Supporting Information

# Cascade C-H functionalization/annulation of 2-aryl-1,3-dicarbonyls with Morita-Baylis-Hillman adducts: access to α-iso-/benzochromenyl acrylates

## Table of Contents

**General Information.** $Pd(OAc)_2$ (98%), $Cu(OAc)_2 \cdot H_2O$ (98%), $Cu(OAc)_2$ (>98%), AgOAc (99%), BQ (>98%), 1,3-cyclohexadione, dimedone and aryl iodides of Aldrich and TCI chemicals were used as received. Acetonitrile, $CH_2Cl_2$, MeOH and EtOH were dried prior to use as per the standard procedure. Silica gel-G/GF254 plates (Merck) were used for TLC analysis with a mixture of hexane and EtOAc as the eluent. Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record ($^1H$, $^{13}C$ and $^{19}F$) NMR spectra using $CDCl_3$ and DMSO-$d_6$ as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. Mestrenova software was used throughout the spectral analysis. Q-Tof ESI-MS instrument was used for recording HRMS data. Infrared spectra were recorded on Perkin Elmer FT-IR instrument. Single crystal X-ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/-Kα radiation and the structure was solved by direct method using SHELXL-18 (Göttingen, Germany).

**Sample Preparation for Crystal Growth.** Compound **4a** dissolved in a 1:1 mixture of $CH_2Cl_2$ and hexane (2 mL) and kept at room temperature for slow evaporation (3 days). Block shaped crystals were formed, which were then subjected to *X*-ray diffraction.

**Crystal Structure and Data of 4a.**

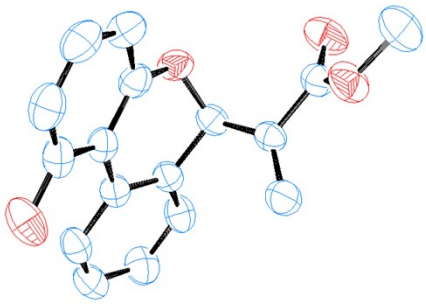
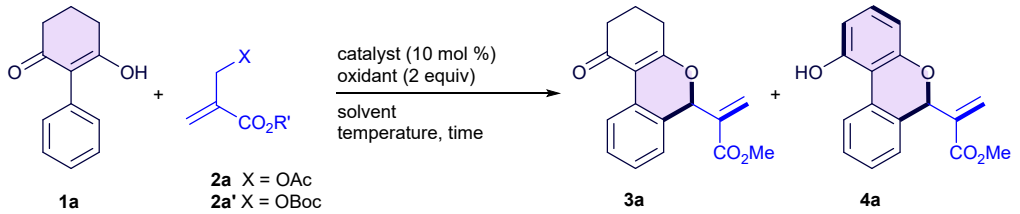


**Figure S1.** ORTEP diagram of methyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate **4a** (CCDC No 2367382) with 50% ellipsoid. H-Atoms are omitted for clarity.

| | |
|---|---|
| CCDC No. | 2367382 |
| Identification code | **4a** |
| Empirical formula | $C_{17}\ H_{14}\ O_4$ |
| Formula weight | 282.298 |
| Crystal habit, colour | Block, colorless |
| Temperature, *T*/K | 293K |
| Wavelength, λ/Å | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C 1 c 1 |
| Unit cell dimensions | a = 17.442 (13) Å<br>b = 7.489 (5) Å<br>c = 12.142 (10) Å<br>α = 90<br>β = 117.13 (3)<br>γ = 90 |
| Volume, *V*/Å$^3$ | 1411.4(18) Å$^3$ |
| *Z* | 4 |
| Calculated density, Mg·m$^{-3}$ | 1.328 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.095 |
| *F* (000) | 592 |
| $\theta$ range for data collection | 2.62 to 24.72 |
| Limiting indices | $-20 \leq h \leq 20$, $-8 \leq k \leq 8$, $-14 \leq l \leq 14$ |
| Reflection collected / unique | 2390/2026 |
| Completeness to $\theta$ | 99.75 % |
| Absorption correction | Multi-scan |
| Refinement method | 'SHELXT 2018/2 (Sheldrick, 2018)' |
| Data / restraints / parameters | 2390/2/201 |
| Goodness-of-fit on $F^2$ | 1.0939 |
| Final *R* indices [*I* >2sigma(*I*)] | $R_1$ = 0.0404, $wR_2$ = 0.0806 |
| R indices (all data) | $R_1$ = 0.0543, $wR_2$ = 0.0898 |

**Table S1. Optimization of Reaction Conditions**[a]




| entry | catalyst | oxidant | solvent | yield **3a**[b] | yield **4a**[b] |
|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | $Cu(OAc)_2$ | DMF | 29 | 36 |
| 2 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF | 35 | 46 |
| 3 | $Pd(OAc)_2$ | AgOAc | DMF | 25 | trace |
| 4 | $Pd(OAc)_2$ | BQ | DMF | 32 | n.d. |
| 5 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMSO | 30 | trace |
| 6 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMA | n.d. | n.d. |
| 7 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | Toluene | n.d. | n.d. |
| 8 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | 1,4-Dioxane | n.d. | n.d. |
| 9 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $(CH_2Cl)_2$ | n.d. | n.d. |
| 10 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $^t$AmOH | n.d. | n.d. |
| 11 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $H_2O$ | 81 | n.d. |
| **12**[c] | **$Pd(OAc)_2$** | **$Cu(OAc)_2{\cdot}H_2O$** | **$H_2O$** | **85** | **n.d.** |
| 13[c] | $Pd(TFA)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $H_2O$ | 65 | n.d. |
| 14[c] | $PdCl_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $H_2O$ | n.d. | n.d. |
| 15[c] | $Pd(PPh_3)_2Cl_2$ | $Cu(OAc)_2{\cdot}H_2O$ | $H_2O$ | n.d. | n.d. |
| 16 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF+$H_2O$[d] | 46 | 21 |
| 17 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF+$H_2O$[e] | 42 | 29 |
| 18 | $Pd(OAc)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF+$H_2O$[f] | trace | 72 |
| **19**[g] | **$Pd(OAc)_2$** | **$Cu(OAc)_2{\cdot}H_2O$** | **DMF + $H_2O$[f]** | **trace** | **78** |
| 20 | $Pd(TFA)_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF + $H_2O$ | 37 | n.d. |
| 21 | $PdCl_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF + $H_2O$ | n.d. | n.d. |
| 22 | $Pd(PPh_3)_2Cl_2$ | $Cu(OAc)_2{\cdot}H_2O$ | DMF + $H_2O$ | n.d. | n.d. |
| 23[h] | - | $Cu(OAc)_2{\cdot}H_2O$ | DMF + $H_2O$ | n.d. | n.d. |
| 24[h] | - | $Cu(OAc)_2{\cdot}H_2O$ | $H_2O$ | n.d. | n.d. |

| | | | | | |
|---|---|---|---|---|---|
| 25[c,i] | $Pd(OAc)_2$ | $Cu(OAc)_2·H_2O$ | $H_2O$ | 52 | n.d. |
| 26[g,i] | $Pd(OAc)_2$ | $Cu(OAc)_2·H_2O$ | DMF + $H_2O$ | n.d. | 49 |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (10 mol %), oxidant (2 equiv), solvent (1 mL), 120 °C, 6 h. [b]Isolated yield (in %). [c]Reaction temperature is 110 °C. [d](DMF:$H_2O$ = 3:7). [e](DMF:$H_2O$ = 1:1), [f](DMF:$H_2O$ = 9:1). [g]Reaction time is 8 h. [h]In absence of catalyst. [i]Methyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate **2a'** used. n.d. = not detected.

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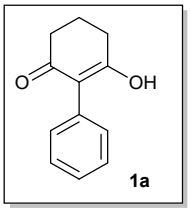
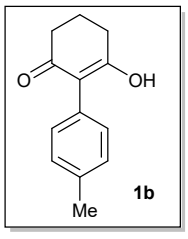
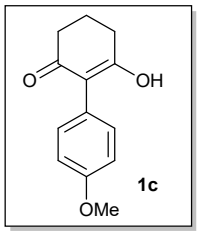
**General Procedure for the Preparation of 2-Aryl-1,3-Dicarbonyl Compounds 1.**[1a] To a stirred solution of 1,3-dicarbonyl compound (9 mmol), CuI (57 mg, 10 mol%), L-proline (69 mg, 20 mol%) and $K_2CO_3$ (1.7 g, 12 mmol) in DMSO (12 mL), aryl iodide (3 mmol) was added. The resultant mixture was stirred at 90 °C for 48 h. The mixture was cooled to 0 °C, acidified with 2 N HCl until the pH became 3-4 and extracted using EtOAc (2 x 50 mL). The combined organic layer was washed with brine (1 x 20 mL) and water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford the 2-aryl-1,3-dicarbonyl compound **1**.



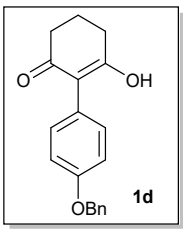

**6-Hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1a.**[1a] Pale yellow solid; yield 62% (350 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.21-7.19 (m, 2H), 6.10 (bs, 1H), 2.58-2.53 (m, 4H), 2.12-2.06 (m, 2H).



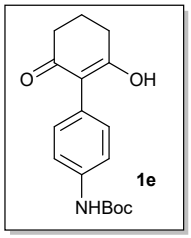

**6-Hydroxy-4'-methyl-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1b.**[1a] Brown solid; yield 65% (394 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.10 (bs, 1H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.49 (t, *J* = 6.4 Hz, 2H), 2.36 (s, 3H), 2.11-2.05 (m, 2H).



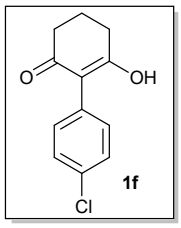

**6-Hydroxy-4'-methoxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1c.**[1a] Colorless solid; yield 54% (353 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.24 (bs, 1H), 3.81 (s, 3H), 2.58-2.49 (m, 4H), 2.10-2.03 (m, 2H).



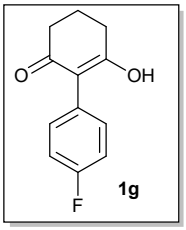

**4'-(Benzyloxy)-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1d.**[1c] Colorless solid; yield 48% (423 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 4H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.06 (s, 1H), 5.08 (s, 2H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.49 (t, *J* = 6.0 Hz, 2H), 2.11-2.04 (m, 2H).



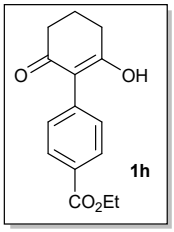

***tert*-Butyl (6'-hydroxy-2'-oxo-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)-carbamate 1e.**[1b] Colorless solid; yield 42% (382 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.53 (s, 1H), 5.99 (bs, 1H), 2.61 (t, *J* = 5.6 Hz, 2H), 2.49 (t, *J* = 5.6 Hz, 2H), 2.11-2.04 (m, 2H), 1.52 (s, 9H).



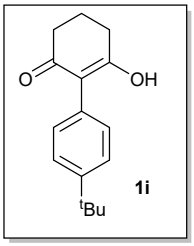

**4'-Chloro-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1f.**[1b] Yellow solid; yield 35% (334 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.59-2.51 (m, 4H), 2.11-2.05 (m, 2H).



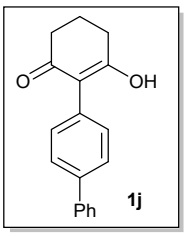

**4'-Fluoro-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1g.**[1b] Colorless solid; yield 55% (340 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.20-7.11 (m, 4H), 5.99 (s, 1H), 2.62-2.60 (m, 2H), 2.51-2.48 (m, 2H), 2.12-2.05 (m, 2H).



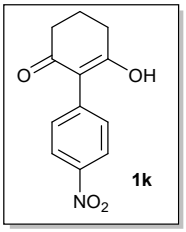

**Ethyl 6'-hydroxy-2'-oxo-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate 1h.**[1c] Colorless solid; yield 62% (484 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J$ = 8.4 Hz, 2H), 7.26 (d, $J$ = 8.4 Hz, 2H), 4.37 (q, $J$ = 7.2 Hz, 2H), 2.62-2.46 (m, 4H), 2.10-2.04 (m, 2H), 1.38 (t, $J$ = 7.2 Hz, 3H).



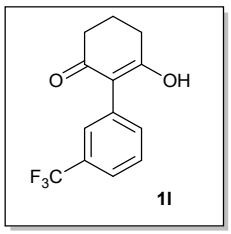

**4'-(*tert*-Butyl)-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1i.**[1c] Brown solid; yield 61% (447 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J$ = 8.8 Hz, 2H), 7.12 (d, $J$ = 8.4 Hz, 2H), 6.11 (bs, 1H), 2.61 (t, $J$ = 6.4 Hz, 2H), 2.50 (d, $J$ = 6.0 Hz, 2H), 2.12-2.05 (m, 2H), 1.32 (s, 9H).



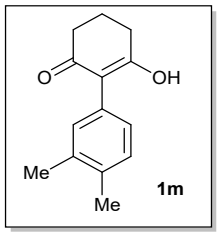

**6-Hydroxy-4,5-dihydro-[1,1':4',1''-terphenyl]-2(3*H*)-one 1j.**[1c] Yellow solid; yield 48% (381 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, $J$ = 8.4 Hz, 2H), 7.59 (d, $J$ = 7.2 Hz, 2H), 7.45 (t, $J$ = 7.2 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.28 (d, $J$ = 8.4 Hz, 2H), 6.07 (bs, 1H), 2.65 (t, $J$ = 6.4 Hz, 2H), 2.54 (t, $J$ = 6.4 Hz, 2H), 2.15-2.08 (m, 2H).



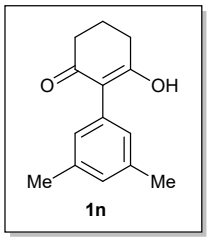

**6-Hydroxy-4'-nitro-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1k.**[1d] Yellow solid; yield 62% (350 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 2.62-2.58 (m, 4H), 2.15-2.08 (m, 2H).



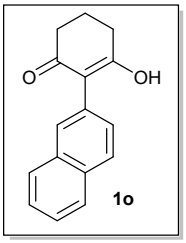

**6-Hydroxy-3'-(trifluoromethyl)-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1l.**[1a] Colorless solid; yield 32% (246 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.46-7.41 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.48-2.44 (m, 4H), 2.02-1.96 (m, 2H).



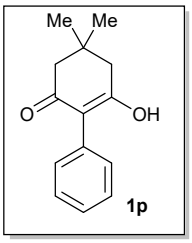

**6-Hydroxy-3',4'-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1m.**[1c] Colorless solid; yield 56% (363 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 6H), 2.11-2.05 (m, 2H).



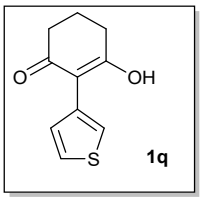

**6-Hydroxy-3',5'-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1n.**[1b] Brown solid; yield 49% (318 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.80 (s, 2H), 6.10 (bs, 1H), 2.59-2.49 (m, 4H), 2.32 (s, 6H), 2.10-2.04 (m, 2H).




**3-Hydroxy-2-(naphthalen-2-yl)cyclohex-2-en-1-one 1o.**[1b] Yellow solid; yield 26% (186 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.86-7.80 (m, 2H), 7.69 (s, 1H), 7.52-7.47 (m, 2H), 7.31-7.28 (m, 1H), 2.61-2.58 (m, 4H), 2.15-2.09 (m, 2H).




**6-Hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one 1p.**[1a] Colorless solid; yield 41% (266 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.06 (bs, 1H), 2.48 (s, 2H), 2.38 (s, 2H), 1.17 (s, 6H).



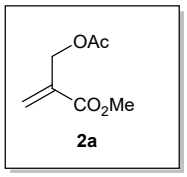

**3-Hydroxy-2-(thiophen-3-yl)cyclohex-2-en-1-one 1q.**[1b] Colorless solid; yield 32% (186 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.24 (dd, *J* = 2.8, 1.3 Hz, 1H), 7.05 (dd, *J* = 4.9, 1.3 Hz, 1H), 2.55 (t, *J* = 6.4 Hz, 4H), 2.10-2.04 (m, 2H).

**General Procedure for the Preparation of MBH Adducts 2a-g.**[2a]

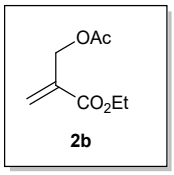
**Step-1:** To a stirred solution of aldehyde (2 mmol) in dioxane/water (1:1) (5 mL), acrylate (6 mmol) and DABCO (224 mg, 2 mmol) were added and stirred at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford the MBH alcohol.

**Step 2:** To a stirred solution of the MBH product (1 mmol), DMAP (244 mg, 0.1 mmol) and $Et_3N$ (139 µL, 1 mmol) in $CH_2Cl_2$ (5 mL), $Ac_2O$ (95 µL, 1 mmol) was added dropwise and the resultant mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), the reaction mixture was poured into an aqueous 2 N HCl and extracted with $CH_2Cl_2$ (2 x 20 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on

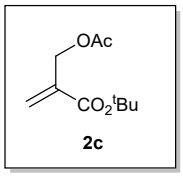
silica gel column chromatography using hexane and EtOAc as eluent to afford the MBH acetate **2**.



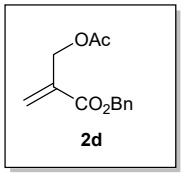

**Methyl 2-(acetoxymethyl)acrylate 2a.**[2a] Colorless liquid; yield 86% (134 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.85 (s, 1H), 4.80 (s, 2H), 3.78 (s, 3H), 2.10 (s, 3H).



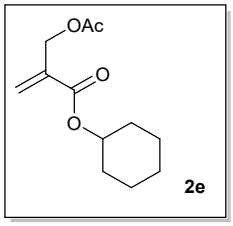

**Benzyl 2-(acetoxymethyl)acrylate 2b.**[2a] Colorless liquid; yield 82% (141 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 5.81 (s, 1H), 4.79 (s, 2H), 4.23 (q, $J$ = 7.2 Hz, 2H), 2.08 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H).




***tert*-Butyl 2-(acetoxymethyl)acrylate 2c.**[2b] Yellow liquid; yield 77% (154 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 5.74 (s, 1H), 4.77 (s, 2H), 2.10 (s, 3H), 1.49 (s, 9H).

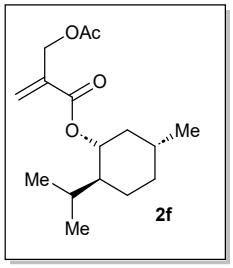



**Benzyl 2-(acetoxymethyl)acrylate 2d.**[2a] Colorless liquid; yield 85% (199 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.38-7.33 (m, 5H), 6.41 (s, 1H), 5.87 (s, 1H), 5.23 (s, 2H), 4.83 (s, 2H), 2.08 (s, 3H).

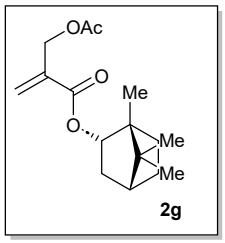



**Cyclohexyl 2-(acetoxymethyl)acrylate 2e.** Analytical TLC on silica gel, 1:9 EtOAc/hexane $R_f$ = 0.5; colorless liquid**;** yield 73% (165 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 5.80 (s, 1H), 4.91-4.85 (m, 1H), 4.81 (s, 2H), 2.10 (s, 3H), 1.87-1.82 (m, 2H), 1.76-1.69 (m, 2H), 1.54-1.28 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.5, 164.6, 136.0, 127.0, 73.3, 62.6, 31.5, 25.4, 23.6, 20.9; FT-IR (neat) 2937, 1725, 2861, 1745, 1717, 1368,

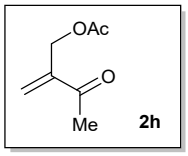
1226, 1170, 1039 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{12}H_{19}O_4$: 227.1278; Found 227.1278.




**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(acetoxymethyl)-acrylate 2f.**[2a] Colorless liquid; yield 72% (203 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 5.81 (s, 1H), 4.82-4.75 (m, 3H), 2.10 (s, 3H), 2.02-2.00 (m, 1H), 1.89-1.83 (m, 1H), 1.71-1.67 (m, 2H), 1.51-1.40 (m, 2H), 1.09-1.00 (m, 2H), 0.92-0.88 (m, 7H), 0.75 (d, *J* = 6.8 Hz, 3H).



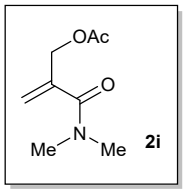

**(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(acetoxymethyl)-acrylate 2g.**[2a] Yellow liquid; yield 75% (210 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 5.82 (s, 1H), 4.98-4.94 (m, 1H), 4.82 (s, 2H), 2.44-2.36 (m, 1H), 2.10 (s, 3H), 1.97-1.90 (m, 1H), 1.81-1.73 (m, 1H), 1.70 (t, *J* = 4.4 Hz, 1H), 1.38-1.30 (m, 1H), 1.27-1.20 (m, 1H), 1.04-0.99 (m, 1H), 0.92 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H).




**2-Methylene-3-oxobutyl Acetate 2h. Step-1:**[2c] To a stirred solution of paraformaldehyde (100 mg, 3.32 mmol) in ethanol (0.40 mL, 6.85 mmol), methyl vinyl ketone (166 mg, 2.37 mmol) and DABCO (13 mg, 0.12 mmol) were added and the resultant mixture was stirred for 3 h at room temperature. After completion (monitored by TLC), evaporation of the solvent gave a residue that was purified on silica gel column chromatography using pentane and diethyl ether as eluent to afford the MBH alcohol in 82% (195 mg) yield.

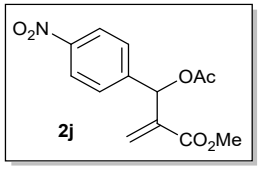
**Step 2:**[2a] To a stirred solution of the MBH alcohol (100 mg, 1 mmol), DMAP (244 mg, 0.1 mmol) and $Et_3N$ (139 µL, 1 mmol) in $CH_2Cl_2$ (5 mL), $Ac_2O$ (95 µL, 1 mmol) was added dropwise and the resultant mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), the reaction mixture was poured into 2 N HCl and extracted with $CH_2Cl_2$ (2 x 20 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford the MBH

acetate **2h** in 73% yield (103 mg) as a colorless liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 6.00 (s, 1H), 4.78 (s, 2H), 2.35 (s, 3H), 2.08 (s, 3H).



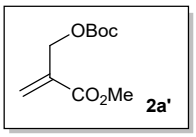

**2-(Dimethylcarbamoyl)allyl Acetate 2i. Step-1:**[2d] To a stirred solution of paraformaldehyde (924 mg, 30 mmol) in $^t$BuOH/$H_2O$ (3:7) (370 µL), DABCO (693 mg, 6 mmol), phenol (141 mg, 1.5 mmol) and *N*,*N*-dimethylacrylamide (618 µL, 6 mmol) were added and the resultant mixture was stirred for 3 days at 55 °C under argon atmosphere. After completion (monitored by TLC), the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (3 x 5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford the MBH alcohol in 74% (573 mg).

**Step 2:**[2a] To a stirred solution of the MBH alcohol (129 mg, 1 mmol), DMAP (244 mg, 0.1 mmol) and $Et_3N$ (139 µL, 1 mmol) in $CH_2Cl_2$ (5 mL), $Ac_2O$ (95 µL, 1 mmol) was added dropwise and the resultant mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), the reaction mixture was poured 2 N HCl and extracted with $CH_2Cl_2$ (2 x 20 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford the MBH acetate **2i** in 84% (144 mg) as a colorless liquid. Analytical TLC on silica gel, 1:1 EtOAc/hexane $R_f$ = 0.5; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 5.26 (s, 1H), 4.75 (s, 2H), 3.05 (s, 3H), 2.98 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.7, 139.6, 117.6, 64.9, 38.9, 34.9, 20.9; FT-IR (neat) 2932, 1729, 1709, 1611, 1060 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_8H_{14}NO_3$: 172.0968; Found 172.0970.



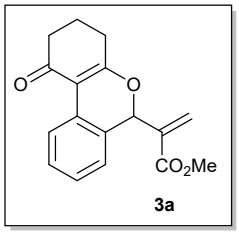

**Methyl 2-(acetoxy(4-nitrophenyl)methyl)acrylate 2j. Step-1:**[2a] To a stirred solution of 4-nitrobenzaldehyde (302 mg, 2 mmol), methyl acrylate (517 mg, 6 mmol) and DABCO (224 mg, 2 mmol) were stirred at room temperature under solvent free condition for 6 h. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford the MBH alcohol.

**Step 2:**[2a] To a stirred solution of the MBH alcohol (237 mg, 1 mmol), DMAP (244 mg, 0.1 mmol) and $Et_3N$ (139 µL, 1 mmol) in $CH_2Cl_2$ (5 mL), $Ac_2O$ (95 µL, 1 mmol) was added dropwise and the resultant mixture was stirred at room temperature for 2 h. After completion (monitored by TLC), the reaction mixture was poured into 2 N HCl and extracted with $CH_2Cl_2$ (2 x 20 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford the MBH acetate **2j** in 86% yield (240 mg) as a yellow liquid. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 6.70 (s, 1H), 6.45 (s, 1H), 5.97 (s, 1H), 3.71 (s, 3H), 2.13 (s, 3H).



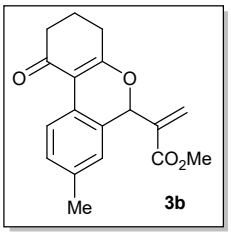

**Methyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate 2a'.**[2e] To a stirred solution of the methyl 2-(hydroxymethyl)acrylate (100 mg, 1 mmol) in $CH_2Cl_2$ (5 mL), $(Boc)_2O$ (0.25 mL, 1.1 mmol) and DMAP (244 mg, 0.05 mmol) were added at 0 °C and the resultant mixture was stirred at room temperature for 16 h. After completion (monitored by TLC), the reaction mixture was quenched with water (5 mL) and extracted with $CH_2Cl_2$ (3 x 5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford **2a'** in 64% yield (138 mg) as a colorless liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 5.86 (s, 1H), 4.77 (s, 2H), 3.76 (s, 3H), 1.47 (s, 9H).

**General Procedure for the Pd-Catalyzed Non-dehydrogenative C-H Functionalization and Annulation of 2-Aryl-3-hydroxy-2-cyclohexenones with MBH Adducts.** In a pressure tube, 2-aryl-3-hydroxy-2-cyclohexenone **1** (0.1 mmol), MBH adduct **2** (0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) were stirred in $H_2O$ (1 mL) at 110 °C for 6 h. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **3**.

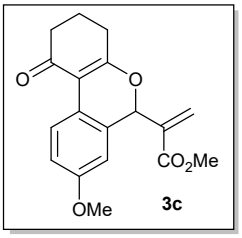



**Methyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3a.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; colorless liquid; yield 85% (24 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.22 (t,

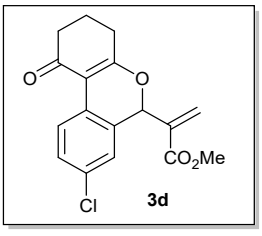
*J* = 7.6 Hz, 1H), 6.94 (d, *J* = 6.4 Hz, 1H), 6.43 (s, 1H), 6.26 (s, 1H), 5.39 (s, 1H), 3.84 (s, 3H), 2.59-2.42 (m, 4H), 2.02-1.96 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 171.7, 166.2, 137.7, 130.5, 129.0, 127.7, 127.5, 127.3, 125.4, 125.1, 112.7, 76.0, 52.5, 38.5, 29.5, 20.1; FT-IR (neat) 2951, 1725, 1657, 1598, 1385, 1288, 1180, 1145 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}O_4$: 285.1121; Found 285.1124.




**Methyl 2-(8-methyl-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3b.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.52; brown liquid; yield 88% (26 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 6.42 (s, 1H), 6.22 (s, 1H), 5.38 (s, 1H), 3.84 (s, 3H), 2.56-2.41 (m, 4H), 2.31 (s, 3H), 2.00-1.94 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.6, 171.0, 166.3, 137.8, 137.1, 130.6, 129.7, 127.5, 125.6, 125.3, 124.9, 112.6, 75.9, 52.4, 38.5, 29.4, 21.3, 20.2; FT-IR (neat) 2951, 1725, 1657, 1600, 1501, 1379, 1288, 1149 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_4$:299.1278; Found 299.1278.

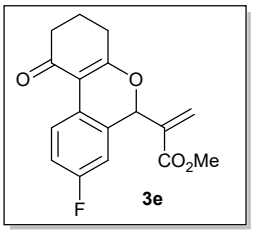



**Methyl 2-(8-methoxy-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3c.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.45; colorless liquid; yield 70% (22 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.50 (s, 1H), 6.42 (s, 1H), 6.22 (s, 1H), 5.40 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.54-2.36 (m, 4H), 2.00-1.95 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.6, 170.0, 166.2, 158.8, 137.6, 130.5, 129.2, 126.9, 120.5, 113.8, 112.4, 111.0, 75.8, 55.5, 52.4, 38.5, 29.3, 20.2; FT-IR (neat) 2925, 1724, 1655, 1602, 1501, 1257, 1146, 1000 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_5$: 315.1227; Found 315.1226.

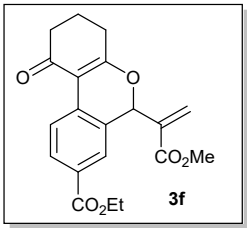



**Methyl 2-(8-chloro-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3d.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; yellow liquid; yield

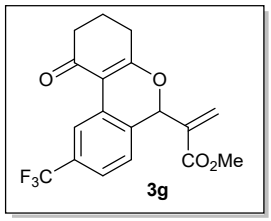
84% (27 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 6.47 (s, 1H), 6.21 (s, 1H), 5.45 (s, 1H), 3.84 (s, 3H), 2.59-2.41 (m, 4H), 2.02-1.96 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.3, 171.9, 165.8, 137.3, 132.7, 130.8, 129.3, 129.0, 126.8, 126.2, 125.1, 112.0, 75.6, 52.5, 38.4, 29.4, 20.1; FT-IR (neat) 2953, 1725, 1658, 1594, 1486, 1378, 1279, 1149, 1001 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}ClO_4$: 319.0732; Found 319.0731.



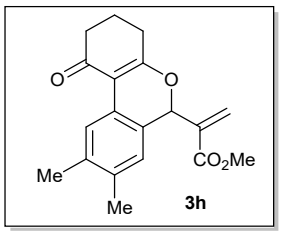

**Methyl 2-(8-fluoro-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]-chromen-6-yl)acrylate 3e.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; colorless liquid; yield 78% (24 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 9.2, 6.0 Hz, 1H), 7.04 (td, *J* = 8.8, 2.8 Hz, 1H), 6.67 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.47 (s, 1H), 6.21 (s, 1H), 5.45 (s, 1H), 3.84 (s, 3H), 2.60-2.39 (m, 4H), 2.02-1.96 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.4, 171.2, 165.9, 162.7 ($J_{C\text{-}F}$ = 245.8 Hz), 137.3, 130.6, 129.8 ($J_{C\text{-}F}$ = 7.2 Hz), 127.5 ($J_{C\text{-}F}$ = 7.6 Hz), 123.8 ($J_{C\text{-}F}$ = 2.9 Hz), 115.8 ($J_{C\text{-}F}$ = 20.5 Hz), 112.2 ($J_{C\text{-}F}$ = 22.9 Hz), 112.1, 75.6 ($J_{C\text{-}F}$ = 2.1 Hz), 52.5, 38.4, 29.3, 20.1; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -114.02; FT-IR (neat) 2953, 1725, 1657, 1582, 1496, 1379, 1250, 1146 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}FO_4$: 303.1027; Found 303.1033.



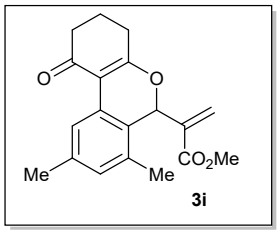

**Ethyl 6-(3-methoxy-3-oxoprop-1-en-2-yl)-1-oxo-2,3,4,6-tetra-hydro-1*H*-benzo[*c*]chromene-8-carboxylate 3f.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.43; colorless liquid; yield 81% (29 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 6.46 (s, 1H), 6.32 (s, 1H), 5.38 (s, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 2.61-2.55 (m, 2H), 2.51-2.44 (m, 2H), 2.02-1.98 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.3, 173.4, 166.2, 165.9, 137.4, 132.0, 131.0, 130.2, 129.1, 127.4, 126.4, 125.2, 112.2, 76.0, 61.2, 52.5, 38.4, 29.6, 20.0, 14.5; FT-IR (neat) 2953, 1718, 1661, 1595, 1381, 1289, 1191, 1001 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{21}O_6$: 357.1333; Found 357.1334.




**Methyl 2-(1-oxo-9-(trifluoromethyl)-2,3,4,6-tetrahydro-1*H*-benzo-[*c*]chromen-6-yl)acrylate 3g.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.51; brown sticky liquid; yield 78% (27 mg); 5:1 mixture of regioisomers; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H, major), 7.57 (d, *J* = 8.0 Hz, 0.2H, minor), 7.51-7.46 (m, 1.2H, major + minor), 7.22 (d, *J* = 7.6 Hz, 0.2H, minor) 7.06 (d, *J* = 8.0 Hz, 1H, major), 6.48 (s, 1H, major), 6.30 (s, 1H, major), 6.06 (s, 0.2H, minor), 5.44 (s, 1H, major), 5.33 (s, 0.2H, minor), 3.84 (s, 3H, major), 3.59 (s, 0.6H, minor), 2.70-2.42 (m, 4.8H, major + minor), 2.04-1.97 (m, 2.4H, major + minor); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 206.3, 196.2, 172.7, 168.2, 165.8, 138.3 ($J_{C\text{-}F}$ = 187.8 Hz), 137.2, 131.3, 131.1, 130.8, 130.7, 130.1, 128.4, 127.4, 125.5, 125.3, 124.0 ($J_{C\text{-}F}$ = 3.5 Hz), 123.1, 122.4 ($J_{C\text{-}F}$ = 3.7 Hz), 111.7, 75.8, 74.6, 52.6, 52.0, 38.9, 38.3, 35.5, 29.5, 20.0, 17.5; $^{19}$F NMR (565 MHz, $CDCl_3$) δ -62.68; FT-IR (neat) 2955, 1725, 1658, 1598, 1326, 1269, 1162, 1124, 1077 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}F_3O_4$: 353.0995; Found 353.1001.

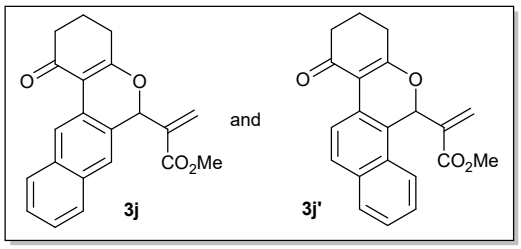



**Methyl 2-(8,9-dimethyl-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]-chromen-6-yl)acrylate 3h.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.53; brown liquid; yield 89% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 6.70 (s, 1H), 6.41 (s, 1H), 6.20 (s, 1H), 5.39 (s, 1H), 3.84 (s, 3H), 2.57-2.35 (m, 4H), 2.28 (s, 3H), 2.22 (s, 3H), 1.99-1.94 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.6, 171.1, 166.3, 137.9, 137.3, 135.8, 130.5, 126.4, 126.2, 125.1, 125.0, 112.7, 75.8, 52.4, 38.5, 29.5, 20.2, 20.1, 19.7; FT-IR (neat) 2950, 1723, 1654, 1596, 1451, 1385, 1251, 1143 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_4$: 313.1434; Found 313.1437.

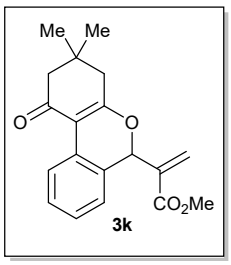



**Methyl 2-(7,9-dimethyl-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]-chromen-6-yl)acrylate 3i.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.53; yellow liquid; yield 72% (22 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 6.90 (s, 1H), 6.47 (s,

1H), 6.34 (s, 1H), 5.21 (s, 1H), 3.87 (s, 3H), 2.57-2.36 (m, 4H), 2.34 (s, 3H), 2.10 (s, 3H), 1.97-1.91 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 170.9, 166.5, 138.4, 136.3, 133.0, 130.9, 130.1, 127.5, 123.8, 122.8, 112.8, 72.8, 52.5, 38.6, 29.6, 21.7, 20.1, 18.3; FT-IR (neat) 2951, 1726, 1657, 1609, 1375, 1274, 1190, 1136, 1072 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_4$: 313.1434; Found 313.1430.

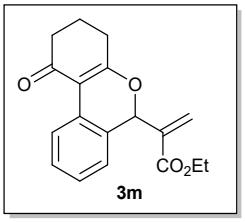



**Methyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-naphtho-[2,3-*c*]chromen-6-yl)acrylate 3j and Methyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-naphtho[2,1-*c*]chromen-6-yl)acrylate 3j`.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.52; brown liquid; yield 81% (27 mg); 2:1 mixture of regioisomers; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H, major), 8.56 (d, *J* = 8.8 Hz, 0.5H, minor), 7.91-7.83 (m, 1.7H, major + minor), 7.71 (d, *J* = 7.6 Hz, 1H, major), 7.55 (d, *J* = 7.2 Hz, 0.5H, minor), 7.48-7.41 (m, 4.5H, major + minor), 7.15 (s, 0.5H, minor), 6.46 (s, 1H, major), 6.40 (s, 1H, major), 6.35 (s, 0.5H, minor), 5.43 (s, 1H, major), 5.18 (s, 0.5H, minor), 3.93 (s, 1.5H, minor), 3.85 (s, 3H, major), 2.66- 2.45 (m, 6H, major + minor), 2.06-1.99 (m, 3H, major + minor); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.9 (major), 196.4 (minor), 172.1 (major), 171.4 (minor), 166.5 (minor), 166.2 (major), 138.2 (major), 135.7 (minor), 134.0 (major), 132.8 (minor), 132.3 (major), 131.6 (minor), 130.5 (major), 129.0 (major), 128.8 (minor), 128.7 (major), 127.5 (major), 126.9 (minor), 126.5 (major), 126.2 (minor), 126.1 (major), 125.6 (minor), 124.7 (minor), 124.3 (major), 124.2 (major), 123.7 (minor), 122.1 (major), 120.9 (minor), 113.0 (minor), 112.6 (major), 76.3 (major), 72.7 (minor), 52.6 (minor), 52.5 (major), 38.7 (major), 38.5 (minor), 29.7 (major), 29.6 (minor), 20.15 (major), 20.13 (minor); FT-IR (neat) 2955, 1728, 1655, 1585, 1398, 1191, 1073 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}O_4$: 335.1278; Found 335.1279.

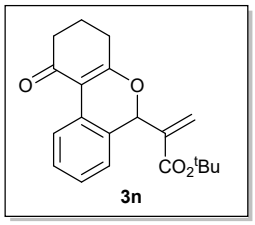



**Methyl 2-(3,3-dimethyl-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3k.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.60; brown sticky liquid; yield 91% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 6.27 (s, 1H), 5.36

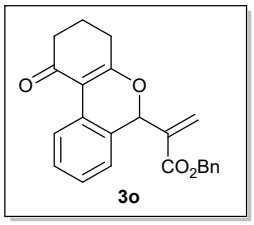
(s, 1H), 3.84 (s, 3H), 2.44-2.29 (m, 4H), 1.08 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 170.3, 166.2, 138.0, 130.3, 129.0, 127.6, 127.3, 127.2, 125.2, 125.1, 111.4, 76.0, 52.4, 52.3, 43.2, 31.8, 29.0, 27.6; FT-IR (neat) 2956, 1726, 1657, 1602, 1443, 1382, 1287, 1149, 1035 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_4$: 313.1434; Found 313.1436.




**Ethyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3m.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.55; yellow liquid; yield 85% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 6.26 (s, 1H), 5.39 (s, 1H), 4.33-4.27 (m, 2H), 2.60-2.39 (m, 4H), 2.02-1.95 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 171.8, 165.7, 138.1, 130.0, 129.0, 127.7, 127.6, 127.3, 125.3, 125.1, 112.7, 76.1, 61.4, 38.5, 29.5, 20.1, 14.3; FT-IR (neat) 2949, 1720, 1658, 1599, 1490, 1385, 1287, 1178, 1106 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_4$: 299.1278; Found 299.1275.

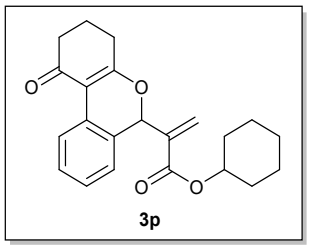



***tert*-Butyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)-acrylate 3n.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.40; colorless liquid; yield 82% (27 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 6.20 (s, 1H), 5.30 (s, 1H), 2.55-2.43 (m, 4H), 2.00-1.96 (m, 2H), 1.51 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 196.5, 171.9, 165.0, 139.5, 129.0, 128.9, 127.8, 127.6, 127.2, 125.3, 125.1, 112.6, 81.9, 76.4, 38.5, 29.4, 28.2, 20.1; FT-IR (neat) 2932, 1716, 1659, 1599, 1491, 1386, 1147, 1106 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{23}O_4$: 327.1591; Found 327.1585.

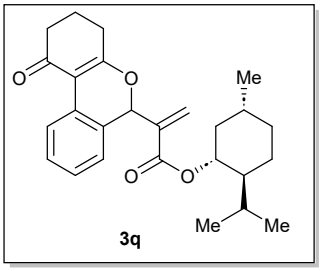



**Benzyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)-acrylate 3o.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.53; colorless liquid; yield

81% (29 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.0 Hz, 1H), 7.38-7.34 (m, 6H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 1H), 6.46 (s, 1H), 6.28 (s, 1H), 5.40 (s, 1H), 5.29 (q, *J* = 12.5 Hz, 2H), 2.55-2.35 (m, 4H), 1.98-1.93 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 171.7, 165.5, 137.9, 135.8, 130.7, 129.0, 128.7, 128.5, 128.3, 127.6, 127.4, 127.3, 125.4, 125.1, 112.6, 76.1, 67.1, 38.4, 29.4, 20.1; FT-IR (neat) 2927, 1722, 1657, 1599, 1384, 1148, 1106 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}O_4$: 361.1434; Found 361.1438.

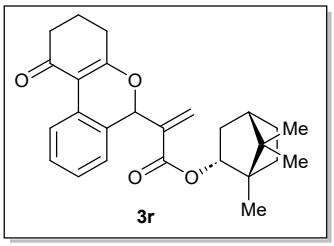



**Cyclohexyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3p.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.42; brown liquid; yield 74% (26 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.40 (s, 1H), 6.24 (s, 1H), 5.37 (s, 1H), 4.97-4.91 (m, 1H), 2.57-2.42 (m, 4H), 2.02-1.96 (m, 2H), 1.90-1.83 (m, 2H), 1.74-1.68 (m, 2H), 1.53-1.28 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 171.9, 165.1, 138.6, 129.7, 128.9, 127.7, 127.6, 127.2, 125.3, 125.1, 112.6, 76.4, 73.6, 38.5, 31.6, 31.5, 29.5, 25.5, 23.7, 23.6, 20.2; FT-IR (neat) 2936, 1718, 1655, 1597, 1452, 1386, 1285, 1179, 1008 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{25}O_4$: 353.1747; Found 353.1752.

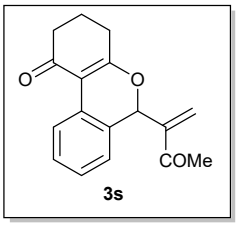



**(1*R*,2*S*,5*R*)-2-isoPropyl-5-methylcyclohexyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3q.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.50; yellow liquid; 1.2:1 mixture of diastereomers; yield 72% (29 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, *J* = 7.2 Hz, 1.85H, major + minor), 7.35 (t, *J* = 7.6 Hz, 1.86H, major + minor), 7.21 (t, *J* = 7.6 Hz, 1.85H, major + minor), 6.97-6.95 (m, 1.88H, major + minor), 6.38 (s, 1.84H, major + minor), 6.26 (s, 1H, major), 6.23 (s, 0.82H, minor) , 5.35 (s, 0.85H, minor), 5.30 (s, 1H, major), 4.88-4.80 (m, 1.86H, major + minor), 2.57-2.37 (m, 7.49H, major + minor), 2.09-2.06 (m, 1H, major), 2.02-1.97 (m, 4.53H, major + minor), 1.89-1.82 (m, 1.85H, major + minor), 1.72-1.68 (m, 3.79H, major + minor), 1.52-1.39 (m, 3.76H, major + minor), 1.10-1.00 (m, 3.74H, major + minor), 0.94-0.87 (m, 13H, major + minor), 0.79 (d, *J* = 7.2 Hz, 2.62H, minor), 0.75 (d, *J* = 6.8 Hz, 3H, major); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.5

(major), 171.8 (minor), 171.6 (major), 165.4 (major), 165.3 (minor), 138.5 (major), 129.7 (minor), 129.5 (major), 128.9 (major), 127.7 (major), 127.6 (minor), 127.5 (major), 127.2 (major), 125.4 (major), 125.3 (minor), 125.1 (major), 125.0 (minor), 112.7 (minor), 112.5 (major), 76.4 (minor), 76.3 (major), 75.5 (major), 75.4 (minor), 47.2 (major), 47.1 (minor), 41.0 (major), 40.8 (minor), 38.5 (minor), 38.4 (major), 34.4 (major), 34.3 (minor), 31.6 (major), 31.5 (minor), 29.4 (major), 26.7 (minor), 26.1 (major), 23.7 (minor), 23.3 (major), 22.2 (major), 22.1 (minor), 21.0 (major), 20.8 (minor), 20.2 (major), 20.1 (minor), 16.7 (minor), 16.2 (major); FT-IR (neat) 2954, 1719, 1659, 1599, 1455, 1386, 1179 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{33}O_4$: 409.2373; Found 409.2372.




**(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate 3r.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.45; yellow liquid; 1:1 mixture of diastereomers; yield 68% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.00-6.97 (m, 2H), 6.49-6.48 (m, 2H), 6.25-6.23 (m, 2H), 5.42 (d, *J* = 6.8 Hz, 2H), 5.08-5.00 (m, 2H), 2.61-2.52 (m, 4H), 2.48-2.41 (m, 4H), 2.04-1.98 (m, 4H), 1.92- 1.71 (m, 10H), 1.15-1.06 (m, 2H), 0.95-0.94 (m, 6H), 0.90-0.83 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.5 (major), 171.8 (major), 166.0 (minor), 138.3 (major), 138.2 (minor), 130.3 (major), 130.2 (minor), 128.93 (major), 128.91 (minor), 127.7 (major), 127.66 (minor), 127.61 (major), 127.58 (minor), 127.2 (major), 125.3 (major), 125.0 (minor), 124.9 (major), 112.6 (major), 81.3 (major), 81.2 (minor), 76.8 (major), 76.6 (minor), 49.2 (major), 49.0 (minor), 48.0 (major), 45.1 (major), 45.0 (minor), 38.5 (major), 36.9 (major), 29.5 (major), 29.4 (minor), 28.2 (major), 28.1 (minor), 27.4 (major), 27.3 (minor), 20.2 (major), 19.8 (major), 19.0 (major), 13.7 (major), 13.6 (minor); FT-IR (neat) 2954, 1714, 1598, 1453, 1386, 1259, 1221, 1013 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{31}O_4$: 407.2217; Found 407.2219.

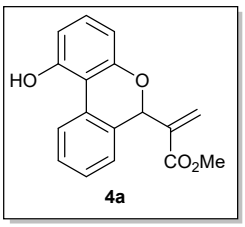



**6-(3-Oxobut-1-en-2-yl)-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-one 3s.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.45; colorless liquid; yield 46% (12 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.20 (t,

*J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 6.30 (s, 1H), 5.62 (s, 1H), 2.58-2.54 (m, 2H), 2.50-2.38 (m, 5H), 2.00-1.95 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 198.0, 196.4, 172.0, 145.6, 129.9, 128.9, 127.9, 127.6, 127.3, 125.3, 125.1, 112.6, 74.9, 38.5, 29.5, 26.6, 20.1; FT-IR (neat) 2952, 1715, 1651, 1596, 1389, 1285, 1151 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}O_3$: 269.1172; Found 269.1171.

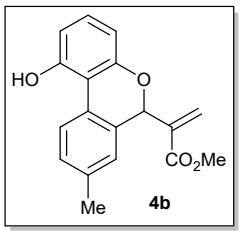
**Scale-up Synthesis of 3a.** In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (376 mg, 2 mmol), methyl 2-(acetoxymethyl)acrylate **2a** (474 mg, 3 mmol), $Pd(OAc)_2$ (45 mg, 10 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (799 mg, 4 mmol) were stirred in $H_2O$ (20 mL) at 110 °C for 6 h. The work up and purification were performed as described in the general procedure to produce **3a** in 72% (409 mg) yield.

**General Procedure for the Pd-Catalyzed Dehydrogenative C-H Functionalization and Annulation of 2-Aryl-3-hydroxy-2-cyclohexenones with MBH Adducts.** In a pressure tube, 2-aryl-3-hydroxy-2-cyclohexenone **1** (0.1 mmol), MBH adduct **2** (0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) were stirred in DMF:$H_2O$ (9:1) (1 mL) at 120 °C for 8 h. After completion (monitored by TLC), the reaction mixture was quenched with ice-cold water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **4**.

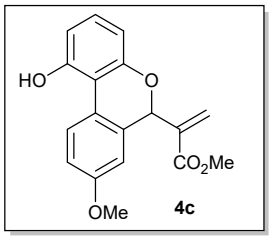


**4a**

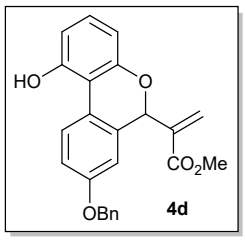
**Methyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4a.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.48; colorless solid; mp =187 °C; yield 78% (22 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 6.11 (s, 1H), 5.50 (s, 1H), 5.48 (bs, 1H), 3.83 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 154.8, 153.7, 138.5, 132.2, 129.7, 129.3, 128.9, 128.7, 127.4, 126.5, 125.9, 111.4, 110.9, 110.4, 74.8, 52.4; FT-IR (neat) 3402, 2952, 1708, 1602, 1439, 1278, 1152, 1036 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}O_4$: 283.0965; Found 283.0966.




**Methyl 2-(1-hydroxy-8-methyl-6*H*-benzo[*c*]chromen-6-yl)-acrylate 4b.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; brown sticky liquid; yield 81% (24 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 6.08 (s, 1H), 5.48 (s, 1H), 5.42 (s, 1H), 3.83 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.7, 154.5, 153.5, 138.6, 137.3, 132.2, 129.7, 129.4, 128.8, 126.5, 126.4, 126.1, 111.5, 110.8, 110.3, 74.8, 52.3, 21.4; FT-IR (neat) 3413, 2952, 1710, 1612, 1458, 1344, 1278, 1130, 1041 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}O_4$: 297.1121; Found 297.1118.

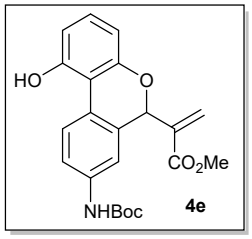



**Methyl 2-(1-hydroxy-8-methoxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4c.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.43; brown liquid; yield 85% (27 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.66 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 6.09 (s, 1H), 5.48 (s, 1H), 5.35 (bs, 1H), 3.83-3.82 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 158.9, 154.0, 153.0, 138.3, 133.9, 129.7, 128.3, 128.1, 121.7, 113.9, 111.5, 111.3, 110.9, 110.3, 74.8, 55.5, 52.3; FT-IR (neat) 3410, 2928, 1715, 1613, 1466, 1270, 1152, 1033 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}O_5$: 313.1071; Found 313.1068.

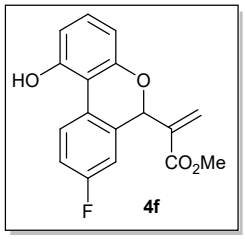



**Methyl 2-(8-(benzyloxy)-1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)-acrylate 4d.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; colorless solid; mp =160 °C; yield 82% (32 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 1H), 7.44-7.37 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.02-6.95 (m, 2H), 6.73 (d, *J* = 2.8 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 6.07 (s, 1H), 5.50-5.46 (m, 2H), 5.08 (s, 2H), 3.82 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 158.0, 154.0, 153.1, 138.3, 136.8, 133.9, 129.8, 128.8, 128.3, 128.2, 128.1, 127.7, 122.0, 114.8, 112.4, 111.3, 110.7, 110.4, 74.8, 70.2,

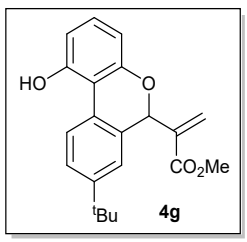
52.4; FT-IR (neat) 3405, 2927, 1702, 1613, 1466, 1270, 1147, 1027 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{21}O_5$: 389.1384; Found 389.1385.




**Methyl 2-(8-((*tert*-butoxycarbonyl)amino)-1-hydroxy-6*H*-benzo[*c*]-chromen-6-yl)acrylate 4e.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.35; brown liquid; yield 79% (31 mg); $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.56-6.54 (m, 2H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 6.10 (s, 1H), 5.82 (bs, 1H), 5.44 (s, 1H), 3.83 (s, 3H), 1.53 (s, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 166.6, 154.1, 153.5, 152.8, 138.2, 137.4, 133.0, 129.9, 128.6, 127.6, 124.0, 118.5, 115.7, 111.1, 110.7, 110.4, 81.0, 74.7, 52.3, 28.5; FT-IR (neat) 3336, 2978, 1704, 1527, 1459, 1416, 1244, 1158, 1062, $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{22}H_{23}NO_6Na$: 420.1418; Found 420.1416.

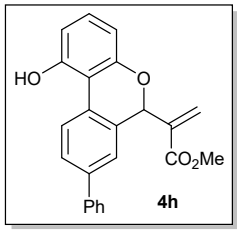



**Methyl 2-(8-fluoro-1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)-acrylate 4f.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.48; colorless solid; mp =171 °C; yield 74% (22 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.08 (td, *J* = 8.8, 2.8 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.39 (s, 1H), 6.07 (s, 1H), 5.55 (s, 1H), 5.49 (bs, 1H), 3.84 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 166.4, 162.8 ($J_{C\text{-}F}$ = 246.2 Hz), 154.4, 153.4, 138.0, 134.5 ($J_{C\text{-}F}$ = 7 Hz), 129.9, 129.1, 128.8 ($J_{C\text{-}F}$ = 7.7 Hz), 125.2 ($J_{C\text{-}F}$ = 3.2 Hz), 115.5 ($J_{C\text{-}F}$ = 20.6 Hz), 112.9 ($J_{C\text{-}F}$ = 22.5 Hz), 110.8, 110.7, 110.4, 74.6 ($J_{C\text{-}F}$ = 2.0 Hz), 52.4; $^{19}F$ NMR (470 MHz, $CDCl_3$) δ -113.98; FT-IR (neat) 3406, 2952, 1707, 1612, 1467, 1272, 1152, 1038 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}FO_4$: 301.0871; Found 301.0871.

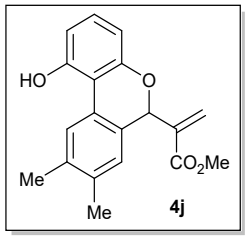



**Methyl 2-(8-(*tert*-butyl)-1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4g.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.55; colorless solid; mp =143 °C;

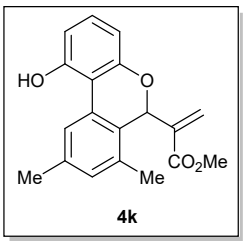
yield 74% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 6.13 (s, 1H), 5.44-5.42 (m, 2H), 3.83 (s, 3H), 1.32 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.8, 154.4, 153.5, 150.6, 138.6, 131.7, 129.6, 128.9, 126.1, 126.0, 125.7, 122.9, 111.3, 110.8, 110.2, 75.1, 52.3, 34.8, 31.4; FT-IR (neat) 3408, 2959, 1708, 1613, 1462, 1277, 1220, 1039 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{23}O_4$: 339.1591; Found 339.1598.



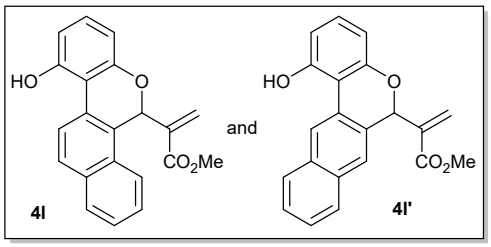

**Methyl 2-(1-hydroxy-8-phenyl-6*H*-benzo[*c*]chromen-6-yl)-acrylate 4h.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; brown sticky liquid; yield 81% (29 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.62-7.60 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.37-7.34 (m, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 6.20 (s, 1H), 5.54 (s, 1H), 5.40 (bs, 1H), 3.84 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 154.7, 153.7, 140.5, 140.1, 138.5, 132.6, 129.8, 129.3, 129.0, 128.0, 127.6, 127.3, 127.1, 127.0, 124.4, 111.2, 111.0, 110.4, 75.0, 52.4; FT-IR (neat) 3406, 2926, 1706, 1596, 1464, 1443, 1277, 1132, 1032 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}O_4$: 359.1278; Found 359.1268.



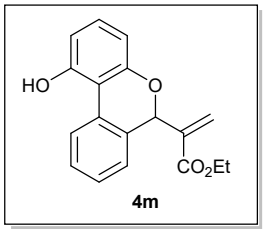

**Methyl 2-(1-hydroxy-8,9-dimethyl-6*H*-benzo[*c*]chromen-6-yl)acrylate 4j.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.51; brown liquid; yield 83% (26 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 6.06 (s, 1H), 5.48 (s, 1H), 5.40 (s, 1H), 3.83 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.7, 154.6, 153.4, 138.7, 136.9, 136.0, 129.9, 129.6, 128.7, 127.3, 127.1, 126.4, 111.5, 110.8, 110.3, 74.6, 52.3, 20.2, 19.8; FT-IR (neat) 3214, 2950, 1705, 1610, 1445, 1339, 1273, 1148, 1042 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; Found 311.1275.



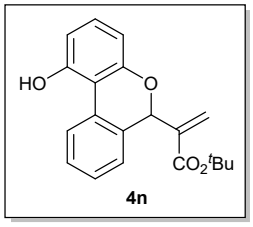

**Methyl 2-(1-hydroxy-7,9-dimethyl-6*H*-benzo[*c*]chromen-6-yl)acrylate 4k.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.51; brown sticky liquid; yield 71% (22 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.01-6.97 (m, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 6.20 (s, 1H), 5.30 (bs, 1H), 5.20 (s, 1H), 3.85 (s, 3H), 2.38 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.8, 153.8, 153.4, 138.0, 137.0, 133.9, 130.3, 129.9, 129.1, 128.7, 127.7, 124.7, 111.7, 111.3, 110.4, 71.5, 52.3, 21.8, 18.6; FT-IR (neat) 3423, 2925, 1726, 1609, 1428, 1346, 1286, 1139, 1040 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; Found 311.1264.



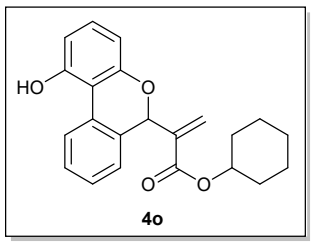

**Methyl 2-(1-hydroxy-6*H*-naphtho[2,1-*c*]chromen-6-yl)acrylate 4l and Methyl 2-(1-hydroxy-6*H*-naphtho[2,3-*c*]chromen-6-yl)-acrylate 4l'.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.50; brown sticky liquid; 1.2:1 mixture of regioisomers; yield 80% (27 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 8.91 (s, 0.86H, minor), 8.61 (d, *J* = 8.4 Hz, 1H, major), 7.91-7.87 (m, 3.20H, major + minor), 7.78 (d, *J* = 8.4 Hz, 0.88H, minor), 7.71 (d, *J* = 8.4 Hz, 1H, major), 7.56 (s, 1H, minor), 7.51-7.46 (m, 3.71H, major + minor), 7.07 (q, *J* = 7.8 Hz, 2H, major + minor), 7.02 (s, 1H, major), 6.64-6.61 (m, 1.86H, major + minor), 6.54 (d, *J* = 7.2 Hz, 0.87H, minor), 6.48 (d, *J* = 8.4 Hz, 1H, major), 6.40 (s, 0.88H, minor), 6.26 (s, 0.85H, minor), 6.22 (s, 1H, major), 5.67 (bs, 0.71H, major), 5.53-5.52 (m, 1.63H, major + minor), 5.18 (s, 1H, major), 3.92 (s, 3H, major), 3.85 (s, 2.59H, minor); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.9 (major), 166.6 (minor), 155.3 (minor), 154.1 (major), 153.6 (minor), 153.5 (major), 139.0 (minor), 136.4 (major), 133.8 (major), 132.6 (major), 132.3 (minor), 131.5 (minor), 130.7 (major), 129.8 (minor), 129.6 (major), 129.4 (minor), 129.3 (major), 128.7 (minor), 128.6 (major), 128.5 (minor), 127.7 (major), 127.1 (minor), 127.0 (major), 126.5 (minor), 126.46 (major), 126.44 (minor), 126.40 (major), 126.0 (major), 125.7 (minor), 124.7 (minor), 124.6 (major), 122.8 (minor), 111.7 (major), 111.6 (minor), 111.2 (major), 111.1 (minor), 110.5 (major), 75.3 (minor), 71.4 (major), 52.5 (major), 52.4 (minor); FT-IR (neat) 3406, 3057, 2952, 1708, 1610, 1462, 1336, 1280, 1144 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{17}O_4$: 333.1121; Found 333.1115.




**Ethyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4m.** Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.53; colorless liquid; yield 76% (23 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 6.11 (s, 1H), 5.50 (s, 1H), 5.30 (bs, 1H), 4.30 (q, *J* = 6.8 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.1, 154.9, 153.6, 138.9, 132.3, 129.3, 129.2, 128.9, 128.6, 127.4, 126.4, 125.9, 111.4, 110.9, 110.3, 74.9, 61.2, 14.4; FT-IR (neat) 3402, 2986, 1701, 1609, 1439, 1277, 1150, 1029 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}O_4$: 297.1121; Found 297.1125.

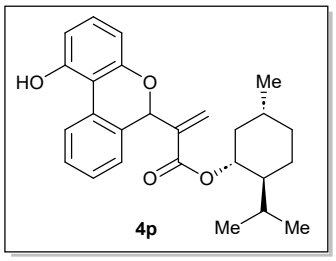



***tert*-Butyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4n.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.38; yellow liquid; yield 70% (23 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.24 (s, 1H), 6.05 (s, 1H), 5.45 (bs, 1H), 5.42 (s, 1H), 1.52 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.4, 155.1, 153.7, 140.4, 132.7, 129.2, 128.9, 128.5, 128.0, 127.3, 126.4, 125.9, 111.5, 110.8, 110.3, 81.6, 75.1, 28.2; FT-IR (neat) 3397, 2980, 2932, 1697, 1602, 1439, 1282, 1149, 1031 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{21}O_4$: 325.1434; Found 325.1436.

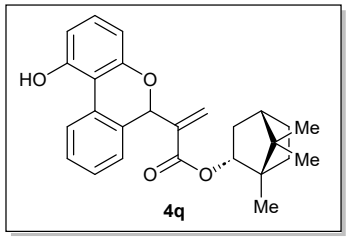



**Cyclohexyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4o.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.40; brown sticky liquid; yield 73% (26 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29-7.25 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 6.10 (s, 1H), 5.48-5,46 (m, 2H), 4.98-4.91 (m, 1H), 1.90-1.86 (m, 2H), 1.74-1.70 (m, 2H), 1.53-1.32 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.6, 155.0,

153.7, 139.4, 132.5, 129.3, 128.9, 128.8, 128.6, 127.3, 126.4, 125.9, 111.5, 110.8, 110.3, 75.1, 73.5, 31.6, 25.5, 23.7; FT-IR (neat) 3394, 2936, 2859, 1695, 1609, 1439, 1277, 1164, 1031 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}O_4$: 351.1591; Found 351.1593.




**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4p.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.48; yellow liquid; 1:1 mixture of diastereomers; yield 66% (27 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 10.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29-7.26 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.02 (td, *J* = 8.4, 2.8 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 2H), 6.30 (s, 1H), 6.28 (s, 1H), 6.11 (s, 2H), 5.42-5.40 (m, 4H), 4.89-4.81 (m, 2H), 2.09-1.99 (m, 3H), 1.83-1.79 (m, 1H), 1.71-1.66 (m, 4H), 1.52-1.37 (m, 4H), 1.10-1.00 (m, 4H), 0.93-0.89 (m, 10H), 0.84 (d, *J* = 6.8 Hz, 4H), 0.78 (d, *J* = 6.8 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.8 (major), 165.7 (minor), 154.9 (major), 153.7 (major), 153.6 (minor), 139.5 (minor), 139.4 (major), 132.4 (minor), 132.3 (major), 129.3 (major), 129.2 (minor), 129.0 (minor), 128.9 (major), 128.8 (major), 128.6 (minor), 128.5 (major), 127.3 (major), 126.4 (major), 125.94 (minor), 125.92 (major), 111.5 (major), 111.4 (minor), 110.8 (major), 110.7 (minor), 110.3 (major), 110.2 (minor), 77.4 (major), 75.3 (minor), 75.1 (major), 75.0 (minor), 47.2 (major), 47.1 (minor), 40.9 (major), 34.4 (major), 31.58 (major), 31.56 (minor), 26.4 (minor), 26.1 (major), 23.6 (minor), 23.4 (major), 22.2 (major), 21.0 (major), 20.9 (minor), 16.6 (minor), 16.3 (major); FT-IR (neat) 3390, 2955, 2868, 1689, 1630, 1437, 1278, 1167 $cm^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{31}O_4$: 407.2217; Found 407.2216.




**(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate 4q.** Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.43; colorless solid; mp = 201 °C; 1:1 mixture of diastereomers; yield 62% (25 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 2H), 7.30-7.26 (m, 2H), 7.12-7.10 (m, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 6.38-6.37 (m, 2H), 6.08-6.07 (m, 2H), 5.50-5.42 (m, 4H), 5.05-5.00 (m, 2H), 2.46-2.38 (m, 2H), 1.94-1.84 (m, 2H), 1.76-1.70 (m, 6H), 1.08-1.01 (m, 2H), 0.93-0.92 (m,

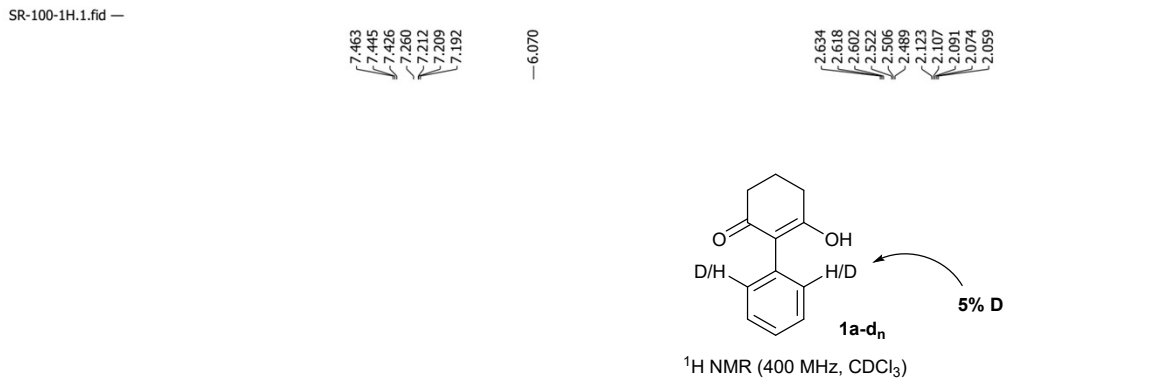
6H), 0.87-0.84 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.44 (major), 166.43 (minor), 155.0 (minor), 153.6 (major), 139.3 (minor), 139.2 (major), 132.5 (minor), 132.4 (major), 129.3 (major), 129.2 (major), 128.9 (minor), 128.6 (major), 127.3 (major), 126.4 (major), 125.84 (minor), 125.81 (major), 111.4 (minor), 110.8 (major), 110.7 (minor), 110.3 (major), 81.0 (major), 80.9 (minor), 77.4 (major), 75.3 (major), 75.2 (minor), 49.2 (major), 49.1 (minor), 48.0 (major), 45.1 (major), 45.0 (minor), 37.0 (major), 36.9 (minor), 28.2 (minor), 28.1 (major), 27.37 (minor), 27.36 (major), 19.8 (major), 19.0 (major), 13.68 (major), 13.67 (minor); FT-IR (neat) 3396, 2954, 1697, 1595, 1438, 1278, 1235, 1032 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{26}H_{28}NaO_4$: 427.1880; Found 427.1862.

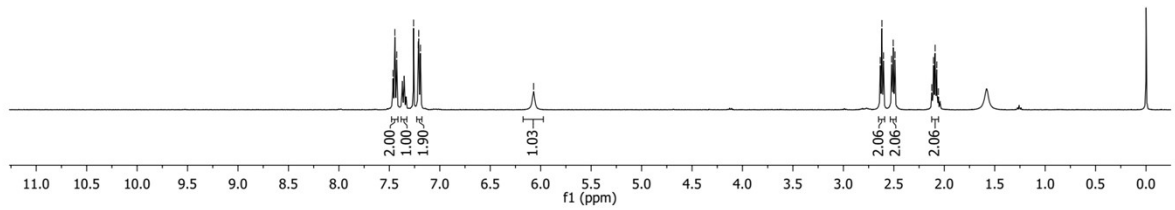
**Scale-up Synthesis of 4a**. In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (376 mg, 2 mmol), methyl 2-(acetoxymethyl)acrylate **2a** (474 mg, 3 mmol), $Pd(OAc)_2$ (45 mg, 10 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (799 mg, 4 mmol) were stirred in DMF:$H_2O$ (9:1) (20 mL) at 120 °C for 8 h. The work up and purification were carried out as described in the general procedure to afford **4a** in 67% (378 mg) yield.

## Mechanistic Investigations

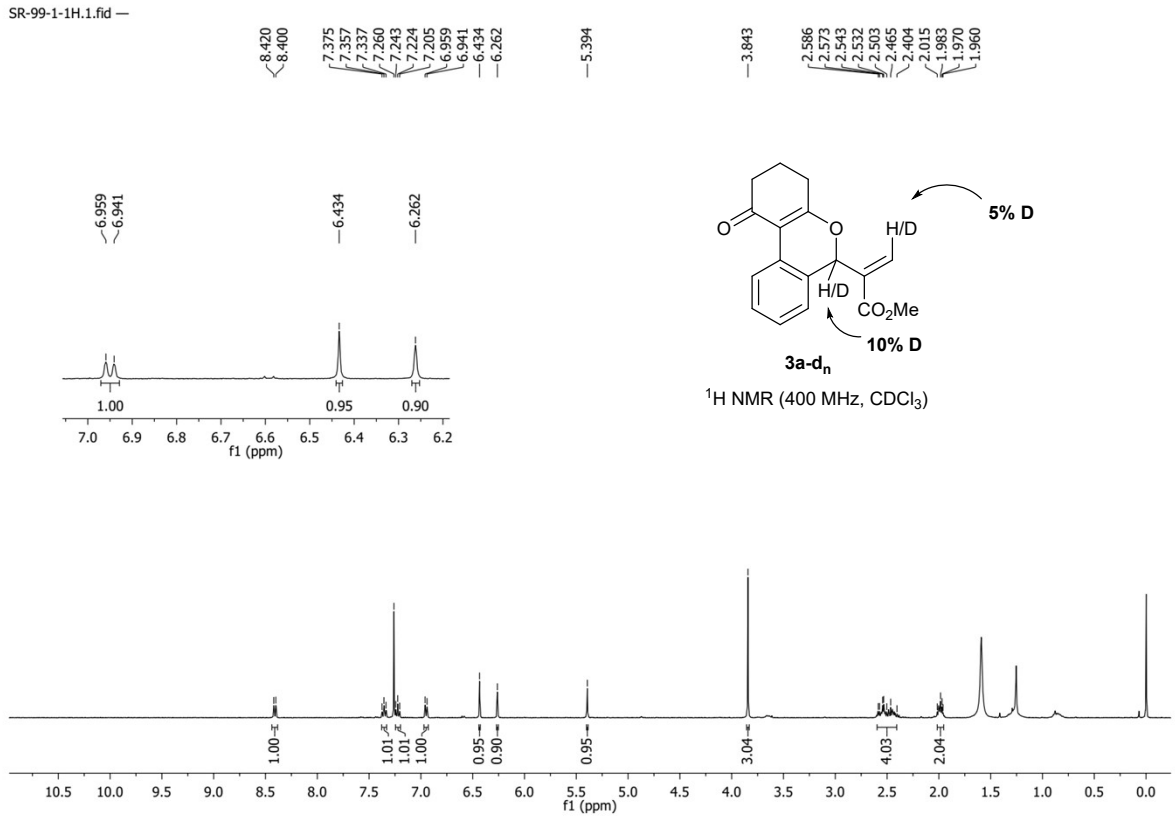
### Non-dehydrogenative C-H Functionalization/Annulation

**H/D Exchange Experiment of 1a with $D_2O$ in Absence of 2a.** In a pressure tube, **1a** (19 mg, 0.1 mmol), $Pd(OAc)_2$ (2 mg, 10 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) were stirred in $D_2O$ (1 mL) at 110 °C temperature for 15 mins and extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **1a-*d*$_n$.** Deuterium incorporation in **1a-*d*$_n$** was observed from 400 MHz $^1$H NMR spectrum.



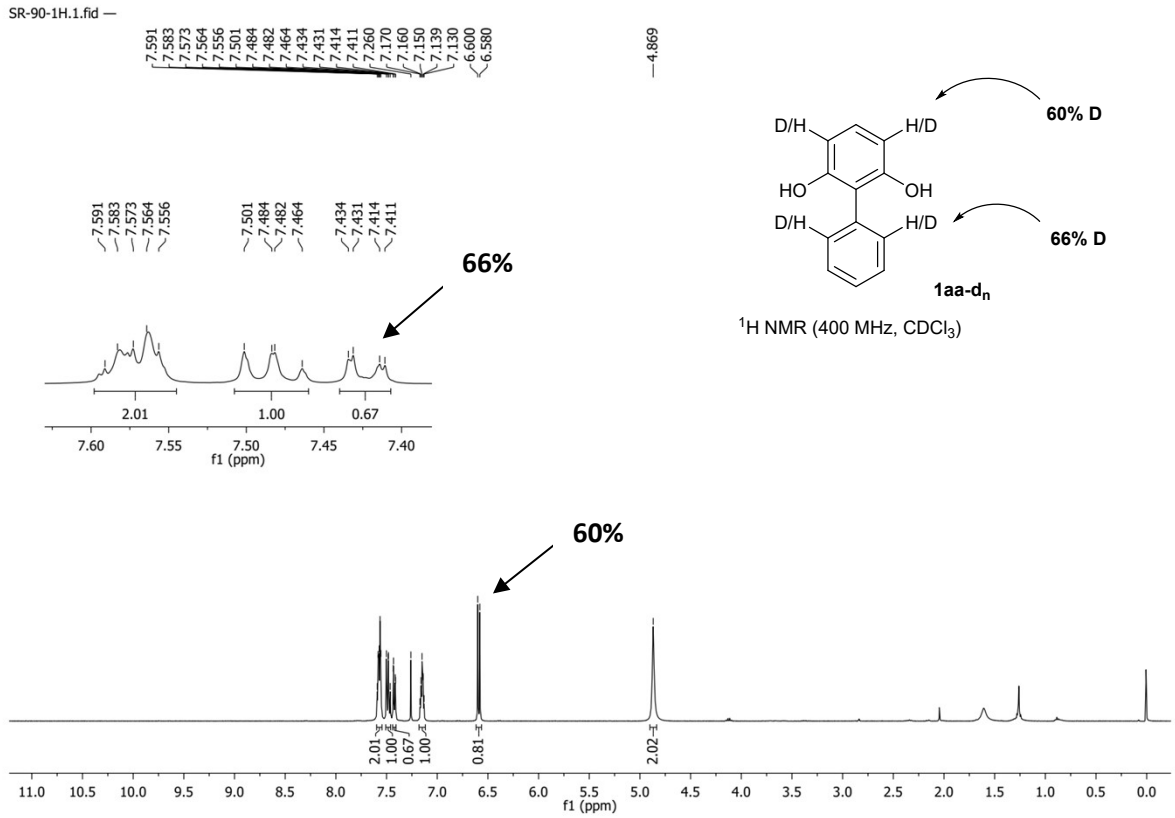




**H/D Exchange Experiment of 1a with $D_2O$ in Presence of 2a.** In a pressure tube, **1a** (19 mg, 0.1 mmol), **2a** (24 mg, 0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol %) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) were stirred in $D_2O$ (1 mL) at 110 °C for 2 h and extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **3a-*d*$_n$.** Deuterium incorporation in **3a-*d*$_n$** was observed from 400 MHz $^1$H NMR spectrum.

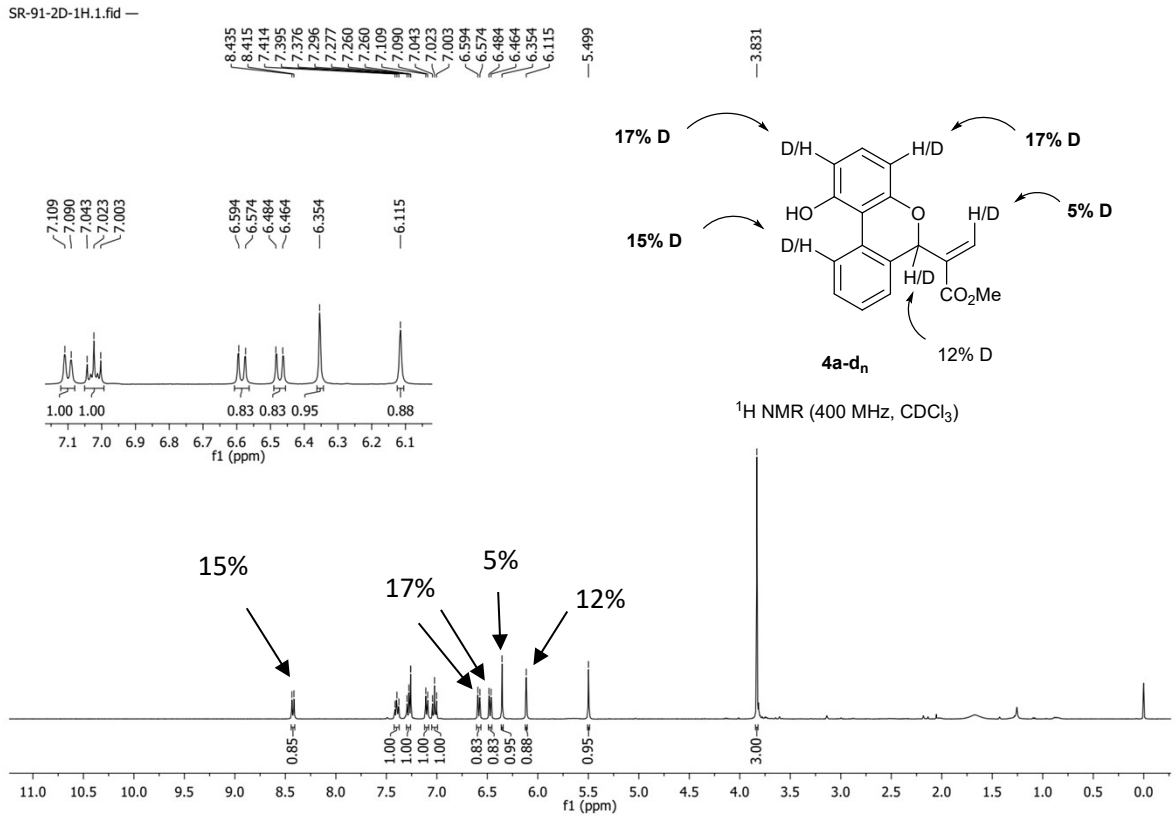



**Dehydrogenative C-H Functionalization/Annulation**

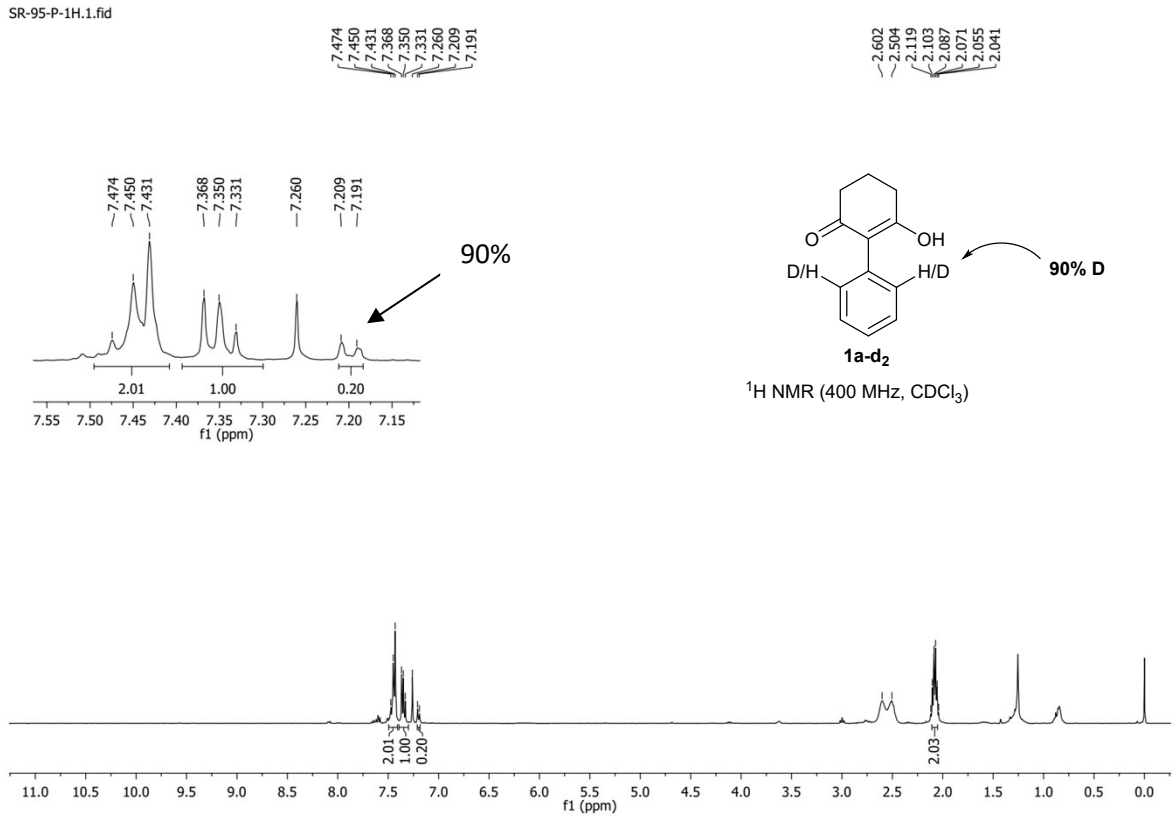
**H/D Exchange Experiment of 1a with $D_2O$ in Absence of 2a.** In a pressure tube, **1a** (19 mg, 0.1 mmol), $Pd(OAc)_2$ (2 mg, 10 mol %) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) were stirred in DMF:$D_2O$ (9:1) (1 mL) at 120 °C for 15 mins, quenched with ice-cold water (5 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to afford **1aa-*d*$_n$.** Deuterium incorporation in **1aa-*d*$_n$** was observed from 400 MHz $^1$H NMR spectrum.




**H/D Exchange Experiment of 1a with $D_2O$ in Presence of 2a.** In a pressure tube, **1a** (19 mg, 0.1 mmol), **2a** (24 mg, 0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) were stirred in DMF:$D_2O$ (9:1) (1 mL) at 120 °C for 2 h. The reaction mixture was quenched with ice-cold water (5 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified on silica gel column chromatography to afford **4a-*d*$_n$**. Deuterium incorporation in **4a-*d*$_n$** was observed from 400 MHz $^1$H NMR spectrum.



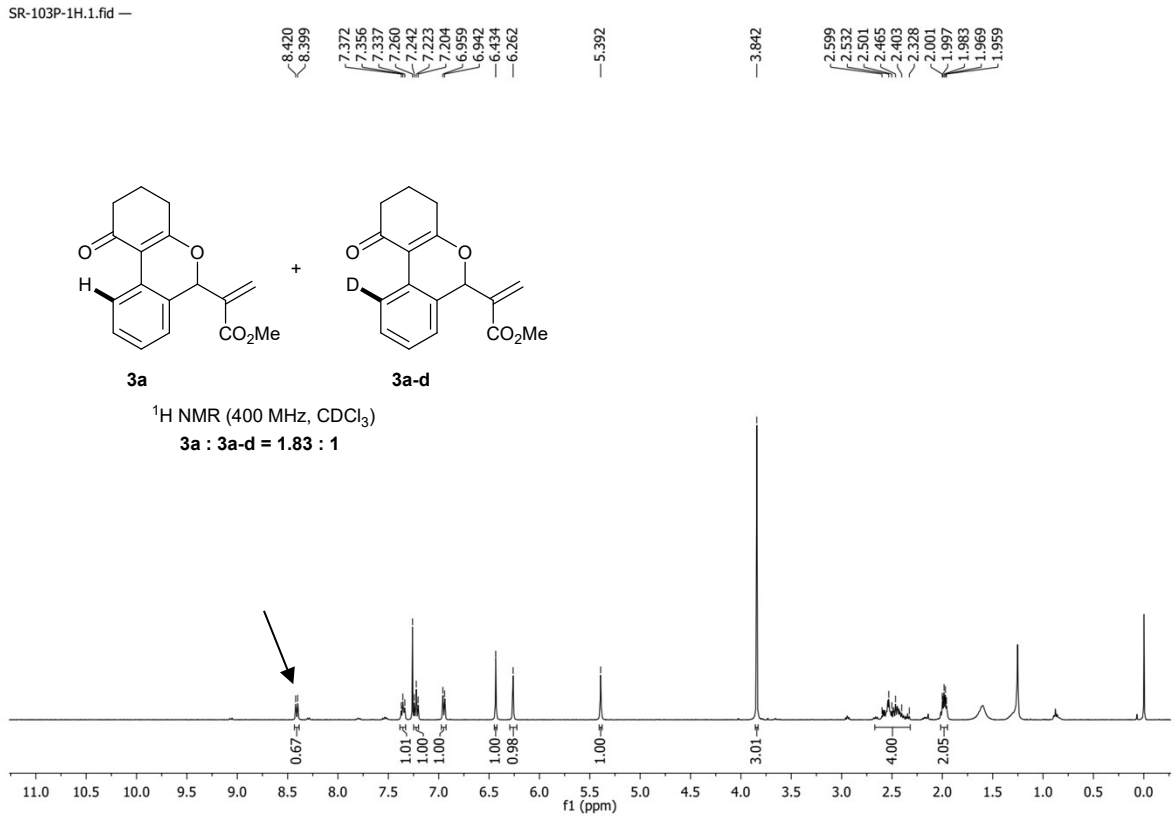

**Preparation of 6-Hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one-2',6'-*d*$_2$ 1a-*d*$_2$.**[1c] In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (39.6 mg, 0.2 mmol), [Ru(*p*-cymene)$Cl_2$]$_2$ (6.2 mg, 5.0 mol %), KOAc (19.6 mg, 0.2 mmol), AcOH (11 µL, 0.2 mmol) and $D_2O$ (100 µL) were stirred in 1,2-dichloroethane (1 mL) at 100 °C for 24 h. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 10 mL), washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford the **1a-*d*$_2$** with 90% deuteriation at the *ortho*-position of the aryl ring (see the following $^1$H NMR spectrum).



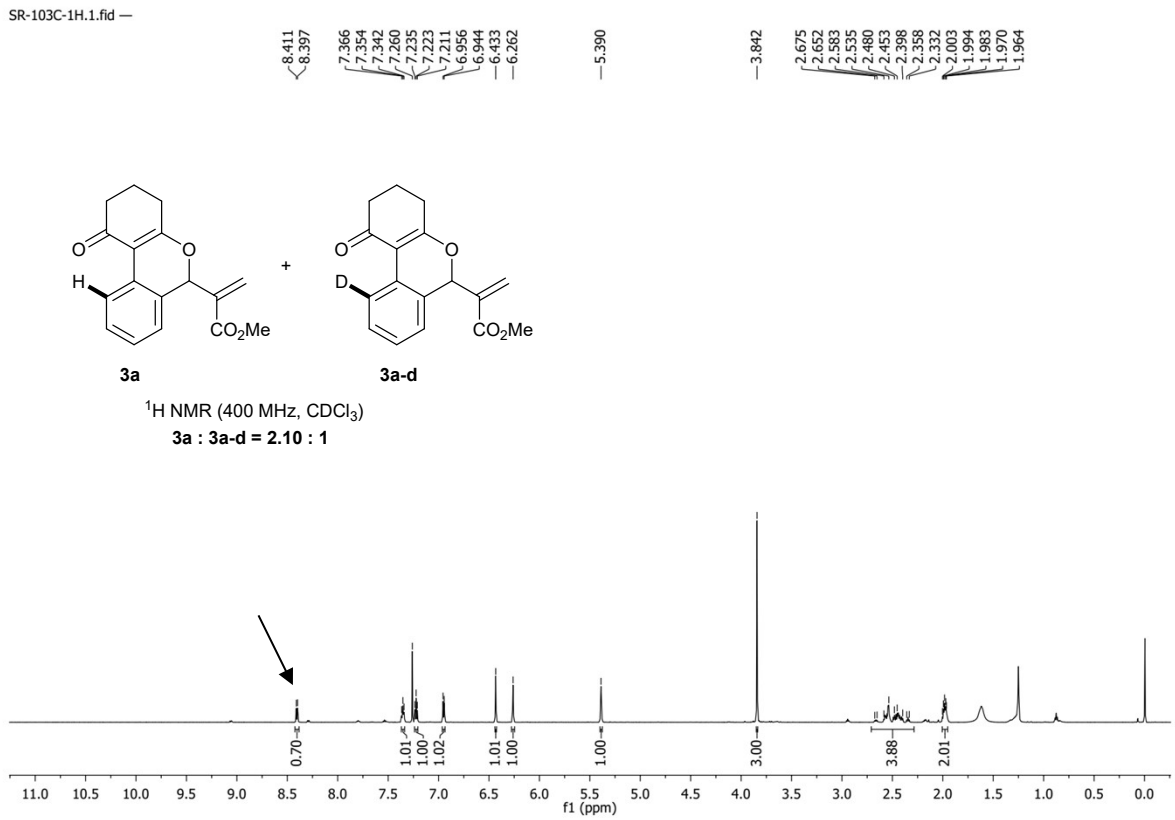

## Kinetic Isotope Effect Experiments

### Non-Dehydrogenative C-H Functionalization/Annulation

**Parallel Reactions.** In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (18.8 mg, 0.1 mmol) and 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one-2',6'-$d_2$ **1a-*d*$_2$** (19.0 mg, 0.1 mmol) [90% D] were separately reacted with methyl 2-(acetoxymethyl)acrylate **2a** (24 mg, 0.15 mmol) in $H_2O$ (1 mL) for 2 h at the standard conditions A. Then the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give **3a** and **3a-*d***, whose 400 MHz $^1$H NMR analysis showed $k_H/k_D$ = 1.83.

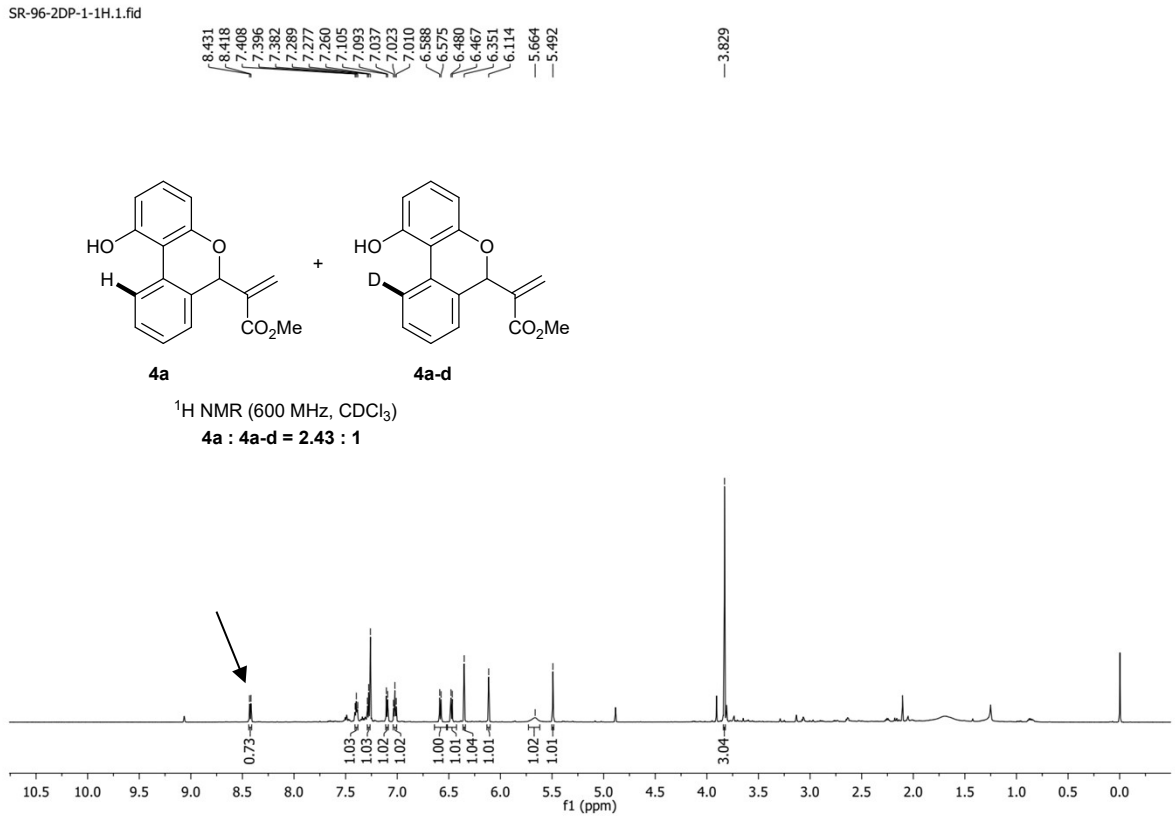



**Competitive Reactions:** In a pressure tube, a mixture of 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (18.8 mg, 0.1 mmol) and 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one-2',6'-$d_2$ **1a-*d*$_2$** (19.0 mg, 0.1 mmol) [90% D] was reacted with methyl 2-(acetoxymethyl)acrylate **2a** (48 mg, 0.3 mmol) in $H_2O$ (1 mL) for 2 h at standard reaction conditions A. Then, the reaction mixture was extracted with EtOAc (3 x 10 mL), washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to afford a mixture of **3a**/**3a-*d***, whose 400 MHz $^1$H NMR analysis showed $k_H/k_D = 2.10$.

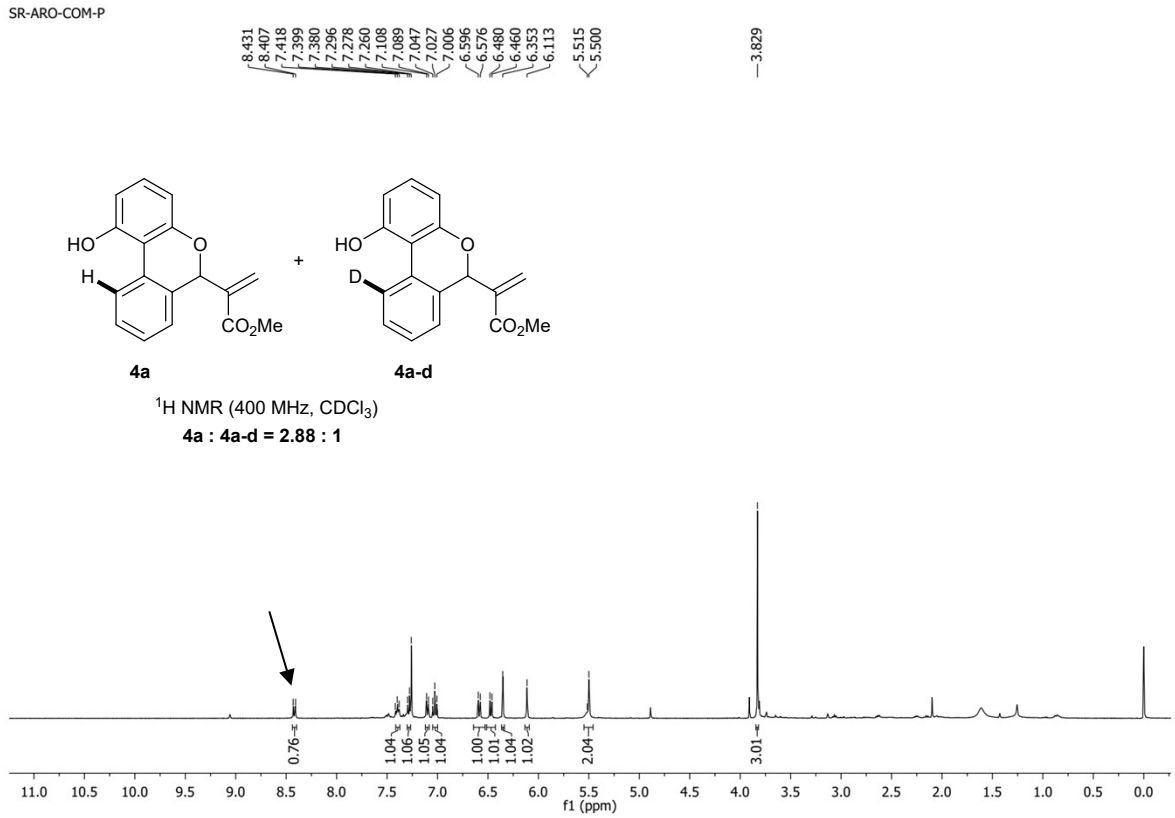



## Dehydrogenative C-H Functionalization/Annulation

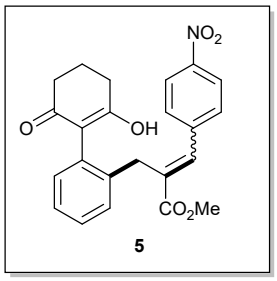
**Parallel Reactions.** In a pressure tube, 6-Hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one **1a** (18.8 mg, 0.1 mmol) and 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one-2',6'-$d_2$ **1a-*d*$_2$** (19.0 mg, 0.1 mmol) [90% D] were separately reacted with methyl 2-(acetoxymethyl)acrylate **2a** (24 mg, 0.15 mmol) in DMF:$H_2O$ (9:1) (1 mL) for 2 h at the standard reaction conditions B. Then the reaction mixture was quenched with ice-cold water (10 mL) and extracted with EtOAc (3 x 10 mL), washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give **4a** and **4a-*d***, whose 400 MHz $^1$H NMR analysis showed $k_H/k_D$ = 2.43.




**Competitive Reactions:** In a pressure tube, a mixture of 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one **1a** (18.8 mg, 0.1 mmol) and 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one-2',6'-$d_2$ **1a-*d*$_2$** (19.0 mg, 0.1 mmol) [90% D] was reacted with methyl 2-(acetoxymethyl)acrylate **2a** (48 mg, 0.3 mmol) in DMF:$H_2O$ (9:1) (1 mL) for 2 h at standard reaction conditions B. Then, the reaction mixture was quenched with ice-cold water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give a mixture of **4a**/**4a-*d***, whose 400 MHz $^1$H NMR analysis showed $k_H/k_D = 2.88$.

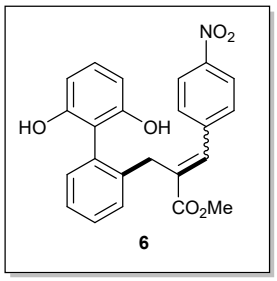



## I) Control Experiment




**Methyl 2-((6'-hydroxy-2'-oxo-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)-3-(4-nitrophenyl)acrylate 5.** In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (19 mg, 0.1 mmol), methyl 2-(acetoxy(4-nitrophenyl)methyl)acrylate **2j** (42 mg, 0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol%) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) were stirred in $H_2O$ (1 mL) at 110 °C for 6 h. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **5**. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.25; colorless liquid; yield 64% (26 mg); 7:1 mixture of diastereomers; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, $J$ = 9.0 Hz, 2H), 7.44-7.42 (m, 3H), 7.27-7.26 (m, 2H), 6.98 (d, $J$ = 8.0 Hz, 2H), 3.71 (s, 3H), 3.23 (s, 2H), 2.70-2.59 (m, 4H), 2.04-1.96 (m, 1H), 1.77-1.71 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 207.1, 169.1, 147.1, 142.5, 137.3, 136.5, 132.7, 130.0, 129.7, 128.6, 128.3, 127.3, 126.9, 123.7, 72.9,

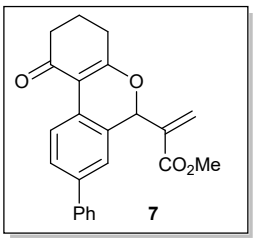
52.4, 38.2, 33.6, 17.3; FT-IR (neat) 2959, 1725, 1712, 1564, 1354, 1337, 1301, 1262, 1207 cm-1; HRMS (ESI-TOF) m/z [M+H]+ calcd for $C_{23}H_{22}NO_6$: 408.1442; Found 408.1441.



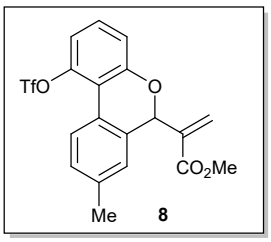

**Methyl 2-((2',6'-dihydroxy-[1,1'-biphenyl]-2-yl)methyl)-3-(4-nitrophenyl)acrylate 6.** In a pressure tube, 6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3*H*)-one **1a** (19 mg, 0.1 mmol), methyl 2-(acetoxy(4-nitrophenyl)methyl)acrylate **2j** (42 mg, 0.15 mmol), $Pd(OAc)_2$ (2 mg, 10 mol%) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) were stirred in DMF:$H_2O$ (9:1) (1 mL) at 120 °C for 8 h. After completion (monitored by TLC), the reaction mixture was quenched with ice-cold water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **6**. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.35; brown sticky liquid; yield 57% (23 mg); 5:1 mixture of diastereomers; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43-7.41 (m, 2H), 7.33 (m, 1H), 7.28-7.26 (m, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 2H), 5.22 (bs, 2H), 3.76 (s, 3H), 3.69 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.8, 153.9, 147.8, 141.5, 139.9, 139.3, 133.7, 132.4, 130.1, 130.0, 129.8, 128.9, 128.2, 127.9, 124.0, 114.7, 108.3, 52.9, 31.0; FT-IR (neat) 2952, 1724, 1716, 1651, 1592, 1378, 1220, 1001 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}NO_6$: 406.1285; Found 406.1267.

## II) Control Experiment

In a pressure tube, methyl 2-(1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)-acrylate **3a** (28 mg, 0.1 mmol), $Pd(OAc)_2$ (2 mg, 10 mol%) and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) were stirred in DMF:$H_2O$ (9:1) (1 mL) at 120 °C for 8 h. After completion (monitored by TLC), the reaction mixture was quenched with ice-cold water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **4a** in 43% (12 mg) yield.

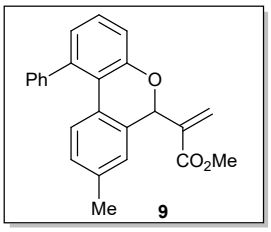



**Methyl 2-(1-oxo-8-phenyl-2,3,4,6-tetrahydro-1*H*-benzo[*c*]-chromen-6-yl)acrylate 7**. To a stirred solution of methyl 2-(8-chloro-1-oxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-6-yl)acrylate **3d** (32 mg, 0.1 mmol), phenylboronic acid (12 mg, 0.1 mmol), $K_2CO_3$ (28 mg, 0.2 mmol) and $H_2O$ (0.1 mL) in 1,4-dioxane (2 ml), $Pd(PPh_3)_4$ (6 mg, 5 mol%) was added. The resultant mixture was stirred at 70 °C for 6 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (2 x 10 mL) and washed with brine (1 x 5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel chromatography using hexane and EtOAc as eluent to afford **7**. Analytical TLC on silica gel, 3:7 EtOAc/hexane $R_f$ = 0.52; yellow liquid; yield 78% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.57-7.55 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 6.46 (s, 1H), 6.35 (s, 1H), 5.46 (s, 1H), 3.85 (s, 3H), 2.62-2.41 (m, 4H), 2.04-1.98 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 196.5, 171.7, 166.2, 140.4, 140.0, 137.8, 130.7, 129.0, 128.0, 127.6, 127.5, 127.0, 126.7, 125.8, 123.7, 112.4, 76.1, 52.5, 38.5, 29.5, 20.2; FT-IR (neat) 2952, 1724, 1656, 1597, 1379, 1220, 1001 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}O_4$: 361.1434; Found 361.1429.

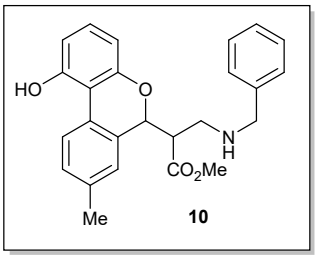



**Methyl 2-(8-methyl-1-(((trifluoromethyl)sulfonyl)oxy)-6*H*-benzo[*c*]-chromen-6-yl)acry-late 8**. To a stirred solution of methyl 2-(1-hydroxy-8-methyl-6*H*-benzo[*c*]chromen-6-yl)acrylate **4b** (30 mg, 0.1 mmol) in $CH_2Cl_2$ (2 mL), $Et_3N$ (20 µL, 0.15 mmol) and triflic anhydride (25 µL, 0.15 mmol) were added at -78 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h under air. After completion (monitored by TLC), the reaction mixture was quenched with 10% aqueous HCl (3 mL) and extracted with EtOAc (2 x 5 mL). The combined organic layer was washed with aqueous saturated $NaHCO_3$ (2 x 5 mL) and brine (1 x 5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as eluent to afford **8**. Analytical TLC on silica gel, 1:9 EtOAc/hexane $R_f$ = 0.45; colorless liquid; yield 75% (32 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.23-7.26 (m, 1H), 7.20 (t, *J* = 8.4 Hz, 1H), 7.00-6.96 (m, 3H), 6.37 (s, 1H), 6.18 (s, 1H), 5.44

(s, 1H), 3.84 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.3, 154.4, 146.3, 139.5, 137.2, 135.1, 132.7, 131.3 ($J_{C\text{-}F}$ = 3.1 Hz), 130.1, 128.9, 127.1, 126.4, 123.8, 118.7, 118.2, 116.1, 75.1, 52.4, 21.5; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -73.13; FT-IR (neat) 2918, 2851, 1727, 1459, 1427, 1214, 1144 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{16}F_3O_6S$: 429.0614; Found 429.0610.

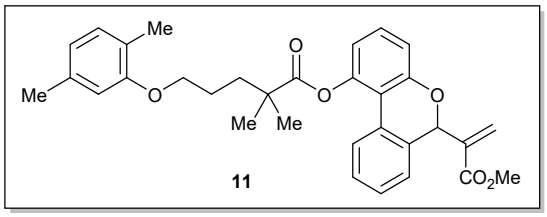



**Methyl 2-(8-methyl-1-phenyl-6*H*-benzo[*c*]chromen-6-yl)acrylate 9.** To a stirred solution of methyl 2-(8-methyl-1-(((trifluoromethyl)sulfonyl)oxy)-6*H*-benzo[*c*]-chromen-6-yl)acrylate **8** (43 mg, 0.1 mmol), phenylboronic acid (12 mg, 0.1 mmol), $K_2CO_3$ (28 mg, 0.2 mmol) and $H_2O$ (0.1 mL) in 1,4-dioxane (2 ml), $Pd(PPh_3)_4$ (6 mg, 5 mol%) was added. The resultant mixture was stirred at 70 °C for 6 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was extracted with EtOAc (2 x 10 mL) and washed with brine (1 x 5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel chromatography using hexane and EtOAc as eluent to afford **9**. Analytical TLC on silica gel, 1:9 EtOAc/hexane $R_f$ = 0.47; colorless liquid; yield 71% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.99-6.94 (m, 2H), 6.87 (s, 1H), 6.75 (d, *J* = 6.8 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 6.09 (s, 1H), 5.71 (s, 1H), 3.86 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 154.0, 142.4, 140.0, 138.5, 137.1, 133.4, 129.7, 129.4, 128.8, 128.7, 128.5, 127.7, 127.4, 127.3, 126.3, 125.4, 121.7, 117.0, 74.9, 52.4, 21.3; FT-IR (neat) 2923, 1709, 1603, 1474, 1439, 1127, 1035 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{21}O_3$: 357.1485; Found 357.1471.




**Methyl 3-(benzylamino)-2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)propanoate 10**. To a stirred solution of methyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate **4a** (28 mg, 0.1 mmol) in EtOH (1 ml), $BnNH_2$ (22 µL, 0.2 mmol) was added. The reaction mixture was stirred at 80 °C for 16 h under $N_2$ atmosphere. After completion (monitored by TLC), evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **10**. Analytical TLC on

silica gel, 3:7 EtOAc/hexane $R_f$ = 0.37; colorless liquid; yield 41% (16 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.6 Hz, 1H), 7.34-7.26 (m, 6H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 9.2 Hz, 1H), 3.84-3.72 (m, 2H), 3.49 (s, 3H), 3.25-3.20 (m, 1H), 3.17-3.06 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.1, 154.5, 153.5, 139.2, 132.0, 129.4, 128.6, 128.5, 128.4, 128.1, 127.4, 126.9, 126.8, 125.3, 111.0, 110.7, 110.0, 77.0, 53.7, 51.9, 49.4, 47.8; FT-IR (neat) 2941, 2917, 1727, 1460, 1427, 1215, 1132 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{24}NO_4$: 390.1700; Found 390.1702.



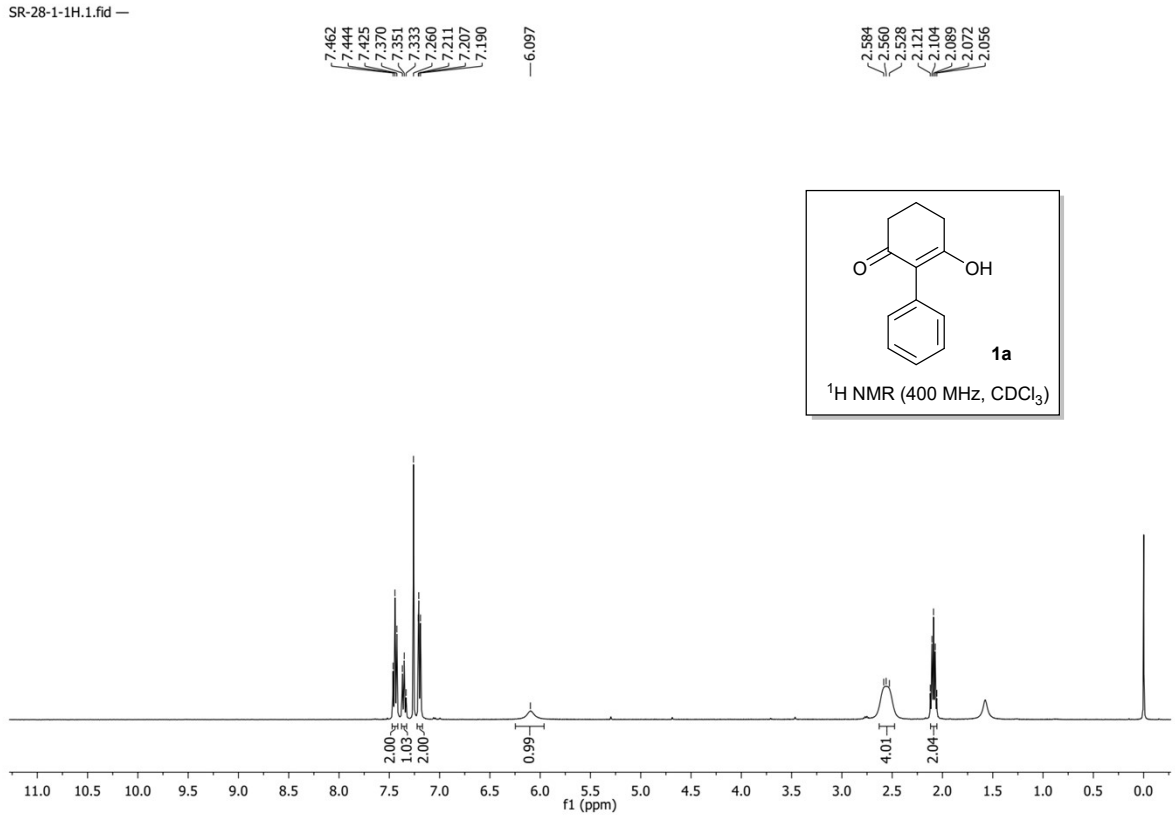
**11**

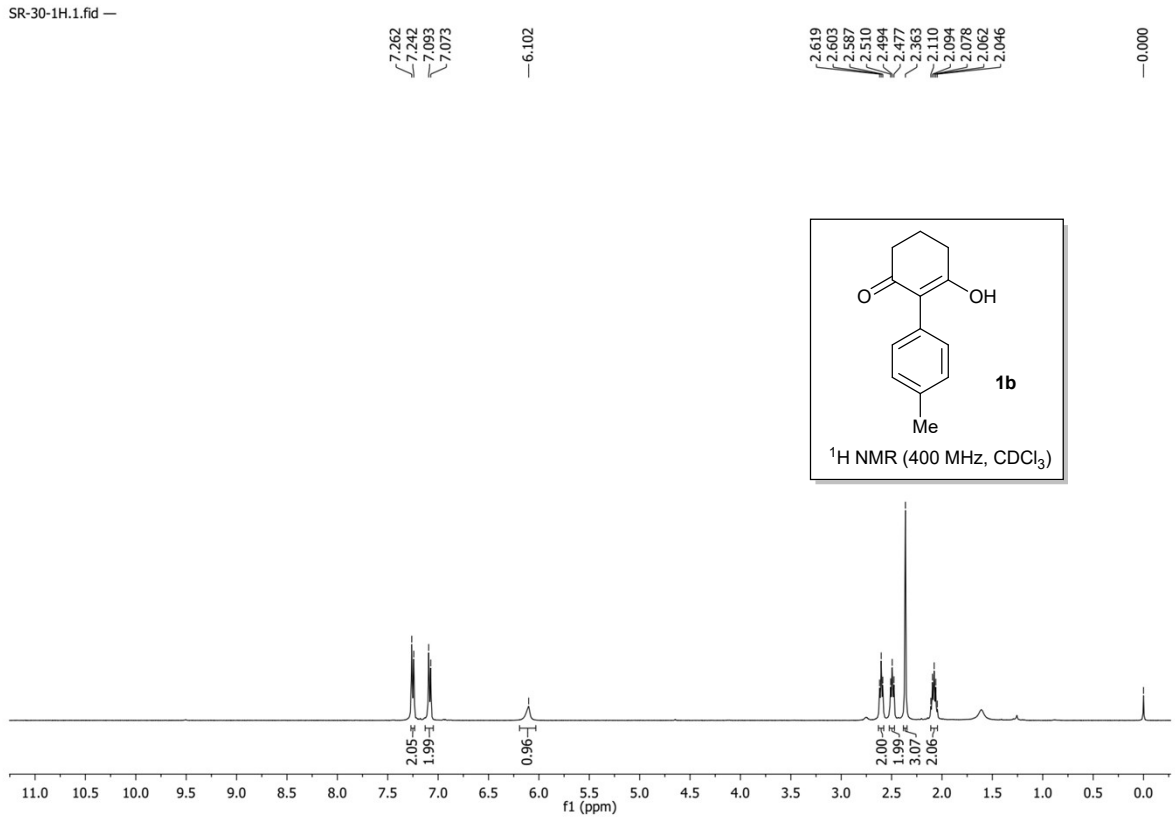
**6-(3-Methoxy-3-oxoprop-1-en-2-yl)-6*H*-benzo-[*c*]chromen-1-yl 5-(2,5-di-methylpheno-xy)-2,2-dimethylpentanoate 11.** To a stirred solution of methyl 2-(1-hydroxy-6*H*-benzo[*c*]chromen-6-yl)acrylate **4a** (28 mg, 0.1 mmol) and gemfibrozil (25 mg, 0.1 mmol) in $CH_2Cl_2$ (2 ml) at 0 °C, DCC (52 mg, 0.25 mmol) and DMAP (6 mg, 0.05 mmol) were added. The reaction mixture was stirred at room temperature for 24 h under air. After completion (monitored by TLC), the reaction mixture was diluted with $CH_2Cl_2$ (5 ml) and passed through a short pad of celite. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and EtOAc as an eluent to afford **11**. Analytical TLC on silica gel, 2:8 EtOAc/hexane $R_f$ = 0.48; colorless sticky liquid; yield 81% (42 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.36-7.27 (m, 2H), 7.17 (t, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.68-6.65 (m, 2H), 6.62 (s, 1H), 6.44 (s, 1H), 6.16 (s, 1H), 5.57 (s, 1H), 3.96 (t, *J* = 5.2 Hz, 2H), 3.83 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.99-1.84 (m, 4H), 1.44 (s, 3H), 1.39 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 175.9, 166.5, 157.0, 154.4, 148.4, 137.3, 136.6, 133.3, 131.1, 130.5, 129.2, 128.4, 128.2, 128.1, 126.1, 126.0, 123.7, 120.9, 117.9, 117.0, 116.1, 112.1, 74.9, 67.9, 52.3, 42.7, 37.4, 25.5, 25.3, 25.1, 21.5, 16.0; FT-IR (neat) 2927, 1751, 1724, 1612, 1508, 1438, 1251, 1102, 1017 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{32}H_{34}NaO_6$: 537.2248; Found 537.2242.

## References


1. (*a*) S. Reddy Chidipudi, I. Khan and H. W. Lam, *Angew. Chem. Int. Ed.*, 2012, **51**, 12115; (*b*) Y. Wada, R. Murata, Y. Fujii, K. Asano and S. Matsubara, *Org. Lett.*, 2020, **22**, 4710; (*c*) S. Mondal, R. Bera, D. Chowdhury, S. Dana and M. Baidya, *Org. Lett.*, 2023, **25**, 70; (*d*) D. J. Burns and H. W. Lam, *Angew. Chem. Int. Ed.*, 2014, **53**, 9931.
2. (*a*) H. Bhattacharyya, S. Saha, K. Verma and T. Punniyamurthy, *Org. Lett.*, 2023, **25**, 6830; (*b*) R. Takagi, Y. Miwa, T. Nerio, Y. Inoue, S. Matsumura and K. Ohkata, *Org. Biomol. Chem.*, 2007, **5**, 286. (*c*) M. Mantel, M. Guder and J. Pietruszka, *Tetrahedron*, 2018, **74**, 5442. (*d*) M. Davoust, J. Brière and P. Metzner, *Org. Biomol. Chem.*, 2006, **4**, 3048. (*e*) N. Kaplaneris, T. Rogge, R. Yin, H. Wang, G. Sirvinskaite and L. Ackermann, *Angew. Chem. Int. Ed.*, 2019, **58**, 3476.

## NMR ($^{1}$H, $^{13}$C and $^{19}$F) Spectra



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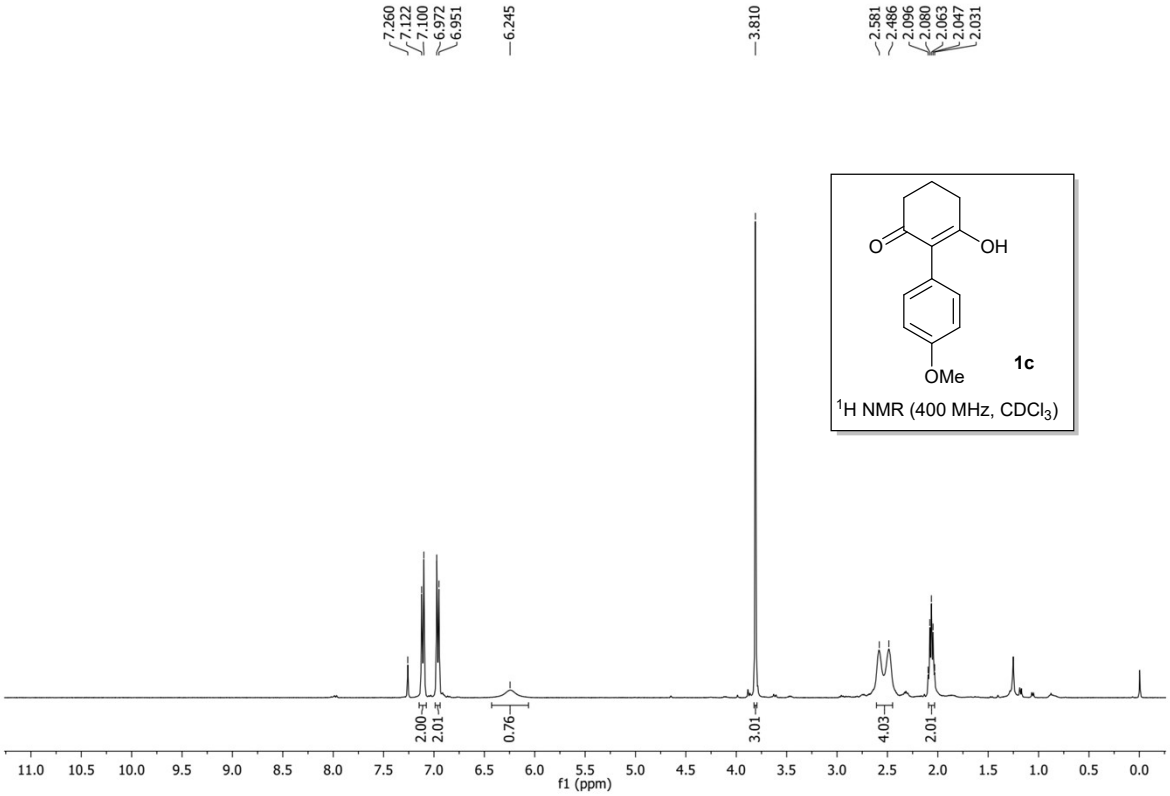


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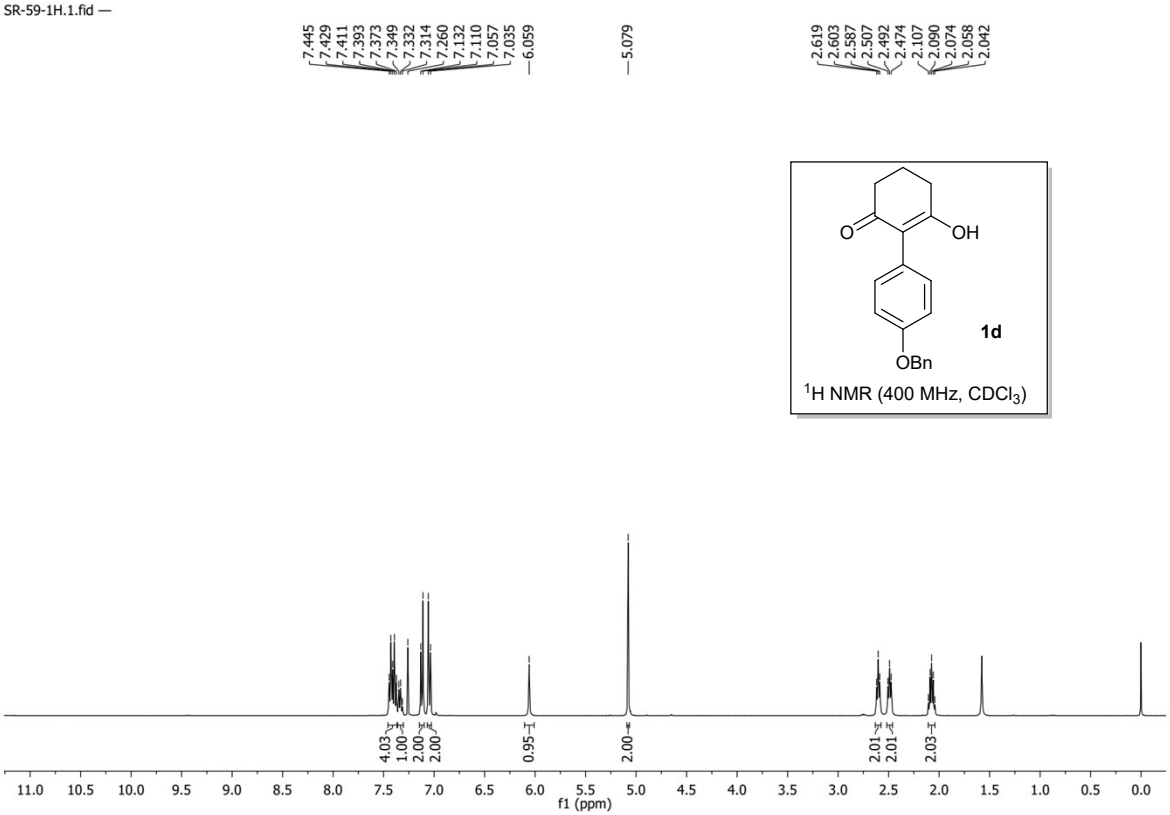

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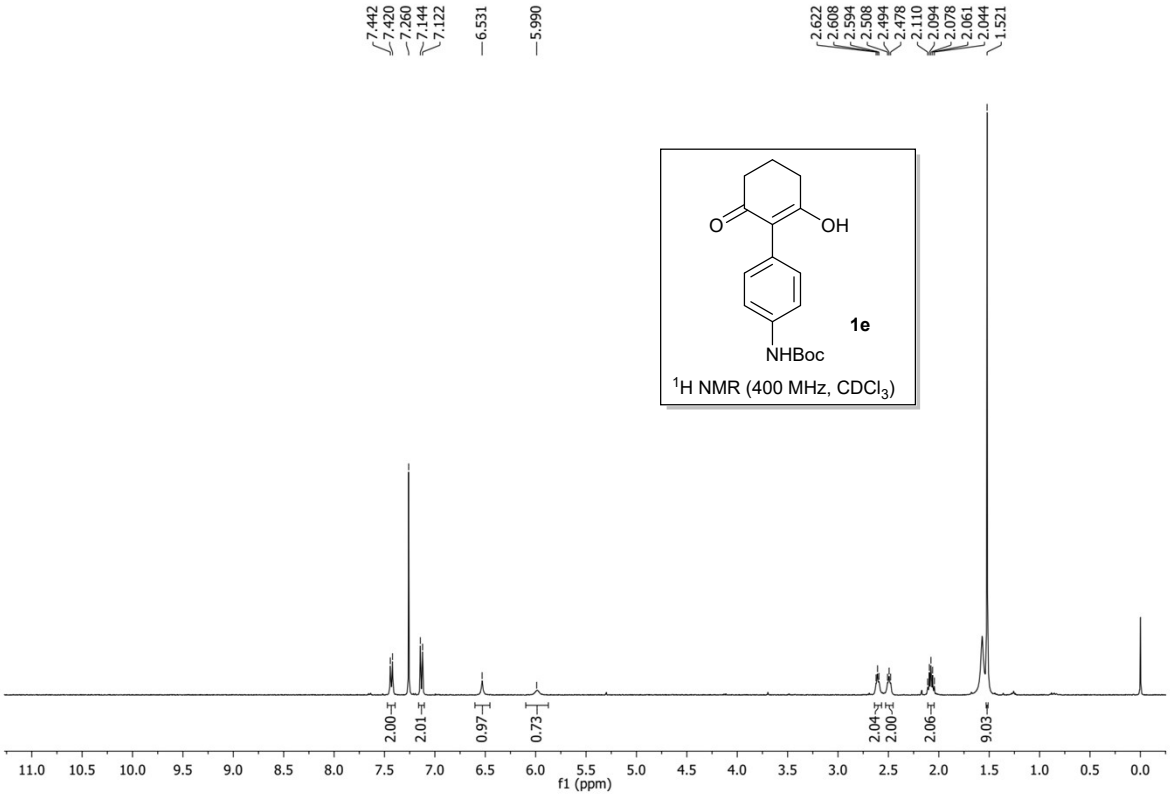


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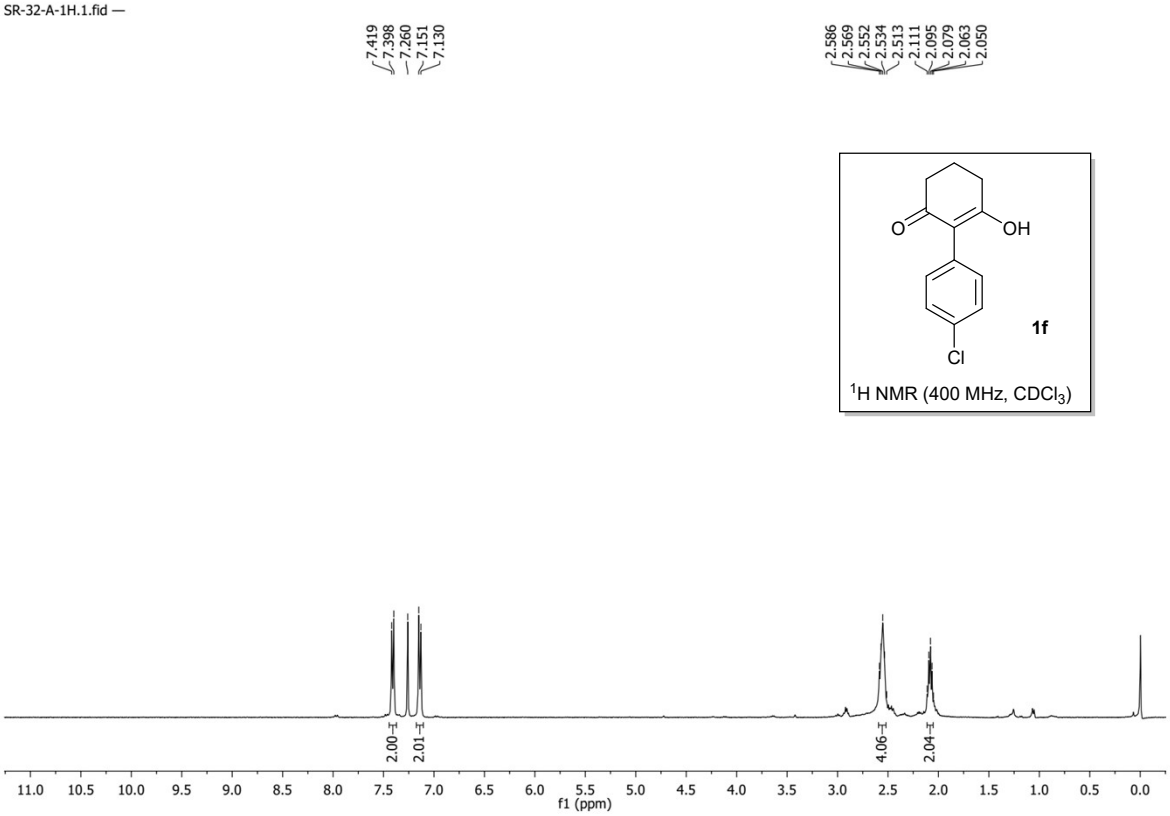

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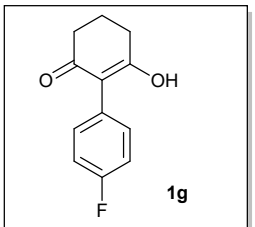


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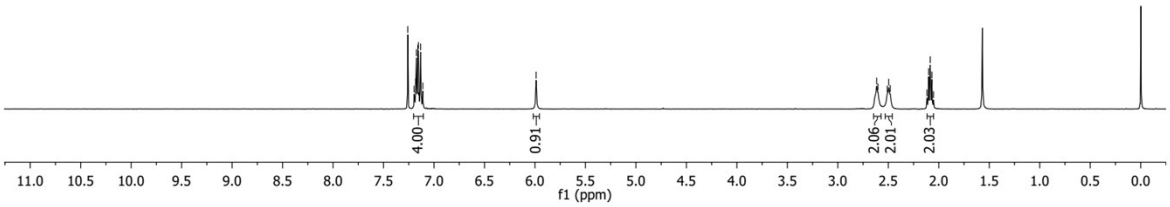
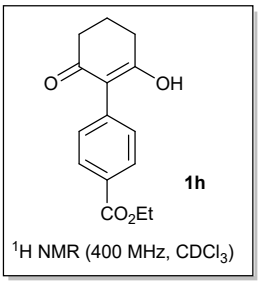
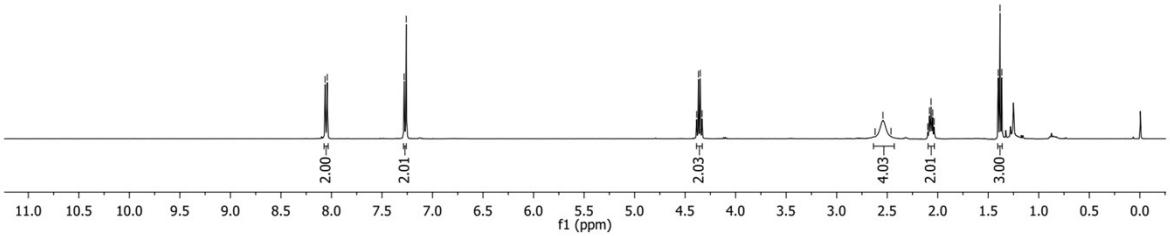


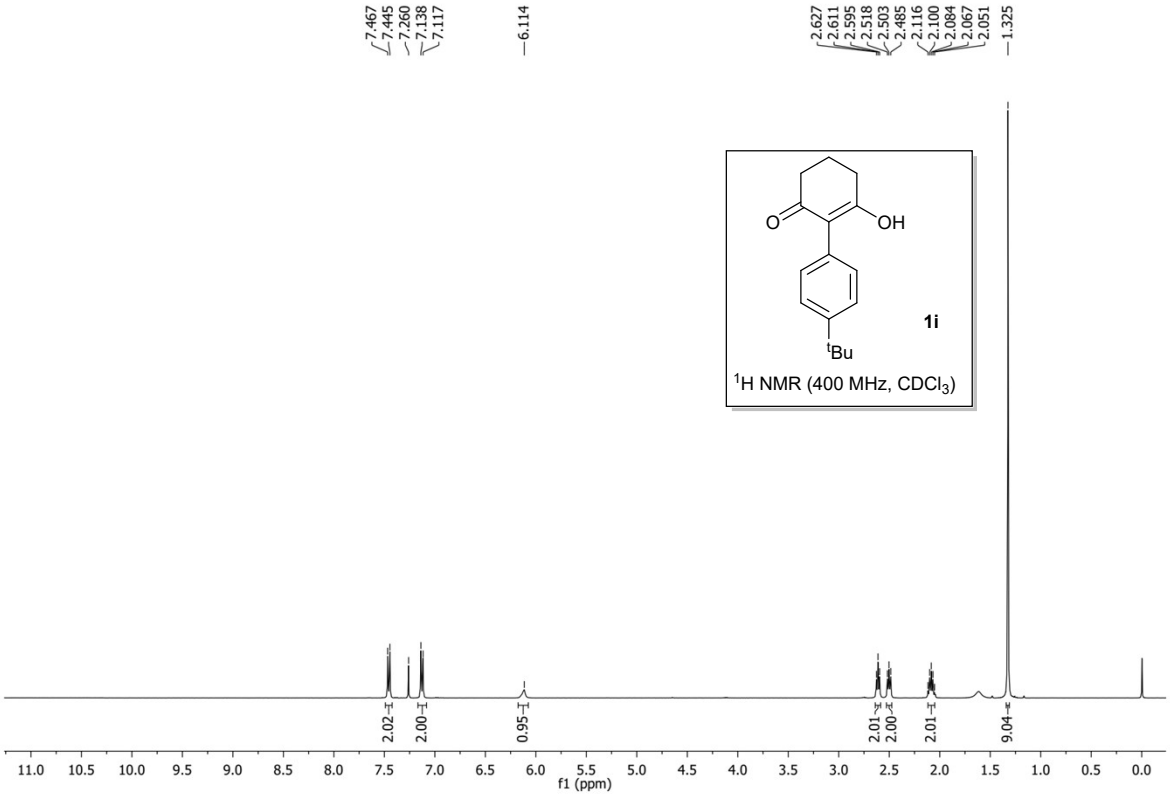

SR-52-A-1H.1.fid —


$^1$H NMR (400 MHz, $CDCl_3$)



SR-36-1-1H.1.fid

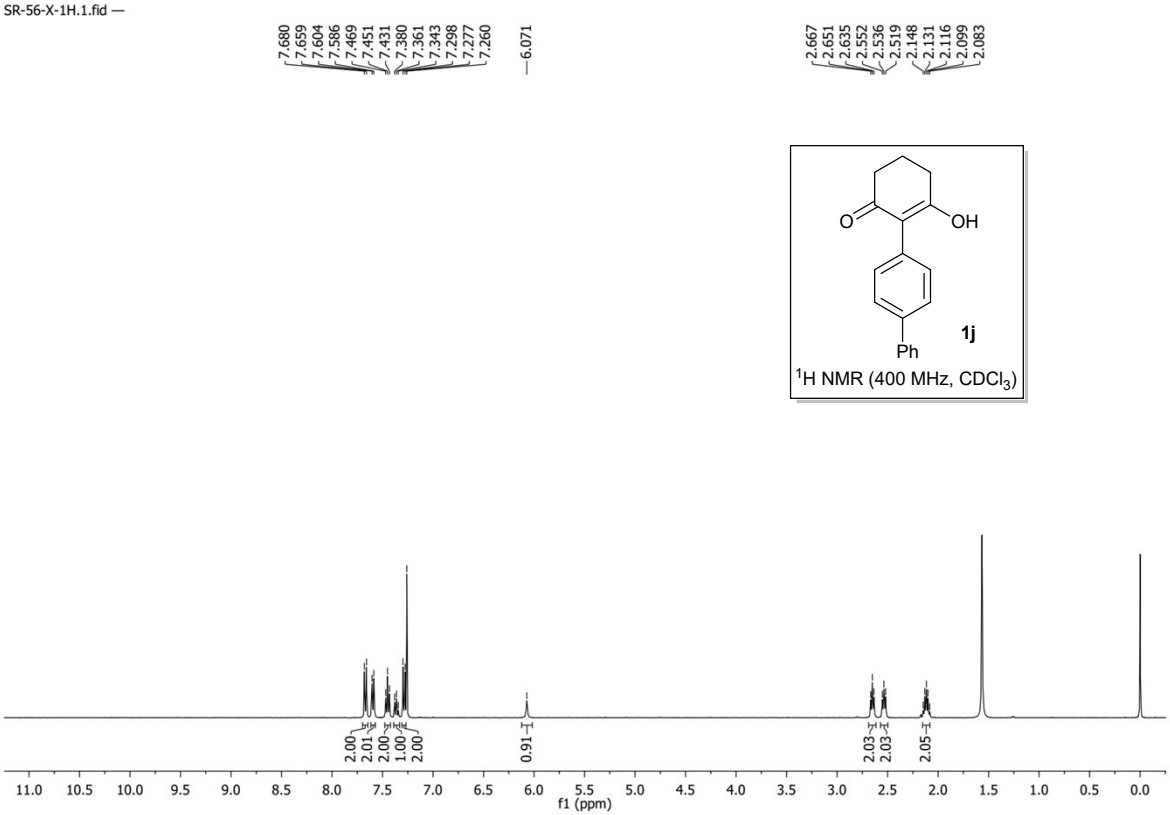






$^1$H NMR (400 MHz, $CDCl_3$)

SR-56-X-1H.1.fid

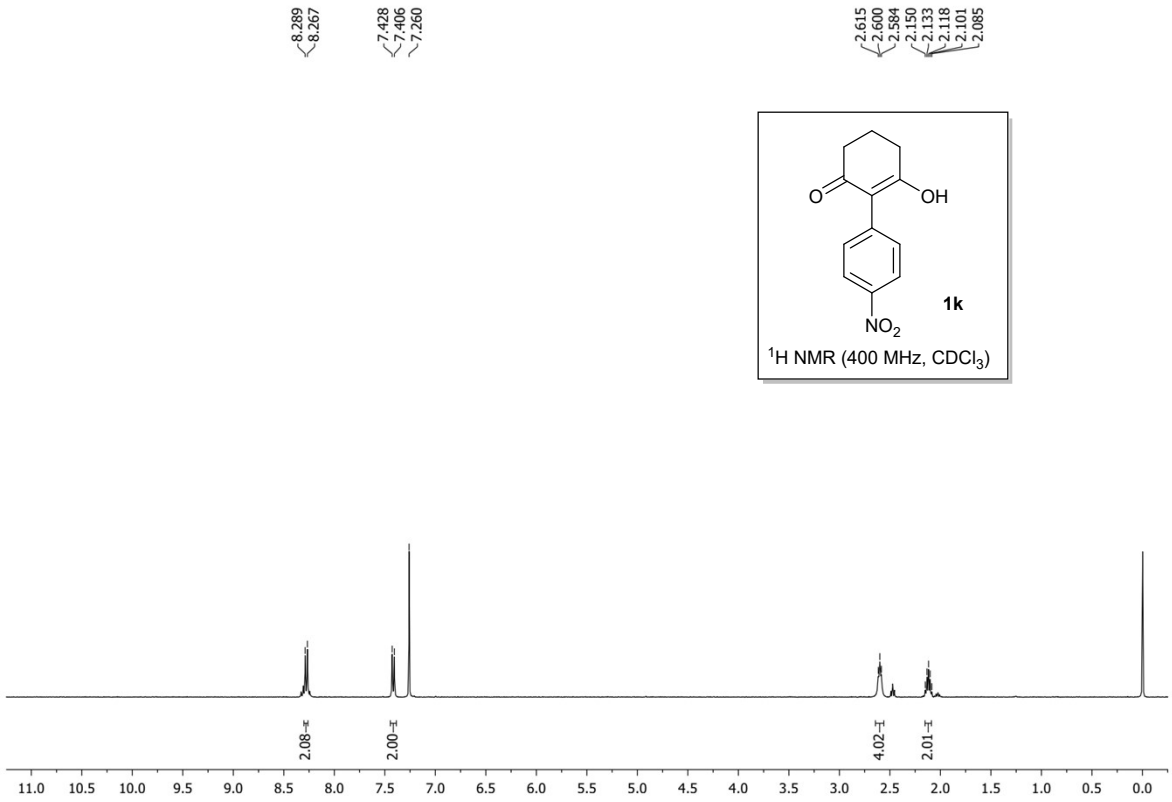




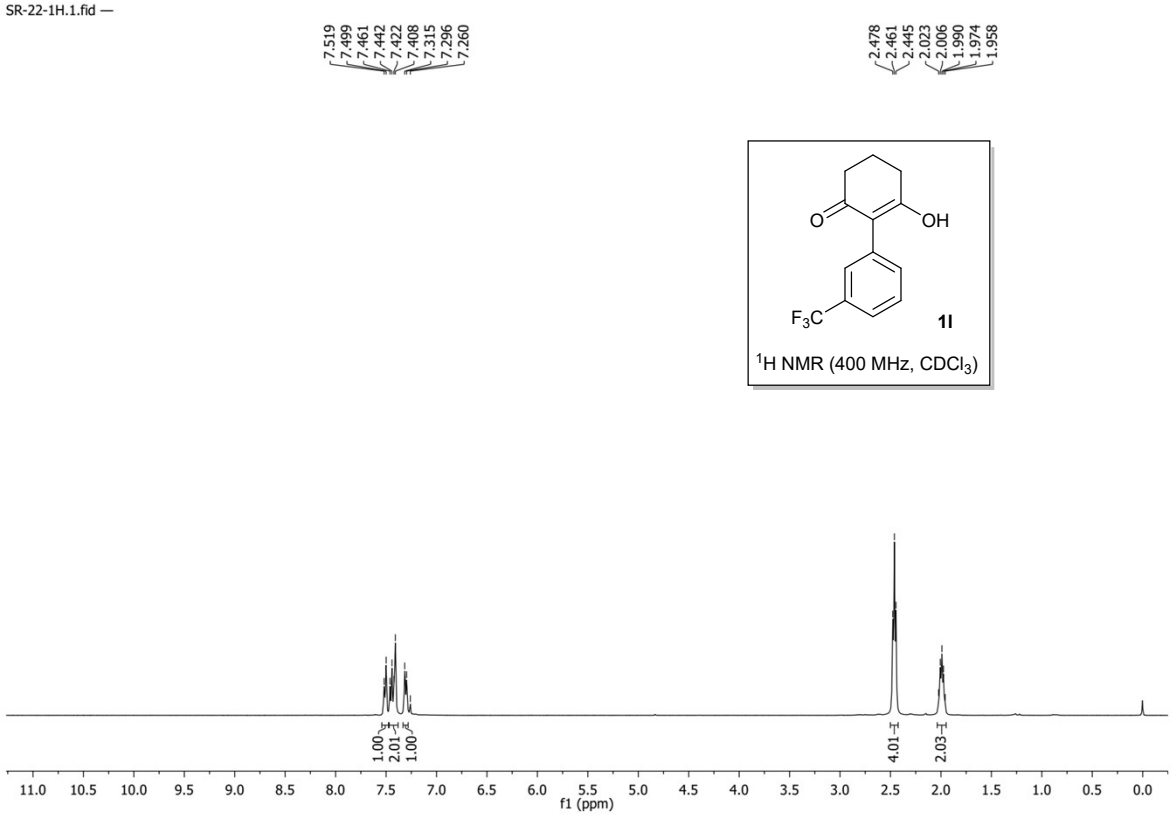


$^1$H NMR (400 MHz, $CDCl_3$)

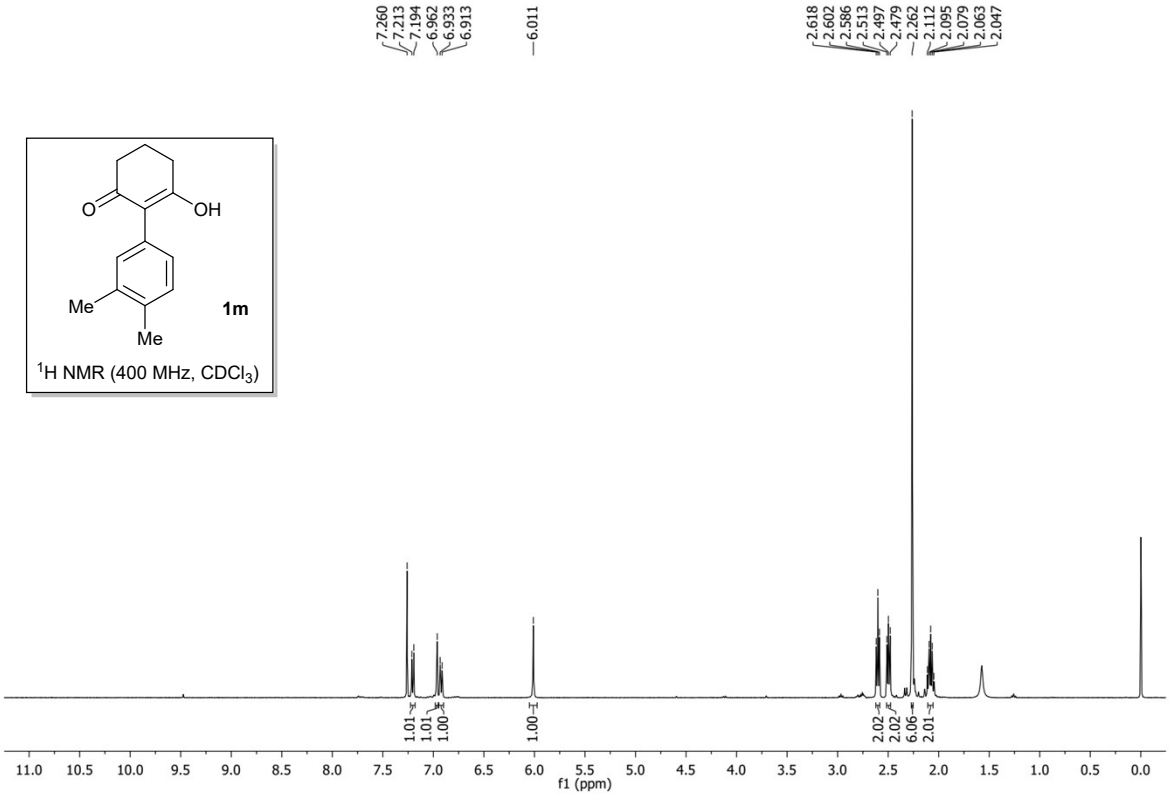
SR-42-1H.1.fid




SR-22-1H.1.fid —



SR-57-1H.1.fid —

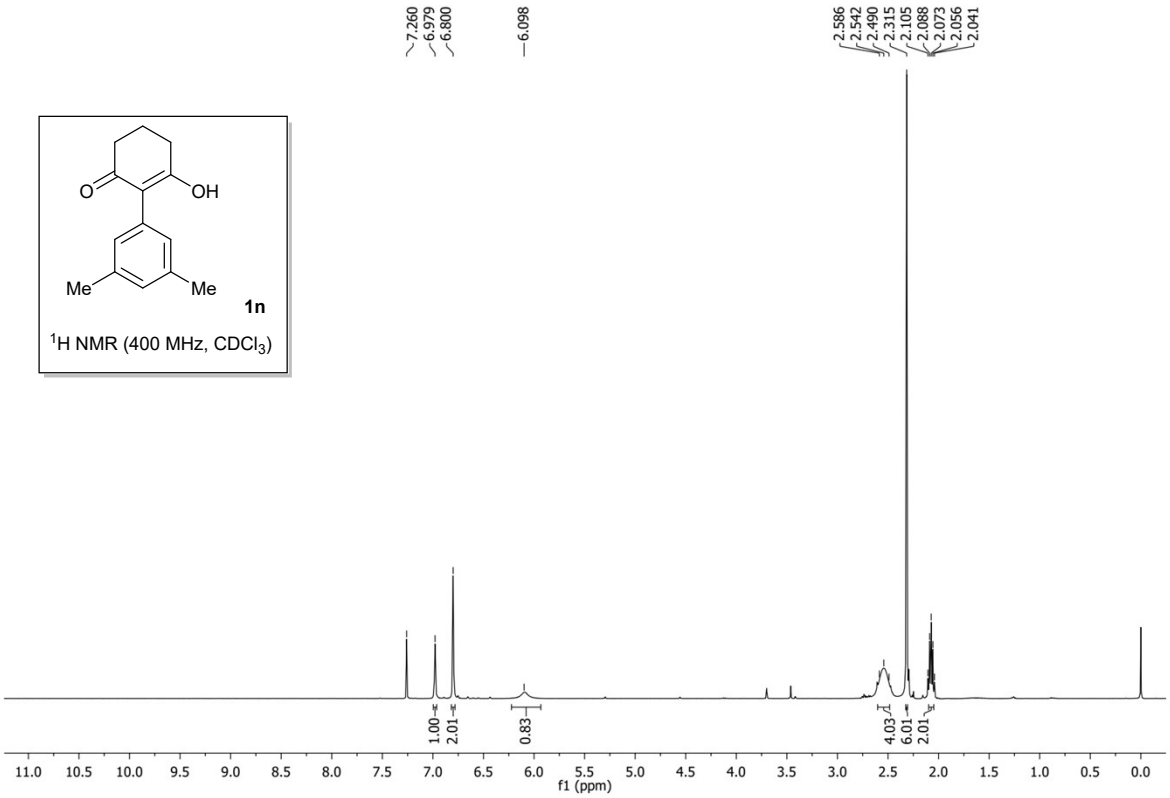






$^1$H NMR (400 MHz, $CDCl_3$)

SR-64-1H.1.fid —

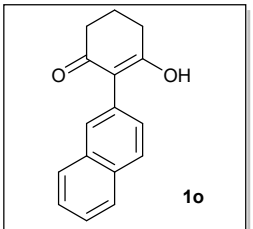




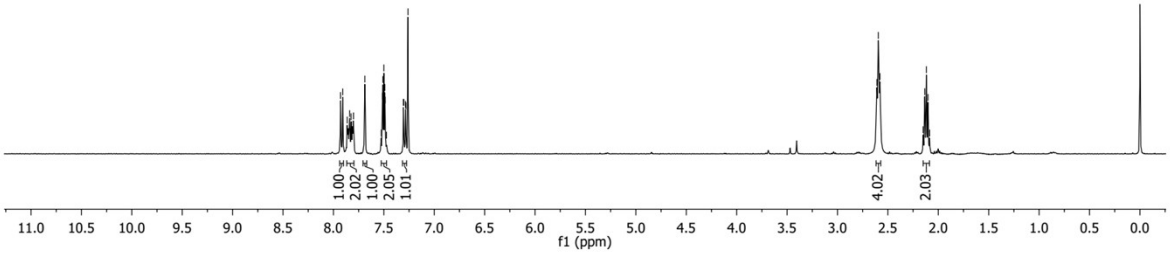


$^1$H NMR (400 MHz, $CDCl_3$)

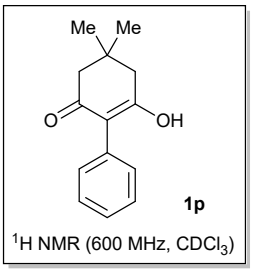
SR-67-1H.1.fid —

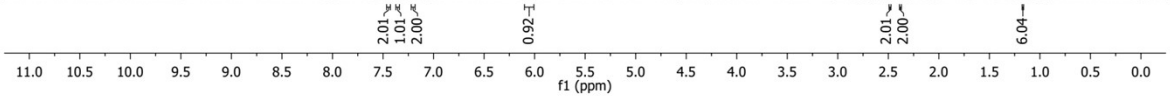

$^1$H NMR (400 MHz, $CDCl_3$)



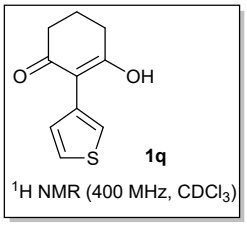

SR-55-1H.1.fid —

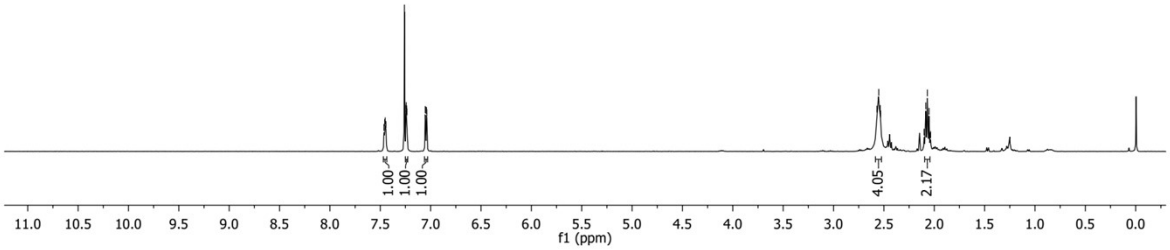

$^1$H NMR (600 MHz, $CDCl_3$)



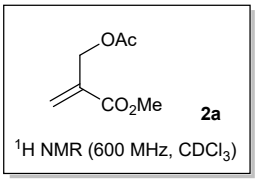
SR-196-THIO-1H.1.fid —

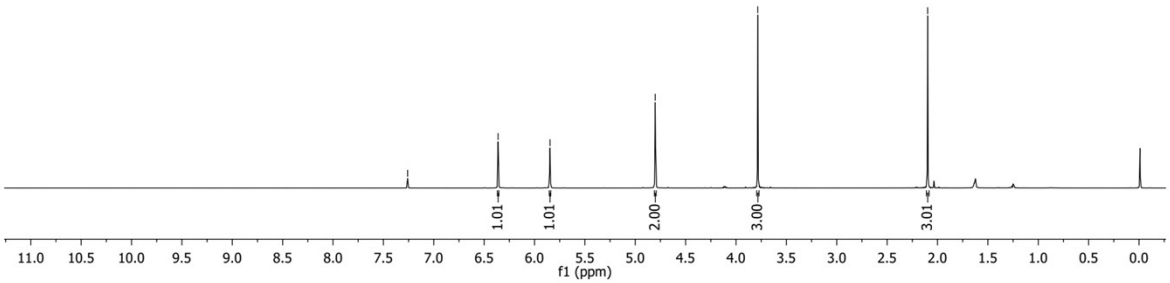

$^1$H NMR (400 MHz, $CDCl_3$)



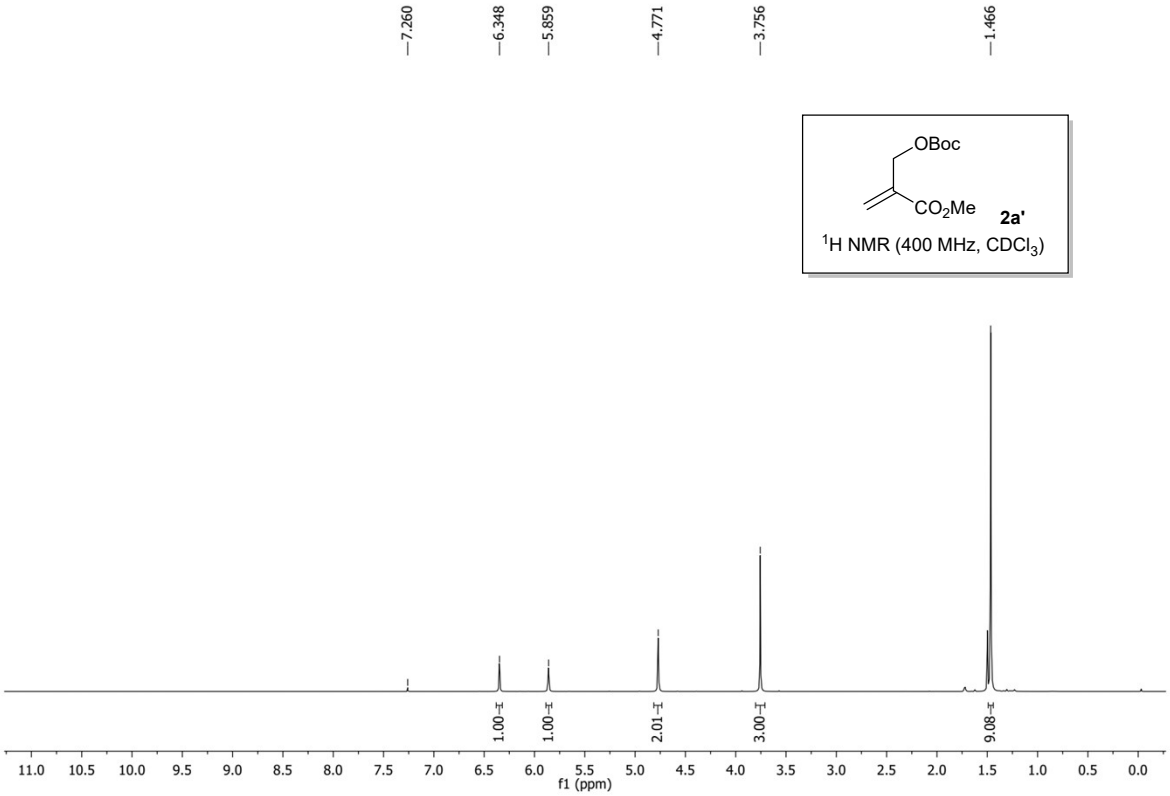

SR-12.1.fid —

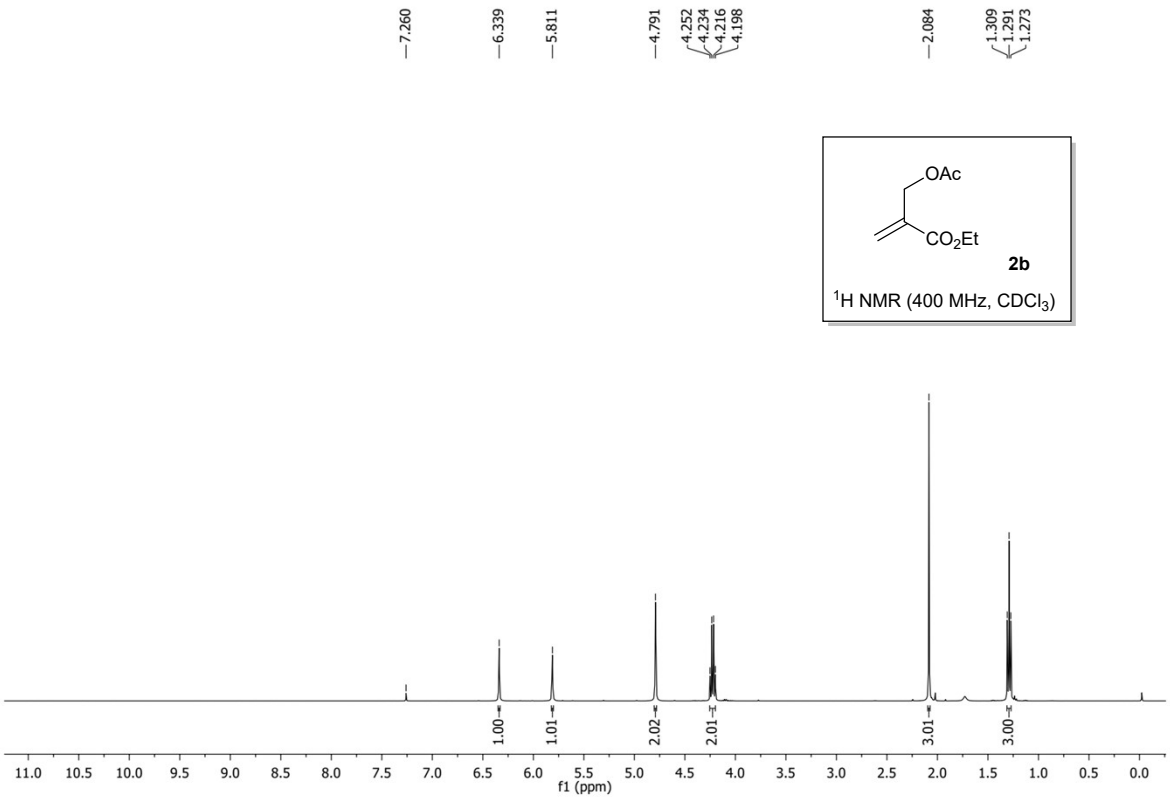

$^1$H NMR (600 MHz, $CDCl_3$)



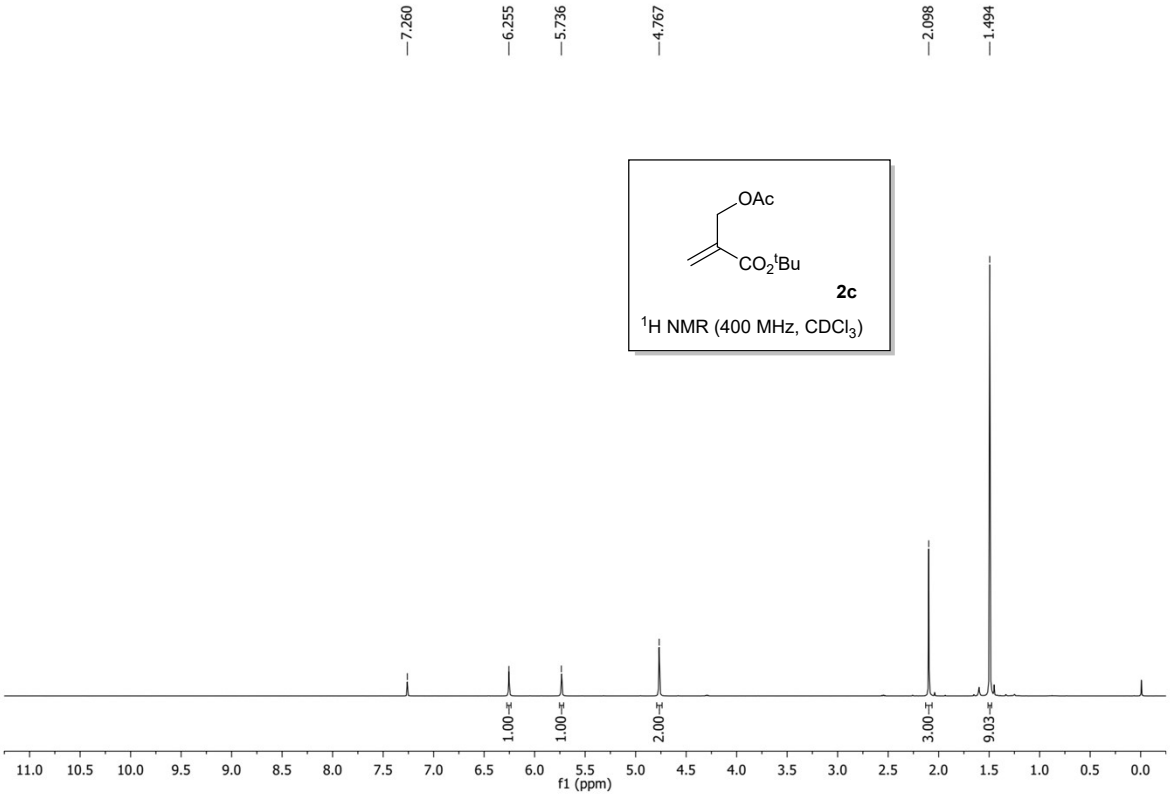
SR-Boc MBH



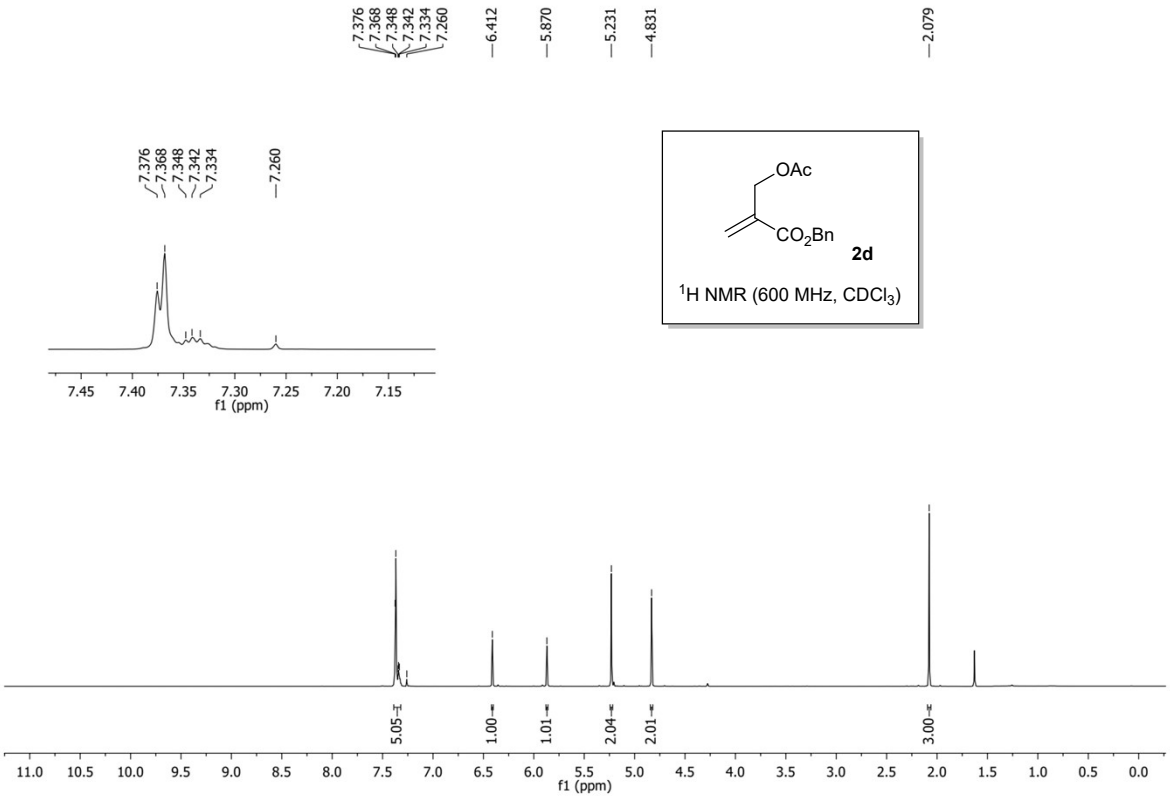

SR-43-1H.1.fid —



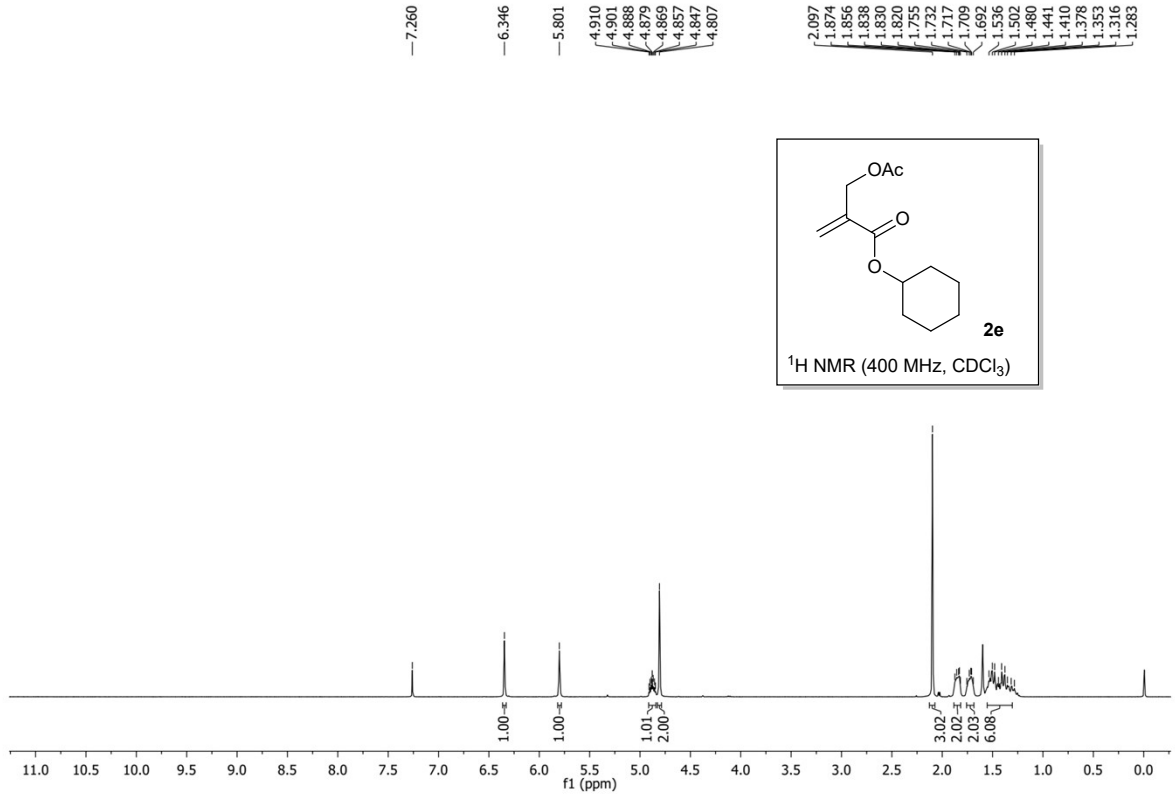
SR-73-1H.1.fid —



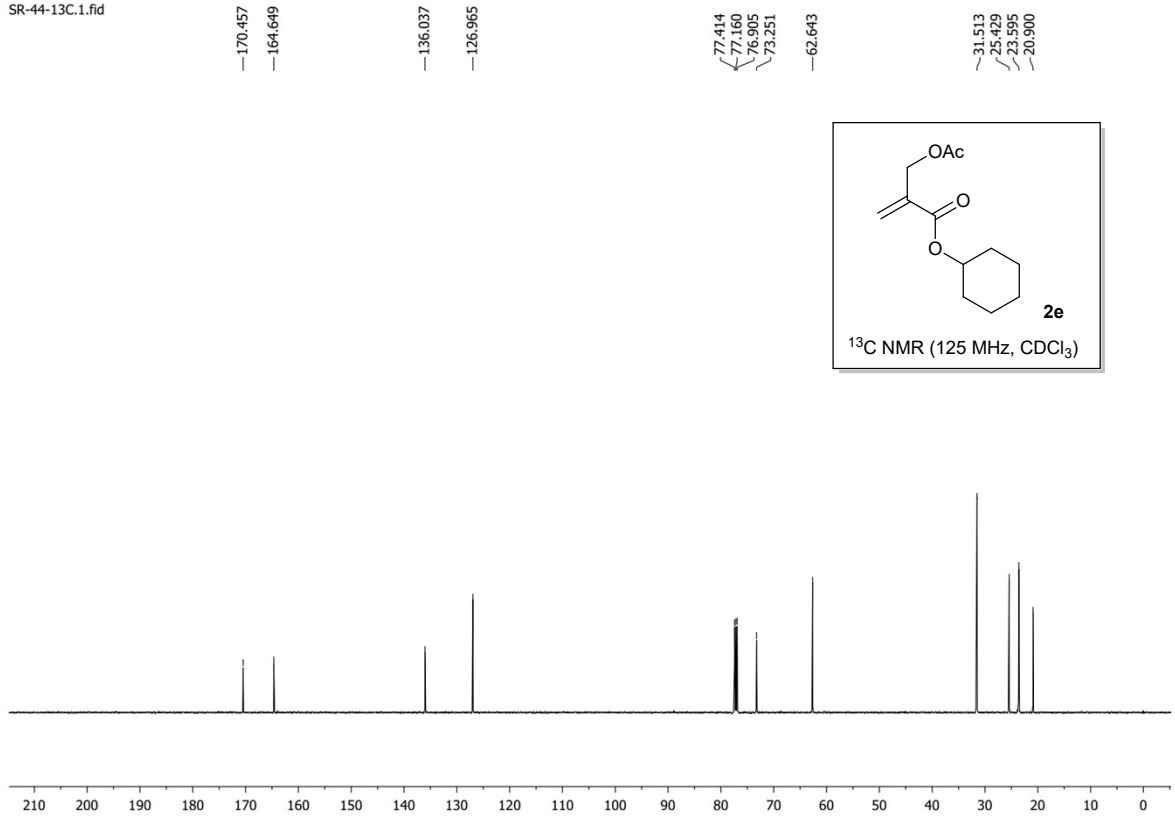

SR-34-1H.1 fid



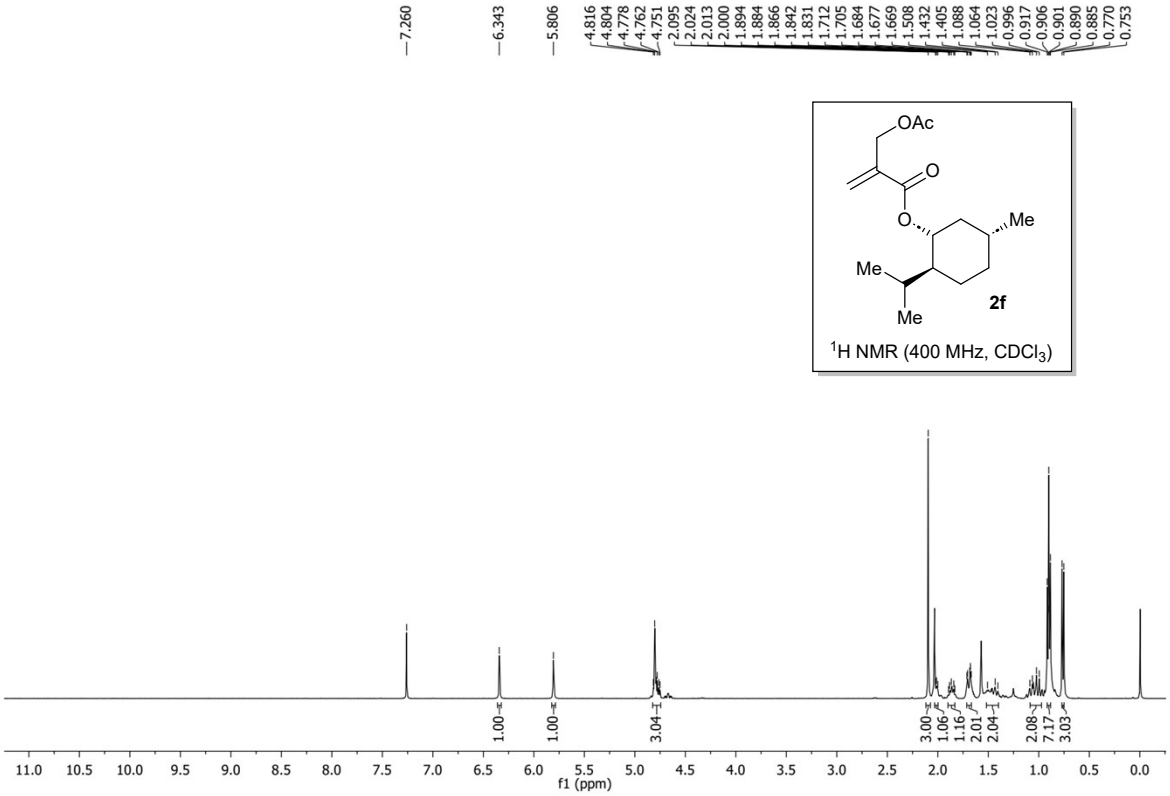
SR-44-1H.1.fid



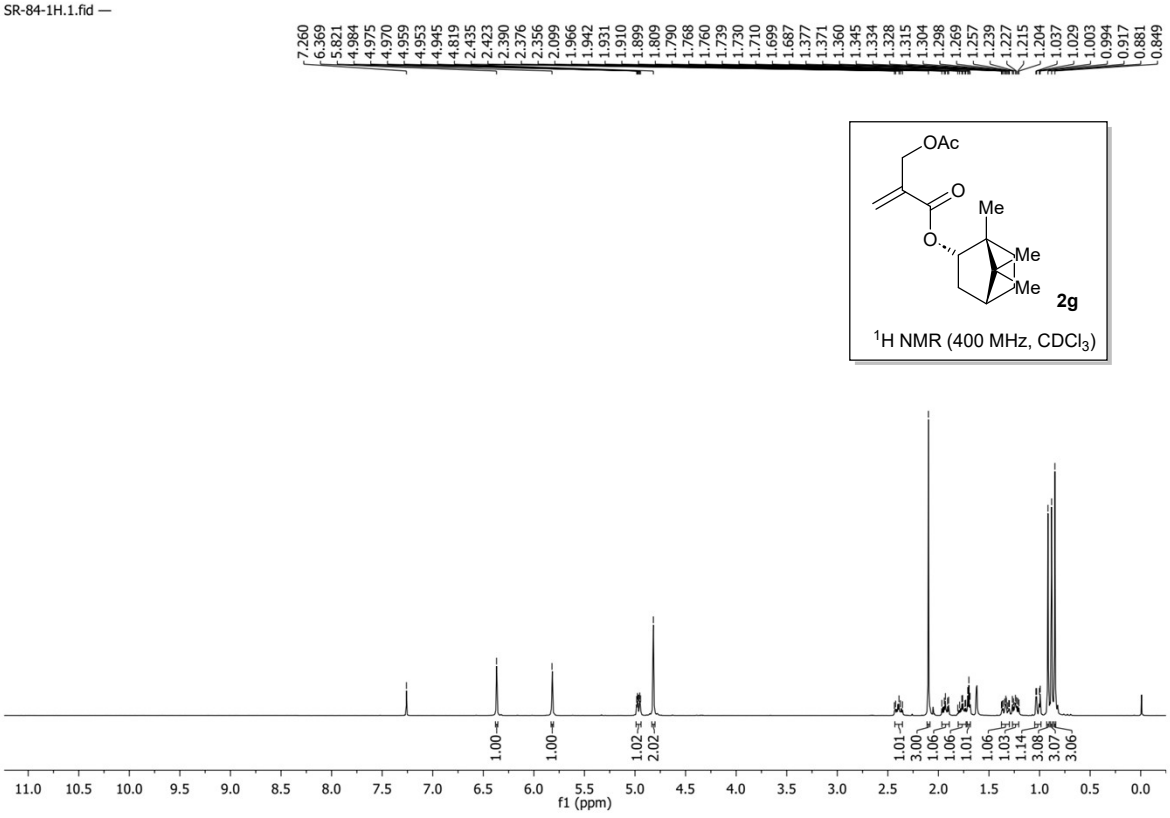

SR-44-13C.1.fid



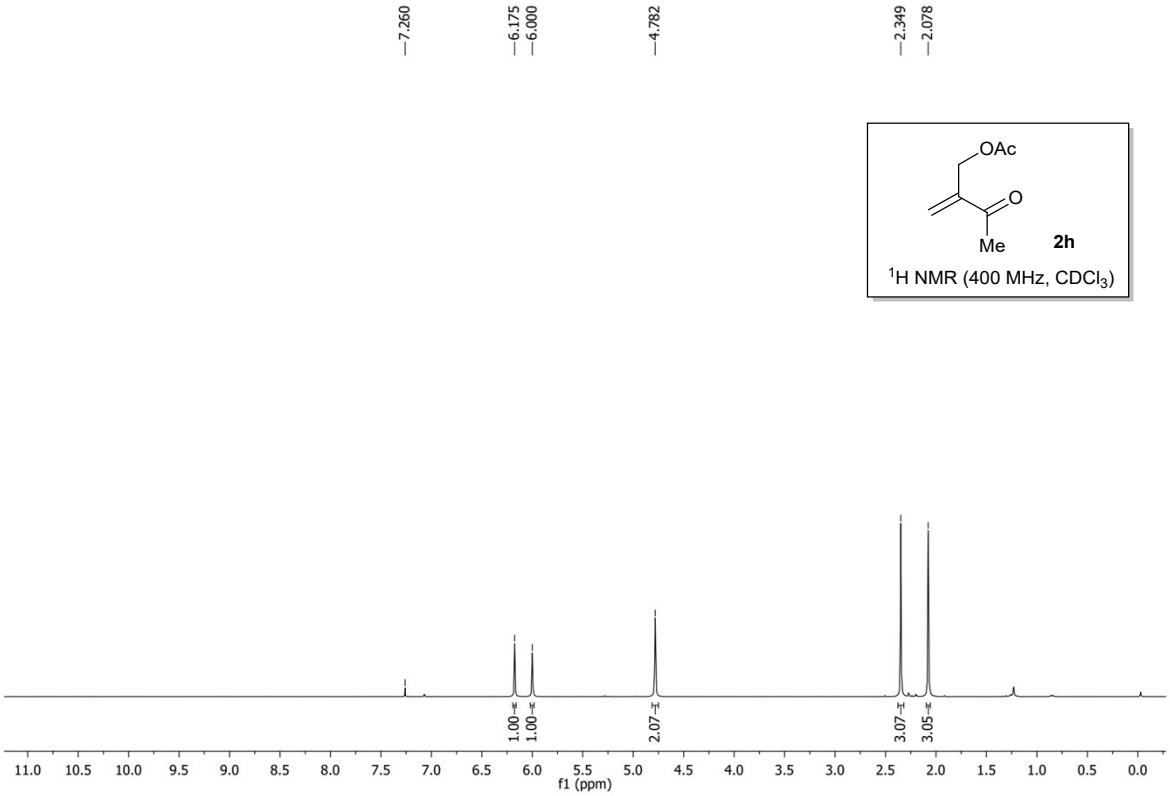
SR-82-1H.1.fid —



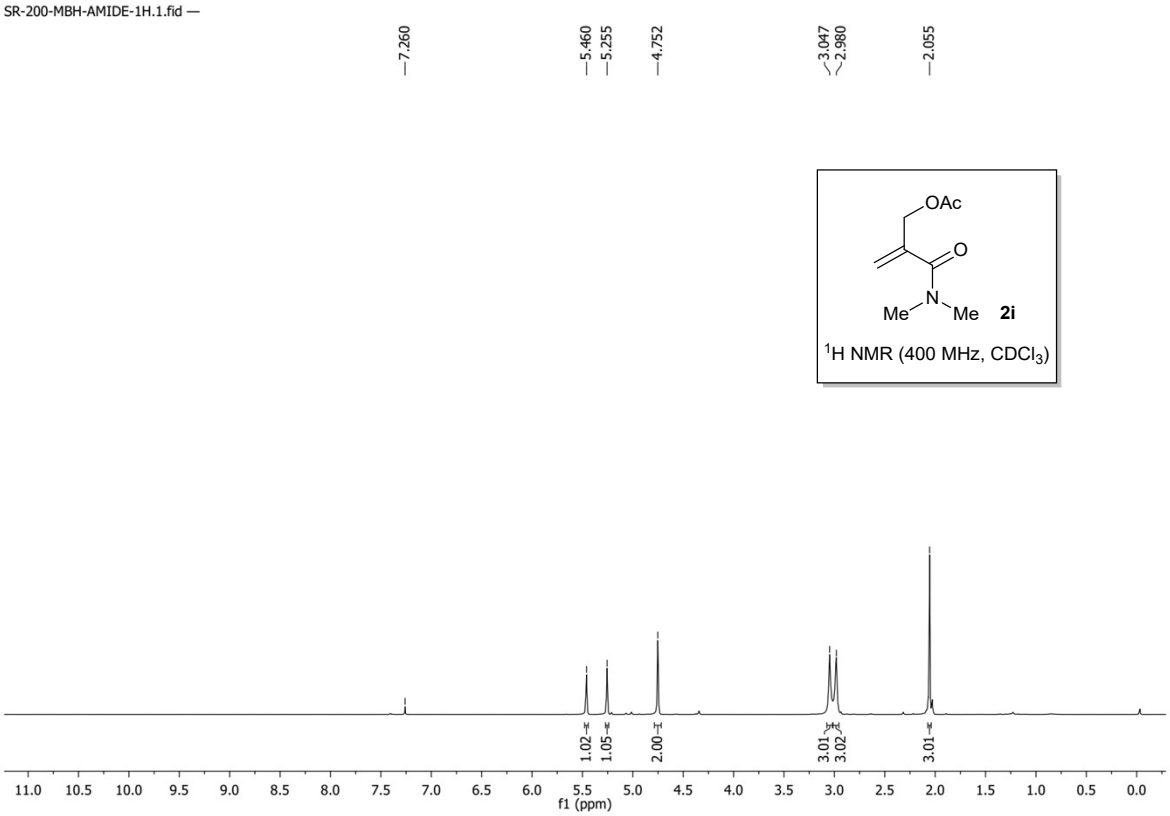

SR-84-1H.1.fid —



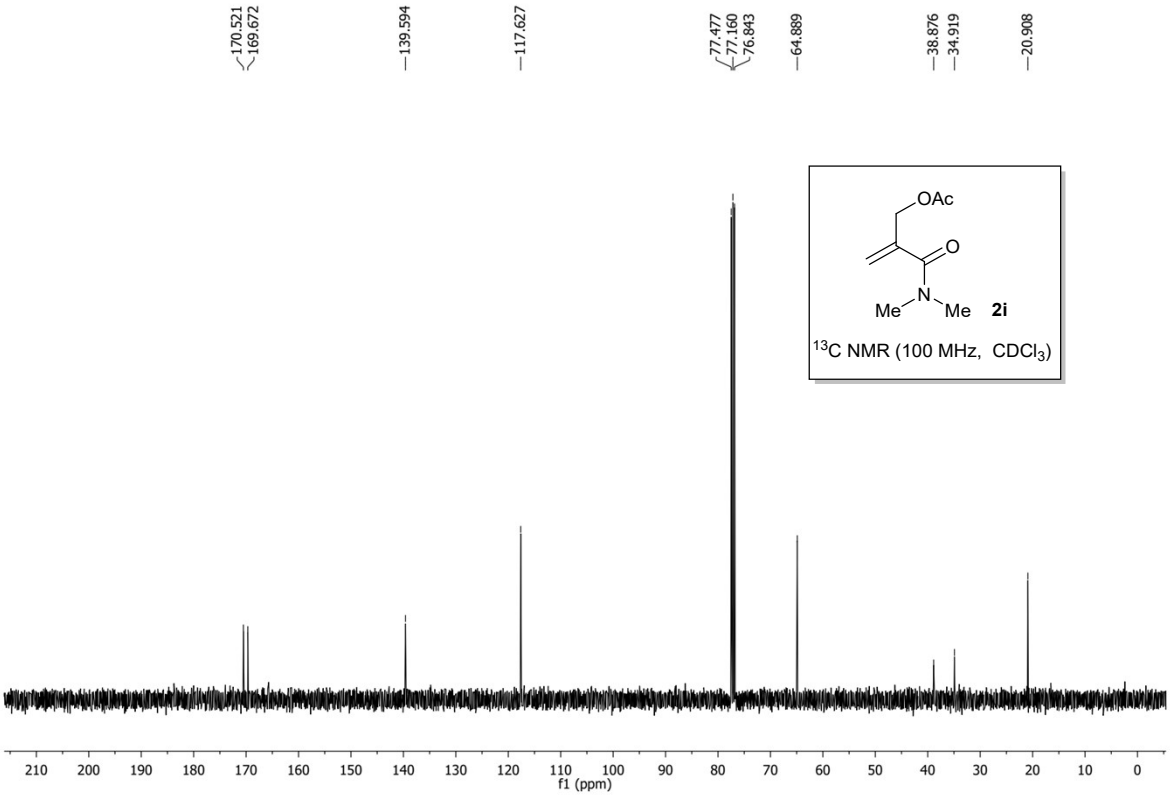
SR-199-1H.1.fid —



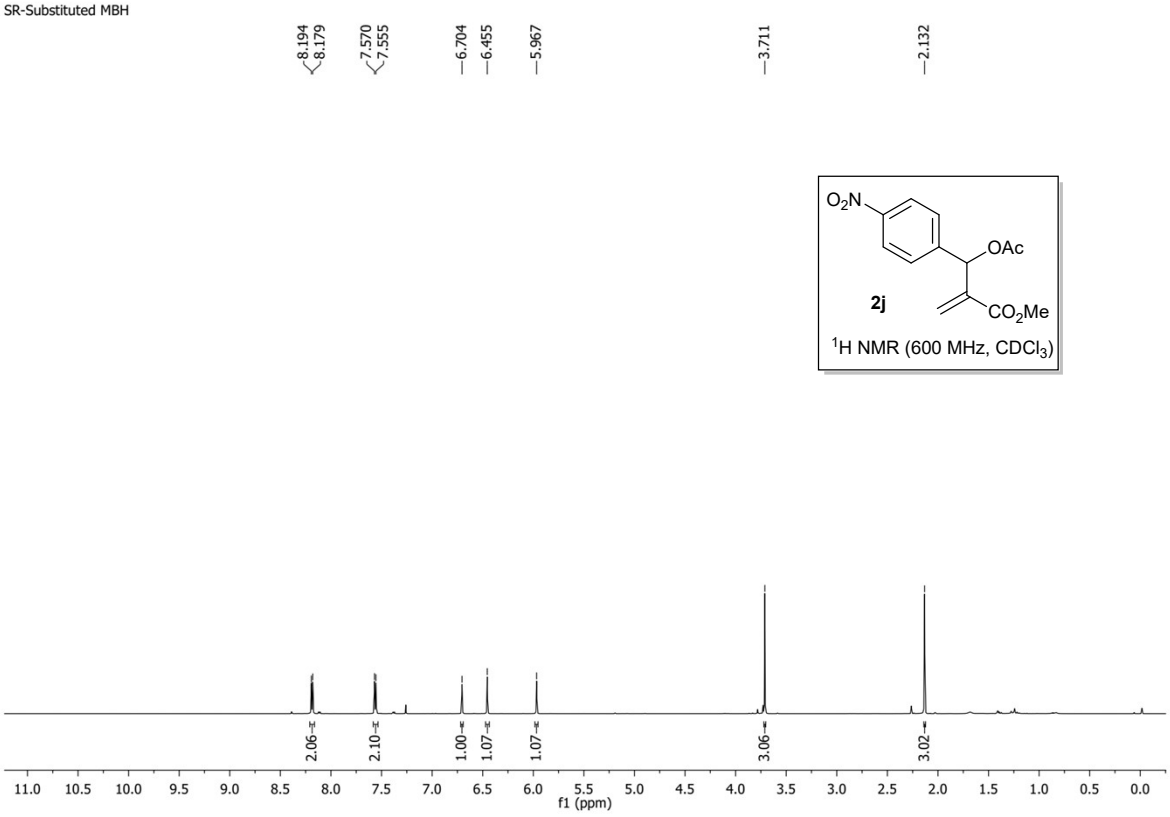

SR-200-MBH-AMIDE-1H.1.fid —

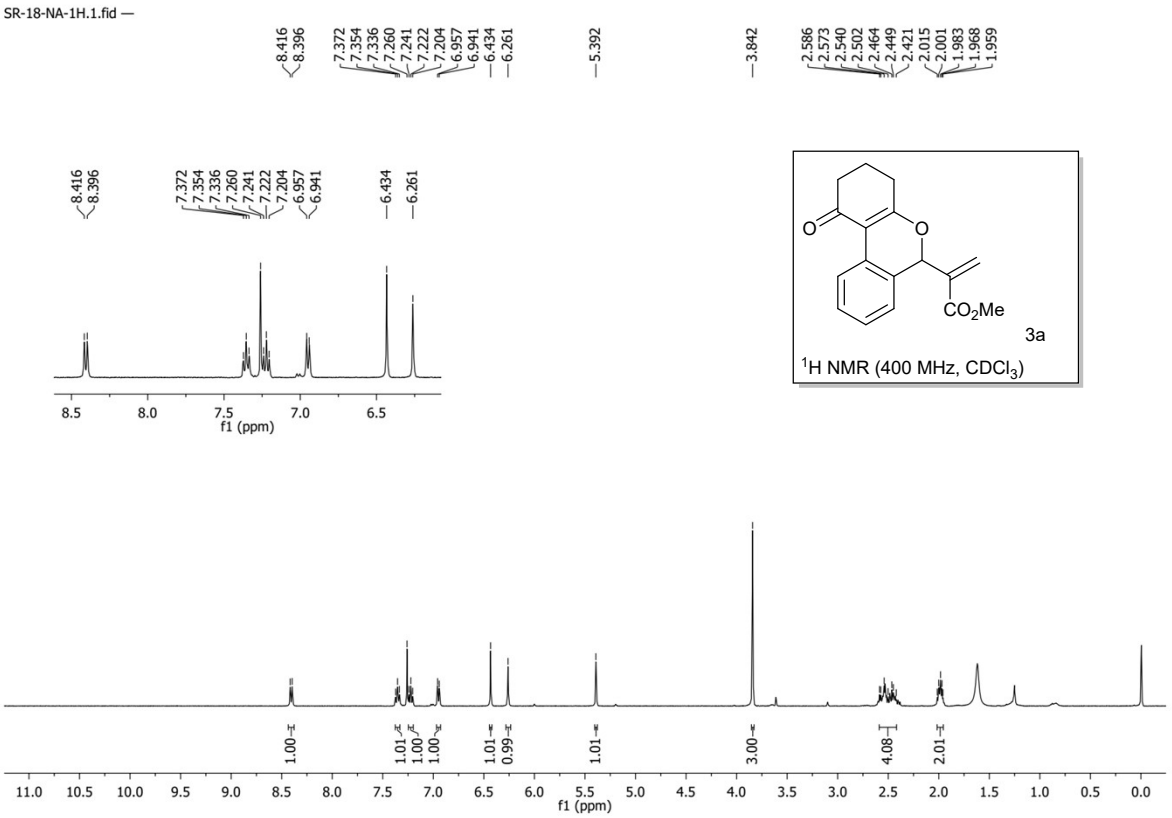


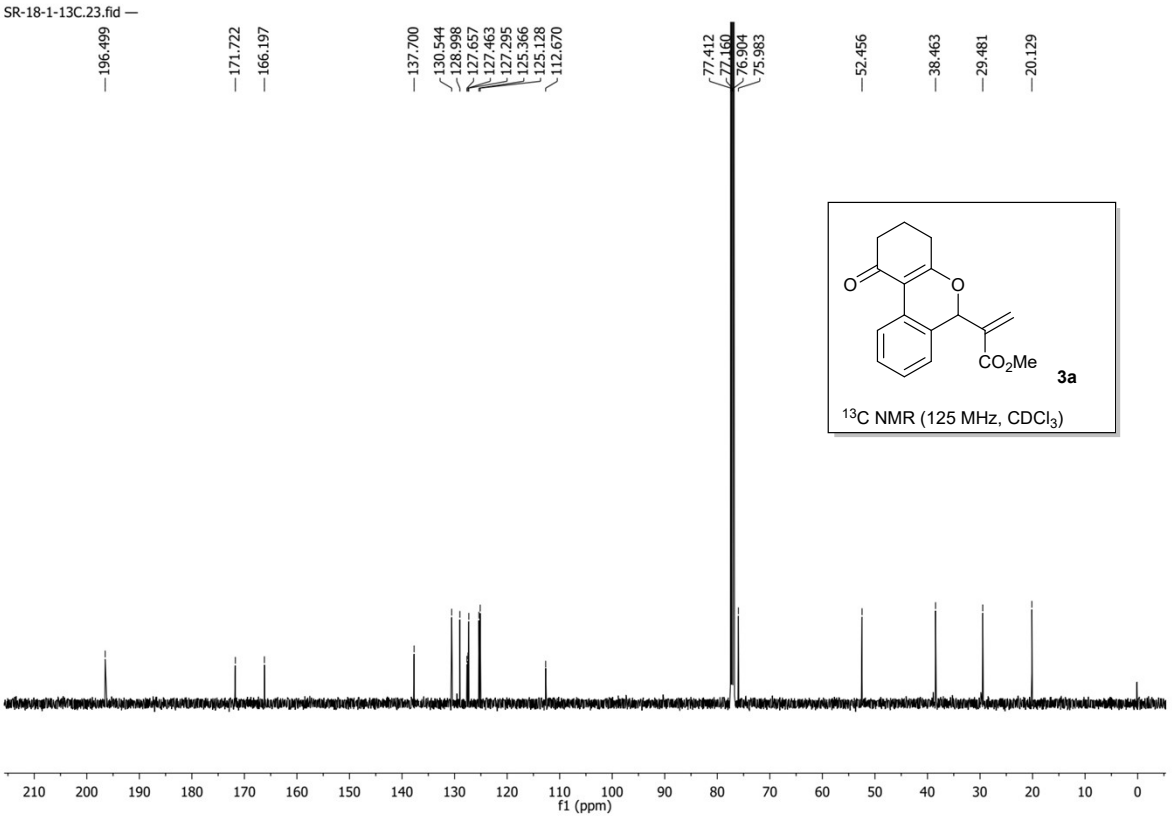
SR-200-MBH-AMIDE-1H.2.fid

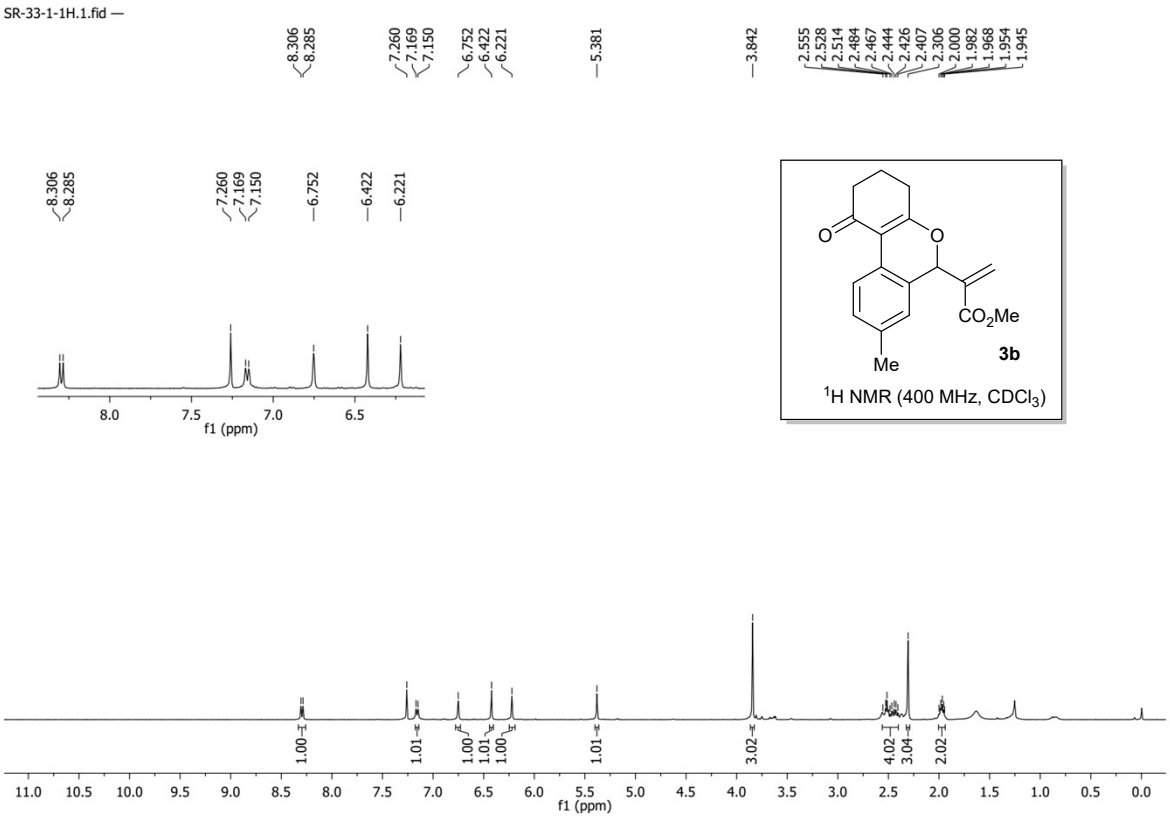


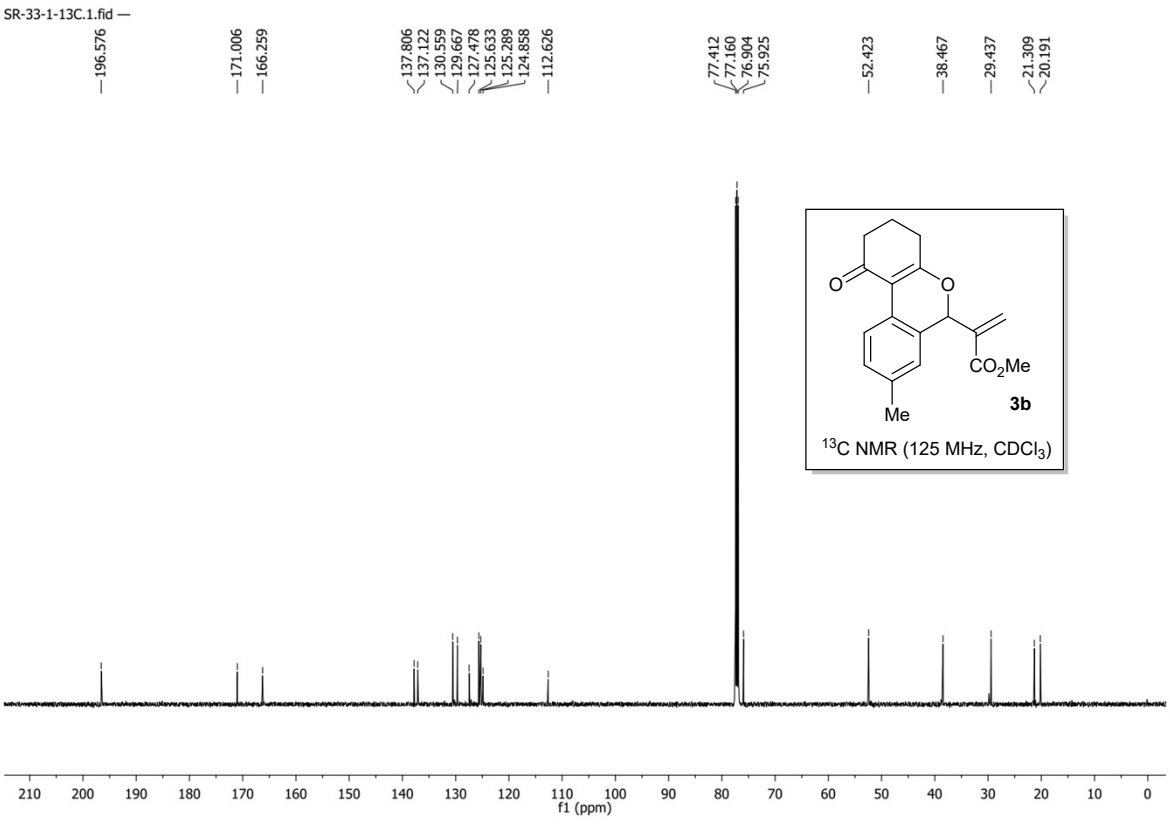

SR-Substituted MBH



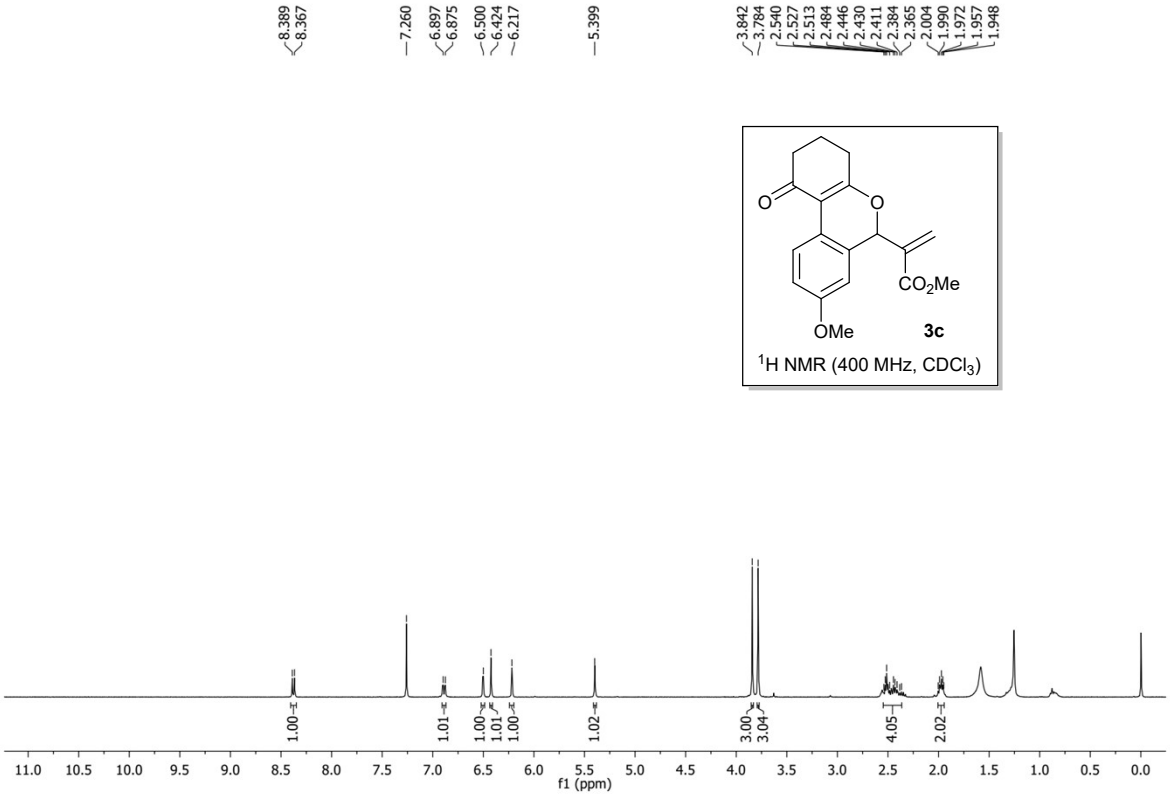

SR-18-NA-1H.1.fid
8.416
8.396
7.372
7.354
7.336
7.260
7.241
7.222
7.204
6.957
6.941
6.434
6.261
5.392
3.842
2.586
2.573
2.540
2.502
2.464
2.449
2.421
2.015
2.001
1.983
1.968
1.959
f1 (ppm)
O
O
CO2Me
3a
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.00
1.00
1.01
0.99
1.01
3.00
4.08
2.01


SR-18-1-13C.23.fid
196.499
171.722
166.197
137.700
130.544
128.998
127.657
127.463
127.295
125.366
125.128
112.670
77.412
77.160
76.904
75.983
52.456
38.463
29.481
20.129
f1 (ppm)
O
O
CO2Me
3a
13C NMR (125 MHz, CDCl3)

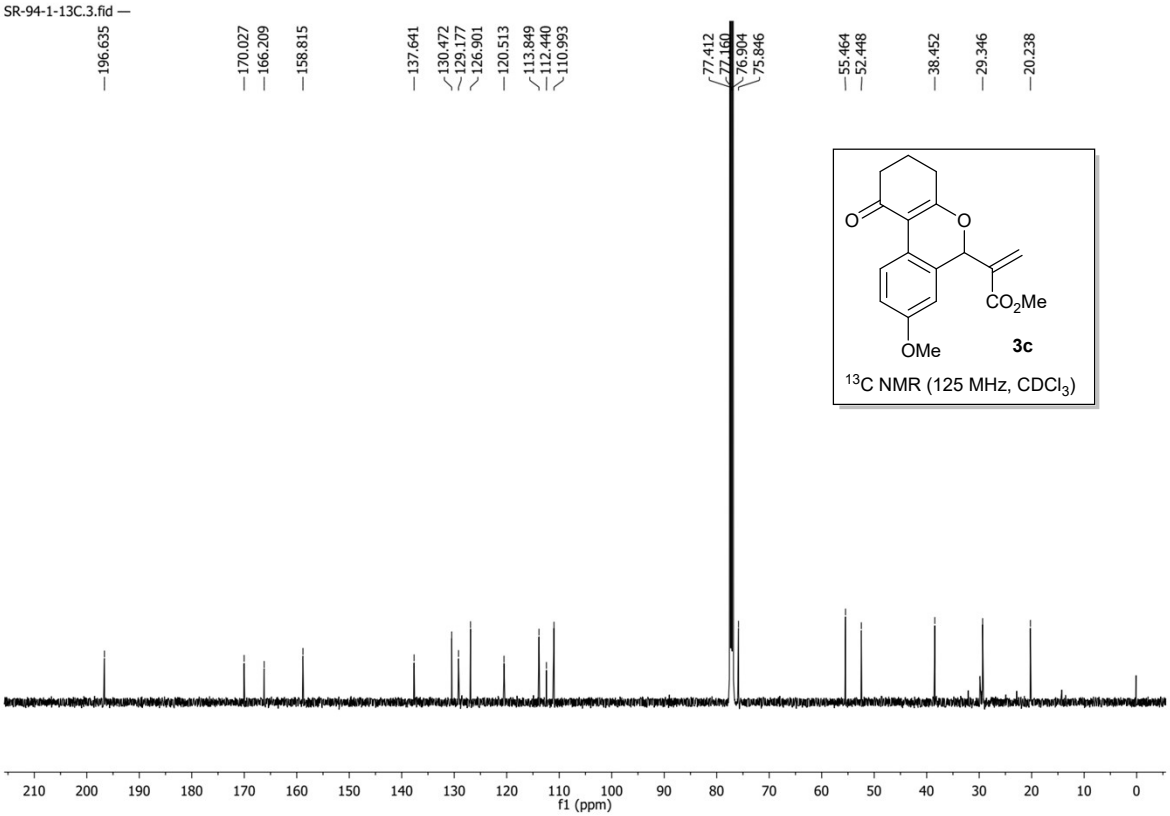

SR-33-1-1H.1.fid
8.306
8.285
7.260
7.169
7.150
6.752
6.422
6.221
5.381
3.842
2.555
2.528
2.514
2.484
2.467
2.444
2.426
2.407
2.306
2.000
1.982
1.968
1.954
1.945
f1 (ppm)
O
O
CO2Me
Me
3b
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.00
1.01
1.00
1.01
3.02
4.02
3.04
2.02

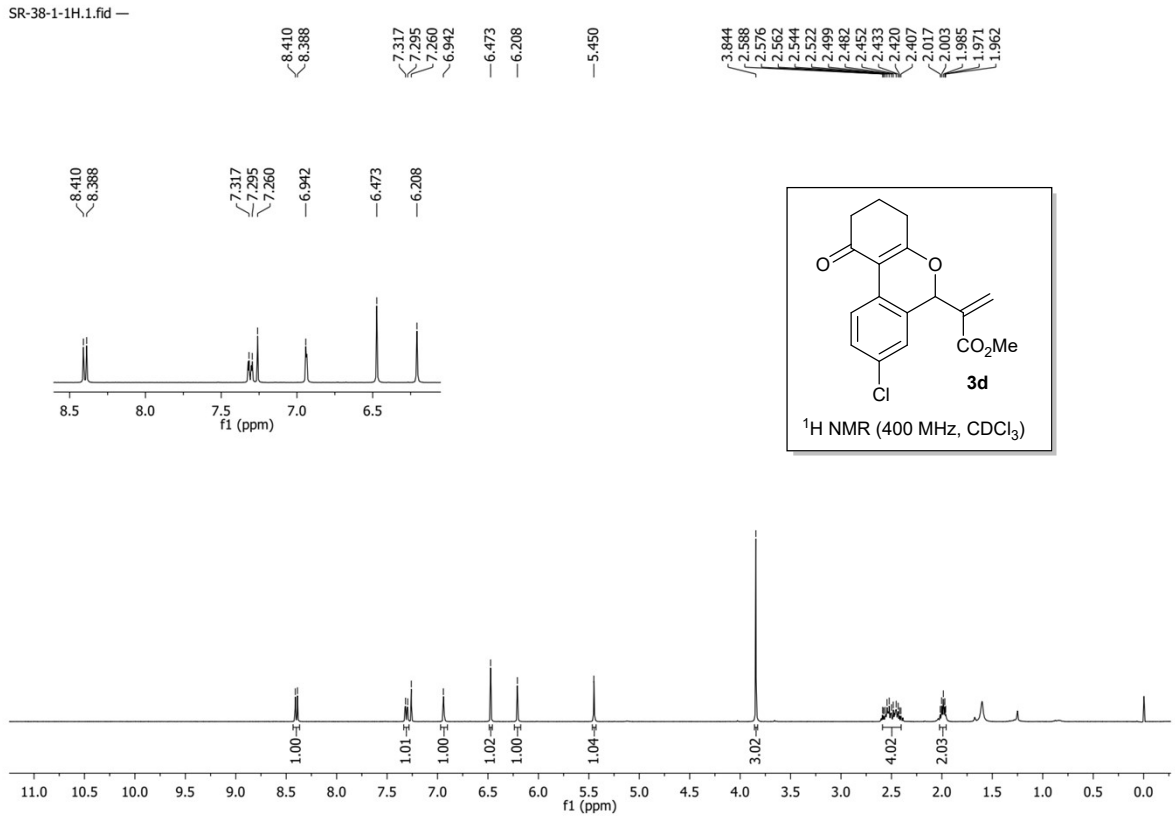

SR-33-1-13C.1.fid
196.576
171.006
166.259
137.806
137.122
130.559
129.667
127.478
125.633
125.289
124.858
112.626
77.412
77.160
76.904
75.925
52.423
38.467
29.437
21.309
20.191
f1 (ppm)
O
O
CO2Me
Me
3b
13C NMR (125 MHz, CDCl3)

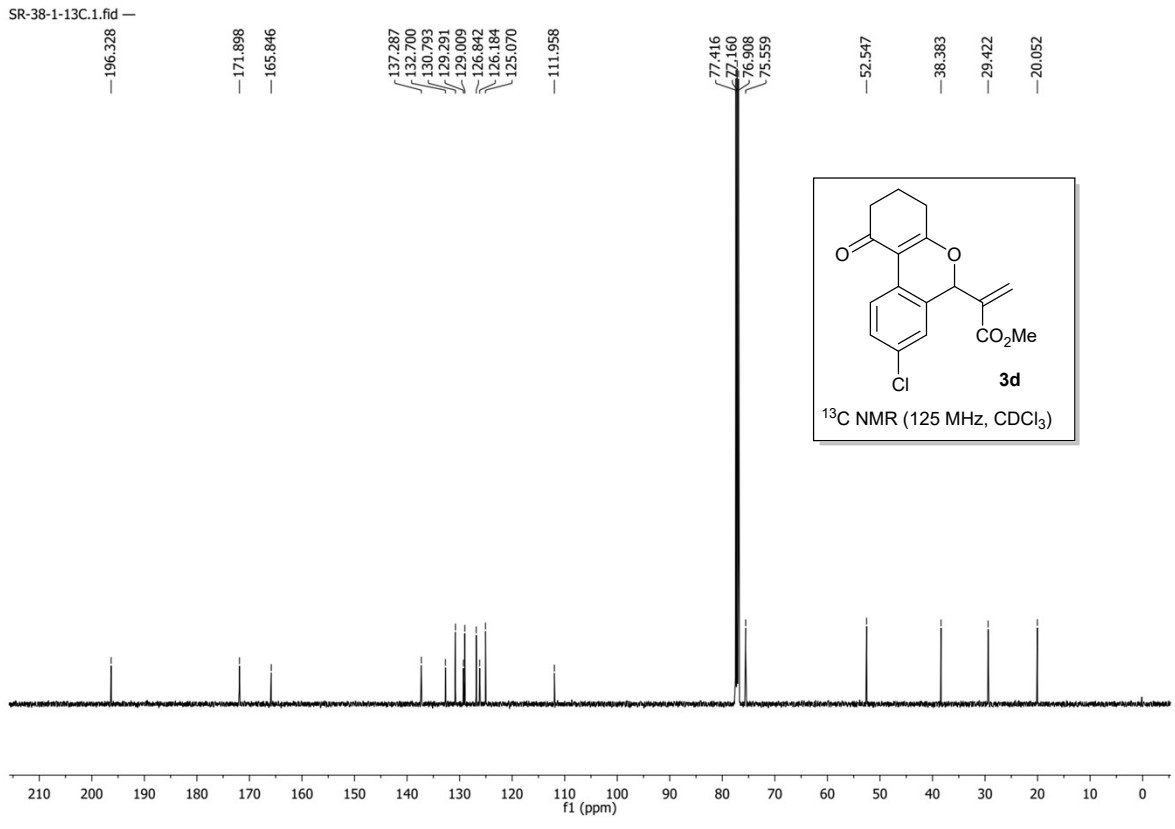
SR-94-1-1H.1.fid

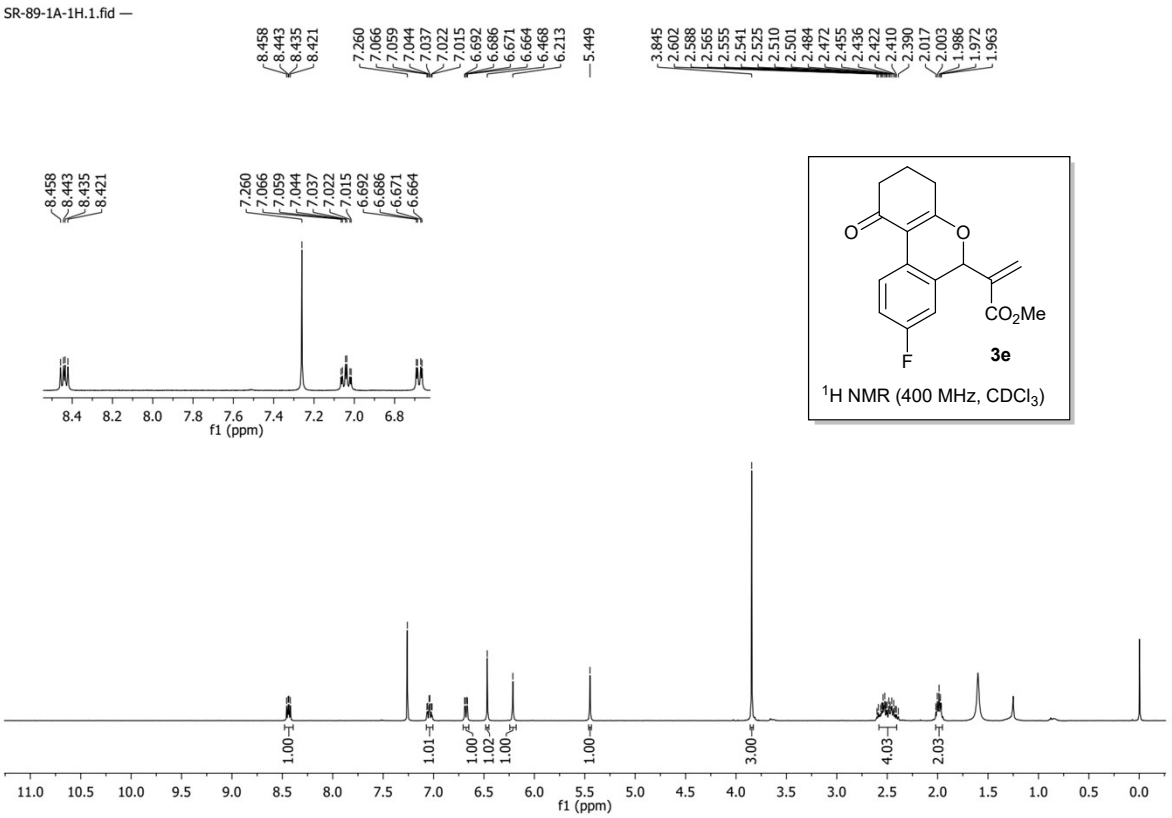


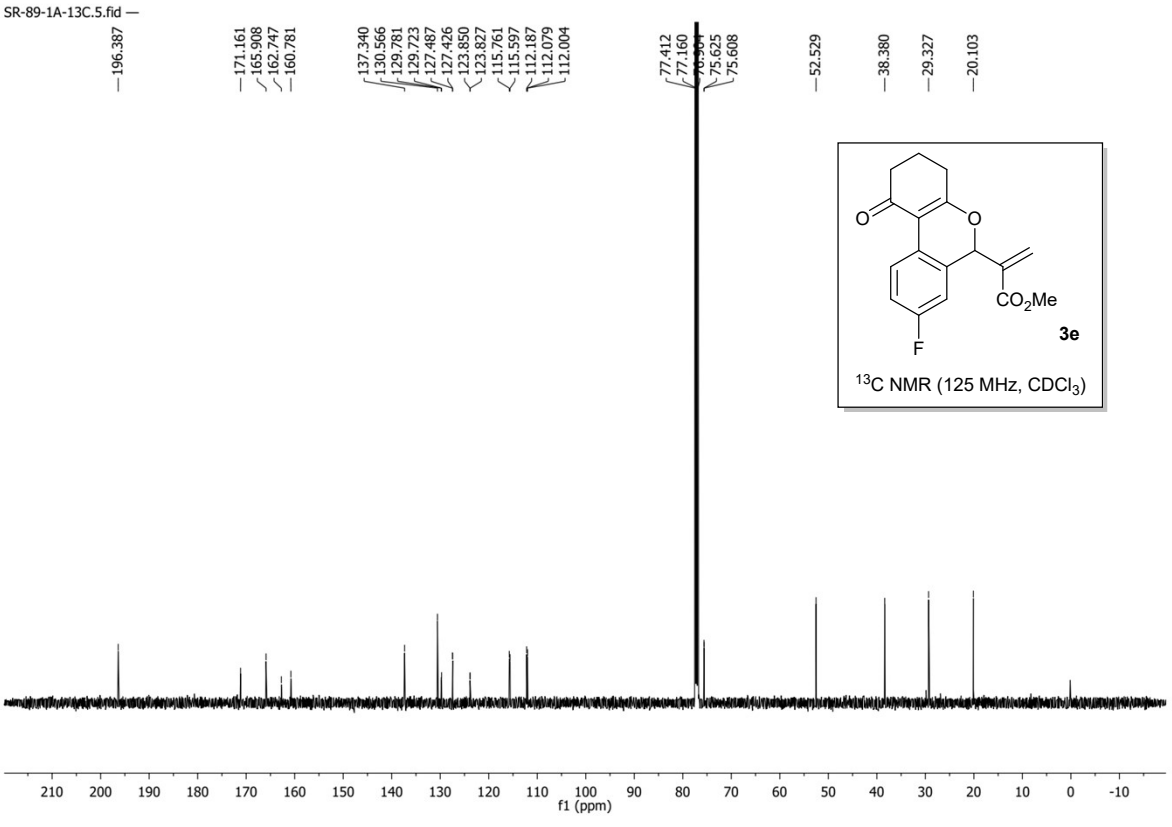

SR-94-1-13C.3.fid



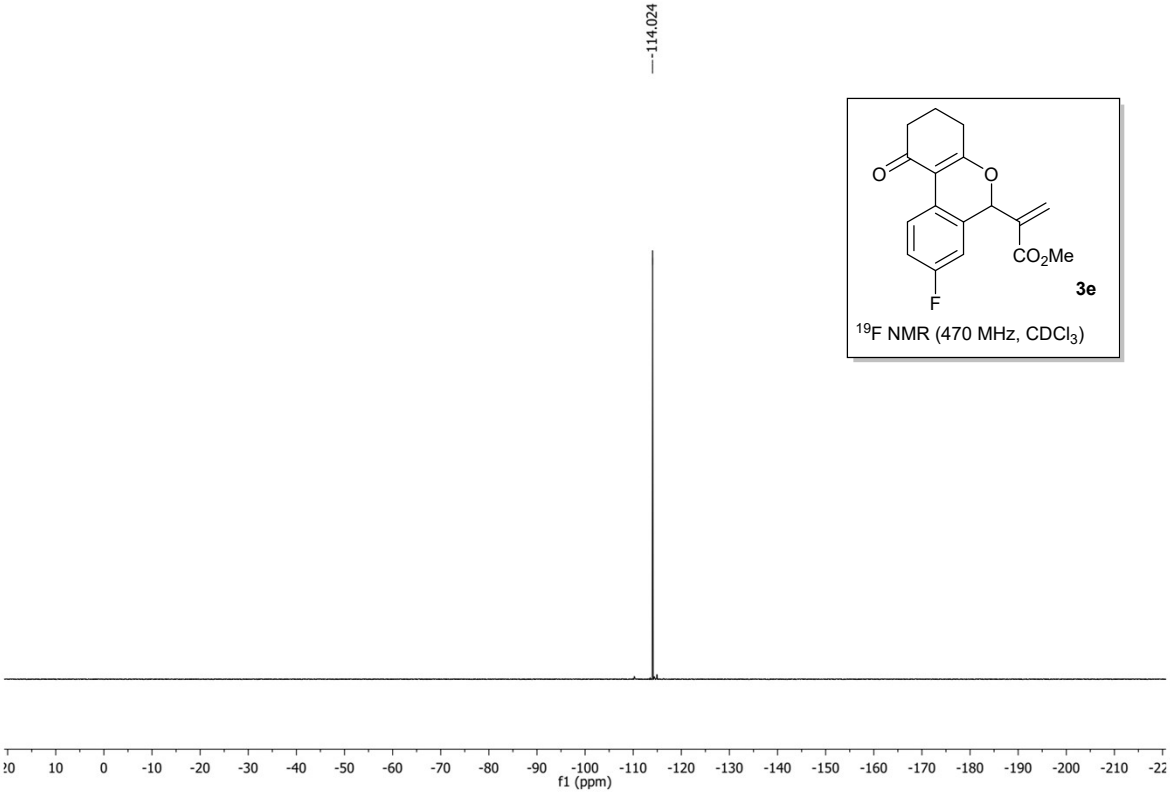

SR-38-1-1H.1.fid
8.410
8.388
7.317
7.295
7.260
6.942
6.473
6.208
5.450
3.844
2.588
2.576
2.562
2.544
2.522
2.499
2.482
2.452
2.433
2.420
2.407
2.017
2.003
1.985
1.971
1.962
f1 (ppm)
O
O
CO2Me
Cl
3d
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.00
1.02
1.00
1.04
3.02
4.02
2.03


SR-38-1-13C.1.fid
196.328
171.898
165.846
137.287
132.700
130.793
129.291
129.009
126.842
126.184
125.070
111.958
77.416
77.160
76.908
75.559
52.547
38.383
29.422
20.052
f1 (ppm)
O
O
CO2Me
Cl
3d
13C NMR (125 MHz, CDCl3)


SR-89-1A-1H.1.fid
8.458
8.443
8.435
8.421
7.260
7.066
7.059
7.044
7.037
7.022
7.015
6.692
6.686
6.671
6.664
6.468
6.213
5.449
3.845
2.602
2.588
2.565
2.555
2.541
2.525
2.510
2.501
2.484
2.472
2.455
2.436
2.422
2.410
2.390
2.017
2.003
1.986
1.972
1.963
O
O
CO2Me
F
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)
1.00
1.01
1.00
1.02
1.00
1.00
3.00
4.03
2.03


SR-89-1A-13C.5.fid
196.387
171.161
165.908
162.747
160.781
137.340
130.566
129.781
129.723
127.487
127.426
123.850
123.827
115.761
115.597
112.187
112.079
112.004
77.412
77.160
76.909
75.625
75.608
52.529
38.380
29.327
20.103
O
O
CO2Me
F
3e
13C NMR (125 MHz, CDCl3)
f1 (ppm)

SR-89-1A-19F.4.fid —



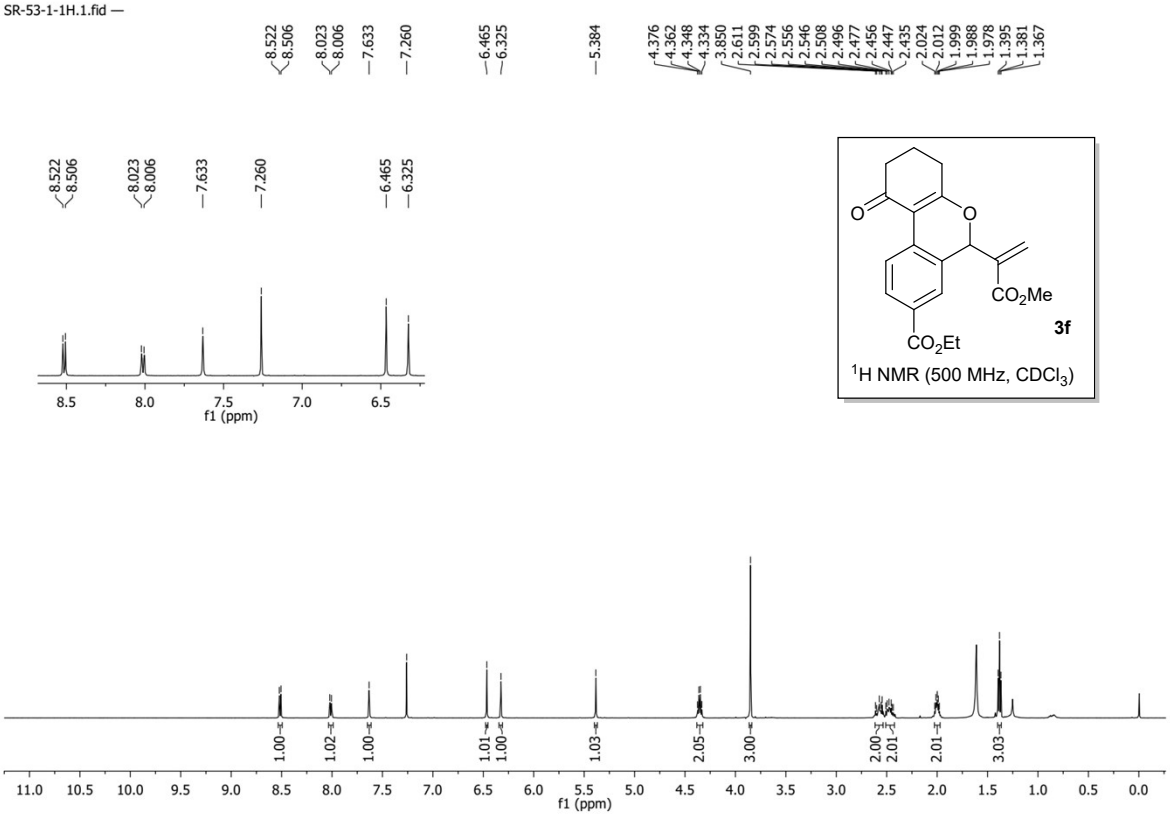




**3e**

$^{19}$F NMR (470 MHz, $CDCl_3$)

SR-53-1-1H.1.fid —

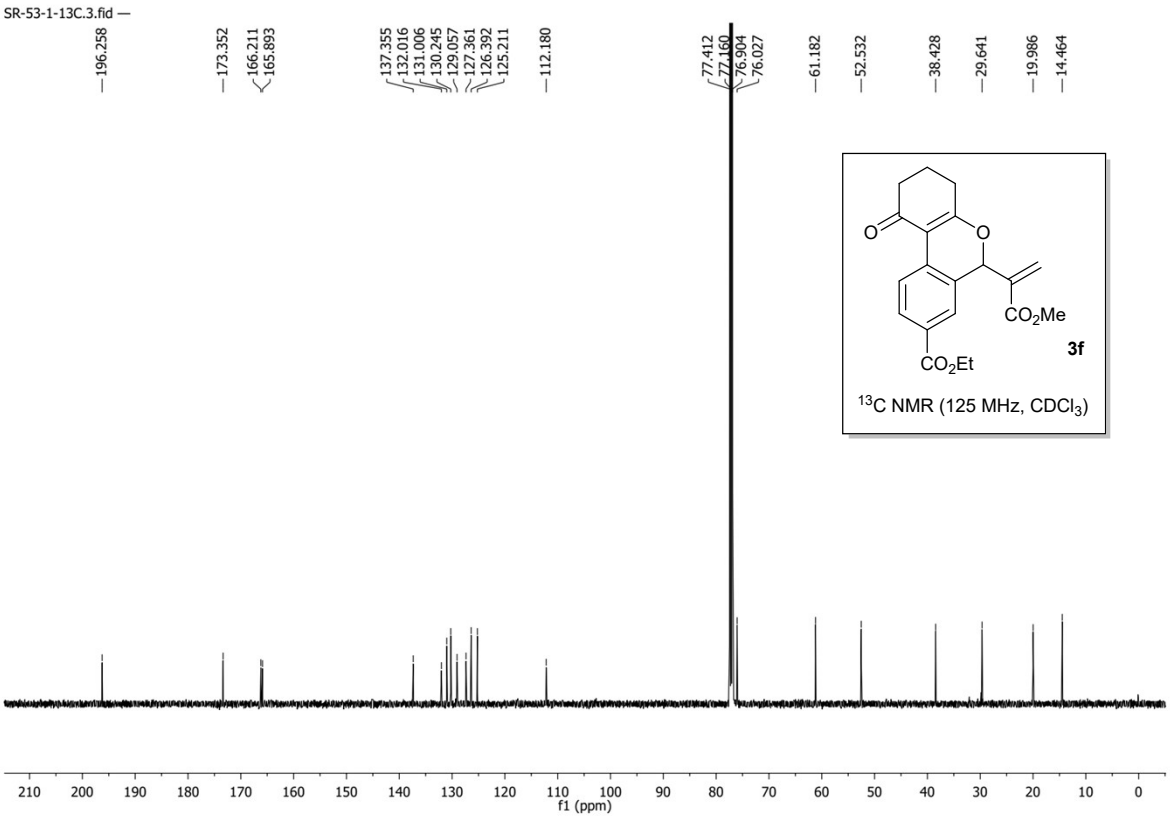


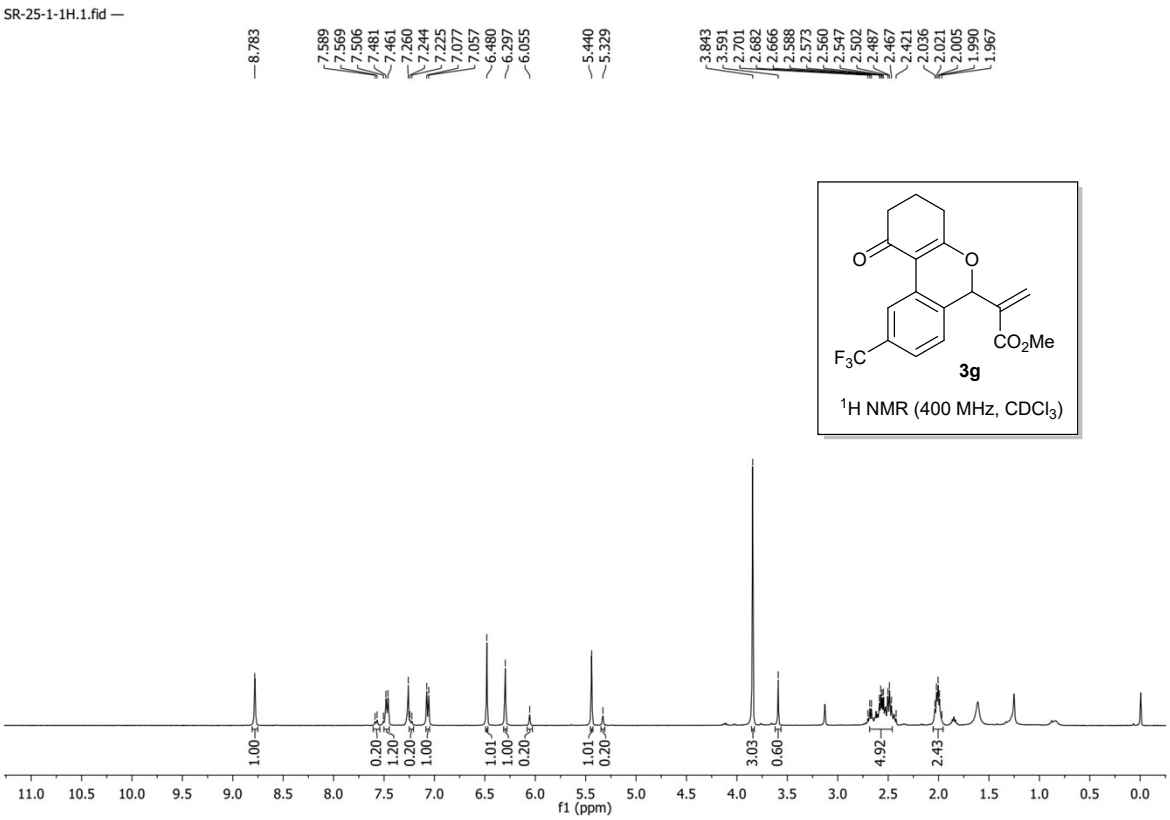


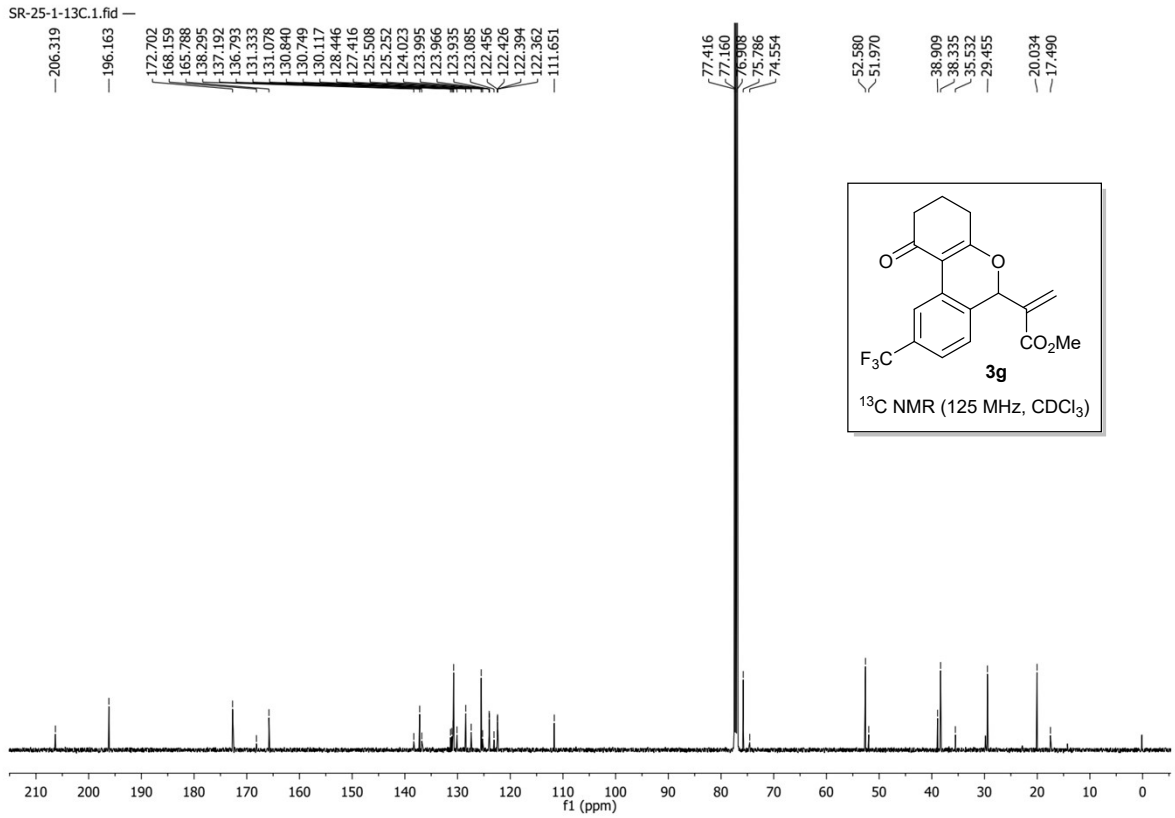


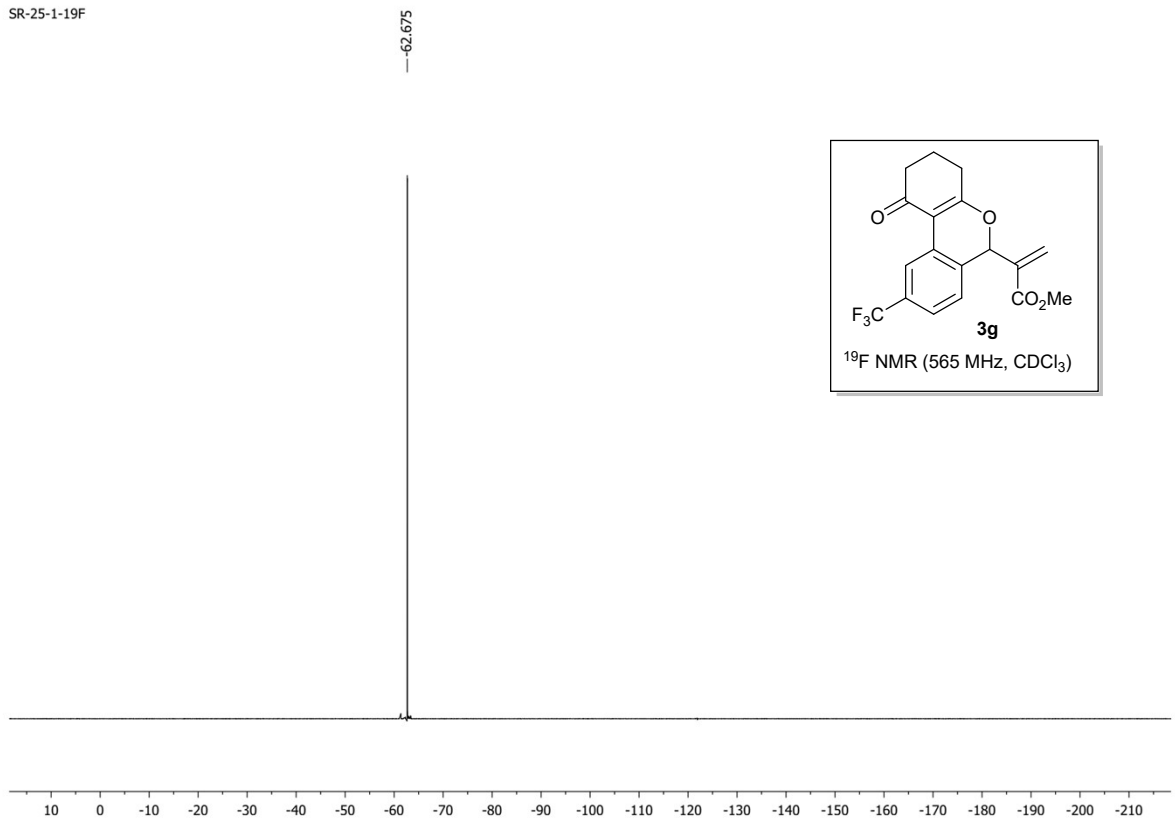
**3f**

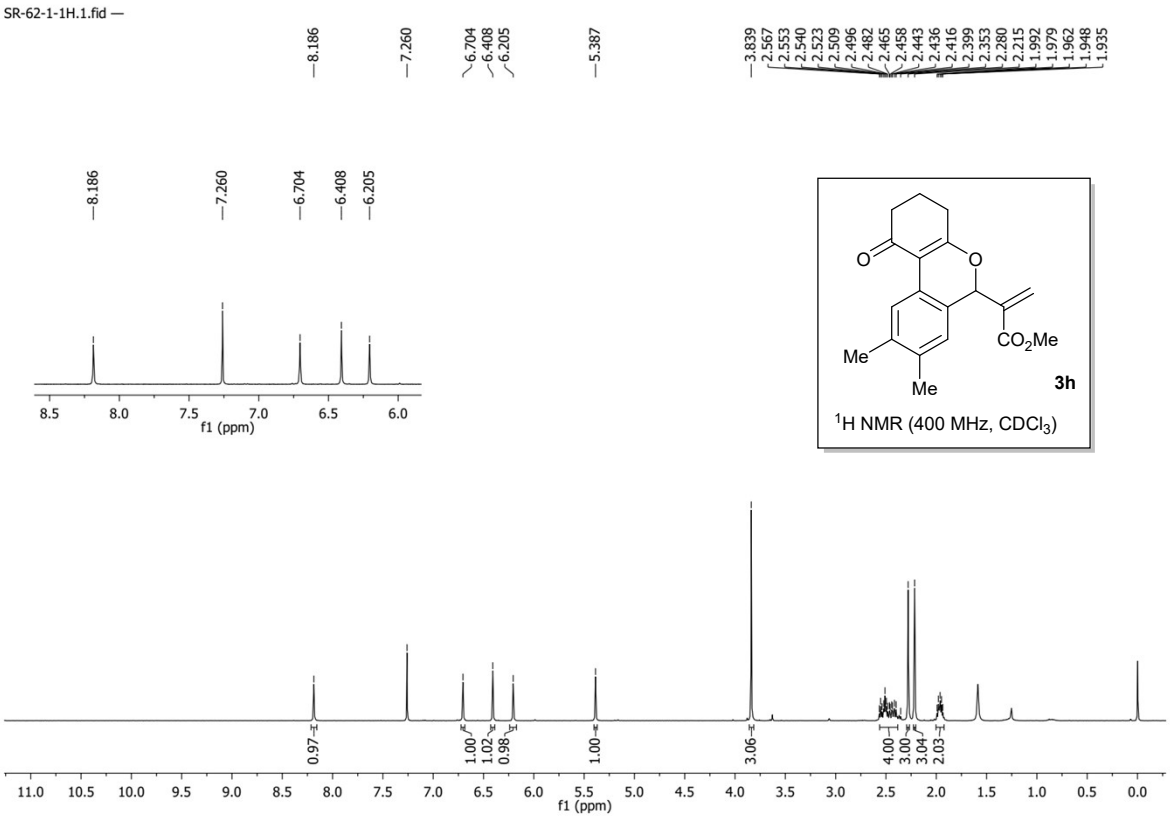
$^{1}$H NMR (500 MHz, $CDCl_3$)

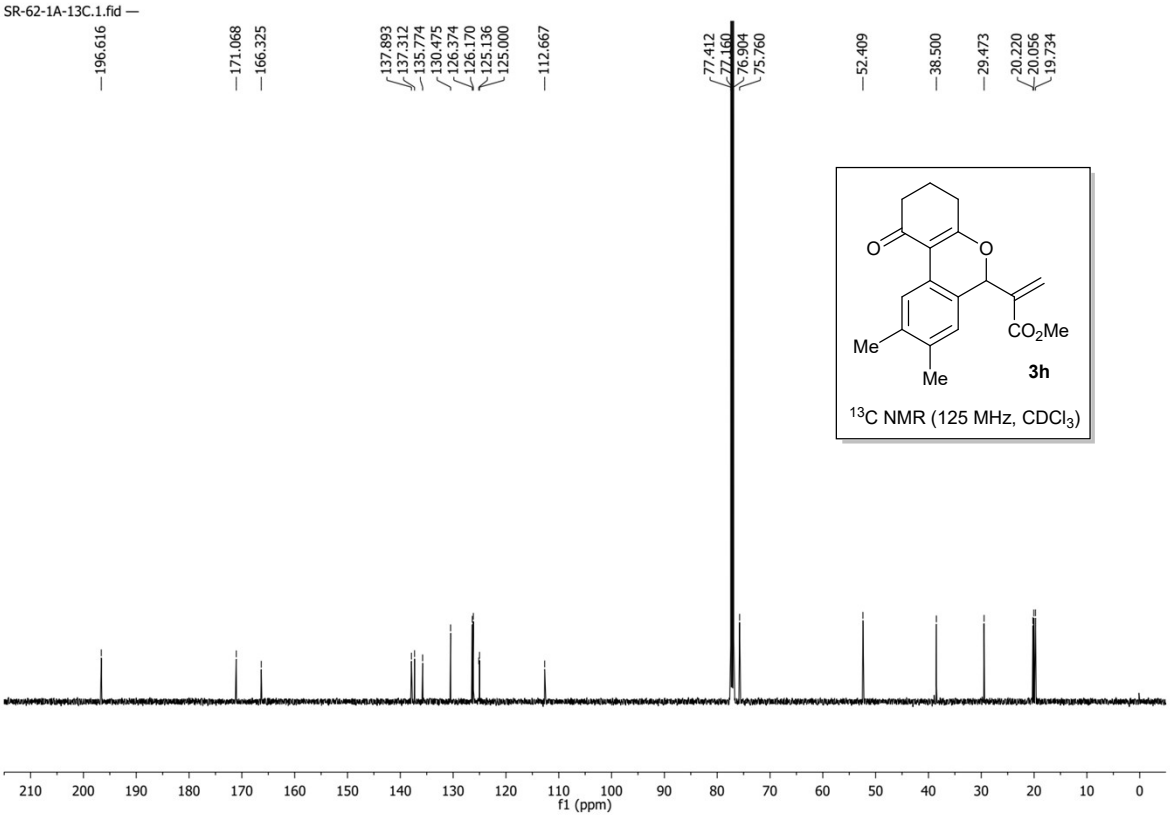

SR-53-1-13C.3.fid
196.258
173.352
166.211
165.893
137.355
132.016
131.006
130.245
129.057
127.361
126.392
125.211
112.180
77.412
77.160
76.904
76.027
61.182
52.532
38.428
29.641
19.986
14.464
O
O
CO2Me
CO2Et
3f
13C NMR (125 MHz, CDCl3)
f1 (ppm)

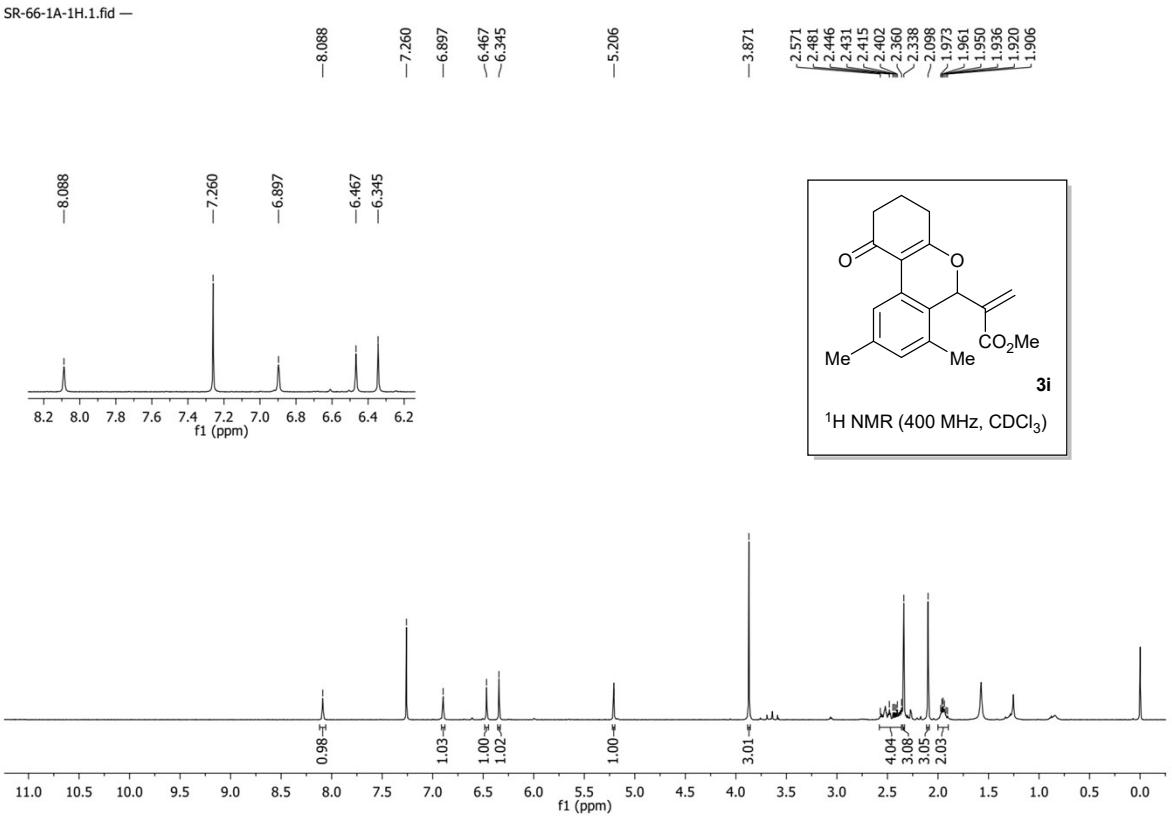

SR-25-1-1H.1.fid
8.783
7.589
7.569
7.506
7.481
7.461
7.260
7.244
7.225
7.077
7.057
6.480
6.297
6.055
5.440
5.329
3.843
3.591
2.701
2.682
2.666
2.588
2.573
2.560
2.547
2.502
2.487
2.467
2.421
2.036
2.021
2.005
1.990
1.967
O
O
CO2Me
F3C
3g
1H NMR (400 MHz, CDCl3)
1.00
0.20
1.20
0.20
1.00
1.01
1.00
0.20
1.01
0.20
3.03
0.60
4.92
2.43
f1 (ppm)

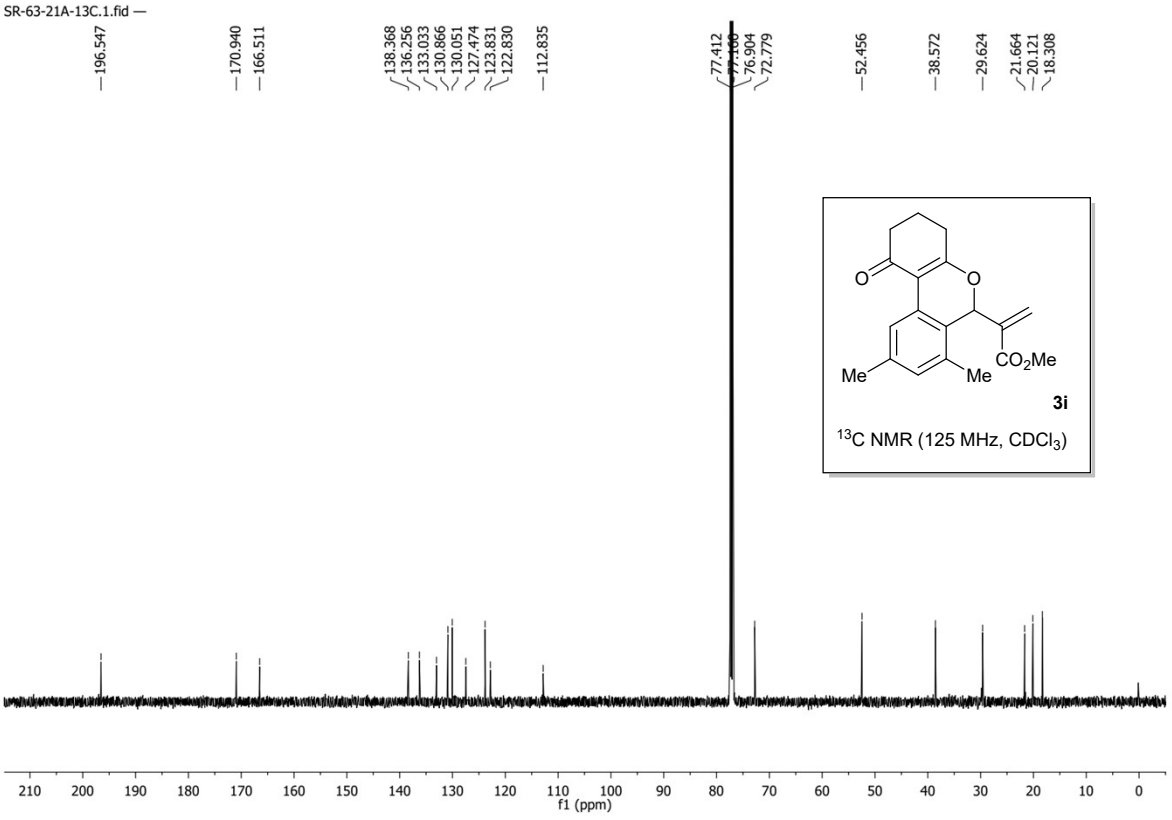

SR-25-1-13C.1.fid
206.319
196.163
172.702
168.159
165.788
138.295
137.192
136.793
131.333
131.078
130.840
130.749
130.117
128.446
127.416
125.508
125.252
124.023
123.995
123.966
123.935
123.085
122.456
122.426
122.394
122.362
111.651
77.416
77.160
76.908
75.786
74.554
52.580
51.970
38.909
38.335
35.532
29.455
20.034
17.490
O
O
F3C
CO2Me
3g
13C NMR (125 MHz, CDCl3)
f1 (ppm)

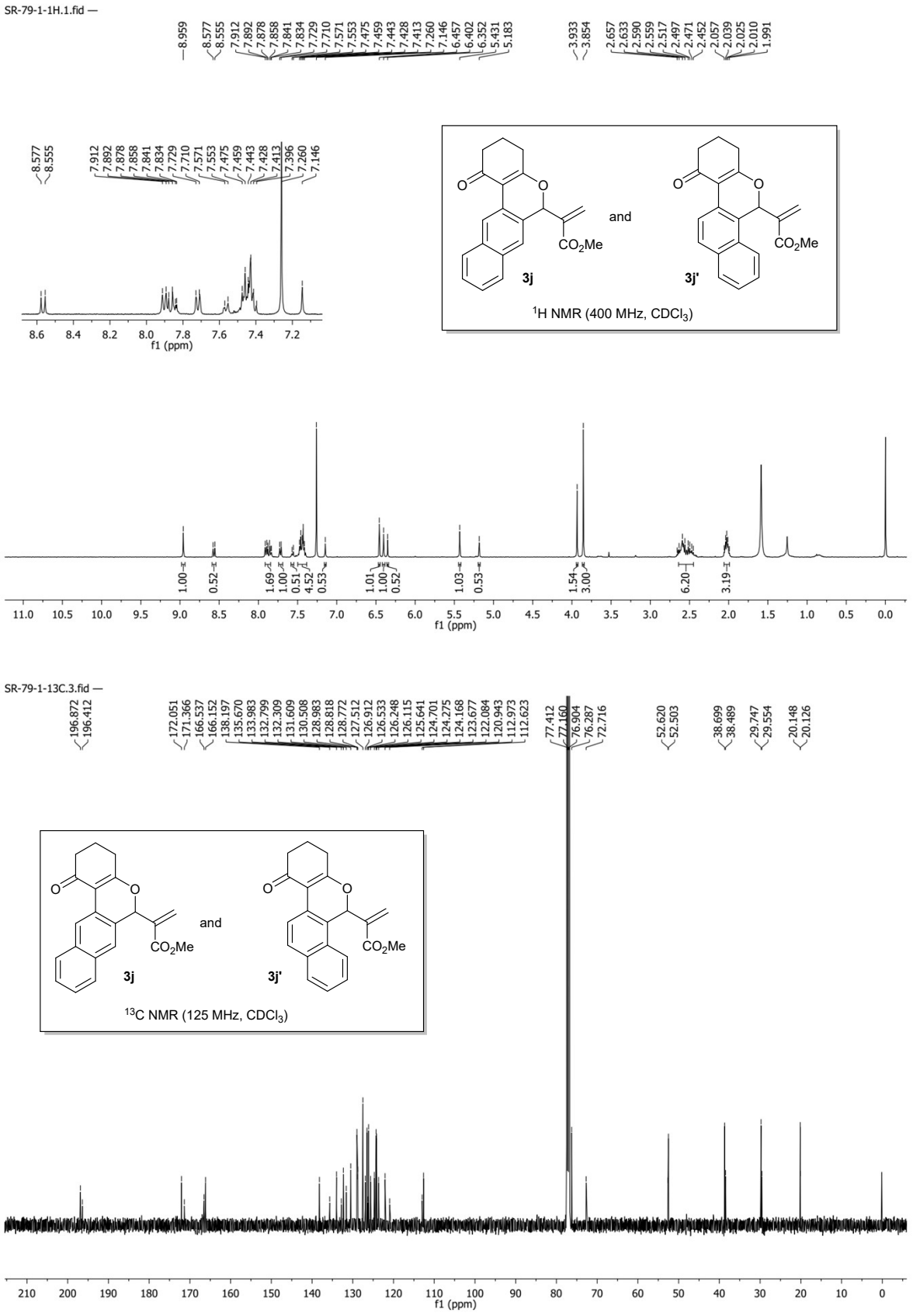

SR-25-1-19F
-62.675
O
O
F3C
CO2Me
3g
19F NMR (565 MHz, CDCl3)

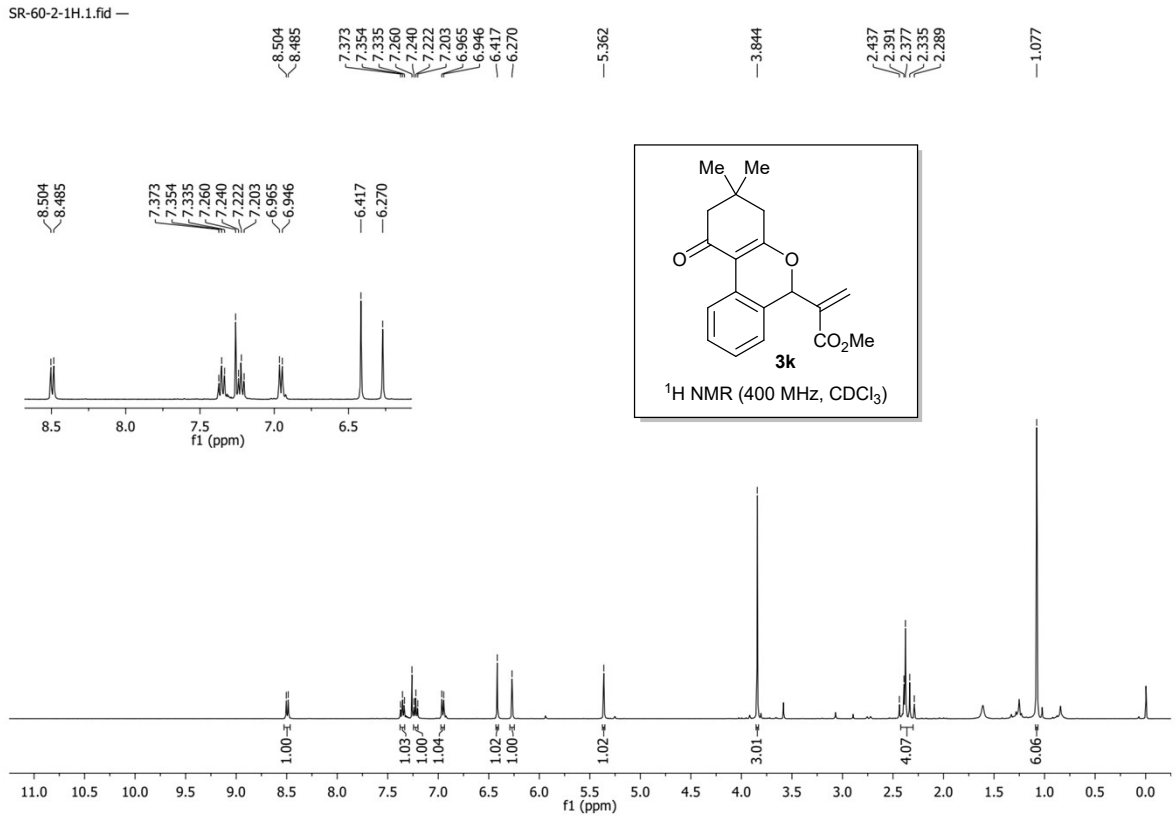

SR-62-1-1H.1.fid
8.186
7.260
6.704
6.408
6.205
5.387
3.839
2.567
2.553
2.540
2.523
2.509
2.496
2.482
2.465
2.458
2.443
2.436
2.416
2.399
2.353
2.280
2.215
1.992
1.979
1.962
1.948
1.935
O
O
Me
Me
CO2Me
3h
1H NMR (400 MHz, CDCl3)
f1 (ppm)
0.97
1.00
1.02
0.98
1.00
3.06
4.00
3.00
3.04
2.03

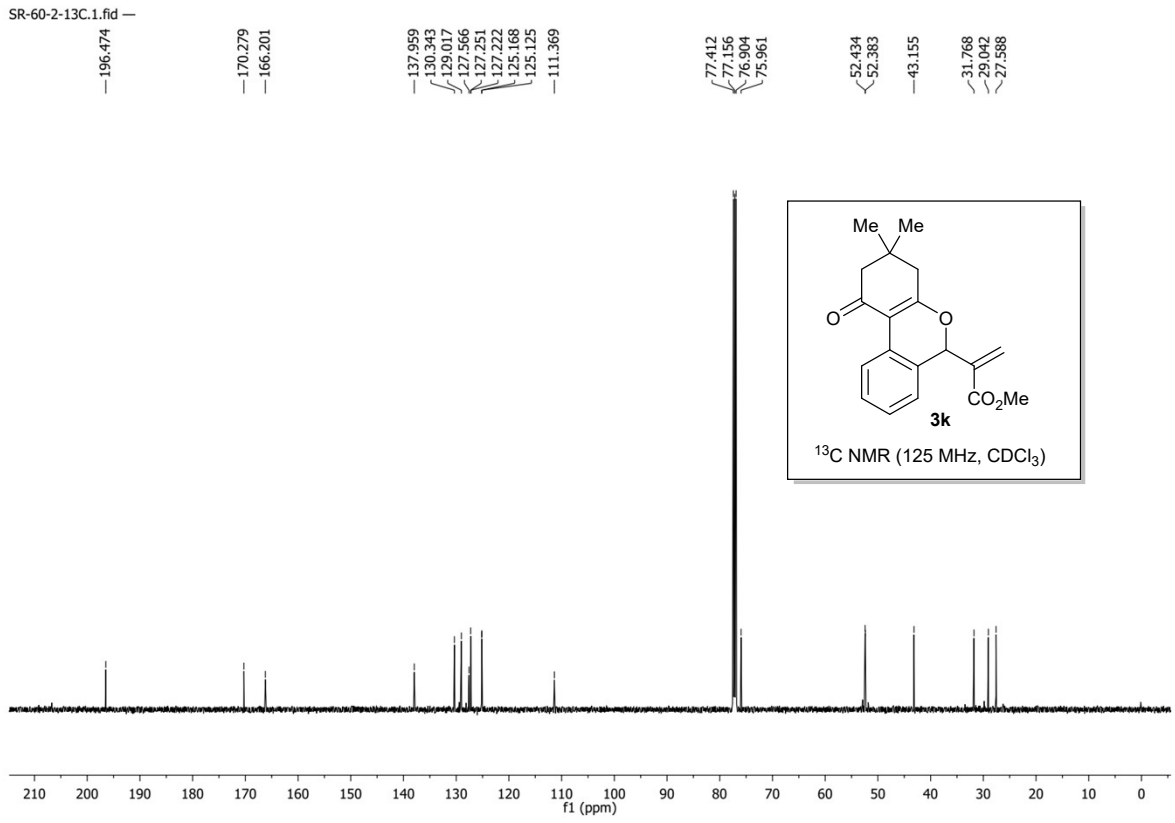

SR-62-1A-13C.1.fid
196.616
171.068
166.325
137.893
137.312
135.774
130.475
126.374
126.170
125.136
125.000
112.667
77.412
77.160
76.904
75.760
52.409
38.500
29.473
20.220
20.056
19.734
O
O
Me
Me
CO2Me
3h
13C NMR (125 MHz, CDCl3)
f1 (ppm)

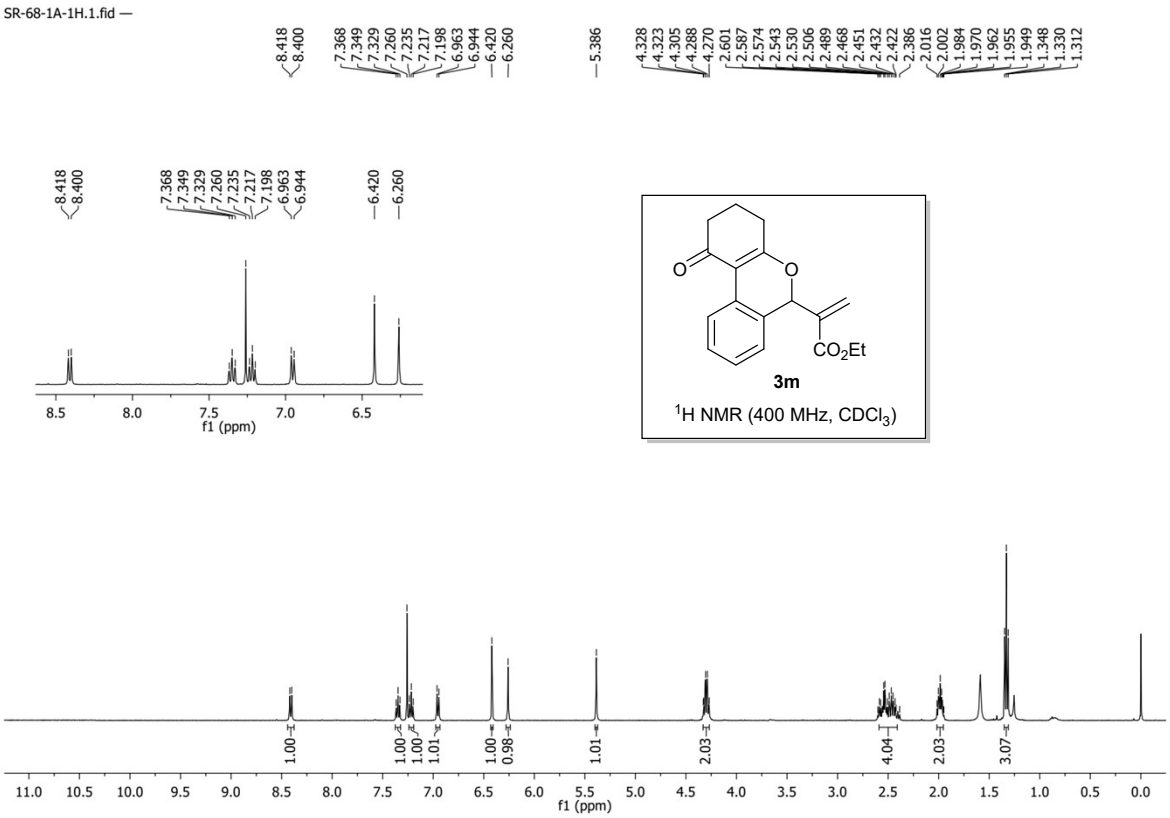

SR-66-1A-1H.1.fid
8.088
7.260
6.897
6.467
6.345
5.206
3.871
2.571
2.481
2.446
2.431
2.415
2.402
2.360
2.338
2.098
1.973
1.961
1.950
1.936
1.920
1.906
f1 (ppm)
O
O
Me
Me
CO2Me
3i
1H NMR (400 MHz, CDCl3)
0.98
1.03
1.00
1.02
1.00
3.01
4.04
3.08
3.05
2.03

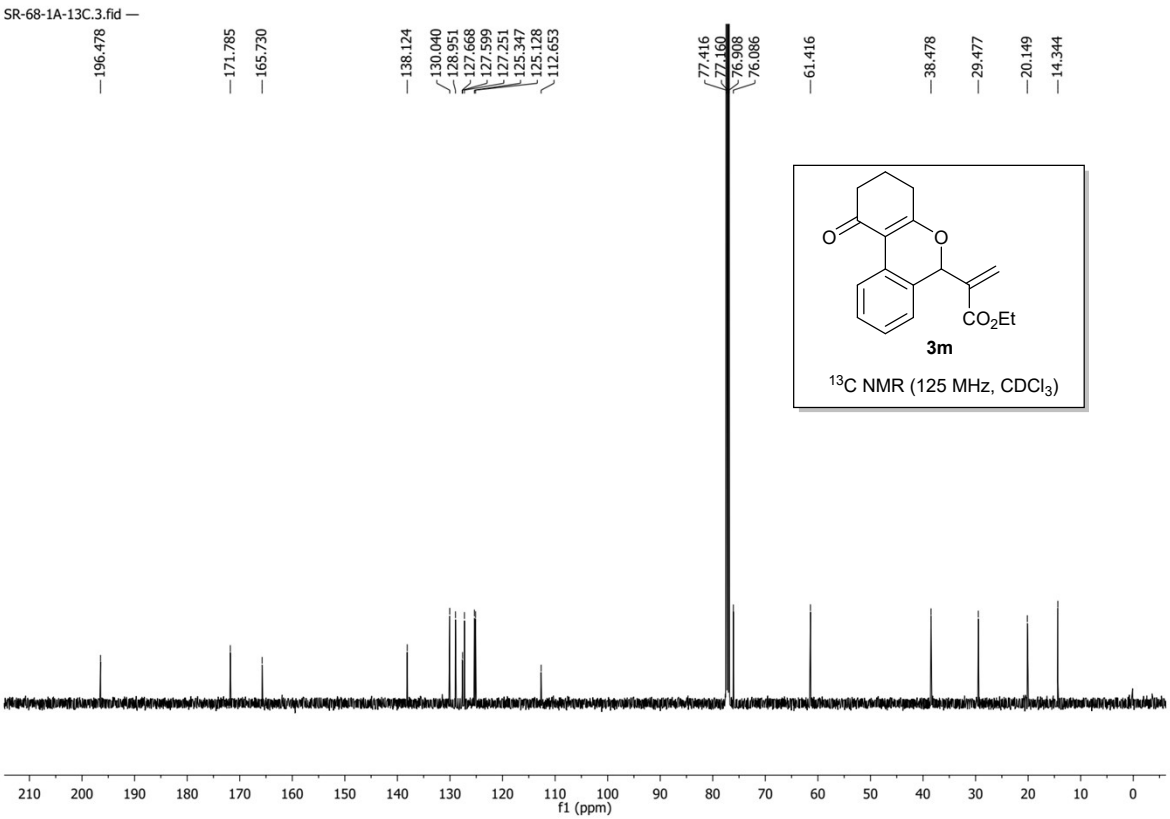

SR-63-21A-13C.1.fid
196.547
170.940
166.511
138.368
136.256
133.033
130.866
130.051
127.474
123.831
122.830
112.835
77.412
77.100
76.904
72.779
52.456
38.572
29.624
21.664
20.121
18.308
f1 (ppm)
O
O
Me
Me
CO2Me
3i
13C NMR (125 MHz, CDCl3)

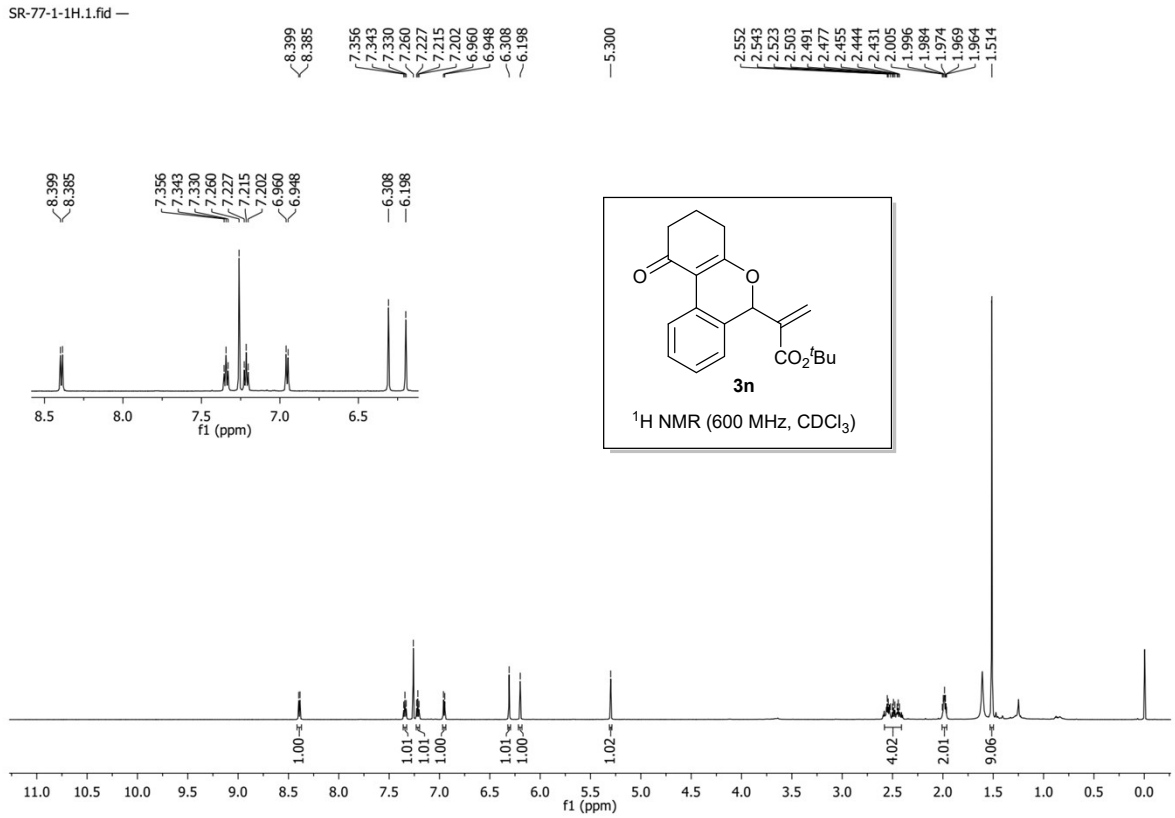

SR-79-1-1H.1.fid
8.959
8.577
8.555
7.912
7.892
7.878
7.858
7.841
7.834
7.729
7.710
7.571
7.553
7.475
7.459
7.443
7.428
7.413
7.260
7.146
6.457
6.402
6.352
5.431
5.183
3.933
3.854
2.657
2.633
2.590
2.559
2.517
2.497
2.471
2.452
2.057
2.039
2.025
2.010
1.991
f1 (ppm)
and
CO2Me
3j
3j'
1H NMR (400 MHz, CDCl3)
1.00
0.52
1.69
1.00
0.51
4.52
0.53
1.01
1.00
0.52
1.03
0.53
1.54
3.00
6.20
3.19
SR-79-1-13C.3.fid
196.872
196.412
172.051
171.366
166.537
166.152
138.197
135.670
133.983
132.799
132.309
131.609
130.508
128.983
128.818
128.772
127.512
126.912
126.533
126.248
126.115
125.641
124.701
124.275
124.168
123.677
122.084
120.943
112.973
112.623
77.412
77.160
76.904
76.287
72.716
52.620
52.503
38.699
38.489
29.747
29.554
20.148
20.126
3j
3j'
13C NMR (125 MHz, CDCl3)

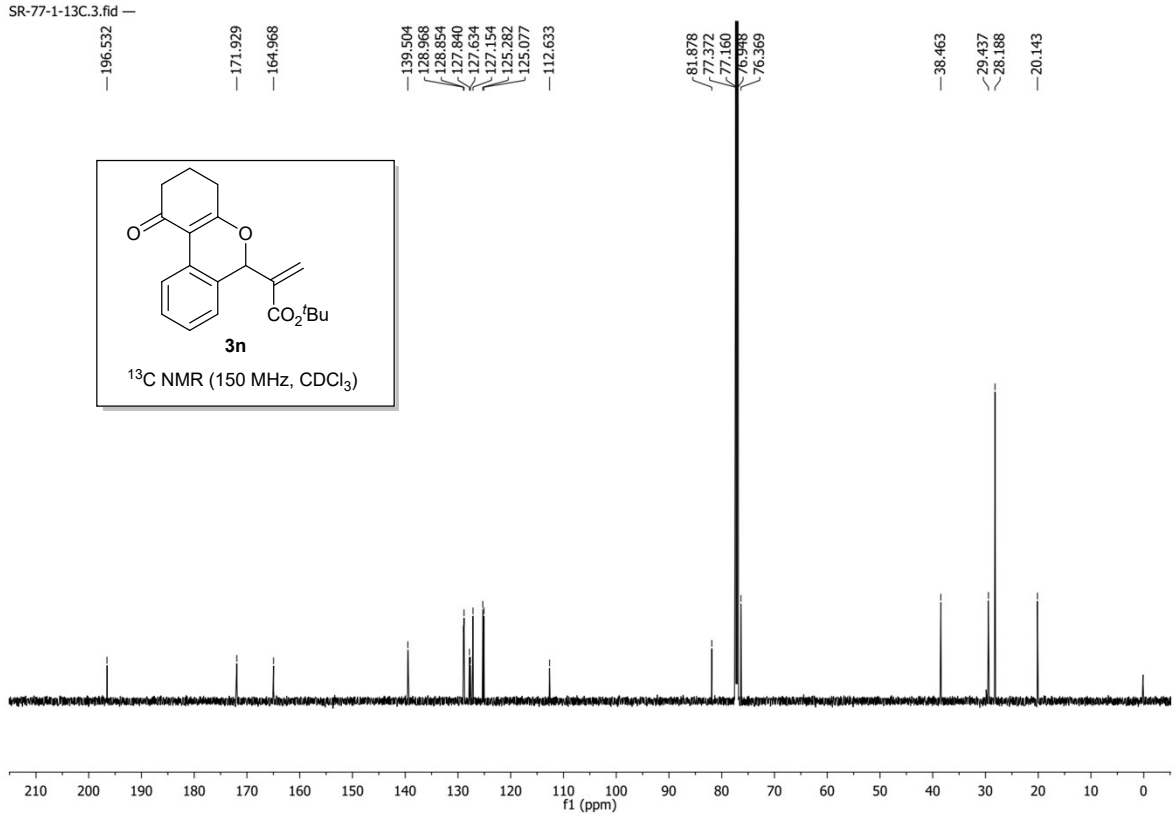

SR-60-2-1H.1.fid
8.504
8.485
7.373
7.354
7.335
7.260
7.240
7.222
7.203
6.965
6.946
6.417
6.270
5.362
3.844
2.437
2.391
2.377
2.335
2.289
1.077
Me Me
O
O
CO2Me
3k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

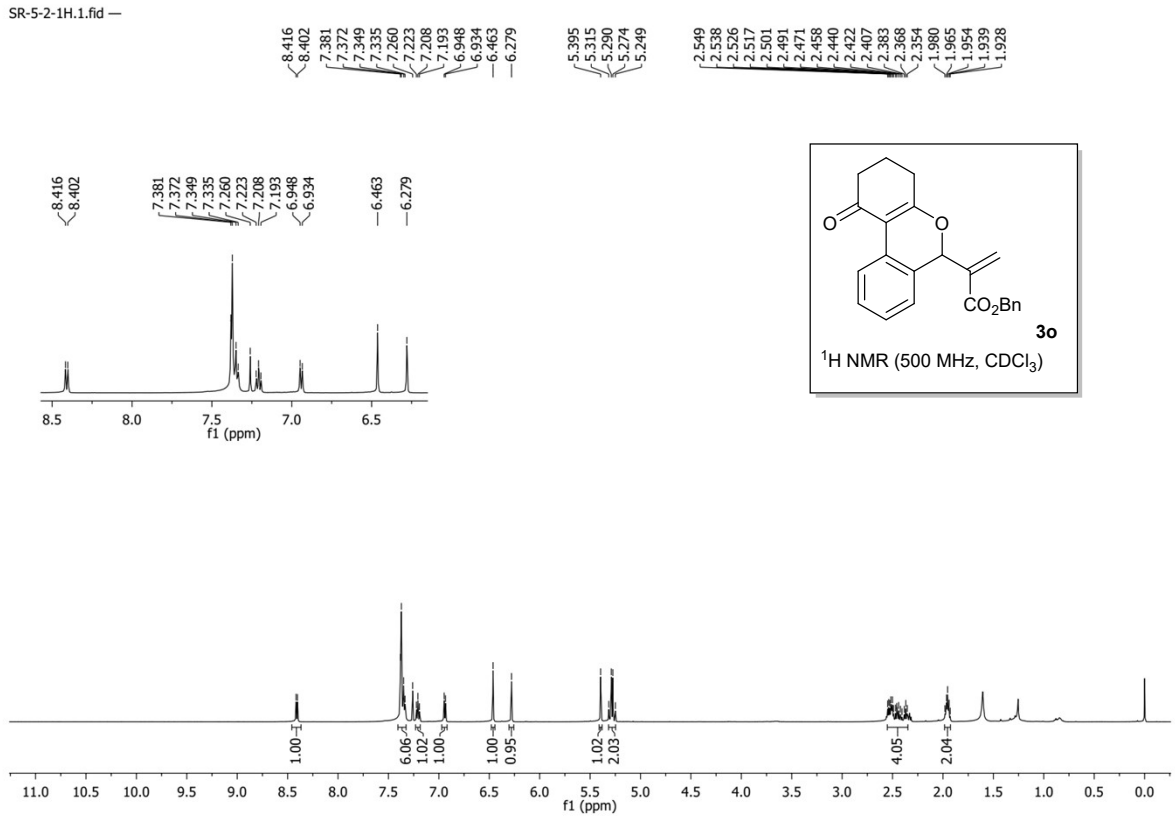

SR-60-2-13C.1.fid
196.474
170.279
166.201
137.959
130.343
129.017
127.566
127.251
127.222
125.168
125.125
111.369
77.412
77.156
76.904
75.961
52.434
52.383
43.155
31.768
29.042
27.588
Me Me
O
O
CO2Me
3k
13C NMR (125 MHz, CDCl3)
f1 (ppm)

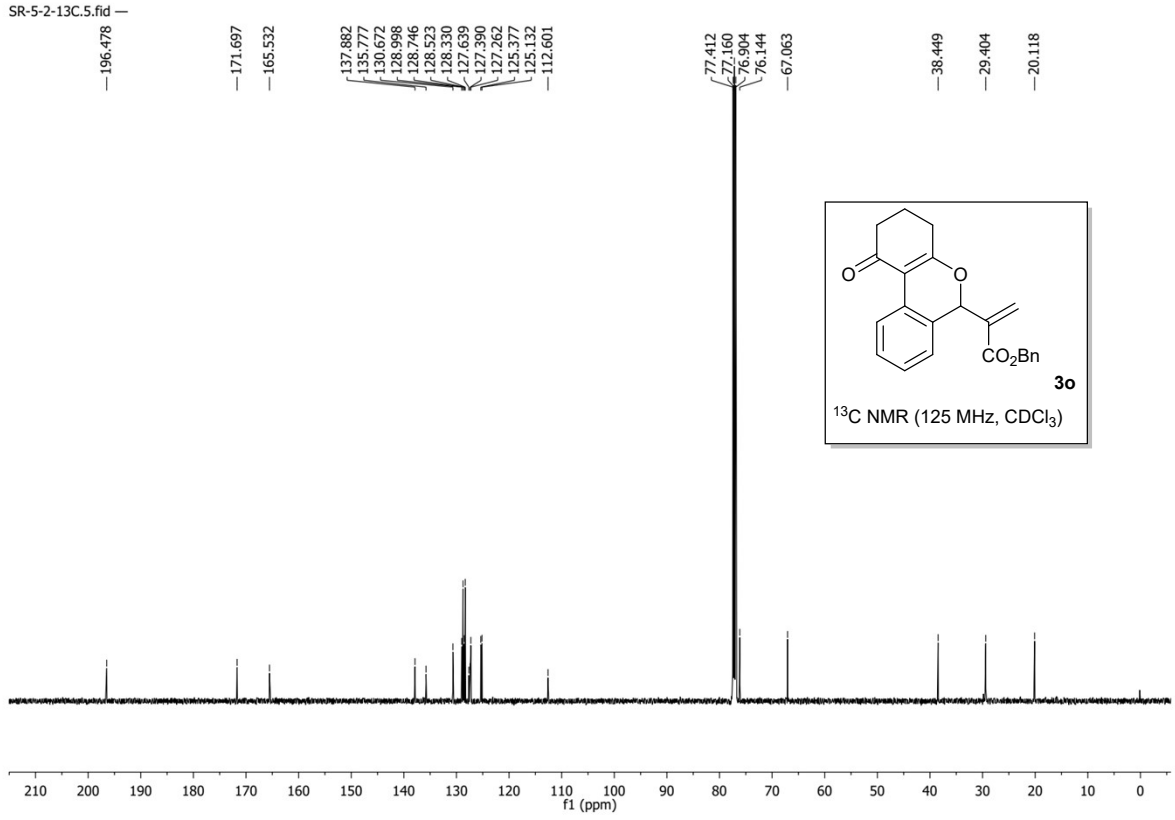

SR-68-1A-1H.1.fid
8.418
8.400
7.368
7.349
7.329
7.260
7.235
7.217
7.198
6.963
6.944
6.420
6.260
5.386
4.328
4.323
4.305
4.288
4.270
2.601
2.587
2.574
2.543
2.530
2.506
2.489
2.468
2.451
2.432
2.422
2.386
2.016
2.002
1.984
1.970
1.962
1.955
1.949
1.348
1.330
1.312
f1 (ppm)
1.00
1.00
1.00
1.01
1.00
0.98
1.01
2.03
4.04
2.03
3.07
3m
$^1$H NMR (400 MHz, $CDCl_3$)

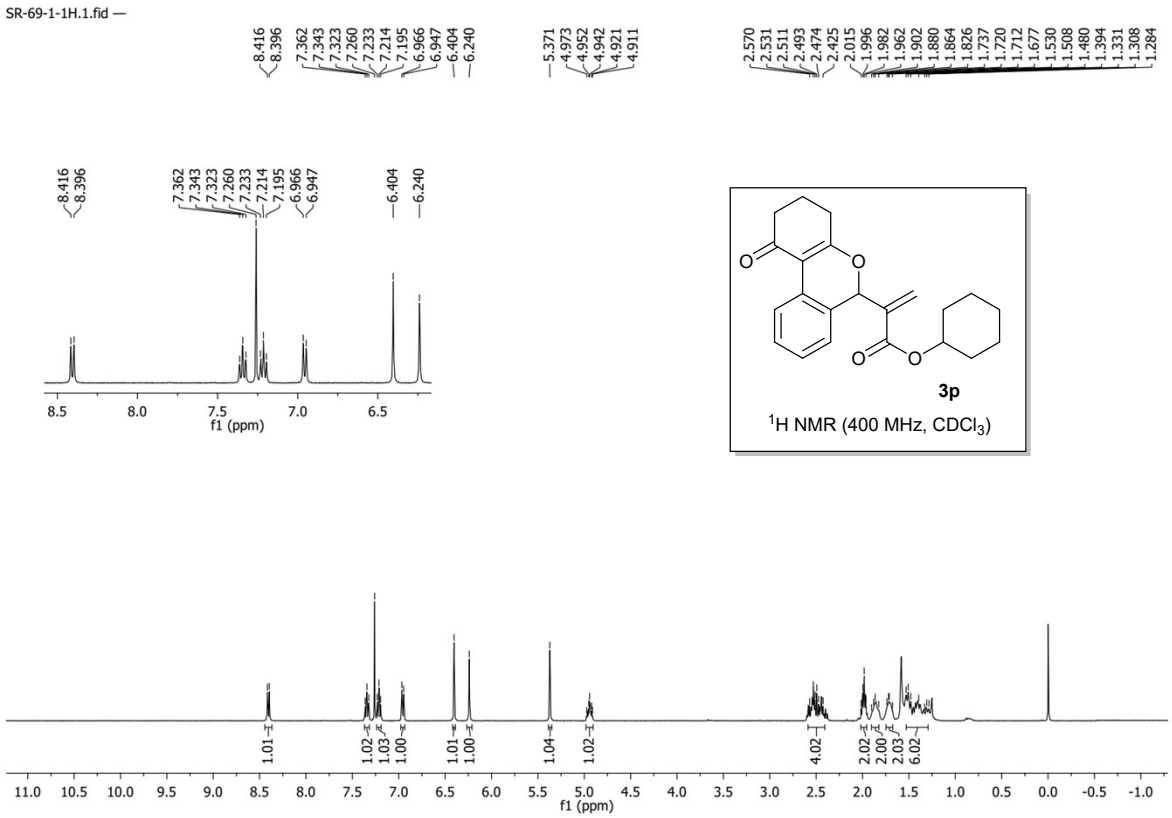

SR-68-1A-13C.3.fid
196.478
171.785
165.730
138.124
130.040
128.951
127.668
127.599
127.251
125.347
125.128
112.653
77.416
77.160
76.908
76.086
61.416
38.478
29.477
20.149
14.344
f1 (ppm)
3m
$^{13}$C NMR (125 MHz, $CDCl_3$)

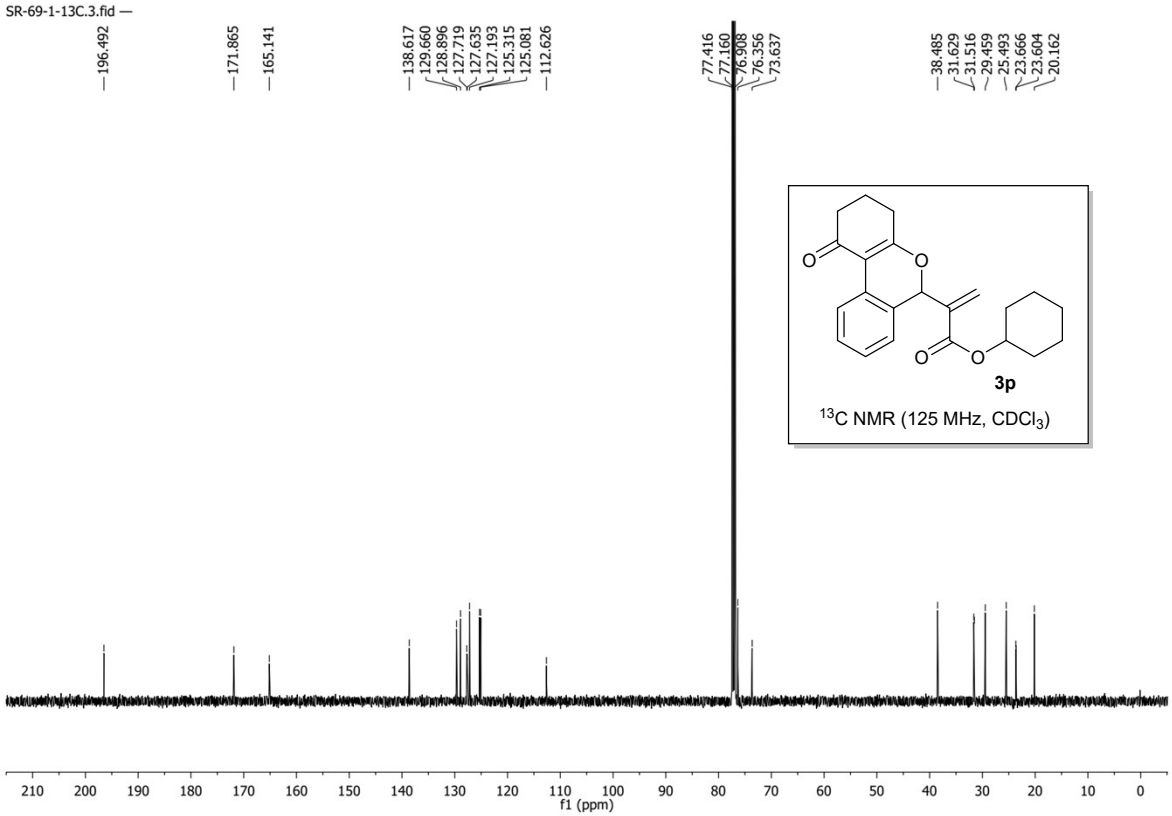

SR-77-1-1H.1.fid
8.399
8.385
7.356
7.343
7.330
7.260
7.227
7.215
7.202
6.960
6.948
6.308
6.198
5.300
2.552
2.543
2.523
2.503
2.491
2.477
2.455
2.444
2.431
2.005
1.996
1.984
1.974
1.969
1.964
1.514
f1 (ppm)
3n
1H NMR (600 MHz, CDCl3)
1.00
1.01
1.01
1.00
1.01
1.00
1.02
4.02
2.01
9.06

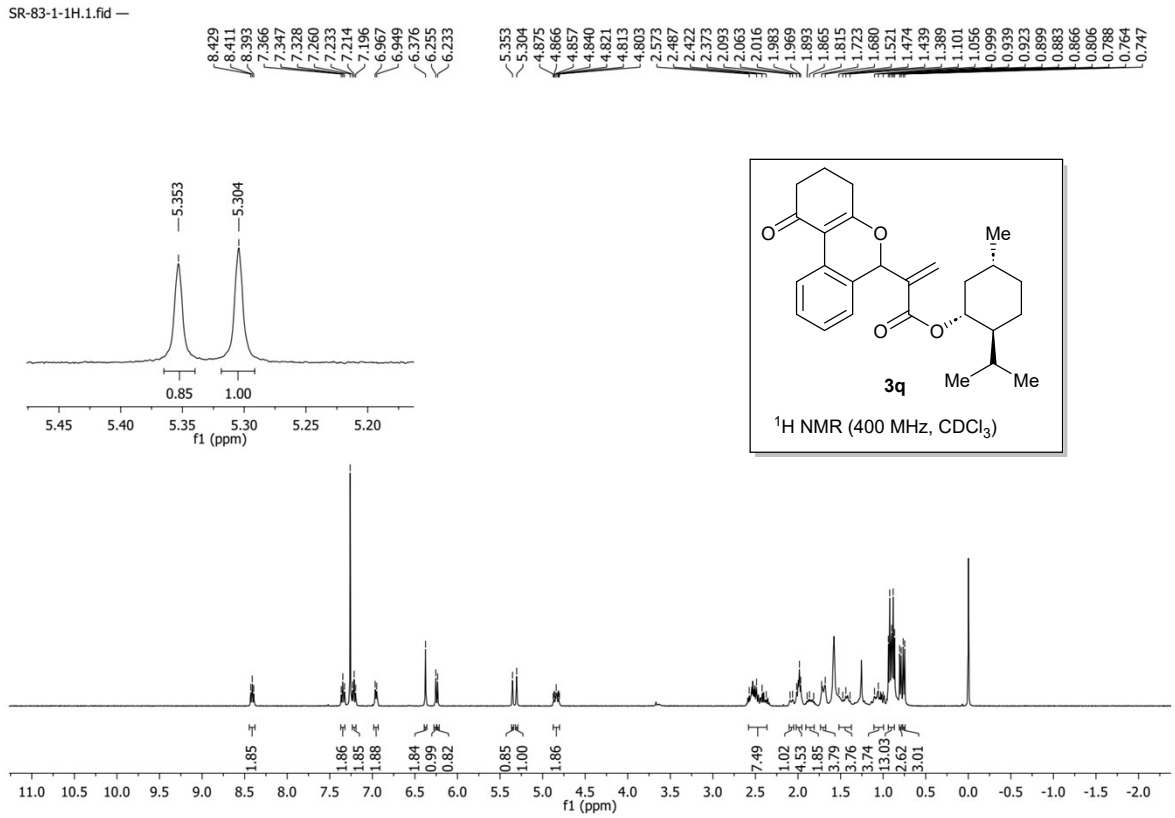

SR-77-1-13C.3.fid
196.532
171.929
164.968
139.504
128.968
128.854
127.840
127.634
127.154
125.282
125.077
112.633
81.878
77.372
77.160
76.948
76.369
38.463
29.437
28.188
20.143
f1 (ppm)
3n
13C NMR (150 MHz, CDCl3)

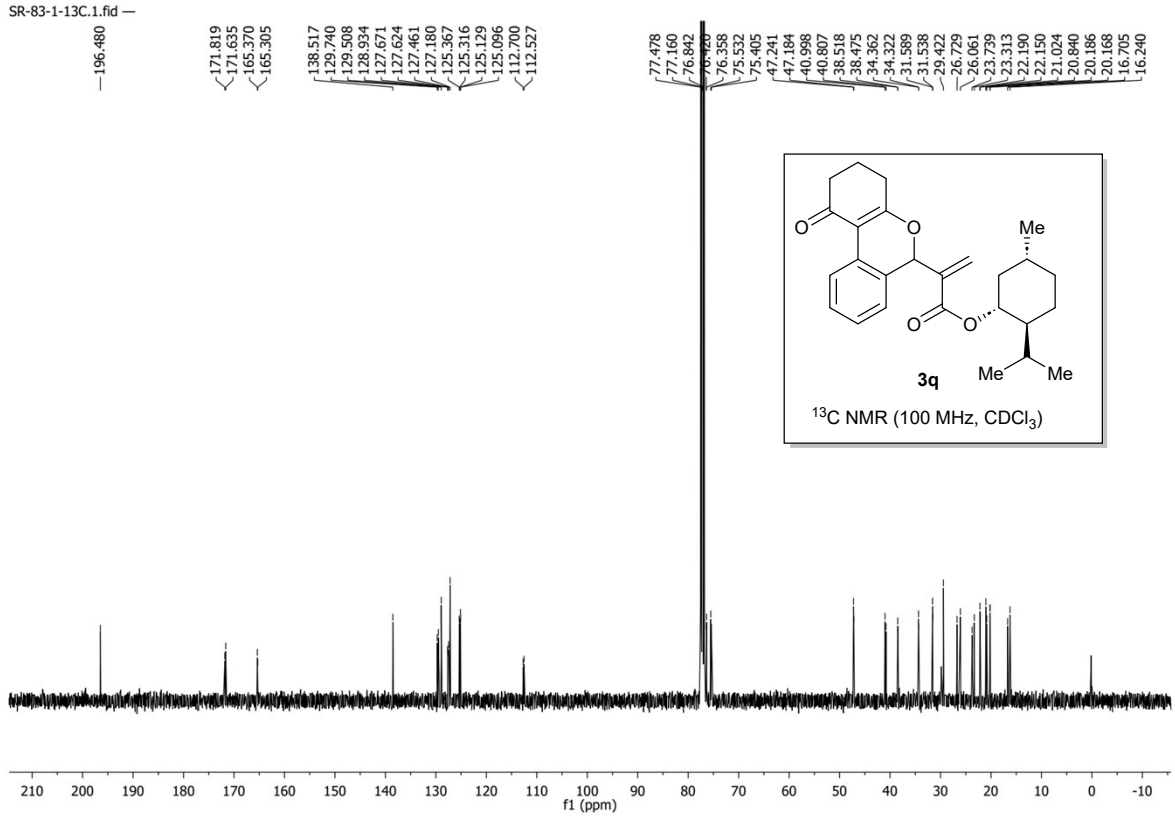

SR-5-2-1H.1.fid
8.416
8.402
7.381
7.372
7.349
7.335
7.260
7.223
7.208
7.193
6.948
6.934
6.463
6.279
5.395
5.315
5.290
5.274
5.249
2.549
2.538
2.526
2.517
2.501
2.491
2.471
2.458
2.440
2.422
2.407
2.383
2.368
2.354
1.980
1.965
1.954
1.939
1.928
f1 (ppm)
O
O
CO2Bn
3o
1H NMR (500 MHz, CDCl3)
1.00
6.06
1.02
1.00
1.00
0.95
1.02
2.03
4.05
2.04

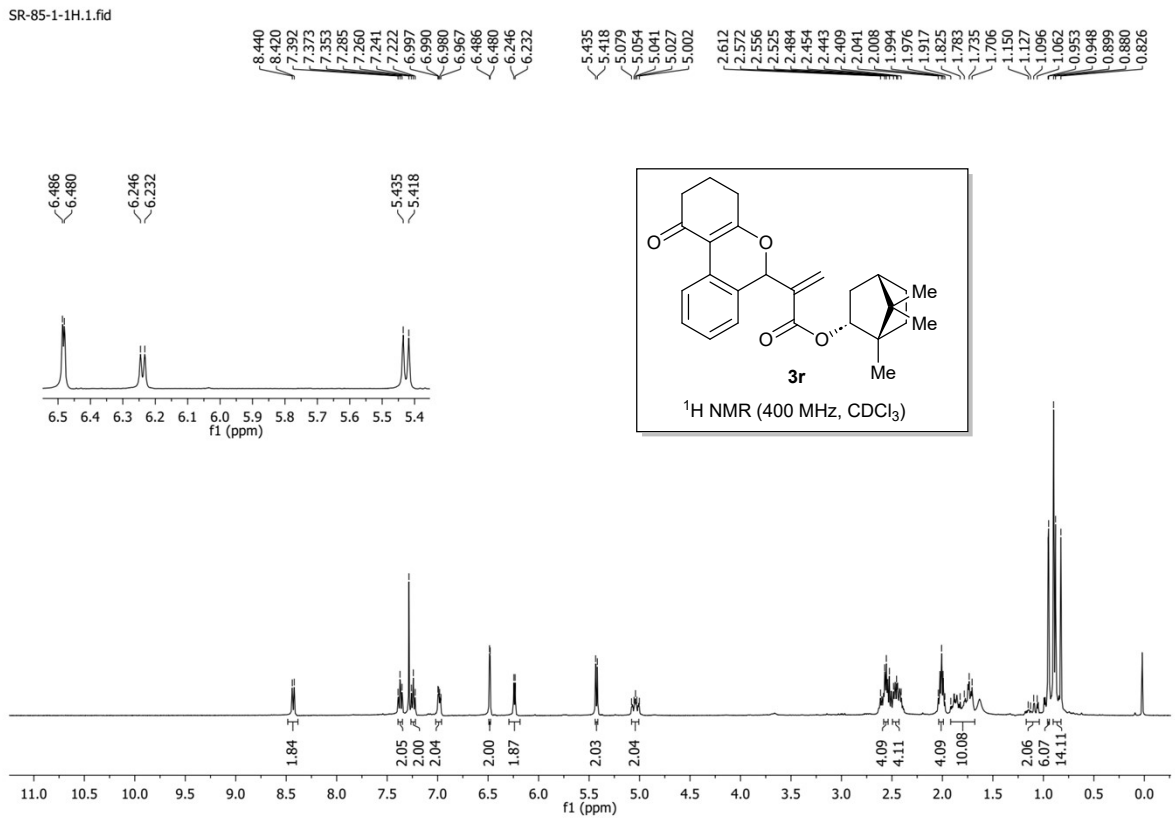

SR-5-2-13C.5.fid
196.478
171.697
165.532
137.882
135.777
130.672
128.998
128.746
128.523
128.330
127.639
127.390
127.262
125.377
125.132
112.601
77.412
77.160
76.904
76.144
67.063
38.449
29.404
20.118
f1 (ppm)
O
O
CO2Bn
3o
13C NMR (125 MHz, CDCl3)

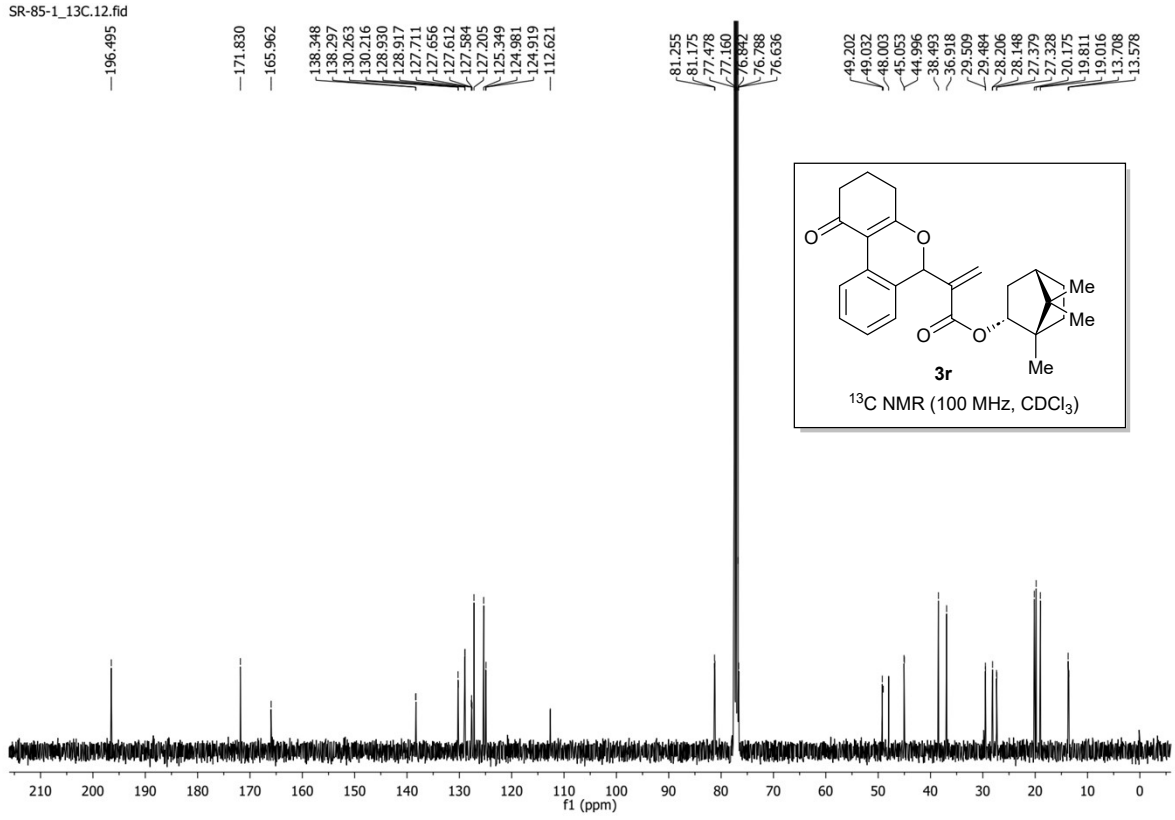

SR-69-1-1H.1.fid
8.416
8.396
7.362
7.343
7.323
7.260
7.233
7.214
7.195
6.966
6.947
6.404
6.240
5.371
4.973
4.952
4.942
4.921
4.911
2.570
2.531
2.511
2.493
2.474
2.425
2.015
1.996
1.982
1.962
1.902
1.880
1.864
1.826
1.737
1.720
1.712
1.677
1.530
1.508
1.480
1.394
1.331
1.308
1.284
f1 (ppm)
1.01
1.02
1.03
1.00
1.01
1.00
1.04
1.02
4.02
2.02
2.00
2.03
6.02
3p
1H NMR (400 MHz, CDCl3)


SR-69-1-13C.3.fid
196.492
171.865
165.141
138.617
129.660
128.896
127.719
127.635
127.193
125.315
125.081
112.626
77.416
77.160
76.908
76.356
73.637
38.485
31.629
31.516
29.459
25.493
23.666
23.604
20.162
f1 (ppm)
3p
13C NMR (125 MHz, CDCl3)

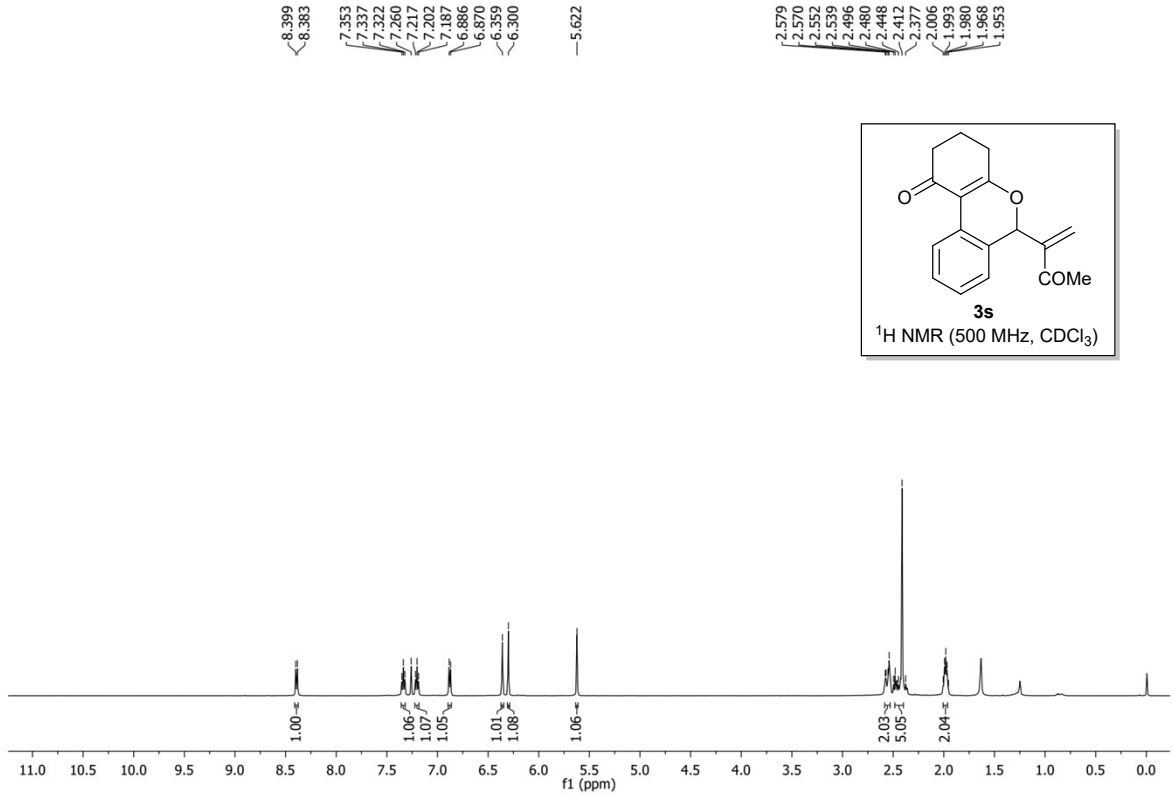

SR-83-1-1H.1.fid
8.429 8.411 8.393 7.366 7.347 7.328 7.260 7.233 7.214 7.196 6.967 6.949 6.376 6.255 6.233
5.353 5.304 4.875 4.866 4.857 4.840 4.821 4.813 4.803 2.573 2.487 2.422 2.373 2.093 2.063 2.016 1.983 1.969 1.893 1.865 1.815 1.723 1.680 1.521 1.474 1.439 1.389 1.101 1.056 0.999 0.939 0.923 0.899 0.883 0.866 0.806 0.788 0.764 0.747
5.353
5.304
0.85
1.00
5.45 5.40 5.35 5.30 5.25 5.20
f1 (ppm)
O
O
O
O
Me
Me
Me
3q
1H NMR (400 MHz, CDCl3)
1.85 1.86 1.85 1.88 1.84 0.99 0.82 0.85 1.00 1.86 7.49 1.02 4.53 1.85 3.79 3.76 3.74 13.03 2.62 3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


SR-83-1-13C.1.fid
196.480
171.819 171.635 165.370 165.305
138.517 129.740 129.508 128.934 127.671 127.624 127.461 127.180 125.367 125.316 125.129 125.096 112.700 112.527
77.478 77.160 76.842 76.358 75.532 75.405 47.241 47.184 40.998 40.807 38.518 38.475 34.362 34.322 31.589 31.538 29.422 26.729 26.061 23.739 23.313 22.190 22.150 21.024 20.840 20.186 20.168 16.705 16.240
O
O
O
O
Me
Me
Me
3q
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SR-85-1-1H.1.fid
3r
$^1$H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


SR-85-1_13C.12.fid
3r
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

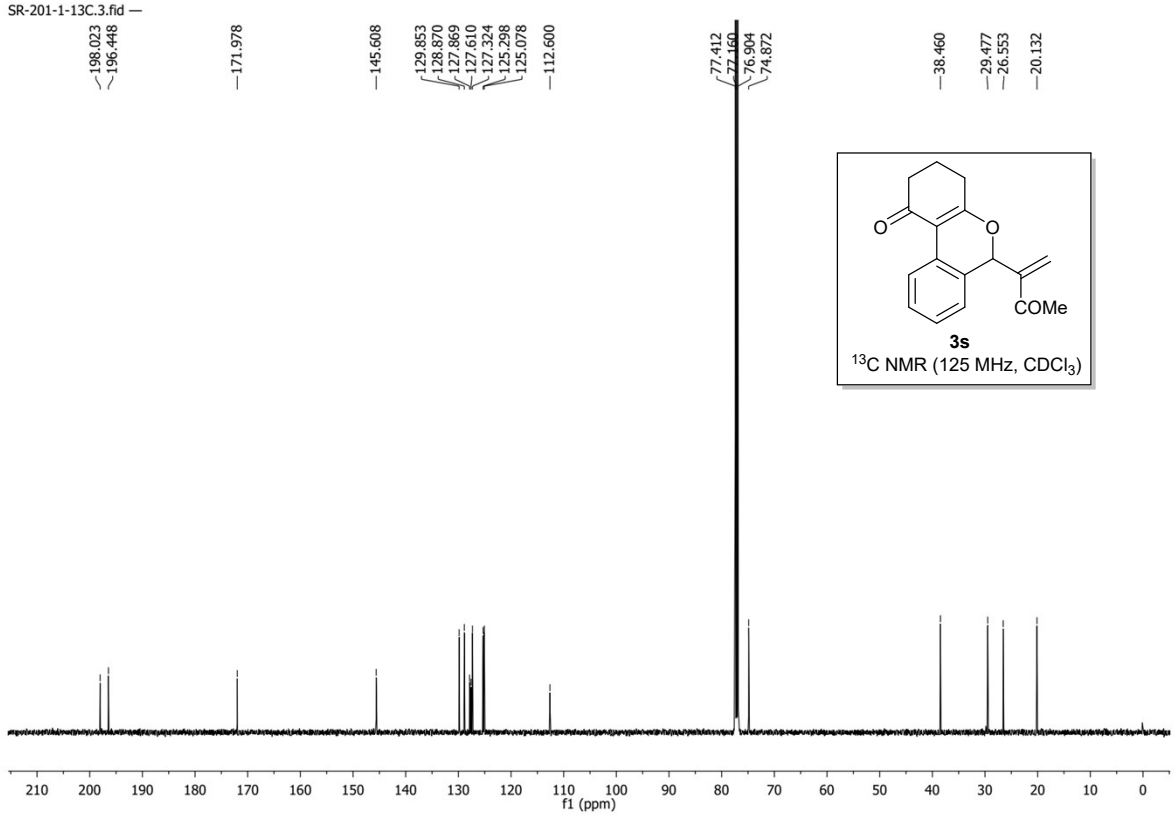
SR-201-1-1H.1.fid —




**3s**

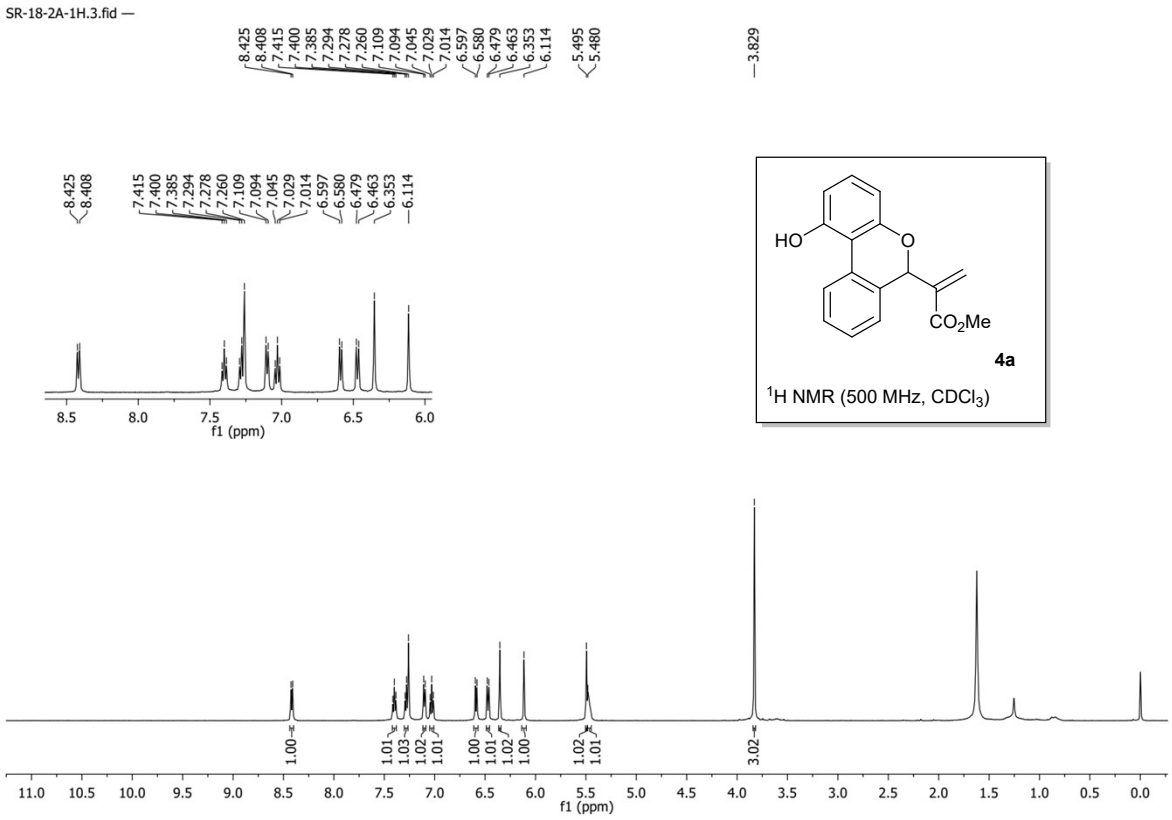
$^{1}$H NMR (500 MHz, $CDCl_3$)

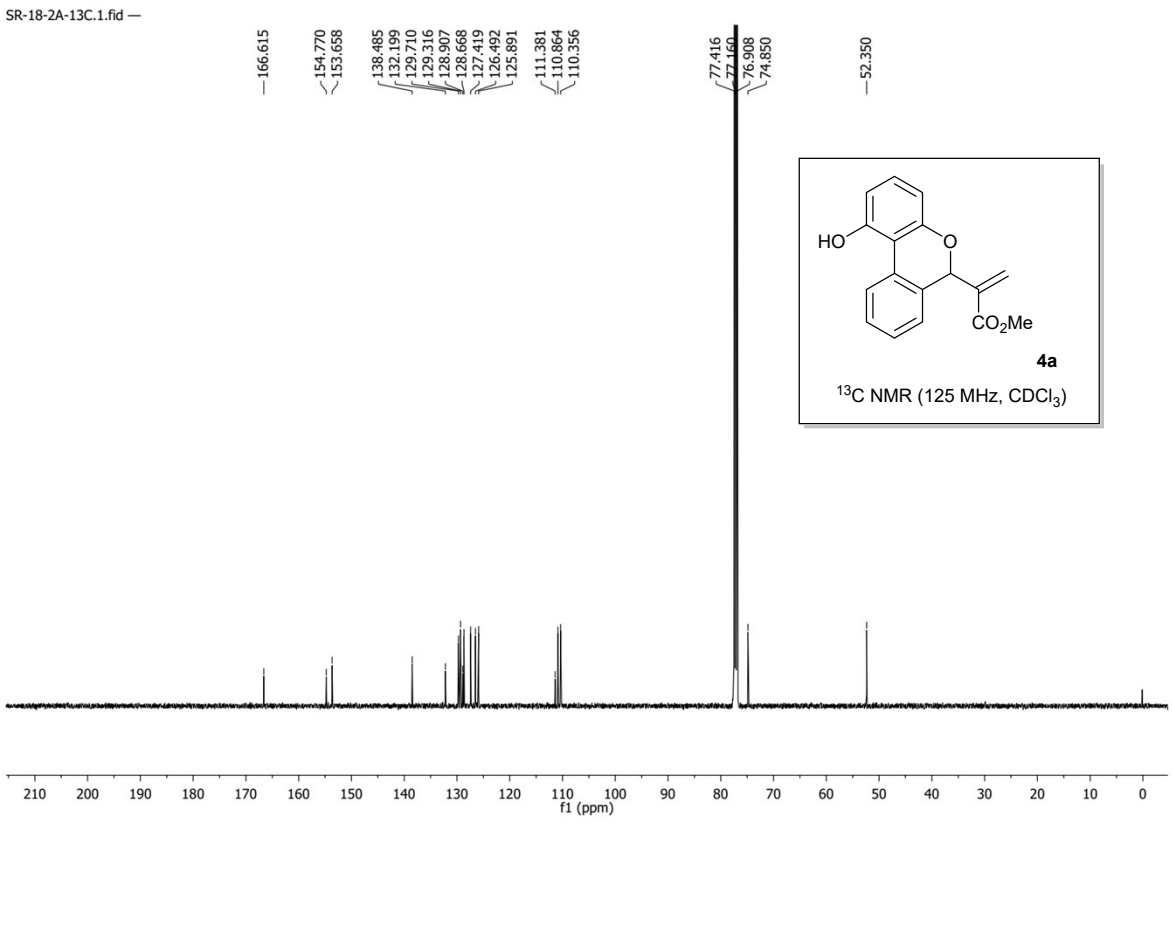
SR-201-1-13C.3.fid —




**3s**

$^{13}$C NMR (125 MHz, $CDCl_3$)


SR-18-2A-1H.fid
8.425
8.408
7.415
7.400
7.385
7.294
7.278
7.260
7.109
7.094
7.045
7.029
7.014
6.597
6.580
6.479
6.463
6.353
6.114
5.495
5.480
3.829
HO
O
CO2Me
4a
1H NMR (500 MHz, CDCl3)
f1 (ppm)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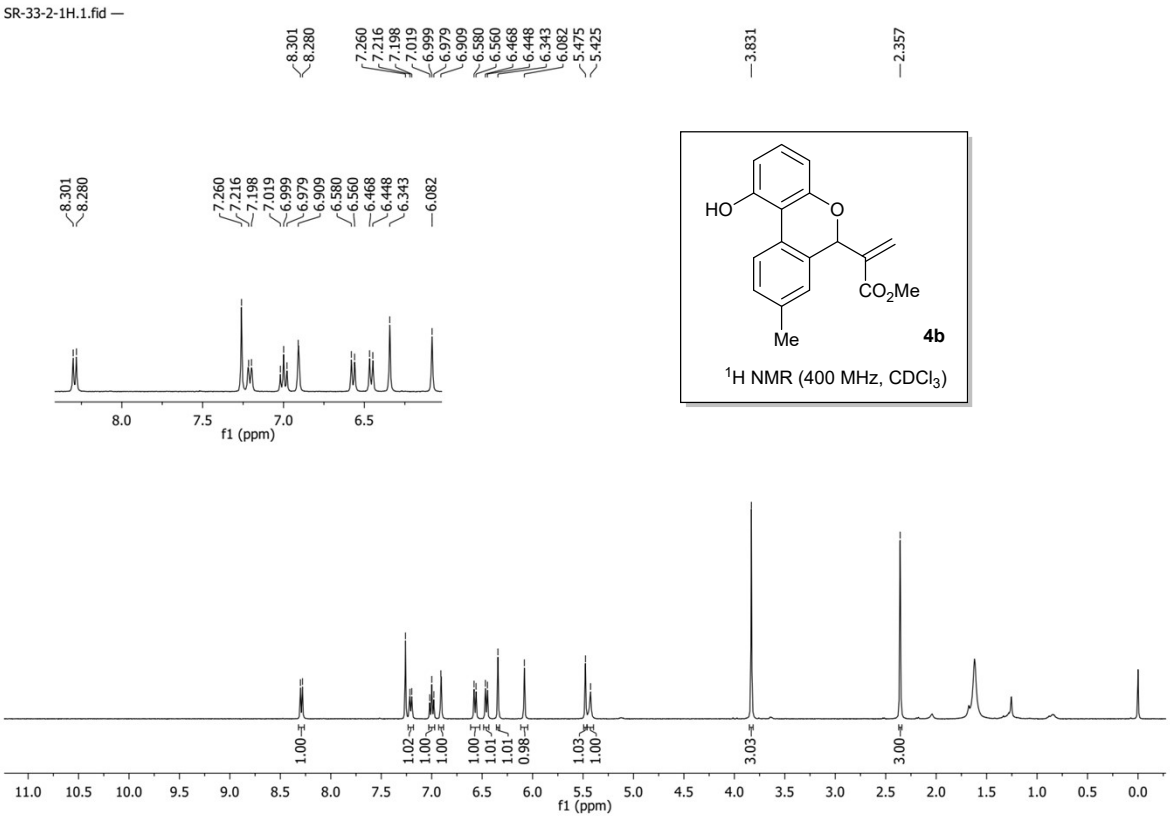
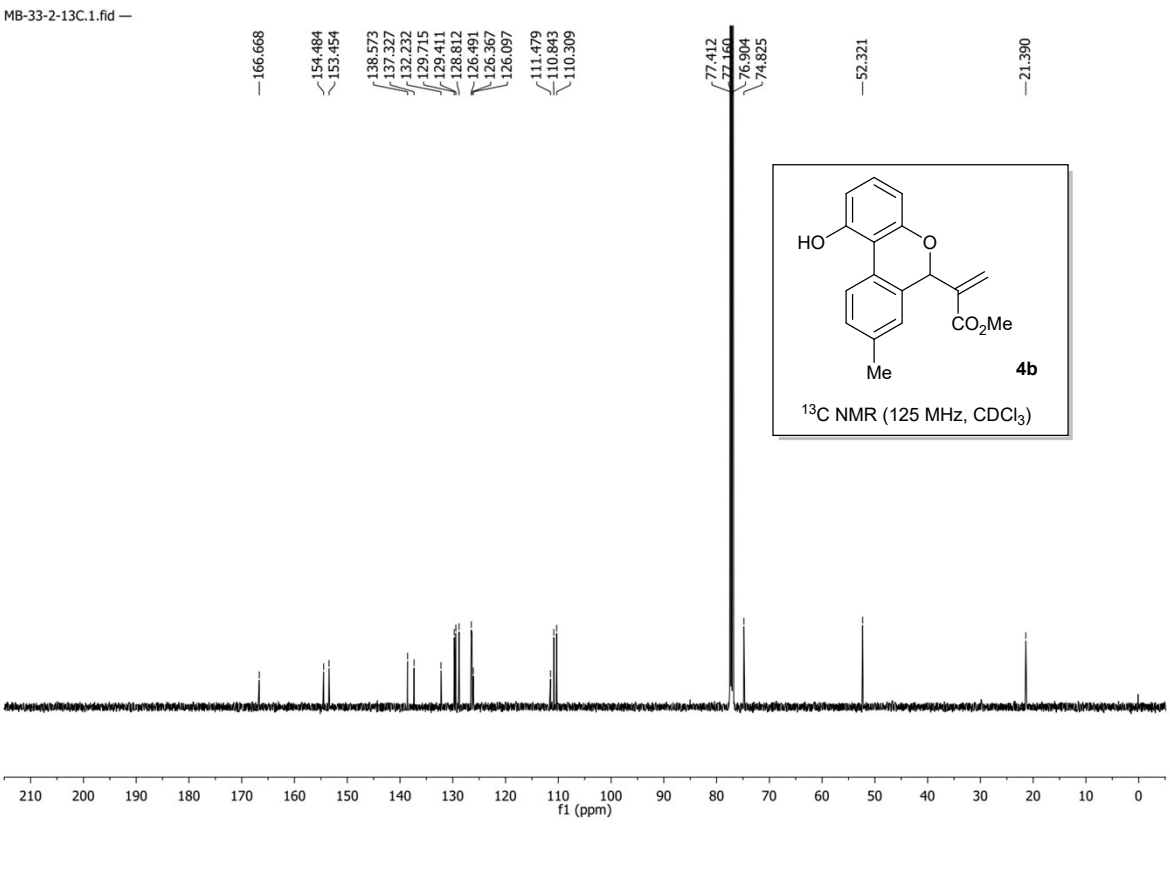
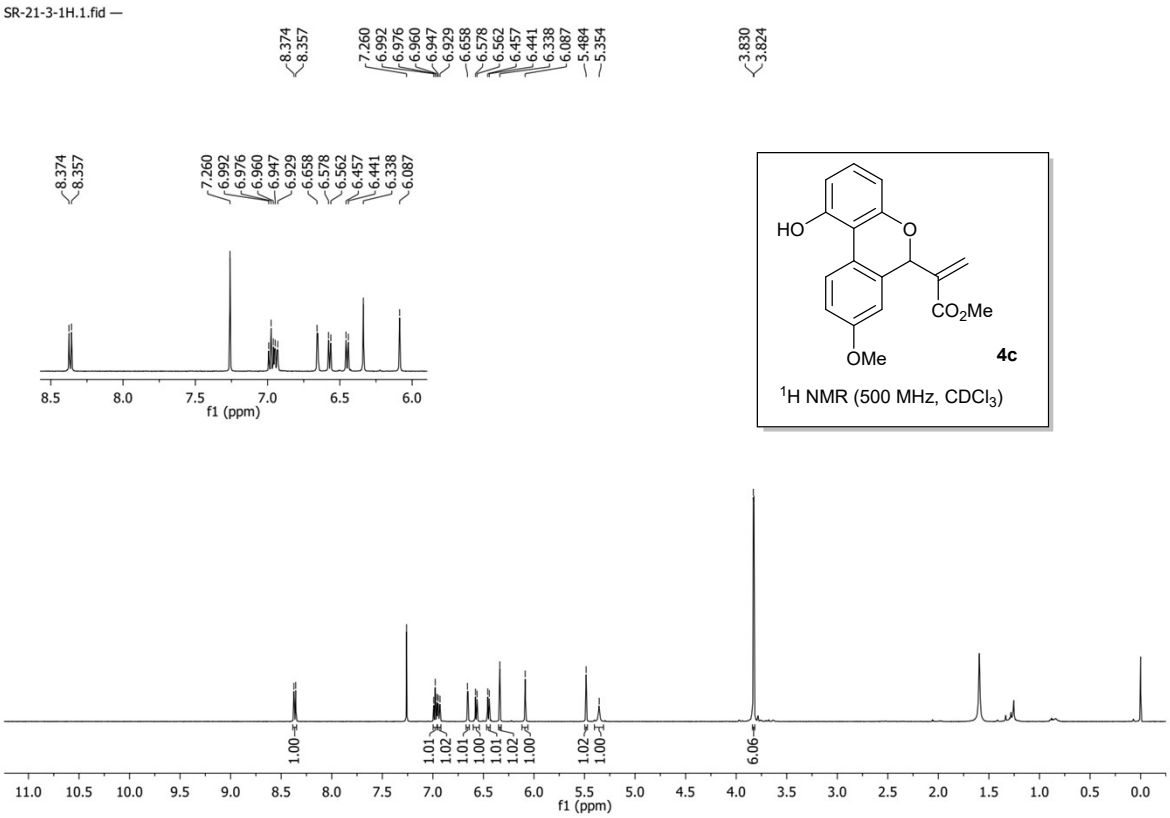
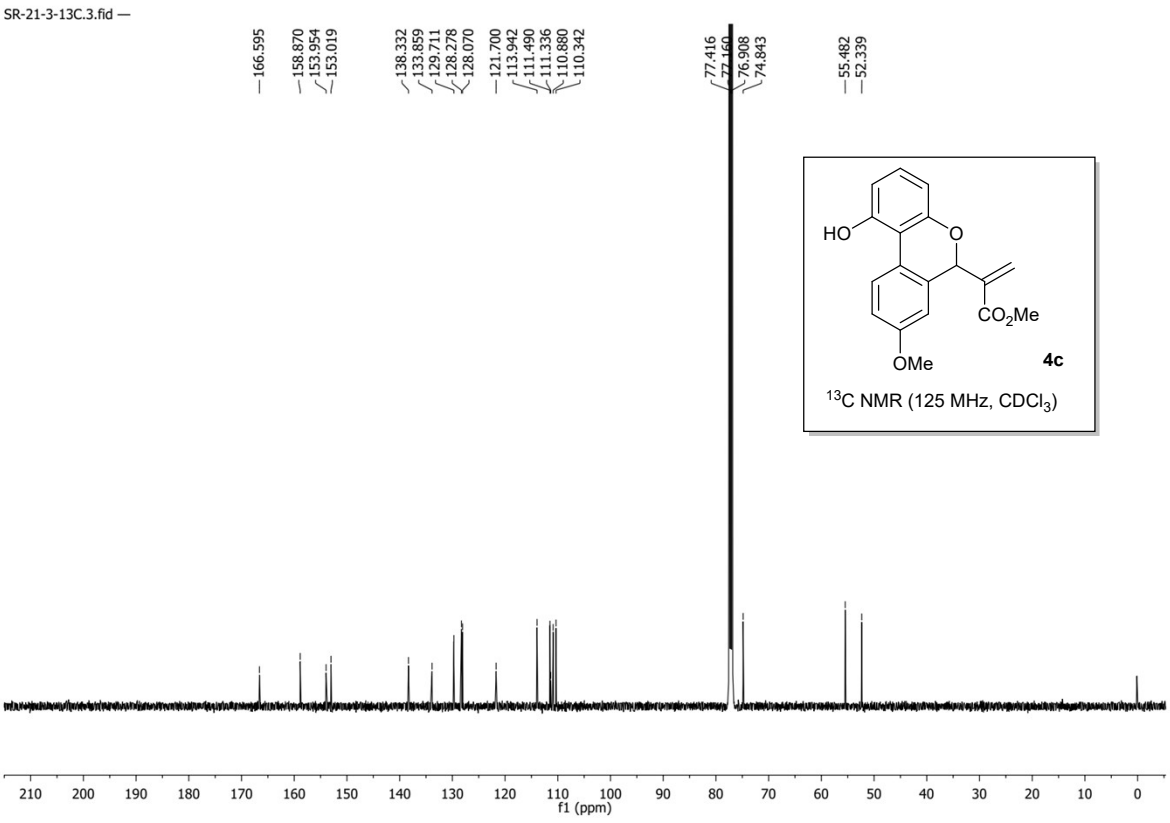
166.615
154.770
153.658
138.485
132.199
129.710
129.316
128.907
128.668
127.419
126.492
125.891
111.381
110.864
110.356
77.416
77.160
76.908
74.850
52.350
HO
O
CO2Me
4a
13C NMR (125 MHz, CDCl3)
f1 (ppm)

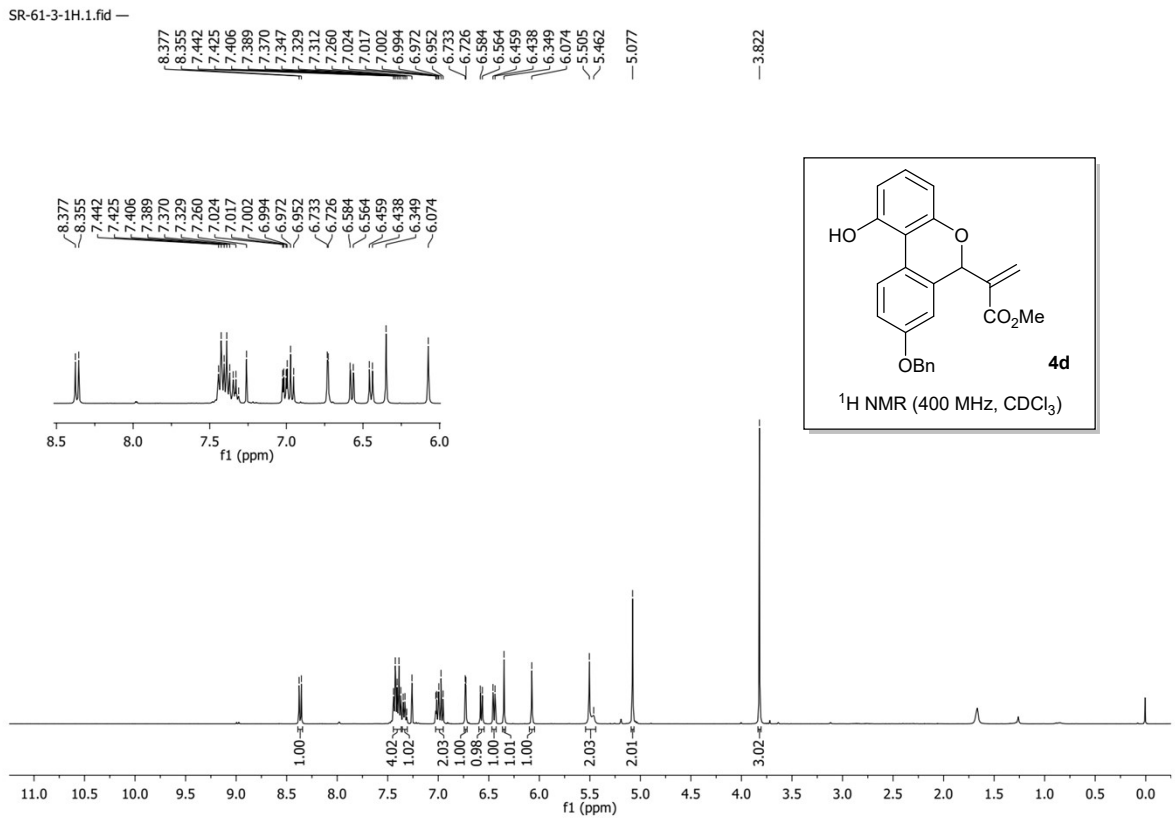

SR-33-2-1H.1.fid
8.301
8.280
7.260
7.216
7.198
7.019
6.999
6.979
6.909
6.580
6.560
6.468
6.448
6.343
6.082
5.475
5.425
3.831
2.357
HO
O
CO2Me
Me
4b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

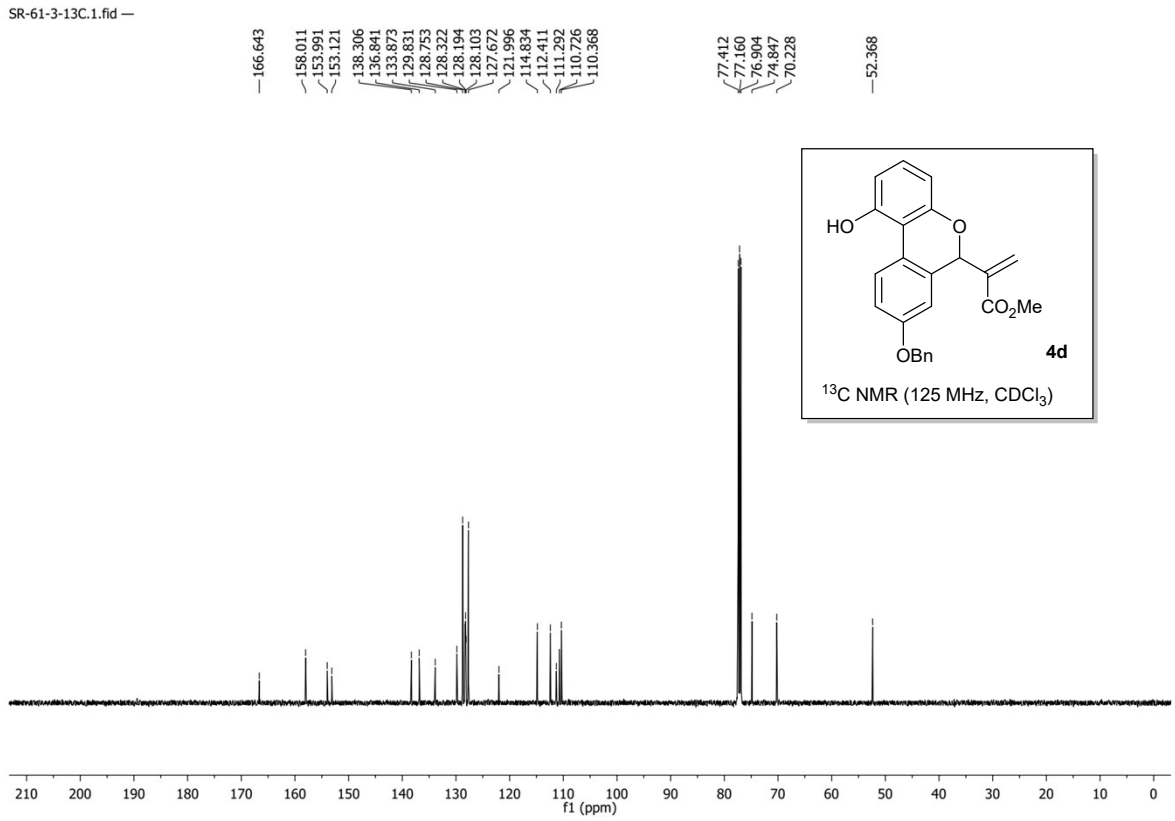

1.00
1.02
1.00
1.00
1.00
1.01
1.01
0.98
1.03
1.00
3.03
3.00
f1 (ppm)

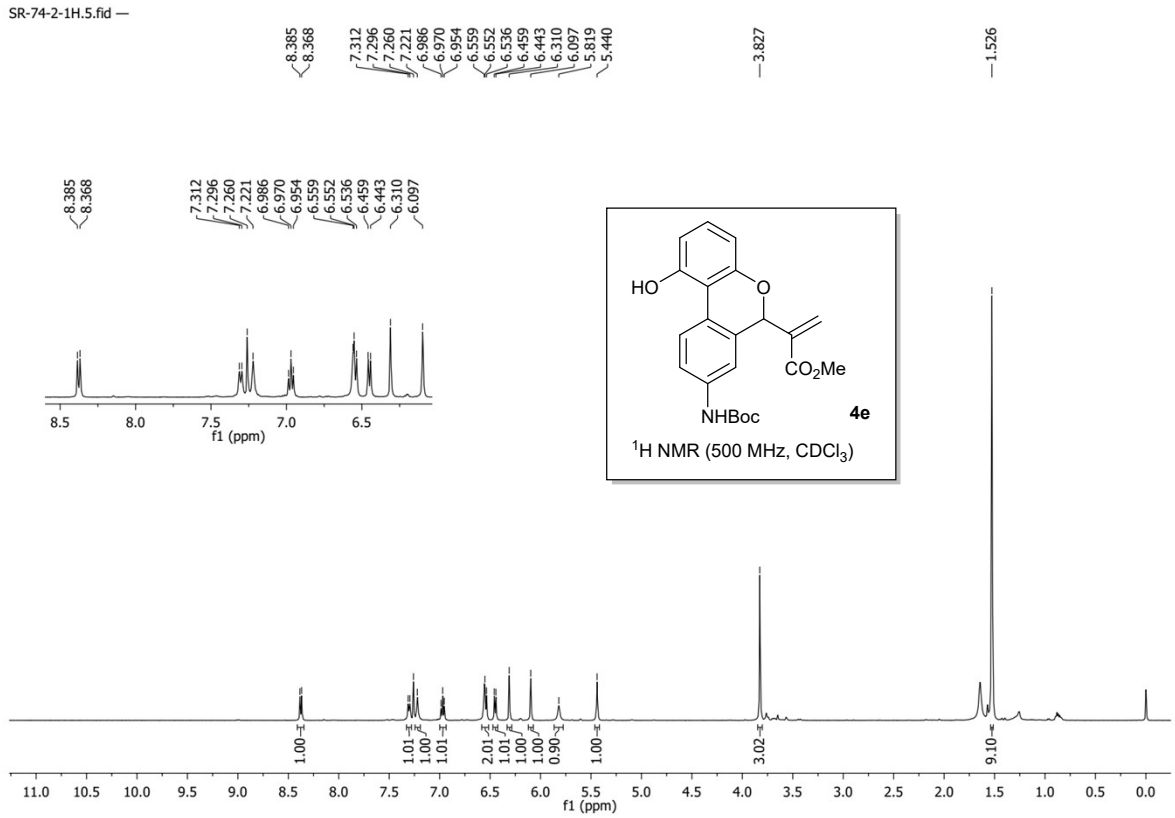

MB-33-2-13C.1.fid
166.668
154.484
153.454
138.573
137.327
132.232
129.715
129.411
128.812
126.491
126.367
126.097
111.479
110.843
110.309
77.412
77.160
76.904
74.825
52.321
21.390
HO
O
CO2Me
Me
4b
13C NMR (125 MHz, CDCl3)
f1 (ppm)

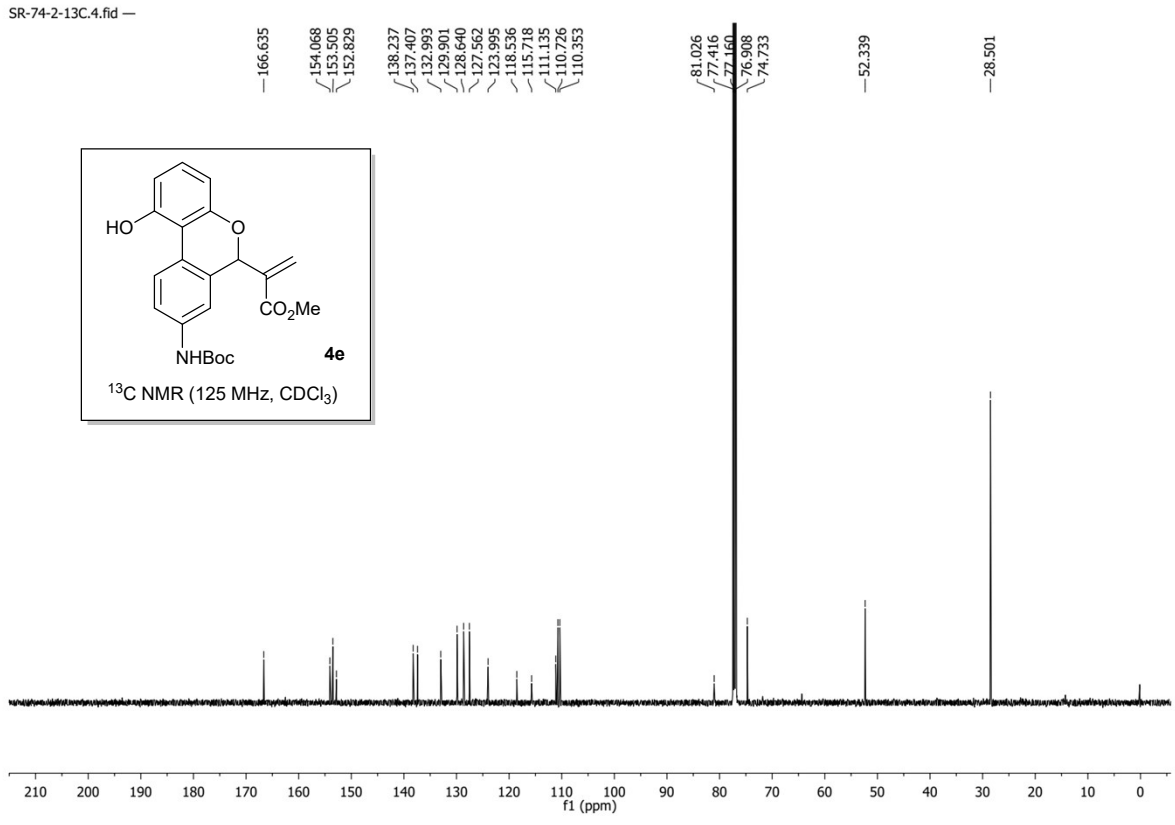

SR-21-3-1H.1.fid
8.374
8.357
7.260
6.992
6.976
6.960
6.947
6.929
6.658
6.578
6.562
6.457
6.441
6.338
6.087
5.484
5.354
3.830
3.824
f1 (ppm)
HO
O
CO2Me
OMe
4c
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.02
1.01
1.00
1.01
1.02
1.00
1.02
1.00
6.06

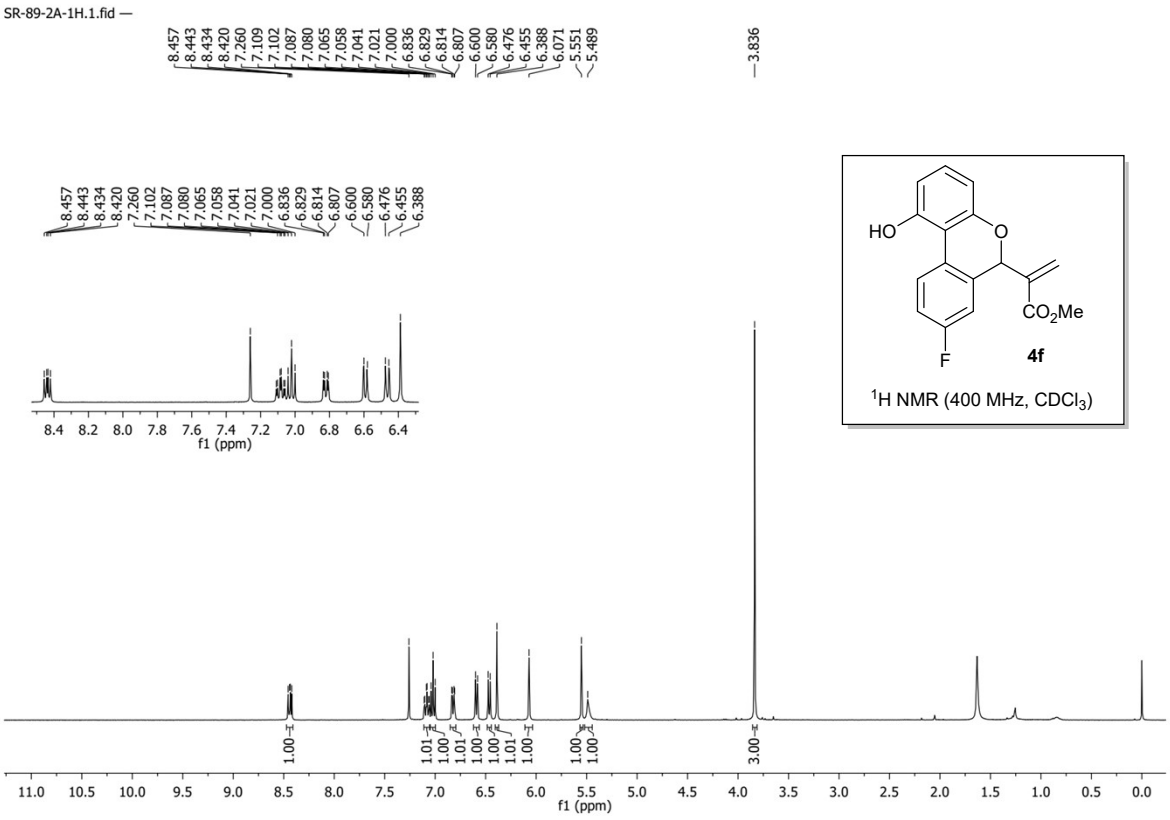

SR-21-3-13C.3.fid
166.595
158.870
153.954
153.019
138.332
133.859
129.711
128.278
128.070
121.700
113.942
111.490
111.336
110.880
110.342
77.416
77.160
76.908
74.843
55.482
52.339
f1 (ppm)
HO
O
CO2Me
OMe
4c
13C NMR (125 MHz, CDCl3)

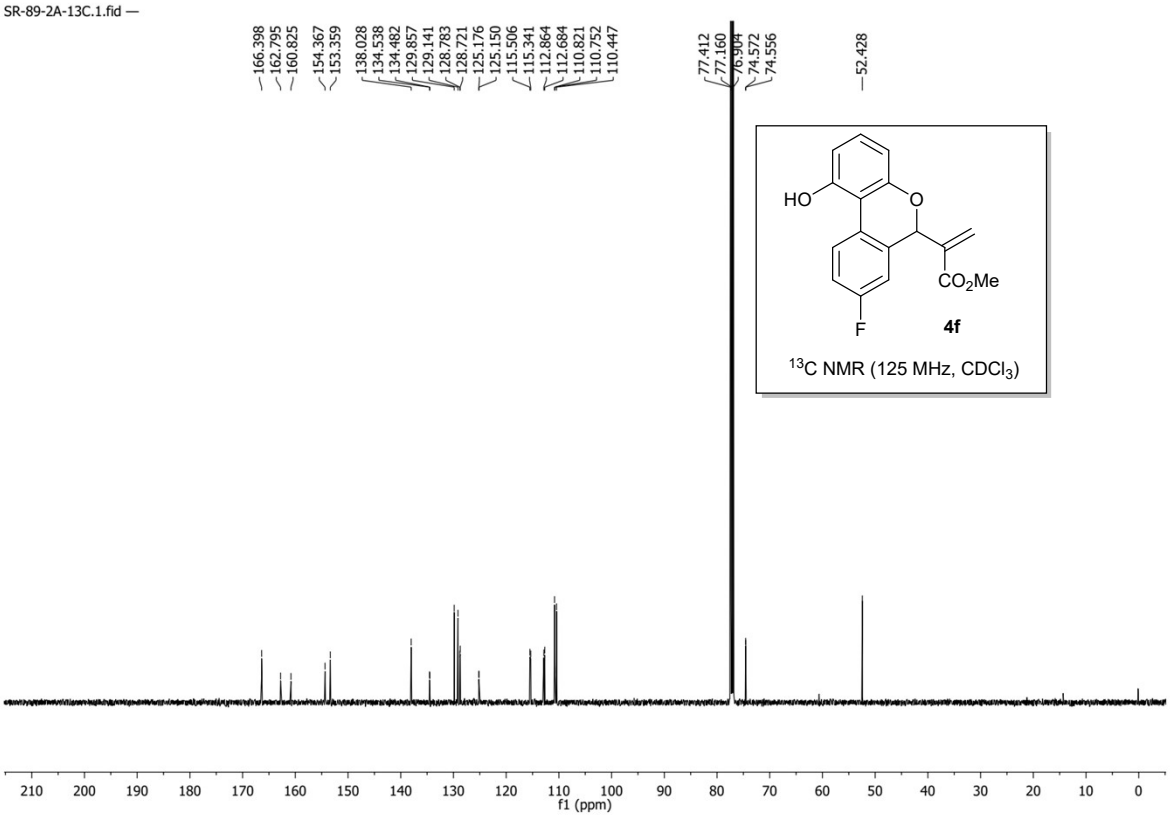

SR-61-3-1H.1.fid
HO
O
CO2Me
OBn
4d
1H NMR (400 MHz, CDCl3)
f1 (ppm)


SR-61-3-13C.1.fid
HO
O
CO2Me
OBn
4d
13C NMR (125 MHz, CDCl3)
f1 (ppm)

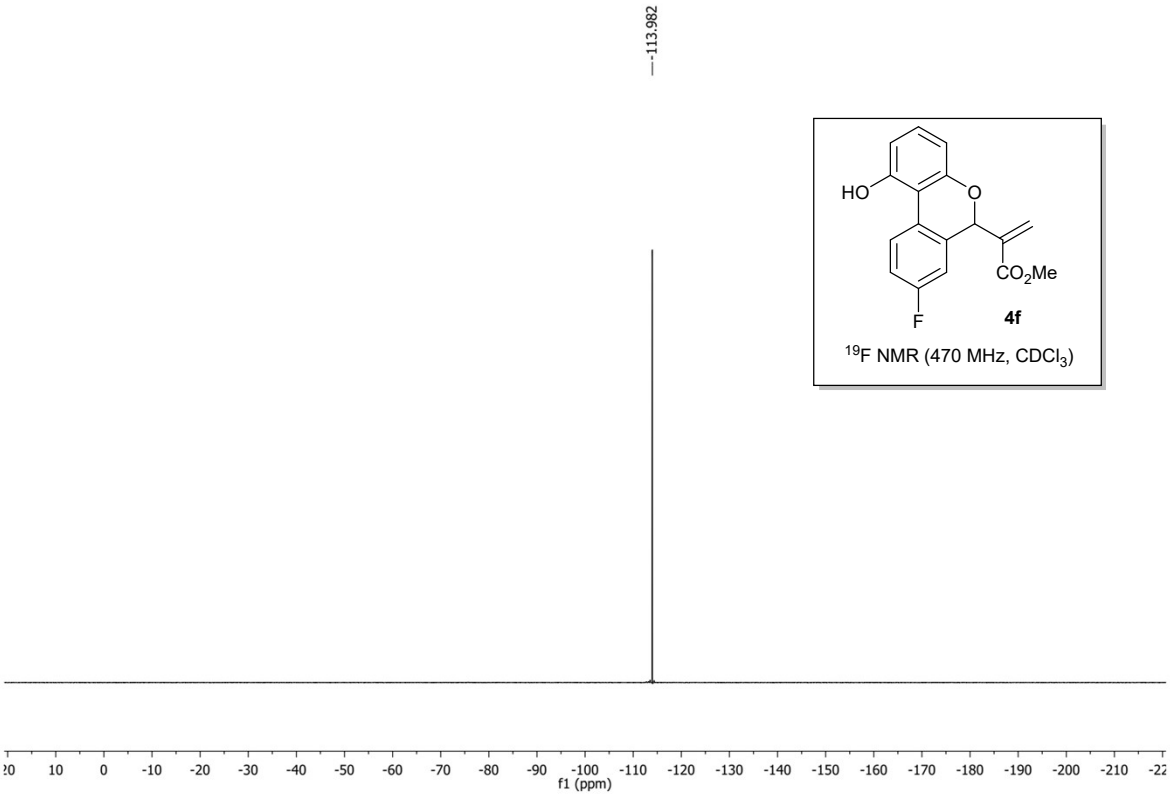

SR-74-2-1H.5.fid
8.385
8.368
7.312
7.296
7.260
7.221
6.986
6.970
6.954
6.559
6.552
6.536
6.459
6.443
6.310
6.097
5.819
5.440
3.827
1.526
HO
O
CO2Me
NHBoc
4e
1H NMR (500 MHz, CDCl3)
f1 (ppm)


SR-74-2-13C.4.fid
166.635
154.068
153.505
152.829
138.237
137.407
132.993
129.901
128.640
127.562
123.995
118.536
115.718
111.135
110.726
110.353
81.026
77.416
77.160
76.908
74.733
52.339
28.501
HO
O
CO2Me
NHBoc
4e
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SR-89-2A-1H.1.fid
8.457
8.443
8.434
8.420
7.260
7.109
7.102
7.087
7.080
7.065
7.058
7.041
7.021
7.000
6.836
6.829
6.814
6.807
6.600
6.580
6.476
6.455
6.388
6.071
5.551
5.489
3.836
HO
O
CO2Me
F
4f
1H NMR (400 MHz, CDCl3)
f1 (ppm)
1.00
1.01
1.00
1.01
1.00
1.00
1.01
1.00
1.00
1.00
3.00


SR-89-2A-13C.1.fid
166.398
162.795
160.825
154.367
153.359
138.028
134.538
134.482
129.857
129.141
128.783
128.721
125.176
125.150
115.506
115.341
112.864
112.684
110.821
110.752
110.447
77.412
77.160
76.904
74.572
74.556
52.428
HO
O
CO2Me
F
4f
13C NMR (125 MHz, CDCl3)
f1 (ppm)

SR-89-2A-19F.3.fid —



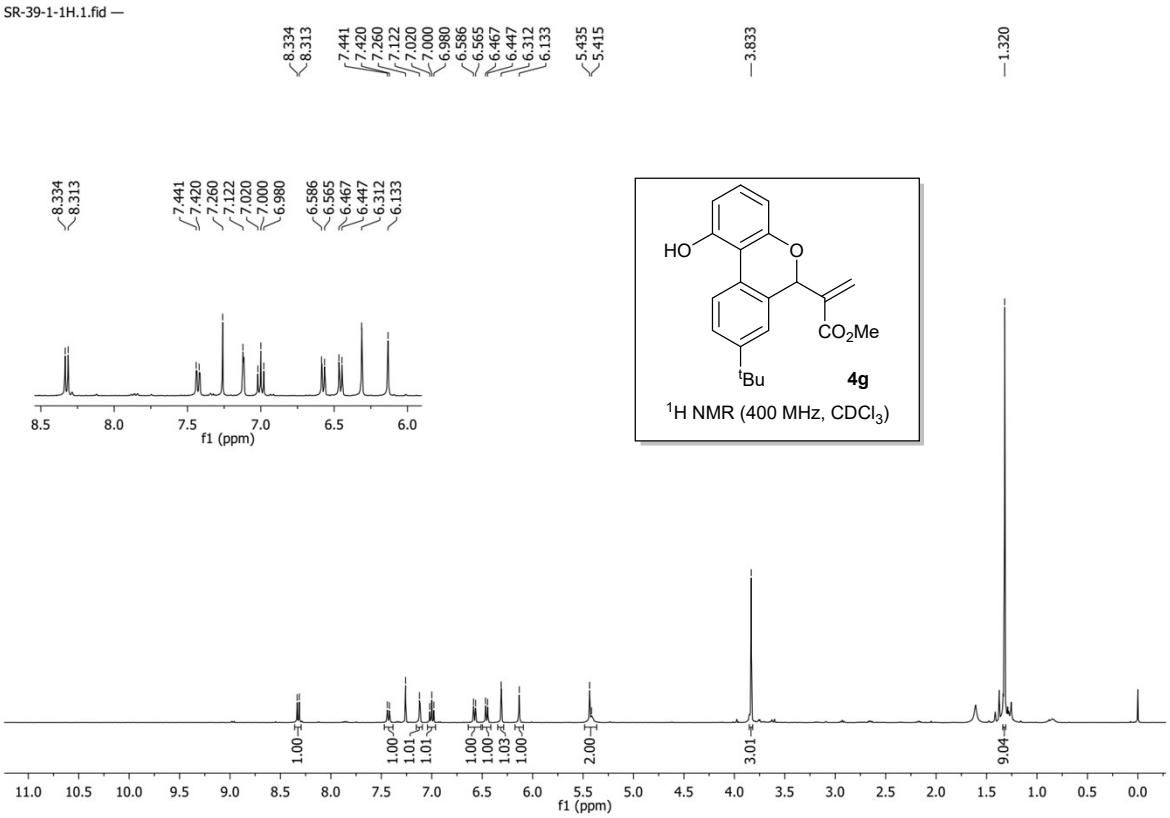




**4f**

$^{19}$F NMR (470 MHz, $CDCl_3$)

SR-39-1-1H.1.fid —

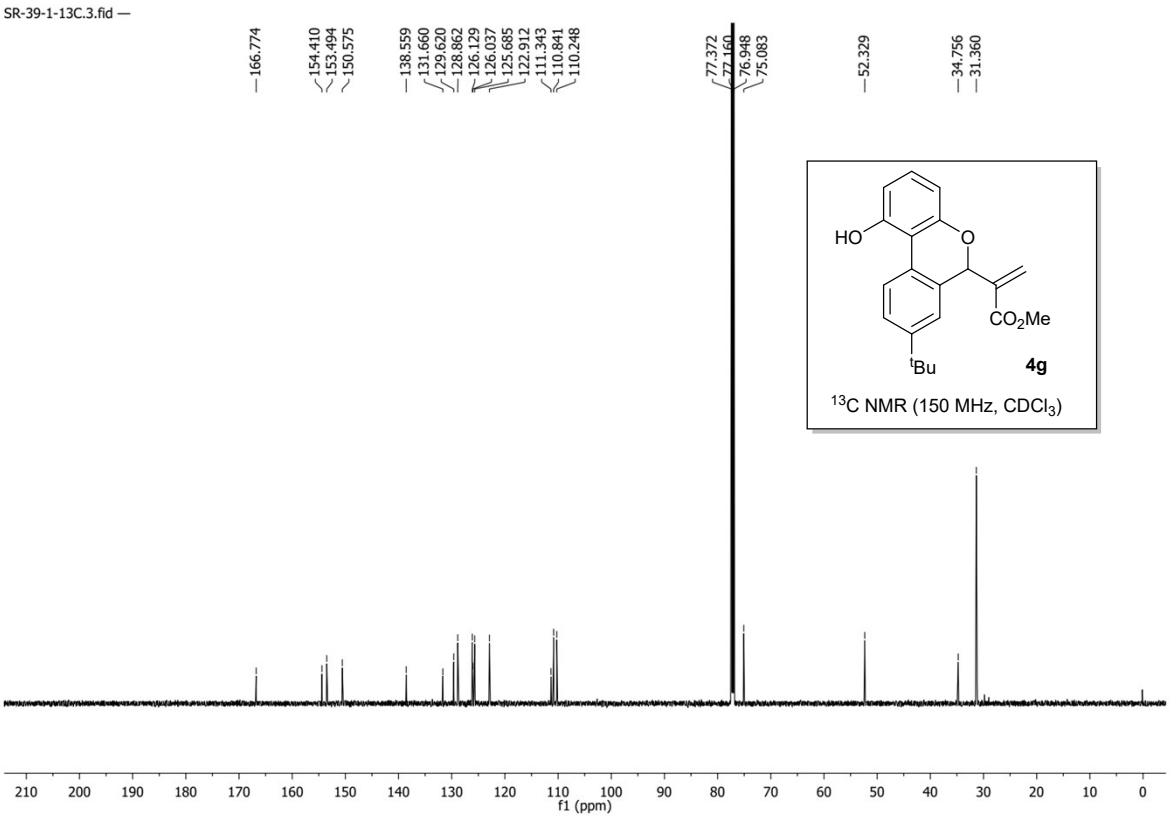


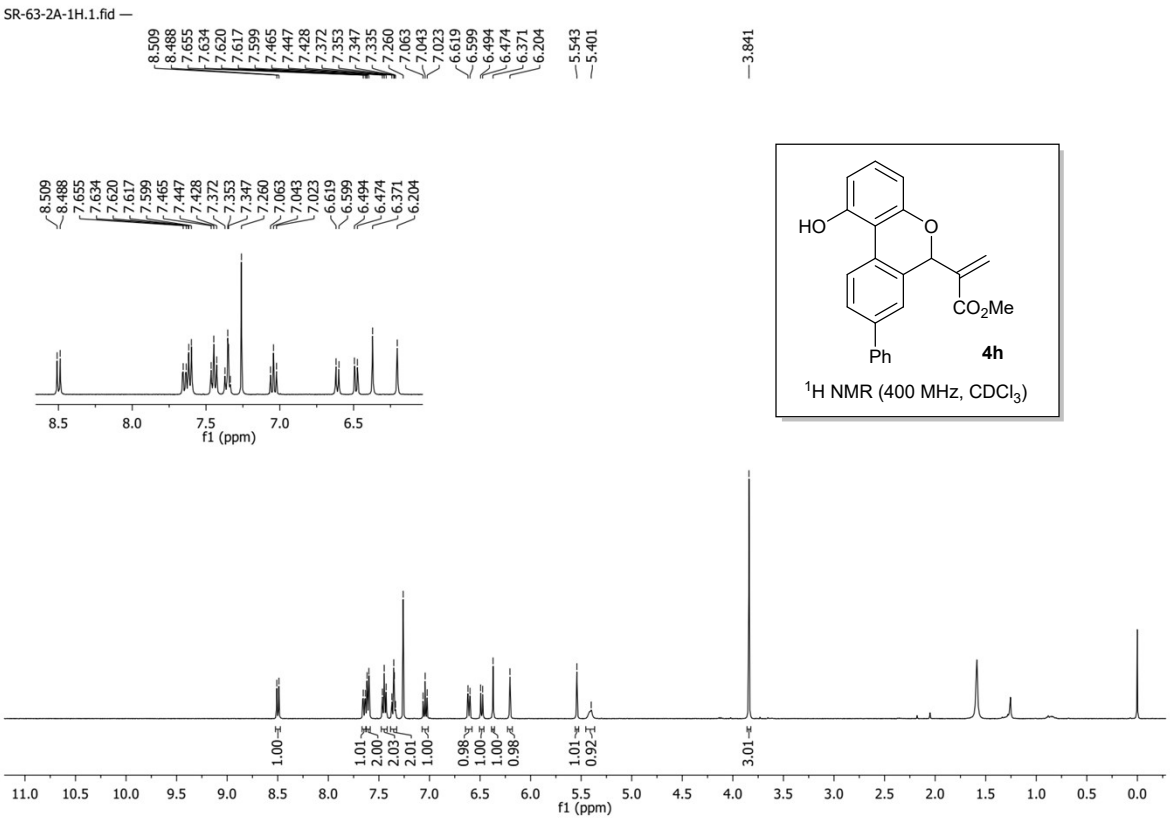


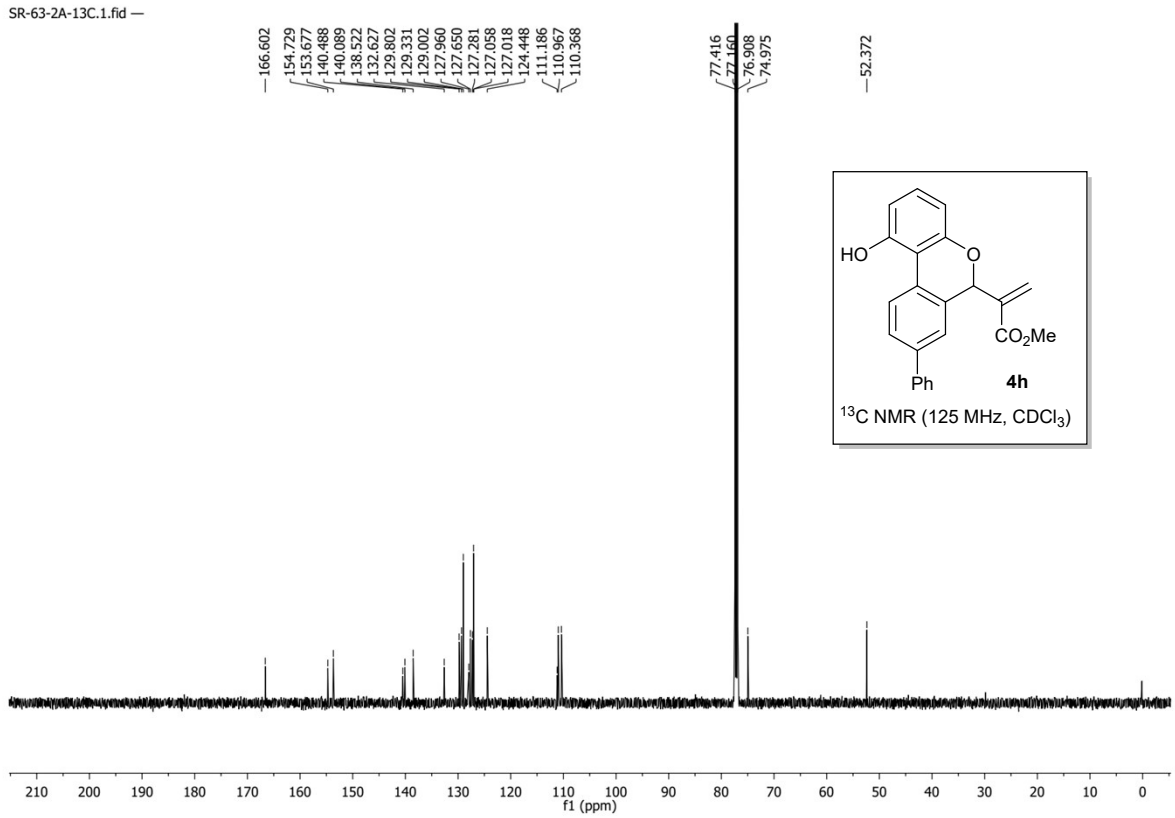


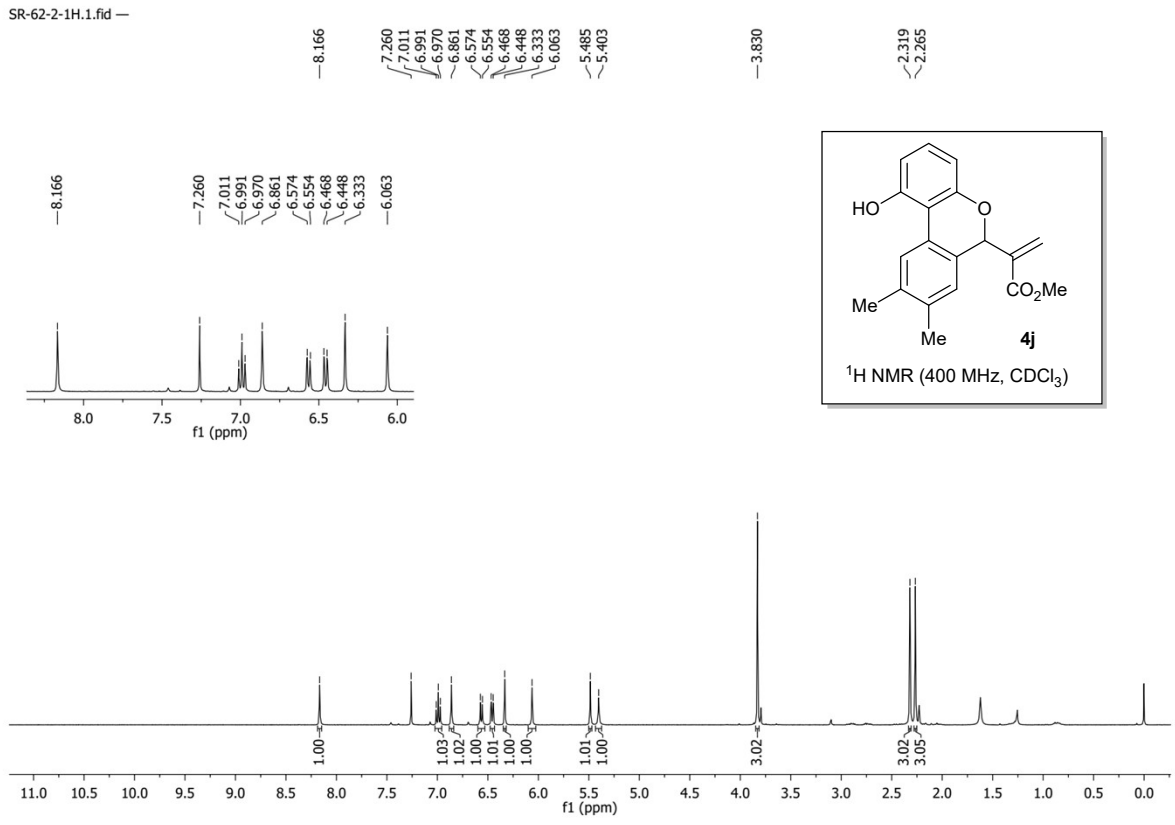
**4g**

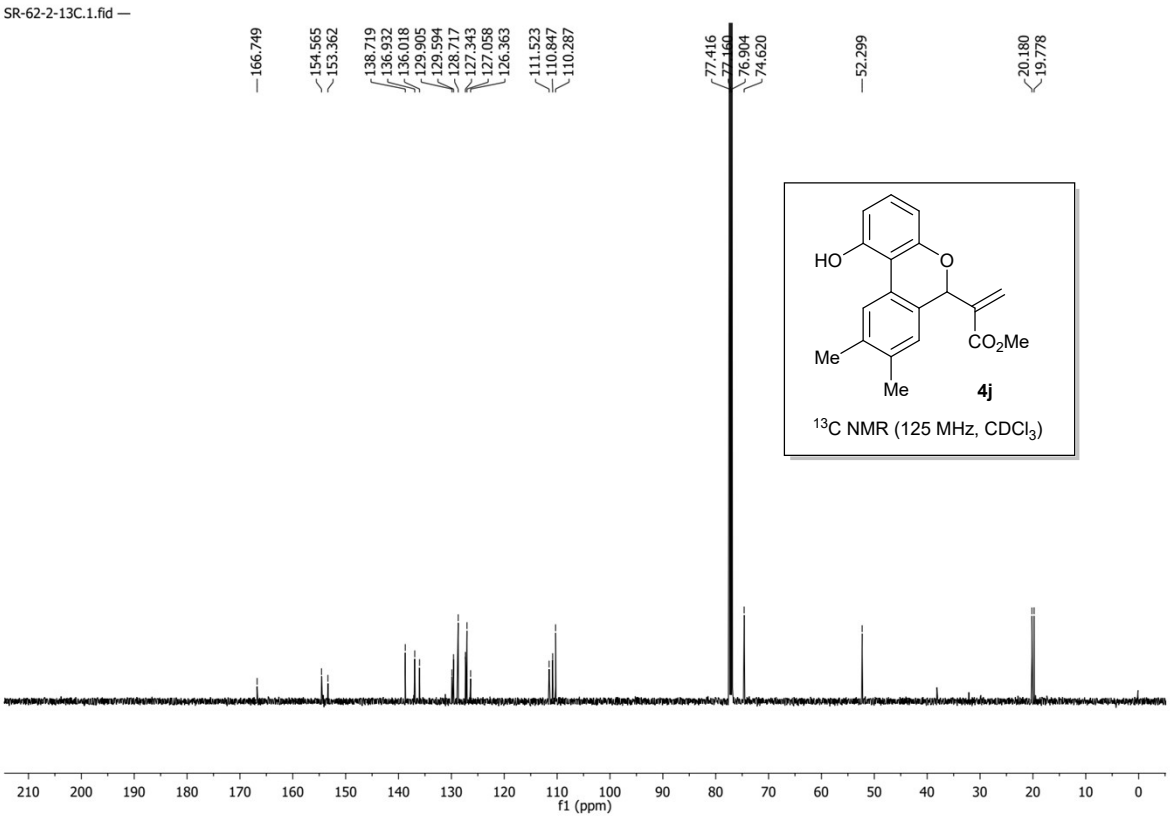
$^{1}$H NMR (400 MHz, $CDCl_3$)

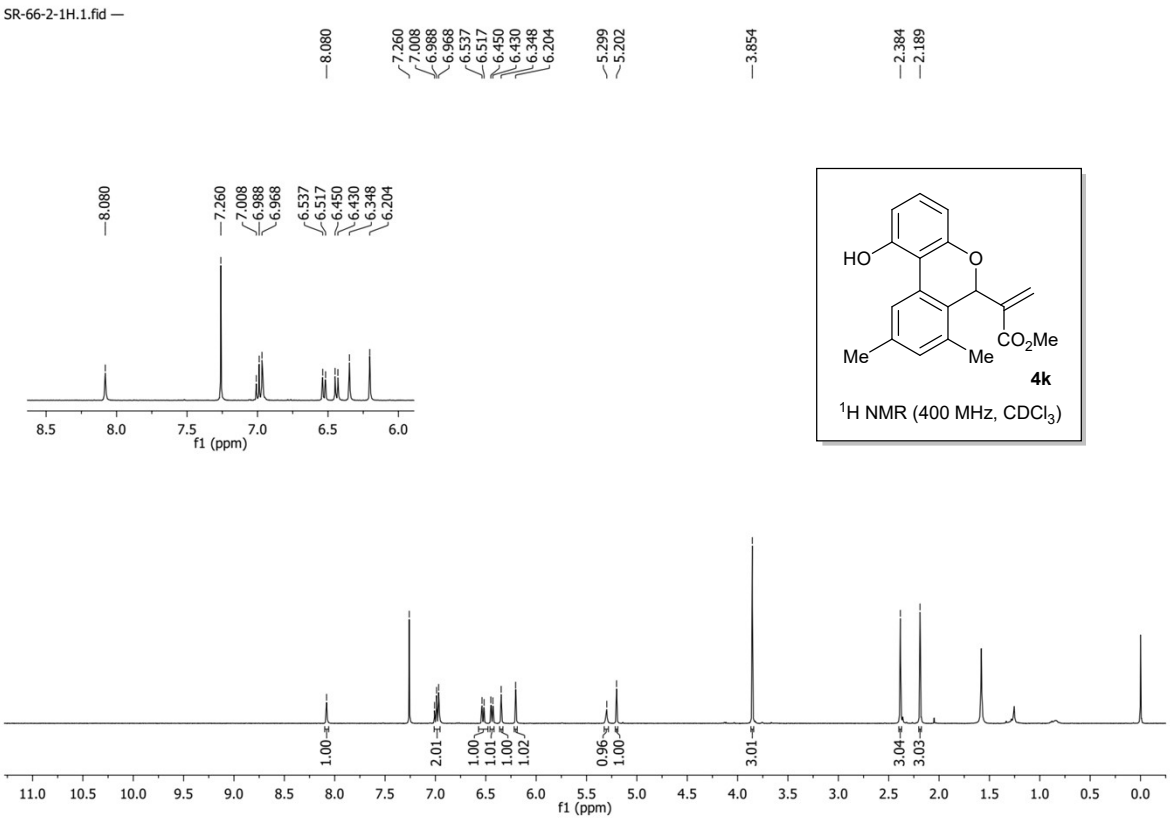

SR-39-1-13C.3.fid
166.774
154.410
153.494
150.575
138.559
131.660
129.620
128.862
126.129
126.037
125.685
122.912
111.343
110.841
110.248
77.372
77.160
76.948
75.083
52.329
34.756
31.360
HO
O
CO2Me
tBu
4g
13C NMR (150 MHz, CDCl3)
f1 (ppm)

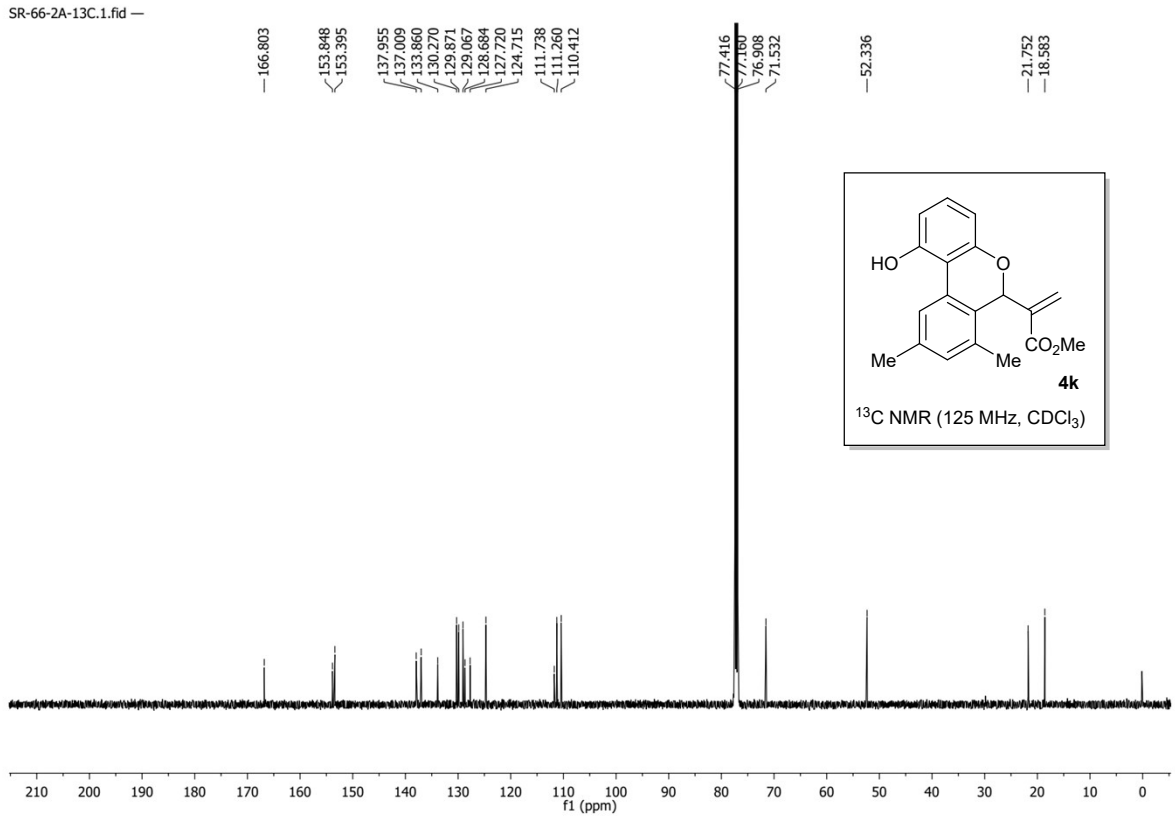

SR-63-2A-1H.1.fid
8.509
8.488
7.655
7.634
7.620
7.617
7.599
7.465
7.447
7.428
7.372
7.353
7.347
7.335
7.260
7.063
7.043
7.023
6.619
6.599
6.494
6.474
6.371
6.204
5.543
5.401
3.841
HO
O
CO2Me
Ph
4h
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.00
2.03
2.01
1.00
0.98
1.00
1.00
0.98
1.01
0.92
3.01
f1 (ppm)

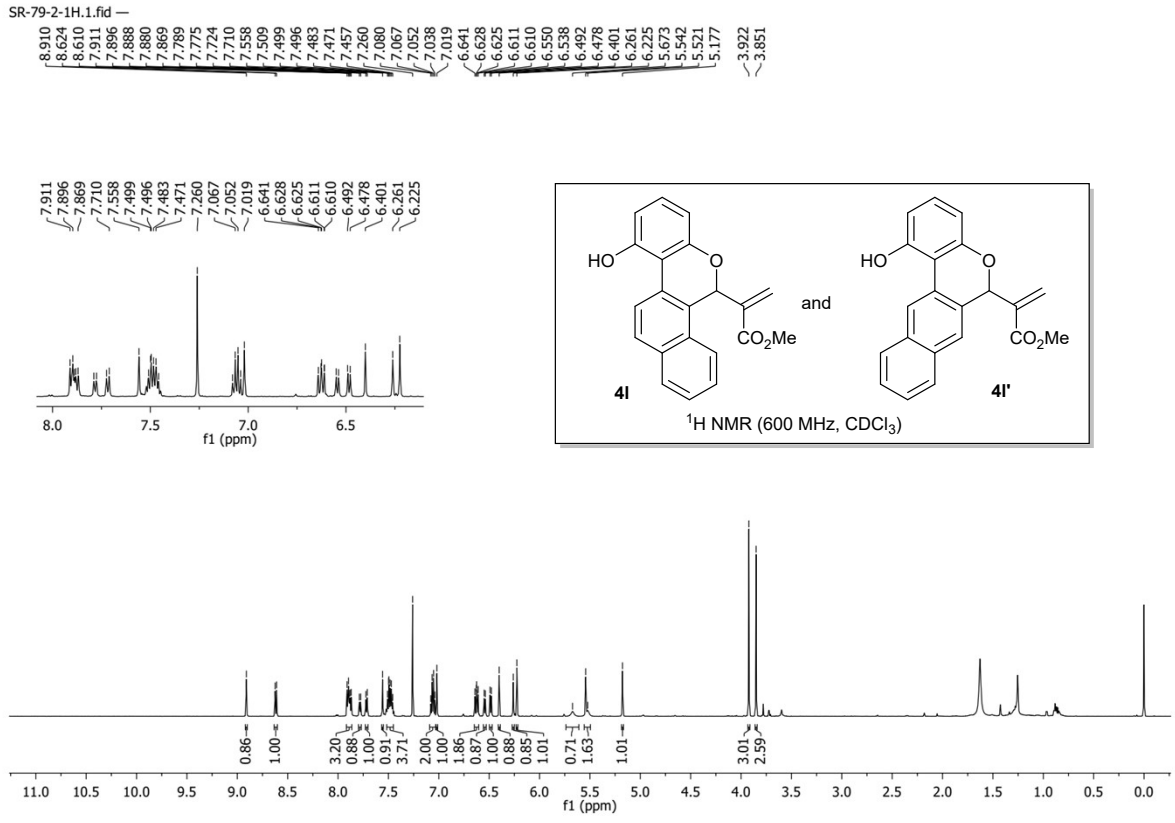

SR-63-2A-13C.1.fid
166.602
154.729
153.677
140.488
140.089
138.522
132.627
129.802
129.331
129.002
127.960
127.650
127.281
127.058
127.018
124.448
111.186
110.967
110.368
77.416
77.160
76.908
74.975
52.372
HO
O
CO2Me
Ph
4h
13C NMR (125 MHz, CDCl3)
f1 (ppm)

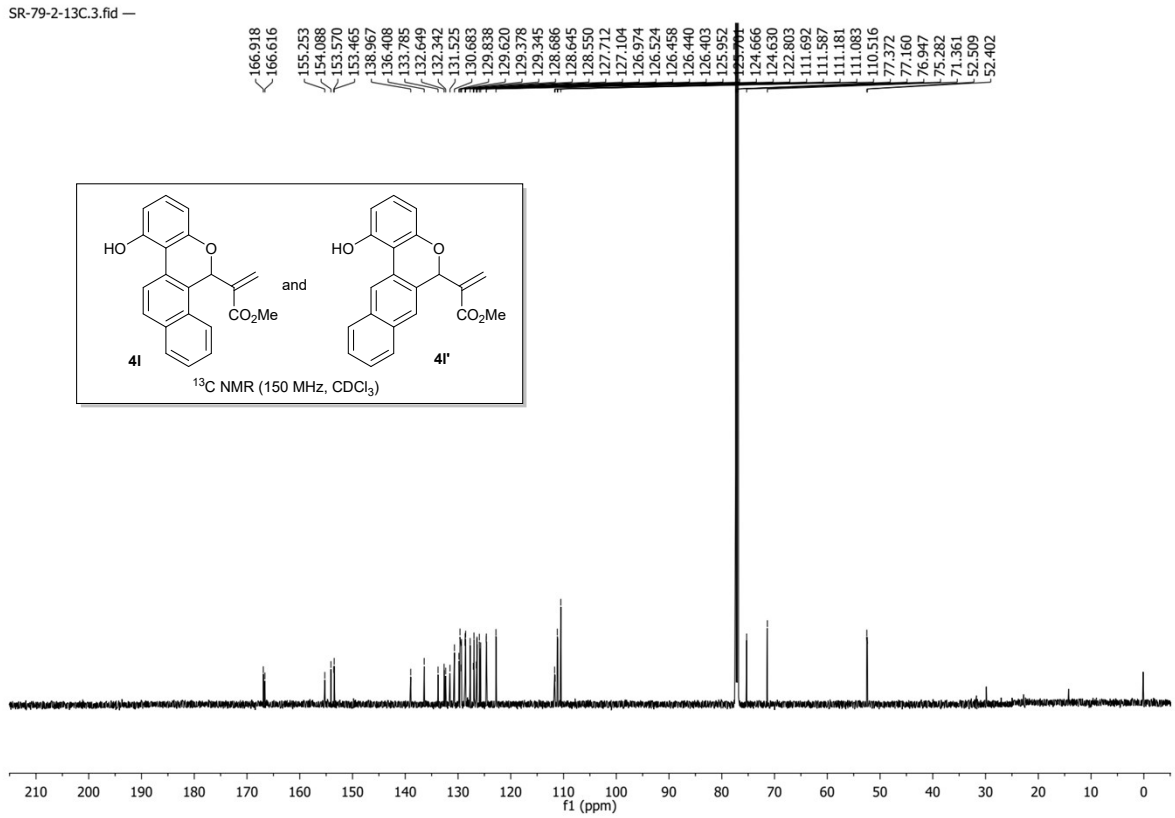

SR-62-2-1H.1.fid
8.166
7.260
7.011
6.991
6.970
6.861
6.574
6.554
6.468
6.448
6.333
6.063
5.485
5.403
3.830
2.319
2.265
HO
O
CO2Me
Me
Me
4j
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.02
1.00
1.01
1.00
1.00
1.01
1.00
3.02
3.02
3.05
f1 (ppm)

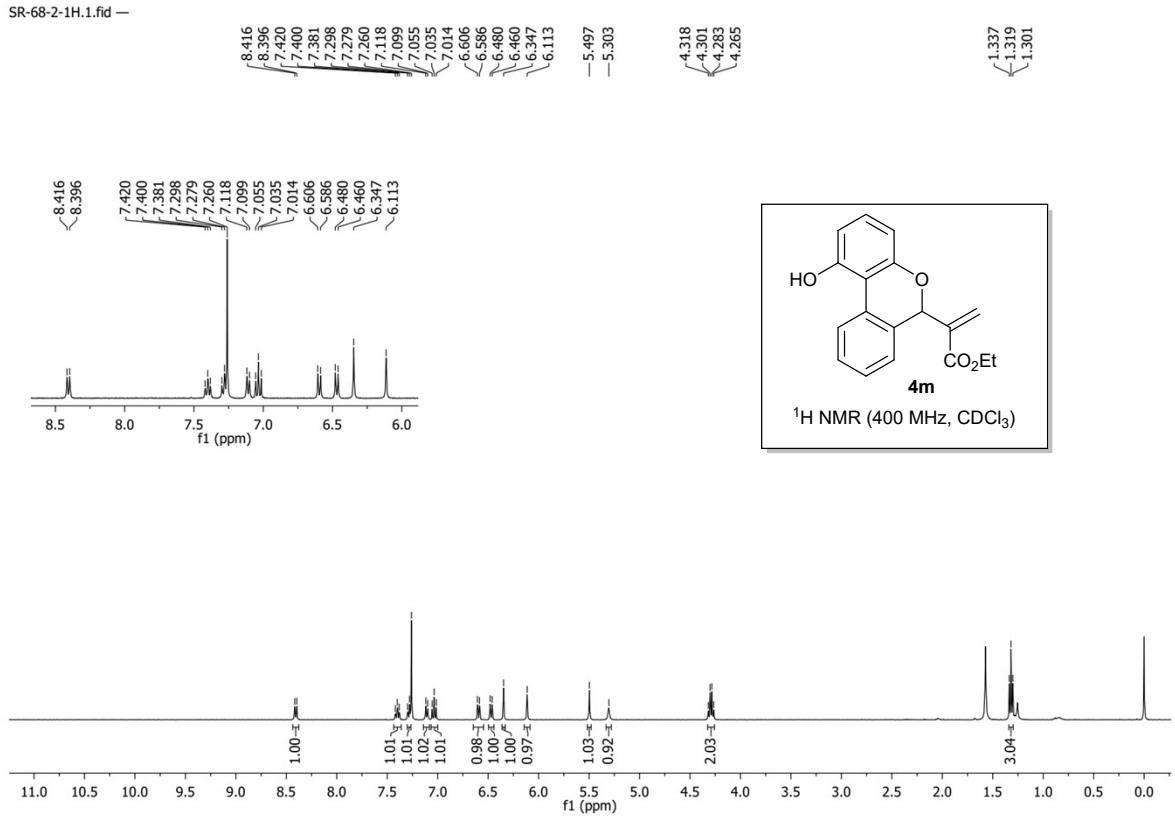

SR-62-2-13C.1.fid
166.749
154.565
153.362
138.719
136.932
136.018
129.905
129.594
128.717
127.343
127.058
126.363
111.523
110.847
110.287
77.416
77.160
76.904
74.620
52.299
20.180
19.778
HO
O
Me
Me
CO2Me
4j
13C NMR (125 MHz, CDCl3)
f1 (ppm)

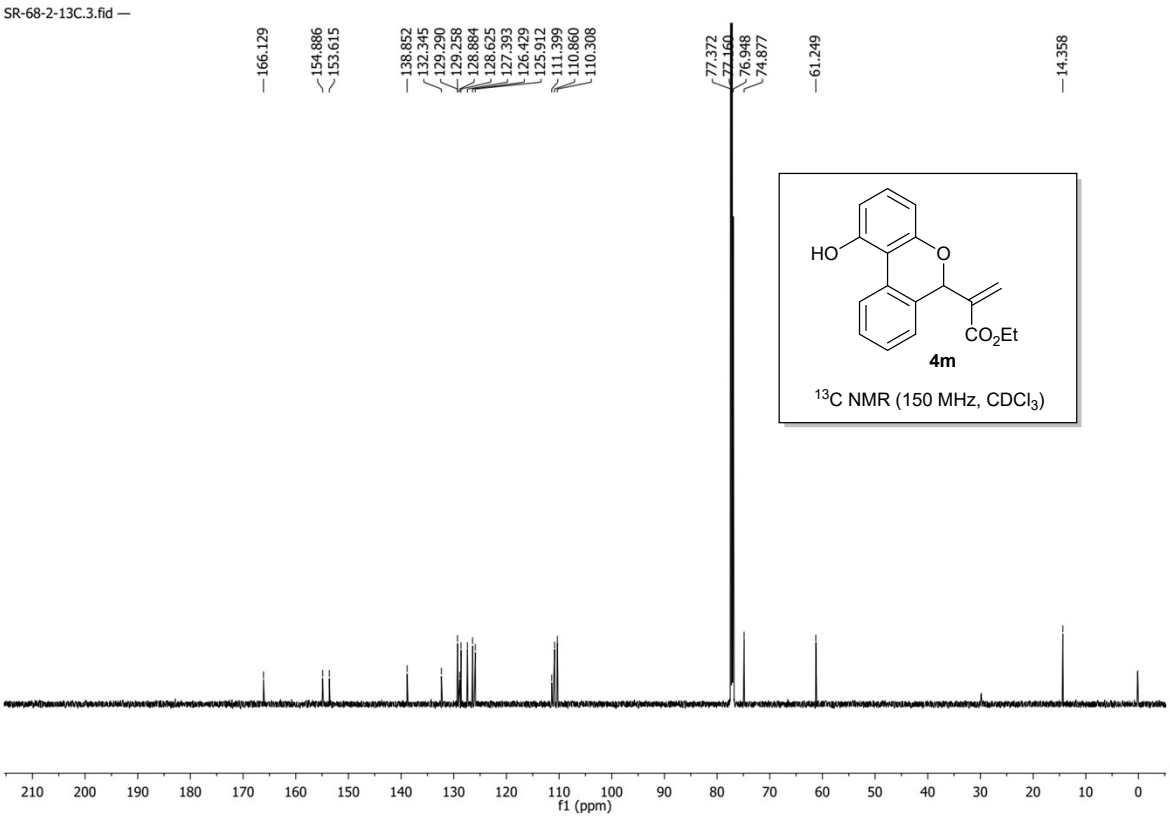

SR-66-2-1H.1.fid
8.080
7.260
7.008
6.988
6.968
6.537
6.517
6.450
6.430
6.348
6.204
5.299
5.202
3.854
2.384
2.189
HO
O
Me
Me
CO2Me
4k
1H NMR (400 MHz, CDCl3)
1.00
2.01
1.00
1.01
1.00
1.02
0.96
1.00
3.01
3.04
3.03
f1 (ppm)

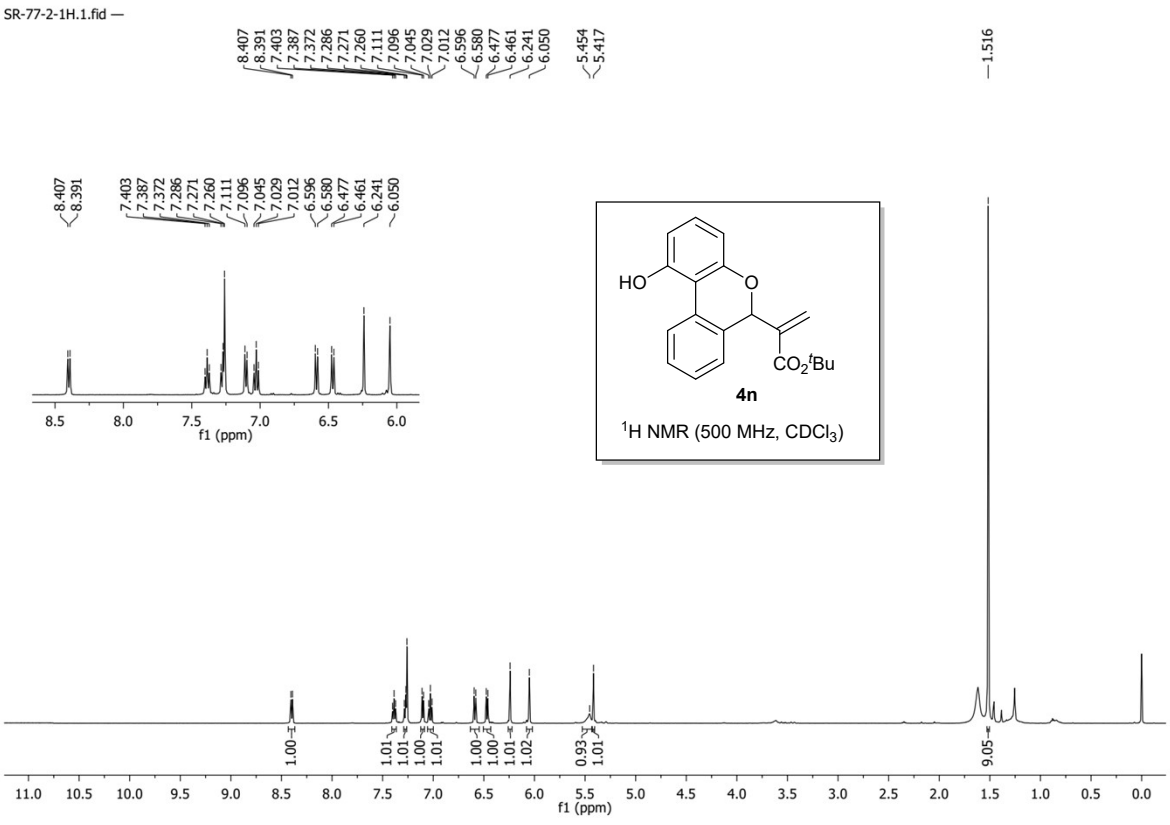

SR-66-2A-13C.1.fid
166.803
153.848
153.395
137.955
137.009
133.860
130.270
129.871
129.067
128.684
127.720
124.715
111.738
111.260
110.412
77.416
77.160
76.908
71.532
52.336
21.752
18.583
HO
O
CO2Me
Me
Me
4k
13C NMR (125 MHz, CDCl3)
f1 (ppm)

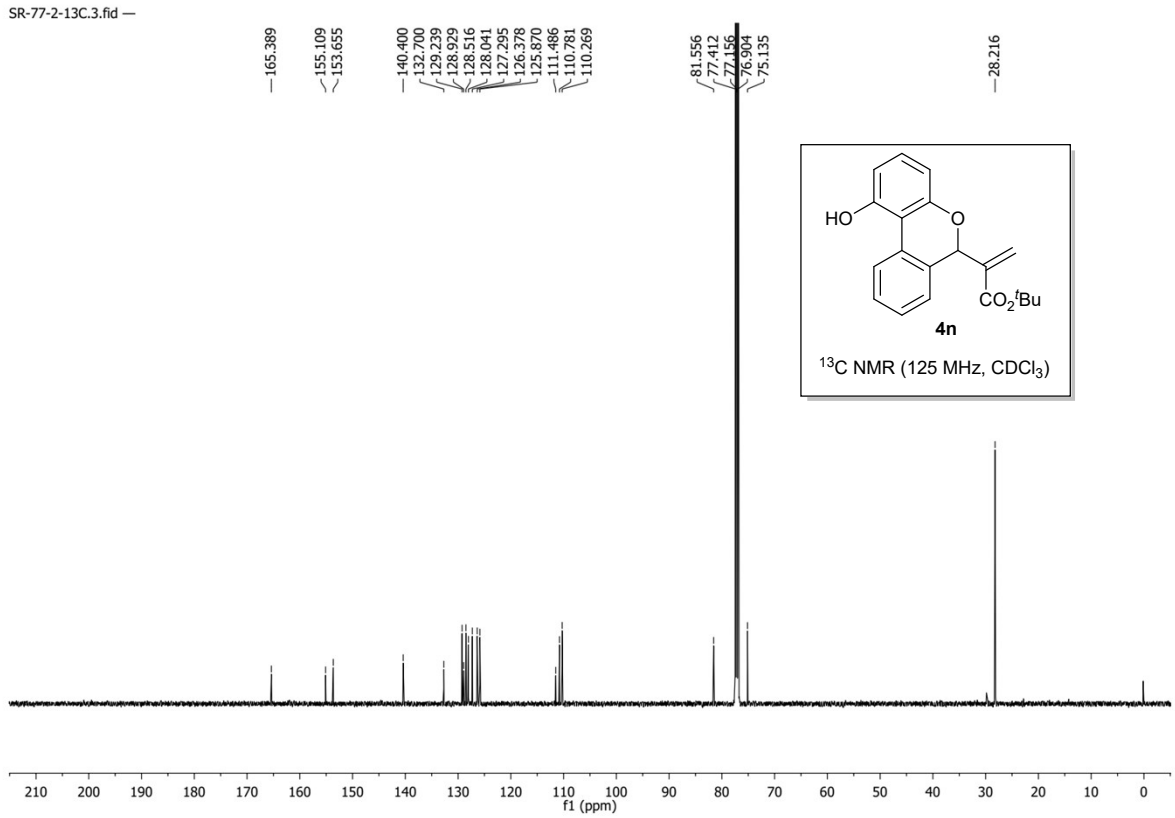

SR-79-2-1H.1.fid
8.910
8.624
8.610
7.911
7.896
7.888
7.880
7.869
7.789
7.775
7.724
7.710
7.558
7.509
7.499
7.496
7.483
7.471
7.457
7.260
7.080
7.067
7.052
7.038
7.019
6.641
6.628
6.625
6.611
6.610
6.550
6.538
6.492
6.478
6.401
6.261
6.225
5.673
5.542
5.521
5.177
3.922
3.851
HO
O
CO2Me
and
HO
O
CO2Me
4l
4l'
1H NMR (600 MHz, CDCl3)
f1 (ppm)

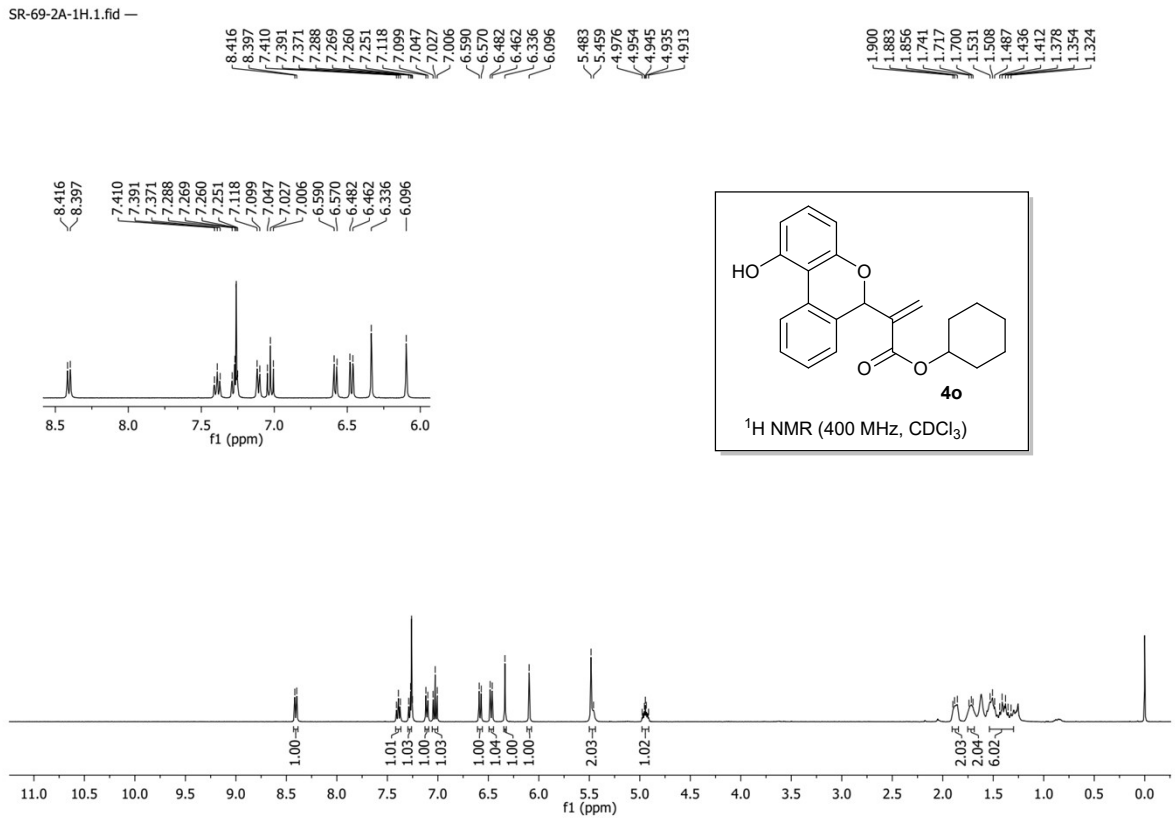

SR-79-2-13C.3.fid
166.918
166.616
155.253
154.088
153.570
153.465
138.967
136.408
133.785
132.649
132.342
131.525
130.683
129.838
129.620
129.378
129.345
128.686
128.645
128.550
127.712
127.104
126.974
126.524
126.458
126.440
126.403
125.952
124.666
124.630
122.803
111.692
111.587
111.181
111.083
110.516
77.372
77.160
76.947
75.282
71.361
52.509
52.402
HO
O
CO2Me
and
HO
O
CO2Me
4l
4l'
13C NMR (150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

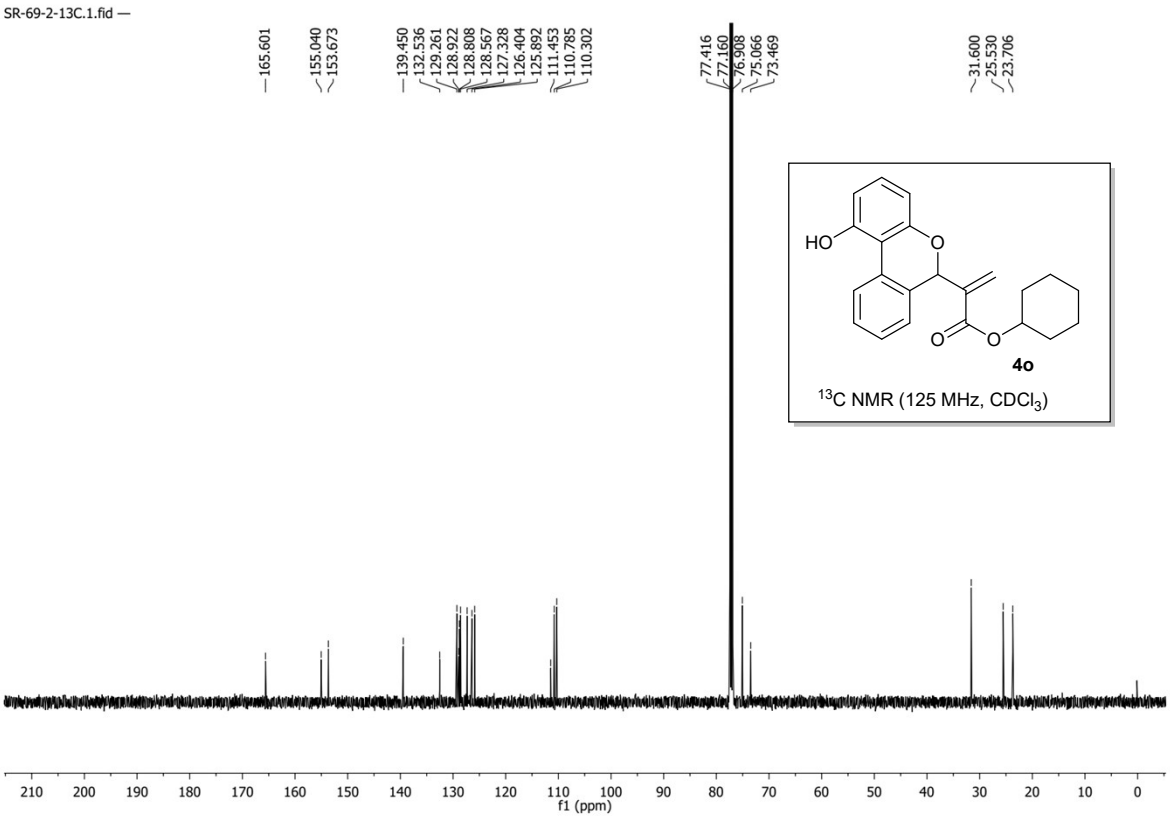

SR-68-2-1H.1.fid
8.416
8.396
7.420
7.400
7.381
7.298
7.279
7.260
7.118
7.099
7.055
7.035
7.014
6.606
6.586
6.480
6.460
6.347
6.113
5.497
5.303
4.318
4.301
4.283
4.265
1.337
1.319
1.301
HO
O
CO2Et
4m
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.01
1.02
1.01
0.98
1.00
1.00
0.97
1.03
0.92
2.03
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

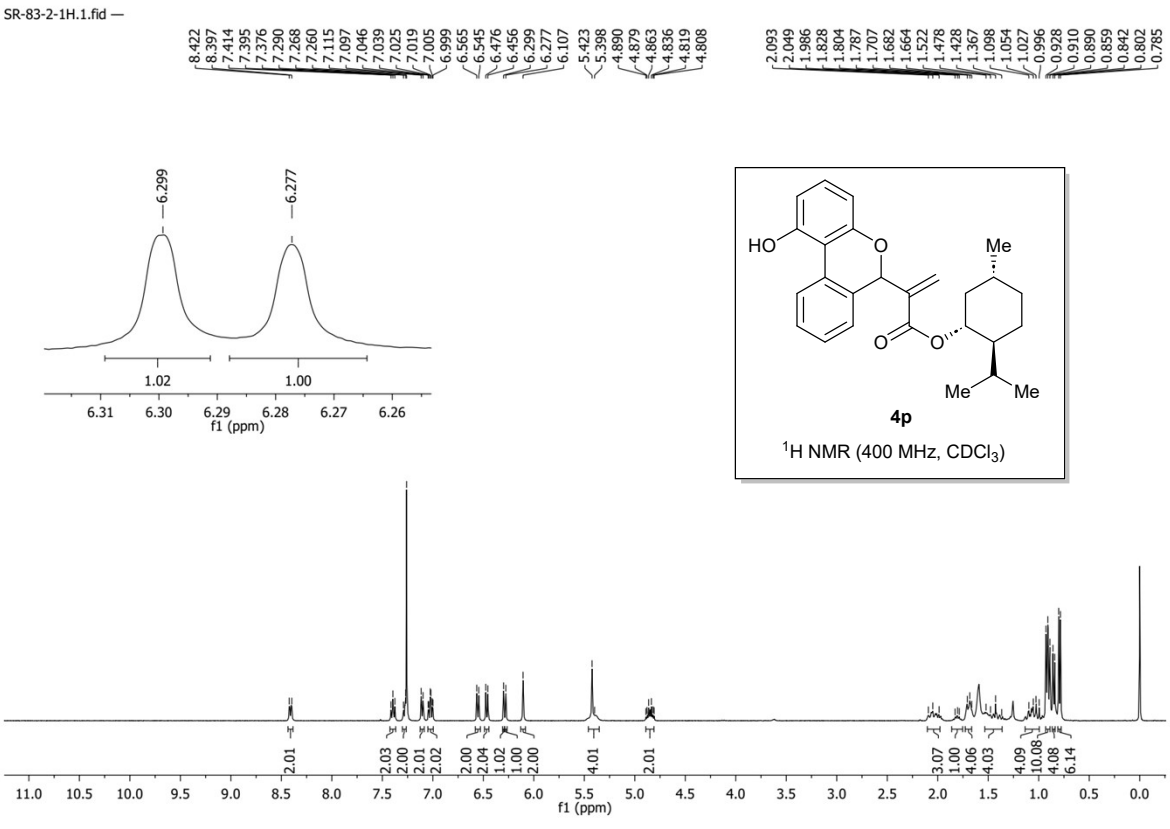

SR-68-2-13C.3.fid
166.129
154.886
153.615
138.852
132.345
129.290
129.258
128.884
128.625
127.393
126.429
125.912
111.399
110.860
110.308
77.372
77.160
76.948
74.877
61.249
14.358
HO
O
CO2Et
4m
13C NMR (150 MHz, CDCl3)
f1 (ppm)

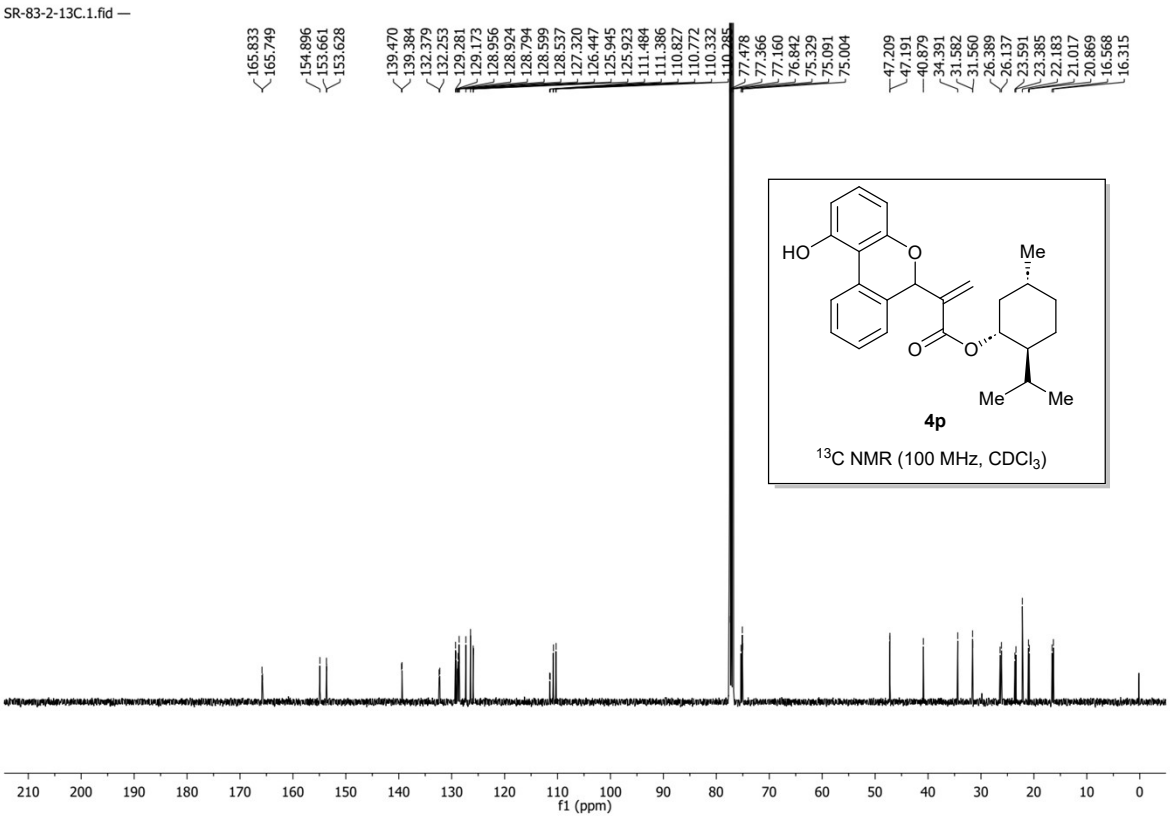

SR-77-2-1H.1.fid
8.407
8.391
7.403
7.387
7.372
7.286
7.271
7.260
7.111
7.096
7.045
7.029
7.012
6.596
6.580
6.477
6.461
6.241
6.050
5.454
5.417
1.516
HO
O
CO2tBu
4n
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.01
1.00
1.01
1.00
1.00
1.01
1.02
0.93
1.01
9.05
f1 (ppm)

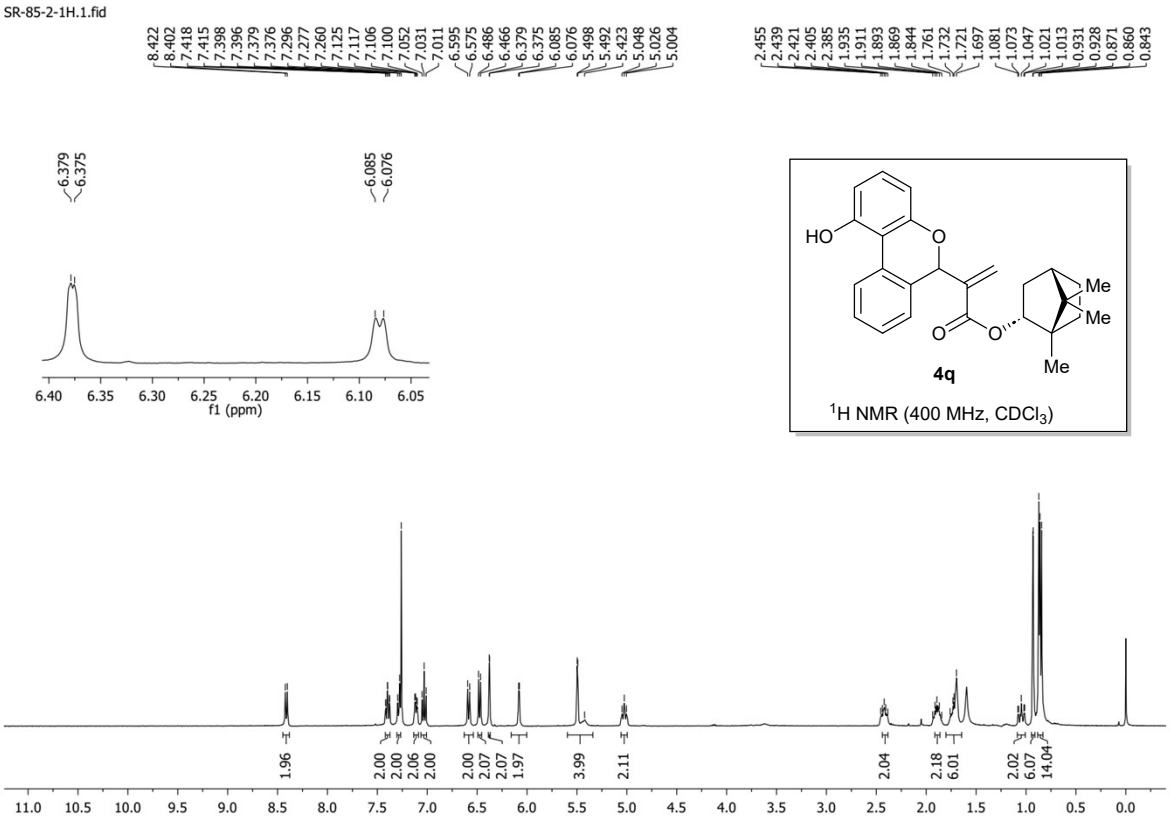

SR-77-2-13C.3.fid
165.389
155.109
153.655
140.400
132.700
129.239
128.929
128.516
128.041
127.295
126.378
125.870
111.486
110.781
110.269
81.556
77.412
77.156
76.904
75.135
28.216
HO
O
CO2tBu
4n
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SR-69-2A-1H.1.fid
8.416
8.397
7.410
7.391
7.371
7.288
7.269
7.260
7.251
7.118
7.099
7.047
7.027
7.006
6.590
6.570
6.482
6.462
6.336
6.096
5.483
5.459
4.976
4.954
4.945
4.935
4.913
1.900
1.883
1.856
1.741
1.717
1.700
1.531
1.508
1.487
1.436
1.412
1.378
1.354
1.324
HO
O
O
O
4o
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.03
1.00
1.03
1.00
1.04
1.00
1.00
2.03
1.02
2.03
2.04
6.02
f1 (ppm)

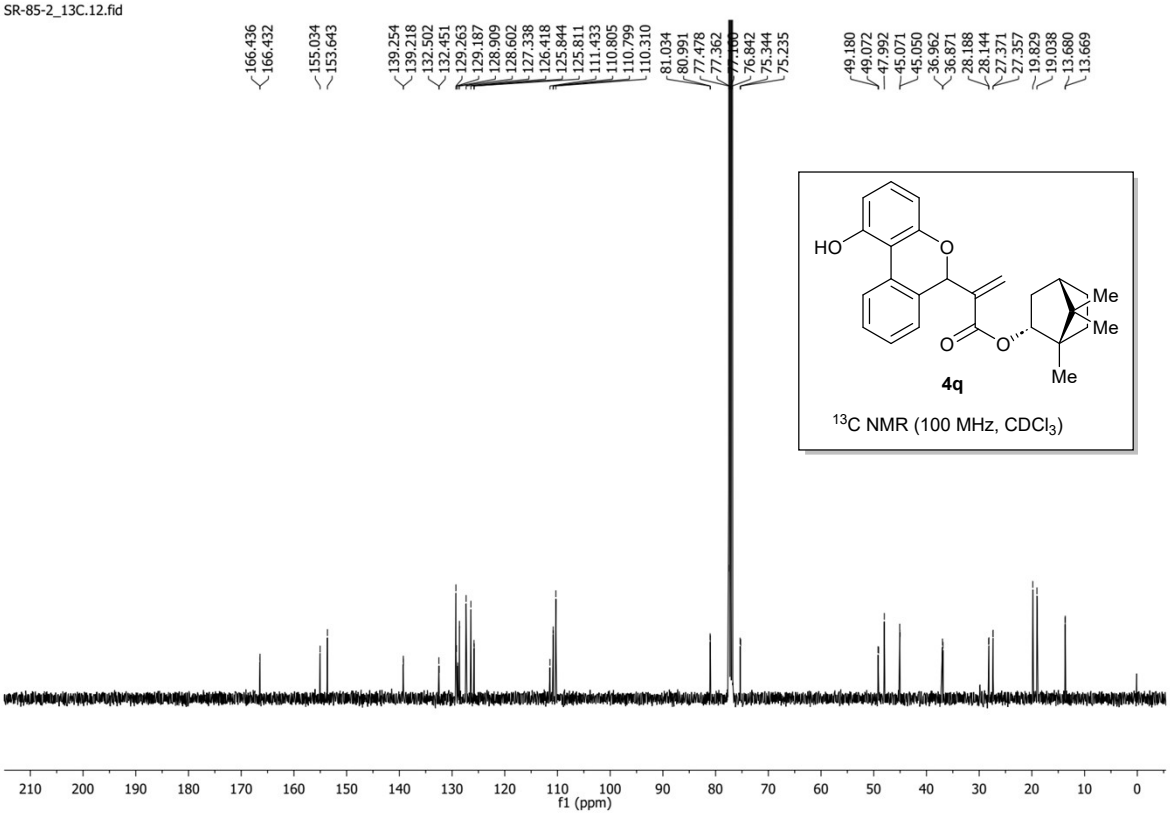

SR-69-2-13C.1.fid
165.601
155.040
153.673
139.450
132.536
129.261
128.922
128.808
128.567
127.328
126.404
125.892
111.453
110.785
110.302
77.416
77.160
76.908
75.066
73.469
31.600
25.530
23.706
HO
O
O
O
4o
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SR-83-2-1H.1.fid
8.422
8.397
7.414
7.395
7.376
7.290
7.268
7.260
7.115
7.097
7.046
7.039
7.025
7.019
7.005
6.999
6.565
6.545
6.476
6.456
6.299
6.277
6.107
5.423
5.398
4.890
4.879
4.863
4.836
4.819
4.808
2.093
2.049
1.986
1.828
1.804
1.787
1.707
1.682
1.664
1.522
1.478
1.428
1.367
1.098
1.054
1.027
0.996
0.928
0.910
0.890
0.859
0.842
0.802
0.785
6.299
6.277
1.02
1.00
f1 (ppm)
HO
O
O
O
Me
Me
Me
4p
1H NMR (400 MHz, CDCl3)
2.01
2.03
2.00
2.01
2.02
2.00
2.04
1.02
1.00
2.00
4.01
2.01
3.07
1.00
4.06
4.03
4.09
10.08
4.08
6.14
f1 (ppm)

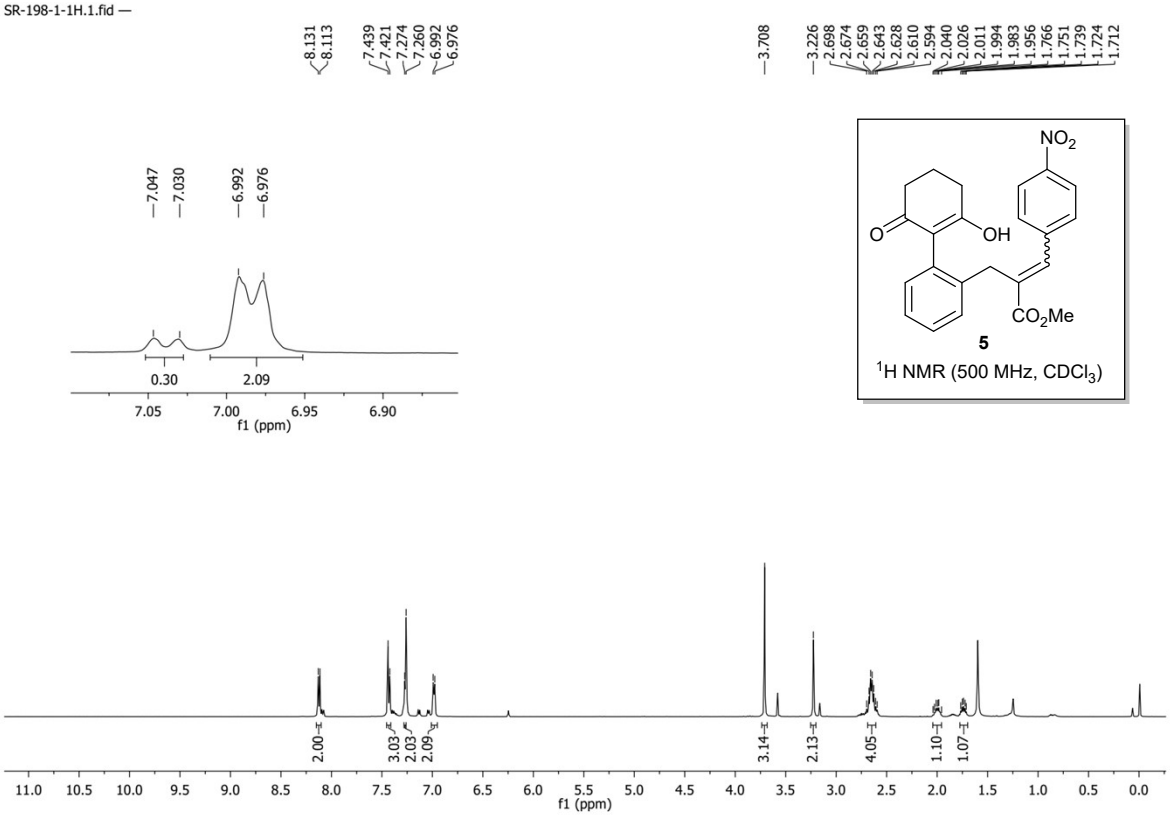

SR-83-2-13C.1.fid
HO
O
Me
O
O
Me
Me
4p
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

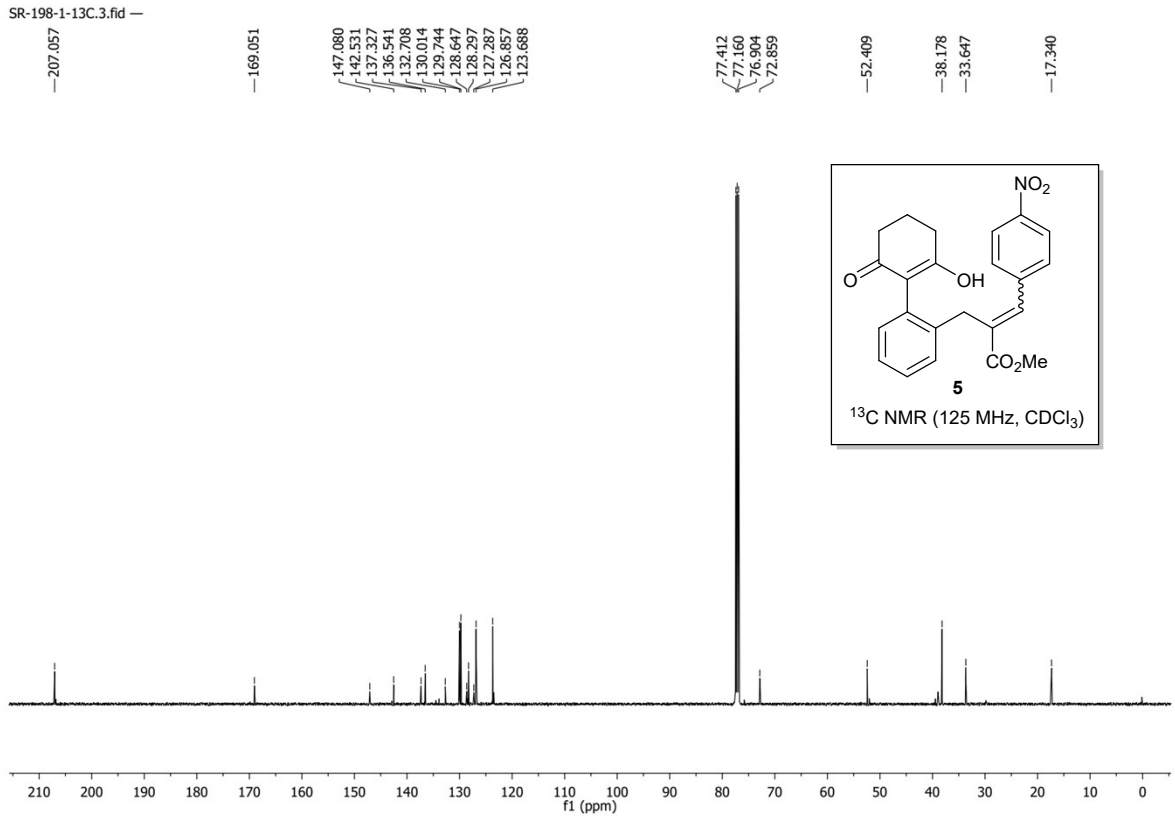

SR-85-2-1H.1.fid
HO
O
Me
O
O
Me
Me
4q
$^{1}$H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

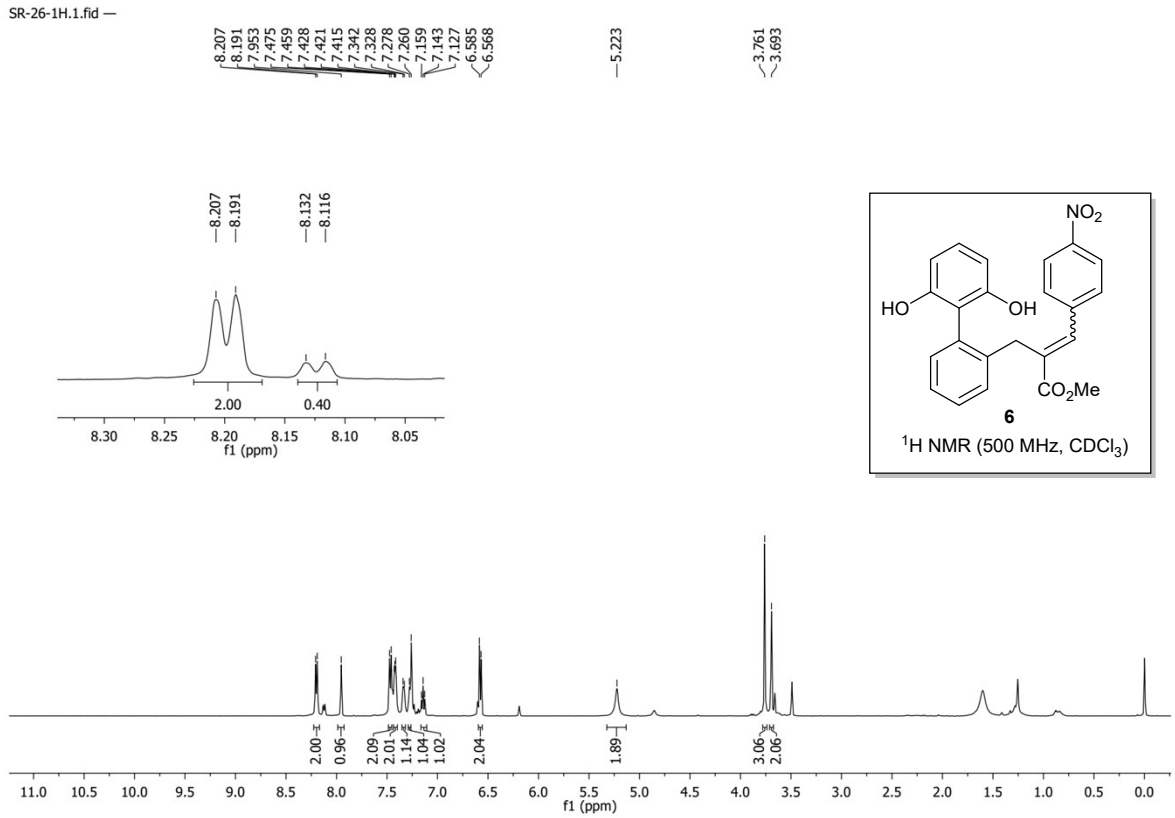
SR-85-2_13C.12.fid

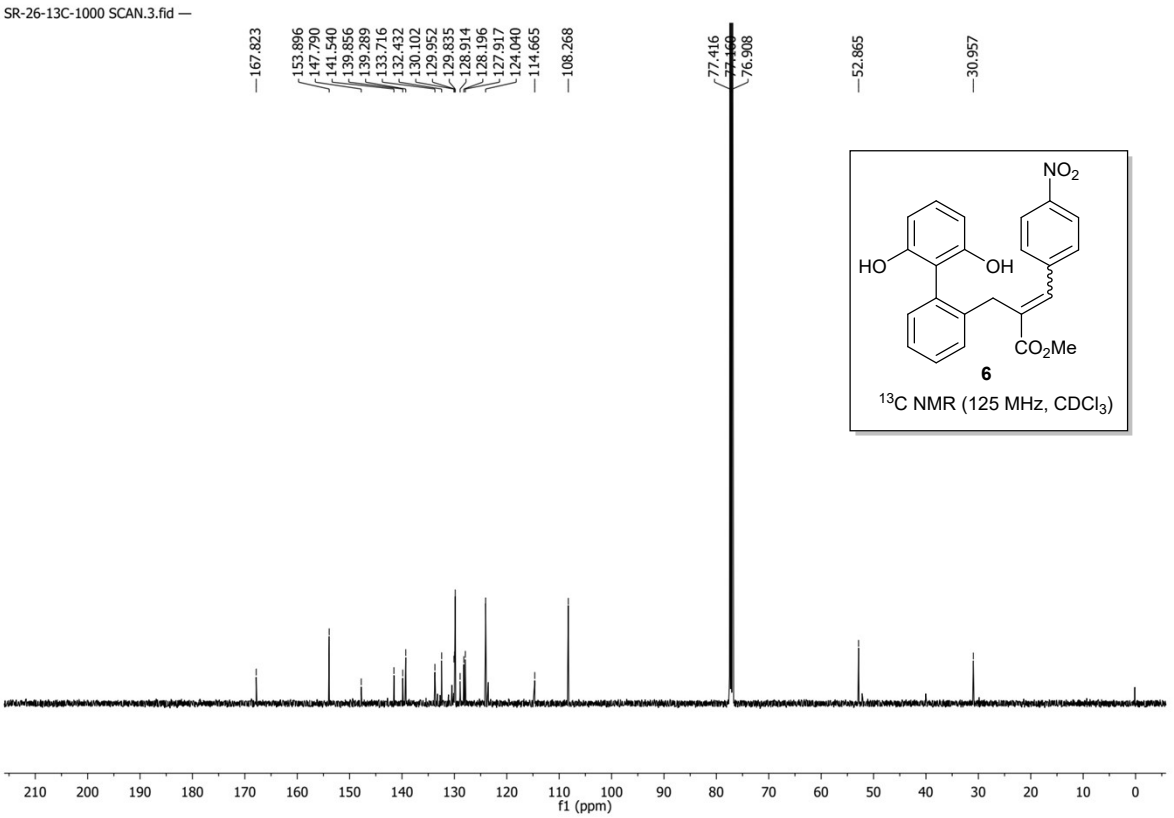


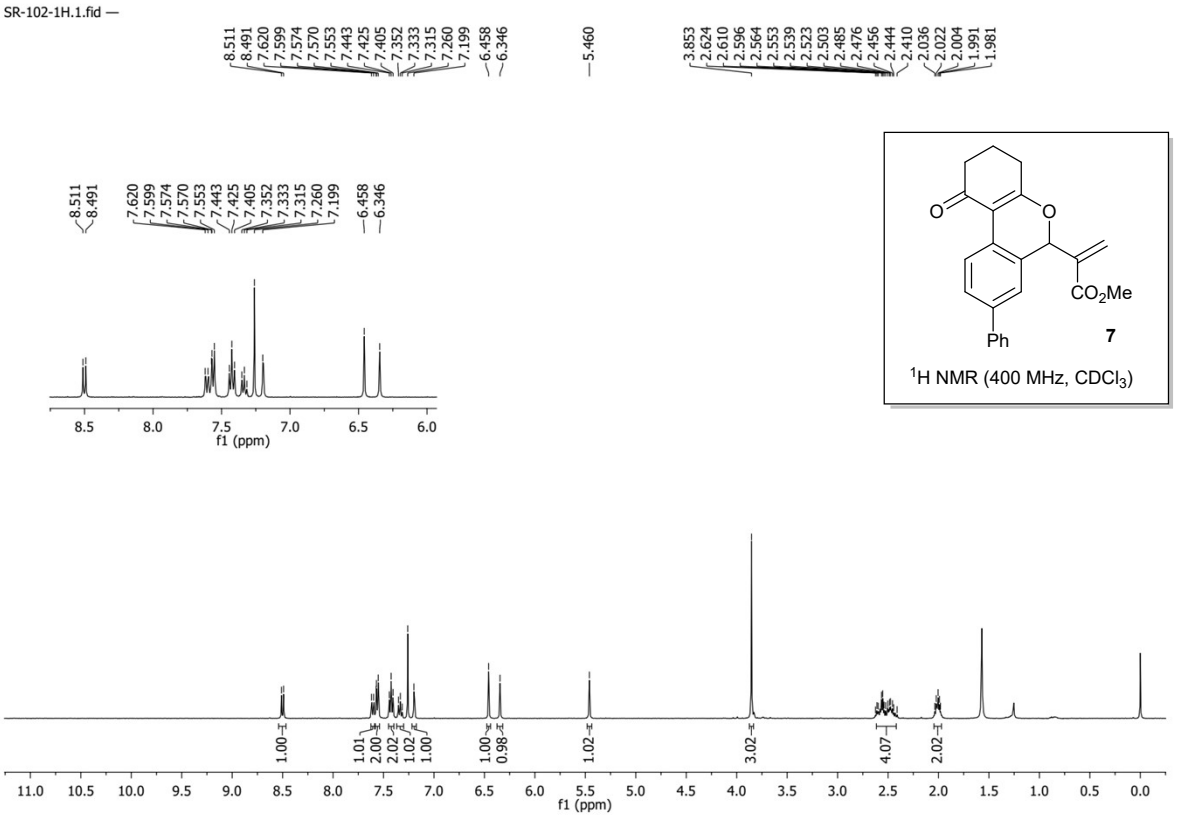

SR-198-1-1H.1.fid —

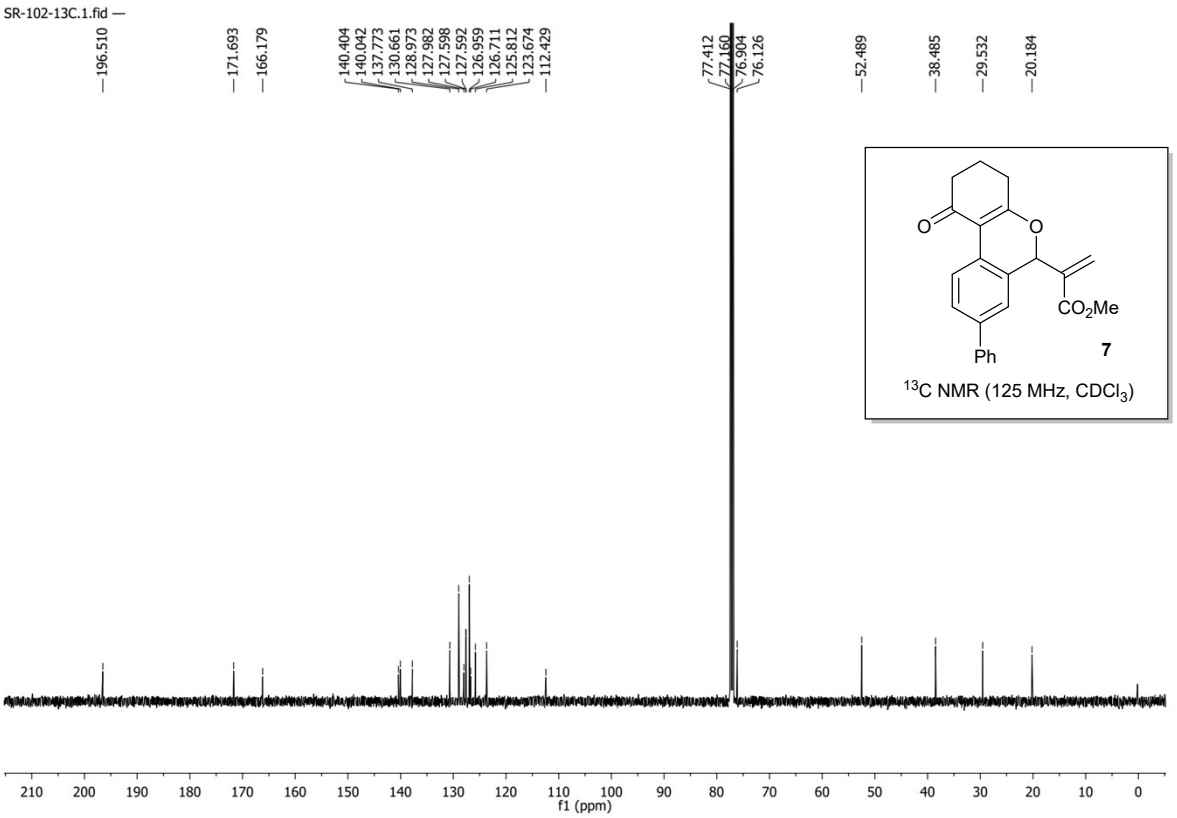


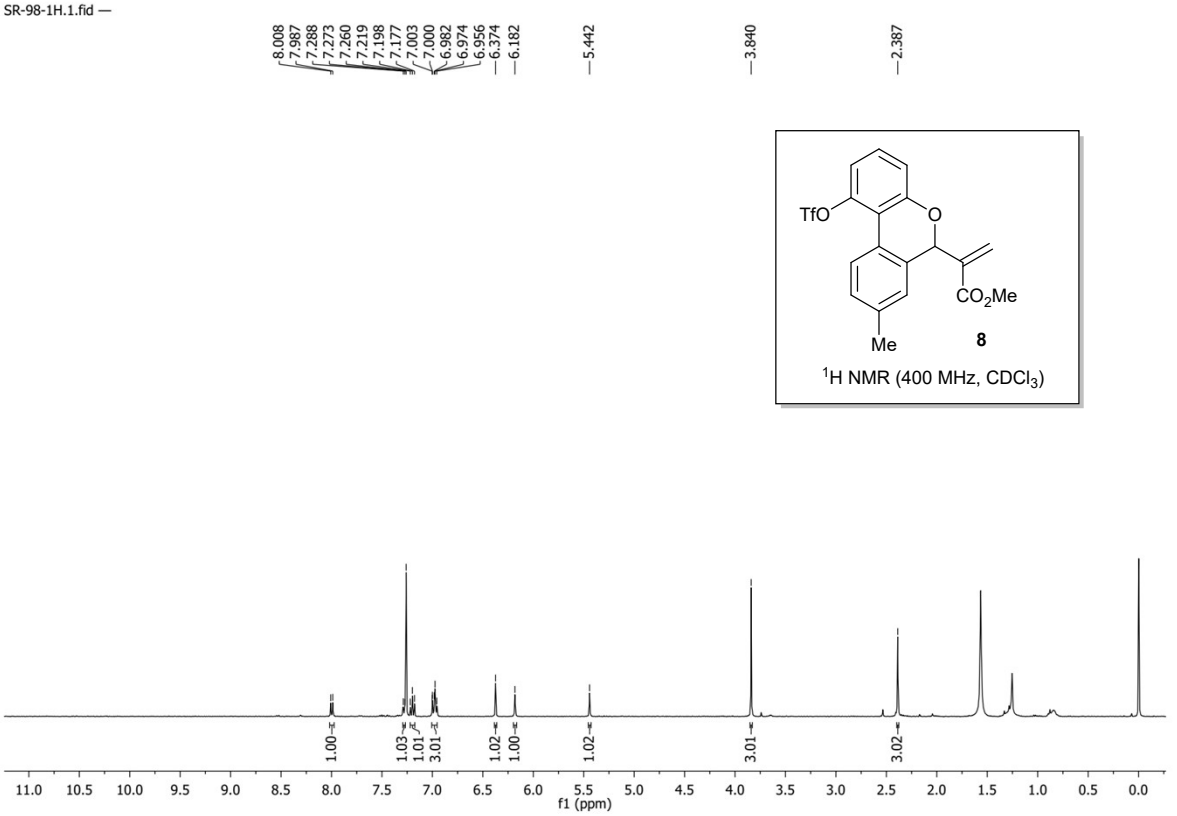

SR-198-1-13C.3.fid
207.057
169.051
147.080
142.531
137.327
136.541
132.708
130.014
129.744
128.647
128.297
127.287
126.857
123.688
77.412
77.160
76.904
72.859
52.409
38.178
33.647
17.340
NO2
OH
O
CO2Me
5
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SR-26-1H.1.fid
8.207
8.191
7.953
7.475
7.459
7.428
7.421
7.415
7.342
7.328
7.278
7.260
7.159
7.143
7.127
6.585
6.568
5.223
3.761
3.693
8.207
8.191
8.132
8.116
2.00
0.40
f1 (ppm)
NO2
HO
OH
CO2Me
6
1H NMR (500 MHz, CDCl3)
2.00
0.96
2.09
2.01
1.14
1.04
1.02
2.04
1.89
3.06
2.06
f1 (ppm)

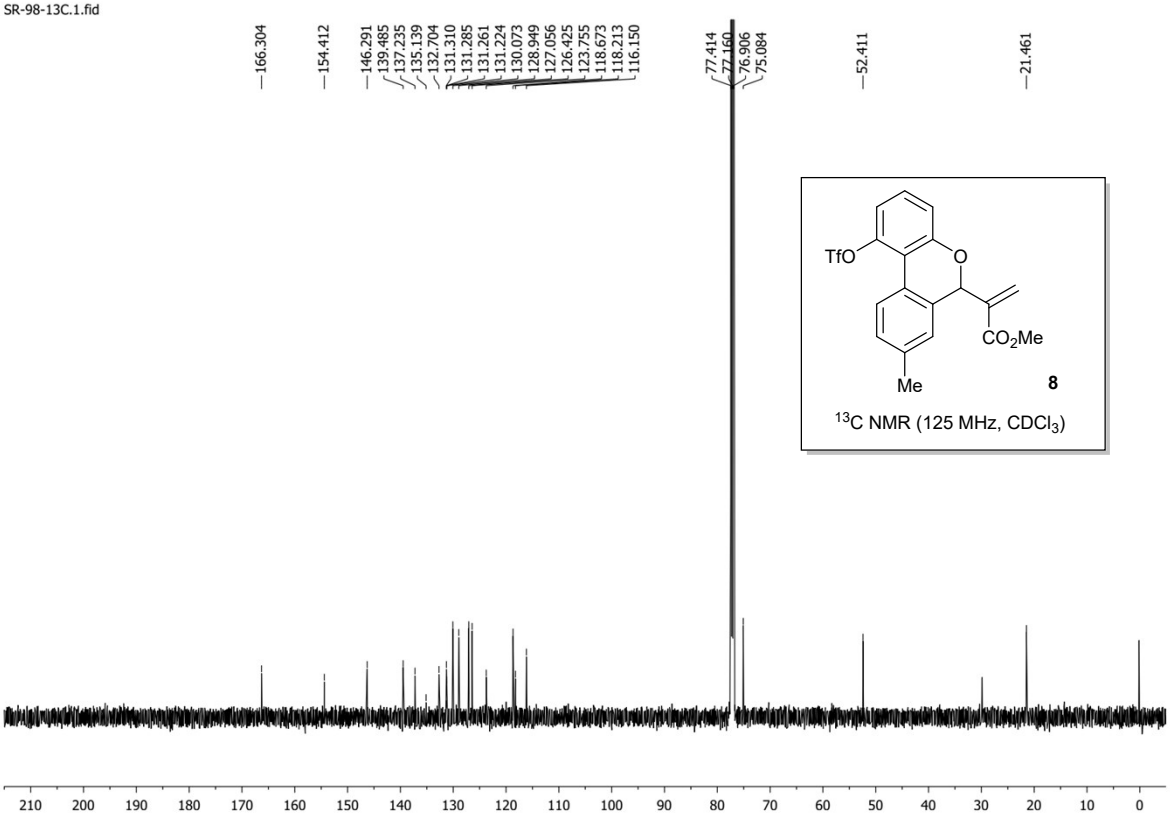

SR-26-13C-1000 SCAN.3.fid
167.823
153.896
147.790
141.540
139.856
139.289
133.716
132.432
130.102
129.952
129.835
128.914
128.196
127.917
124.040
114.665
108.268
77.416
77.160
76.908
52.865
30.957
NO2
HO
OH
CO2Me
6
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SR-102-1H.1.fid
8.511
8.491
7.620
7.599
7.574
7.570
7.553
7.443
7.425
7.405
7.352
7.333
7.315
7.260
7.199
6.458
6.346
5.460
3.853
2.624
2.610
2.596
2.564
2.553
2.539
2.523
2.503
2.485
2.476
2.456
2.444
2.410
2.036
2.022
2.004
1.991
1.981
O
O
CO2Me
Ph
7
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.00
2.02
1.02
1.00
1.00
0.98
1.02
3.02
4.07
2.02
f1 (ppm)

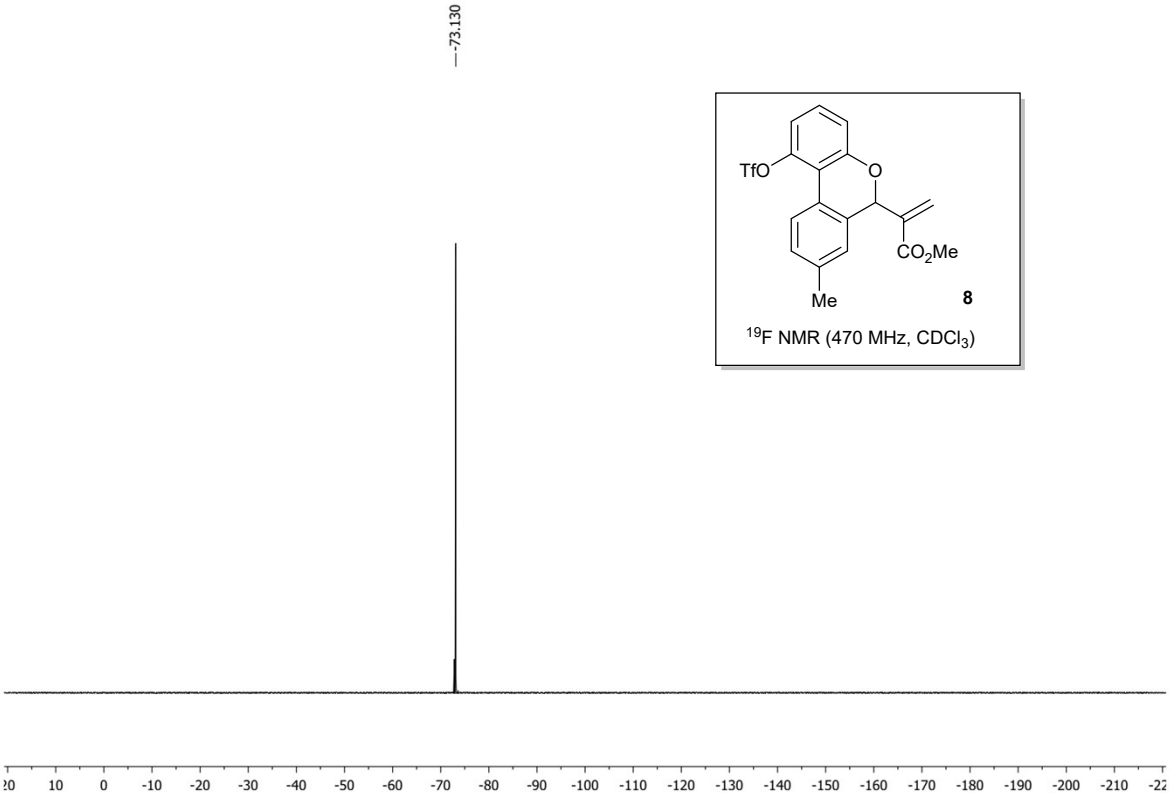

SR-102-13C.1.fid
196.510
171.693
166.179
140.404
140.042
137.773
130.661
128.973
127.982
127.598
127.592
126.959
126.711
125.812
123.674
112.429
77.412
77.160
76.904
76.126
52.489
38.485
29.532
20.184
O
O
CO2Me
Ph
7
13C NMR (125 MHz, CDCl3)
f1 (ppm)

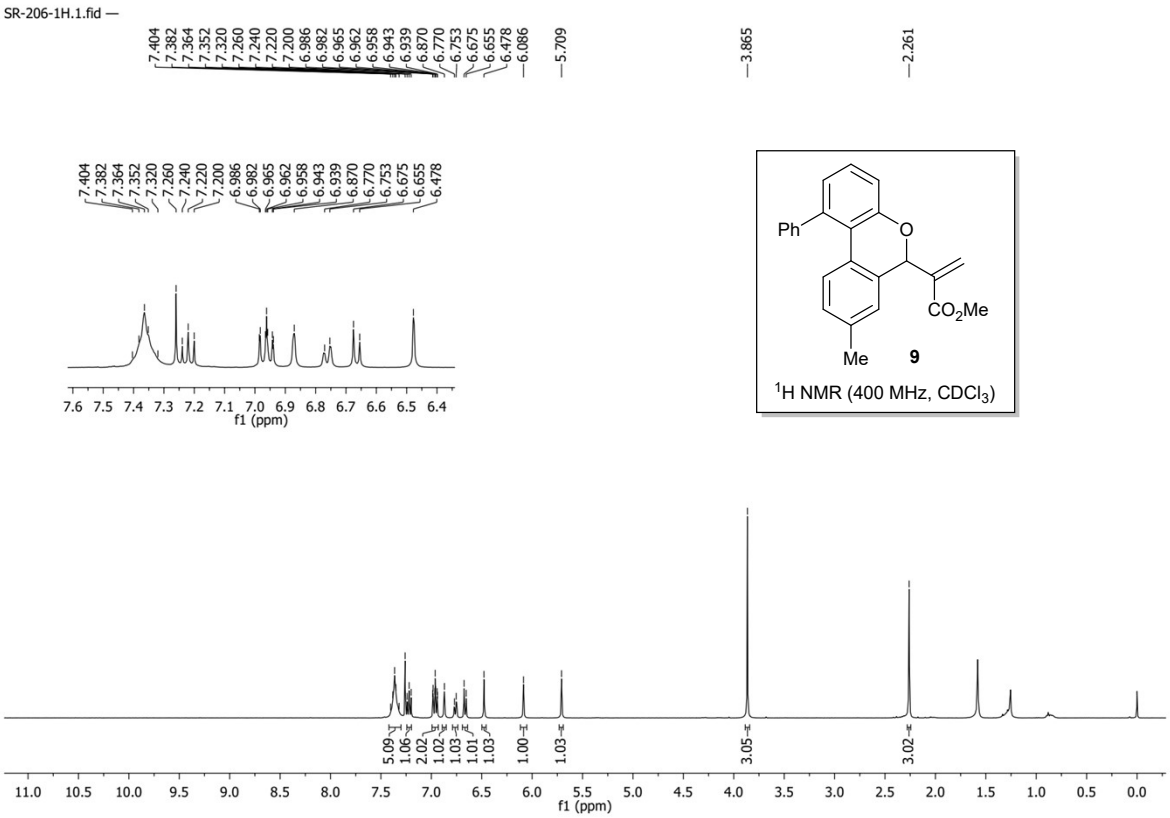

SR-98-1H.1.fid
8.008
7.987
7.288
7.273
7.260
7.219
7.198
7.177
7.003
7.000
6.982
6.974
6.956
6.374
6.182
5.442
3.840
2.387
TfO
O
CO2Me
Me
8
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.01
3.01
1.02
1.00
1.02
3.01
3.02
f1 (ppm)

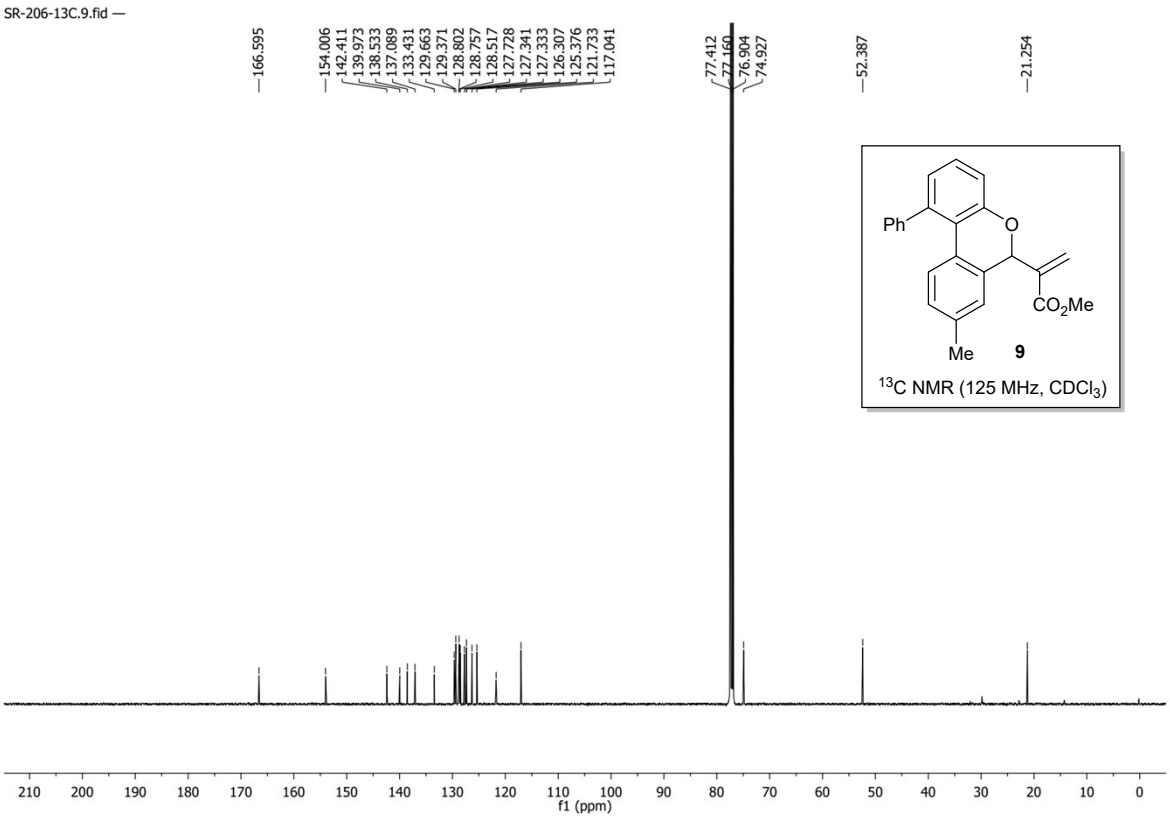
SR-98-13C.1.fid



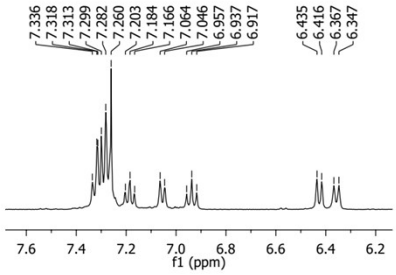

SR-98-19F.3.fid

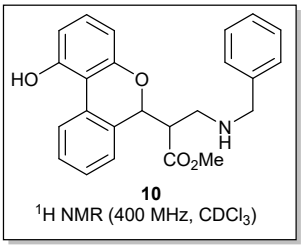



SR-206-1H.1.fid
7.404
7.382
7.364
7.352
7.320
7.260
7.240
7.220
7.200
6.986
6.982
6.965
6.962
6.958
6.943
6.939
6.870
6.770
6.753
6.675
6.655
6.478
6.086
5.709
3.865
2.261
Ph
O
CO2Me
Me
9
1H NMR (400 MHz, CDCl3)
5.09
1.06
2.02
1.02
1.03
1.01
1.03
1.00
1.03
3.05
3.02
f1 (ppm)


SR-206-13C.9.fid
166.595
154.006
142.411
139.973
138.533
137.089
133.431
129.663
129.371
128.802
128.757
128.517
127.728
127.341
127.333
126.307
125.376
121.733
117.041
77.412
77.160
76.904
74.927
52.387
21.254
Ph
O
CO2Me
Me
9
13C NMR (125 MHz, CDCl3)
f1 (ppm)

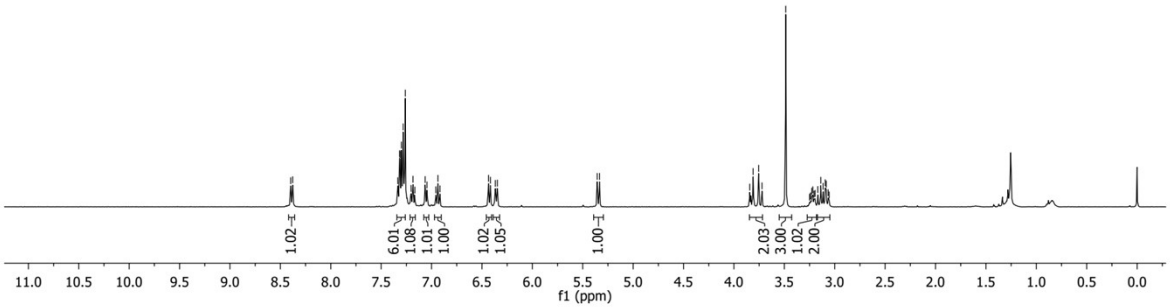
SR-202-2-1H.1.fid —



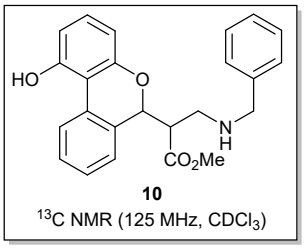



**10**

$^{1}$H NMR (400 MHz, $CDCl_3$)

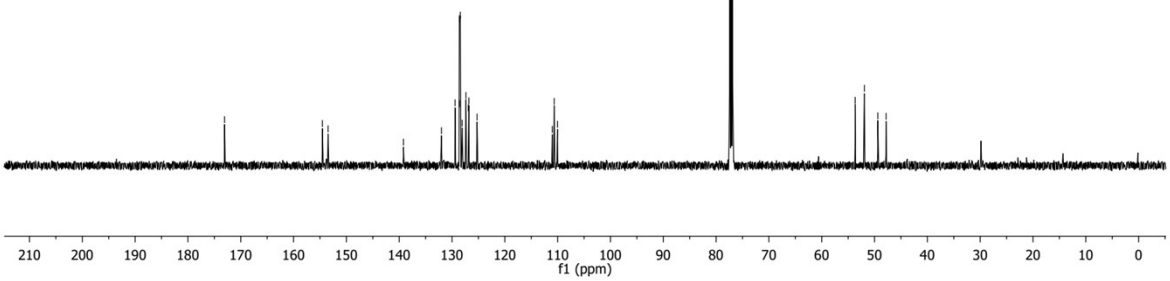


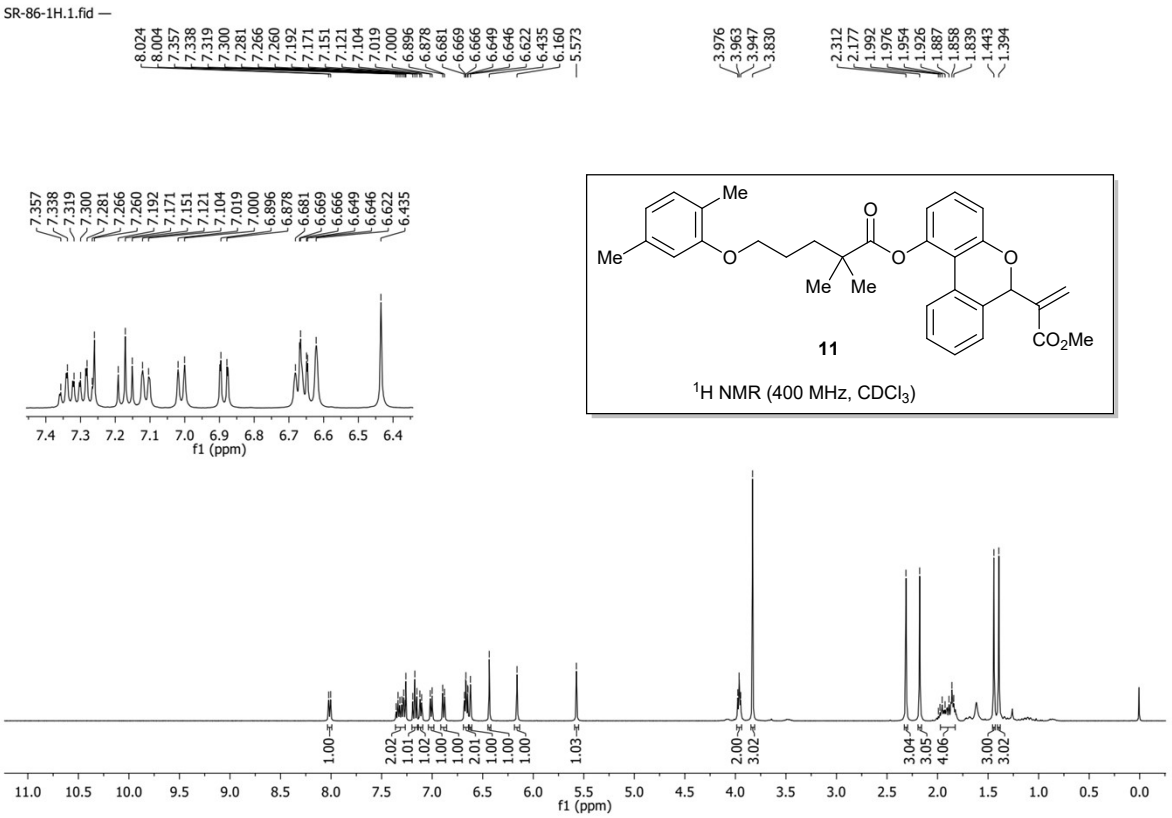
SR-202-2-13C.3.fid —

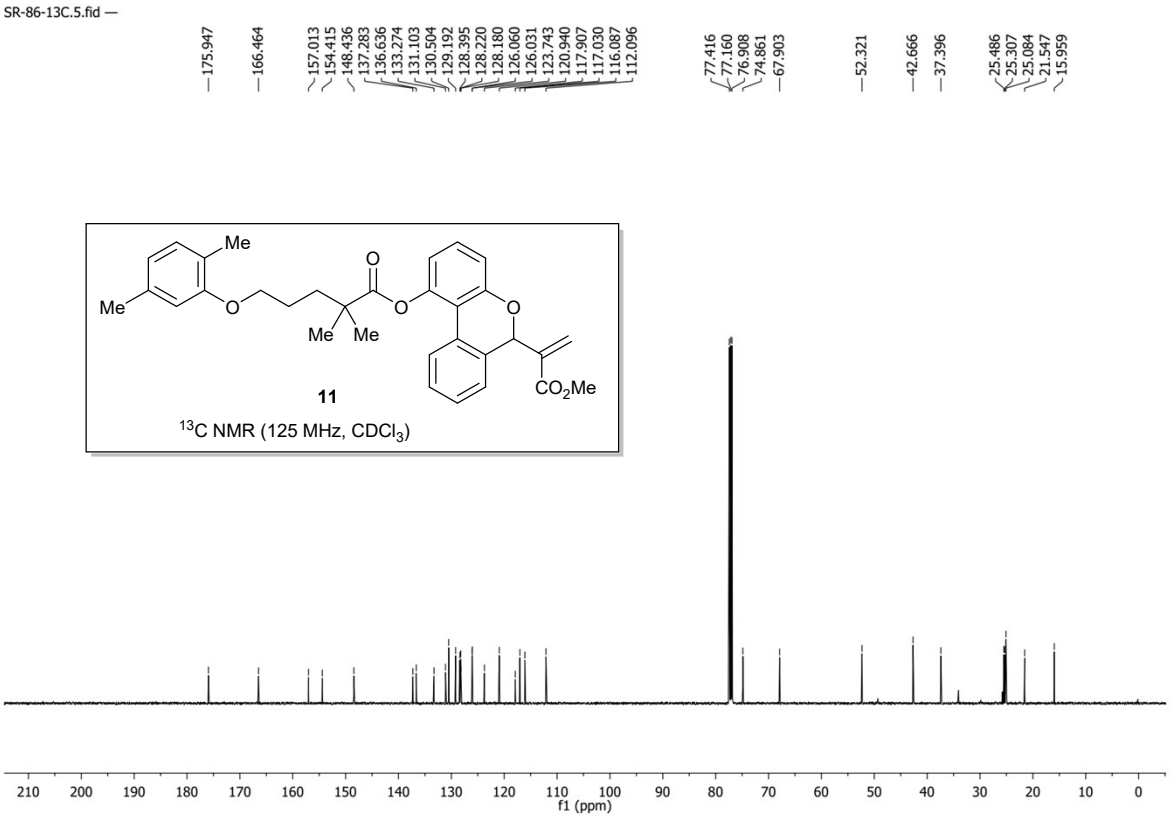



**10**

$^{13}$C NMR (125 MHz, $CDCl_3$)




SR-86-1H.1.fid
11
$^1$H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


SR-86-13C.5.fid
11
$^{13}$C NMR (125 MHz, $CDCl_3$)
f1 (ppm)