

Supporting Information

Visible-Light-Promoted Atom Transfer Radical Cyclization of Unactivated Alkyl Iodides

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General Considerations

Reagents: Unless otherwise noted, all reactions were carried out in Schlenk tubes with screw cap using standard Schlenk techniques for the manipulation of solvents and reagents. [Ir(ppy)₂(dtbbpy)]PF₆ was prepared following the reported literature method.¹ **1f**,² **1g**,³ **1u**⁴ and **4c**⁵ were all prepared following the reported literature protocols. *t*-BuCN was purchased from Alfa Aesar and used as received. All other reagents were purchased from commercial sources and used as received.

Analytical Methods: ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra and melting points (where applicable) are included for all new compounds. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 300 MHz, a Bruker 400 MHz or a Bruker 500 MHz at 20 °C. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CHCl₃ (7.26 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CHCl₃ (77.16 ppm) and were obtained with ¹H decoupling. Coupling constants, *J*, are reported in hertz (Hz). In the case of diastereisomeric mixtures, a crude NMR was recorded to determine the ratio. Melting points were measured using open glass capillaries in a Büchi B540 apparatus. Infrared spectra were recorded on a Bruker Tensor 27. Mass spectra were recorded on a Waters LCT Premier spectrometer. Gas chromatographic analyses were performed on HewlettPackard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase. Flash chromatography was performed with EM Science silica gel 60 (230- 400 mesh) and using KMnO₄ TLC stain. All electrochemical experiments were performed on a PAR 263A EG&G potentiostat or on an IJ-Cambria HI-660 potentiostat, using a three-electrode cell. Glassy carbon (S = 0.07 cm²) as working electrode, platinum mesh as counter electrode, and MSE or SSCE as reference electrode unless otherwise indicated. *E*_{1/2} values reported in this work were estimated from Cyclic Voltammetry (CV) experiments as the average of the oxidative and reductive peak potentials. Fluorescence measurements were carried out on a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with photomultiplier detector, double monochromator and Xenon light source. UV-Vis measurements were carried out on a Shimadzu UV-1700PC spectrophotometer equipped with a photomultiplier detector, double beam optics and D2 and W light

sources. Lifetime measurements were carried out on a Edinburgh Instruments LifeSpec-II based on the time-correlated single photon counting (TCSPC) technique, equipped with a PMT detector, double subtractive monochromator and picosecond pulsed diode lasers source. The yields reported in Table 2 and Scheme 2 refer to isolated yields and represent an average of at least two independent runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in the tables of the manuscript.

Optimization details

General procedure for screening reactions: A 12.0 mL Schlenk tube with screw cap containing a stirring bar was charged with the photocatalyst (1 mol%). The tube was then evacuated and back-filled with argon. The alkyl iodide **1a** (0.2 mmol, 1 equiv, 58.0 mg) was added with a microsyringe followed by addition of the corresponding solvent (1.0 mL, 0.2 M) and amine (0.2 mmol, 1 equiv) under a positive Ar flow. Then three freeze-pump-thaw cycles were conducted in liquid nitrogen. Finally, the reaction was placed on the photoreactor, consisting of a 150 mL beaker surrounded by blue LED strips (FlexLed Inspire. 20 LEDs, 1.7 W, 0.364 mW/cm²). A mini-fan was necessary on the top to keep internal temperature between 30 and 35°C. The reaction was stirred for 12 h. After that time, decane (0.2 mmol, 1 equiv, 39 μ L) was added via microsyringe followed by 9 mL of EtOAc. An aliquot was filtered through a plug of silica and celite and analyzed by GC with FID detector.

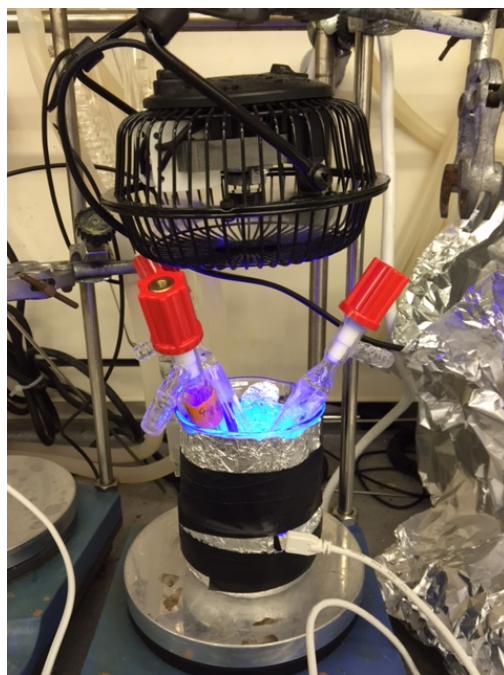
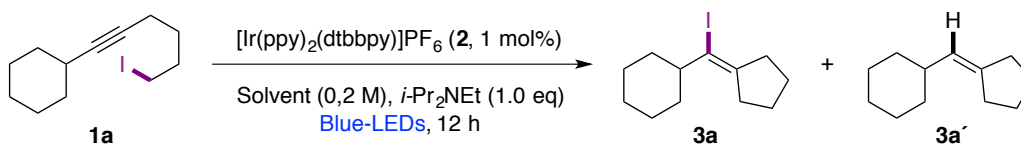


Table S1: Screening of Solvents



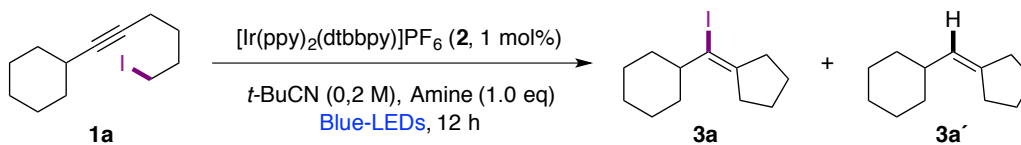
Entry	Solvent	Conversion (%) ^a	3a (%) ^a	3a' (%) ^a
1	ACN	98	68	25
2	EtCN	53	30	20
3	<i>i</i> PrCN	47	30	11
4	<i>t</i>BuCN	93	89	0
5	DMF	58	35	13
6	DMSO	100	82	7
7	Acetone	47	33	6
8 ^b	<i>t</i> BuCN	85	76	1
9 ^c	<i>t</i> BuCN	45	39	0

^a Determined by GC using decane as an internal standard.

^b Without freeze-pump-thaw.

^c Under air.

Table S2: Screening of Amines

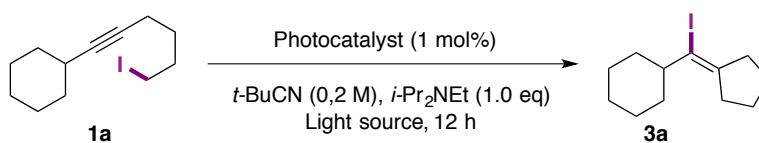


Entry	Amine	Conversion (%) ^a	3a (%) ^a	3a' (%) ^a
1	<i>i</i> -Pr ₂ NEt (1.0 eq)	93	89	0
2	Et ₃ N (1.0 eq)	100	88	2
3	Bu ₃ N (1.0 eq)	100	87	0
4	Cy ₂ NMe (1.0 eq)	100	82	0
5	PMP (1.0 eq)	100	85	5
6	<i>i</i> -Pr ₂ NEt (0.5 eq)	93	86	0
7	<i>i</i> -Pr ₂ NEt (0.25 eq)	84	84	0
8 ^b	<i>i</i> -Pr ₂ NEt (0.125 eq)	69	67 (83)	0

^a Determined by GC using decane as an internal standard.

^b 48h. PMP: 1,2,2,6,6-Pentamethyl piperidine.

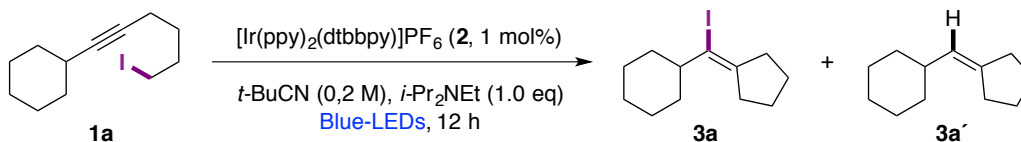
Table S3: Screening of Photocatalysts and Light Sources



Entry	Photocatalyst	Emission (nm) ^b	<i>E</i> (M/M ⁺) (V) ^b	Light source	Conversion ^a	Yield of 3a ^a
1	Ru(bpy) ₃ (PF ₆) ₂	615	-1.33	Blue-LED	56 %	53 %
2	Ir(ppy) ₃	494	-2.19	Blue-LED	63 %	58 %
3	Ir(dfCF ₃ ppy) ₂ (dtbbpy)(PF ₆)	470	-1.37	Blue-LED	91 %	83 %
4	Ru(bpz) ₃ (PF ₆) ₂	591	-0.80	Blue-LED	12 %	8 %
5	Pt(ppy)(acac)			CFL (23w x 2)	98 %	86 %
6	Fluorescein			CFL (23w x 2)	78 %	71 %
7	Fluorescein			Green Bulb	22 %	20 %
8	Fluorescein			Green-LEDs	32 %	26 %
9	Fluorescein Sodium			Green-LEDs	77 %	70 %

^a Determined by GC using decane as an internal standard. ^b Ref 6.

Table S4: Control Experiments



Entry	Deviation from standard condition	Conversion (%) ^a	3a (%) ^a	3a' (%) ^a
1	in the dark	-	trace	-
2	no <i>i</i> -Pr ₂ NEt	-	≤ 1	-
3	no photocatalyst (2)	-	2	-
4	2 (0.5 mol%)	78	78	-
5	CFL (2*23 W) instead of Blue-LEDs	87	78	2

^a Determined by GC using decane as an internal standard.

Synthesis of starting materials

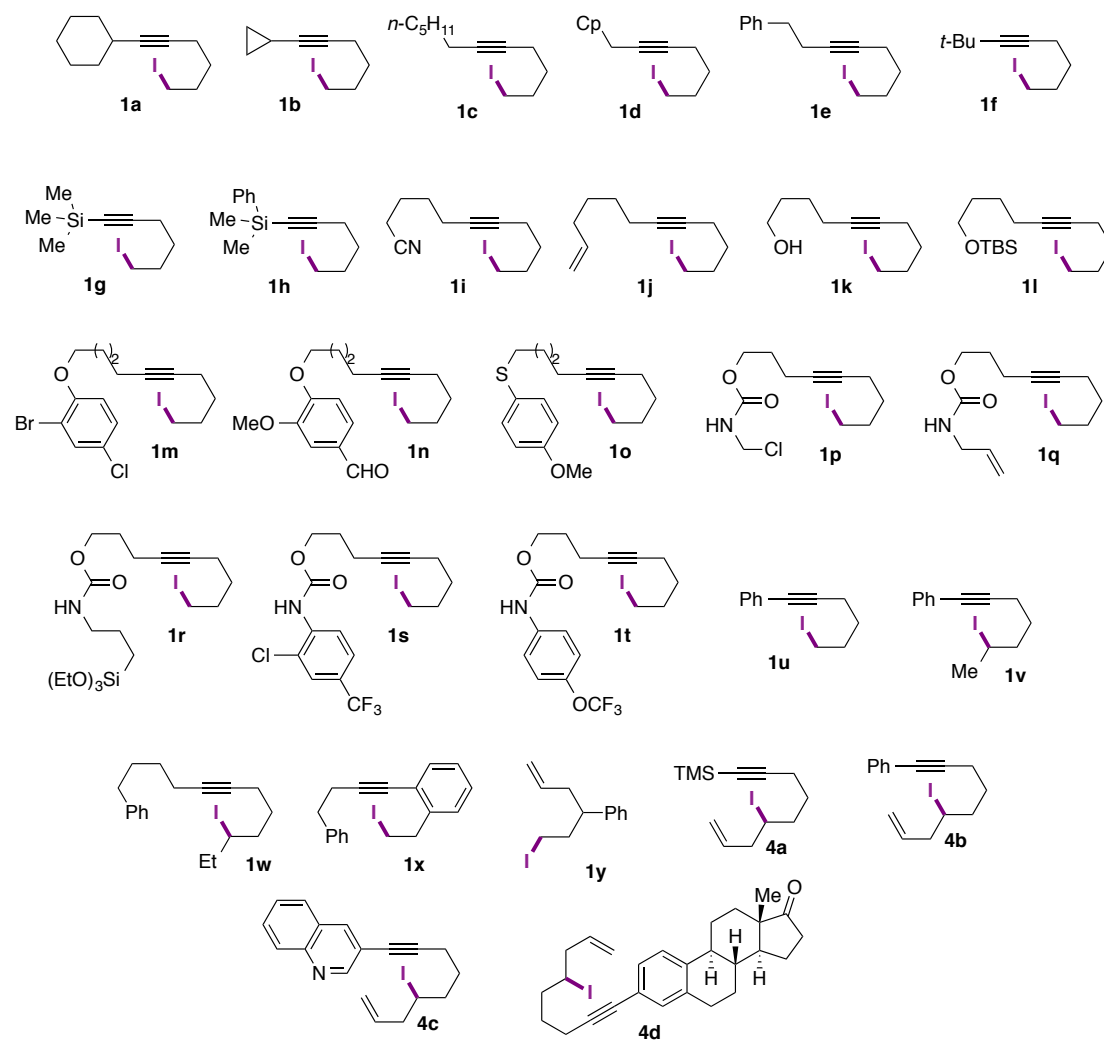
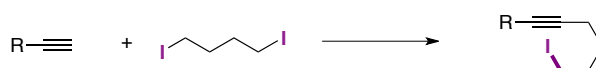
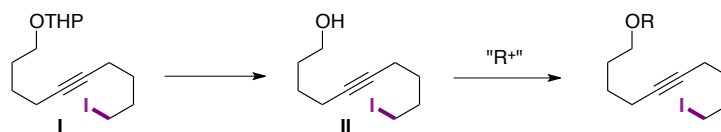


Figure S1. Synthesized starting materials

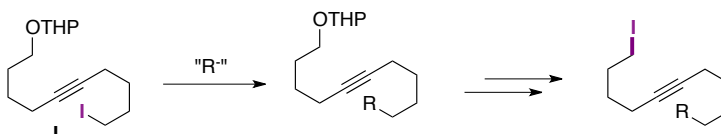
Method A:



Method B:



Method C:



Method D:

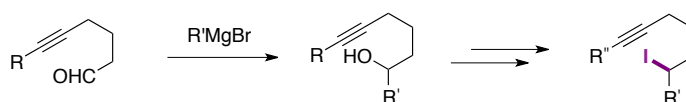


Figure S2. General conditions to prepare starting materials.

General conditions A (Figure S2):⁴ To a stirred solution of the terminal alkyne (1.0 eq) in dry THF (0.3 M) under Ar at -78°C , $n\text{-BuLi}$ (2.5 M, 1.03 eq) was slowly added by syringe. The reaction mixture was stirred for 30 min and then warmed up to room temperature. Then, 1,4-diiodobutane (1.5 eq) was added and the mixture was refluxed until total consumption of the alkyne. The reaction was then cooled down to room temperature, diluted with diethyl ether, washed with water (2x), sodium thiosulfate (aq. 10%) and brine (2x). The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated under vacuum. The residue was purified by silica gel flash chromatography to deliver the corresponding alkyl iodide.

General conditions B (Figure S2):

Step 1. To a stirred solution of $\text{TsOH}\cdot\text{H}_2\text{O}$ (0.1 eq) in MeOH (0.1 M) at room temperature, the protected alcohol (**I**) was added (1.0 eq). The reaction was allowed to stir overnight at room temperature. Then the solvent was removed under vacuum and the crude diluted with EtOAc, washed with a saturated solution of NaHCO_3 (2x) and brine (2x). The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated under vacuum. The residue was purified by silica gel flash chromatography to afford the unprotected alcohol **II**.

Step 2.⁷ To a stirred solution of alcohol **II** (1.0 equiv) in anhydrous DCM (0.1 M) at 0 °C, NEt₃ (3 equiv) and corresponding electrophile (1.2 equiv) were consecutively added and the reaction was stirred overnight at room temperature. The mixture was then concentrated and the residue purified by silica gel column chromatography to afford the corresponding starting material.

General conditions C (Figure S2):

Step 1. The corresponding nucleophile (1.0 equiv) and K₂CO₃ (1.3 equiv) were added to a solution of the protected alcohol **I** (1.0 equiv) in DMF (0.1 M) at room temperature. The mixture was allowed to stir overnight at room temperature. After completion, the reaction was diluted with Et₂O and the mixture washed with water (2x) and brine (2x). The organic layer was separated, dried over MgSO₄ anhydrous and the solvent evaporated. The crude product was used in the next step without further purification.

Step 2. The crude compound from step 1 was added to a stirred solution of TsOH·H₂O (0.1 eq) in MeOH (0.1 M) at room temperature. The reaction was allowed to stir overnight at room temperature. Then the solvent was removed under vacuum and the crude diluted with EtOAc, washed with a saturated solution of NaHCO₃ (2x) and brine (2x). The organic layer was dried over anhydrous MgSO₄, filtered and concentrated under *vacuum*. The residue was purified by silica gel flash chromatography to afford the corresponding unprotected alcohol.

Step 3. To a solution of triphenylphosphine (1.3 equiv) in anhydrous DCM (0.5 M) was added imidazole (1.3 equiv) at room temperature. Then, I₂ (1.3 equiv) was added in portions over 5 minutes, followed by additional 10 min of stirring in the dark. A solution of the alcohol from the previous step (1.0 equiv) in DCM was added dropwise and the mixture was stirred overnight. After completion, the mixture was diluted with Et₂O and filtered through a short pad of silica. The filtrate was then concentrated and the residue purified by silica gel flash chromatography to give the corresponding starting material.

General conditions D (Figure S2):⁵

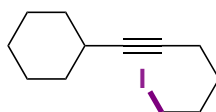
Step 1. The corresponding aldehyde (1.0 eq) was dissolved in THF (0.1 M) and the corresponding Grignard reagent R¹MgBr (2.0 eq) was added slowly at -30 °C. After completion, the reaction was allowed to warm up at room temperature and stirred for

3 h. Then, the mixture was carefully quenched at 0° C upon addition of NH₄Cl (aq. 10%), and then extracted with EtOAc (3x). The organic phase was washed with water (1x), brine (2x), filtered and concentrated. The residue was utilized in the next step without further purification.

Step 2 (R ≠ H). To a solution of triphenylphosphine (1.3 equiv) in anhydrous DCM (0.5 M) was added imidazole (1.3 equiv) at room temperature. Then, I₂ (1.3 equiv) was added in portions over 5 minutes, followed by additional 10 min of stirring in the dark. After that, a solution of the alcohol obtained in the previous step (1.0 equiv) in DCM was added dropwise and the mixture stirred overnight. After completion, the mixture was diluted with Et₂O and filtered through a short pad of silica. The filtrate was then concentrated and the residue purified by silica gel flash chromatography to give the corresponding starting material.

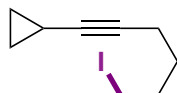
Step 2 (R = H). To a suspension of Pd(PPh₃)₂Cl₂ (5 mol%) in anhydrous DMF (0.33M), the corresponding terminal alkyne (1.2 equiv), aryl (pseudo)halide (1.0 equiv) and NEt₃ (2.0 equiv) were added. The mixture was stirred at room temperature for 5 minutes. After that, CuI (5 mol%) was added and the mixture was heated to 80 °C for 24 h. Then, the reaction was cooled down to room temperature, quenched with H₂O and extracted with Et₂O (3x). The combined organic phases were washed with H₂O (2x), brine (2x), dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel flash chromatography giving rise to the cross-coupled product.

Step 3 (R = H). To a solution of triphenylphosphine (1.3 equiv) in anhydrous DCM (0.5 M) was added imidazole (1.3 equiv) at room temperature. Then, I₂ (1.3 equiv) was added in portions over 5 minutes, followed by additional 10 min of stirring in the dark. After that, a solution of the secondary alcohol obtained in the previous step (1.0 equiv) in DCM was added dropwise and the mixture stirred overnight. After completion, the mixture was diluted with Et₂O and filtered through a short pad of silica. The filtrate was then concentrated and the residue purified by silica gel flash chromatography to give the corresponding starting material.

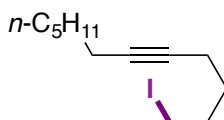


(6-Iodohept-1-yn-1-yl)cyclohexane (1a): Following reaction conditions A. 80% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 3.21 (t, *J* = 7.2 Hz, 2H), 2.31 (b, 1H),

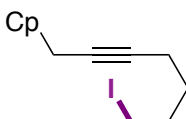
2.19 (dt, $J = 6.9, 2.1$ Hz, 2H), 1.93 (quint, $J = 7.2$ Hz, 2H), 1.78-1.24 (m, 12H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 85.5, 79.0, 33.2, 32.6, 29.8, 29.2, 26.0, 25.0, 17.8, 6.6 ppm. IR (neat, cm^{-1}): 2925, 2851, 1447, 1286, 1211, 1164, 888. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{20}\text{I})$ $[\text{M}+\text{H}]^+$: 291.0604, *found* 291.0603.



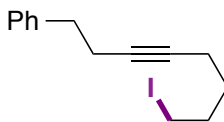
(6-Iodohept-1-yn-1-yl)cyclopropane (1b): Following reaction conditions A. 67% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.20 (t, $J = 6.0$ Hz, 2H), 2.16 (dt, $J = 6.0, 2.1$ Hz, 2H), 1.91 (quint, $J = 7.2$ Hz, 2H) 1.57 (quint, $J = 7.2$ Hz, 2H), 1.24-1.14 (m, 1H), 0.74-0.65 (m, 2H), 0.65-0.57 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): 84.1, 74.7, 32.6, 29.8, 17.9, 8.1, 6.5, -0.38 ppm. IR (neat, cm^{-1}): 3009, 2937, 2203, 1700, 1666, 1426, 1168. HRMS *calcd.* for $(\text{C}_9\text{H}_{14}\text{I})$ $[\text{M}+\text{H}]^+$: 249.0135, *found* 249.0131.



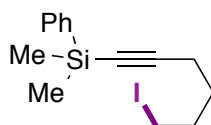
1-Iodododec-5-yne (1c): Following reaction conditions A. 46% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.21 (t, $J = 6.9$ Hz, 2H), 2.22-2.10 (m, 4H), 1.93 (quint, $J = 6.9$ Hz, 2H), 1.63-1.54 (m, 2H), 1.52-1.26 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 81.2, 79.2, 32.6, 31.5, 29.9, 29.2, 28.7, 22.7, 18.9, 17.9, 14.2, 6.5 ppm. IR (neat, cm^{-1}): 2927, 2856, 1455, 1331, 1287, 1211, 1165. HRMS *calcd.* for $(\text{C}_{13}\text{H}_{26}\text{IO})$ $[\text{M}+\text{CH}_3\text{OH}+\text{H}]^+$: 325.1023, *found* 325.1020.



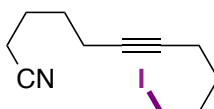
(7-Iodohept-2-yn-1-yl)cyclopentane (1d): Following reaction conditions A. 56% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.21 (t, $J = 6.9$ Hz, 2H), 2.22-2.12 (m, 4H), 2.07-1.89 (m, 3H), 1.78-1.73 (m, 2H), 1.63-1.52 (m, 6H), 1.31-1.19 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 80.6, 79.3, 39.5, 32.6, 32.1, 29.9, 25.4, 24.7, 17.9, 6.6 ppm. IR (neat, cm^{-1}): 2943, 2862, 1450, 1429, 1328, 1286, 1211. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{20}\text{I})$ $[\text{M}+\text{H}]^+$: 291.0604, *found* 291.0601.



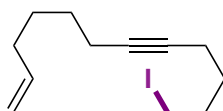
(8-Iodooct-3-yn-1-yl)benzene (1e): Following reaction conditions A. 85% yield. Pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.20 (m, 5H), 3.23-3.14 (m, 2H), 2.86-2.76 (m, 2H), 2.50-2.44 (m, 2H), 2.23-2.16 (m, 2H), 1.95-1.82 (m, 2H), 1.64-1.53 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 141.0, 128.5, 128.4, 126.3, 80.3, 80.1, 35.6, 32.5, 29.7, 21.0, 17.8, 6.6 ppm. IR (neat, cm^{-1}): 3061, 3026, 2928, 2859, 2212, 1453, 1339. HRMS calcd. for $(\text{C}_{14}\text{H}_{18}\text{I})$ $[\text{M}+\text{H}]^+$: 313.0448, found 313.0446.



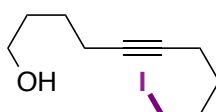
(6-Iodohex-1-yn-1-yl)dimethyl(phenyl)silane (1h): Following reaction conditions A. 75% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.66-7.63 (m, 2H), 7.41-7.37 (m, 3H), 3.23 (t, $J = 6.9$ Hz, 2H), 2.33 (t, $J = 7.0$ Hz, 2H), 1.98 (quint, $J = 7.0$ Hz, 2H), 1.68 (quint, $J = 7.1$ Hz, 2H), 0.41 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 137.6, 133.7, 129.4, 128.0, 108.4, 83.4, 32.5, 29.3, 19.1, 6.3, 0.5 ppm. IR (neat, cm^{-1}): 3068, 3048, 2957, 2173, 1427, 1248, 1114. HRMS calcd. for $(\text{C}_{14}\text{H}_{20}\text{ISi})$ $[\text{M}+\text{H}]^+$: 343.0374, found 343.0371.



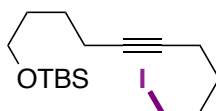
11-Iodoundec-6-ynenitrile (1i): Following reaction conditions C, but using KCN (3.0 equiv) as nucleophile in DMSO (0.25 M) in step 1. 75% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.21 (t, $J = 6.9$ Hz, 2H), 2.38 (t, $J = 7.2$ Hz, 2H), 2.25-2.15 (m, 4 H), 1.97-1.87 (m, 2H), 1.83-1.74 (m, 2H), 1.68-1.54 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 119.7, 80.5, 79.5, 32.6, 29.8, 27.8, 24.6, 18.1, 17.8, 16.9, 6.4 ppm. IR (neat, cm^{-1}): 2935, 2866, 2246, 2211, 1672, 1426, 1212. HRMS calcd. for $(\text{C}_{11}\text{H}_{17}\text{IN})$ $[\text{M}+\text{H}]^+$: 290.0400, found 290.0392.



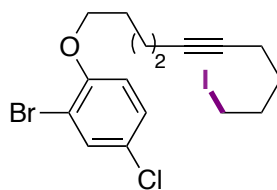
12-Iodododec-1-en-7-yne (1j): Following reaction conditions A. 75% yield. Colorless oil. ^1H NMR (300 MHz): δ 5.87-5.74 (m, 1H), 5.04-4.93 (m, 2H), 3.20 (t, J = 6.9 Hz, 2H), 2.21-2.05 (m, 6H), 1.93 (quint, J = 7.2 Hz, 2H), 1.63-1.46 (m, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 138.8, 114.6, 80.9, 79.4, 33.4, 32.6, 29.8, 28.6, 28.1, 18.7, 17.8, 6.5 ppm. IR (neat, cm^{-1}): 3075, 2931, 2857, 1640, 1432, 1332, 1211. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{20}\text{I})$ $[\text{M}]^+$: 291.0604, *found* 291.0596.



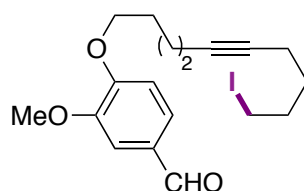
10-Iododec-5-yn-1-ol (1k): Following reaction conditions B. 90% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.67 (t, J = 4.2 Hz, 2H), 3.20 (t, J = 6.9 Hz, 2H), 2.21-2.16 (m, 4H), 1.93 (quint, J = 7.2 Hz, 2H), 1.71-1.53 (m, 6H), 1.38 (br, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 80.6, 79.6, 62.4, 32.5, 31.8, 29.7, 25.3, 18.5, 17.7, 6.5 ppm. IR (neat, cm^{-1}): 3341, 2935, 2862, 1431, 1286, 1211, 1165, 1056. HRMS *calcd.* for $(\text{C}_{10}\text{H}_{18}\text{OI})$ $[\text{M}+\text{H}]^+$: 281.0397, *found* 281.0394.



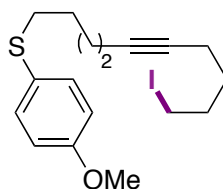
Tert-butyl((10-iododec-5-yn-1-yl)oxy)dimethylsilane (1l): Following reaction conditions B. 79% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.62 (t, J = 6.0 Hz, 2H), 3.21 (t, J = 6.9 Hz, 2H), 2.21-2.14 (m, 4H), 1.98-1.89 (m, 2H), 1.63-1.52 (m, 6H), 0.89 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 80.9, 79.5, 62.9, 32.6, 32.1, 29.9, 26.1, 25.6, 18.7, 18.5, 17.9, 6.5, -5.1 ppm. IR (neat, cm^{-1}): 2929, 2856, 1471, 1253, 1102, 834, 774. HRMS *calcd.* for $(\text{C}_{16}\text{H}_{32}\text{IOSi})$ $[\text{M}+\text{H}]^+$: 395.1262, *found* 395.1252.



2-Bromo-4-chloro-1-((10-iododec-5-yn-1-yl)oxy)benzene (1m): Following reaction conditions C. 43% yield. Brown oil. ^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, $J = 2.7$ Hz, 1H), 7.21 (dd, $J = 8.7, 2.7$ Hz, 1H), 6.80 (d, $J = 8.7$ Hz, 1H), 4.02 (t, $J = 6.3$ Hz, 2H), 3.21 (t, $J = 6.9$ Hz, 2H), 2.28-2.15 (m, 4H), 1.98-1.88 (m, 4H), 1.75-1.66 (m, 2H), 1.63-1.54 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 154.4, 132.9, 128.3, 126.0, 113.8, 112.9, 80.5, 79.9, 69.1, 32.7, 29.8, 28.3, 25.6, 18.6, 17.9, 6.5 ppm. IR (neat, cm^{-1}): 2937, 2212, 1672, 1479, 1465, 1262, 1046. HRMS *calcd.* for ($\text{C}_{16}\text{H}_{19}\text{OClBrI}$): 467.9353, *found* 467.9347.

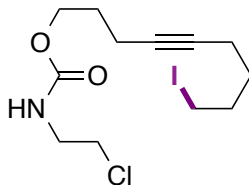


4-((10-Iododec-5-yn-1-yl)oxy)-3-methoxybenzaldehyde (1n): Following reaction conditions C. 30% yield. Pale yellow solid. M.P. = 54.7 °C. ^1H NMR (300 MHz, CDCl_3): δ 9.85 (s, 1H), 7.45-7.40 (m, 2H), 6.97 (d, $J = 8.1$ Hz, 1H), 4.13 (t, $J = 6.6$ Hz, 2H), 3.93 (s, 3H), 3.20 (t, $J = 6.9$ Hz, 2H), 2.28-2.15 (m, 4H), 2.02-1.87 (m, 4H), 1.73-1.53 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 191.0, 154.2, 150.0, 130.1, 126.9, 111.5, 109.4, 80.3, 80.0, 68.7, 56.2, 32.6, 29.8, 28.2, 25.5, 18.6, 17.8, 6.5 ppm. IR (neat, cm^{-1}): 3071, 2942, 2925, 1670, 1583, 1508, 1259. HRMS *calcd.* for ($\text{C}_{18}\text{H}_{23}\text{I}\text{NaO}_3$) $[\text{M}+\text{Na}]^+$: 437.0584, *found* 437.0589.

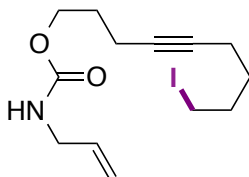


(10-Iododec-5-yn-1-yl)(4-methoxyphenyl)sulfane (1o): Following reaction conditions C. 50% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.34 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H), 3.19 (t, $J = 6.9$ Hz, 2H), 2.83 (t, $J = 6.9$ Hz, 2H), 2.16-2.14 (m, 4H), 1.95-1.86 (m, 2H), 1.73-1.51 (m, 6H) ppm. ^{13}C NMR

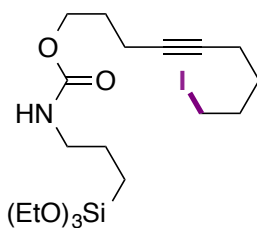
(75 MHz, CDCl₃): 158.9, 133.2, 126.7, 114.6, 80.4, 79.8, 55.5, 35.5, 32.6, 29.8, 28.5, 28.0, 18.4, 17.8, 6.5 ppm. IR (neat, cm⁻¹): 2999, 2934, 1591, 1492, 1439, 1240, 1030. HRMS *calcd.* for (C₁₇H₂₄IOS) [M+H]⁺: 403.0587, *found* 403.0593.



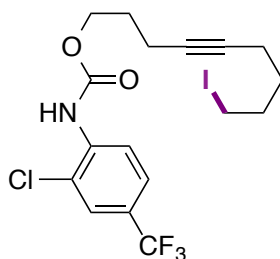
9-Iodonon-4-yn-1-yl (2-chloroethyl)carbamate (1p): Following reaction conditions B. 75% yield. White solid. M.P. = 48.0 °C. ¹H NMR (300 MHz, CDCl₃): δ 5.14 (b, 1H), 4.14 (t, *J* = 6.3 Hz, 2H), 3.61-3.47 (m, 4H), 3.19 (t, *J* = 6.9 Hz, 2H), 2.25-2.14 (m, 4H), 1.93-1.80 (m, 2H), 1.78-1.74 (m, 2H), 1.61-1.52 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): 156.4, 80.1, 79.4, 63.9, 44.2, 42.8, 32.5, 29.7, 28.5, 17.7, 15.5, 6.5 ppm. IR (neat, cm⁻¹): 3344, 2936, 1690, 1539, 1317, 1257, 1152. HRMS *calcd.* for (C₁₂H₁₉ClINaO₂) [M+Na]⁺: 394.0041, *found* 394.0042.



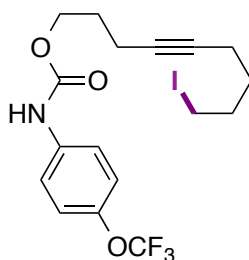
9-Iodonon-4-yn-1-yl allylcarbamate (1q): Following reaction conditions B. 83% yield. Brown oil. ¹H NMR (400 MHz, CDCl₃): δ 5.87-5.77 (m, 1H), 5.20-5.08 (m, 2H), 4.79 (b, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 3.78 (b, 2H), 3.54-3.18 (m, 2H), 2.24-2.13 (m, 4H), 1.94-1.74 (m, 4H), 1.64-1.53 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): 156.5, 134.6, 116.0, 80.09, 80.03, 79.55, 79.52, 68.9, 63.7, 44.7, 43.5, 32.5, 31.6, 29.7, 28.60, 26.2, 18.1, 17.7, 15.1, 6.4 ppm. IR (neat, cm⁻¹): 3337, 2934, 1698, 1518, 1432, 1239, 1144. HRMS *calcd.* for (C₁₃H₂₀INNaO₂) [M+Na]⁺: 372.0431, *found* 372.0415.



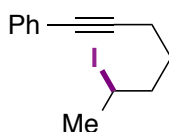
9-Iodonon-4-yn-1-yl (3-(triethoxysilyl)propyl)carbamate (1r): Following reaction conditions B. 60% yield. Brown oil. ^1H NMR (300 MHz, CDCl_3): δ 4.9 (b, 1H), 4.10 (t, $J = 6.0$ Hz, 2H), 3.80 (q, $J = 6.9$ Hz, 6H), 3.21-3.12 (m, 4H), 2.21-2.14 (m, 4H), 1.93-1.54 (m, 8H), 1.21 (t, $J = 6.9$ Hz, 9H), 0.61 (t, $J = 8.1$ Hz, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 156.6, 79.9, 79.6, 63.5, 58.5, 43.4, 32.5, 29.7, 28.6, 23.4, 18.4, 17.8, 15.5, 7.7, 6.4 ppm. IR (neat, cm^{-1}): 3346, 2972, 2927, 1702, 1525, 1240, 1073. HRMS *calcd.* for $(\text{C}_{19}\text{H}_{36}\text{INaO}_5\text{Si})$ $[\text{M}+\text{Na}]^+$: 536.1300, *found* 536.1300.



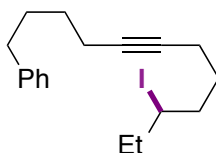
9-Iodonon-4-yn-1-yl (2-chloro-4-(trifluoromethyl)phenyl)carbamate (1s): Following reaction conditions B. 78% yield. Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 8.52 (b, 1H), 7.44 (d, $J = 8.1$ Hz, 1H), 7.24-7.20 (m, 2H), 4.30 (t, $J = 6.3$ Hz, 2H), 3.18 (t, $J = 6.9$ Hz, 2H), 2.32-2.26 (m, 2H), 2.20-2.14 (m, 2H), 1.96-1.83 (m, 4H), 1.62-1.53 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 152.9, 135.5, 130.3 (q, $J_{\text{C-F}} = 32.7$ Hz), 129.6, 125.1, 123.6 (q, $J_{\text{C-F}} = 270.8$ Hz), 120.1 (q, $J_{\text{C-F}} = 3.8$ Hz), 116.6 (q, $J_{\text{C-F}} = 3.8$ Hz), 80.4, 79.1, 64.8, 32.6, 29.7, 28.2, 17.8, 15.5, 6.4 ppm. ^{19}F NMR (376 MHz, CDCl_3): -62.883 ppm. IR (neat, cm^{-1}): 3422, 2939, 1739, 1591, 1527, 1434, 1330. HRMS *calcd.* for $(\text{C}_{17}\text{H}_{18}\text{ClF}_3\text{INaO}_2)$ $[\text{M}+\text{Na}]^+$: 509.9915, *found* 509.9903.



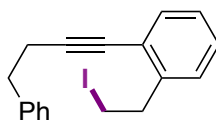
9-Iodonon-4-yn-1-yl (4-(trifluoromethoxy)phenyl)carbamates (1t): Following reaction conditions B. 89% yield. White solid. M.P. = 50.3 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.40 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 6.73 (b, 1H), 4.26 (t, J = 6.3 Hz, 2H), 3.20 (t, J = 6.9 Hz, 2H), 2.31-2.25 (m, 2H), 2.21-2.16 (m, 2H), 1.97-1.80 (m, 4H), 1.63-1.53 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 153.5, 144.8, 136.7, 122.0, 120.6 (q, $J_{\text{C-F}}$ = 255.1 Hz), 119.8, 80.4, 79.3, 64.3, 32.6, 29.7, 28.4, 17.8, 15.5, 6.5 ppm. ^{19}F NMR (376 MHz, CDCl_3): -58.304 ppm. IR (neat, cm^{-1}): 3330, 2935, 2859, 1702, 1604, 1528, 1153. HRMS *calcd.* for $(\text{C}_{17}\text{H}_{19}\text{F}_3\text{INaO}_3)$ $[\text{M}+\text{Na}]^+$: 492.0254, *found* 492.0257.



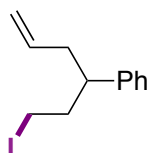
(6-Iodohept-1-yn-1-yl)benzene (1v): Following reaction conditions D. 65% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.42-7.38 (m, 2H), 7.31-7.26 (m, 3H), 4.30-4.19 (m, 1H), 2.46 (t, J = 6.9 Hz, 2H), 2.03-1.64 (m, 7H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 131.6, 128.3, 127.7, 123.9, 89.4, 81.3, 41.9, 29.6, 29.1, 28.9, 18.7 ppm. IR (neat, cm^{-1}): 2943, 1702, 1489, 1442, 1137, 754, 690. HRMS *calcd.* for $(\text{C}_{13}\text{H}_{15})$ $[\text{M-I}]^+$: 171.1168, *found* 171.1174.



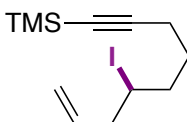
(10-Iodododec-5-yn-1-yl)benzene (1w): Following reaction conditions D. 70% yield. Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.30-7.25 (m, 2H), 7.19-7.15 (m, 3H), 4.13-4.04 (m, 1H), 2.62 (t, J = 7.5 Hz, 2H), 2.20-2.15 (m, 4H), 2.00-1.47 (m, 10 H), 1.01 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 142.5, 128.5, 128.4, 125.8, 80.7, 79.7, 41.6, 39.3, 35.5, 33.9, 30.7, 29.0, 28.7, 18.7, 18.1, 14.2 ppm. IR (neat, cm^{-1}): 3025, 2933, 2858, 1495, 1453, 1332, 1298. HRMS *calcd.* for $(\text{C}_{18}\text{H}_{26}\text{I})$ $[\text{M}+\text{H}]^+$: 369.1074, *found* 369.1074.



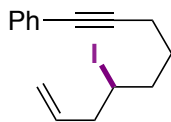
(6-Iodonon-8-en-1-yn-1-yl)trimethylsilane (1x): Compound **1x** was prepared following a reported procedure.² 78% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.37-7.13 (m, 9H), 3.34-3.20 (m, 4H), 2.96 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): 142.5, 140.6, 132.5, 129.0, 128.6, 128.5, 128.0, 126.9, 126.5, 123.2, 93.9, 79.3, 39.3, 35.2, 21.7, 4.8 ppm. IR (neat, cm⁻¹): 3061, 3025, 2926, 2221, 1483, 1451, 1172. HRMS *calcd.* for (C₁₈H₁₈I) [M+H]⁺: 361.0448, *found* 361.0449.



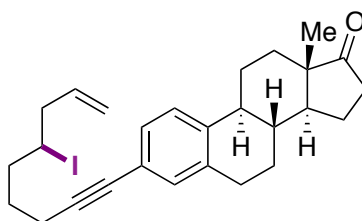
1-(2-Iodoethyl)-2-(4-phenylbut-1-yn-1-yl)benzene (1y): Following reaction conditions D. 95% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.33-7.28 (m, 2H), 7.25-7.16 (m, 3H), 5.73-5.59 (m, 1H), 5.02-4.94 (m, 2H), 3.12-3.04 (m, 1H), 2.90-2.74 (m, 2H), 2.41-2.36 (m, 2H), 2.28-2.17 (m, 1H), 2.10-1.98 (m, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): 143.2, 136.3, 128.7, 127.8, 126.7, 116.6, 46.3, 40.8, 39.6, 5.1 ppm. IR (neat, cm⁻¹): 3062, 6026, 2923, 1493, 1453, 1226, 913.



(6-Iodonon-8-en-1-yn-1-yl)trimethylsilane (4a): Following reaction conditions D. 83% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 5.89-5.75 (m, 1H), 5.17-5.10 (m, 2H), 4.16-4.08 (m, 1H), 2.74-2.57 (m, 2H), 2.26 (t, J = 6.9 Hz, 2H), 1.92-1.57 (m, 4H), 0.15 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃): 136.3, 117.8, 106.6, 85.3, 45.0, 38.7, 36.0, 28.4, 19.1, 0.28 ppm. IR (neat, cm⁻¹): 3079, 2955, 2924, 2174, 1432, 1248, 838.



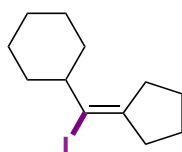
(1-Iodohex-5-en-3-yl)benzene (4b): Following reaction conditions D. 75% yield. Pale yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.42-7.39 (m, 2H), 7.31-7.28 (m, 3H), 5.91-5.78 (m, 1H), 5.19-5.12 (m, 2H), 4.20-4.12 (m, 1H), 2.68 (q, J = 6.3 Hz, 2H), 2.46 (t, J = 6.9 Hz, 2H), 2.00-1.65 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 136.3, 131.7, 128.3, 127.8, 123.9, 117.9, 89.4, 81.3, 44.9, 38.9, 36.2, 28.7, 18.7 ppm. IR (neat, cm^{-1}): 3077, 2944, 2834, 1489, 961, 754, 690. HRMS *calcd.* for $(\text{C}_{15}\text{H}_{17})$ $[\text{M}-\text{I}]^+$: 179.1325, *found* 179.1319.



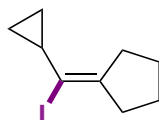
3-(6-Iodonon-8-en-1-yn-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4d): Following reaction conditions D. 35% yield. Yellow solid. M.P. = 75.4 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.26-7.14 (m, 3H), 5.90-5.77 (m, 1H), 5.18-5.11 (m, 2H), 4.19-4.11 (m, 1H), 2.90-2.85 (m, 2H), 2.70-2.64 (m, 2H), 2.55-1.39 (m, 19H), 0.91 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 220.8, 139.6, 136.5, 136.3, 132.1, 128.9, 125.4, 121.2, 117.8, 88.7, 81.2, 50.6, 48.0, 44.9, 44.5, 38.9, 38.1, 36.2, 35.9, 31.6, 29.2, 28.7, 26.5, 25.7, 21.7, 18.7, 13.9 ppm. IR (neat, cm^{-1}): 2930, 2874, 1732, 1495, 1454, 1084, 1006. HRMS *calcd.* for $(\text{C}_{27}\text{H}_{33}\text{INaO})$ $[\text{M}+\text{Na}]^+$: 523.1468, *found* 523.1461.

Iodine transfer radical cyclization (Table 2 and Scheme 2)

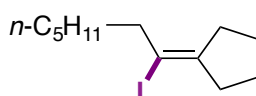
General Procedure. A 12.0 mL Schlenk tube with screw cap containing a stirring bar was charged with $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (**2**, 1 mol%, 1.8 mg). The tube was then evacuated and back-filled with argon. The alkyl iodide **1** (0.2 mmol, 1 equiv) was added with a microsyringe followed by addition of *t*-BuCN (1.0 mL, 0.2 M) and *i*-Pr₂NEt (0.2 mmol, 1 equiv, 35 μL) under a positive Ar flow. Then three freeze-pump-thaw cycles were conducted in liquid nitrogen. Finally, the reaction was placed on the photoreactor, consisting of a 150 mL beaker surrounded by blue LED strips (FlexLed Inspire. 20 LEDs, 1.7 W, 0.364 mW/cm²). A mini-fan was necessary on the top to keep internal temperature between 30 and 35°C. The reaction was stirred for 12-96 h, and then the solvent was evaporated under vacuum and the residue purified on silica gel column chromatography.



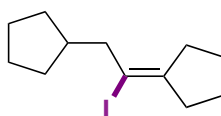
(Cyclopentylideneiodomethyl)cyclohexane (3a). Following the general procedure, the corresponding vinyl iodide **3a** was obtained in 87% yield in 24 h as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 2.37-2.27 (m, 4H), 1.86-1.17 (m, 15H) ppm. ¹³C NMR (100 MHz, CDCl₃): 146.9, 108.1, 45.7, 41.6, 33.6, 32.4, 28.2, 25.9, 25.8, 25.5 ppm. IR (neat, cm⁻¹): 2924, 2851, 1448, 1427, 1230, 1173, 890. HRMS *calcd.* for (C₁₂H₂₀I) [M+H]⁺: 291.0604, *found* 291.0603.



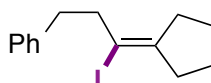
(Cyclopropylideneiodomethylene)cyclopentane (3b). Following the general procedure, the corresponding vinyl iodide **3b** was obtained in 70% yield in 32 h as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 2.45 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.85 (quint, *J* = 7.2 Hz, 2H), 1.66 (quint, *J* = 7.0 Hz, 2H), 1.44-1.35 (m, 1H), 0.76-0.68 (m, 2H), 0.68-0.61 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): 150.1, 100.7, 42.0, 32.9, 28.4, 25.7, 19.9, 9.8 ppm. IR (neat, cm⁻¹): 2956, 2870, 1736, 1373, 1237, 1045, 981. HRMS *calcd.* for (C₉H₁₃I) [M]⁺: 248.0056, *found* 248.0054.



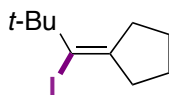
(1-Iodoheptylidene)cyclopentane (3c). Following the general procedure, the corresponding vinyl iodide **3c** was obtained in 96% yield in 24 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 2.41 (t, $J = 7.2$ Hz, 2H), 2.34-2.26 (m, 4H), 1.82 (quint, $J = 6.9$ Hz, 2H), 1.66 (quint, $J = 6.9$ Hz, 2H), 1.51-1.45 (m, 2H), 1.35-1.26 (6H), 0.91-0.87 (m, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 148.6, 97.5, 41.9, 41.4, 31.9, 31.8, 29.4, 28.4, 28.3, 25.9, 22.8, 14.2 ppm. IR (neat, cm^{-1}): 2954, 2926, 2855, 1452, 1428, 1377, 1305. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{21})$ $[\text{M}-\text{I}]^+$: 165.1638, *found* 165.1637.



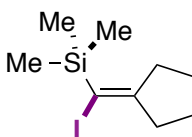
(2-cyclopentyl-1-iodoethylidene)cyclopentane (3d). Following the general procedure, the corresponding vinyl iodide **3d** was obtained in 91% yield in 12 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 2.44-2.14 (m, 7H), 1.88-1.54 (m, 10H), 1.22-1.10 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 148.8, 97.5, 47.4, 41.5, 40.5, 32.4, 31.8, 28.4, 25.8, 25.2 ppm. IR (neat, cm^{-1}): 2974, 2865, 1450, 1427, 1305, 1231, 1174. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{19})$ $[\text{M}-\text{I}]^+$: 163.1481, *found* 163.1481.



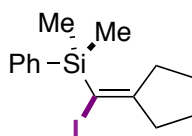
(3-cyclopentylidene-3-iodopropyl)benzene (3e). Following the general procedure, the corresponding vinyl iodide **3e** was obtained in 88% yield in 24 h as colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.72 (t, $J = 7.0$ Hz, 2H), 2.27 (t, $J = 7.4$ Hz, 2H), 2.04 (t, $J = 7.2$ Hz, 2H), 1.73-1.58 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): 150.1, 141.1, 128.9, 128.3, 126.1, 95.6, 44.3, 41.4, 35.4, 31.6, 28.3, 25.8 ppm. IR (neat, cm^{-1}): 3061, 3026, 2939, 2864, 1493, 747, 697. HRMS *calcd.* for $(\text{C}_{14}\text{H}_{17})$ $[\text{M}-\text{I}]^+$: 185.1325, *found* 185.1322.



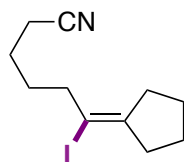
(1-Iodo-2,2-dimethylpropylidene)cyclopentane (3f). Following the general procedure, the corresponding vinyl iodide **3f** was obtained in 60% yield in 48 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 2.51 (dt, $J = 7.2, 1.2$ Hz, 2H), 2.44 (dt, $J = 7.2, 1.2$ Hz, 2H), 1.85 (quint, $J = 6.9$ Hz, 2H), 1.56 (quint, $J = 6.9$ Hz, 2H), 1.31 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 146.6, 115.7, 48.2, 41.4, 33.0, 32.5, 29.9, 25.4 ppm. IR (neat, cm^{-1}): 2954, 2923, 2864, 1453, 1362, 1220, 764. HRMS *calcd.* for ($\text{C}_{10}\text{H}_{17}$) $[\text{M}-\text{I}]^+$: 137.1325, *found* 137.1322.



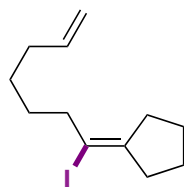
(Cyclopentylideneiodomethyl)trimethylsilane (3g). Following the general procedure, the corresponding vinyl iodide **3g** was obtained in 81% yield in 24 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 2.41 (t, $J = 7.2$ Hz, 2H), 2.34 (t, $J = 6.9$ Hz, 2H), 1.89 (quint, $J = 6.9$ Hz, 2H), 1.67 (quint, $J = 7.2$ Hz, 2H), 0.25 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 164.4, 100.5, 45.8, 34.7, 29.5, 25.6, 1.1 ppm. IR (neat, cm^{-1}): 2954, 2868, 1595, 1419, 1247, 877, 834. HRMS *calcd.* for ($\text{C}_9\text{H}_{17}\text{Si}$): 280.0144, *found* 280.0155.



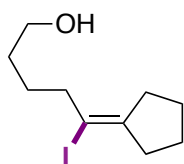
(Cyclopentylideneiodomethyl)dimethyl(phenyl)silane (3h). Following the general procedure but using **1h** (5.8 mmol), **2** (0.1 mol%) and $t\text{-BuCN}$ (0.6 M), the corresponding vinyl iodide **3h** was obtained in 84% yield in 24 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.60-7.56 (m, 2H), 7.40-7.33 (m, 3H), 2.44 (t, $J = 7.2$ Hz, 2H), 2.08 (t, $J = 7.2$ Hz, 2H), 1.78 (quint, $J = 6.6$ Hz, 2H), 1.65 (quint, $J = 7.2$ Hz, 2H), 0.54 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 166.7, 138.2, 134.1, 129.3, 128.0, 96.9, 45.9, 35.2, 29.4, 25.6, 0.4 ppm. IR (neat, cm^{-1}): 3067, 3048, 2954, 2867, 1593, 1427, 1247. HRMS *calcd.* for ($\text{C}_{14}\text{H}_{20}\text{Si}$) $[\text{M}+\text{H}]^+$: 343.0374, *found* 343.0374.



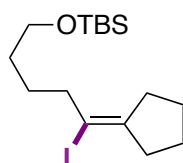
6-Cyclopentylidene-6-iodohexanenitrile (3i). Following the general procedure, the corresponding vinyl iodide **3i** was obtained in 66% yield in 48 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 2.47 (br, 2H), 2.38-2.26 (m, 6H), 1.88-1.79 (m, 2H), 1.71-1.64 (m, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 150.0, 119.7, 95.3, 41.5, 40.8, 32.0, 28.5, 28.4, 25.8, 24.3, 17.3 ppm. IR (neat, cm^{-1}): 2941, 2866, 2246, 1451, 1425, 1305, 1176. HRMS *calcd.* for $(\text{C}_{11}\text{H}_{16}\text{INa})$ $[\text{M}+\text{Na}]^+$: 312.0220, *found* 312.0215.



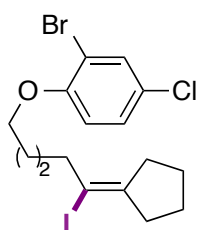
(1-Iodohept-6-en-1-ylidene)cyclopentane (3j). Following the general procedure, the corresponding vinyl iodide **3j** was obtained in 78% yield in 32 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 5.88-5.75 (m, 1H), 5.05-4.93 (m, 2H), 2.43 (t, $J = 7.2$ Hz, 2H), 2.34-2.26 (m, 4H), 2.11-2.04 (m, 2H), 1.82 (quint, $J = 6.9$ Hz, 2H), 1.66 (quint, $J = 6.9$ Hz, 2H), 1.57-1.47 (m, 2H), 1.43-1.34 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 148.8, 138.9, 114.5, 97.1, 41.7, 41.4, 33.8, 31.8, 28.9, 28.4, 27.8, 25.9 ppm. IR (neat, cm^{-1}): 2933, 2859, 1709, 1430, 1373, 1234, 1172. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{18}\text{I})$ $[\text{M}-\text{H}]^+$: 289.0448, *found* 289.0447.



5-Cyclopentylidene-5-iodopentan-1-ol (3k). Following the general procedure, the corresponding vinyl iodide **3k** was obtained in 89% yield in 32 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.67-3.61 (m, 2H), 2.47-2.43 (m, 2H), 2.34-2.25 (m, 4H), 1.86-1.77 (m, 2H), 1.70-1.52 (m, 7H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 149.2, 96.8, 62.9, 41.4, 31.9, 31.5, 28.4, 25.9, 25.6 ppm. IR (neat, cm^{-1}): 3497, 2937, 2864, 1438, 1351, 1201, 1159. HRMS *calcd.* for $(\text{C}_{10}\text{H}_{18}\text{OI})$ $[\text{M}+\text{H}]^+$: 281.0397, *found* 281.0394.

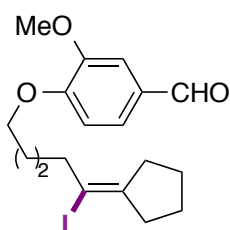


Tert-butyl((5-cyclopentylidene-5-iodopentyl)oxy)dimethylsilane (3l). Following the general procedure, the corresponding vinyl iodide **3l** was obtained in 93% yield in 32 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.62 (t, J = 6.0 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 2.34-2.26 (m, 4H), 1.87-1.77 (m, 2H), 1.71-1.51 (m, 6H), 0.90 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 148.9, 97.2, 63.2, 41.6, 41.4, 31.8, 31.7, 28.4, 26.1, 25.9, 25.8, 18.5, -5.1 ppm. IR (neat, cm^{-1}): 2934, 2863, 1451, 1428, 1051, 836, 781. HRMS *calcd.* for $(\text{C}_{10}\text{H}_{16}\text{I}) [\text{M-OTBS}]^+$: 263.0291, *found* 263.0280.



2-Bromo-4-chloro-1-((5-cyclopentylidene-5-iodopentyl)oxy)benzene (3m).

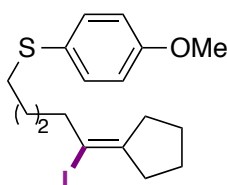
Following the general procedure, the corresponding vinyl iodide **3m** was obtained in 92% yield in 48 h as yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 8.7, 2.4 Hz, 1H), 6.79 (d, J = 8.7 Hz, 1H), 4.00 (t, J = 6.0 Hz, 2H), 2.51 (t, J = 6.9 Hz, 2H), 2.35-2.27 (m, 4H), 1.87-1.65 (m, 8H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 154.4, 149.4, 132.9, 128.3, 125.9, 113.9, 112.8, 96.5, 69.5, 41.5, 41.3, 31.9, 28.4, 27.9, 25.9, 25.9 ppm. IR (neat, cm^{-1}): 2942, 2866, 1585, 1479, 1464, 1284, 1047.



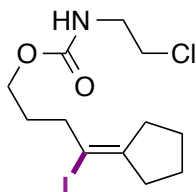
4-((5-Cyclopentylidene-5-iodopentyl)oxy)-3-methoxybenzaldehyde (3n).

Following the general procedure, the corresponding vinyl iodide **3n** was obtained in 93% yield in 48 h as slight yellow solid. M.P. = 63.5 °C. ^1H NMR (300 MHz, CDCl_3): δ 9.83 (s, 1H), 7.44-7.38 (m, 2H), 6.95 (d, J = 8.4 Hz, 1H), 4.09 (t, J = 6.9

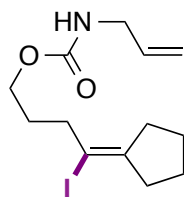
Hz, 2H), 3.90 (s, 3H), 2.49 (t, $J = 7.2$ Hz, 2H), 2.33-2.24 (m, 4H), 1.91-1.76 (m, 4H), 1.73-1.60 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 191.0, 154.1, 149.9, 149.5, 130.0, 126.9, 111.5, 109.3, 96.4, 69.1, 56.1, 41.4, 41.2, 31.9, 28.4, 27.7, 25.8 ppm. IR (neat, cm^{-1}): 3078, 2944, 2866, 1677, 1582, 1506, 1465. HRMS *calcd.* for $(\text{C}_{18}\text{H}_{23}\text{INaO}_3) [\text{M}+\text{Na}]^+$: 437.0584, *found* 437.0579.



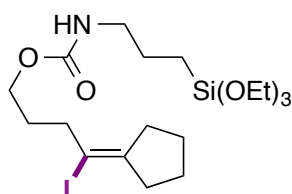
(5-Cyclopentylidene-5-iodopentyl)(4-methoxyphenyl)sulfane (3o). Following the general procedure, the corresponding vinyl iodide **3o** was obtained in 88% yield in 48 h as yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.37-7.31 (m, 2H), 6.87-6.82 (m, 2H), 3.79 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.41 (t, $J = 6.6$ Hz, 2H), 2.27 (t, $J = 7.2$ Hz, 4H), 1.85-1.76 (m, 2H), 1.70-1.56 (m, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 158.9, 149.2, 133.4, 114.6, 96.6, 55.5, 41.4, 41.3, 35.9, 31.8, 28.4, 28.4, 28.2, 25.9 ppm. IR (neat, cm^{-1}): 2936, 2862, 2833, 1591, 1492, 1240, 824. HRMS *calcd.* for $(\text{C}_{17}\text{H}_{24}\text{IOS}) [\text{M}+\text{H}]^+$: 403.0587, *found* 403.0590.



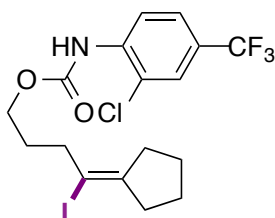
4-Cyclopentylidene-4-iodobutyl (2-chloroethyl)carbamates (3p). Following the general procedure, the corresponding vinyl iodide **3p** was obtained in 95% yield in 48 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 5.15 (b, 1H), 4.05 (t, $J = 6.3$ Hz, 2H), 3.61-3.47 (m, 4H), 2.50 (t, $J = 7.2$ Hz, 2H), 2.28 (q, $J = 7.5$ Hz, 4H), 1.87-1.76 (m, 4H), 1.70-1.60 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 156.5, 150.0, 95.1, 63.8, 44.2, 42.8, 41.4, 38.0, 31.7, 28.6, 28.3, 25.8 ppm. IR (neat, cm^{-1}): 3332, 2954, 1695, 1518, 1430, 1244, 1146. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{19}\text{ClINNaO}_2) [\text{M}+\text{Na}]^+$: 394.0041, *found* 394.0043.



4-Cyclopentylidene-4-iodobutyl allylcarbamate (3q). Following the general procedure, the corresponding vinyl iodide **3q** was obtained in 72% yield in 96 h as brown oil. ^1H NMR (300 MHz, CDCl_3): δ 5.90-5.77 (m, 1H), 5.22-5.09 (m, 2H), 4.76 (b, 1H), 4.05 (t, J = 6.3 Hz, 2H), 3.79 (t, J = 5.4 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.29 (q, J = 7.5 Hz, 4H), 1.87-1.77 (m, 4H), 1.70-1.61 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 156.5, 149.9, 134.7, 116.0, 95.3, 63.6, 43.5, 41.4, 38.1, 31.7, 28.7, 28.3, 25.8 ppm. IR (neat, cm^{-1}): 3339, 2954, 1679, 1520, 1427, 1244, 1060. HRMS *calcd.* for $(\text{C}_{13}\text{H}_{20}\text{INNaO}_2)$ $[\text{M}+\text{Na}]^+$: 372.0431, *found* 372.0440.

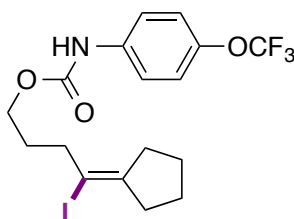


4-Cyclopentylidene-4-iodobutyl (3-(triethoxysilyl)propyl)carbamates (3r). Following the general procedure, the corresponding vinyl iodide **3r** was obtained in 61% yield in 48 h as brown oil. ^1H NMR (300 MHz, CDCl_3): δ 4.92 (b, 1H), 4.01 (t, J = 6.3 Hz, 2H), 3.80 (q, J = 6.9 Hz, 6H), 3.15 (q, J = 6.6 Hz, 2H), 2.49 (t, J = 6.9 Hz, 2H), 2.28 (q, J = 7.8 Hz, 4H), 1.85-1.75 (m, 4H), 1.69-1.55 (m, 4H), 1.20 (t, J = 6.9 Hz, 9H), 0.60 (t, J = 8.1 Hz, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 156.7, 149.8, 95.3, 63.3, 58.5, 43.4, 41.3, 38.1, 31.7, 28.7, 28.3, 25.8, 23.4, 18.3, 7.7 ppm. IR (neat, cm^{-1}): 3324, 2929, 1689, 1529, 1445, 1248, 1120.



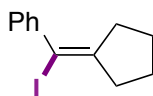
4-Cyclopentylidene-4-iodobutyl (2-chloro-4-(trifluoromethyl)phenyl)carbamates (3s). Following the general procedure, the corresponding vinyl iodide **3s** was obtained in 89% yield in 48 h as white solid. M.P. = 54.1 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ

8.53 (b, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.26-7.23 (m, 2H), 4.21 (t, $J = 6.3$ Hz, 2H), 2.57 (t, $J = 6.9$ Hz, 2H), 2.36-2.27 (m, 4H), 1.99-1.90 (m, 2H), 1.87-1.78 (m, 2H), 1.71-1.62 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 153.0, 150.3, 135.5, 130.4 (q, $J_{\text{C-F}} = 32.8$ Hz), 129.6, 125.2, 123.6 (q, $J_{\text{C-F}} = 270.8$ Hz), 120.3 (q, $J_{\text{C-F}} = 3.8$ Hz), 116.8 (q, $J_{\text{C-F}} = 3.8$ Hz), 94.8, 64.7, 41.4, 38.0, 31.8, 28.4, 28.3, 25.8 ppm. ^{19}F NMR (376 MHz, CDCl_3): -62.89 ppm. IR (neat, cm^{-1}): 3303, 2950, 2846, 1738, 1712, 1588, 1536. HRMS *calcd.* for $(\text{C}_{17}\text{H}_{18}\text{ClF}_3\text{NNaO}_2)$ $[\text{M}+\text{Na}]^+$: 509.9915, *found* 509.9919.

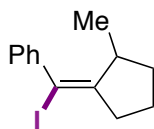


4-Cyclopentylidene-4-iodobutyl (4-(trifluoromethoxy)phenyl)carbamates (3t).

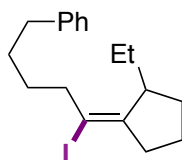
Following the general procedure, the corresponding vinyl iodide **3t** was obtained in 90% yield in 48 h as white solid. M.P. = 79.4 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.41 (d, $J = 9.0$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.73 (s, 1H), 4.17 (t, $J = 6.3$ Hz, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.34-2.26 (q, $J = 7.5$ Hz, 4H), 1.95-1.77 (m, 4H), 1.70-1.61 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 153.6, 150.2, 144.8, 136.7, 122.0, 120.6 (q, $J_{\text{C-F}} = 255.0$ Hz), 119.9 (br), 118.9, 94.9, 64.3, 41.4, 38.1, 31.8, 28.6, 28.3, 25.8 ppm. ^{19}F NMR (376 MHz, CDCl_3): -58.31 ppm. IR (neat, cm^{-1}): 3327, 2958, 2862, 1699, 1541, 1414, 1270. HRMS *calcd.* for $(\text{C}_{17}\text{H}_{19}\text{F}_3\text{INNaO}_3)$ $[\text{M}+\text{Na}]^+$: 492.0254, *found* 492.0266.



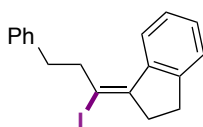
(Cyclopentylideneiodomethyl)benzene (3u). Following the general procedure, the corresponding vinyl iodide **3u** was obtained in 73% yield in 32 h (5% of **3u'** was observed) as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.33-7.15 (m, 5H), 2.48-2.43 (m, 2H), 2.32-2.28 (m, 2H), 1.81-1.74 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 152.7, 144.2, 128.9, 128.1, 127.4, 89.4, 42.0, 33.8, 28.7, 26.0 ppm. IR (neat, cm^{-1}): 3077, 2953, 2831, 1441, 1305, 1156, 657. HRMS *calcd.* for $(\text{C}_{12}\text{H}_{14}\text{I})$ $[\text{M}+\text{H}]^+$: 285.0135, *found* 285.0142.



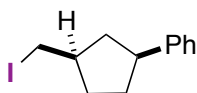
(Iodo(2-methylcyclopentylidene)methyl)benzene (3v). Following the general procedure, the corresponding vinyl iodide **3v** (E/Z mixture = 1.3: 1) was obtained in 95% yield in 72 h as colorless oil. ^1H NMR (major isomer, 300 MHz, CDCl_3): δ 7.36-7.20 (m, 5H), 2.93-2.78 (m, 1H), 2.68-2.20 (m, 2H), 2.05-1.54 (m, 4H), 0.75 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (major isomer, 75 MHz, CDCl_3): 157.0, 144.6, 128.6, 128.2, 127.5, 90.4, 41.8, 36.8, 33.7, 23.1, 19.5 ppm. IR (neat, cm^{-1}): 3056, 2953, 2865, 1441, 1370, 749, 696. HRMS *calcd.* for ($\text{C}_{13}\text{H}_{15}$) $[\text{M}-\text{I}]^+$: 171.1168, *found* 171.1167.



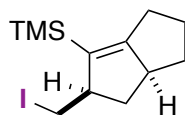
(5-(2-Ethylcyclopentylidene)-5-iodopentyl)benzene (3w). Following the general procedure, the corresponding vinyl iodide **3w** (E/Z mixture = 1: 1) was obtained in 88% yield in 32 h as colorless oil. ^1H NMR (major isomer, 300 MHz, CDCl_3): δ 7.33-7.28 (m, 2H), 7.23-7.18 (m, 3H), 2.69-2.21 (m, 7H), 1.87-1.55 (m, 8H), 1.43-1.12 (m, 2H), 0.98-0.89 (m, 3H) ppm. ^{13}C NMR (major isomer, 75 MHz, CDCl_3): 152.9, 142.64, 128.5, 125.8, 100.1, 52.4, 41.9, 40.9, 36.0, 32.2, 30.4, 30.1, 29.0, 25.5, 22.7, 12.4 ppm. IR (neat, cm^{-1}): 3025, 2929, 2857, 1453, 1160, 744, 697. HRMS *calcd.* for ($\text{C}_{18}\text{H}_{25}$) $[\text{M}-\text{I}]^+$: 241.1951, *found* 241.1946.



(Z)-1-(1-Iodo-3-phenylpropylidene)-2,3-dihydro-1H-indene (3x). Following the general procedure, the corresponding vinyl iodide **3x** was obtained in 47% yield in 72 h as colorless oil (E/Z mixture = 1:1). Z isomer spectroscopic data: ^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, J = 7.5 Hz, 1H), 7.35-7.27 (m, 4H), 7.24-7.13 (m, 4H), 3.35-3.29 (m, 2H), 3.03-2.93 (m, 4H), 2.89-2.84 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 149.7, 147.1, 140.7, 137.9, 128.6, 128.6, 128.1, 126.6, 126.3, 126.2, 124.0, 100.6, 44.7, 42.9, 35.1, 29.4 ppm. IR (neat, cm^{-1}): 3019, 2921, 2851, 1455, 1376, 749, 699. HRMS *calcd.* for ($\text{C}_{18}\text{H}_{18}\text{I}$) $[\text{M}+\text{H}]^+$: 361.0448, *found* 361.0446.

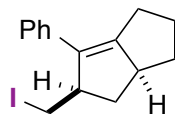


3-(Iodomethyl)cyclopentylbenzene (3y). Following the general procedure, the corresponding alkyl iodide **3y** was obtained in 80% yield in 32 h (cis/trans mixture = 10:1) as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.31-7.15 (m, 5H), 3.29-3.25 (m, 2H), 3.18-3.06 (m, 1H), 2.53-2.26 (2H), 2.16-2.08 (m, 1H), 2.05-1.85 (m, 1H), 1.83-1.70 (m, 1H), 1.59-1.48 (m, 1H), 1.43-1.31 (m, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 145.3, 128.4, 127.0, 126.1, 46.2, 42.7, 42.4, 33.5, 32.6, 14.1 ppm. IR (neat, cm^{-1}): 3025, 2947, 2863, 1492, 1447, 1181, 752, 697. HRMS calcd. for ($\text{C}_{12}\text{H}_{15}\text{I}$): 286.0219, found 286.0223.



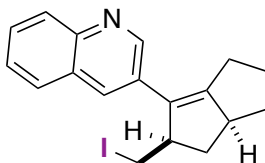
2-(Iodomethyl)-2,3,3a,4,5,6-hexahdropentalen-1-yl)trimethylsilane (5a).

Following the general procedure, the corresponding alkyl iodide **5a** (single isomer) was obtained in 70% yield in 72 h as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.62 (dd, $J = 9.0, 3.0$ Hz, 1H), 3.41-3.31 (m, 1H), 3.065 (t, $J = 9.3$ Hz, 1H), 2.79-2.71 (m, 1H), 2.40-2.33 (m, 1H), 2.21-2.15 (m, 2H), 2.07-1.84 (m, 3H), 1.11-0.97 (m, 2H), 0.13 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 169.4, 130.4, 59.0, 53.7, 40.5, 31.6, 28.5, 25.8, 17.2, 0.28 ppm. IR (neat, cm^{-1}): 2922, 2852, 1460, 1377, 1249, 839.

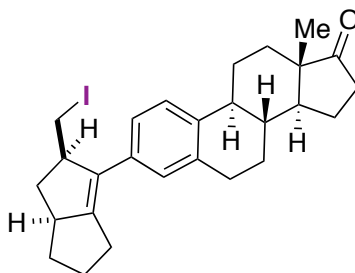


5-(Iodomethyl)-6-phenyl-1,2,3,3a,4,5-hexahdropentalene (5b). Following the general procedure, the corresponding alkyl iodide **5b** was obtained in 72% yield in 60 h as yellow oil (dr = 25:1). ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.20 (m, 5H), 3.75-3.66 (m, 1H), 3.53 (dd, $J = 9.6$ Hz, 3.2 Hz, 1H), 3.13 (dd, $J = 9.6$ Hz, 8.4 Hz, 1H), 2.97-2.88 (m, 1H), 2.63-2.46 (m, 2H), 2.23-2.11 (m, 2H), 2.04-1.92 (m, 2H), 1.35-1.25 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3): 153.5, 137.3, 130.6, 128.5, 127.1, 126.2, 54.4, 51.6, 38.3, 32.2, 28.8, 24.4, 16.5 ppm. IR (neat, cm^{-1}): 3053, 3025, 2953,

2865, 1488, 743, 693. HRMS *calcd.* for (C₁₅H₁₈I) [M+H]⁺: 325.0448, *found* 325.0442.



3-(2-(Iodomethyl)-2,3,3a,4,5,6-hexahydro-pentalen-1-yl)quinolone (5c). Following the general procedure, the corresponding alkyl iodide **5c** was obtained in 63% yield in 96 h as brown oil. The spectroscopic data correspond to those previously reported in the literature.⁵ ¹H NMR (300 MHz, CDCl₃): δ 8.90 (d, *J* = 2.1 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 2.1 Hz, 1H), 7.79-7.76 (m, 1H), 7.69-7.63 (m, 1H), 7.55-7.49 (m, 1H), 3.77-3.66 (m, 1H), 3.47 (dd, *J* = 10.2, 3 Hz, 1H), 3.19 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.02-2.93 (m, 1H), 2.67-2.56 (m, 1H), 2.51-2.42 (m, 1H), 2.27-2.12 (m, 2H), 2.05-1.90 (m, 2H), 1.44-1.31 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): 156.5, 150.2, 146.6, 132.7, 130.5, 129.3, 129.0, 128.0, 127.8, 127.6, 126.9, 53.9, 52.0, 37.9, 31.9, 28.7, 24.4, 16.0 ppm.



3-(2-(iodomethyl)-2,3,3a,4,5,6-hexahydro-pentalen-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5d). Following the general procedure but using **2** (2 mol%), the corresponding alkyl iodide **5c** was obtained in 44% yield in 72 h as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.24 (d, *J* = 9.3 Hz, 1H), 7.08-7.03 (m, 1H), 6.99-6.97 (d, *J* = 4.5 Hz, 1H), 3.70-3.62 (m, 1H), 3.52 (dt, *J* = 9.6, 2.4 Hz, 1H), 3.07 (dt, 9.0, 2.4 Hz, 1H), 2.92-2.85 (m, 3H), 2.56-1.91 (m, 14H), 1.68-1.44 (m, 7H), 0.92 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): 221.0, 153.03, 152.99, 137.78, 137.75, 136.49, 136.46, 134.79, 134.77, 130.33, 130.31, 127.54, 127.41, 125.4, 124.70, 124.59, 54.5, 51.5, 50.6, 48.1, 44.5, 44.5, 38.4, 38.2, 36.0, 32.1, 31.7, 29.6, 28.7, 26.7, 25.7, 24.4, 21.7, 14.0 ppm. IR (neat, cm⁻¹): 2924, 2854, 1736, 1453, 1374, 1260, 1084. (MALDI) HRMS *calcd.* for (C₂₇H₃₃IO) [M]⁺: 500.1570, *found* 500.1549.

Determination of redox potentials by cyclic voltammetry

A cyclic voltammetry study was carried out to investigate the feasibility of the electron transfer between the Ir photocatalyst **2** and the unactivated alkyl iodide **1a** in *t*-BuCN. [Ir(ppy)₂(dtbbpy)]PF₆ (**2**) showed a quasi-reversible redox behavior (Table S5, $E_{1/2}^{\text{red}} = -1.42$ V), whereas **1a** showed an irreversible reduction below -2.5 V (Table S5) under the same conditions. These results suggested that a direct electron transfer between the reduced Ir(II) complex and compound **1a** is unlikely under the reaction conditions.

Table S5. Electrochemical data for 1a and 2

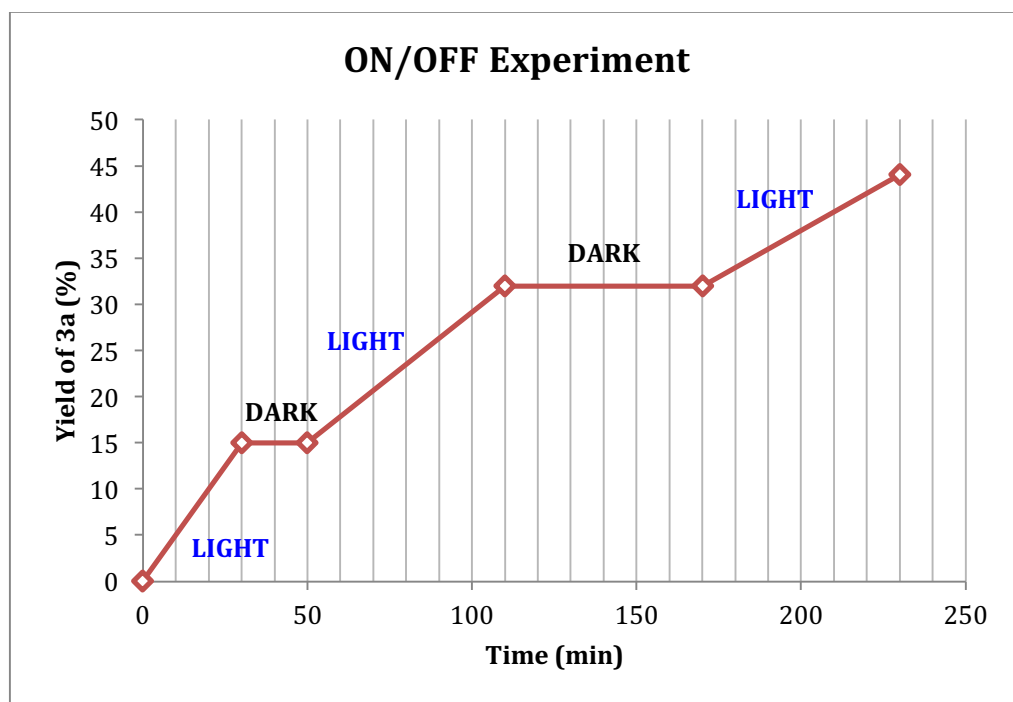
	$E_{1/2}$ (vs SCE)	E_p (vs SCE)	Electrolyte
Ferrocene	0.4 V	-	0.1 M Bu ₄ NPF ₆ (MeCN)
	0.51 V	-	0.1 M Bu ₄ NPF ₆ (<i>t</i> BuCN)
	-	-	0.1 M Bu ₄ NPF ₆ (DMF)
[Ir(ppy) ₂ (dtbbpy)]PF ₆	-1.48 V	-	0.1 M Bu ₄ NPF ₆ (MeCN)
	-1.42 V	-	0.1 M Bu ₄ NPF ₆ (<i>t</i> BuCN)
	-1.39 V	-	0.1 M Bu ₄ NPF ₆ (DMF)
1a	-	≤ -2.5 V	0.1 M Bu ₄ NPF ₆ (MeCN)
	-	≤ -2.5V	0.1 M Bu ₄ NPF ₆ (<i>t</i> BuCN)
	-	-	0.1 M Bu ₄ NPF ₆ (DMF)

The redox potentials (vs SCE) were determined by cyclic voltammetry using 5.0 mM solutions of **1a** and **2** in a 0.1 M solution of NBu₄PF₆ with a glassy carbon disk electrode at a scan rate of 0.1 V/s. The counter-electrode was a platinum disk. Solutions were purged with argon for 30 min prior to the measurement to displace oxygen.

Mechanistic studies

ON/OFF experiment.

A 12.0 mL Schlenk tube with screw cap containing a stirring bar was charged with $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (**2**, 1 mol%, 1.8 mg). The tube was then evacuated and back-filled with argon. The alkyl iodide **1a** (0.2 mmol, 1 equiv, 58.0 mg) and decane (0.2 mmol, 1 equiv, 39 μL) were added with a microsyringe follow by addition of *t*-BuCN (1.0 mL, 0.2 M) and *i*-Pr₂NEt (0.2 mmol, 1 equiv, 35 μL) under a positive Ar flow. Then three freeze-pump-thaw cycles were conducted in liquid nitrogen. Finally, the reaction was placed on the photoreactor, consisting of a 150 mL beaker surrounded by blue LED strips (FlexLed Inspire. 20 LEDs, 1.7 W, 0.364 mW/cm^2) and was alternatively irradiated under light/dark regimes. A mini-fan was necessary on the top to keep internal temperature between 30 and 35°C. After a certain time, aliquots were taken, diluted with EtOAc (9 mL), filtered through a plug of silica and analyzed by GC with FID detector.



Luminescence quenching experiments.

Luminescence quenching experiments were carried out using the Stern–Volmer relationship:

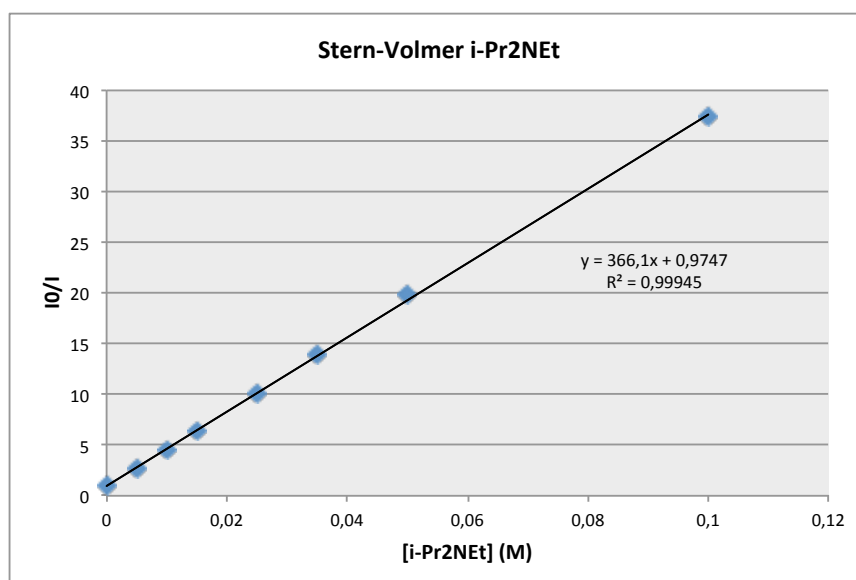
$$I/I_0 = k_q \tau_0 [\text{quencher}]$$

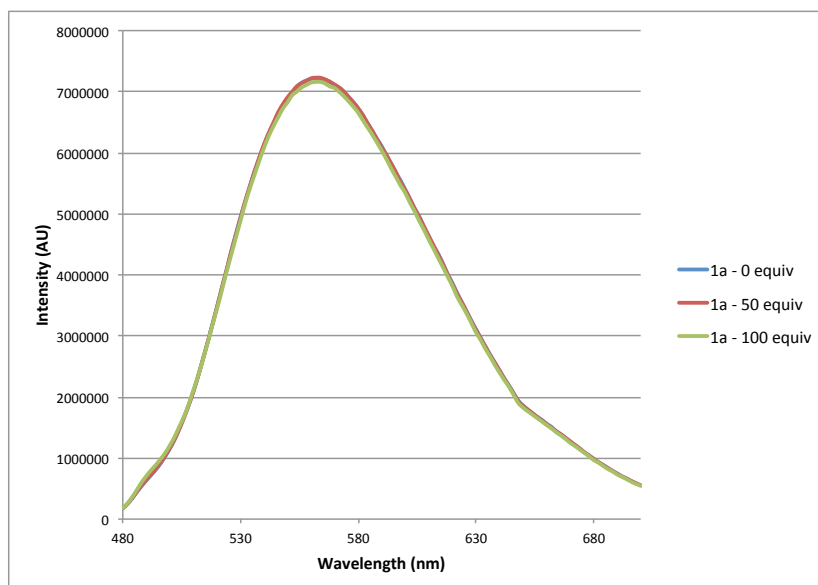
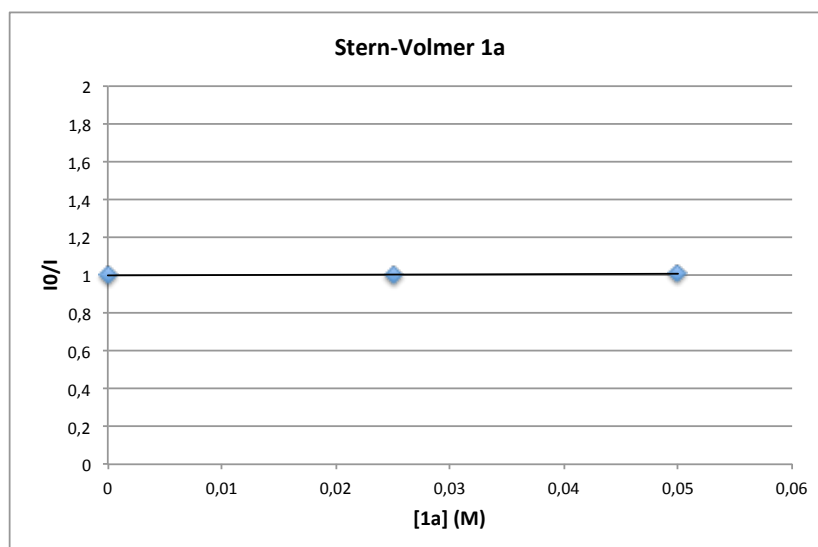
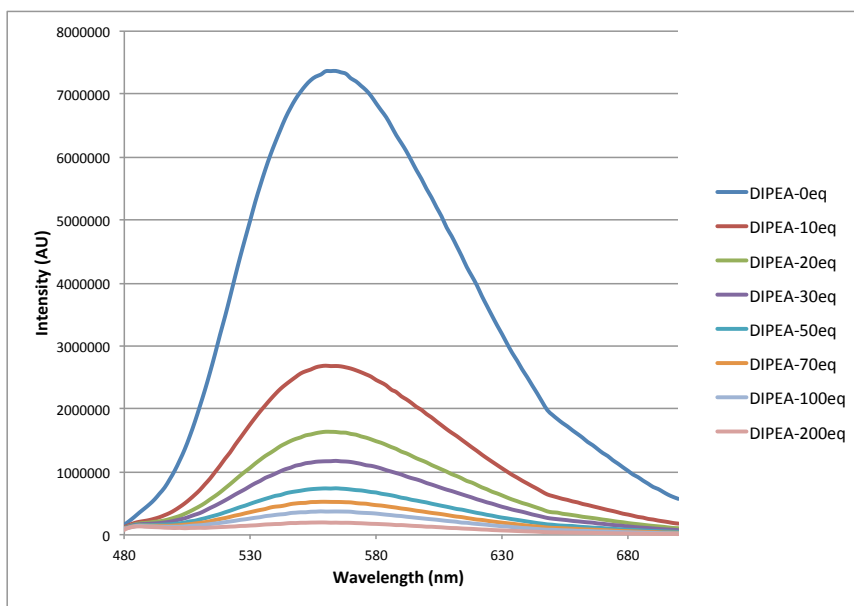
I_0 stands for the luminescence intensity of the photocatalyst (**2**) whereas I represents the intensity of luminescence in the presence of the quencher. τ_0 is the lifetime of **2**, determined to be 661.04 ± 0.75 ns (5.0×10^{-5} M in *t*-BuCN) using a time-correlated single photon counting (TCSPC) technique.

Samples for the quenching experiments were prepared in 2 mL glass cuvette with a septum screw cap. Different amounts of quenchers were added to a solution of the photocatalyst **2** in *t*-BuCN (5.0×10^{-5} M). Samples were irradiated at 470 nm and emission was measured at 560 nm.

Quenching with *i*-Pr₂NEt: $k_q = 5.58 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Quenching with **1a**: No quenching was observed.





Quantum yield determination.

The determination of the quantum yield of the reaction was carried out using two light sources: (a) a spectrophotometer and (b) using blue LED strip (photoreactor). All manipulations and preparation of samples were carried out in a dark lab with red irradiation. The measurement of the photon flux of both light sources was determined by standard ferrioxalate actinometry following already reported procedures.^{8,9,10,11}

Spectrophotometer (Irradiation at 468 nm, slit 3 nm).

Photon flux (average of 3 measurements) = 5.86×10^{-9} einstein s⁻¹

Blue LED strip photoreactor (Irradiation at 450 nm) (QY of ferrioxalate at 450 nm estimated to be 0.95).

Photon flux (average of 3 measurements) = 1.56×10^{-8} einstein s⁻¹

→ Quantum yield determination using a spectrophotometer.

In a dark lab, a cuvette was charge with with [Ir(ppy)₂(dtbbpy)]PF₆ (**2**, 1 mol%, 3.6 mg), **1a** (0.4 mmol, 1 equiv, 116.0 mg), *i*-Pr₂NEt (0.4 mmol, 1 equiv, 70 μL), decane (0.4 mmol, 1 equiv, 78 μL) and *t*-BuCN (2.0 mL, 0.2 M). The cuvette was then closed with a septum screw cap and degassed for 30 min. The sample was irradiated at 468 nm (slit 3 nm) for 1800 s (30 min). An aliquot was filtered through a plug of silica and celite and analyzed by GC with FID detector. **3a** was detected in 6% yield.

Under these conditions, the fraction of light absorbed by **2** was $f = 0.974$.

$$\Phi = \frac{\text{mol of } \mathbf{3a}}{\text{flux} \cdot t \cdot f}$$

$$\Phi = \frac{2.4 \times 10^{-5} \text{ mol}}{5.86 \times 10^{-9} \text{ einstein s}^{-1} \cdot 1800 \text{ s} \cdot 0.974} = 2.34$$

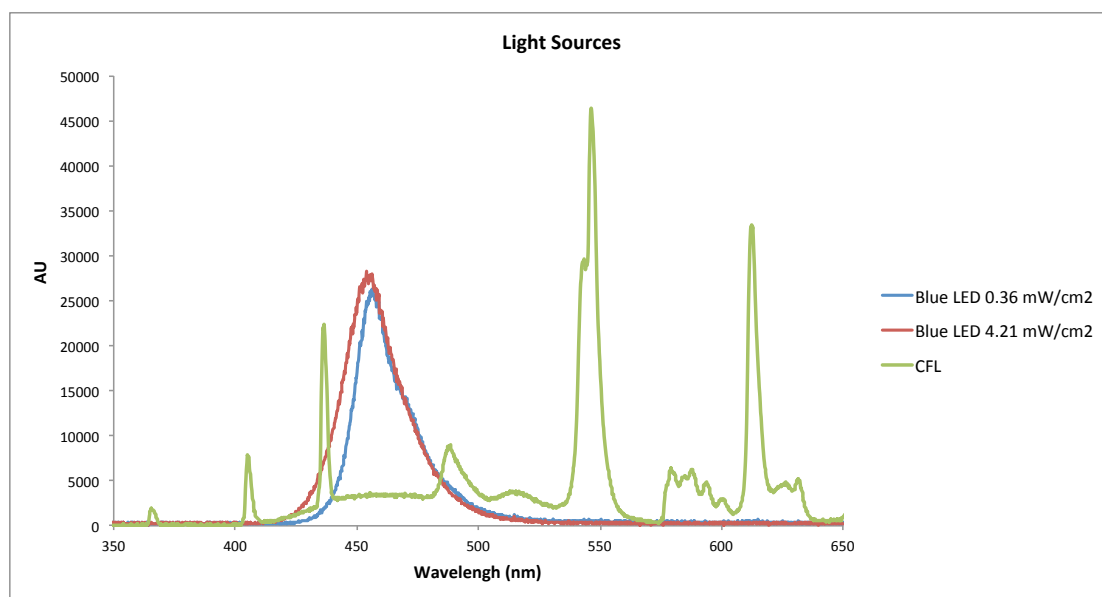
→ Quantum yield determination using the blue LED photoreactor. A 12.0 mL Schlenk tube with screw cap containing a stirring bar was charged with [Ir(ppy)₂(dtbbpy)]PF₆ (**2**, 1 mol%, 3.6 mg). The tube was then evacuated and back-filled with argon. **1a** (0.4 mmol, 1 equiv, 116 mg) was added with a microsyringe

followed by addition of decane (0.4 mmol, 1 equiv, 78 μ L), *t*-BuCN (2.0 mL, 0.2 M) and *i*-Pr₂NEt (0.4 mmol, 1 equiv, 70 μ L) under a positive Ar flow. Then three freeze-pump-thaw cycles were conducted in liquid nitrogen. The sample was irradiated with the blue LED photoreactor (FlexLed Inspire. 20 LEDs, 1.7 W, 0.364 mW/cm²) for 1800 s (30 min). An aliquot was filtered through a plug of silica and celite and analyzed by GC with FID detector. **3a** was detected in 15% yield. Under these conditions, the fraction of light absorbed by **2** was $f = 0.974$.

$$\Phi = \frac{\text{mol of } \mathbf{3a}}{\text{flux} \cdot t \cdot f}$$

$$\Phi = \frac{6.0 \times 10^{-5} \text{ mol}}{1.56 \times 10^{-8} \text{ einstein s}^{-1} \cdot 1800 \text{ s} \cdot 0.974} = 2.19$$

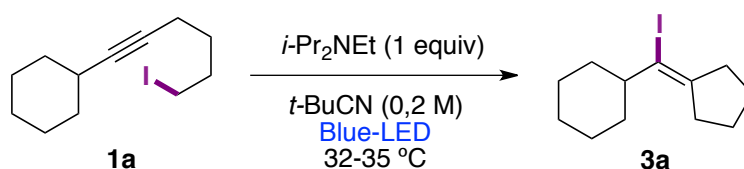
Emission spectra of different light sources.



Ir-free atom transfer radical cyclization of **1a** (Scheme 3).

A 12.0 mL Schlenk tube with screw cap containing a stirring bar was charged with **1a** (0.2 mmol, 1 equiv, 58.0 mg), *i*-Pr₂NEt (0.2 mmol, 1 equiv, 35 μ L) and *t*-BuCN (1.0 mL, 0.2 M). Then three freeze-pump-thaw cycles were conducted in liquid nitrogen. Finally, the reaction was placed on the corresponding photoreactor, consisting of a 150 mL beaker surrounded by blue LED strips. A mini-fan was necessary on the top to keep internal temperature between 30 and 35°C. The reaction was stirred for 48-60 h. After that time, the solvent was evaporated under vacuum and the residue purified on silica gel column chromatography to yield **3a** as a colorless oil.

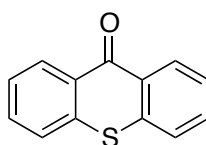
Table S6. ATRC of **1a in the absence of photocatalyst**



Entry	Light source	Irradiation time	3a (%) ^a	3a' (%) ^a
1	Blue LED (0.364 mW/cm ²)	60 h	12	0
2	Blue LED (4.21 mW/cm ²)	60 h	44	0
3	Blue LED (4.21 mW/cm ²) ^b	48 h	16	0
4	Blue LED (4.21 mW/cm ²) ^{b,c}	48 h	25	0
5	Blue LED (4.21 mW/cm ²) ^d	48 h	70	10
6	Blue LED (4.21 mW/cm ²) ^{d,e}	84 h	15	70

^a Isolated yields. ^b 25 °C. ^c In the presence of 1 eq of thioxanthone.

^d DMSO as solvent ^e *i*-Pr₂NEt (10 equiv)



Mechanistic discussion.

In principle, a number of different pathways can be considered for our visible light-mediated atom transfer radical cyclization of unactivated alkyl iodides, although some of them can be ruled out on the basis of our experimental information.

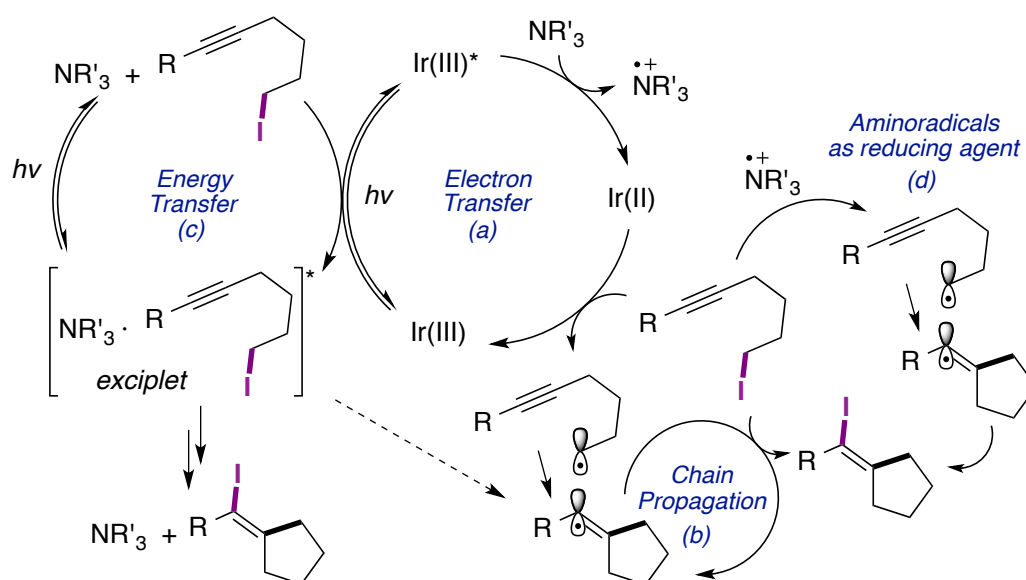


Figure S3. Mechanistic considerations

The behavior of the amine as quenching agent for the triplet-excited state of the photocatalyst (**2**) in contrast to **1a** pointed towards a reductive pathway for the photocatalytic transformation. However, the absence of double cyclization products with substrates **1j** and **1k** (Table 2), and the fact that substoichiometric amounts of amine are sufficient to efficiently promote the reaction (entry 6, Table 1) rules out the formation of cationic vinyl intermediates. Therefore, we considered the possibility of a radical-chain propagation process photoinitiated by **2** (Figure S3, *pathways a and b*). In order to characterize this event, we measured the quantum yield of the ATRC reaction obtaining values in the range 2.2-2.4, which indeed involved this possibility. Unexpectedly, we found that the ATRC of **1a** was also possible in the absence of **2**, although the reaction rate was significantly slower. These results could be explained by the formation of an exciplex under blue irradiation, which could potentially trigger the chain-process giving rise to **3a**. Formation of exciplex is a well-documented phenomenon between electron-rich amines and alkyl halides.¹²⁻¹⁵ Although an in depth mechanistic study should await further investigations, we speculate that in the presence of **2**, formation of an exciplex might be accelerated via energy transfer from

the triplet excited state of **2** (pathway c), thus suggesting that a prototypical SET from **2** to **1a** might not take place. Although tentative, this pathway explains the successful ATRC encountered with photocatalysts unable to promote SET to **1a** due to a significant thermodynamic gap between their redox potentials (see entries 1 or 8, Table 1). At present we cannot totally rule out that chain-processes might occur from in situ generated α -amino radicals generated by deprotonation of the corresponding amine radical cation (pathway d).¹⁶ Further mechanistic studies are ongoing in our laboratories.

X-Ray crystallographic data for 3t

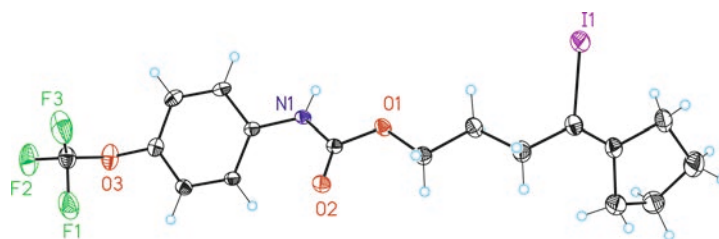


Table S7. Crystal data and structure refinement for **3t**.

Identification code	yshen03-431a
Empirical formula	C ₁₇ H ₁₉ F ₃ I N O ₃
Formula weight	469.23
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 47.1143(6) Å a = 90° b = 4.86847(8) Å b = 97.7446(11)° c = 16.0241(2) Å γ = 90°
Volume	3642.00(9) Å ³
Z	8
Density (calculated)	1.712 Mg/m ³
Absorption coefficient	1.803 mm ⁻¹
F(000)	1856
Crystal size	0.25 x 0.20 x 0.15 mm ³
Theta range for data collection	2.566 to 34.164°
Index ranges	-74 ≤ h ≤ 74, -7 ≤ k ≤ 7, -25 ≤ l ≤ 24
Reflections collected	55197
Independent reflections	7329 [R(int) = 0.0289]
Completeness to theta = 34.164°	97.299995%
Absorption correction	Multi-scan
Max. and min. transmission	0.840 and 0.646
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7329 / 3 / 262
Goodness-of-fit on F ²	1.033
Final R indices [I > 2σ(I)]	R1 = 0.0328, wR2 = 0.0949
R indices (all data)	R1 = 0.0363, wR2 = 0.0972
Largest diff. peak and hole	2.049 and -1.418 e. Å ⁻³

Table S8. Bond lengths [\AA] and angles [$^\circ$] for yshen03-431a.

Bond lengths----	
C1-C13	1.326(2)
C1-C2	1.507(2)
C1-I1	2.1234(17)
C2-C3	1.529(2)
C3-C4	1.509(2)
C4-O1	1.4502(19)
C5-O2	1.2209(16)
C5-O1	1.3430(17)
C5-N1	1.3560(18)
C6-C7	1.3970(19)
C6-C11	1.3978(19)
C6-N1	1.4118(19)
C7-C8	1.387(2)
C8-C9	1.385(2)
C9-C10	1.389(2)
C9-O3	1.411(2)
C10-C11	1.389(2)
C12-F1'	1.252(4)
C12-F2	1.268(8)
C12-F3	1.285(3)
C12-F2'	1.321(8)
C12-O3	1.325(2)
C12-F3'	1.374(4)
C12-F1	1.396(4)
C13-C14	1.518(3)
C13-C17	1.519(3)
C14-C15	1.538(3)
C15-C16'	1.450(6)
C15-C16	1.484(5)
C16-C17	1.501(5)
C16'-C17	1.599(4)
Angles-----	
C13-C1-C2	127.27(16)
C13-C1-I1	118.64(13)
C2-C1-I1	114.09(12)
C1-C2-C3	112.80(14)

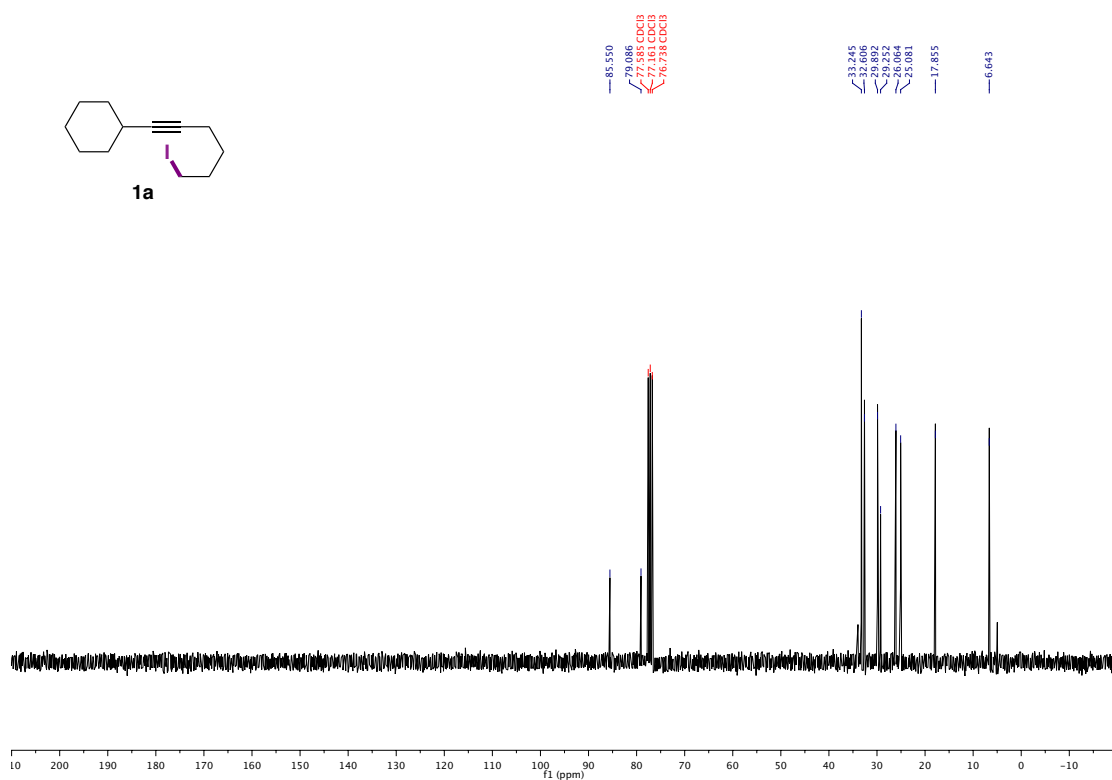
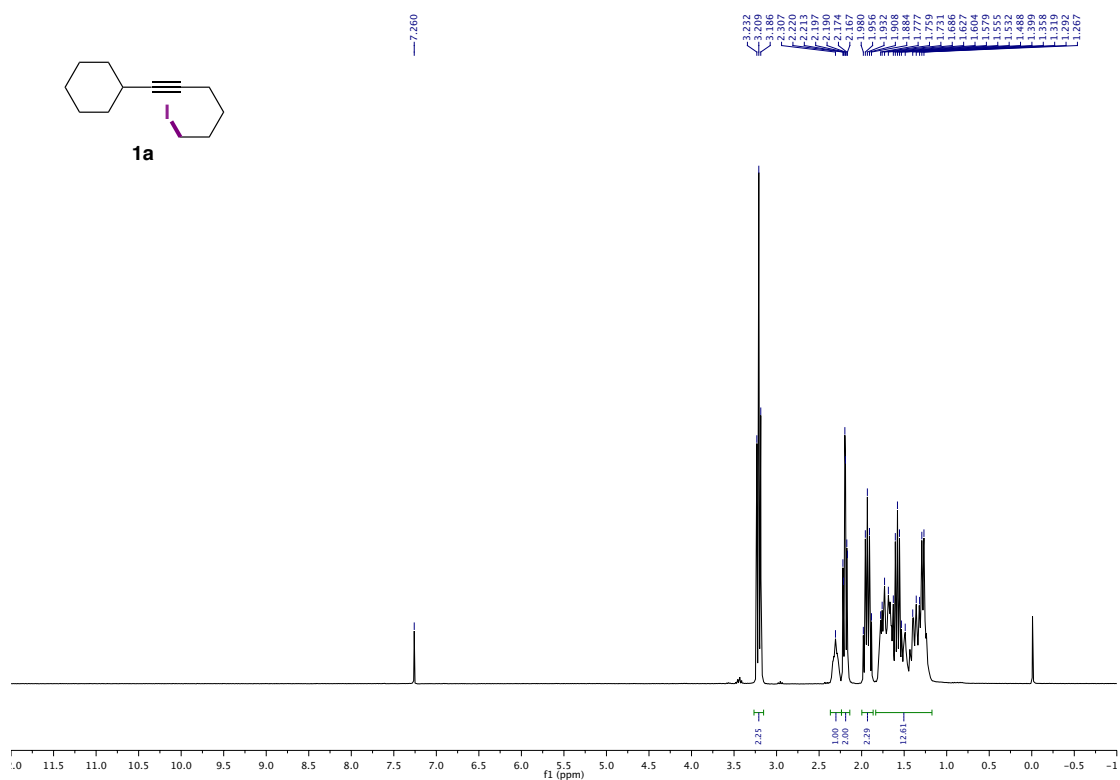
C4-C3-C2	111.39(13)
O1-C4-C3	106.40(12)
O2-C5-O1	123.94(13)
O2-C5-N1	126.11(13)
O1-C5-N1	109.93(11)
C7-C6-C11	119.63(13)
C7-C6-N1	123.00(12)
C11-C6-N1	117.28(12)
C8-C7-C6	120.01(13)
C9-C8-C7	119.42(13)
C8-C9-C10	121.67(14)
C8-C9-O3	118.93(15)
C10-C9-O3	119.18(14)
C11-C10-C9	118.62(13)
C10-C11-C6	120.64(13)
F2-C12-F3	114.1(5)
F1'-C12-F2'	110.0(6)
F1'-C12-O3	121.4(2)
F2-C12-O3	112.6(5)
F3-C12-O3	119.3(2)
F2'-C12-O3	110.0(5)
F1'-C12-F3'	106.3(4)
F2'-C12-F3'	103.1(4)
O3-C12-F3'	104.2(2)
F2-C12-F1	104.8(5)
F3-C12-F1	100.9(4)
O3-C12-F1	102.4(2)
C1-C13-C14	126.45(17)
C1-C13-C17	125.08(17)
C14-C13-C17	108.47(16)
C13-C14-C15	104.43(17)
C16'-C15-C14	108.2(3)
C16-C15-C14	104.4(2)
C15-C16-C17	105.9(3)
C15-C16'-C17	102.7(3)
C16-C17-C13	102.6(2)
C13-C17-C16'	102.8(2)
C5-N1-C6	125.36(11)
C5-O1-C4	115.50(11)
C12-O3-C9	118.07(13)

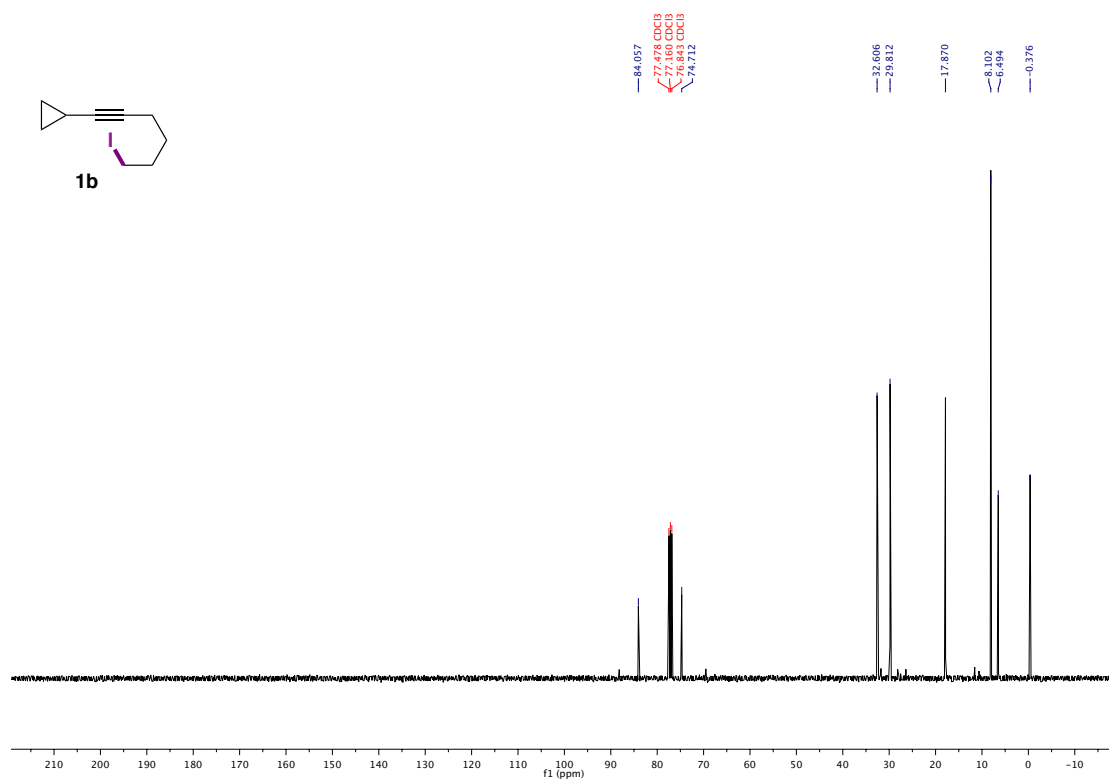
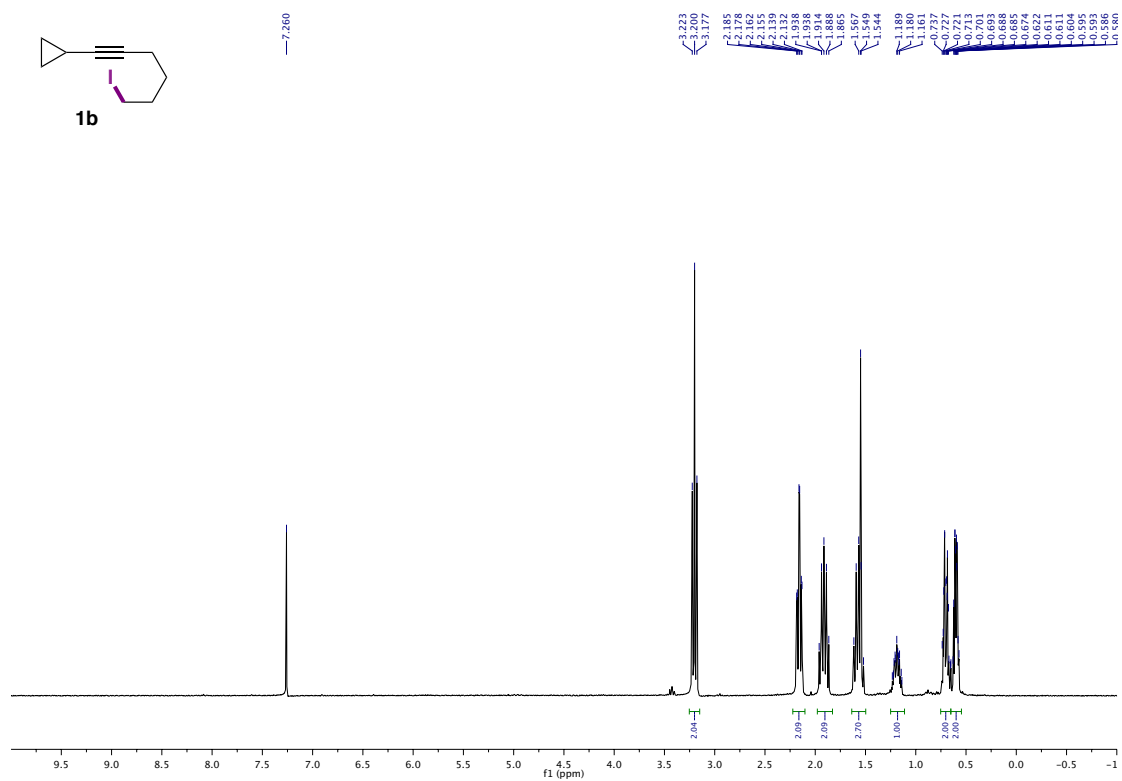
Table S9. Torsion angles [$^{\circ}$] for yshen03-431a.

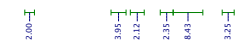
C13-C1-C2-C3	-115.7(2)
I1-C1-C2-C3	64.30(17)
C1-C2-C3-C4	178.08(14)
C2-C3-C4-O1	175.28(13)
C11-C6-C7-C8	1.1(2)
N1-C6-C7-C8	-175.41(13)
C6-C7-C8-C9	-0.5(2)
C7-C8-C9-C10	-0.3(2)
C7-C8-C9-O3	174.26(13)
C8-C9-C10-C11	0.4(2)
O3-C9-C10-C11	-174.14(13)
C9-C10-C11-C6	0.2(2)
C7-C6-C11-C10	-0.9(2)
N1-C6-C11-C10	175.72(13)
C2-C1-C13-C14	178.19(18)
I1-C1-C13-C14	-1.8(3)
C2-C1-C13-C17	-2.0(3)
I1-C1-C13-C17	178.02(16)
C1-C13-C14-C15	179.0(2)
C17-C13-C14-C15	-0.8(2)
C13-C14-C15-C16'	-22.8(3)
C13-C14-C15-C16	22.9(3)
C16'-C15-C16-C17	64.2(4)
C14-C15-C16-C17	-37.3(4)
C16-C15-C16'-C17	-56.4(3)
C14-C15-C16'-C17	35.6(4)
C15-C16-C17-C13	36.1(4)
C15-C16-C17-C16'	-59.0(4)
C1-C13-C17-C16	159.0(3)
C14-C13-C17-C16	-21.1(3)
C1-C13-C17-C16'	-158.6(3)
C14-C13-C17-C16'	21.3(3)
C15-C16'-C17-C16	59.9(4)
C15-C16'-C17-C13	-34.7(3)
O2-C5-N1-C6	-8.5(2)
O1-C5-N1-C6	172.60(12)
C7-C6-N1-C5	-25.7(2)
C11-C6-N1-C5	157.75(13)

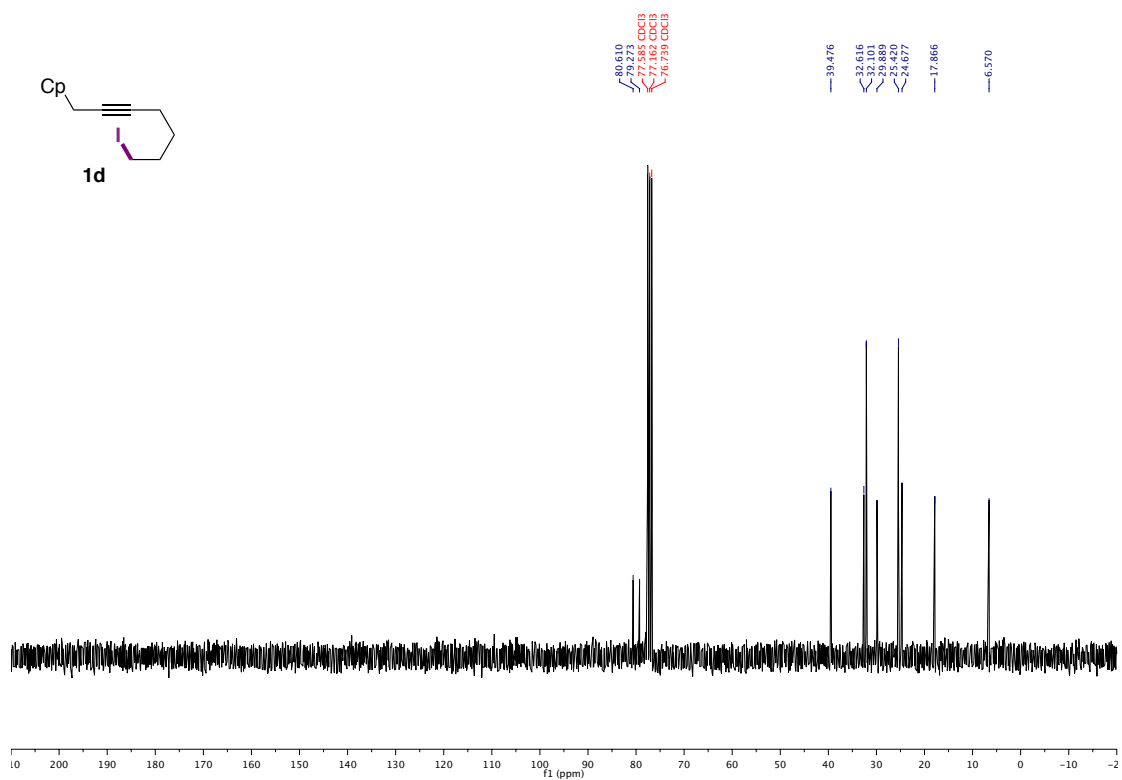
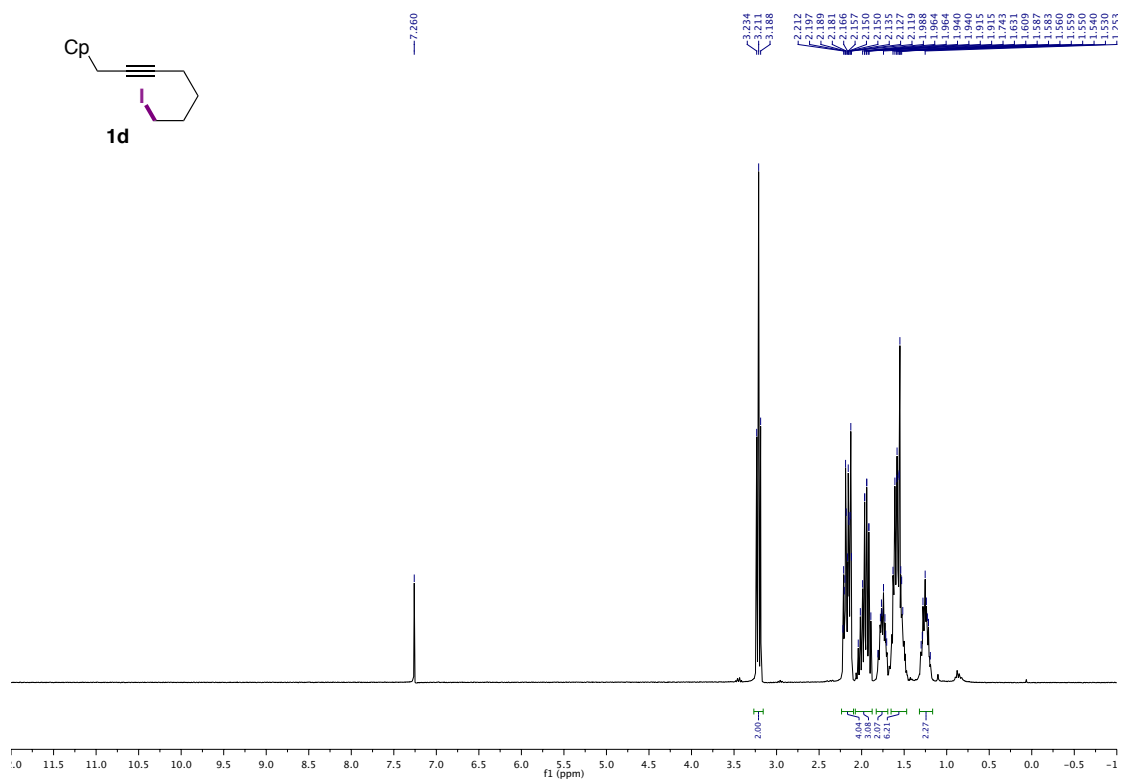
O2-C5-O1-C4	1.7(2)
N1-C5-O1-C4	-179.35(11)
C3-C4-O1-C5	-179.60(12)
F1'-C12-O3-C9	-41.9(5)
F2-C12-O3-C9	170.6(4)
F3-C12-O3-C9	32.8(4)
F2'-C12-O3-C9	-172.3(4)
F3'-C12-O3-C9	77.8(3)
F1-C12-O3-C9	-77.5(3)
C8-C9-O3-C12	91.1(2)
C10-C9-O3-C12	-94.3(2)

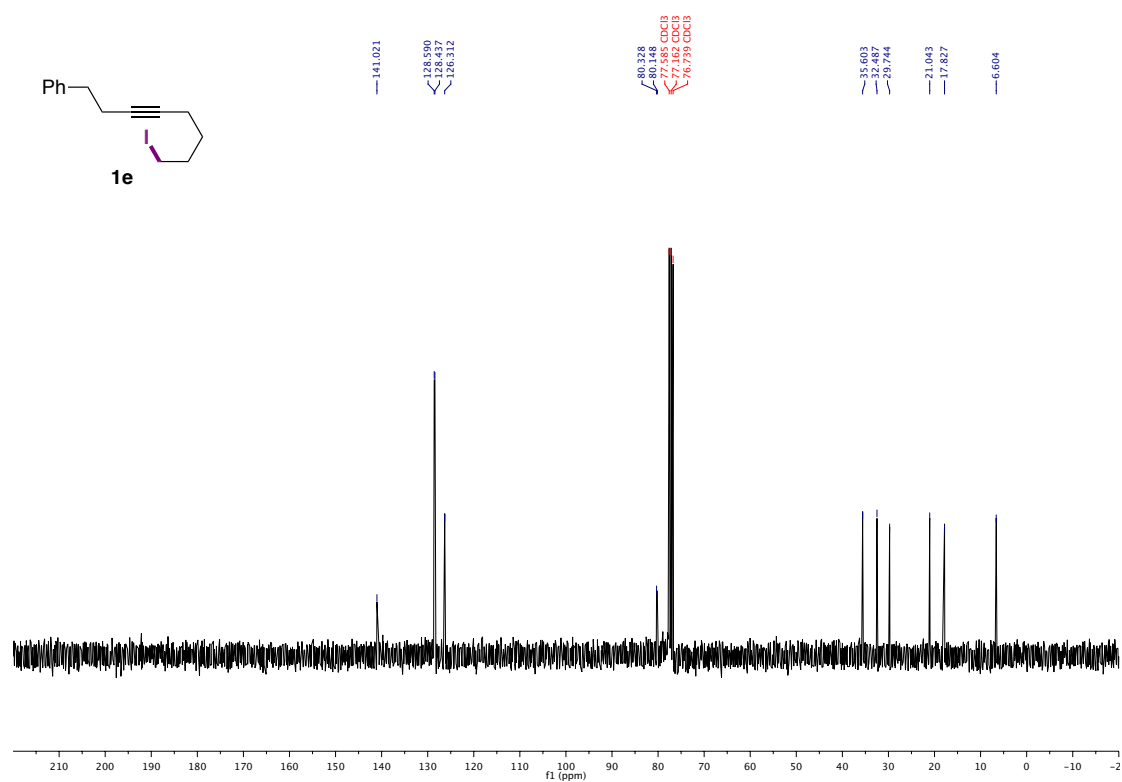
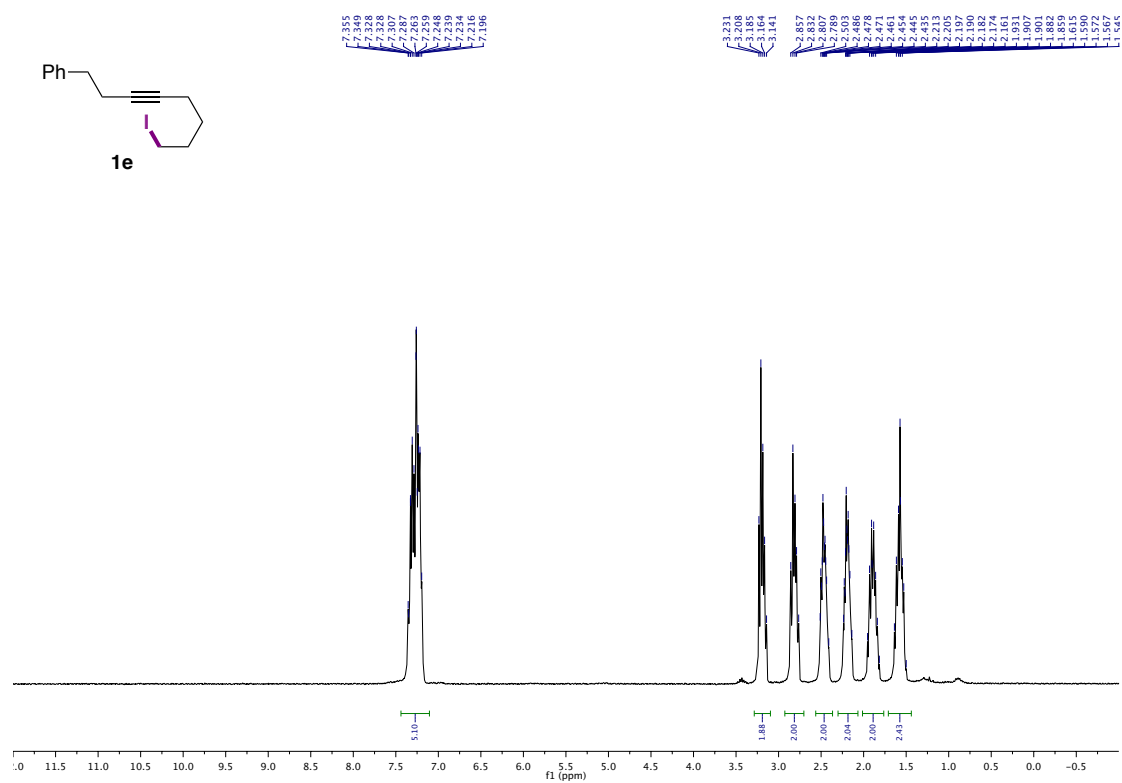
^1H , ^{13}C and ^{19}F NMR spectra

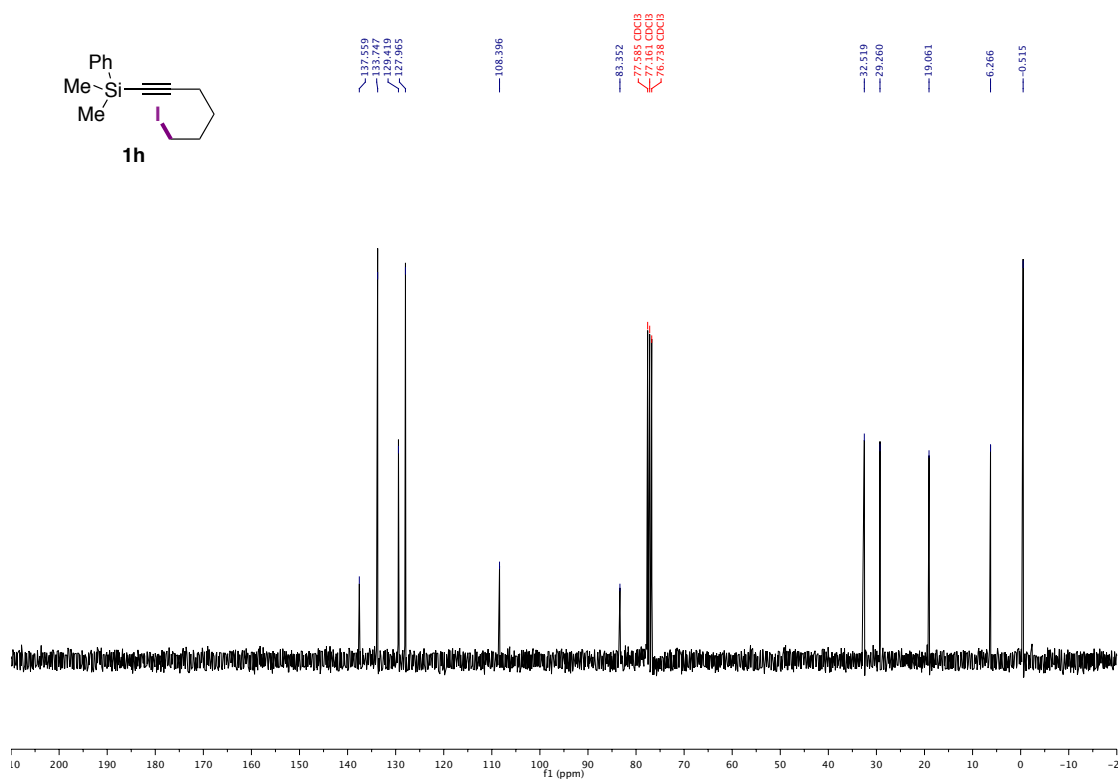
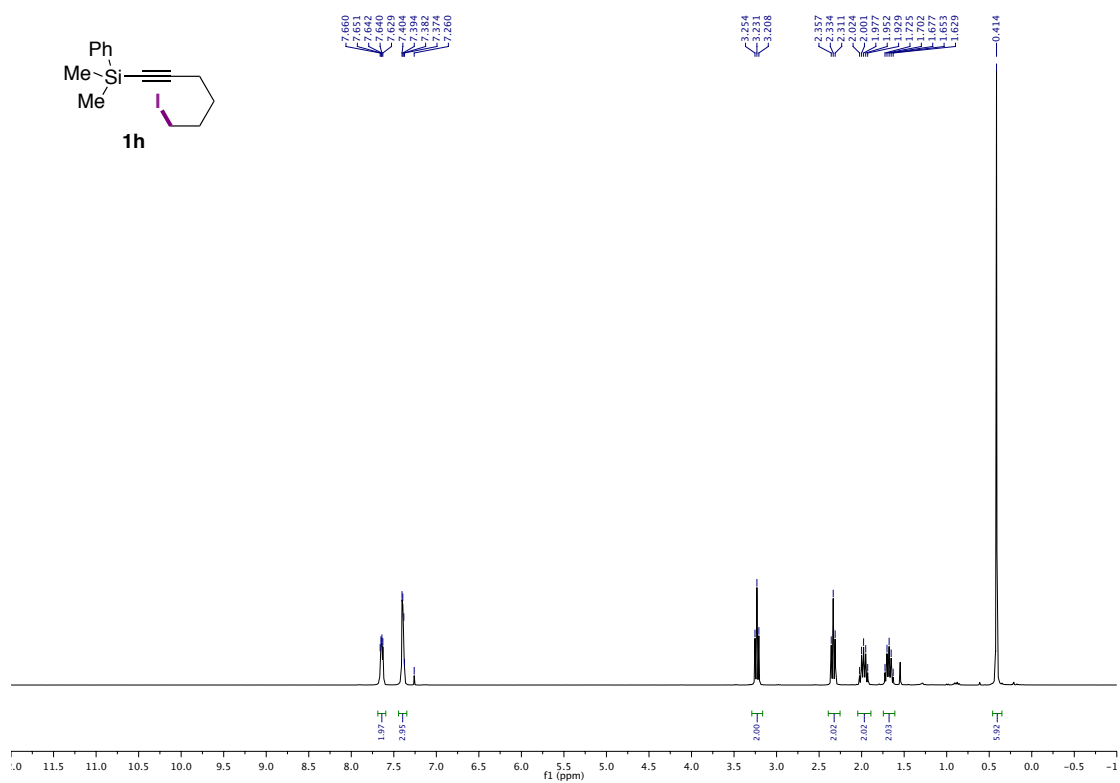


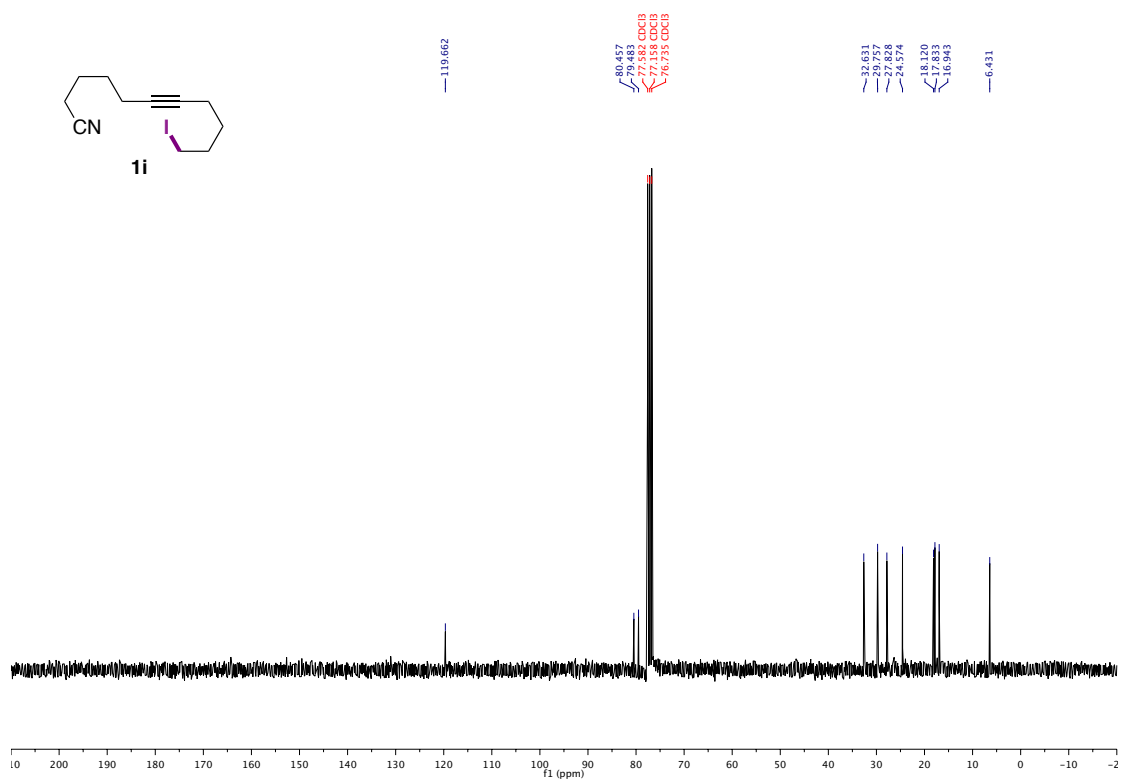
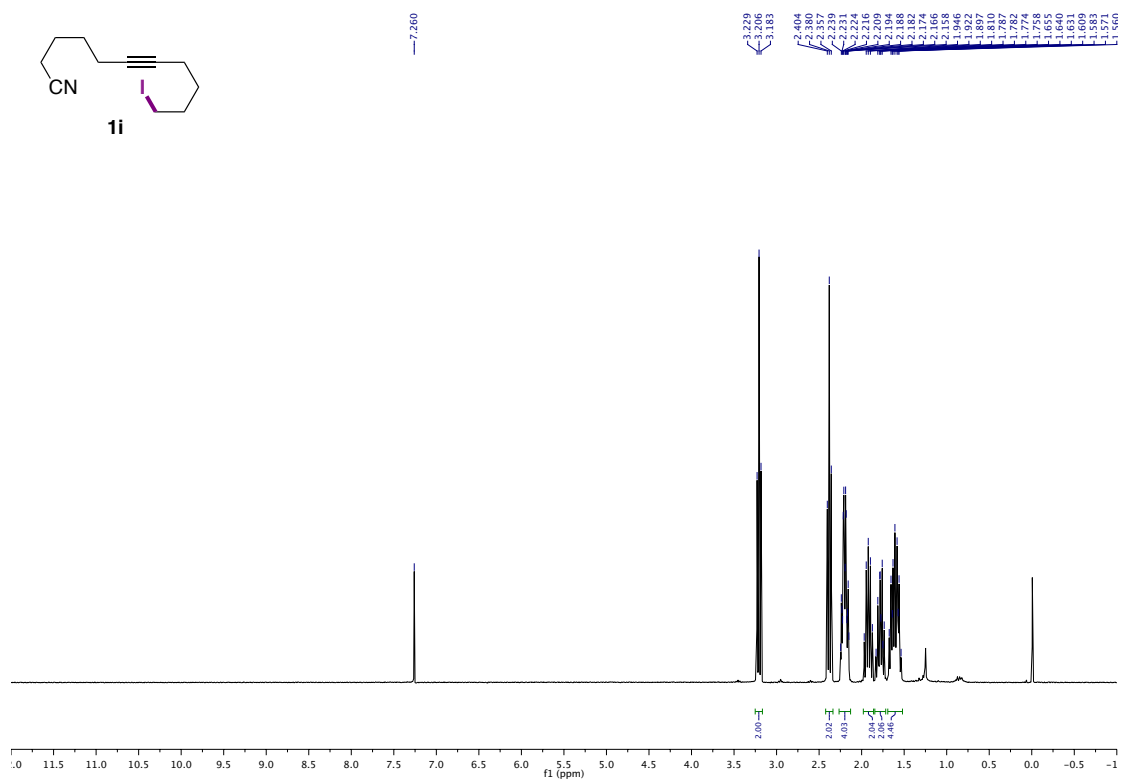


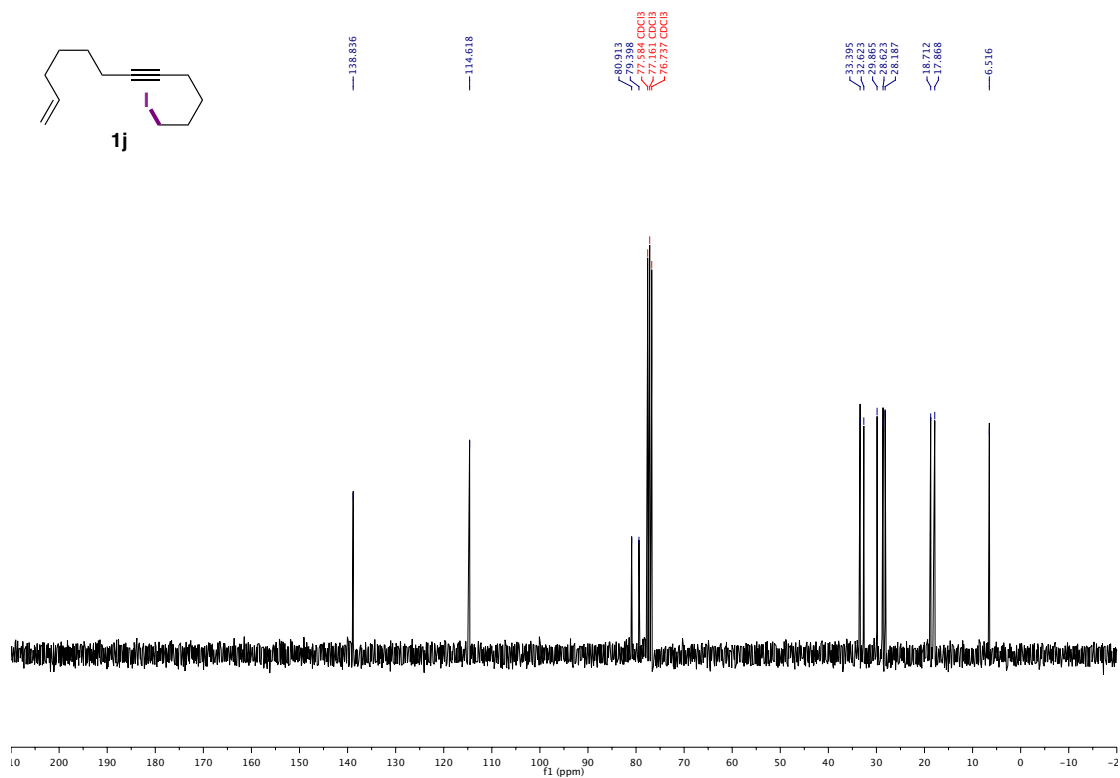
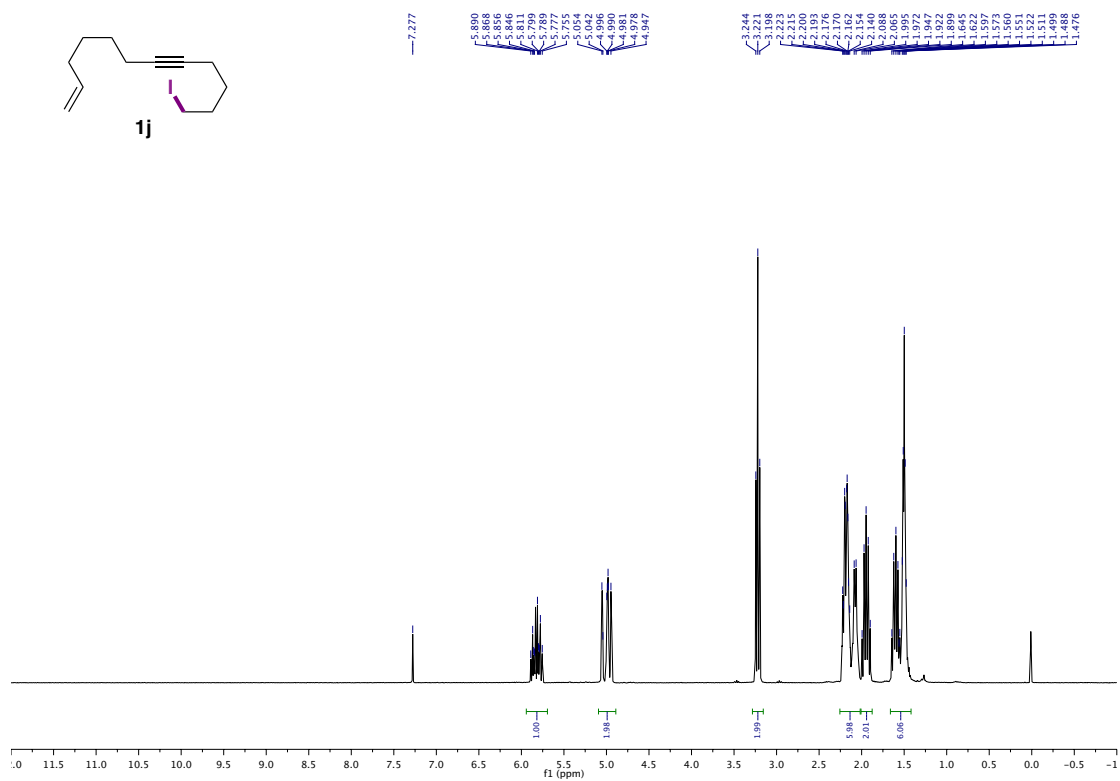


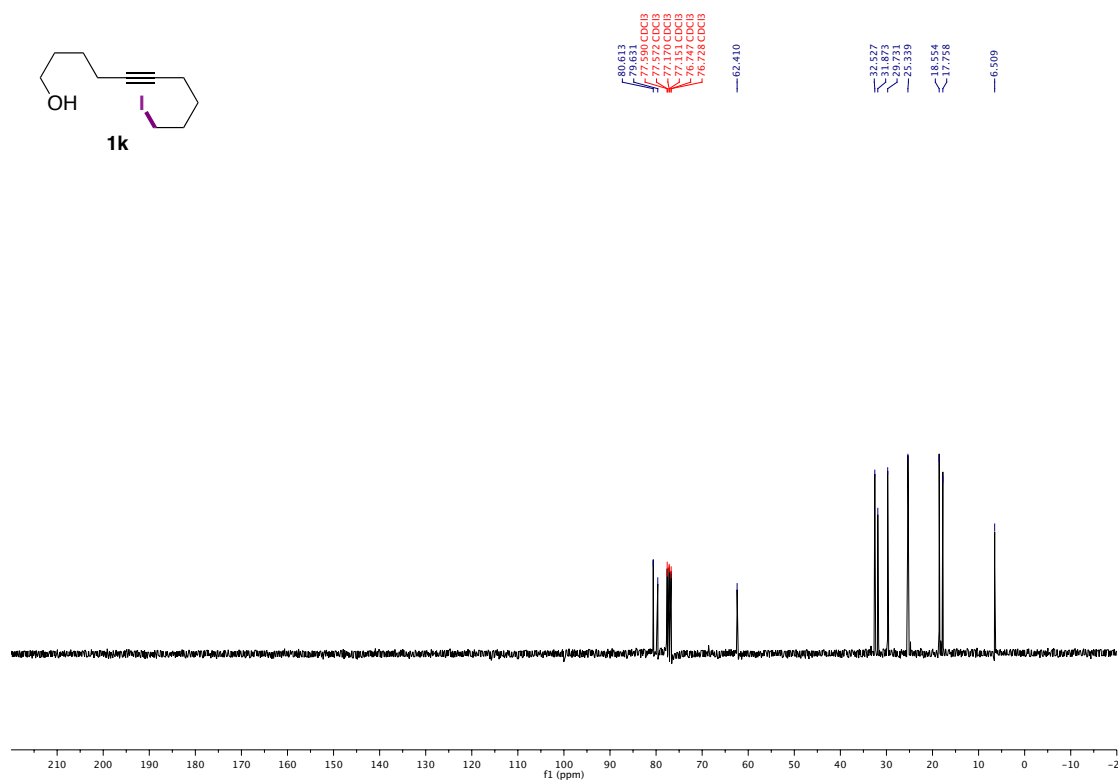
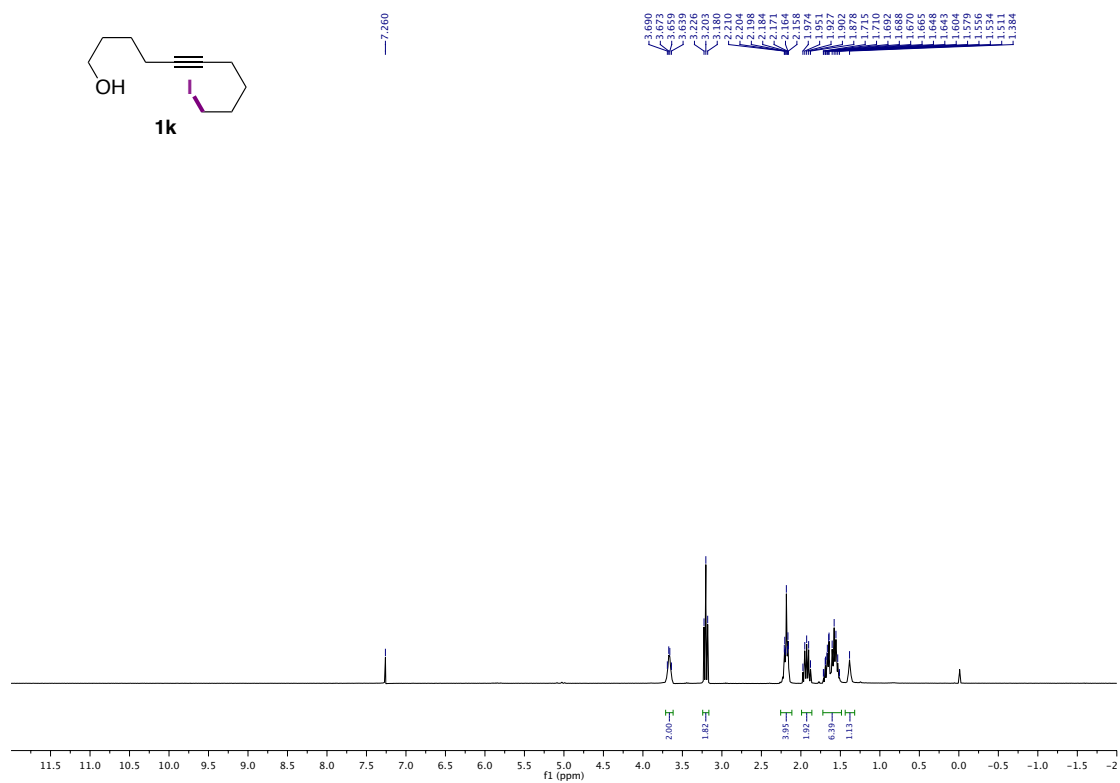


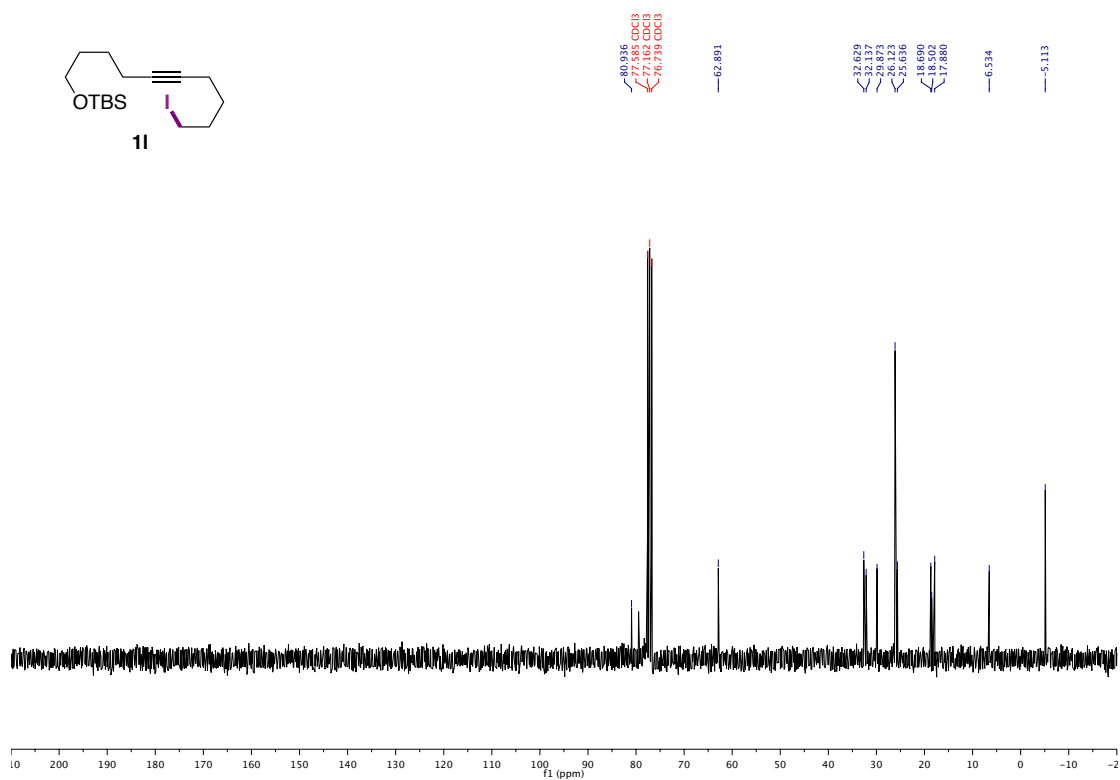
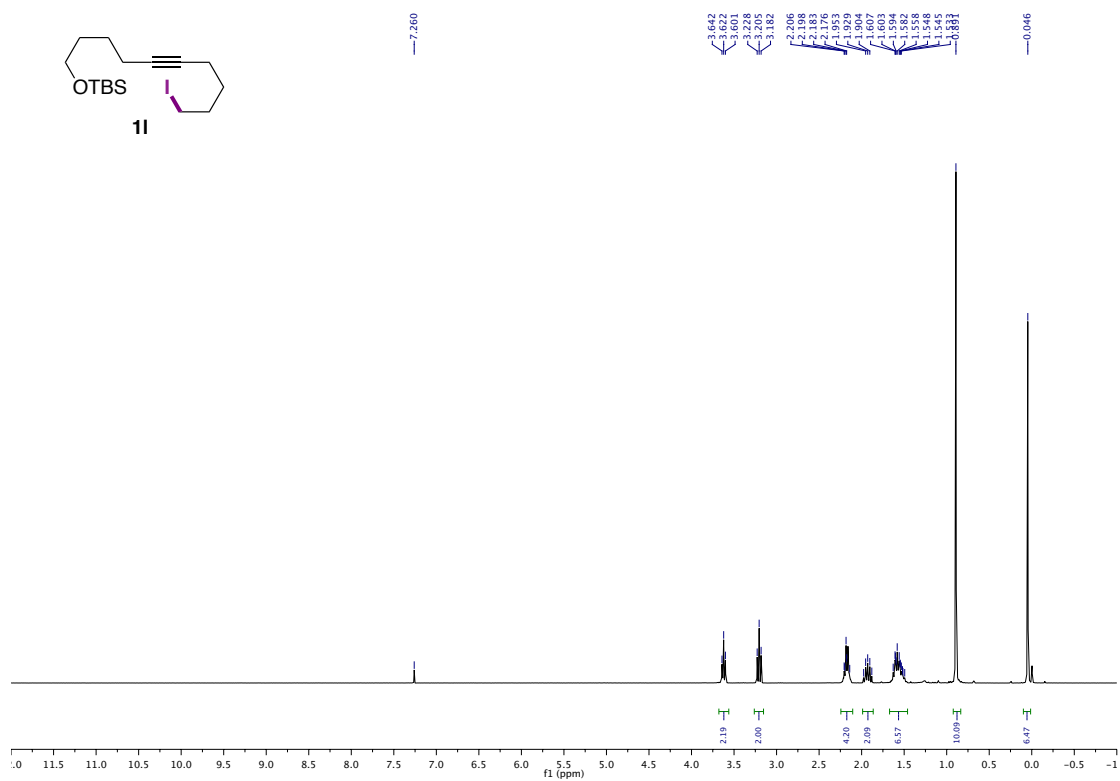


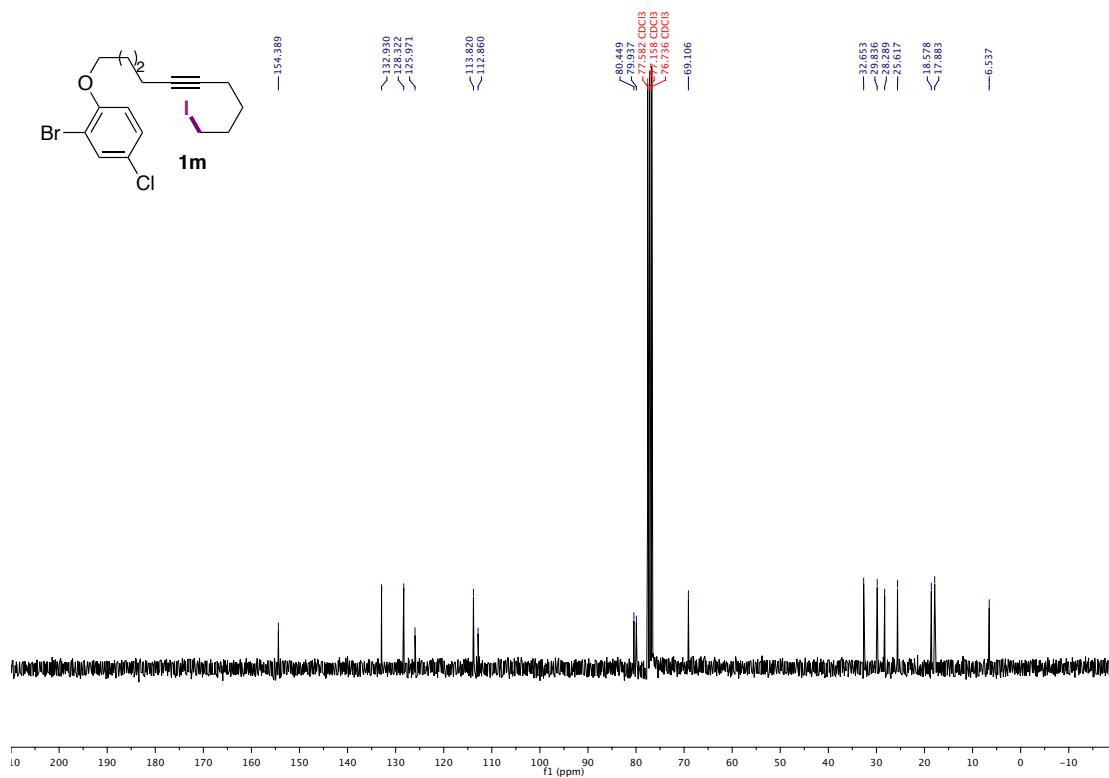
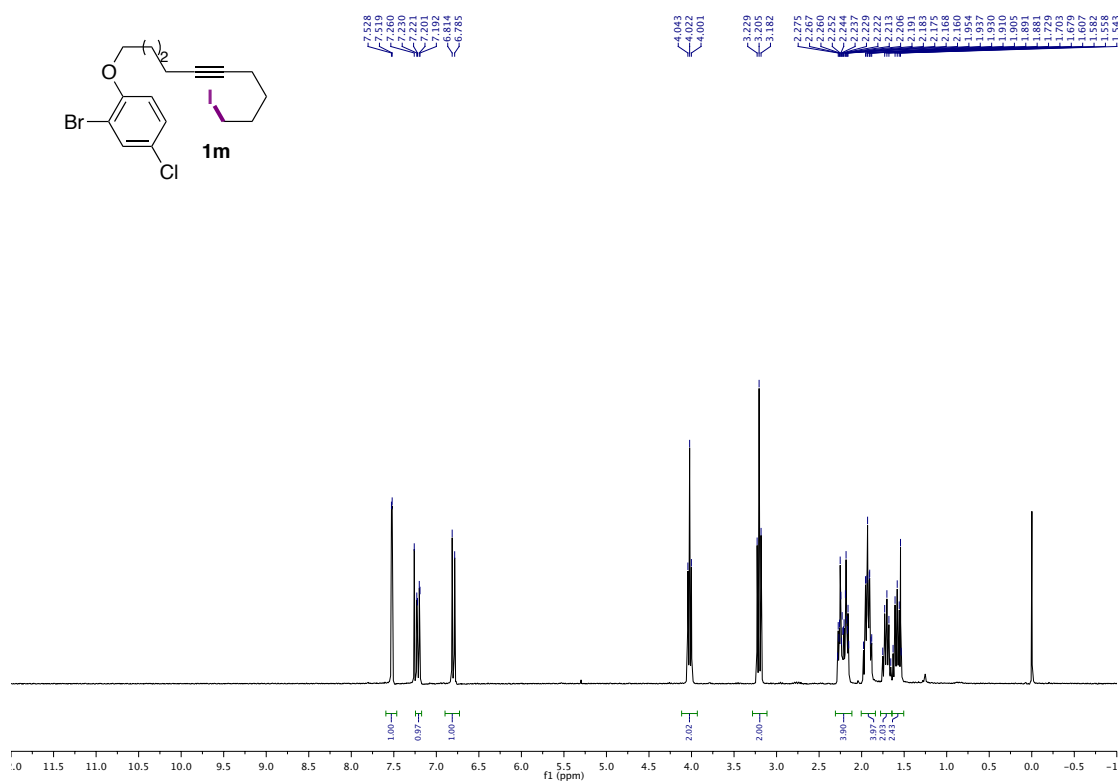


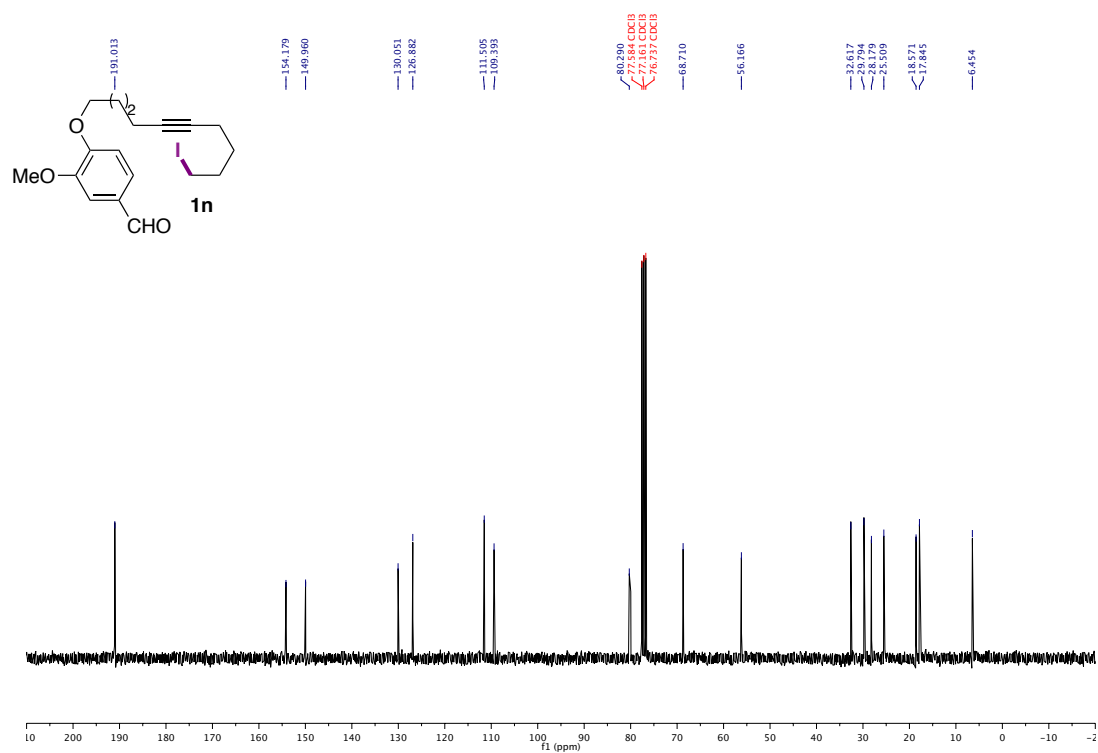
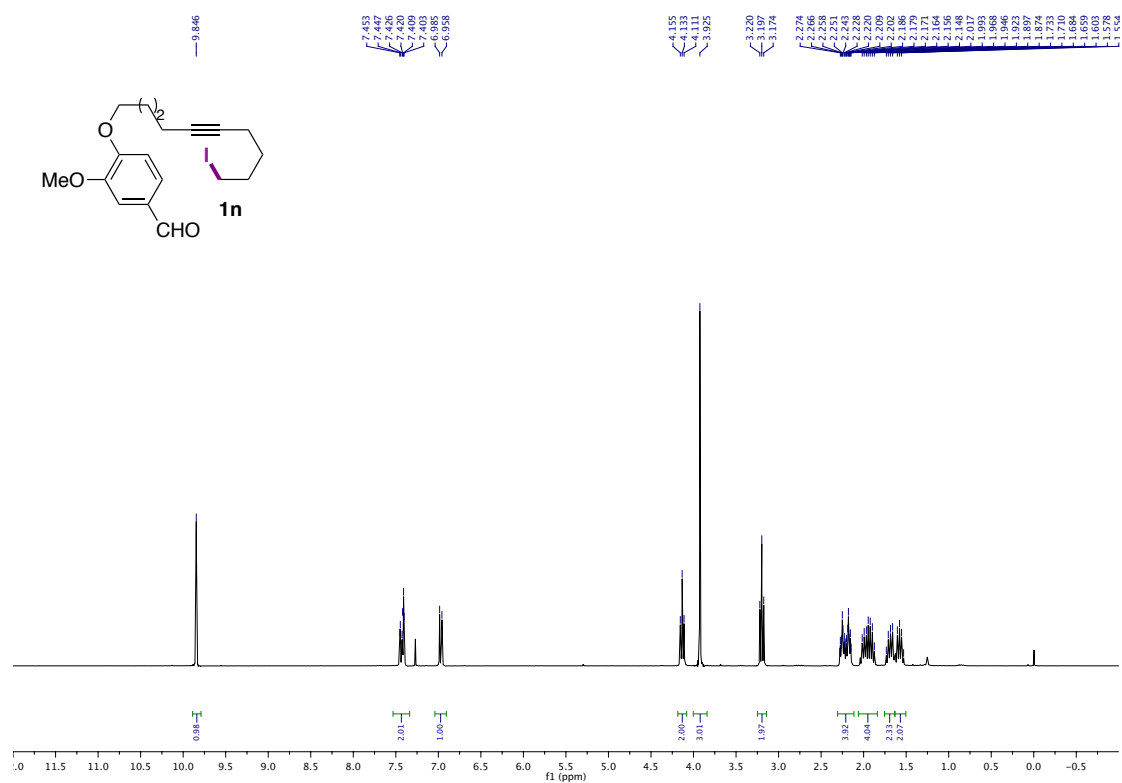


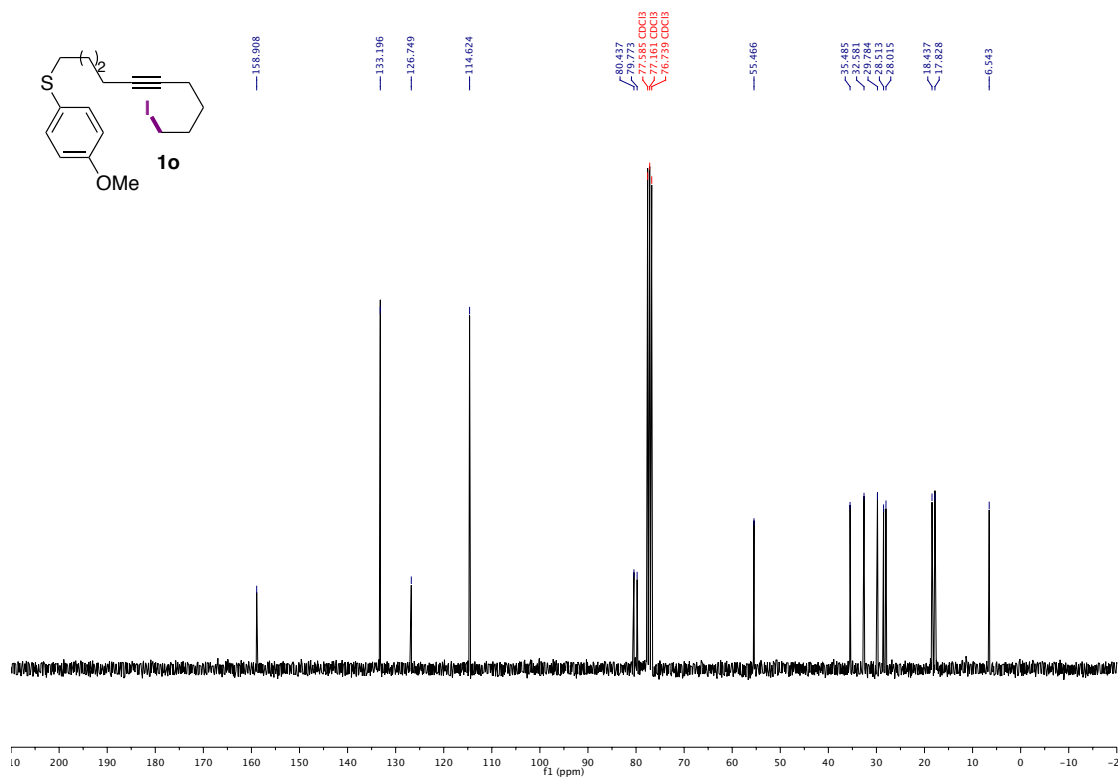
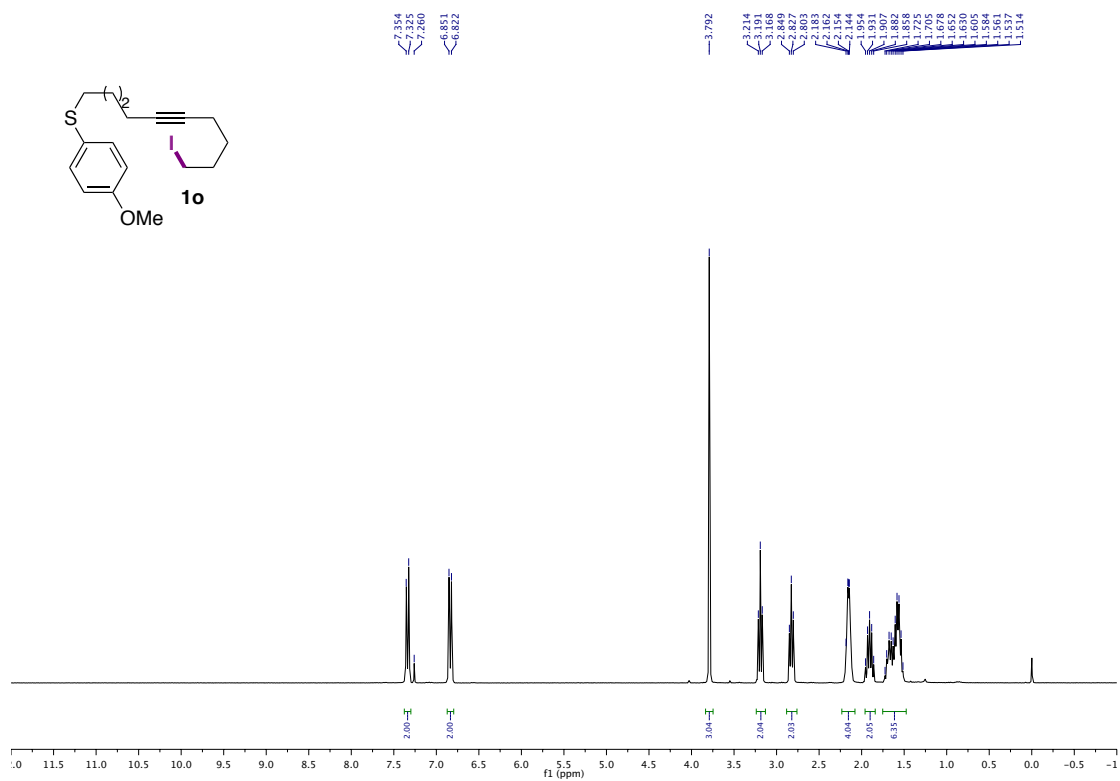


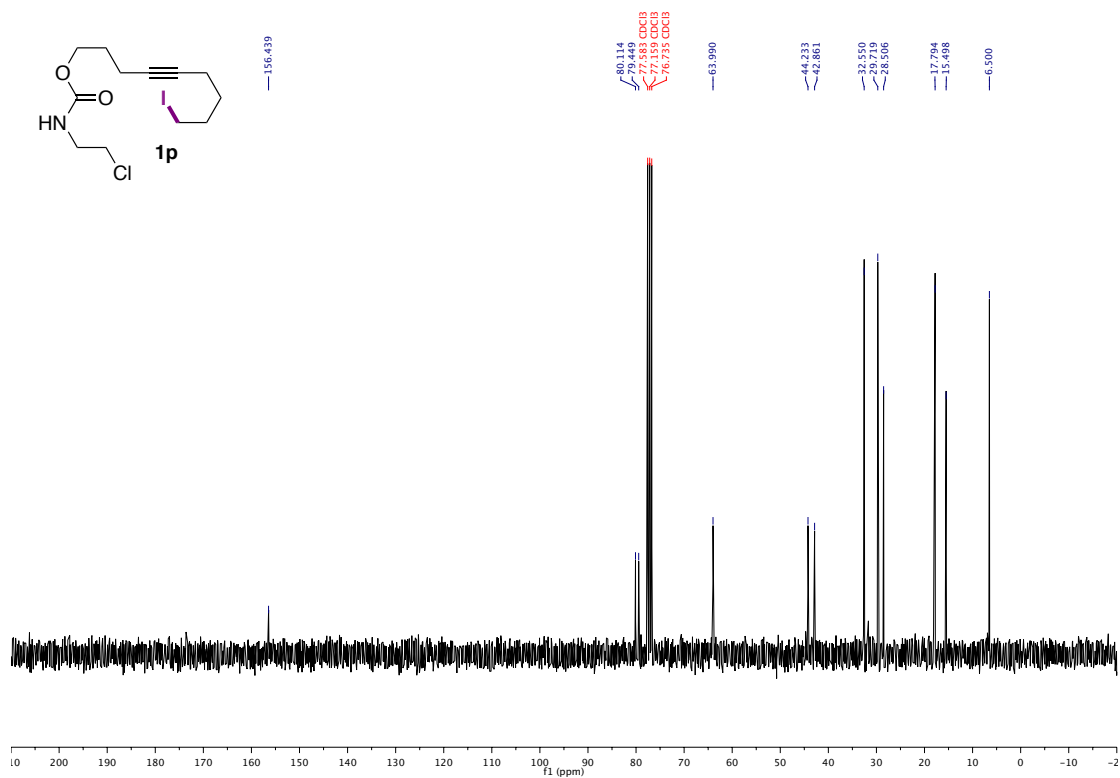
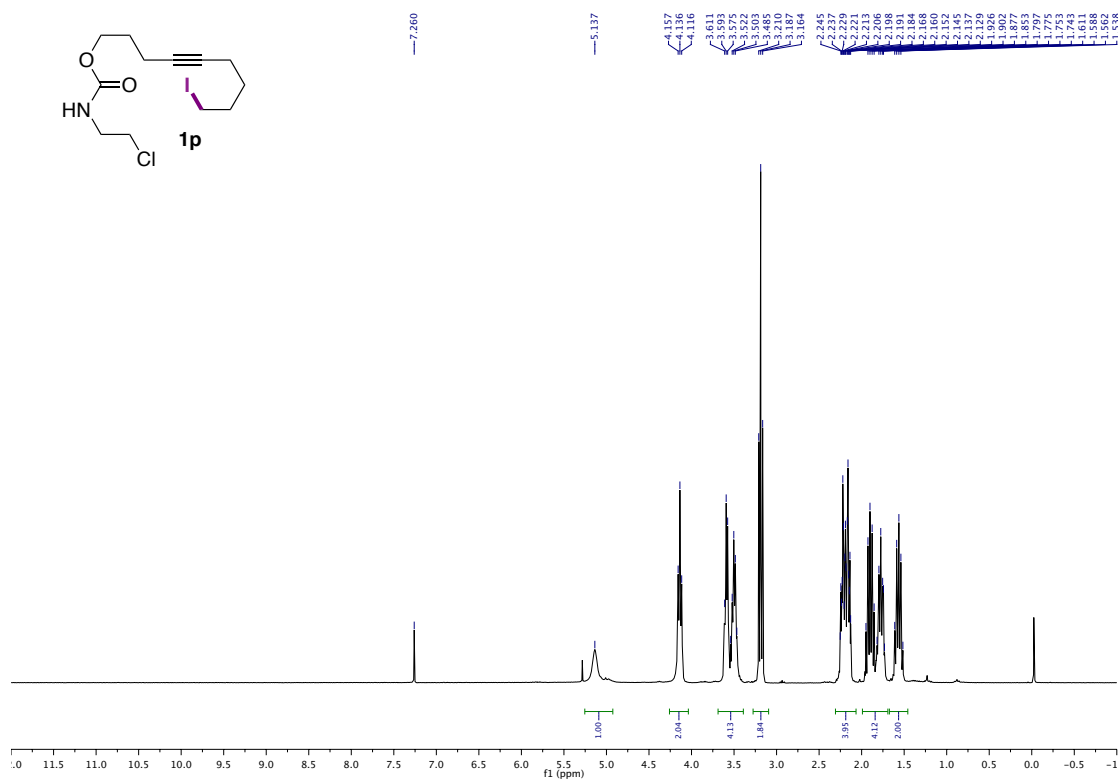


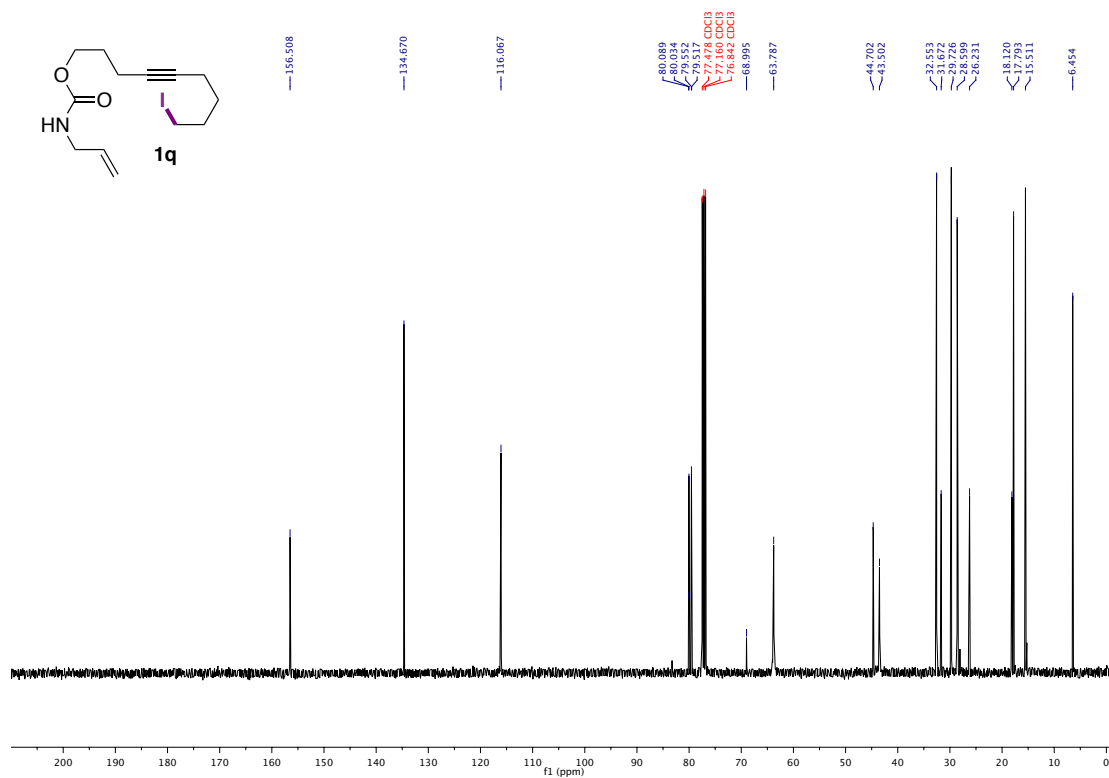
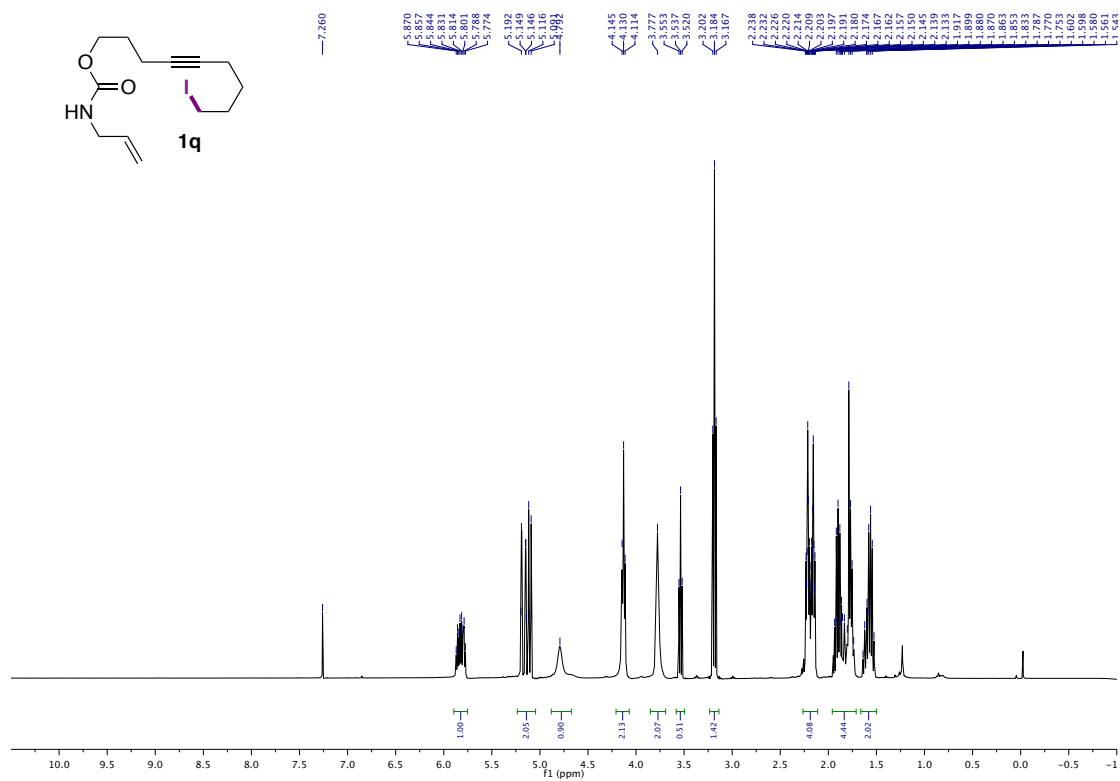


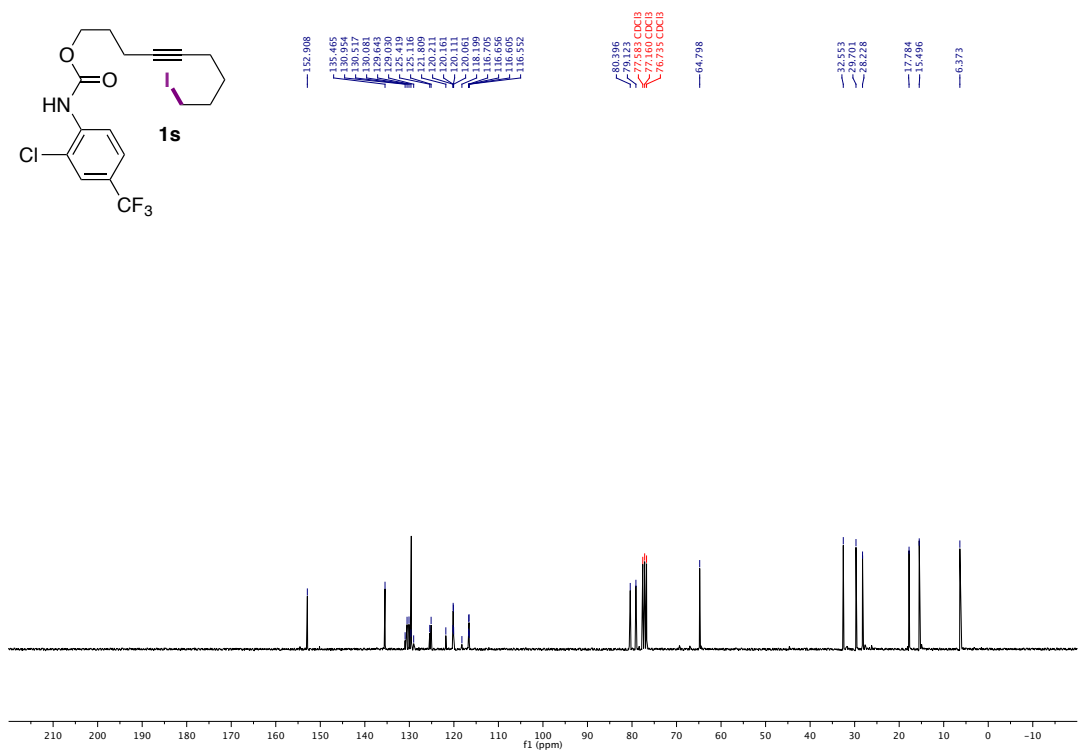
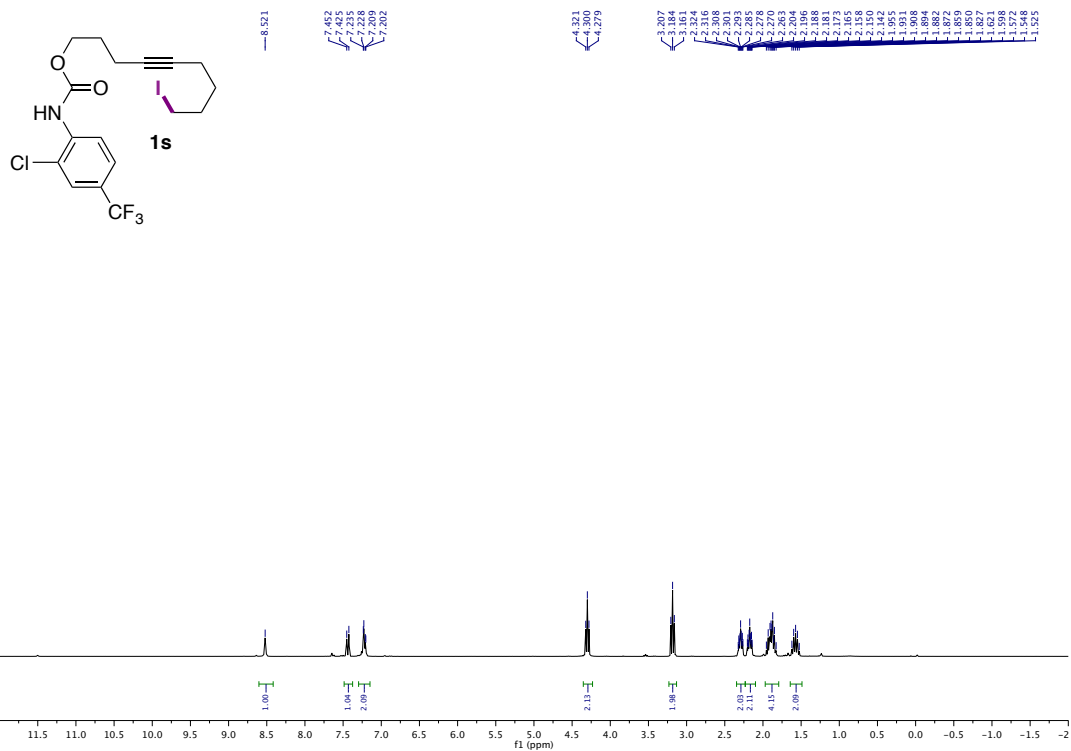


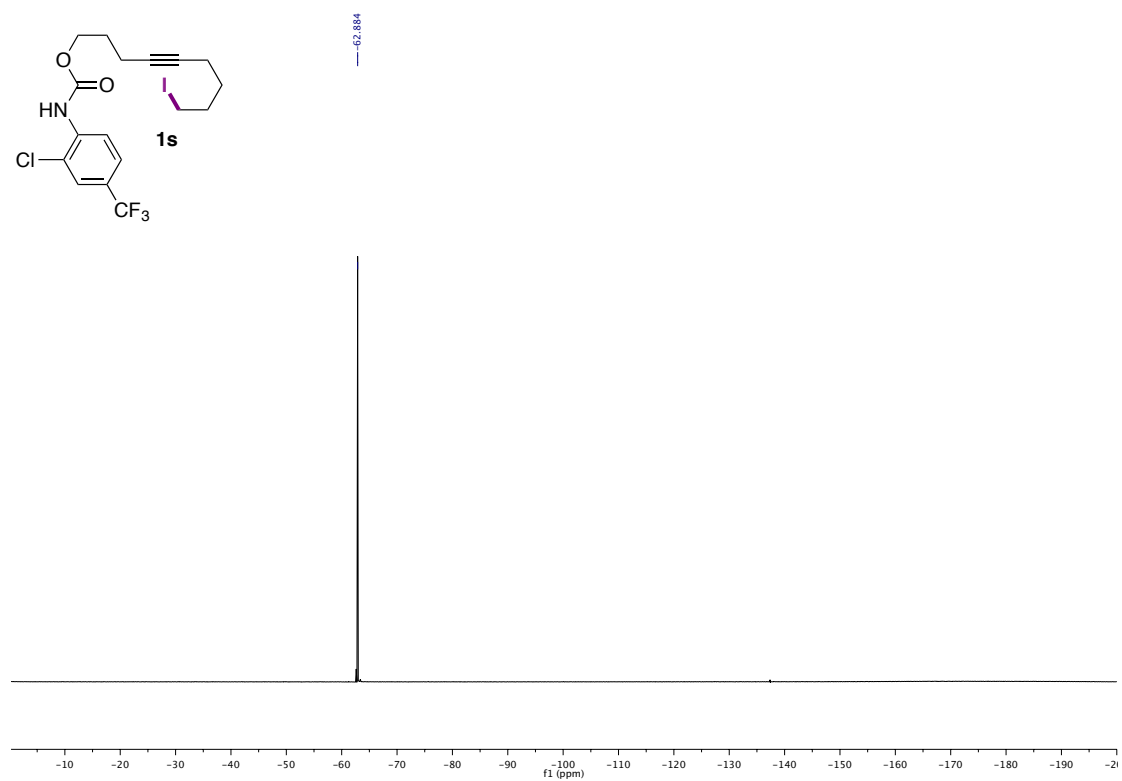


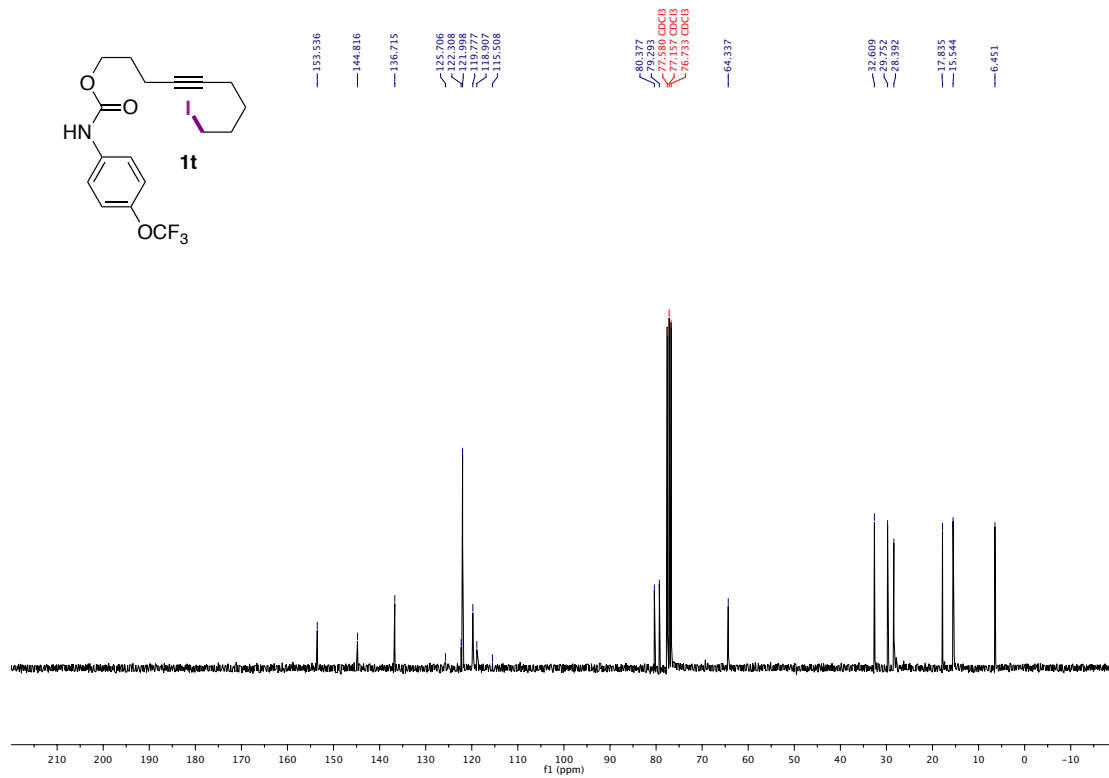
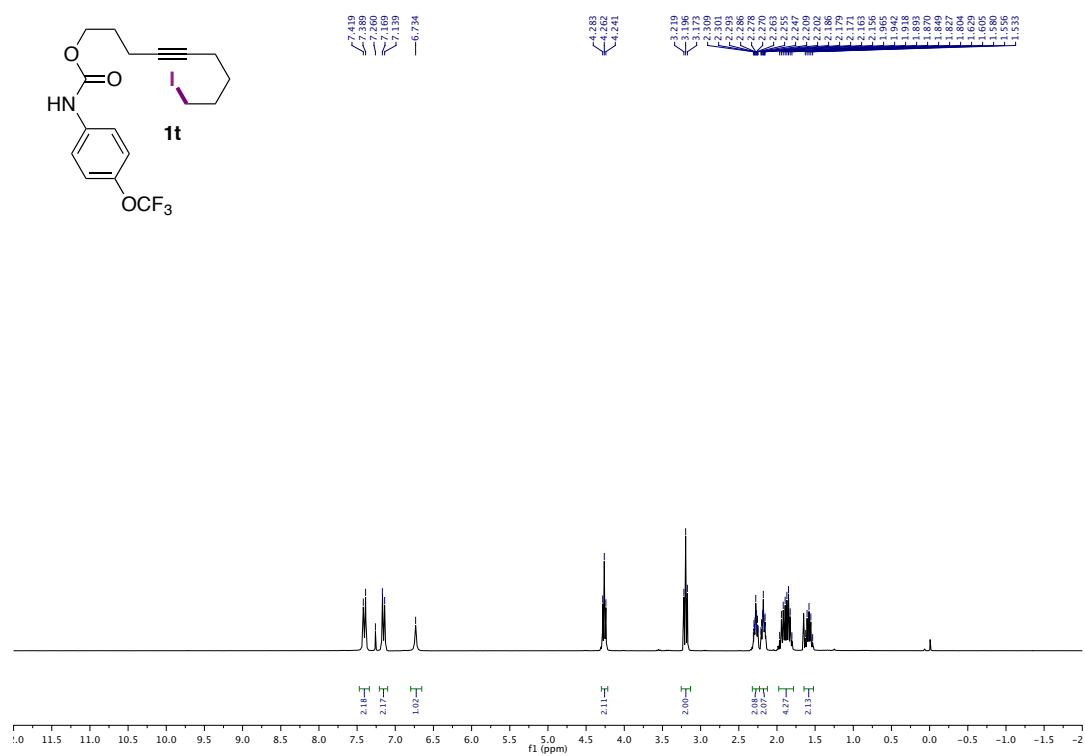


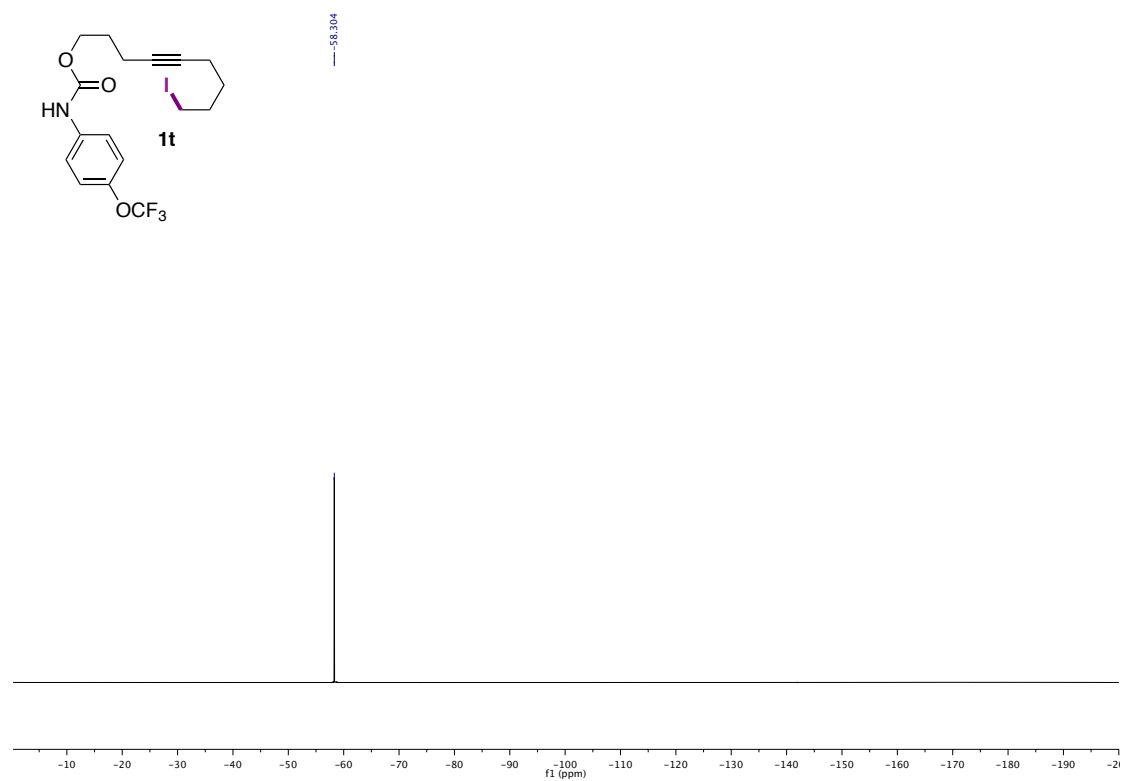


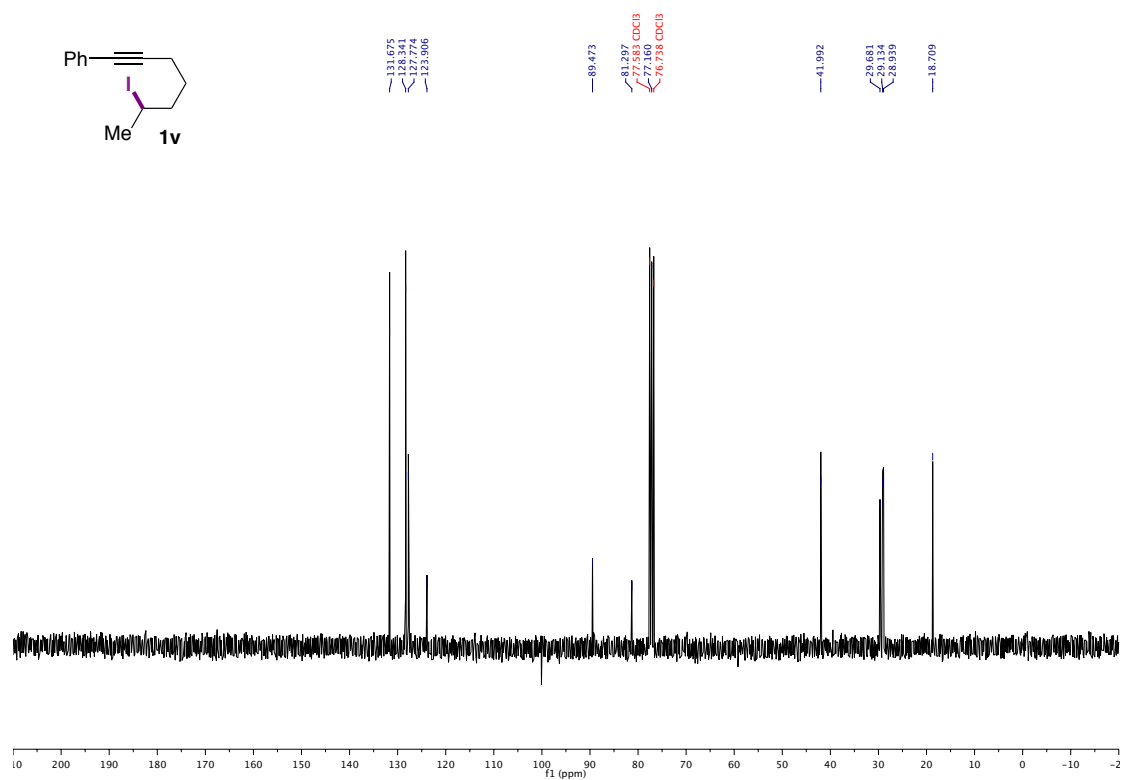
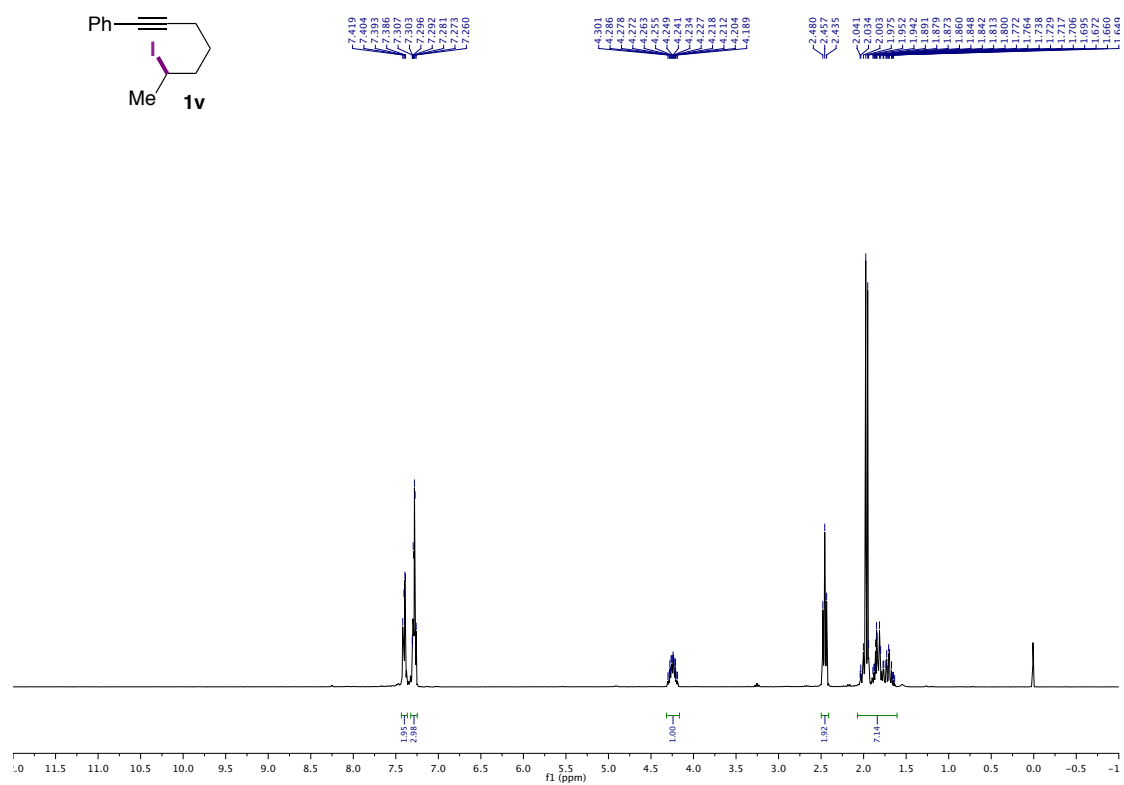


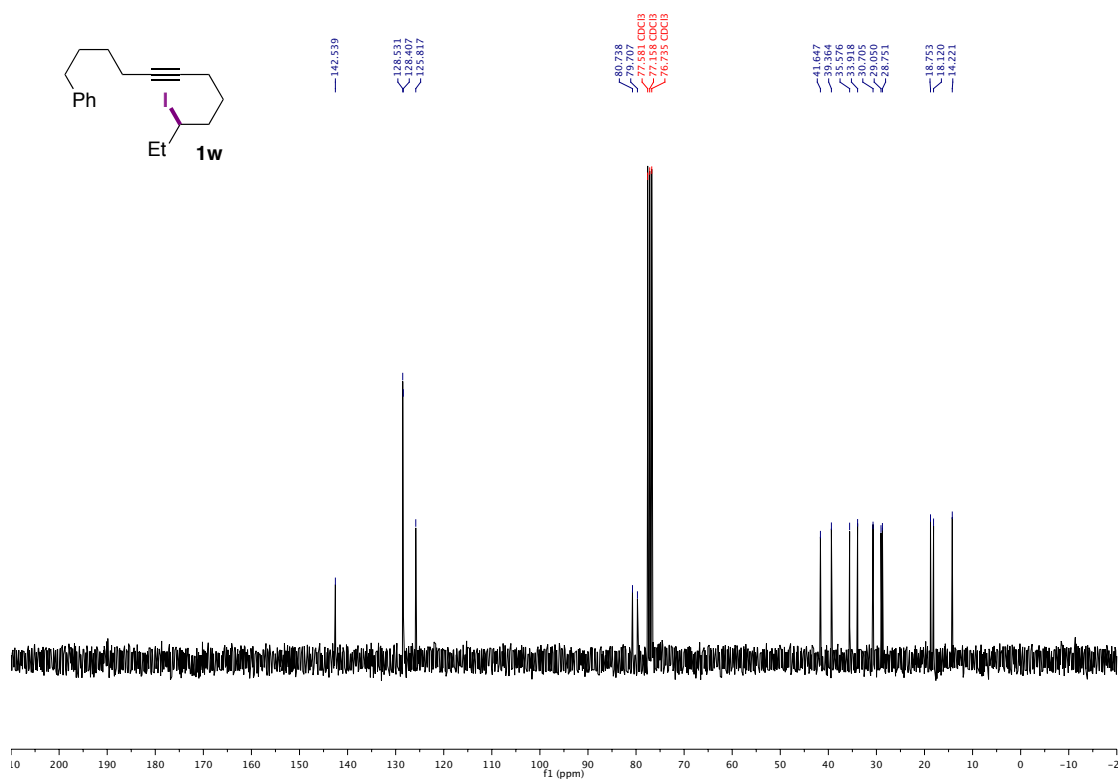
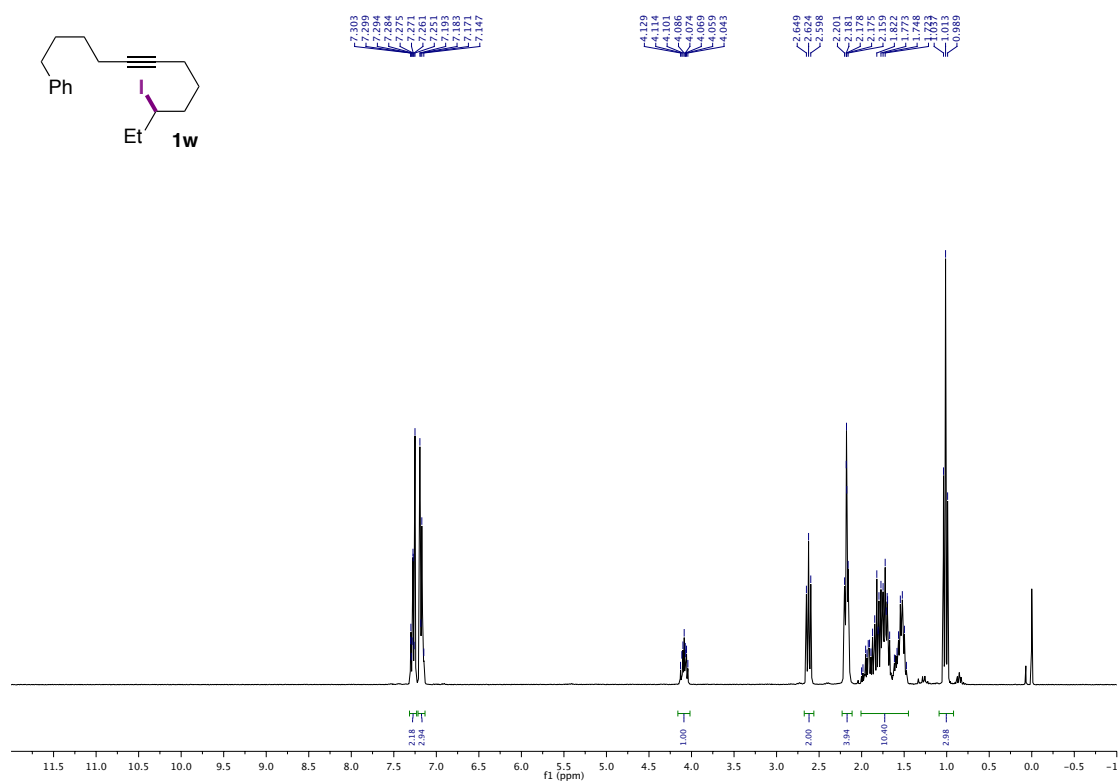


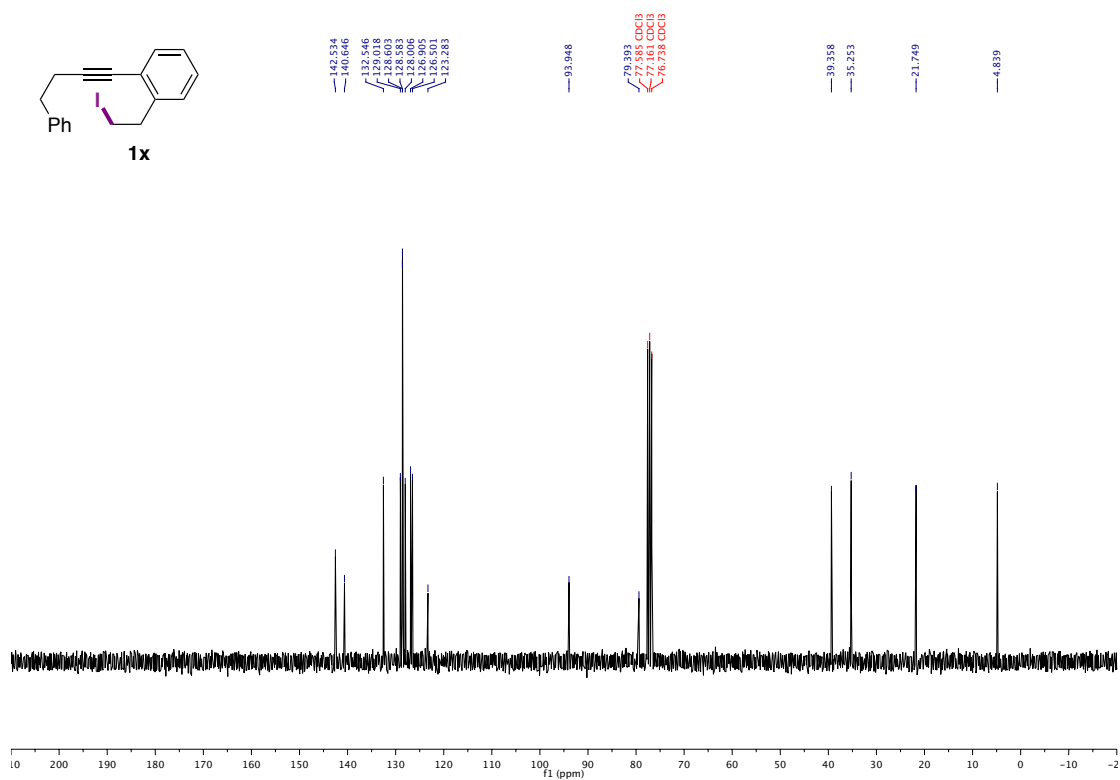
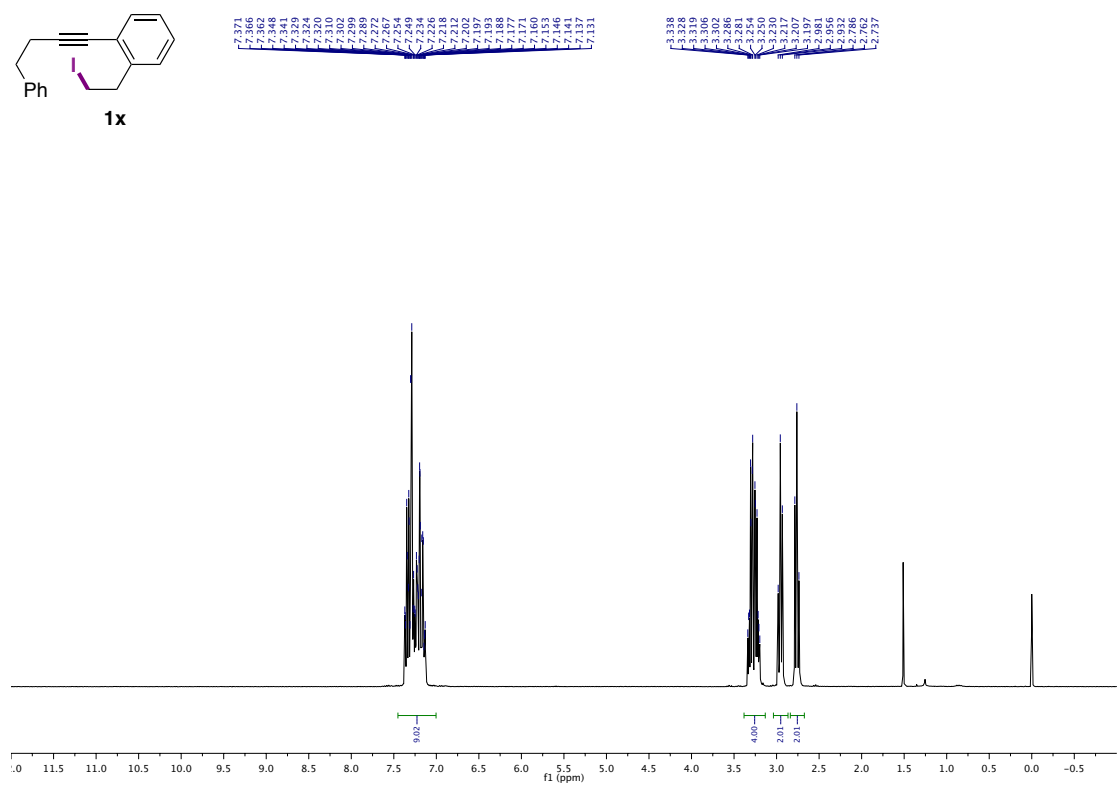


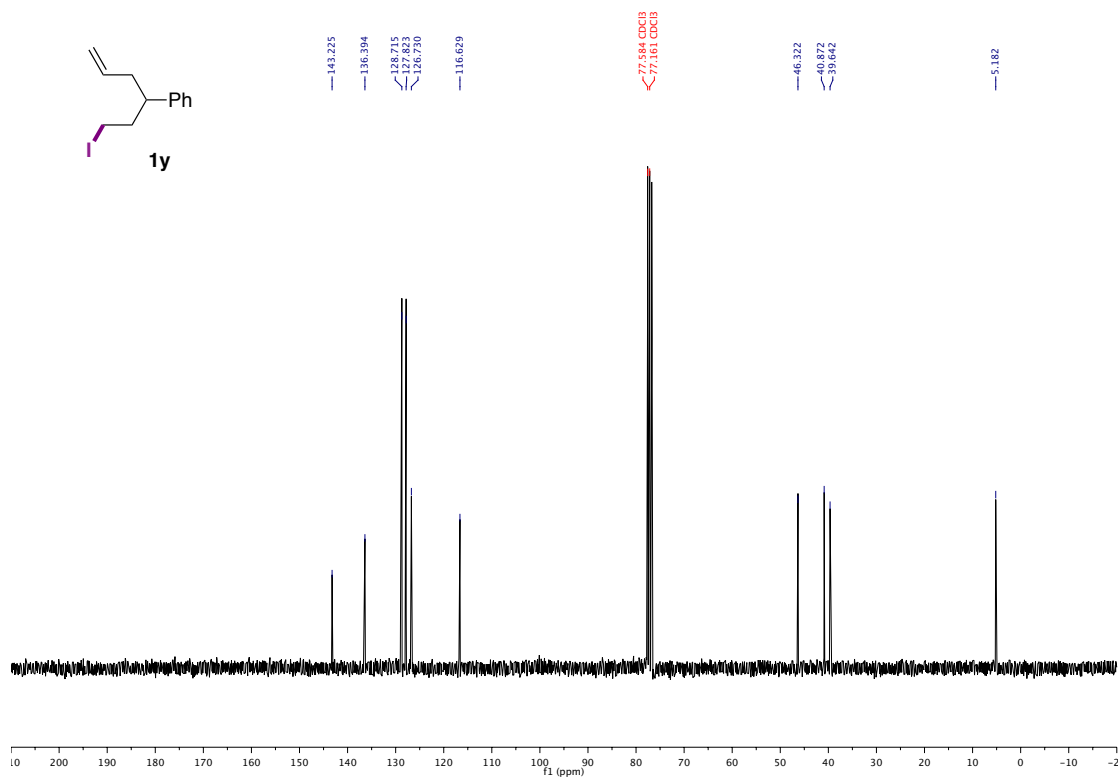
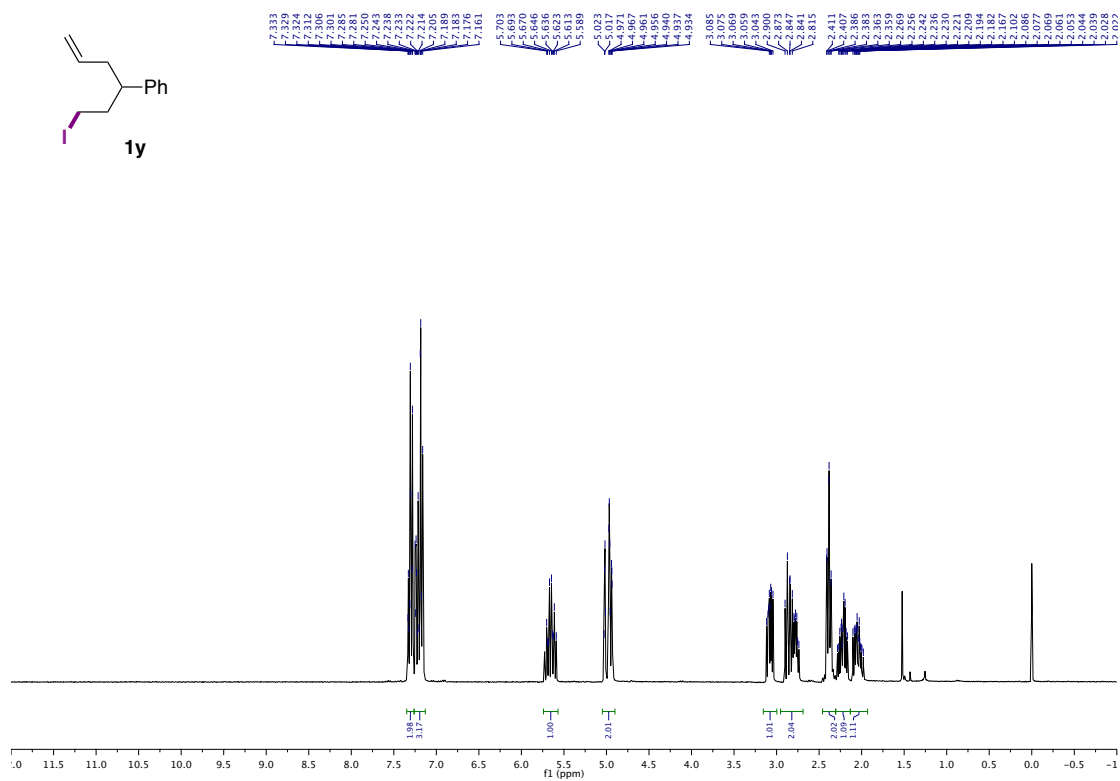


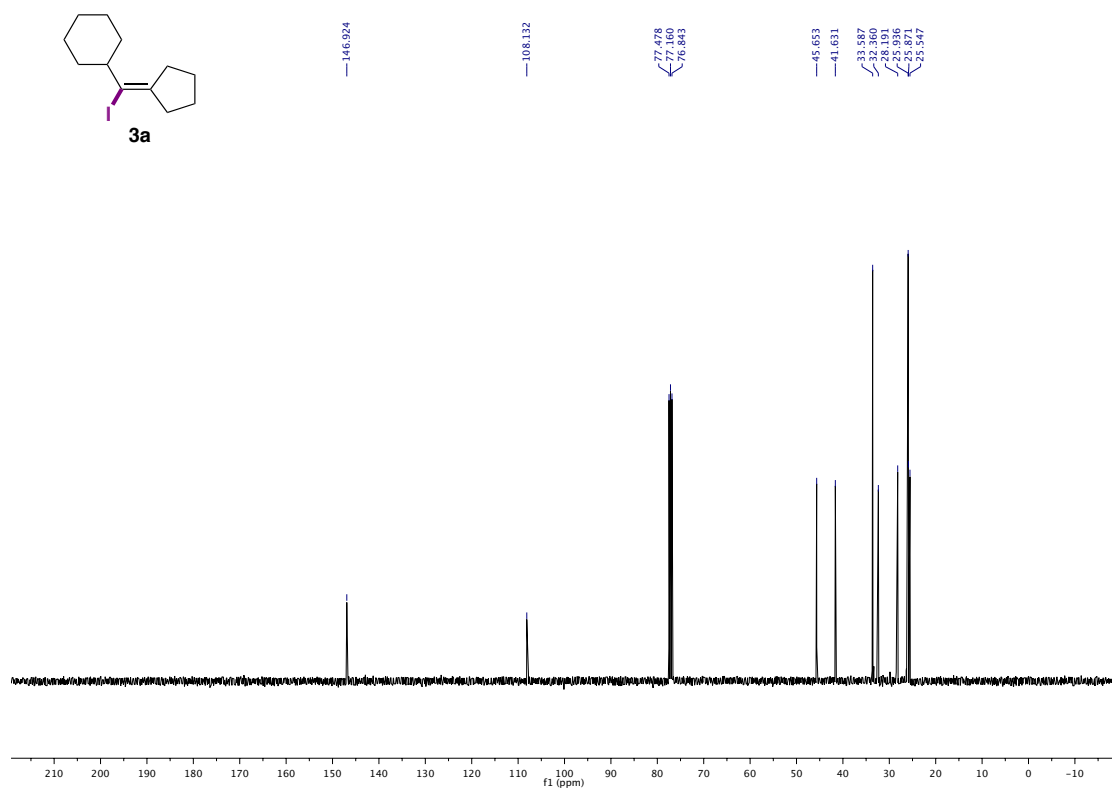
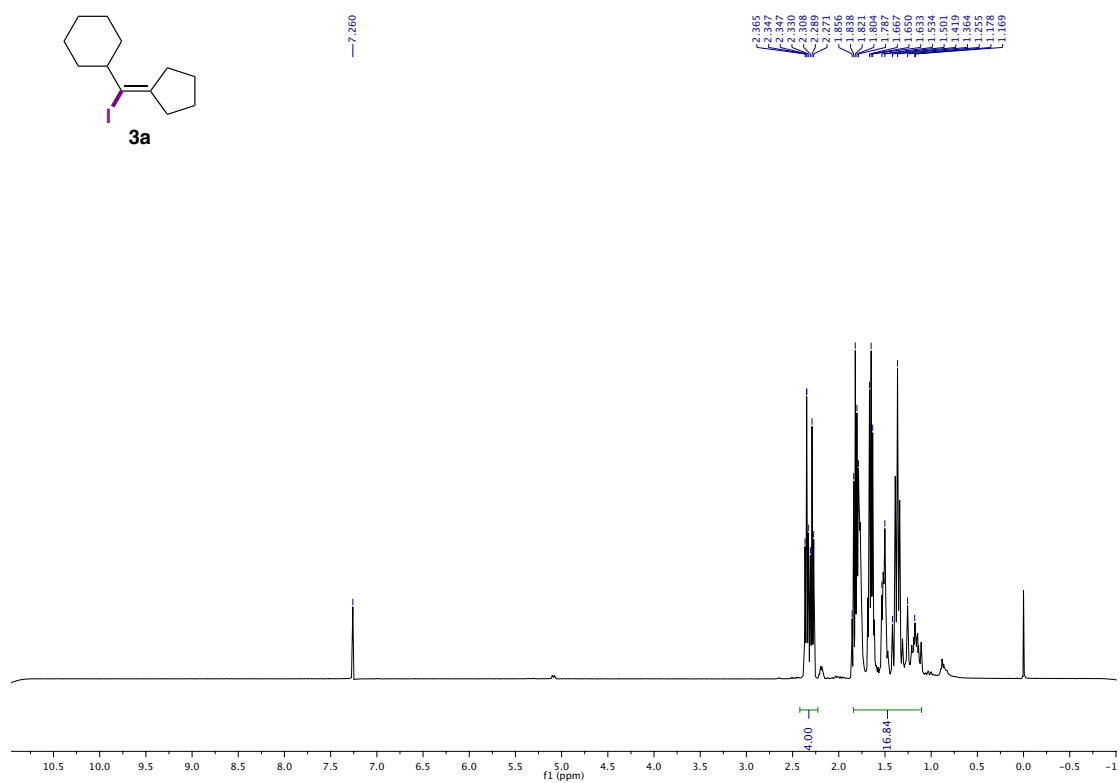


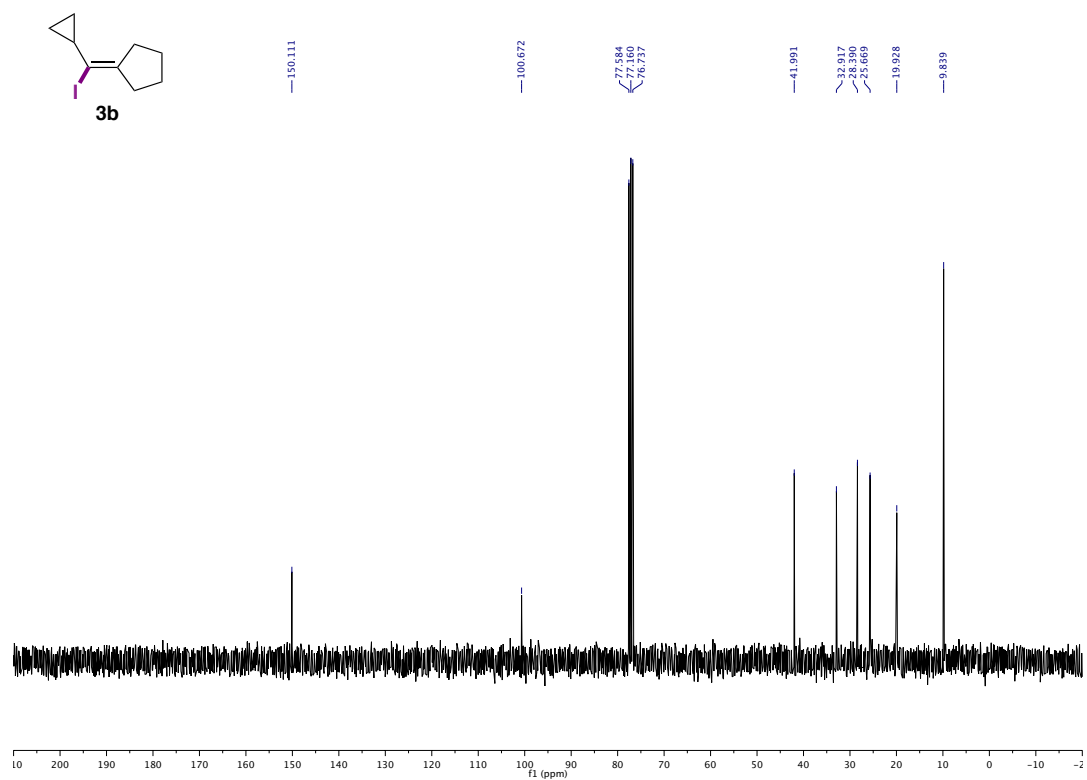
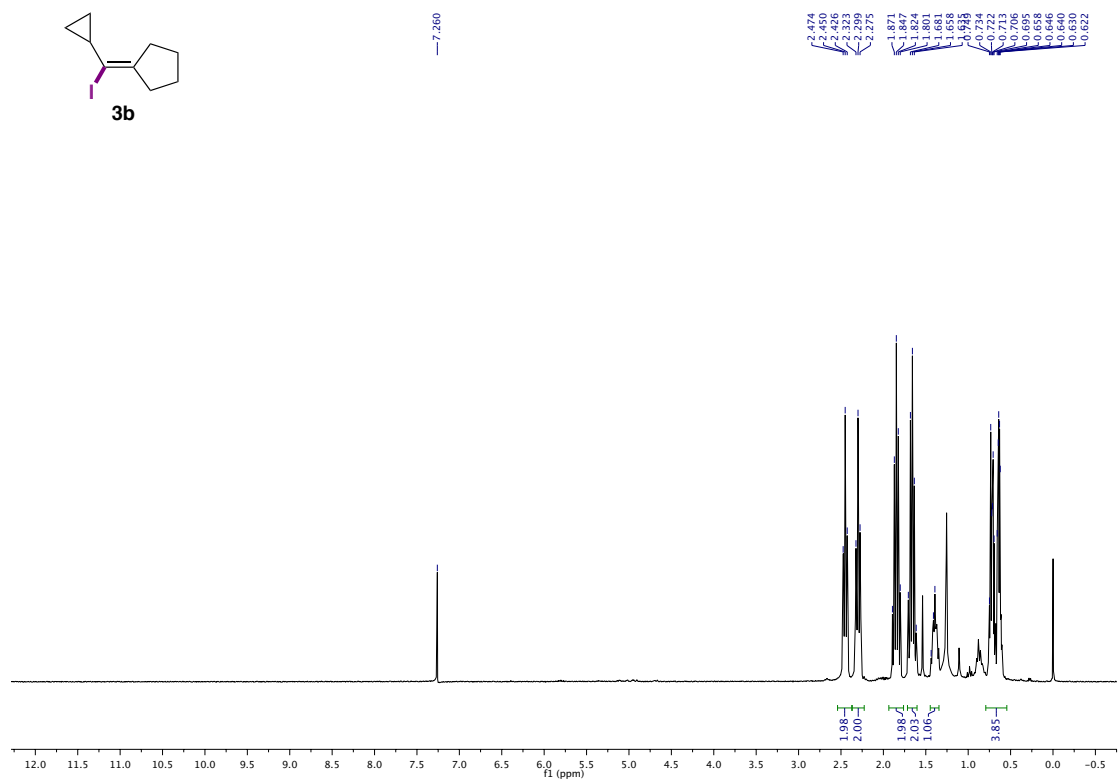


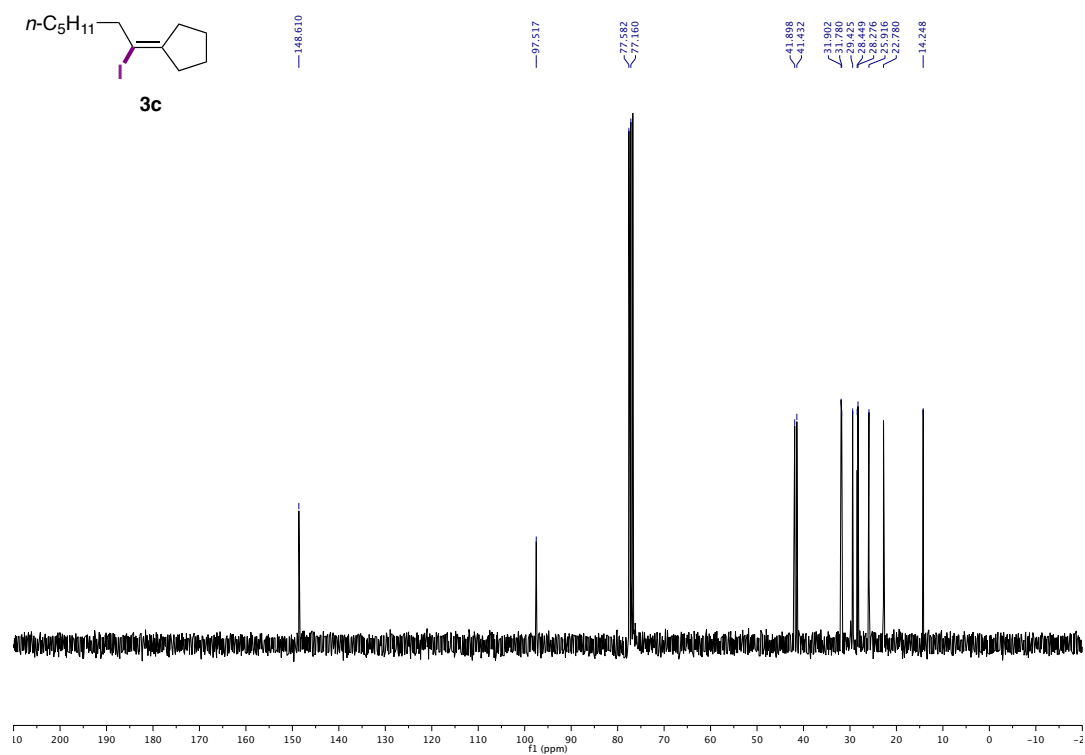
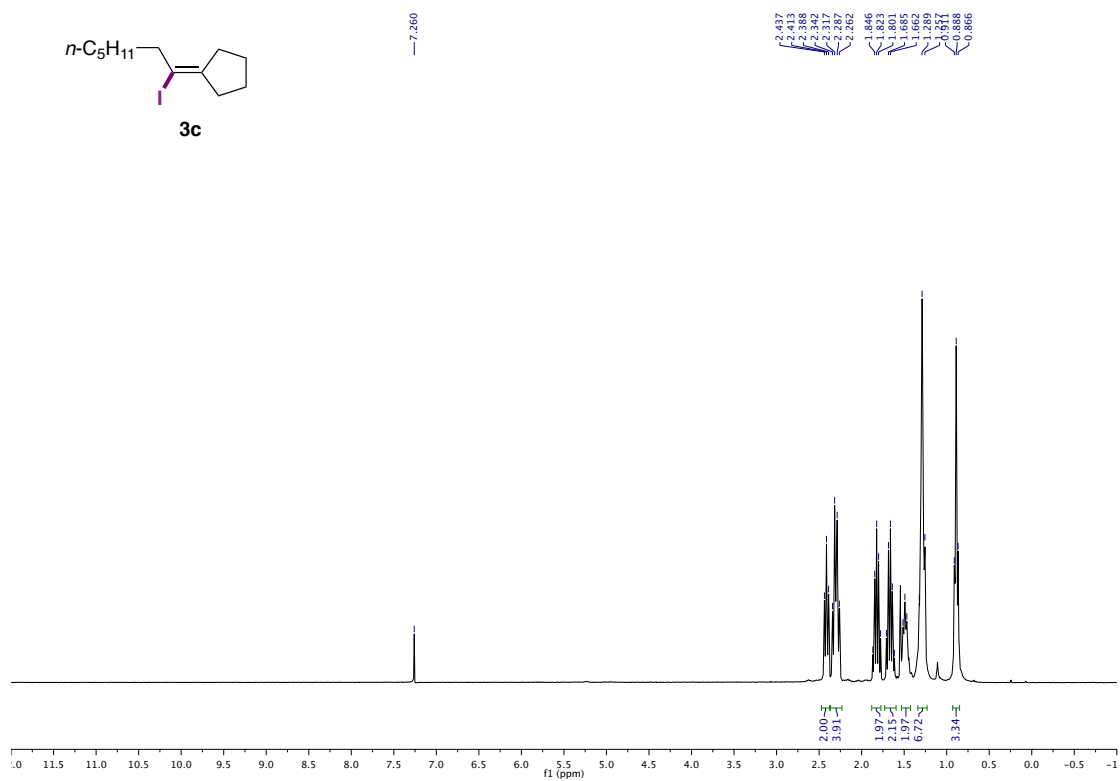


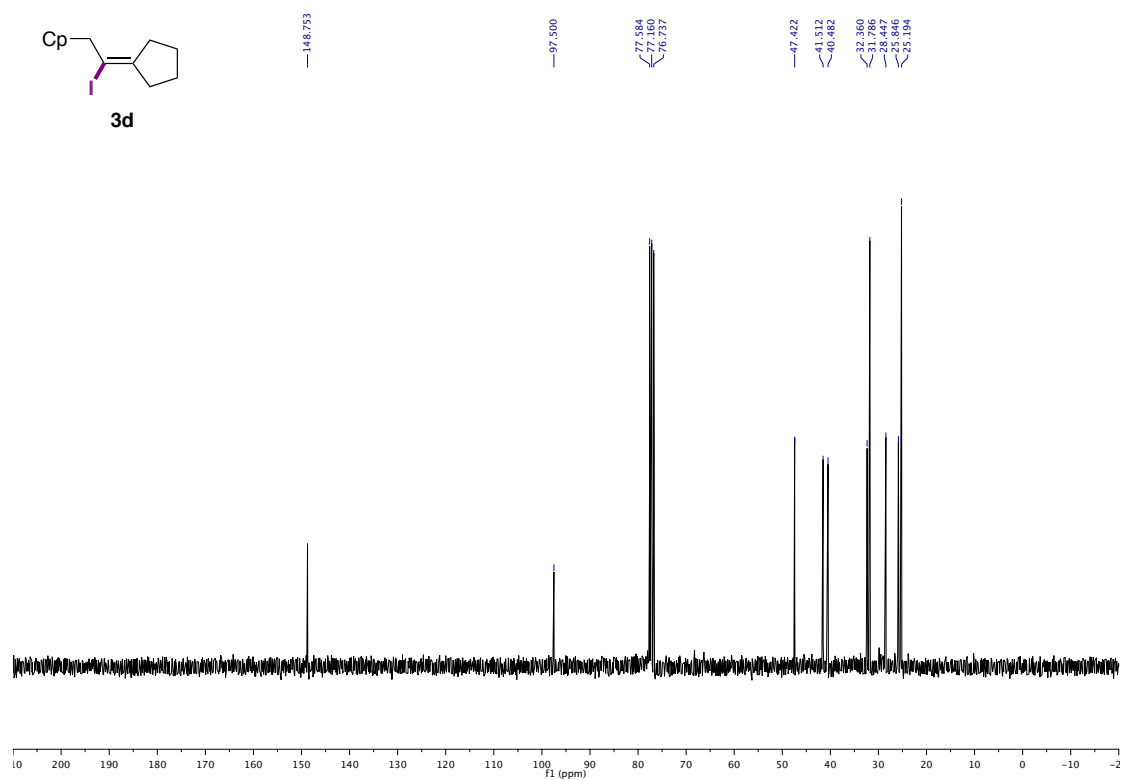
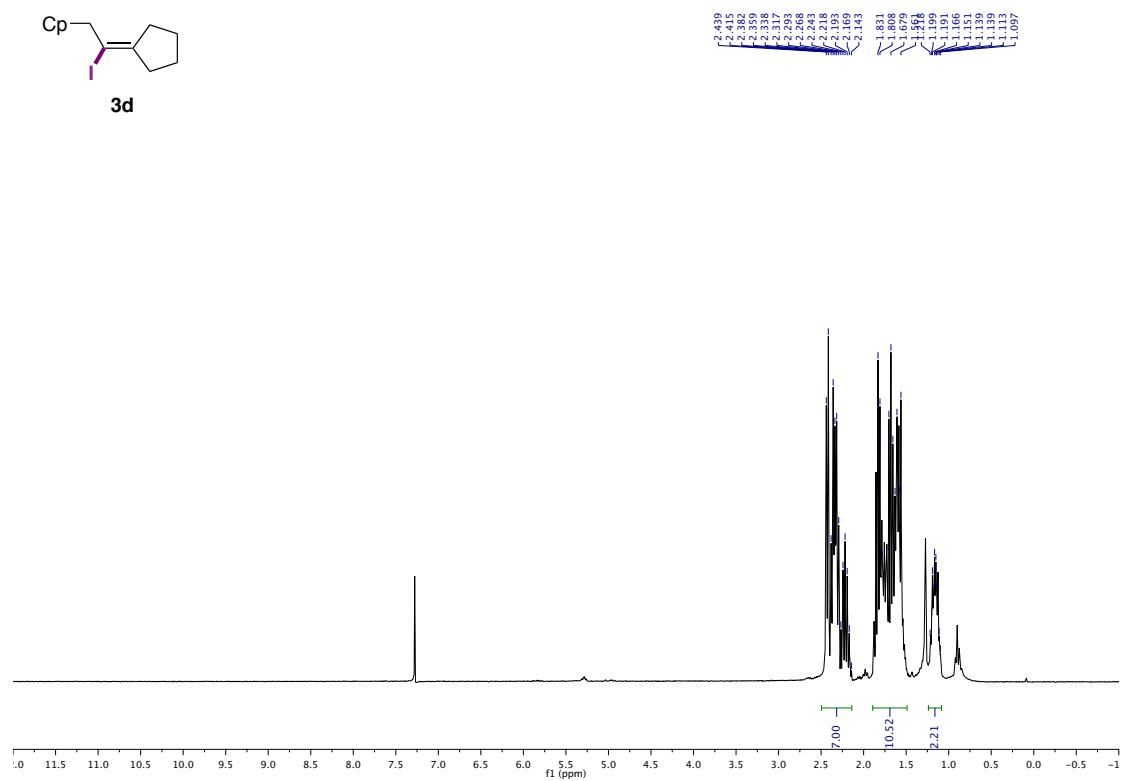


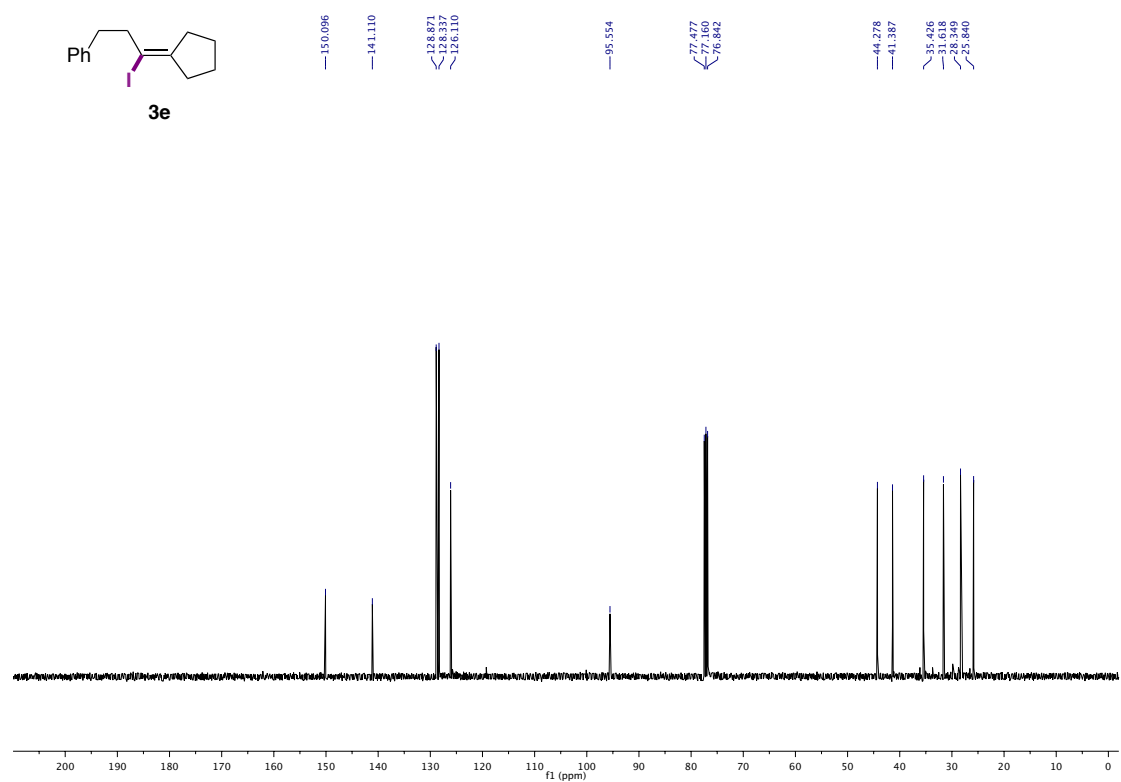
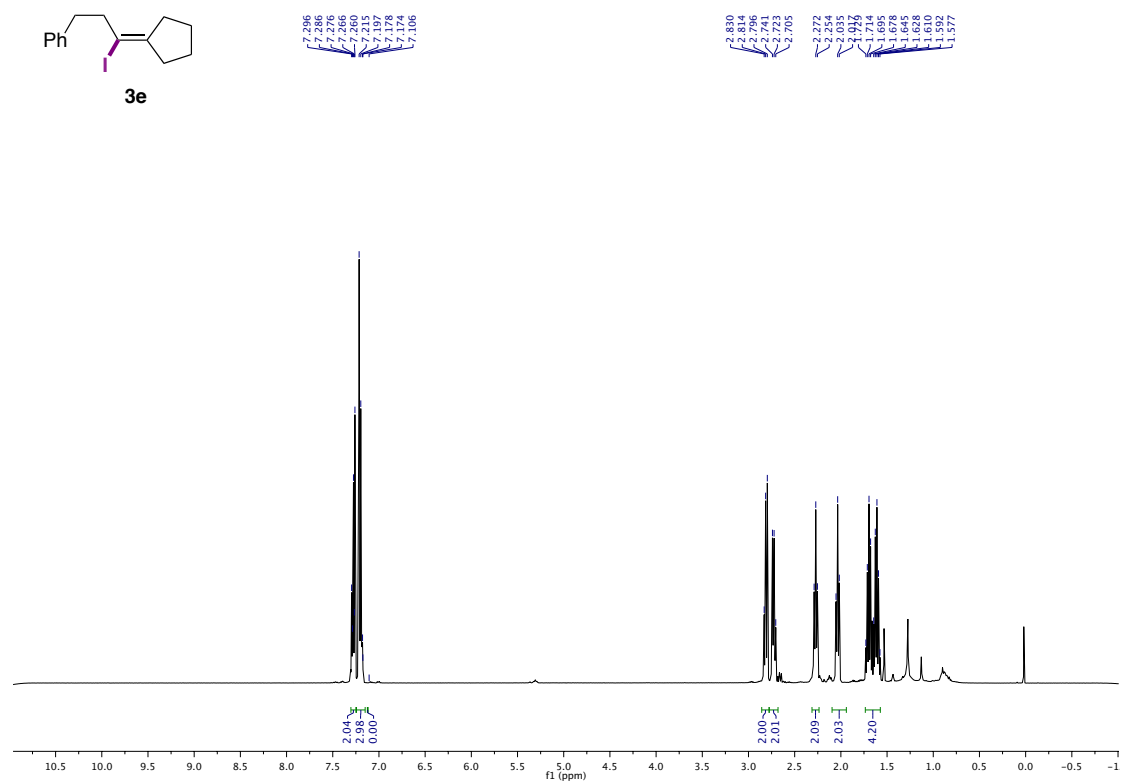


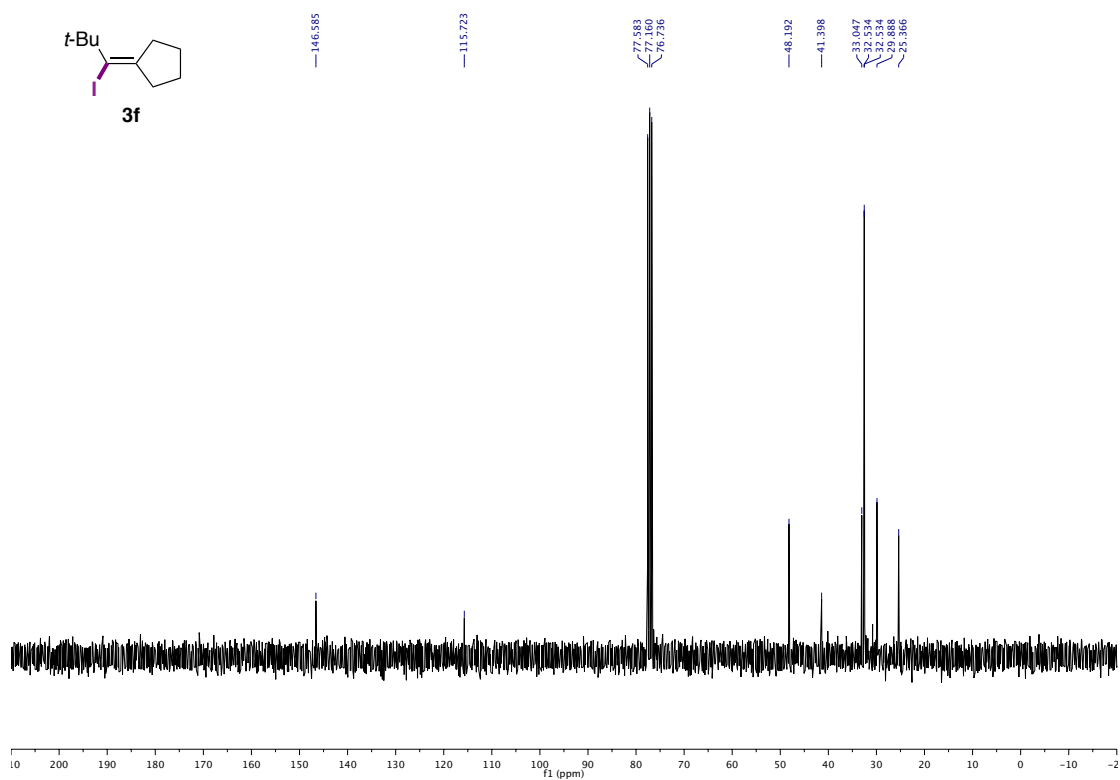
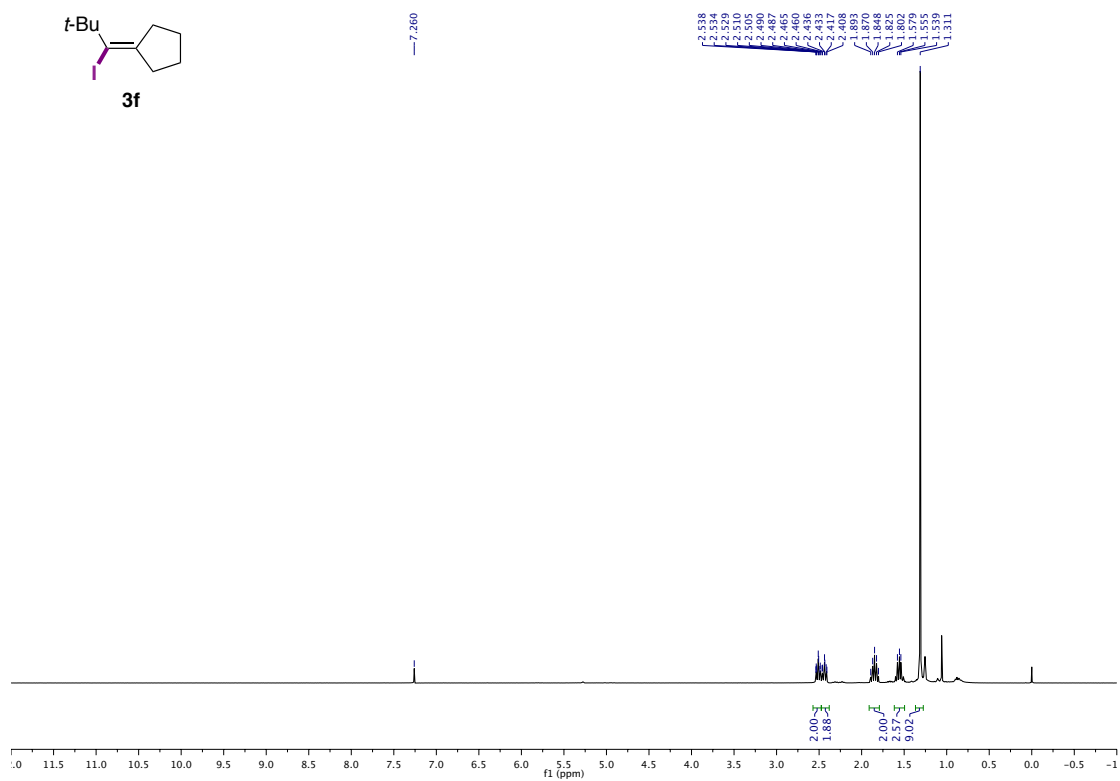


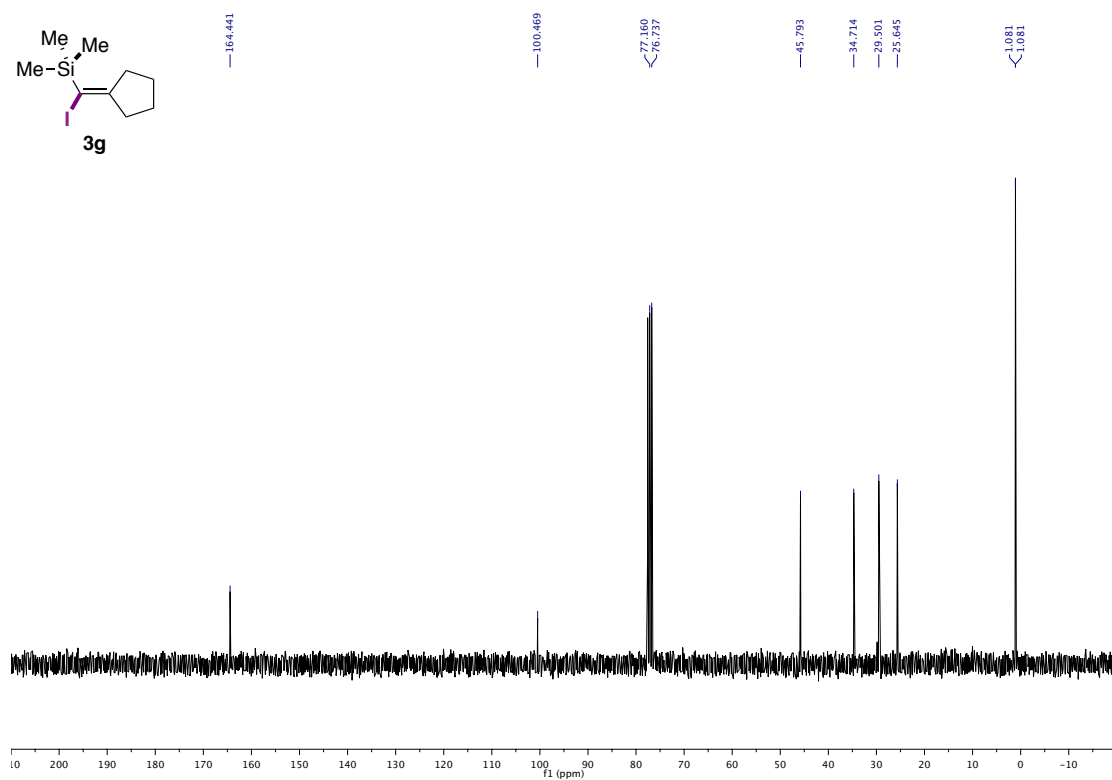
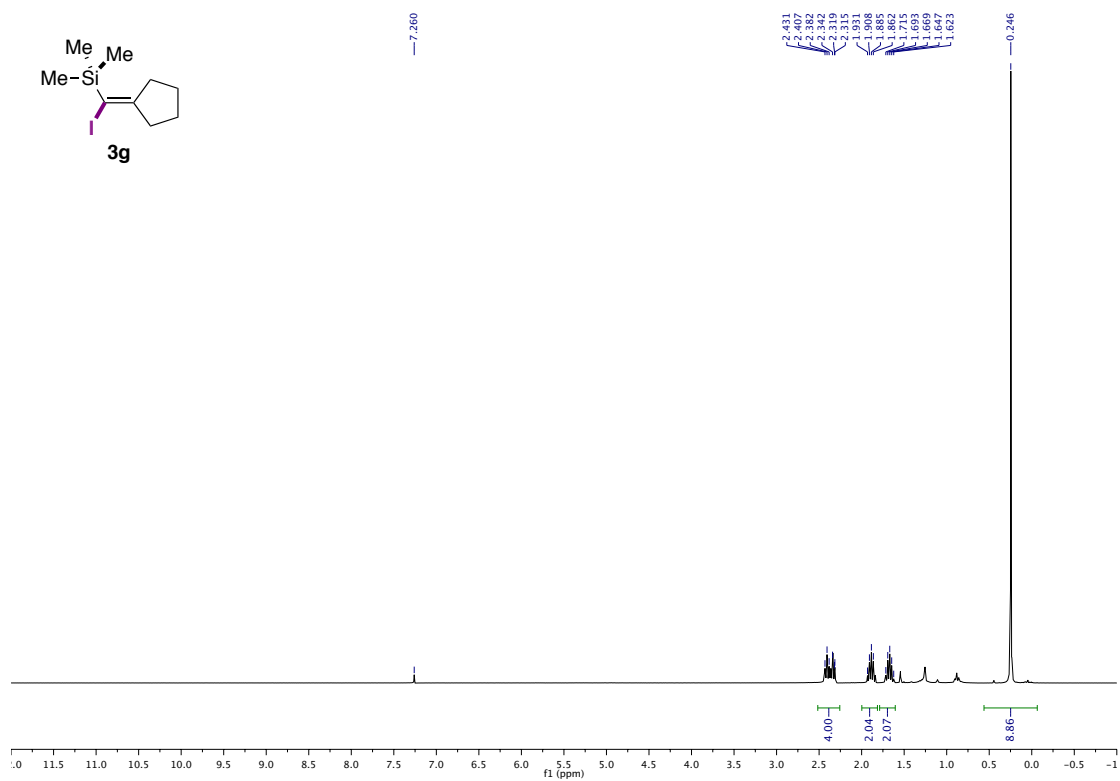


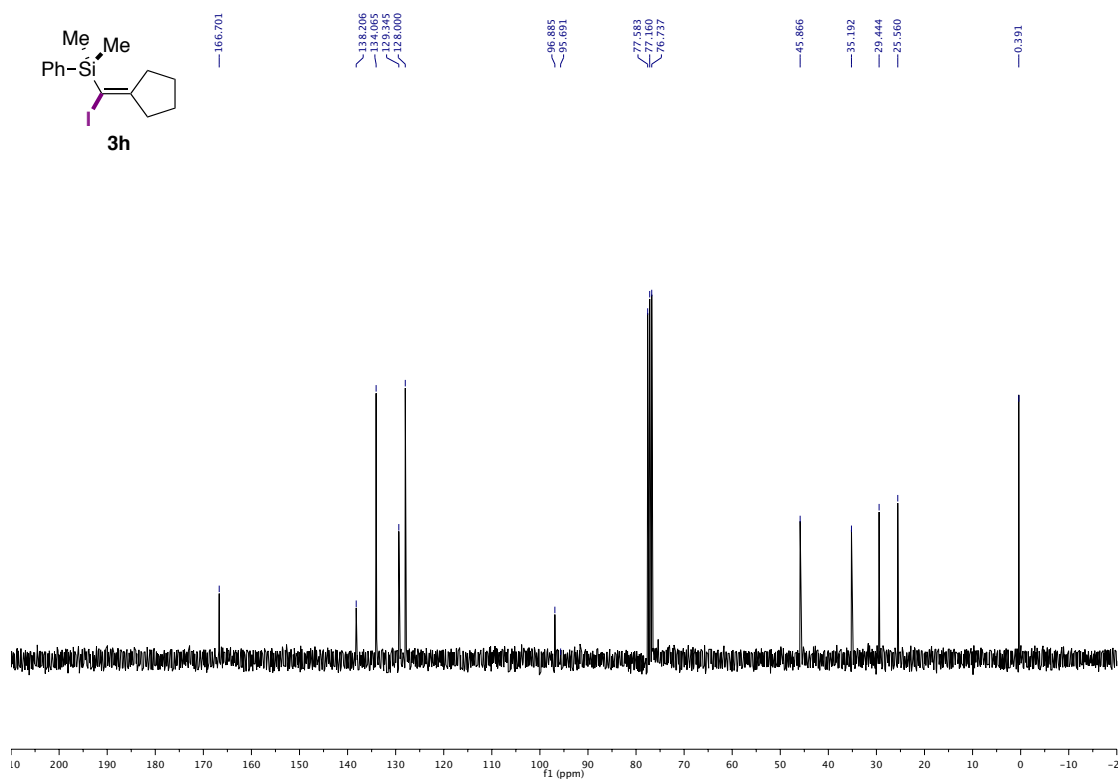
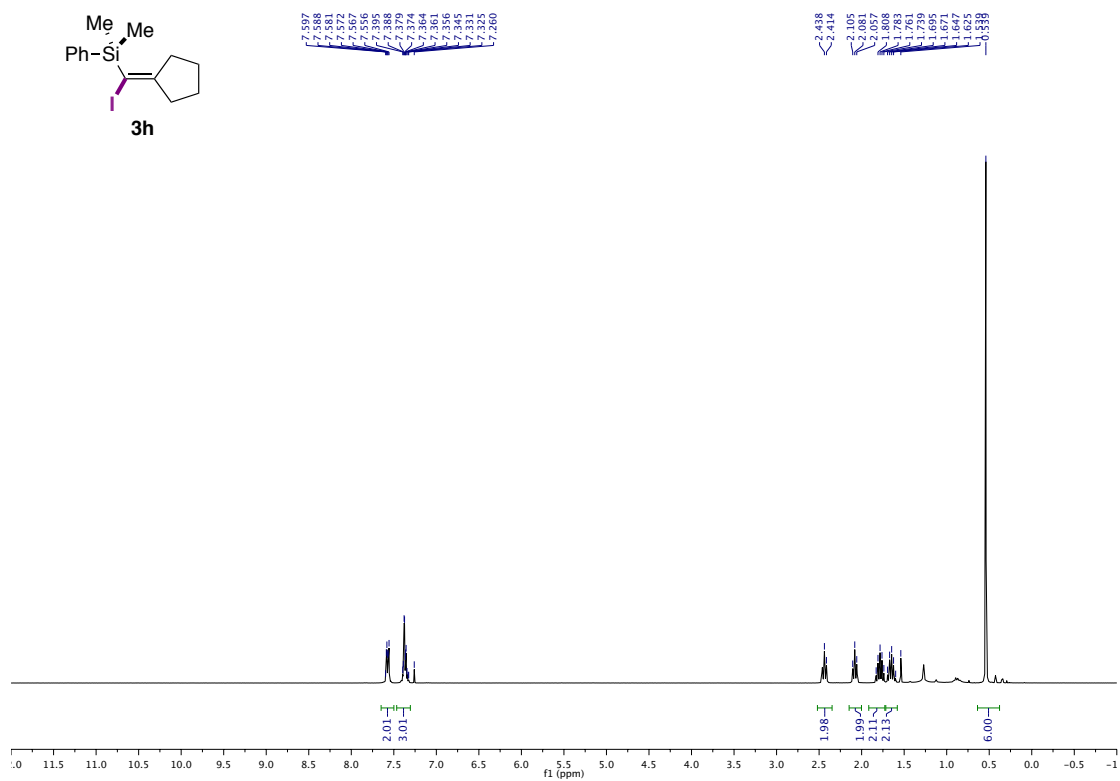


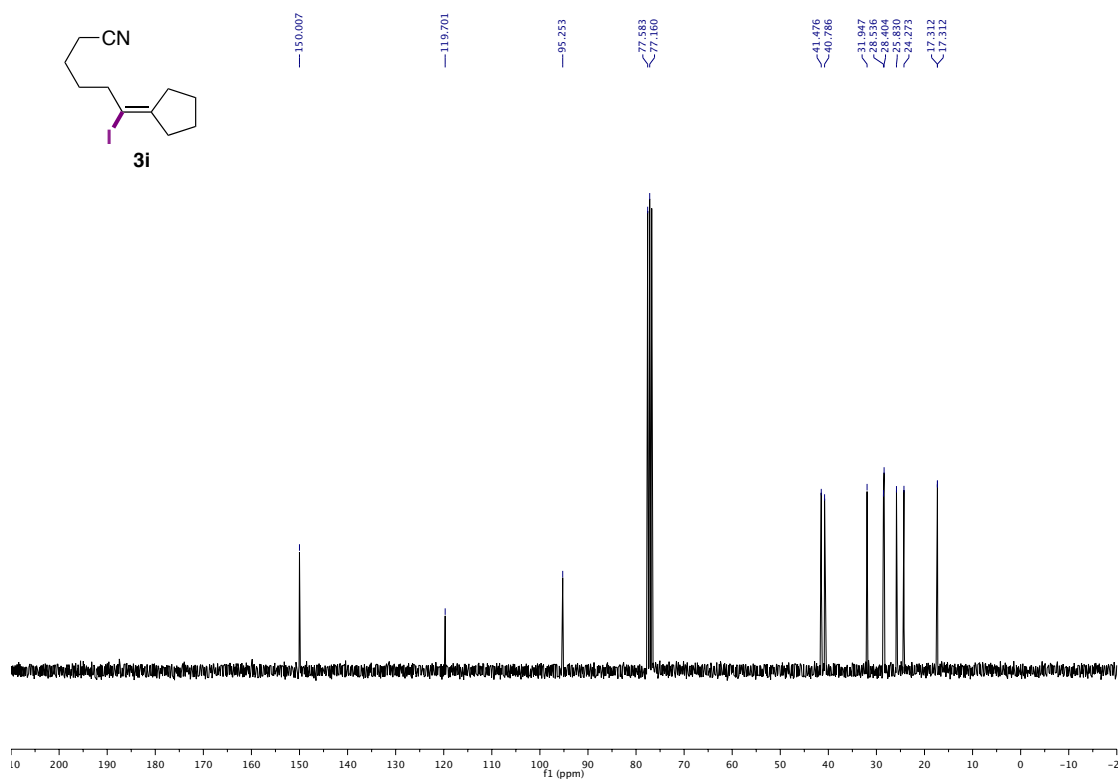
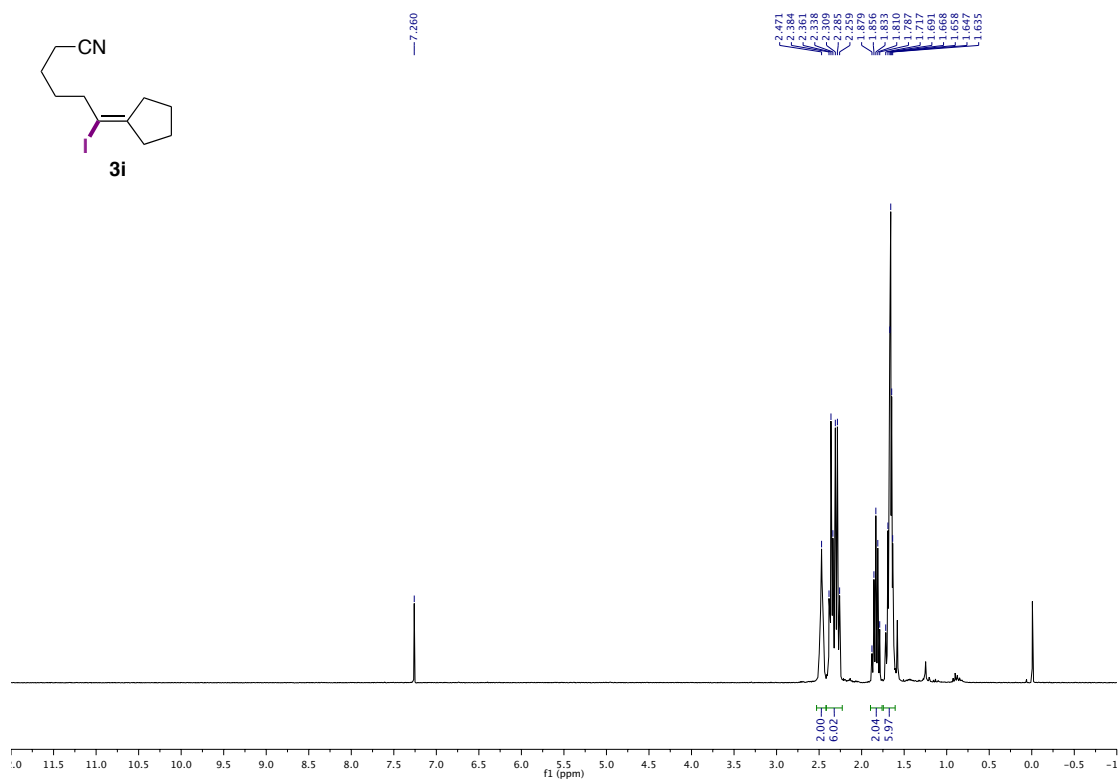


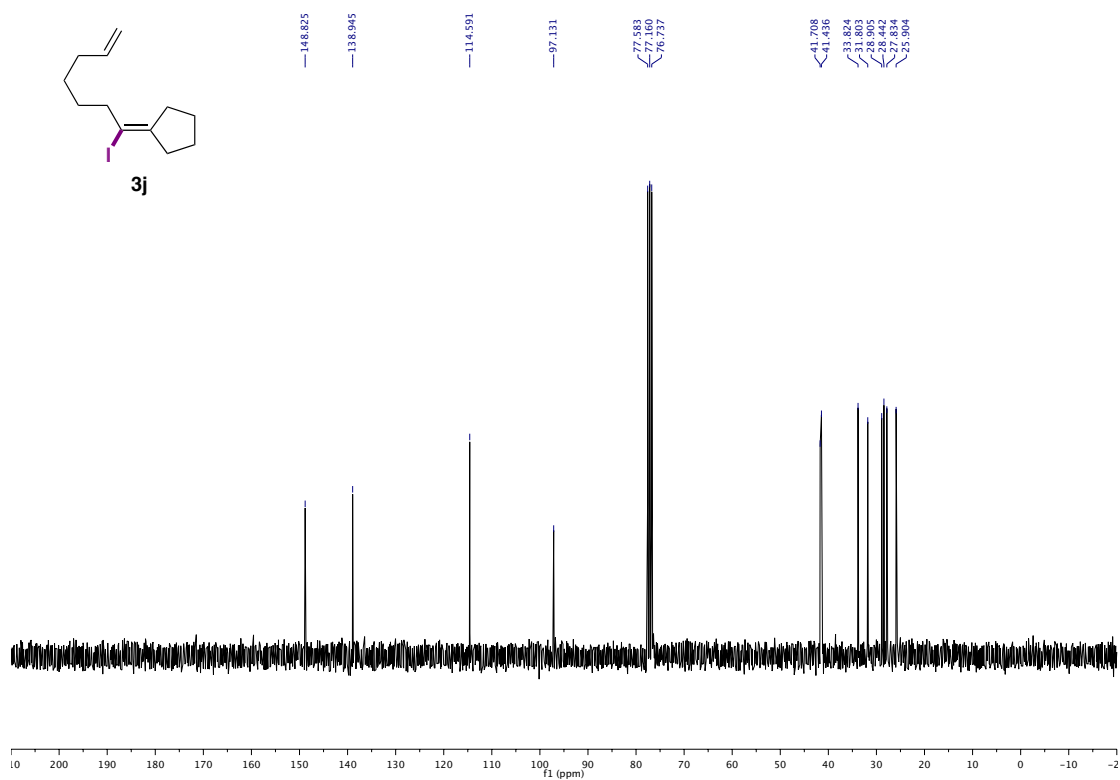
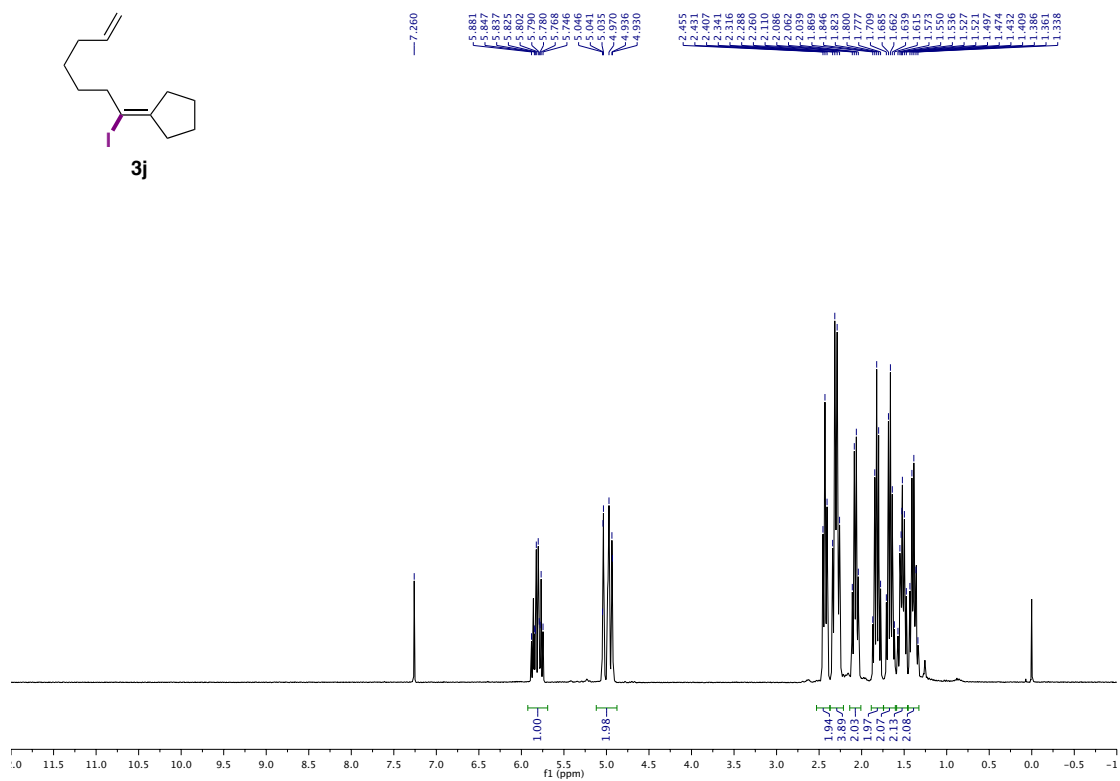


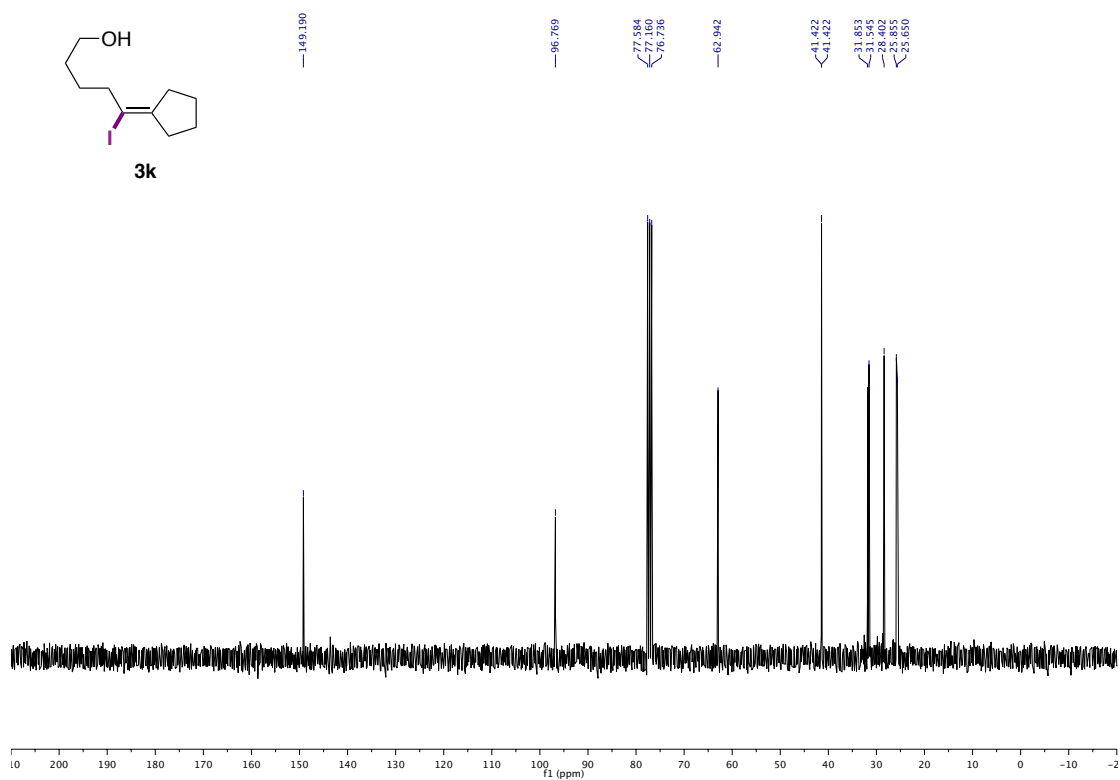
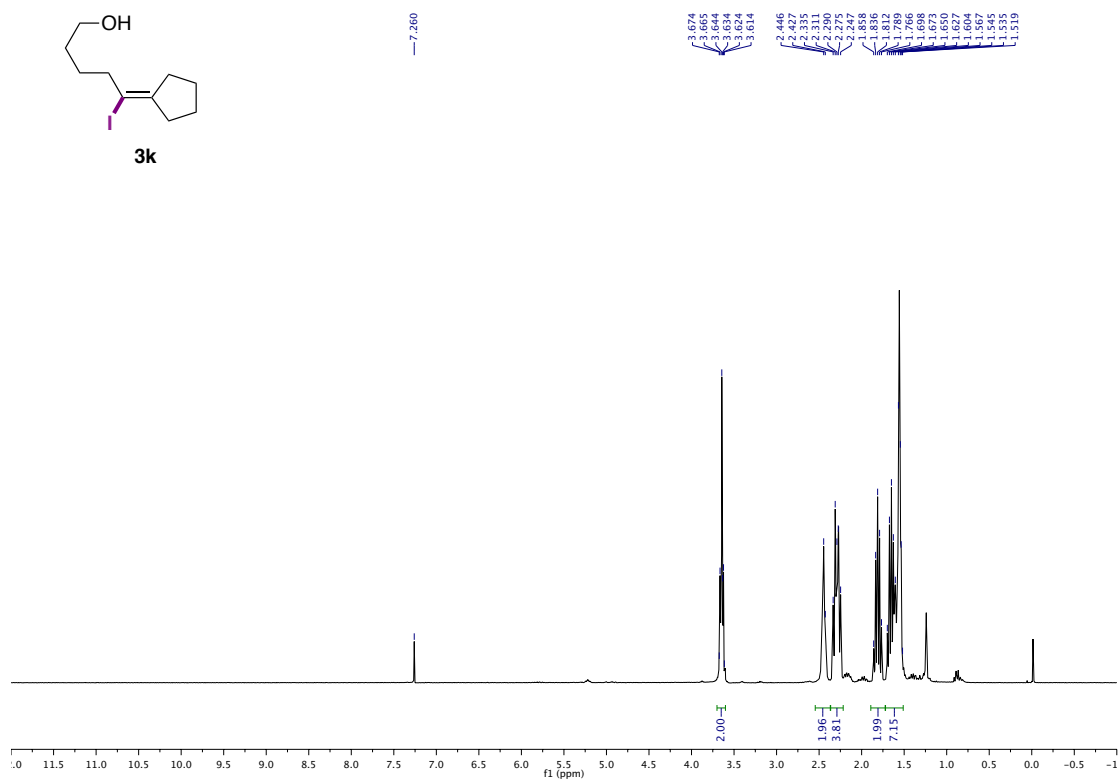


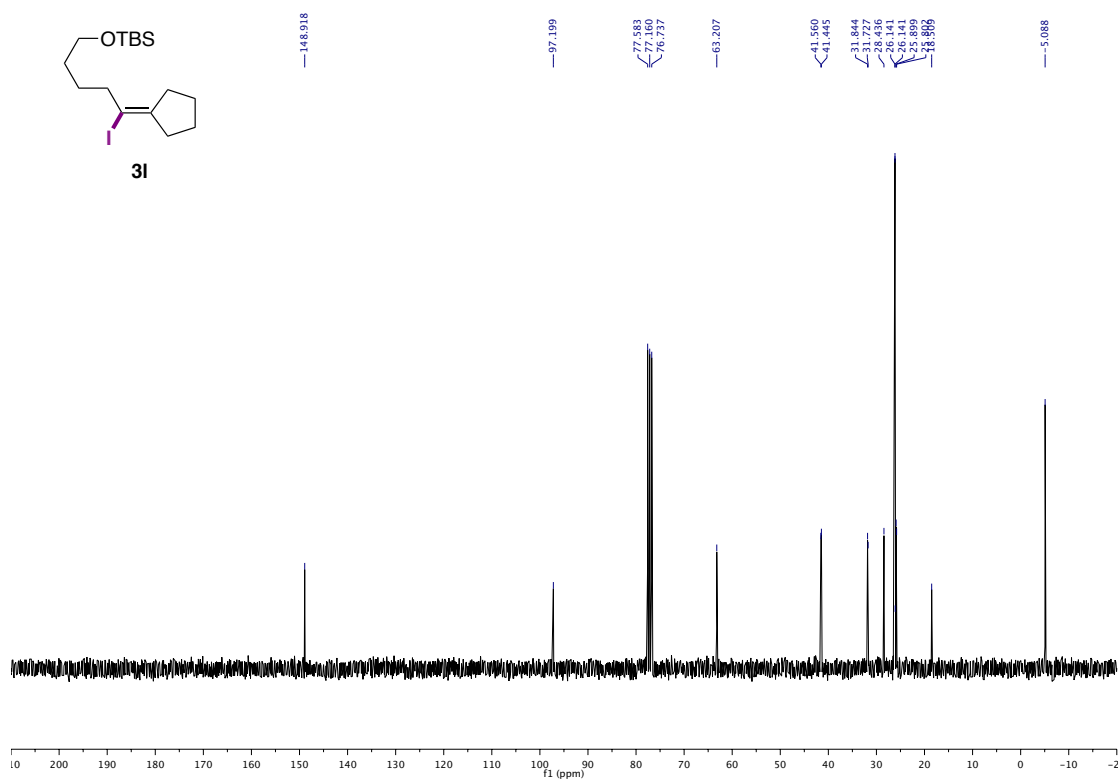
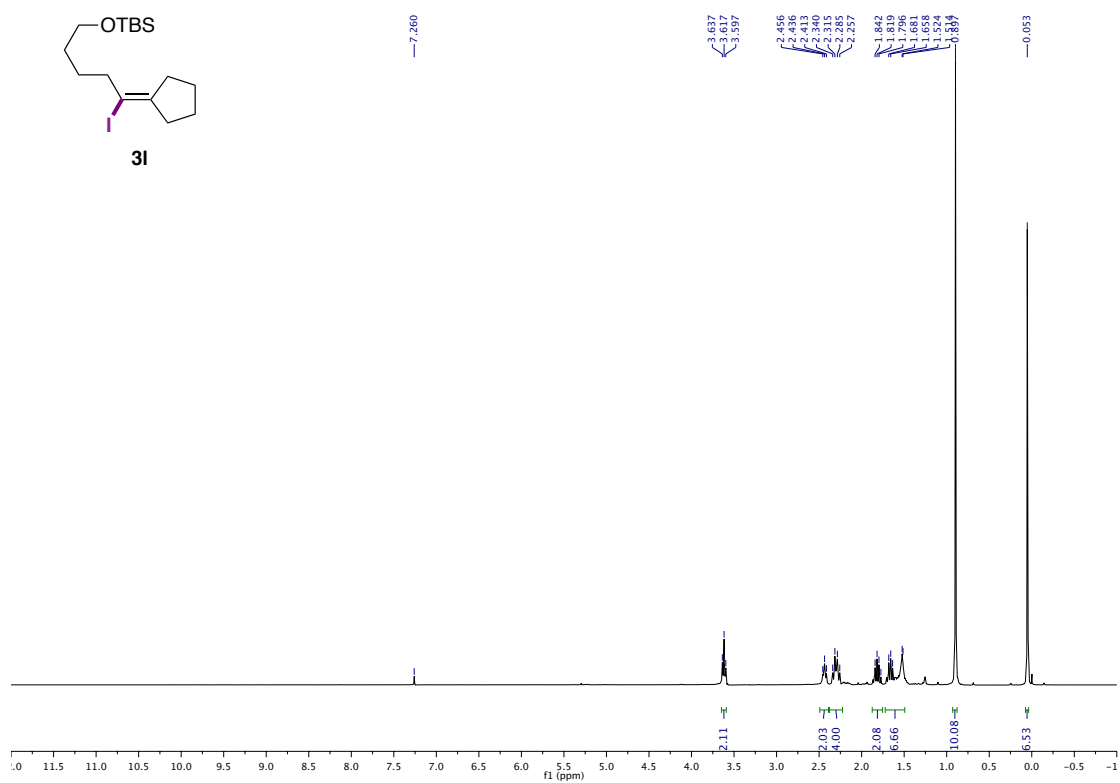


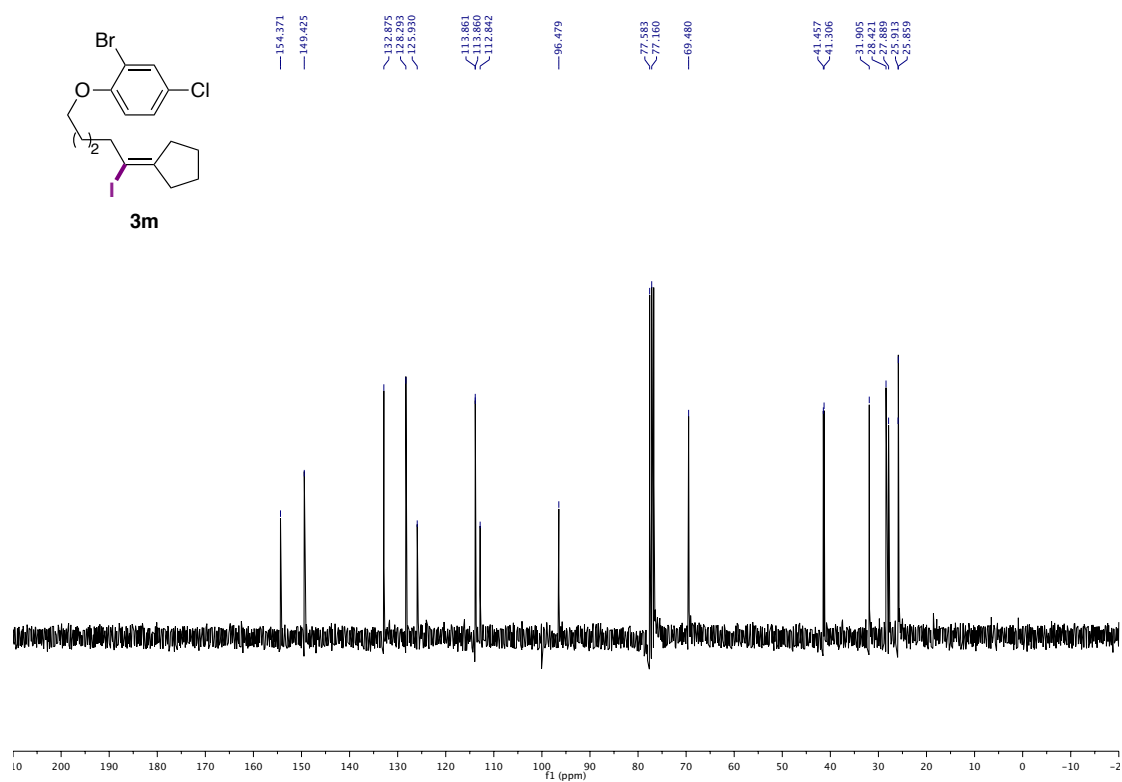
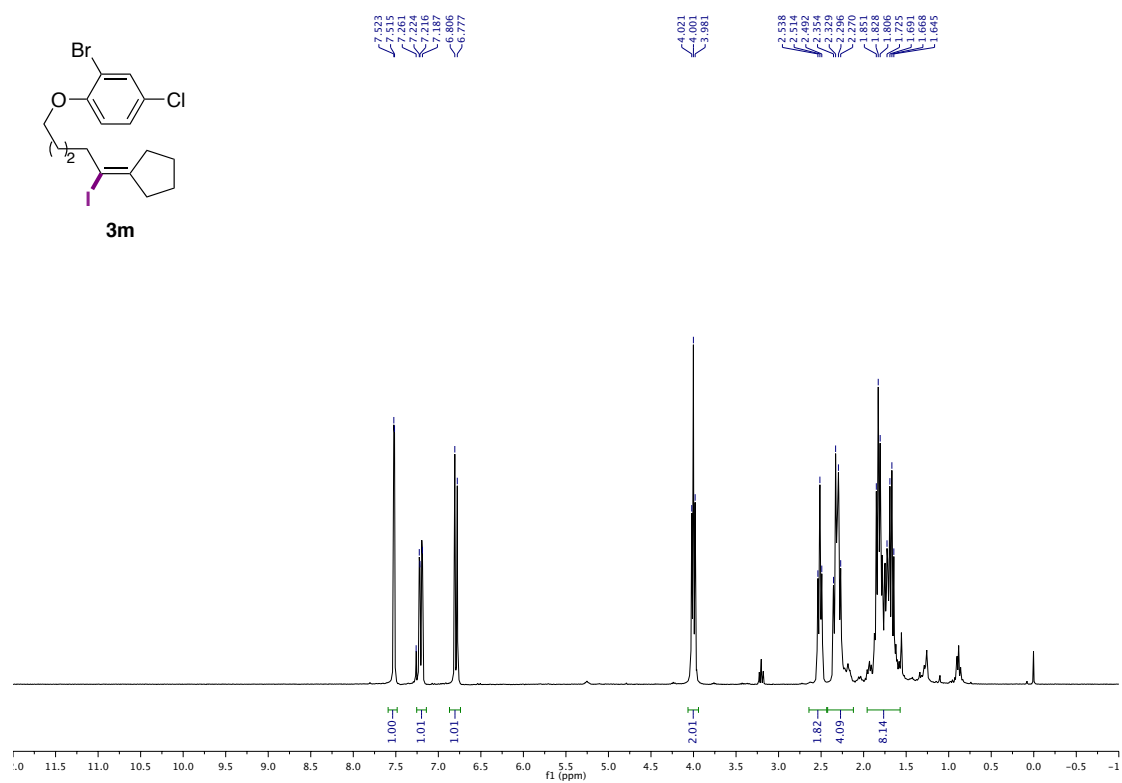


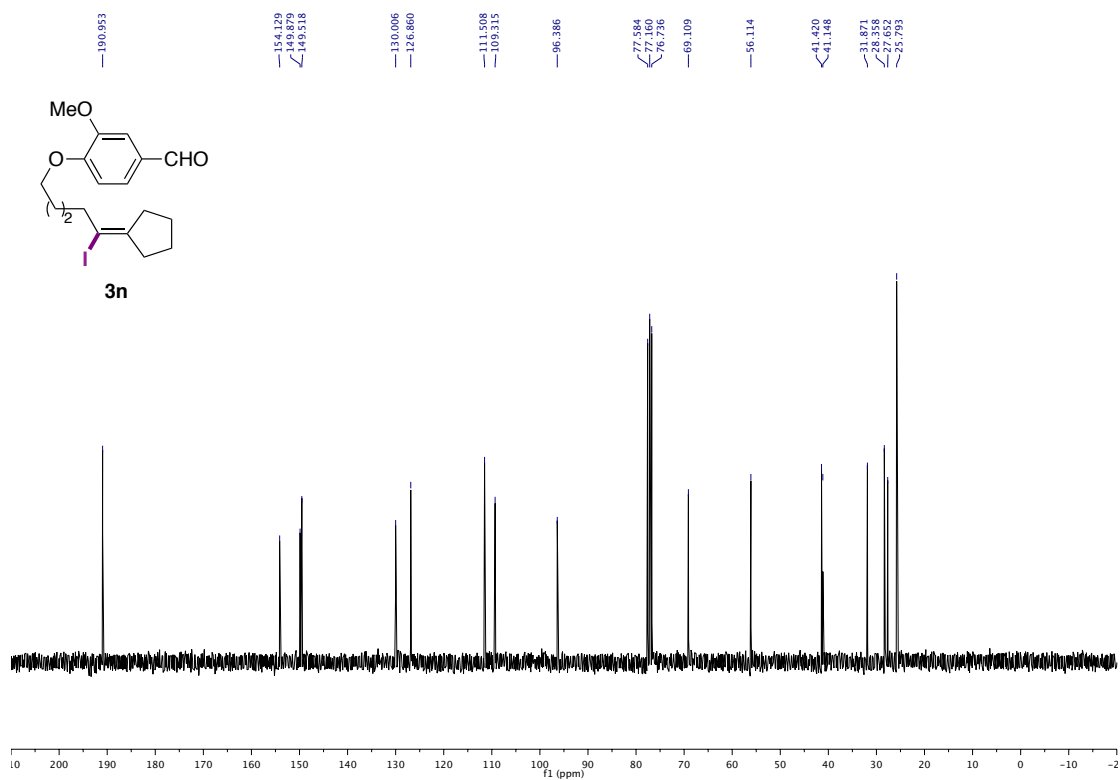
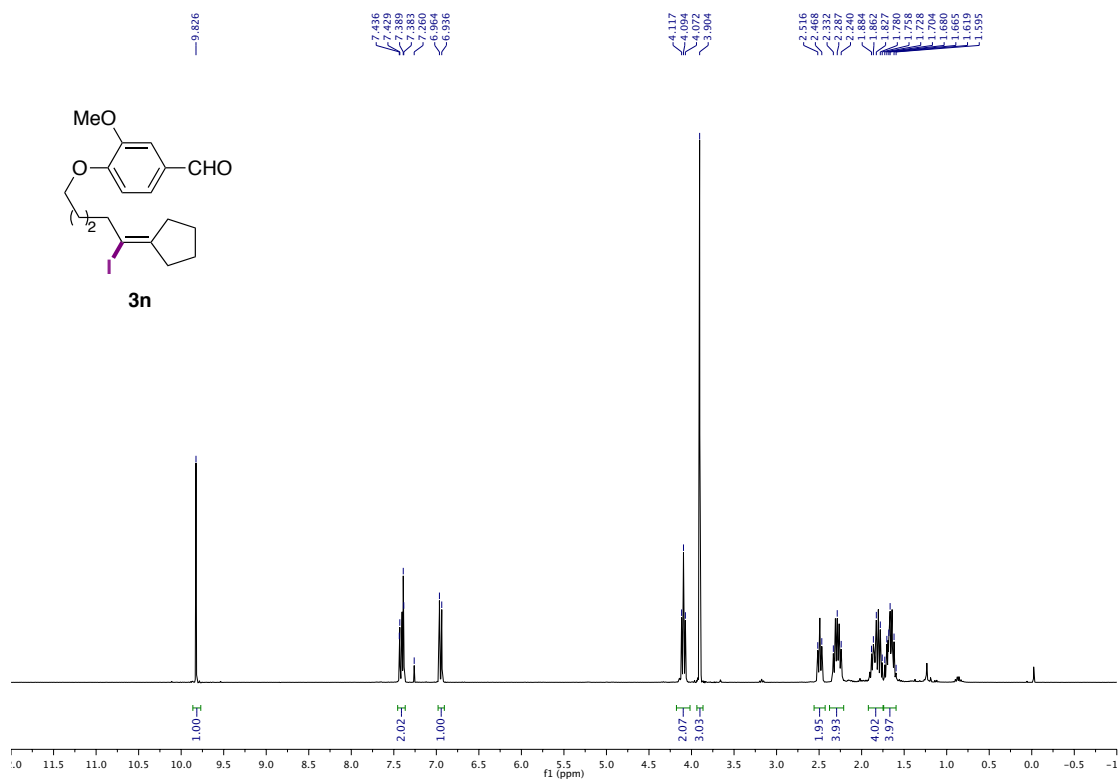


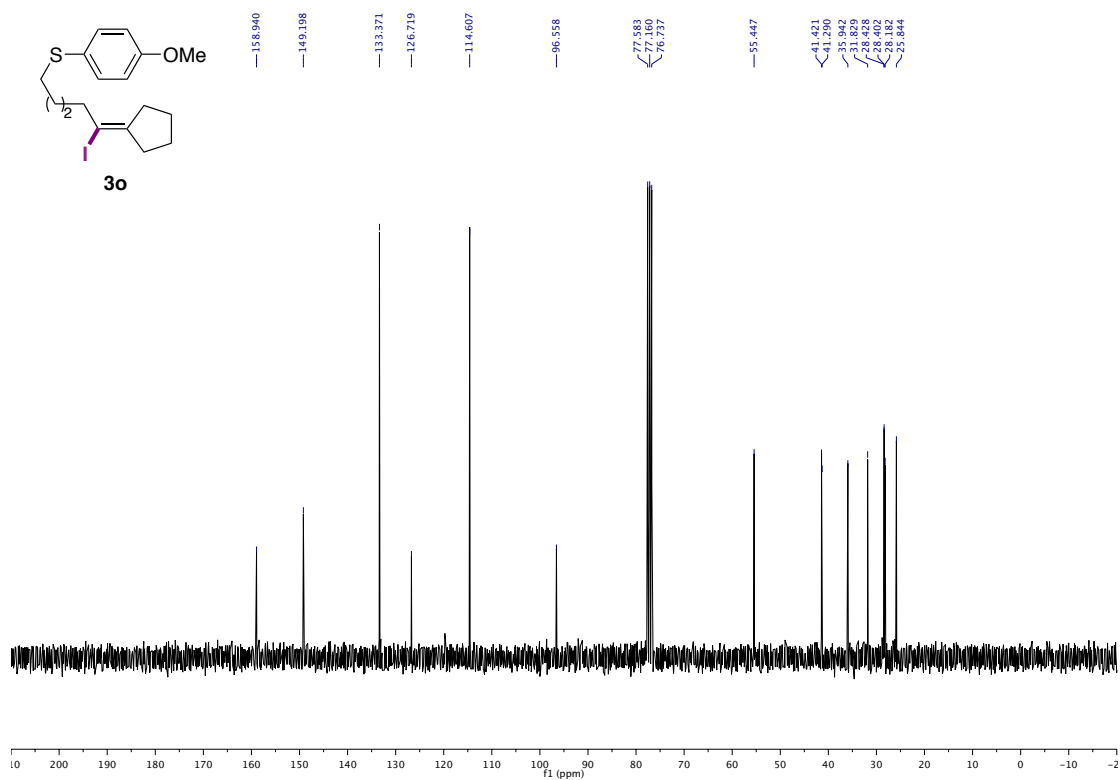
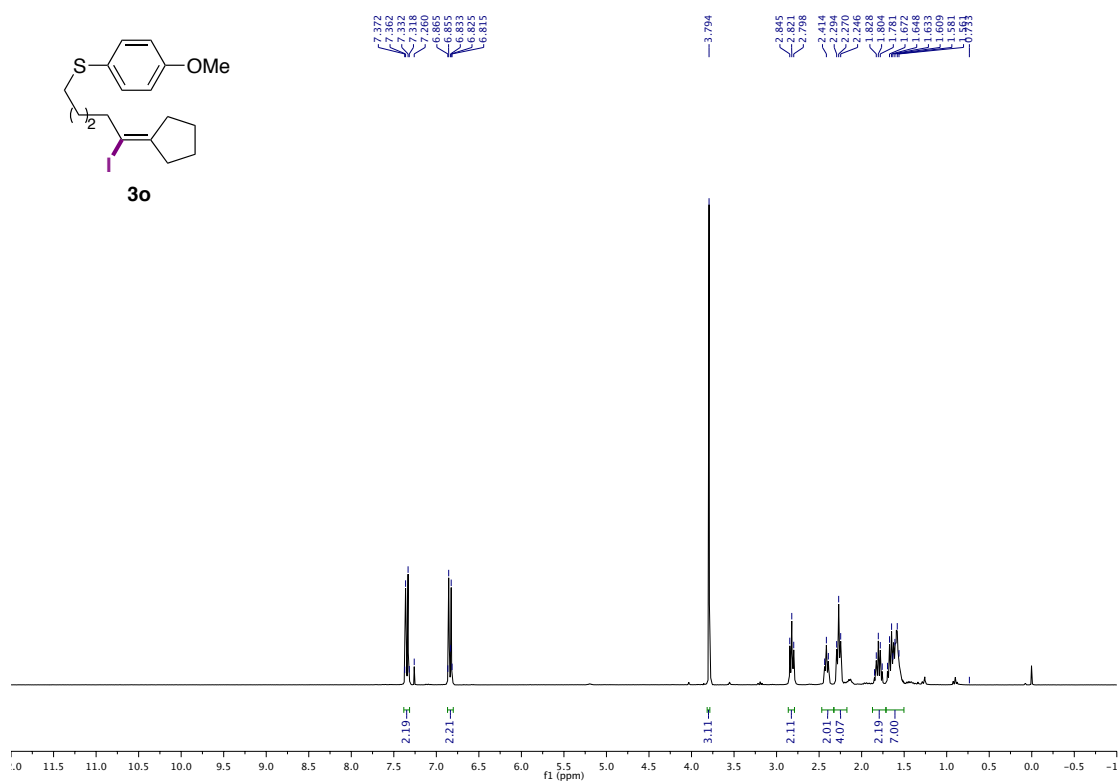


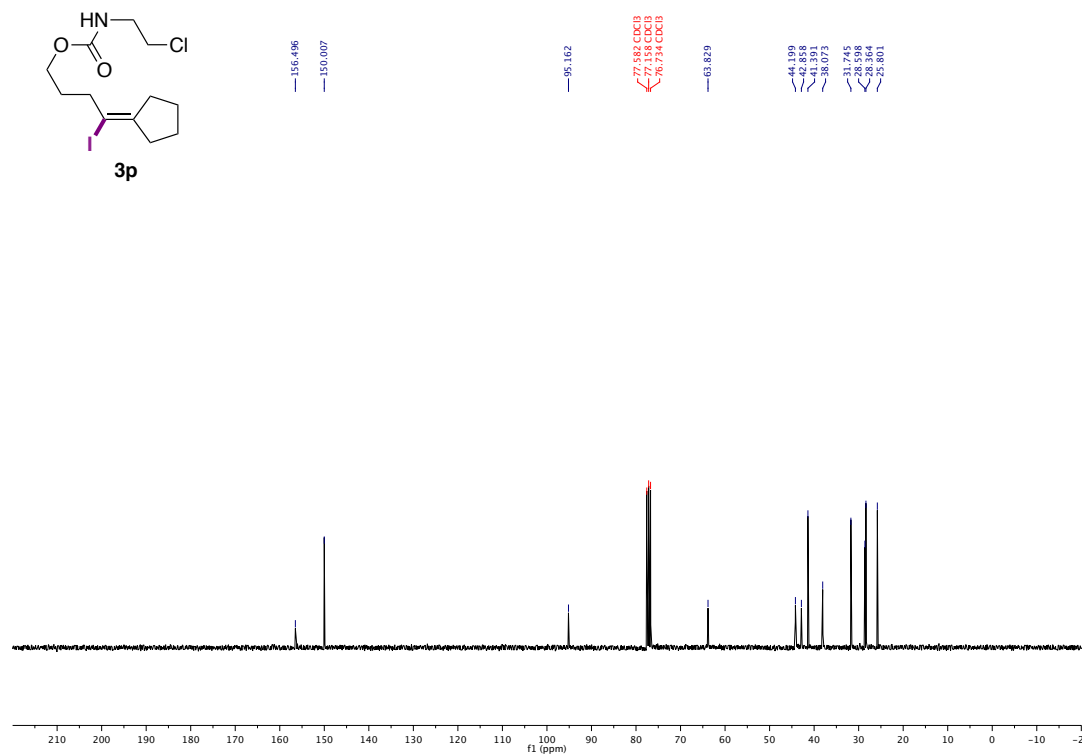
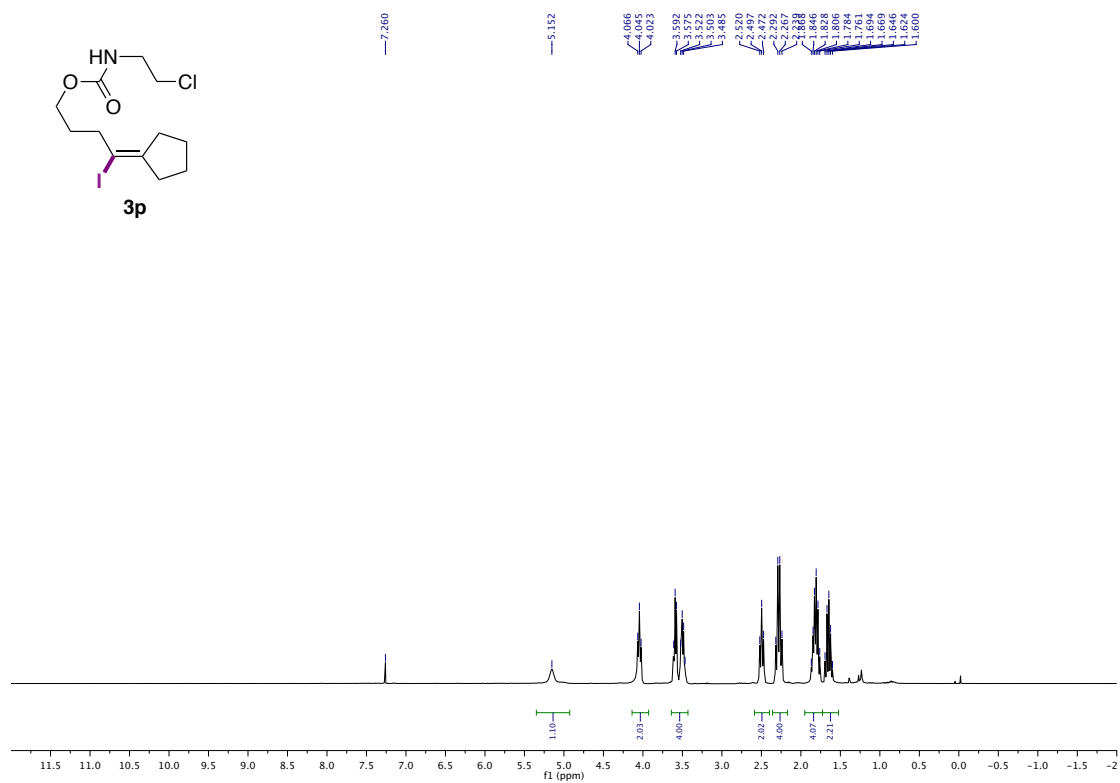


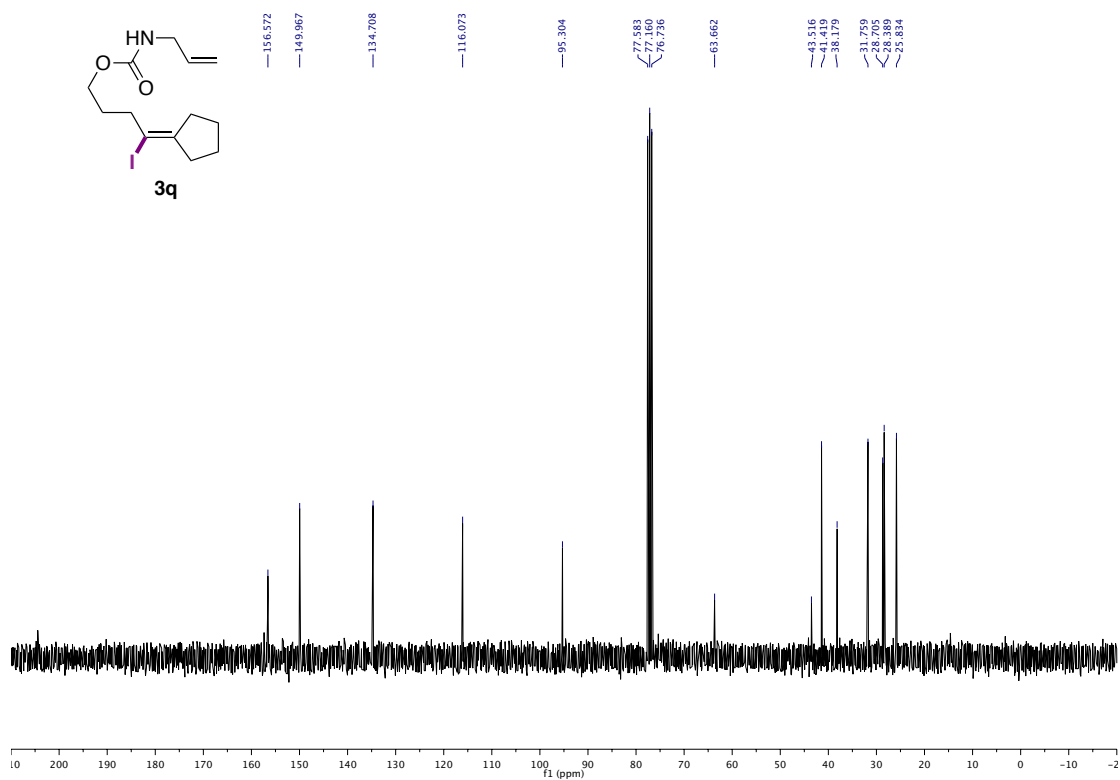
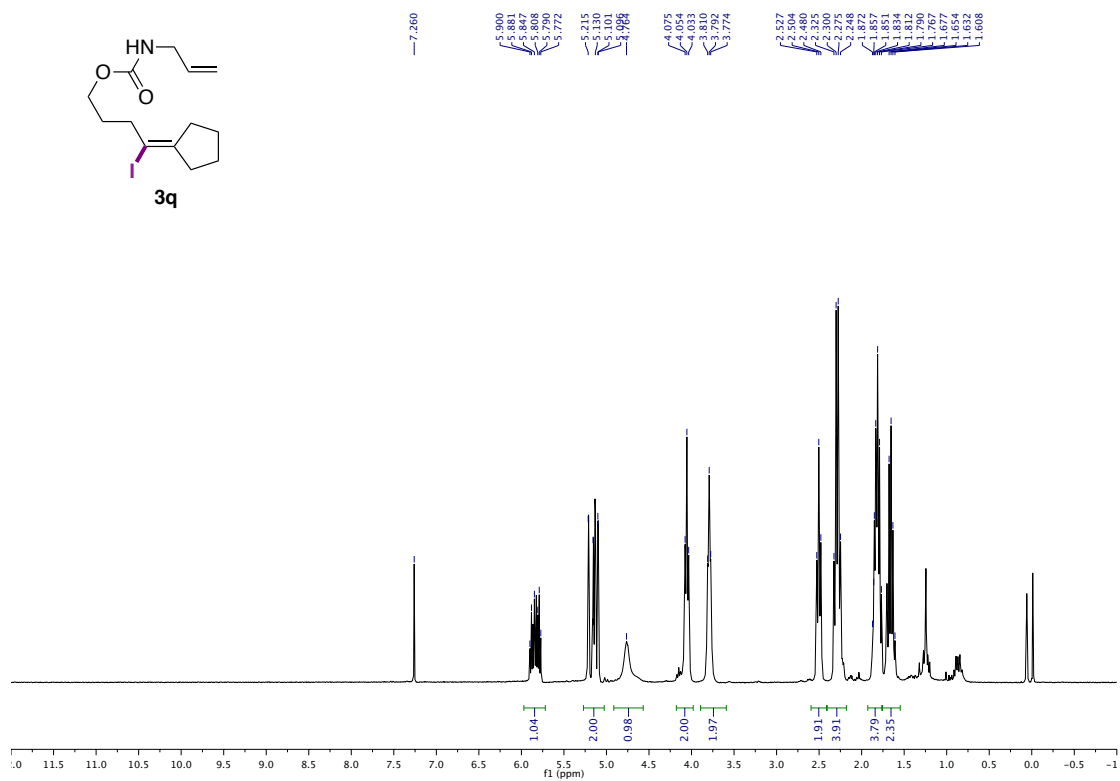


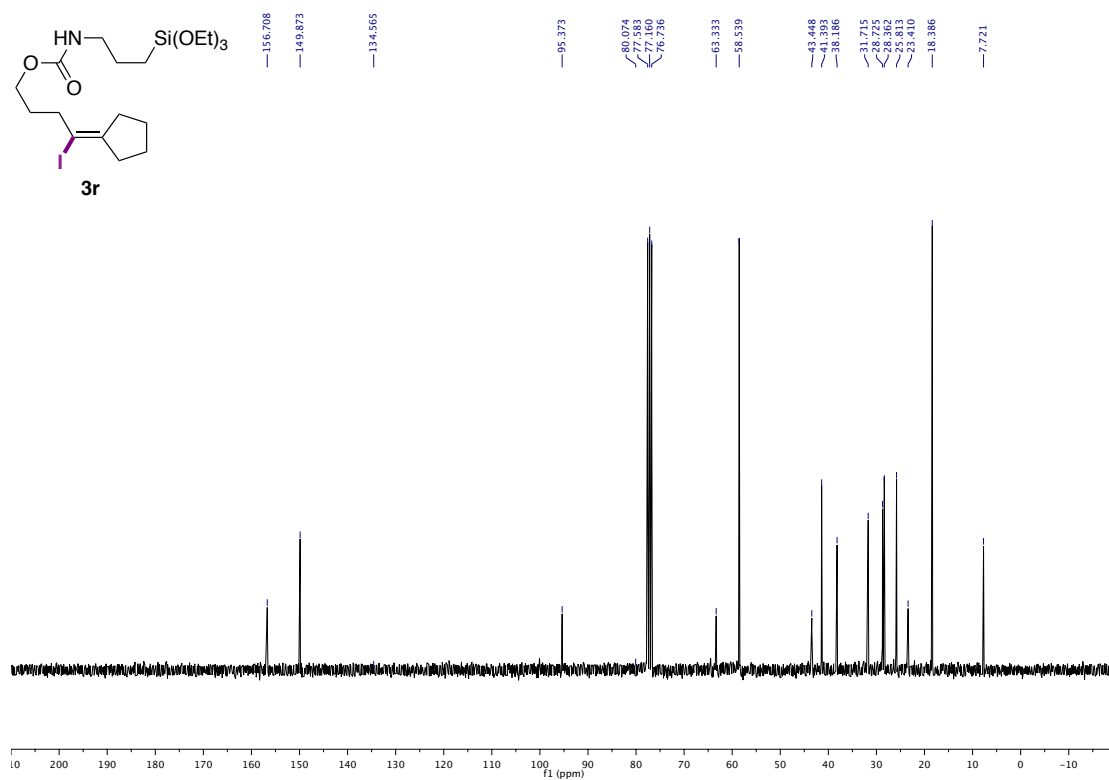
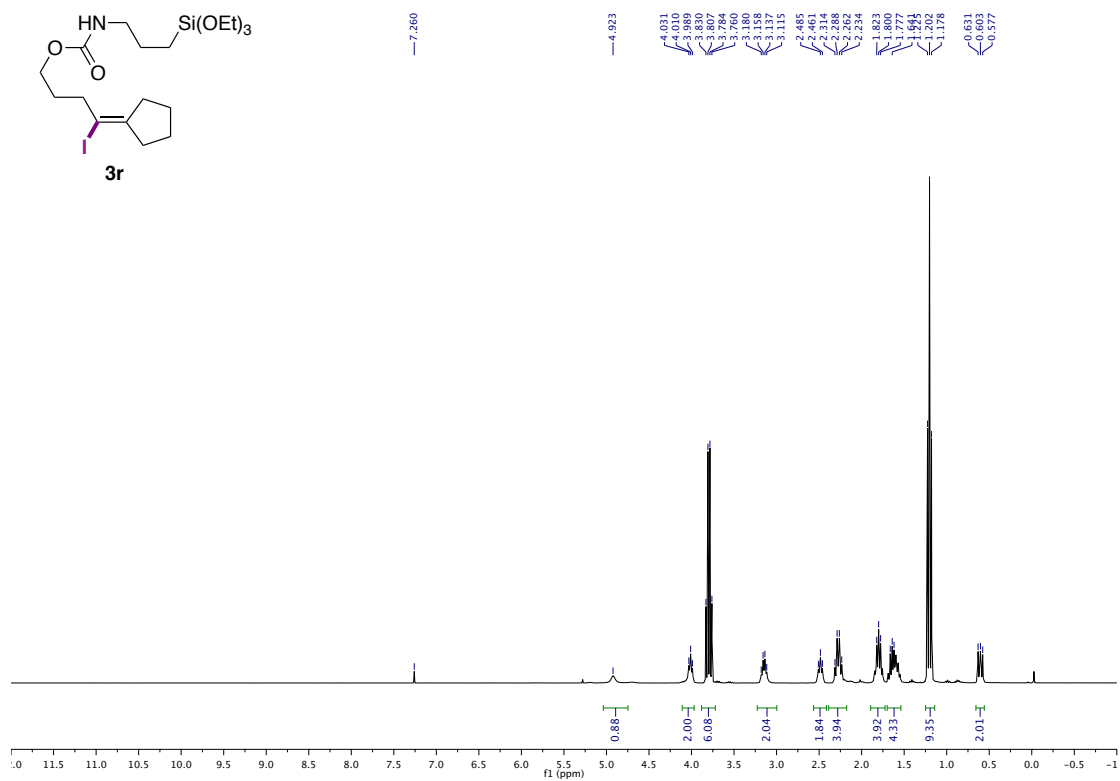


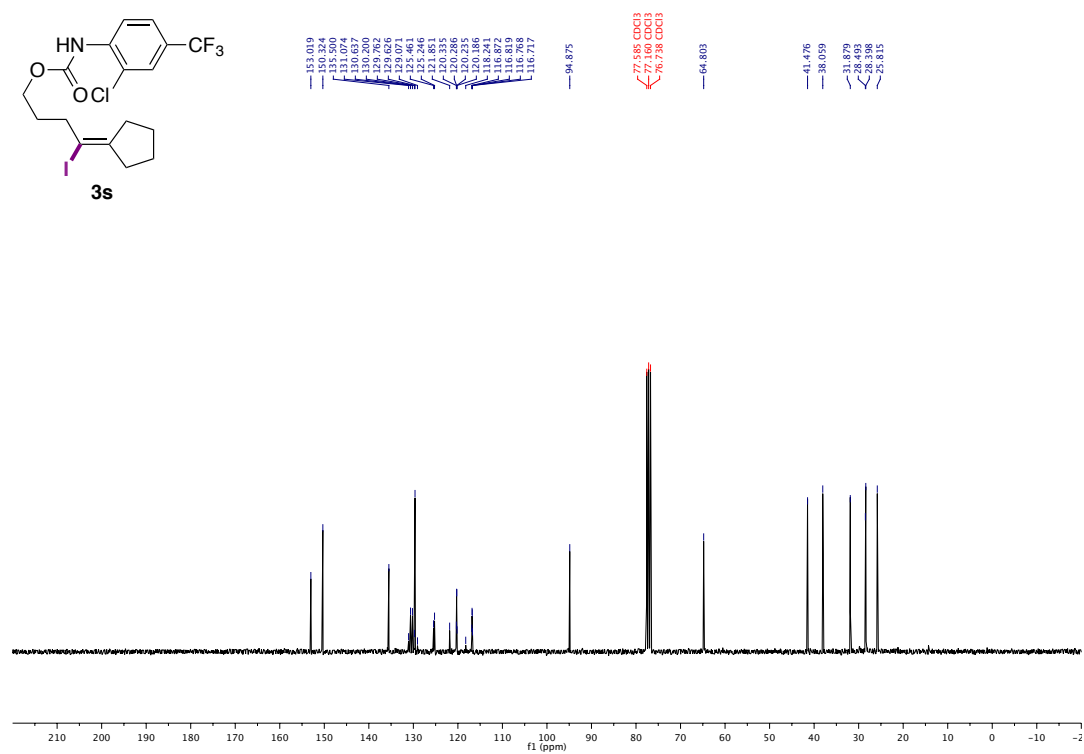
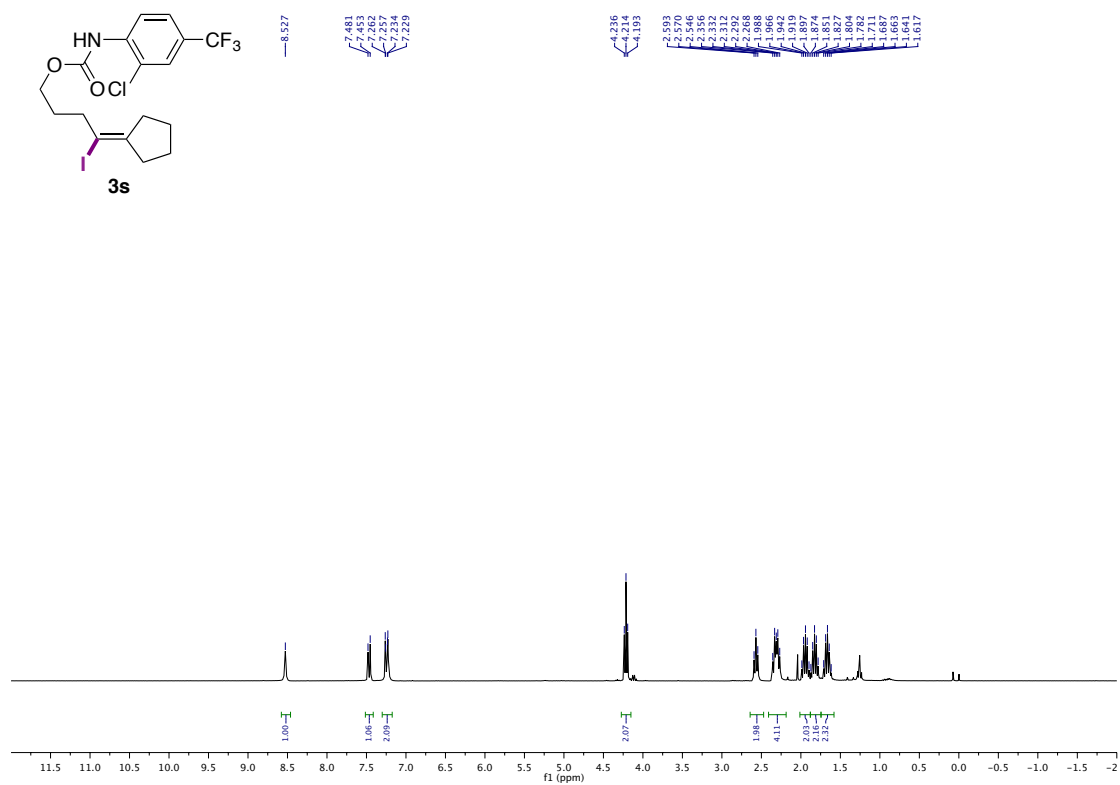


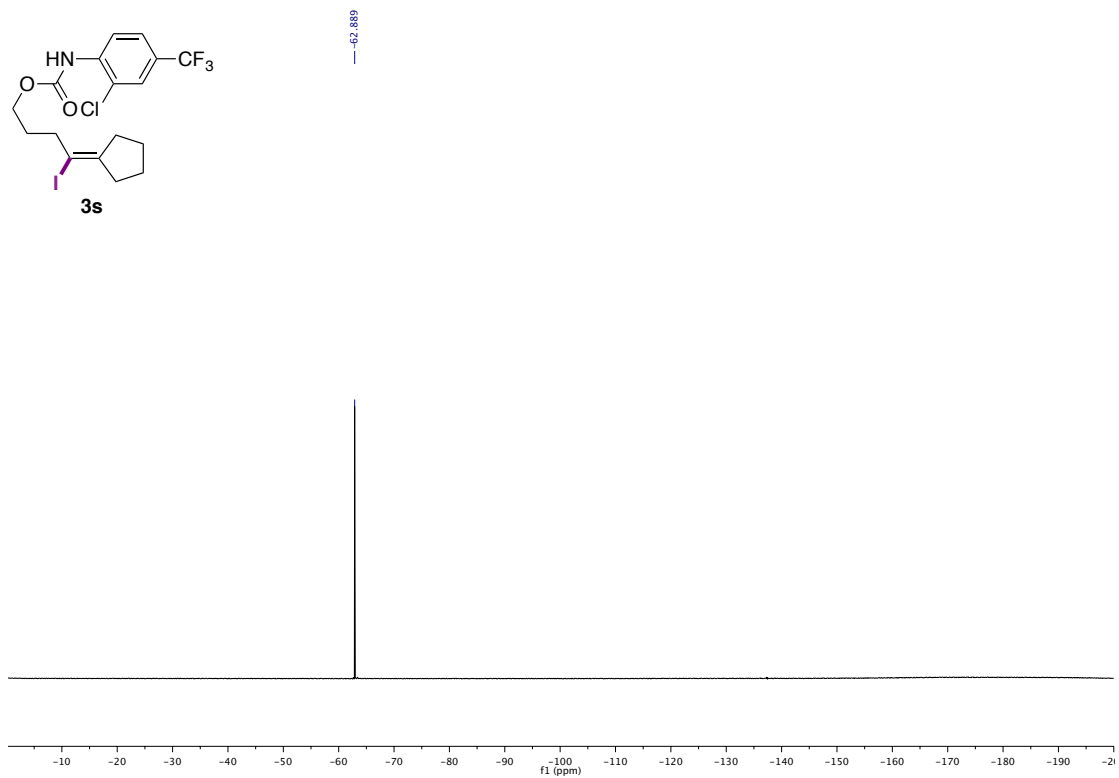


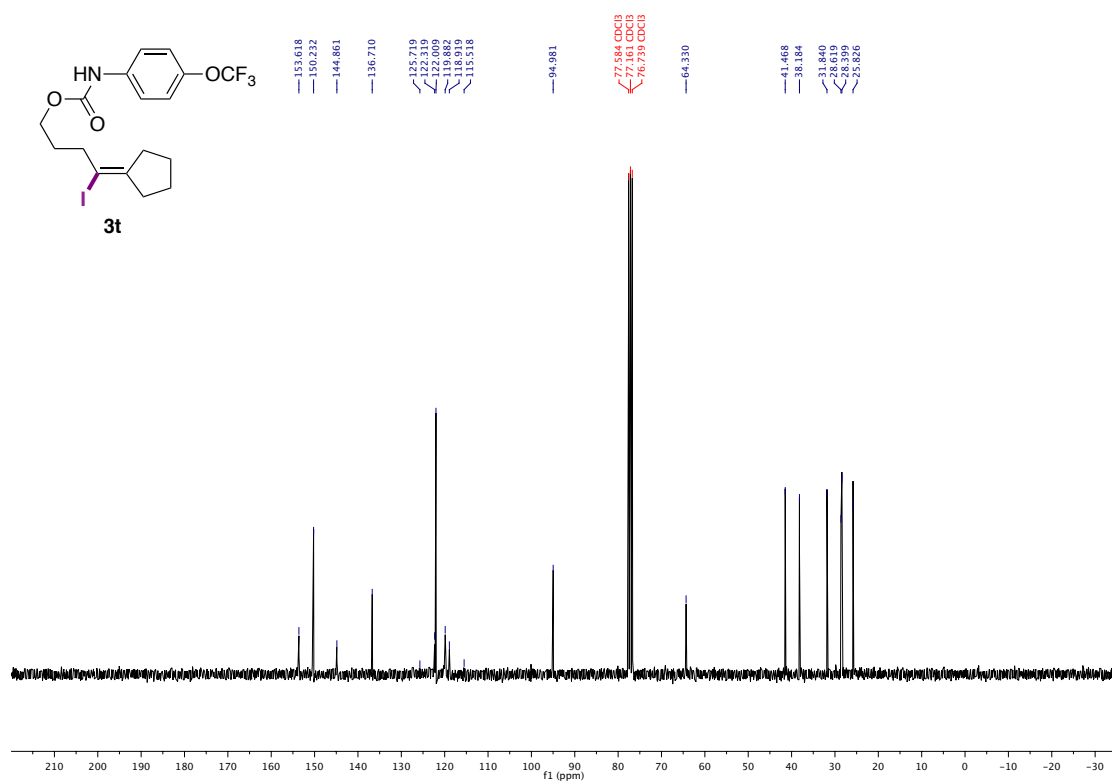
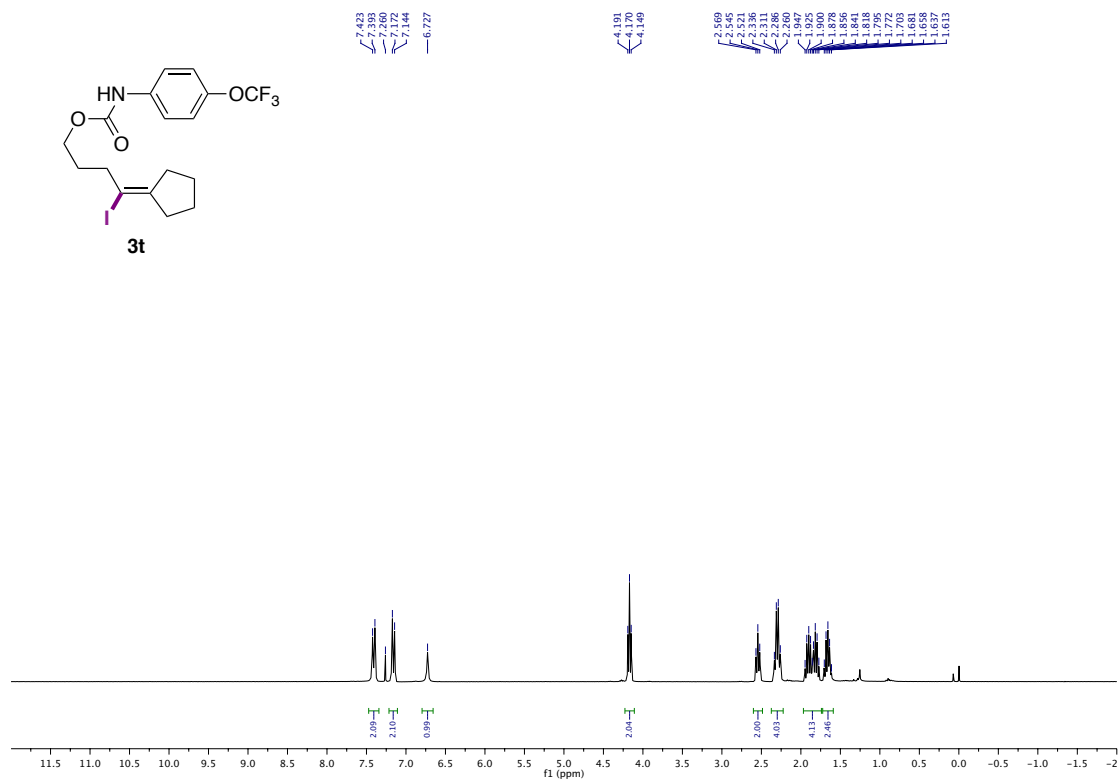


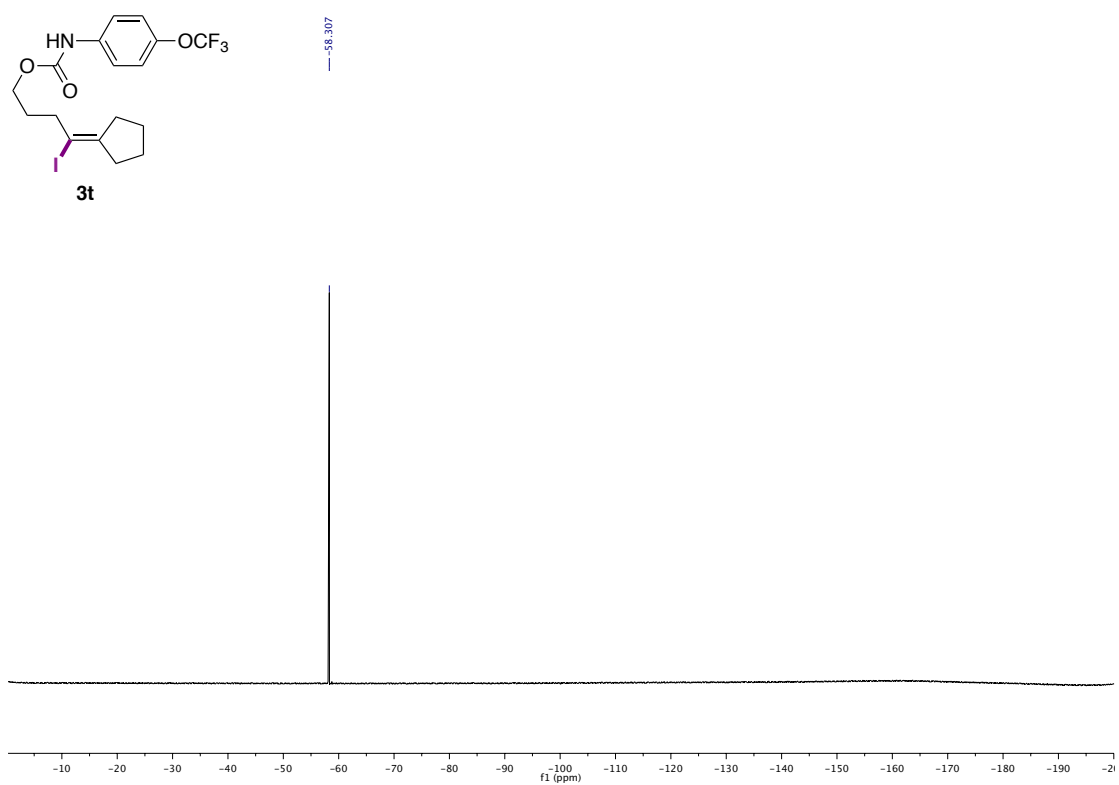


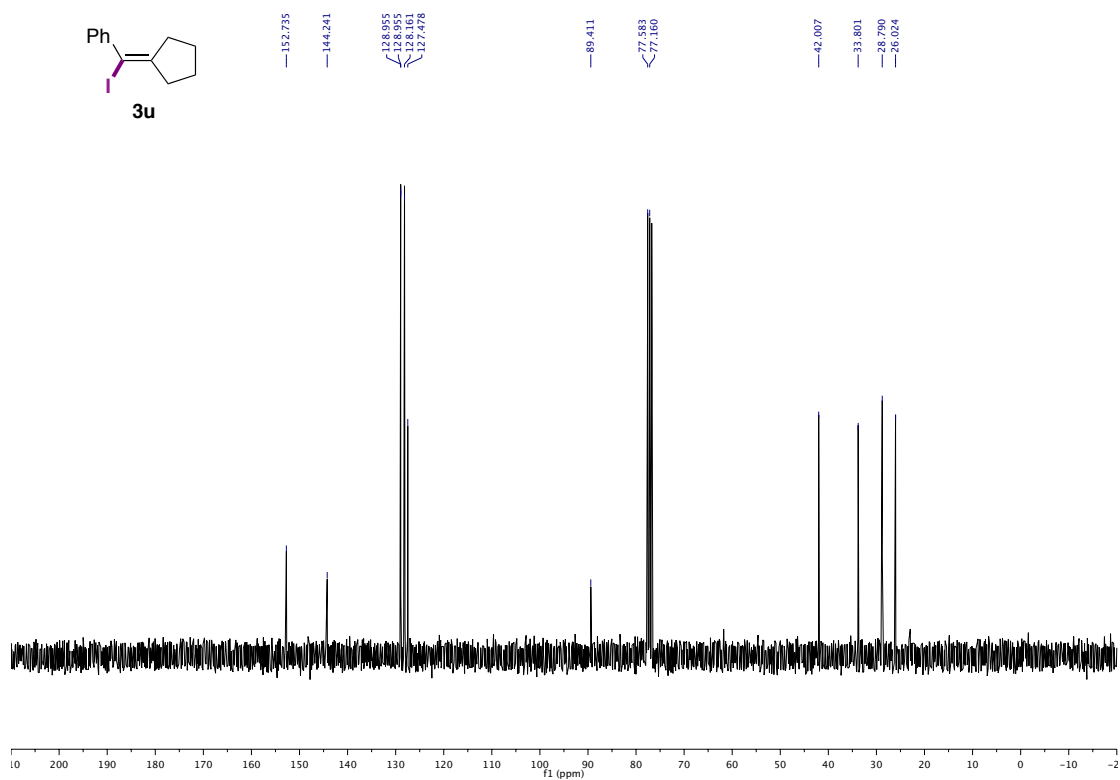
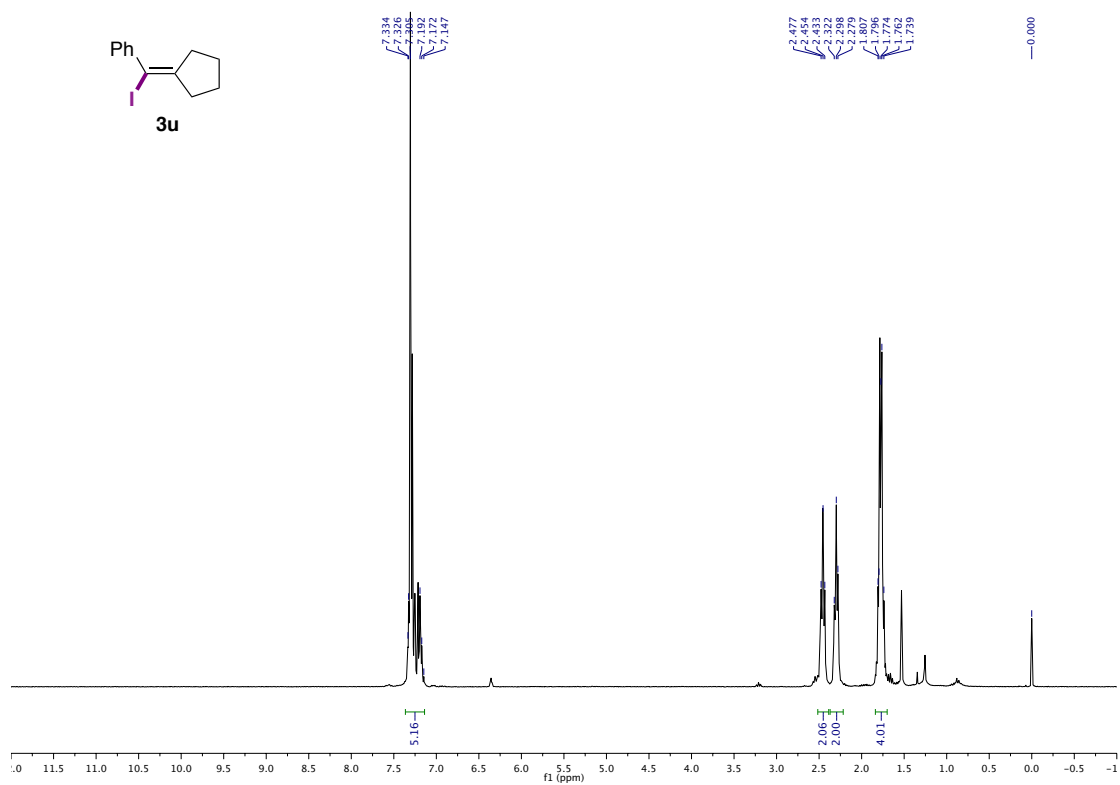


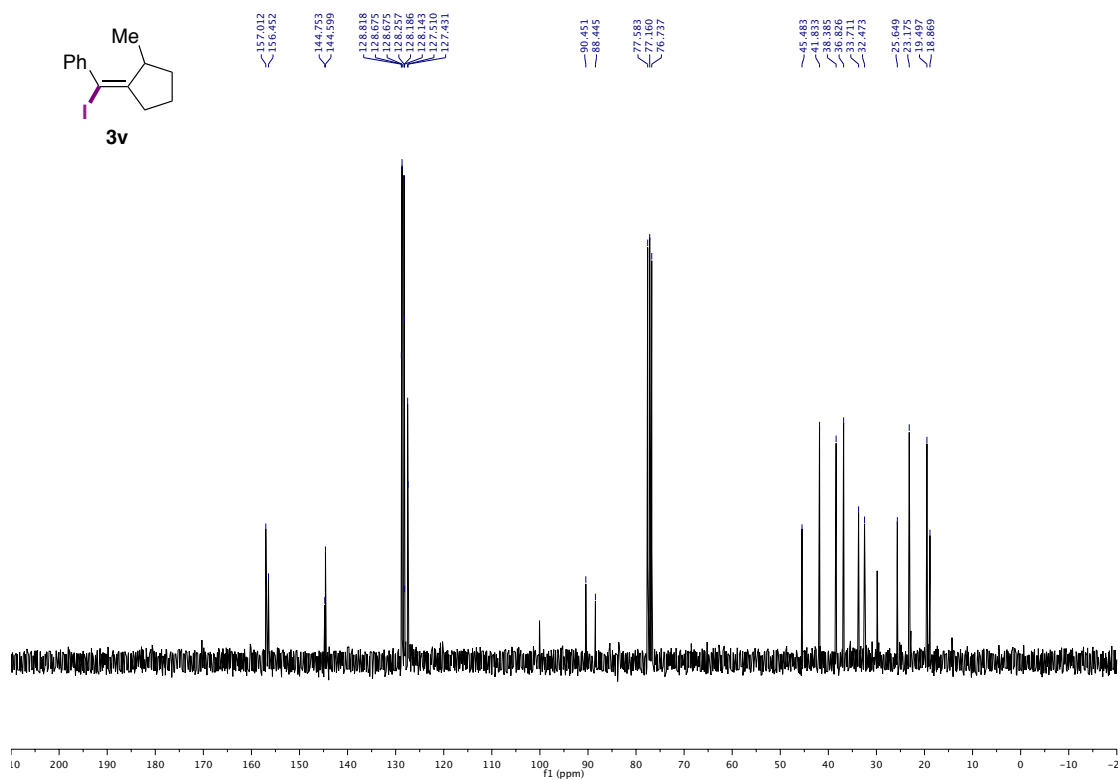
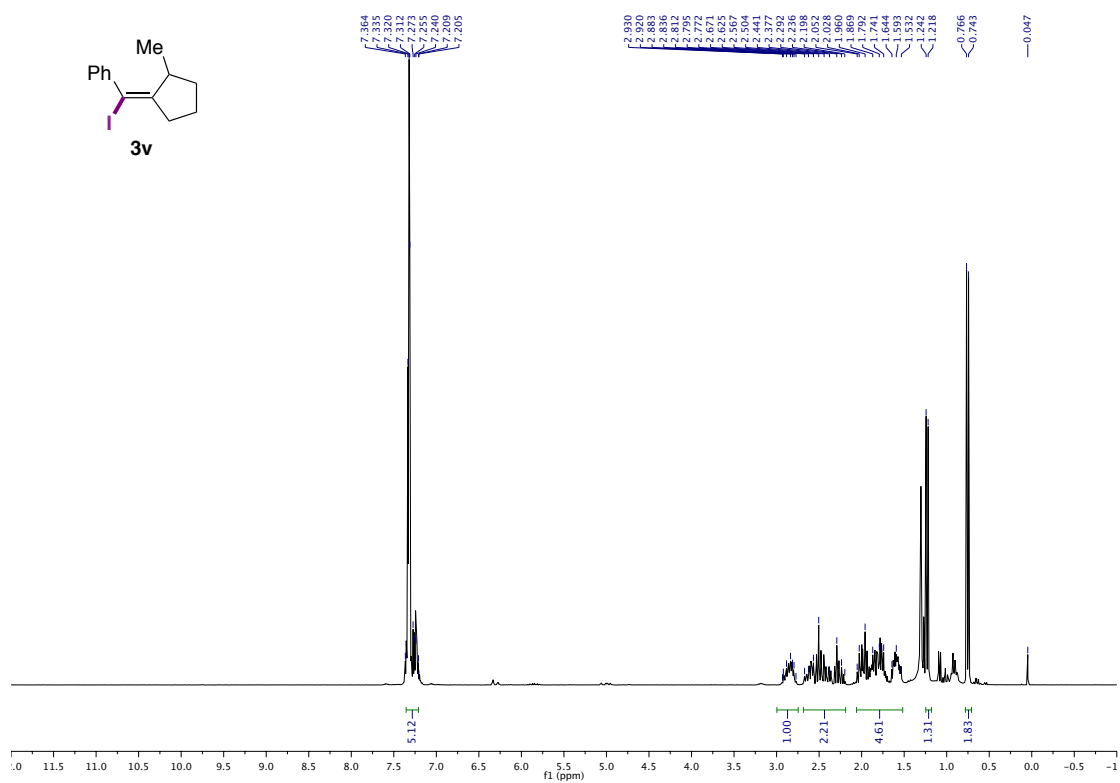


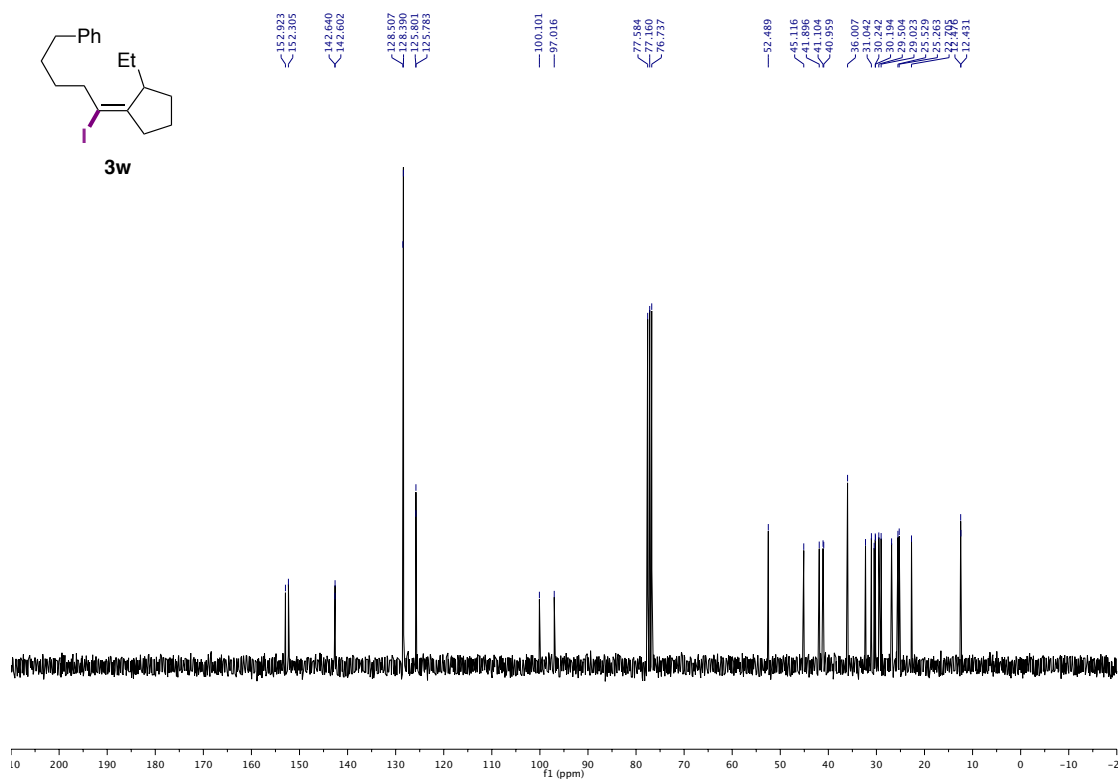
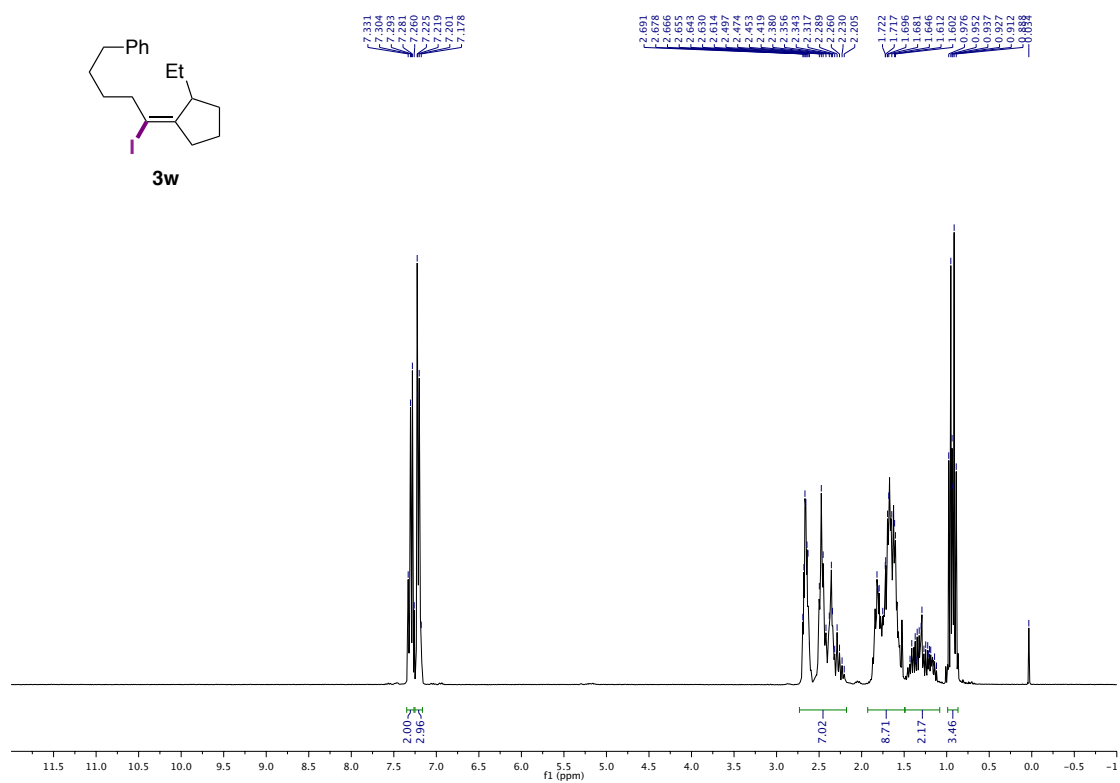


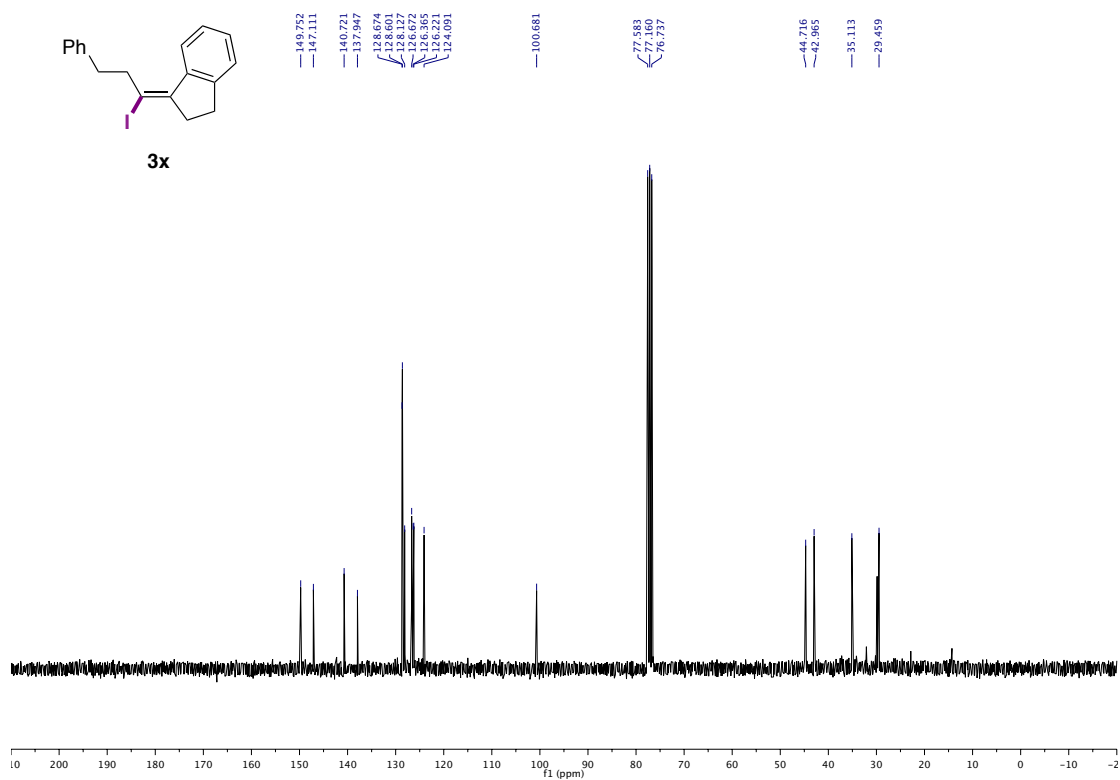
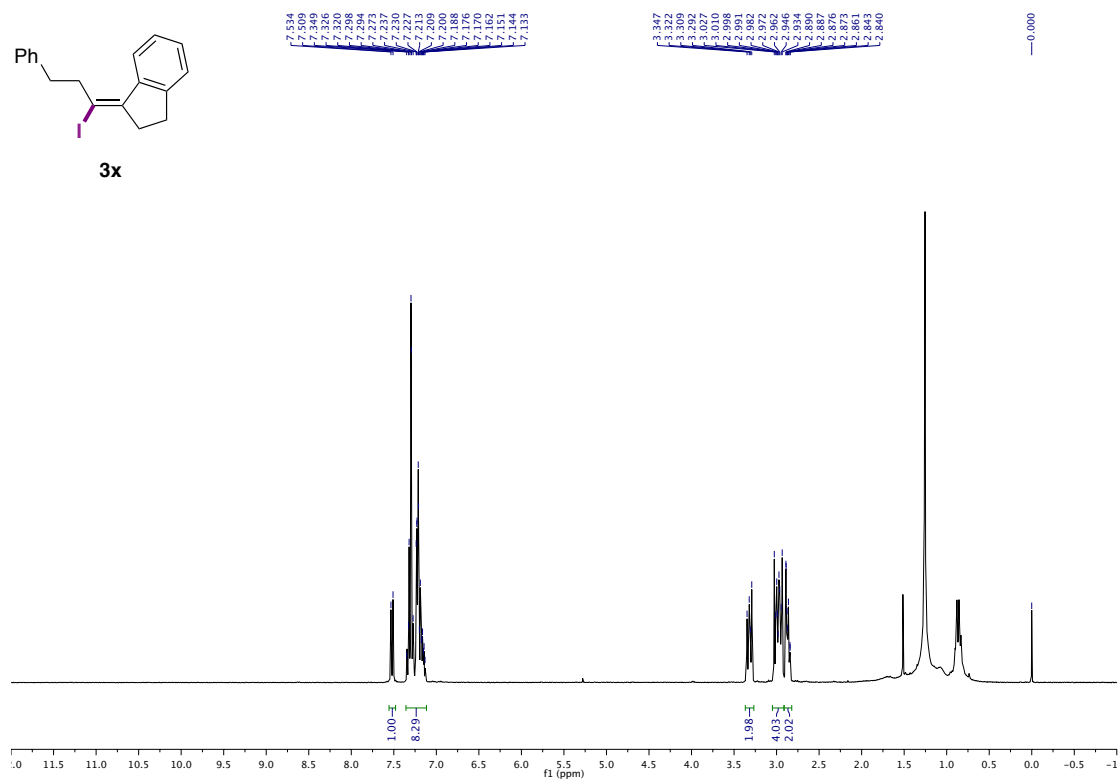


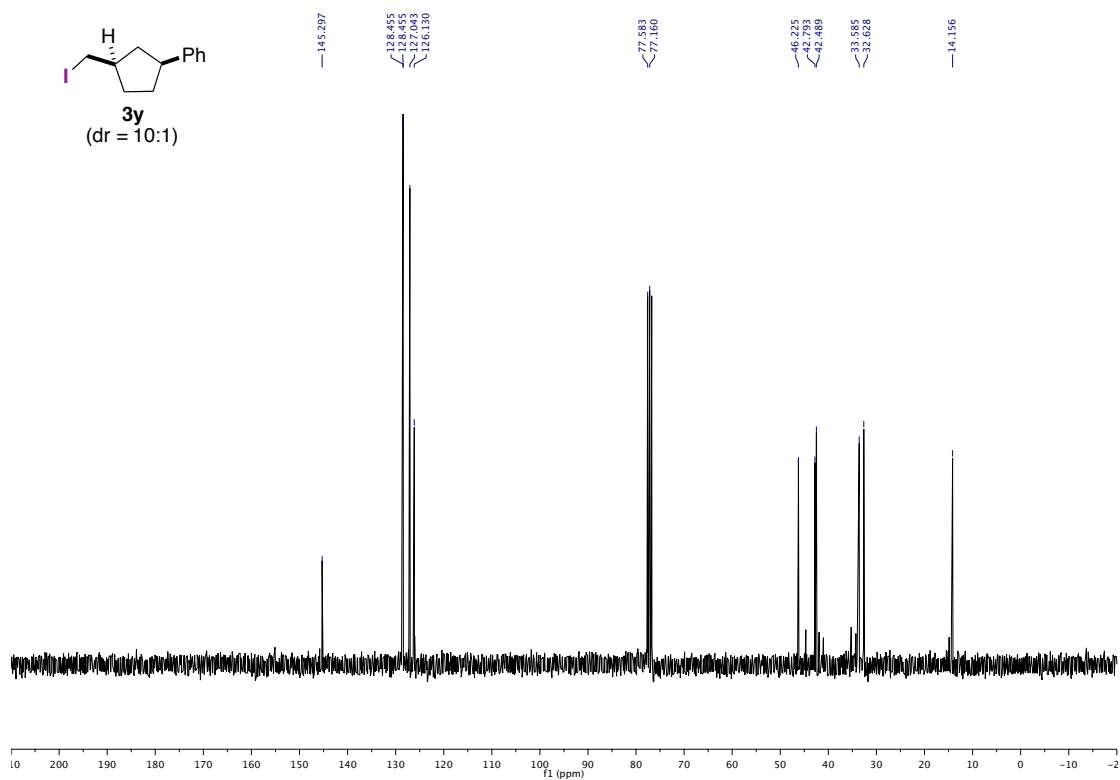
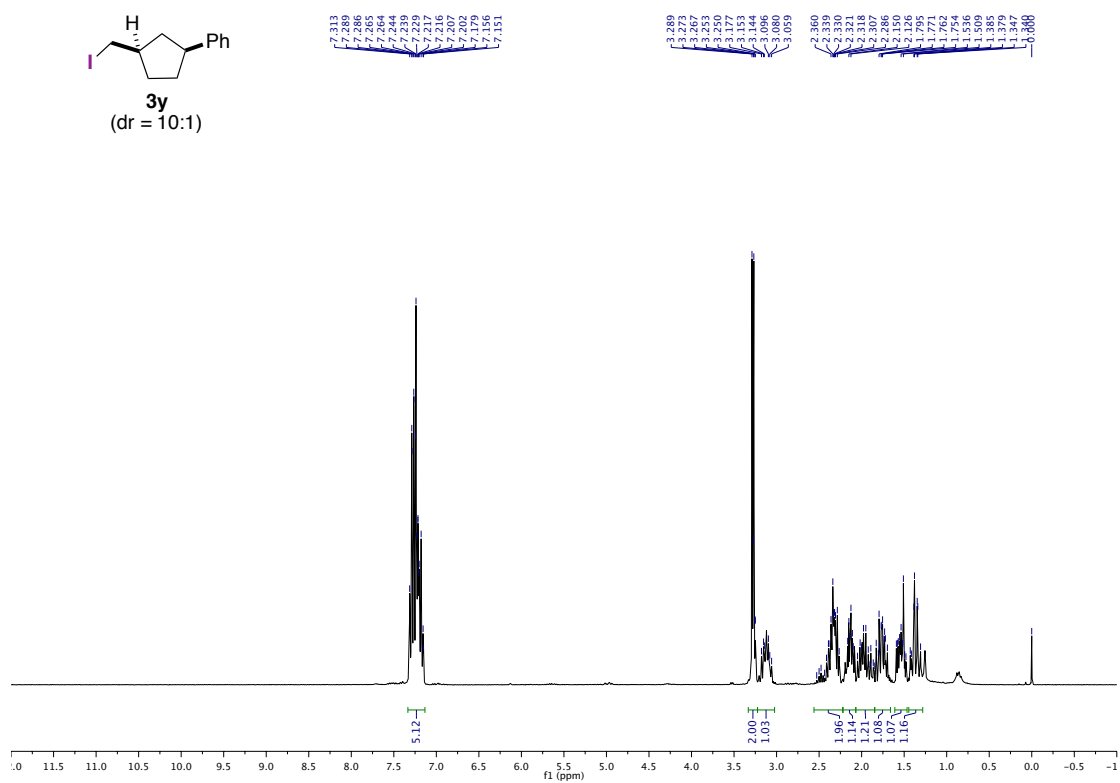


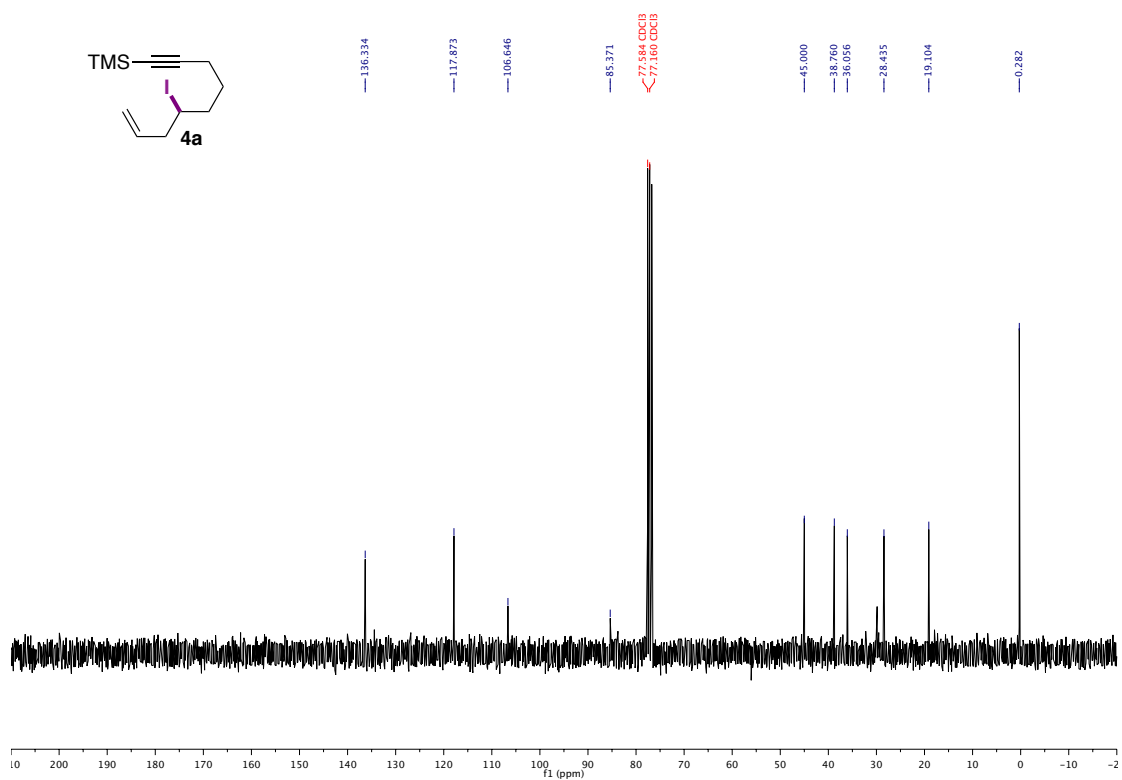
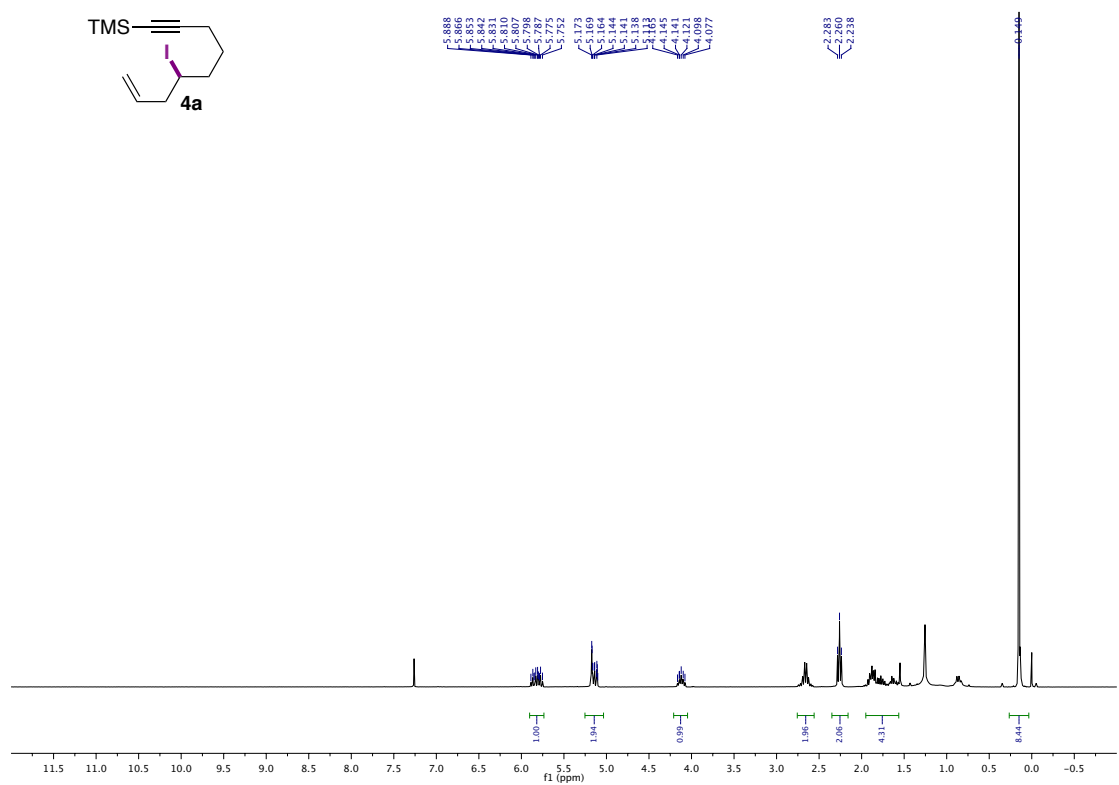


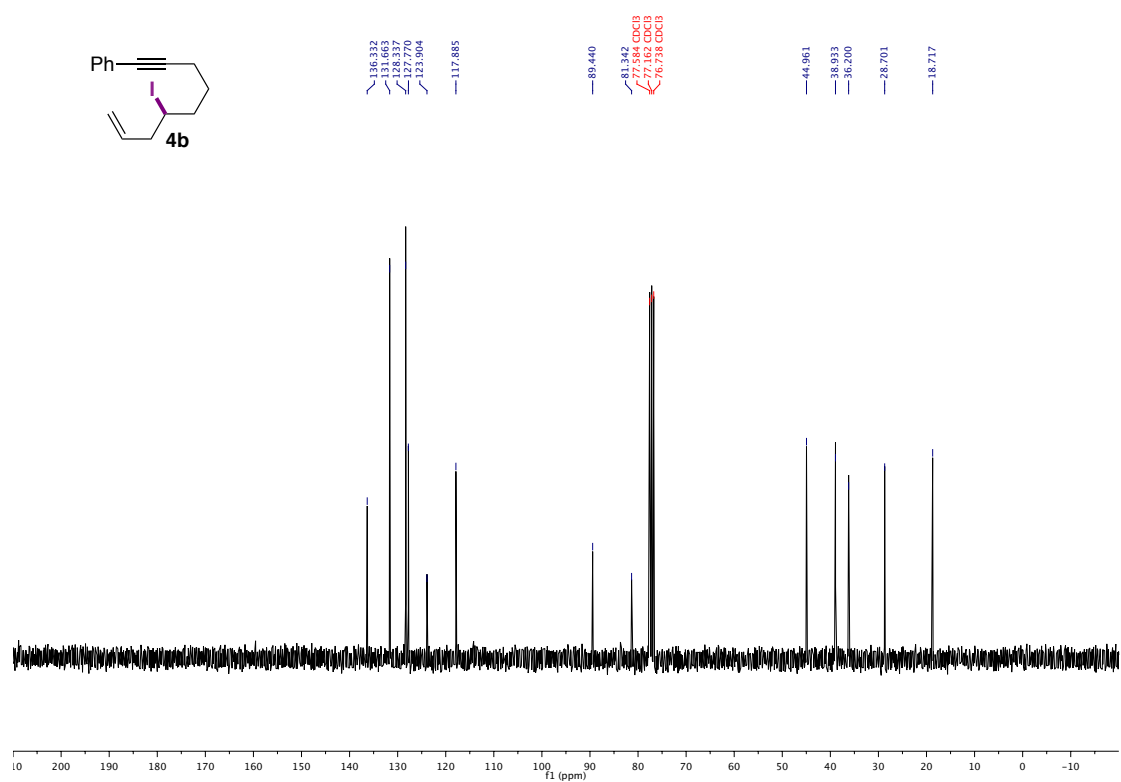
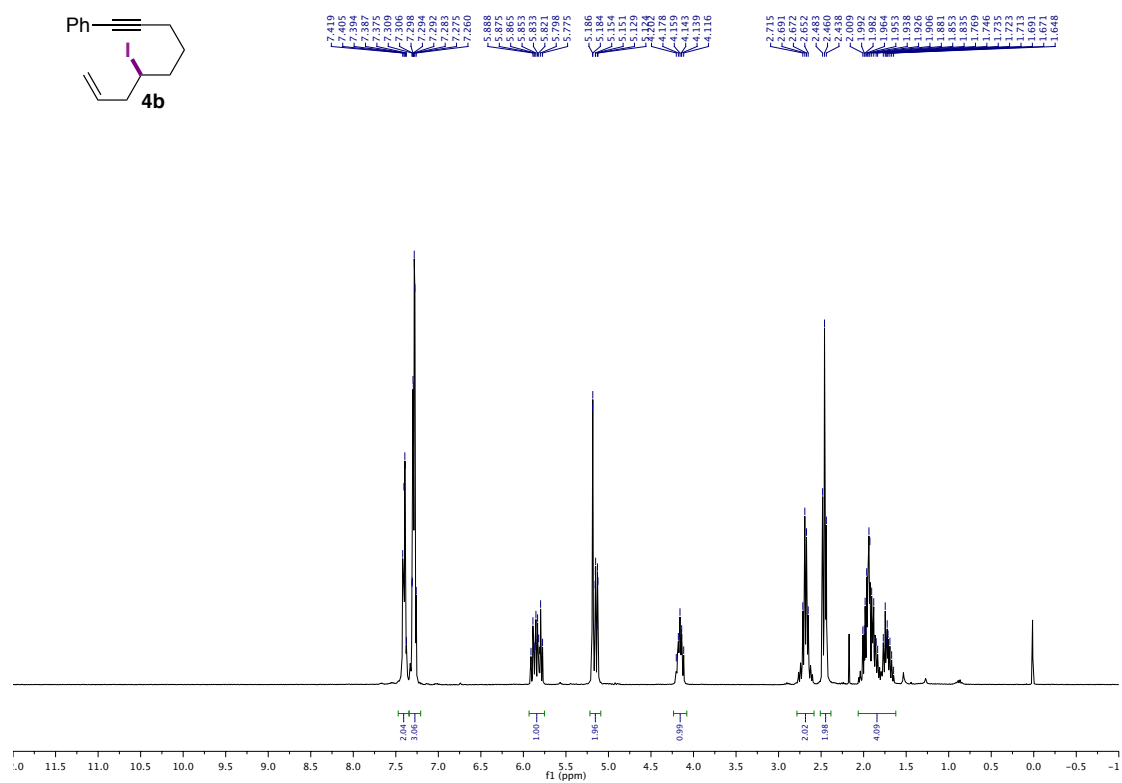


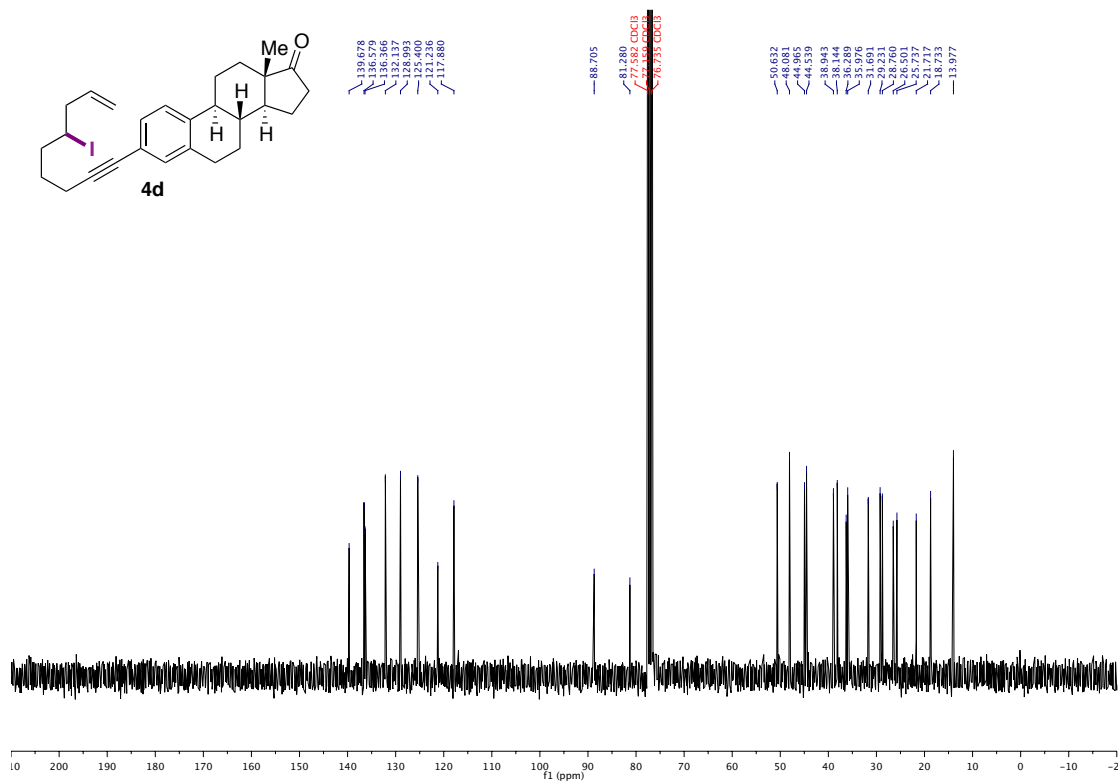
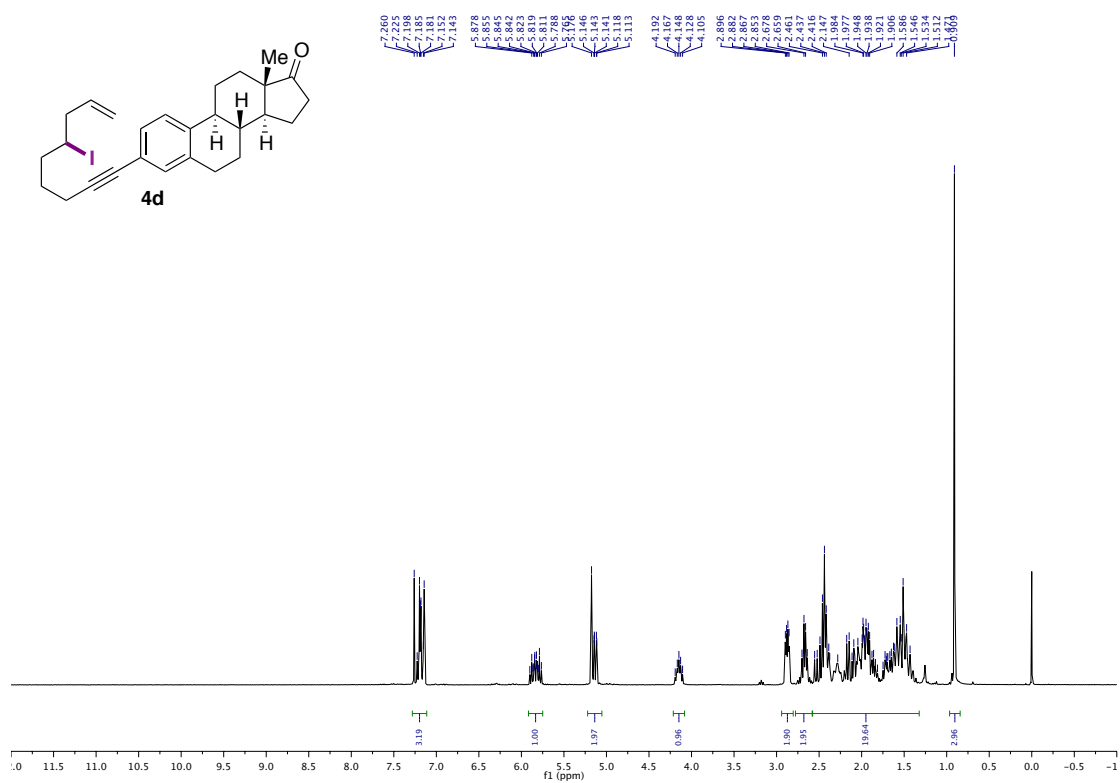


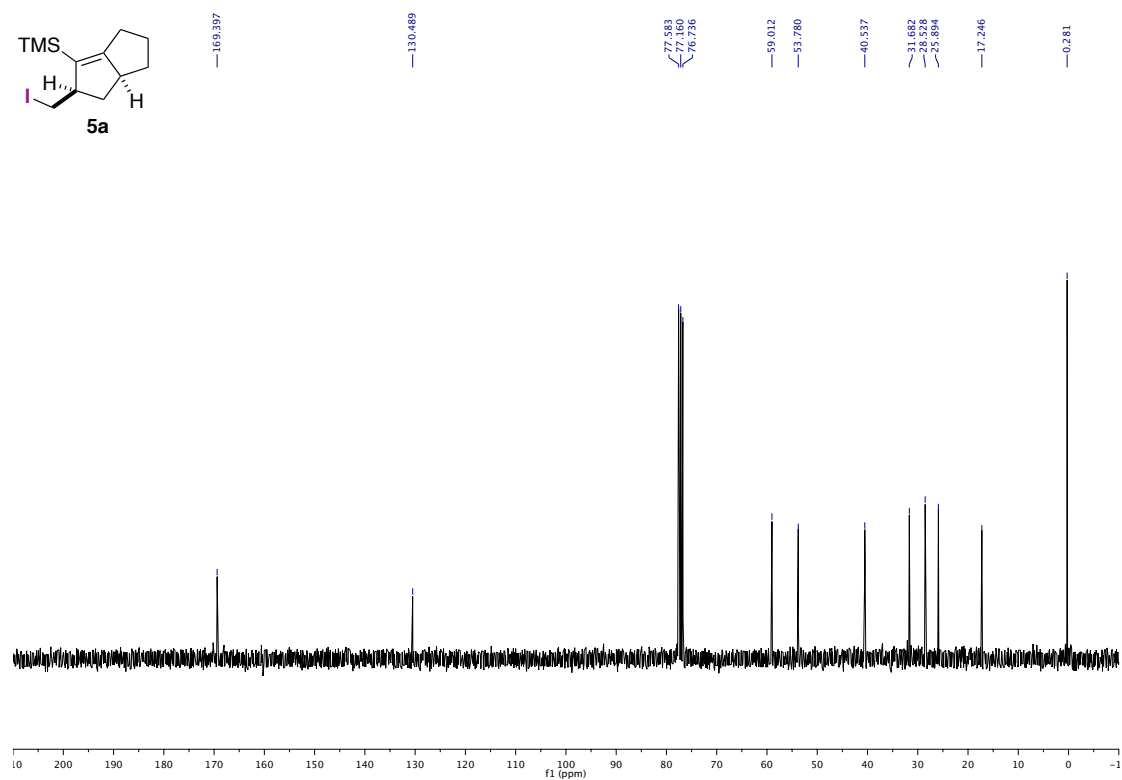


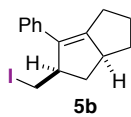
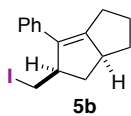


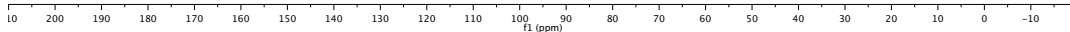
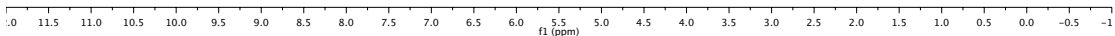












References

- (1) Tordera, D.; Delgado, M.; Ortí, E.; Bolink, H. J.; Frey, J.; Nazeeruddin M. K.; Baranoff, E. *Chem. Mater.* **2012**, *24*, 1896-1903.
- (2) Monks, B. M.; Cook, S. P. *J. Am. Chem. Soc.* **2012**, *134*, 15297-15300.
- (3) Hodgson, D. M.; Labande, A. H.; Pierard, F. Y. T. M.; Castro, M. Á. E. *J. Org. Chem.* **2003**, *68*, 6153-6159.
- (4) Lu, B.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 14070-14072.
- (5) Monks, B. M.; Cook, S. P. *Angew. Chem. Int. Ed.* **2013**, *52*, 14214-14218.
- (6) Prier, C. K.; Rankic, D. A.; MacMillan D. W. C. *Chem. Rev.* **2013**, *113*, 5322-5363.
- (7) Choi, G. J.; Knowles, R. R. *J. Am. Chem. Soc.* **2015**, *137*, 9226-9229.
- (8) Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A235*, 518-536.
- (9) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105-2146.
- (10) Mnalti, M. and co-workers. *Chemical Actinometry. Handbook of Photochemistry*, 3rd ed.; Taylor & Francis Group. **2006**, 601-616.
- (11) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.*, **2015**, *6*, 5426-5434.
- (12) Kropp, P. J., *Photobehavior of Alkyl Halides. CRC Handbook of organic photochemistry and photobiology*, 2nd ed.; **2004**, *1*, 1-32.
- (13) For triethylamine-mediated radical dehalogenation of unactivated alkyl halides via formation of an exciplex see: (a) Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709-2717. (b) Kropp, P. J.; Poindexter, G.S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135-8144.
- (14) Exciplex formation between amines and alkyl halides followed by SET process between these two species have also been reported under visible-light irradiation at high concentrations of the amine, see: Lautenberger, W. J.; Jones, E. N.; Miller, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 1110-1115.
- (15) For an example of a radical-chain process triggered by the formation of an *exciplex*, see: Biaselle, C. J.; Miller, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 3813-3816.
- (16) For reduction processes involving α -amino radicals, see: (a) Ismaili, H.; Pitre, S. P.; Scaiano, J. C. *Catal. Sci. Technol.* **2013**, *3*, 935-937. (b) Lanterna, A. E.; Elhage, A.; Scaiano, J. C. *Catal. Sci. Technol.* **2015**, *5*, 4336-4340.