Supporting Information

Rh(III)-Catalyzed Diastereoselective Cascade Annulation of Enone-Tethered Cyclohexadienones via a C(sp^2)−H Bond Activation

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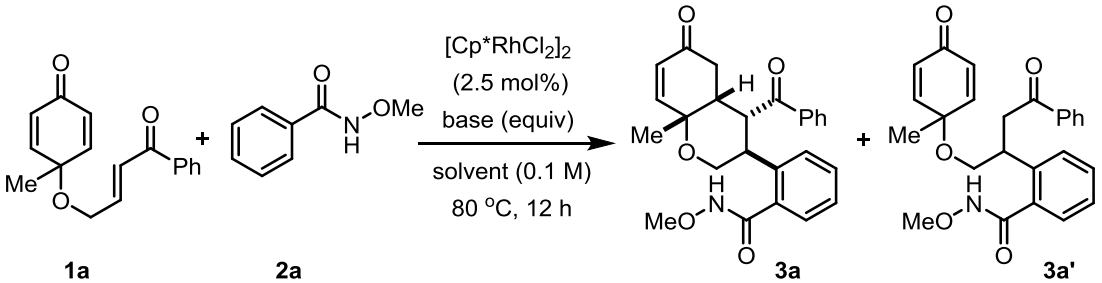
1. General details

***General information*:** Unless otherwise noted, all reagents, catalysts were purchased from commercial suppliers and used without further purification. 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 100-200 mesh silica gel packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) and CD_3OD (H: δ = 4.870 ppm and 3.310 ppm and C: δ = 49.00 ppm) as internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublet, m = multiplet), coupling constants (Hz) and integration. HRMS were recorded using ESI-TOF techniques and diastereomer ratio (*dr*) values were determined by ^{1}H NMR analysis.

2. Experimental procedures and analytical data

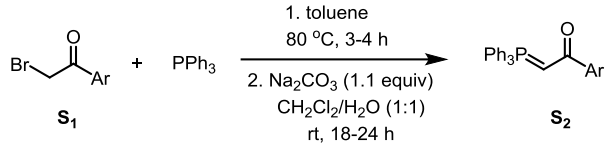
2a. Table S1: Complete Optimization of reaction conditions[a,b,c]



entry	base *(equiv)*	solvent	**3a** yield [%]	**3a'** yield [%]	*dr* (**3a**)
1	CsOAc (0.3)	THF	12	73	7:1
2	CsOAc (1.0)	THF	30	47	7:1
3	CsOAc (1.5)	THF	61	25	9:1
4	CsOAc (2.0)	THF	91	-	15:1
5	CsOAc (2.0) at rt	THF	31	58	6:1
6	NaOAc (2.0)	THF	<10	-	-
7	$Cu(OAc)_2$ (2.0)	THF	<10	<10	-
8	CuOAc (2.0)	THF	<10	-	5:1
9	KOAc (2.0)	THF	34	-	11:1
10	CsOAc (2.0)	$CHCl_3$	38	-	5:1
11	CsOAc (2.0)	DCE	41	12	3:1
12	CsOAc (2.0)	CH_3CN	84	-	10:1
13	CsOAc (2.0)	DMF	57	-	8:1
14	CsOAc (2.0)	DMSO	45	21	6:1
15	CsOAc (2.0)	CH_2Cl_2	31	25	3:1
16	CsOAc (2.0)	1,4-dioxane	34	30	4:1
17	CsOAc (2.0)	toluene	20	35	5:1
18	CsOAc (2.0)	MeOH	<10	78	-

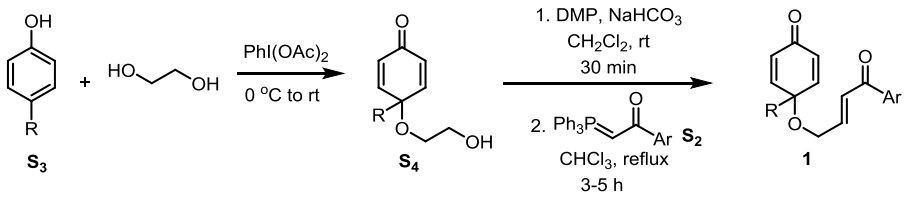
[a]Reaction conditions: **1a** (60 mg, 0.22 mmol), *N*-Methoxybenzamide (33.2 mg, 0.22 mmol), $[Cp^*RhCl_2]_2$ (3.4 mg, 2.5 mol %), base (2.0 equiv). [b]Isolated yields of inseparable diastereomers after column chromatography. [c]The diastereomeric ratio (*dr*) was assigned by ^1H NMR analysis.

2b. General Procedure for the Preparation of Phosphoranes:[1]



To a solution of 2-bromoacetophenone **S1** (10 mmol) in toluene (0.3 M) was added PPh_3 (11 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 3-4 h. Then the resulting precipitate was filtered, washed with more Et_2O, dried and concentrated *in vacuo* to give the phosphonium salt. To a solution of phosphonium salt in CH_2Cl_2 and was added Na_2CO_3 (11 mmol) in H_2O (1 M) and the resulting biphasic solution was stirred vigorously at room temperature for 18-24 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 Wittig reagent **S2** was used for next reaction without further purification.

2c. 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 (16.7 mL, 300 mmol) was added $PhI(OAc)_2$ (4.84g, 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**.[2]

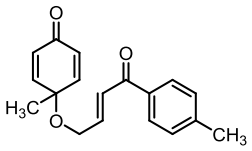
To a stirred solution of pure alcohol **S4** (10 mmol) in CH_2Cl_2 (0.1 M) was added Dess Martin periodinane (5.9 g, 12 mmol) in one portion at room-temperature and stirred the reaction mixture for 30 minutes to 1 hour under nitrogen atmosphere. The reaction mixture was diluted with hexanes (30 mL) and filtered through Celite and then concentrated in *vacuo.* The crude product was purified by column chromatography (EtOAc/hexane) to give aldehyde in excellent yields.[2]

The solution of aldehyde in $CHCl_3$ (0.3 M) was added desired phosphorene **S2** (12 mmol, 1.2 equiv) in one portion at room temperature under nitrogen atmosphere. The reaction mixture stirred at 65 °C for 3 to 5 h and then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography (EtOAc/Hexanes) to give enone-tethered cyclohexadienones **1** in good yields with excellent diastereoselectivity (*dr* = >20:1). All enone-tethered cyclohexadienones **1** were prepared according to a previously reported procedure unless otherwise mentioned below.[1]

Enone-tethered cyclohexadienones **1a, 1ag, 1ak, 1ai,** and **1ae** were prepared according to a previously reported procedure.[3]

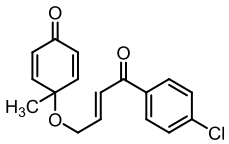
Compounds **1z** and **1al** were prepared according to a previously reported procedure.[4]

(*E*)-4-Methyl-4-((4-oxo-4-(*p*-tolyl)but-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1y):



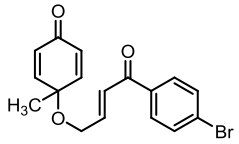
Prepared according to the general procedure as described above in 63% yield (1.1 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford as a yellow semi solid (*dr* = >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (dt, *J* = 15.4, 1.9 Hz, 1H), 6.97 (dt, *J* = 15.4, 4.2 Hz, 1H), 6.82 (d, *J* = 10.2 Hz, 2H), 6.33 (d, *J* = 10.2 Hz, 2H), 4.12 (dd, *J* = 4.2, 1.9 Hz, 2H), 2.42 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 185.0, 151.2, 143.9, 143.7, 135.1, 130.6, 129.4, 128.8, 125.1, 72.9, 64.9, 26.4, 21.8; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329; found: 283.1315.

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



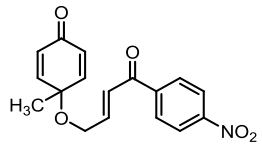
Prepared according to the general procedure as described above in 60% yield (1.1 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford as a pale yellow oil (*dr* = >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.10 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.98 (dt, *J* = 15.4, 4.0 Hz, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.32 (d, *J* = 10.2 Hz, 2H), 4.11 (dd, *J* = 4.0, 2.0 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 184.9, 151.0, 144.8, 139.5, 136.0, 130.7, 130.1, 129.0, 124.5, 73.0, 64.8, 26.4; HRMS (ESI) calcd for $C_{17}H_{16}O_3Cl$ $[M+H]^+$: 303.0783; found: 303.0771.

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



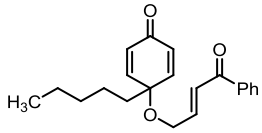
Prepared according to the general procedure as described above in 62% yield (1.3 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.4) to afford as a yellow semi solid (*dr* = >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.59 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.08 (dd, *J* = 15.4, 1.3 Hz, 1H), 6.97 (dtd, *J* = 15.4, 3.9, 1.5 Hz, 1H), 6.79 (d, *J* = 10.1 Hz, 2H), 6.30 (dd, *J* = 10.0, 1.6 Hz, 2H), 4.10 (dd, *J* = 3.7, 1.8 Hz, 2H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 184.9, 150.9, 144.8, 136.4, 132.0, 130.6, 130.2, 128.1, 124.4, 72.9, 64.8, 26.4; HRMS (ESI) calcd for $C_{17}H_{16}BrO_3$ $[M+H]^+$: 347.0277; found: 347.0268.

(*E*)-4-Methyl-4-((4-(4-nitrophenyl)-4-oxobut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ac):



Prepared according to the general procedure as described above in 48% yield (0.9 gm). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford as a pale yellow oil (*dr* = >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.7, 1.8 Hz, 2H), 8.07 (dd, *J* = 8.7, 1.4 Hz, 2H), 7.13 (dt, *J* = 15.5, 1.4 Hz, 1H), 7.04 (dtd, *J* = 15.5, 3.8, 1.4 Hz, 1H), 6.80 (d, *J* = 10.2 Hz, 2H), 6.33 (dd, *J* = 10.0, 1.5 Hz, 2H), 4.14 (dd, *J* = 3.3, 1.8 Hz, 2H), 1.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 184.9, 150.8, 150.2, 146.5, 142.4, 130.8, 129.6, 124.3, 123.9, 73.0, 64.7, 26.3; HRMS (ESI) calcd for $C_{17}H_{16}O_5N$ $[M+H]^+$: 314.1023; found: 314.1014.

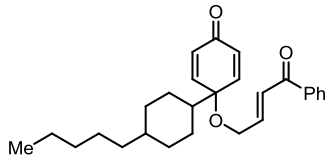
(*E*)-4-((4-Oxo-4-phenylbut-2-en-1-yl)oxy)-4-pentylcyclohexa-2,5-dien-1-one (1ah):



Prepared according to the general procedure as described above in 62% yield (0.9 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford a pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.66 – 7.51 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.15 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.98 (dt, *J* = 15.4, 4.1 Hz, 1H), 6.77 (d, *J* = 10.2 Hz, 2H), 6.36 (d, *J* = 10.2 Hz, 2H), 4.12 (dd, *J* = 4.1, 2.0 Hz, 2H), 1.88 – 1.74 (m, 2H), 1.39 – 1.16 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101

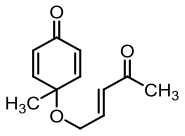
MHz, $CDCl_3$) δ 190.3, 185.3, 150.6, 144.5, 137.7, 133.0, 131.5, 128.7, 124.9, 76.1, 64.6, 39.5, 32.0, 23.2, 22.5, 14.0; HRMS (ESI) calcd for $C_{21}H_{24}O_3Na$ $[M+Na]^+$: 347.1623; found: 347.1621.

(*E*)-1-((4-Oxo-4-phenylbut-2-en-1-yl)oxy)-4'-pentyl-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (1am):



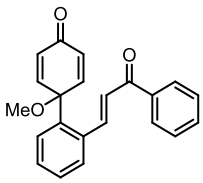
Prepared according to the general procedure as described above in 61% yield (0.8 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford as a yellow semi solid (*dr* =10:1 ratio of inseparable *E/Z* diastereomers); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.14 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.97 (dt, *J* = 15.5, 4.1 Hz, 1H), 6.77 (d, *J* = 10.3 Hz, 2H), 6.38 (d, *J* = 10.3 Hz, 2H), 4.11 (dd, *J* = 4.0, 2.0 Hz, 2H), 1.94 (d, *J* = 11.9 Hz, 2H), 1.80 (d, *J* = 11.4 Hz, 2H), 1.74 (tt, *J* = 12.2, 3.1 Hz, 2H), 1.34 – 1.19 (m, 7H), 1.19 – 1.08 (m, 3H), 1.03 (ddd, *J* = 25.0, 12.7, 2.9 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 185.6, 149.9, 144.8, 137.7, 133.0, 132.1, 128.7, 128.7, 125.0, 78.3, 64.4, 46.8, 37.7, 37.2, 33.1, 32.2, 27.3, 26.7, 22.8, 14.2; HRMS (ESI) calcd for $C_{27}H_{35}O_3$ $[M+H]^+$: 407.2586; found: 407.2584.

(*E*)-4-Methyl-4-((4-oxopent-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1af):



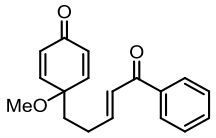
Prepared according to the general procedure as described above in 66% yield (0.8 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford as a pale yellow oil (*dr* = >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 10.2 Hz, 2H), 6.77 (dt, *J* = 16.1, 4.3 Hz, 1H), 6.39 – 6.22 (m, 3H), 4.07 (dd, *J* = 4.4, 2.1 Hz, 2H), 2.27 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 184.1, 150.5, 142.6, 129.9, 129.5, 72.2, 63.7, 26.6, 25.6; HRMS (ESI) calcd for $C_{12}H_{15}O_3Na$ $[M+ Na]^+$: 229.0841; found: 229.0838.

(*E*)-1-Methoxy-2'-(3-oxo-3-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-4(1*H*)-one (SM-1):



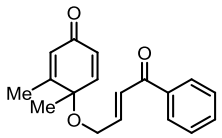
Prepared according to the general procedure as described above in 48% yield (0.7 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as a yellow semi solid (*dr* = >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 15.5 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.67 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.43 – 7.34 (m, 2H), 7.26 (d, *J* = 15.5 Hz, 1H), 6.93 (d, *J* = 9.9 Hz, 2H), 6.44 (d, *J* = 10.0 Hz, 2H), 3.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 185.0, 148.4, 144.7, 138.0, 137.9, 135.4, 132.9, 130.8, 130.1, 129.2, 128.7, 128.6, 126.8, 124.4, 76.9, 52.2; HRMS (ESI) calcd for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1329; found: 331.1323.

(*E*)-4-Methoxy-4-(5-oxo-5-phenylpent-3-en-1-yl)cyclohexa-2,5-dien-1-one (SM-2):



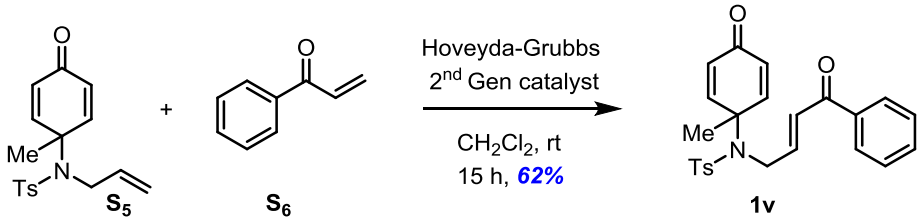
Prepared according to the general procedure as described above in 70% yield (1.1 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as an orange semi solid (*dr* = >20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.38 (m, 2H), 6.98 (dt, *J* = 15.4, 6.5 Hz, 1H), 6.86 (dt, *J* = 15.4, 1.3 Hz, 1H), 6.76 (d, *J* = 10.3 Hz, 2H), 6.40 (d, *J* = 10.3 Hz, 2H), 3.22 (s, 3H), 2.40 – 2.24 (m, 2H), 2.00 – 1.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 185.2, 150.5, 147.8, 137.8, 132.9, 132.0, 128.7, 128.6, 126.3, 75.3, 53.3, 37.8, 27.1; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329; found: 283.1322.

(*E*)-3,4-Dimethyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (SM-3):



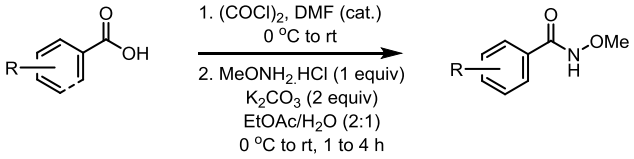
Prepared according to the general procedure as described above in 46% yield (0.7 gm). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford as a yellow semi solid (*dr* = >20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.51 – 7.45 (m, 2H), 7.17 (dt, *J* = 15.4, 2.0 Hz, 1H), 6.98 (dt, *J* = 11.4, 4.1 Hz, 1H), 6.80 (d, *J* = 10.0 Hz, 1H), 6.30 (dd, *J* = 10.0, 1.6 Hz, 1H), 6.20 (s, 1H), 4.04 (ddd, *J* = 16.2, 4.1, 2.0 Hz, 1H), 3.87 (ddd, *J* = 16.2, 4.1, 2.0 Hz, 1H), 2.00 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 185.4, 160.0, 151.5, 143.9, 137.7, 133.1, 130.3, 129.3, 128.7, 128.7, 125.0, 74.8, 64.4, 25.6, 18.0; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1329; found: 283.1321.

(E)-4-Methyl-N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-N-(4-oxo-4-phenylbut-2-en-1-yl)benzenesulfonamide[5] (1x):



Second generation Hoveyda-Grubbs catalyst (11.3 mg, 0.018 mmol) was added to the mixture of *p*-quinamine **S5** (190 mg, 0.6 mmol) and enone **S6** (0.239 µL, 1.8 mmol 3 equiv) in degassed CH_2Cl_2 (15 mL). The reaction was stirred at rt for 3 h and another 3.0 equiv of enone (0.239 µL, 1.8 mmol) was added to the reaction mixture and stirring was continued for 12 h. After completion of the reaction (monitored by TLC), the solution was evaporated and purified by flash column chromatography (30% EtOAc/hexanes; R_f = 0.3) to give substrate **1v** as a white solid in 62% yield (157 mg, *dr* = >20:1); mp = 201–203°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.46 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (dt, *J* = 15.4, 1.3 Hz, 1H), 7.01 – 6.94 (m, 1H), 6.89 (d, *J* = 10.2 Hz, 2H), 6.17 (d, *J* = 10.2 Hz, 2H), 4.19 (dd, *J* = 5.5, 1.3 Hz, 2H), 2.42 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 184.2, 150.6, 144.5, 144.4, 138.9, 137.4, 133.3, 130.1, 128.8, 128.7, 128.6, 127.6, 127.6, 60.5, 48.7, 26.1, 21.7; HRMS (ESI) calcd for $C_{24}H_{24}NO_4S$ $[M+H]^+$: 422.1426; found: 422.1420.

2d. Synthesis of *N*-methoxybenzamide/acrylamide 1



Following same procedure by Guimond and Fagnou *et. al.*[8]

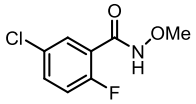
To a stirred solution of the carboxylic acid (10.0 mmol, 1.0 eq.) in dry CH_2Cl_2 (30 mL) at 0 °C under inert atmosphere was added dropwise oxalyl chloride (1.14 mL, 12.0 mmol, 1.2 eq.) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature until completion monitored by TLC (~8h). The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride.

Methoxyamine hydrochloride (1.2 equiv.) was added to a biphasic mixture of K_2CO_3 (2.0 equiv.) in a 2:1 mixture of EtOAc and H_2O (0.3 M). The resulting solution was cooled to 0°C followed by dropwise

addition of the crude acid chloride dissolved in a minimum amount of EtOAc. The reaction was allowed to stir at room temperature for 8h. The reaction mixture was then diluted with EtOAc, the layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The pure products were obtained without any further purification.

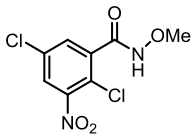
N-methoxybenzamides, *N*-methoxyacrylamides and *N*-(pivaloyloxy) benzamide **2a,**[6] **2t,**[6] **2b,**[7] **2d,**[7] **2c,**[8] **2g,**[8] **2o**[8]**, 2i,**[9] **2j,** [10] **2e,**[11] **2f,**[12] **2h,**[13] **2k,**[14] **2q,**[14] **2s,**[15] **2r,**[16] **2w**[16] were prepared according to a previously reported procedure.[8]

5-Chloro-2-fluoro-*N*-methoxybenzamideone (2l):



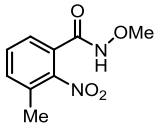
Prepared according to the general procedure as described above in 96% yield (1.9 gm). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 173–175°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.30 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.16 (dd, *J* = 8.1, 2.7 Hz, 1H), 7.09 – 7.00 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 161.0 (d, J_{CF} = 249.3 Hz), 133.7 (d, J_{CF}= 6.7 Hz), 131.8 (d, J_{CF} = 7.7 Hz), 126.4, 119.0 (d, J_{CF} = 22.7 Hz), 117.2 (d, J_{CF} = 24.8 Hz), 64.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.78 (s, 1F); HRMS (ESI) calcd for $C_8H_8ClFNO_2$ $[M+H]^+$: 204.0228; found: 204.0237.

2,5-Dichloro-*N*-methoxy-3-nitrobenzamide (2m):



Prepared according to the general procedure as described above in 93% yield (2.45 gm). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 178–180°C; ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD) δ 7.80 (s, 1H), 7.57 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$+ CD_3OD) δ 161.5, 149.0, 137.2, 133.6, 132.4, 126.4, 123.0, 64.2; HRMS (ESI) calcd for $C_8H_7Cl_2N_2O_4$ $[M+H]^+$: 264.9783; found: 264.9790.

***N*-Methoxy-3-methyl-2-nitrobenzamide (2n):**

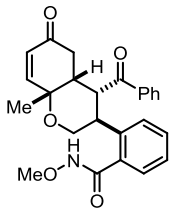


Prepared according to the general procedure as described above in 98% yield (2.58 gm). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 215–217°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 151.1, 134.2, 131.7, 128.6, 125.5, 125.0, 64.6, 20.4; HRMS (ESI) calcd for $C_9H_{11}N_2O_4$ $[M+H]^+$: 211.0719; found: 211.0727.

2e. General procedure for the Rh(III)-catalyzed C–H functionalization:

An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (4.6 mg, 2.5 mol%), cyclohexadienone **1** (0.3 mmol) and benzamide **2** (0.3 mmol) in THF (3 mL, 0.1 M) solvent and then to it was added CsOAc (115.2 mg, 0.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 ^{o}C for 12 h. Later, it was cooled down to room temperature, diluted with water (10 mL) and extracted with EtOAc (10 mL × 2). Combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude product was subjected to flash column chromatography on silica gel (EtOAc/Hexanes) to afford desired cyclized product **3** and its minor isomer ***3′*** as inseparable diastereomers. [The diastereomeric ratio (*dr*) was assigned by ^{1}H NMR analysis].

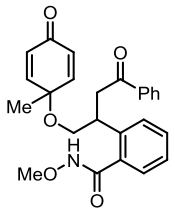
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-N-methoxybenzamide (3a):



Prepared according to the general procedure as described above in 91% yield (114 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 226–228°C; (*dr* =15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.88 (dd, *J* = 11.9, 4.7 Hz, 2H), 7.62 (dd, *J* = 17.6, 10.2 Hz, 1H), 7.47 (dd, *J* = 10.7, 4.7 Hz, 3H), 7.36 – 7.21 (m, 3H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 4.67 (d, *J* = 6.1 Hz, 1H), 4.00 (s, 3H), 3.95 – 3.84 (m, 2H), 3.81 – 3.69 (m, 1H), 2.83 (dd, *J*

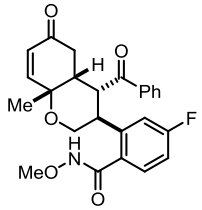
= 15.9, 13.8 Hz, 1H), 2.52 (dt, *J* = 13.7, 3.9 Hz, 1H), 1.93 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 198.3, 167.6, 150.4, 136.2, 135.6, 135.1, 134.5, 130.7, 129.5, 129.4, 129.0, 128.5, 127.6, 125.4, 69.9, 66.3, 64.6, 47.3, 39.3, 34.9, 34.1, 22.4; HRMS (ESI) calcd for $C_{25}H_{26}O_5N$ $[M+H]^+$: 420.1809; found: 420.1811.

***N*-Methoxy-2-(1-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)-4-oxo-4-phenylbutan-2-yl)benzamide (3a'):**



It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 216–218°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 11.1, 4.1 Hz, 2H), 7.33 (d, *J* = 15.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.72 (dd, *J* = 9.8, 2.5 Hz, 1H), 6.42 (dd, *J* = 10.2, 2.9 Hz, 1H), 6.25 – 6.20 (m, 1H), 6.19 – 6.13 (m, 1H), 3.94 (s, 3H), 3.92 – 3.85 (m, 1H), 3.55 (dd, *J* = 18.2, 8.9 Hz, 1H), 3.46 (dt, *J* = 13.1, 5.7 Hz, 2H), 3.41 – 3.34 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 185.0, 167.6, 151.2, 138.6, 136.5, 134.9, 133.8, 130.5, 130.4, 130.3, 129.1, 128.8, 128.2, 127.2, 126.1, 72.7, 69.9, 64.5, 41.3, 37.4, 26.2; HRMS (ESI) calcd for $C_{25}H_{26}NO_5$ $[M+H]^+$: 420.1811; found: 420.1818.

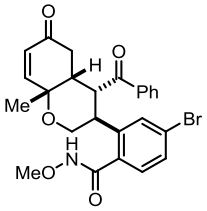
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-fluoro-*N*-methoxybenzamide (3b):



Prepared according to the general procedure as described above in 87% yield (114 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 248–250°C; (*dr* =30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.91 – 7.86 (m, 2H), 7.67 – 7.57 (m, 1H), 7.54 – 7.46 (m, 3H), 6.94 (dd, *J* = 7.9, 6.9 Hz, 2H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.1 Hz, 1H), 4.60 – 4.51 (m, 1H), 3.99 (s, 3H), 3.95 – 3.88 (m, 2H), 3.80 – 3.64 (m, 1H), 2.80 (dd, *J* = 15.9, 13.8 Hz, 1H), 2.54 (dt, *J* = 13.7, 3.9 Hz, 1H), 1.92 (dd, *J* = 15.9, 3.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 198.1, 166.7, 163.8 (d, J_{CF} = 250.8 Hz), 150.2, 139.3, 135.6 (d, J_{CF} = 25.4 Hz), 134.9, 134.7, 131.8 (d, J_{CF} = 8.5 Hz), 129.5, 129.1, 128.5, 114.9 (d, J_{CF} = 21.9 Hz), 112.7 (d, J_{CF} = 20.2 Hz), 70.0, 66.1, 64.6, 47.4,

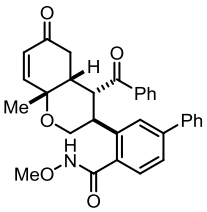
39.3, 34.9, 34.3, 22.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.8 (s, 1F); HRMS (ESI) calcd for $C_{25}H_{25}O_5NF$ $[M+H]^+$: 438.1711; found: 438.1714.

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



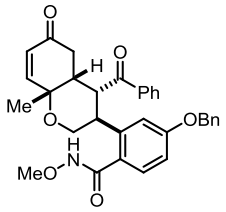
Prepared according to the general procedure as described above in 81% yield (121 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 256–258°C; (*dr* =19:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.51 – 7.45 (m, 2H), 7.42 – 7.31 (m, 3H), 6.63 (d, *J* = 10.0 Hz, 1H), 5.96 (d, *J* = 10.1 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 1H), 3.97 (s, 3H), 3.92 – 3.80 (m, 2H), 3.72 (d, *J* = 9.7 Hz, 1H), 2.77 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.53 (d, *J* = 13.6 Hz, 1H), 1.89 (dd, *J* = 16.0, 3.7 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 198.0, 166.6, 150.3, 138.7, 134.8, 134.6, 131.0, 130.8, 129.4, 128.9, 128.7, 128.5, 128.1, 124.9, 69.9, 66.0, 64.5, 47.3, 39.2, 34.7, 34.2, 22.4; HRMS (ESI) calcd for $C_{25}H_{25}O_5NBr$ $[M+H]^+$: 498.0916; found: 498.0919.

3,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-N-methoxy-[1,1'-biphenyl]-4-carboxamide (3d):



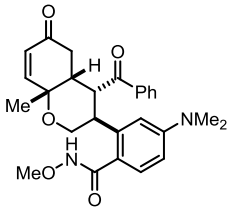
Prepared according to the general procedure as described above in 87% yield (129 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 212–214°C; (*dr* =14:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.90 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.59 – 7.53 (m, 1H), 7.50 – 7.47 (m, 2H), 7.46 – 7.35 (m, 7H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.87 – 4.52 (m, 1H), 4.02 (s, 3H), 4.01 – 3.92 (m, 2H), 3.84 – 3.69 (m, 1H), 2.86 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.59 – 2.52 (m, 1H), 1.96 (dd, *J* = 16.0, 3.6 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 198.3, 167.5, 150.3, 143.8, 140.3, 136.8, 135.2, 134.5, 130.0, 129.4, 129.0, 128.5, 128.3, 128.2, 127.4, 127.2, 126.7, 124.3, 70.0, 66.4, 64.6, 47.3, 39.3, 34.9, 34.2, 22.5; HRMS (ESI) calcd for $C_{31}H_{29}O_5Na$ $[M+Na]^+$: 518.1940; found: 518.1950.

2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-(benzyloxy)-*N*-methoxybenzamide (3e):



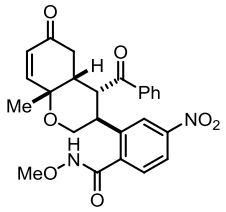
Prepared according to the general procedure as described above in 90% yield (142 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =16:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.88 – 7.81 (m, 2H), 7.66 – 7.57 (m, 1H), 7.52 – 7.43 (m, 3H), 7.40 – 7.31 (m, 5H), 6.85 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.64 (dd, *J* = 10.5, 4.5 Hz, 1H), 5.98 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.99 (s, 2H), 4.54 (d, *J* = 9.6 Hz, 1H), 3.99 (s, 3H), 3.97 – 3.84 (m, 2H), 3.65 (dd, *J* = 26.6, 16.4 Hz, 1H), 2.81 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.50 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.92 (dd, *J* = 16.0, 3.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 198.3, 167.4, 160.4, 150.3, 138.2, 136.3, 135.0, 134.5, 131.4, 129.4, 129.0, 128.9, 128.6, 128.5, 128.4, 127.8, 113.8, 112.3, 70.5, 69.9, 66.4, 64.6, 47.4, 39.4, 34.9, 34.0, 22.3; HRMS (ESI) calcd for $C_{32}H_{32}O_6N$ $[M+H]^+$: 526.2224; found: 526.2232.

2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-(dimethylamino)-*N*-methoxybenzamide (3f):



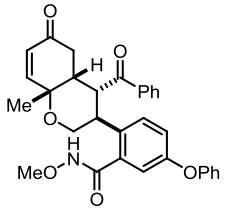
Prepared according to the general procedure as described above in 77% yield (107 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 264–266°C; (*dr* =14:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.72 (s, 1H), 7.88 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.39 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.63 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.62 (d, *J* = 10.0 Hz, 1H), 5.94 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 3.99 (s, 3H), 3.83 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.78 – 3.70 (m, 2H), 2.86 (s, 6H), 2.81 (dd, *J* = 16.6, 2.9 Hz, 1H), 2.48 (dt, *J* = 13.6, 3.9 Hz, 1H), 1.92 (dd, *J* = 15.8, 3.7 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 198.5, 168.1, 150.5, 149.4, 135.9, 135.2, 134.3, 129.2, 128.8, 128.5, 126.2, 122.5, 114.5, 112.6, 69.8, 66.5, 64.4, 47.2, 40.3, 39.3, 34.9, 33.0, 22.3; HRMS (ESI) calcd for $C_{27}H_{31}O_5N_2$ $[M+H]^+$: 463.2228; found: 463.2228.

2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-4-nitrobenzamide (3g):



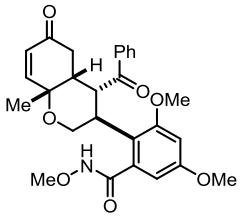
Prepared according to the general procedure as described above in 65% yield (91 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 255–257°C; (*dr* =10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.15 – 8.07 (m, 2H), 7.91 – 7.85 (m, 2H), 7.70 – 7.61 (m, 2H), 7.55 – 7.44 (m, 2H), 6.66 (d, *J* = 10.1 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.65 (d, *J* = 7.7 Hz, 1H), 4.02 (s, 2H), 3.98 – 3.89 (m, 2H), 3.85 – 3.63 (m, 2H), 2.79 (dd, *J* = 15.7, 13.9 Hz, 1H), 2.60 (dt, *J* = 13.7, 3.9 Hz, 1H), 1.92 (dd, *J* = 15.8, 3.7 Hz, 1H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 197.8, 165.6, 150.1, 149.0, 141.6, 138.8, 135.0, 134.6, 130.9, 129.6, 129.1, 128.6, 122.7, 120.6, 70.0, 65.8, 64.8, 47.6, 39.4, 34.8, 34.6, 22.4; HRMS (ESI) calcd for $C_{25}H_{25}O_7N_2$ $[M+H]^+$: 465.1662; found: 465.1659.

2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-5-phenoxybenzamide (3h):



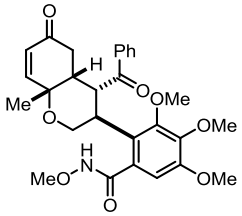
Prepared according to the general procedure as described above in 90% yield (138 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =13:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.89 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 6.99 – 6.90 (m, 3H), 6.64 (d, *J* = 10.1 Hz, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 10.1 Hz, 1H), 3.98 (s, 3H), 3.92 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.82 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.71 (dd, *J* = 26.7, 16.6 Hz, 1H), 2.83 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.52 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.93 (dd, *J* = 16.0, 3.4 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 198.3, 166.9, 157.0, 156.0, 150.3, 137.1, 135.1, 134.6, 130.2, 130.1, 129.4, 129.0, 128.5, 126.9, 124.3, 120.4, 119.8, 118.6, 69.9, 66.3, 64.6, 47.4, 39.4, 34.9, 33.6, 22.4; HRMS (ESI) calcd for $C_{31}H_{30}O_6N$ $[M+H]^+$: 512.2068; found: 512.2076.

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



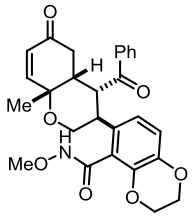
Prepared according to the general procedure as described above in 92% yield (132 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =23:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.64 – 7.59 (m, 1H), 7.54 – 7.48 (m, 2H), 6.87 (s, 2H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.55 (t, *J* = 2.2 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 4.95 (s, 1H), 4.72 (td, *J* = 11.3, 5.7 Hz, 1H), 4.13 (t, *J* = 11.4 Hz, 1H), 3.97 – 3.78 (m, 1H), 3.84 (s, 6H), 3.61 (s, 3H), 2.68 – 2.44 (m, 2H), 1.94 (d, *J* = 12.9 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 197.6, 171.8, 160.7, 150.0, 136.2, 135.5, 134.1, 129.4, 129.3, 128.4, 105.9, 103.7, 70.0, 63.6, 60.3, 55.8, 53.8, 42.7, 39.6, 35.2, 22.2; HRMS (ESI) calcd for $C_{27}H_{30}O_7N$ $[M+H]^+$: 480.2017; found: 480.2024.

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



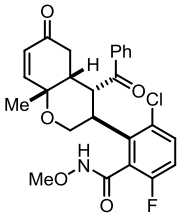
Prepared according to the general procedure as described above in 87% yield (133 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.2) to afford as a white solid; mp = 240–242°C; (*dr* =22:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (s, 1H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.52 (m, 1H), 7.52 – 7.26 (m, 2H), 6.75 (s, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 5.40 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.11 (dd, *J* = 22.3, 10.8 Hz, 1H), 3.97 (s, 6H), 3.80 (s, 3H), 3.83 – 3.77 (m, 1H), 3.70 (s, 3H), 3.73 – 3.66 (m, 1H), 2.82 (dd, *J* = 15.8, 13.9 Hz, 1H), 2.43 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.89 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 198.7, 167.7, 153.1, 152.6, 150.6, 143.6, 135.5, 134.3, 131.9, 129.2, 129.0, 128.5, 120.3, 108.0, 70.0, 64.4, 63.1, 61.6, 60.6, 56.0, 44.7, 39.6, 34.6, 34.4, 22.3; HRMS (ESI) calcd for $C_{28}H_{32}O_8N$ $[M+H]^+$: 510.2128; found: 510.2130.

6,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-2,3-dihydrobenzo[*b*][1,4]dioxine-5-carboxamide (3k):



Prepared according to the general procedure as described above in 80% yield (115 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 224–226°C; (*dr* =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.94 – 7.74 (m, 2H), 7.65 – 7.54 (m, 1H), 7.53 – 7.43 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 5.96 (dd, *J* = 10.0, 0.6 Hz, 1H), 4.57 (d, *J* = 8.7 Hz, 1H), 4.33 – 4.27 (m, 1H), 4.26 – 4.17 (m, 3H), 4.01 (s, 3H), 3.92 (dd, *J* = 11.9, 5.3 Hz, 1H), 3.70 (t, *J* = 11.5 Hz, 1H), 3.59 – 3.51 (m, 1H), 2.79 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.48 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.90 (dd, *J* = 16.0, 3.5 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.9, 198.5, 165.0, 150.5, 142.8, 141.9, 135.3, 134.4, 129.5, 129.4, 128.9, 128.4, 124.8, 118.9, 117.7, 69.8, 66.2, 64.6, 64.6, 64.2, 47.1, 39.3, 34.9, 33.8, 22.3; HRMS (ESI) calcd for $C_{27}H_{28}O_7N$ $[M+H]^+$: 478.1860; found: 478.1868.

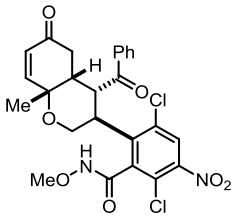
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-3-chloro-6-fluoro-*N*-methoxybenzamide (3l):



Prepared according to the general procedure as described above in 74% yield (105 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a Brown solid; mp = 176–178°C; (*dr* =05:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.57 (m, 1H), 7.55 – 7.46 (m, 2H), 7.30 (dd, *J* = 8.7, 4.6 Hz, 1H), 7.00 (td, *J* = 8.4, 2.8 Hz, 1H), 6.89 (dd, *J* = 7.8, 2.5 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 5.39 (d, *J* = 7.8 Hz, 1H), 4.75 – 4.60 (m, 1H), 4.32 (t, *J* = 11.4 Hz, 1H), 4.15 (dd, *J* = 16.5, 11.1 Hz, 1H), 3.50 (s, 3H), 2.77 (dd, *J* = 15.9, 14.2 Hz, 1H), 2.52 (dt, *J* = 13.8, 4.3 Hz, 1H), 2.00 (dd, *J* = 16.3, 3.6 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 198. 1, 168.7, 160.8 (d, J_{CF} = 249.6 Hz), 150.2, 136.9 (d, J_{CF} = 6.4 Hz), 135.7, 134.0, 131.0 (d, J_{CF} = 7.6 Hz), 129.3, 129.3, 128.4, 125.6 (d, J_{CF} = 2.5 Hz), 117.5 (d, J_{CF} = 22.5 Hz), 114.8 (d, J_{CF} = 24.9 Hz),

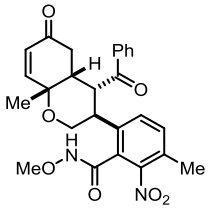
70.2, 63.2, 59.4, 53.7, 42.7, 39.7, 35.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6 (s, 1F); HRMS (ESI) calcd for $C_{25}H_{24}ClFO_5N$ $[M+H]^+$: 472.1327; found: 472.1335.

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



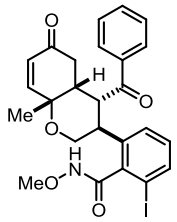
Prepared according to the general procedure as described above in 77% yield (123 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a Brown semi solid (*dr* =09:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.72 – 7.54 (m, 1H), 7.56 – 7.47 (m, 2H), 7.35 (s, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.0 Hz, 1H), 5.35 (d, *J* = 6.1 Hz, 1H), 4.68 (d, *J* = 4.9 Hz, 1H), 4.28 (t, *J* = 11.4 Hz, 1H), 4.14 (dd, *J* = 11.3, 5.8 Hz, 1H), 3.55 (s, 3H), 2.74 (dd, *J* = 25.2, 11.3 Hz, 1H), 2.54 (dt, *J* = 13.8, 4.2 Hz, 1H), 1.99 (dd, *J* = 16.2, 3.9 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 198.0, 166.7, 150.0, 148.5, 139.6, 135.5, 134.2, 133.6, 130.7, 129.4, 129.3, 128.4, 125.9, 122.2, 70.3, 63.4, 59.3, 53.9, 42.7, 39.8, 35.0, 22.4; HRMS (ESI) calcd for $C_{25}H_{23}O_7N_2Cl_2$ $[M+H]^+$: 533.0882; found: 533.0880.

6,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-3-methyl-2-nitrobenzamide (3n):



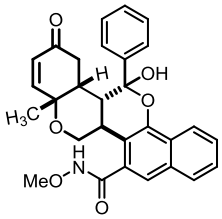
Prepared according to the general procedure as described above in 79% yield (113 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 235–237°C; (*dr* =14:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.92 – 7.82 (m, 3H), 7.69 – 7.55 (m, 1H), 7.53 – 7.43 (m, 3H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.1 Hz, 1H), 4.62 (d, *J* = 7.9 Hz, 1H), 4.00 (s, 3H), 3.95 – 3.83 (m, 2H), 3.82 – 3.70 (m, 1H), 2.77 (dd, *J* = 15.8, 13.8 Hz, 1H), 2.57 (dt, *J* = 7.9, 3.6 Hz, 1H), 2.52 (s, 3H), 1.90 (dd, *J* = 15.8, 3.7 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 197.9, 165.5, 150.2, 149.9, 139.9, 135.9, 134.9, 134.7, 134.1, 133.4, 129.5, 129.0, 128.6, 122.0, 70.0, 65.9, 64.7, 47.6, 39.3, 34.7, 34.1, 22.4, 20.1; HRMS (ESI) calcd for $C_{26}H_{27}O_7N_2$ $[M+H]^+$: 479.1818; found: 479.1830.

2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-6-iodo-*N*-methoxybenzamide (3o):



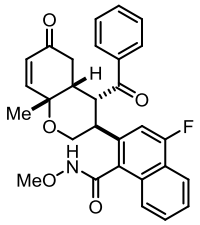
Prepared according to the general procedure as described above in 78% yield (128 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =03:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.46 (m, 3H), 7.35 – 7.23 (m, 1H), 7.17 – 6.96 (m, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 5.49 (d, *J* = 7.6 Hz, 1H), 4.74 – 4.56 (m, 1H), 4.41 (t, *J* = 11.4 Hz, 1H), 4.20 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.47 (s, 3H), 2.86 – 2.72 (m, 1H), 2.50 (dt, *J* = 13.7, 4.3 Hz, 1H), 2.00 (dd, *J* = 16.2, 3.1 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 198.4, 172.1, 150.3, 141.7, 139.0, 135.9, 133.9, 130.4, 129.3, 129.3, 128.8, 128.5, 127.6, 127.2, 70.2, 62.8, 59.4, 53.5, 42.7, 39.7, 35.1, 22.5; HRMS (ESI) calcd for $C_{25}H_{25}IO_5N$ $[M+H]^+$: 546.0778; found: 546.0777.

14-Hydroxy-*N*-methoxy-4a-methyl-2-oxo-14-phenyl-1,2,4a,6,6a,14,14a,14b-octahydrobenzo[*h*]chromeno[4,3-c]chromene-7-carboxamide (3p):



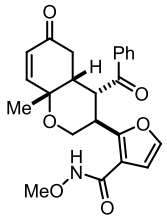
Prepared according to the general procedure as described above in 60% yield (87 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.2) to afford as a white semi solid (*dr* =08:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.34 (s, 1H), 8.02 – 7.94 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.55 – 7.46 (m, 3H), 7.39 – 7.30 (m, 2H), 6.61 (d, *J* = 10.0 Hz, 1H), 5.94 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.92 (td, *J* = 11.3, 5.7 Hz, 1H), 4.24 (dd, *J* = 14.0, 8.7 Hz, 1H), 4.09 (dd, *J* = 11.4, 5.6 Hz, 1H), 3.67 (s, 3H), 2.64 – 2.52 (m, 2H), 1.94 (d, *J* = 12.9 Hz, 1H), 1.80 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 154.9, 149.8, 136.7, 135.3, 134.2, 130.5, 129.4, 129.4, 129.2, 129.0, 128.8, 128.5, 127.3, 126.4, 124.2, 118.3, 112.4, 70.1, 64.1, 60.4, 55.2, 42.8, 39.8, 35.1, 22.3; HRMS (ESI) calcd for $C_{29}H_{28}NO_6$ $[M+H]^+$: 486.1916; found: 486.1909.

2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-fluoro-*N*-methoxy-1-naphthamide (3q):



Prepared according to the general procedure as described above in 67% yield (98 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as an orange semi solid (*dr* =03:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.99 (dd, *J* = 8.3, 3.2 Hz, 2H), 7.93 – 7.82 (m, 2H), 7.61 – 7.46 (m, 5H), 7.01 (d, *J* = 11.4 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.3 Hz, 1H), 4.67 (dd, *J* = 10.8, 4.2 Hz, 1H), 4.09 (s, 3H), 4.02 – 3.93 (m, 2H), 3.88 – 3.80 (m, 1H), 2.84 (dd, *J* = 15.9, 13.8 Hz, 1H), 2.57 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.94 (dd, *J* = 15.9, 3.6 Hz, 1H), 1.84 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 198.1, 166.7, 160.0 (d, J_{CF} = 255.9 Hz), 150.3, 134.8, 134.7, 134.0 (d, J_{CF} = 7.2 Hz), 132.9 (d, J_{CF} = 5.5 Hz), 129.4, 129.0, 128.9, 128.5, 127.1, 125.4, 122.8 (d, J_{CF} = 16.6 Hz), 120.6 (d, J_{CF} = 4.7 Hz), 120.6, 110.6 (d, J_{CF} = 20.0 Hz), 105.9 (d, J_{CF} = 20.9 Hz), 65.6, 64.6, 46.8, 39.3, 35.2, 34.9, 22.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.1 (s, 1F); HRMS (ESI) calcd for $C_{29}H_{27}FO_5N$ $[M+H]^+$: 488.1873; found: 488.1872.

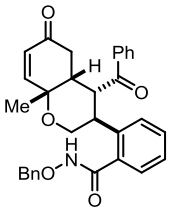
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxyfuran-3-carboxamide (3r):



Prepared according to the general procedure as described above in 83% yield (102 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 228–230°C; (*dr* =19:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.72 – 7.57 (m, 1H), 7.53 – 7.36 (m, 2H), 7.23 (d, *J* = 1.7 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 6.54 (d, *J* = 1.7 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 4.83 (dd, *J* = 11.1, 4.2 Hz, 1H), 4.11 – 3.95 (m, 2H), 3.90 (dd, *J* = 7.7, 3.2 Hz, 1H), 3.89 (s, 3H), 2.76 (dd, *J* = 15.9, 13.9 Hz, 1H), 2.49 (dt, *J* = 13.6, 4.0 Hz, 1H), 1.90 (dd, *J* = 16.1, 3.9 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 198.2, 162.1, 153.4, 150.5, 142.1, 134.8, 134.5, 129.3,

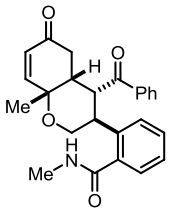
129.1, 128.6, 117.0, 110.6, 70.0, 64.7, 62.7, 45.1, 38.7, 34.7, 31.8, 22.3; HRMS (ESI) calcd for $C_{23}H_{24}O_6N$ $[M+H]^+$: 410.1604; found: 410.1611.

2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-(benzyloxy)benzamide (3s):



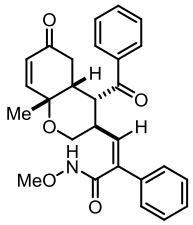
Prepared according to the general procedure as described above in 91% yield (135 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =34:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.61 – 7.51 (m, 3H), 7.49 – 7.38 (m, 5H), 7.37 – 7.18 (m, 4H), 6.62 (d, *J* = 10.0 Hz, 1H), 5.96 (d, *J* = 10.0 Hz, 1H), 5.21 (d, *J* = 11.3 Hz, 1H), 5.13 (d, *J* = 11.3 Hz, 1H), 4.62 (s, 1H), 3.93 – 3.82 (m, 2H), 3.80 – 3.65 (m, 1H), 2.75 – 2.65 (m, 1H), 2.47 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.91 – 1.71 (m, 1H), 1.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 198.4, 167.6, 150.3, 136.4, 135.7, 135.1, 134.4, 130.6, 129.6, 129.3, 129.2, 129.0, 128.9, 128.7, 128.4, 127.5, 125.5, 78.3, 69.8, 66.2, 47.2, 39.2, 34.9, 34.0, 22.4; HRMS (ESI) calcd for $C_{31}H_{30}O_5N$ $[M+H]^+$: 496.2124; found: 496.2122.

2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2H-chromen-3-yl)-N-methylbenzamide (3u):



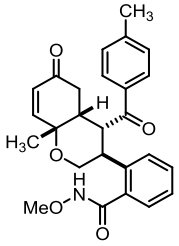
Prepared according to the general procedure as described above in 79% yield (96 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as an orange solid; mp = 211–213°C; (*dr* =14:1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.69 – 7.55 (m, 1H), 7.53 – 7.41 (m, 3H), 7.31 – 7.17 (m, 3H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 10.0 Hz, 1H), 4.70 (d, *J* = 4.5 Hz, 1H), 4.06 – 3.86 (m, 2H), 3.84 – 3.61 (m, 1H), 3.09 (d, *J* = 4.5 Hz, 3H), 2.80 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.52 (dt, *J* = 13.6, 4.0 Hz, 1H), 1.93 (dd, *J* = 16.0, 3.9 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 198.5, 170.5, 150.6, 138.9, 135.5, 135.3, 134.3, 129.9, 129.3, 129.0, 129.0, 128.4, 127.5, 125.3, 69.9, 66.5, 47.0, 39.3, 34.9, 34.0, 26.8, 22.4; HRMS (ESI) calcd for $C_{25}H_{26}NO_4$ $[M+H]^+$: 404.1862; found: 404.1852.

(*Z*)-3-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-2-phenylacrylamide (3w):



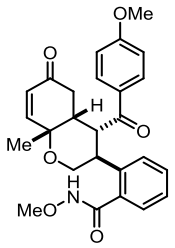
Prepared according to the general procedure as described above in 51% yield (68 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as an orange semi solid (*dr* =03:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.27 (m, 8H), 6.83 (dd, *J* = 10.4, 2.1 Hz, 1H), 6.36 (d, *J* = 11.0 Hz, 1H), 6.13 (d, *J* = 10.4 Hz, 1H), 3.99 (s, 3H), 3.84 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.39 – 3.20 (m, 3H), 3.12 (ddd, *J* = 18.3, 10.4, 7.9 Hz, 1H), 2.76 (dd, *J* = 17.6, 5.2 Hz, 1H), 2.27 (d, *J* = 17.7 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 197.2, 165.4, 155.3, 136.8, 136.3, 134.2, 133.9, 130.8, 129.2, 128.9, 128.6, 128.2, 127.2, 126.3, 74.3, 68.0, 64.0, 46.7, 40.1, 37.4, 37.2, 26.6; HRMS (ESI) calcd for $C_{27}H_{28}O_5N$ $[M+H]^+$: 446.1968; found: 446.1968.

***N*-Methoxy-2-(8a-methyl-4-(4-methylbenzoyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)benzamide (3y):**



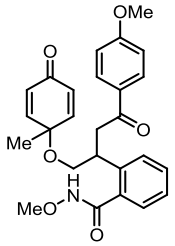
Prepared according to the general procedure as described above in 92% yield (120 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 200–202°C; (*dr* =14:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.45 (m, 1H), 7.34 – 7.21 (m, 5H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 7.2 Hz, 1H), 3.99 (s, 3H), 3.93 – 3.83 (m, 2H), 3.82 – 3.64 (m, 1H), 2.82 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.51 (dt, *J* = 13.8, 4.0 Hz, 1H), 2.40 (s, 3H), 1.93 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 198.4, 167.6, 150.4, 145.7, 136.2, 135.6, 132.6, 130.6, 130.0, 129.6, 129.0, 128.7, 127.6, 125.5, 69.9, 66.3, 64.6, 47.1, 39.5, 34.9, 34.2, 22.4, 21.8; HRMS (ESI) calcd for $C_{26}H_{28}O_5N$ $[M+H]^+$: 434.1968; found: 434.1965.

***N*-Methoxy-2-(4-(4-methoxybenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)benzamide (3z):**



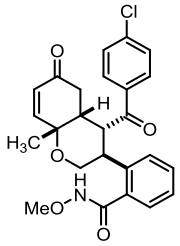
Prepared according to the general procedure as described above in 70% yield (94 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 208–210°C; (*dr* =28:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.89 – 7.83 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.21 (m, 2H), 6.95 – 6.91 (m, 2H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.97 (dd, *J* = 10.0, 0.7 Hz, 1H), 4.61 (d, *J* = 7.3 Hz, 1H), 3.99 (s, 3H), 3.91 – 3.81 (m, 2H), 3.85 (s, 3H), 3.78 – 3.68 (m, 1H), 2.82 (dd, *J* = 16.0, 13.7 Hz, 1H), 2.51 (dt, *J* = 13.6, 4.0 Hz, 1H), 1.95 (dd, *J* = 16.0, 3.3 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 198.5, 167.5, 164.6, 150.4, 136.1, 135.6, 131.0, 130.6, 129.6, 129.0, 128.0, 127.6, 125.5, 114.5, 69.9, 66.4, 64.5, 55.8, 46.9, 39.7, 34.9, 34.2, 22.4; HRMS (ESI) calcd for $C_{26}H_{28}O_6N$ $[M+H]^+$: 450.1911; found: 450.1920.

***N*-Methoxy-2-(4-(4-methoxyphenyl)-1-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)-4-oxobutan-2-yl)benzamideone (3z'):**



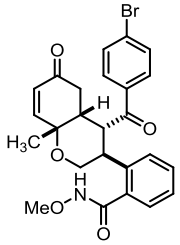
Prepared according to the general procedure as described above in 21% yield (28 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.5) to afford as a white semi solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.52 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.30 – 7.24 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.73 (dd, *J* = 10.2, 3.1 Hz, 1H), 6.42 (dd, *J* = 10.2, 3.1 Hz, 1H), 6.25 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.17 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.97 (s, 3H), 3.93 – 3.81 (m, 1H), 3.86 (s, 3H), 3.52 (dd, *J* = 18.1, 9.3 Hz, 1H), 3.47 – 3.40 (m, 2H), 3.39 – 3.32 (m, 1H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 185.1, 167.7, 164.1, 151.2, 138.7, 135.1, 130.6, 130.5, 130.4, 130.4, 129.6, 129.2, 127.3, 126.0, 114.0, 72.8, 70.1, 64.6, 55.7, 40.9, 37.5, 26.3; HRMS (ESI) calcd for $C_{26}H_{28}O_6N$ $[M+H]^+$: 450.1911; found: 450.1919.

2-(4-(4-Chlorobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3aa):



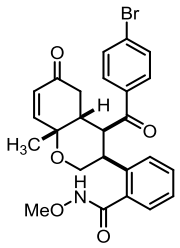
Prepared according to the general procedure as described above in 85% yield (116 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.4) to afford as a white semi solid (*dr* =17:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.85 – 7.75 (m, 2H), 7.52 – 7.41 (m, 3H), 7.37 – 7.29 (m, 1H), 7.29 – 7.22 (m, 2H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.60 (d, *J* = 3.3 Hz, 1H), 3.99 (s, 3H), 3.95 – 3.83 (m, 2H), 3.80 – 3.65 (m, 1H), 2.83 (dd, *J* = 15.8, 13.9 Hz, 1H), 2.53 – 2.42 (m, 1H), 1.89 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 198.1, 167.6, 150.3, 141.8, 136.1, 135.7, 133.4, 130.7, 129.9, 129.7, 129.5, 129.0, 127.7, 125.3, 69.9, 66.2, 64.6, 47.3, 39.3, 34.9, 34.1, 22.4; HRMS (ESI) calcd for $C_{25}H_{25}O_5NCl$ $[M+H]^+$: 454.1416; found: 454.1423.

2-(4-(4-Bromobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ab):



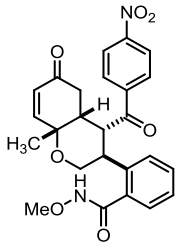
Prepared according to the general procedure as described above in 69% yield (103 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.4) to afford as a white solid; mp = 220–222°C; (*dr* =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.28 – 7.20 (m, 2H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 4.59 (s, 1H), 3.98 (s, 3H), 3.94 – 3.79 (m, 2H), 3.81 – 3.60 (m, 1H), 2.82 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.47 (d, *J* = 13.6 Hz, 1H), 1.88 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 198.1, 167.6, 150.3, 136.1, 135.6, 133.8, 132.7, 130.7, 129.9, 129.4, 129.0, 127.7, 125.4, 69.9, 66.1, 64.6, 47.3, 39.2, 34.9, 34.1, 22.4; HRMS (ESI) calcd for $C_{25}H_{24}O_5NBrNa$ $[M+Na]^+$: 520.0730; found: 520.0738.

2-(4-(4-Bromobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ab'): (minor isomer)



Prepared according to the general procedure as described above in 7% yield (10 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.4) to afford as a white solid; mp = 232–234°C; (*dr* =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.53 – 7.48 (m, 2H), 7.44 (td, *J* = 7.8, 1.5 Hz, 1H), 7.30 (s, 1H), 7.21 (td, *J* = 7.5, 1.1 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.86 (dd, *J* = 10.4, 2.2 Hz, 1H), 6.17 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.13 (dd, *J* = 12.2, 3.4 Hz, 1H), 4.02 (dd, *J* = 12.2, 1.2 Hz, 1H), 3.88 (dd, *J* = 11.7, 6.2 Hz, 1H), 3.82 (s, 1H), 3.54 (s, 3H), 3.31 – 3.20 (m, 1H), 2.76 (dd, *J* = 17.7, 5.2 Hz, 1H), 2.23 (ddd, *J* = 17.7, 2.0, 1.4 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 197.2, 167.9, 155.1, 139.2, 135.5, 132.9, 132.4, 131.8, 131.0, 130.9, 129.6, 128.9, 127.3, 127.0, 73.9, 67.5, 64.4, 46.7, 40.3, 37.8, 37.1, 26.8; HRMS (ESI) calcd for $C_{25}H_{24}O_5NBrNa$ $[M+Na]^+$: 520.0730; found: 520.0738.

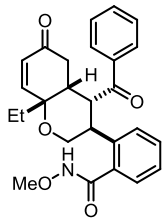
***N*-Methoxy-2-(8a-methyl-4-(4-nitrobenzoyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)benzamide (3ac):**



Prepared according to the general procedure as described above in 67% yield (93 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 262–264°C; (*dr* =14:1); ^{1}H NMR (500 MHz, CD_3OD+$CDCl_3$) δ 8.30 – 8.15 (m, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.16 – 7.02 (m, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 5.88 (d, *J* = 10.0 Hz, 1H), 4.63 (s, 1H), 3.97 – 3.85 (m, 1H), 3.79 – 3.65 (m, 1H), 3.72 (s, 3H), 3.52 (d, *J* = 24.6 Hz, 1H), 2.76 (dd, *J* = 16.1, 14.0 Hz, 1H), 2.35 (d, *J* = 12.5 Hz, 1H), 1.73 (s, 3H), 1.73 (dd, *J* = 15.8, 4.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD +$CDCl_3$) δ 199.1, 198.6, 167.9, 150.8, 150.6, 139.8, 136.7, 131.0, 130.7, 129.4, 129.1,

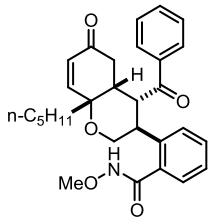
128.6, 127.5, 127.3, 124.3, 69.8, 65.7, 64.2, 47.4, 38.5, 34.7, 22.1, 13.6 ; HRMS (ESI) calcd for $C_{25}H_{24}O_7N_2Na$ $[M+Na]^+$: 487.1476; found: 487.1484.

2-(4-Benzoyl-8a-ethyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ag):



Prepared according to the general procedure as described above in 94% yield (122 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 215–217°C; (*dr* =23:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.90 – 7.77 (m, 2H), 7.68 – 7.56 (m, 1H), 7.47 (dd, *J* = 9.7, 5.8 Hz, 3H), 7.41 – 7.18 (m, 3H), 6.69 (d, *J* = 10.2 Hz, 1H), 6.02 (d, *J* = 10.2 Hz, 1H), 4.64 (d, *J* = 8.1 Hz, 1H), 3.99 (s, 3H), 3.93 – 3.80 (m, 2H), 3.74 – 3.47 (m, 1H), 2.85 (dd, *J* = 15.9, 13.7 Hz, 1H), 2.58 (dt, *J* = 13.6, 4.0 Hz, 1H), 2.36 – 2.14 (m, 2H), 1.94 (dd, *J* = 15.9, 3.8 Hz, 1H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 198.4, 167.6, 148.6, 136.2, 135.6, 135.2, 134.5, 130.6, 130.1, 129.5, 129.3, 128.4, 127.6, 125.5, 72.3, 66.2, 64.5, 46.9, 36.5, 34.9, 33.8, 26.3, 7.9; HRMS (ESI) calcd for $C_{26}H_{28}O_5N$ $[M+H]^+$: 434.1967; found: 434.1967.

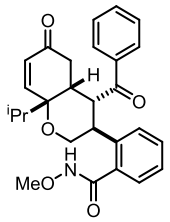
2-(4-Benzoyl-6-oxo-8a-pentyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ah):



Prepared according to the general procedure as described above in 89% yield (127 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =19:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.66 – 7.55 (m, 1H), 7.52 – 7.46 (m, 3H), 7.39 – 7.27 (m, 1H), 7.29 – 7.20 (m, 2H), 6.69 (d, *J* = 10.2 Hz, 1H), 6.03 (dd, *J* = 10.2, 0.6 Hz, 1H), 4.62 (d, *J* = 8.5 Hz, 1H), 4.01 (s, 3H), 3.97 – 3.85 (m, 2H), 3.80 – 3.60 (m, 1H), 2.86 (dd, *J* = 15.9, 13.7 Hz, 1H), 2.59 (dt, *J* = 13.6, 4.0 Hz, 1H), 2.25 (ddd, *J* = 16.9, 13.9, 11.4 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.94 (dd, *J* = 15.9, 3.5 Hz, 1H), 1.56 – 1.37 (m, 6H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 198.4, 167.7, 149.1, 135.2, 134.5, 132.2, 130.7, 130.0, 129.6, 129.4, 128.8, 128.5, 127.7, 127.5,

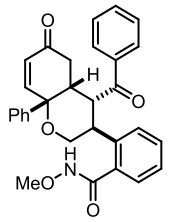
72.2, 66.3, 64.6, 47.1, 36.8, 34.9, 33.8, 32.6, 29.8, 23.4, 22.8, 14.2; HRMS (ESI) calcd for $C_{29}H_{34}O_5N$ $[M+H]^+$: 476.2432; found: 476.2441.

2-(4-Benzoyl-8a-isopropyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ai):



Prepared according to the general procedure as described above in 91% yield (122 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 250–252°C; (*dr* =21:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.92 – 7.82 (m, 2H), 7.66 – 7.56 (m, 1H), 7.55 – 7.41 (m, 3H), 7.36 – 7.30 (m, 1H), 7.29 – 7.22 (m, 2H), 6.82 – 6.61 (m, 1H), 6.08 (d, *J* = 10.3 Hz, 1H), 4.65 (d, *J* = 9.9 Hz, 1H), 4.01 (s, 3H), 3.98 – 3.82 (m, 2H), 3.71 – 3.51 (m, 1H), 3.15 – 3.01 (m, 1H), 2.89 (dd, *J* = 15.2, 13.6 Hz, 1H), 2.78 (dt, *J* = 13.5, 3.6 Hz, 1H), 1.95 (ddd, *J* = 8.5, 5.8, 4.1 Hz, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 198.5, 167.6, 145.6, 136.3, 135.7, 135.2, 134.5, 131.2, 130.6, 129.6, 129.4, 128.4, 127.6, 125.5, 74.5, 66.0, 64.6, 46.7, 35.2, 35.2, 33.6, 27.7, 18.3, 15.2; HRMS (ESI) calcd for $C_{27}H_{30}O_5N$ $[M+H]^+$: 448.2119; found: 448.2128.

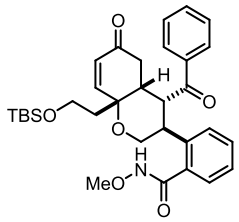
2-(4-Benzoyl-6-oxo-8a-phenyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3aj):



Prepared according to the general procedure as described above in 97% yield (140 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 235–237°C; (*dr* =35:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.47 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.20 – 7.12 (m, 3H), 7.10 – 7.05 (m, 1H), 6.85 – 6.75 (m, 2H), 6.41 (dd, *J* = 6.3, 2.6 Hz, 1H), 6.20 – 6.02 (m, 1H), 5.52 (dd, *J* = 9.9, 0.7 Hz, 1H), 3.96 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.67 (s, 3H), 3.65 – 3.60 (m, 2H), 3.43 – 3.30 (m, 1H), 2.98 (dt, *J* = 13.5, 3.8 Hz, 1H), 2.73 (dd, *J* = 15.8, 13.6 Hz, 1H), 1.86 – 1.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 198.3, 167.6, 150.5, 140.2, 135.9, 135.5, 134.5, 130.5, 130.1, 129.4,

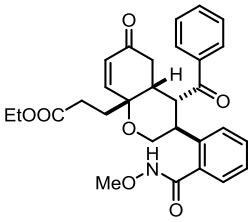
128.9, 128.4, 127.6, 127.4, 126.4, 125.4, 75.6, 67.3, 64.6, 48.0, 36.4, 35.2, 33.8; HRMS (ESI) calcd for $C_{30}H_{28}O_5N$ $[M+H]^+$: 482.1968; found: 482.1974.

2-(4-Benzoyl-8a-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ak):



Prepared according to the general procedure as described above in 73% yield (123 mg). It was purified by flash chromatography (30% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 188–190°C; (*dr* =15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.88 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.69 – 7.57 (m, 1H), 7.53 – 7.45 (m, 3H), 7.38 – 7.29 (m, 1H), 7.30 – 7.20 (m, 2H), 6.84 (d, *J* = 10.2 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 1H), 4.67 (d, *J* = 7.5 Hz, 1H), 4.01 (s, 3H), 3.96 – 3.83 (m, 4H), 3.82 – 3.61 (m, 1H), 2.84 (dd, *J* = 15.8, 13.7 Hz, 1H), 2.65 (dt, *J* = 13.8, 4.0 Hz, 1H), 2.48 (t, *J* = 6.6 Hz, 2H), 1.94 (dd, *J* = 15.8, 3.4 Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 198.2, 167.6, 148.6, 136.2, 135.6, 135.3, 134.5, 134.0, 130.7, 129.6, 129.4, 128.5, 127.7, 125.5, 71.4, 66.5, 64.6, 58.6, 47.1, 37.6, 36.7, 35.0, 29.8, 26.1, 18.5, -5.2; HRMS (ESI) calcd for $C_{32}H_{42}O_6NSi$ $[M+H]^+$: 564.2782; found: 564.2787.

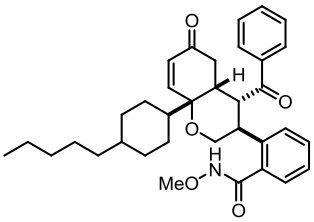
Ethyl 3-(4-benzoyl-3-(2-(methoxycarbamoyl)phenyl)-6-oxo-2,3,4,4a,5,6-hexahydro-8a*H*-chromen-8a-yl)propanoate (3al):



Prepared according to the general procedure as described above in 81% yield (123 mg). It was purified by flash chromatography (50% EtOAc/hexanes; R_f = 0.3) to afford as a white semi solid (*dr* =24:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.93 – 7.84 (m, 2H), 7.66 – 7.52 (m, 1H), 7.48 (dd, *J* = 10.1, 5.4 Hz, 3H), 7.39 – 7.28 (m, 2H), 7.24 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.64 (d, *J* = 10.2 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 4.71 (d, *J* = 7.8 Hz, 1H), 4.23 (qd, *J* = 7.1, 1.7 Hz, 2H), 4.01 (s, 3H), 3.95 – 3.83 (m, 2H), 3.63 (dd, *J* = 26.1, 15.5 Hz, 1H), 2.84 (dd, *J* = 15.9, 13.7 Hz, 1H), 2.82 – 2.75 (m, 1H), 2.61 – 2.43 (m, 3H), 2.35 (ddd, *J* = 15.5, 10.1, 5.7 Hz, 1H), 1.95 (dd, *J* = 16.0, 3.8 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 198.0, 173.2, 167.7, 147.1, 136.0, 135.6, 135.1, 134.6, 130.8, 130.1, 129.5, 129.4,

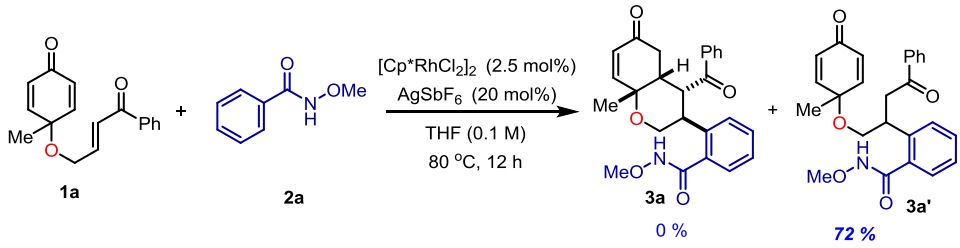
128.6, 127.7, 125.6, 71.5, 66.3, 64.6, 61.3, 47.0, 37.4, 35.0, 33.8, 28.5, 28.0, 14.4; HRMS (ESI) calcd for $C_{29}H_{32}O_7N$ $[M+H]^+$: 506.2179; found: 506.2179.

2-(4-Benzoyl-6-oxo-8a-(4-pentylcyclohexyl)-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3am):



Prepared according to the general procedure as described above in 88% yield (147 mg). It was purified by flash chromatography (40% EtOAc/hexanes; R_f = 0.4) to afford as a white semi solid (*dr* =22:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.89 – 7.78 (m, 2H), 7.67 – 7.53 (m, 1H), 7.53 – 7.42 (m, 3H), 7.34 (td, *J* = 7.7, 1.4 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.74 (d, *J* = 10.4 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 4.65 (d, *J* = 9.5 Hz, 1H), 4.00 (s, 3H), 3.97 – 3.82 (m, 2H), 3.70 – 3.47 (m, 1H), 2.86 (dd, *J* = 29.1, 14.1 Hz, 1H), 2.79 (dt, *J* = 13.6, 3.2 Hz, 1H), 2.66 – 2.43 (m, 1H), 2.10 – 1.87 (m, 3H), 1.63 (d, *J* = 12.5 Hz, 1H), 1.44 – 1.06 (m, 14H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 198.5, 167.5, 146.5, 136.3, 135.6, 135.2, 134.5, 130.6, 130.5, 129.6, 129.4, 128.4, 127.6, 125.4, 74.1, 66.2, 64.6, 46.9, 38.9, 37.8, 37.3, 35.0, 33.6, 33.1, 32.3, 28.8, 26.7, 24.7, 22.8, 14.2; HRMS (ESI) calcd for $C_{35}H_{44}O_5N$ $[M+H]^+$: 558.3214; found: 558.3215.

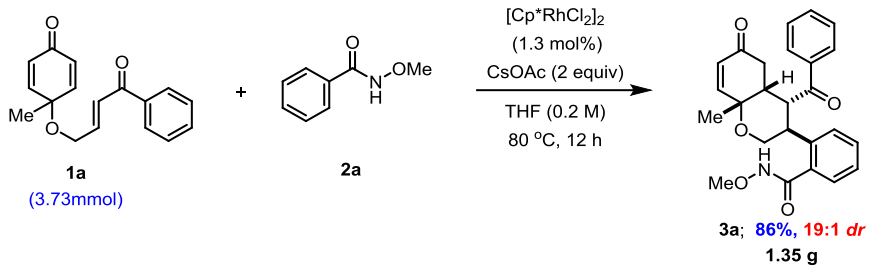
The Rh(III)-catalyzed C–H functionalization in presence of silver salt without base:



An oven-dried pressure tube containing teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (4.6 mg, 2.5 mol%), cyclohexadienone **1a** (80.4 mg, 0.3 mmol) and benzamide **2a** (45.3 mg, 0.3 mmol) in THF (3 mL, 0.1 M) solvent and then added $AgSbF_6$ (20.6 mg, 20 mol%) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 °C for 12 h. Later, reaction mixture was cooled down to room temperature, diluted with water (10 mL) and extracted with EtOAc (10 mL × 2). Combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude product was subjected to flash column chromatography on silica gel (EtOAc/Hexanes) to afford uncyclized compound **3a′** with 72% yield (95 mg).

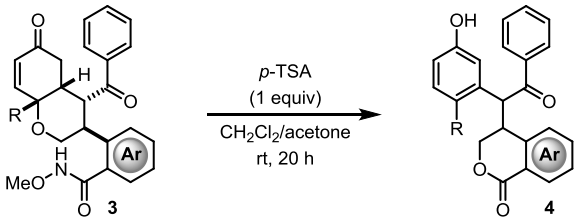
2f. Gram-scale reaction and synthetic utility

Gram-scale synthesis of 3a:



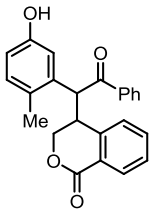
In an oven-dried pressure tube with Teflon-coated magnetic stir bar, $[Cp^*RhCl_2]_2$ catalyst (30.0 mg, 1.3 mol%), cyclohexadienone **1** (1.0 gm, 3.73 mmol) and benzamide **2** (563 mg, 3.73 mmol) were dissolved in THF followed by cesium acetate (1.43 gm, 7.46 mmol) under nitrogen atmosphere. The reaction mixture was then stirred in a pre-heated oil bath at 80 °C for 12 h. The reaction mixture was cooled down to room temperature, diluted with water (30 mL) and extracted with EtOAc (30 mL × 3), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel (EtOAc/Hexanes:2/3) to give desired cyclized product **3a** in 86% yield (1.35 g) as a white semi solid (*dr* =19:1).

Acid catalyzed ring-opening reaction:



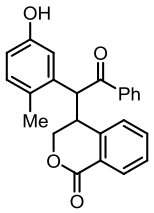
To a stirred solulation of compound **3** (0.15 mmol) in acetone/CH_2Cl_2 sovent(1:1 ratio, 1.5 mL, 0.1 M) was additon of *p*-TSA catalyst (29 mg, 0.15 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 20 h and then solvent was removed under reduced pressure. The crude residue was directly subjected to flash column chromatography on silica gel (EtOAc in hexanes) to afford acid-catalyzed ring-opening product **4**.

4-(1-(5-Hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4a):



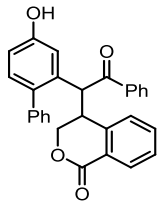
Prepared according to the general procedure as described above in 67% yield (42 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 262–264°C; (*dr* =06:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.38 – 7.33 (m, 1H), 7.31 – 7.25 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.72 (dd, *J* = 8.3, 2.7 Hz, 1H), 5.96 (s, 1H), 5.04 (d, *J* = 10.7 Hz, 1H), 4.39 (dd, *J* = 11.5, 3.0 Hz, 1H), 4.08 (dd, *J* = 11.5, 1.4 Hz, 1H), 3.92 (dd, *J* = 10.7, 1.5 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 165.4, 154.9, 142.0, 137.2, 135.1, 134.0, 133.5, 132.8, 130.6, 129.3, 129.1, 128.8, 128.4, 128.2, 124.6, 115.6, 114.2, 69.6, 51.9, 40.5, 19.1; HRMS (ESI) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1440; found: 373.1445.

4-(1-(5-Hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (Minor Isomer)(4a'):



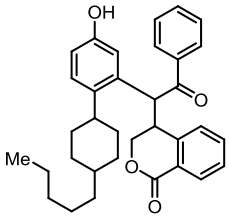
Prepared according to the general procedure as described above in 7% yield (5 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 249–251°C; (*dr* =06:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.42 (m, 1H), 7.42 – 7.30 (m, 3H), 7.22 – 7.13 (m, 1H), 6.86 – 6.72 (m, 2H), 6.59 (d, *J* = 6.2 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 5.12 (d, *J* = 11.1 Hz, 1H), 5.04 (s, 1H), 4.70 – 4.55 (m, 2H), 3.73 (d, *J* = 11.1 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 165.5, 154.3, 140.5, 136.6, 135.8, 133.7, 133.0, 132.3, 130.1, 128.9, 128.8, 128.7, 128.6, 128.3, 125.3, 115.2, 114.2, 70.4, 49.6, 41.2, 18.2; HRMS (ESI) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1440; found: 373.1432.

4-(1-(4-Hydroxy-[1,1'-biphenyl]-2-yl)-2-oxo-2-phenylethyl)isochroman-1-one (4b):



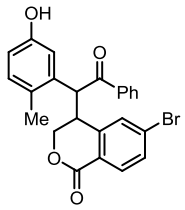
Prepared according to the general procedure as described above in 81% yield (53 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 226–228°C; (*dr* =>20:1); ^{1}H NMR (400 MHz, CD_3OD + $CDCl_3$) δ 8.68 (d, *J* = 7.4 Hz, 1H), 8.13 – 7.82 (m, 9H), 7.77 – 7.67 (m, 3H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.44 (m, 1H), 5.83 (d, *J* = 11.3 Hz, 1H), 5.23 (dd, *J* = 30.9, 7.9 Hz, 2H), 4.72 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD + $CDCl_3$) δ 200.6, 165.3, 156.8, 141.2, 140.3, 136.4, 135.5, 134.0, 133.7, 133.0, 131.7, 130.3, 129.9, 128.9, 128.5, 128.3, 128.0, 126.9, 124.0, 115.0, 114.1, 69.2, 50.4, 40.2; HRMS (ESI) calcd for $C_{29}H_{23}O_4$ $[M+H]^+$: 435.1596; found: 435.1598.

4-(1-(5-Hydroxy-2-(4-pentylcyclohexyl)phenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4c):



Prepared according to the general procedure as described above in 74% yield (54 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.5) to afford as a white semi solid (*dr* =08:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.33 (m, 4H), 7.30 – 7.24 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.77 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 4.39 (dd, *J* = 11.4, 2.8 Hz, 1H), 4.10 (d, *J* = 10.6 Hz, 1H), 3.91 (d, *J* = 10.7 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.00 (dd, *J* = 29.7, 10.4 Hz, 2H), 1.77 (d, *J* = 12.7 Hz, 1H), 1.46 – 1.17 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 165.3, 154.2, 139.3, 137.2, 133.9, 133.5, 133.4, 130.6, 129.3, 129.2, 128.6, 128.3, 128.3, 124.7, 122.2, 116.0, 113.6, 69.3, 40.8, 37.6, 37.4, 35.4, 34.8, 33.9, 33.8, 32.3, 26.9, 22.9, 14.3; HRMS (ESI) calcd for $C_{34}H_{39}O_4$ $[M+H]^+$: 511.2848; found: 511.2845.

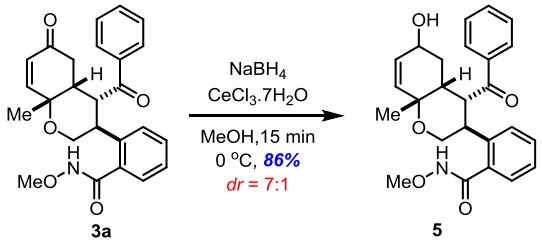
6-Bromo-4-(1-(5-hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4d):



Prepared according to the general procedure as described above in 64% yield (43 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford as a white solid; mp = 236–238°C; (*dr* =10:1); ^{1}H NMR (400 MHz, CD_3OD+$CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.79 (m, 3H), 7.71 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.55 – 7.42 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.59 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.08 (d, *J* = 9.5 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD+$CDCl_3$) δ 198.4, 164.7, 155.4, 143.6, 136.6, 134.0, 132.8, 132.0, 131.9, 131.3, 131.1, 128.3, 128.1, 127.4, 127.1, 122.8, 114.9, 113.3, 69.0, 51.6, 39.5, 17.8; HRMS (ESI) calcd for $C_{24}H_{20}BrO_4$ $[M+H]^+$: 451.0545; found: 451.0544.

Selective Reduction:

2-(4-Benzoyl-6-hydroxy-8a-methyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide[17] (5):

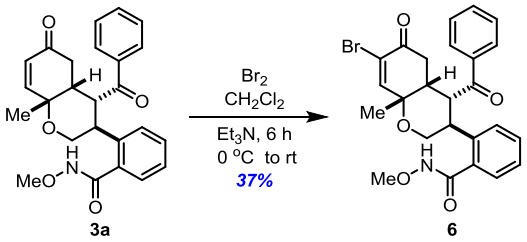


In an oven dried 10 mL round-bottom flask charged with enone **3a** (63 mg, 0.15 mmol) and $CeCl_3.7H_2O$ (74 mg, 0.30 mmol) in 2.0 mL of absolute methanol under nitrogen atmosphere and the resulting solution was stirred for 20 minutes at room temperature and then cooled to 0 °C. Later $NaBH_4$ (5.7 mg, 0.15 mmol) was added to the reaction mixture in one portion and the resulting mixture was stirred at 0 °C. After 15 min, reaction mixture was quenched with 2 mL of saturated NH_4Cl solution and diluted with 5 mL CH_2Cl_2 and extracted with additional CH_2Cl_2 (2 × 5 mL). Combined organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture (with dr = 7:1, as obtained from ^{1}H-NMR) was purified by silica-gel flash column chromatography (60% EtOAc/hexanes; R_f = 0.3) to obtain **5** as a white semi-solid (55 mg, 86% yield); *dr* = >07:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 7.93 – 7.85

(m, 2H), 7.65 – 7.57 (m, 1H), 7.51 – 7.45 (m, 3H), 7.34 – 7.28 (m, 1H), 7.26 – 7.18 (m, 2H), 5.78 (dt, *J* = 10.0, 1.4 Hz, 1H), 5.62 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.60 (dd, *J* = 37.5, 10.1 Hz, 1H), 3.99 (s, 3H), 3.96 – 3.91 (m, 1H), 3.89 – 3.78 (m, 2H), 3.69 (dd, *J* = 29.6, 17.0 Hz, 1H), 2.05 – 2.01 (m, 1H), 1.84 (dd, *J* = 12.6, 2.1 Hz, 1H), 1.67 (s, 3H), 1.60 – 1.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 167.5, 137.0, 135.4, 134.2, 133.6, 133.3, 130.6, 129.6, 129.3, 128.5, 128.0, 127.4, 125.3, 70.4, 68.5, 66.9, 64.5, 48.0, 39.4, 34.9, 29.7, 22.3; HRMS (ESI) calcd for $C_{25}H_{28}O_5N$ $[M+H]^+$: 422.1968; found: 422.1962.

α-Bromination:

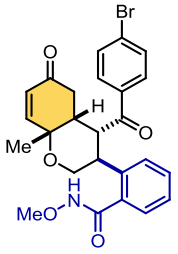
2-(4-Benzoyl-7-bromo-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide[18] (6):



To a stirred solution of enone **3a** (126 mg, 0.3 mmol) in CH_2Cl_2 (3.0 mL,0.1M) was added a solution of bromine (15.5 μL, 0.3 mmol) in CH_2Cl_2 at 0 °C. Then the reaction mixture was stirred at same temperature for 30 minutes and then Et_3N (125 μL, 0.9 mmol) was added. The resulting mixture was warmed to room temperature and the reaction was continued to stir for 6 hours. The mixture was then concentrated *in vacuo* and the purification of residue was performed by column chromatography in silica-gel (40% EtOAc/hexanes; Rf = 0.4) affording α-bromo compound **6** (55 mg, 37 %) as a brown semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.92 – 7.82 (m, 2H), 7.73 – 7.56 (m, 1H), 7.53 – 7.43 (m, 3H), 7.36 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 7.11 (s, 1H), 4.77 – 4.54 (m, 1H), 4.01 (s, 3H), 3.97 – 3.84 (m, 2H), 3.83 – 3.64 (m, 1H), 3.01 (dd, *J* = 16.0, 13.8 Hz, 1H), 2.59 (dt, *J* = 13.7, 3.9 Hz, 1H), 2.20 (dd, *J* = 16.0, 3.9 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 190.3, 167.6, 150.6, 136.0, 135.7, 135.0, 134.7, 130.7, 129.5, 129.5, 128.5, 127.8, 126.0, 125.4, 72.7, 66.4, 64.7, 47.0, 39.3, 35.2, 33.9, 22.4; HRMS (ESI) calcd for $C_{25}H_{25}BrNO_5$ $[M+H]^+$: 498.0916; found: 498.0915.

3. X-Ray crystallographic data

3a. X-ray crystallographic data for compound 3ab (major isomer):



3ab *(major isomer)*

The pure major isomer **3ab** was dissolved in a mixed solvent of dichloromethane/*n*-hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colourless crystals were collected after few days for X-ray analysis.

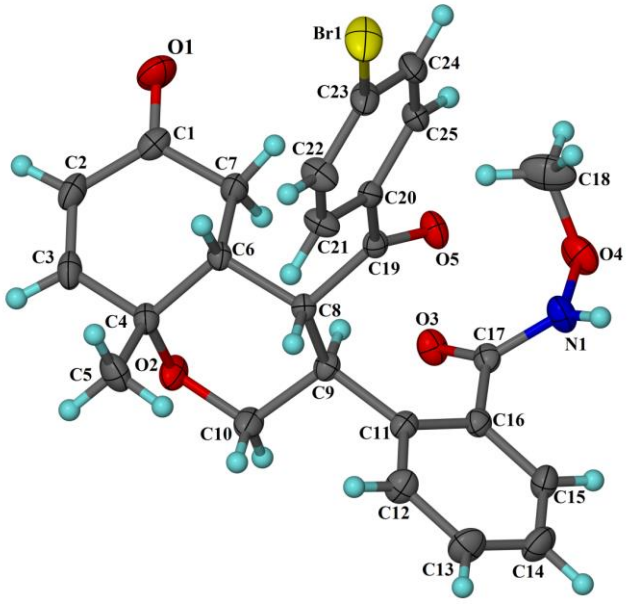
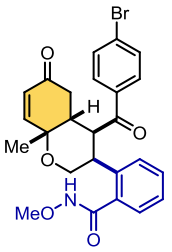


Figure caption: ORTEP diagram of compound **3ab** (KB23) with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 3ab (KB23): $C_{25}H_{24}N_1O_5Br_1$, M = 498.36, Monoclinic, Space group $P2_1/n$ (No.14), a = 12.333(5)Å, b = 13.046(5)Å, c = 15.250(5)Å, α = 90°, β = 106.607(8)°, γ = 90°, V = 2351.2(15)Å^3, Z = 4, D_c = 1.408 g/cm^3, F_{000} = 1024, Bruker D8 QUEST PHOTON-100, Mo-Kα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 55°, μ= 1.784 mm^{-1}, 37041 reflections collected, 5393 unique (R_{int} = 0.0623), 304

parameters, *R1* = 0.0354, *wR2* =0.0870, *R* indices based on 4024 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.039, largest difference hole and peak = -0.297 and 0.392 e.Å^{-3}.

3b. X-ray crystallographic data for compound 3ab′ (minor isomer):



3ab' *(minor isomer)*

The pure minor isomer **3ab′** was dissolved in a mixed solvent of dichloromethane/*n*-hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colourless crystals were collected after few days for X-ray analysis.

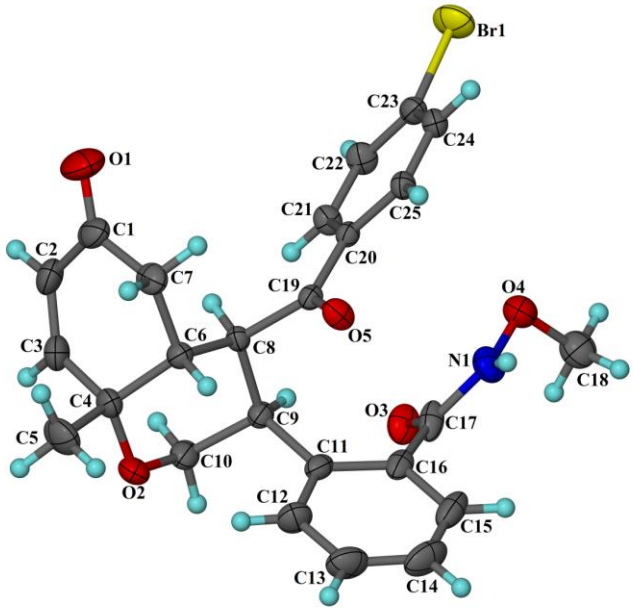


Figure caption: ORTEP diagram of compound **3ab′** (KB60) with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for 3ab′ (KB60): $C_{25}H_{24}N_1O_5Br_1$, *M* = 498.36, Monoclinic, Space group $P2_1$ (No.4), *a* = 11.355(4)Å, *b* =7.423(2)Å, *c* = 14.224(5)Å, *α* = 90°, *β* = 107.513(7)°, *γ* = 90°, *V* = 1143.3(7)Å^3, *Z* = 2, D_c = 1.448 g/cm^3, F_{000} = 512, Bruker D8 QUEST PHOTON-100, Mo-Kα radiation, λ = 0.71073 Å, *T* =

293(2)K, $2\theta_{max}$ = 55º, μ= 1.834 mm^{-1}, 29073 reflections collected, 5218 unique (R_{int} = 0.0553), 319 parameters, *R1* = 0.0419, *wR2* = 0.0967, *R* indices based on 4106 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.030, largest difference hole and peak = -0.382 and 0.512 e.$Å^{-3}$.

Data collection and Structure solution details:

X-ray data for the compounds (KB23 and KB60) were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. The N bound H atoms were located in the difference Fourier map and their positional coordinates were refined. The crystal data of KB60 compound was refined as a 2-component inversion twin [3]. The Bromine atom in KB23 crystal was disordered over two sites. The site occupancy factor (SOF) for the major (Br1) and minor (Br1d) component of the disordered atoms are 0.59(2) and 0.41(2) respectively. In KB60 data, the methoxy benzamide side chain is disordered over two sites. The site occupancy factor (SOF) for the major (C18-O4-N1) and minor (C18D-O4D-N1D) component of the disordered atoms are 0.62(1) and 0.38(1) respectively. **CCDC 2101384-2101385** deposition numbers contain the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

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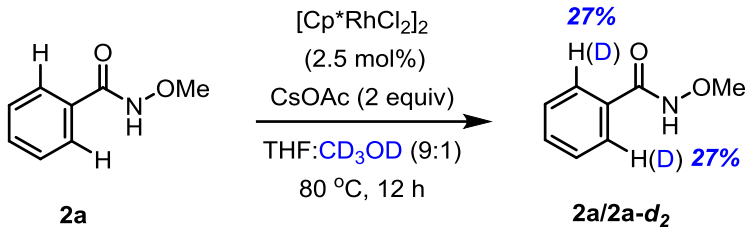
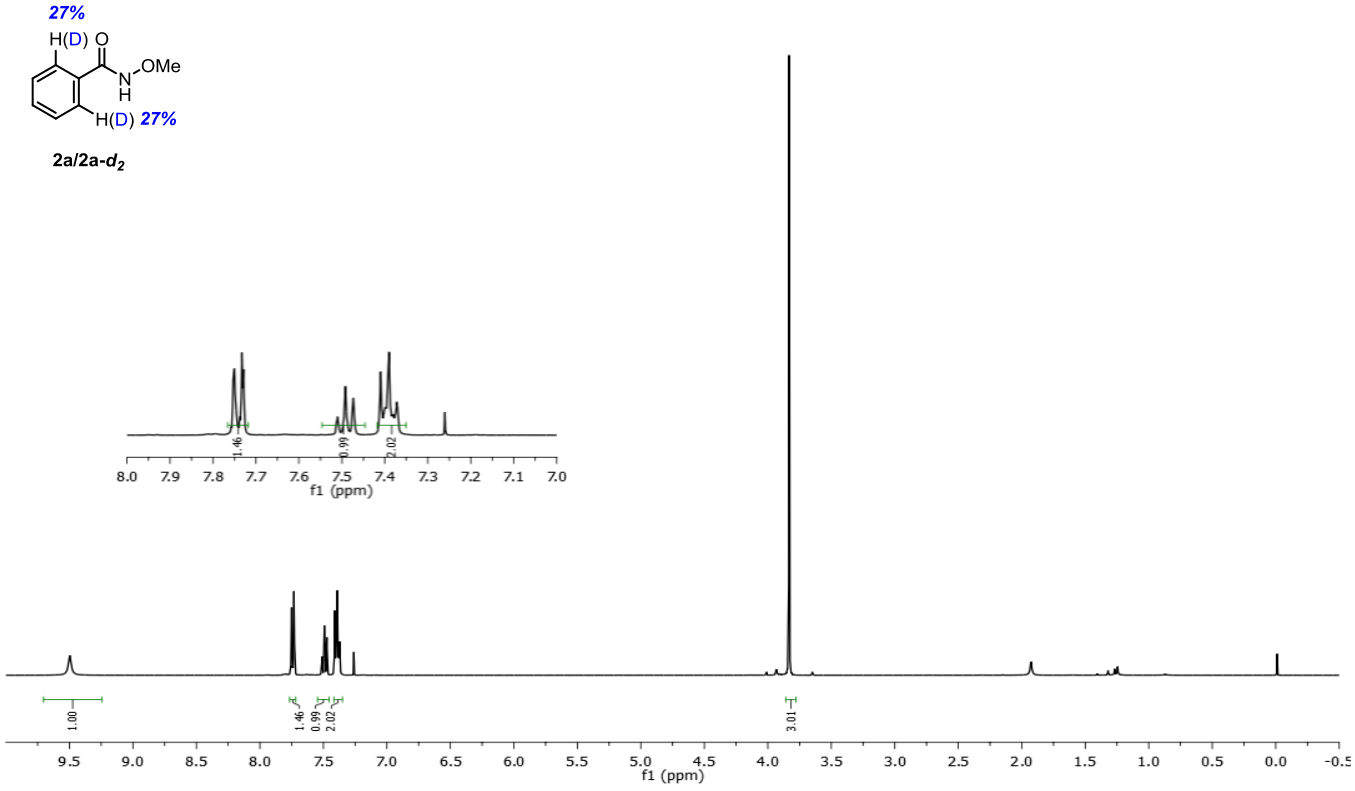
4. Study of the Kinetic Isotope Effects and Competition Experiments

4a. H/D Exchange Study

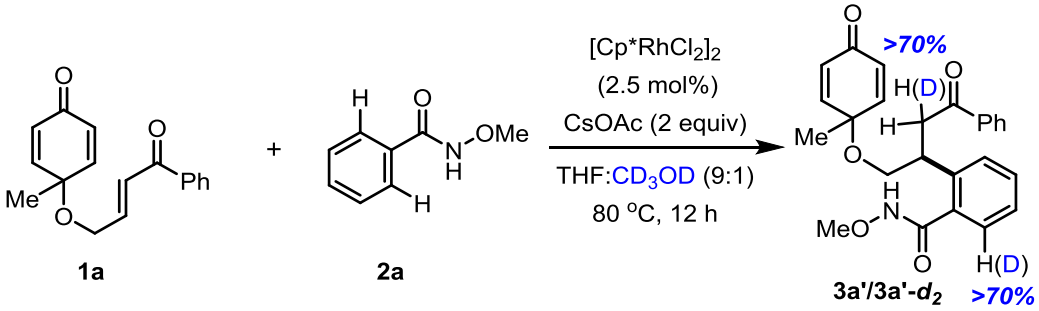


27% Deuterium incorporation at ortho-position

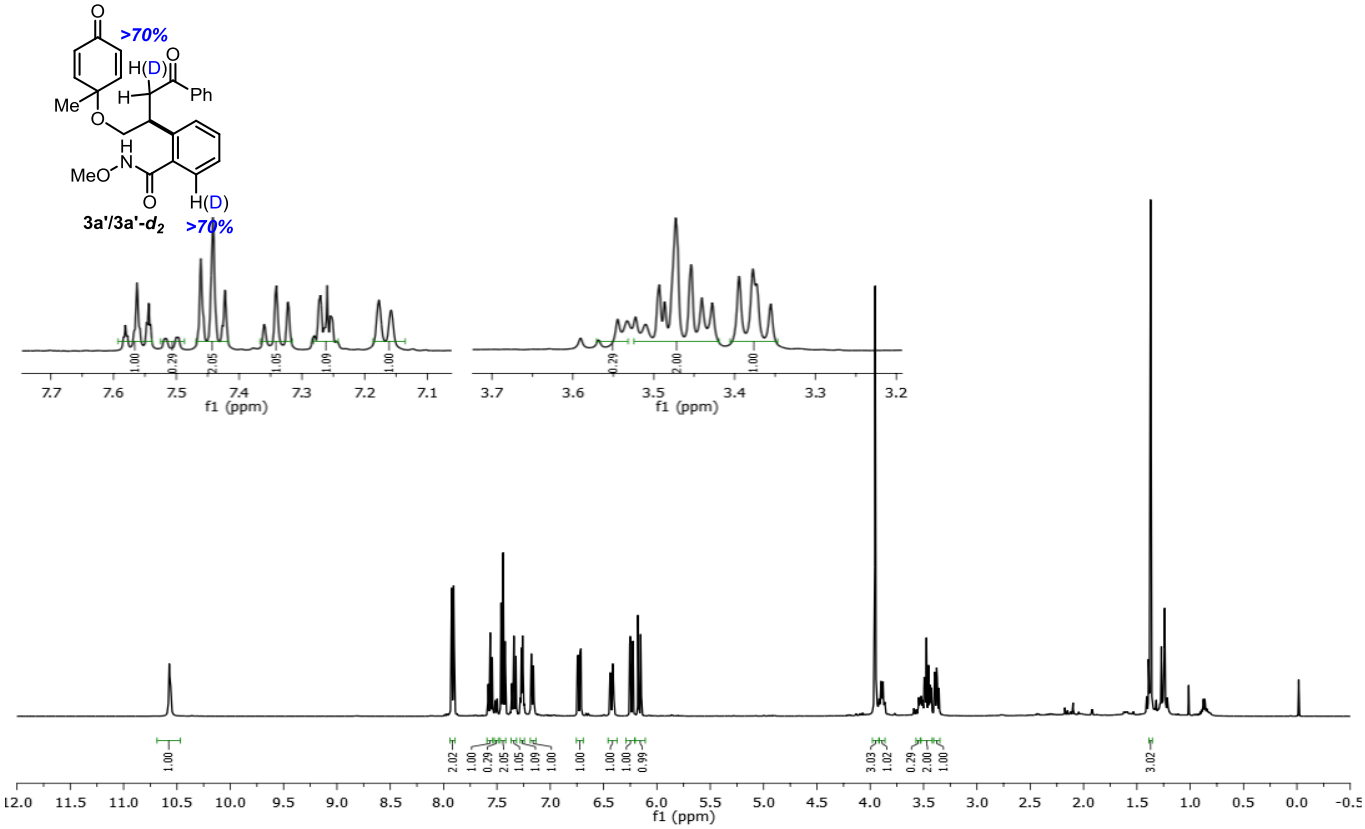
An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (4.6 mg, 2.5 mol%), benzamide **2a** (45.3 mg, 0.3 mmol) in THF:CD_3OD (9:1 ratio) (3.0 mL, 0.1 M) solvent and then to it was added CsOAc (115.2 mg, 0.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 °C for 12 h. Later, it was cooled down to room temperature and solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc: 2/1) to give the desired product **2a/2a-d2** **(**99 % Yield) as white solid with 27% deuterium incorporation at the *ortho*-position, as estimated ^1H NMR spectroscopy.



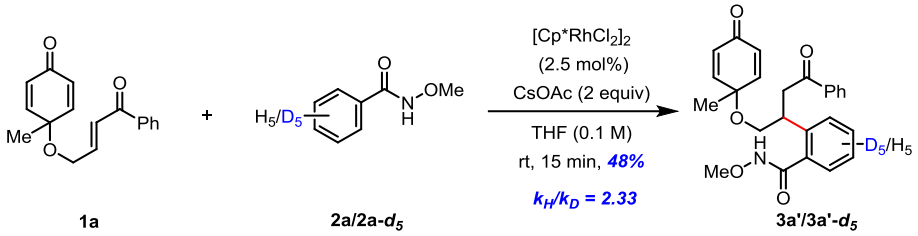
4b. H/D Exchange Study



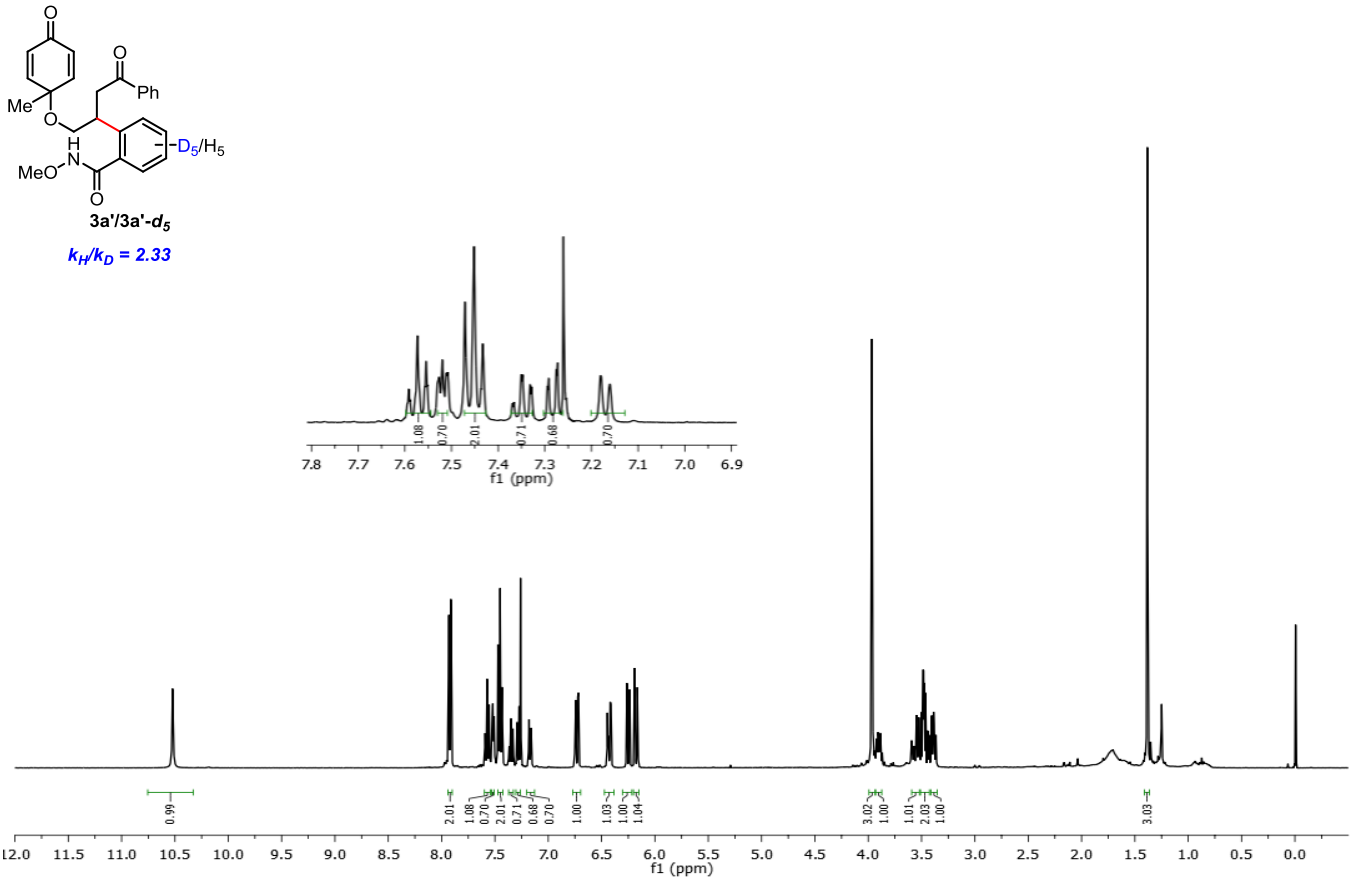
An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (4.6 mg, 2.5 mol%), cyclohexadienone **1a** (80.4 mg, 0.3 mmol) and benzamide **2a** (45.3 mg, 0.3 mmol) in THF:CD_3OD (9:1 ratio) (3.0 mL, 0.1 M) solvent and then added CsOAc (115.2 mg, 0.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 °C for 12 h. Later, it was cooled down to room temperature and solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (30% EtOAc in hexane) to give the desired product **3a'/3a'-d2** (73% Yield) as white solid with 70% deuterium incorporation at the *ortho*-position, as estimated ^{1}H NMR spectroscopy.



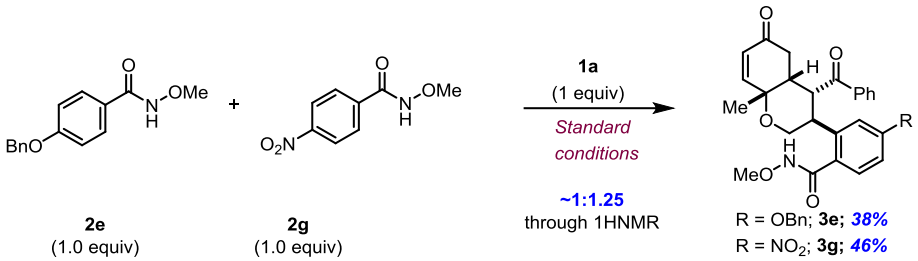
4c. Intermolecular Kinetic Isotope Effect:



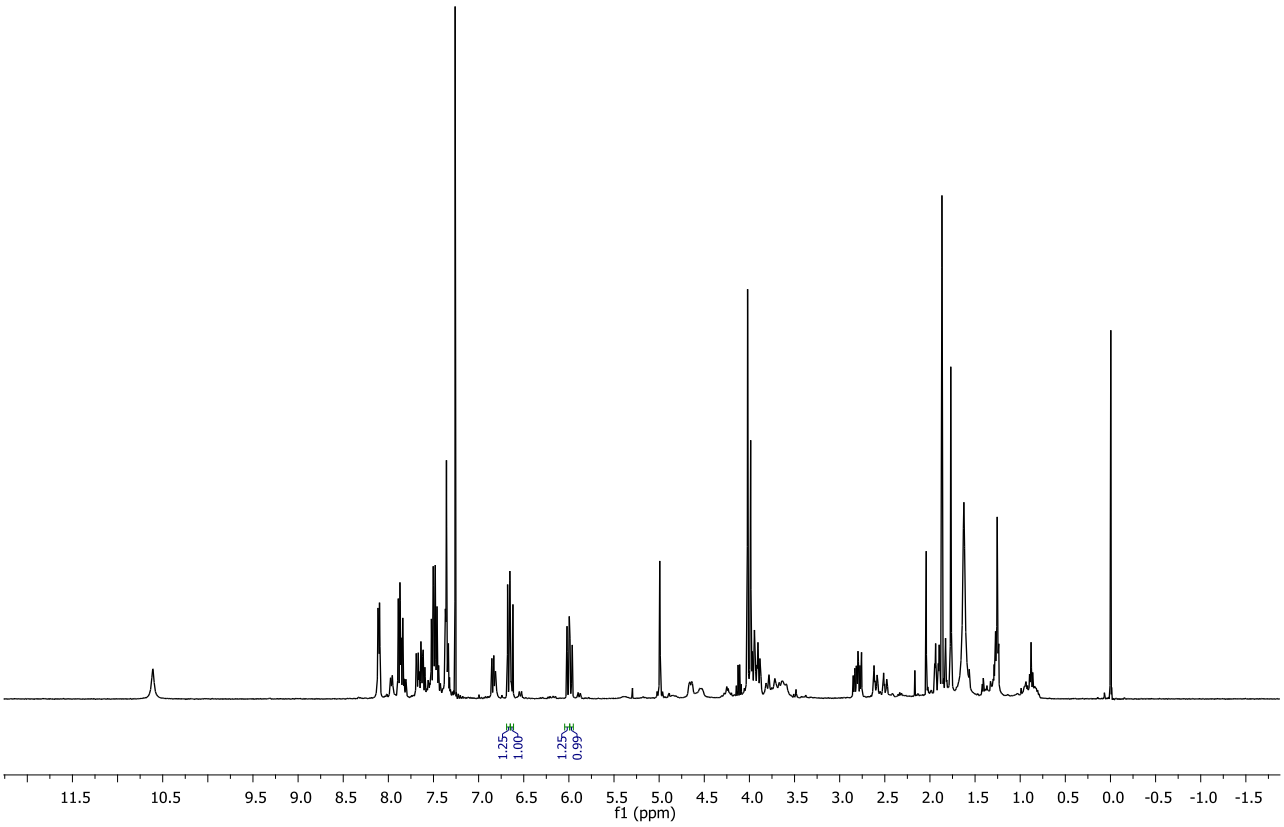
An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (4.6 mg, 2.5 mol%), cyclohexadienone **1a** (0.3 mmol) and benzamide **2a/2a-d$_5$** (0.3 mmol, 1:1 ratio) in THF (3 mL, 0.1 M) solvent and then added CsOAc (115.2 mg, 0.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred at rt for 15 min. Later, solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (30% EtOAc in hexane) to give the uncyclized product **3a'/3a'-d$_5$** as white solid in 48% yield. The kinetic isotopic effect of this reaction was thus determined to be $k_H/k_D \approx 2.33$ utilizing ^{1}H NMR spectroscopy.



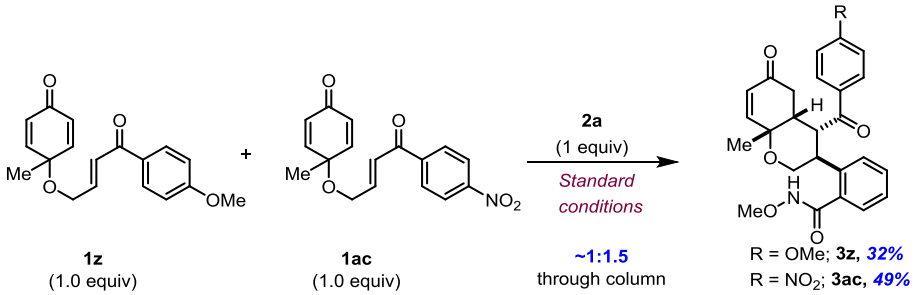
4d. Intermolecular competition between benzamides:



An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (2.3 mg, 2.5 mol%), cyclohexadienone **1** (40.2 mg, 0.15 mmol) and benzamide **2e** (38.6 mg, 0.15 mmol), **2g** (29.4 mg, 0.15 mmol) in THF (3 mL, 0.05 M) solvent and then added CsOAc (57.6 mg, 0.3 mmol) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 ^oC for 12 h. Later, it was cooled down to room temperature, diluted with water (15 mL) and extracted with EtOAc (15 mL × 2). Combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude ^1H NMR revealed the formation of products **3e** and **3g** in 1:1.25 ratio. The product formation is more favourable from electron-deficient benzamide **2g**.



4e. Intermolecular competition between enones:



An oven-dried pressure tube containing Teflon-coated magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ catalyst (2.3 mg, 2.5 mol%), enone **1z** (45 mg, 0.15 mmol), **1ac** (47 mg, 0.15 mmol) and benzamide **2** (22.7 mg, 0.15 mmol) in THF (3 mL, 0.05 M) solvent and then added CsOAc (57.6 mg, 0.3 mmol) under nitrogen atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 80 ^oC for 12 h. Later, it was cooled down to room temperature, diluted with water (15 mL) and extracted with EtOAc (15 mL × 2). Combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude product was subjected to column chromatography on silica gel (EtOAc/Hexanes) to afford desired cyclized products **3z** (21.7 mg, 32% yield) and **3ac** (34.1 mg, 49% yield). An intermolecular competition reaction revealed that alkene insertion of electron-deficient enone **1ac** undergoes preferentially faster than electron-rich enone **1z**.

5. References:

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16. S.-S. Zhang, J.-Q. Wu, Y.-X. Lao, X.-G. Liu, Y. Liu, W.-X. Lv, D.-H. Tan, Y.-F. Zeng and H. Wang, *Org. Lett.*, 2014, ***16***, 6412−6415.
17. H. Liang, X. Zhao, L. Zheng and J. Wang, *J. Org. Chem.*, 2019, ***84***, 11306–11315.
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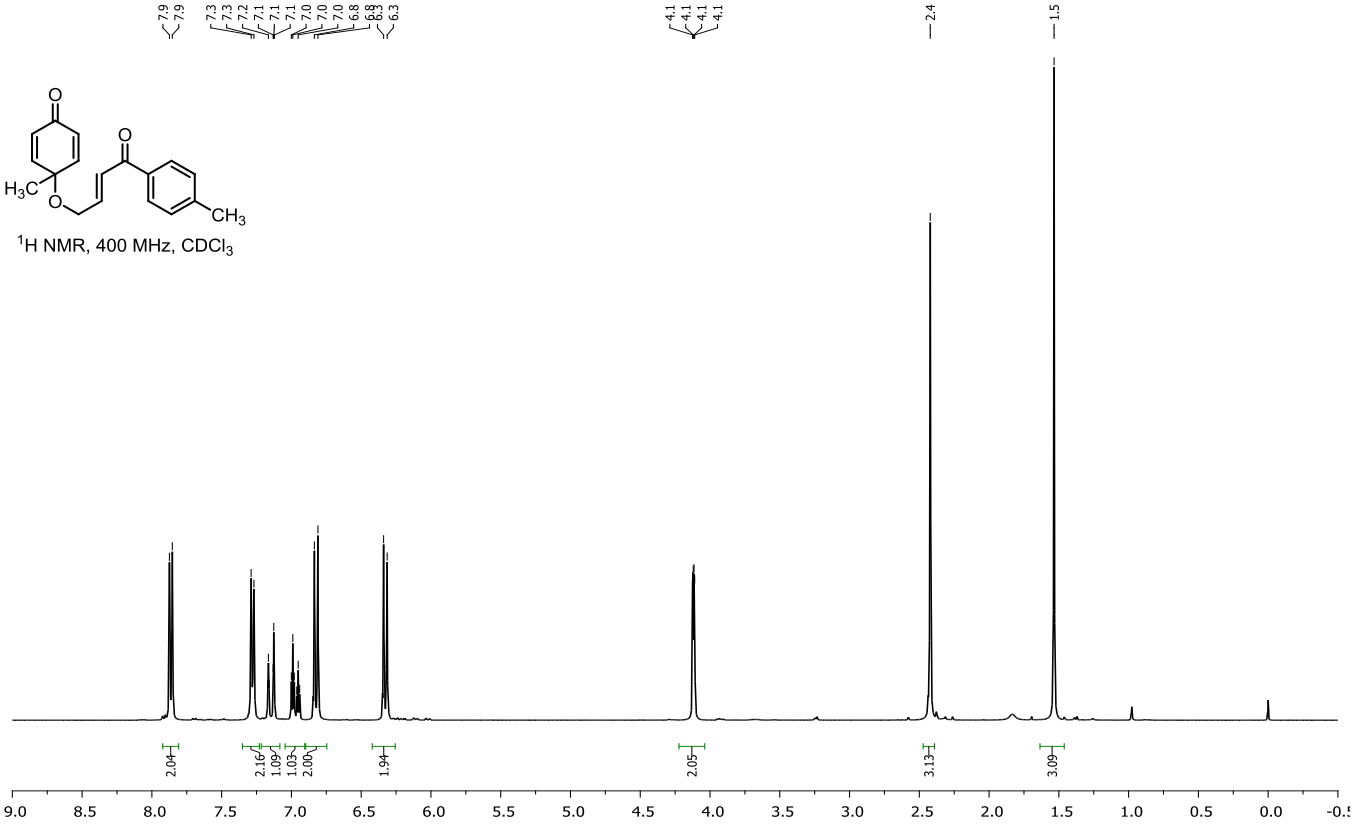
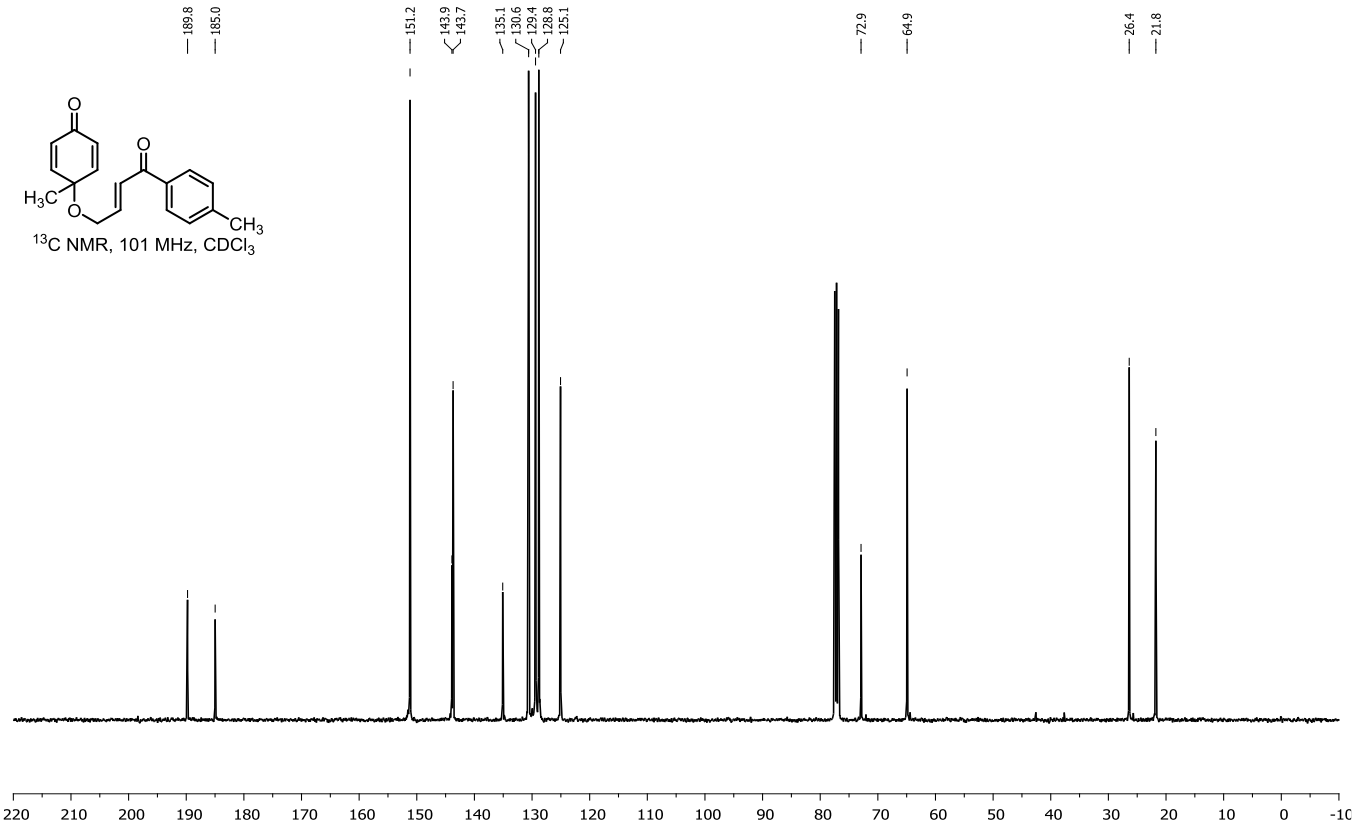
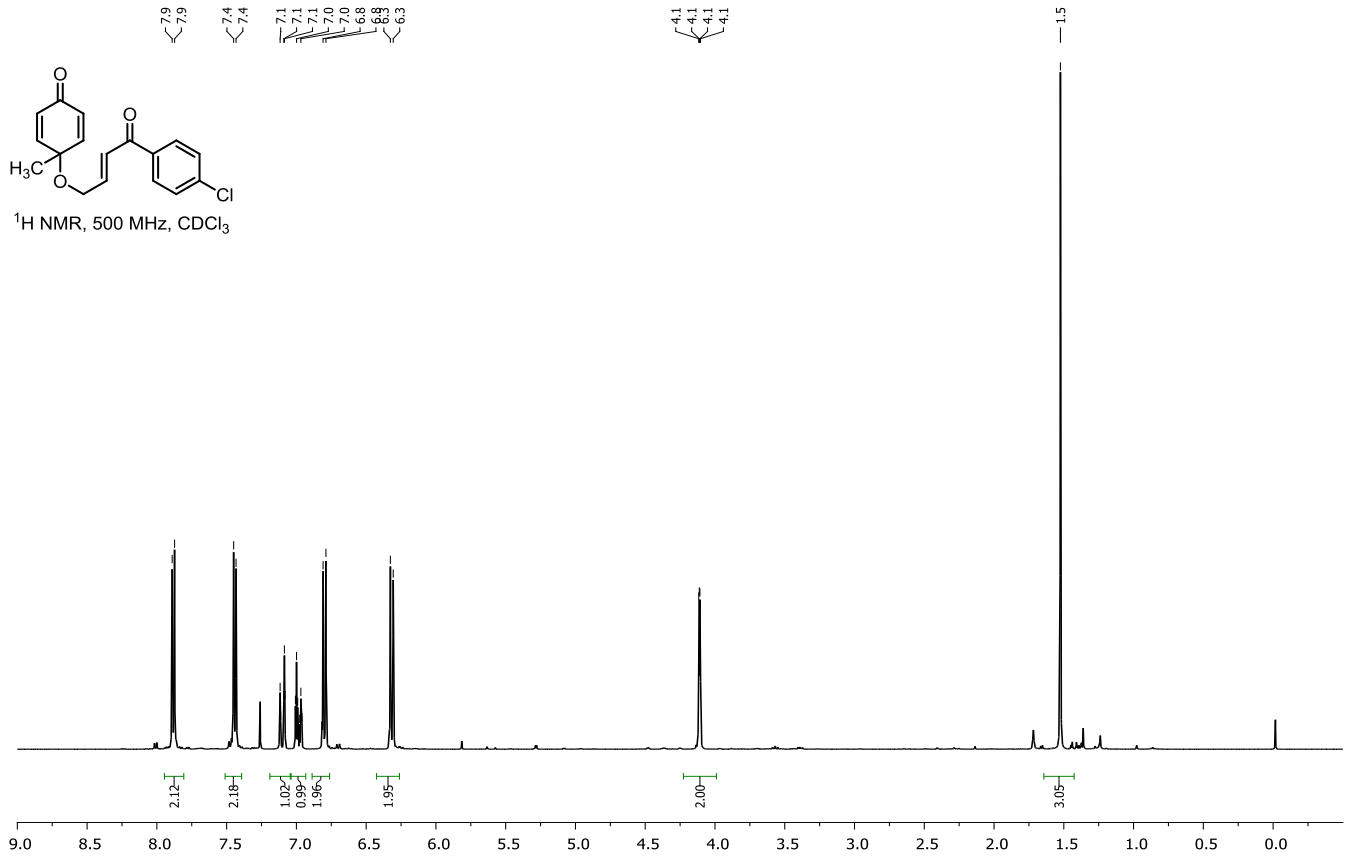
6. ^{1}H &^{13}C NMR Spectra:

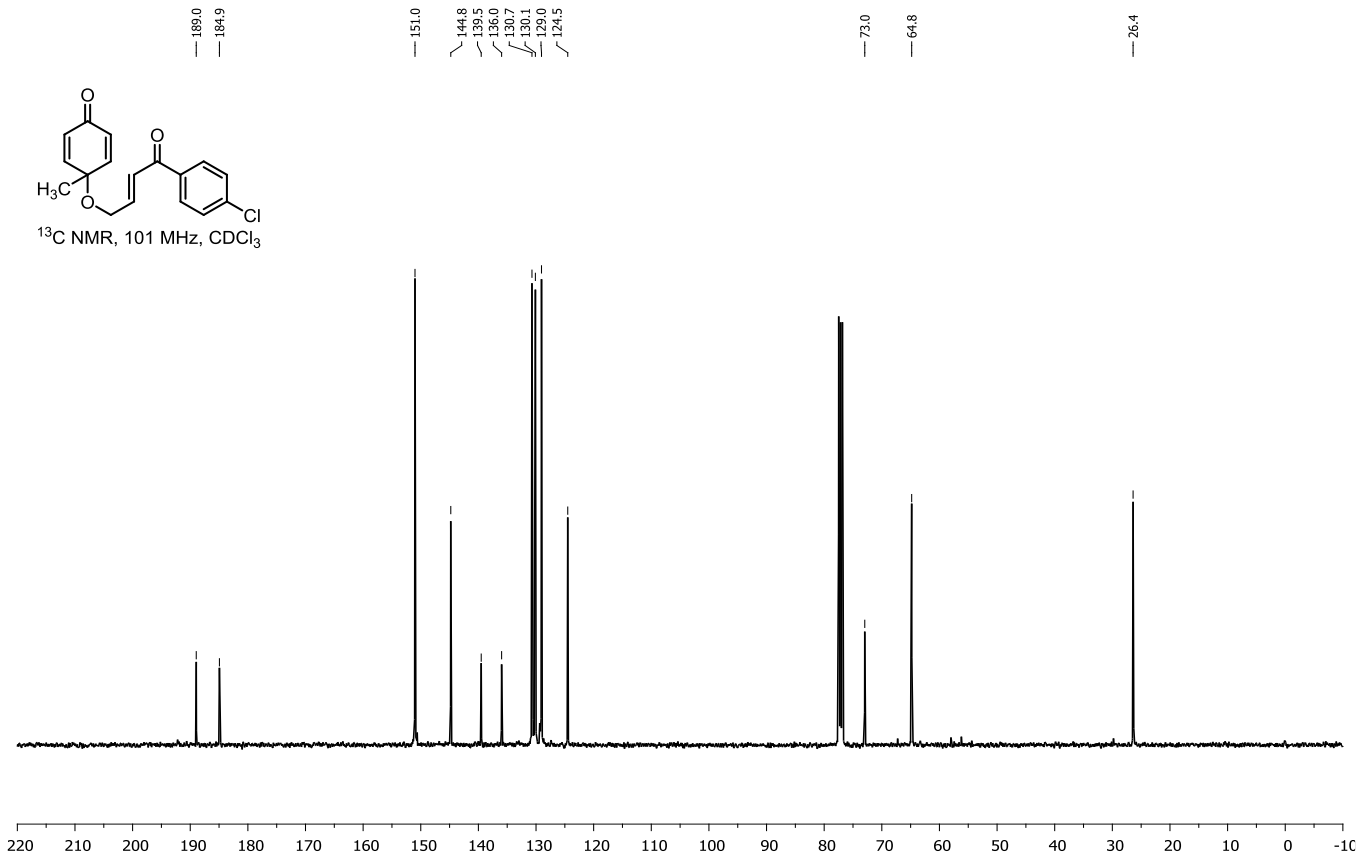
(*E*)-4-Methyl-4-((4-oxo-4-(*p*-tolyl)but-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1y):



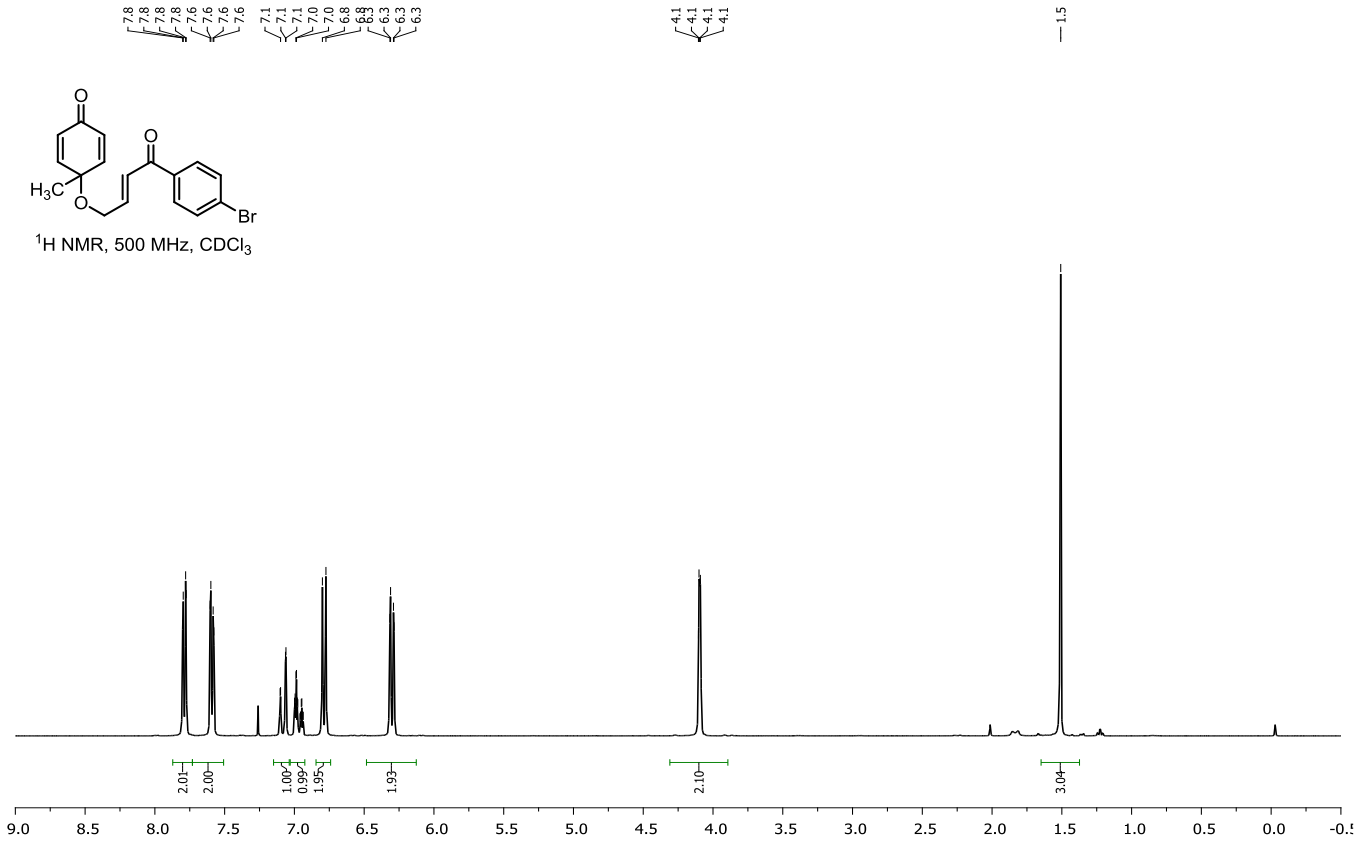


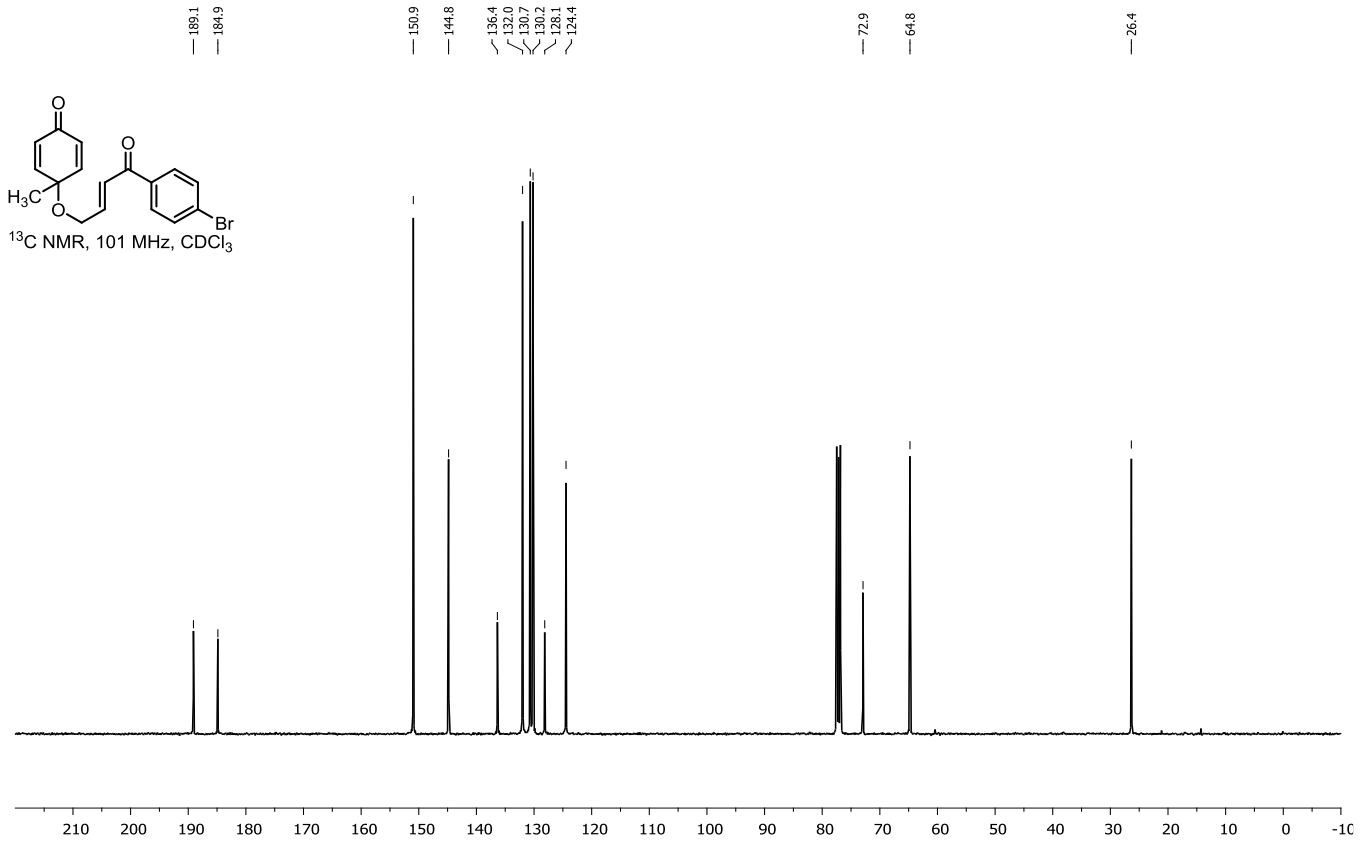
(*E*)-4-((4-(4-Chlorophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1aa):



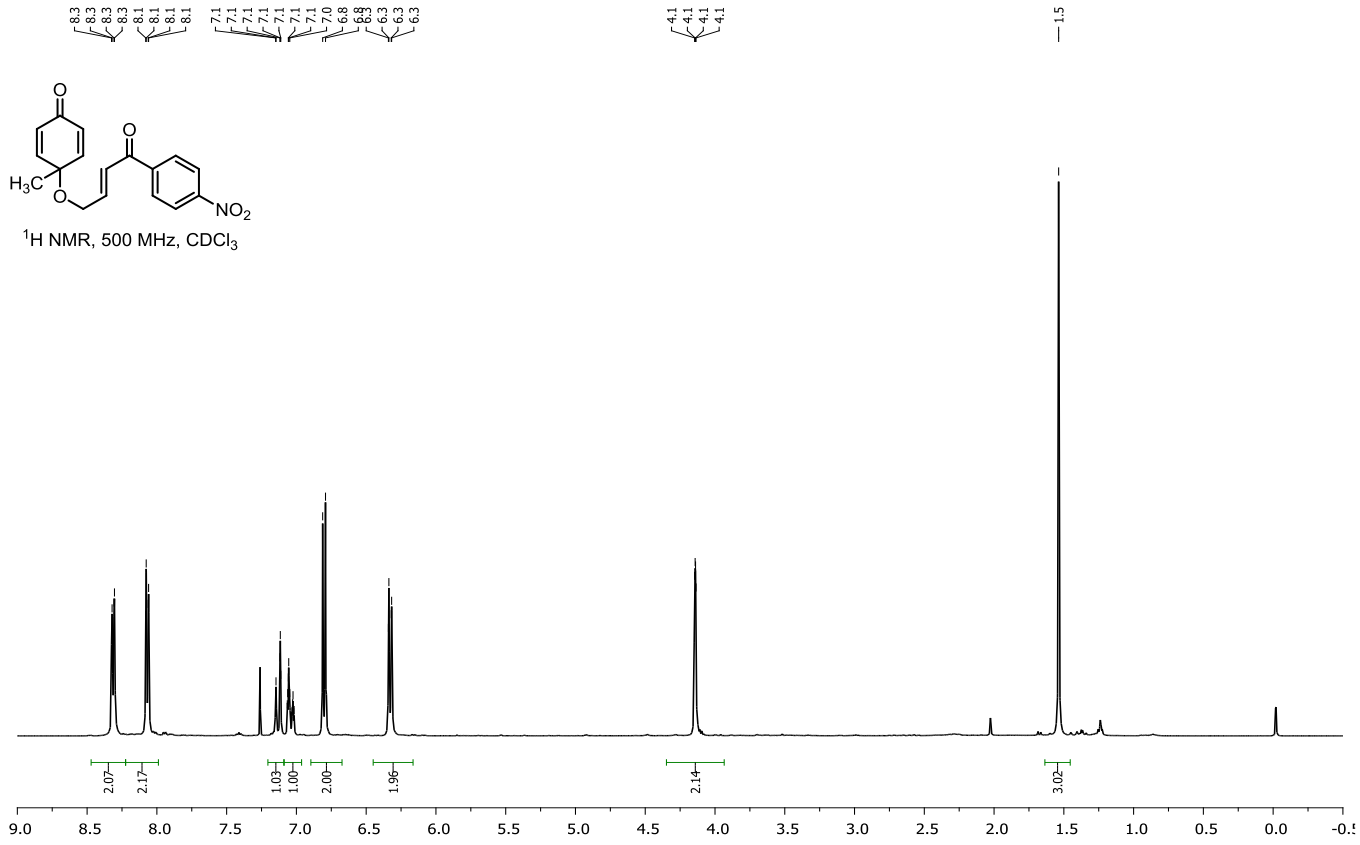


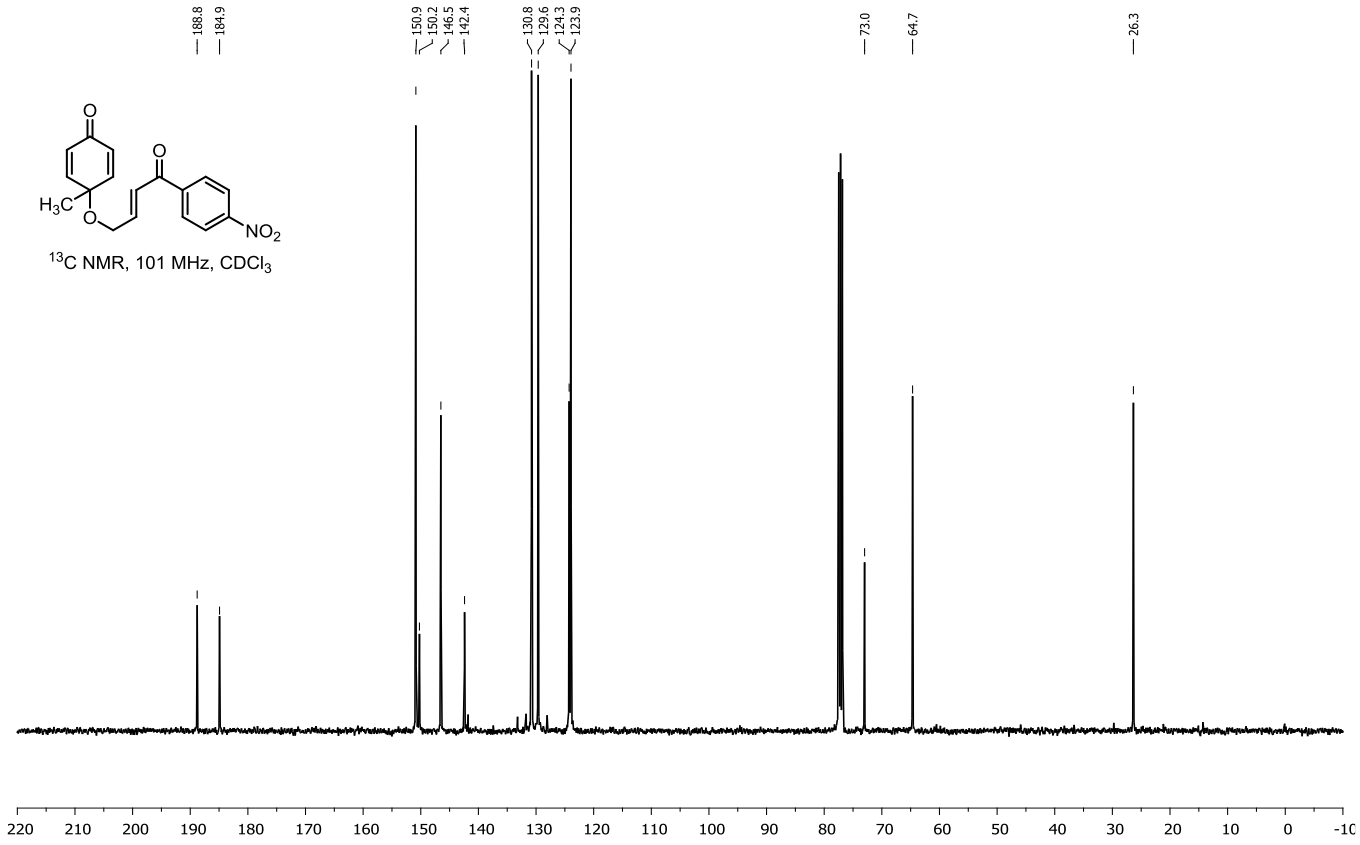
(*E*)-4-((4-(4-Bromophenyl)-4-oxobut-2-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (1ab):



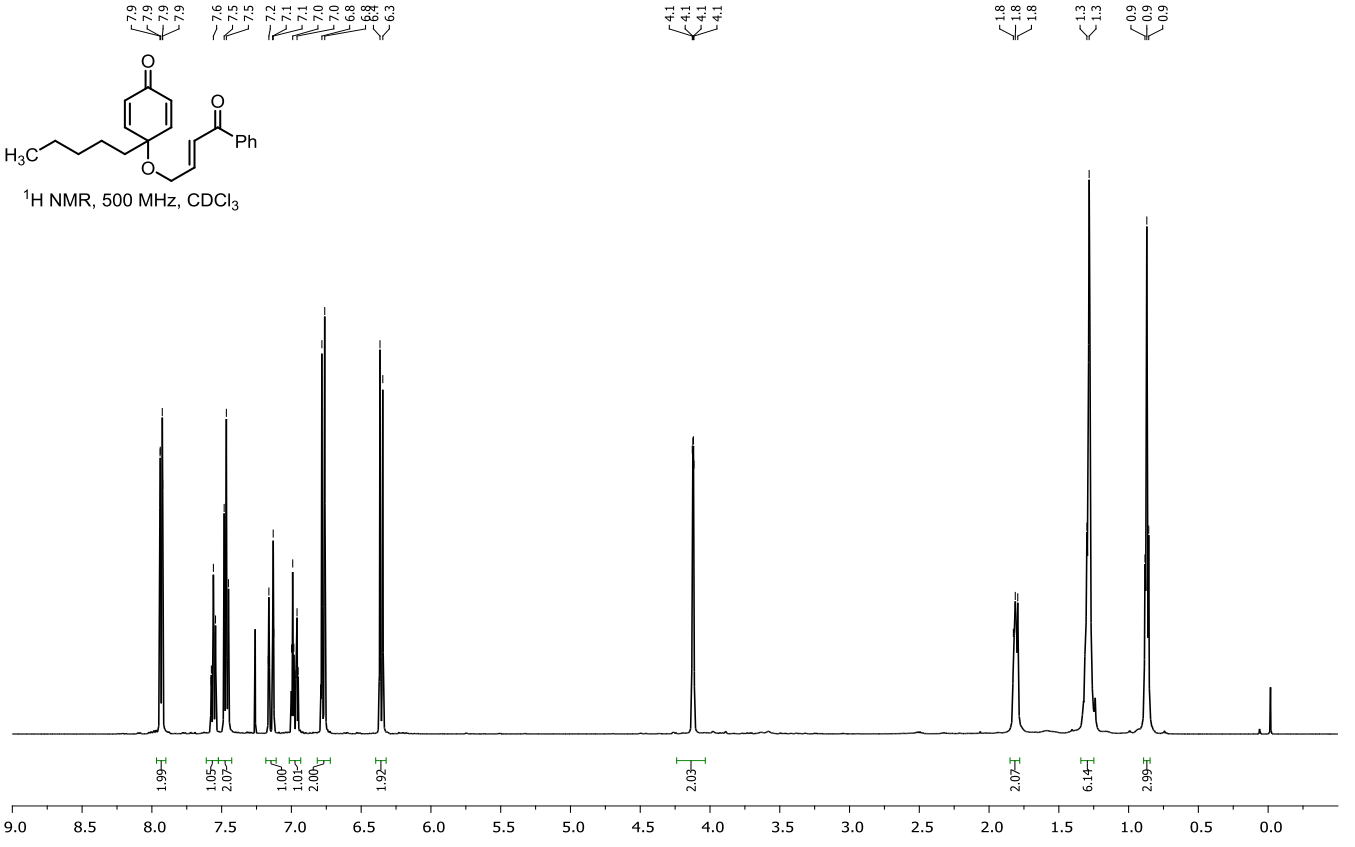


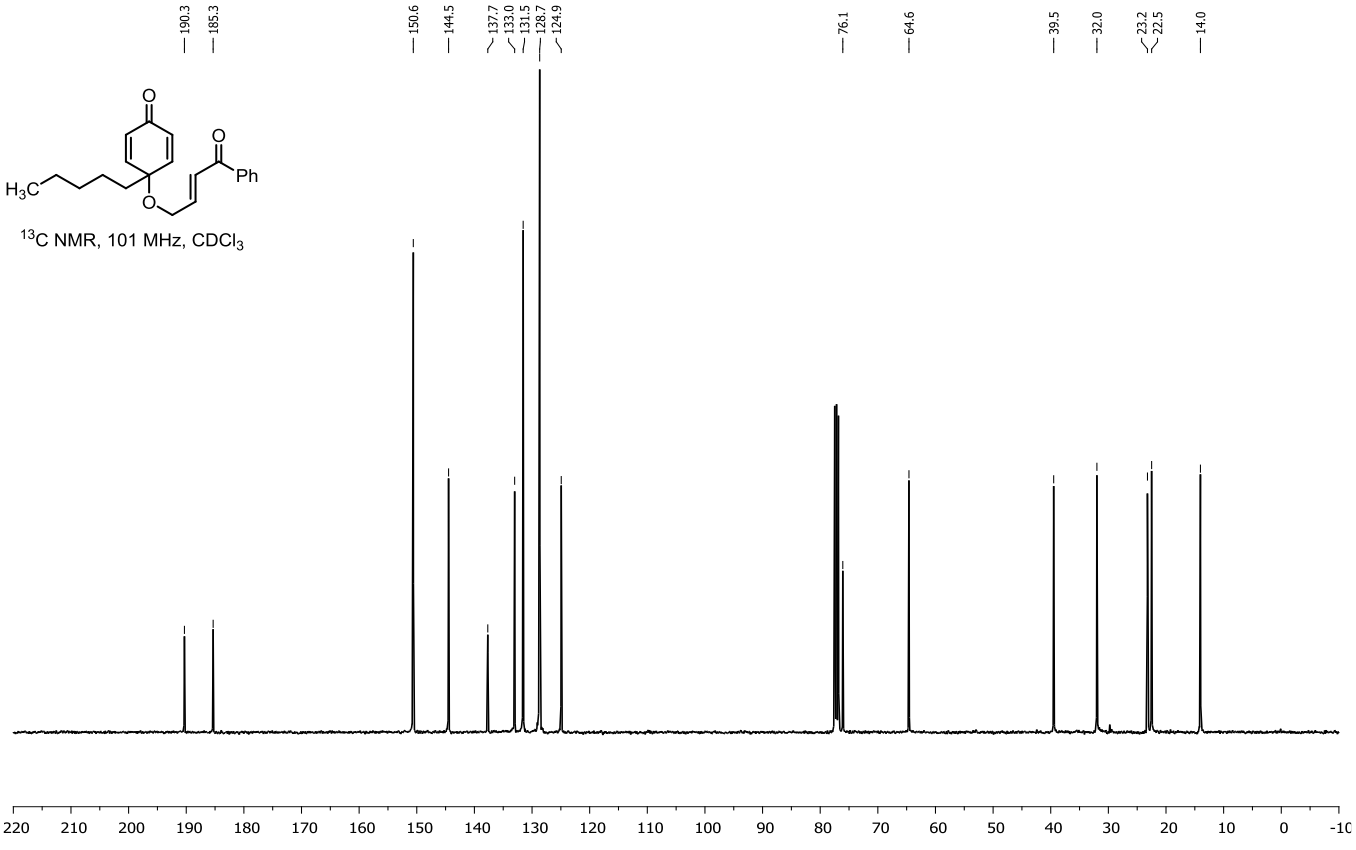
(*E*)-4-Methyl-4-((4-(4-nitrophenyl)-4-oxobut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1ac):



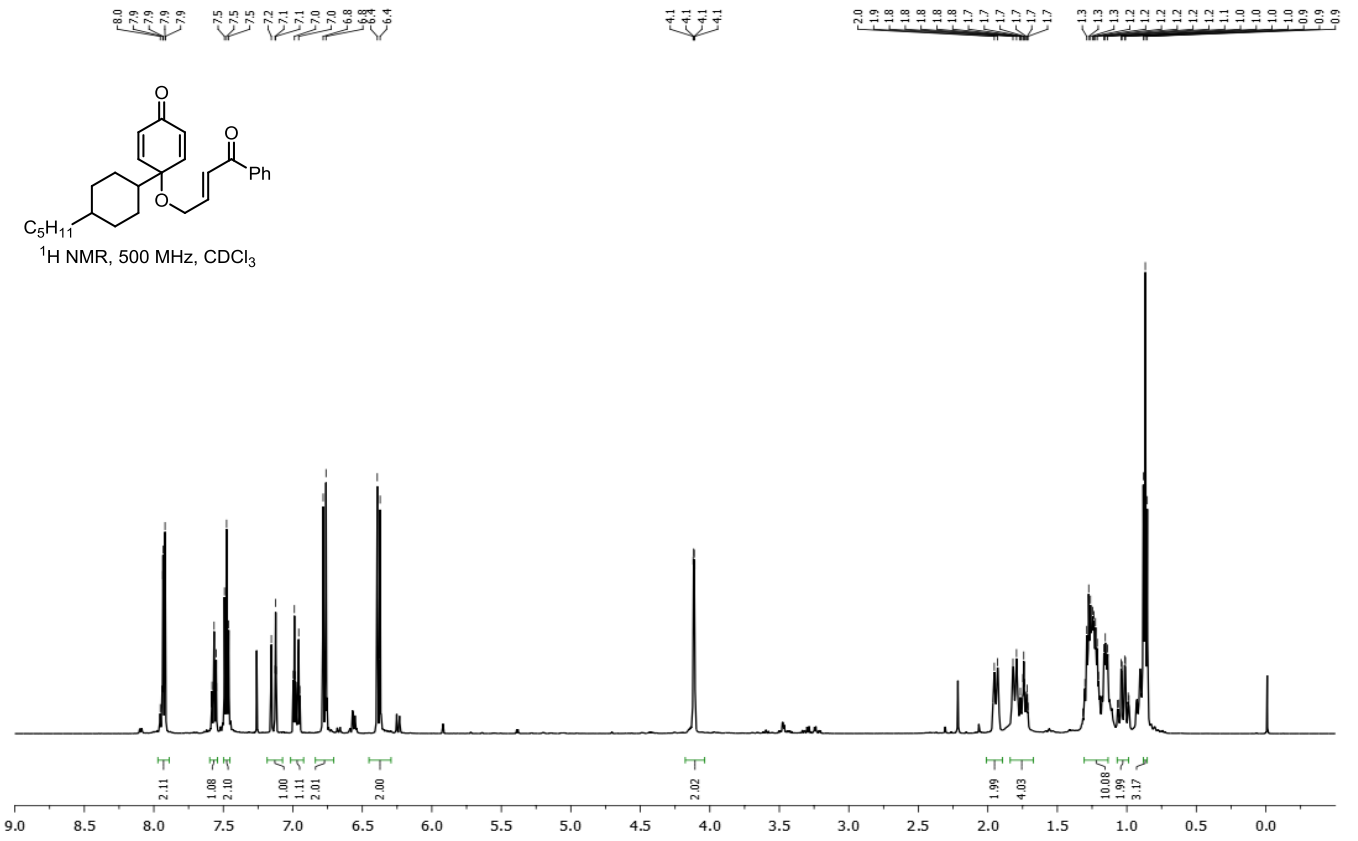


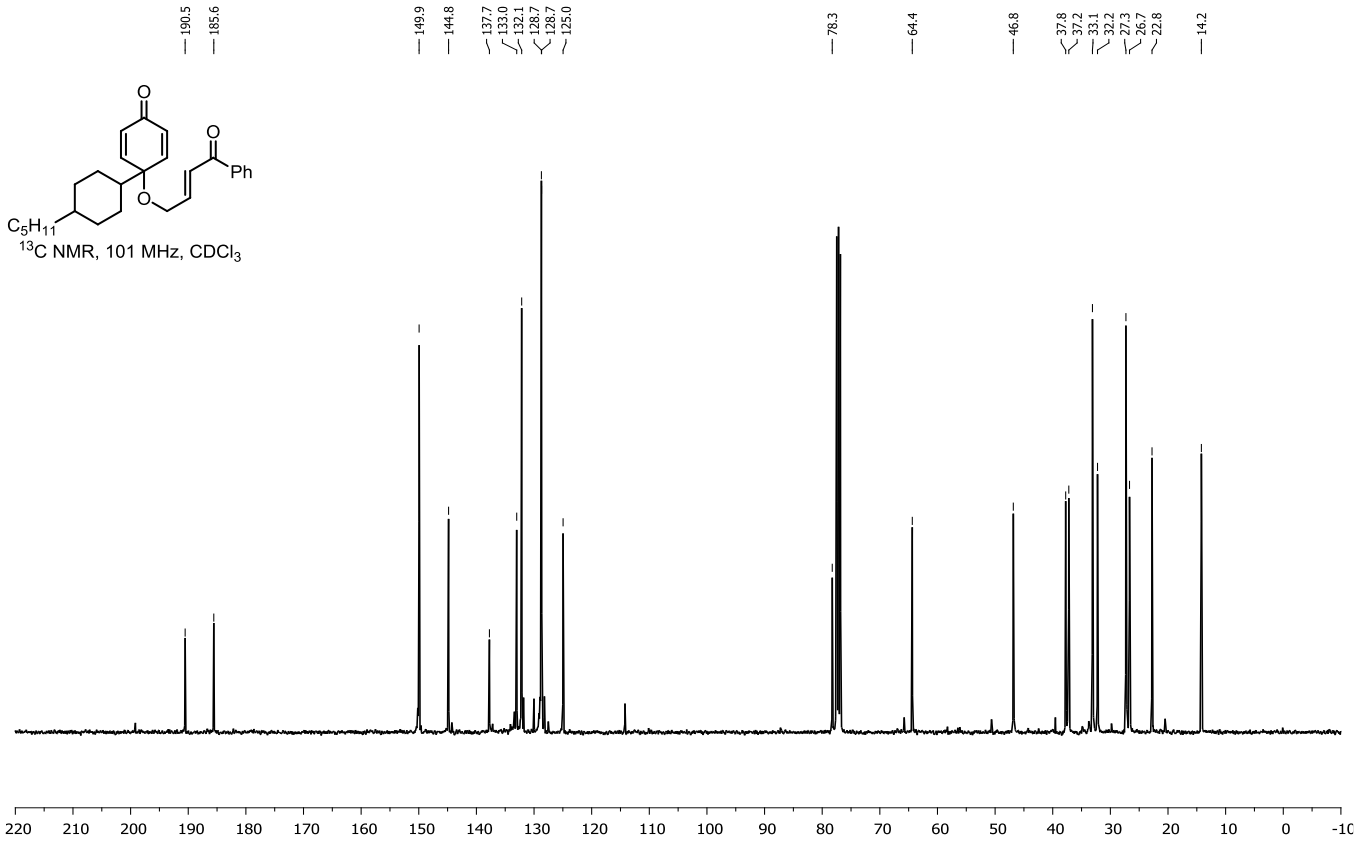
(*E*)-4-((4-Oxo-4-phenylbut-2-en-1-yl)oxy)-4-pentylcyclohexa-2,5-dien-1-one (1ah):



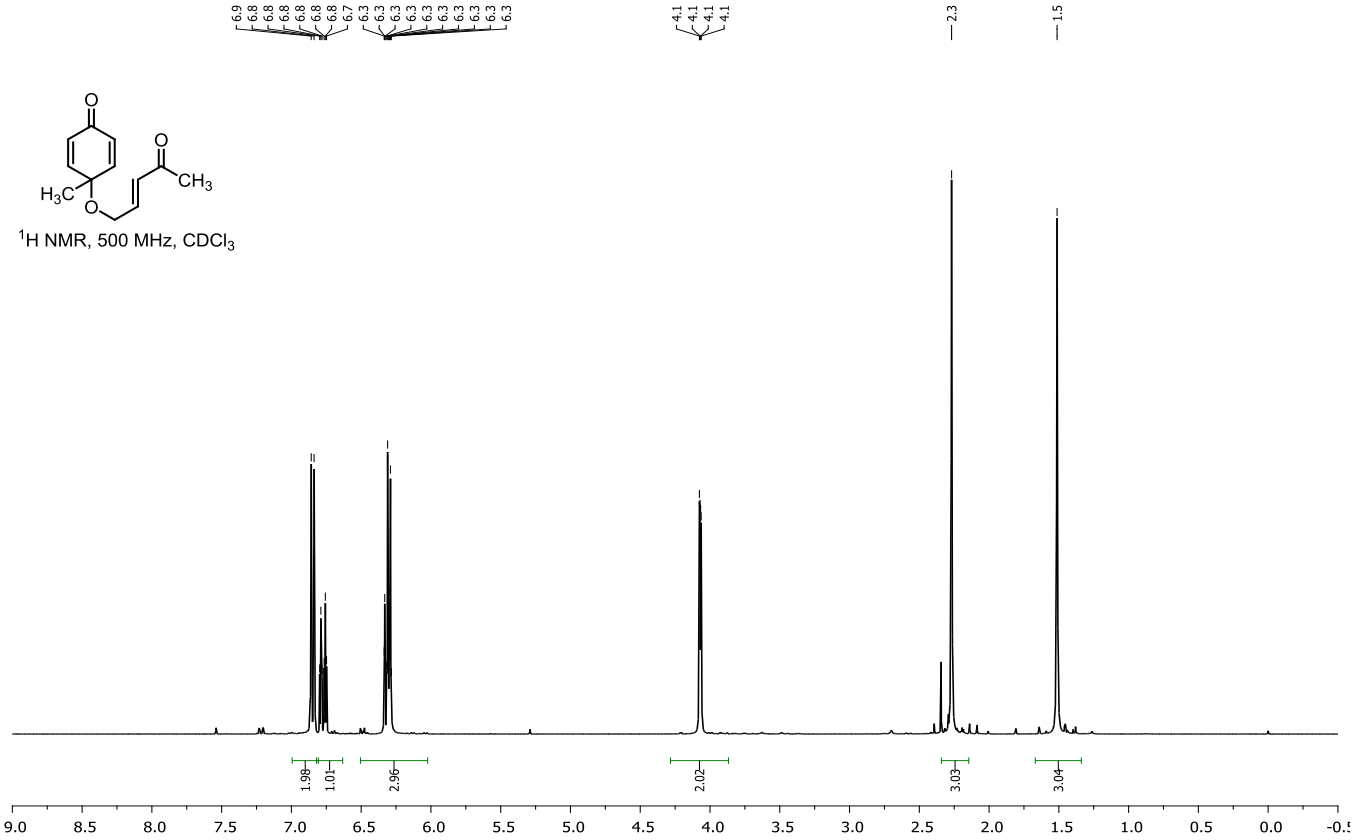


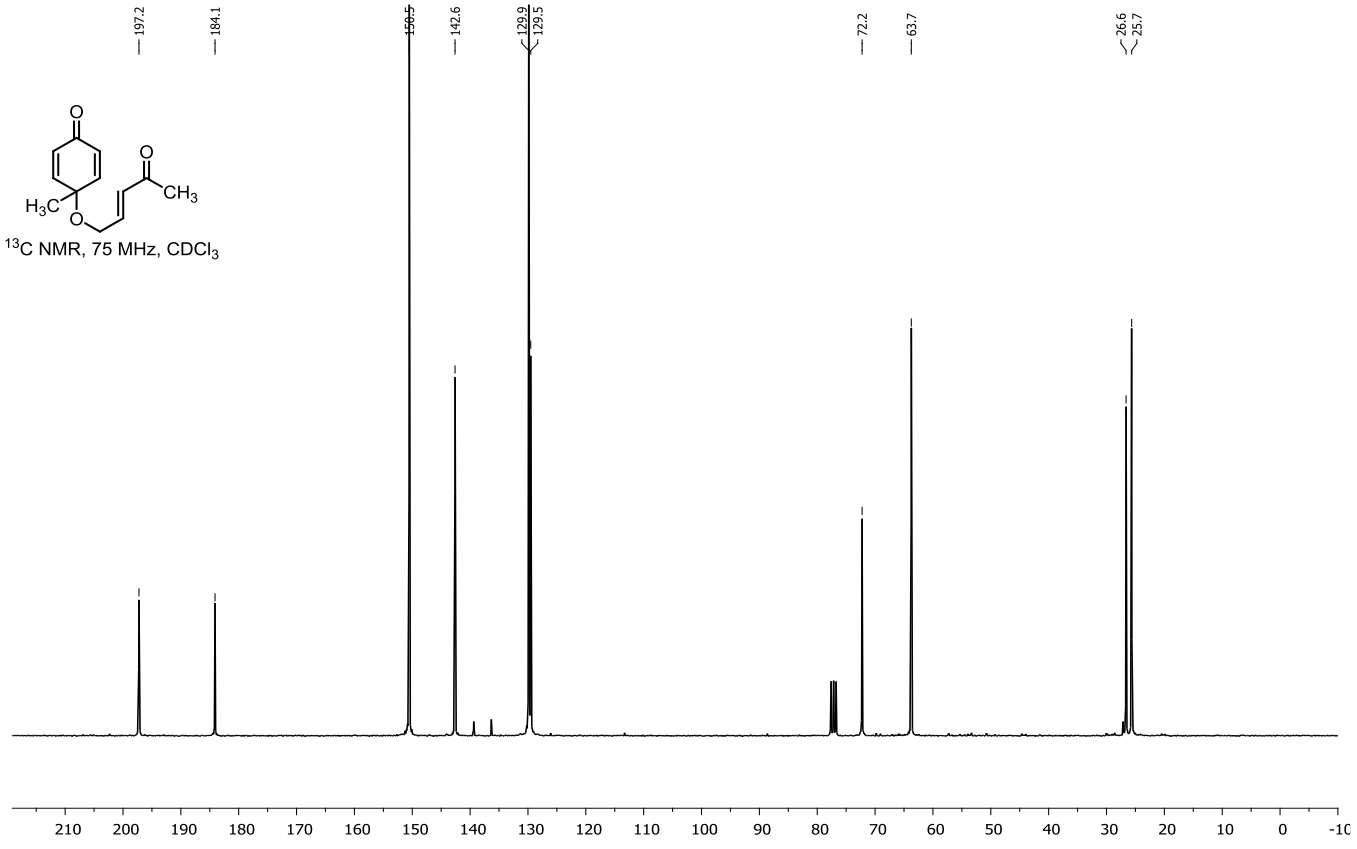
(*E*)-1-((4-Oxo-4-phenylbut-2-en-1-yl)oxy)-4'-pentyl-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (1am):



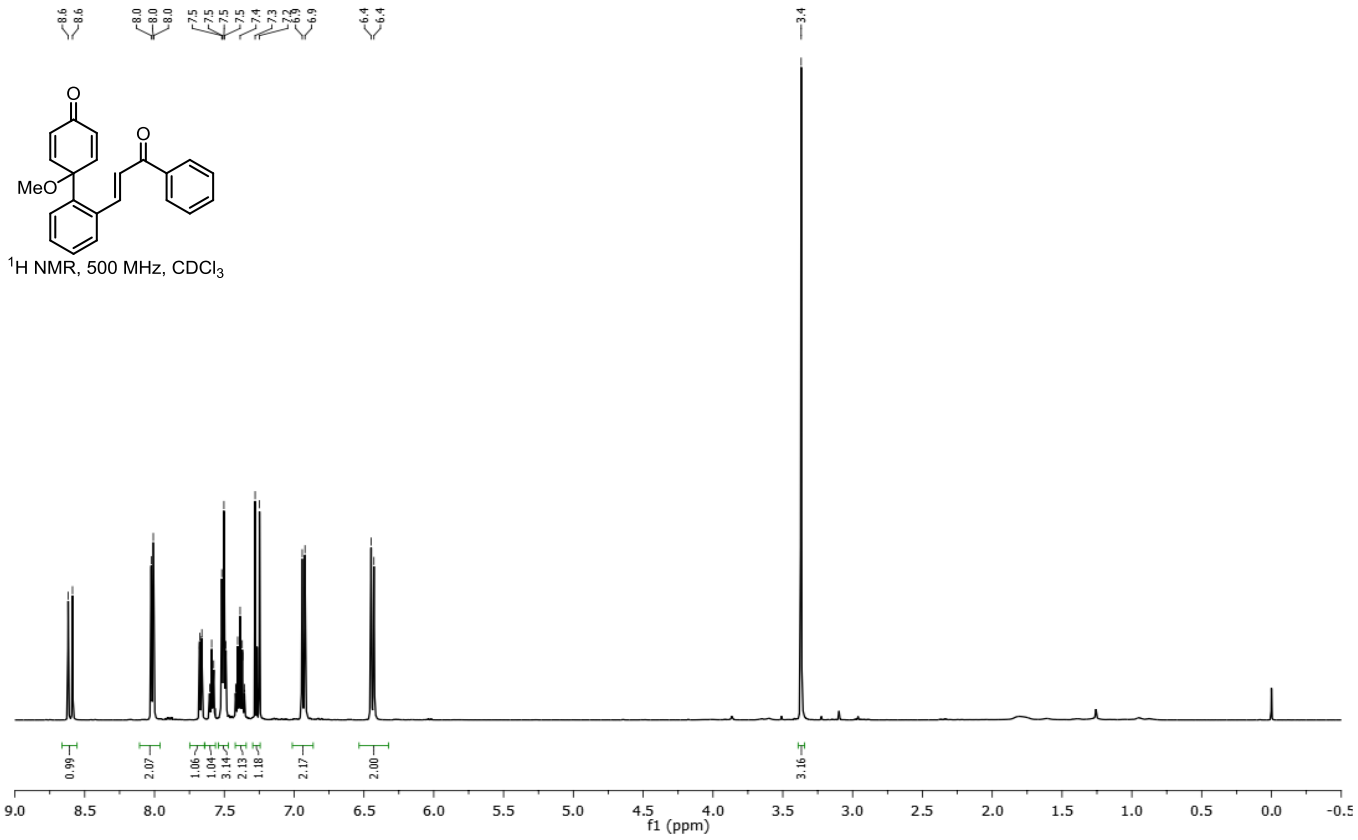


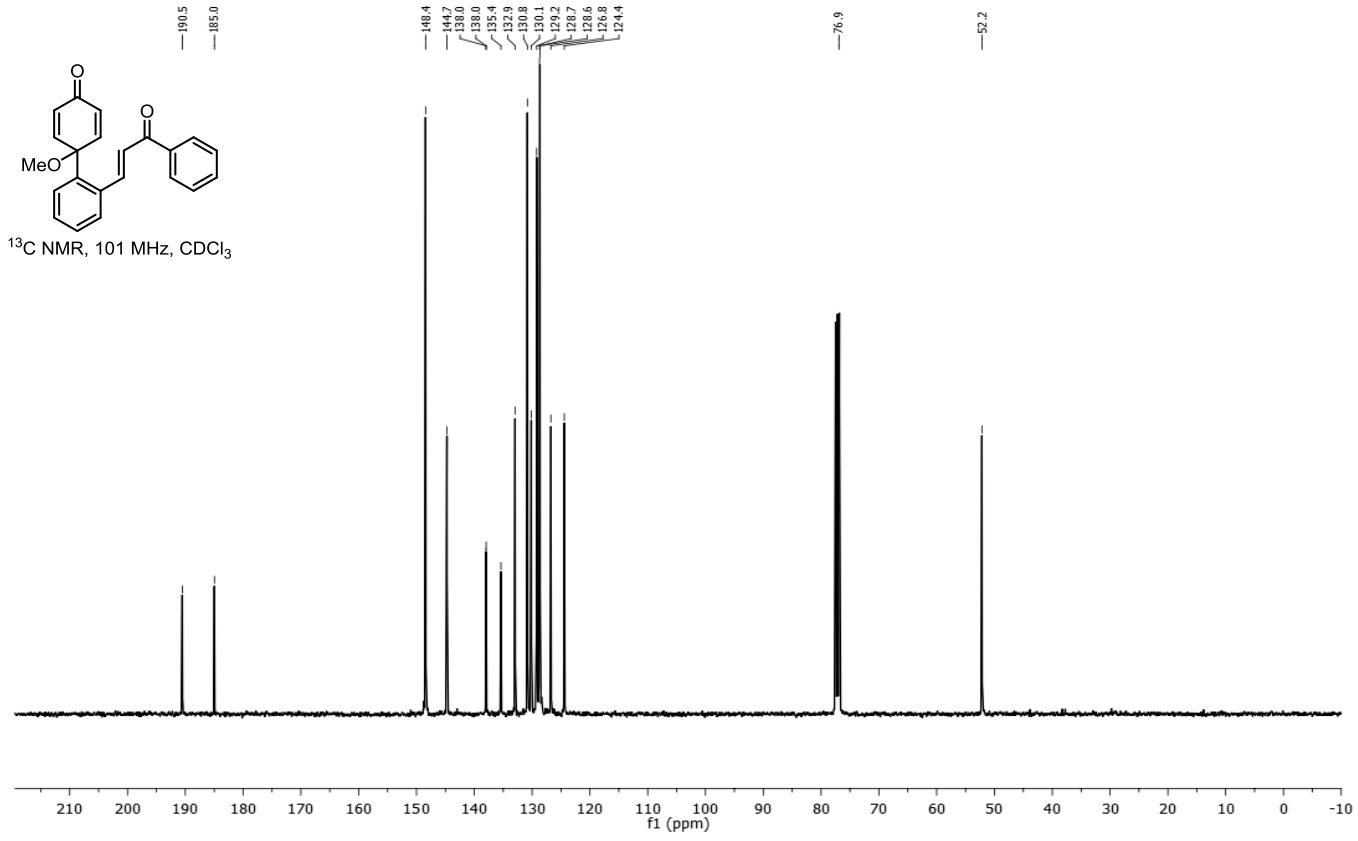
(*E*)-4-Methyl-4-((4-oxopent-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (1af):



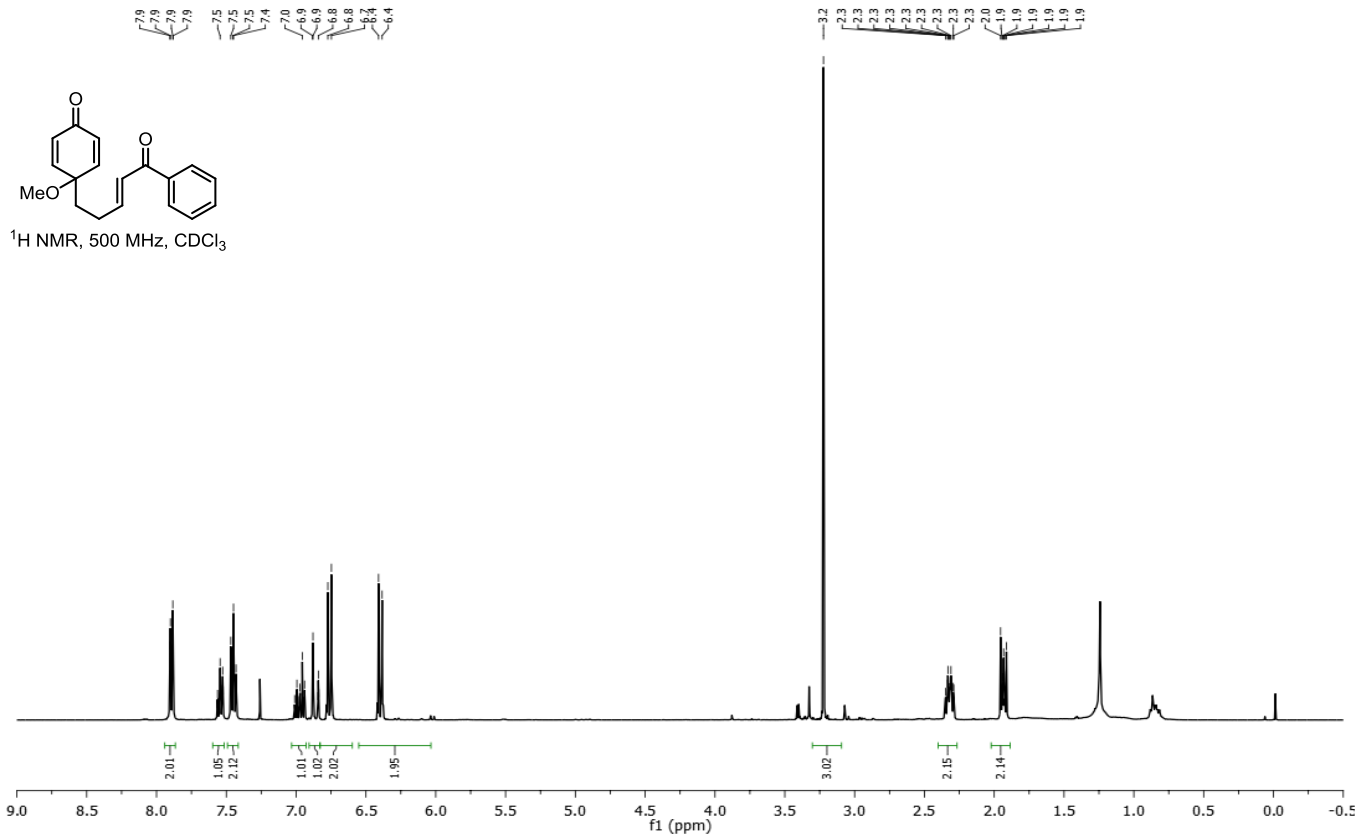


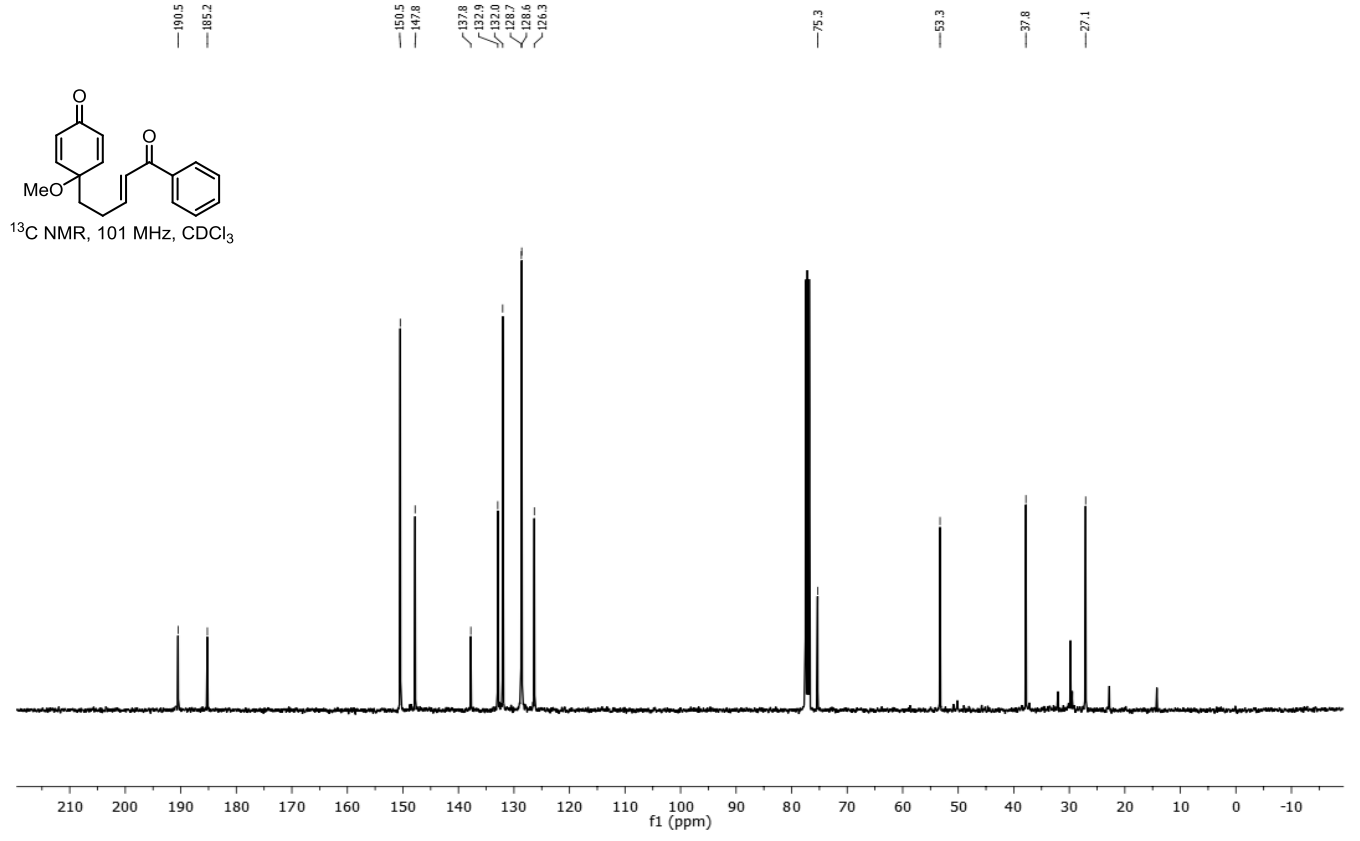
(*E*)-1-Methoxy-2'-(3-oxo-3-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-4(1*H*)-one (SM-1):



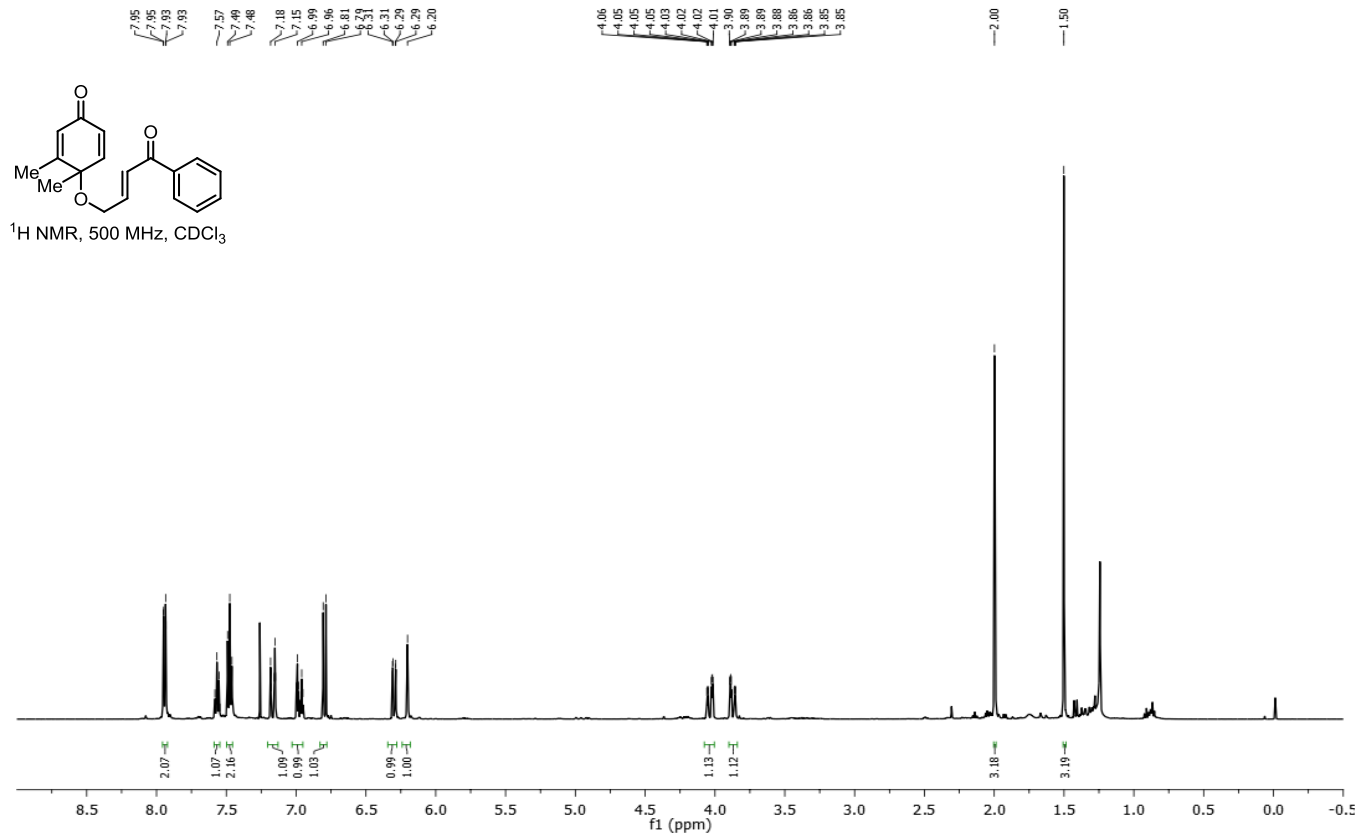


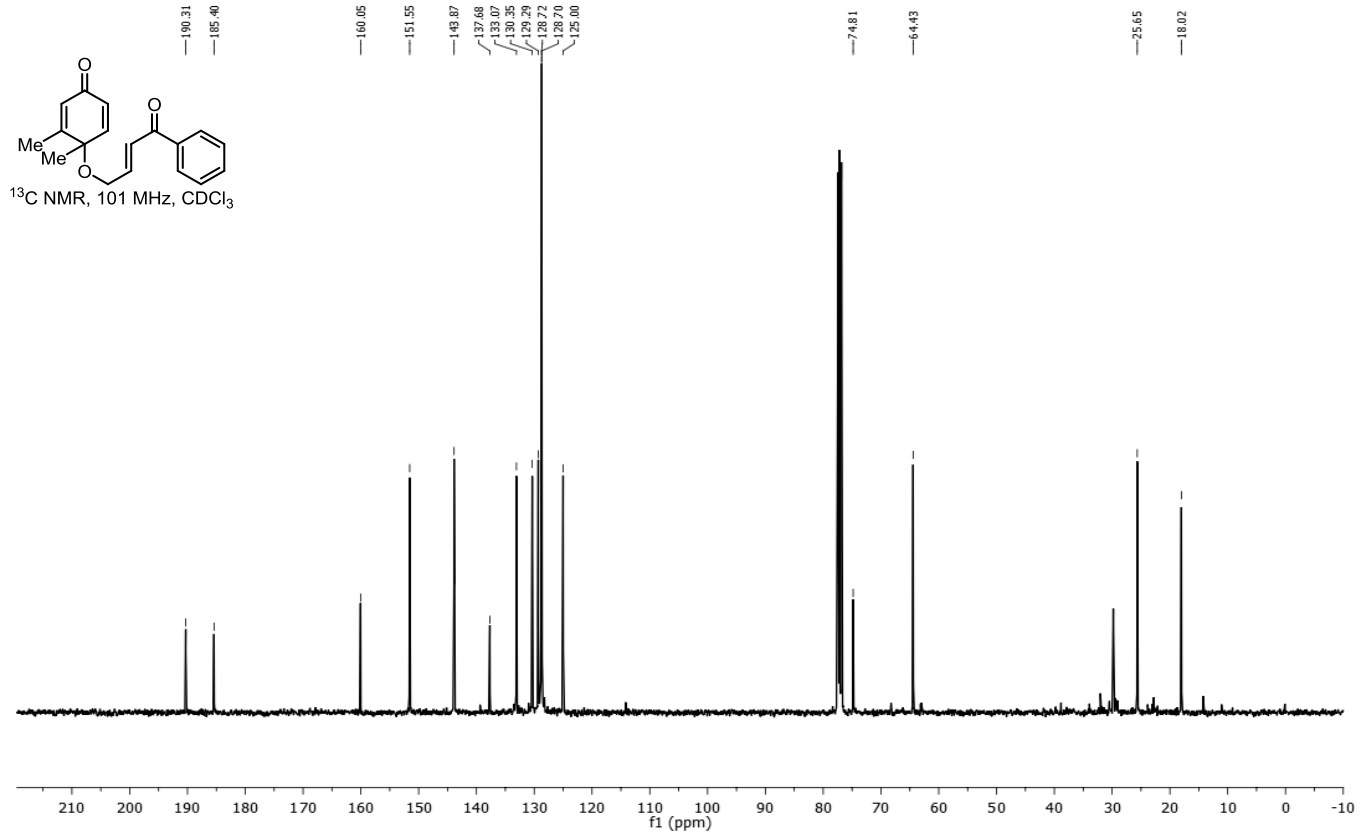
(*E*)-4-Methoxy-4-(5-oxo-5-phenylpent-3-en-1-yl)cyclohexa-2,5-dien-1-one (SM-2):



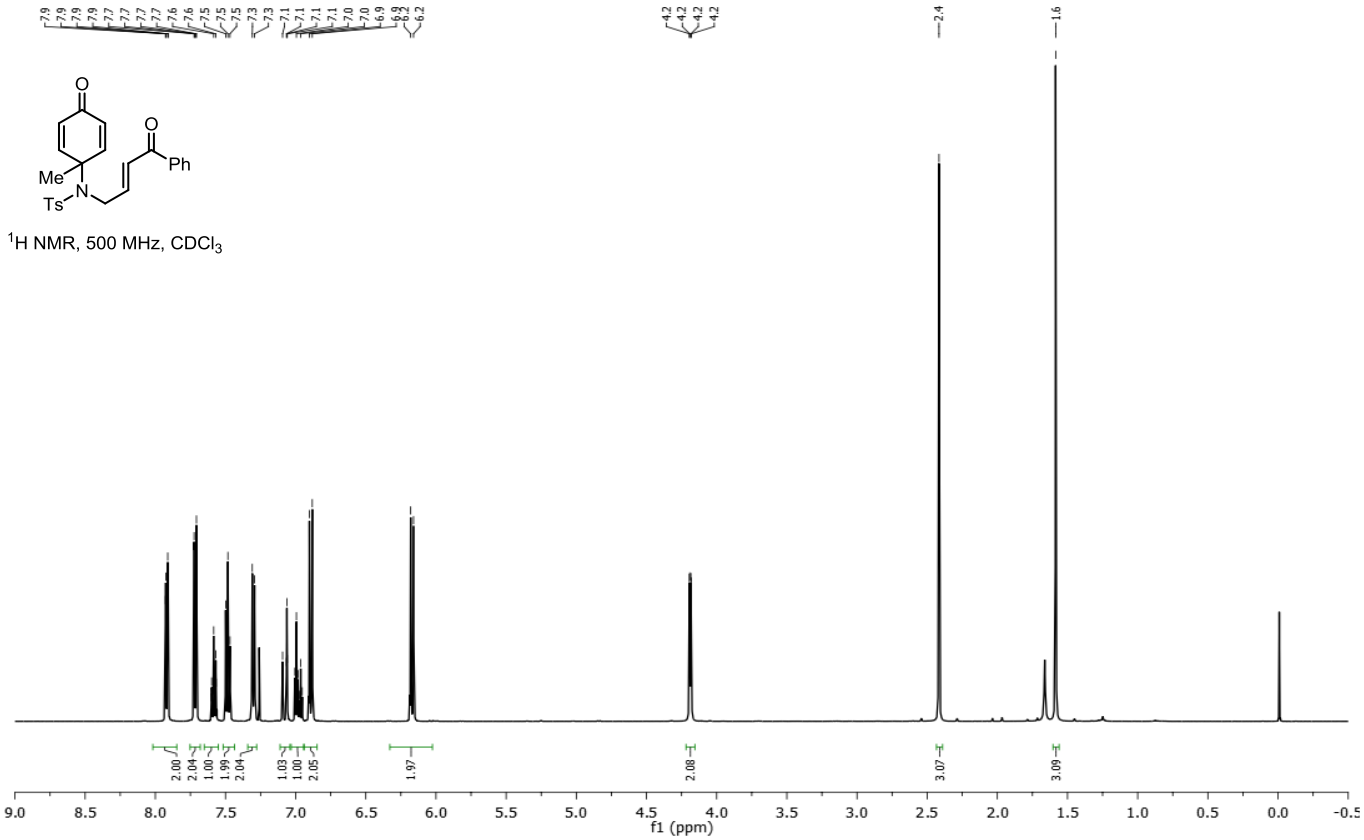


(*E*)-3,4-Dimethyl-4-((4-oxo-4-phenylbut-2-en-1-yl)oxy)cyclohexa-2,5-dien-1-one (SM-3):

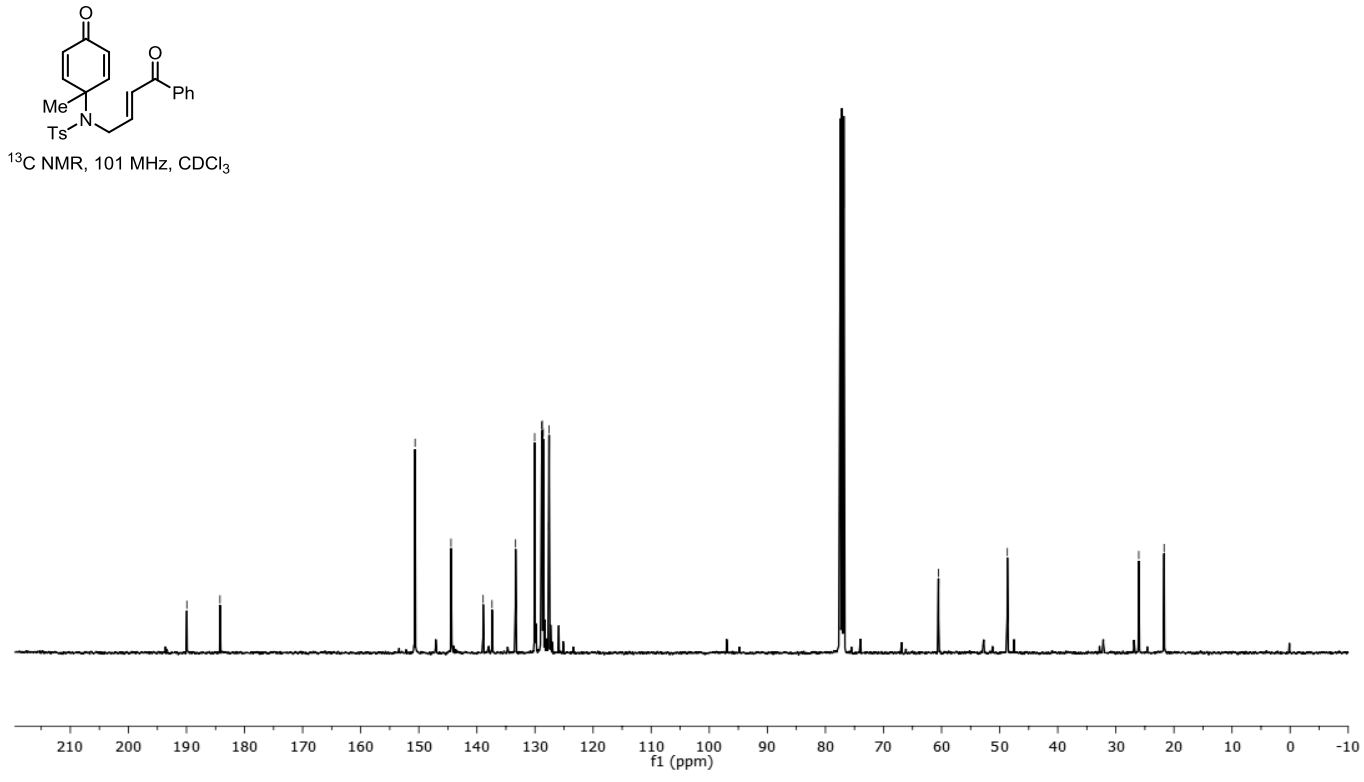




(*E*)-4-Methyl-N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-N-(4-oxo-4-phenylbut-2-en-1-yl)benzenesulfonamide (1x):

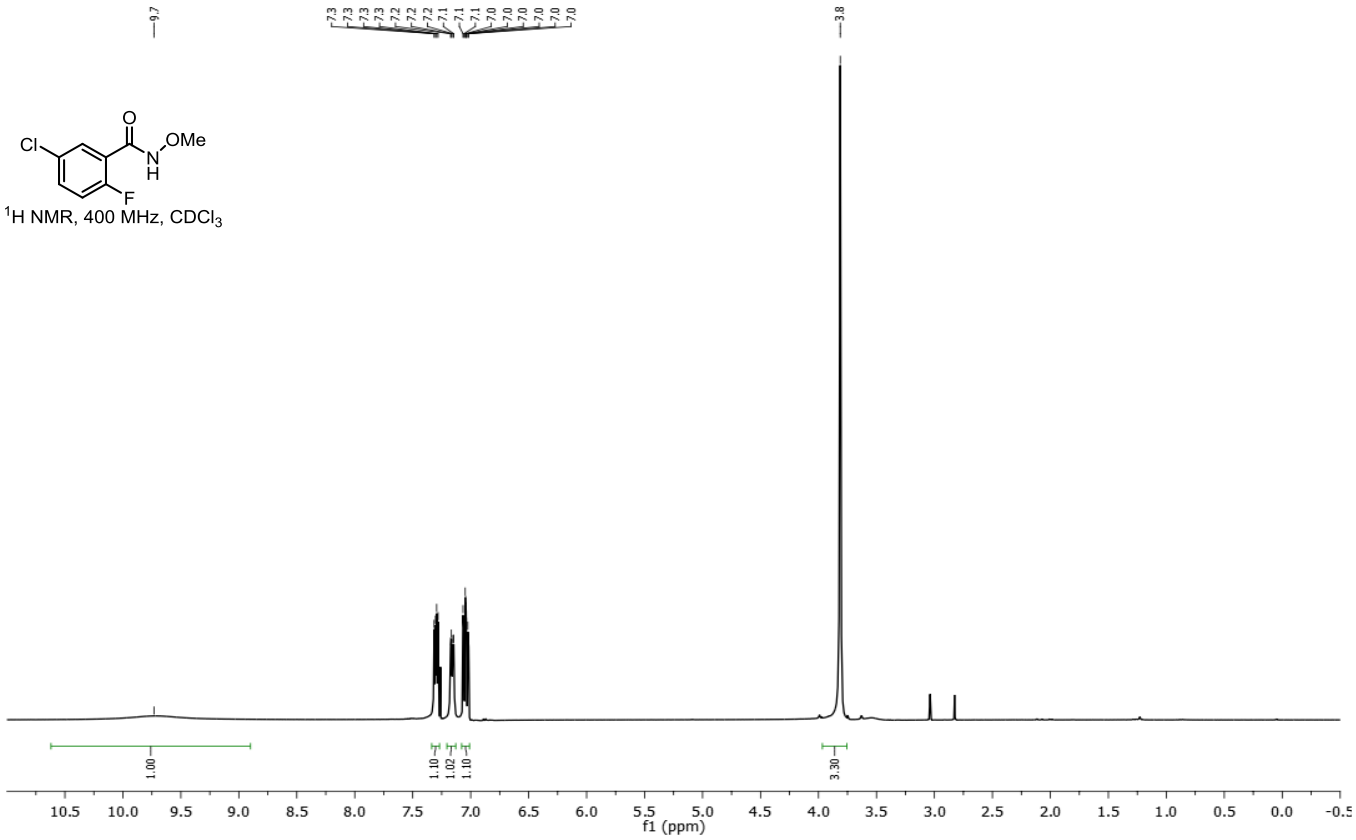


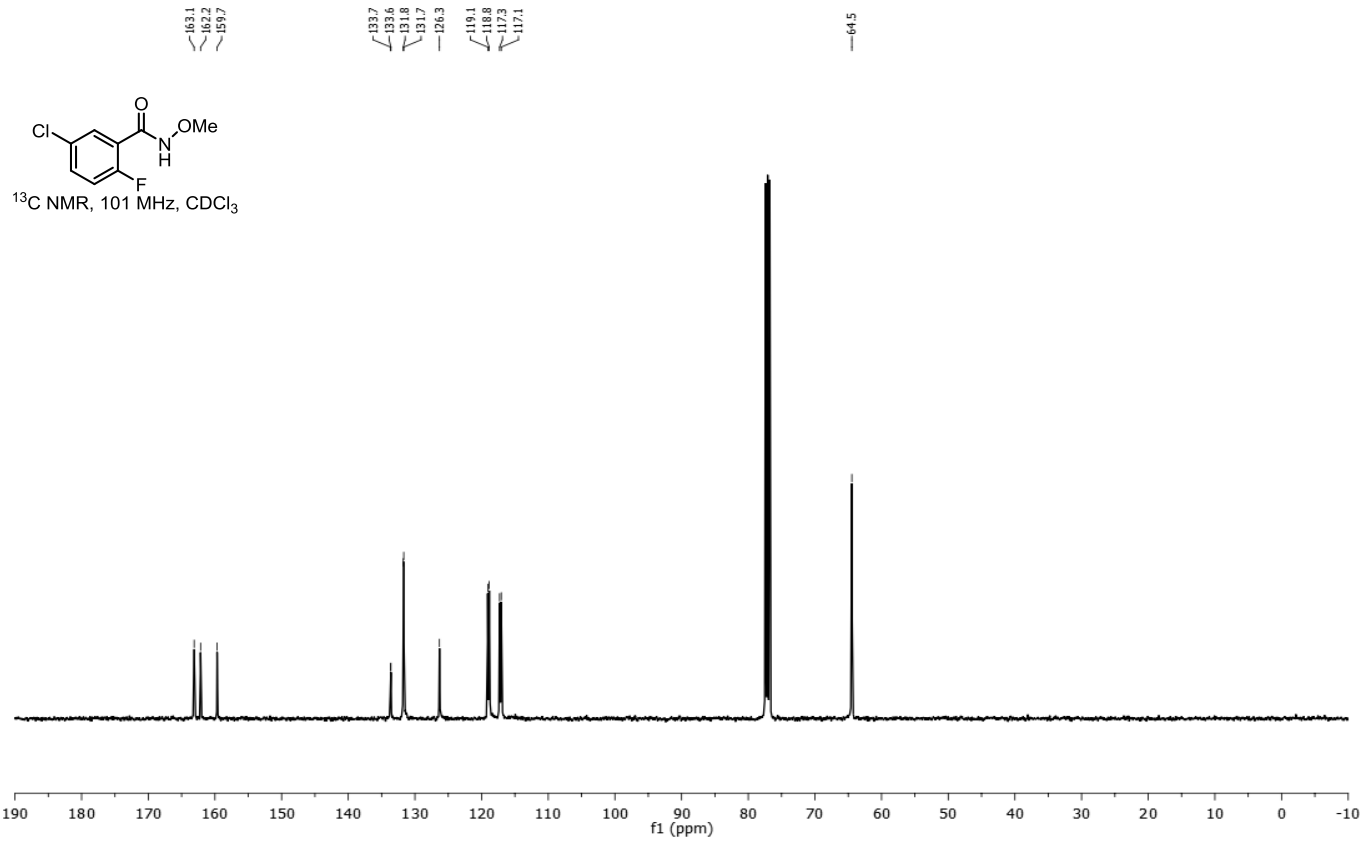
^{1}H NMR, 500 MHz, $CDCl_3$

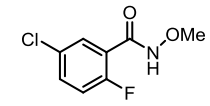


^{13}C NMR, 101 MHz, $CDCl_3$

5-Chloro-2-fluoro-*N*-methoxybenzamideone (1l):

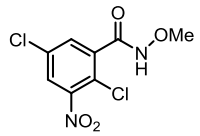




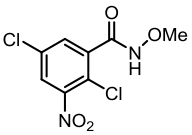


^{19}F NMR, 376 MHz, $CDCl_3$

2,5-Dichloro-*N*-methoxy-3-nitrobenzamide (1m):

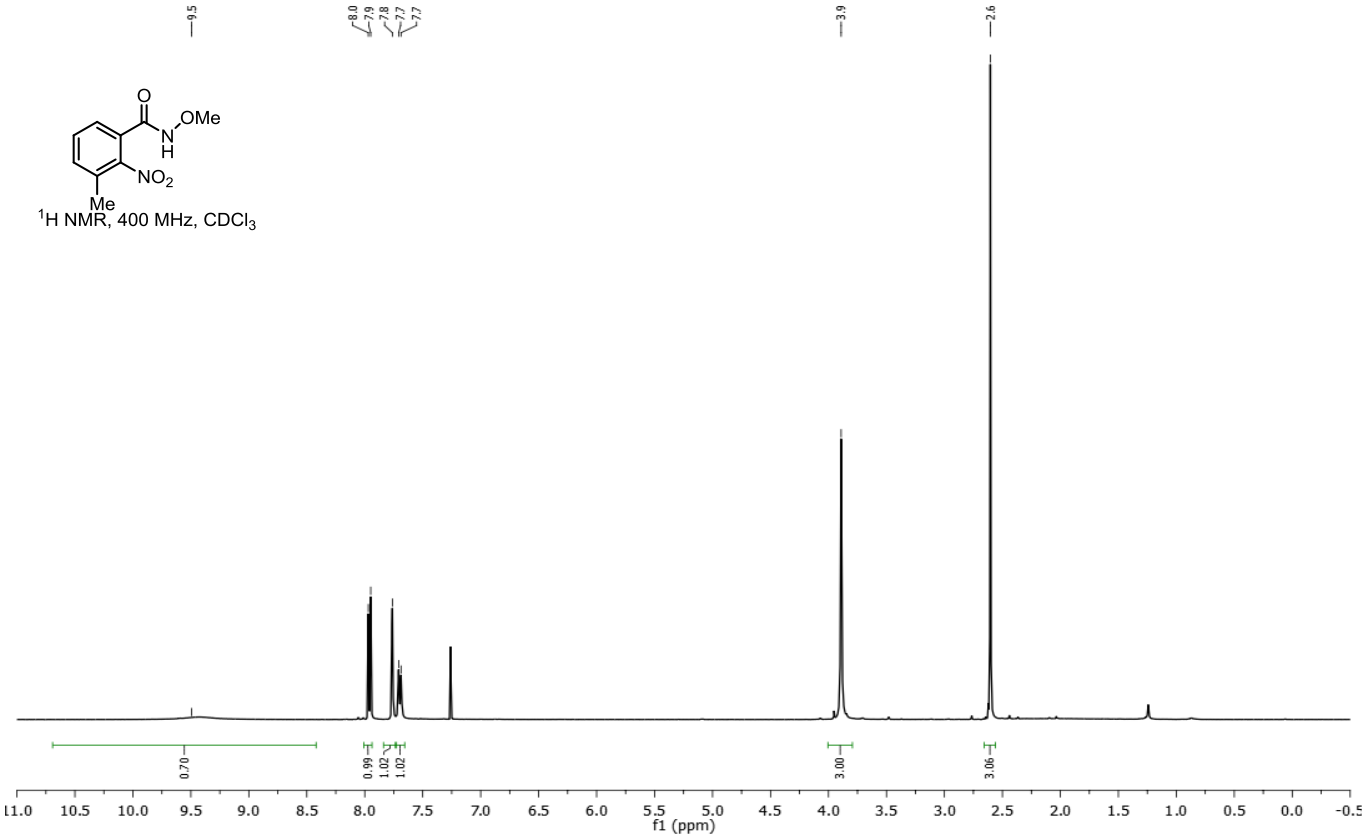


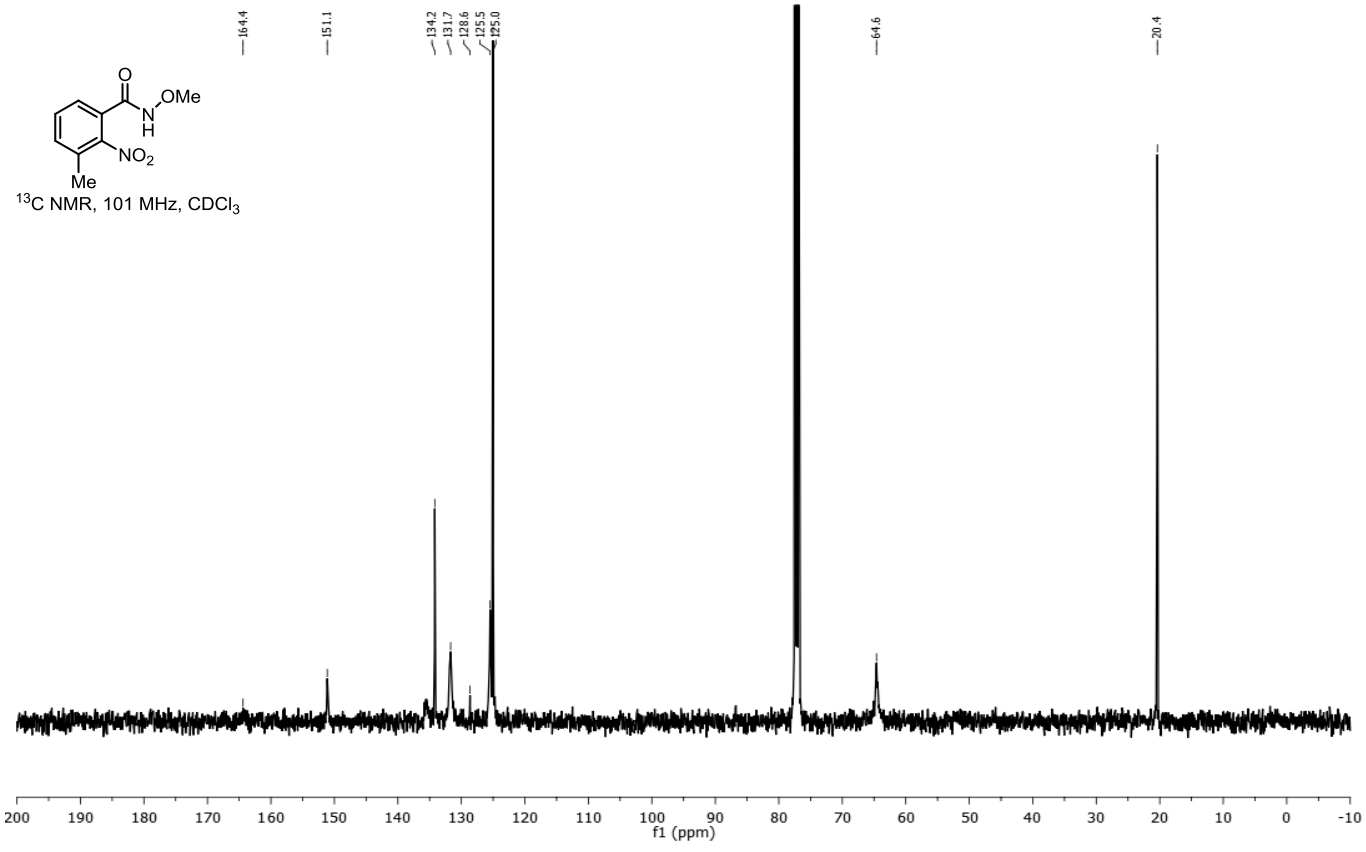
^{1}H NMR, 400 MHz, $CDCl_3$+CD_3OD



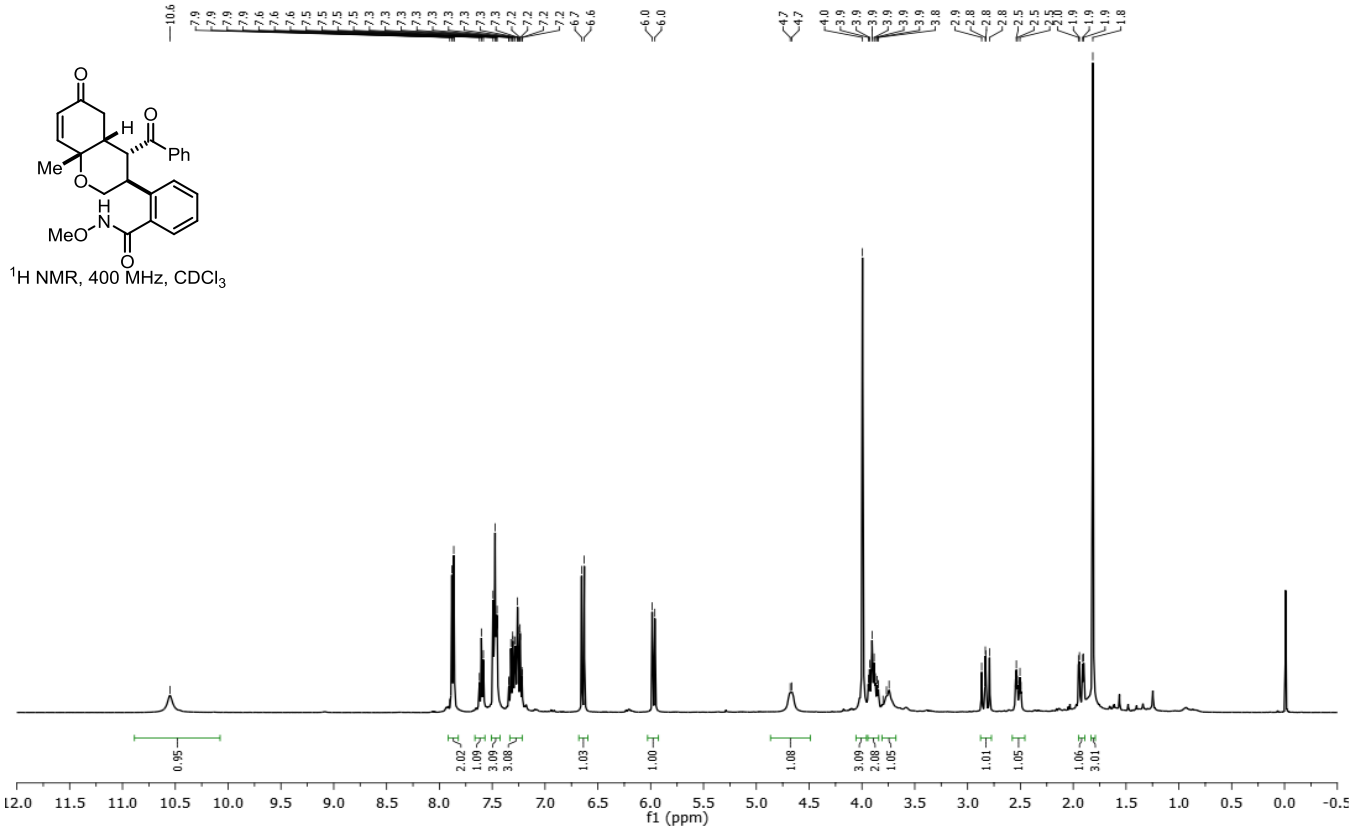
^{13}C NMR, 101 MHz, $CDCl_3$+CD_3OD

N-Methoxy-3-methyl-2-nitrobenzamide (1n):

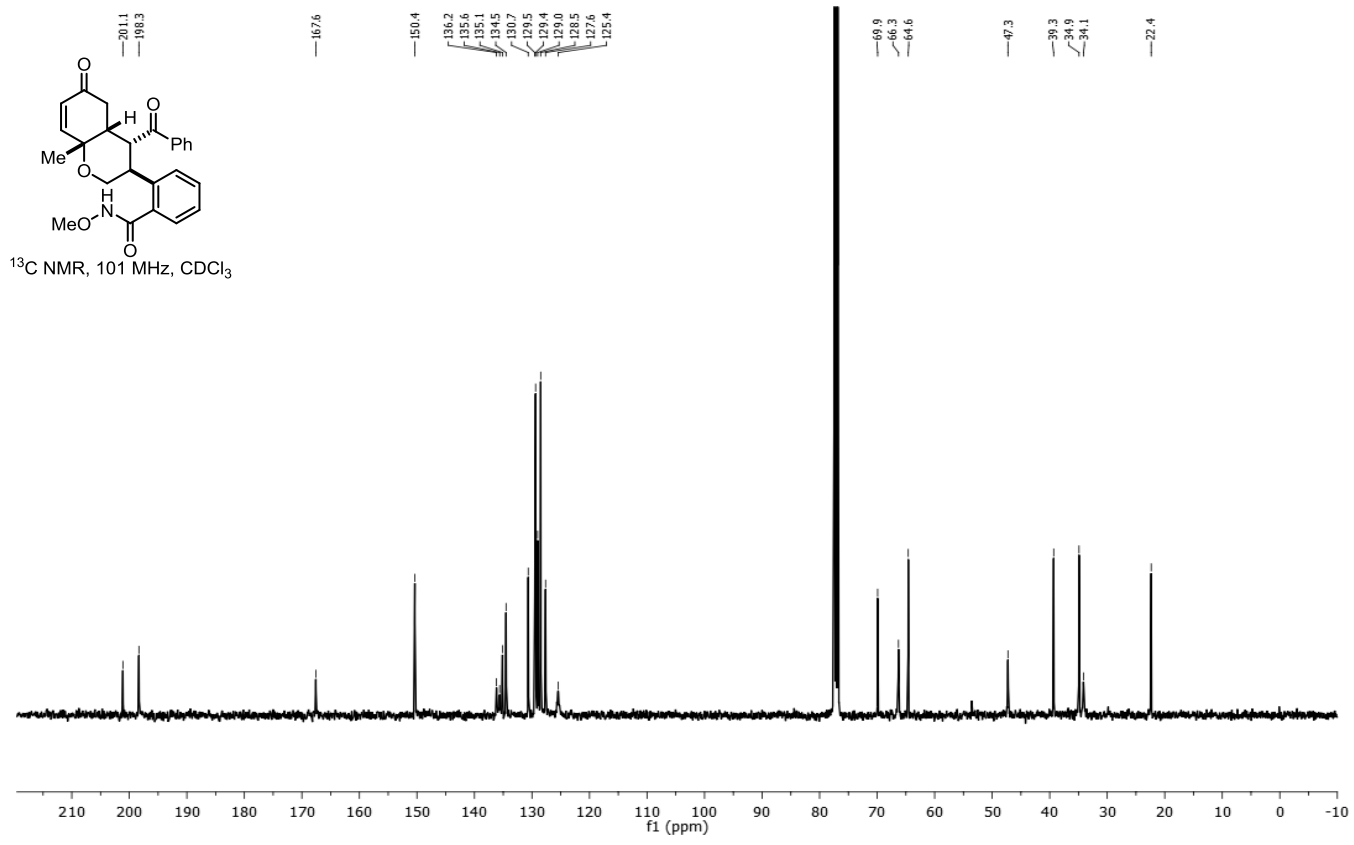




2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3a):

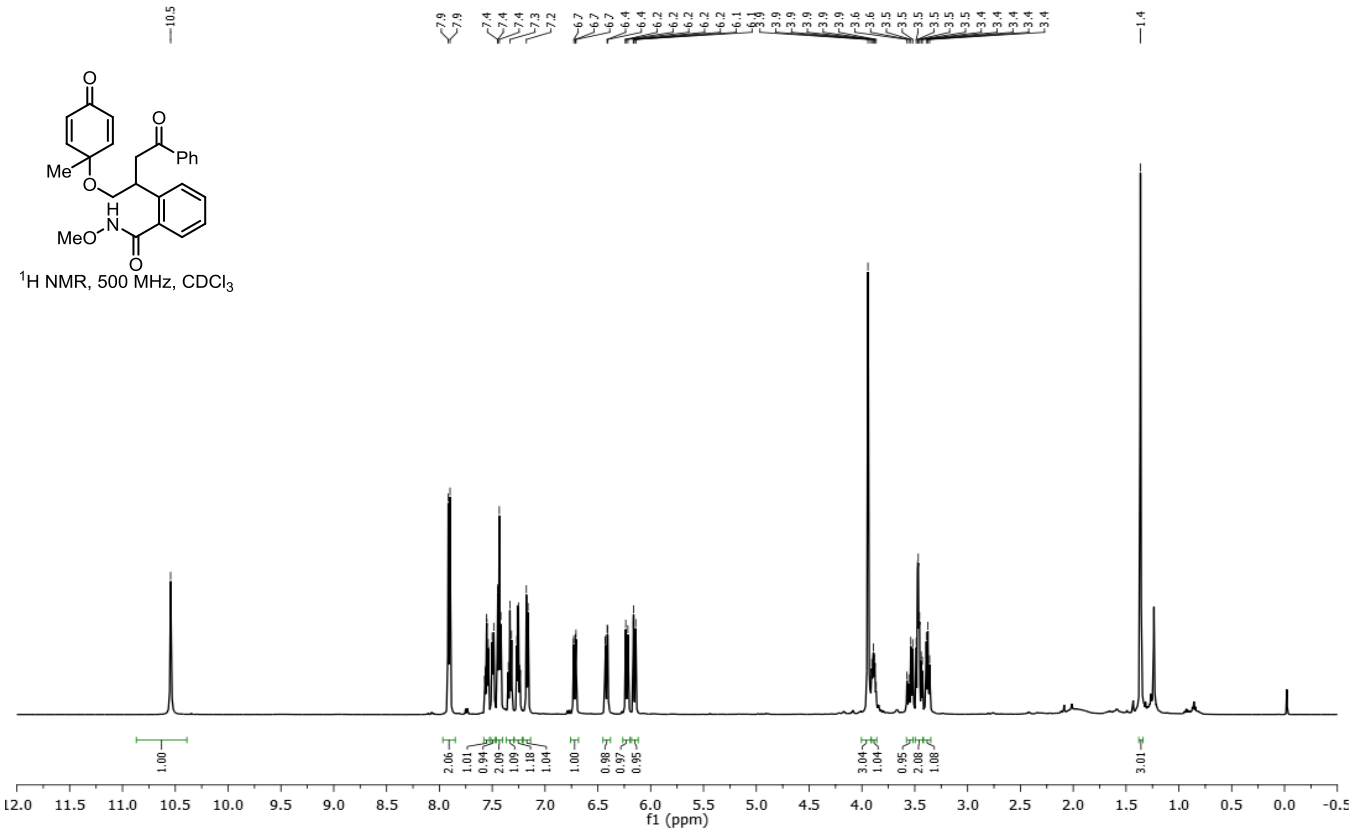


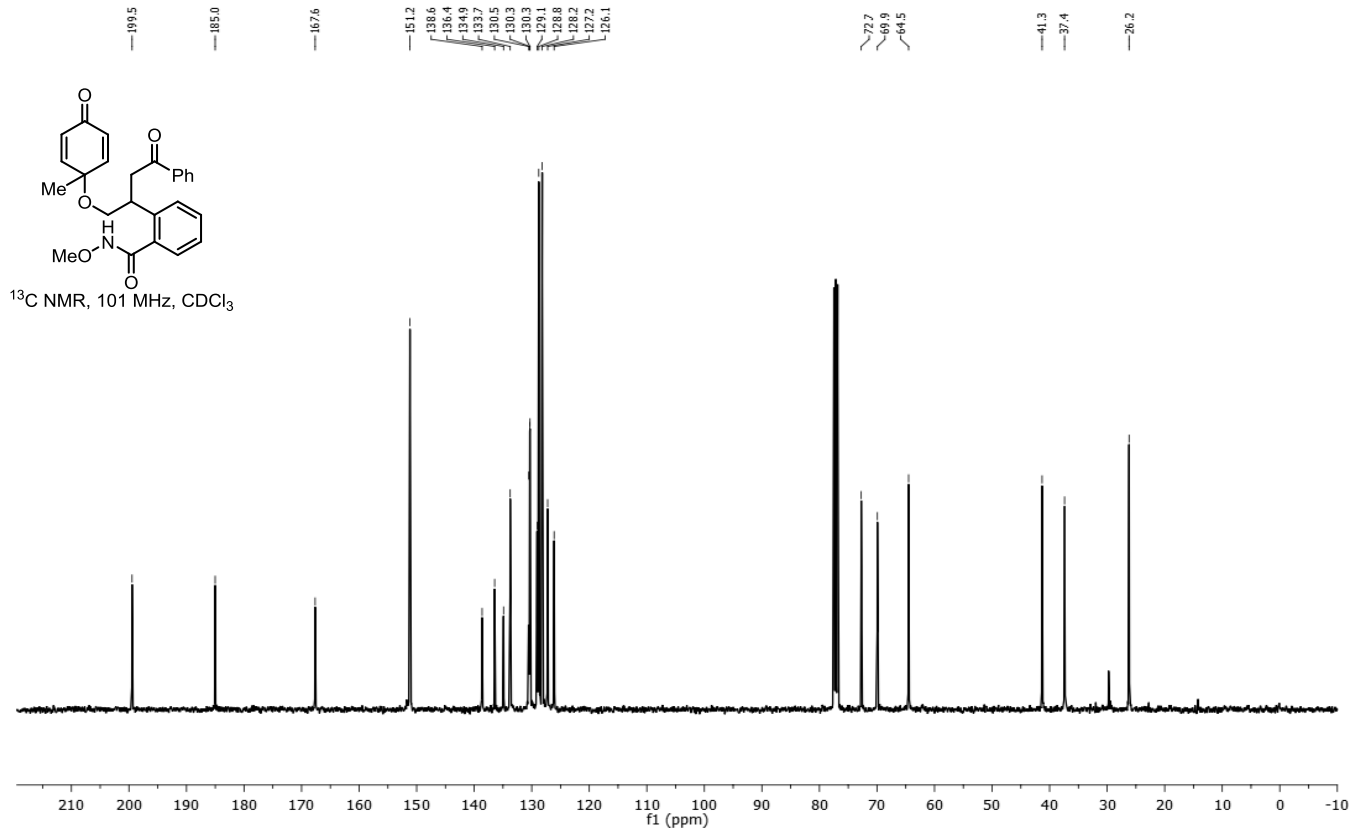
^{1}H NMR, 400 MHz, $CDCl_3$



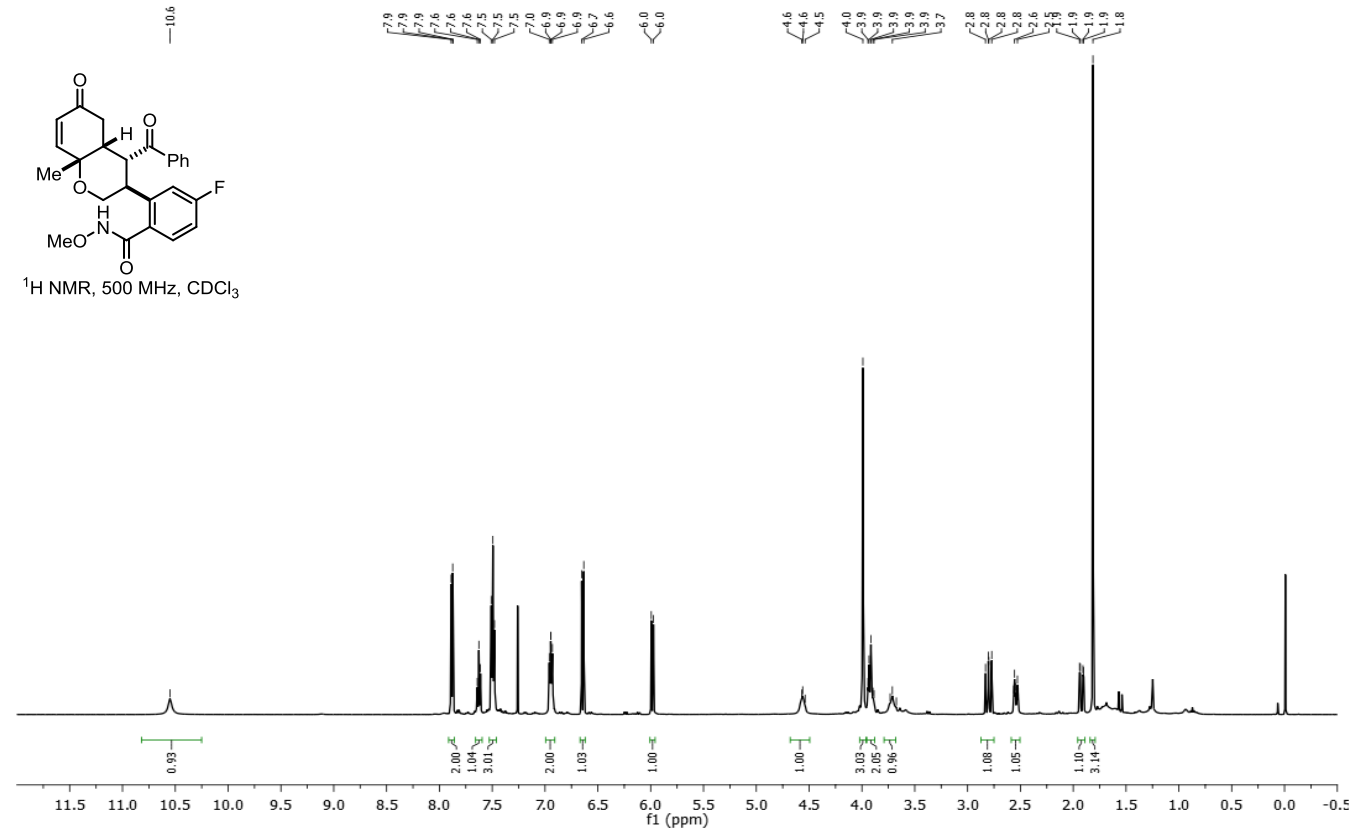
^{13}C NMR, 101 MHz, $CDCl_3$

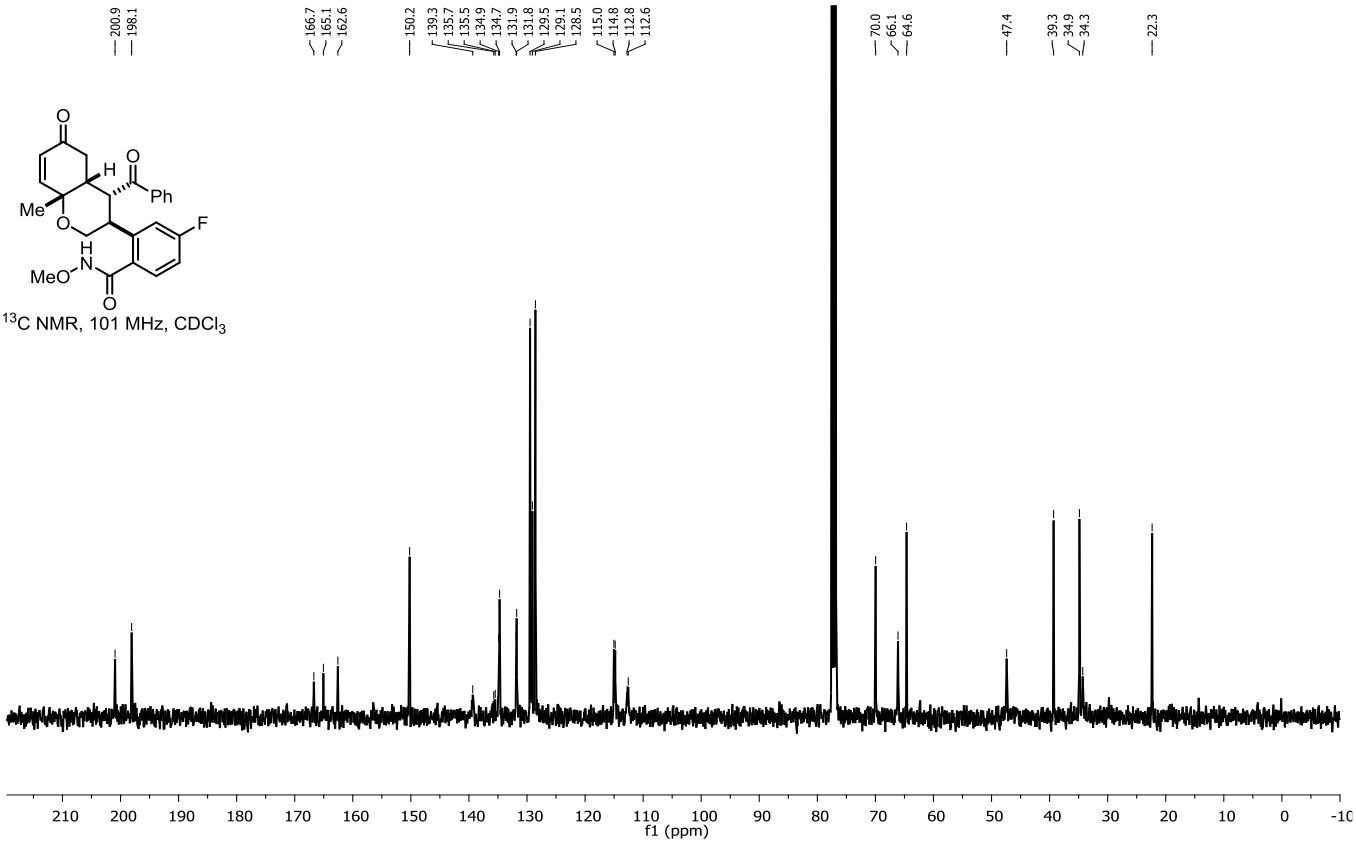
_N_-Methoxy-2-(1-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)-4-oxo-4-phenylbutan-2-yl)benzamide (3a'):

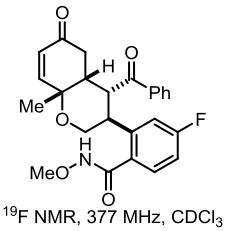




2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-fluoro-*N*-methoxybenzamide (3b):

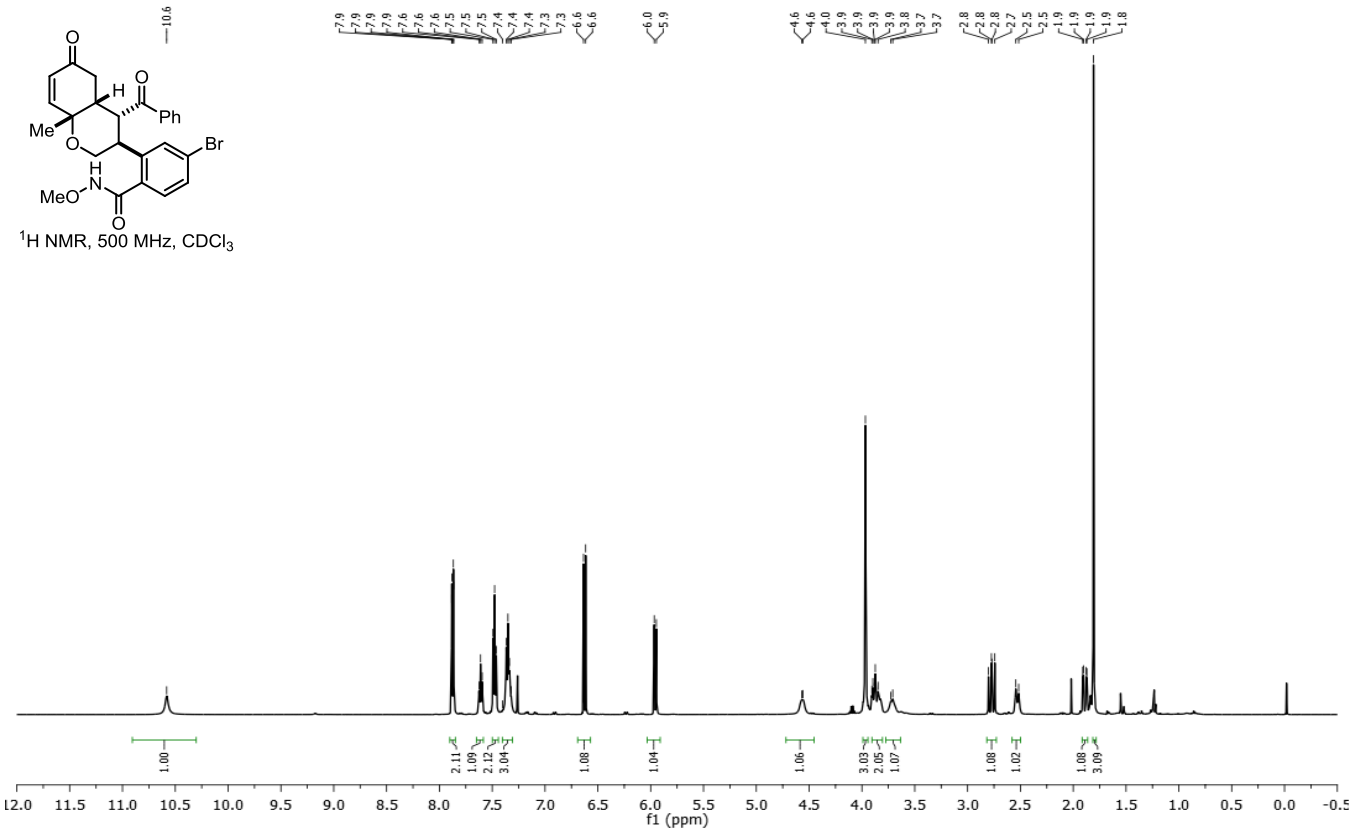


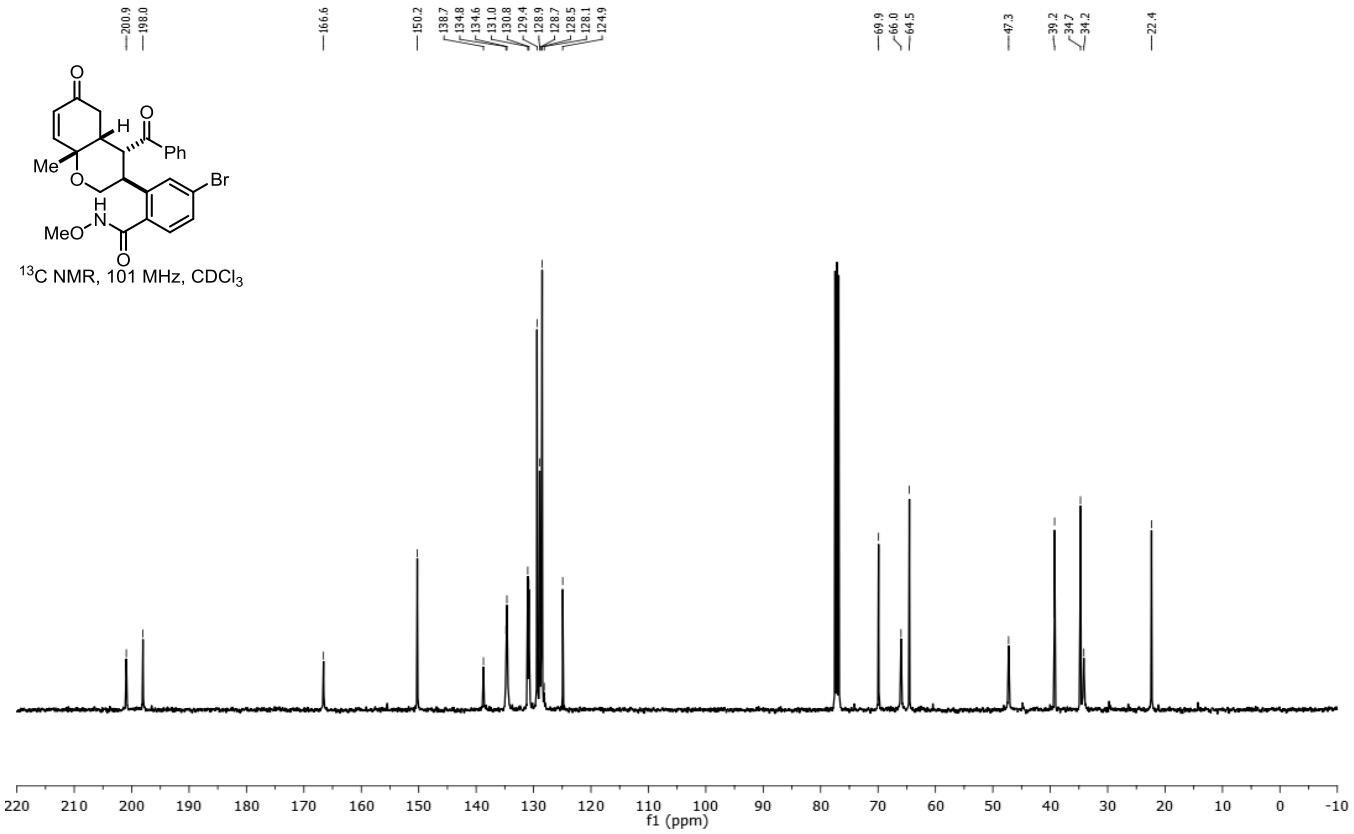




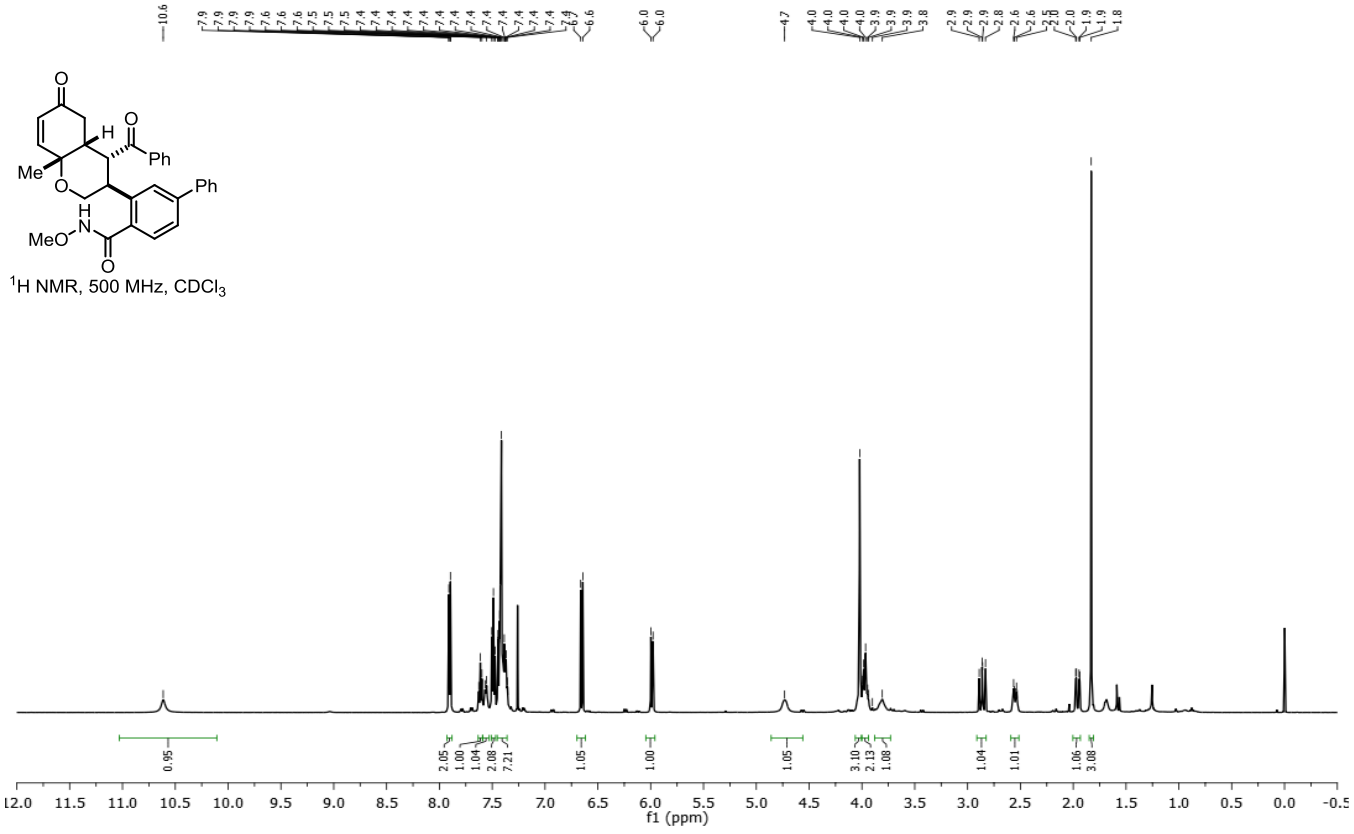
^{19}F NMR, 377 MHz, $CDCl_3$

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

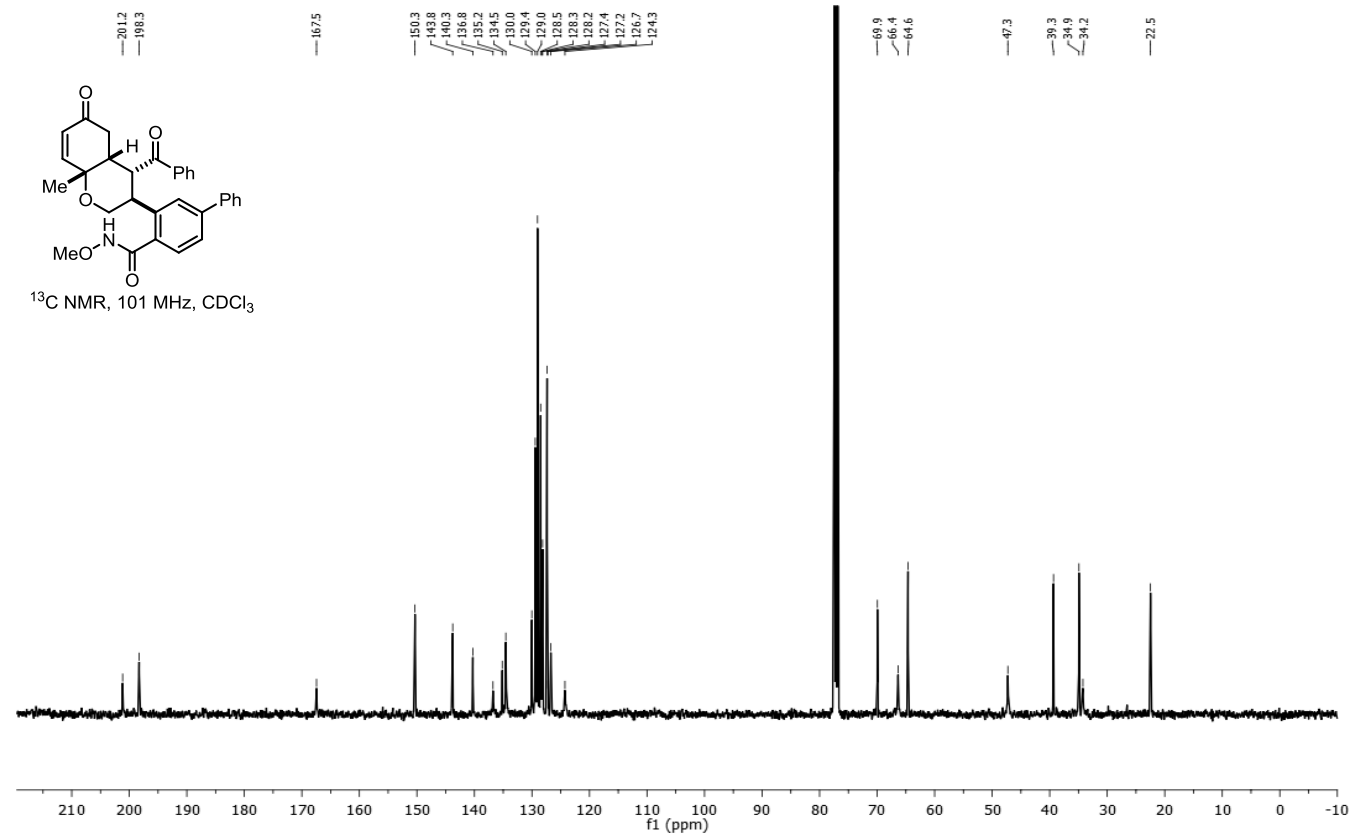




3,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-[1,1'-biphenyl]-4-carboxamide (3d):

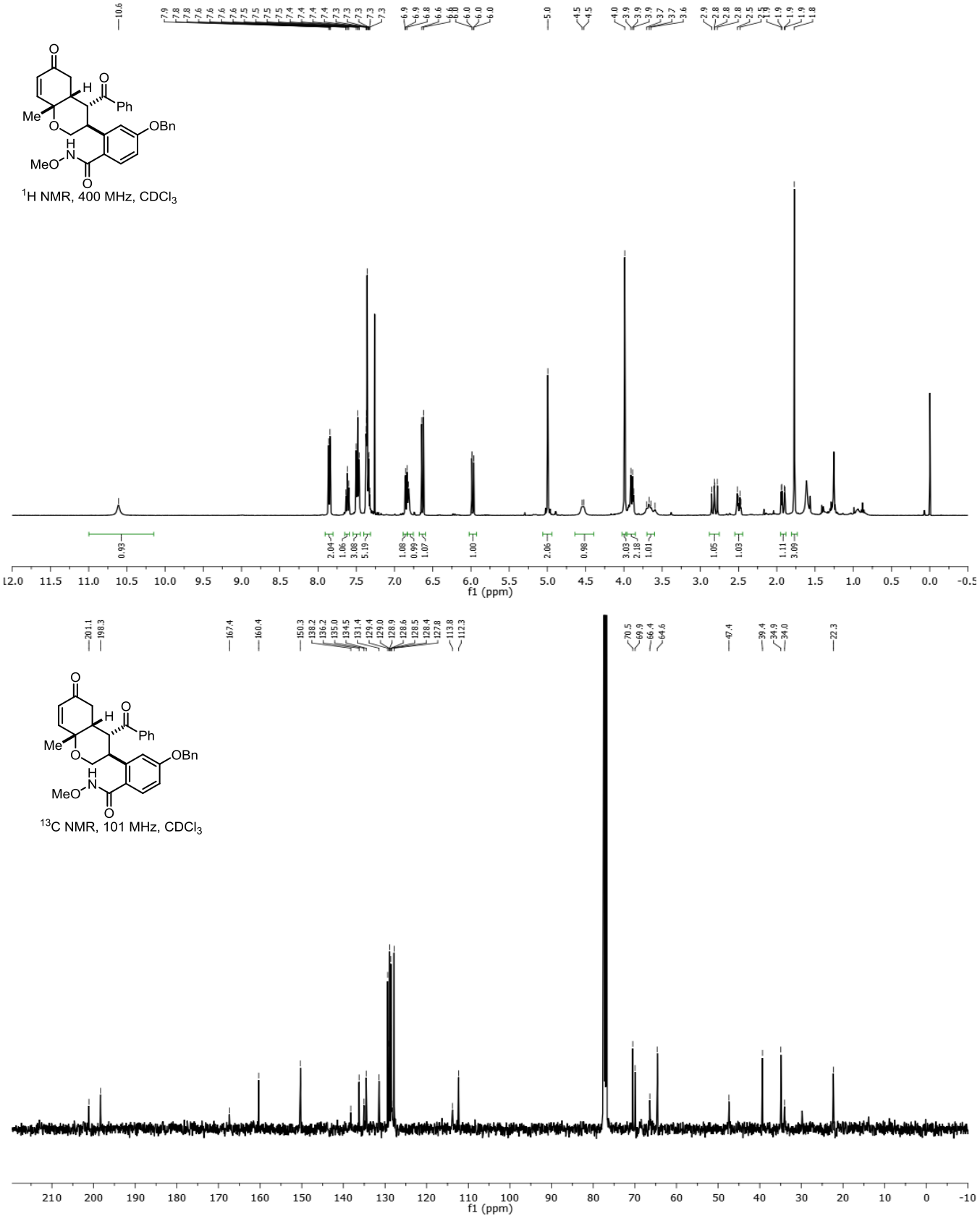


^{1}H NMR, 500 MHz, $CDCl_3$

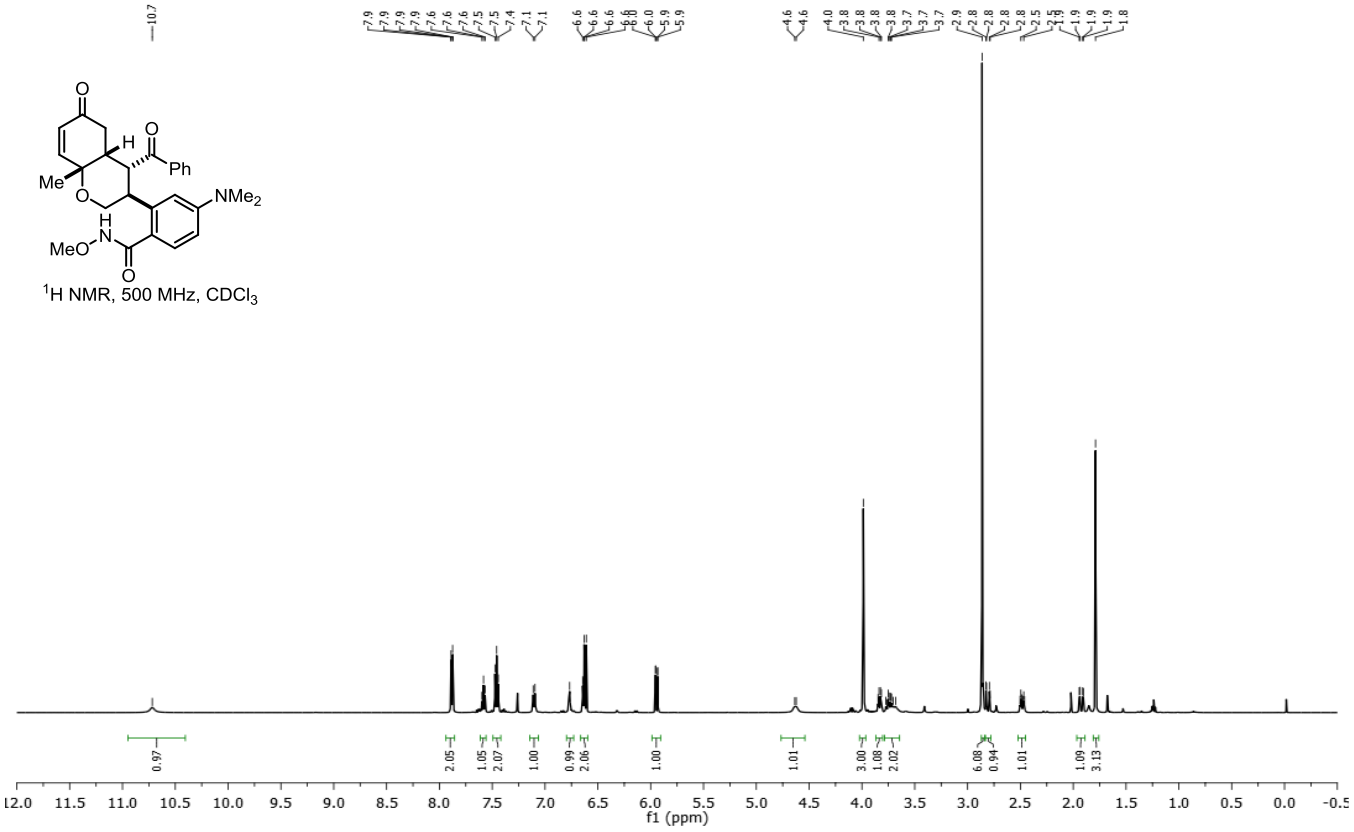


^{13}C NMR, 101 MHz, $CDCl_3$

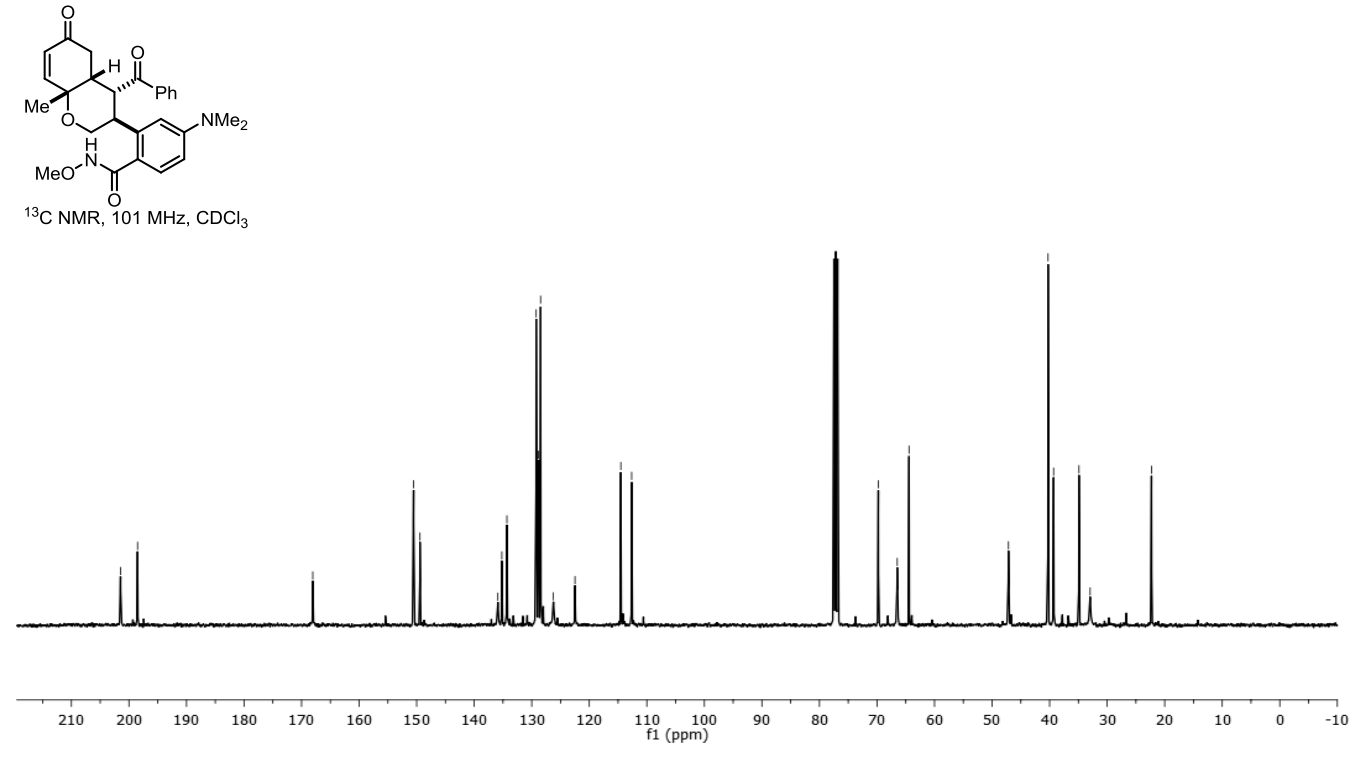
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-(benzyloxy)-*N*-methoxybenzamide (3e):



2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-(dimethylamino)-*N*-methoxybenzamide (3f):

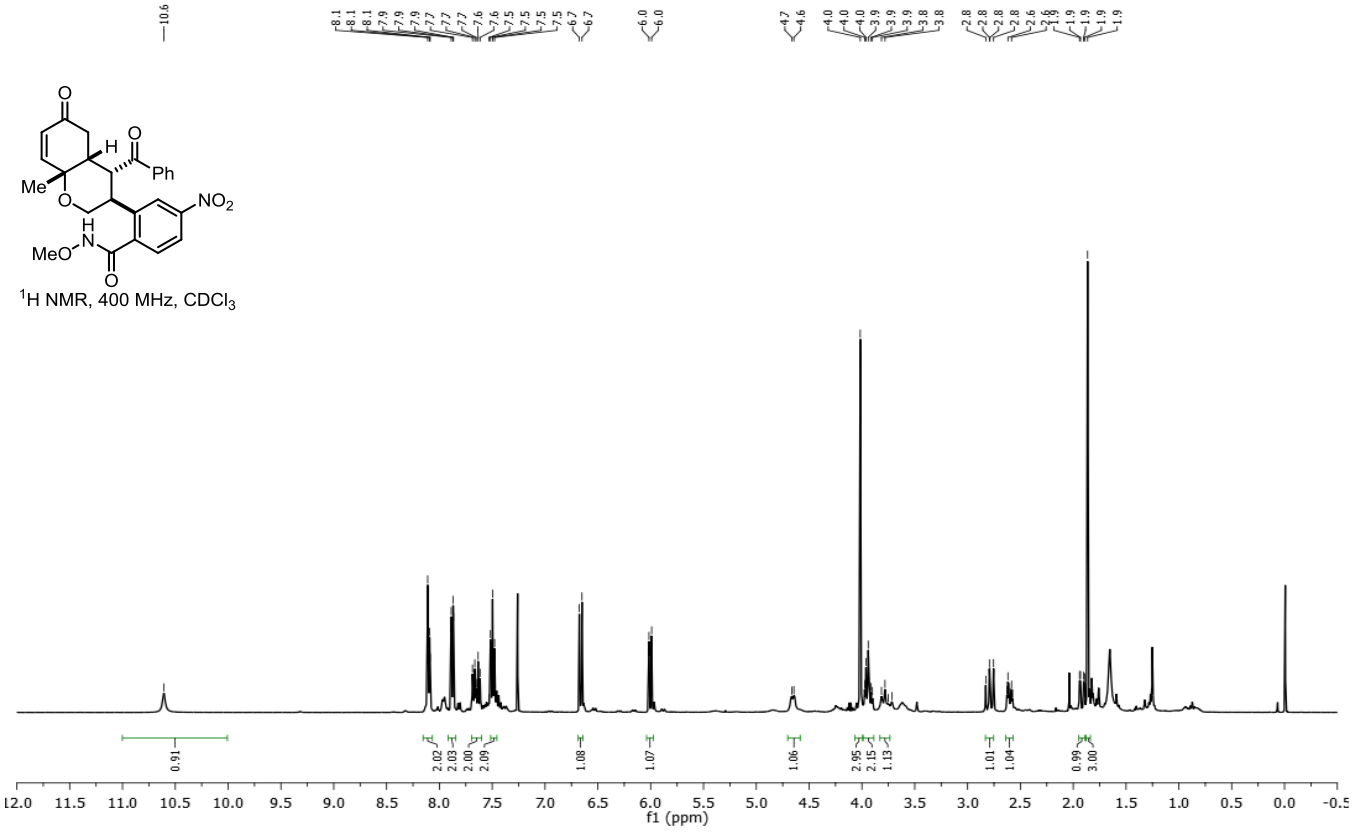


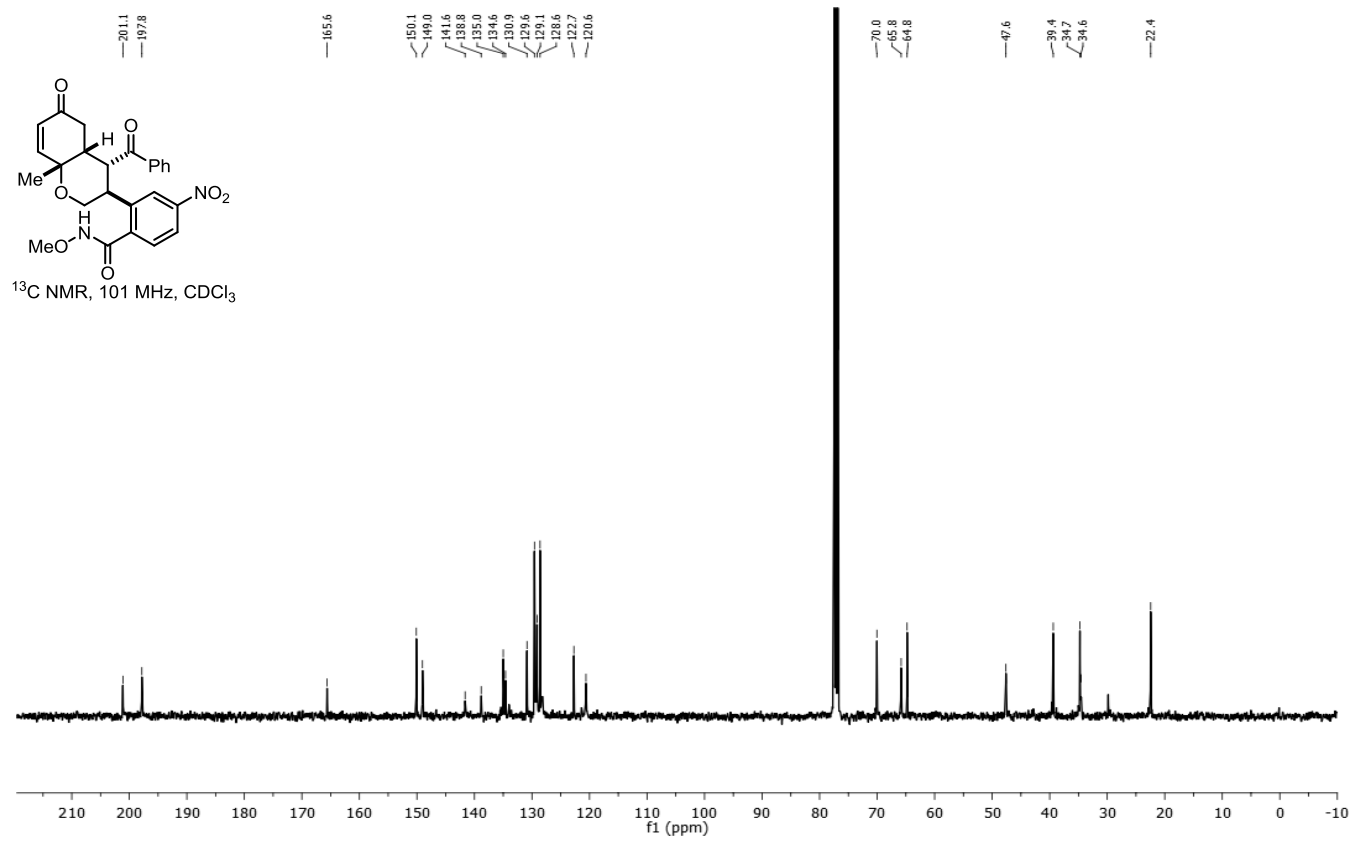
^{1}H NMR, 500 MHz, $CDCl_3$



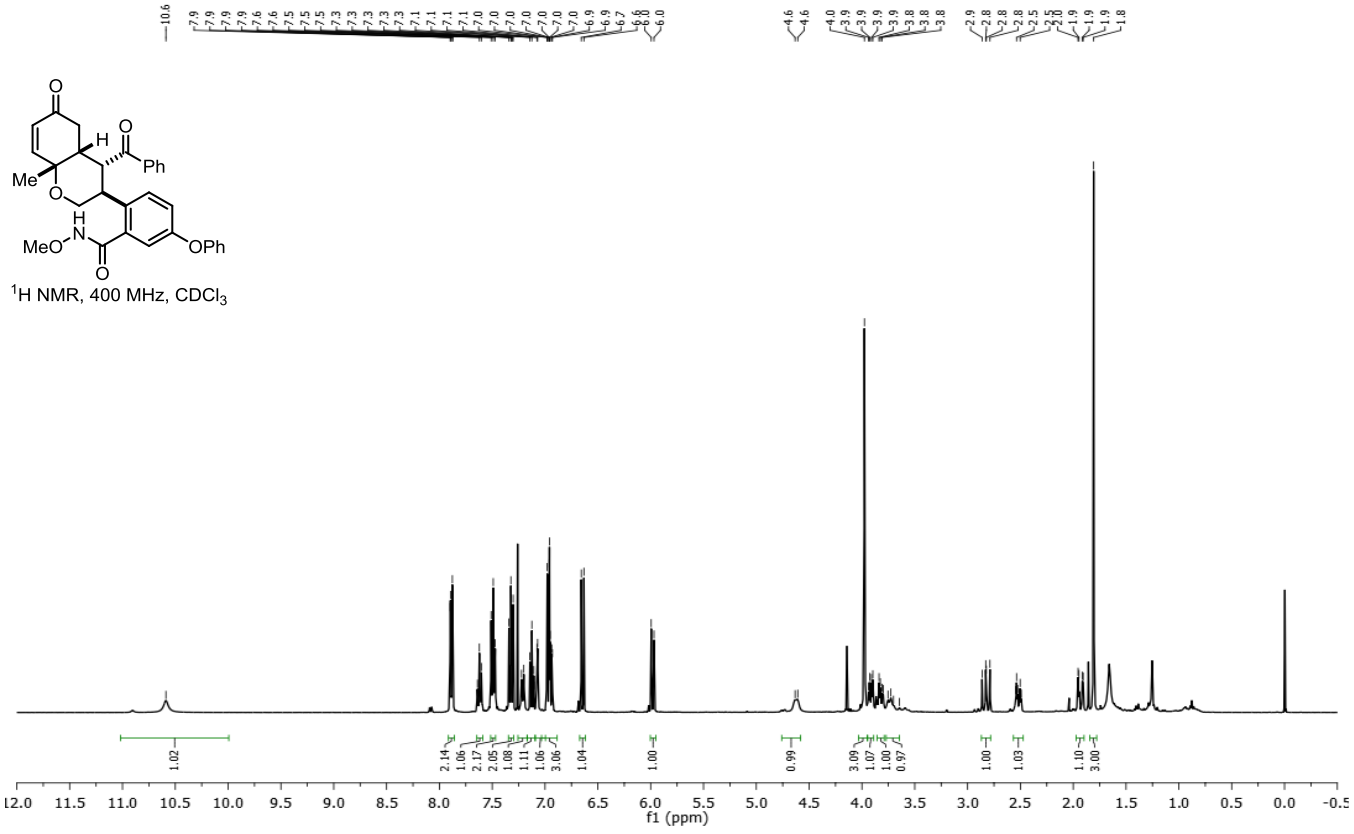
^{13}C NMR, 101 MHz, $CDCl_3$

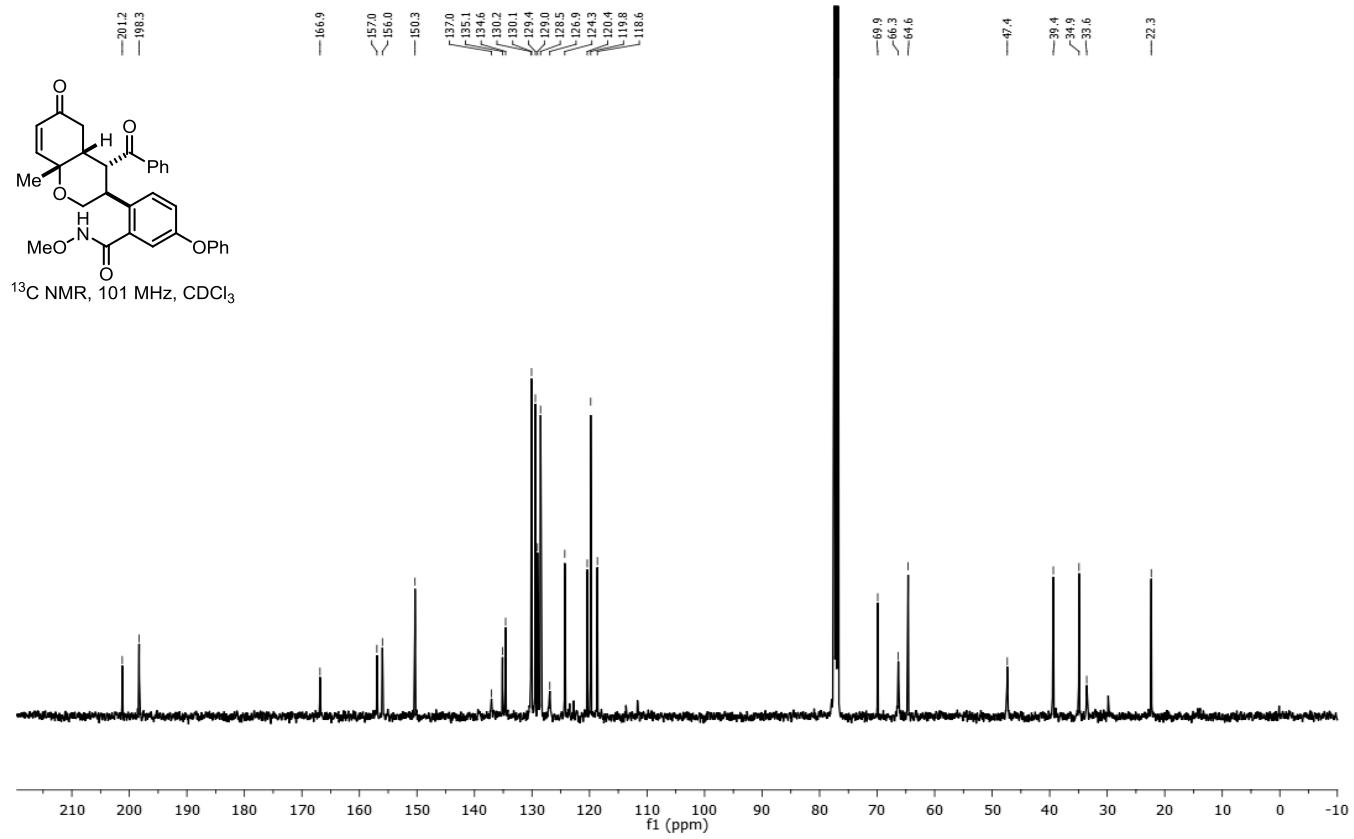
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-4-nitrobenzamide (3g):



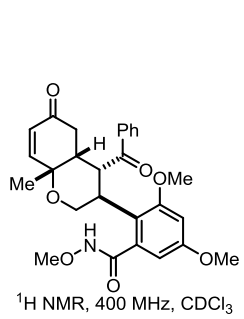


2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-5-phenoxybenzamide (3h):

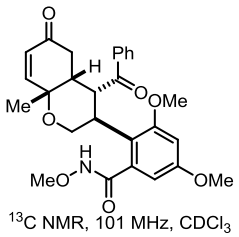




2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*,3,5-trimethoxybenzamide (3i):

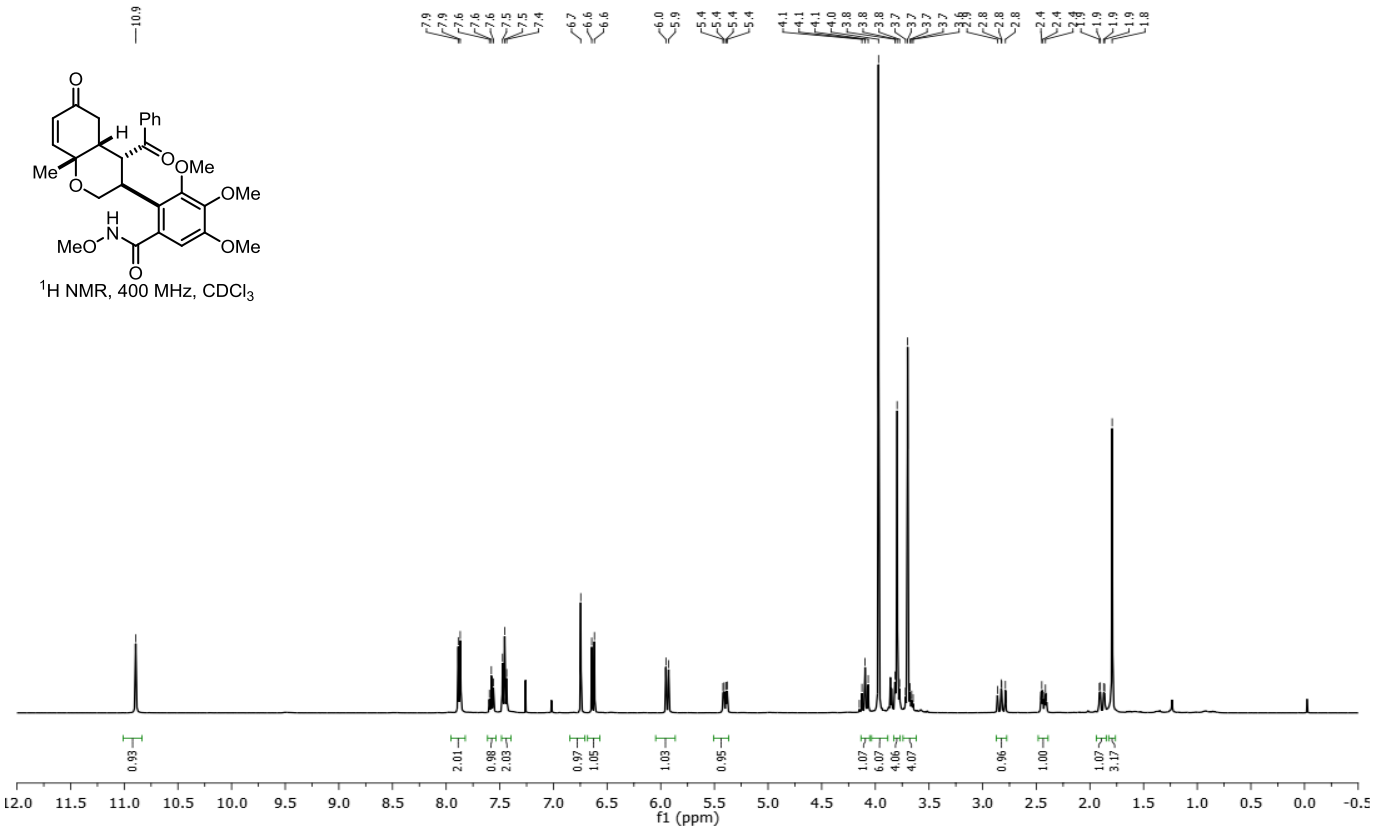


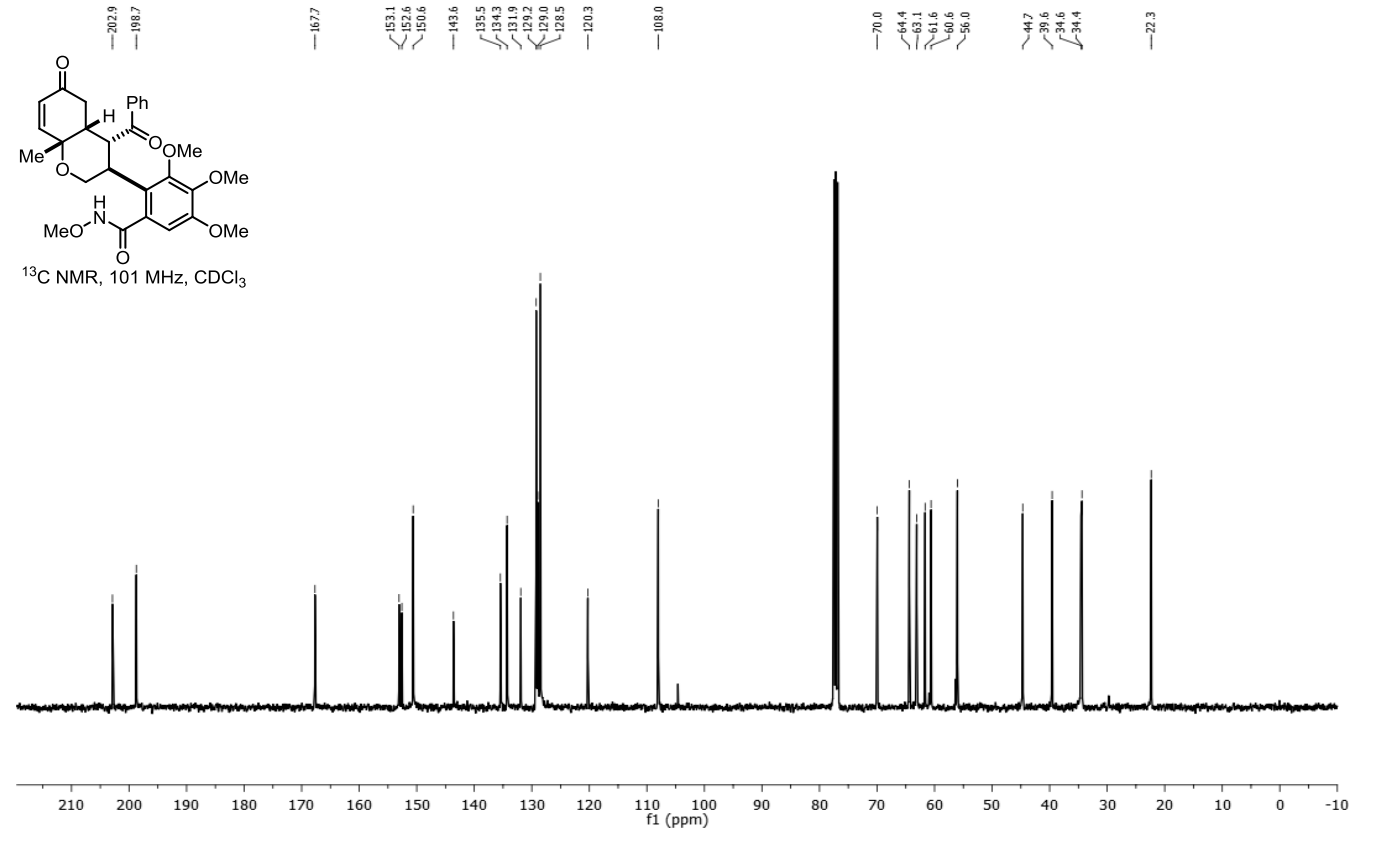
^{1}H NMR, 400 MHz, $CDCl_3$



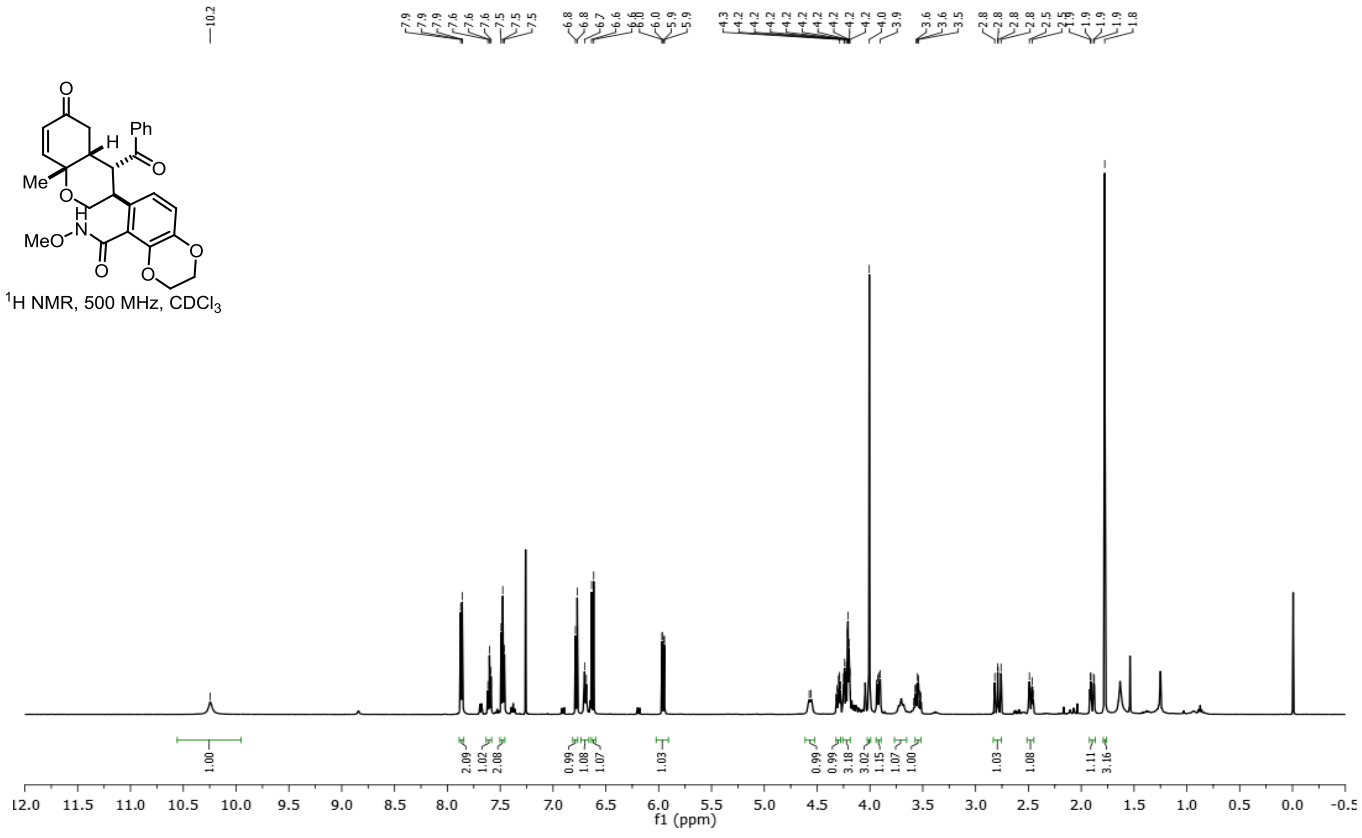
^{13}C NMR, 101 MHz, $CDCl_3$

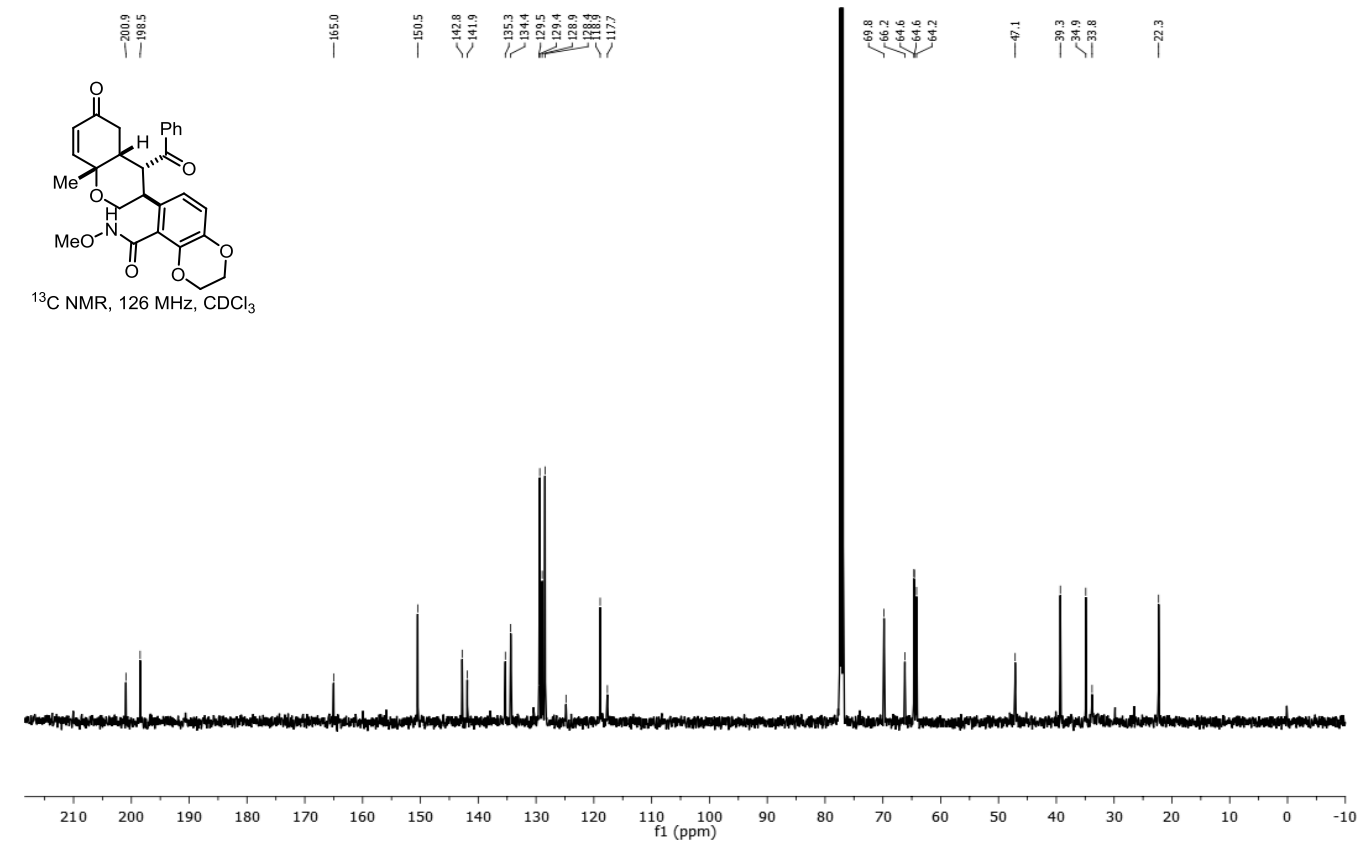
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*,3,4,5-tetramethoxybenzamide (3j)



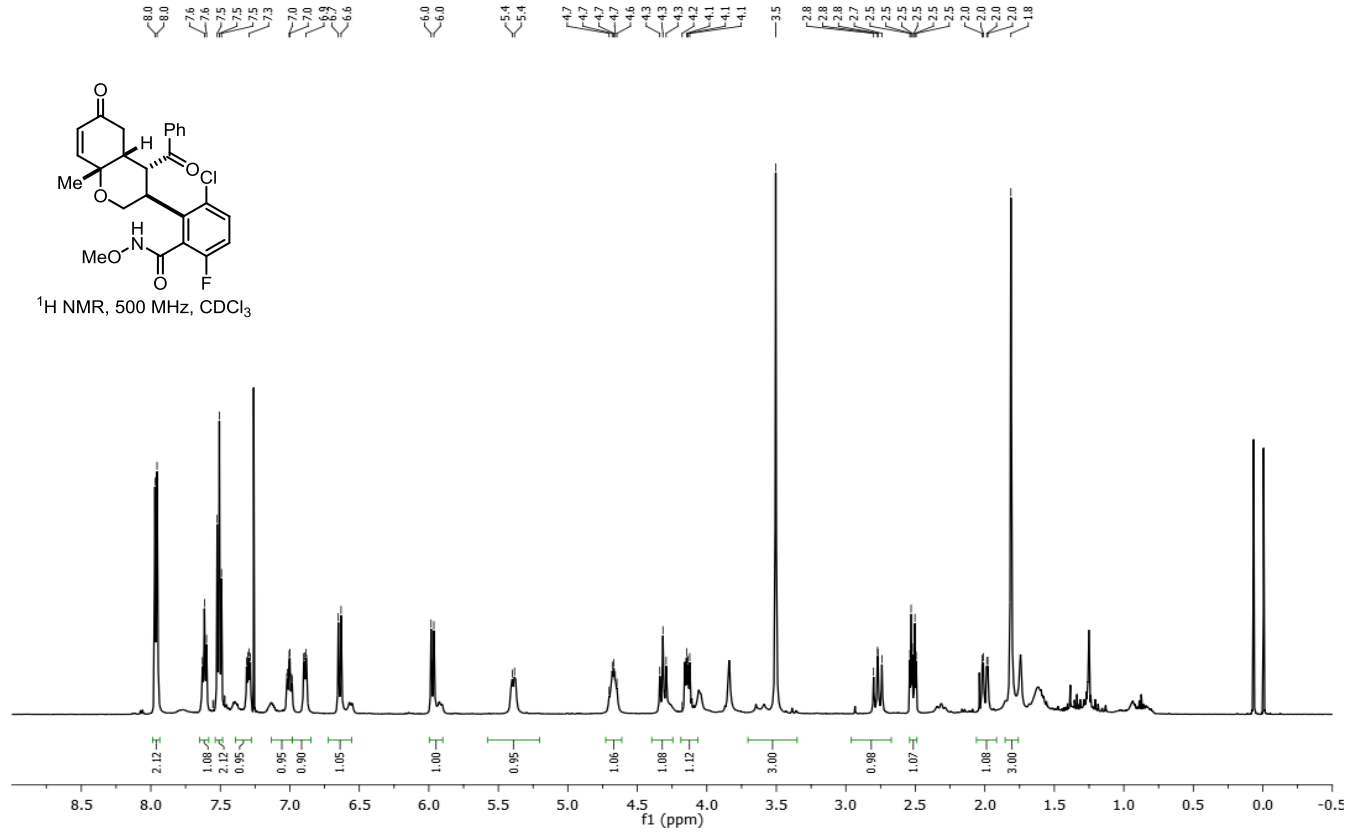


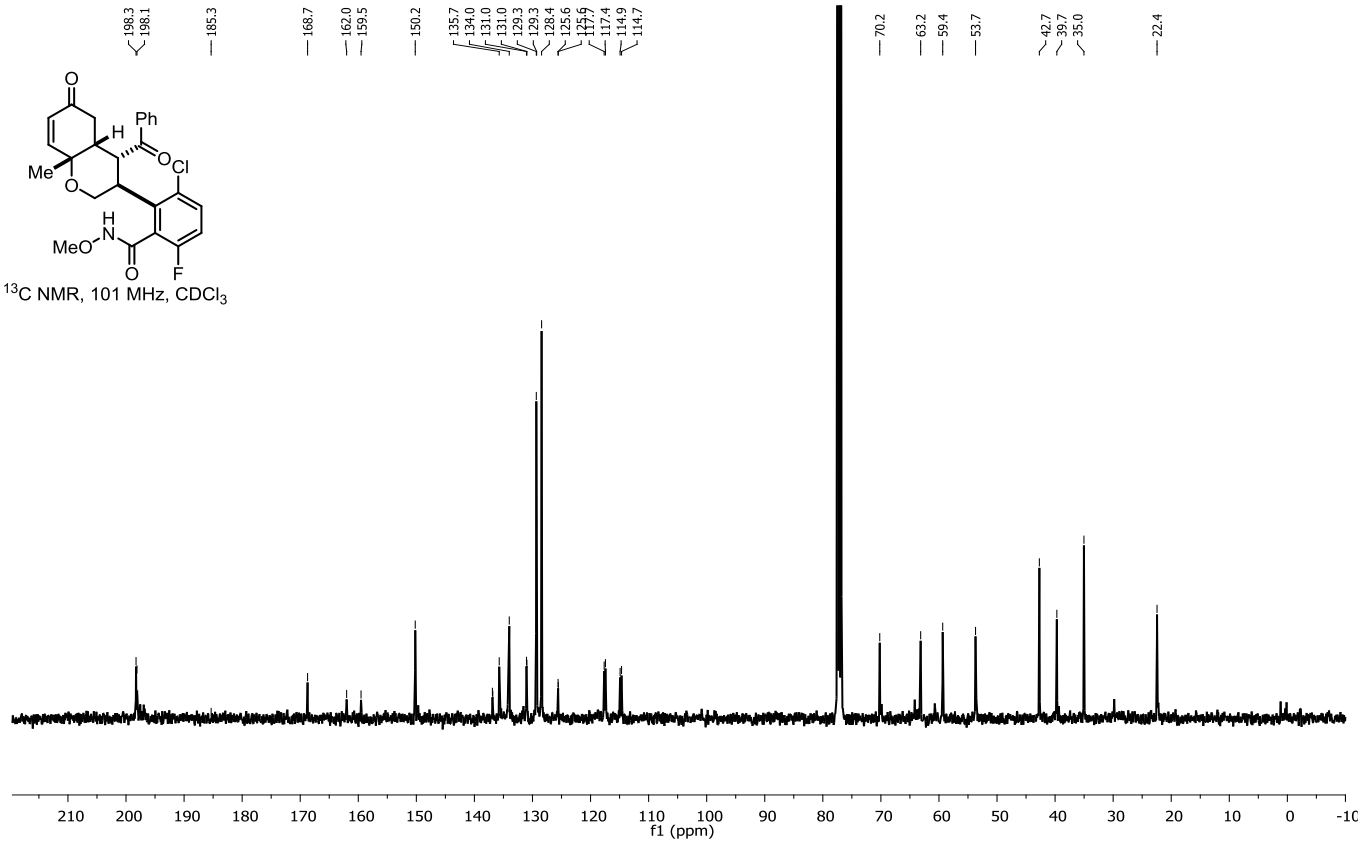
6,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-2,3-dihydrobenzo[*b*][1,4]dioxine-5-carboxamide (3k):

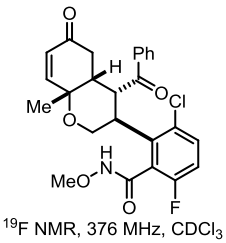




2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-3-chloro-6-fluoro-*N*-methoxybenzamide (3l):

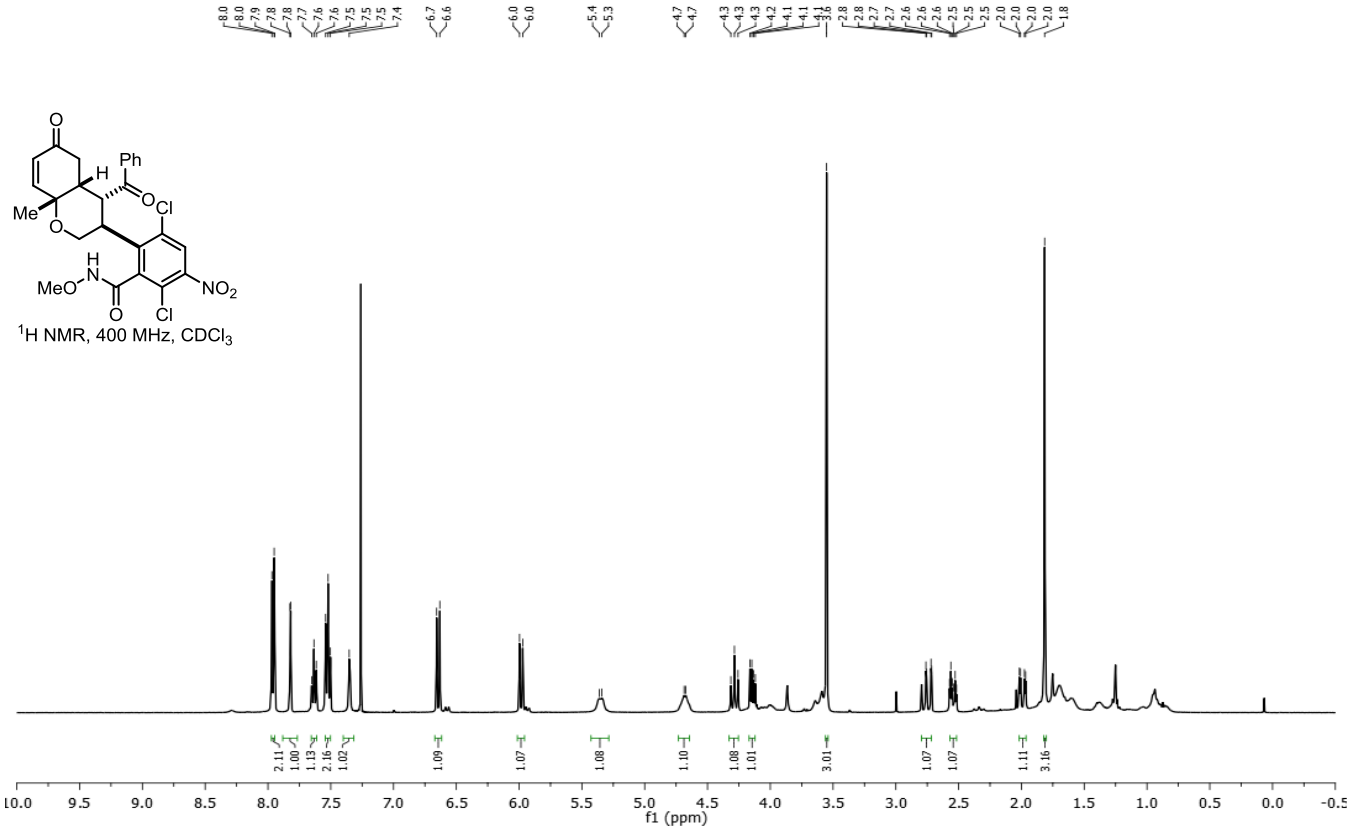


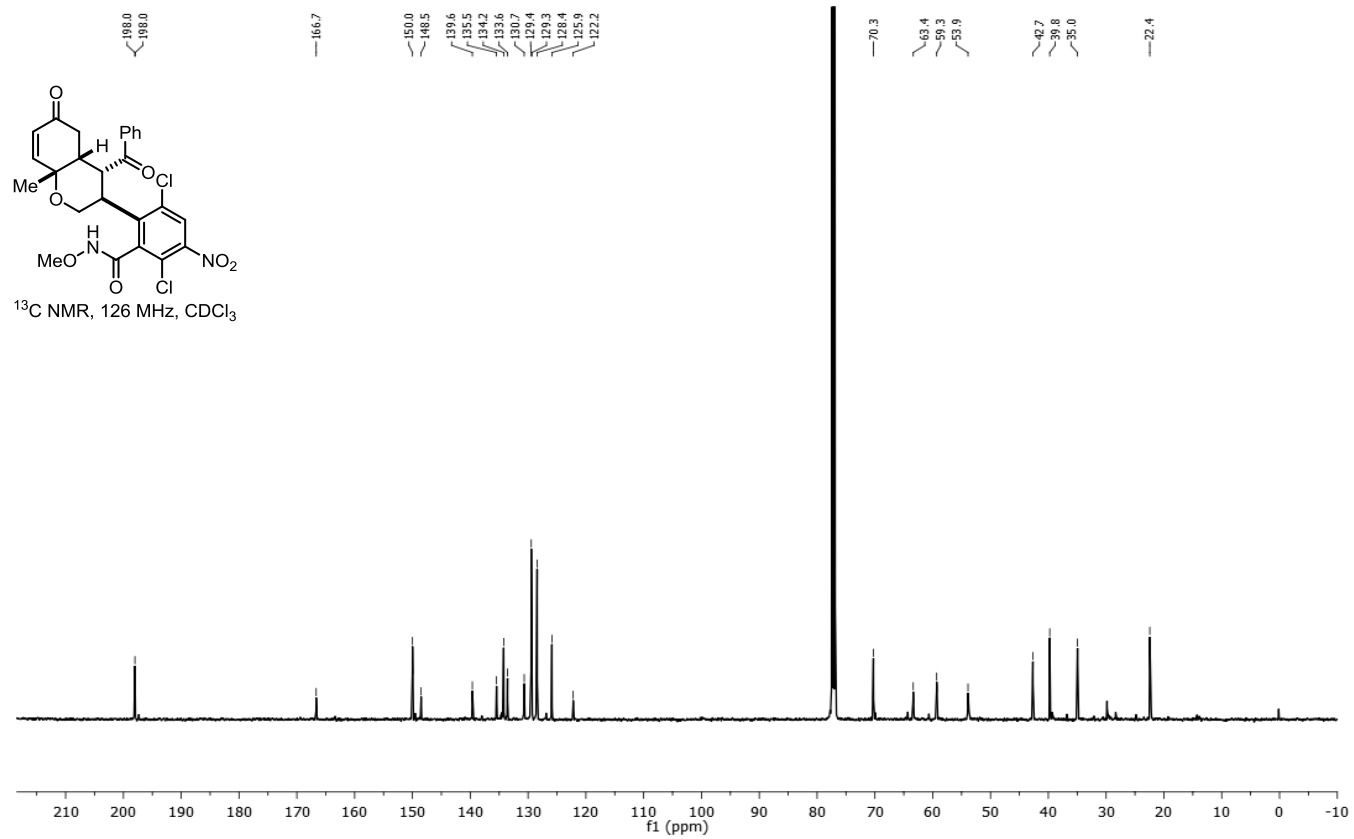




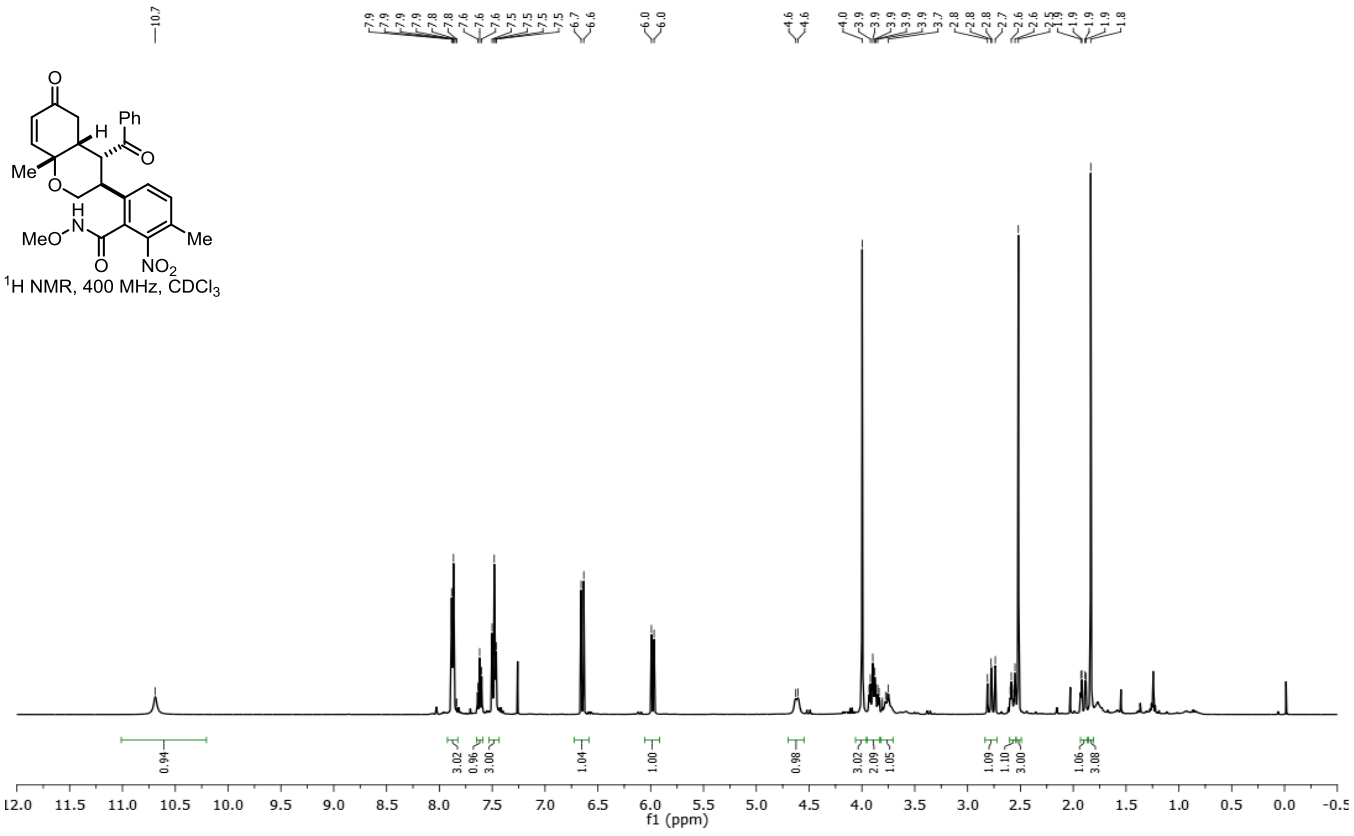
^{19}F NMR, 376 MHz, $CDCl_3$

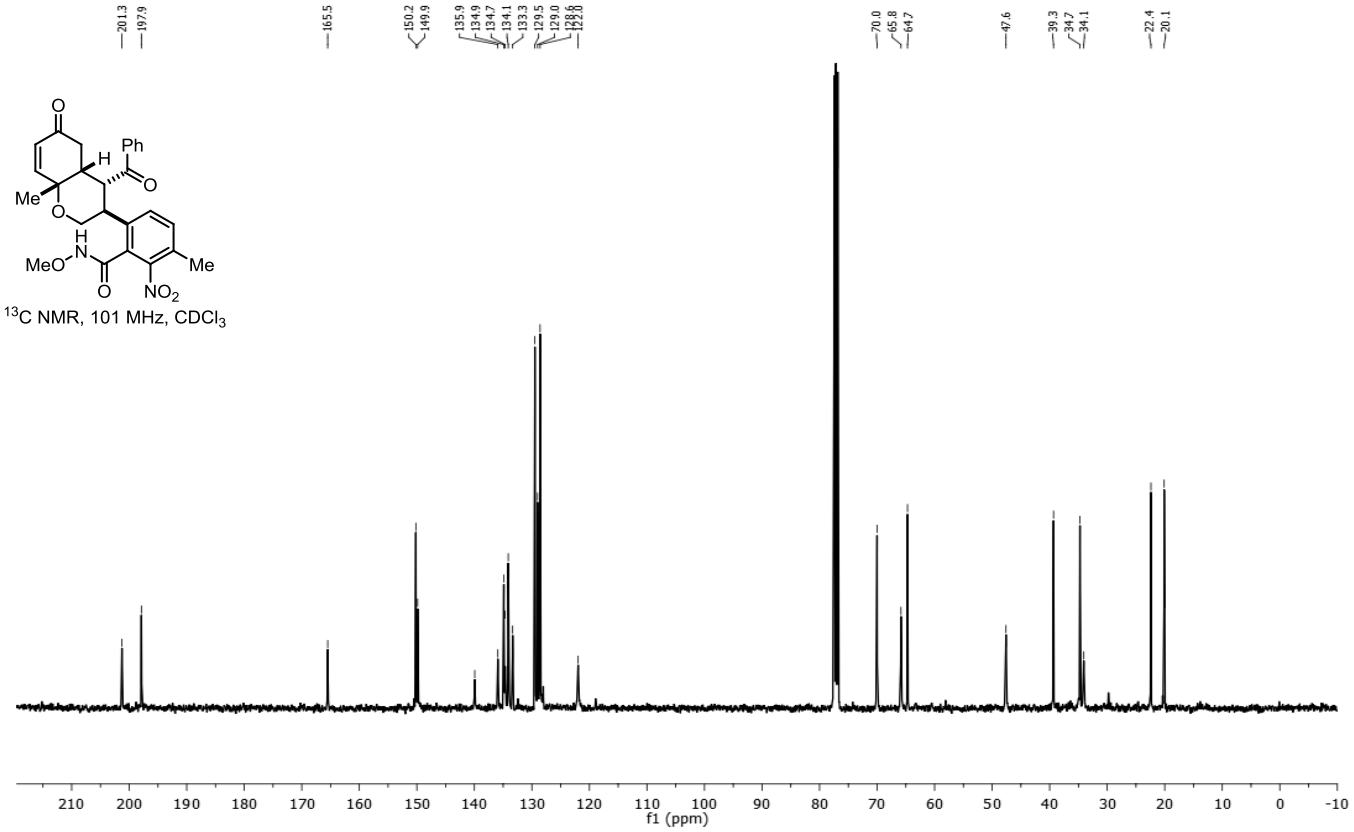
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-3,6-dichloro-*N*-methoxy-5-nitrobenzamide (3m):



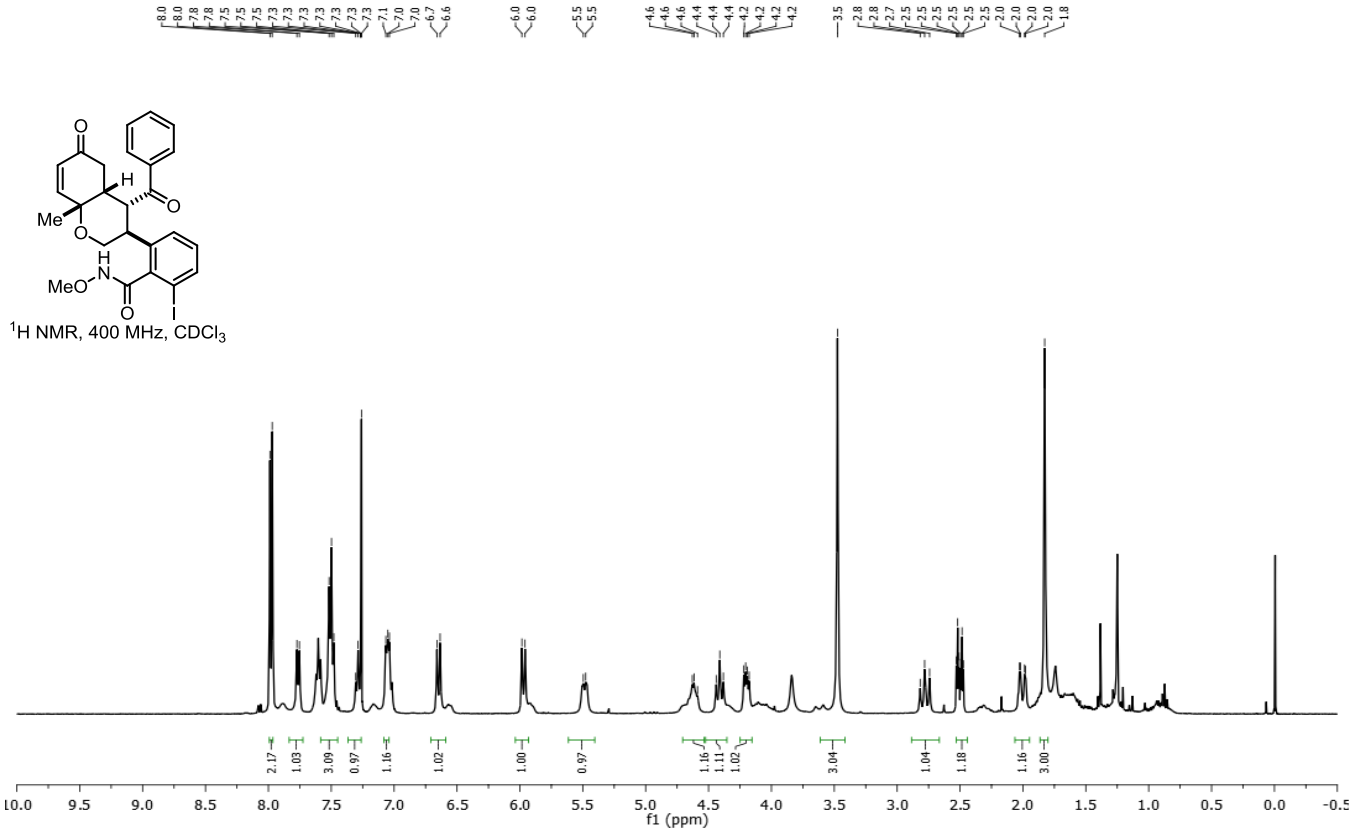


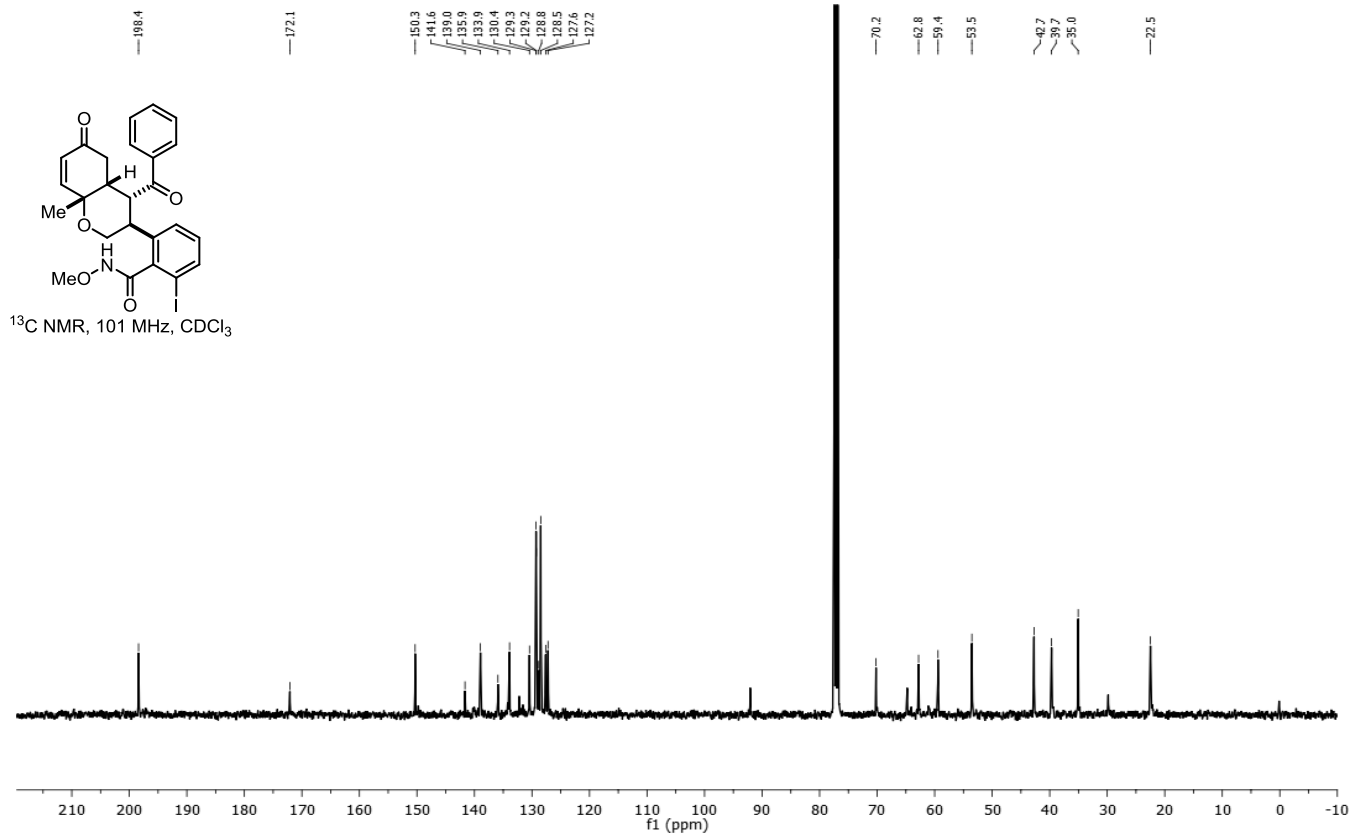
6,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-3-methyl-2-nitrobenzamide (3n):



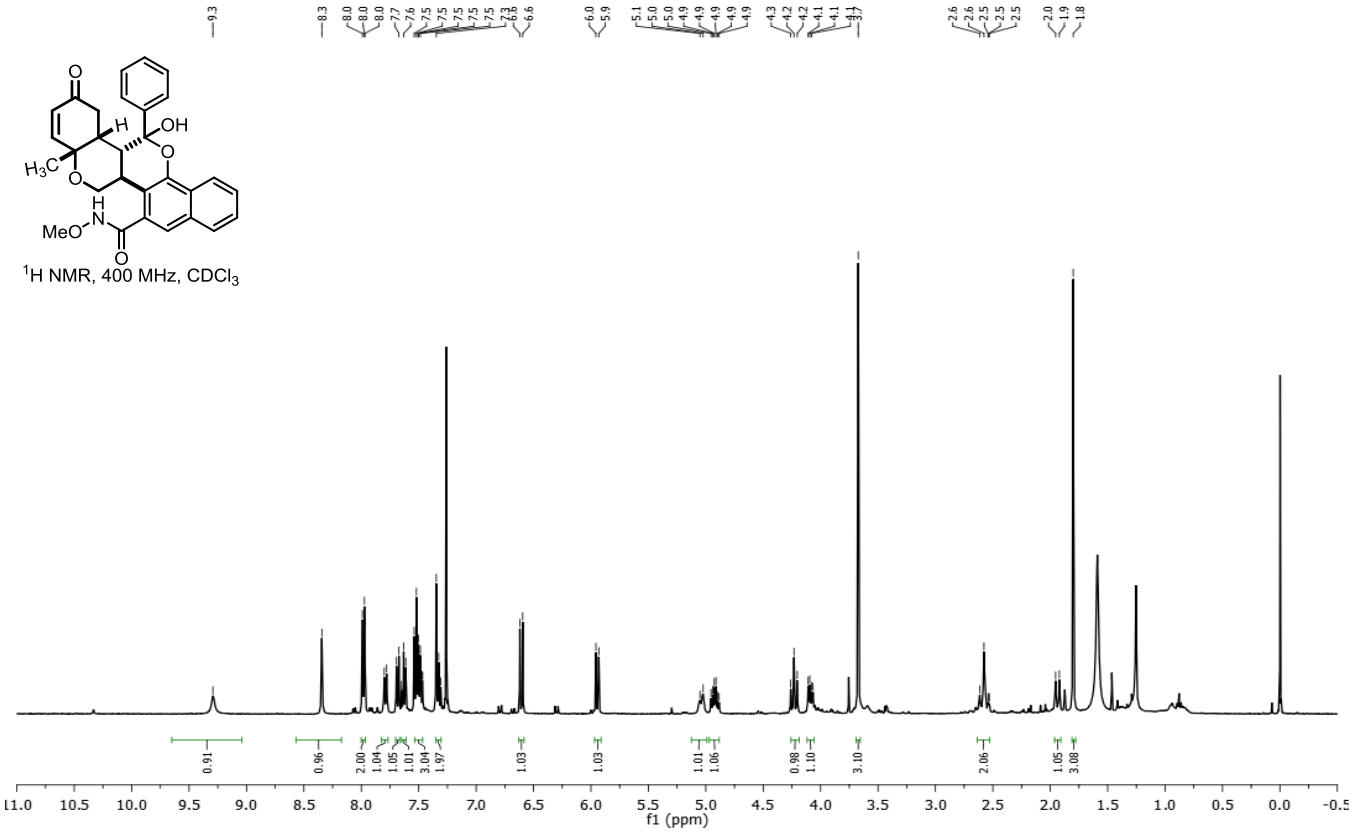


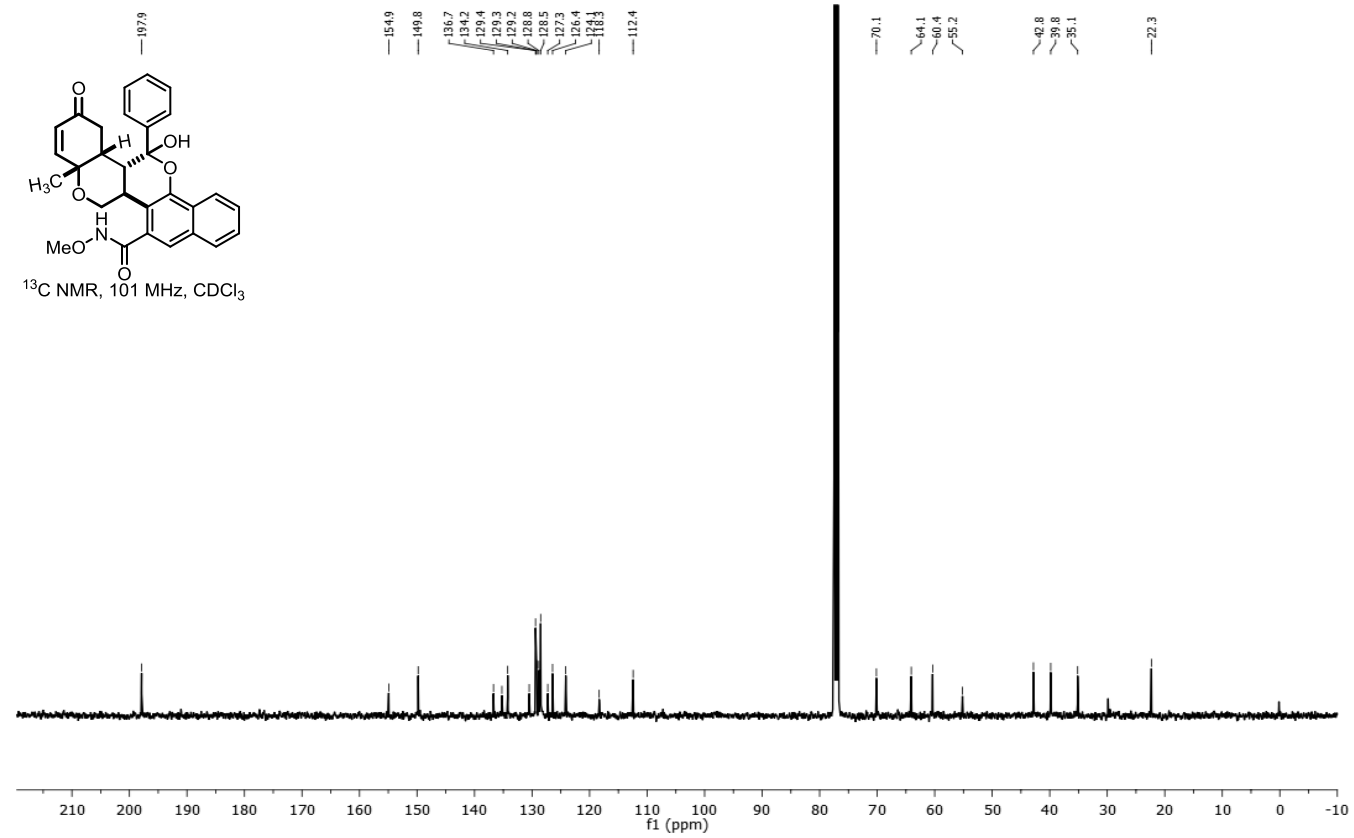
2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-6-iodo-*N*-methoxybenzamide (3o):



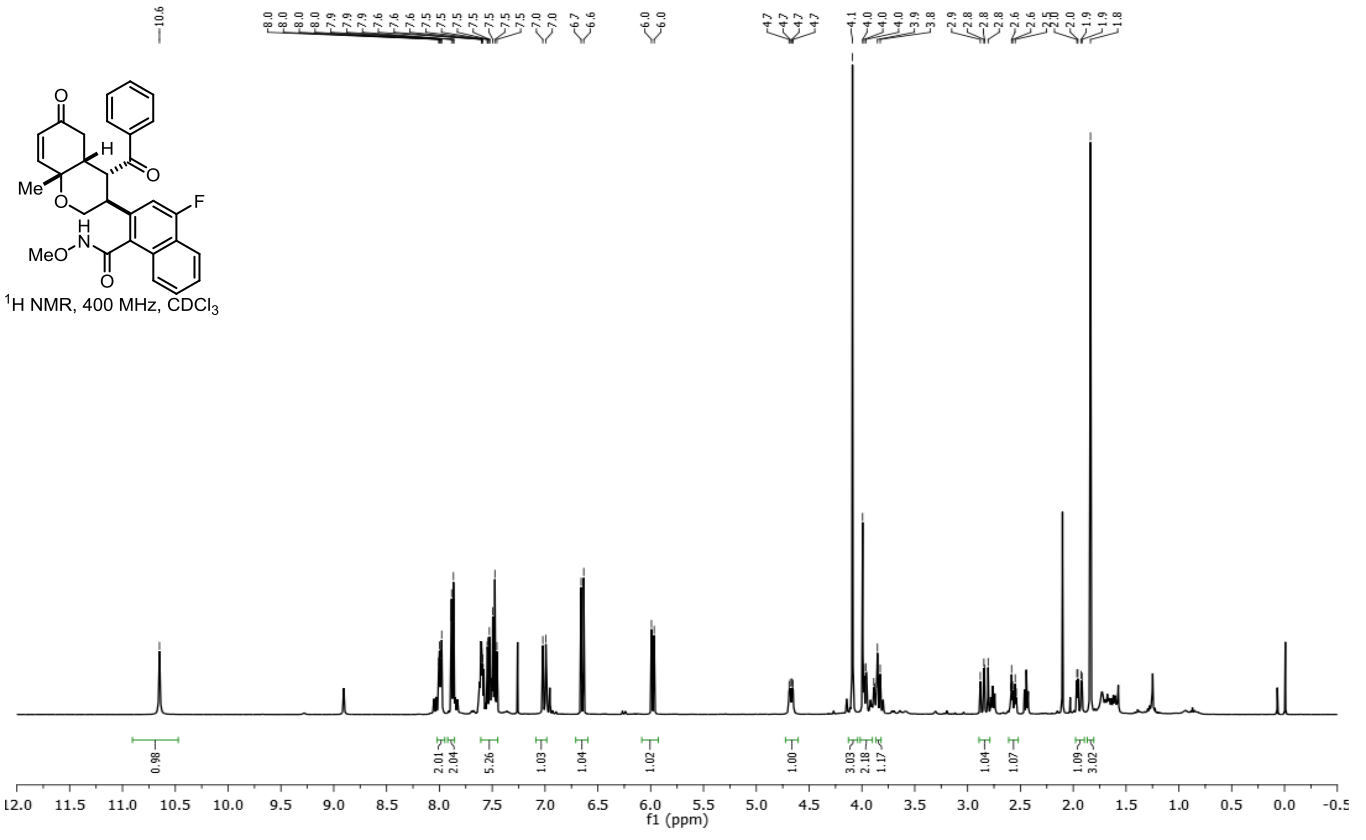


14-Hydroxy-*N*-methoxy-4a-methyl-2-oxo-14-phenyl-1,2,4a,6,6a,14,14a,14*b*-octahydrobenzo[h]chromeno[4,3-*c*]chromene-7-carboxamide (3p):

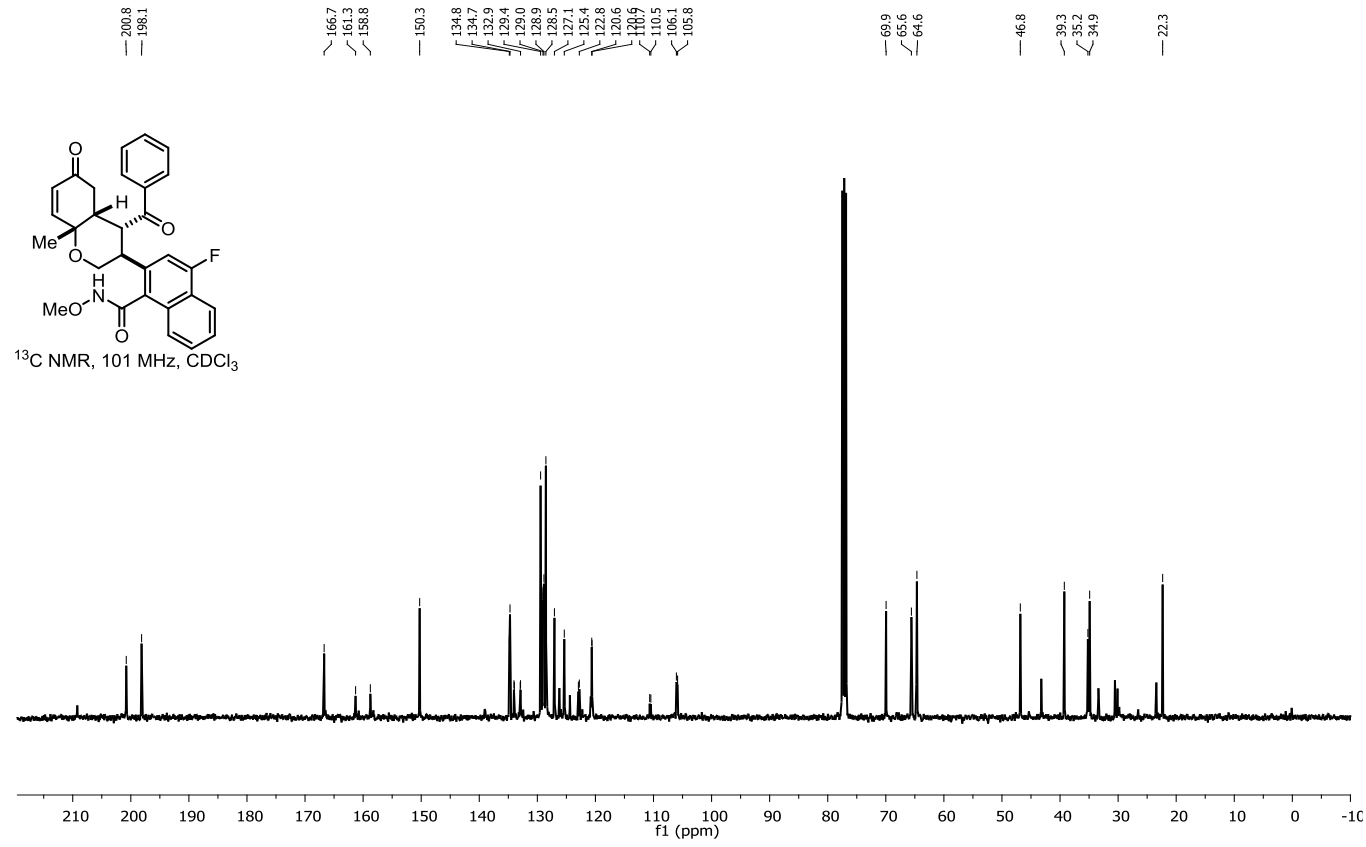




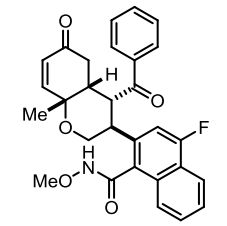
2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-4-fluoro-*N*-methoxy-1-naphthamide (3q):



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

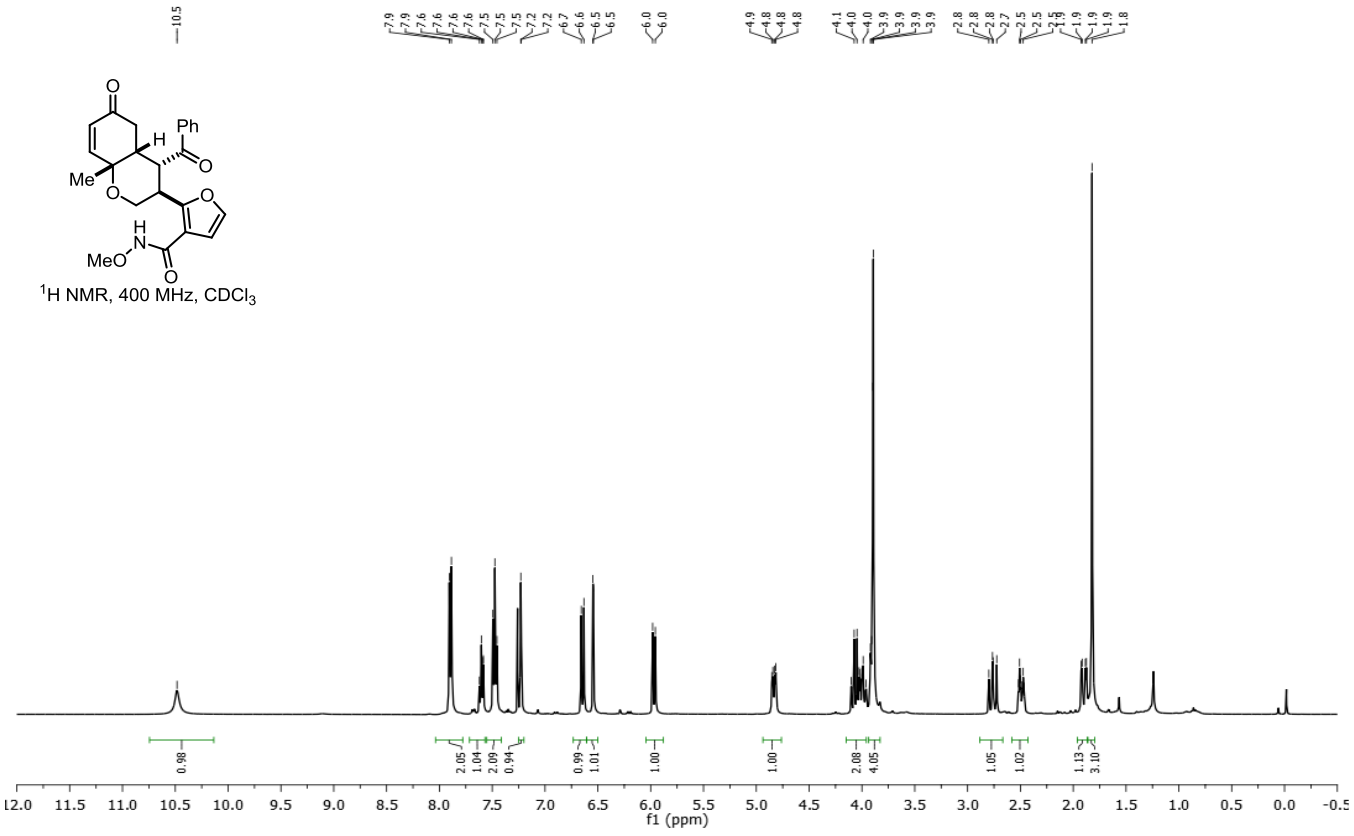


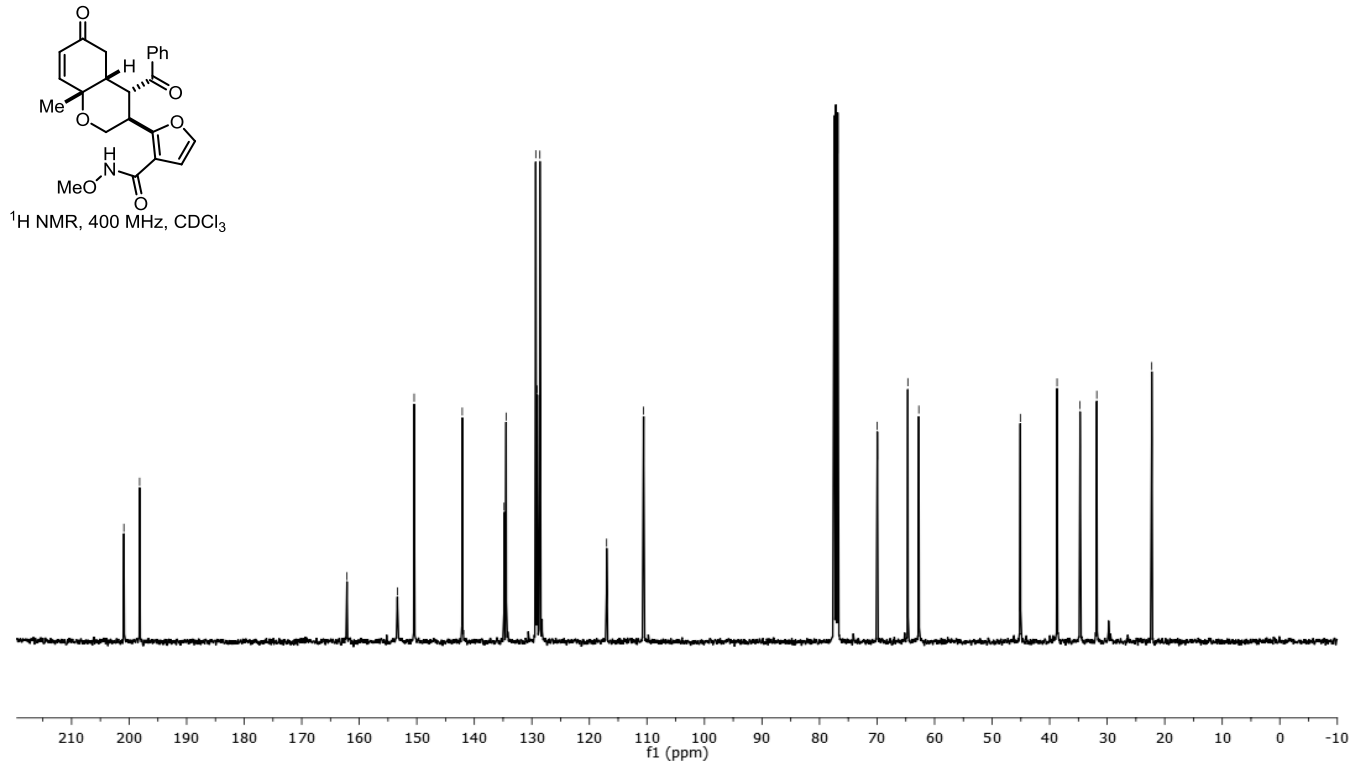
^{13}C NMR, 101 MHz, $CDCl_3$



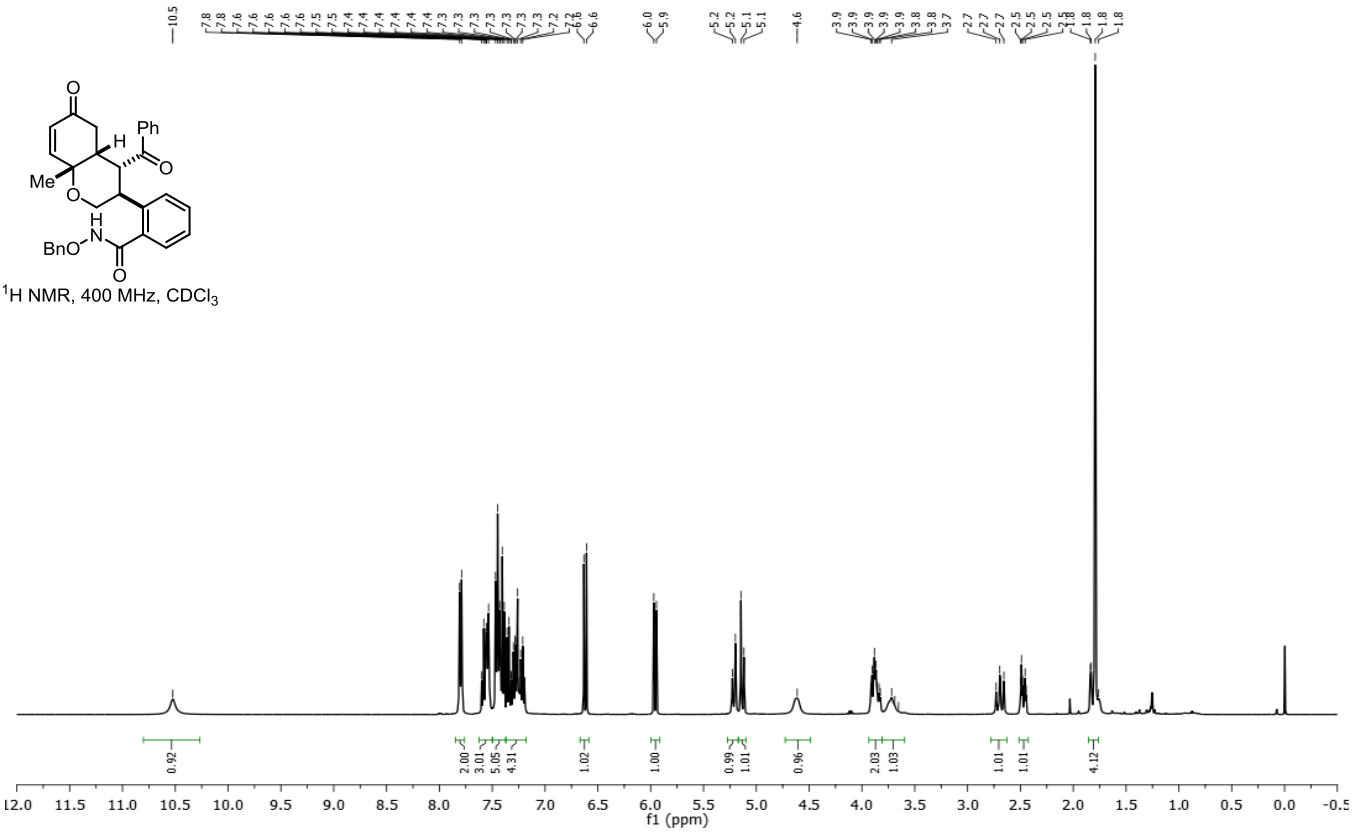
^{19}F NMR, 471 MHz, $CDCl_3$

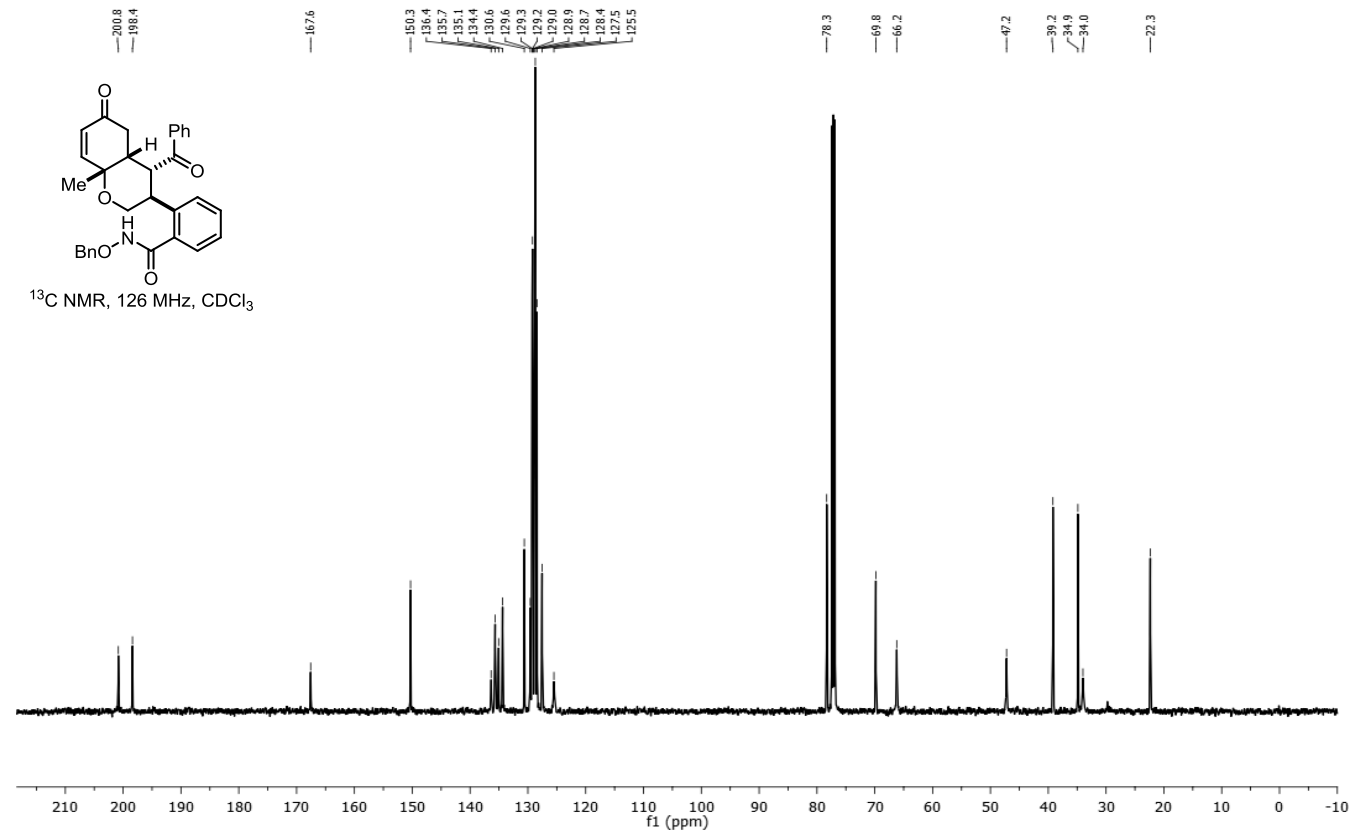
2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxyfuran-3-carboxamide (3r):



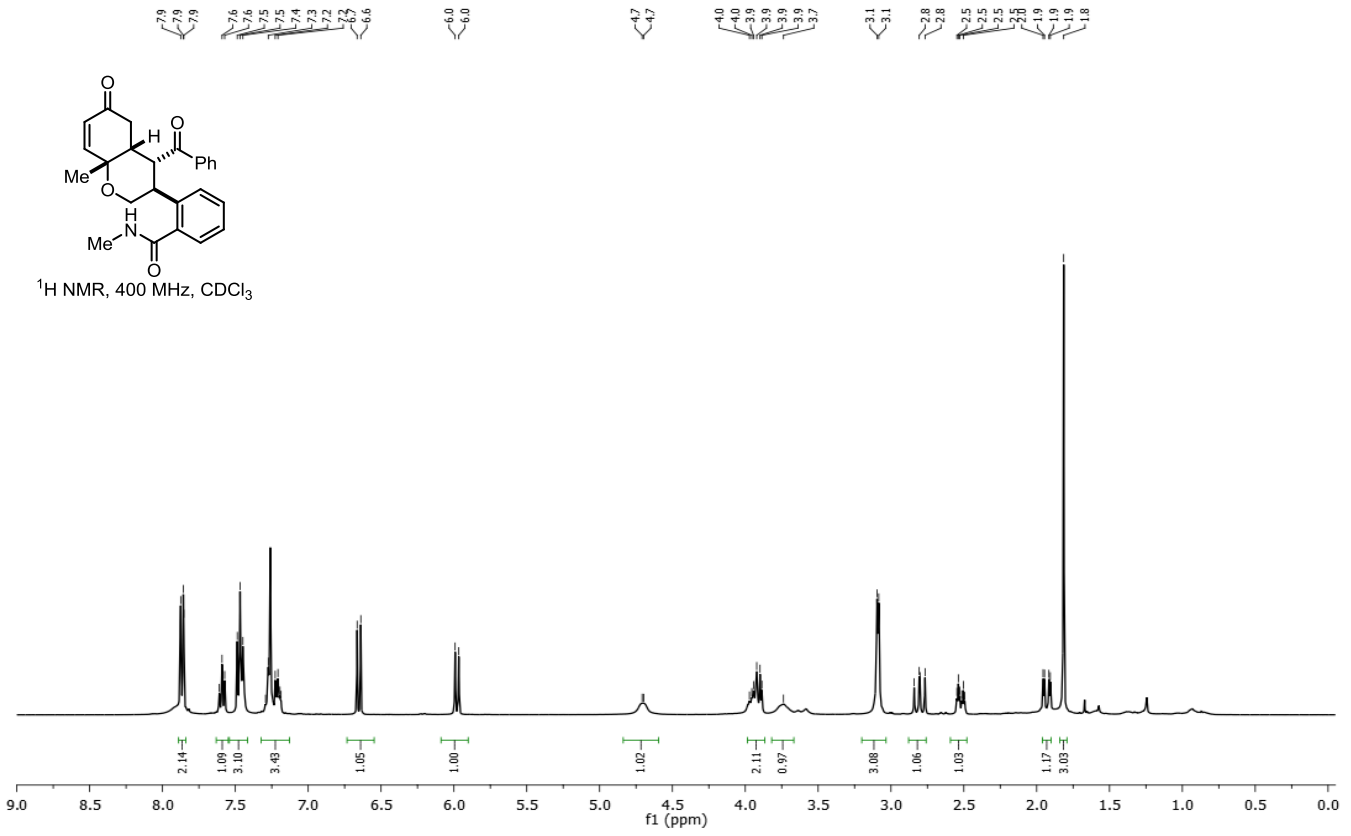


2,4-Benzoyl-(8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-(benzyloxy)benzamide (3s):

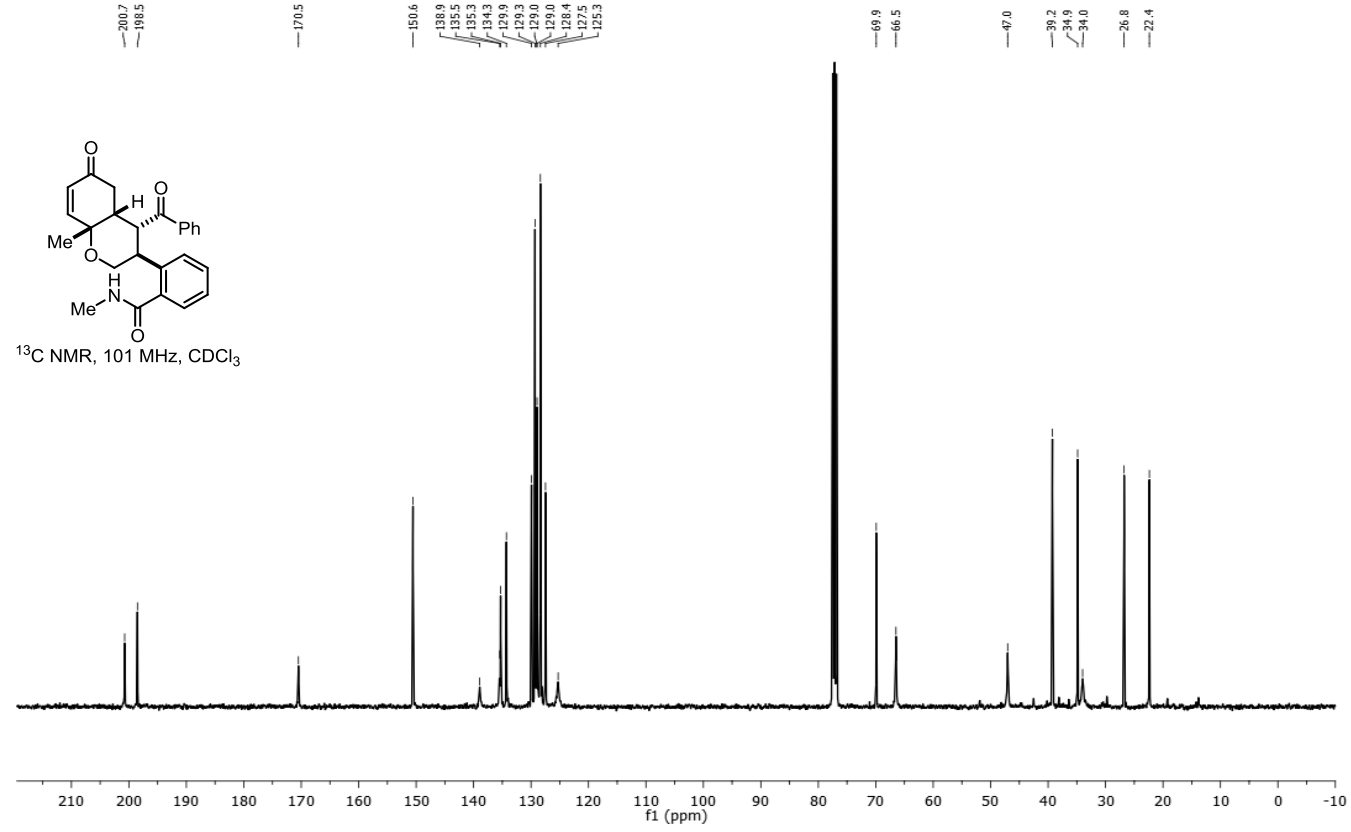




2-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2H-chromen-3-yl)-N-methylbenzamide (3u):

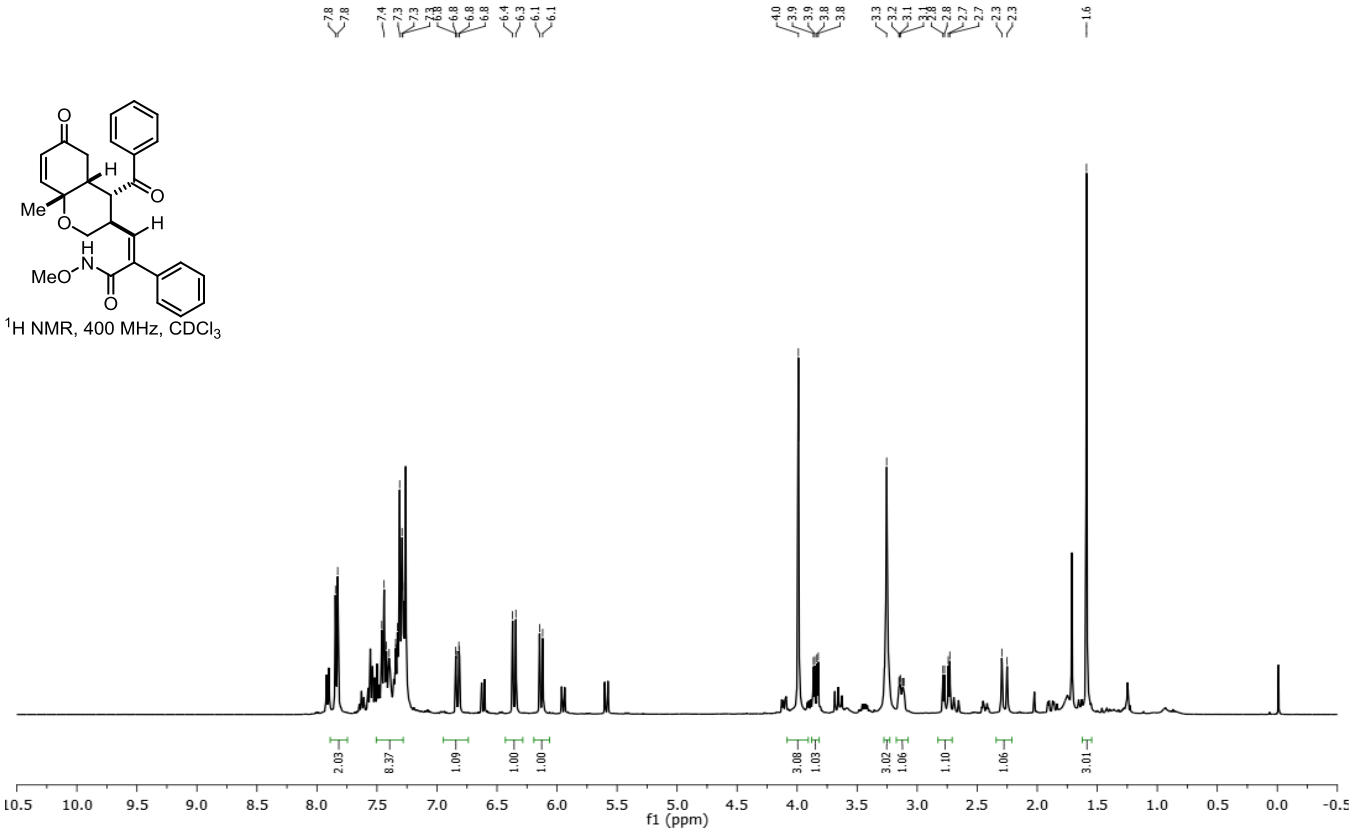


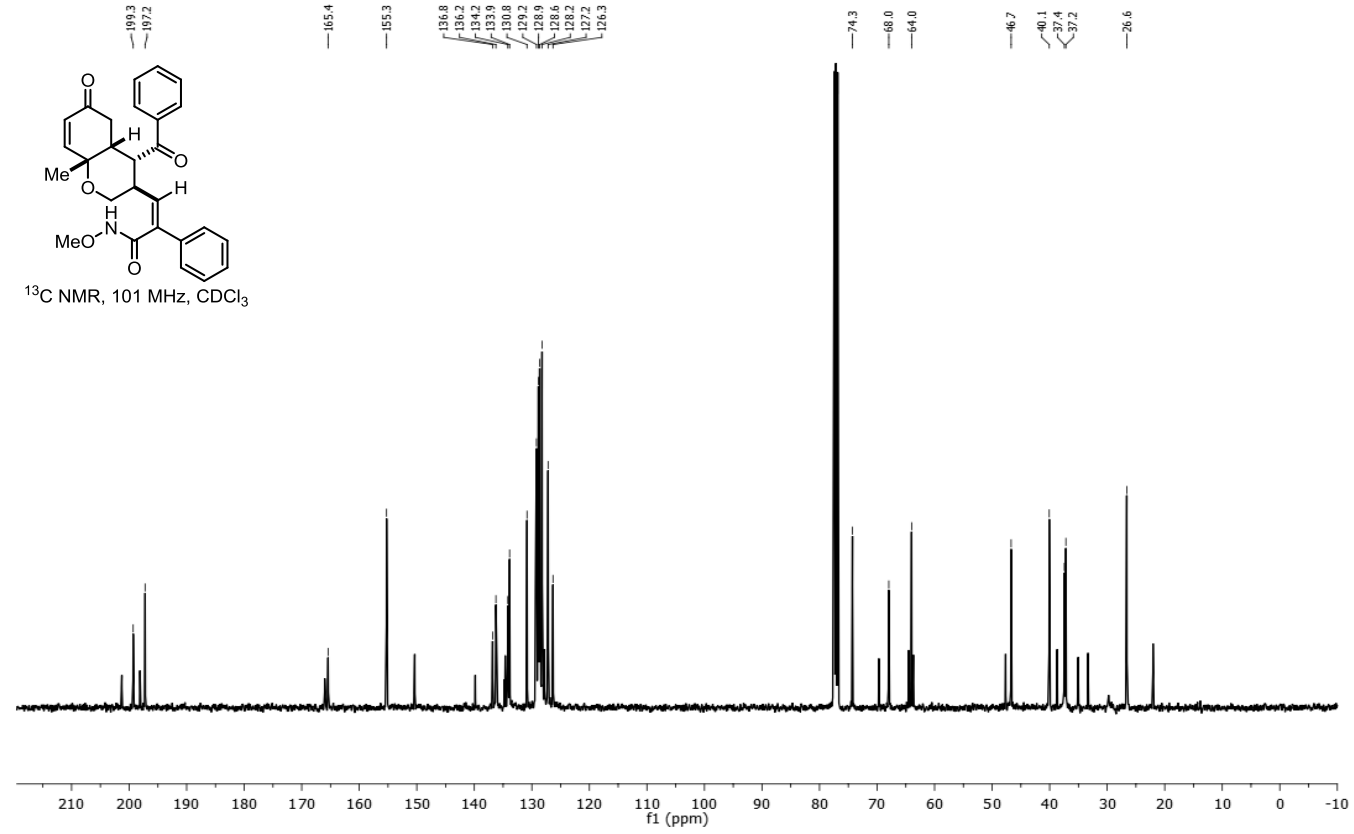
^{1}H NMR, 400 MHz, $CDCl_3$



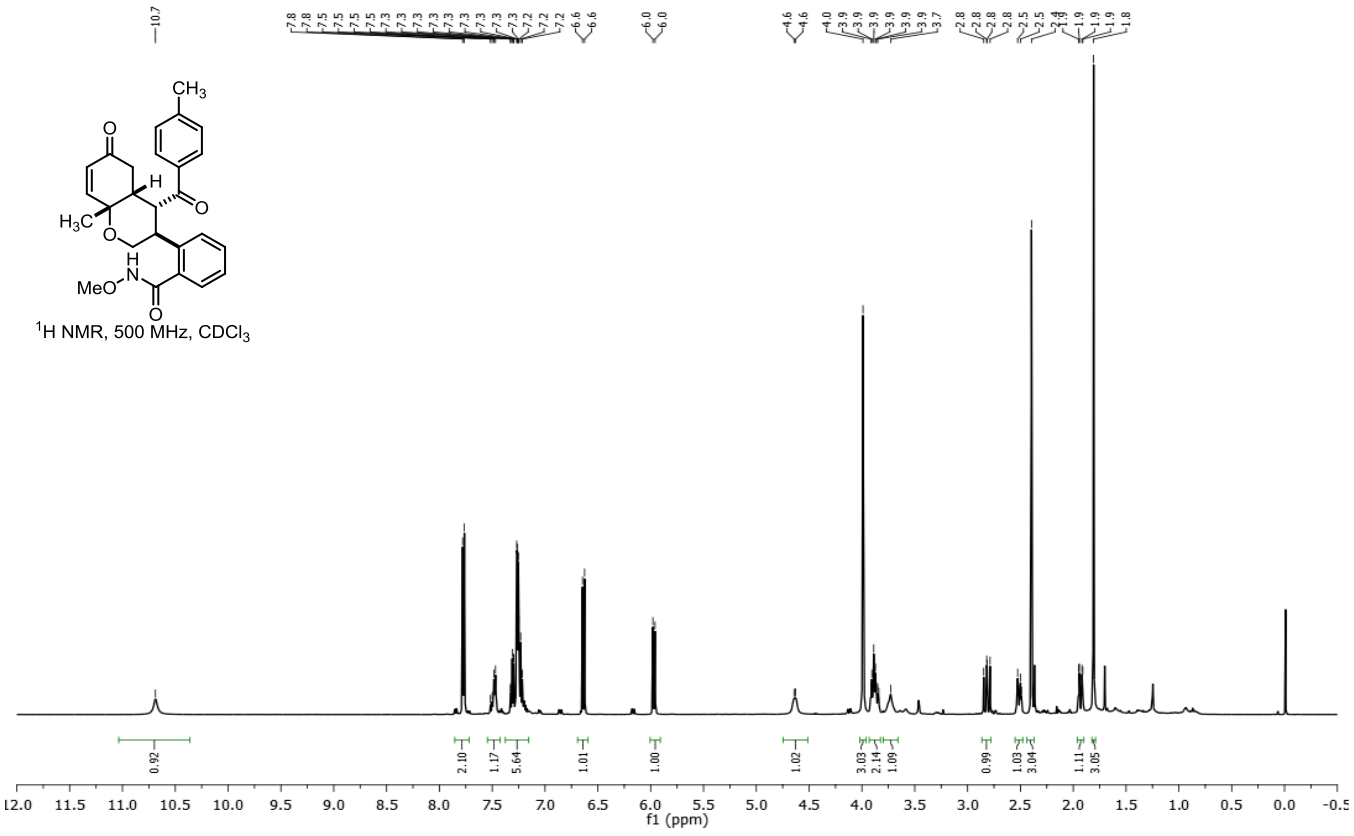
^{13}C NMR, 101 MHz, $CDCl_3$

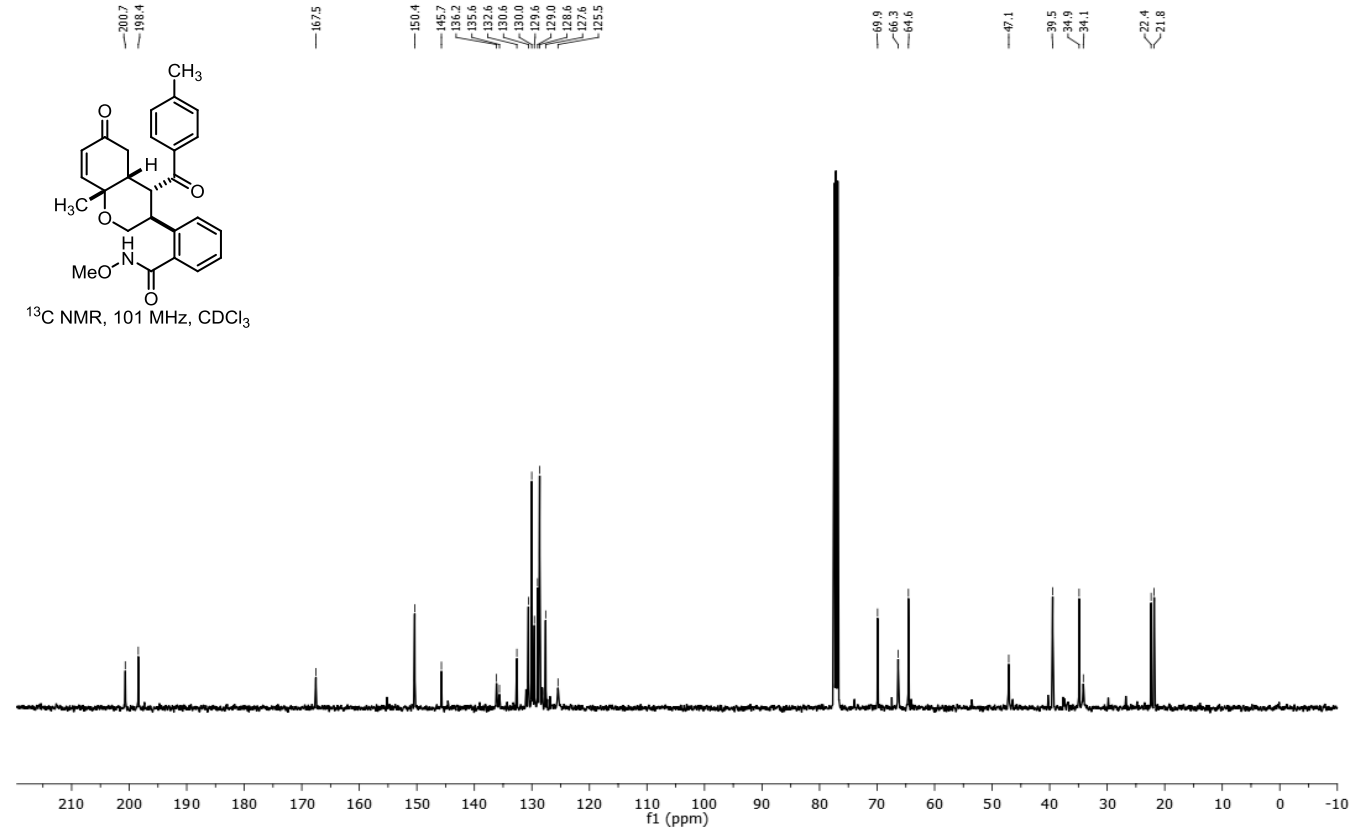
(*Z*)-3-(4-Benzoyl-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxy-2-phenylacrylamide (3w):



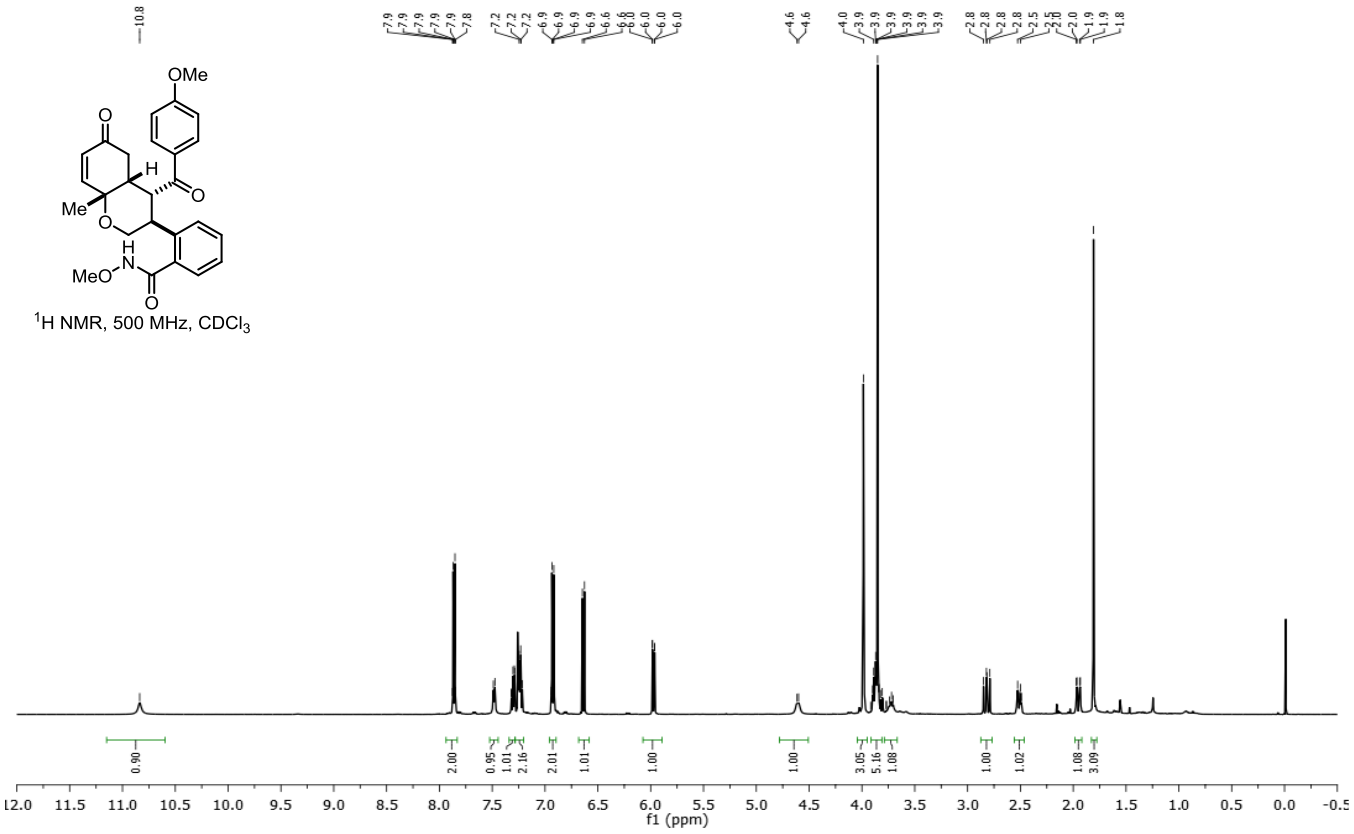


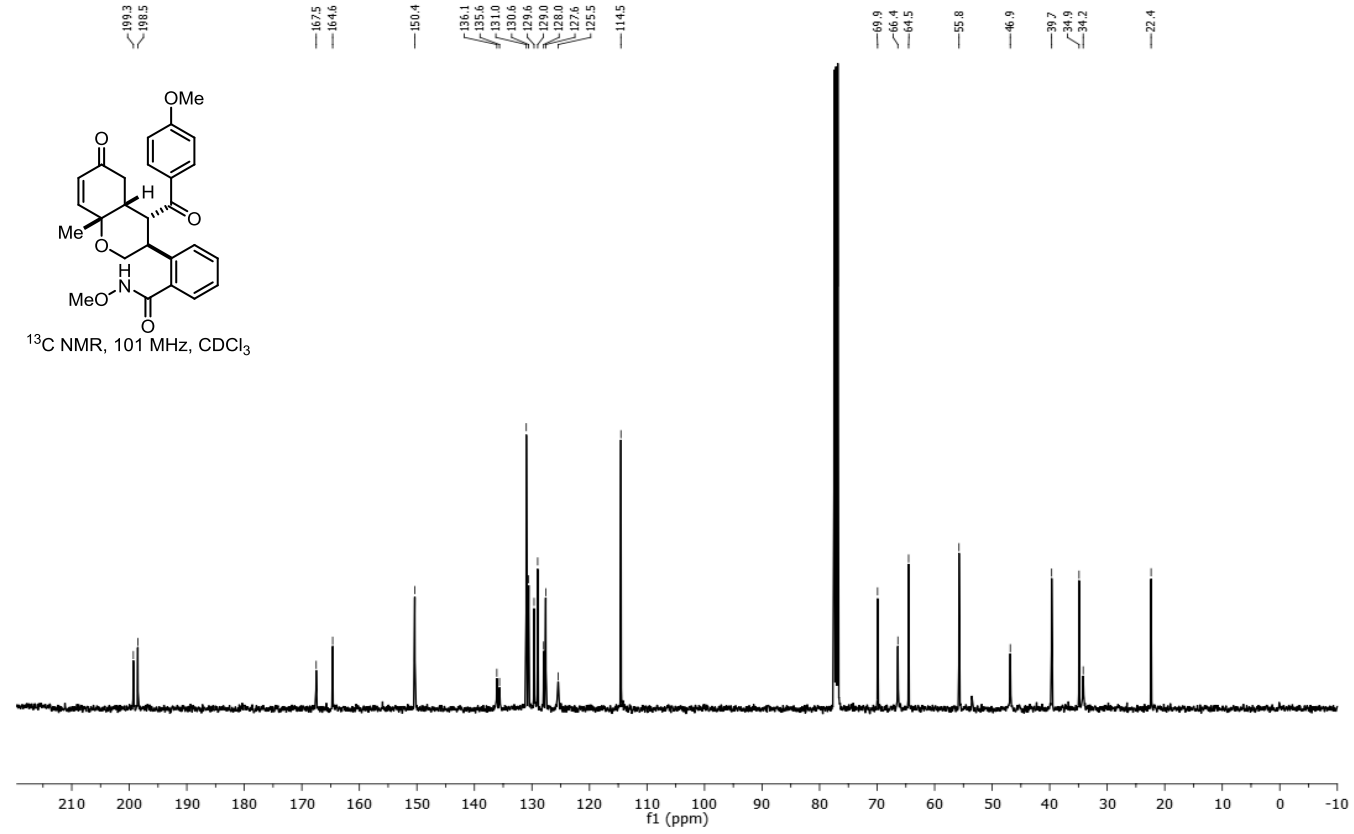
_N_-Methoxy-2-(8a-methyl-4-(4-methylbenzoyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2_H_-chromen-3-yl)benzamide (3y):



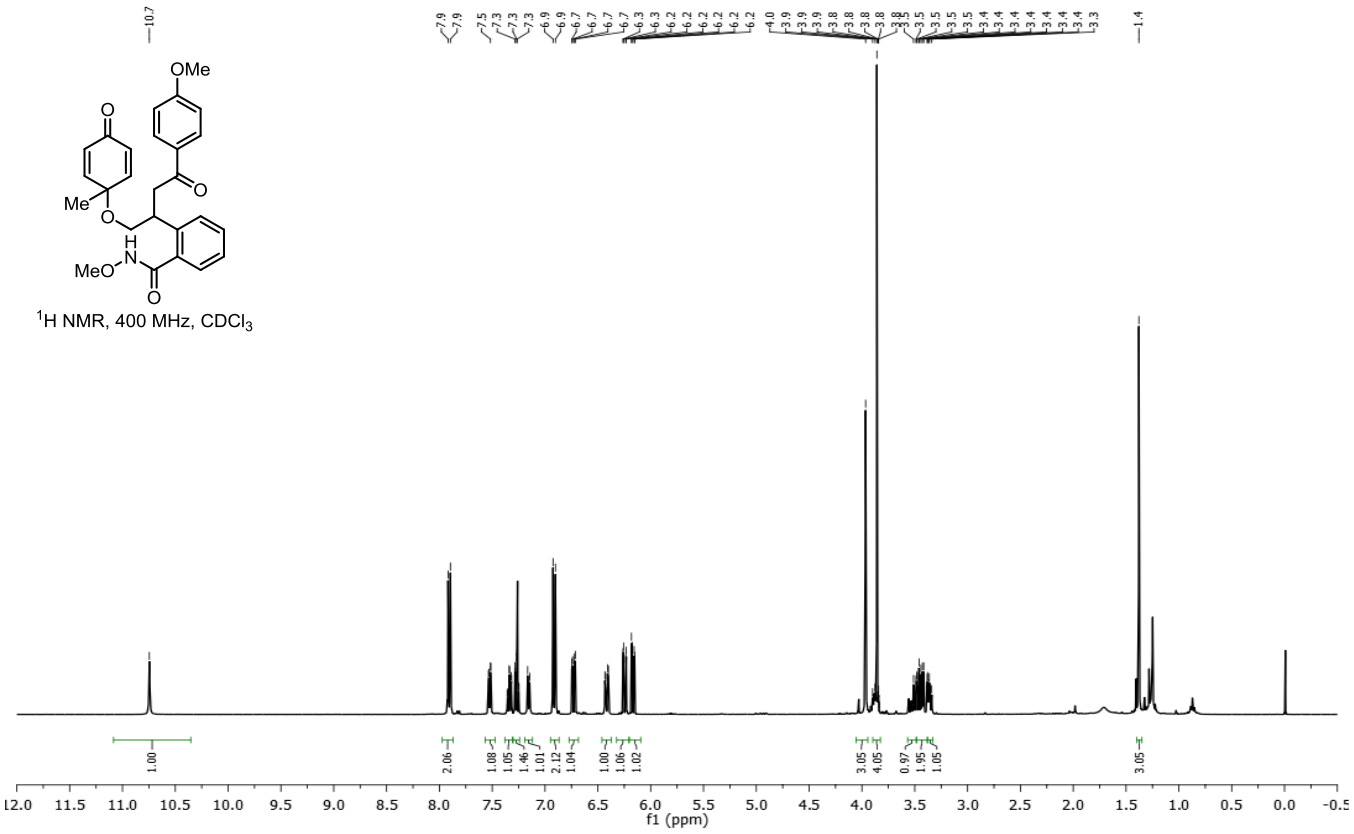


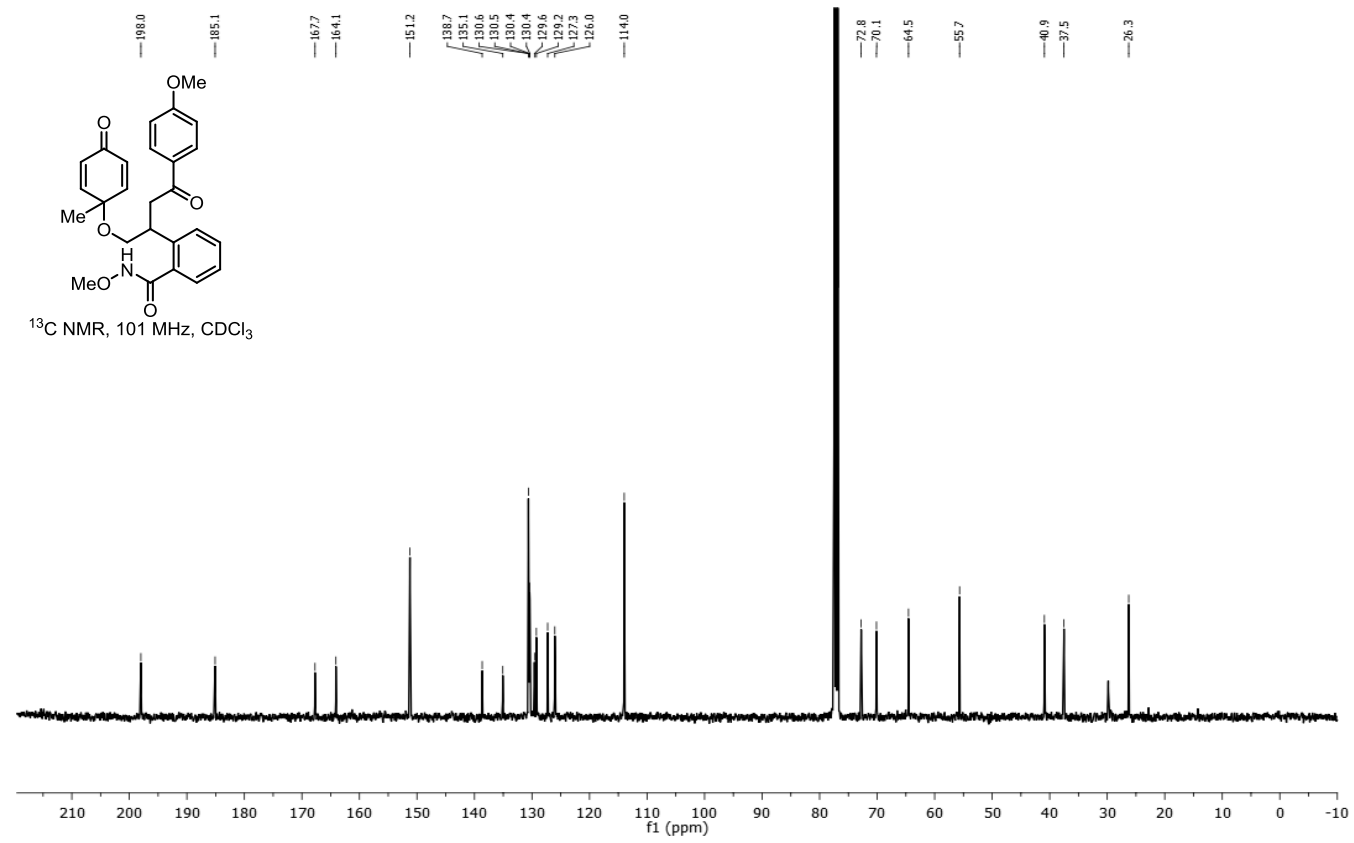
_N_-Methoxy-2-(4-(4-methoxybenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2_H_-chromen-3-yl)benzamide (3z):



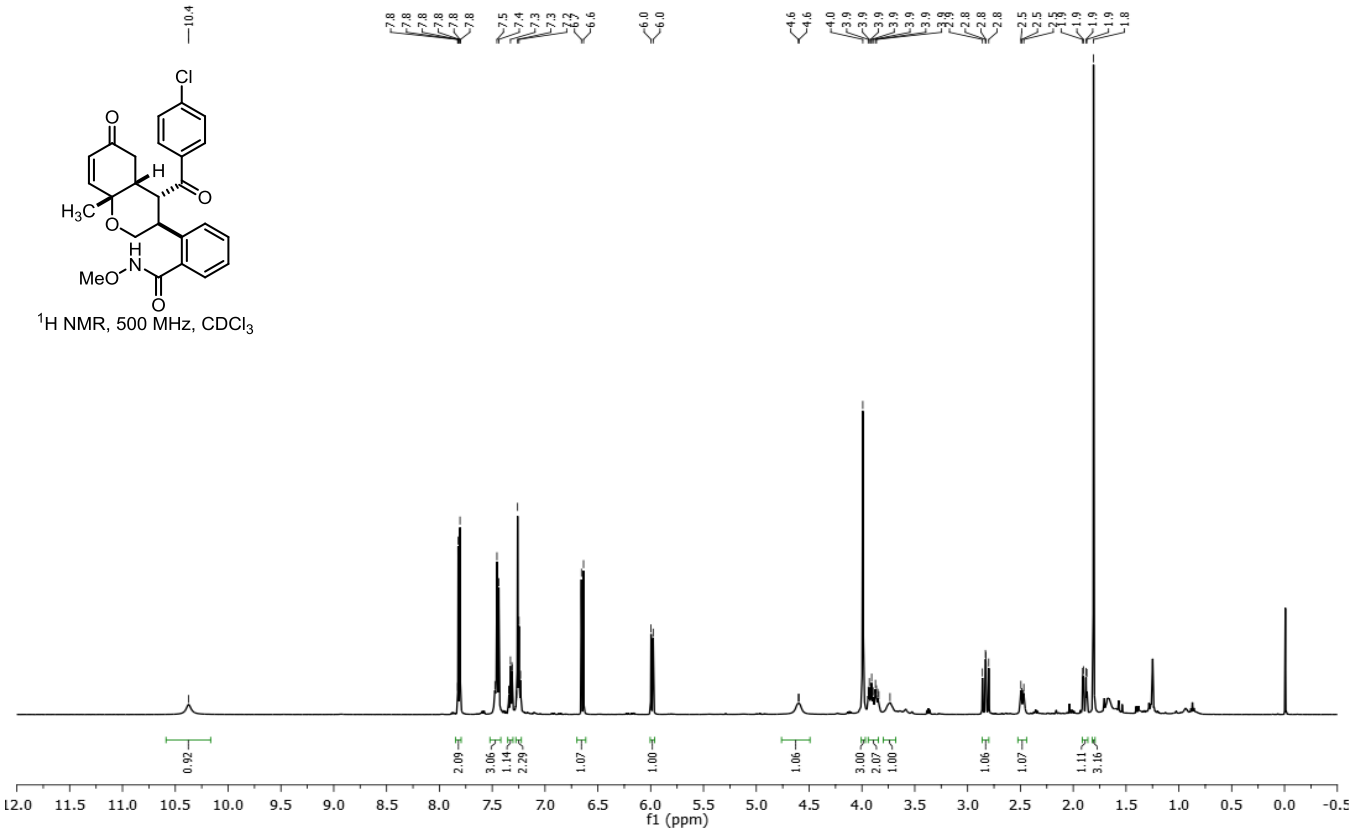


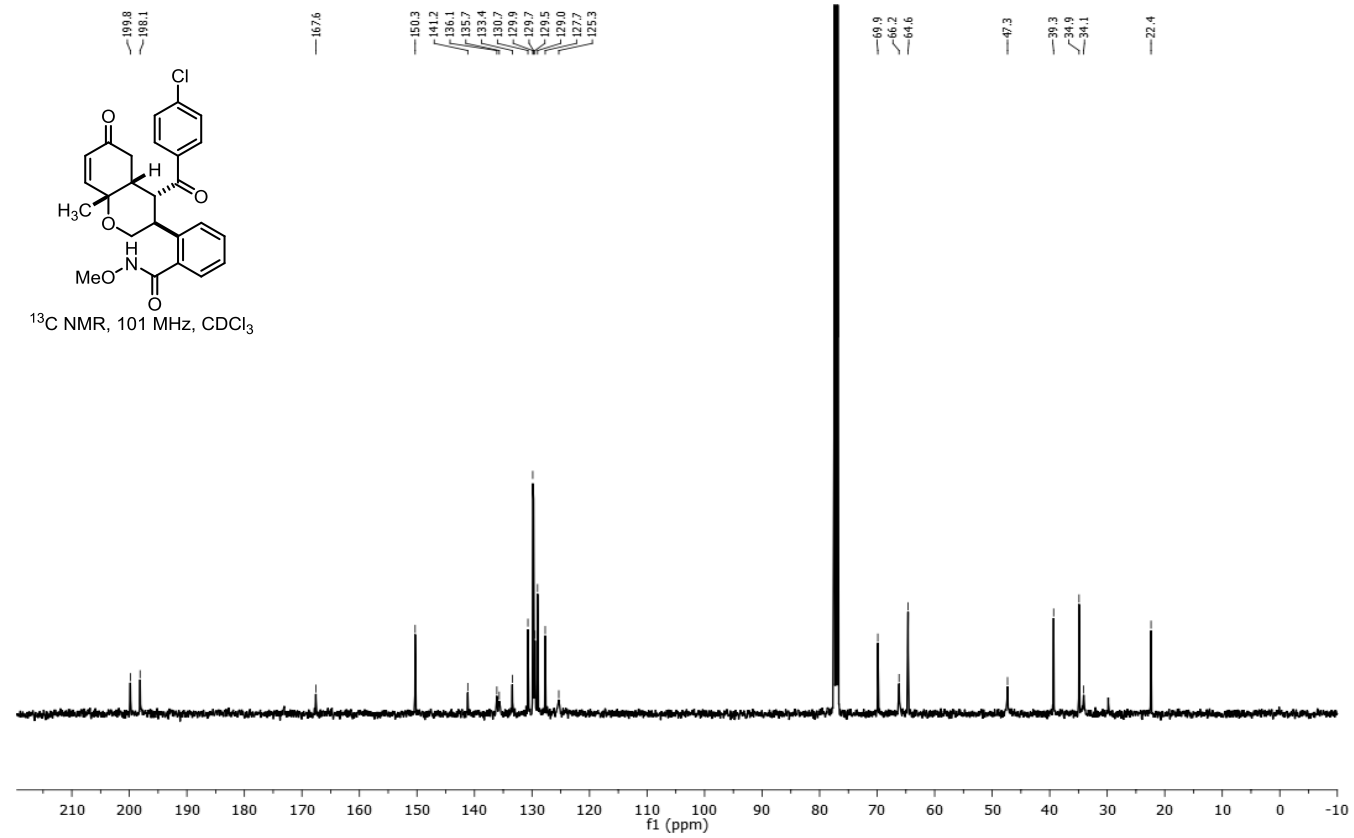
***N*-Methoxy-2-(4-(4-methoxyphenyl)-1-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)oxy)-4-oxobutan-2-yl)benzamideone (3z'):**



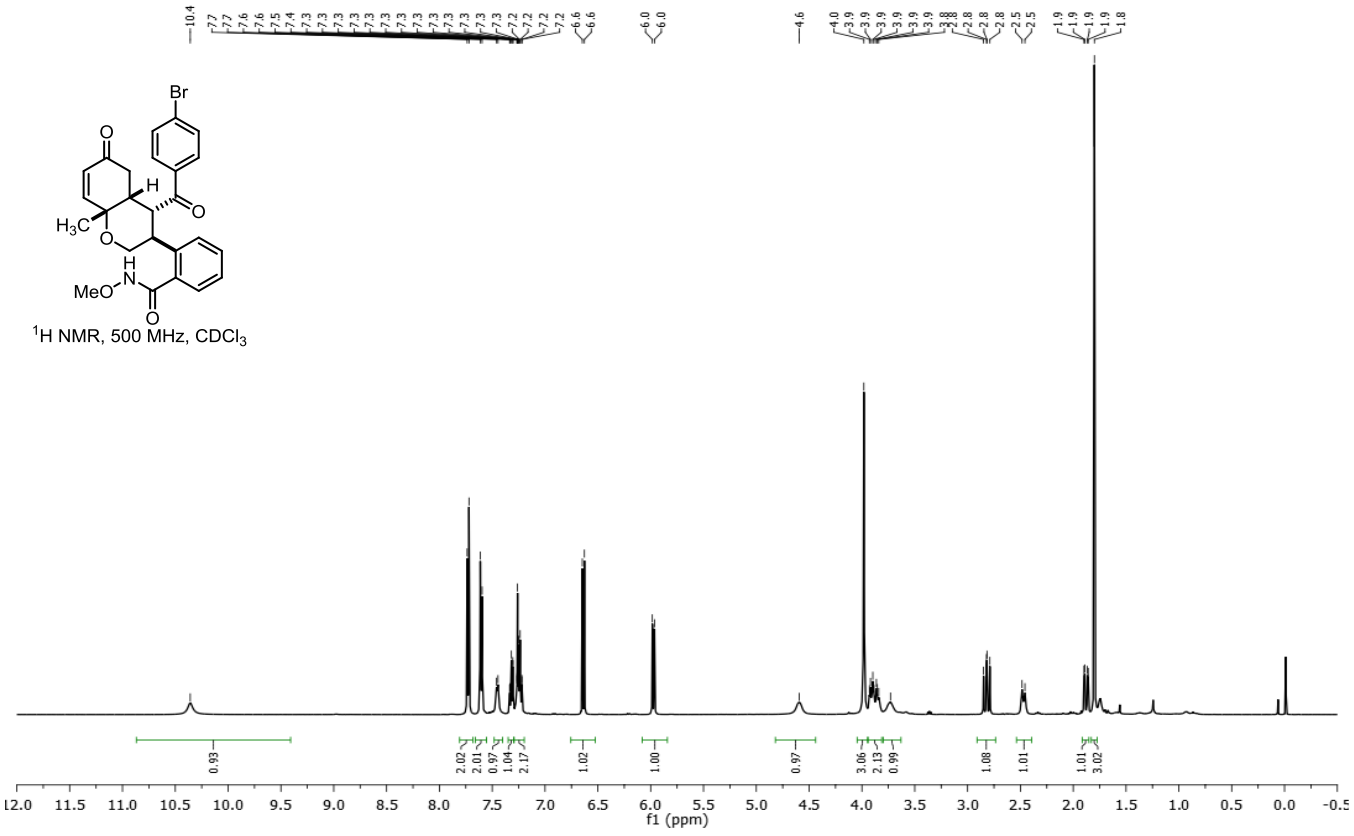


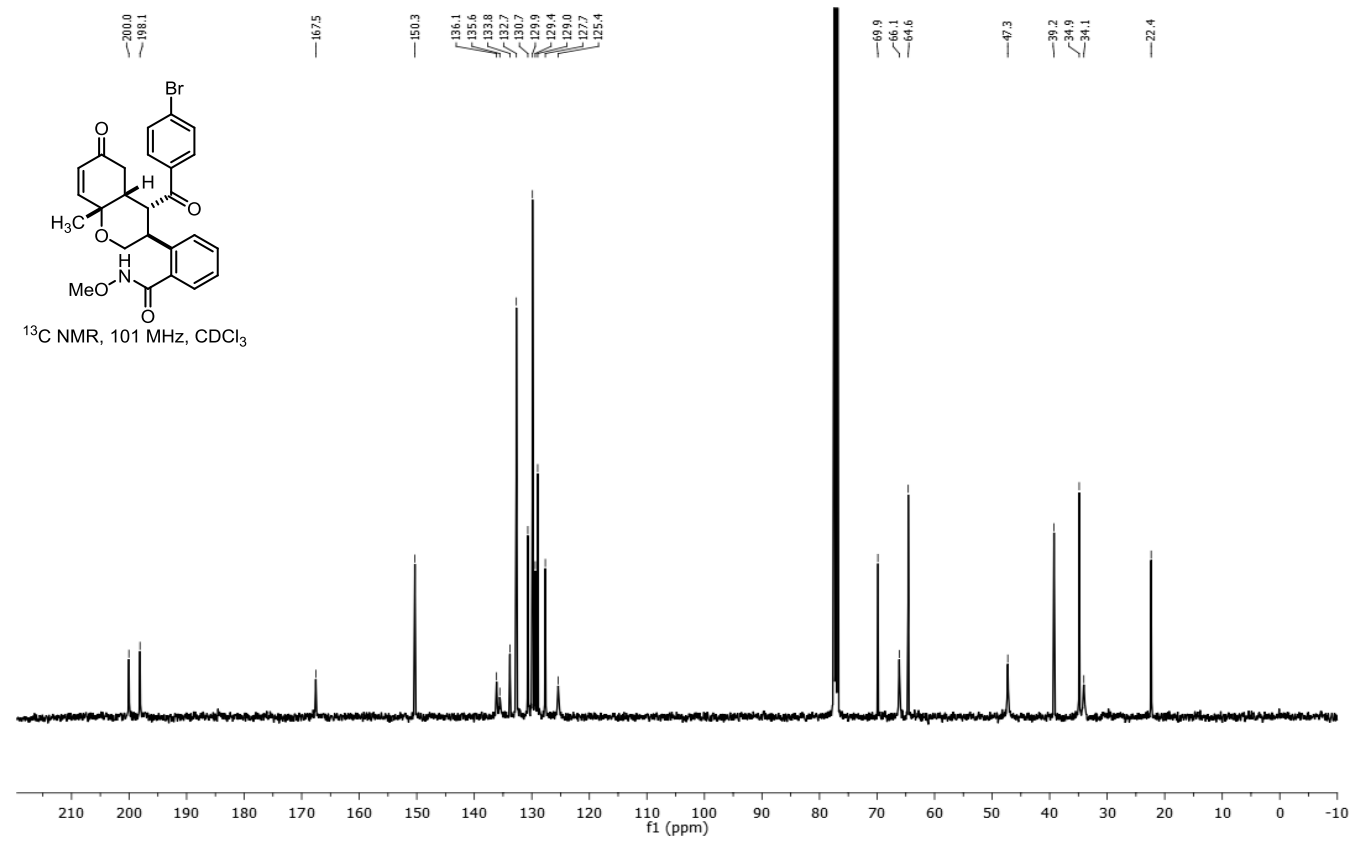
2-(4-(4-Chlorobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3aa):



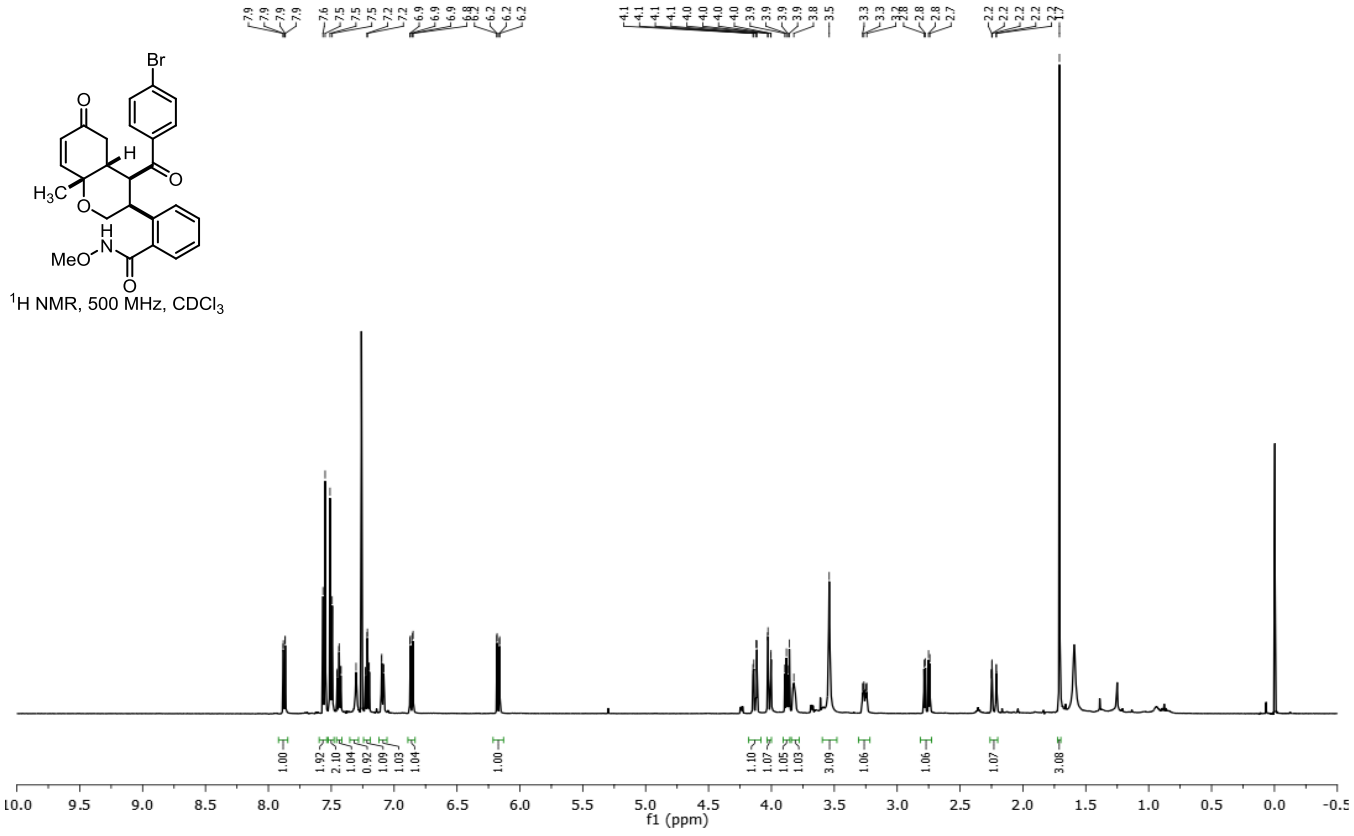


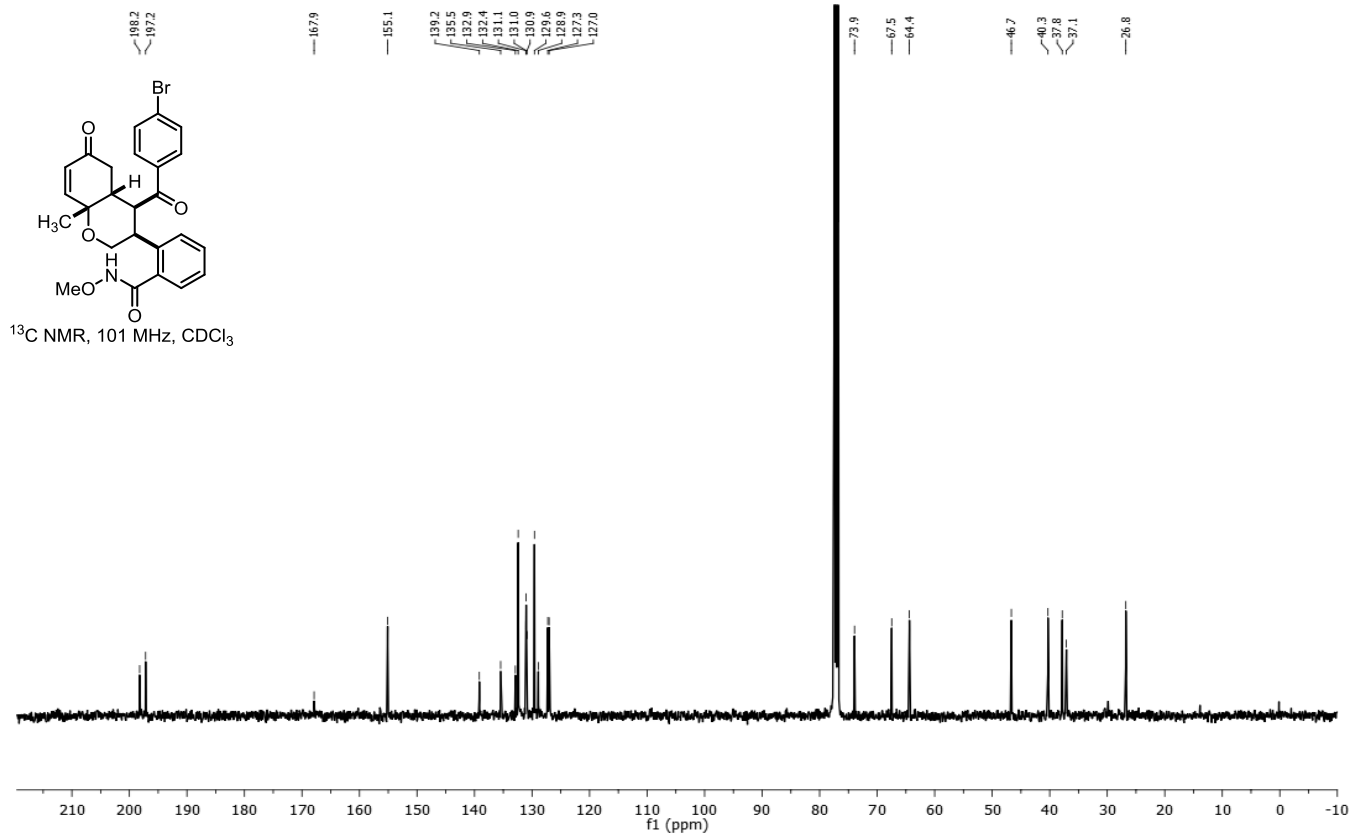
2-(4-(4-Bromobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ab):



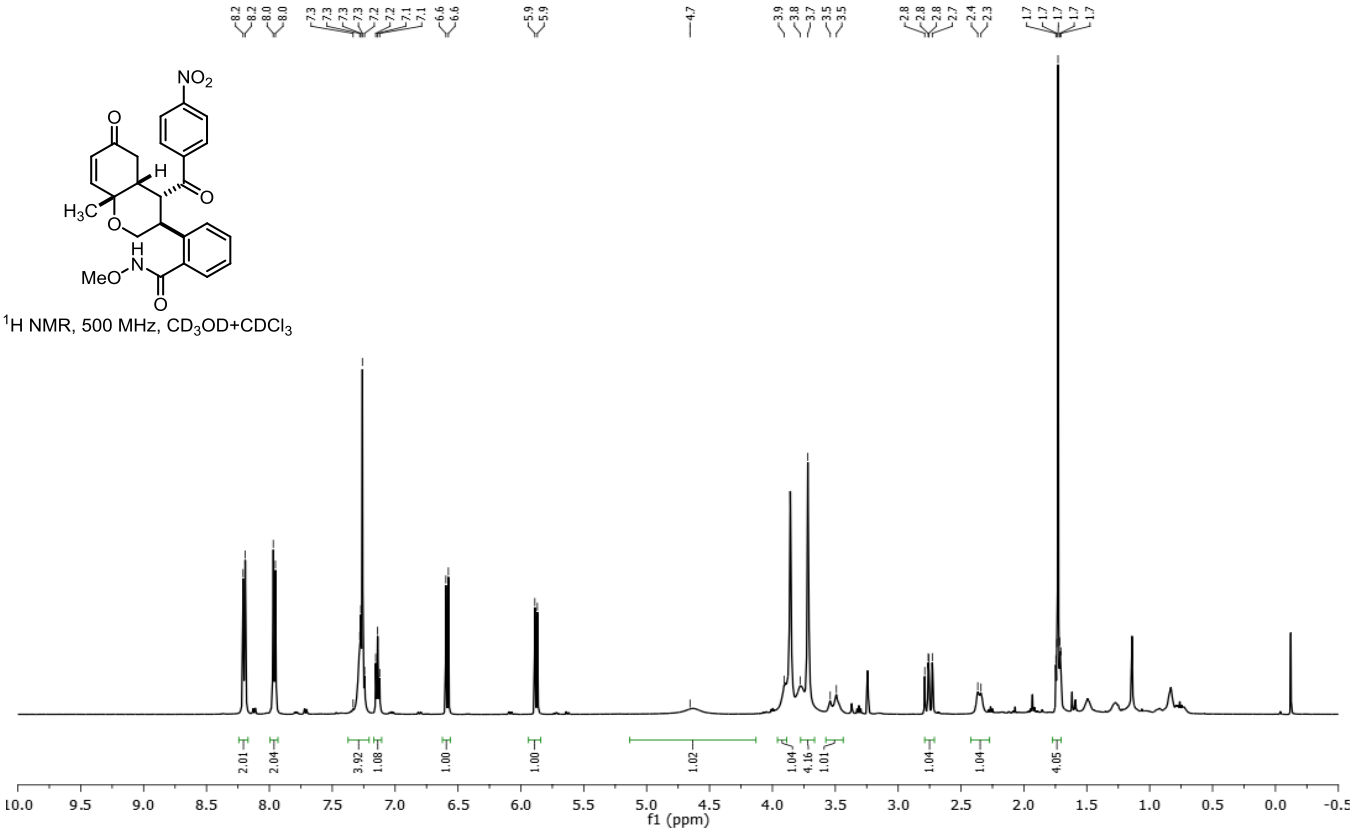


2-(4-(4-Bromobenzoyl)-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ab'): (minor isomer)

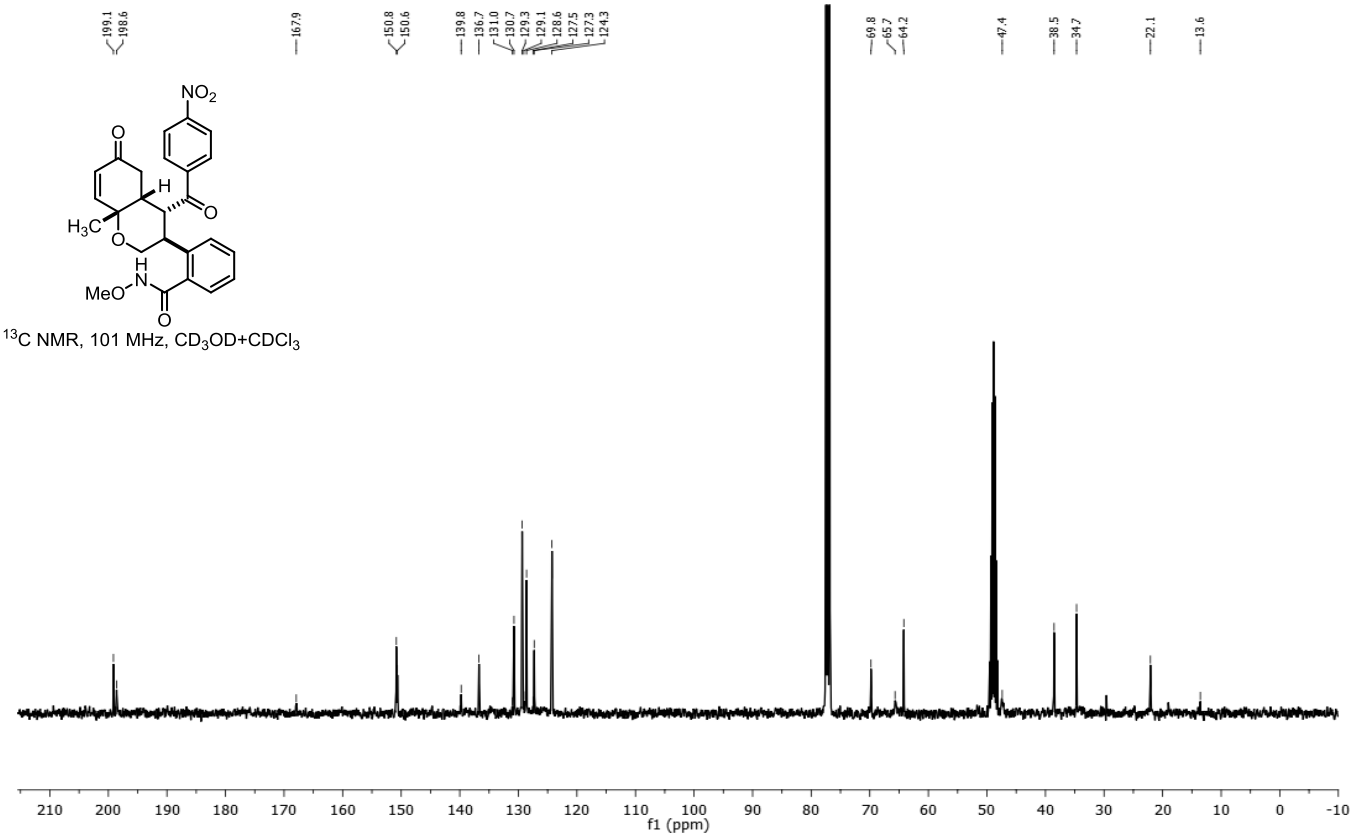




_N_-Methoxy-2-(8a-methyl-4-(4-nitrobenzoyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2_H_-chromen-3-yl)benzamide (3ac):

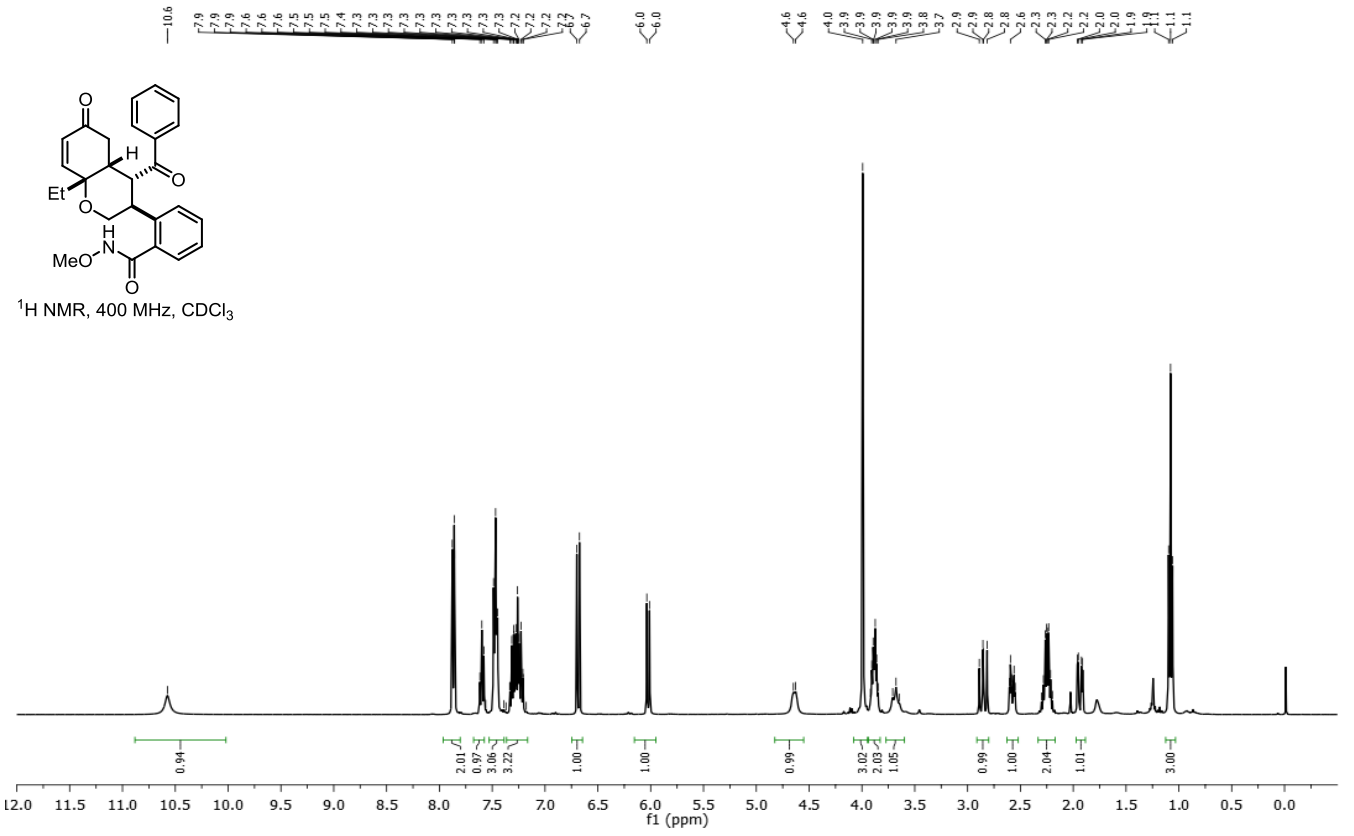


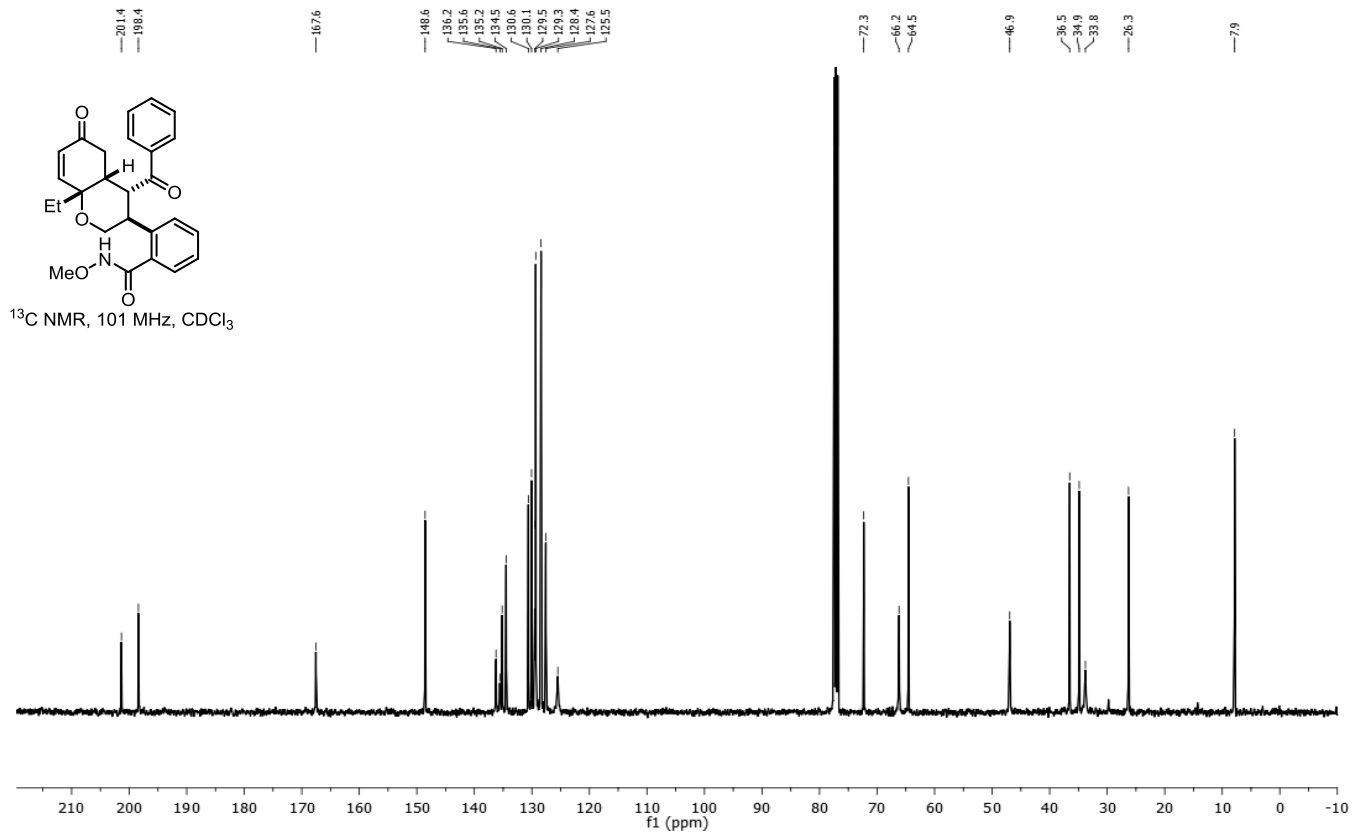
^{1}H NMR, 500 MHz, CD_3OD+$CDCl_3$



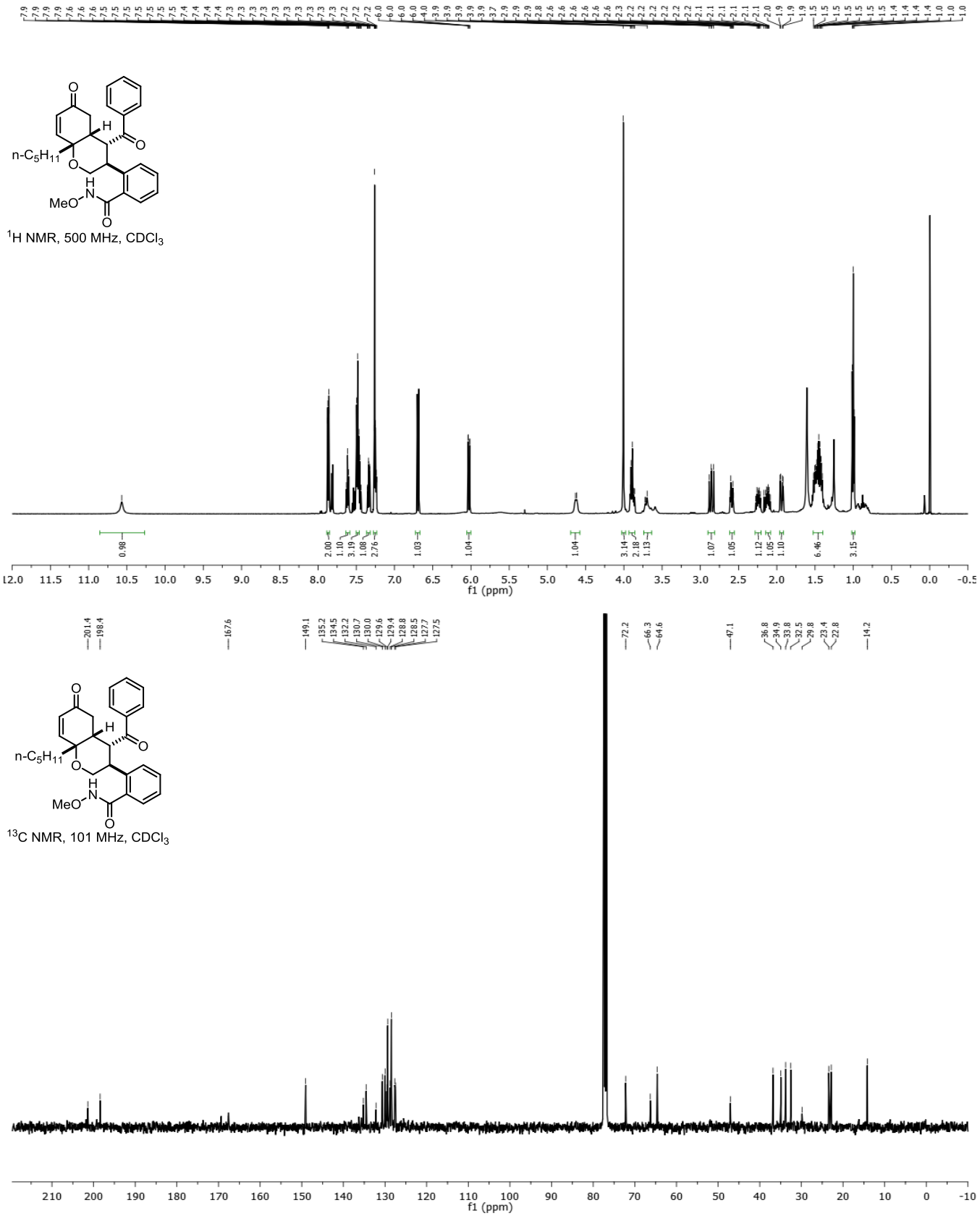
^{13}C NMR, 101 MHz, CD_3OD+$CDCl_3$

2-(4-Benzoyl-8a-ethyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ag):

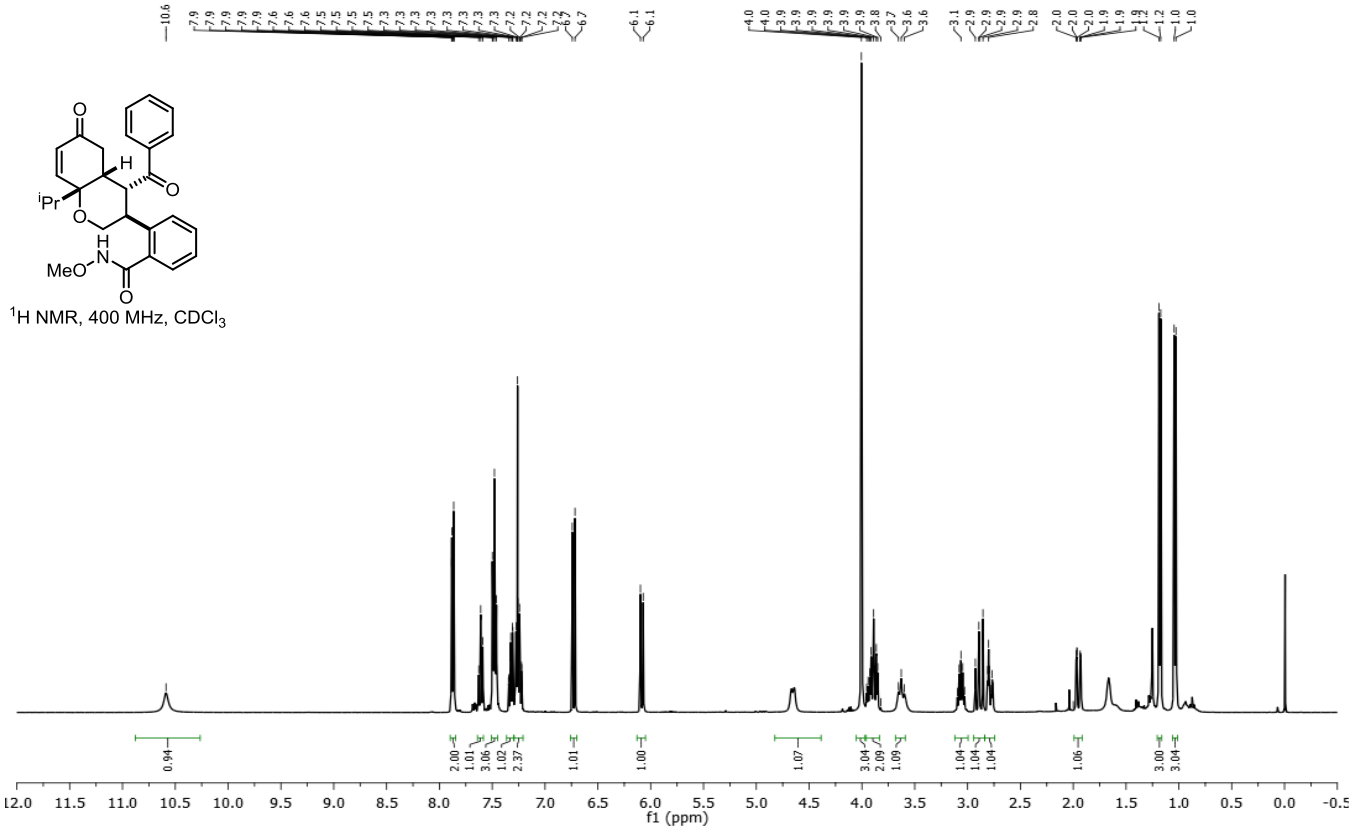


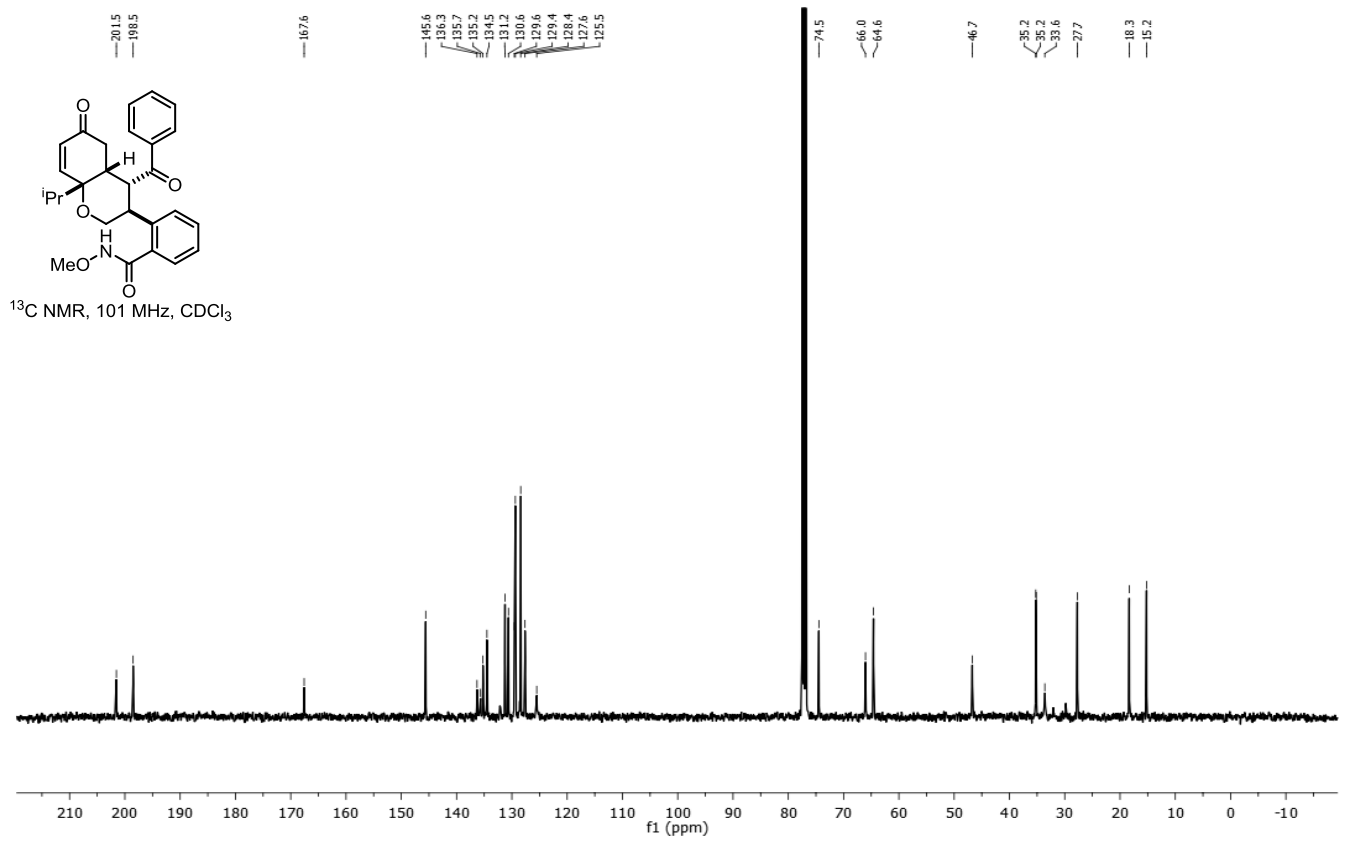


2-(4-Benzoyl-6-oxo-8a-pentyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ah):

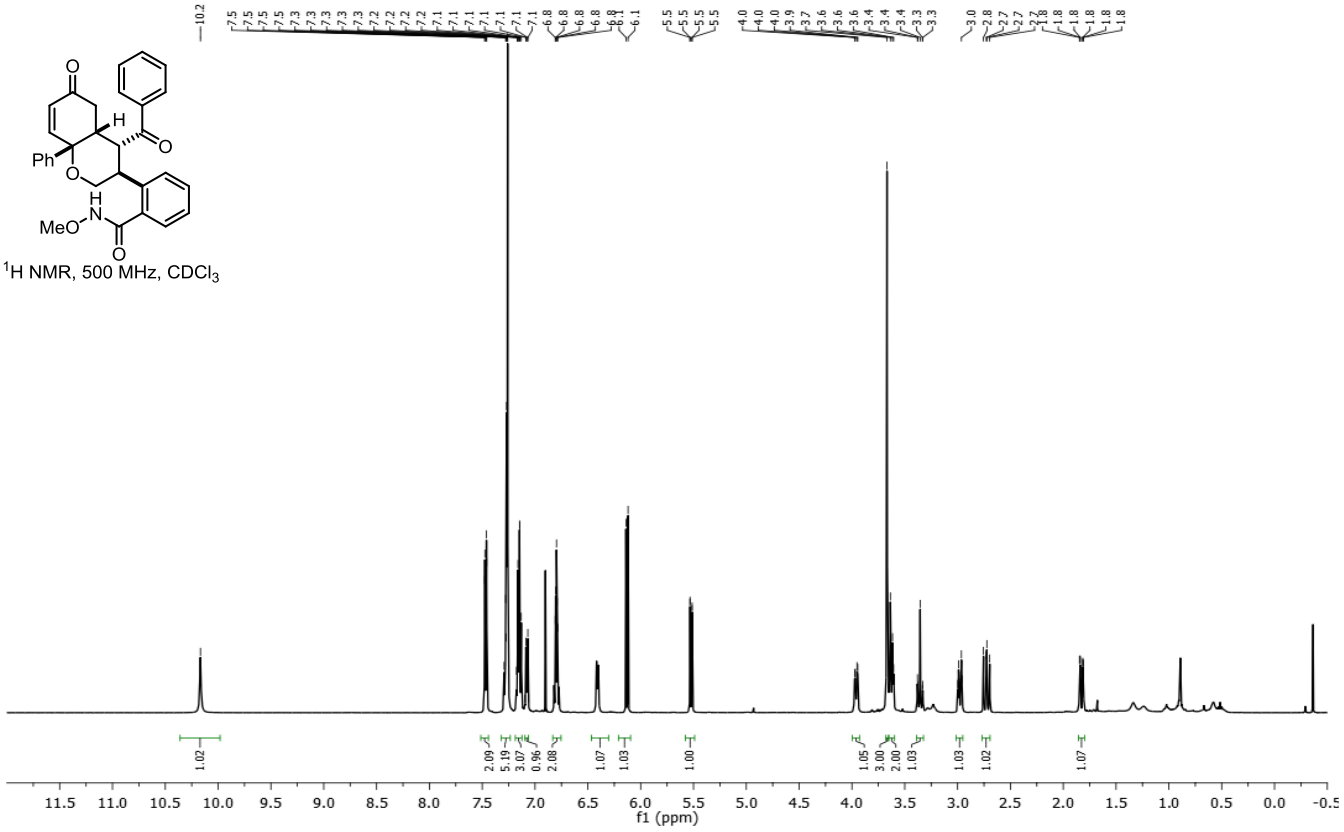


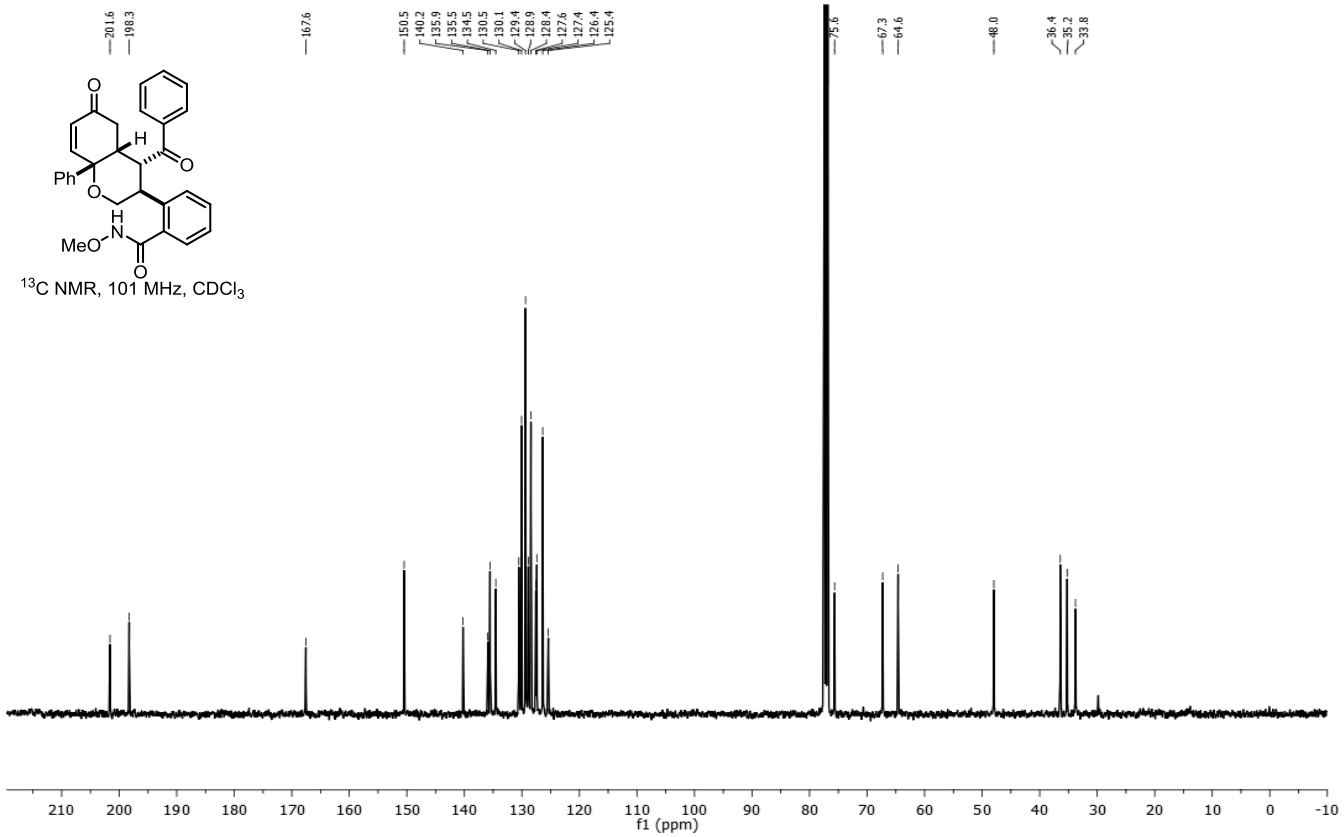
2-(4-Benzoyl-8a-isopropyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ai):



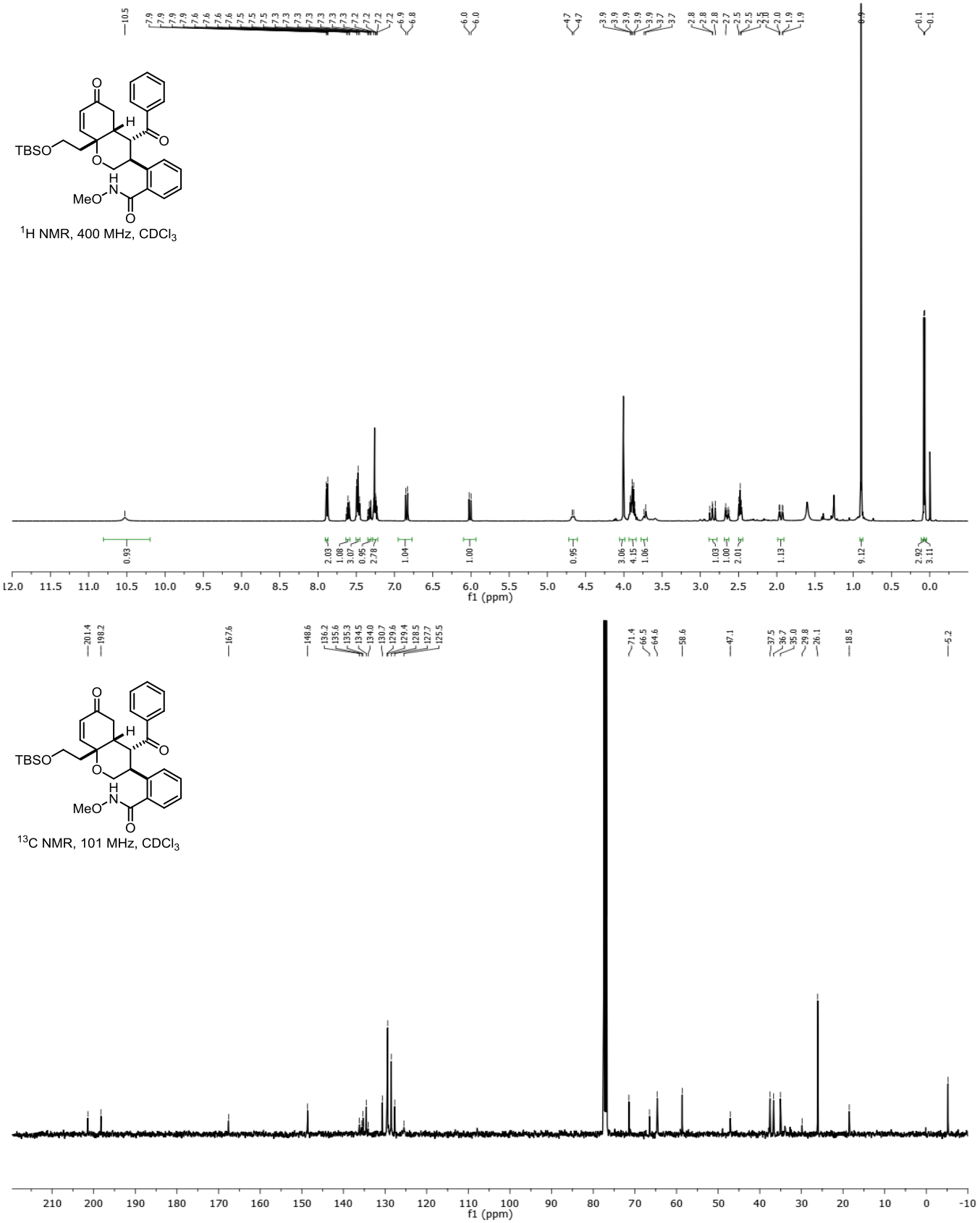


2-(4-Benzoyl-6-oxo-8a-phenyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3aj):

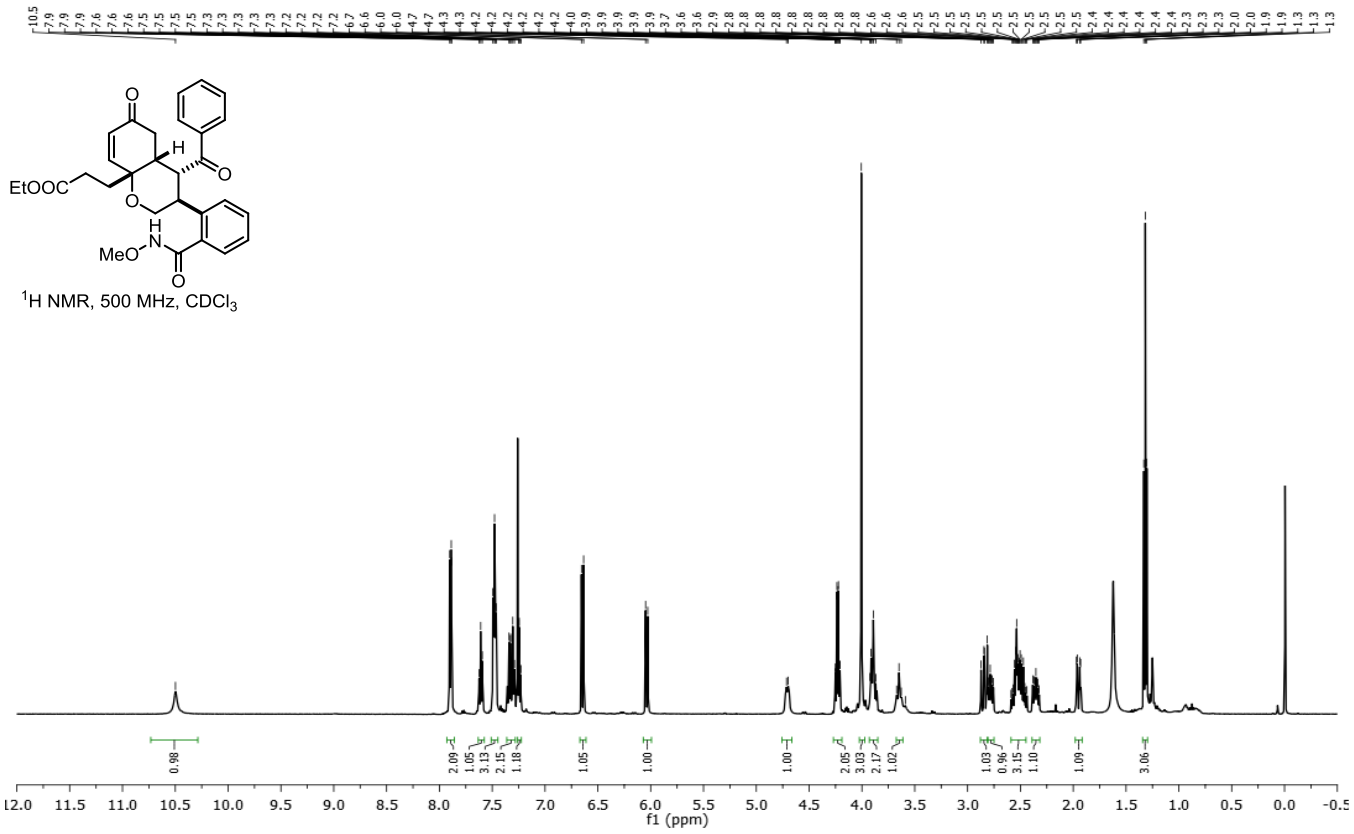


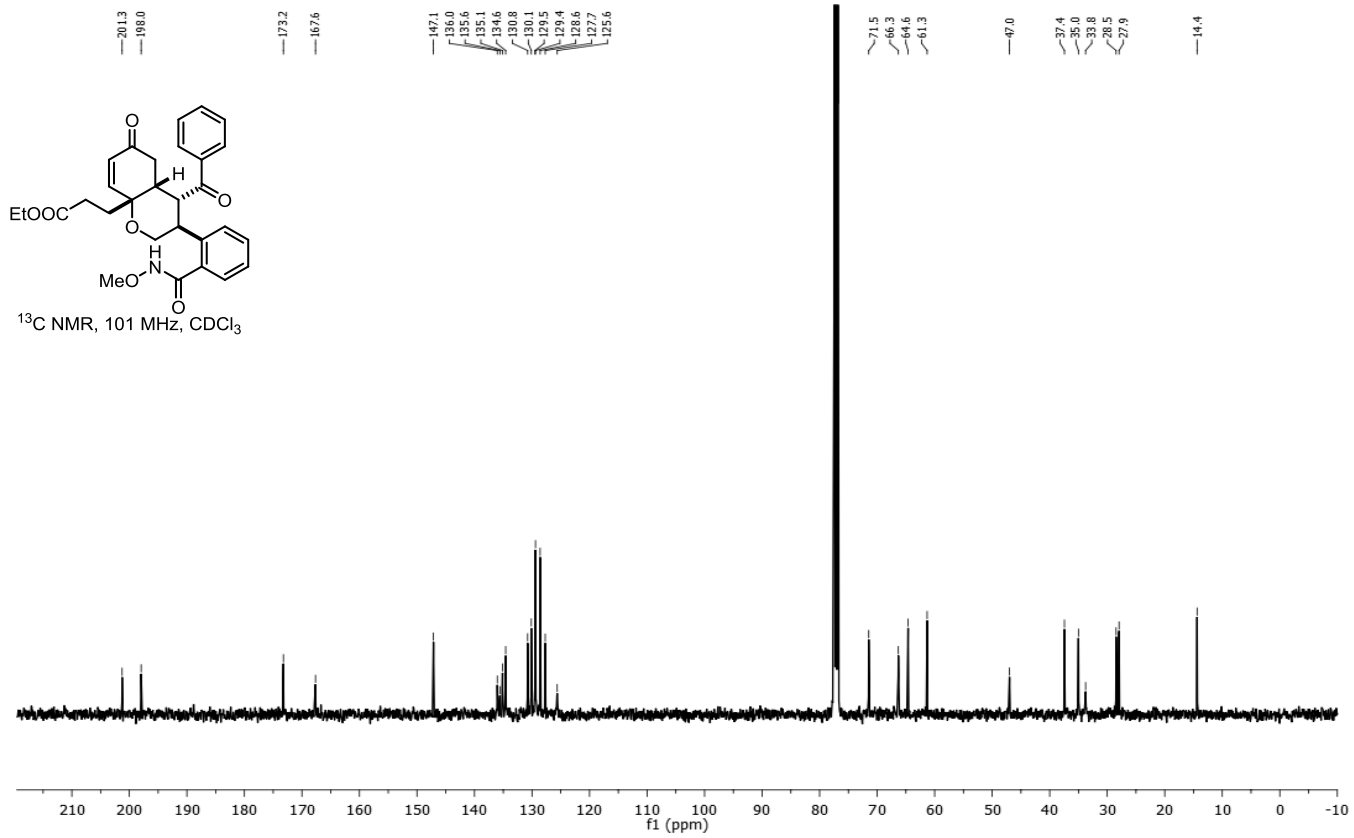


2-(4-Benzoyl-8a-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3ak):

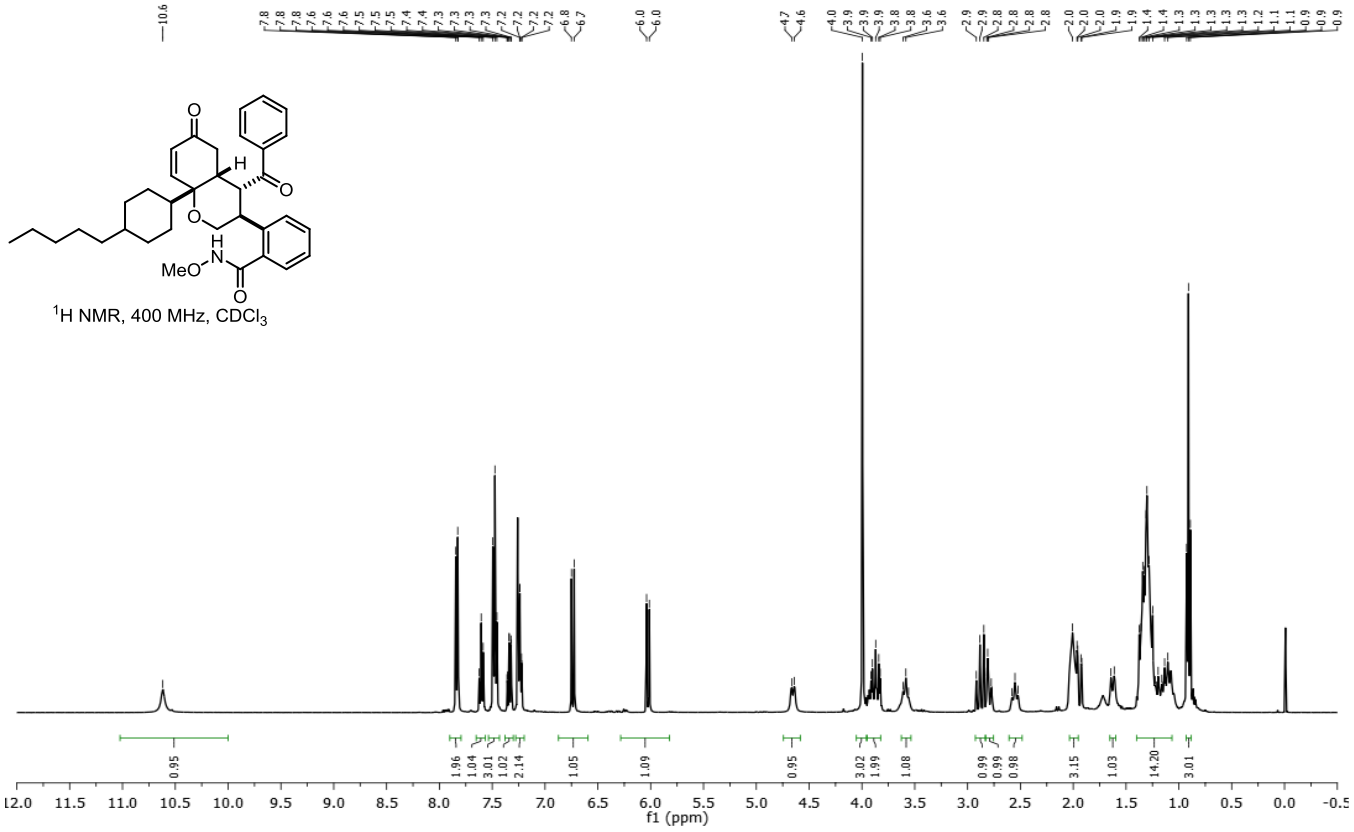


Ethyl 3-(4-benzoyl-3-(2-(methoxycarbamoyl)phenyl)-6-oxo-2,3,4,4a,5,6-hexahydro-8a*H*-chromen-8a-yl)propanoate (3al):

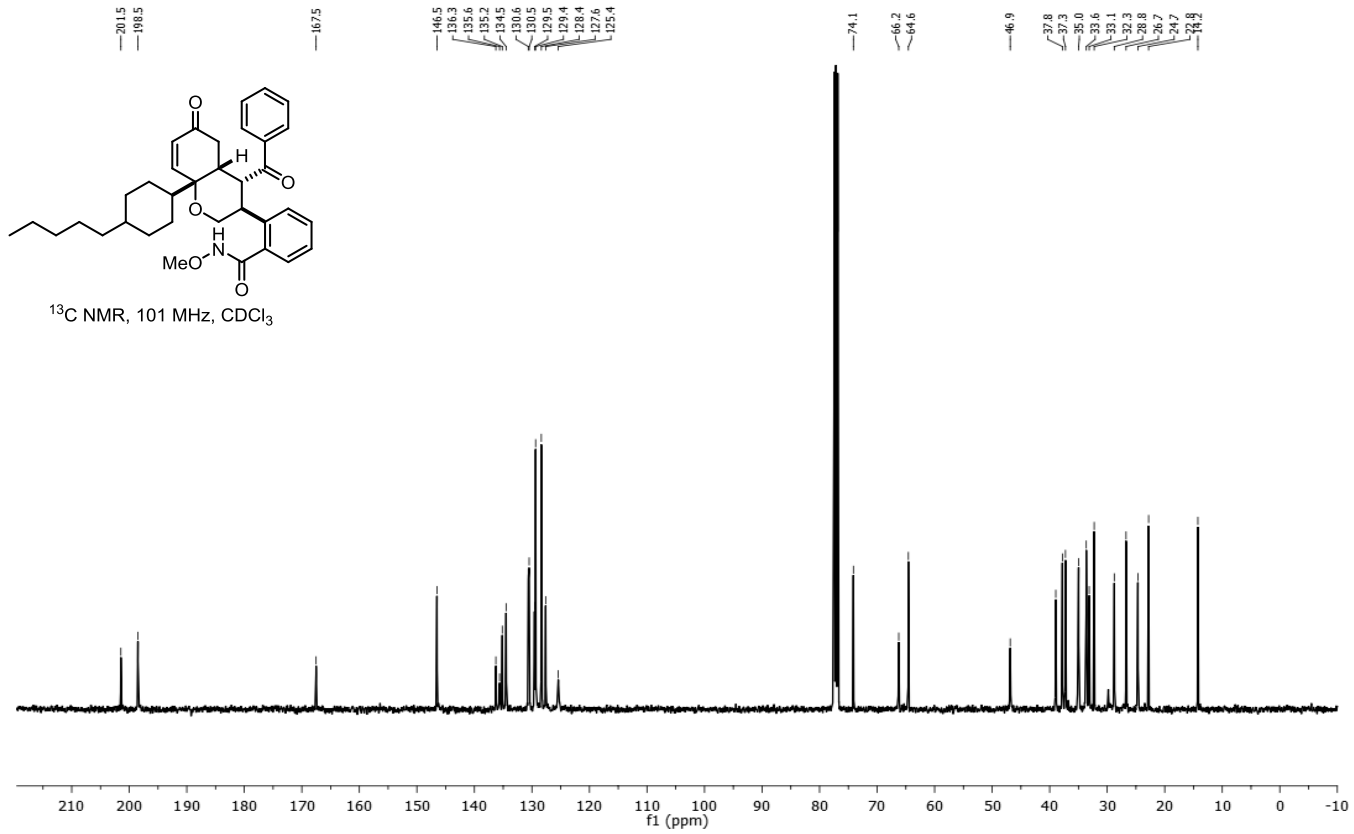




2-(4-Benzoyl-6-oxo-8a-(4-pentylcyclohexyl)-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (3am):

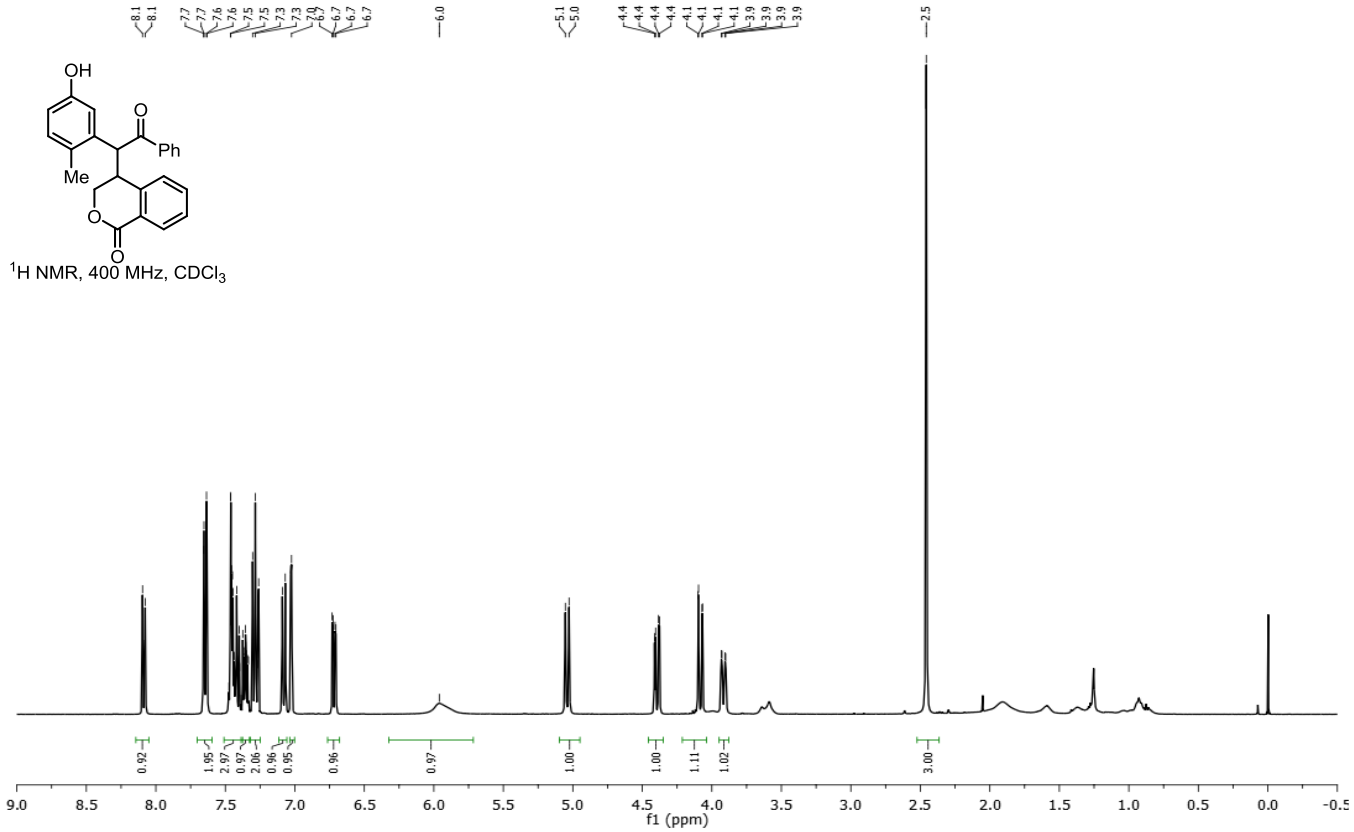


^{1}H NMR, 400 MHz, $CDCl_3$

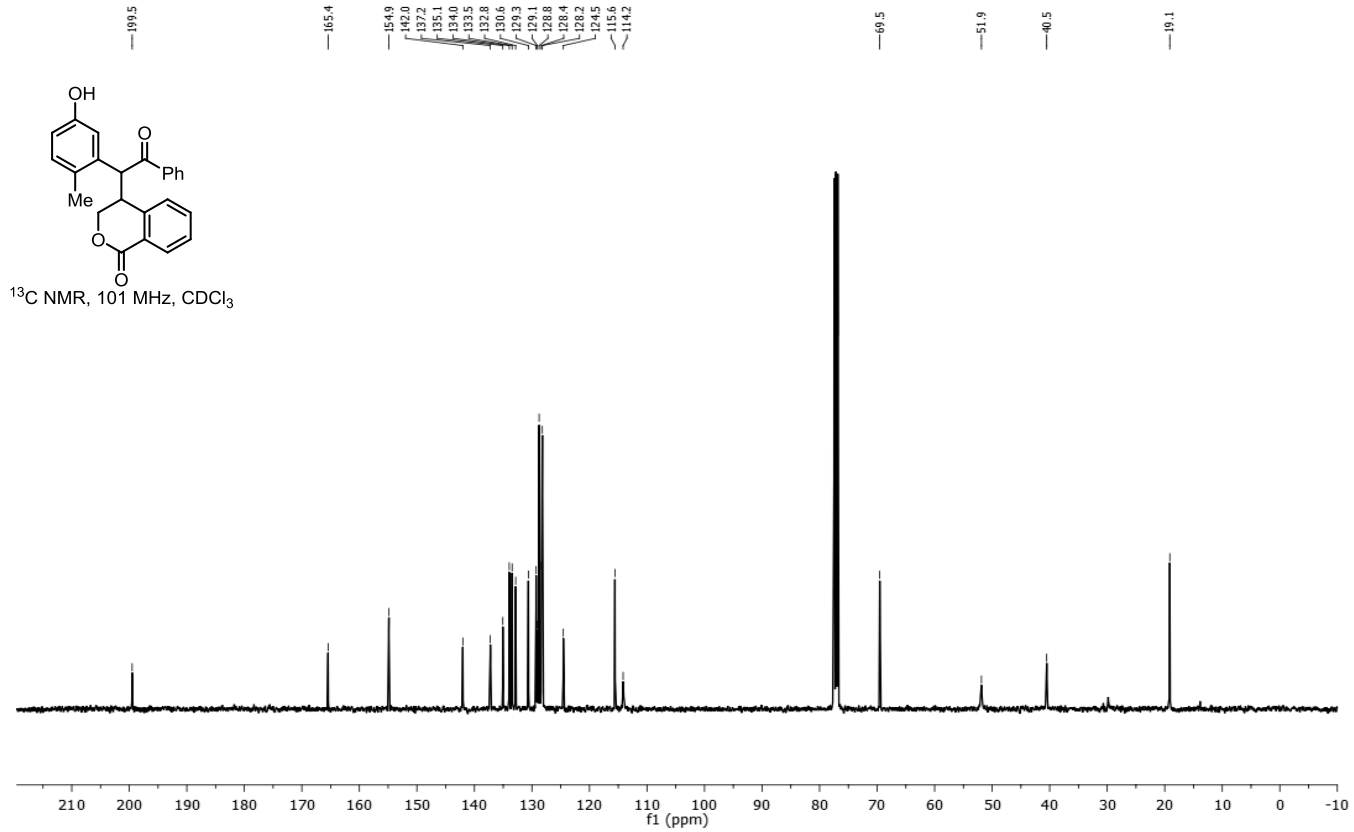


^{13}C NMR, 101 MHz, $CDCl_3$

4-(1-(5-Hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4a):

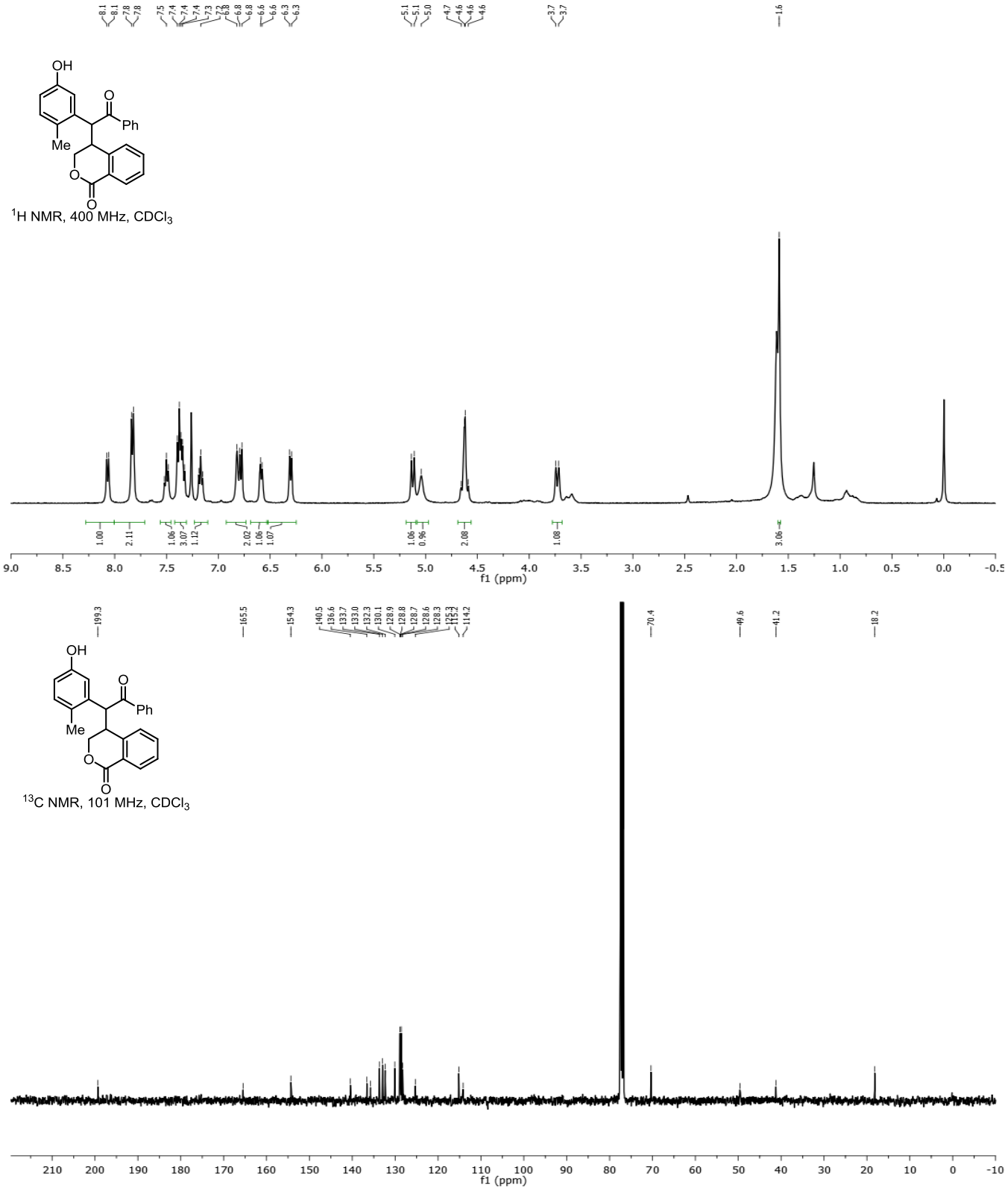


^{1}H NMR, 400 MHz, $CDCl_3$

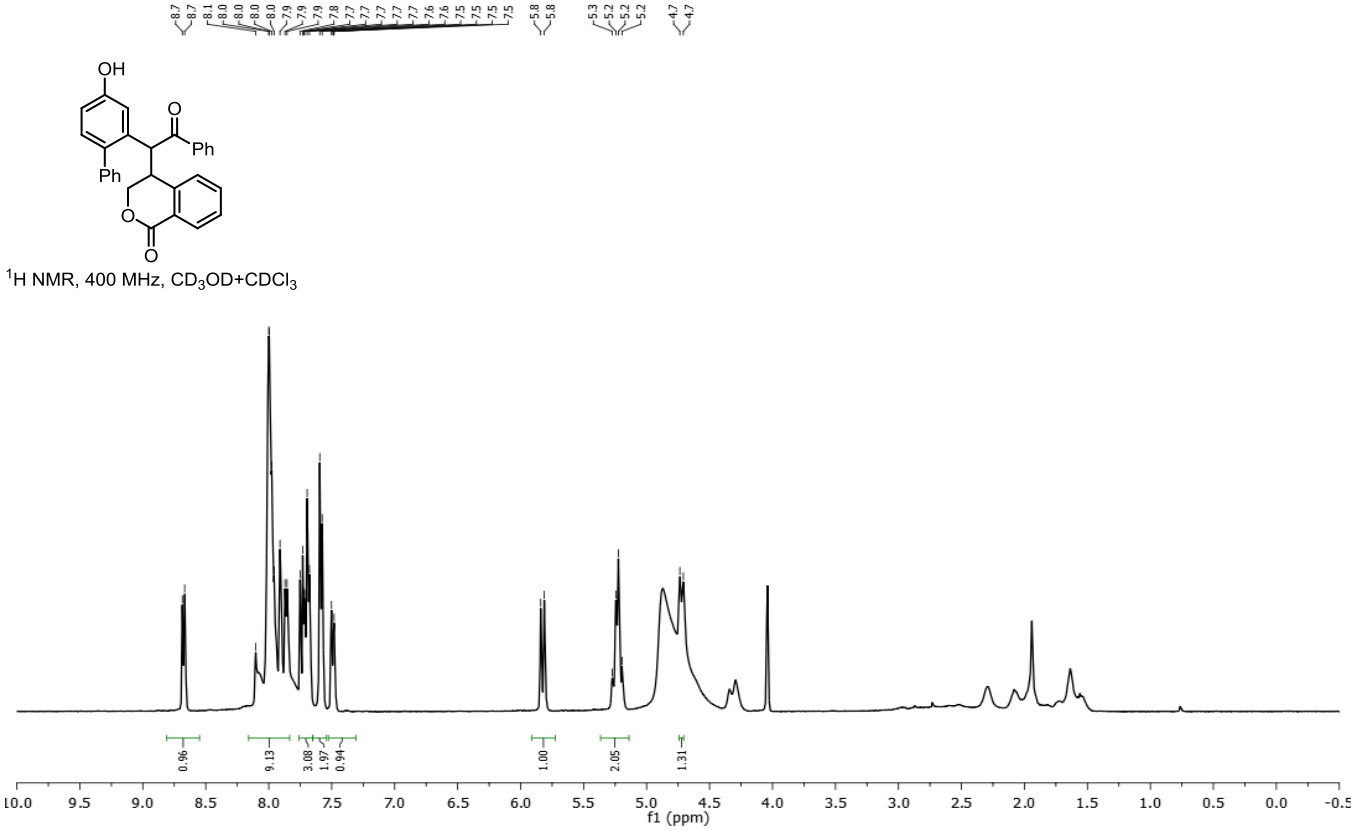


^{13}C NMR, 101 MHz, $CDCl_3$

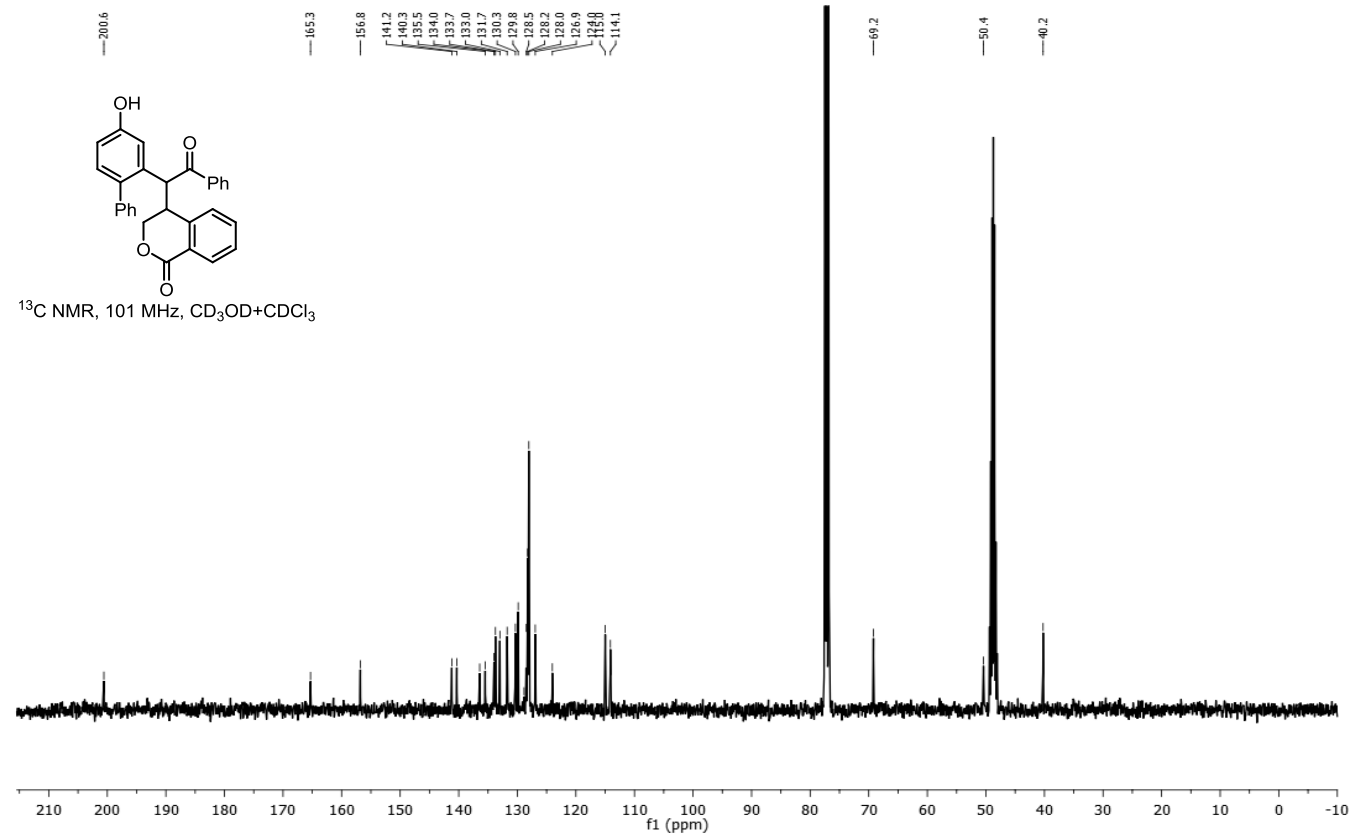
4-(1-(5-Hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (Minor Isomer)(4a'):



4-(1-(4-Hydroxy-[1,1'-biphenyl]-2-yl)-2-oxo-2-phenylethyl)isochroman-1-one (4b):

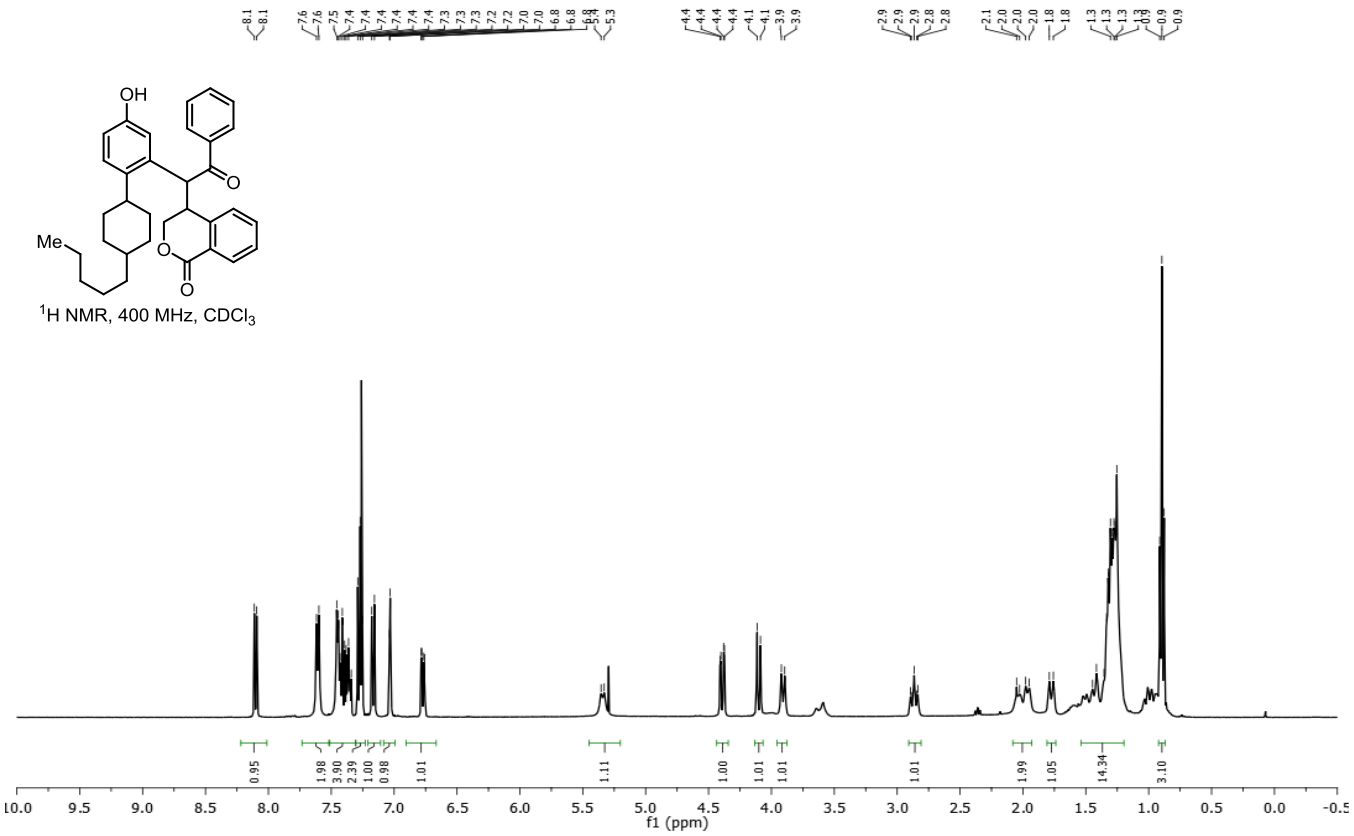


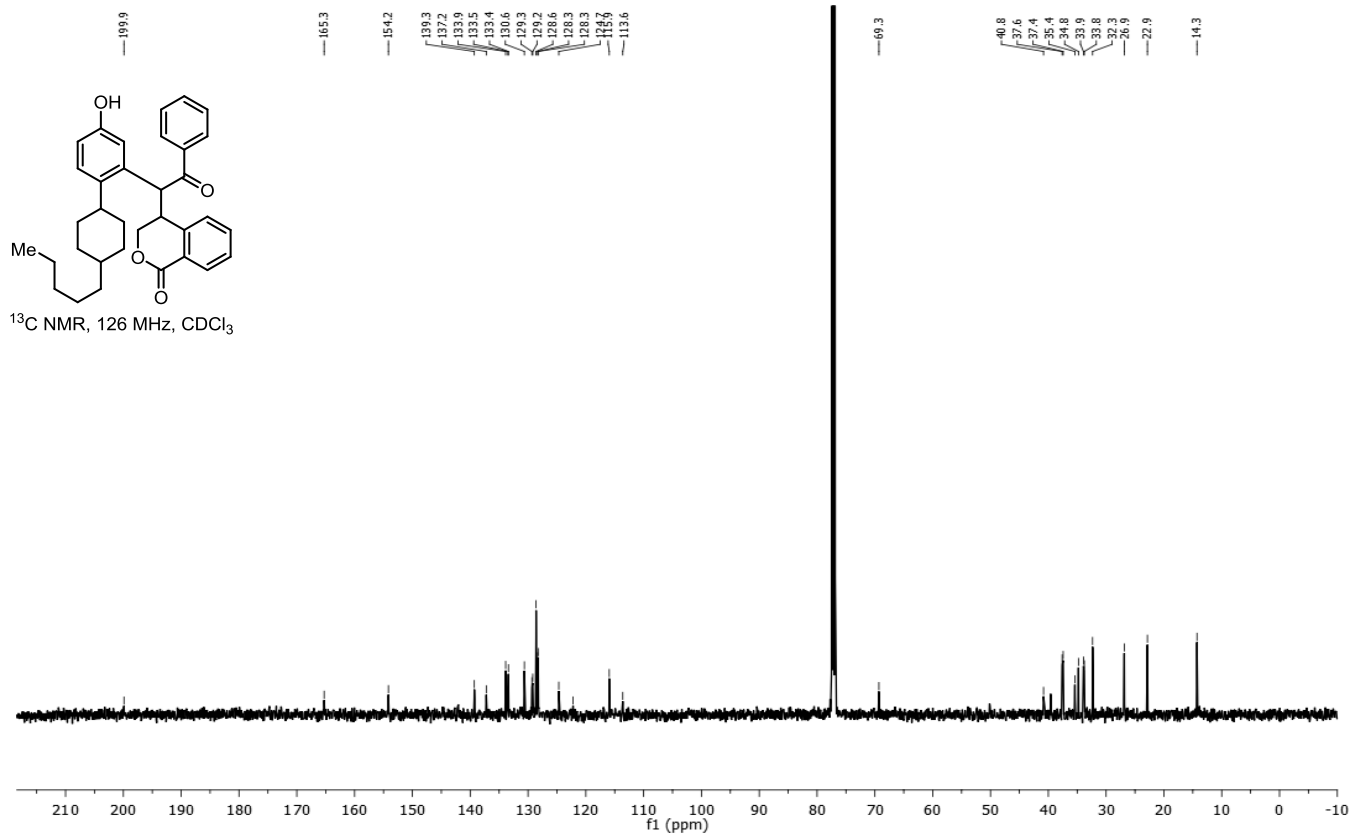
^{1}H NMR, 400 MHz, $CD_3OD+CDCl_3$



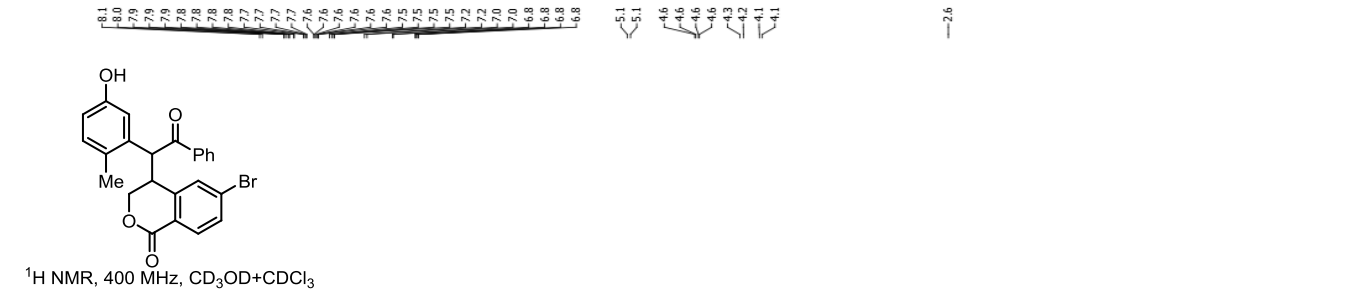
^{13}C NMR, 101 MHz, $CD_3OD+CDCl_3$

4-(1-(5-Hydroxy-2-(4-pentylcyclohexyl)phenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4c):

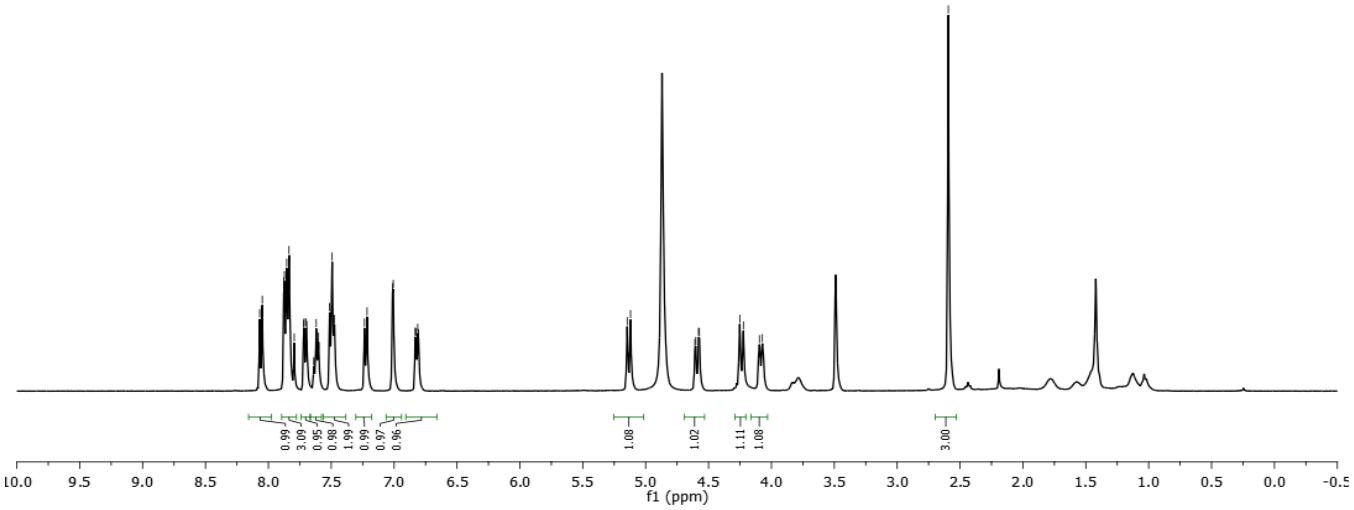


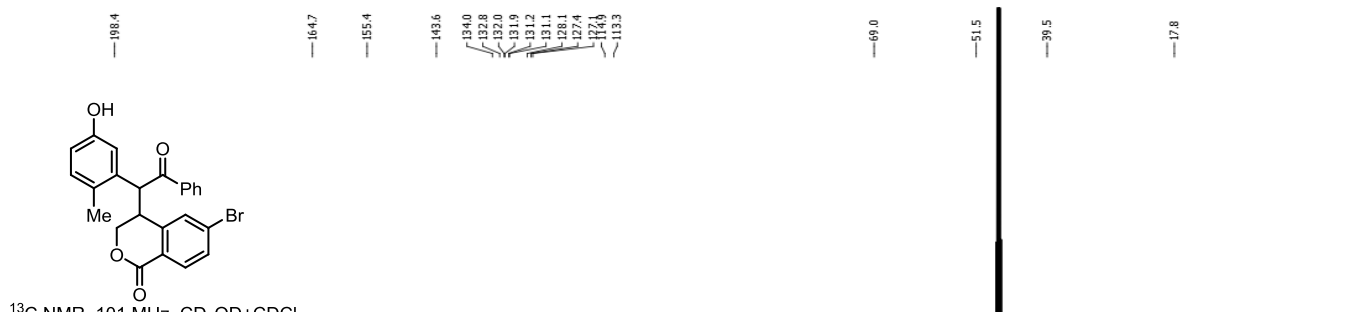


6-Bromo-4-(1-(5-hydroxy-2-methylphenyl)-2-oxo-2-phenylethyl)isochroman-1-one (4d):



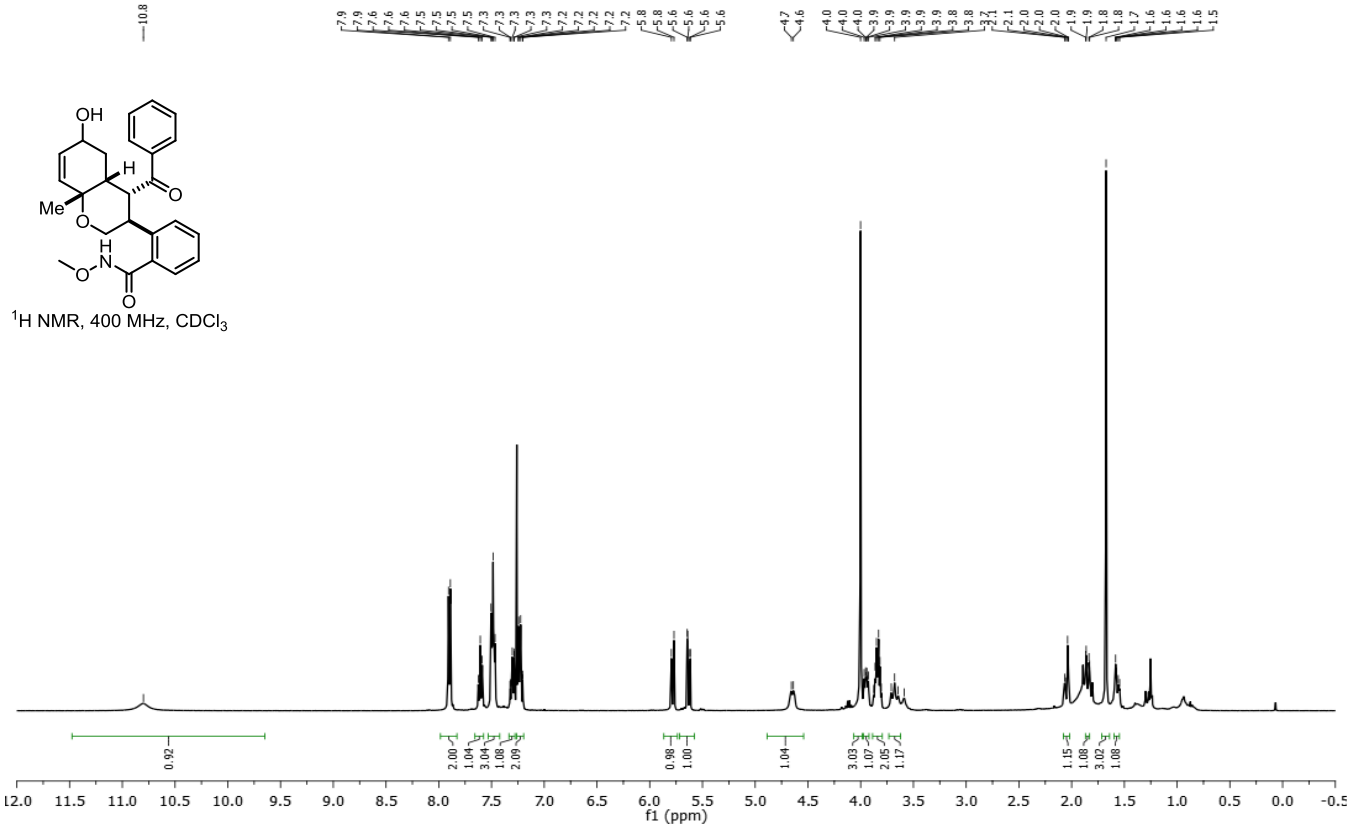
^{1}H NMR, 400 MHz, $CD_3OD+CDCl_3$

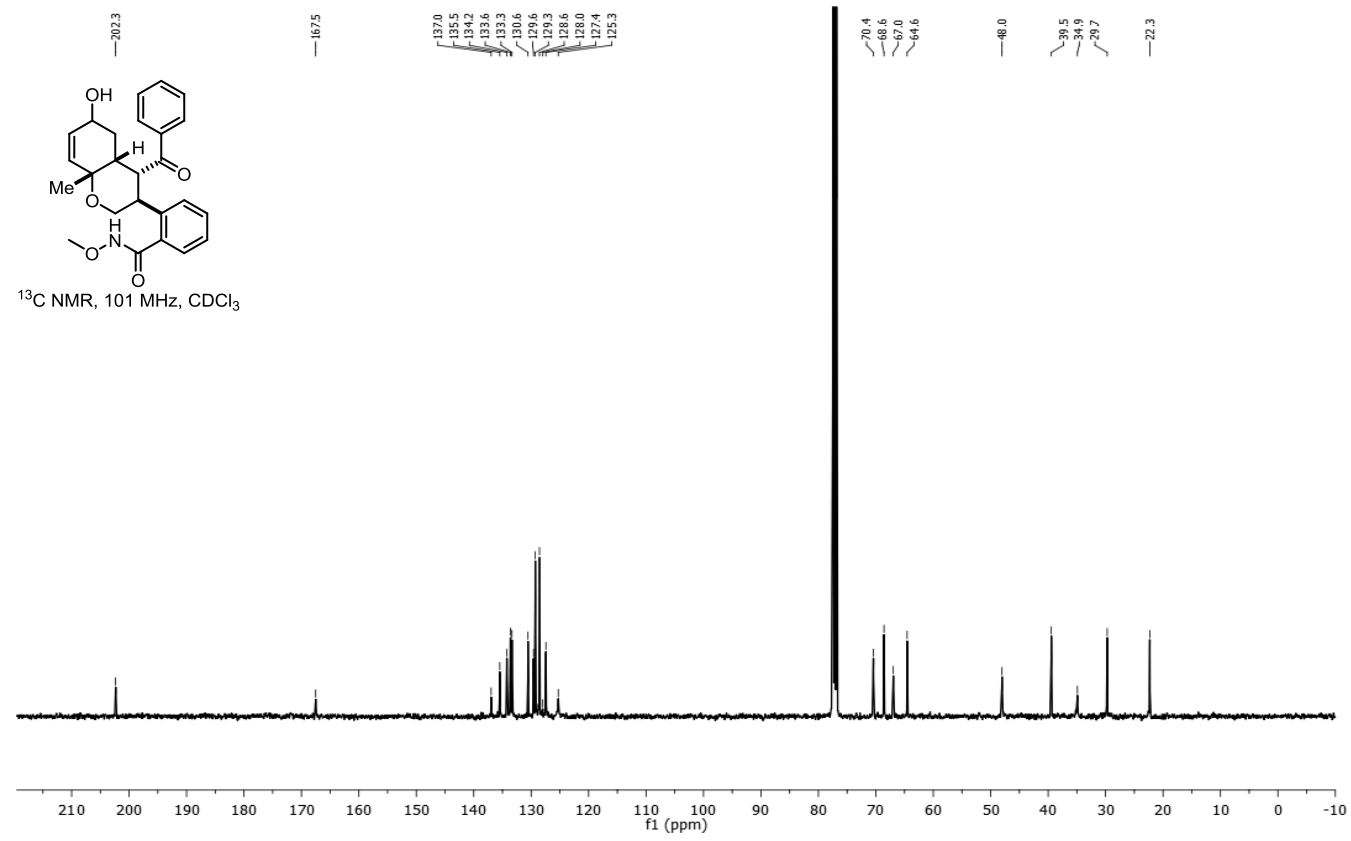




^{13}C NMR, 101 MHz, $CD_3OD+CDCl_3$

2-(4-Benzoyl-6-hydroxy-8a-methyl-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-N-methoxybenzamide (5):





2-(4-Benzoyl-7-bromo-8a-methyl-6-oxo-3,4,4a,5,6,8a-hexahydro-2*H*-chromen-3-yl)-*N*-methoxybenzamide (6):