# N-Heterocyclic Carbene-Catalyzed Cascade Reaction Involving the Hydroacylation of Unactivated Alkynes

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## Supporting Information

## 1. General Information

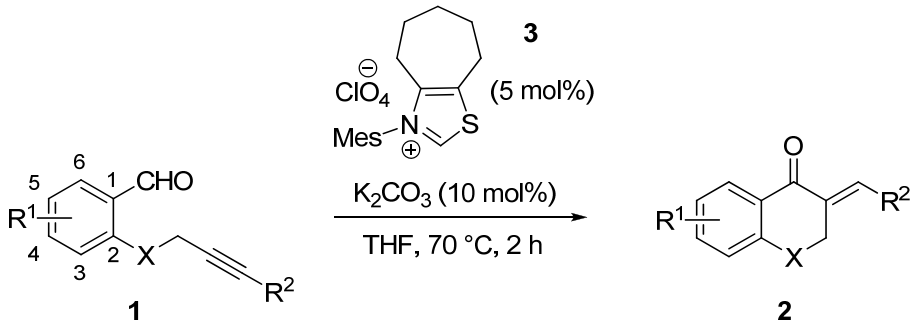
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. THF was purified by distillation over Na-benzophenone and was transferred under argon. Dry DMF was purchased from Acros and stored under argon over 4 Å molecular sieves. The salicylaldehydes were purchased from Acros or Alfa Aesar and used as received. The other aldehydes were purchased from Aldrich, Acros or Alfa Aesar and were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether, prior to use. The propargyl bromide (80% solution in toluene) was purchased from Acros. $K_2CO_3$ was dried by heating at 110 °C for 12 h and left to cool under argon.

Analytical thin layer chromatography was performed on Polygram SIL G/$UV_{254}$ plates. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker AV 300, AV 400 or Varian 500 MHz INOVA instruments in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.16 ppm).

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in $cm^{-1}$. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Elemental analyses were recorded on Vario EL III of Fa. Elementar Analysensysteme GmbH, Hanau.

## 2. General Procedure for the NHC-Catalyzed Hydroacylation of Internal Alkynes.



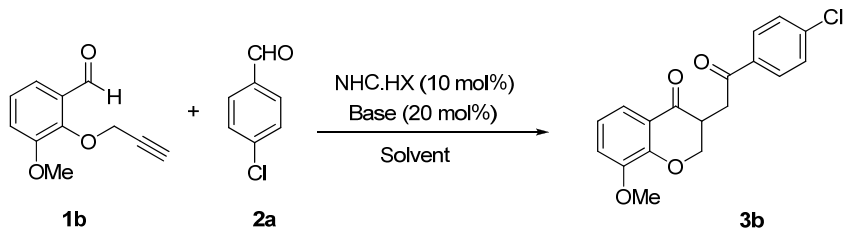

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde derivative **1** (1.0 mmol, 1.0 eq., weighing was carried out in air). To this was added the thiazolium salt **3** (0.019 mg, 0.05 mmol, 0.05 eq.) and dry $K_2CO_3$ (0.14 g, 0.1 mmol, 0.1 eq.) in a glove box. Outside the glove box, the mixture was dissolved in 2.0 mL of THF under argon. The resulting mixture was then stirred in a pre-heated oil bath at 70 °C for 2 h. After the reaction was complete, the reaction mixture was cooled to room temperature, pre-adsorbed on silica gel and purified by flash column chromatography on silica gel.

Control experiments show that *weighing the reactants in air* and performing the reaction under argon atmosphere provides slightly reduced yields (83%) for **2a** as compared to 93% yield under standard conditions (Argon throughout). It is important to note that the reaction does not work when performed in air.

| Entry | Condition | Yield [a] (%) |
|---|---|---|
| 1 | Standard | 93 |
| 2 | Air/Argon | 83 |
| 3 | Air | 0 |

[a]The yields were determined by $^1$H NMR analysis of crude products using $CH_2Br_2$ as the internal standard.

## 3. General Procedure for the Screening of the Cascade Reaction



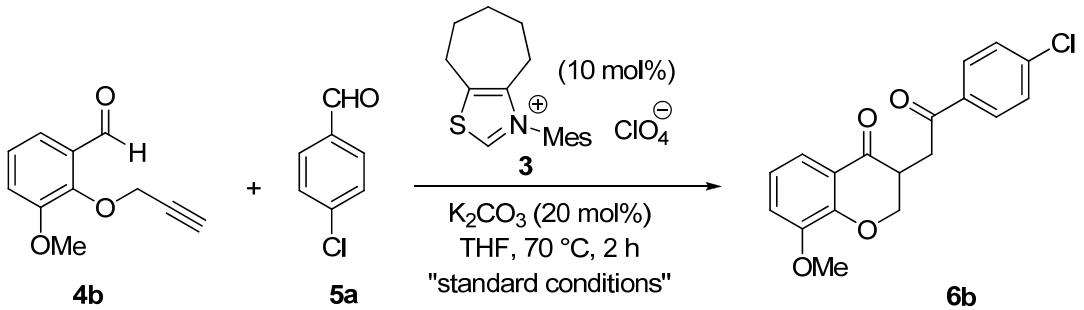

**1b** **2a** **3b**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 3-methoxy 2-prop-2-ynyloxy-benzaldehyde **1b** (0.048 g, 0.25 mmol, 1 eq.). 4-Chlorobenzaldehyde (0.035 g, 0.25 mmol, 1 eq.) and NHC.HX (0.025 mmol, 0.1 eq.) were added in a glove box. Outside the glove box, the mixture was dissolved in 0.5 mL of the solvent under argon. After addition of the base (0.05 mmol, 0.2 eq.) the resulting mixture was stirred in a pre-heated oil bath at the indicated temperature for the specified time. After the reaction was complete, the reaction mixture was cooled to room temperature, then diluted with $CH_2Cl_2$ (1 mL) and filtered through a small pad of silica gel. It was further eluted with $CH_2Cl_2$ (5 mL). The solvent was evaporated to obtain the crude product whose yield was determined by $^1H$ NMR analysis using $CH_2Br_2$ as the internal standard.

## 4. Optimization Studies for the NHC-Catalyzed Hydroacylation-Stetter Reaction Cascade.

Our optimization study commenced with treating O-propargylated *o*-vanillin **4b** with 4-chlorobenzaldehyde, leading to the formation of the chromanone derivative **6b** (Table S1). The NHC generated from thiazolium salt **3** showed excellent reactivity and the desired chromanone was formed in 99% yield (based on $^1$NMR, entry 1). Remarkably, in contrast to this NHC, other common NHCs derived from **A**-D are far less effective (entries 2-5). The choice of $K_2CO_3$ as base is important: other common bases resulted only in low yield of **3b** (entries 6-9). Lowering the reaction temperature below 70 °C was not found to be not beneficial (entry 10) and other solvents than THF were deleterious (entries 11-13). Additionally, when the carbene precursor **3** and $K_2CO_3$ were weighed outside the glove box (under air) and the reaction was carried out under argon atmosphere, **6b** was formed in 94% yield (entry 14). However, the reaction did not work at all when it was carried out in air (entry 15). Finally, reducing the catalyst loading to 5 mol% **3** and 10 mol% $K_2CO_3$ maintained the reactivity, providing chromanone **6b** in 96% isolated yield (entry 17).

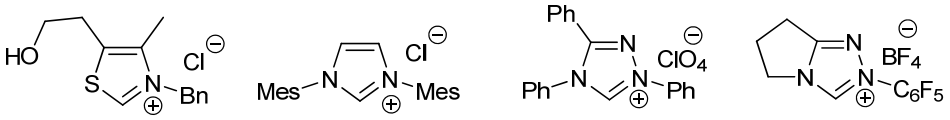
**Table S1.** Optimization of the reaction conditions.




| Entry | Variation of the standard conditions[a] | Yield of **6b** (%)[b] |
|---|---|---|
| 1 | None | 99 |
| 2 | **A** instead of **3** | 8 |

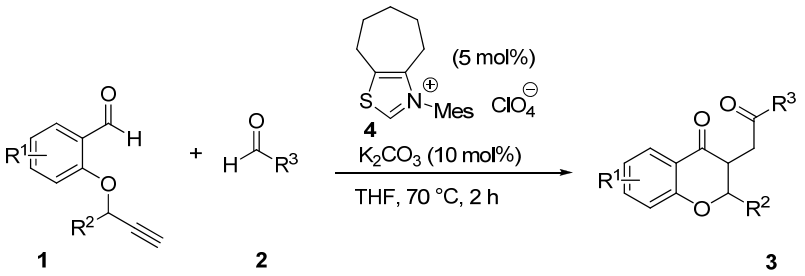
| | | |
|---|---|---|
| 3 | **B** instead of **3** | 0 |
| 4 | **C** instead of **3** | 0 |
| 5 | **D** instead of **3** | 10 |
| 6 | KO*t*-Bu instead of $K_2CO_3$ | 14 |
| 7 | DBU instead of $K_2CO_3$ | 72 |
| 8 | $Cs_2CO_3$ instead of $K_2CO_3$ | 16 |
| 9 | NaH instead of $K_2CO_3$ | 26 |
| 10 | 60 °C instead of 70 °C, 5 h | 86 |
| 11 | 1,4-dioxane instead of THF | 96 |
| 12 | DMF instead of THF | 0 |
| 13 | DME instead of THF | 64 |
| 14 | **3** and $K_2CO_3$ weighed outside glove box | 94 |
| 15 | Reaction carried out in air | 0 |
| 16 | 3 mol% **3** and 6 mol% $K_2CO_3$ | 73 |
| **17** | **5 mol% 3 and 10 mol% $K_2CO_3$** | **99 (96)[c]** |

[a]Standard conditions: **4b** (0.25 mmol), **5a** (0.25 mmol), NHC·HX (10 mol%), $K_2CO_3$ (20 mol%), THF (0.5 mL), 70 °C and 2 h. [b]The yields were determined by $^1$H NMR analysis of crude products using $CH_2Br_2$ as the internal standard. [c] Isolated yield in parentheses.




**A** **B** **C** **D**

## 5. General Procedure for the NHC-Catalyzed Hydroacylation-Stetter Reaction Cascade.

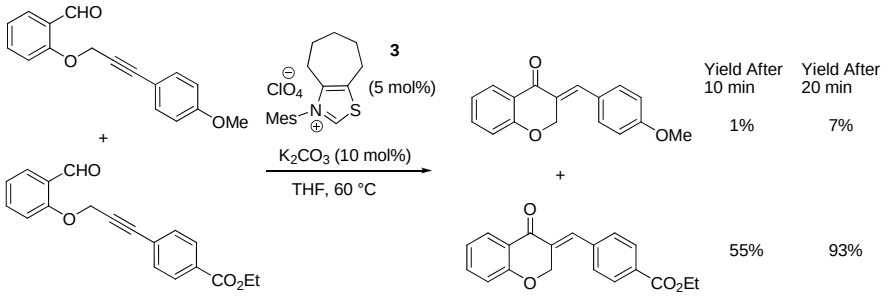



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-prop-2-ynyloxy-benzaldehyde derivative **1** (1.0 mmol, 1.0 eq.). To this was added the thiazolium salt **4** (0.019 mg, 0.05 mmol, 0.05 eq.) and dry $K_2CO_3$ (0.14 g, 0.1 mmol, 0.1 eq.) in a glove box. The aldehyde **2** (1.0 mmol, 1.0 eq.) was added outside the glove box (*solid* aldehydes were weighed in air and *liquid* aldehydes were transferred via syringe) and the mixture was dissolved in 2.0 mL of THF under argon. The resulting mixture was then stirred in a pre-heated oil bath at 70 °C for 2 h. After the reaction was complete, the reaction mixture was cooled to room temperature, pre-adsorbed on silica gel and purified by flash column chromatography on silica gel.

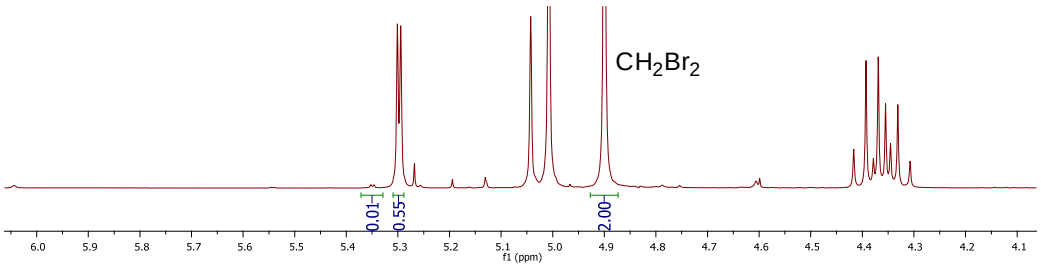
## 6. Competition Experiments

### Competition Experiments with Substrates 1e and 1g

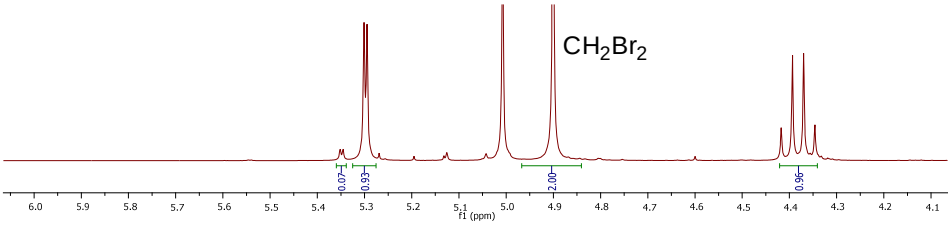
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-[3-(4-methoxyphenyl)-prop-2-ynyloxy)-benzaldehyde **1e** (33.3 mg, 0.125 mmol) and 2-[3-(4-carboethoxyphenyl)-prop-2-ynyloxy)-benzaldehyde **1g** (38.5 mg, 0.125 mmol). To this was added the thiazolium salt **3** (5 mg, 0.0125 mmol) and dry $K_2CO_3$ (4 mg, 0.025) in a glove box. The mixture was dissolved in 0.5 mL of THF under argon. The resulting mixture was then stirred in a pre-heated oil bath at 60 °C for either 10 or 20 minutes. The reaction mixture was cooled to room temperature immediately, then diluted with $CH_2Cl_2$ (1 mL) and filtered through a small pad of silica gel. It was further eluted with $CH_2Cl_2$ (2 mL). The solvent was evaporated to obtain the crude products whose yield was determined by $^1$H NMR analysis using $CH_2Br_2$ (18 µL, 0.25 mmol) as the internal standard.




### Section of $^1$H NMR after 10 minutes

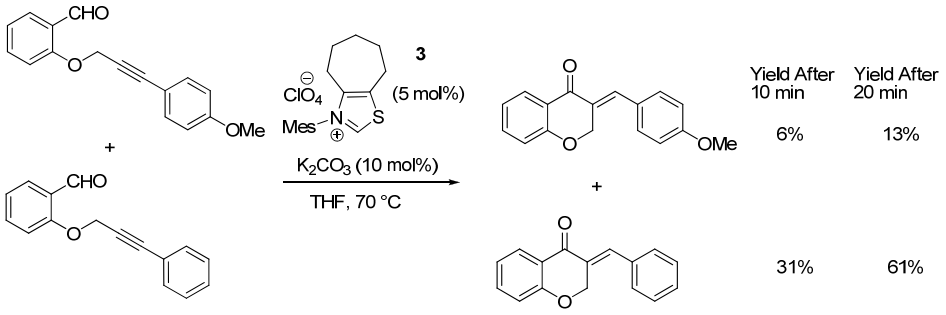



### Section of $^1$H NMR after 20 minutes

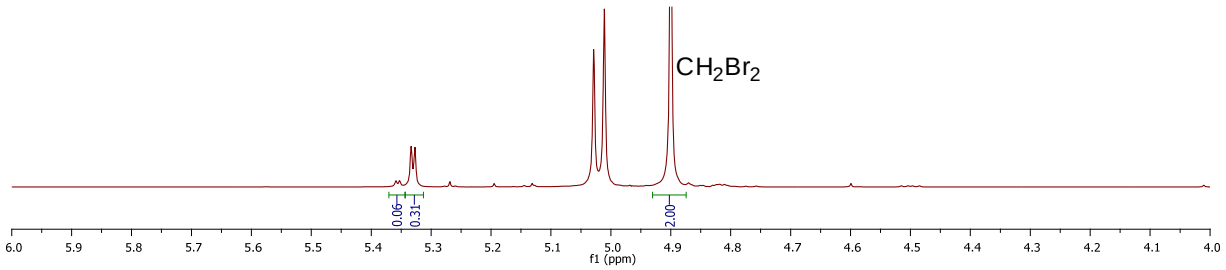


**Competition Experiments with Substrates 1a and 1e**

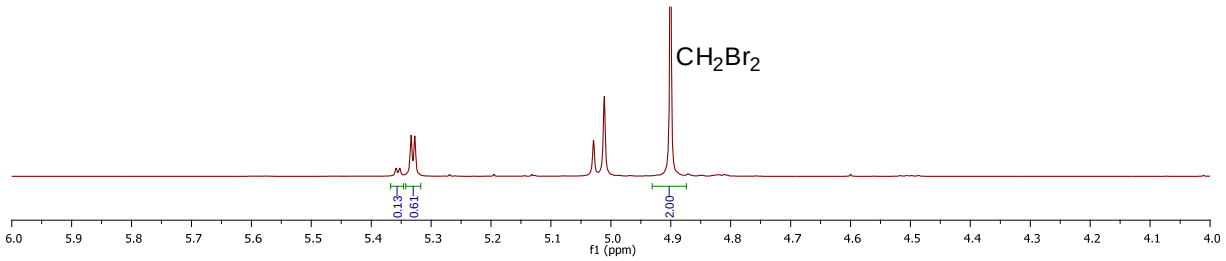
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde **1a** (29.5 mg, 0.125 mmol) and 2-[3-(4-methoxyphenyl)-prop-2-ynyloxy)-benzaldehyde **1e** (33.3 mg, 0.125 mmol). To this was added the thiazolium salt **3** (5 mg, 0.0125 mmol) and dry $K_2CO_3$ (4 mg, 0.025) in a glove box. The mixture was dissolved in 0.5 mL of THF under argon. The resulting mixture was then stirred in a pre-heated oil bath at 70 °C for either 10 or 20 minutes. The reaction mixture was cooled to room temperature immediately, then diluted with $CH_2Cl_2$ (1 mL) and filtered through a small pad of silica gel. It was further eluted with $CH_2Cl_2$ (2 mL). The solvent was evaporated to obtain the crude products whose yield was determined by $^1$H NMR analysis using $CH_2Br_2$ (18 µL, 0.25 mmol) as the internal standard.




**Section of $^1$H NMR after 10 minutes**

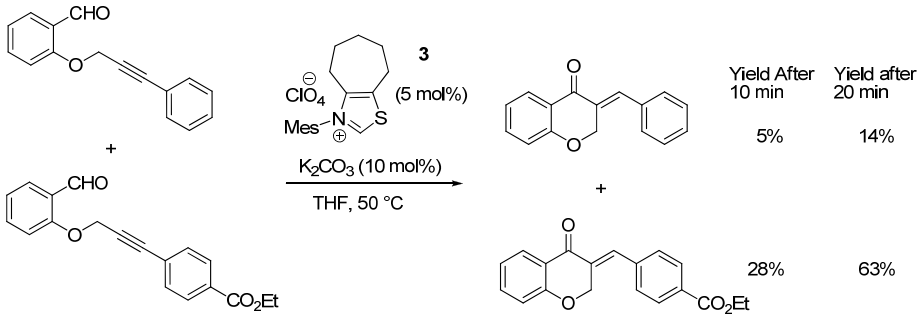



**Section of $^1$H NMR after 20 minutes**

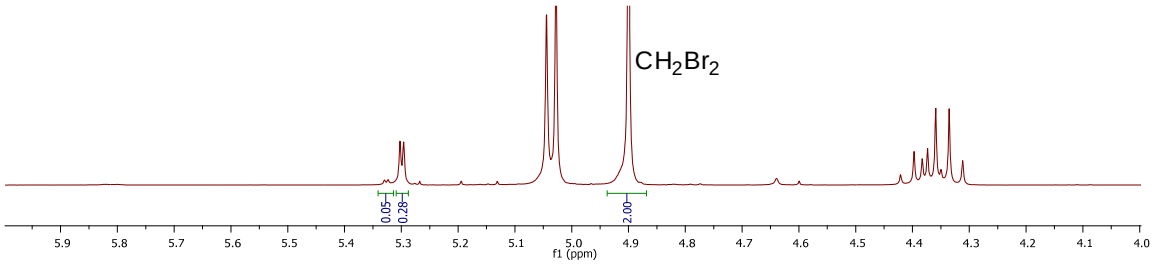


**Competition Experiments with Substrates 1a and 1g**

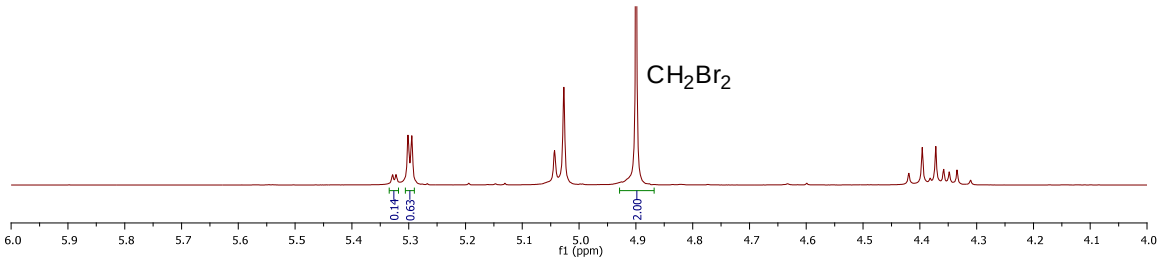
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde **1a** (29.5 mg, 0.125 mmol) and 2-[3-(4-carboethoxyphenyl)-prop-2-ynyloxy)-benzaldehyde **1g** (38.5 mg, 0.125 mmol). To this was added the thiazolium salt **3** (5 mg, 0.0125 mmol) and dry $K_2CO_3$ (4 mg, 0.025) in a glove box. The mixture was dissolved in 0.5 mL of THF under argon. The resulting mixture was then stirred in a pre-heated oil bath at 50 °C for either 10 or 20 minutes. The reaction mixture was cooled to room temperature immediately, then diluted with $CH_2Cl_2$ (1 mL) and filtered through a small pad of silica gel. It was further eluted with $CH_2Cl_2$ (2 mL). The solvent was evaporated to obtain the crude products whose yield was determined by $^1$H NMR analysis using $CH_2Br_2$ (18 µL, 0.25 mmol) as the internal standard.




**Section of $^1$H NMR after 10 minutes**




**Section of $^1$H NMR after 20 minutes**



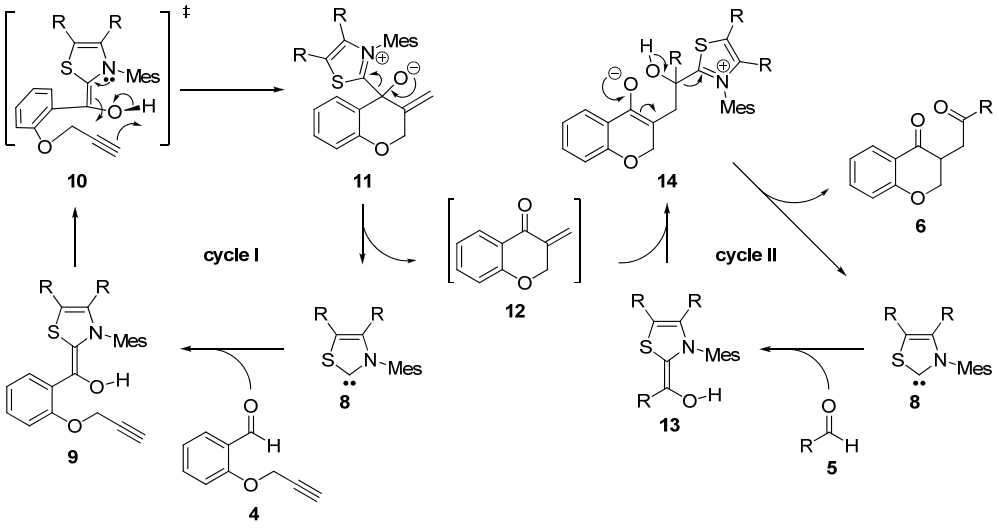
## Conclusions of the Competition Experiments

Arguably, the result of the competition experiments (ester substituted substrate **1g** reacting about 55 times faster than the methoxy substituted substrate **1e**) allows three assumptions:

1.) Formation of the Breslow intermediate is reversible under the reaction conditions.
2.) The alkyne plays an active role in the rate-determining step.
3.) Electron-poor alkynes react faster than electron-rich ones.

## 7. Proposed Mechanism for the Hydroacylation Cascade

A mechanistic rationale for the reaction may be advanced along the following lines as in Scheme below. The thiazolylidene **8** derived from thiazolium salt **3** adds to the carbonyl group of *o*-propargyloxybenzaldehyde **4** to form the Breslow-intermediate **9**. This can transform to the tetrahedral intermediate **11** through a concerted five-membered transition state **10**.[1] Liberation of carbene from **11** furnishes the enone **12.** At the same time, aldehyde **5** also reacts with NHC **8** to form the Breslow intermediate **13**, which can undergo a 1,4-addition to the generated enone **12** to form the zwitterionic intermediate **14**, which liberates the desired product **6** and the carbene. The mechanism presented herein is in good agreement with the observation that in the absence of aldehyde **5**, enone **12** adds to another molecule of **4a** to form the dimer **4a'**.




**Scheme S1.** Proposed mechanism.

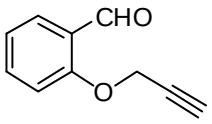
[1] For analogous transformations proceeding through five membered transition states see: (a) Roveda, J. G.; Clavette, C.; Hunt, A. D.; Gorelsky, S. I.; Whipp, C. J.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2009**, *131*, 8740. (b) Beauchemin, A. M.; Moran, J.; Lebrun, M.-E.; Séguin, C.; Dimitrijevic, E.; Zhang, L.; Gorelsky, S. I. *Angew. Chem., Int. Ed.* **2008**, *47*, 1410. (c) Moran, J.; Gorelsky, S. I.; Dimitrijevic, E.; Lebrun, M.-E.; Bédard, A.-C.; Séguin, C.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2008**, *130,* 17893. (d) Oppolzer, W.; Spivey, A. C.; Bochet, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 3139.

## 8. Synthesis and Characterization of Substrates

### General Procedure for the Synthesis of 2-propargyloxy Benzaldehyde Derivatives

Following a known procedure,[2] the salicylaldehyde derivative (41.0 mmol, 1.0 eq.) was dissolved in DMF (20 mL). To the stirred solution, potassium carbonate (45.04 mmol, 1.1 eq.) was added followed by the dropwise addition of propargyl bromide (45.04 mmol, 1.1 eq. 80% solution in toluene). The reaction mixture was stirred at room temperature for 15 h. Water (100 mL) was then added and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were washed with water (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography to afford the 2-prop-2-ynyloxy-benzaldehyde derivatives.

**2-Prop-2-ynyloxy-benzaldehyde (4a)**

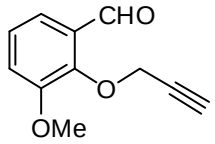



Following the general procedure, treatment of salicylaldehyde (5.0 g, 41.0 mmol, 1.0 eq.) with propargyl bromide (5.36 g, 4.69 mL, 45.04 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (6.22 g, 45.04 mmol, 1.1 eq.) in DMF (25 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 2-prop-2-ynyloxy-benzaldehyde **4a** as white solid (5.32 g, 80%).

**$R_f$** (pentane/EtOAc = 80/20): 0.45; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.47 (s, 1H, CHO), 7.85 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.62-7.51 (m, 1H, $H_{ar}$), 7.15-7.03 (m, 2H, $H_{ar}$), 4.82 (d, *J* = 2.4 Hz, 2H, $OCH_2$), 2.57 (t, *J* = 2.4 Hz, 1H, CCH). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 189.66, 159.86, 135.84, 128.67, 125.57, 121.79, 113.30, 77.78, 76.62, 56.48. **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_8O_2Na$: 183.0417, found: 183.0419; **ATR-FTIR ($cm^{-1}$)**: 3269, 2973, 2875, 1679, 1663, 1595, 1480, 1455, 1398, 1349, 1286, 1263, 1220, 1192, 1165, 1104, 1044, 1006, 925.

[2] F. Birbaum, A. Neels, C. G. Bochet, *Org. Lett.* **2008**, *10*, 3175.

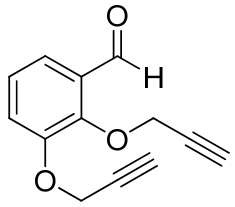
**3-Methoxy-2-prop-2-ynyloxy-benzaldehyde (4b)**




Following the general procedure, treatment of 3-methoxy salicylaldehyde (4.0 g, 26.3 mmol, 1.0 eq.) with propargyl bromide (3.44 g, 3.0 mL, 28.92 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (3.99 g, 28.92 mmol, 1.1 eq.) in DMF (15 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** as white solid (4.32 g, 87%).

**$R_f$** (pentane/EtOAc = 80/20): 0.34; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.47 (s, 1H, CHO), 7.43 (dd, *J* = 6.5 Hz, 2.9 Hz, 1H, $H_{ar}$), 7.17-7.11 (m, 2H, $H_{ar}$), 4.86 (d, *J* = 2.4 Hz, 2H, $OCH_2$), 3.88 (s, 3H, $OCH_3$), 2.47 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 190.63, 152.89, 149.50, 131.17, 124.98, 118.87, 117.80, 78.32, 77.02, 60.89, 56.08; **ESI-MS**: calculated $[M+Na]^+$ for $C_{11}H_{10}O_3Na$: 213.0522, found: 213.0526; **ATR-FTIR ($cm^{-1}$)**: 3266, 2940, 2891, 1681, 1582, 1477, 1438, 1383, 1316, 1248, 1203, 1178, 1065, 982, 912, 802.

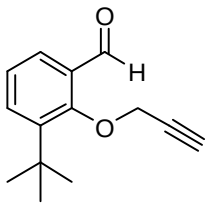
**2,3-Bis-prop-2-ynyloxy-benzaldehyde (4c)**




Following the general procedure, treatment of 3-hydroxysalicylaldehyde (1.0 g, 7.24 mmol, 1.0 eq.) with propargyl bromide (2.151 g, 2.01 mL, 18.09 mmol, 2.5 eq.) and potassium carbonate (3.0 g, 21.7 mmol, 3 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded 2,3-bis-prop-2-ynyloxy-benzaldehyde **4c** as a white solid (1.164 g, 75%).

**$R_f$** (pentane/EtOAc = 90/10): 0.38; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.49 (s, 1H, CHO), 7.53 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.6 Hz, 1H, $H_{ar}$), 7.30 (dd, $J_1$ = 8.1 Hz, $J_2$ = 1.6 Hz, 1H, $H_{ar}$), 7.20 (td, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz, 1H, $H_{ar}$), 4.90 (d, *J* = 2.4 Hz, 2H, $CH_2$), 4.80 (d, *J* = 2.4 Hz, 2H, $CH_2$), 2.56 (t, *J* = 2.4 Hz, 1H, CCH), 2.49 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 190.47, 150.80, 150.16, 131.49, 124.91, 120.25, 120.10, 78.22, 77.78, 77.22, 76.62, 61.27, 56.88; **ESI-MS:** calculated $[M+Na]^+$ for $C_{13}H_{10}O_3Na$: 237.0522, found: 237.0522; **ATR-FTIR ($cm^{-1}$):** 2879, 2119, 1681, 1583, 1478, 1448, 1394, 1356, 1309, 1272, 1246, 1205, 1168, 1087, 1054, 1003, 985, 952, 892.

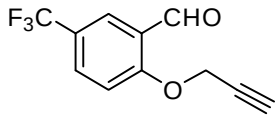
**3-*tert*-Butyl-2-prop-2-ynyloxybenzaldehyde (4d)**



Following the general procedure, treatment of 3-*ter*t-butylsalicylaldehyde (1.0 g, 5.61 mmol, 1.0 eq.) with propargyl bromide (0.734 g, 0.55 mL, 6.17 mmol, 1.1 eq.) and potassium carbonate (0.853 g, 6.17 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 3-*tert*-butyl-2-prop-2-ynyloxybenzaldehyde **4d** as a white solid (1.17 g, 97%).

**$R_f$** (pentane/EtOAc = 95/5): 0.45; **$^1$H NMR (400 MHz, $CDCl_3$)** δ = 10.36 (s, 1H, CHO), 7.71 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.8 Hz, 1H, $H_{ar}$), 7.61 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.8 Hz, 1H, $H_{ar}$), 7.19 (t, $J$ = 8.0 Hz, 1H, $H_{ar}$), 4.68 (d, $J$ = 2.5 Hz, 2H, $OCH_2$), 2.61 (t, $J$ = 2.5 Hz, 1H, CCH), 1.45 (s, 9H, $C(CH_3)_3$); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ = 190.54, 160.45, 144.28, 133.81, 130.43, 128.53, 124.67, 78.06, 77.04, 65.07, 35.34, 31.09; **ESI-MS**: calculated $[M+Na]^+$ for $C_{14}H_{16}O_2Na$: 239.1043, found: 239.1035; **ATR-FTIR (cm$^{-1}$):** 2965, 2875, 2129,0 1678, 1579, 1469, 1432, 1401, 1362, 1252, 1207, 1179, 1139, 1087, 1002, 985, 899, 841, 795, 726, 667, 623.

**2-Prop-2-ynyloxy-4-trifluoromethyl-benzaldehyde (4e)**

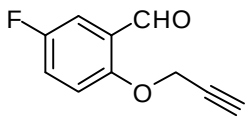


Following the general procedure, treatment of 4-trifluoromethyl salicylaldehyde (0.834 g, 4.39 mmol, 1.0 eq.) with propargyl bromide (0.574 g, 0.49 mL, 4.83 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (0.668 g, 4.83 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 2-prop-2-ynyloxy-4-trifluoromethyl-benzaldehyde **4e** as white solid (5.318 g, 80%).

**$R_f$** (pentane/EtOAc = 80/20): 0.59; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.49 (s, 1H, CHO), 7.94 (d, $J$ = 8.0 Hz, 1H, $H_{ar}$), 7.45-7.28 (m, 2H, $H_{ar}$), 4.89 (d, $J$ = 2.4 Hz, 2H, $OCH_2$), 2.63 (t, $J$ = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 188.63, 159.56, 136.54, 129.36, 127.72, 125.15, 118.50, 110.62, 77.49, 76.85, 56.85; **ESI-MS**: calculated $[M+Na]^+$ for $C_{11}H_7F_3O_2Na$: 251.0290, found: 251.0312; **ATR-FTIR (cm$^{-1}$)**: 3260, 1679,

1618, 1584, 1499, 1461, 1433, 1399, 1370, 1323, 1284, 1212, 1160, 1125, 1077, 1015, 931, 887.

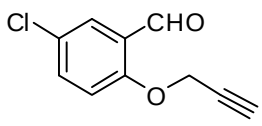
**5-Fluoro-2-prop-2-ynyloxy-benzaldehyde (4f)**




Following the general procedure, treatment of 5-fluoro salicylaldehyde (1.0 g, 7.14 mmol, 1.0 eq.) with propargyl bromide (0.934 g, 0.81 mL, 7.85 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (1.08 g, 7.85 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 5-fluoro-2-prop-2-ynyloxy-benzaldehyde **4f** as white solid (1.222 g, 96%).

**$R_f$** (pentane/EtOAc = 80/20): 0.43; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.41 (d, *J* = 3.1 Hz, 1H, CHO), 7.51 (dd, *J* = 8.2 Hz, 3.2 Hz, 1H, $H_{ar}$), 7.26 (m, 1H, $H_{ar}$), 7.10 (dd, *J* = 9.1 Hz, 3.9 Hz, 1H, $H_{ar}$), 4.81 (d, *J* = 2.4 Hz, 2H, $OCH_2$), 2.58 (t, *J* = 2.4 Hz, 1H, CCH). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 188.58, 157.61 (d, $J_{(C-F)}$ = 242.43 Hz), 156.11 (d, $J_{(C-F)}$ = 2.08 Hz), 126.62 (d, $J_{(C-F)}$ = 6.20 Hz), 122.44 (d, $J_{(C-F)}$ = 23.85 Hz), 115.39 (d, $J_{(C-F)}$ = 7.43 Hz), 114.31 (d, $J_{(C-F)}$ = 23.55 Hz), 77.54, 76.92, 57.23. **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_7FO_2Na$: 201.0322, found: 201.0315; **ATR-FTIR ($cm^{-1}$)**: 3230, 2909, 1672, 1609, 1484, 1452, 1426, 1403, 1380, 1266, 1250, 1198, 1157, 1021, 972, 884, 812.

**5-Chloro-2-prop-2-ynyloxy-benzaldehyde (4g)**

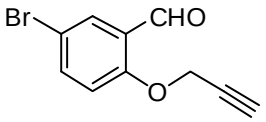



Following the general procedure, treatment of 5-chloro salicylaldehyde (1.0 g, 6.37 mmol, 1.0 eq.) with propargyl bromide (0.836 g, 0.73 mL, 7.03 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (0.972 g, 7.03 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 5-chloro-2-prop-2-ynyloxy-benzaldehyde **4g** as white solid (1.119 g, 90%).

**$R_f$** (pentane/EtOAc = 80/20): 0.43; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.39 (s, 1H, CHO), 7.79 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 7.50 (dd, *J* = 8.9, 2.7 Hz, 1H, $H_{ar}$), 7.08 (d, *J* = 8.9 Hz, 1H, $H_{ar}$), 4.82 (d, *J* = 2.4 Hz, 2H, $OCH_2$), 2.59 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 188.33, 158.24, 135.32, 128.21, 127.54, 126.48, 115.08, 77.32, 77.08, 56.84; **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_7ClO_2Na$: 217.0027, found: 217.0023; **ATR-FTIR**

**(cm$^{-1}$)**: 3242, 2880, 1673, 1594, 1479, 1446, 1396, 1369, 1271, 1219, 1184, 1131, 1003, 928, 896.

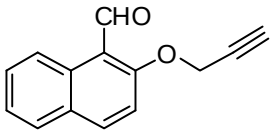
**5-Bromo-2-prop-2-ynyloxy-benzaldehyde (4h)**




Following the general procedure, treatment of 5-bromo salicylaldehyde (4.0 g, 19.90 mmol, 1.0 eq.) with propargyl bromide (2.604 g, 2.27 mL, 21.89 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (3.025 g, 21.89 mmol, 1.1 eq.) in DMF (15 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 5-bromo-2-prop-2-ynyloxy-benzaldehyde **4h** as white solid (3.95 g, 83%).

**R$_f$** (pentane/EtOAc = 80/20): 0.43; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 10.36 (s, 1H, CHO), 7.91 (d, *J* = 2.6 Hz, 1H, H$_{ar}$), 7.62 (dd, *J* = 8.9 Hz, 2.6 Hz, 1H, H$_{ar}$), 7.01 (d, *J* = 8.9 Hz, 1H, H$_{ar}$), 4.81 (d, *J* = 2.4 Hz, 2H, OCH$_2$), 2.59 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 188.16, 158.67, 138.17, 131.18, 126.80, 115.42, 114.64, 77.26, 77.11, 56.74; **ESI-MS**: calculated [M+Na]$^+$ for $C_{10}H_7O_2BrNa$: 260.9522, found: 260.9515; **ATR-FTIR (cm$^{-1}$)**: 3283, 2870, 1681, 1589, 1472, 1395, 1275, 1216, 1182, 1154, 1123, 1011, 928, 907, 876.

**2-Prop-2-ynyloxy-naphthalene-1-carbaldehyde (4i)**

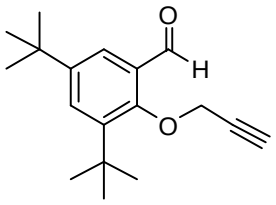



Following the general procedure, treatment of 2-hydroxy-1-naphthaldehyde (4.0 g, 23.23 mmol, 1.0 eq.) with propargyl bromide (3.039 g, 2.64 mL, 25.55 mmol, 1.1 eq., 80% in toluene) and potassium carbonate (3.51 g, 25.55 mmol, 1.1 eq.) in DMF (15 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 2-prop-2-ynyloxy-naphthalene-1-carbaldehyde **4i** as white solid (3.81 g, 78%).

**R$_f$** (pentane/EtOAc = 80/20): 0.36; **$^1$H NMR (300 MHz, CDCl$_3$)** δ 10.90 (s, 1H, CHO), 9.28 (d, *J* = 8.7 Hz, 1H, H$_{ar}$), 8.06 (d, *J* = 9.1 Hz, 1H, H$_{ar}$), 7.78 (d, *J* = 8.1 Hz, 1H, H$_{ar}$), 7.62 (dd, *J* = 11.4 Hz, 4.1 Hz, 1H, H$_{ar}$), 7.48-7.33 (m, 2H, H$_{ar}$), 4.93 (d, *J* = 1.9 Hz, 2H, OCH$_2$), 2.58 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ 192.08, 161.98, 137.39, 131.53, 130.00, 129.21, 128.35, 125.31, 125.20, 118.09, 114.09, 77.77, 76.90,

57.47; **ESI-MS**: calculated $[M+Na]^+$ for $C_{14}H_{10}O_2Na$: 233.0573, found: 233.0564; **ATR-FTIR (cm$^{-1}$)**: 3252, 2893, 1654, 1619, 1588, 1511, 1457, 1435, 1365, 1343, 1266, 1209, 1147, 1053, 1023, 947, 913, 858.

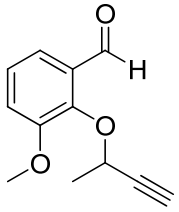
**3,5-Di-*tert*-butyl-2-prop-2-ynyloxy-benzaldehyde (4j)**



Following the general procedure, treatment of 3,5-di-*tert*-butyl-salicylaldehyde (1.0 g, 4.26 mmol, 1.0 eq.) with propargyl bromide (0.556 mg, 0.52 mL, 4.67 mmol, 1.1 eq.) and potassium carbonate (0.645 g, 4.67 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 3,5-di-*tert*-butyl-2-prop-2-ynyloxy-benzaldehyde **4j** as a white solid (1.056 g, 91%).

**R$_f$** (pentane/EtOAc = 95:5): 0.44; **$^1$H NMR (300 MHz, CDCl$_3$)** δ = 10.37 (s, 1H, CHO), 7.71 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 7.63 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 4.63 (d, *J* = 2.5 Hz, 2H, $OCH_2$), 2.61 (t, *J* = 2.5 Hz, 1H, CCH), 1.45 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$); **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ = 190.84, 158.53, 147.26, 143.41, 131.13, 129.73, 124.77, 78.30, 76.81, 65.12, 35.51, 34.88, 31.42, 31.19; **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{24}O_2Na$: 295.1669, found: 295.1661; **ATR-FTIR (cm$^{-1}$):** 2958, 2871, 2361, 2131, 1691, 1594, 1392, 1365, 1264, 1235, 1217, 1201, 1161, 1113, 990, 961.

**3-Methoxy-2-(1-methyl-prop-2-ynyloxy)-benzaldehyde (4k)**



Following the general procedure, treatment of 3-methoxysalicylaldehyde (1.0 g, 6.57 mmol, 1.0 eq.) with 3-bromo-but-1-yne (1.74 g, 13.1 mmol, 2.0 eq.) and potassium carbonate (1.363 g, 6.17 mmol, 1.1 eq.) in DMF (10 mL), followed by work-up of the reaction mixture in diethyl ether and flash column chromatography afforded the 3-methoxy-2-(1-methyl-prop-2-ynyloxy)-benzaldehyde **4k** as a white solid (343 mg, 26%).

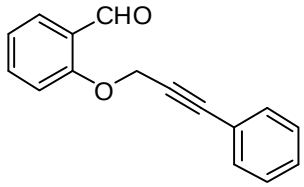
**R*f*** (pentane/EtOAc = 90/10): 0.50; **$^1$H NMR (300 MHz, CDCl$_3$)** δ = 10.49 (s, 1H, CHO), 7.46 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.7 Hz, 1H, $H_{ar}$), 7.19 – 7.13 (m, 2H, $H_{ar}$), 5.13 (qd, $J_1$ = 6.6 Hz, $J_2$ = 2.1 Hz, 1H, OCH), 3.89 (s, 3H, $OCH_3$), 2.42 (s, 1H, CCH), 1.70 (d, *J* = 6.6 Hz, 3H, CHC$H_3$); **$^{13}$C NMR (75 MHz, CDCl$_3$)** δ = 191.06, 153.11, 149.53, 131.46,

124.85, 118.85, 117.65, 82.38, 75.50, 68.73, 56.15, 22.23; **ESI-MS:** calculated $[M+Na]^+$ for $C_{12}H_{12}O_3Na$: 227.0679, found: 227.0666; **ATR-FTIR ($cm^{-1}$):** 3006, 2876, 2107, 1689, 1583, 1480, 1439, 1390, 1312, 1250, 1214, 1186, 1067, 1023, 312.

## General Procedure for the Synthesis of Internal Alkynes

Following a reported procedure,[3] a solution of 2-prop-2-ynyloxy-benzaldehyde derivative **4** (5.0 mmol, 1.0 equiv.) in dry DMSO (10 mL) was added iodobenzene derivative (5.0 mmol, 1.0 equiv.), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol, 1 mol%) and CuI (0.029 g, 0.15 mmol, 3 mol%) followed by triethylamine (0.759 g, 7.5 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 8 h under an Argon atmosphere. The reaction mixture was diluted with EtOAc (30 mL) and washed with water (3 x 30 mL) followed by brine (20 mL) and then dried over anhydrous $Na_2SO_4$. The residue obtained after evaporation of the solvent was purified by silica gel column chromatography to afford 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde derivatives **1** as a white solid (64-88%).

### 2-(3-Phenyl-prop-2-ynyloxy)-benzaldehyde (1a)



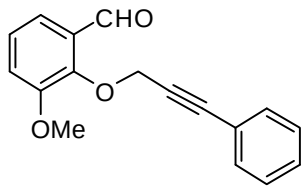

Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.800 g, 5 mmol) with iodobenzene (1.22 g, 0.67 mL, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) CuI (0.029 g, 0.15 mmol) and triethylamine (0.759 g, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde **1a** as a white solid (1.041 g, 88%).

**$R_f$** (pentane/EtOAc = 80/20): 0.58; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.54 (s, 1H, CHO), 7.88 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H, $H_{ar}$), 7.66-7.51 (m, 1H, $H_{ar}$), 7.48-7.38 (m, 2H, $H_{ar}$), 7.38-7.27 (m, 3H, $H_{ar}$), 7.21 (d, *J* = 8.4 Hz, 1H, $H_{ar}$), 7.15-7.03 (m, 1H, $H_{ar}$), 5.06 (s, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 189.86, 160.18, 135.88, 131.91, 129.06, 128.57,

[3] V. S. P. Rao Lingam, R. Vinodkumar, K. Mukkanti, A. Thomas, B. Gopalan, *Tetrahedron Lett.* **2008**, *49*, 4260

125.62, 121.98, 121.65, 113.53, 88.20, 83.04, 57.40. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{12}O_2Na$: 259.0730, found: 259.0726; **ATR-FTIR ($cm^{-1}$)**: 2962, 2887, 1678, 1660, 1595, 1479, 1459, 1400, 1305, 1284, 1261, 1221, 1190, 1164, 1106, 1069, 1042, 1029, 1006, 958.

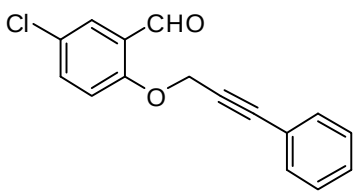
**3-Methoxy 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1b)**




Following the general procedure, treatment of 3-methoxy 2-prop-2-ynyloxy-benzaldehyde **4b** (0.950 g, 5 mmol) with iodobenzene (1.02 g, 0.56 mL, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) and CuI (0.029 g, 0.15 mmol) and triethylamine (0.759 g, 1.05 mL, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 3-methoxy 2-prop-2-ynyloxy-benzaldehyde **1b** as white solid (0.845 g, 64%).

**$R_f$** (pentane/EtOAc = 80/20): 0.38; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.59 (s, 1H, CHO), 7.48 (dd, *J* = 6.8 Hz, 2.7 Hz, 1H, $H_{ar}$), 7.35-7.23 (m, 5H, $H_{ar}$), 7.18 (dd, *J* = 6.1 Hz, 1.5 Hz, 2H, $H_{ar}$), 5.09 (s, 2H, $OCH_2$), 3.92 (s, 3H, $OCH_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 190.68, 153.11, 149.77, 131.56, 128.78, 128.41, 125.04, 122.01, 118.88, 117.76, 88.91, 83.67, 61.92, 56.15. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_3Na$ : 289.0835, found: 289.0836; **ATR-FTIR ($cm^{-1}$)**: 2965, 2937, 1684, 1582, 1478, 1448, 1437, 1390, 1350, 1312, 1268, 1249, 1196, 1177, 1065, 982, 950, 911.

**5-Chloro 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1c)**

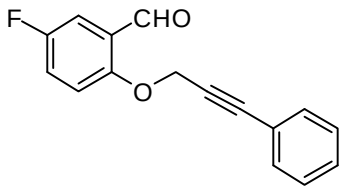



Following the general procedure, treatment of 5-chloro 2-prop-2-ynyloxy-benzaldehyde **4g** (0.720 g, 3.7 mmol) with iodobenzene (0.755 g, 0.41 mL, 3.7 mmol), $(PPh_3)_4Pd$ (0.043 g, 0.04 mmol) and CuI (0.021 g, 0.12 mmol) and triethylamine (0.562 g, 0.77 mL, 5.5 mmol) in dry DMSO (8 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 5-chloro 2-prop-2-ynyloxy-benzaldehyde **1c** as white solid (0.651 g, 65%).

**$R_f$** (pentane/EtOAc = 90/10): 0.30; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.45 (s, 1H, CHO), 7.81 (d, *J* = 2.7 Hz, 1H, $H_{ar}$), 7.51 (dd, *J* = 8.9, 2.8 Hz, 1H, $H_{ar}$), 7.42 (dd, *J* = 7.5, 2.0 Hz,

2H, $H_{ar}$), 7.37-7.27 (m, 3H, $H_{ar}$), 7.17 (d, $J$ = 8.9 Hz, 1H, $H_{ar}$), 5.04 (s, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 188.44, 158.53, 135.31, 131.89, 129.18, 128.51, 128.13, 127.35, 126.50, 121.73, 115.27, 88.62, 82.52, 57.72. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2ClNa$ : 293.0340, found: 293.0345; **ATR-FTIR (cm$^{-1}$)**: 2985, 2884, 1673, 1591, 1473, 1450, 1400, 1382, 1290, 1276, 1258, 1224, 1181, 1126, 1029, 994, 957, 900.

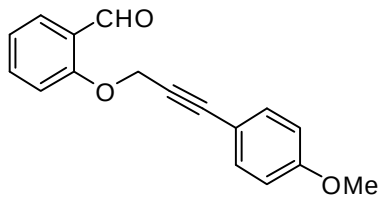
**5-Fluoro 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1d)**




Following the general procedure, treatment of 5-fluoro 2-prop-2-ynyloxy-benzaldehyde **4f** (0.760 g, 4.27 mmol) with iodobenzene (0.871 g, 0.48 mL, 4.27 mmol), $(PPh_3)_4Pd$ (0.049 g, 0.043 mmol) and CuI (0.024 g, 0.13 mmol) and triethylamine (0.649 g, 0.89 mL, 6.41 mmol) in dry DMSO (8 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 5-fluoro 2-prop-2-ynyloxy-benzaldehyde **1d** as white solid (0.834 g, 77%).

**$R_f$** (pentane/EtOAc = 90/10): 0.30; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.48 (d, $J$ = 3.2 Hz, 1H, CHO), 7.55 (dd, $J$ = 8.2 Hz, 3.2 Hz, 1H, $H_{ar}$), 7.42 (dd, $J$ = 7.5 Hz, 2.1 Hz, 2H, $H_{ar}$), 7.37-7.25 (m, 4H, $H_{ar}$), 7.19 (dd, $J$ = 9.1 Hz, 4.0 Hz, 1H, $H_{ar}$), 5.04 (s, 2H, $OCH_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 188.69, 157.56 (d, $J_{(C-F)}$ = 243.34 Hz), 156.40 (d, $J_{(C-F)}$ = 2.16 Hz), 131.87, 129.14, 128.50, 126.68 (d, $J_{(C-F)}$ = 6.13 Hz), 122.44 (d, $J_{(C-F)}$ = 23.99 Hz), 121.81, 115.66 (d, $J_{(C-F)}$ = 7.26 Hz), 114.21 (d, $J_{(C-F)}$ = 23.56 Hz), 88.50, 82.76, 58.18. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2FNa$ : 277.0635, found: 277.0630; **ATR-FTIR (cm$^{-1}$)**: 2972, 2890, 1679, 1609, 1482, 1454, 1429, 1399, 1297, 1267, 1234, 1199, 1151, 1007, 954, 892.

**2-[3-(4-Methoxy phenyl)-prop-2-ynyloxy]-benzaldehyde (1e)**

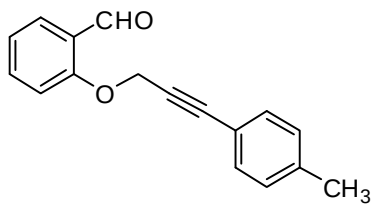



Following the general procedure, treatment of 3-methoxy 2-prop-2-ynyloxy-benzaldehyde **4a** (0.950 g, 5 mmol) with iodobenzene (1.22 g, 0.67 mL, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) and CuI (0.029 g, 0.15 mmol) and

triethylamine (0.759 g, 1.05 mL, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 2-[3-(4-methoxy phenyl)-prop-2-ynyloxy]-benzaldehyde **1e** as white solid (0.953 g, 72%).

**$R_f$** (pentane/EtOAc = 80/20): 0.32; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.53 (s, 1H, CHO), 7.86 (d, *J* = 7.5 Hz, 1H, $H_{ar}$), 7.57 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 7.44-7.31 (m, 2H, $H_{ar}$), 7.20 (d, *J* = 8.4 Hz, 1H, $H_{ar}$), 7.07 (t, *J* = 7.5 Hz, 1H, $H_{ar}$), 6.83 (d, *J* = 8.6 Hz, 2H, $H_{ar}$), 5.03 (s, 2H, $OCH_2$), 3.79 (s, 3H, $OCH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 189.83, 160.22, 160.15, 135.83, 133.43, 128.54, 125.56, 121.52, 114.02, 113.54, 88.19, 81.72, 57.49, 55.38. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_3Na$ : 289.0835, found: 289.0829; **ATR-FTIR ($cm^{-1}$)**: 2962, 2893, 1680, 1595, 1510, 1480, 1459, 1401, 1290, 1266, 1250, 1226, 1189, 1167, 1103, 1030, 1000, 958, 825.

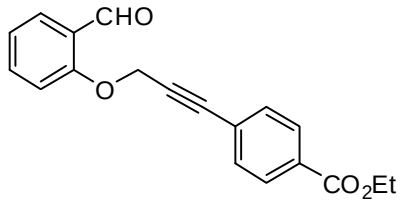
**2-[3-(4-Methyl phenyl)-prop-2-ynyloxy]-benzaldehyde (1f)**




Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.801 g, 5 mmol) with 4-iodotoluene (1.09 g, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) and CuI (0.029 g, 0.15 mmol) and triethylamine (0.759 g, 1.05 mL, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 2-[3-(4-methyl phenyl)-prop-2-ynyloxy]-benzaldehyde **1f** as white solid (0.926 g, 74%).

**$R_f$** (pentane/EtOAc = 90/10): 0.32; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.53 (s, 1H, CHO), 7.87 (dd, *J* = 7.7 Hz, 1.8 Hz, 1H, $H_{ar}$), 7.58 (td, *J* = 8.4 Hz, 1.7 Hz, 1H, $H_{ar}$), 7.38-7.28 (m, 2H, $H_{ar}$), 7.20 (d, *J* = 8.4 Hz, 1H, $H_{ar}$), 7.09 (dd, *J* = 14.8 Hz, 7.7 Hz, 3H, $H_{ar}$), 5.04 (s, 2H, $OCH_2$), 2.34 (s, 3H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 189.83, 160.21, 139.27, 135.85, 131.80, 129.22, 128.57, 125.57, 121.56, 118.88, 113.53, 88.36, 82.38, 57.44, 21.61. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_2Na$ : 273.0886, found: 273.0870; **ATR-FTIR ($cm^{-1}$)**: 2981, 2893, 1678, 1595, 1507, 1477, 1458, 1403, 1382, 1288, 1267, 1223, 1190, 1164, 1103, 1044, 1001, 958, 830, 818.

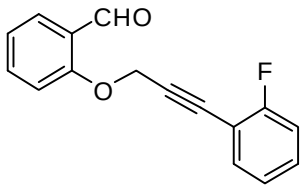
**2-[3-(4-Carboethoxy phenyl)-prop-2-ynyloxy]-benzaldehyde (1g)**




Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.801 g, 5 mmol) with methyl 4-iodo benzoate (1.38 g, 0.84 mL, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) and CuI (0.029 g, 0.15 mmol) and triethylamine (0.759 g, 1.05 mL, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 2-[3-(4-carboethoxy phenyl)-prop-2-ynyloxy]-benzaldehyde **1g** as white solid (1.355 g, 88%).

**$R_f$** (pentane/EtOAc = 80/20): 0.28; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.52 (s, 1H, CHO), 7.98 (d, *J* = 8.3 Hz, 2H, $H_{ar}$), 7.87 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.64-7.54 (m, 1H, $H_{ar}$), 7.47 (d, *J* = 8.3 Hz, 2H, $H_{ar}$), 7.18 (d, *J* = 8.4 Hz, 1H, $H_{ar}$), 7.09 (t, *J* = 7.5 Hz, 1H, $H_{ar}$), 5.06 (s, 2H, $OCH_2$), 4.36 (q, *J* = 7.1 Hz, 2H, $OCH_2CH_3$), 1.38 (t, *J* = 7.1 Hz, 3H, $OCH_2CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 189.57, 165.86, 159.93, 135.82, 131.69, 130.56, 129.49, 128.61, 126.36, 125.52, 121.69, 113.33, 87.26, 85.81, 61.26, 57.15, 14.32. **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{16}O_4Na$ : 331.0941, found: 331.0939; **ATR-FTIR ($cm^{-1}$)**: 2987, 2865, 1721, 1690, 1600, 1482, 1461, 1403, 1368, 1263, 1224, 1174, 1104, 1045, 1008, 960, 859.

**2-[3-(2-Fluoro phenyl)-prop-2-ynyloxy]-benzaldehyde (1h)**

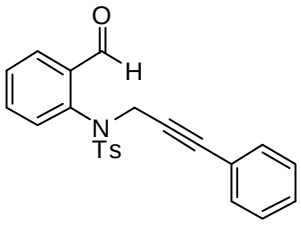



Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.801 g, 5 mmol) with 2-fluoro iodobenzene (1.11 g, 0.58 mL, 5 mmol), $(PPh_3)_4Pd$ (0.058 g, 0.05 mmol) and CuI (0.029 g, 0.15 mmol) and triethylamine (0.759 g, 1.05 mL, 7.5 mmol) in dry DMSO (10 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the 2-[3-(2-fluoro phenyl)-prop-2-ynyloxy]-benzaldehyde **1h** as white solid (0.852 g, 67%).

**$R_f$** (pentane/EtOAc = 90/10): 0.23; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.53 (s, 1H, CHO), 7.87 (d, *J* = 7.7 Hz, 1H, $H_{ar}$), 7.65-7.54 (m, 1H, $H_{ar}$), 7.41 (dd, *J* = 11.7 Hz, 4.5 Hz, 1H, $H_{ar}$), 7.30 (dd, *J* = 9.9 Hz, 4.1 Hz, 1H, $H_{ar}$), 7.22 (d, *J* = 8.4 Hz, 1H, $H_{ar}$), 7.07 (dd, *J* = 15.5 Hz, 8.1 Hz, 3H, $H_{ar}$), 5.08 (s, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 189.78,

163.06 (d, $J_{(C-F)}$ = 252.08 Hz), 160.07, 135.89, 133.78, 130.90 (d, $J_{(C-F)}$ = 8.09 Hz), 128.63, 125.61, 124.13 (d, $J_{(C-F)}$ = 3.79 Hz), 121.72, 115.69 (d, $J_{(C-F)}$ = 21.21 Hz), 113.55, 110.58 (d, $J_{(C-F)}$ = 15.24 Hz), 88.20, 81.68, 57.32. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2FNa$ : 277.0635, found: 277.0631; **ATR-FTIR (cm$^{-1}$)**: 2873, 2768, 1679, 1597, 1491, 1480, 1459, 1395, 1363, 1287, 1259, 1215, 1191, 1168, 1106, 1043, 1008, 965, 832.

***N*-(3-Phenyl-prop-2-ynyloxy)-*N*-(2-formyl-phenyl)-4-methyl-benzenesulfonamide (1i)**

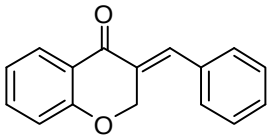



Following the general procedure, treatment of *N*-Propynyloxy-*N*-(2-formyl-phenyl)-4-methyl-benzenesulfonamide (0.490 g, 1.56 mmol) with iodobenzene (0.318 g, 0.18 mL, 1.56 mmol), $(PPh_3)_4Pd$ (0.018 g, 0.016 mmol) and CuI (0.009 g, 0.05 mmol) and triethylamine (0.236 g, 0.33 mL, 2.34 mmol) in dry DMSO (8 mL) followed by work-up of the reaction mixture in EtOAc and flash column chromatography afforded the *N*-(3-phenyl-prop-2-ynyloxy)-*N*-(2-formyl-phenyl)-4-methyl-benzenesulfonamide **1i** as white solid (0.399 g, 66%).

**$R_f$** (pentane/EtOAc = 70/30): 0.44; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 10.51 (s, 1H, CHO), 8.17-7.98 (m, 1H, $H_{ar}$), 7.71-7.49 (m, 4H, $H_{ar}$), 7.40-7.25 (m, 5H, $H_{ar}$), 7.24-7.15 (m, 2H, $H_{ar}$), 7.14-7.01 (m, 1H, $H_{ar}$), 4.76 (s, 2H, $NCH_2$), 2.46 (s, 3H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 190.23, 144.48, 141.55, 136.12, 135.18, 134.33, 131.55, 129.77, 129.32, 128.90, 128.81, 128.64, 128.38, 128.35, 121.97, 86.65, 82.46, 42.88, 21.68. **ESI-MS**: calculated $[M+Na]^+$ for $C_{23}H_{19}O_3NSNa$ : 412.0978, found: 412.0979; **ATR-FTIR (cm$^{-1}$)**: 3062, 2884, 1686, 1595, 1487, 1454, 1391, 1347, 1299, 1267, 1221, 1189, 1162, 1092, 1075, 1006, 970, 920, 866.

## 9. Synthesis and Characterization of Functionalized Chromanones

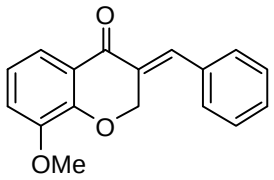
**3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2a)**[4]



Following the general procedure, treatment of 2-(3-phenyl-prop-2-ynyloxy) benzaldehyde **1a** (0.236 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-phenyl-meth-(E)-ylidene]-chroman-4-one **2a** as a white solid (0.202 g, 86%).

**$R_f$** (pentane/EtOAc = 80/20): 0.60; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.03 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.88 (s, 1H, C=C*H*), 7.59-7.36 (m, 4H, $H_{ar}$), 7.36-7.27 (m, 2H, $H_{ar}$), 7.15-7.02 (m, 1H, $H_{ar}$), 6.97 (d, *J* = 8.3 Hz, 1H, $H_{ar}$), 5.35 (d, *J* = 1.6 Hz, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 182.35, 161.21, 137.61, 135.99, 134.46, 130.99, 130.09, 129.58, 128.83, 128.04, 122.11, 122.02, 118.02, 67.69. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{12}O_2Na$: 259.0730, found: 259.0724; **ATR-FTIR (cm$^{-1}$)**: 2857, 1666, 1600, 1492, 1466, 1450, 1391, 1307, 1265, 1210, 1145, 1102, 1030, 1014, 993, 965, 934.

**3-[1-Phenyl-meth-(E)-ylidene]-8-methoxy-chroman-4-one (2b)**



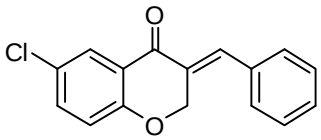
Following the general procedure, treatment of 3-methoxy 2-prop-2-ynyloxy-benzaldehyde **1b** (0.266 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-Phenyl-meth-(E)-ylidene]-8-methoxy-chroman-4-one **2b** as a white solid (0.253 g, 95%).

**$R_f$** (pentane/EtOAc = 80/20): 0.26; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.87 (s, 1H, $CH_{olefin}$), 7.62 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H, $H_{ar}$), 7.41 (t, *J* = 7.3 Hz, 3H, $H_{ar}$), 7.35-7.27 (m, 2H, $H_{ar}$), 7.11-6.95 (m, 2H, $H_{ar}$), 5.42 (d, *J* = 1.7 Hz, 2H, $OCH_2$), 3.89 (s, 3H, $OCH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 182.34, 151.14, 148.91, 137.77, 134.34, 130.64, 130.02, 129.60, 128.83, 122.73, 121.48, 119.15, 116.74, 68.13, 56.35. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_3Na$: 289.0835, found: 289.0836; **ATR-FTIR (cm$^{-1}$)**: 2996, 2834,

[4] Basavaiah, M. Bakthadiss, S. Pandiraju, *Chem. Commun*, **1998**, 1639.

1670, 1607, 1584, 1487, 1445, 1383, 1338, 1303, 1270, 1251, 1215, 1185, 1077, 1015, 994, 979, 944, 923.

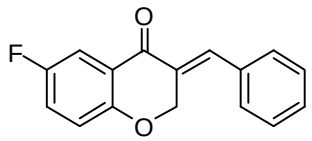
**6-Chloro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2c)**



Following the general procedure, treatment of 5-chloro 2-prop-2-ynyloxy-benzaldehyde **1c** (0.271 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 6-Chloro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one **2c** as a white solid (0.211 g, 78%).

**$R_f$** (pentane/EtOAc = 90/10): 0.52; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 7.88 (s, 1H, $CH_{olefin}$), 7.42 (dt, *J* = 8.8 Hz, 5.0 Hz, 4H, $H_{ar}$), 7.34-7.27 (m, 2H, $H_{ar}$), 6.92 (d, *J* = 8.8 Hz, 1H, $H_{ar}$), 5.34 (d, *J* = 1.8 Hz, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 181.28, 159.62, 138.46, 135.78, 134.21, 130.16, 130.12, 129.83, 128.90, 127.46, 127.30, 122.86, 119.78, 67.82. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2ClNa$: 293.0340, found: 293.0342; **ATR-FTIR (cm$^{-1}$)**: 3057, 3030, 1673, 1609, 1574, 1470, 1448, 1421, 1317, 1280, 1241, 1200, 1154, 1123, 1082, 1031, 1008, 996, 966, 929, 913, 896.

**6-Fluoro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2d)**

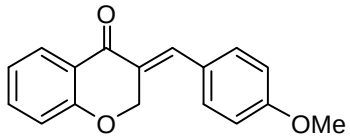


Following the general procedure, treatment of 5-fluoro 2-prop-2-ynyloxy-benzaldehyde **1d** (0.254 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 6-Fluoro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one **2d** as a white solid (0.213 g, 84%).

**$R_f$** (pentane/EtOAc = 90/10): 0.48; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.89 (s, 1H, $CH_{olefin}$), 7.66 (dd, *J* = 8.3 Hz, 3.2 Hz, 1H, $H_{ar}$), 7.53-7.38 (m, 3H, $H_{ar}$), 7.35-7.27 (m, 2H, $H_{ar}$), 7.20 (ddd, *J* = 9.0 Hz, 7.8 Hz, 3.2 Hz, 1H, $H_{ar}$), 6.95 (dd, *J* = 9.0 Hz, 4.2 Hz, 1H, $H_{ar}$), 5.33 (d, *J* = 1.8 Hz, 2H, $OCH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 181.65, 157.69 (d, $J_{(C-F)}$ = 242.04 Hz), 157.43 (d, $J_{(C-F)}$ = 1.72 Hz), 138.30, 134.28, 130.35, 130.14, 129.78, 128.89,

123.47 (d, $J_{(C-F)}$ = 25.14 Hz), 122.66 (d, $J_{(C-F)}$ = 6.79 Hz), 119.70 (d, $J_{(C-F)}$ = 7.62 Hz), 112.97 (d, $J_{(C-F)}$ = 23.54 Hz), 67.82. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2FNa$: 277.0635, found: 277.0629; **ATR-FTIR (cm$^{-1}$)**: 3028, 2858, 1668, 1605, 1617, 1574, 1482, 1436, 1323, 1280, 1228, 1196, 1128, 1080, 1030, 1014, 984, 942.

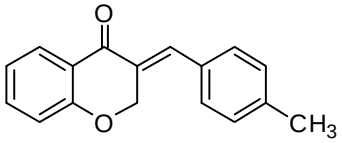
**3-[1-(4-methoxy phenyl)-meth-(E)-ylidene]-chroman-4-one (2e)**




Following the general procedure, treatment of 2-[3-(4-methoxy phenyl)-prop-2-ynyloxy]-benzaldehyde **1e** (0.266 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-(4-methoxy phenyl)-meth-(E)-ylidene]-chroman-4-one **2e** as a white solid (0.191 g, 72%).

**$R_f$** (pentane/EtOAc = 90/10): 0.23; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.84 (s, 1H, $CH_{olefin}$), 7.56-7.40 (m, 1H, $H_{ar}$), 7.36-7.23 (m, 2H, $H_{ar}$), 7.13-7.02 (m, 1H, $H_{ar}$), 7.02-6.85 (m, 3H, $H_{ar}$), 5.38 (d, *J* = 1.8 Hz, 2H, $OCH_2$), 3.86 (s, 3H, $OCH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 182.32, 161.07, 160.82, 137.46, 135.80, 132.19, 128.99, 128.00, 127.11, 122.23, 121.96, 117.94, 114.38, 67.89, 55.54. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_3Na$: 289.0835, found: 289.0827; **ATR-FTIR (cm$^{-1}$)**: 2959, 2896, 1664, 1595, 1509, 1477, 1460, 1416, 1296, 1248, 1227, 1171, 1147, 1106, 1028, 998, 957, 917, 867.

**3-[1-(4-methyl phenyl)-meth-(E)-ylidene]-chroman-4-one (2f)**

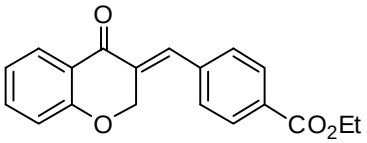



Following the general procedure, treatment of 2-[3-(4-methyl phenyl)-prop-2-ynyloxy]-benzaldehyde **1f** (0.250 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-(4-methoxy phenyl)-meth-(E)-ylidene]-chroman-4-one **2f** as a white solid (0.184 g, 74%).

**$R_f$** (pentane/EtOAc = 90/10): 0.50; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.85 (s, 1H, $CH_{olefin}$), 7.47 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.8 Hz, 1H, $H_{ar}$), 7.31-7.17 (m, 4H, $H_{ar}$), 7.06 (ddd, *J* = 8.1 Hz, 7.3 Hz, 1.1 Hz, 1H, $H_{ar}$), 6.96 (dd, *J* = 8.3

Hz, 0.7 Hz, 1H, $H_{ar}$), 5.35 (d, *J* = 1.9 Hz, 2H, $OCH_2$), 2.40 (s, 3H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 182.27, 161.11, 140.00, 137.63, 135.83, 131.61, 130.23, 130.12, 129.54, 127.96, 122.11, 121.91, 117.94, 67.77, 21.55. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{14}O_2Na$: 273.0886, found: 273.0880; **ATR-FTIR (cm$^{-1}$)**: 3032, 2853, 1665, 1595, 1510, 1465, 1412, 1307, 1266, 1216, 1184, 1147, 1113, 1019, 994, 957.

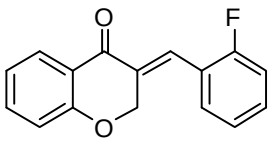
**3-[1-(4-Carboethoxy phenyl)-meth-(E)-ylidene]-chroman-4-one (2g)**




Following the general procedure, treatment of 2-[3-(4-carboethoxy phenyl)-prop-2-ynyloxy]-benzaldehyde **1g** (0.308 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-(4-Carboethoxy phenyl)-meth-(E)-ylidene]-chroman-4-one **2g** as a white solid (0.241 g, 78%).

**$R_f$** (pentane/EtOAc = 90/10): 0.34; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.3 Hz, 2H, $H_{ar}$), 8.03 (d, *J* = 7.8 Hz, 1H, $H_{ar}$), 7.88 (s, 1H, $CH_{olefin}$), 7.58-7.44 (m, 1H, $H_{ar}$), 7.37 (d, *J* = 8.2 Hz, 2H, $H_{ar}$), 7.09 (t, *J* = 7.5 Hz, 1H, $H_{ar}$), 6.98 (d, *J* = 8.3 Hz, 1H, $H_{ar}$), 5.33 (d, *J* = 1.6 Hz, 2H, $OCH_2$), 4.41 (q, *J* = 7.1 Hz, 2H, $OCH_2CH_3$), 1.42 (t, *J* = 7.1 Hz, 3H, $OCH_2CH_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 182.06, 166.05, 161.29, 138.73, 136.25, 132.60, 131.13, 129.99, 129.86, 128.13, 122.22, 122.00, 118.12, 67.57, 61.42, 14.45. **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{16}O_4Na$: 331.0941, found: 331.0927; **ATR-FTIR (cm$^{-1}$)**: 2985, 2908, 1708, 1673, 1606, 1463, 1413, 1369, 1326, 1313, 1268, 1218, 1181, 1145, 1100, 1012, 986, 955, 921, 869.

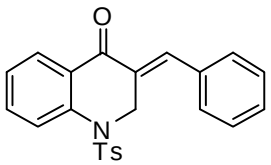
**3-[1-(2-Fluoro phenyl)-meth-(E)-ylidene]-chroman-4-one (2h)**




Following the general procedure, treatment of 2-[3-(2-fluoro phenyl)-prop-2-ynyloxy]-benzaldehyde **1g** (0.254 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[1-(2-fluoro phenyl)-meth-(E)-ylidene]-chroman-4-one **2g** as a white solid (0.203 g, 80%).

**$R_f$** (pentane/EtOAc = 90/10): 0.43; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.03 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.85 (s, 1H, $CH_{olefin}$), 7.58-7.36 (m, 2H, $H_{ar}$), 7.25-7.03 (m, 4H, $H_{ar}$), 6.97 (d, *J* = 8.3 Hz, 1H, $H_{ar}$), 5.19 (s, 2H, $OCH_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 182.02, 161.48, 160.63 (d, $J_{(C-F)}$ = 250.38 Hz), 136.11, 132.95, 131.54 (d, $J_{(C-F)}$ = 8.21 Hz), 131.03 (d, $J_{(C-F)}$ = 2.84 Hz), 130.43 (d, $J_{(C-F)}$ = 2.74 Hz), 128.12, 124.32 (d, $J_{(C-F)}$ = 3.68 Hz), 122.47 (d, $J_{(C-F)}$ = 14.45 Hz), 122.09, 122.05, 118.09, 116.21(d, $J_{(C-F)}$ = 21.40 Hz), 68.00. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{11}O_2FNa$: 277.0635, found: 277.0627; **ATR-FTIR (cm$^{-1}$)**: 3069, 3037, 2907, 1678, 1607, 1576, 1465, 1448, 1380, 1325, 1309, 1271, 1224, 1211, 1184, 1142, 1095, 1019, 989, 957, 916, 864.

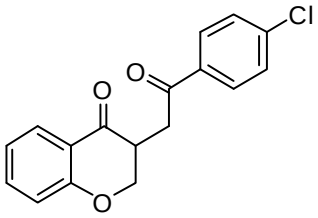
**3-[1-(2- Phenyl)-meth-(E)-ylidene]-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-quinolin-4-one (2i)**




Following the general procedure, treatment of 2 *N*-(3-phenyl prop-2-ynyloxy)-*N*-(2-formyl-phenyl)-4-methyl-benzene sulfonamide **1i** (0.135 g, 0.35 mmol) with thiazolium salt **3** (12.9 mg, 0.035 mmol) and $K_2CO_3$ (9.7 mg, 0.035 mmol) in THF (1 mL) at 70 °C for 4 h followed by column chromatography afforded 3-[1-(2-phenyl)-meth-(E)-ylidene]-1-(toluene-4-sulfonyl)-2,3-dihydro-1H quinolin-4-one **2i** as a white solid (0.85 g, 63%).

**$R_f$** (pentane/EtOAc = 70/30): 0.49; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.82 (dd, *J* = 8.2 Hz, 0.7 Hz, 1H, $H_{ar}$), 7.71-7.59 (m, 1H, $H_{ar}$), 7.56-7.43 (m, 4H, $H_{ar}$, $CH_{olefin}$), 7.42-7.35 (m, 1H, $H_{ar}$), 7.35-7.27 (m, 2H, $H_{ar}$), 7.08-6.91 (m, 4H, $H_{ar}$), 5.06 (d, *J* = 1.7 Hz, 2H, $NCH_2$), 2.34 (s, 3H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 182.68, 144.31, 141.41, 138.52, 134.47, 134.32, 134.23, 130.13, 130.01, 129.66, 129.61, 129.06, 128.95, 128.30, 127.54, 127.44, 127.27, 48.03, 21.71. **ESI-MS**: calculated $[M+Na]^+$ for $C_{23}H_{19}O_3NSNa$: 412.0978, found: 412.0983; **ATR-FTIR (cm$^{-1}$)**: 3052, 1671, 1599, 1458, 1403, 1350, 1299, 1249, 1201, 1153, 1090, 1056, 1031, 997, 960, 876.

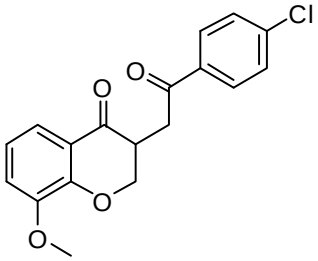
**3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6a)**



Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.160 g, 1 mmol) and 4-chloro benzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one **6a** as a white solid (0.213 g, 71%).

**$R_f$** (pentane/EtOAc = 80/20): 0.47; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.00-7.85 (m, 3H, $H_{ar}$), 7.54-7.41 (m, 3H, $H_{ar}$), 7.02 (dd, *J* = 16.8 Hz, 8.3 Hz, 2H, $H_{ar}$), 4.64 (dd, *J* = 11.0 Hz, 5.2 Hz, 1H, $OCH_2$), 4.31 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.72-3.53 (m, 2H, CHCO, $CH_2CO$), 2.97 (dd, *J* = 17.7 Hz, 7.7 Hz, 1H, $CH_2CO$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.95, 193.42, 161.94, 140.08, 136.22, 134.87, 129.70, 129.16, 127.51, 121.64, 120.69, 118.02, 70.47, 41.96, 34.42. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{13}ClO_3Na$: 323.0445, found: 323.0447; **ATR-FTIR (cm$^{-1}$)**: 2916, 2884, 1680, 1604, 1587, 1478, 1457, 1413, 1398, 1360, 1320, 1303, 1258, 1214, 1181, 1147, 1090, 1050, 1032, 1006, 995, 885.

**3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6b)**

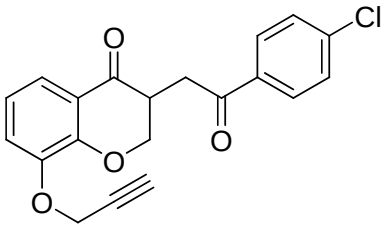


Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-8 methoxy-chroman-4-one **6b** as a white solid (0.317 g, 96%)

**$R_f$** (pentane/EtOAc = 80/20): 0.16; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.6 Hz, 2H, $H_{ar}$), 7.59-7.37 (m, 3H, $H_{ar}$), 7.10-7.02 (m, 1H, $H_{ar}$), 6.96 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.73 (dd, $J_1$ = 11.2 Hz, $J_2$ = 5.1 Hz, 1H, $OCH_2$), 4.39 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.60 (m, 2H, CHCO, $CH_2CO$), 3.01 (dd, *J* = 19.0 Hz, 8.8 Hz, 1H, $CH_2CO$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.74, 193.32, 151.81, 148.86, 139.99, 134.83, 129.65 129.10, 121.20, 118.58, 116.80, 70.94, 56.34, 41.78, 34.39. **ESI-MS**: calculated $[M+Na]^+$

for $C_{18}H_{15}ClO_4Na$: 353.0551, found: 353.0550; **ATR-FTIR ($cm^{-1}$)**: 2901, 2840, 1677, 1586, 1489, 1444, 1400, 1338, 1287, 1270, 1236, 1211, 1091, 1045, 986, 922, 880, 840, 817.

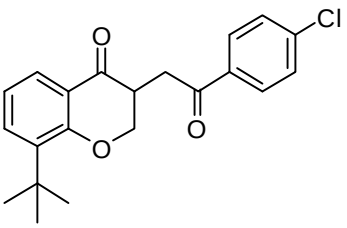
**3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-8-prop-2-ynyloxy-chroman-4-one (6c)**




Following the general procedure, treatment of 2,3-bis-prop-2-ynyloxy-benzaldehyde **4c** (0.214 g, 1.0 mmol, 1.0 eq.) and 4-chlorobenzaldehyde (141 mg, 1.0 mmol, 1.0 eq.) with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-8-prop-2-ynyloxy-chroman-4-one **6c** as a white solid (0.333 g, 94%).

**$R_f$** (pentane/EtOAc = 80/20): 0.47; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 7.91 (d, *J* = 8.7 Hz, 2H, $H_{ar}$), 7.54 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.5 Hz, 1H, $H_{ar}$), 7.42 (m, 2H, $H_{ar}$), 7.21 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.5 Hz, 1H, $H_{ar}$), 6.96 (t, *J* = 8.0 Hz, 1H, $H_{ar}$), 4.78 (d, *J* = 2.4 Hz, 2H, OC$H_2$CCH), 4.72 (dd, $J_1$ =11.2 Hz, $J_2$ = 5.2 Hz, 1H, OC$H_2$CH), 4.37 (t, *J* = 11.3 Hz, 1H, OC$H_2$CH), 3.60 (m, 2H, CHCO/$CH_2$CO), 3.00 (m, 1H, CHCO/$CH_2$CO), 2.55 (t, *J* = 2.4 Hz, 1H, CCH); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 196.01, 193.10, 152.33, 146.52, 139.96, 134.76, 129.62, 129.07, 121.59, 120.91, 119.97, 119.82, 77.94, 76.55, 70.85, 57.09, 41.73, 34.32; **ESI-MS:** calculated $[M+Na]^+$ for $C_{20}H_{15}ClO_4Na$: 377.0551, found: 377.0647; **ATR-FTIR ($cm^{-1}$):** 2925, 2894, 2360, 2129, 1952, 1695, 1679, 1604, 1585, 1489, 1448, 1402, 1373, 1361, 1339, 1298, 1256, 1235, 1210, 1193, 1177, 1128, 1093, 1063, 1040, 1011, 993, 955, 904.

**8-*tert*-Butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6d)**

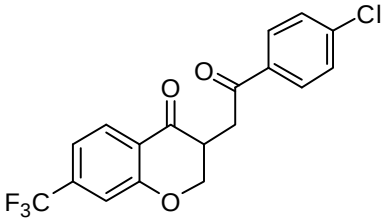



Following the general procedure, treatment of 3-*tert*-butyl-2-prop-2-ynyloxybenzaldehyde **4d** (0.216 g, 1.0 mmol, 1.0 eq.) and 4-chlorobenzaldehyde (141 mg, 1.0 mmol, 1.0 eq.) with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 8-

*tert*-butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one **6d** as a white solid (0.339 g, 95%) after flash column chromatography.

**$R_f$** (pentane/EtOAc = 97:3): 0.47; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.00 – 7.92 (m, 2H, $H_{ar}$), 7.81 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.7 Hz, 1H, $H_{ar}$), 7.51-7.44 (m, 3H, $H_{ar}$), 6.97 (t, $J$ = 7.7 Hz, 1H, $H_{ar}$), 4.70 (dd, $J_1$ = 11.0 Hz, $J_2$ = 5.3 Hz, 1H, $OCH_2$), 4.35 – 4.21 (m, 1H, $OCH_2$), 3.69 (dd, $J_1$ = 17.9 Hz, $J_2$ = 3.9 Hz, 1H, $CH_2CO$), 3.59 (m, 1H, CH), 2.97 (dd, $J_1$ = 17.9 Hz, $J_2$ = 8.1 Hz, 1H, $CH_2CO$), 1.39 (s, 9H, $C(CH_3)_3$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 196.19, 194.11, 161.15, 140.07, 139.15, 134.91, 133.18, 129.72, 129.17, 125.63, 121.49, 121.16, 70.00, 41.89, 35.06, 34.54, 29.74; **ESI-MS:** calculated $[M+Na]^+$ for $C_{21}H_{21}ClO_3Na$: 379.1071, found: 379.1068; **ATR-FTIR (cm$^{-1}$):** 2955, 2906, 1676, 1588, 1475, 1429, 1402, 1383, 1343, 1288, 1269, 1244, 1192, 1141, 1090, 1056, 1022, 992, 970, 915, 875, 830, 811.

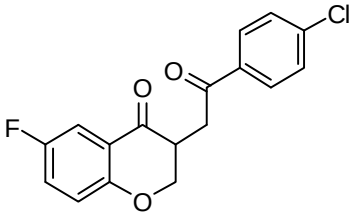
**3-(2-Oxo-2-phenyl-ethyl)-7-trifluoromethyl-chroman-4-one (6e)**




Following the general procedure, treatment of 2-prop-2-ynyloxy-4-trifluoromethyl-benzaldehyde **4e** (0.228 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-(2-oxo-2-phenyl-ethyl)-7-trifluoromethyl-chroman-4-one **6e** as a white solid (0.267 g, 72%)

**$R_f$** (pentane/EtOAc = 80/20): 0.54; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.08-7.81 (m, 3H, $H_{ar}$), 7.54-7.36 (m, 2H, $H_{ar}$), 7.25 (d, $J$ = 7.0 Hz, 2H, $H_{ar}$), 4.78-4.59 (m, 1H, $OCH_2$), 4.36 (t, $J$ = 11.6 Hz, 1H, $OCH_2$), 3.64 (m, 2H, $CH_2CO$, CHCO), 3.01 (dd, $J$ = 18.9 Hz, 8.4 Hz, 1H, $CH_2CO$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.50, 192.55, 161.69, 140.23, 134.68, 129.67, 129.20, 128.48, 125.02, 122.80, 121.40, 117.96, 115.72, 70.69, 41.89, 34.20; **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{12}ClF_3O_3Na$: 391.0319, found: 391.0317; **ATR-FTIR (cm$^{-1}$)**: 3078, 2937, 1682, 1626, 1589, 1495, 1470, 1432, 1333, 1312, 1292, 1257, 1220, 1196, 1152, 1123, 1091, 1073, 1048, 1024, 990, 943, 887, 834.

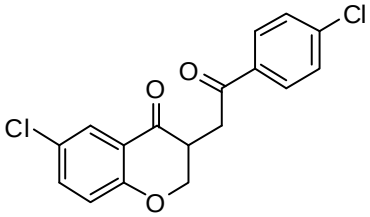
**3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-6-fluoro-chroman-4-one (6f)**



Following the general procedure, treatment of 5-fluoro-2-prop-2-ynyloxy-benzaldehyde **4f** (0.178 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-6-fluoro-chroman-4-one **6f** as a white solid (0.281g, 88%).

**$R_f$** (pentane/EtOAc = 80/20): 0.38; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.03-7.81 (m, 2H, $H_{ar}$), 7.54 (dd, *J* = 8.3 Hz, 3.2 Hz, 1H, $H_{ar}$), 7.50-7.40 (m, 2H, $H_{ar}$), 7.27-7.17 (m, 1H, $H_{ar}$), 6.97 (dd, *J* = 9.1 Hz, 4.2 Hz, 1H, $H_{ar}$), 4.63 (dd, *J* = 11.1 Hz, 5.2 Hz, 1H, $OCH_2$), 4.30 (t, *J* = 11.4 Hz, 1H, $OCH_2$), 3.74-3.48 (m, 2H, $CH_2CO$, CHCO), 3.00 (dd, *J* = 17.8 Hz, 7.6 Hz, 1H, $CH_2CO$); **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 195.73, 192.73, 158.23 (d, $J_{(C-F)}$ = 1.76 Hz), 157.42 (d, $J_{(C-F)}$ = 242.48 Hz), 140.19, 134.79, 129.69, 129.21, 123.77 (d, $J_{(C-F)}$ = 25.06 Hz), 121. 12 (d, $J_{(C-F)}$ = 6.66 Hz), 119.72 (d, $J_{(C-F)}$ = 7.54 Hz), 112.44 (d, $J_{(C-F)}$ = 23.45 Hz), 70.65, 41.83, 34.37; **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{12}ClFO_3Na$: 341.0351, found: 341.0351; **ATR-FTIR ($cm^{-1}$)**: 2890, 1674, 1619, 1587, 1484, 1437, 1400, 1368, 1280, 1229, 1193, 1150, 1092, 1046, 1015, 994, 901, 821.

**6-Chloro-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6g)**

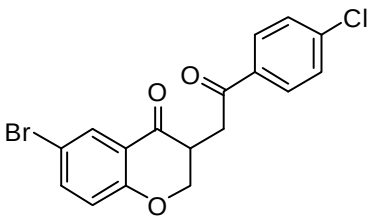


Following the general procedure, treatment of 5-chloro-2-prop-2-ynyloxy-benzaldehyde **4g** (0.195 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 6-chloro-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one **6g** as a white solid (0.285 g, 85%).

**$R_f$** (pentane/EtOAc = 80/20): 0.51; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.97-7.88 (m, 2H, $H_{ar}$), 7.83 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 7.50-7.36 (m, 3H, $H_{ar}$), 6.95 (d, *J* = 8.8 Hz, 1H, $H_{ar}$), 4.64 (dd, *J* = 11.1 Hz, 5.3 Hz, 1H, $OCH_2$), 4.30 (t, *J* = 11.4 Hz, 1H, $OCH_2$), 3.75-3.47 (m, 2H, $CH_2CO$, CHCO), 2.99 (dd, *J* = 17.9 Hz, 7.7 Hz, 1H, $CH_2CO$); **$^{13}$C NMR (75 MHz,**

**$CDCl_3$)** δ 195.65, 192.27, 160.41, 140.19, 136.00, 134.81, 129.68, 129.20, 127.19, 126.80, 121.50, 119.77, 70.60, 41.77, 34.33; **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{12}Cl_2O_3Na$: 357.0056, found: 357.0070; **ATR-FTIR ($cm^{-1}$)**: 2914, 2891, 1671, 1604, 1587, 1478, 1461, 1420, 1400, 1367, 1308, 1278, 1258, 1232, 1206, 1180, 1134, 1090, 1048, 1017, 990, 906, 881.

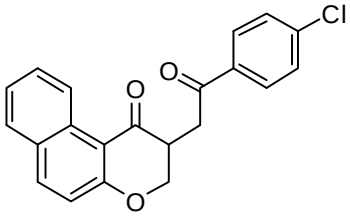
**6-Bromo-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6h)**




Following the general procedure, treatment of 5-bromo-2-prop-2-ynyloxy-benzaldehyde **4h** (0.239 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 6-bromo-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one **6h** as a white solid (0.281 g, 74%).

**$R_f$** (pentane/EtOAc = 80/20): 0.49; **$^1$H NMR (300 MHz, CDCl3)** δ 7.98 (d, *J* = 2.5 Hz, 1H, $H_{ar}$), 7.96-7.89 (m, 2H, $H_{ar}$), 7.55 (dd, *J* = 8.8 Hz, 2.5 Hz, 1H, $H_{ar}$), 7.48 – 7.41 (m, 2H, $H_{ar}$), 6.89 (d, *J* = 8.8 Hz, 1H, $H_{ar}$), 4.64 (dd, *J* = 11.1 Hz, 5.3 Hz, 1H, $OCH_2$), 4.29 (t, *J* = 11.5 Hz, 1H, $OCH_2$), 3.69-3.50 (m, 2H, $CH_2CO$, CHCO), 2.99 (dd, *J* = 17.9 Hz, 7.7 Hz, 1H, $CH_2CO$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.62, 192.17, 160.82, 140.17, 138.77, 134.71, 129.77, 129.18, 121.94, 120.12, 114.28, 70.52, 41.65, 34.29. **ESI-MS**: calculated $[M+Na]^+$ for $C_{17}H_{12}BrClO_3Na$: 402.9530, found: 402.9529; **ATR-FTIR ($cm^{-1}$)**: 2898, 1687, 1673, 1588, 1476, 1460, 1417, 1362, 1280, 1204, 1180, 1137, 1092, 1049, 1018, 991, 904, 839.

**2-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-2,3-dihydro-benzo[*f*]chromen-1-one (6i)**

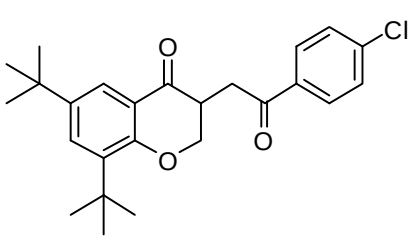



Following the general procedure, treatment of 2-prop-2-ynyloxy-naphthalene-1-carbaldehyde **4i** (0.210 g, 1 mmol) and 4-chlorobenzaldehyde (0.141 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by

column chromatography afforded 2-[2-(4-chloro-phenyl)-2-oxo-ethyl]-2,3-dihydro-benzo[*f*] chromen-1-one **6i** as a white solid (0.326 g, 93%).

**$R_f$** (pentane/EtOAc = 80/20): 0.50; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 9.41 (d, *J* = 8.7 Hz, 1H, $H_{ar}$), 7.95 (dd, *J* = 12.8 Hz, 6.0 Hz, 3H, $H_{ar}$), 7.75 (d, *J* = 8.0 Hz, 1H, $H_{ar}$), 7.62 (ddd, *J* = 8.6 Hz, 7.0 Hz, 1.4 Hz, 1H, $H_{ar}$), 7.52-7.37 (m, 3H, $H_{ar}$), 7.10 (d, *J* = 9.0 Hz, 1H, $H_{ar}$), 4.72 (dd, *J* = 11.0 Hz, 5.1 Hz, 1H, $OCH_2$), 4.42 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.82-3.57 (m, 2H, $CH_2CO$, CHCO), 3.11-2.87 (m, 1H, $CH_2CO$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 196.27, 194.28, 163.92, 139.98, 137.73, 134.96, 131.70, 129.75, 129.23, 128.57, 125.87, 125.02, 118.80, 112.25, 70.34, 42.53, 34.78. **ESI-MS**: calculated $[M+Na]^+$ for $C_{21}H_{15}ClO_3Na$: 373.0602, found: 373.0616; **ATR-FTIR ($cm^{-1}$)**: 2908, 2878, 1665, 1618, 1586, 1567, 1510, 1471, 1434, 1401, 1363, 1342, 1277, 1233, 1203, 1167, 1138, 1090, 1054, 1026, 986, 897, 876.

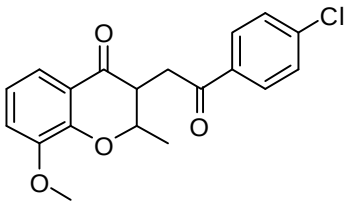
**6,8-Di-*tert*-butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6j)**




Following the general procedure, treatment of 3,5-di-*tert*-butyl-2-prop-2-ynyloxybenzaldehyde **4j** (0.272 g, 1.0 mmol, 1.0 eq.) and 4-chlorobenzaldehyde (141 mg, 1.0 mmol, 1.0 eq.) with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 6,8-di-*tert*-butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one **6j** as a white solid (0.374 g, 91%) after flash column chromatography.

**$R_f$** (pentane/EtOAc = 90/10): 0.83; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 7.97-7.94 (m, 2H, $H_{ar}$), 7.81 (d, *J* = 2.6 Hz, 1H, $H_{ar}$), 7.56 (d, *J* = 2.6 Hz, 1H), 7.47-7.44 (m, 2H, $H_{ar}$), 4.60 (dd, $J_1$ = 10.9 Hz, $J_2$ = 5.2 Hz, 1H, $OCH_2$), 4.19 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.60 (dd, $J_1$ = 17.7 Hz, $J_2$ = 3.9 Hz, 1H, $CH_2CO$), 3.53-3.43 (m, 1H, CHCO), 2.90 (dd, $J_1$ = 17.7 Hz, $J_2$ = 8.1 Hz, 1H, $CH_2CO$), 1.40 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 196.28, 194.40, 159.11, 143.52, 139.98, 138.47, 134.96, 130.93, 129.71, 129.13, 121.46, 120.69, 69.94, 42.01, 35.21, 34.61, 31.43, 29.80; **ESI-MS:** calculated $[M+Na]^+$ for $C_{25}H_{29}ClO_3Na$: 435.1697, found: 435.1704; **ATR-FTIR ($cm^{-1}$):** 2953, 2360, 1679, 1600, 1587, 1478, 1443, 1400, 1361, 1327, 1286, 1272, 1248, 1220, 1196, 1169, 1107, 1089, 1006.

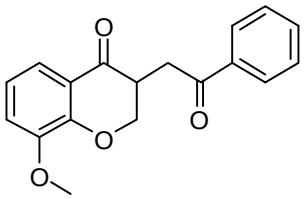
**4-(4-Chloro-phenyl)-1-(2-hydroxy-3-methoxy-phenyl)-2-isopropyl-butane-1,4-dione (6k)**



Following the general procedure, treatment of 3-methoxy-2-(1-methyl-prop-2-ynyloxy)-benzaldehyde **4k** (0.102 g, 0.5 mmol, 1 eq.) and 4-chlorobenzaldehyde (71 mg, 0.5 mmol, 1 eq.) with thiazolium salt **3** (9.3 mg, 0.025 mmol, 0.05 eq.) and potassium carbonate (7.9 mg, 0.05 mmol, 0.1 eq.) gave 4-(4-chloro-phenyl)-1-(2-hydroxy-3-methoxy-phenyl)-2-isopropyl-butane-1,4-dione **6k** as a white solid (0.121 g, 70%) after flash column chromatography, as a mixture of diastereomers in a 3:1, (*trans: cis*) ratio. The major *trans* diastereomer was isolated by recrystallization from $CH_2Cl_2$/pentane.

**$R_f$** (pentane/EtOAc = 80:20): 0.36; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.94 (d, $J$ = 8.5 Hz, 2H, $H_{ar}$), 7.55 – 7.40 (m, 3H, $H_{ar}$), 7.07 (m, 1H, $H_{ar}$), 6.96 (t, $J$ = 7.9 Hz, 1H, $H_{ar}$), 4.72 (dq, $J_1$ = 12.5 Hz, $J_2$ = 6.3 Hz, 1H, OCH), 3.91 (s, 3H, $OCH_3$), 3.51 (dd, $J_1$ = 17.5 Hz, $J_2$ = 4.8 Hz, 1H, $CH_2$), 3.44 – 3.31 (m, 1H, CHCO), 3.19 (dd, $J_1$ = 17.5 Hz, $J_2$ = 5.6 Hz, 1H, $CH_2$), 1.56 (d, $J$ = 6.3 Hz, 3H, CHC$H_3$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 196.12, 193.63, 151.28, 148.89, 139.93, 135.07, 129.72, 129.13, 121.02, 120.997, 118.62, 116.91, 77.95, 56.38, 48.20, 34.64, 19.74; **ESI-MS:** calculated $[M+Na]^+$ for $C_{19}H_{17}ClO_4Na$: 367.0708, found: 367.0708; **ATR-FTIR (cm$^{-1}$):** 2936, 2362, 1682, 1585, 1486, 1443, 1400, 1342, 1301, 1259, 1211, 1185, 1068, 1002, 980, 919.

**8-Methoxy-3-(2-oxo-2-phenyl-ethyl)-chroman-4-one (6l)**

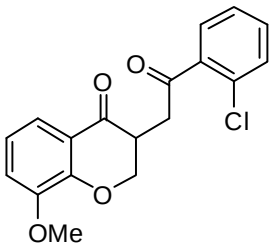


Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1.0 mmol, 1.0 eq.) and benzaldehyde (106 mg, 1.0 mmol, 1.0 eq.) with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 8-methoxy-3-(2-oxo-2-phenyl-ethyl)-chroman-4-one **6l** as a white solid (0.268 g, 90%).

**$R_f$** (pentane/EtOAc = 80/20): 0.33; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 7.99-7.95 (m, 2H, $H_{ar}$), 7.57-7.45 (m, 4H, $H_{ar}$), 7.06-6.93 (m, 2H, $H_{ar}$), 4.74 (dd, $J_1$ = 11.0 Hz, $J_2$ = 5.1 Hz,

1H, $OCH_2$), 4.39 (t, $J$ = 11.2 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.65 (m, 2H, CH + $CH_2CO$ ), 3.05 (dd, $J_1$ = 17.8 Hz, $J_2$ = 7.8 Hz, 1H, $CH_2CO$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 196.88, 193.43, 151.80, 148.83, 136.47, 133.52, 128.75, 128.20, 121.30, 121.04, 118.57, 116.72, 70.97, 56.31, 41.75, 34.41; **ESI-MS:** calculated $[M+Na]^+$ for $C_{18}H_{16}O_4Na$: 319.0941, found: 319.0936; **ATR-FTIR (cm$^{-1}$):** 2399, 2283, 1680, 1601, 1582, 1489, 1449, 1346, 1289, 1270, 1247, 1209, 1046, 1012, 989, 964.

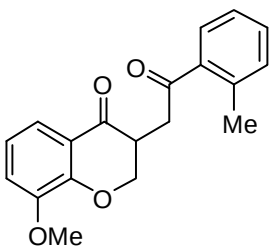
**3-[2-(2-Chloro-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6m)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 2-chlorobenzaldehyde (0.141 g, 0.113 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(2-chloro-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one **6m** as a white solid (0.218 g, 66%).

**$R_f$** (pentane/EtOAc = 80/20): 0.17; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.63-7.56 (m, 1H, $H_{ar}$), 7.45 (dd, $J$ = 7.9 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.40-7.29 (m, 3H, $H_{ar}$), 7.04 (dd, $J$ = 8.0 Hz, 1.3 Hz, 1H, $H_{ar}$), 6.93 (t, $J$ = 7.9 Hz, 1H, $H_{ar}$), 4.73 (dd, $J$ = 11.1 Hz, 5.3 Hz, 1H, $OCH_2$), 4.45-4.32 (m, 1H, $OCH_2$), 3.88 (s, 3H, $OCH_3$), 3.70-3.55 (m, 1H, CHCO), 3.48 (dd, $J$ = 17.9 Hz, 5.3 Hz, 1H, $CH_2CO$), 3.02 (dd, $J$ = 17.9 Hz, 7.1 Hz, 1H, $CH_2CO$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 200.13, 193.01, 151.73, 148.78, 138.79, 132.08, 130.85, 130.57, 129.45, 127.11, 121.10, 118.46, 116.75, 70.82, 56.27, 42.38, 38.70. **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{15}ClO_4Na$: 353.0551, found: 353.0547; **ATR-FTIR (cm$^{-1}$)**: 2940, 2909, 1685, 1604, 1584, 1490, 1438, 1385, 1344, 1290, 1267, 1212, 1188, 1130, 1061, 1041, 1016, 991, 922.

**8-Methoxy-3-(2-oxo-2-*o*-tolyl-ethyl)-chroman-4-one (6n)**

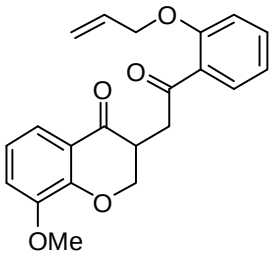



Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and *o*-tolualdehyde (0.120 g, 0.12 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2

mL) at 70 °C for 2 h followed by column chromatography afforded 8-methoxy-3-(2-oxo-2-*o*-tolyl-ethyl)-chroman-4-one **6n** as a white solid (0.208 g, 67%).

**$R_f$** (pentane/EtOAc = 80/20): 0.25; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.78-7.66 (m, 1H, $H_{ar}$), 7.49 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.43-7.33 (m, 1H, $H_{ar}$), 7.26 (t, *J* = 6.5 Hz, 2H, $H_{ar}$), 7.06 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H, $H_{ar}$), 6.96 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.72 (dd, *J* = 11.1 Hz, 5.2 Hz, 1H, $OCH_2$), 4.42 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.75-3.36 (m, 2H, $CH_2CO$, CHCO), 2.98 (dd, *J* = 17.7 Hz, 7.4 Hz, 1H, $CH_2CO$), 2.52 (s, 3H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 200.56, 193.39, 151.73, 148.78, 138.44, 137.27, 132.09, 131.68, 128.64, 125.79, 121.27, 121.00, 118.50, 116.68, 70.93, 56.26, 42.12, 37.13, 21.42. **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{18}O_4Na$ :333.1097, found: 333.1090; **ATR-FTIR ($cm^{-1}$)**: 2966, 2841, 1678, 1602, 1580, 1488, 1442, 1404, 1381, 1351, 1289, 1269, 1247, 1206, 1138, 1077, 1060, 1045, 1013, 982, 958, 921.

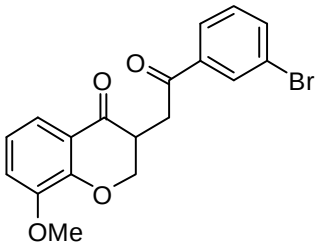
**3-[2-(2-Allyloxy-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6o)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 2-allyloxybenzaldehyde (0.162 g, 0.15 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(2-allyloxy-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one **6o** as a white solid (0.229 g, 65%).

**$R_f$** (pentane/EtOAc = 80/20): 0.20; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.76 (dd, *J* = 7.7 Hz, 1.8 Hz, 1H, Har), 7.55-7.32 (m, 2H, Har), 7.10-6.90 (m, 4H, Har), 6.05 (ddt, *J* = 17.2 Hz, 10.6 Hz, 5.3 Hz, 1H, C*H*=$CH_2$), 5.48-5.24 (m, 2H, CH=C$H_2$), 4.76-4.68 (m, 1H, $OCH_2$), 4.64 (dt, *J* = 5.3 Hz, 1.4 Hz, 2H, $OCH_2$), 4.38 (t, *J* = 11.4 Hz, 1H, $OCH_2$), 3.91 (s, 3H, $OCH_3$), 3.73-3.50 (m, 2H, $CH_2CO$, CHCO), 3.14 (dd, *J* = 17.9 Hz, 7.6 Hz, 1H, CHCO); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 199.17, 193.62, 157.81, 151.83, 148.84, 133.87, 132.56, 130.74, 127.96, 121.46, 121.01, 118.60, 116.57, 112.88, 71.17, 69.56, 56.34, 42.31, 39.81; **ESI-MS**: calculated $[M+Na]^+$ for $C_{21}H_{20}O_5Na$: 375.1203, found: 375.1206; **ATR-FTIR ($cm^{-1}$)**: 3005, 1688, 1654, 1593, 1486, 1450, 1392, 1360, 1295, 1265, 1242, 1215, 1175, 1111, 1080, 1056, 1012, 994, 955, 930, 870.

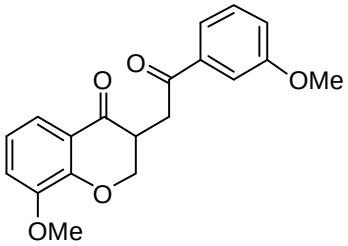
**3-[2-(3-Bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6p)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 3-bromobenzaldehyde (0.185 g, 0.12 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(3-bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one **6p** as a white solid (0.308 g, 82%).

**$R_f$** (pentane/EtOAc = 80/20): 0.21; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.10 (t, *J* = 1.7 Hz, 1H, $H_{ar}$), 7.95-7.84 (m, 1H, $H_{ar}$), 7.69 (ddd, *J* = 7.9 Hz, 1.9 Hz, 1.0 Hz, 1H, $H_{ar}$), 7.48 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.34 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 7.06 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H, $H_{ar}$), 6.96 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.73 (dd, *J* = 11.2 Hz, 5.0 Hz, 1H, $OCH_2$), 4.38 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.70-3.51 (m, 2H, $CH_2CO$, CHCO), 3.00 (dd, *J* = 19.0 Hz, 8.7 Hz, 1H, CHCO). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.62, 193.22, 151.78, 148.85, 138.20, 136.36, 131.30, 130.38, 126.75, 123.13, 121.18, 118.58, 116.81, 70.89, 56.34, 41.74, 34.49. **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{15}BrO_4Na$: 397.0046, found: 397.0046; **ATR-FTIR (cm$^{-1}$)**: 2969, 2942, 1683, 1584, 1473, 1412, 1368, 1256, 1211, 1173, 1088, 1057, 991, 922, 889, 856.

**8-Methoxy-3-[2-(3-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one (6q)**

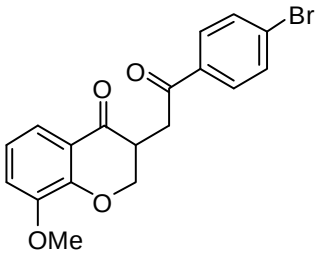



Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 3-methoxybenzaldehyde (0.136 g, 0.12 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 8-methoxy-3-[2-(3-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one **6q** as a white solid (0.279 g, 86%).

**$R_f$** (pentane/EtOAc = 80/20): 0.14; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.62-7.45 (m, 3H, $H_{ar}$), 7.36 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 7.16-7.02 (m, 2H, $H_{ar}$), 6.96 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.73 (dd, *J* = 11.1 Hz, 5.1 Hz, 1H, $OCH_2$), 4.39 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.84 (s, 3H, $OCH_3$), 3.66-3.58 (m, 2H, $CH_2CO$, CHCO), 3.05 (dd, *J* = 17.8 Hz,

7.8 Hz, 1H, CHCO). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 196.74, 193.43, 159.93, 151.81, 148.84, 137.82, 129.76, 121.06, 120.15, 118.58, 116.72, 112.26, 70.98, 56.32, 55.54, 41.80, 34.56. **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{18}O_5Na$: 349.1046, found: 349.1056; **ATR-FTIR ($cm^{-1}$)**: 2962, 2910, 1678, 1583, 1490, 1434, 1359, 1305, 1290, 1261, 1221, 1182, 1165, 1134, 1083, 1044, 1015, 993, 957, 880.

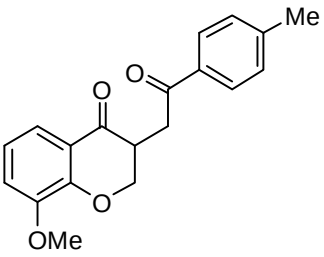
**3-[2-(4-Bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6r)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 4-bromobenzaldehyde (0.185 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-(4-bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one **6r** as a white solid (0.348 g, 93%).

**$R_f$** (pentane/EtOAc = 80/20): 0.23; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.89-7.78 (m, 2H, $H_{ar}$), 7.67-7.52 (m, 2H, $H_{ar}$), 7.50-7.44 (m, 1H, $H_{ar}$), 7.05 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.00-6.84 (m, 1H, $H_{ar}$), 4.73 (dd, *J* = 11.2 Hz, 5.1 Hz, 1H, $OCH_2$), 4.38 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.90 (s, 3H, $OCH_3$), 3.59 (m, 2H, $CH_2CO$, CHCO), 3.00 (dd, *J* = 19.0 Hz, 8.7 Hz, 1H, CHCO). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 195.92, 193.28, 151.78, 148.83, 135.21, 132.07, 129.72, 128.72, 121.17, 118.55, 116.78, 70.90, 56.32, 41.75, 34.34. **ESI-MS**: calculated $[M+Na]^+$ for $C_{18}H_{15}BrO_4Na$: 397.0046, found: 397.0046; **ATR-FTIR ($cm^{-1}$)**: 2964, 2898, 1676, 1605, 1583, 1489, 1443, 1388, 1337, 1291, 1272, 1255, 1237, 1210, 1071, 1047, 1003, 984, 923, 903, 879.

**8-Methoxy-3-(2-oxo-2-*p*-tolyl-ethyl)-chroman-4-one (6s)**

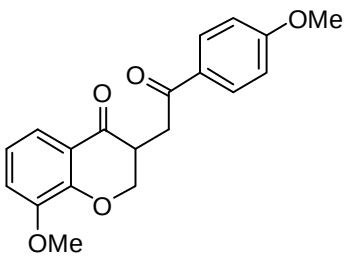



Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 4-tolualdehyde (0.120 g, 0.118 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column

chromatography afforded 8-methoxy-3-(2-oxo-2-*p*-tolyl-ethyl)-chroman-4-one **6s** as a white solid (0.278 g, 90%).

**$R_f$** (pentane/EtOAc = 80/20): 0.21; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.2 Hz, 2H, $H_{ar}$), 7.51 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.33-7.20 (m, 2H, $H_{ar}$), 7.07 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H, $H_{ar}$), 6.97 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.74 (dd, *J* = 11.1 Hz, 5.0 Hz, 1H, $OCH_2$), 4.39 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.91 (s, 3H, $OCH_3$), 3.63 (dt, *J* = 8.8 Hz, 4.5 Hz, 2H, $CH_2CO$, CHCO), 3.04 (dd, *J* = 17.7 Hz, 7.9 Hz, 1H, CHCO), 2.41 (s, 3H, $CH_3$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 196.55, 193.62, 151.88, 148.89, 144.43, 134.07, 129.48, 128.37, 121.39, 121.06, 118.65, 116.74, 71.08, 56.37, 41.82, 34.35, 21.81. **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{18}O_4Na$: 333.1097, found: 333.1101; **ATR-FTIR ($cm^{-1}$)**: 2914, 2892, 1670, 1604, 1580, 1490, 1439, 1408, 1378, 1336, 1283, 1264, 1209, 1180, 1081, 1059, 987, 923.

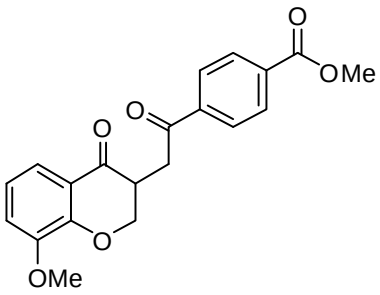
**8-Methoxy-3-[2-(4-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one (6t)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 4-methoxybenzaldehyde (0.136 g, 0.12 mL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 8-methoxy-3-[2-(4-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one **6t** as a white solid (0.288 g, 88%).

**$R_f$** (pentane/EtOAc = 60/40): 0.22; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.04-7.91 (m, 2H, $H_{ar}$), 7.51 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H, $H_{ar}$), 7.06 (dd, *J* = 8.0, 1.4 Hz, 1H, $H_{ar}$), 7.00-6.88 (m, 3H, $H_{ar}$), 4.74 (dd, *J* = 11.2 Hz, 5.1 Hz, 1H, $OCH_2$), 4.39 (t, *J* = 11.2 Hz, 1H, $OCH_2$), 3.91 (s, 3H, $OCH_3$), 3.87 (s, 3H, $OCH_3$), 3.66-3.52 (m, 2H, $CH_2CO$, CHCO), 3.02 (dd, *J* = 18.5 Hz, 8.9 Hz, 1H, CHCO). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 195.39, 193.67, 163.84, 151.89, 148.89, 130.54, 129.63, 121.40, 121.04, 118.64, 116.74, 113.92, 71.11, 56.36, 55.61, 41.87, 34.09; **ESI-MS**: calculated $[M+Na]^+$ for $C_{19}H_{18}O_5Na$: 349.1046, found: 349.1051; **ATR-FTIR ($cm^{-1}$)**: 2971, 2912, 1688, 1669, 1595, 1511, 1489, 1465, 1443, 1419, 1388, 1365, 1345, 1305, 1287, 1265, 1240, 1214, 1184, 1168, 1071, 1043, 1025, 1004, 986, 969, 833.

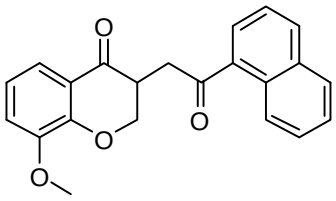
**4-[2-(8-Methoxy-4-oxo-chroman-3-yl)-acetyl]-benzoic acid methyl ester (6u)**



Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 4-formyl methyl benzoate (0.164 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 4-[2-(8-methoxy-4-oxo-chroman-3-yl)-acetyl]-benzoic acid methyl ester **6u** as a white solid (0.272 g, 77%).

**$R_f$** (pentane/EtOAc = 60/40): 0.18; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.17-8.09 (m, 2H, $H_{ar}$), 8.07-8.00 (m, 2H, $H_{ar}$), 7.50 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H, $H_{ar}$), 7.15-6.90 (m, 2H, $H_{ar}$), 4.75 (dd, *J* = 11.1 Hz, 5.0 Hz, 1H, $OCH_2$), 4.41 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.95 (s, 3H, $OCH_3$), 3.91 (s, 3H, $OCH_3$), 3.76-3.53 (m, 2H, $CH_2CO$, CHCO), 3.20-2.91 (m, 1H, CHCO); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 196.51, 193.28, 166.24, 151.81, 148.87, 139.69, 134.26, 130.01, 128.17, 121.22, 118.61, 116.82, 70.92, 56.36, 52.62, 41.79, 34.80; **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{18}O_6Na$: 377.0996, found: 377.0999; **ATR-FTIR ($cm^{-1}$)**: 3014, 2954, 1713, 1682, 1605, 1582, 1489, 1442, 1404, 1388, 1346, 1284, 1266, 1209, 1186, 1110, 1088, 1049, 1005, 992, 966.

**8-Methoxy-3-(2-naphthalen-1-yl-2-oxo-ethyl)-chroman-4-one (6v)**

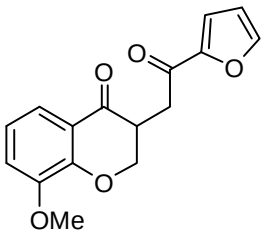


Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxybenzaldehyde **4b** (0.190 g, 1.0 mmol, 1.0 eq.) and naphthalene-1-carbaldehyde (156 mg, 1.0 mmol, 1.0 eq.) with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 8-methoxy-3-(2-naphthalen-1-yl-2-oxo-ethyl)-chroman-4-one **6v** as a white oil (0.298 g, 86%) after flash column chromatography.

**$R_f$** (pentane/EtOAc = 80/20): 0.24; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 8.63 (d, *J* = 8.5 Hz, 1H, $H_{ar}$), 7.95 (t, *J* = 7.7 Hz, 2H, $H_{ar}$), 7.84 (d, *J* = 7.5 Hz, 1H, $H_{ar}$), 7.53 (m, 4H, $H_{ar}$), 7.03 (d, *J* = 6.5 Hz, 1H, $H_{ar}$), 6.94 (t, *J* = 7.9 Hz, 1H, $H_{ar}$), 4.82 – 4.73 (m, 1H, $OCH_2$), 4.45 (t, *J* = 11.3 Hz, 1H, $OCH_2$), 3.88 (s, 3H, $OCH_3$), 3.64 (m, 2H, CH + $CH_2CO$), 3.09

(dd, $J_1$ = 17.5 Hz, $J_2$ = 7.2 Hz, 1H, $CH_2CO$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 200.91, 193.45, 151.82, 148.86, 135.37, 134.05, 133.15, 130.20, 128.54, 128.24, 127.97, 126.66, 125.83, 124.45, 121.35, 121.12, 118.61, 116.76, 71.05, 56.35, 42.38, 37.78; **ESI-MS:** calculated $[M+Na]^+$ for $C_{22}H_{18}O_4Na$: 369.1097, found: 369.1105; **ATR-FTIR (cm$^{-1}$):** 2908, 2838, 2360, 1682, 1604, 1583, 1490, 1442, 1384, 1343, 1290, 1266, 1213, 1187, 1173, 1064, 1041, 1017, 971.

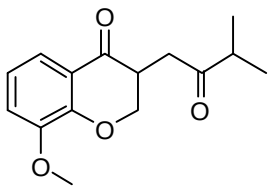
**3-(2-Furan-2-yl-2-oxo-ethyl)-8-methoxy-chroman-4-one (6w)**




Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol) and 2-furaldehyde (0.096 g, 83 µL, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-(2-furan-2-yl-2-oxo-ethyl)-8-methoxy-chroman-4-one **6w** as a white solid (0.244 g, 85%).

**$R_f$** (pentane/EtOAc = 60/40): 0.14; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.57 (s, 1H, $H_{ar}$), 7.46 (dd, $J$ = 7.9 Hz, 1.2 Hz, 1H, $H_{ar}$), 7.22 (d, $J$ = 3.6 Hz, 1H, $H_{ar}$), 7.10-7.00 (m, 1H, $H_{ar}$), 6.93 (t, $J$ = 7.9 Hz, 1H, $H_{ar}$), 6.52 (dd, $J$ = 3.4 Hz, 1.5 Hz, 1H, $H_{ar}$), 4.71 (dd, $J$ = 11.1 Hz, 5.1 Hz, 1H, $OCH_2$), 4.36 (t, $J$ = 11.3 Hz, 1H, $OCH_2$), 3.88 (s, 3H, $OCH_3$), 3.72-3.31 (m, 2H, $CH_2CO$, CHCO), 2.89 (dd, $J$ = 17.5 Hz, 7.7 Hz, 1H, CHCO); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 193.06, 186.05, 152.28, 151.73, 148.78, 146.66, 121.10, 118.50, 117.52, 116.71, 112.47, 70.88, 56.28, 41.44, 34.04; **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{14}O_5Na$: 309.0733, found: 309.0742; **ATR-FTIR (cm$^{-1}$)**: 2941, 2913, 1672, 1604, 1585, 1569, 1465, 1385, 1268, 1214, 1179, 1080, 1052, 1027, 989, 912, 883, 837.

**8-Methoxy-3-(3-methyl-2-oxo-butyl)-2,3,4a,8a-tetrahydro-chromen-4-one (6x)**

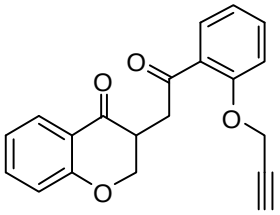



Following the general procedure, treatment of 3-methoxy-2-prop-2-ynyloxybenzaldehyde **4b** (0.190 g, 1.0 mmol, 1.0 eq.) and 2-methyl-propionaldehyde (0.079 mL, 2.0 mmol, 2.0 eq.), with thiazolium salt **3** (18.6 mg, 0.05 mmol, 0.05 eq.) and potassium carbonate (13.8 mg, 0.1 mmol, 0.1 eq.) gave 8-

methoxy-3-(3-methyl-2-oxo-butyl)-2,3,4a,8a-tetrahydro-chromen-4-one **6x** as a white solid (0.176 g, 68%) after flash column chromatography.

**$R_f$** (pentane/EtOAc = 80:20): 0.47; **$^1$H NMR (300 MHz, $CDCl_3$)** δ = 7.43 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.5 Hz, 1H, $H_{ar}$), 7.02 (dd, $J_1$ = 7.9 Hz, $J_2$ = 1.5 Hz, 1H, $H_{ar}$), 6.92 (t, $J$ = 7.9 Hz, 1H, $H_{ar}$), 4.60 (dd, $J_1$ = 11.1 Hz, $J_2$ = 5.2 Hz, 1H, $OCH_2$), 4.29 (t, $J$ = 11.3 Hz, 1H, $OCH_2$), 3.88 (s, 3H, $OCH_3$), 3.44–3.36 (m, 1H, C*H*$CH_2$), 3.00 (dd, $J_1$ = 18.0 Hz, $J_2$ = 4.7 Hz, 1H, CHC*H*$_2$), 2.71–2.62 (m, 1H, C*H*$CH_3$), 2.53 (dd, $J_1$ = 18.0 Hz, $J_2$ = 7.5 Hz, 1H, CHC*H*$_2$), 1.12 (dd, $J_1$ = 6.9 Hz, $J_2$ = 4.1 Hz, 6H, CHC*H*$_3$); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ = 211.47, 193.47, 151.71, 148.77, 121.24, 120.99, 118.46, 116.64, 70.89, 56.27, 41.64, 41.19, 35.90, 18.31; **ESI-MS:** calculated $[M+Na]^+$ for $C_{15}H_{18}O_4Na$: 285.1097, found: 285.1096; **ATR-FTIR ($cm^{-1}$):** 2971, 2936, 2877, 1687, 1604, 1584, 1490, 1465, 1445, 1384, 1345, 1260, 1268, 1213, 1188, 1020, 1048, 1015, 966.

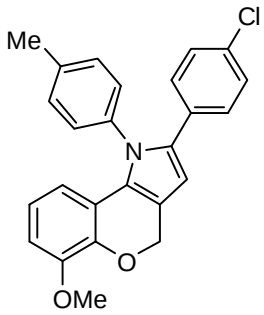
**3-[2-Oxo-2-(2-prop-2-ynyloxy-phenyl)-ethyl]-chroman-4-one (4a')**



Following the general procedure, treatment of 2-prop-2-ynyloxy-benzaldehyde **4a** (0.160 g, 1 mmol) with thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) at 70 °C for 2 h followed by column chromatography afforded 3-[2-oxo-2-(2-prop-2-ynyloxy-phenyl)-ethyl]-chroman-4-one **4a'** as a white solid (0.137 g, 86%).

**$R_f$** (pentane/EtOAc = 80/20): 0.33; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.90 (dd, $J$ = 7.9 Hz, 1.7 Hz, 1H), 7.78 (dd, $J$ = 7.9 Hz, 1.8 Hz, 1H), 7.56-7.41 (m, 2H), 7.17-6.92 (m, 4H), 4.81 (d, $J$ = 2.4 Hz, 2H), 4.69-4.54 (m, 1H), 4.32 (t, $J$ = 11.4 Hz, 1H), 3.76-3.49 (m, 2H), 3.11 (dd, $J$ = 17.8 Hz, 7.6 Hz, 1H), 2.53 (t, $J$ = 2.4 Hz, 1H); **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 199.12, 193.71, 161.97, 156.64, 135.96, 133.80, 130.85, 128.44, 127.50, 121.91, 121.47, 120.89, 117.97, 113.17, 77.85, 76.53, 70.66, 56.35, 42.47, 39.80; **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{16}O_4Na$ : 343.0941, found: 343.0930; **ATR-FTIR ($cm^{-1}$)**: 3243, 2904, 1681, 1663, 1596, 1480, 1454, 1380, 1326, 1287, 1232, 1198, 1169, 1146, 1117, 1010, 979, 949, 896.

**2-(4-Chloro-phenyl)-6-methoxy-1-*p*-tolyl-1,4-dihydro-chromeno[4,3-*b*]pyrrole (7)**[5]



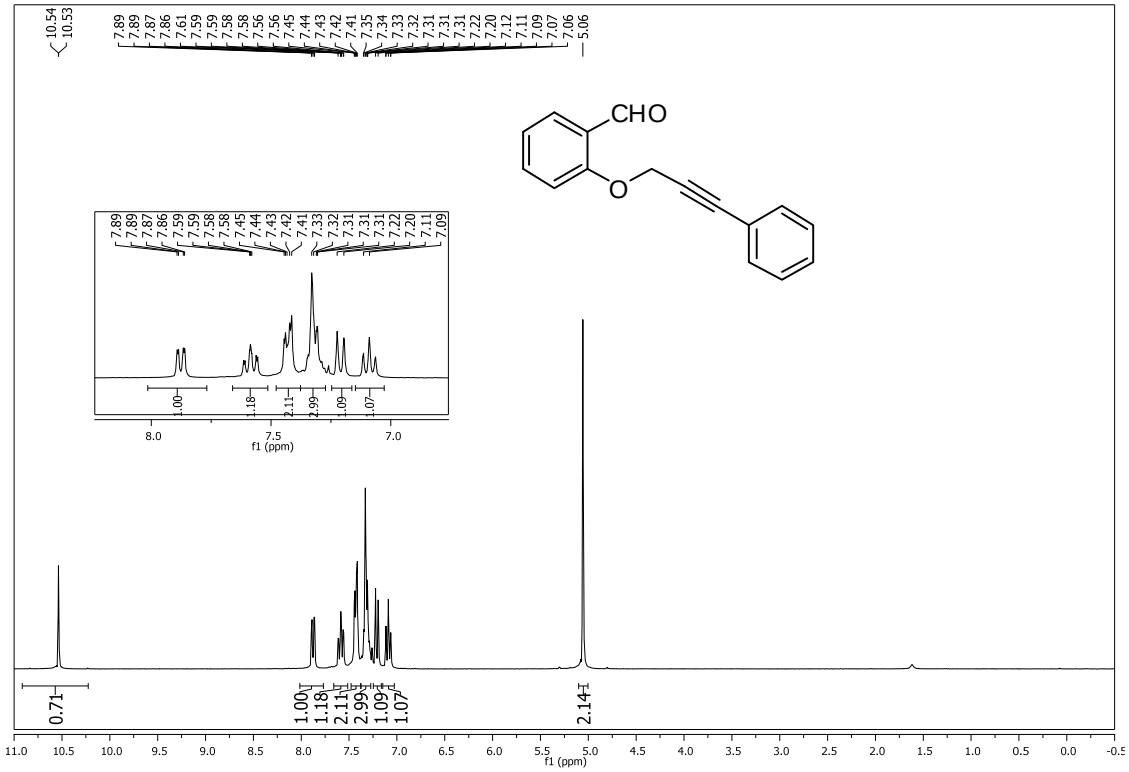

Following the general procedure, a solution of 3-methoxy-2-prop-2-ynyloxy-benzaldehyde **4b** (0.190 g, 1 mmol), 4-chlorobenzaldehyde (0.141 g, 1 mmol), thiazolium salt **3** (18.6 mg, 0.05 mmol) and $K_2CO_3$ (13.8 mg, 0.1 mmol) in THF (2 mL) was heated at 70 °C for 2 h. The mixture was then cooled, and AcOH (3 mL) and *p*-toluidine (0.322 g, 3 mmol) were added and the mixture was heated at 110 °C for 12 h. The reaction mixture was cooled to room temperature, poured into cold water (20 mL) and extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic fractions were washed with $NaHCO_3$ (3 x 20 mL), brine (1 x 20 mL) and water (1 x 20 mL), dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography to afford 2-(4-chloro-phenyl)-6-methoxy-1-*p*-tolyl-1,4-dihydro-chromeno[4,3-*b*]pyrrole **7** as a white solid (204 mg, 51%).

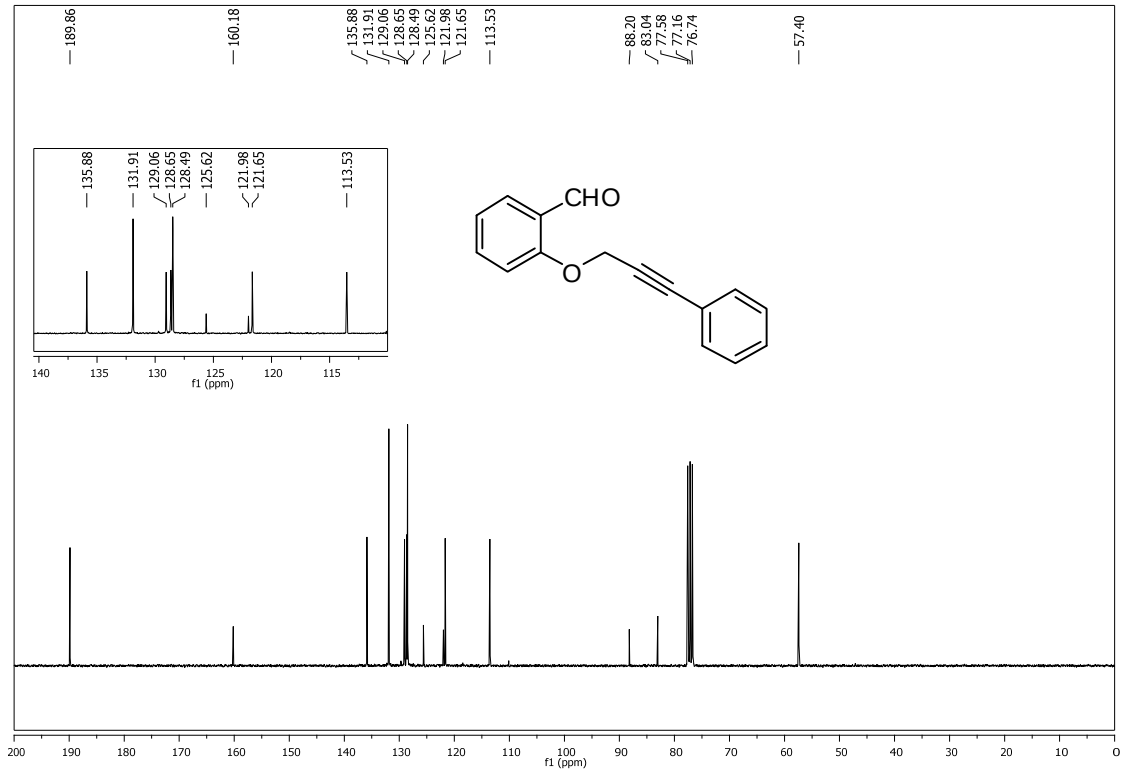
**$R_f$** (pentane/EtOAc = 80/20): 0.40; **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.22-7.11 (m, 6H, $H_{ar}$), 7.06-6.94 (m, 2H, $H_{ar}$), 6.66 (dd, *J* = 8.2 Hz, 1.3 Hz, 1H, $H_{ar}$),, 6.57 (d, *J* = 8.0 Hz, 1H, $H_{ar}$), 6.24 (s, 1H, C*H*=C), 5.93 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H, $H_{ar}$), 5.36 (s, 2H, $OCH_2$), 3.87 (s, 3H, OCH3), 2.43 (s, 3H, CH3). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 148.94, 138.77, 136.31, 135.80, 132.48, 130.19, 129.81, 128.79, 128.33, 126.03, 120.84, 119.97, 117.20, 113.72, 109.87, 105.59, 66.35, 56.15, 21.45. **ESI-MS**: calculated $[M+Na]^+$ for $C_{25}H_{20}ClNO_2Na$: 424.1075, found: 424.1071; **Elemental analysis:** calcd. (%) for $C_{25}H_{20}ClNO_2$ (401.1183): C 74.71, H 5.02, N 3.49, found: C 74.28, H 4.99, N 3.90. **ATR-FTIR ($cm^{-1}$)**: 2952, 2842, 1601, 1585, 1553, 1513, 1475, 1453, 1427, 1405, 1367, 1333, 1282, 1264, 1235, 1203, 1173, 1098, 1031, 998, 945, 887.

[5] For the synthesis of pyrroles from 1,4-diketones, see: R. Martinez, J. G. Avila, M. T. Ramirez, A. Perez, A. Martinez, *Bioorg. Med. Chem.* **2006**, *14*, 4007.

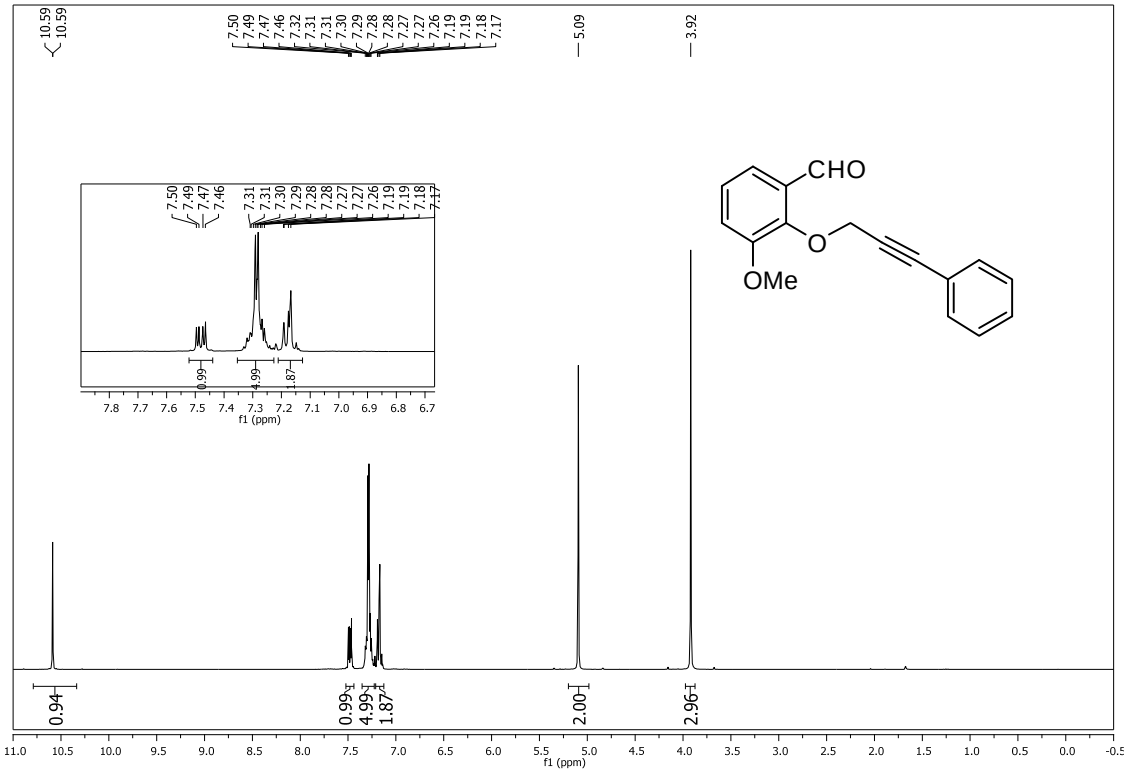
## 6. $^{1}H$ and $^{13}C$ NMR Spectra of Substrates

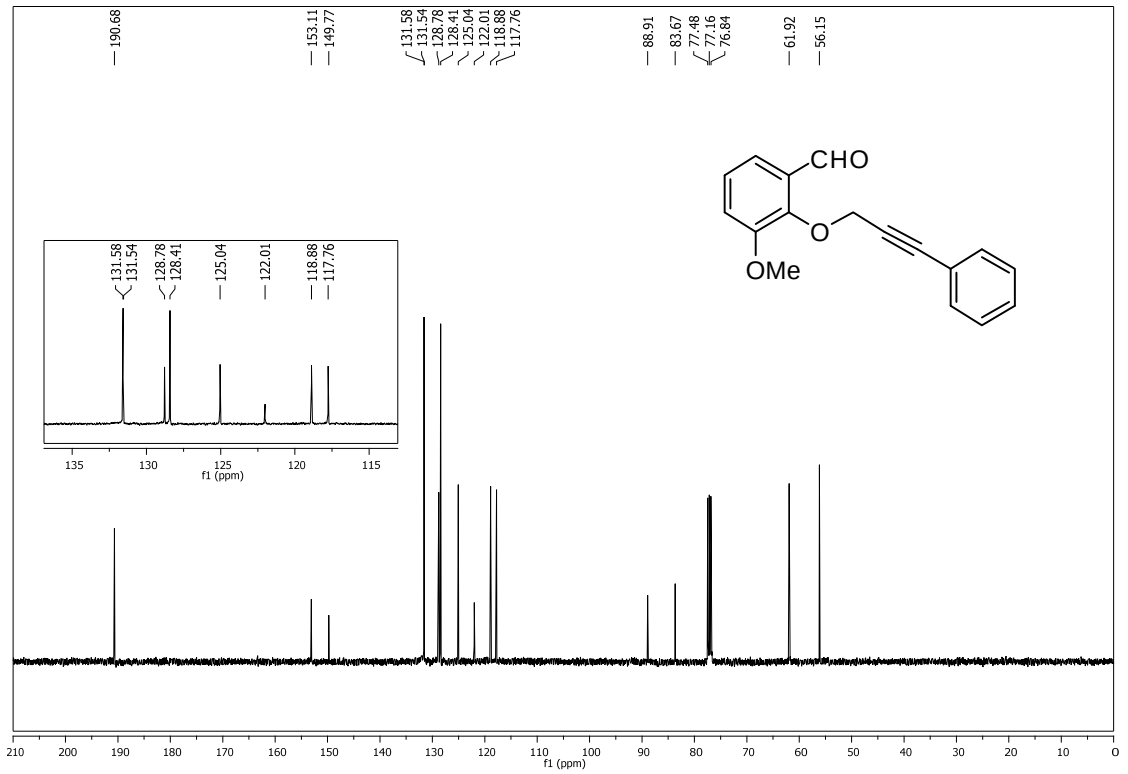
### 2-(3-Phenyl-prop-2-ynyloxy)-benzaldehyde (1a)



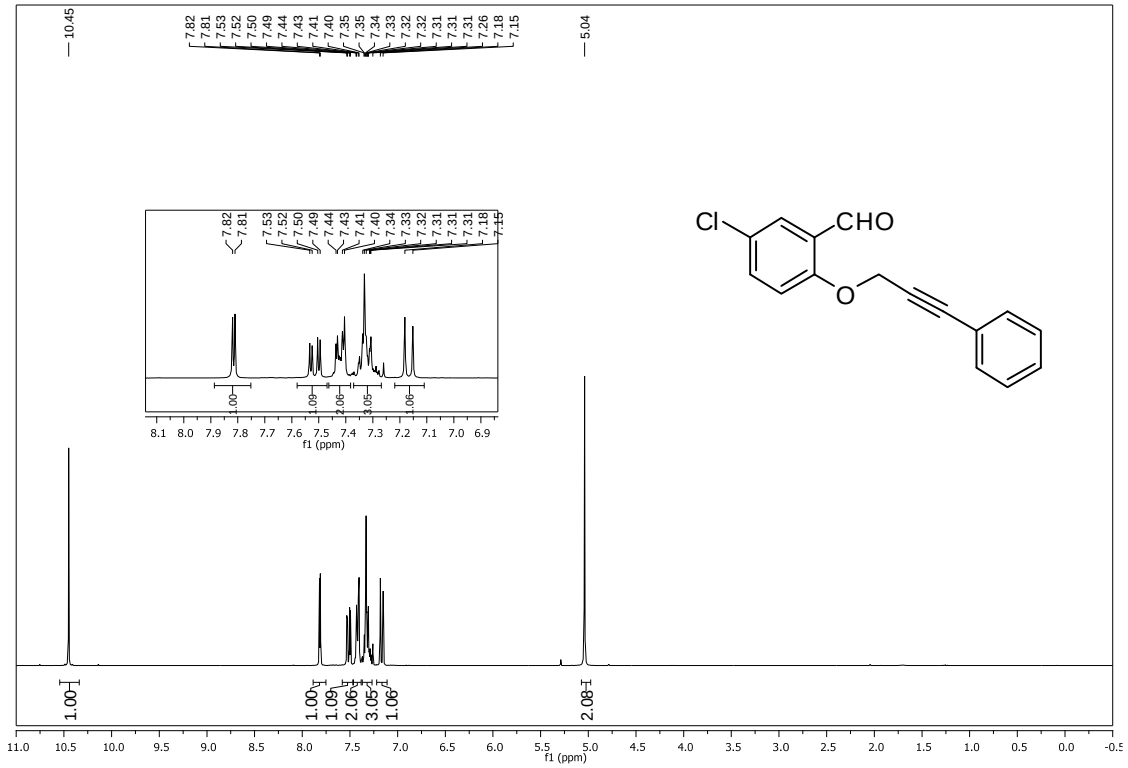



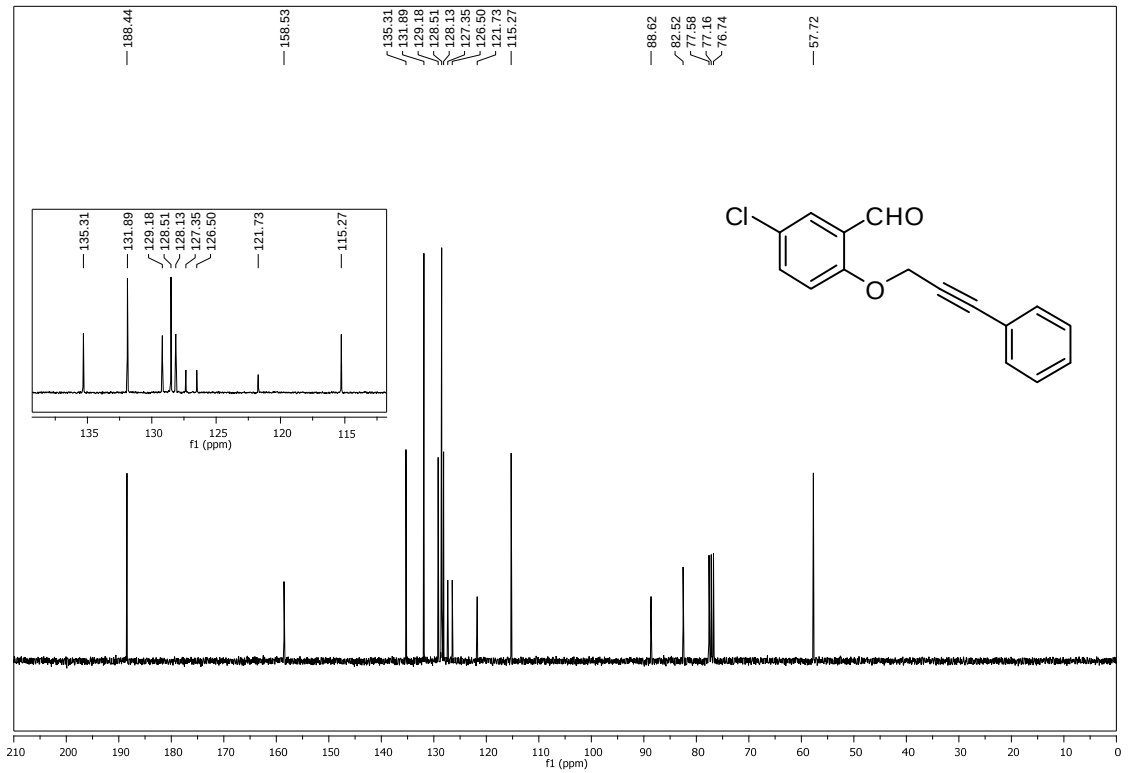
## 3-Methoxy 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1b)



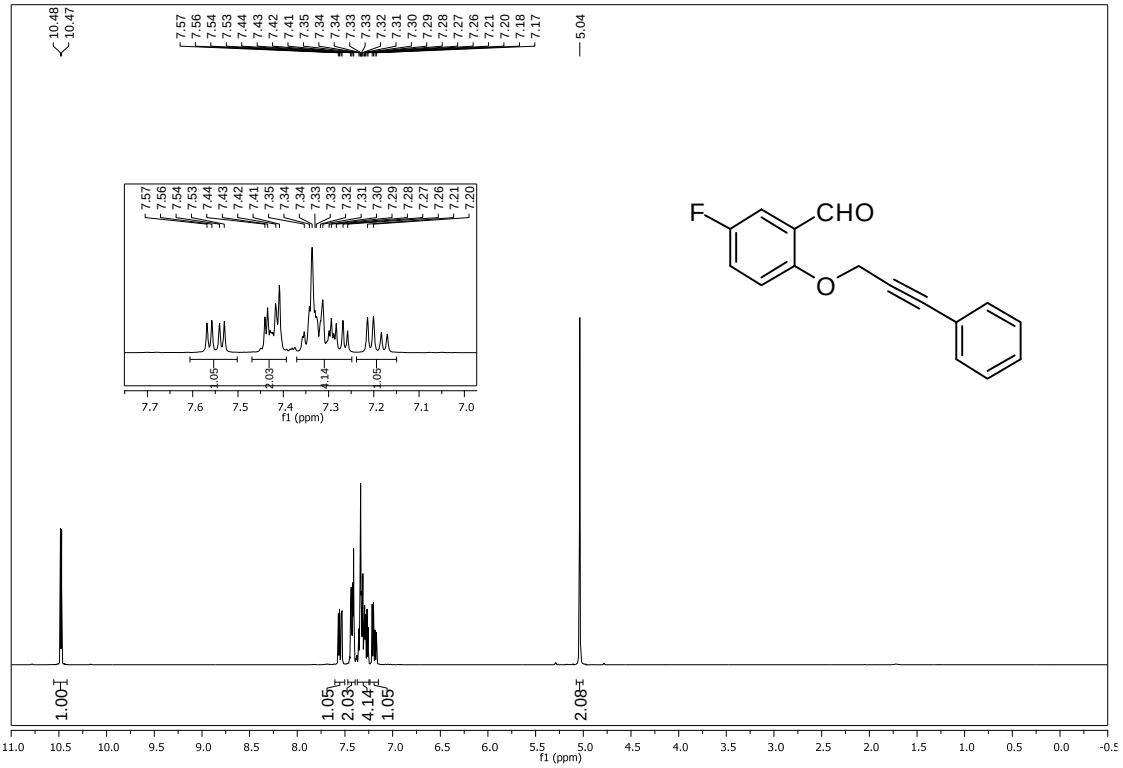



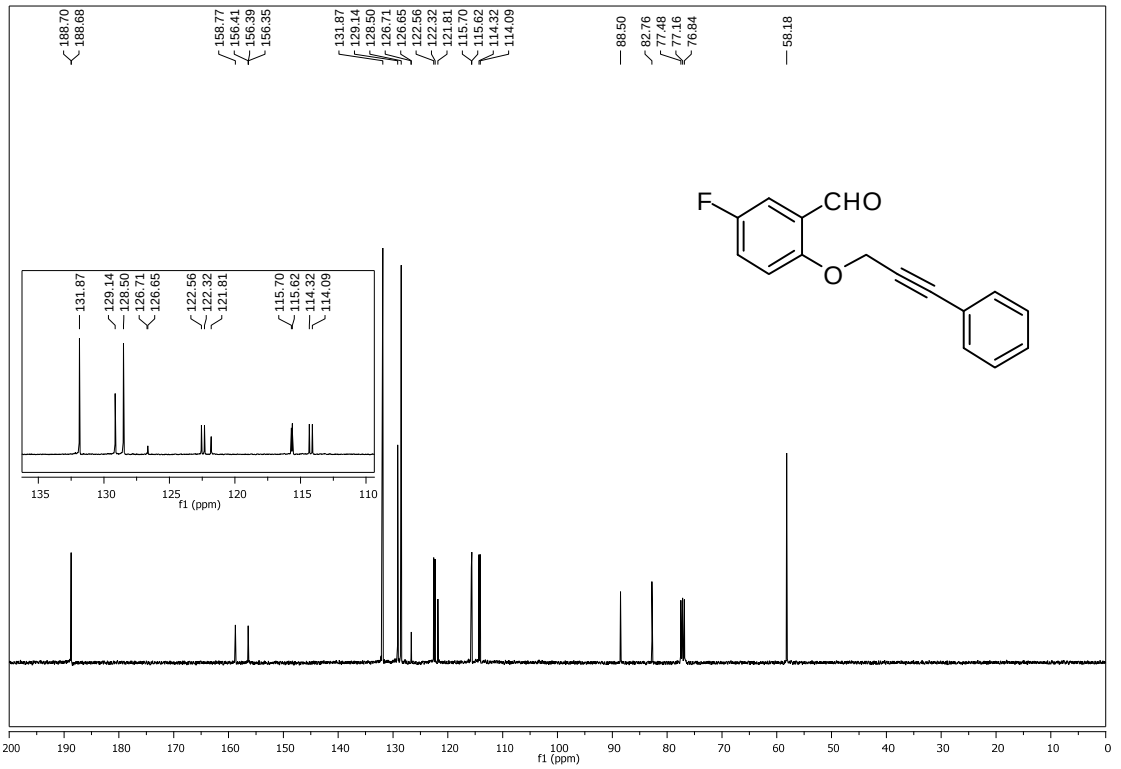
## 5-Chloro 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1c)



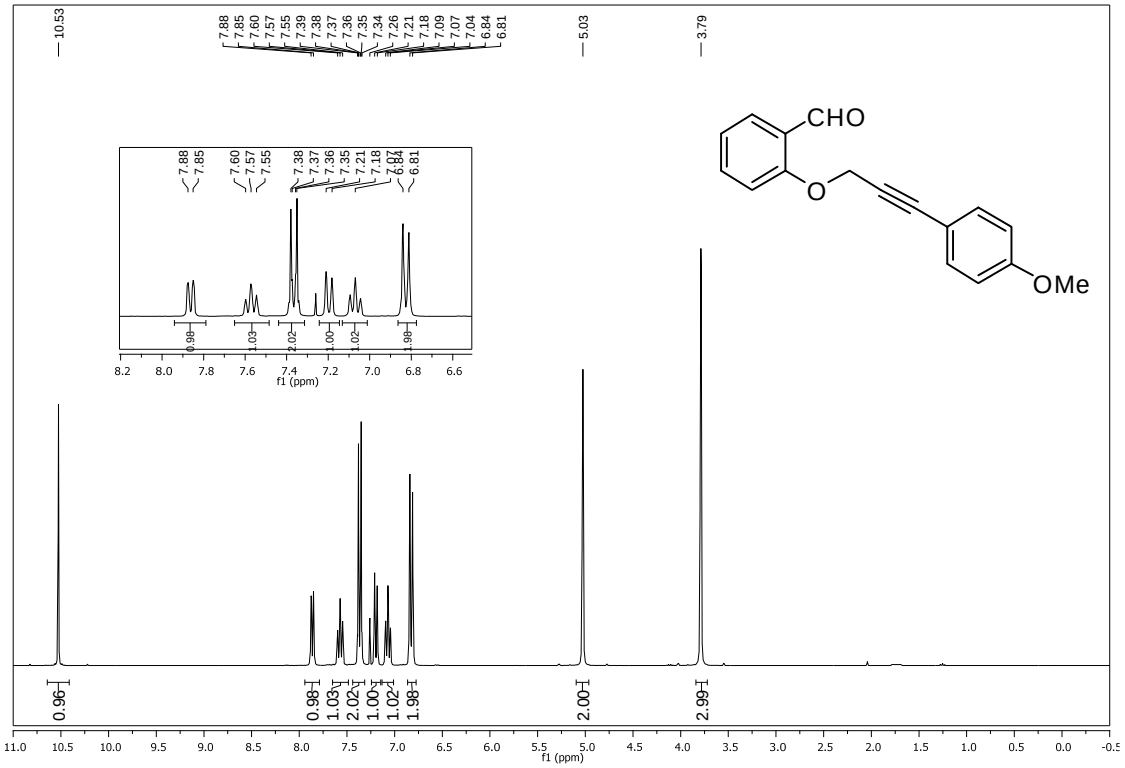



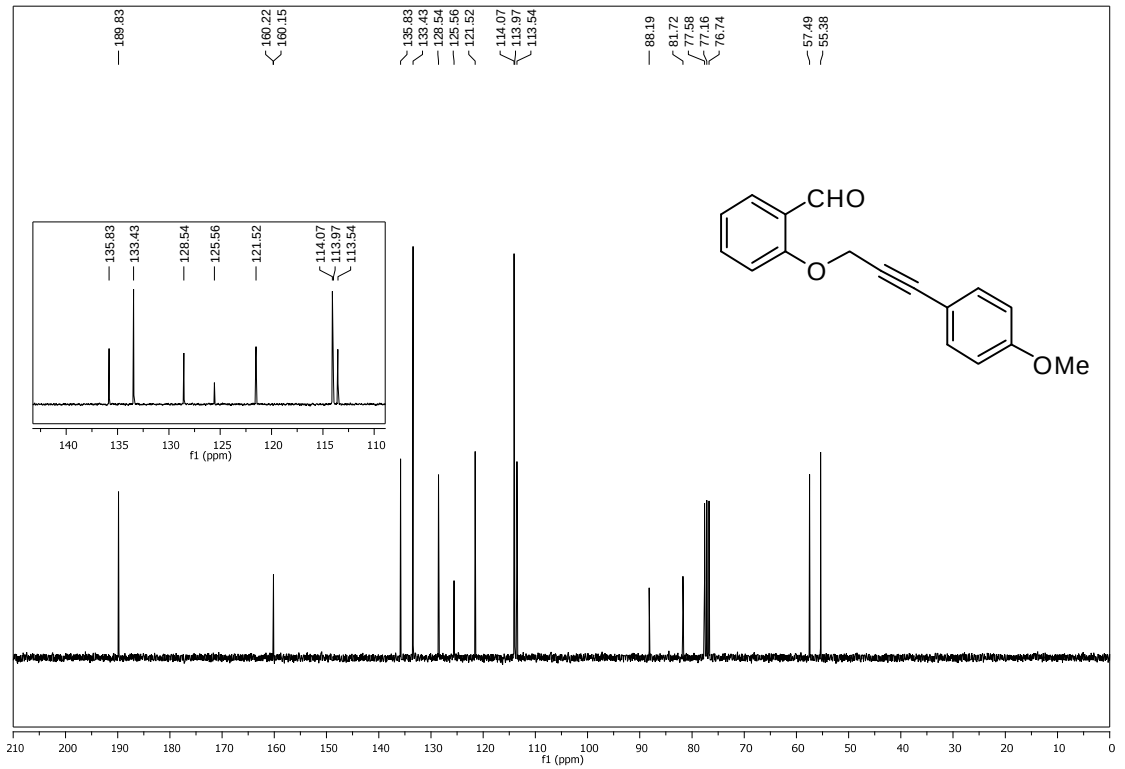
## 5-Fluoro 2-(3-phenyl-prop-2-ynyloxy)-benzaldehyde (1d)



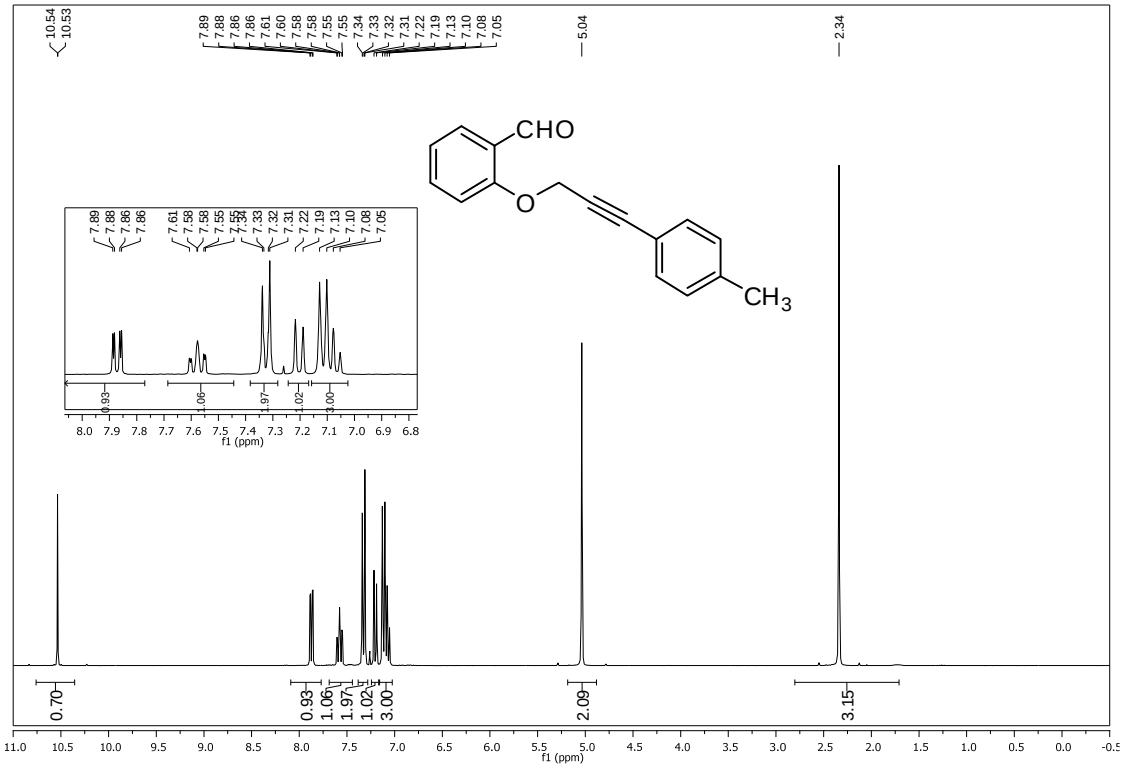



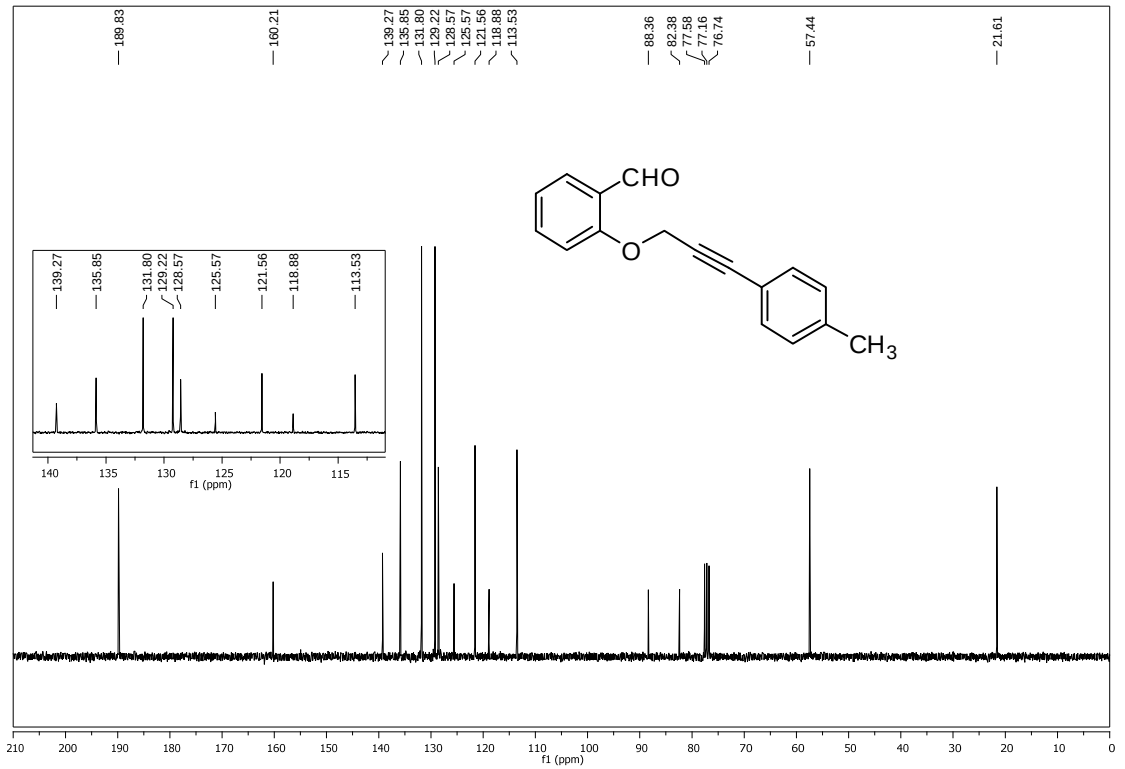
## 2-[3-(4-Methoxy phenyl)-prop-2-ynyloxy]-benzaldehyde (1e)



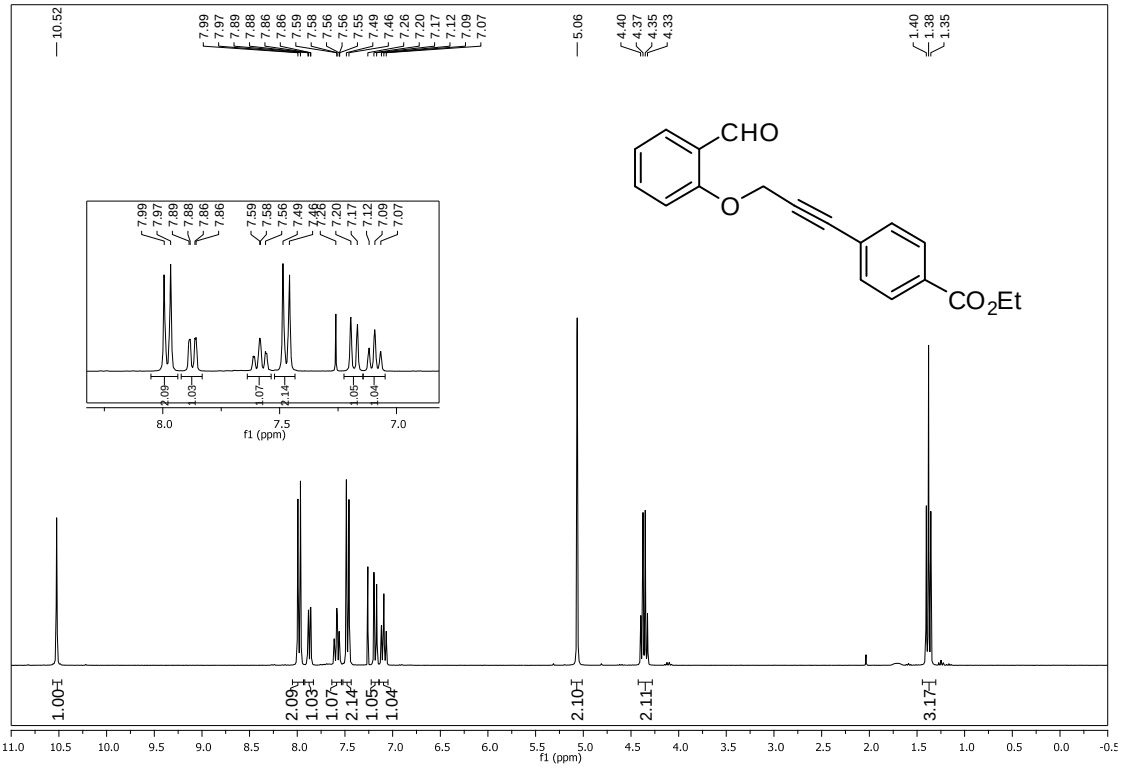



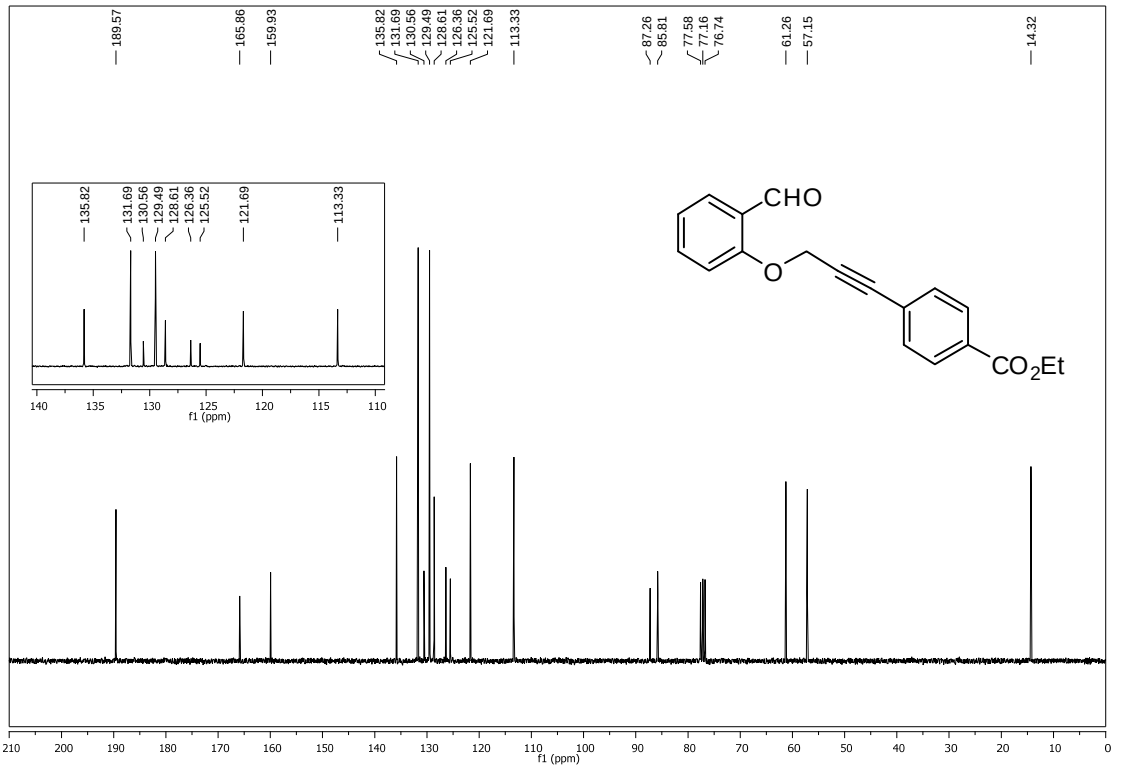
## 2-[3-(4-Methyl phenyl)-prop-2-ynyloxy]-benzaldehyde (1f)



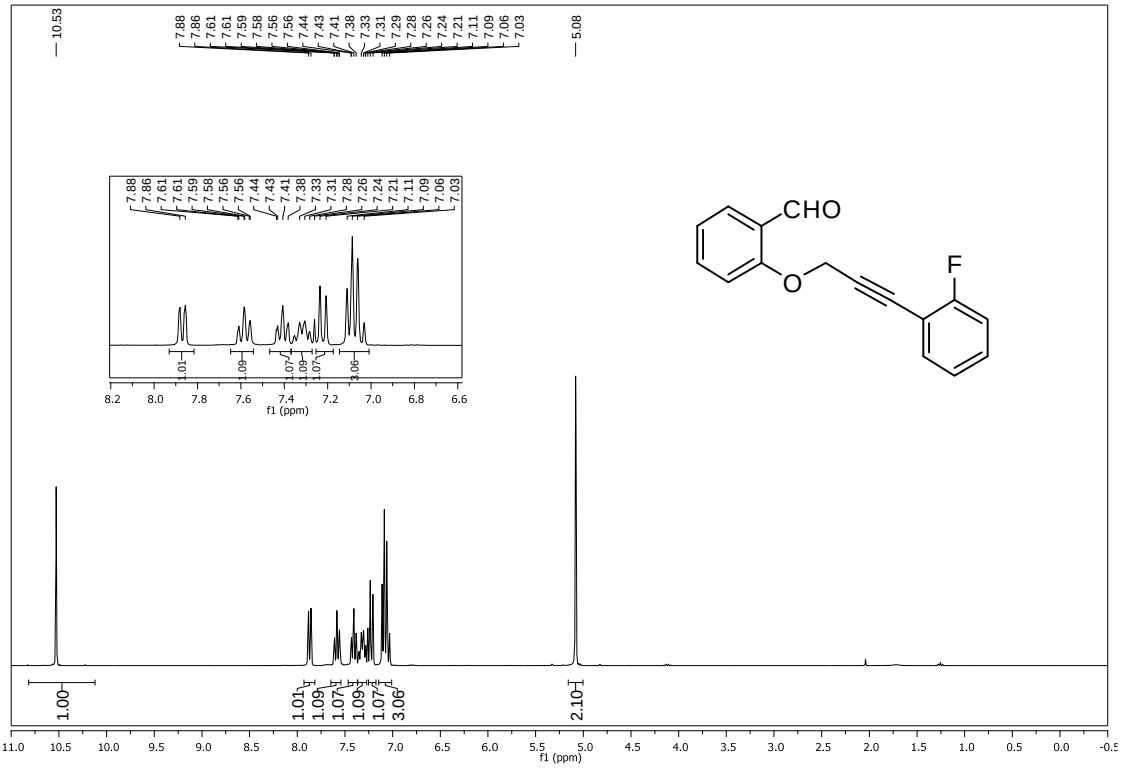



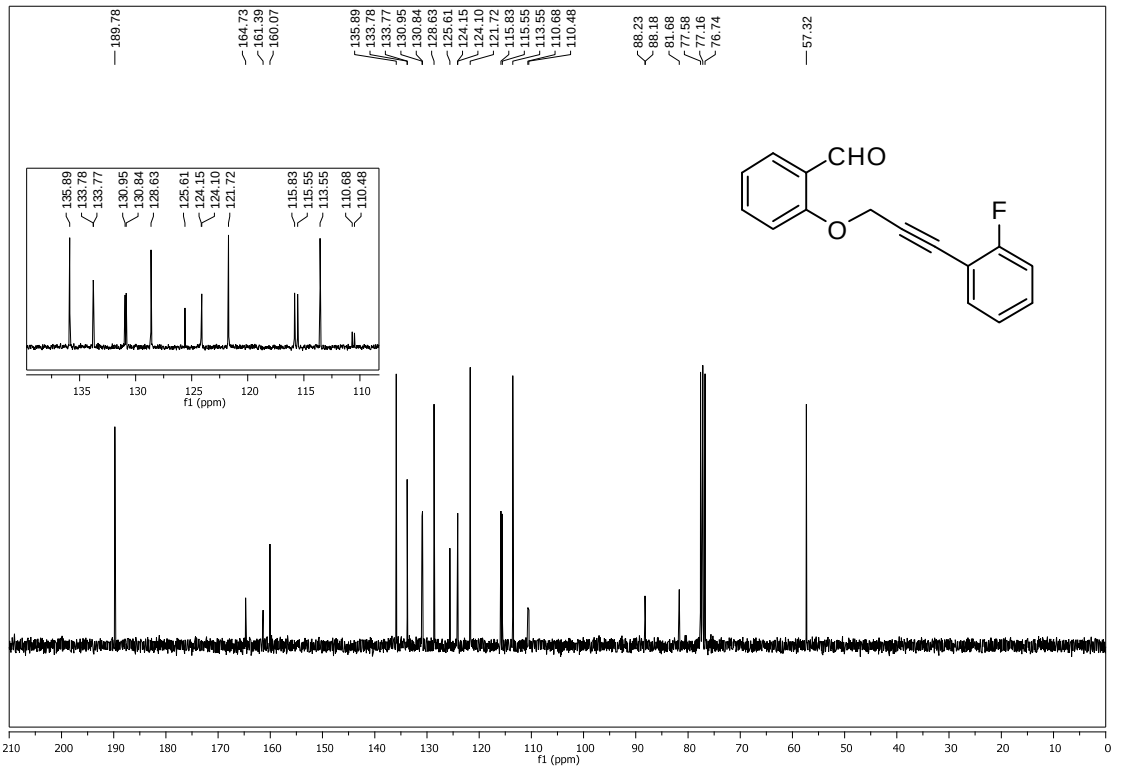
## 2-[3-(4-Carboethoxy phenyl)-prop-2-ynyloxy]-benzaldehyde (1g)



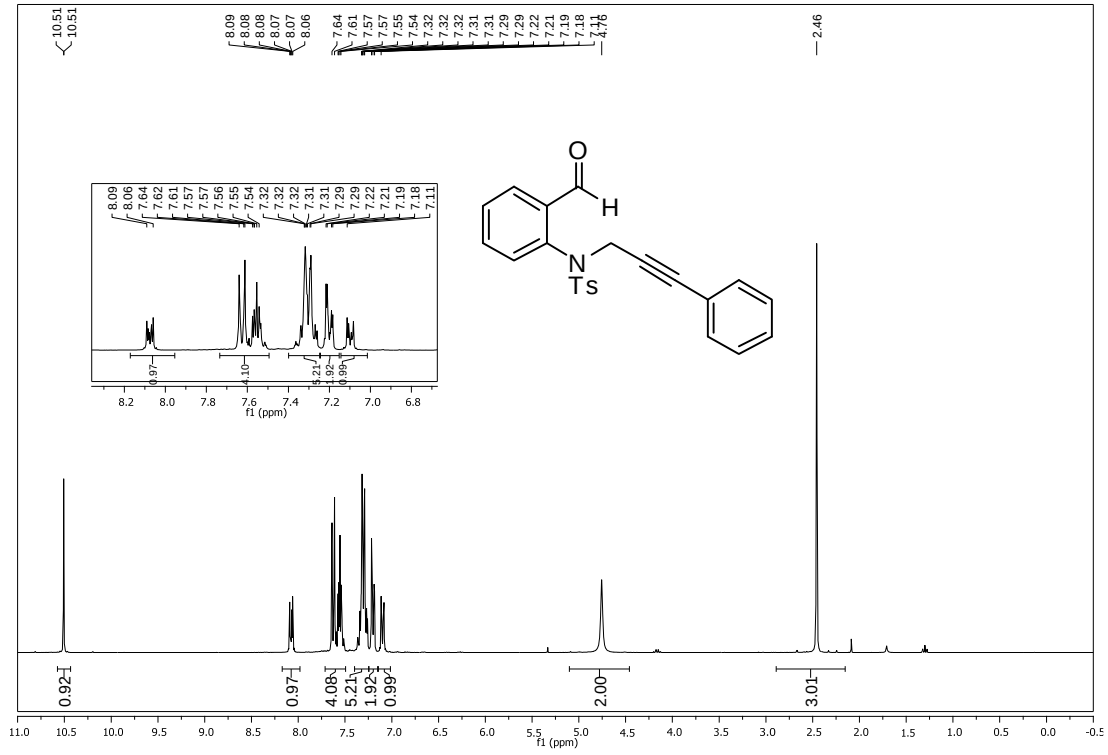



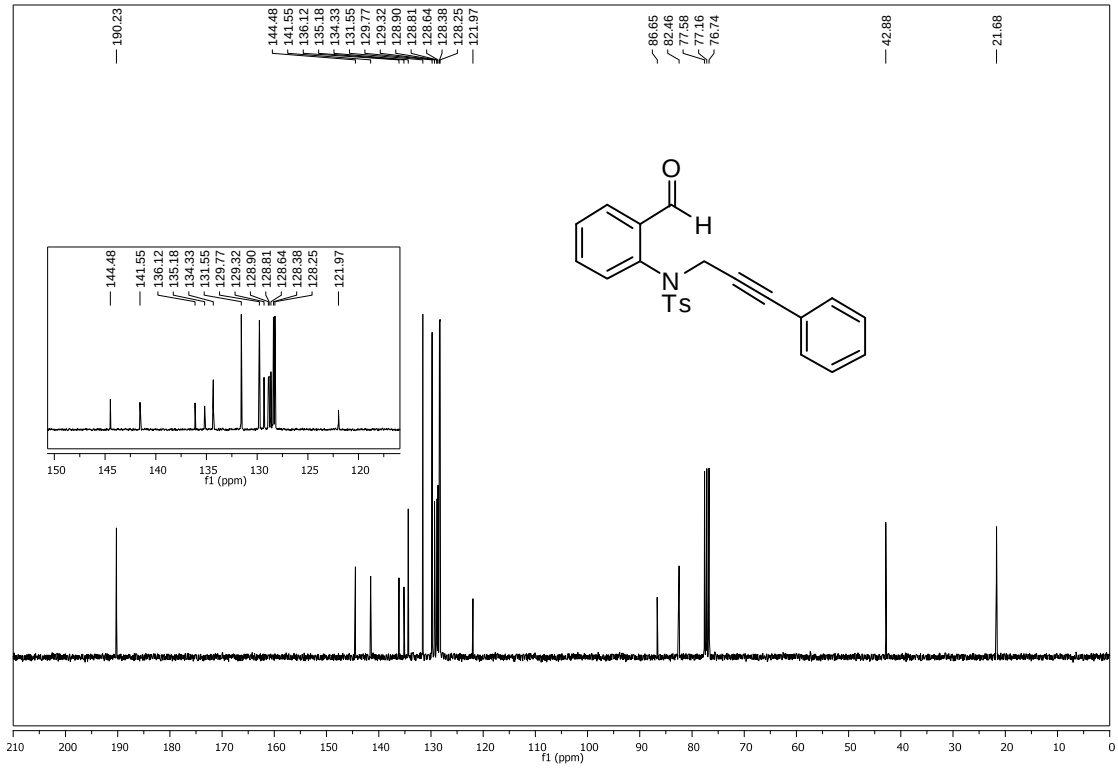
## 2-[3-(2-Fluoro phenyl)-prop-2-ynyloxy]-benzaldehyde (1h)



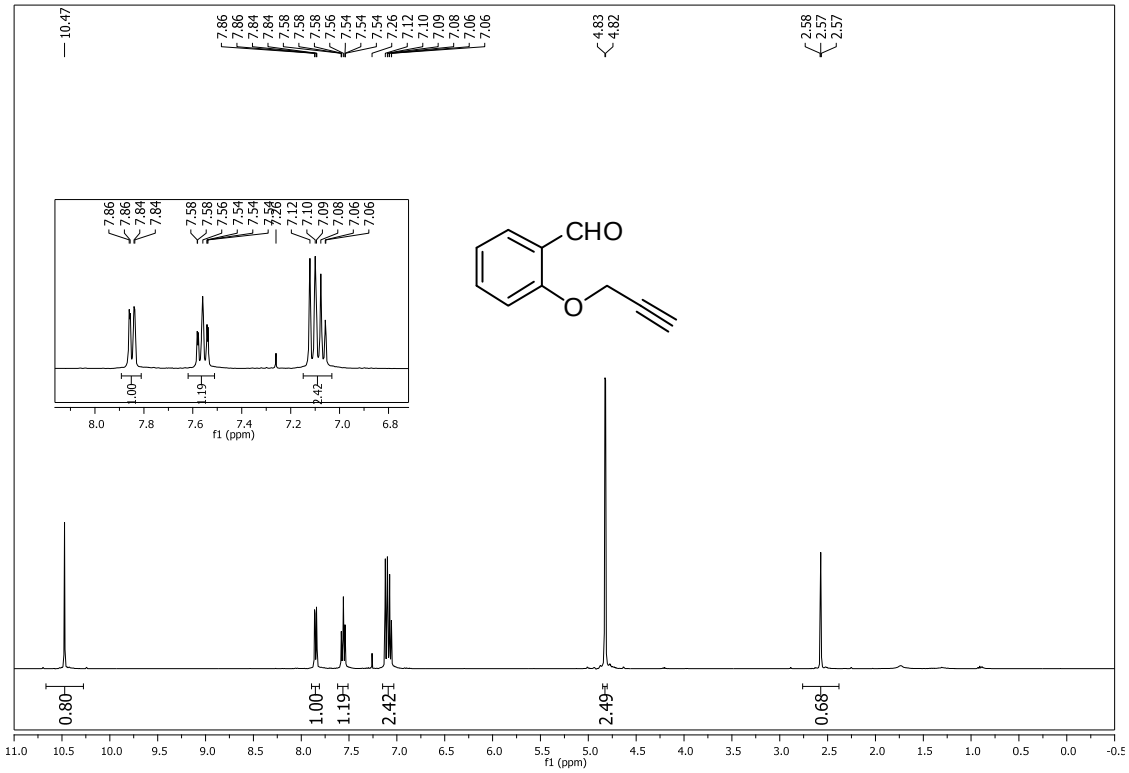



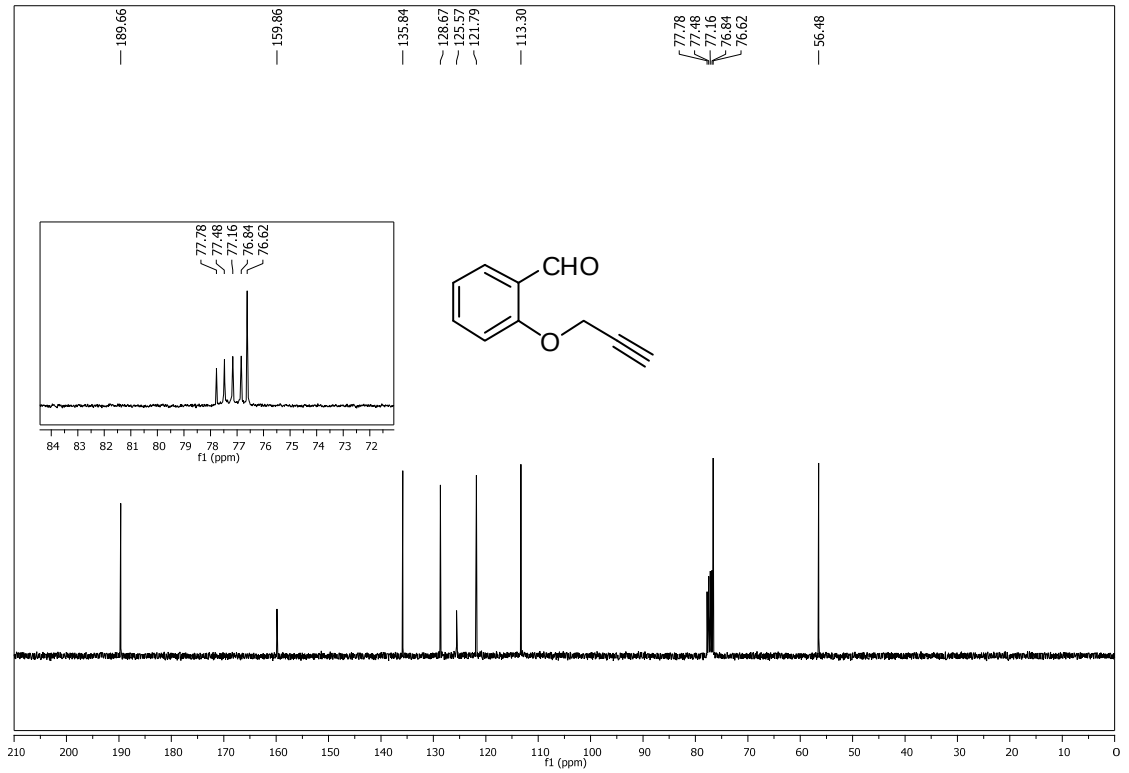
**_N_-(3-Phenyl-prop-2-ynyloxy)-_N_-(2-formyl-phenyl)-4-methyl-benzenesulfonamide (1i)**



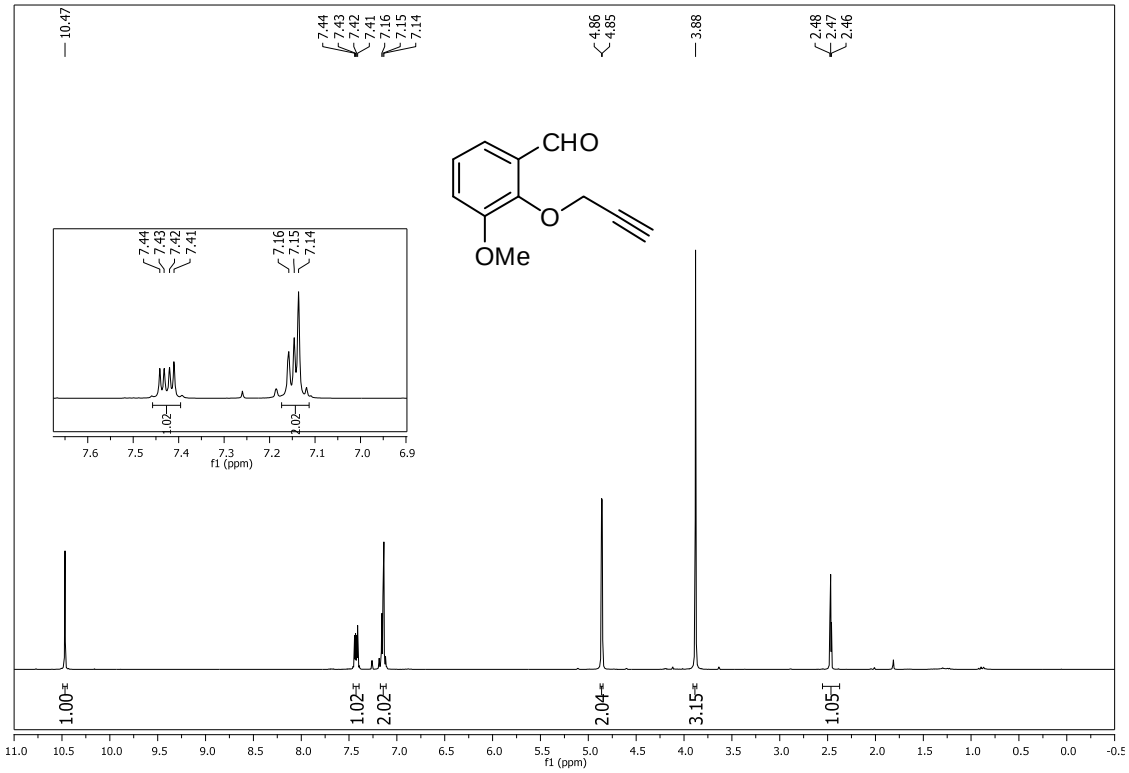



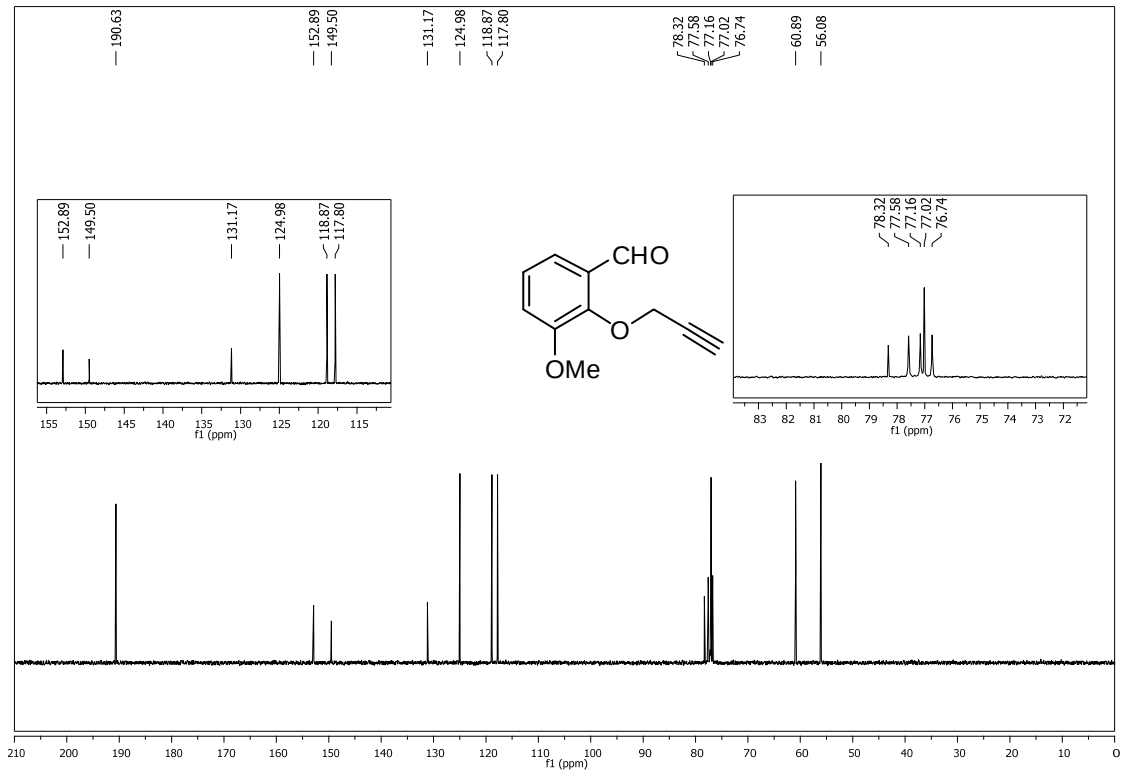
## 2-Prop-2-ynyloxy-benzaldehyde (4a)



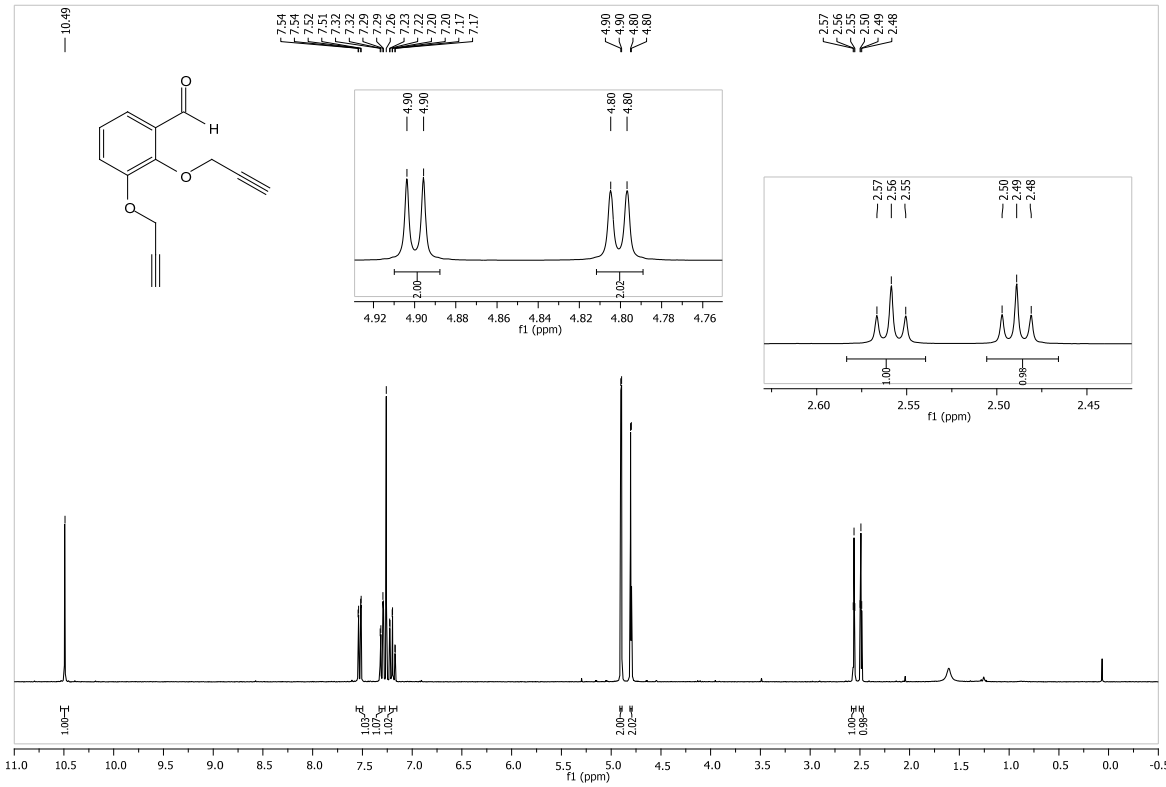



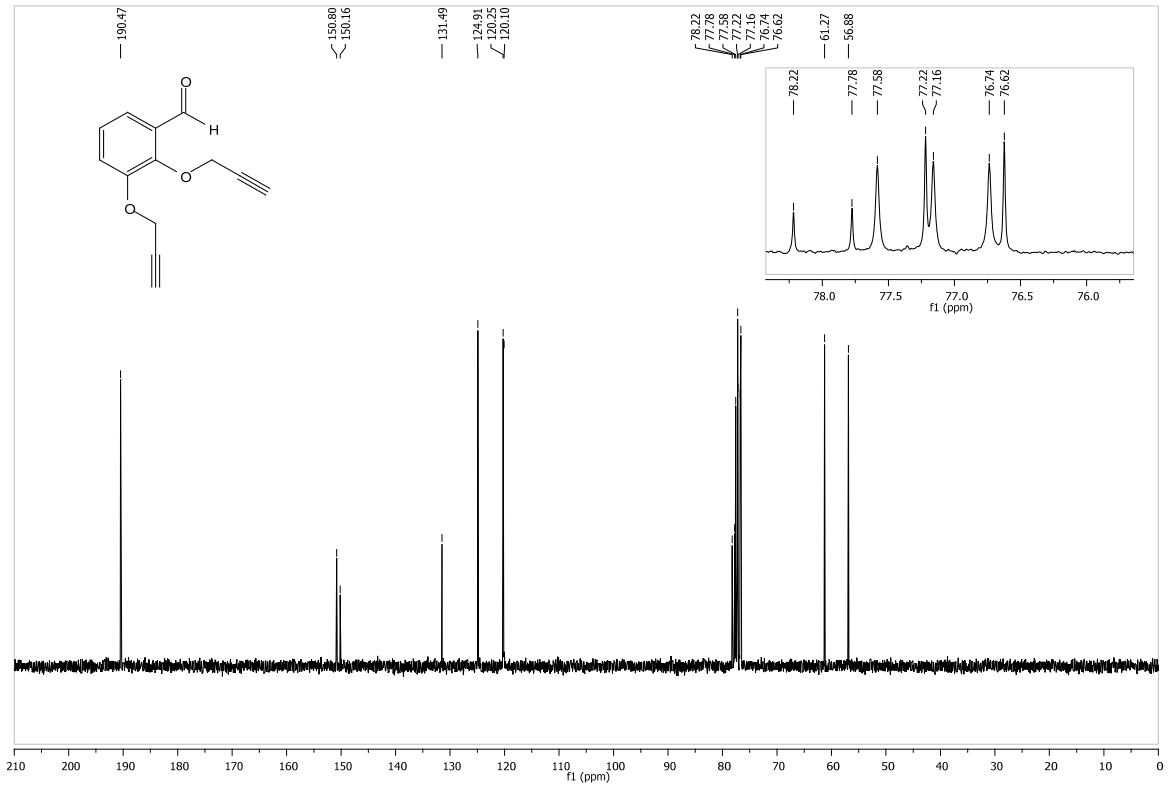
## 3-Methoxy-2-prop-2-ynyloxy-benzaldehyde (4b)



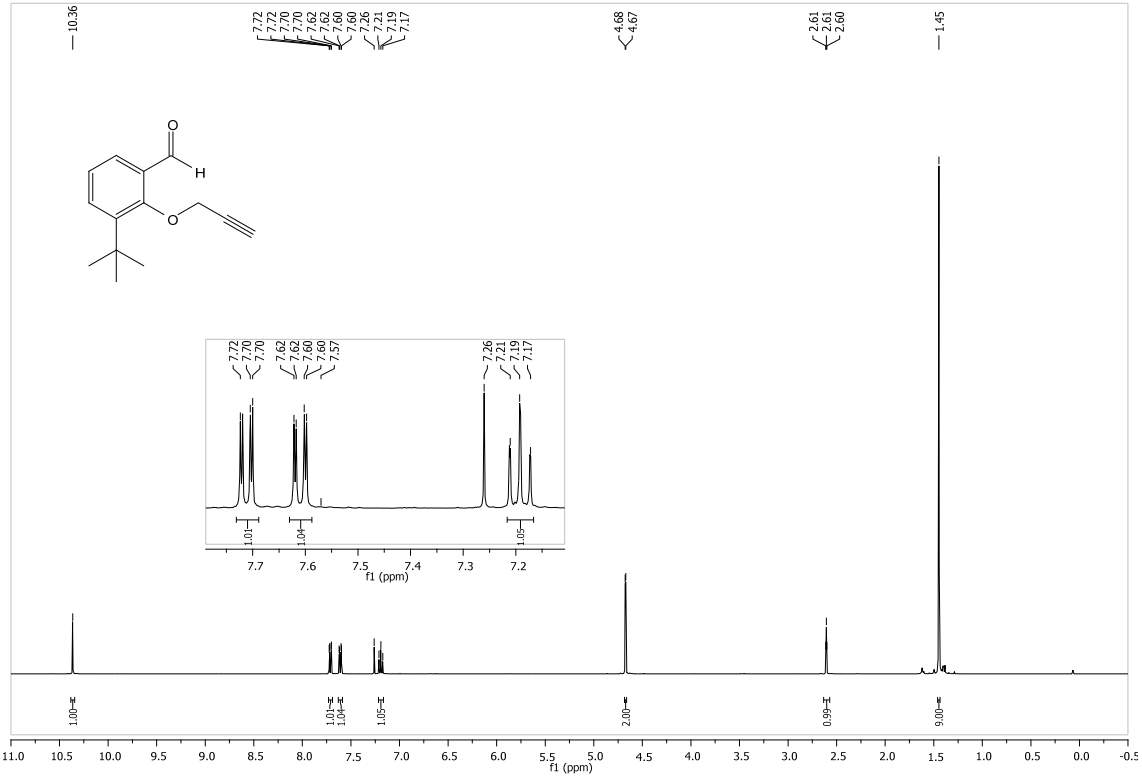



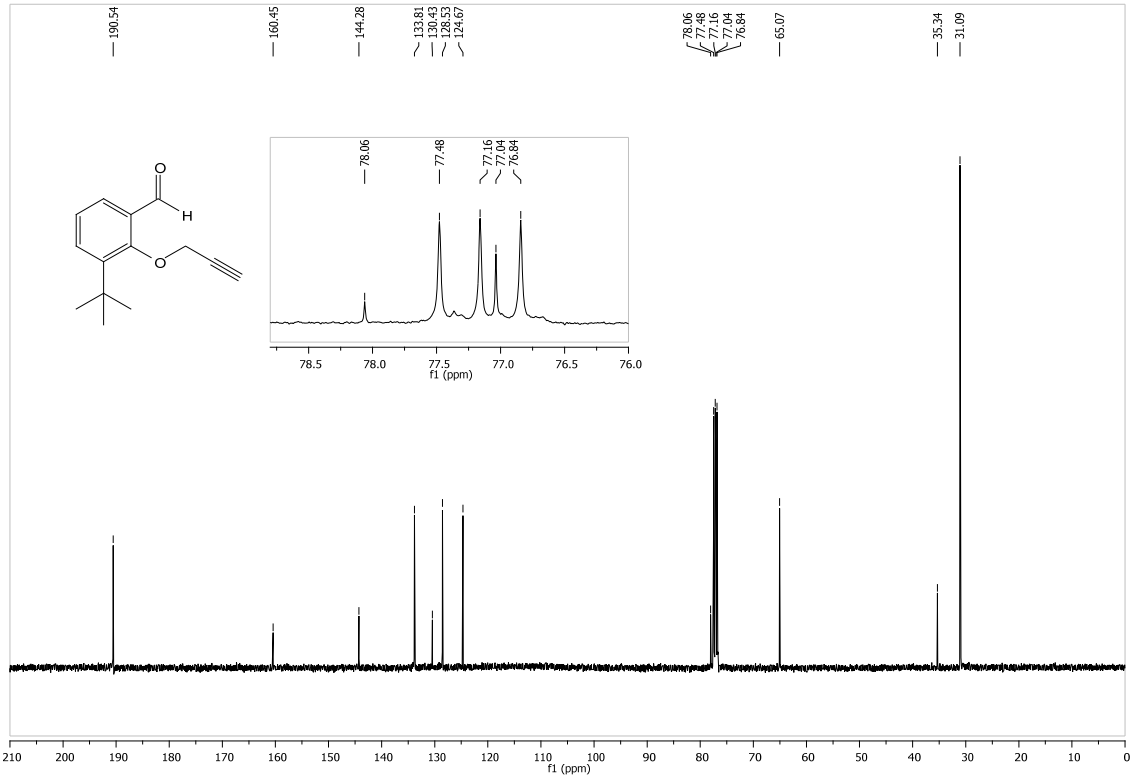
## 2,3-Bis-prop-2-ynyloxy-benzaldehyde (4c)



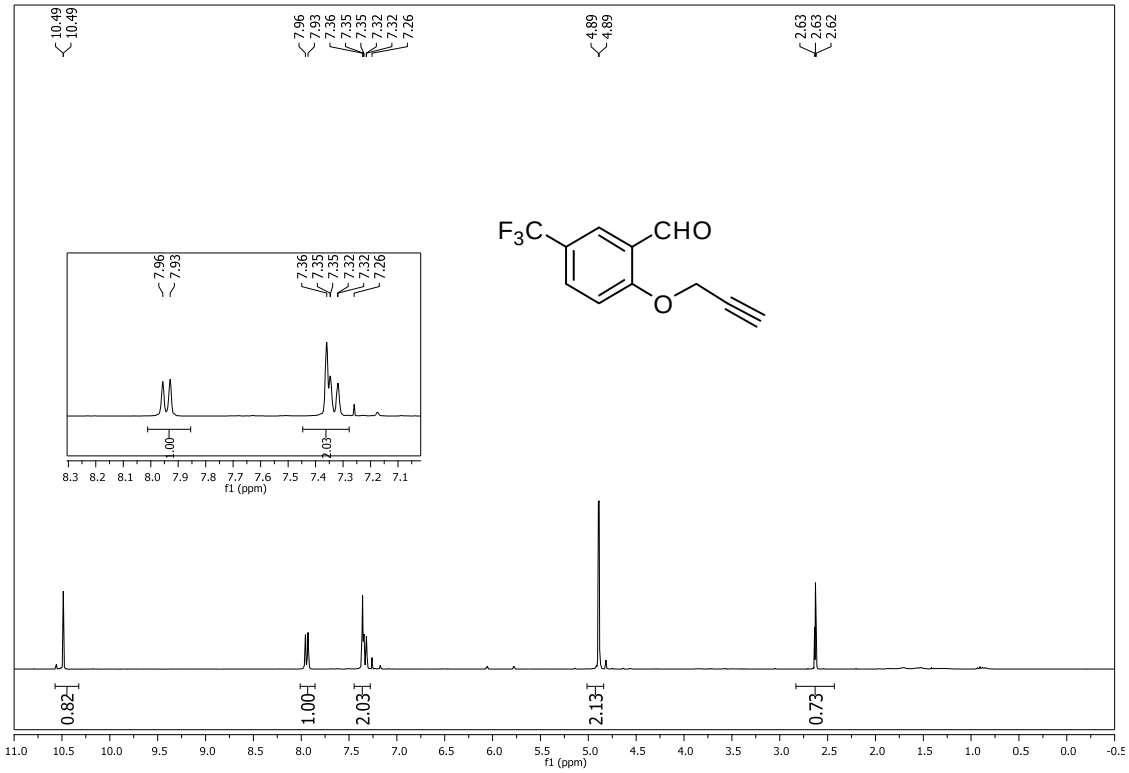



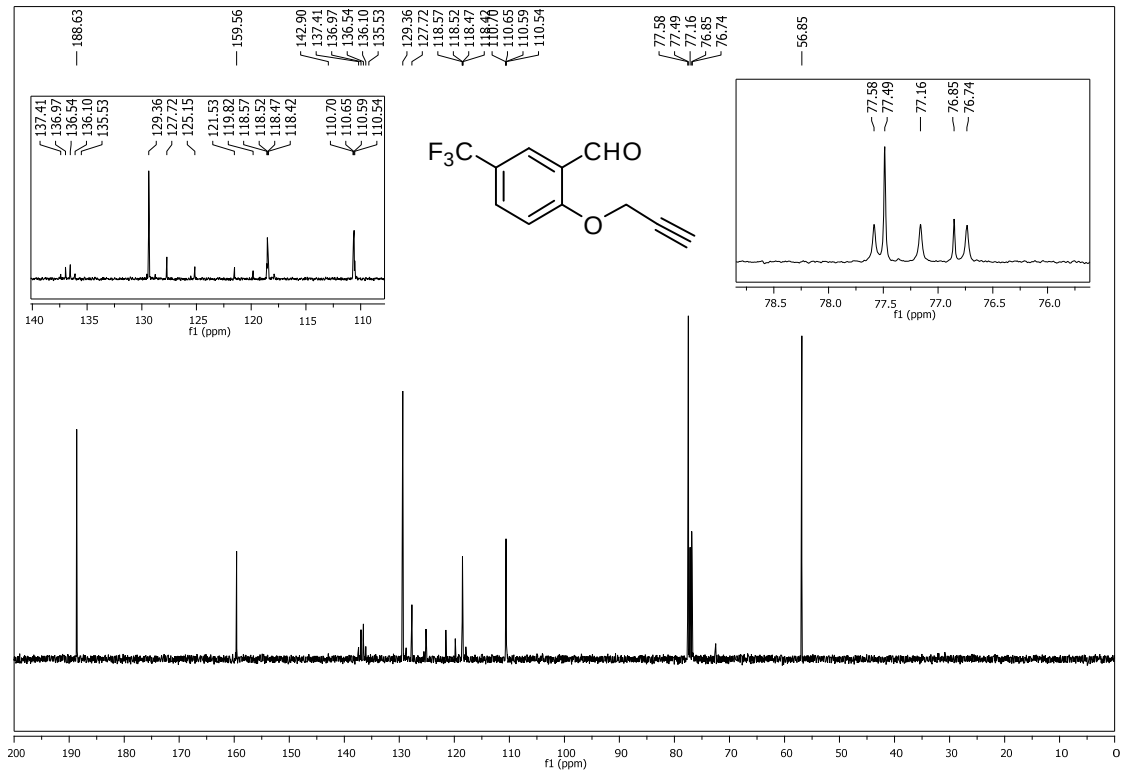
## 3-*tert*-Butyl-2-prop-2-ynyloxybenzaldehyde (4d)



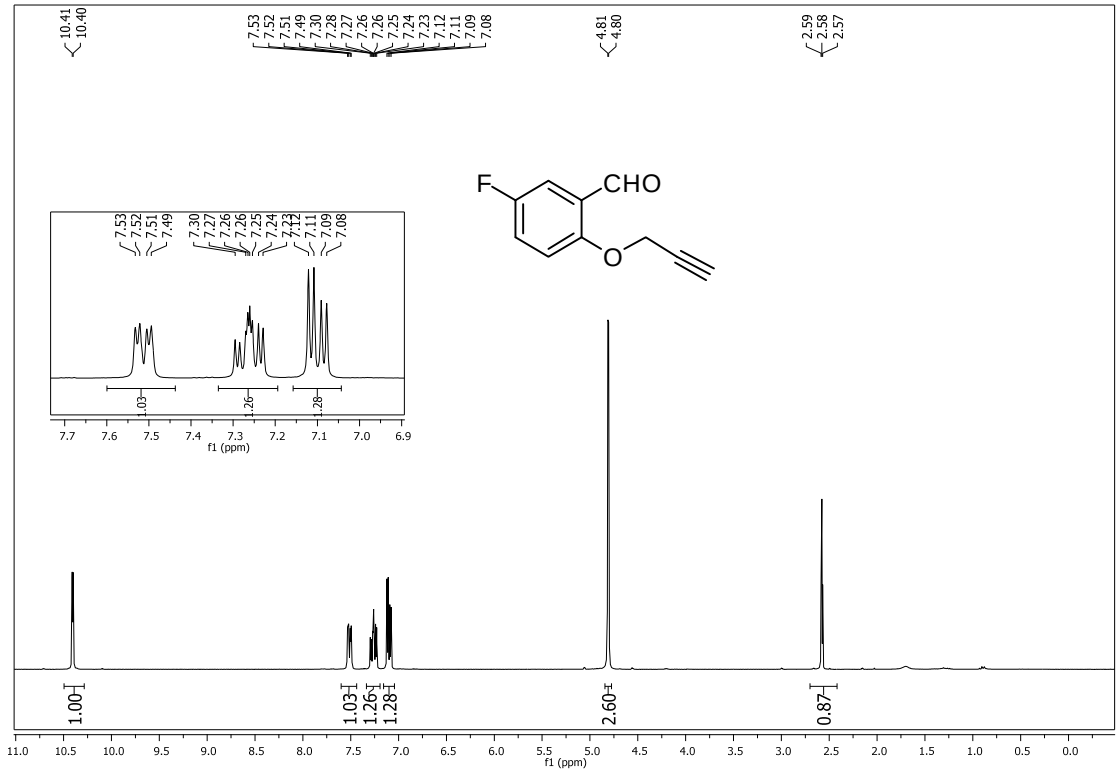



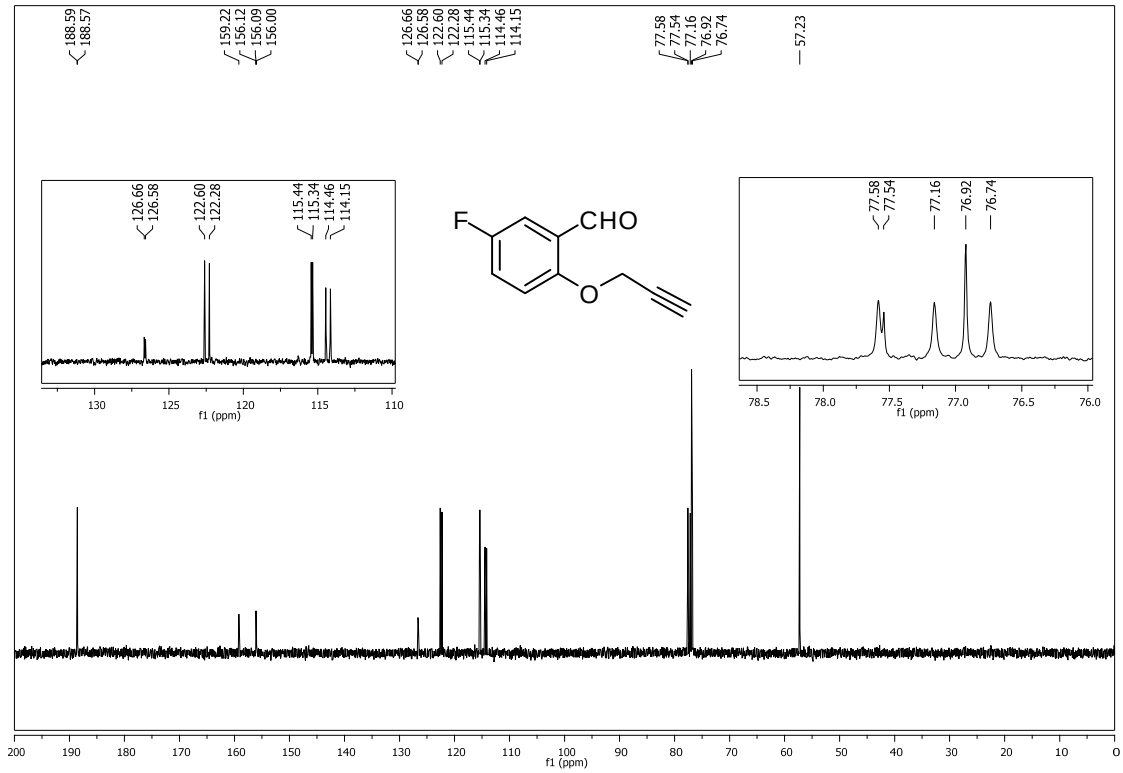
## 2-Prop-2-ynyloxy-4-trifluoromethyl-benzaldehyde (4e)



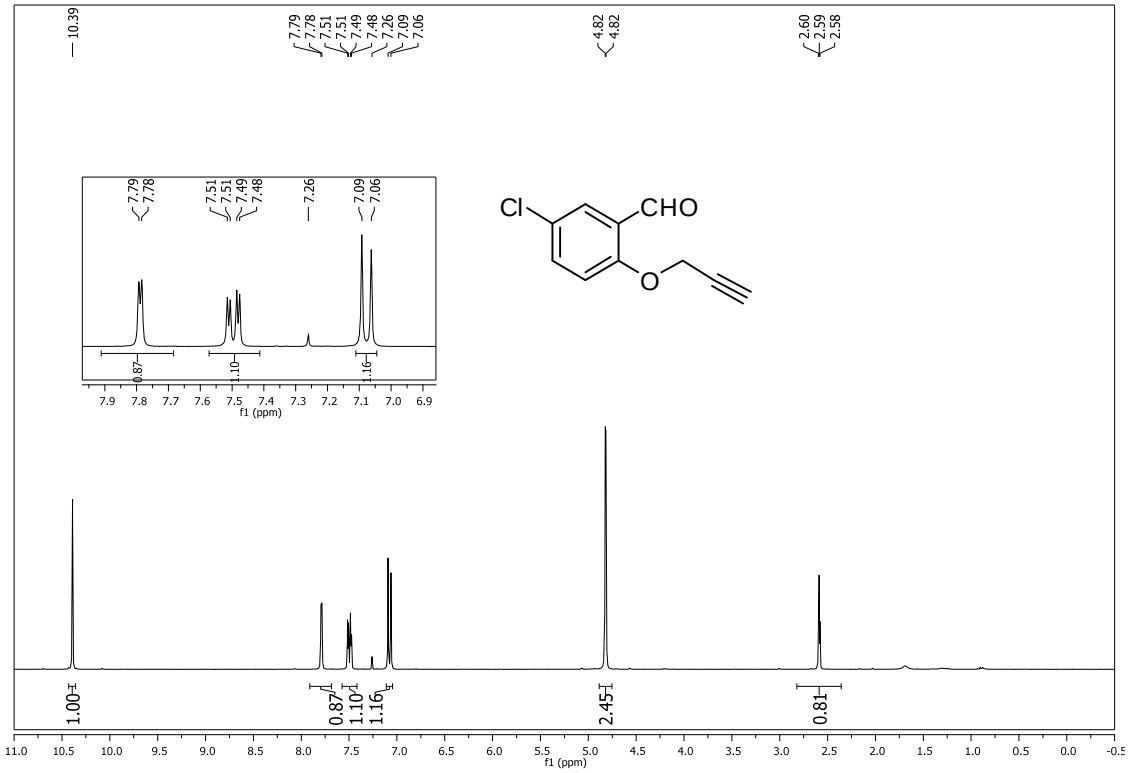



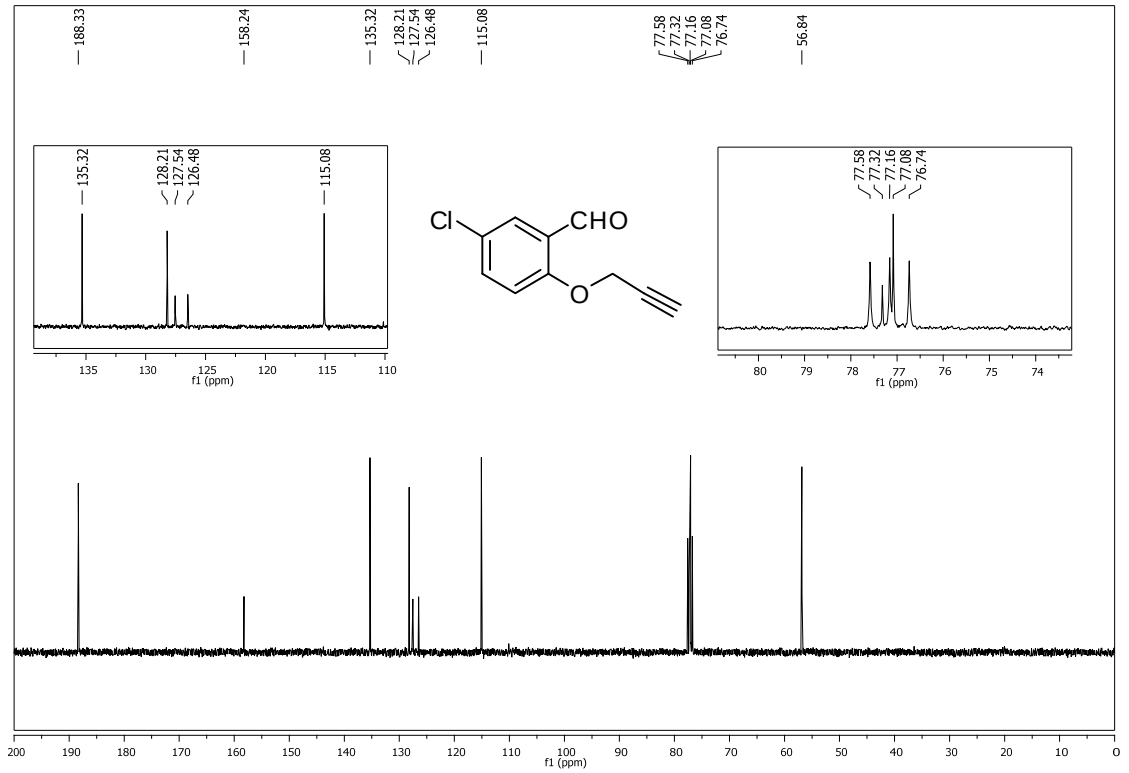
## 5-Fluoro-2-prop-2-ynyloxy-benzaldehyde (4f)



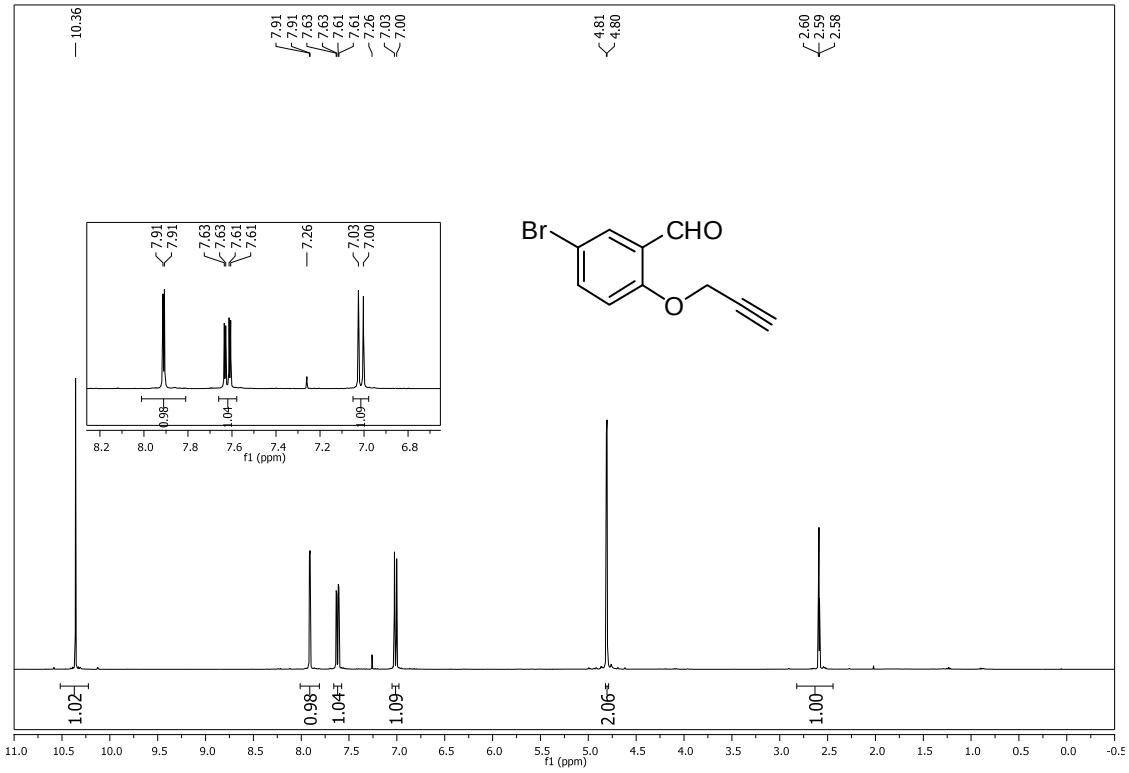



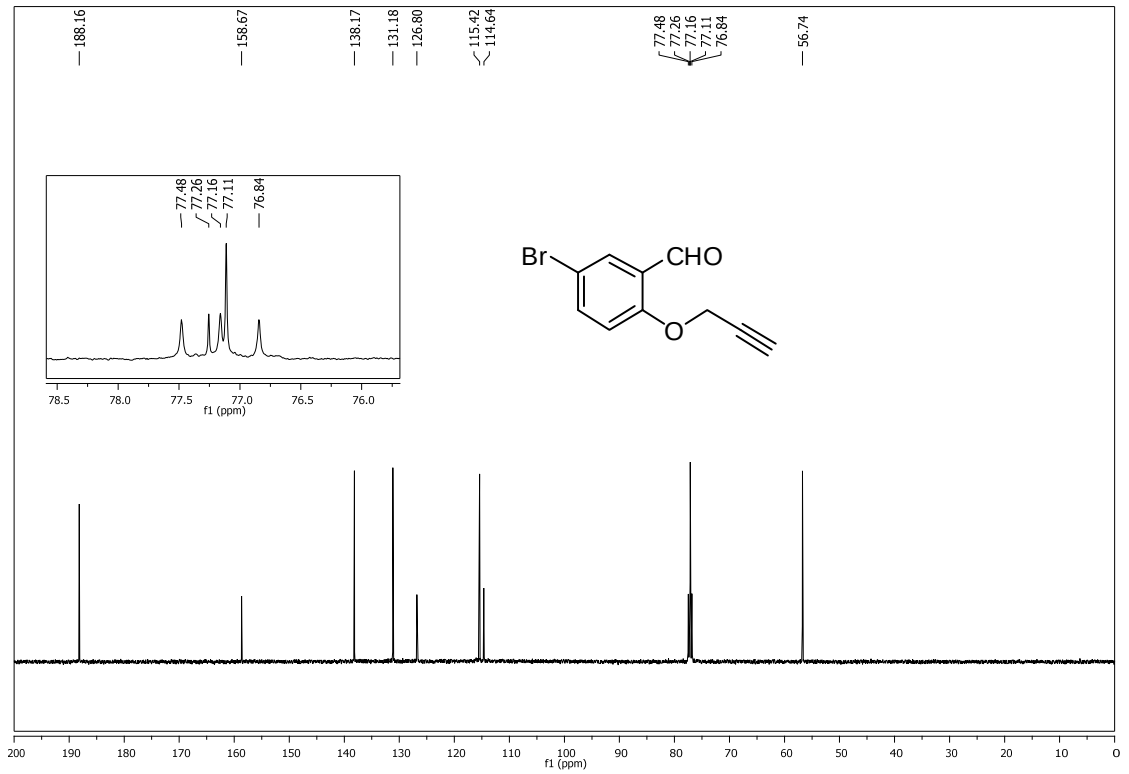
## 5-Chloro-2-prop-2-ynyloxy-benzaldehyde (4g)



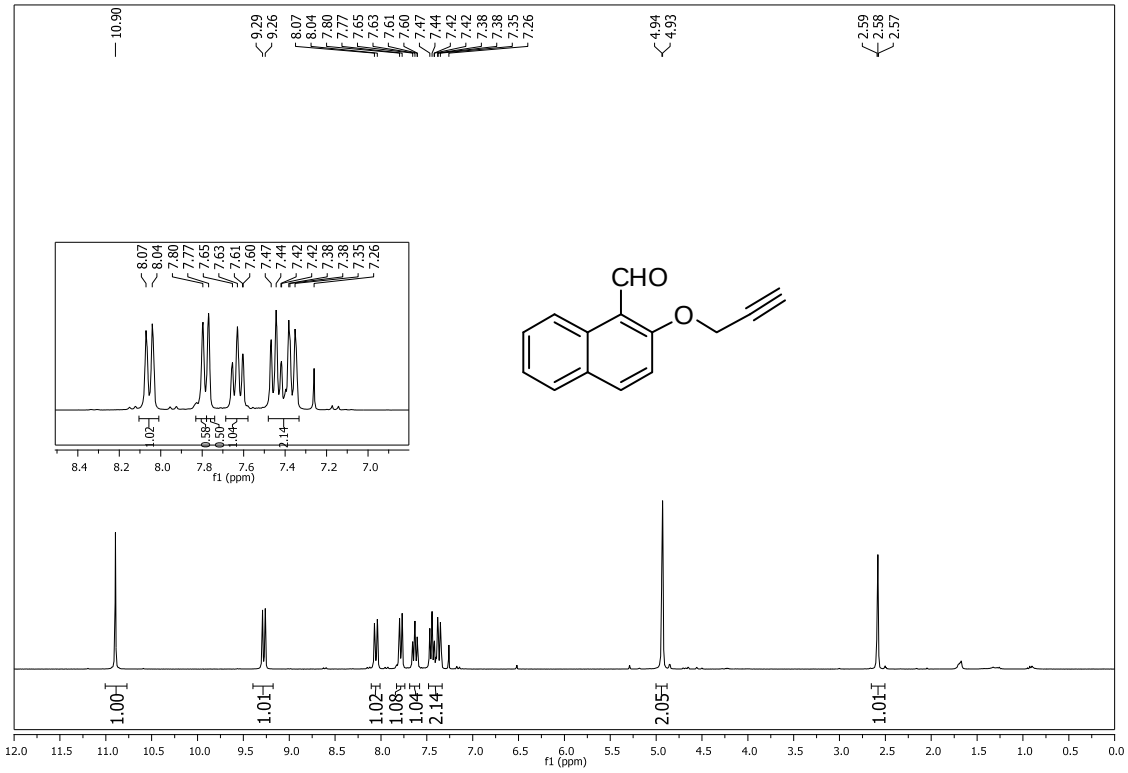



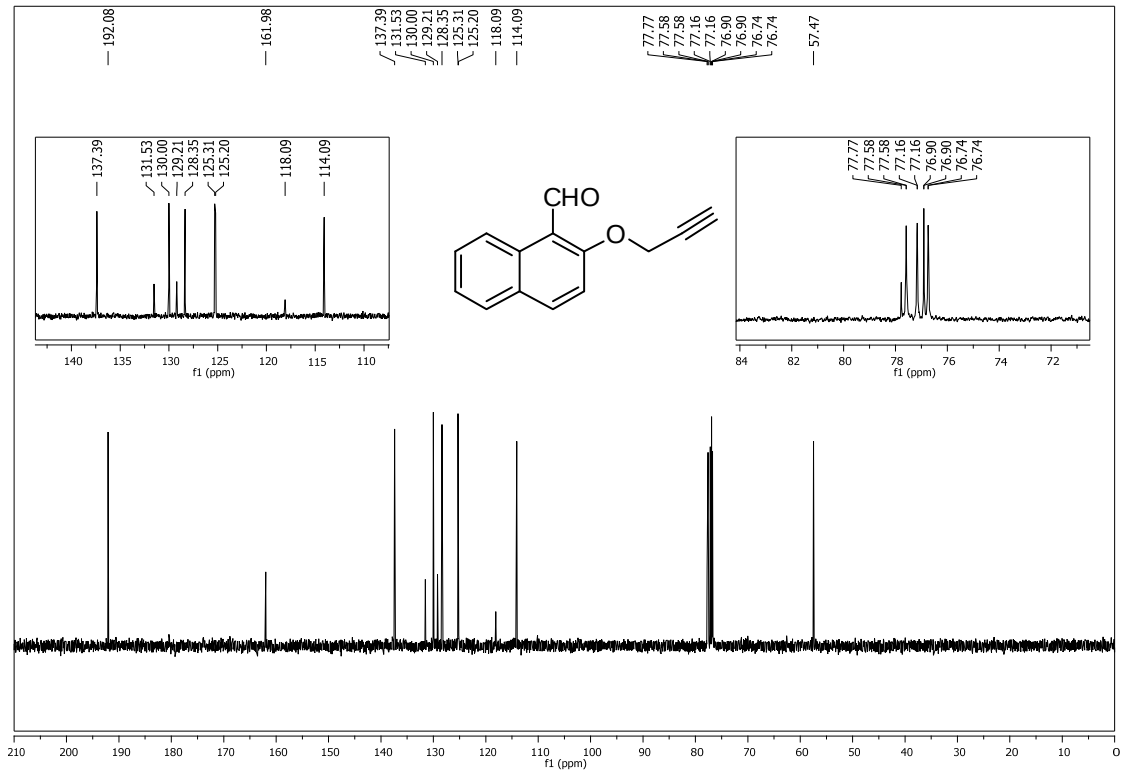
## 5-Bromo-2-prop-2-ynyloxy-benzaldehyde (4h)



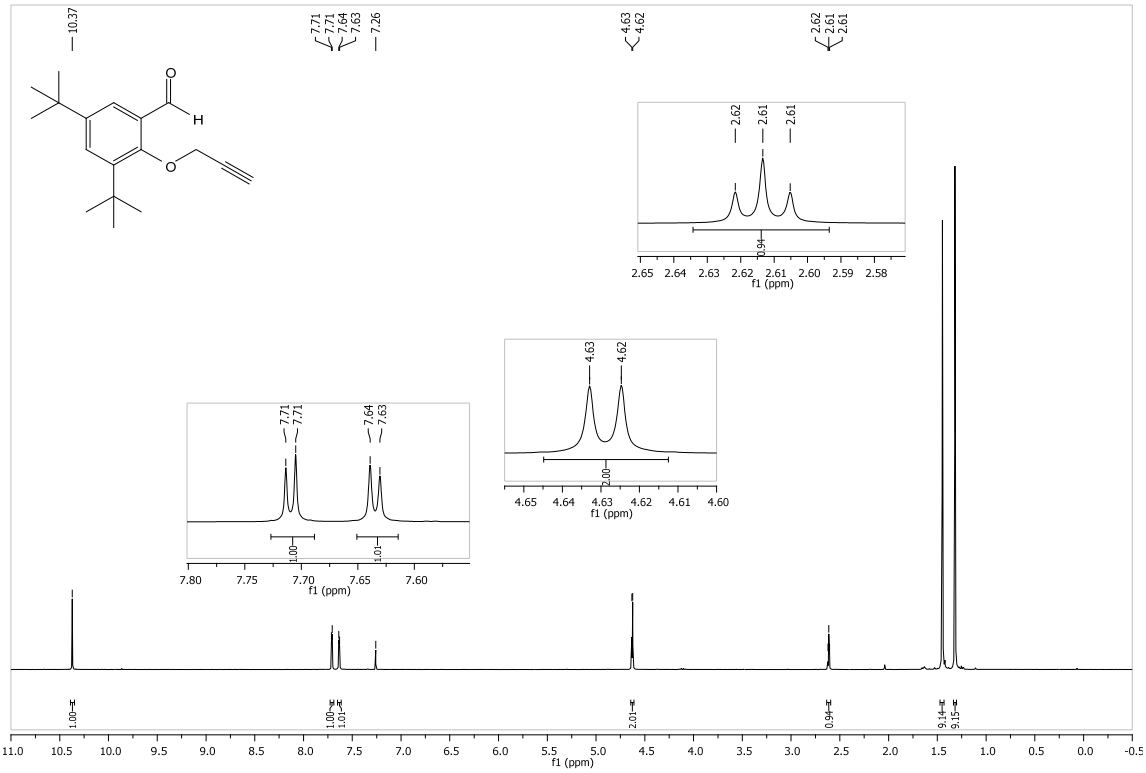



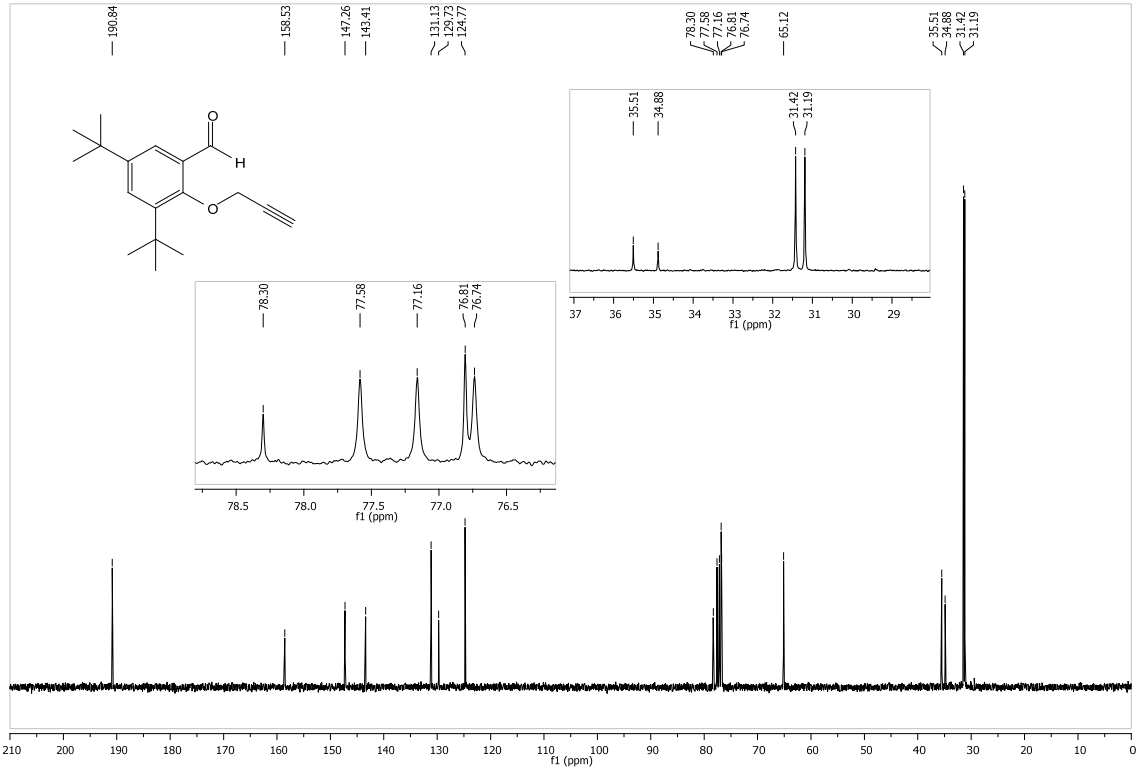
## 2-Prop-2-ynyloxy-naphthalene-1-carbaldehyde (4i)



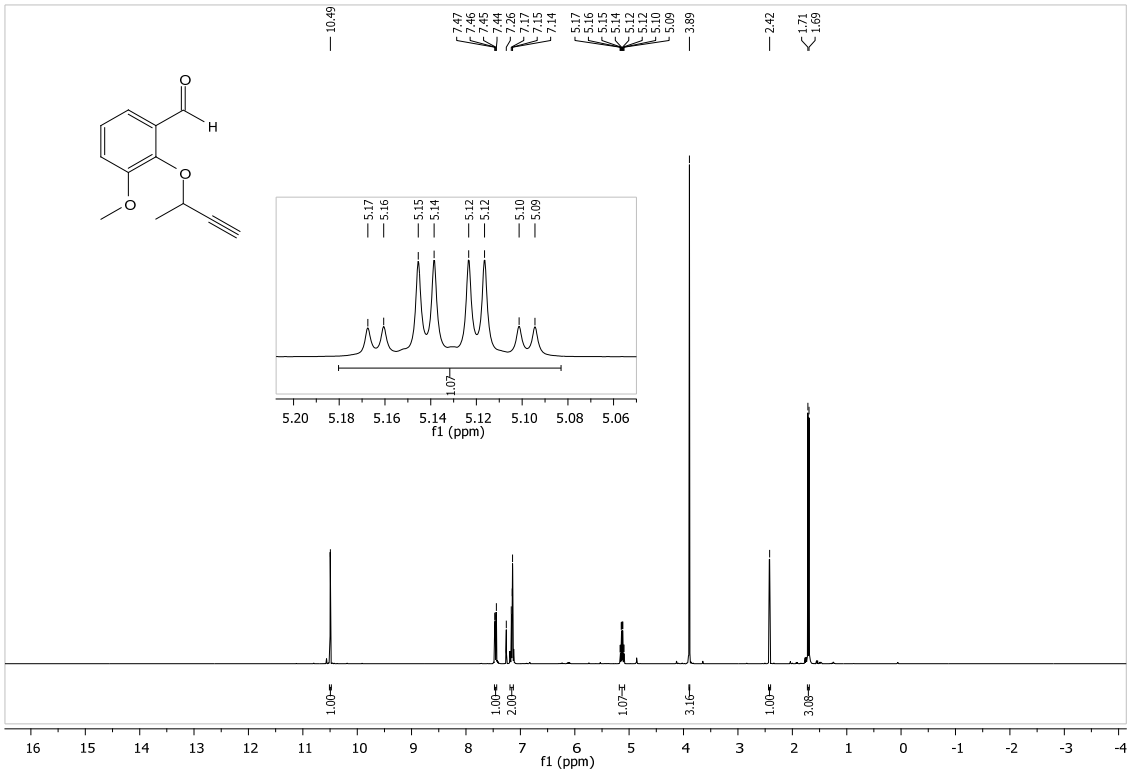



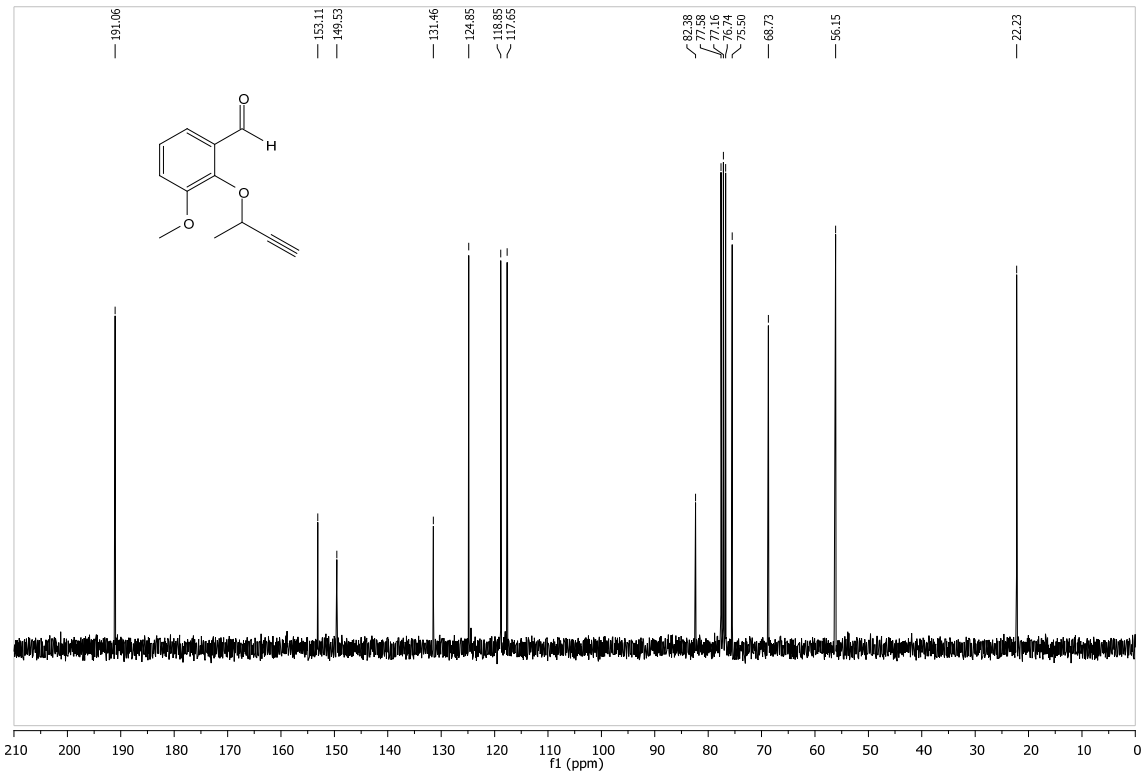
## 3,5-Di-*tert*-butyl-2-prop-2-ynyloxy-benzaldehyde (4j)



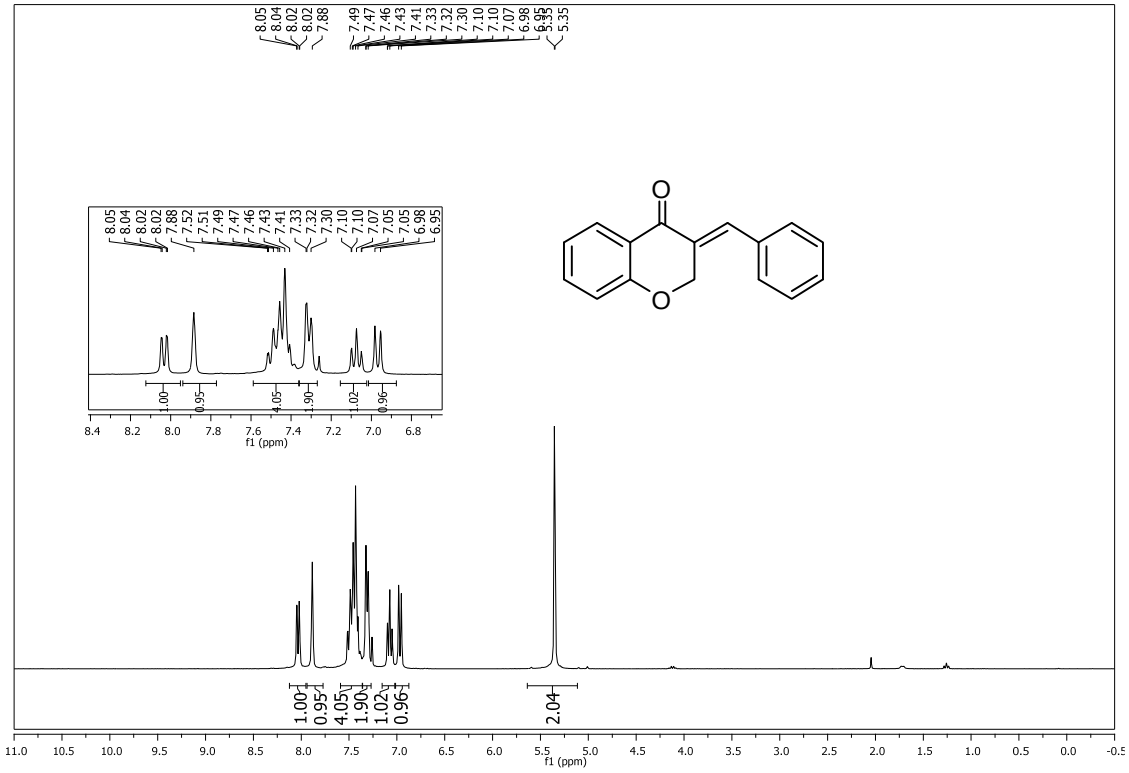
## 3-Methoxy-2-(1-methyl-prop-2-ynyloxy)-benzaldehyde (4k)

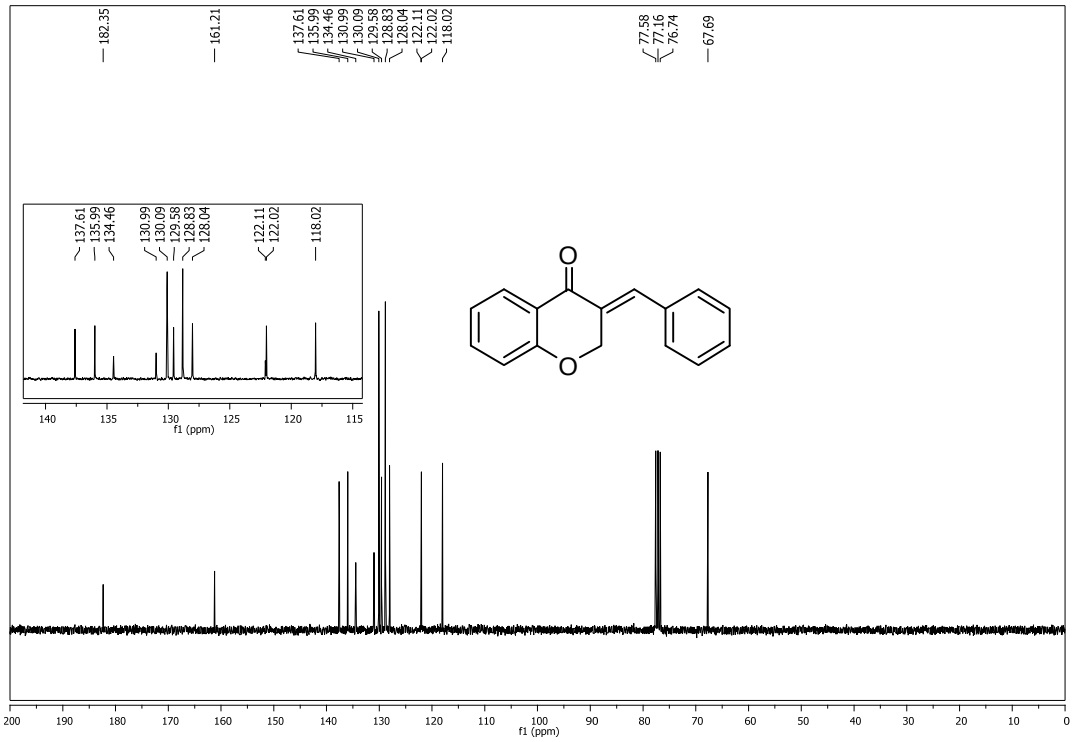


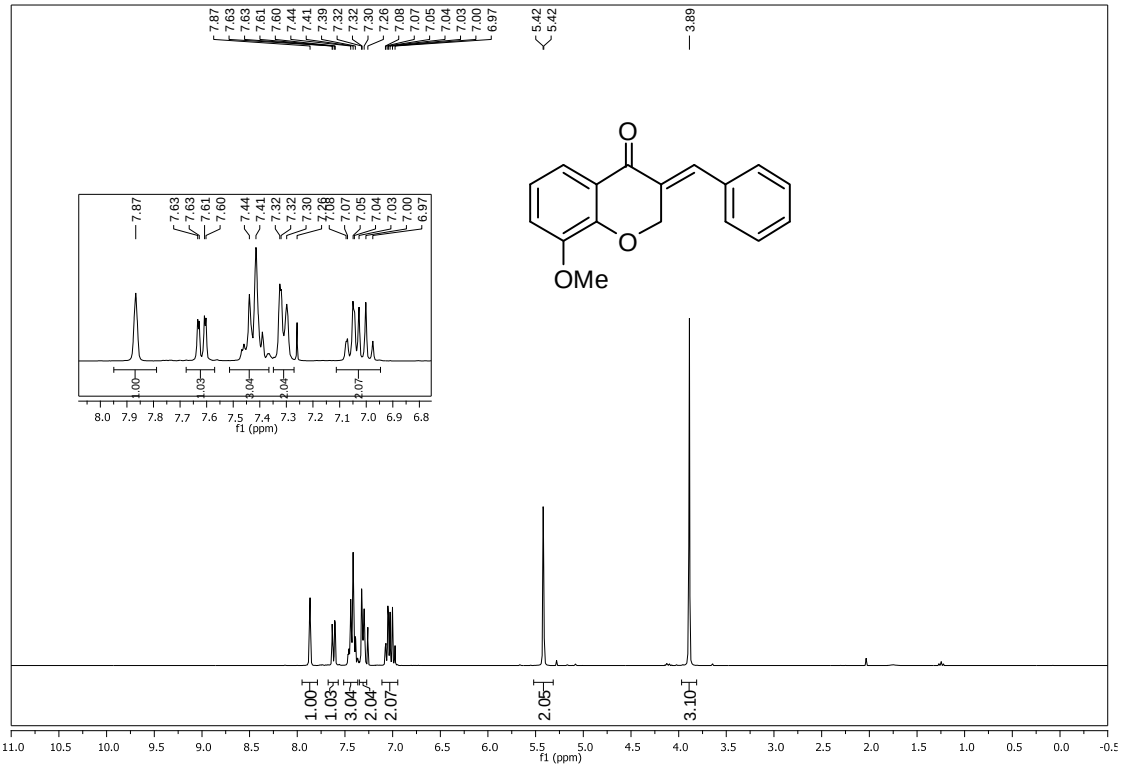
# 7. $^{1}H$ and $^{13}C$ NMR Spectra of Functionalized Chromanones

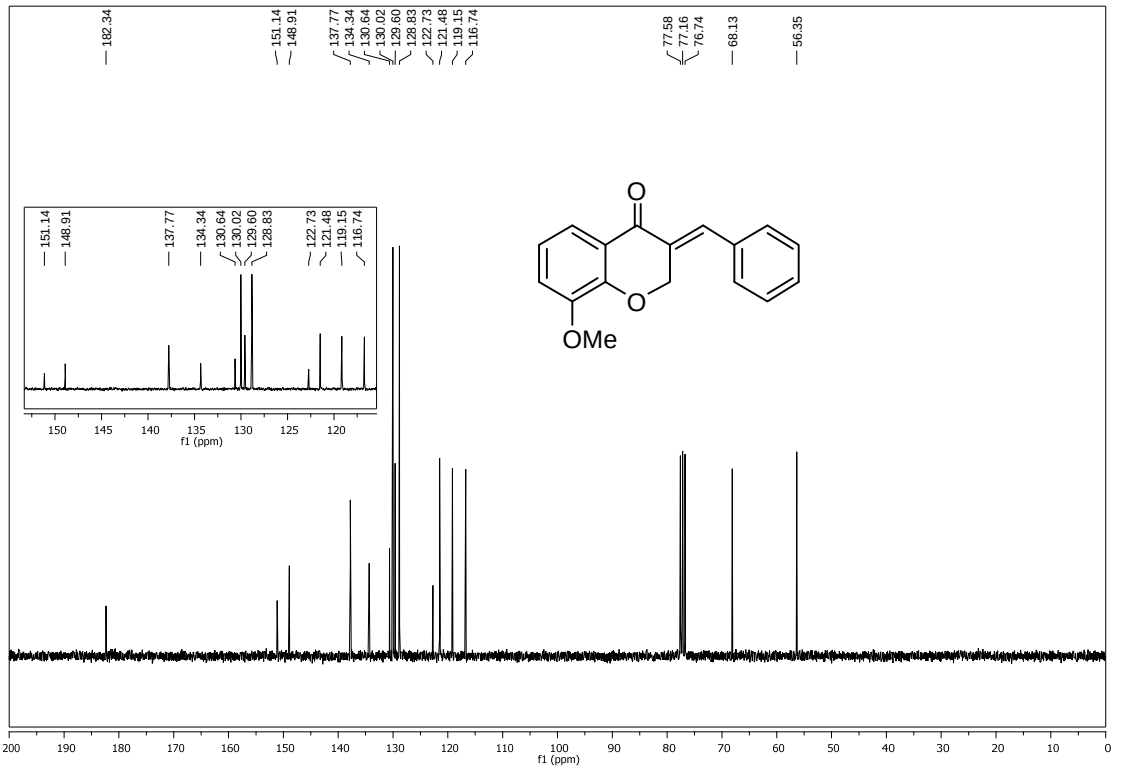
## 3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2a)



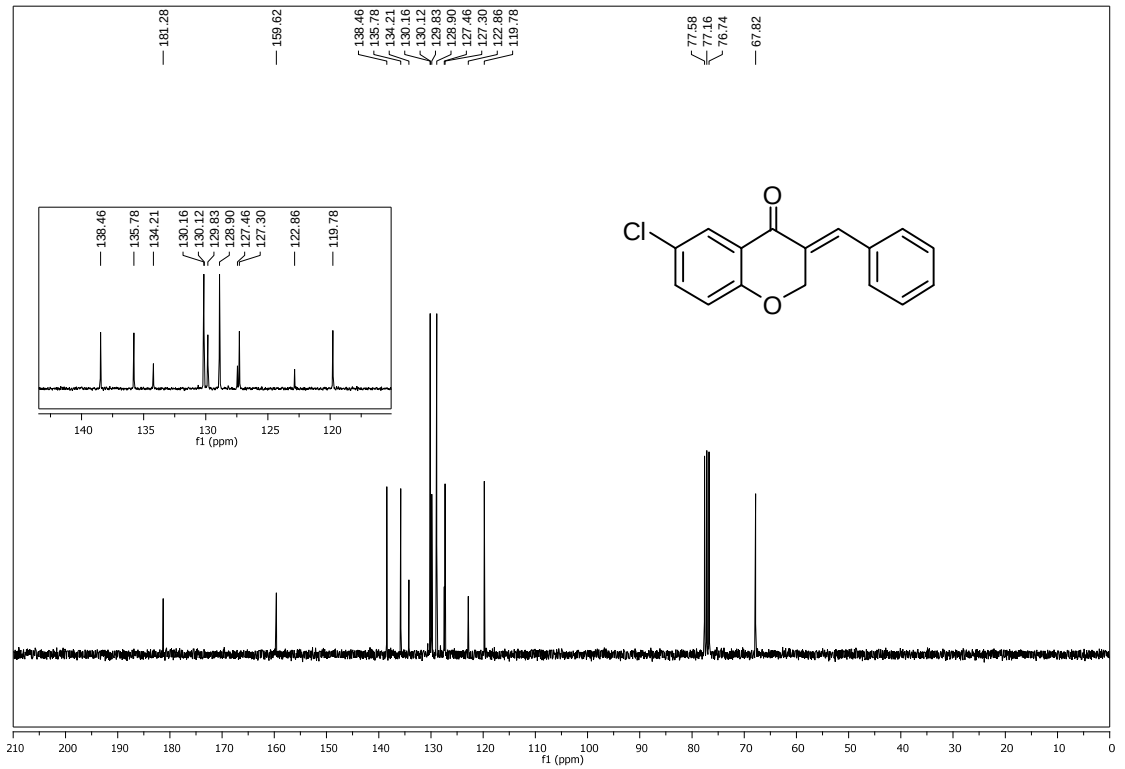



## 3-[1-Phenyl-meth-(E)-ylidene]-8-methoxy-chroman-4-one (2b)

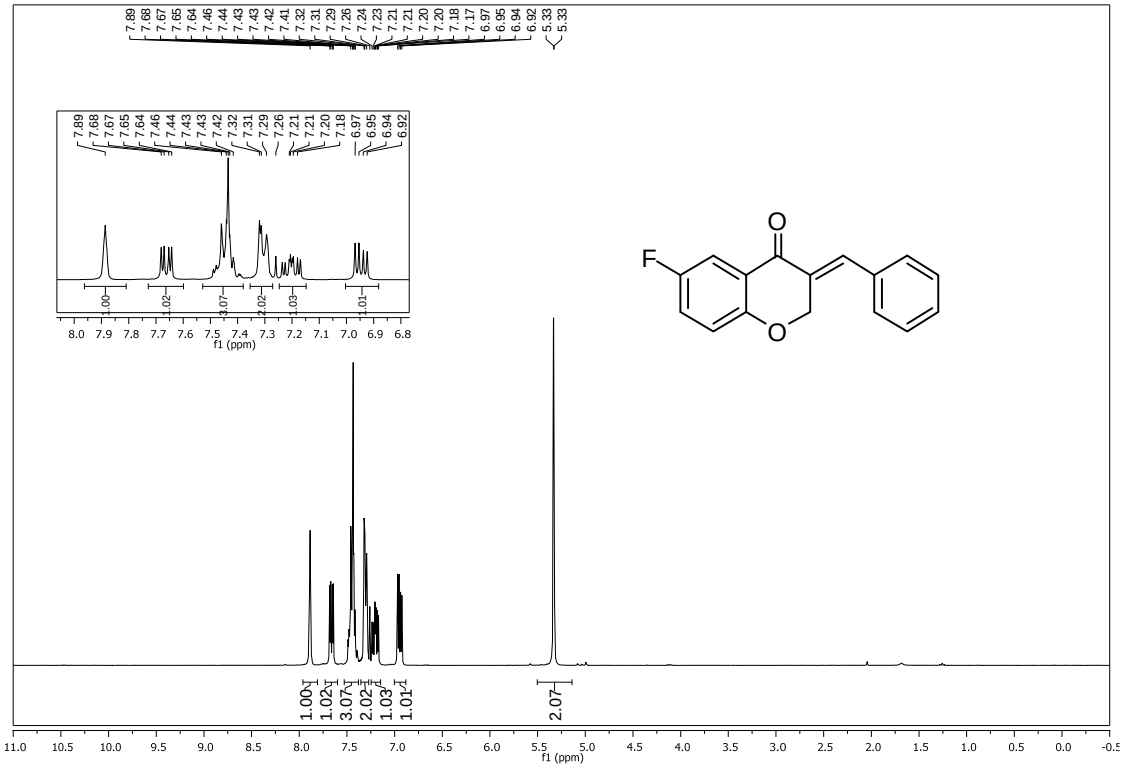


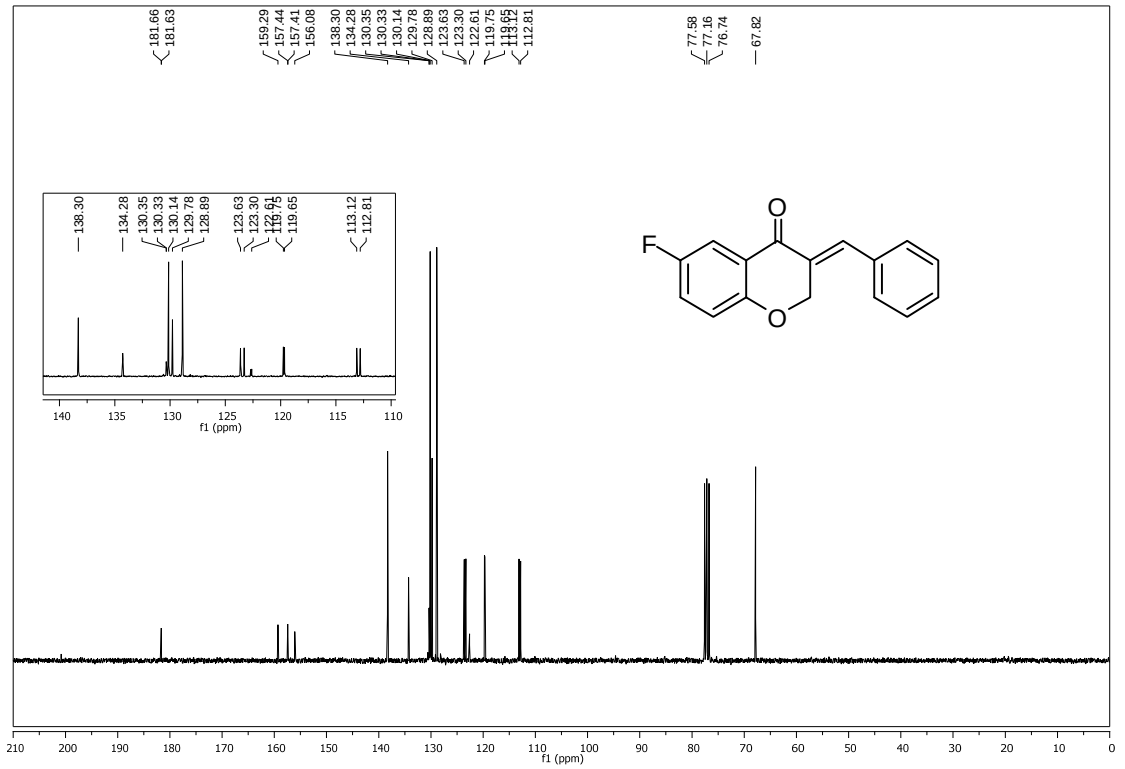



## 5-Chloro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2c)

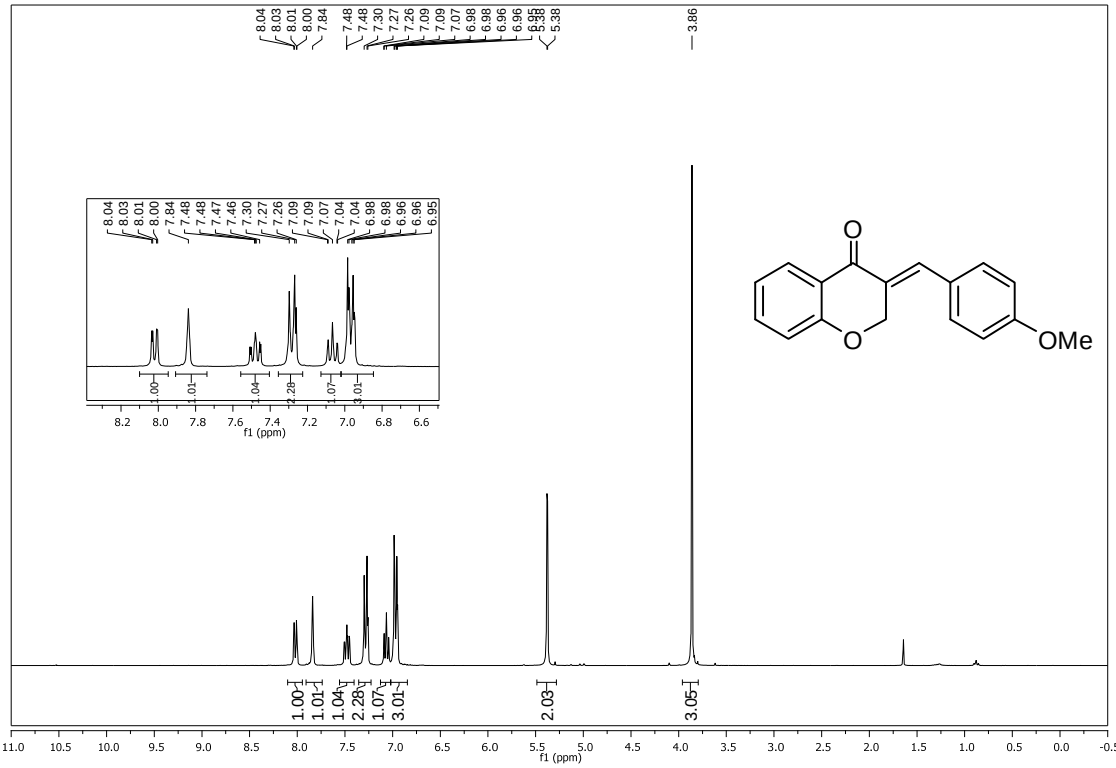



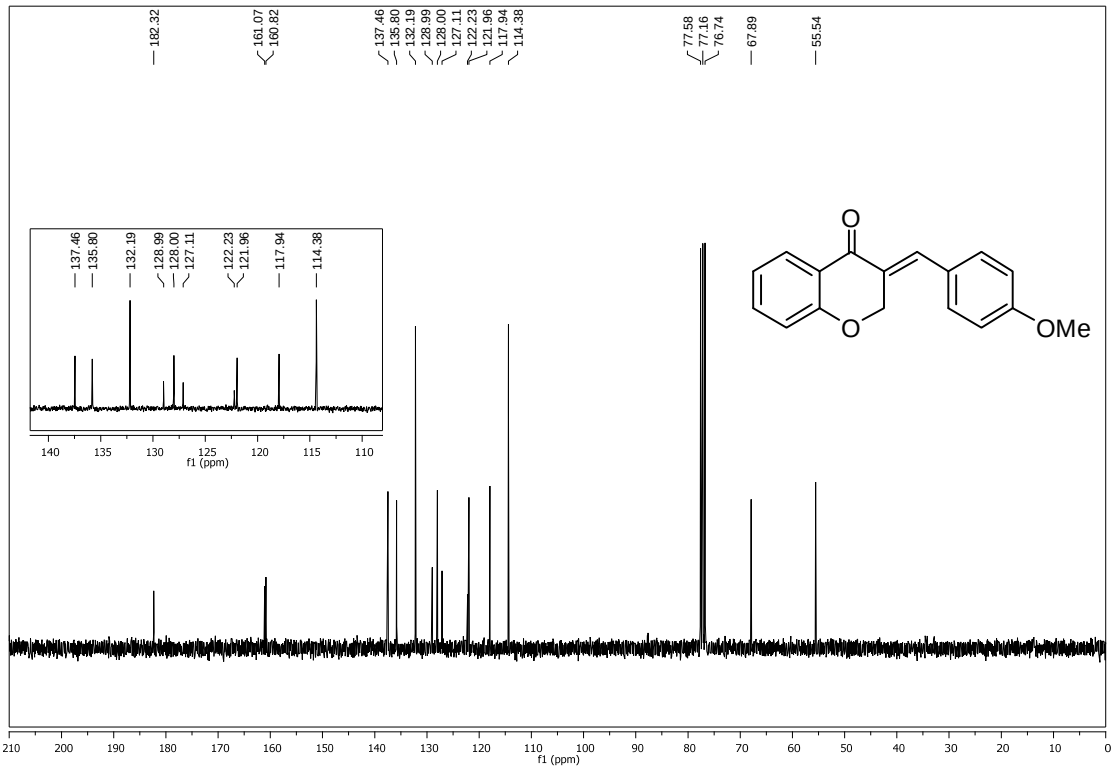
## 6-Fluoro-3-[1-Phenyl-meth-(E)-ylidene]-chroman-4-one (2d)



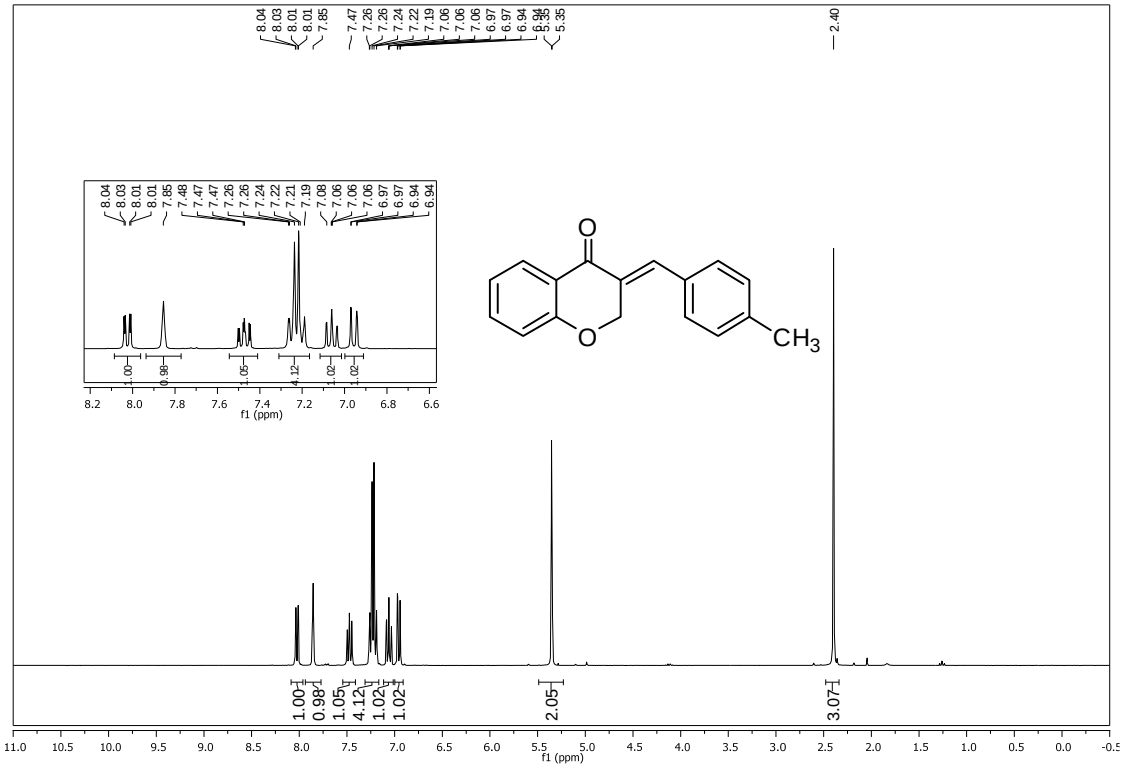



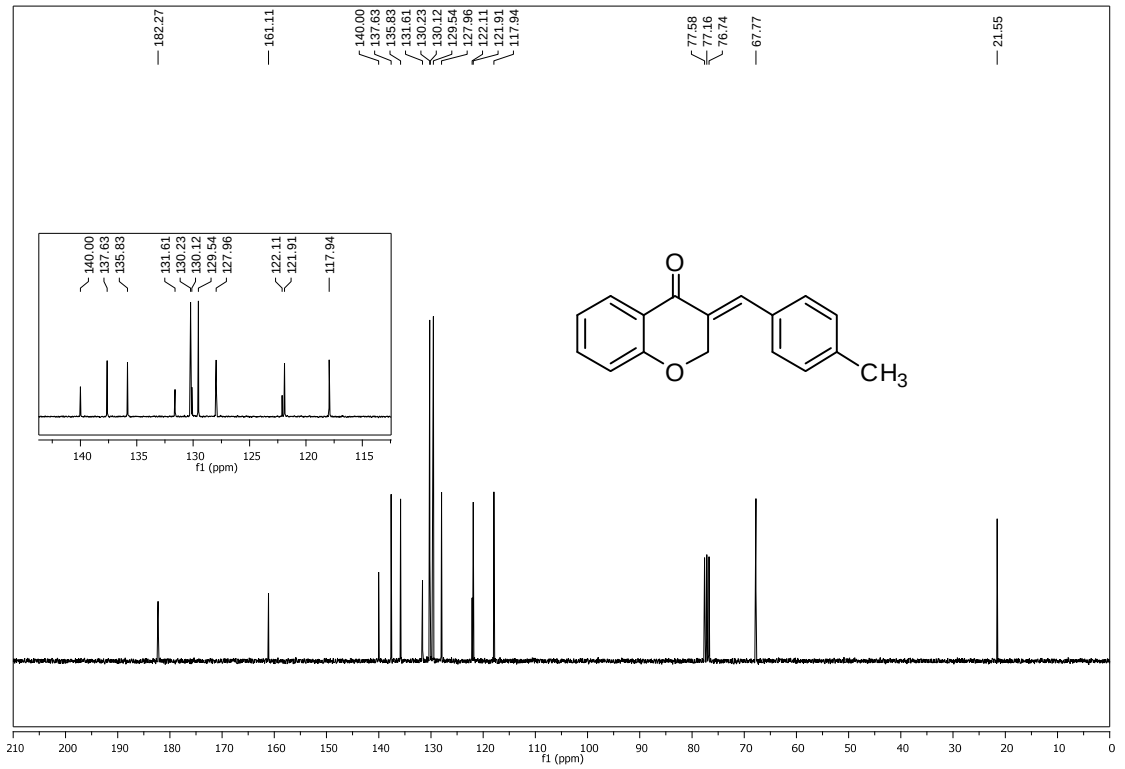
## 3-[1-(4-Methoxy phenyl)-meth-(E)-ylidene]-chroman-4-one (2e)



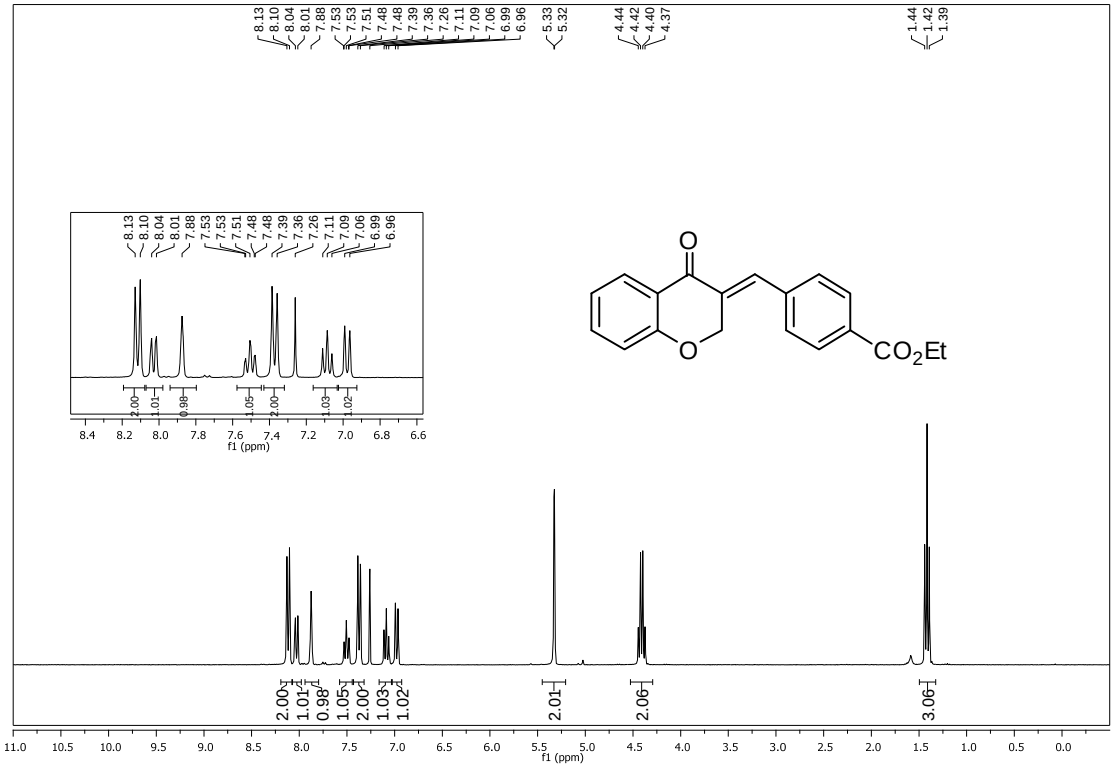



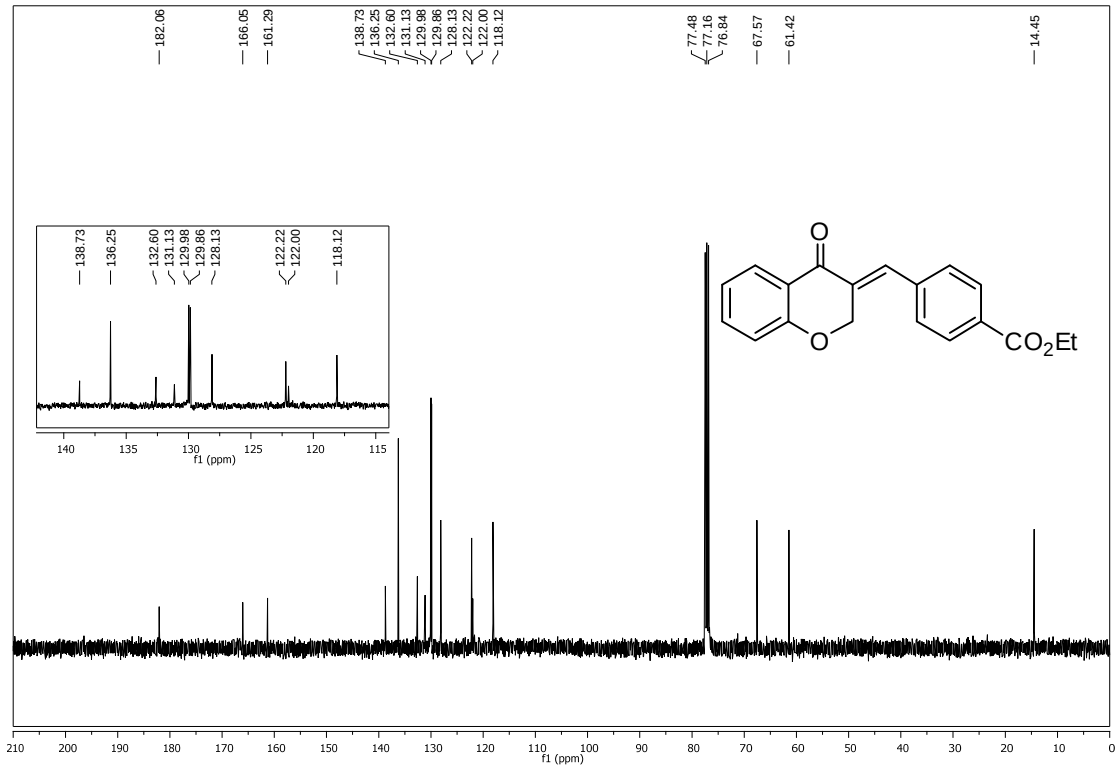
## 3-[1-(4-Methyl phenyl)-meth-(E)-ylidene]-chroman-4-one (2f)



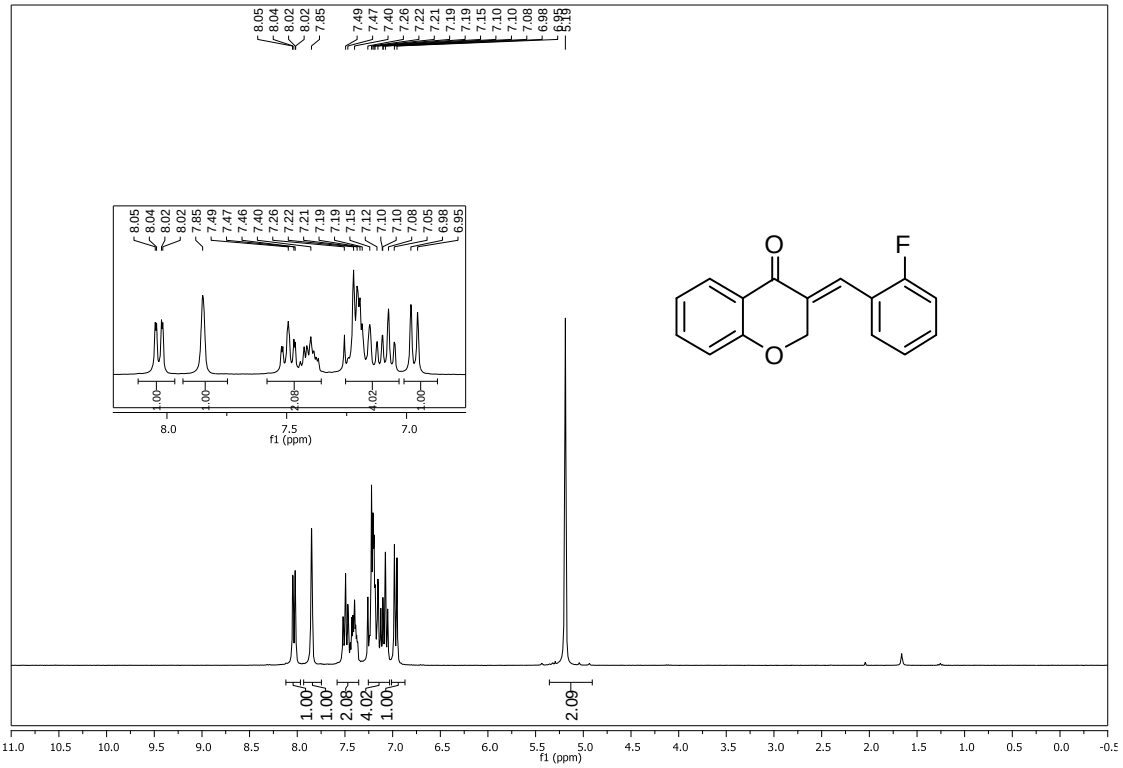



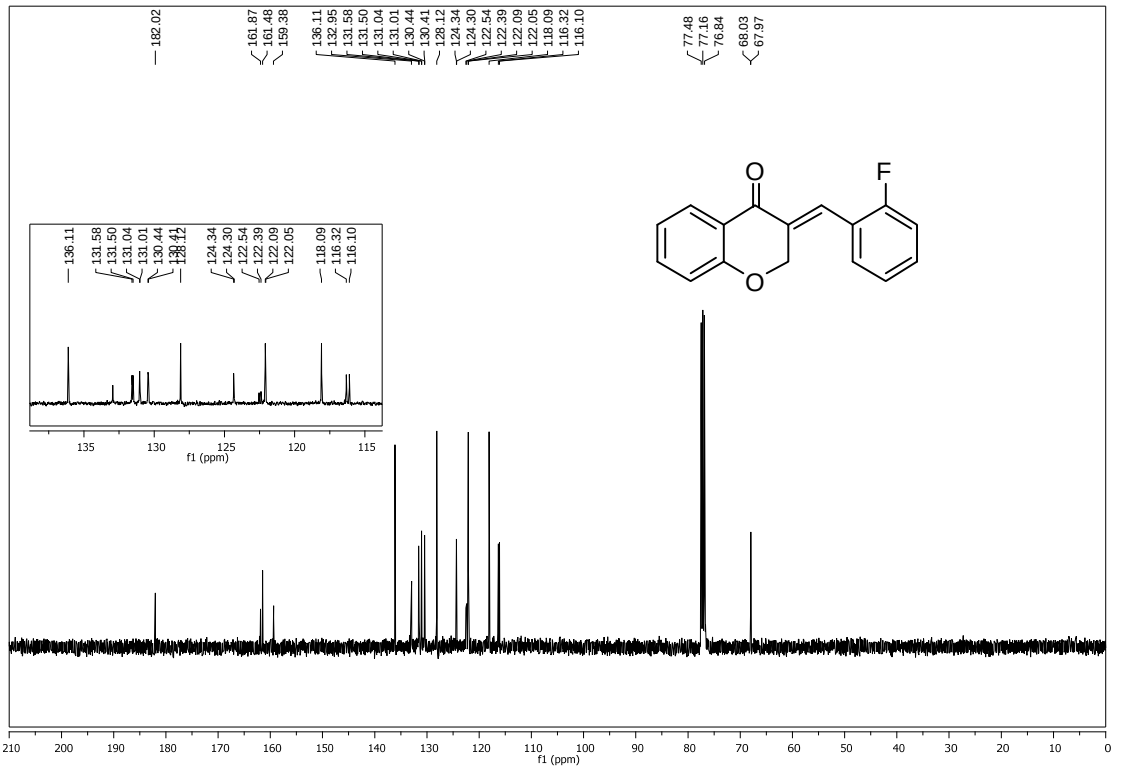
## 3-[1-(4-Carboethoxy phenyl)-meth-(E)-ylidene]-chroman-4-one (2g)



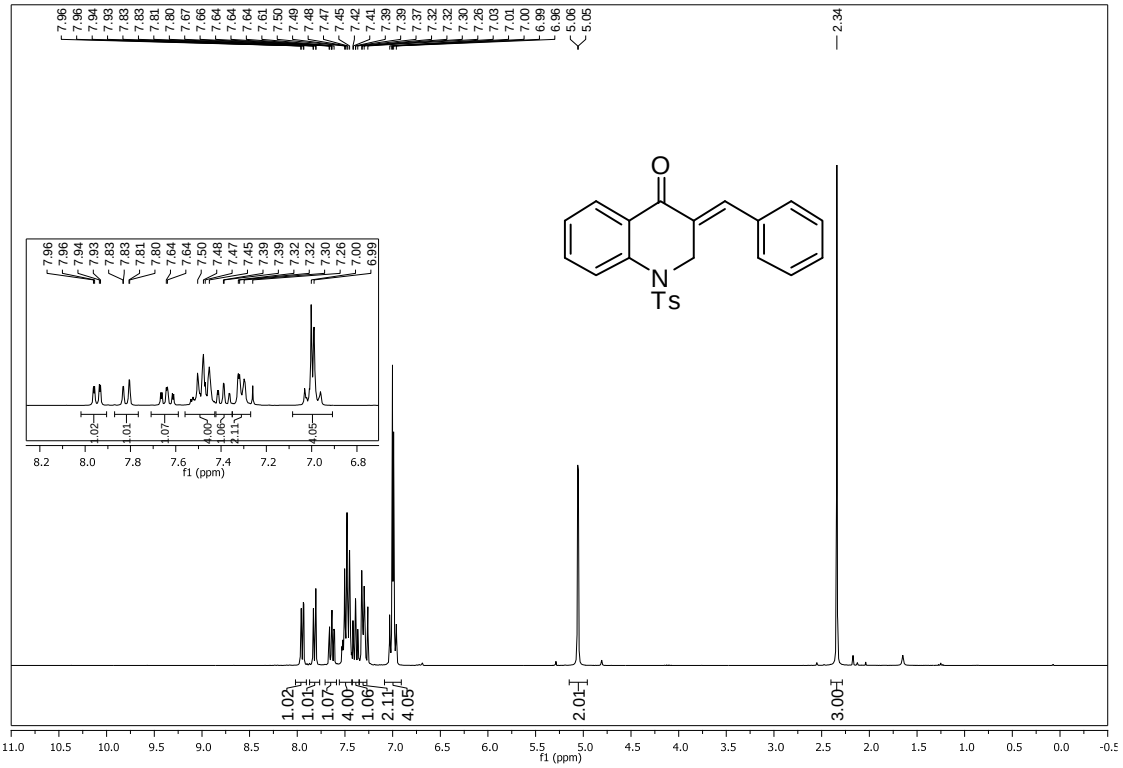



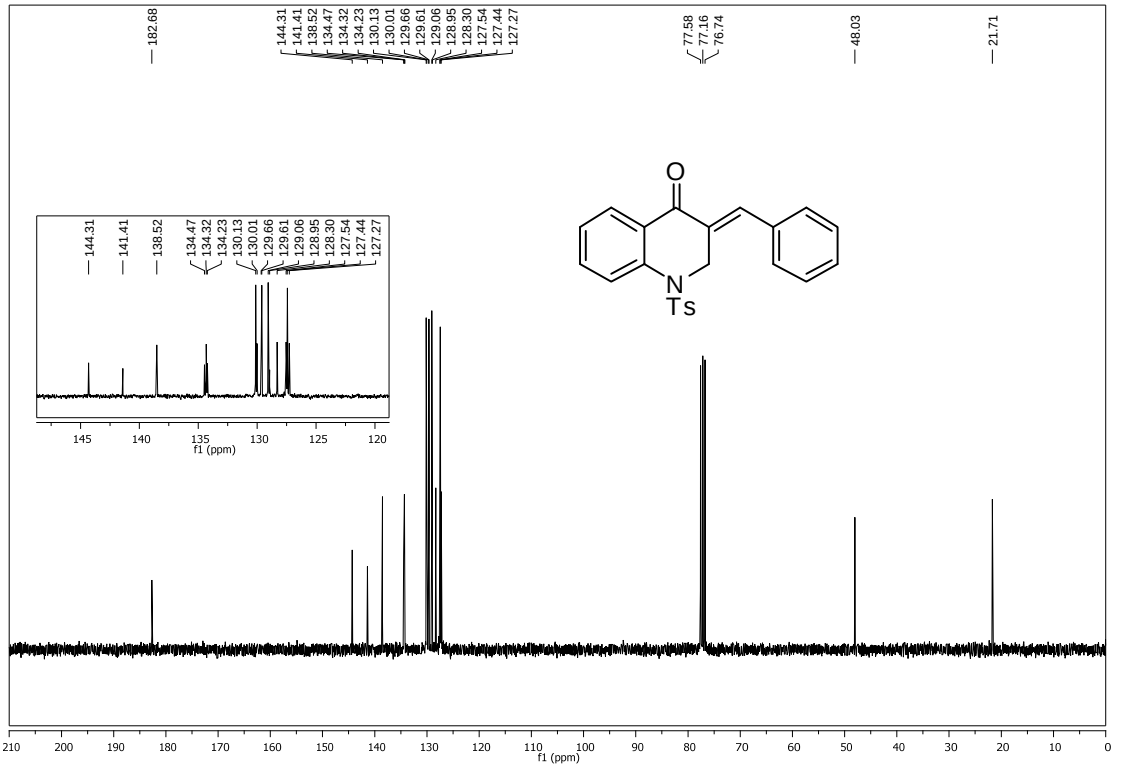
## 3-[1-(2-Fluoro phenyl)-meth-(E)-ylidene]-chroman-4-one (2h)



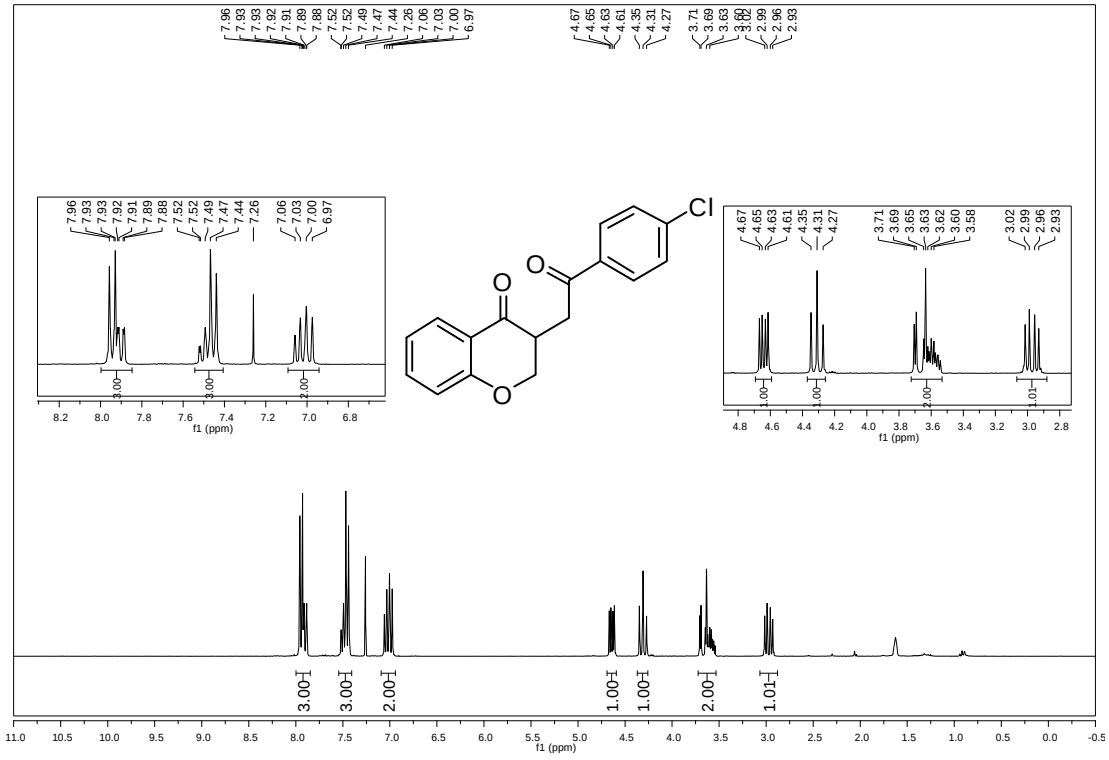



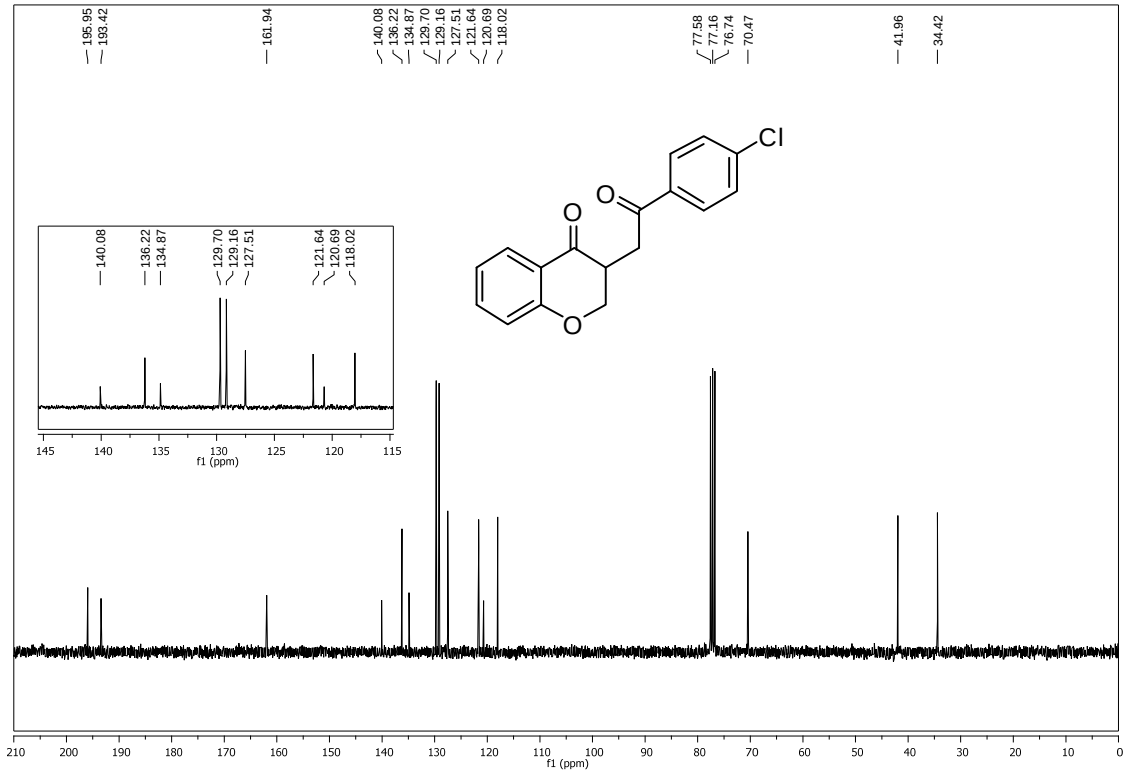
**3-[1-(2- Phenyl)-meth-(E)-ylidene]-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-quinolin-4-one (2i)**



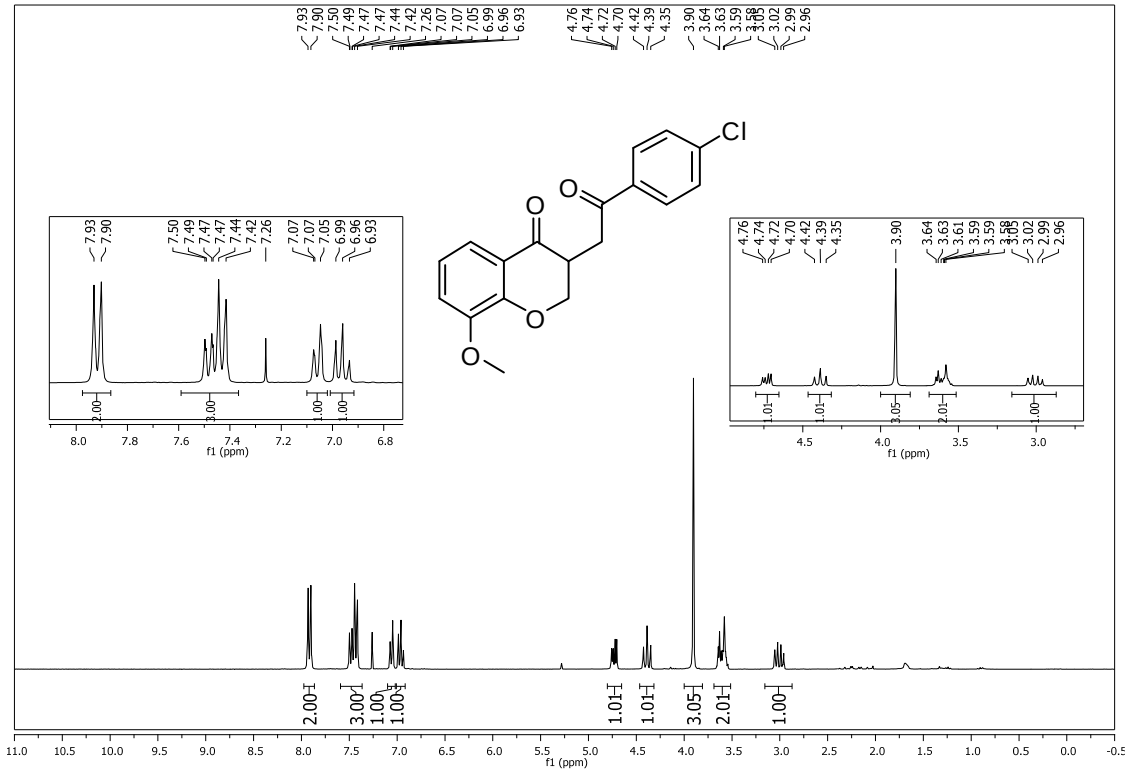



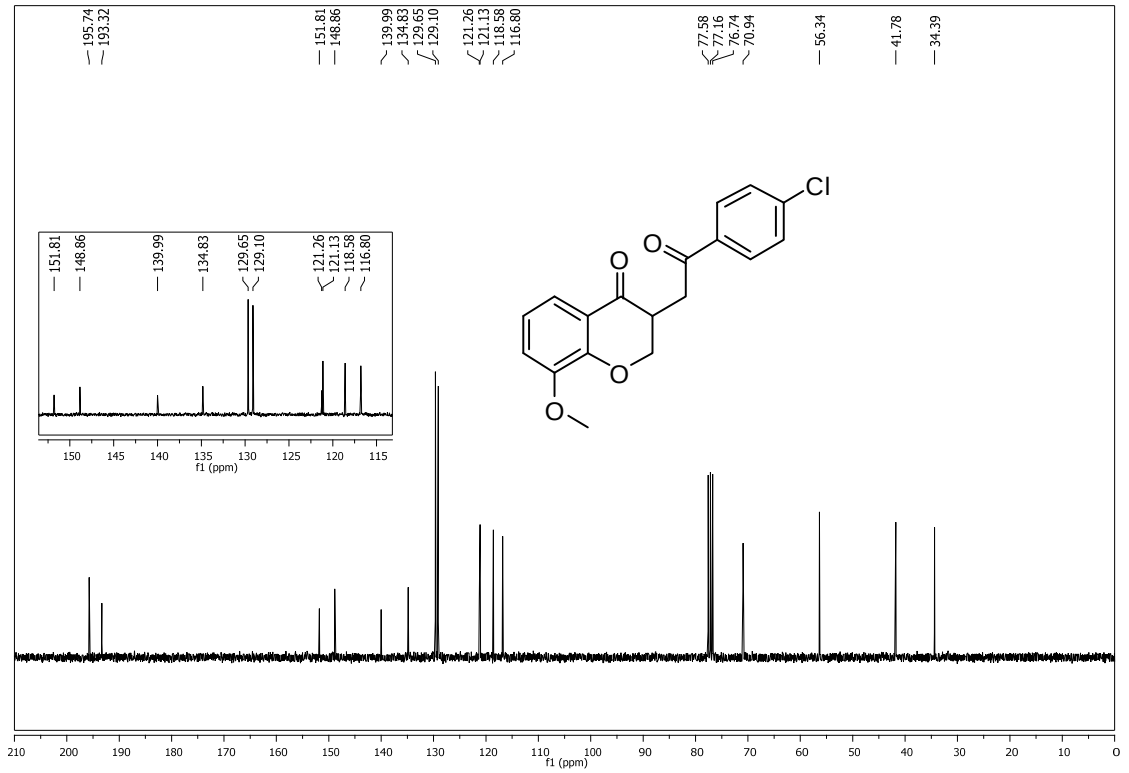
## 3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6a)



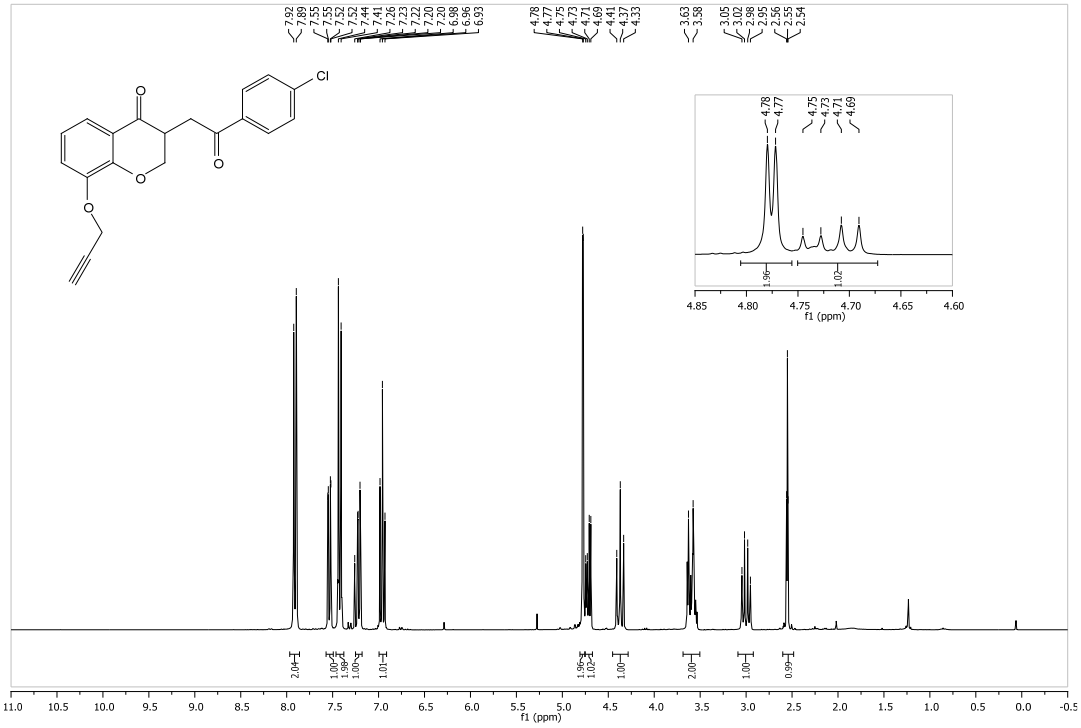



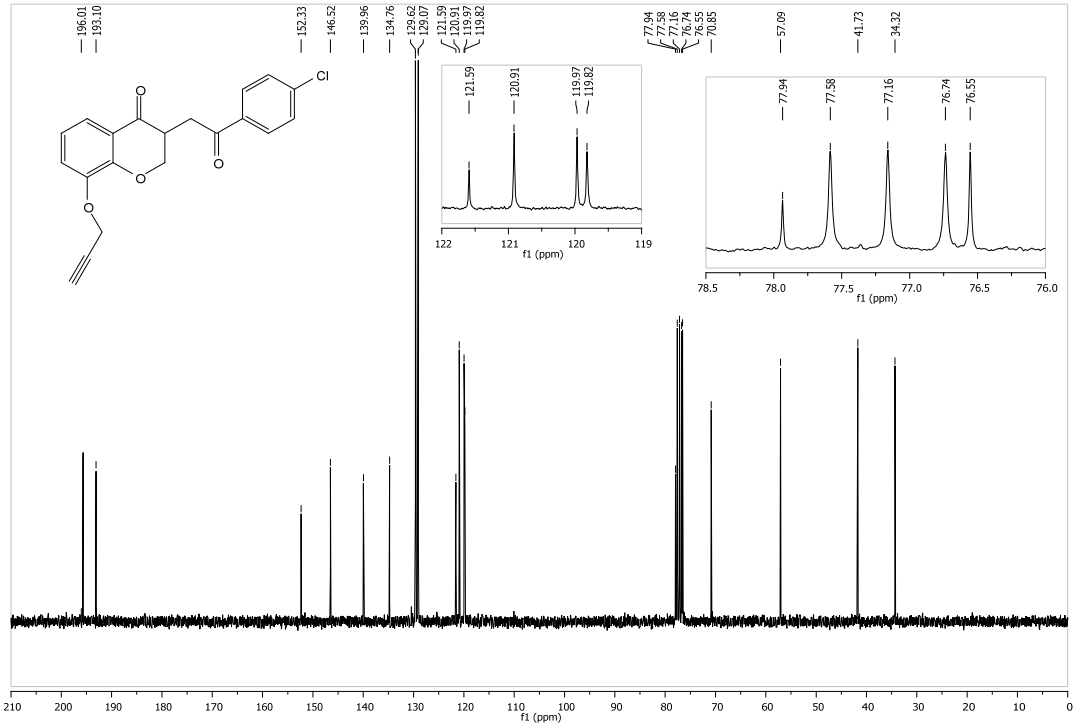
## 3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6b)



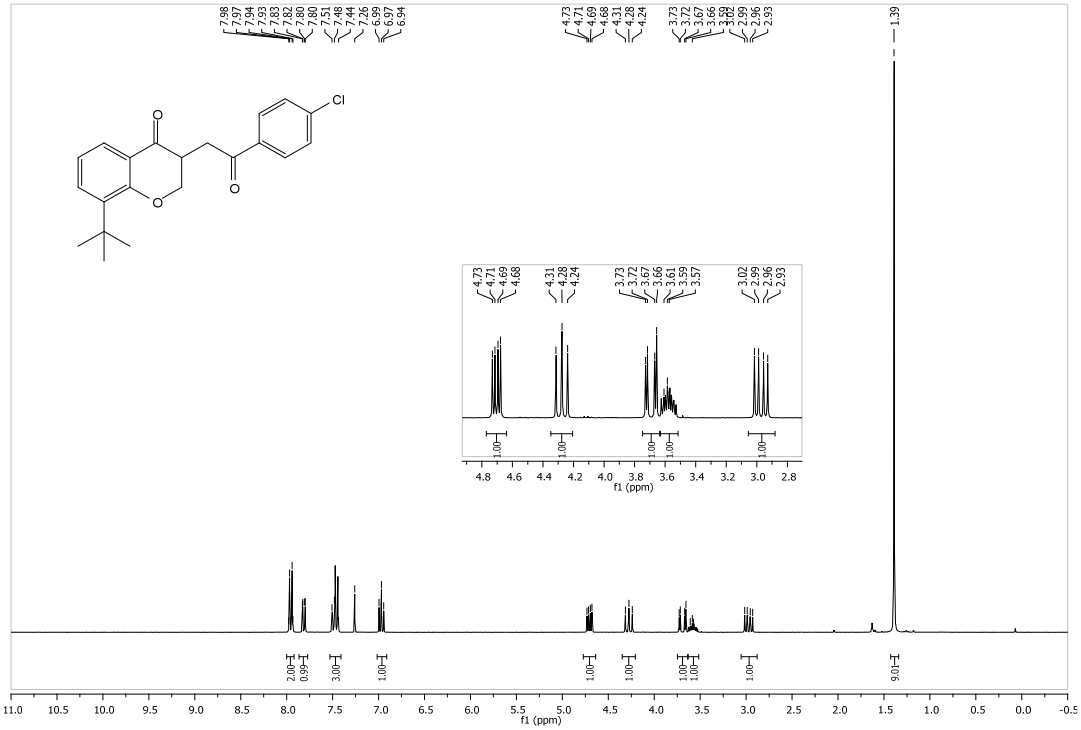



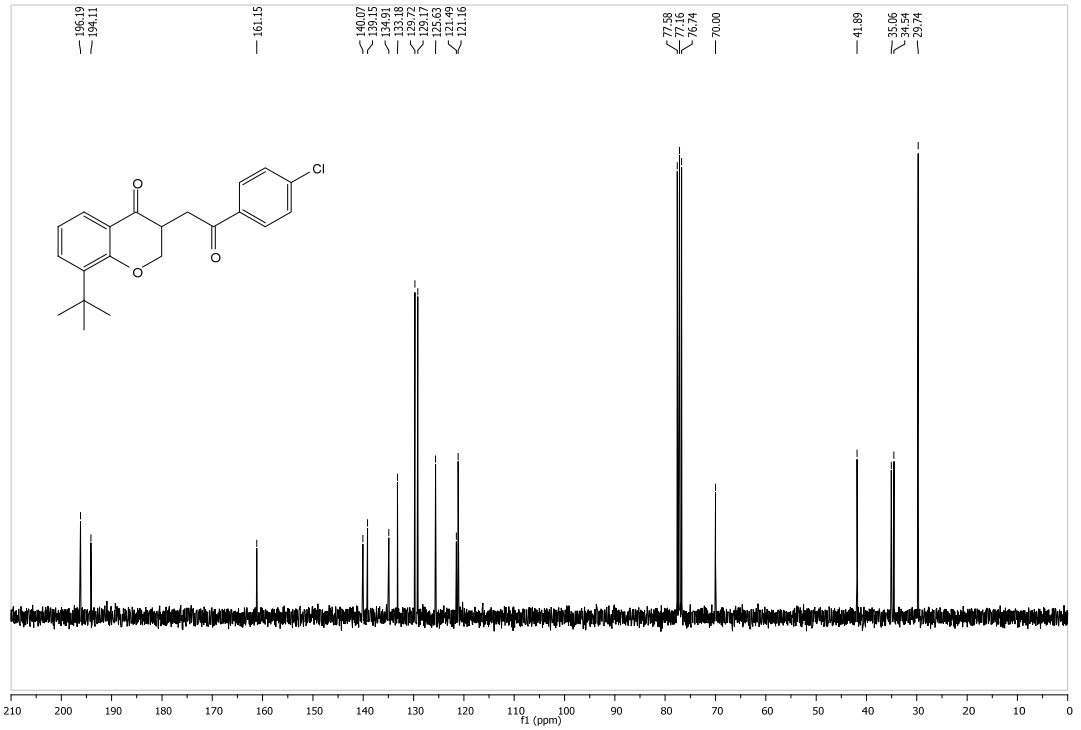
## 3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-8-prop-2-ynyloxy-chroman-4-one (6c)



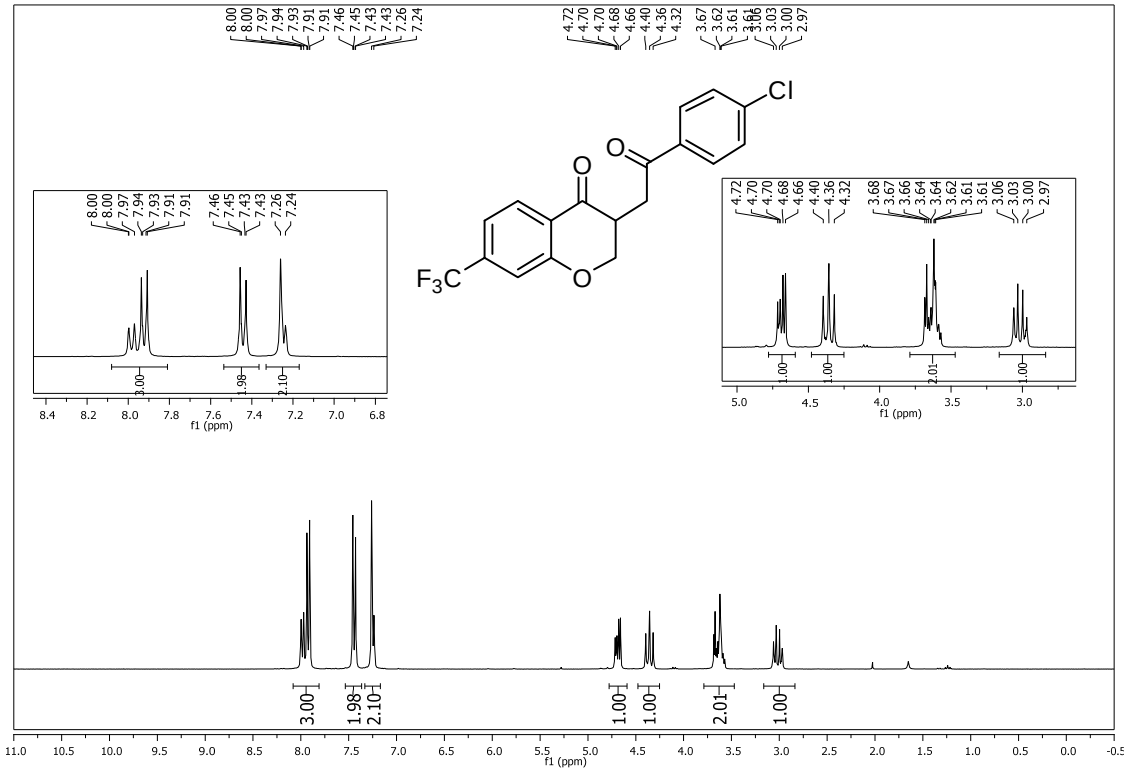


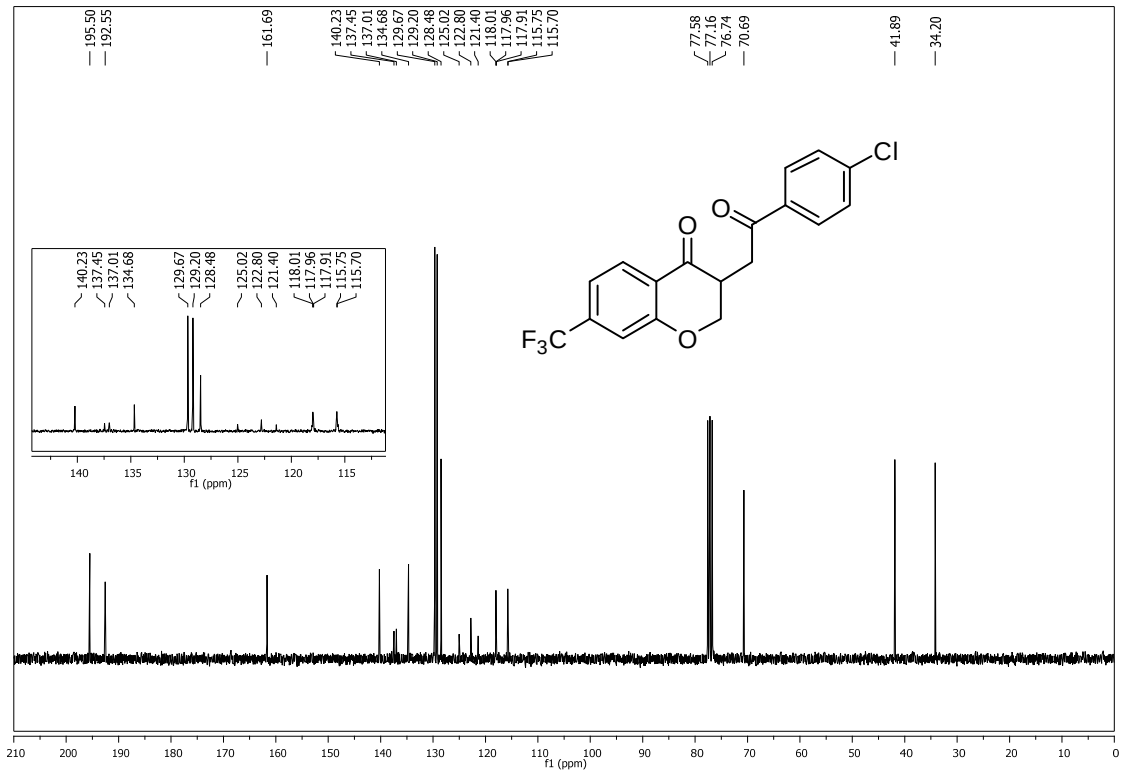
## 8-*tert*-Butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6d)



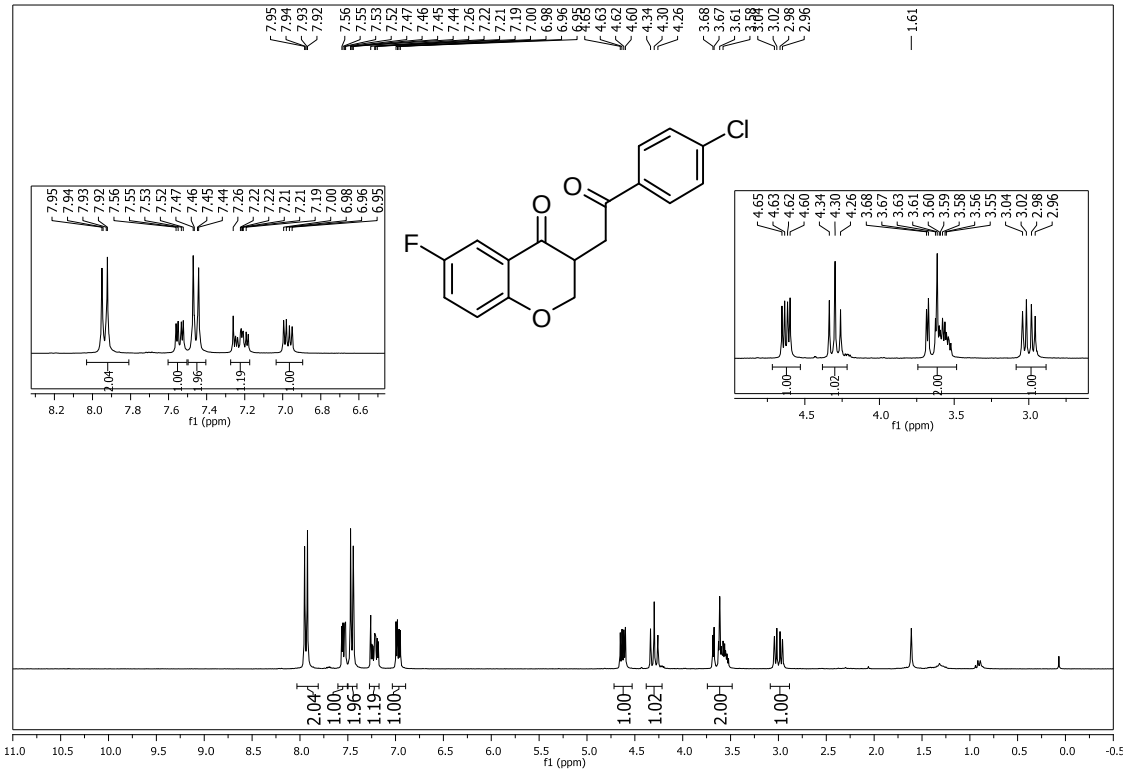



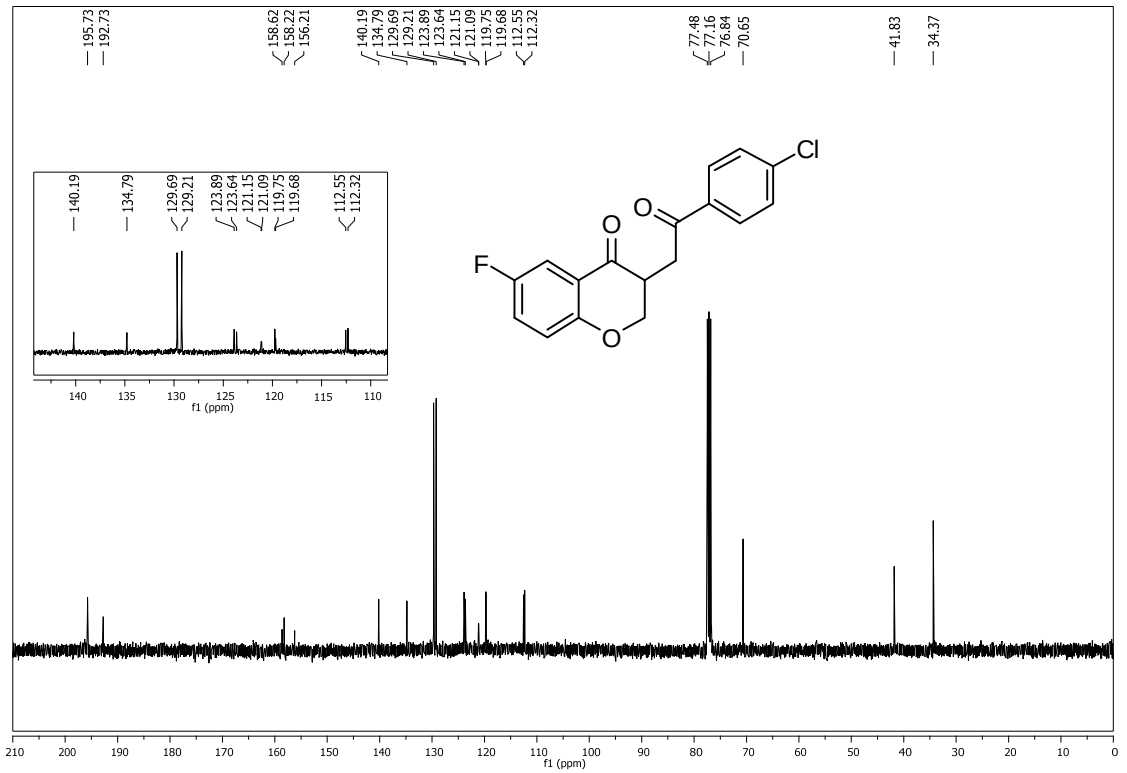
## 3-(2-Oxo-2-phenyl-ethyl)-7-trifluoromethyl-chroman-4-one (6e)



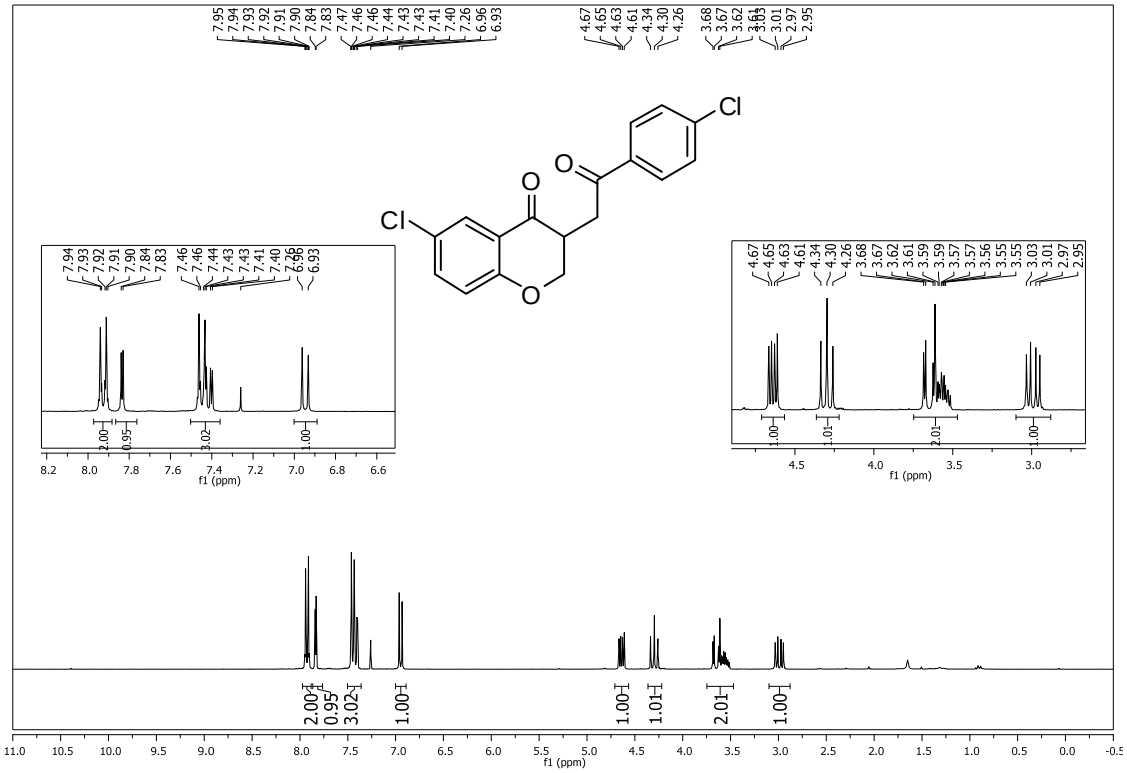



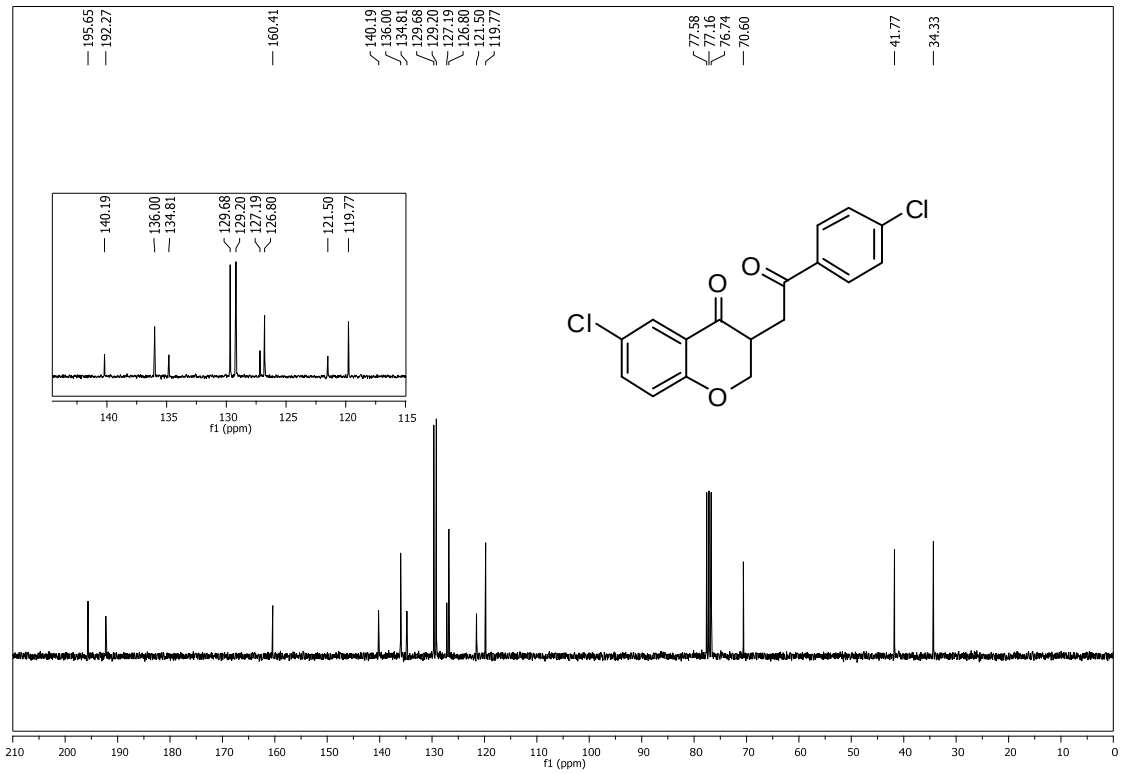
## 3-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-6-fluoro-chroman-4-one (6f)



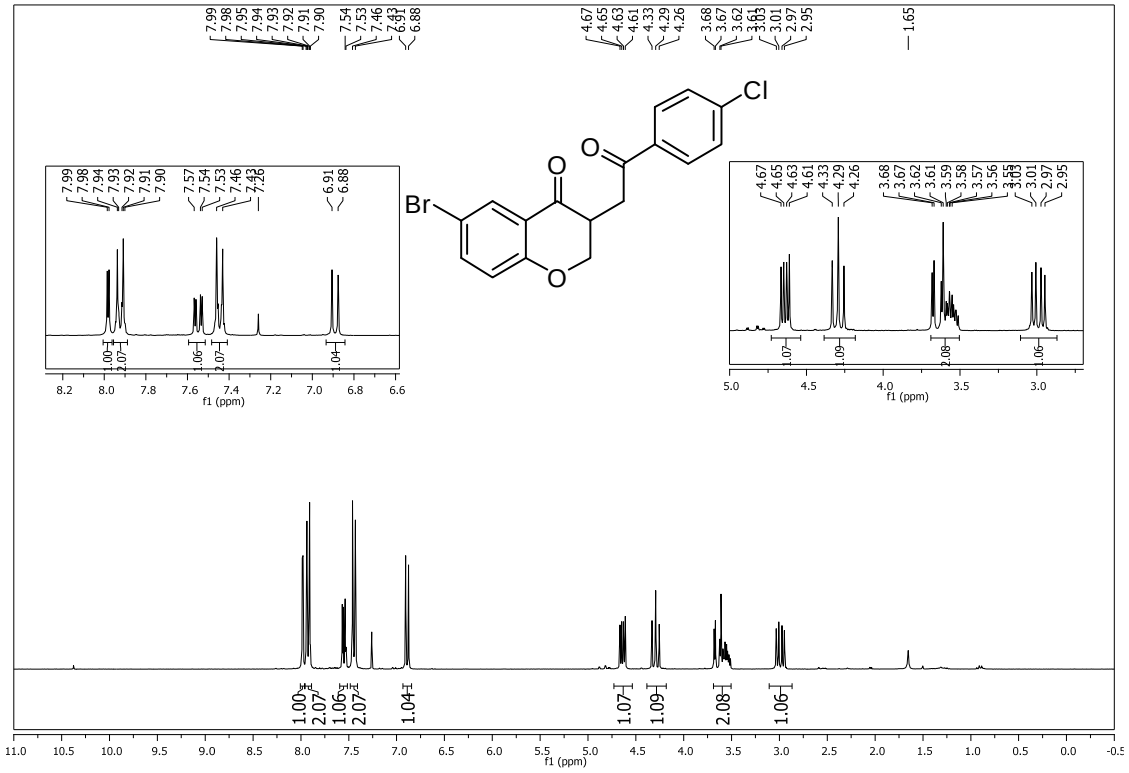



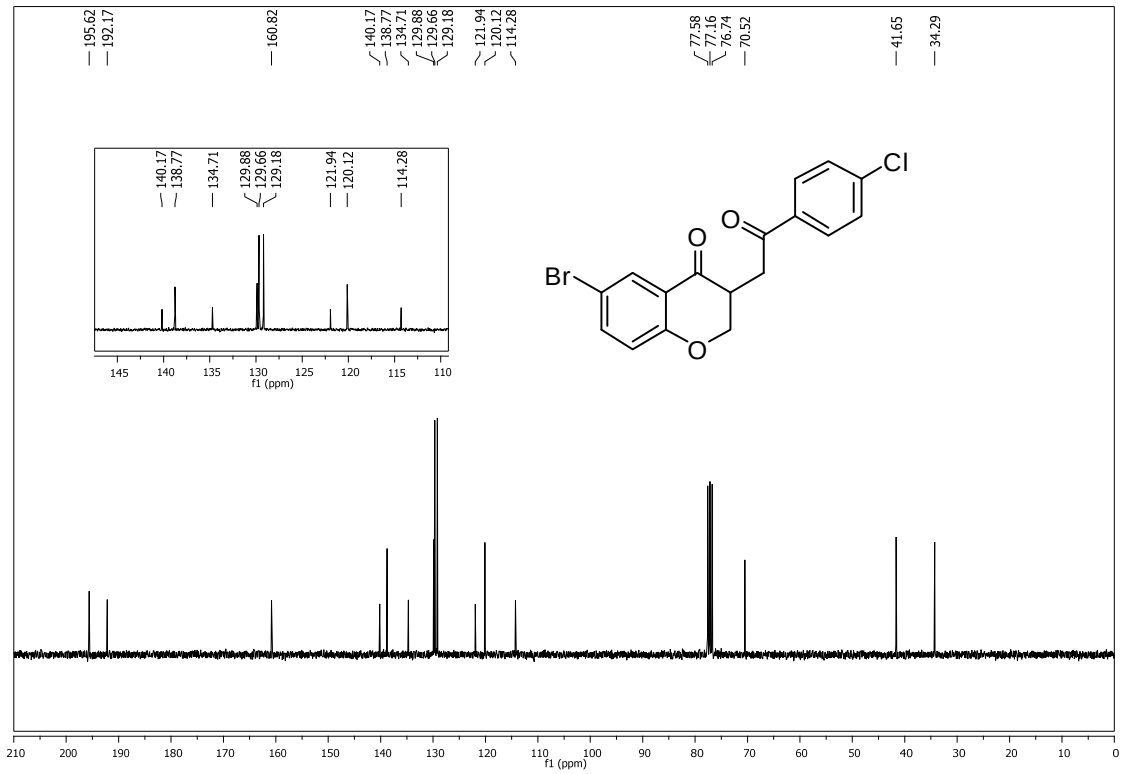
## 6-Chloro-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6g)



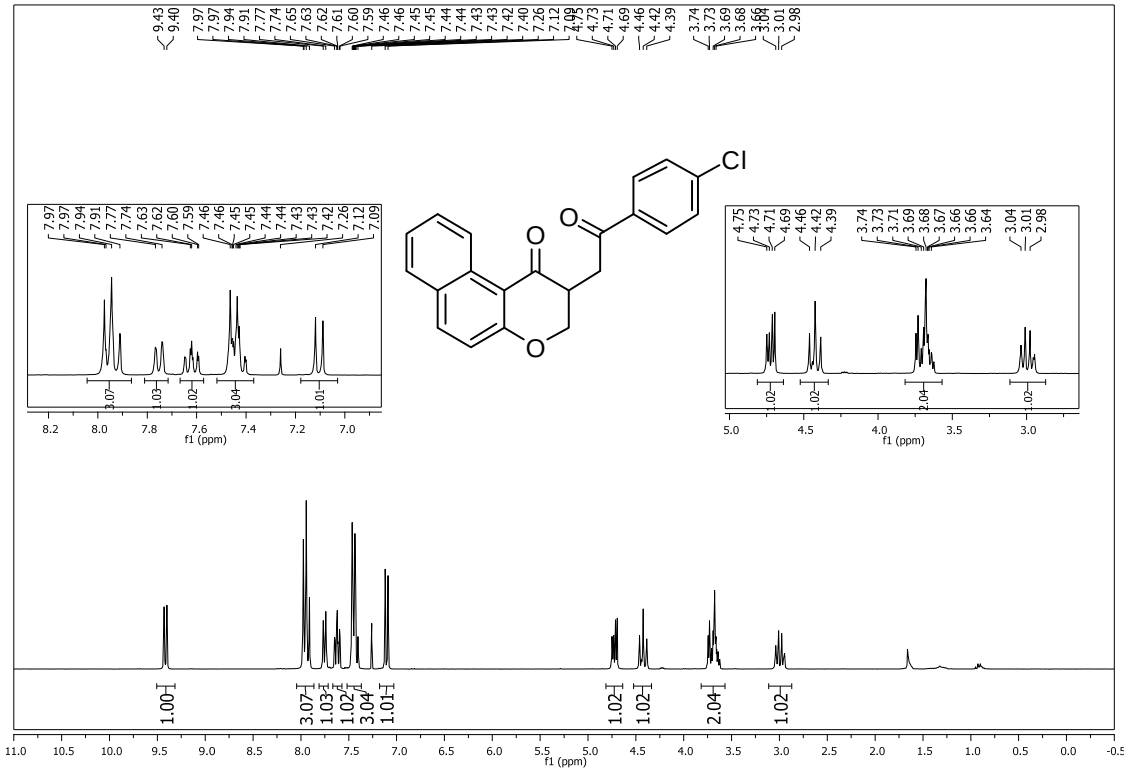



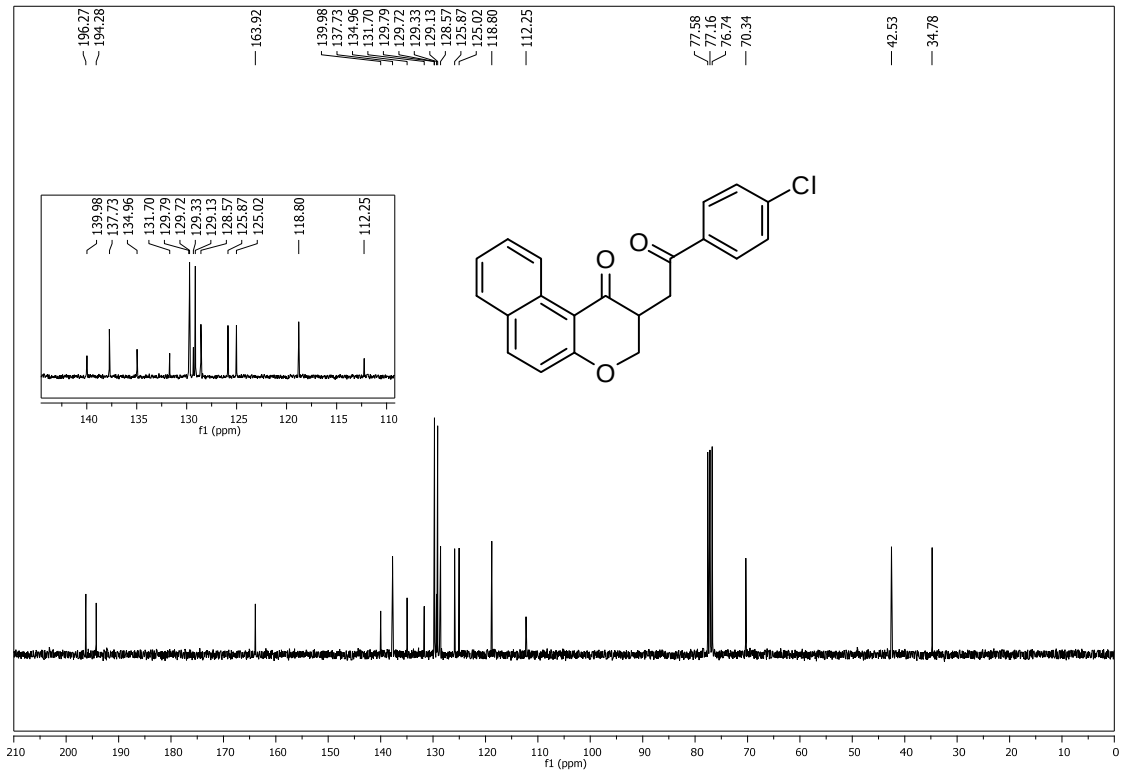
## 6-Bromo-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6h)



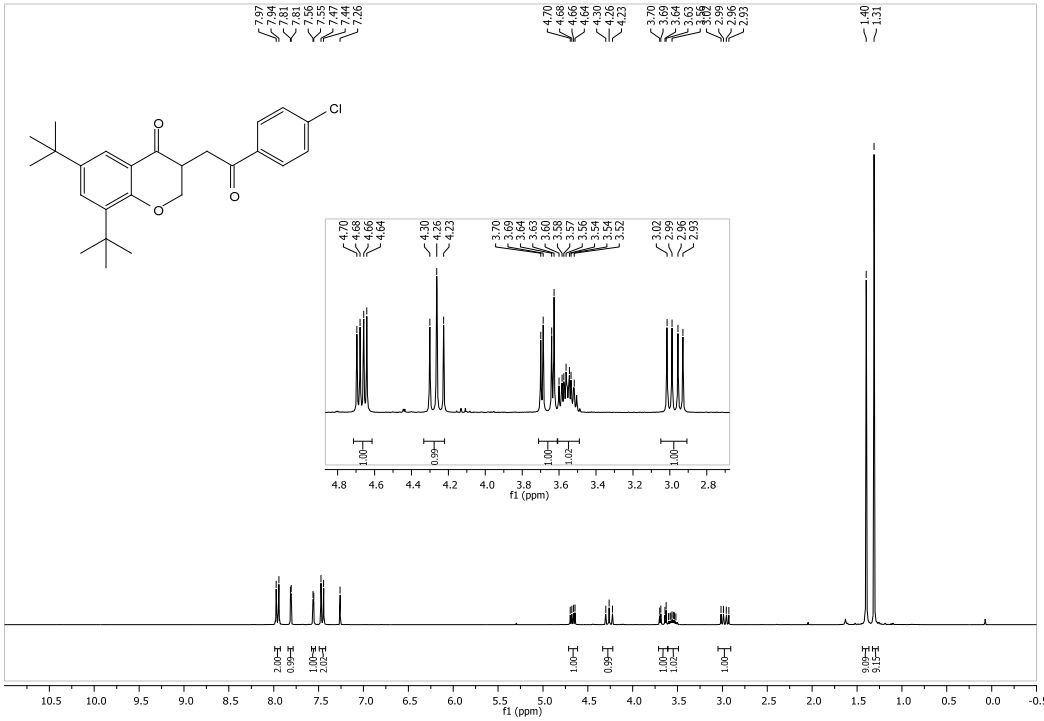



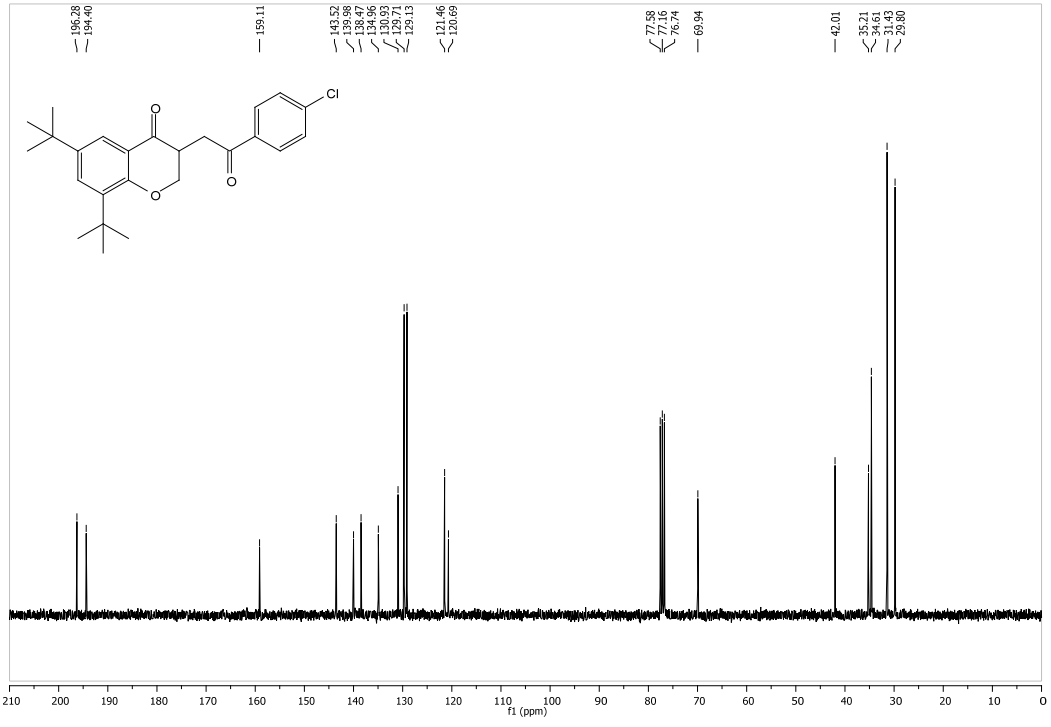
## 2-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-2,3-dihydro-benzo[*f*]chromen-1-one (6i)



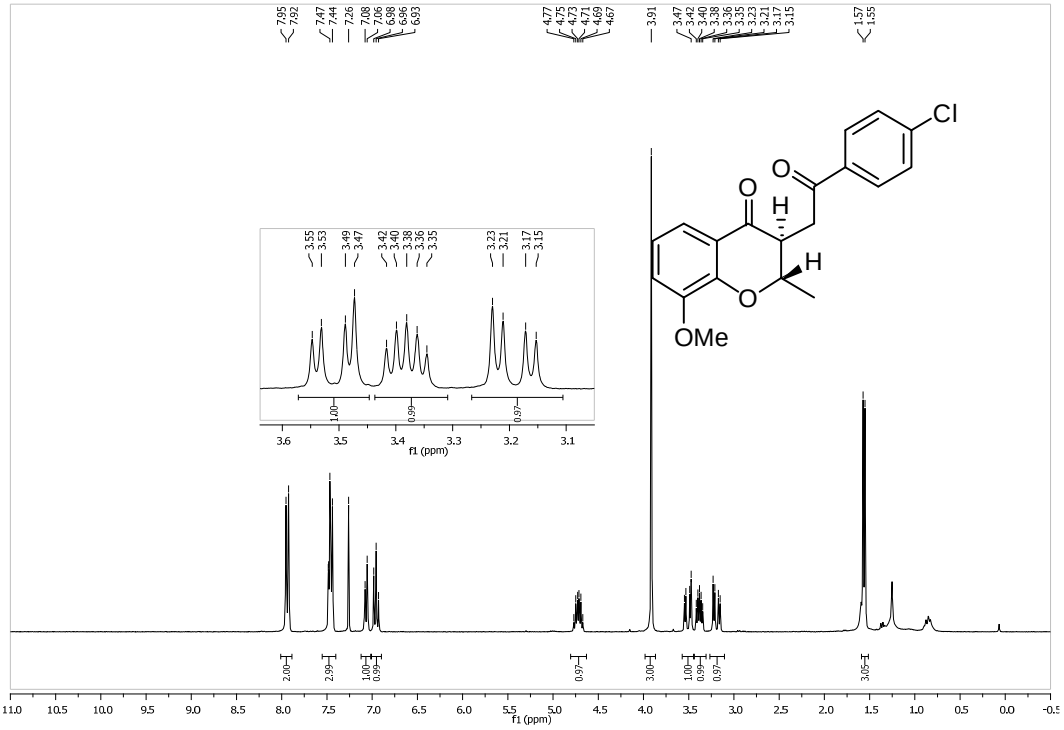



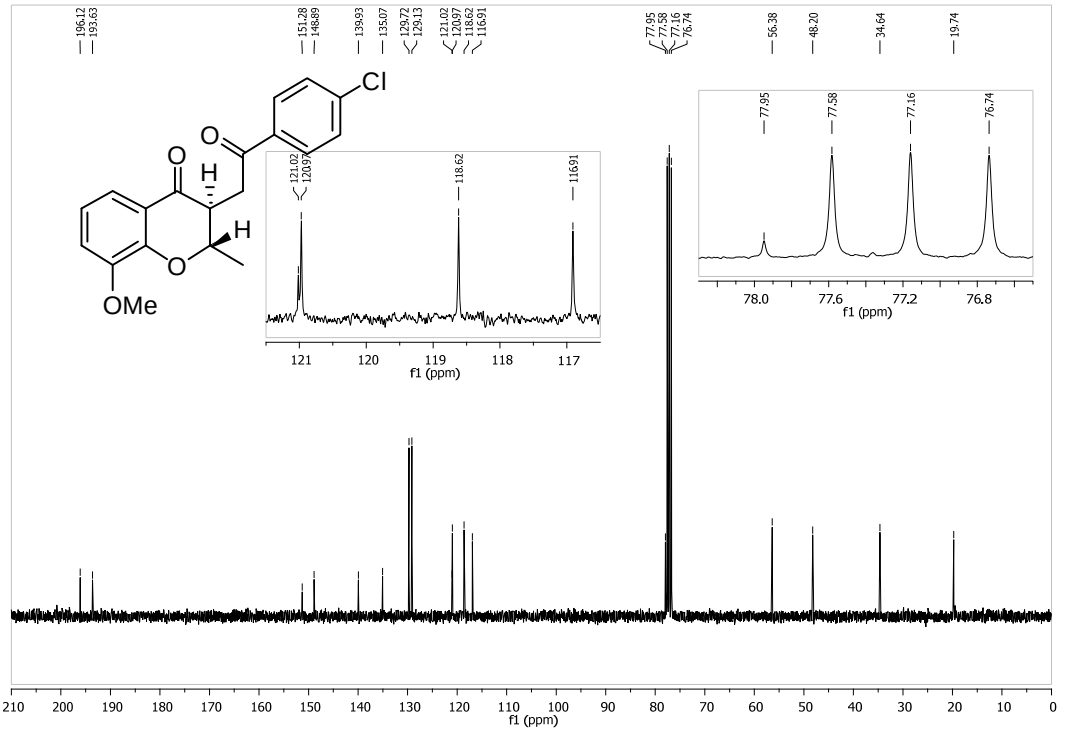
## 6,8-Di-*tert*-butyl-3-[2-(4-chloro-phenyl)-2-oxo-ethyl]-chroman-4-one (6j)



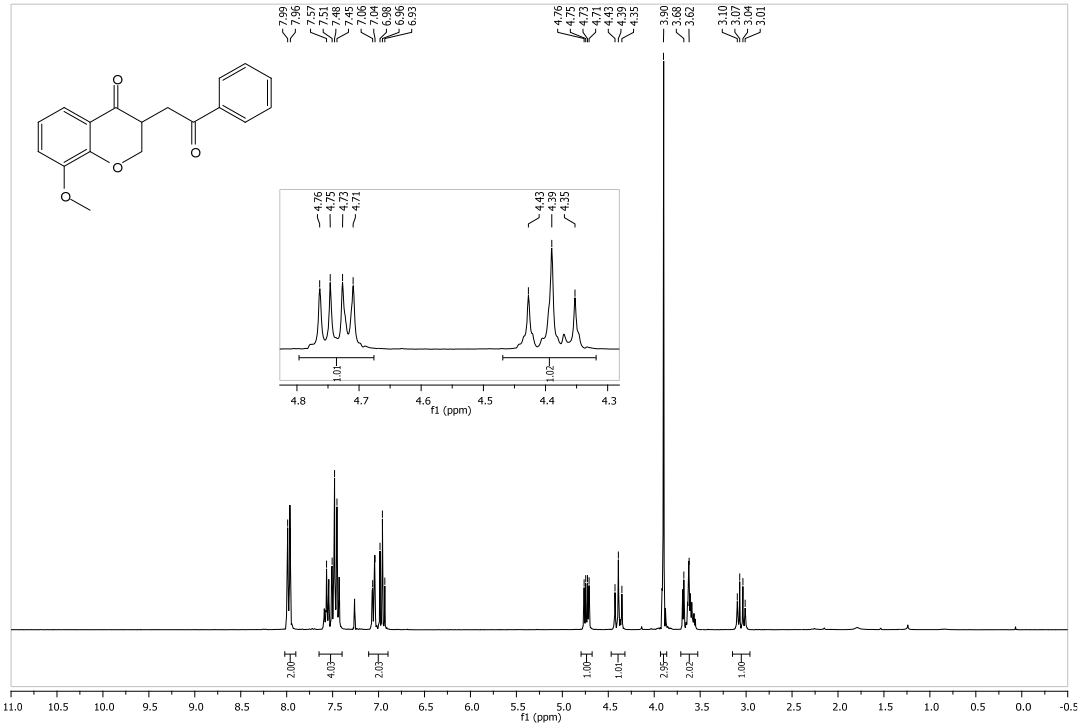



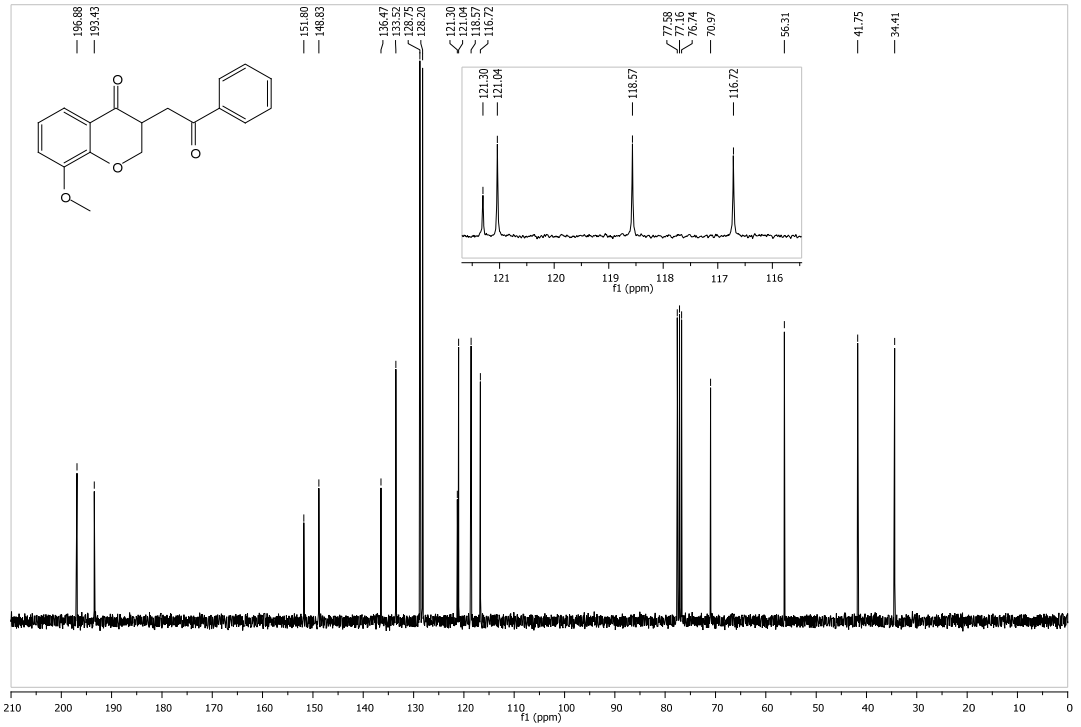
**4-(4-Chloro-phenyl)-1-(2-hydroxy-3-methoxy-phenyl)-2-isopropyl-butane-1,4-dione (6k)**



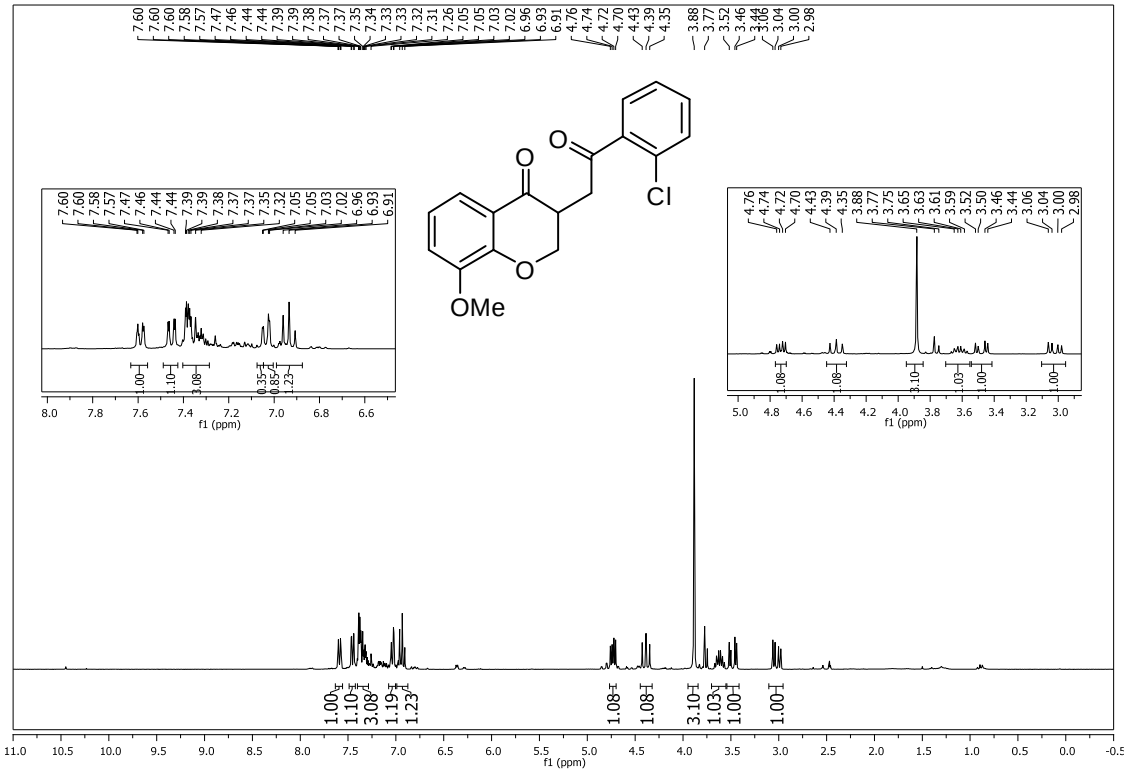



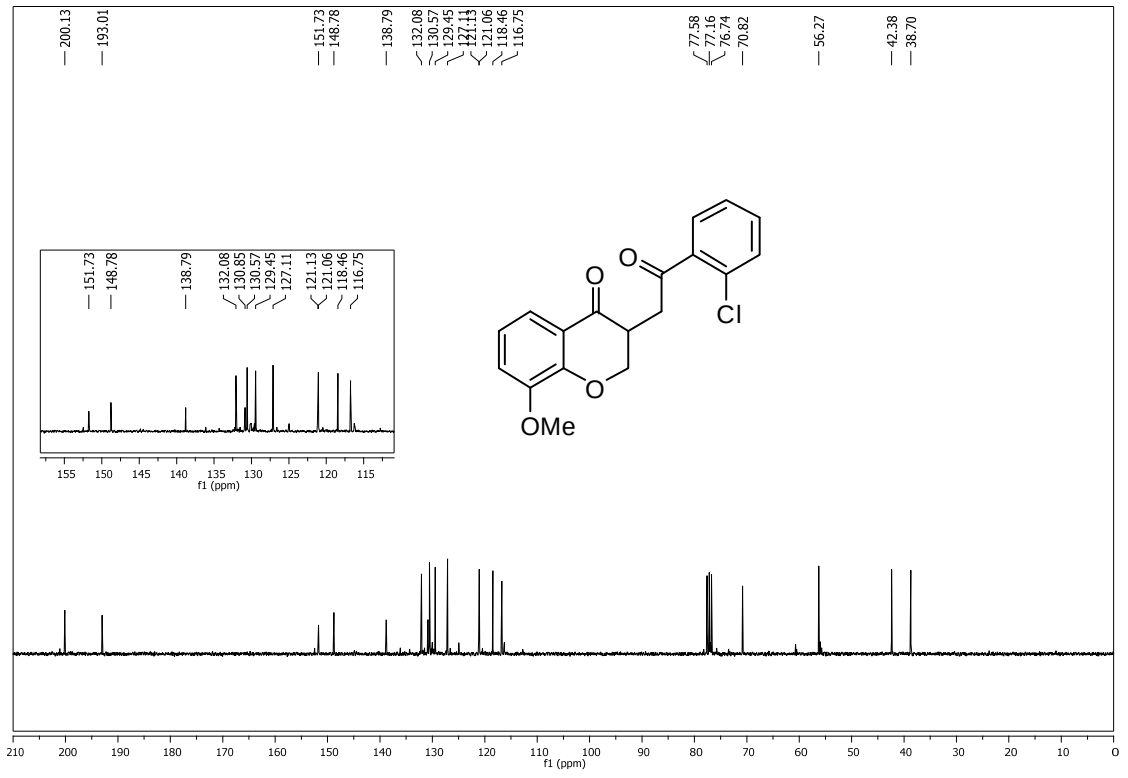
## 8-Methoxy-3-(2-oxo-2-phenyl-ethyl)-chroman-4-one (6l)



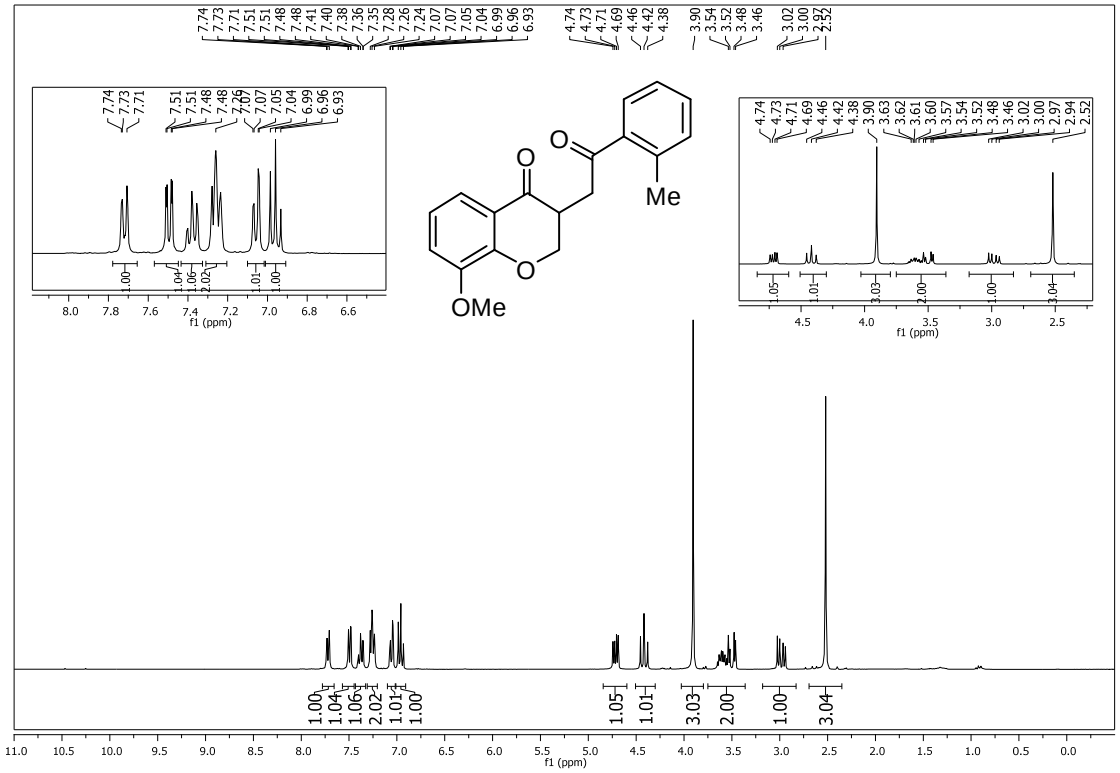


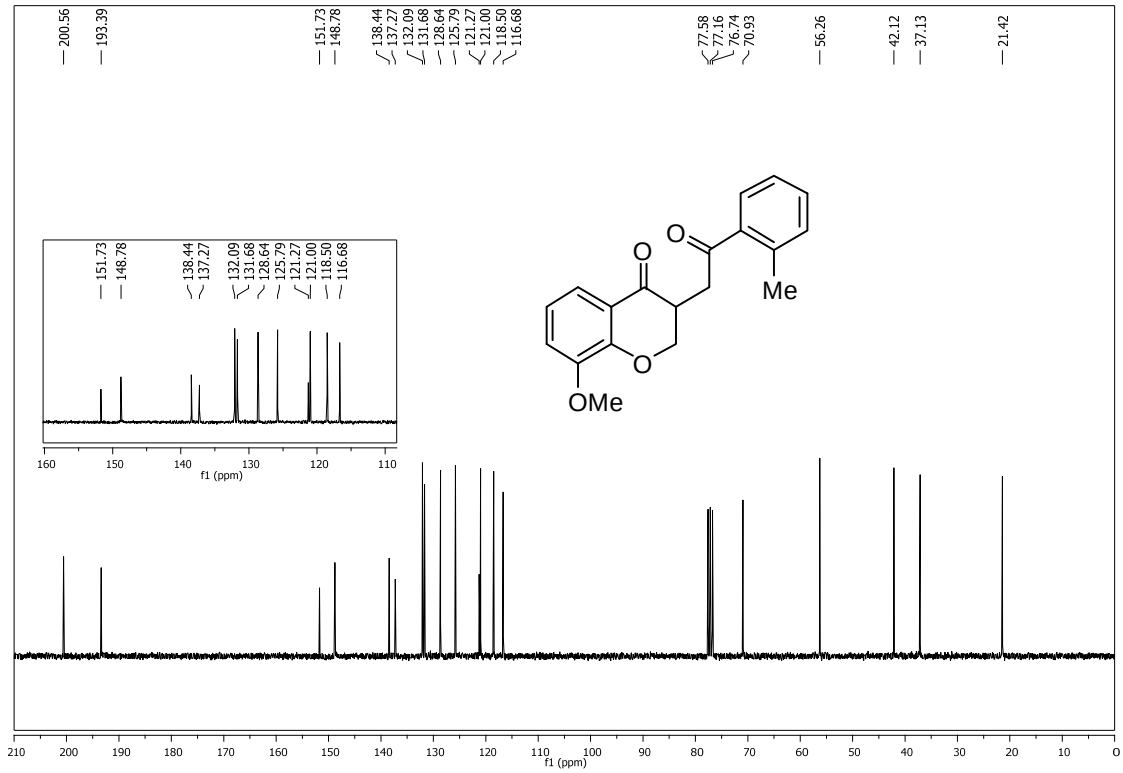
## 3-[2-(2-Chloro-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6m)



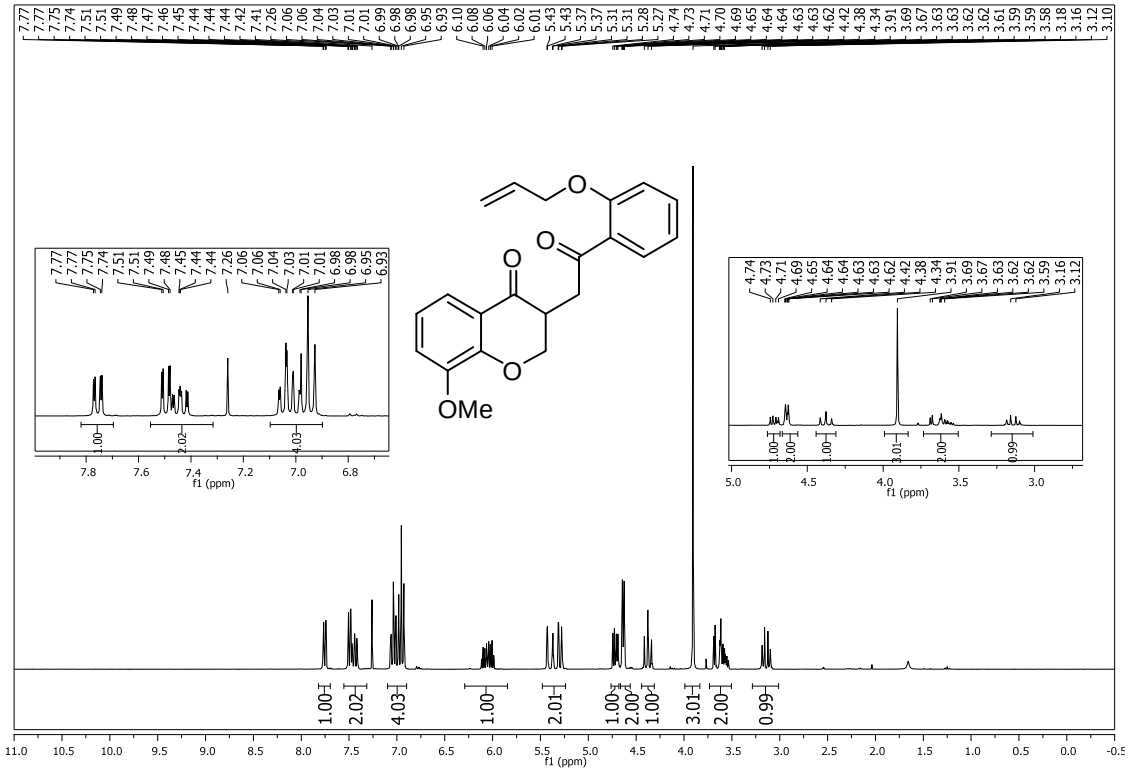



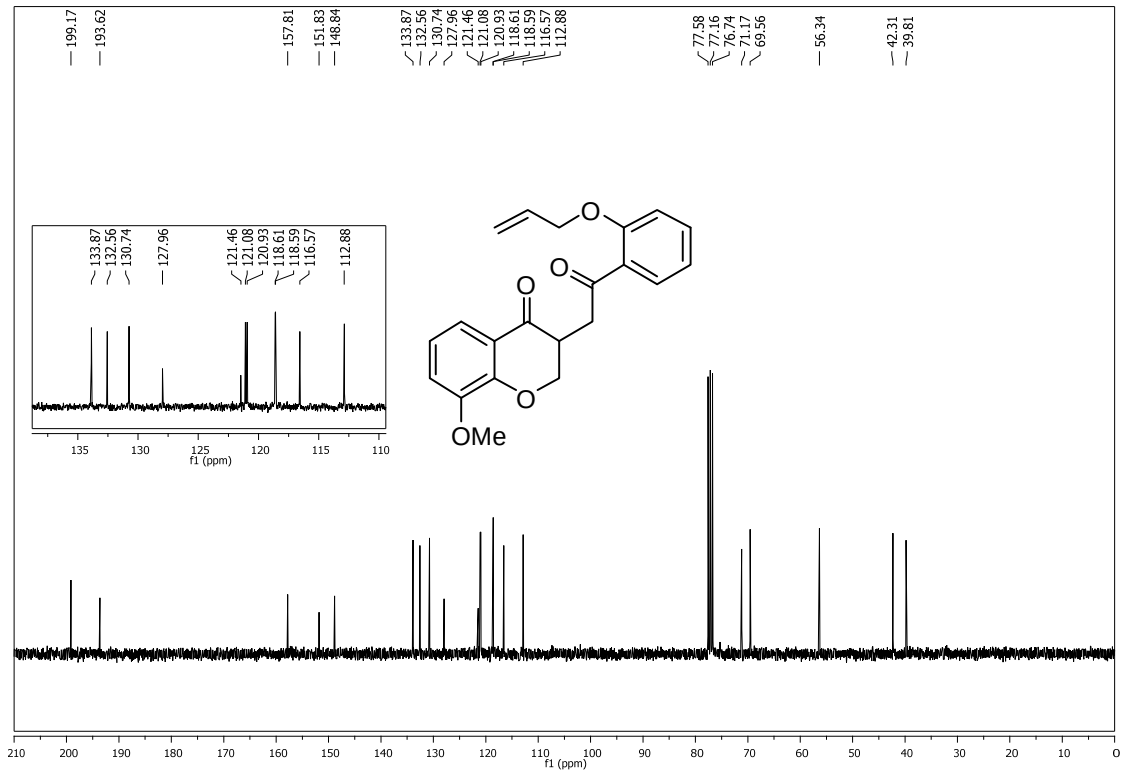
## 8-Methoxy-3-(2-oxo-2-*o*-tolyl-ethyl)-chroman-4-one (6n)



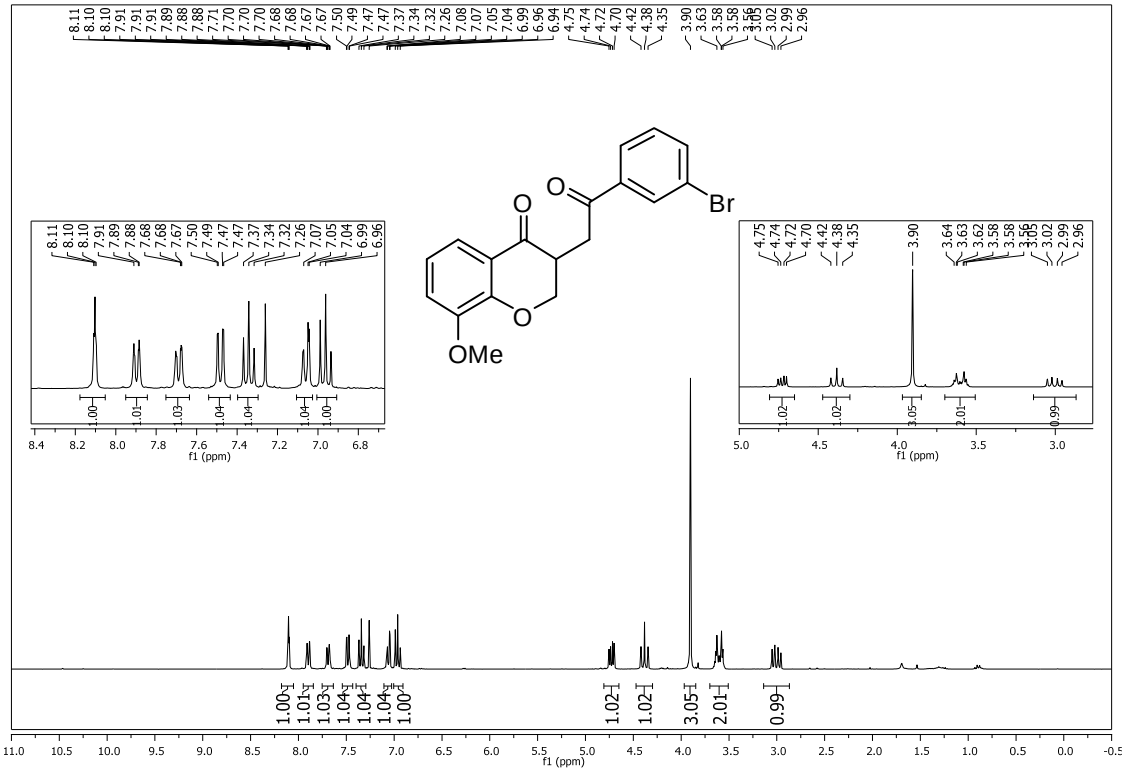



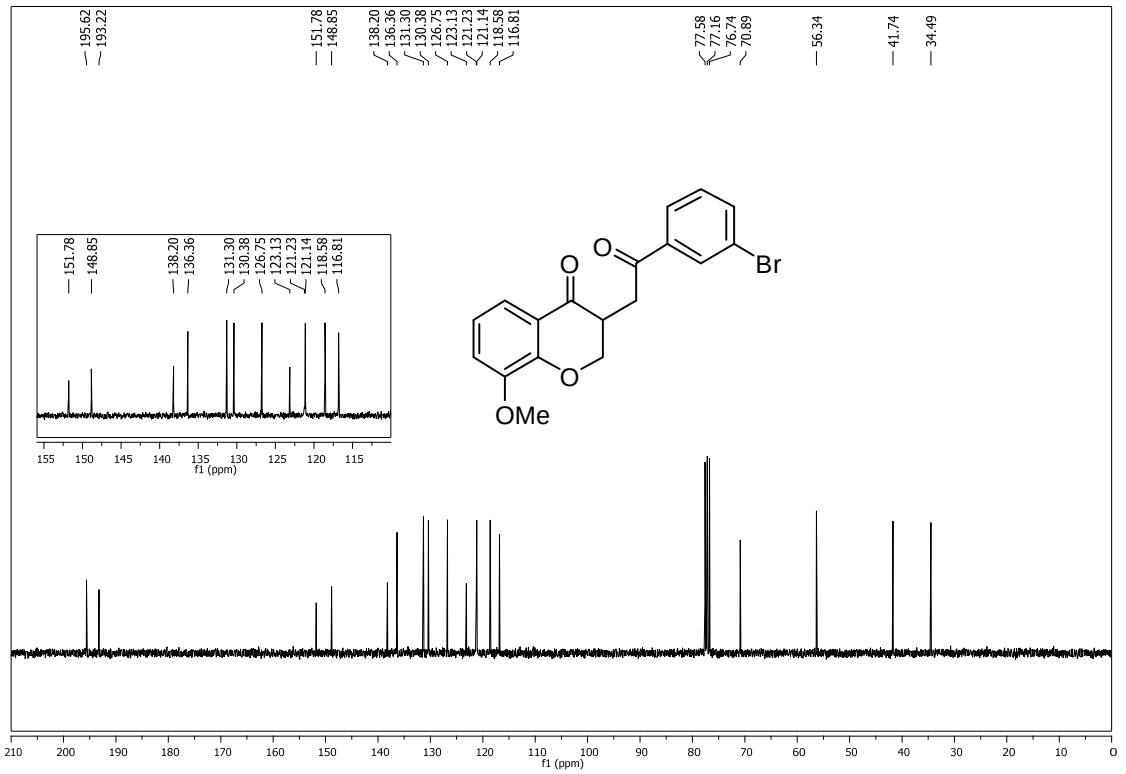
## 3-[2-(2-Allyloxy-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6o)



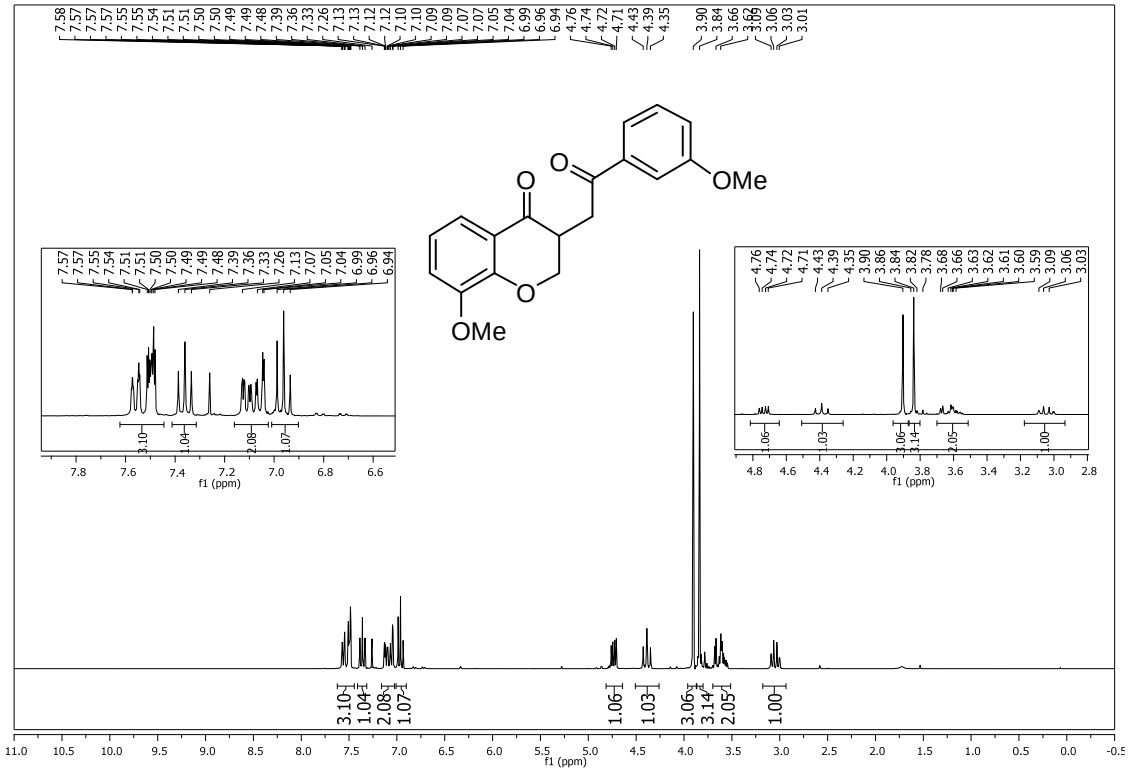



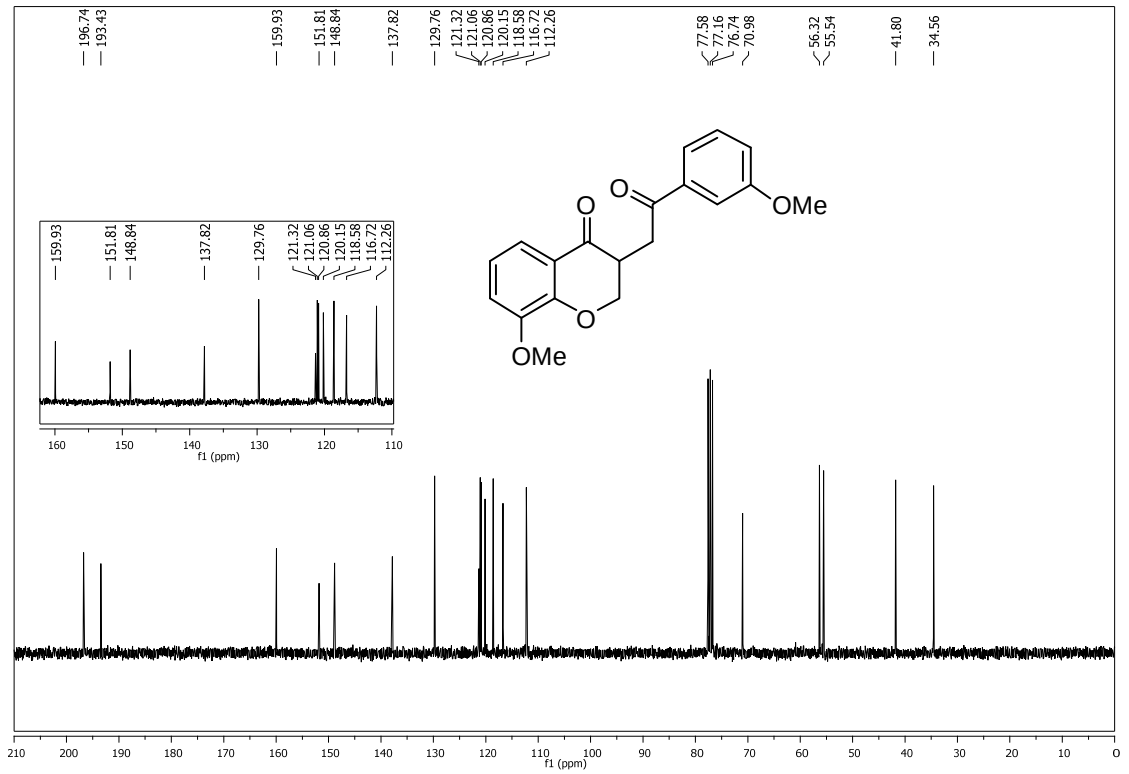
## 3-[2-(3-Bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6p)



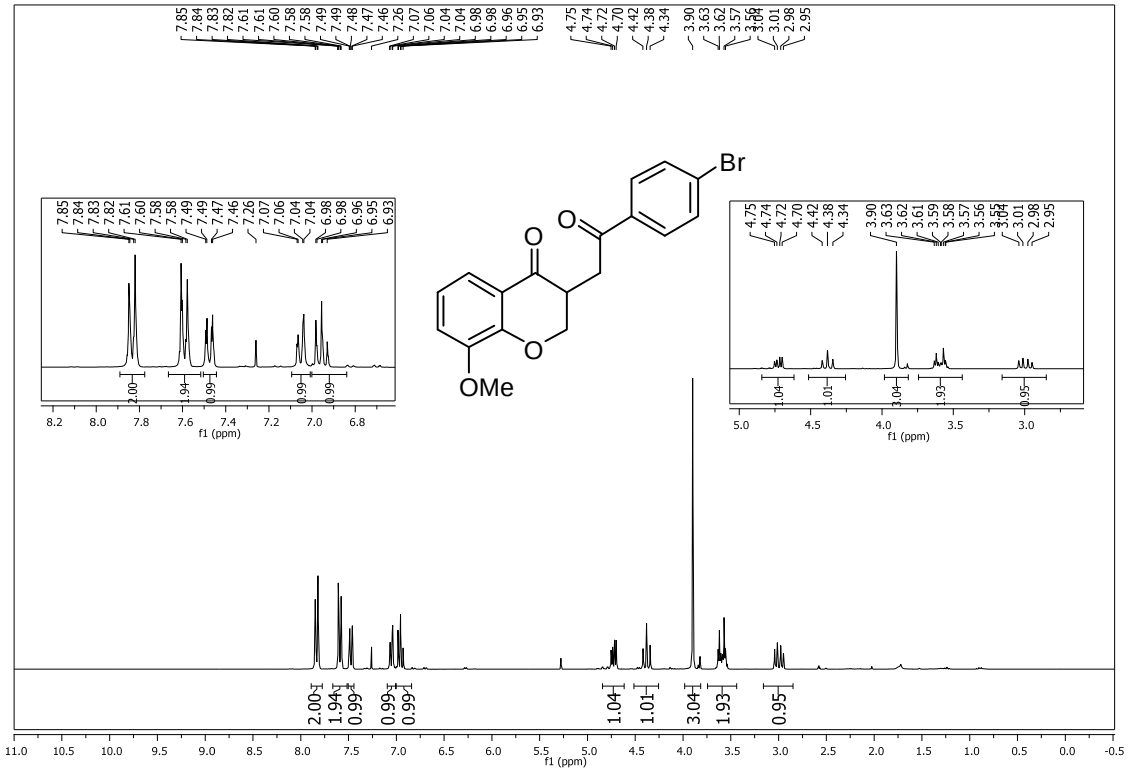



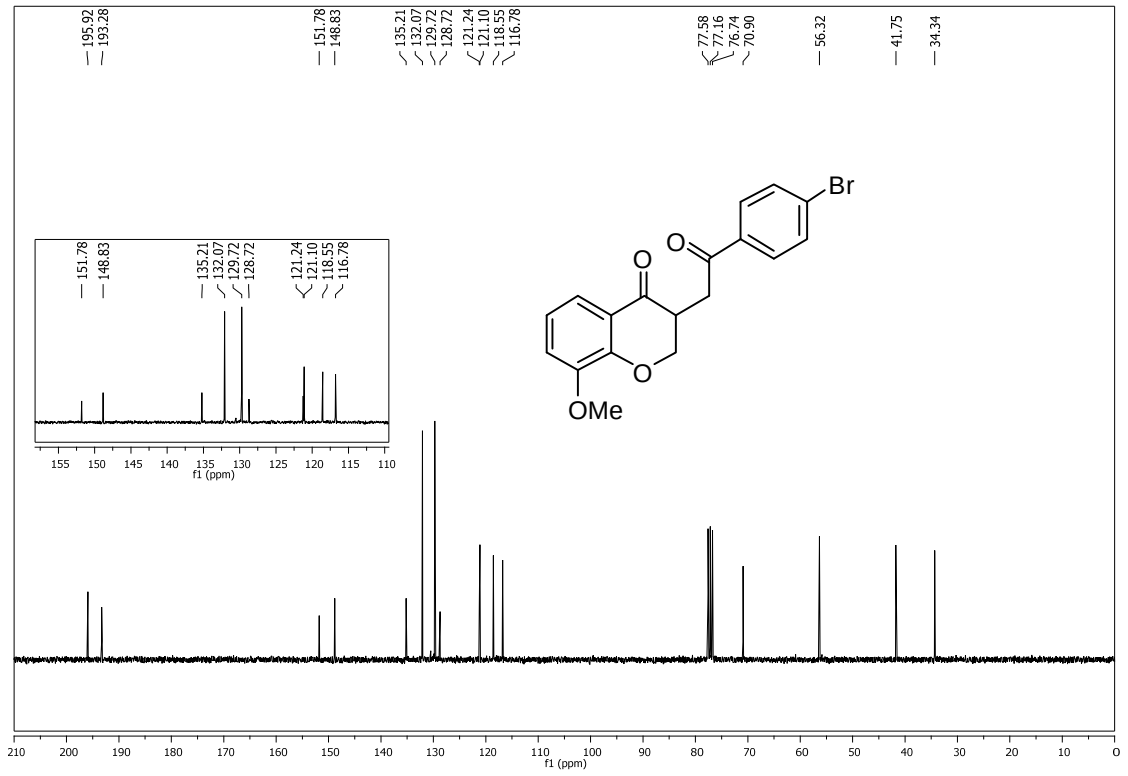
## 8-Methoxy-3-[2-(3-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one (6q)



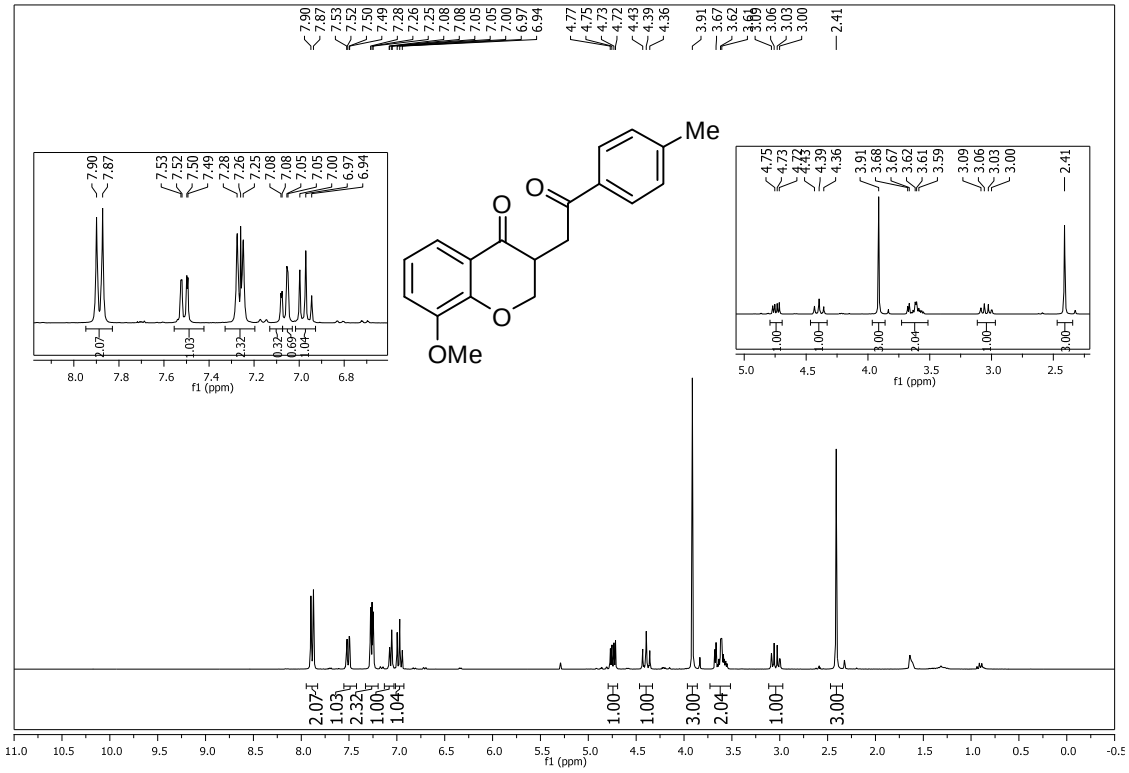



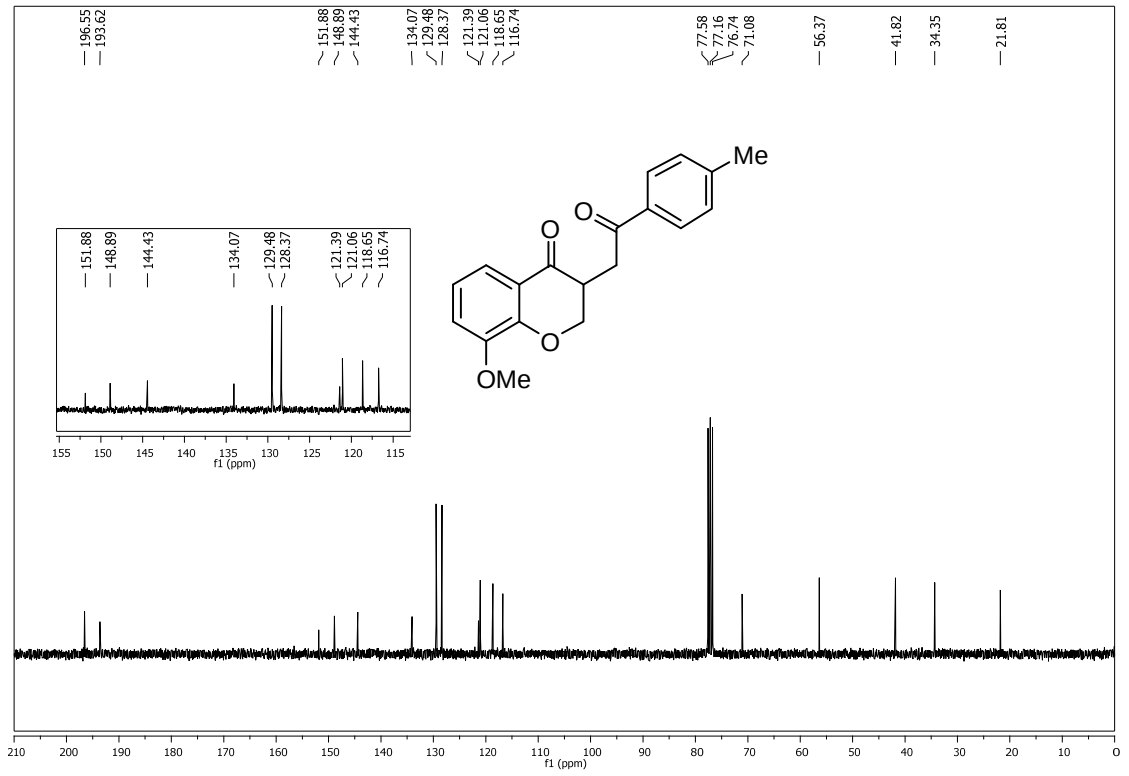
## 3-[2-(4-Bromo-phenyl)-2-oxo-ethyl]-8-methoxy-chroman-4-one (6r)



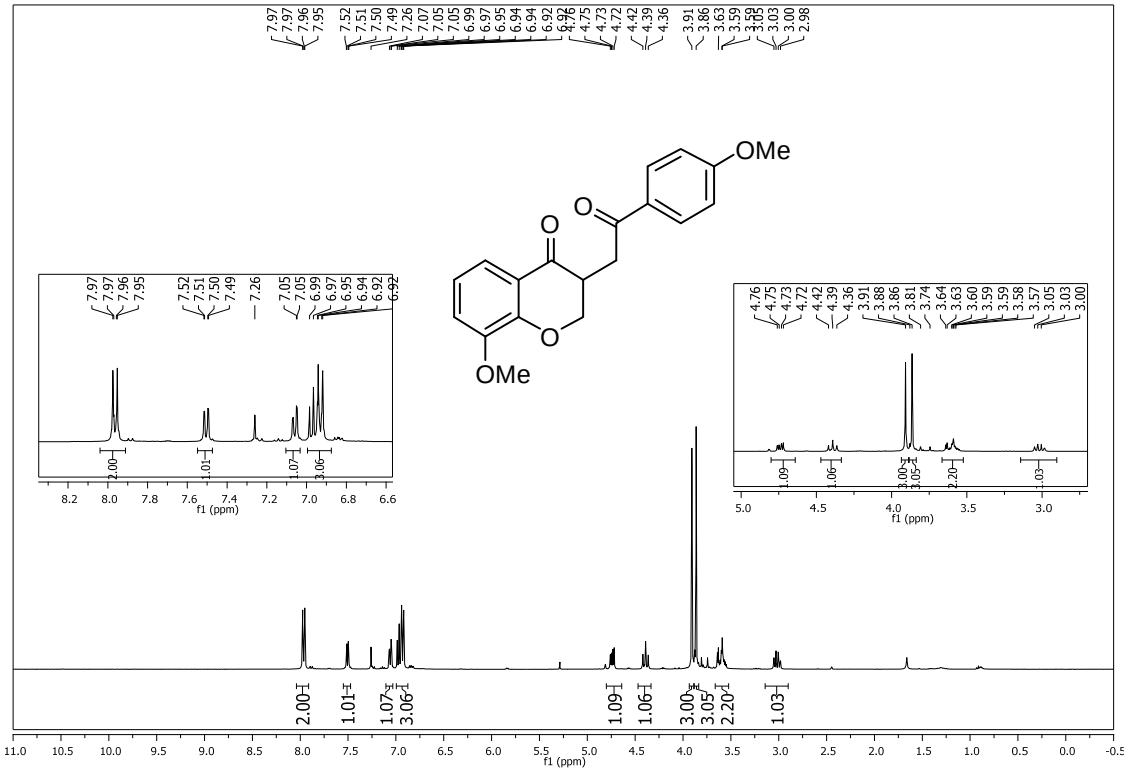



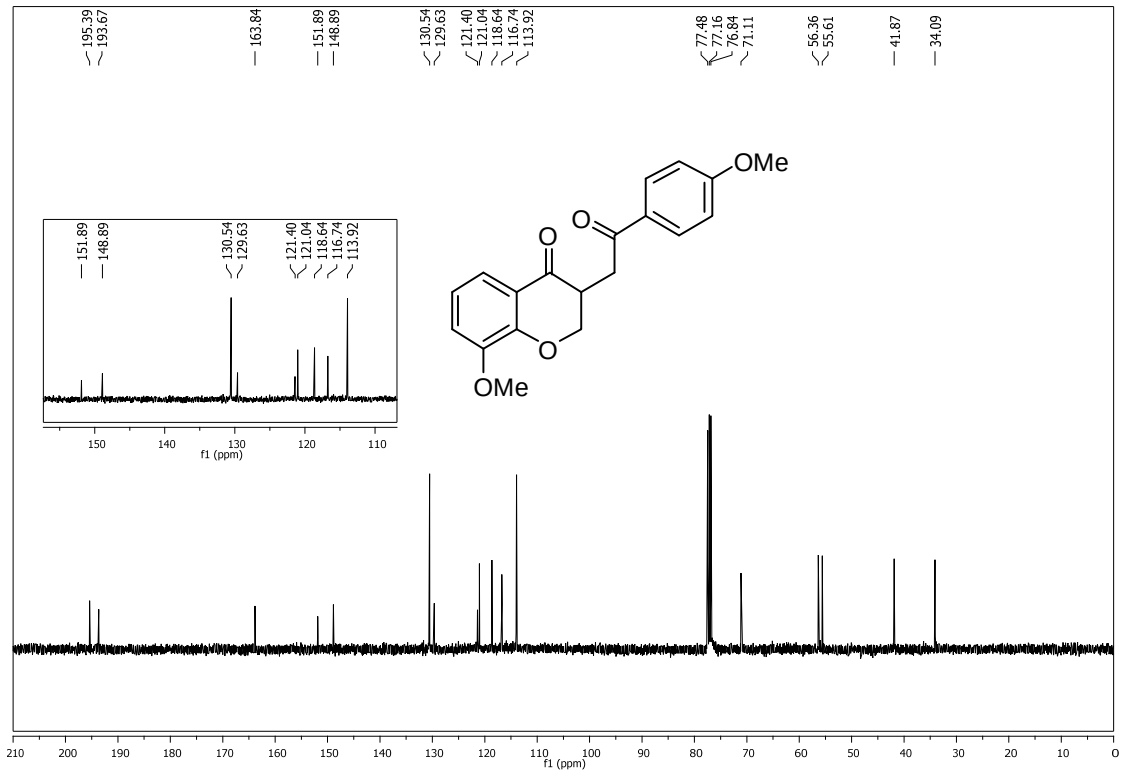
## 8-Methoxy-3-(2-oxo-2-*p*-tolyl-ethyl)-chroman-4-one (6s)



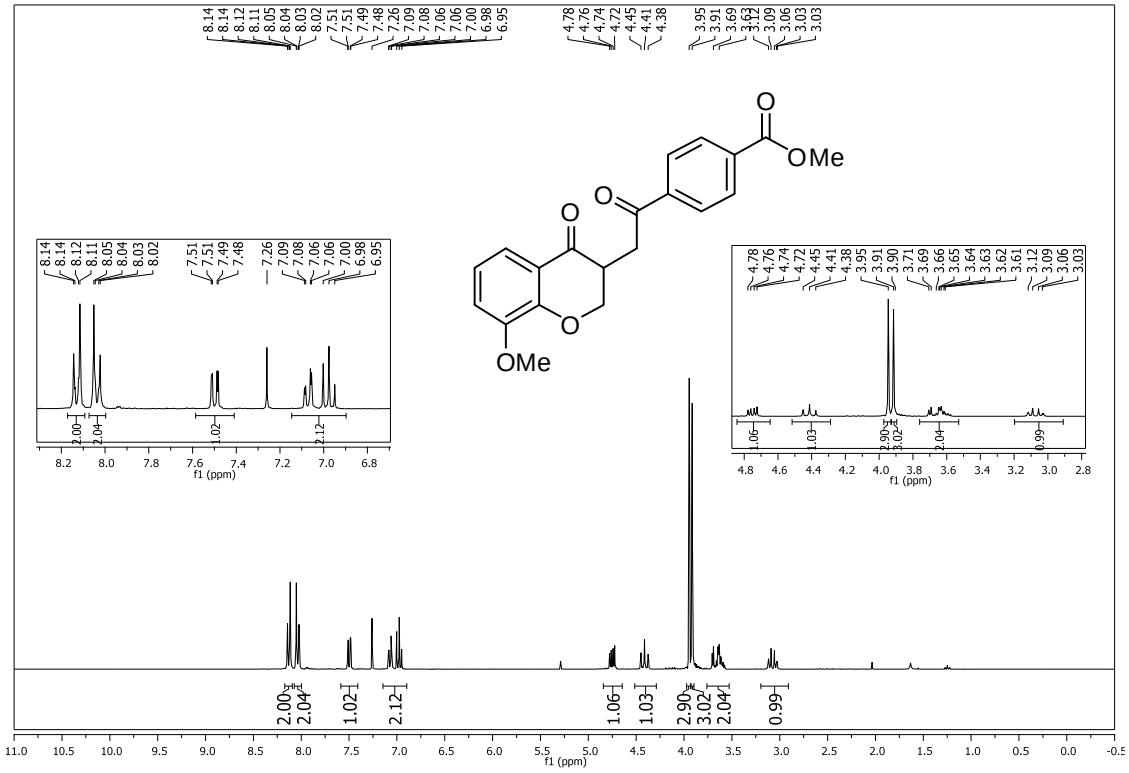



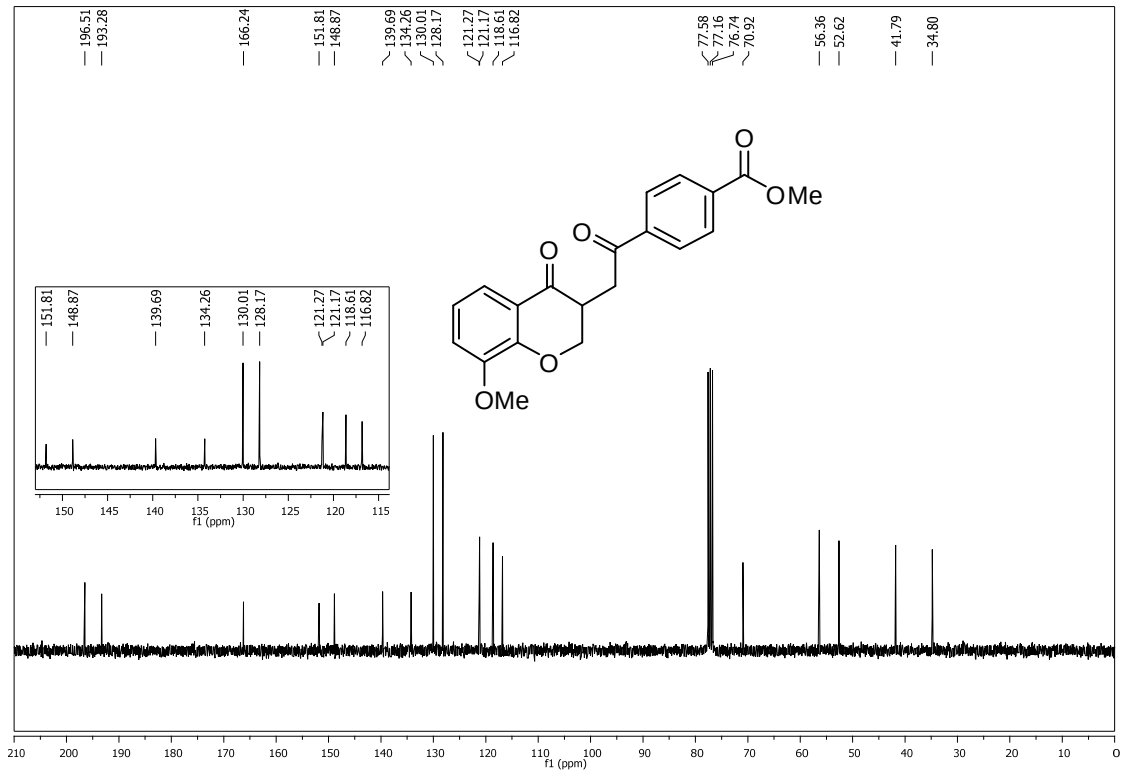
## 8-Methoxy-3-[2-(4-methoxy-phenyl)-2-oxo-ethyl]-chroman-4-one (6t)



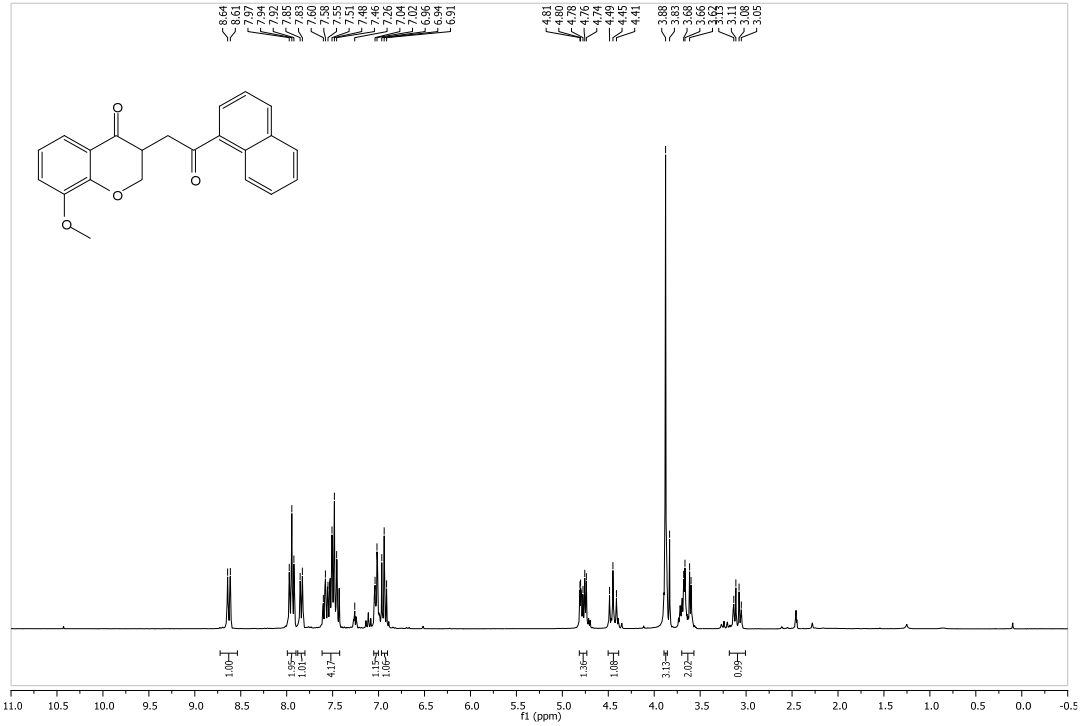



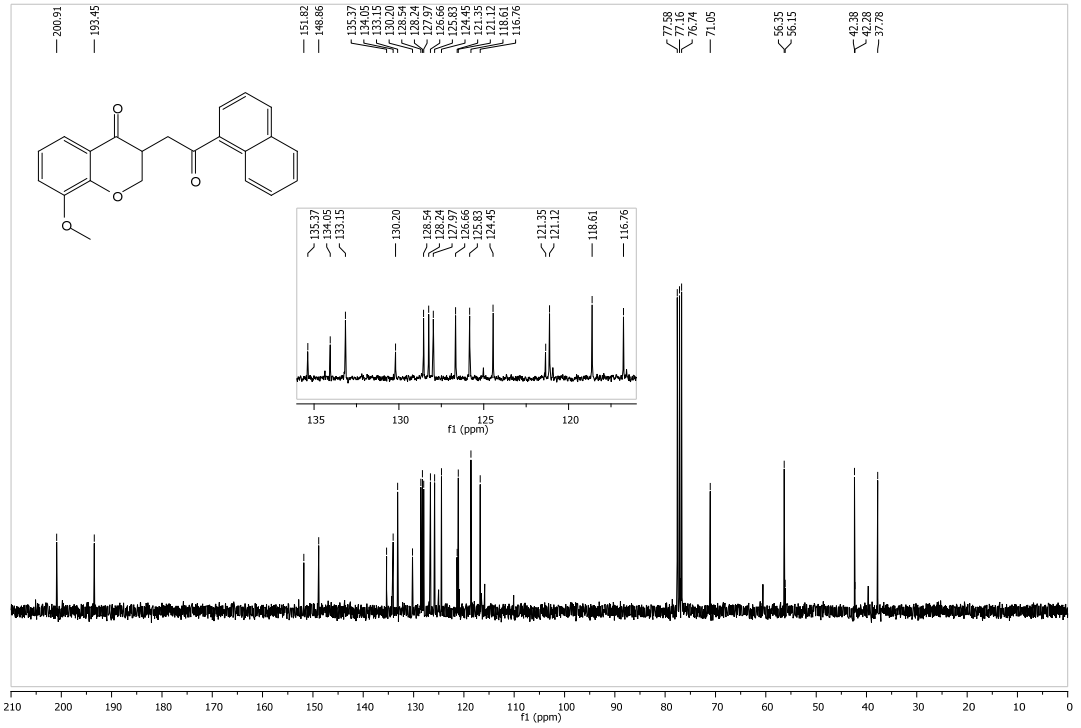
## 4-[2-(8-Methoxy-4-oxo-chroman-3-yl)-acetyl]-benzoic acid methyl ester (6u)



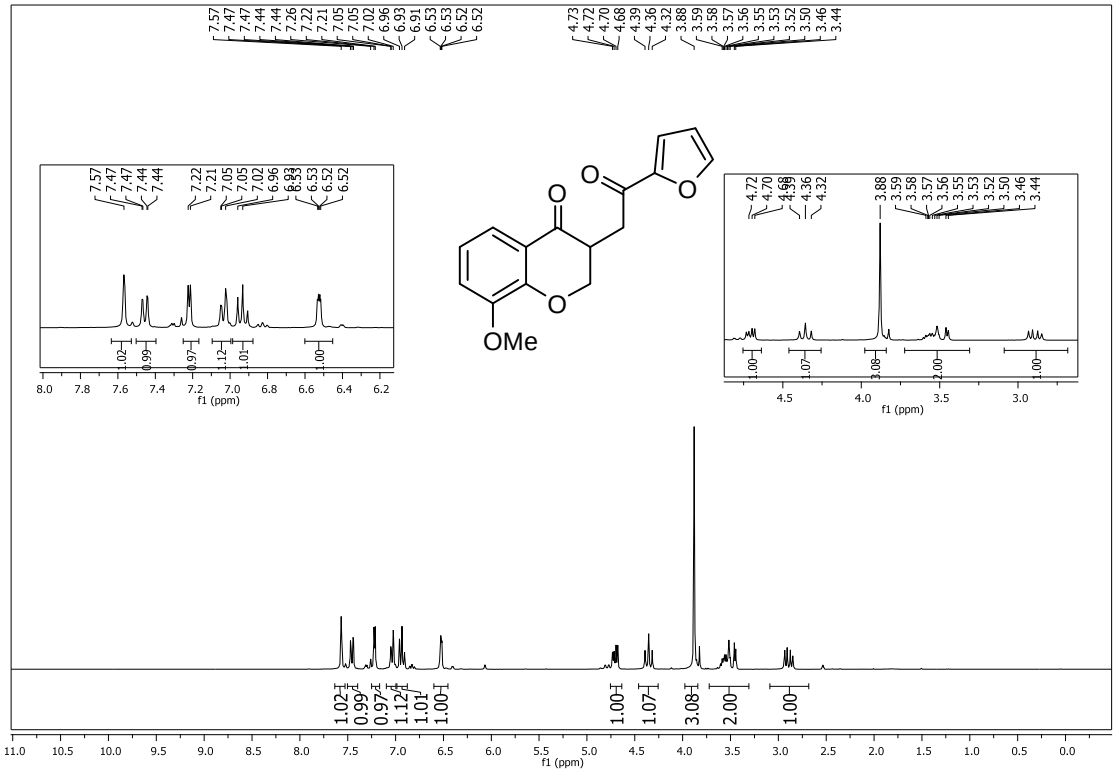


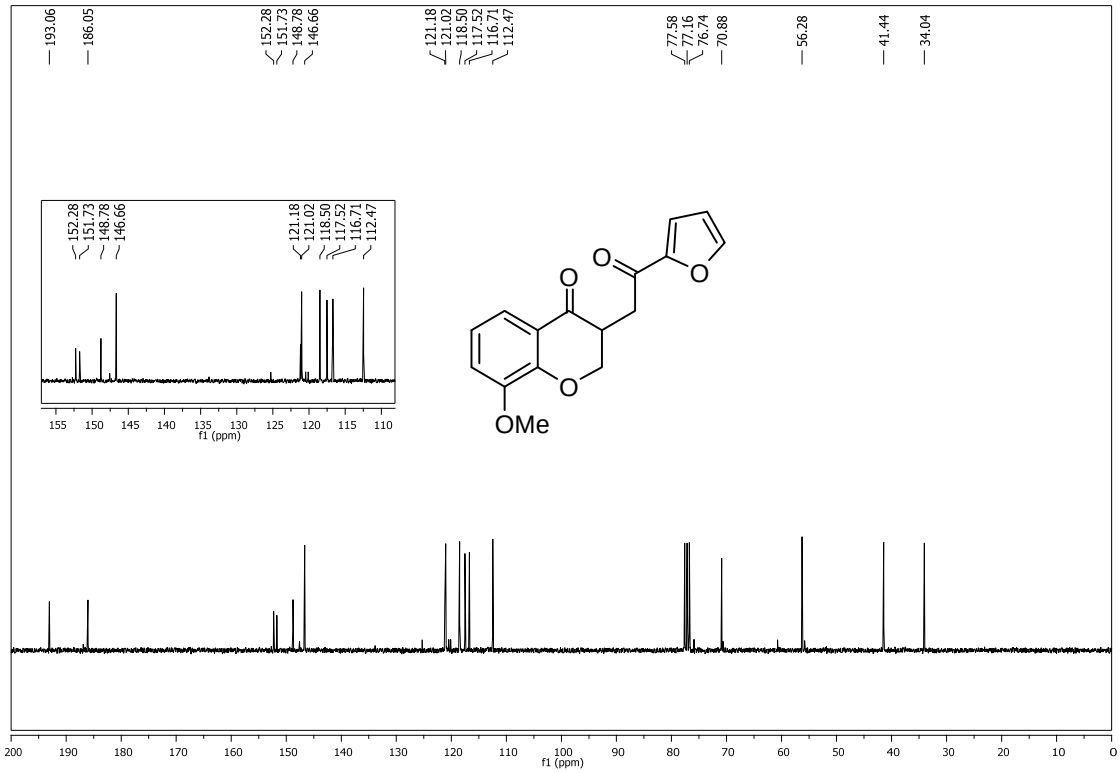
## 8-Methoxy-3-(2-naphthalen-1-yl-2-oxo-ethyl)-chroman-4-one (6v)



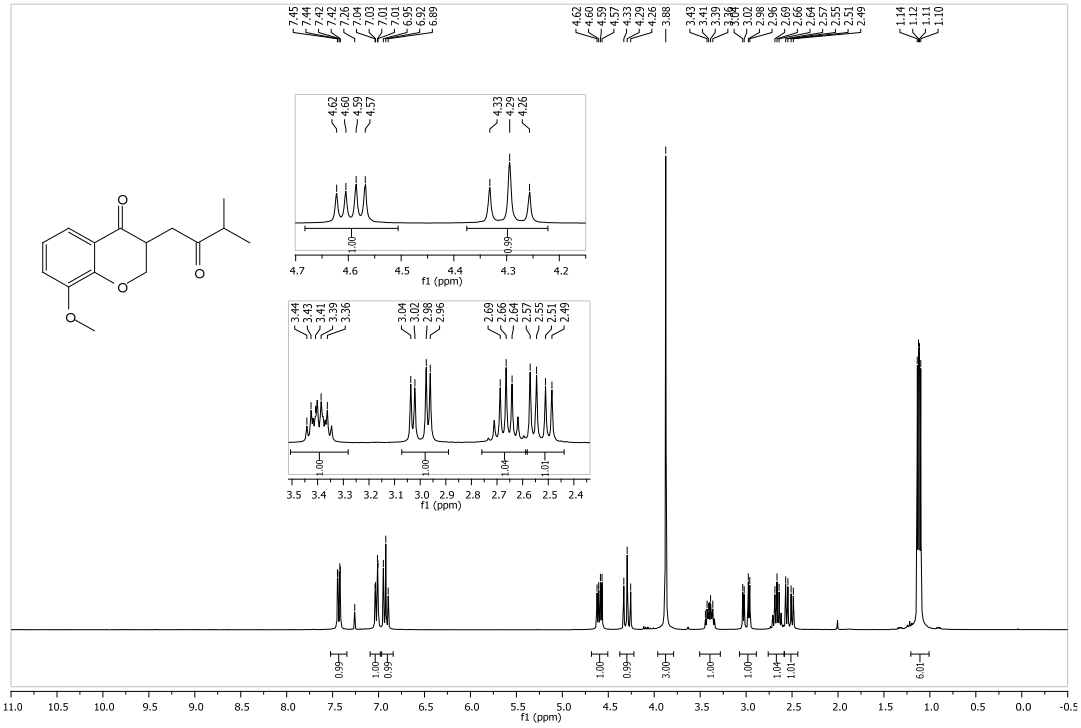



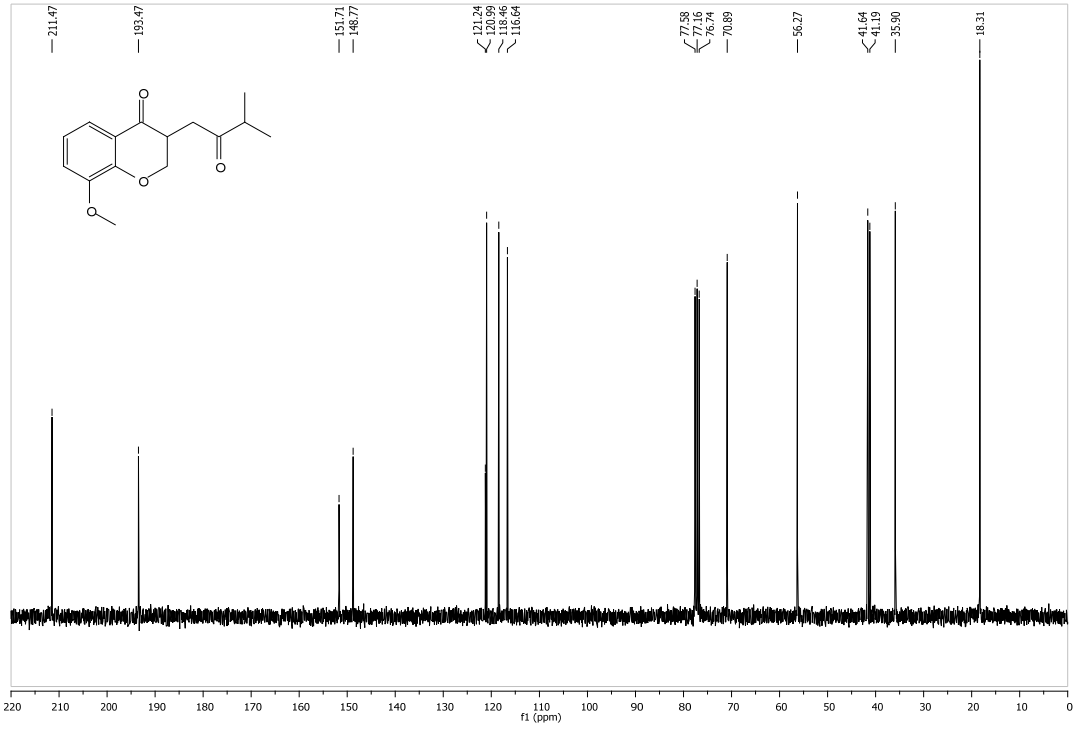
## 3-(2-Furan-2-yl-2-oxo-ethyl)-8-methoxy-chroman-4-one (6w)



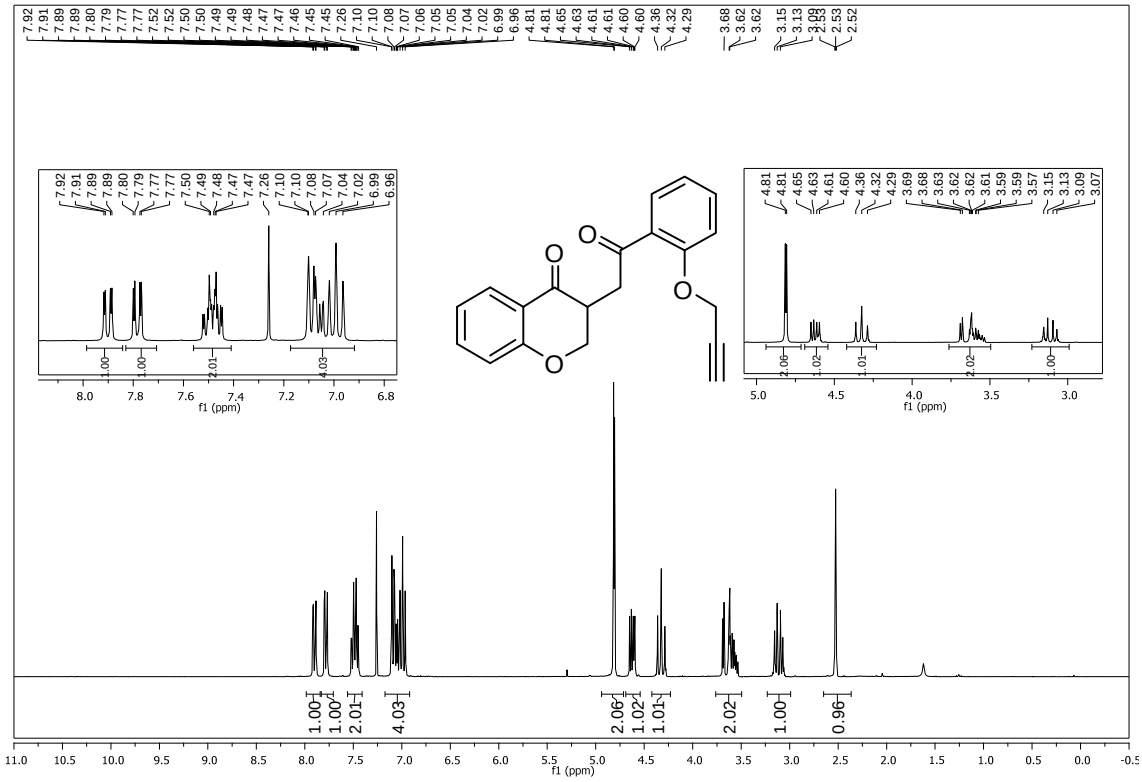



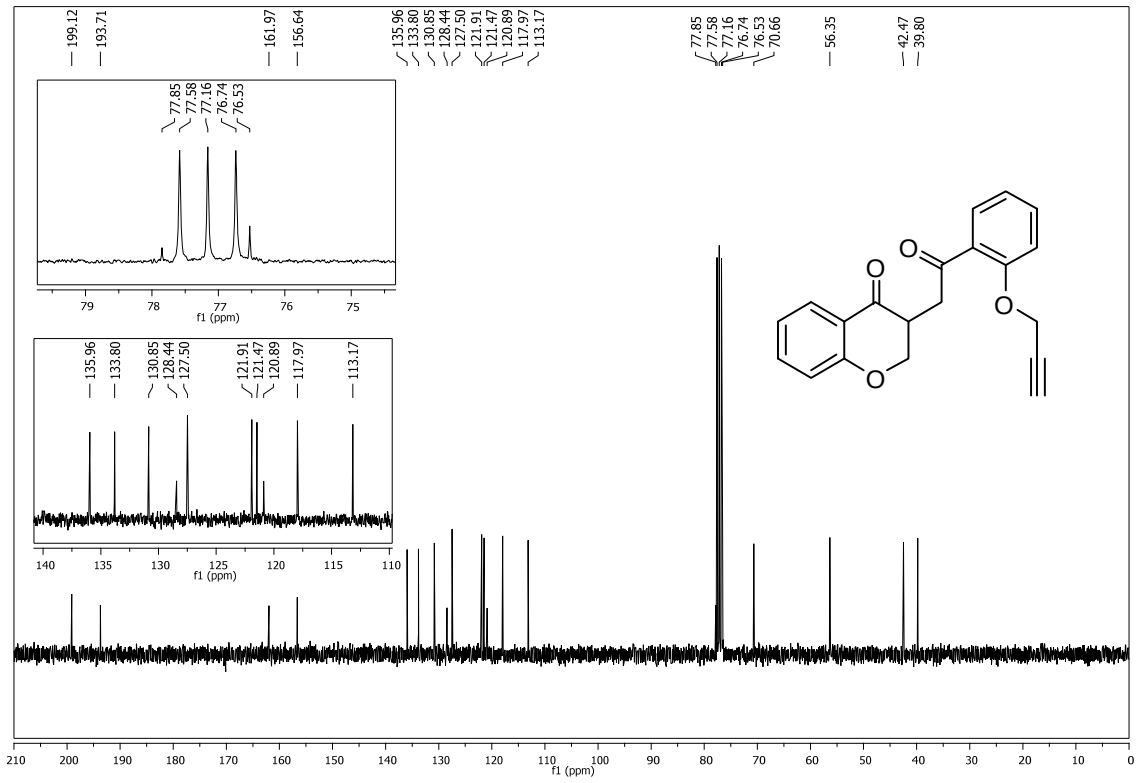
**8-Methoxy-3-(3-methyl-2-oxo-butyl)-2,3,4a,8a-tetrahydro-chromen-4-one (6x)**





## 3-[2-Oxo-2-(2-prop-2-ynyloxy-phenyl)-ethyl]-chroman-4-one (3a’)





**2-(4-Chloro-phenyl)-6-methoxy-1-*p*-tolyl-1,4-dihydro-chromeno[4,3-*b*]pyrrole (7)**