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Supporting Information

Investigation of Olefin as a Cocatalyst for Halonium Catalysis

Alex M. Nguyen[a], Nur-E Alom,[a] Madison Martin Erickson, Jonathon T. Truong, Adedapo O. Olosunde, Kristi Shrestha, Zhichang Yin, Michelle M. Huynh, Xiche Hu*, and Wei Li*[a]

Department of Chemistry and Biochemistry, School of Green Chemistry and Engineering, The University of Toledo, 2801 West Bancroft Street, Toledo, Ohio-43606, United States

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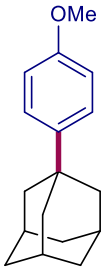
1. General Information. Commercial reagents and solvents were purchased from Sigma Aldrich, Oakwood Chemicals, Alfa Aesar, Matrix Scientific, Acros Organic, and were used as received. The alcohol substrates were synthesized according to the reported procedure. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an acetone-dry ice bath. Chromatographic purification of products was accomplished using flash chromatography on 230-400 mesh silica gel. Thin-layer chromatography (TLC) was performed on Analtech 250 mm silica gel HLF UV-254 plates. Visualization of the developed plates was performed by fluorescence quenching, potassium permanganate, and iodine-silica gel system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 600 instrument (600 and 150 MHz) or INOVA 600 (600 and 150 MHz) and are internally referenced to residual protio solvent signals (for $CDCl_3$, δ 7.26 and 77.0 ppm, MeOH-d_4 δ 3.31, 4.90 and 49.0 ppm, DMSO-d_6 δ 2.50 and 39.53 respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. IR spectra were recorded on a PerkinElmer FT-IR spectrophotometer and are reported in terms of wavenumber of absorption (cm^{-1}). High resolution mass spectra were obtained on Waters Synapt High-Definition Mass Spectrometer (HDMS) by electrospray ionization at The University of Toledo, OH, USA.

2. Experimental Procedures

General Procedure A: The 1-adamantanol (38mg, 0.25 mmol) and anisole (41 mL, 0.375 mmol), 1-methyl-1-cyclohexene (3 µL, 10 mol%), NIS (5.6 mg, 10 mol%) were added to 8 mL vial. Then, HFIP (1.5 mL) was added to the reaction mixture and stirred at room temperature for 16 h. After the reaction, HFIP was removed by rotavapor. The reaction was quenched with 20% $Na_2S_2O_3$ (1 mL) and EtOAc (2 mL) was added. The organic layer was separated, and aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic solution was dried with anhydrous Na_2SO_4, filtered, concentrated *in vacuo* by rotavapor and purified by flash chromatography on SiO_2 to provide the desired product.

3. Spectral Characterization of the Products



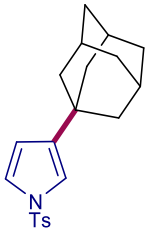
1-(4-methoxyphenyl)adamantane (4): This compound was prepared according to the General Procedure A using 1-adamantanol (38 mg, 0.25 mmol), anisole (41 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a colorless liquid (60 mg, 99% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33-7.28 (d, *J* = 8.5 Hz, 2 H), 6.91-6.85 (d, *J* = 8.5 Hz, 2 H), 3.81 (s, 3 H), 2.10 (br. s., 3 H), 1.91 (br. s., 6 H), 1.83-1.71 (m, 6 H);

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.3, 143.7, 125.8, 113.4, 55.2, 43.4, 36.8, 35.5, 29.0;

IR (neat): 2904.5, 1509.7, 1244.7, 1029.25, 801.8 cm^{-1};

HRMS (ESI) *m/z* calcd for $C_{17}H_{23}O$ [$(M+H)^+$] 243.1743, found 243.1708



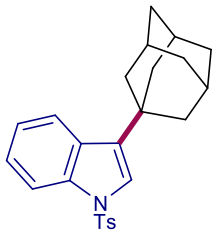
3-adamantan-1-yl-1-tosyl-1H-pyrrole (5): This compound was prepared according to the General Procedure A using 1-adamantanol (38 mg, 0.25 mmol), 1-tosyl-1H-pyrrole (83 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a white solid (79 mg, 89% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.06 (t, *J* = 2.2 Hz, 1 H), 6.85 (s, 1 H), 6.27-6.22 (m, 1 H), 2.40 (s, 3 H), 2.00 (br. s., 3 H), 1.78-1.67 (m, 12 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 140.9, 136.4, 129.9, 126.7, 120.6, 114.8, 111.7, 43.2, 36.7, 32.6, 28.6, 21.6

IR (neat): 2905.9, 2850.8, 1737.5, 1352.8, 670 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{21}H_{26}NO_2S$ [$(M+Na)^+$] 378.1498, found 378.1493.



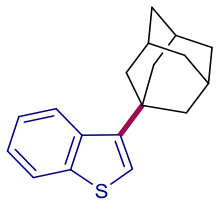
3-(adamantan-1-yl)-1-tosyl-1H-indole (6): This compound was prepared according to the General Procedure A using 1-adamantanol (38 mg, 0.25 mmol), 1-tosyl-1H-indole (102 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a white solid (98 mg, 97% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.27-7.22 (m, 2 H), 7.22-7.14 (m, 3 H), 2.32 (s, 3 H), 2.08 (br. s., 3 H), 2.03 (br. s., 6 H), 1.85-1.76 (m, 6 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 135.9, 135.3, 132.8, 129.7, 129.3, 126.7, 123.9, 122.3, 122.0, 121.0, 113.9, 42.1, 36.9, 34.0, 28.5, 21.5

IR (neat): 2930, 2909.8, 1353.6, 1149.3, 671.0 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{25}H_{28}NO_2S$ [$(M+ Na)^+$] 428.1654, found 428.1658

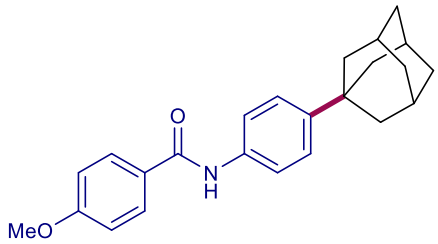


3-(adamantan-1-yl)benzo[b]thiophene (7): This compound was prepared according to the General Procedure A using 1-adamantanol (38 mg, 0.25 mmol), benzo[b]thiophene (50 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (hexanes), the title compound was isolated as a white solid (53 mg, 79% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 7.8 Hz, 1 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 7.29 (t, *J* = 7.3 Hz, 1 H), 7.07 (s, 1 H), 2.18 (s, 6 H), 2.14 (br. s., 3 H), 1.85 (br. s., 6 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.1, 141.7, 137.5, 124.6, 123.4, 123.3, 123.0, 119.7, 42.0, 37.0, 36.9, 28.8

HRMS (ESI) *m/z* calcd for $C_{18}H_{21}S$ [$(M+H)^+$] 269.1358, found 269.1318



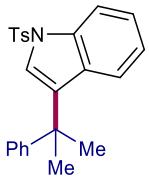
N-(4-adamantan-1-yl)phenyl)-4-methoxybenzamide (8): This compound was prepared according to the General Procedure A using 1-adamantanol (38 mg, 0.25 mmol), 4-methoxy-N-phenylbenzamide (85 mg, 0.375 mmol) at 50 ºC. After purification by column chromatography on SiO_2 (20% EtOAc in hexanes), the title compound was isolated as a white solid (58 mg, 64% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.60-7.53 (m, *J* = 8.5 Hz, 2 H), 7.36-7.29 (m, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H), 2.10 (br. s., 3 H), 1.90 (br. s., 6 H), 1.83-1.69 (m, 6 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 162.2, 147.5, 135.5, 128.9, 127.2, 125.4, 120.1, 113.8, 55.4, 43.1, 36.7, 35.8, 28.9

IR (neat): 3369.10, 3309.6, 2900, 2847.2, 1649.84, 1523.8, 1271.3, 547.2 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{24}H_{28}NO_2$ [$(M+ Na)^+$] 384.1934, found 384.1947.



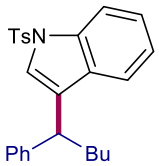
3-(2-phenylpropan-2-yl)-1-tosyl-1H-indole (9): This compound was prepared according to the General Procedure B using 2-phenylpropan-2-ol (36 mg, 0.25 mmol), 1-tosyl-1H-indole (102 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a white solid (72 mg, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.3 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.56 (s, 1 H), 7.29-7.14 (m, 8 H), 6.97 (t, *J* = 7.4 Hz, 1 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 2.37 (s, 3 H), 1.73 (s, 6 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.9, 144.7, 136.0, 135.2, 132.2, 129.8, 129.5, 128.2, 126.7, 126.0, 125.9, 124.1, 122.6, 122.3, 121.9, 113.7, 39.0, 30.0, 21.5

IR (neat): 2960.4, 2924.6, 1364.33, 703.9 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{24}H_{24}NO_2S$ [(M+ Na)$^+$] 412.1341, found 412.1347



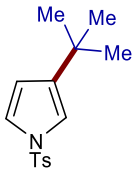
3-(1-phenylpentyl)-1-tosyl-1H-indole (10): This compound was prepared according to the General Procedure B using -1-phenylpentan-1-ol (41 mg, 0.25 mmol), 1-tosyl-1H-indole (102 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a white solid (74 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.3 Hz, 1 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.44 (s, 1 H), 7.25-7.13 (m, 9 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 3.99 (t, *J* = 7.4 Hz, 1 H), 2.34 (s, 3 H), 2.15-2.06 (m, 1 H), 2.00-1.92 (m, 1 H), 1.39-1.19 (m, 4 H), 0.87 (t, *J* = 7.1 Hz, 3 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.7, 143.6, 135.6, 135.2, 130.7, 129.7, 128.4, 127.8, 127.0, 126.7, 126.3, 124.6, 123.0, 122.7, 120.1, 113.7, 42.6, 35.3, 30.0, 22.7, 21.5, 14.0

IR (neat): 2955.6, 1365.2, 1171.4, 1092, 744, cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{26}H_{28}NO_2S$ [(M+ Na)$^+$] 440.1654, found 440.1655



3-(tert-butyl)-1-tosyl-1H-pyrrole (11): This compound was prepared according to the General Procedure A using *tert*-butanol (19 mg, 0.25 mmol), 1-tosyl-1H-pyrrole (83 mg, 0.375 mmol) at

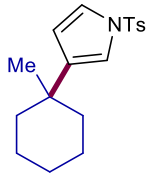
50 ˚C. After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a colorless liquid (55 mg, 79%, 93:7 rr yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74-7.70 (m, *J* = 8.1 Hz, 2 H), 7.31-7.27 (m, *J* = 8.1 Hz, 2 H), 7.06 (t, *J* = 2.6 Hz, 1 H), 6.88 (s, 1 H), 6.25-6.22 (m, 1 H), 2.40 (s, 3 H), 1.17 (s, 9 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 140.4, 136.3, 129.9, 126.7, 120.7, 114.9, 112.5, 30.9, 30.7, 21.6

IR (neat): 2959.2, 1364.7, 1168.3, 1061.7, 672.6 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NO_2S$ [(M+ Na)$^+$] 300.1028, found 300.1032



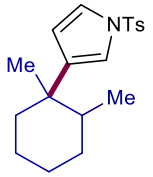
3-(1-methylcyclohexyl)-1-tosyl-1H-pyrrole (12): This compound was prepared according to the General Procedure A using 1-methylcyclohexan-1-ol (29 mg, 0.25 mmol), 1-tosyl-1H-pyrrole (83 mg, 0.375 mmol). After purification by column chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a colorless liquid (57 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.3 Hz, 2 H), 7.27-7.21 (m, 2 H), 7.03 (t, *J* = 2.7 Hz, 1 H), 6.87 (s, 1 H), 6.19 (dd, *J* = 1.6, 3.1 Hz, 1 H), 2.37 (s, 3 H), 1.72-1.62 (m, 2 H), 1.47-1.38 (m, 4 H), 1.38-1.29 (m, 4 H), 1.06 (s, 3 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.6, 139.5, 136.4, 129.8, 126.6, 120.8, 116.1, 112.7, 38.1, 34.1, 29.7, 26.2, 22.4, 21.6

IR (neat): 2924.5, 2852.5, 1170, 672.74 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{18}H_{24}NO_2S$ [(M+ Na)$^+$] 340.1341, found 340.1348



3-(1,2-dimethylcyclohexyl)-1-tosyl-1H-pyrrole (13): This compound was prepared according to the General Procedure A using 1,2-dimethylcyclohexan-1-ol (32 mg, 0.25 mmol), 1-tosyl-1H-pyrrole (83 mg, 0.375 mmol), NIS (20 mol%), catalyst (20 mol%). After purification by column

chromatography on SiO_2 (2% EtOAc in hexanes), the title compound was isolated as a colorless liquid (41 mg, 49% yield, 13:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 7.08-7.02 (m, 1 H), 6.93-6.87 (m, 1 H), 6.24 (dd, *J* = 1.5, 2.9 Hz, 1 H), 2.39 (s, 3 H), 1.70 (d, *J* = 12.7 Hz, 1 H), 1.60 (ddd, *J* = 3.9, 6.8, 10.9 Hz, 1 H), 1.54-1.41 (m, 5 H), 1.33-1.17 (m, 2 H), 1.09-1.04 (m, 3 H), 0.56 (d, *J* = 6.8 Hz, 3 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.5, 140.6, 136.4, 129.8, 126.6, 120.8, 116.5, 112.7, 41.3, 39.7, 37.4, 30.3, 26.4, 22.1, 21.6, 16.8, 16.4

IR (neat): 2924.6, 2856.9, 1168.8, 671.2 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{19}H_{26}NO_2S$ [(M+ Na)$^+$] 354.1498, found 354.1504

4. Alkene rate dependence studies

4.1 Procedure for dehydrative arylation of alcohols via Gas chromatography time courses

To a 10 mL round bottom flask equipped with magnetic stir bar was added 1-adamantanol (152 mg, 1.0 mmol), anisole (0.162 mL, 1.5 mmol), and 6 mL HFIP (0.67 M). Then to the flask was added alkene (0.1 mmol), 1,3-dibromobenzene (0.120 mL, 1.0 mmol, internal standard), and N-iodosuccinimide (22.5 mg, 0.1 mmol). Time courses were monitored using GC by taking aliquot. The aliquots were quenched by filtering through a plug of sodium thiosulfate. The initial rates of the reactions were obtained from the reaction time courses.

	Catalyst								
Time	**D**	**E**	**3**	**F**	**B**	**C**	**A**	**3-Pregen**	**H**
Min	**M**	**M**	**M**	**M**	**M**	**M**	**M**	**M**	**M**
1	0	0	0	0	0	0	0	----	----
5	0	0	0	0	0	0	0	0.012	0.005
10	0	0	0.001	0.003	0	0	0	0.030	0.011
15	0	0	0.001	0.008	0	0	0	0.037	0.013
20	0.003	0	0.002	0.012	0.002	0	0	0.048	0.019
30	0.012	0	0.005	0.018	0.009	0	0	0.067	0.025
40	0.022	0	0.007	0.023	0.02	0	0	0.100	0.034
50	0.032	0	0.007	0.031	0.032	0	0	0.118	0.042
60	0.046	0	0.01	0.038	0.043	0	0	0.138	0.049
90	---	0	0.02	0.066	0.091	0	0	0.166	0.101
120	0.092	0.001	---	0.085	---	0	0	0.176	0.093
240	0.136	0.002	0.048	0.134	0.157	0	0.035	0.169	0.191
360	0.154	0.006	0.078	0.151	---	0.002	----	0.157	0.166
420	0.161	0.008	0.096	---	0.153	0.005	0.135	----	----
480	0.162	0.01	0.106	0.152	0.157	0.004	0.135	0.167	0.168

Table S1. Raw data for dehydrative arylation of alcohols gas chromatography time courses. A = para-trifluoromethyl-styrene, B = styrene, C = para-methoxy-styrene, D = vinyl cyclohexane, E = Trans-dec-5-ene, F = 1, 2-dimethyl-but-2-ene, 3 = 1-methylcyclohexene, 3-pregen = 1-methylcyclohexene after 2hr prestiring with NIS, and H = dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate

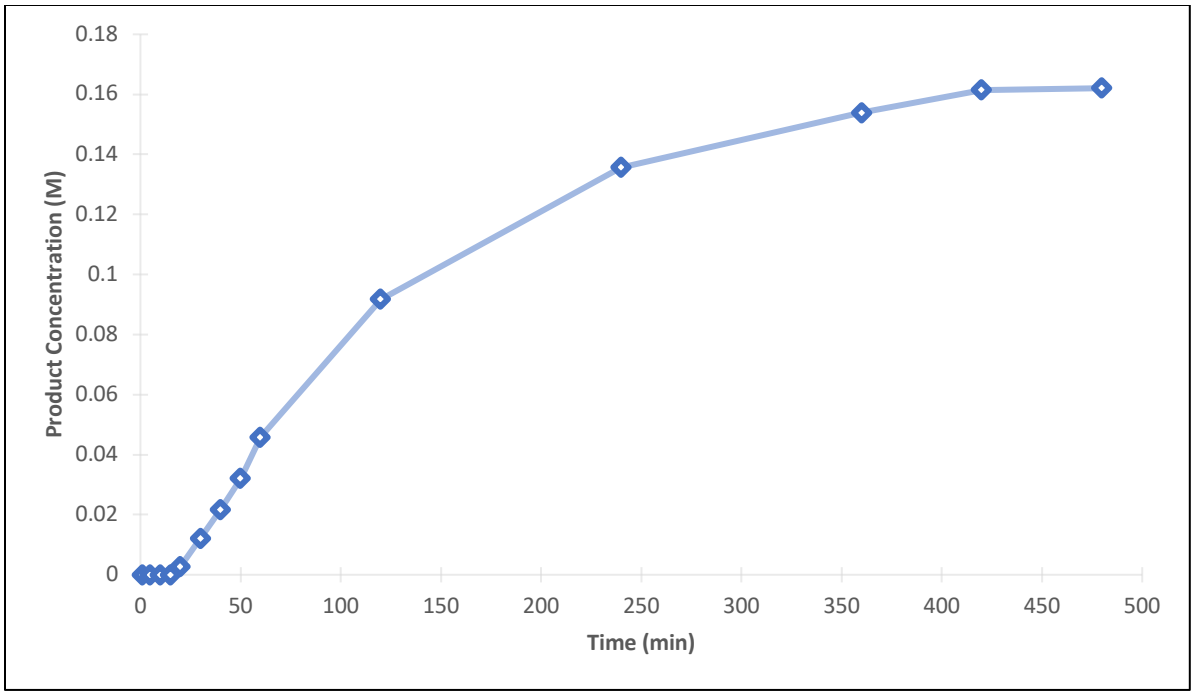


Figure S1. Alkene rate dependence for vinyl cyclohexane

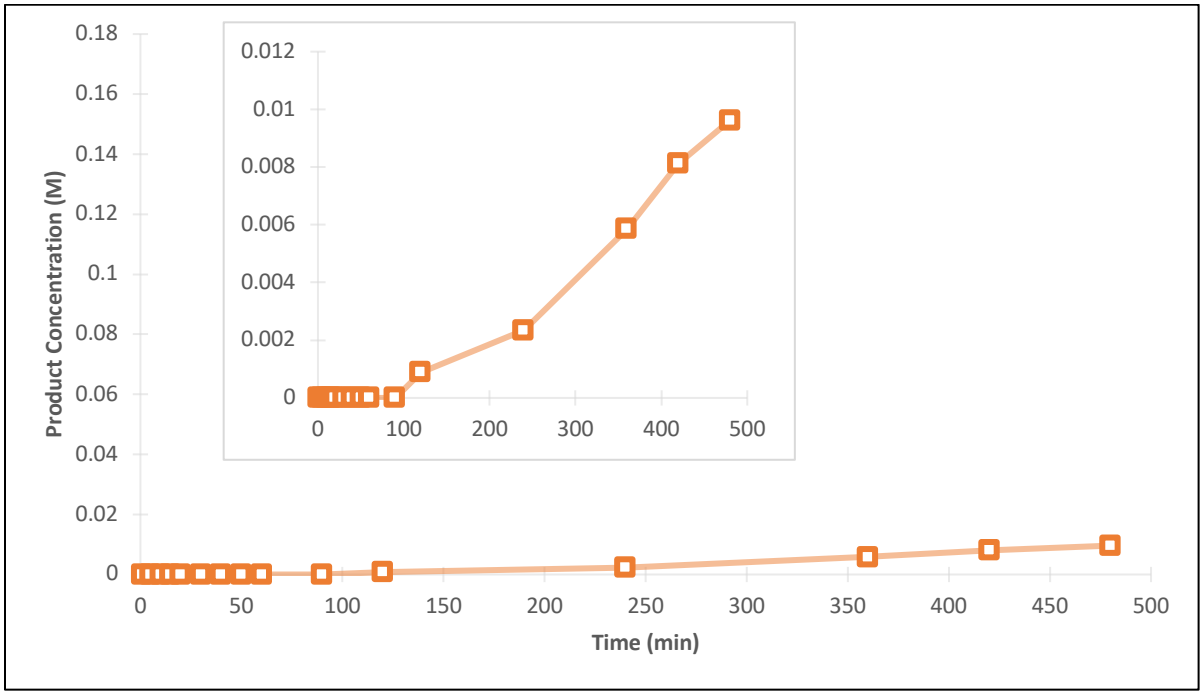


Figure S2. Alkene rate dependence for Trans-dec-5-ene

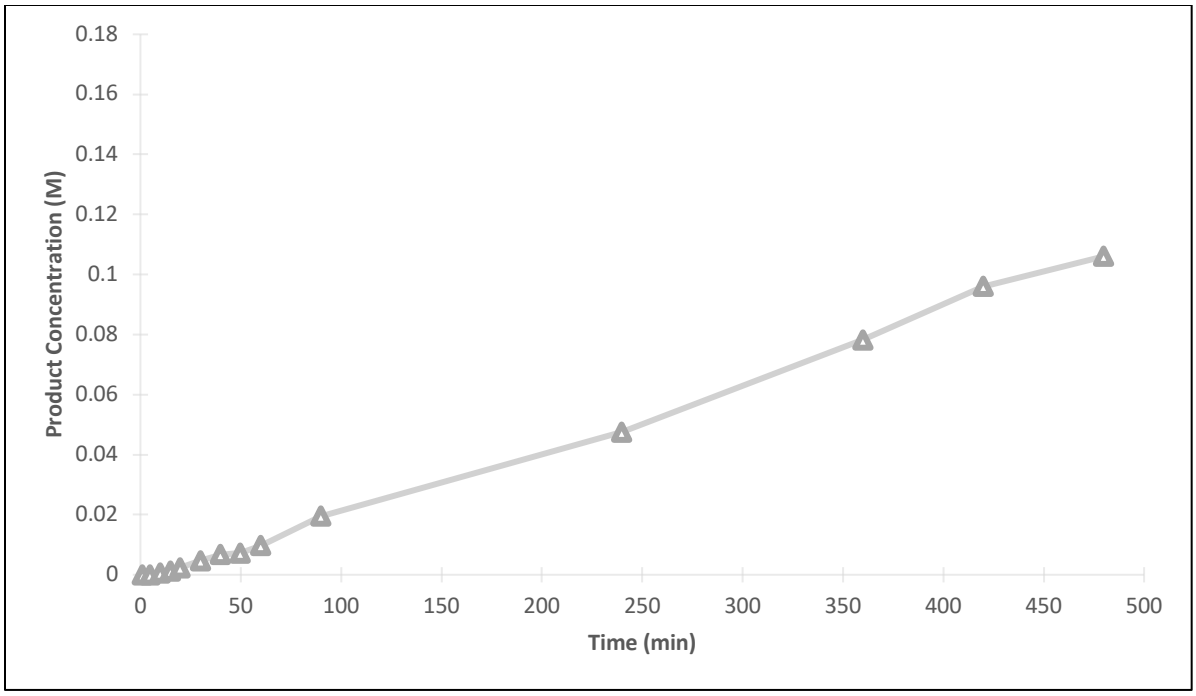


Figure S3. Alkene rate dependence for 1-methylcyclohexene

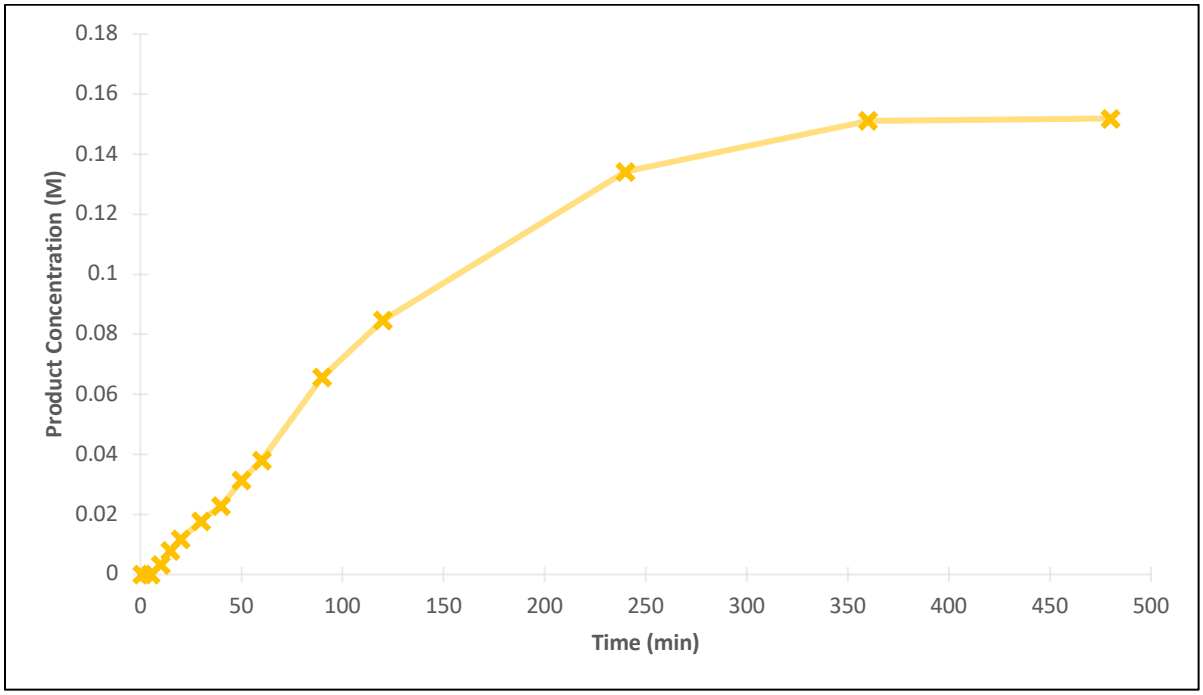


Figure S4. Alkene rate dependence for 1, 2-dimethyl-but-2-ene

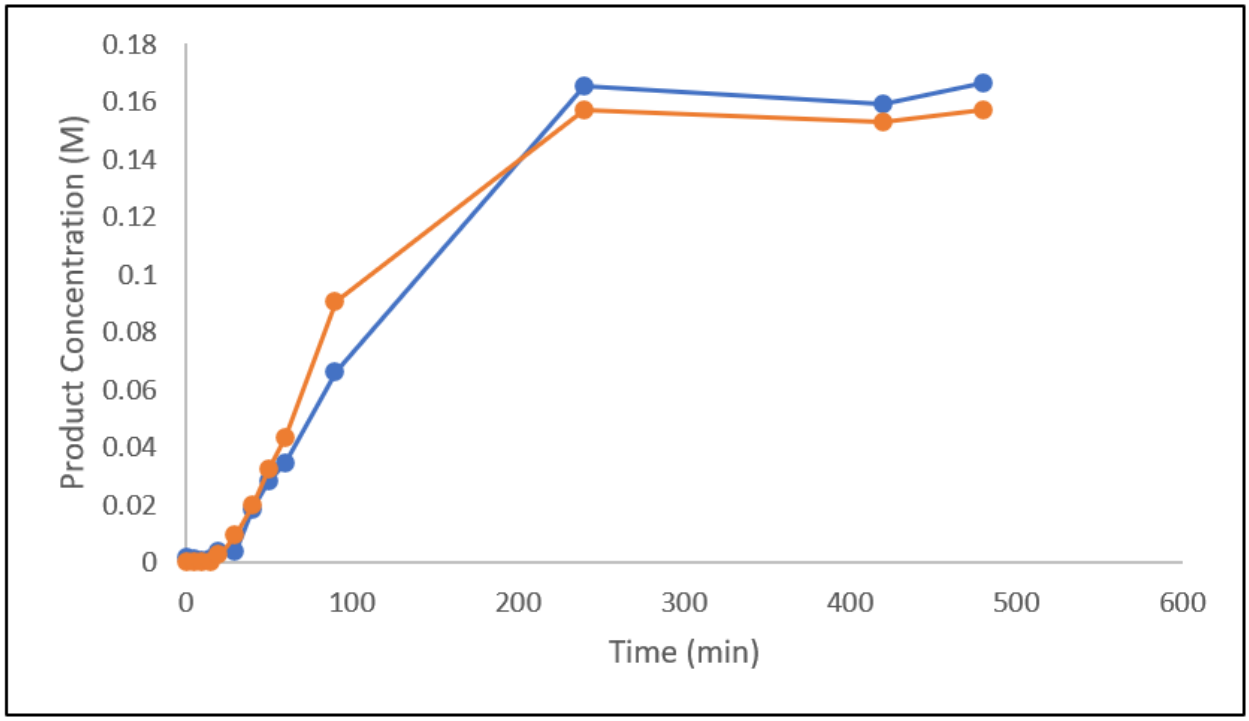


Figure S5. Alkene rate dependence for styrene

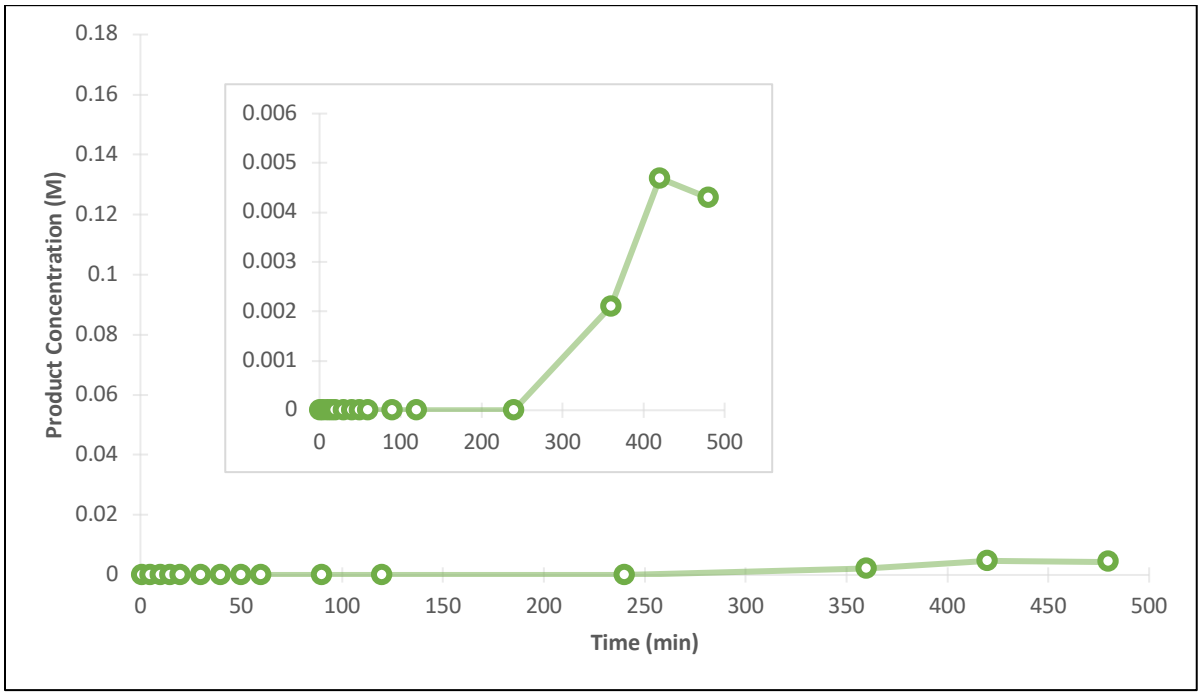


Figure S6. Alkene rate dependence for para-methoxy-styrene

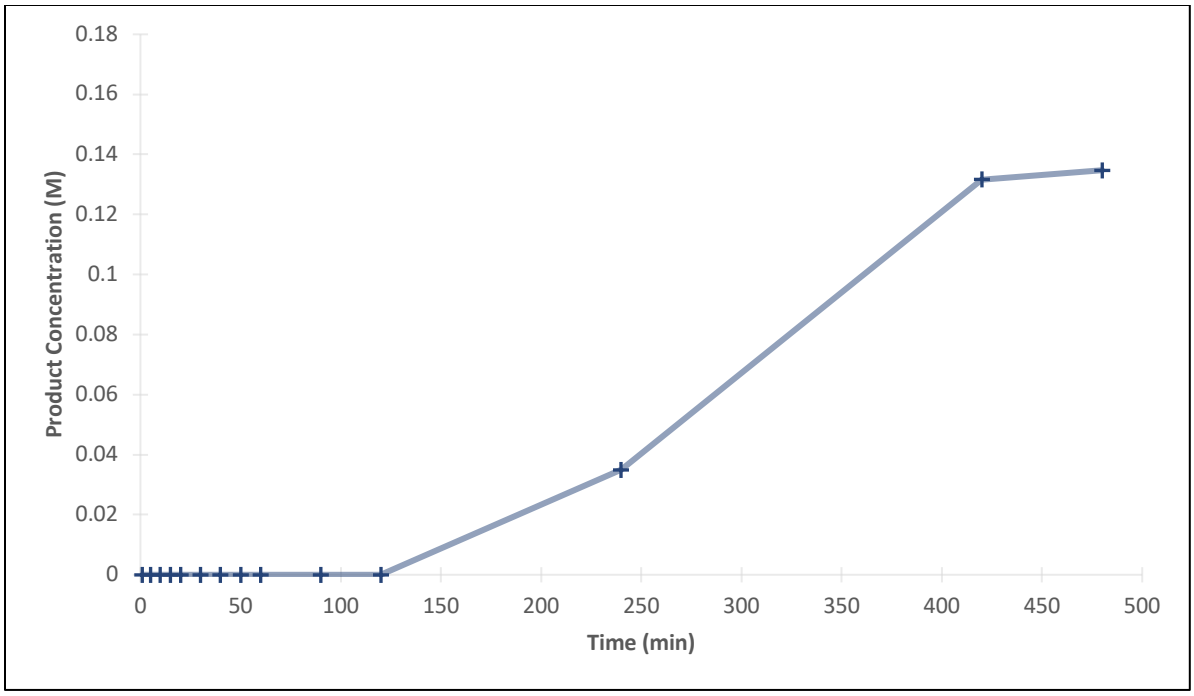


Figure S7. Alkene rate dependence for para-trifluoromethyl-styrene

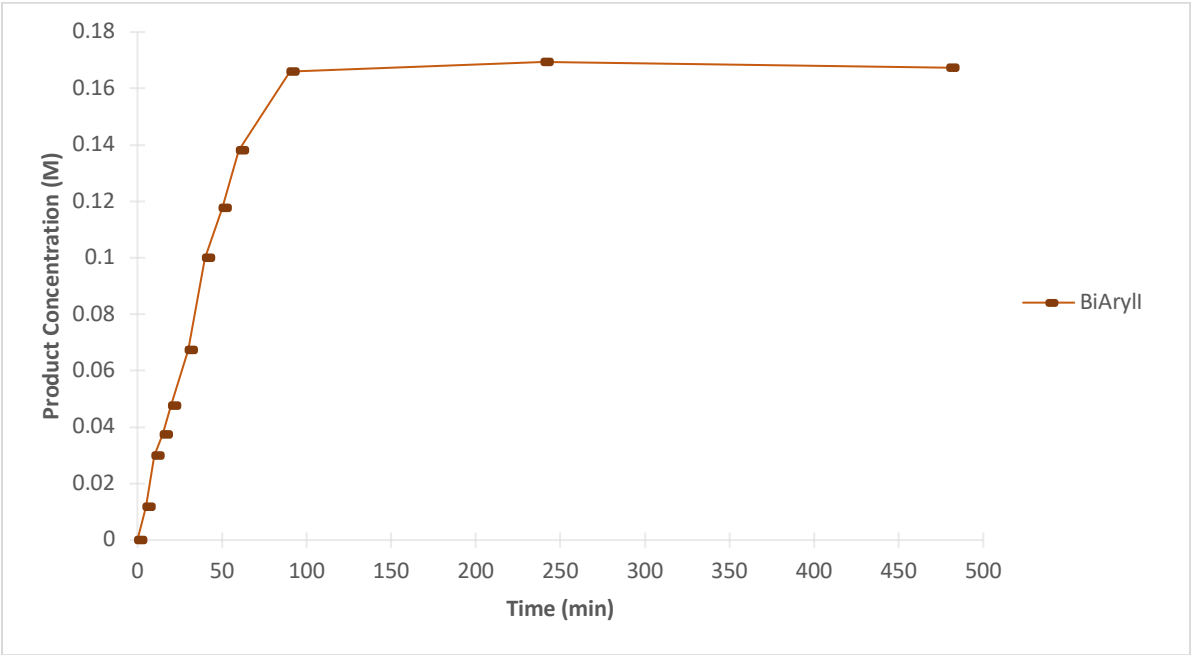


Figure S8. Alkene rate dependence for dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate

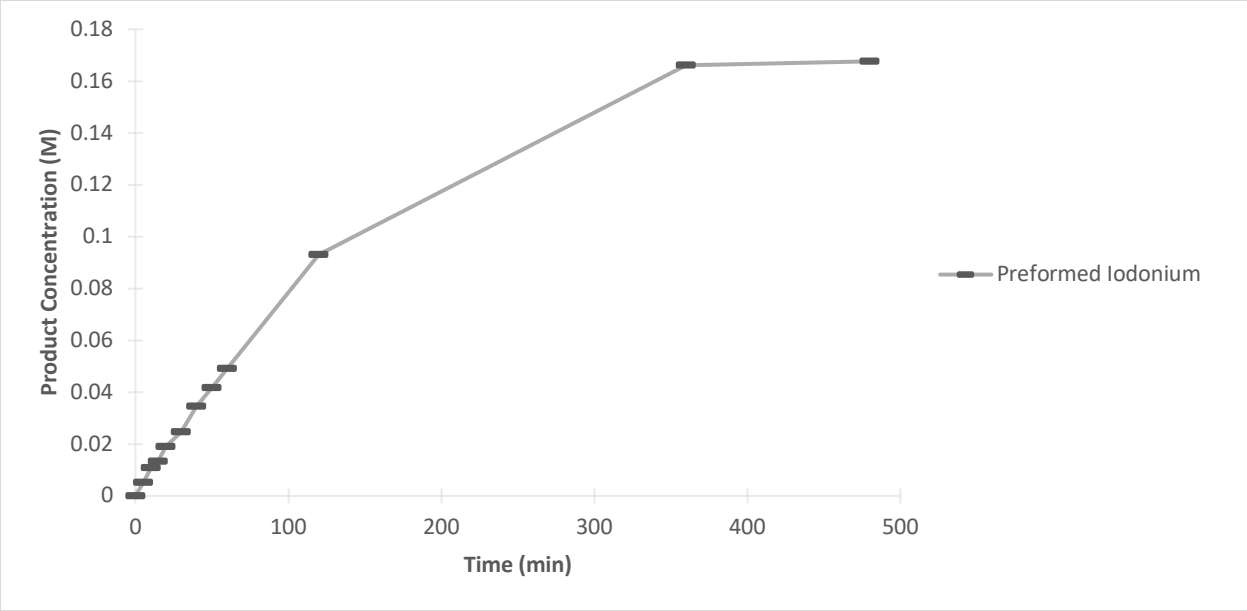


Figure S9. Alkene rate dependence for 1-methylcyclohexene after 2hr prestiring with NIS

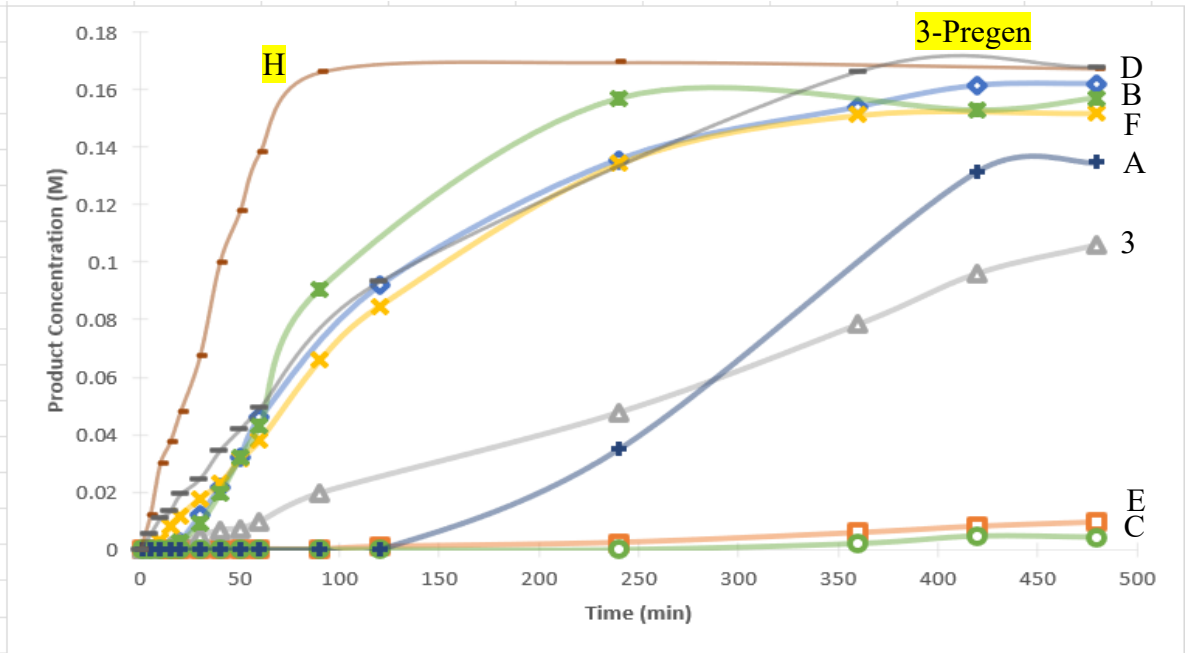


Figure S10. Combined alkene rate dependence where A = para-trifluoromethyl-styrene, B = styrene, C = para-methoxy-styrene, D = vinyl cyclohexane, E = Trans-dec-5-ene, F = 1, 2-dimethyl-but-2-ene, 3 = 1-methylcyclohexene, 3-Pregen = 1-methylcyclohexene after 2hr prestiring with NIS, and H = dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate

5 Hammett Plot Study

5.1 Procedure for dehydrative arylation of alcohols using NMR.

To a 10 mL RBF was equipped with magnetic stir bar was added benzylic alcohol (1.0 mmol), and 1-tosylindoline (410 mg, 1.5 mmol). To the vial was added 6mL HFIP (0.67 M) 1-methylcyclohexene (11.8µL, 0.1 mmol), and then N-iodosuccinimide (22.5 mg, 0.1 mmol). Timecourses were monitored using NMR by taking aliquots.

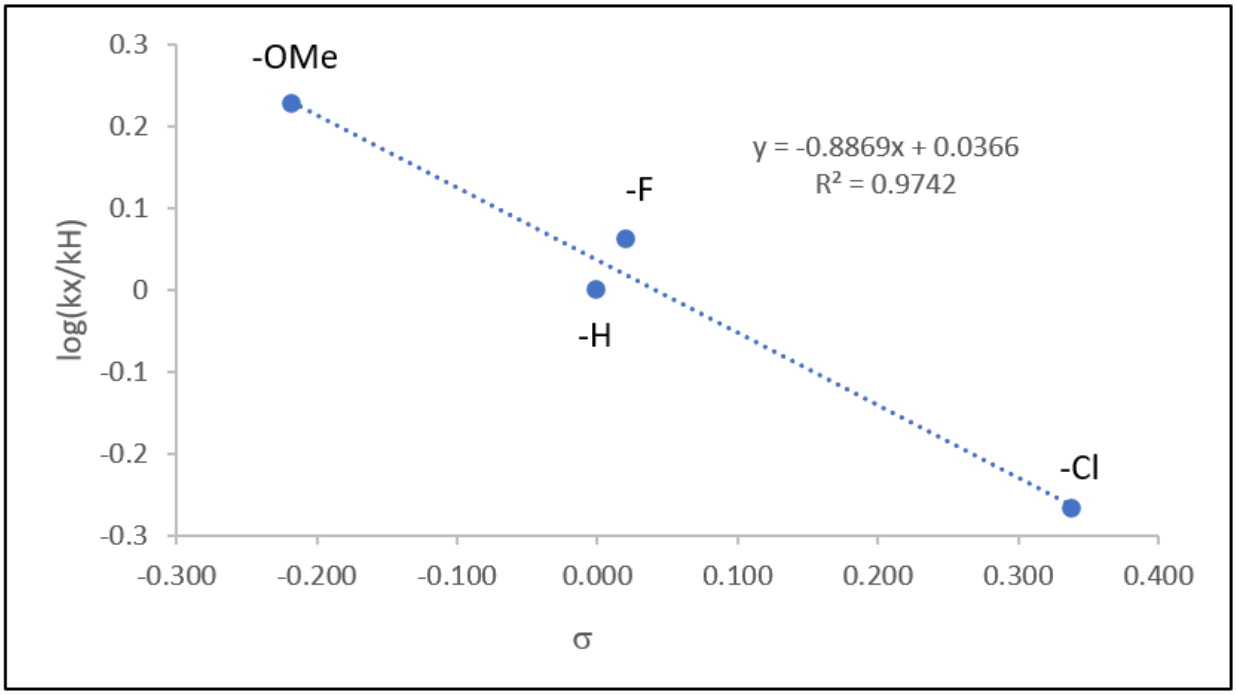


Figure S11. Hammett Plot study for dehydration arylation

Functional Group	Rate (M/min)	Log(kx/kH)	σ
p-OMe	7.63E-04	0.338	-0.268
p-H	3.50E-04	0.000	0
p-Cl	2.12E-04	-0.218	0.227
p-F	3.67E-04	0.021	0.062

Table S2. Raw data for dehydration arylation of benzylic alcohols

6. Alkene Rate Order Study

To a 10 mL round bottom flask equipped with magnetic stir bar was added 1-adamantanol (152 mg, 1.0 mmol), anisole (0.162 mL, 1.5 mmol), and 6 mL HFIP (0.67 M). Then to the flask was added alkene,1,3-dibromobenzene (0.120 mL, 1.0 mmol, internal standard), and N-iodosuccinimide (22.5 mg, 0.1 mmol). Time courses were monitored using GC

by taking aliquot. The aliquots were quenched by filtering through a plug of sodium thiosulfate. The initial rates of the reactions were obtained from the reaction time courses.

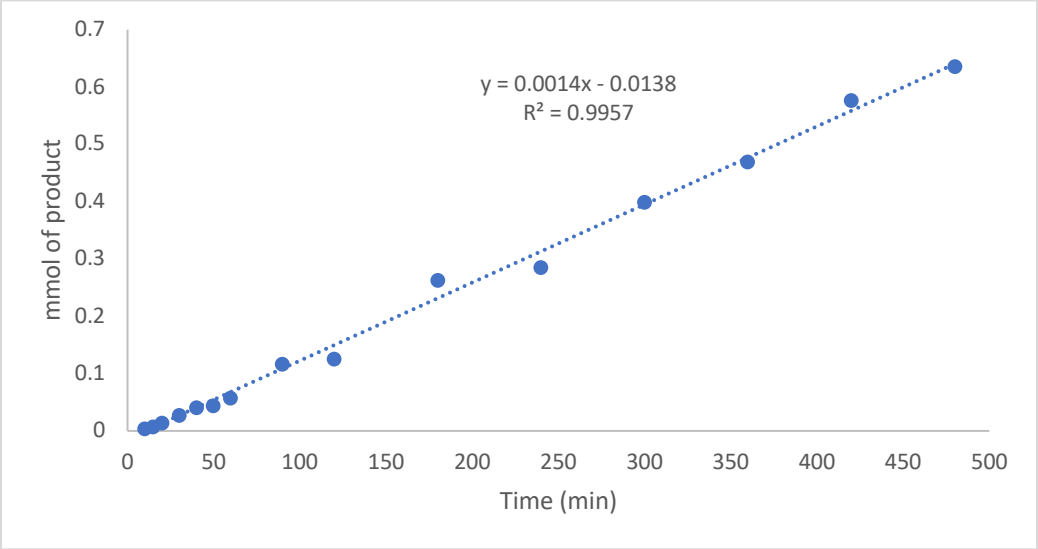


Figure S12. Kinetics of reaction with 10 mol% 1-methylcyclohexene

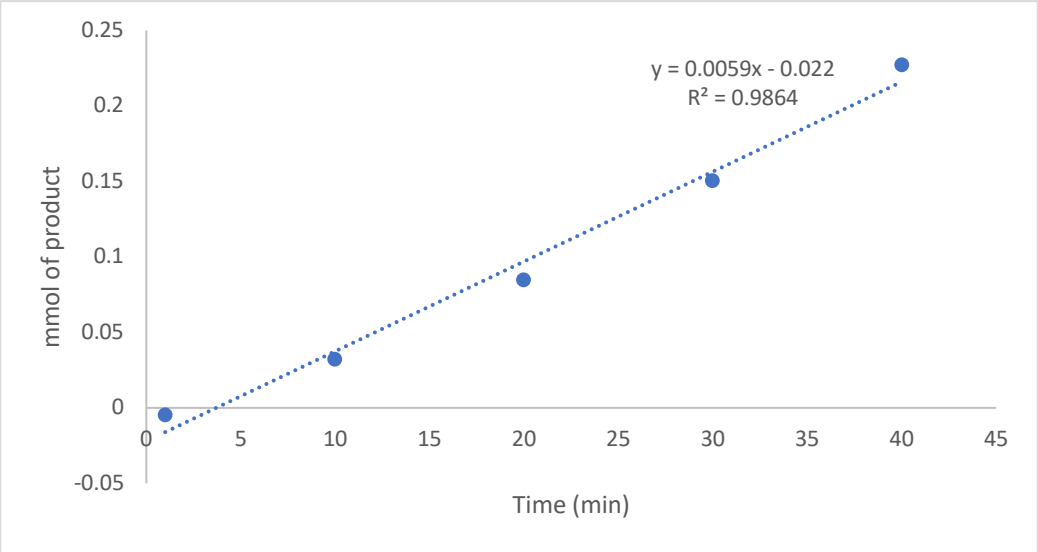


Figure S13. Kinetics of reaction with 20 mol% 1-methylcyclohexene

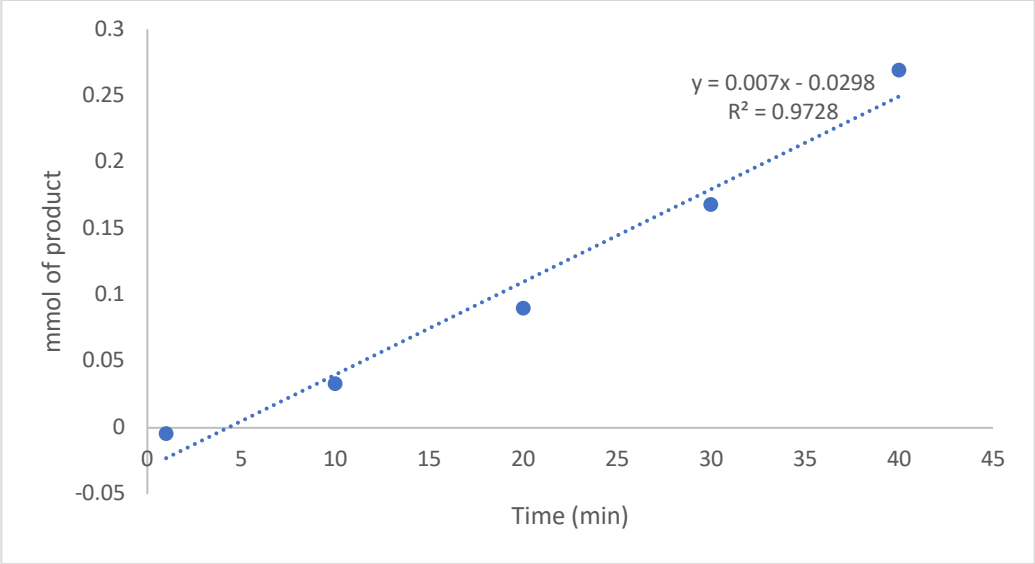


Figure S14. Kinetics of reaction with 30 mol% 1-methylcyclohexene

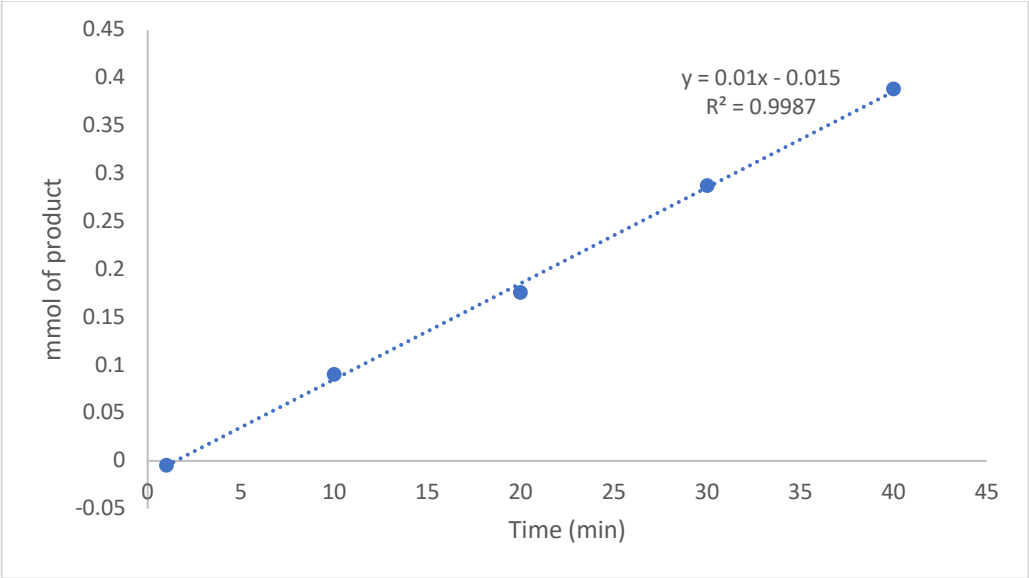


Figure S15. Kinetics of reaction with 40 mol% 1-methylcyclohexene

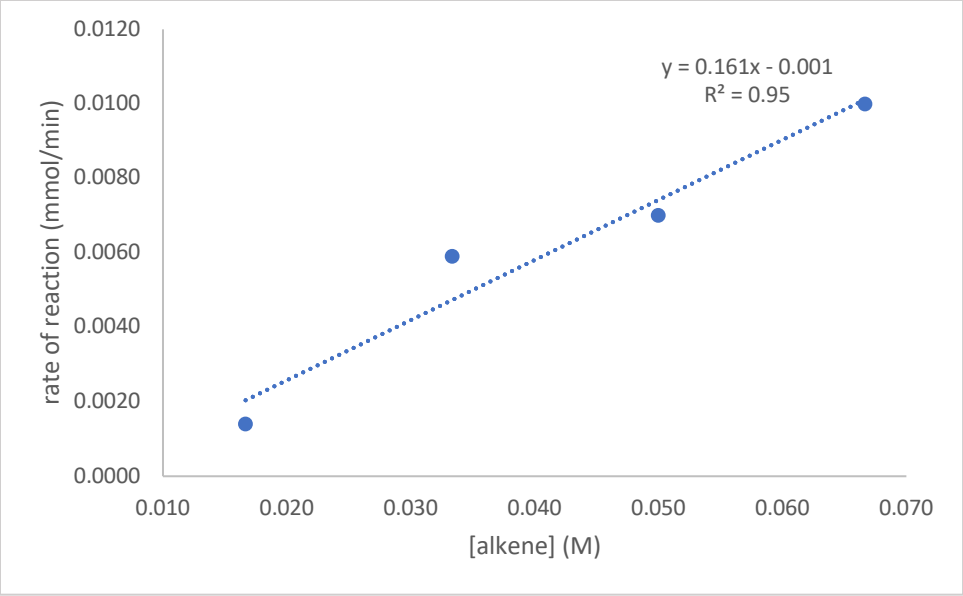


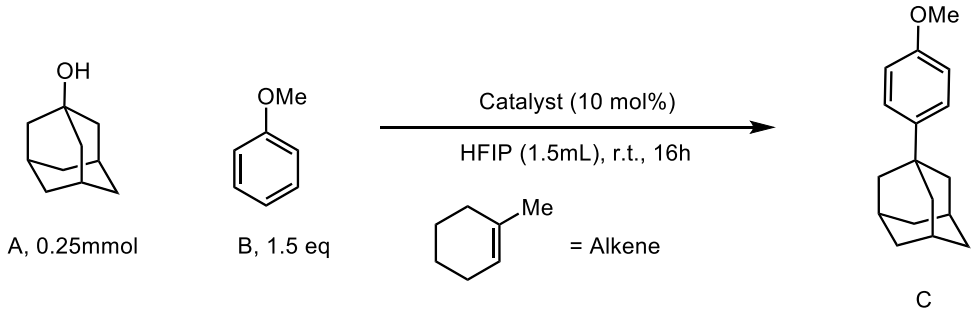
Figure S16. Rate order of 1-methylcyclohexene for dehydrative arylation reaction

[alkene] (M)	rate (mmol/min)
0.017	0.0014
0.033	0.0059
0.050	0.0070
0.067	0.0100

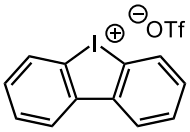
Table S3. Raw data for rate order of 1-methylcyclohexene for dehydrative arylation reaction

7. Iodonium benchmarking with Lewis/ Bronsted acids and Controls

To 8 mL vial was added 1-adamantanol (38mg, 0.25 mmol), anisole (41 mL, 0.375 mmol), and the respective catalyst (10 mol%) Then, HFIP (1.5 mL) was added to the reaction mixture and stirred at room temperature for 16 h. After the reaction, HFIP was removed by rotavapor. The reaction was quenched with 20% $Na_2S_2O_3$ (1 mL) and EtOAc (2 mL) was added. The organic layer was separated, and aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic solution was dried with anhydrous Na_2SO_4, filtered, concentrated in vacuo by rotavapor. Yields were determined by ^{1}H NMR with 1,3-benzodioxole as internal standard.



biaryl-iodonium =



Catalyst	C Yield	SM A Yield
HOAc	0%	99%
HOTf	88%	0%
$Sc(OTf)_3$	100%	0%
BF_3*Et_2O	100%	0%
biaryl-iodonium	89%	0%
Schreiner's Catalyst	0%	92%
I_2(10%), alkene (10%) $AgBF_4$ (10%)	100%	0%
Alkene (10 mol%), NIS (10 mol%)	99%	0%
Alkene (10 mol%)	0%	99%
NIS (10 mol%)	0%	99%

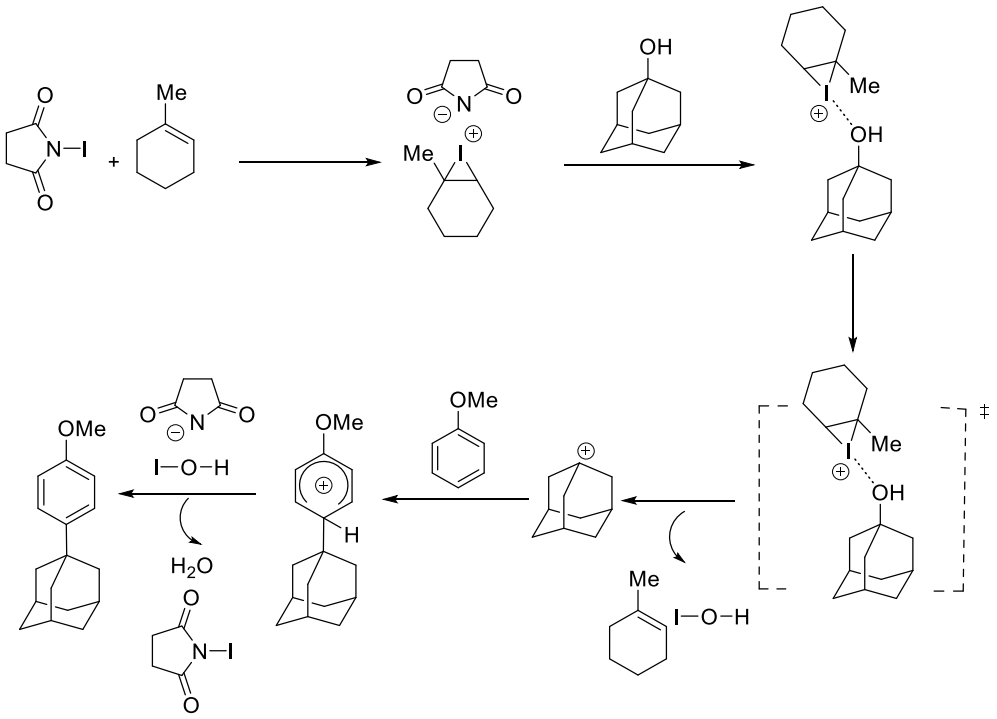
Table S4. Iodonium benchmarking with Lewis/ Bronsted acids with electronically activated alcohol. Yields were determined by 1H NMR with 1,3-benzodioxole as internal standard.

8. Computational Support

A. DFT Calculations

All DFT calculations were carried out using Gaussian 16 (Rev. C01) via the Ohio Supercomputer Center.[1] Geometry optimization and frequency calculations were performed at the M06-2X/def2-TZVP level of theory. Additional diffuse functions (def2-

TZVP(D)) were used for iodine in conjunction with SMD, solvation model of HFIP.[2, 3] The corresponding pseudopotential for iodine was employed.[3] Stable geometry minima were confirmed by the absence of imaginary frequencies while transition states geometries were verified by the existence of one negative frequency. Energies were further improved by performing single-point calculations at the M06-2X-D3/def2-TZVP(D) level of theory for all atoms with the same solvent effects and pseudopotential for iodine. All reported energies correspond to Gibbs free energies evaluated at 298.15 K and 1 atm, obtained by adding the thermal free energy corrections computed at the lower level of theory to the higher-level single-point electronic energies.



Scheme S1. Iodonium-catalyzed reaction pathway

List of input files and the resulting Gibbs free energies for all chemical species*

* Cartesian Coordinates in Å, Gibbs free energies, as calculated by adding the thermal Gibbs energy correction to the electronic energy, in Hartree.

C_7H_{12}

M06-2X/def2-TZVP level Gibbs free energy in HFIP= -273.7857619 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP= -273.7868939 a.u.

0 1

C	-0.69471623	-0.53816046	0.00000000
C	0.70044377	-0.53816046	0.00000000
C	1.39798177	0.66959054	0.00000000
C	0.70032777	1.87809954	-0.00119900
C	-0.69449723	1.87802154	-0.00167800
C	-1.39209823	0.66981554	-0.00068200
H	-1.01091108	-1.08629619	-0.86282561
H	1.01659625	-1.08584790	0.86312576
H	1.25052777	2.83024254	-0.00125800
H	-1.01099294	2.42655869	0.86078212
H	-2.02466927	0.66923312	-0.86367304
C	2.93798151	0.66970257	0.00088786
H	3.29522846	0.68211659	-1.00763607
H	3.29428773	1.53711991	0.51618683
H	3.29442771	-0.21005099	0.49472972
H	1.01659625	-1.08584790	-0.86312576
H	-1.01091108	-1.08532157	0.86344400
H	-2.02428090	0.67043195	0.86259356
H	-1.01040002	2.42479328	-0.86547548

NIS

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -657.6128475 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -657.6100275 a.u.

0 1

C	-1.40368862	0.71721310	0.00000000
C	0.11816938	0.71721310	0.00000000
C	-0.64079762	3.05464610	-0.13318600
C	-1.87289462	2.16153310	-0.10359000
H	-1.79565062	0.11476810	-0.85750800
H	-1.79380362	0.24680210	0.93750400
H	-2.52527262	2.42333510	0.76707400
H	-2.48464062	2.30915510	-1.02879300
N	0.58694238	2.16507810	0.00000000
O	-0.59080848	3.79268900	-1.35698899
O	0.61469129	0.03419413	-1.15405853
I	2.50984085	2.79798723	0.15095537

Anisole

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -346.6434631 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -346.644926 a.u.

0 1

C	-0.46544426	-1.10719321	0.00000000
C	0.92971574	-1.10719321	0.00000000
C	1.62725374	0.10055779	0.00000000
C	0.92959974	1.30906679	-0.00119900
C	-0.46522526	1.30898879	-0.00167800
C	-1.16282626	0.10078279	-0.00068200
H	-1.01520326	-2.05951021	0.00045000
H	1.47922374	-2.05970621	0.00131500
H	2.72693374	0.10063779	0.00063400
H	-1.01534726	2.26126979	-0.00263100
H	-2.26243026	0.10096579	-0.00086200
O	1.64506780	2.54721275	-0.00127572

C	2.36000084	3.78453674	-0.05419184
H	3.30274394	3.67313389	0.43949313
H	2.52247081	4.05918921	-1.07549959
H	1.78973739	4.54711659	0.43383642

1-Adamantanol

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -465.7044371 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -465.7072157 a.u.

0 1

C	0.08650519	0.03460208	0.00000000
H	1.20629119	0.03460208	0.00000000
H	-0.25978581	1.09948608	0.00000000
C	-0.43015681	-0.67699392	1.24678900
H	-0.04939481	-0.15262592	2.16300500
C	-0.43045181	-0.67716992	-1.24655200
C	0.05928319	-2.12213292	-1.24512500
H	1.17880319	-2.14330092	-1.25765600
H	-0.30721081	-2.64785992	-2.16338000
C	0.05963219	-2.12194392	1.24538300
H	-0.30656981	-2.64756392	2.16381800
H	1.17915519	-2.14306392	1.25757100
C	-0.45730681	-2.83623492	0.00025600
H	-0.09648981	-3.89887392	0.00028500
C	-1.98285781	-2.81549492	0.00044400
H	-2.36965981	-3.34813692	-0.90542000
H	-2.36939681	-3.34799292	0.90650500
C	-1.95573881	-0.65877892	1.24557000
H	-2.32252481	0.39915208	1.25798800
H	-2.34197281	-1.16992392	2.16398300
C	-1.95603781	-0.65885392	-1.24490700
H	-2.32273681	0.39911408	-1.25719400

H	-2.34258481	-1.16992092	-2.16322300
C	-2.47495881	-1.37133592	0.00041000
H	-3.59709581	-1.35729592	0.00055900
O	0.05448379	-0.00918982	-2.41425918
H	1.01446570	-0.01211659	-2.40914284

Iodonium Formation

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -931.3665548 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -931.3650138 a.u.

0 1

C	4.22153800	1.20799800	0.36313700
C	3.20206000	0.69245300	1.38330200
C	1.77539900	0.73706500	0.88847600
C	1.49891300	0.85823300	-0.52492500
C	2.58803700	1.09521100	-1.52632900
C	3.96609900	0.66364800	-1.03792200
H	4.16977100	2.29978400	0.33384100
H	3.44067100	-0.32425200	1.69847400
H	0.50300900	1.20779500	-0.78315500
H	2.32161100	0.63652200	-2.48023500
H	4.72325400	1.03503700	-1.73073900
C	0.72199600	1.08492800	1.88750800
H	-0.28855600	0.96201300	1.49676200
H	0.85574800	0.52331200	2.81126000
H	0.88464500	2.14625900	2.12006700
C	-3.85967800	1.75320700	-0.51558500
C	-2.82283000	0.66419000	-0.30658200
C	-4.70156600	-0.35579000	0.17685400
C	-5.16187700	1.04283600	-0.19129800
H	-3.62786000	2.58666400	0.15102100
H	-3.79330300	2.11977400	-1.54052400

H	-5.85159800	0.97180400	-1.03436300
H	-5.70849800	1.47168000	0.64988700
N	-3.35593000	-0.51388900	0.08087000
O	-5.48795400	-1.24685900	0.51244200
O	-1.61448600	0.86169300	-0.47973100
I	1.11403700	-1.31347500	-0.12016000
H	3.22973700	1.29637900	2.29514900
H	2.57607900	2.18021000	-1.69178900
H	4.03945700	-0.42806500	-1.03897600
H	5.22433100	0.94393600	0.70420400

Halogen Exchange to Adamantanol

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -1036.934422 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -1036.936665 a.u.

1 1

C	3.23922843	0.46581824	0.00000000
C	2.85227243	1.90899224	0.31399000
C	1.74742843	2.09770124	1.29532900
C	1.66891743	1.15072424	2.37717200
C	2.76647843	0.14843224	2.52453300
C	3.23627343	-0.48624776	1.21506000
H	2.54488843	0.09201824	-0.75397200
H	3.68806343	2.41900024	0.81958700
H	1.15098743	1.47631724	3.27383800
H	3.57892343	0.73114724	2.98056300
H	2.58541643	-1.33498976	1.00054100
C	1.13955643	3.45055824	1.42134300
H	0.79347143	3.82005524	0.45731300
H	0.33244543	3.47430724	2.15103200
H	1.94376443	4.11191624	1.76430000
I	0.00247843	0.52463324	1.01869000

H	2.48264743	-0.61307776	3.24938400
H	4.23274143	-0.89456376	1.37967300
H	4.22321443	0.48099724	-0.46726300
H	2.65214843	2.47671224	-0.59449800
C	-4.08292777	-0.48830335	0.97452159
H	-4.46308853	0.53763559	1.03316032
H	-3.82458447	-0.68821546	-0.07010657
C	-5.14045063	-1.48097462	1.47374065
H	-6.04082847	-1.39281777	0.86084169
C	-2.82194737	-0.60756004	1.82915610
C	-3.15864443	-0.29657031	3.28677265
H	-3.53305484	0.73056844	3.35957370
H	-2.24385743	-0.36039710	3.88430934
C	-5.47683798	-1.16895241	2.93692219
H	-6.24037342	-1.86378482	3.29975317
H	-5.89104749	-0.15917555	3.01872935
C	-4.21223913	-1.28834360	3.79596158
H	-4.45103669	-1.06292213	4.83819921
C	-3.65496377	-2.71264439	3.68834735
H	-2.76081099	-2.81282335	4.31135720
H	-4.39256419	-3.43035096	4.06024468
C	-4.58111671	-2.90484965	1.37124887
H	-4.35307216	-3.14323792	0.32776599
H	-5.33074002	-3.62505165	1.71306485
C	-2.26671869	-2.02403644	1.72466449
H	-2.00361740	-2.22660167	0.68167990
H	-1.34941750	-2.09089084	2.31809649
C	-3.31384846	-3.02531779	2.22631516
H	-2.91228626	-4.03860623	2.14984875
O	-1.79993064	0.26185740	1.34860152
H	-2.10730306	1.17685737	1.39468246

Halogen Exchange to Adamantanol Transition State

M06-2X-D3/def2-TZVP(D) level Gibbs free energy in HFIP = -1036.887112 a.u.

1 1

C	-3.65372200	1.17969600	0.27761800
C	-5.12342800	1.55820200	0.12078500
C	-5.98920400	0.38675100	-0.26980400
C	-5.55792200	-0.87064800	-0.18012300
C	-4.20393900	-1.26722200	0.34199300
C	-3.55397400	-0.10791800	1.08326900
H	-3.21973800	1.02887600	-0.71646700
H	-5.50618200	1.98387900	1.05606200
H	-6.21514900	-1.67811700	-0.49165700
H	-4.30276300	-2.13235700	1.00212600
H	-2.51643100	-0.36037400	1.38933800
C	-7.36312100	0.73178100	-0.75738500
H	-7.31089200	1.34203400	-1.66396100
H	-7.95301600	-0.15939800	-0.97419300
H	-7.89774500	1.32634400	-0.00993500
I	-0.56108800	-0.50524200	0.07114100
H	-3.57377900	-1.59494300	-0.49442300
H	-4.04495000	0.03434400	2.05162900
H	-3.10041400	1.98941600	0.75713800
H	-5.22963000	2.34602900	-0.63095700
C	3.53493700	-0.61272300	-1.51343800
H	3.53761600	-1.69994900	-1.63673700
H	3.25146300	-0.15256800	-2.46270700
C	4.91969400	-0.11837400	-1.05788600
H	5.65011200	-0.39471300	-1.82011100
C	2.53903600	-0.21833500	-0.43680600
C	2.84686900	-0.89622100	0.88092400

H	2.84616600	-1.98178200	0.75289900
H	2.09728600	-0.63274700	1.63265600
C	5.27655100	-0.77579500	0.27866800
H	6.26546100	-0.44059400	0.60224200
H	5.32016400	-1.86253500	0.16385700
C	4.23250400	-0.39828100	1.33478800
H	4.47579400	-0.87069900	2.28770700
C	4.18948700	1.12525800	1.49884000
H	3.45465100	1.40064100	2.26070500
H	5.16373200	1.48675000	1.83806000
C	4.87726500	1.40411500	-0.89462500
H	4.63638300	1.87853600	-1.85002700
H	5.86032500	1.76928100	-0.58591300
C	2.44656000	1.28474300	-0.29331600
H	2.16304400	1.73099800	-1.24942000
H	1.69741900	1.55620400	0.45629000
C	3.83245900	1.78165100	0.16052700
H	3.79026400	2.86582900	0.27479400
O	1.20180900	-0.69351600	-0.97025600
H	1.28368900	-1.57248100	-1.39160500

Adamantane Cation Formation

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -389.6723363 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -389.6738393 a.u.

1 1

C	7.03336398	-3.30154772	0.39789100
H	7.23236098	-4.21577772	0.96757700
H	6.78860698	-3.59322772	-0.62798300
C	8.25669398	-2.37676172	0.42452100
H	9.11292598	-2.89643372	-0.01175300
C	5.83451398	-2.57875572	1.00872800

C	6.14236298	-2.19712572	2.45472500
H	6.33613498	-3.10547272	3.03529400
H	5.26736798	-1.70282872	2.88958800
C	8.56754498	-1.99055272	1.87530000
H	9.44655398	-1.33992572	1.90673300
H	8.80436698	-2.88549872	2.45887900
C	7.36233998	-1.26741172	2.48845900
H	7.58220398	-0.99503772	3.52337000
C	7.05564998	-0.00558872	1.67325000
H	6.20628798	0.52683628	2.11253000
H	7.91362498	0.67269828	1.69994900
C	7.94805998	-1.11302872	-0.38661000
H	7.74013898	-1.37748172	-1.42791100
H	8.81743998	-0.44884272	-0.38678600
C	5.52360798	-1.32389172	0.20055600
H	5.27022798	-1.61125872	-0.82485400
H	4.65150398	-0.82209872	0.63221200
C	6.74085298	-0.39074872	0.22267700
H	6.51607698	0.50717428	-0.35750000

Anisole Carbocation Formation

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -736.3162926 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -736.3206099 a.u.

1 1

C	-0.87445482	-0.04772757	-0.64692429
C	-1.63387949	-1.17402600	-0.34003415
C	-2.93020258	-1.29286028	-0.80596596
C	-3.48104612	-0.27898704	-1.58805409
C	-2.73554390	0.85080253	-1.90252327
C	-1.43160348	0.95385998	-1.42480883
H	-0.17413167	-0.16794738	-1.71242284

H	-1.21168253	-1.96568084	0.26742374
H	-3.53798031	-2.16064469	-0.57867011
H	-3.14941136	1.64525283	-2.50803266
H	-0.85135539	1.83524838	-1.67070305
O	-4.76842415	-0.48666985	-2.00161353
C	-5.38204343	0.50976898	-2.79854360
H	-6.38553646	0.14688615	-3.01041858
H	-5.44540969	1.45997982	-2.26228218
H	-4.84160074	0.65177071	-3.73783308
C	0.90157294	0.70608820	-1.19243158
H	0.78540273	0.67506951	-2.27315524
H	0.42149182	1.57492130	-0.74854575
C	2.47176898	0.75723129	-0.84787076
H	2.83747225	1.67749793	-1.30235034
C	0.58047011	-0.54204194	-0.53320702
C	0.96962563	-1.77483901	-1.18468552
H	0.85187749	-1.75775614	-2.26548056
H	0.53889688	-2.66586014	-0.73437008
C	3.13437436	-0.47367185	-1.45664644
H	4.20750238	-0.44332852	-1.25296863
H	3.00619872	-0.48011327	-2.54085586
C	2.54069195	-1.73631167	-0.84160182
H	2.95627177	-2.63745953	-1.29159018
C	2.69914611	-1.73936404	0.67461619
H	2.26228688	-2.64368860	1.10254993
H	3.76254135	-1.73759614	0.92608058
C	2.62897495	0.77657400	0.66861666
H	2.14221827	1.65733907	1.09201941
H	3.69065005	0.83510546	0.92044663
C	0.47158965	-0.54051685	0.91007752
H	0.00122827	0.35223957	1.31500166

H	0.04927452	-1.45453176	1.32033406
C	2.03985927	-0.49716520	1.26452871
H	2.08961531	-0.49318598	2.35301720

Final Structure

M06-2X/def2-TZVP level Gibbs free energy in HFIP = -735.928468 a.u.
M06-2X-D3/def2-TZVP(D) level corrected energy in HFIP = -735.9327381 a.u.

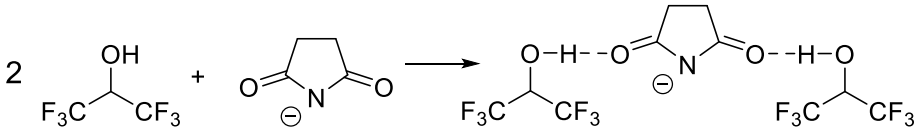
0 1

C	0.67118500	-0.39785900	1.06709900
C	1.34964200	-1.55641300	0.45428700
C	2.58154300	-1.48904100	-0.07631500
C	3.29131500	-0.25256500	-0.04346100
C	2.74337000	0.90025100	0.58777400
C	1.50642100	0.81527900	1.11688300
H	0.82114400	-2.50090300	0.43041800
H	3.07249900	-2.33714300	-0.53570100
H	3.31603200	1.81420700	0.65086100
H	1.10287600	1.68210700	1.62487700
O	4.45488200	-0.27436500	-0.60476100
C	5.29423600	0.89110800	-0.65311000
H	6.18041100	0.57444700	-1.19357700
H	4.78473500	1.68985800	-1.18993100
H	5.55429400	1.19816300	0.35888300
C	-1.41631100	1.08606300	1.09443600
H	-1.46893800	0.94671800	2.17959400
H	-0.81918900	1.98034300	0.90370800
C	-2.81672100	1.31455000	0.51278700
H	-3.25536400	2.19399200	0.99060800
C	-0.76355300	-0.14423300	0.44356800
C	-1.66101800	-1.36524700	0.70547500
H	-1.73263300	-1.54049700	1.78397900

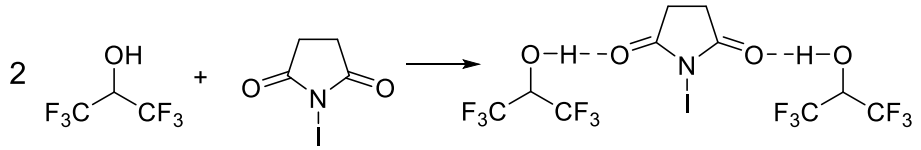
H	-1.23568700	-2.26405500	0.25375400
C	-3.69587500	0.08970000	0.77109400
H	-4.69811300	0.25501300	0.36448600
H	-3.80378700	-0.07588400	1.84752500
C	-3.05651800	-1.13455100	0.11315700
H	-3.66887400	-2.01982400	0.30109400
C	-2.93181300	-0.90267100	-1.39683800
H	-2.49377400	-1.78376400	-1.87623500
H	-3.92348100	-0.75367900	-1.83434300
C	-2.69431000	1.55282600	-0.99630300
H	-2.08644500	2.44280200	-1.18691700
H	-3.68324900	1.73592300	-1.42700800
C	-0.65836300	0.09052500	-1.07047900
H	-0.01368400	0.95371300	-1.26947400
H	-0.20061700	-0.77917000	-1.55282400
C	-2.05608700	0.32759800	-1.65816200
H	-1.96447700	0.49405200	-2.73425400

B. Microsolvation Correction

The negatively charged pyrrolidine-2,5-dione ion, also known as succinimide (SOC), possesses a strong hydrogen-bonding capability, and when embedded in the highly polar solvent HFIP, the resulting specific hydrogen bonding interactions can contribute substantially to the overall stabilization energy. Because the SMD model treats solvation implicitly, it cannot explicitly describe such directional hydrogen-bonding interactions [4, 5]. Consequently, a microsolvation correction [6] was applied to account for these effects. This correction was implemented as an enthalpic adjustment to the calculated Gibbs free energies of all species that contain the negatively charged SOC ion in the iodonium-catalyzed reaction pathway. As microsolvated SOC originates from microsolvated N-Iodosuccinimide (NIS), the enthalpic adjustment was calculated as the difference of enthalpy of microsolvation of SOC (Scheme 2) and that of NIS (Scheme S3).



Scheme S2. Microsolvation of the negatively charged succinimide (SOC) by HFIP molecules.



Scheme S3. Microsolvation of N-Iodosuccinimide (NIS) by HFIP molecules..

Enthalpies were computed for the relevant molecular species, including the isolated solute, HFIP solvent molecules, and the corresponding solute–solvent hydrogen-bonded complexes, at the M06-2X/def2-TZVP(D) level of theory. Enthalpies of microsolvation were calculated as enthalpy of reaction for Scheme 2 and Scheme 3. The calculated enthalpy of microsolvation for formation of the SOC^{-}–HFIP complex (Scheme S2) is −18.53 kcal/mol, reflecting strong stabilization arising from the formation of dual hydrogen bonds. However, this stabilization is partially offset by the energetic cost of disrupting the hydrogen-bonding interactions between NIS and two HFIP molecules. The enthalpy of microsolvation for formation of the NIS–HFIP complex (Scheme S3) was calculated to be −8.88 kcal/mol. Accordingly, the net enthalpic stabilization associated with SOC–HFIP hydrogen bonding, relative to microsolvated NIS, is −9.64 kcal/mol. This value was applied as a correction to all states in which the negatively charged pyrrolidine-2,5-dione ion exists as an isolated or uncomplexed anion.

Figure S17 presents the Gibbs free energy profile for the NIS-based iodonium pathway, with enthalpy corrections applied to all molecular states containing the uncomplexed negatively charged pyrrolidine-2,5-dione ion. In this figure, ΔG is defined as the free energy difference between a given state and the immediately preceding state, rather than relative to the initial reactant state, which differs from the standard convention.

The enthalpy correction has a pronounced impact on the computed activation barrier of the key transition state. Prior to applying this correction, the activation free

energy is 32.3 kcal/mol. Upon inclusion of the enthalpy correction, the Gibbs free energy of the transition state is substantially lowered, resulting in a reduced activation free energy of 22.6 kcal/mol. This corrected barrier is in good agreement with the experimentally observed activation free energy of approximately 23–25 kcal/mol. Theoretically speaking, an activation barrier of 32.3 kcal/mol would be difficult to surmount by thermal energy at room temperature, indicating that explicit solute–solvent interactions play a critical energetic role in facilitating transition-state formation.

Overall, the Gibbs free energy change for the entire reaction pathway is −10.4 kcal/mol, confirming that the process is thermodynamically favorable.

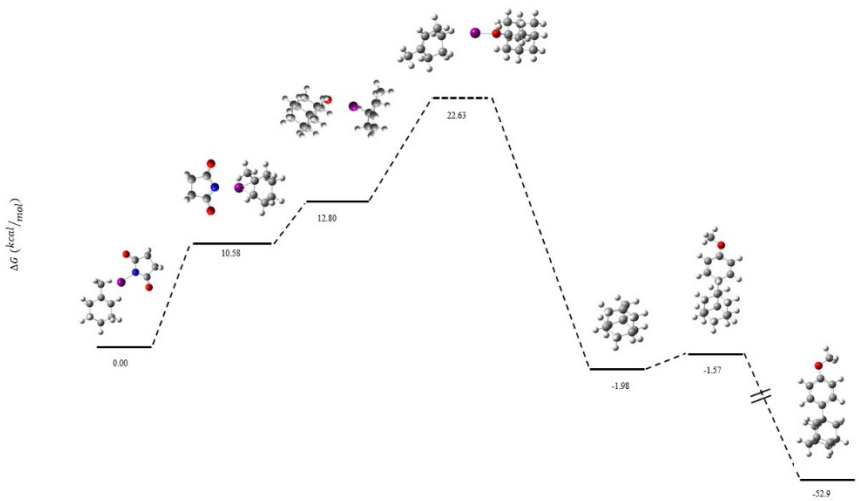


Figure S17. Energy profile for the NIS based iodonium pathway. ΔG is defined as the free energy difference between a given state and the immediately preceding state.

List of input files and the resulting Enthalpy for all chemical species*

* Cartesian Coordinates in Å, enthalpies, as calculated by adding the thermal enthalpy correction to the electronic energy, in Hartree.

<u>NIS</u>

M06-2X/def2-TZVP(D) level Enthalpy in HFIP= -657.599332 a.u.

0 1

C	0.87987491	-4.01190816	-4.85752092
C	1.40351394	-5.42915329	-5.06576457

C	1.94933937	-3.31809054	-4.04956495
C	2.73856287	-5.45422724	-4.36419372
N	2.97465959	-4.20920479	-3.82637923
O	3.49515471	-6.39611095	-4.27130200
O	1.93105269	-2.17392679	-3.65159897
H	-0.05395473	-3.96983815	-4.29831137
H	0.73967948	-3.45932955	-5.78570362
H	0.76892374	-6.19641786	-4.62466213
H	1.56148674	-5.68488675	-6.11295270
I	4.66474172	-3.73498230	-2.80675409

SOC

M06-2X/def2-TZVP level Enthalpy in HFIP = -360.126058 a.u.

-1 1

C	-2.017473	1.012417	-0.023291
C	-2.227591	-0.488133	-0.014262
C	-0.476891	1.149736	-0.002382
C	-0.783983	-1.043098	0.010924
N	0.137461	-0.054156	0.016143
O	-0.576857	-2.250791	0.023596
O	0.054074	2.254112	-0.003751
H	-2.425598	1.530206	0.846022
H	-2.400483	1.516148	-0.912075
H	-2.760885	-0.863654	0.860356
H	-2.735555	-0.877794	-0.897729

HFIP

M06-2X/def2-TZVP level Enthalpy in HFIP= -789.829873 a.u.

0 1

F	-3.39700000	1.05800000	-5.03800000
F	-2.54500000	-1.11700000	-4.29000000

H	-0.91300000	0.39900000	-2.32400000
F	-3.81700000	0.29800000	-2.73900000
F	-1.80100000	3.58300000	-4.06600000
F	-2.48000000	2.90000000	-1.80600000
F	-0.10200000	3.20600000	-2.33900000
C	-2.78100000	0.32200000	-3.85500000
C	-1.42800000	2.69600000	-2.88800000
C	-1.26900000	1.02500000	-3.34600000
O	-0.20212903	0.94148946	-4.56178537
H	0.44500000	0.02100000	-4.33400000

SOC-HFIP Complex

M06-2X/def2-TZVP level Enthalpy in HFIP= -1939.815327 a.u.

-1 1

C	0.87987491	-4.01190816	-4.85752092
C	1.40351394	-5.42915329	-5.06576457
C	1.94933937	-3.31809054	-4.04956495
C	2.73856287	-5.45422724	-4.36419372
N	2.97465959	-4.20920479	-3.82637923
O	3.49515471	-6.39611095	-4.27130200
O	1.93105269	-2.17392679	-3.65159897
H	-0.05395473	-3.96983815	-4.29831137
H	0.73967948	-3.45932955	-5.78570362
H	0.76892374	-6.19641786	-4.62466213
H	1.56148674	-5.68488675	-6.11295270
F	8.91673854	-10.53972502	-5.04821087
F	8.20079447	-8.59543080	-4.47189664
H	6.70683005	-9.83294413	-2.73327389
F	9.26073822	-9.81368237	-3.04877038
F	7.45048148	-12.69191856	-4.15051761
F	8.02151186	-12.03901759	-2.17821296

F	5.94037510	-12.27664528	-2.67775360
C	8.37160309	-9.84797496	-4.04456591
C	7.12135604	-11.87212116	-3.15106243
C	7.02352516	-10.41892891	-3.60384097
O	6.12262329	-10.35984339	-4.65809223
H	5.55800000	-9.53600000	-4.53000000
F	-3.39700000	1.05800000	-5.03800000
F	-2.54500000	-1.11700000	-4.29000000
H	-0.91300000	0.39900000	-2.32400000
F	-3.81700000	0.29800000	-2.73900000
F	-1.80100000	3.58300000	-4.06600000
F	-2.48000000	2.90000000	-1.80600000
F	-0.10200000	3.20600000	-2.33900000
C	-2.78100000	0.32200000	-3.85500000
C	-1.42800000	2.69600000	-2.88800000
C	-1.26900000	1.02500000	-3.34600000
O	-0.20212903	0.94148946	-4.56178537
H	0.44500000	0.02100000	-4.33400000

NIS-HFIP Complex

M06-2X/def2-TZVP(D) level Enthalpy in HFIP= -2237.273231 a.u.

0 1

C	0.87987491	-4.01190816	-4.85752092
C	1.40351394	-5.42915329	-5.06576457
C	1.94933937	-3.31809054	-4.04956495
C	2.73856287	-5.45422724	-4.36419372
N	2.97465959	-4.20920479	-3.82637923
O	3.49515471	-6.39611095	-4.27130200
O	1.93105269	-2.17392679	-3.65159897
H	-0.05395473	-3.96983815	-4.29831137
H	0.73967948	-3.45932955	-5.78570362

H	0.76892374	-6.19641786	-4.62466213
H	1.56148674	-5.68488675	-6.11295270
F	8.91673854	-10.53972502	-5.04821087
F	8.20079447	-8.59543080	-4.47189664
H	6.70683005	-9.83294413	-2.73327389
F	9.26073822	-9.81368237	-3.04877038
F	7.45048148	-12.69191856	-4.15051761
F	8.02151186	-12.03901759	-2.17821296
F	5.94037510	-12.27664528	-2.67775360
C	8.37160309	-9.84797496	-4.04456591
C	7.12135604	-11.87212116	-3.15106243
C	7.02352516	-10.41892891	-3.60384097
O	6.12262329	-10.35984339	-4.65809223
H	5.55800000	-9.53600000	-4.53000000
F	-3.39700000	1.05800000	-5.03800000
F	-2.54500000	-1.11700000	-4.29000000
H	-0.91300000	0.39900000	-2.32400000
F	-3.81700000	0.29800000	-2.73900000
F	-1.80100000	3.58300000	-4.06600000
F	-2.48000000	2.90000000	-1.80600000
F	-0.10200000	3.20600000	-2.33900000
C	-2.78100000	0.32200000	-3.85500000
C	-1.42800000	2.69600000	-2.88800000
C	-1.26900000	1.02500000	-3.34600000
O	-0.20212903	0.94148946	-4.56178537
H	0.44500000	0.02100000	-4.33400000
I	4.66474172	-3.73498230	-2.80675409

9. NMR iodonium Studies

9.1 NMR iodonium studies procedure: To an NMR tube was added NIS (87.5 mg, 0.5 mmol), 1-methylcyclohexene (12µL, 0.1mmol), HFIP (21µL, 0.2 mmol) followed by $CDCl_3$ (0.6 mL) and was stirred 2h over dark conditions at room temperature.

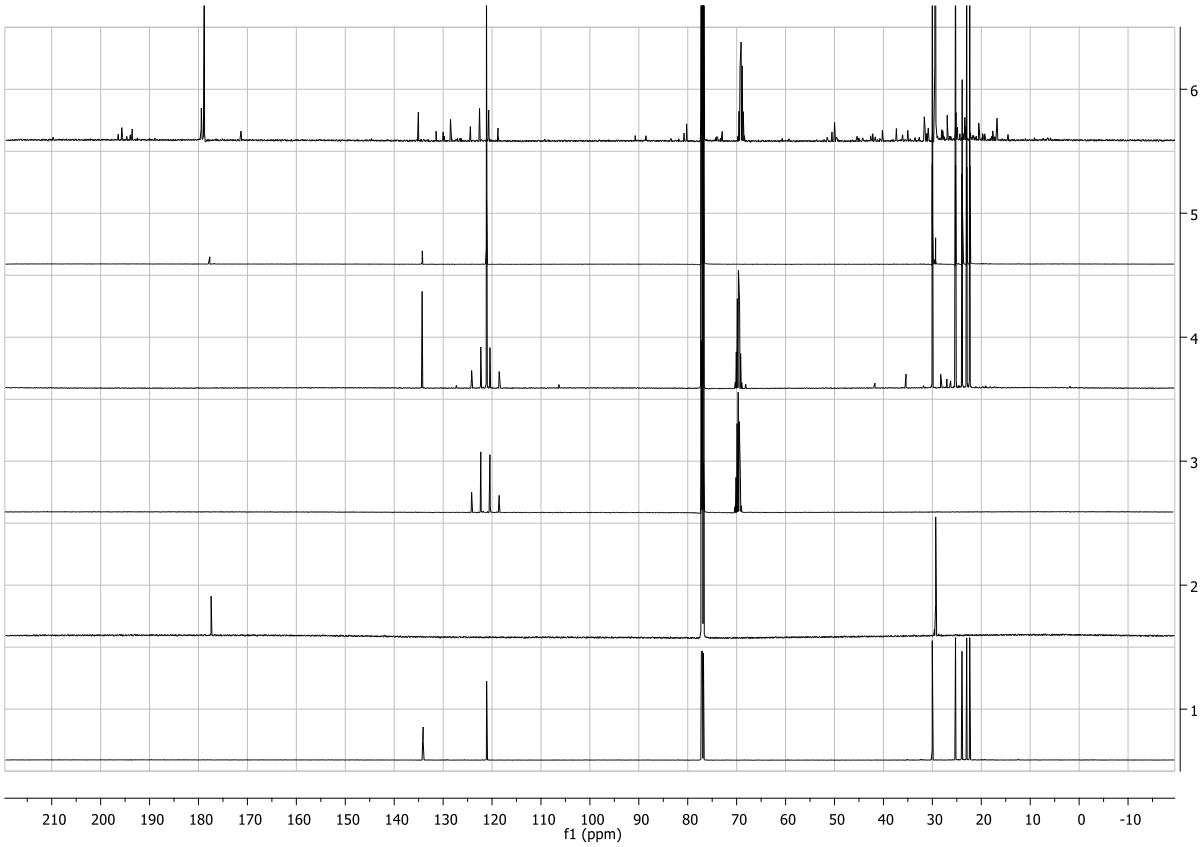


Figure S18. NMR studies of *in-situ* iodonium from top to bottom

Spectrum 6 = 1-methyl-cyclohexene + NIS + HFIP
Spectrum 5 = NIS + 1-methyl-cyclohexene
Spectrum 4 = HFIP + 1-methyl-cyclohexene
Spectrum 3 = HFIP
Spectrum 2 = NIS
Spectrum 1 = 1-methyl-cyclohexene

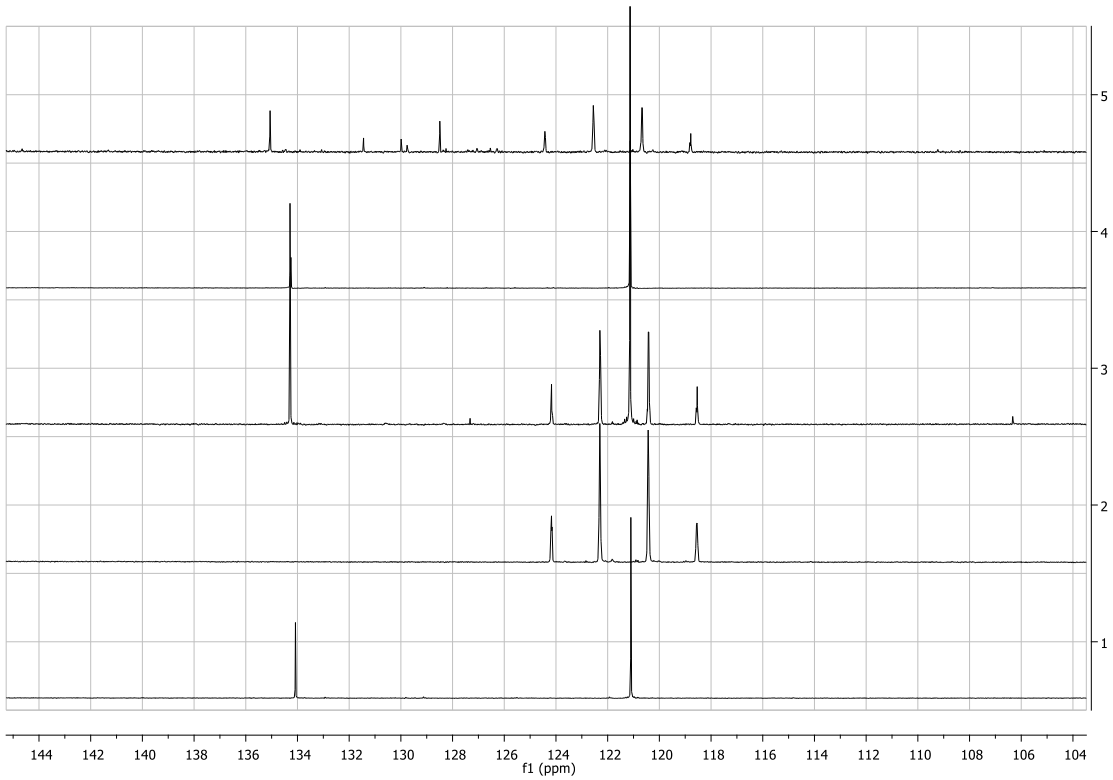


Figure S19. NMR studies of *in-situ* iodonium from top to bottom
Spectrum 5 = 1-methyl-cyclohexene + NIS + HFIP
Spectrum 4 = NIS + 1-methyl-cyclohexene
Spectrum 3 = HFIP + 1-methyl-cyclohexene
Spectrum 2 = HFIP
Spectrum 1 = 1-methyl-cyclohexene

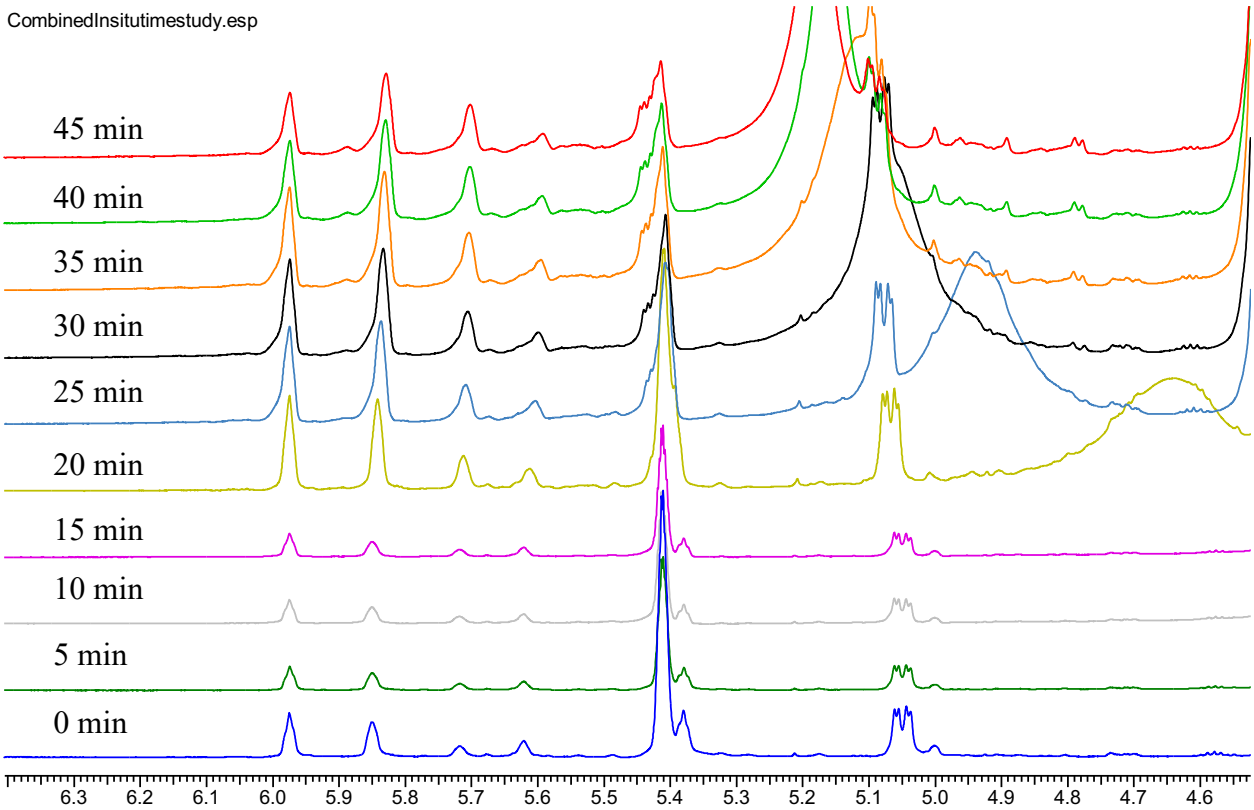


Figure S20. 1H-NMR of in-situ generated iodonium over 45 min with alkene **3** (0.1mmol), NIS (0.5mmol), and HFIP (0.2 mmol) in $CDCl_3$.

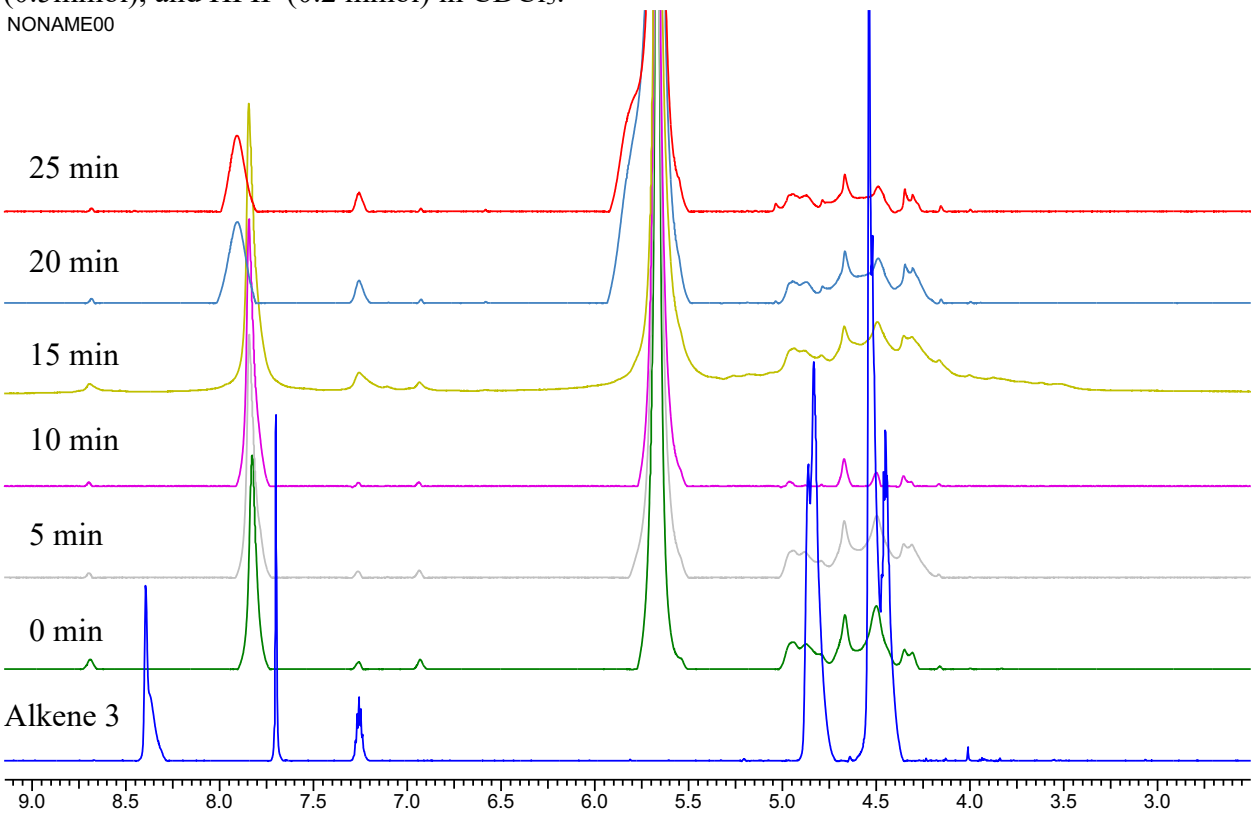


Figure S21. In-situ generated iodonium with HFIP-d2 (0.6mL) as solvent with 1-methylcyclohexene (0.1 mmol) and NIS (0.5mmol)

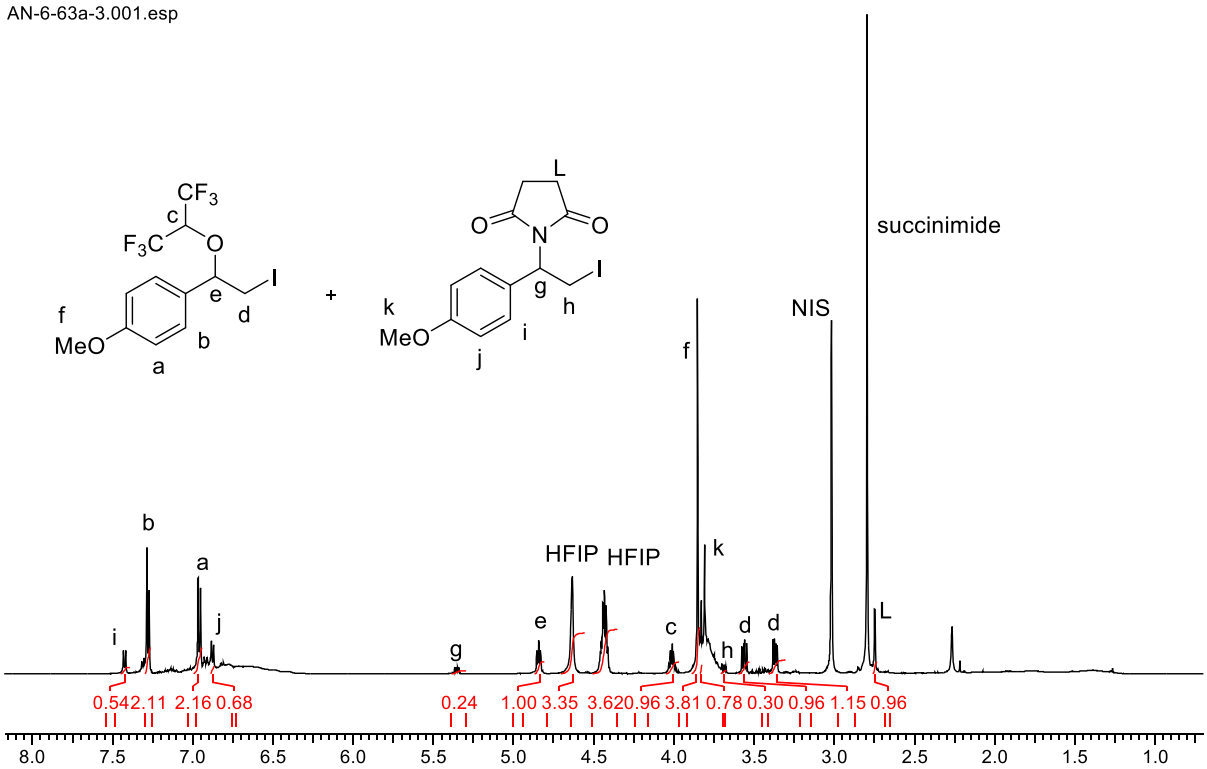


Figure S22. NMR study for p-methoxy styrene (0.1mmol), NIS (0.5mmol), and HFIP (0.2 mmol) in $CDCl_3$.

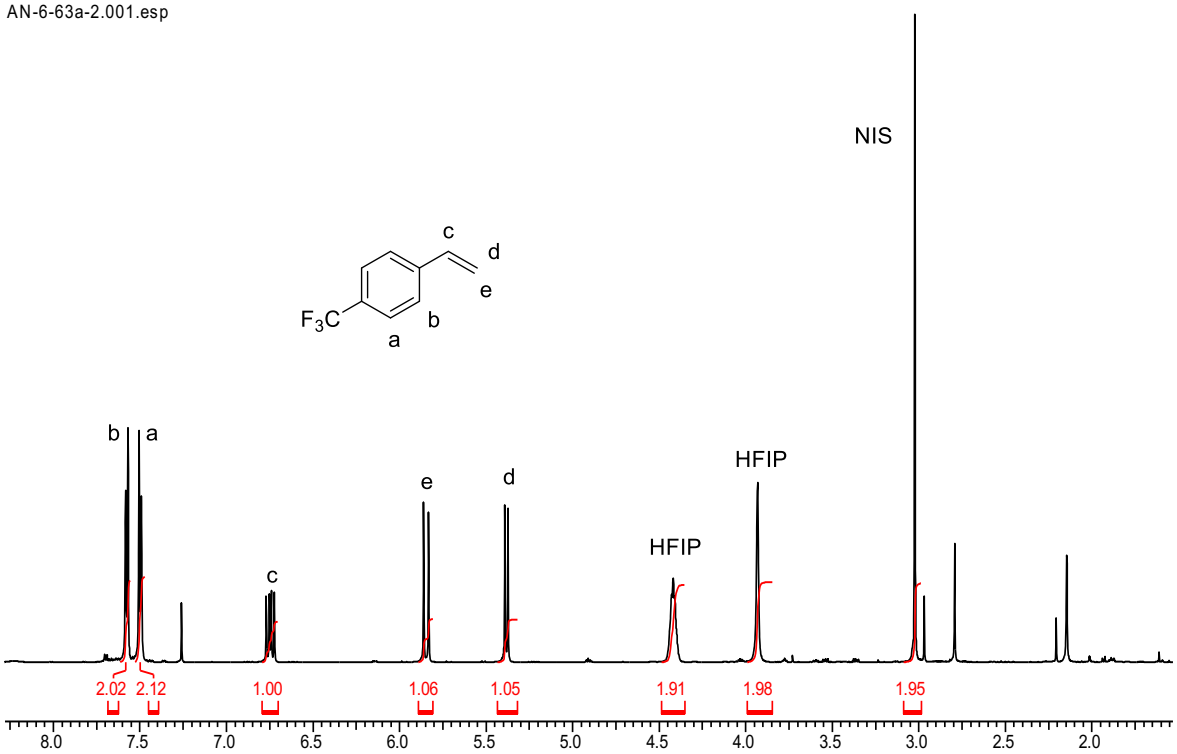


Figure S23. NMR study for p-trifluoromethyl styrene (0.1mmol), NIS (0.5mmol), and HFIP (0.2 mmol) in $CDCl_3$.

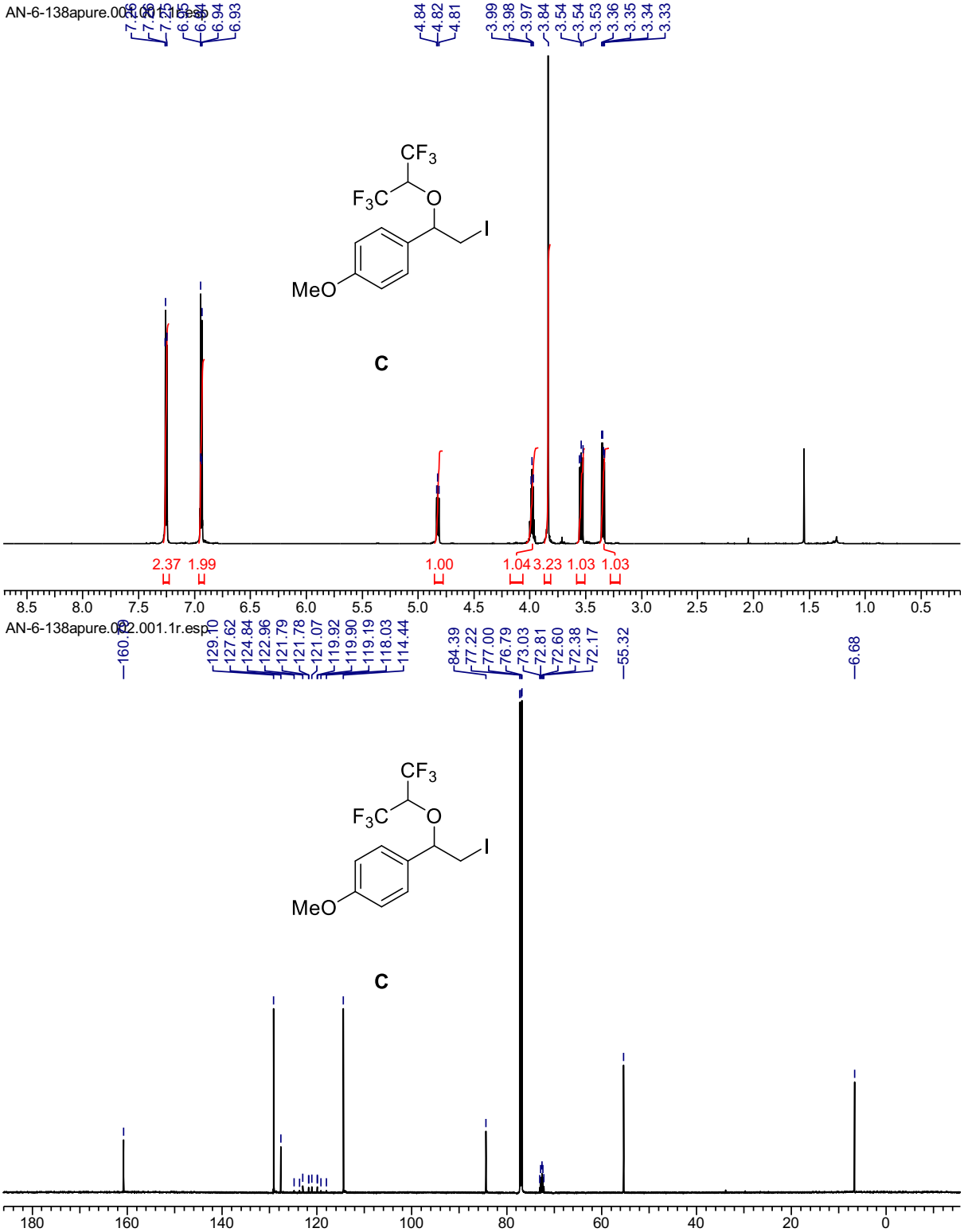
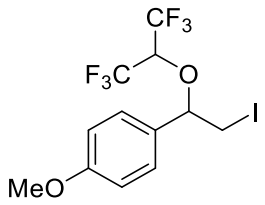


Figure S24. 1H-NMR of isolated iodo ether trapped byproduct



1-(1-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2-iodoethyl)-4-methoxybenzene (C): To 8 mL vial was added p-methoxystyrene (33.5 µL, 0.25 mmol), NIS (281 mg, 5 eq), $CHCl_3$ (0.6mL), and HFIP (52.5 µL, 2 eq). The reaction mixture was stirred at room temperature under dark for 2 h. After the reaction, the reaction was quenched with 20% $Na_2S_2O_3$ (1 mL) and extracted with EtOAc (3 x 2 mL). The combined organic solution was dried with anhydrous Na_2SO_4, filtered, concentrated *in vacuo* by rotavapor and purified by flash chromatography on SiO_2 to provide the desired product.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.6 Hz, 2 H), 6.94 (d, J = 8.6 Hz, 2 H), 4.82 (dd, J = 6.3, 7.2 Hz, 1 H), 4.03 - 3.92 (m, 1 H), 3.84 (s, 3 H), 3.54 (dd, J = 7.8, 10.5 Hz, 1 H), 3.35 (dd, J = 6.0, 10.5 Hz, 1 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.8, 129.1, 127.6, 122.0 (td, J=286.10, 283.90 Hz), 120.8 (td, J=282.80, 280.60 Hz), 114.4, 84.4, 72.6 (quin, J=31.91 Hz), 55.3, 6.7

IR (neat): 2927, 2841, 1611, 1514, 1284, 1189, 1175, 1190, 1100, 1120,833, 689, 573 cm^{-1}

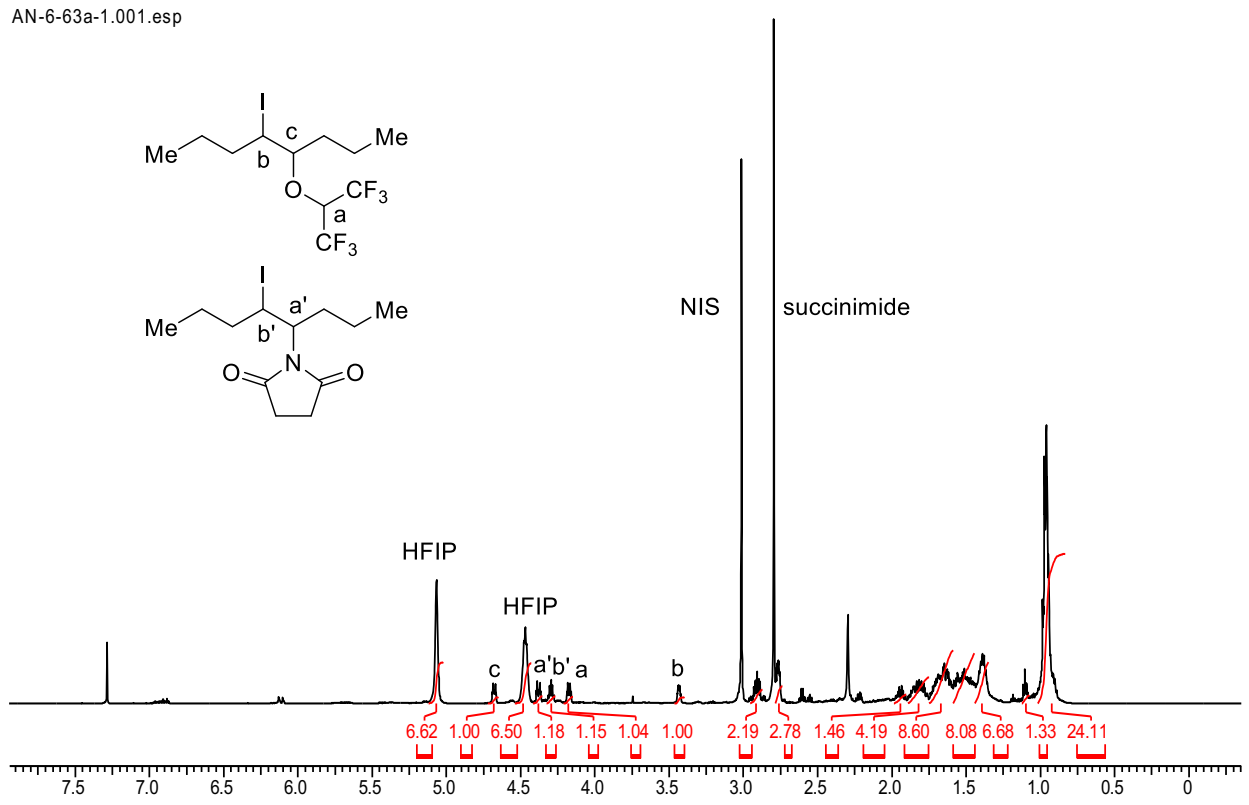
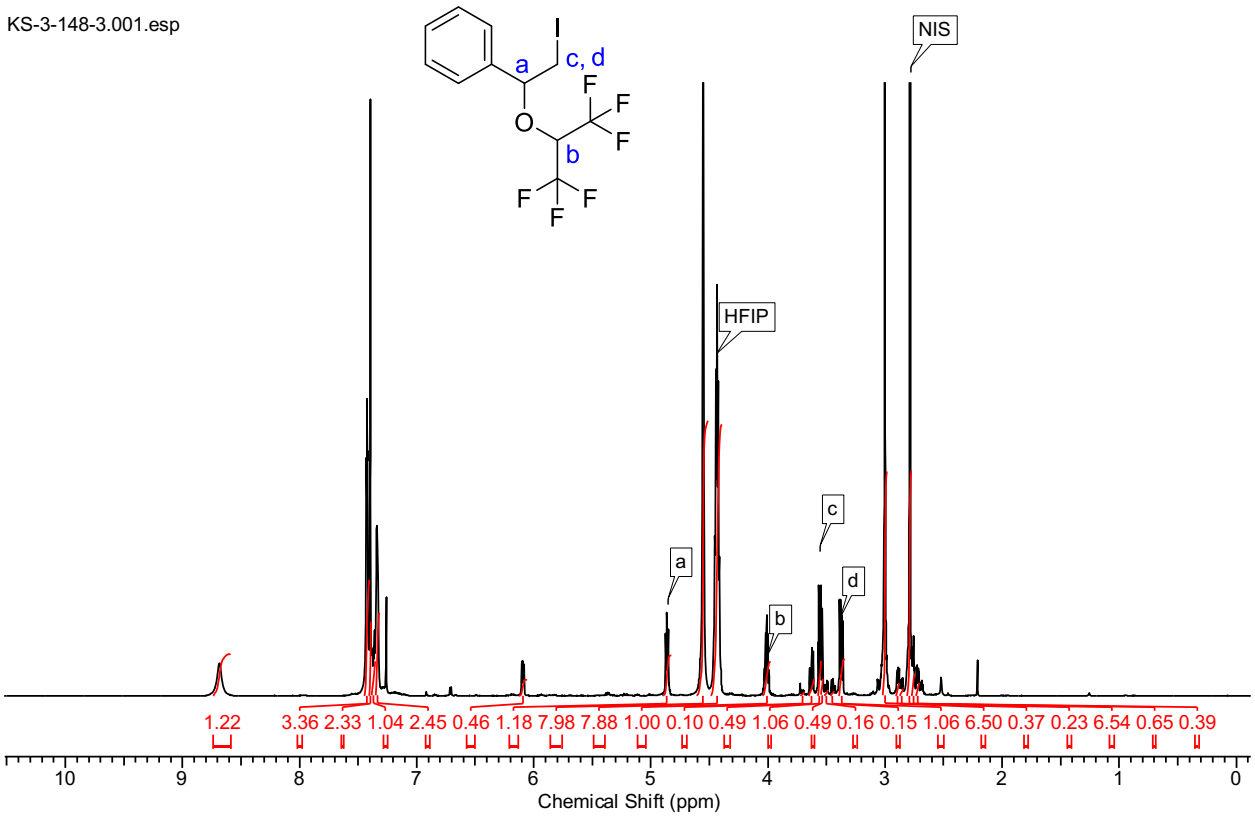


Figure S25. NMR study for trans-4-octene



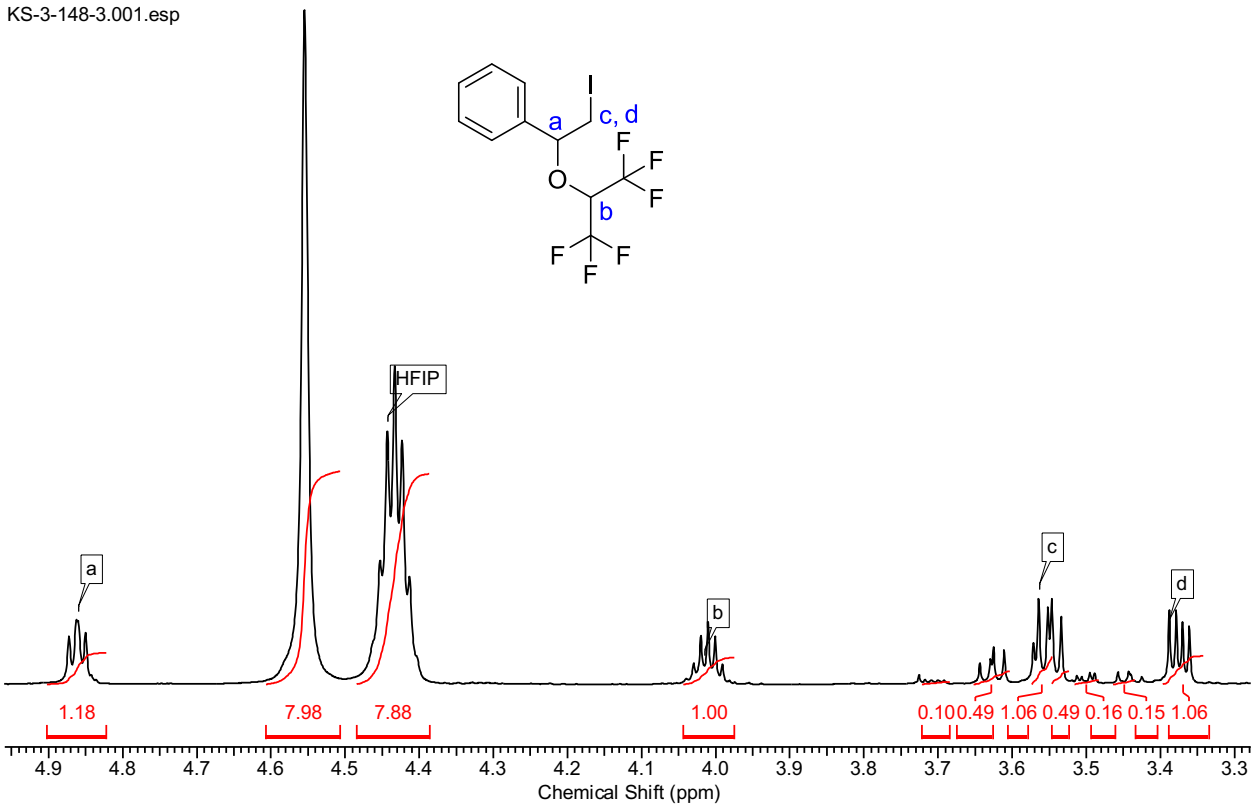


Figure S26. NMR study for styrene

10. FT-IR Iodonium in-situ generation study

10.1 FT-IR study procedure: To an 8mL vial was added NIS (22.5 mg, 0.1 mmol), 1-methylcyclohexene (12µL, 0.1mmol), HFIP (0.6 mL) and over dark conditions at room temperature. Time aliquots were sampled and directed subjected to IR spectroscopy.

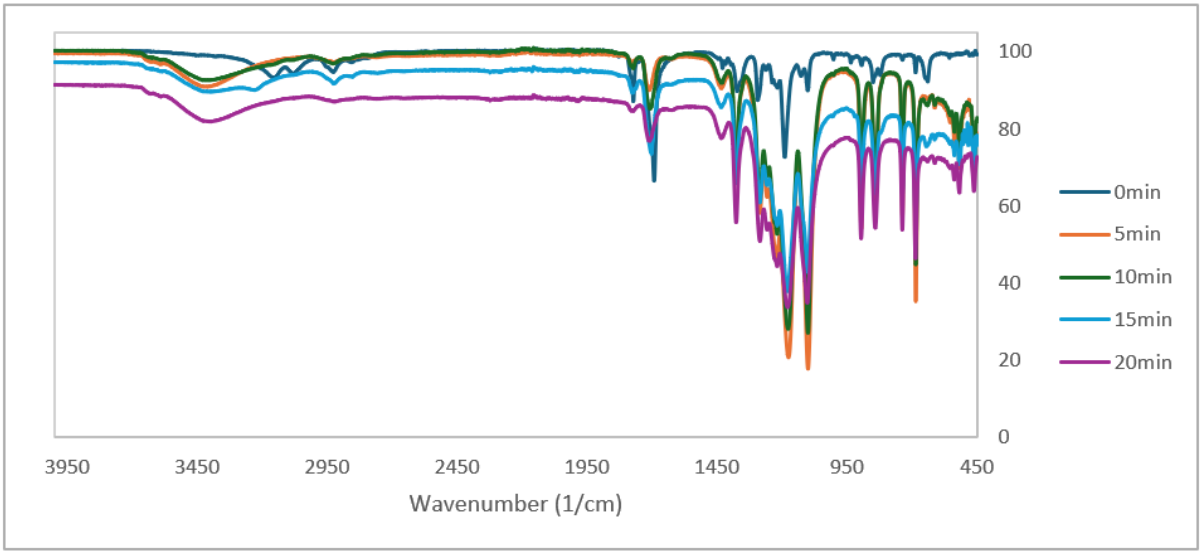


Figure S27. IR spectroscopy of in-situ generated iodonium over 20min

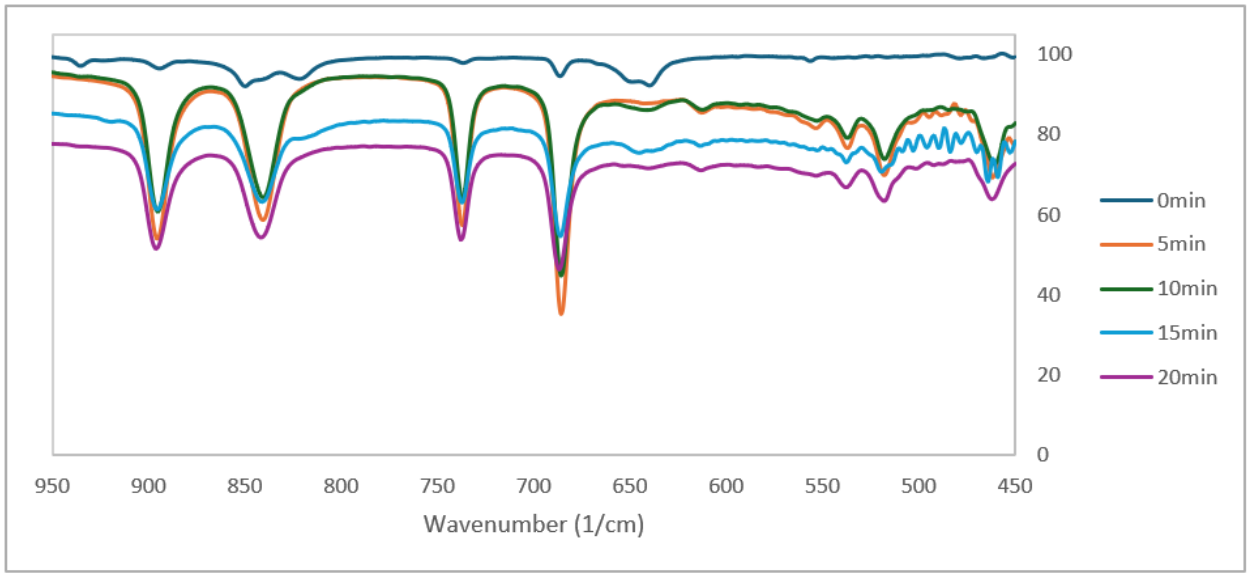


Figure S28. IR spectroscopy of in-situ generated iodonium over 20min from 950 to 450 cm^{-1}

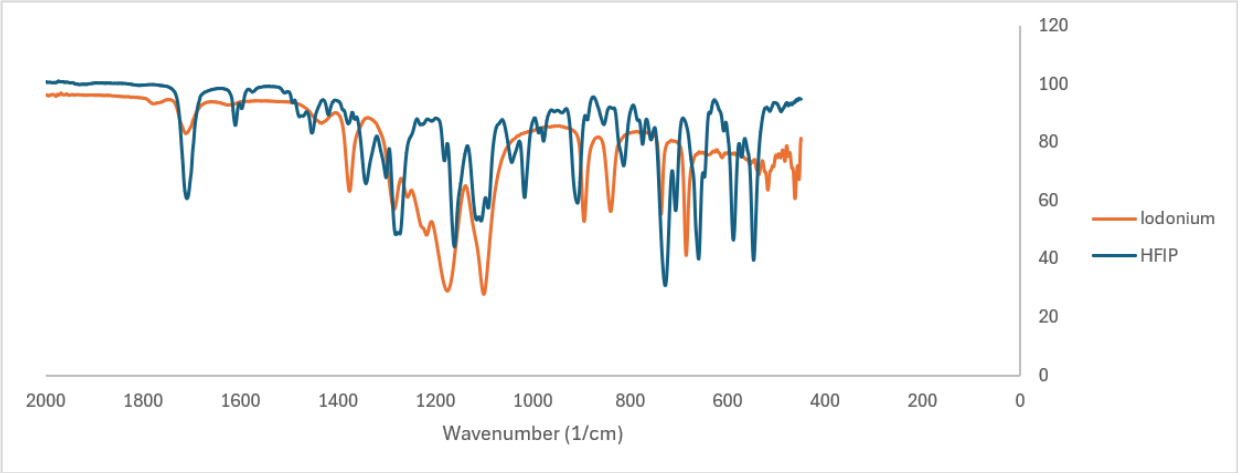


Figure S29. IR spectroscopy of proposed Iodonium versus HFIP control

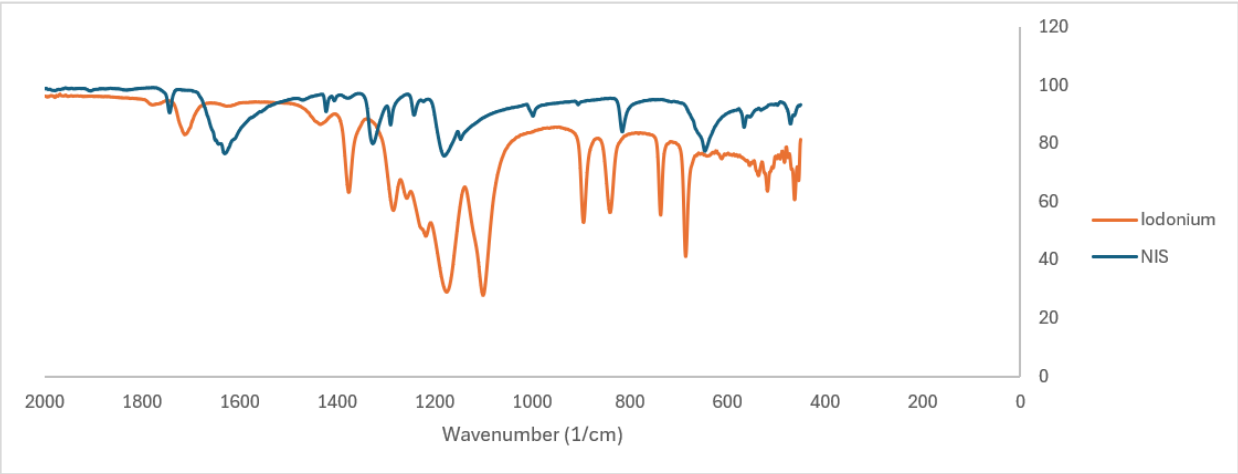


Figure S30. IR spectroscopy of proposed Iodonium versus NS control

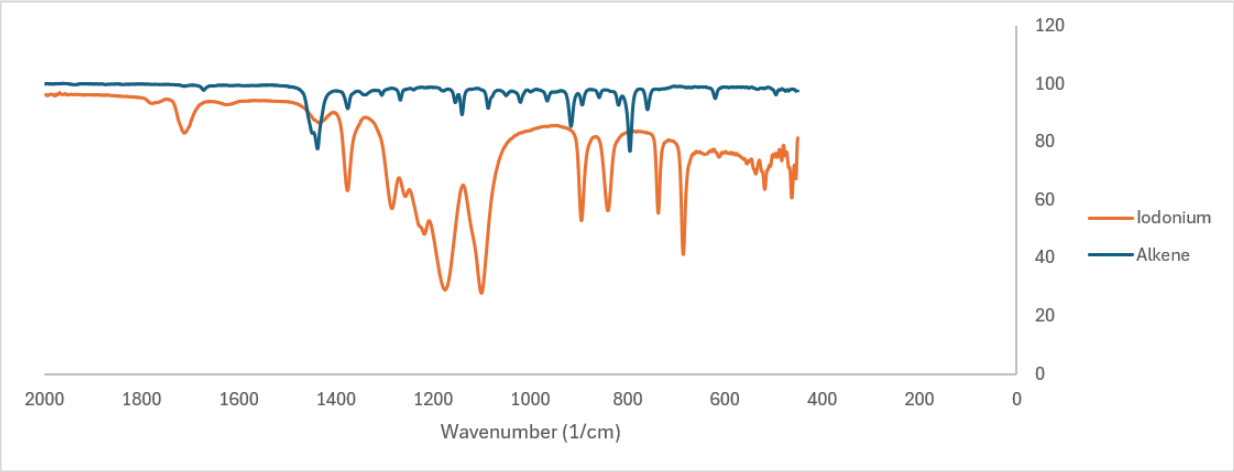


Figure S31. IR spectroscopy of proposed Iodonium versus 1-methylcyclohexene control

11. Spectral Data

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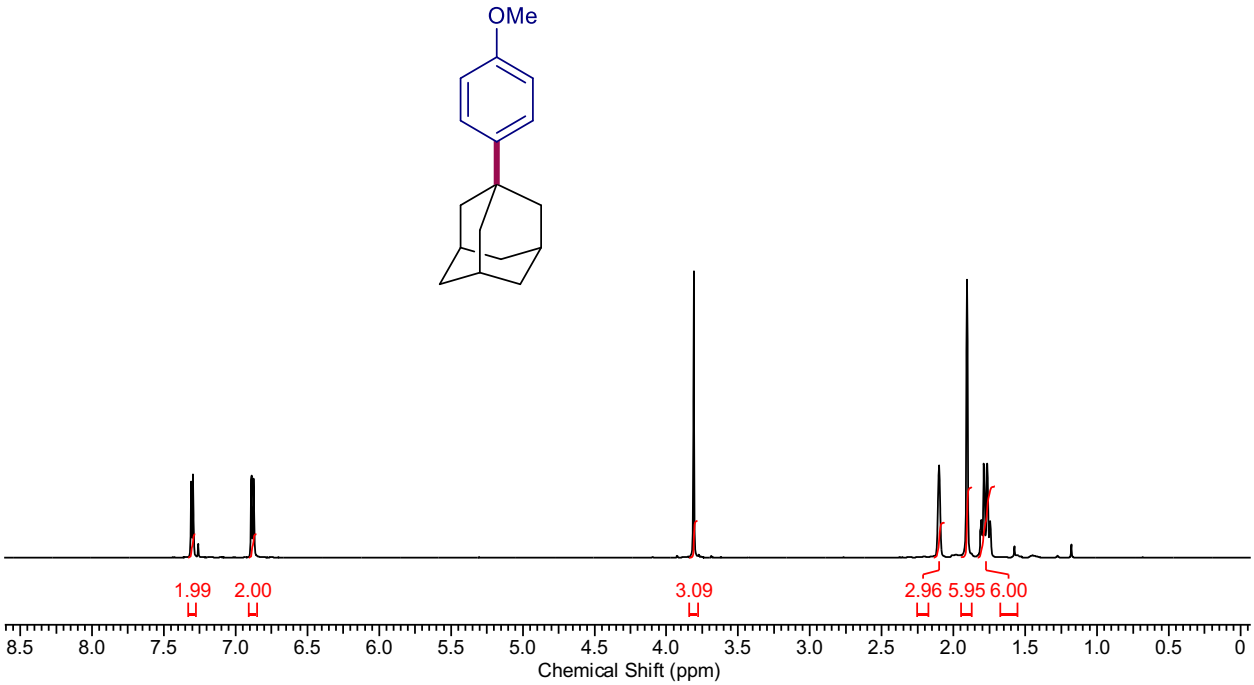

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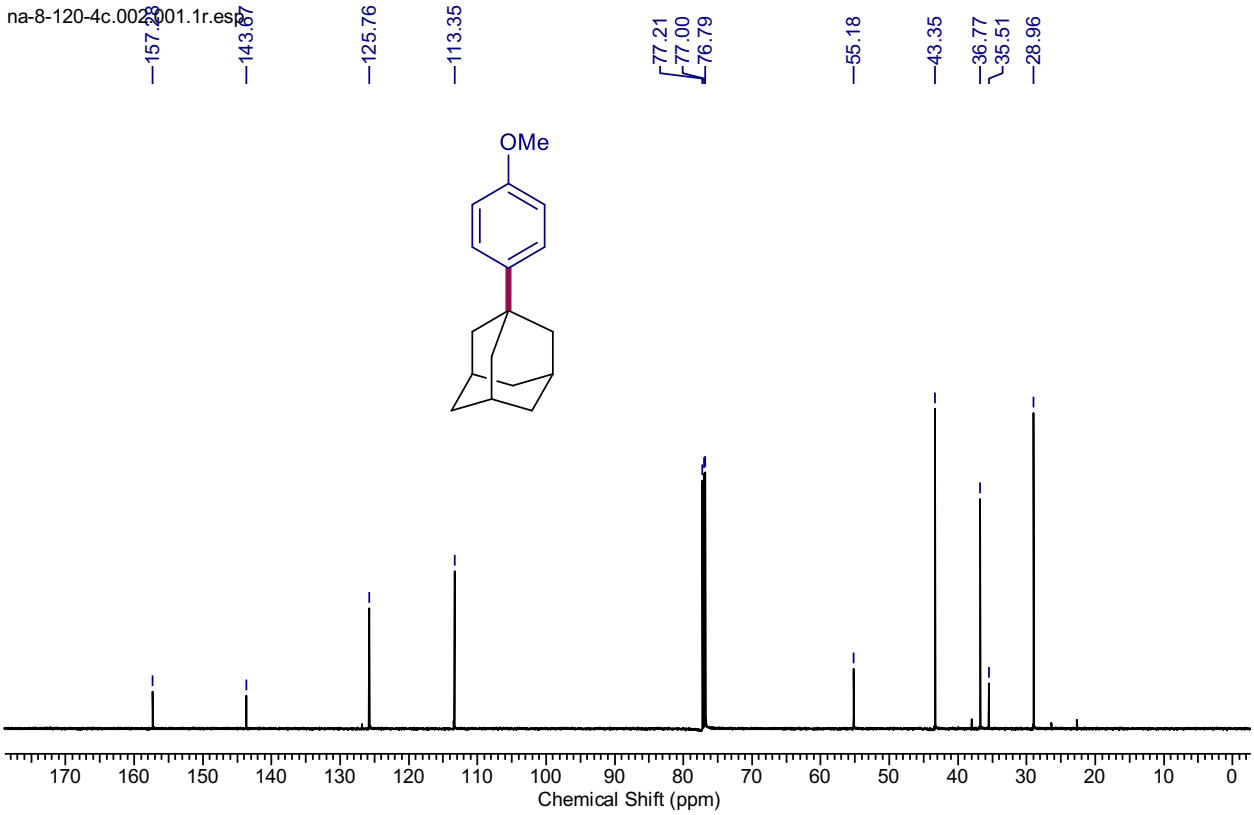

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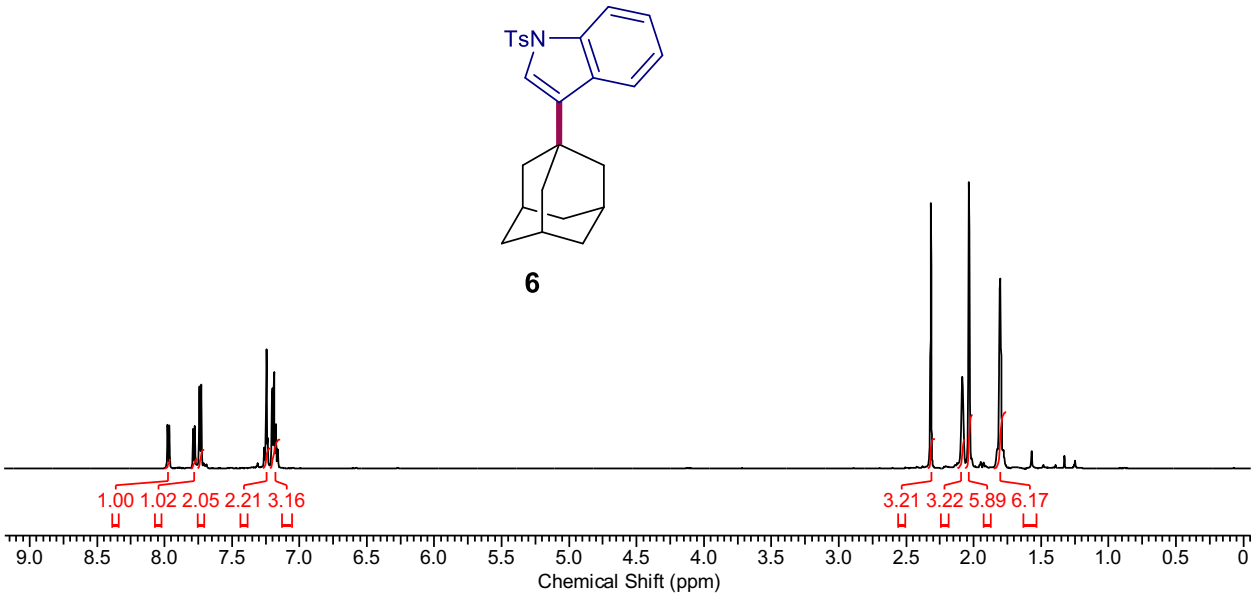

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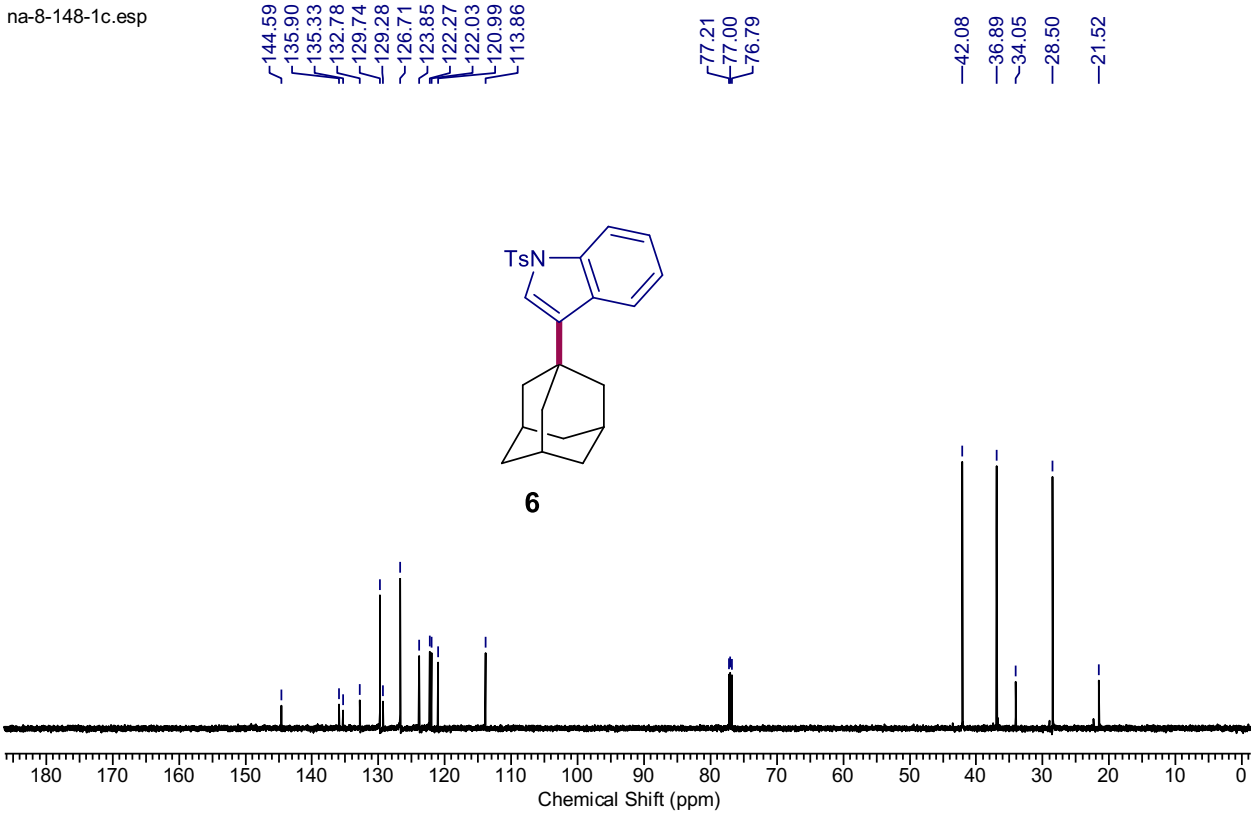

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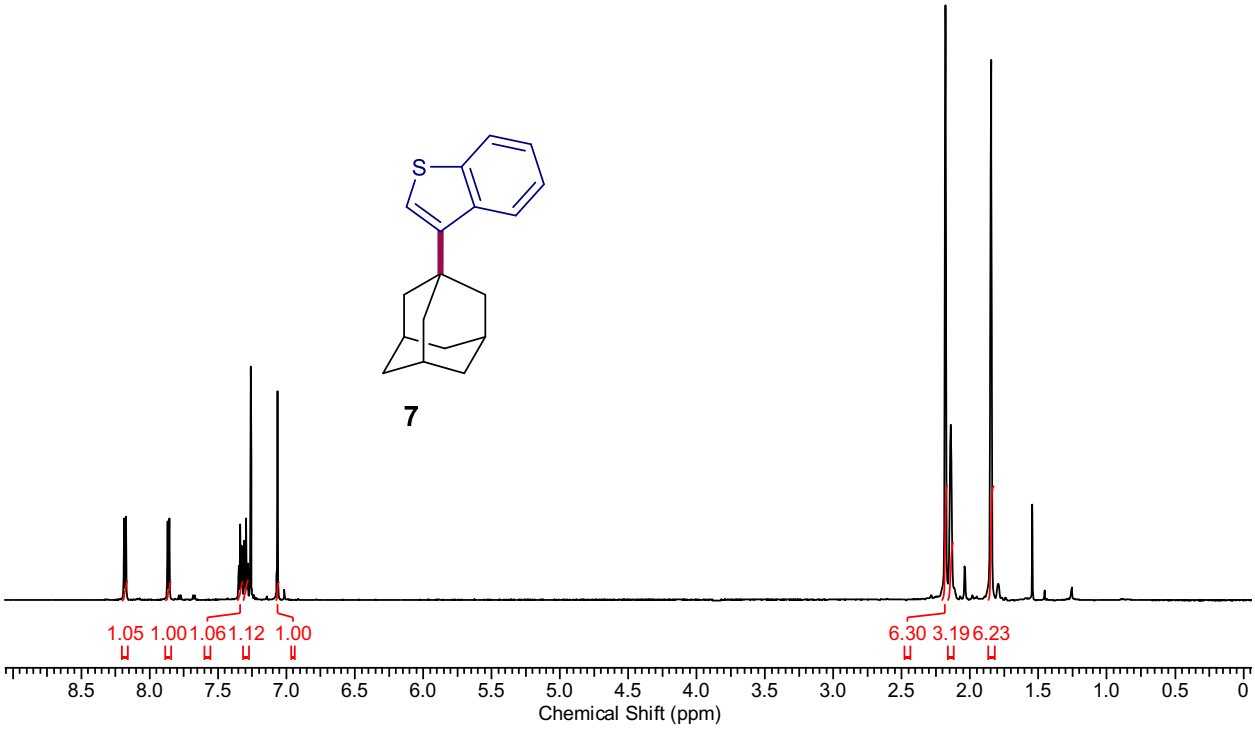

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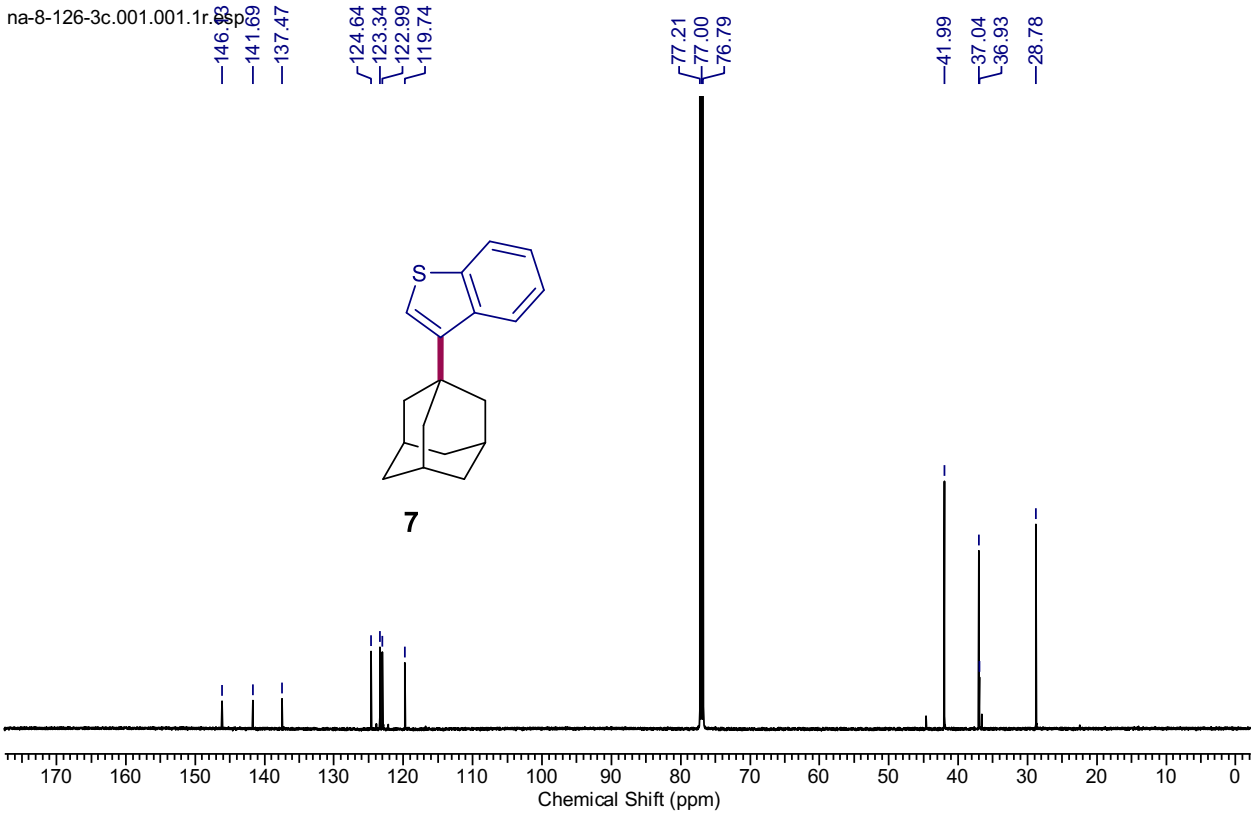

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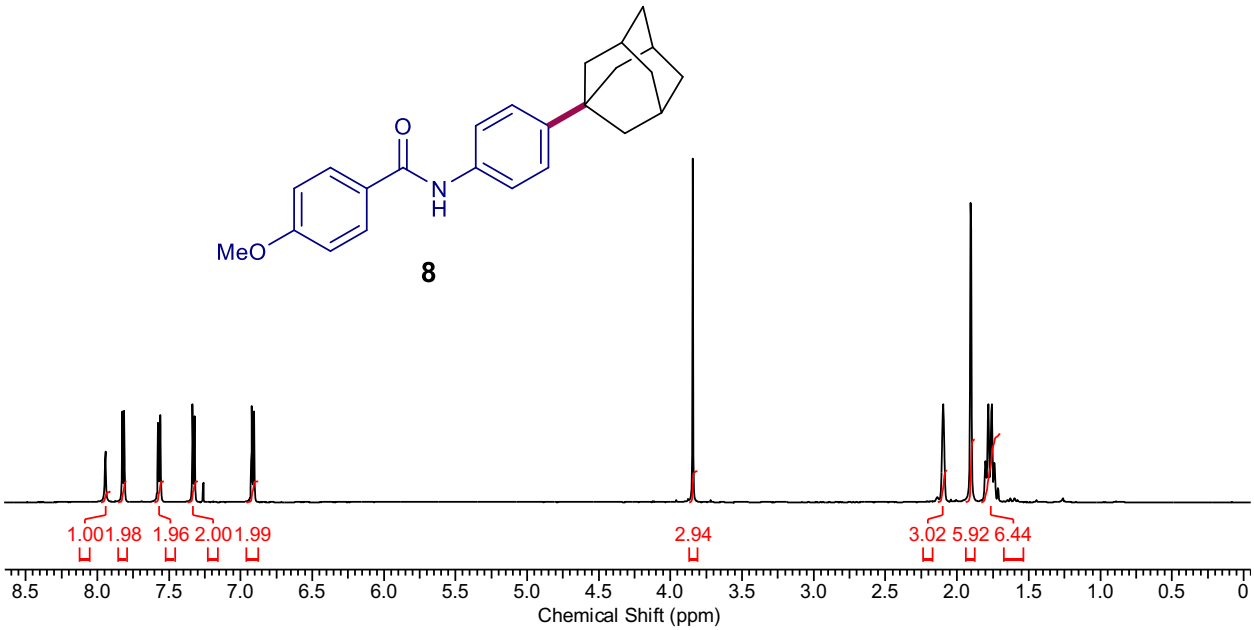

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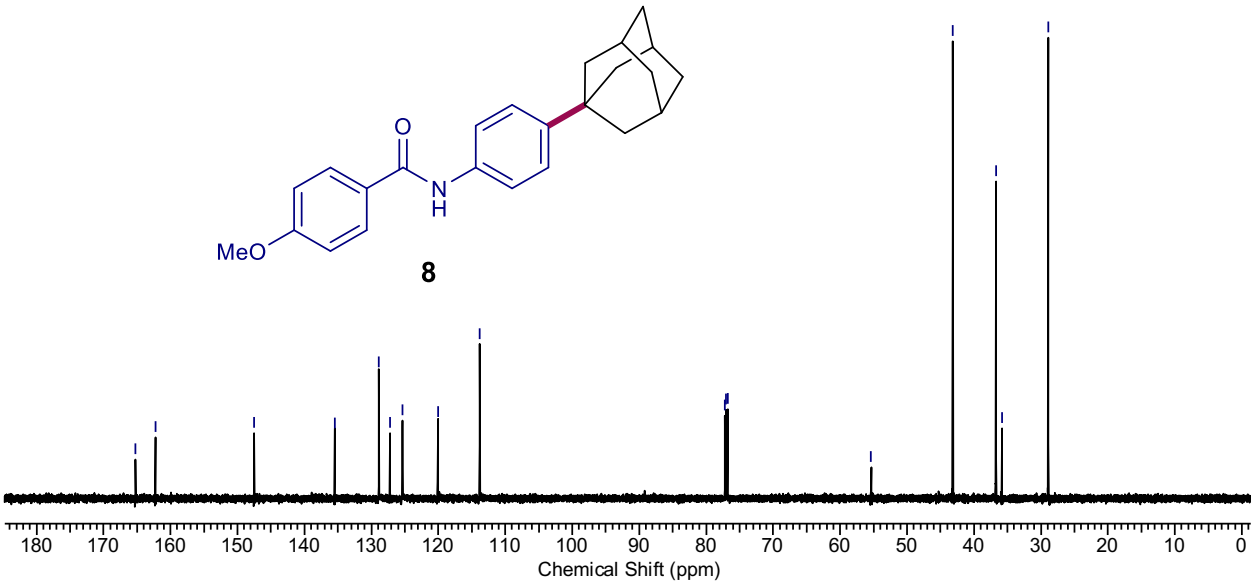

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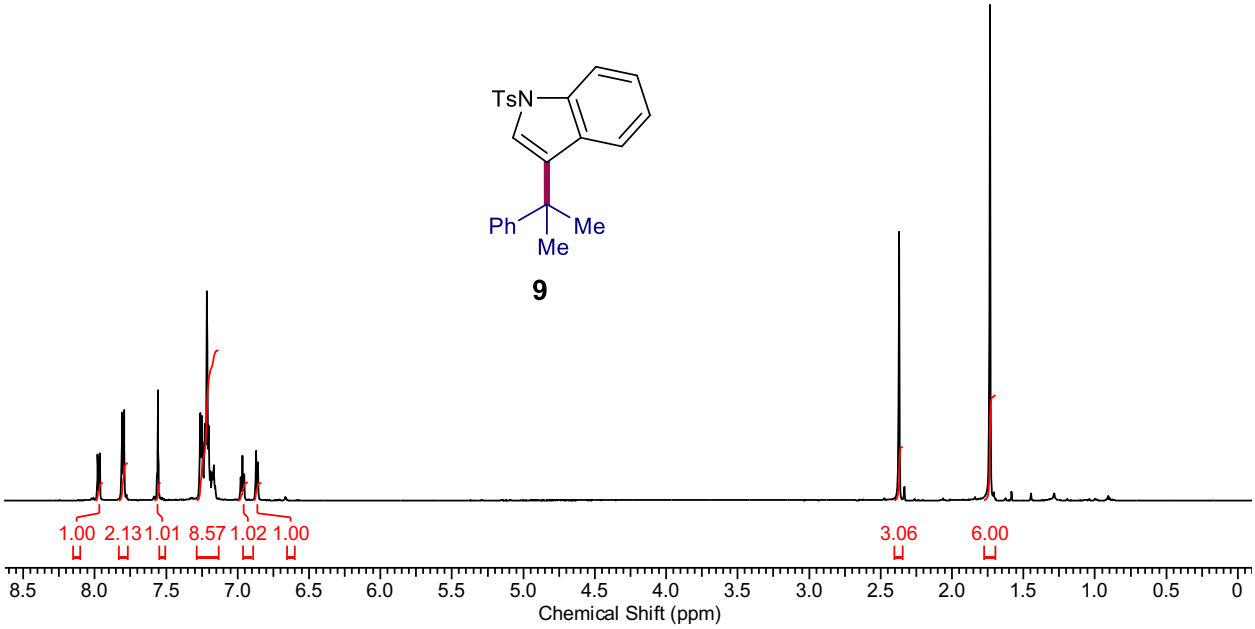

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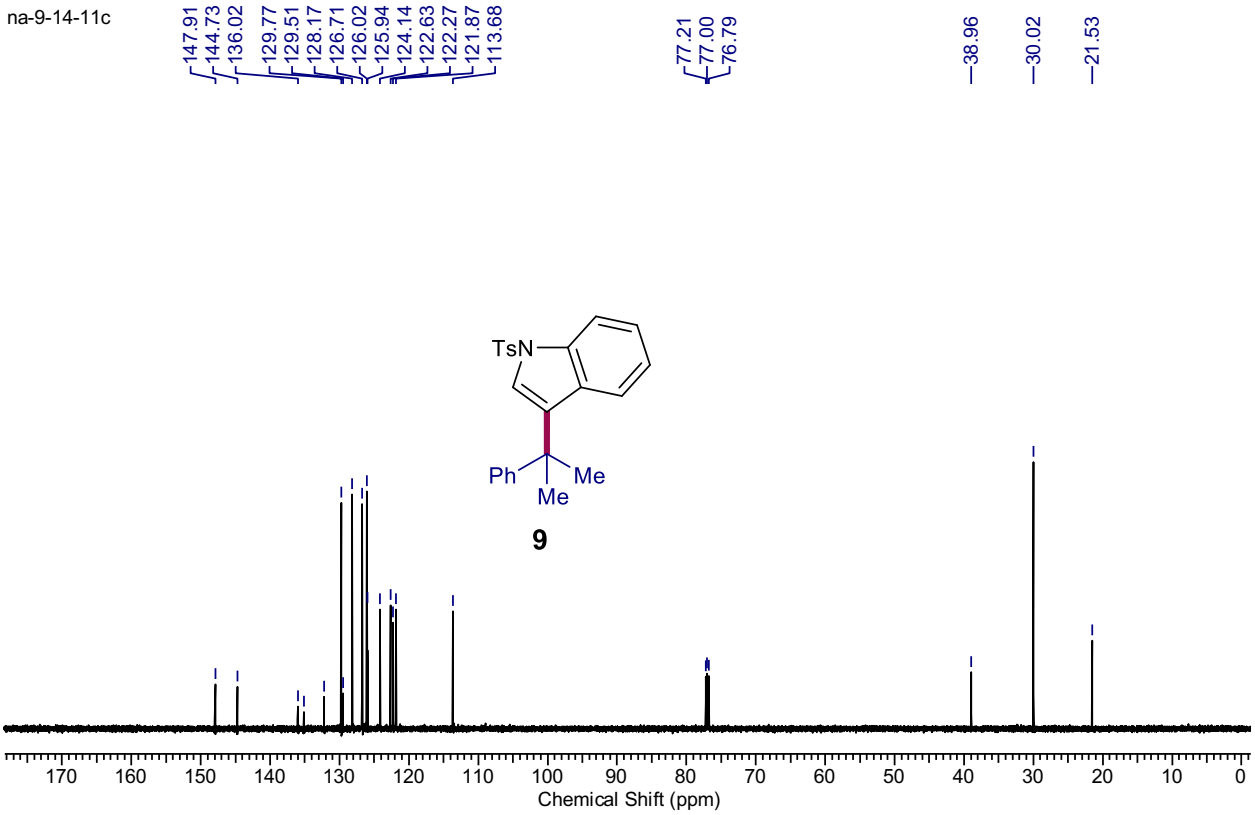

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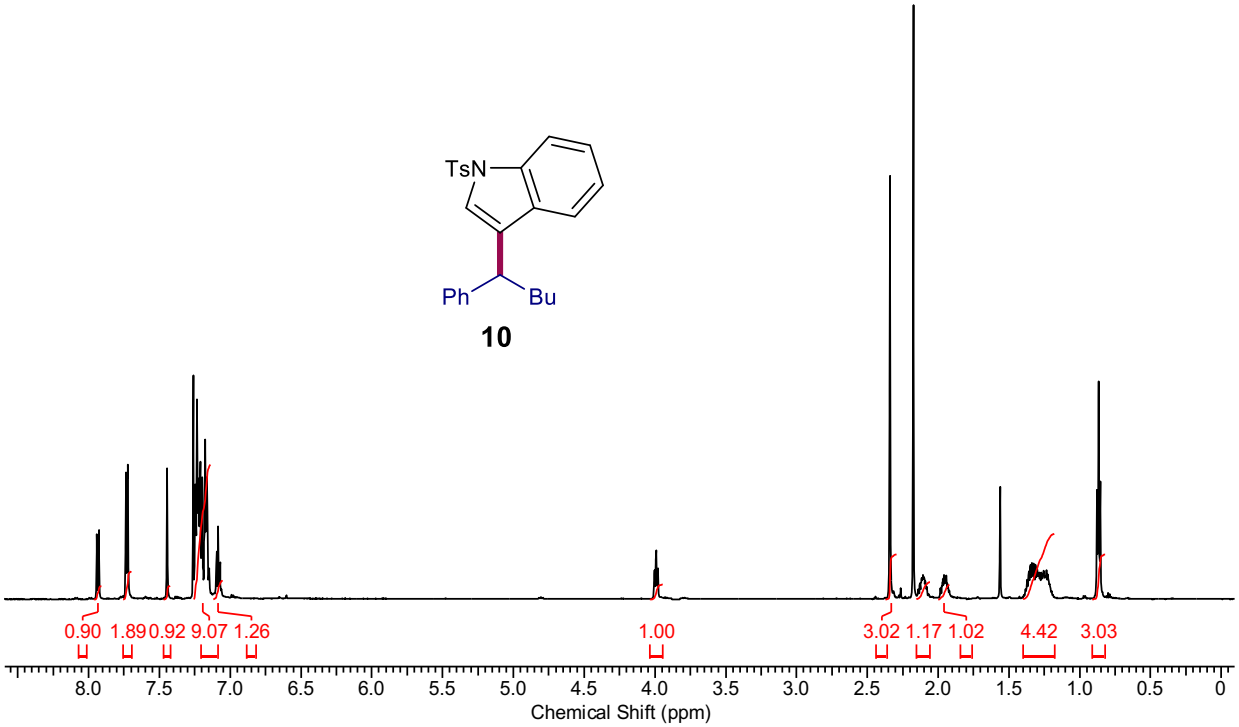

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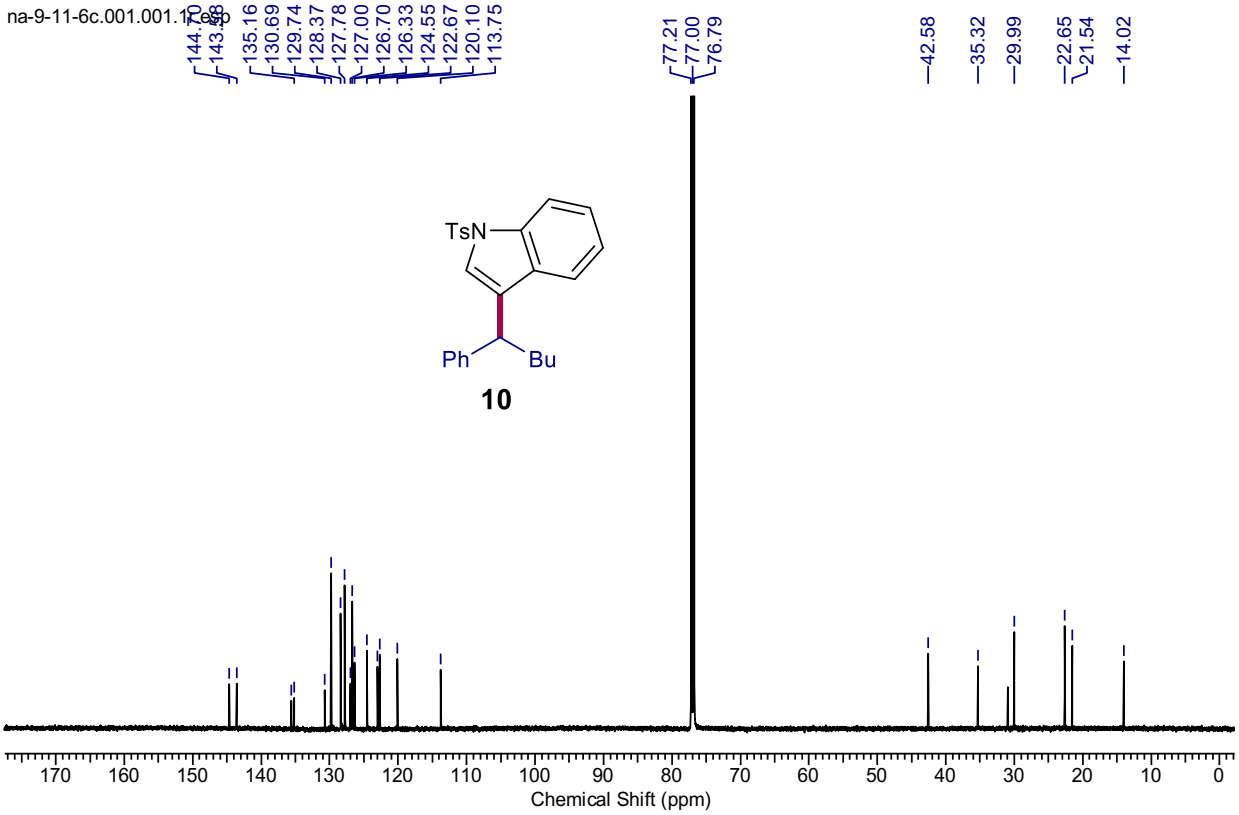

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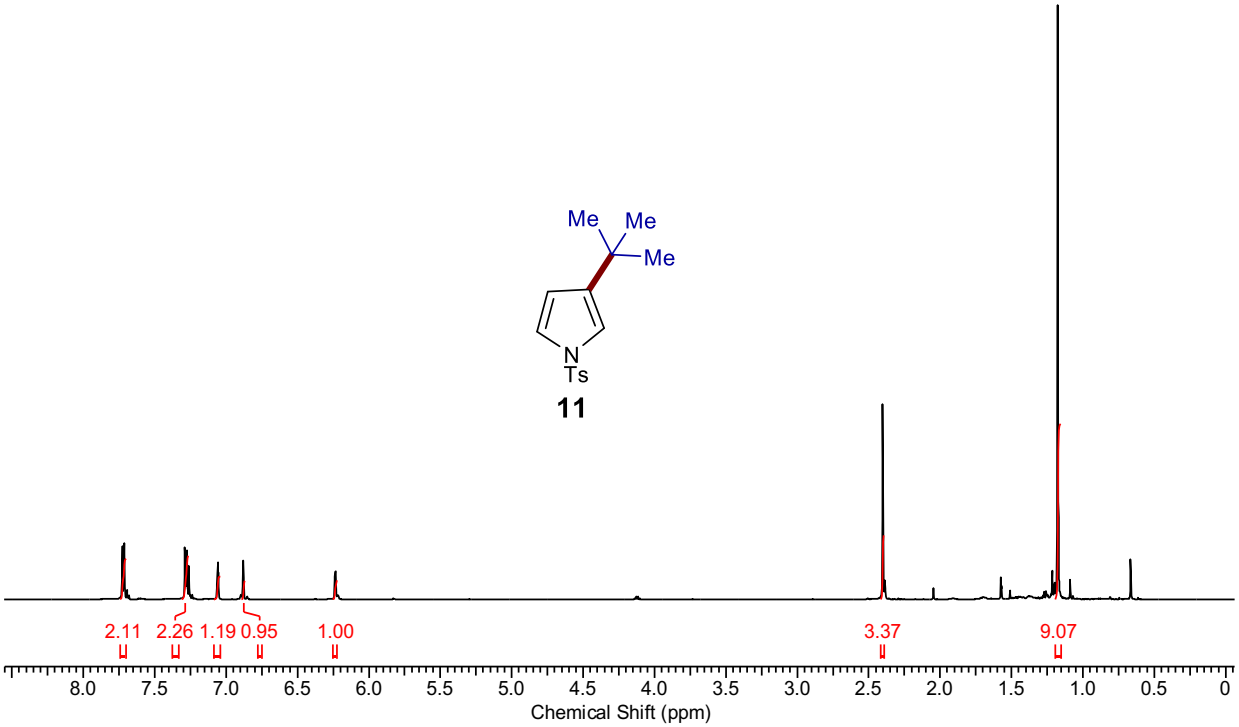

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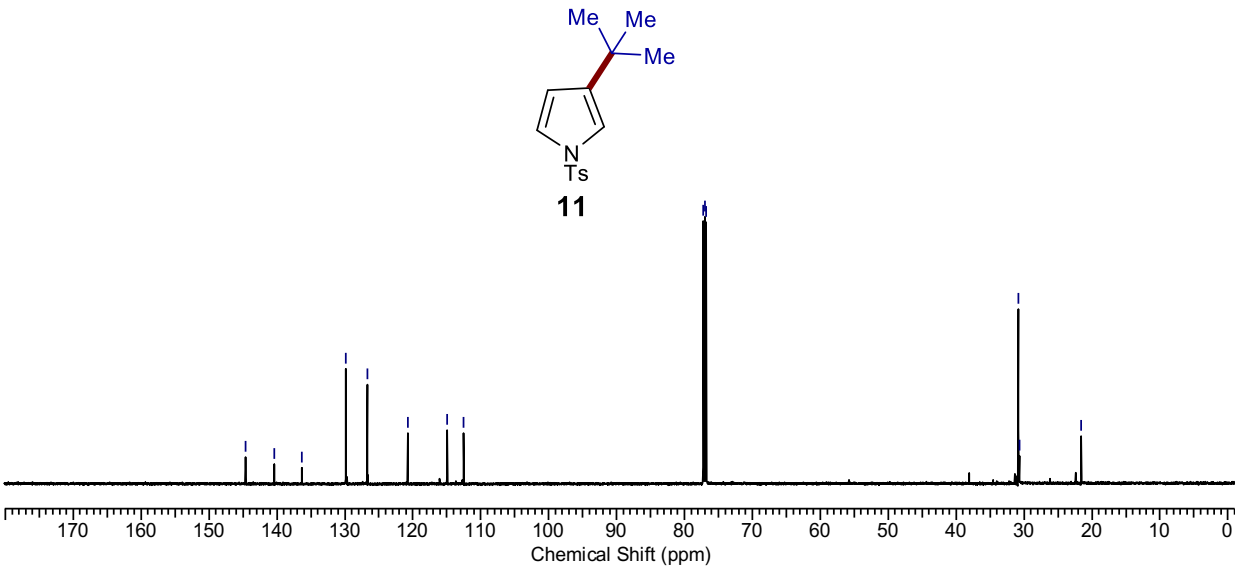

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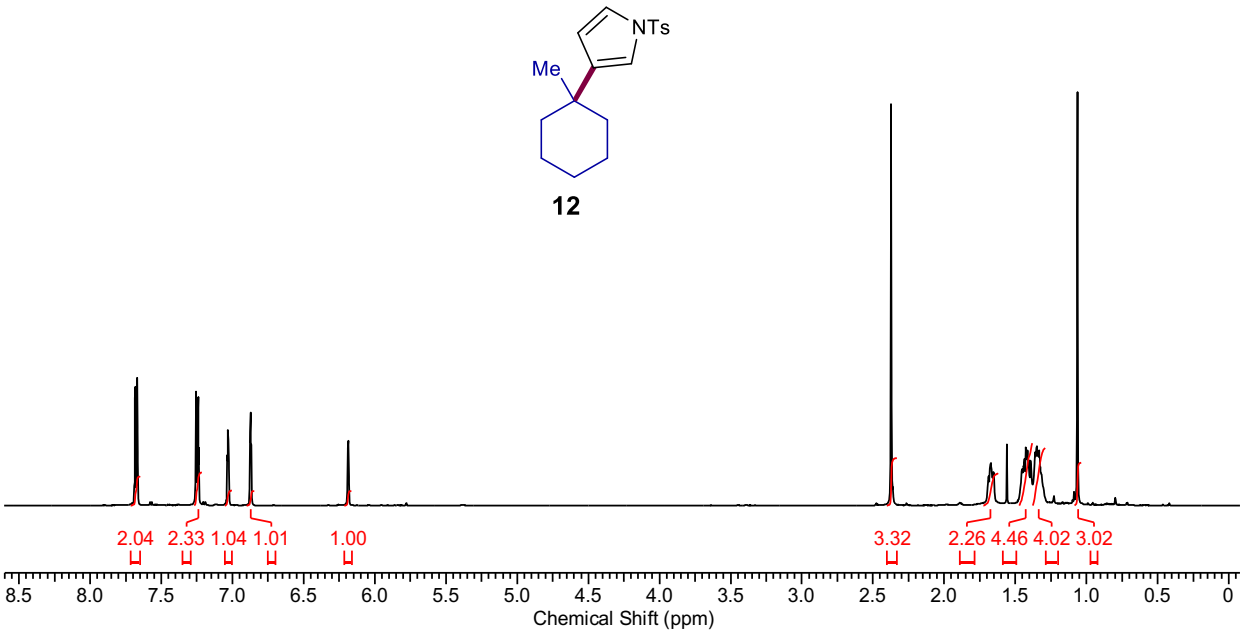
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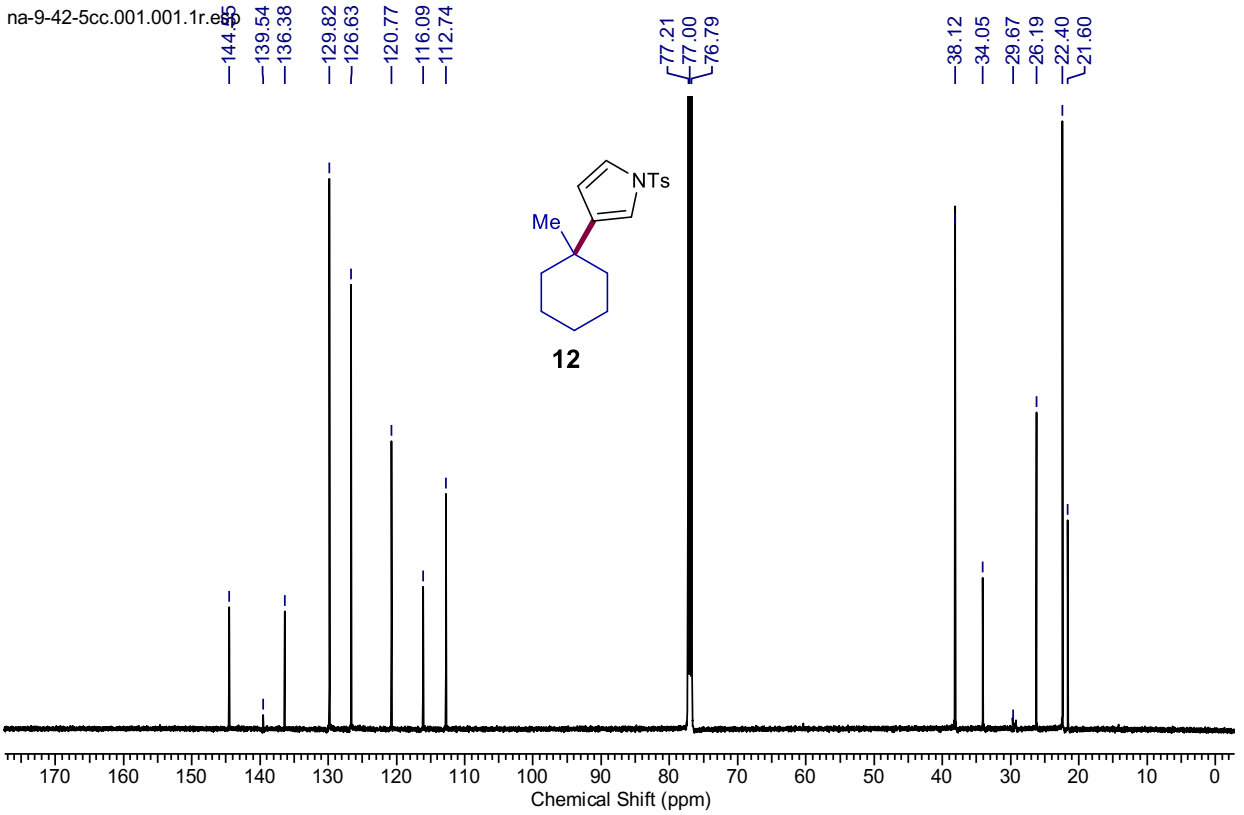
Chemical Shift (ppm)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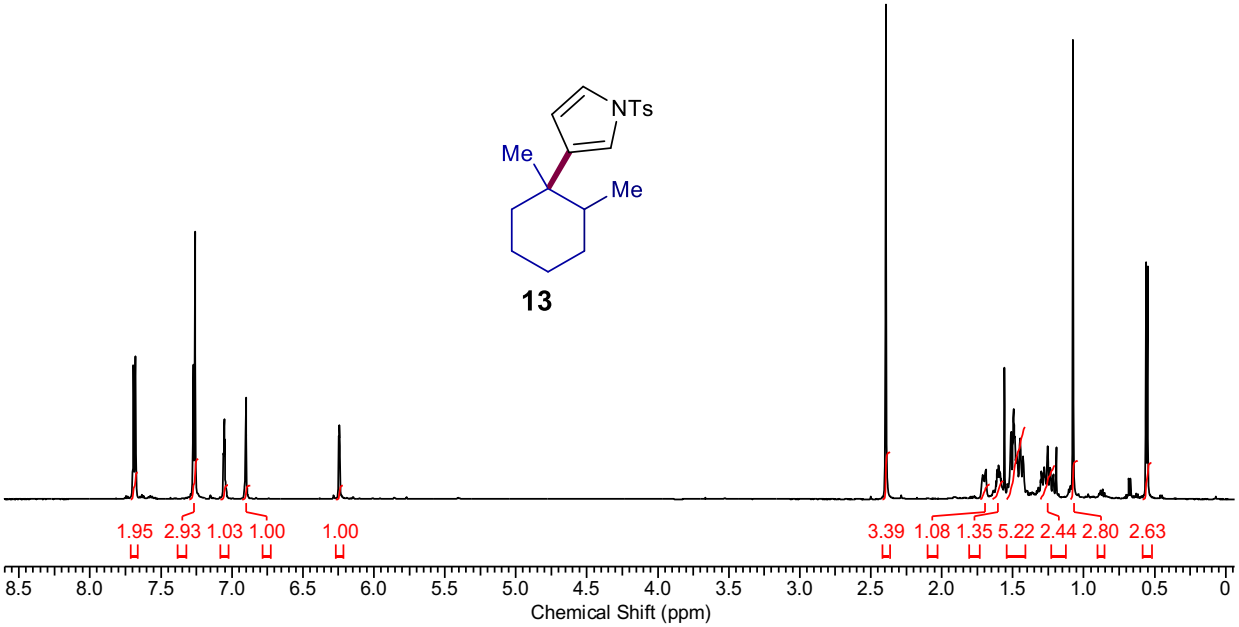

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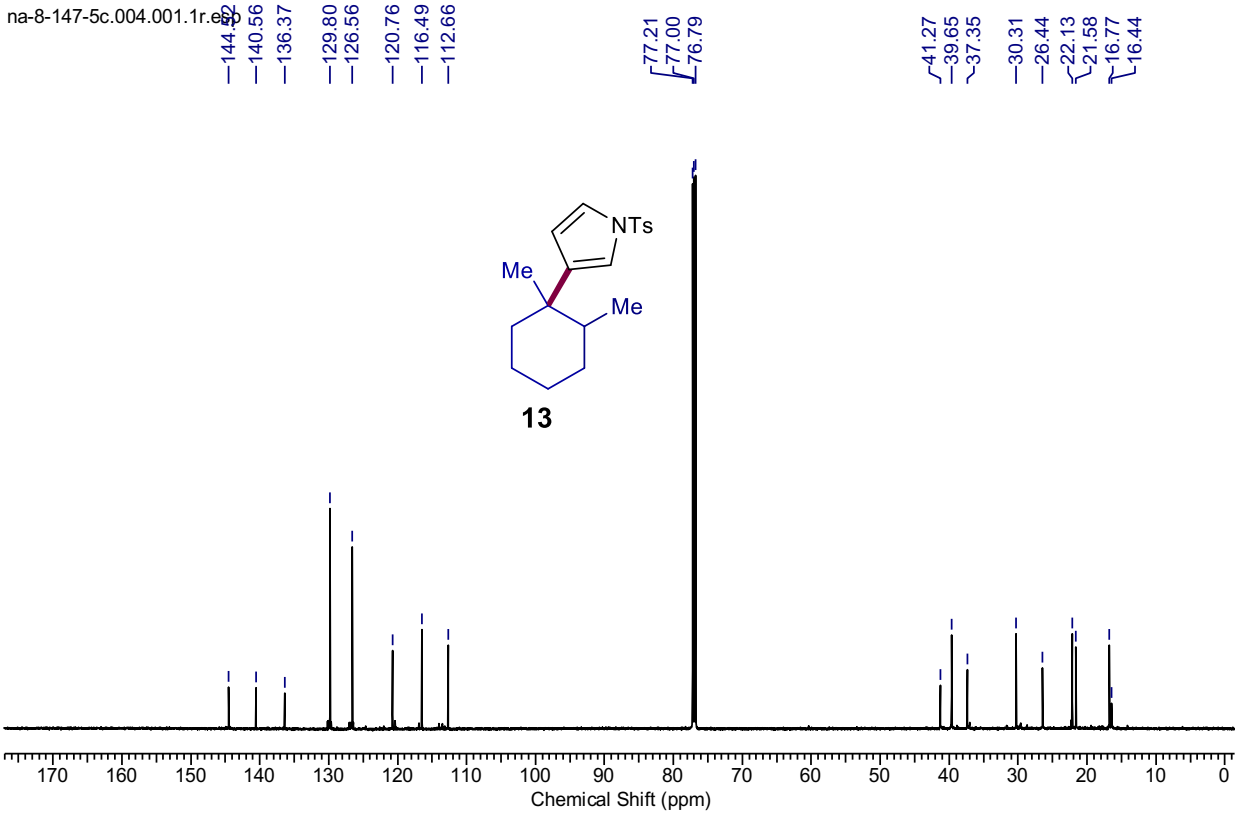

References

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