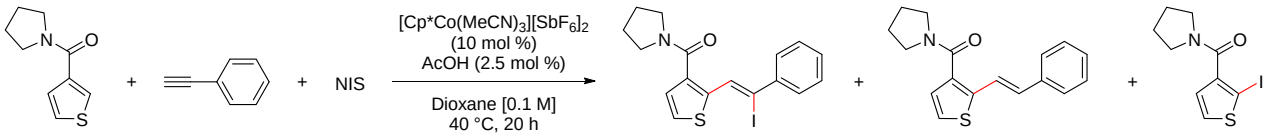
# Supporting Information

# I. Supplemental Optimization Table S1:




**1a** **2a** **3a** ***"standard conditions"*** **4a** **5a**

| Entry | Variation from the standard conditions | Yield 4a (%) | Yield 5a (%) | Yield (%) |
|---|---|---|---|---|
| 1 | None | 70 (71)[c] | 17 | < 5 |
| 2 | No catalyst | 0 | 0 | < 5 |
| 3 | No additive | 27 | 3 | < 5 |
| 4 | AcOH (10 mol %) | 38 | 47 | < 5 |
| 5 | LiOAc (20 mol %) | 67 | 8 | < 5 |
| 6 | Run at 60 °C | 53 | 11 | < 5 |
| 7 | Run at 1.0 M | 43 | 8 | < 5 |
| 8 | In 1,2-DCE | 64 | 27 | < 5 |
| 9 | In THF | 57 | 15 | < 5 |
| 10 | $[Cp^*Co(C_6H_6)][B(C_6F_5)]_2$ (10 mol %) as catalyst system | 3 | 0 | < 5 |
| 11 | $[Cp^*Co(CO)I_2]$ (10 mol %) and $AgSbF_6$ (20 mol %) as catalyst system | 24 | 4 | < 5 |
| 12 | $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) as catalyst system | 8 | 3 | < 5 |
| 13 | No **2a** | -- | -- | 59[d] |
| 14 | No **3a** | -- | 30% | -- |
| 15 | No **3a**, AcOH (10 mol %) | -- | 92%[e] | -- |

[a]Conditions: **1a**, (1.0 equiv), **2a** (1.2 equiv), **3a** (1.5 equiv) using above parameters. [b]Yields determined by $^1$H NMR analysis with 1,3,5-trimethoxybenzene as an external standard. [c]Isolated yield based for a 0.2 mmol scale reaction. [d]Another mono-iodinated product was also detected as a minor product, but the structure was not elucidated. [e]Isolated yield based on a 0.4 mmol scale reaction.

# II. General Information:

Unless otherwise indicated, all Co(III)-catalyzed reactions were set up in a $N_2$ filled glovebox, using glassware that was oven-dried (150 °C) and evacuated while hot prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a $N_2$ atmosphere. Solvents were purified by elution through a column of activated alumina under $N_2$ before use. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Microwave vials and caps were purchased from Biotage with part numbers 351521 and 352298 respectively. Products and starting materials were visualized on TLC using UV-light or by staining with $KMnO_4$ or p-anisaldehyde. The diastereoselectivity and regioselectivity of the reactions was evaluated by NMR analysis of unpurified material. Flash-

column chromatography was preformed on SiliaFlash® P60 (230-400 mesh) silica gel, and preparative thin-layer chromatrography with plates from Analtech (1 mm $SiO_2$, 20 x 20 cm). NMR chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 ppm for $^1H$ and 77.16 ppm for $^{13}C$). For IR spectra, only partial data are provided. Melting points are reported uncorrected. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time of flight (TOF) mass spectrometer.

## III. Preparation of Starting Materials:

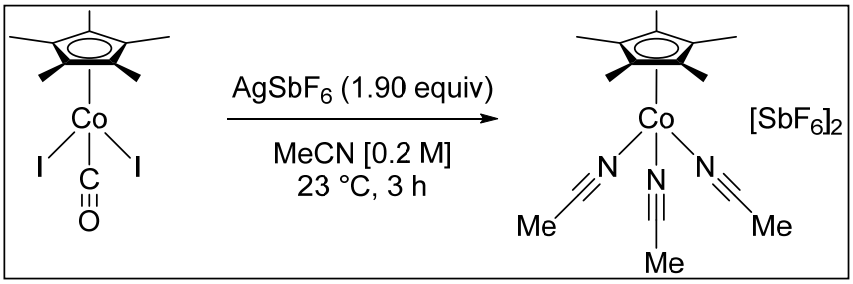
### Catalysts/Additives:

$[Cp^*RhCl_2]_2$,[S1] $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$,[S2] $[Cp^*Co(C_6H_6)][PF_6]_2$,[S3] $[Cp^*Co(CO)I_2]$,[S4] were each synthesized according to literature procedures. Lithium acetate was dried under high vacuum at 75 °C for 20 h.

### Substrates:

*Tert*-butyldimethyl(pent-4-yn-1-yloxy)silane,[S5] ethyl hex-5-ynoate,[S6] *N*,*N*-dimethyl-1*H*-pyrrole-1-carboxamide,[S7] 1-(*m*-tolyl)-1*H*-pyrazole,[S8] and 5-vinylidenenonane[S9] were each synthesized according to literature procedures. All other C–H activation substrates were purchased from commercial sources and used without further purification.

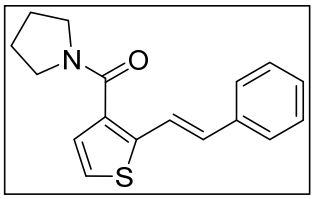
## IV. Preparation of $[Cp^*Co(MeCN)_3][SbF_6]_2$:




In an $N_2$-filled glove box, to a suspension of $[Cp^*Co(CO)I_2]$[S4] (4.76 g, 10.0 mmol) in dried MeCN (25 mL) in a 250 mL single necked round bottom flask, a solution of $AgSbF_6$ (6.53 g, 19.0 mmol) in dried MeCN (25 mL) was added in 5 mL portions over ca. 5 min, causing AgI to precipitate immediately. The reaction flask was sealed with a rubber septa, removed from the glove box, and the reaction mixture was stirred with a $N_2$ inlet at 23 °C in a water bath for 3 h. Then the solid was filtered through celite in air to remove AgI and washed with MeCN (3 × 50 mL, 200 mL total volume). The product complex was then precipitated via the rapid addition of $Et_2O$ (800 mL) and a purple solid precipitated immediately. The purple solid was collected by filtration under vacuum using a medium fritted funnel in air, washed with $CH_2Cl_2$ (3 × 50 mL) and $Et_2O$ (2 × 50 mL), collected and dried under reduced pressure to furnish the product as a purple solid (5.97 g, 7.57 mmol, 80%). The analytical data for this compound are consistent with previously reported data.[S10]

## V. Preparation of Alkene 5a:

**Procedure for Synthesis of (*E*)-pyrrolidin-1-yl(2-styrylthiophen-3-yl)methanone:**



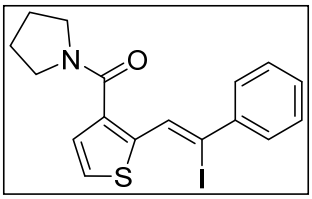

In a $N_2$-filled glove box, a 2.0–5.0 mL microwave vial was charged with $[Cp^*Co(MeCN)_3][SbF_6]_2$ (31.6 mg, 0.0400 mmol, 0.10 equiv). Following this, a 0.0200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg (0.200 mmol) of acetic acid to 10.0 mL of 1,4-dioxane. Then 2.0 mL of this solution was added to the solid mixture, followed by 2.0 mL of 1,4-dioxane (10 mol % total acetic acid relative to the C–H activation substrate, 4.0 mL of total solvent). Pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (72.5 mg, 0.400 mmol, 1.0 equiv) and

ethynylbenzene (49.0 mg, 0.480 mmol, 1.2 equiv) were then added successively. The reaction vial was equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction solution was stirred at 40 °C in an oil bath for 20 h. The reaction vial was then uncapped, and the reaction mixture was concentrated followed by through a silica plug using ~ 20 mL of ethyl acetate as the eluent. After concentration, the residue was purified by silica gel chromatography eluting with a 30:60:10 acetone: hexanes: $CH_2Cl_2$ to afford the desired product **5a** as a yellow oil (104.5 mg, 92% yield). IR (film): 2971, 2874, 1611, 1518, 1430, 954, 715, 691 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.39–7.31 (m, 3H), 7.26-7.23 (m, 1H), 7.13 (d, *J* = 5.2 Hz, 1H), 7.02 (d, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 3.67 (t, *J* = 6.9 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 2H), 1.97–1.92 (m, 2H), 1.88–1.82 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.67, 141.70, 136.69, 135.45, 130.39, 128.76, 128.06, 127.12, 126.69, 123.71, 120.31, 48.77, 46.00, 26.20, 24.60; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{18}NOS^+$: 284.1104. Found 284.1088.

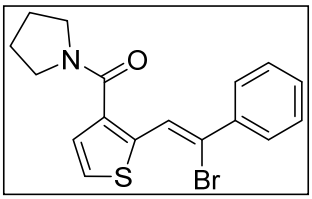
## VI. Procedures for Co(III)-Catalyzed Three-Component Synthesis of Alkenyl Halides:

### General Procedure:

In a $N_2$-filled glove box, a 2.0–5.0 mL microwave vial was charged with $[Cp^*Co(MeCN)_3][SbF_6]_2$ (15.8 mg, 0.0200 mmol, 0.10 equiv) and halogenating agent **3** (0.300 mmol, 1.5 equiv). Following this, a 0.0200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg (0.200 mmol) of acetic acid to 10.0 mL of 1,4-dioxane. Then 250 μL of this solution was added to the solid mixture, followed by 1.75 mL of 1,4-dioxane (2.5 mol % total acetic acid relative to C–H activation partner **1**, 2 mL of total solvent). The indicated C–H bond partner **1** (0.200 mmol, 1.0 equiv) and alkyne **2** (0.240 mmol, 1.2 equiv) were then added successively. The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction solution was stirred at 40 °C in an oil bath for 20 h. The reaction vial was then uncapped, and the reaction mixture was concentrated followed by eluting the resulting residue through a silica plug using ~ 20 mL of ethyl acetate as the eluent. After concentration, the residue was purified by the chromatographic method and eluent indicated in the specific procedure to afford the desired product.

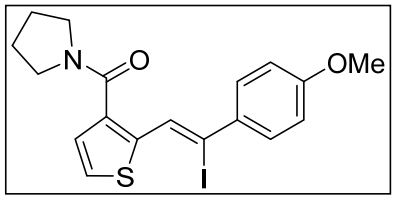



**(*Z*)-(2-(2-Iodo-2-phenylvinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4a):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and *N*-iodosuccinimide (NIS) (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4a** (58.5 mg, 71% yield) as a yellow oil. IR (film): 2969, 2873, 1610, 1504, 1486, 1425, 718, 692 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.35–7.31 (m, 3H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 5.2 Hz, 1H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.30 (t, *J* = 6.4 Hz, 2H), 1.96–1.91 (m, 2H), 1.88–1.83 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.87, 144.30, 139.90, 138.87, 129.74, 128.96, 128.70, 128.47, 125.94, 125.30, 101.47, 48.88, 46.04, 26.22, 24.61; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{17}INOS^+$: 410.0070. Found 410.0082.



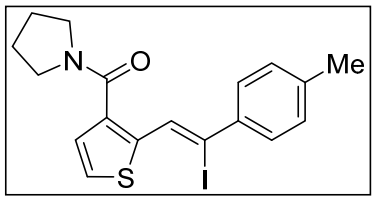

**(*Z*)-(2-(2-Bromo-2-phenylvinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4b):** Slightly modified conditions: Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and *N*-bromosuccinimide

(NBS) (53.4 mg, 0.300 mmol, 1.5 equiv). For this reaction 1 mL of acetic acid stock solution was added along with 1 mL of dioxane (10 mol % total acetic acid relative to the C–H activation partner **1a**, 2 mL total solvent). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4b** (48.1 mg, 66% yield) as a yellow-orange oil. IR (film): 2971, 2876, 1611, 1509, 1426, 1363, 719, 691 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.38–7.35 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 5.2 Hz, 1H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.31 (t, *J* = 6.2 Hz, 2H), 1.97–1.92 (m, 2H), 1.88–1.84 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.92, 140.33, 139.14, 138.08, 128.93, 128.56, 127.90, 126.27, 125.74, 123.62, 122.13, 48.94, 46.09, 26.24, 24.62; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{17}BrNOS^+$: 362.0209. Found 362.0200.

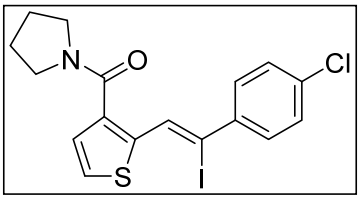



**(*Z*)-(2-(2-Iodo-2-(4-methoxyphenyl)vinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4c):** Slightly modified conditions: Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 1-ethynyl-4-methoxybenzene (31.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). For this reaction 0.5 mL of acetic acid stock solution was added along with 1.5 mL of dioxane (5 mol % total acetic acid relative to the C–H activation partner **1a**, 2 mL total solvent). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford

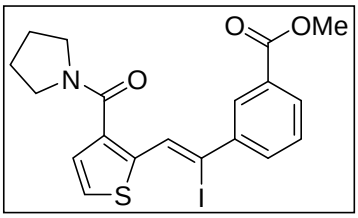
product **4c** (52.5 mg, 60% yield) as a yellow oil. IR (film): 2968, 2875, 1601, 1503, 1428, 1248, 1172, 828 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 5.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.62 (t, *J* = 6.9 Hz, 2H), 3.30 (t, *J* = 6.6 Hz, 2H), 1.96–1.90 (m, 2H), 1.88–1.83 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.99, 160.05, 139.44, 139.13, 136.88, 130.24, 128.33, 125.90, 124.98, 113.75, 101.66, 55.55, 48.87, 46.04, 26.22, 24.62.; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{19}INO_2S^+$: 440.0176. Found 440.0185.




**(*Z*)-(2-(2-Iodo-2-(*p*-tolyl)vinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4d):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 1-ethynyl-4-methylbenzene (27.9 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4d** (54.1 mg, 64% yield) as a yellow oil. IR (film): 2971, 2874, 1609, 1502, 1426, 1362, 816, 720 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 5.2 Hz, 1H), 7.14–7.12 (m, 3H), 3.62 (t, *J* = 7.3 Hz, 2H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.36 (s, 3H), 1.94–1.92 (m, 2H), 1.86–1.84 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.95, 141.52, 139.70, 138.92, 138.82, 129.12, 128.96, 128.84, 125.89, 125.16, 101.82, 48.86, 46.03, 26.20, 24.62, 21.22; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{19}INOS^+$: 424.0227. Found 424.0233.

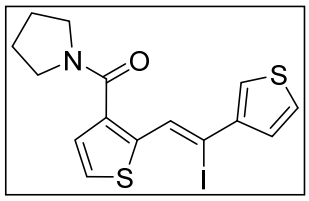



**(*Z*)-(2-(2-(4-Chlorophenyl)-2-iodovinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4e):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 1-chloro-4-ethynylbenzene (32.8 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4e** (60.3 mg, 68% yield) as a yellow waxy solid. IR (film): 2966, 2876, 1603, 1483, 1429, 1089, 826, 721 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 5.1 Hz, 1H), 7.29 (d, $J$ = 8.5 Hz, 2H), 7.13 (d, $J$ = 5.2 Hz, 1H), 3.62 (t, $J$ = 6.9 Hz, 2H), 3.30 (t, $J$ = 6.6 Hz, 2H), 1.95–1.91 (m, 2H), 1.88–1.83 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.73, 142.78, 139.94, 138.80, 134.56, 130.15, 128.54, 126.00, 125.52, 99.47, 48.94, 46.09, 26.23, 24.58; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{16}ClINOS^+$: 443.9680. Found 443.9675.



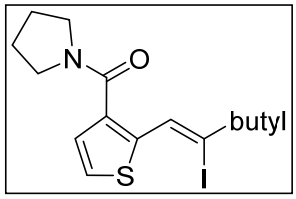

**Methyl (*Z*)-3-(1-iodo-2-(3-(pyrrolidine-1-carbonyl)thiophen-2-yl)vinyl)benzoate (4f):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), methyl 3-ethynylbenzoate (38.4 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5

equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4f** (54.7 mg, 58% yield) as a yellow waxy solid. IR (film): 2969, 2873, 1718, 1603, 1436, 1278, 1209, 722 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.94 (d, *J* = 7.8, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.66 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H), 3.93 (s, 3H), 3.62 (t, *J* = 7.0 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 2H), 1.97–1.93 (m, 2H), 1.90–1.86 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 166.60, 165.76, 144.76, 140.20, 138.47, 133.10, 130.60, 130.45, 130.00, 129.67, 128.67, 126.06, 125.67, 99.50, 52.42, 48.94, 46.12, 26.22, 24.60; HRMS (ESI/[M+H]+) calcd. for $C_{19}H_{19}INO_3S^+$: 468.0125. Found 468.0121.

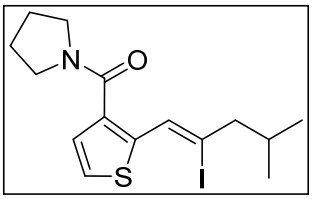



**(*Z*)-(2-(2-Iodo-2-(thiophen-3-yl)vinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4g):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 3-ethynylthiophene (26.0 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed

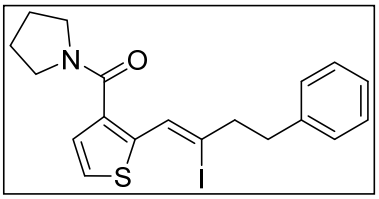
with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4g** (46.3 mg, 56% yield) as a yellow oil. IR (film): 3100, 2969, 2873, 1607, 1426, 1360, 1232, 717 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.47 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.37 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.33–7.32 (m, 2H), 7.13 (d, *J* = 5.2 Hz, 1H), 3.66–3.63 (m, 2H), 3.31–3.29 (m, 2H), 1.96–1.94 (m, 2H), 1.87–1.85 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.91, 145.09, 139.49, 138.87, 127.96, 126.47, 126.39, 126.24, 126.03, 125.51, 94.10, 48.94, 46.12, 26.24, 24.65; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{15}INOS_2^+$: 415.9634. Found 415.9637.



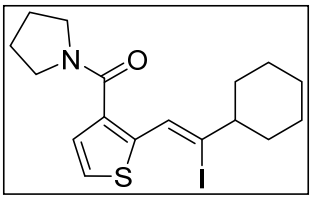

**(*Z*)-(2-(2-Iodohex-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4h):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), hex-1-yne (19.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4h** (66.5 mg, 85% yield) as a yellow oil. IR (film): 2954, 2928, 2871, 1614, 1425, 1361, 1232, 717 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 5.2 Hz, 1H), 7.20 (s, 1H), 7.05 (d, *J* = 5.2 Hz, 1H), 3.62 (t, *J* = 7.0 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.68 (d, *J* = 7.2 Hz, 2H), 1.96–1.91 (m, 2H), 1.87–1.83 (m, 2H), 1.59–1.54 (m, 2H), 1.36–1.29 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 165.99, 138.47, 138.19, 126.82, 125.66, 124.49, 108.06, 48.75, 47.37, 45.97, 32.07, 26.19, 24.64, 21.47, 14.00; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{21}INOS^+$: 390.0383. Found 390.0380.



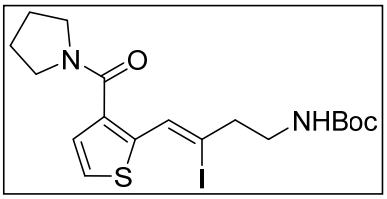
**(*Z*)-(2-(2-Iodo-4-methylpent-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4i):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 4-methylpent-1-yne (19.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 40:50:10 mixture of acetone: hexanes: $CH_2Cl_2$ to afford product **4i** (65.7 mg, 84% yield) as a yellow oil. IR (film): 2953, 2870, 1615, 1427, 1362, 1239, 844, 718 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.23 (d, $J$ = 5.2 Hz, 1H), 7.15 (s, 1H), 7.05 (d, $J$ = 5.2 Hz, 1H), 3.62 (t, $J$ = 7.0 Hz, 2H), 3.25 (t, $J$ = 6.7 Hz, 2H), 2.52 (dd, $J$ = 7.1, 0.8 Hz, 2H), 2.08–2.00 (m, 1H), 1.95–1.90 (m, 2H), 1.87–1.82 (m, 2H), 0.91 (d, $J$ = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.00, 138.35, 138.28, 127.66, 125.65, 124.59, 107.31, 56.37, 48.72, 45.96, 28.38, 26.16, 24.65, 21.61; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{21}INOS^+$: 390.0383 Found 390.0385.



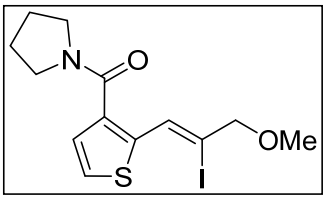
**(*Z*)-(2-(2-Iodo-4-phenylbut-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4j):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), but-3-yn-1-ylbenzene (31.2 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone: hexanes: $CH_2Cl_2$ to afford product **4j** (64.6 mg, 74% yield) as a yellow oil. IR (film): 2971, 2874, 1614, 1427, 1361, 1336, 718, 698 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 3H), 7.21–7.16 (m, 3H), 7.12 (s, 1H), 7.04 (d, $J$ = 4.9 Hz, 1H), 3.58 (t, $J$ = 6.5 Hz, 2H), 3.09 (t, $J$ = 6.1 Hz, 2H), 3.00–2.98 (m, 2H), 2.93–2.90 (m, 2H), 1.91–1.87 (m, 2H), 1.82–1.78 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.89, 140.32, 138.58, 138.04, 128.80, 128.46, 127.63, 126.24, 125.71, 124.70, 105.98, 49.67, 48.59, 45.91, 36.26, 26.14, 24.56; HRMS (ESI/[M+H]+) calcd. for $C_{19}H_{21}INOS^+$: 438.0383. Found 438.0382.



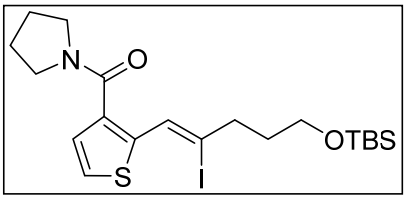
**(*Z*)-(2-(2-Cyclohexyl-2-iodovinyl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4k):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), ethynylcyclohexane (26.0 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone: hexanes: $CH_2Cl_2$ to afford product **4k** (64.6 mg, 74% yield) as a yellow oil. IR (film): 2925, 2851, 1613, 1426, 1358, 1238, 844, 717 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.23 (d, $J$ = 5.2 Hz, 1H), 7.07 (d, $J$ = 5.2 Hz, 1H), 3.64 (t, $J$ = 6.7 Hz, 2H), 3.28 (t, $J$ = 6.3 Hz, 2H), 2.16–2.11 (m, 1H), 1.98–1.93 (m, 2H), 1.89–1.79 (m, 6H), 1.69–1.66 (m, 1H), 1.44–1.31 (m, 4H), 1.22–1.14 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.11, 139.07, 138.30, 125.75, 124.89, 124.44, 117.14, 53.28, 48.80, 46.05, 34.07, 26.27, 26.00, 25.99, 24.69; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{23}INOS^+$: 416.0540. Found 416.0565.



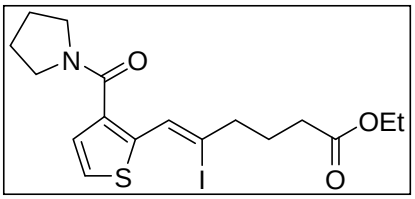
***Tert*-butyl (*Z*)-(3-iodo-4-(3-(pyrrolidine-1-carbonyl)thiophen-2-yl)but-3-en-1-yl)carbamate (4l):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), *tert*-butyl but-3-yn-1-ylcarbamate (40.6 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4l** (76.0 mg, 80% yield) as a yellow oil. IR (film): 3324 (br), 2974, 2879, 1696, 1609, 1433, 1363, 1164 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.07 (d, $J$ = 5.2 Hz, 1H), 4.76 (s, 1H), 3.61 (t, $J$ = 6.8 Hz, 2H), 3.36–3.35 (m, 2H), 3.28 (t, $J$ = 6.5 Hz, 2H), 2.85 (t, $J$ = 6.2 Hz, 2H), 1.96–1.91 (m, 2H), 1.89–1.83 (m, 2H), 1.41 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.66, 155.93, 138.59, 138.52, 129.14, 125.86, 124.85, 103.53, 48.84, 47.52, 46.06, 40.42, 29.38, 28.50, 26.24, 24.57; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{26}IN_2O_3S^+$: 477.0703. Found 477.0722.



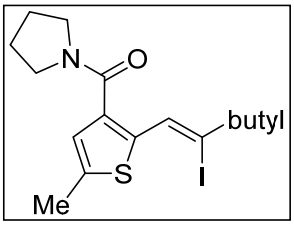

**(*Z*)-(2-(2-Iodo-3-methoxyprop-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4m):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), 3-methoxyprop-1-yne (16.8 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 70:20:10 mixture of ethyl ether:pentane:$CH_2Cl_2$ to afford product **4m** (63.0 mg, 83% yield) as a yellow oil. IR (film): 2973, 2875, 2822, 1611, 1428, 1359, 1104, 718 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.30 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 5.2 Hz, 1H), 4.25 (s, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.35 (s, 3H), 3.26 (t, *J* = 6.6 Hz, 2H), 1.97–1.91 (m, 2H), 1.88–1.83 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.66, 139.37, 137.62, 128.24, 125.90, 125.41, 101.83, 82.00, 57.77, 48.82, 46.03, 26.21, 24.60; HRMS (ESI/[M+H]+) calcd. for $C_{13}H_{17}INO_2S^+$: 378.0019. Found 378.0010.



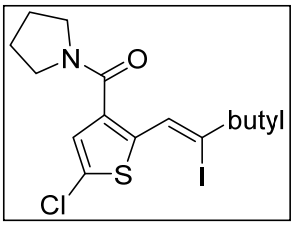

**(*Z*)-(2-(5-((*Tert*-butyldimethylsilyl)oxy)-2-iodopent-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4n):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane[S5] (47.6 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4n** (85.9 mg, 85% yield) as a yellow oil. IR (film): 3408 (br), 2951, 2855, 1611, 1429, 1250, 1095, 833 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.24–7.23 (m, 2H), 7.06 (d, *J* = 5.2 Hz, 1H), 3.64–3.61 (m, 4H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.78–2.75 (m, 2H), 1.96–1.91 (m, 2H), 1.88–1.78 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.90, 138.49, 138.29, 127.14, 125.78, 124.52, 107.37, 61.60, 48.76, 45.97, 44.33, 33.30, 26.22, 26.08, 24.63, 18.41, -5.14; HRMS (ESI/[M+H]+) calcd. for $C_{20}H_{33}INO_2SSi^+$: 506.1040. Found 506.1027.



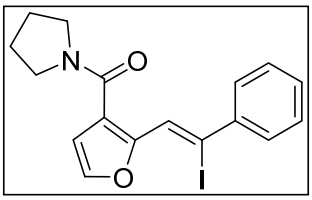

**Ethyl (*Z*)-5-iodo-6-(3-(pyrrolidine-1-carbonyl)thiophen-2-yl)hex-5-enoate (4o):** Derived from pyrrolidin-1-yl(thiophen-3-yl)methanone **1a** (36.3 mg, 0.200 mmol, 1.0 equiv), ethyl hex-5-ynoate[S6] (33.6 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4o** (81.4 mg, 91% yield) as a yellow-orange waxy solid. IR (film): 2974, 2876, 1726, 1615, 1429, 1232, 1180, 718 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.05 (d, *J* = 5.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 7.0 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.96–1.89 (m, 4H), 1.88–1.83 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 173.12, 165.82, 138.48, 138.24, 127.82, 125.72, 124.69, 106.00, 60.48, 48.78, 46.73, 45.98, 32.70, 26.18, 25.15, 24.59, 14.34; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{23}INO_3S^+$: 448.0438. Found 448.0429.




**(*Z*)-(2-(2-Iodohex-1-en-1-yl)-5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone (4p):** Derived from (5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone **1b** (39.0 mg, 0.200 mmol, 1.0 equiv), hex-1-yne (19.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4p** (68.9 mg, 85% yield) as a yellow oil. IR (film): 2954, 2927, 2871, 1615, 1452, 1407, 1352, 769 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.71 (s, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.95–1.90 (m, 2H), 1.87–1.82 (m, 2H), 1.57–1.52 (m, 2H), 1.35–1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 166.08, 139.31, 138.37, 135.87, 126.96, 123.85, 106.20, 48.70, 47.29, 45.88, 32.09, 26.16, 24.66, 21.47, 15.41, 14.00; HRMS (ESI/[M+H]+) calcd. for $C_{16}H_{23}INOS^+$: 404.0540. Found 404.0533.

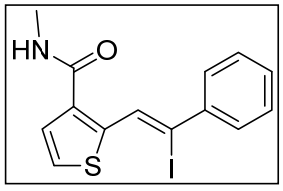



**(*Z*)-(5-Chloro-2-(2-iodohex-1-en-1-yl)thiophen-3-yl)(pyrrolidin-1-yl)methanone (4q):** Derived from (5-chlorothiophen-3-yl)(pyrrolidin-1-yl)methanone **1c** (43.1 mg, 0.200 mmol, 1.0 equiv), hex-1-yne (19.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4q** (63.4 mg, 75% yield) as a yellow oil. IR (film): 2955, 2929, 2871, 1618, 1432, 1409, 1222, 837 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.90 (s, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.96–1.91 (m, 2H), 1.89–1.85 (m, 2H), 1.57–1.52 (m, 2H), 1.35–1.28 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 164.64, 137.31, 136.91, 129.16, 126.52, 124.58, 108.20, 48.76, 47.30, 46.05, 32.06, 26.19, 24.61, 21.48, 13.98; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{20}ClINOS^+$: 423.9993. Found 424.0002.



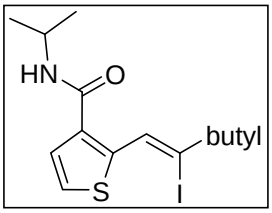

**(*Z*)-(2-(2-Iodo-2-phenylvinyl)furan-3-yl)(pyrrolidin-1-yl)methanone (4r):** Slightly modified conditions: Derived from furan-3-yl(pyrrolidin-1-yl)methanone **1d** (33.0 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). For this reaction 0.5 mL of acetic acid stock solution was added along with 1.5 mL of dioxane (5 mol % total acetic acid relative to the C–H activation partner **1d**, 2 mL total solvent). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed

with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated. The residual material was then purified through silica gel chromatography eluting with a 50:50 mixture of ethyl acetate/hexanes to afford product **4r** (35.2 mg, 45% yield) as a yellow oil. IR (film): 2972, 2875, 1605, 1478, 1442, 1419, 722, 692 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.56 (d, $J$ = 7.8 Hz, 2H), 7.50 (s, 1H), 7.30 (t, $J$ = 7.5 Hz, 2H), 7.25 (t, $J$ = 7.2 Hz, 1H), 6.60 (s, 1H), 3.57 (t, $J$ = 6.4 Hz, 2H), 3.49 (t, $J$ = 6.1 Hz, 2H), 1.92–1.88 (m, 4H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 163.66, 150.82, 144.46, 141.37, 128.91, 128.81, 128.34, 124.94, 122.21, 111.01, 99.62, 48.93, 46.39, 26.53, 24.42; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{17}INO_2^+$: 394.0298. Found 394.0294.

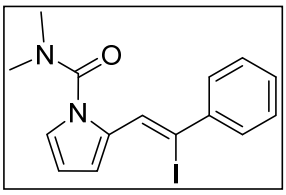



**(*Z*)-2-(2-Iodo-2-phenylvinyl)-*N*-methylthiophene-3-carboxamide (4s):** Derived from *N*-methylthiophene-3-carboxamide **1e** (28.2 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4s** (37.6 mg, 51% yield) as an off-white solid (mp: 117–118 °C). IR (film): 3272 (br), 3043, 2924, 1623, 1542, 1295, 752, 678 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.60 (d, $J$ = 7.2 Hz, 2H), 7.35–7.31 (m, 3H), 7.30–7.27 (m, 1H), 7.23 (d, $J$ = 5.3 Hz, 1H), 6.00 (s, 1H), 2.95 (d, $J$ = 4.9 Hz, 3H); $^{13}C\{^1H\}$ NMR

(126 MHz, $CDCl_3$): δ 165.35, 144.15, 142.47, 136.45, 130.45, 129.09, 128.84, 128.49, 126.42, 125.14, 104.04, 26.85; HRMS (ESI/[M+H]+) calcd. for $C_{14}H_{13}INOS^+$: 369.9757. Found 369.9763.

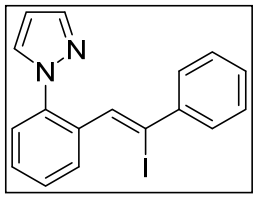



**(*Z*)-2-(2-Iodohex-1-en-1-yl)-*N*-isopropylthiophene-3-carboxamide (4t):** Slightly modified conditions: Derived from *N*-isopropylthiophene-3-carboxamide **1f** (33.8 mg, 0.200 mmol, 1.0 equiv), hex-1-yne (19.7 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). For this reaction 1 mL of acetic acid stock solution was added along with 1 mL of dioxane (10 mol % total acetic acid relative to the C–H activation substrate **1f**, 2 mL total solvent). The product was then purified by silica gel chromatography eluting with a 30:60:10 mixture of acetone:hexanes:$CH_2Cl_2$ to afford product **4t** (47.3 mg, 63% yield) as an off-white solid (mp: 102–103 °C). IR (film): 3285 (br), 2953, 2868, 1625, 1535, 1455, 1281, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.23–7.20 (m, 2H), 5.73 (d, $J$ = 6.1 Hz, 1H), 4.28–4.18 (m, 1H), 2.73 (t, $J$ = 7.4 Hz, 2H), 1.64–1.58 (m, 2H), 1.40–1.32 (m, 2H), 1.23 (d, $J$ = 6.6 Hz, 6H), 0.94 (t, $J$ = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.72, 141.75, 135.59, 127.47, 126.71, 124.39, 111.33, 47.40, 41.86, 32.08, 23.00, 21.65, 14.05; HRMS (ESI/[M+H]+) calcd. for $C_{14}H_{21}INOS^+$: 378.0383. Found 378.0380.

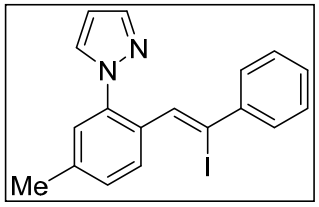



**(*Z*)-2-(2-Iodo-2-phenylvinyl)-N,N-dimethyl-1*H*-pyrrole-1-carboxamide (4u):** Slightly modified conditions: Derived from *N*,*N*-dimethyl-1*H*-pyrrole-1-carboxamide[S7] **1g** (41.4 mg, 0.300 mmol, 1.5 equiv), ethynylbenzene (20.4 mg, 0.200 mmol, 1.0 equiv), and NIS (49.5 mg, 0.220 mmol, 1.1 equiv). Lithium acetate (2.7 mg, 0.041 mmol, 0.2 equiv) was used in place of acetic acid, and the reaction was heated at 60 °C. The product was then purified by silica gel chromatography eluting with a 95:5 mixture of $CH_2Cl_2$:ethyl acetate to afford product **4u** (44.7 mg, 61% yield) as a yellow-orange oil. IR (film): 2929, 1681, 1487, 1441, 1385, 1272, 1060, 724

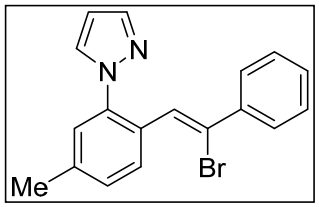
$cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 2.8 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.10 (s, 1H), 6.92 (s, 1H), 6.34 (t, *J* = 2.9 Hz, 1H), 2.98 (s, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 154.37, 144.50, 131.12, 128.81, 128.42, 128.40, 126.59, 121.57, 112.21, 110.01, 99.12, 38.19; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{16}IN_2O^+$: 367.0302. Found 367.0306.



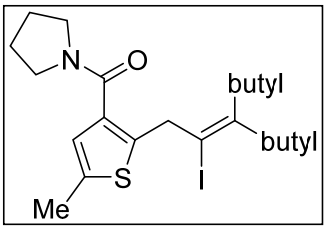

**(*Z*)-1-(2-(2-Iodo-2-phenylvinyl)phenyl)-1*H*-pyrazole (4v):** Derived from 1-phenyl-1*H*-pyrazole **1h** (28.8 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified first by silica gel chromatography using a 10:90 mixture of ethyl acetate/hexanes to give a yellow oil that was then purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4v** (38.1 mg, 51% yield) as a light yellow oil. IR (film): 2921, 2849, 1516, 1491, 1442, 1392, 748, 692 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.51–7.44 (m, 4H), 7.34–7.28 (m, 3H), 6.90 (s, 1H), 6.43 (t, *J* = 2.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 143.14, 141.00, 139.00, 134.93, 134.31, 131.28, 130.81, 129.18, 128.93, 128.80, 128.46, 127.66, 125.23, 107.40, 106.93; HRMS (ESI/[M+H]+) calcd. for $C_{17}H_{14}IN_2^+$: 373.0196. Found 373.0189.



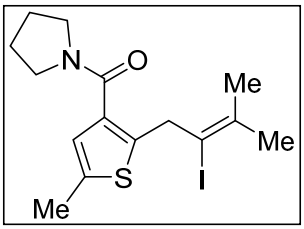

**(*Z*)-1-(2-(2-Iodo-2-phenylvinyl)-5-methylphenyl)-1*H*-pyrazole (4w):** Derived from 1-(*m*-tolyl)-1*H*-pyrazole[S8] **1i** (31.6 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4w** (57.2 mg, 74% yield) as a yellow oil. IR (film): 2919, 1516, 1442, 1400, 1036, 750, 692, 618 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.70 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.41 (s, 1H), 7.33–7.26 (m, 4H), 6.85 (s, 1H), 6.42 (s, 1H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.21, 140.87, 139.54, 138.84, 134.86, 131.26, 131.12, 130.51, 128.81, 128.78, 128.41, 128.36, 125.71, 106.95, 106.81, 21.35; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{16}IN_2^+$: 387.0353. Found 387.0354.



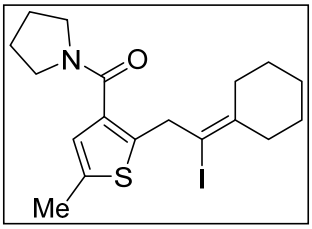

**(*Z*)-1-(2-(2-Bromo-2-phenylvinyl)-5-methylphenyl)-1*H*-pyrazole (4x):** Slightly modified conditions: Derived from 1-(*m*-tolyl)-1*H*-pyrazole[S8] **1i** (31.6 mg, 0.200 mmol, 1.0 equiv), ethynylbenzene (24.5 mg, 0.240 mmol, 1.2 equiv), and *N*-bromosuccinimide (NBS) (53.4 mg, 0.300 mmol, 1.5 equiv). For this reaction 1 mL of acetic acid stock solution was added along with 1 mL of dioxane (10 mol % total acetic acid relative to the C–H activation partner **1i**, 2 mL total solvent). The product was then purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **4x** (51.8 mg, 76% yield) as a light yellow oil. IR (film): 2920, 1614, 1516, 1443, 1036, 949, 751, 692 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 1.4 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.58–7.56 (m, 2H), 7.40 (s, 1H), 7.37–7.32 (m, 3H), 7.27–7.26 (m, 1H), 7.02 (s, 1H), 6.42 (t, *J* = 2.0 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 140.93, 140.12, 139.44, 139.20, 131.31, 130.48, 129.02, 128.47, 128.45, 128.37, 127.86, 126.85, 126.73, 125.87, 106.82, 21.32; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{16}BrN_2^+$: 339.0491. Found 339.0494.




**(2-(3-Butyl-2-iodohept-2-en-1-yl)-5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone (9a):** Slightly modified conditions: Derived from (5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone **1b** (39.0 mg, 0.200 mmol, 1.0 equiv), 5-vinylidenenonane[S9] (36.5 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). Reaction was run at 60 °C. The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **9a** (61.7 mg, 65% yield) as a yellow oil. IR (film): 2954, 2927, 2870, 1621, 1417, 1226, 1168, 769 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) 6.60 (s, 1H), 4.14 (s, 2H), 3.57 (t, $J$ = 7.0 Hz, 2H), 3.44 (t, $J$ = 6.6 Hz, 2H), 2.39 (s, 3H), 2.29–2.26 (m, 2H), 2.24–2.22 (m, 2H), 1.94–1.90 (m, 2H), 1.87–1.83 (m, 2H), 1.43–1.37 (m, 4H), 1.36–1.28 (m, 4H), 0.94–0.88 (m, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 166.04, 146.91, 140.89, 137.94, 135.22, 123.89, 100.54, 49.12, 45.80, 42.22, 40.62, 31.78, 31.33, 29.88, 26.36, 24.67, 22.88, 22.87, 15.44, 14.14, 14.08; HRMS (ESI/[M+H]+) calcd. for $C_{21}H_{33}INOS^+$: 474.1322. Found 474.1329.




**(2-(2-Iodo-3-methylbut-2-en-1-yl)-5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone (9b):** Slightly modified conditions: Derived from (5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone **1b** (39.0 mg, 0.200 mmol, 1.0 equiv), 3-methylbuta-1,2-diene (16.4 mg, 0.241 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). Reaction was run at 60 °C. The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **9b** (39.1 mg, 50% yield) as a yellow oil. IR (film): 2918, 2874, 1615, 1490, 1418, 1125, 768, 728 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 6.59 (s, 1H), 4.16 (s, 2H), 3.56 (t, $J$ = 6.9 Hz, 2H), 3.41 (t, $J$ = 6.6 Hz, 2H), 2.39 (s, 3H), 1.95–1.89 (m, 8H), 1.87–1.82 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.08, 140.13, 138.46, 137.86, 135.10, 123.88, 98.90, 49.11, 45.80, 40.77, 31.72, 26.34, 24.68, 19.85, 15.39; HRMS (ESI/[M+H]+) calcd. for $C_{15}H_{21}INOS^+$: 390.0383. Found 390.0384.

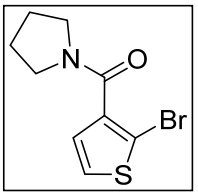



**(2-(2-Cyclohexylidene-2-iodoethyl)-5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone (9c):** Slightly modified conditions: Derived from (5-methylthiophen-3-yl)(pyrrolidin-1-yl)methanone

**1b** (39.0 mg, 0.200 mmol, 1.0 equiv), vinylidenecyclohexane (26.0 mg, 0.240 mmol, 1.2 equiv), and NIS (67.5 mg, 0.300 mmol, 1.5 equiv). Reaction was run at 60 °C. The product was purified by C18 reverse phase column chromatography with loading of the isolated material onto a C18 precolumn, transferring with ~ 0.3 mL of DMSO. The vial with the residual material was then washed 2x with ~0.2 mL of DMSO and loaded onto the precolumn to ensure full transfer of material. The precolumn was then hooked up to a 250 mL vacuum jacketed erlenmeyer flask and reduced pressure was used to pull the all material into the precolumn. The precolumn was then connected to the reverse phase instrument and purification was performed with 15.5 g of reverse phase media and a 100 column volume gradient from 10 to 90% $CH_3CN$:$H_2O$ containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were then washed with brine (100 mL), dried over $Na_2SO_4$, and concentrated to afford product **9c** (55.2 mg, 64% yield) as a yellow oil. IR (film): 2925, 2853, 1615, 1490, 1418, 1223, 912, 728 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 6.60 (s, 1H), 4.22 (s, 2H), 3.58 (t, $J$ = 6.9 Hz, 2H), 3.43 (t, $J$ = 6.6 Hz, 2H), 2.44–2.43 (m, 2H), 2.39–2.38 (m, 5H), 1.95–1.90 (m, 2H), 1.87–1.82 (m, 2H), 1.56 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.05, 145.76, 140.53, 137.83, 135.20, 123.97, 96.79, 49.09, 45.82, 42.24, 40.40, 31.00, 27.92, 27.58, 26.52, 26.39, 24.69, 15.37; HRMS (ESI/[M+H]+) calcd. for $C_{18}H_{25}INOS^+$: 430.0696. Found 430.0691.

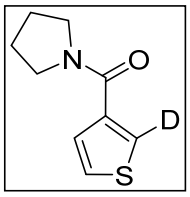
## VII. Mechanism Experiments:

**Procedure for the synthesis of (2-bromothiophen-3-yl)(pyrrolidin-1-yl)methanone:**



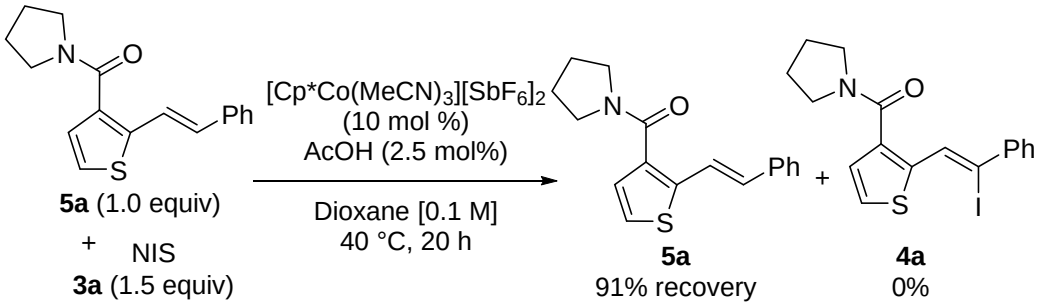

In a 50 mL RB flask, 2-bromothiophene-3-carboxylic acid (828 mg, 4.00 mmol, 1.0 equiv) was added along with a stir bar. The flask was flushed with nitrogen, followed by the addition of excess thionyl chloride (4 mL). The mixture was then refluxed at 85 °C for 30 min, and was then allowed to cool back to rt. The mixture was then concentrated in the same flask, leaving the acid chloride as a tan-colored solid. The flash was then flushed with nitrogen again, followed by the addition of dichloromethane (10 mL). The solution was cooled to 0 °C in an ice-bath, followed by the dropwise addition of pyrrolidine (0.40 mL, 4.9 mmol, 1.2 equiv). After 1 min, triethylamine (0.70 mL, 5.0 mmol, 1.2 equiv) was added dropwise, and stirring was continued for 5 min. After 5 min, the ice-bath was removed to allow the mixture to warm to rt, with stirring for an additional 2 h. The mixture was then transferred to a separatory funnel and the organic layer was washed with water (1x), sat. $NaHCO_3$ solution (1x), and brine (1x) successively. The organic layer was then dried over $Na_2SO_4$ and was concentrated. The residual oil was then dissolved in a minimal amounts of ethyl acetate (~5 mL) and purified by silica gel chromatography using ethyl acetate as the eluent. After concentration of the combined fractions, the desired amide was obtained (930 mg, 89%) as a white solid (mp: 48–49 °C). IR (film): 3066, 2966, 2881, 1610, 1527, 1435, 1392, 735 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) 7.25 (d, $J$ = 5.7 Hz, 1H), 6.94 (d, $J$ = 5.7 Hz, 1H), 3.62 (t, $J$ = 6.9 Hz, 2H), 3.33 (t, $J$ = 6.7 Hz, 2H), 1.97–1.93 (m, 2H), 1.91–1.87 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 164.16, 138.84, 127.29, 126.79, 110.58, 48.10, 45.87, 26.08, 24.60; HRMS (ESI/[M+H]+) calcd. for $C_9H_{11}BrNOS^+$: 259.9739. Found 259.9737.

**Procedure for the synthesis of pyrrolidin-1-yl(thiophen-3-yl-2-d)methanone:**



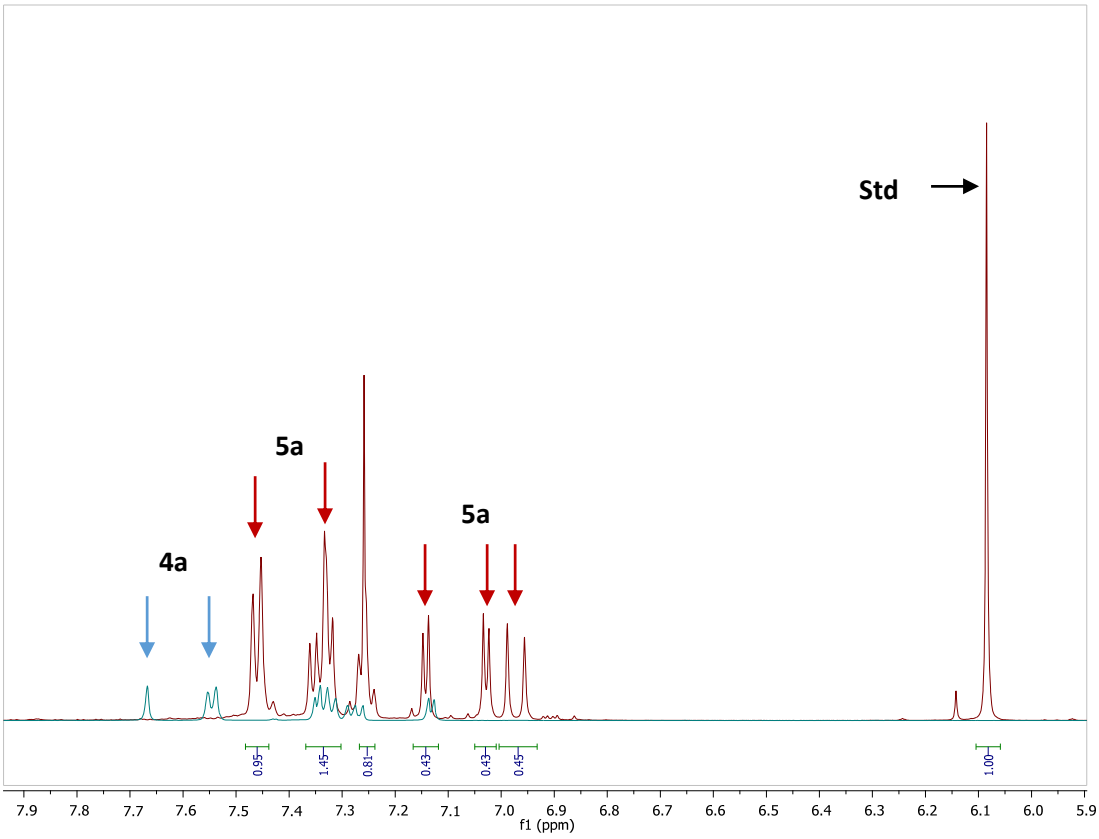

In a 50 mL RB flask, (2-bromothiophen-3-yl)(pyrrolidin-1-yl)methanone (520 mg, 2.00 mmol, 1.0 equiv) was added along with a stir bar. The flask was flushed with nitrogen, followed by the addition of diethyl ether (10 mL). The mixture was then cooled to -78 °C, followed by dropwise addition of *n*-BuLi (2.5 M solution in hexanes, 1.2 mL, 3.0 mmol, 1.5 equiv). The mixture was stirred for 15 min, followed by the addition of $CD_3OD$ (0.41 mL, 10 mmol, 5 equiv). The mixture was then allowed to warm to rt and was stirred for 1 h. The reaction was then quenched with sat. $NH_4Cl$ solution, and resulting mixture was extracted with ethyl acetate (3x). The combined organic layers were washed with brine (1x), dried over $Na_2SO_4$, and concentrated. The residual oil was dissolved in minimal amounts of ethyl acetate (~5 mL) and purified by silica gel chromatography using ethyl acetate as the eluent. After concentration of the combined fractions, the desired amide **1a-D** was obtained (299 mg, 82%) as a white solid (mp: 70–71 °C). IR (film): 3081, 2872, 1581, 1504, 1434, 1348, 1333, 729 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.35 (d, $J$ = 5.0 Hz, 1H), 7.27 (d, $J$ = 5.0 Hz, 1H), 3.62 (t, $J$ = 6.5 Hz, 2H), 3.57 (t, $J$ = 6.2 Hz, 2H), 1.94–1.89 (m, 4H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.44, 137.99, 127.77, 127.09 (t, $J$ = 28.5 Hz), 125.23, 49.27, 46.57, 26.61, 24.38; HRMS (ESI/[M+H]+) calcd. for $C_9H_{11}DNOS^+$: 183.0697. Found 183.0690.

**Subjecting two-component product 5a to NIS under optimal reaction conditions**

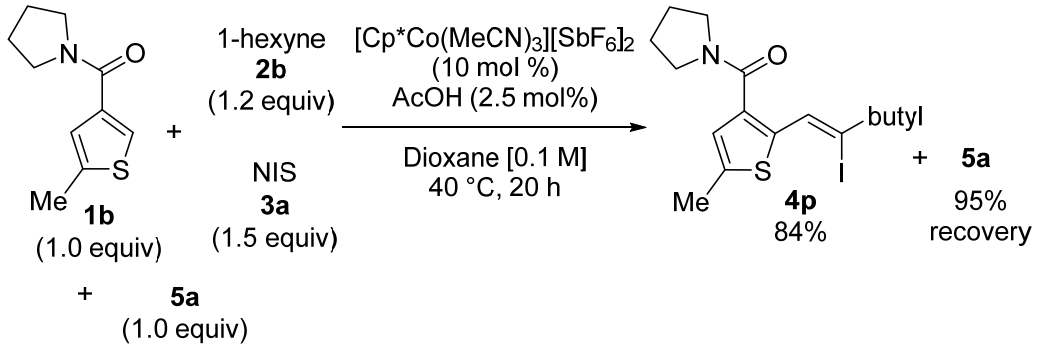



In a $N_2$-filled glove box, a 2.0–5.0 mL microwave vial was charged with $[Cp^*Co(MeCN)_3][SbF_6]_2$ (7.9 mg, 0.010 mmol, 0.10 equiv) and *N*-iodosuccinimide (NIS) (33.8 mg, 0.150 mmol, 1.5 equiv).

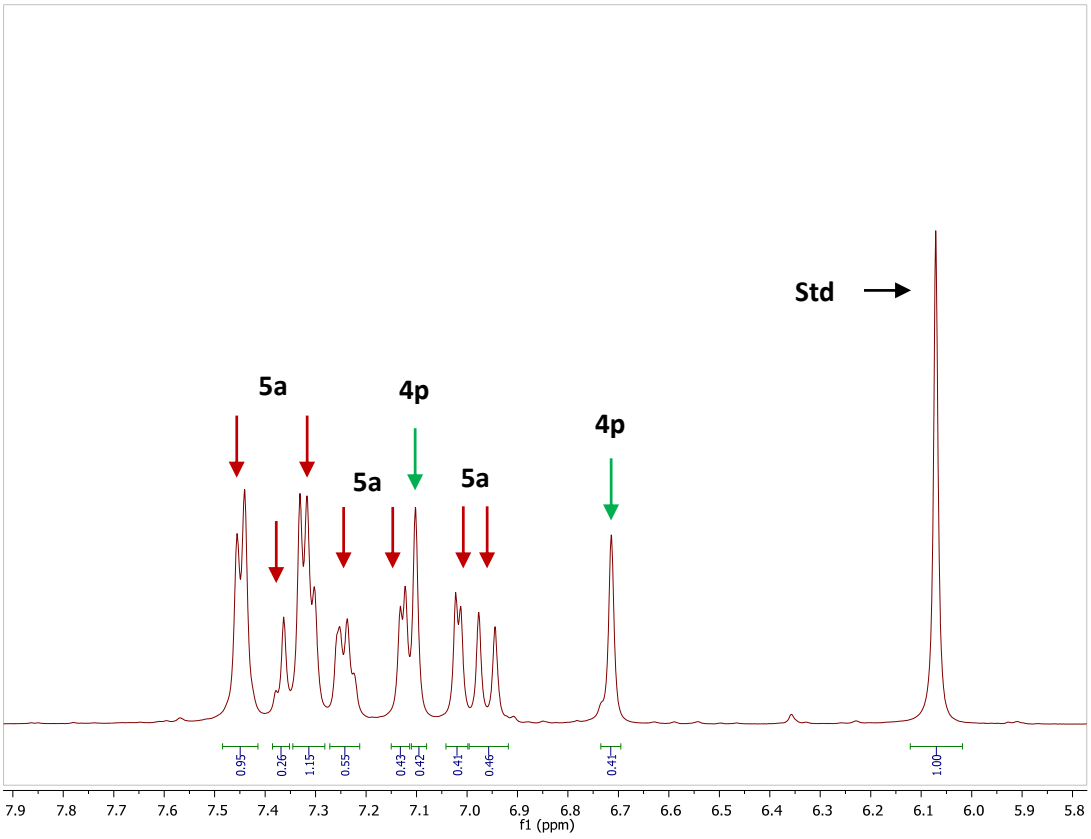
Following this, a 0.0200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg (0.200 mmol) of acetic acid to 10.0 mL of 1,4-dioxane. Then 125 µL of this solution was added to the solid mixture, followed by 0.875 mL of 1,4-dioxane (2.5 mol % total acetic acid relative to two-component product **5a**, 1 mL of total solvent). The two-component product **5a** (28.3 mg, 0.0999 mmol, 1.0 equiv) was then added, and the reaction vial was equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction solution was stirred at 40 °C in an oil bath for 20 h. The reaction vial was then uncapped and transferred with dichloromethane (20 mL) to a 125 mL separatory funnel containing 75 mL of a sat. $NaHCO_3$ solution, and immediately extracted. The aqueous layer was further extracted 3x with fresh dichloromethane (20 mL), and the combined organic layers were then dried over $Na_2SO_4$, and concentrated. The concentrated mixture was then charged with a 11.3 mg of 1,3,5-trimethoxybenzene as external standard and the mixture was then analyzed by $^1H$ NMR using $CDCl_3$ to analyze the amounts of two-component product **5a** and three-component product **4a** present. (The crude NMR is shown below in red, with red arrows indicating peaks for **5a** with the superimposed spectra in blue for product **4a**.)



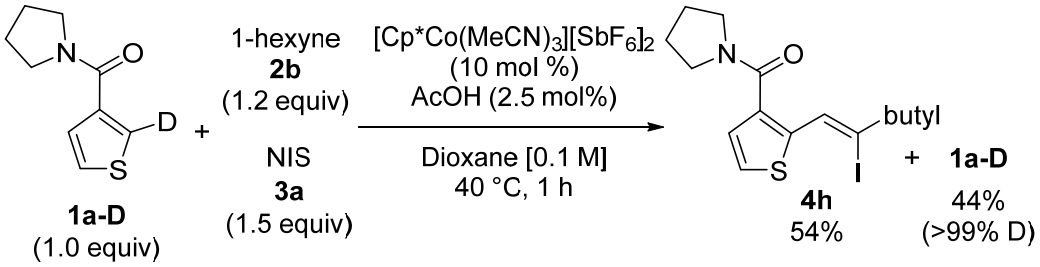
**Subjecting 1b, 1-hexyne, and NIS under optimal reaction conditions in the presence of two-component product 5a**




In a $N_2$-filled glove box, a 2.0–5.0 mL microwave vial was charged with $[Cp^*Co(MeCN)_3][SbF_6]_2$ (7.9 mg, 0.010 mmol, 0.10 equiv) and **3a**, *N*-iodosuccinimide (NIS) (33.8 mg, 0.150 mmol, 1.5 equiv). Following this, a 0.0200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg (0.200 mmol) of acetic acid to 10.0 mL of 1,4-dioxane. Then 125 µL of this solution was added to the solid mixture, followed by 0.875 mL of 1,4-dioxane (2.5 mol % total acetic acid relative to C–H bond partner **1b**, 1 mL of total solvent). The two-component product **5a** (27.3 mg, 0.0963 mmol, 0.96 equiv) was then added, followed by the addition of **1b** (19.5 mg, 0.0999 mmol, 1.0 equiv) and 1-hexyne (9.9 mg, 0.12 mmol, 1.2 equiv). The reaction vial was equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction solution was stirred at 40 °C in an oil bath for 20 h. The reaction vial was then uncapped and transferred with dichloromethane (20 mL) to a 125 mL separatory funnel containing 75 mL of a sat. $NaHCO_3$ solution, and immediately extracted. The aqueous layer was further extracted 3x with fresh dichloromethane (20 mL), and the combined organic layers were then dried over $Na_2SO_4$, and concentrated. The concentrated mixture was then charged with a 11.5 mg of 1,3,5-trimethoxybenzene as external standard and the mixture was then analyzed by $^1H$ NMR using $CDCl_3$ to analyze the amounts of two-component product **5a** and three-component product **4p** present. (The crude NMR is shown below in red, with green arrows indicating peaks for product **4p**, and red arrows indicating peaks for **5a**.)

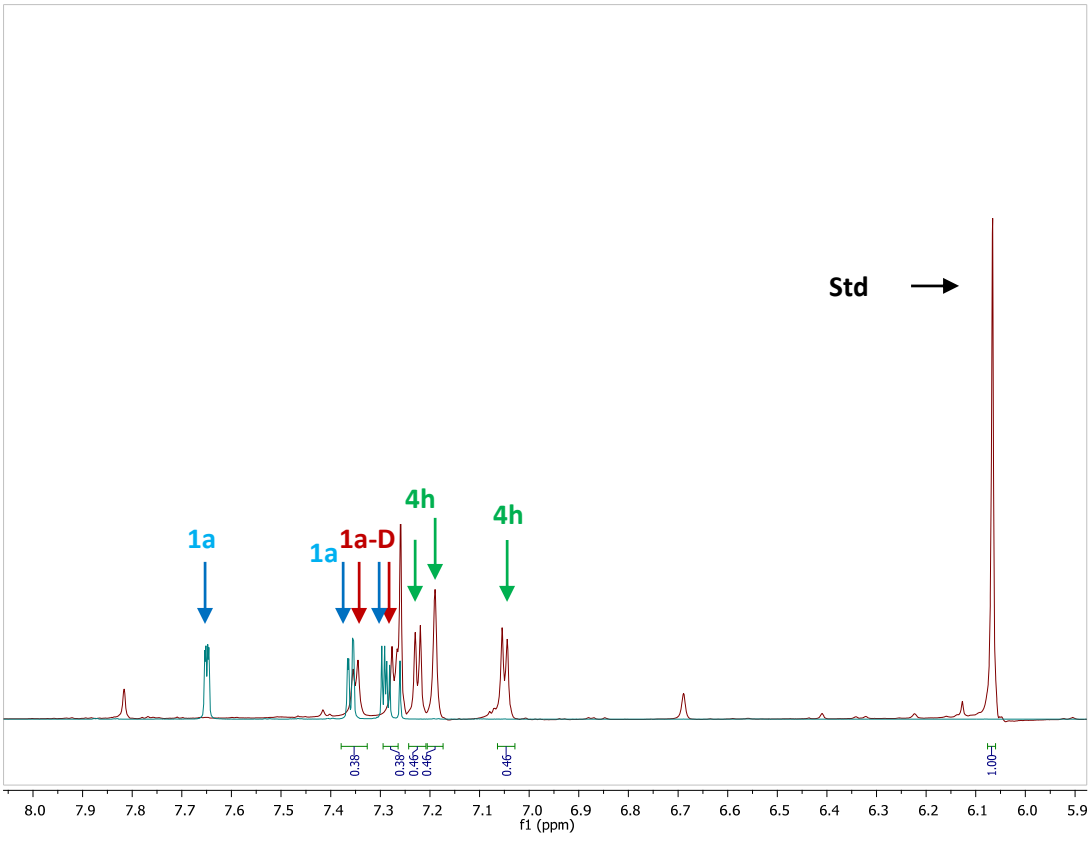



**Subjecting 1a-D under optimal reaction conditions for a shortened reaction time**

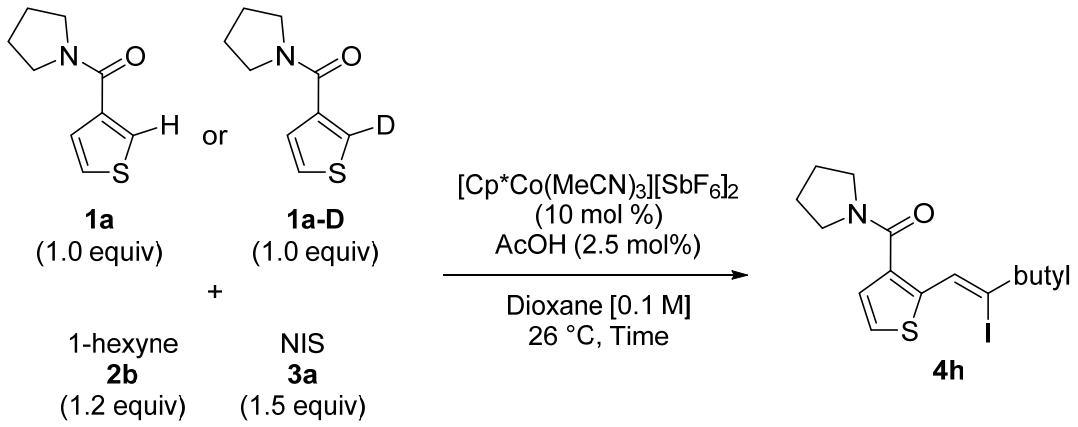



In a $N_2$-filled glove box, a 2.0–5.0 mL microwave vial was charged with $[Cp^*Co(MeCN)_3][SbF_6]_2$ (15.8 mg, 0.0200 mmol, 0.10 equiv) and *N*-iodosuccinimide (NIS) (67.5 mg, 0.300 mmol, 1.5 equiv). Following this, a 0.0200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg (0.200 mmol) of acetic acid to 10.0 mL of 1,4-dioxane. Then 250 µL of this solution was added to the solid mixture, followed by 1.75 mL of 1,4-dioxane (2.5 mol % total acetic acid relative

to C–H bond partner **1a-D**, 2 mL of total solvent). This was then followed by the addition of **1a-D** (36.5 mg, 0.200 mmol, 1.0 equiv) and 1-hexyne (19.7 mg, 0.240 mmol, 1.2 equiv). The reaction vial was equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction solution was stirred at 40 °C in an oil bath for 1 h. The reaction vial was then uncapped and transferred with dichloromethane (20 mL) to a 125 mL separatory funnel containing 75 mL of a sat. $NaHCO_3$ solution, and immediately extracted. The aqueous layer was further extracted 3x with fresh dichloromethane (20 mL), and the combined organic layers were then dried over $Na_2SO_4$, and concentrated. The concentrated mixture was then charged with a 13.1 mg of 1,3,5-trimethoxybenzene as external standard and each mixture was then analyzed by $^1H$ NMR using $CDCl_3$ to analyze the amounts of **1a-D**, **1a**, and three-component product **4h** present. (The crude NMR is shown below in red, with green arrows indicating peaks for product **4h**, and red arrows indicating peaks for **1a-D**. The blue superimposed spectra is shown for **1a** with blue arrows indicating specific peaks.)



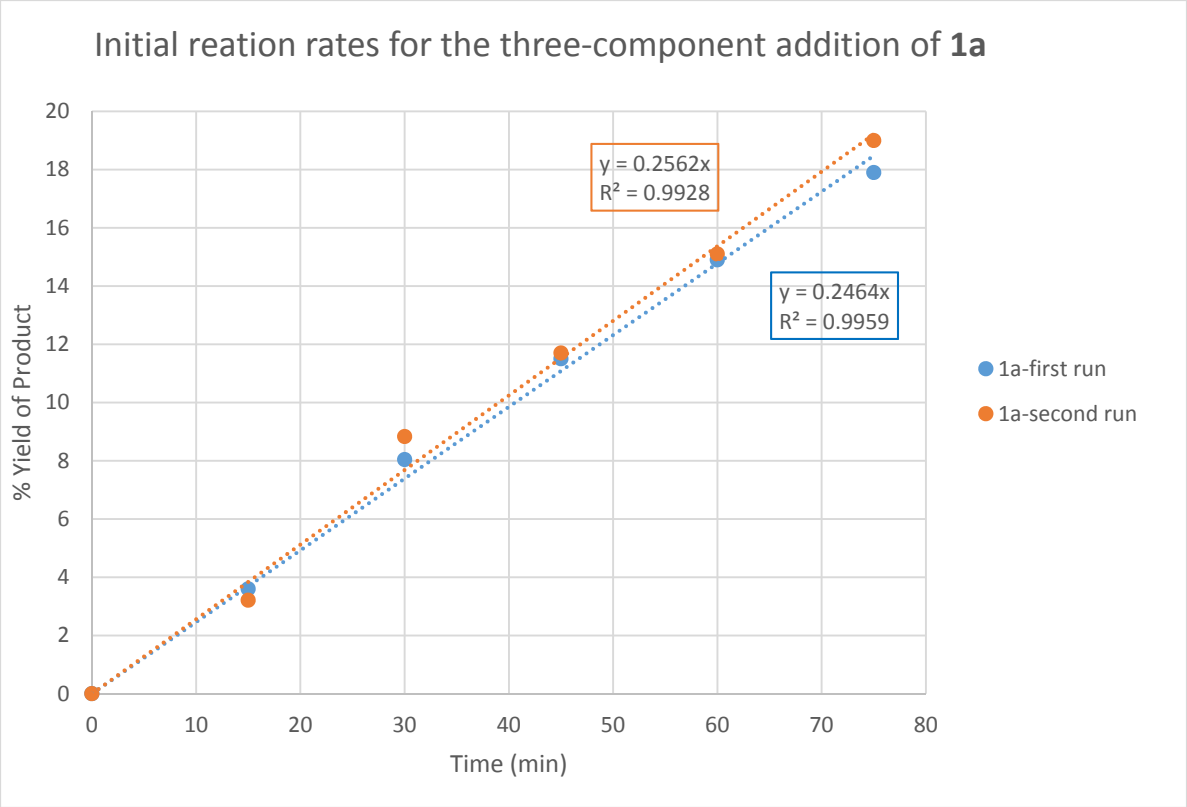
**Initial rate measurements and KIE determination**



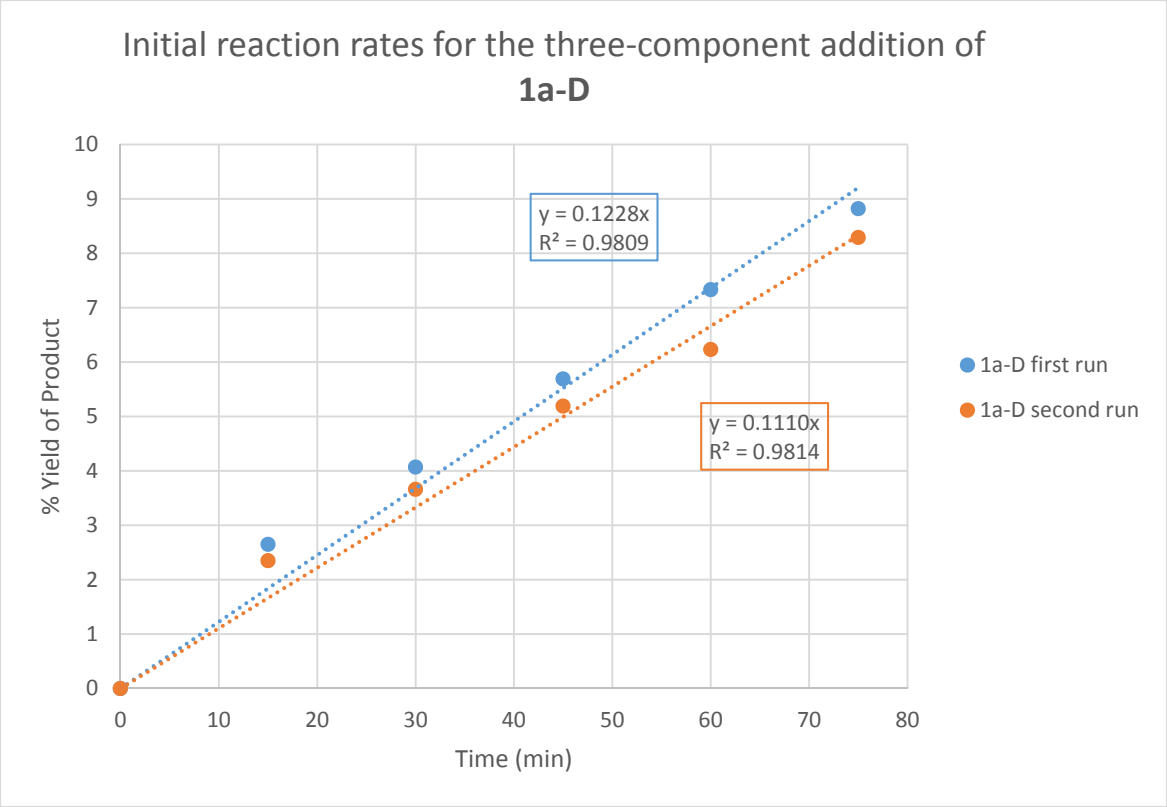

In a $N_2$-filled glovebox a 0.200 mM solution of acetic acid in 1,4-dioxane was prepared by adding 12.0 mg of acetic acid to 10.0 mL of 1,4-dioxane. Following this, an oven-dried scintillation vial was charged $[Cp^*Co(MeCN)_3][SbF_6]_2$ (39.5 mg, 0.0501 mmol, 0.10 equiv) and *N*-iodosuccinimide (NIS) (168.8 mg, 0.7503 mmol, 1.5 equiv). To the solid mixture was added 625 µL of the 0.200 mM acetic acid in dioxane solution followed by 4.375 mL of 1,4-dioxane (2.5 mol % total acetic acid relative to the C–H activation coupling partner, 5 mL of total solvent system added). This mixture was shaken for 1 minute to fully dissolve the catalyst and NIS. At this point the indicated C–H bond partner **1a** or **1a-D** (0.500 mmol, 1.0 equiv [exact amounts shown in table below]) and 1-hexyne (49.3 mg, 0.600 mmol, 1.2 equiv), were added successively. The vial was then capped and shaken for about 15 seconds to ensure homogeneity. Following this, the 5 mL mixture was pipetted into five separate oven-dried 2.0–5.0 mL microwave vials containing stir bars (exactly 1 mL of the reaction solution to each vial, 0.100 mmol scale with respect to **1a** or **1a-D**). The vials were capped with a microwave cap and taken out of the glove box, and the reaction mixtures were stirred in a preset oil bath at 26 °C. At a given time point, one vial was removed at 15 min, 30 min, 45 min, 60 min, or 75 min, was uncapped and the reaction solution was transferred with dichloromethane (20 mL) to a 125 mL separatory funnel containing 75 mL of a sat. $NaHCO_3$ solution, and immediately extracted. The aqueous layer was further extracted 3x with fresh dichloromethane (20 mL), and the combined organic layers were then dried over $Na_2SO_4$, and concentrated. The concentrated mixtures were then charged with a known amount of 1,3,5-trimethoxybenzene as external standard and each

mixture was then analyzed by $^{1}H$ NMR using $CDCl_3$ as the solvent to obtain NMR yields of the three-component product **4h**.

| Raw Data for three-component addition of **1a** | | |
|---|---|---|
| | | |
| First Run (Amount of **1a** added = 90.5 mg) | | |
| Time (min) | Amount of Std (mg) | Yield of Product (%) |
| 0 | 0 | 0 |
| 15 | 10.7 | 3.60 |
| 30 | 12.2 | 8.04 |
| 45 | 10.8 | 11.5 |
| 60 | 10.4 | 14.9 |
| 75 | 14.0 | 17.9 |
| | | |
| Second Run (Amount of **1a** added = 90.8 mg) | | |
| Time (min) | Amount of Std (mg) | Yield of Product (%) |
| 0 | 0 | 0 |
| 15 | 11.3 | 3.21 |
| 30 | 11.5 | 8.83 |
| 45 | 12.8 | 11.7 |
| 60 | 11.3 | 15.1 |
| 75 | 12.3 | 19.0 |
| | | |
| Average of both runs | | |
| Time (min) | Yield of Product (%) | Standard Deviation (%) |
| 0 | 0 | 0 |
| 15 | 3.41 | 0.276 |
| 30 | 8.44 | 0.559 |
| 45 | 11.6 | 0.141 |
| 60 | 15.0 | 0.141 |
| 75 | 18.5 | 0.778 |


Initial reation rates for the three-component addition of **1a**
% Yield of Product
Time (min)
y = 0.2562x
R² = 0.9928
y = 0.2464x
R² = 0.9959
1a-first run
1a-second run
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80

| Raw Data for three-component addition of **1a-D** | | |
|---|---|---|
| | | |
| First Run (Amount of **1a-D** added = 91.0 mg) | | |
| Time (min) | Amount of Std (mg) | Yield of Product (%) |
| 0 | 0 | 0 |
| 15 | 10.5 | 2.65 |
| 30 | 11.0 | 4.07 |
| 45 | 13.0 | 5.69 |
| 60 | 12.2 | 7.33 |
| 75 | 12.4 | 8.82 |
| | | |
| Second Run (Amount of **1a-D** added = 91.4 mg) | | |
| Time (min) | Amount of Std (mg) | Yield of Product (%) |
| 0 | 0 | 0 |
| 15 | 19.4 | 2.35 |
| 30 | 10.6 | 3.66 |
| 45 | 14.5 | 5.19 |
| 60 | 14.0 | 6.23 |
| 75 | 14.2 | 8.29 |
| | | |
| Average of both runs | | |
| Time (min) | Yield of Product (%) | Standard Deviation (%) |
| 0 | 0 | 0 |
| 15 | 2.50 | 0.212 |
| 30 | 3.87 | 0.290 |
| 45 | 5.44 | 0.354 |
| 60 | 6.78 | 0.778 |
| 75 | 8.56 | 0.375 |




| | |
|---|---|
| Initial rates for **1a** | |
| | |
| Slope First Run | 0.2464 |
| Slope Second Run | 0.2562 |
| Average Slope | 0.2513 |
| Standard Deviation | 0.006930 |
| | |
| Initial rates for **1a-D** | |
| | |
| Slope First Run | 0.1228 |
| Slope Second Run | 0.1110 |
| Average Slope | 0.1169 |
| Standard Deviation | 0.008344 |
| | |
| KIE | 2.15 |
| Standard Deviation | 0.164 |

## VIII. X-Ray Crystallographic Data:

Single crystals of **4s** were obtained by layering of diethyl ether (~1 mL) to a concentrated solution of product **4s** in dichloromethane (roughly 10 mg in 0.05 mL). The mixture was allowed to slowly evaporate to yield the desired crystals.

***Experimental***

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **4s**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against $F^2$ on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H1, which was found in the difference map and semi-freely refined with and N-H distance restraint of 0.88(2) Å. The full numbering scheme of compound **4s** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1548918 (**4s**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

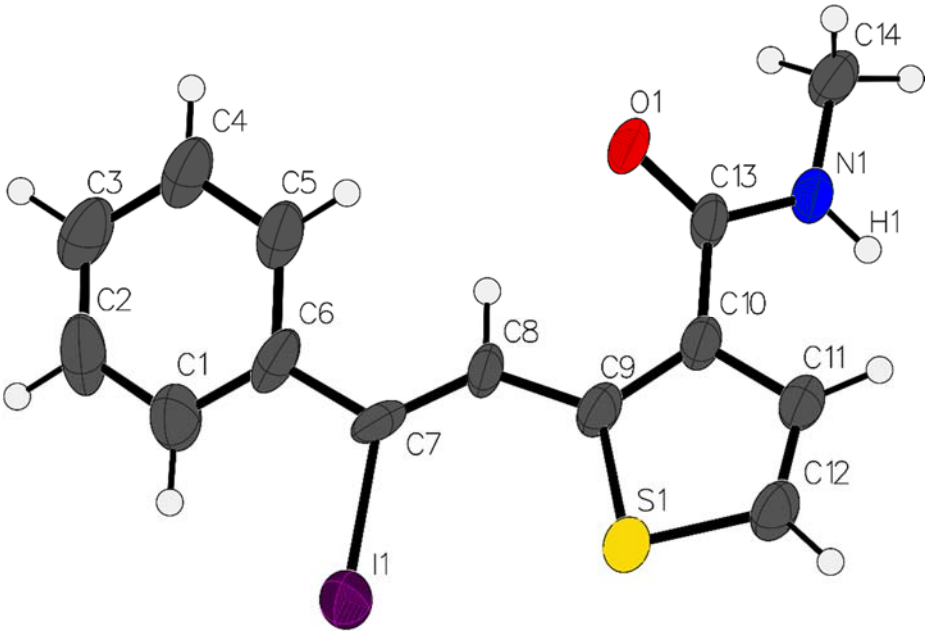



Figure 1. The complete numbering scheme of **4s** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

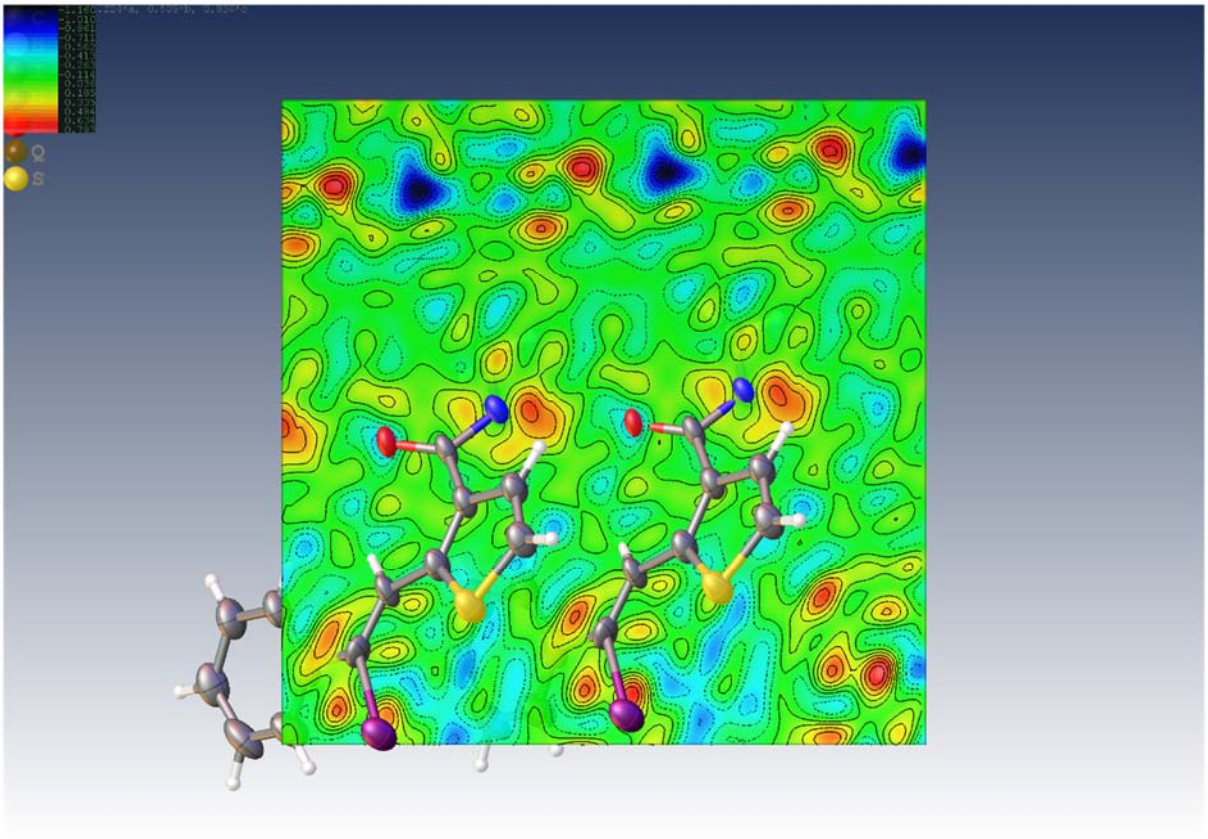


Figure 2. The Fourier difference map of total electron density in **4s** (0.8*e*/Å$^3$ isolines) highlights the plane of the amide {N1 H1 O1}, excluding contributions from H3 so as to show its effective position.

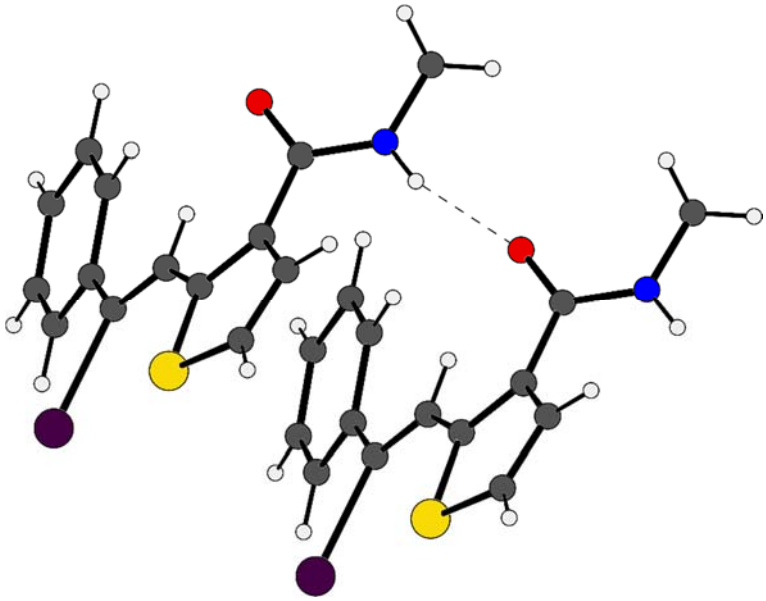


Figure 3. The hydrogen bonding in **4s** with all atoms shown as circles for clarity. The hydrogen bond interaction is highlighted with a dashed line.

Table 1. Crystal data and structure refinement for **4s**.

| | | |
|---|---|---|
| Identification code | 007b-17010 | |
| Empirical formula | C14 H12 I N O S | |
| Formula weight | 369.21 | |
| Temperature | 93(2) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 4.9263(4) Å | α= 82.007(6)°. |
| | b = 11.5372(8) Å | β= 82.519(7)°. |
| | c = 12.1743(9) Å | γ = 79.760(7)°. |
| Volume | 670.34(9) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.829 $Mg/m^3$ | |
| Absorption coefficient | 20.113 $mm^{-1}$ | |
| F(000) | 360 | |
| Crystal size | 0.200 x 0.010 x 0.010 $mm^3$ | |
| Theta range for data collection | 3.688 to 68.326°. | |
| Index ranges | -5<=h<=5, -13<=k<=13, -14<=l<=14 | |
| Reflections collected | 18612 | |
| Independent reflections | 2359 [R(int) = 0.1119] | |
| Completeness to theta = 67.684° | 97.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.62092 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2359 / 1 / 169 | |
| Goodness-of-fit on $F^2$ | 1.166 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0858, wR2 = 0.2324 | |
| R indices (all data) | R1 = 0.0934, wR2 = 0.2476 | |
| Extinction coefficient | 0.0067(15) | |
| Largest diff. peak and hole | 1.951 and -2.890 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4s**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 4655(2) | -18(1) | 7451(1) | 52(1) |
| S(1) | 7581(6) | 1200(2) | 9234(2) | 44(1) |
| O(1) | 3568(14) | 5113(6) | 8180(7) | 42(2) |
| N(1) | 7846(18) | 5452(8) | 8381(8) | 39(2) |
| C(1) | 1190(30) | 1472(12) | 5411(11) | 58(3) |
| C(2) | -570(30) | 1875(14) | 4584(13) | 65(4) |
| C(3) | -2070(30) | 2998(13) | 4509(11) | 57(3) |
| C(4) | -1710(30) | 3768(13) | 5265(11) | 55(3) |
| C(5) | 50(20) | 3376(11) | 6094(10) | 49(3) |
| C(6) | 1580(20) | 2197(10) | 6167(10) | 45(3) |
| C(7) | 3430(20) | 1838(9) | 7072(10) | 41(2) |
| C(8) | 4290(20) | 2612(9) | 7629(9) | 37(2) |
| C(9) | 6110(20) | 2507(9) | 8503(9) | 39(2) |
| C(10) | 6910(20) | 3462(9) | 8855(9) | 36(2) |
| C(11) | 8780(20) | 3123(10) | 9699(10) | 42(2) |
| C(12) | 9290(20) | 1945(11) | 9993(10) | 44(3) |
| C(13) | 5953(19) | 4728(9) | 8439(9) | 36(2) |
| C(14) | 7180(20) | 6715(10) | 8014(10) | 44(3) |

Table 3. Bond lengths [Å] and angles [°] for **4s**.

| | |
|---|---|
| I(1)-C(7) | 2.122(10) |
| S(1)-C(12) | 1.728(12) |
| S(1)-C(9) | 1.731(10) |
| O(1)-C(13) | 1.245(12) |
| N(1)-C(13) | 1.348(12) |
| N(1)-C(14) | 1.455(13) |
| N(1)-H(1) | 0.88(2) |
| C(1)-C(6) | 1.379(18) |
| C(1)-C(2) | 1.390(19) |
| C(1)-H(1A) | 0.9500 |
| C(2)-C(3) | 1.37(2) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.41(2) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.391(16) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.430(17) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.488(14) |
| C(7)-C(8) | 1.346(15) |
| C(8)-C(9) | 1.459(13) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.372(15) |
| C(10)-C(11) | 1.437(14) |
| C(10)-C(13) | 1.491(14) |
| C(11)-C(12) | 1.344(17) |
| C(11)-H(11) | 0.9500 |
| C(12)-H(12) | 0.9500 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| | |
| C(12)-S(1)-C(9) | 92.3(5) |
| C(13)-N(1)-C(14) | 121.4(8) |

| | |
|---|---|
| C(13)-N(1)-H(1) | 122(9) |
| C(14)-N(1)-H(1) | 117(9) |
| C(6)-C(1)-C(2) | 121.6(13) |
| C(6)-C(1)-H(1A) | 119.2 |
| C(2)-C(1)-H(1A) | 119.2 |
| C(3)-C(2)-C(1) | 121.4(13) |
| C(3)-C(2)-H(2) | 119.3 |
| C(1)-C(2)-H(2) | 119.3 |
| C(2)-C(3)-C(4) | 118.6(12) |
| C(2)-C(3)-H(3) | 120.7 |
| C(4)-C(3)-H(3) | 120.7 |
| C(5)-C(4)-C(3) | 120.5(13) |
| C(5)-C(4)-H(4) | 119.8 |
| C(3)-C(4)-H(4) | 119.8 |
| C(4)-C(5)-C(6) | 120.2(12) |
| C(4)-C(5)-H(5) | 119.9 |
| C(6)-C(5)-H(5) | 119.9 |
| C(1)-C(6)-C(5) | 117.7(10) |
| C(1)-C(6)-C(7) | 125.0(11) |
| C(5)-C(6)-C(7) | 117.3(11) |
| C(8)-C(7)-C(6) | 123.8(9) |
| C(8)-C(7)-I(1) | 121.1(7) |
| C(6)-C(7)-I(1) | 115.1(8) |
| C(7)-C(8)-C(9) | 134.9(9) |
| C(7)-C(8)-H(8) | 112.6 |
| C(9)-C(8)-H(8) | 112.6 |
| C(10)-C(9)-C(8) | 123.5(9) |
| C(10)-C(9)-S(1) | 110.4(8) |
| C(8)-C(9)-S(1) | 126.1(8) |
| C(9)-C(10)-C(11) | 112.8(9) |
| C(9)-C(10)-C(13) | 125.0(9) |
| C(11)-C(10)-C(13) | 122.2(9) |
| C(12)-C(11)-C(10) | 113.0(10) |
| C(12)-C(11)-H(11) | 123.5 |
| C(10)-C(11)-H(11) | 123.5 |
| C(11)-C(12)-S(1) | 111.5(8) |

| | |
|---|---|
| C(11)-C(12)-H(12) | 124.2 |
| S(1)-C(12)-H(12) | 124.2 |
| O(1)-C(13)-N(1) | 121.3(9) |
| O(1)-C(13)-C(10) | 123.4(9) |
| N(1)-C(13)-C(10) | 115.3(8) |
| N(1)-C(14)-H(14A) | 109.5 |
| N(1)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| N(1)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4s**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 59(1) | 40(1) | 60(1) | -1(1) | -28(1) | -10(1) |
| S(1) | 47(2) | 37(1) | 51(2) | 4(1) | -26(1) | -10(1) |
| O(1) | 28(3) | 42(4) | 61(5) | 1(3) | -22(3) | -9(3) |
| N(1) | 34(4) | 35(4) | 53(5) | 3(4) | -20(4) | -12(4) |
| C(1) | 70(8) | 53(7) | 60(7) | -6(6) | -34(7) | -14(6) |
| C(2) | 79(9) | 71(9) | 62(8) | -1(7) | -35(7) | -38(8) |
| C(3) | 53(7) | 69(9) | 52(7) | 15(6) | -28(6) | -15(6) |
| C(4) | 45(6) | 70(8) | 55(7) | 0(6) | -26(5) | -11(6) |
| C(5) | 41(6) | 61(7) | 51(6) | -2(5) | -21(5) | -14(5) |
| C(6) | 31(5) | 55(6) | 51(6) | 16(5) | -21(5) | -13(5) |
| C(7) | 28(5) | 34(5) | 57(6) | 2(4) | -17(4) | 8(4) |
| C(8) | 33(5) | 35(5) | 49(6) | 5(4) | -25(4) | -12(4) |
| C(9) | 35(5) | 39(5) | 46(6) | 5(4) | -22(4) | -7(4) |
| C(10) | 31(5) | 37(5) | 42(5) | 3(4) | -17(4) | -10(4) |
| C(11) | 36(5) | 42(6) | 50(6) | -2(5) | -19(5) | -7(4) |
| C(12) | 45(6) | 46(6) | 45(6) | 8(5) | -24(5) | -10(5) |
| C(13) | 29(5) | 36(5) | 47(5) | 4(4) | -18(4) | -15(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(14) | 34(5) | 44(6) | 57(6) | 7(5) | -21(5) | -7(4) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **4s**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 9560(110) | 5180(110) | 8530(110) | 60(40) |
| H(1A) | 2139 | 678 | 5457 | 70 |
| H(2) | -738 | 1360 | 4061 | 78 |
| H(3) | -3317 | 3254 | 3959 | 69 |
| H(4) | -2676 | 4560 | 5208 | 66 |
| H(5) | 237 | 3893 | 6613 | 59 |
| H(8) | 3530 | 3412 | 7399 | 44 |
| H(11) | 9573 | 3675 | 10016 | 50 |
| H(12) | 10454 | 1568 | 10548 | 53 |
| H(14A) | 6538 | 6830 | 7273 | 67 |
| H(14B) | 8846 | 7082 | 7980 | 67 |
| H(14C) | 5724 | 7084 | 8543 | 67 |

Table 6. Torsion angles [°] for **4s**.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -2(2) |
| C(1)-C(2)-C(3)-C(4) | 3(2) |
| C(2)-C(3)-C(4)-C(5) | -2(2) |
| C(3)-C(4)-C(5)-C(6) | 1.9(19) |
| C(2)-C(1)-C(6)-C(5) | 2(2) |
| C(2)-C(1)-C(6)-C(7) | -179.7(12) |
| C(4)-C(5)-C(6)-C(1) | -1.6(17) |
| C(4)-C(5)-C(6)-C(7) | 179.9(11) |
| C(1)-C(6)-C(7)-C(8) | 163.9(12) |

| | |
|---|---|
| C(5)-C(6)-C(7)-C(8) | -17.6(16) |
| C(1)-C(6)-C(7)-I(1) | -16.3(15) |
| C(5)-C(6)-C(7)-I(1) | 162.2(8) |
| C(6)-C(7)-C(8)-C(9) | -177.9(11) |
| I(1)-C(7)-C(8)-C(9) | 2.3(18) |
| C(7)-C(8)-C(9)-C(10) | 172.5(12) |
| C(7)-C(8)-C(9)-S(1) | -7.1(19) |
| C(12)-S(1)-C(9)-C(10) | -0.7(9) |
| C(12)-S(1)-C(9)-C(8) | 178.9(10) |
| C(8)-C(9)-C(10)-C(11) | -178.1(10) |
| S(1)-C(9)-C(10)-C(11) | 1.6(12) |
| C(8)-C(9)-C(10)-C(13) | 2.8(17) |
| S(1)-C(9)-C(10)-C(13) | -177.6(8) |
| C(9)-C(10)-C(11)-C(12) | -1.9(14) |
| C(13)-C(10)-C(11)-C(12) | 177.3(10) |
| C(10)-C(11)-C(12)-S(1) | 1.3(13) |
| C(9)-S(1)-C(12)-C(11) | -0.3(10) |
| C(14)-N(1)-C(13)-O(1) | 0.0(17) |
| C(14)-N(1)-C(13)-C(10) | -178.6(10) |
| C(9)-C(10)-C(13)-O(1) | 35.6(17) |
| C(11)-C(10)-C(13)-O(1) | -143.5(11) |
| C(9)-C(10)-C(13)-N(1) | -145.9(11) |
| C(11)-C(10)-C(13)-N(1) | 35.0(15) |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **4s** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)...O(1)#1 | 0.88(2) | 1.95(7) | 2.759(11) | 152(13) |

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

## IX. References:


S1. K.-I. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, *Org. Lett*. **2004**, *6*, 2785.

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S8. P. M. Liu, C. G. Frost, *Org. Lett*. **2013**, *15*, 5862.

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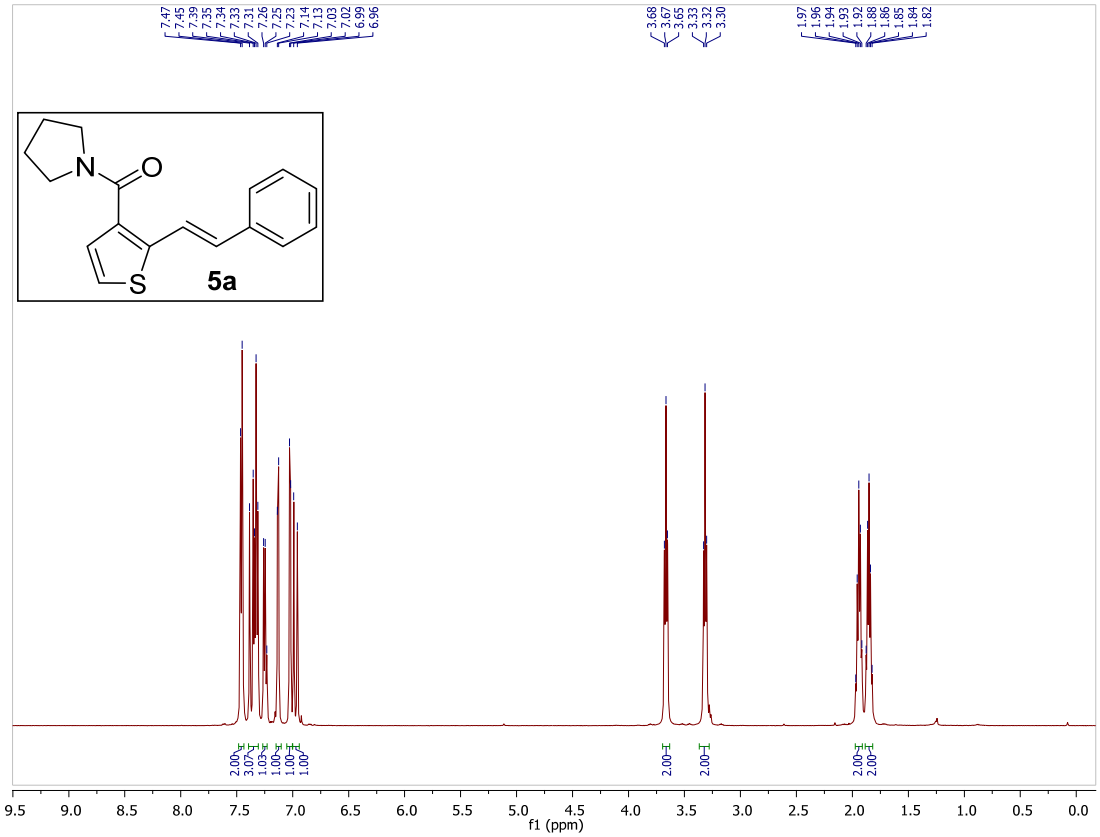
# X: NMR Data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7.02
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6.96
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3.67
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3.33
3.32
3.30
1.97
1.96
1.94
1.93
1.92
1.88
1.86
1.85
1.84
1.82
N
O
S
5a
2.00
3.07
1.03
1.00
1.00
1.00
2.00
2.00
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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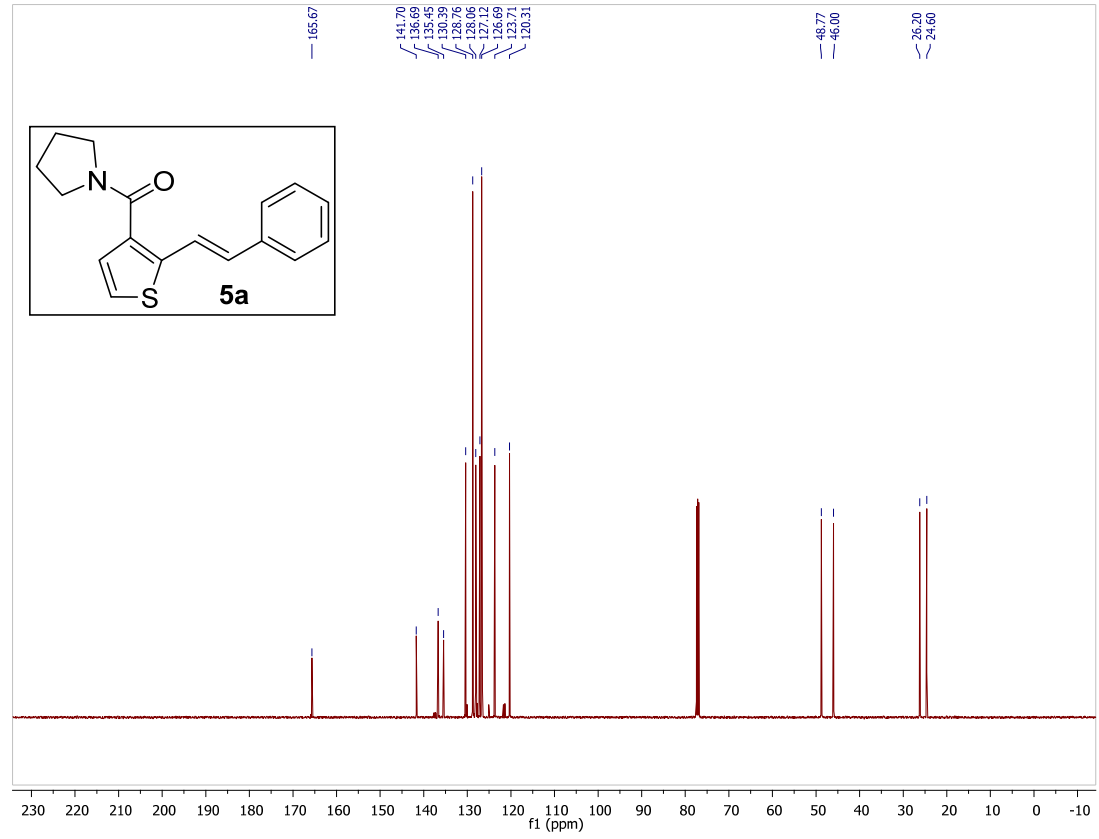
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24.60
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O
S
5a
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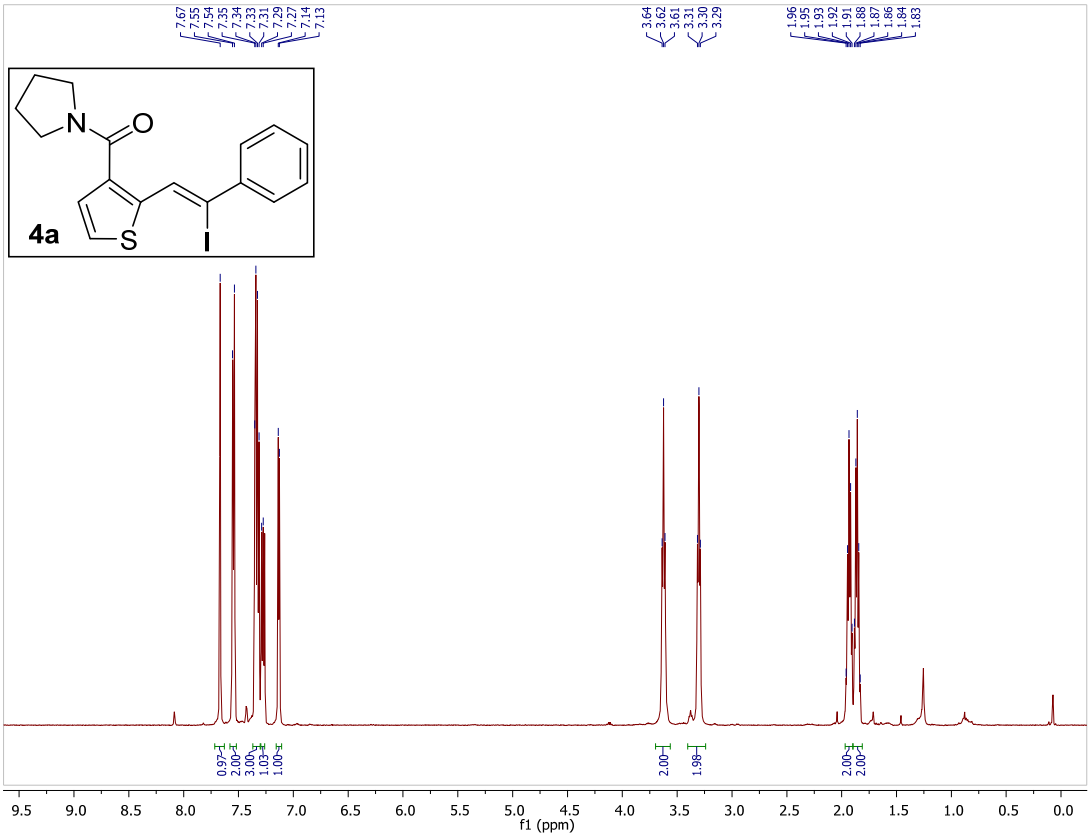
f1 (ppm)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7.55
7.54
7.35
7.34
7.33
7.31
7.29
7.27
7.14
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3.61
3.31
3.30
3.29
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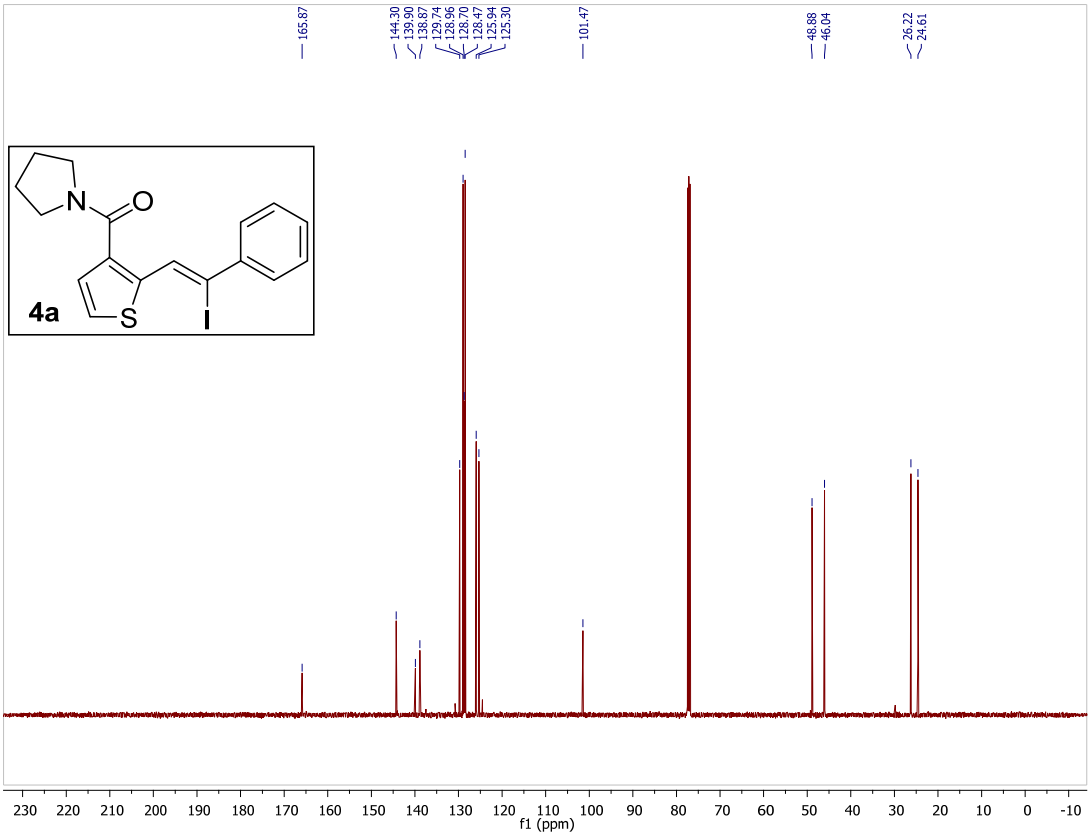
1.95
1.93
1.92
1.91
1.88
1.87
1.86
1.84
1.83
N
O
S
I
4a
0.97
2.00
3.00
1.03
1.00
2.00
1.98
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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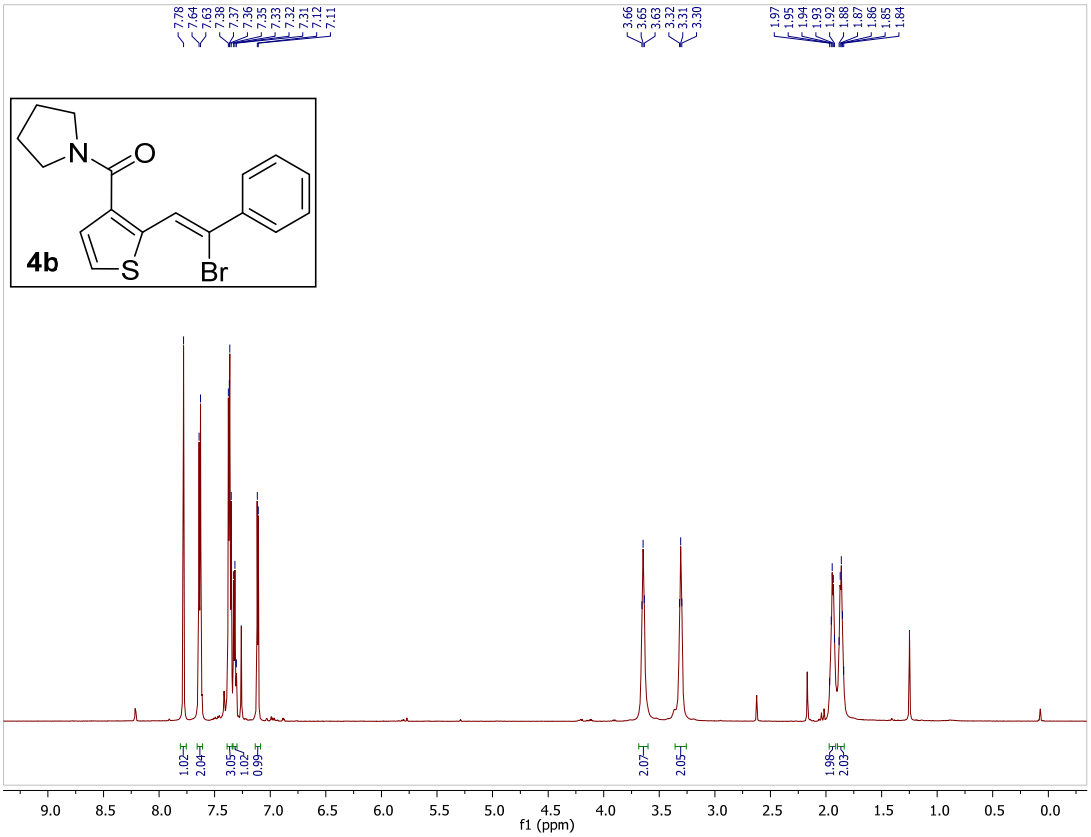
26.22
24.61
N
O
S
I
4a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.11
3.66
3.65
3.63
3.32
3.31
3.30
1.97
1.95
1.94
1.93
1.92
1.88
1.87
1.86
1.85
1.84
4b
N
O
S
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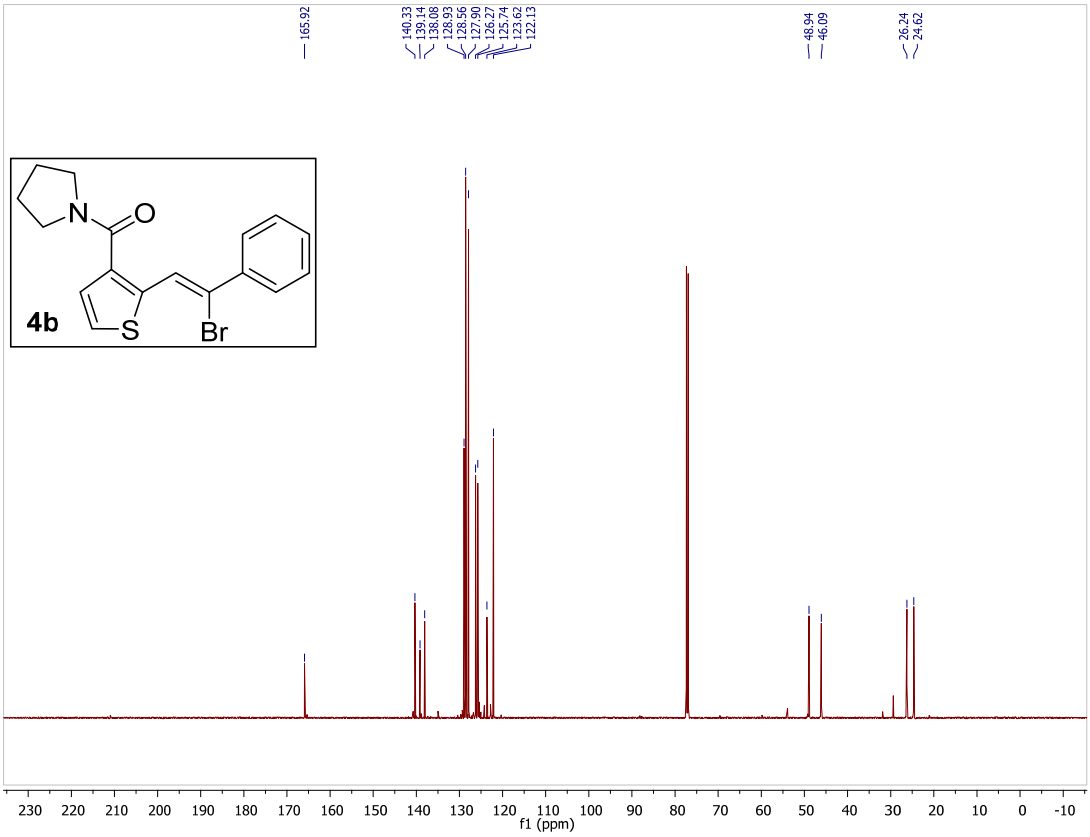
2.05
1.98
2.03
f1 (ppm)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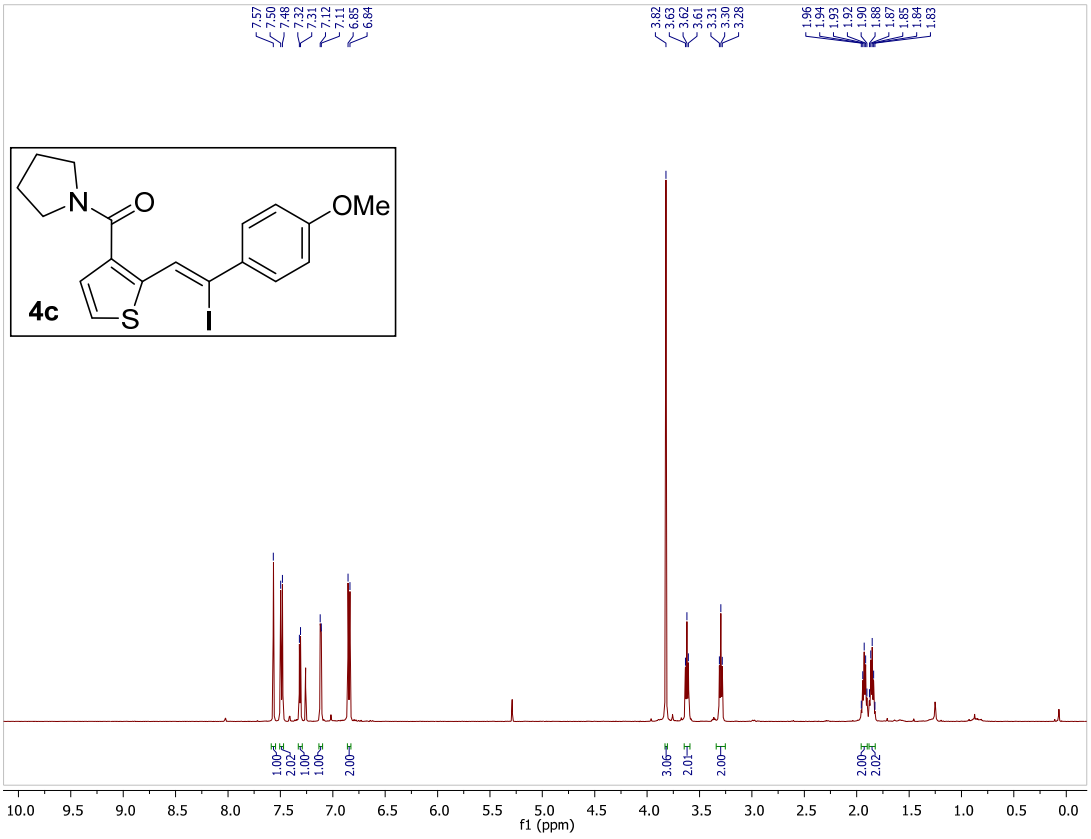
4b
N
O
S
Br
f1 (ppm)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3.30
3.28
1.96
1.94
1.93
1.92
1.90
1.88
1.87
1.85
1.84
1.83
N
O
OMe
S
I
4c
1.00
2.02
1.00
1.00
2.00
3.06
2.01
2.00
2.00
2.02
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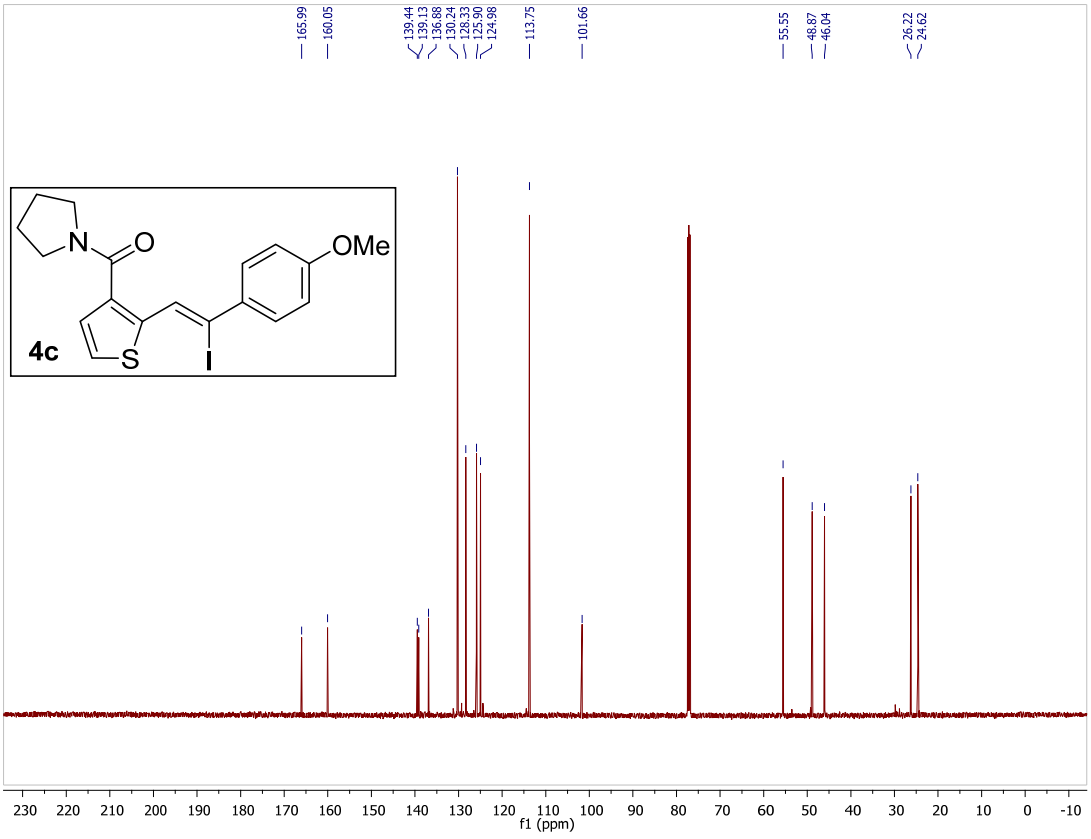
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26.22
24.62
N
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OMe
S
I
4c
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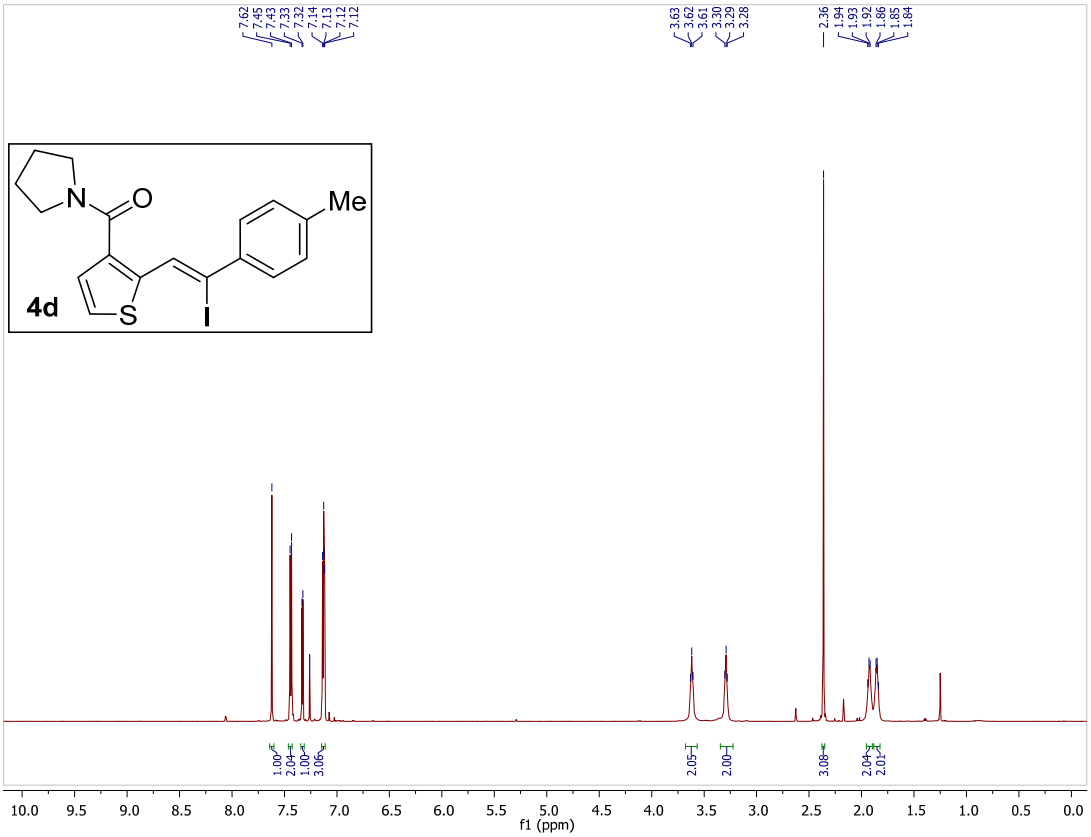
f1 (ppm)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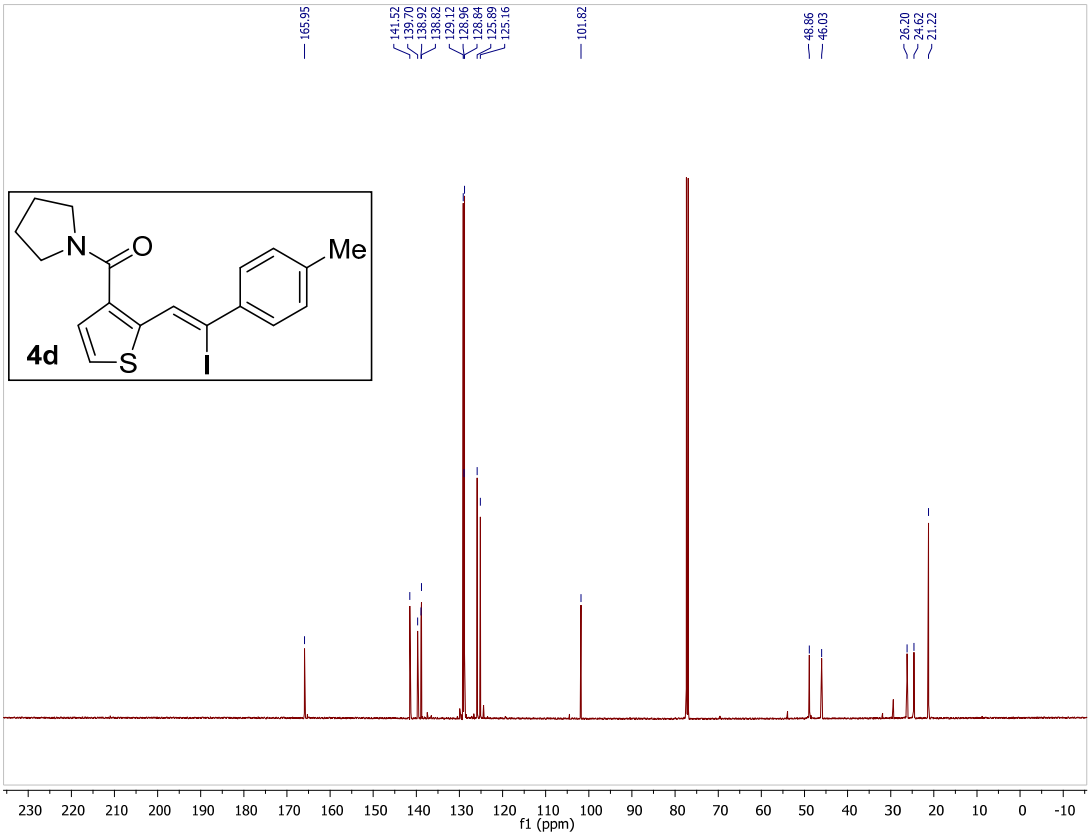
3.62
3.61
3.30
3.29
3.28
2.36
1.94
1.93
1.92
1.86
1.85
1.84
N
O
Me
S
I
4d
1.00
2.04
1.00
3.06
2.05
2.00
3.08
2.04
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.12
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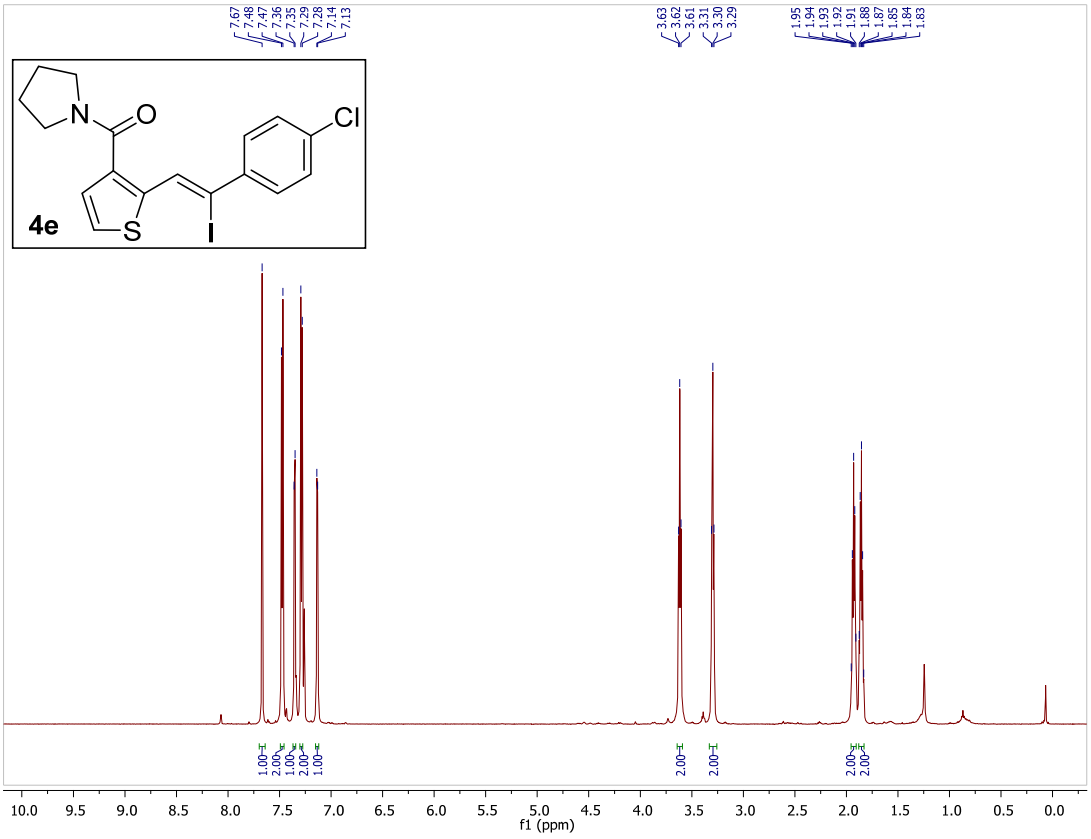
125.16
101.82
48.86
46.03
26.20
24.62
21.22
N
O
Me
S
I
4d
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.62
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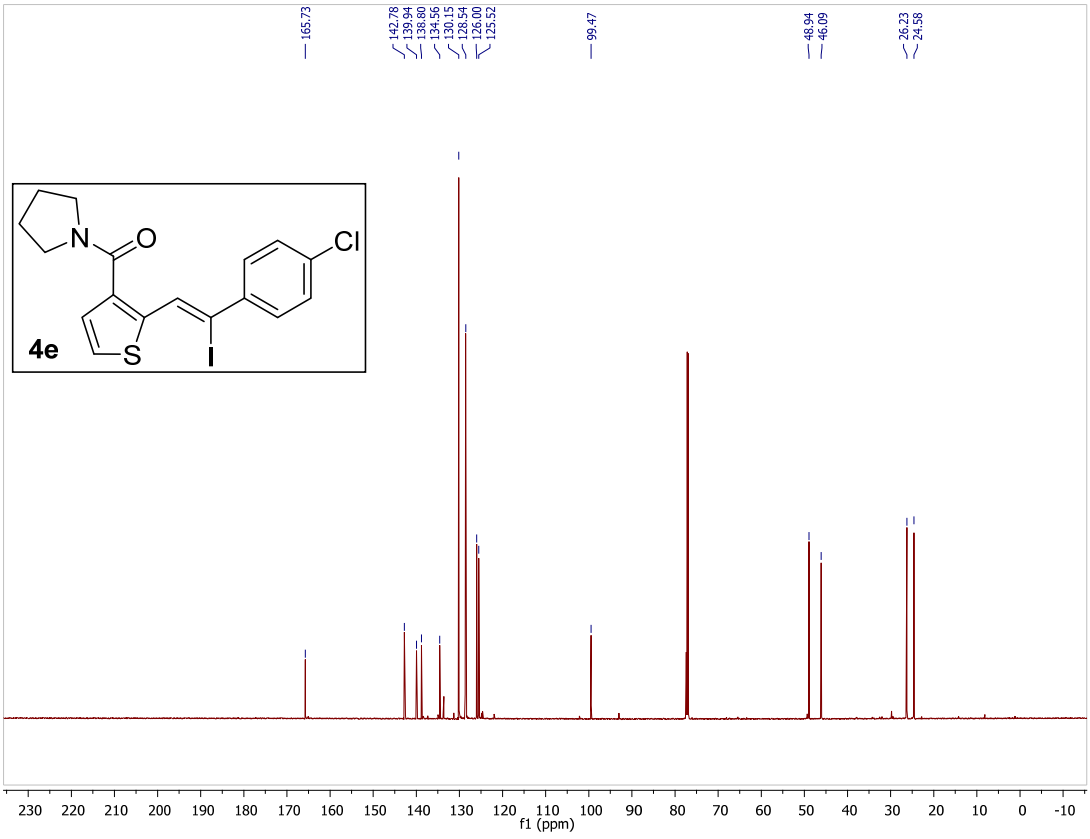
3.30
3.29
1.95
1.94
1.93
1.92
1.91
1.88
1.87
1.85
1.84
1.83
N
O
Cl
S
I
4e
1.00
2.00
1.00
1.00
2.00
1.00
2.00
2.00
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.54
126.00
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99.47
48.94
46.09
26.23
24.58
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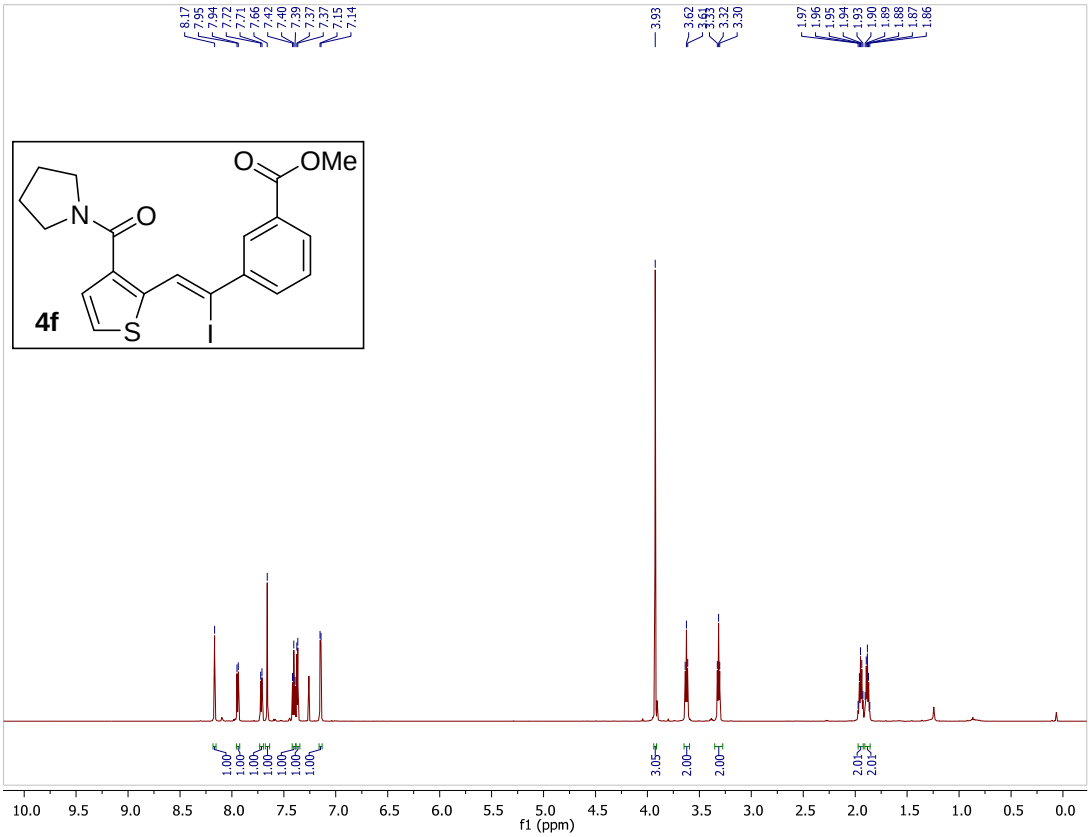
O
Cl
S
I
4e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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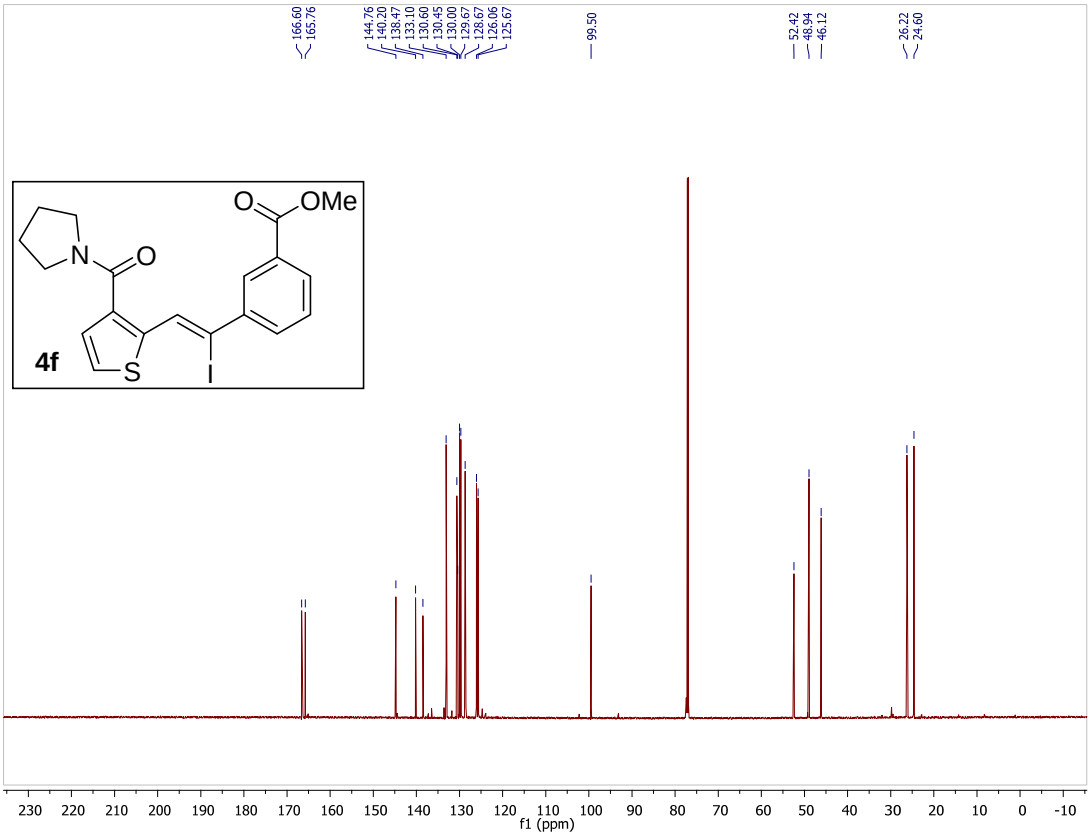
7.37
7.37
7.15
7.14
3.93
3.62
3.61
3.33
3.32
3.30
1.97
1.96
1.95
1.94
1.93
1.90
1.89
1.88
1.87
1.86
O
OMe
N
O
4f
S
I
1.00
1.00
1.00
1.00
1.00
1.00
3.05
2.00
2.00
2.01
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.76
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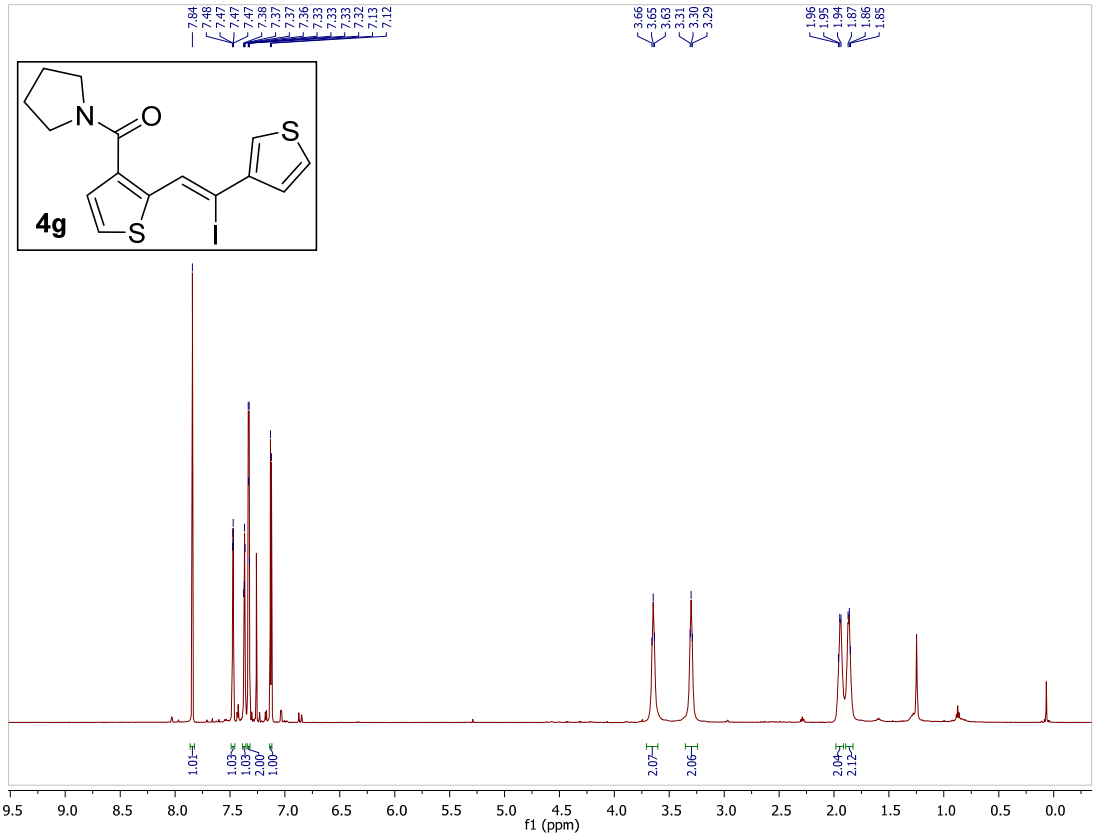
133.10
130.60
130.45
130.00
129.67
128.67
126.06
125.67
99.50
52.42
48.94
46.12
26.22
24.60
O
OMe
N
O
4f
S
I
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.65
3.63
3.31
3.30
3.29
1.96
1.95
1.94
1.87
1.86
1.85
N
O
S
S
I
4g
1.01
1.03
1.03
2.00
1.00
2.07
2.06
2.04
2.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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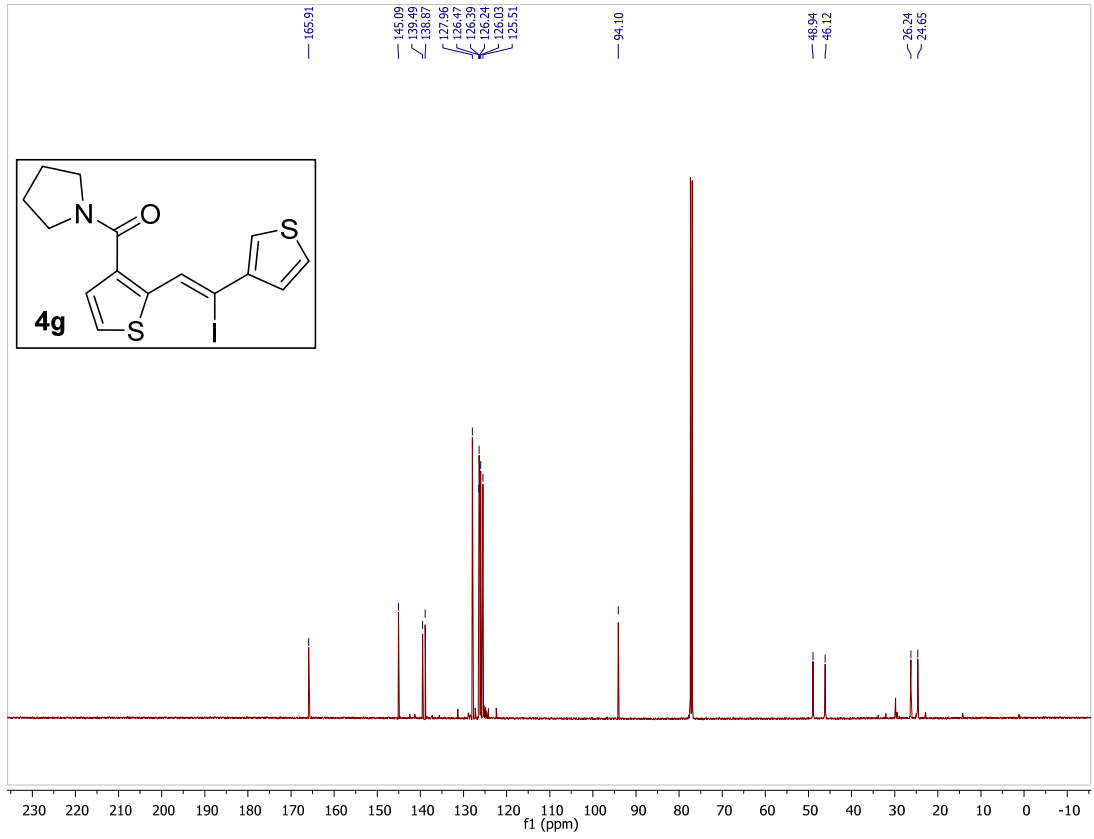
0.0
f1 (ppm)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126.24
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125.51
94.10
48.94
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26.24
24.65
N
O
S
S
I
4g
230
220
210
200
190
180
170
160
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120
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100
90
80
70
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50
40
30
20
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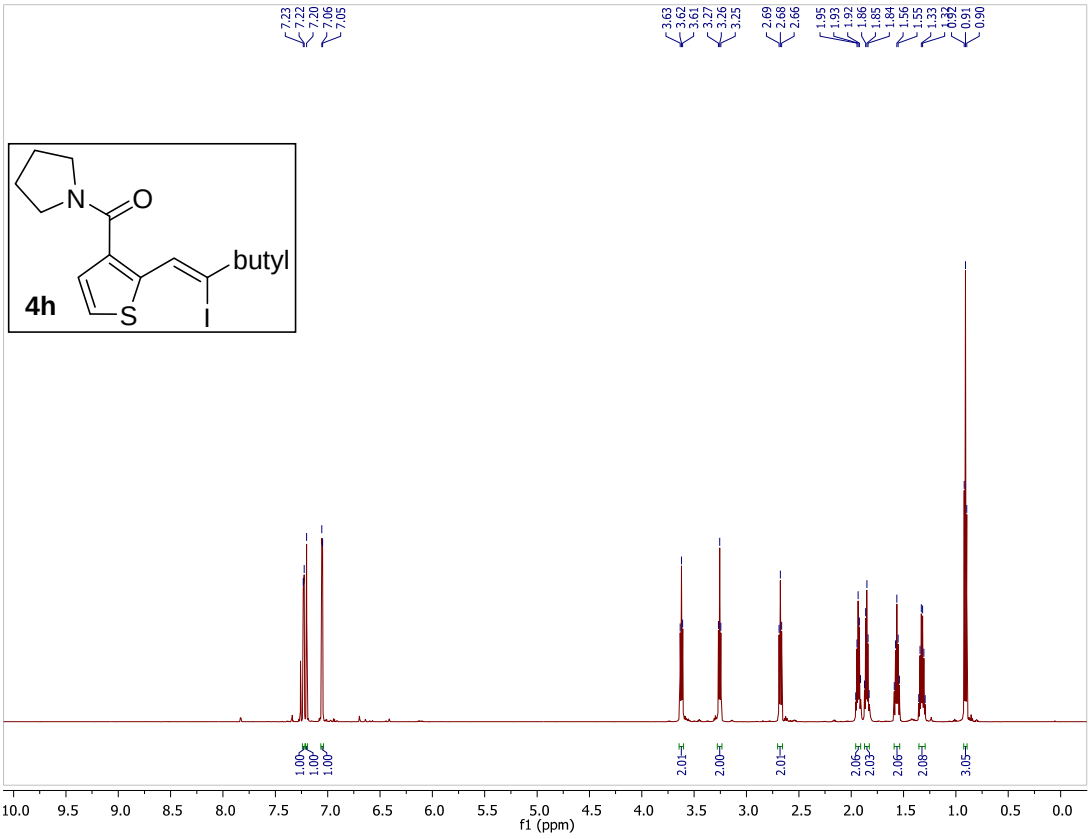
0
-10
f1 (ppm)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3.26
3.25
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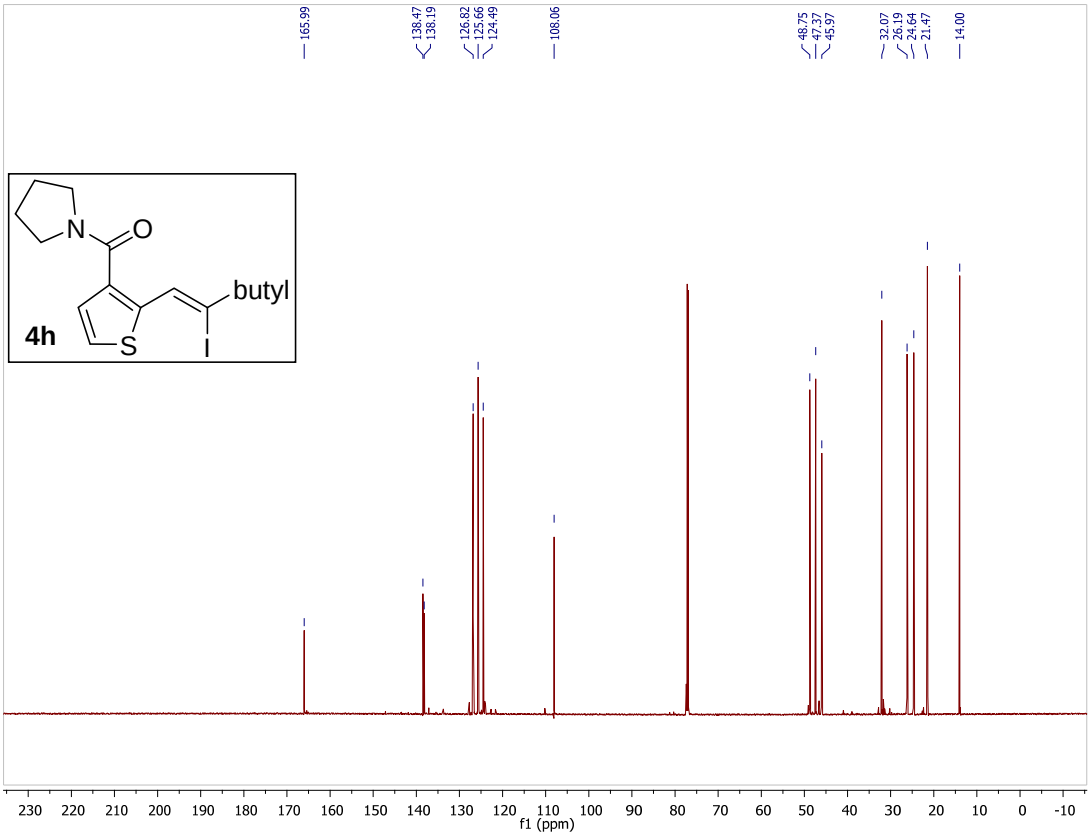
2.68
2.66
1.95
1.93
1.92
1.86
1.85
1.84
1.56
1.55
1.33
0.92
0.91
0.90
N
O
butyl
4h
S
I
1.00
1.00
1.00
2.01
2.00
2.01
2.06
2.03
2.06
2.08
3.05
f1 (ppm)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124.49
108.06
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26.19
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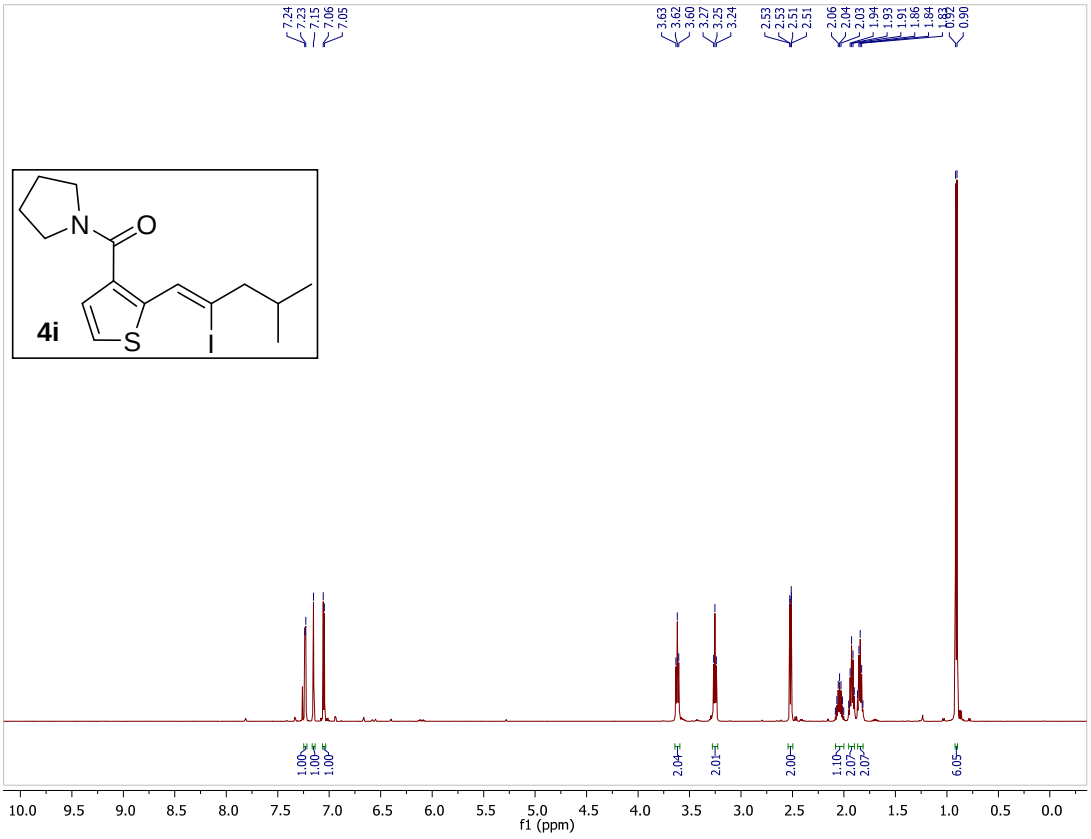
21.47
14.00
N
O
butyl
4h
S
I
f1 (ppm)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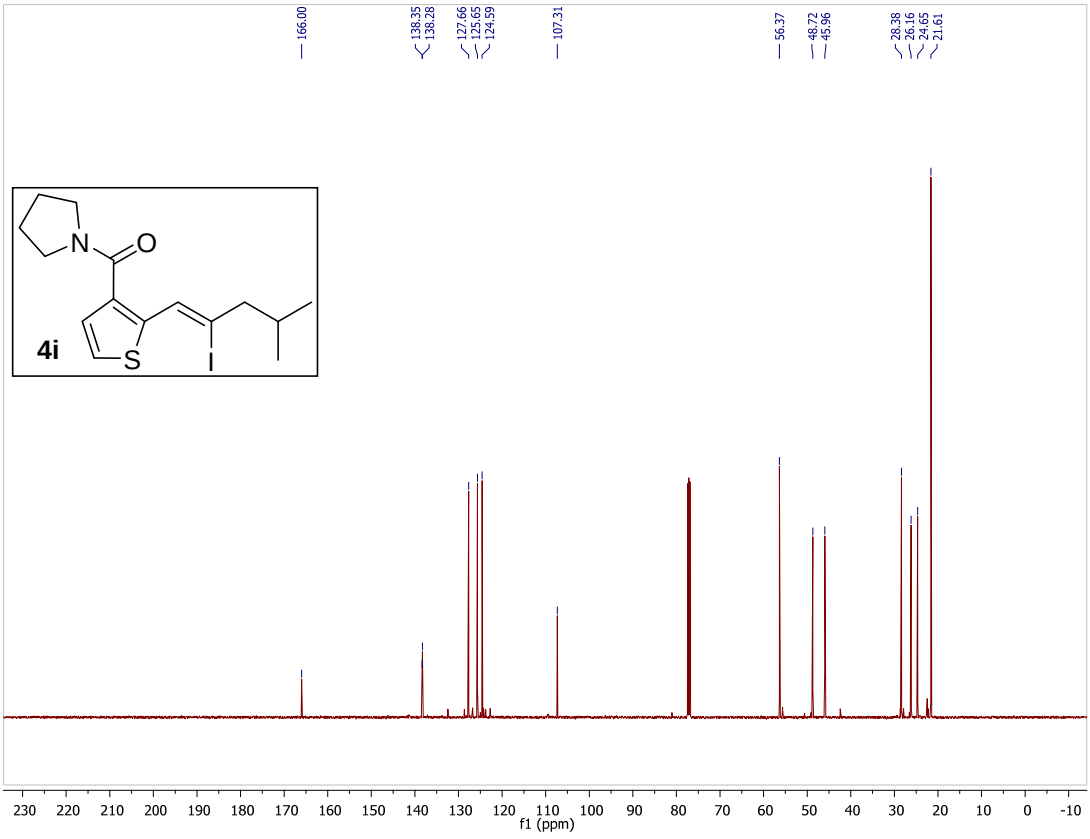
3.25
3.24
2.53
2.53
2.51
2.51
2.06
2.04
2.03
1.94
1.93
1.91
1.86
1.84
0.92
0.90
N
O
S
I
4i
1.00
1.00
1.00
2.04
2.01
2.00
1.10
2.07
2.07
6.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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28.38
26.16
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N
O
S
I
4i
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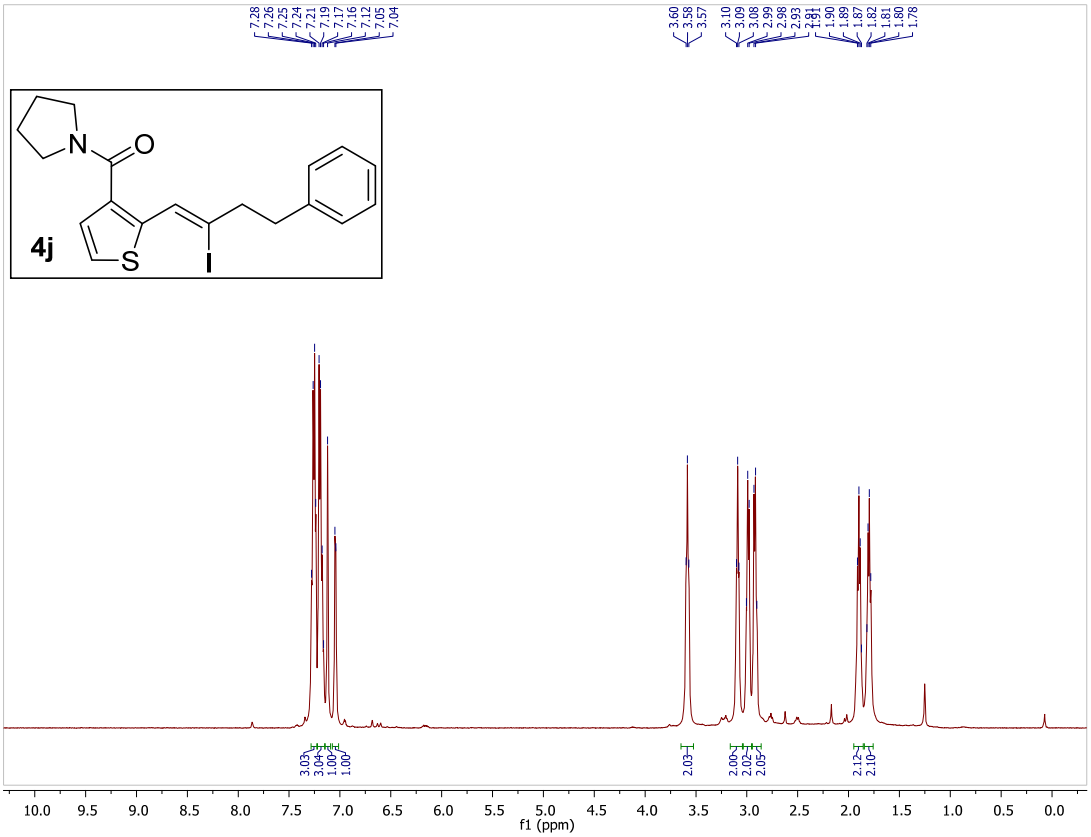
f1 (ppm)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3.58
3.57
3.10
3.09
3.08
2.99
2.98
2.93
1.91
1.90
1.89
1.87
1.82
1.81
1.80
1.78
N
O
S
I
4j
3.03
3.04
3.09
1.00
2.03
2.00
2.02
2.05
2.12
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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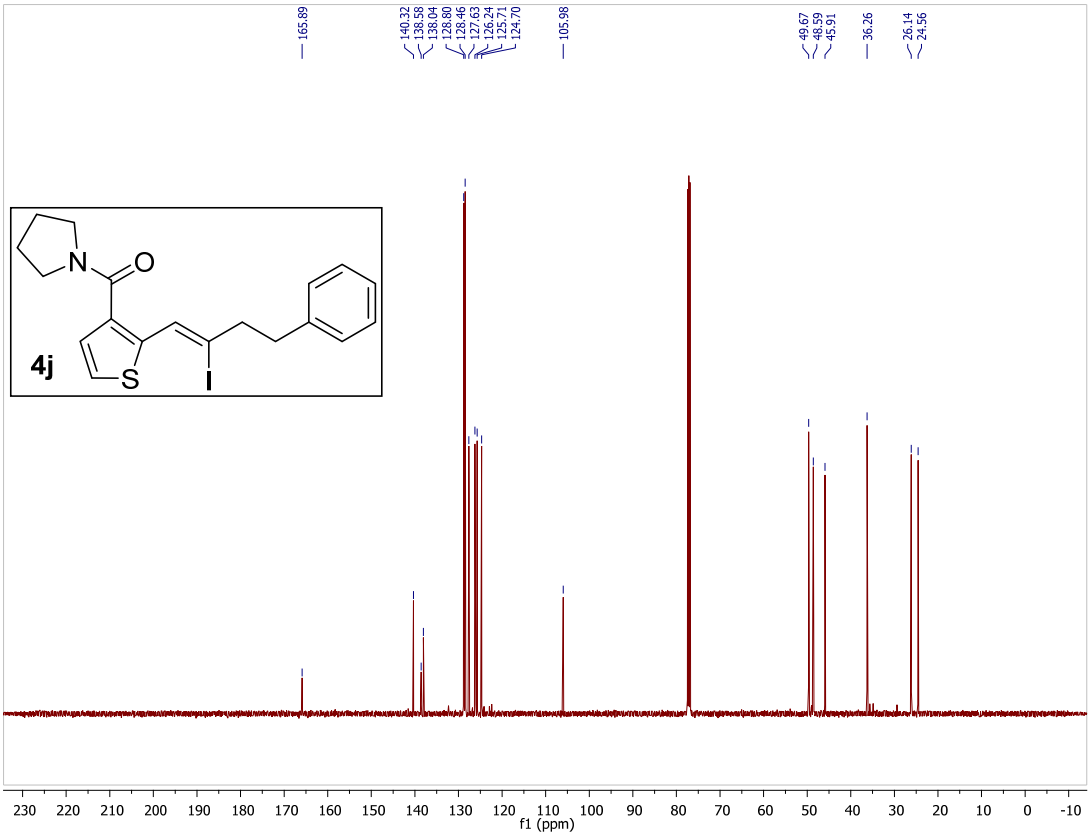
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126.24
125.71
124.70
105.98
49.67
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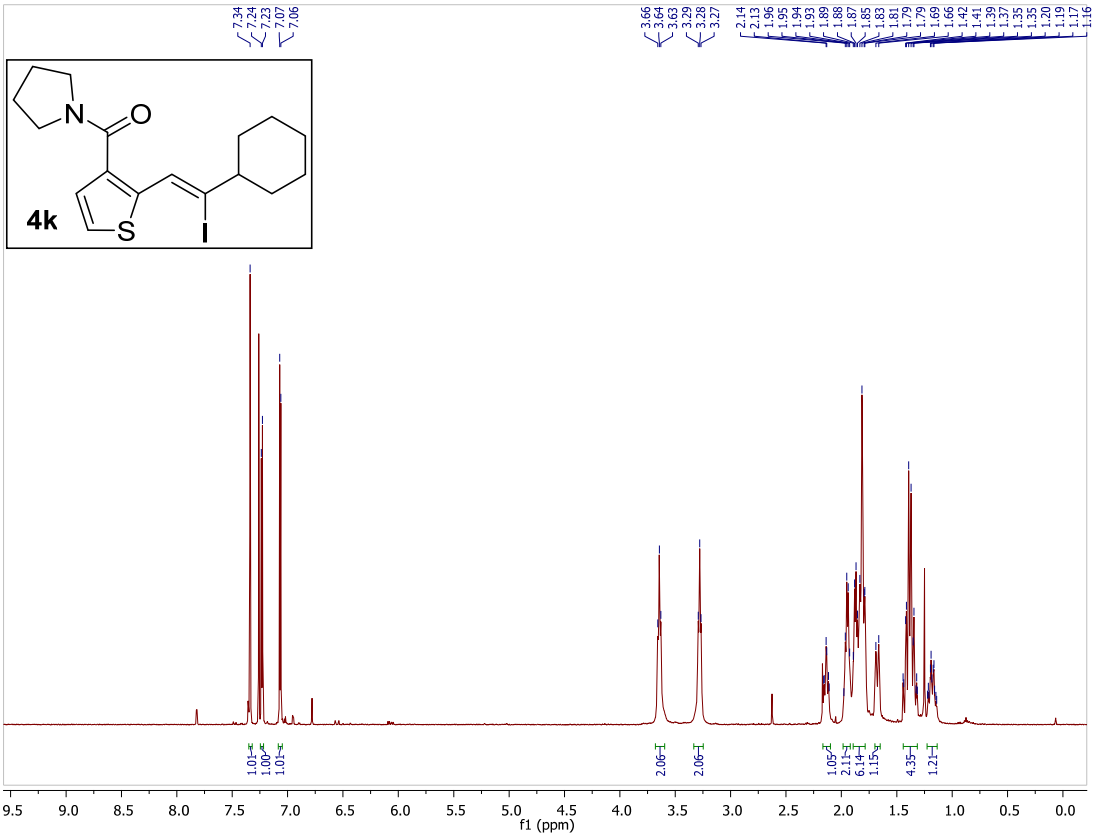
45.91
36.26
26.14
24.56
N
O
S
I
4j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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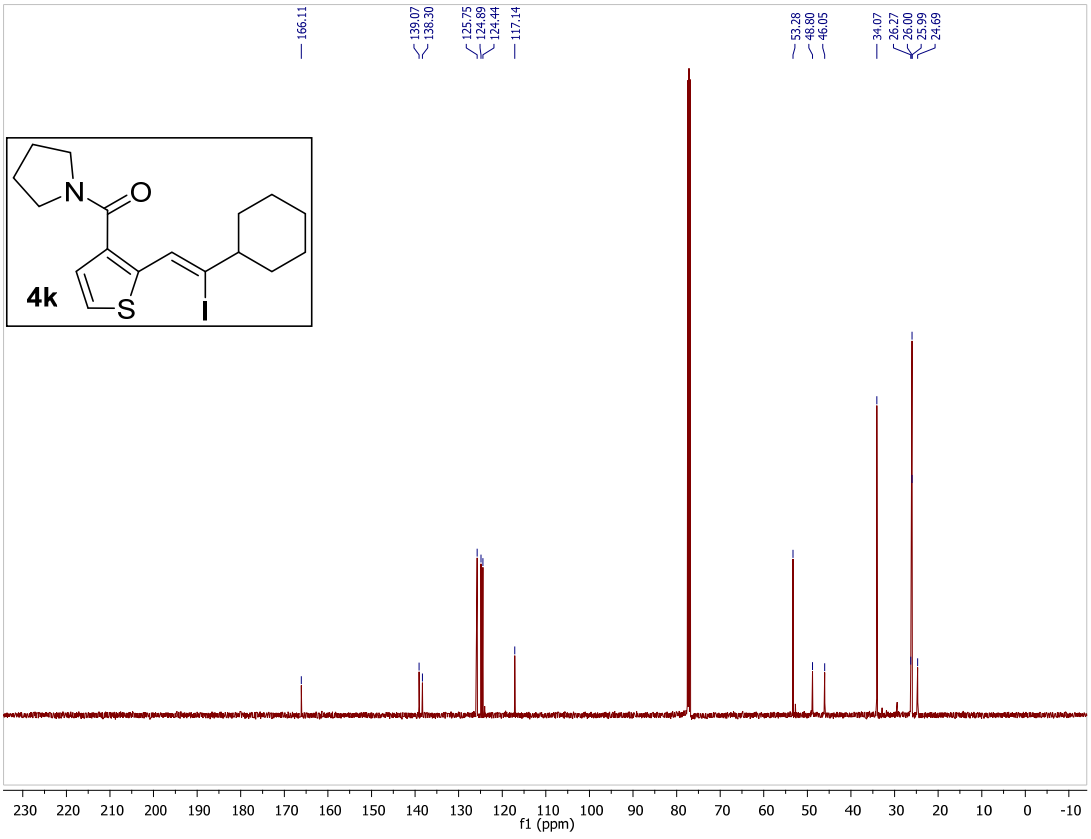
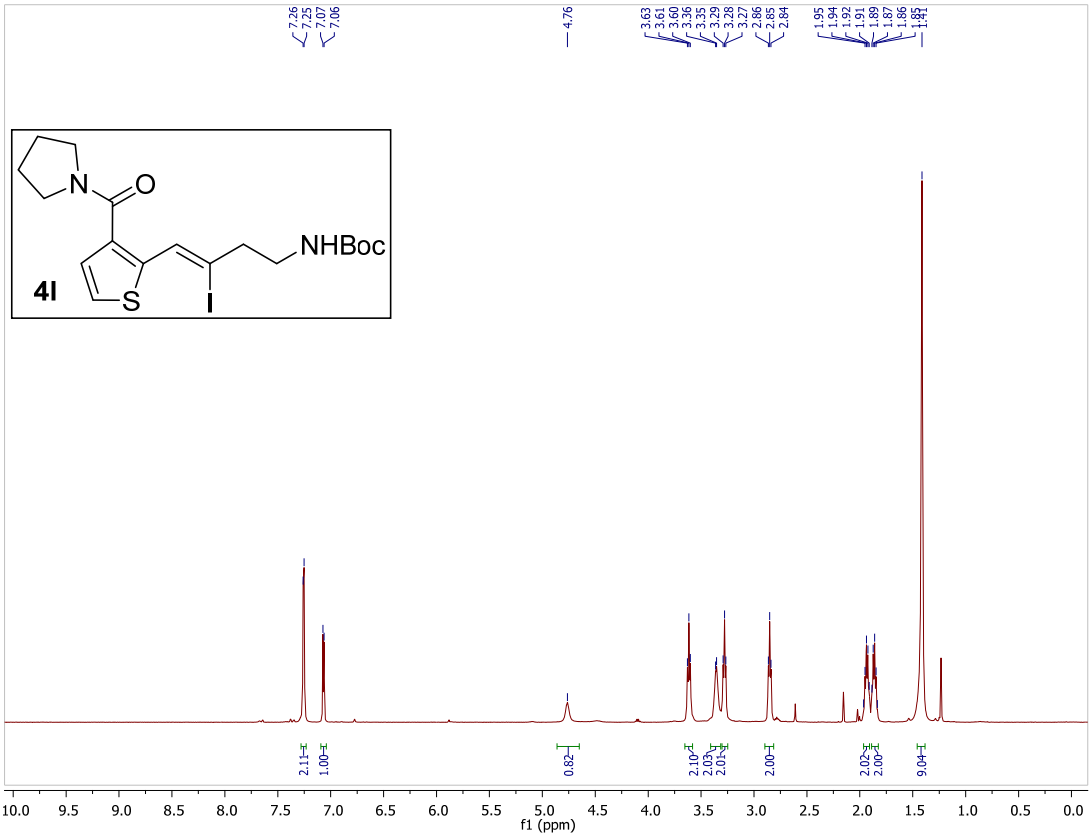

4k
f1 (ppm)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3.35
3.29
3.28
3.27
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2.85
2.84
1.95
1.94
1.92
1.91
1.89
1.87
1.86
1.85
1.41
N
O
NHBoc
S
I
4l
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0.82
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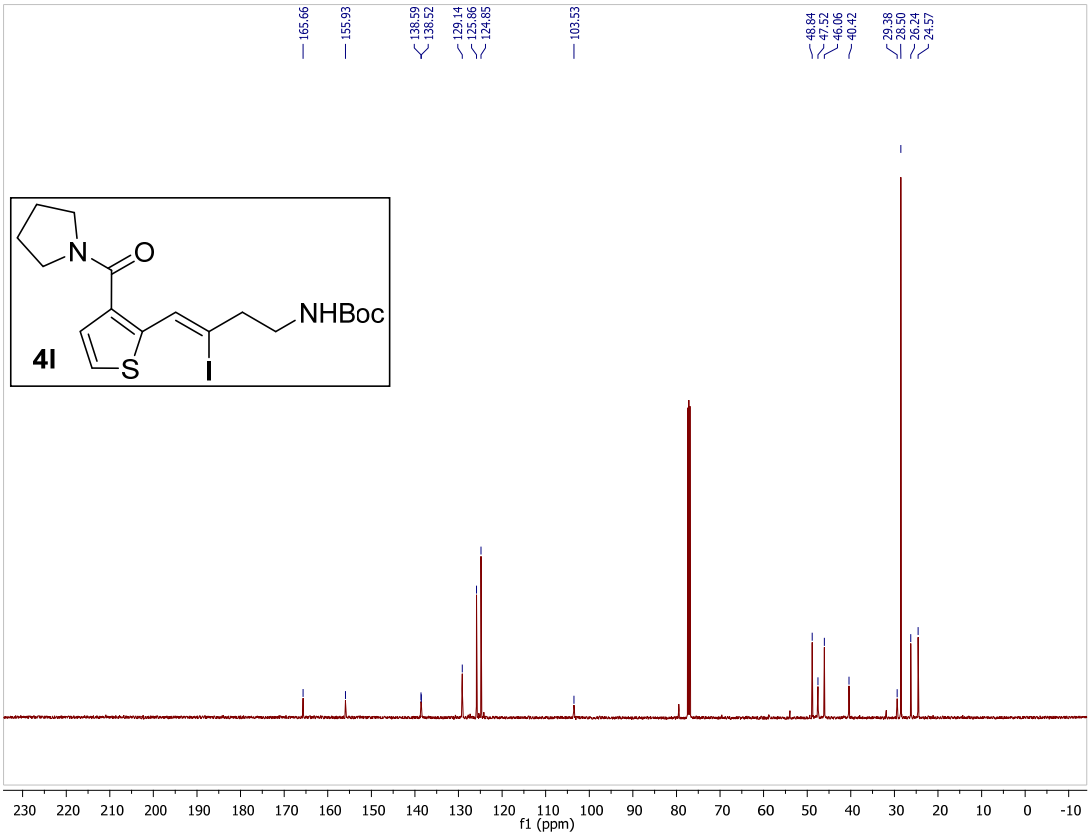
2.03
2.01
2.00
2.02
2.00
9.04
f1 (ppm)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28.50
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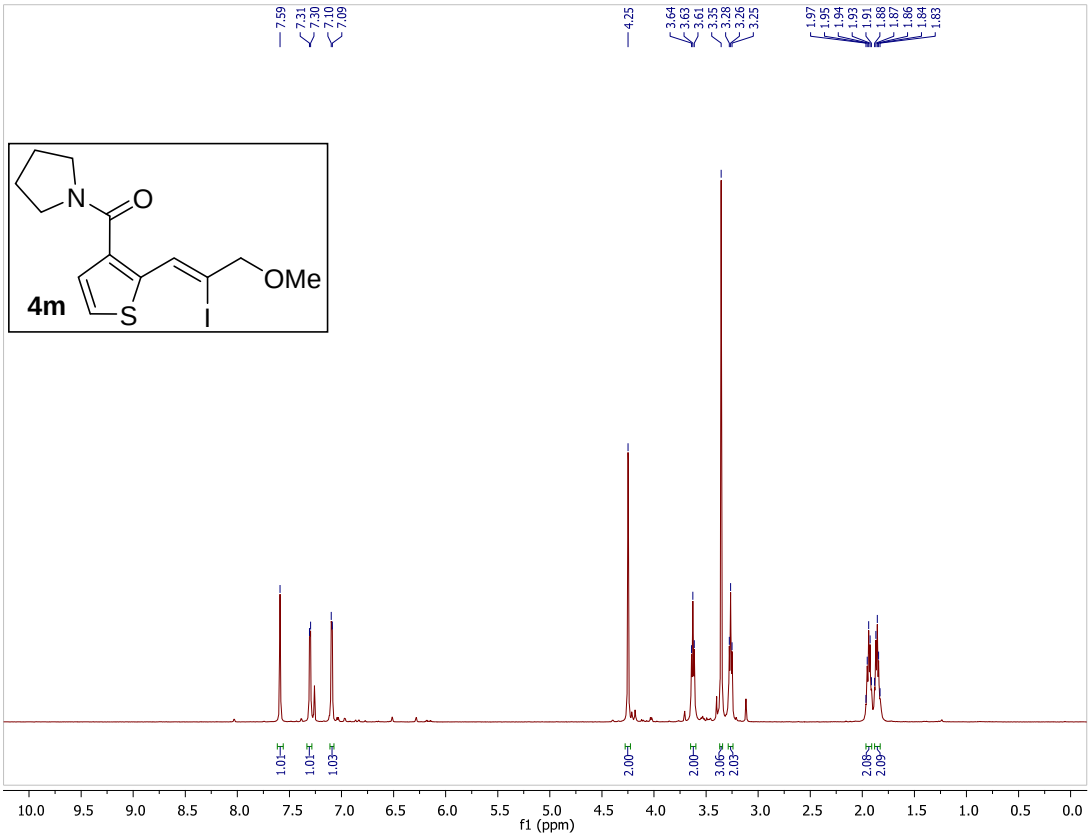
24.57
N
O
NHBoc
S
I
4l
f1 (ppm)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3.26
3.25
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1.95
1.94
1.93
1.91
1.88
1.87
1.86
1.84
1.83
1.01
1.01
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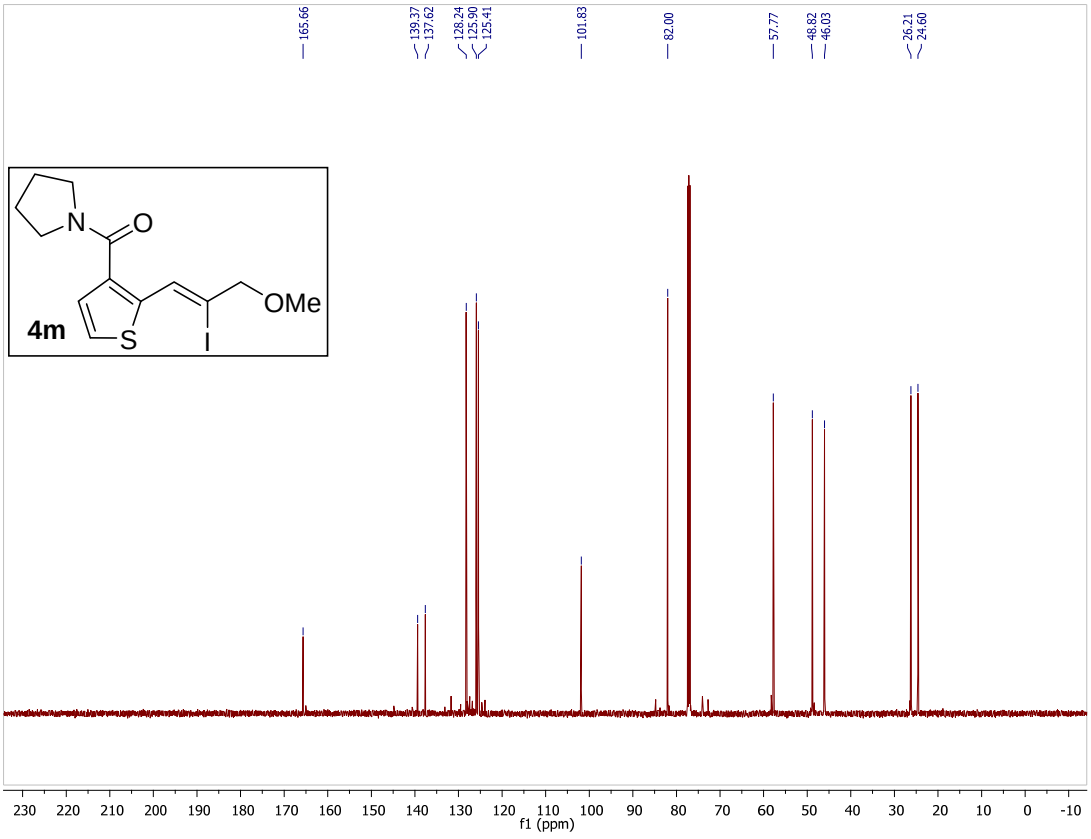
2.08
2.09
N
O
OMe
4m
S
I
f1 (ppm)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82.00
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48.82
46.03
26.21
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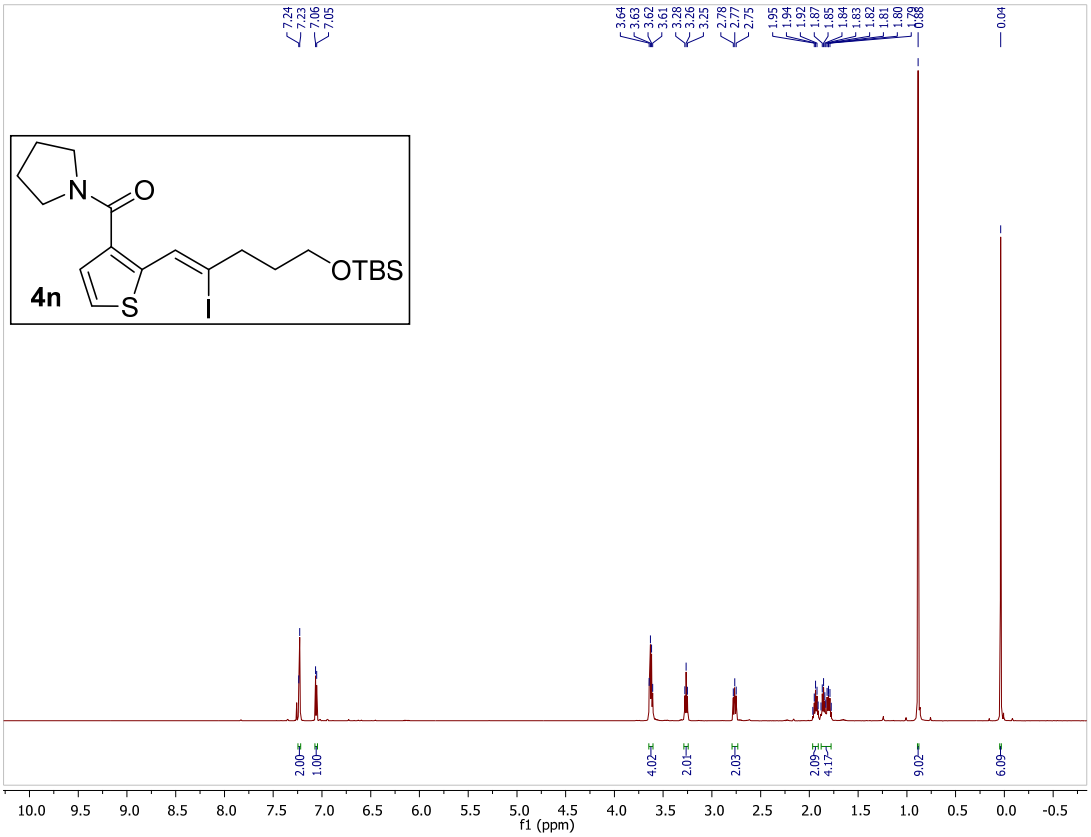
N
O
OMe
4m
S
I
f1 (ppm)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3.26
3.25
2.78
2.77
2.75
1.95
1.94
1.92
1.87
1.85
1.84
1.83
1.82
1.81
1.80
0.88
0.04
N
O
OTBS
4n
S
I
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1.00
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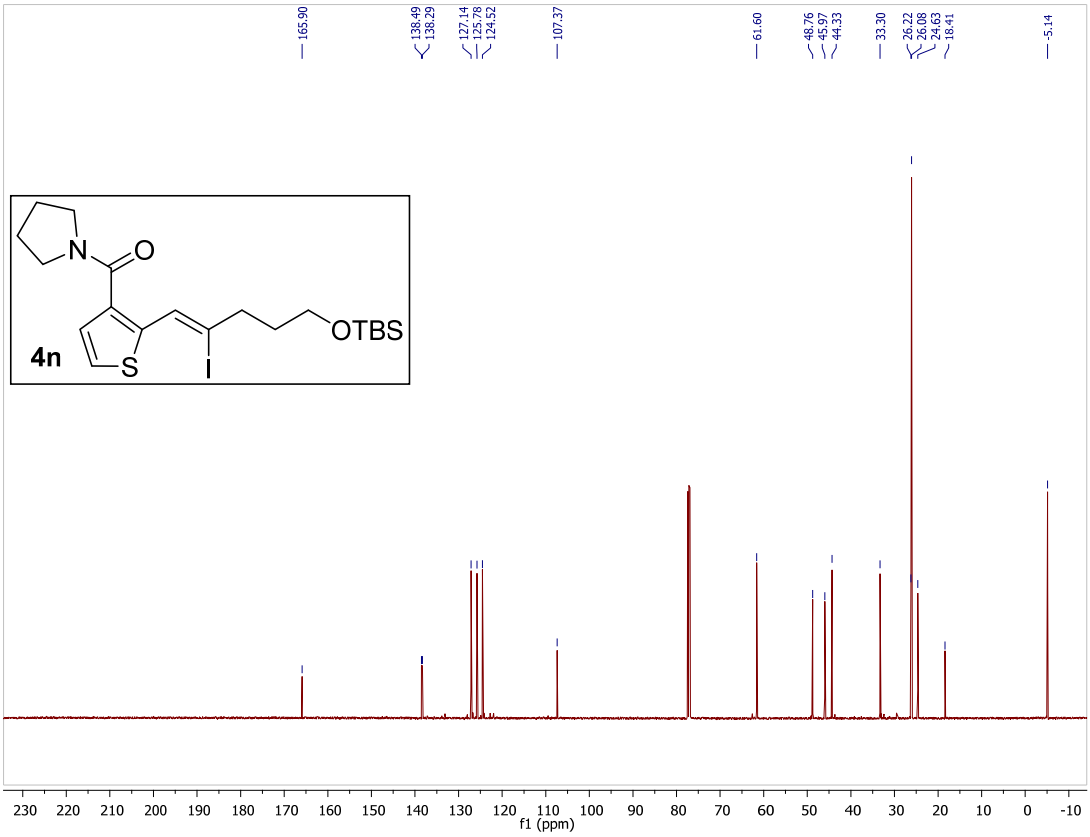
2.01
2.03
2.09
4.17
9.02
6.09
f1 (ppm)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45.97
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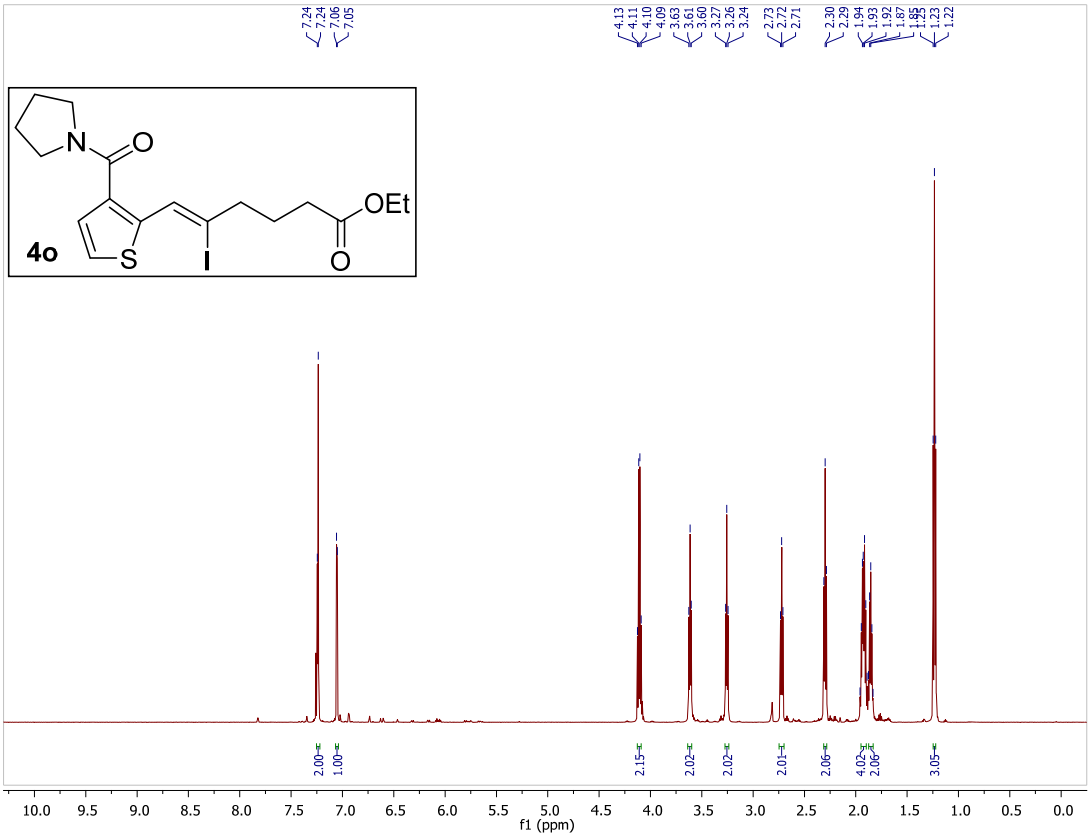
26.08
24.63
18.41
-5.14
N
O
OTBS
4n
S
I
f1 (ppm)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7.05
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3.27
3.26
3.24
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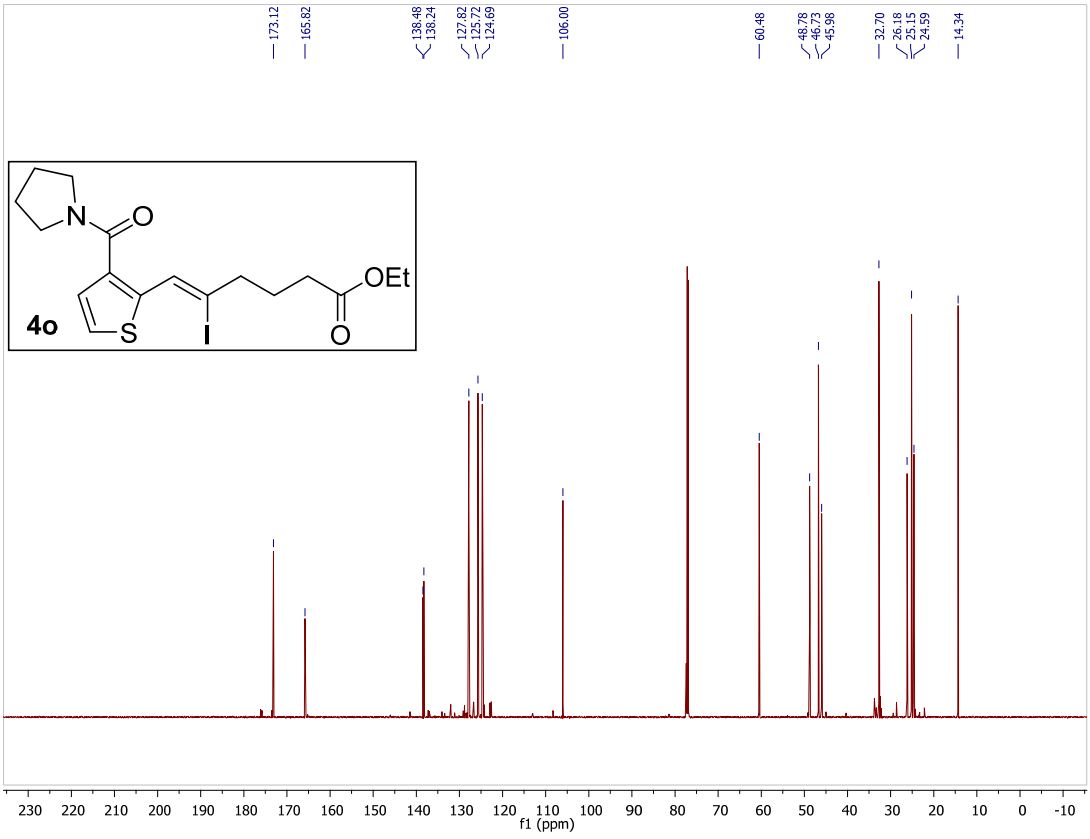
2.72
2.71
2.30
2.29
1.94
1.93
1.92
1.87
1.85
1.23
1.22
N
O
OEt
4o
S
I
O
2.00
1.00
2.15
2.02
2.02
2.01
2.06
4.02
2.06
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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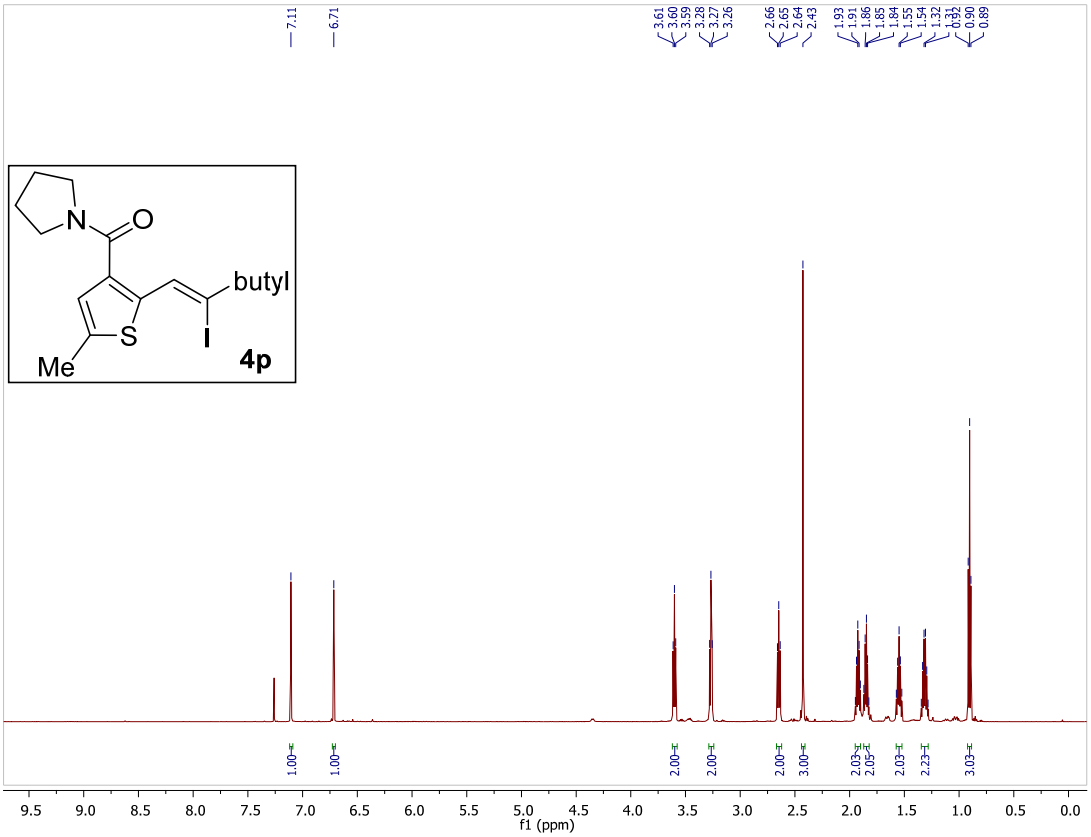
48.78
46.73
45.98
32.70
26.18
25.15
24.59
14.34
N
O
OEt
4o
S
I
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.64
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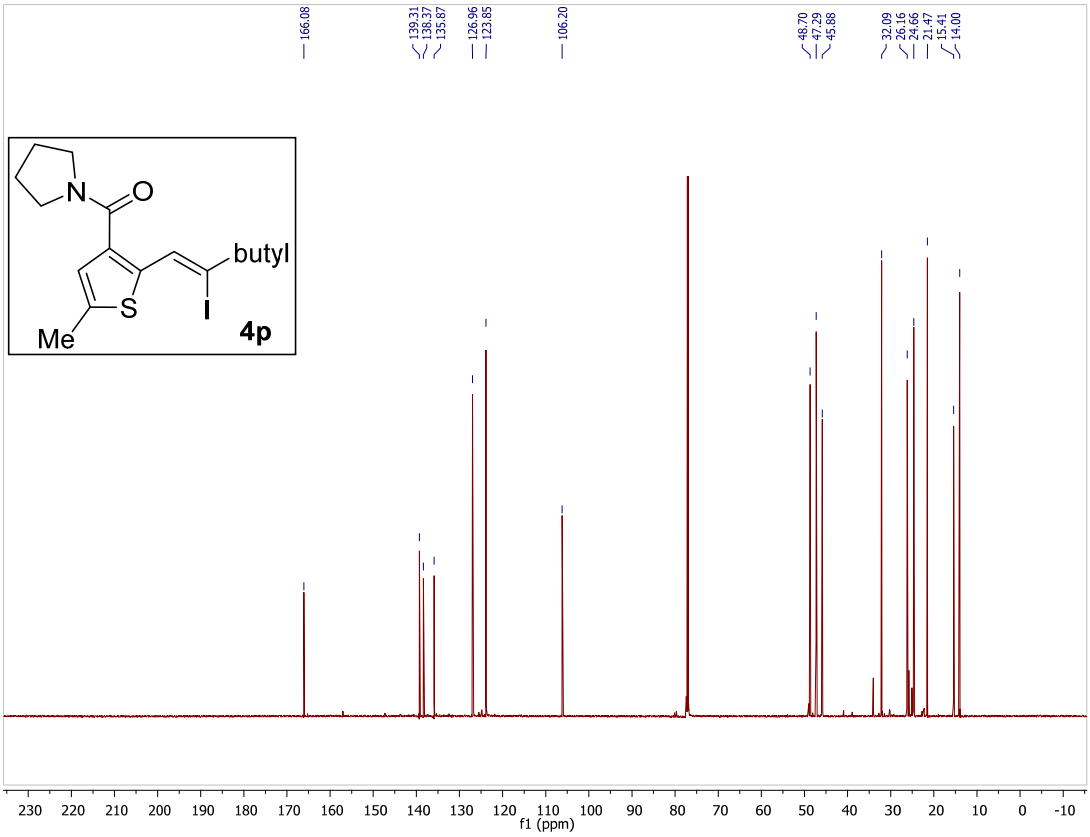
1.91
1.86
1.85
1.84
1.55
1.54
1.32
1.31
0.92
0.90
0.89
1.00
1.00
2.00
2.00
2.00
3.00
2.03
2.05
2.03
2.23
3.03
N
O
butyl
S
I
Me
4p
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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45.88
32.09
26.16
24.66
21.47
15.41
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N
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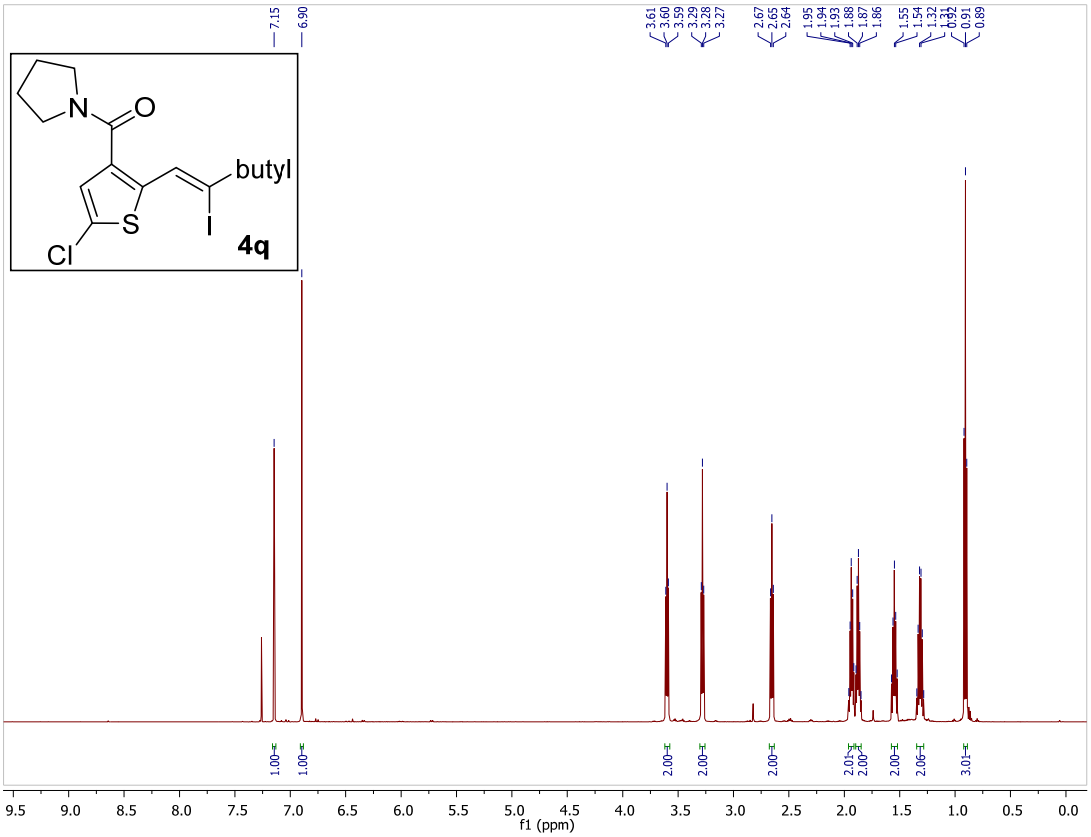
S
I
Me
4p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1.94
1.93
1.88
1.87
1.86
1.55
1.54
1.32
1.31
0.92
0.91
0.89
N
O
butyl
S
I
Cl
4q
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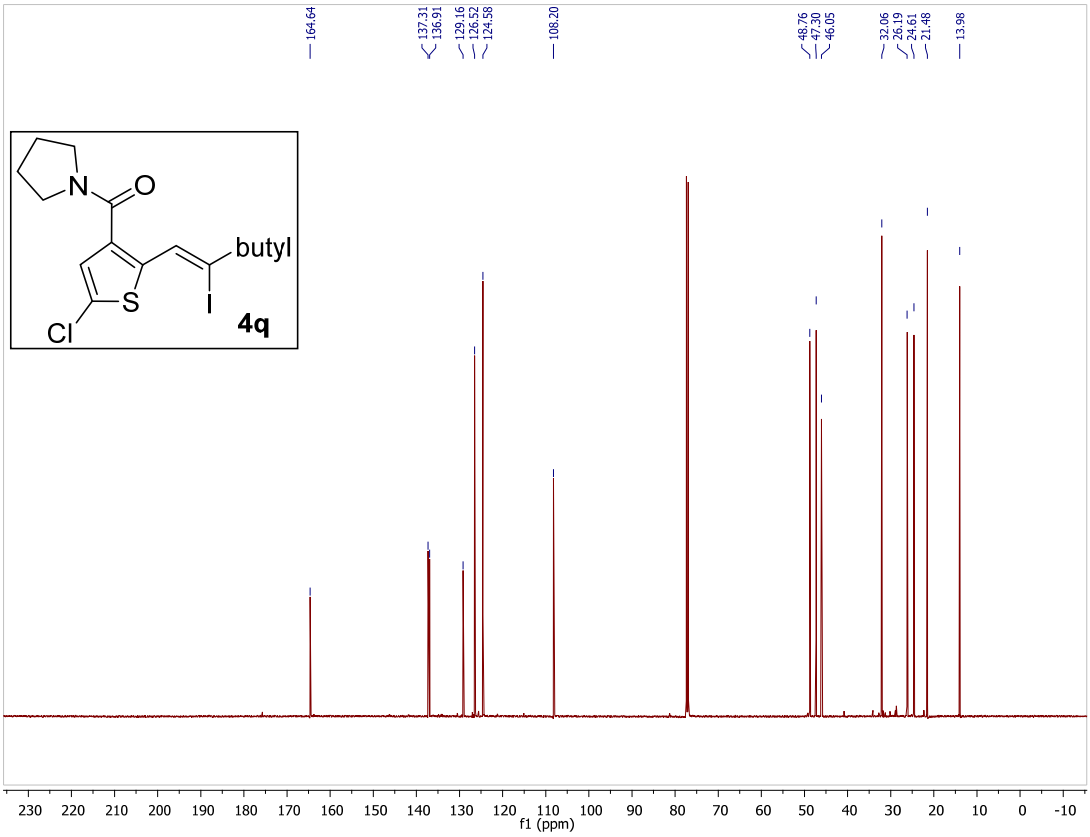
2.00
2.00
2.01
2.00
2.00
2.06
3.01
f1 (ppm)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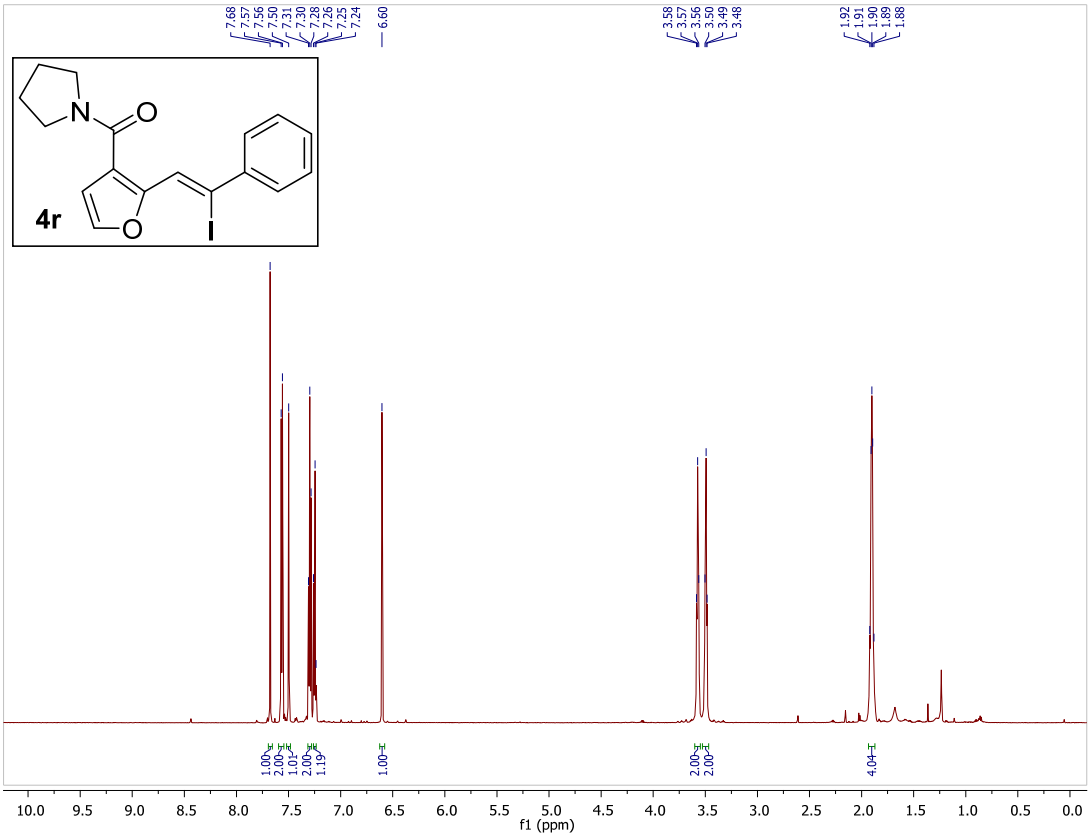
26.19
24.61
21.48
13.98
N
O
butyl
S
I
Cl
4q
f1 (ppm)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7.56
7.50
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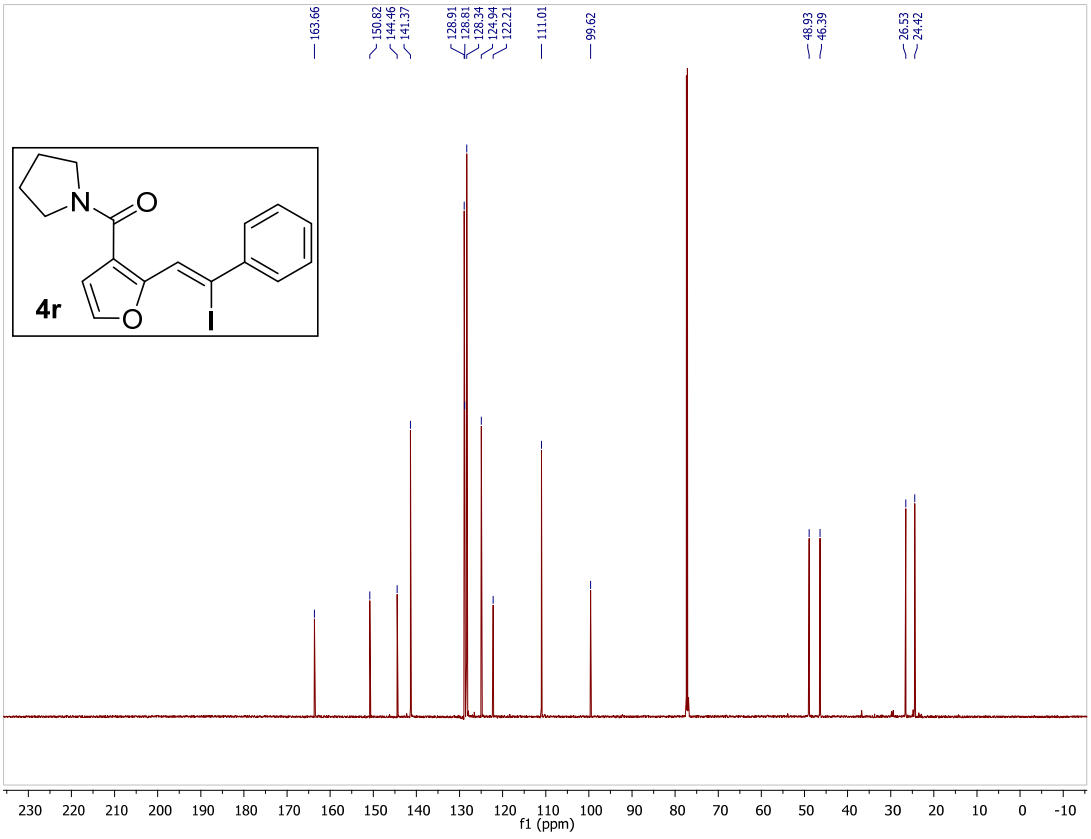
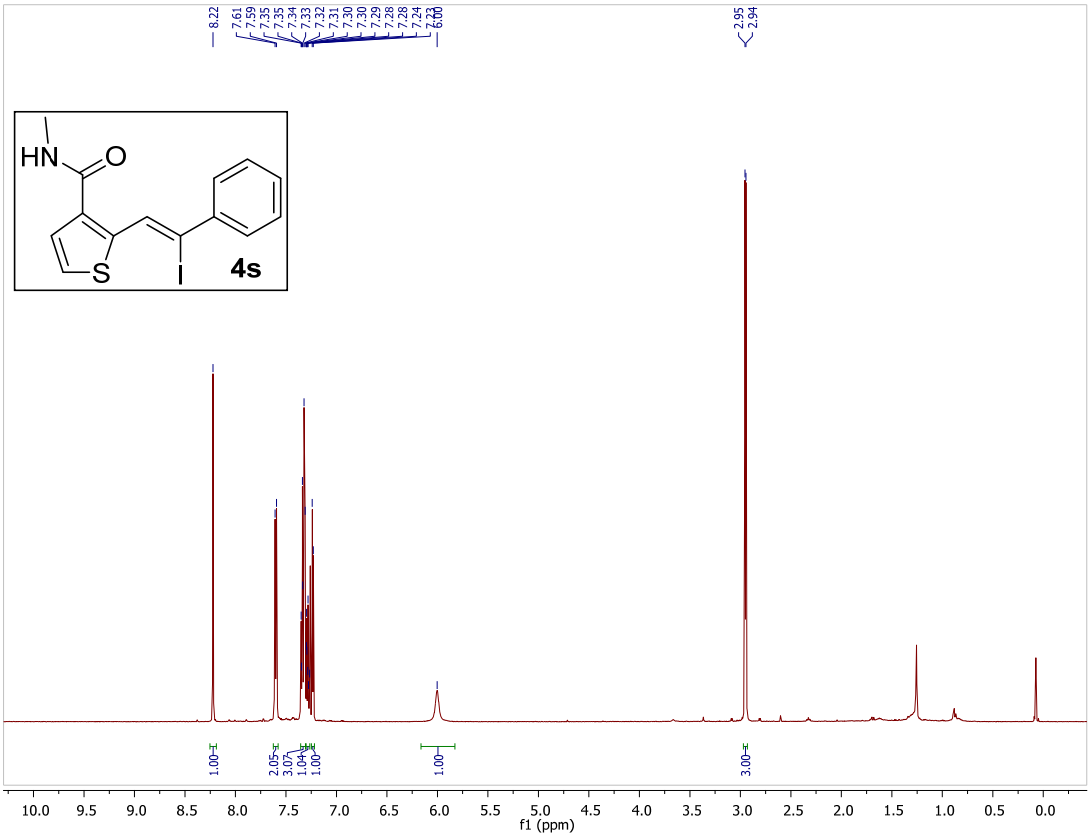
7.30
7.28
7.26
7.25
7.24
6.60
3.58
3.57
3.56
3.50
3.49
3.48
1.92
1.91
1.90
1.89
1.88
4r
1.00
2.00
1.01
2.00
1.19
1.00
2.00
2.00
4.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.66
150.82
144.46
141.37
128.91
128.81
128.34
124.94
122.21
111.01
99.62
48.93
46.39
26.53
24.42
4r
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.59
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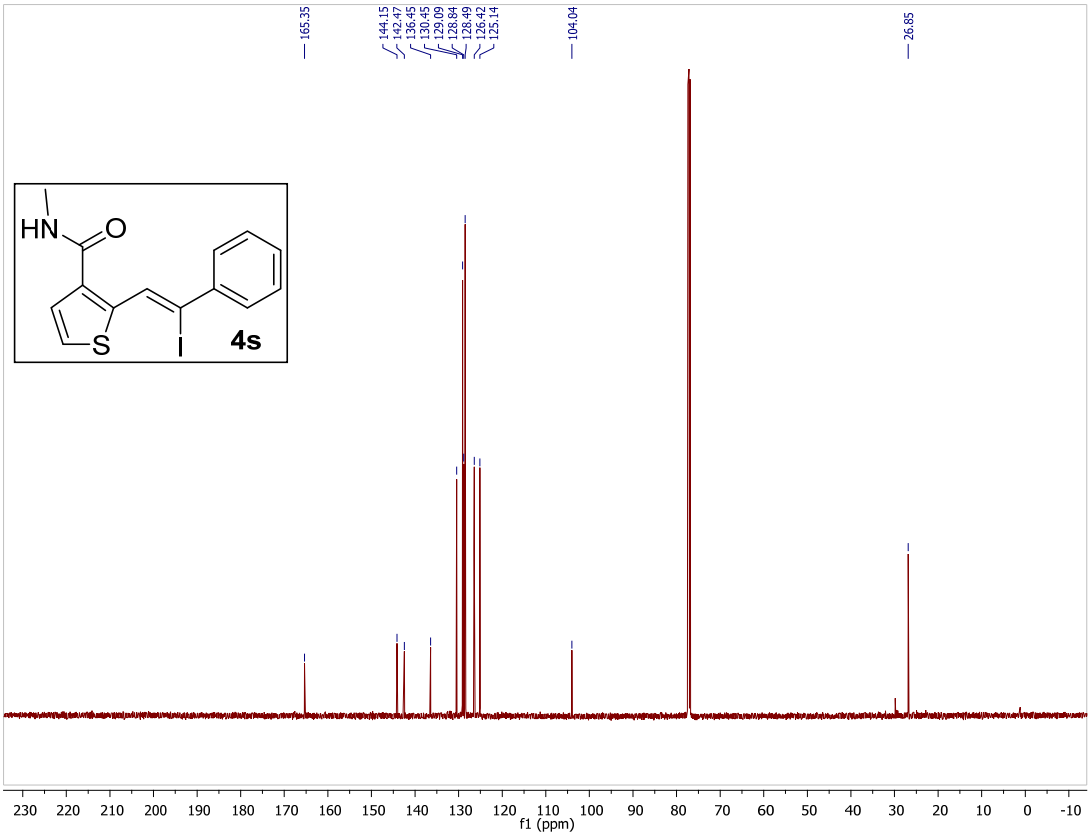
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.24
7.23
6.00
2.95
2.94
HN
O
S
I
4s
1.00
2.05
3.07
1.04
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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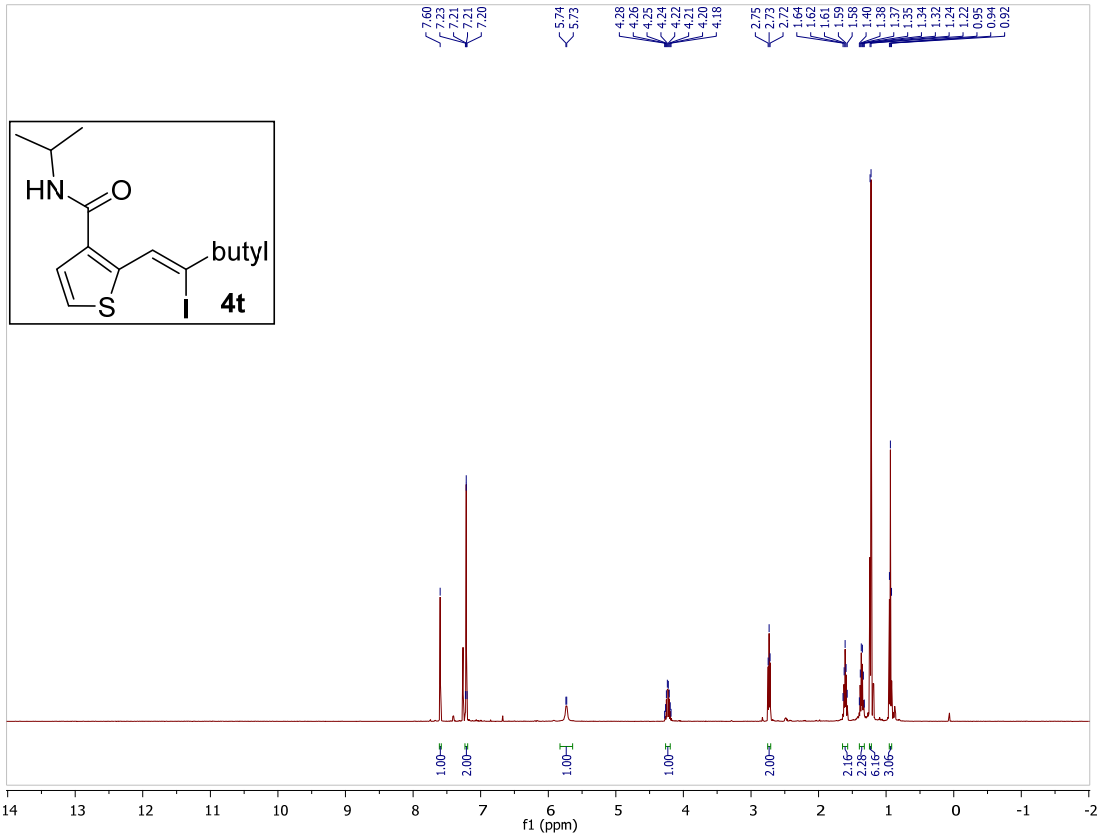
144.15
142.47
136.45
130.45
129.09
128.84
128.49
126.42
125.14
104.04
26.85
HN
O
S
I
4s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.21
7.21
7.20
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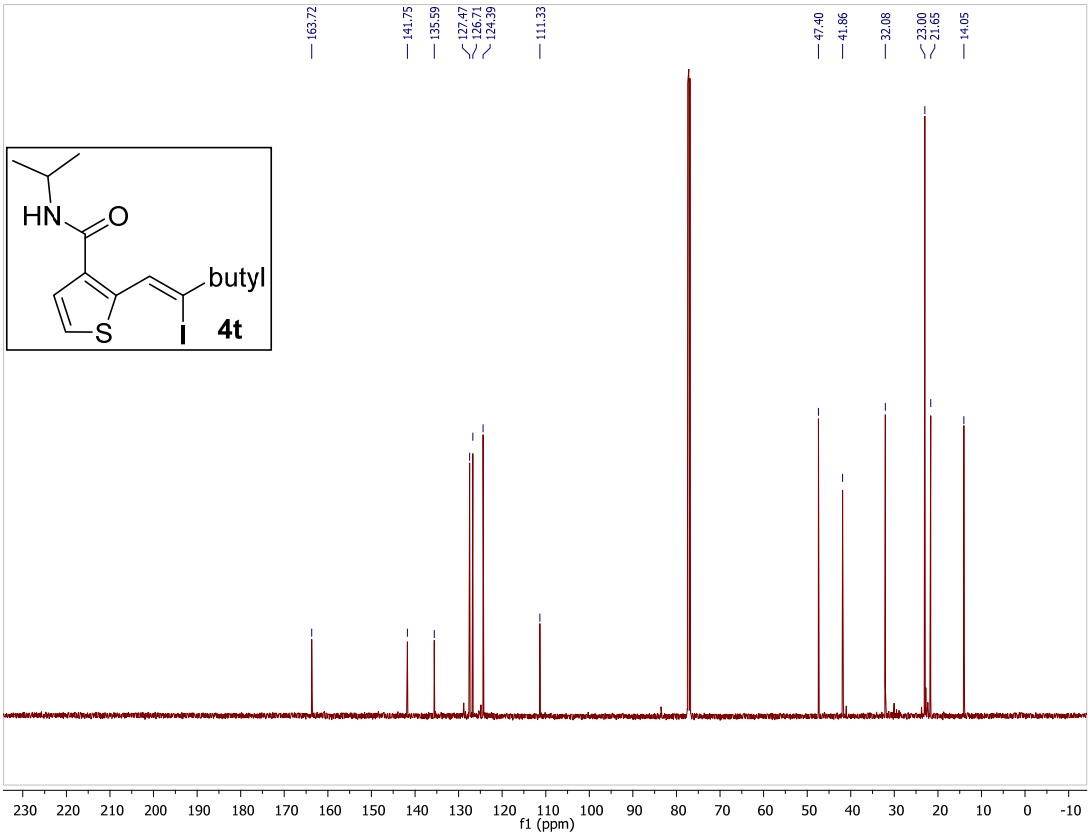
5.73
4.28
4.26
4.25
4.24
4.22
4.21
4.20
4.18
2.75
2.73
2.72
1.64
1.62
1.61
1.59
1.58
1.40
1.38
1.37
1.35
1.34
1.32
1.24
1.22
0.95
0.94
0.92
HN
O
butyl
S
I
4t
1.00
2.00
1.00
1.00
2.00
2.16
2.28
6.16
3.06
f1 (ppm)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141.75
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126.71
124.39
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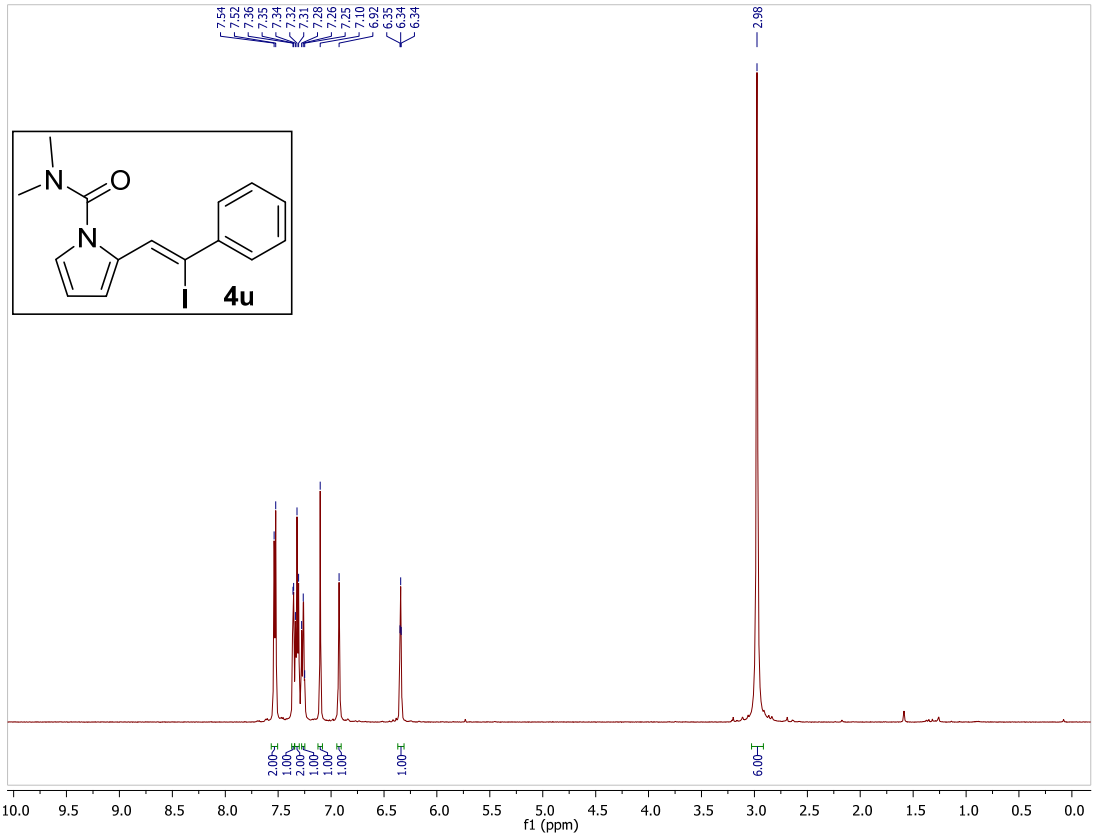
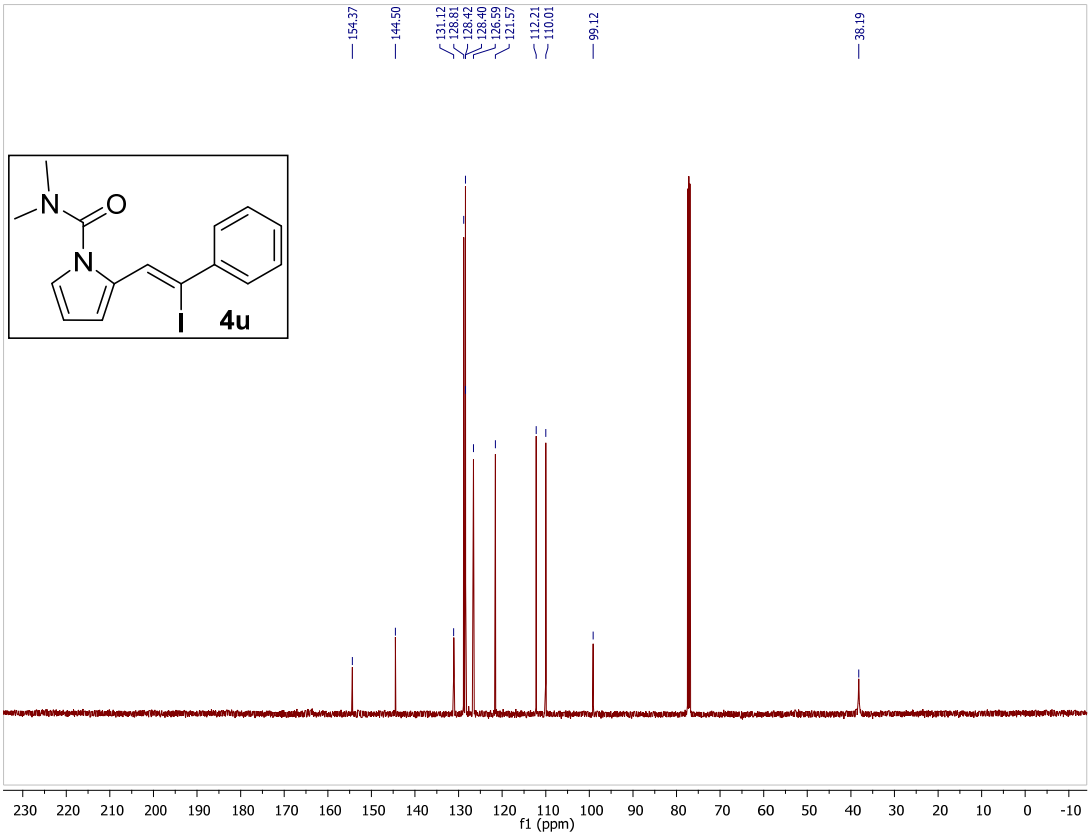
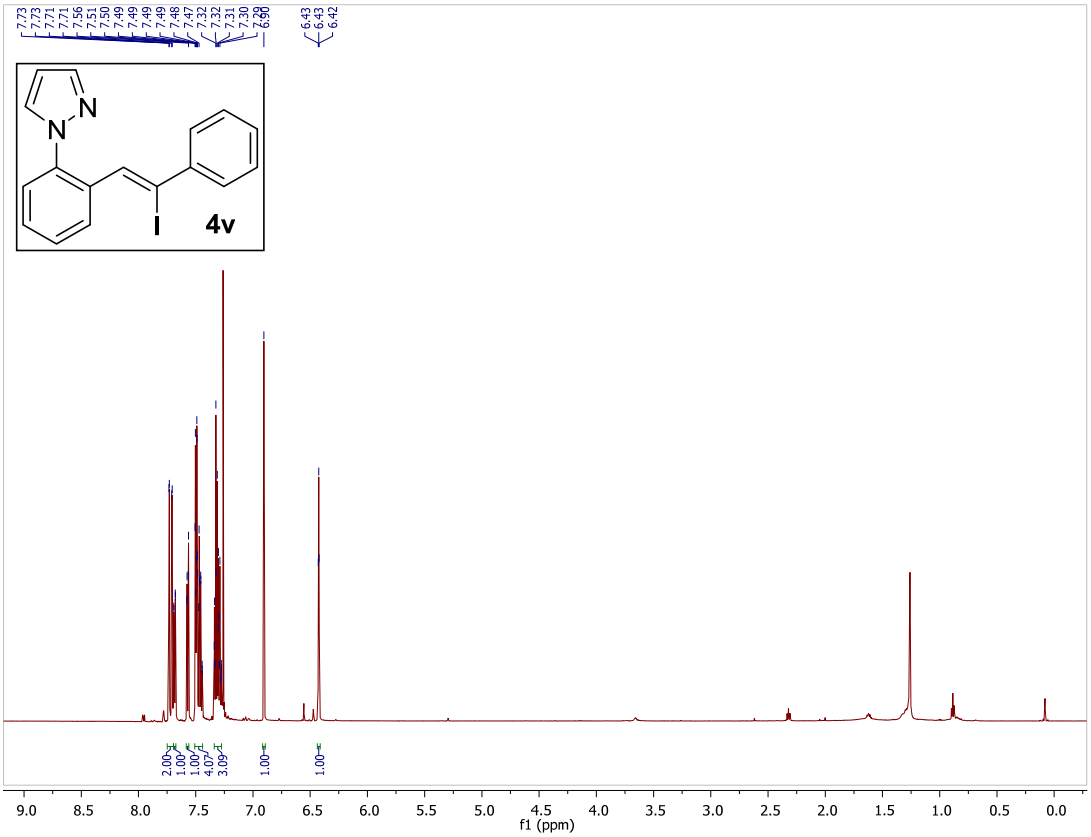
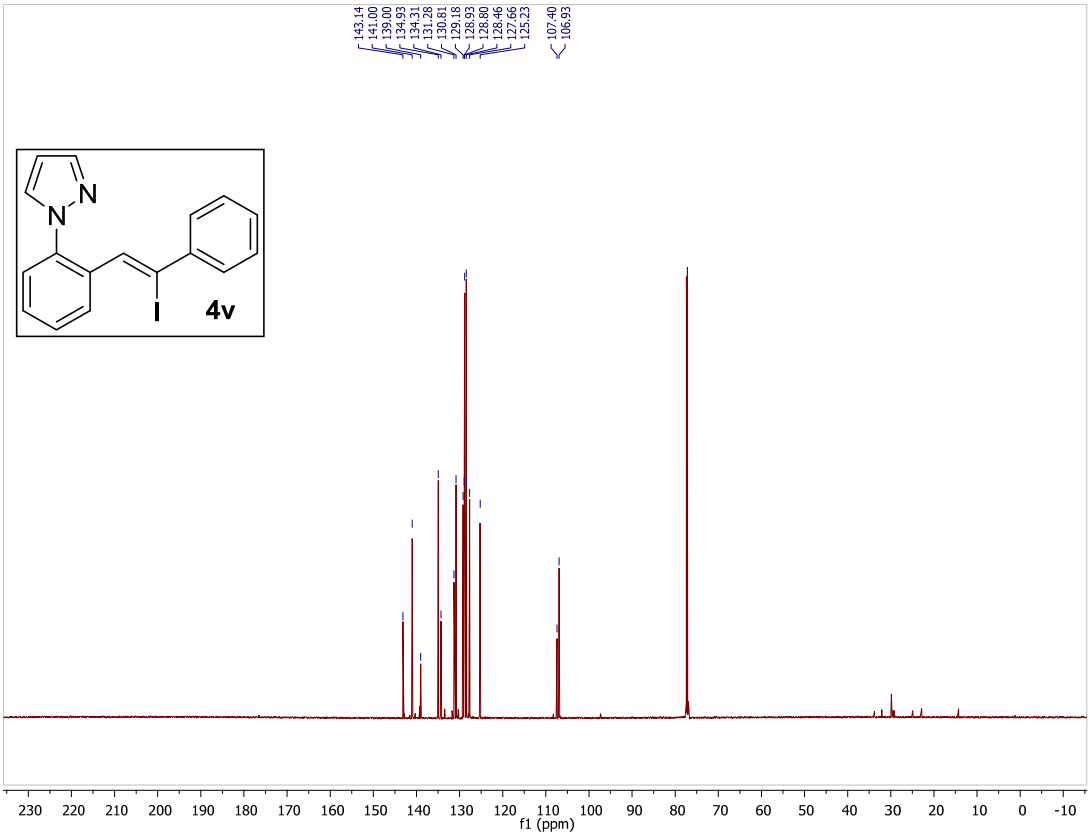
32.08
23.00
21.65
14.05
HN
O
butyl
S
I
4t
f1 (ppm)


7.54
7.52
7.36
7.35
7.34
7.32
7.31
7.28
7.26
7.25
7.10
6.92
6.35
6.34
6.34
2.98
4u
2.00
1.00
2.00
1.00
1.00
1.00
1.00
6.00
f1 (ppm)


154.37
144.50
131.12
128.81
128.42
128.40
126.59
121.57
112.21
110.01
99.12
38.19
4u
f1 (ppm)


7.73
7.73
7.71
7.71
7.56
7.51
7.50
7.49
7.49
7.49
7.49
7.48
7.47
7.32
7.32
7.31
7.30
7.29
6.90
6.43
6.43
6.42
N
N
I
4v
2.00
1.00
1.00
1.00
4.07
3.09
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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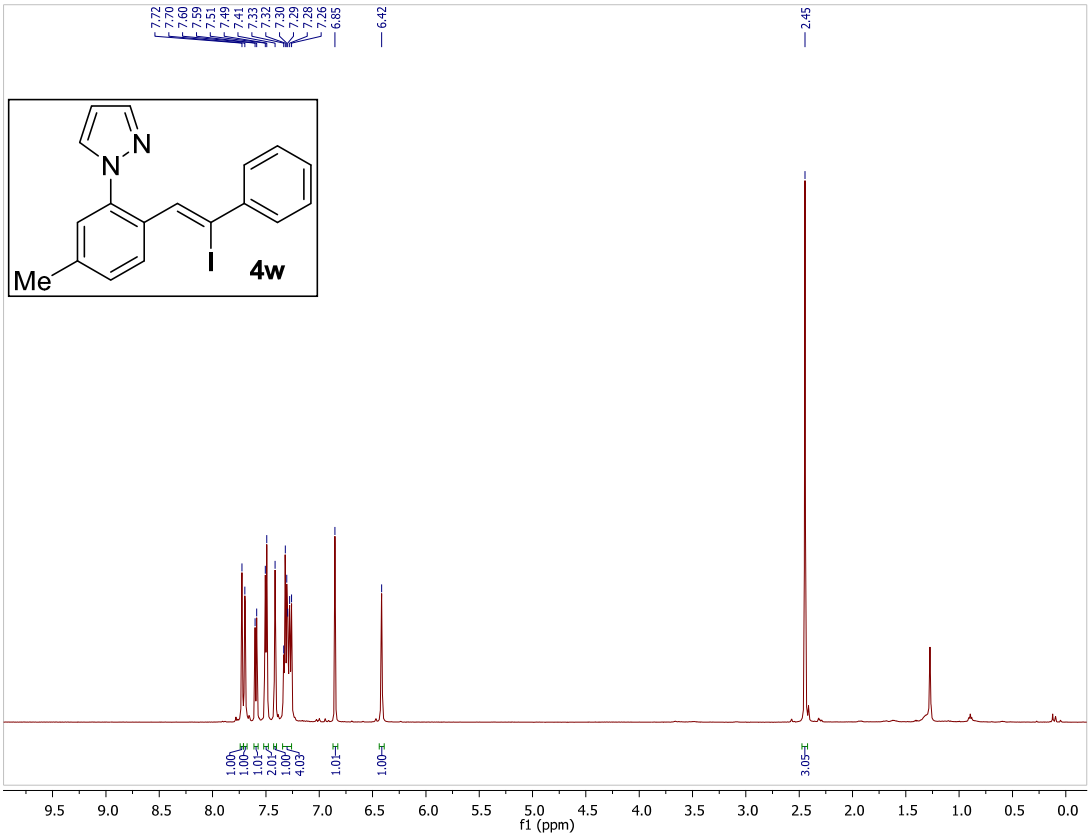
141.00
139.00
134.93
134.31
131.28
130.81
129.18
128.93
128.80
128.46
127.66
125.23
107.40
106.93
N
N
I
4v
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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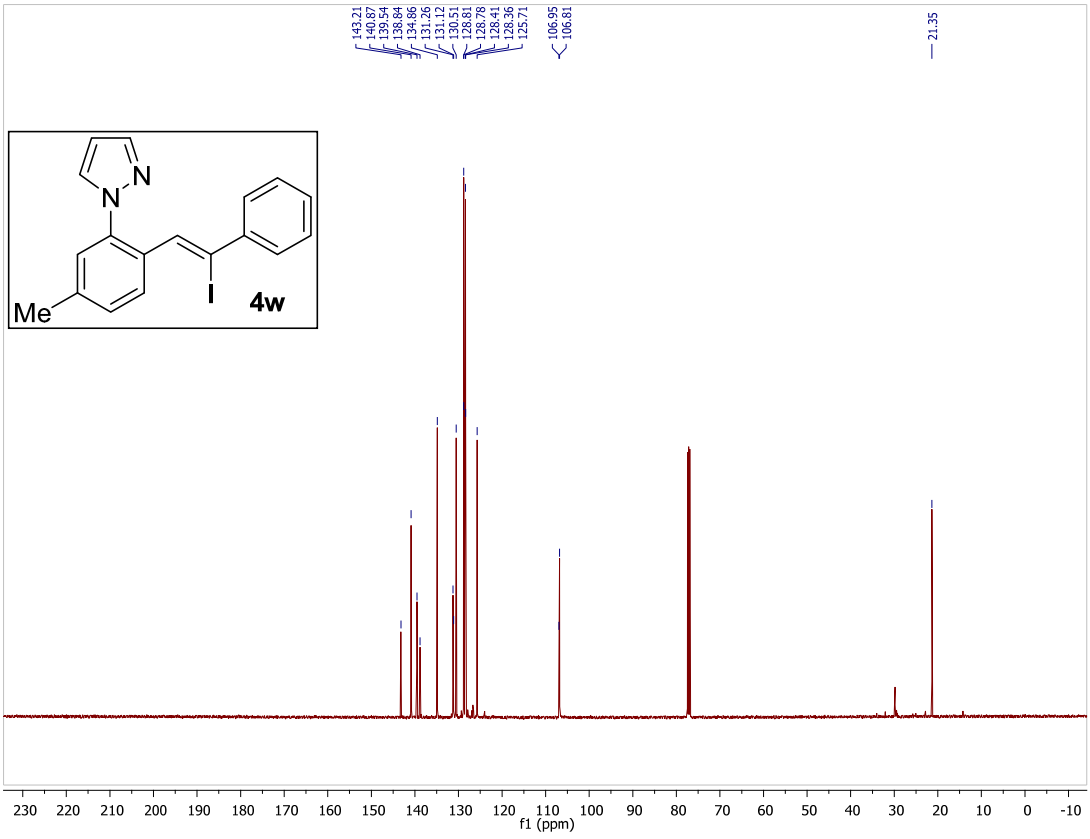
7.70
7.60
7.59
7.51
7.49
7.41
7.33
7.32
7.30
7.29
7.28
7.26
6.85
6.42
2.45
N
N
Me
I
4w
1.00
1.00
1.01
2.01
1.00
4.03
1.01
1.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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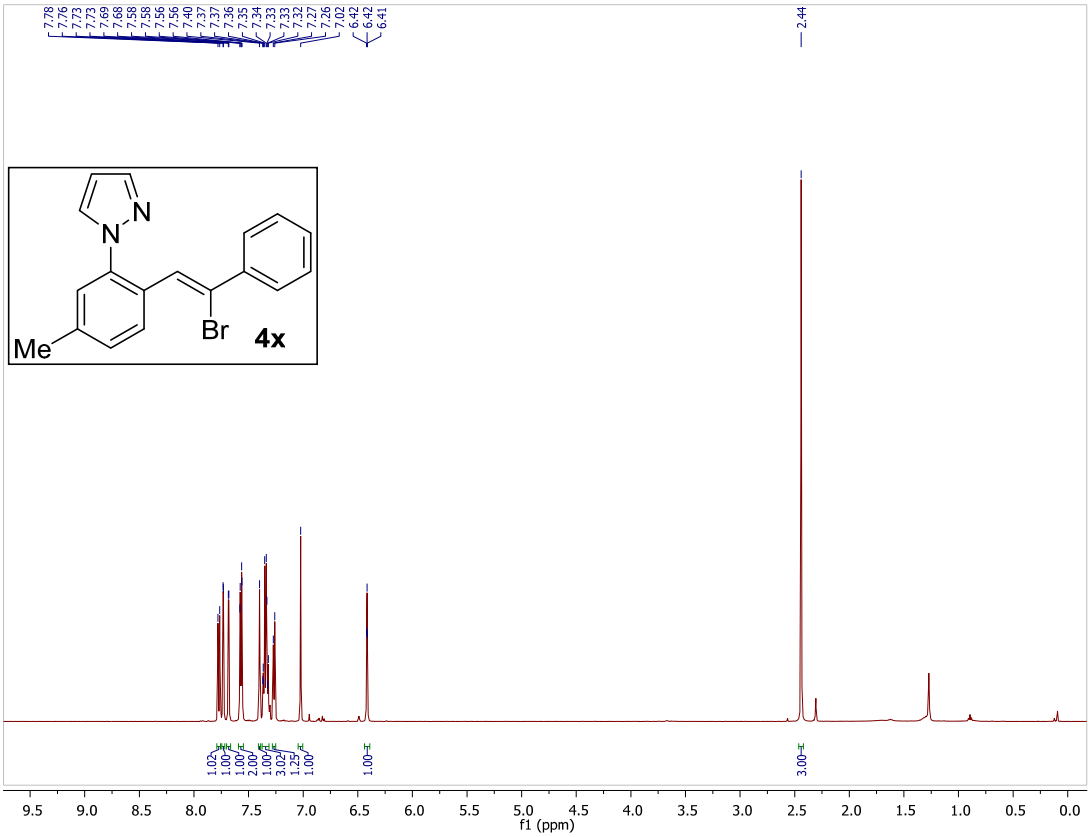
140.87
139.54
138.84
134.86
131.26
131.12
130.51
128.81
128.78
128.41
128.36
125.71
106.95
106.81
21.35
N
N
Me
I
4w
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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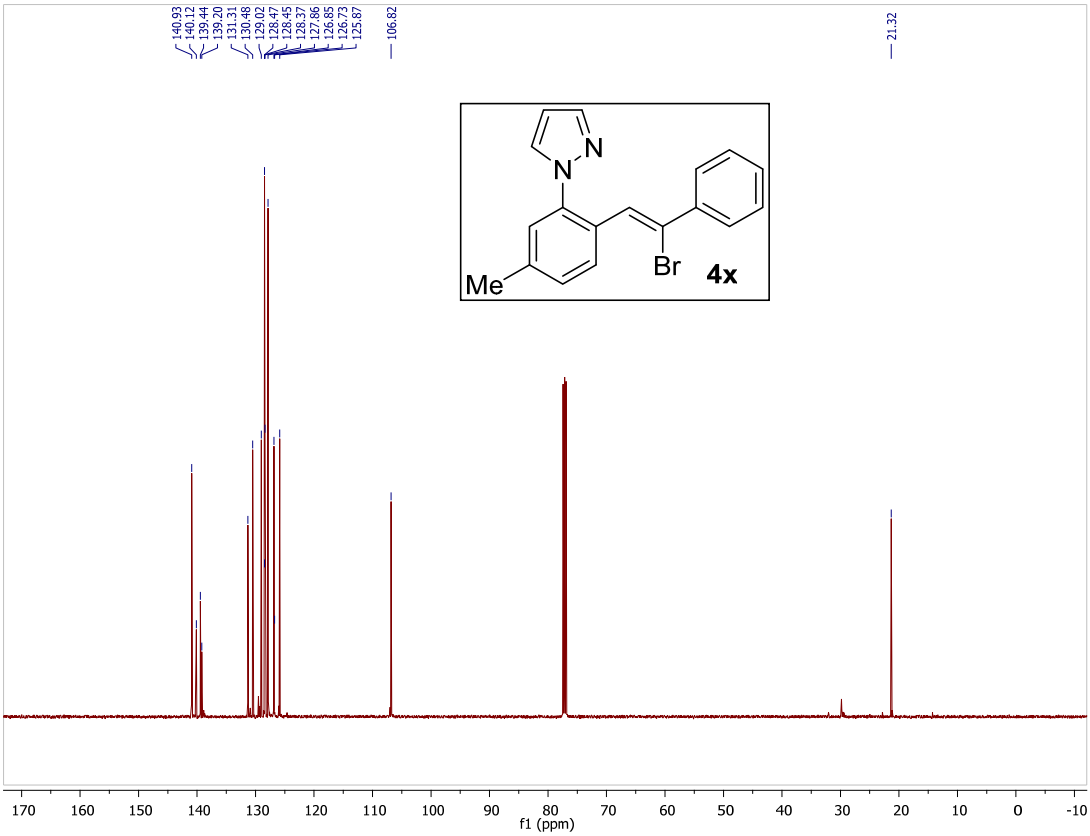
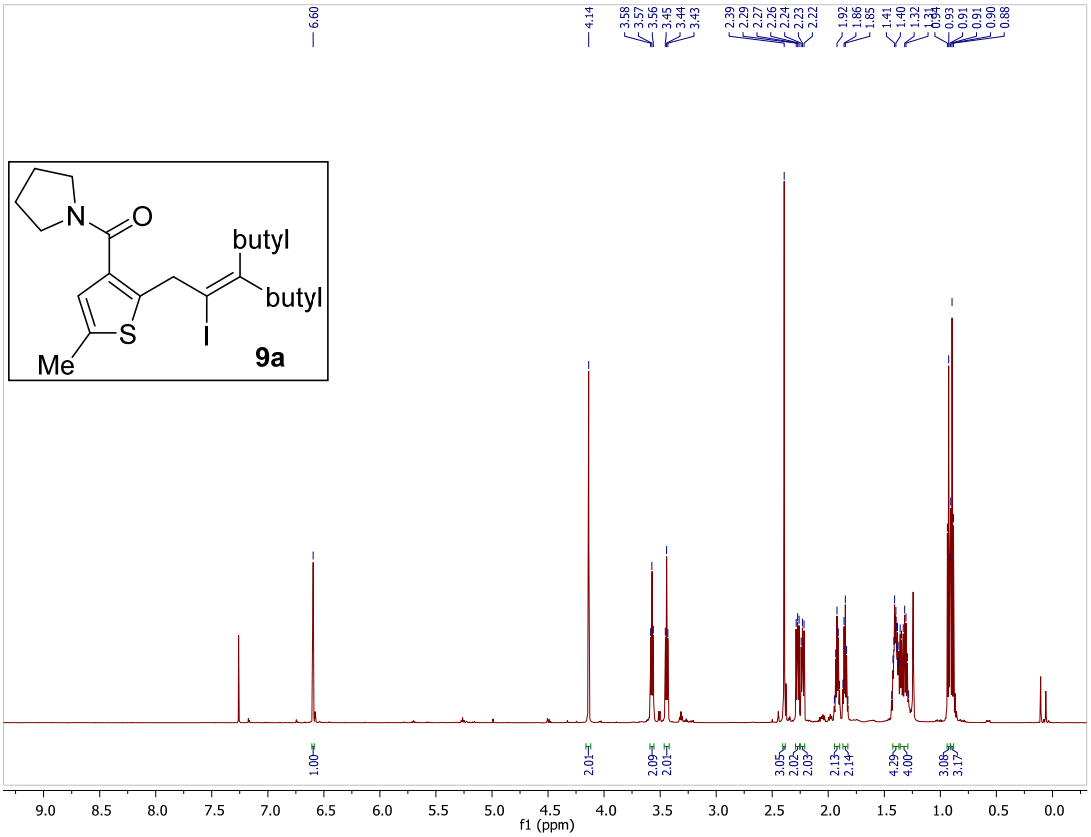
7.76
7.73
7.73
7.69
7.68
7.58
7.58
7.56
7.56
7.40
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.27
7.26
7.02
6.42
6.41
2.44
N
N
Me
Br
4x
1.02
1.00
1.00
2.00
1.00
3.02
1.25
1.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.93
140.12
139.44
139.20
131.31
130.48
129.02
128.47
128.45
128.37
127.86
126.85
126.73
125.87
106.82
21.32
N
N
Me
Br
4x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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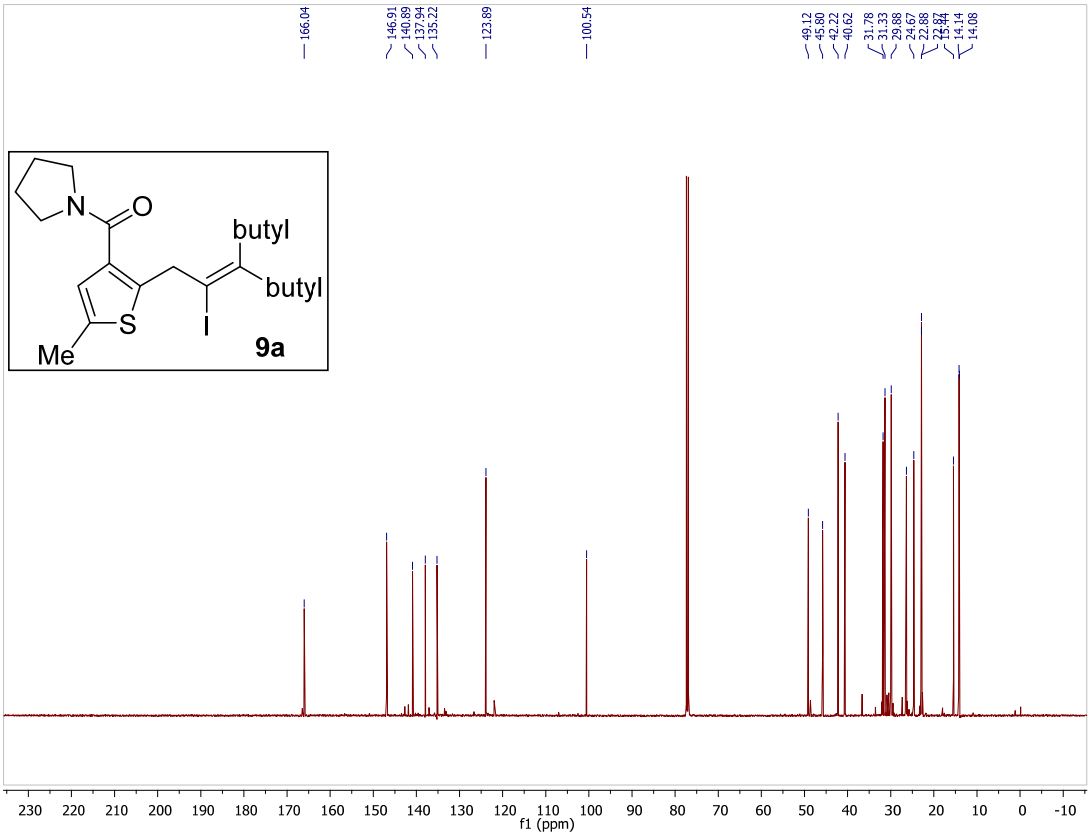
4.14
3.58
3.57
3.56
3.45
3.44
3.43
2.39
2.29
2.27
2.26
2.24
2.23
2.22
1.92
1.86
1.85
1.41
1.40
1.32
1.31
0.94
0.93
0.91
0.91
0.90
0.88
N
O
butyl
butyl
S
I
Me
9a
1.00
2.01
2.09
2.01
3.05
2.02
2.09
2.13
2.14
4.29
4.00
3.08
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.04
146.91
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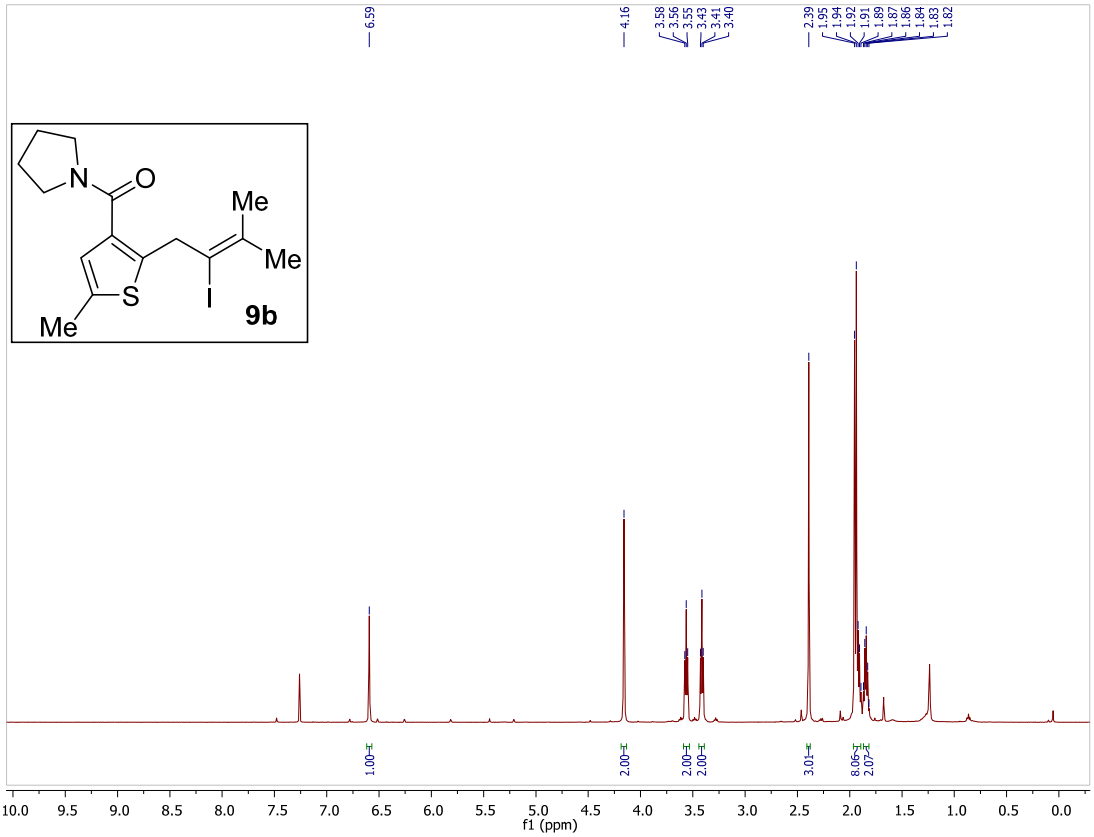
137.94
135.22
123.89
100.54
49.12
45.80
42.22
40.62
31.78
31.33
29.88
24.67
22.88
14.14
14.08
N
O
butyl
butyl
S
I
Me
9a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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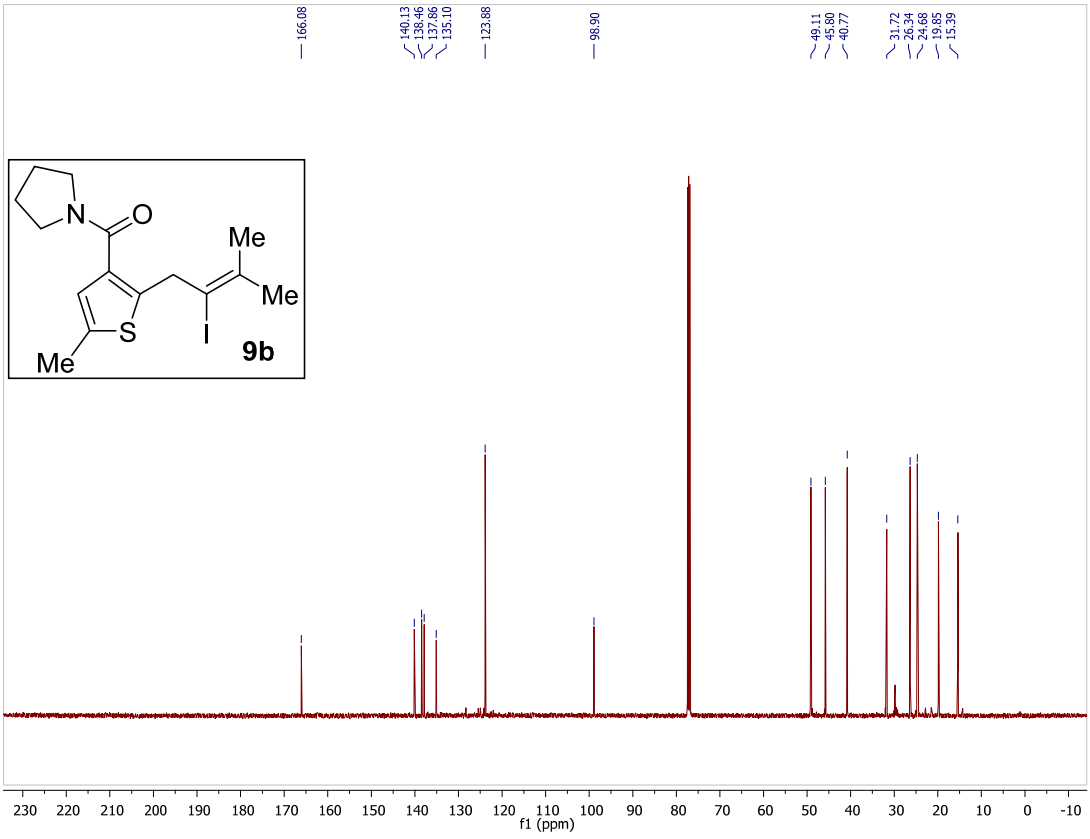
3.41
3.40
2.39
1.95
1.94
1.92
1.91
1.89
1.87
1.86
1.84
1.83
1.82
N
O
Me
Me
S
I
Me
9b
1.00
2.00
2.00
2.00
3.01
8.06
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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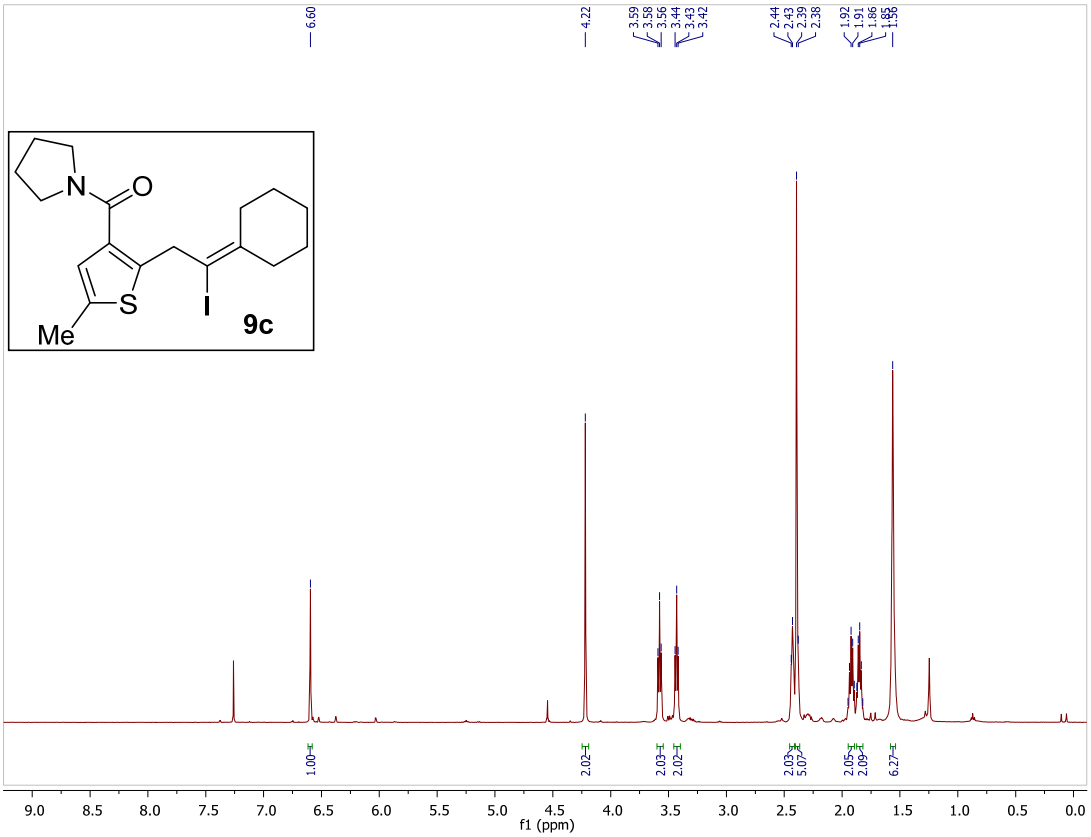
137.86
135.10
123.88
98.90
49.11
45.80
40.77
31.72
26.34
24.68
19.85
15.39
N
O
Me
Me
S
I
Me
9b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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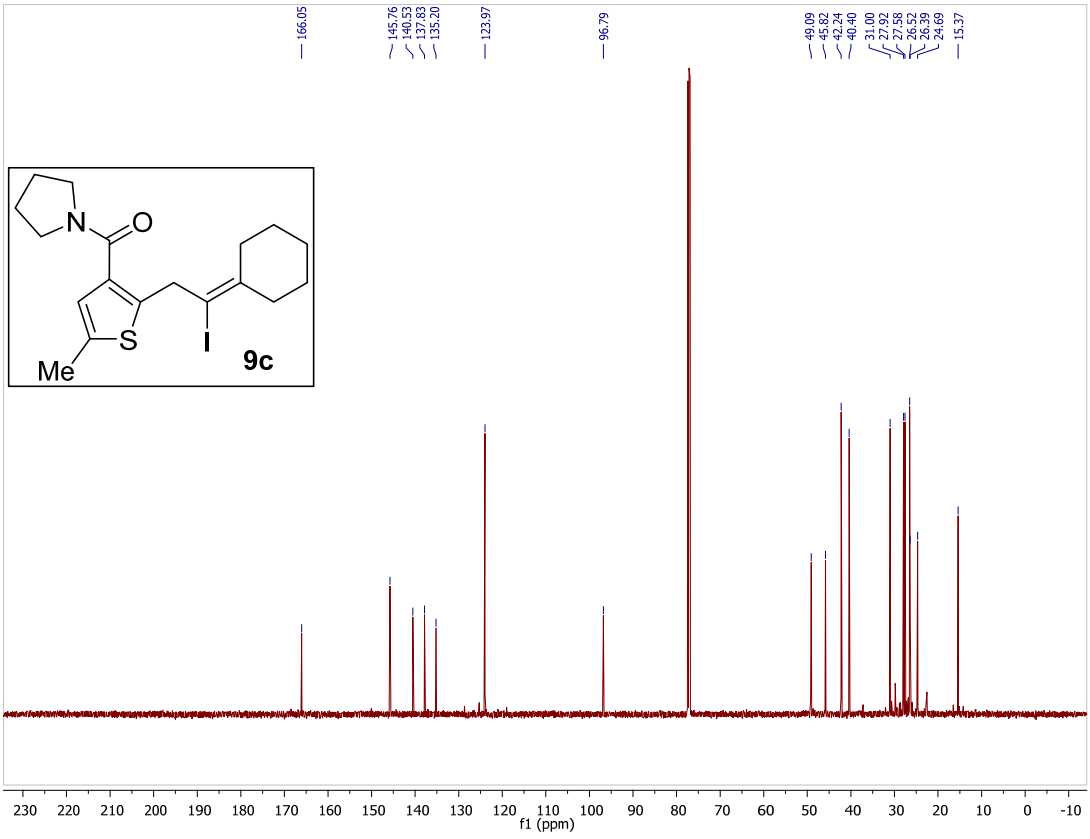
4.22
3.59
3.58
3.56
3.44
3.43
3.42
2.44
2.43
2.39
2.38
1.92
1.91
1.86
1.85
1.58
N
O
S
I
Me
9c
1.00
2.02
2.03
2.02
2.03
5.07
2.05
2.09
6.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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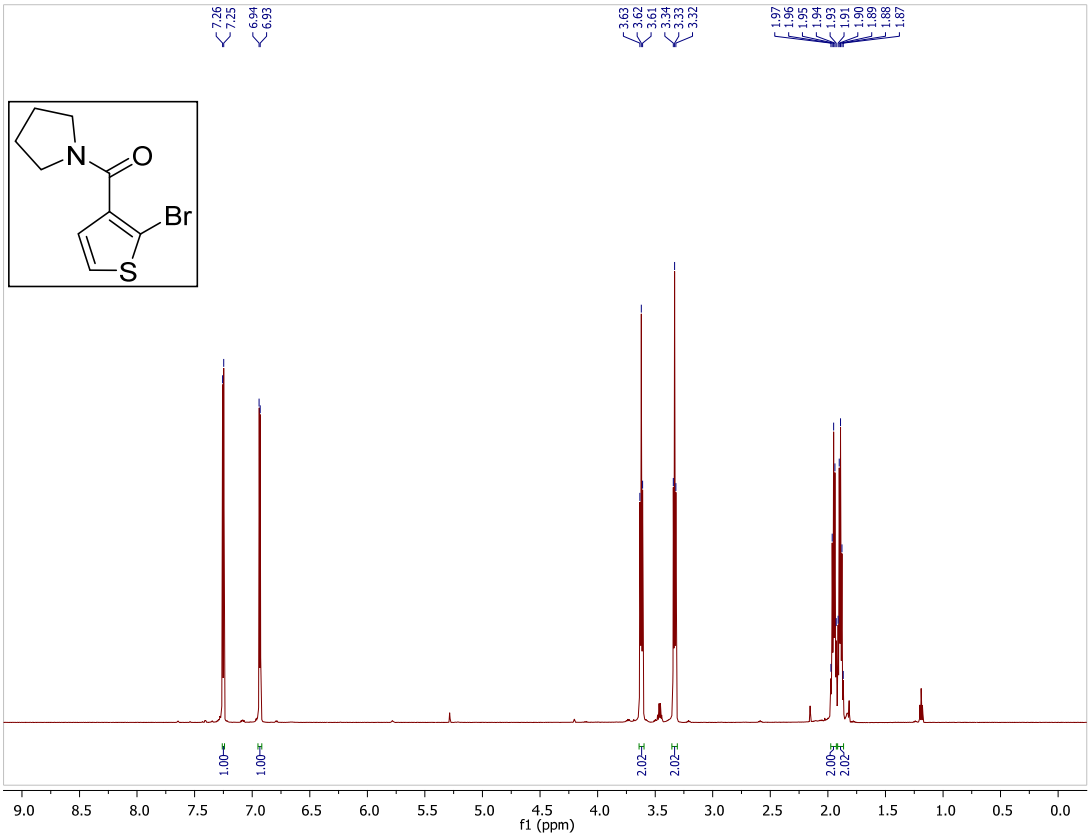
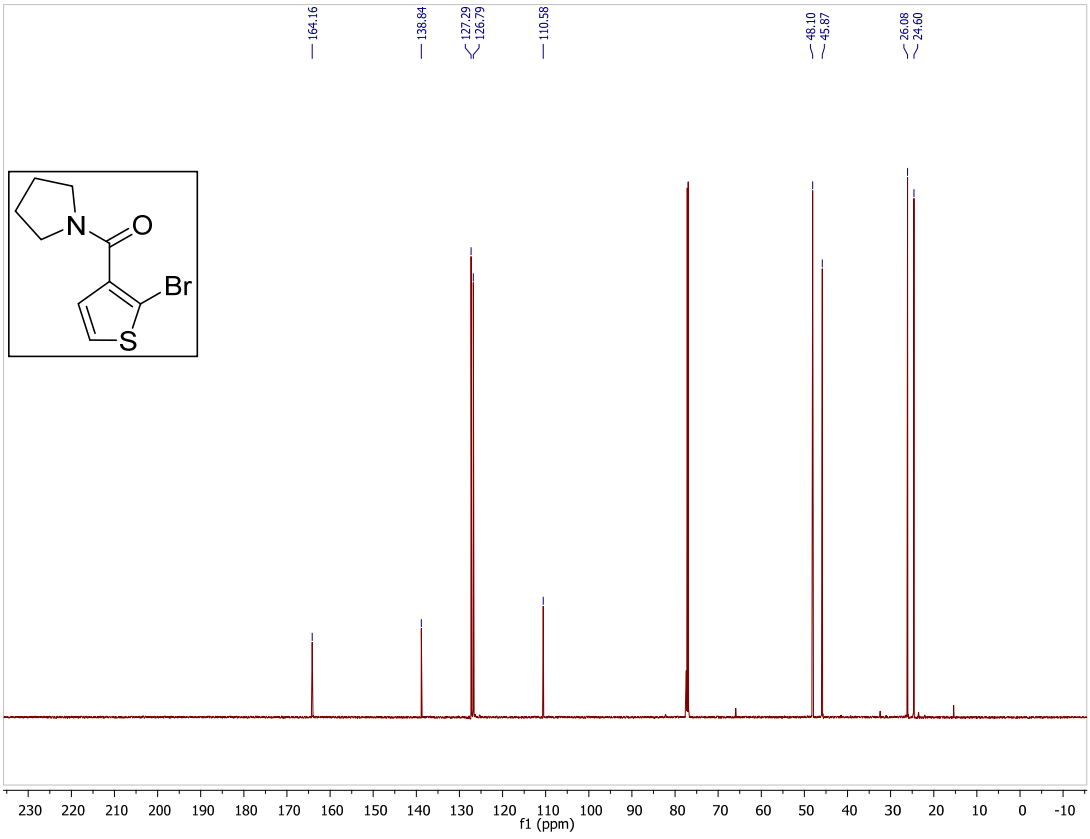
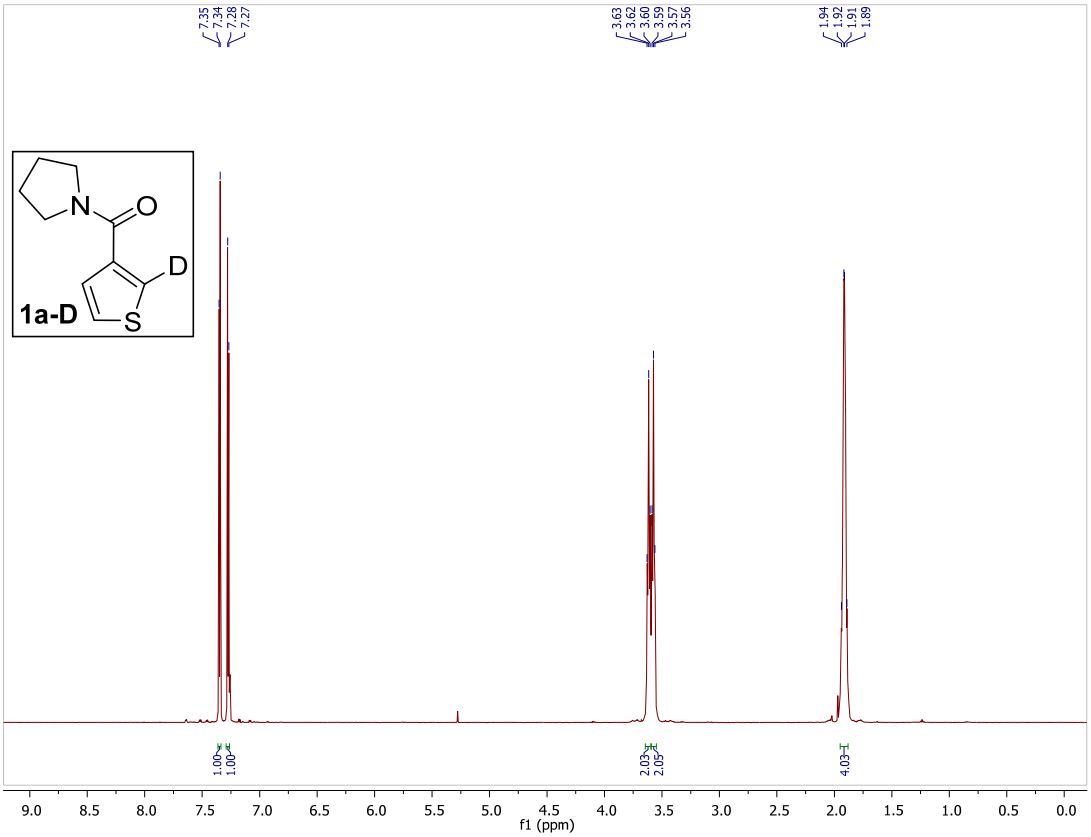
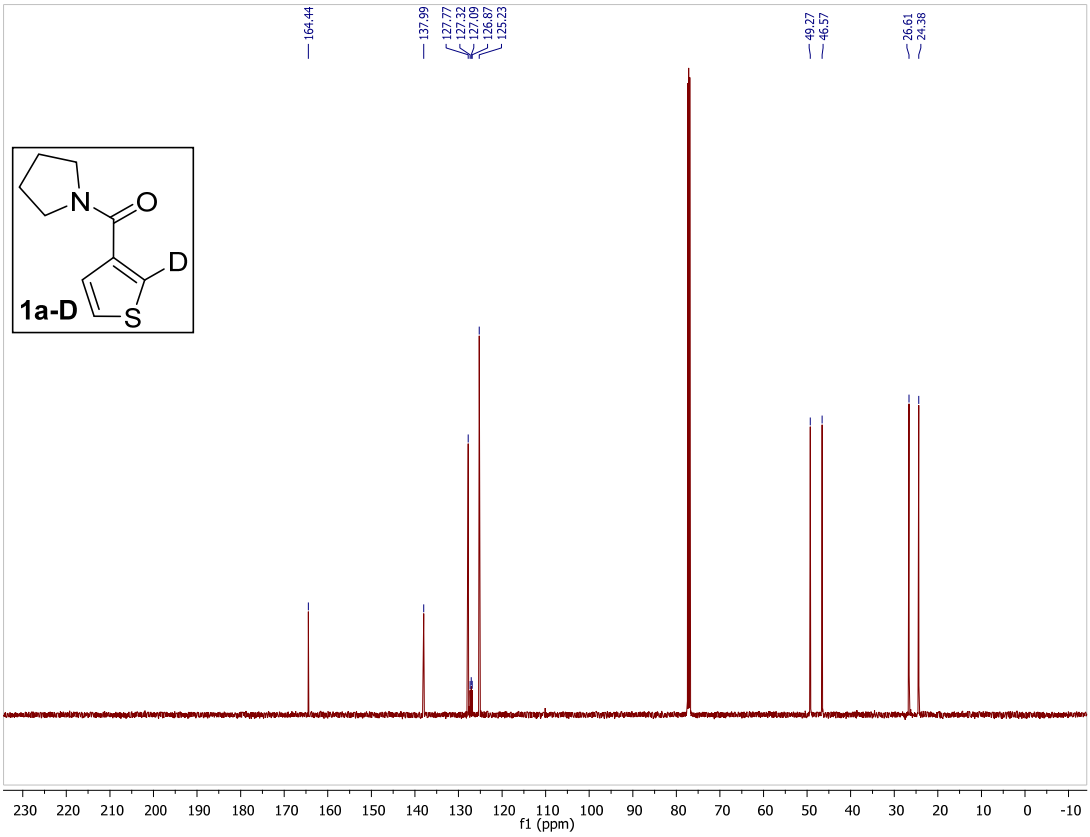
140.53
137.83
135.20
123.97
96.79
49.09
45.82
42.24
40.40
31.00
27.92
27.58
26.52
26.39
24.69
15.37
N
O
S
I
Me
9c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
7.25
6.94
6.93
3.63
3.62
3.61
3.34
3.33
3.32
1.97
1.96
1.95
1.94
1.93
1.91
1.90
1.89
1.88
1.87
N
O
Br
S
1.00
1.00
2.02
2.02
2.00
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.16
138.84
127.29
126.79
110.58
48.10
45.87
26.08
24.60
N
O
Br
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.35
7.34
7.28
7.27
3.63
3.62
3.60
3.59
3.57
3.56
1.94
1.92
1.91
1.89
N
O
D
S
1a-D
1.00
1.00
2.03
2.05
4.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.44
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127.32
127.09
126.87
125.23
49.27
46.57
26.61
24.38
N
O
D
S
1a-D
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)