Supporting Information

Rh-Catalyzed Diastereoselective Desymmetrization of Enone Tethered-Cyclohexadienone via Tandem Arylative Cyclization

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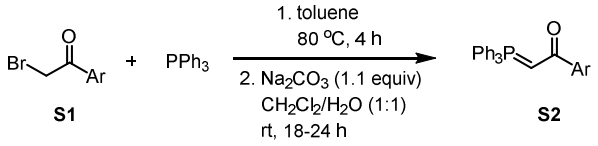
I. General details

***General information*:** Unless otherwise noted, all reagents were used as received from commercial suppliers. All reactions were performed under nitrogen atmosphere and in a flame-dried or oven-dried glassware with magnetic stirring. All solvents were dried before use following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain or *β*-naphthol stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 100, 125 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: $\delta = 7.26$ and C: $\delta = 77.16$ ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

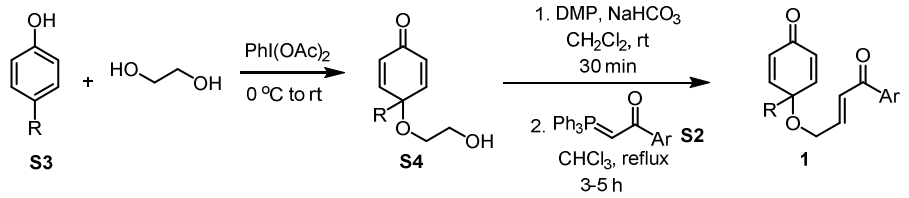
II. Experimental procedures and analytical data

IIa. General Procedure for the Preparation of Phosphoranes



To a stirred solution of 2-bromoacetophenone **S1** (1 equiv) in toluene (0.3 M) was added PPh_3 (1.1 equiv) at room temperature. The resulting reaction mixture was stirred at 80 °Cfor 4 h. Then the resulting precipitate was filtered, washed with more Et_2O, and dried in *vacuo* to give the phosphonium salt. To a solution of phosphonium salt in CH_2Cl_2 and was added Na_2CO_3 (1.1 equiv) in H_2O (1 M) and the resulting biphasic solution was stirred vigorously at room temperature for 18 h. The layers were separated and the aqueous layers was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in *vacuo* to give the phosphorene **S2**. The crude Witting reagent **S2** was used for next reaction without further purification.

IIb. General Procedure for the Synthesis of Enone Tethered-Cyclohexadienones 1:

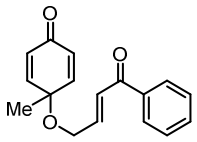


To a stirred solution of phenol **S3** (10 mmol) in CH_2Cl_2 (2 mL) and ethylene glycol (300 mmol) was added $PhI(OAc)_2$ (15 mmol, dissolved in 40 ml CH_2Cl_2) dropwise over 2 hours at room temperature under inert atmosphere. After completion of addition, the reaction mixture was stirred for another 30 minutes and then concentrated in *vacuo*. The crude residue was purified by column chromatography (EtOAc/hexane) to give the desired alcohol **S4**.

To a stirred solution of pure alcohol **S4** in CH_2Cl_2 (0.1 M) was added Dess Martin periodinane (1.2 equiv) in one portion at room-temperature and stirred the raction mixture for 1 hour under nitrogen atmosphere. The reaction mixture was filtered through Celite and then concentrated in *vacuo.* The crude product was purified by column chromatography (EtOAc/hexane) to give aldehyde in excellent yields.

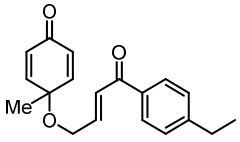
The solution of aldehyde in $CHCl_3$ (0.3 M) was added desired phosphorene **S2** (1.2 equiv) in one portion at room temperature under nitrogen atmosphere. The reaction mixture stirred at 65 ^oC for 3 to 5 h and then concentrated in *vacuo*. The crude reaction mixture was purified by column chromatography (EtOAc/petroleum ether) to give enone tethered-cyclohexadienones **1** in good yields.

(*E*)-4-methyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1a):



Prepared according to the general procedure as described above in 67% yield (541 mg). It was purified by flash chromatography (20% EtOAc/hexanes; $R_f = 0.4$) to afford as a orange liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.60 – 7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.18 – 7.11 (m, 1H), 6.98 (dt, J = 15.4, 4.1 Hz, 1H), 6.84 – 6.78 (m, 2H), 6.35 – 6.30 (m, 2H), 4.12 (dd, J = 4.1, 2.2 Hz, 2H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 185.0, 151.2, 144.3, 137.7, 133.0, 130.7, 128.7, 125.0, 73.0, 64.9, 26.4; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $[M+H]^+$: 269.1178; found: 269.1178.

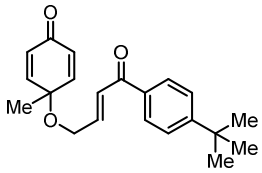
(*E*)-4-((4-(4-Ethylphenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1u):



Prepared according to the general procedure as described above in 68% yield (549 mg). It was purified by flash chromatography (20% EtOAc/hexanes; $R_f = 0.4$) to afford as a orange semi solid; ^1H NMR

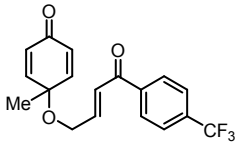
(500 MHz, CDCl3) δ 7.90 – 7.85 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.14 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.96 (dt, *J* = 15.4, 4.3 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.37 – 6.27 (m, 2H), 4.11 (dd, *J* = 4.2, 2.3 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.52 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 185.0, 151.2, 150.1, 143.7, 135.4, 130.6, 129.0, 128.2, 125.1, 73.0, 65.0, 29.0, 26.4, 15.3; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1491; found: 297.1496.

(*E*)-4-((4-(4-(*tert*-Butyl)phenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1v):



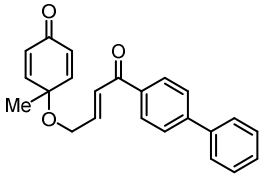
Prepared according to the general procedure as described above in 70% yield (683 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a orange solid; mp = 97–99°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H),), 7.13 (dt, *J* = 15.5, 2.0 Hz, 1H), 6.96 (dt, J = 15.4, 4.2 Hz, 1H), 6.81 (d, *J* = 10.2 Hz, 2H), 6.31 (d, *J* = 10.2 Hz, 2H), 4.11 (dd, *J* = 4.2, 2.0 Hz, 2H), 1.52 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 185.0, 156.8, 151.2, 143.7, 135.0, 130.6, 128.7, 125.7, 125.1, 72.9, 64.9, 35.2, 31.2, 26.4; HRMS (ESI) calcd for $C_{21}H_{25}O_3$ $[M+H]^+$: 325.1804; found: 325.1801.

(*E*)-4-methyl-4-((4-Oxo-4-(4-(Trifluoromethyl)phenyl)but-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1w):



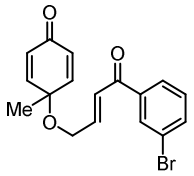
Prepared according to the general procedure as described above in 64% yield (637 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.76 – 7.69 (m, 2H), 7.16 – 7.08 (m, 1H), 7.04 – 6.97 (m, 1H), 6.82 – 6.77 (m, 2H), 6.34 – 6.29 (m, 2H), 4.12 (dd, *J* = 3.9, 1.9 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4 , 184.9, 150.9 , 145.7, 140.5, 134.2 (q, J_{CF} = 32.5 Hz), 130.7, 129.0, 125.7 (q, J_{CF} = 3.5 Hz), 123.7 (q, J_{CF} = 272.1 Hz), 124.5, 73.0, 64.7, 26.3; ; ^{19}F NMR ($CDCl_3$) δ -63.09 (s); HRMS (ESI) calcd for $C_{18}H_{16}O_3F_3$ $[M+H]^+$: 337.1052; found: 337.1046

(*E*)-4-((4-([1,1'-Biphenyl]-4-yl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1x):



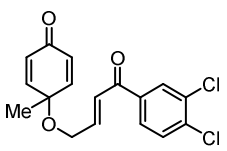
Prepared according to the general procedure as described above in 65% yield (674 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 136-138°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.20 (dt, *J* = 15.4, 2.0 Hz, 1H), 7.02 (dt, *J* = 15.4, 4.2 Hz, 1H), 6.83 (d, *J* = 10.3 Hz, 2H), 6.33 (d, *J* = 10.3 Hz, 2H), 4.14 (dd, *J* = 4.2, 2.0 Hz, 2H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 185.0, 151.1, 145.8, 144.1, 140.0, 136.4, 130.7, 129.3, 129.1, 128.4, 127.4, 125.0, 73.0, 64.9, 26.4; HRMS (ESI) calcd for $C_{23}H_{21}O_3$ $[M+H]^+$: 345.1491; found: 345.1483.

(*E*)-4-((4-(3-Bromophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1y):



Prepared according to the general procedure as described above in 63% yield (656 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 1H), 7.85 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.68 (ddd, *J* = 7.9, 1.9, 0.9 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.09 (dd, *J* = 15.4, 1.8 Hz, 1H), 6.99 (dt, *J* = 15.4, 3.8 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.34 – 6.30 (m, 2H), 4.11 (dd, *J* = 3.7, 1.6 Hz, 2H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 185.0, 151.0, 145.3, 139.4, 135.9, 131.7, 130.7, 130.3, 127.2, 124.4, 123.0, 73.0, 64.8, 26.4; HRMS (ESI) calcd for $C_{17}H_{16}O_3Br$ $[M+H]^+$: 347.0283; found: 347.0278.

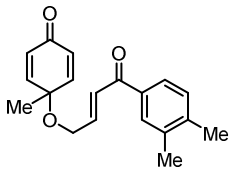
(*E*)-4-((4-(3,4-Dichlorophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1z):



Prepared according to the general procedure as described above in 62% yield (627 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford a orange solid; mp = 68–70°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 1H), 7.78 – 7.72 (m, 1H), 7.57 – 7.50 (m, 1H), 7.06 (dd,

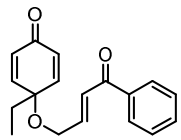
J = 15.4, 1.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.81 – 6.77 (m, 2H), 6.34 – 6.27 (m, 2H), 4.11 (dd, *J* = 3.6, 1.7 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.8, 184.9, 150.9, 145.6, 137.6, 137.2, 133.3, 130.8, 130.7, 130.6, 127.7, 123.9, 72.9, 64.7, 26.3; HRMS (ESI) calcd for $C_{17}H_{15}O_3Cl_2$ $[M+H]^+$: 337.0398; found: 337.0399.

(*E*)-4-((4-(3,4-Dimethylphenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1aa):



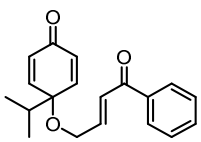
Prepared according to the general procedure as described above in 68% yield (606 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a orange solid; mp = 71–73°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.5 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.12 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.95 (dt, *J* = 15.4, 4.2 Hz, 1H), 6.81 (d, *J* = 10.2 Hz, 2H), 6.31 (d, *J* = 10.2 Hz, 2H), 4.11 (dd, *J* = 4.3, 2.0 Hz, 2H), 2.32 (s, 6H), 1.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 185.0, 151.2, 143.5, 142.7, 137.1, 135.5, 130.6, 129.9, 129.8, 126.5, 125.2, 73.0, 65.0, 26.4, 20.2, 19.9; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1491; found: 297.1489.

(*E*)-4-Ethyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ab):



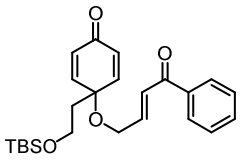
Prepared according to the general procedure as described above in 70% yield (410 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a orange oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.95 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.49 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.17 (dt, *J* = 15.4, 2.0 Hz, 1H), 7.00 (ddd, *J* = 15.5, 4.4, 3.7 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.43 – 6.37 (m, 2H), 4.18 – 4.14 (m, 2H), 1.89 (q, *J* = 7.6 Hz, 2H), 0.91 (dd, *J* = 9.5, 5.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 185.3, 150.3, 144.4, 137.6, 133.0, 131.8, 128.6, 128.7, 124.9, 76.5, 64.7, 32.4, 7.9; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1334; found: 283.1329.

(*E*)-4-Isopropyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ac):



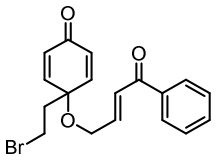
Prepared according to the general procedure as described above in 65% yield (588 mg). It was purified by flash chromatography (20% EtOAc/hexanes; $R_f = 0.4$) to afford a yellow oil; 1H NMR (400 MHz, CDCl3) δ 7.97 – 7.87 (m, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.20 – 7.13 (m, 1H), 7.02 – 6.95 (m, 1H), 6.79 – 6.73 (m, 2H), 6.43 – 6.38 (m, 2H), 4.12 (dd, *J* = 4.0, 2.0 Hz, 2H), 2.10 (hept, *J* = 7.0 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 185.3, 149.6, 144.7, 137.7, 133.0, 132.4, 128.7, 128.6, 124.7, 78.5, 64.5, 36.8 , 17.2; HRMS (ESI) calcd for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1491; found: 297.1488.

(*E*)-4-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ad):



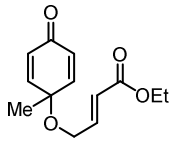
Prepared according to the general procedure as described above in 71% yield (180 mg). It was purified by flash chromatography (10% EtOAc/hexanes; $R_f = 0.4$) to afford a pale yellow oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.94 – 7.89 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 14.0, 6.7 Hz, 2H), 7.16 – 7.09 (m, 1H), 6.96 (dt, *J* = 15.4, 4.0 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.34 – 6.29 (m, 2H), 4.10 (dd, *J* = 4.0, 1.9 Hz, 2H), 3.75 (t, *J* = 6.2 Hz, 2H), 2.03 (t, *J* = 6.2 Hz, 2H), 0.84 (s, 9H), 0.00 (s, *J* = 3.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 185.3, 150.5, 144.3, 137.6, 133.0, 130.9, 128.7, 128.6, 124.8, 74.6, 64.3, 58.0, 43.0 , 25.9, 18.2, -5.4; HRMS (ESI) calcd for $C_{24}H_{32}SiNaO_4$ $[M+Na]^+$: 435.1968; found: 435.1975.

(*E*)-4-(2-Bromoethyl)-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (5):



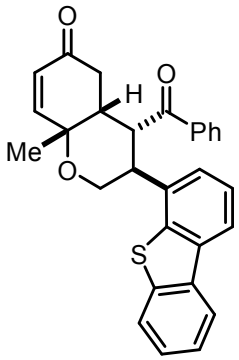
Prepared according to the general procedure as described above in 68% yield (179 mg). It was purified by flash chromatography (10% EtOAc/hexanes; $R_f = 0.4$) to afford a pale orange oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.98 – 7.92 (m, 2H), 7.62 – 7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 7.14 (dt, *J* = 15.5, 2.0 Hz, 1H), 6.97 (dt, *J* = 15.5, 4.1 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.46 – 6.38 (m, 2H), 4.14 (dd, *J* = 4.1, 2.1 Hz, 2H), 3.42 (t, *J* = 8.1 Hz, 2H), 2.44 (t, *J* = 8.1 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 184.5, 148.8, 143.6, 137.5, 133.1, 132.1, 128.7, 128.6, 125.0, 75.2, 64.6, 42.9, 25.3; HRMS (ESI) calcd for $C_{18}H_{18}BrO_3$ $[M+H]^+$: 361.0439; found: 361.0435.

Ethyl (*E*)-4-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)but-2-enoate (6):



Prepared according to the general procedure as described above in 58% yield (412 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a yellow semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.80 (m, 1H), 6.77 – 6.71 (m, 2H), 6.29 – 6.22 (m, 2H), 6.08 – 6.00 (m, 1H), 4.14 (q, *J* = 7.1 Hz 2H), 3.95 (dd, *J* = 4.2, 2.1 Hz, 2H), 1.44 (s, 3H), 1.23 (t, *J* = 7.1 Hz 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 166.2, 151.0, 144.0, 130.5, 121.3, 72.8, 64.3, 60.5, 26.2, 14.3; HRMS (ESI) calcd for $C_{13}H_{17}O_4$ $[M+H]^+$: 237.1127; found: 237.1125.

III. X-ray crystallographic data for compound 3t:



compound **3t**

Crystallographic data for 3t

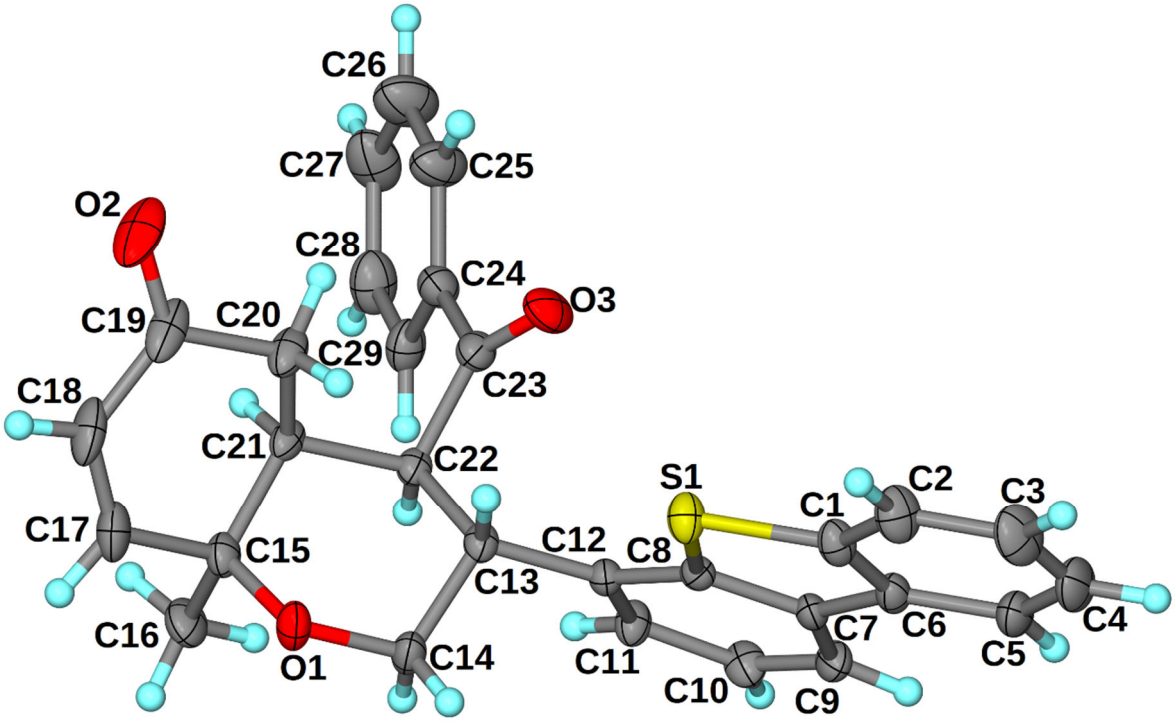


Figure caption: The molecular structure of **3t** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Only major component of the disordered atoms is shown for clarity. **CCDC 1866550** contains the supplementary crystallographic data.

Table 1: Crystal data and structure refinement.

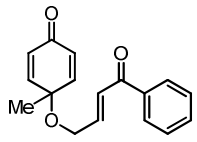
Identification code	Compound **3t**
CCDC Deposition Number	CCDC 1866550
Chemical formula	C29 H24 O3 S
Molecular weight	452.54
Temperature	293(2)
Wavelength	0.71073
Crystal system ; space group	orthorhombic ; $P2_12_12_1$
Unit cell dimentions	a = 7.942(4)Å ; b = 16.844(10)Å ; c = 17.488(11)Å α = 90 ° ; β = 90 ° ; γ = 90 °
Volume	2339(2) Å³
Z, Calculated density	4, 1.285 g/cm³
Absorption coefficient	0.167 1/mm
F(000)	952
Theta range for data collection	2.329° to 27.497°
Limiting indices	-10 <= h <= 10 ; -21 <= k <= 21 ; -22 <= l <= 22
Reflection collected / unique	25848 / 5384 [R(int) = 0.0665]
Completness to theta max	100.0 %
Refinement method	Full-matrix least-square on F²
Data / restraints / parameters	5384 / 204 / 330
Goodness of fit on F²	0.922
Final R indices [I>2sigma(I)]	R1 = 0.0529 ; wR2 = 0.1230
Final R indices [all data]	R1 = 0.1013 ; wR2 = 0.1498
Absolute structure parameter (Flack)	0.01(4)
Largest diff peak and hole	0.158 and -0.211 e/Å³

Data collection and structure solution of comound 3t: Single crystal X-ray data for two compounds were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo source (λ=0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Unit cell dimensions were determined using 8030 reflections. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[2-3] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms. The phenyl ring was disordered over two sites, with the site occupancy factor of 0.729(19) for C24/C25/C26/C27/C28/C29 atoms (major component) & 0.271(19) for C24/C25/C26/C27/C28/C29 atoms (minor component). The anisotropic displacement parameters of the disordered carbon atoms were restrained to be similar (SIMU instruction) and the direction of motion along the axis between these atoms was also restrained (DELU instruction).[3] The C-C bond distances of disordered ethyl groups were restrained to their expected values with DFIX instruction and performed the final cycle of refinement. The phenyl ring atoms were also treated as split models joining isopropyl group major and minor components respectively.

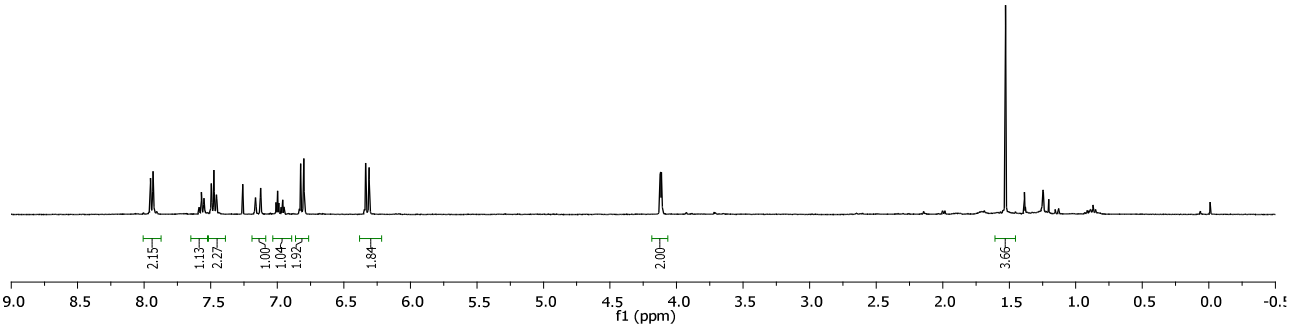
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac.gwdg.de/SHELX/index.php
3. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

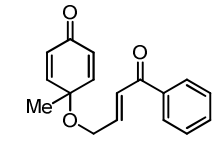
IV. ^{1}H NMR, ^{13}C NMR spectra:

(*E*)-4-Methyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1a):



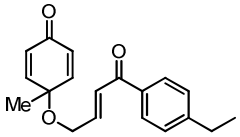
1H NMR (400 MHz, CDCl3)



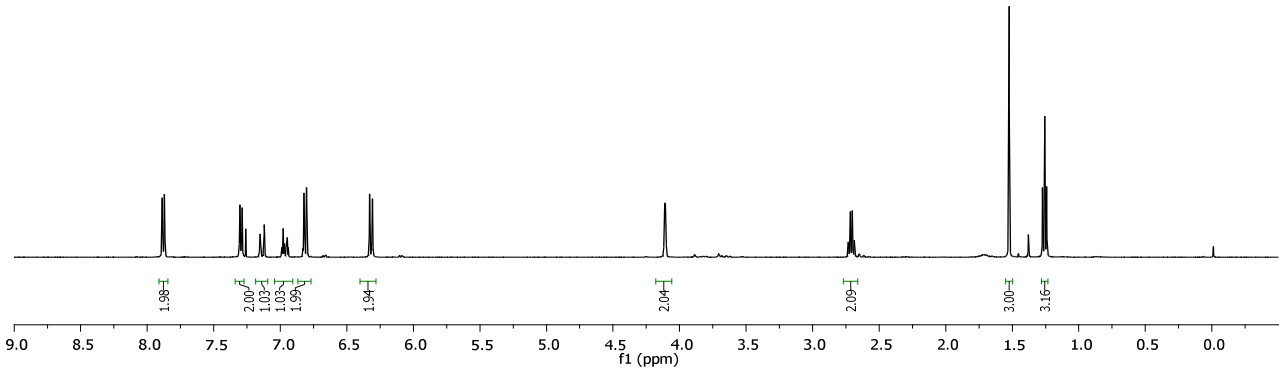


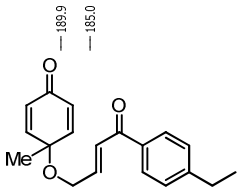
13C NMR (101 MHz, CDCl3)

(*E*)-4-((4-(4-Ethylphenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1u):



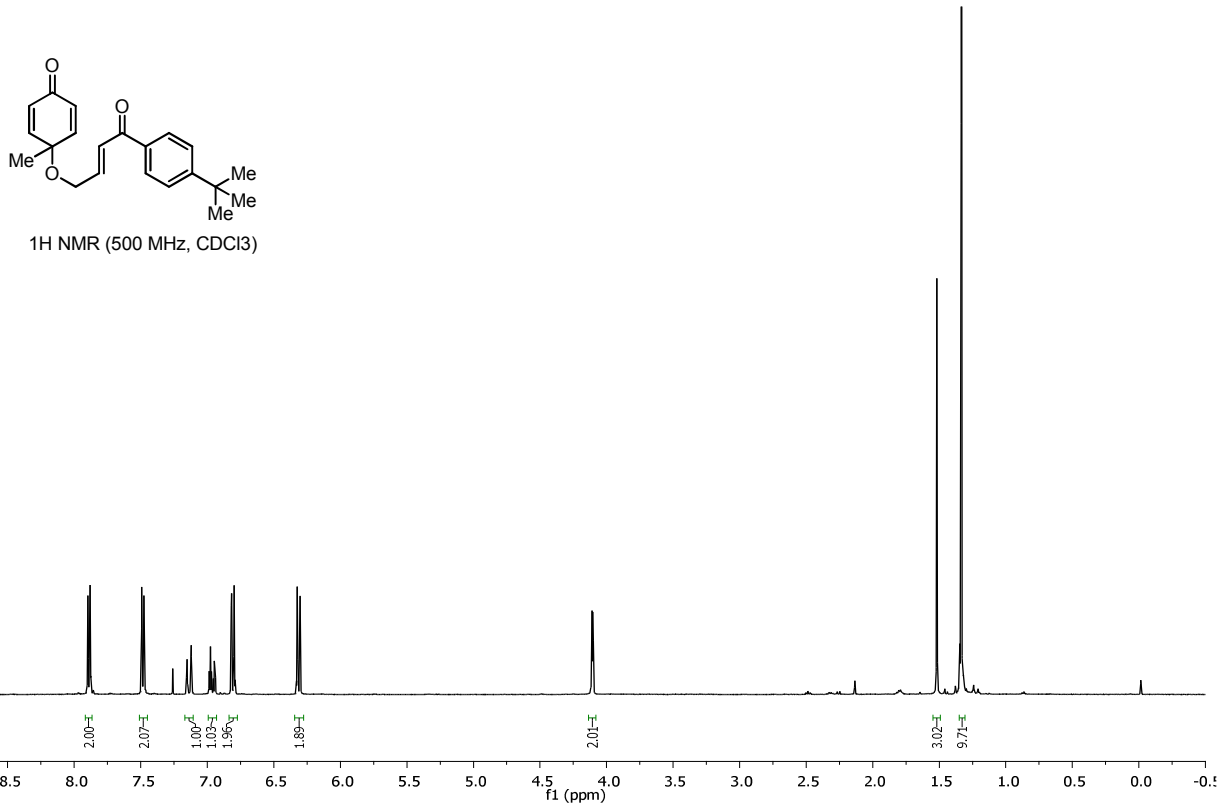
1H NMR (500 MHz, CDCl3)

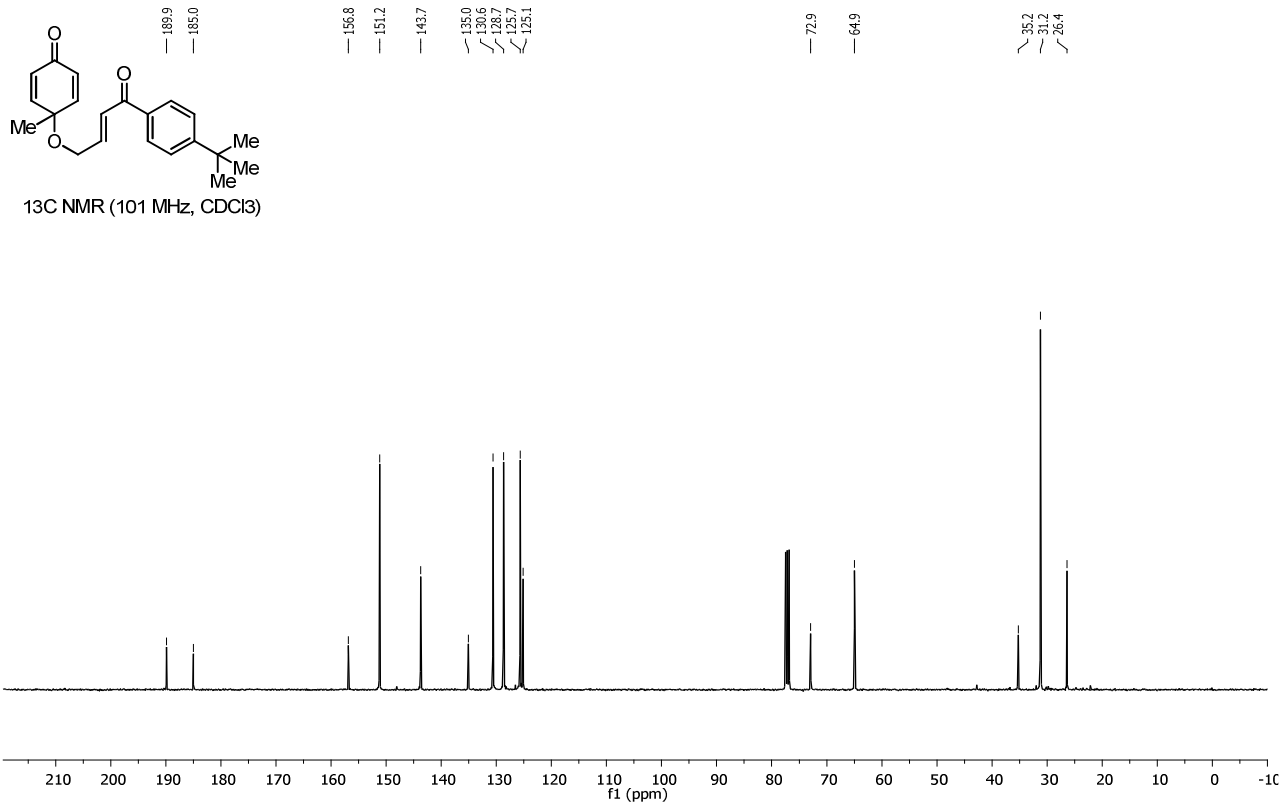




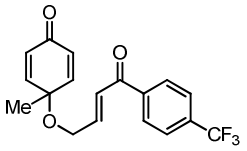
13C NMR (126 MHz, CDCl3)

(*E*)-4-((4-(4-(*tert*-Butyl)phenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1v):

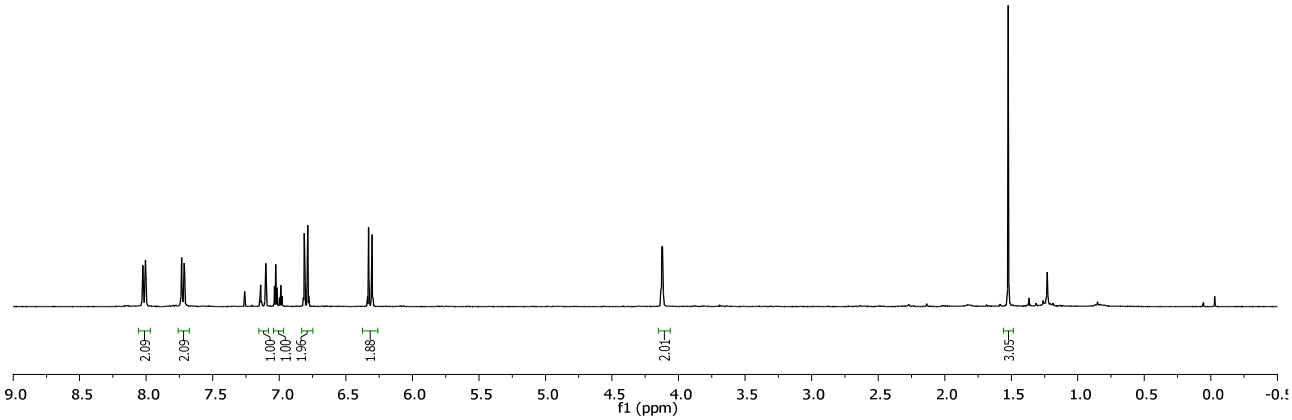


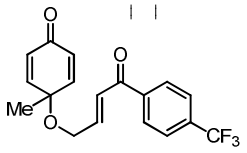


(*E*)-4-Methyl-4-((4-Oxo-4-(4-(Trifluoromethyl)phenyl)but-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1w):



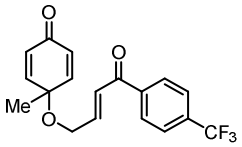
1H NMR (400 MHz, CDCl3)



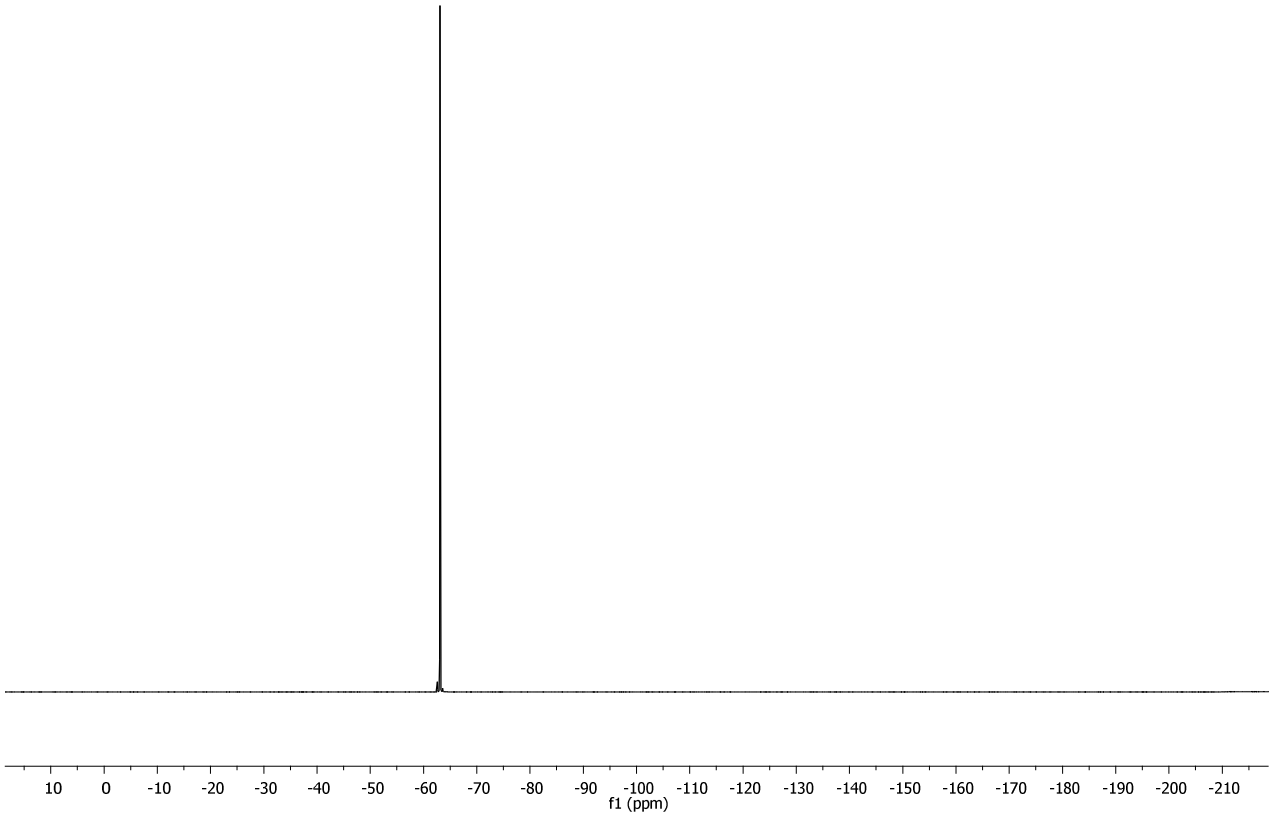


13C NMR (101 MHz, CDCl3)

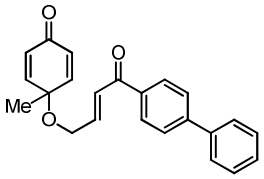
^{19}F NMR spectrum of compound 1w in $CDCl_3$



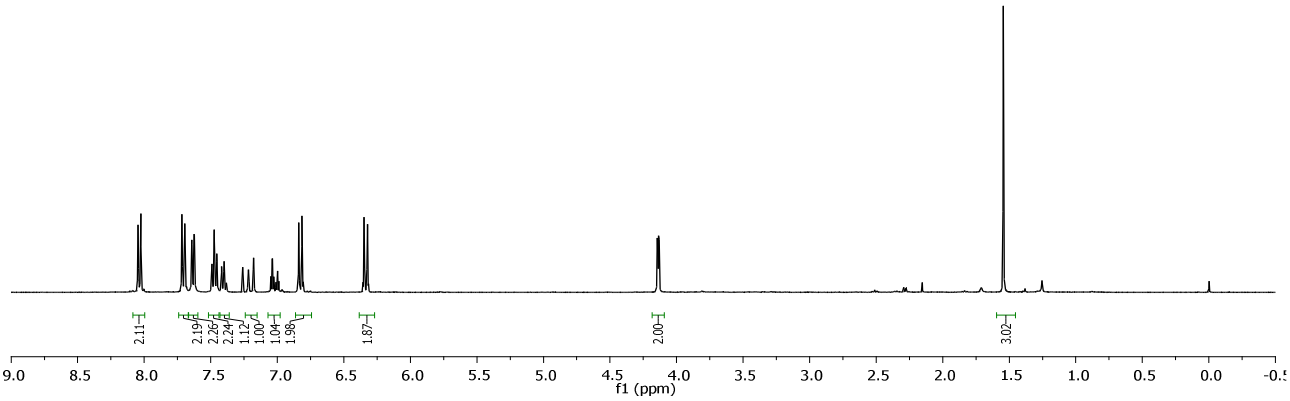
compound **1w**

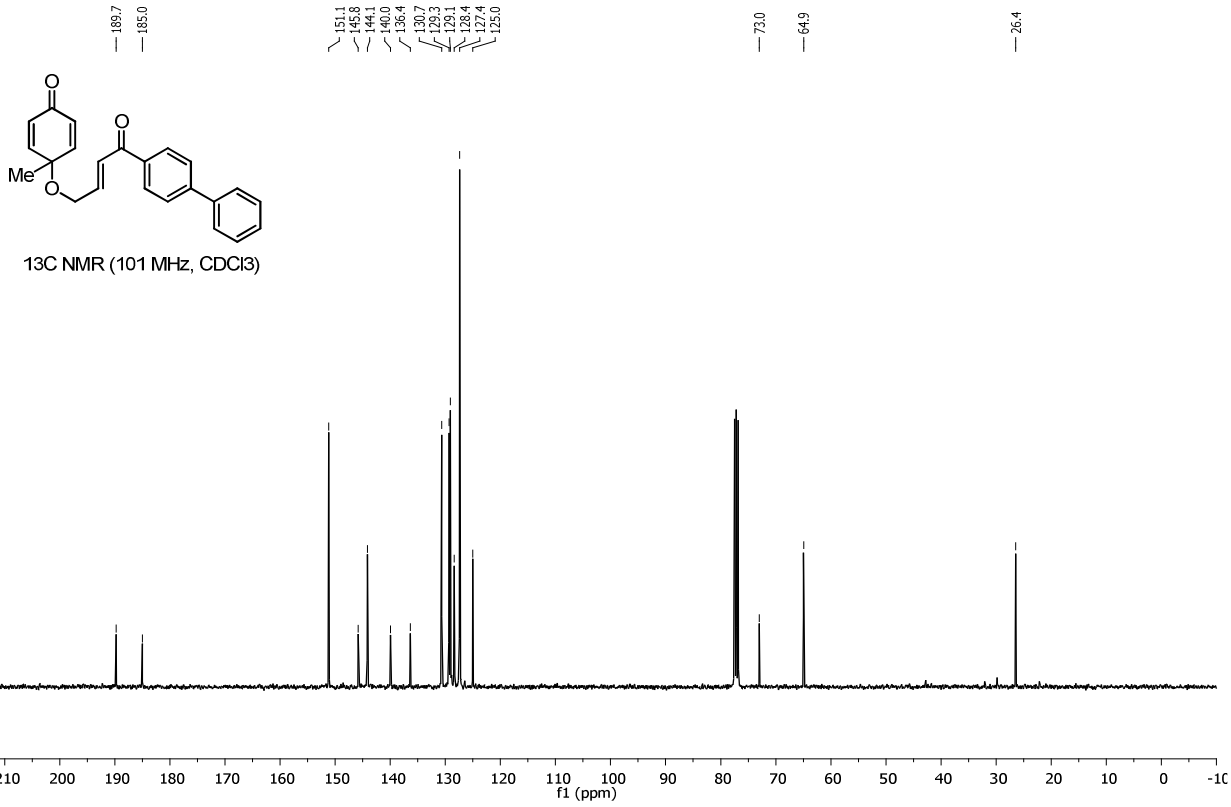


(*E*)-4-((4-([1,1'-Biphenyl]-4-yl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1x):



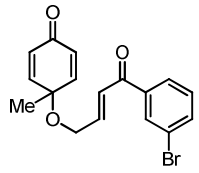
1H NMR (400 MHz, CDCl3)



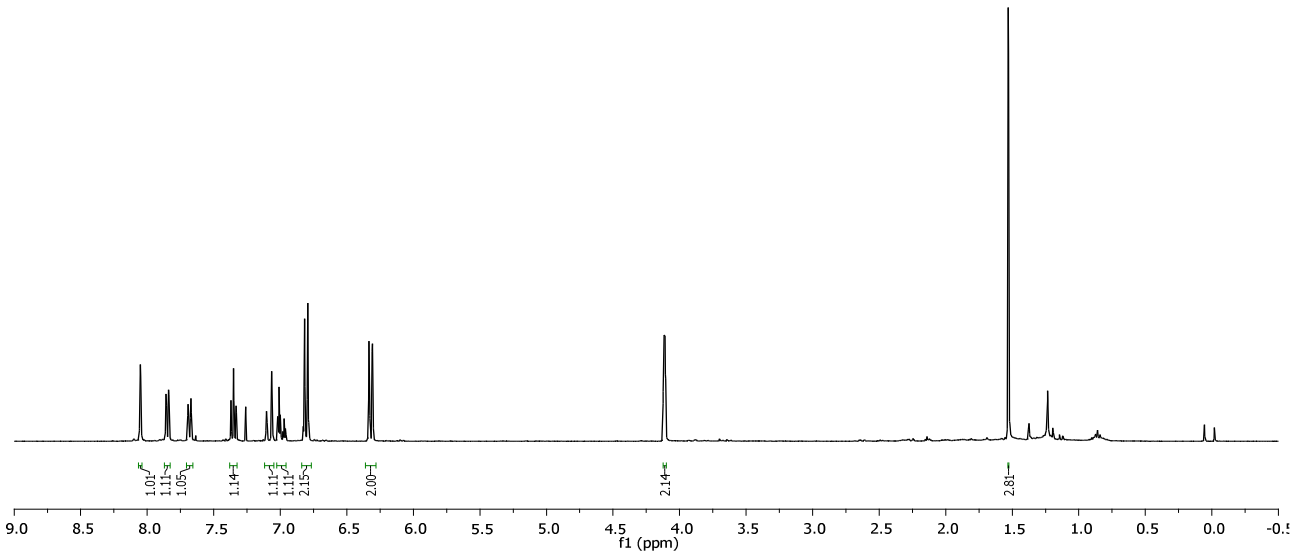


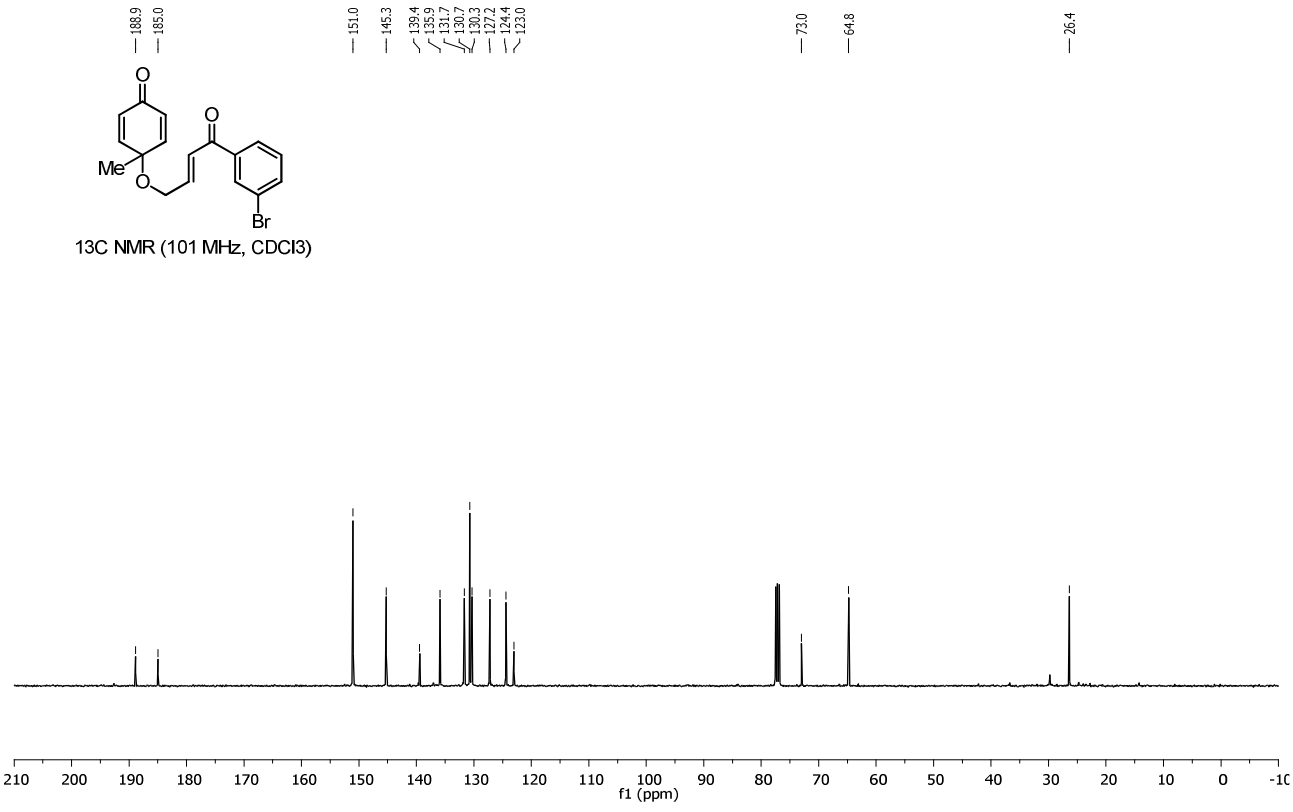
13C NMR (101 MHz, CDCl3)

(E)-4-((4-(3-Bromophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1y):



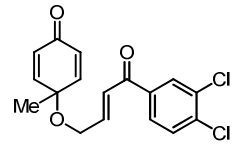
1H NMR (400 MHz, CDCl3)



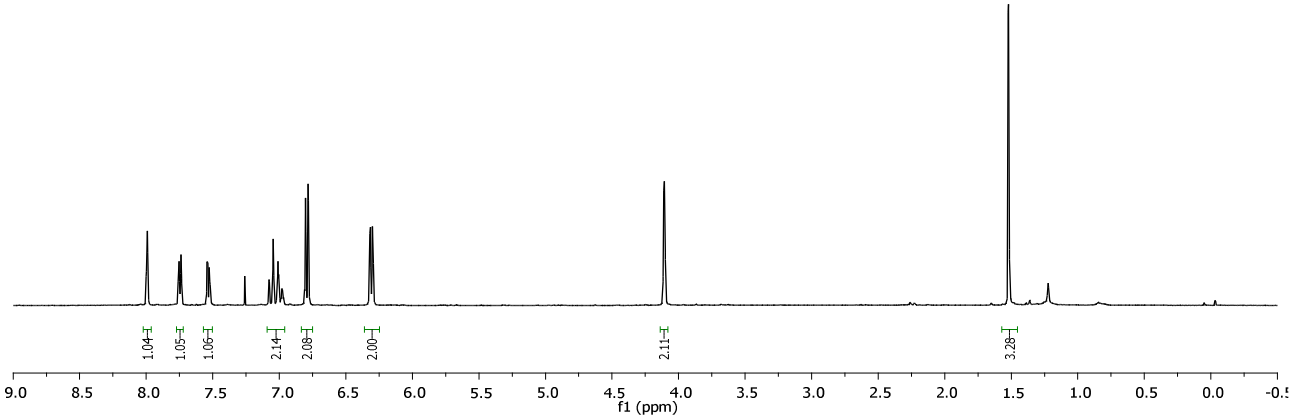


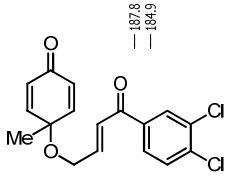
13C NMR (101 MHz, CDCl3)

(*E*)-4-((4-(3,4-Dichlorophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1z):



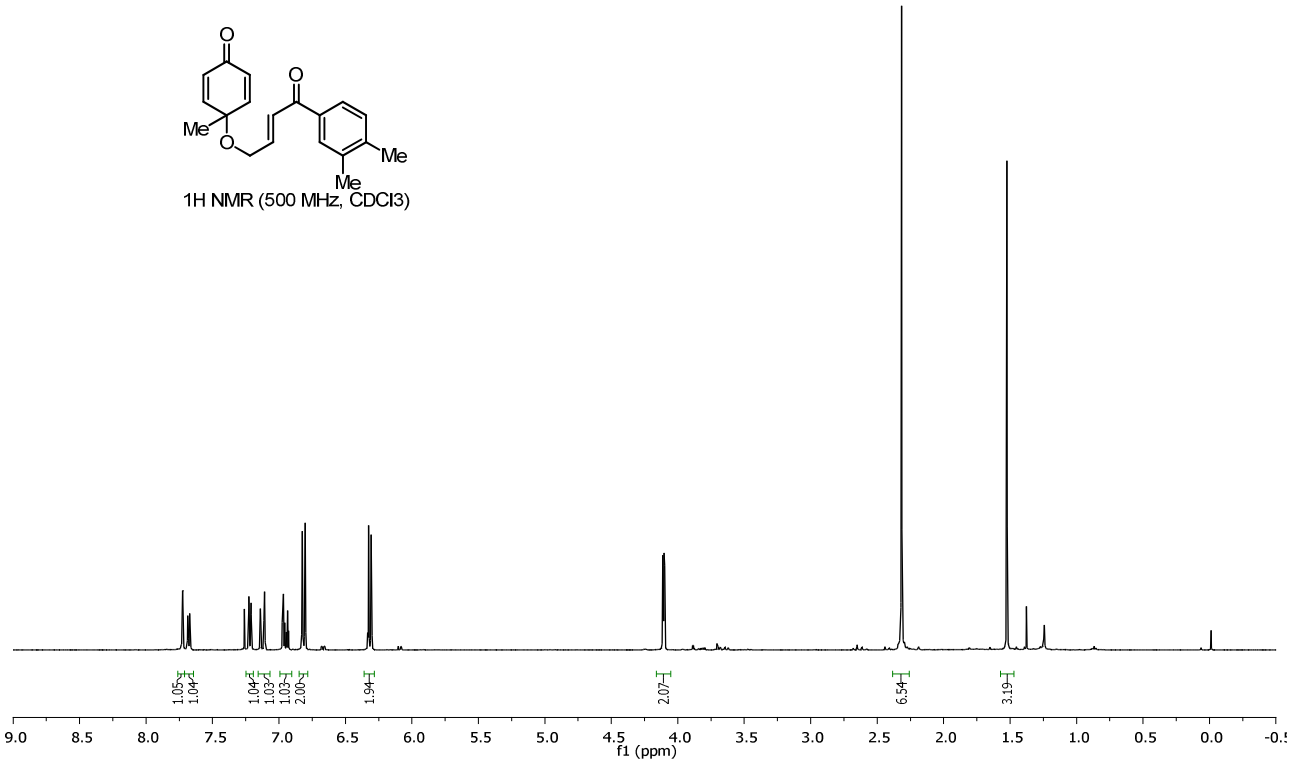
1H NMR (500 MHz, CDCl3)

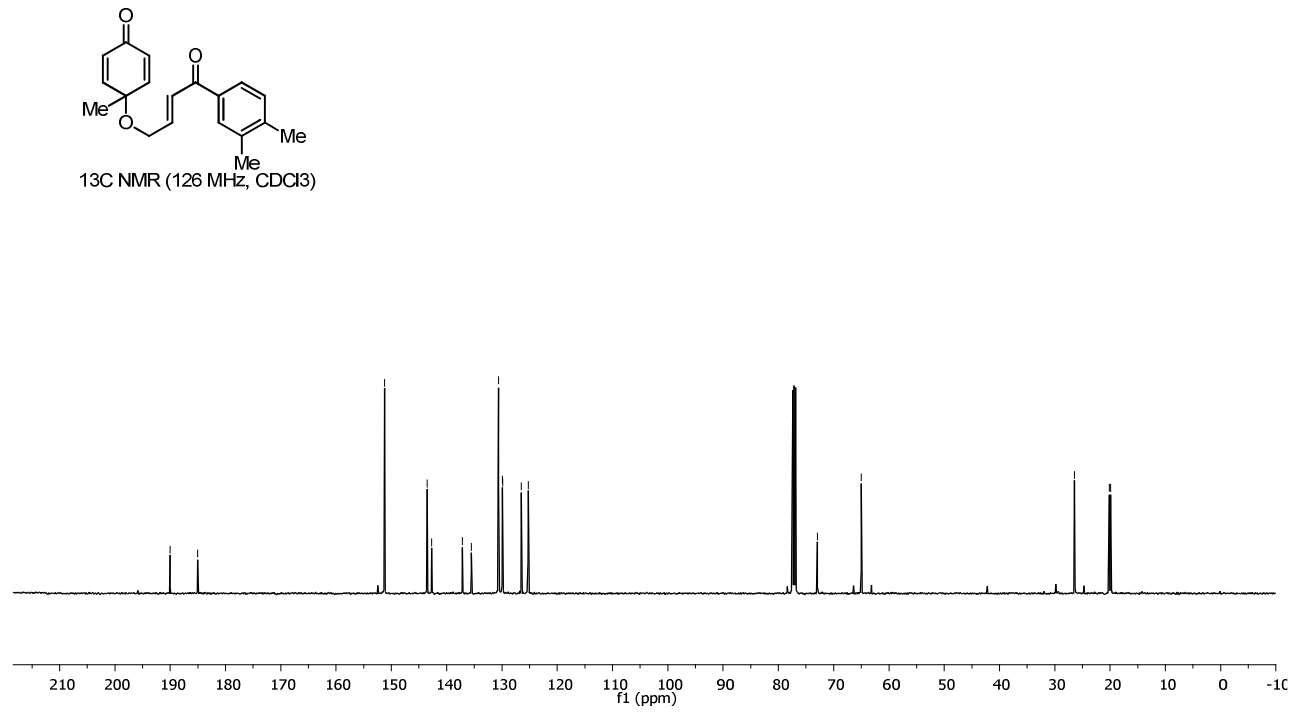




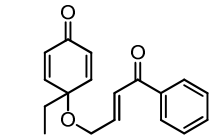
13C NMR (126 MHz, CDCl3)

(*E*)-4-((4-(3,4-Dimethylphenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1aa):

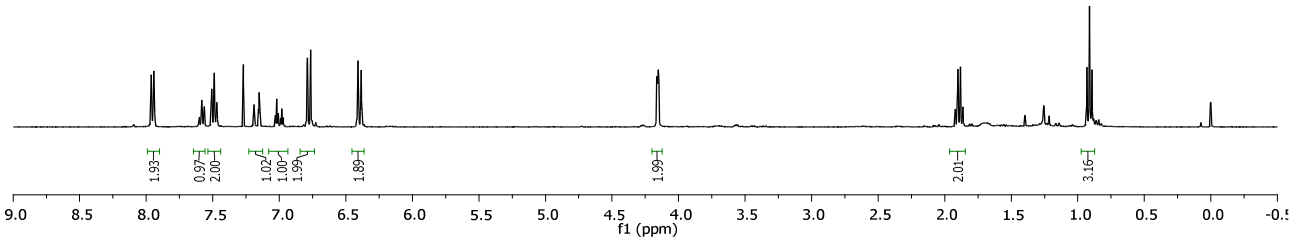


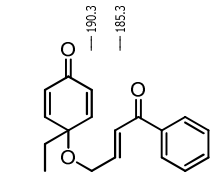


(*E*)-4-Ethyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ab):



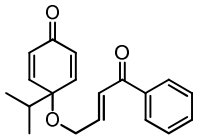
1H NMR (400 MHz, CDCl3)



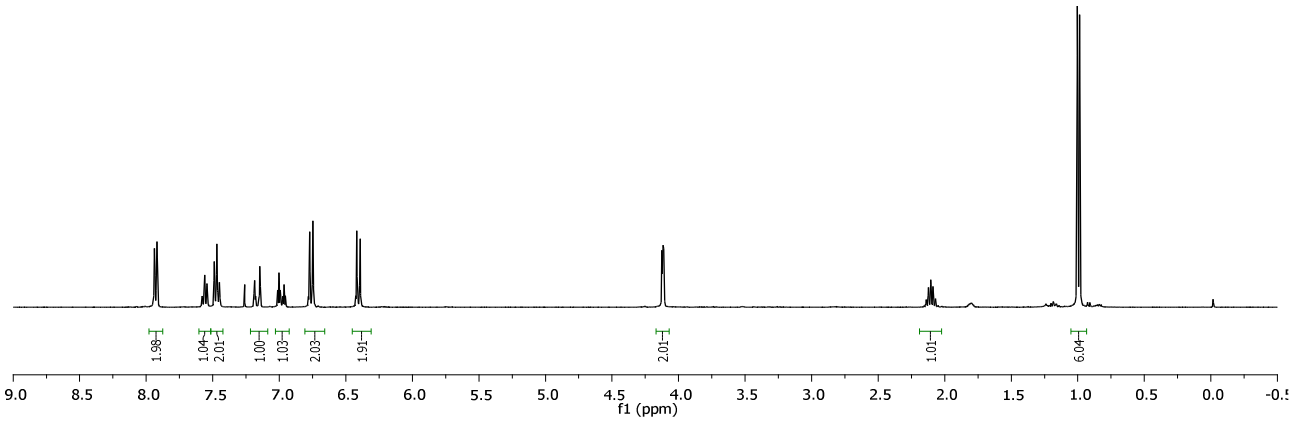


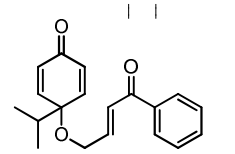
13C NMR (101 MHz, CDCl3)

(*E*)-4-Isopropyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ac):



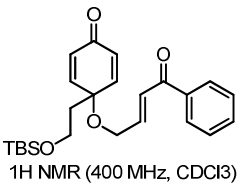
1H NMR (400 MHz, CDCl3)



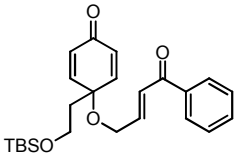


13C NMR (101 MHz, CDCl3)

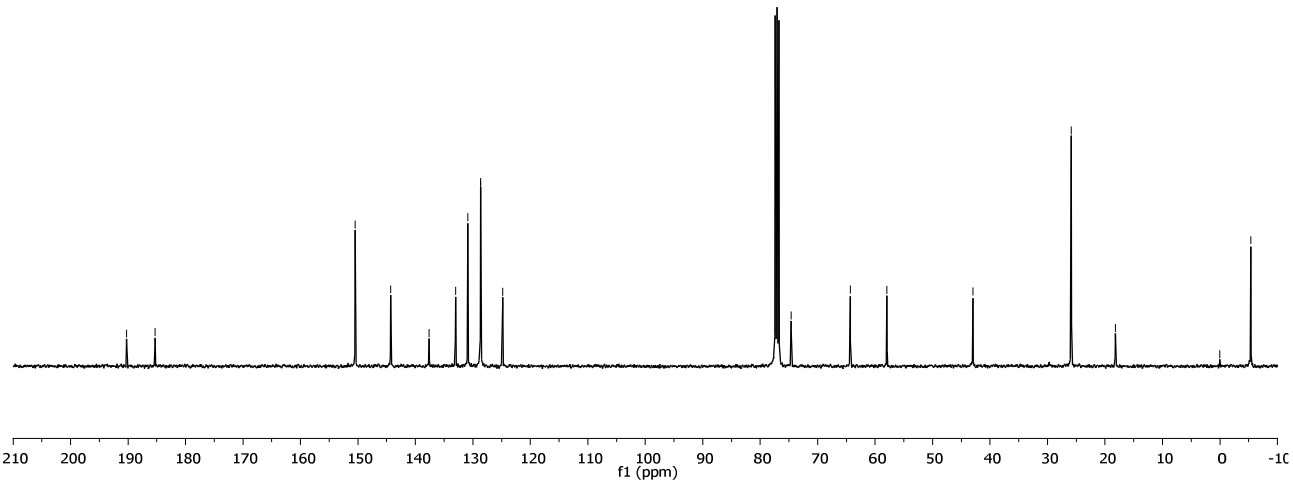
(*E*)-4-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ad):



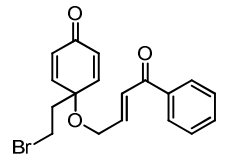
1H NMR (400 MHz, CDCl3)



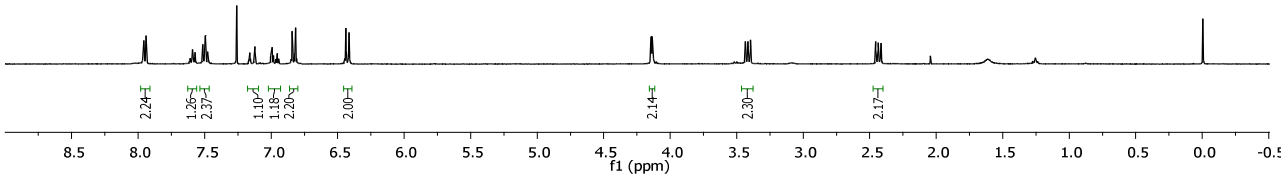
13C NMR (101 MHz, CDCl3)

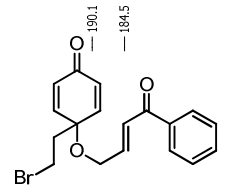


(*E*)-4-(2-Bromoethyl)-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (5):



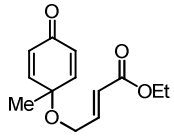
1H NMR (400 MHz, CDCl3)



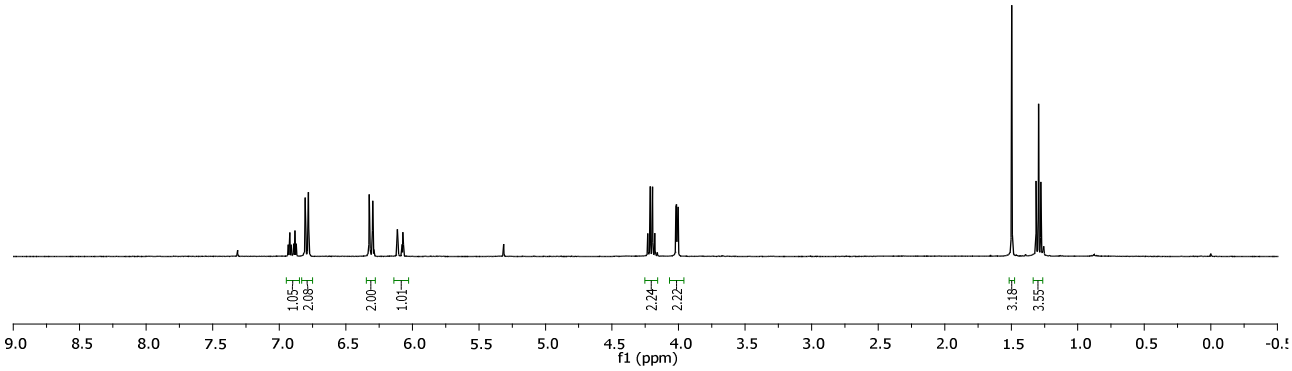


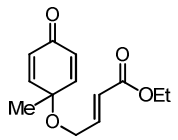
13C NMR (101 MHz, CDCl3)

Ethyl (*E*)-4-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)but-2-enoate (6):

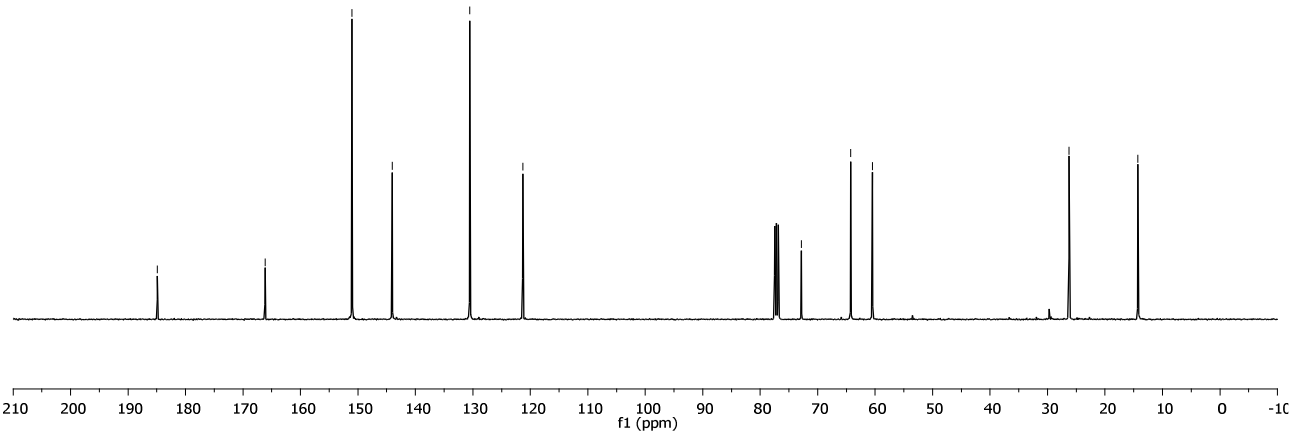


1H NMR (400 MHz, CDCl3)

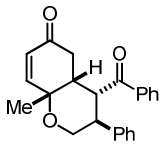




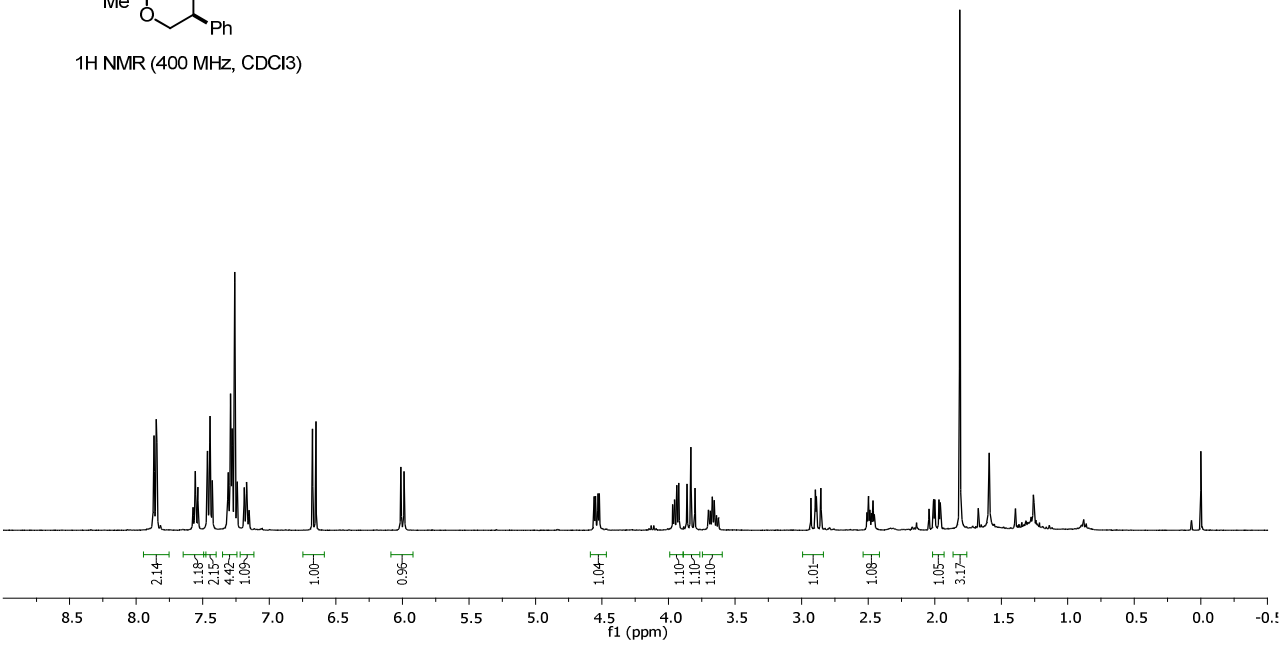
13C NMR (101 MHz, CDCl3)

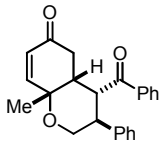


4-Benzoyl-8a-methyl-3-phenyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3a):



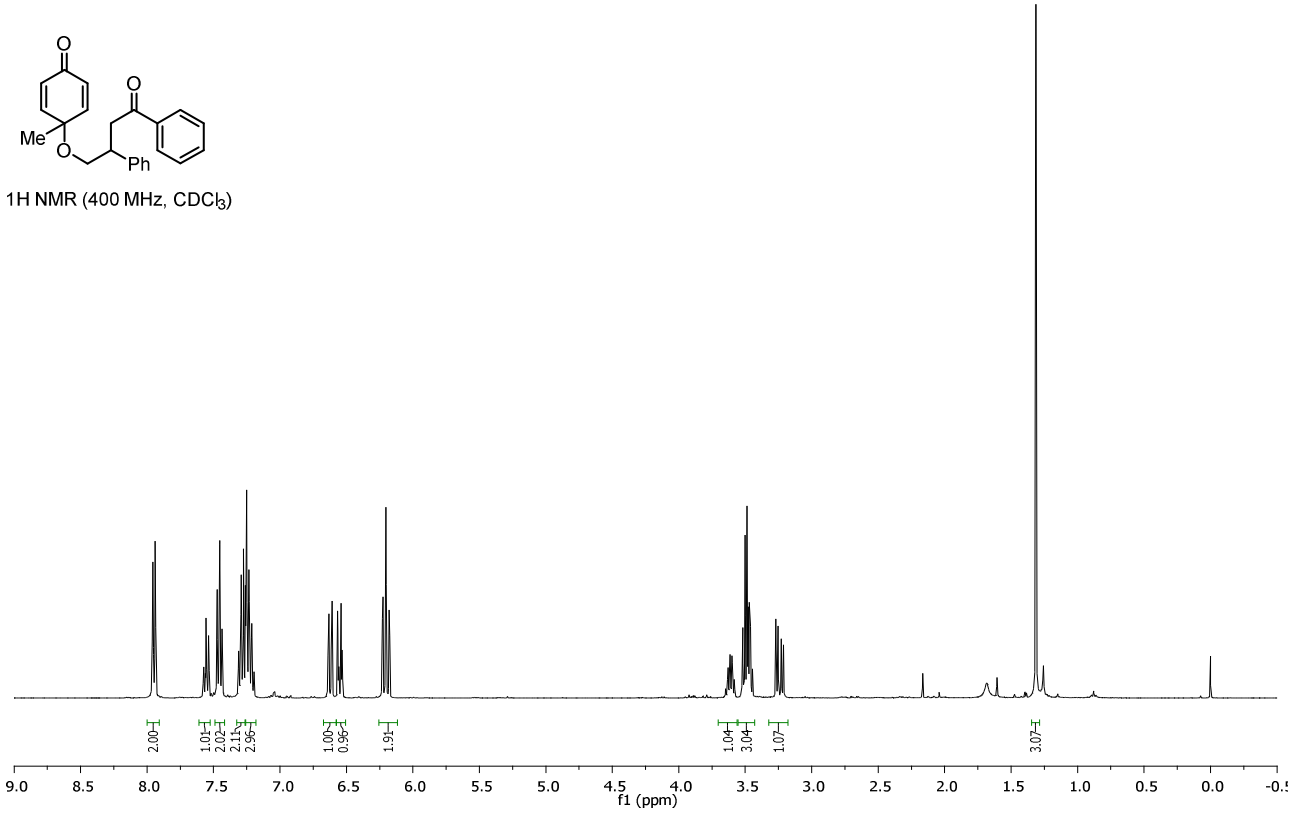
1H NMR (400 MHz, CDCl3)

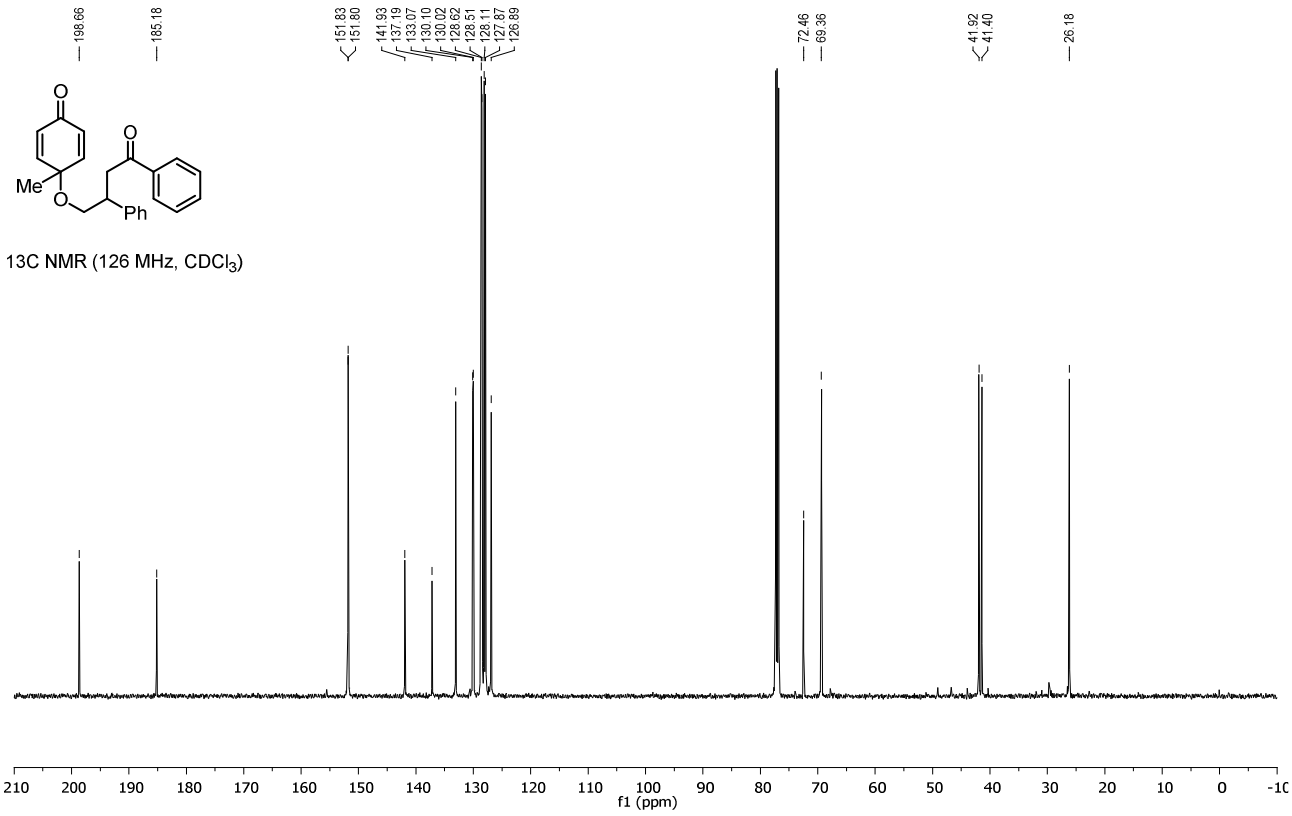




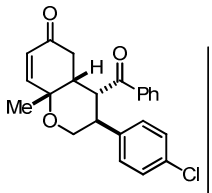
13C NMR (101 MHz, CDCl3)

4-Methyl-4-(4-oxo-2,4-diphenylbutoxy)cyclohexa-2,5-dienone (4a):

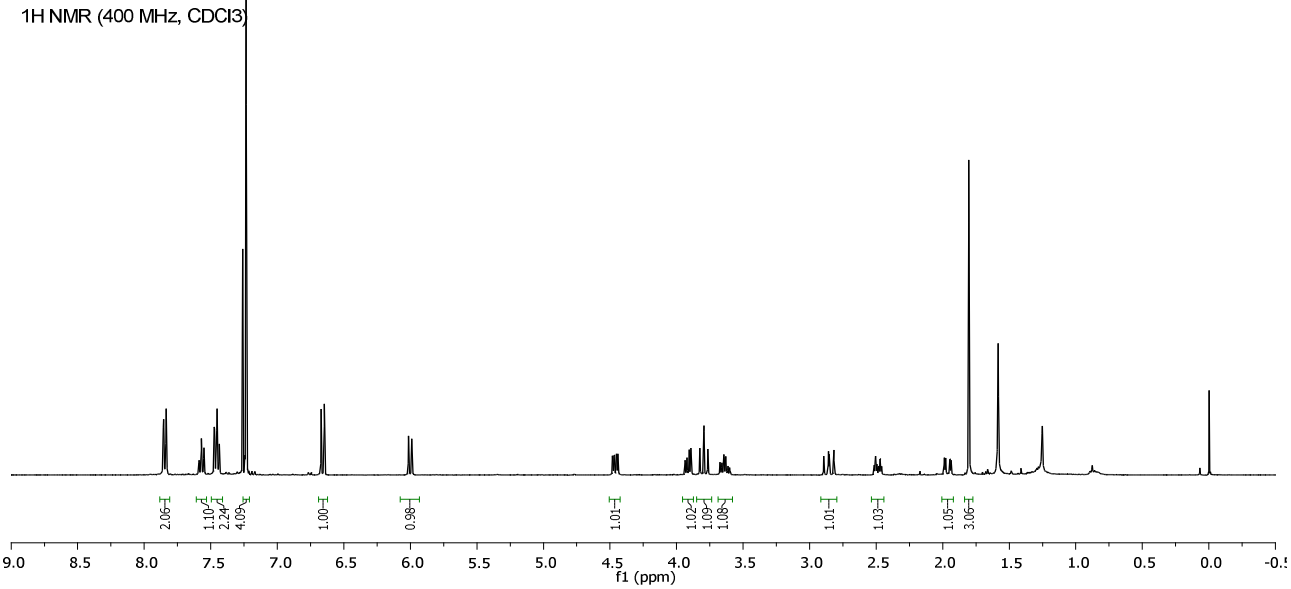


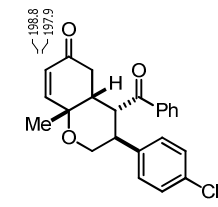


4-Benzoyl-3-(4-chlorophenyl)-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3b):



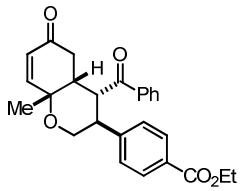
1H NMR (400 MHz, CDCl3)



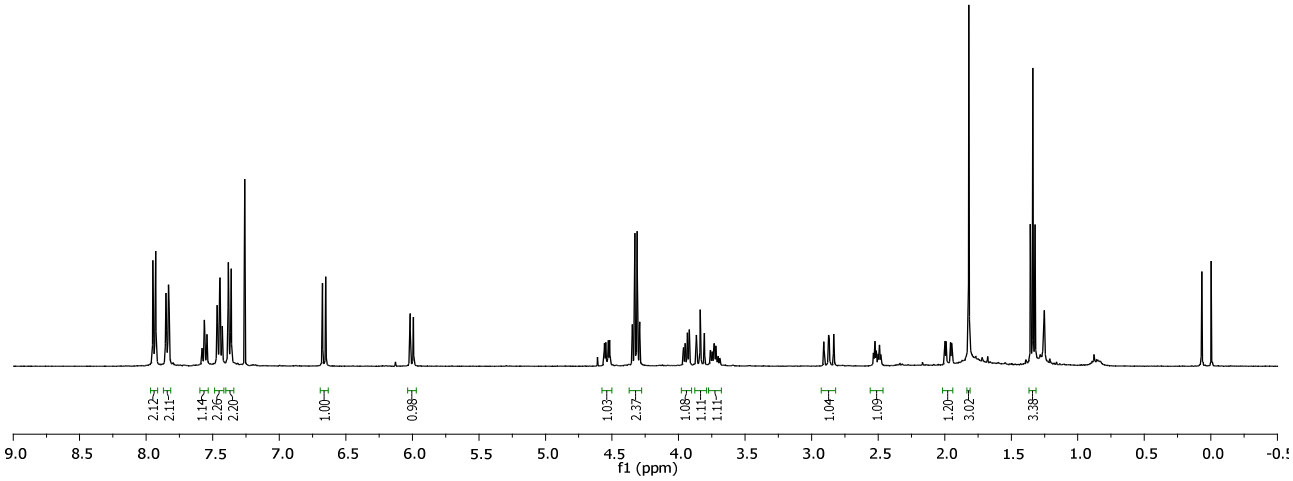


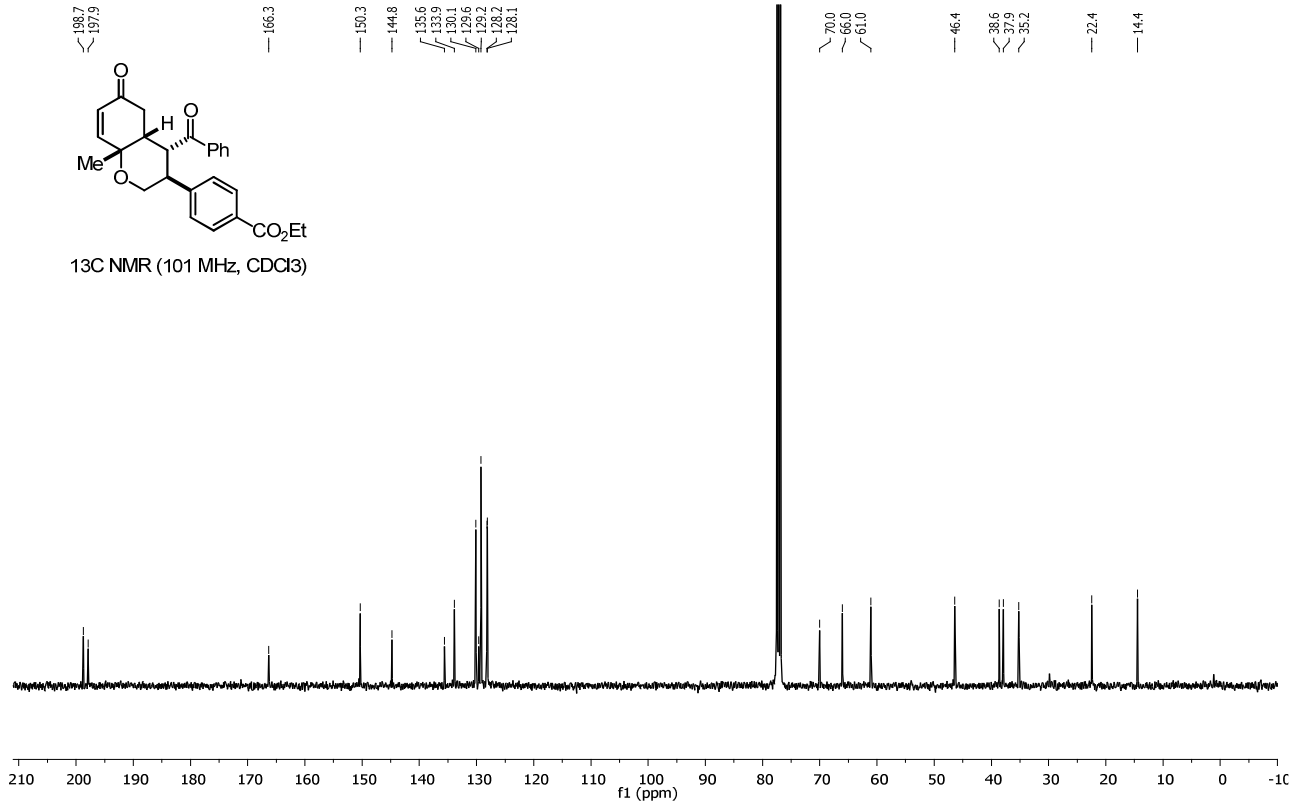
13C NMR (101 MHz, CDCl3)

4-|Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)benzoate (3c):



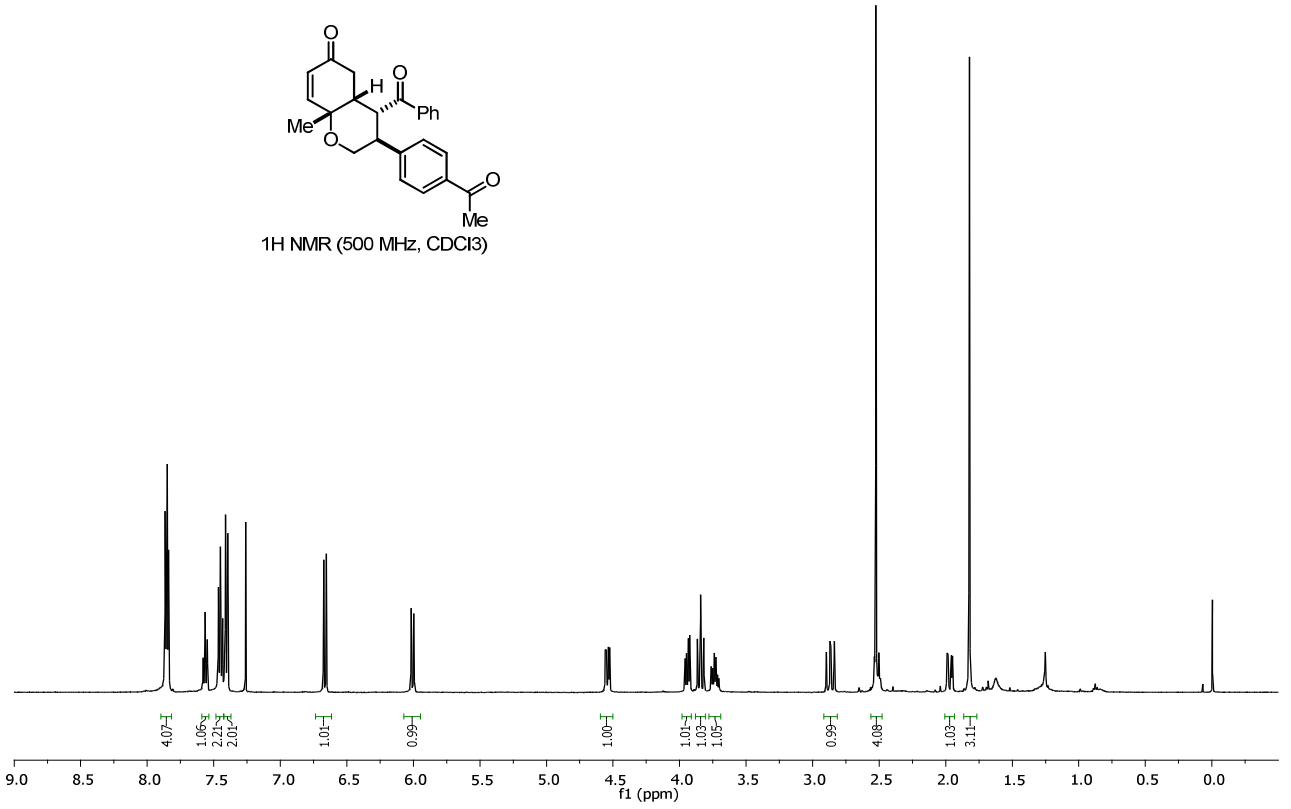
1H NMR (400 MHz, CDCl3)

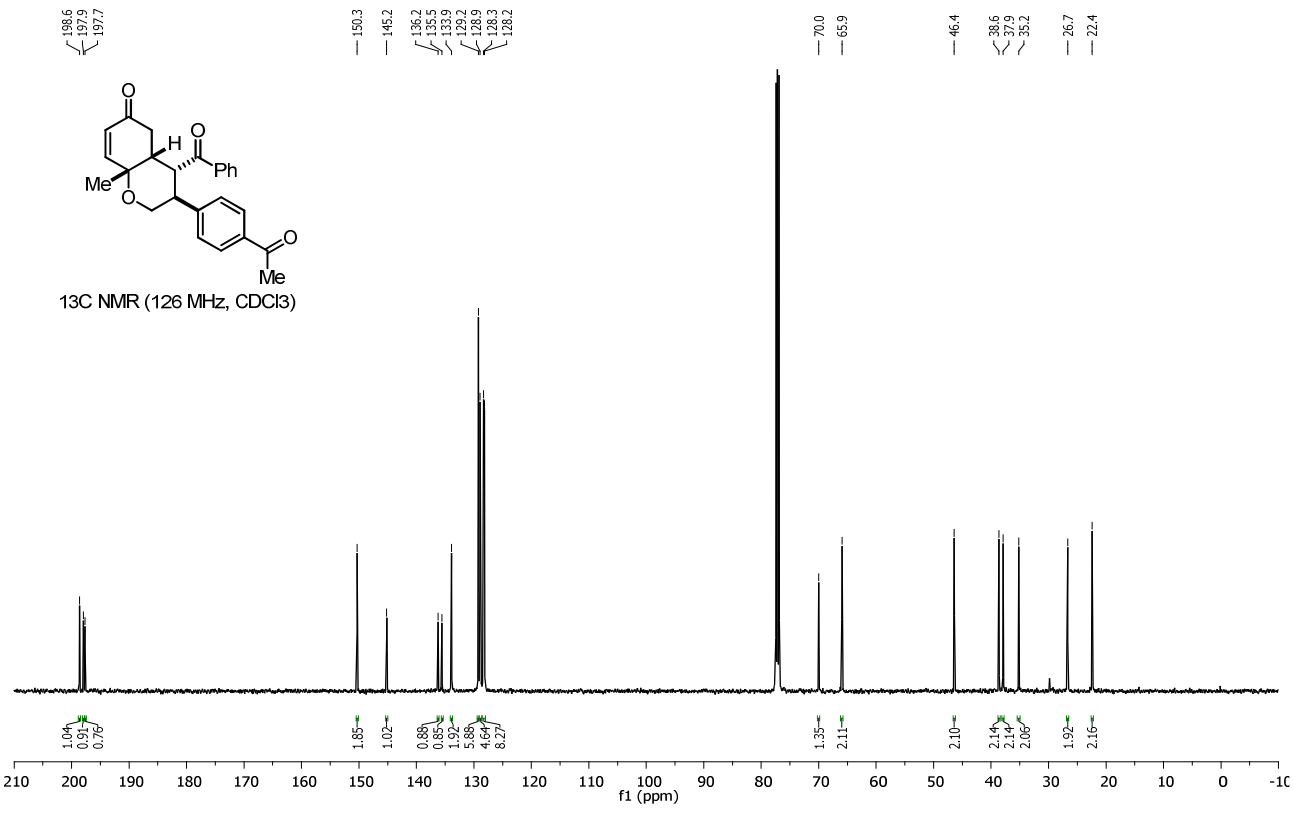




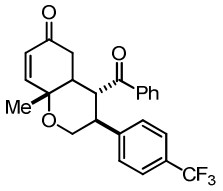
13C NMR (101 MHz, CDCl3)

3-(4-Acetylphenyl)-4-benzoyl-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3d):

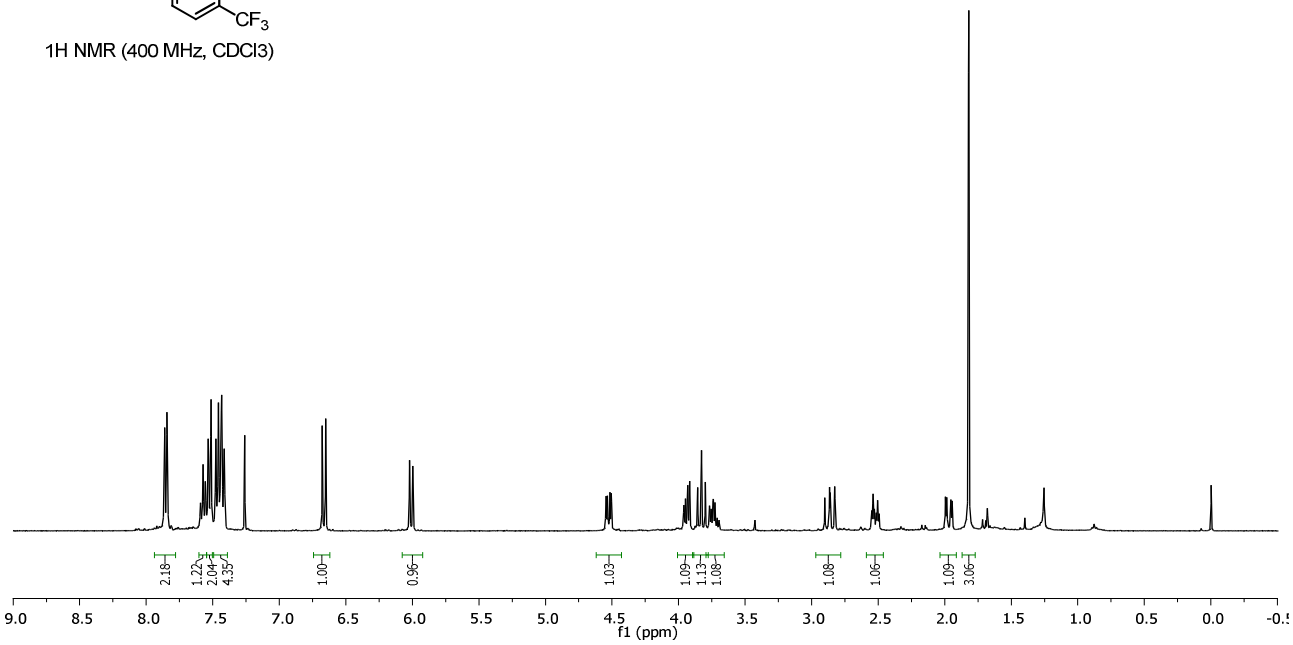


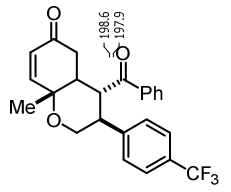


4-Benzoyl-8a-methyl-3-(4-(trifluoromethyl)phenyl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3e):



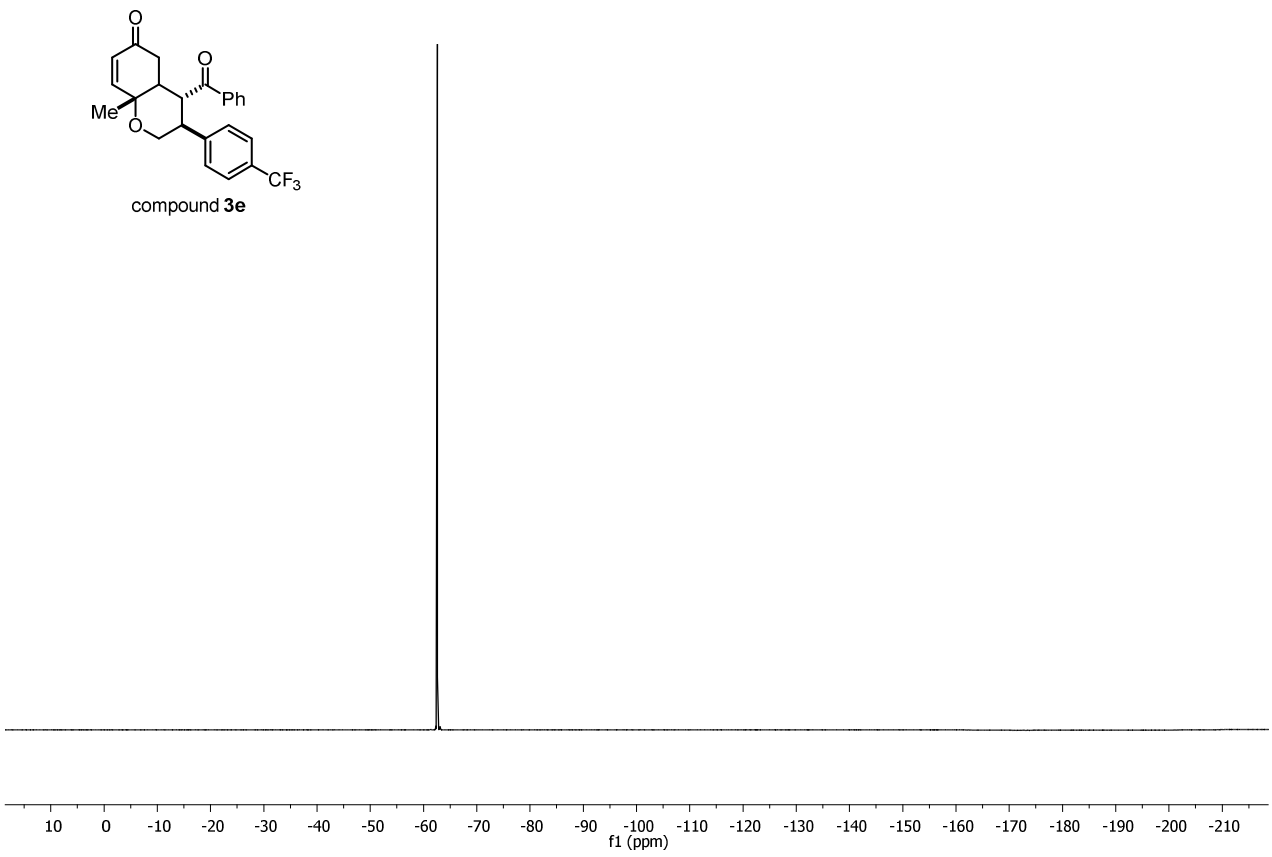
1H NMR (400 MHz, CDCl3)



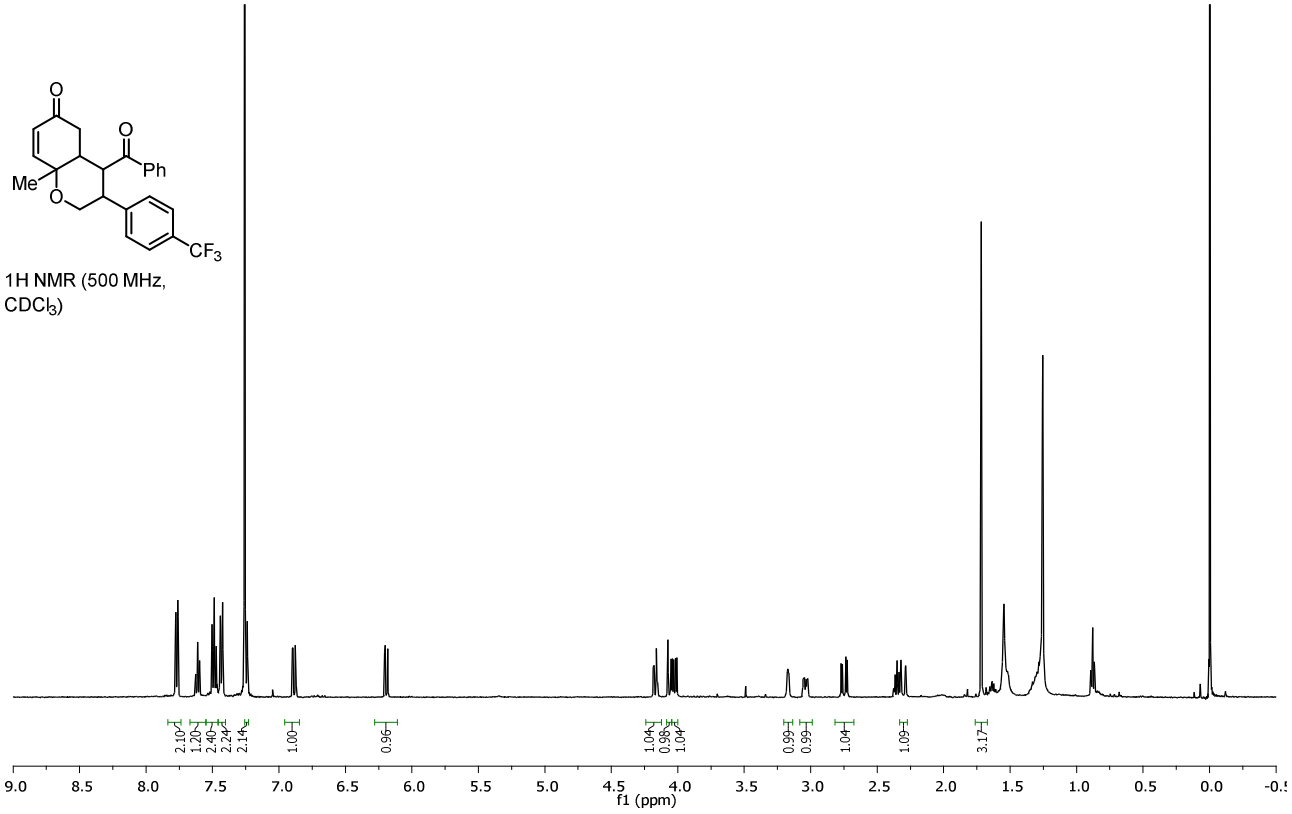


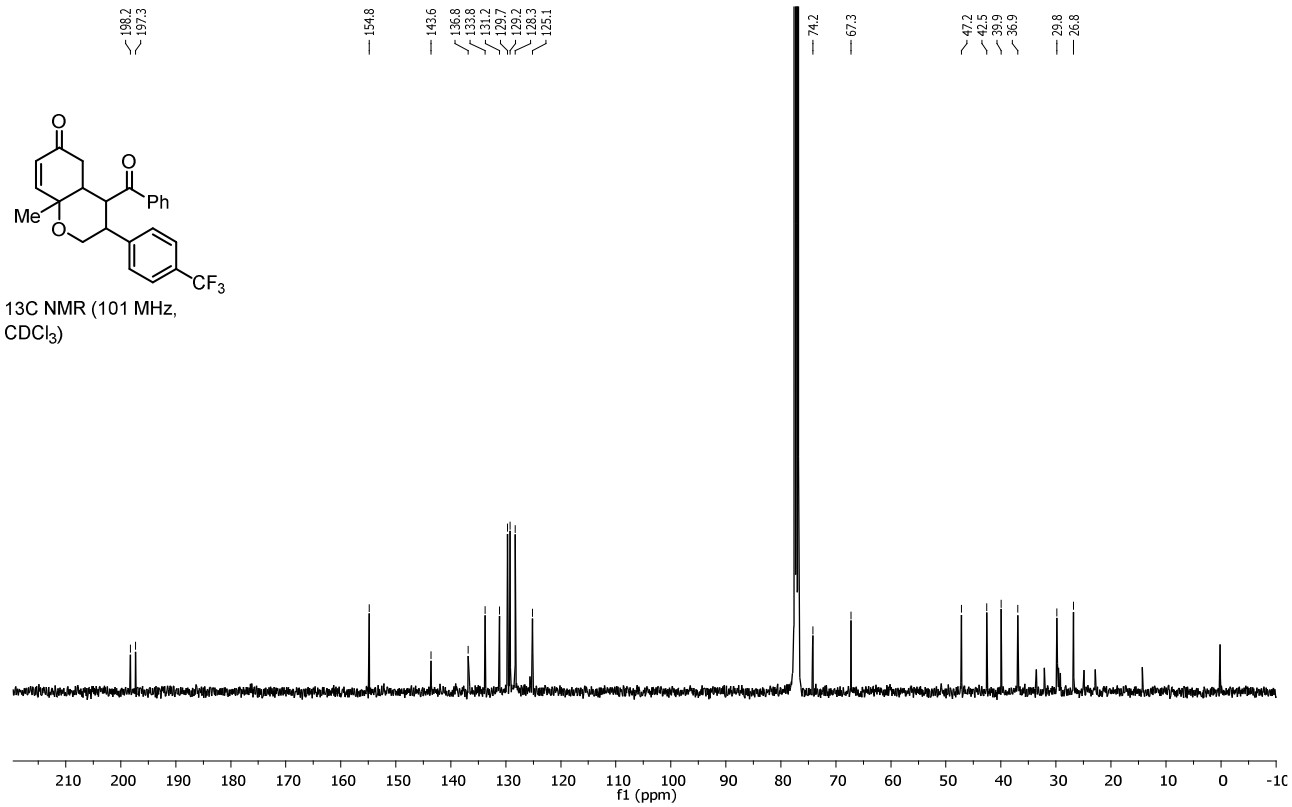
13C NMR (101 MHz, CDCl3)

^{19}F NMR spectrum of compound 3e in $CDCl_3$

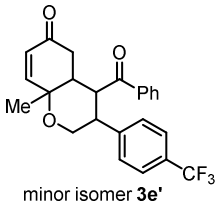


Minor isomer 3e':

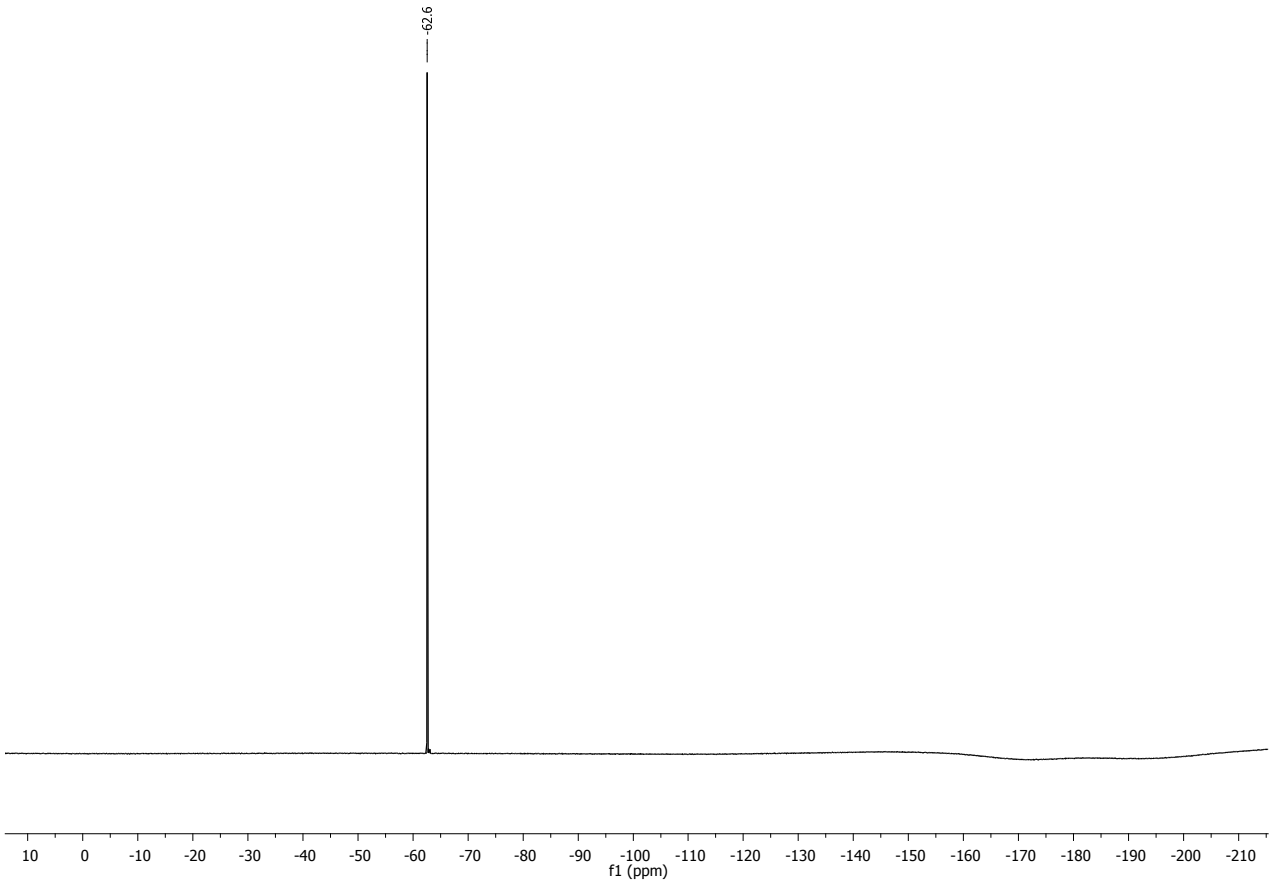




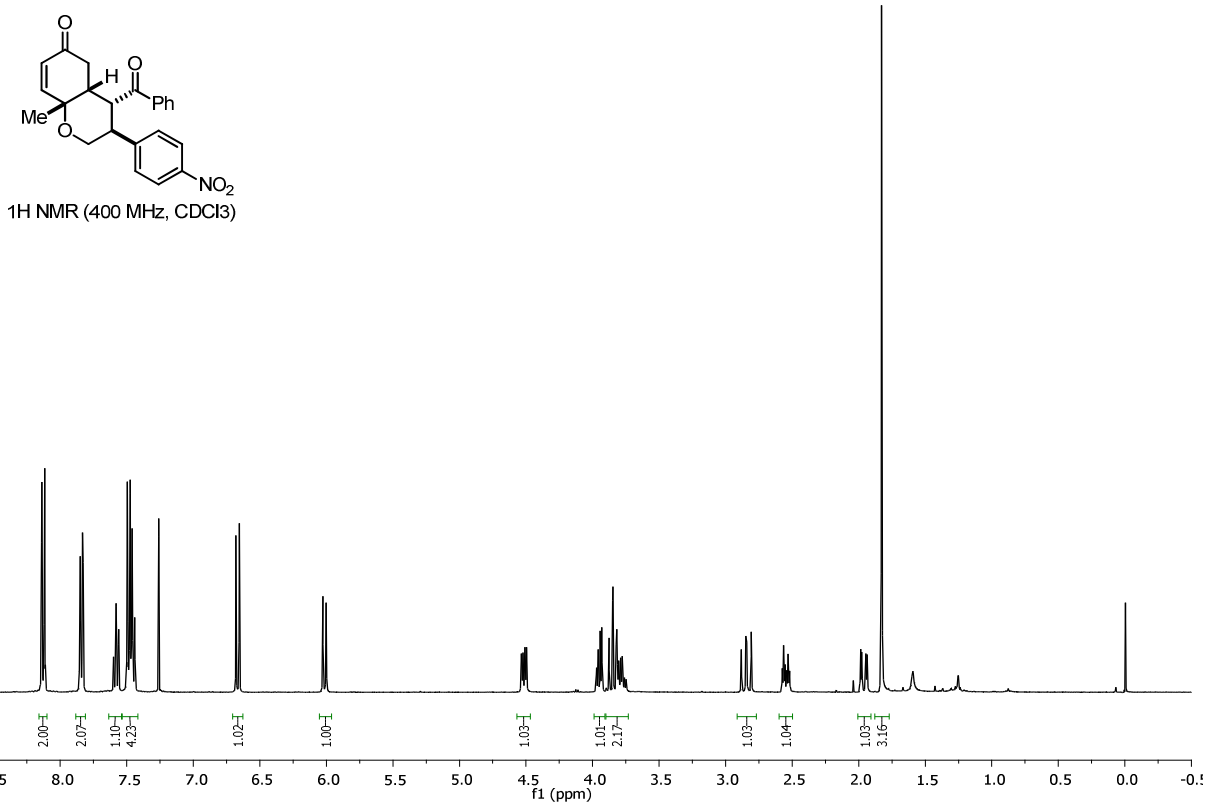
^{19}F NMR spectrum of compound 3e' in $CDCl_3$

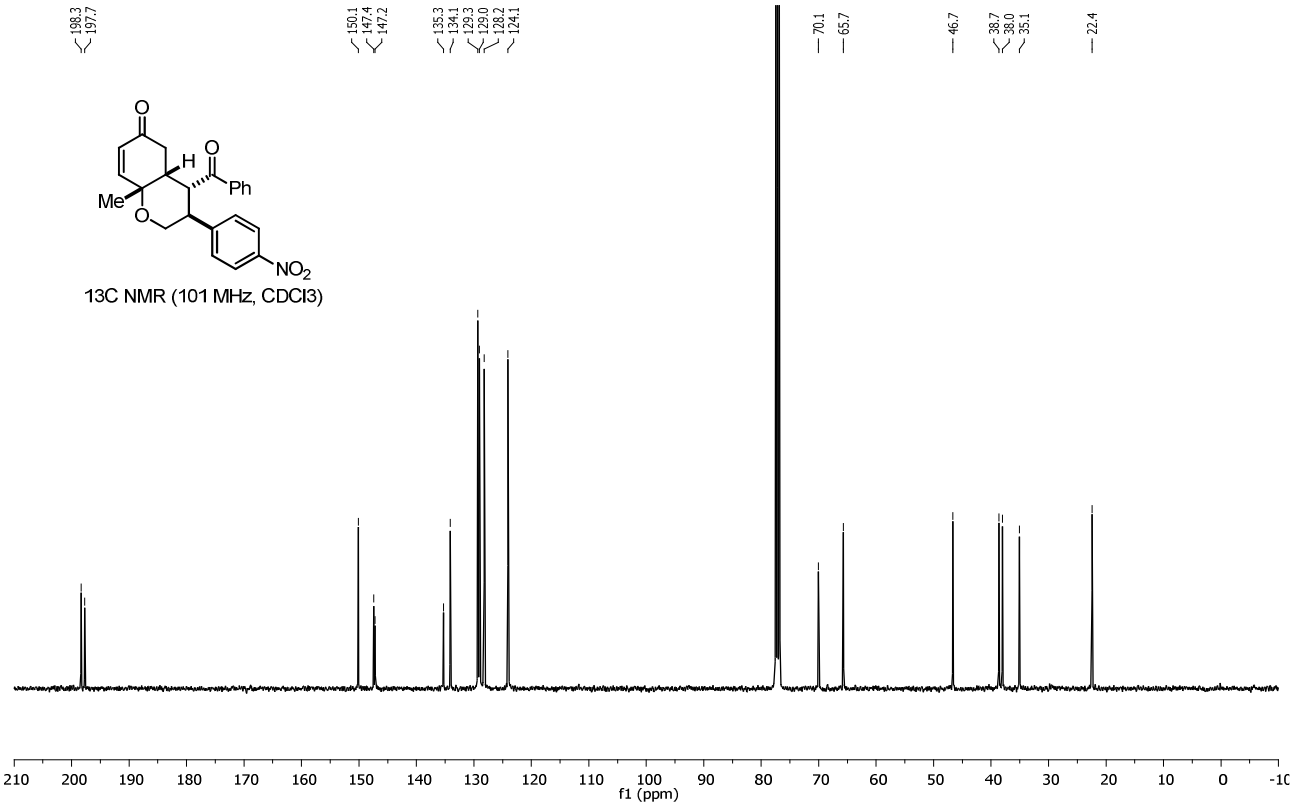


minor isomer **3e'**

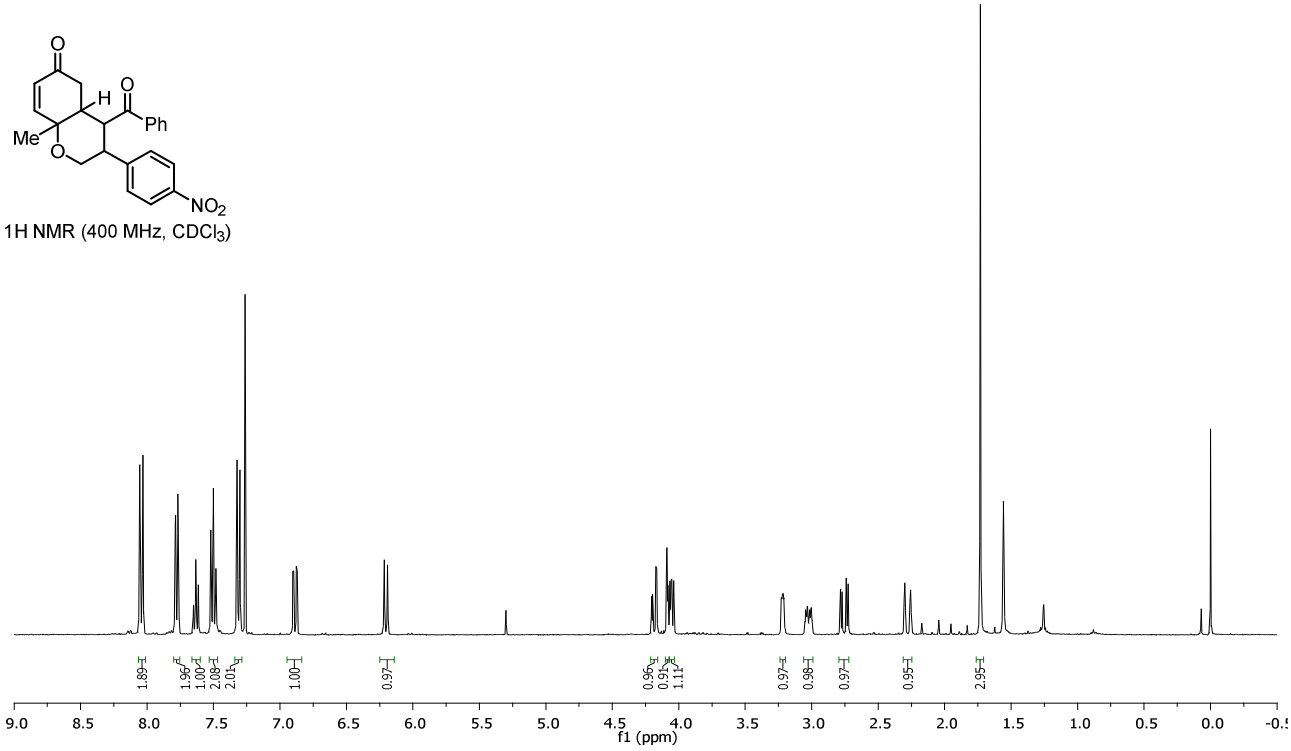


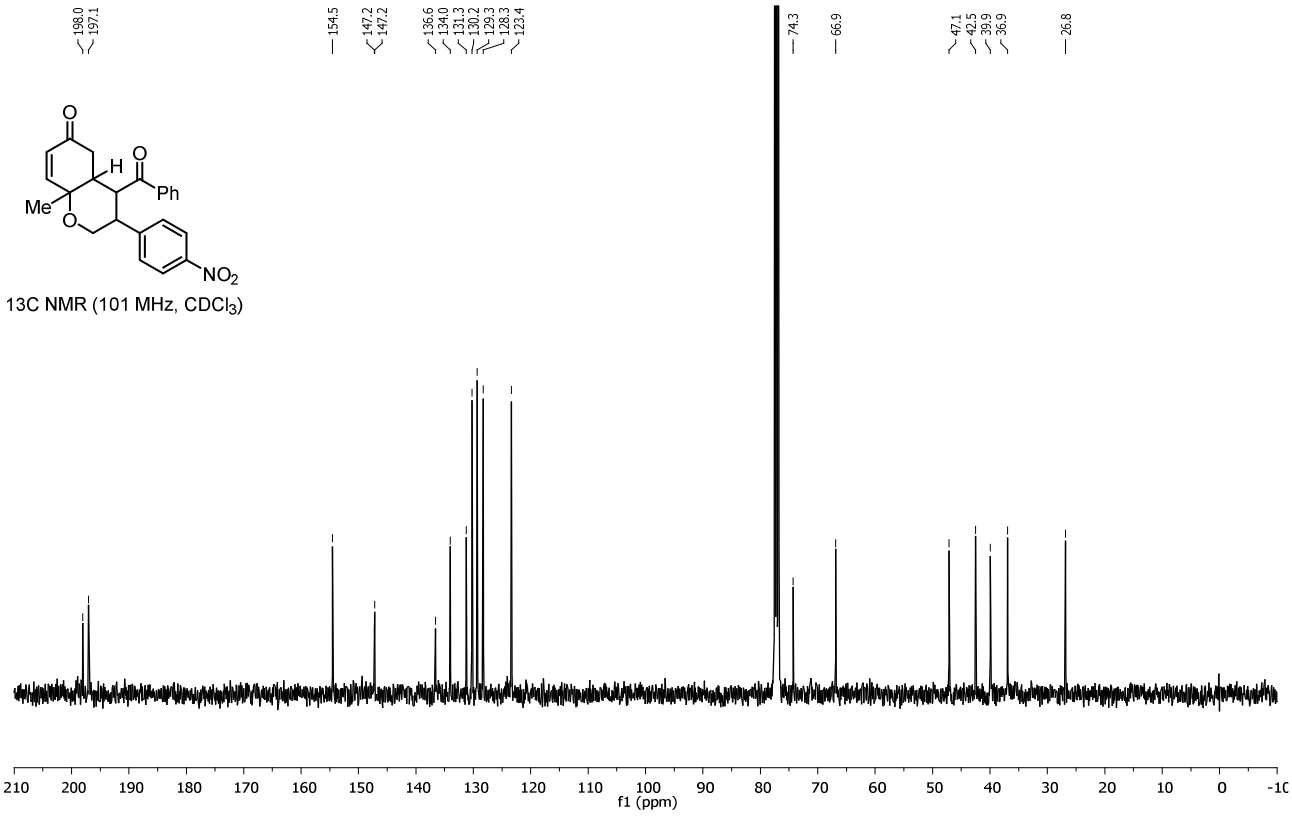
4-Benzoyl-8a-methyl-3-(4-nitrophenyl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3f):



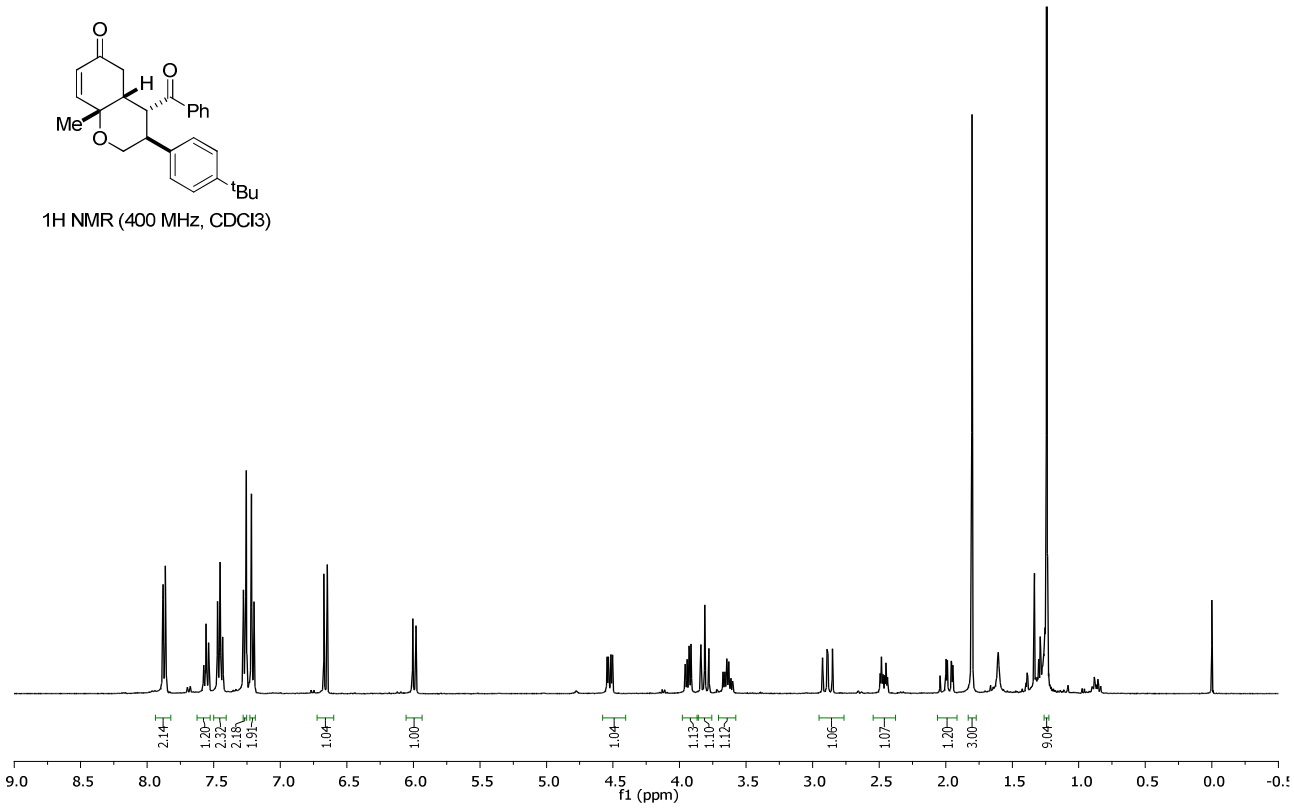


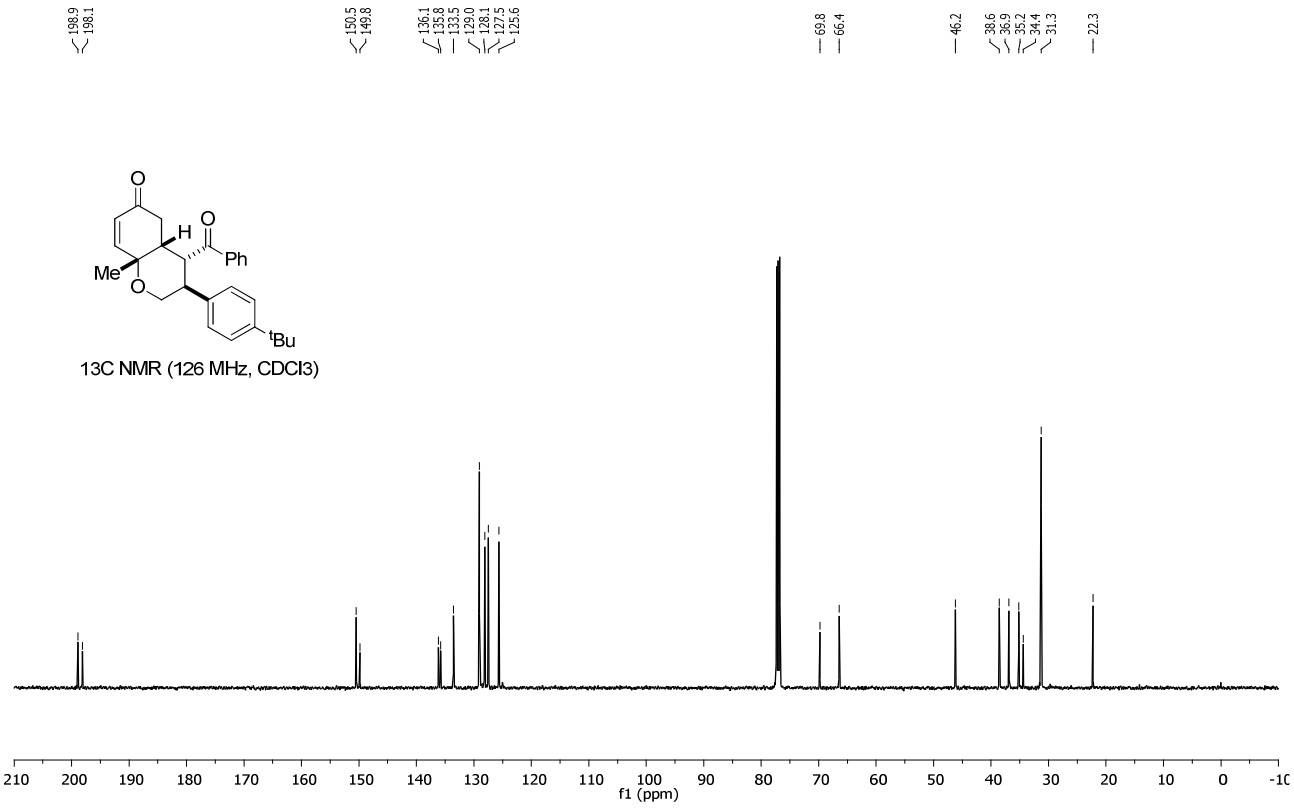
Minor isomer 3f':



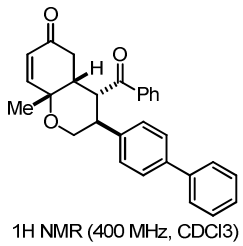


4-Benzoyl-3-(4-(tert-butyl)phenyl)-8a-methyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3g):

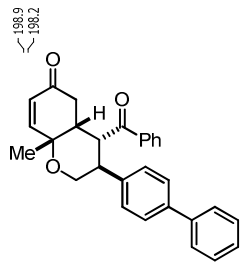




3-([1,1'-Biphenyl]-4-yl)-4-benzoyl-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3h):

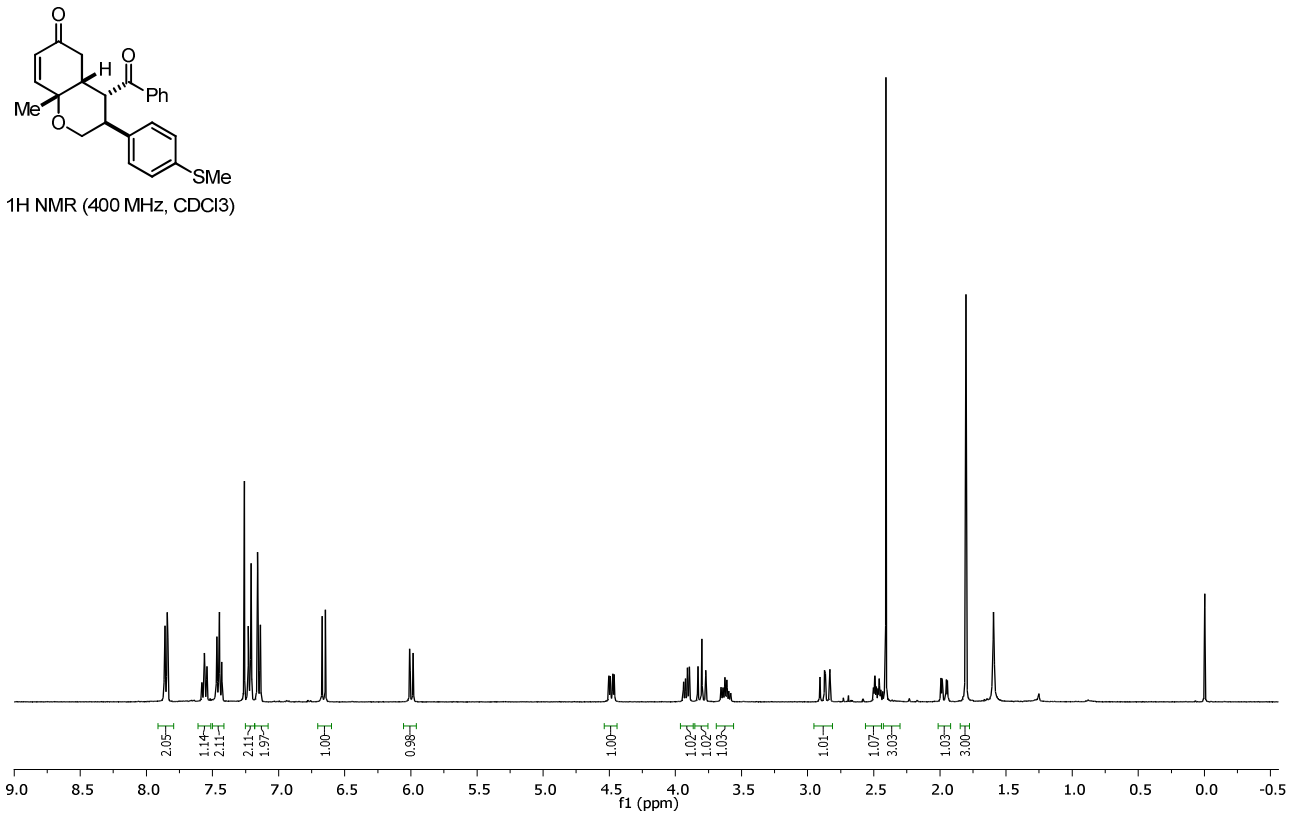


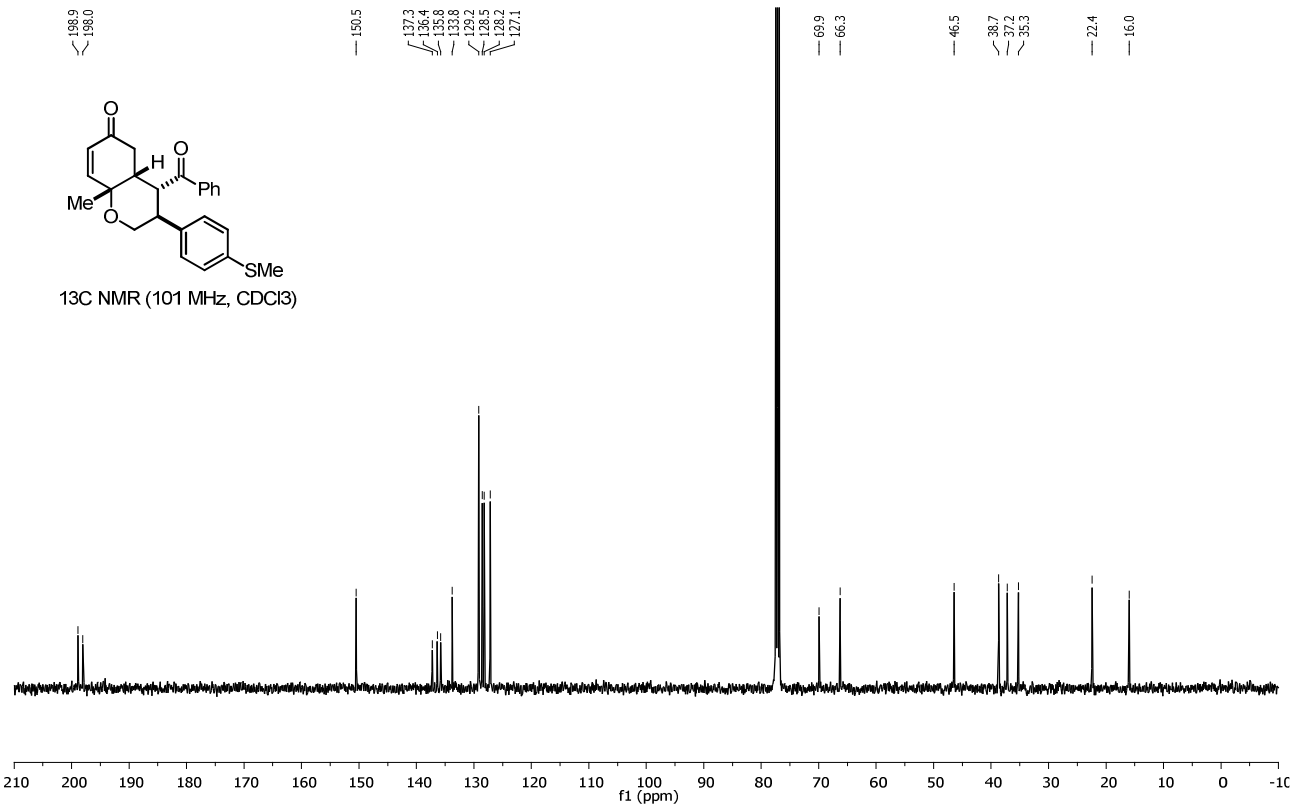
1H NMR (400 MHz, CDCl3)



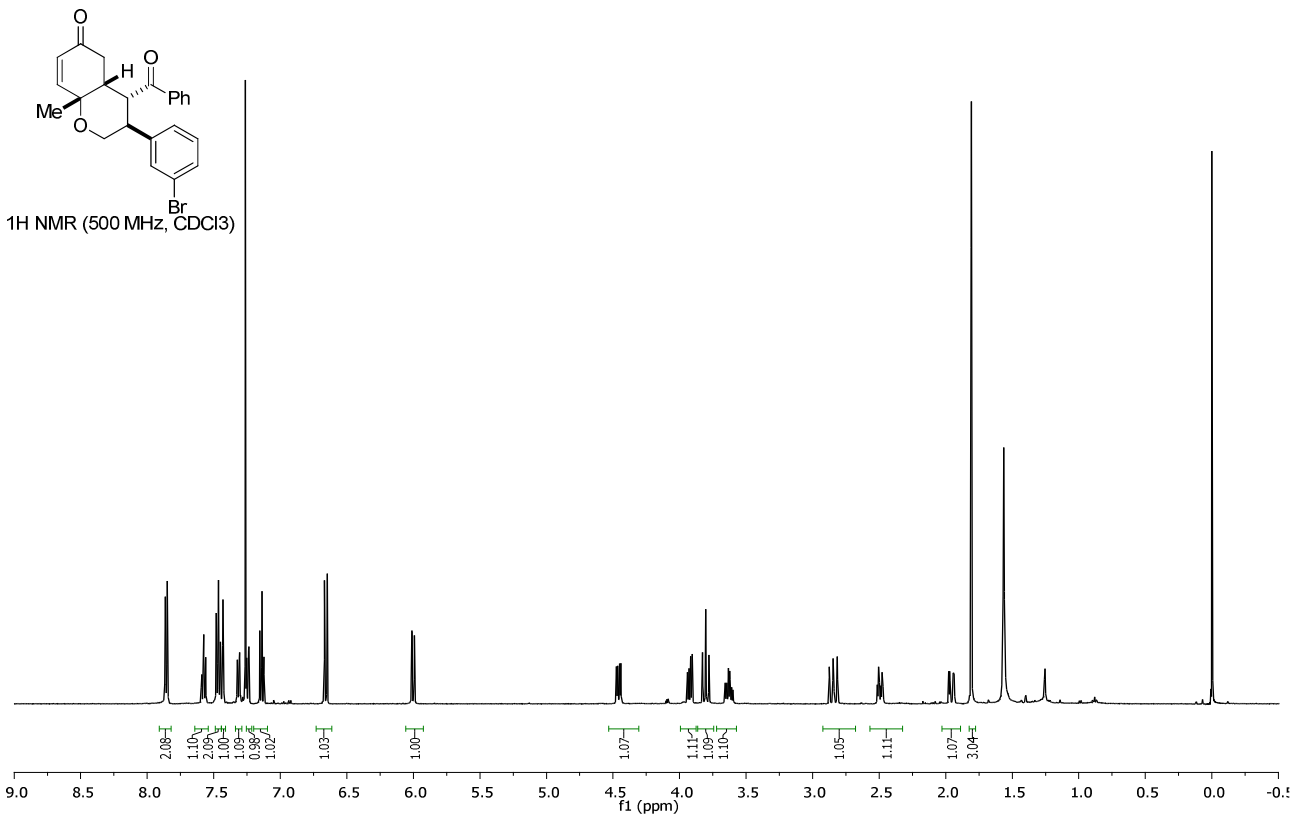
13C NMR (101 MHz, CDCl3)

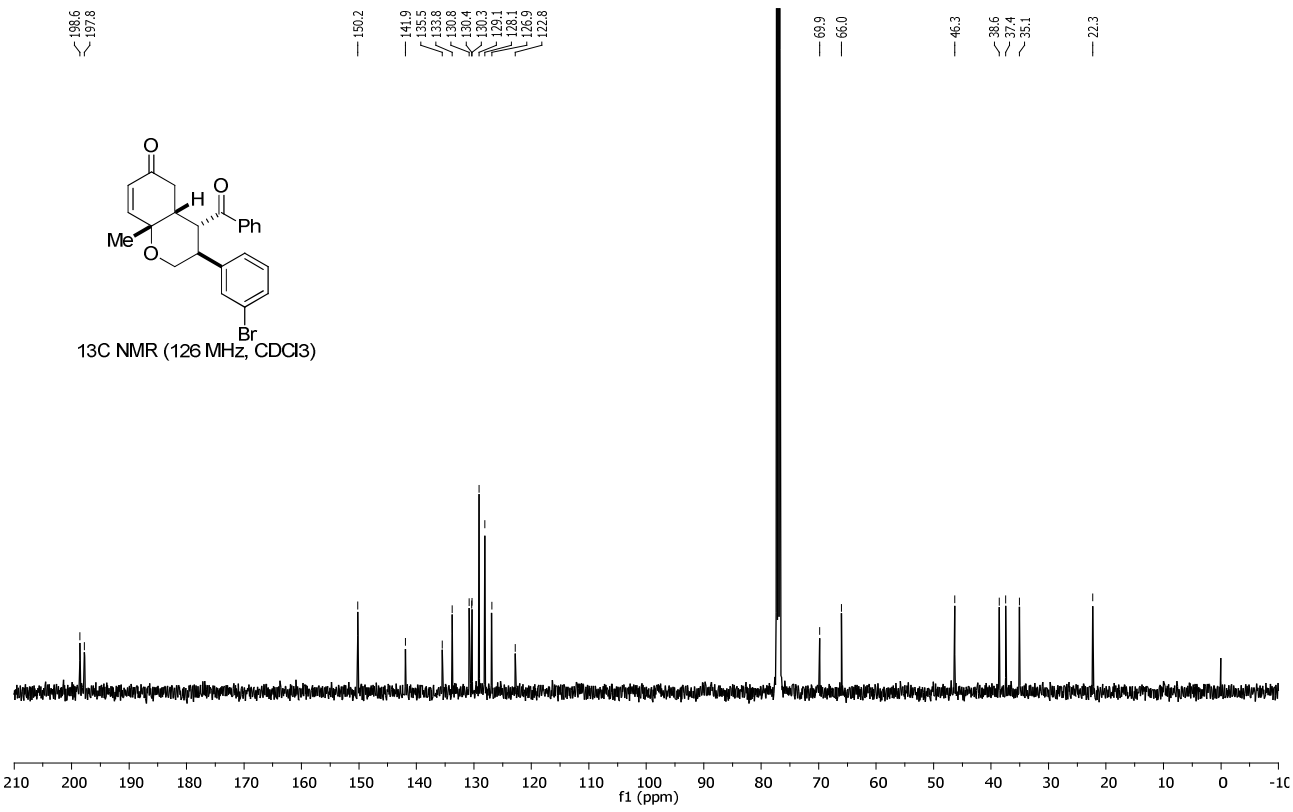
4-Benzoyl-8a-methyl-3-(4-(methylthio)phenyl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3i):



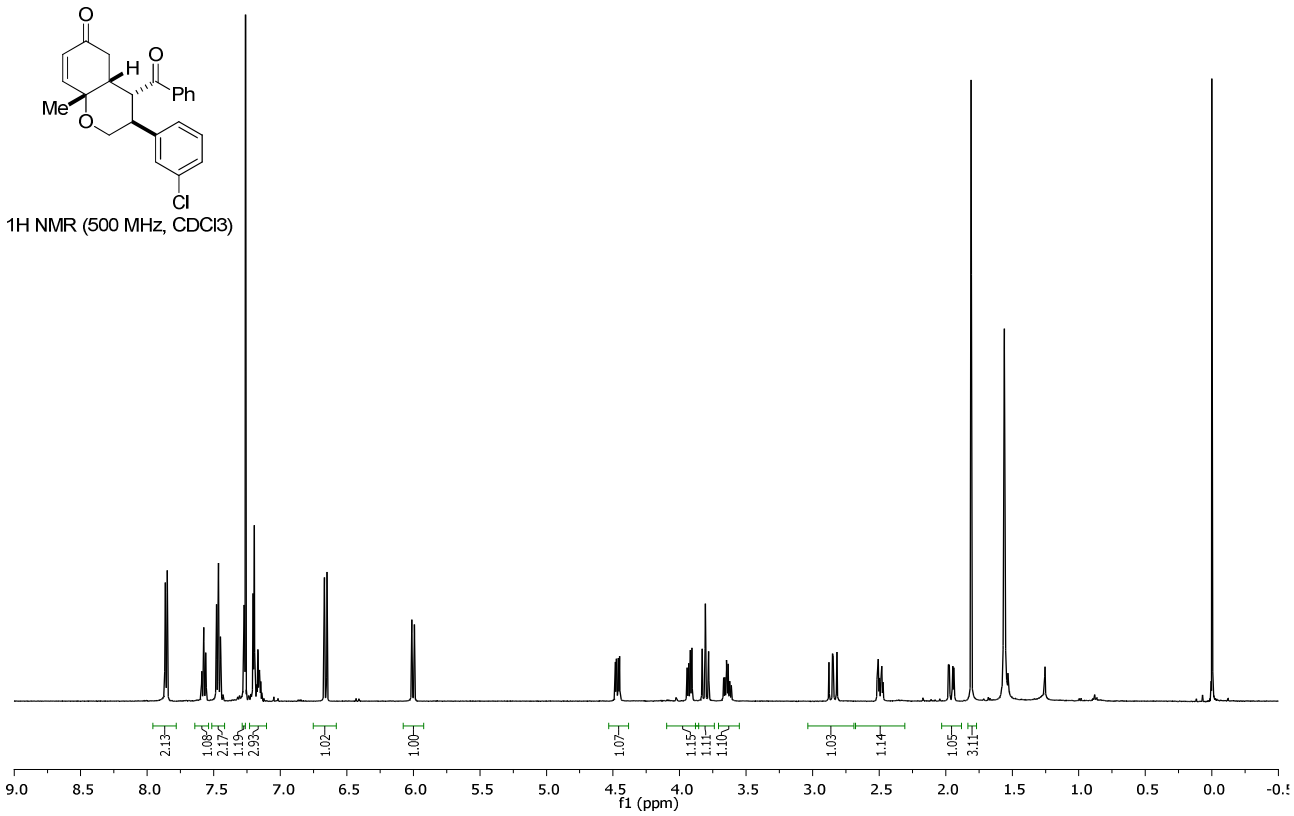


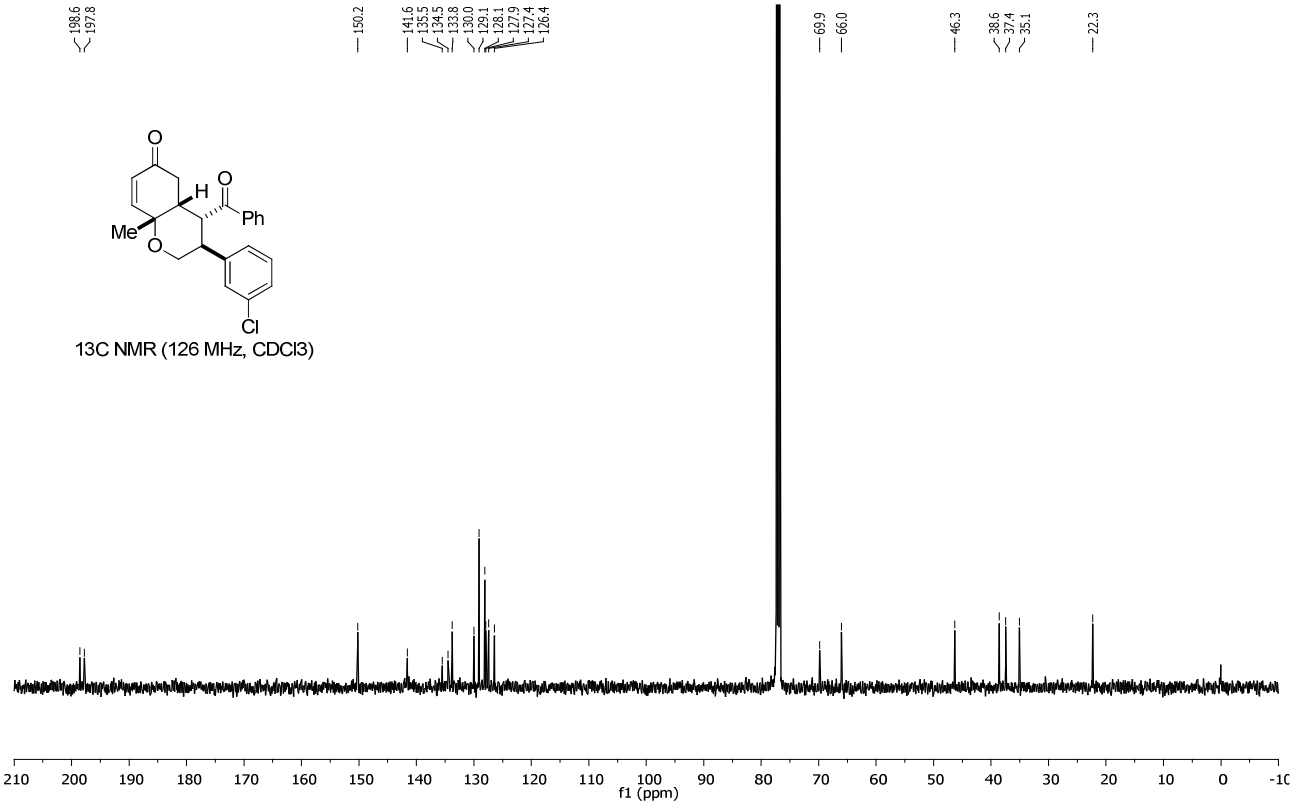
(4-Benzoyl-3-(3-bromophenyl)-8a-methyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3j):



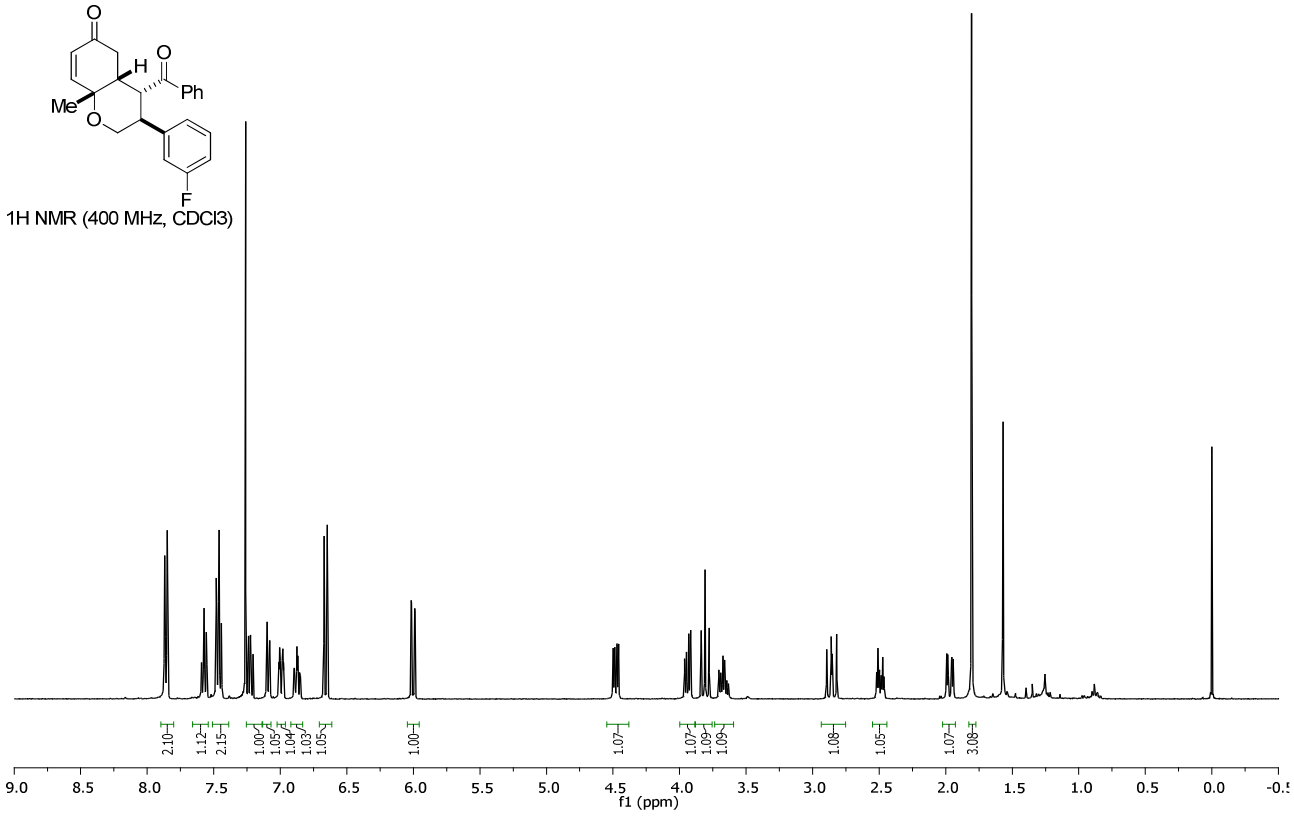


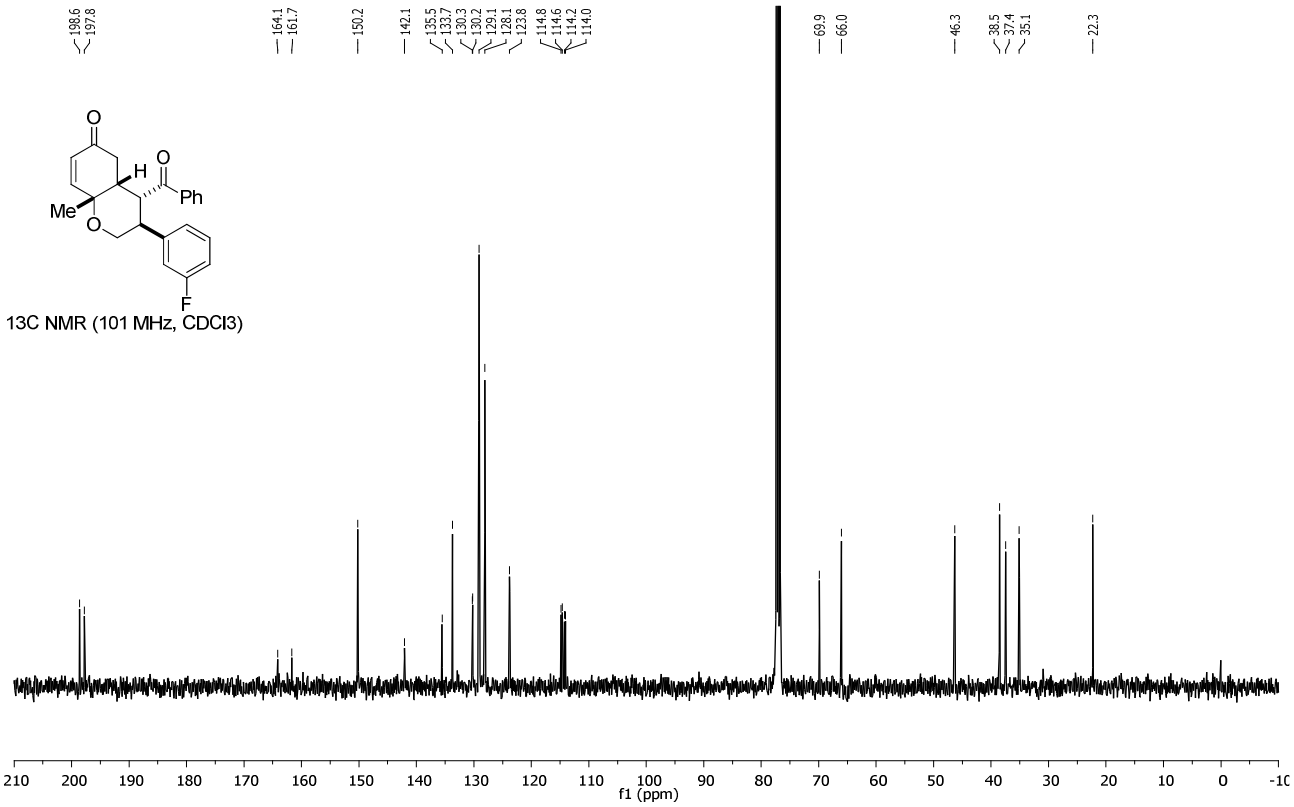
4-Benzoyl-3-(3-chlorophenyl)-8a-methyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3k):



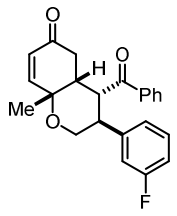


4-Benzoyl-3-(3-fluorophenyl)-8a-methyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3l):



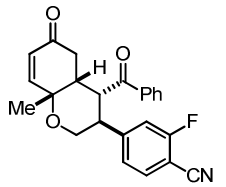


^{19}F NMR spectrum of compound 3l in $CDCl_3$

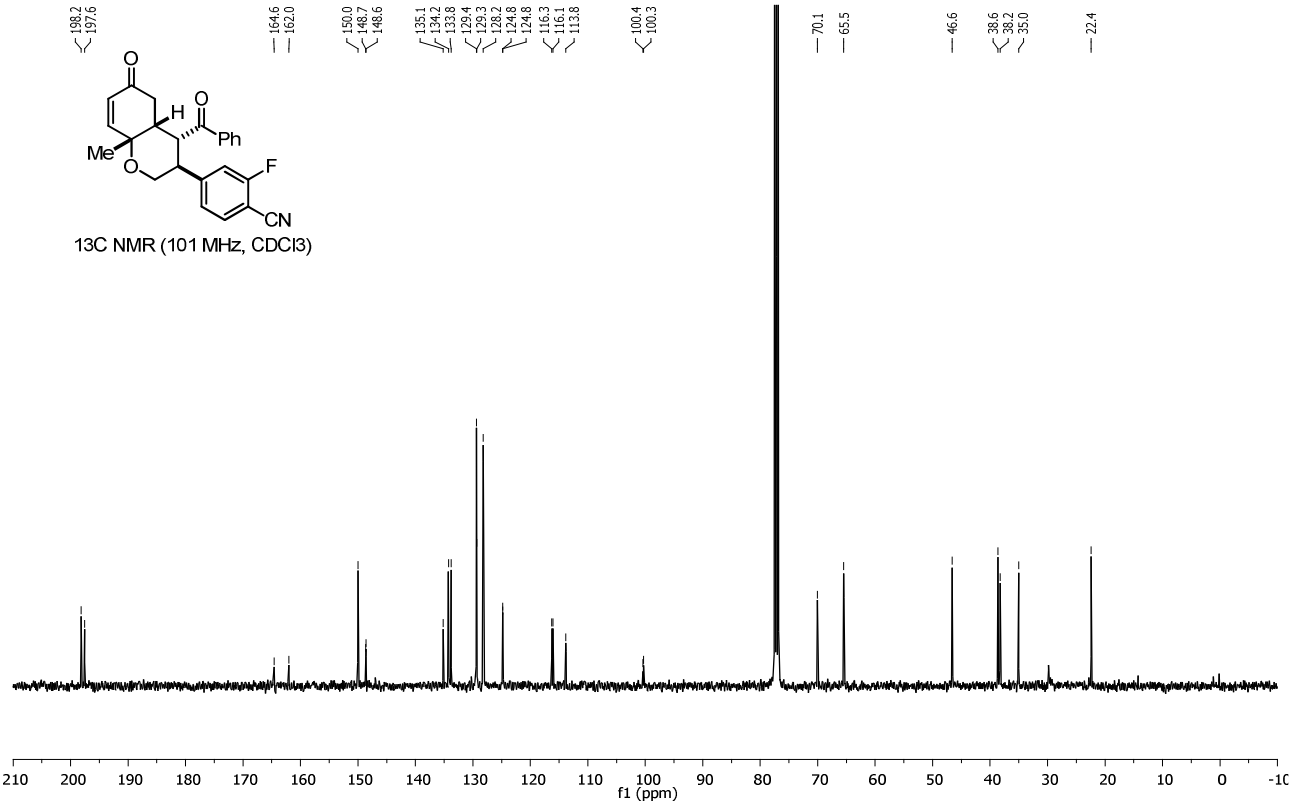


compound **3l**

4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-2-fluorobenzonitrile (3m):

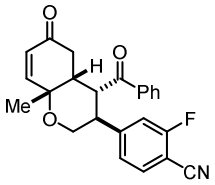


1H NMR (400 MHz, CDCl3)

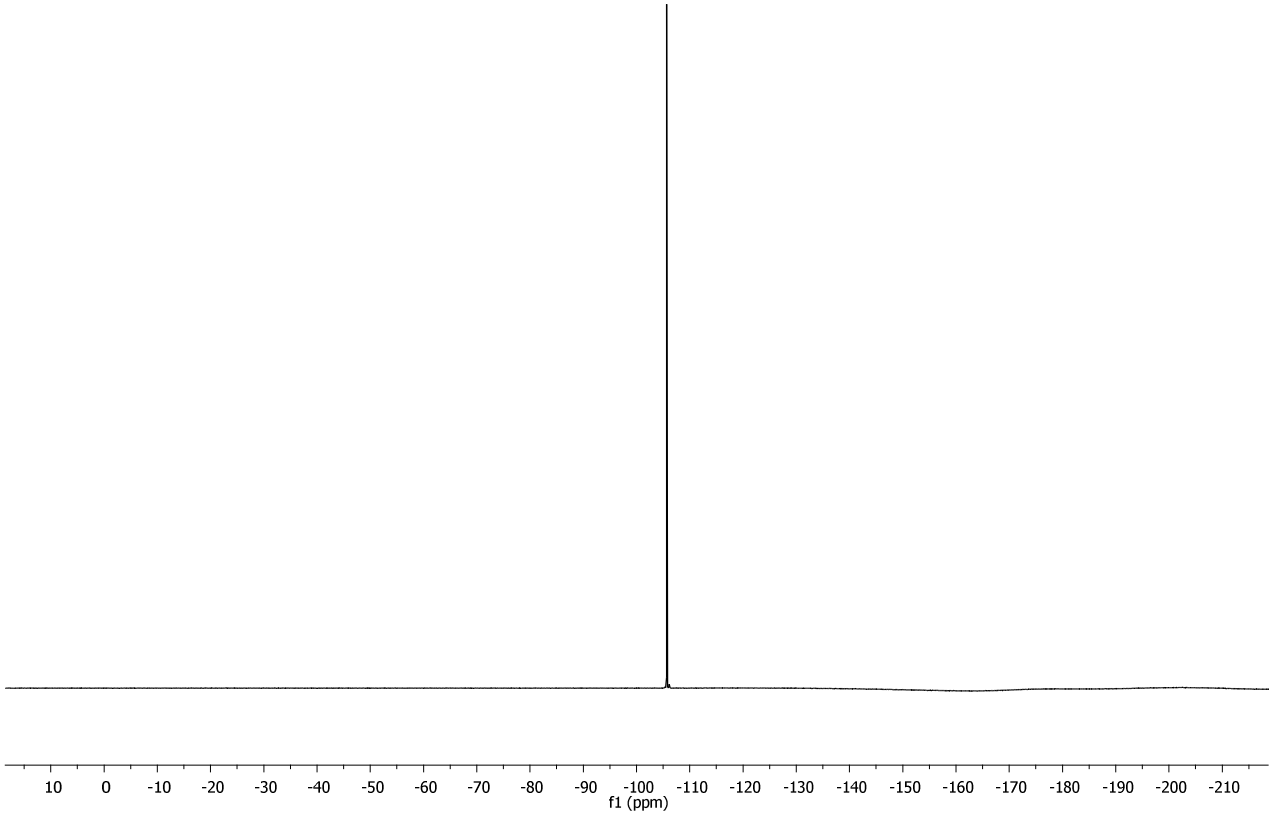


13C NMR (101 MHz, CDCl3)

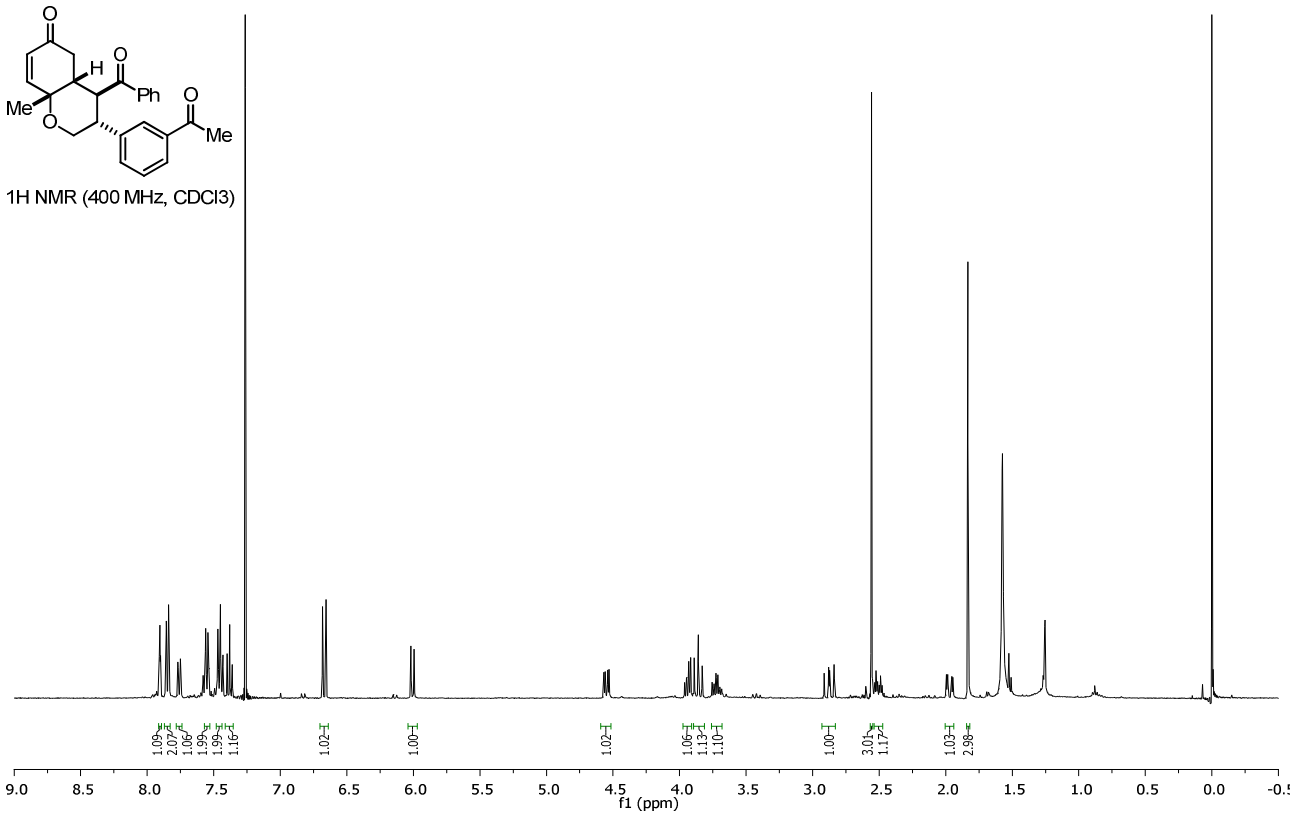
^{19}F NMR spectrum of compound 3m in $CDCl_3$

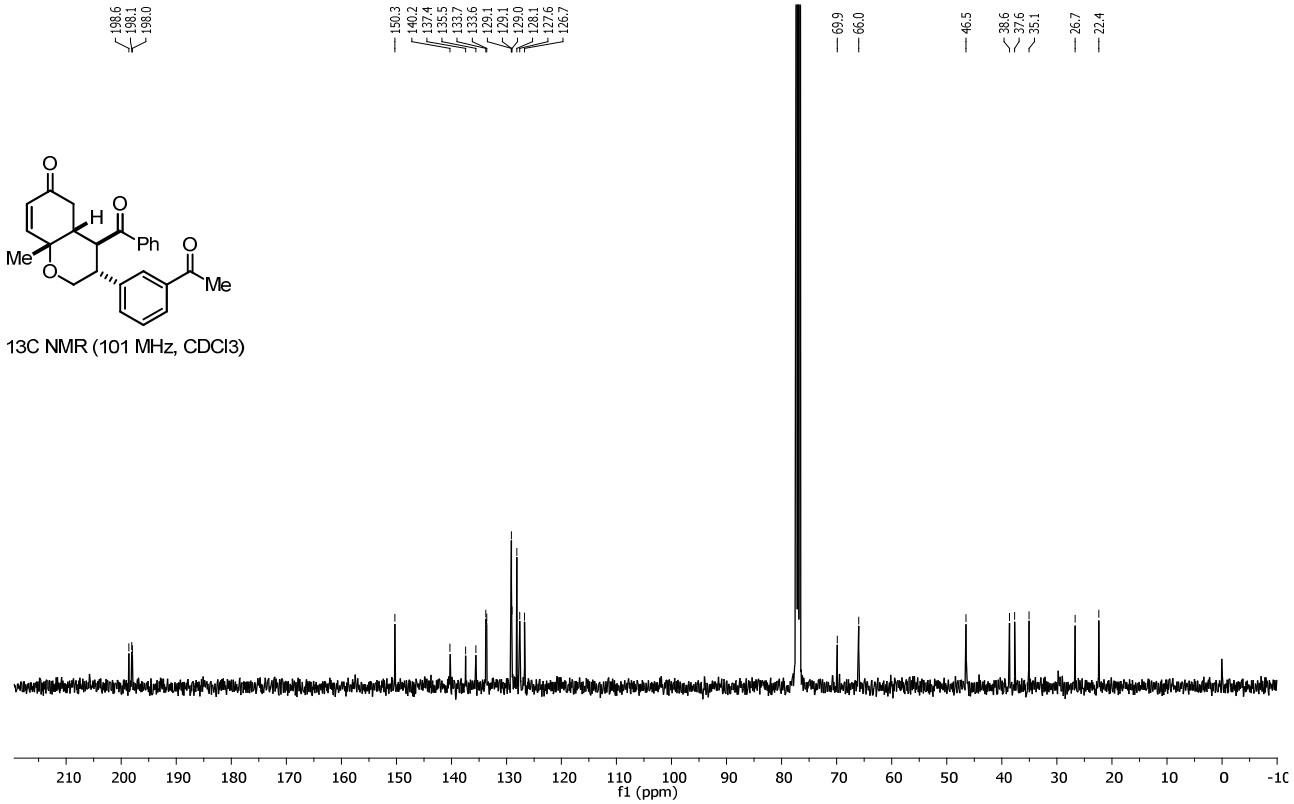


compound **3m**

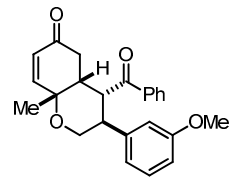


3-(3-Acetylphenyl)-4-benzoyl-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3n):

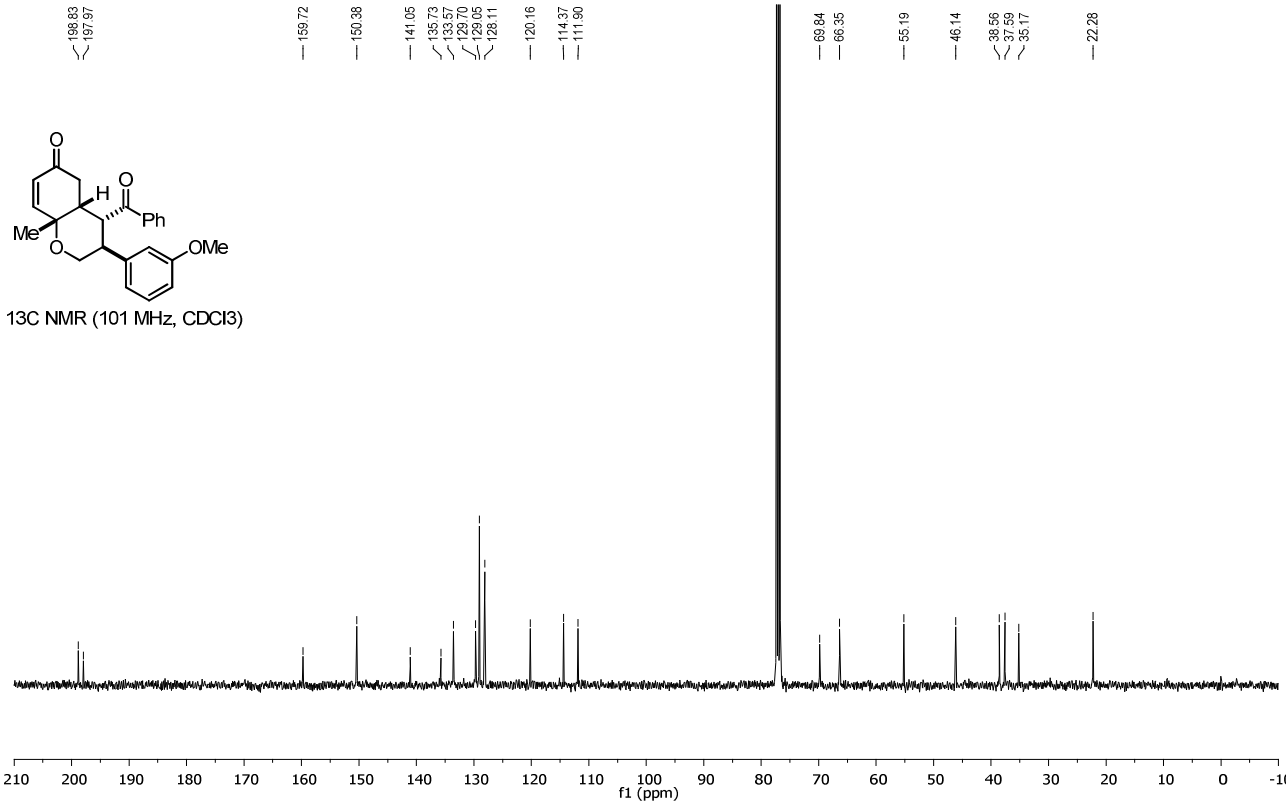




4-Benzoyl-3-(3-methoxyphenyl)-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3o):

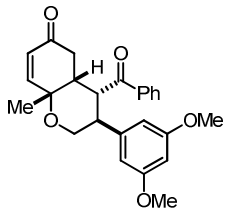


1H NMR (500 MHz, CDCl3)

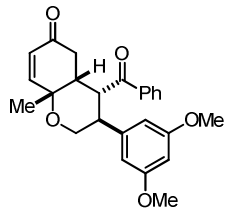


13C NMR (101 MHz, CDCl3)

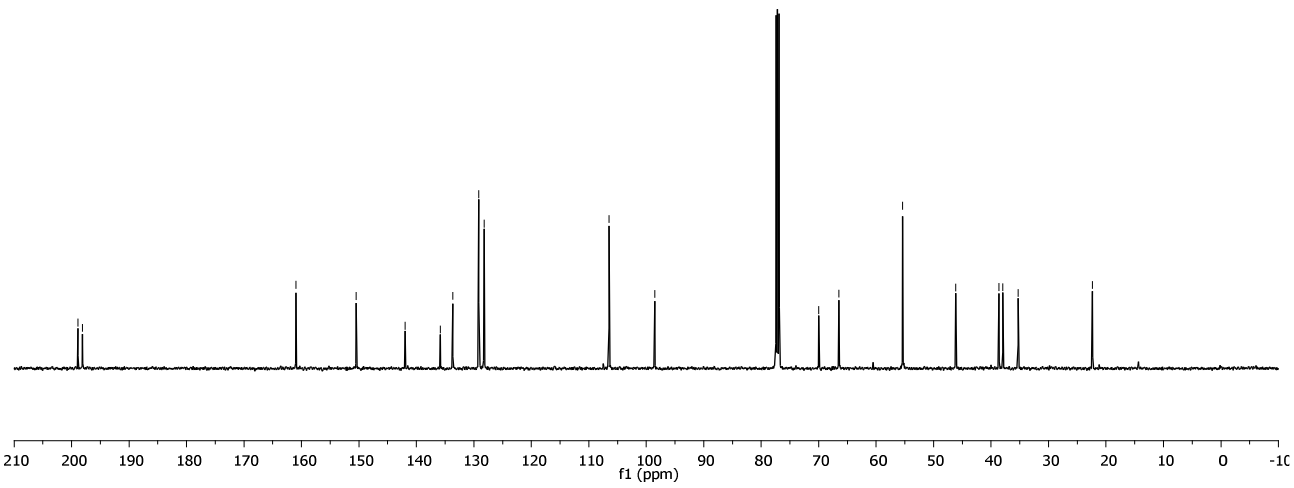
4-Benzoyl-3-(3,5-dimethoxyphenyl)-8a-methyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3p):



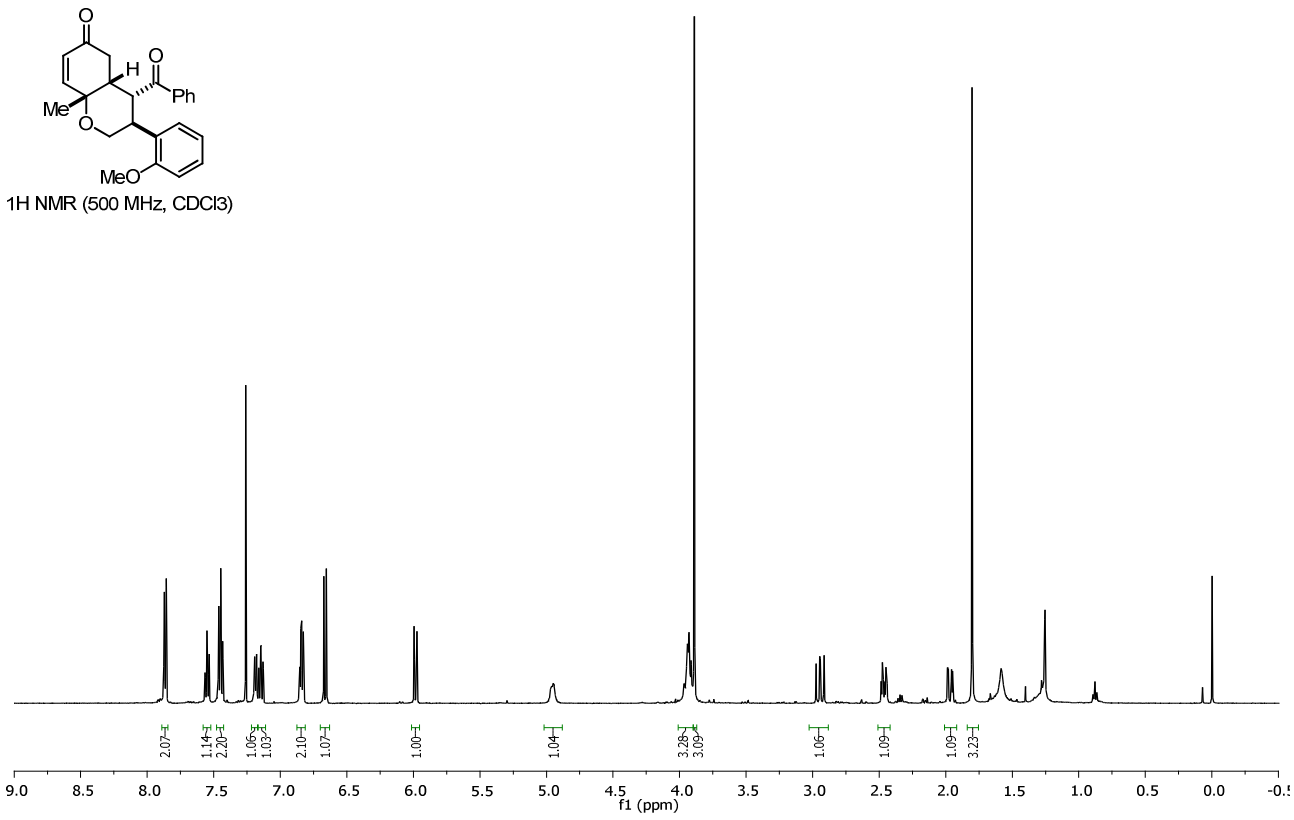
1H NMR (400 MHz, CDCl3)

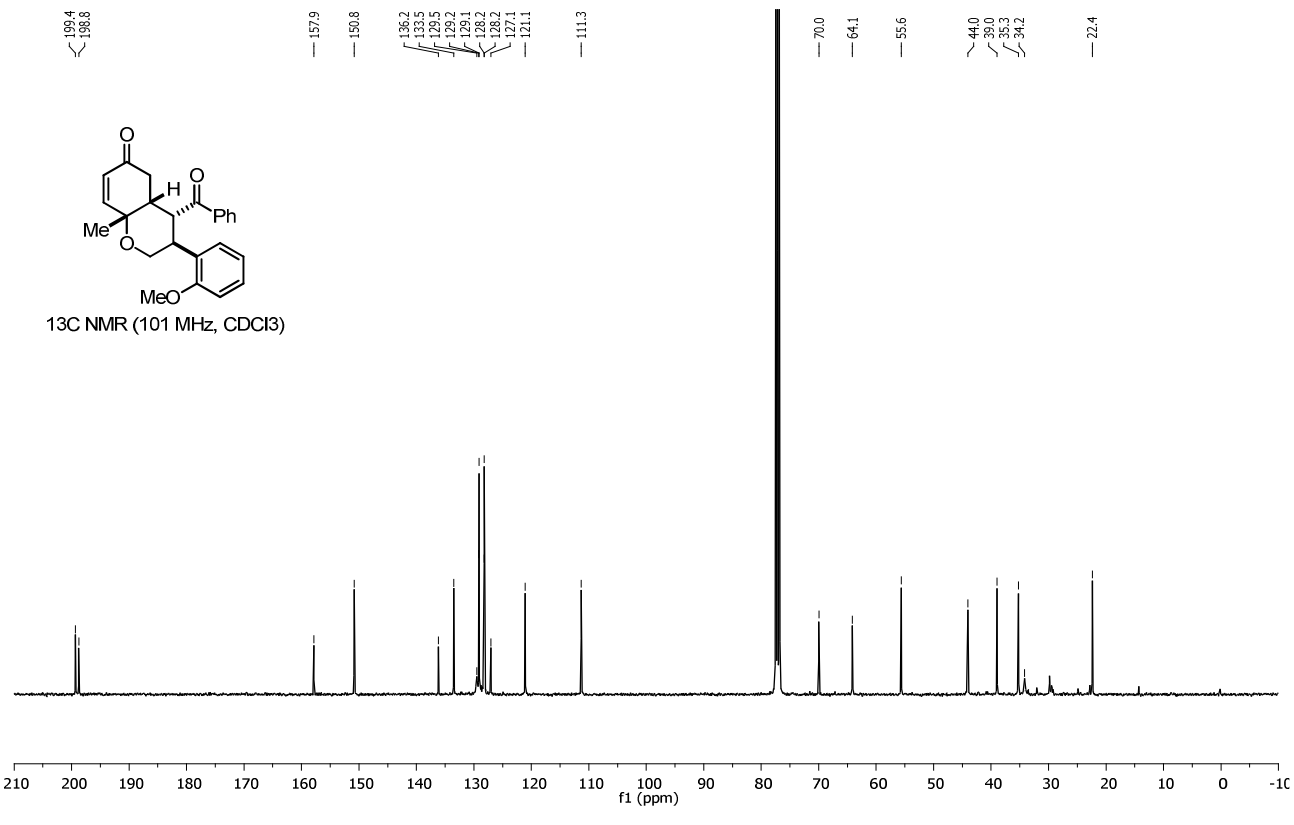


13C NMR (126 MHz, CDCl3)

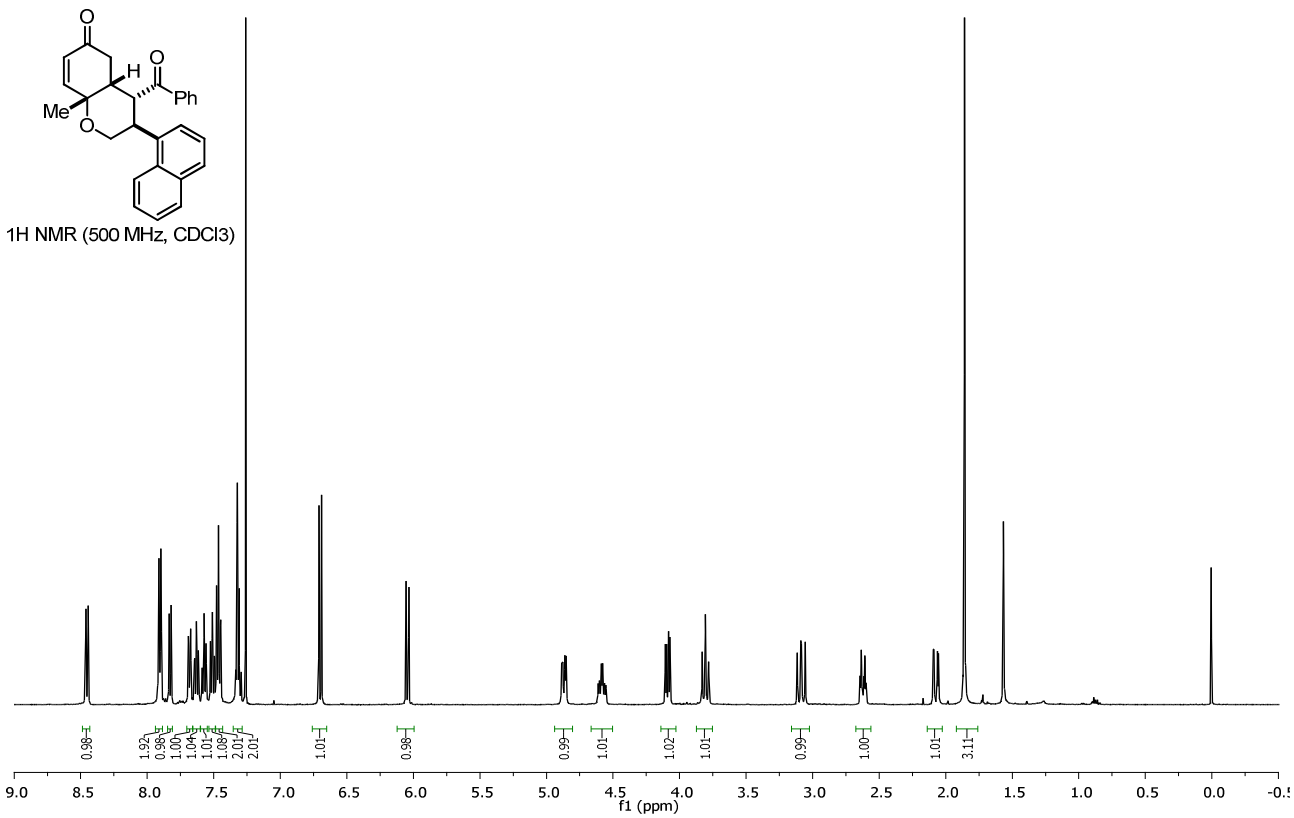


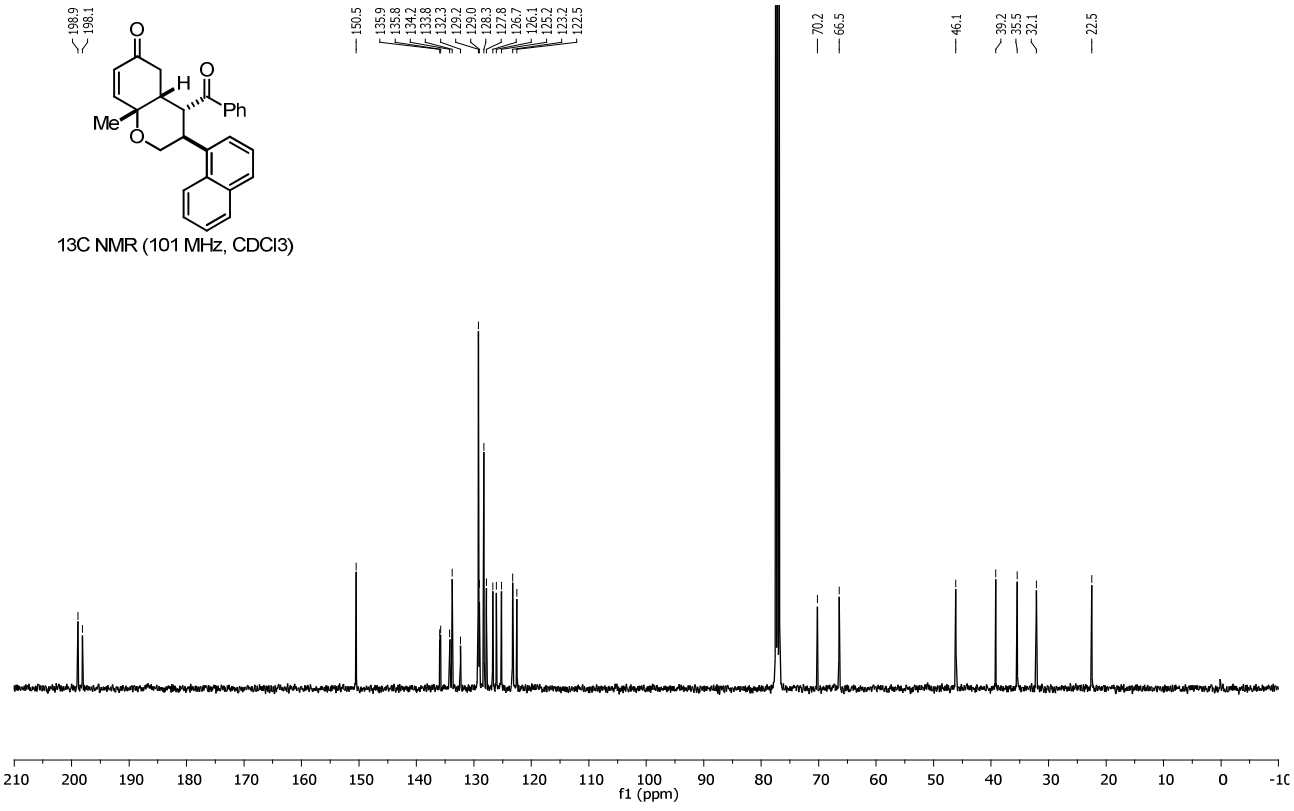
4-Benzoyl-3-(2-methoxyphenyl)-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3q):



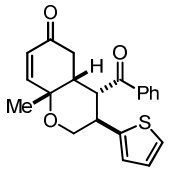


4-Benzoyl-8a-methyl-3-(naphthalen-1-yl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3r):

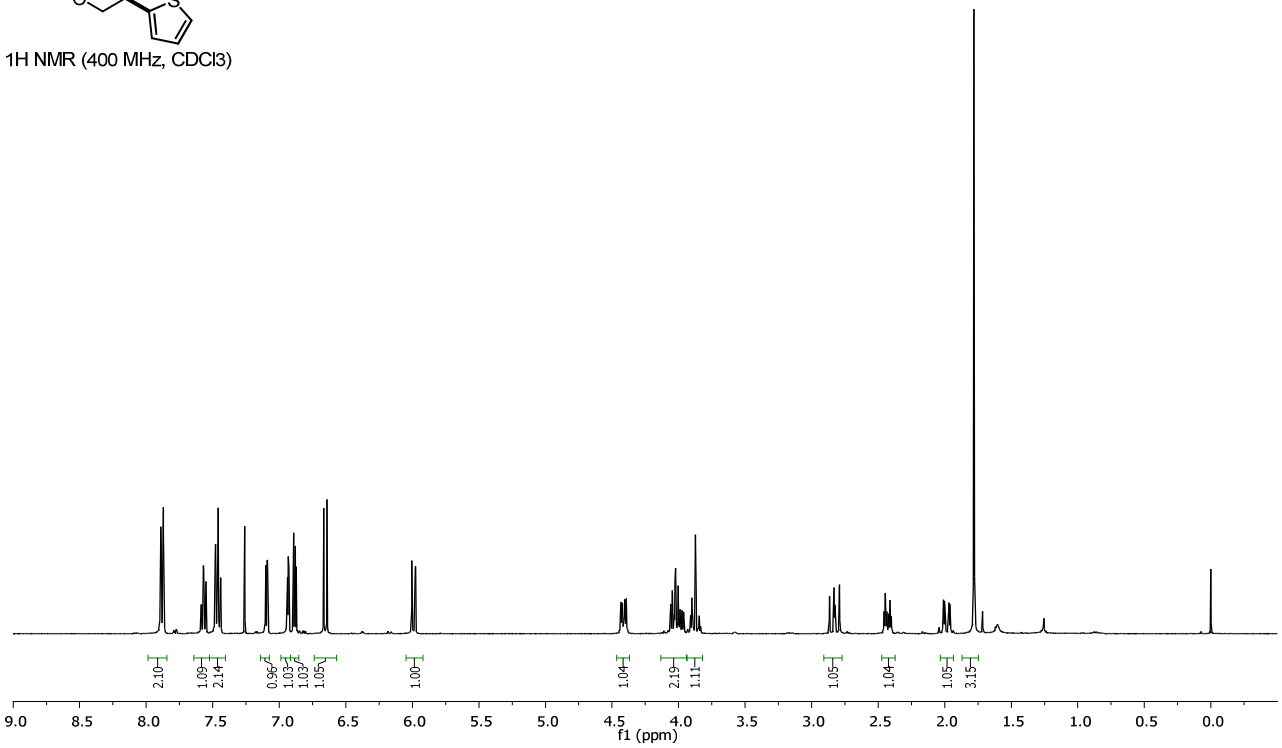


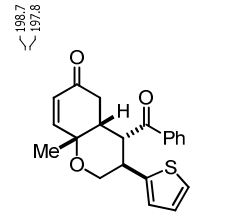


4-Benzoyl-8a-methyl-3-(thiophen-2-yl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3s):



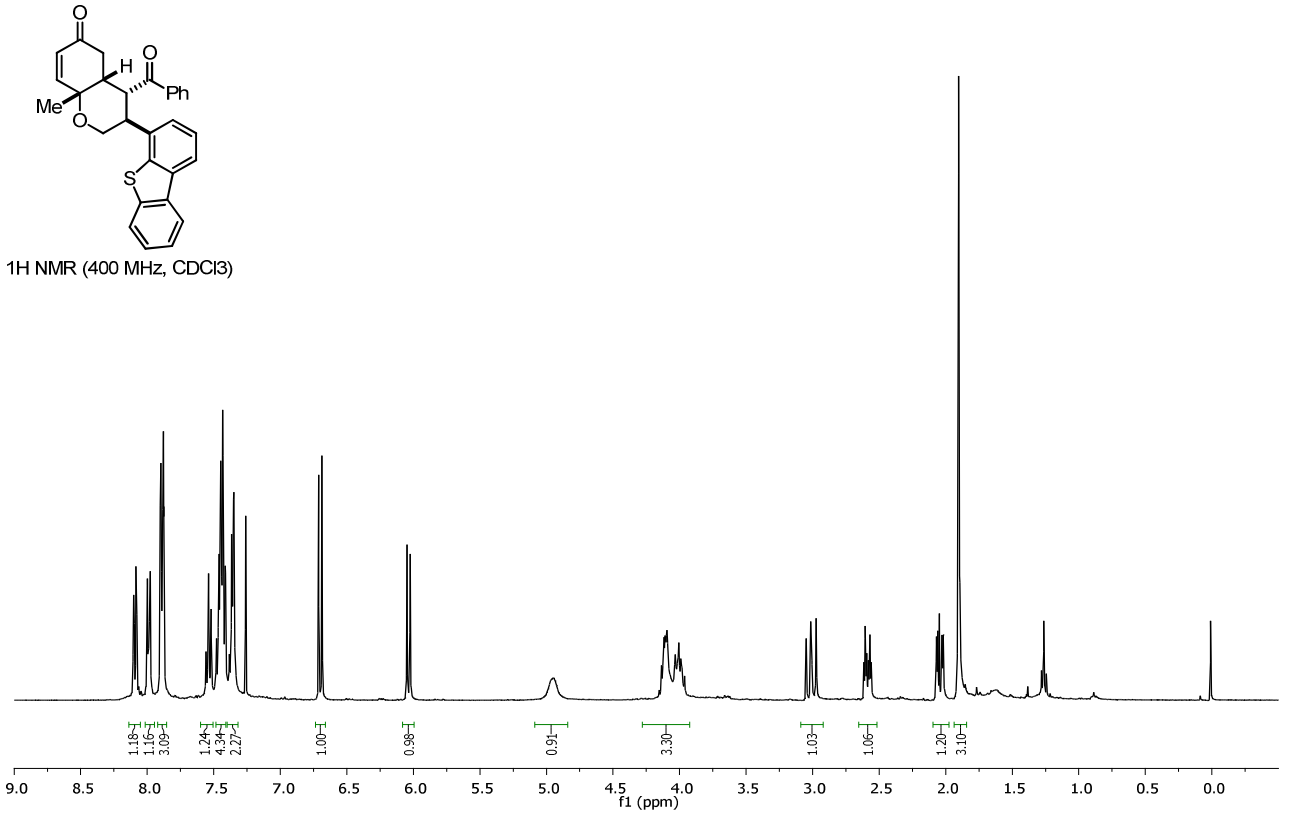
1H NMR (400 MHz, CDCl3)

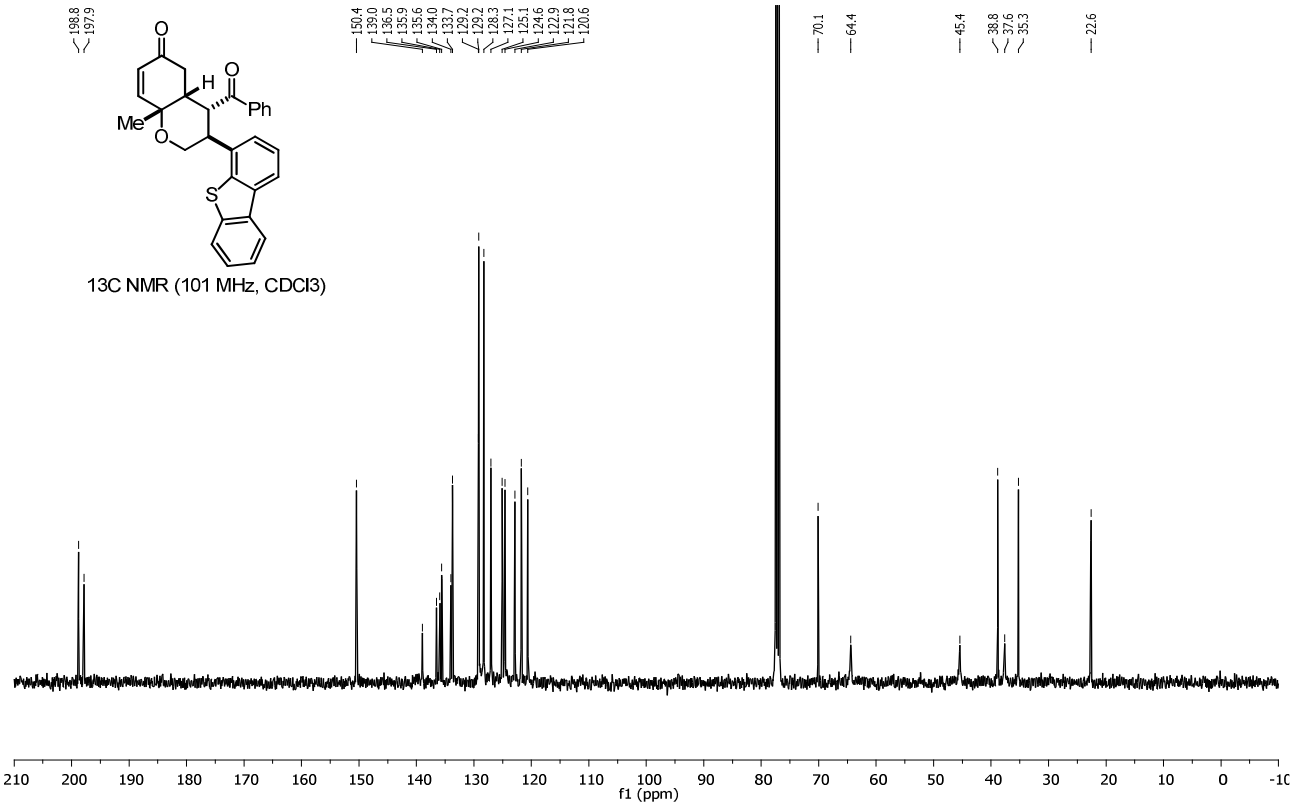




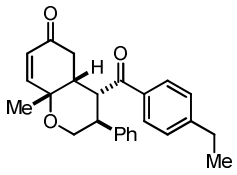
13C NMR (101 MHz, CDCl3)

4-Benzoyl-3-(dibenzo[b,d]thiophen-4-yl)-8a-methyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3t):

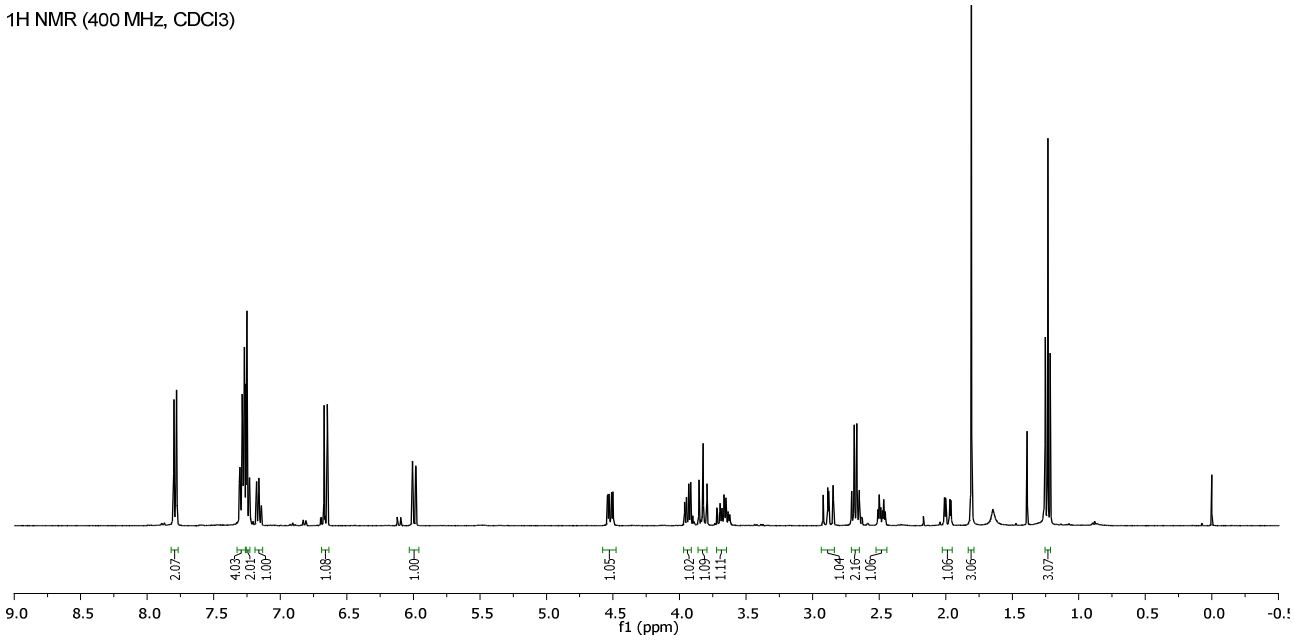


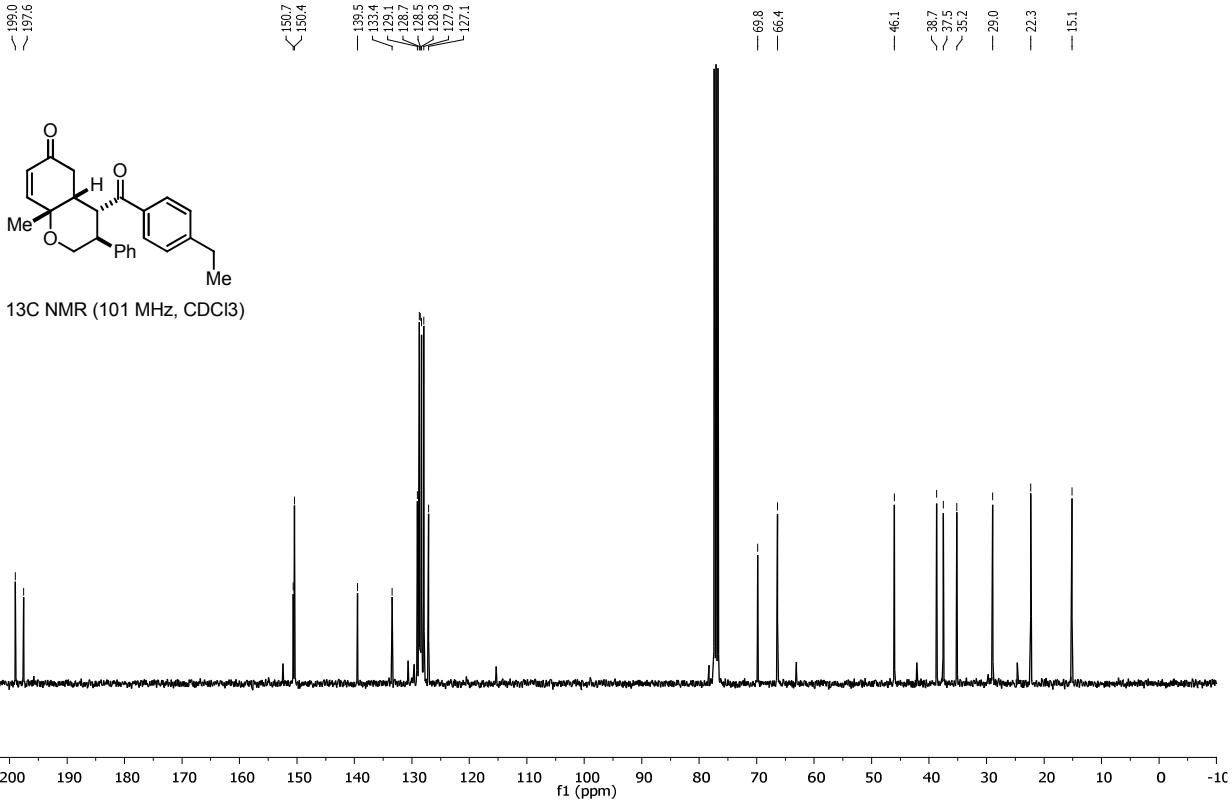


4-(4-Ethylbenzoyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3u):



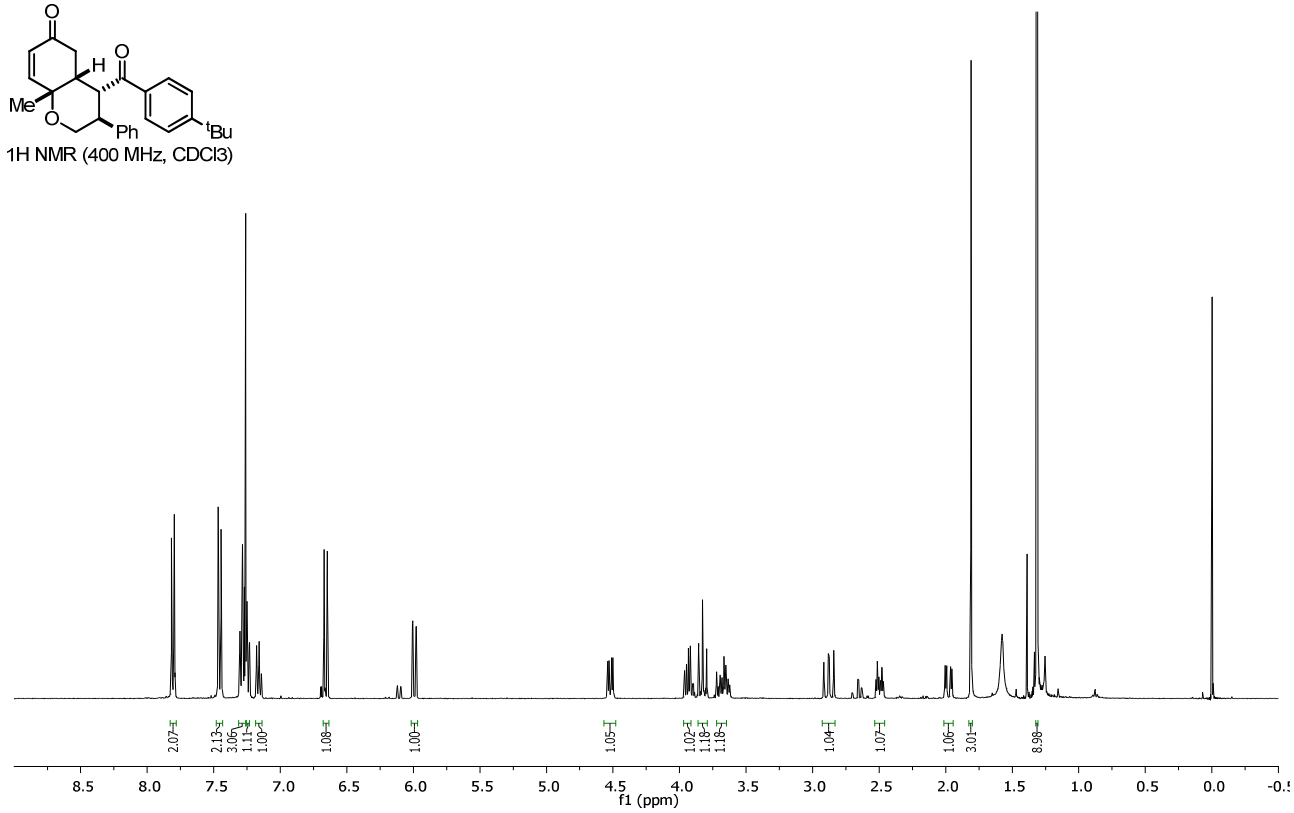
1H NMR (400 MHz, CDCl3)

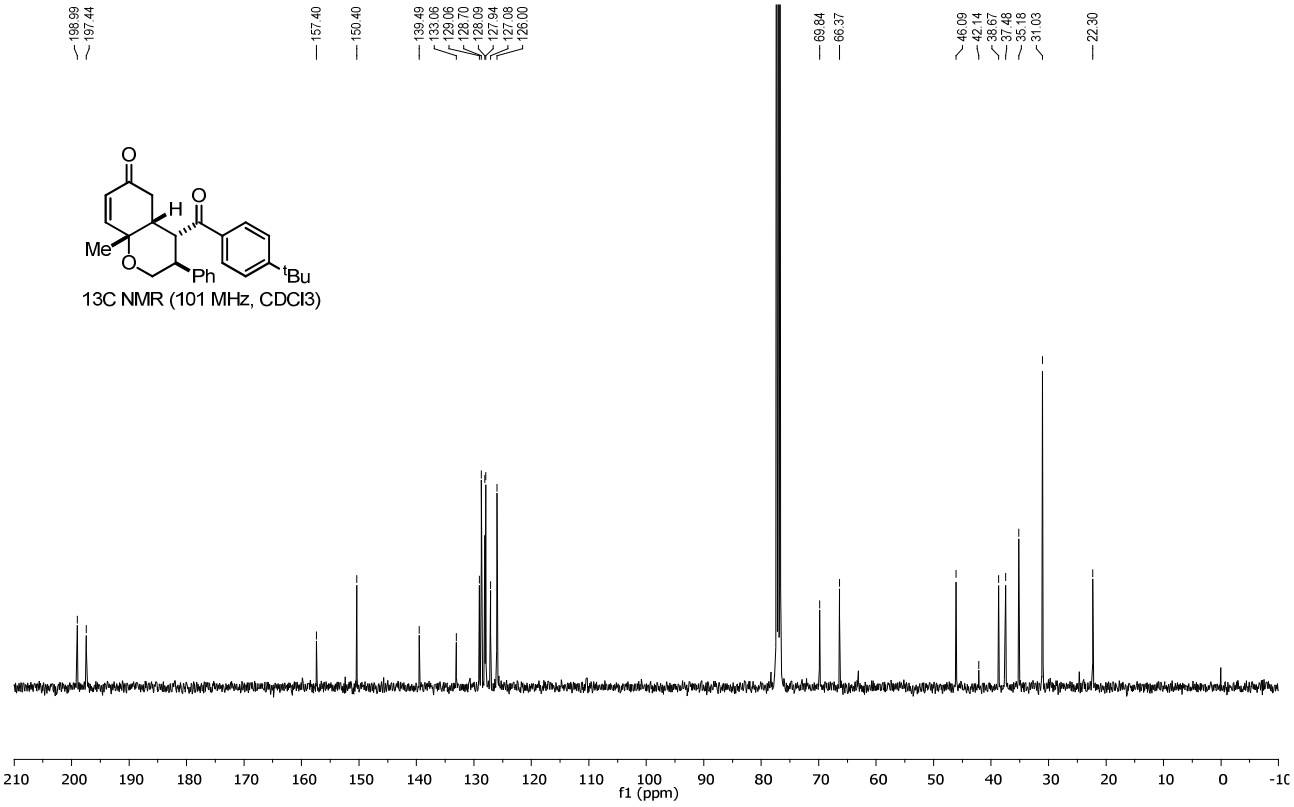




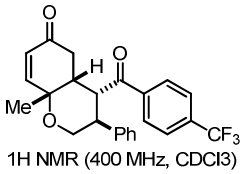
13C NMR (101 MHz, CDCl3)

4-(4-(*tert*-Butyl)benzoyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3v):

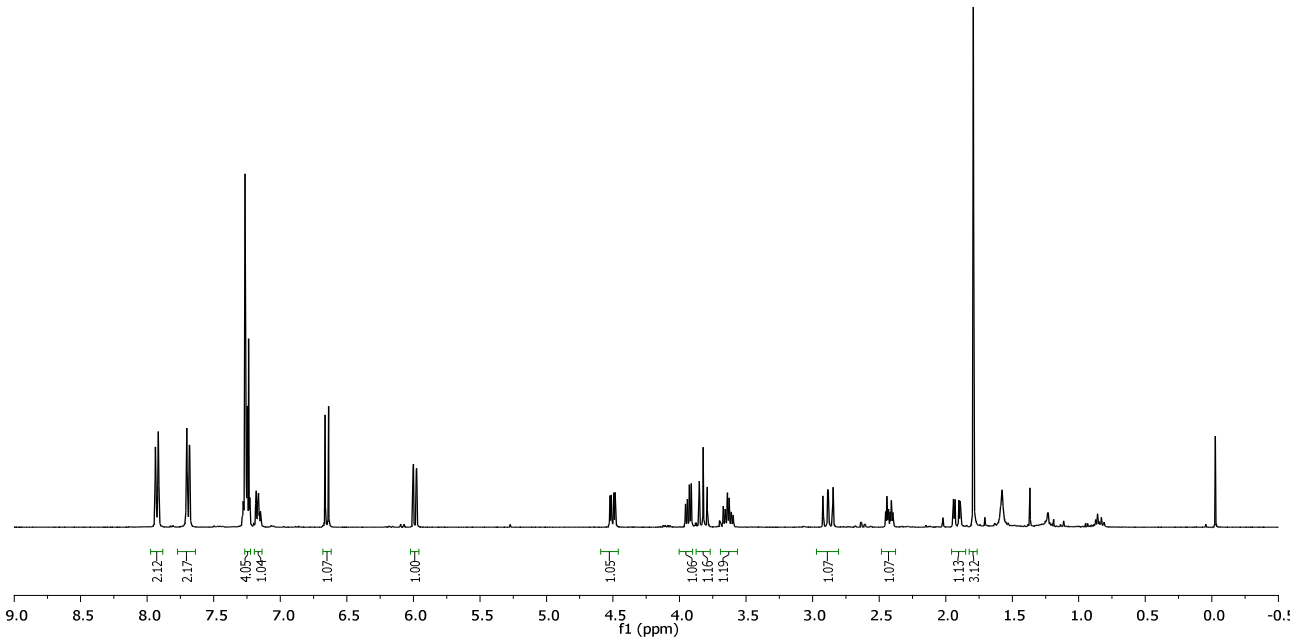


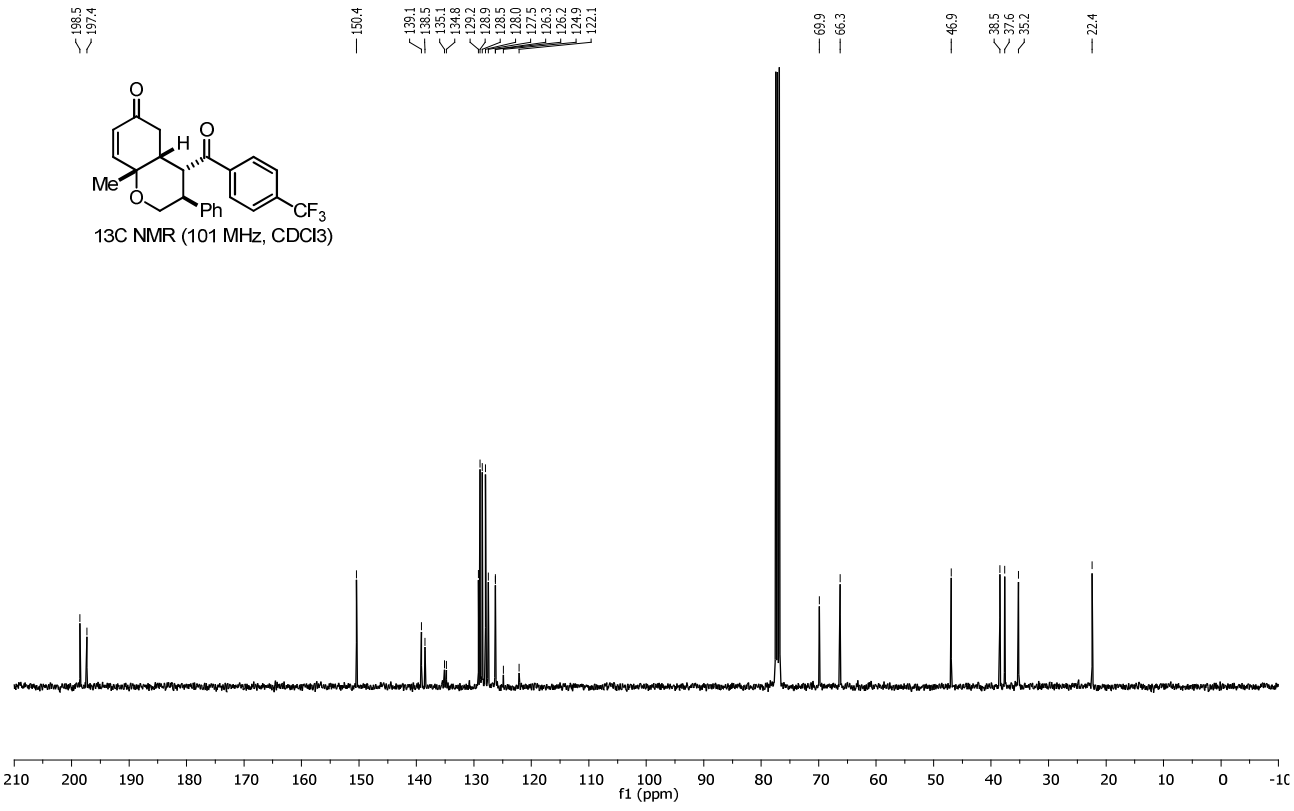


8a-Methyl-3-phenyl-4-(4-(trifluoromethyl)benzoyl)-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3w):



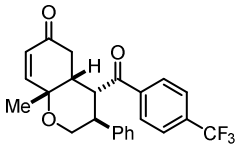
1H NMR (400 MHz, CDCl3)



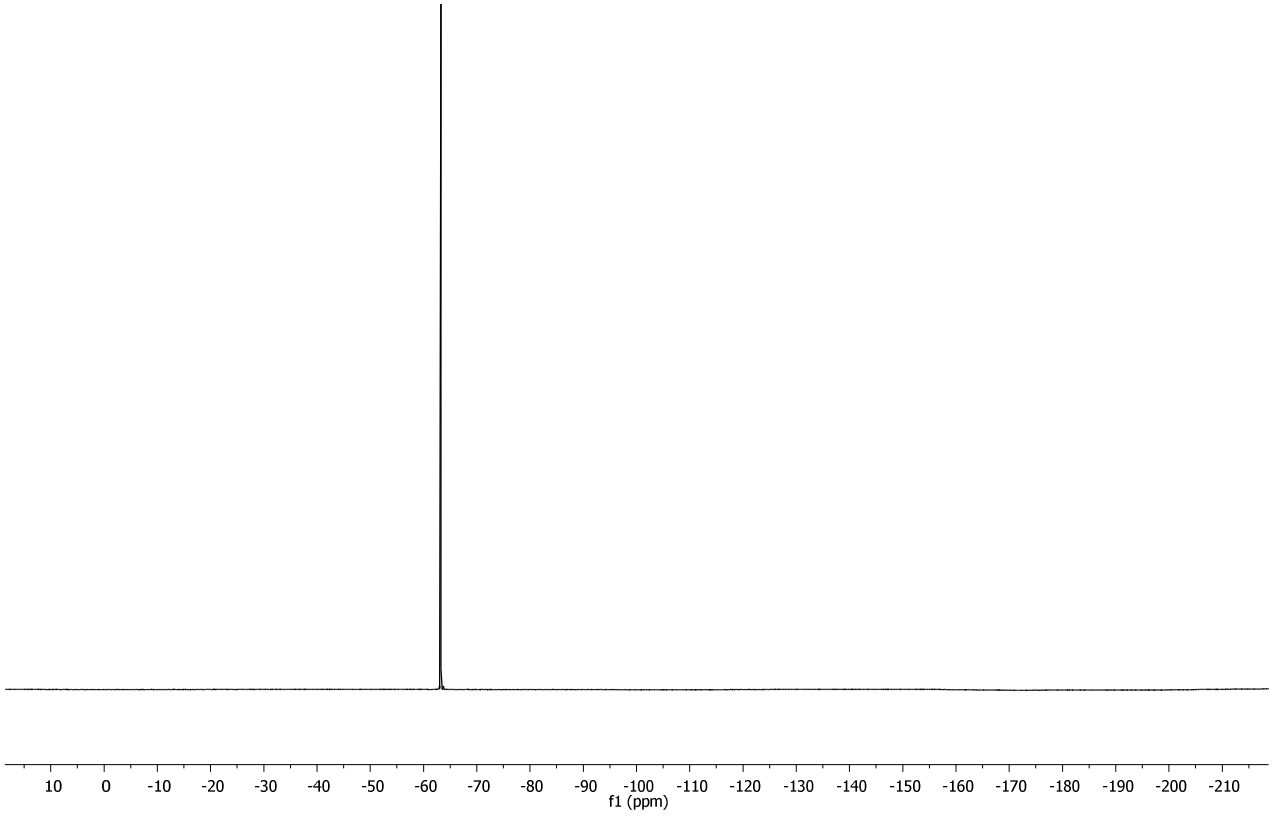


13C NMR (101 MHz, CDCl3)

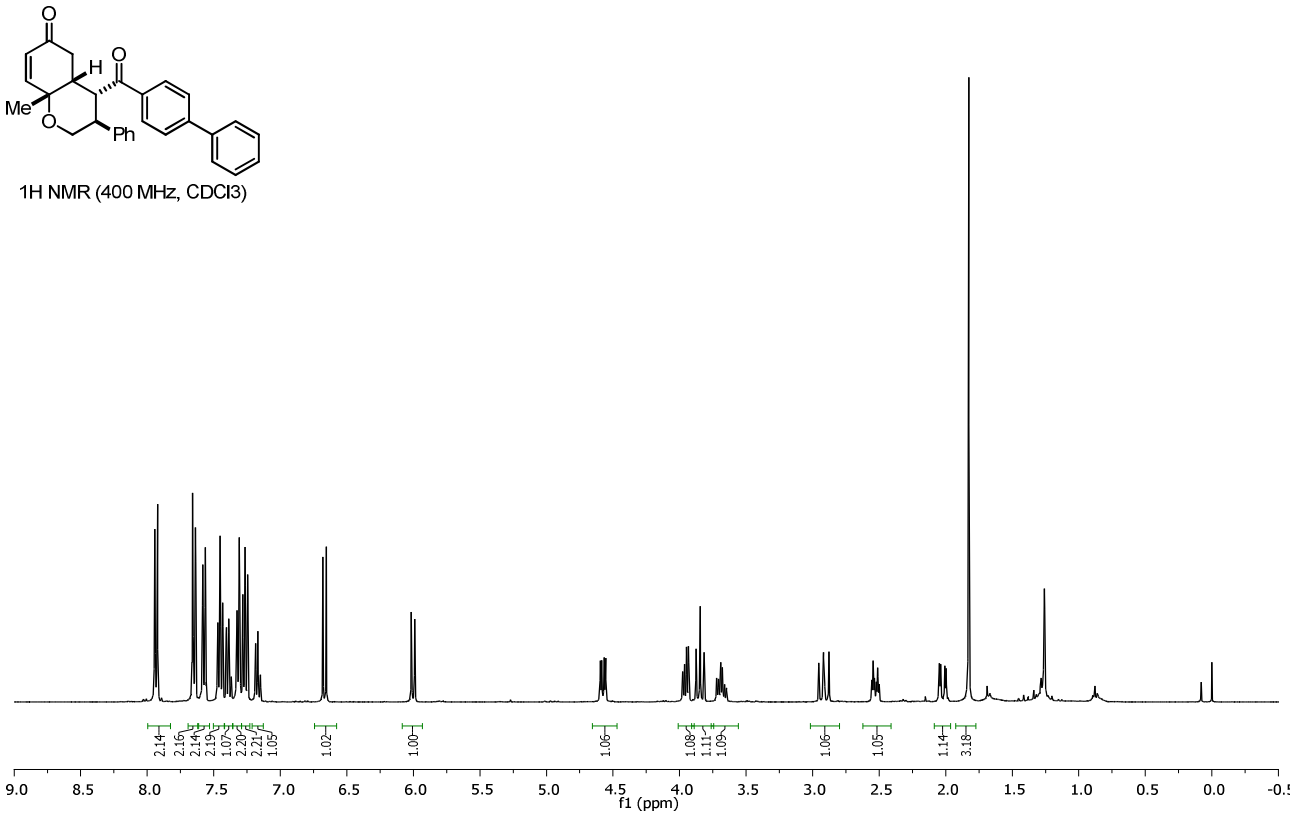
^{19}F NMR spectrum of compound 3w in $CDCl_3$

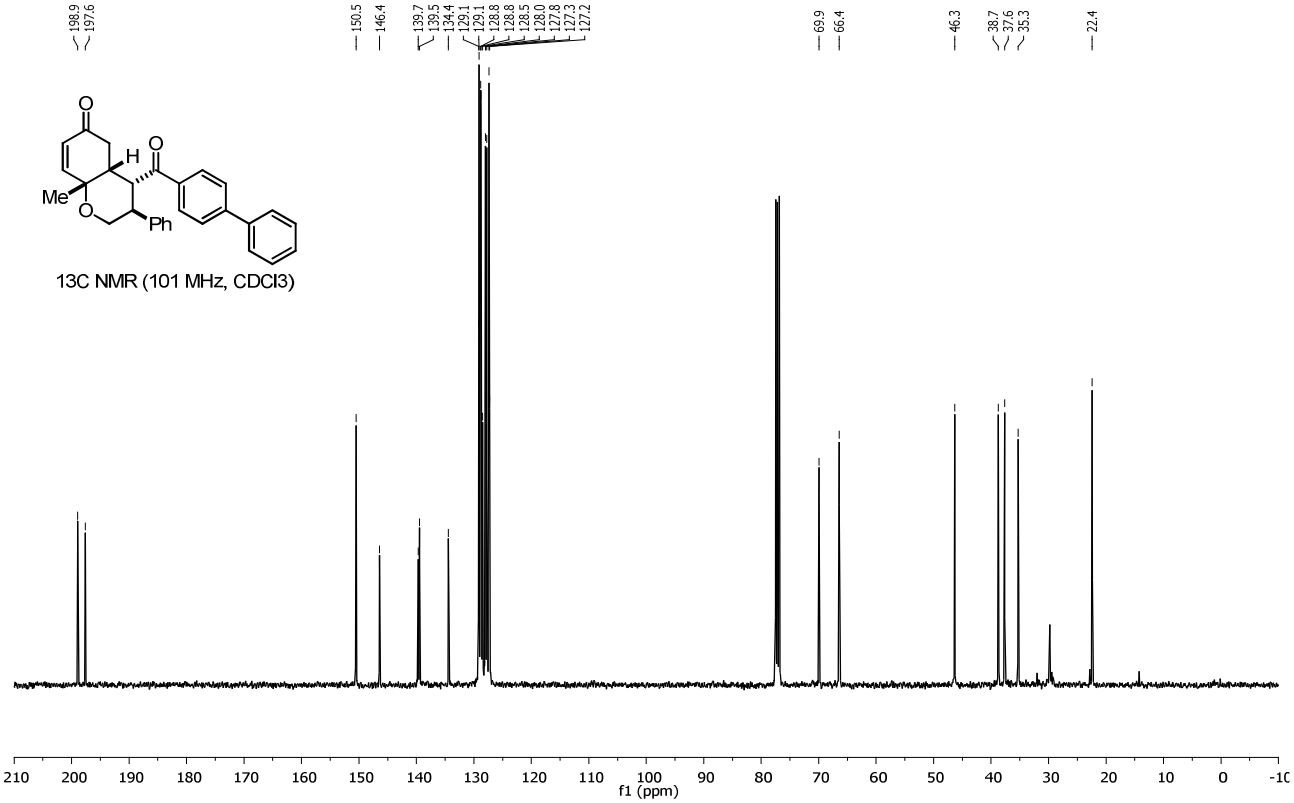


compound **3w**

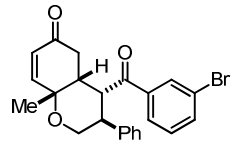


4-([1,1'-Biphenyl]-4-carbonyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3x):

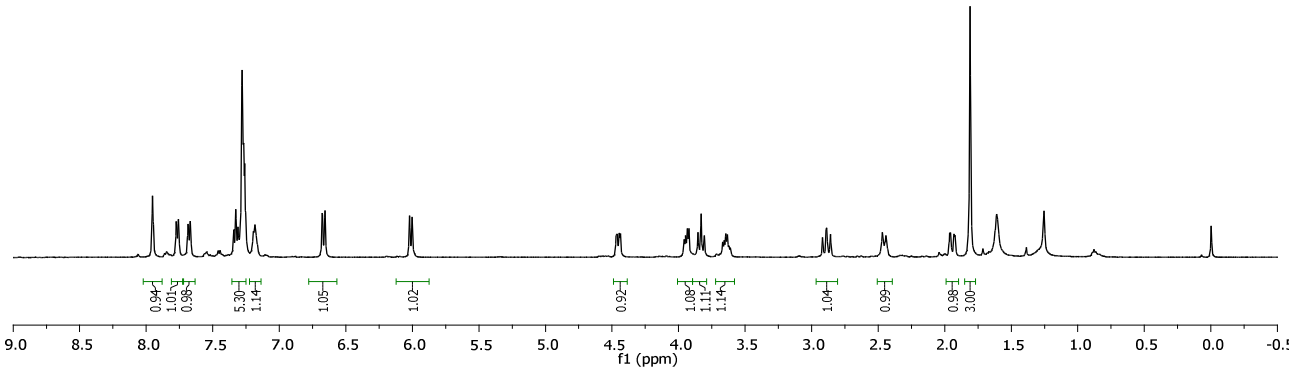


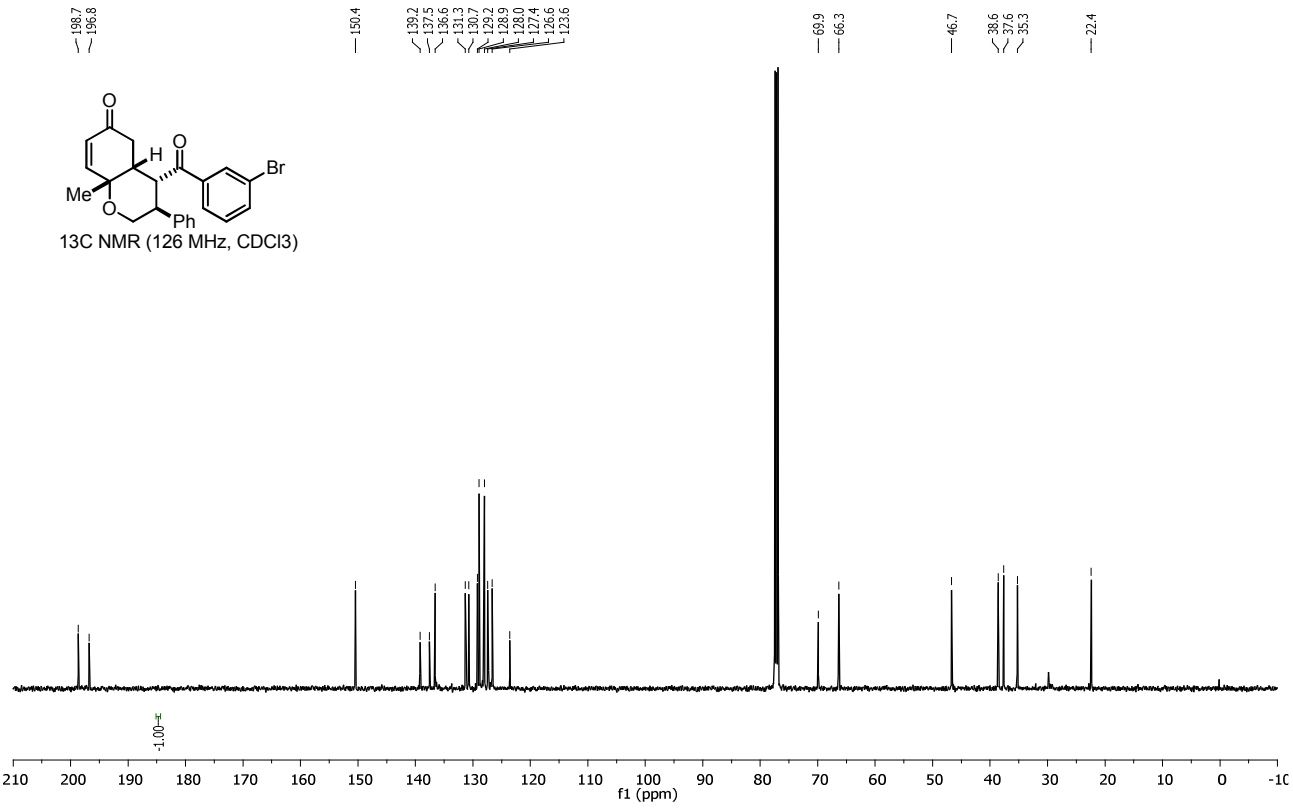


4-(3-Bromobenzoyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3y):



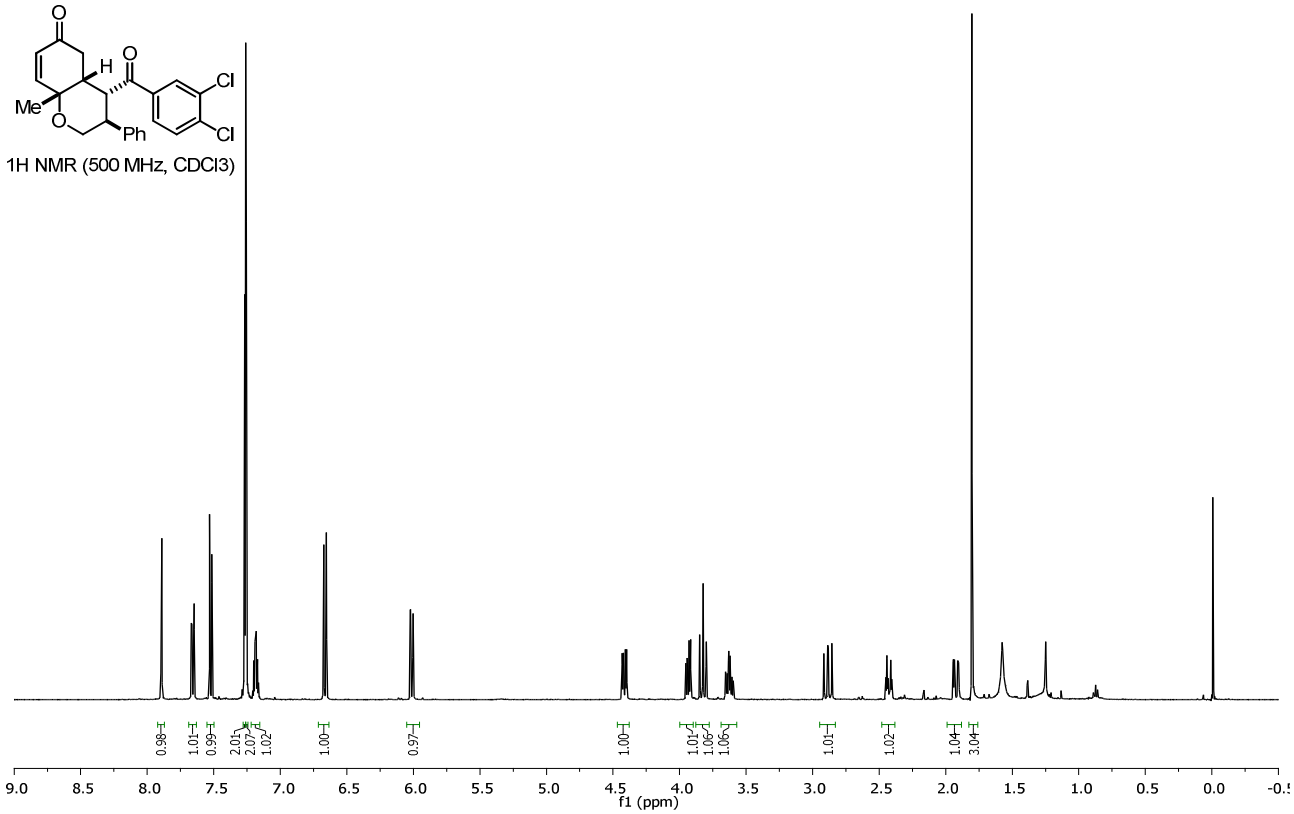
1H NMR (500 MHz, CDCl3)

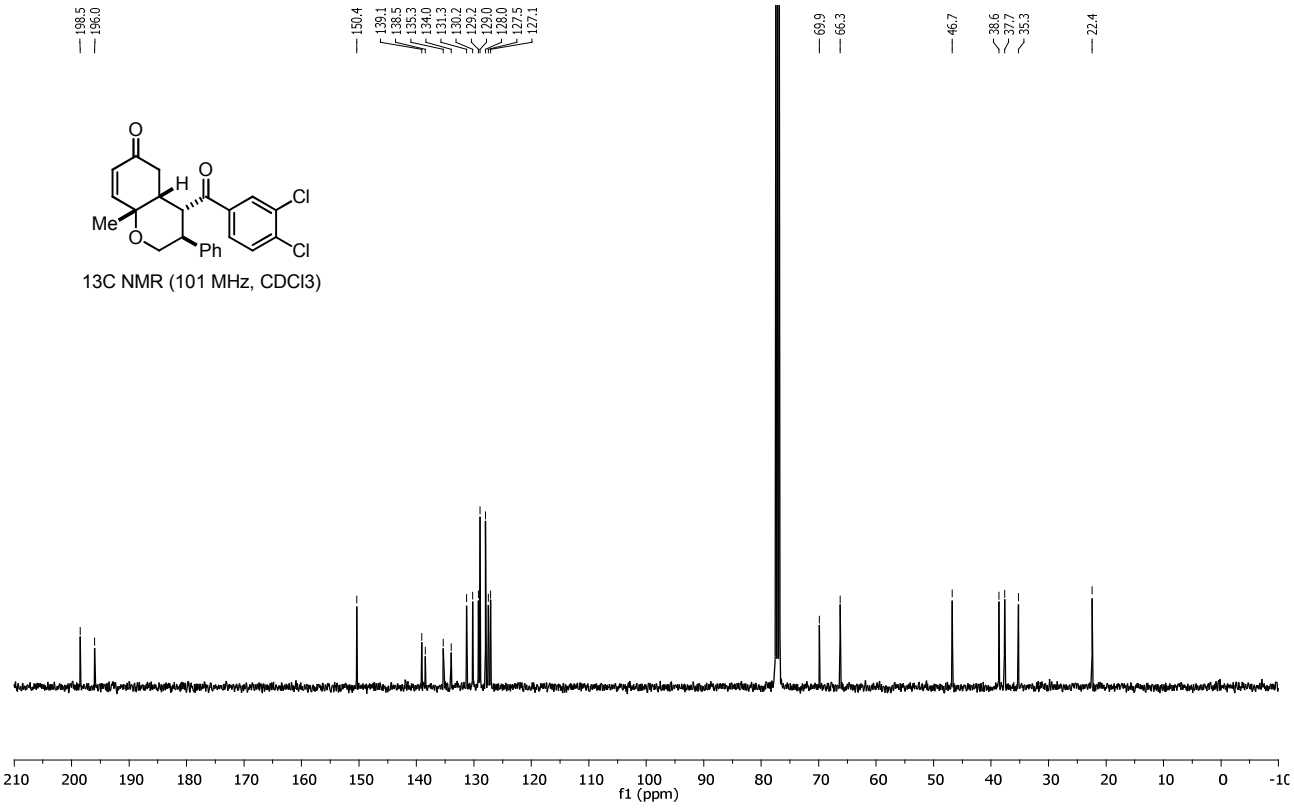




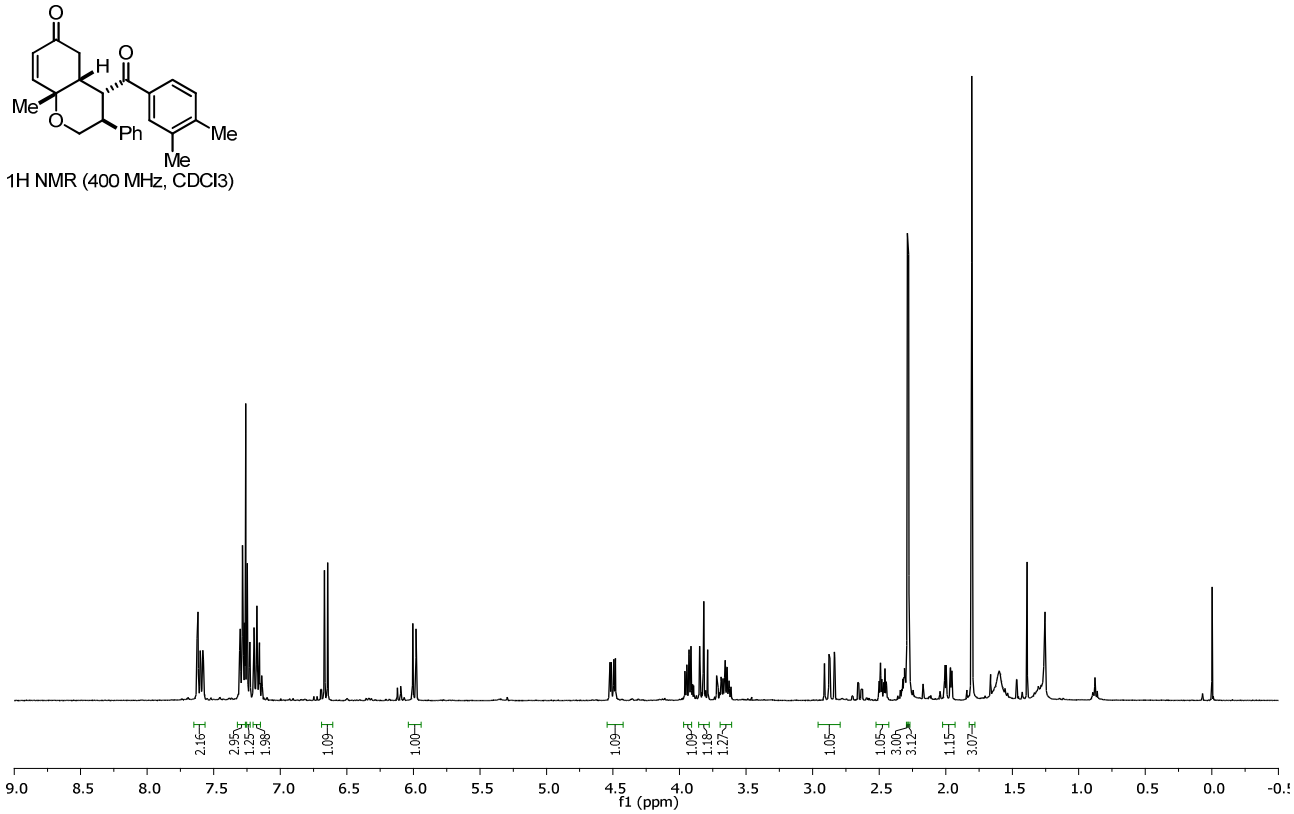
13C NMR (126 MHz, CDCl3)

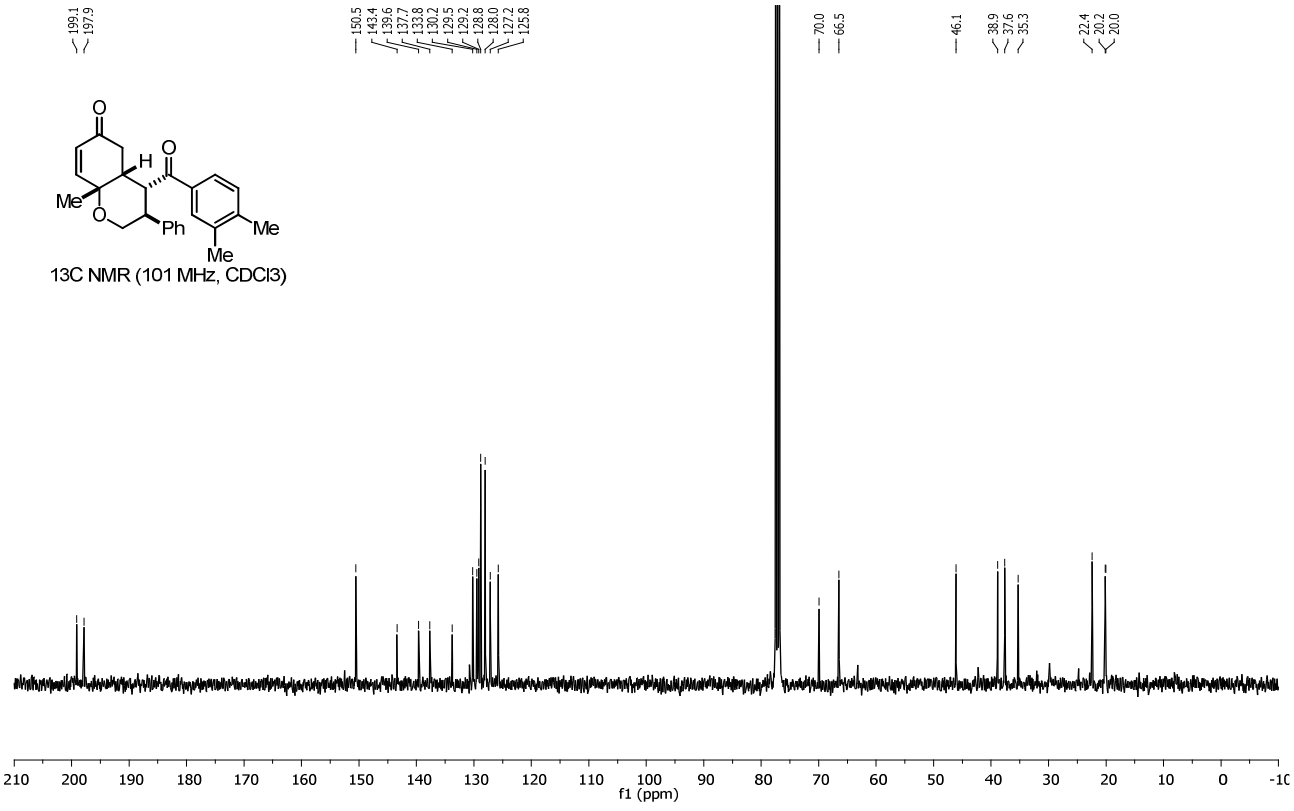
4-(3,4-Dichlorobenzoyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3z):



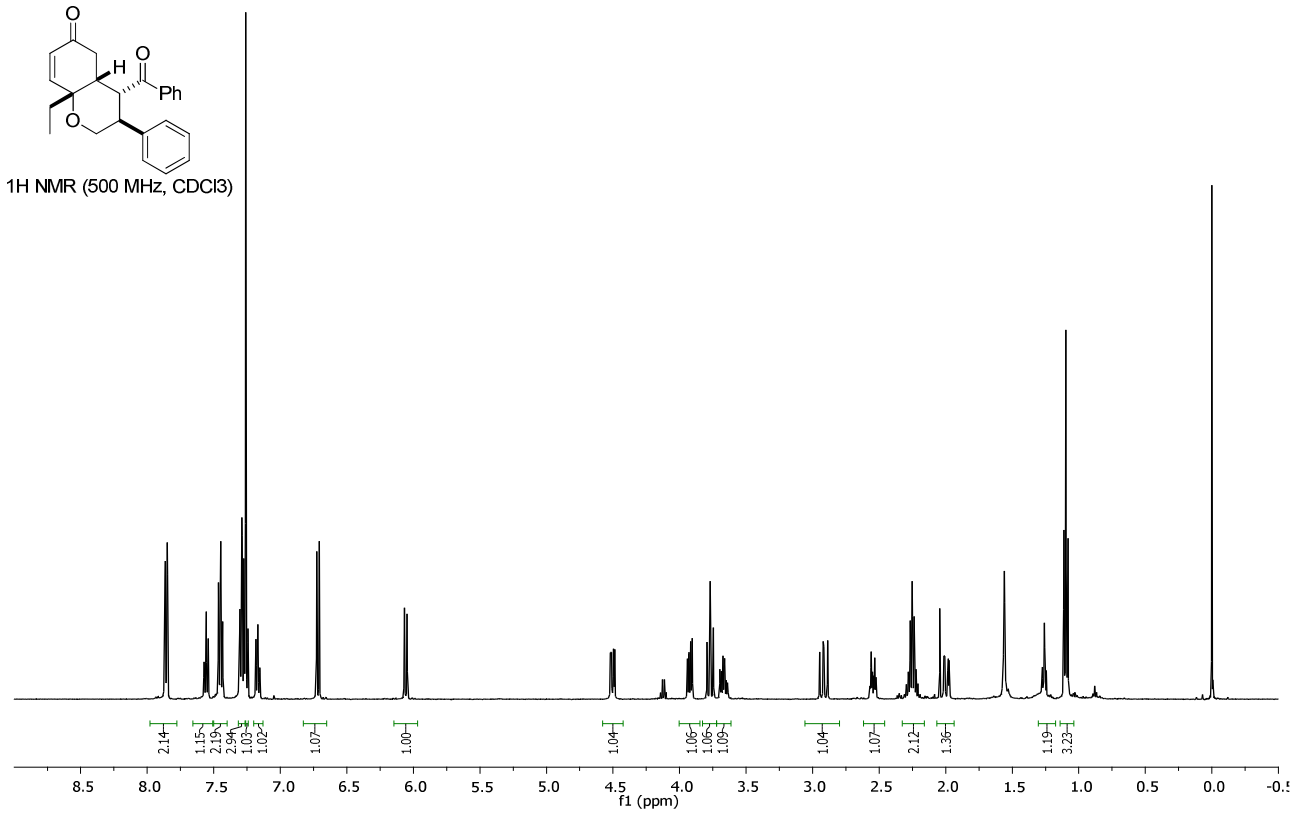


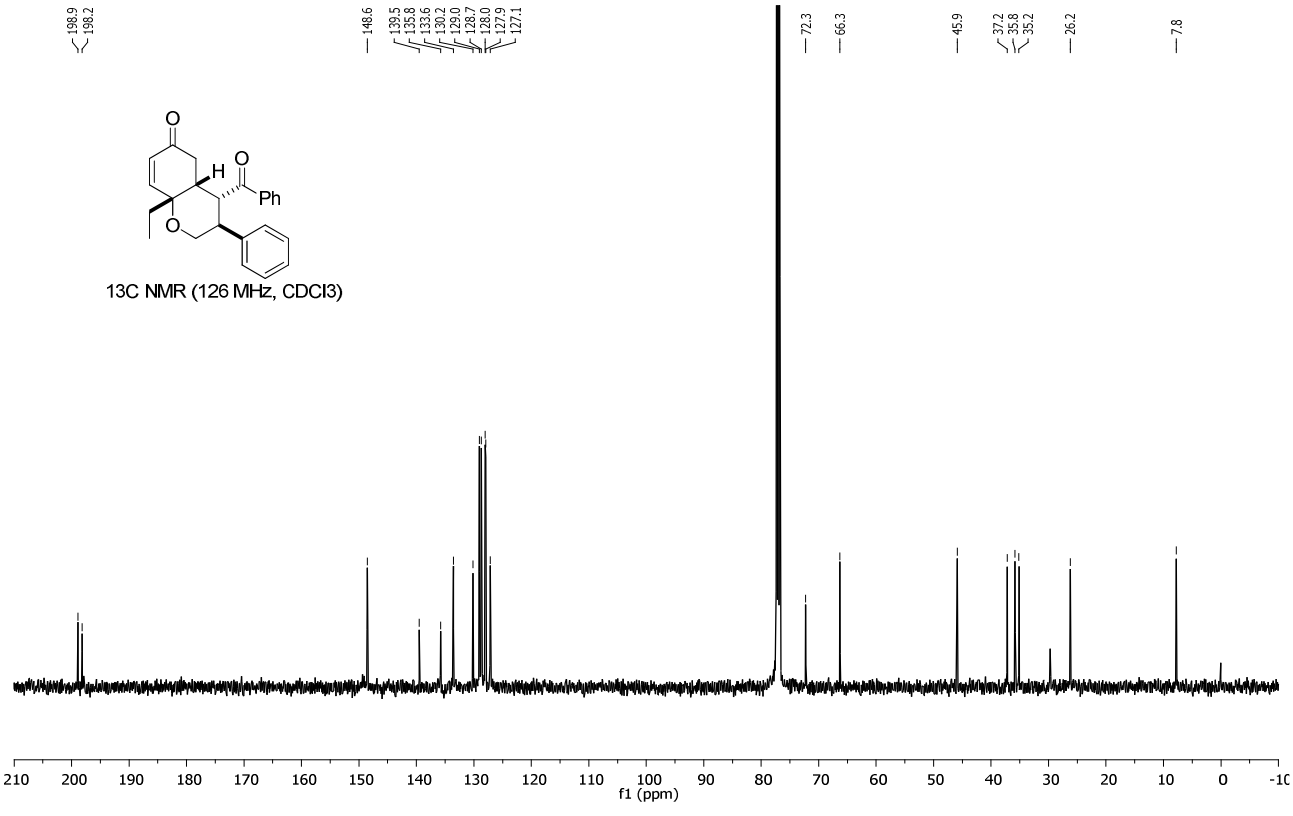
4-(3,4-Dimethylbenzoyl)-8a-methyl-3-phenyl-3,4,4a,5-tetrahydro-2*H*-chromen-6(8a*H*)-one (3aa):



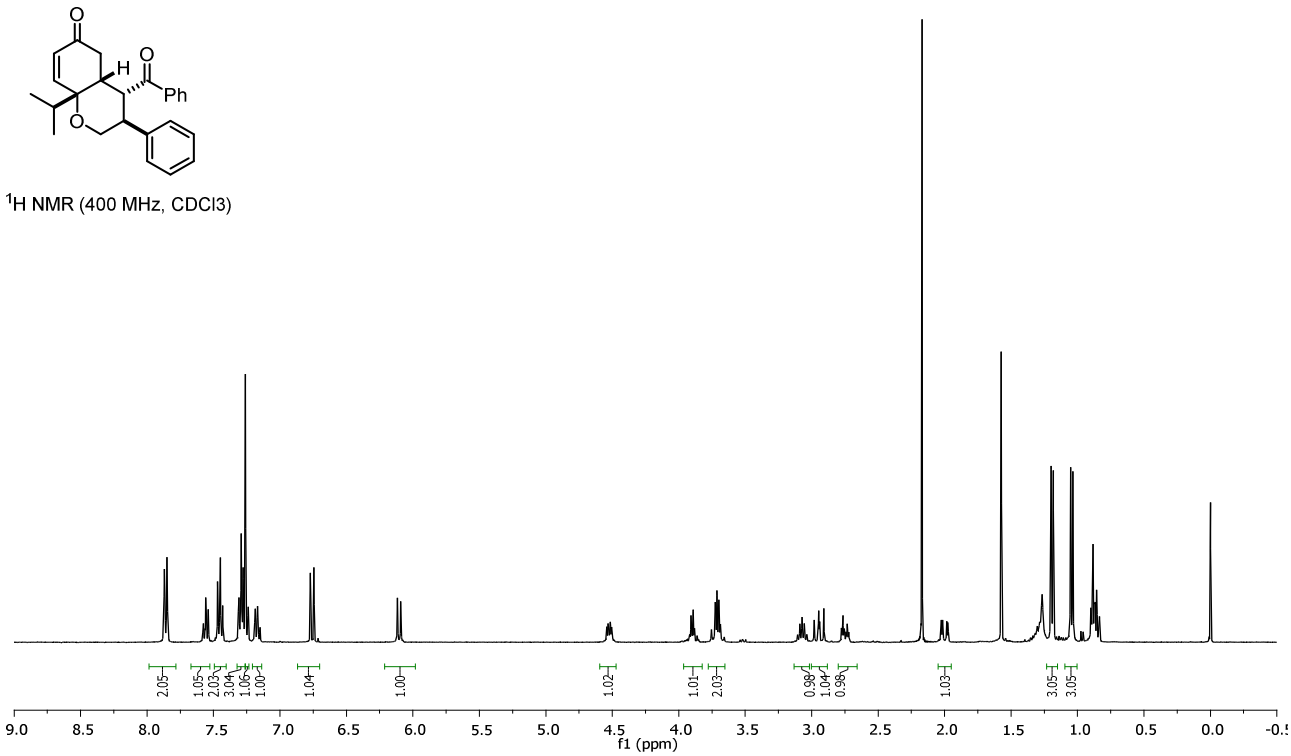


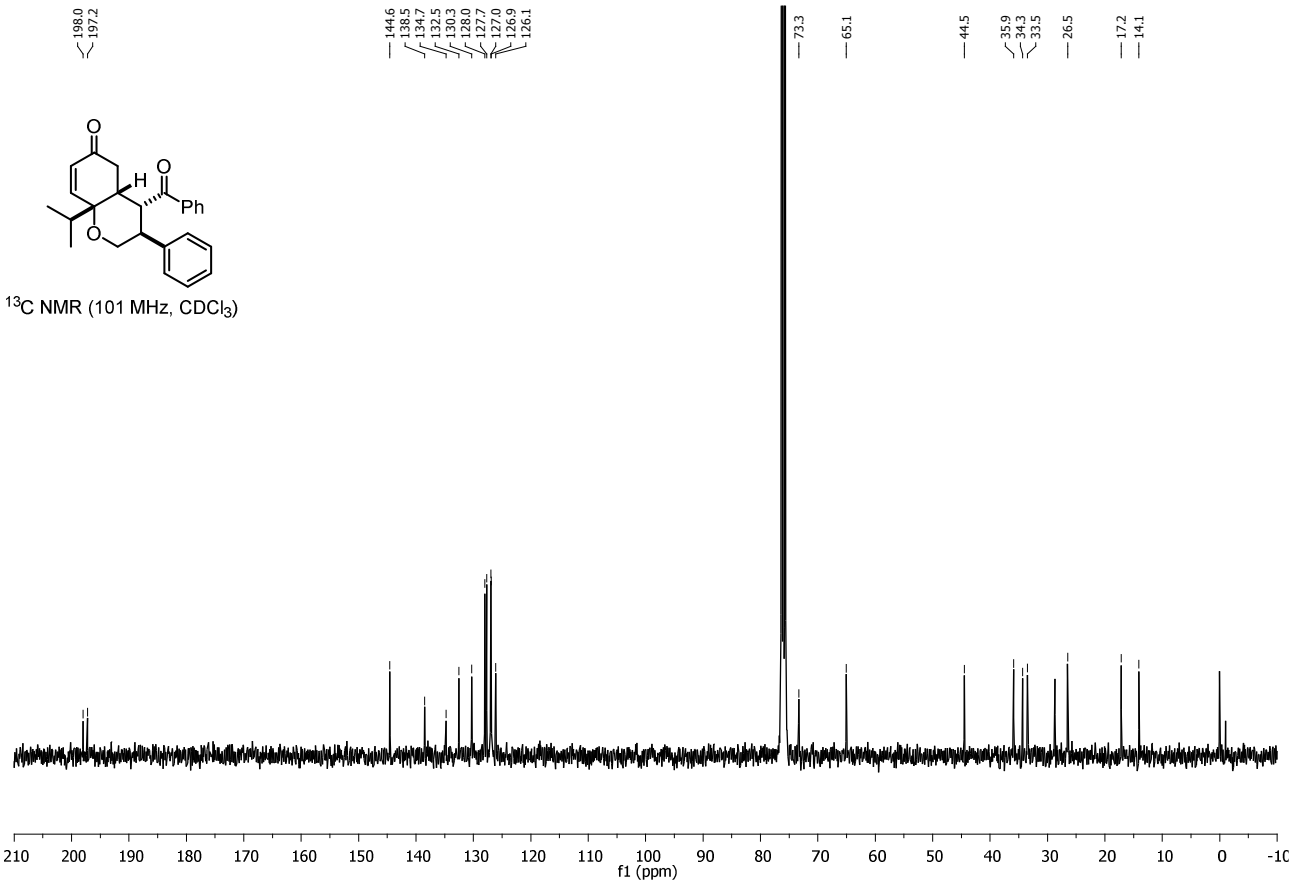
4-Benzoyl-8a-ethyl-3-phenyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3ab):



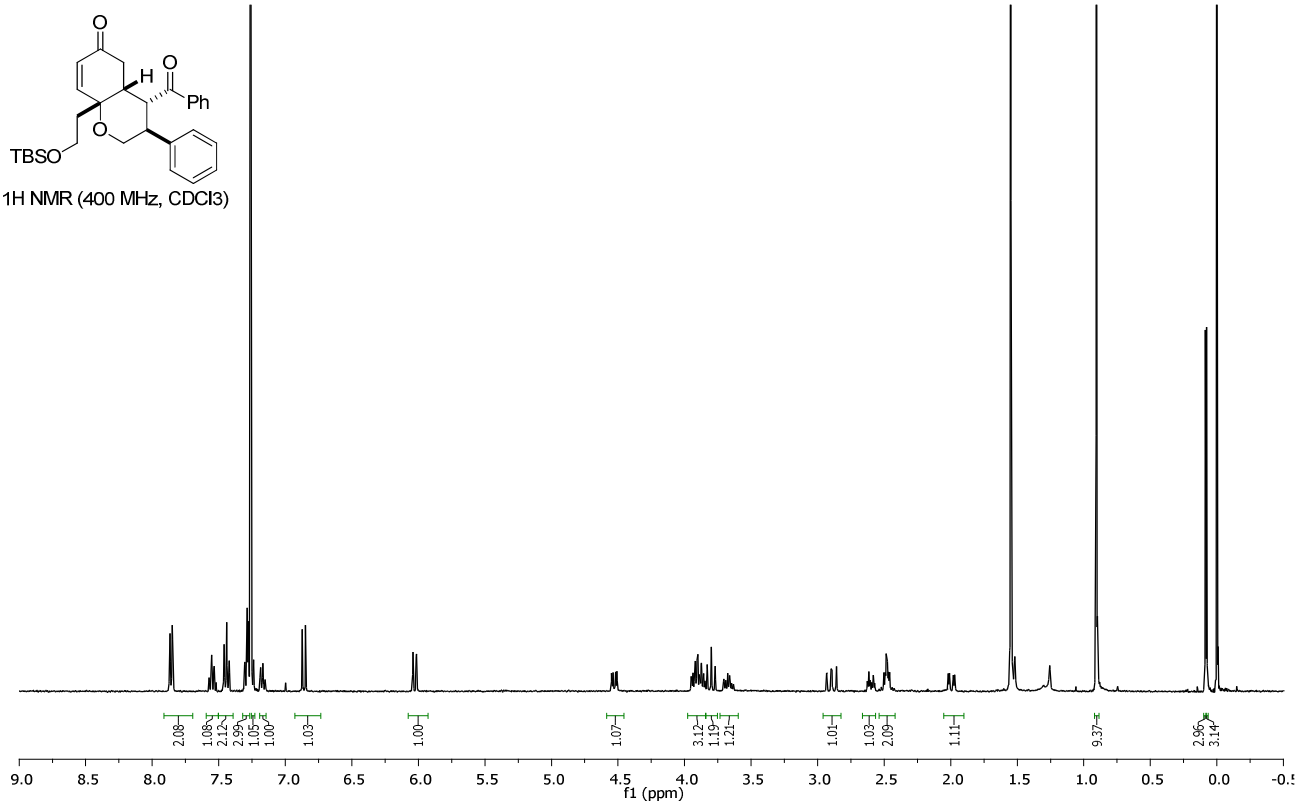


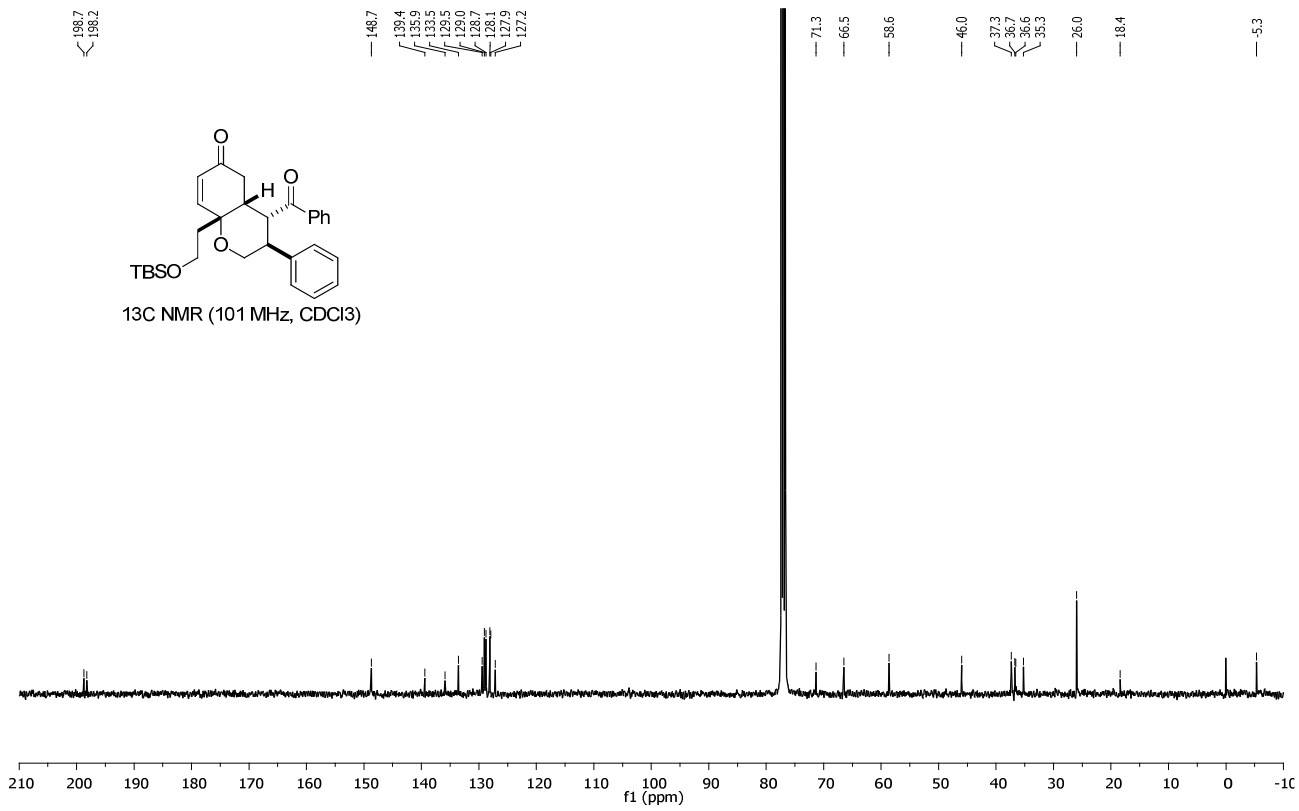
4-Benzoyl-8a-isopropyl-3-phenyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3ac):





4-Benzoyl-8a-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-3-phenyl-3,4,4a,8a-tetrahydro-2*H*-chromen-6(5*H*)-one (3ad):





4-Benzoyl-3-phenyloctahydrofuro[2,3-i]chromen-6(2*H*)-one (8):