Supplementary Material

Evolving utility of C(sp^3)-substituted hypervalent iodine reagents: improved synthesis of aryl((arylsulfonyl)methyl)iodoniums

*Ashley Paige Kreth, Bhuran Z. Khan, Amanda Jordan Rup, Joshuah G. Tavarez, Eric David Finkelstein, Patrick Starmach, Keisnalall Garib, John Thomas Lund, Laila Aaliyah Roman, Jonathan M. Nidam, Parizoda Boymurodova, I. F. Dempsey Hyatt**

Department of Chemistry, Adelphi University, Garden City, New York 11530, United States
Email: ihyatt@adelphi.edu

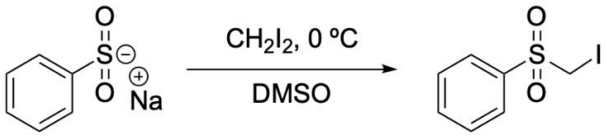
Table of Contents

General Information

All moisture-sensitive reactions were conducted using oven-dried glassware under a nitrogen atmosphere. Unless otherwise specified, all solvents and reagents were procured from commercial suppliers and utilized without additional purification. Iodomethylsulfonyl benzene derivatives **1a-c** were prepared according to the literature.[1-3] Aryl(arylsulfonyl)methyl)iodonium triflate derivatives **4a-h** were synthesized as described in their respective procedures. A Bruker Avance III^{TM} HD 500 MHz spectrometer was used to record the ^{1}H, ^{13}C, and ^{19}F NMR spectra in $CDCl_3$, CD_3CN, DMSO-d_6, CD_3OD, and d_6-acetone. ^{1}H NMR data are reported as chemical shift (δ ppm), multiplicity, coupling constants (J, Hz), and integration; multiplicity is abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR and ^{19}F NMR data are reported as coupling chemical shift (δ ppm) and coupling constants (J, Hz).

Experimental Procedures

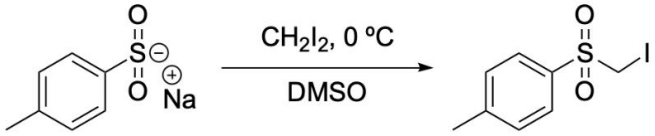
Procedures and Characterization of Iodomethylsulfonyl Benzene Derivatives



((Iodomethyl)sulfonyl)benzene (1a)

Procedure A: A solution of sodium benzenesulfinate (18.27 mmol, 3.0 g, 1.00 equiv.) and diiodomethane (30.95 mmol, 2.49 mL, 1.69 equiv.) in DMSO (60 mL) was stirred for two days at 50 ºC. The crude reaction mixture was extracted with DCM and deionized water. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo at 2 torr to give **1a** in 76% yield (3922 mg). Spectral data were consistent with previously reported values.[1]

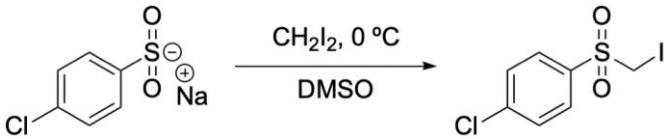
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 4.48 (s, 2 *H*) 7.62 (tt, *J* = 7.7, 1.8 Hz, 2 *H*) 7.72 (tt, *J* = 7.6, 1.9 Hz, 1 *H*) 7.99 (d, *J* = 7.3 Hz, 2 *H*).



1-((iodomethyl)sulfonyl)-4-methylbenzene (1b)

Procedure B: A solution of sodium p-toluenesulfinate (16.83 mmol, 3.01 g, 1.00 equiv.) and diiodomethane (28.51 mmol, 2.15 mL, 1.69 equiv.) in DMSO (60.0 mL) was stirred for two days at 50 °C. The reaction is cooled to 25 °C and quenched with deionized water (300 mL). The reaction is then filtered, and the desired product is desiccated to give **1b** in 82% yield (4283 mg). Spectral data were consistent with previously reported values.[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 2.49 (s, 3 *H*) 4.45 (s, 2 *H*) 7.40 (dd, *J* = 8.6, 0.6 Hz, 2 *H*) 7.86 (d, *J* = 8.2 Hz, 2 *H*).

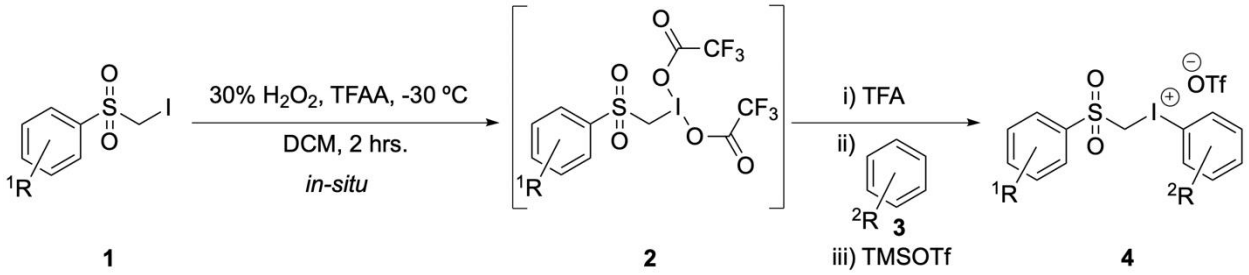


1-chloro-4-((iodomethyl)sulfonyl)benzene (1c)

Procedure C: A solution of sodium 4-chlorobenzenesulfinate (5.04 mmol, 1.0 g, 1.00 equiv.) and diiodomethane (8.33 mmol, 0.69 mL, 1.65 equiv.) in DMSO (20 mL) was stirred for two days at 50 ºC. The crude reaction mixture was extracted with DCM and deionized water. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo at 2 torr to give 1c in 77% yield (2441 mg). Spectral data were consistent with previously reported values.[3]

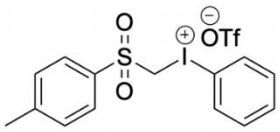
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 4.47 (s, 2 *H*) 7.59 (d, *J* = 8.9 Hz, 2 *H*) 7.93 (d, *J* = 8.8 Hz, 2 *H*).

General Procedure for *in-situ* Synthesis of aryl(arylsulfonyl)methyl)iodonium Triflate Derivatives



General Procedure A: A solution of 30% hydrogen peroxide (7.45 equiv.) and trifluoroacetic anhydride (11.41 equiv.) was stirred at -30 ºC for 10 min. The system was warmed to 25 ºC, agitated for 10 min, and subsequently re-cooled to -30 ºC. A mixture of the iodomethylsulfonyl benzene derivative (1.00 equiv.) in DCM (2.0-4.0 mL) was added and maintained at -30 ºC for 0.5-3.5 h. The reaction mixture was evaporated under reduced pressure for 35 min. The resulting residue was treated with trifluoroacetic acid (17.4 equiv.), the respective aryl reagent (2.11 equiv.), anhydrous DCM (2.0-3.0 mL), and TMSOTf (2.21 equiv.). The reaction was stirred at 25 ºC for 24-72 h. The crude product was concentrated *in vacuo*, precipitated with diethyl ether (10-20 mL), and collected via filtration.

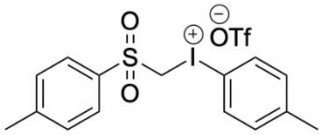
Spectroscopic Data of Compounds



phenyl(tosylmethyl)iodonium triflate (4a)

Following **General Procedure A,** a solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was agitated at -30 ºC for 10 min, warmed to 25 ºC, and subsequently re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-((iodomethyl)sulfonyl)-4-methylbenzene (**1b**, 1.50 mmol, 0.444 g) in DCM (2.0 mL) was added, and the mixture was stirred for 3.5 h at -30 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2.0 mL), benzene (3.16 mmol, 0.28 mL), anhydrous DCM (2.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (10 mL) afforded **4a** in 41% yield (318 mg).

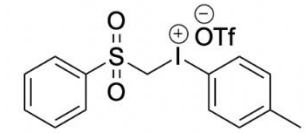
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.47 (s, 3 *H*) 5.51 (s, 2 *H*) 7.46 (d, *J* = 8.2 Hz, 2 *H*) 7.54 (t, *J* = 7.7 Hz, 2 *H*) 7.77 (t, *J* = 7.6 Hz, 1 *H*) 7.81 (d, *J* = 8.2 Hz, 2 *H*) 8.04 (dd, *J* = 8.5, 1.2 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 21.90 (s, 1 *C*), 52.96 (s, 1 *C*), 110.51 (s, 1 *C*) 130.20 (s, 2 *C*) 131.63 (s, 2 *C*) 133.20 (s, 2 *C*) 133.29 (s, 1 *C*) 134.69 (s, 1 *C*) 138.20 (s, 2 *C*) 148.78 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.34 (s, 3 *F*).



***p*-tolyl(tosylmethyl)iodonium triflate (4b)**

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was agitated at -30 ºC for 10 min, warmed to 25 ºC, and subsequently re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-((iodomethyl)sulfonyl)-4-methylbenzene (**1b**) (1.50 mmol, 0.443 g) in DCM (2.0 mL) was added, and the mixture was stirred for 3.5 hours at -30 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2.0 mL), toluene (3.16 mmol, 0.33 mL), anhydrous DCM (2.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (10 mL) afforded **4b** in 36% yield (286 mg).

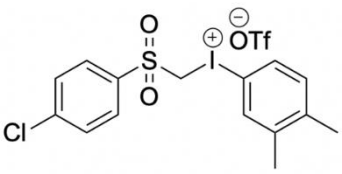
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.44 (s, 3 *H*) 2.46 (s, 3 *H*) 5.50 (s, 2 *H*) 7.33 (d, *J* = 8.2 Hz, 2 *H*) 7.44 (d, *J* = 8.6 Hz, 2 *H*) 7.79 (d, *J* = 8.2 Hz, 2 *H*) 7.90 (d, *J* = 8.5 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 21.63 (s, 1 *C*) 21.89 (s, 1 *C*) 52.55 (s, 1 *C*) 106.61 (s, 1 *C*) 130.07 (s, 2 *C*) 131.56 (s, 2 *C*) 133.50 (s, 1 *C*) 133.77 (s, 2 *C*) 138.10 (s, 2 *C*) 146.08 (s, 1 *C*) 148.61 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.22 (s, 3 *F*).



((phenylsulfonyl)methyl)(*p*-tolyl)iodonium triflate (4c)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was agitated at -30 ºC for 10 min, warmed to 25 ºC, and subsequently re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of ((iodomethyl)sulfonyl)benzene (**1a**) (1.32 mmol, 0.372 g) in DCM (2.0 mL) was added and stirred for 1.5 hours at -30 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2 mL), toluene (3.16 mmol, 0.33 mL), anhydrous DCM (2.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (10 mL) afforded **4c** in 58% yield (457 mg).

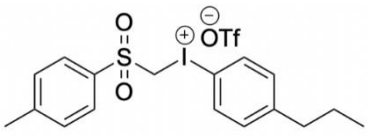
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.44 (s, 3 *H*) 5.51 (s, 2 *H*) 7.34 (d, *J* = 8.3 Hz, 2 *H*) 7.65 (t, *J* = 8.2 Hz, 2 *H*) 7.81 (tt, *J* = 7.5, 1.1 Hz, 1 *H*) 7.92 – 7.94 (m, 4 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 21.79 (s, 1 *C*) 52.58 (s, 1 *C*) 106.84 (s, 1 *C*) 130.24 (s, 2 *C*) 131.24 (s, 2 *C*) 134.00 (s, 2 *C*) 136.66 (s, 1 *C*) 137.05 (s, 1 *C*) 138.36 (s, 2 *C*) 146.35 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.24 (s, 3 *F*).



(((4-chlorophenyl)sulfonyl)methyl)(3,4-dimethylphenyl)iodonium triflate (4d)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was stirred at -30 ºC for 10 min. The reaction mixture was brought to 25 ºC and stirred for 10 min, then re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-chloro-4-((iodomethyl)sulfonyl)benzene (**1c**) (1.50 mmol, 0.475 g) in DCM (2.0 mL) was added, and the mixture was stirred for 45 min at -30 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2 mL), *o*-xylene (3.16 mmol, 0.383 mL), anhydrous DCM (3.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (10 mL) afforded **4d** in 24% yield (205 mg).

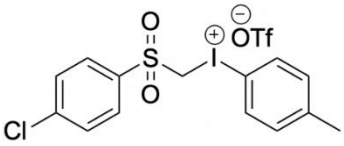
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.28 (s, 3 *H*) 2.35 (s, 3 *H*) 5.55 (s, 2 *H*) 7.26 (d, *J* = 8.8 Hz, 1 *H*) 7.60 (d, *J* = 8.8 Hz, 2 *H*) 7.73 – 7.74 (m, 2 *H*) 7.86 (d, *J* = 8.6 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 19.91 (s, 1 *C*) 20.04 (s, 1 *C*) 51.45 (s, 1 *C*) 106.51 (s, 1 *C*) 131.16 (s, 2 *C*) 131.79 (s, 2 *C*) 133.94 (s, 1 *C*) 135.37 (s, 1 *C*) 135.41 (s, 1 *C*) 138.09 (s, 1 *C*) 142.78 (s, 1 *C*) 142.91 (s, 1 *C*) 144.87 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.22 (s, 3 *F*).



(4-propylphenyl)(tosylmethyl)iodonium triflate (4e)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was stirred at -30 ºC for 10 min. The reaction mixture was brought to 25 ºC and stirred for 10 min, then re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-((iodomethyl)sulfonyl)-4-methylbenzene (**1b**) (1.50 mmol, 0.444 g) in DCM (2.0 mL) was added, and the mixture was stirred for 45 min at -35 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2 mL), *n*-propylbenzene (3.16 mmol, 0.442 mL), anhydrous DCM (3.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (15 mL) afforded **4e** in 48% yield (406 mg).

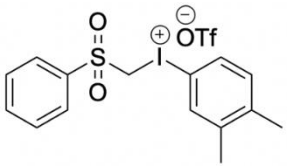
^{1}H NMR (500 MHz, CD_3CN): δ ppm 0.94 (t, *J* = 7.3 Hz, 3 *H*) 1.64 (sxt, *J* = 7.1 Hz, 2 *H*) 2.46 (s, 3 *H*) 2.68 (t, *J* = 7.8 Hz, 2 *H*) 5.51 (s, 2 *H*) 7.33 (d, *J* = 8.5 Hz, 2 *H*) 7.44 (d, *J* = 8.5 Hz, 2 *H*) 7.79 (d, *J* = 8.5, 2 *H*) 7.91 (d, *J* = 8.5 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 13.84 (s, 1 *C*) 21.75 (s, 1 *C*) 24.91 (s, 1 *C*) 38.04 (s, 1 *C*) 52.43 (s, 1 *C*) 106.73 (s, 1 *C*) 129.91 (s, 2 *C*) 131.40 (s, 2 *C*) 133.00 (s, 2 *C*) 133.35 (s, 1 *C*) 137.93 (s, 2 *C*) 148.42 (s, 1 *C*) 150.32 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.21 (s, 3 *F*).



(((4-chlorophenyl)sulfonyl)methyl)(*p*-tolyl)iodonium triflate (4f)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was stirred at -30 ºC for 10 min. The reaction mixture was brought to 25 ºC and stirred for 10 min, then re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-chloro-4-((iodomethyl)sulfonyl)benzene (**1c**) (1.50 mmol, 0.475 g) in DCM (2.0 mL) was added, and the mixture was stirred for 45 min at -35 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2 mL), toluene (3.16 mmol, 0.336 mL), anhydrous DCM (3.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (15 mL) afforded **4f** in 28% yield (231 mg).

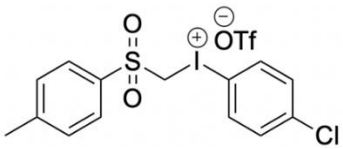
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.45 (s, 3 *H*) 5.54 (s, 2 *H*) 7.34 (d, *J* = 8.2 Hz, 2 *H*) 7.63 (d, *J* = 8.8 Hz, 2 *H*) 7.88 (d, *J* = 8.8 Hz, 2 *H*) 7.92 (d, *J* = 8.5 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 21.65 (s, 1 *C*) 51.90 (s, 1 *C*) 106.68 (s, 1 *C*) 131.23 (s, 2 *C*) 131.85 (s, 2 *C*) 133.83 (s, 2 *C*) 135.25 (s, 1 *C*) 138.07 (s, 2 *C*) 143.01 (s, 1 *C*) 146.18 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.21 (s, 3 *F*).



(3,4-dimethylphenyl)((phenylsulfonyl)methyl)iodonium triflate (4g)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (11.18 mmol, 0.36 mL) and trifluoroacetic anhydride (17.12 mmol, 2.4 mL) was stirred at -35 ºC for 10 min. The reaction mixture was brought to 25 ºC and stirred for 10 min, then re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of ((iodomethyl)sulfonyl)benzene (**1a**) (1.50 mmol, 0.423 g) in DCM (2.0 mL) was added and stirred for 45 min at -35 ºC. The resulting residue was treated with trifluoracetic acid (26.1 mmol, 2.0 mL), *o*-xylene (3.16 mmol, 0.382 mL), anhydrous DCM (3.0 mL), and TMSOTf (3.32 mmol, 0.64 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (15 mL) afforded **4g** in 53% (429.6) yield.

^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.27 (s, 3 *H*) 2.34 (s, 3 *H*) 5.52 (s, 2 *H*) 7.27 (d, *J* = 7.9 Hz, 1 *H*) 7.64 (t, *J* = 7.9 Hz, 2 *H*) 7.75 – 7.77 (m, 2 *H*) 7.80 (t, *J* = 7.5, 1 *H*) 7.91 (dd, *J* = 8.0, 1.3 Hz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): δ ppm 20.11 (s, 1 *C*) 20.19 (s, 1 *C*) 52.29 (s, 1 *C*) 106.74 (s, 1 *C*) 130.20 (s, 2 *C*) 131.19 (s, 2 *C*) 134.11 (s, 1 *C*) 135.70 (s, 1 *C*) 136.74 (s, 1 *C*) 136.98 (s, 1 *C*) 138.41 (s, 1 *C*) 142.92 (s, 1 *C*) 145.06 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): δ ppm -79.22 (s, 3 *F*).

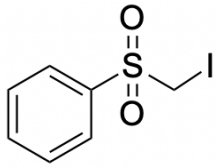


(4-chlorophenyl)(tosylmethyl)iodonium triflate (4h)

Following **General Procedure A,** A solution of 30% hydrogen peroxide (22.36 mmol, 0.72 mL) and trifluoroacetic anhydride (34.24 mmol, 4.8 mL) was stirred at -35 ºC for 10 min. The reaction mixture was brought to 25 ºC and stirred for 10 min, then re-cooled to -30 ºC. The reaction mixture was evaporated under reduced pressure for 35 min. A solution of 1-((iodomethyl)sulfonyl)-4-methylbenzene (**1b**) (3.0 mmol, 0.888 g) in DCM (4.0 mL) was added, and the mixture was stirred for 2 h at -35 ºC. The resulting residue was treated with trifluoracetic acid (52.2 mmol, 4.0 mL), chlorobenzene (6.32 mmol, 0.642 mL), anhydrous DCM (4.0 mL), and TMSOTf (6.64 mmol, 1.28 mL). The reaction mixture was stirred for 24 h. Precipitation with diethyl ether (20 mL) afforded **4h** in 22% yield (364 mg).

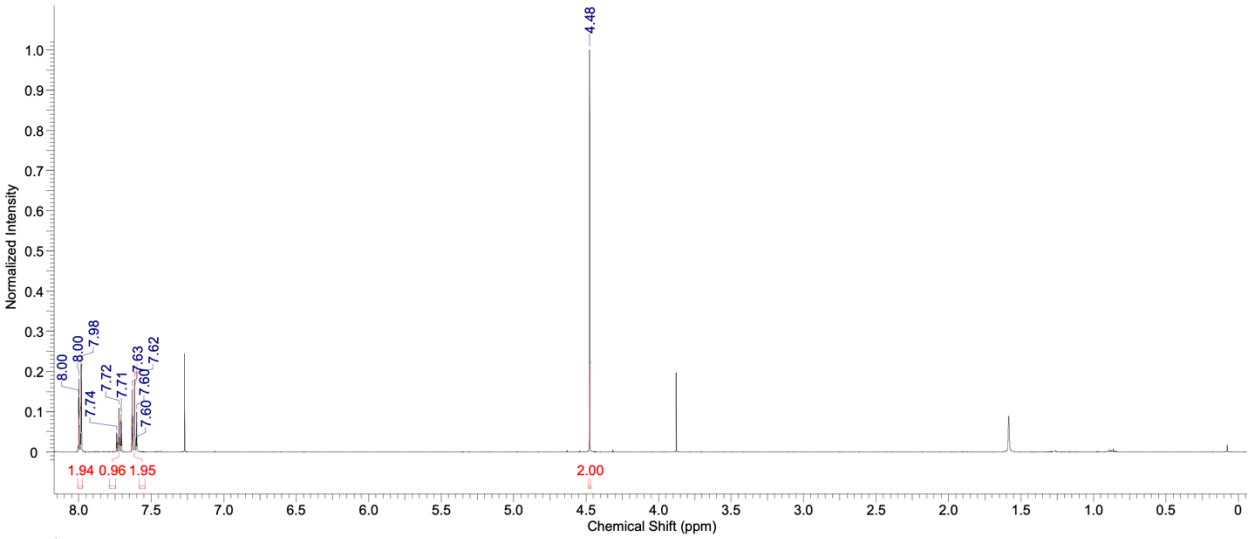
^{1}H NMR (500 MHz, CD_3CN): δ ppm 2.47 (s, 3 *H*) 5.53 (s, 2 *H*) 7.44 (d, *J* = 8.2 MHz, 2 *H*) 7.52 (d, *J* = 8.8 MHz, 2 *H*) 7.79 (d, *J* = 8.2 MHz, 2 *H*) 8.01 (d, *J* = 9.2 MHz, 2 *H*). ^{13}C NMR (126 MHz, CD_3CN): 21.74 (s, 1 *C*) 52.84 (s, 1 *C*) 107.64 (s, 1 *C*) 129.97 (s, 2 *C*) 131.43 (s, 2 *C*) 132.90 (s, 2 *C*) 133.24 (s, 1 *C*) 139.61 (s, 2 *C*) 140.73 (s, 1 *C*) 148.57 (s, 1 *C*). ^{19}F NMR (470 MHz, CD_3CN): -79.23 (s, 3 *F*).

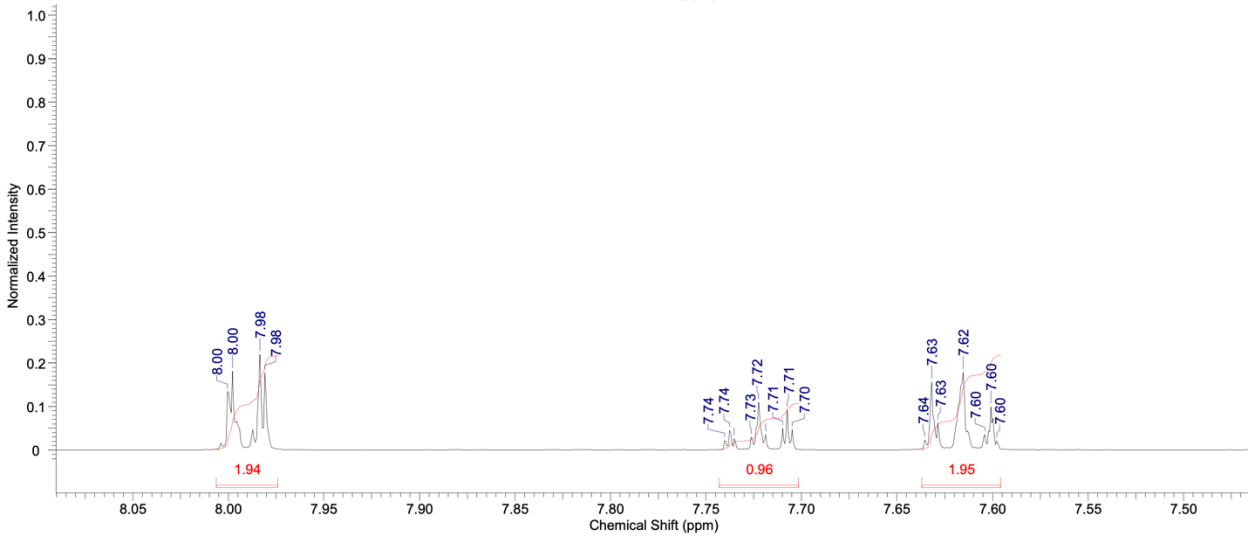
$^{1}H/^{13}C$ NMR Spectra

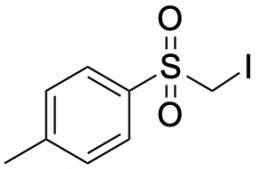


((iodomethyl)sulfonyl)benzene (1a)

^{1}H NMR

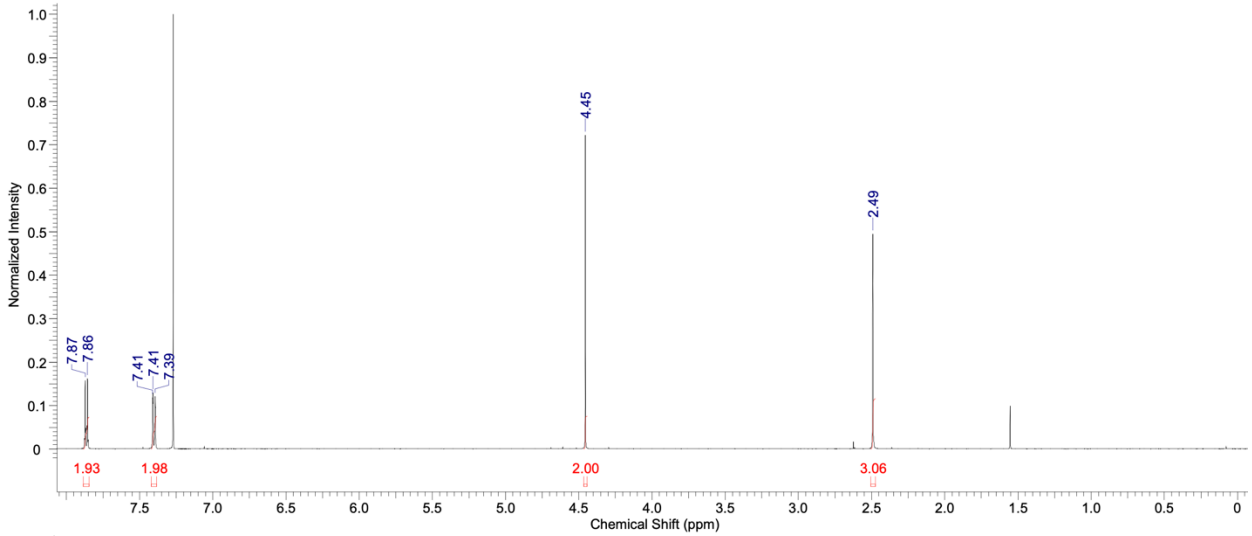


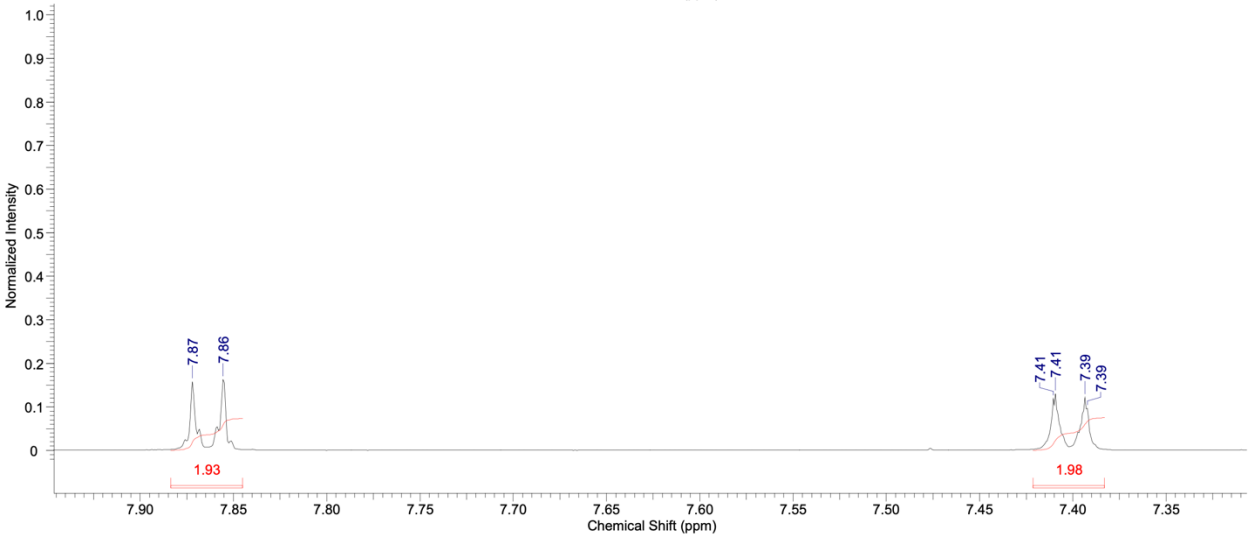


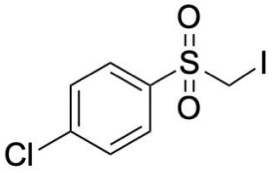


1-((iodomethyl)sulfonyl)-4-methylbenzene (1b)

^{1}H NMR

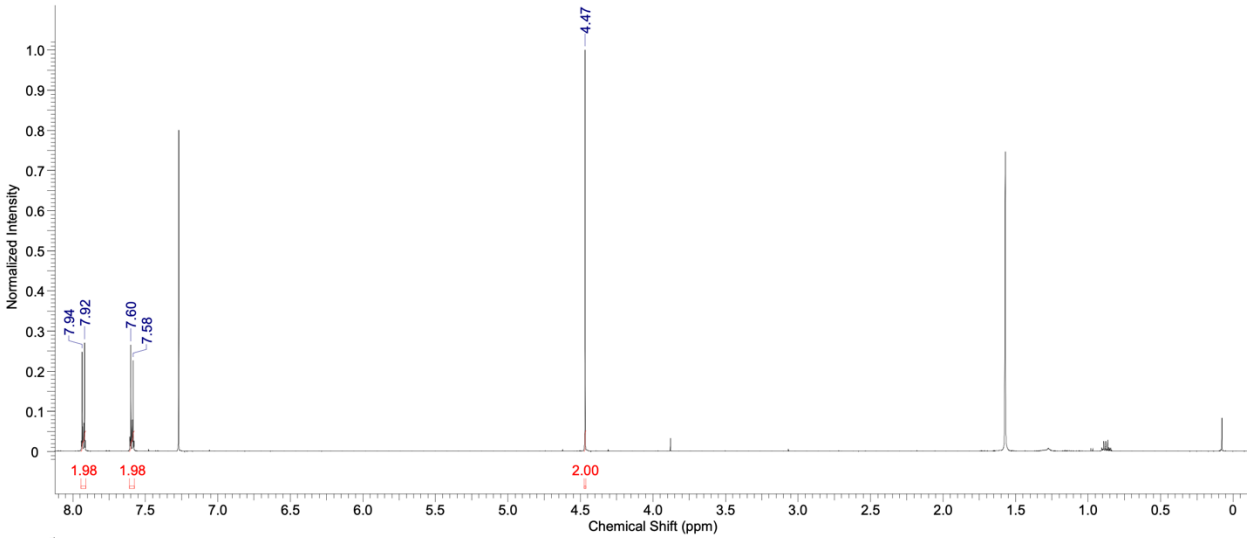


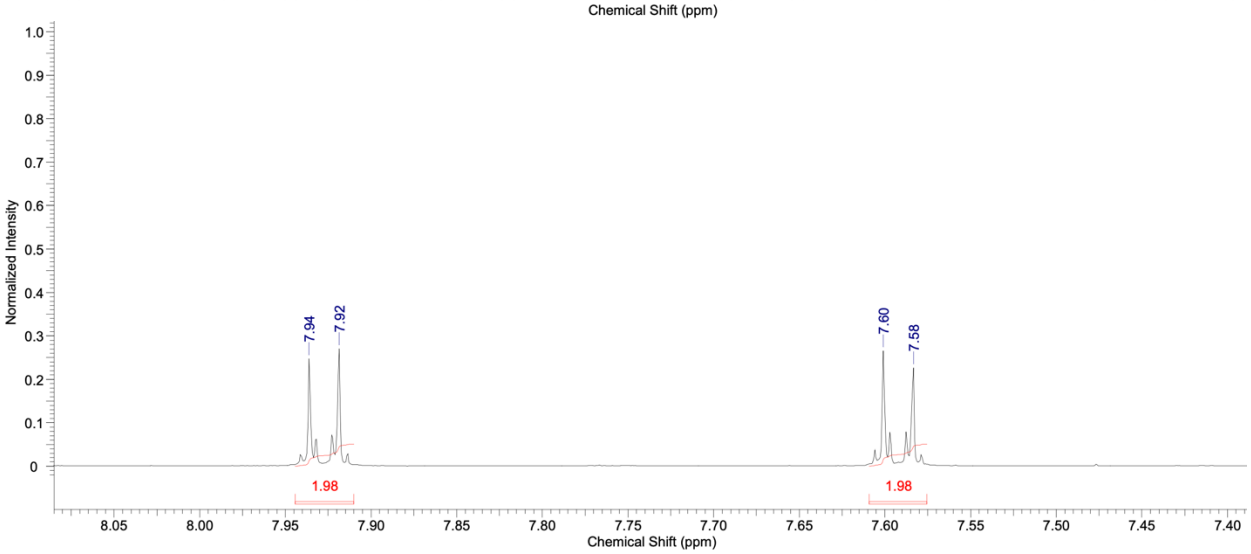


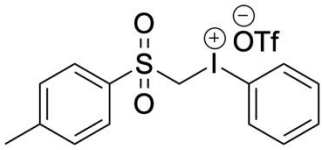


1-chloro-4-((iodomethyl)sulfonyl)benzene (1c) (water impurity)

^{1}H NMR

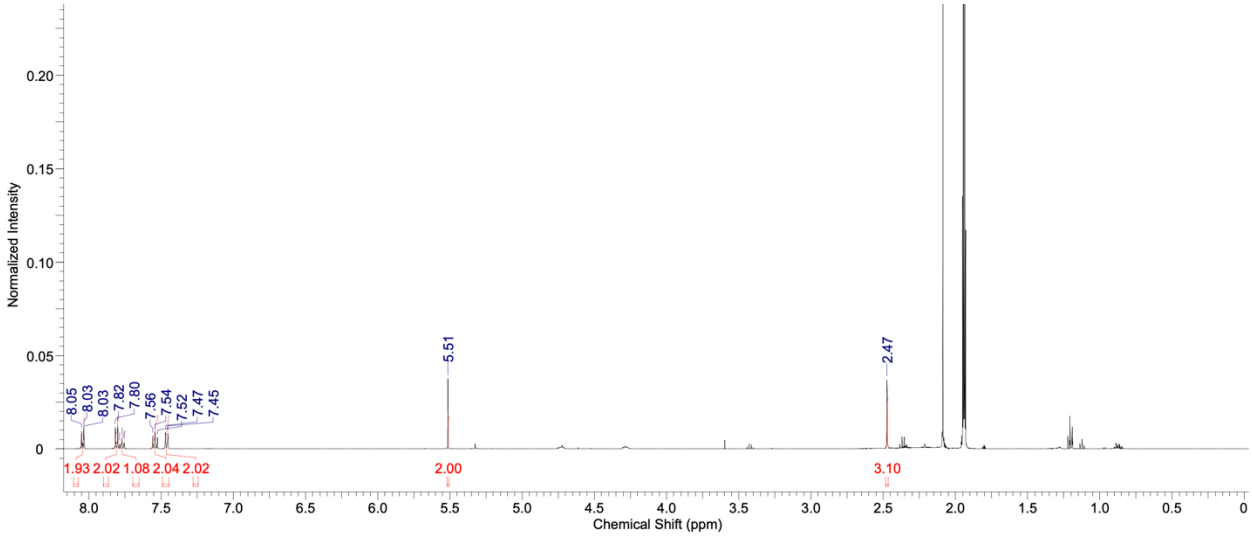


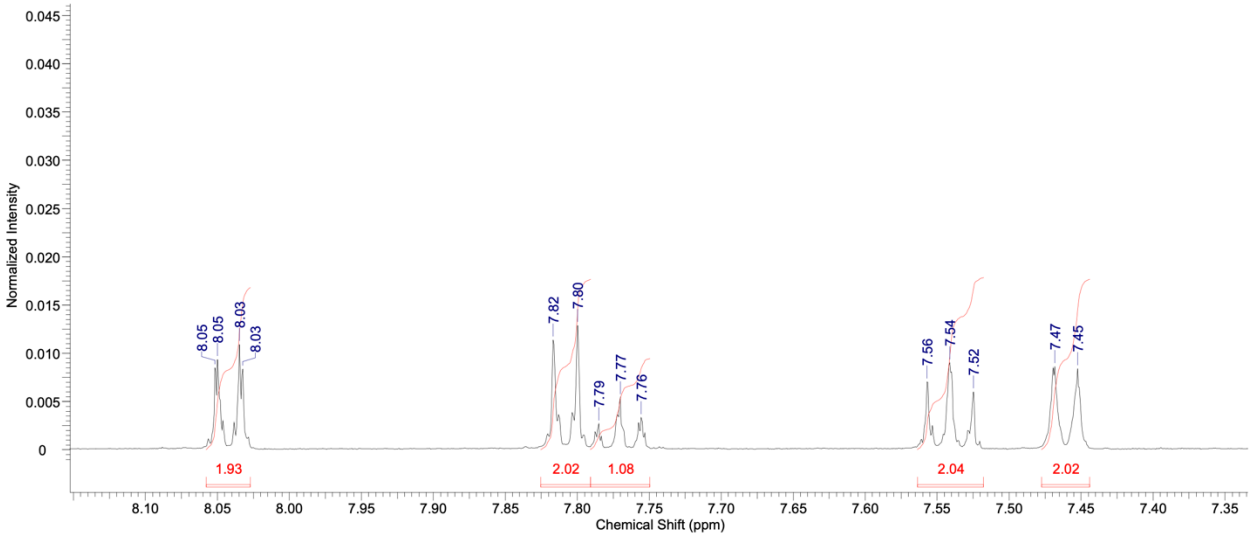




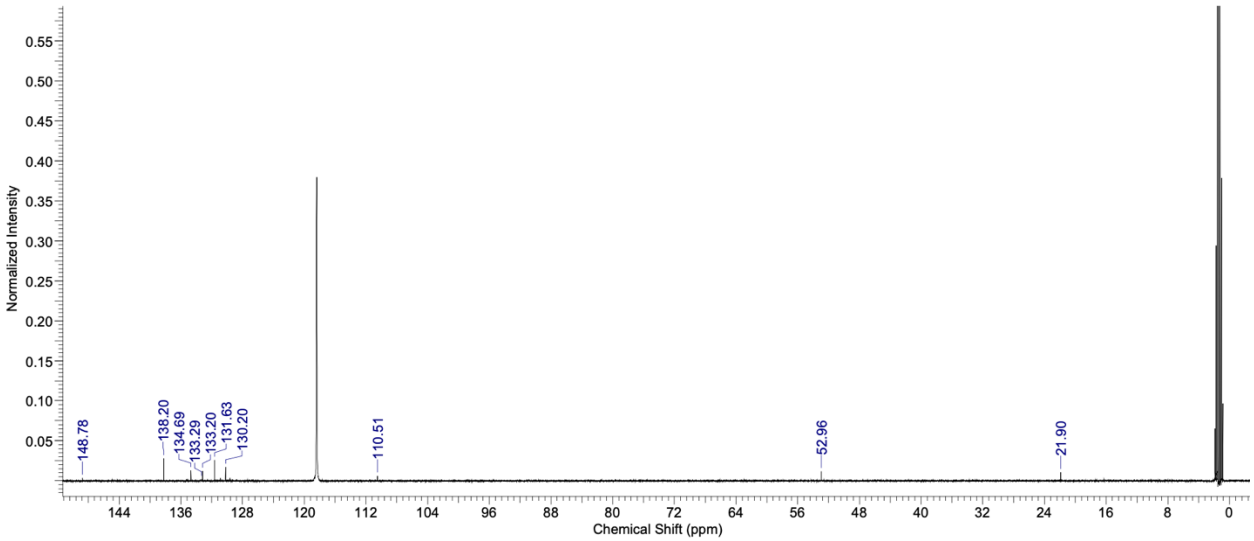
phenyl(tosylmethyl)iodonium triflate (4a) (acetone impurity)

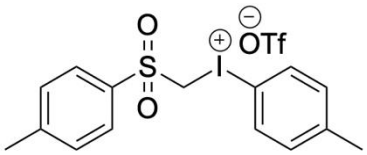
^{1}H NMR





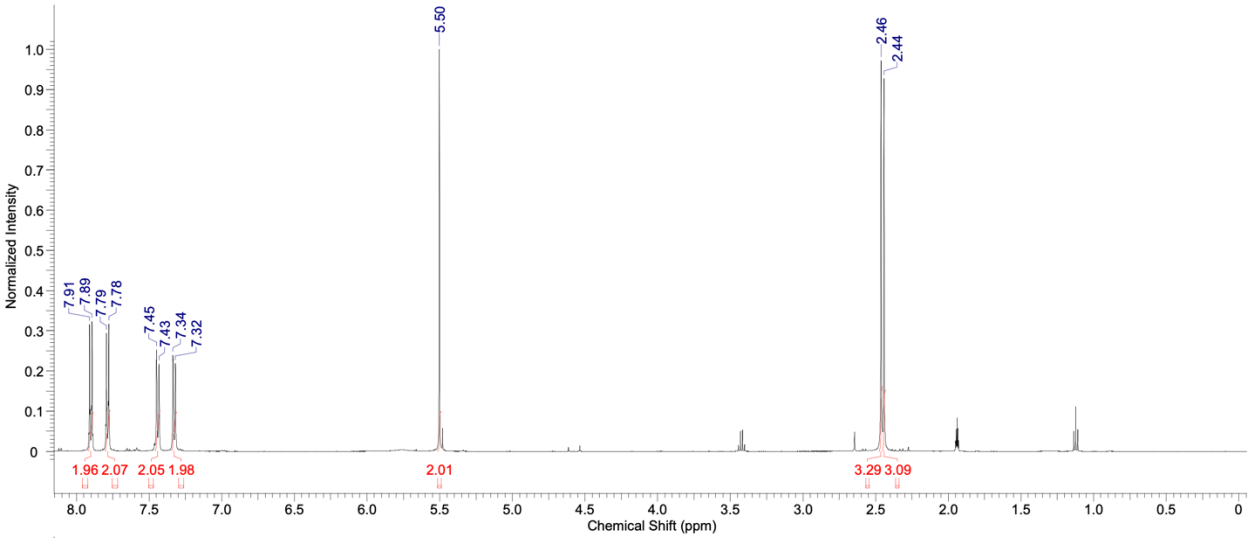
^{13}C NMR

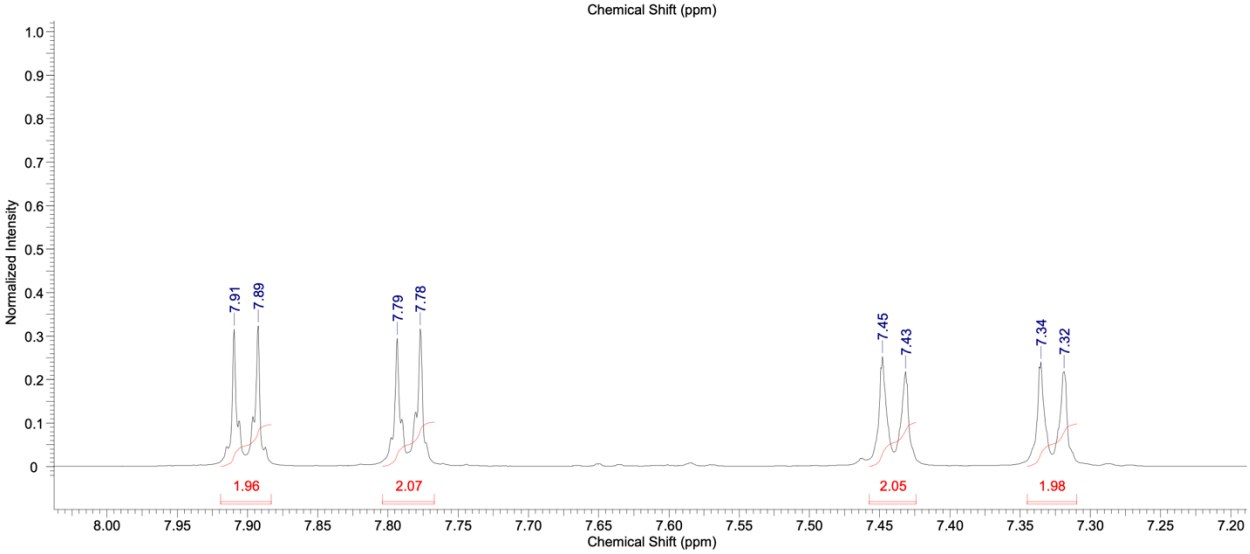




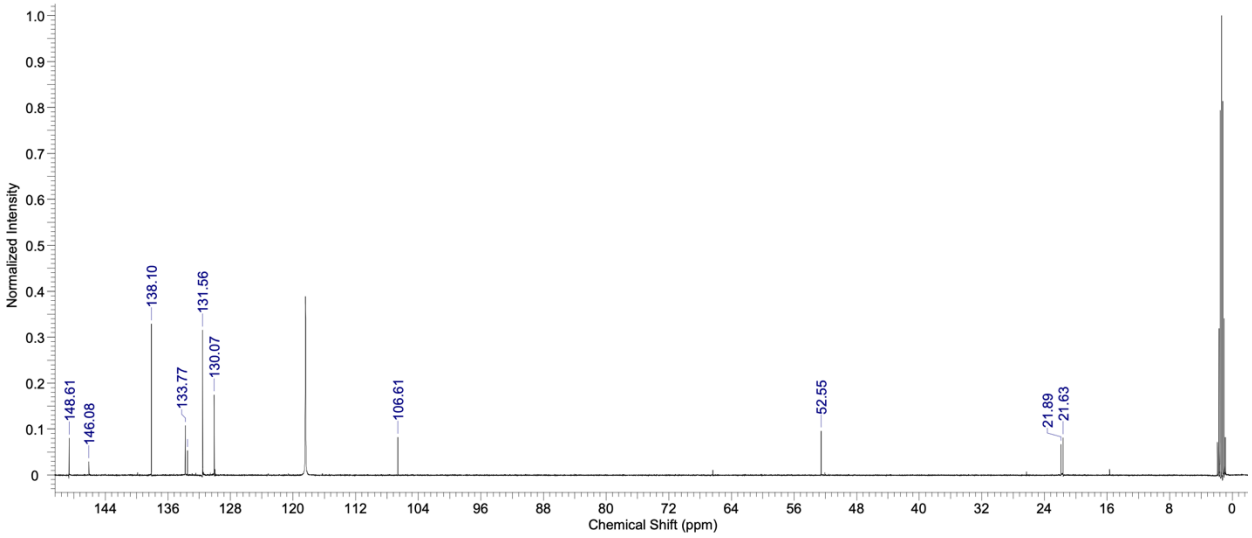
***p*-tolyl(tosylmethyl)iodonium triflate (4b)** (acetone impurity)

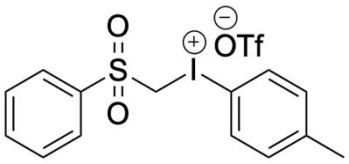
^{1}H NMR





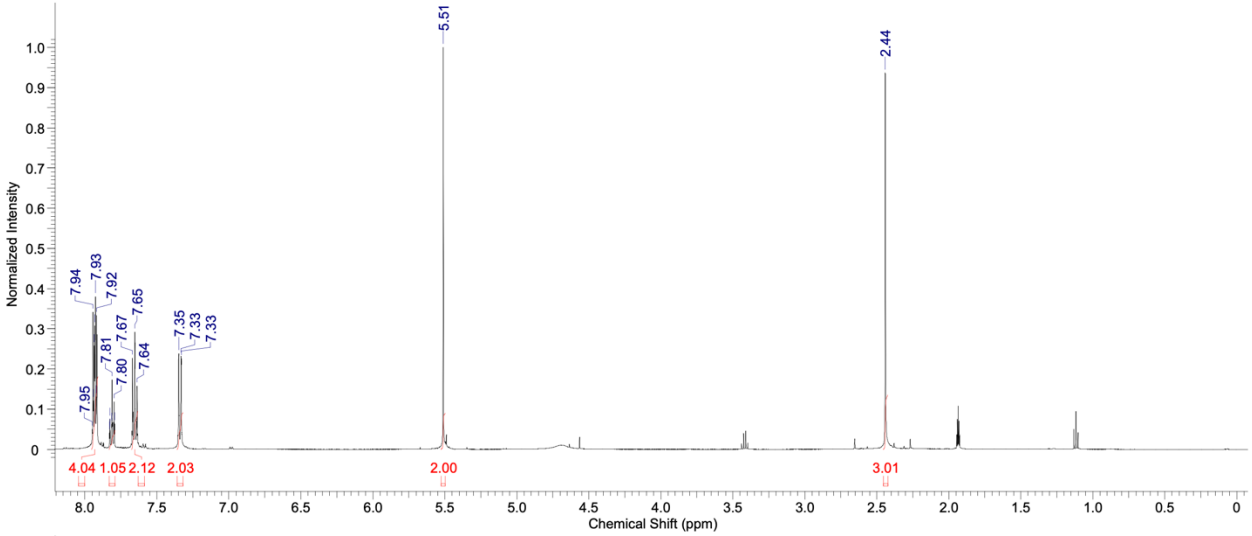
^{13}C NMR

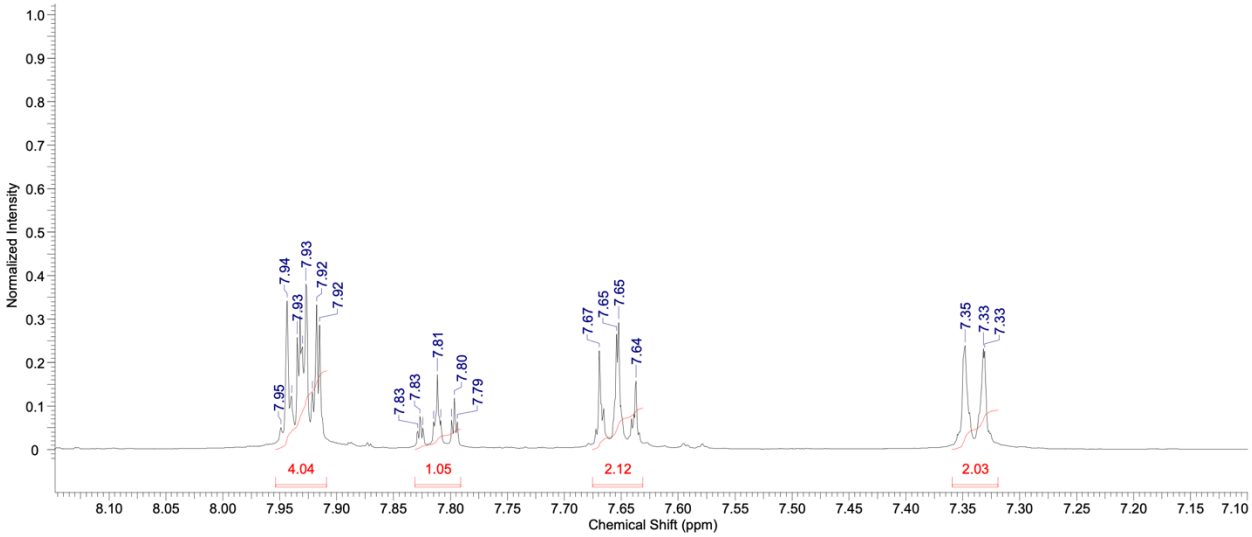




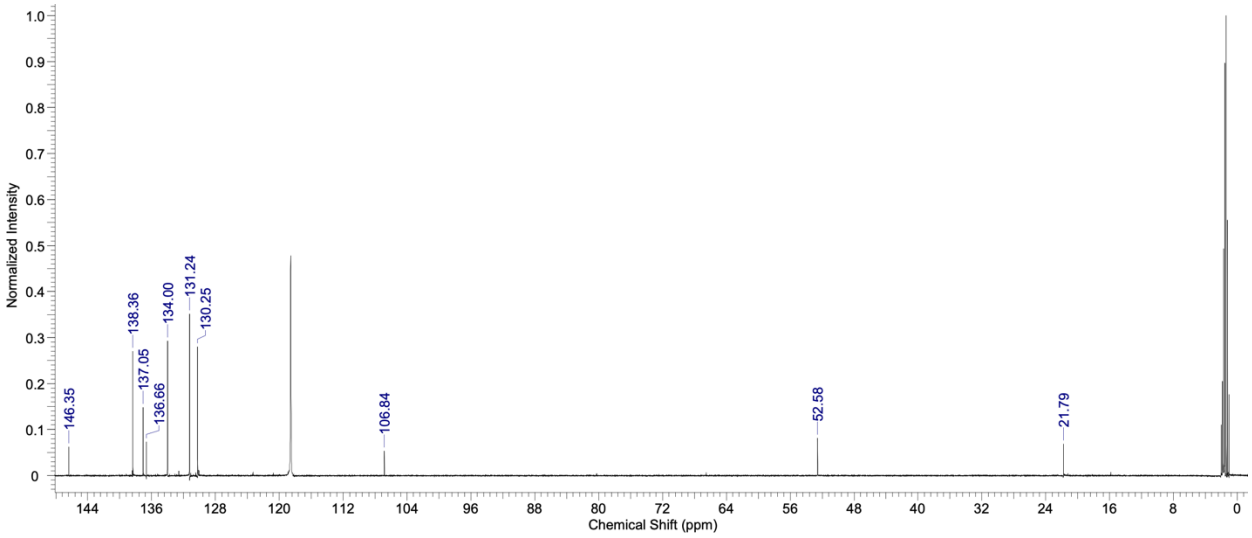
((phenylsulfonyl)methyl)(*p*-tolyl)iodonium triflate (4c)

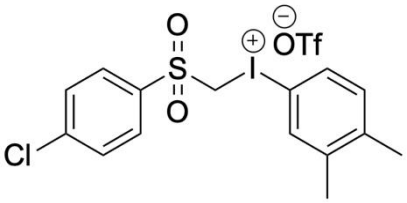
^{1}H NMR





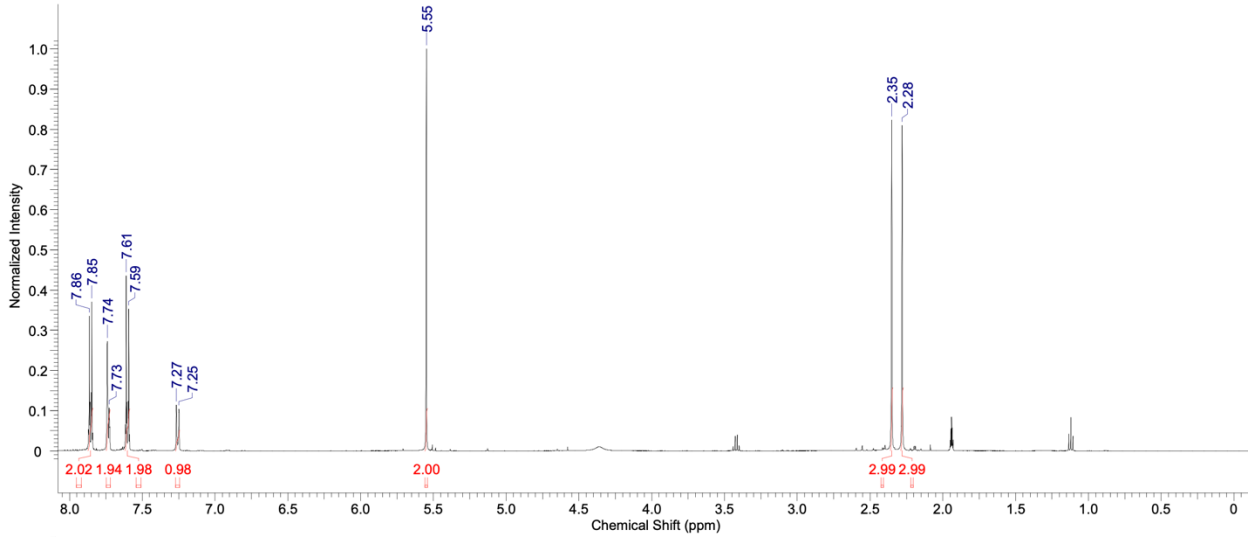
^{13}C NMR

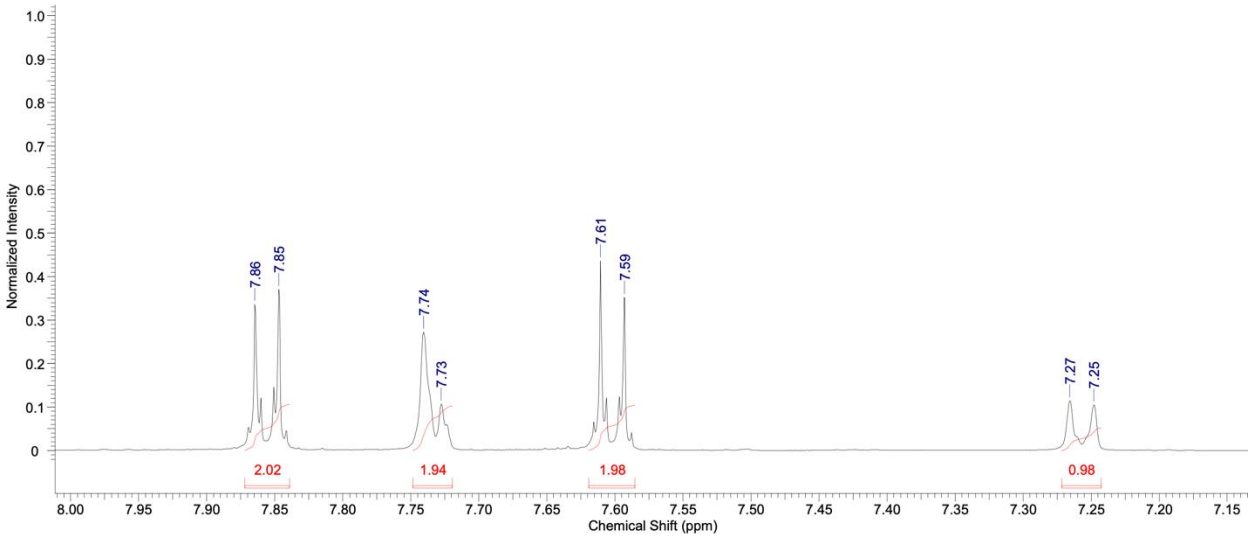




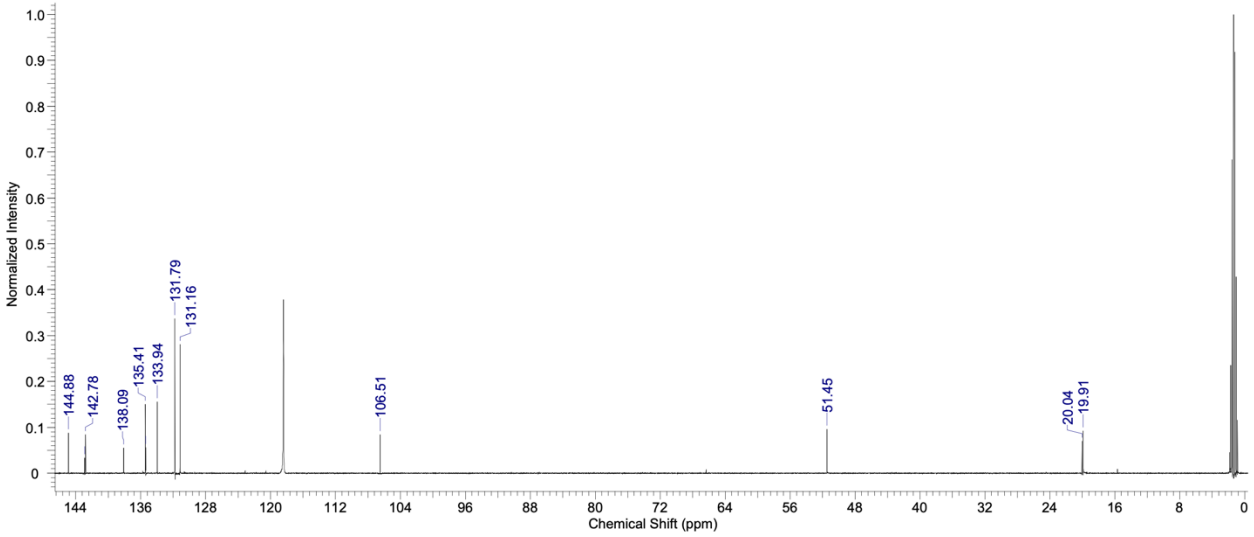
(((4-chlorophenyl)sulfonyl)methyl)(3,4-dimethylphenyl)iodonium triflate (4d)

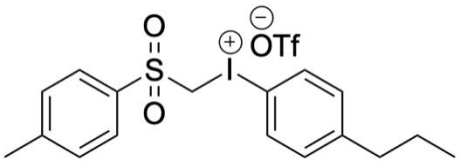
^{1}H NMR





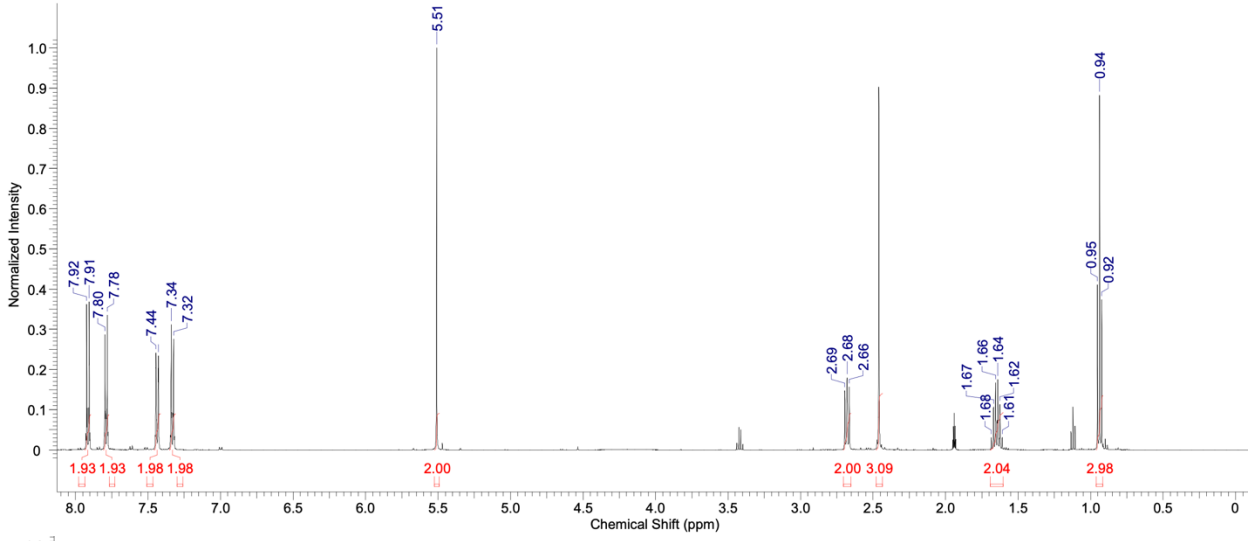
^{13}C NMR

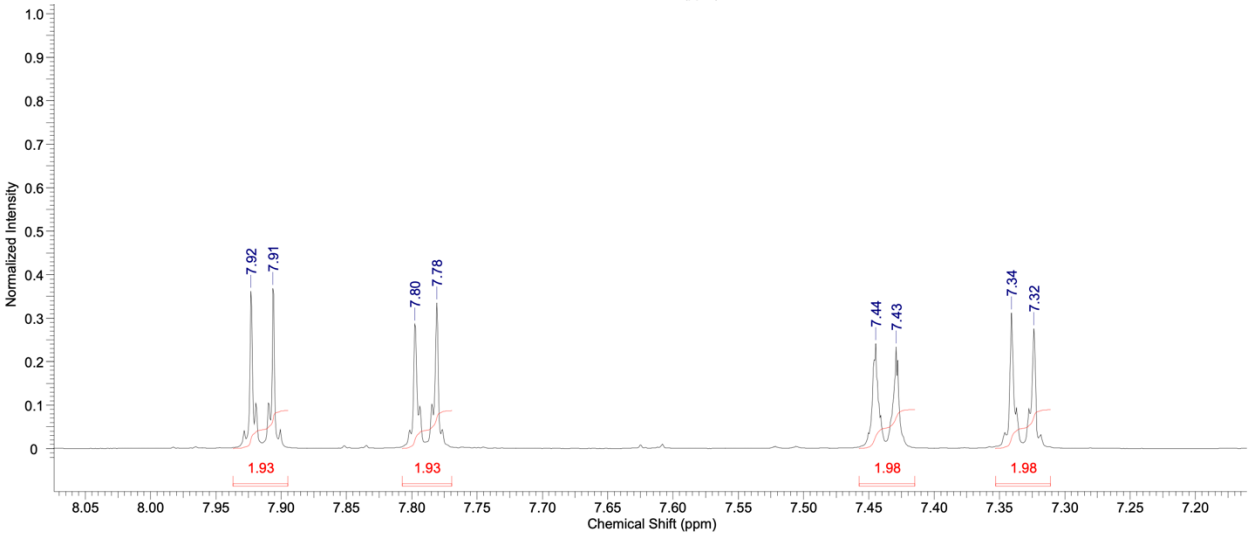




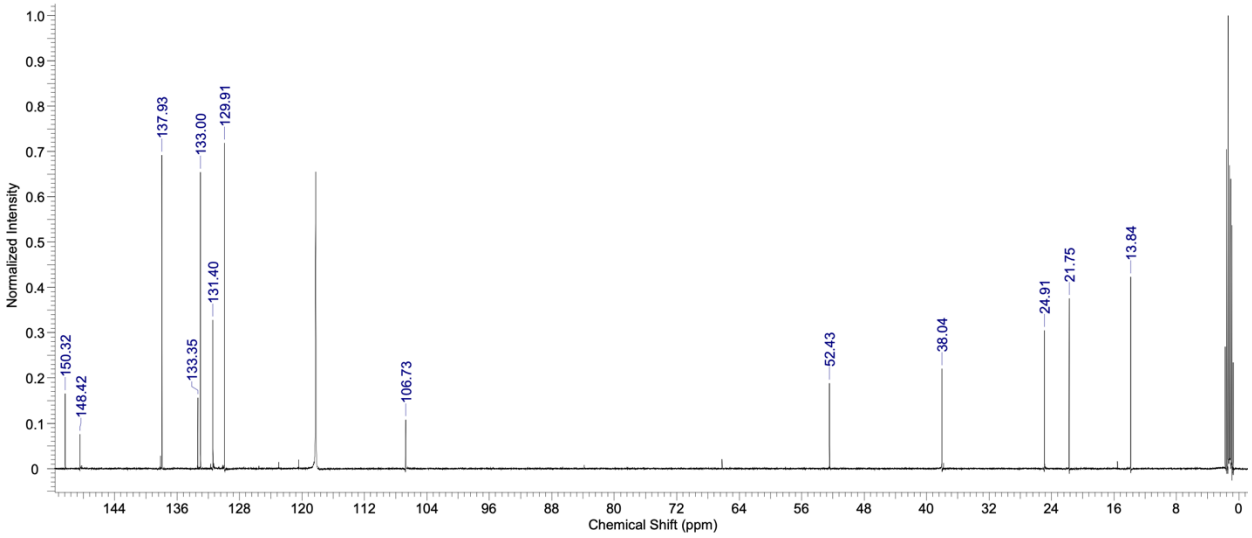
(4-propylphenyl)(tosylmethyl)iodonium triflate (4e)

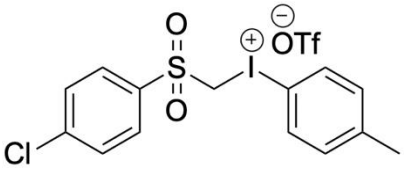
^{1}H NMR





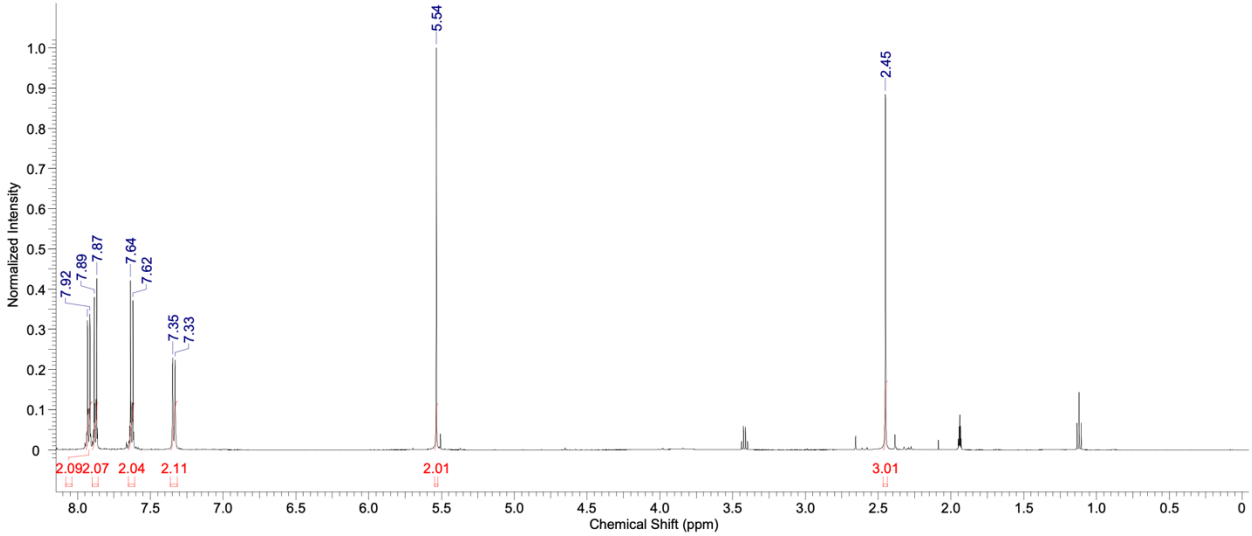
^{13}C NMR

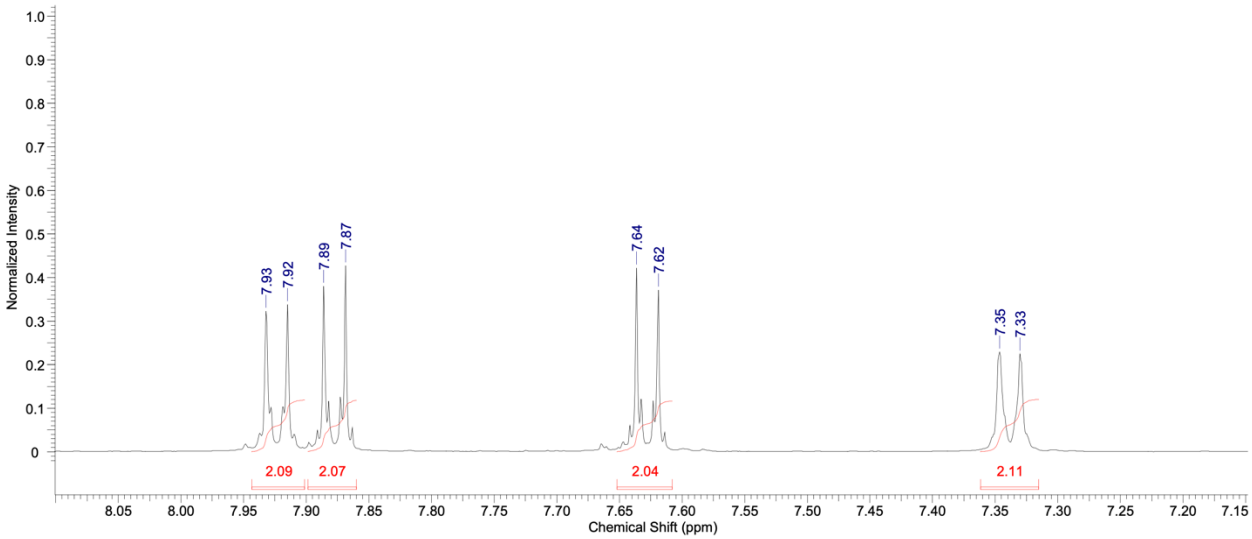




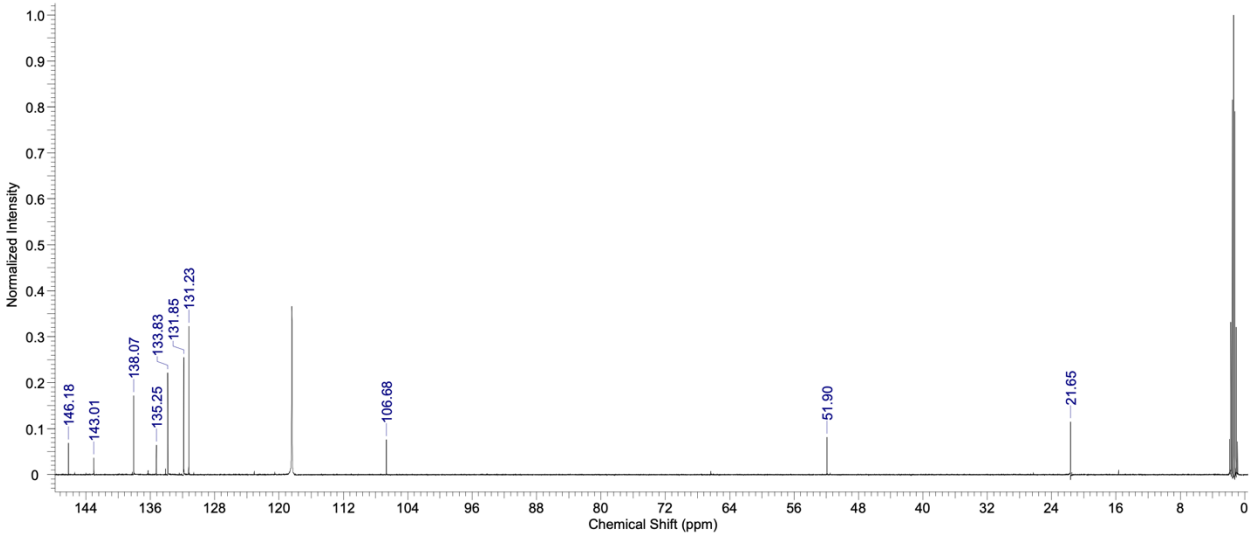
(((4-chlorophenyl)sulfonyl)methyl)(*p*-tolyl)iodonium triflate (4f)

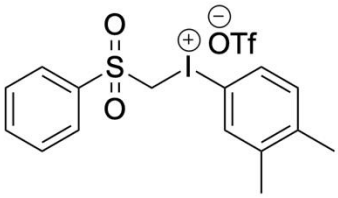
^{1}H NMR





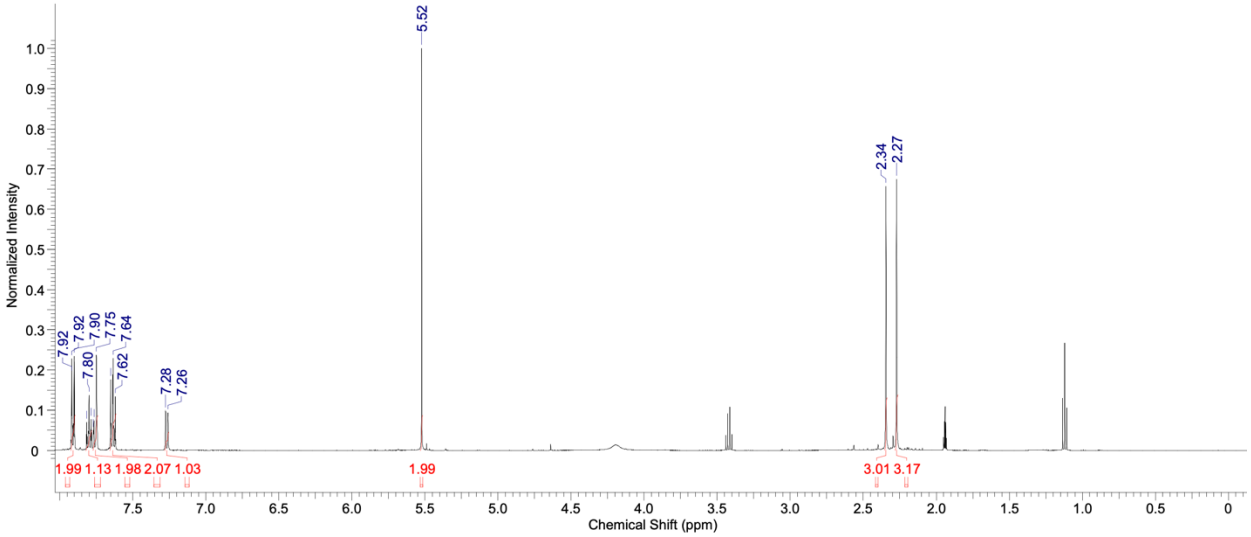
^{13}C NMR

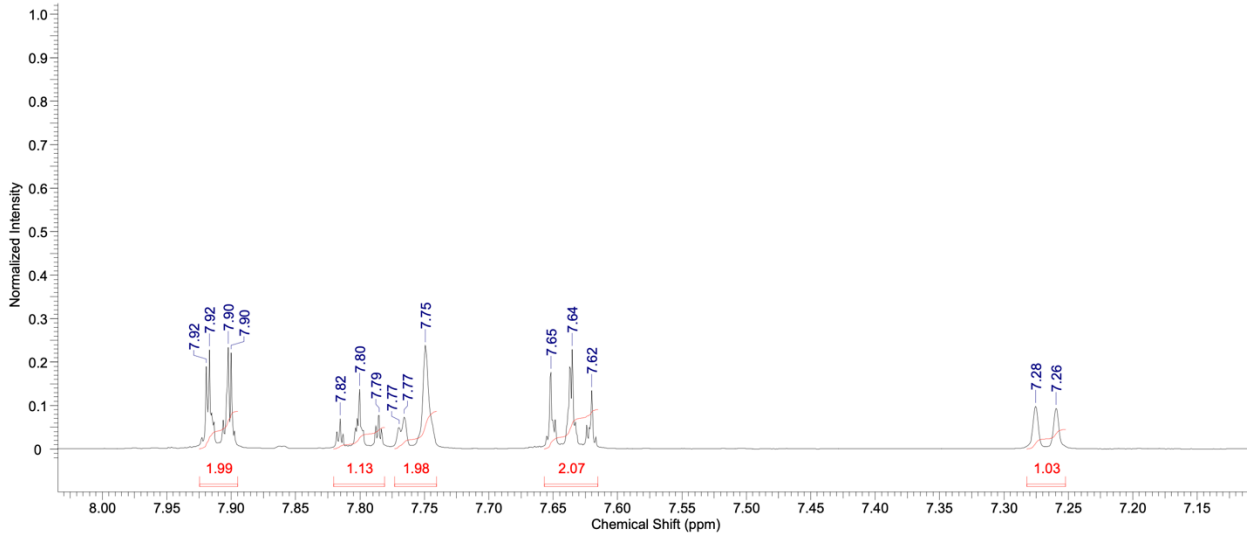




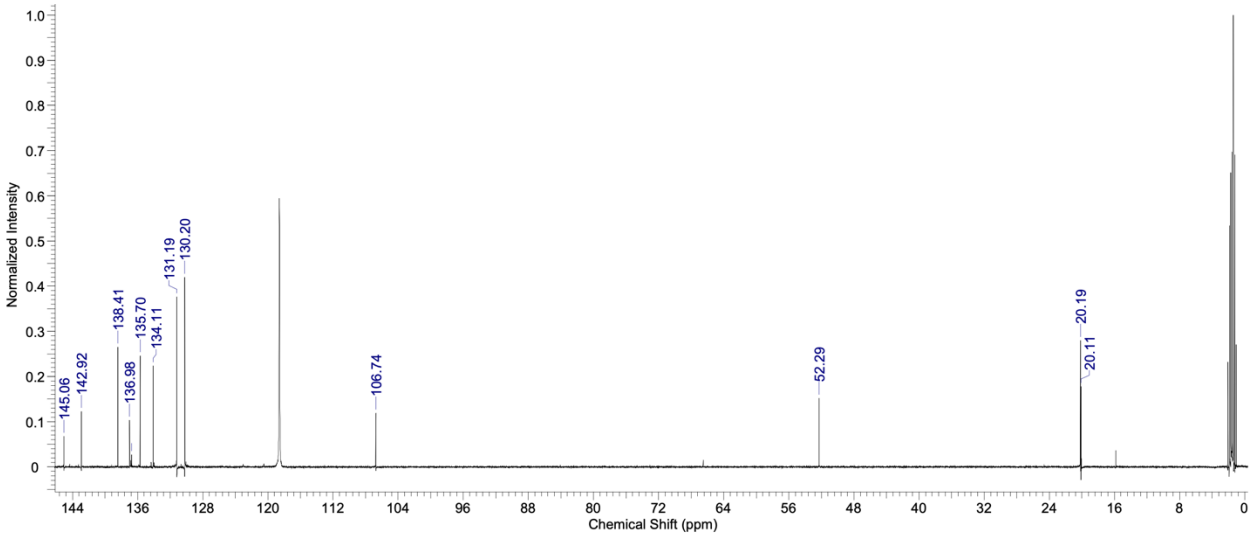
(3,4-dimethylphenyl)((phenylsulfonyl)methyl)iodonium triflate (4g)

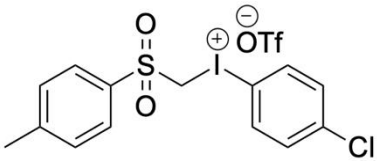
^{1}H NMR





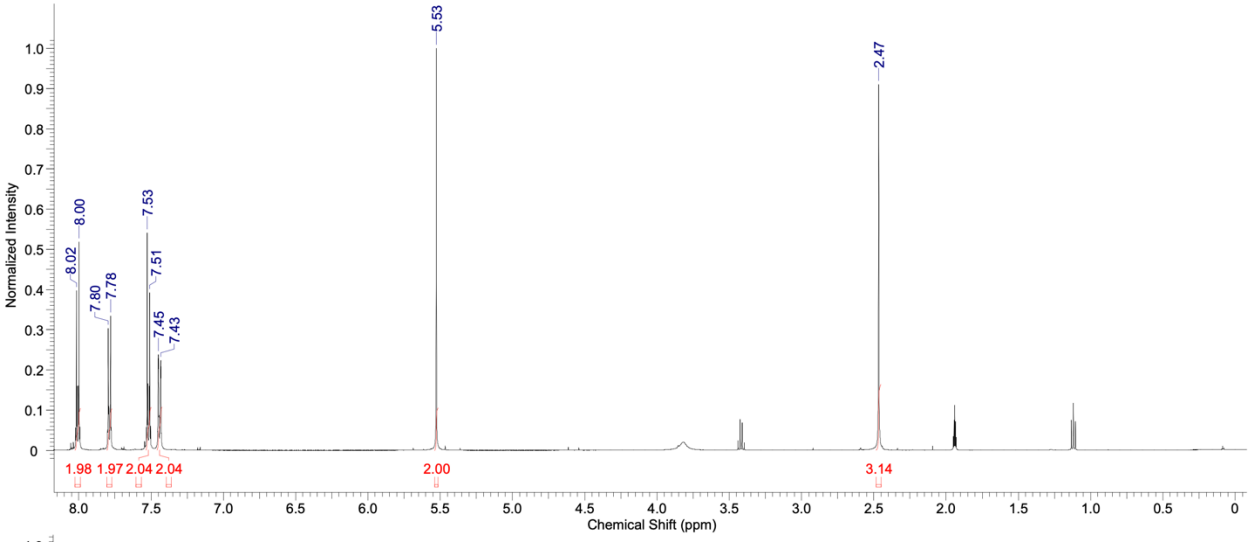
^{13}C NMR

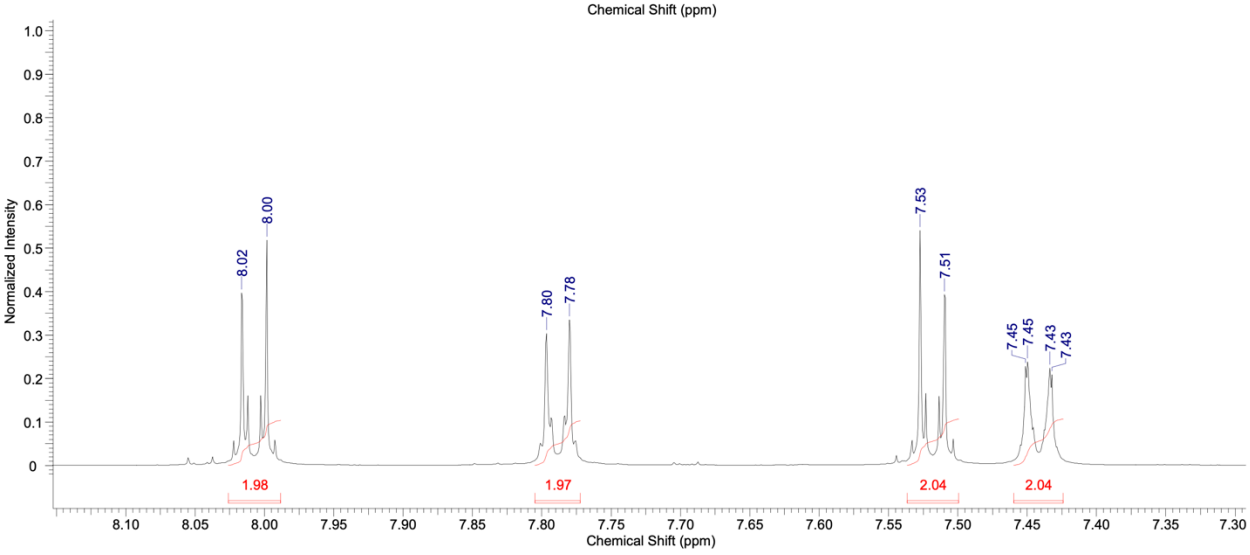




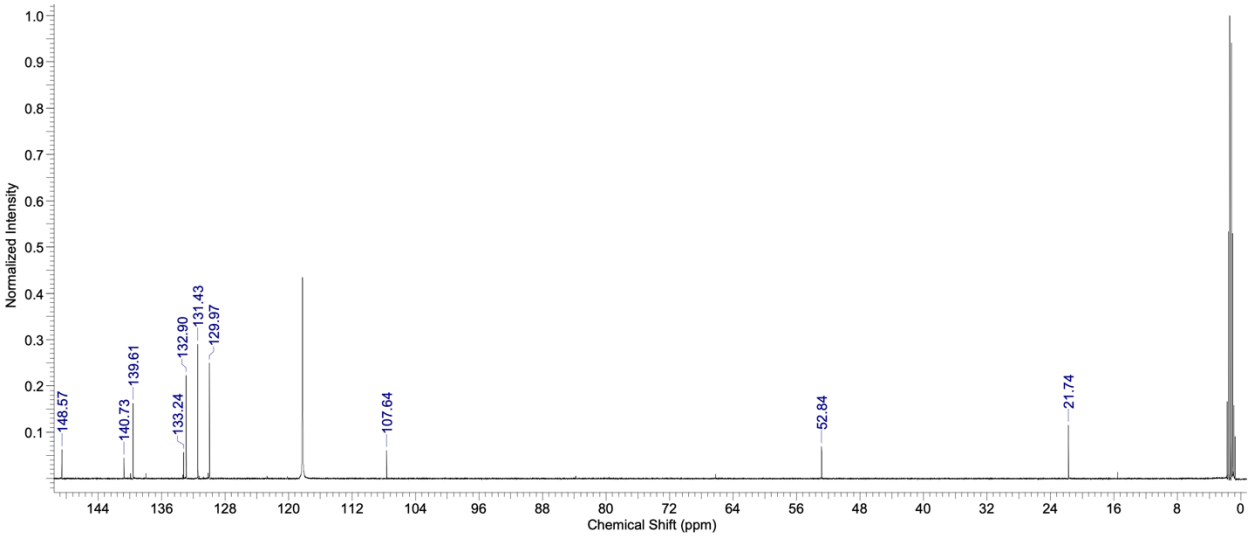
(4-chlorophenyl)(tosylmethyl)iodonium triflate (4h)

^{1}H NMR





^{13}C NMR

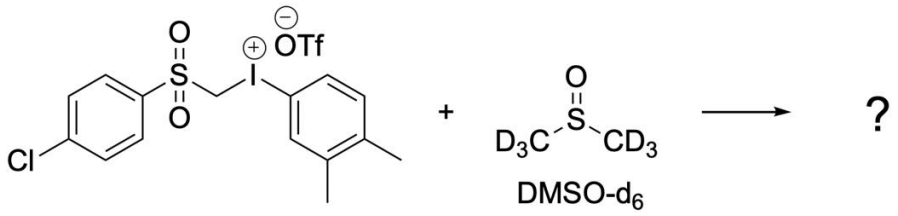


Degradation Behavior in Deuterated Solvents

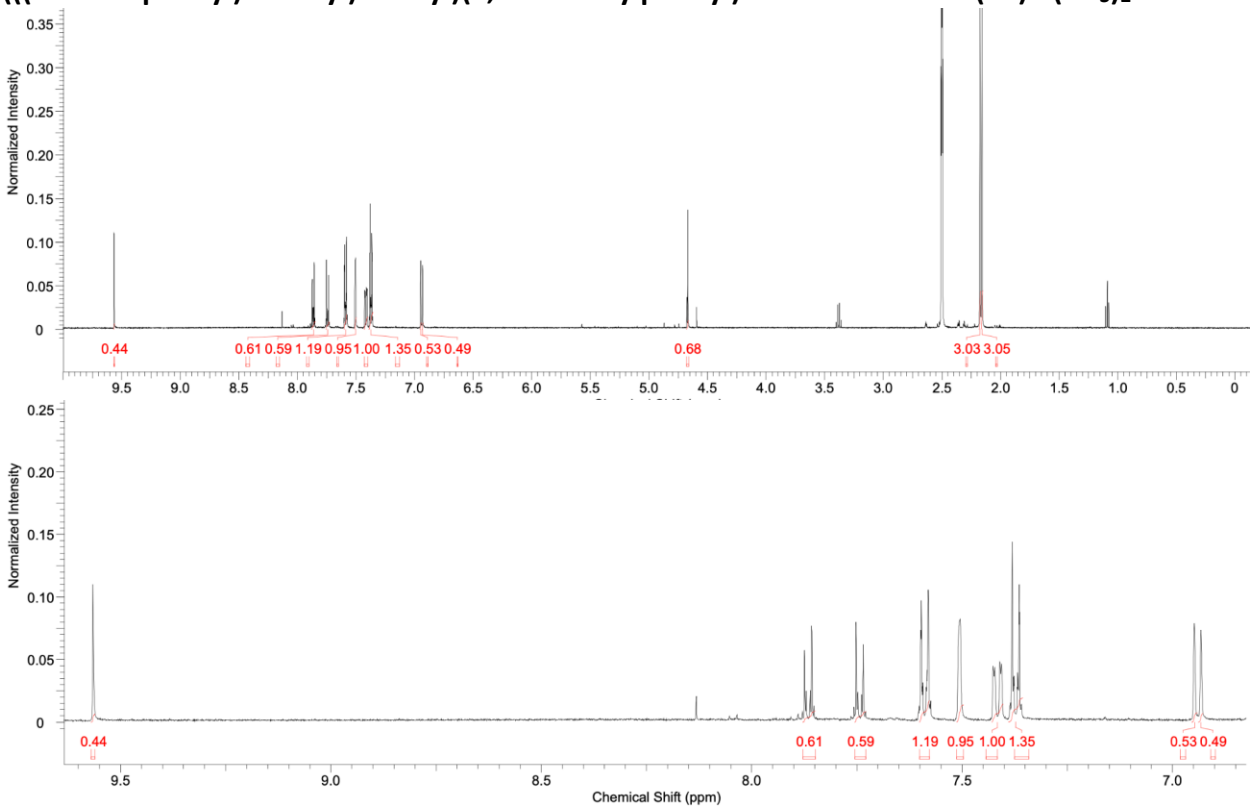
The stability of the synthesized aryl((arylsulfonyl)methyl)iodonium triflate derivatives was found to be highly dependent on the choice of deuterated NMR solvents, with specific degradations observed in less than 4 hours (exception: deuterated acetonitrile was 8 hours).

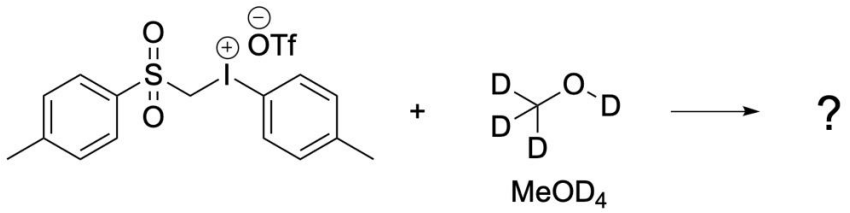
Distinct degradation pathways were observed:

- $(CD_3)SO$: In the presence of DMSO, the aryl((arylsulfonyl)methyl)iodonium triflate undergoes a Kornblum-type oxidation that likely leads to the formation of a sulfonyl aldehyde and the iodomethylsulfone, as assessed by the NMR spectrum.
- CD_3OD: Deuterated methanol appears to attack the methylene, or a possible diiodo-complex is formed, as evidenced by a new peak at approximately 4.9 ppm. yielding unreacted starting material and 4-iodotoluene as the primary degradation products.
- Acetonitrile-d_3: Acetonitrile facilitates reductive elimination of the hypervalent iodine center, leading to a mixture of the iodonium triflate salt, unreacted starting material, and 4-iodotoluene.
- Acetone-d_6: Acetone provides a complex mixture of products, such as starting material, 4-iodotoluene, and a potential secondary hypervalent iodine species.

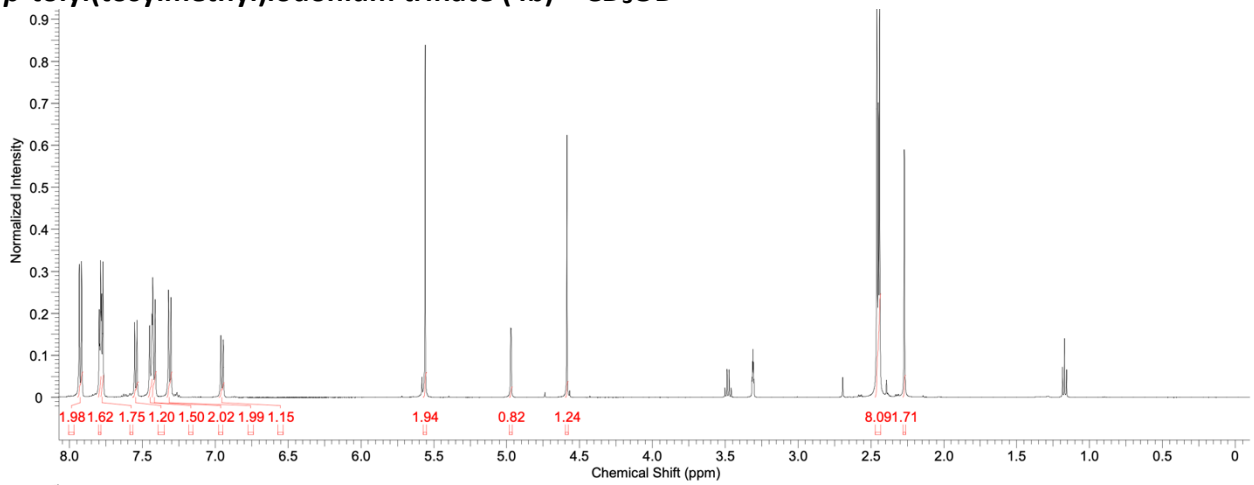


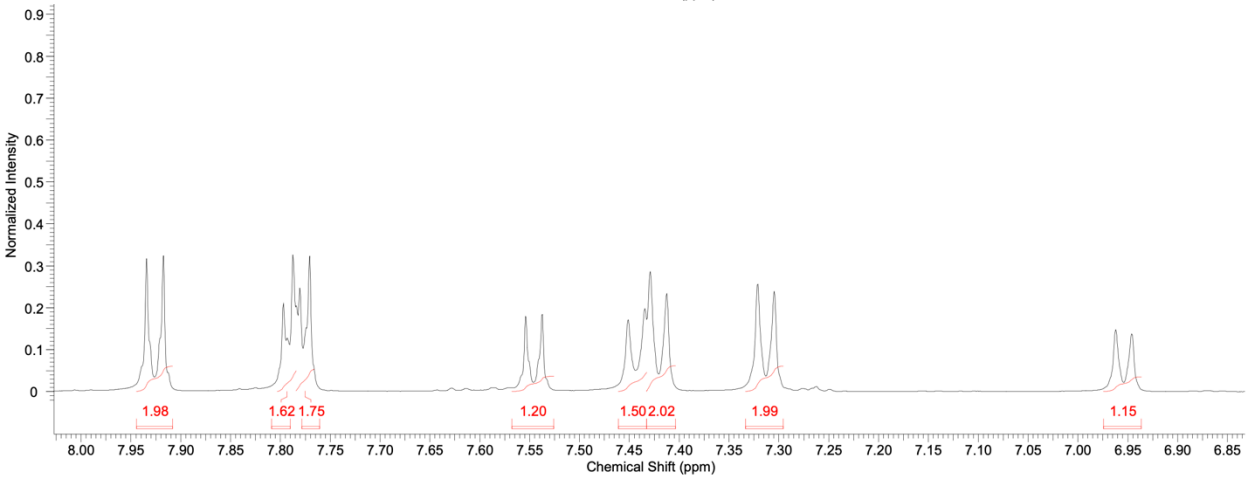
(((4-chlorophenyl)sulfonyl)methyl)(3,4-dimethylphenyl)iodonium triflate (4d) - $(CD_3)_2SO$

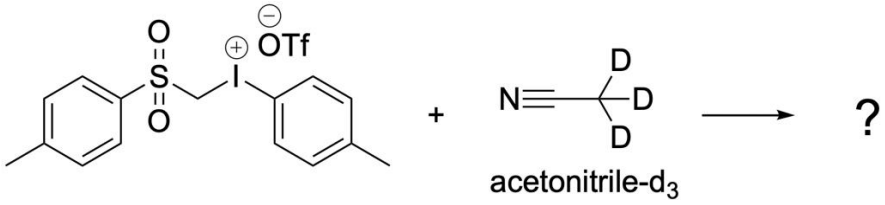




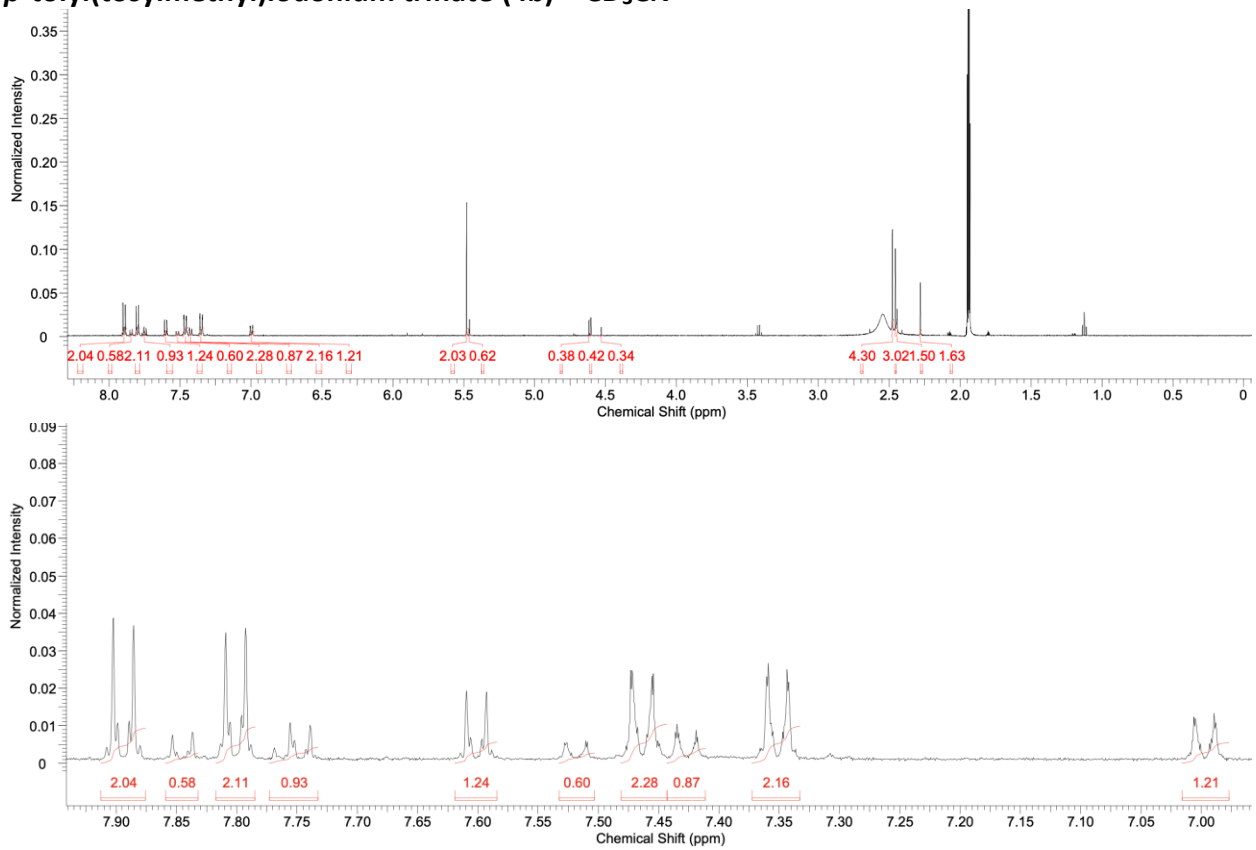
p-tolyl(tosylmethyl)iodonium triflate (4b) – CD_3OD

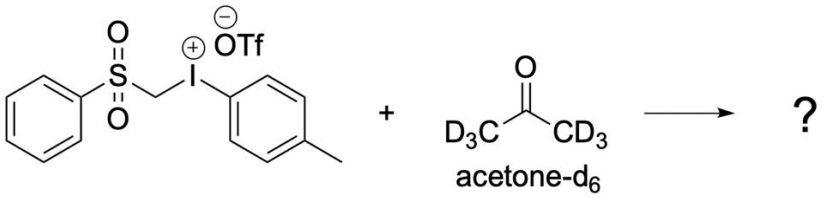




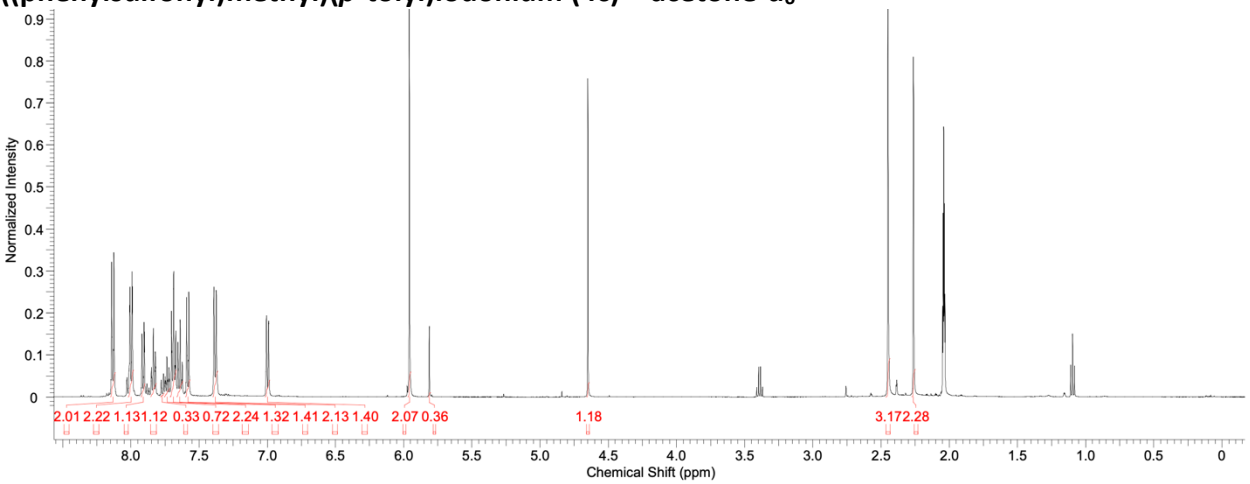


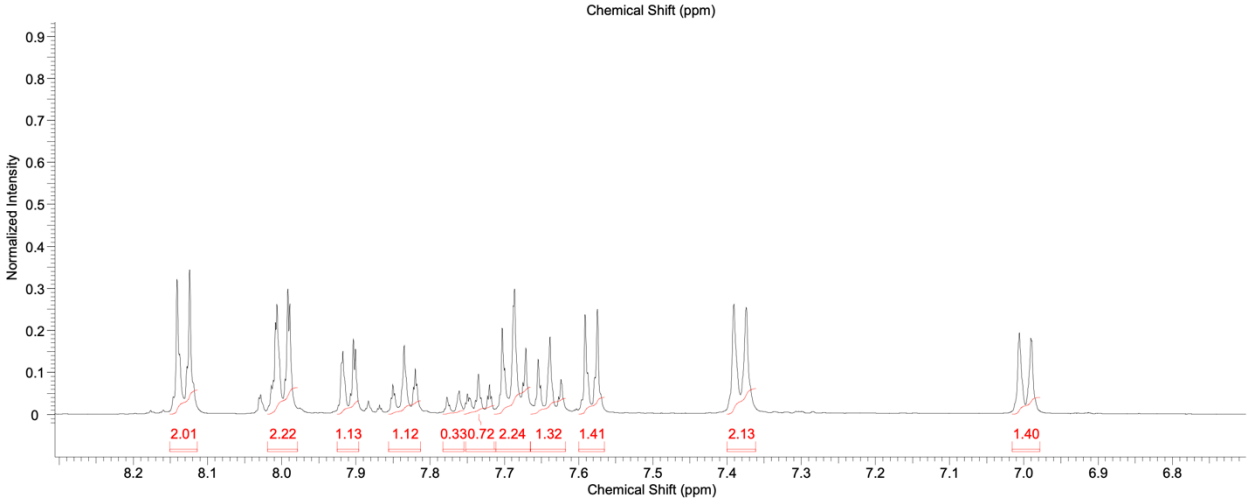
_p_-tolyl(tosylmethyl)iodonium triflate (4b) – CD_3CN



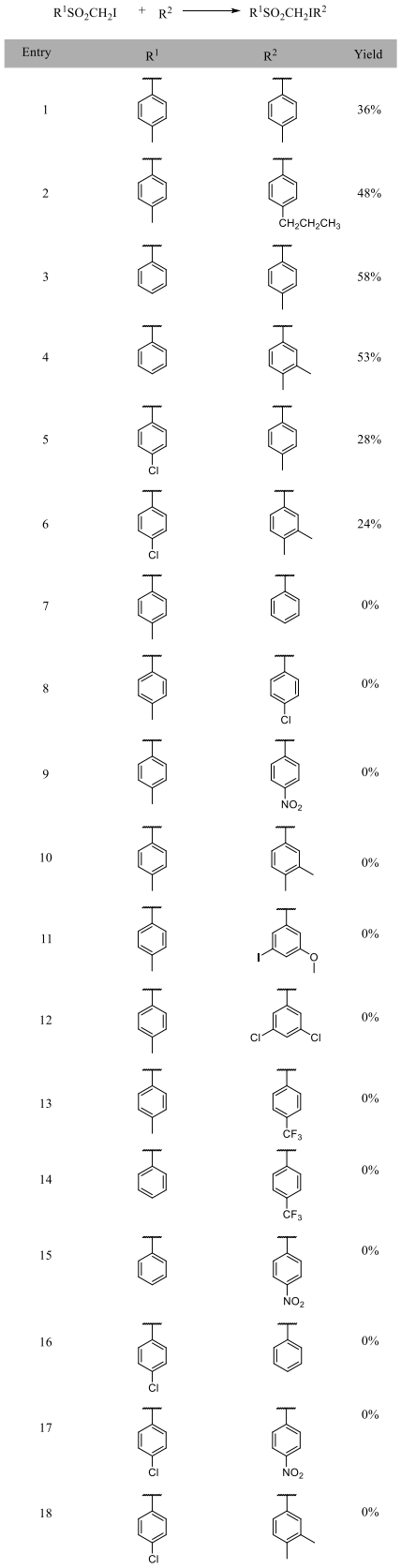


((phenylsulfonyl)methyl)(*p*-tolyl)iodonium (4c) – acetone-d$_6$





Substrate Scope of Isolated Compounds



References

[1] Suryakiran, N., Prabhakar, P., Srikanth Reddy, T., Chinni Mahesh, K., Rajesh, K., & Venkateswarlu, Y. (**2007**). Chemoselective mono halogenation of β-keto-sulfones using potassium halide and hydrogen peroxide;

synthesis of halomethyl sulfones and dihalomethyl sulfones. *Tetrahedron Letters*, *48*(5), 877–881. https://doi.org/10.1016/J.TETLET.2006.11.129

[2] Suryakiran, N., Srikanth Reddy, T., Suresh, V., Lakshman, M., & Venkateswarlu, Y. (**2006**). Synthesis of α-iodo β-ketosulfones and α-iodo methylsulfones using iodine monochloride. *Tetrahedron Letters*, *47*(26), 4319–4323. https://doi.org/10.1016/J.TETLET.2006.04.123

[3] Shen, J., Li, H., Li, Y., Zhu, Z., Luo, K., & Wu, L. (**2024**). Visible-Light-Promoted Radical Cascade Sulfone Alkylation/Cyclization of 2-Isocyanoaryl Thioethers Enabled by Electron Donor–Acceptor Complex Formation. *The Journal of Organic Chemistry*, *89*(14), 10223–10233. https://doi.org/10.1021/ACS.JOC.4C01100

