

*Supporting information*

**Regio- and Stereoselective Cyanotriflation of Alkynes Using  
Aryl(cyano)iodonium Triflates**

Xi Wang, and Armido Studer\*

*Institute of Organic Chemistry, University of Münster, Corrensstrasse 40, 48149*

*Münster, Germany*

*E-mail: [studer@uni-muenster.de](mailto:studer@uni-muenster.de)*

**Table of Contents**

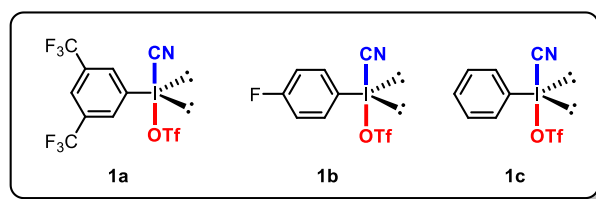
1. General .....	2
2. Preparation of starting materials.....	2
General procedure for the preparation of alkynes <b>3</b> from the corresponding aryl iodides or aryl bromides ( <b>GP1</b> ).....	4
3. Regio- and stereoselective cyanotriflation of alkynes using aryl(cyano)-iodonium triflates.....	18
General procedure for cyanotriflation of alkynes ( <b>GP2</b> ).....	18
Scale-up experiment .....	19
Screening of reaction conditions .....	35
Mechanistic study .....	36
4. Derivatization of vinyl triflates .....	38
5. Spectra .....	46
Spectra of alkynes <b>3</b> .....	46
Spectra of cyanotriflation products <b>2</b> .....	72
Spectra of products <b>4-11</b> in follow-up chemistry .....	125
6. References .....	138

## 1. General

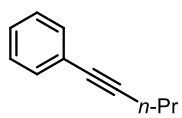
All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The alkynes were synthesized according to literature procedures. IR spectra were recorded on a *Digilab FTS 4000* with a *Specac MKII Golden Gate Single Reflexion ART System*.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a *DPX 300*, *AV 400* or *DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift:  $\text{CHCl}_3$  ( $\delta = 7.26$  for  $^1\text{H}$  NMR and  $\delta = 77.0$  for  $^{13}\text{C}$  NMR). TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of  $\text{KMnO}_4$  (1.5 g in 400 mL  $\text{H}_2\text{O}$ , 5 g  $\text{NaHCO}_3$ ), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63  $\mu\text{m}$ ) applying a pressure of about 0.2 bar. Mass spectra were recorded on a *Finnigan MAT 4200S*, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quattro LCZ* (ESI); peaks are given in  $m/z$  (% of basis peak).

## 2. Preparation of starting materials

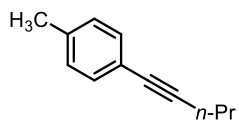
Aryl(cyano)iodonium triflates **1a**, **1b**, **1c** were prepared according to the previously reported literature procedures.<sup>[1]</sup>



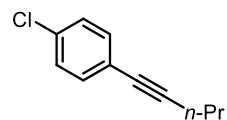
Alkyne **3a** is commercially available from Alfa Aesar and was used as received. Alkyne **3t** was prepared according to a previously reported literature procedure.<sup>[2]</sup>



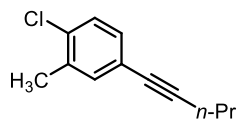
3a



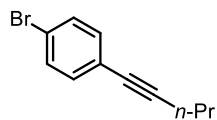
3b



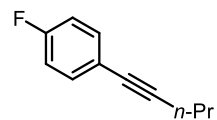
3c



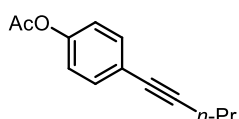
3d



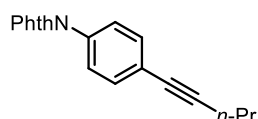
3e



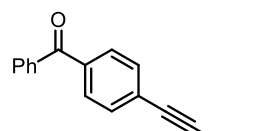
3f



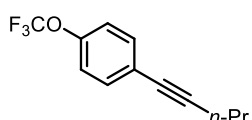
3g



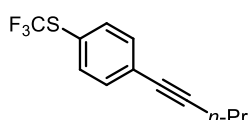
3h



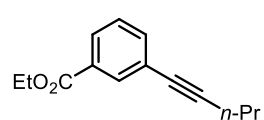
3i



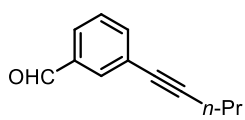
3j



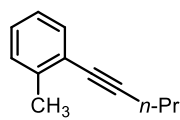
3k



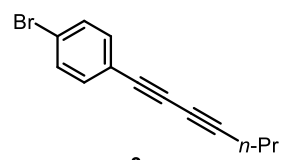
3l



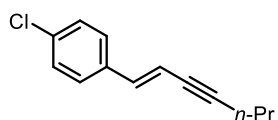
3m



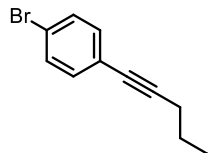
3n



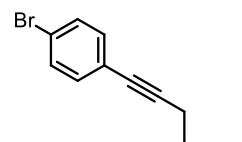
3o



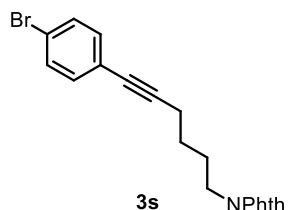
3p



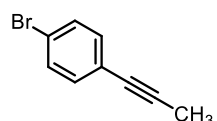
3q



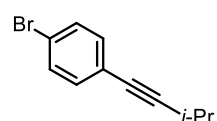
3r



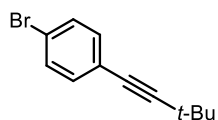
3s



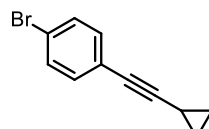
3t



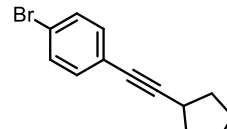
3u



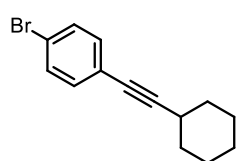
3v



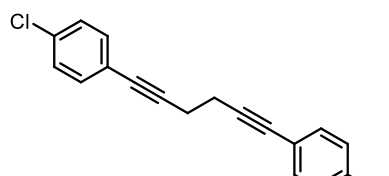
3w



3x

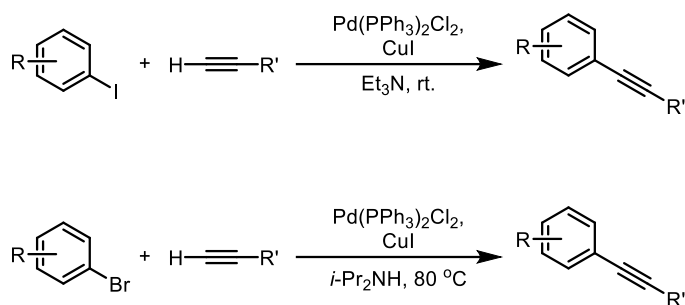


3y

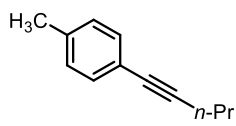


3z

**General procedure for the preparation of alkynes **3** from the corresponding aryl iodides or aryl bromides (GP1)**



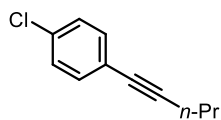
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride, copper(I) iodide, aryl iodide or aryl bromide, sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before triethylamine or diisopropylamine was added. The corresponding terminal alkyne was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature or 80 °C for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding pure alkynes **3**.



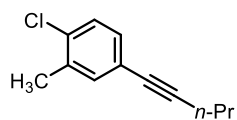
**1-Methyl-4-(pent-1-yn-1-yl)benzene (**3b**):** The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70.2 mg, 0.100 mmol, 1.0 mol%), CuI (38.1 mg, 0.200 mmol, 2.0 mol%), 1-iodo-4-methylbenzene (2.180 g, 10.00 mmol, 1.0 equiv), and pent-1-yne (0.817 g, 12.0 mmol, 1.2 equiv) in Et<sub>3</sub>N (10 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3b** as a yellow oil in 94% yield (1.482 g). **TLC** *R<sub>f</sub>* = 0.85 (Pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.21 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 1.55 (tq, *J*<sup>1</sup> = 7.2 Hz, *J*<sup>2</sup> = 7.2 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 137.4 (C), 131.4 (CH),



128.9 (CH), 121.0 (C), 89.4 (C), 80.7 (C), 22.3 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 21.3 (CH<sub>3</sub>), 13.5 (CH<sub>3</sub>); **EI-MS** (*m/z*, relative intensity): 158 (M<sup>+</sup>, 34), 143 (38), 129 (100), 128 (63), 115 (25), 102 (7), 91 (4), 74 (10), 77 (11), 63 (6), 51 (4); **IR** (neat, cm<sup>-1</sup>): 3029<sub>w</sub>, 2963<sub>m</sub>, 2933<sub>m</sub>, 2872<sub>w</sub>, 2233<sub>w</sub>, 1509<sub>s</sub>, 1460<sub>m</sub>, 1379<sub>w</sub>, 1338<sub>w</sub>, 1284<sub>w</sub>, 1180<sub>w</sub>, 1106<sub>w</sub>, 1040<sub>w</sub>, 945<sub>w</sub>, 816<sub>s</sub>.

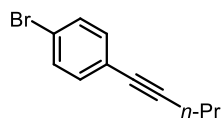


**1-Chloro-4-(pent-1-yn-1-yl)benzene (3c)**<sup>[3]</sup>: The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70.2 mg, 0.100 mmol, 1.0 mol%), CuI (38.1 mg, 0.200 mmol, 2.0 mol%), 1-chloro-4-iodobenzene (2.385 g, 10.00 mmol, 1.0 equiv), and pent-1-yne (0.817 g, 12.0 mmol, 1.2 equiv) in Et<sub>3</sub>N (10 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3c** as a light yellow oil in 86% yield (1.532 g). **TLC** R<sub>f</sub> = 0.85 (Pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.35 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.66 (tq, *J*<sup>1</sup> = 7.2 Hz, *J*<sup>2</sup> = 7.2 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 133.4 (C), 132.8 (CH), 128.5 (CH), 122.6 (C), 91.3 (C), 79.7 (C), 22.1 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>).

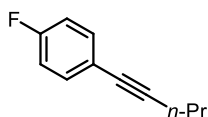


**1-Chloro-2-methyl-4-(pent-1-yn-1-yl)benzene (3d)**: The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (112.3 mg, 160.0 μmol, 2.0 mol%), CuI (61.0 mg, 320.0 μmol, 4.0 mol%), 4-bromo-1-chloro-2-methylbenzene (1.631 g, 8.000 mmol, 1.0 equiv), and pent-1-yne (1.306 g, 19.20 mmol, 2.4 equiv) in *i*-Pr<sub>2</sub>NH (15 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3d** as a light yellow solid in 61% yield (0.933 g). **TLC** R<sub>f</sub> = 0.85 (Pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.18 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.07 (dd, *J*<sup>1</sup> = 8.2 Hz, *J*<sup>2</sup> = 1.8 Hz, 1H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 1.55 (tq, *J*<sup>1</sup> = 7.2 Hz, *J*<sup>2</sup> = 7.2 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 135.9 (C), 133.9 (CH), 133.7 (C), 130.1 (CH), 128.9 (CH), 122.6 (C), 90.8 (C), 79.9 (C), 22.2 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 19.8 (CH<sub>3</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* =

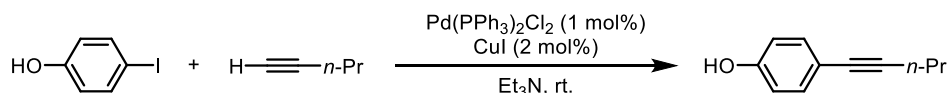
298.97512 calcd. for  $C_{12}H_{13}ClAg [M+Ag]^+$ , found: 298.97533; **IR** (neat,  $cm^{-1}$ ): 2963<sub>w</sub>, 2872<sub>m</sub>, 2230<sub>w</sub>, 1888<sub>w</sub>, 1761<sub>w</sub>, 1594<sub>w</sub>, 1478<sub>s</sub>, 1381<sub>w</sub>, 1338<sub>w</sub>, 1272<sub>w</sub>, 1180<sub>w</sub>, 1137<sub>w</sub>, 1051<sub>s</sub>, 883<sub>m</sub>, 819<sub>s</sub>, 773<sub>w</sub>, 705<sub>w</sub>.

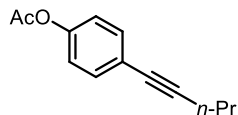
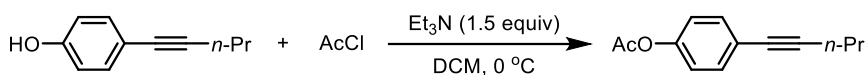


**1-Bromo-4-(pent-1-yn-1-yl)benzene (3e)**<sup>[4]</sup>: The title compound was prepared according to general procedure (**GP1**) with  $Pd(PPh_3)_2Cl_2$  (70.2 mg, 0.100 mmol, 1.0 mol%), CuI (38.1 mg, 0.200 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (8.490 g, 30.00 mmol, 3.0 equiv), and pent-1-yne (0.681 g, 10.0 mmol, 1.0 equiv) in  $Et_3N$  (10 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3e** as a light yellow oil in 75% yield (1.670 g). **TLC**  $R_f$  = 0.85 (Pentane);  **$^1H$  NMR** (300 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 7.33 (d,  $J$  = 8.5 Hz, 2H), 7.17 (d,  $J$  = 8.5 Hz, 2H), 2.29 (t,  $J$  = 7.0 Hz, 2H), 1.55 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.5 Hz, 2H), 0.97 (t,  $J$  = 7.4 Hz, 3H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 133.0 (CH), 131.4 (CH), 123.1 (C), 121.5 (C), 91.6 (C), 79.7 (C), 22.1 ( $CH_2$ ), 21.4 ( $CH_2$ ), 13.5 ( $CH_3$ ).



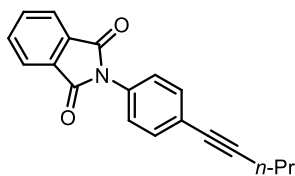
**1-Fluoro-4-(pent-1-yn-1-yl)benzene (3f)**<sup>[5]</sup>: The title compound was prepared according to general procedure (**GP1**) with  $Pd(PPh_3)_2Cl_2$  (56.2 mg, 80.0  $\mu$ mol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), 1-fluoro-4-iodobenzene (1.776 g, 8.000 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in  $Et_3N$  (8 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3f** as a light yellow oil in 92% yield (1.195 g). **TLC**  $R_f$  = 0.85 (Pentane);  **$^1H$  NMR** (300 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 7.32 – 7.27 (m, 2H), 6.90 (t,  $J$  = 8.6 Hz, 2H), 2.30 (t,  $J$  = 7.0 Hz, 2H), 1.55 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.2 Hz, 2H), 0.97 (t,  $J$  = 7.4 Hz, 3H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 162.0 (d,  $J$  = 248.0 Hz, CF), 133.3 (d,  $J$  = 8.2 Hz, CH), 120.2 (d,  $J$  = 3.5 Hz, C), 115.3 (d,  $J$  = 22.0 Hz, CH), 89.9 (C), 79.6 (C), 22.2 ( $CH_2$ ), 21.3 ( $CH_2$ ), 13.5 ( $CH_3$ );  **$^{19}F$  NMR** (282 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = -112.5 (s, 3F).





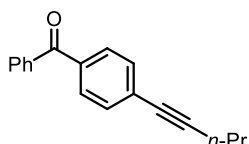
**4-(Pent-1-yn-1-yl)phenyl acetate (3g):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with

bis(triphenylphosphine)palladium(II) dichloride (70.2 mg, 0.100 mmol, 1.0 mol%) and copper(I) iodide (38.1 mg, 0.200 mmol, 2.0 mol%), 4-iodophenol (2.200 g, 10.00 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before Et<sub>3</sub>N (10 mL) was added. Pent-1-yne (0.820 g, 12.0 mmol, 1.2 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and filtrated through a pad of silica gel to remove most impurity. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was used in next step without further purification. Acetyl chloride (0.640 g, 8.13 mmol, 1.3 equiv) was slowly added to a solution of the crude 4-(pent-1-yn-1-yl)phenol (1.000 g, 6.250 mmol, 1.0 equiv), triethylamine (0.950 g, 9.38 mmol, 1.5 equiv) and in DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 6 h, before being diluted with hexanes (30 mL). The solid precipitates were filtered off and the filtrate obtained was concentrated under reduced pressure with the aid of a rotary evaporator. The crude residue was purified through silica gel flash column chromatography (Pentane:EtOAc = 12:1) to give pure **3g** as light yellow oil in 65% yield (0.818 g). **TLC** *R<sub>f</sub>* = 0.65 (Pentane:EtOAc = 4:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.32 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.20 (s, 3H), 1.55 (tq, *J*<sup>1</sup> = 7.2 Hz, *J*<sup>2</sup> = 7.2 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 169.1 (C), 149.8 (C), 132.6 (CH), 121.8 (C), 121.4 (CH), 90.3 (C), 79.9 (C), 22.1 (CH<sub>2</sub>), 21.3 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* = 225.0886 calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 225.0889; **IR** (neat, cm<sup>-1</sup>): 2964<sub>w</sub>, 2396<sub>w</sub>, 2238<sub>w</sub>, 1765<sub>s</sub>, 1601<sub>w</sub>, 1504<sub>s</sub>, 1369<sub>m</sub>, 1189<sub>s</sub>, 1098<sub>w</sub>, 1014<sub>m</sub>, 909<sub>s</sub>, 847<sub>s</sub>, 726<sub>w</sub>, 690<sub>w</sub>.



**2-(4-(Pent-1-yn-1-yl)phenyl)isoindoline-1,3-dione (3h):**

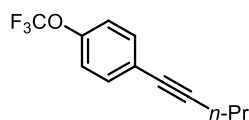
The title compound was prepared according to general procedure (GP1) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (112.4 mg, 0.1600 mmol, 2.0 mol%),  $\text{CuI}$  (61.0 mg, 0.320 mmol, 4.0 mol%), 2-(4-bromophenyl)isoindoline-1,3-dione (2.41 g, 8.0 mmol, 1.0 equiv), and pent-1-yne (1.308 g, 19.20 mmol, 2.4 equiv) in *i*-Pr<sub>2</sub>NH (16 mL) and THF (16 mL) at 80 °C for 24 hours. Purification via silica gel chromatography (Pentane:EtOAc = 16:1) gave the desired product **3h** as a gray solid in 58% yield (1.360 g). **TLC**  $R_f$  = 0.55 (Pentane:EtOAc = 4:1); **MP**: 119 °C, (decomp.); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.95 (dd,  $J^1$  = 5.5 Hz,  $J^2$  = 3.0 Hz, 2H), 7.78 (dd,  $J^1$  = 5.5 Hz,  $J^2$  = 3.1 Hz, 2H), 7.51 (d,  $J$  = 8.6 Hz, 2H), 7.39 (d,  $J$  = 8.7 Hz, 2H), 2.40 (t,  $J$  = 7.0 Hz, 2H), 1.64 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.2 Hz, 2H), 1.06 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) =  $\delta$  167.0 (C), 134.4 (CH), 132.2 (CH), 131.7 (C), 130.8 (C), 126.1 (CH), 124.0 (C), 123.7 (CH), 91.4 (C), 80.1 (C), 22.1 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI)  $m/z$  = 312.0995 calcd. for C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 312.1001; **IR** (neat, cm<sup>-1</sup>): 3052w, 2966w, 2240w, 1709s, 1610w, 1513s, 1465w, 1382s, 1285w, 1222s, 1177w, 1116m, 1080m, 948w, 883m, 834m, 790w, 714s, 667w.



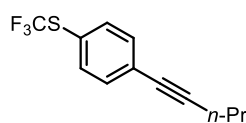
**(4-(Pent-1-yn-1-yl)phenyl)(phenyl)methanone (3i):** The title compound was prepared according to general procedure (GP1)

with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), (4-bromophenyl)(phenyl)methanone (2.09 g, 8.00 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in *i*-Pr<sub>2</sub>NH (10 mL) and at 80 °C for 24 hours. Purification via silica gel chromatography (Pentane:EtOAc = 200:1, then 50:1) gave the desired product **3i** as a yellow solid in 92% yield (1.836 g). **TLC**  $R_f$  = 0.55 (Pentane:EtOAc = 20:1); **MP**: 28 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.78 – 7.72 (m, 4H), 7.61 – 7.55 (m, 1H), 7.50 – 7.45 (m, 4H), 2.42 (t,  $J$  = 7.0 Hz, 2H), 1.66 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.2 Hz, 2H), 1.06 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 196.0 (C), 137.6 (C), 136.1 (C), 132.4 (CH), 131.4 (CH), 130.0 (CH), 129.9 (CH), 128.6 (CH), 128.3 (C), 93.9 (C), 80.3 (C), 22.0 (CH<sub>2</sub>),

21.5 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI)  $m/z$  = 271.1093 calcd. for C<sub>18</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup>, found: 271.1094; **IR** (neat, cm<sup>-1</sup>): 3058<sub>w</sub>, 2964<sub>w</sub>, 2361<sub>w</sub>, 2237<sub>w</sub>, 1659<sub>s</sub>, 1600<sub>s</sub>, 1447<sub>w</sub>, 1404<sub>w</sub>, 1276<sub>s</sub>, 1176<sub>w</sub>, 937<sub>w</sub>, 852<sub>w</sub>, 792<sub>w</sub>, 741<sub>w</sub>, 700<sub>m</sub>, 665<sub>w</sub>.

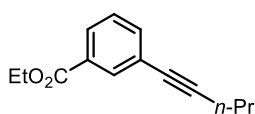


**1-(Pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene (3j):** The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (56.2 mg, 80.0 μmol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), 1-iodo-4-(trifluoromethoxy)benzene (2.304 g, 8.000 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in Et<sub>3</sub>N (8 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane:EtOAc = 200:1) gave the desired product **3j** as a light yellow oil in 81% yield (1.469 g). **TLC**  $R_f$  = 0.8 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.41 (d,  $J$  = 8.7 Hz, 2H), 7.13 (d,  $J$  = 8.7 Hz, 2H), 2.38 (t,  $J$  = 7.0 Hz, 2H), 1.63 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.2 Hz, 2H), 1.05 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 148.4 (C), 133.0 (CH), 123.0 (C), 120.6 (CH), 120.4 (q,  $J$  = 257.4 Hz, CF<sub>3</sub>), 91.3 (C), 79.4 (C), 22.1 (CH<sub>2</sub>), 21.3 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -57.9 (s, 3F); **EI-MS** ( $m/z$ , relative intensity) 228 (M<sup>+</sup>, 72), 199 (70), 143 (73), 133 (31), 128 (68), 127 (100), 115 (55), 102 (77), 69 (35); **IR** (neat, cm<sup>-1</sup>): 2967<sub>w</sub>, 2232<sub>w</sub>, 1507<sub>s</sub>, 1463<sub>w</sub>, 1255<sub>s</sub>, 1220<sub>s</sub>, 1166<sub>s</sub>, 1019<sub>w</sub>, 922<sub>w</sub>, 850<sub>m</sub>, 666<sub>w</sub>.



**(4-(Pent-1-yn-1-yl)phenyl)(trifluoromethyl)sulfane (3k):** The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (56.2 mg, 80.0 μmol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), (4-bromophenyl)(trifluoromethyl)sulfane (2.057 g, 8.0 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in *i*-Pr<sub>2</sub>NH (10 mL) at 80 °C for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3k** as a light yellow oil in 61% yield (1.191 g). **TLC**  $R_f$  = 0.7 (Pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.48 (d,  $J$  = 8.2 Hz, 2H), 7.34 (d,  $J$  = 8.4 Hz, 2H), 2.32 (t,  $J$  = 7.0 Hz, 2H), 1.56 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.2 Hz, 2H),

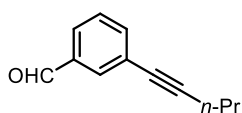
0.97 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 136.0 (CH), 132.4 (CH), 129.5 (q,  $J = 308.2$  Hz,  $\text{CF}_3$ ), 127.1 (C), 123.3 (q,  $J = 2.0$  Hz, C), 93.5 (C), 79.7 (C), 22.0 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_2$ ), 13.5 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -42.7 (s, 3F); **EI-MS** ( $m/z$ , relative intensity): 244 ( $\text{M}^+$ , 100), 215 (74), 146 (47), 128 (61), 115 (18), 102 (17), 89 (9), 69 (11), 45 (4), 39 (5); **IR** (neat,  $\text{cm}^{-1}$ ): 2967 $w$ , 2875 $w$ , 2238 $w$ , 1592 $w$ , 1491 $w$ , 1397 $w$ , 1339 $w$ , 1283 $w$ , 1115 $s$ , 1016 $w$ , 833 $m$ , 756 $w$ .



**Ethyl 3-(pent-1-yn-1-yl)benzoate (3l):** The title compound

was prepared according to general procedure (**GP1**) with

$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), ethyl 3-iodobenzoate (2.209 g, 8.000 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in  $\text{Et}_3\text{N}$  (8 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane:EtOAc = 100:1) gave the desired product **3l** as a light yellow oil in 95% yield (1.648 g). **TLC**  $R_f$  = 0.5 (Pentane:EtOAc = 20:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.99 (s, 1H), 7.86 (dd,  $J^1 = 7.8$  Hz,  $J^2 = 1.1$  Hz, 1H), 7.48 (dd,  $J^1 = 7.7$  Hz,  $J^2 = 1.0$  Hz, 1H), 7.27 (t,  $J = 7.8$  Hz, 1H), 4.30 (q,  $J = 7.1$  Hz, 2H), 2.32 (t,  $J = 7.0$  Hz, 2H), 1.57 (tq,  $J^1 = 7.2$  Hz,  $J^2 = 6.9$  Hz, 2H), 1.31 (t,  $J = 7.1$  Hz, 3H), 0.98 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 166.0 (C), 135.6 (CH), 132.6 (CH), 130.6 (C), 128.5 (CH), 128.2 (CH), 124.5 (C), 91.3 (C), 79.9 (C), 61.1 ( $\text{CH}_2$ ), 22.1 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_2$ ), 14.3 ( $\text{CH}_3$ ), 13.5 ( $\text{CH}_3$ ); **HRMS** (ESI)  $m/z$  = 239.1043 calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ , found: 239.1049; **IR** (neat,  $\text{cm}^{-1}$ ): 2965 $w$ , 2234 $w$ , 2065 $w$ , 1721 $s$ , 1602 $w$ , 1464 $w$ , 1368 $w$ , 1292 $s$ , 1224 $s$ , 1169 $w$ , 1105 $s$ , 1024 $m$ , 913 $w$ , 817 $w$ , 754 $s$ , 685 $w$ .

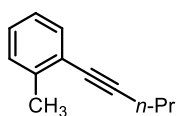


**3-(Pent-1-yn-1-yl)benzaldehyde (3m):** The title compound was

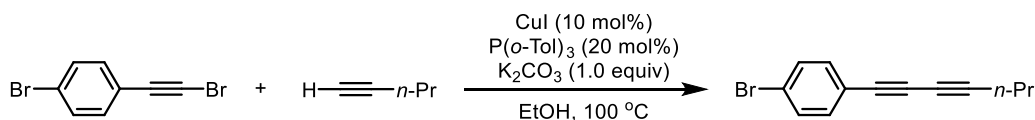
prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$

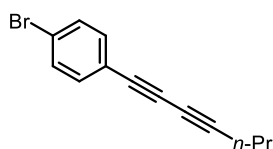
(112.3 mg, 160.0  $\mu\text{mol}$ , 2.0 mol%), CuI (61.0 mg, 320.0  $\mu\text{mol}$ , 4.0 mol%), 3-bromobenzaldehyde (1.48 g, 8.00 mmol, 1.0 equiv), and pent-1-yne (1.308 g, 19.20 mmol, 2.4 equiv) in  $i\text{-Pr}_2\text{NH}$  (8 mL) and at 80  $^\circ\text{C}$  for 24 hours. Purification via silica gel chromatography (Pentane:EtOAc = 200:1) gave the desired

product **3m** as a yellow oil in 69% yield (0.953 g). **TLC**  $R_f$  = 0.6 (Pentane:EtOAc = 20:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 9.90 (s, 1H), 7.81 (s, 1H), 7.69 (dt,  $J^1 = 7.7$  Hz,  $J^2 = 1.4$  Hz, 1H), 7.55 (dt,  $J^1 = 7.7$  Hz,  $J^2 = 1.4$  Hz, 1H), 7.37 (t,  $J = 7.7$  Hz, 1H), 2.33 (t,  $J = 7.0$  Hz, 2H), 1.57 (tq,  $J^1 = 7.2$  Hz,  $J^2 = 7.5$  Hz, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 191.7 (CH), 137.1 (CH), 136.4 (C), 132.9 (CH), 128.9 (C), 128.2 (CH), 125.3 (C), 92.1 (C), 79.4 (C), 22.0 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_2$ ), 13.5 ( $\text{CH}_3$ ); **HRMS** (ESI)  $m/z$  = 195.0780 calcd. for  $\text{C}_{12}\text{H}_{12}\text{ONa}$   $[\text{M}+\text{Na}]^+$ , found: 195.0783; **IR** (neat,  $\text{cm}^{-1}$ ): 2965w, 2873w, 2725w, 2232w, 1797w, 1700s, 1600w, 1434w, 1382w, 1284w, 1159w, 1031w, 1031w, 1031w, 1031w, 1031w, 910, 796, 757, 684, 649.

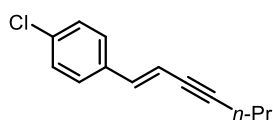
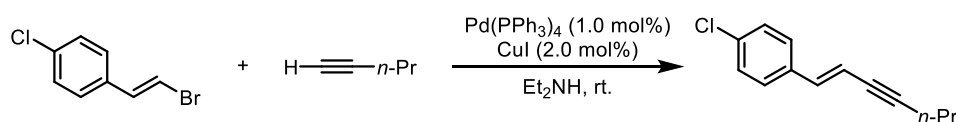


**1-Methyl-2-(pent-1-yn-1-yl)benzene (3n):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-iodo-2-methylbenzene (1.744 g, 8.000 mmol, 1.0 equiv), and pent-1-yne (0.654 g, 9.60 mmol, 1.2 equiv) in  $\text{Et}_3\text{N}$  (8 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3n** as a light yellow oil in 81% yield (1.023 g). **TLC**  $R_f$  = 0.8 (Pentane);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.42 (d,  $J = 7.2$  Hz, 1H), 7.22 – 7.20 (m, 2H), 7.19 – 7.12 (m, 1H), 2.48 (t,  $J = 6.9$  Hz, 2H), 2.47 (s, 3H), 1.70 (tq,  $J^1 = 7.2$  Hz,  $J^2 = 7.2$  Hz, 2H), 1.12 (t,  $J = 7.4$  Hz, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 139.9 (C), 131.8 (CH), 129.2 (CH), 127.4 (CH), 125.4 (CH), 123.9 (C), 94.2 (C), 79.6 (C), 22.4 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_2$ ), 20.7 ( $\text{CH}_3$ ), 13.5 ( $\text{CH}_3$ ); **EI-MS** ( $m/z$ , relative intensity): 158 ( $\text{M}^+$ , 29), 143 (25), 129 (86), 128 (100), 127 (33), 115 (31), 102 (10), 89 (4), 77 (10), 63 (5), 51 (4); **IR** (neat,  $\text{cm}^{-1}$ ): 3023w, 2964w, 2872w, 2233w, 1601w, 1457w, 1379s, 1338w, 1279w, 1115w, 1041w, 942w, 879s, 756s.





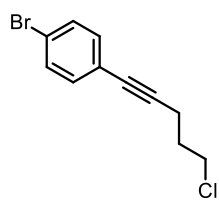
**1-Bromo-4-(hepta-1, 3-diyn-1-yl)benzene (3o)**<sup>[6]</sup>: A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with copper(I) iodide (95.2 mg, 0.500 mmol, 10 mol%), tri(*o*-tolyl)phosphine (30.4 mg, 1.00 mmol, 20 mol%), potassium carbonate (0.691 g, 5.00 mmol, 1.0 equiv), and 1-bromo-4-(bromoethynyl)benzene<sup>[7]</sup> (1.290 g, 5.000 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before anhydrous ethanol (20 mL) was added. Pent-1-yne (0.409 g, 6.00 mmol, 1.2 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at 100 °C for 24 hours. After the reaction was complete, the reaction mixture was diluted with EtOAc (50 mL) and filtrated through filtered through a pad of Celite. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane) to give pure 1,3-diyne **3o** as a white solid in 70% yield (0.858 g). **TLC**  $R_f$  = 0.8 (Pentane); **MP**: 85 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.35 (d,  $J$  = 8.6 Hz, 2H), 7.24 (d,  $J$  = 8.6 Hz, 2H), 2.26 (t,  $J$  = 7.0 Hz, 2H), 1.53 (tq,  $J^1$  = 7.2 Hz,  $J^2$  = 7.5 Hz, 2H), 0.95 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 133.8 (CH), 131.6 (CH), 123.1 (C), 121.1 (C), 85.4 (C), 75.6 (C), 73.5 (C), 65.1 (C), 21.7 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI)  $m/z$  = 254.90691 calcd. for C<sub>13</sub>H<sub>11</sub>BrAg [M+Ag]<sup>+</sup>, found: 354.90750; **IR** (neat, cm<sup>-1</sup>): 3086w, 2959m, 2867w, 2243w, 2156w, 1904w, 1647w, 1582w, 1473m, 1390m, 1346w, 1267m, 1096w, 1065m, 1007m, 907m, 820s, 732s, 650w.



**(E)-1-Chloro-4-(hept-1-en-3-yn-1-yl)benzene (3p)**<sup>[8]</sup>: A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (57.7 mg, 50.0  $\mu$ mol, 1.0 mol%), copper(I) iodide (19.0 mg, 0.100 mmol, 2.0 mol%),

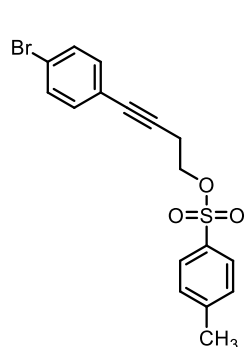


and (*E*)-1-(2-bromovinyl)-4-chlorobenzene<sup>[9]</sup> (1.080 g, 5.000 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before diethylamine (12 mL) was added. Pent-1-yne (0.409 g, 0.600 mmol, 1.2 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane) to give pure 1,3 enyne **3p** as a white solid in 56% yield (0.570 g). **TLC** *R<sub>f</sub>* = 0.7 (Pentane); **MP**: 32 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.28 (s, 4H), 6.81 (d, *J* = 16.2 Hz, 1H), 6.13 (dt, *J*<sup>1</sup> = 16.2 Hz, *J*<sup>2</sup> = 2.2 Hz, 1H), 2.35 (td, *J*<sup>1</sup> = 7.0, *J*<sup>2</sup> = 1.9 Hz, 2H), 1.68 – 1.51 (tq, *J*<sup>1</sup> = 7.2 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 138.6 (CH), 135.1 (C), 133.9 (C), 128.8 (CH), 127.2 (CH), 109.6 (CH), 93.5 (C), 79.6 (C), 22.2 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>), 13.5 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* = 310.97512 calcd. for C<sub>13</sub>H<sub>13</sub>ClAg [M+Ag]<sup>+</sup>, found: 310.97507; **IR** (neat, cm<sup>-1</sup>): 3033w, 2964m, 2872w, 2211w, 2159w, 1616w, 1490s, 1338w, 1277m, 1226m, 1178w, 1091s, 1012m, 954s, 852m, 806s, 745w, 682w.



**1-Bromo-4-(5-chloropent-1-yn-1-yl)benzene (3q):** The title compound was prepared according to general procedure (**GPI**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (56.2 mg, 80.0 μmol, 1.0 mol%), CuI (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.395 g, 12.00 mmol, 1.5 equiv), and 5-chloropent-1-yne (0.820 g, 8.00 mmol, 1.0 equiv) in Et<sub>3</sub>N (8 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3q** as a light yellow oil in 36% yield (0.732 g). **TLC** *R<sub>f</sub>* = 0.45 (Pentane); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.35 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.98 (p, *J* = 6.6 Hz, 2H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 133.1 (CH), 131.5 (CH), 122.6 (C), 121.9 (C), 89.4 (C), 80.5 (C), 43.7 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 16.9 (CH<sub>2</sub>); **EI-MS** (*m/z*, relative intensity): 258 (M+2<sup>+</sup>, 100), 256 (M<sup>+</sup>, 100), 220 (71), 193 (33), 162 (8),

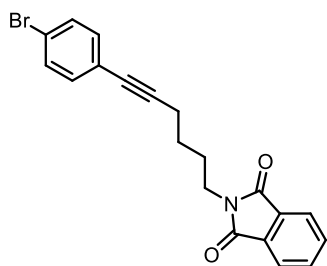
149 (10); **IR** (neat,  $\text{cm}^{-1}$ ): 2959 $w$ , 2230 $w$ , 1901 $w$ , 1646 $w$ , 1586 $w$ , 1485 $s$ , 1438 $w$ , 1394 $w$ , 1352 $w$ , 1290 $m$ , 1070 $s$ , 1010 $s$ , 969 $w$ , 823 $s$ , 785 $w$ , 723 $w$ , 656 $m$ .



**4-(4-Bromophenyl)but-3-yn-1-yl 4-methylbenzenesulfonate**

**(3r):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol, 1.5 equiv), and but-3-yn-1-yl 4-methylbenzenesulfonate (1.79 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (8

mL) at room temperature for 12 hours. Purification via silica gel chromatography gave the desired product **3r** as a light yellow solid in 51% yield (1.530 g). **TLC**  $R_f$  = 0.2 (Pentane:EtOAc = 10:1); **MP**: 65  $^\circ\text{C}$ ;  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.72 (d,  $J$  = 8.3 Hz, 2H), 7.31 (d,  $J$  = 8.5 Hz, 2H), 7.22 (d,  $J$  = 8.1 Hz, 2H), 7.09 (d,  $J$  = 8.5 Hz, 2H), 4.09 (t,  $J$  = 6.9 Hz, 2H), 2.67 (t,  $J$  = 6.9 Hz, 2H), 2.32 (s, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 144.9 (C), 133.0 (CH), 132.7 (C), 131.4 (CH), 129.8 (CH), 127.8 (CH), 122.2 (C), 121.8 (C), 85.2 (C), 81.5 (C), 67.5 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_3$ ), 20.3 ( $\text{CH}_2$ ); **HRMS** (ESI)  $m/z$  = 402.9797 calcd. for  $\text{C}_{17}\text{H}_{15}\text{BrO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 402.9790; **IR** (neat,  $\text{cm}^{-1}$ ): 2961 $w$ , 2178 $w$ , 1975 $w$ , 1598 $w$ , 1486 $m$ , 1361 $s$ , 1306 $w$ , 1176 $s$ , 1071 $w$ , 980 $s$ , 903 $m$ , 822 $s$ , 767 $m$ , 664 $m$ .

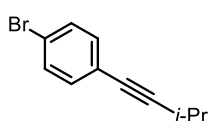


**2-(6-(4-Bromophenyl)hex-5-yn-1-yl)isoindoline-1,3-dione**

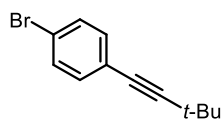
**(3s):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol,

1.5 equiv), and 2-(hex-5-yn-1-yl)isoindoline-1,3-dione (1.82 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography gave the desired product **3s** as a brown solid in 83% yield (2.530 g). **TLC**  $R_f$  = 0.5 (Pentane:EtOAc = 5:1); **MP**: 89  $^\circ\text{C}$ ;  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.76 (dt,  $J^1$  = 4.8,  $J^2$  = 3.6 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.32 (d,  $J$  = 7.9 Hz,

2H), 7.18 (dd,  $J^1 = 10.4$  Hz,  $J^2 = 4.4$  Hz, 2H), 3.68 (t,  $J = 6.9$  Hz, 2H), 2.38 (t,  $J = 6.9$  Hz, 2H), 1.84 – 1.75 (m, 2H), 1.59 (dd,  $J^1 = 15.1$ ,  $J^2 = 7.4$  Hz, 2H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 168.4 (C), 133.9 (CH), 133.0 (CH), 132.1 (C), 131.4 (CH), 123.2 (CH), 122.8 (C), 121.6 (C), 90.7 (C), 80.1 (C), 37.5 ( $\text{CH}_2$ ), 27.8 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_2$ ), 19.0 ( $\text{CH}_2$ ); **HRMS** (ESI)  $m/z = 404.0257$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{BrNO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ , found: 404.0246; **IR** (neat,  $\text{cm}^{-1}$ ): 2942w, 2237w, 1904w, 1771m, 1706s, 1615w, 1485w, 1436w, 1395s, 1188w, 1116w, 1037m, 921w, 825m, 718s.

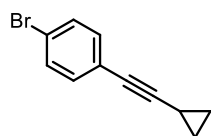


**1-Bromo-4-(3-methylbut-1-yn-1-yl)benzene (3u):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol, 1.5 equiv), and 3-methylbut-1-yne (0.545 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3u** as a yellow oil in 88% yield (1.562 g). **TLC**  $R_f = 0.75$  (Pentane);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.33 (d,  $J = 8.5$  Hz, 2H), 7.17 (d,  $J = 8.5$  Hz, 2H), 2.68 (hept,  $J = 6.9$  Hz, 1H), 1.18 (d,  $J = 6.9$  Hz, 6H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 133.0 (CH), 131.4 (CH), 123.0 (C), 121.5 (C), 97.0 (C), 78.8 (C), 22.9 ( $\text{CH}_3$ ), 21.1 (CH); **HRMS** (ESI)  $m/z = 360.89674$  calcd. for  $\text{C}_{11}\text{H}_{11}\text{BrAgO}_2$   $[\text{M}+\text{AgO}_2]^+$ , found: 360.89740; **IR** (neat,  $\text{cm}^{-1}$ ): 3091w, 2964w, 2925w, 2869w, 2227w, 1642w, 1424s, 1212s, 1132s, 1072m, 1000s, 837s, 762w, 735w, 686w, 655w.

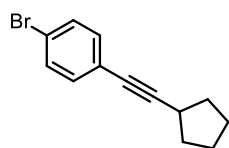


**1-Bromo-4-(3,3-dimethylbut-1-yn-1-yl)benzene (3v):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol, 1.5 equiv), and 3,3-dimethylbut-1-yne (0.657 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3v** as a white solid in 85% yield (1.617 g). **TLC**  $R_f = 0.75$  (Pentane); **MP**: 50  $^\circ\text{C}$ ;  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.32 (d,  $J = 8.6$  Hz, 2H),

7.16 (d,  $J = 8.6$  Hz, 2H), 1.23 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 133.0 (CH), 131.3 (CH), 123.1 (C), 121.4 (C), 99.7 (C), 78.09 (C), 30.9 ( $\text{CH}_3$ ), 28.0 (C); **EI-MS** ( $m/z$ , relative intensity): 236 ( $\text{M}^+$ , 24), 221 (47), 157 (14), 142 (100), 141 (75), 126 (22), 115 (44), 102 (18), 77 (17), 71 (16), 63 (12); **IR** (neat,  $\text{cm}^{-1}$ ): 2989s, 2236w, 1484s, 1392w, 1362m, 1291s, 1203w, 1071s, 1010s, 916w, 823s.

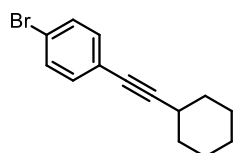


**1-Bromo-4-(cyclopropylethynyl)benzene (3w):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol, 1.5 equiv), and ethynylcyclopropane (0.53 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3w** as a white solid in 75% yield (1.314 g). **TLC**  $R_f = 0.7$  (Pentane); **MP**: 32  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.31 (d,  $J = 8.4$  Hz, 2H), 7.15 (d,  $J = 8.4$  Hz, 2H), 1.38 – 1.31 (m, 1H), 0.95 – 0.67 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 133.0 (CH), 131.4 (CH), 122.9 (C), 121.5 (C), 94.7 (C), 74.8 (C), 8.6 ( $\text{CH}_2$ ), 0.2 (CH); **EI-MS** ( $m/z$ , relative intensity): 220 ( $\text{M}^+$ , 18), 141 (48), 139 (19), 115 (100), 113 (39), 101 (5), 87 (16), 74 (10), 70 (12), 63 (21), 50 (8); **IR** (neat,  $\text{cm}^{-1}$ ): 3012w, 2233w, 1899w, 1782w, 1645w, 1587w, 1485s, 1393w, 1361w, 1179w, 1069s, 1028w, 953s, 822s.



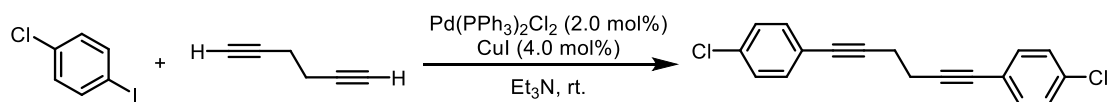
**1-Bromo-4-(cyclopentylethynyl)benzene (3x):** The title compound was prepared according to general procedure (**GP1**) with  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (56.2 mg, 80.0  $\mu\text{mol}$ , 1.0 mol%),  $\text{CuI}$  (30.5 mg, 0.160 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0 mmol, 1.5 equiv), and ethynylcyclopentane (0.753 g, 8.0 mmol, 1.0 equiv) in  $\text{Et}_3\text{N}$  (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3x** as a white solid in 84% yield (1.667 g). **TLC**  $R_f = 0.85$  (Pentane); **MP**: 29  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.32 (d,  $J = 8.5$  Hz, 2H), 7.17 (d,  $J = 8.5$  Hz, 2H), 2.73 (p,  $J = 7.5$  Hz, 1H), 1.97 – 1.86 (m, 2H), 1.77 – 1.51 (m,

6H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 133.0 (CH), 131.4 (CH), 123.2 (C), 121.4 (C), 95.9 (C), 79.1 (C), 33.8 (CH<sub>2</sub>), 30.8 (CH), 25.1 (CH<sub>2</sub>); **EI-MS** (*m/z*, relative intensity): 248 (M<sup>+</sup>, 32), 221 (13), 169 (25), 154 (19), 141 (100), 127 (22), 115 (17), 101 (11), 91 (11), 77 (10), 63 (12), 41 (10); **IR** (neat, cm<sup>-1</sup>): 2961<sub>s</sub>, 2870<sub>m</sub>, 2225<sub>w</sub>, 1911<sub>w</sub>, 1644<sub>w</sub>, 1486<sub>s</sub>, 1393<sub>w</sub>, 1341<sub>w</sub>, 1300<sub>w</sub>, 1071<sub>s</sub>, 1010<sub>s</sub>, 941<sub>w</sub>, 991<sub>w</sub>, 823<sub>s</sub>, 703<sub>w</sub>.



**1-Bromo-4-(cyclohexylethynyl)benzene (3y):** The title compound was prepared according to general procedure (**GP1**) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70.2 mg, 0.100 mmol, 1.0 mol%), CuI (38.1 mg, 0.200 mmol, 2.0 mol%), 1-bromo-4-iodobenzene (3.40 g, 12.0

mmol, 1.2 equiv), and ethynylcyclohexane (1.08 g, 10.0 mmol, 1.0 equiv) in Et<sub>3</sub>N (15 mL) at room temperature for 12 hours. Purification via silica gel chromatography (Pentane) gave the desired product **3y** as a light yellow solid in 95% yield (2.495 g). **TLC** R<sub>f</sub> = 0.85 (Pentane); **MP**: 62 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.32 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 2.49 (ddd, *J*<sup>1</sup> = 12.7 Hz, *J*<sup>2</sup> = 8.8 Hz, *J*<sup>3</sup> = 3.6 Hz, 1H), 1.81 – 1.77 (m, 2H), 1.67 (dd, *J*<sup>1</sup> = 8.9 Hz, *J*<sup>2</sup> = 3.7 Hz, 2H), 1.45 (dd, *J*<sup>1</sup> = 22.3 Hz, *J*<sup>2</sup> = 8.9 Hz, 3H), 1.27-1.21 (m, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 133.0 (CH), 131.3 (CH), 123.2 (C), 121.4 (C), 95.7 (C), 79.5 (C), 32.6 (CH<sub>2</sub>), 29.7 (CH), 25.9 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>); **EI-MS** (*m/z*, relative intensity): 264 (M+2<sup>+</sup>, 48), 262 (M<sup>+</sup>, 47), 221 (21), 183 (21), 154 (52), 141 (100), 127 (44), 115 (25), 77 (28), 41 (28); **IR** (neat, cm<sup>-1</sup>): 2929<sub>s</sub>, 2854<sub>s</sub>, 2230<sub>w</sub>, 1485<sub>s</sub>, 1448<sub>m</sub>, 1393<sub>w</sub>, 1359<sub>w</sub>, 1300<sub>w</sub>, 1257<sub>w</sub>, 1070<sub>s</sub>, 1011<sub>s</sub>, 952<sub>w</sub>, 888<sub>s</sub>, 745<sub>w</sub>.



**1,6-Bis(4-chlorophenyl)hexa-1,5-diyne (3z):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride

(180 mg, 0.256 mmol, 2.0 mol%) and copper(I) iodide (97.6 mg, 0.512 mmol, 4.0 mol%), 1-chloro-4-iodobenzene (7.332 g, 30.75 mmol, 2.4 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before triethylamine (24 mL) was added. 1,5-hexadiyne (50% in pentane) (1.000 g, 12.81 mmol, 1.0 equiv) was added to the resulting suspension subsequently. The reaction mixture was then stirred at room temperature for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane, then Pentane:EtOAc = 250:1) to give pure 1,5 diynes **3z** as a light yellow solid in 47% yield (1.802 g). **TLC** *R<sub>f</sub>* = 0.9 (Pentane); **MP**: 148 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.26 (d, *J* = 8.6 Hz, 4H), 7.18 (d, *J* = 8.7 Hz, 4H), 2.63 (s, 4H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 133.8 (C), 132.8 (CH), 128.5 (CH), 122.1 (C), 89.2 (C), 80.6 (C), 19.7 (CH<sub>2</sub>); **HRMS** (ESI) *m/z* = 404.93615 calcd. for C<sub>18</sub>H<sub>12</sub>Cl<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 404.93621; **IR** (neat, cm<sup>-1</sup>): 2916<sub>w</sub>, 2001<sub>w</sub>, 1912<sub>w</sub>, 1663<sub>w</sub>, 1591<sub>w</sub>, 1488<sub>s</sub>, 1438<sub>w</sub>, 1397<sub>w</sub>, 1274<sub>w</sub>, 1095<sub>s</sub>, 1015<sub>m</sub>, 830<sub>s</sub>, 744<sub>w</sub>.

### 3. Regio- and stereoselective cyanotriflation of alkynes using aryl(cyano)-iodonium triflates

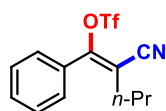
#### General procedure for cyanotriflation of alkynes (GP2)

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with iron(II) acetate (3.5 mg, 0.020 mmol, 10 mmol%) and 1,10-phenanthroline (3.6 mg, 0.020 mmol, 10 mmol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (1 mL) was added. The resulting suspension was stirred for 5 min at room temperature. The corresponding alkyne **3** (0.200 mmol, 1.0 equiv) and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 45 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary

evaporator. The crude residue was purified by silica gel column chromatography to afford pure cyanotriflated product **2**.

### Scale-up experiment

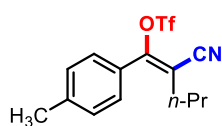
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with iron(II) acetate (87.0 mg, 0.500 mmol, 10 mmol%) and 1,10-phenanthroline (90.1 mg, 0.500 mmol, 10 mmol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (25 mL) was added. The resulting suspension was stirred for 5 min at room temperature. The corresponding alkyne 1-bromo-4-(pent-1-yn-1-yl)benzene **3e** (1.116 g, 5.000 mmol, 1.0 equiv) and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (5.664 g, 11.00 mmol, 2.2 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 45 °C for 24 hours. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography (Pentane:EtOAc = 200:1) to afford pure cyanotriflated product **2e** as a light yellow oil in 88% yield (1.741 g, dr>20:1); TLC  $R_f$  = 0.50 (Pentane:EtOAc = 20:1).



#### (Z)-2-Cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate (**2a**):

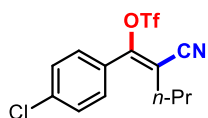
The title compound was prepared according to general procedure (GP2) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), pent-1-yn-1-ylbenzene **3a** (28.8 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography gave the desired product **2a** as a yellow oil in 40% yield (25.5 mg). TLC  $R_f$  = 0.50 (Pentane:EtOAc = 20:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.77 – 7.31 (m, 5H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.62 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 155.6 (C), 131.8 (CH), 129.8 (C), 129.0 (CH), 128.8 (CH), 118.1 (q, *J* = 320.9 Hz, CF<sub>3</sub>), 114.3 (C), 109.5 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.5

(s, 3F); **HRMS** (ESI)  $m/z$  = 342.0382, calcd. for  $C_{13}H_{12}F_3NO_3SNa$   $[M+Na]^+$ , found: 342.0385; **IR** (neat,  $cm^{-1}$ ): 2970 $w$ , 2878 $w$ , 2226 $w$ , 1644 $w$ , 1426 $s$ , 1216 $s$ , 1136 $s$ , 1093 $w$ , 1000 $m$ , 929 $w$ , 859 $w$ , 820 $m$ , 770 $w$ , 698 $w$ .



**(Z)-2-Cyano-1-(p-tolyl)pent-1-en-1-yl trifluoromethanesulfonate (2b):**

The title compound was prepared according to general procedure (**GP2**) with  $Fe(OAc)_2$  (3.5 mg, 20  $\mu$ mol, 10 mol%), **L1** (3.6 mg, 20  $\mu$ mol, 10 mol%), 1-methyl-4-(pent-1-yn-1-yl)benzene **3b** (31.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography gave the desired product **2b** as a light yellow oil in 41% yield (27.1 mg). **TLC**  $R_f$  = 0.50 (Pentane:EtOAc = 20:1);  **$^1H$  NMR** (300 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 7.23 (m, 4H), 2.34 (s, 3H), 2.23 (t,  $J$  = 7.5 Hz, 2H), 1.60 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.5 Hz, 2H), 0.85 (t,  $J$  = 7.4 Hz, 3H);  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 155.9 (C), 142.6 (C), 129.7 (CH), 128.7 (CH), 126.9 (C), 118.1 (q,  $J$  = 320.9 Hz,  $CF_3$ ), 114.5 (C), 108.7 (C), 31.4 ( $CH_2$ ), 21.5 ( $CH_3$ ), 21.4 ( $CH_2$ ), 13.1 ( $CH_3$ );  **$^{19}F$  NMR** (282 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = -73.6 (s, 3F); **HRMS** (ESI)  $m/z$  = 356.0539, calcd. for  $C_{14}H_{14}F_3NO_3SNa$   $[M+Na]^+$ , found: 356.0552; **IR** (neat,  $cm^{-1}$ ): 2969 $w$ , 2257 $w$ , 2227 $w$ , 1644 $w$ , 1426 $w$ , 1218 $m$ , 1136 $m$ , 1092 $w$ , 997 $m$ , 905 $s$ , 830 $w$ , 725 $s$ , 649 $w$ , 607 $w$ .

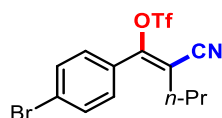


**(Z)-1-(4-Chlorophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate (2c):**

The title compound was prepared according to general procedure (**GP2**) with  $Fe(OAc)_2$  (3.5 mg, 20  $\mu$ mol, 10 mol%), **L1** (3.6 mg, 20  $\mu$ mol, 10 mol%), 1-chloro-4-(pent-1-yn-1-yl)benzene **3c** (35.7 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2c** as a light yellow oil in 81% yield (57.1 mg). **TLC**  $R_f$  = 0.35 (Pentane:EtOAc = 20:1);  **$^1H$  NMR** (300 MHz,  $CDCl_3$ , 300 K):  $\delta$  (ppm) = 7.41 (d,  $J$  = 8.6 Hz, 2H), 7.31 (d,  $J$  = 8.7 Hz, 2H), 2.21 (t,  $J$  = 7.5 Hz, 2H), 1.60 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.5 Hz, 2H), 0.86 (t,  $J$  = 7.4

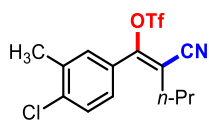


Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 154.3 (C), 138.3 (C), 130.1 (CH), 129.5 (CH), 128.1 (C), 118.1 (q,  $J$  = 320.9 Hz,  $\text{CF}_3$ ), 114.0 (C), 110.1 (C), 31.4 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_2$ ), 13.1 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); HRMS (ESI)  $m/z$  = 375.9992, calcd. for  $\text{C}_{13}\text{H}_{11}\text{ClF}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 375.9990; IR (neat,  $\text{cm}^{-1}$ ): 2969w, 2938w, 2878w, 2227w, 1644w, 1594w, 1489w, 1425s, 1346w, 1211s, 1133s, 1093s, 997s, 914w, 838s, 811s, 763w, 739s, 686w.



**(Z)-1-(4-Chloro-3-methylphenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate (2d)**

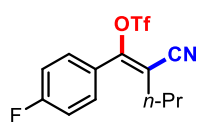
**fluoromethanesulfonate (2d):** The title compound was prepared according to general procedure (GP2) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-chloro-2-methyl-4-(pent-1-yn-1-yl)benzene **3d** (38.4 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45  $^\circ\text{C}$  for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 400:1) gave the desired product **2d** as a slight yellow oil in 76% yield (55.7 mg). TLC  $R_f$  = 0.5 (Pentane:EtOAc = 20:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.40 (d,  $J$  = 8.3 Hz, 1H), 7.23 (d,  $J$  = 1.7 Hz, 1H), 7.14 (dd,  $J^1$  = 8.3 Hz,  $J^2$  = 1.9 Hz, 1H), 2.36 (s, 1H), 2.27 – 2.15 (t,  $J$  = 7.5 Hz, 2H), 1.61 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.2 Hz, 2H), 0.87 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 154.6 (C), 138.4 (C), 137.5 (C), 131.0 (CH), 129.9 (CH), 128.2 (C), 127.5 (CH), 118.1 (q,  $J$  = 321.0 Hz,  $\text{CF}_3$ ), 114.1 (C), 109.7 (C), 31.4 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_2$ ), 20.1 ( $\text{CH}_3$ ), 13.2 ( $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); HRMS (ESI)  $m/z$  = 390.0149 calcd. for  $\text{C}_{14}\text{H}_{13}\text{ClF}_3\text{NNaO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 390.0148; IR (neat,  $\text{cm}^{-1}$ ): 2969w, 2878w, 2227w, 1643w, 1596w, 1426s, 1300w, 1214s, 1135s, 1094w, 1054m, 1021m, 946w, 894m, 817m, 764w, 690w.



**(Z)-1-(4-Bromophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate (2e)**

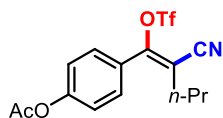
**sulfonate (2e):** The title compound was prepared according to general procedure (GP2) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-bromo-4-(pent-1-yn-1-yl)benzene **3e** (44.4 mg,

0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2e** as a colorless oil in 90% yield (71.1 mg). **TLC**  $R_f$  = 0.35 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.58 (d,  $J$  = 8.3 Hz, 2H), 7.24 (d,  $J$  = 8.3 Hz, 2H), 2.21 (t,  $J$  = 7.5 Hz, 2H), 1.61 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.4 Hz, 2H), 0.86 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 154.4 (C), 132.5 (CH), 130.4 (CH), 128.6 (C), 126.7 (C), 118.1 (q,  $J$  = 321.0 Hz, CF<sub>3</sub>), 114.0 (C), 110.1 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.1 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); **HRMS** (ESI)  $m/z$  = 419.9487 calcd. for C<sub>13</sub>H<sub>11</sub>BrF<sub>3</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup>, found: 419.9499; **IR** (neat, cm<sup>-1</sup>): 2968w, 2226w, 1642w, 1588w, 1425s, 1211s, 1133s, 1073m, 996s, 836s, 763w, 685w.



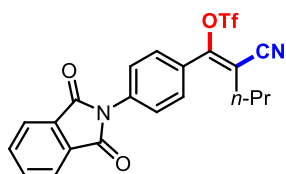
**(Z)-2-Cyano-1-(4-fluorophenyl)pent-1-en-1-yl trifluoromethanesulfonate (2f):** The title compound was prepared according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20  $\mu$ mol, 10 mol%),

**L1** (3.6 mg, 20  $\mu$ mol, 10 mol%), 1-fluoro-4-(pent-1-yn-1-yl)benzene **3f** (32.4 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1, then 200:1) gave the desired product **2f** as a colorless oil in 50% yield (33.7 mg). **TLC**  $R_f$  = 0.3 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.41 – 7.36 (m, 2H), 7.19 – 7.10 (m, 2H), 2.21 (t,  $J$  = 7.5 Hz, 2H), 1.61 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.5 Hz, 2H), 0.87 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 164.4 (d,  $J$  = 254.8 Hz, C), 154.5 (C), 131.2 (d,  $J$  = 9.0 Hz, CH), 125.9 (d,  $J$  = 3.7 Hz, C), 118.1 (q,  $J$  = 321.1 Hz, CF<sub>3</sub>), 116.5 (d,  $J$  = 22.3 Hz, CH), 114.1 (C), 109.8 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = -73.5 (s, 3F), -105.7 (s, 1F); **HRMS** (ESI)  $m/z$  = 360.0288 calcd. for C<sub>13</sub>H<sub>11</sub>F<sub>4</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup>, found: 360.0294; **IR** (neat, cm<sup>-1</sup>): 2970w, 2879w, 2227w, 1646w, 1603m, 1508m, 1425s, 1212s, 1135w, 1092m, 999s, 847s, 813s, 764w, 690w.



**(Z)-4-(2-Cyano-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl) phenyl acetate (2g):**

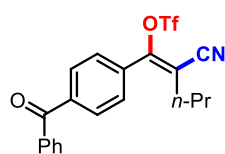
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 4-(pent-1-yn-1-yl)phenyl acetate **3g** (40.4 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 30:1, then 25:1) gave the desired product **2g** as a colorless oil in 54% yield (40.6 mg). **TLC**  $R_f$  = 0.3 (Pentane:EtOAc = 5:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.39 (d,  $J$  = 8.6 Hz, 2H), 7.19 (d,  $J$  = 8.6 Hz, 2H), 2.26 (s, 3H), 2.25 (t,  $J$  = 8.1 Hz, 2H) 1.62 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.2 Hz, 2H), 0.87 (t,  $J$  = 7.3 Hz, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 168.6 (C), 154.6 (C), 153.1 (C), 130.2 (CH), 127.1 (C), 122.4 (CH), 118.1 (q,  $J$  = 321.0 Hz,  $\text{CF}_3$ ), 114.2 (C), 109.8 (C), 31.4 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_2$ ), 21.1 ( $\text{CH}_3$ ), 13.2 ( $\text{CH}_3$ );  **$^{19}\text{F}$  NMR** (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); **HRMS** (ESI)  $m/z$  = 400.0437 calcd. for  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{NO}_5\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ , found: 400.0438; **IR** (neat,  $\text{cm}^{-1}$ ): 2969w, 2226w, 1772s, 1642w, 1603w, 1505w, 1425s, 1371m, 1195s, 1135m, 1092w, 998s, 911m, 852m, 818m, 764w, 679w.



**(Z)-2-Cyano-1-(4-(1,3-dioxoisindolin-2-yl)phenyl)pent-1-en-1-yl trifluoromethanesulfonate (2h):**

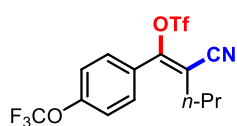
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 2-(4-(pent-1-yn-1-yl)phenyl)isoindoline-1,3-dione **3h** (57.8 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 20:1, the 12:1) gave the desired product **2h** as a colorless oil in 71% yield (65.5 mg). **TLC**  $R_f$  = 0.35 (Pentane:EtOAc = 4:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.91 (dd,  $J^1$  = 5.3 Hz,  $J^2$  = 3.1 Hz, 2H), 7.76 (dd,  $J^1$  = 5.5 Hz,  $J^2$  = 3.0 Hz, 2H), 7.64 (d,  $J$  = 8.5 Hz, 2H), 7.51 (d,  $J$  = 8.4 Hz, 2H), 2.29 (t,  $J$  = 7.5 Hz, 2H), 1.64 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.2 Hz, 2H), 0.89 (t,  $J$  = 7.3 Hz,

3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 166.6 (C), 154.5 (C), 135.1 (C), 134.8 (CH), 131.4 (C), 129.5 (CH), 128.6 (C), 126.2 (CH), 124.0 (CH), 114.2 (C), 118.2 (q, *J* = 319.0 Hz, CF<sub>3</sub>), 110.2 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.3 (s, 3F); **HRMS** (APCI) *m/z* = 487.0546 calcd. for C<sub>21</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>5</sub>SSNa [M+Na]<sup>+</sup>, found: 487.0555; **IR** (neat, cm<sup>-1</sup>): 3074<sub>w</sub>, 2968<sub>w</sub>, 2871<sub>w</sub>, 2225<sub>w</sub>, 1716<sub>s</sub>, 1605<sub>w</sub>, 1512<sub>m</sub>, 1423<sub>s</sub>, 1367<sub>s</sub>, 1212<sub>s</sub>, 1133<sub>s</sub>, 1078<sub>s</sub>, 998<sub>s</sub>, 840<sub>s</sub>.



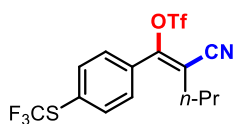
**(Z)-1-(4-Benzoylphenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate (2i):** The title compound was prepared according to general procedure (GP2) with Fe(OAc)<sub>2</sub> (3.5 mg, 20

μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), (4-(pent-1-yn-1-yl)phenyl)(phenyl)methanone **3i** (49.7 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Then further portions of Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv), and DCE (1 mL) were added. The stirring was continued at 45 °C for further 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 150:1, then 80:1) gave the desired product **2i** as a light yellow oil in 37% yield (31.1 mg). **TLC** *R<sub>f</sub>* = 0.20 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.84 (d, *J* = 8.5 Hz, 2H), 7.74 – 7.71 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.64 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 195.2 (C), 154.3 (C), 140.3 (C), 136.6 (C), 133.1 (CH), 130.3 (CH), 130.0 (CH), 128.8 (CH), 128.6 (CH), 118.1 (q, *J* = 319.1 Hz, CF<sub>3</sub>), 114.0 (C), 110.8 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.3 (s, 3F); **HRMS** (ESI) *m/z* = 446.0644, calcd. for C<sub>20</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>4</sub>SSNa [M+Na]<sup>+</sup>, found: 446.0646; **IR** (neat, cm<sup>-1</sup>): 3065<sub>w</sub>, 2969<sub>w</sub>, 2877<sub>w</sub>, 2226<sub>w</sub>, 1662<sub>m</sub>, 1600<sub>w</sub>, 1426<sub>s</sub>, 1276<sub>s</sub>, 1212<sub>s</sub>, 1134<sub>s</sub>, 1092<sub>w</sub>, 1000<sub>s</sub>, 924<sub>w</sub>, 857<sub>s</sub>, 816<sub>s</sub>, 701<sub>s</sub>, 654<sub>s</sub>.



**(Z)-2-Cyano-1-(4-(trifluoromethoxy)phenyl)pent-1-en-1-yl trifluoromethanesulfonate (2j):** The title compound was prepared

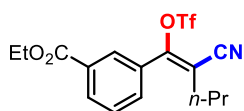
according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-(pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene **3j** (45.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2j** as a colorless oil in 89% yield (71.7 mg). **TLC**  $R_f$  = 0.3 (Pentane:EtOAc = 20:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.43 (d,  $J$  = 8.6 Hz, 2H), 7.27 (d,  $J$  = 8.5 Hz, 2H), 2.22 (t,  $J$  = 7.7 Hz, 2H), 1.62 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.5 Hz, 2H), 0.88 (t,  $J$  = 7.4 Hz, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 154.0 (C), 151.5 (C), 130.8 (CH), 128.1 (C), 121.0 (CH), 120.3 (q,  $J$  = 259.0 Hz,  $\text{OCF}_3$ ), 118.1 (q,  $J$  = 321.0 Hz,  $\text{CF}_3$ ), 114.0 (C), 110.5 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>);  **$^{19}\text{F}$  NMR** (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -57.8 (s, 3F), -73.4 (s, 3F); **HRMS** (ESI)  $m/z$  = 426.0205 calcd. for  $\text{C}_{14}\text{H}_{11}\text{F}_6\text{NO}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 426.0211; **IR** (neat,  $\text{cm}^{-1}$ ): 2935 $w$ , 2227 $w$ , 1644 $w$ , 1607 $w$ , 1427 $s$ , 1206 $s$ , 1169 $s$ , 1133 $s$ , 1000 $s$ , 915 $w$ , 853 $s$ , 815 $s$ , 764 $m$ , 659 $w$ .



**(Z)-2-Cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate (2k):** The title compound was

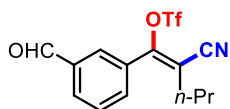
prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), (4-(pent-1-yn-1-yl)phenyl)(trifluoromethyl)sulfane **3k** (48.9 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Then further portions of  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv), and DCE (1 mL) were added. The stirring was continued at 45 °C for further 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 250:1) gave the desired product **2k** as a light yellow oil in 61% yield (51.2 mg). **TLC**  $R_f$  = 0.25 (Pentane:EtOAc

= 40:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.71 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 2.24 (t, *J* = 7.7 Hz, 2H), 1.64 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 153.9 (C), 136.0 (CH), 132.0 (C), 129.7 (CH), 129.2 (C), 129.2 (q, *J* = 308.6 Hz, SCF<sub>3</sub>), 118.1 (q, *J* = 321.0 Hz, CF<sub>3</sub>), 113.9 (C), 111.1 (C), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -41.7 (s, 3F), -73.3 (s, 3F); **HRMS** (ESI) *m/z* = 441.9977 calcd. for C<sub>14</sub>H<sub>11</sub>F<sub>6</sub>NO<sub>3</sub>S<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 441.9971; **IR** (neat, cm<sup>-1</sup>): 2970<sub>w</sub>, 2228<sub>w</sub>, 1644<sub>s</sub>, 1427<sub>s</sub>, 1215<sub>s</sub>, 1113<sub>s</sub>, 1000<sub>s</sub>, 843<sub>s</sub>, 811<sub>s</sub>, 758<sub>m</sub>, 688<sub>w</sub>.



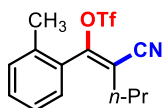
**(Z)-2-Cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate (2l):** The title compound was

prepared according to general procedure (GP2) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 1-(pent-1-yn-1-yl)- ethyl 3-(pent-1-yn-1-yl)benzoate **3l** (43.3 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 100:1, then 60:1) gave the desired product **2l** as a colorless oil in 48% yield (37.6 mg). **TLC** *R<sub>f</sub>* = 0.4 (Pentane:EtOAc = 10:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 8.15 (d, *J* = 6.9 Hz, 1H), 8.05 (s, 1H), 7.64 – 7.51 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.64 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 165.0 (C), 154.4 (C), 132.7 (CH), 132.6 (CH), 131.6 (C), 130.1 (C), 129.9 (CH), 129.3 (CH), 118.1 (q, *J* = 320.9 Hz, CF<sub>3</sub>), 114.1 (C), 110.5 (C), 61.7 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.3 (s, 3F); **HRMS** (ESI) *m/z* = 414.0593 calcd. for C<sub>16</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>5</sub>SNa [M+Na]<sup>+</sup>, found: 414.0599; **IR** (neat, cm<sup>-1</sup>): 2924<sub>w</sub>, 2227<sub>w</sub>, 1723<sub>s</sub>, 1645<sub>w</sub>, 1427<sub>s</sub>, 1370<sub>w</sub>, 1302<sub>m</sub>, 1221<sub>s</sub>, 1135<sub>s</sub>, 1012<sub>m</sub>, 894<sub>w</sub>, 824<sub>m</sub>, 763<sub>w</sub>, 727<sub>w</sub>, 684<sub>w</sub>.



**(Z)-2-Cyano-1-(3-formylphenyl)pent-1-en-1-yl trifluoromethanesulfonate (2m):** The title compound was prepared

according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 3-(pent-1-yn-1-yl)benzaldehyde **3m** (34.5 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 35:1, then 20:1) gave the desired product **2m** as a light yellow oil in 13% yield (9.0 mg). **TLC** *R*<sub>f</sub> = 0.25 (Pentane:EtOAc = 7:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 10.00 (s, 1H), 8.01 – 7.98 (m, 1H), 7.88 (s, 1H), 7.65 – 7.64 (m, 2H), 2.24 (t, *J* = 7.9 Hz, 2H), 1.64 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 190.4 (CH), 153.9 (C), 136.9 (C), 134.1 (CH), 132.7 (CH), 131.0 (C), 130.0 (CH), 129.6 (CH), 118.1 (q, *J* = 321.1 Hz, CF<sub>3</sub>), 113.9 (C), 110.9 (C), 31.5 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.3 (s, 3F); **HRMS** (ESI) *m/z* = 370.0331 calcd. for C<sub>14</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>4</sub>SNa [M+Na]<sup>+</sup>, found: 370.0339; **IR** (neat, cm<sup>-1</sup>): 3064w, 2930w, 2853w, 2735w, 2359w, 2227w, 1705s, 1649w, 1601w, 1426s, 1213s, 1134s, 1092w, 1016m, 951w, 895w, 818s, 763w.

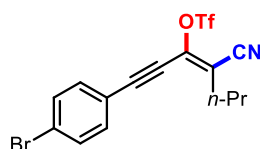


**(Z)-2-Cyano-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate**

**(2n)**: The title compound was prepared according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 1-methyl-2-(pent-1-yn-1-yl)benzene **3n** (31.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2n** as a colorless oil in 30% yield (20.0 mg). **TLC** *R*<sub>f</sub> = 0.45 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.39 – 7.32 (m, 1H), 7.25 – 7.19 (m, 3H), 2.28 (s, 3H), 2.05 (q, *J* = 7.5 Hz, 2H), 1.57 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.4 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 155.8 (C), 137.7 (C), 131.8 (CH), 131.0 (CH), 130.2 (CH), 128.6 (C), 126.1 (CH), 118.1 (q, *J* = 320.9 Hz, CF<sub>3</sub>), 114.1 (C), 110.7 (C), 31.4 (CH<sub>2</sub>), 21.0 (CH<sub>2</sub>), 19.4 (CH<sub>3</sub>), 13.1 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -74.0 (s, 3F); **HRMS** (ESI) *m/z* = 356.0539, calcd. for C<sub>14</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>3</sub>SNa

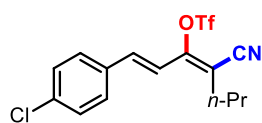


[M+Na]<sup>+</sup>, found: 356.0541; **IR** (neat, cm<sup>-1</sup>): 2968<sub>w</sub>, 2834<sub>w</sub>, 2257<sub>w</sub>, 2228<sub>w</sub>, 1649<sub>w</sub>, 1425<sub>m</sub>, 1214<sub>s</sub>, 1135<sub>s</sub>, 1091<sub>m</sub>, 990<sub>m</sub>, 908<sub>s</sub>, 867<sub>w</sub>, 820<sub>s</sub>, 768<sub>w</sub>, 728<sub>s</sub>, 649<sub>w</sub>.



**(Z)-1-(4-Bromophenyl)-4-cyanohept-3-en-1-yn-3-yl trifluoromethanesulfonate (2o):**

The title compound was prepared according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 1-bromo-4-(hepta-1,3-diyn-1-yl)benzene **3o** (49.4 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 400:1, then 300:1) gave the desired product **2o** as a yellow oil in 61% yield (51.0 mg). **TLC** R<sub>f</sub> = 0.5 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.49 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.67 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 137.3 (C), 133.3 (CH), 132.3 (CH), 126.0 (C), 118.4 (q, *J* = 319.1 Hz, CF<sub>3</sub>), 118.3 (C), 114.8 (C), 113.7 (C), 104.4 (C), 79.3 (C), 32.6 (CH<sub>2</sub>), 21.0 (CH<sub>2</sub>), 13.1 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -72.9 (s, 3F); **HRMS** (ESI) *m/z* = 445.9487, calcd. for C<sub>15</sub>H<sub>11</sub>BrF<sub>3</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup>, found: 445.9481; **IR** (neat, cm<sup>-1</sup>): 2968<sub>w</sub>, 2877<sub>w</sub>, 2200<sub>w</sub>, 1618<sub>w</sub>, 1582<sub>w</sub>, 1486<sub>w</sub>, 1430<sub>s</sub>, 1306<sub>w</sub>, 1212<sub>s</sub>, 1134<sub>s</sub>, 1083<sub>s</sub>, 1011<sub>m</sub>, 969<sub>s</sub>, 889<sub>w</sub>, 817<sub>s</sub>, 760<sub>w</sub>, 703<sub>w</sub>.

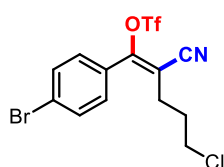


**(1E, 3Z)-1-(4-Chlorophenyl)-4-cyanohepta-1,3-dien-3-yl trifluoromethanesulfonate (2p):**

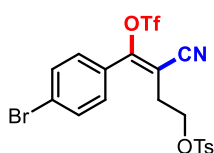
The title compound was prepared according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), (*E*)-1-chloro-4-(hept-1-en-3-yn-1-yl)benzene **3p** (40.8 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2p** as a yellow oil in 20% yield (15.2 mg). **TLC** R<sub>f</sub> = 0.35 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300



K):  $\delta$  (ppm) = 7.36 (d,  $J$  = 8.6 Hz, 2H), 7.30 (d,  $J$  = 8.7 Hz, 2H), 7.11 (d,  $J$  = 15.8 Hz, 1H), 6.78 (d,  $J$  = 15.8 Hz, 1H), 2.38 (t,  $J$  = 7.4 Hz, 2H), 1.64 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.2 Hz, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 152.9 (C), 137.9 (CH), 136.6 (C), 132.8 (C), 129.4 (CH), 129.0 (CH), 116.1 (CH), 118.3 (q,  $J$  = 320.8 Hz,  $\text{CF}_3$ ), 115.0 (C), 108.0 (C), 31.3 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_2$ ), 13.2 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -72.5 (s, 3F); HRMS (ESI)  $m/z$  = 402.0149, calcd. for  $\text{C}_{15}\text{H}_{13}\text{ClF}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 402.0161; IR (neat,  $\text{cm}^{-1}$ ): 2968w, 2877w, 2217w, 1624m, 1587w, 1491w, 1410s, 1331w, 1209s, 1133s, 1091s, 958s, 894m, 807s, 743w, 655w.

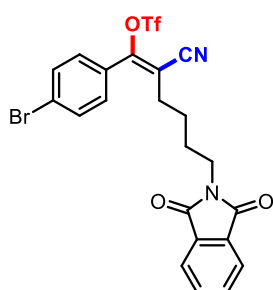


**(Z)-1-(4-Bromophenyl)-5-chloro-2-cyanopent-1-en-1-yl tri-fluoromethanesulfonate (2q):** The title compound was prepared according to general procedure (GP2) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-bromo-4-(5-chloropent-1-yn-1-yl)benzene **3q** (51.5 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45  $^\circ\text{C}$  for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 200:1, then 100:1) gave the desired product **2q** as a yellow oil in 72% yield (61.8 mg). TLC  $R_f$  = 0.2 (Pentane:EtOAc = 20:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.60 (d,  $J$  = 8.5 Hz, 2H), 7.27 (d,  $J$  = 8.5 Hz, 2H), 3.48 (t,  $J$  = 6.0 Hz, 2H), 2.49 – 2.44 (m, 2H), 2.10 – 2.01 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 155.3 (C), 132.6 (CH), 130.2 (CH), 128.3 (C), 127.0 (C), 118.1 (q,  $J$  = 319.1 Hz,  $\text{CF}_3$ ), 113.8 (C), 108.4 (C), 43.0 ( $\text{CH}_2$ ), 30.3 ( $\text{CH}_2$ ), 26.9 ( $\text{CH}_2$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.3 (s, 3F); HRMS (ESI)  $m/z$  = 455.9098 calcd. for  $\text{C}_{13}\text{H}_{10}\text{BrClF}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 455.9093; IR (neat,  $\text{cm}^{-1}$ ): 2970m, 2933w, 1872w, 2230w, 1899w, 1646w, 1485s, 1393s, 1322s, 1256w, 1157w, 1071s, 1011s, 942m, 822s, 708w.



**(Z)-4-(4-Bromophenyl)-3-cyano-4-(((trifluoromethyl)sulfonyl)-oxy)but-3-en-1-yl 4-methylbenzenesulfonate (2r):**

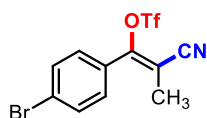
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 4-(4-bromophenyl)but-3-yn-1-yl 4-methylbenzenesulfonate **3r** (75.9 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Then further portions of  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv), and DCE (1 mL) were added. The stirring was continued at 45 °C for further 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 30:1, then 10:1) gave the desired product **2r** as a yellow oil in 46% yield (51.1 mg). **TLC**  $R_f$  = 0.25 (Pentane:EtOAc = 7:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.69 (d,  $J$  = 8.3 Hz, 2H), 7.58 (d,  $J$  = 8.4 Hz, 2H), 7.30 (d,  $J$  = 8.2 Hz, 2H), 7.26 (d,  $J$  = 8.6 Hz, 2H), 4.15 (t,  $J$  = 5.9 Hz, 2H), 2.58 (t,  $J$  = 5.9 Hz, 2H), 2.39 (s, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 157.0 (C), 146.0 (C), 132.6 (CH), 132.1 (C), 130.4 (CH), 130.1 (CH), 127.9 (CH), 127.7 (C), 127.3 (C), 118.0 (q,  $J$  = 321.1 Hz,  $\text{CF}_3$ ), 113.1 (C), 105.0 (C), 65.5 ( $\text{CH}_2$ ), 29.7 ( $\text{CH}_2$ ), 21.6 ( $\text{CH}_3$ );  **$^{19}\text{F}$  NMR** (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.2 (s, 3F); **HRMS** (ESI)  $m/z$  = 577.9368, calcd. for  $\text{C}_{19}\text{H}_{15}\text{BrF}_3\text{NO}_6\text{S}_2\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ , found: 577.9389; **IR** (neat,  $\text{cm}^{-1}$ ): 2963 $w$ , 2228 $w$ , 1644 $w$ , 1589 $w$ , 1486 $w$ , 1426 $s$ , 1364 $m$ , 1216 $s$ , 1176 $s$ , 1134 $s$ , 1072 $m$ , 991 $s$ , 906 $m$ , 838 $s$ , 807 $s$ , 763 $s$ , 663 $m$ , 838 $s$ .



**(Z)-1-(4-Bromophenyl)-2-cyano-6-(1,3-dioxoisindolin-2-yl)hex-1-en-1-yl trifluoromethanesulfonate (2s):**

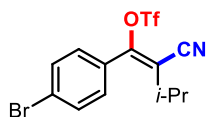
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 2-(6-(4-bromophenyl)hex-5-yn-1-yl)isoindoline-1,3-dione **3s** (76.5 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography

(Pentane:EtOAc = 30:1, then 14:1) gave the desired product **2s** as a light yellow oil in 93% yield (103.9 mg). **TLC**  $R_f$  = 0.25 (Pentane:EtOAc = 7:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.79 – 7.73 (m, 2H), 7.67 – 7.63 (m, 2H), 7.57 (d,  $J$  = 8.5 Hz, 2H), 7.25 (d,  $J$  = 8.5 Hz, 2H), 3.56 (t,  $J$  = 6.0 Hz, 2H), 2.30 (t,  $J$  = 6.8 Hz, 2H), 1.63 – 1.59 (m, 4H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 168.2 (C), 154.6 (C), 134.0 (CH), 132.5 (CH), 131.9 (C), 130.2 (CH), 128.4 (C), 126.8 (C), 123.2 (CH), 113.8 (C), 118.1 (q,  $J$  = 318.8 Hz,  $\text{CF}_3$ ), 109.4 (C), 37.0 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 27.5 ( $\text{CH}_2$ ), 25.1 ( $\text{CH}_2$ );  **$^{19}\text{F}$  NMR** (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.3 (s, 3F); **HRMS** (ESI)  $m/z$  = 580.9787 calcd. for  $\text{C}_{22}\text{H}_{16}\text{BrF}_3\text{N}_2\text{O}_5\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 580.9796; **IR** (neat,  $\text{cm}^{-1}$ ): 2926w, 2856w, 2227w, 1771w, 1707s, 1642w, 1588w, 1397s, 1214s, 1133s, 1072m, 1018m, 995s, 912m, 839s, 720s.



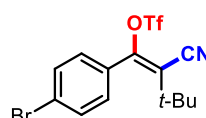
**(Z)-1-(4-Bromophenyl)-2-cyanoprop-1-en-1-yl trifluoromethanesulfonate (2t):**

The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-bromo-4-(prop-1-yn-1-yl)benzene **3t** (38.8 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 200:1) gave the desired product **2t** as a light yellow oil in 72% yield (52.7 mg). **TLC**  $R_f$  = 0.25 (Pentane:EtOAc = 7:1);  **$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.59 (d,  $J$  = 8.4 Hz, 2H), 7.26 (d,  $J$  = 8.5 Hz, 2H), 2.00 (s, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 154.5 (C), 132.5 (CH), 130.2 (CH), 128.5 (C), 126.8 (C), 118.1 (q,  $J$  = 320.9 Hz,  $\text{CF}_3$ ), 114.9 (C), 104.4 (C), 16.5 ( $\text{CH}_3$ );  **$^{19}\text{F}$  NMR** (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.3 (s, 3F); **HRMS** (ESI)  $m/z$  = 391.9174, calcd. for  $\text{C}_{11}\text{H}_7\text{BrF}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 391.9177; **IR** (neat,  $\text{cm}^{-1}$ ): 2929w, 2228w, 1647w, 1588w, 1485w, 1424s, 1209s, 1132s, 1052s, 987s, 836s, 766m, 733m, 686w, 601s.



**(Z)-1-(4-Bromophenyl)-2-cyano-3-methylbut-1-en-1-yl trifluoromethanesulfonate (2u)**

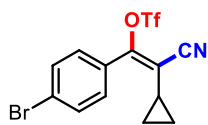
The title compound was prepared according to general procedure (GP2) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene **3u** (44.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1, then 200:1) gave the desired product **2u** as a white solid in 81% yield (64.6 mg). **TLC** *R<sub>f</sub>* = 0.35 (Pentane:EtOAc = 40:1); **MP**: 66 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.58 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 2.65 – 2.54 (m, 1H), 1.15 (d, *J* = 6.7 Hz, 6H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): 152.9 (C), 132.5 (CH), 130.0 (CH), 128.7 (C), 126.7 (C), 118.1 (q, *J* = 320.9 Hz, CF<sub>3</sub>), 116.8 (C), 112.6 (C), 29.2 (CH), 21.2 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = -73.4 (s, 3F); **HRMS** (ESI) *m/z* = 421.9467, calcd. for C<sub>13</sub>H<sub>11</sub>BrF<sub>3</sub>NO<sub>3</sub>S [M+Na]<sup>+</sup>, found: 421.9465; **IR** (neat, cm<sup>-1</sup>): 2976<sub>w</sub>, 2254<sub>w</sub>, 1629<sub>w</sub>, 1429<sub>w</sub>, 1224<sub>m</sub>, 1135<sub>w</sub>, 1073<sub>w</sub>, 998<sub>m</sub>, 904<sub>s</sub>, 834<sub>w</sub>, 724<sub>s</sub>, 649<sub>s</sub>.



**(Z)-1-(4-Bromophenyl)-2-cyano-3,3-dimethylbut-1-en-1-yl trifluoromethanesulfonate (2v)**

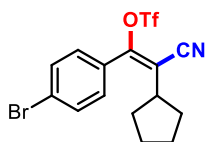
The title compound was prepared according to general procedure (GP2) with Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 1-bromo-4-(3,3-dimethylbut-1-yn-1-yl)benzene **3v** (47.4 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Then further portions of Fe(OAc)<sub>2</sub> (3.5 mg, 20 μmol, 10 mol%), **L1** (3.6 mg, 20 μmol, 10 mol%), 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv), and DCE (1 mL) were added. The stirring was continued at 45 °C for further 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2v** as a light yellow oil in 60% yield (49.0 mg). **TLC** *R<sub>f</sub>* = 0.55 (Pentane:EtOAc = 20:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.55 (d, *J* = 8.3 Hz, 2H), 7.23

(d,  $J = 8.3$  Hz, 2H), 1.06 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 154.1 (C), 132.0 (CH), 131.6 (CH), 129.4 (C), 126.6 (C), 121.7 (C), 118.0 (q,  $J = 321.0$  Hz,  $\text{CF}_3$ ), 114.1 (C), 34.9 (C), 30.3 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.8 (s, 3F); **HRMS** (ESI)  $m/z = 435.9623$ , calcd. for  $\text{C}_{14}\text{H}_{13}\text{BrF}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 435.9619; **IR** (neat,  $\text{cm}^{-1}$ ): 2975 $w$ , 2232 $w$ , 1636 $w$ , 1586 $w$ , 1481 $w$ , 1423 $s$ , 1209 $s$ , 1134 $s$ , 1071 $m$ , 1014 $m$ , 963 $s$ , 893 $m$ , 842 $s$ , 787 $m$ , 758 $m$ , 703 $m$ .



**(Z)-1-(4-Bromophenyl)-2-cyano-2-cyclopropylvinyl trifluoromethanesulfonate (2w):**

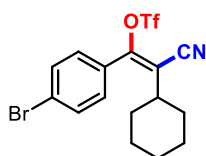
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-bromo-4-(cyclopropylethynyl)benzene **3w** (44.2 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45  $^\circ\text{C}$  for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2w** as a colorless oil in 42% yield (32.6 mg). **TLC**  $R_f = 0.45$  (Pentane:EtOAc = 20:1);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 7.59 (d,  $J = 8.4$  Hz, 2H), 7.39 (d,  $J = 8.6$  Hz, 2H), 1.61 – 1.52 (m, 1H), 0.93 – 0.90 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K): 153.0 (C), 132.4 (CH), 130.4 (CH), 129.0 (C), 126.5 (C), 118.1 (q,  $J = 321.2$  Hz,  $\text{CF}_3$ ), 113.2 (C), 112.1 (C), 10.7 (CH), 7.9 ( $\text{CH}_2$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -73.3 (s, 3F); **HRMS** (ESI)  $m/z = 419.9310$ , calcd. for  $\text{C}_{13}\text{H}_9\text{BrF}_3\text{NO}_3\text{S}$   $[\text{M}+\text{Na}]^+$ , found: 419.9314; **IR** (neat,  $\text{cm}^{-1}$ ): 3093 $w$ , 2228 $w$ , 1629 $w$ , 1588 $w$ , 1486 $s$ , 1426 $s$ , 1363 $w$ , 1216 $s$ , 1134 $s$ , 1072 $m$ , 1002 $s$ , 915 $m$ , 869 $m$ , 835 $m$ , 798 $m$ , 759 $m$ , 684 $w$ , 610 $m$ .



**(Z)-1-(4-Bromophenyl)-2-cyano-2-cyclopentylvinyl trifluoromethanesulfonate (2x):**

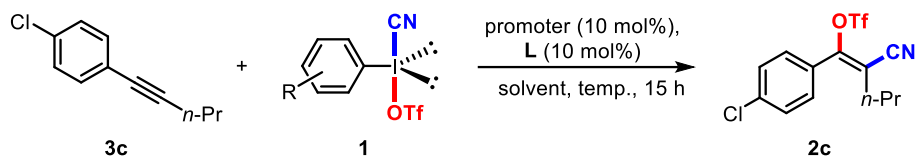
The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1-bromo-4-(cyclopentylethynyl)benzene **3x** (49.8 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv)

in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2x** as a colorless oil in 70% yield (58.8 mg). **TLC**  $R_f$  = 0.4 (Pentane:EtOAc = 40:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.57 (d,  $J$  = 8.4 Hz, 2H), 7.24 (d,  $J$  = 8.4 Hz, 2H), 2.58 (p,  $J$  = 8.3 Hz, 1H), 1.83 – 1.50 (m, 8H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 153.1 (C), 132.5 (CH), 130.2 (CH), 128.9 (C), 126.6 (C), 118.1 (q,  $J$  = 321.0 Hz, CF<sub>3</sub>), 115.1 (C), 113.2 (C), 39.4 (CH), 32.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); **HRMS** (ESI)  $m/z$  = 447.9624, calcd. for C<sub>15</sub>H<sub>13</sub>BrF<sub>3</sub>NO<sub>3</sub>S [M+Na]<sup>+</sup>, found: 447.9628; **IR** (neat, cm<sup>-1</sup>): 2959<sub>w</sub>, 2872<sub>w</sub>, 2226<sub>w</sub>, 1638<sub>w</sub>, 1588<sub>w</sub>, 1486<sub>w</sub>, 1425<sub>s</sub>, 1212<sub>s</sub>, 1134<sub>s</sub>, 1072<sub>m</sub>, 1001<sub>s</sub>, 871<sub>m</sub>, 825<sub>s</sub>, 759<sub>w</sub>, 684<sub>w</sub>.



**(Z)-1-(4-Bromophenyl)-2-cyano-2-cyclohexylvinyl trifluoromethanesulfonate (2y):** The title compound was prepared according to general procedure (**GP2**) with Fe(OAc)<sub>2</sub> (3.5 mg, 20  $\mu$ mol, 10 mol%), **L1** (3.6 mg, 20  $\mu$ mol, 10 mol%), 1-bromo-4-(cyclohexylethynyl)benzene **3y** (52.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 300:1) gave the desired product **2y** as a colorless oil in 60% yield (52.6 mg). **TLC**  $R_f$  = 0.45 (Pentane:EtOAc = 40:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.59 (d,  $J$  = 8.4 Hz, 2H), 7.23 (d,  $J$  = 8.4 Hz, 2H), 2.21 (tt,  $J^1$  = 11.7 Hz,  $J^2$  = 3.5 Hz, 1H), 1.75 – 1.04 (m, 10H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 153.3 (C), 132.5 (CH), 130.0 (CH), 128.9 (C), 126.7 (C), 118.1 (q,  $J$  = 321.0 Hz, CF<sub>3</sub>), 115.8 (C), 113.2 (C), 38.6 (CH), 31.3 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = -73.4 (s, 3F); **HRMS** (ESI)  $m/z$  = 461.9780, calcd. for C<sub>16</sub>H<sub>15</sub>BrF<sub>3</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup>, found: 461.9782; **IR** (neat, cm<sup>-1</sup>): 2933<sub>m</sub>, 2857<sub>w</sub>, 2225<sub>w</sub>, 1639<sub>w</sub>, 1588<sub>w</sub>, 1486<sub>w</sub>, 1425<sub>s</sub>, 1210<sub>s</sub>, 1133<sub>s</sub>, 1072<sub>m</sub>, 1004<sub>s</sub>, 982<sub>s</sub>, 909<sub>w</sub>, 835<sub>s</sub>, 787<sub>m</sub>, 763<sub>m</sub>, 685<sub>w</sub>.

## Screening of reaction conditions



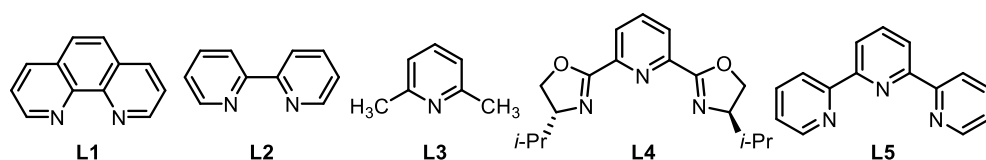
entry <sup>a</sup>	promotor	ligand	<b>1</b>	solvent	temperature	yield (%) <sup>b</sup>
<b>1</b>	<b>Fe(OAc)<sub>2</sub></b>	<b>L1</b>	<b>1a</b>	<b>DCE</b>	<b>45 °C</b>	<b>78, 81<sup>c</sup>, (72:1)</b>
2	none	none	<b>1a</b>	DCE	45 °C	trace, (NA)
3	Fe(OAc) <sub>2</sub>	none	<b>1a</b>	DCE	45 °C	36, (26:1)
4	Fe(OAc) <sub>2</sub>	<b>L2</b>	<b>1a</b>	DCE	45 °C	51, (61:1)
5	Fe(OAc) <sub>2</sub>	<b>L3</b>	<b>1a</b>	DCE	45 °C	20, (24:1)
6	Fe(OAc) <sub>2</sub>	<b>L4</b>	<b>1a</b>	DCE	45 °C	24, (18:1)
7	Fe(OAc) <sub>2</sub>	<b>L5</b>	<b>1a</b>	DCE	45 °C	31, (23:1)
8	Fe(OAc) <sub>2</sub>	<b>L1</b>	<b>1b</b>	DCE	45 °C	22, (22:1)
9	Fe(OAc) <sub>2</sub>	<b>L1</b>	<b>1c</b>	DCE	45 °C	40, (54:1)
10	Fe(OAc) <sub>2</sub>	<b>L1</b>	<b>1a</b>	DCM	45 °C	63, (42:1)
11	Fe(OAc) <sub>2</sub>	<b>L1</b>	<b>1a</b>	MeCN	45 °C	trace, (NA)
12	Fe(OAc) <sub>2</sub>	<b>L1</b>	<b>1a</b>	DCE	rt.	64, (91:1)
13	Fe(OTf) <sub>2</sub>	<b>L1</b>	<b>1a</b>	DCE	45 °C	23, (4:1)
14	FeCl <sub>2</sub>	<b>L1</b>	<b>1a</b>	DCE	45 °C	49, (15:1)
15	FeCl <sub>3</sub>	<b>L1</b>	<b>1a</b>	DCE	45 °C	55, (21:1)
16	CuCl	none	<b>1a</b>	DCE	45 °C	trace, (NA)
17	BF <sub>3</sub> ·Et <sub>2</sub> O	none	<b>1a</b>	DCE	45 °C	12, (NA)
18	HOTf	none	<b>1a</b>	DCE	45 °C	trace, (NA)
19	AlCl <sub>3</sub>	none	<b>1a</b>	DCE	45 °C	12, (2:1)
20	TBAI	none	<b>1a</b>	DCE	45 °C	32, (9:1)

<sup>a</sup>Reaction condition: **3c** (0.20 mmol, 1.0 equiv.), reagent **1** (0.44 mmol, 2.2 equiv.), promoter (0.02 mmol, 10 mol%), ligand (0.02 mmol, 10 mol%), solvent (1 mL), 45 °C, 15 h.

<sup>b</sup>Yield determined by <sup>19</sup>F NMR analysis using PhCF<sub>3</sub> as an internal standard; isomer ratio in parentheses determined by GC-MS analysis on the crude product; NA, not applicable;

<sup>c</sup>Isolated yield.

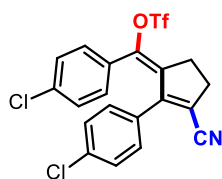
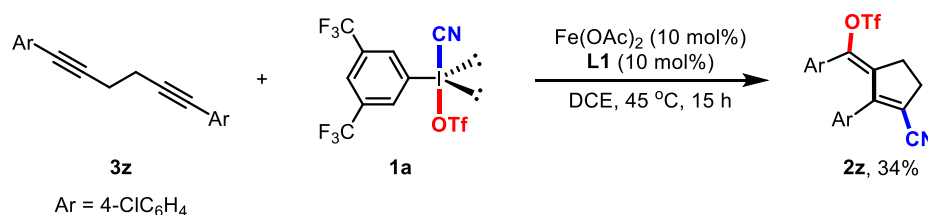
ligand =



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with promoter (0.020 mmol, 10 mmol%) and ligand (0.020 mmol, 10 mmol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (1 mL) was added. The resulting suspension was stirred for 5 min

at room temperature. 1-Chloro-4-(pent-1-yn-1-yl)benzene **1c** (35.7 mg, 0.200 mmol, 1.0 equiv) and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (0.440 mmol, 227 mg, 2.2 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 45 °C for 15 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was analyzed by GC-MS and  $^{19}\text{F}$  NMR.

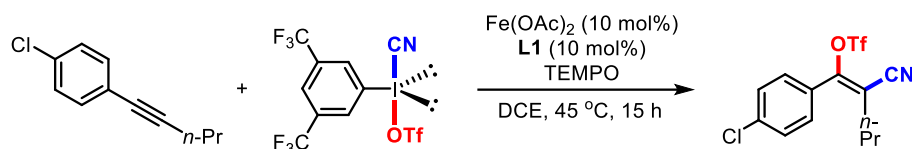
### Mechanistic study



**(E)-(4-Chlorophenyl)(2-(4-chlorophenyl)-3-cyanocyclopent-2-en-1-ylidene)methyl trifluoromethanesulfonate (2z):** The title compound was prepared according to general procedure (**GP2**) with  $\text{Fe}(\text{OAc})_2$  (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%), **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), 1,6-bis(4-chlorophenyl)hexa-1,5-diyne **3z** (59.6 mg, 0.200 mmol, 1.0 equiv), and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv) in DCE (1 mL) at 45 °C for 15 h. Purification via silica gel chromatography (Pentane:EtOAc = 100:1) gave the desired product **2z** as an off-white solid in 34% yield (32.1 mg). **TLC**  $R_f$  = 0.35 (Pentane:EtOAc = 10:1); **MP**: 79 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 6.93 (dd,  $J^1$  = 10.9 Hz,  $J^2$  = 8.6 Hz, 4H), 6.74 (dd,  $J^1$  = 16.0 Hz,  $J^2$  = 8.5 Hz, 4H), 3.14 – 3.10 (m, 2H), 2.89 – 2.85 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = 153.6 (C), 143.3 (C), 139.0 (C), 136.6 (C), 135.2 (C), 131.0 (CH), 129.5 (CH), 129.3 (C), 128.9 (C), 128.2 (CH), 128.0 (CH), 122.5 (C), 118.06 (q,  $J$  = 320.5 Hz,  $\text{CF}_3$ ), 115.7 (C), 32.2 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ );  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 300 K):  $\delta$  (ppm) = -74.2 (s, 3F); **HRMS** (ESI)  $m/z$  = 495.9759, calcd. for  $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{F}_3\text{NO}_3\text{SNa}$   $[\text{M}+\text{Na}]^+$ , found: 495.9743; **IR** (neat,  $\text{cm}^{-1}$ ): 2934w, 2216w,

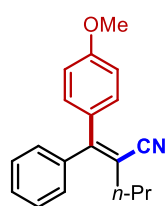
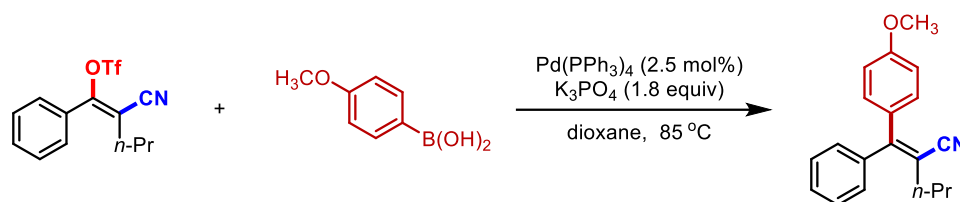


1648<sub>w</sub>, 1594<sub>w</sub>, 1489<sub>m</sub>, 1412<sub>s</sub>, 1347<sub>w</sub>, 1213<sub>s</sub>, 1136<sub>s</sub>, 1092<sub>m</sub>, 1018<sub>m</sub>, 929<sub>m</sub>, 859<sub>s</sub>, 831<sub>s</sub>, 734<sub>w</sub>, 667<sub>w</sub>.



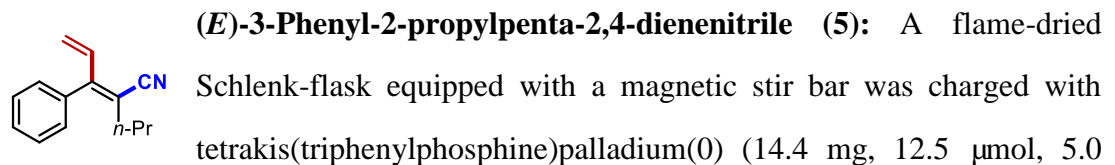
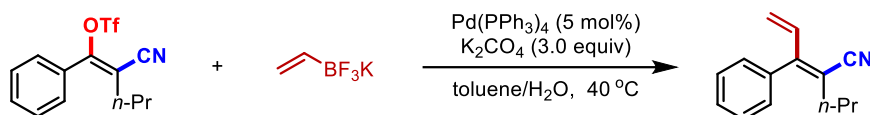
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with iron(II) acetate (3.5 mg, 20  $\mu\text{mol}$ , 10 mol%) and 1,10-phenanthroline **L1** (3.6 mg, 20  $\mu\text{mol}$ , 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DCE (1 mL) was added. The resulting suspension was stirred for 5 min at room temperature. The corresponding alkyne 1-chloro-4-(pent-1-yn-1-yl)benzene **1c** (35.7 mg, 0.200 mmol, 1.0 equiv) and 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate **1a** (227 mg, 0.440 mmol, 2.2 equiv), and 2,2,6,6-Tetramethylpiperidine 1-oxyl (68.7 mg, 0.440 mmol, 2.2 equiv) were added successively under a flow of argon. The reaction mixture was then stirred at 45 °C for 24 hours. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. No desired product **2c** and TEMPO-CN adduct was detected by GC-MS and  $^{19}\text{F}$  NMR analysis.

#### 4. Derivatization of vinyl triflates

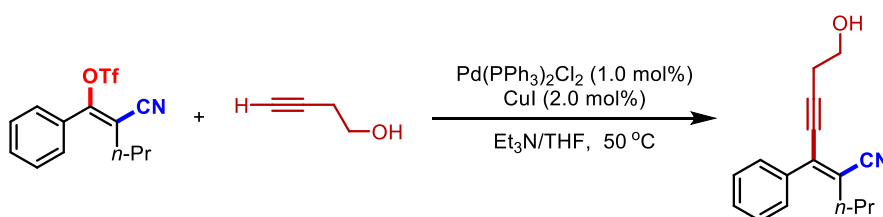


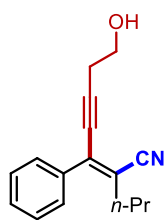
#### (Z)-2-((4-Methoxyphenyl)(phenyl)methylene)pentanenitrile (**4**): A

flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (5.8 mg, 5.0  $\mu$ mol, 2.5 mol%), (4-methoxyphenyl)boronic acid (54.7 mg, 0.360 mmol, 1.8 equiv), tripotassium phosphate (76.4 mg, 0.360 mmol, 1.8 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dioxane (2 mL) was added. (Z)-2-Cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (63.9 mg, 0.200 mmol, 1.0 equiv, dr>20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 85 °C for 24 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 200:1) to give pure product **4** as a light yellow oil in 86% yield (47.8 mg, dr>20:1). **TLC** *R<sub>f</sub>* = 0.55 (Pentane:EtOAc = 10:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.30 – 7.25 (m, 3H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.04 – 7.01 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 2.20 (t, *J* = 7.7 Hz, 2H), 1.59 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 160.3 (C), 156.7 (C), 139.2 (C), 132.2 (C), 130.8 (CH), 129.1 (CH), 128.5 (CH), 128.3 (CH), 120.1 (C), 113.6 (CH), 110.5 (C), 55.2 (CH<sub>3</sub>), 34.1 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 13.3 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* = 300.1359, calcd. for C<sub>19</sub>H<sub>19</sub>NONa [M+Na]<sup>+</sup>, found: 300.1354; **IR** (neat, cm<sup>-1</sup>): 2961w, 2205w, 1605s, 1509s, 1461m, 1289m, 1250s, 1174s, 1114w, 1075w, 1030s, 908w, 829s, 759m, 702s, 656w.



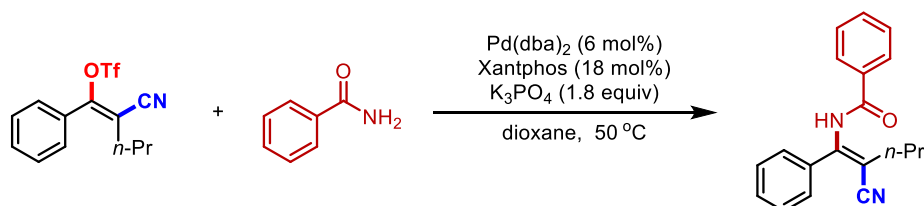
Schlenk-flask equipped with a magnetic stir bar was charged with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 12.5  $\mu$ mol, 5.0 mol%), potassium vinyltrifluoroborate (53.5 mg, 0.400 mmol, 1.6 equiv), potassium carbonate (0.104 g, 0.750 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before toluene (5 mL) and H<sub>2</sub>O (1 mL) was added. (Z)-2-Cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (79.8 mg, 0.250 mmol, 1.0 equiv, dr>20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 40 °C for 24 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 300:1) to give pure product **5** as a yellow oil in 90% yield (44.4 mg, dr>20:1). *R*<sub>f</sub> = 0.6 (Pentane:EtOAc = 20:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.37 – 7.26 (m, 3H), 7.11 (dd, *J*<sup>1</sup> = 17.0 Hz, *J*<sup>2</sup> = 10.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 5.38 (dd, *J*<sup>1</sup> = 10.5 Hz, *J*<sup>2</sup> = 0.8 Hz, 1H), 4.88 (dd, *J*<sup>1</sup> = 16.9 Hz, *J*<sup>2</sup> = 0.7 Hz, 1H), 1.96 (t, *J* = 7.2 Hz, 2H), 1.47 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.75 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 154.4 (C), 136.4 (CH), 135.1 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 123.8 (CH<sub>2</sub>), 118.3 (C), 113.5 (C), 33.0 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>), 13.3 (CH<sub>3</sub>); HRMS (ESI) *m/z* = 220.1097, calcd. for C<sub>14</sub>H<sub>15</sub>NNa [M+Na]<sup>+</sup>, found: 220.1091; IR (neat, cm<sup>-1</sup>): 2963<sub>w</sub>, 2874<sub>w</sub>, 2208<sub>w</sub>, 1574<sub>w</sub>, 1461<sub>w</sub>, 1409<sub>w</sub>, 1312<sub>w</sub>, 1260<sub>w</sub>, 1088<sub>w</sub>, 1027<sub>w</sub>, 985<sub>w</sub>, 928<sub>m</sub>, 765<sub>m</sub>, 701<sub>s</sub>.

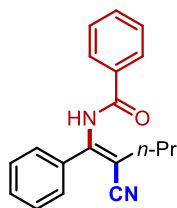




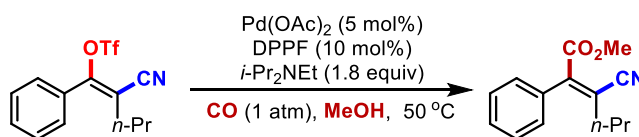
**(Z)-7-Hydroxy-3-phenyl-2-propylhept-2-en-4-ynenitrile (6):** A

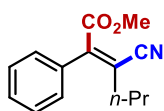
flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(triphenylphosphine)palladium(II) dichloride (1.4 mg, 2  $\mu$ mol, 1.0 mol%), copper(I) iodide (0.8 mg, 4  $\mu$ mol, 2.0 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before tetrahydrofuran (1 mL) and triethylamine (1 mL) was added. (Z)-2-Cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (63.9 mg, 0.200 mmol, 1.0 equiv, dr>20:1) and but-3-yn-1-ol (28.0 mg, 0.400 mmol, 2.0 equiv) was added to the resulting suspension successively. The reaction mixture was stirred at 50  $^{\circ}$ C for 24 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 8:1) to give pure product **6** as a light yellow oil in 84% yield (40.2 mg, dr>20:1). **R<sub>f</sub>** = 0.2 (Pentane:EtOAc = 4:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.39 – 7.30 (m, 3H), 7.28 – 7.22 (m, 2H), 3.74 (t,  $J$  = 6.1 Hz, 2H), 2.62 (t,  $J$  = 6.1 Hz, 2H), 2.26 – 2.20 (m, 3H), 1.54 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.5 Hz, 2H), 0.82 (t,  $J$  = 7.3 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 138.3 (C), 135.4 (C), 129.1 (CH), 128.5 (CH), 128.3 (CH), 120.1 (C), 119.6 (C), 97.0 (C), 81.8 (C), 60.8 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>), 13.3 (CH<sub>3</sub>); **HRMS** (ESI)  $m/z$  = 262.1202, calcd. for C<sub>16</sub>H<sub>17</sub>NONa [M+Na]<sup>+</sup>, found: 262.1227; **IR** (neat, cm<sup>-1</sup>): 3418 $br$ , 3062 $w$ , 2926 $m$ , 2208 $m$ , 1718 $w$ , 1565 $w$ , 1461 $m$ , 1380 $m$ , 1334 $m$ , 1243 $w$ , 1153 $w$ , 1047 $s$ , 962 $w$ , 924 $w$ , 846 $w$ , 761 $s$ , 700 $s$ .



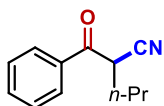
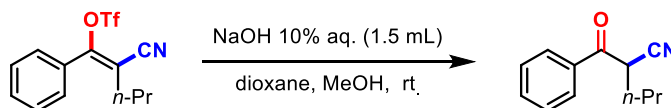


**(E)-N-(2-Cyano-1-phenylpent-1-en-1-yl)benzamide (7):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with bis(dibenzylideneacetone)palladium(0) (6.9 mg, 12  $\mu$ mol, 6.0 mol%), Xantphos (20.8 mg, 36.0  $\mu$ mol, 18 mol%), tripotassium phosphate (0.076 g, 0.36 mmol, 1.8 equiv), and benzamide (36.3 mg, 0.300 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dioxane (2 mL) was added. (Z)-2-Cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (63.9 mg, 0.200 mmol, 1.0 equiv, dr>20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 50  $^{\circ}$ C for 12 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 12:1, then 8:1) to give pure product **7** as a yellow solid in 58% yield (33.9 mg, containing 11% of imine tautomer). **R<sub>f</sub>** = 0.25 (Pentane:EtOAc = 5:1); enamine tautomer: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 8.14 (s, 1H), 7.78 – 7.75 (m, 2H), 7.51 – 7.45 (m, 1H), 7.39 (dd,  $J^1$  = 6.4 Hz,  $J^2$  = 1.4 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.30 – 7.26 (m, 2H), 2.23 – 2.06 (t,  $J$  = 7.5 Hz, 2H), 1.54 (tq,  $J^1$  = 7.5 Hz,  $J^2$  = 7.2 Hz, 2H), 0.83 (t,  $J$  = 7.4 Hz, 2H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 165.0 (C), 149.2 (C), 133.7 (C), 133.2 (C), 132.6 (CH), 129.7 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 127.5 (CH), 118.2 (C), 101.8 (C), 30.7 (CH<sub>2</sub>), 22.1 (CH<sub>2</sub>), 13.3 (CH<sub>3</sub>); **HRMS** (ESI)  $m/z$  = 313.1311, calcd. for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>ONa [M+Na]<sup>+</sup>, found: 313.1317; **IR** (neat, cm<sup>-1</sup>): 3271<sub>br</sub>, 3062<sub>w</sub>, 2962<sub>w</sub>, 2929<sub>w</sub>, 2873<sub>w</sub>, 2208<sub>w</sub>, 1661<sub>s</sub>, 1603<sub>m</sub>, 1479<sub>s</sub>, 1270<sub>s</sub>, 1151<sub>w</sub>, 1076<sub>w</sub>, 1027<sub>w</sub>, 915<sub>w</sub>.



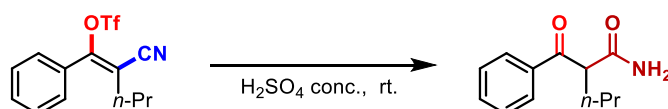


**Methyl (Z)-3-cyano-2-phenylhex-2-enoate (8):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with palladium(II) acetate (2.8 mg, 13  $\mu$ mol, 5.0 mol%), DPPF (13.9 mg, 25.0  $\mu$ mol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before methanol (1.5 mL) was added. *N,N*-diisopropylethylamine (32.3 mg, 0.250 mmol, 1.0 equiv) and (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (79.8 mg, 0.250 mmol, 1.0 equiv, dr>20:1) were then added successively. The flask fitted with a balloon of carbon monoxide gas and partially evacuated followed by purging with carbon monoxide. This process was repeated three times. The reaction mixture was stirred at 60  $^{\circ}$ C for 18 hours. After the reaction was complete, the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 100:1) to give pure product **8** as a colorless oil in 92% yield (52.8 mg, dr>20:1). *R*<sub>f</sub> = 0.5 (Pentane:EtOAc = 10:1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 7.38 – 7.32 (m, 3H), 7.13 – 7.09 (m, 2H), 3.73 (s, 3H), 2.14 (t, *J* = 7.5 Hz, 2H), 1.56 (tq, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = 165.4 (C), 146.4 (C), 133.2 (C), 129.0 (CH), 128.5 (CH), 128.3 (CH), 121.8 (C), 117.1 (C), 52.8 (CH<sub>3</sub>), 34.0 (CH<sub>2</sub>), 21.1 (CH<sub>2</sub>), 13.2 (CH<sub>3</sub>); HRMS (ESI) *m/z* = 252.0995, calcd. for C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 252.0996; IR (neat, cm<sup>-1</sup>): 2964<sub>w</sub>, 2875<sub>w</sub>, 2362<sub>w</sub>, 2218<sub>w</sub>, 2029<sub>w</sub>, 1972<sub>w</sub>, 1728<sub>s</sub>, 1615<sub>w</sub>, 1436<sub>w</sub>, 1298<sub>m</sub>, 1224<sub>s</sub>, 1085<sub>w</sub>, 1015<sub>w</sub>, 846<sub>w</sub>, 791<sub>w</sub>, 752<sub>w</sub>, 701<sub>m</sub>.



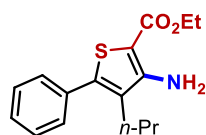
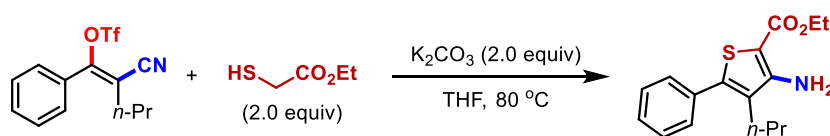
**2-Benzoylpentanenitrile (9):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (63.9 mg, 0.200 mmol, 1.0 equiv,

dr>20:1), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before dioxane (3 mL) and methanol (1 mL) was added. Sodium hydroxide (10% aqueous solution) (1.5 mL) was added dropwise to the resulting solution. The reaction mixture was stirred at room temperature for 10 hours. After the reaction was complete, the reaction mixture was quenched with 10 mL of NH<sub>4</sub>Cl (saturated aq. solution) and extracted with Et<sub>2</sub>O (3 x 10 mL). After drying over Na<sub>2</sub>SO<sub>4</sub> and filtration, the solvent was removed under reduced pressure with the aid of a rotary evaporator to give pure product **9** as a yellow oil in 95% yield (35.6 mg). **R<sub>f</sub>** = 0.35 (Pentane:EtOAc = 10:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.87 – 7.90 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.30 (t, *J* = 7.1 Hz, 1H), 1.90 (dt, *J*<sup>1</sup> = 7.8, *J*<sup>2</sup> = 7.2 Hz, 2H), 1.64 – 1.39 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 190.9 (C), 134.4 (CH), 134.0 (C), 129.0 (CH), 128.7 (CH), 117.3 (C), 39.8 (CH), 31.8 (CH<sub>2</sub>), 20.4 (CH<sub>2</sub>), 13.4 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* = 210.0889, calcd. for C<sub>12</sub>H<sub>13</sub>NONa [M+Na]<sup>+</sup>, found: 210.0894; **IR** (neat, cm<sup>-1</sup>): 3064<sub>w</sub>, 2963<sub>w</sub>, 2875<sub>w</sub>, 2249<sub>w</sub>, 1691<sub>s</sub>, 1597<sub>s</sub>, 1449<sub>m</sub>, 1344<sub>w</sub>, 1262<sub>m</sub>, 1226<sub>s</sub>, 1090<sub>w</sub>, 986<sub>w</sub>, 918<sub>w</sub>, 803<sub>w</sub>, 780<sub>w</sub>, 693<sub>s</sub>.



**2-Benzoylpentanamide (10):** A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (127.7 mg, 0.4000 mmol, 1.0 equiv, dr>20:1), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before concentrated sulfuric acid (1 mL) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirring at room temperature was continued for 24 hours. After the reaction was complete, the reaction mixture was then poured into ice water, basified with 28% ammonium hydroxide solution and extracted with EtOAc. The organic phase

was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>. After drying over Na<sub>2</sub>SO<sub>4</sub> and filtration, the solvent was removed under reduced pressure with the aid of a rotary evaporator to give pure product **10** as a white solid in 96% yield (78.4 mg). *R*<sub>f</sub> = 0.2 (Pentane:EtOAc = 2:1); **MP**: 158 °C; **<sup>1</sup>H NMR** (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ (ppm) = 7.98 – 7.95 (m, 2H), 7.59 – 7.54 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.30 (s, 1H), 5.53 (s, 1H), 4.27 (t, *J* = 7.2 Hz, 1H), 1.99 – 1.79 (m, 2H), 1.37 – 1.29 (m, 2H), 0.91 – 0.85 (m, 3H); **<sup>13</sup>C NMR** (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ (ppm) = 199.6 (C), 171.6 (C), 137.2 (C), 134.4 (CH), 129.4 (CH), 129.1 (CH), 56.2 (CH), 34.7 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>); **HRMS** (ESI) *m/z* = 228.0995, calcd. for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>, found: 228.1007; **IR** (neat, cm<sup>-1</sup>): 3405*br*, 3178*br*, 2957*w*, 2873*w*, 2195*w*, 1681*s*, 1650*s*, 1449*w*, 1394*w*, 1337*w*, 1275*w*, 1209*w*, 1122*w*, 983*w*, 821*w*, 769*w*, 704*w*, 628*w*.



#### **Ethyl 3-amino-5-phenyl-4-propylthiophene-2-carboxylate (**11**):**

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with anhydrous potassium carbonate (0.055 g, 0.4 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the freshly distilled THF (2 mL) was added. (*Z*)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate **2a** (63.9 mg, 0.200 mmol, 1.0 equiv, dr>20:1) was added to the resulting suspension subsequently. The reaction mixture was stirred at 80 °C for 5 hours. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (Pentane:EtOAc = 100:1) to give pure product **11** as a colorless oil in 48% yield (27.6 mg). *R*<sub>f</sub> = 0.25 (Pentane:EtOAc = 10:1); **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 7.35 – 7.23 (m, 5H), 4.87 (br, 2H) 4.24 (q, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 8.1 Hz, 2H), 1.48 (tq, *J*<sup>1</sup> = 7.8 Hz, *J*<sup>2</sup> = 7.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ (ppm) = 164.9 (C), 153.0 (C), 144.3 (C), 134.3 (C), 129.1

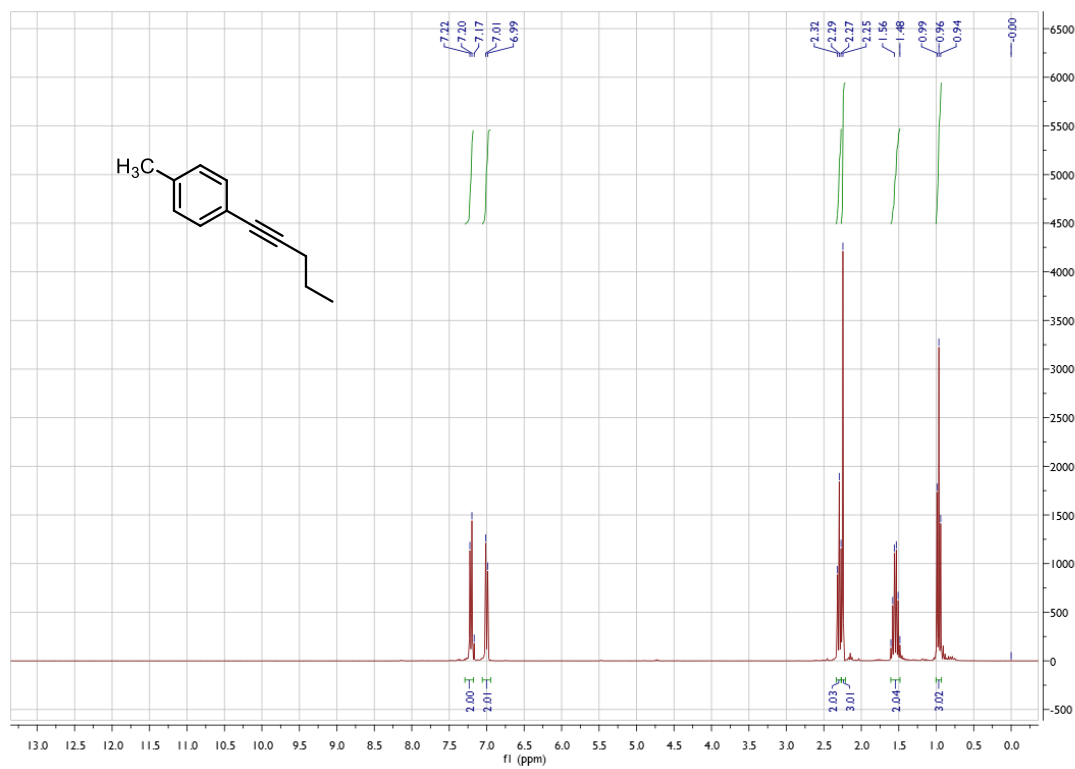


(CH), 128.6 (CH), 128.5 (C), 128.3 (CH), 100.3 (C), 60.0 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 14.6 (CH<sub>3</sub>), 14.1 (CH<sub>3</sub>); **<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  (ppm) = -73.5 (s, 3F); **HRMS** (ESI)  $m/z$  = 312.1029, calcd. for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup>, found: 312.1033; **IR** (neat, cm<sup>-1</sup>): 3479<sub>w</sub>, 3362<sub>w</sub>, 2961<sub>w</sub>, 2871<sub>w</sub>, 2253<sub>w</sub>, 2157<sub>w</sub>, 1669<sub>s</sub>, 1599<sub>s</sub>, 1549<sub>w</sub>, 1469<sub>m</sub>, 1369<sub>w</sub>, 1306<sub>s</sub>, 1234<sub>m</sub>, 1172<sub>w</sub>, 1126<sub>m</sub>, 1084<sub>m</sub>, 1028<sub>w</sub>, 763<sub>m</sub>, 698<sub>m</sub>, 616<sub>w</sub>.

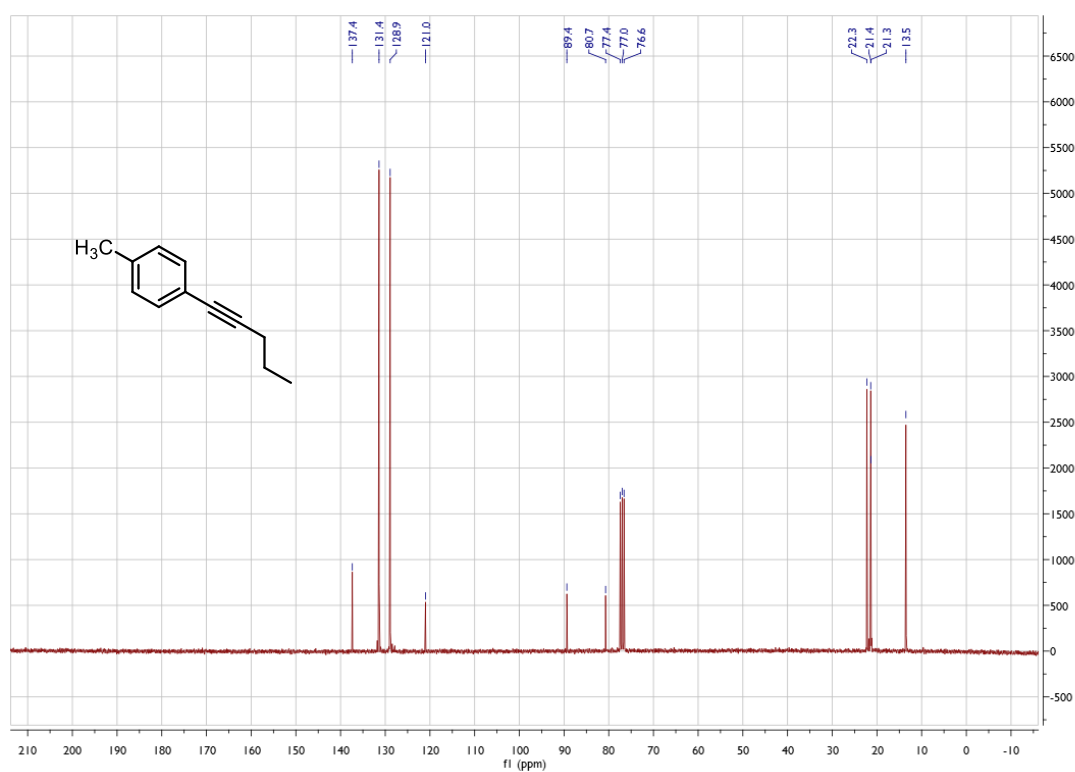
## 5. Spectra

### Spectra of alkynes 3

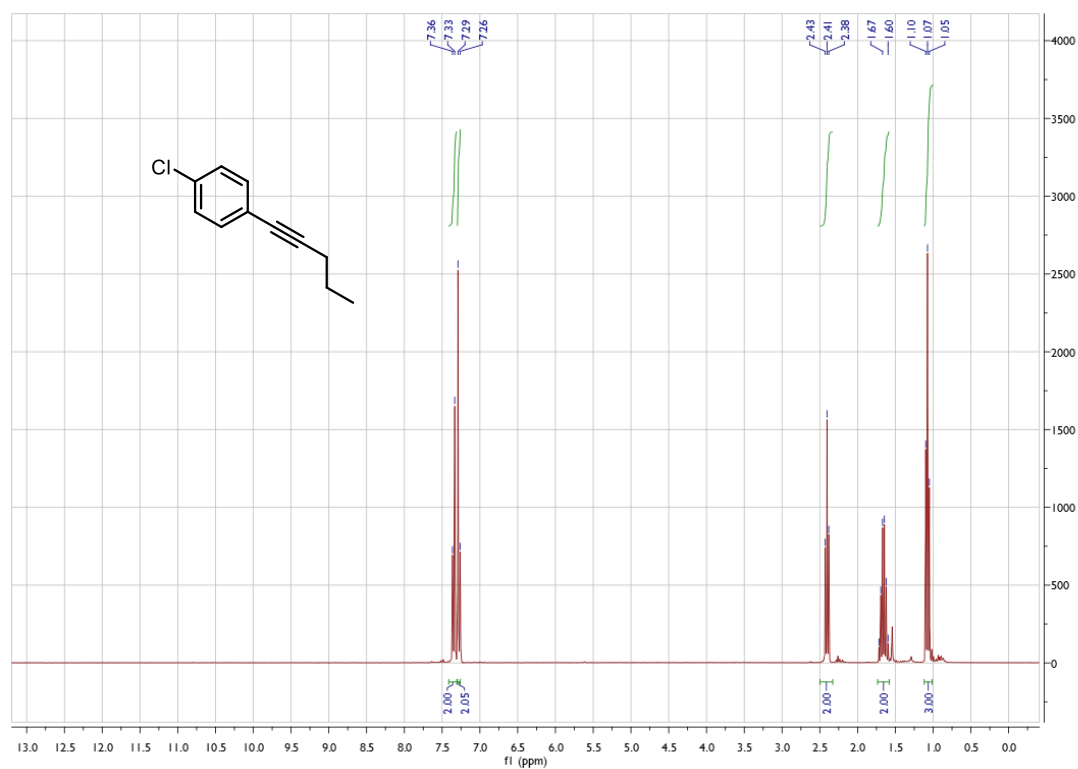
#### $^1\text{H}$ NMR Spectrum of 1-methyl-4-(pent-1-yn-1-yl)benzene 3b



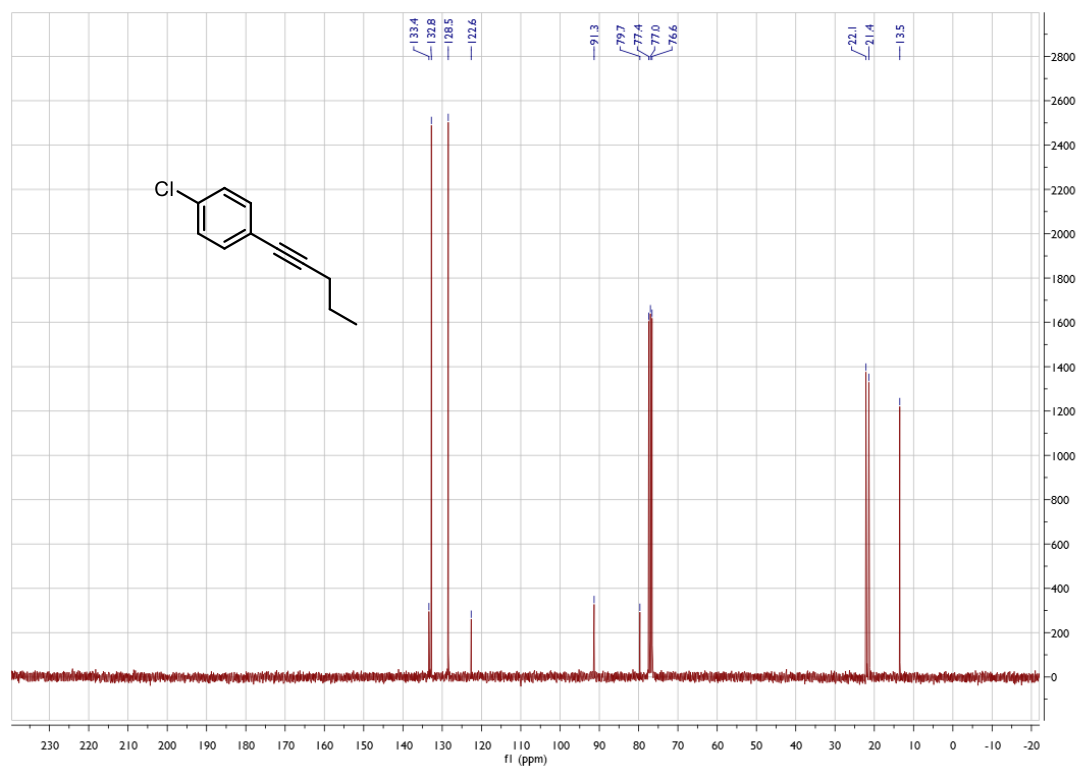
#### $^{13}\text{C}$ NMR Spectrum of 1-methyl-4-(pent-1-yn-1-yl)benzene 3b



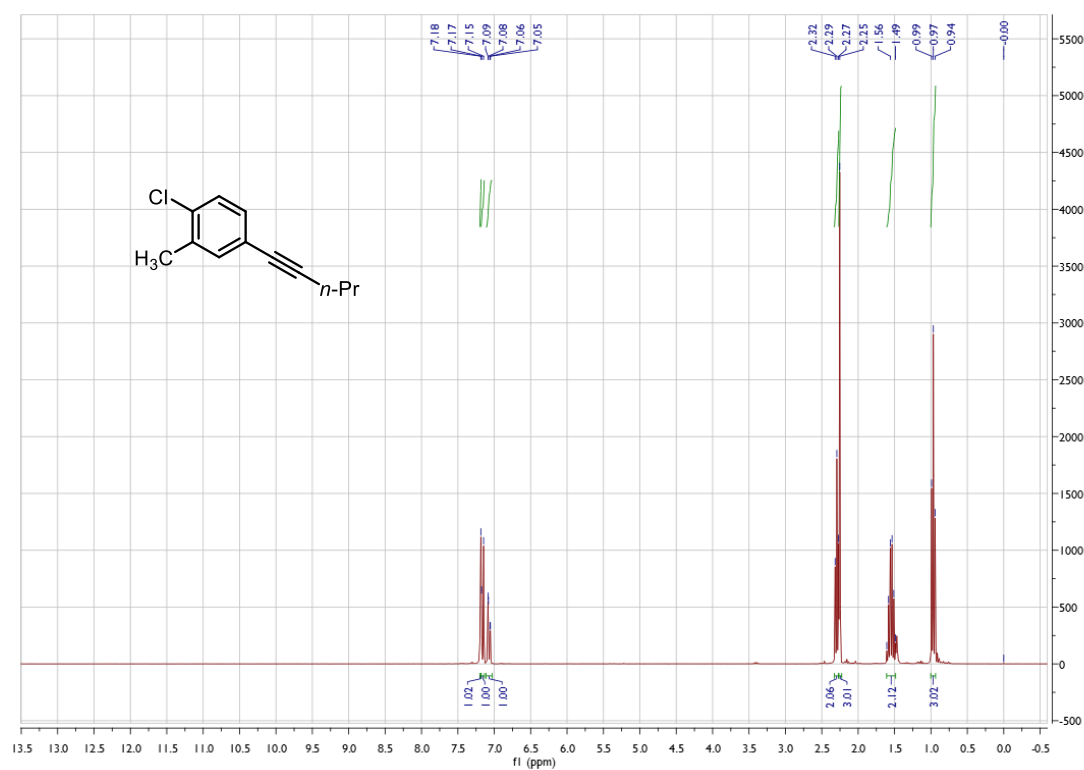
### <sup>1</sup>H NMR Spectrum of 1-chloro-4-(pent-1-yn-1-yl)benzene **3c**



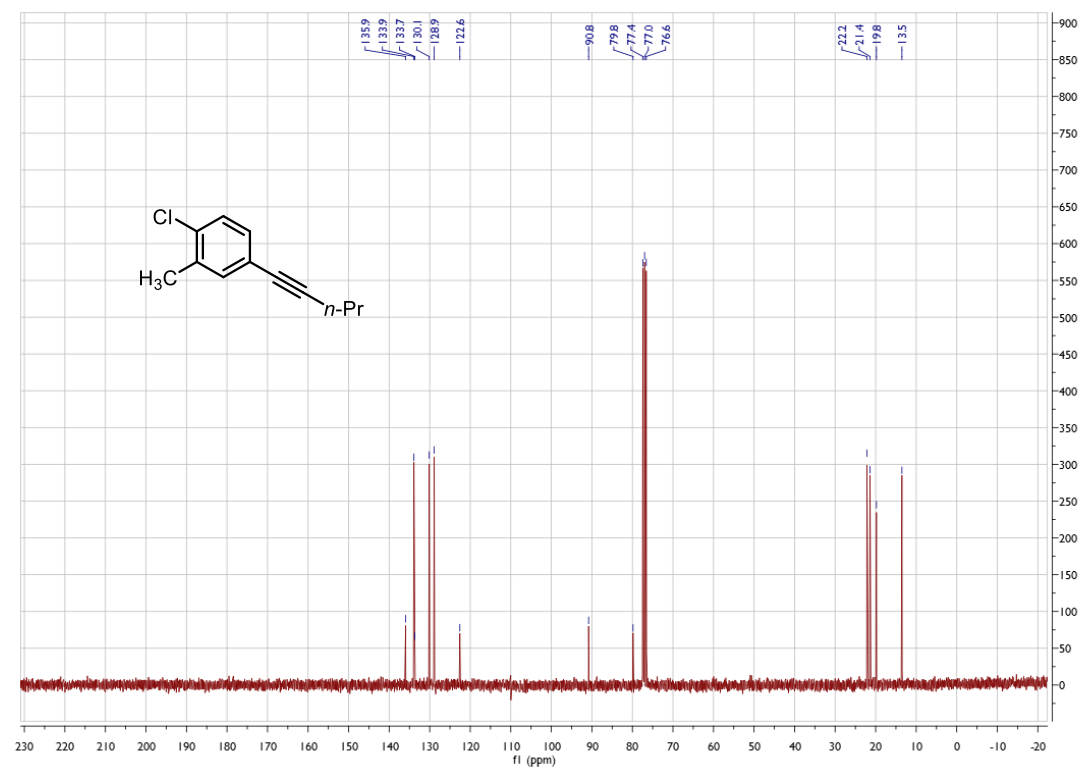
### <sup>13</sup>C NMR Spectrum of 1-chloro-4-(pent-1-yn-1-yl)benzene **3c**



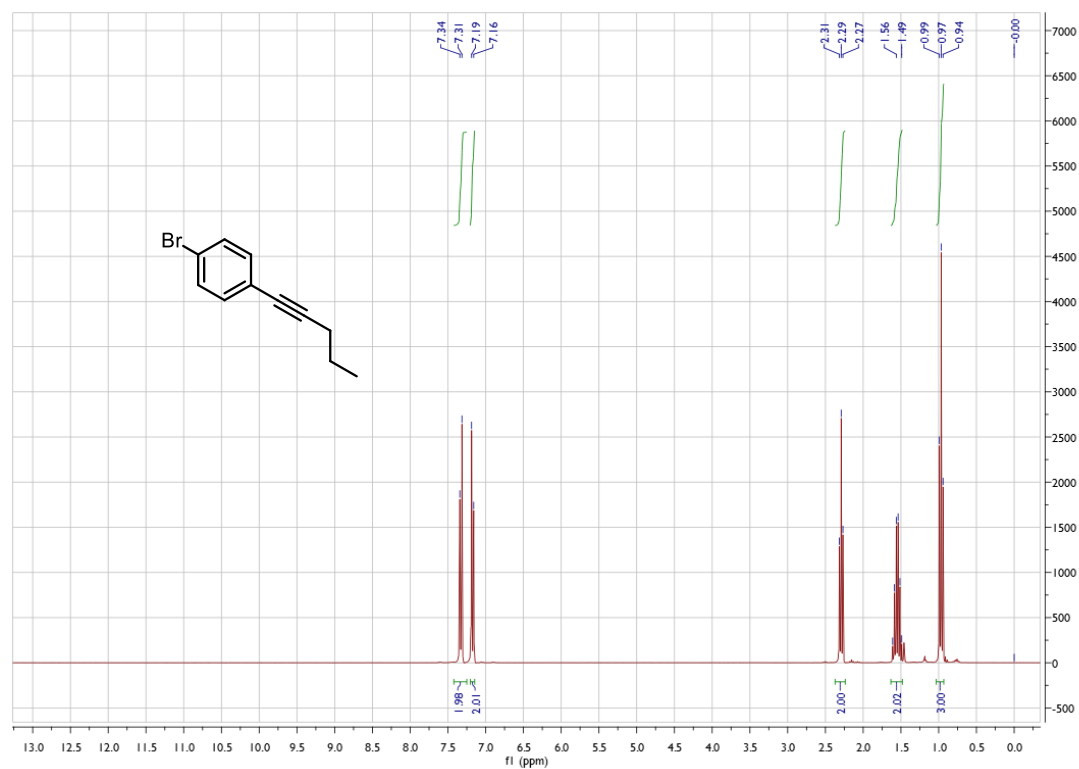
### <sup>1</sup>H NMR Spectrum of 1-Chloro-2-methyl-4-(pent-1-yn-1-yl)benzene 3d



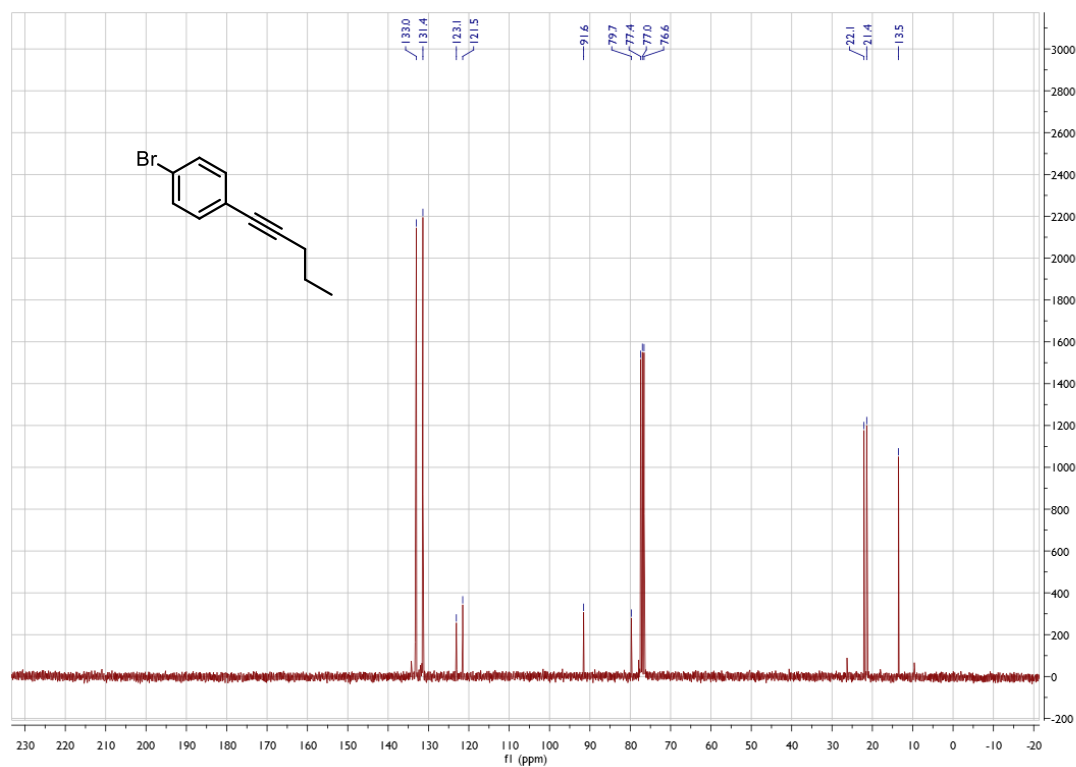
### <sup>13</sup>C NMR Spectrum of 1-Chloro-2-methyl-4-(pent-1-yn-1-yl)benzene 3d



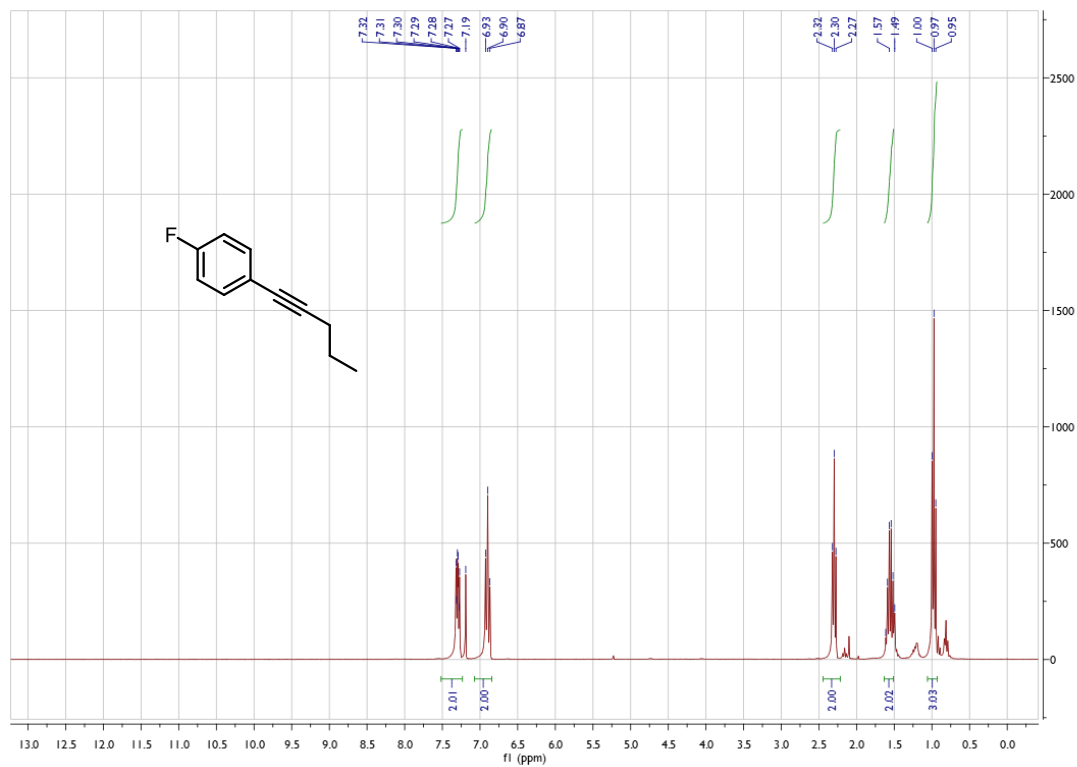
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(pent-1-yn-1-yl)benzene **3e**



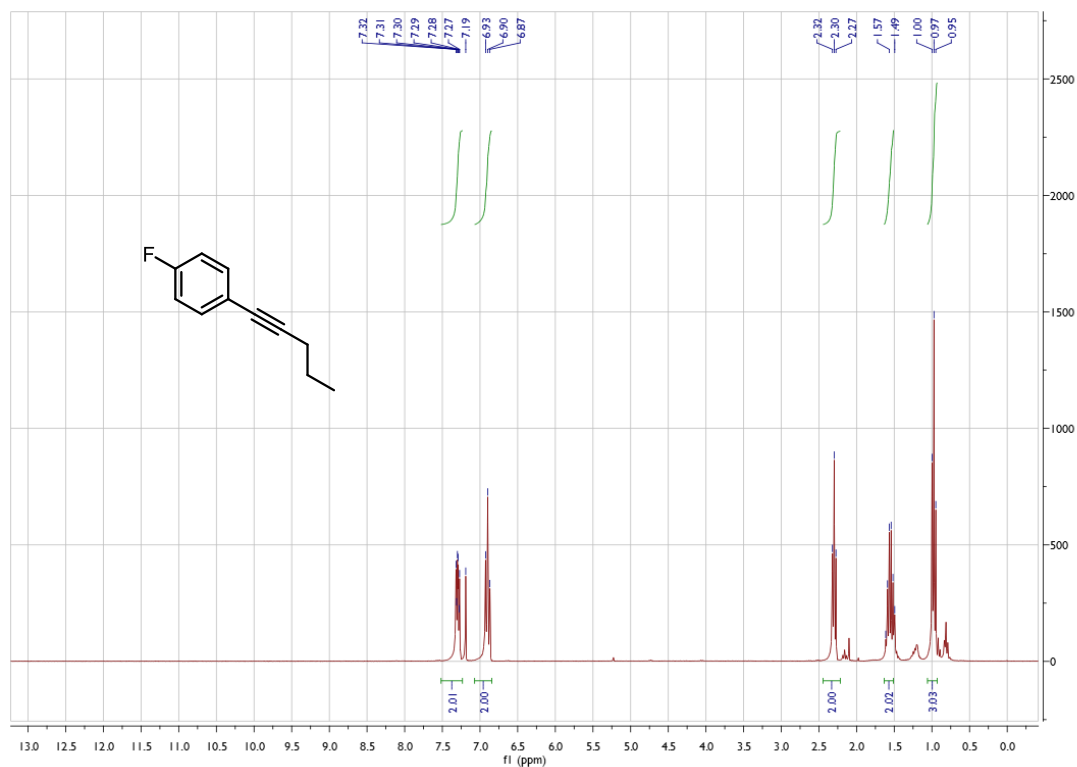
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(pent-1-yn-1-yl)benzene **3e**



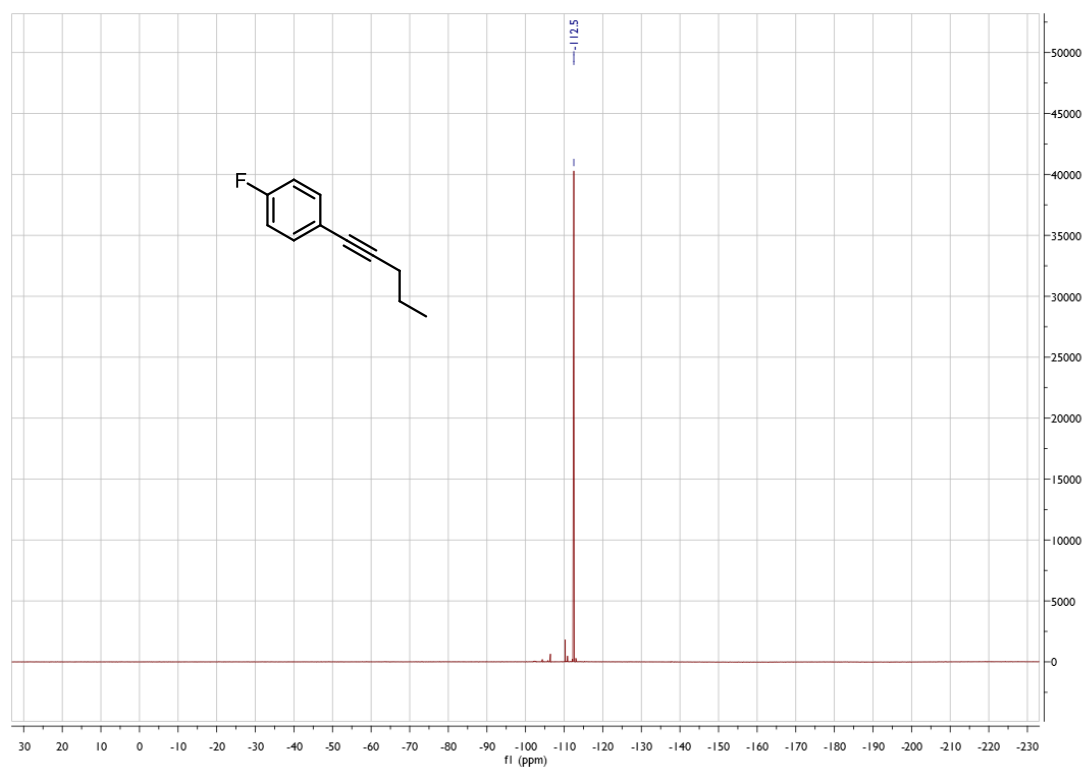
### <sup>1</sup>H NMR Spectrum of 1-fluoro-4-(pent-1-yn-1-yl)benzene 3f



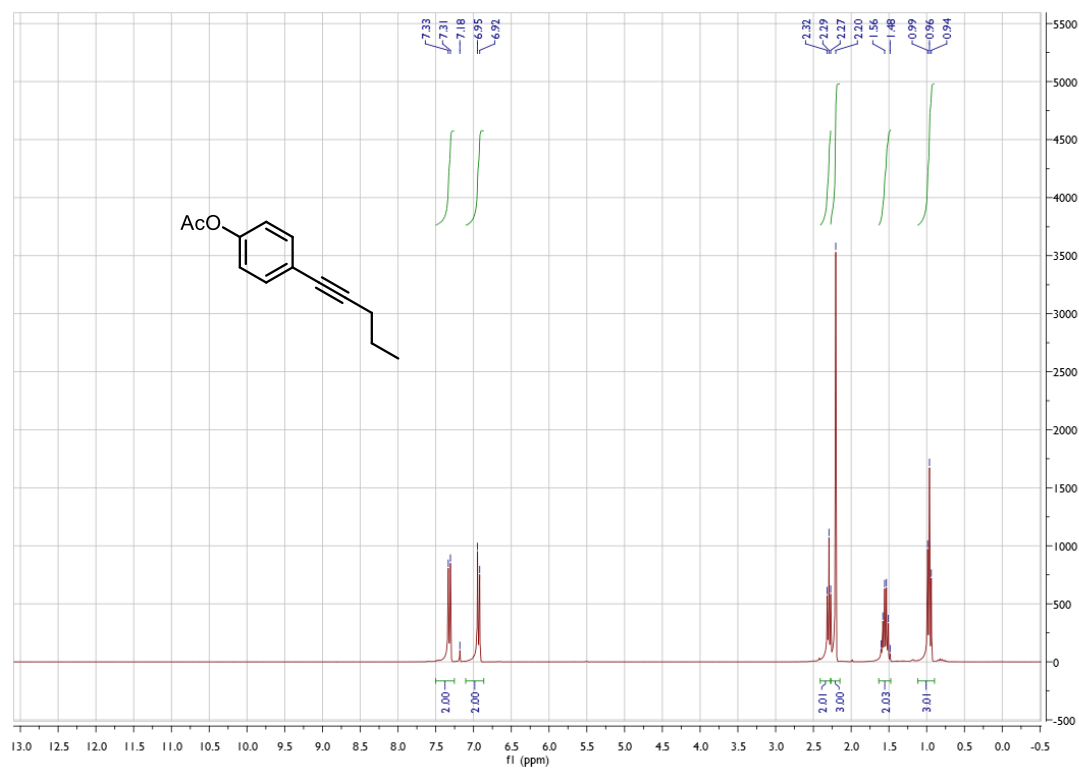
### <sup>13</sup>C NMR Spectrum of 1-fluoro-4-(pent-1-yn-1-yl)benzene 3f



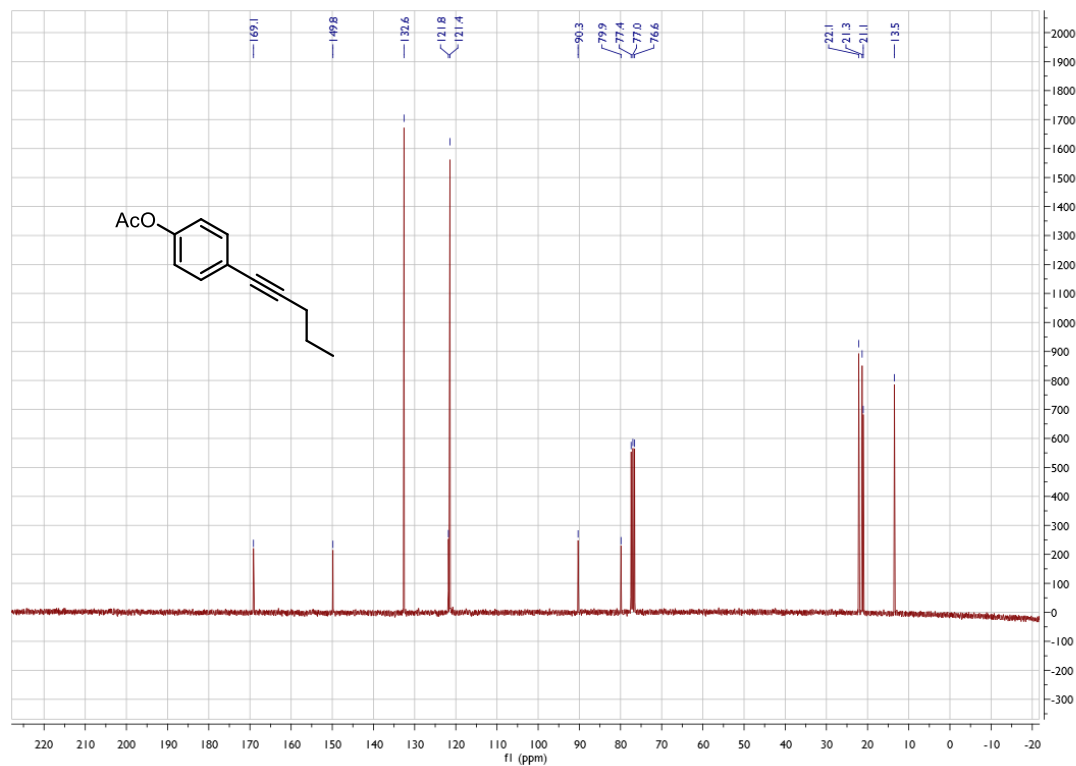
# <sup>19</sup>F NMR Spectrum of 1-fluoro-4-(pent-1-yn-1-yl)benzene 3f



### <sup>1</sup>H NMR Spectrum of 4-(pent-1-yn-1-yl)phenyl acetate 3g

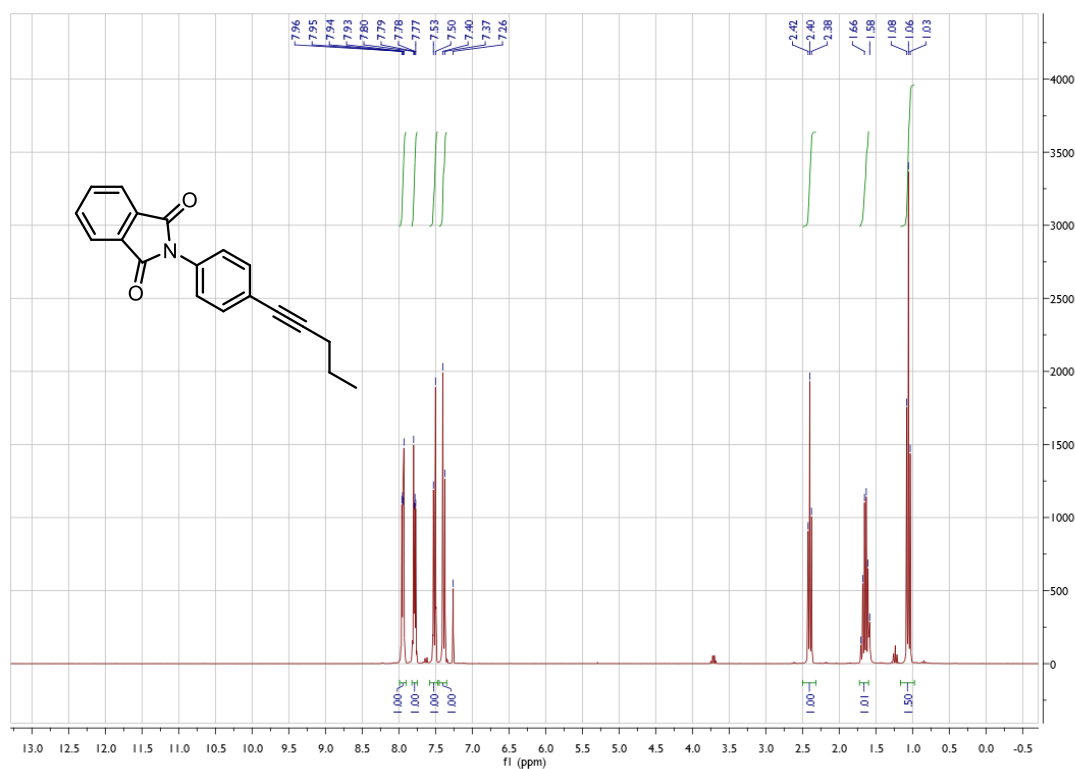


### <sup>13</sup>C NMR Spectrum of 4-(pent-1-yn-1-yl)phenyl acetate 3g

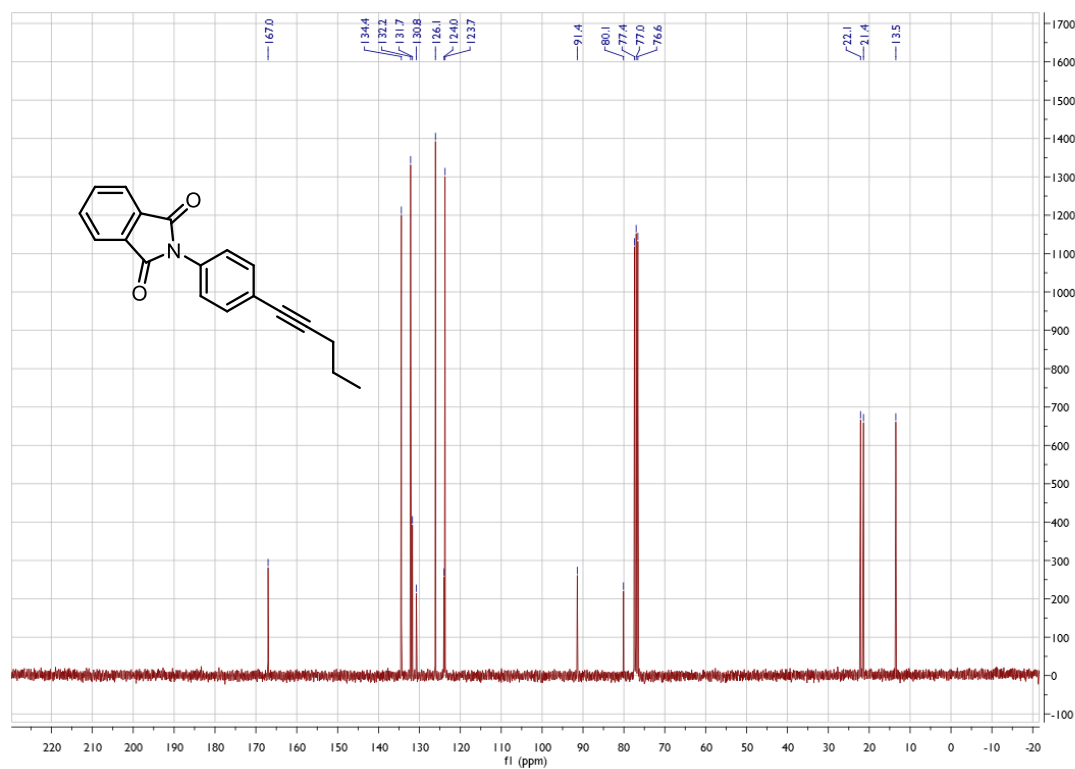




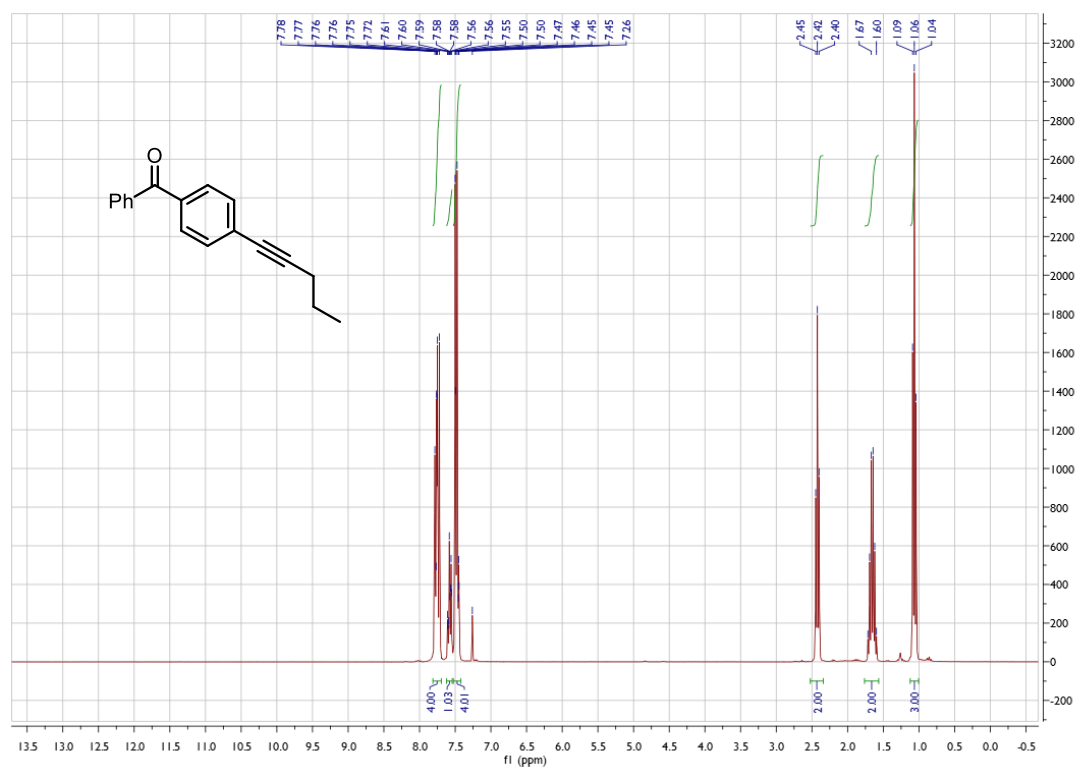
# <sup>1</sup>H NMR Spectrum of 2-(4-(pent-1-yn-1-yl)phenyl)isoindoline-1,3-dione 3h



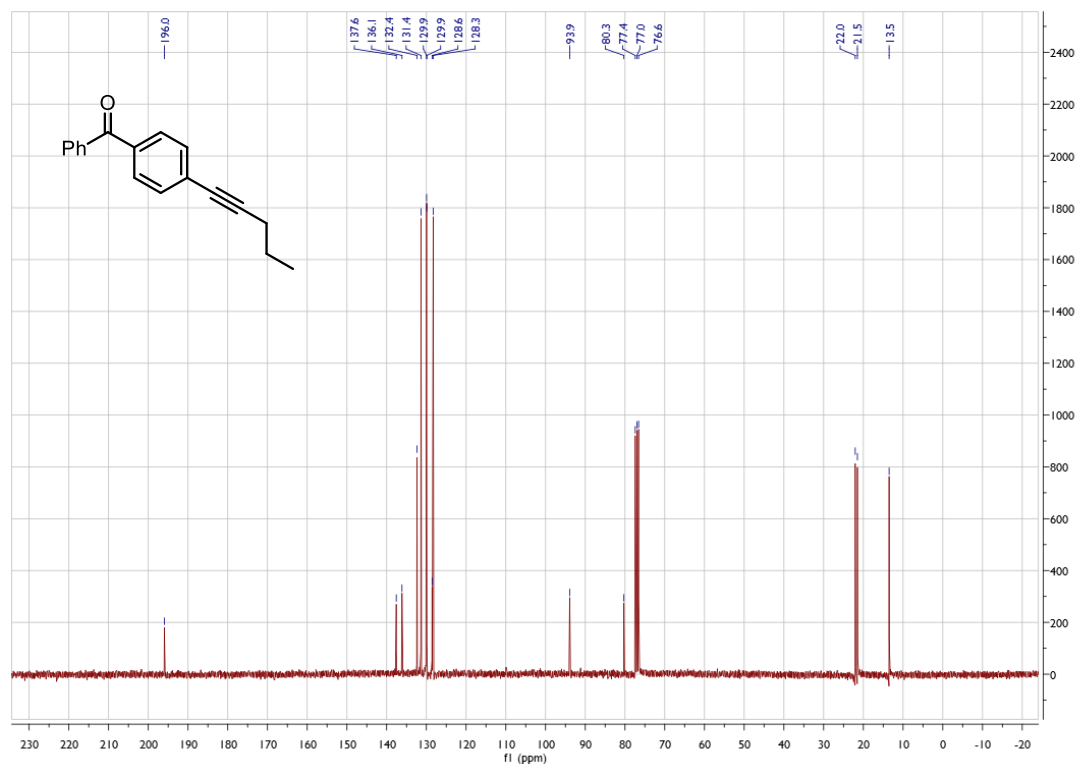
# <sup>13</sup>C NMR Spectrum of 2-(4-(pent-1-yn-1-yl)phenyl)isoindoline-1,3-dione 3h



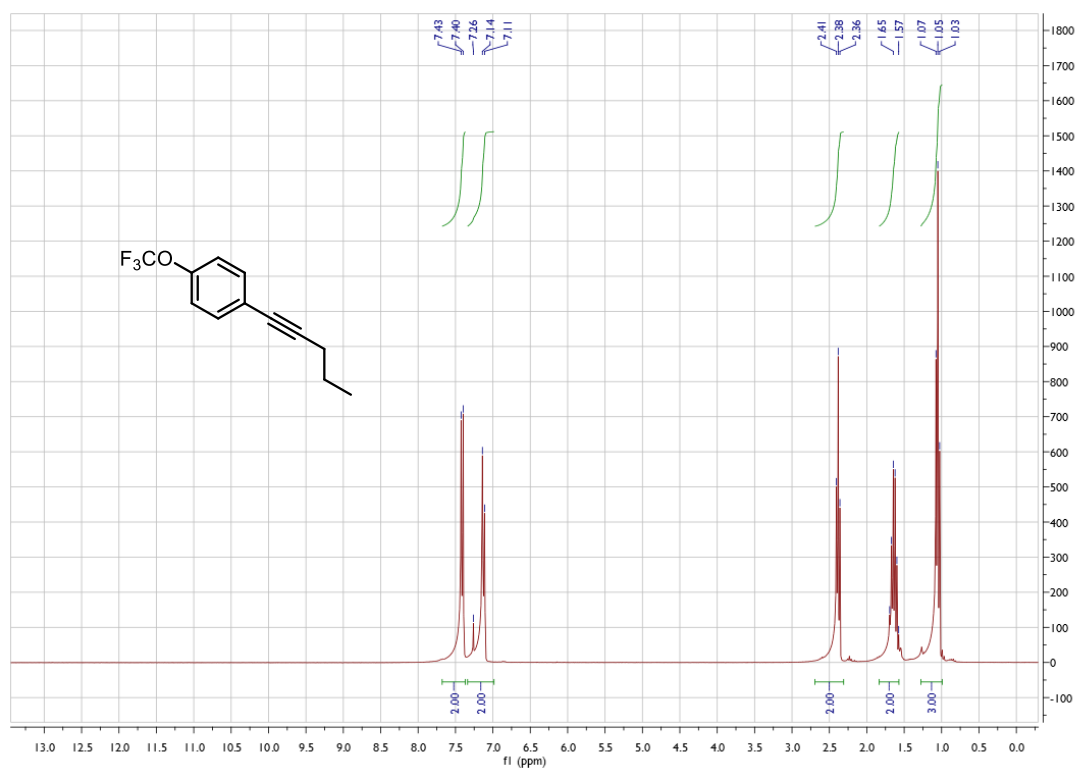
# <sup>1</sup>H NMR Spectrum of (4-(pent-1-yn-1-yl)phenyl)(phenyl)methanone 3i



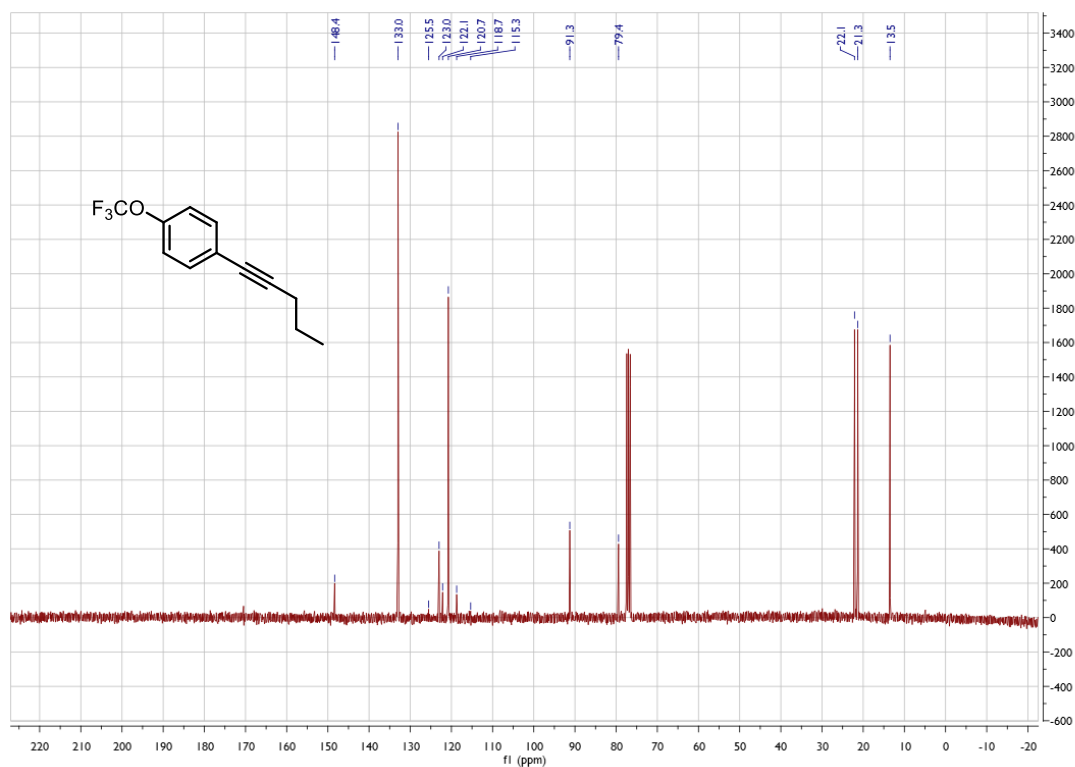
# <sup>13</sup>C NMR Spectrum of (4-(pent-1-yn-1-yl)phenyl)(phenyl)methanone 3i



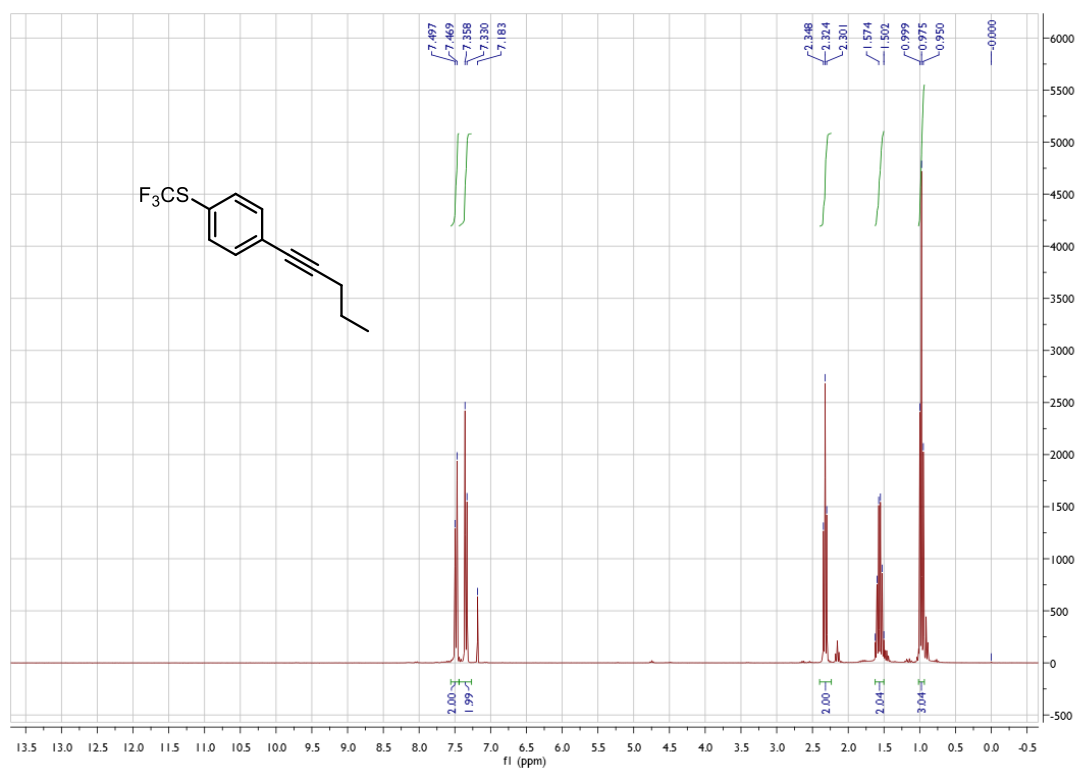
### <sup>1</sup>H NMR Spectrum of 1-(pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene **3j**



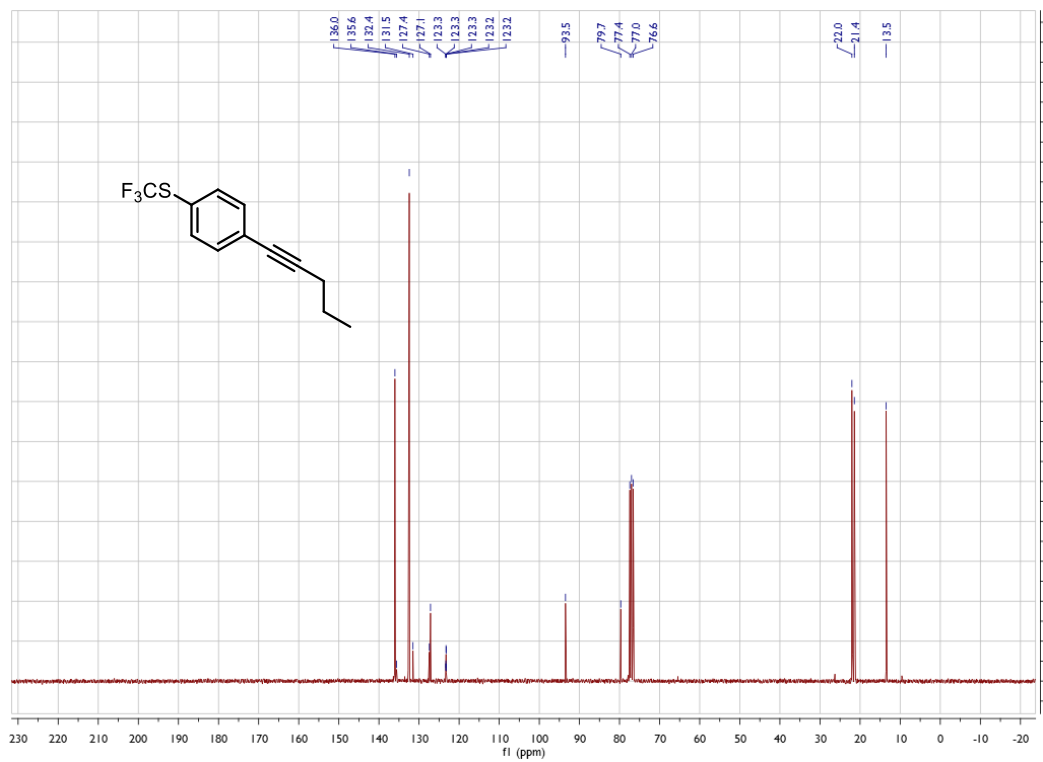
### <sup>1</sup>H NMR Spectrum of 1-(pent-1-yn-1-yl)-4-(trifluoromethoxy)benzene **3j**



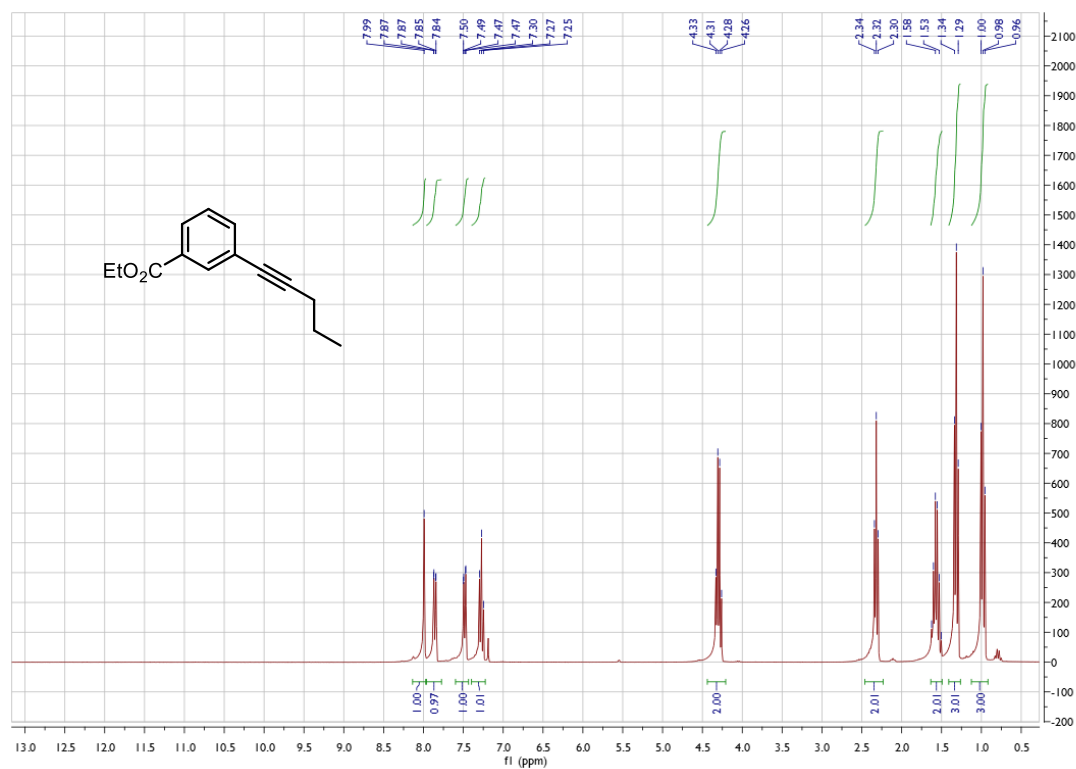
### <sup>1</sup>H NMR Spectrum of (4-(pent-1-yn-1-yl)phenyl)(trifluoromethyl)sulfane 3k



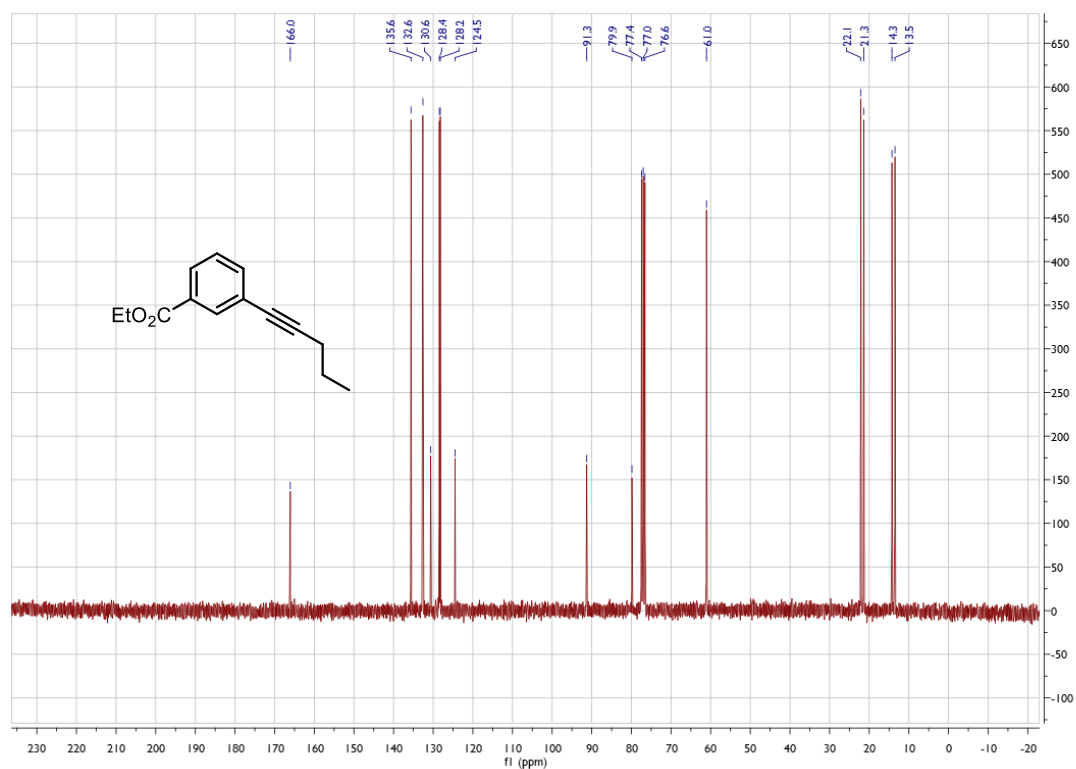
### <sup>13</sup>C NMR Spectrum of (4-(pent-1-yn-1-yl)phenyl)(trifluoromethyl)sulfane 3k



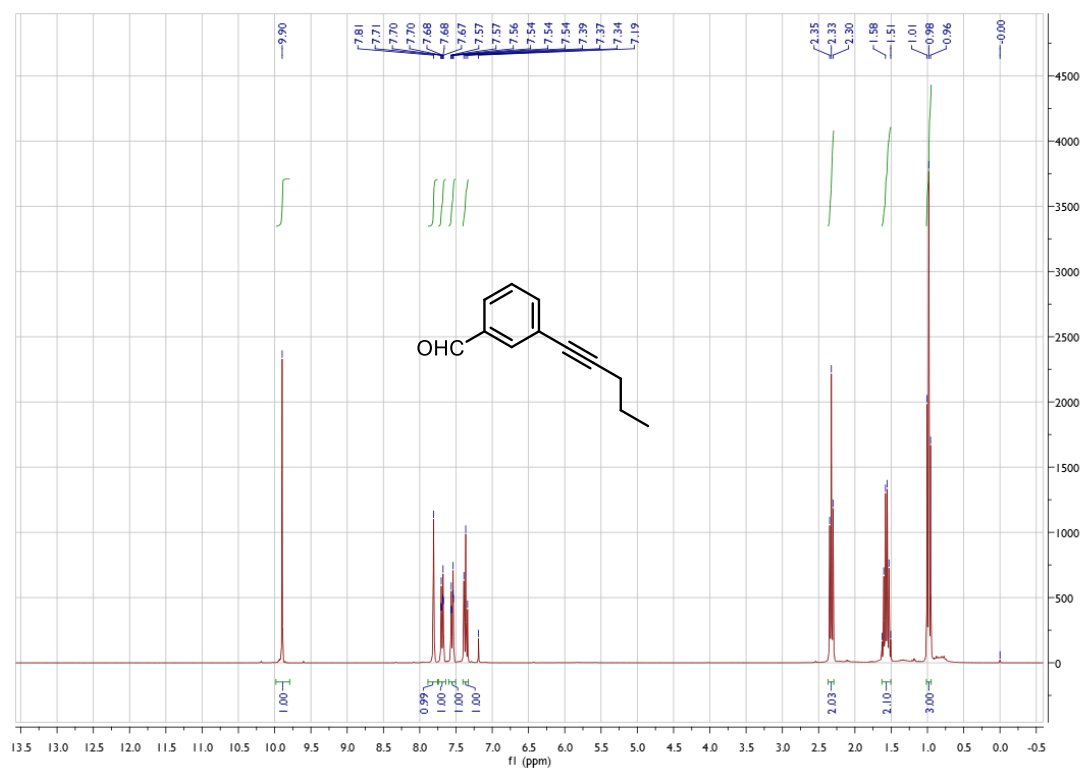
# <sup>1</sup>H NMR Spectrum of ethyl 3-(pent-1-yn-1-yl)benzoate 3l



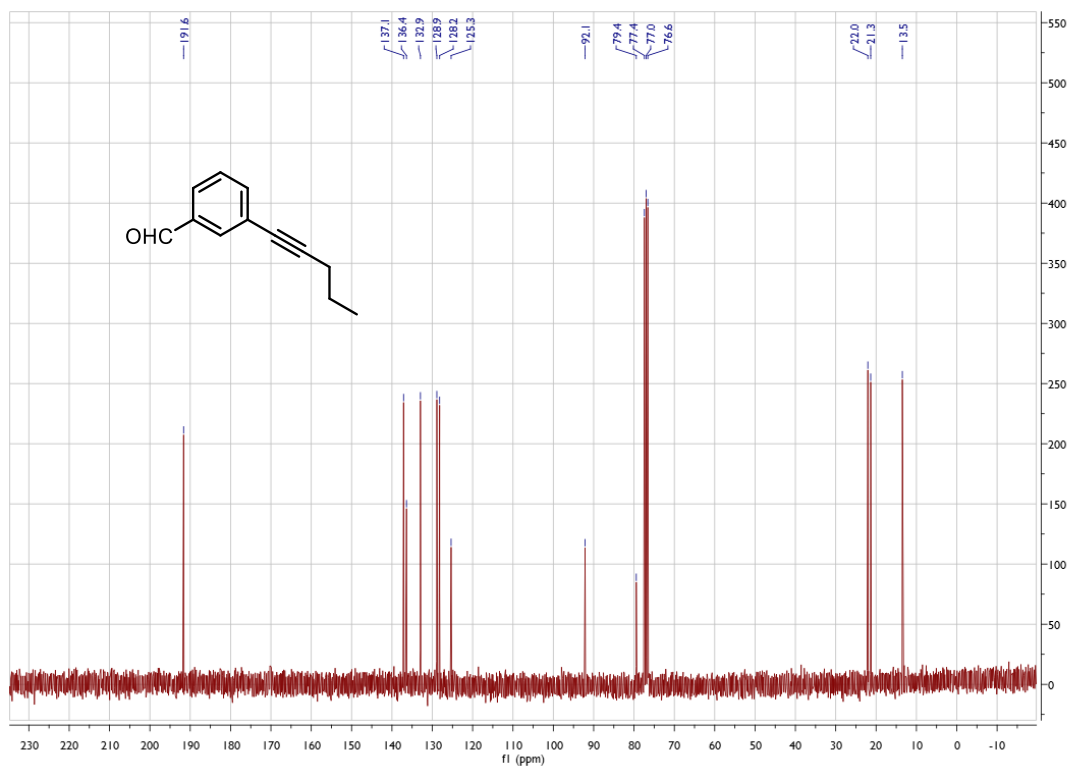
# <sup>13</sup>C NMR Spectrum of ethyl 3-(pent-1-yn-1-yl)benzoate 3l



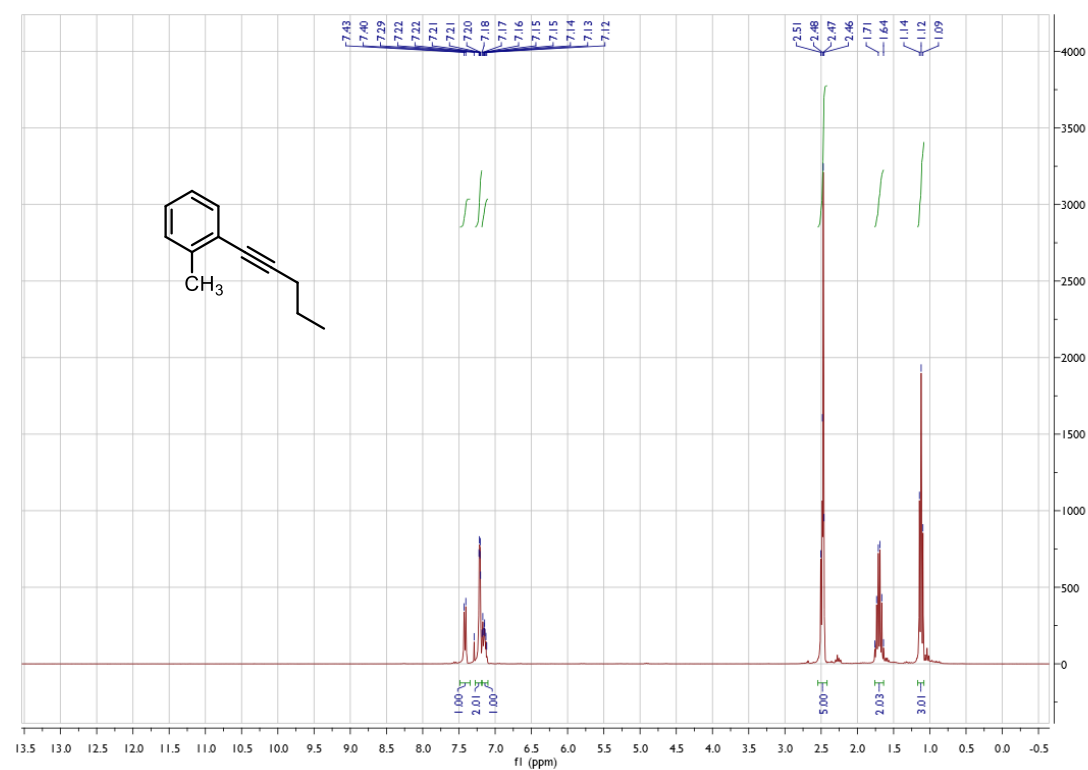
# <sup>1</sup>H NMR Spectrum of 3-(Pent-1-yn-1-yl)benzaldehyde 3m



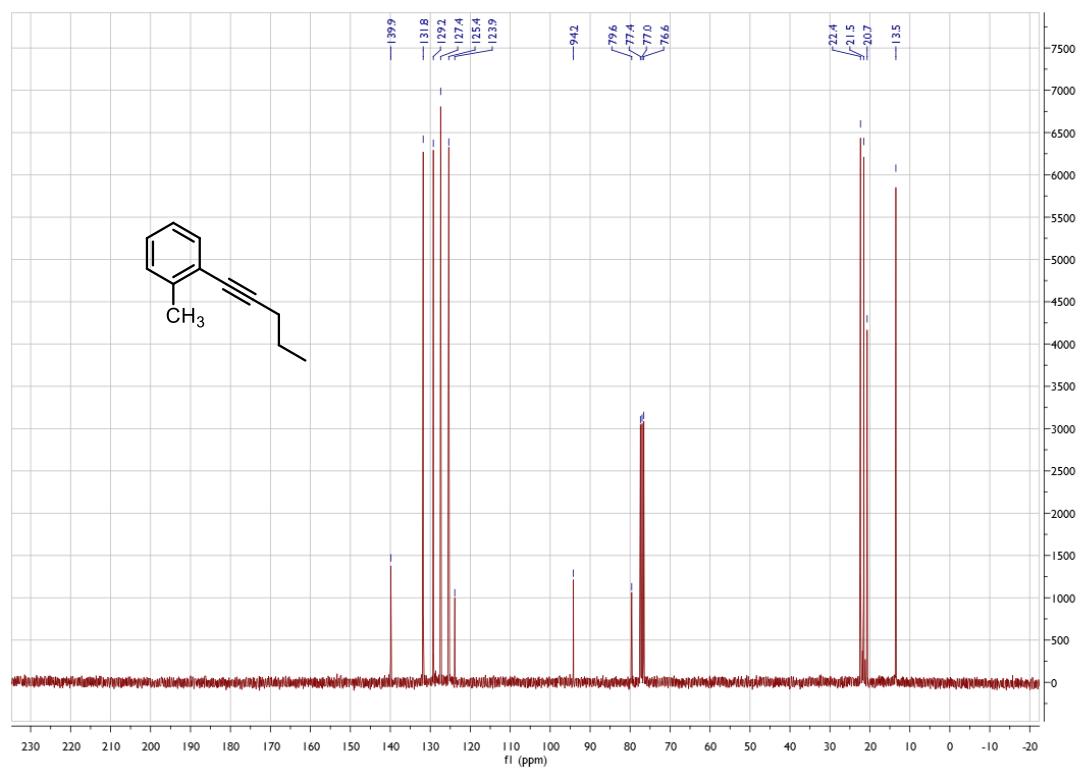
# <sup>13</sup>C NMR Spectrum of 3-(Pent-1-yn-1-yl)benzaldehyde 3m



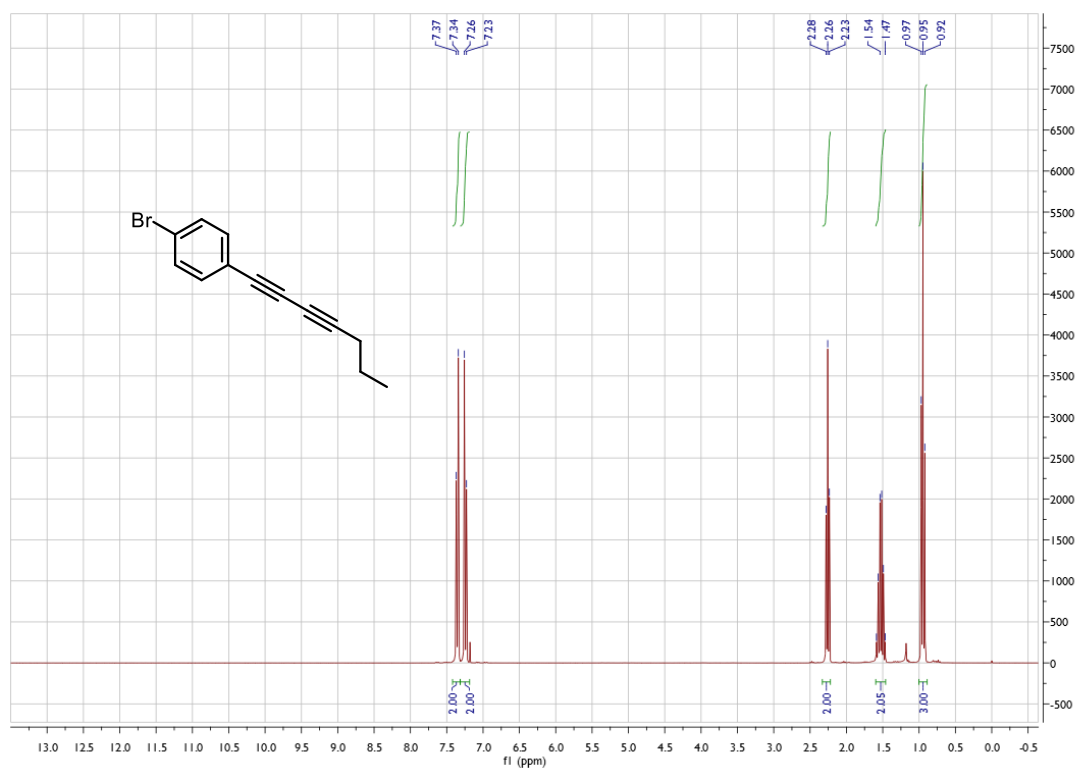
# <sup>1</sup>H NMR Spectrum of 1-methyl-2-(pent-1-yn-1-yl)benzene 3n



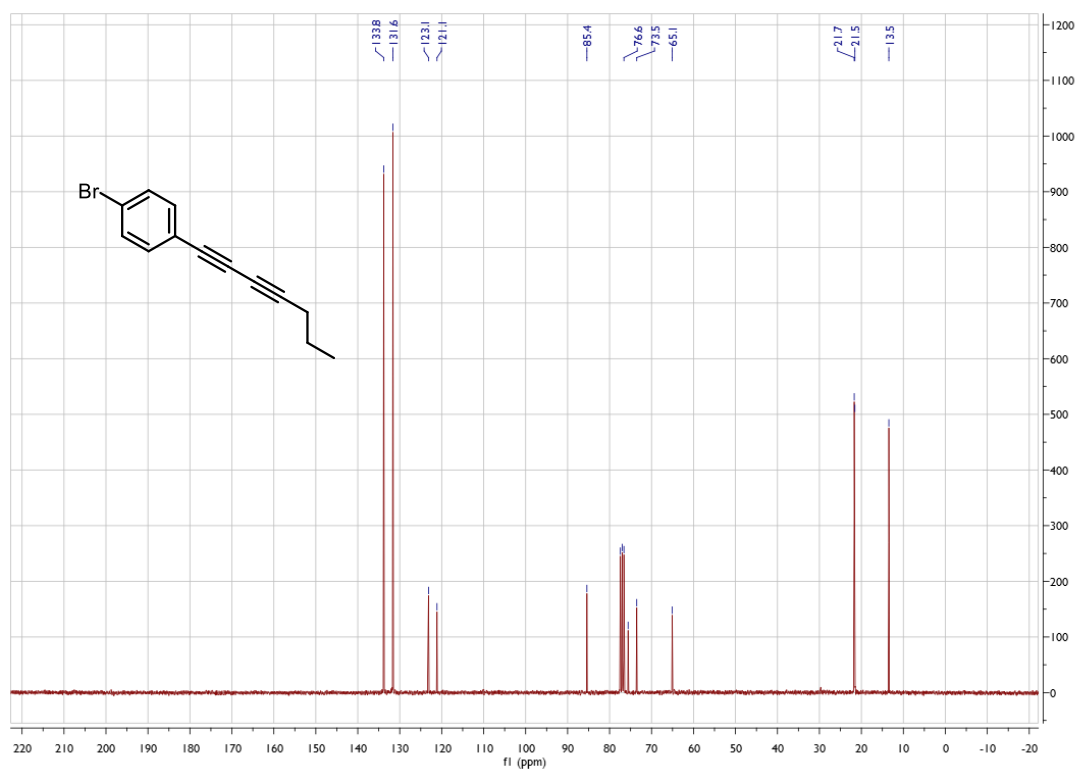
# <sup>13</sup>C NMR Spectrum of 1-methyl-2-(pent-1-yn-1-yl)benzene 3n



### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(hepta-1, 3-diyne-1-yl)benzene **3o**

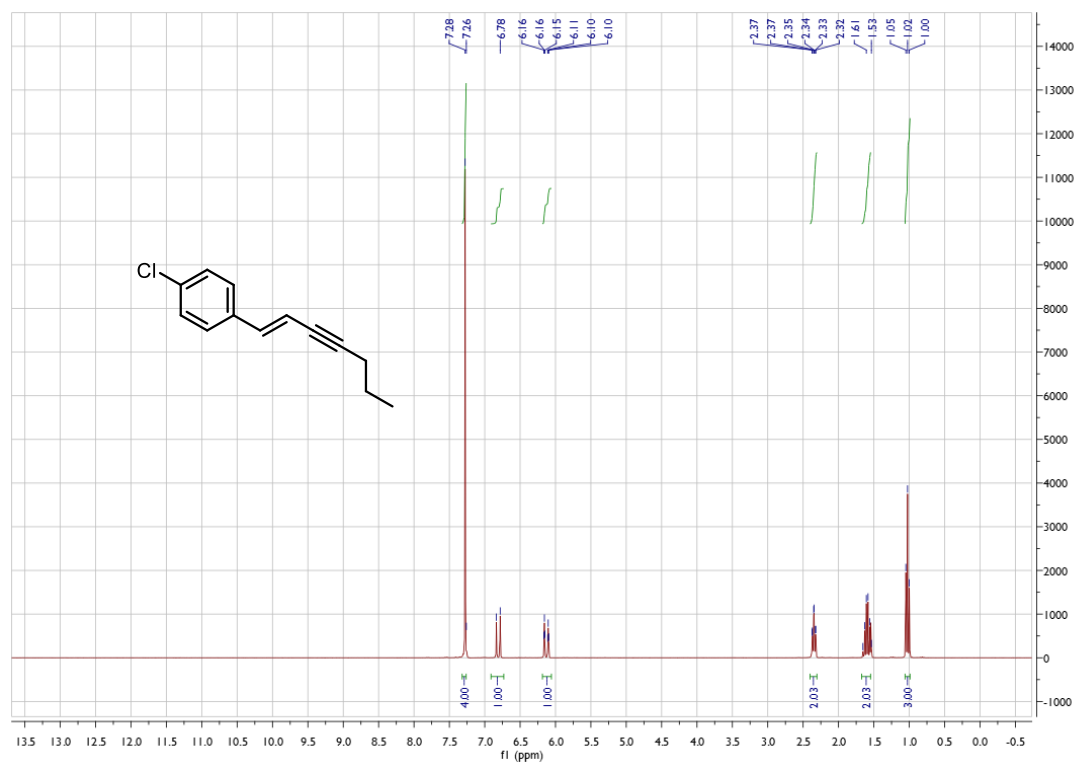


### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(hepta-1, 3-diyne-1-yl)benzene **3o**

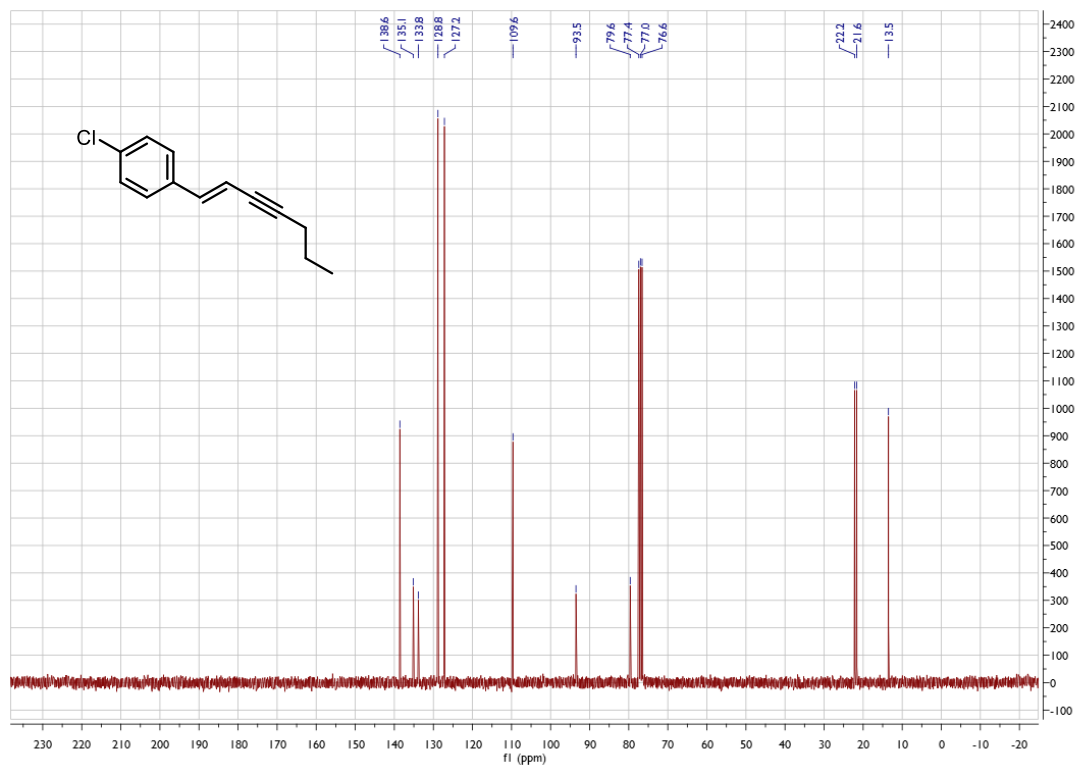




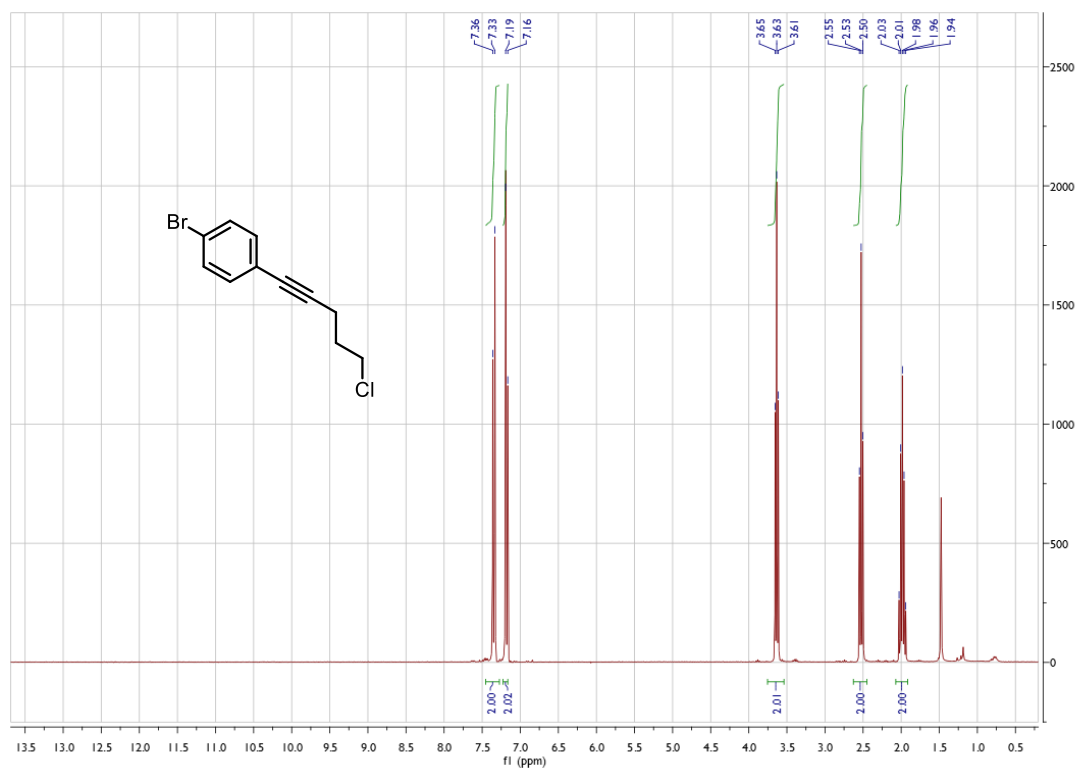
# <sup>1</sup>H NMR Spectrum of (*E*)-1-chloro-4-(hept-1-en-3-yn-1-yl)benzene 3p



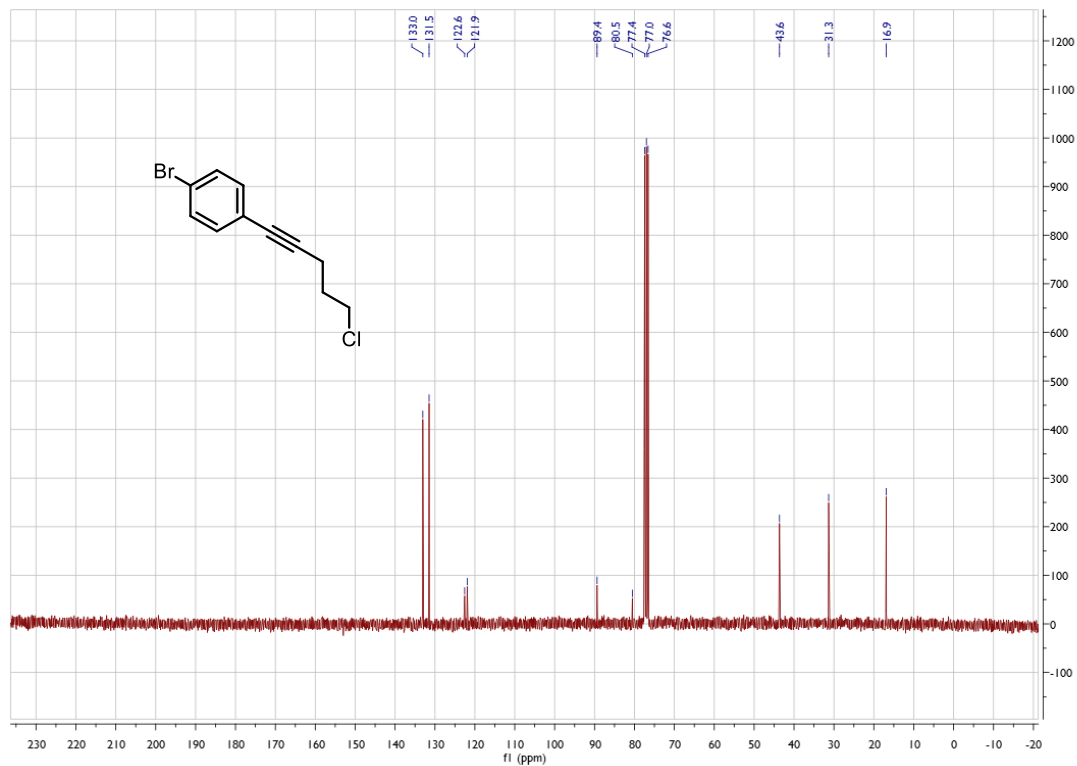
# <sup>13</sup>C NMR Spectrum of (*E*)-1-chloro-4-(hept-1-en-3-yn-1-yl)benzene 3p



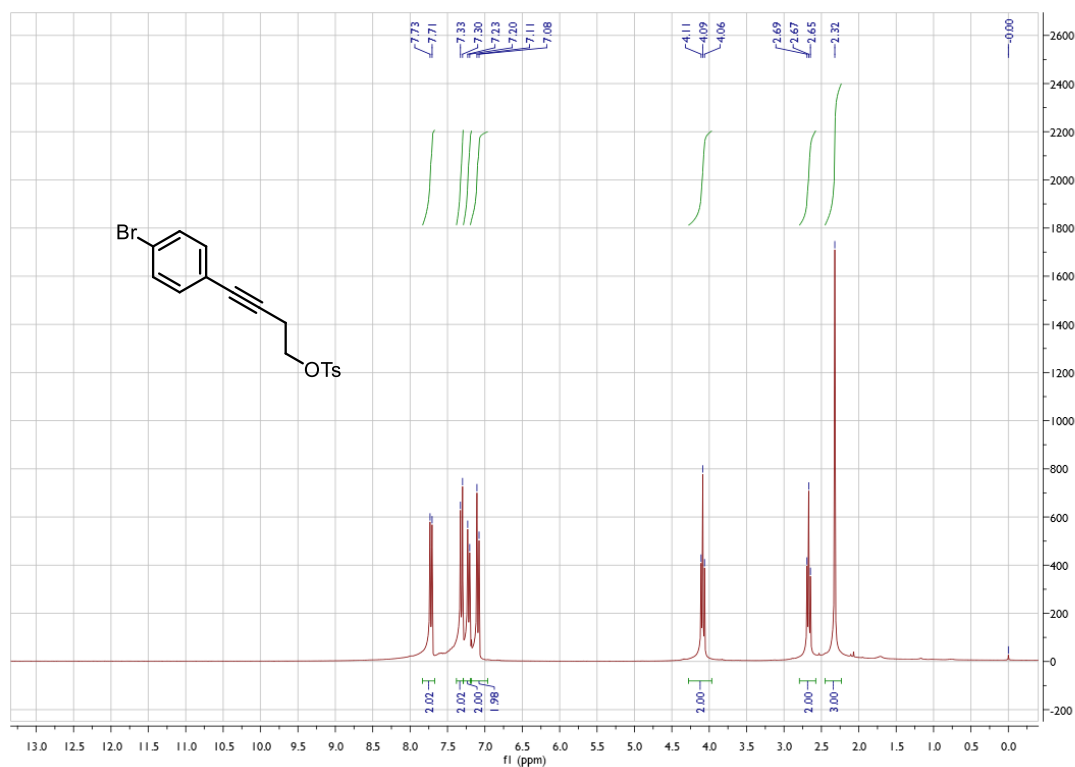
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(5-chloropent-1-yn-1-yl)benzene 3q



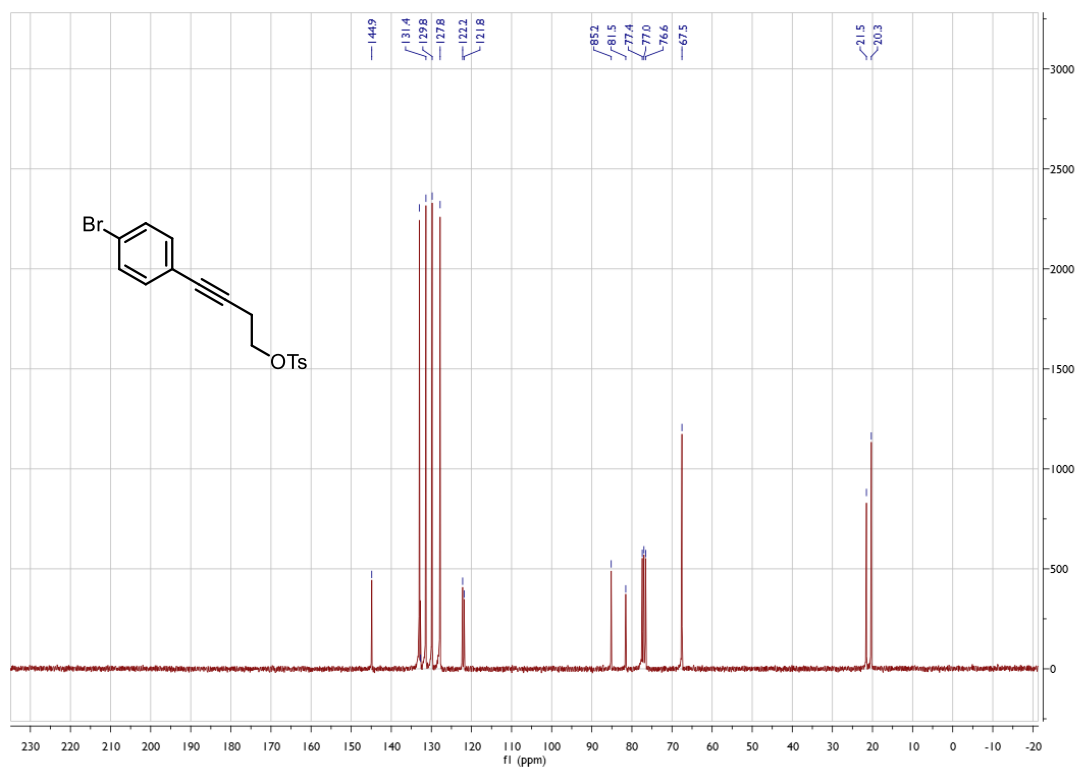
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(5-chloropent-1-yn-1-yl)benzene 3q



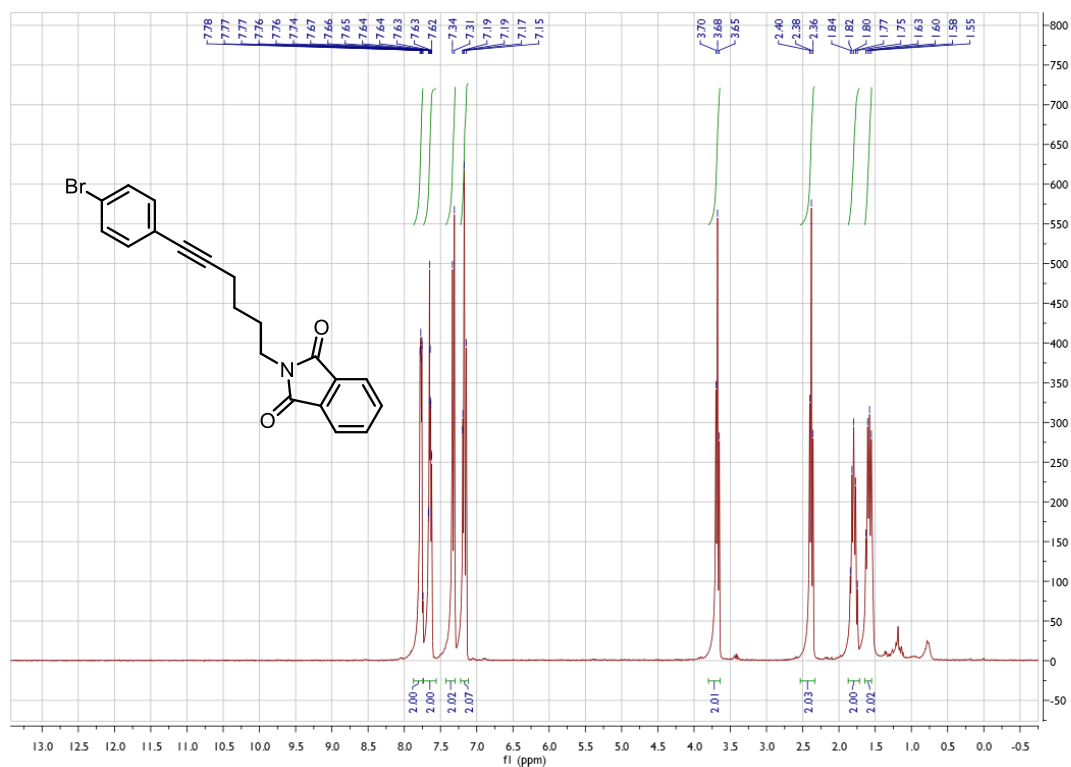
**<sup>1</sup>H NMR Spectrum of 4-(4-bromophenyl)but-3-yn-1-yl 4-methylbenzenesulfonate  
3r**



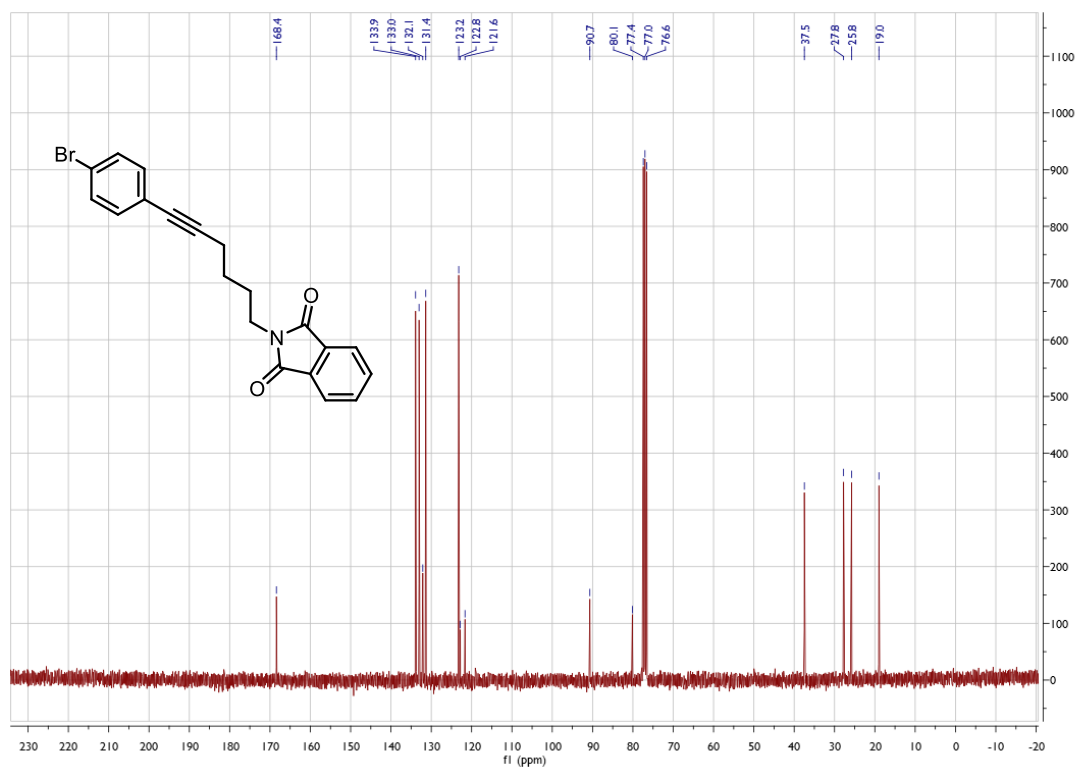
**<sup>13</sup>C NMR Spectrum of 4-(4-bromophenyl)but-3-yn-1-yl 4-methylbenzenesulfonate  
3r**



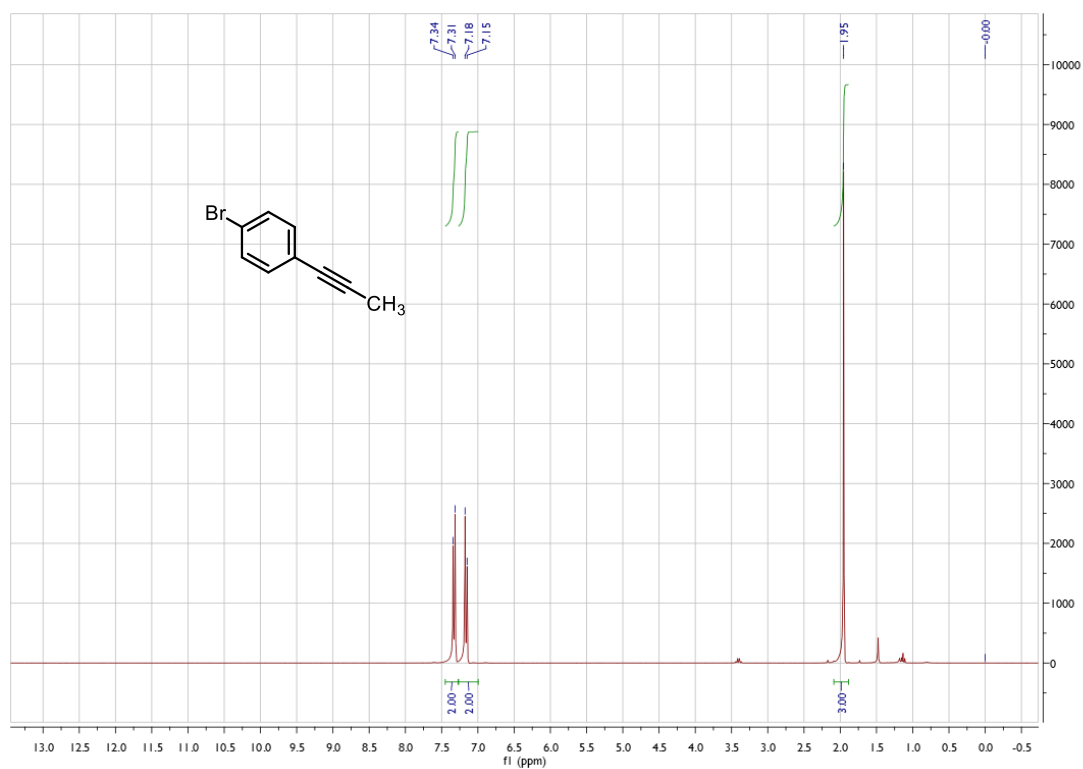
### <sup>1</sup>H NMR Spectrum of 2-(6-(4-bromophenyl)hex-5-yn-1-yl)isoindoline-1,3-dione **3s**



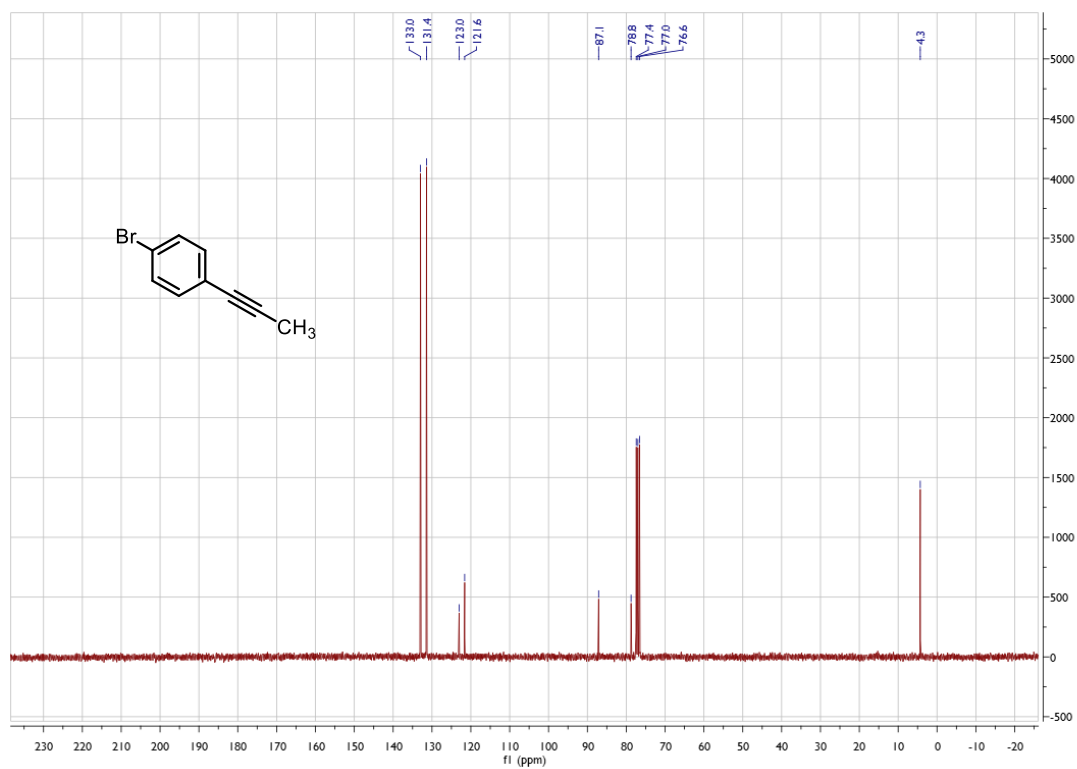
### <sup>13</sup>C NMR Spectrum of 2-(6-(4-bromophenyl)hex-5-yn-1-yl)isoindoline-1,3-dione **3s**



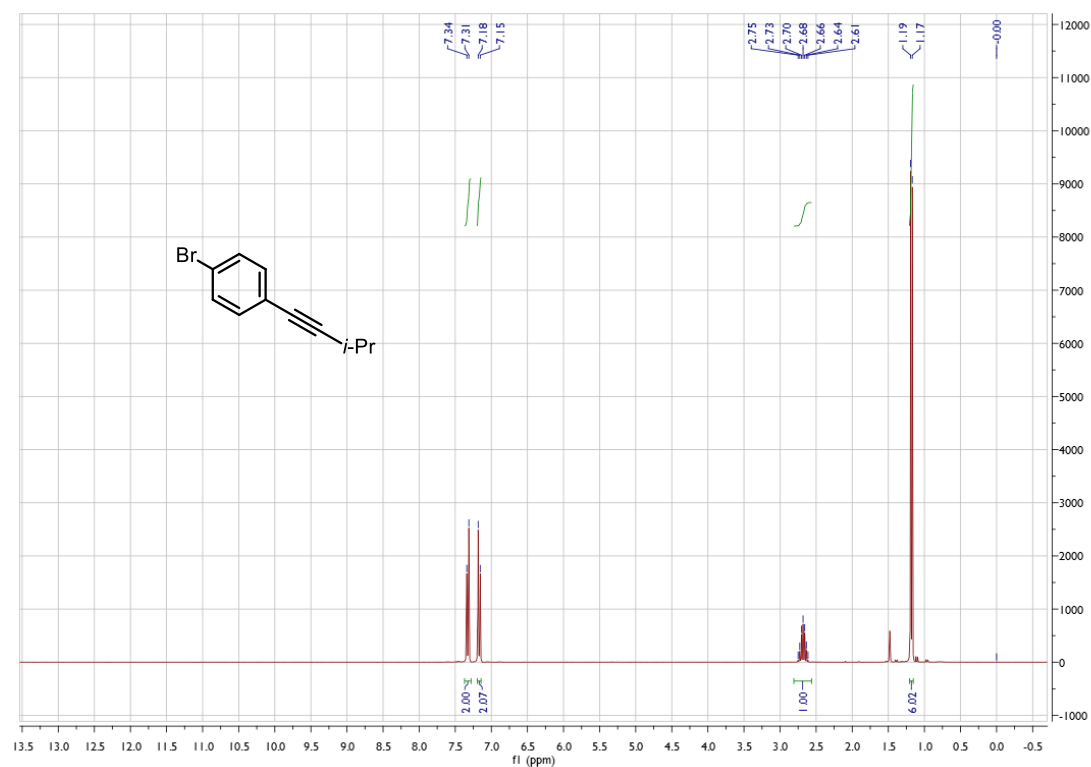
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(prop-1-yn-1-yl)benzene 3t



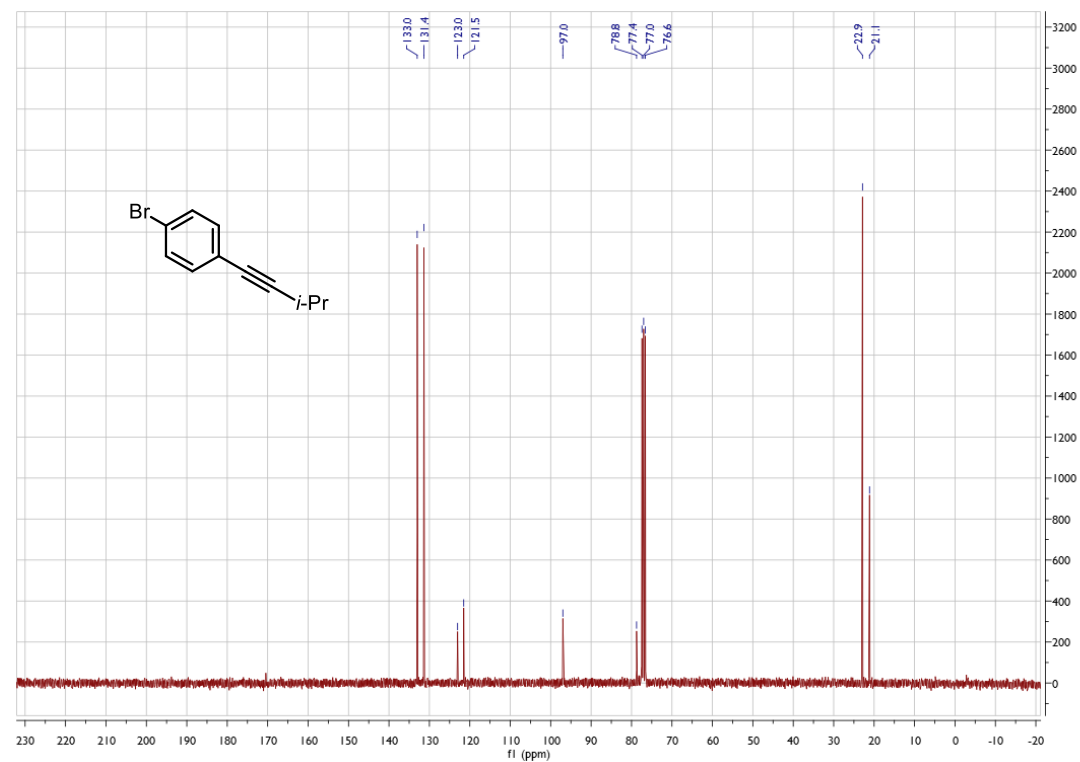
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(prop-1-yn-1-yl)benzene 3t



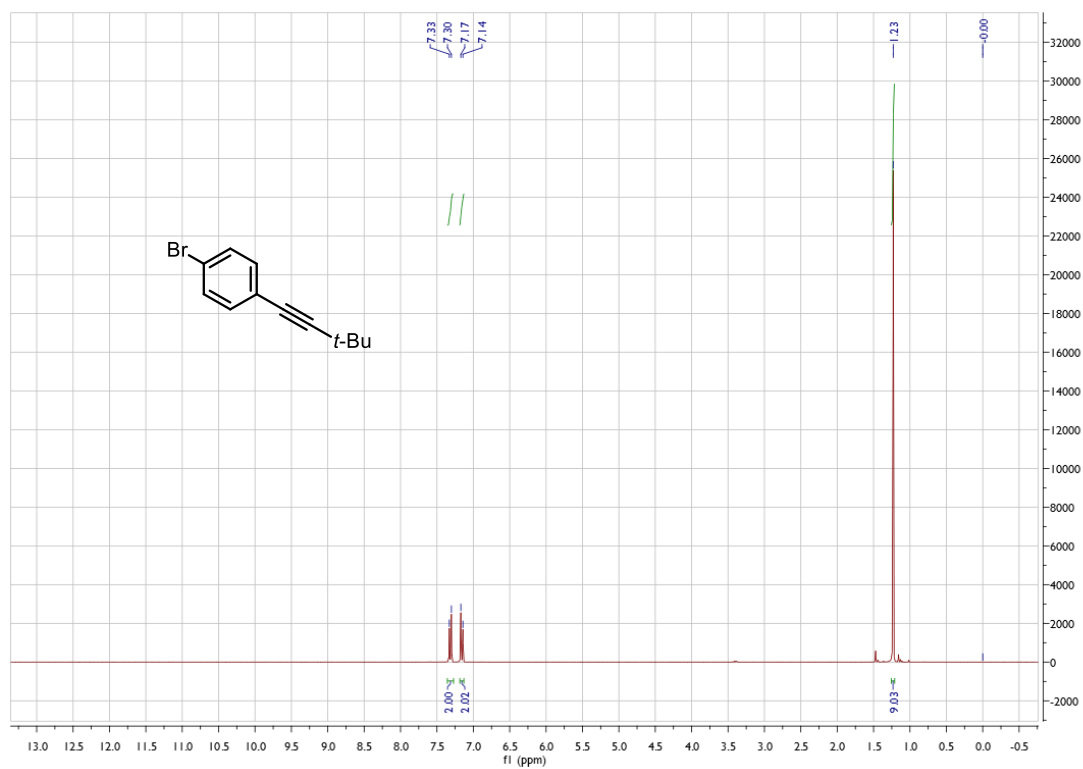
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene **3u**



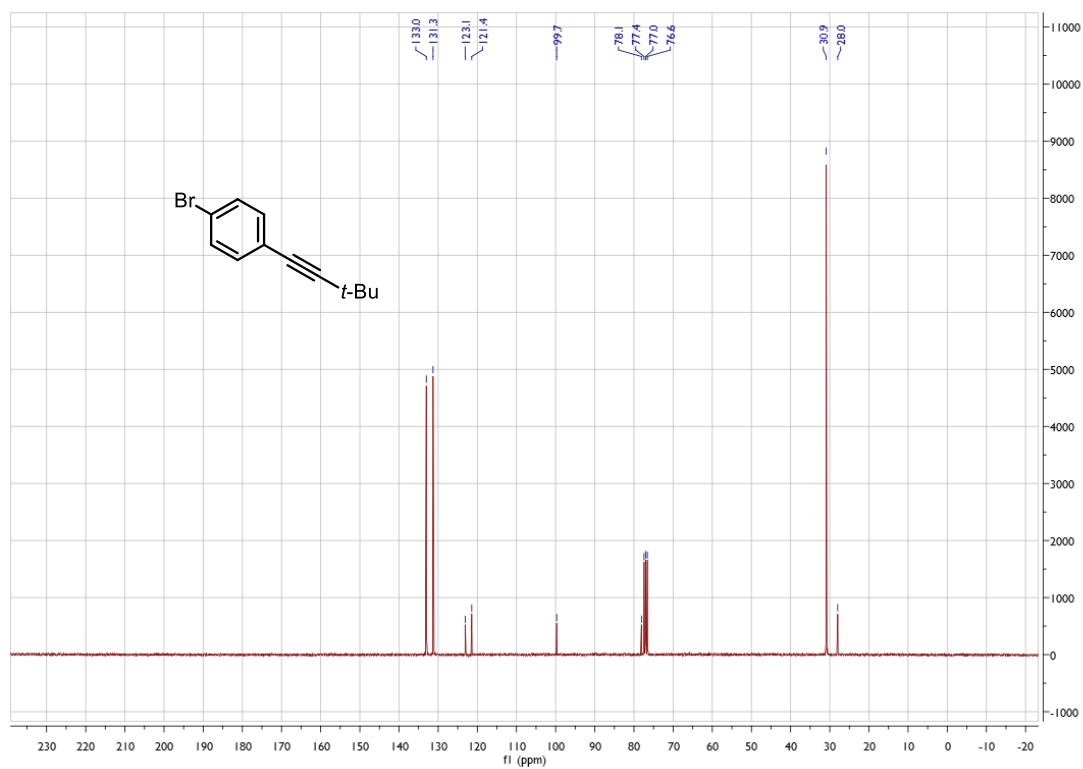
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(3-methylbut-1-yn-1-yl)benzene **3u**



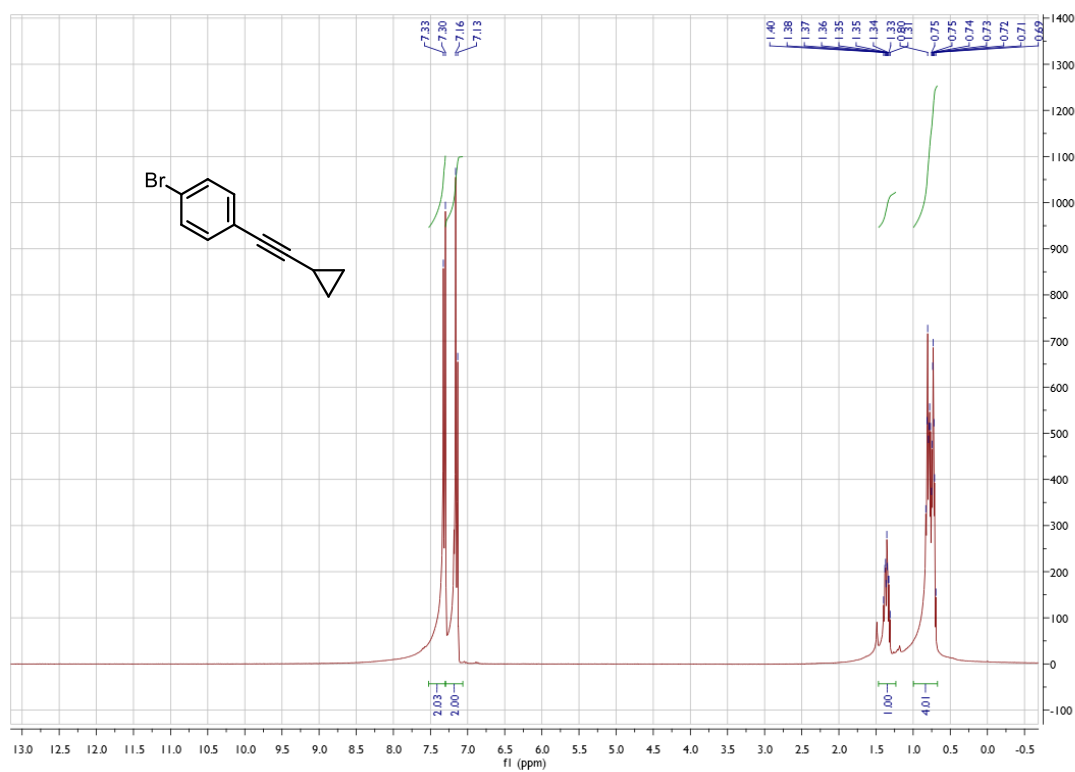
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(3,3-dimethylbut-1-yn-1-yl)benzene 3v



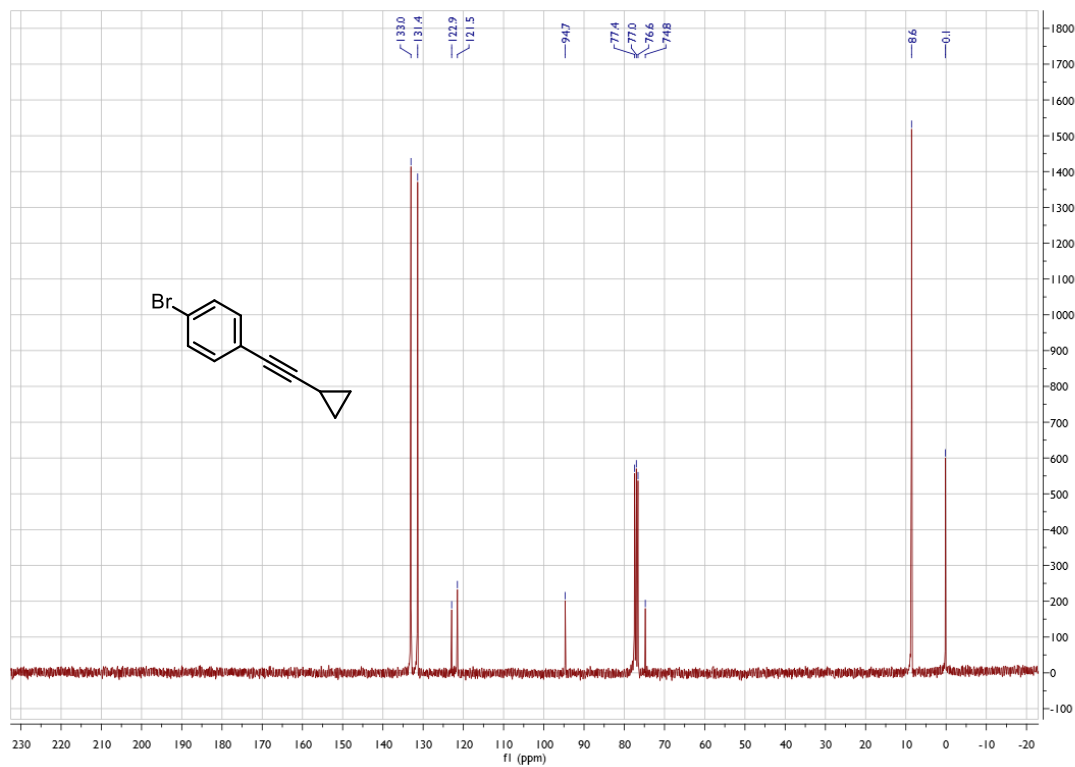
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(3,3-dimethylbut-1-yn-1-yl)benzene 3v



### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(cyclopropylethynyl)benzene 3w

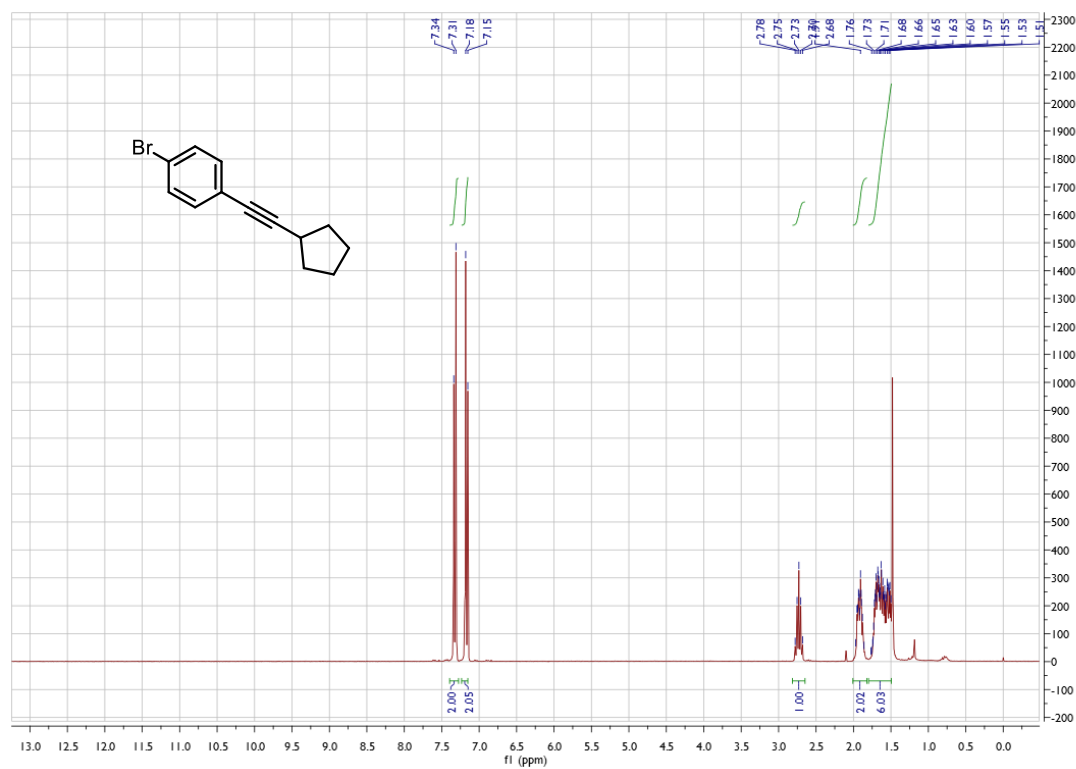


### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(cyclopropylethynyl)benzene 3w

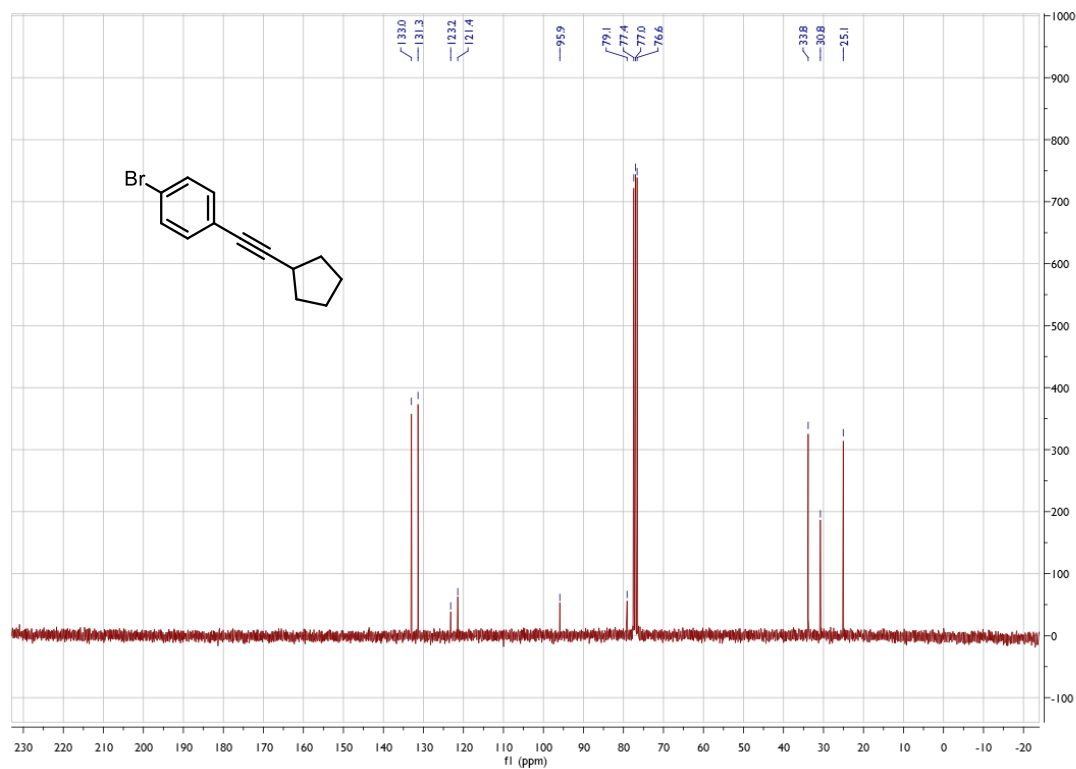




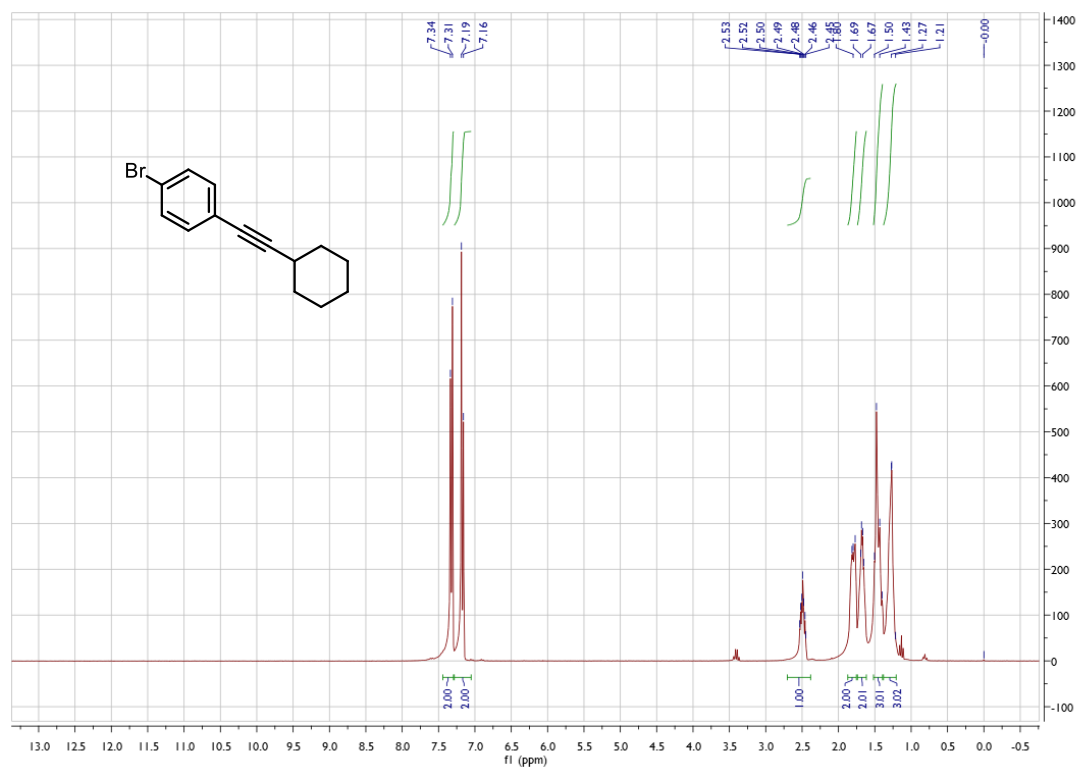
# <sup>1</sup>H NMR Spectrum of 1-bromo-4-(cyclopentylethynyl)benzene 3x



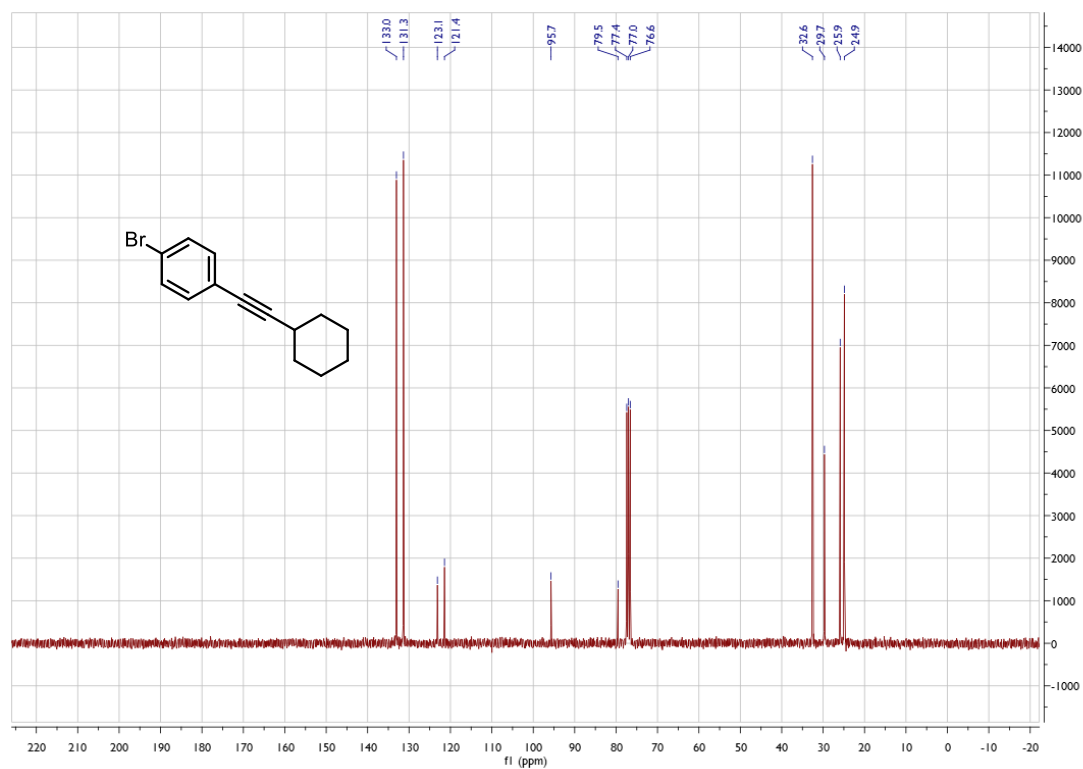
# <sup>13</sup>C NMR Spectrum of 1-bromo-4-(cyclopentylethynyl)benzene 3x



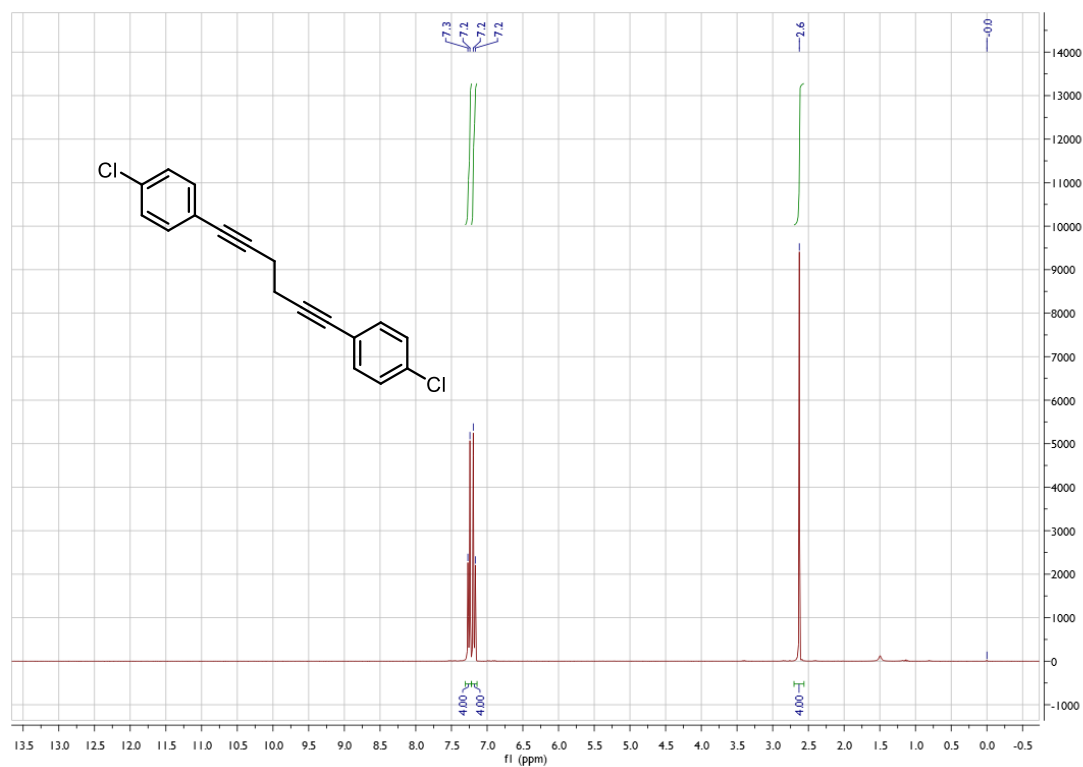
### <sup>1</sup>H NMR Spectrum of 1-bromo-4-(cyclohexylethynyl)benzene **3y**



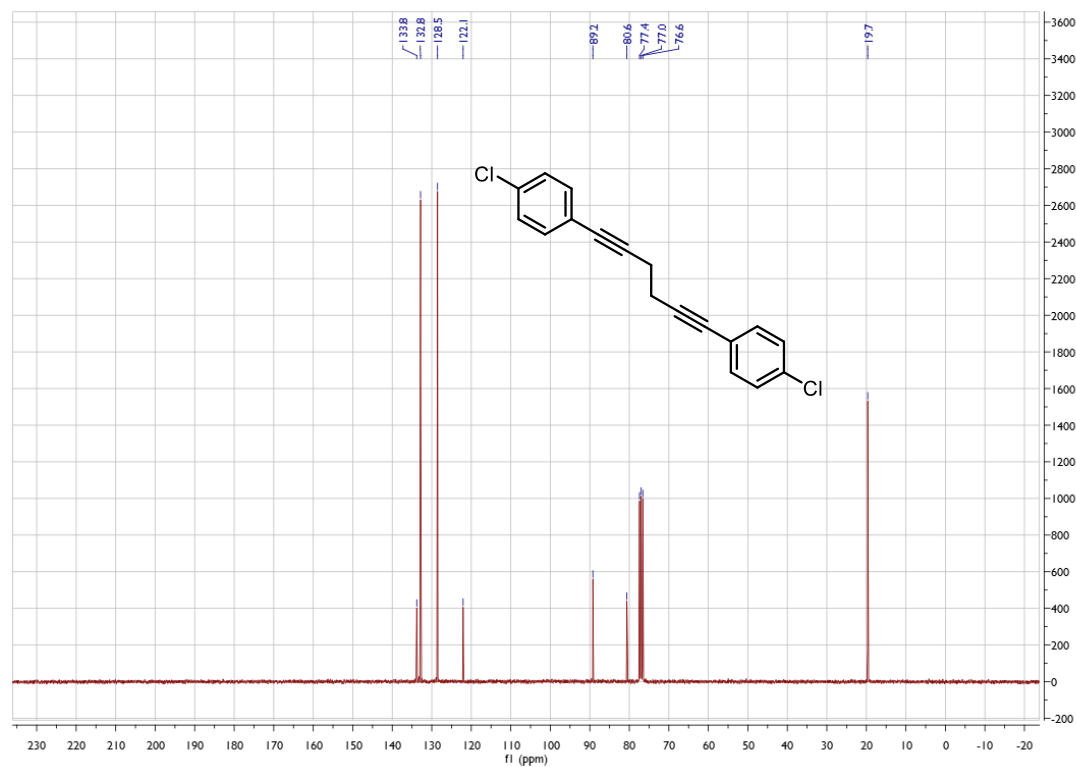
### <sup>13</sup>C NMR Spectrum of 1-bromo-4-(cyclohexylethynyl)benzene **3y**



### <sup>1</sup>H NMR Spectrum of 1, 6-bis(4-chlorophenyl)hexa-1,5-diyne 3z

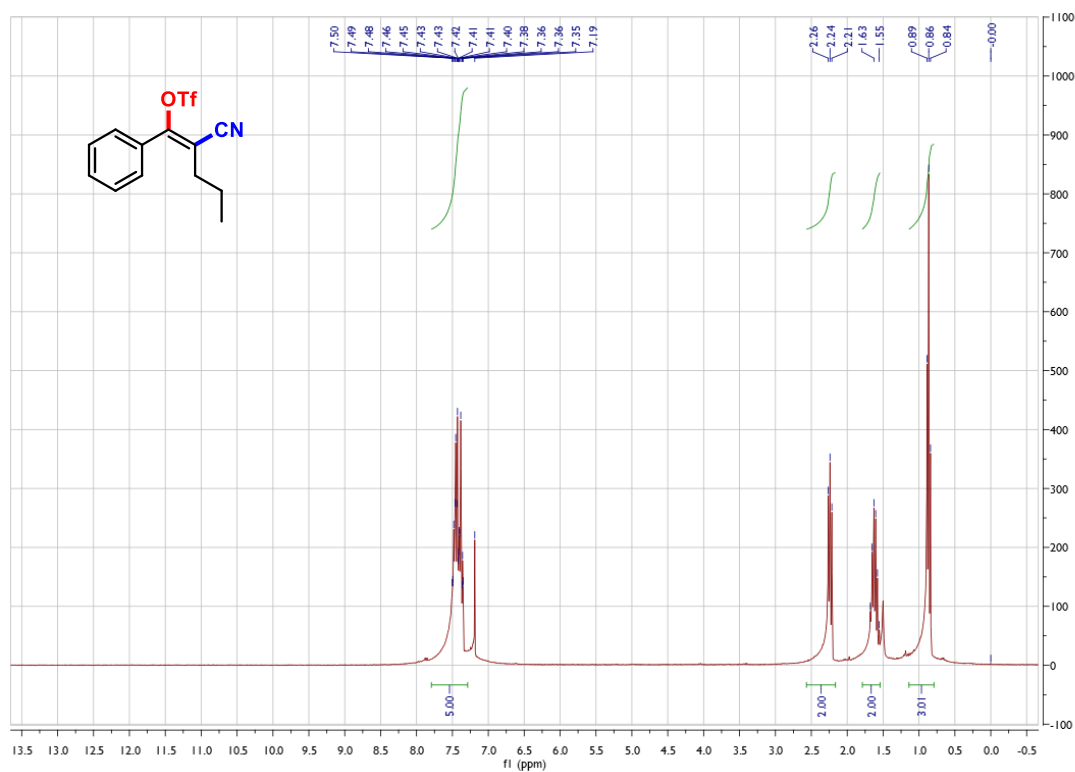


### <sup>13</sup>C NMR Spectrum of 1, 6-bis(4-chlorophenyl)hexa-1,5-diyne 3z

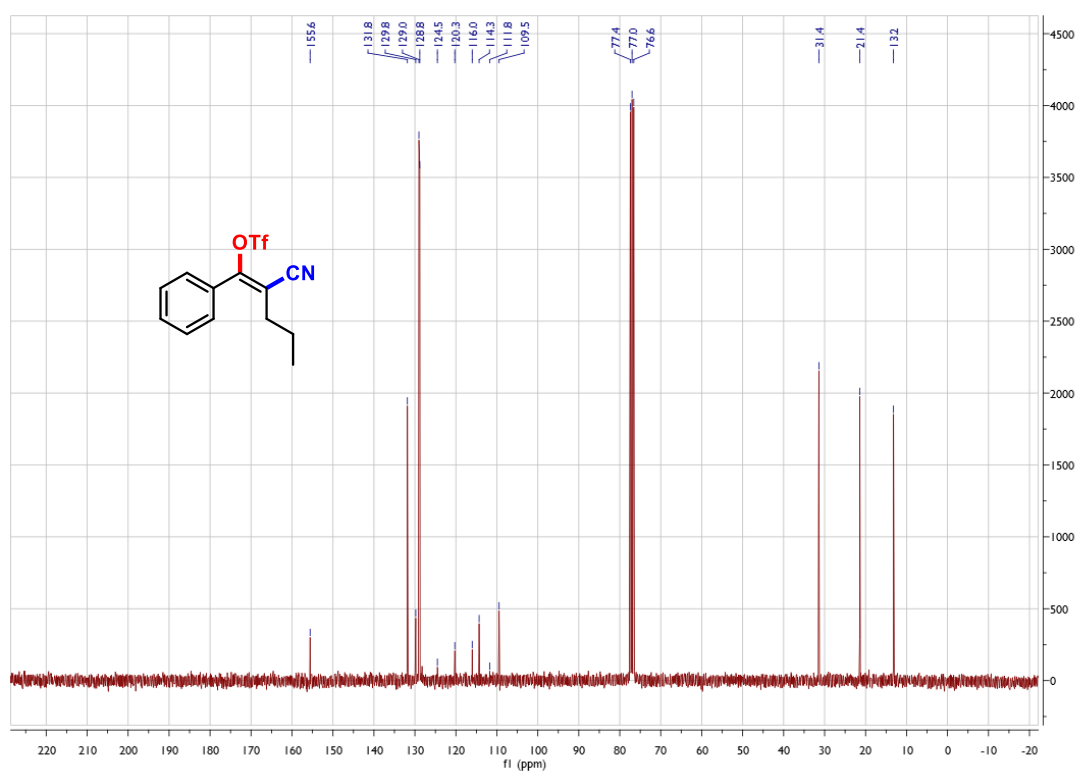


## Spectra of cyanotriflation products 2

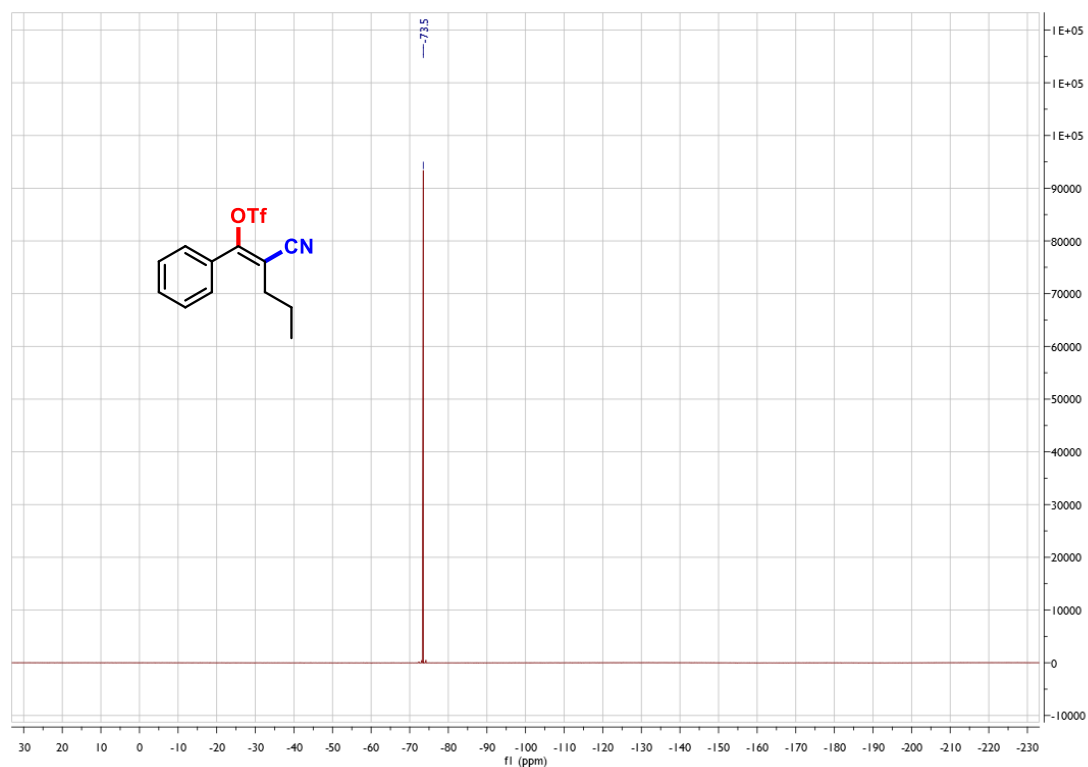
### <sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate 2a



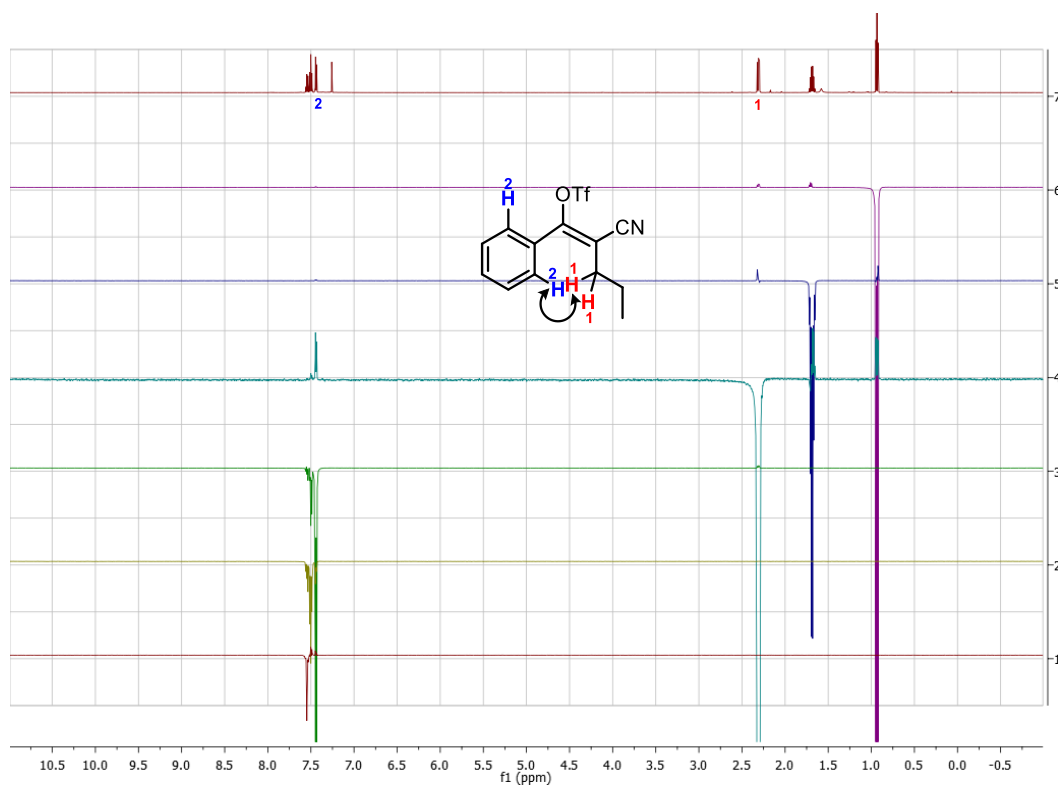
### <sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate 2a



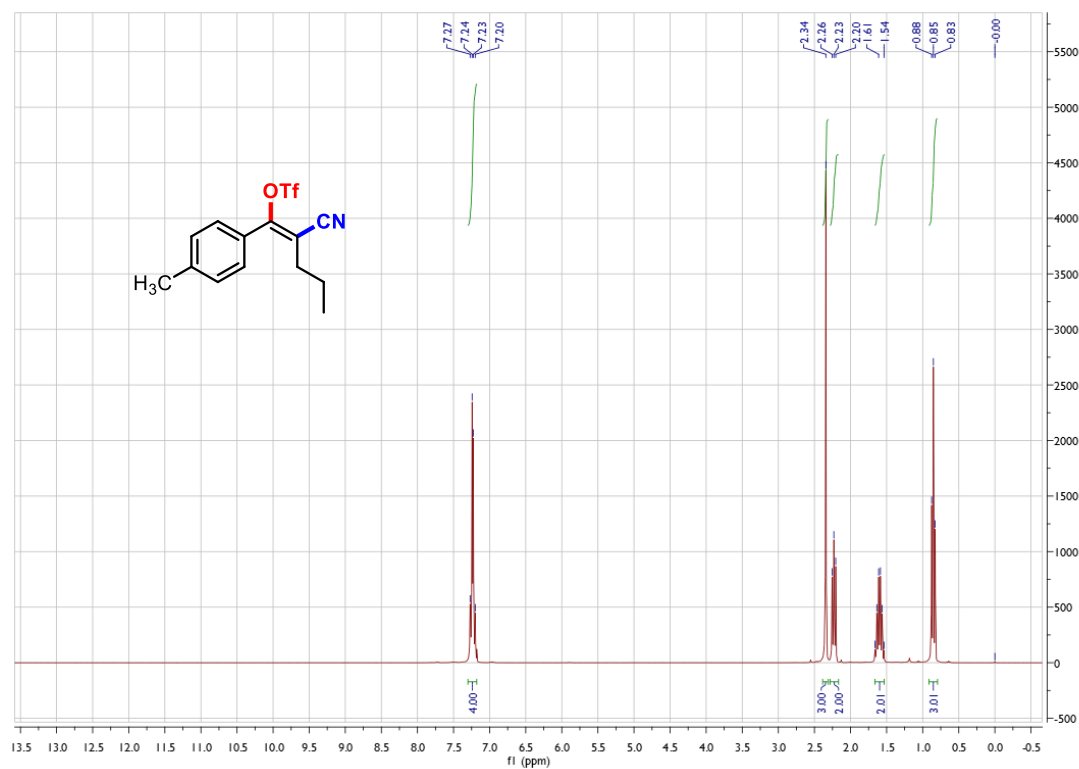
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate 2a**



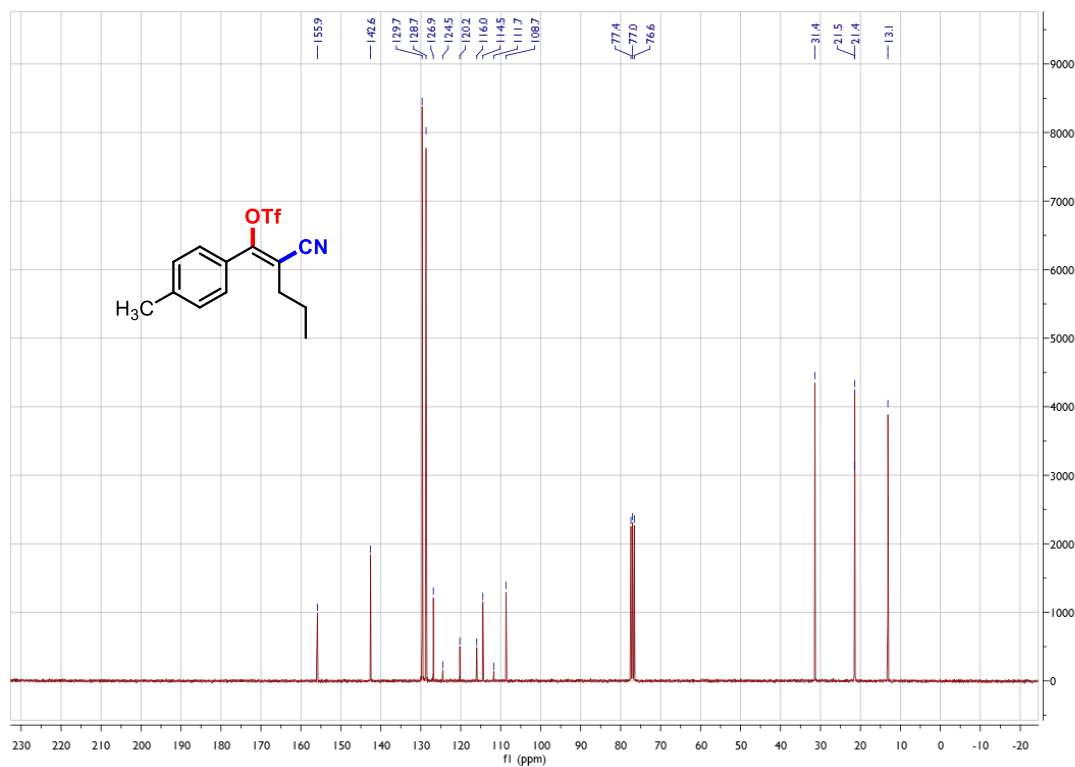
**NOESY1D Spectrum of (Z)-2-cyano-1-phenylpent-1-en-1-yl trifluoromethanesulfonate 2a**



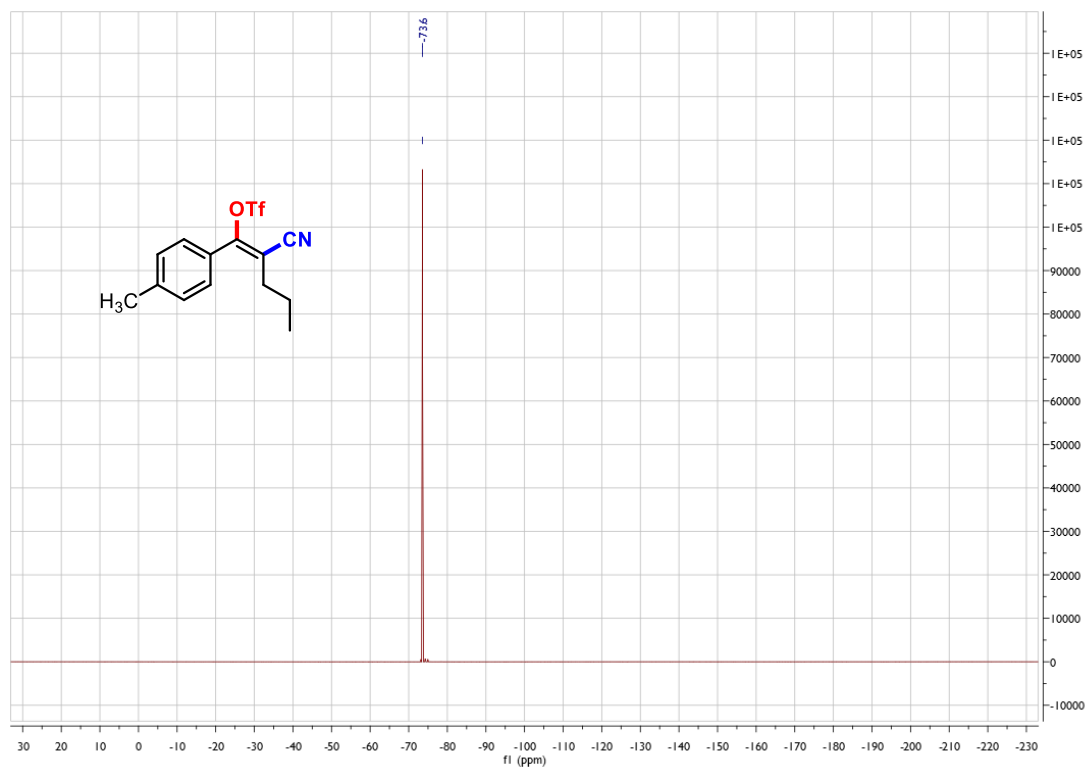
**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(p-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2b**



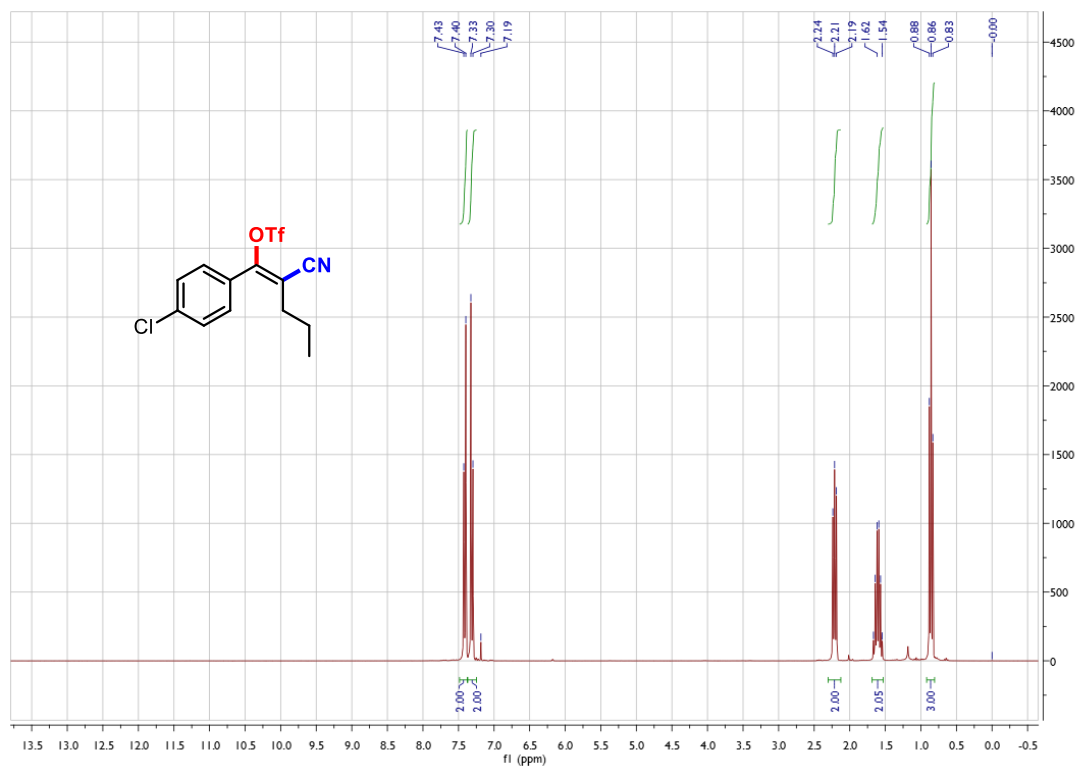
**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(p-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2b**



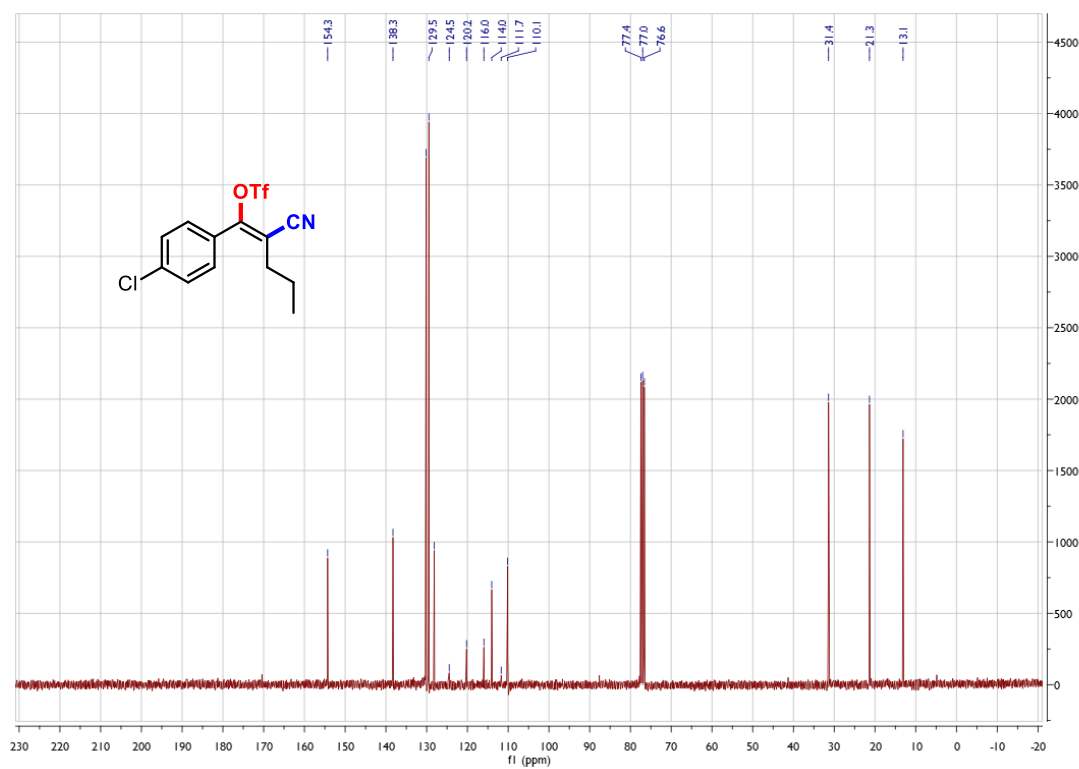
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(p-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2b**



**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-chlorophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2c**

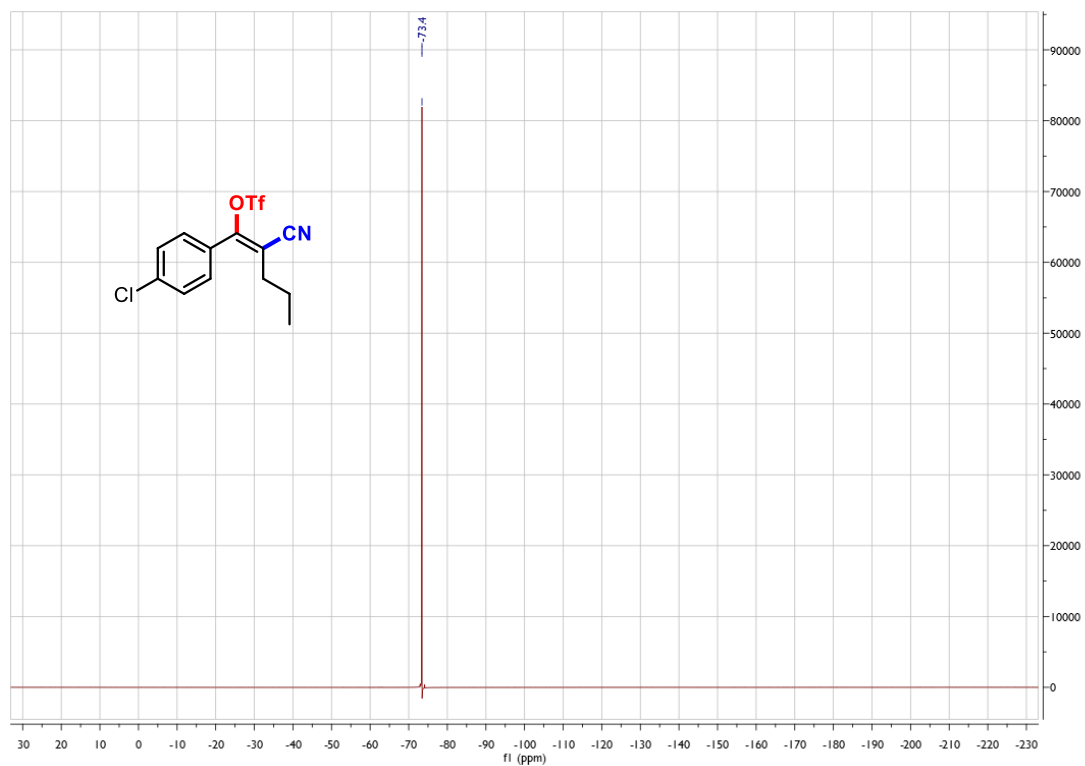


**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-chlorophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2c**

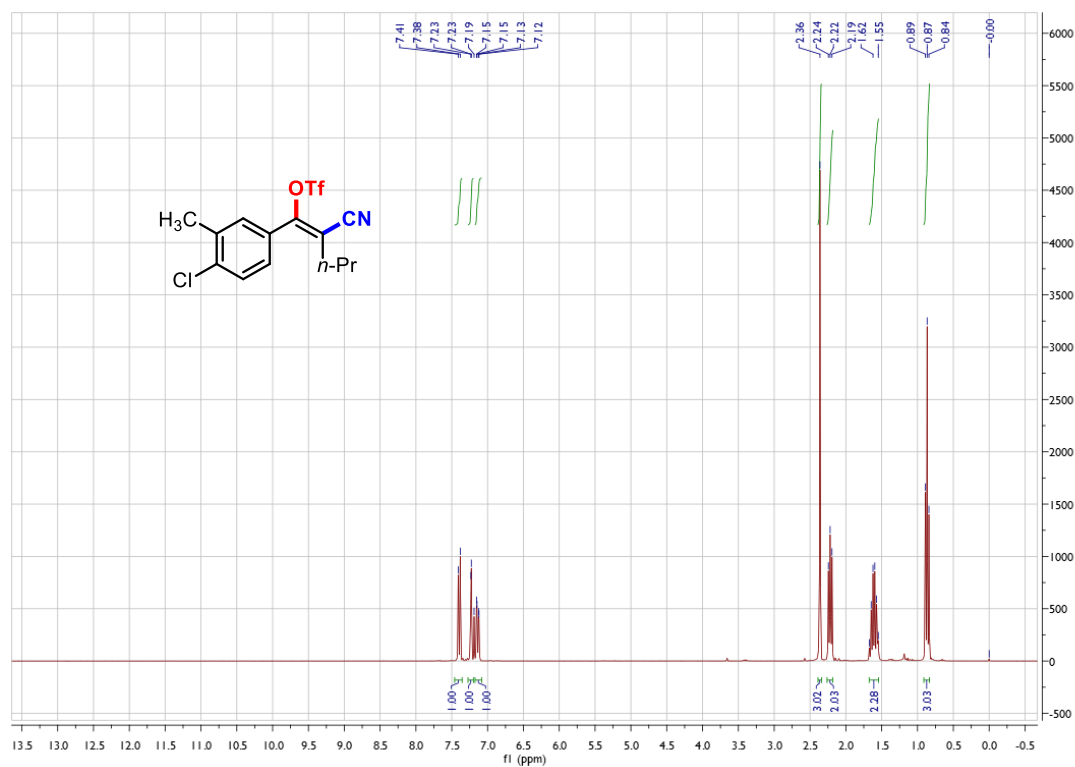




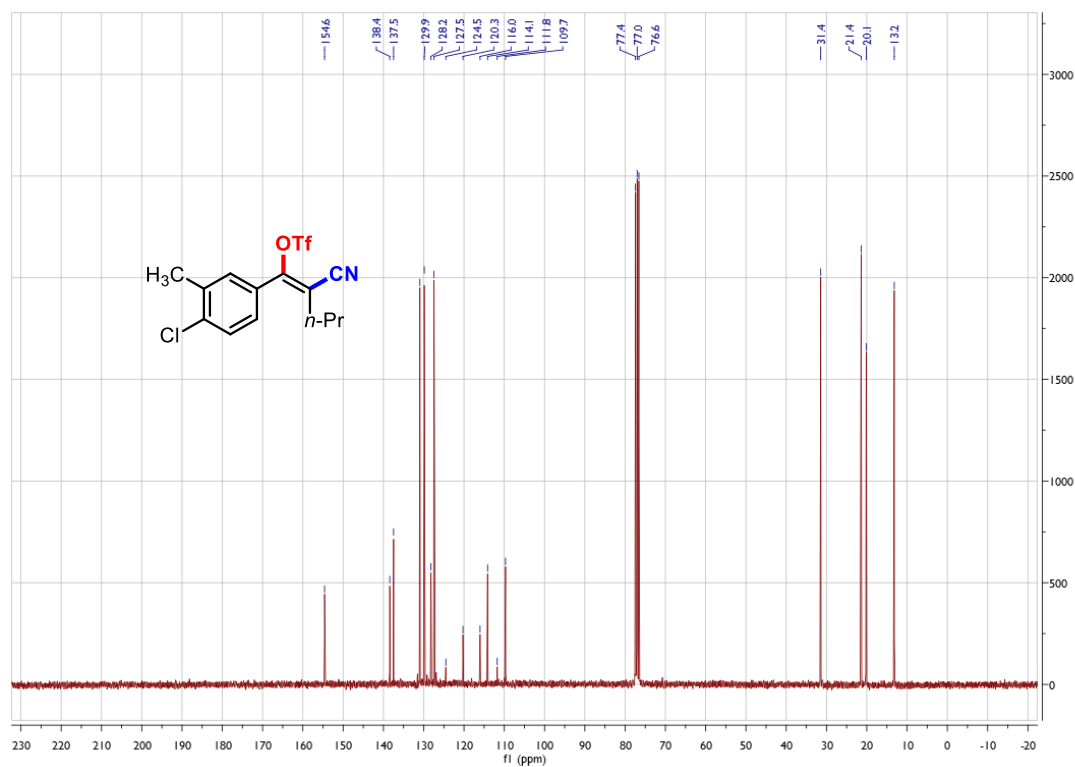
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-chlorophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2c**



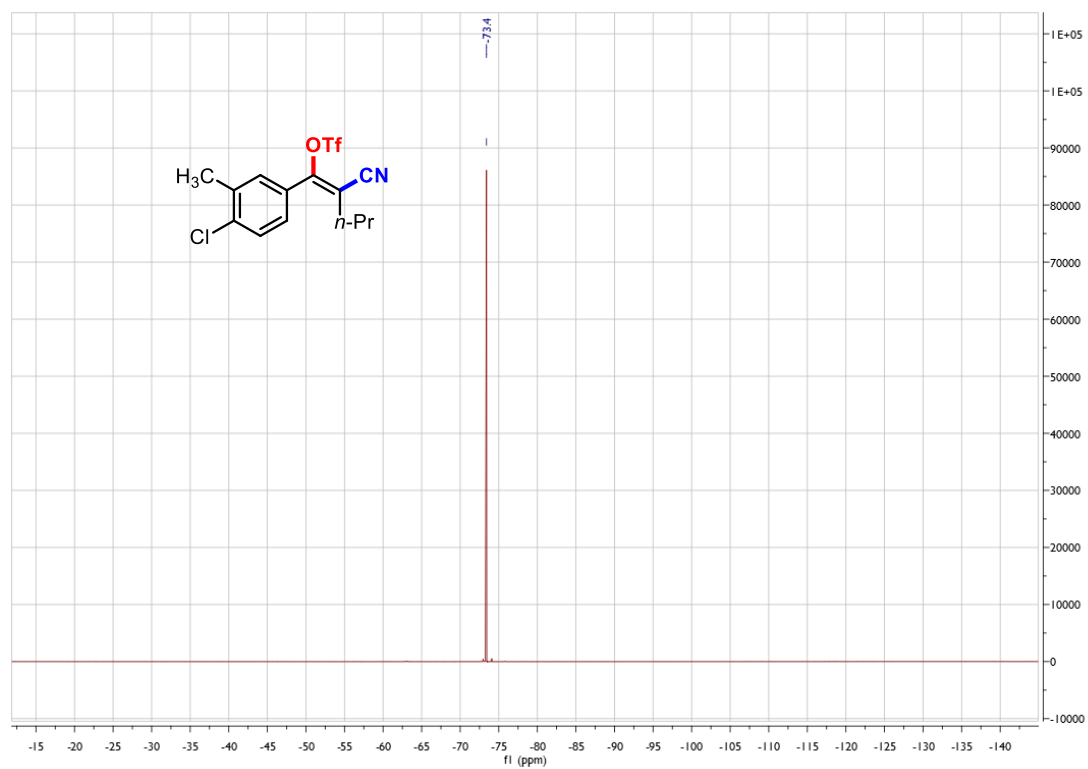
**$^1\text{H}$  NMR Spectrum of (Z)-1-(4-chloro-3-methylphenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2d**



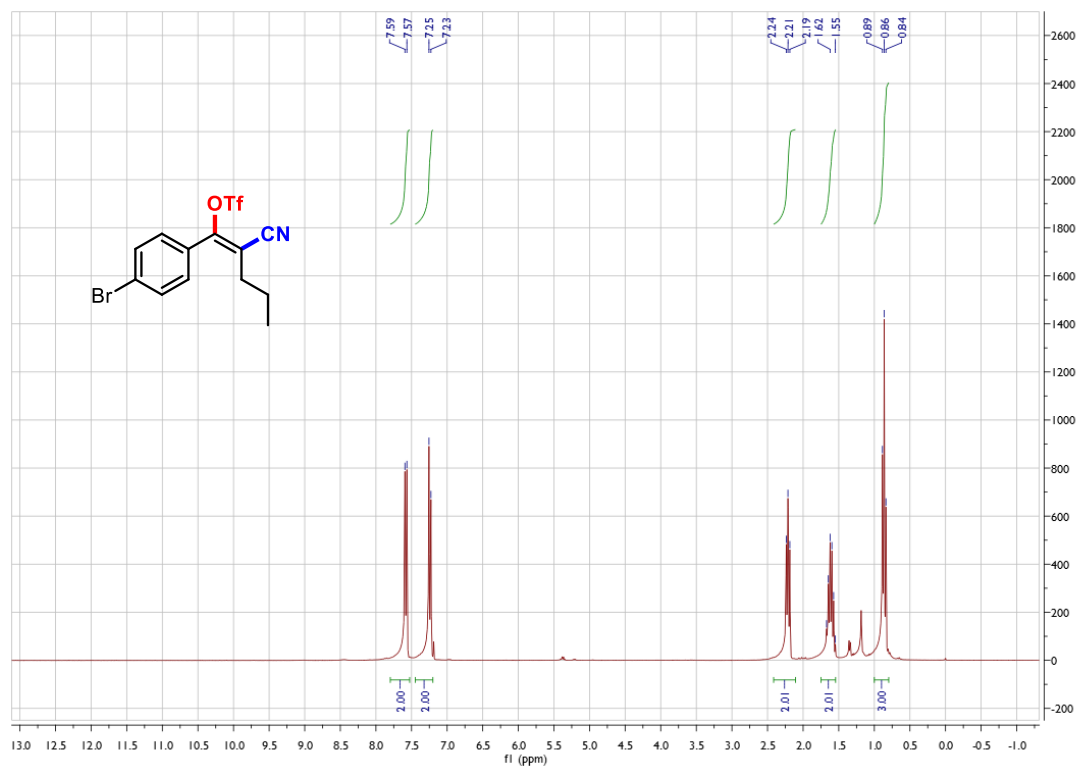
**$^{13}\text{C}$  NMR Spectrum of (Z)-1-(4-chloro-3-methylphenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2d**



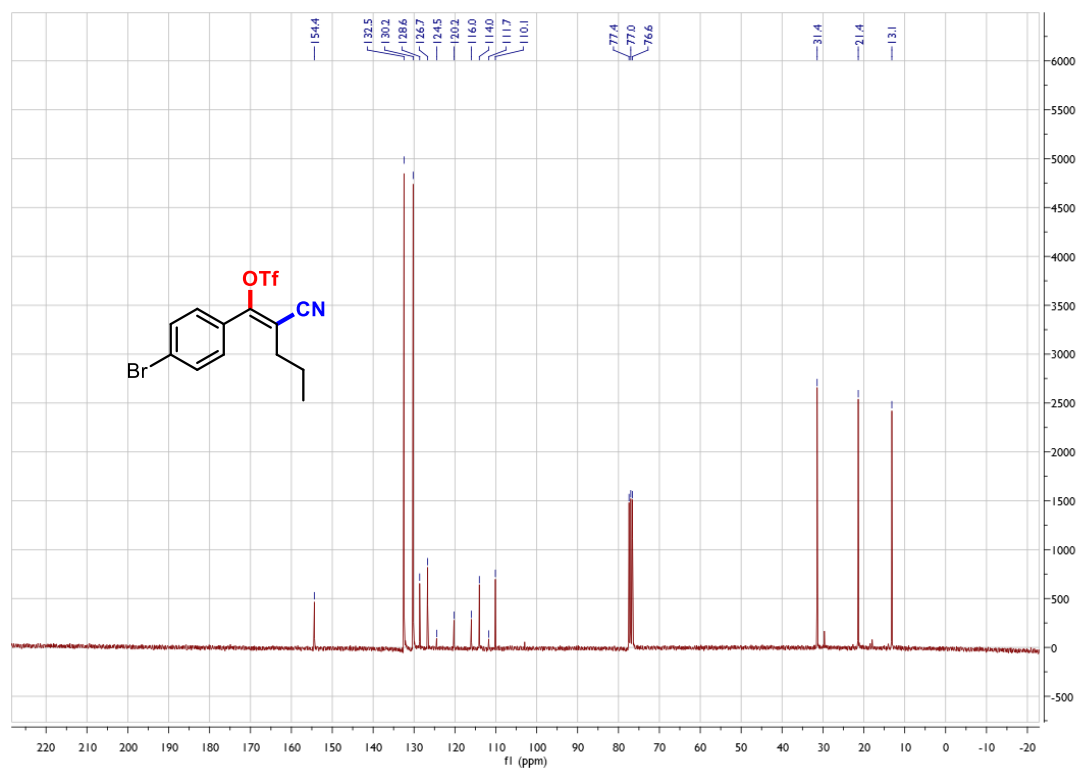
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-chloro-3-methylphenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2d**



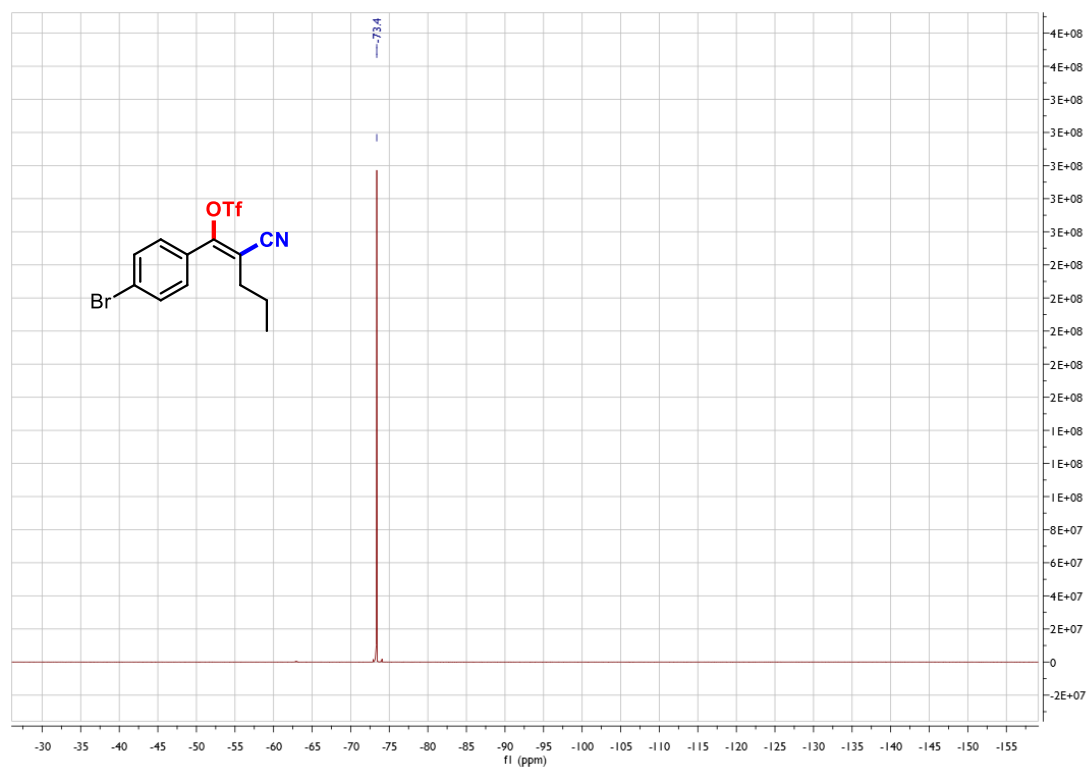
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2e**



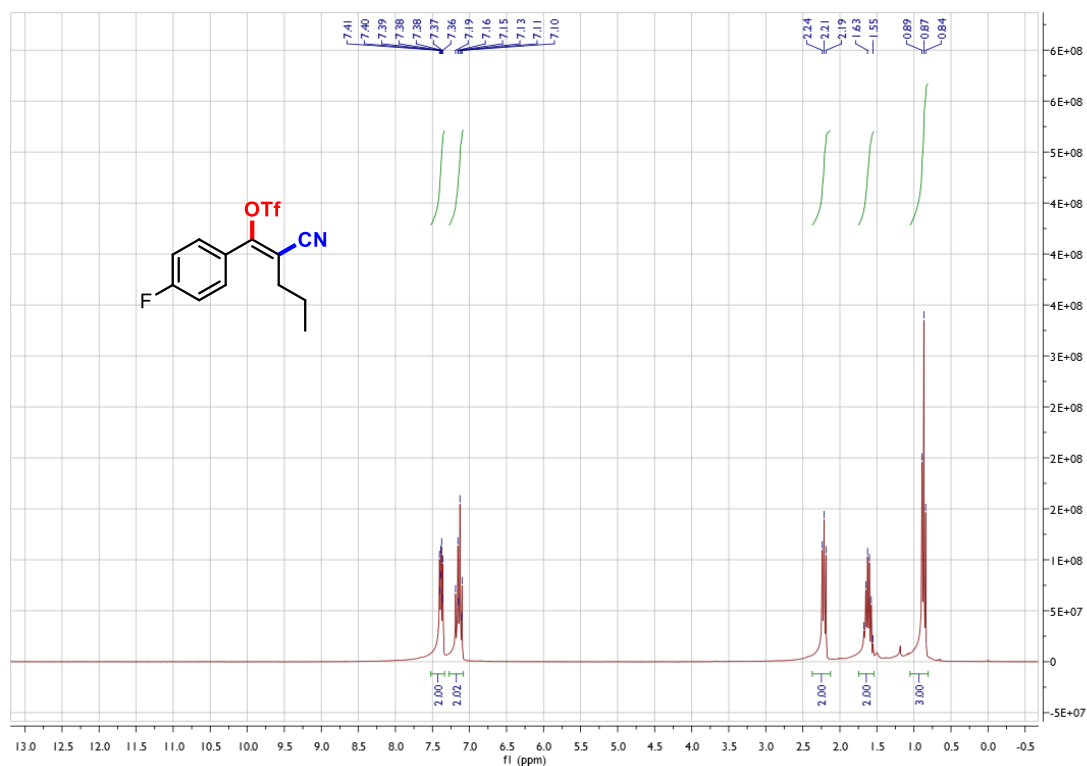
**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2e**



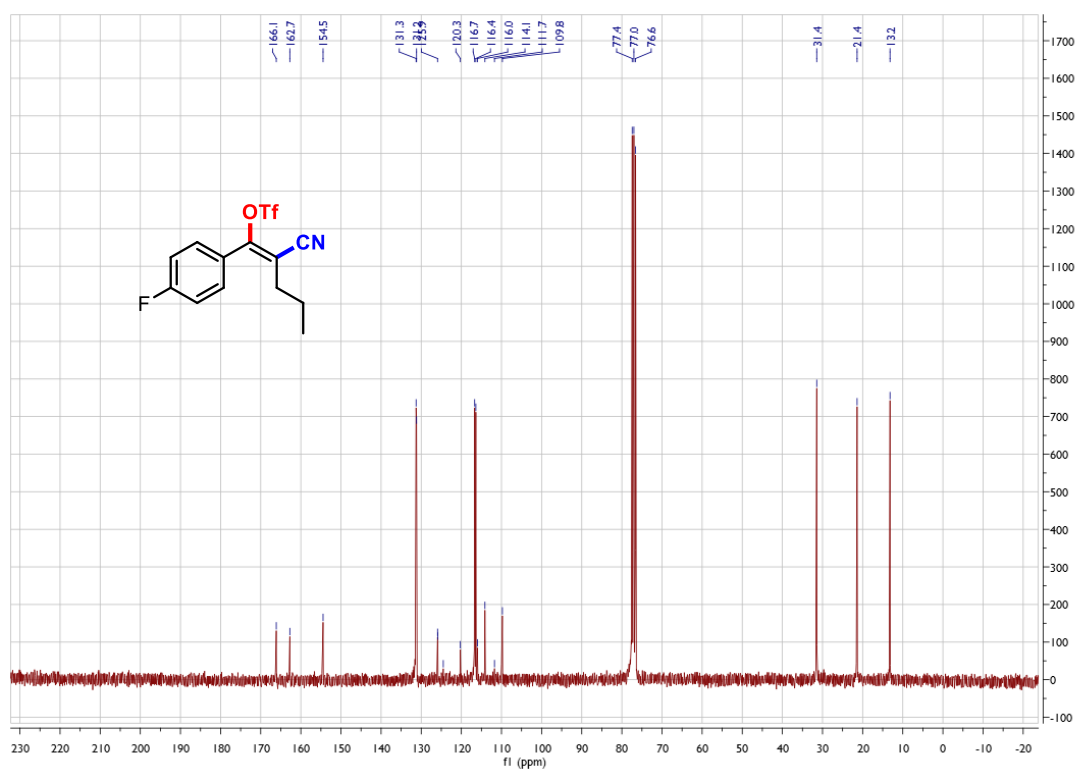
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanopent-1-en-1-yl trifluoromethanesulfonate 2e**



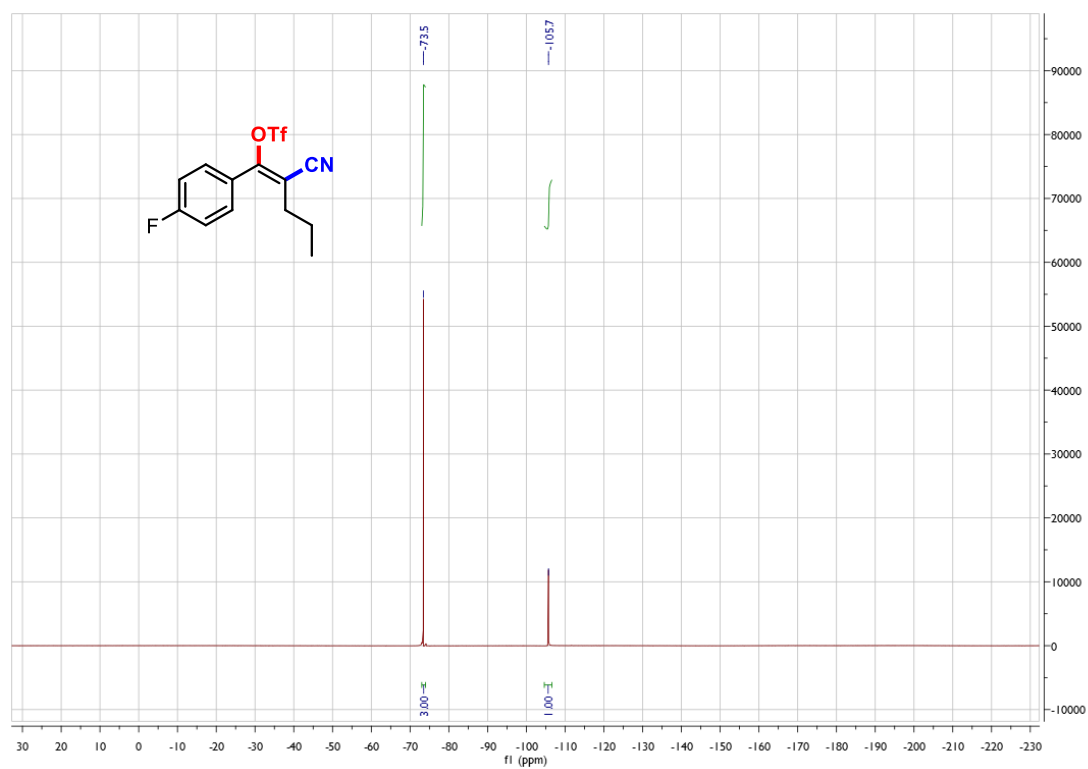
**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(4-fluorophenyl)pent-1-en-1-yl trifluoromethanesulfonate 2f**



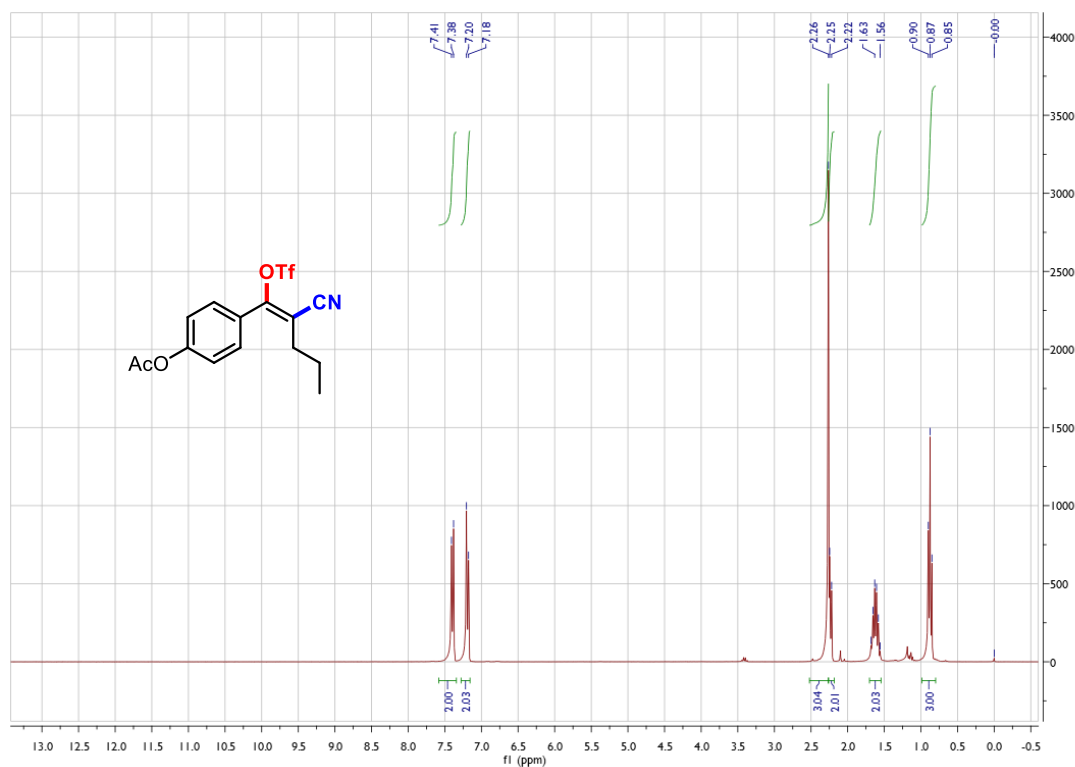
**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(4-fluorophenyl)pent-1-en-1-yl trifluoromethanesulfonate 2f**



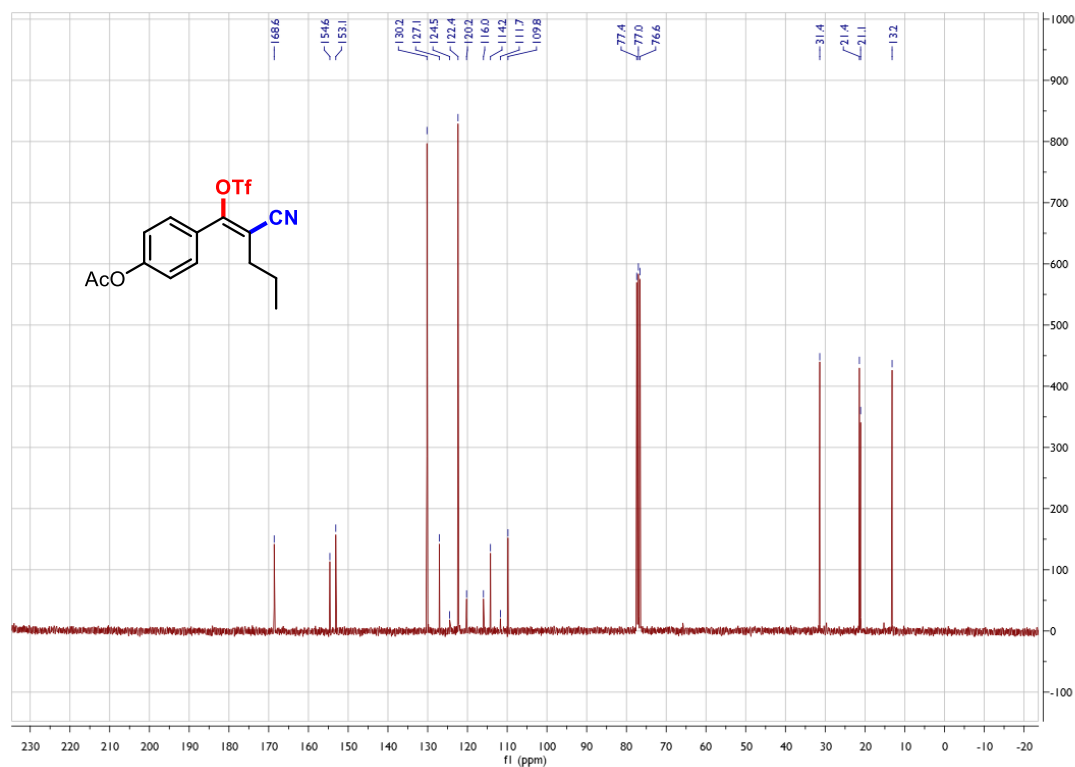
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(4-fluorophenyl)pent-1-en-1-yl trifluoromethanesulfonate 2f**



**<sup>1</sup>H NMR Spectrum of (Z)-4-(2-cyano-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl acetate 2g**

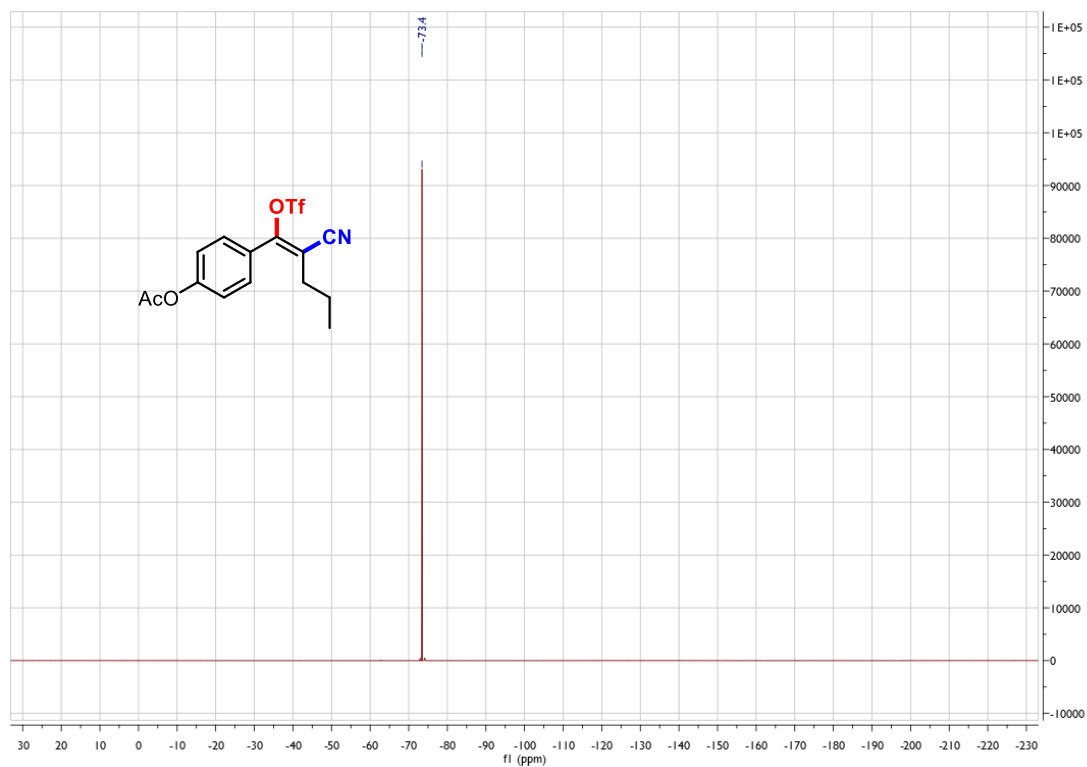


**<sup>13</sup>C NMR Spectrum of (Z)-4-(2-cyano-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl acetate 2g**

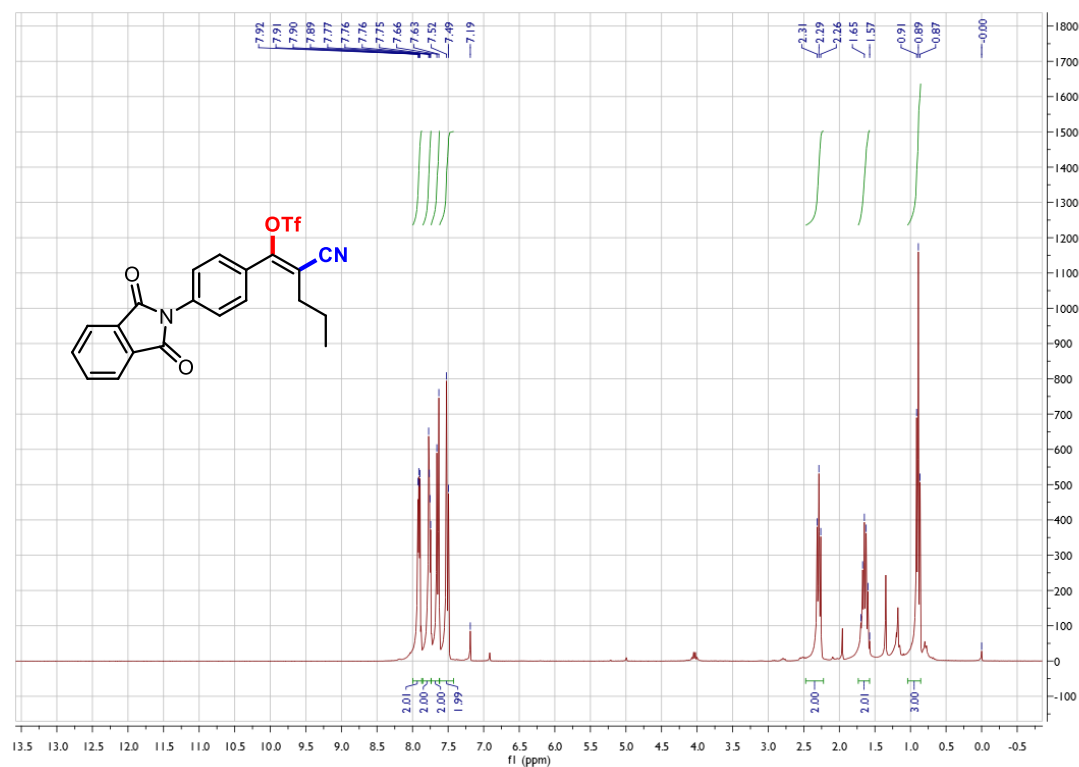




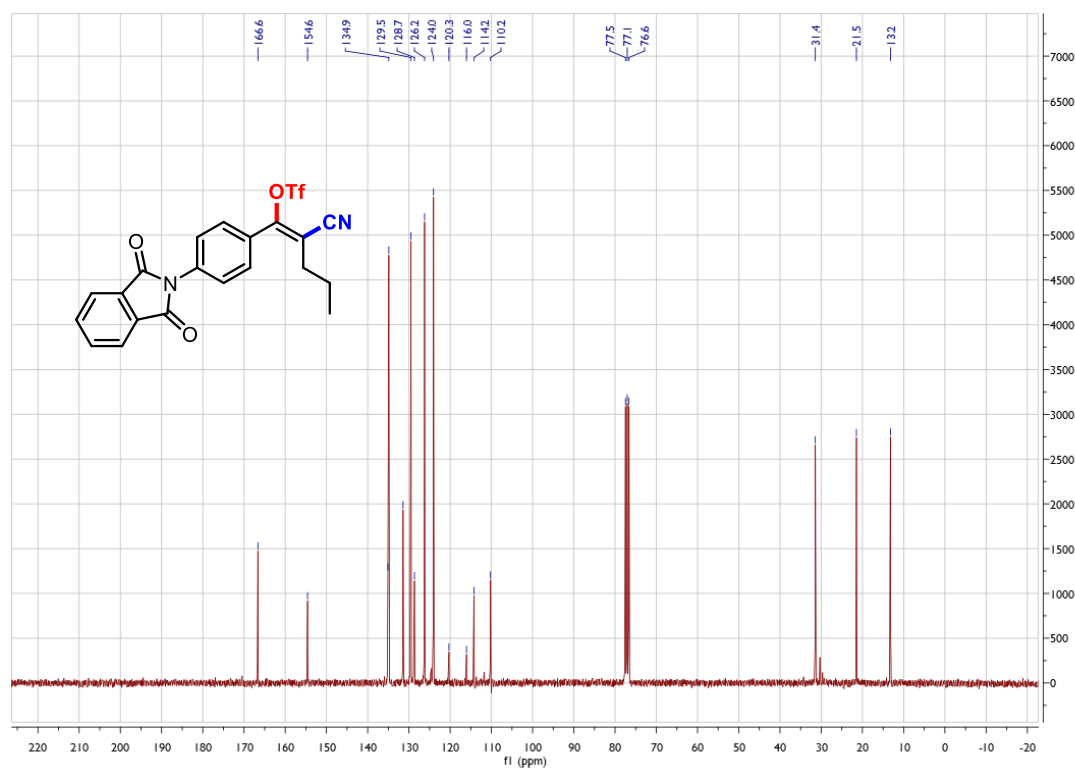
**$^{19}\text{F}$  NMR Spectrum of (Z)-4-(2-cyano-1-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)phenyl acetate 2g**



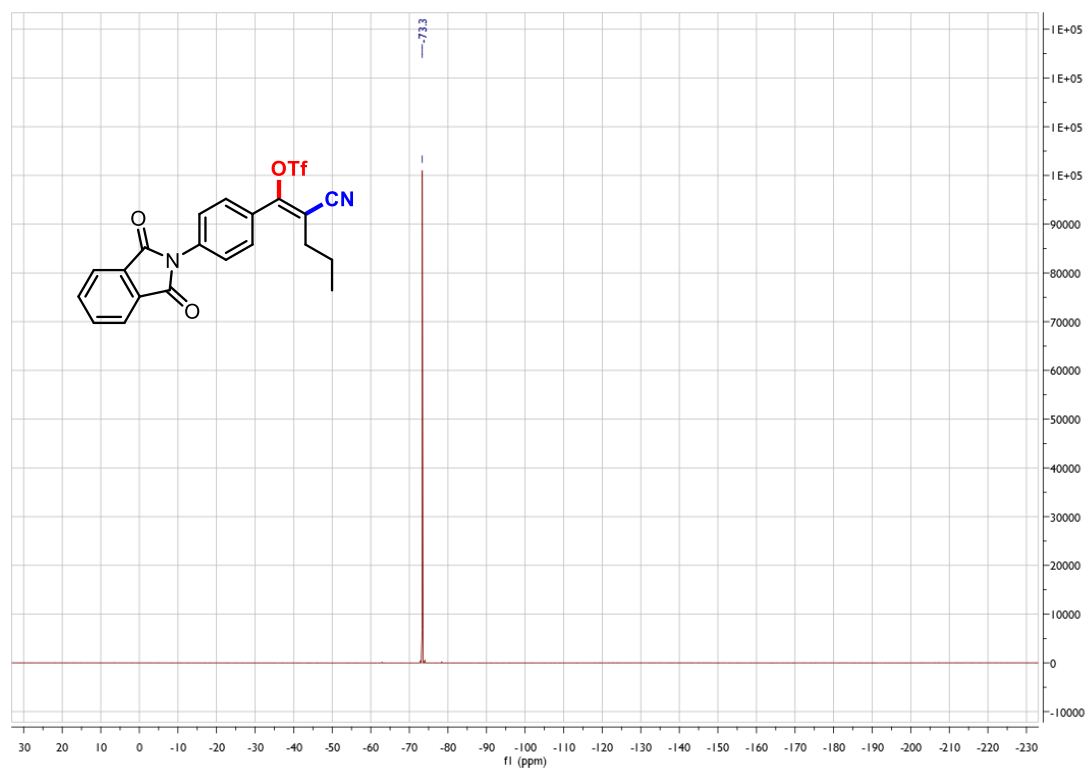
**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(4-(1,3-dioxoisindolin-2-yl)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2h**



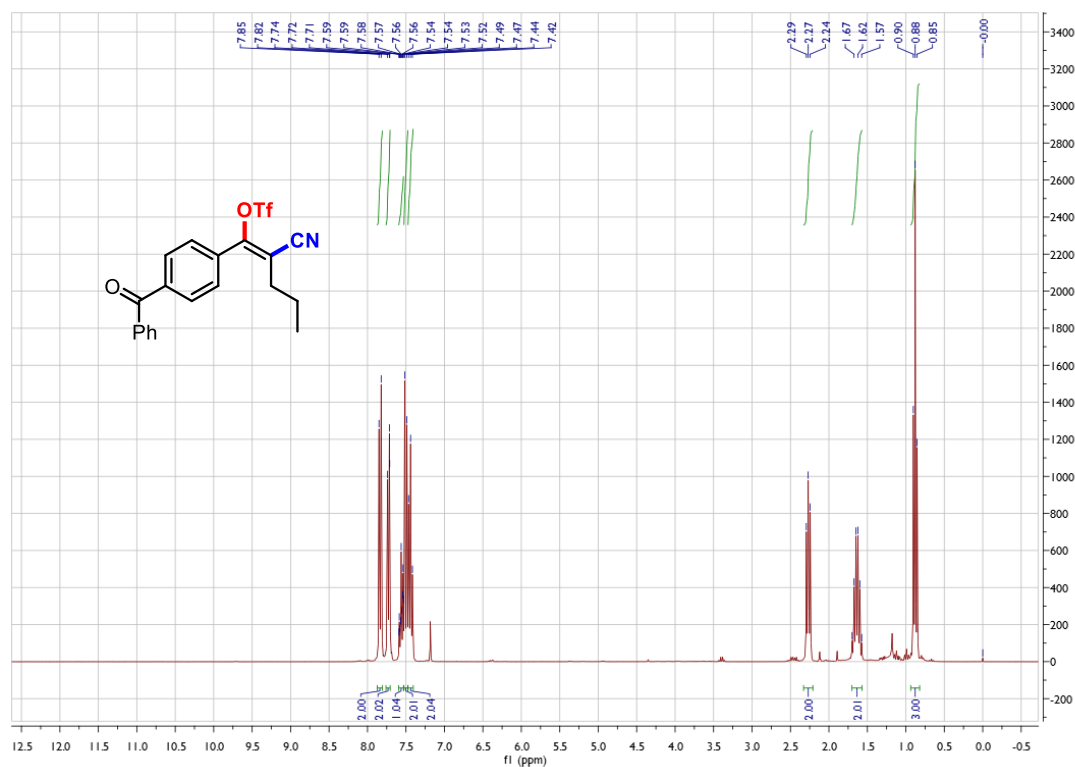
**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(4-(1,3-dioxoisindolin-2-yl)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2h**



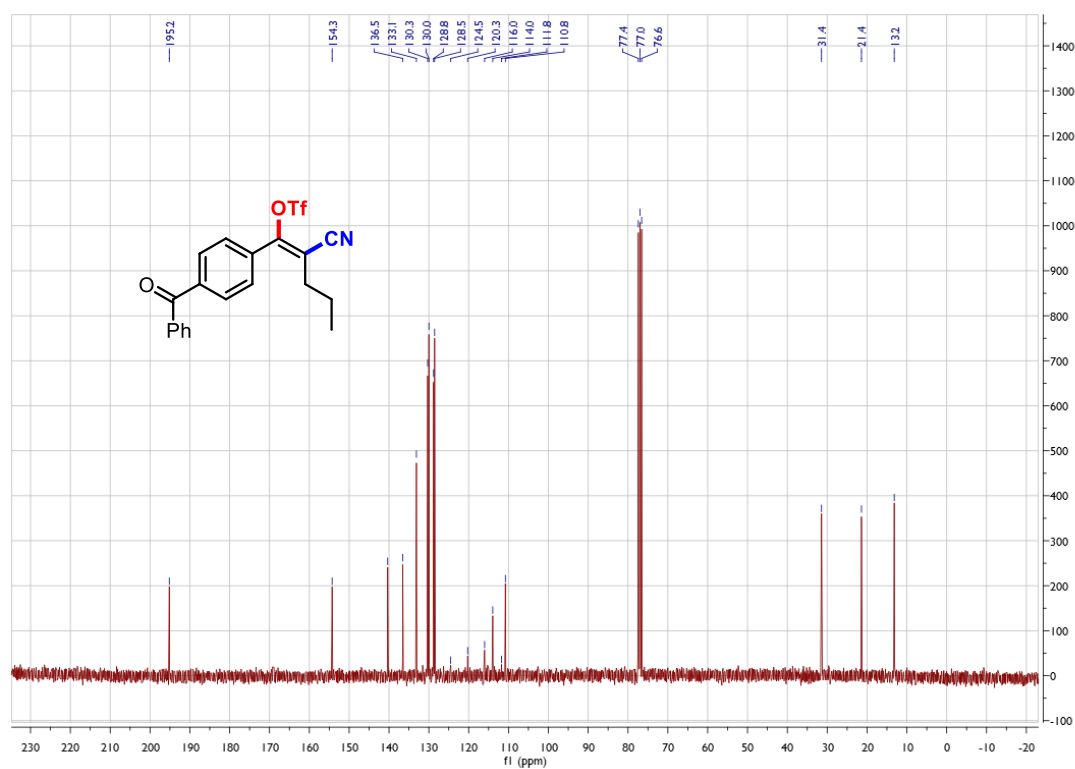
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(4-(1,3-dioxoisindolin-2-yl)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2h**



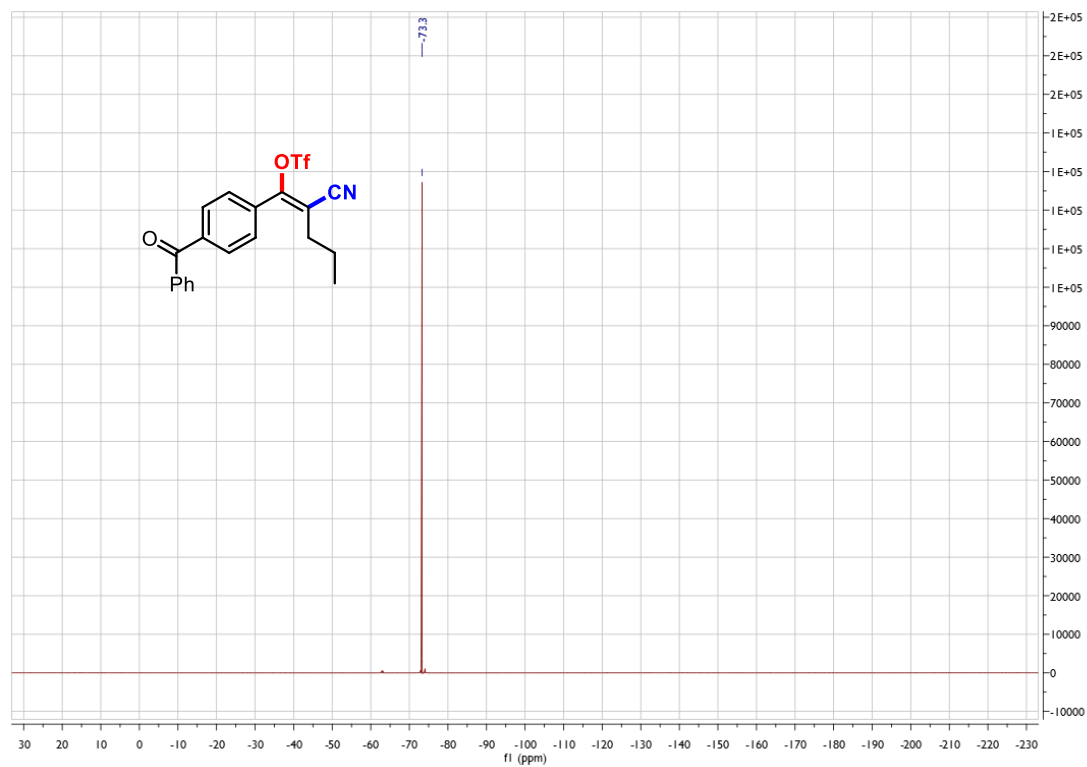
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-Benzoylphenyl)-2-cyanopent-1-en-1-yl trifluoroethanesulfonate 2i**



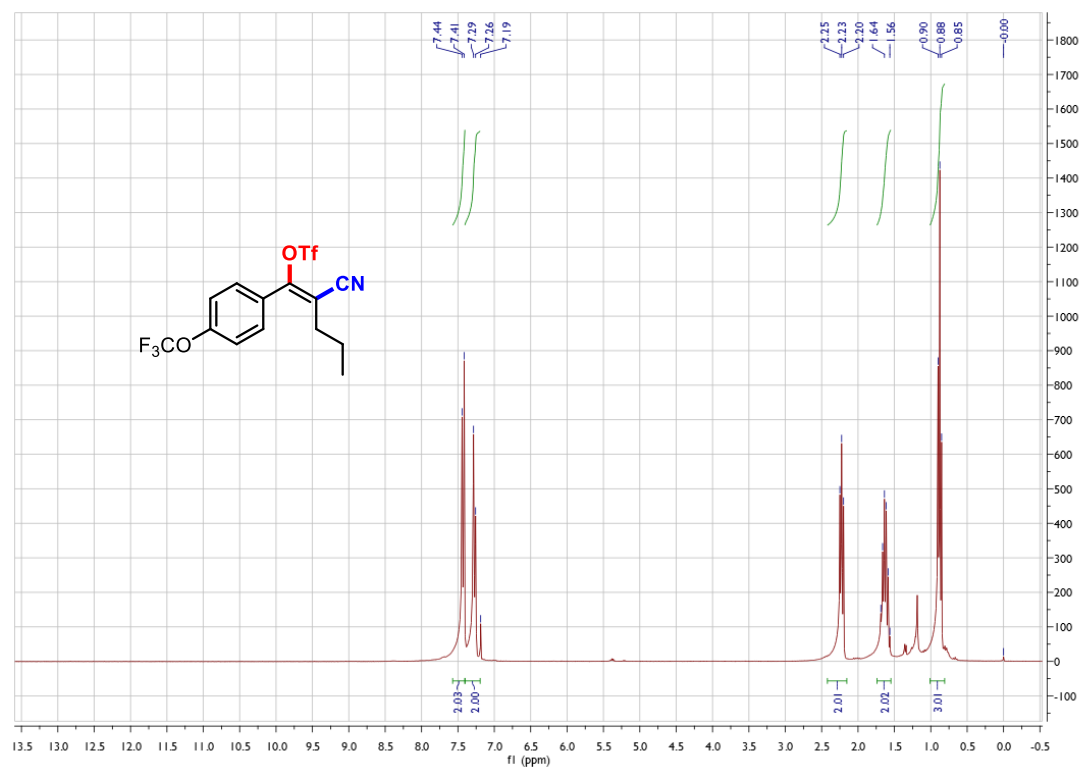
**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-Benzoylphenyl)-2-cyanopent-1-en-1-yl trifluoroethanesulfonate 2i**



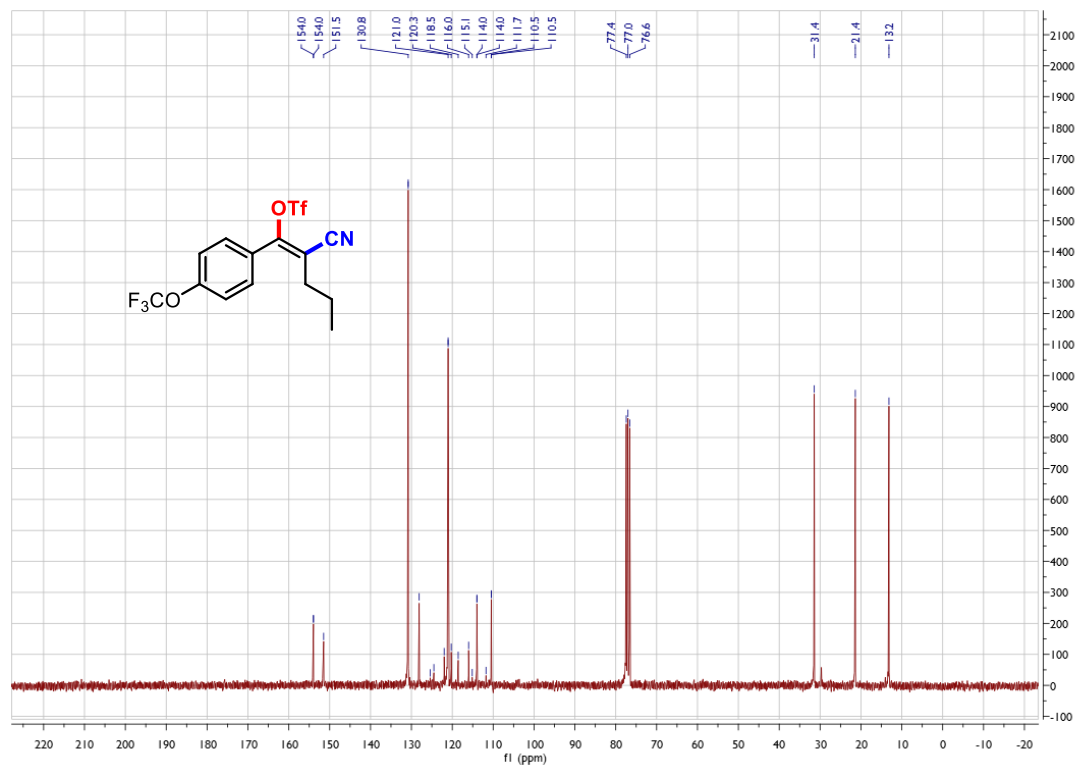
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-Benzoylphenyl)-2-cyanopent-1-en-1-yl trifluoroethanesulfonate **2i****



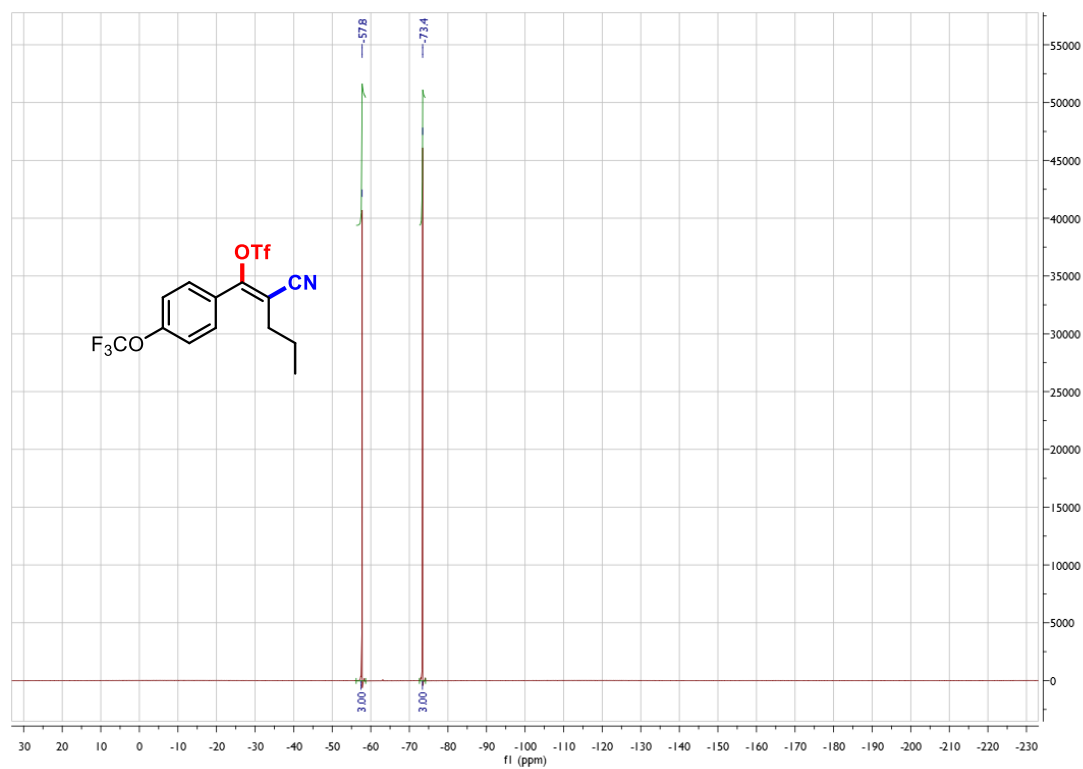
**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(4-(trifluoromethoxy)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2j**



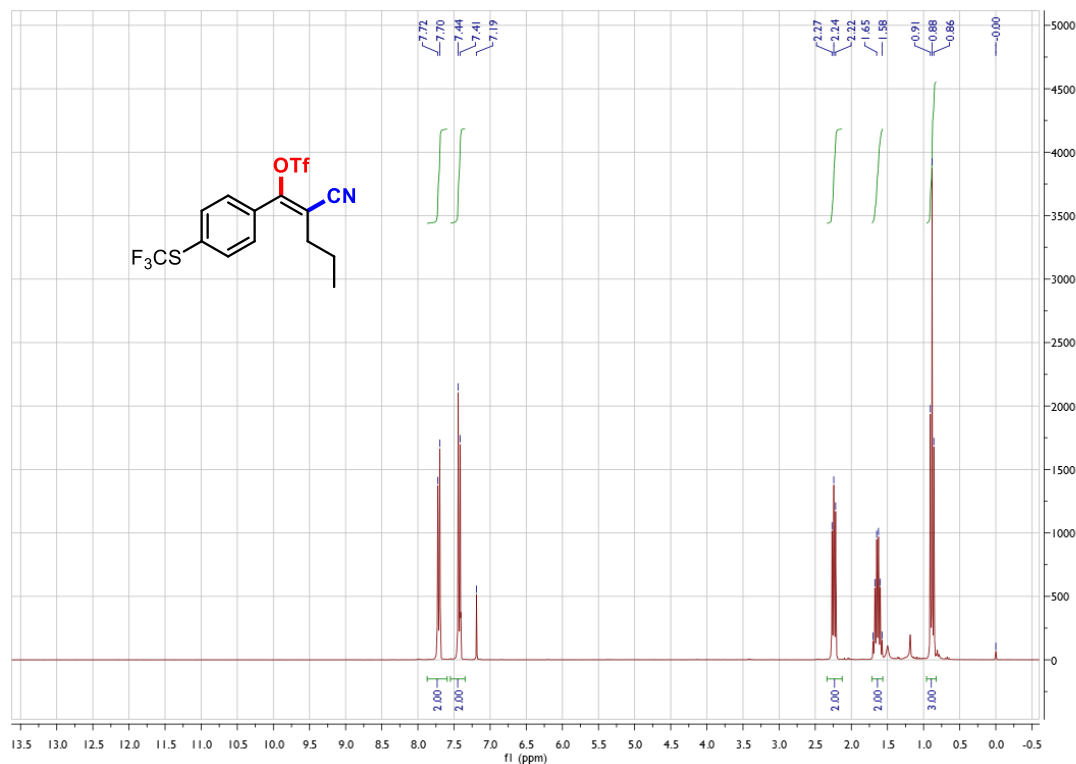
**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(4-(trifluoromethoxy)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2j**



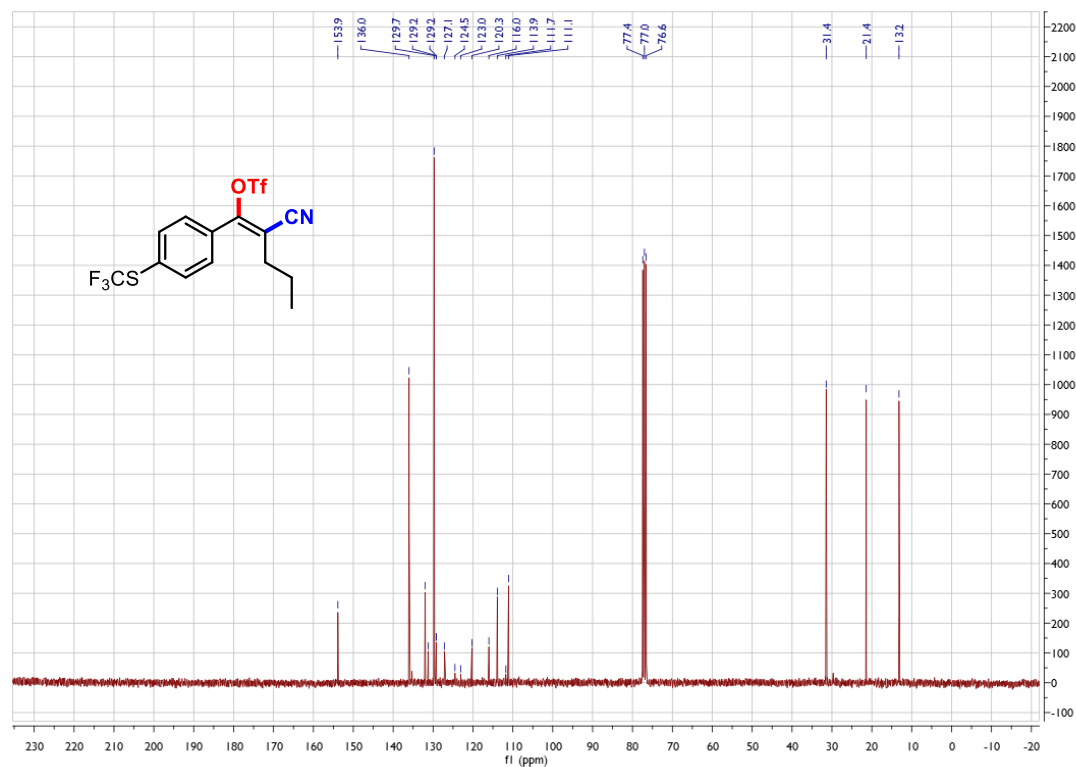
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(4-(trifluoromethoxy)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2j**



**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2k**

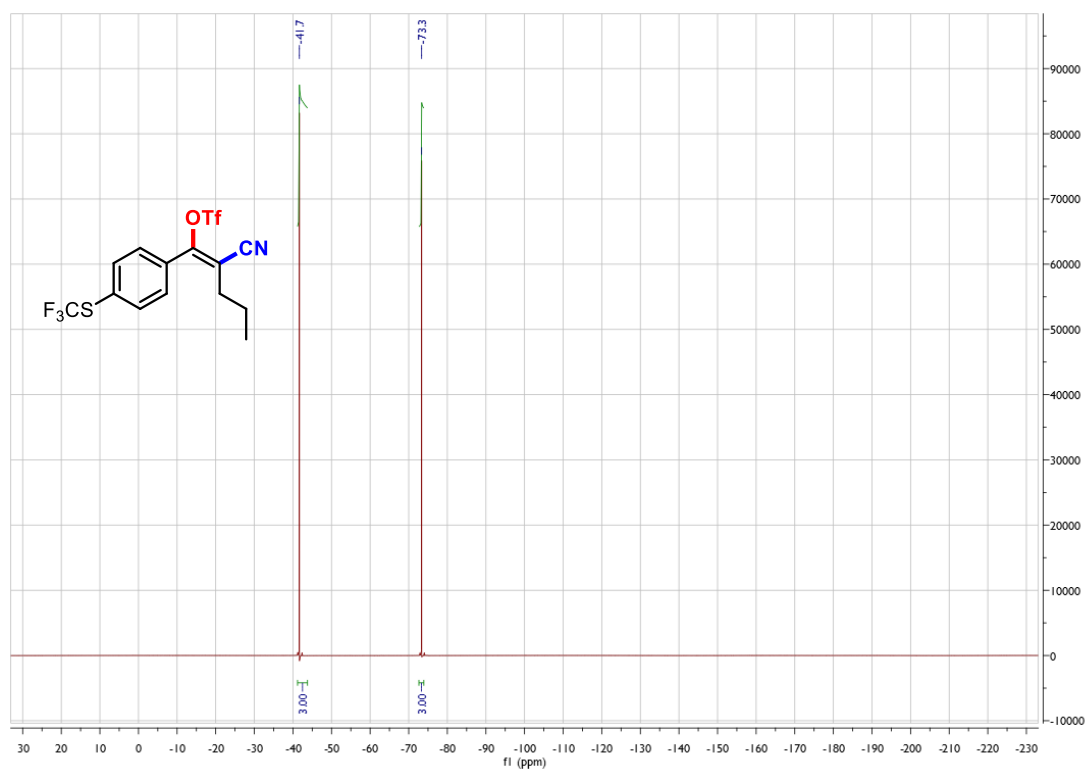


**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2k**

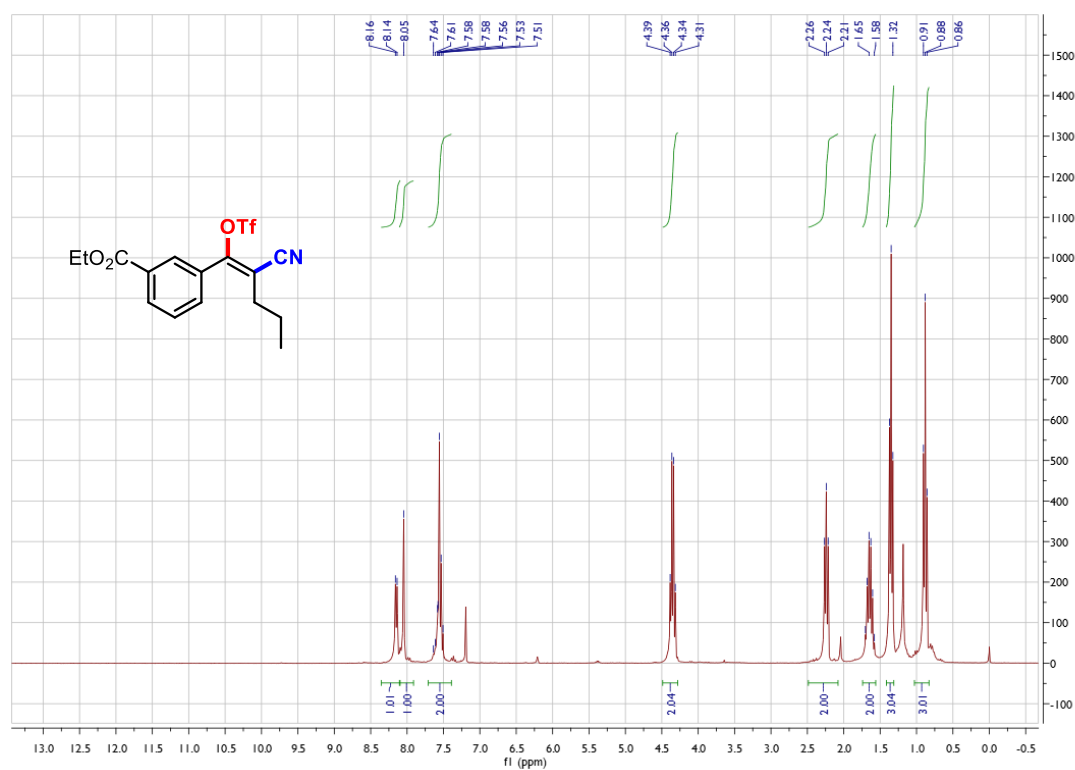




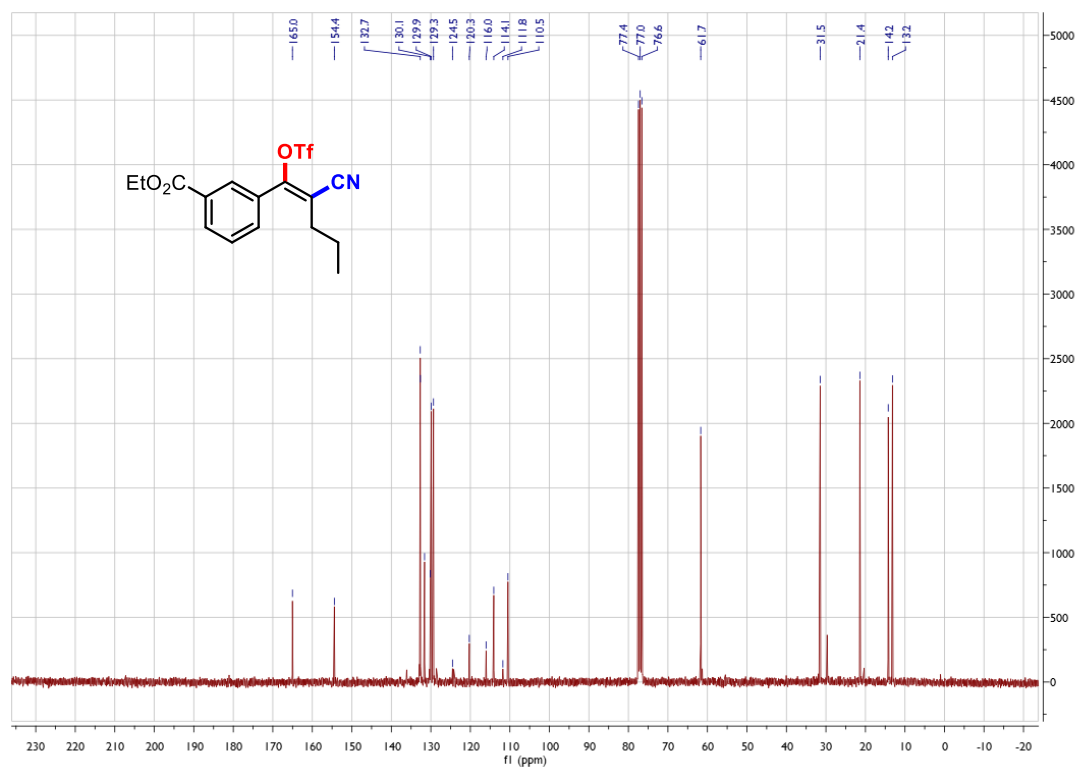
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2k**



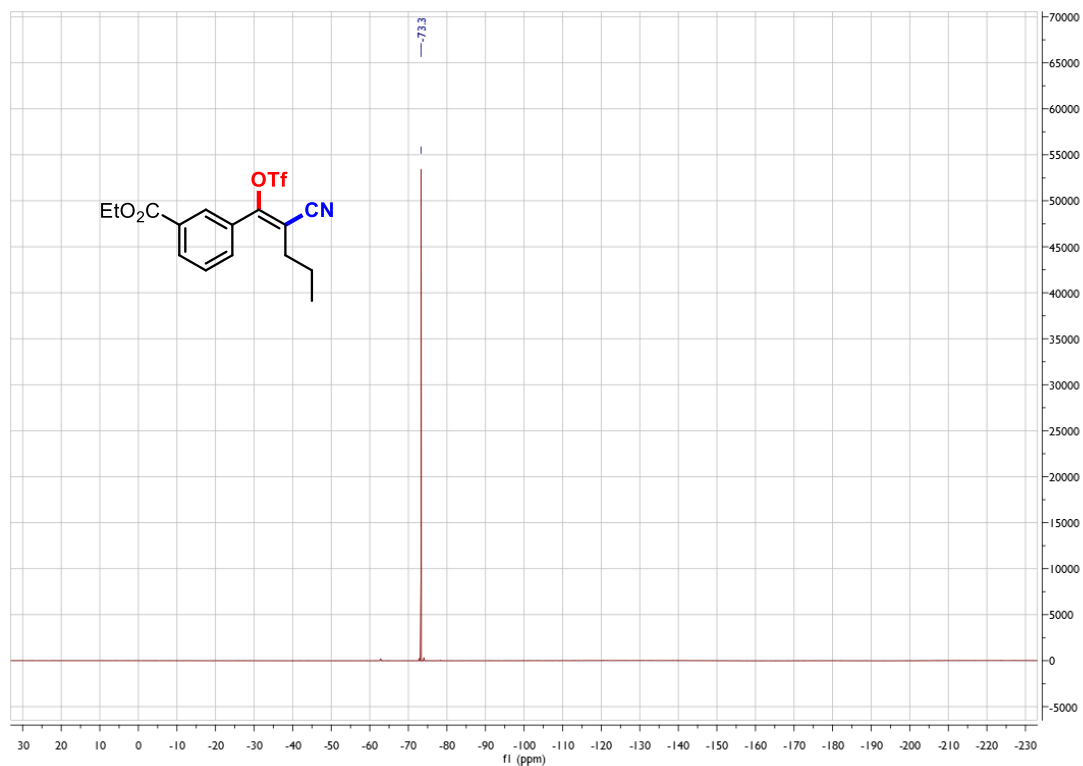
**<sup>1</sup>H NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2l**



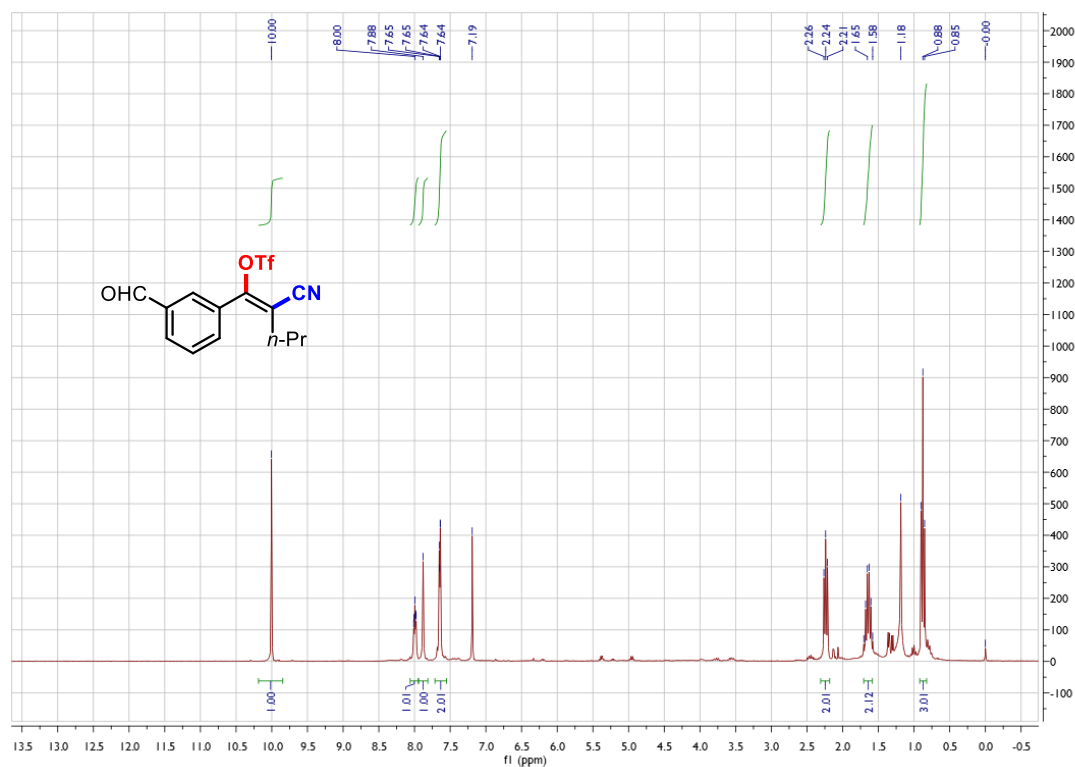
**<sup>13</sup>C NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2l**



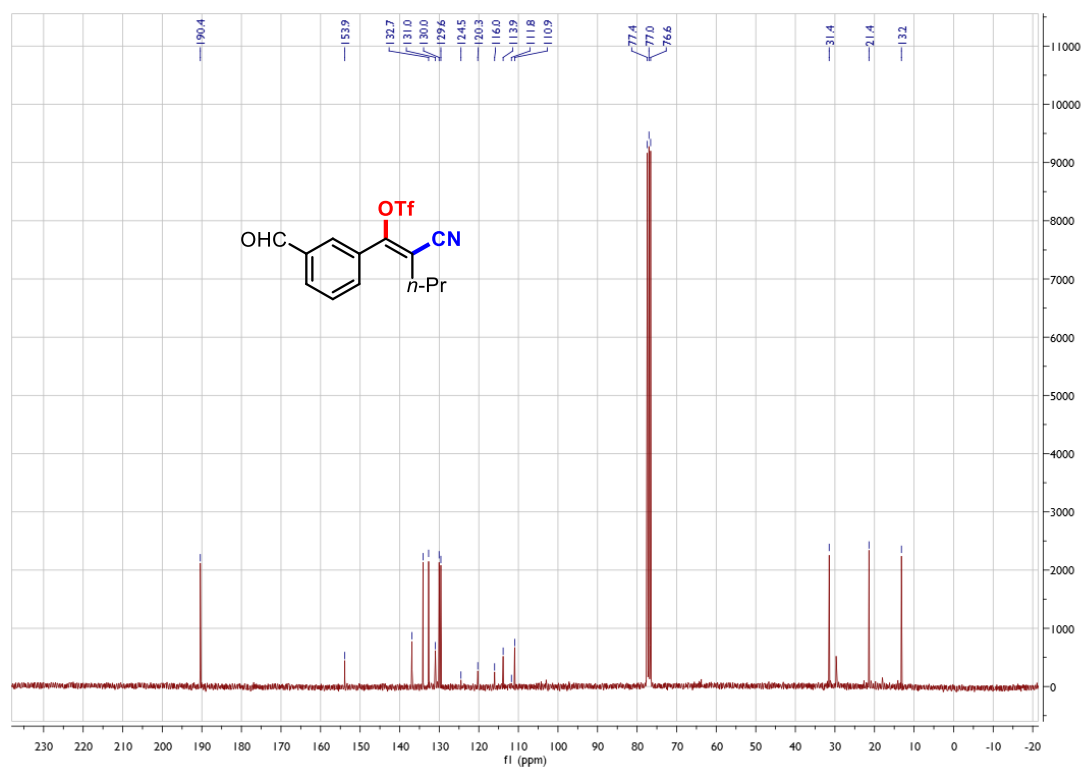
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(4-((trifluoromethyl)thio)phenyl)pent-1-en-1-yl trifluoromethanesulfonate 2l**



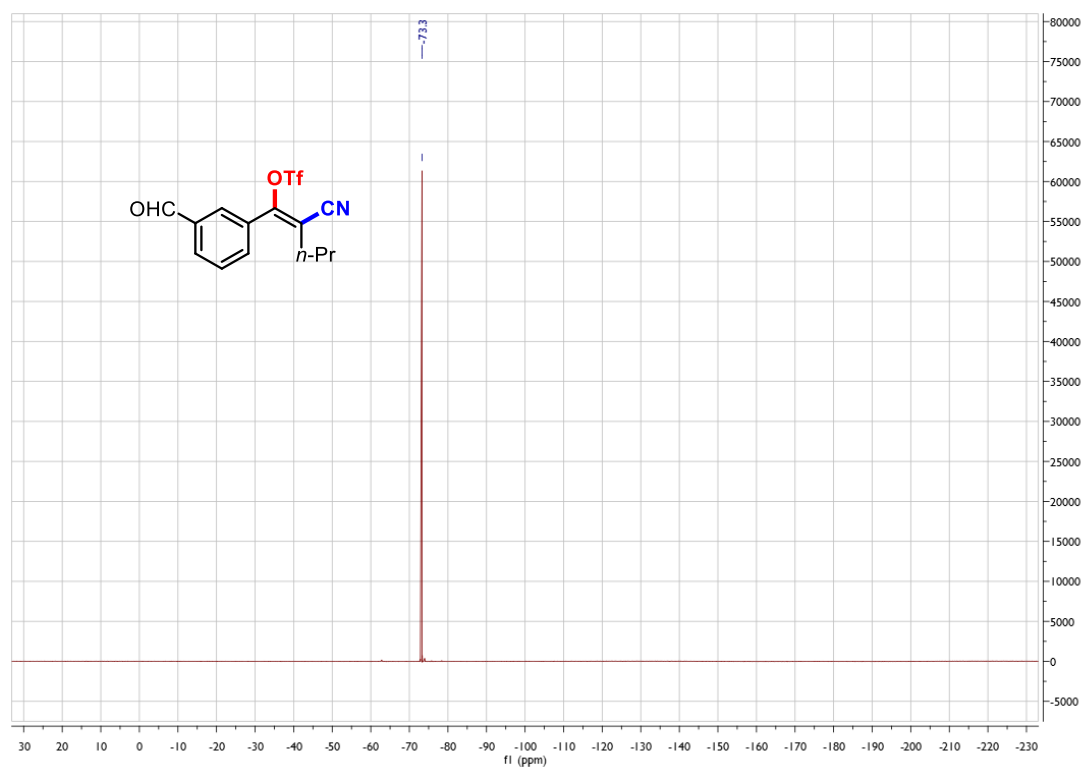
**$^1\text{H}$  NMR Spectrum of (Z)-2-cyano-1-(3-formylphenyl)pent-1-en-1-yl trifluoromethanesulfonate 2m**



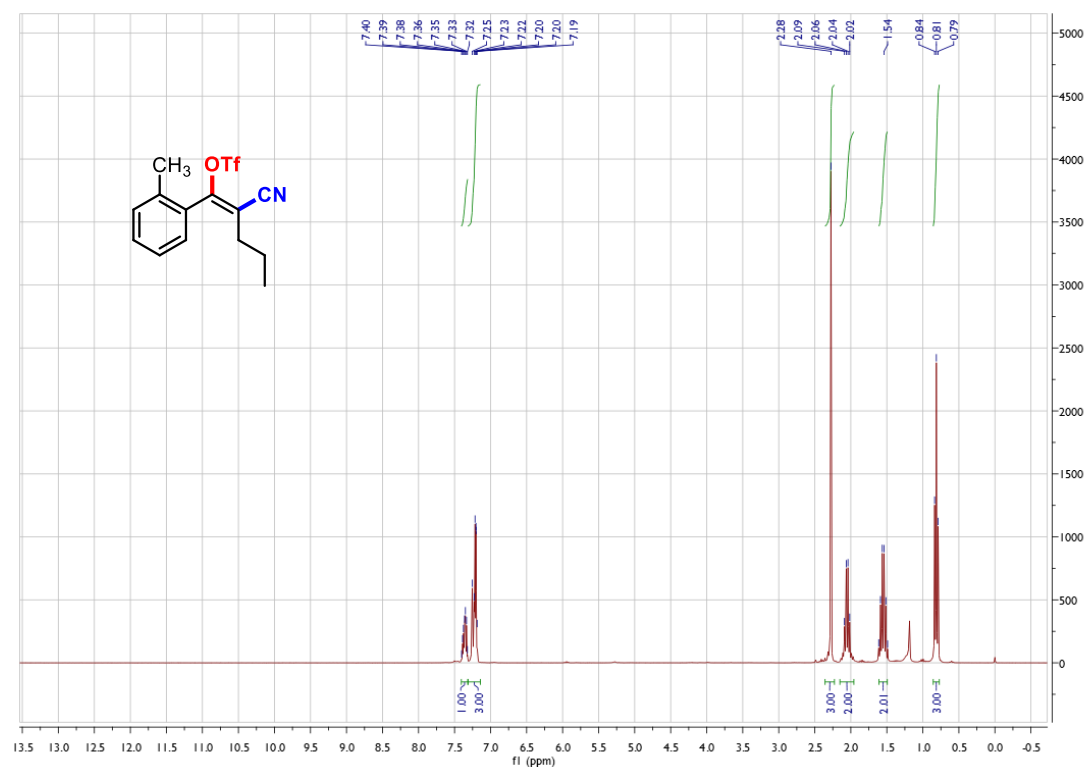
**$^{13}\text{C}$  NMR Spectrum of (Z)-2-cyano-1-(3-formylphenyl)pent-1-en-1-yl trifluoromethanesulfonate 2m**



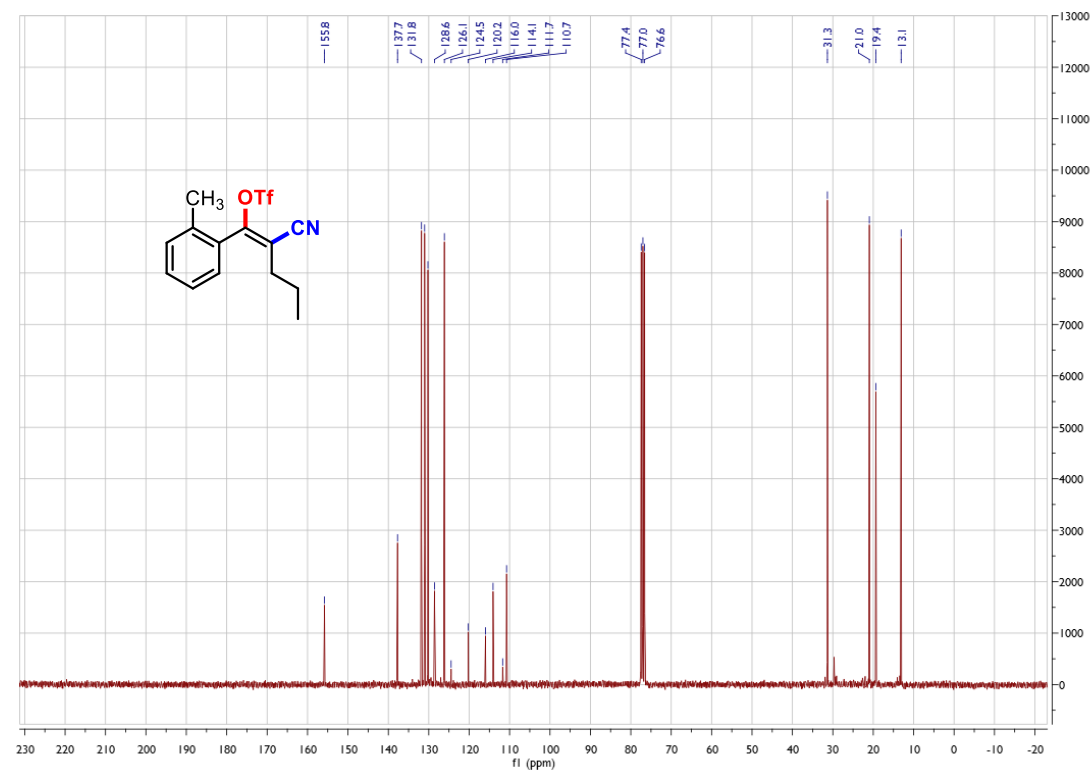
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(3-formylphenyl)pent-1-en-1-yl trifluoroethanesulfonate 2m**



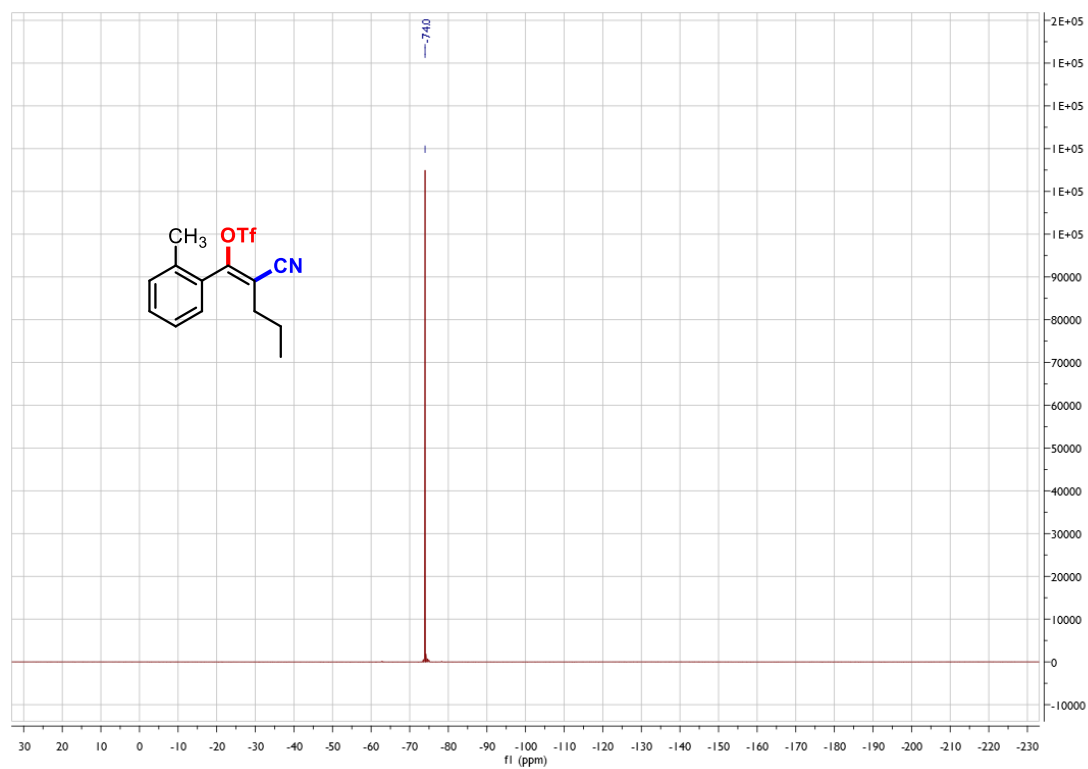
**$^1\text{H}$  NMR Spectrum of (Z)-2-cyano-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2n**



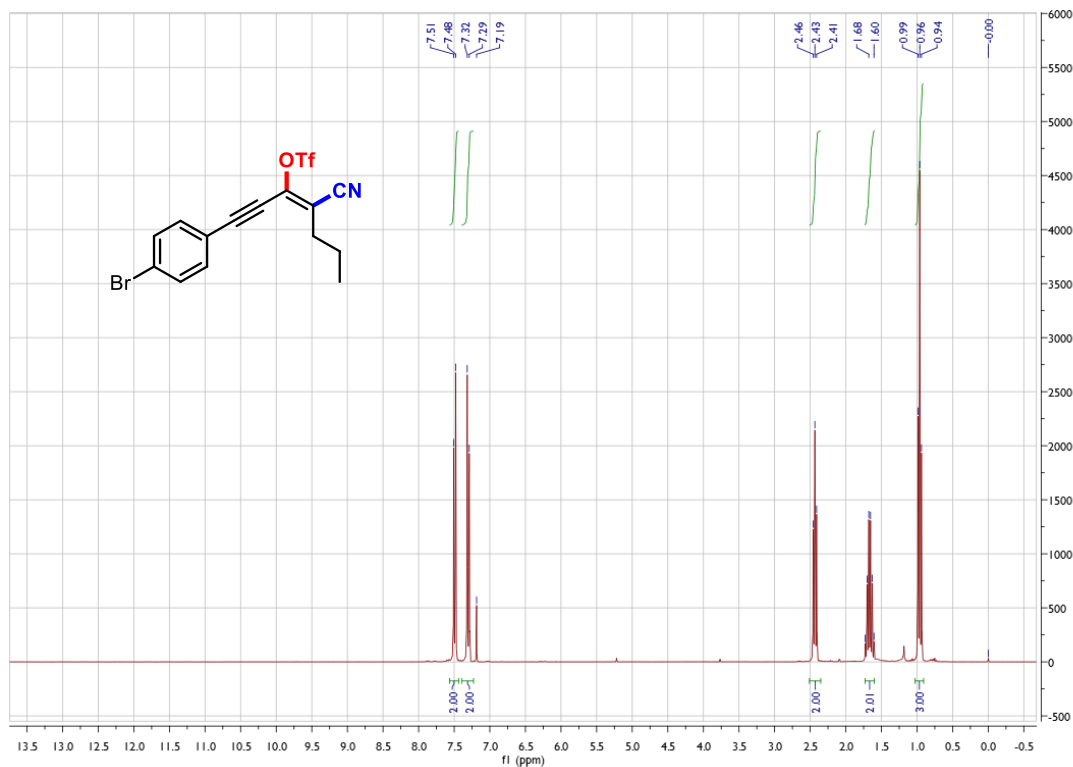
**$^{13}\text{C}$  NMR Spectrum of (Z)-2-cyano-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2n**



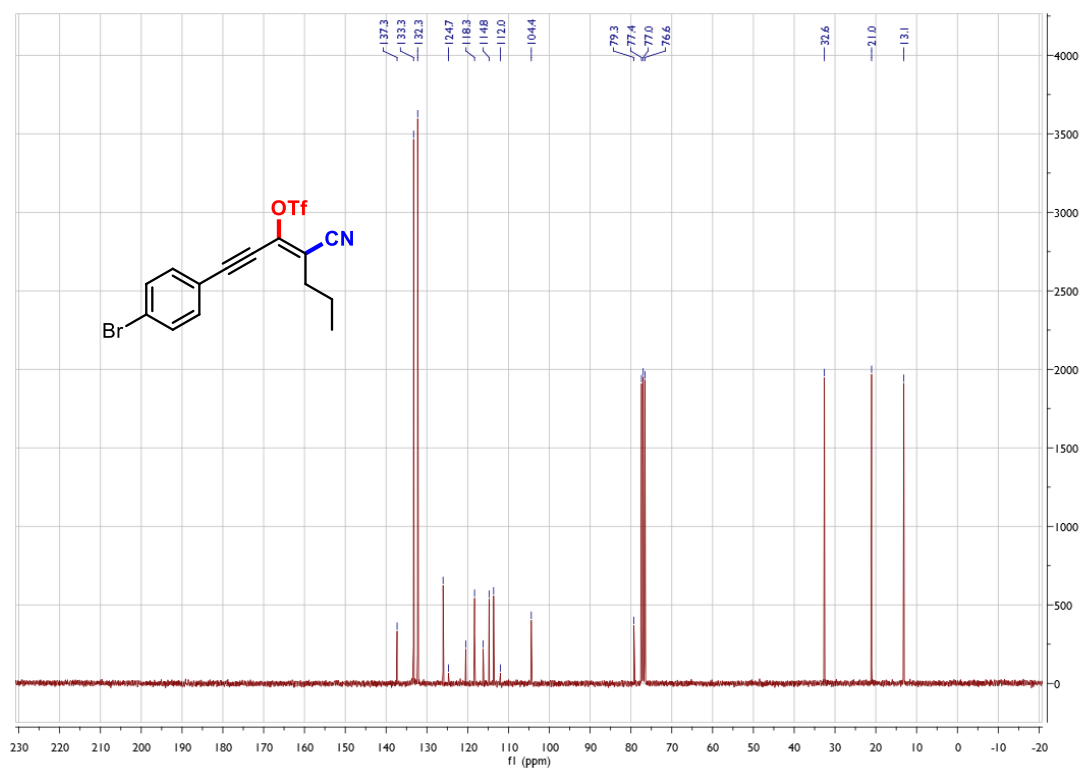
**$^{19}\text{F}$  NMR Spectrum of (Z)-2-cyano-1-(*o*-tolyl)pent-1-en-1-yl trifluoromethanesulfonate 2n**



**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-4-cyanohept-3-en-1-yn-3-yl tri-fluoromethanesulfonate 2o**

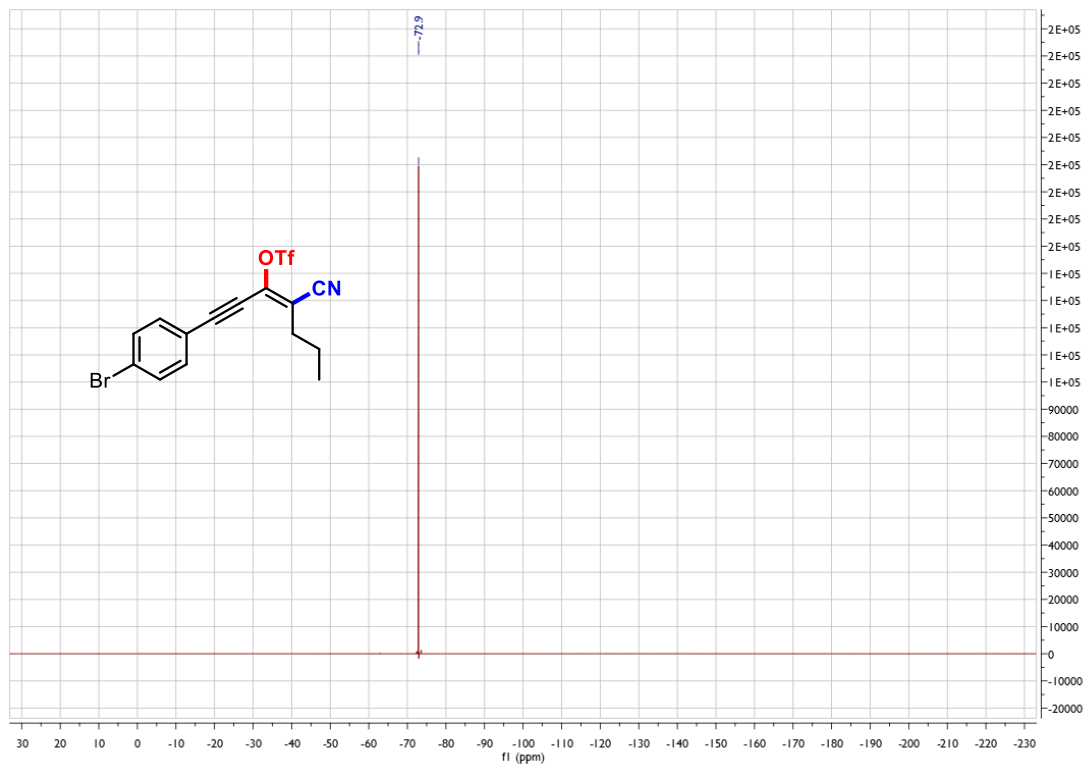


**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-4-cyanohept-3-en-1-yn-3-yl tri-fluoromethanesulfonate 2o**

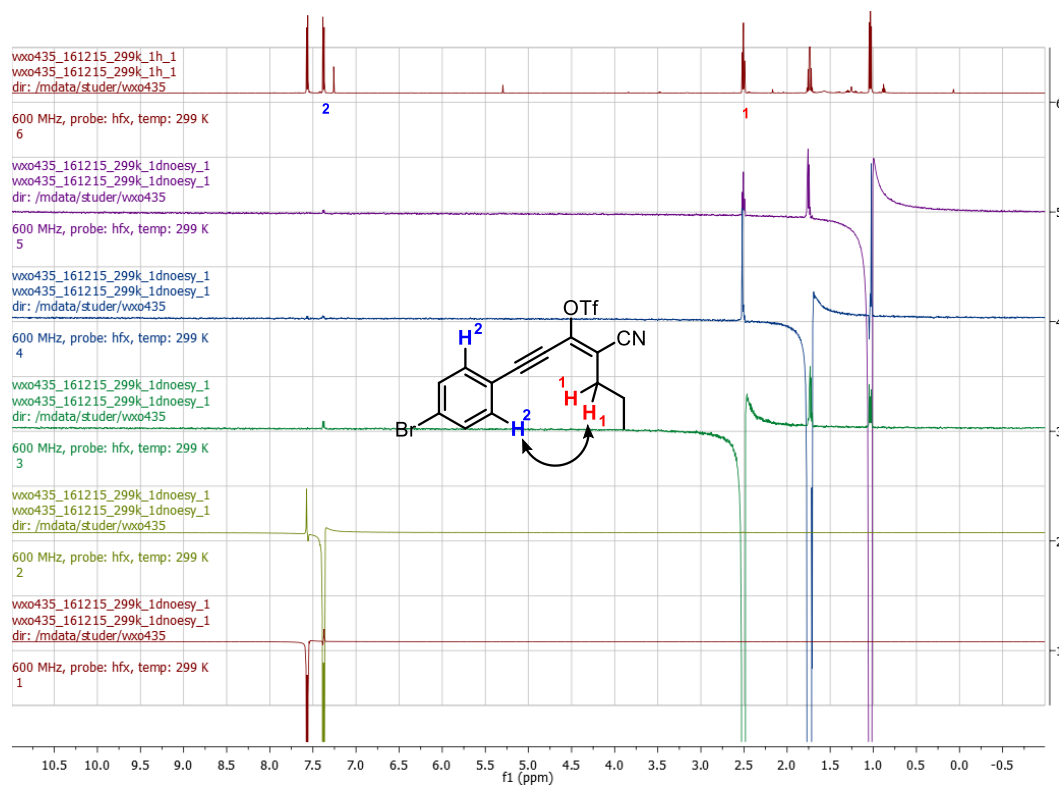




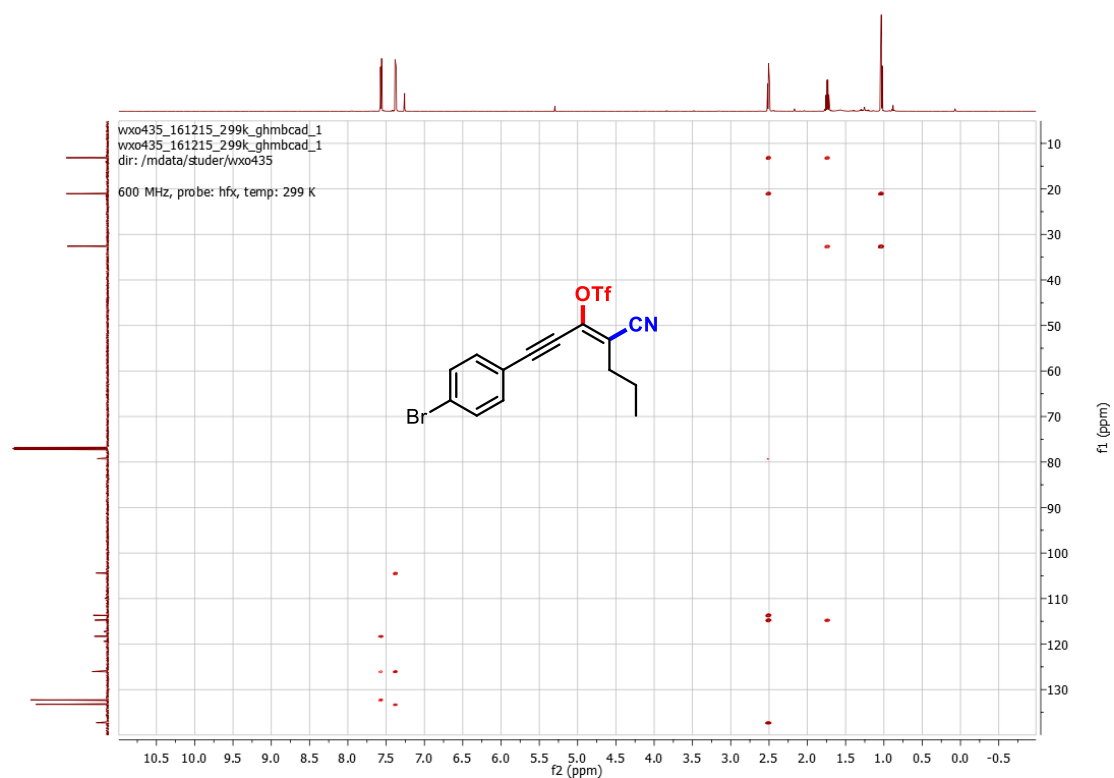
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-4-cyanohept-3-en-1-yn-3-yl tri-fluoromethanesulfonate 2o**



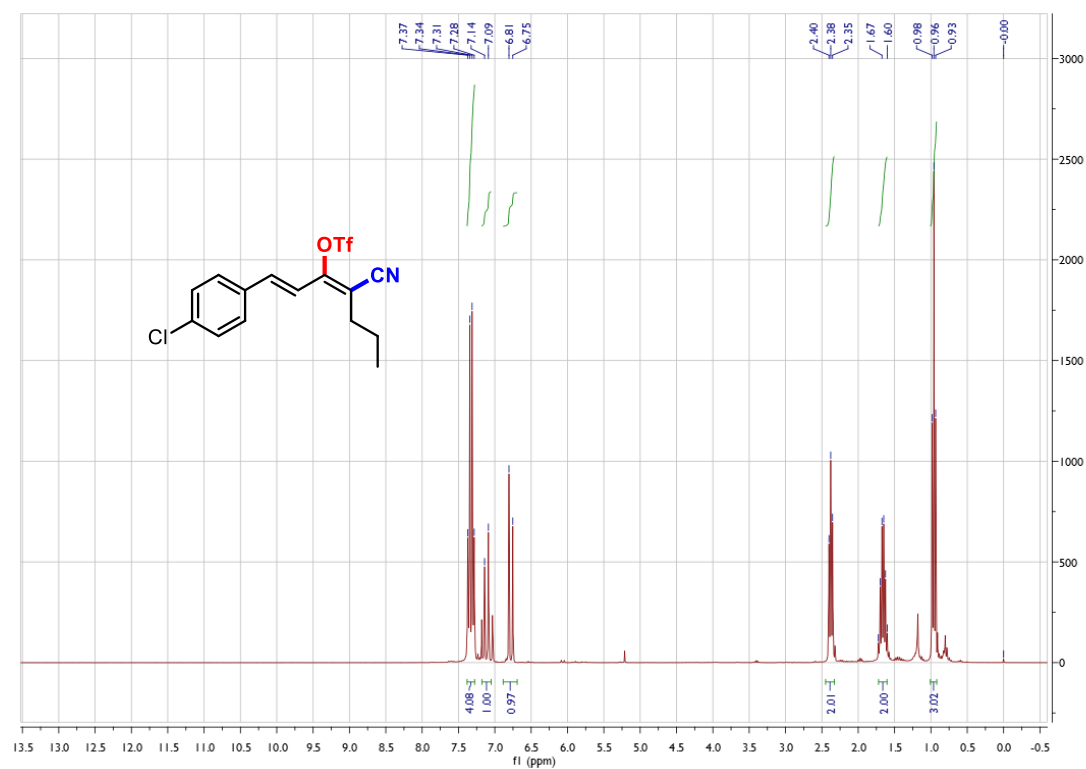
**NOESY1D Spectrum of (Z)-1-(4-bromophenyl)-4-cyanohept-3-en-1-yn-3-yl tri-fluoromethanesulfonate 2o**



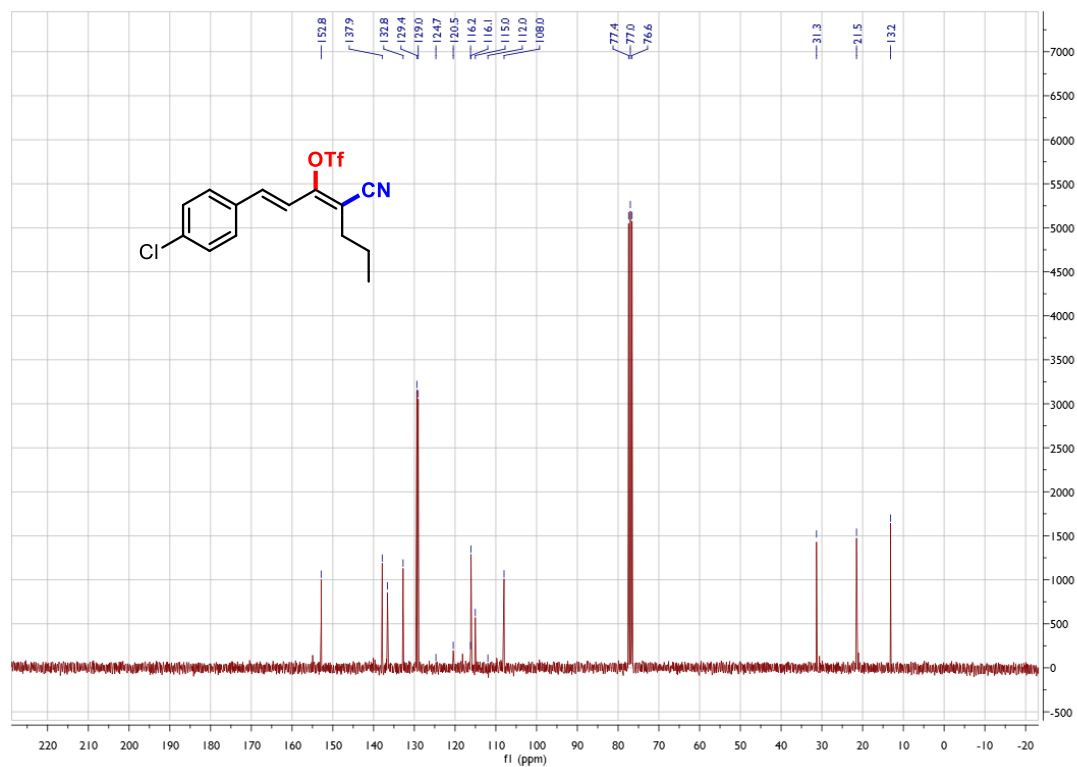
**$^{13}\text{C}/^1\text{H}$  GHMBCAD Spectrum of (Z)-1-(4-bromophenyl)-4-cyanohept-3-en-1-yn-3-yl trifluoromethanesulfonate 2o**



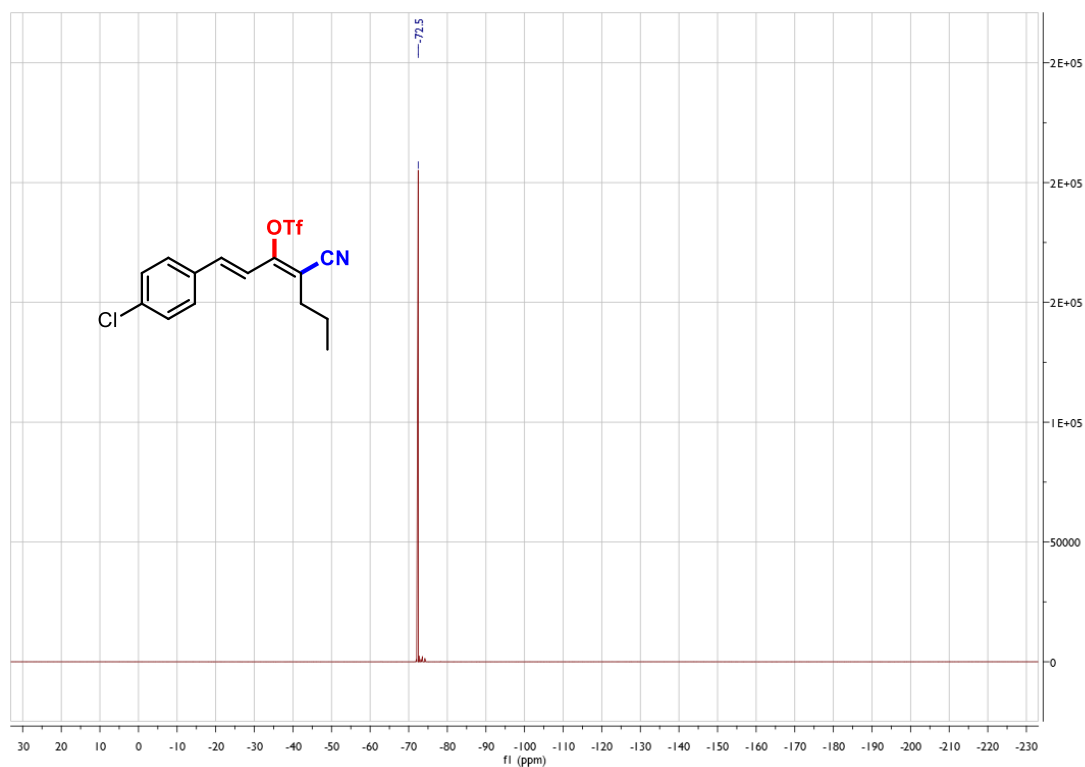
**$^1\text{H}$  NMR Spectrum of (1*E*, 3*Z*)-1-(4-chlorophenyl)-4-cyanohepta-1,3-dien-3-yl trifluoromethanesulfonate 2p**



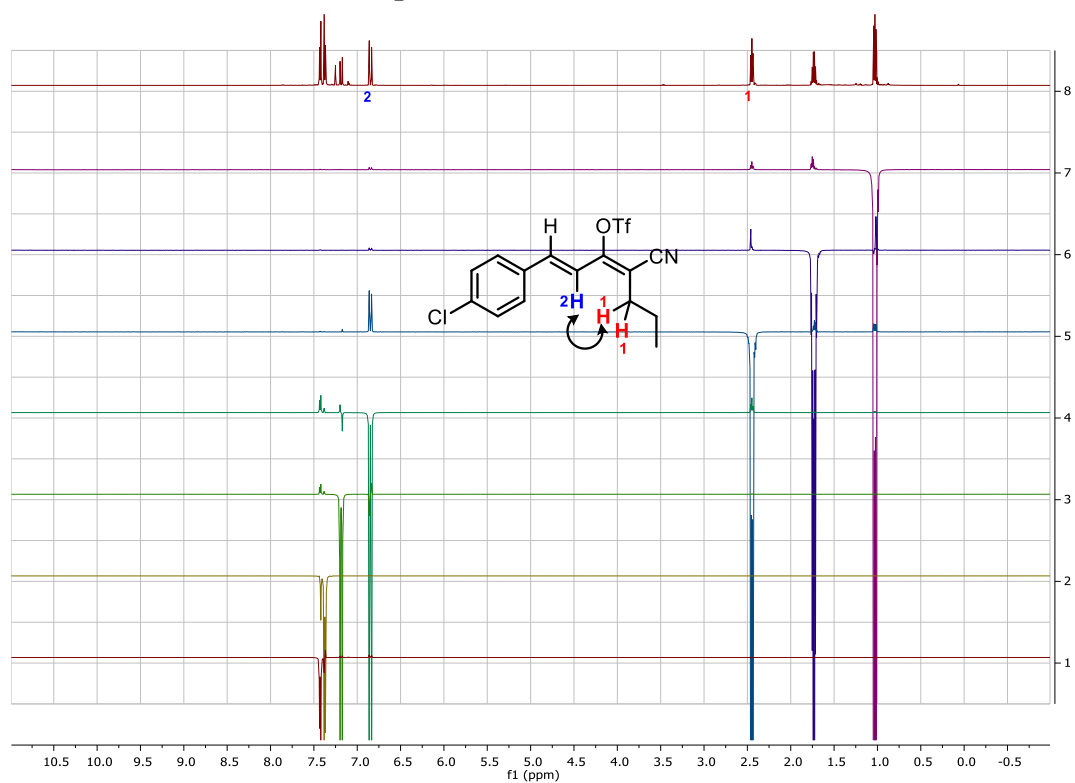
**$^{13}\text{C}$  NMR Spectrum of (1*E*, 3*Z*)-1-(4-chlorophenyl)-4-cyanohepta-1,3-dien-3-yl trifluoromethanesulfonate 2p**



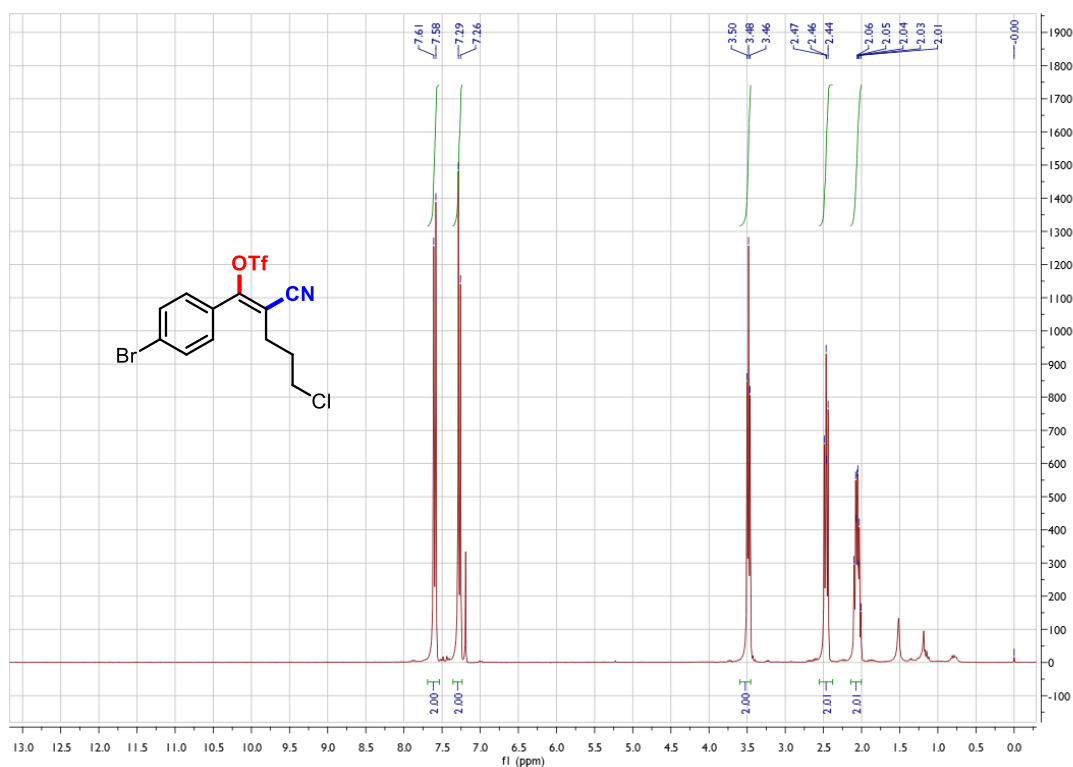
**$^{19}\text{F}$  NMR Spectrum of (1*E*, 3*Z*)-1-(4-chlorophenyl)-4-cyanohepta-1,3-dien-3-yl trifluoromethanesulfonate 2p**



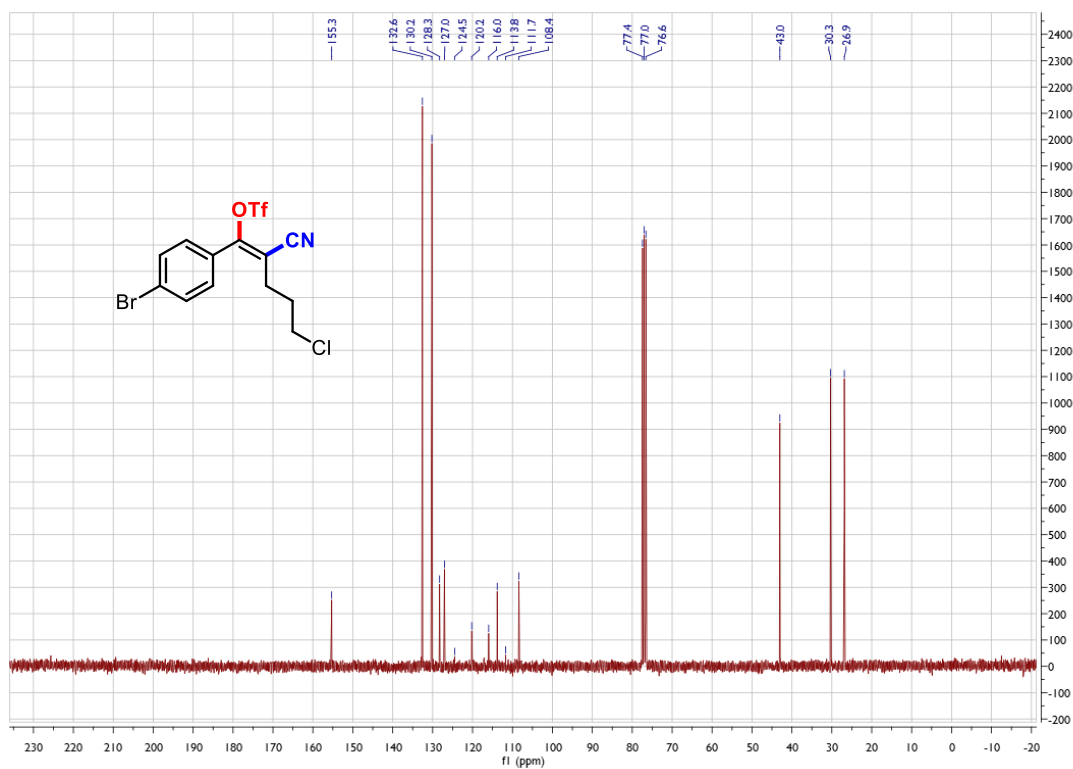
**NOESY1D Spectrum of (1*E*, 3*Z*)-1-(4-chlorophenyl)-4-cyanohepta-1,3-dien-3-yl trifluoromethanesulfonate 2p**



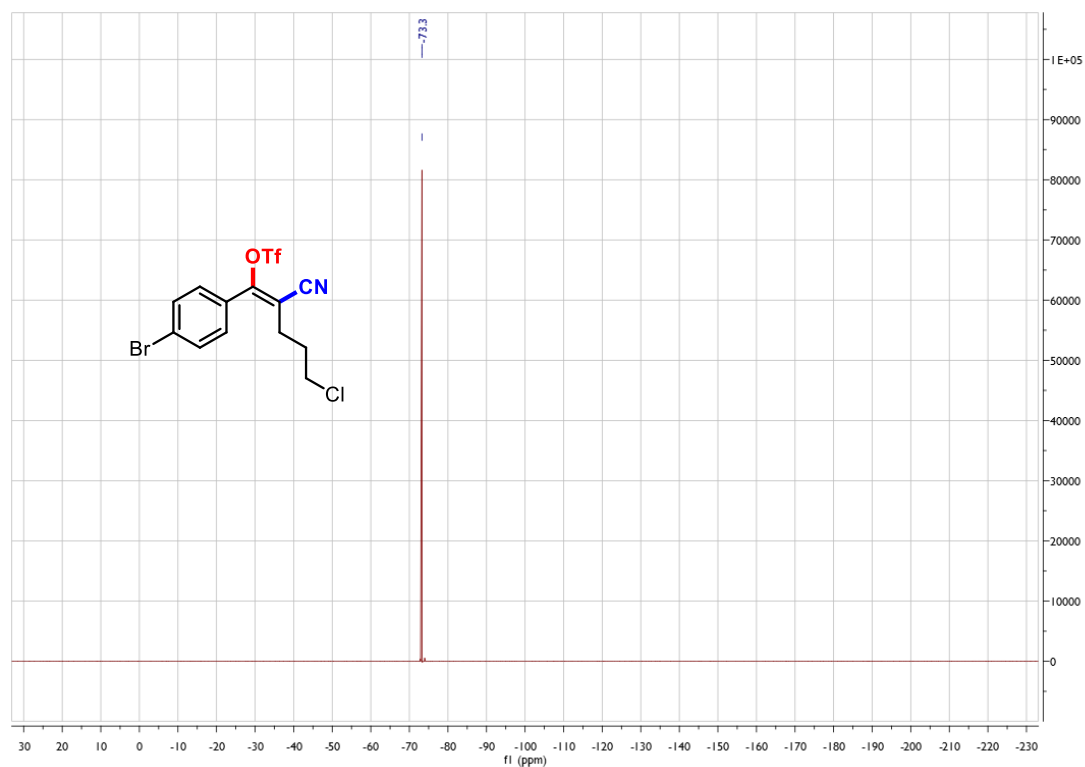
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-5-chloro-2-cyanopent-1-en-1-yl tri-fluoromethanesulfonate 2q**



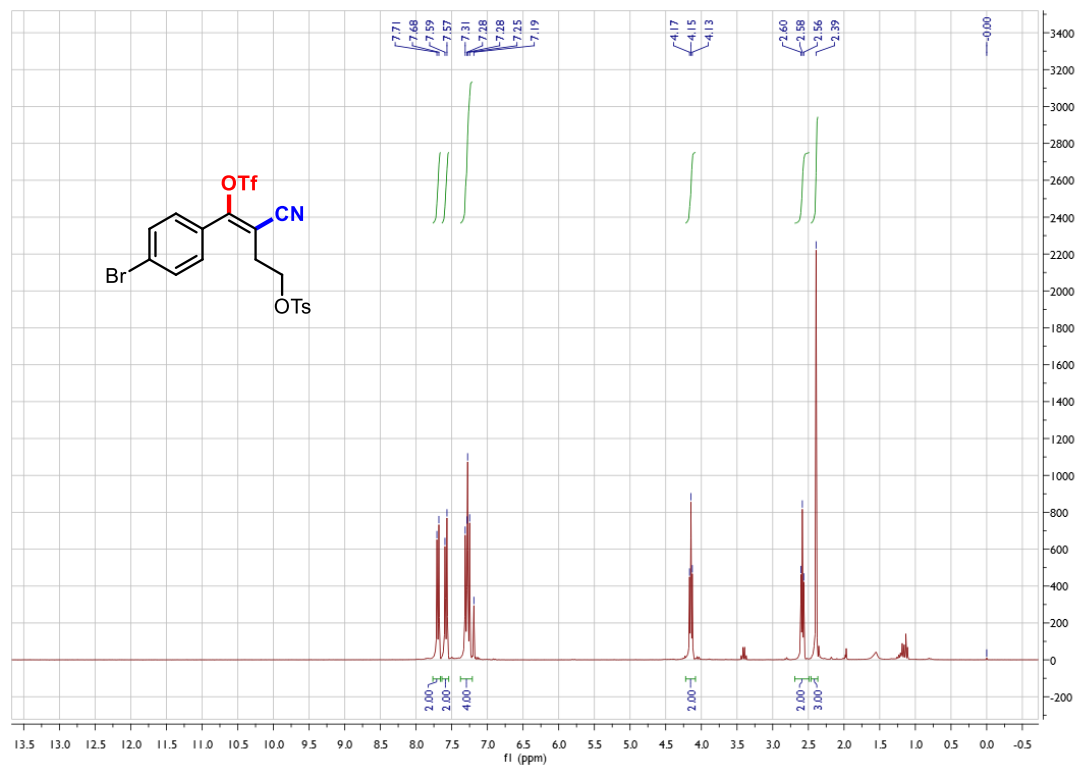
**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-5-chloro-2-cyanopent-1-en-1-yl tri-fluoromethanesulfonate 2q**



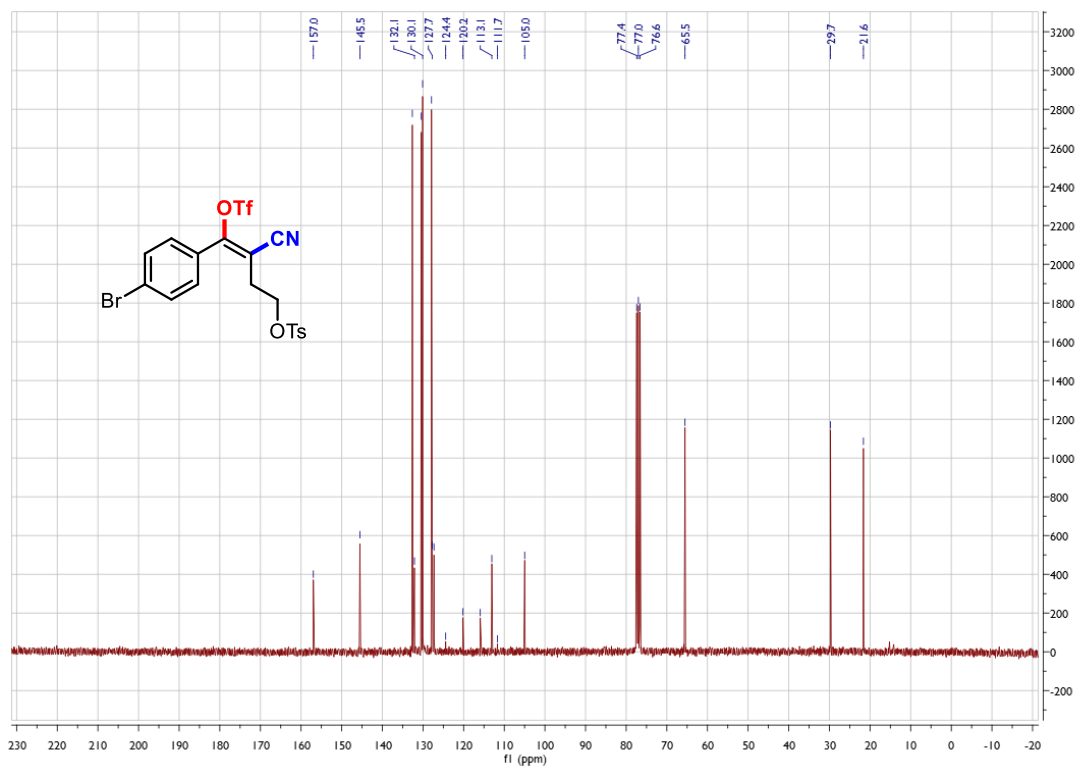
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-5-chloro-2-cyanopent-1-en-1-yl tri-fluoromethanesulfonate 2q**



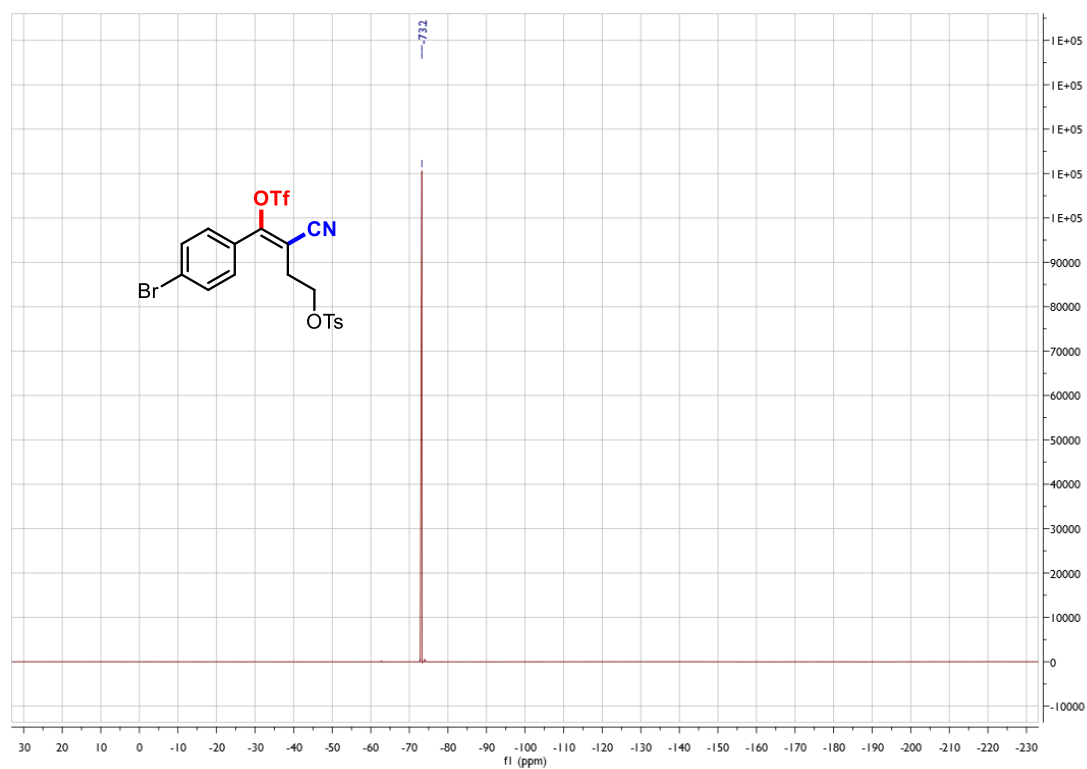
**<sup>1</sup>H NMR Spectrum of (Z)-4-(4-bromophenyl)-3-cyano-4-(((trifluoromethyl)sulfonyl)-oxy)but-3-en-1-yl 4-methylbenzenesulfonate 2r**



**<sup>13</sup>C NMR Spectrum of (Z)-4-(4-bromophenyl)-3-cyano-4-(((trifluoromethyl)sulfonyl)-oxy)but-3-en-1-yl 4-methylbenzenesulfonate 2r**

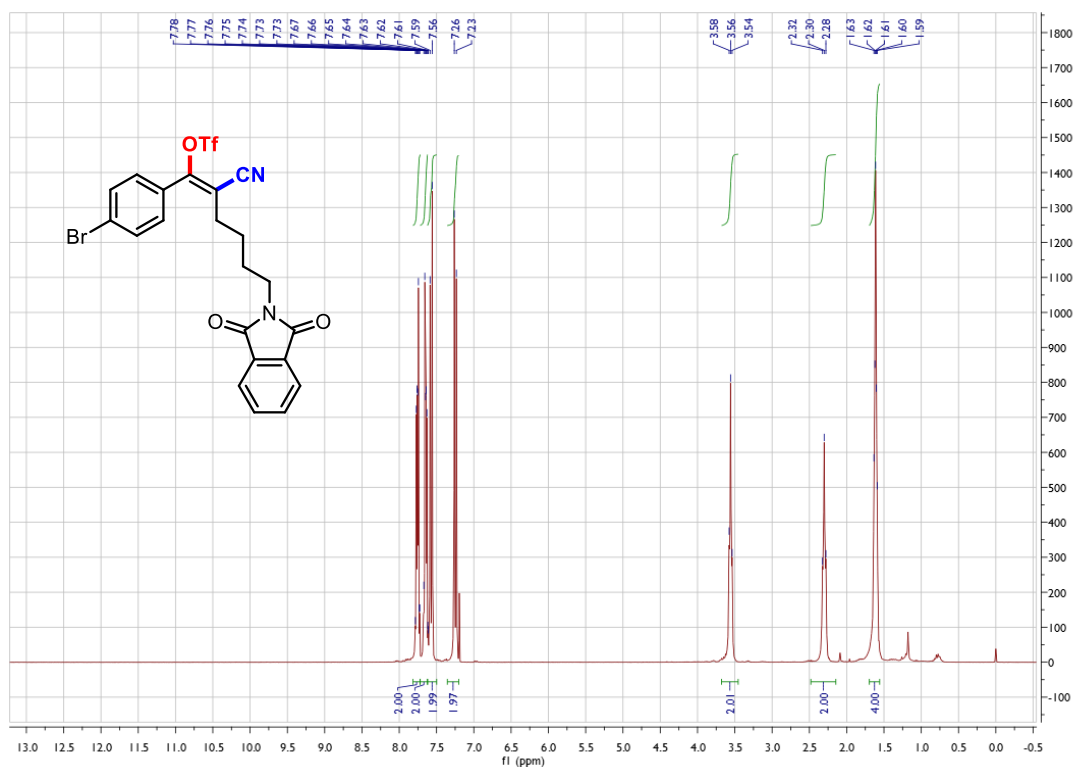


**$^{19}\text{F}$  NMR Spectrum of (Z)-4-(4-bromophenyl)-3-cyano-4-(((trifluoromethyl)sulfonyl)-oxy)but-3-en-1-yl 4-methylbenzenesulfonate 2r**

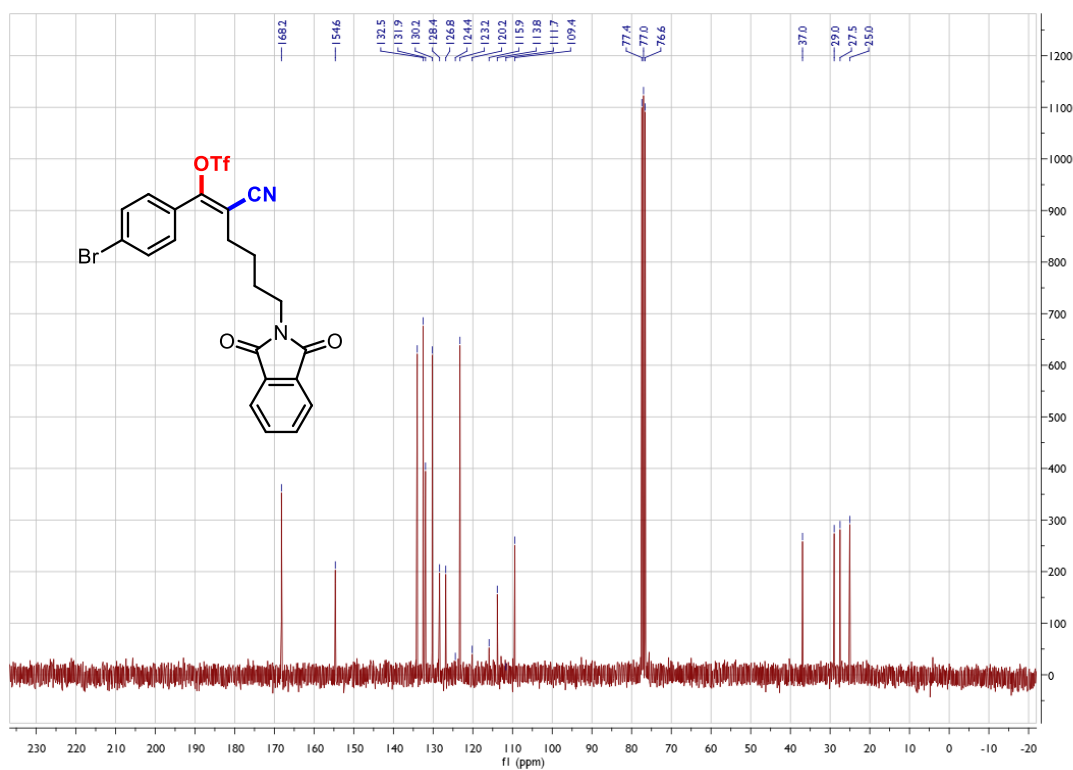




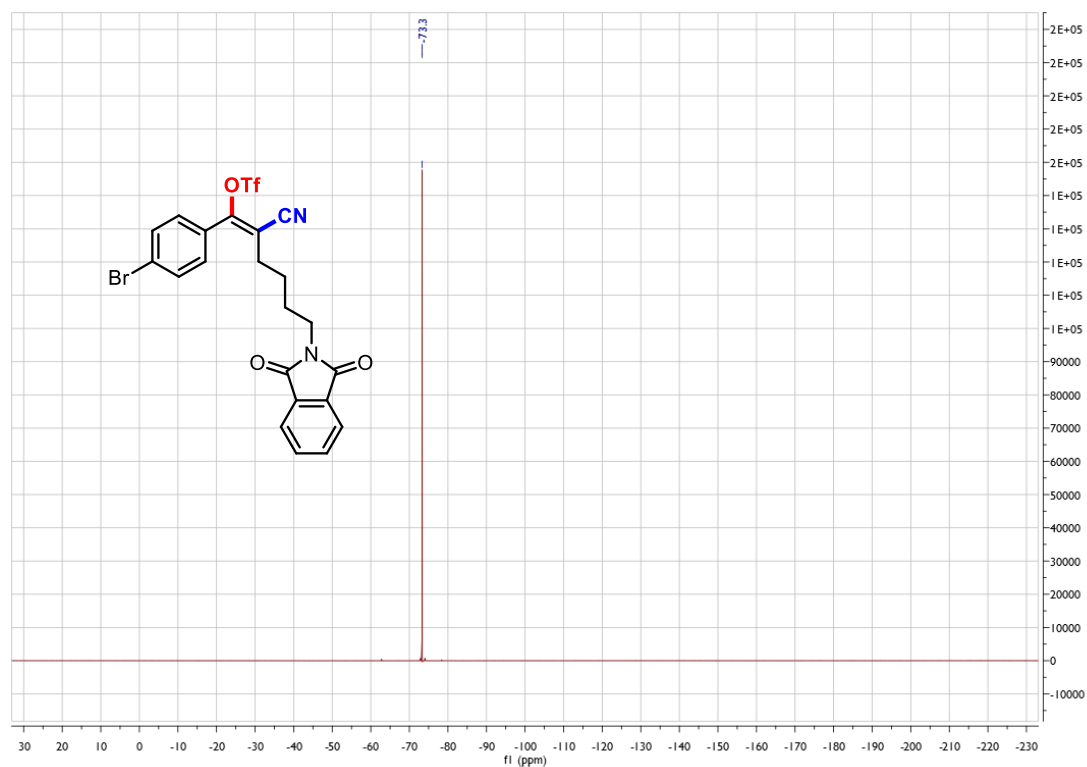
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-6-(1,3-dioxisoindolin-2-yl)hex-1-en-1-yl trifluoromethanesulfonate 2s**



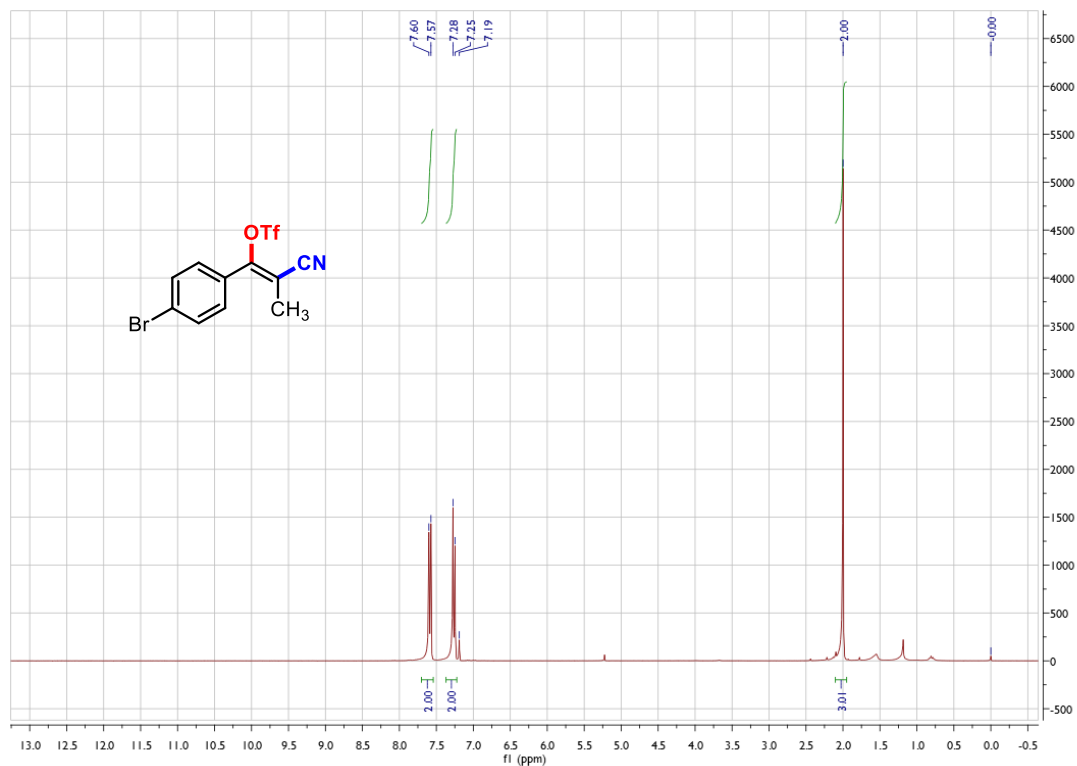
**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-6-(1,3-dioxisoindolin-2-yl)hex-1-en-1-yl trifluoromethanesulfonate 2s**



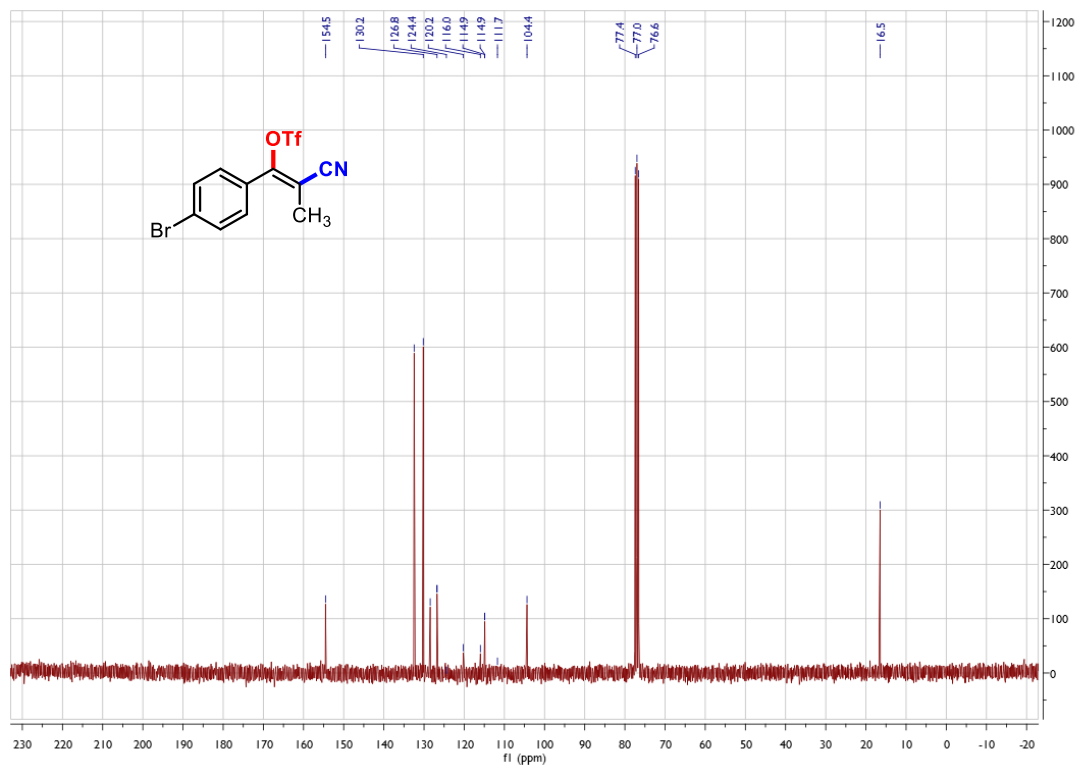
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-6-(1,3-dioxisoindolin-2-yl)hex-1-en-1-yl trifluoromethanesulfonate 2s**



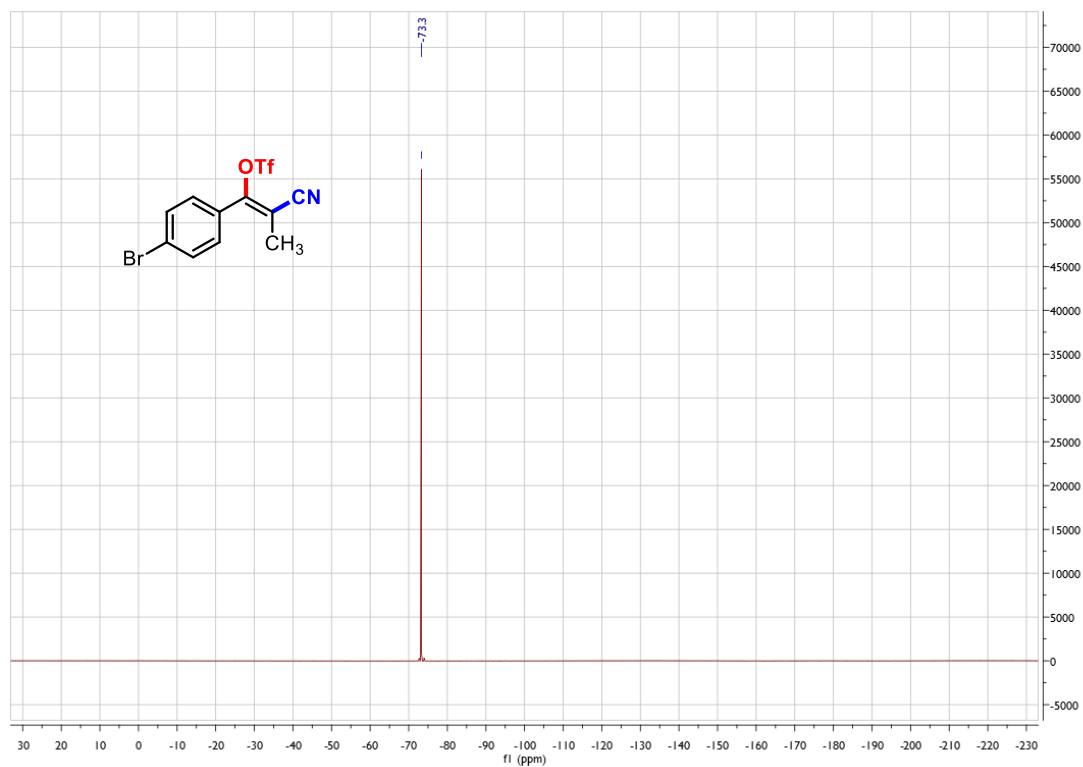
**$^1\text{H}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanoprop-1-en-1-yl trifluoromethanesulfonate 2t**



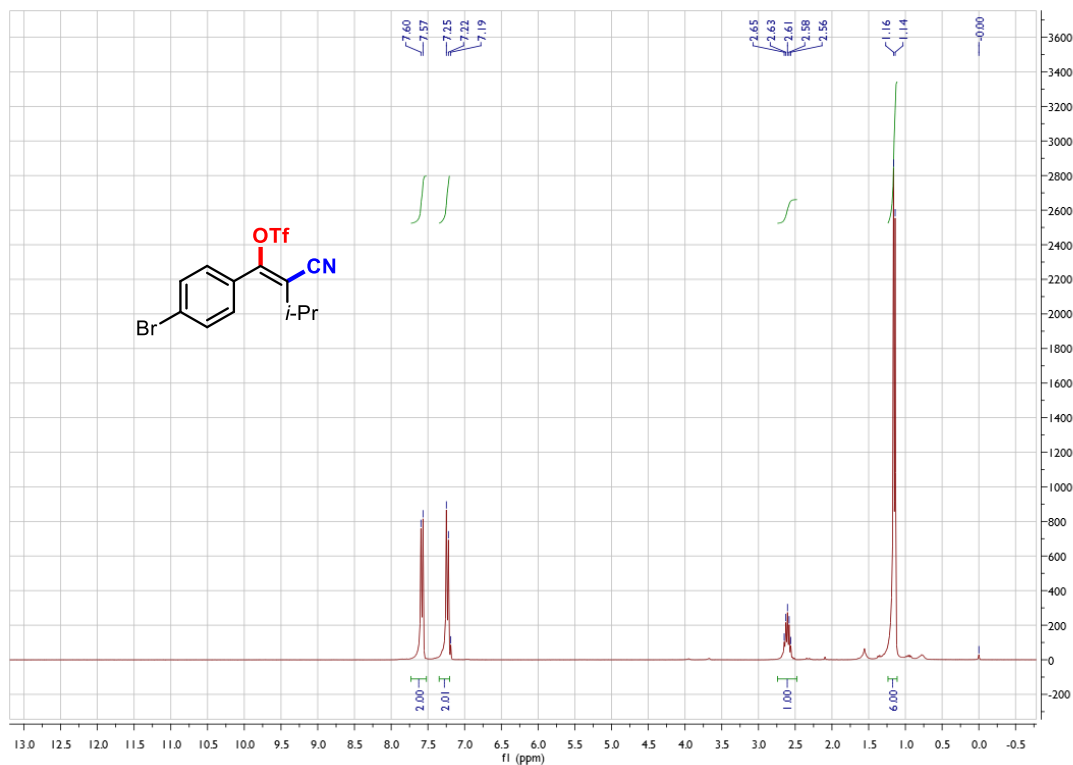
**$^{13}\text{C}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanoprop-1-en-1-yl trifluoromethanesulfonate 2t**



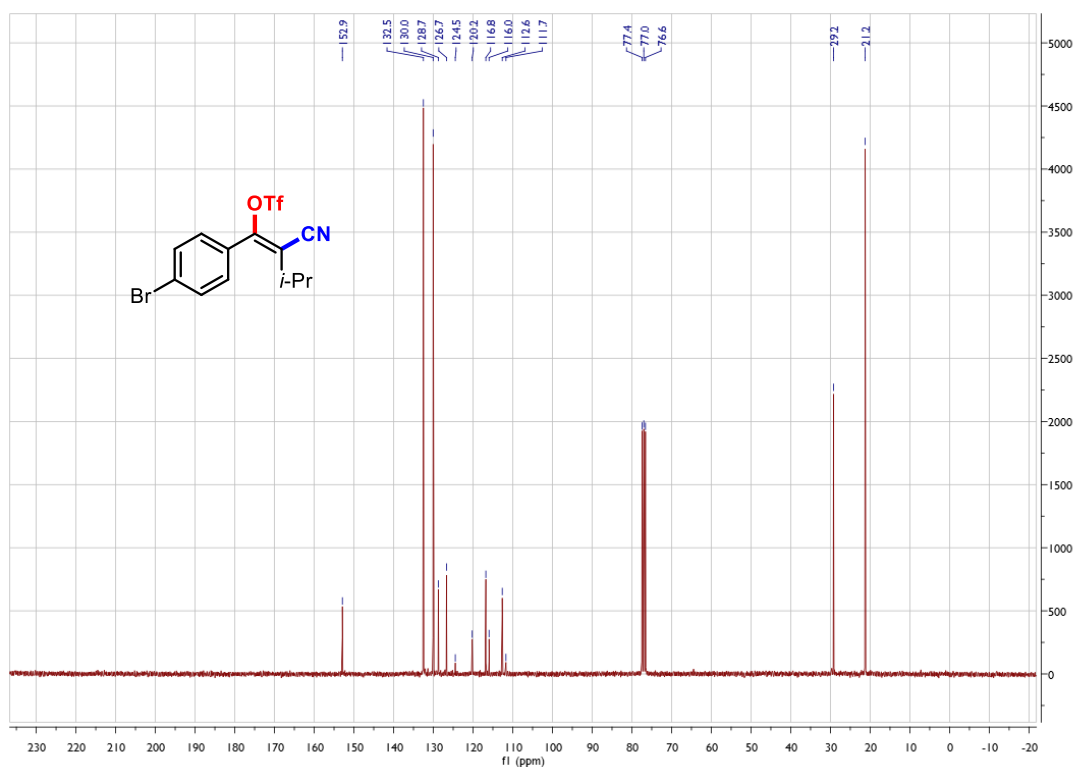
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyanoprop-1-en-1-yl trifluoromethanesulfonate 2t**



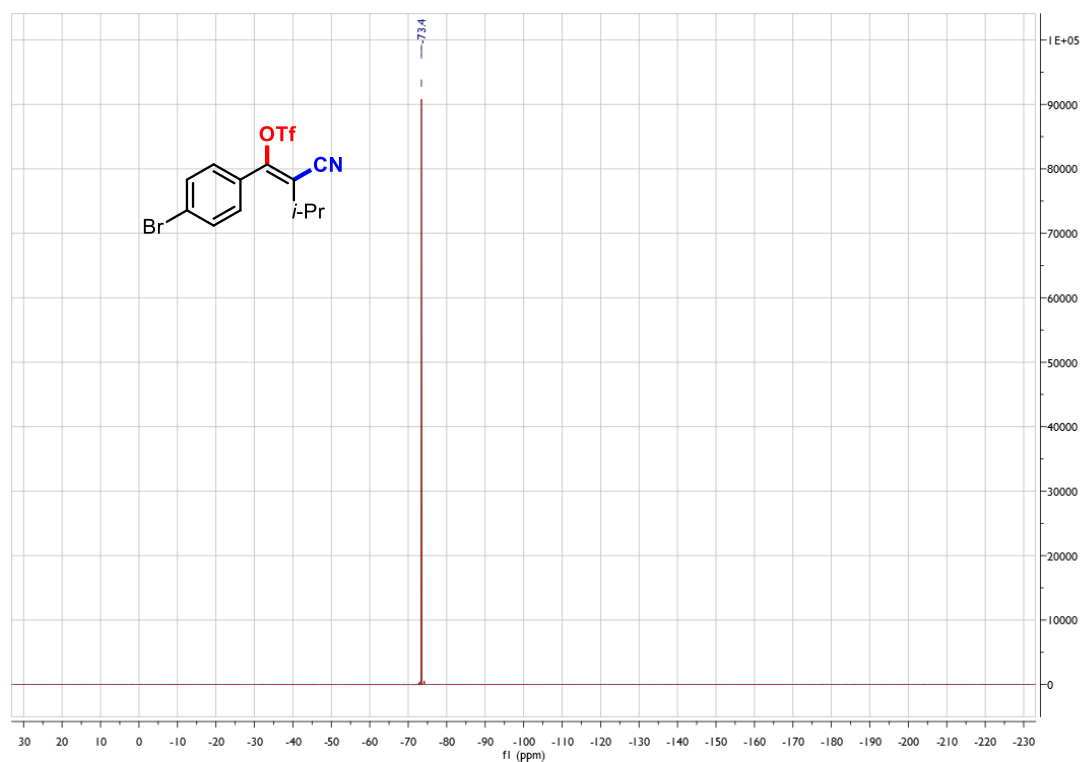
**$^1\text{H}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3-methylbut-1-en-1-yl tri-fluoromethanesulfonate 2u**



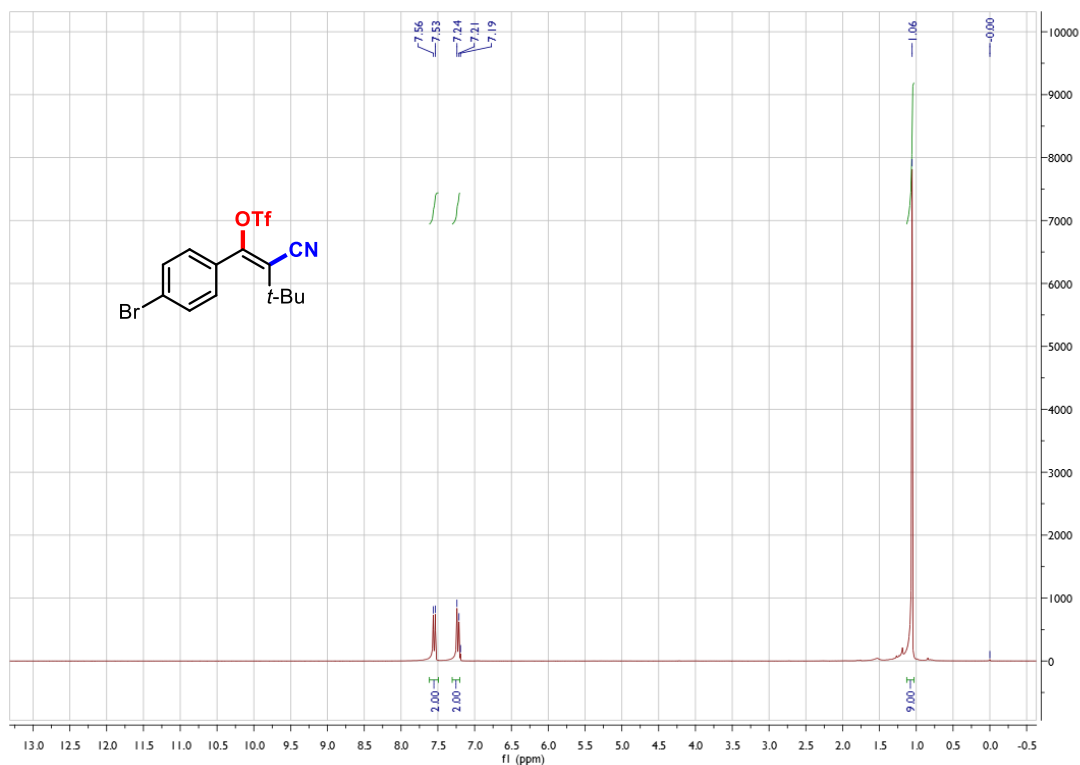
**$^{13}\text{C}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3-methylbut-1-en-1-yl tri-fluoromethanesulfonate 2u**



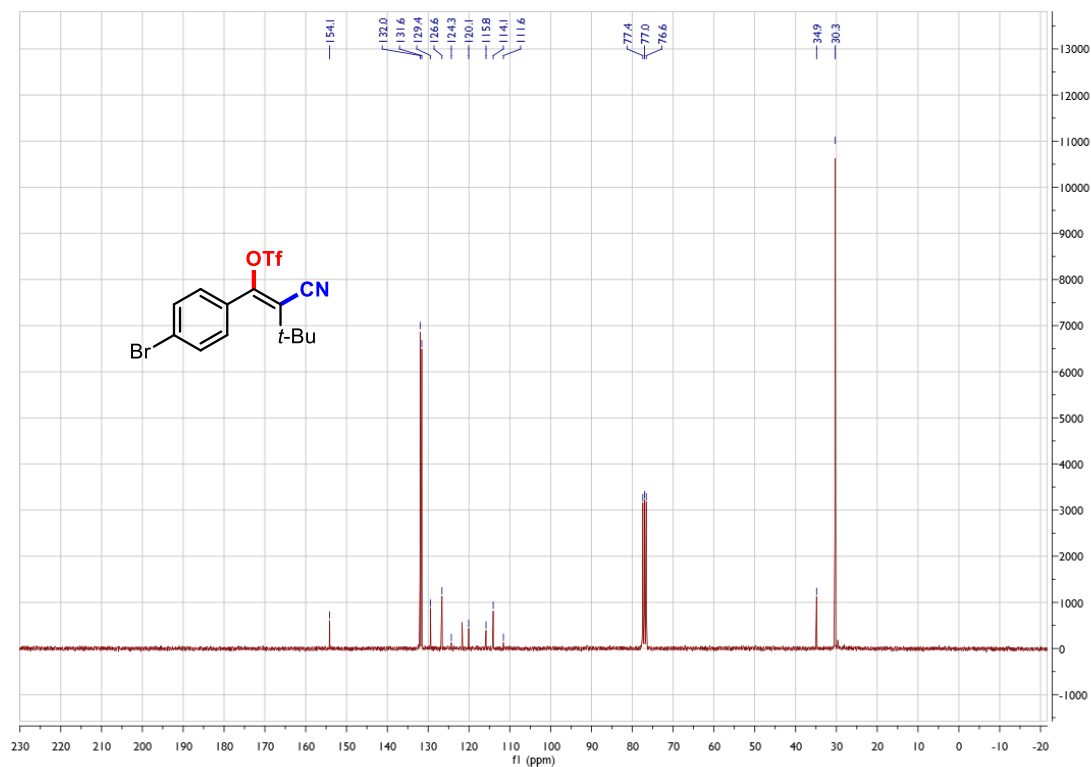
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3-methylbut-1-en-1-yl tri-fluoromethanesulfonate 2u**



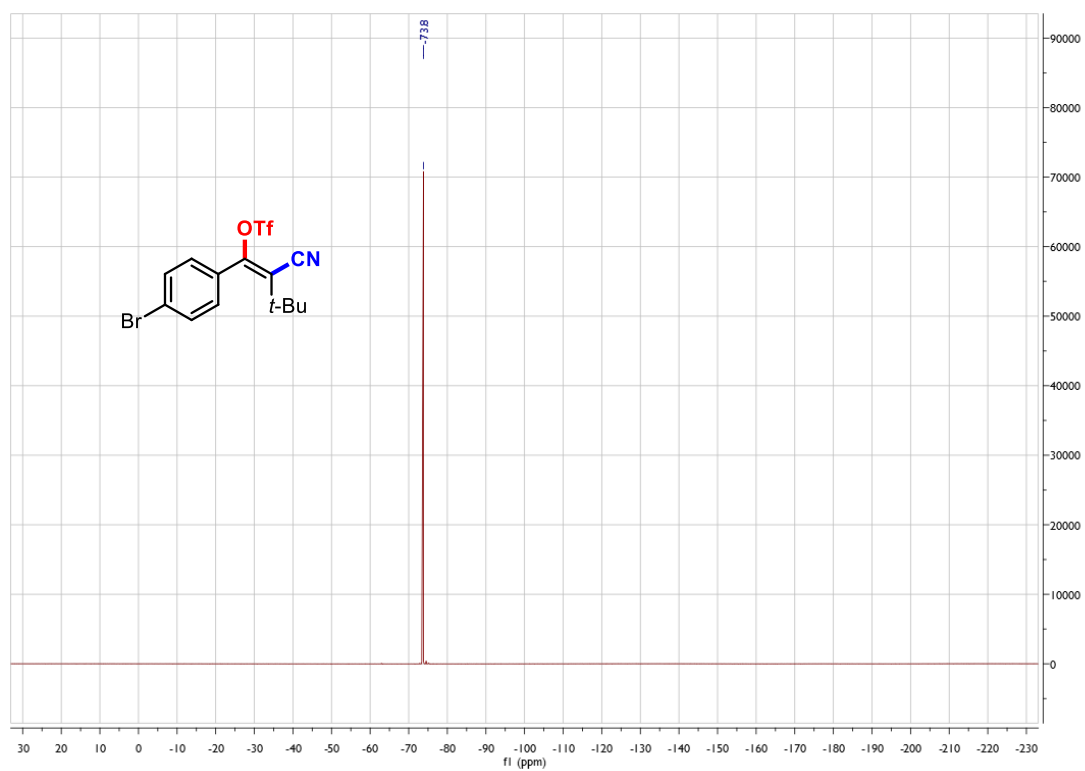
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3,3-dimethylbut-1-en-1-yl trifluoromethanesulfonate 2v**



**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3,3-dimethylbut-1-en-1-yl trifluoromethanesulfonate 2v**

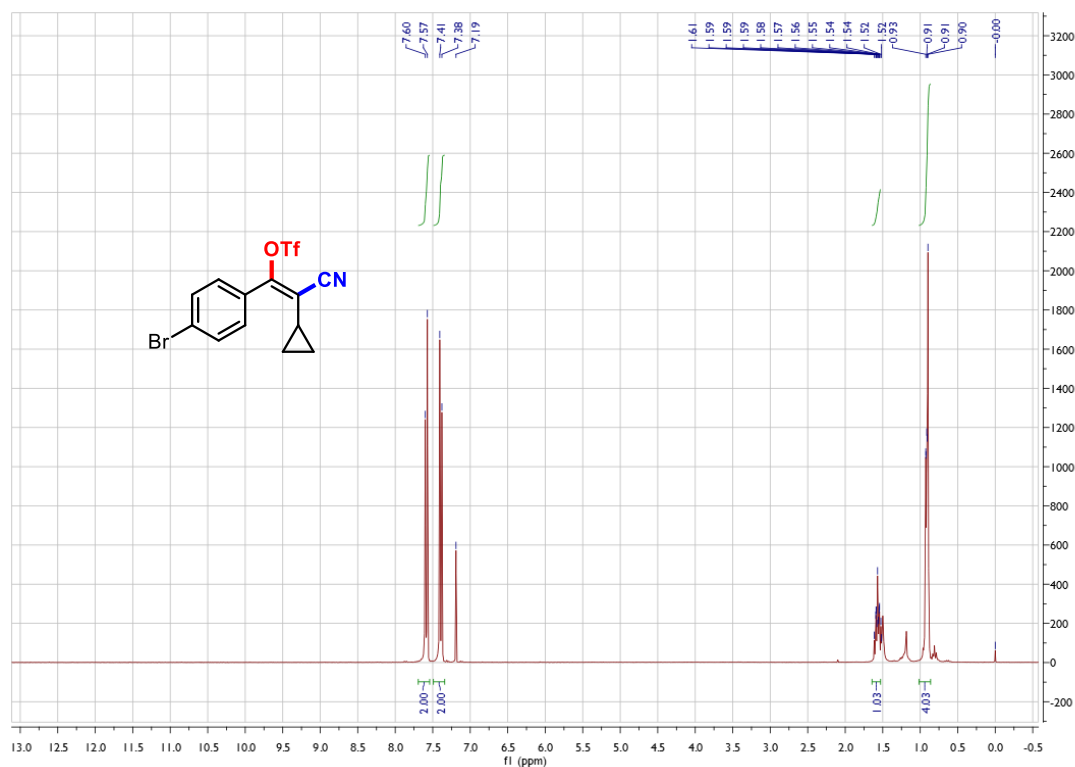


**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-3,3-dimethylbut-1-en-1-yl trifluoromethanesulfonate **2v****

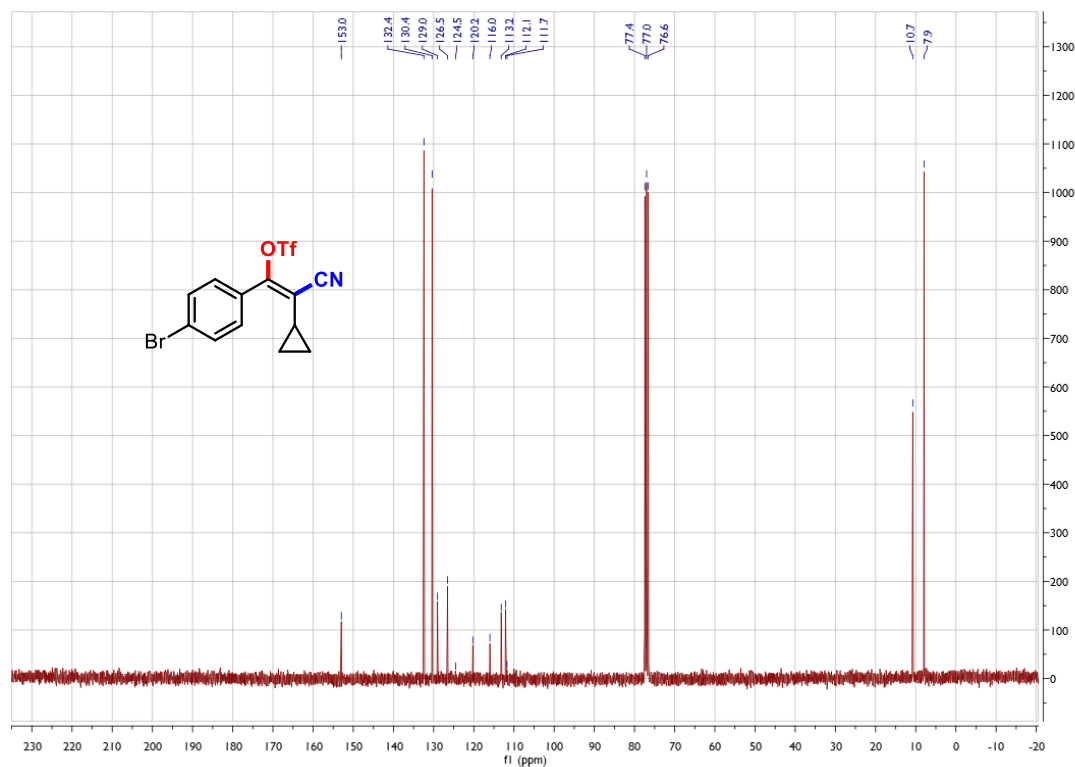




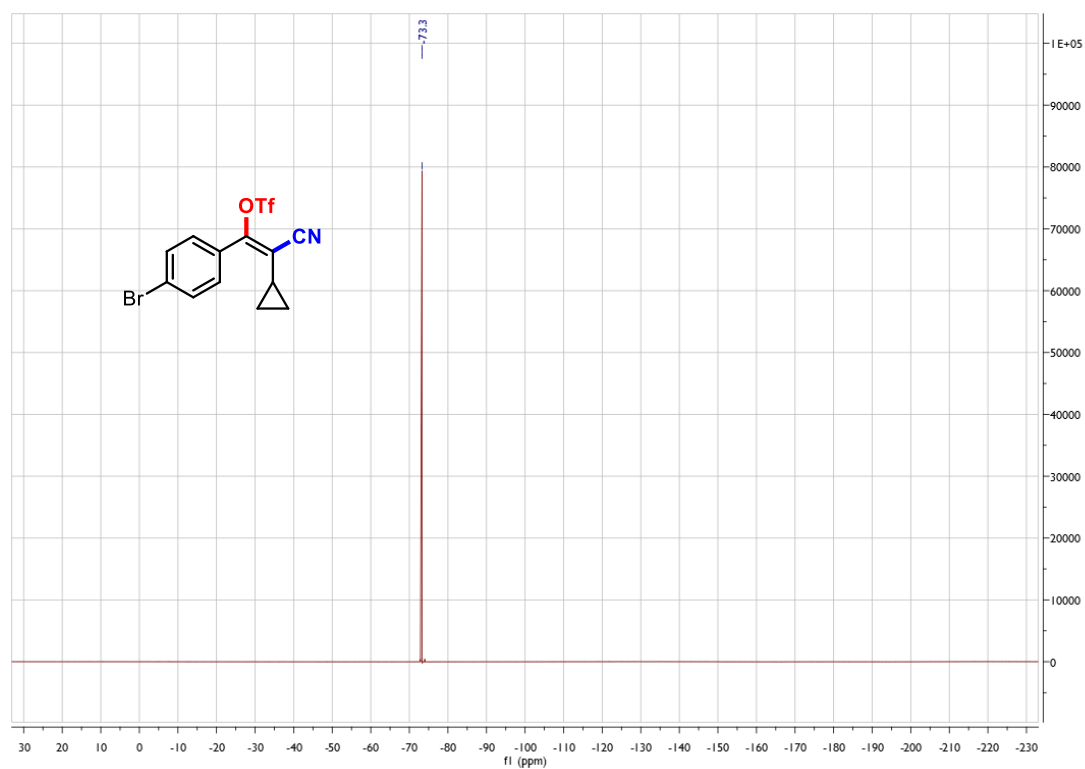
**$^1\text{H}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopropylvinyl trifluoromethanesulfonate 2w**



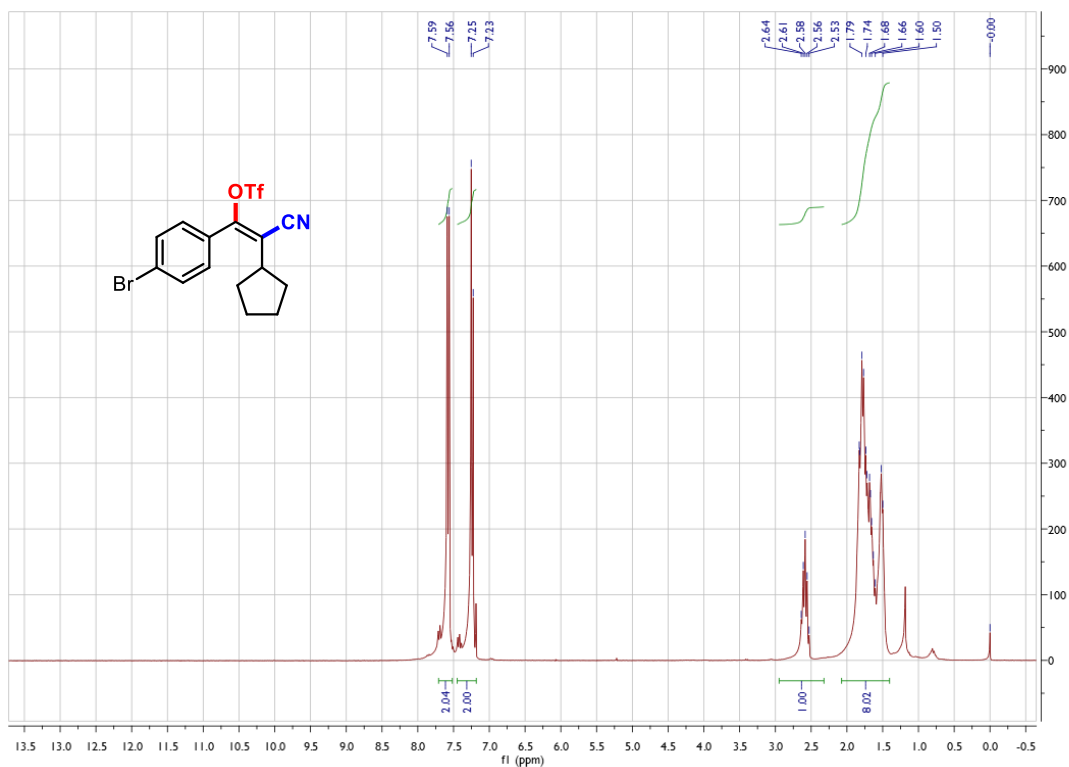
**$^{13}\text{C}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopropylvinyl trifluoromethanesulfonate 2w**



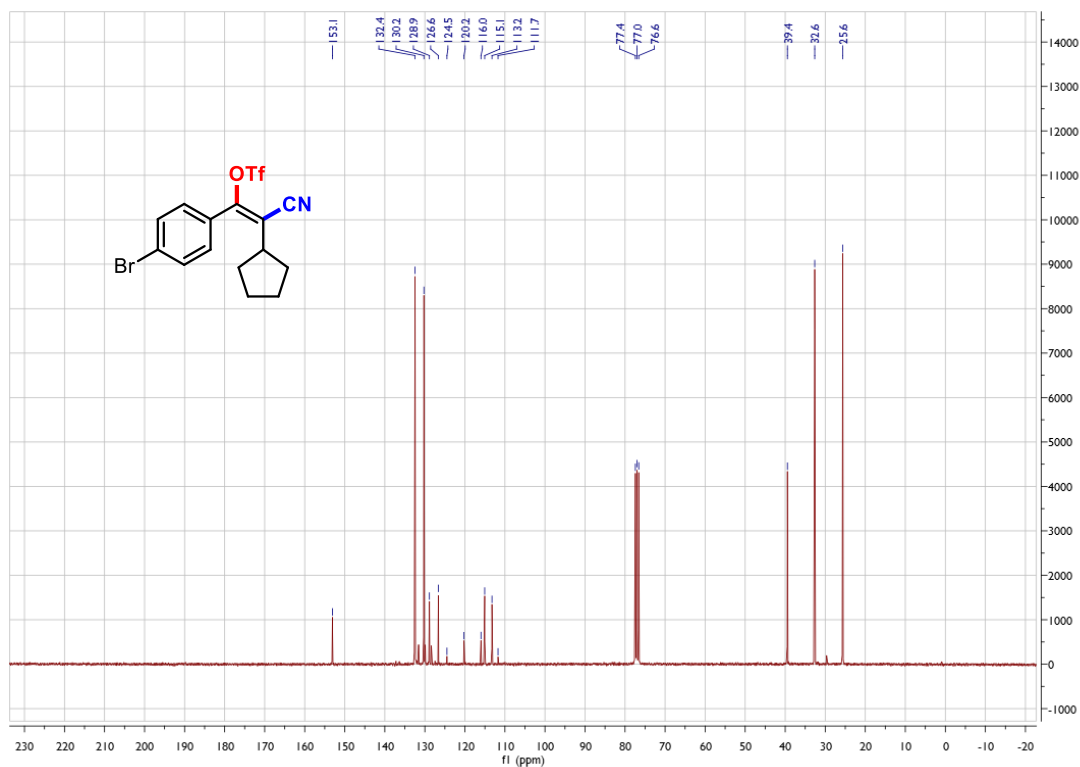
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopropylvinyl trifluoromethanesulfonate 2w**



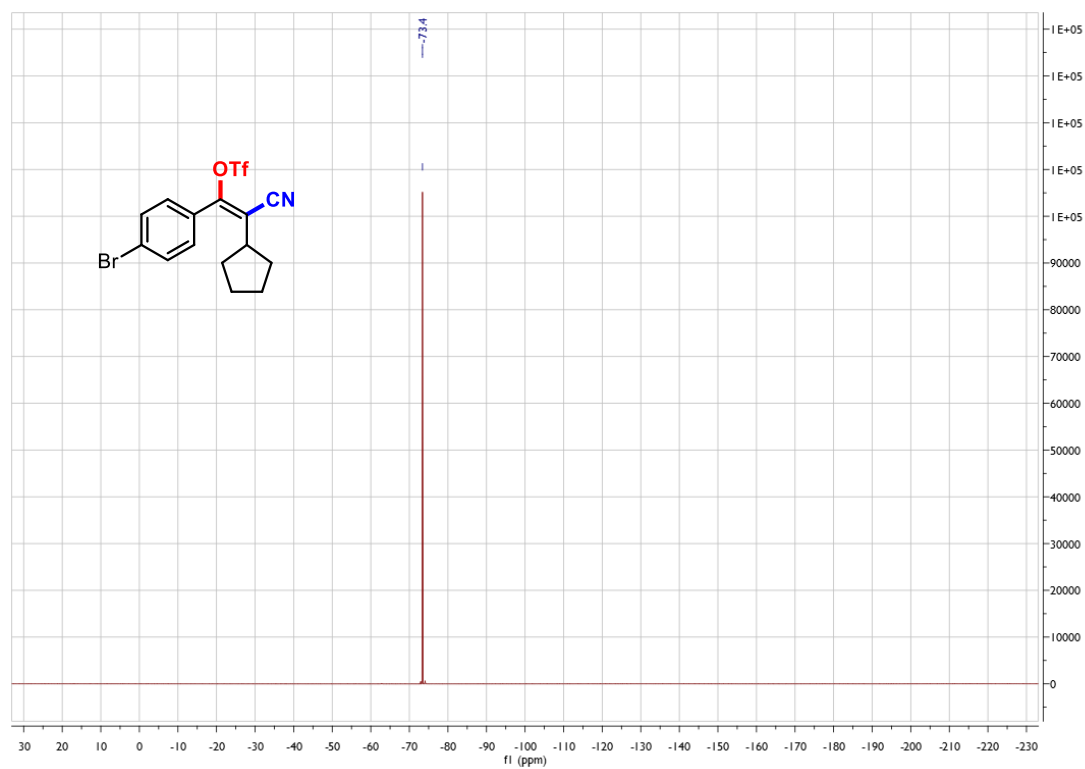
**<sup>1</sup>H NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopentylvinyl trifluoromethanesulfonate 2x**



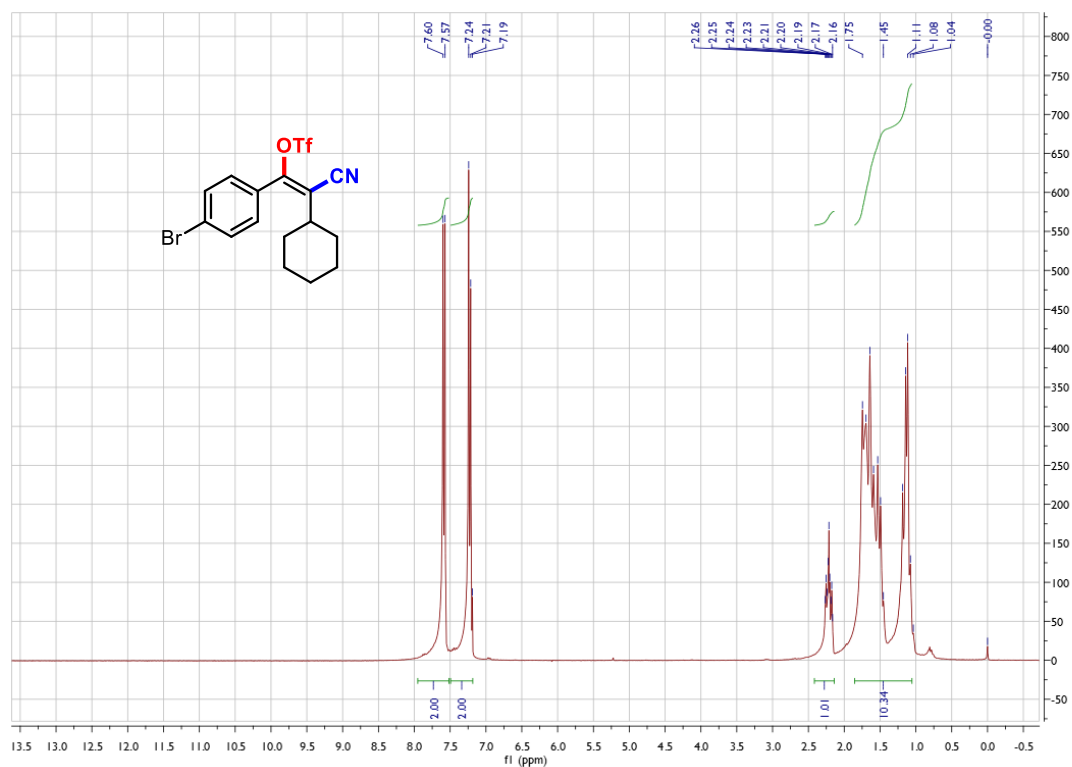
**<sup>13</sup>C NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopentylvinyl trifluoromethanesulfonate 2x**



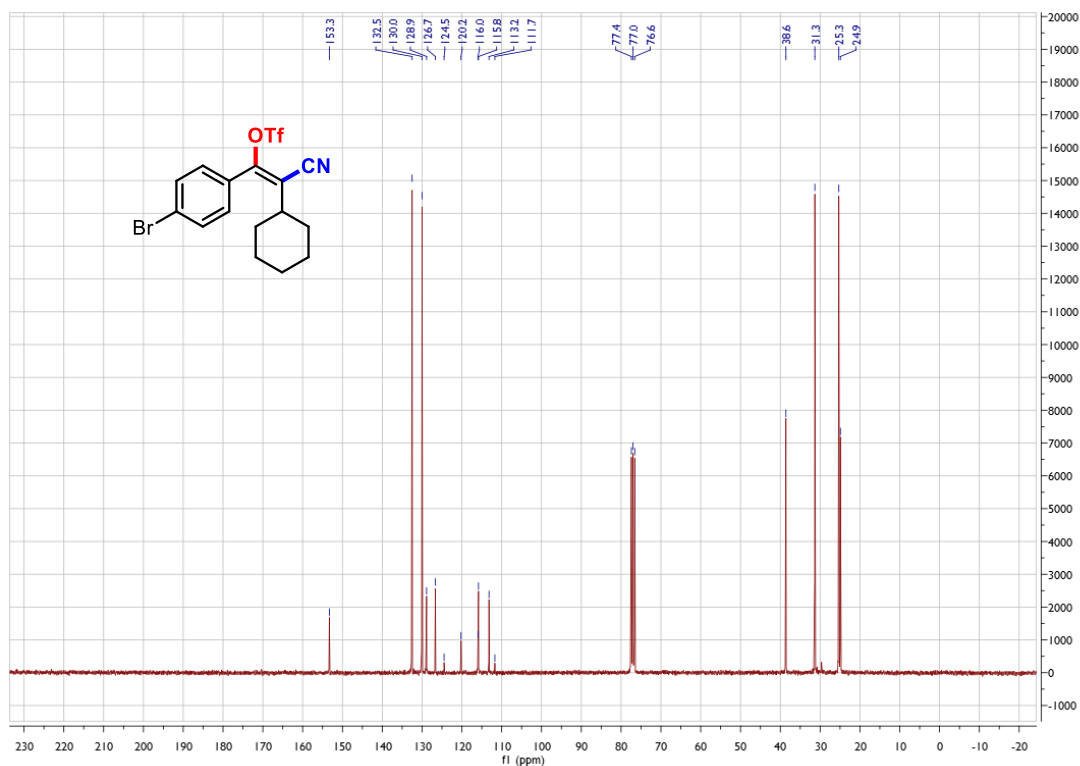
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclopentylvinyl trifluoromethanesulfonate 2x**



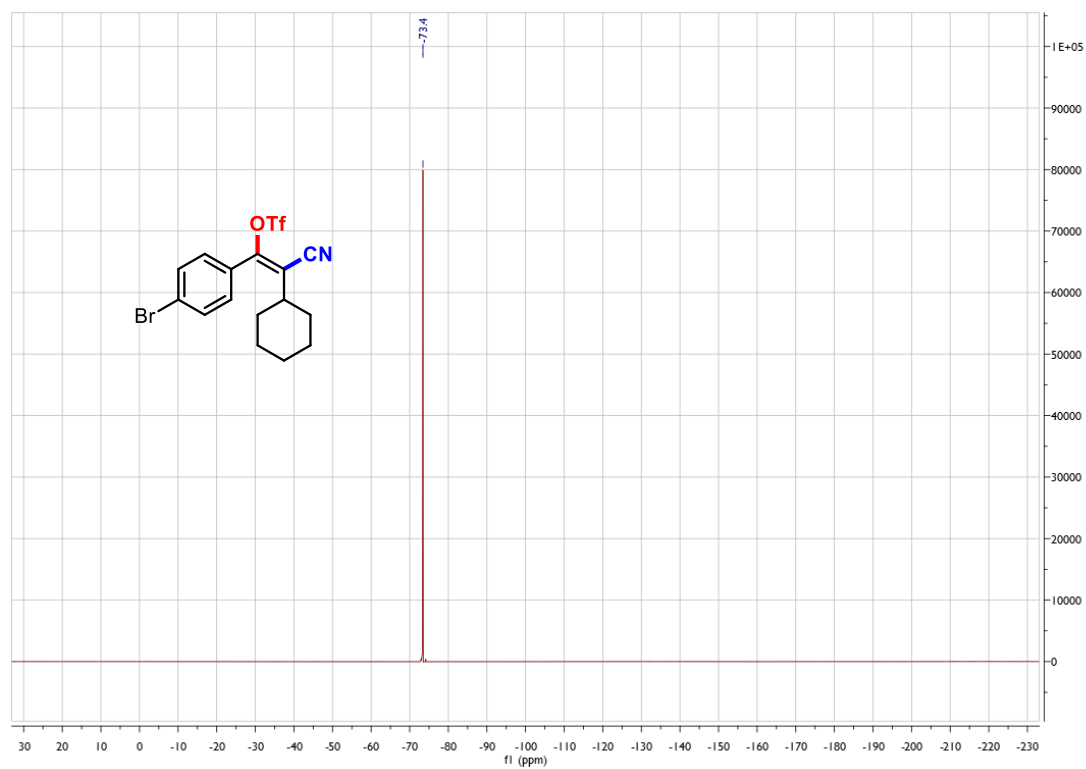
**$^1\text{H}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclohexylvinyl trifluoromethanesulfonate 2y**



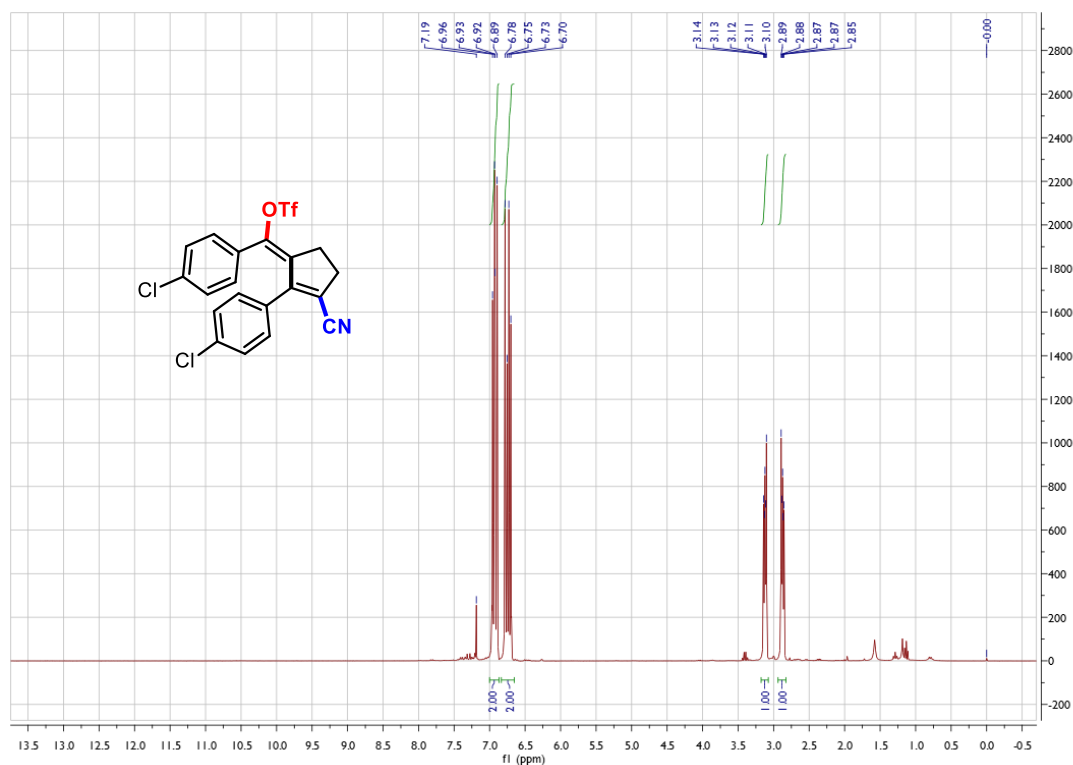
**$^{13}\text{C}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclohexylvinyl trifluoromethanesulfonate 2y**



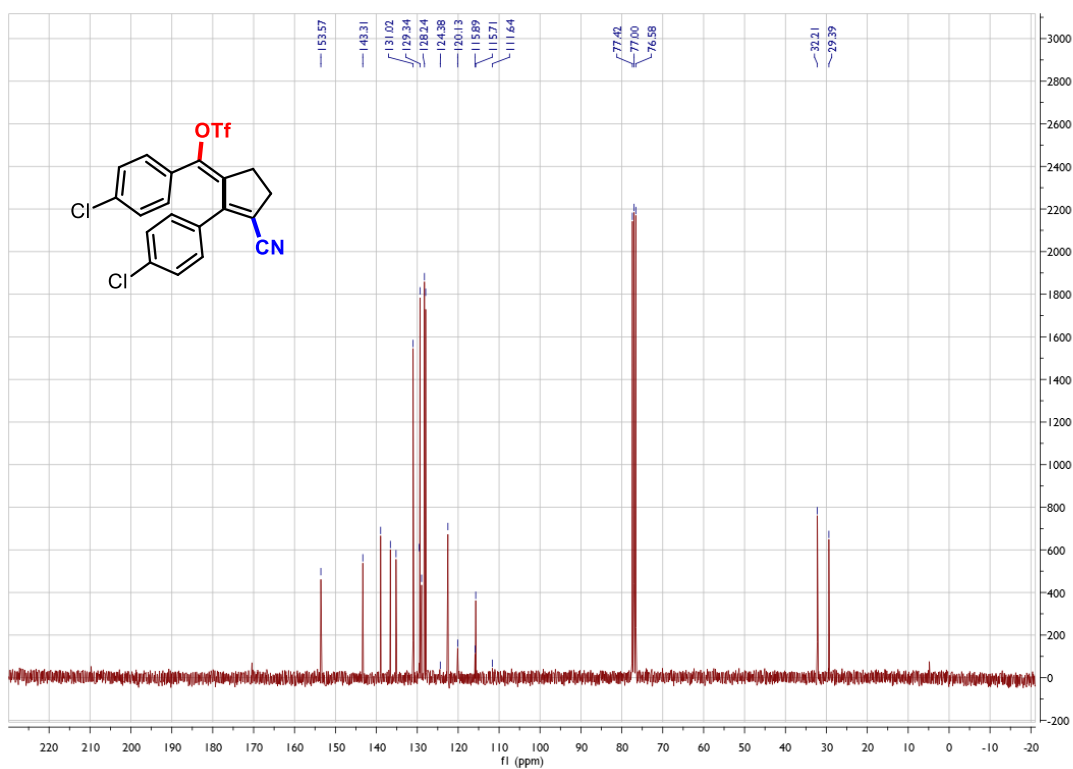
**$^{19}\text{F}$  NMR Spectrum of (Z)-1-(4-bromophenyl)-2-cyano-2-cyclohexylvinyl trifluoromethanesulfonate 2y**



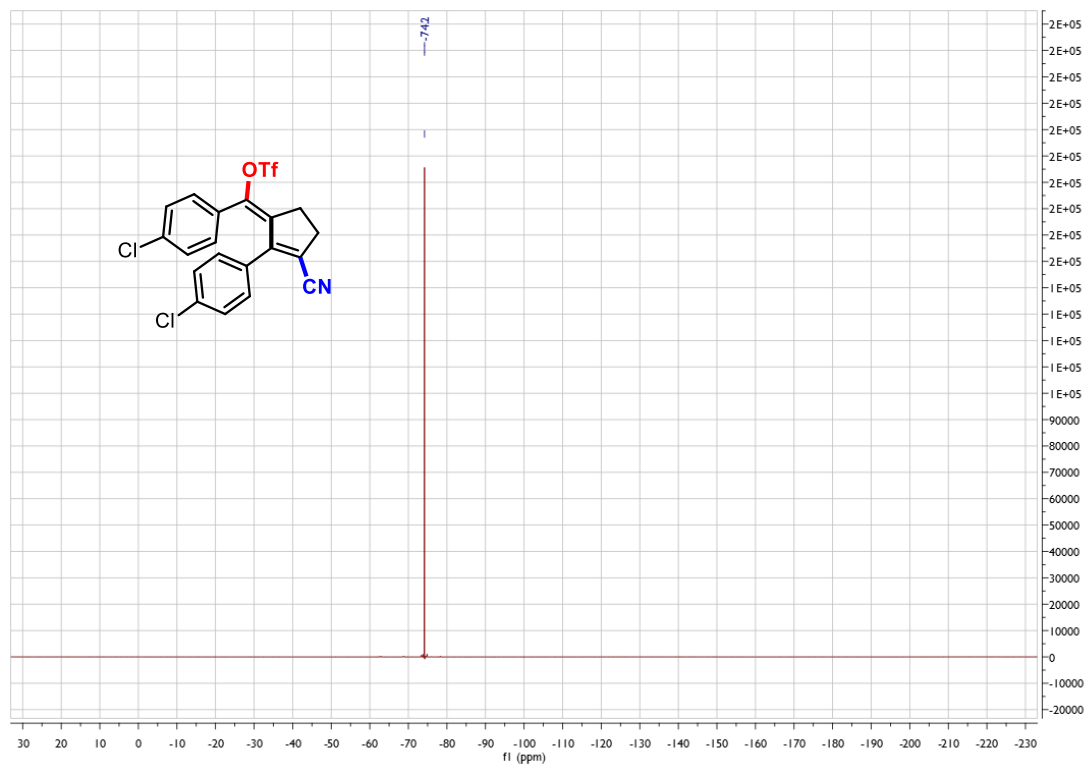
**<sup>1</sup>H NMR Spectrum of (*E*)-(4-chlorophenyl)(2-(4-chlorophenyl)-3-cyanocyclopent-2-en-1-ylidene)methyl trifluoromethanesulfonate **2z****



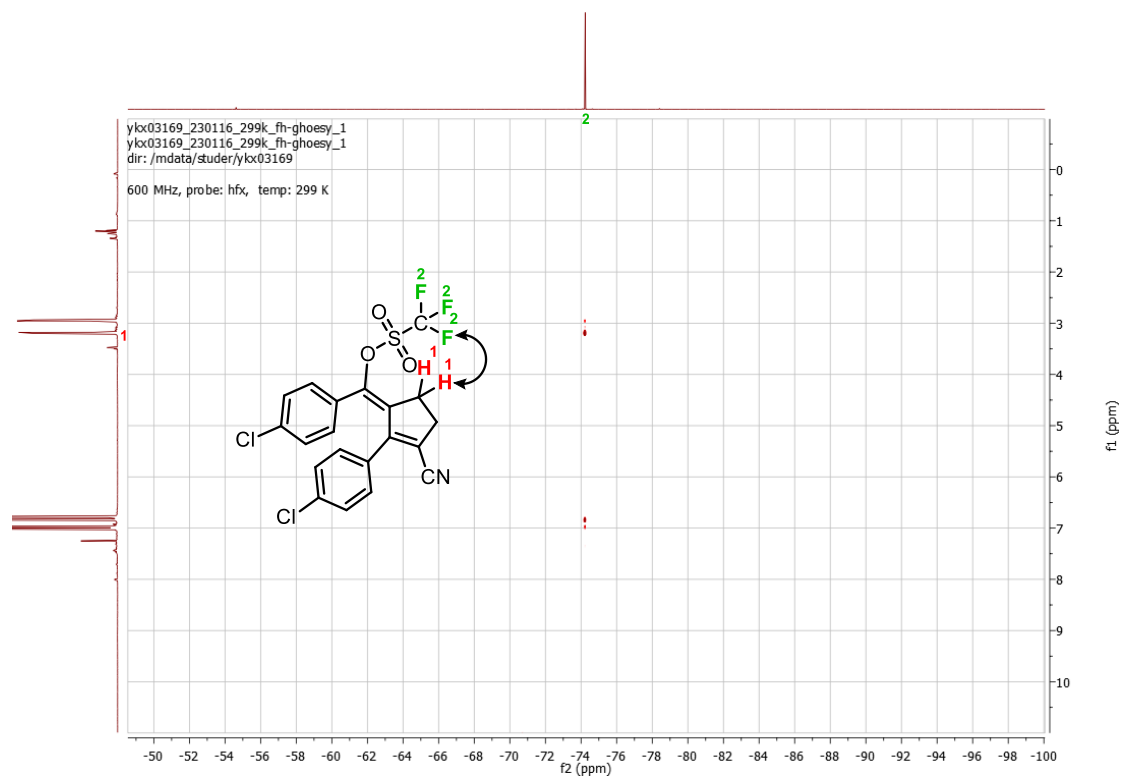
**<sup>13</sup>C NMR Spectrum of (*E*)-(4-chlorophenyl)(2-(4-chlorophenyl)-3-cyanocyclopent-2-en-1-ylidene)methyl trifluoromethanesulfonate **2z****



**$^{19}\text{F}$  NMR Spectrum of (*E*)-(4-chlorophenyl)(2-(4-chlorophenyl)-3-cyanocyclopent-2-en-1-ylidene)methyl trifluoromethanesulfonate **2z****



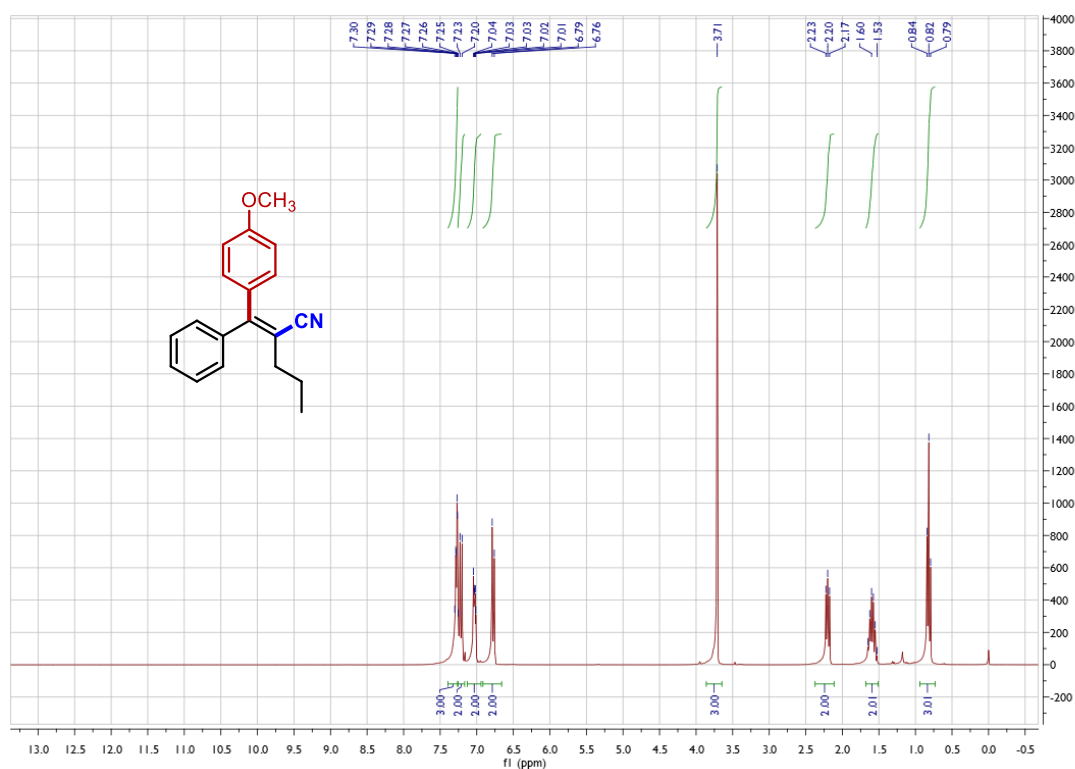
**$^{19}\text{F}/^1\text{H}$ -GHOESY Spectrum of (*E*)-(4-chlorophenyl)(2-(4-chlorophenyl)-3-cyanocyclopent-2-en-1-ylidene)methyl trifluoromethanesulfonate **2z****



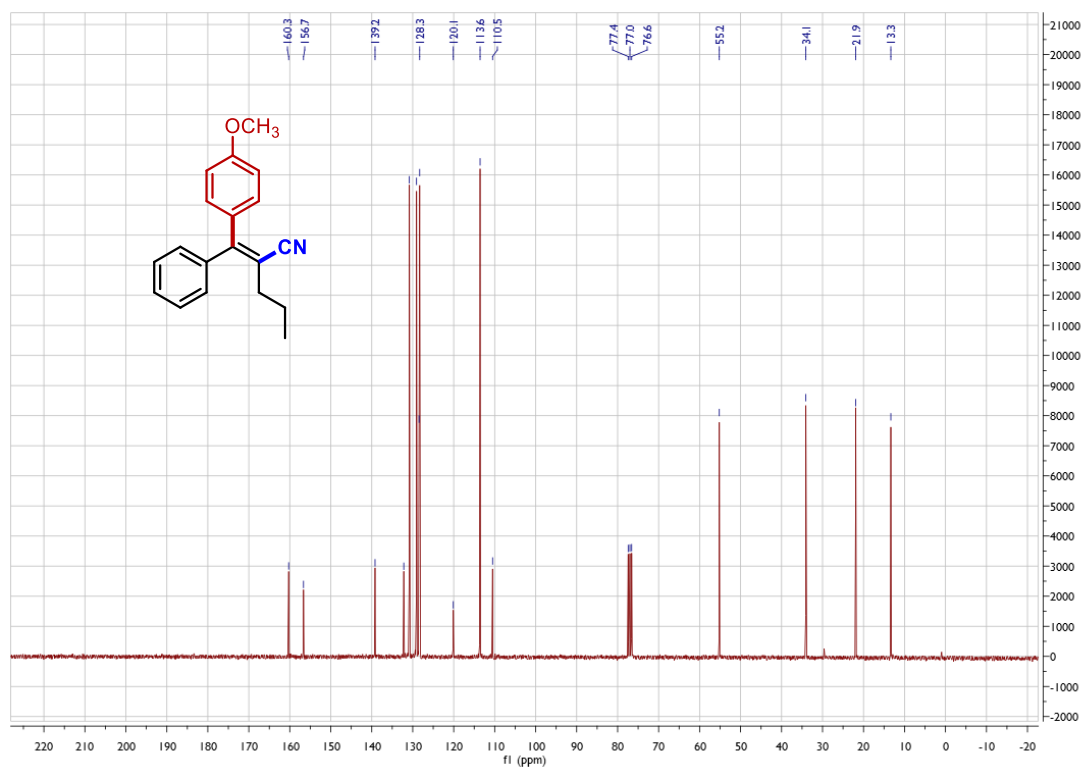


## Spectra of products 4-11 in follow-up chemistry

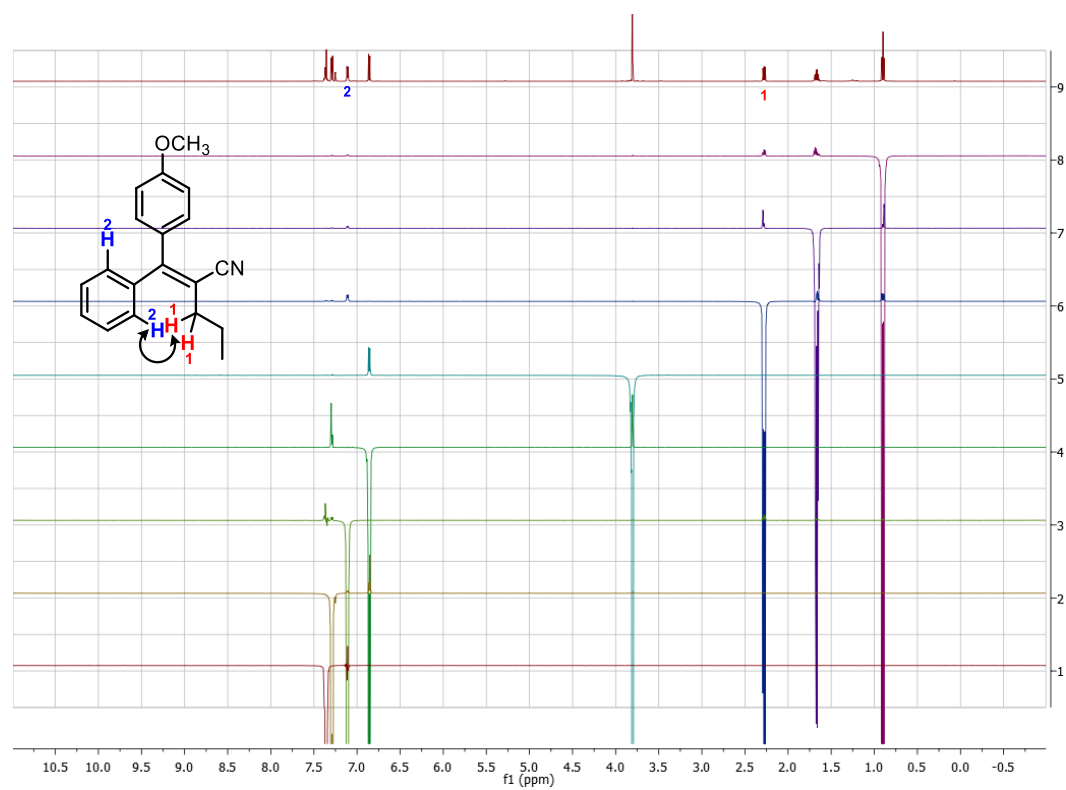
### <sup>1</sup>H NMR Spectrum of (Z)-2-((4-methoxyphenyl)(phenyl)methylene)pentanenitrile 4



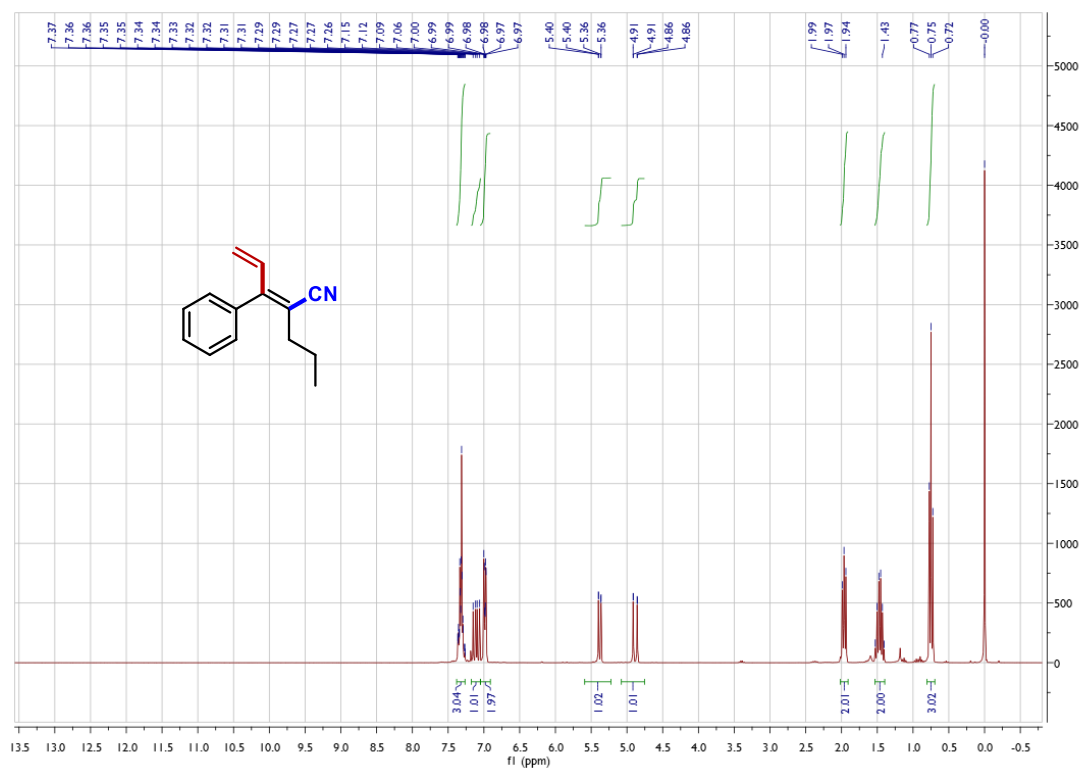
### <sup>13</sup>C NMR Spectrum of (Z)-2-((4-methoxyphenyl)(phenyl)methylene)pentanenitrile 4



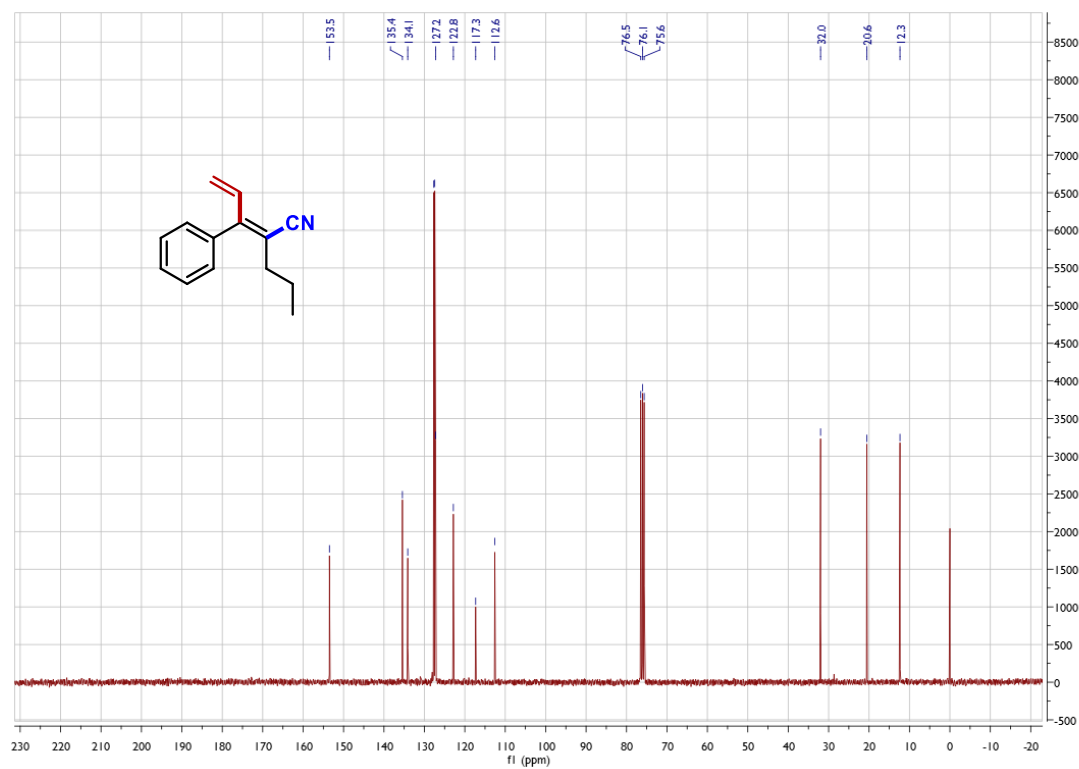
**NOESY1D Spectrum of (Z)-2-((4-methoxyphenyl)(phenyl)methylene)pentanenitrile 4**



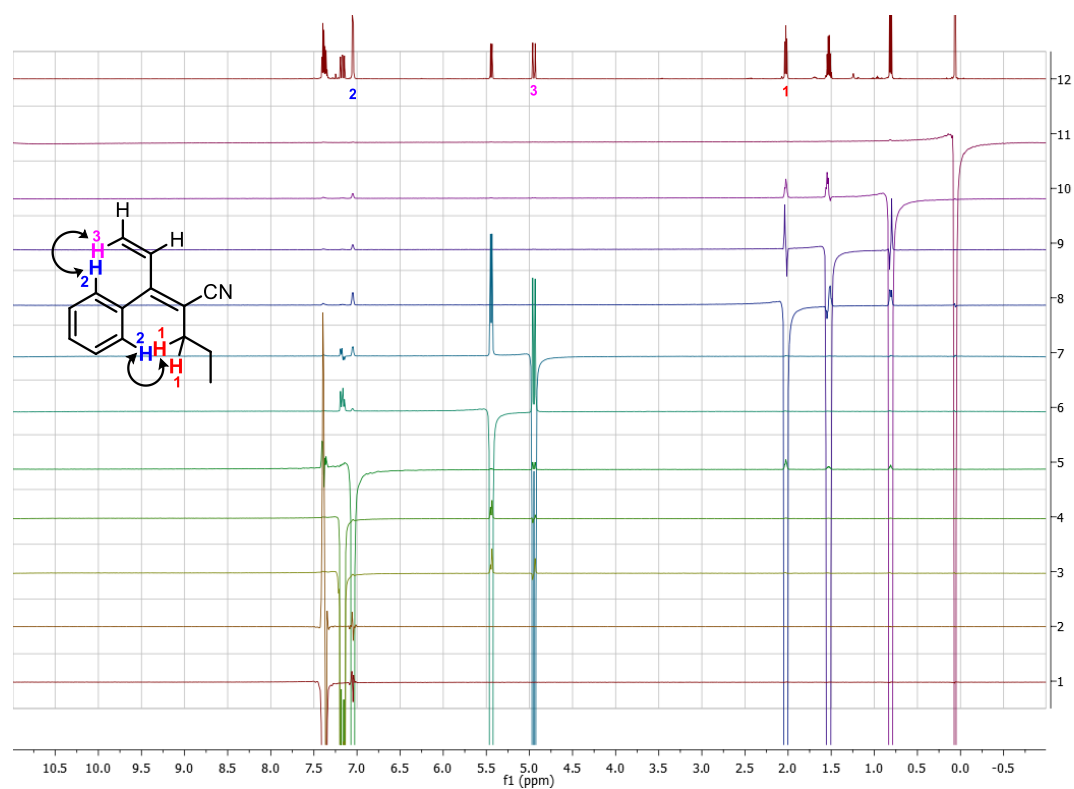
# <sup>1</sup>H NMR Spectrum of (*E*)-3-phenyl-2-propylpenta-2, 4-dienitrile 5



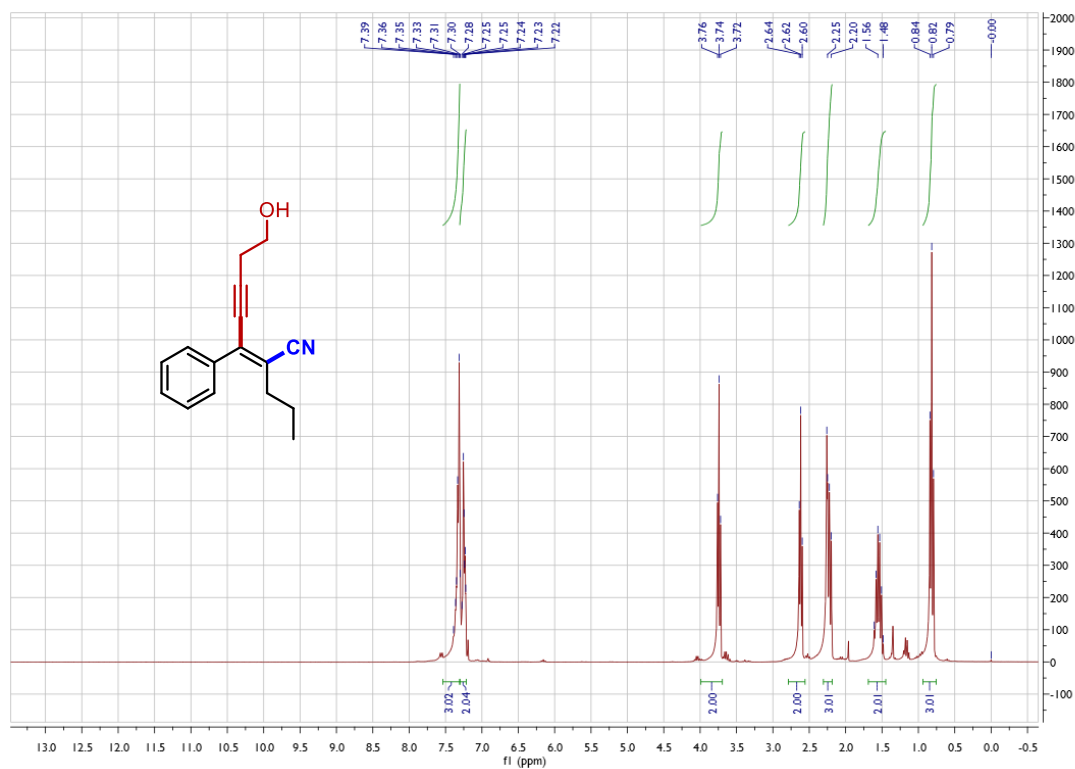
# <sup>13</sup>C NMR Spectrum of (*E*)-3-phenyl-2-propylpenta-2, 4-dienitrile 5



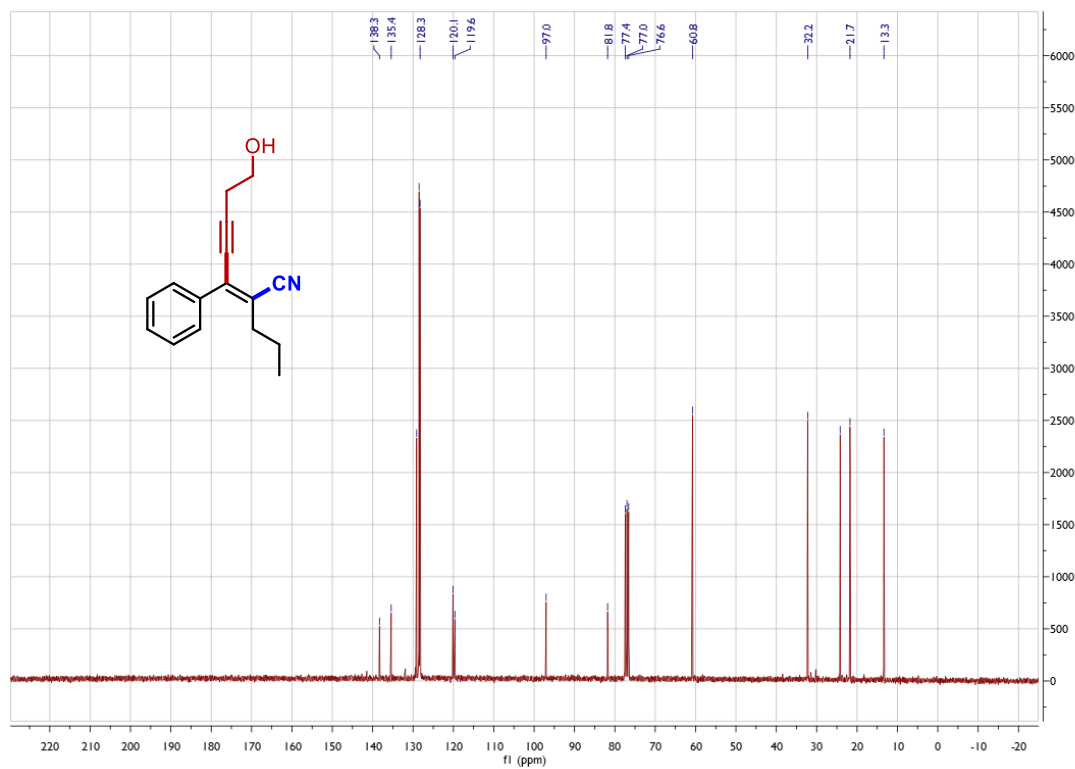
# NOESY1D Spectrum of (*E*)-3-phenyl-2-propylpenta-2,4-dienitrile 5



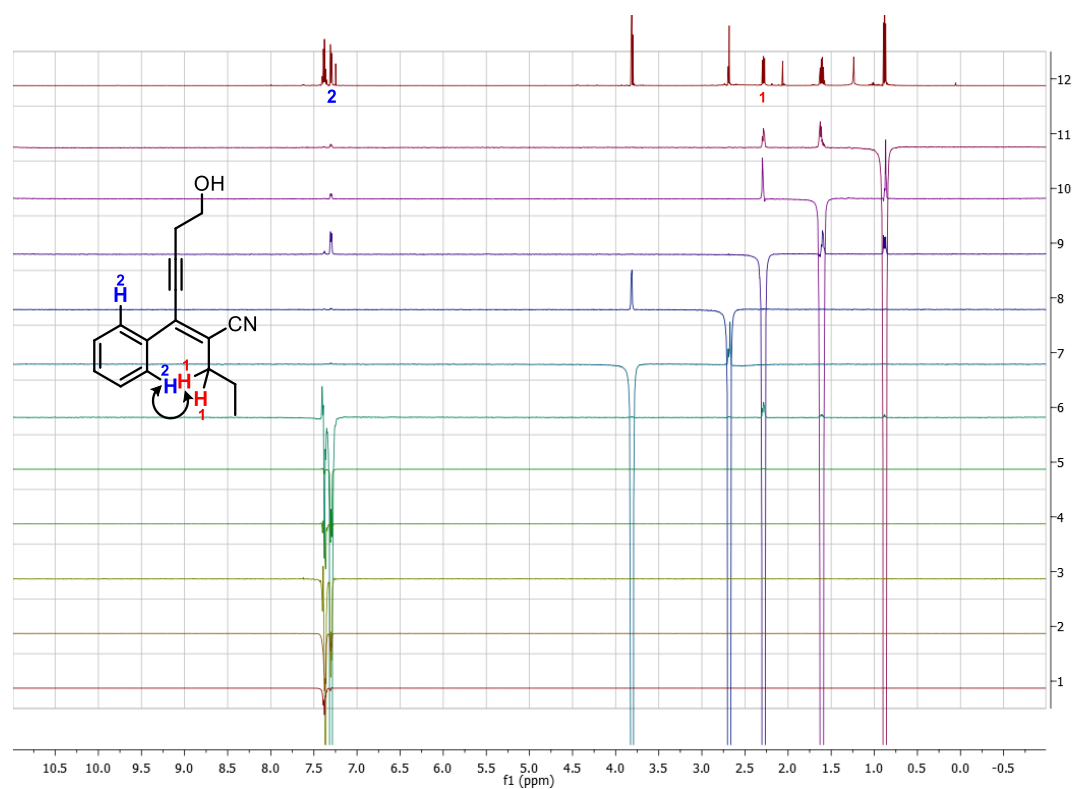
# <sup>1</sup>H NMR Spectrum of (Z)-7-hydroxy-3-phenyl-2-propylhept-2-en-4-ynenitrile 6



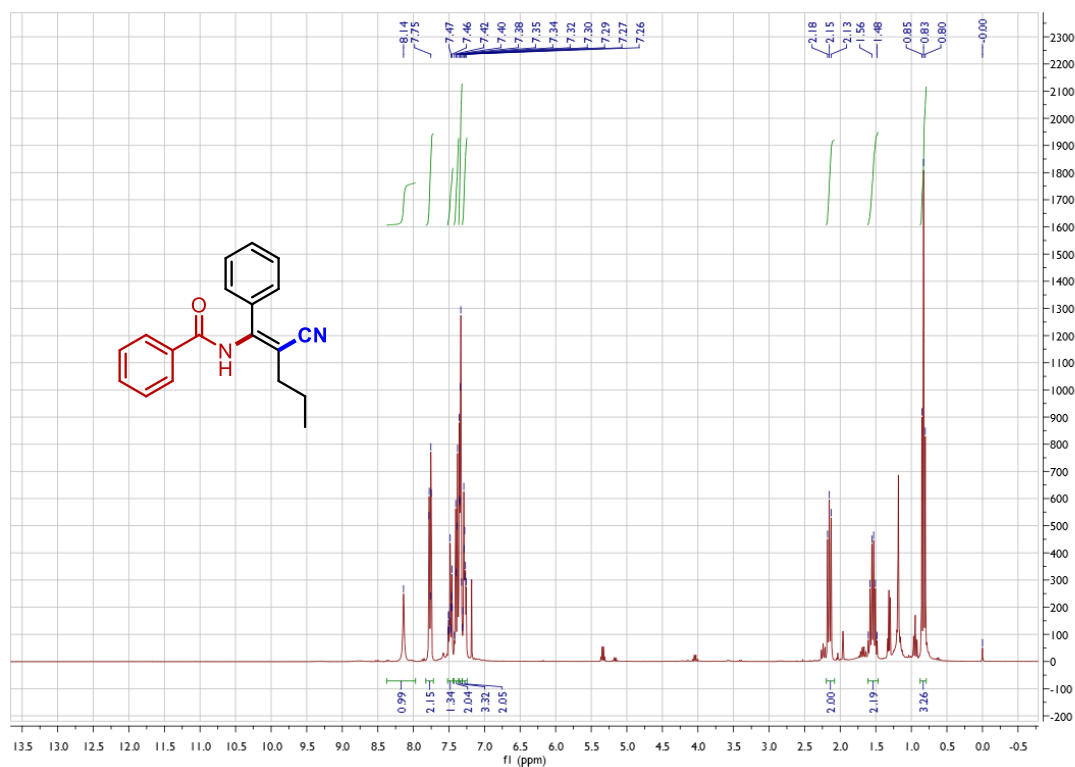
# <sup>13</sup>C NMR Spectrum of (Z)-7-hydroxy-3-phenyl-2-propylhept-2-en-4-ynenitrile 6



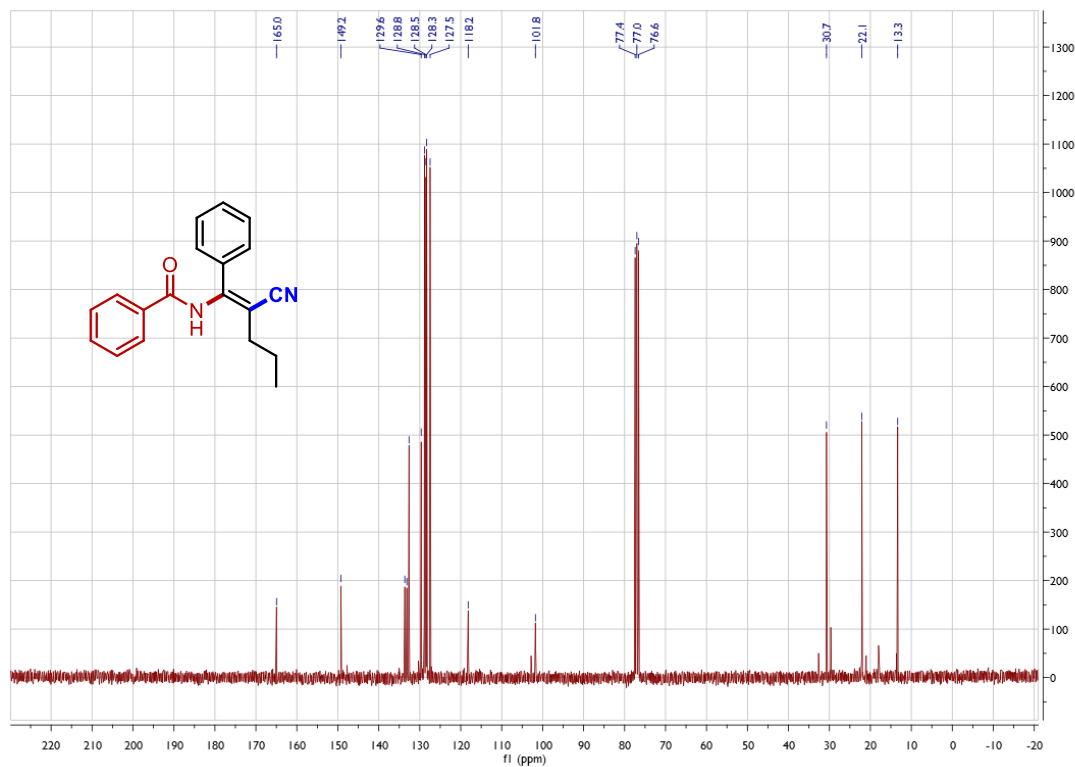
# NOESZ1D Spectrum of (Z)-7-hydroxy-3-phenyl-2-propylhept-2-en-4-yne nitrile **6**



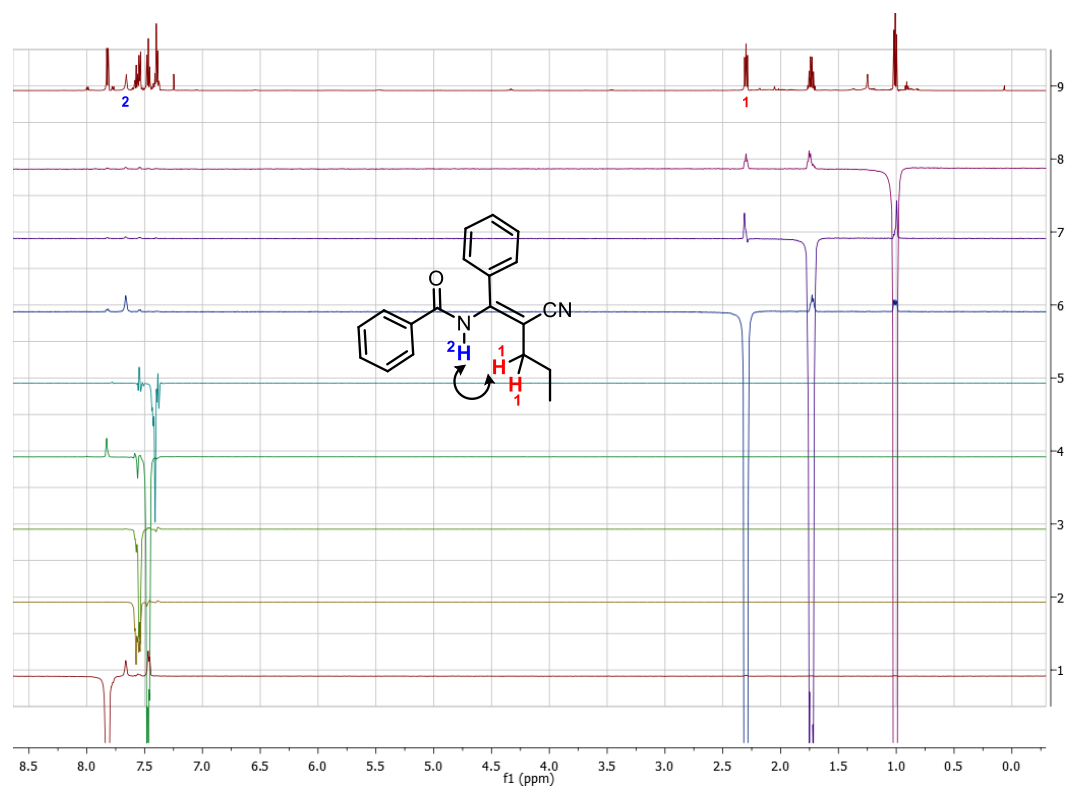
### <sup>1</sup>H NMR Spectrum of (*E*)-*N*-(2-cyano-1-phenylpent-1-en-1-yl)benzamide 7



### <sup>13</sup>C NMR Spectrum of (*E*)-*N*-(2-cyano-1-phenylpent-1-en-1-yl)benzamide 7

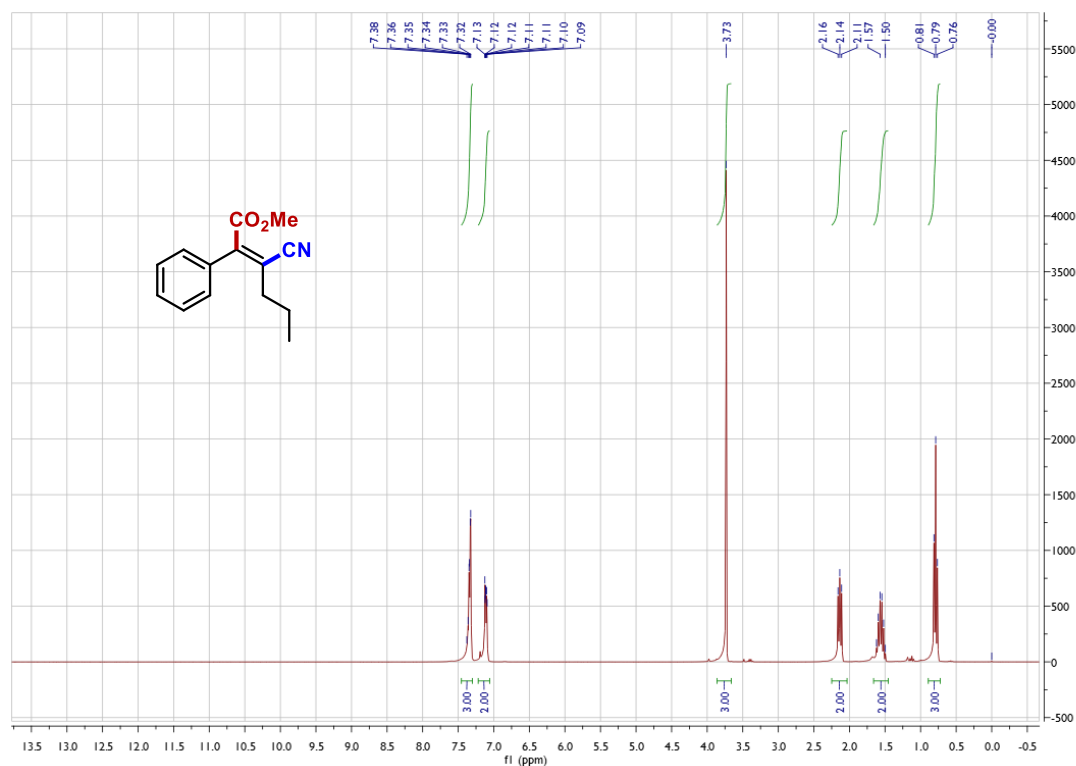


**NOESY1D Spectrum of (*E*)-*N*-(2-cyano-1-phenylpent-1-en-1-yl)benzamide **7****

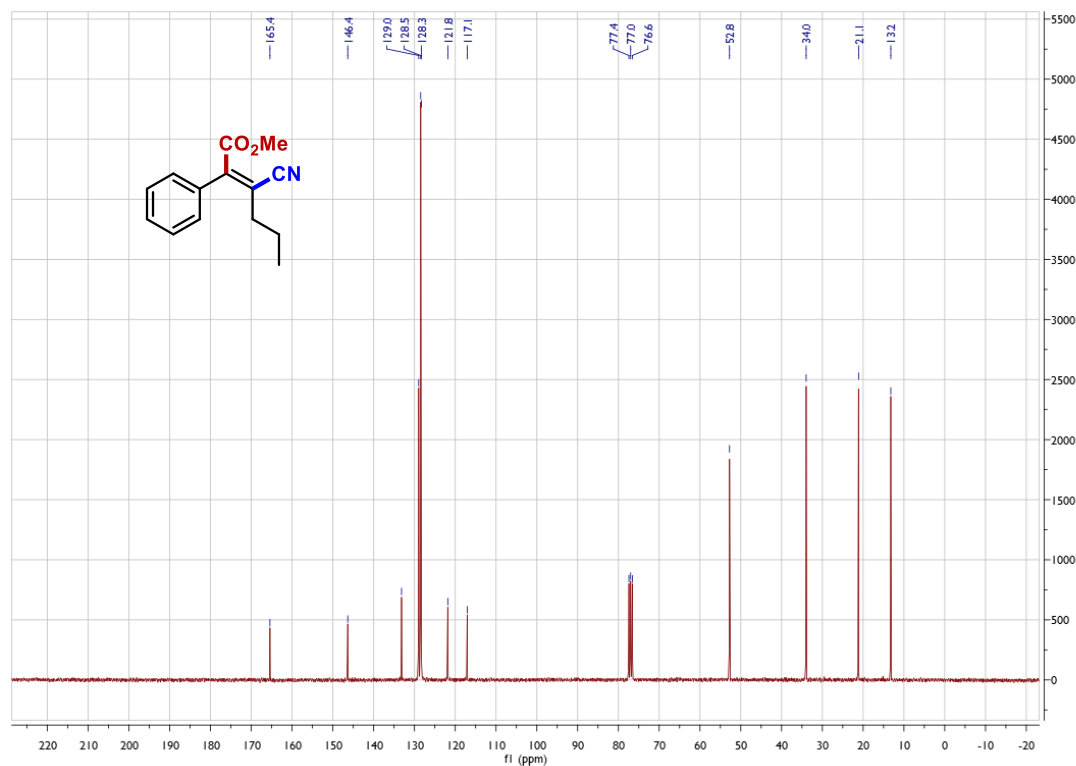




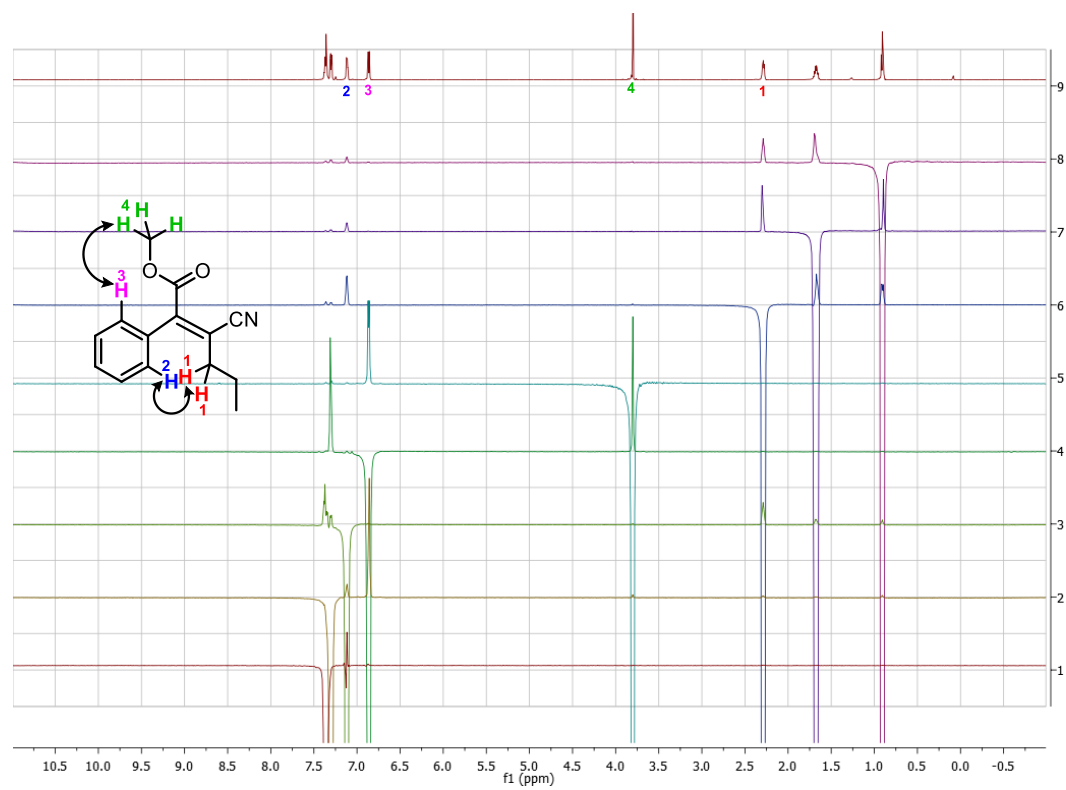
### <sup>1</sup>H NMR Spectrum of methyl (Z)-3-cyano-2-phenylhex-2-enoate 8



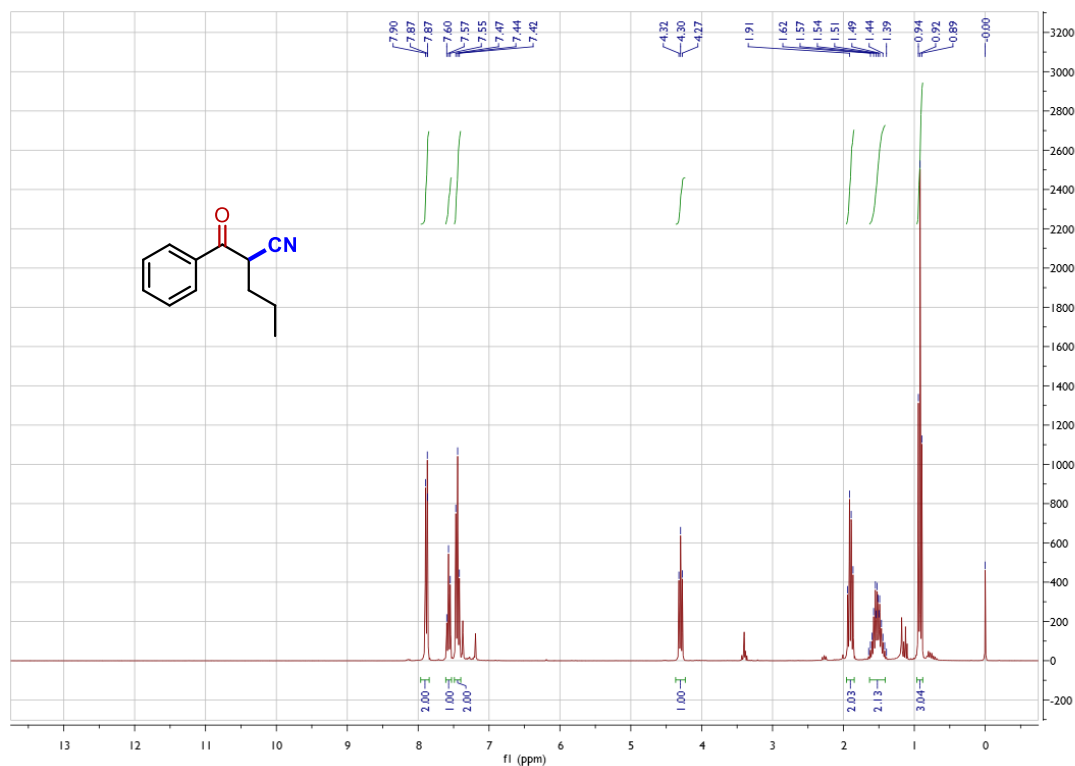
### <sup>13</sup>C NMR Spectrum of methyl (Z)-3-cyano-2-phenylhex-2-enoate 8



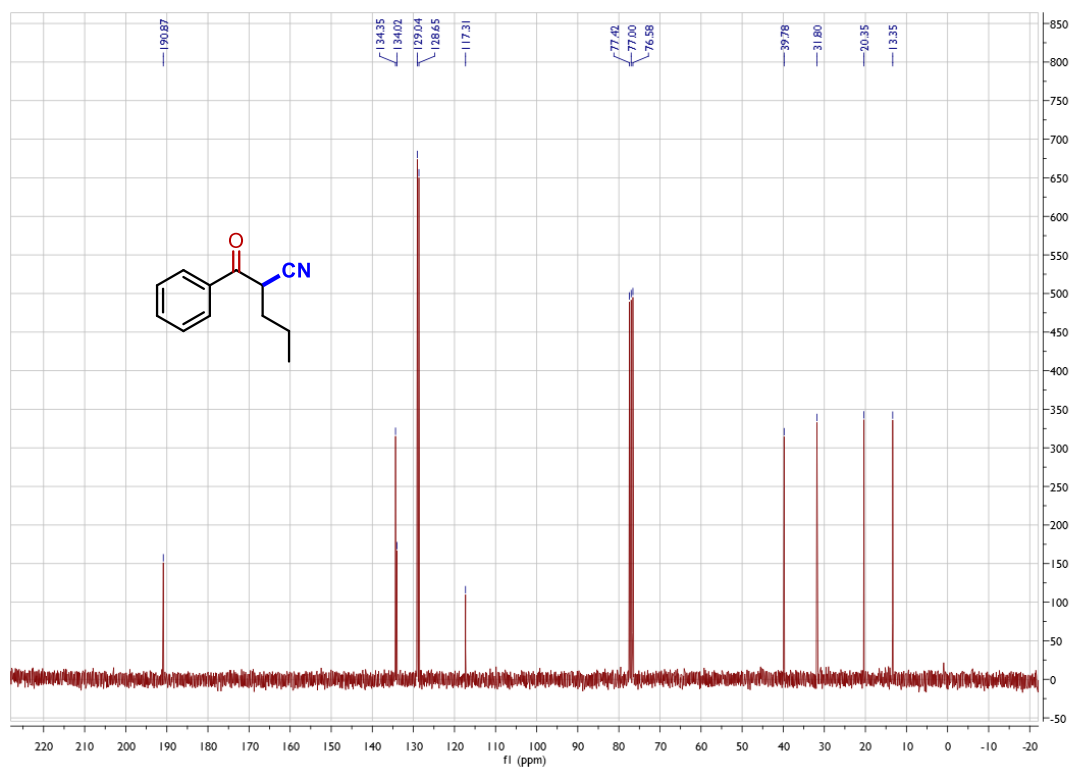
# NOESY1D Spectrum of methyl (Z)-3-cyano-2-phenylhex-2-enoate 8



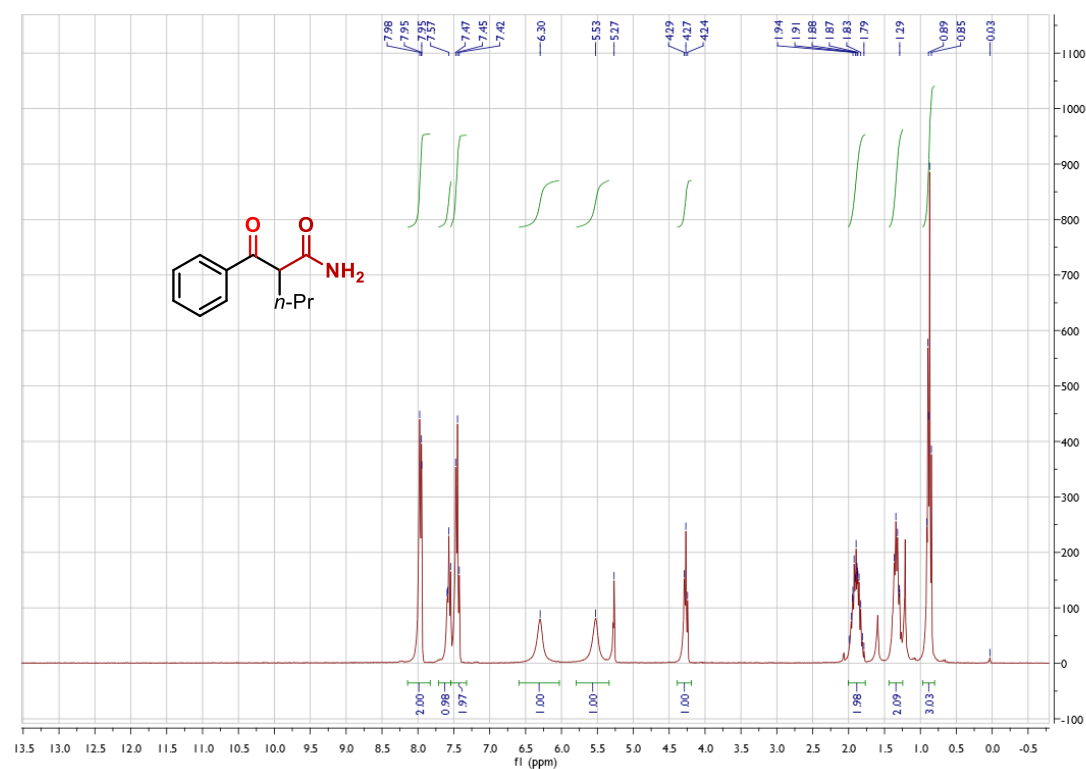
## $^1\text{H}$ NMR Spectrum of 2-benzoylpentanenitrile **9**



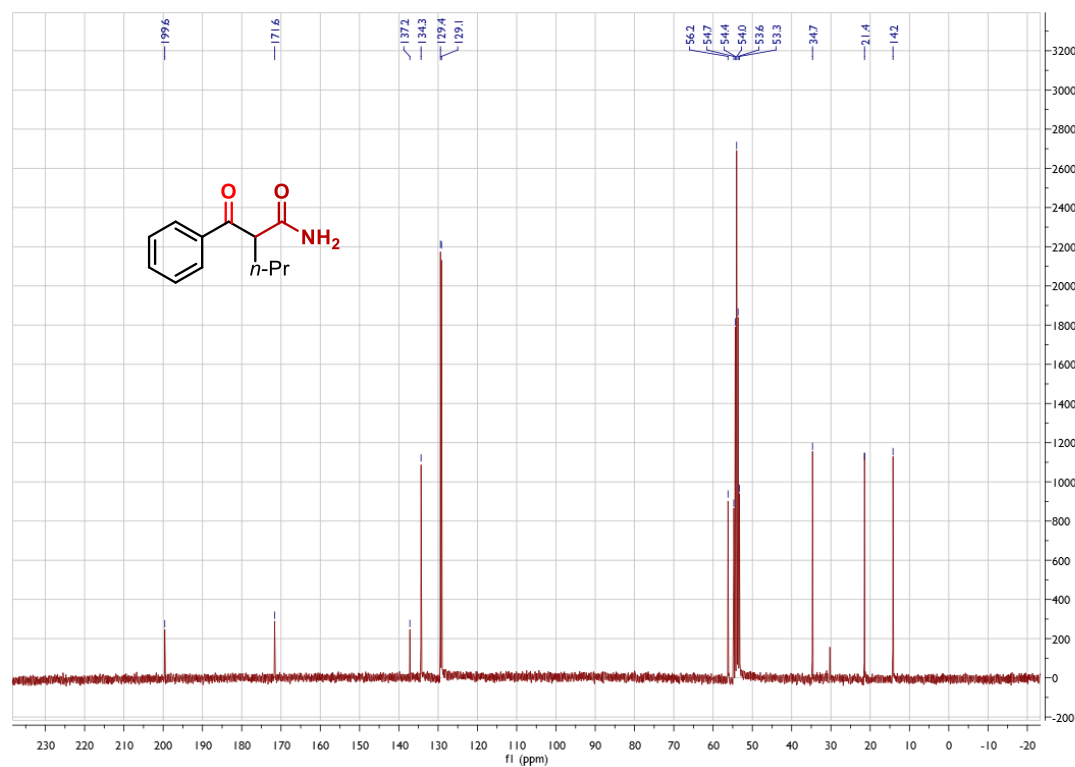
## $^{13}\text{C}$ NMR Spectrum of 2-benzoylpentanenitrile **9**



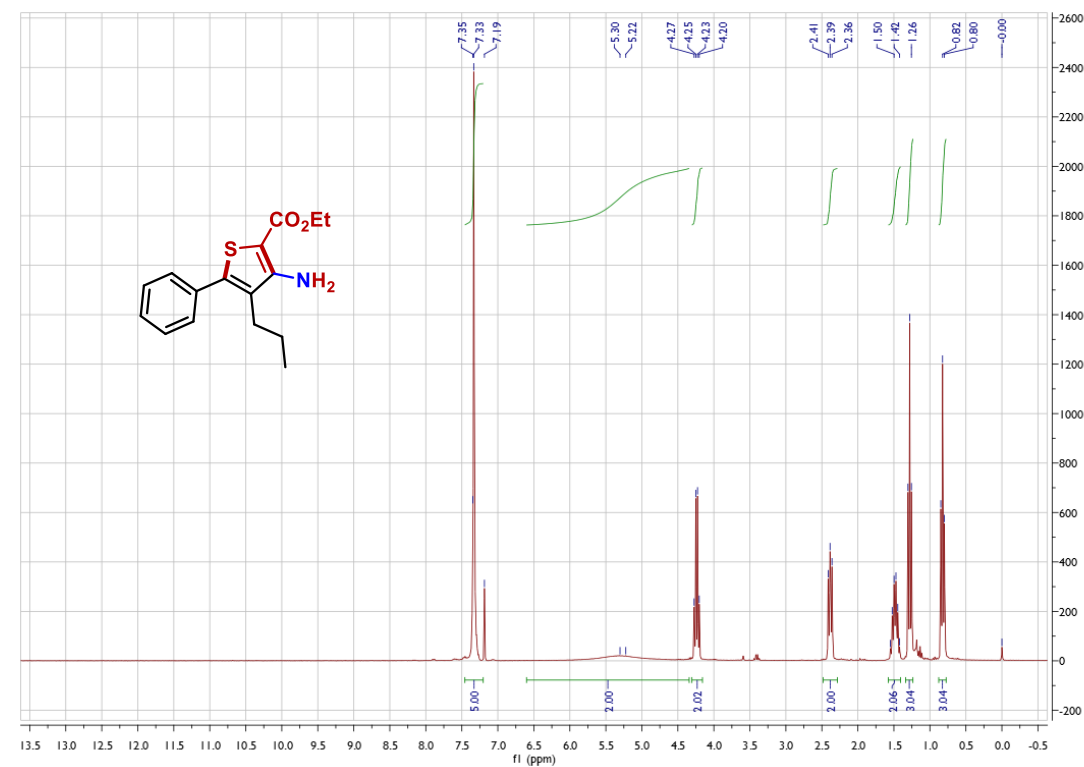
## <sup>1</sup>H NMR Spectrum of 2-Benzoylpentanamide 10



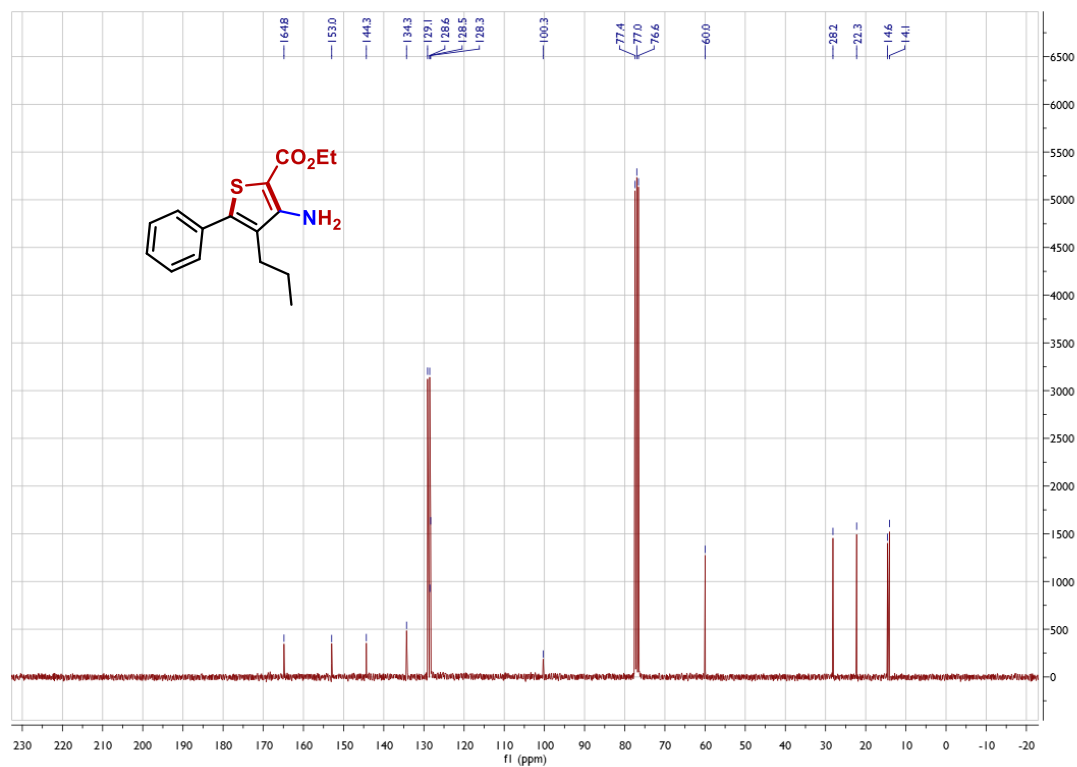
## <sup>13</sup>C NMR Spectrum of 2-Benzoylpentanamide 10



# <sup>1</sup>H NMR Spectrum of Ethyl 3-amino-5-phenyl-4-propylthiophene-2-carboxylate



# <sup>13</sup>C NMR Spectrum of Ethyl 3-amino-5-phenyl-4-propylthiophene-2-carboxylate



## 6. References

- [1] (a) Frei, R.; Courant, T.; Wodrich, M. D.; Waser, J. *Chem. Eur. J.* **2015**, *21*, 2662–2668; (b) Zhu, D.; Chang, D.; Shi, L. *Chem. Commun.* **2015**, *51*, 7180–7183; (c) Zhdankin, V. V.; Scheuller M. C.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853–6856.
- [2] Songis, O.; Mišek, J.; Schmid, M. B.; Kollárovič, A.; Stará, I. G.; Saman, D.; Císařová, I.; Stary, I. *J. Org. Chem.* **2010**, *75*, 6889–6899.
- [3] Miersch, A.; Hilt, G. *Chem. Eur. J.* **2012**, *18*, 9798–9801.
- [4] Tong, L.; Qin, A.; Zhang, X.; Mao, Y.; Sun, J.; Tang, B. Z. *Science China: Chemistry*, **2011**, *54*, 1948–1954.
- [5] Siebeneicher, H.; Doye, S. *Eur. J. Org. Chem.* **2002**, 1213–1220.
- [6] Wang, S.; Yu, L.; Li, P.; Meng, L.; Wang, L. *Synthesis* **2011**, *10*, 1541–1546.
- [7] Chen, Z.; Jiang, H.; Li, Y.; Qi, C. *Chem. Commun.* **2010**, *46*, 8049–8051.
- [8] Li, X.; Peng, F.; Zhou, M.; Mo, M.; Zhao, R.; Shao Z. *Chem. Commun.* **2014**, *50*, 1745–1747.
- [9] You, H.-W.; Lee, K.-J. *Synlett* **2001**, *1*, 105–107.