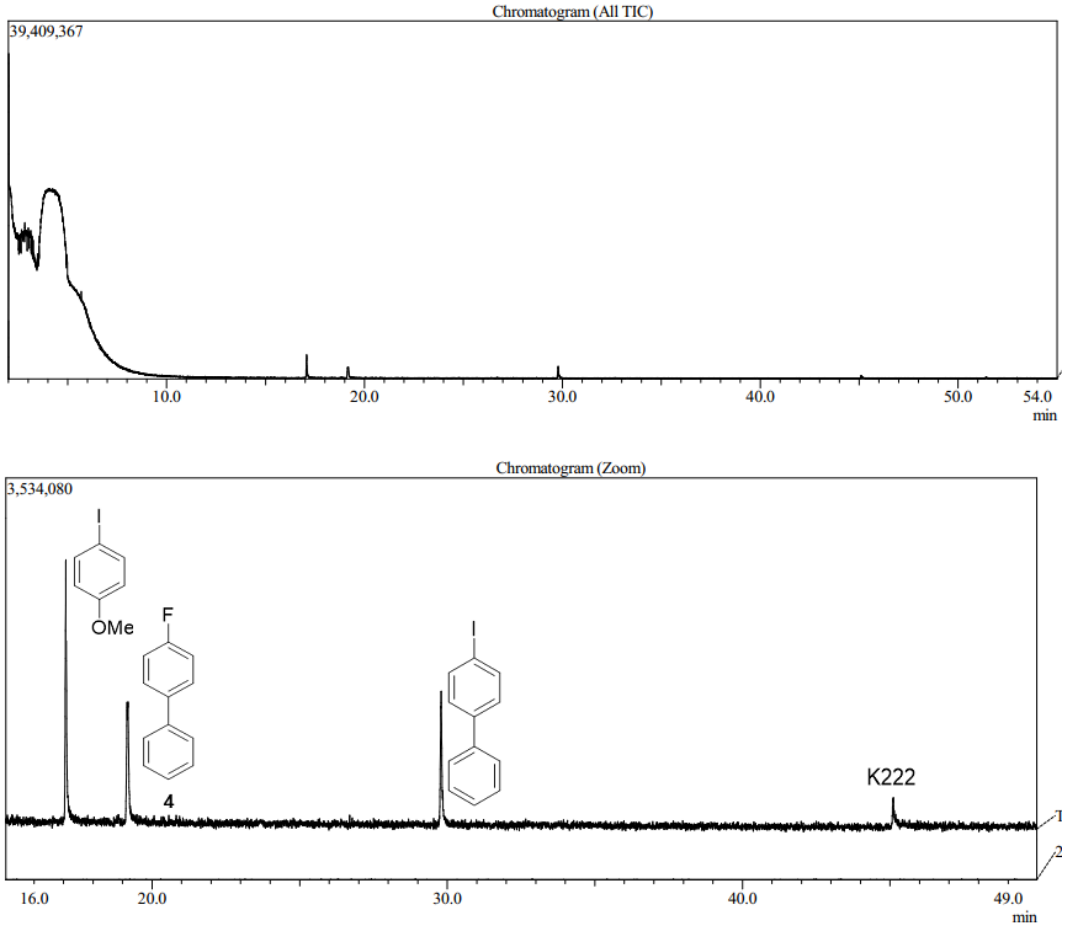


**Figure S53** GC-MS chromatogram of the crude 20-minute fluorination reaction using diaryliodonium salt **2-OTs** (Method C).

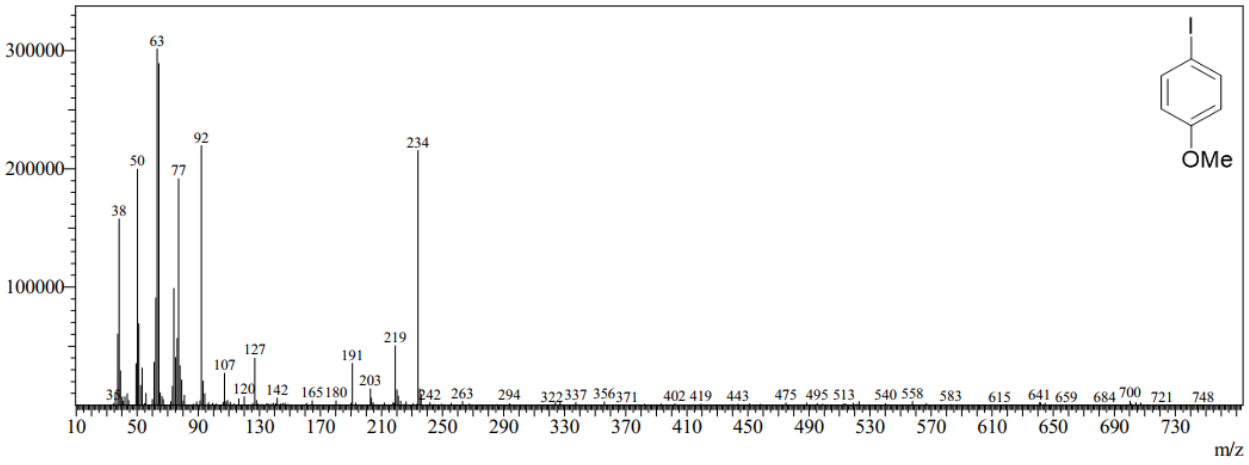


**Figure S54**: MS spectrum of 4-iodoanisole (17.1 min). Calculated mass for $C_7H_7IO^+$ = 234.

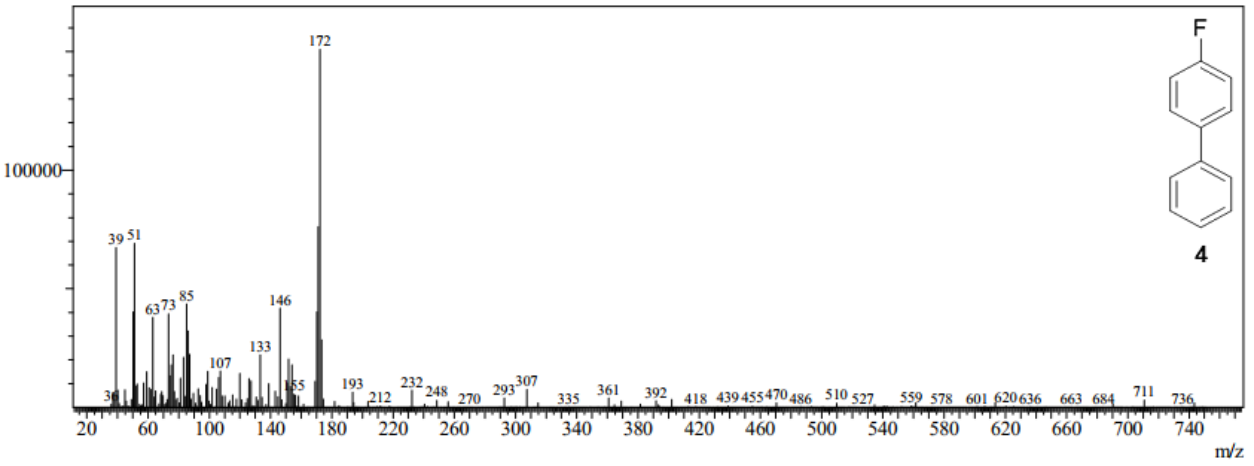


**Figure S55**: MS spectrum of 4-fluorobiphenyl (**4**) (19.2 min). Calculated mass for $C_{12}H_9F^+$ = 172.

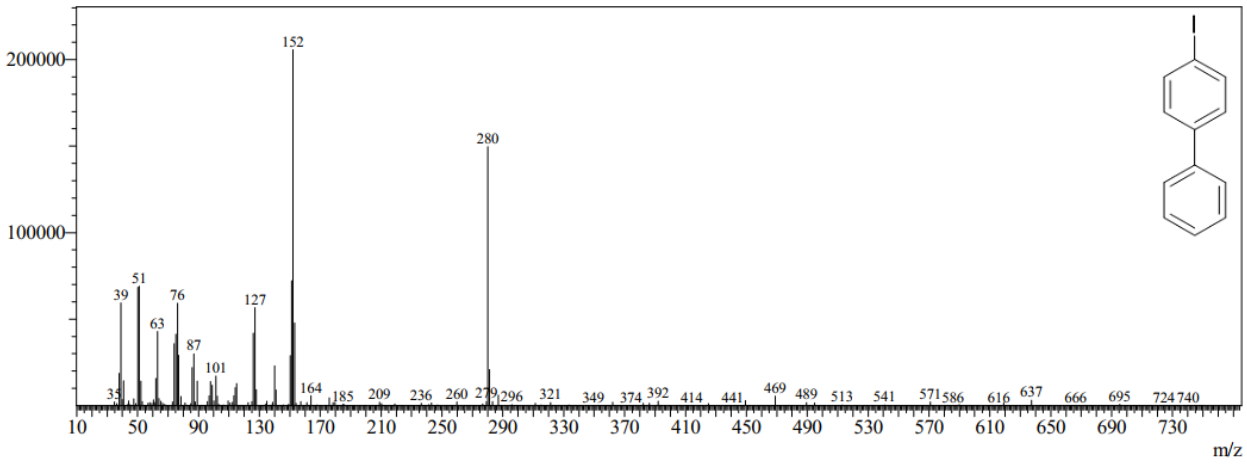


**Figure S56:** MS spectrum of 4-iodobiphenyl (29.8 min). Calculated mass for $C_{12}H_9I^+$ = 280.

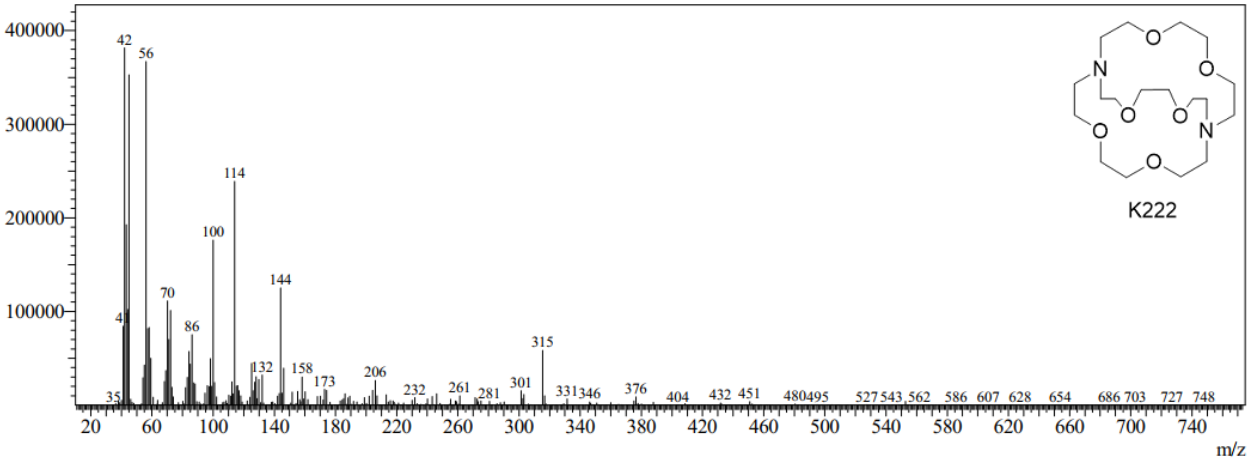


**Figure S57**: MS spectrum of K222 (45.1 min). Calculated mass for $C_{18}H_{36}N_2O_6^+$ = 376.

Reference spectra for fluorination reactions

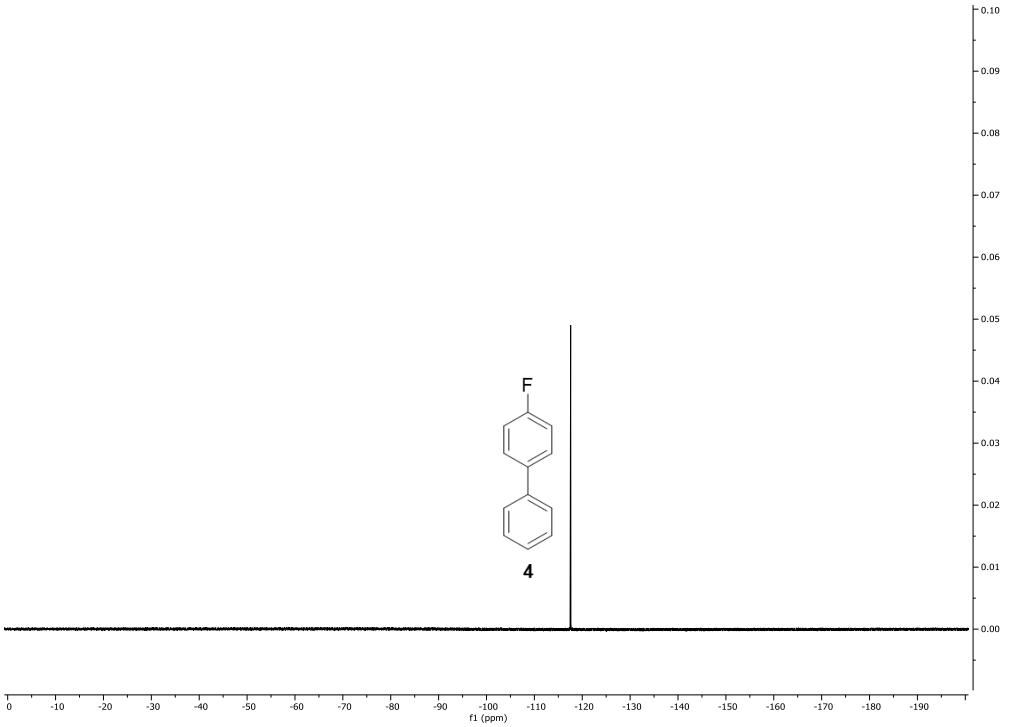


**Figure S58:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of commercial 4-fluorobiphenyl (**4**).

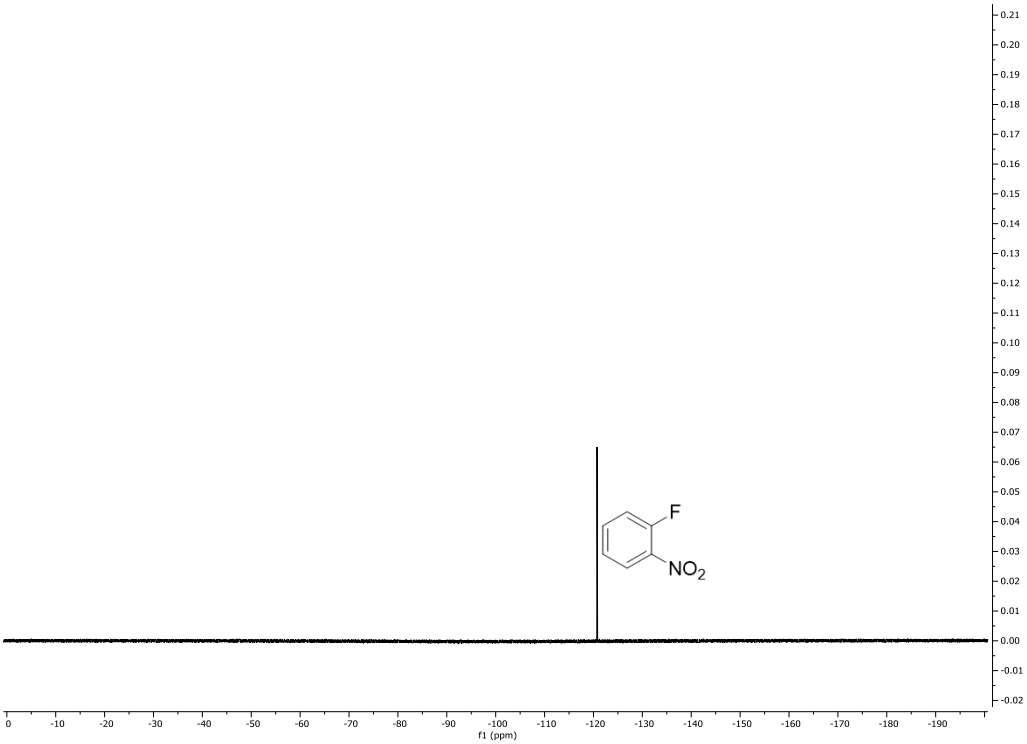


**Figure S59:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of 1-fluoro-2-nitrobenzene.

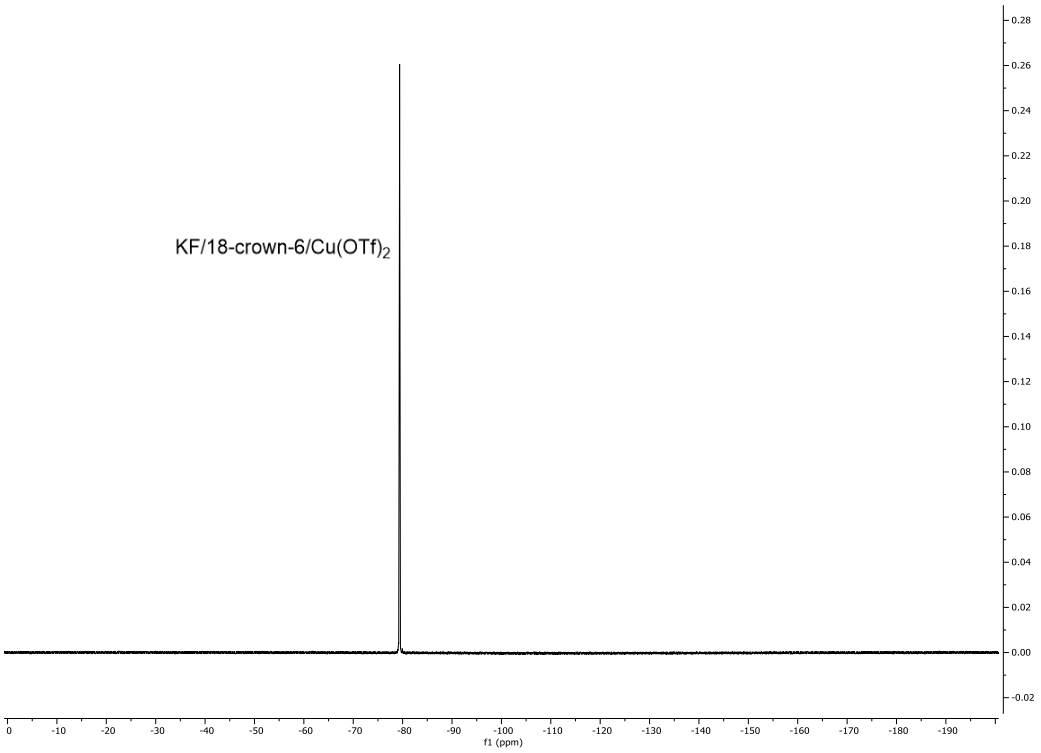


**Figure S60:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of a mixture of KF (3.2 mg, 55 µmol), 18-crown-6 (5.3 mg, 20 µmol), and $Cu(OTf)_2$ (3.6 mg, 10 µmol).

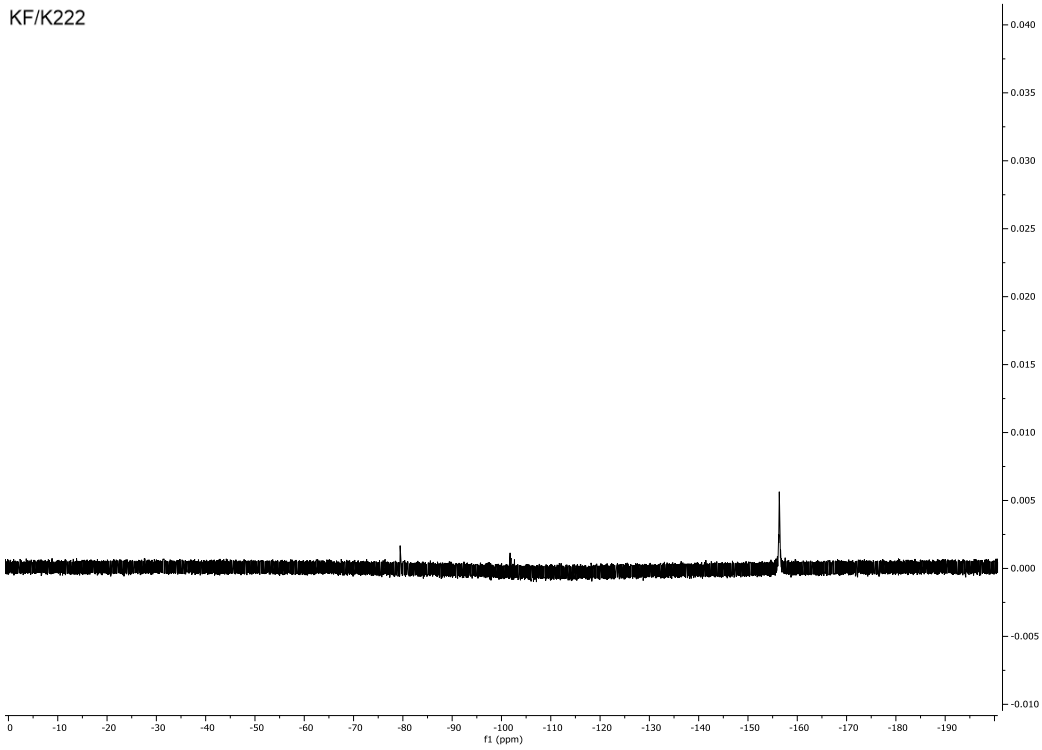


**Figure S61:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of a mixture of KF (1.9 mg, 33 µmol) and K222 (11 mg, 30 µmol).

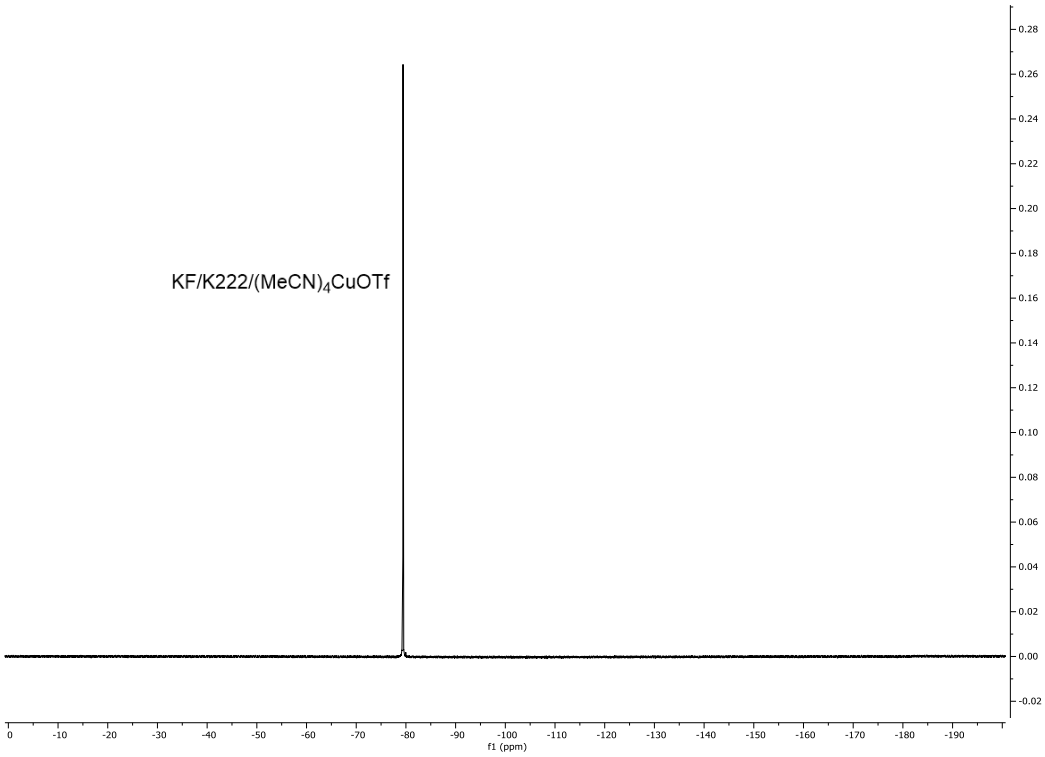


**Figure S62:** $^{19}F$ NMR spectrum (DMF/$CDCl_3$ 4:1, 376 MHz) of a mixture of KF (1.9 mg, 33 µmol), K222 (11 mg, 30 µmol), and $(MeCN)_4CuOTf$ (11 mg, 30 µmol).

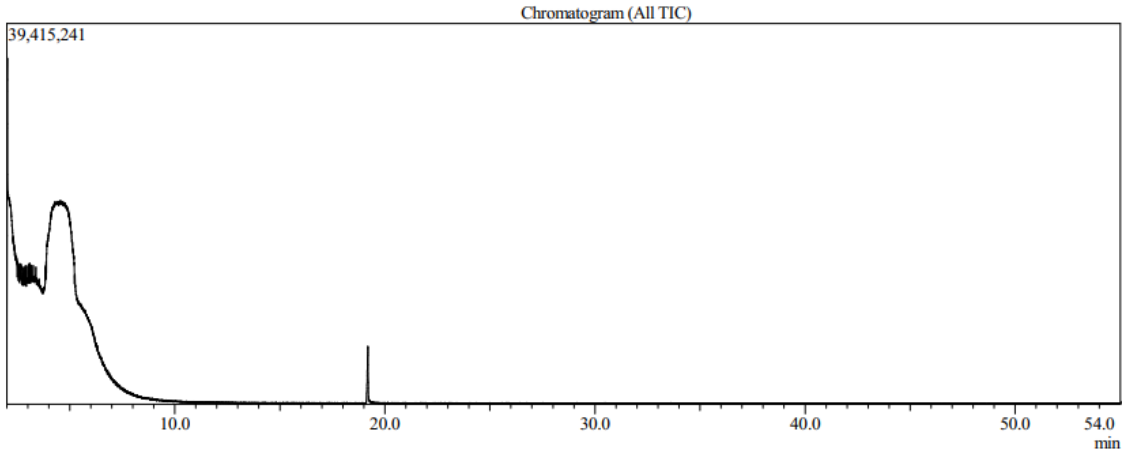


**Figure S63:** GC-MS chromatogram of commercial 4-fluorobiphenyl (**4**).

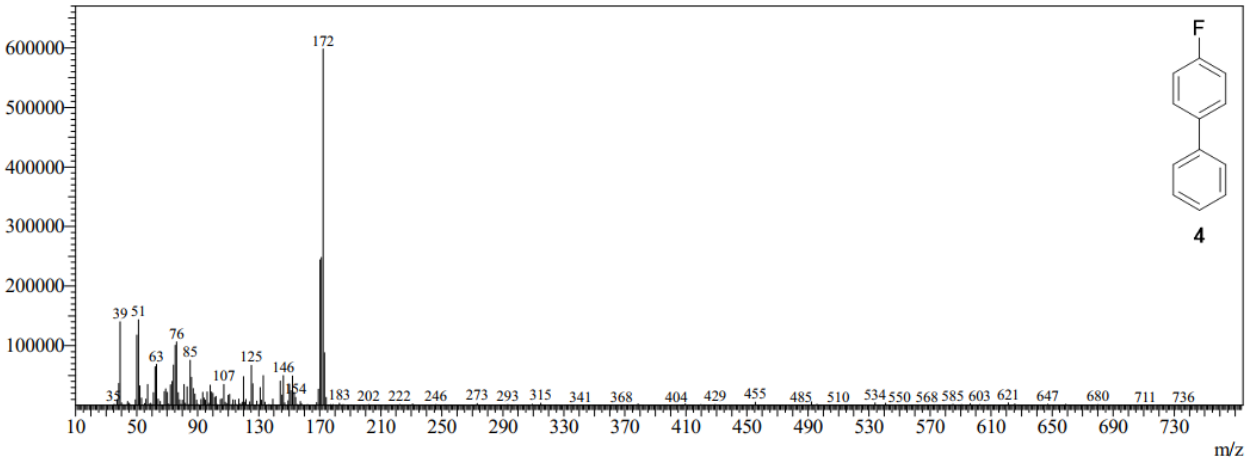


**Figure S64:** MS spectrum of commercial 4-fluorobiphenyl (**4**) (19.2 min). Calculated mass for $C_{12}H_9F^+$ = 172.