Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

for

Anion-Accelerated Asymmetric Nazarov Cyclization: Access to Vicinal All-Carbon Quaternary Stereocenters

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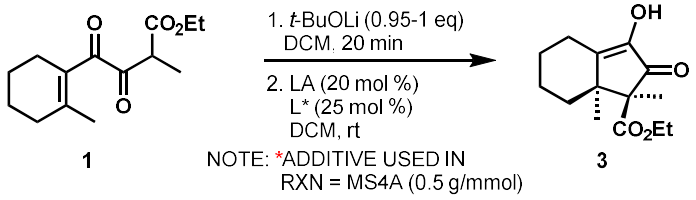
1. General Methods

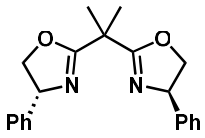
All moisture and air sensitive reactions were performed under an argon atmosphere in oven-dried or flame-dried glassware. Reactions that required heating where carried with a stir-hot plate using a heated external oil bath. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried using a Glass Contour solvent purification system. Acetonitrile (MeCN) was purchased from Fisher (HPLC grade) and used without further purification. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Varian Mecury-300 (300 MHz/75 MHz), Agilent 400 DD2 (400 MHz/100 MHz), or Agilent 600 DD2 (600 MHz/150 MHz) spectrometer at ambient temperature. Chemical shifts are reported in parts per million (ppm) and are referenced to the solvent (***e.g.,*** δ 7.26 for $CHCl_3$; δ 77.0 for $CDCl_3$). ^{19}F NMR spectra were measured on a Varian Mercury-300 (282 MHz), Varian INOVA-500 (470 MHz), or an Agilent 600 DD2 (565 MHz) spectrometer and reported in ppm relative to TFA (−76.5 ppm). Multiplicities are indicated as follows: br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), sext (sextet), sept (septet), etc. or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a ThermoFisher Nicolet Summit FTIR spectrophotometer. Optical rotations ($[\alpha]_D$) were measured on a JASCO-DIP-370 polarimeter. High performance liquid chromatography (HPLC) analyses were performed using a Thermo-Fisher UltiMate 3000 instrument using Chiralpak AD-H, OD-H, or OJ-H columns (4.6 mm x 250 mm, UV detection at 261 nm) and *i*-PrOH and hexane as eluents. High-resolution mass spectra (HRMS) were obtained with an Agilent 1100 quaternary LC system or were measured at the University of Illinois Mass Spectrometry Laboratory (Dr. Furong Sun, Dr. Xiuli Mao, and Dr. Haijun Yao). Melting points were recorded on a DigiMelt MPA160 instrument and are uncorrected. Thin layer chromatography (TLC) was performed on glass plates, 250 μm, particle size 5–17 μm, pore size 60 Å. All reactions were monitored by TLC and analyzed under UV (254 and/or 365 nm) light and visualized using either PAA, $KMnO_4$, PMA, CAM, or DNP stains. Flash column chromatography was performed on silica gel, 200–400 mesh or premium silica gel, 60 Å, 40–75 μm. Purity and homogeneity of all materials was determined by TLC, ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, and LCMS.

2. *Initial Cyclization Results*

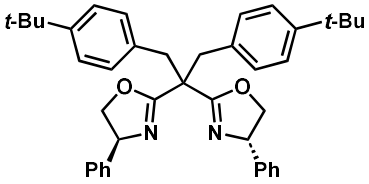
Below is a partial list of results of our initial survey of catalysts on the cyclization of diketoester **1** focused on metal BOX/PyBOX catalyst systems and is shown below. We were unable to improve the e.r. of cyclopentenone **3** upon further optimization of the reaction conditions using the best catalysts shown in the below list.



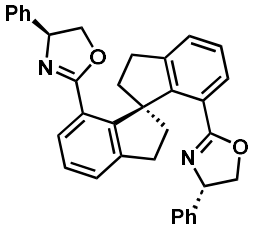
1 3



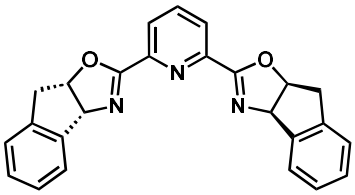
$Cu(OTf)_2$: 55:45 er
$Zn(OTf)_2$: 52:48 er
$Yb(OTf)_3$: 50:50 er
$Mg(OTf)_2$: 50:50 er
(in PhMe)



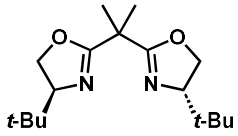
$Cu(OTf)_2$: 41:59 er
$Zn(OTf)_2$: 46:54 er



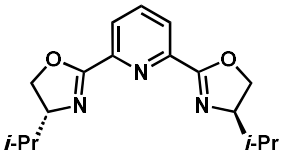
$Cu(OTf)_2$: 50:50 er
$Zn(OTf)_2$: 48:52 er



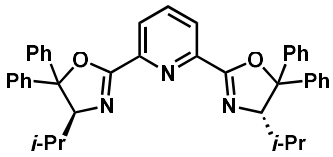
$Cu(OTf)_2$: 53:47 er
$Zn(OTf)_2$: 48:52 er



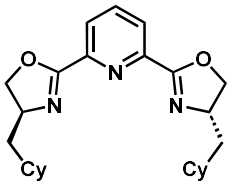
$Cu(OTf)_2$: 62:38 er
$Zn(OTf)_2$: 38:62 er
Note: No base used



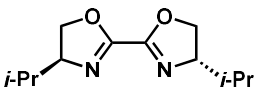
$Cu(OTf)_2$: 60:40 er
$Zn(OTf)_2$: 54:46 er
$Cu(OTf)_2$* : 63:37, 66:34, 65:35 er



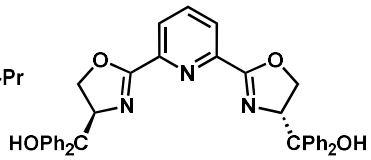
$Cu(OTf)_2$: 40:60 er
$Zn(OTf)_2$: 44:56 er



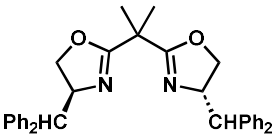
$Cu(OTf)_2$: 43:57 er
$Zn(OTf)_2$: 46:54 er



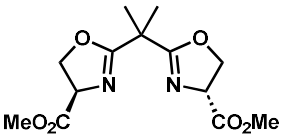
$Cu(OTf)_2$*: 51:49 er



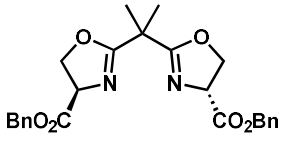
$Cu(OTf)_2$*: 47.5:52.5 er



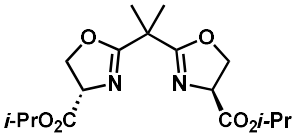
$Cu(OTf)_2$*: 48:52 er



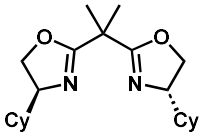
$Cu(OTf)_2$*: 39:61 er



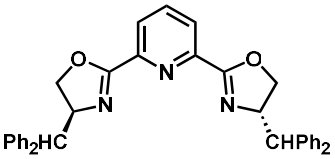
$Cu(OTf)_2$*: 40:60 er



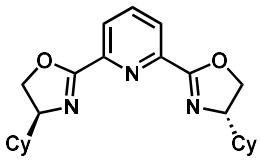
$Cu(OTf)_2$*: 66:34 er



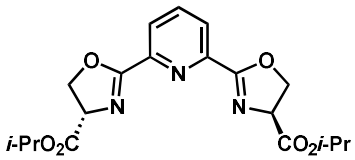
$Cu(OTf)_2$*: 46:54 er



$Cu(OTf)_2$*: 46:54 er



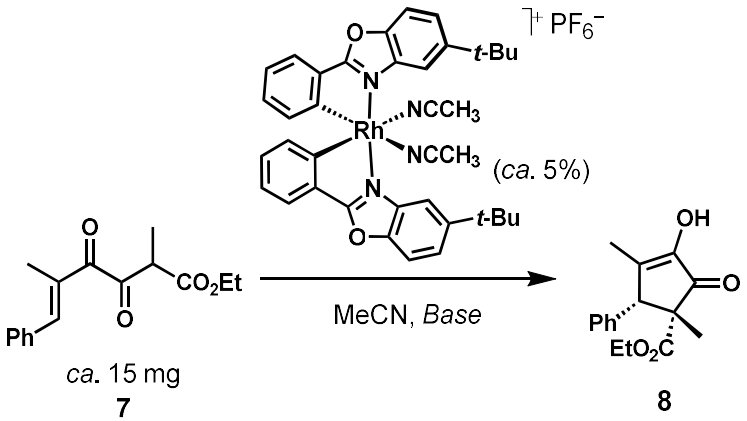
$Cu(OTf)_2$*: 35.5:64.5 er



$Cu(OTf)_2$*: 52:48 er

We decided to refocus our reaction screening efforts using diketoester **7** as the substrate since it is more easily accessible from commercially available starting materials and is more activated towards cyclization. Our initial screening of conditions for the cyclization of compound **7** is shown in **Table S1**. We chose to use Meggers' catalyst (Λ-Rh*O*t*Bu, *ca*. 5 mol%) in MeCN as the starting point for the cyclization conditions. First, in the absence of base the reaction was slow and stoichiometric with respect to the Rh-catalyst (entry 1). The trace amount of cyclopentenone **8** that was produced had an e.r. of 86/14. The reaction did not progress upon prolonged reaction times or heating. In a separate experiment, diisopropylethylamine was added at the outset to the reaction mixture. The reaction went to completion at room temperature overnight and resulted in cyclopentenone **8** with an e.r. of 86/14, regardless if the amine base was used stoichiometrically or catalytically (entries 2 and 3). Performing the reaction with either catalytic dicyclohexylamine or DABCO (entries 4 and 5) did not change the outcome of the reaction. The use of *t*-BuOLi as base led to erosion of the e.r. of cyclopentenone **8** (entries 6 and 7), for the reasons described in the manuscript. Based on the above experiments we decided to use diisopropylethylamine as the base for this reaction.

Table S1: Initial results and base screen.



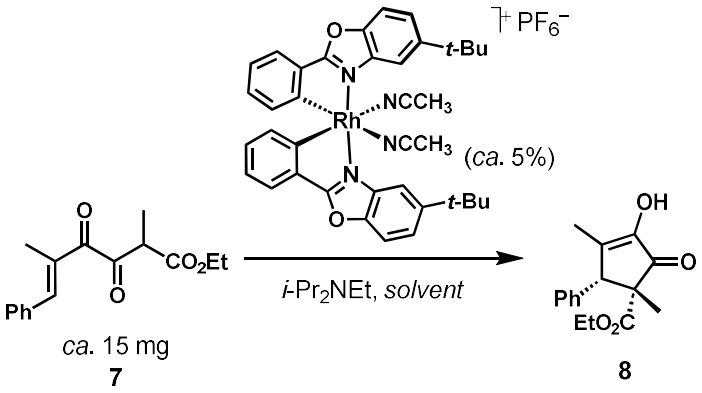
Entry	Base	e.r.
1	None[a]	86/14
2	*i*-Pr$_2$NEt (1.0 eq)	86/14
3	*i*-Pr$_2$NEt (0.2 eq)	86/14
4	NMeCy$_2$ (0.2 eq)	86/14
5	DABCO (0.2 eq)	86/14
6	*t*-BuOLi (1.0 eq)	56/44
7	*t*-BuOLi (0.2 eq)	78/22

[a] reaction was not catalytic.

3. *Solvent Screen*

We were encouraged by the initial results of the catalytic cyclization and e.r. of the cyclopentenone **8**. We wanted to determine if the e.r. could be improved by a change of solvent in both the presence and absence of *i*-Pr_2NEt. **Table S2** lists the results of the solvent screen. In the presence of base, the e.r. of **8** had a strong correlation to the dielectric constant[1] of the reaction solvent. In polar, aprotic solvents (DMSO, MeCN, DMF) the e.r. of **8** was much higher than in non-polar solvents (EtOAc, PhMe, isooctane). However, in the absence of base the e.r. of **8** was less affected by the solvent polarity (compare entries 2, 8, 10–12), but the reaction was not catalytic. Interestingly, the reaction was catalytic in the absence of base when carried out in DMF or polar protic solvents (entries 3, 14, and 15), but the e.r. of **8** was poor.

Table S2: Solvent screen.



Entry	Solvent	*er* with base	*er* without base	ε_r
1	DMSO	86/14	-	47.2
2	MeCN	86/14	86/14	36.6
3	DMF	83/17	79/21[a][b]	38.3
4	EtCN	80/20	-	29.7
5	Acetone	78/22	-	21.0
6	PhCN	76/24	-	25.9
7	EtOAc	70/30	-	6.1
8	PhMe	61/39	86/14	2.4
9	Isooctane	59/41	-	1.9
10	PhF	-	86/14	5.5
11	DCM	-	85/15	8.9
12	$CHCl_3$	-	86/14	4.8
13	THF	-	74/26	7.5
14	EtOH	-	71/29[a]	25.3
15	*i*-PrOH	-	73/27[a]	20.2

[a] these reactions were catalytic in the absence of *i*-Pr_2NEt. [b] The DMF was used as is and was most likely not dimethylamine free.

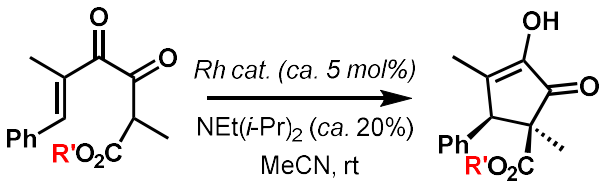
From these results we hypothesized that when an amine base is employed in polar, aprotic solvents the conjugate acid of the amine is completely dissociated from the keto-enolate of **7** and a bidentate chelate between the keto-enolate of **7** and the Rh-catalyst is formed (see manuscript). This bidentate chelation is essential in order to transfer asymmetry effectively. As the solvent polarity decreases, less bidentate chelation occurs as a result of stronger ion pairing of the amine conjugate acid and the enolate. This competition between monodentate and bidentate chelation increasingly favors the monodentate chelate in very non-polar solvents. It is interesting that in polar, protic solvents a catalytic reaction in the absence of base occurs. This is likely a result of

hydrogen-bonding between **8** and the solvent, allowing for decomplexation of the cyclopentenone from the Rh center, whereas in aprotic solvents a strong complex between the product and Rh exists and is not as easily displaced (in the absence of added base). Based on these results, we chose to keep MeCN as the solvent since it provided good e.r. of **8** in the presence or absence of base, resulted in a fast catalytic reaction in the presence of base, and is relatively easy to keep anhydrous.

4. Catalyst & Ester Screens

The results of our catalyst and ester screen are shown in **Table S3**. We started our study by first screening Rh-catalysts for the cyclization of compound **7**. See **Scheme S1** (section 5) for the structures of the catalysts used. The best results were obtained with Rh-catalysts that had a tertiary alkyl side arm (entries 1 and 2, e.r. 86/14). Other catalysts were much less effective and no clear trend could be observed. Next, we changed the size of the ester substituent. We screened a number of catalysts using the phenyl ester **7a**. In general, the e.r. of cyclopentenone **8a** was lower than that of cyclopentenone **8**. The larger size of the phenyl ester apparently introduces unfavorable steric interactions that precludes discrimination of the two helical enolate-conformers in the pocket of the catalyst. Lastly, we screened the methyl ester **7b** using the three best Rh-catalysts found from screening ethyl ester **7** (entries 1-3). We observed minor improvement in the e.r. with the smaller methyl ester. Based on these results, we used Λ-Rh catalyst **11** in further screens.

Table S3: Catalyst and ester screening.



ca. 15 mg

R' = Et, **7**
Ph, **7a**
Me, **7b**

R' = Et, **8**
Ph, **8a**
Me, **8b**

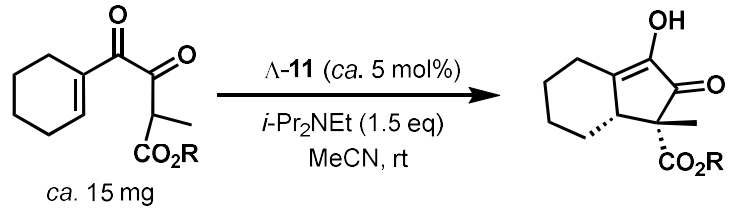
Entry	Rh cat.	*er* (R')		
		Me	Et	Ph
1	Λ-**11**[a]	**88/12**	**86/14**	-
2	Λ-**C18**	**86/14**	**86/14**	77/23
3	Δ-**C8**	**14/86**	19/81	-
4	Δ-**C15**	-	17/83	19/81
5	Δ-**C11**	-	20/80	-
6	Δ-**C9**	-	20/80	29/71
7	Δ-**C13**	-	25/75	-
8	Δ-**C14**	-	26/74	28/72
9	Λ-**C19**	-	72/28	59/41
10	Δ-**C10**	-	30/70	25/75
11	Δ-**C12**	-	31/69	-
12	Δ-**C16**	-	36/64	40/60
13	Δ-**C17**	-	47/53	-

[a] Use of either TFA salt of PF_6 salt gave identical results.

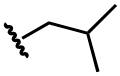
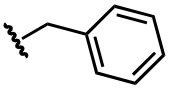
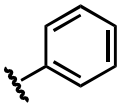
Since we were more interested in the all-aliphatic cases, we used Λ-Rh catalyst **11** to study the cyclization of diketoester **DK16a** using the standard conditions. Cyclopentenone **28a** was formed in 92:8 e.r. Changing the ethyl ester to a phenyl ester also led to a marked decrease in e.r. of cyclopentenone **28c** (80:20 e.r.). Moving the bulk one carbon atom further on the ethyl ester chain as in isobutyl or benzyl esters **DK16b** and **DK16**, respectively, led to an improved e.r. of 95/5 for both cyclopentenones **28b** and **28**. Bulk at the end of the ethyl chain provides a beneficial steric interaction with Rh catalyst **11**.

We chose to use the benzyl ester for further substrate screening since it led to an improved e.r. for the trisubstituted case shown here, can be easily removed in a number of different ways, and also for the reasons discussed in the manuscript regarding the cyclization of diketones **9**.

Table S4: Ester screening.

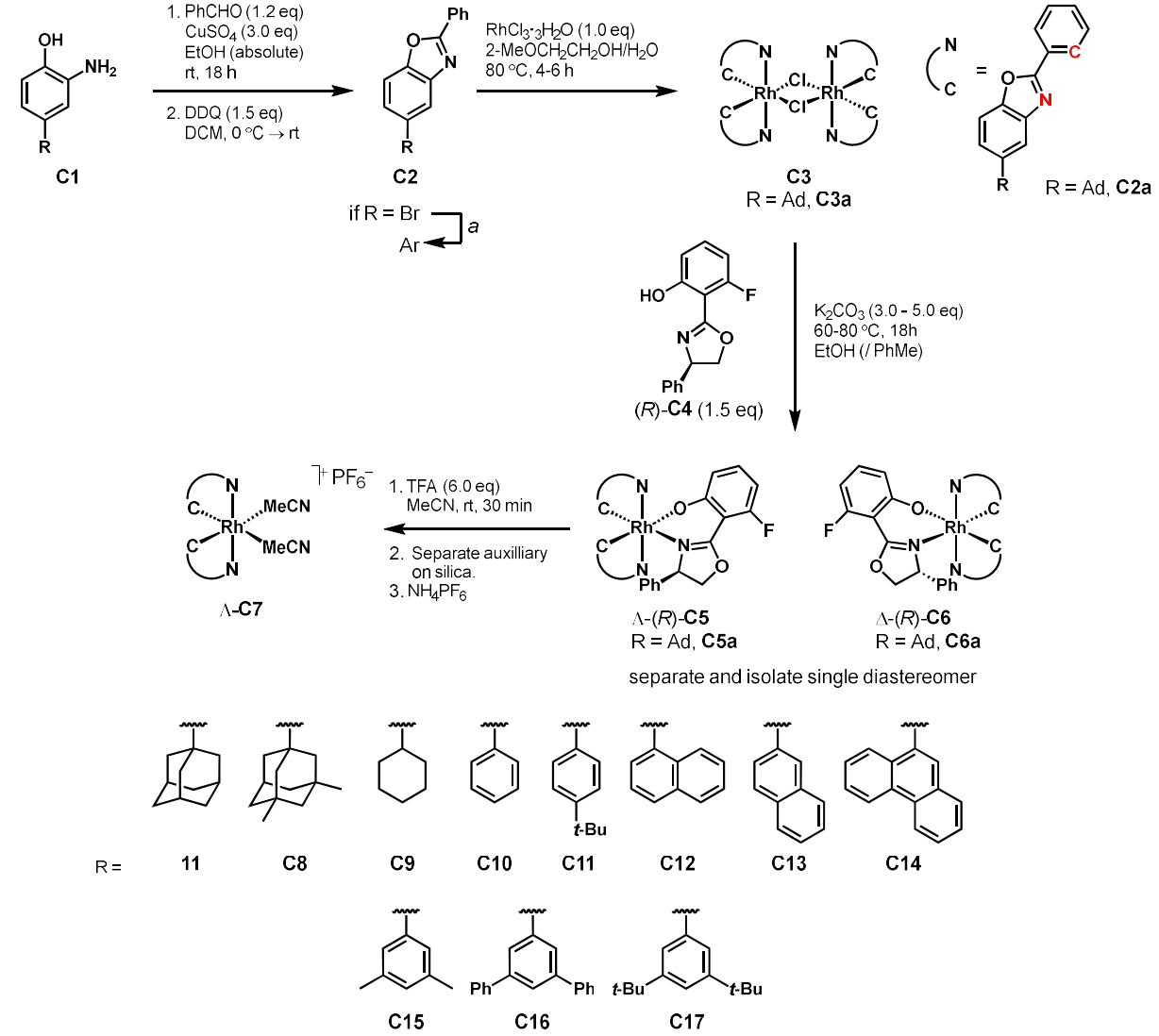


ca. 15 mg

	R	e.r.	
DK16a		92/8	**28a**
DK16b		**95/5**	**28b**
DK16		**95/5**	**28**
DK16c		80/20	**28c**

5. *Synthesis of Rh Catalysts*

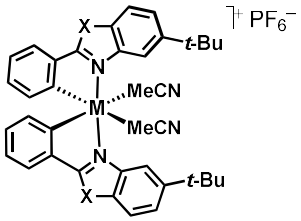
The general synthetic scheme used to prepare the Rh-catalysts used in this study are shown in **Scheme S1**.



Scheme S1: Synthesis of chiral-at-rhodium complexes. a. For **C11–C17**: $Pd_2(dba)_3$ (5 mol%), PPh_3 (40 mol%), $RB(OH)_2$ (2.0 equiv), Cs_2CO_3 (4.0 equiv), PhMe, 100 °C; for **C9**: $Pd(OAc)_2$ (5 mol%), CPhos (15 mol%), CyZnI·LiCl (2.0 equiv), THF, rt.

Complexes **C18**[2] and **C19**[3] were prepared according to Meggers' protocols**.**

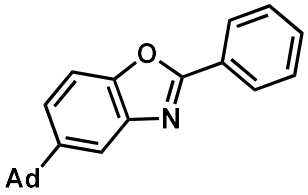
Λ-**C18** M = Rh, X = O
Λ-**C19** M = Rh, X = S



*Synthesis of Chiral-at-Rhodium Complex **11***

The general procedure follows that described by Meggers[3] with some minor changes.

Preparation of Oxazole:



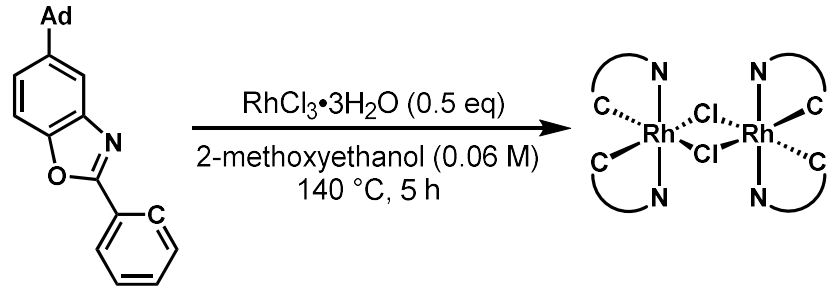
5-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-phenylbenzo[*d*]oxazole (**C2a**)

Starting from commercially available 4-(1-adamantyl)-2-aminophenol (Combi-blocks).

A solution of benzaldehyde (109 mg, 1.03 mmol, 1.0 equiv) and 4-(1-adamantyl)-2-aminophenol (300 mg, 1.23 mmol, 1.2 equiv) in absolute ethanol (15 mL) was added anhydrous $CuSO_4$ (247 mg, 1.55 mmol, 1.5 equiv) and a spatula tip of *p*-TsOH. The reaction mixture was stirred vigorously at room temperature overnight, filtered through Celite, and washed with DCM. After concentration, the crude solid was placed under an inert atmosphere and dissolved in DCM (30 mL) and cooled to 0 °C. DDQ (352 mg, 1.55 mmol, 1.5 equiv) was added at once to the reaction mixture and allowed to warm to room temperature. After 1.5 hrs., the reaction mixture was quenched by the addition of a saturated aqueous $NaHCO_3$ solution. The phases were separated and the aqueous phase extracted with DCM (x3). The combined organic extracts were washed with $NaHCO_3$ (sat. aq., x2), and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed *in vacuo* to afford a crude solid. The crude solid was dry loaded onto a silica gel column and eluted with 10, 20, 30, 40% DCM in hexane. 5-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-phenylbenzo[*d*]oxazole was isolated as an off-white solid that could be recrystallized from hexane to afford fluffy white needles (297 mg, 88%).

m.p. = 194–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 8.29 – 8.23 (m, 2H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.54 – 7.47 (m, 4H), 7.40 (dd, *J* = 8.6, 1.9 Hz, 1H), 2.19 – 2.07 (m, 3H), 2.03 – 1.93 (m, 6H), 1.86 – 1.73 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 163.1, 148.8, 148.5, 142.0, 131.4, 128.9, 127.6, 127.3, 122.5, 116.2, 109.8, 43.7, 36.87, 36.4, 29.0; IR (neat, cm^{-1}) 2901, 2846, 1550, 1474, 1448, 1425, 1332, 1321, 1283, 1263, 1426, 1201, 1052, 1024; HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1852; found: 330.1855.

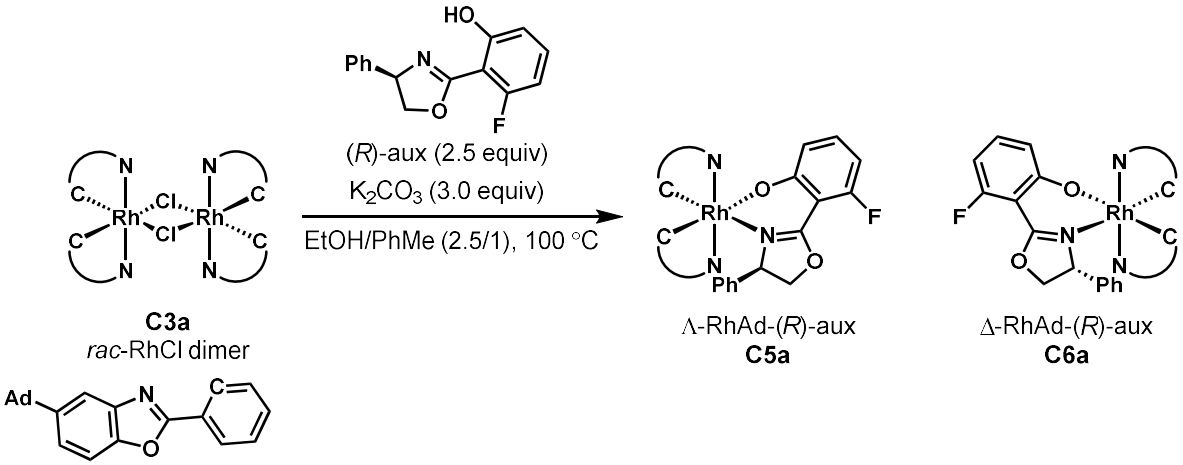
Preparation of Rh dimer:



C2a **C3a**

A stirred suspension of oxazole **C2a** (988 mg, 3.0 mmol) and $RhCl_3 \cdot 3H_2O$ (402 mg, 1.5 mmol) in 2-methoxyethanol (0.06 M) was heated to 140 °C in a glass pressure tube for five hours. A yellow solid precipitated. After cooling to room temperature, the reaction was diluted with water and filtered through Celite. The filter cake was washed with water and methanol. Into a separate flask, the filter cake was washed with hot toluene and the filtrate concentrated *in vacuo* to afford a yellow solid **C3a** (1.59 g, quant.) which was used immediately in the next step without further purification.

Preparation of Λ- and Δ-RhAd-(R)-aux:



A vigorously stirred suspension of **C3a** (1.03 g, 0.65 mmol), K_2CO_3 (269 mg, 1.95 mmol), and (*R*)-chiral auxiliary **C4** (418 mg, 1.63 mmol) in an ethanol/toluene (2.5/1.0) mixture were heated to 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered over Celite and washed with toluene. The filtrate was concentrated *in vacuo* and the crude solid was taken up in hot ethanol, and the insoluble solid filtered and washed with hot ethanol. The filtrate contains primarily Δ-(*R*)-**C6a** while the insoluble residue contains primarily Λ-(*R*)-**C5a**.

Separation of Δ-(*R*)-**C6a** from Λ-(*R*)-**C5a** can be achieved by differential solubility in ethanol. In a typical procedure, the insoluble solid, described above, was washed with hot ethanol until the Δ-(*R*)-**C6a** was not detectable by TLC (1% Et_2O in PhMe). Further purification of Λ-(*R*)-**C5a** can be achieved by flash column chromatography (0, 1, 5% Et_2O in PhMe) to afford a yellow solid (405 mg, 30%). This typically provided Λ-(*R*)-**C5a** of ≥ 99.5% purity (as judged by ^{1}H and ^{19}F NMR). No trace amounts of Δ-(*R*)-**C6a** were detected.

Λ-(*R*)-**C5a**: ^{1}H NMR (600 MHz, $CDCl_3$*) 8.09 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.57 – 7.56 (m, 2H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.37 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.96 – 6.87 (m, 4H), 6.94 (td, *J* = 7.5, 1.5 Hz, 1H), 6.78 – 6.74 (m, 3H), 6.72 (td, *J* = 7.4, 1.0 Hz, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.35 – 6.32 (m, 2H), 6.04 (d, *J* = 7.8 Hz, 1H), 5.93 (ddd, *J* = 11.4, 8.0, 1.1 Hz, 1H), 4.33 (dd, *J* = 10.1, 8.8 Hz, 1H), 4.24 (t, *J* = 8.3 Hz, 1H), 4.17 (dd, *J* = 10.1, 7.9 Hz, 1H), 2.19 – 2.17 (m, 3H), 2.04 – 1.94 (m, 9H), 1.91 – 1.81 (m, 12H), 1.73 – 1.67 (m, 6H); ^{13}C NMR** (150 MHz, $CDCl_3$*) 174.5 (d, *J* = 3.6 Hz), 171.5 (d, *J* = 3.9 Hz), 171.4 (d, *J* = 3.4 Hz), 167.9 (d, *J* = 31.9 Hz), 166.7 (d, *J* = 30.7 Hz), 166.2, 162.5 (d, J_{CF} = 253.7 Hz), 150.6, 149.2, 148.3, 147.7, 140.6, 138.7, 138.4, 135.3, 133.1, 132.2 (d, *J* = 13.2 Hz), 131.1 (d, *J* = 1.5 Hz), 130.6, 130.0 (d, *J* = 1.7 Hz), 129.7, 128.1, 127.1, 126.8, 125.02, 124.99, 122.8, 122.6, 122.2, 121.7, 119.2 (d, *J* = 2.4 Hz), 114.8, 113.5, 110.3, 110.2, 102.8 (d, J_{CF} = 8.2 Hz), 98.7 (d, J_{CF} = 22.1 Hz), 75.3, 68.7, 43.4, 43.1, 36.7, 36.53, 36.49, 29.0, 28.8; ^{19}F NMR (564 NMR, $CDCl_3$) –107.92 (dd, *J* = 11.5, 7.4 Hz); IR (neat, cm^{-1}) 3058, 2035, 2905, 2849, 1620, 1592, 1527, 1478, 1448, 1380, 1224, 1035; HRMS (ESI^+) *m*/*z* calcd for $C_{46}H_{44}N_2O_2Rh$ $[M-C_{15}H_{11}FNO_2]^+$: 759.2452; found: 759.2445.

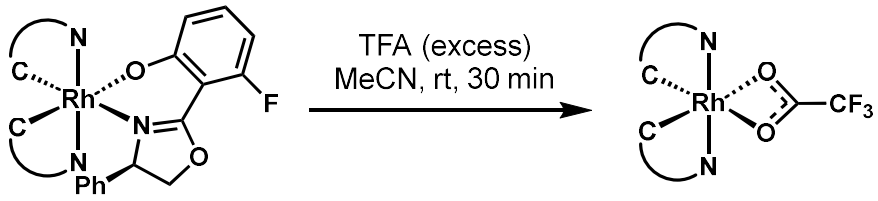
*$CDCl_3$ was passed through basic alumina prior to use. **One of the adamantyl qC atoms was not observed in the ^{13}C NMR.

Separation of Λ-(*R*)-**C5a** from Δ-(*R*)-**C6a** (from the ethanolic solution) can be achieved by flash column chromatography (dry load, 5% EtOAc in hexanes) to afford a yellow solid (454 mg, 34%). This typically provided of Δ-(*R*)-**C6a** ≥99% purity (as judged by ^{1}H and ^{19}F NMR). Approximately < 1% of Λ-(*R*)-**C5a** was detectable by ^{19}F NMR.

Δ-(*R*)-**C6a**: ^{1}H NMR (600 MHz, $CDCl_3$*) 7.94 (d, *J* = 1.9 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.98 – 6.82 (m, 6H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.56 (brs, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 6.19 (brd, *J* = 7.5 Hz, 2H), 5.98 (dd, *J* = 12.7, 7.9 Hz, 1H), 4.92 (dd, *J* = 9.7, 4.4 Hz, 1H), 4.85 (t, *J* = 9.2 Hz, 1H), 4.13 (dd, *J* = 8.7, 4.5 Hz, 1H), 2.17 – 2.16 (m, 3H), 2.06 – 2.05 (m, 3H), 2.01 – 1.98 (m, 6H), 1.91 – 1.86 (m, 6H), 1.84 – 1.79 (m, 6H), 1.76 – 1.70 (m, 6H); ^{13}C NMR** (150 MHz, $CDCl_3$*) 174.7 (d, *J* = 3.1 Hz), 171.7 (d, *J* = 3.4 Hz), 170.1 (d, *J* = 4.0 Hz), 168.5 (d, *J* = 30.0 Hz), 166.8 (d, *J* = 31.4 Hz), 165.0 (d, *J* = 3.7 Hz), 163.7 (d, *J* = 257.8 Hz), 149.9, 149.8, 148.1, 148.0, 140.9, 138.9, 138.3, 134.1, 133.0, 132.8 (d, *J* = 14.0 Hz), 131.5, 130.9, 130.3 (d, *J* = 1.1 Hz), 127.5, 126.9, 125.3 (brd),125.13, 125.06, 122.6, 122.3, 122.0, 121.8, 120.2 (d, *J* = 2.1 Hz), 115.1, 112.5, 110.8, 109.8, 99.9 (d, J_{CF} = 6.4 Hz), 98.6 (d, J_{CF} = 24.2 Hz), 74.4, 69.5, 43.5, 43.4, 36.67, 36.63, 36.58, 36.49, 29.94, 29.93; ^{19}F NMR (564 MHz, $CDCl_3$) −104.94 (dd, *J* = 12.8, 7.0 Hz); IR (neat, cm^{-1}) 3057, 3031, 2904, 2849, 1618, 1592, 1528, 1477, 1447, 1431, 1381, 1265, 1220, 1036; HRMS (ESI^+) *m*/*z* calcd for $C_{61}H_{56}FN_3O_4Rh$ $[M+H]^+$: 1016.3304; found: 1016.3328.

*$CDCl_3$ was passed through basic alumina prior to use. **Two carbon atoms were not observed in the ^{13}C NMR.

*Preparation of Λ- and Δ-**11** TFA Catalyst:*



Λ-(*R*)-**C5a** Λ-**11** TFA

To a suspension of Λ-(*R*)-**C5a** (377 mg, 0.376 mmol) in MeCN (30 mL, HPLC grade) was added trifluoroacetic acid (0.5 mL) at room temperature. The reaction mixture become homogeneous upon the addition of trifluoroacetic acid and was allowed to stir for 30 min before being concentrated *in vacuo*. The residue was purified by flash column chromatography (0, 1, 5% MeCN in DCM doped with 1 – 2% TFA) to afford **11** as a pale-yellow solid (282 mg, 86%).

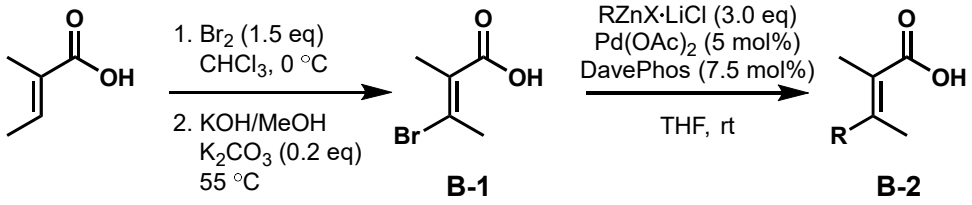
^{1}H NMR (600 MHz, $CDCl_3$*) 7.90 (brs, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.47 (d, *J* = 7.6 Hz, 2H), 2.11 (brs, 6H), 1.97 (s, 12H), 1.80 – 1.74 (m, 12H); ^{13}C NMR** (150 MHz, $CDCl_3$*) 170.6, 159.1 (br), 150.7 (br), 148.2, 138.1 (br), 134.3 (br), 131.3, 130.7, 125.5, 123.4, 123.2, 114.0 (br), 110.7, 43.4, 36.6, 36.6, 28.9; ^{19}F NMR (564 MHz, $CDCl_3$) −75.15 (brs); IR (neat, cm^{-1}) 3054, 2905, 2850, 1781, 1652, 1617, 1592, 1529, 1478, 1452, 1431, 1386, 1347, 13319, 1267, 1199, 1162, 1117, 1081, 1036, 931, 821, 797, 738; HRMS (ESI^+) *m*/*z* calcd for $C_{46}H_{44}N_2O_2Rh$ $[M\text{-}TFA]^+$: 759.2452; found 759.2436.

*$CDCl_3$ was passed through basic alumina prior to use.

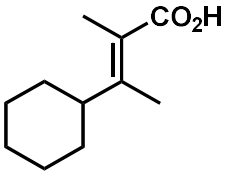
**The two carbon signals belonging to the TFA anion were not observed in the ^{13}C NMR.

6. Preparation of Carboxylic Acids

A majority of the tetrasubstituted carboxylic acids used in this study could be prepared from our previously described method;[4, 5] however, we have found it useful to use a Pd-catalyzed Negishi cross coupling of the vinyl bromide **B-1** shown below, which was prepared according to a procedure found in the literature.[6] Tiglic acid, (*E*)-2-methylpent-2-enoic acid, cyclohex-1-ene-1-carboxylic acid were purchased from commercial sources.



A typical procedure for the Negishi cross coupling is as follows:

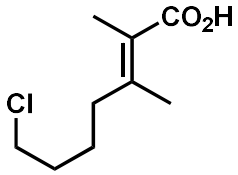


(*E*)-3-cyclohexyl-2-methylbut-2-enoic acid (**B-3**)

To a solution of $Pd(OAc)_2$ (168 mg, 0.75 mmol, 5 mol%), DavePhos (442 mg, 1.1 mmol, 7.5 mol%), and bromide **B-1** (2.90 g, 16.2 mmol, 1.0 equiv) in THF (15 mL) at 0 °C was added dropwise freshly prepared CyZnI·LiCl (25 mL, 37.5 mmol, 2.5 equiv, 1.35 M soln in THF). The reaction was allowed to warm to room temperature overnight. The reaction was quenched with 1M HCl and diluted with diethyl ether. The phases were separated and the aqueous phase extracted with diethyl ether (x3). The combined organic extracts were washed a sodium sulfite solution* and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* to afford a crude solid. Compound **B-3** was isolated from the crude material using silica gel chromatography (dry load, 0, 3, 5, 10, 15% ethyl acetate in hexane) as a white solid (1.83 g, 62%). ^{1}H and ^{13}C spectra matched the previously reported values.

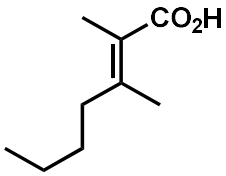
*A sodium sulfite wash was only necessary if the organozinc was prepared from the corresponding alkyl iodide.

In some cases, small amounts of angelic acid were detectable by ^{1}H NMR analysis. Angelic acid could be removed from the bulk material by sublimation under high vacuum at room temperature over the course of 18–24 hours or until a constant mass was reached. Also, in some cases traces of a highly colored red compound (presumably a Pd-complex) carried through the silica gel column. Although it does not interfere in subsequent reactions it can be removed by an aqueous acid-base extraction of the acid.



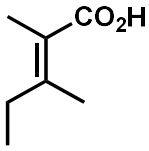
(*E*)-7-chloro-2,3-dimethylhept-2-enoic acid (**B-4**)

Brown oil (2.65 g, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) 3.56 (t, *J* = 6.6 Hz, 2H), 2.22 – 2.20 (m, 2H), 2.09 (q, *J* = 1.4 Hz, 3H), 1.09 (q, *J* = 1.4 Hz, 3H), 1.84 – 178 (m, 2H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 174.3, 150.7, 122.0, 44.7, 36.0, 32.3, 24.5, 21.4, 15.2; IR (neat, cm^{-1}) 3055, 2954, 2867, 2673, 2621, 1683, 1445, 1405, 1375, 1287, 1233, 1116; HRMS (ESI^-) calcd for $C_9H_{14}ClO_2$ $[M-H]^-$: 189.0688; found 189.0692.



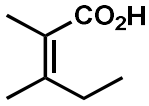
(*E*)-2,3-dimethylhept-2-enoic acid (**B-5**)

Colorless oil (1.57 g, 79%); ^{1}H NMR matched previously reported values.[4, 5] ^{1}H NMR (300 MHz, $CDCl_3$) 11.24 (brs, 1H), 2.17 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.09 (q, *J* = 1.5 Hz, 3H), 1.89 (q, *J* = 1.5 Hz, 3H), 1.47 – 1.28 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).



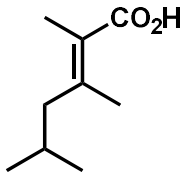
(*E*)-2,3-dimethylpent-2-enoic acid (**B-6**)

Deliquescent white solid (629 mg, 59%); ^{1}H NMR matched previously reported values.[4] ^{1}H NMR (300 MHz, $CDCl_3$) 2.19 (q, *J* = 7.6 Hz, 2H), 2.09 (q, *J* = 1.5 Hz, 3H), 1.89 (q, *J* = 1.5 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H).



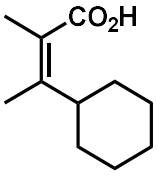
(*Z*)-2,3-dimethylpent-2-enoic acid (**B-7**)

Prepared from ethyl (*Z*)-2-methyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-enoate and hydrolyzed according to a protocol found in the literature.[4] Deliquescent white solid (1.21 g, 77% over 2 steps). ^{1}H NMR (300 MHz, $CDCl_3$) 12.10 (brs, 1H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.87 (q, *J* = 1.5 Hz, 3H), 1.83 (q, *J* = 1.5 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H).



(*E*)-2,3,5-trimethylhex-2-enoic acid (**B-8**)

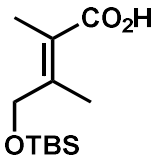
White solid (1.38 g, 59%); ^{1}H NMR matched previously reported values. [4] ^{1}H NMR (300 MHz, $CDCl_3$) 8.27 (brs, 1H), 2.11 – 2.06 (m, 5H), 1.94 – 1.82 (m, 4H), 0.92 (d, *J* = 6.6 Hz, 6H).



(*Z*)-3-cyclohexyl-2-methylbut-2-enoic acid (**B-9**)

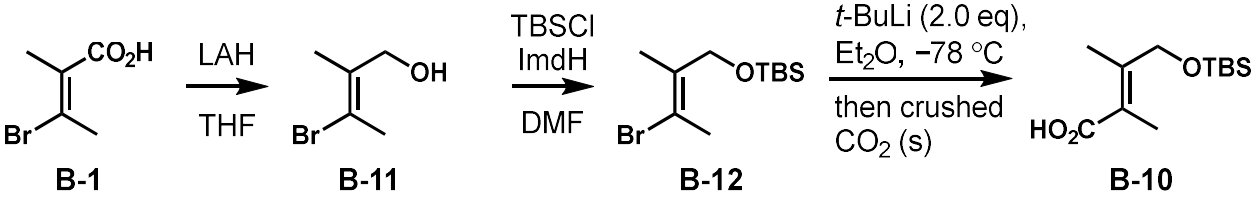
Prepared from ethyl (*Z*)-2-methyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-enoate and hydrolyzed according to a protocol found in the literature.[4] White solid (1.03 g, 57% over 2 steps). m.p. = 113 – 115 °C.

^{1}H NMR (300 MHz, $CDCl_3$) 11.52 (brs, 1H), 3.22 – 3.09 (m, 1H), 1.89 (s, 3H), 1.83 – 1.52 (m, 5H), 1.73 (s, 3H), 1.41 – 1.06 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.9, 153.4, 121.1, 42.9, 30.8, 26.2, 26.1, 16.0, 15.6; IR (neat, cm^{-1}) 2936, 2850, 2655, 1669, 1621, 1444, 1408, 1377, 1295, 1226, 1126; HRMS (EI$^+$) *m*/*z* calcd for $[M]^+$: 182.1301; found: 182.1303.



(*E*)-4-((tert-butyldimethylsilyl)oxy)-2,3-dimethylbut-2-enoic acid (**B-10**)

Compound **B-10** was prepared according to the scheme shown below.



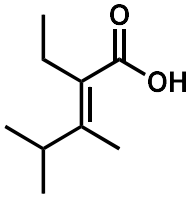
Carboxylic acid **B-1** (2.68 g) was reduced to allylic alcohol **B-11** according to a protocol found in the literature.[6]

A solution of crude allylic alcohol **B-11** (1.85 g, 11.2 mmol, 1.0 eq) was added to stirred mixture of TBSCl and imidazole in DMF at 0 °C. The reaction mixture was allowed to warm to room temperature and after 2 hours was quenched by the addition of water and diethyl ether. The phases were separated and the aqueous phase extracted with diethyl ether (x2). The combined organic extracts were washed with 1M HCl, water, and brine, followed by drying over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* and the crude material (2.60 g) used in the next step without further purification.

To a solution of crude TBS-protected vinyl bromide **B-12** (2.60 g, 9.32 mmol, 1.0 eq) in diethyl ether (50 mL) at −78 °C was added a solution *t*-BuLi (9.3 mL, 18.6 mmol, 2.0 eq., 2.0 M in pentane) dropwise. After stirring for 10-15 min, the solution was poured onto dry ice and allowed to warm to room temperature. The reaction mixture was diluted with 1M HCl and the aqueous phase was extracted with diethyl ether (x2). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* and the crude material subjected to column chromatography (0, 10, 25% ethyl acetate in

hexanes). The isolated carboxylic acid was still contaminated by pivalic acid. Pivalic acid could be removed by sublimation at room temperature under a high vacuum to afford **B-10** as a white solid (1.40 g, 61% yield, 70% yield BRSM).

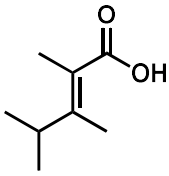
^{1}H NMR (300 MHz, $CDCl_3$) 4.26 (s, 2H), 2.12 (q, *J* = 1.6 Hz, 3H), 1.89 – 1.86 (m, 3H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.2, 149.8, 121.8, 64.2, 25.9, 18.3, 17.6, 14.6, −5.4; IR (neat, cm^{-1}) 3038, 2954, 2930, 2885, 2857, 2709, 2609, 1679, 1664, 1626, 1471, 1462, 1406, 1387, 1374, 1312, 1294, 1256, 1220, 1081; HRMS (ESI^-) *m*/*z* calcd for $[M-H]^-$: 243.1421; found 243.1415.



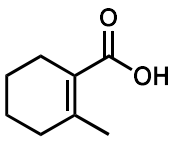
(*E*)-2-ethyl-3,4-dimethylpent-2-enoic acid (**B-13**)

Acid **B-13** was prepared according a protocol found in the literature[4] using ethyl 2-ethyl-3-oxobutanoate as the starting material.

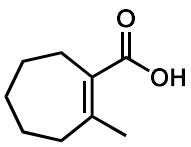
White solid (1.01 g, 84% yield over two steps); ^{1}H NMR (300 MHz) 11.33 (brs, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.37 (q, *J* = 7.4 Hz, 2H), 1.91 (s, 3H), 1.06 – 1.01 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.9, 154.0, 127.5, 31.2, 22.3, 20.3, 14.9, 14.4; IR (neat, cm^{-1}) 3051, 2964, 2936, 2875, 2799, 2706, 2618, 2521, 1682, 1604, 1467, 1310, 1257, 1241; HRMS (ESI^-) *m*/*z* calcd for $C_9H_{15}O_2$ $[M-H]^-$: 155.1078; found: 155.1082.



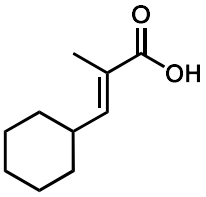
B-14



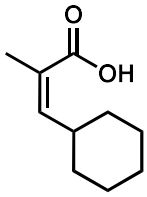
B-15



B-16



B-17



B-18

Acid **B-14** was prepared according to a protocol found in the literature.[4]

Acids **B-15** and **-16** were prepared according to a protocol found in the literature.[5]

Acids **B-17** and **-18** were prepared according to a protocol found in the literature.[7, 8]

7. Preparation of Benzyl Propiolate

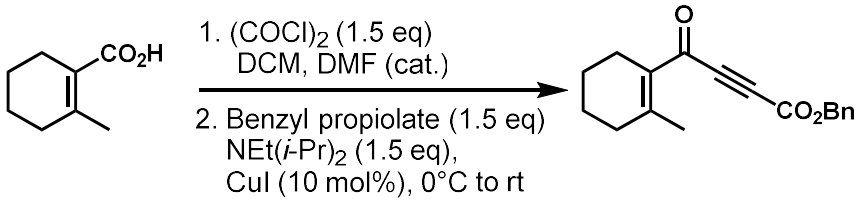
Benzyl propiolate was prepared according to a protocol found in the literature.[9]

To a stirred suspension of K_2CO_3 (15.2 g, 110 mmol, 1.5 equiv) in DMF (100 mL) at 0 °C was added propiolic acid (7.70 g, 110 mmol, 1.1 equiv). After stirring at this temperature for ten minutes, benzyl bromide (11.9 mL, 100 mmol, 1.0 equiv) was added. The reaction mixture was allowed to warm to room temperature and diluted with water and diethyl ether at 0 °C. The phases were separated and the aqueous phase extracted with diethyl ether (x3). The combined organic extracts were washed with water (x2) and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* to afford a crude oil. The crude oil was subjected to silica gel column chromatography (dry load, 0, 2, 5% diethyl ether in hexane) to afford benzyl propiolate as a colorless oil (14.4 g, 90%). ^{1}H and ^{13}C NMR spectra matched the previously reported values.[9]

^{1}H NMR (300 MHz, $CDCl_3$) 7.42 – 7.34 (m, 5H), 5.23 (s, 2H), 2.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.6, 134.5, 128.8, 128.7, 128.6, 75.2, 74.6, 68.0; IR (neat, cm^{-1}) 3277, 3091, 3068, 2960, 2121, 1716, 1498, 1456, 1375, 1220.

8. Synthesis of Ynones

Representative procedure:



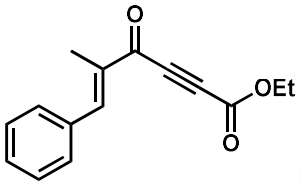
Benzyl 4-(2-methylcyclohex-1-en-1-yl)-4-oxobut-2-ynoate (**5**)

To a solution of 2-methylcyclohex-1-ene-1-carboxylic acid (612 mg, 4.37 mmol) in DCM (1 M) was added oxalyl chloride (0.56 mL, 6.56 mmol) dropwise followed by two drops of anhydrous DMF from a Pasteur pipet. Once the evolution of gas ceased (approx. 2 to 3 h), the mixture was cooled to 0 °C. In a separate flask, Hünig's base (1.1 mL, 6.56 mmol) was added to a stirred suspension of benzyl propiolate (1.05 g, 6.56 mmol) and CuI (83 mg, 0.44 mmol). Once the mixture became homogenous it was added dropwise to the acid chloride at 0 °C and then allowed to warm to room temperature. The reaction was quenched by the addition of a saturated aqueous ammonium chloride solution and was extracted with DCM (x2). The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution (x2) and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed *in vacuo* and the crude oil purified by flash column chromatography (0, 1, 2, 5, 7% Et_2O in hexanes) to afford **5** as a pale-yellow oil (4.19 g, 96%).

^{1}H NMR (300 MHz, $CDCl_3$) 7.45 – 7.31 (m, 5H), 5.25 (s, 2H), 2.43 – 2.37 (m, 2H), 2.25 – 2.17 (m, 2H), 2.14 – 2.12 (m, 3H), 1.68 – 1.55 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.7, 154.5, 152.5, 134.3, 131.0, 128.9, 128.7, 128.7, 82.9, 79.6, 68.3, 35.0, 26.1, 22.7, 22.1, 21.9; IR (neat, cm^{-1}) 3035, 2937, 2863, 2200, 1717, 1651, 1560, 1498, 1456, 1418, 1375, 1280, 1231, 1179, 941, 747; HRMS (ESI$^+$) m/*z* calcd for $C_{18}H_{18}O_3Na$ $[M+Na]^+$: 305.1148; found: 305.1151.

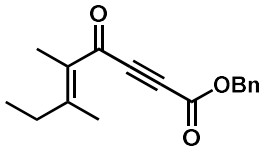
Note: Benzyl propiolate often has very similar chromatographic properties to many of the ynones prepared herein and as a result may appear as a minor, inseparable contaminant. In most cases, the bulk of the excess benzyl propiolate could be separated by silica gel chromatography using 10, 20, 30% PhMe in hexanes followed by 3, 5% ether in hexanes as eluent.

All of the acyclic tetrasubstituted all-aliphatic carboxylic acids used in this study are sensitive to anhydrous acid. exposure to which will cause isomerization of the alkene. In these cases, cyanuric chloride and triethylamine were used to form the acid chloride (see the SI of reference 4) and the copper propiolate, formed as described above, was added directly to the reaction mixture of the acid chloride. In some cases, an adduct of TCT and triethylamine carries over as a chromatographically inseparable contaminant and can be seen by ^{1}H and ^{13}C NMR (marked on the corresponding spectra). This contaminate did not affect the subsequent steps in the reaction sequence and is chromatographically separable from the cyclopentenone.



Ethyl (*E*)-5-methyl-4-oxo-6-phenylhex-5-en-2-ynoate (**A2**)

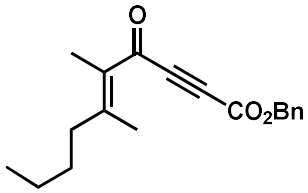
Pale-yellow oil (2.17 g, 89%) ^{1}H NMR (300 MHz, $CDCl_3$) 7.93 (q, *J* = 1.6 Hz, 1H), 7.52 – 7.36 (m, 5H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.11 (d, *J* = 1.6 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.7, 152.5, 148.1, 137.5, 134.8, 130.4, 129.9, 128.7, 80.3, 79.7, 62.9, 14.0, 12.1; IR (neat, cm^{-1}) 3057, 3027, 2986, 2939, 2874, 2229, 1717, 1639, 1618, 1574, 1448, 1393, 1366, 1327, 1299, 1250, 1089, 1018; HRMS (ESI$^+$) *m*/*z* calcd for $[M+H]^+$: 243.1016; found 243.1016.



Benzyl (*E*)-5,6-dimethyl-4-oxooct-5-en-2-ynoate (**A3**)

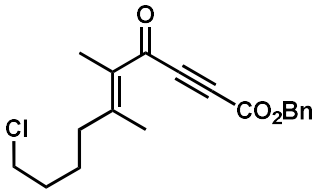
Pale-yellow oil (1.14 g, 60%); ^{1}H NMR* (300 MHz, $CDCl_3$) 7.40 – 7.35 (m, 5H), 5.25 (s, 2H), 2.21 (q, *J* = 7.6 Hz, 2H), 2.14 (q, *J* = 1.4 Hz, 3H), 2.00 (q, *J* = 1.4 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.4, 157.5, 152.5, 134.3, 128.9, 128.73, 128.69, 128.63, 83.1, 79.6, 68.3, 30.8, 21.2, 14.8, 11.4; IR (neat, cm^{-1}) 3067, 3035, 2972, 2937, 2877, 2214, 1717, 1651, 1583, 1536, 1506, 1456, 1375, 1321, 1283, 1228; HRMS (ESI$^+$) calcd for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1148; found 293.1154.

*Inseparable benzyl propiolate contaminant is present.



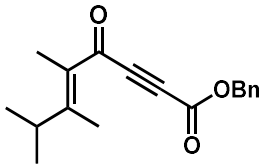
Benzyl (*E*)-5,6-dimethyl-4-oxodec-5-en-2-ynoate (**A4**)

Pale-yellow oil (1.28 g, 54%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.33 (m, 5H), 5.24 (s, 2H), 2.22 – 2.17 (m, 2H), 2.14 (q, *J* = 1.4 Hz, 3H), 2.00 (q, *J* = 1.4 Hz, 3H), 1.47 – 1.29 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.2, 156.5, 152.5, 134.3, 129.0, 128.9, 128.74, 128.67, 83.1, 79.6, 68.3, 37.6, 29.4, 22.9, 21.8, 15.1, 14.0; IR (neat, cm^{-1}) 3066, 3035, 2960, 2932, 2872, 2119, 1717, 1650, 1490, 1476, 1457, 1376, 1350, 1328, 1305, 1230, 1161, 1082, 1031; HRMS (ESI$^+$) *m*/*z* calcd for $C_{19}H_{22}NaO_3$ $[M+Na]^+$: 321.1461; found: 321.1456.



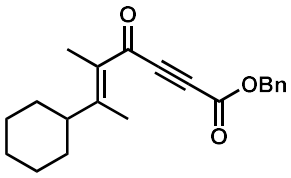
Benzyl (*E*)-10-chloro-5,6-dimethyl-4-oxodec-5-en-2-ynoate (**A5**)

Pale-yellow oil (636 mg, 37%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.32 (m, 5H), 5.24 (s, 2H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.24 – 2.19 (m, 2H), 2.14 – 2.13 (m, 3H), 2.01 – 2.00 (m, 3H), 1.84 (m, 2H), 1.65 – 1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.3, 154.9, 152.4, 134.3, 129.4, 128.9, 128.8, 128.7, 82.9, 79.7, 68.3, 44.6, 36.8, 32.3, 24.4, 21.7, 15.2; IR (neat, cm^{-1}) 3091, 3067, 3035, 2956, 2870, 2216, 1720, 1650, 1601, 1498, 1456, 1375, 1225, 1070, 950; HRMS (ESI$^+$) *m*/*z* calcd for $C_{19}H_{21}ClO_3Na$ [M+Na]$^+$: 355,1071; found: 355.1069.



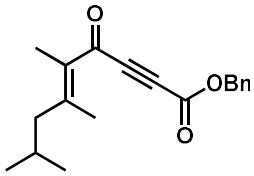
Benzyl (*E*)-5,6,7-trimethyl-4-oxooct-5-en-2-ynoate (**A6**)

Pale-yellow oil (425 mg, 64%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.35 (m, 5H), 5.25 (s, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.02 (q, *J* = 1.3 Hz, 3H), 1.99 (q, *J* = 1.3 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 6H); ^{13}C (75 MHz, $CDCl_3$) 178.9, 160.0, 152.5, 134.3, 128.9, 128.8, 128.7, 83.1, 79.5, 68.3, 32.6, 19.6, 15.4, 14.6; IR (neat, cm^{-1}) 3067, 3035, 2968, 2934, 2873, 2216, 1720, 1648, 1579, 1498, 1457, 1375, 1331, 1304, 1279, 1232, 1152, 1061, 965; HRMS (ESI$^+$) m/*z* calcd for $C_{18}H_{20}O_3Na$ [M+Na]$^+$: 307.1305; found: 307.1314.



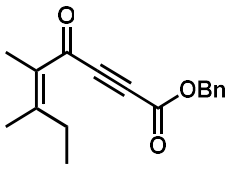
Benzyl (*E*)-6-cyclohexyl-5-methyl-4-oxohept-5-en-2-ynoate (**A7**)

Pale-yellow oil (692 mg, 43%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.34 (m, 5H), 5.24 (s, 2H), 2.54 – 2.44 (m, 1H), 2.02 (s, 6H), 1.85 – 1.10 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.0, 159.4, 152.5, 134.3, 128.9, 128.7, 128.7, 128.4, 83.2, 79.5, 68.3, 44.0, 29.6, 26.2, 26.0, 16.8, 14.7; IR (neat, cm^{-1}) 3035, 2930, 2854, 2214, 1717, 1647, 1574, 1532, 1499, 1451, 1417, 1375, 1300, 1280, 1230, 1143, 1080, 968; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{24}NaO_3$ [M+Na]$^+$: 347.1618; found 347.1604.



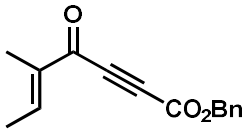
Benzyl (*E*)-5,6,8-trimethyl-4-oxonon-5-en-2-ynoate (**A8**)

Pale-yellow oil (889 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.34 (m, 5H), 5.25 (m, 2H), 2.13 – 2.08 (m, 5H), 2.02 (q, *J* = 1.4 Hz, 3H), 1.95 – 1.84 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$)178.3, 155.3, 152.5, 134.3, 129.8, 128.9, 128.74, 128.69, 83.1, 79.6, 68.3, 46.6, 27.5, 22.7, 22.2, 15.7; IR (neat, cm^{-1}) 3035, 2959, 2870, 2214, 1719, 1650, 1585, 1532, 1499, 1457, 1375, 1332, 1230, 1143, 1072, 987, 952; HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{22}NaO_3$ $[M+Na]^+$ 321.1461; found: 321.1451.



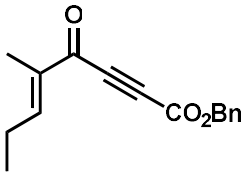
Benzyl (*Z*)-5,6-dimethyl-4-oxooct-5-en-2-ynoate (**A9**)

Pale-yellow oil (747 mg, 28%) ^{1}H NMR (300 MHz, $CDCl_{3)}$) 7.40 – 7.34 (m, 5H), 5.24 (s, 2H), 2.53 (qq, *J* = 7.4, 1.0 Hz, 2H), 1.96 (sext, *J* = 1.0 Hz, 3H), 1.87 (q, *J* = 1.0 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.7, 157.7, 152.5, 134.3, 129.1, 128.9, 128.73, 128.65, 82.9, 79.0, 68.3, 29.6, 21.8, 15.5, 12.9; IR (neat, cm^{-1}) 3035, 2973, 2936, 2875, 2213, 1720, 1651, 1575, 1498, 1457, 1375, 1300, 1262, 1230, 1074; HRMS (ESI^+) calcd for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1148; found 293.1161.



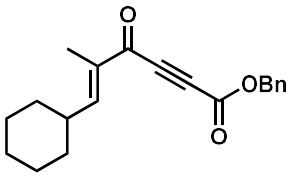
Benzyl (*E*)-5-methyl-4-oxohept-5-en-2-ynoate (**A10**)

Pale-yellow oil (565 mg, 47%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.35 (m, 5H), 7.23 (qq, *J* = 7.0, 0.8 Hz, 1H), 5.25 (s, 2H), 1.96 (dq, *J* = 7.0, 0.8 Hz, 3H), 1.81 (p, *J* = 0.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.0, 152.3, 148.7, 141.9, 139.2, 134.2, 128.9, 128.8, 80.1, 79.1, 68.4, 15.5, 10.1; IR (neat, cm^{-1}) 3036, 2959, 2218, 1720, 1635, 1456, 1378, 1267, 1228, 1113, 1086, 1013, 966, 906; HRMS (ESI^+) m/*z* calcd for $C_{15}H_{14}O_3Na$ $[M+Na]^+$: 265.0835; found 265.0844.



Benzyl (*E*)-5-methyl-4-oxooct-5-en-2-ynoate (**A11**)

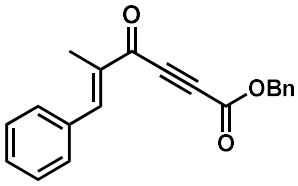
Colorless oil (538 mg, 42%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.42 – 7.33 (m, 5H), 7.10 (tq, *J* = 7.5, 0.8 Hz, 1H), 5.26 (s, 2H), 2.34 (pq, *J* = 7.5, 0.8 Hz, 2H), 1.80 (q, *J* = 0.8 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 178.2, 155.0, 152.4, 148.5, 137.7, 134.2, 128.9, 128.8, 80.3, 79.2, 68.4, 23.0, 12.7, 10.2; IR (neat, cm^{-1}) 3067, 3036, 2971, 2936, 2876, 2225, 1720, 1634, 1499, 1457, 1375, 1227, 1128, 993, 941; HRMS (ESI$^+$) calcd for $C_{16}H_{16}O_3Na$ [M+Na]$^+$: 279.0992; found 279.0996.



Benzyl (*E*)-6-cyclohexyl-5-methyl-4-oxohex-5-en-2-ynoate (**A12**)

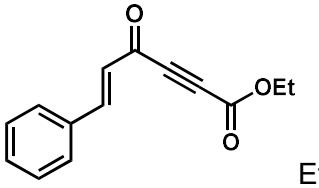
Pale-yellow oil (721 mg, 72%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 – 7.35 (m, 5H), 6.90 (dq, *J* = 9.5, 1.3 Hz, 1H), 5.27 (s, 2H), 2.53 – 2.40 (m, 1H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.81 – 1.64 (m, 5H), 1.39 – 1.16 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$)* 178.5, 158.3, 152.4, 136.3, 134.2, 128.9, 128.8, 80.4, 79.2, 68.4, 38.8, 31.5, 25.7, 25.4, 10.4; IR (neat, cm^{-1}) 3035, 2928, 2853, 2214, 1720, 1633, 1498, 1449, 1375, 1300, 1275, 1260, 1231, 1140, 1082, 996, 967; HRMS (ESI$^+$) *m*/*z* calcd for $C_{20}H_{22}O_3Na$ [M+Na]$^+$: 333.1461; found: 333.1457.

*One carbon signal is not observed in the ^{13}C NMR.



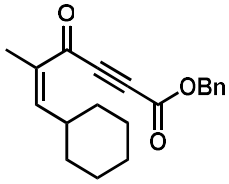
Benzyl (*E*)-5-methyl-4-oxo-6-phenylhex-5-en-2-ynoate (**A13**)

Pale-yellow oil (1.08 g, 71%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.95 (q, *J* = 1.3 Hz, 1H), 7.54 – 7.37 (m, 10H), 5.30 (s, 2H), 2.14 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.7, 152.3, 148.2, 137.6, 134.8, 134.3, 130.4, 130.0, 129.0, 128.8, 128.8, 80.3, 80.1, 68.5, 12.2; IR (neat, cm^{-1}) 3090, 3065, 3034, 2962, 2926, 2222, 1720, 1638, 1619, 1574, 1498, 1449, 1393, 1375, 1327, 1298, 1246, 1184, 1089, 1027, 1002, 931; HRMS (ESI$^+$) m/*z* calcd for $C_{20}H_{16}O_3Na$ [M+Na]$^+$: 327.0992; found: 327.0994.



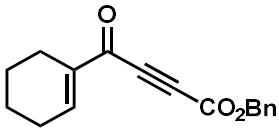
Ethyl (*E*)-4-oxo-6-phenylhex-5-en-2-ynoate (**A14**)

Pale-yellow oil (1.36 g, 60%) ^{1}H NMR (300 MHz, $CDCl_3$) 7.85 (d, *J* = 16.2 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.48 – 7.40 (m, 3H), 6.83 (d, *J* = 16.2 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.2, 152.2, 150.9, 133.5, 131.9, 129.2, 129.0, 127.4, 79.5, 79.3, 63.1, 14.0; IR (neat, cm^{-1}) 3083, 3063, 3027, 2985, 2940, 2906, 1717, 1636, 1597, 1576, 1450, 1368, 1331, 1297, 1256, 1202, 1136, 1022; HRMS (ESI$^+$) *m*/*z* calcd for $[M+H]^+$: 229.0859; found; 229.0860.



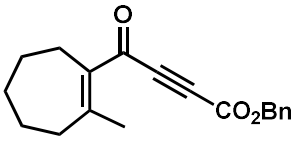
Benzyl (*Z*)-6-cyclohexyl-5-methyl-4-oxohex-5-en-2-ynoate (**A15**)

Pale-yellow oil (774 mg, 50%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 – 7.30 (m, 5H), 6.08 (dq, *J* = 10.3, 1.3 Hz, 1H), 5.26 (s, 2H), 3.19 (qt, *J* = 10.3, 3.4 Hz, 1H), 1.94 (d, *J* = 1.3 Hz, 3H), 1.78 – 1.58 (m, 5H), 1.33 – 1.00 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.3, 153.5, 152.3, 134.2, 132.2, 128.9, 128.7, 82.5, 78.9, 68.4, 37.9, 32.7, 25.8, 25.4, 20.1; IR (neat, cm^{-1}) 3067, 3035, 2927, 2852, 2215, 1720, 1661, 1623, 1498, 1449, 1376, 1352, 1308, 1231, 1142, 1079, 1010, 947, 906; HRMS (ESI$^+$) m/*z* calcd for $C_{20}H_{22}O_3Na$ $[M+Na]^+$: 333.1461; found: 333.1474.



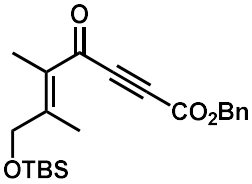
Benzyl 4-(cyclohex-1-en-1-yl)-4-oxobut-2-ynoate (**A16**)

Pale-yellow oil (1.29 g, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.42 – 7.33 (m, 6H), 5.26 (s, 2H), 2.38 – 2.31 (m, 2H), 2.29 – 2.21 (m, 2H), 1.69 – 1.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.3, 152.3, 150.9, 140.4, 134.2, 128.9, 128.8, 80.1, 78.8, 68.4, 26.7, 22.1, 21.5, 21.3; IR (neat, cm^{-1}) 3093, 3067, 3035, 2937, 2863, 2222, 1720, 1630, 1498, 1456, 1418, 1385, 1343, 1234, 1083, 1054, 1029, 966, 905; HRMS (ESI$^+$) m/*z* calcd for $C_{17}H_{16}O_3Na$ $[M+Na]^+$: 291.0992; found 291.0996.



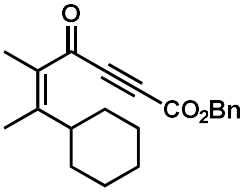
Benzyl 4-(2-methylcyclohept-1-en-1-yl)-4-oxobut-2-ynoate (**A18**)

Pale-yellow oil (724 mg, 62%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.44 – 7.31 (m, 5H), 5.25 (s, 2H), 2.64 – 2.60 (m, 2H), 2.38 – 2.34 (m, 2H), 2.19 (t, *J* = 1.0 Hz, 3H), 1.82 – 1.74 (m, 2H), 1.56 – 1.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.0, 160.6, 152.6, 137.3, 134.3, 128.9, 128.8, 128.7, 83.1, 79.5, 68.3, 39.1, 32.1, 29.3, 26.4, 24.7, 24.0; IR (neat, cm^{-1}) 2924, 2853, 2213, 1719, 1648, 1601, 1498, 1457, 1440, 1375, 1286, 1231, 1180, 942; HRMS (ESI$^+$) m/*z* calcd for $C_{19}H_{20}O_3Na$ $[M+Na]^+$: 319.1305; found: 319.1311.



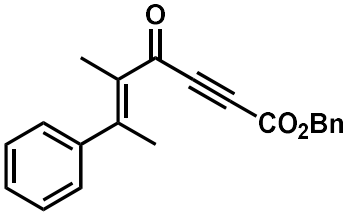
Benzyl (*E*)-7-((tert-butyldimethylsilyl)oxy)-5,6-dimethyl-4-oxohept-5-en-2-ynoate (**A19**)

Pale-yellow oil (945 mg, 47%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.36 (m, 5H), 5.25 (s, 2H), 4.27 (s, 2H), 2.18 (tq, *J* = 1.6, 0.8 Hz, 3H), 1.96 (tq, *J* = 1.5, 0.8 Hz, 3H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.4, 153.9, 152.4, 134.3, 128.9, 128.8, 128.7, 128.6, 82.7, 79.7, 68.3, 64.5, 25.8, 18.3, 17.5, 14.3, −5.4; IR (neat, cm^{-1}) 3036, 2955, 2930, 2886, 2857, 1720, 1655, 1611, 1471, 1375, 1285, 1228, 1089, 1063; This compound was not fully characterized (HRMS) but was fully characterized at the next compound (**DK19**) in the reaction sequence.



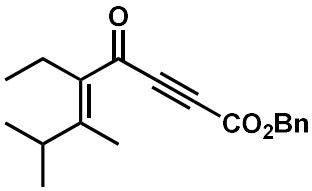
Benzyl (*Z*)-6-cyclohexyl-5-methyl-4-oxohept-5-en-2-ynoate (**A20**)

Pale-yellow oil (753 mg, 45%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.33 (m, 5H), 5.25 (s, 2H), 3.33 – 3.23 (m, 1H), 1.92 (q, *J* = 1.0 Hz, 3H), 1.77 (q, *J* = 1.0 Hz, 3H), 1.73 – 1.49 (m, 5H), 1.41 – 1.21 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.5, 159.3, 152.5, 134.3, 129.5, 128.9, 128.7, 128.7, 83.0, 78.9, 68.3, 42.7, 30.8, 26.0, 25.9, 16.7, 15.6; IR (neat, cm^{-1}) 3035, 2929, 2854, 2213, 1719m 1645, 1602, 1498, 1450, 1375, 1294, 1228, 1083, 1061; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{25}O_3$ $[M+H]^+$: 325.1798; found 325.1804.



Benzyl (*E*)-5-methyl-4-oxo-6-phenylhept-5-en-2-ynoate (**A21**)

Pale-yellow oil (879 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) 7.42 – 7.36 (m, 7H), 7.34 – 7.30 (m, 1H), 7.15 – 7.12 (m, 2H), 5.27 (s, 2H), 2.40 (q, *J* = 1.6 Hz, 3H), 1.90 (q, *J* = 1.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 179.0, 152.8, 152.4, 143.2, 134.2, 130.6, 128.9, 128.73, 128.68, 128.5, 127.7, 126.8, 82.6, 79.8, 68.4, 23.7, 17.3; IR (neat, cm^{-1}) 3061, 3035, 2950, 2120, 1717, 1651, 1586, 1491, 1456, 1442, 1375, 1309, 1243, 1181, 1112; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{18}O_3Na$ $[M+Na]^+$: 341.1148; found: 341.1145.



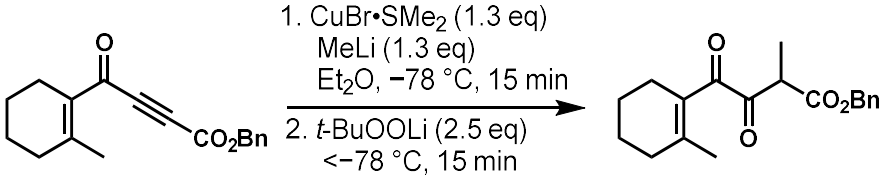
Benzyl (*E*)-5-ethyl-6,7-dimethyl-4-oxooct-5-en-2-ynoate (**A22**)

Pale-yellow oil (1.0 g, yield determined in next step)*; ^{1}H NMR (300 MHz, $CDCl_3$) 7.44 – 7.35 (m, 5H), 5.27 (s, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.99 (s, 3H), 1.10 – 1.04 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.3, 159.2, 152.5, 134.8, 128.9, 128.74, 128.67, 83.2, 78.7, 68.3, 32.0, 22.2, 20.2, 15.3, 14.8; IR (neat, cm^{-1}) 3272, 3067, 3035, 2968, 2934, 2873, 2120, 1717, 1645, 1574, 1456, 1375, 1229, 1080; HRMS (ESI$^+$) *m*/*z* calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461; found: 321.1464.

*isolated as an inseparable mixture with benzyl propiolate

9. *Synthesis of Diketones*

Representative procedure:



To a stirred suspension of freshly prepared CuBr·SMe_2[10] (1.02 g, 4.97 mmol) in Et_2O (0.1 M) was added MeLi (3.3 mL, 4.97 mmol, 1.5 M soln in Et_2O) at −30 °C. After stirring at this temperature for 15 min, the canary yellow solution was cooled to −78 °C and a solution of alkyne **5** (1.08 g, 3.82 mmol) in Et_2O (1.0 M) was added dropwise. After 15 min at this temperature, the reaction mixture was cooled between −94 and −78 °C (liquid N_2/hexane) and a solution of *t*-BuOOLi in Et_2O (preparation described below) at −78 °C was vacuum transferred via cannula to the reaction mixture. After stirring for 15 – 30 min the reaction mixture was quenched by the addition of a saturated aqueous ammonium chloride solution and the reaction mixture was allowed to warm to room temperature. The reaction mixture was extracted with EtOAc (x3). The combined organic extracts were washed with saturated ammonium chloride (x2) and saturated aqueous sodium sulfite, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* and the crude oil purified by flash column chromatography (0, 10, 20, 30, 40, 50% DCM in hexanes) to afford diketone **6** as a yellow oil (613 mg, 51% yield).

Preparation of t-BuOOLi solution:

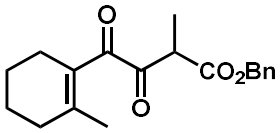
To a solution of 1,10-phenanthroline (spatula tip) in Et_2O (19 mL) was added anhydrous *t*-BuOOH (2.8 mL, 9.55 mmol, 3.4 M ± 5% solution in PhMe*). The solution was cooled to −78 °C and *n*-BuLi (3.8 mL, 9.55 mol, 2.5 M in hexanes) was added dropwise until an endpoint was reached. The mixture was allowed to stir at −78 °C for 5 – 10 min before transferring to the organocopper species.

*Anhydrous *t*-BuOOH in PhMe was prepared according to a Sharpless procedure[11] with one deviation – the extracts were dried over activated 4Å molecular sieves (no azeotropic distillation necessary). We have also found that long-term storage of the solution in an amber glass bottle under an Ar atmosphere at room temperature leads to little change in active oxidant concentration.

Please Note:

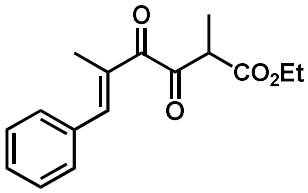
1. Many of these diketones are highly reactive and some have been observed to spontaneously decompose during silica gel column chromatography which may lead to low yields of isolated diketone. Consequently, the diketones used in this study were not as rigorously purified.
2. Many of these diketones are not stable to long term storage and should be used immediately. If storage is necessary, we found it best to store the diketone neat in a sealed vial under Ar in a −20 °C freezer.
3. The ^{1}H and ^{13}C NMR spectral data of the diketones appear complicated because there is *ca.* 10% of the enol tautomer present (mixture of *E*/*Z*).

4. A subtle note regarding the eluent system for column chromatography. The mixing of DCM and hexane is endothermic. Using a cold solution as the eluent leads to poor mobility of the diketone on silica. We regularly prepare the eluent freshly and gently warm the mixture to approximately room temperature in a warm water bath prior to use.



Benzyl 2-methyl-4-(2-methylcyclohex-1-en-1-yl)-3,4-dioxobutanoate (**6**)

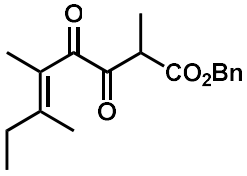
^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.27 (m, 5H), 5.13 (s, 2H), 4.19 (q, *J* = 7.3 Hz, 1H), 2.31 – 1.96 (m, 4H), 1.83 – 1.81 (m, 3H), 1.66 – 1.49 (m, 4H), 1.44 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.6, 194.4, 170.3, 151.9, 135.0, 128.6, 128.49, 128.46, 128.0, 67.3, 47.5, 34.1, 25.5, 22.7, 21.92, 21.91 12.1.; IR (neat, cm^{-1}) 2939, 2862, 1750, 1715, 1672, 1622, 1455, 1379, 1279, 1214, 1176, 1115, 1087; HRMS (ESI$^+$) *m*/*z* calcd for $C_{19}H_{23}O_4$ [M+H]$^+$: 315.1591; found 315.1594.



Ethyl (*E*)-2,5-dimethyl-3,4-dioxo-6-phenylhex-5-enoate (**7**)

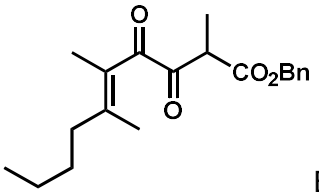
Yellow oil (523 mg, 76%); Spectral data matched the previously reported data.[12, 13]

^{1}H NMR (300 MHz, $CDCl_3$) 7.55 (q, *J* = 1.4 Hz, 1H), 7.49 – 7.33 (m, 5H), 4.26 (q, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.14 (d, *J* = 1.4 Hz, 3H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.4, 194.7, 170.0, 147.0, 135.1, 132.3, 130.3, 130.2, 129.6, 128.62, 128.59, 61.6, 48.5, 14.0, 12.6, 11.7.



Benzyl (*E*)-2,5,6-trimethyl-3,4-dioxooct-5-enoate (**DK3**)

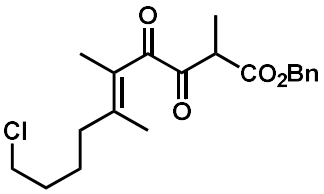
Yellow oil (520 mg, 41%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.25 (m, 5H), 5.13 (s, 2H), 4.20 (q, *J* = 7.7 Hz, 1H), 2.15 (q, *J* = 7.2 Hz, 2H), 1.85 (s, 3H), 1.75 (s, 3H), 1.43 (d, *J* = 7.7 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.2, 194.7, 170.4, 154.8, 135.1, 128.6, 128.5, 128.4, 125.5, 67.3, 47.3, 29.5, 20.9, 14.2, 12.1, 11.4; IR (neat, cm^{-1}) 3034, 2972, 2937, 2877, 1751, 1716, 1675, 1513, 1497, 1456, 1377, 1279, 1253, 1217, 1184, 1131, 1084, 1029; HRMS (ESI$^+$) *m*/*z* calcd for $C_{18}H_{22}NaO_4$ [M+Na]$^+$: 325.1410; found 325.1396.



Benzyl (*E*)-2,5,6-trimethyl-3,4-dioxodec-5-enoate (**DK4**)

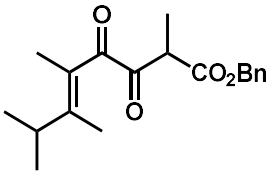
Yellow oil (520 mg, 41%)*; ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.27 (m, 5H), 5.16 (d, *J* = 12.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 1H), 2.20 – 2.09 (m, 2H), 1.85 (q, *J* = 1.4 Hz, 3H), 1.75 (q, *J* = 1.4 Hz, 3H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.44 – 1.30 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.1, 194.7, 170.4, 153.6, 135.1, 128.6, 128.45, 128.4, 125.9, 67.3, 47.3, 36.3, 29.4, 22.9, 21.5, 14.5, 14.0, 12.1; IR (neat, cm^{-1}) 2961, 2933, 2873, 1752, 1717, 1673, 1569, 1492, 1457, 1437, 1378, 1327, 1278, 1257, 1217, 1185, 1132, 1083, 1030; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{26}NaO_4$ $[M+Na]^+$: 353.1723; found: 353.1708.

*Contaminated with an inseparable TCT-triethylamine adduct.



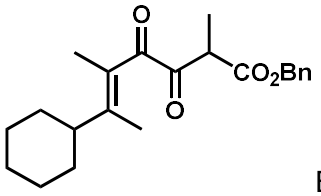
Benzyl (*E*)-10-chloro-2,5,6-trimethyl-3,4-dioxodec-5-enoate (**DK5**)

Yellow oil (303 mg, 44%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.27 (m, 5H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.55 – 2.09 (m, 2H), 1.97 – 1.66 (m, 2H), 1.84 (q, *J* = 1.4 Hz, 3H), 1.75 (q, *J* = 1.4 Hz, 3H), 1.66 – 1.51 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 194.6, 170.4, 151.7, 135.0, 128.6, 128.5, 128.4, 126.5, 67.3, 47.2, 44.7, 35.5, 32.3, 24.4, 21.3, 14.6, 12.1; IR (neat, cm^{-1}) 3066, 3034, 2943, 2870, 1751, 1716, 1673, 1616, 1533, 1498, 1456, 1378, 1216, 1183, 1003; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{25}ClNaO_4$ $[M+Na]^+$ 387.1334; found: 387.1332.



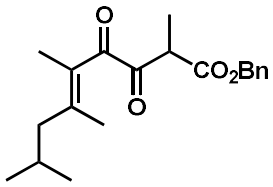
Benzyl (*E*)-2,5,6,7-tetramethyl-3,4-dioxooct-5-enoate (**DK6**)

Yellow oil (198 mg, 44%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.27 (m, 5H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 1H), 2.88 (sept, *J* = 6.9 Hz, 1H), 1.76 (q, *J* = 1.1 Hz, 3H), 1.72 (q, *J* = 1.1 Hz, 3H), 1.43 (q, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 195.1, 170.4, 156.9, 135.1, 128.6, 128.5, 128.4, 124.9, 67.3, 47.2, 31.6, 19.69, 19.67, 15.2, 14.1, 12.2; IR (neat, cm^{-1}) 3067, 3035, 2967, 2874, 1752, 1717, 1674, 1570, 1512, 1498, 1456, 1380, 1308, 1278, 1219, 1188, 1162, 1133, 1082; HRMS (ESI^+) *m*/*z* calcd for $C_{19}H_{24}NaO_4$ $[M+Na]^+$: 339.1567; found 339.1566.



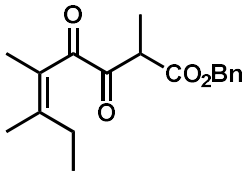
Benzyl (*E*)-6-cyclohexyl-2,5-dimethyl-3,4-dioxohept-5-enoate (**DK7**)

Yellow oil (284 mg, 51%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.27 (m, 5H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 2.53 – 2.42 (m, 1H), 1.87 – 1.49 (m, 11H), 1.43 (d, *J* = 7.3 Hz, 3H), 1.37 – 1.10 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.8, 195.2, 170.4, 156.3, 135.1, 128.6, 128.44, 128.38, 125.2, 67.3, 47.2, 42.9, 29.8, 29.7, 26.31, 26.29, 26.1, 16.7, 14.1, 12.2; IR (neat, cm^{-1}) 3066, 3034, 2930, 2854, 1751, 1717, 1674, 1608, 1535, 1498, 1453, 1379, 1279, 1217, 1177, 1130, 1082, 1029; HRMS (ESI$^+$) *m*/*z* calcd for $C_{22}H_{28}NaO_4$ [M+Na]$^+$: 379.1880; found: 379.1877.



Benzyl (*E*)-2,5,6,8-tetramethyl-3,4-dioxonon-5-enoate (**DK8**)

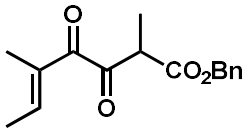
Yellow oil (361 mg, 50%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.28 (m, 5H), 5.16 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 1H), 2.15 – 1.85 (m, 3H), 1.83 (q, *J* = 1.5 Hz, 3H), 1.76 (q, *J* = 1.5 Hz, 3H), 1.43 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 194.9, 170.4, 151.6, 135.1, 128.6, 128.5, 128.4, 126.9, 67.3, 47.2, 45.2, 27.2, 22.7, 22.6, 21.8, 15.0, 12.2; IR (neat, cm^{-1}) 3035, 2958, 2870, 1752, 1717, 1677, 1610, 1498, 1456, 1383, 1303, 1274, 1216, 1176, 108, 1028; HRMS (ESI$^+$) *m*/*z* calcd for $C_{20}H_{26}NaO_4$ [M+Na]$^+$: 353.1723; found: 353.1718.



Benzyl (*Z*)-2,5,6-trimethyl-3,4-dioxooct-5-enoate (**DK9**)

Yellow oil (230 mg, 42%*); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 – 7.28 (m, 5H), 5.14 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 2.23 – 2.08 (m, 2H), 1.80 (q, *J* = 0.9 Hz, 3H), 1.71 (q, *J* = 0.9 Hz, 3H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 194.1, 170.3, 154.6, 135.0, 128.5, 128.35, 128.33, 125.9, 67.2, 47.2, 29.7, 20.1, 14.9, 12.6, 12.0; IR (neat, cm^{-1}) 3034, 2974, 2937, 2876, 1752, 1717, 1676, 1570, 1512, 1492, 1456, 1379, 1327, 1278, 1259, 1216, 1185, 1132, 1082, 1029; HRMS (ESI$^+$) calcd for $C_{18}H_{22}NaO_4$ [M+Na]$^+$: 325.1410; found 325.1421.

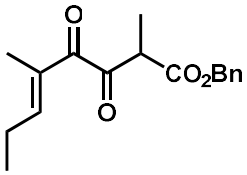
*isolated as an inseparable mixture of geometrical isomers.



Benzyl (*E*)-2,5-dimethyl-3,4-dioxohept-5-enoate (**DK10**)

Yellow oil (233 mg, 36%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.46 – 7.27 (m, 5H), 6.77 (qq, *J* = 7.0, 1.1 Hz, 1H) 5.14 (s, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.82 (dq, *J* = 7.0, 1.1 Hz 3H), 1.78 (p, *J* = 1.1 Hz, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.2, 193.7, 169.8, 147.6, 135.0, 133.9, 128.6, 128.52, 128.47, 67.4, 48.3, 15.4, 11.8, 10.3; IR (neat, cm^{-1}) 3066, 3035, 2943, 1749, 1715, 1658, 1637, 1498, 1456, 1396, 1379, 1264. 1209, 1140, 1084, 1027; HRMS (ESI$^+$) *m*/*z* calcd for $C_{16}H_{18}NaO_4$ $[M+Na]^+$: 297.1097; found 297.1102.

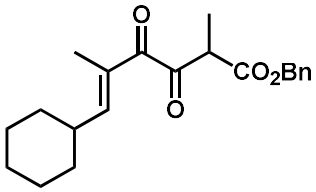
*Significant amounts of the enol tautomer are observed in the ^{1}H and ^{13}C NMR.



Benzyl (*E*)-2,5-dimethyl-3,4-dioxooct-5-enoate (**DK11**)

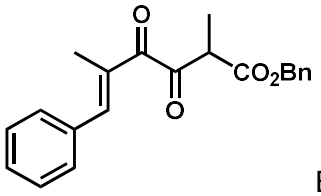
Yellow oil (221 mg, 37%) ^{1}H NMR* (300 MHz, $CDCl_3$) 7.45 – 7.27 (m, 5H), 6.65 (tq, *J* = 7.2, 1.7 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.3 Hz, d), 4.26 (q, *J* = 7.2 Hz, 1H), 2.37 – 2.12 (m, 2H), 1.76 (brs, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.1, 193.9, 169.8, 154.1, 135.0, 132.3, 128.6, 128.5, 128.3, 67.3, 48.4, 22.9, 12.6, 11.8, 10.5; IR (neat, cm^{-1}) 3066, 3035, 2971, 2937, 2877, 1750, 1717, 1657, 1634, 1498, 1456, 1379, 1306, 1246, 1210, 1144, 1086, 1029; HRMS (ESI$^+$) *m*/*z* calcd for $C_{34}H_{40}NaO_8$ $[2M+Na]^+$: 599.2615; found 599.2622.

*Significant amounts of the enol tautomer are observed in the ^{1}H and ^{13}C NMR.



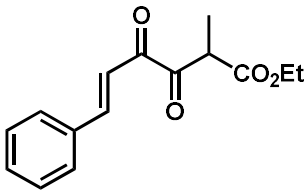
Benzyl (*E*)-6-cyclohexyl-2,5-dimethyl-3,4-dioxohex-5-enoate (**DK12**)

Yellow oil (453 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.42 – 7.28 (m, 5H), 6.50 (d, *J* = 9.5 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 5.10 (d, *J* = 12.1 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 1H), 2.47 – 2.33 (m, 1H), 1.79 (s, 3H), 1.79 – 1.63 (m, 5H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.37 – 0.98 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.3, 194.3, 169.8, 157.4, 135.1, 131.0, 128.6, 128.4, 128.2, 67.2, 48.6, 38.6, 31.4, 31.3, 25.7, 25.38, 25.34, 11.8, 10.6; IR (neat, cm^{-1}) 3034, 2928, 2853, 1751, 1716, 1657, 1633, 1498, 1450, 1381, 1302, 1274, 1259, 1225, 1202, 1154, 1117, 1082, 1028; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{26}NaO_4$ $[M+Na]^+$: 365.1723; found: 365.1731.



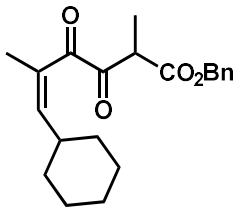
Benzyl (*E*)-2,5-dimethyl-3,4-dioxo-6-phenylhex-5-enoate (**DK13**)

Yellow oil (470 mg, 35%) ^{1}H NMR (300 MHz, $CDCl_3$) 7.55 (q, *J* = 1.4 Hz, 1H), 7.51 – 7.33 (m, 10H), 5.20 (s, 2H), 4.41 (q, *J* = 7.2 Hz, 1H), 2.12 (d, *J* = 1.4 Hz, 3H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.3, 194.6, 169.8, 147.2, 135.1, 134.9, 132.2, 130.4, 129.6, 128.6, 128.5, 128.5, 128.4, 67.5, 48.5, 12.6, 11.8; IR (neat, cm^{-1}) 3065, 3033, 2989, 2943, 1749, 1713, 1655, 1616, 1574, 1497, 1454, 1395, 1382, 1324, 1244, 1217, 1197, 1130, 1081, 1028, 1002; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{20}NaO_4$ [M+Na]$^+$: 359.1254; found 359.1259.



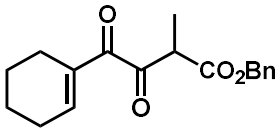
Ethyl (*E*)-2-methyl-3,4-dioxo-6-phenylhex-5-enoate (**DK14**)

Yellow oil (193 mg, 25%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.86 (d, *J* = 16.1 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.47 – 7.35 (m, 4H); 4.27 (q, *J* = 7.2, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.2, 186.6, 170.34 148.2, 134.3, 131.6, 129.1, 129.0, 118.4, 61.6, 46.3, 14.0, 11.9; IR (neat, cm^{-1}) 3063, 2985, 2940, 1717, 1682, 1651, 1607, 1576, 1496, 1450, 1377, 1306, 1206, 1095, 1030; HRMS (EI$^+$) *m*/*z* calcd for $C_{15}H_{16}O_4$ [M]$^+$: 283.1043; found; 283.1040.



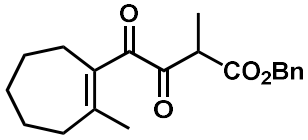
Benzyl (*Z*)-6-cyclohexyl-2,5-dimethyl-3,4-dioxohex-5-enoate (**DK15**)

Yellow oil (412 mg, 61%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.28 (m, 5H), 5.90 (dq, *J* = 10.6, 1.4 Hz, 1H), 5.18 (d, *J* = 12.3 Hz, 1H), 512 (d, *J* = 12.3 Hz, 1H), 4.21 (q, *J* = 7.3 Hz, 1H), 2.36 (qt, *J* = 10.6, 3.5 Hz, 1H), 1.82 (d, *J* = 1.4 Hz, 3H), 1.74 – 1.56 (m, 5H), 1.44 (q, *J* = 7.3 Hz, 3H), 1.28 – 0.96 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 194.4, 170.2, 151.3, 135.1, 128.7, 128.6, 128.5, 128.3, 67.3, 47.4, 39.0, 32.5, 32.2, 25.8, 25.42, 25.38, 19.5, 12.0; IR (neat, cm^{-1}) 3034, 2927, 2852, 1752, 1716, 1679, 1651, 1498, 1449, 1381, 1309, 1257, 1217, 1190, 1112, 1081, 1027; HRMS (ESI$^+$) *m*/*z* calcd for $C_{21}H_{26}NaO_4$ [M+Na]$^+$: 365.1723; found: 365.1734.



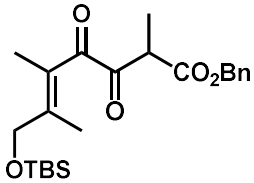
Benzyl 4-(cyclohex-1-en-1-yl)-2-methyl-3,4-dioxobutanoate (**DK16**)

Yellow oil (352 mg, 25%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.27 (m, 5H), 6.94 (tt, *J* = 3.9, 1.5 Hz, 1H), 5.11 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 2.33 – 2.05 (m, 4H), 1.69 – 1.53 (m, 4H), 1.42 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.8, 192.6, 169.9, 149.9, 135.0, 134.7, 128.6, 128.5, 128.4, 67.4, 48.0, 26.6, 22.3, 21.4, 21.2, 11.7; IR (neat, cm^{-1}) 3070, 3035, 2939, 2863, 1750, 1714, 1656, 1630, 1498, 1456, 1382, 1309, 1273, 1235, 1193, 1121, 1082, 1029; HRMS (ESI^+) *m*/*z* calcd for $C_{18}H_{20}NaO_4$ $[M+Na]^+$: 323.1254; found: 323.1257.



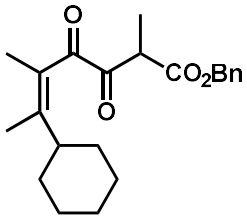
Benzyl 2-methyl-4-(2-methylcyclohept-1-en-1-yl)-3,4-dioxobutanoate (**DK17**)

Yellow oil (474 mg, 59%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.40 – 7.28 (m, 5H), 5.16 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 1H), 2.33 – 2.24 (m, 4H), 1.91 (t, *J* = 0.9 Hz, 3H), 1.80 – 1.70 (m, 2H), 1.85 – 1.41 (m, 4H), 1.43 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 193.8, 190.5, 166.8, 154.5, 131.5, 124.9, 124.8, 124.7, 63.6, 43.6, 34.7, 28.5, 25.4, 22.7, 22.7, 21.1, 20.3, 8.5; IR (neat, cm^{-1}) 2926, 2853, 1750, 1716, 1671, 1612, 1455, 1378, 1284, 1254, 1216, 1176, 1119, 1087; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{25}O_4$ $[M+H]^+$: 329.1747; found 329.1752.



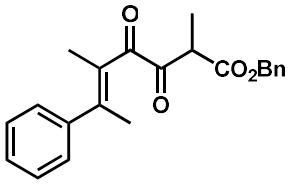
Benzyl (*E*)-7-((tert-butyldimethylsilyl)oxy)-2,5,6-trimethyl-3,4-dioxohept-5-enoate (**DK18**)

Yellow oil (341 mg, 33%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.27 (m, 5H), 5.14 (s, 2H), 4.23 (brs, 2H), 4.21 (q, *J* = 7.2 Hz, 1H), 1.86 (tq, *J* = 1.7, 0.8 Hz, 3H), 1.71 (tq, *J* = 1.6, 0.8 Hz, 3H), 1.43 (d, *J* = 7.2 Hz, 3H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.6, 194.4, 170.3, 151.0, 135.0, 128.6, 128.5, 128.5, 125.6, 67.3, 63.8, 47.2, 25.8, 18.3, 17.6, 13.8, 12.1, -5.4; IR (neat, cm^{-1}) 3067, 3035, 2955, 2930, 2886, 2857, 1753, 1719, 1678, 1649, 1566, 1457, 1375, 1300, 1255, 1216, 1180, 1136; HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{35}O_5Si$ $[M+H]^+$: 419.2248; found: 419.2254.



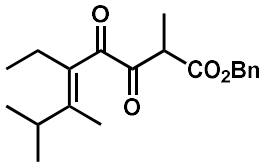
Benzyl (*Z*)-6-cyclohexyl-2,5-dimethyl-3,4-dioxohept-5-enoate (**DK20**)

Yellow oil (295 mg, 42%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.27 (m, 5H), 5.18 (d, *J* = 12.2 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 1H), 2.50 – 2.40 (m, 1H), 1.82 – 1.59 (m, 9H), 1.57 – 1.38 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.35 – 1.11 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.5, 194.9, 170.5, 156.5, 135.2, 128.6, 128.4, 128.3, 125.9, 67.2, 47.3, 44.2, 30.4, 25.98, 25.95, 15.7, 15.1, 12.4; IR (neat, cm^{-1}) 3034, 2930, 2854, 1717, 1672, 1639, 1608, 1452, 1382, 1288, 1214, 1176, 1128, 1080; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{29}O_4$ $[M+H]^+$: 357.2060; found: 357.2066.



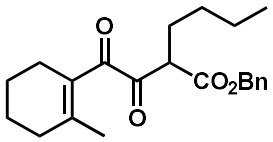
Benzyl (*E*)-2,5-dimethyl-3,4-dioxo-6-phenylhept-5-enoate (**DK21**)

Yellow oil (347 mg, 34% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 7.42 – 7.29 (m, 8H), 7.17 – 7.11 (m, 2H), 5.20 (d, *J* = 12.5 Hz, 1H), 5.15 (d, *J* = 12.5 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 1H), 2.11 (q, *J* = 1.5 Hz, 3H), 1.68 (q, *J* = 1.5 Hz, 3H), 1.48 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.4, 195.2, 170.3, 150.0, 142.7, 135.1, 128.6, 128.5, 128.4, 128.4, 127.9, 127.5, 127.2, 67.4, 47.2, 23.6, 16.6, 12.1; IR (neat, cm^{-1}) 3063, 3033, 2989, 2943, 1753, 1717, 1685, 1611, 1597, 1492, 1455, 1376, 1304, 1238, 1200, 1087, 1026; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{22}O_4Na$ $[M+Na]^+$: 373.1410; found: 373.1412.



Benzyl (*E*)-5-ethyl-2,6,7-trimethyl-3,4-dioxooct-5-enoate (**DK22**)

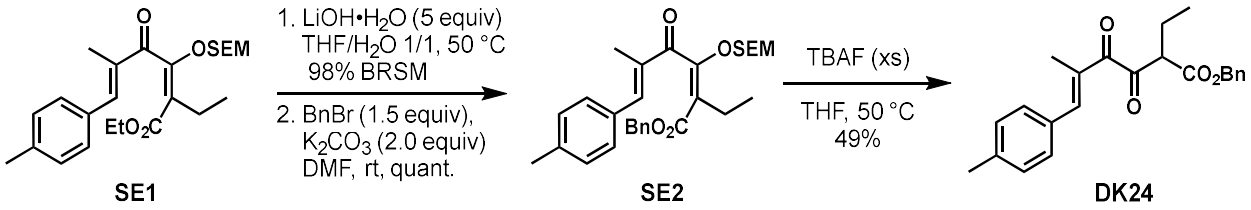
Yellow oil (519 mg, 35% over 2 steps); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41 – 7.28 (m, 5H), 5.15 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 2.91 (hept, *J* = 6.8 Hz, 1H), 2.25 (brq, *J* = 7.6 Hz, 2H), 1.62 (s, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.4, 196.0, 170.4, 154.4, 135.2, 131.8, 128.6, 128.4, 128.3, 67.2, 47.3, 30.9, 21.7, 20.4, 20.3, 15.3, 14.2, 12.5; IR (neat, cm^{-1}) 3067, 3035, 2967, 2937, 2875, 1752, 1719, 1665, 1609, 1498, 1456, 1378, 1306, 1216, 1186, 1133, 1083, 1027; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{26}O_4Na$ $[M+Na]^+$ 353.1723; found: 353.1725.



Benzyl 2-(2-(2-methylcyclohex-1-en-1-yl)-2-oxoacetyl)hexanoate (**DK23**)

Yellow oil (439 mg, 43%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 – 7.26 (m, 5H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 4.07 (t, *J* = 6.9 Hz, 1H), 2.39 – 2.02 (m, 4H), 2.00 – 1.88 (m, 2H), 1.84 (s, 3H), 1.67 – 1.48 (m, 4H), 1.42 – 1.21 (m, 4H), 0.98 – 0.78 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.9, 194.4, 169.8, 151.5, 135.1, 128.5, 128.5, 128.4, 128.1, 67.2, 53.2, 34.0, 29.3, 27.2, 25.5, 22.6, 22.4, 22.0, 21.9, 13.8; IR (neat, cm^{-1}) 3066, 3034, 2933, 2862, 1749, 1716, 1673, 1621, 1498, 1456, 1419, 1378, 1336, 1280, 1214, 1169, 1122, 1082, 1054, 1029, 1002; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{28}O_4Na$ $[M+Na]^+$: 379.1880; found 379.1886.

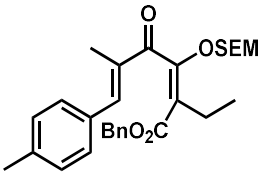
Diketones **DK24** and **DK25** were prepared through the method described below.



SE1 **SE2** **DK24**

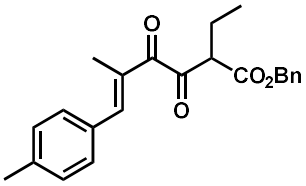
SEM enol ether **SE1** was prepared according to a protocol found in the literature.[13]

Hydrolysis of SEM enol ether **SE1** using lithium hydroxide monohydrate (5.0 equiv) in THF/H_2O (1/1, 0.1 M) at 50 °C overnight led to an incomplete reaction that provided 98% yield (BRSM) of the intermediate carboxylic acid, which was separated from the unreacted starting material by silica gel column chromatography (10% to 20% ethyl acetate in hexanes as eluent). The intermediate acid was immediately esterified to compound **SE2** using benzyl bromide (1.5 equiv) and potassium carbonate (2.0 equiv) in DMF (0.1 M) at room temperature. The reaction mixture was quenched by the addition of water and diethyl ether. The phases were separated and the aqueous phase was extracted with diethyl ether (x2). The combined organic extracts were dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and compound **SE2** was isolated as a colorless oil (314 mg, quantitative yield). Deprotection of the SEM protecting group of **SE2** was achieved using a large excess of TBAF in THF at 50 °C. The diketone was purified using column chromatography (30% DCM/Hex then 4% EtOAc/Hex) and isolated as a yellow oil (95 mg, 49% yield).



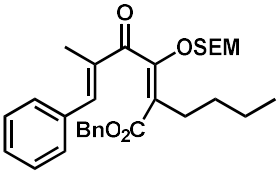
Benzyl (2*E*,5*E*)-2-ethyl-5-methyl-4-oxo-6-(*p*-tolyl)-3-((2-(trimethylsilyl)ethoxy)methoxy)hexa-2,5-dienoate (**SE2**)

Colorless oil (314 mg, quant.); ^{1}H NMR (300 MHz, $CDCl_3$) 7.44 (brs, 1H), 7.31 – 7.22 (m, 9H), 3.73 – 3.68 (m, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.17 (t, *J* = 7.4 Hz, 3H), 0.9 – 0.84 (m, 2H), −0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 194.8, 167.1, 158.3, 142.0, 139.3, 136.5, 135.8, 132.8, 130.2, 129.2, 128.4, 128.2, 128.0, 116.9, 93.2, 66.8, 66.4, 21.4, 19.2, 17.9, 13.5, 12.3, -1.5; IR (neat, cm^{-1}) 3033, 2955, 1703, 1659, 1622, 1510, 1456, 1379, 1359, 1307, 1251, 1184, 1126, 1086, 1059, 1029; HRMS (ESI$^+$) *m*/*z* calcd for $C_{29}H_{38}O_5SiNa$ $[M+Na]^+$ 517.2381; found: 517.2378.



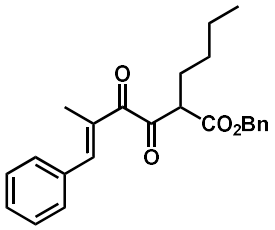
Benzyl (*E*)-2-ethyl-5-methyl-3,4-dioxo-6-(*p*-tolyl)hex-5-enoate (**DK24**)

Yellow oil (95 mg, 49% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 7.47 (q, *J* = 1.3 Hz, 1H), 7.32 – 7.22 (m, 9H), 5.15 (s, 2H), 4.14 (t, *J* = 7.0 Hz, 1H), 2.42 (s, 3H), 2.09 (d, *J* = 1.3 Hz, 3H), 2.04 (q, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.9, 194.7, 169.2, 147.5, 140.2, 135.0, 132.3, 131.4, 130.6, 129.3, 128.6, 128.4, 128.4, 67.3, 55.9, 21.5, 20.8, 12.6, 11.9; IR (neat, cm^{-1}) 2969, 2932, 2878, 1745, 1712, 1685, 1654, 1605, 1456, 1382, 1345, 1244; HRMS (ESI$^+$) *m*/*z* calcd for $C_{23}H_{24}O_4Na$ $[M+Na]^+$ 387.1567; found: 387.1580.



Benzyl (2*E*,5*E*)-2-butyl-5-methyl-4-oxo-6-phenyl-3-((2-(trimethylsilyl)ethoxy)methoxy)hexa-2,5-dienoate (**SE3**)

Colorless oil (237 mg, 73% yield over two steps); ^{1}H NMR (300 MHz, $CDCl_3$) 7.47 (q, *J* = 1.7 Hz, 1H), 7.45 – 7.32 (m, 5H), 7.29 – 7.23 (m, 5H), 5.08 (s, 2H), 5.06 (s, 2H), 3.74 – 3.67 (m, 2H), 2.53 (dd, *J* = 8.3, 6.6 Hz, 2H), 2.00 (d, *J* = 1.3 Hz, 3H), 1.62 – 1.38 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.90 – 0.84 (m, 2H), −0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 194.9, 167.3, 158.4, 141.7, 137.4, 135.8, 135.6, 130.0, 129.0, 128.5, 128.4, 128.2, 128.0, 115.8, 93.1, 66.9, 66.4, 31.0, 25.4, 22.8, 17.9, 14.0, 12.3, −1.6; IR (neat, cm^{-1}) 3033, 2955, 2927, 2872, 1705, 1661, 1621, 1498, 1455, 1378, 1359, 1313, 1279, 1250, 1208, 1127, 1093, 1040, 1029, 1003; HRMS (ESI$^+$) *m*/*z* calcd for $C_{30}H_{40}O_5SiNa$ $[M+Na]^+$: 531.2537; found: 531.2530.

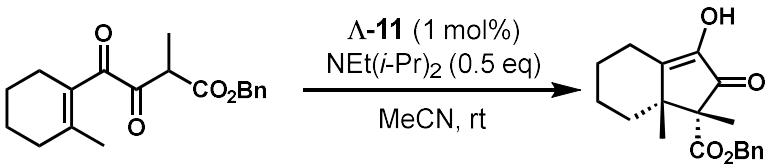


Benzyl (*E*)-2-butyl-5-methyl-3,4-dioxo-6-phenylhex-5-enoate (**DK25**)

Yellow oil (113 mg, 64%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.52 – 7.50 (m, 1H), 7.45 – 7.37 (m, 6H), 7.30 – 7.28 (m, 4H); 5.16 (s, 2H), 4.22 (t, *J* = 7.0 Hz, 1H), 2.09 (d, *J* = 1.3 Hz, 3H), 2.07 – 1.98 (m, 2H), 1.47 – 1.30 (m, 4H), 0.97 – 0.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.8, 194.6, 169.3, 147.2, 135.1, 135.0, 132.3, 130.4, 129.6, 128.6, 128.5, 128.5, 128.4, 67.3, 54.4, 29.5, 27.0, 22.5, 13.9, 12.6; IR (neat, cm^{-1}) 3064, 3033, 2958, 2928, 2858, 1744, 1717, 1655, 1616, 1575, 1497, 1456, 1378, 1326, 1245, 1215, 1169, 1129, 1077, 1029, 1003; HRMS (ESI^+) *m*/*z* calcd for $C_{24}H_{26}O_4Na$ $[M+Na]^+$ 401.1723; found: 401.1721.

10. Synthesis of Cyclopentenones

Representative procedure:



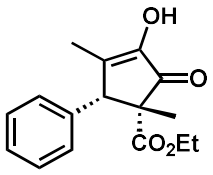
Benzyl (1*R*,7a*R*)-3-hydroxy-1,7a-dimethyl-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-1-carboxylate (**14**)

To a solution of diketone **6** (535 mg, 1.7 mmol) and Λ-**11** TFA (15 mg, 1 mol%) in MeCN (0.05 M) was added *i*-Pr_2NEt (0.15 mL, 0.85 mmol) at ambient temperature. The reaction was monitored by LCMS for ≥95% conversion of diketone, was quenched by the addition of 1 M HCl, and extracted with Et_2O (x3). The combined organic extracts were washed with water (x2) and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* and the crude oil was purified by flash column chromatography (load with PhMe, 0, 5, 10, 15% EtOAc in hexanes) to afford cyclopentenone **14** as a colorless oil (482 mg, 91% yield).

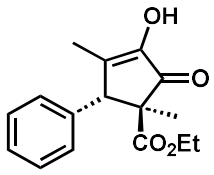
e.r. 97:3; $[\alpha]_D^{20}$ −10.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.37 – 7.27 (m, 5H), 5.97 (brs, 1H), 5.15 (d, *J* = 12.5 Hz, 1H), 5.04 (d, *J* = 12.5 Hz, 1H), 2.87 (ddt, *J* = 14.2, 4.3, 2.0 Hz, 1H), 2.11 (ddd, *J* = 14.2, 13.4, 5.5 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.74 – 1.47 (m, 3H), 1.39 (s, 3H), 1.32 – 1.10 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.3, 171.7, 152.4, 144.2, 135.4, 128.5, 128.2, 128.1, 66.6, 60.1, 44.6, 35.5, 26.0, 22.8, 21.9, 20.8, 16.9; IR (neat, cm^{-1}) 3348, 2942, 2864, 1732, 1705, 1657, 1454, 1399, 1349, 1331, 1256, 1233, 1181, 1158, 1140, 1098, 1082, 1034; HRMS (ESI$^+$) m/*z* calcd for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1416; found: 337.1411; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 11.9 min (minor), t_R = 15.5 min (major).

Please note:

1. Several cyclopentenones prepared here have been observed to discolor in air within minutes when neat and have prompted us to store them immediately in a screw cap vial sealed under an Ar atmosphere and to store them in the freezer (−20 °C). We have found the cyclopentenones to be indefinitely stable under these storage conditions (as long as efforts are made to exclude air).
2. The cyclopentenone racemates that were used as standards for HPLC in this study were prepared in parallel with the enantioenriched cyclopentenones using $Sc(OTf)_3$ (30 mol%) and *i*-Pr_2NEt (1.5 equiv) in MeCN (2 mL) with 10–15 mg of diketone. The Sc-catalyzed cyclizations were not as highly diastereoselective.



8



dia-8

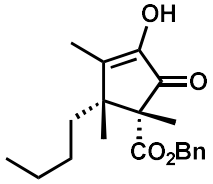
Ethyl (1*R*,5*R*)-3-hydroxy-1,4-dimethyl-2-oxo-5-phenylcyclopent-3-ene-1-carboxylate (**8**) and ethyl (1*S*,5*R*)-3-hydroxy-1,4-dimethyl-2-oxo-5-phenylcyclopent-3-ene-1-carboxylate (***dia*-8**)

Combined yield: 354 mg, 96%; *dr* 4.6/1.0.

8*: White solid; e.r. 86:14;[1]H and [13]C NMR data match previously reported values.[13] [1]H NMR (300 MHz, $CDCl_3$) 7.35 – 7.24 (m, 3H), 7.14 – 7.09 (m, 2H), 6.16 (brs, 1H), 3.71 (q, *J* = 1.4 Hz, 1H), 3.58 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.42 (dq, *J* = 10.8, 7.2 Hz, 1H), 1.93 (d, *J* = 1.4 Hz, 1H), 1.59 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); [13]C NMR (75 MHz, $CDCl_3$) 200.4, 170.0, 148.8, 142.7, 136.6, 129.3, 128.2, 127.8, 61.0, 58.7, 58.4, 21.8, 13.5, 13.0; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 7.18 min (minor), t_R = 14.8 min (major).

***dia-8*:** Colorless oil; e.r. 92:8; $[\alpha]_D^{20}$ +52.6 (*c* 1.2, $CHCl_3$); [1]H NMR (300 MHz, $CDCl_3$) 7.36 – 7.25 (m, 3H), 7.09 – 6.97 (m, 2H), 6.12 (brs, 1H), 4.24 (q, *J* = 1.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.94 (d, *J* = 1.5 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 3H); [13]C NMR (75 MHz, $CDCl_3$) 199.9, 171.9, 148.5, 144.5, 137.0, 129.5, 128.6, 127.7, 61.8, 56.1, 54.7, 17.8, 14.1, 13.3; IR (neat, cm^{-1}) 3442, 3063, 3031, 2987, 2941, 1789, 1733, 1667, 1456, 1379, 1246, 1170, 1106, 1082, 1018; HRMS m/*z* calcd for $C_{16}H_{18}O_4aNa$ $[M+Na]^+$: 297.1103; found: 297.1101; HPLC (Chiralpak OJ-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 95/5, flow 1 mL/min) t_R = 13.5 min (minor), t_R = 43.8 min (major).

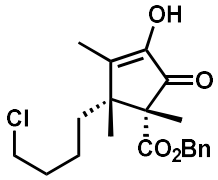
*Absolute stereochemistry was determined by comparison of major enantiomer's retention times to previous work.[12, 13]



Benzyl (1*R*,2*R*)-2-butyl-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**15**)

Colorless oil (147 mg, 79%); e.r. 97:3; $[\alpha]_D^{20}$ +24.3 (*c* 1.2, $CHCl_3$); [1]H NMR (300 MHz, $CDCl_3$) 7.35 – 7.24 (m, 5H), 6.45 (brs, 1H), 5.09* (s, 2H), 1.90 (s, 3H), 1.56 – 1.31 (m, 2H), 1.38 (s, 3H), 1.13 (s, 3H), 1.11 – 0.95 (m, 4H), 0.75 (t, *J* = 7.0 Hz, 3H); [13]C NMR (75 MHz, $CDCl_3$) 200.2, 171.4, 150.2, 146.8, 135.4, 128.5, 128.2, 128.1, 66.8, 59.5, 48.2, 36.8, 26.8, 23.3, 21.6, 19.4, 13.9, 10.2; IR (neat, cm^{-1}) 3354, 3066, 3034, 2957, 2872, 1736, 1702, 1656, 1586, 1498, 1455, 1406, 1385, 1359, 1234, 1191, 1157, 1080, 1030; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{27}O_4$ $[M+H]^+$: 331.1904; found 331.1893. HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 7.1 min (minor), t_R = 9.0 min (major).

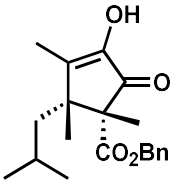
*The benzylic protons coincidentally have the same chemical shift and appear as a singlet.



Benzyl (1*R*,2*R*)-2-(4-chlorobutyl)-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**16**)

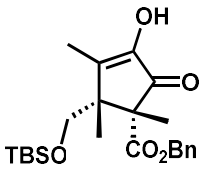
Colorless oil (135 mg, 66%) e.r. 97:3; $[\alpha]_D^{20}$ +14.1 (*c* 0.98, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.37 – 7.27 (m, 5H) 5.15 (d, *J* = 12.4 Hz, 1H), 5.08 (d, *J* = 12.4 Hz, 1H), 3.30 (t, *J* = 6.5 Hz, 2H) 1.90 (s, 3H), 1.54 – 1.21 (m, 6H), 1.39 (s, 3H), 1.14 (s, 3H); ^{13}C NMR* (75 MHz, $CDCl_3$) 199.7, 171.4, 149.0, 146.7, 135.3, 128.6, 128.4, 67.0, 59.4, 48.2, 44.52, 36.3, 32.9, 22.1, 21.6, 19.4, 10.2; IR (neat, cm^{-1}) 3343, 3034, 2954, 2874, 1702, 1658, 1498, 1455, 1405, 1386, 1360, 1259, 1235, 1156, 1076, 1029; HRMS (ESI^+) *m*/*z* calcd for $C_{21}H_{25}ClO_4Na$ $[M+Na]^+$: 387.1334; found 387.1330; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 10.4 min (minor), t_R = 15.0 min (major).

*One carbon signal is not observed in the ^{13}C NMR.



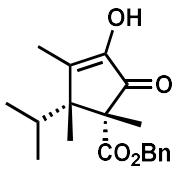
Benzyl (1*R*,2*R*)-4-hydroxy-2-isobutyl-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**17**)

Colorless oil (261 mg, 75%); e.r. 97:3; $[\alpha]_D^{20}$ −33.8 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.36 – 7.26 (m, 5H), 6.48 (brs, 1H), 5.15 (d, *J* = 12.8 Hz, 1H), 5.11 (d, *J* = 12.8 Hz, 1H), 1.90 (s, 3H), 1.53 – 1.34 (m, 3H), 1.40 (s, 3H), 1.18 (s, 3H), 0.77 (d, *J* = 6.2 Hz, 3H), 0.69 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.9, 171.1, 148.9, 146.5, 135.5, 128.6, 128.2, 127.9, 66.7, 59.5, 49.0, 46.5, 25.3, 24.7, 24.5, 21.6, 20.9, 10.6; IR (neat, cm^{-1}) 3346, 3066, 3034, 2957, 2870, 1741, 1702, 1656, 1587, 1498, 1455, 1406, 1386, 1365, 1306, 1250, 1231, 1191, 1155, 1124, 1080, 1049, 1031; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{27}O_4$ $[M+H]^+$: 331.1904; found: 331.1909; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 95/5, flow 1 mL/min) t_R = 12.0 min (minor), t_R = 12.8 min (major).



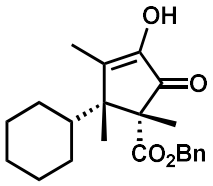
Benzyl (1*R*,2*R*)-2-(((tert-butyldimethylsilyl)oxy)methyl)-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**18**)

Colorless oil (135 mg, 69%); e.r. 96:4; $[\alpha]_D^{20}$ +34.8 (*c* 0.14, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.38 – 7.26 (m, 5H), 6.04 (brs, 1H), 5.17 (d, *J* = 12.7 Hz, 1H), 5.07 (d, *J* = 12.7 Hz, 1H), 3.65 (d, *J* = 9.8 Hz, 1H), 3.49 (d, *J* = 9.8 Hz, 1H), 1.89 (s, 3H), 1.36 (s, 3H), 1.17 (s, 3H), 0.80 (s, 9H), −0.07 (s, 3H), −0.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.4, 170.8, 147.0, 143.8, 135.8, 128.5, 128.0, 127.6, 66.8, 66.4, 56.8, 50.5, 25.7, 21.0, 18.1, 16.8, 10.0, −5.7; IR (neat, cm^{-1}) 3350, 2953, 2929, 2884, 2857, 1719, 1666, 1472, 1407, 1360, 1257, 1199, 1167, 1091, 1067; HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{34}O_5SiNa$ $[M+Na]^+$: 441.2068; found: 441.2073; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 5.3 min (minor), t_R = 6.3 min (major).



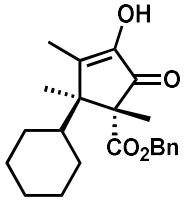
Benzyl (1*R*,2*R*)-4-hydroxy-2-isopropyl-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**19**)

Colorless oil (132 mg, 73%); e.r. 99:1; $[\alpha]_D^{20}$ −20.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.37 – 7.24 (m, 5H), 6.07 (brs, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.09 (d, *J* = 12.5 Hz, 1H), 1.93 (s, 3H), 1.92 (sept, *J* = 7.0 Hz, 1H), 1.39 (s, 3H), 1.20 (s, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.1, 171.7, 147.3, 147.2, 135.3, 128.5, 128.2, 128.0, 66.8, 59.8, 52.3, 35.3, 21.8, 19.3, 18.9, 11.8; IR (neat, cm^{-1}) 3346, 3065, 3033, 2984, 2883, 1699, 1656, 1456, 1405, 1383, 1372, 1360, 1266, 1234, 1193, 1140, 1121, 1078; HRMS (ESI^+) m/*z* calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$: 339.1572; found: 339.1572; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 8.2 min (minor), t_R = 9.8 min (major).



Benzyl (1*R*,2*R*)-2-cyclohexyl-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**20**)

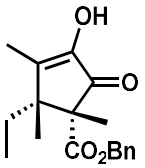
Colorless oil (144 mg, 61%); e.r. 99:1 $[\alpha]_D^{20}$ −40.4 (*c* 0.96, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.38 – 7.26 (m, 5H), 6.34 (brs, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 1.91 (s, 3H), 1.72 – 1.41 (m, 6H), 1.38 (s, 3H), 1.19 (s, 3H), 1.05 – 0.68 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.0, 171.4, 147.1, 146.9, 135.1, 128.6, 128.3, 128.2, 66.7, 60.3, 52.2, 46.2, 30.1, 29.4, 27.4, 26.8, 26.2, 22.7, 17.5, 12.2; IR (neat, cm^{-1}) 3344, 3065, 3033, 2929, 2853, 1698, 1656, 1498, 1448, 1404, 1386, 1362, 1264, 1249, 1219, 1195, 1148, 1129, 1046, 1061; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{28}NaO_4$ $[M+Na]^+$: 279.1880; found 379.1878; HPLC (Chiralpak OD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 5.9 min (minor), t_R = 6.8 min (major).



Benzyl (1*R*,2*S*)-2-cyclohexyl-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**21**)

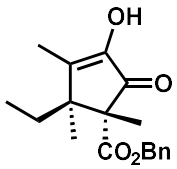
Colorless oil (170 mg, 59%); e.r. 97.5:2.5; ^1H NMR (300 MHz, $CDCl_3$) 7.37 – 7.19 (m, 5H), 6.62 (brs, 1H), 5.06 (d, *J* = 12.7 Hz, 1H), 4.95 (d, *J* = 12.7 Hz, 1H), 1.91 (s, 3H), 1.85 – 1.59 (m, 5H), 1.53 – 1.34 (m, 1H), 1.42 (s, 3H), 1.31 – 0.96 (m, 5H). 0.99 (s, 3H); ^{13}C NMR* (75 MHz, $CDCl_3$) 200.5, 172.2, 149.4 (br), 147.5 (br), 135.3, 128.5, 128.1, 127.6, 66.7, 62.2 (br), 50.7, 44.8 (br), 32.2 (br), 29.3, 27.7, 26.5, 26.3, 17.6 (br), 15.2 (br), 12.1 (br); IR (neat, cm^{-1}) 3339, 2932, 2853, 1737, 1697, 1655, 1455, 1406, 1362, 1233, 1188, 1105, 1080, 1066; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{28}O_4Na$ $[M+Na]^+$: 379.1880; found: 379.1885; HPLC (Chiralpak AI-3®, 4.6 mm x 150 mm, UV 300 nm, hexane/EtOH = 90/10, flow 1 mL/min) t_R = 6.4 min (minor), t_R = 7.1 min (major).

*some ^{13}C NMR signals appear broadened due to hindered rotation at room temperature.



Benzyl (1*R*,2*R*)-2-ethyl-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**22**)

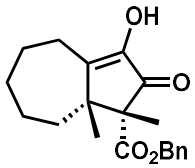
Colorless oil (257 mg, 78%); e.r. 97:3 (> 1/99, recryst. from hex); $[\alpha]_D^{20}$ −25.9 (*c* 1.0, $CHCl_3$) (of the 3/97 *er*); ^{1}H NMR (300 MHz, $CDCl_3$) 7.37 – 7.27 (m, 5H), 5.96 (brs, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.09 (d, *J* = 12.3 Hz, 1H), 1.89 (s, 3H), 1.64 – 1.41 (m, 2H), 1.38 (s, 3H), 1.13 (s, 3H), 0.69 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.0, 171.5, 149.4, 146.7, 135.4, 128.5, 128.2, 128.1, 66.8, 59.2, 48.5, 29.6, 21.1, 19.5, 10.1, 9.2; IR (neat, cm^{-1}) 3348, 3065, 3034, 2974, 2945, 2883, 1701, 1655, 1586, 1498, 1456, 1406, 1361, 1261, 1235, 1196, 1161, 1078, 1029, 970; HRMS (ESI$^+$) *m*/*z* calcd for $C_{18}H_{22}O_4Na$ $[M+Na]^+$: 325.1410; found: 325.1414; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 85/15, flow 1 mL/min) t_R = 7.0 min (minor), t_R = 8.1 min (major).



Benzyl (1*R*,2*S*)-2-ethyl-4-hydroxy-1,2,3-trimethyl-5-oxocyclopent-3-ene-1-carboxylate (**23**)

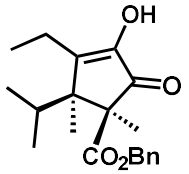
Colorless oil (76 mg, 83%*); e.r. 83:17; ^{1}H NMR (300 MHz, $CDCl_3$) 7.38 – 7.25 (m, 5H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 1.89 (s, 3H), 1.65 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.51 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.42 (s, 3H), 1.01 (s, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.2, 171.9, 148.3, 147.6, 135.4, 128.5, 128.2, 127.9, 66.7, 60.0, 48.0, 29.5, 21.1, 16.0, 10.3, 10.2; IR (neat, cm^{-1}) 3348, 3065, 3034, 2972, 2944, 2883, 1735, 1701, 1656, 1498, 1456, 1407, 1360, 1338, 1234, 1198, 1152, 1077, 1029; HRMS (ESI$^+$) *m*/*z* calcd for $C_{18}H_{22}O_4Na$ $[M+Na]^+$: 325.1410; found: 325.1414; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 9.1 min (minor), t_R = 10.9 min (major).

*Isolated as an inseparable mixture of diastereomers.



Benzyl (1*R*,8a*R*)-3-hydroxy-1,8a-dimethyl-2-oxo-1,2,4,5,6,7,8,8a-octahydroazulene-1-carboxylate (**24**)

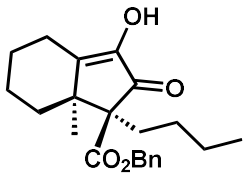
Pale yellow oil (241 mg, 67%); e.r. 85:15; $[\alpha]_D^{20}$ −0.9 (*c* 0.72, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.47 – 7.33 (m, 5H), 6.29 (brs, 1H), 5.21 – 5.12 (m, 2H), 3.02 (ddd, *J* = 14.2, 7.3, 3.8 Hz, 1H), 2.20 (ddd, *J* = 14.2, 10.3, 3.7 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.69 – 1.37 (m, 5H), 1.47 (s, 3H), 1.23 (s, 3H), 1.18 – 1.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 201.1, 172.0, 154.0, 146.7, 135.2, 128.5, 128.2, 127.9, 66.8, 60.3, 48.8, 37.0, 30.7, 27.0, 25.8, 25.4, 24.6, 16.7; IR (neat, cm^{-1}) 3343, 3034, 2932, 2878, 1732, 1697, 1655, 1455, 1398, 1382, 1349, 1236, 1154, 1126, 1070, 1053, 1006; HRMS (ESI^+) m/*z* calcd for $C_{20}H_{24}O_4Na$ $[M+Na]^+$: 351.1572; found: 351.1567; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 10.6 min (minor), t_R = 12.3 min (major).



Benzyl (1*S*,2*S*)-3-ethyl-4-hydroxy-2-isopropyl-1,2-dimethyl-5-oxocyclopent-3-ene-1-carboxylate (**25**)

Colorless oil (161 mg, 70%, 81% BRSM); e.r. 95:5*; $[\alpha]_D^{20}$ −22.4 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.38 – 7.25 (m, 5H), 6.01 (brs, 1H), 5.13 (s, 2H), 2.45 (dq, *J* = 15.3, 7.6 Hz, 1H), 2.19 (dq, *J* = 15.3, 7.6 Hz, 1H), 1.89 (hept, *J* = 6.8 Hz, 1H), 1.39 (s, 3H), 1.22 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H), 0.82 (d, *J* = 7.6 Hz, 3H), 0.75 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.3, 171.5, 151.7, 146.9, 135.3, 128.5, 128.2, 128.0, 66.7, 59.8, 52.8, 36.1, 22.7, 20.3, 19.4, 19.2, 17.7, 12.0; IR (neat, cm^{-1}) 3346, 2969, 2880, 1736, 1694, 1652, 1465, 1456, 1400, 1371, 1313, 1265, 1225, 1193, 1193, 1136, 1093, 1009; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{26}O_4Na$ $[M+Na]^+$: 353.1723; found: 353.1722. HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 7.5 min (major), t_R = 8.8 min (minor).

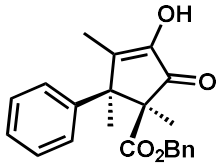
*prepared using Δ-**11**



Benzyl (1*S*,7a*S*)-1-butyl-3-hydroxy-7a-methyl-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-1-carboxylate (**26**)

Pale yellow oil (26 mg, 14%, 47% BRSM); e.r. 88:12*; $[\alpha]_D^{20}$ −3.6 (*c* 0.79, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.47 – 7.28 (m, 5H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 2.82 (ddt, *J* = 13.5, 4.1, 1.8 Hz, 1H), 2.21 – 1.98 (m, 2H), 1.96 – 1.41 (m, 6H), 1.38 – 1.07 (m, 9H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.8, 170.6, 150.8, 143.7, 135.5, 128.5, 128.3, 128.3, 66.5, 62.8, 45.1, 38.1, 33.2, 26.8, 26.7, 23.4, 22.9, 22.0, 18.7, 13.9; IR (neat, cm^{-1}) 3445, 2955, 2935, 2870, 1779, 1756, 1727, 1654, 1456, 1377, 1325, 1259, 1212, 1158, 1108, 1060; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{28}O_4Na$ $[M+Na]^+$: 379.1880; found: 379.1885; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 4.5 min (major), t_R = 12.1 min (minor).

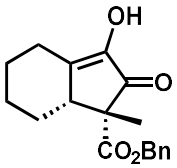
*prepared using Δ-**11**



Benzyl (1*S*,2*S*)-4-hydroxy-1,2,3-trimethyl-5-oxo-2-phenylcyclopent-3-ene-1-carboxylate (**27**)

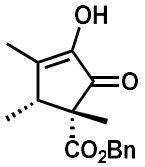
Thick pale-yellow oil (124 mg, 81%); e.r. 87.5/12.5*; $[\alpha]_D^{20}$ +1.8 (*c* 0.95, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.34 – 7.19 (m, 8H), 7.11 – 7.03 (m, 2H), 6.24 (brs, 1H), 4.39 (d, *J* = 12.8 Hz, 1H), 4.20 (d, *J* = 12.8 Hz, 1H), 1.93 (s, 3H), 1.65 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.3, 170.7, 148.4, 147.9, 141.4, 135.2, 128.4, 127.99, 127.97, 127.93, 127.7, 127.2, 66.4, 61.8, 52.9, 21.4, 18.3, 11.0; IR (neat, cm^{-1}) 3346, 3062, 3033, 2984, 2946, 1774, 1709, 1660, 1601, 1496, 1446, 1404, 1386, 1362, 1266, 1192, 1120, 1081, 1030; HRMS (ESI^+) *m*/*z* calcd for $C_{22}H_{22}O_4$ $[M+H]^+$: 351.1591; found: 351.1600; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 9.2 min (major), t_R = 10.4 min (minor).

*prepared using Δ-**11**



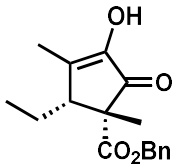
Benzyl (1*R*,7a*R*)-3-hydroxy-1-methyl-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-1-carboxylate (**28**)

Colorless oil (182 mg, 79%); e.r. 95:5; $[\alpha]_D^{20}$ −13.1 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.36 – 7.25 (m, 5H), 6.23 (brs, 1H), 5.10 (s, 2H), 3.08 – 2.91 (m, 1H), 2.33 (ddd, *J* = 12.7, 5.0, 1.8 Hz, 1H) 2.05 – 1.74 (m, 4H), 1.43 (s, 3H), 1.40 – 1.19 (m, 2H), 1.05 – 0.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.7, 171.0, 148.1, 144.5, 135.4, 128.5, 128.2, 128.1, 66.6, 55.3, 49.0, 28.9, 25.6, 25.4, 25.2, 20.6; IR (neat, cm^{-1}) 3344, 2937, 2861, 1736, 1707, 1658, 1456, 1398, 1259, 1216, 1176, 1075, 1032; HRMS (ESI^+) m/*z* calcd for $C_{18}H_{20}O_4Na$ $[M+Na]^+$: 323.1259; found: 323.1254; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 12.6 min (minor), t_R = 17.4 min (major).



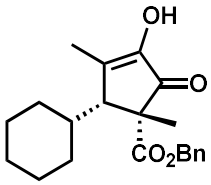
Benzyl (1*R*,5*R*)-3-hydroxy-1,4,5-trimethyl-2-oxocyclopent-3-ene-1-carboxylate (**29**)

Colorless oil (141 mg, 66%); e.r. 94:6; $[\alpha]_D^{20}$ −69.7 (*c* 1.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.38 – 7.28 (m, 5H), 6.56 (brs, 1H), 5.12 (s, 2H), 2.53 (qq, *J* = 7.3, 1.5 Hz, 1H), 1.98 (d, *J* = 1.5 Hz, 3H), 1.45 (s, 3H), 1.06 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.5, 171.2, 147.3, 146.7, 135.4, 128.5, 128.2, 128.1, 66.7, 56.3, 46.2, 20.6, 13.7, 12.1; IR (neat, cm^{-1}) 3348, 3065, 3034, 2976, 2937, 2879, 1705, 1656, 1498, 1456, 1406, 1360, 1309, 1253, 1209, 1178, 1124, 1075, 1049, 1029, 991; HRMS (ESI^+) m/*z* calcd for $C_{16}H_{18}O_4Na$ $[M+Na]^+$: 297.1103; found: 297.1102; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 92/8, flow 1 mL/min) t_R = 12.6 min (minor), t_R = 18.2 min (major).



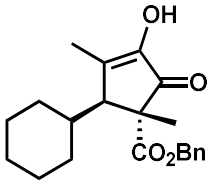
Benzyl (1*R*,2*R*)-2-ethyl-4-hydroxy-1,3-dimethyl-5-oxocyclopent-3-ene-1-carboxylate (**30**)

Pale yellow oil (128 mg, 74%); e.r. 92:8; $[\alpha]_D^{20}$ −3.5 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.36 – 7.24 (m, 5H), 6.12 (brs, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 2.37 (ddq, *J* = 9.9, 4.5, 1.6 Hz, 1H), 1.97 (d, *J* = 1.6 Hz, 3H), 1.76 – 1.62 (m, 1H), 1.45 (s, 3H), 1.41 – 1.23 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.3, 171.1, 147.4, 146.4, 135.3, 128.5, 128.2, 128.2, 66.9, 56.0, 53.9, 22.0, 21.4, 12.8, 12.7; IR (neat, cm^{-1}) 3353, 3066, 3035, 2970, 2936, 2878, 1737, 1703, 1655, 1456, 1406, 1362, 1267, 1228, 1206, 1179, 1129, 1081; HRMS (ESI^+) m/*z* calcd for $C_{17}H_{20}O_4Na$ $[M+Na]^+$: 311.1259; found: 311.1259; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 92/8, flow 1 mL/min) t_R = 8.7 min (minor), t_R = 13.3 min (major).



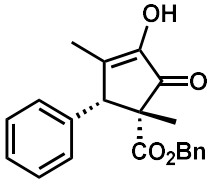
Benzyl (1*R*,2*R*)-2-cyclohexyl-4-hydroxy-1,3-dimethyl-5-oxocyclopent-3-ene-1-carboxylate (**31**)

Colorless oil (110 mg, 71%); e.r. 92:8; $[\alpha]_D^{20}$ −51.4 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.37 – 7.28 (m, 5H), 6.32 (brs, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.4 Hz, 1H), 2.42 – 2.41 (m, 1H), 2.04 (s, 3H), 1.77 – 1.49 (m, 6H), 1.46 (s, 3H), 1.35 – 0.82 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.4, 171.4, 148.0, 144.8, 135.2, 128.6, 128.4, 128.3, 67.0, 58.5, 56.7, 39.4, 33.8, 29.3, 27.2, 26.4, 26.2, 24.0, 15.2; IR (neat, cm^{-1}) 3346, 3034, 2929, 2853, 1735, 1698, 1654, 1452, 1406, 1363, 1296, 1251, 1207, 1179, 1078; HRMS (ESI^+) m/*z* calcd for $C_{21}H_{26}O_4Na$ $[M+Na]^+$: 365.1723; found 365.1706; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 8.5 min (minor), t_R = 9.8 min (major).



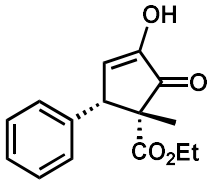
Benzyl (1*R*,2*S*)-2-cyclohexyl-4-hydroxy-1,3-dimethyl-5-oxocyclopent-3-ene-1-carboxylate (**32**)

Pale yellow oil (96 mg, 64% BRSM); e.r. 97:3 (Λ-**9**) and 3:97 (Δ-**9**); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39 – 7.21 (m, 5H), 5.76 (brs, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.5 Hz, 1H), 2.86 – 2.82 (m, 1H), 2.08 (d, *J* = 1.2 Hz, 3H), 1.86 – 1.54 (m, 6H), 1.44 (s, 3H), 1.38 – 1.00 (m, 4H), 0.93 – 0.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.3, 172.1, 148.2, 146.3, 135.6, 128.5, 128.2, 127.6, 67.1, 56.8, 53.4, 38.7, 33.6, 30.0, 27.5, 26.3, 26.2, 15.8, 15.3; IR (neat, cm^{-1}) 3351,3065, 3034, 2929, 2853, 1737, 1702, 1655, 1454, 1404, 1363, 1210, 1176, 1111, 1083; HRMS (ESI$^+$) m/*z* calcd for $C_{21}H_{26}O_4Na$ [M+Na]$^+$: 365.1723; found: 365.1739; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) From Λ-**11**: t_R = 11.0 min (major), t_R = 12.3 min (min).



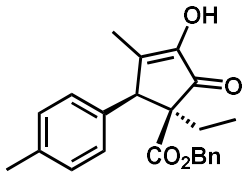
Benzyl (1*R*,5*R*)-3-hydroxy-1,4-dimethyl-2-oxo-5-phenylcyclopent-3-ene-1-carboxylate (**33**)

Pale yellow oil (294 mg, 90%); e.r. 89:11; $[\alpha]_D^{20}$ −20.1 (*c* 0.96, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.36 – 7.25 (m, 6H), 7.17 – 7.07 (m, 4H), 6.85 (brs, 1H), 4.54 (d, *J* = 12.5 Hz, 1H), 4.38 (d, *J* = 12.5 Hz, 1H), 3.77 (q, *J* = 1.4 Hz, 1H), 1.94 (d, *J* = 1.4 Hz, 3H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.6, 170.0, 149.2, 143.6, 136.6, 135.2, 129.3, 128.4, 128.4, 128.0, 127.87, 127.85, 66.6, 58.7, 58.6, 21.7, 13.0; IR (neat, cm^{-1}) 3346, 3064, 3032, 2979, 2934, 2874, 1705, 1659, 1497, 1455, 1406, 1361, 1297, 1273, 1241, 1206, 1173, 1079, 910; HRMS (ESI$^+$) m/*z* calcd for $C_{21}H_{20}O_4Na$ [M+Na]$^+$: 359.1259; found: 359.1256; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 9.8 min (minor), t_R = 17.7 min (major).



Ethyl (1*R*,5*S*)-3-hydroxy-1-methyl-2-oxo-5-phenylcyclopent-3-ene-1-carboxylate (**34**)

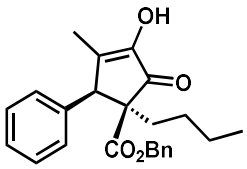
Pale yellow oil (15 mg, 83%); e.r. 86:14; $[\alpha]_D^{20}$ +5.0 (*c* 0.69, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 7.32 – 7.25 (m, 3H), 7.21 – 7.15 (m, 2H), 6.64 (d, *J* = 2.9 Hz, 1H), 3.90 (d, *J* = 2.9 Hz, 1H), 3.57 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.41 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.61 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 201.9, 169.7, 151.8, 137.8, 129.3, 128.6, 128.2, 127.8, 61.1, 58.6, 53.4, 20.2, 13.1; IR (neat, cm^{-1}) 3376, 3061, 3031, 2984, 2935, 1716, 1658, 1634, 1602, 1555, 1496, 1455, 1394, 1377, 1289, 1219, 1106, 1014; HRMS (EI^+) *m*/*z* calcd for $C_{15}H_{16}O_4$ $[M]^+$: 260.1043; found 260.1048; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 85/15, flow 1 mL/min) t_R = 5.9 min (minor), t_R = 7.1 min (major).



Benzyl (1*S*,5*S*)-1-ethyl-3-hydroxy-4-methyl-2-oxo-5-(*p*-tolyl)cyclopent-3-ene-1-carboxylate (**35**)

Pale-yellow oil (78 mg, 82% yield); e.r. 88:12*; d.r. 9:1; ^1H NMR (300 MHz, $CDCl_3$) 7.36 – 7.28 (m, 3H), 7.14 – 6.92 (m, 6H), 6.28 (brs, 1H), 4.53 (d, *J* = 12.5 Hz, 1H), 4.42 (d, *J* = 12.5 Hz, 1H), 3.75 (s, 1H), 2.34 (s, 3H), 2.28 (dq, *J* = 13.4, 7.4 Hz, 1H), 2.05 (dq, *J* = 13.4, 7.4 Hz, 1H), 1.90 (d, *J* = 1.3 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.8, 169.8, 149.7, 143.4, 137.4, 135.3, 133.7, 129.2, 129.0, 128.4, 128.0, 127.9, 66.4, 62.7, 55.3, 28.2, 21.2, 12.8, 8.3; IR (neat, cm^{-1}) 3347, 3065, 3033, 2972, 2940, 2882, 1785, 1735, 1660, 1514, 1456, 1227, 1155, 1131, 1114, 1084; HRMS (ESI^+) *m*/*z* calcd for $C_{23}H_{24}O_4Na$ $[M+Na]^+$: 387.1567; found: 387.1563. HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 9.9 min (major), t_R = 10.7 min (minor).

*prepared using Δ-**11**



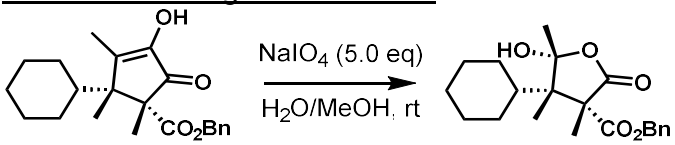
Benzyl (1*S*,5*S*)-1-butyl-3-hydroxy-4-methyl-2-oxo-5-phenylcyclopent-3-ene-1-carboxylate (**36**)

Pale-yellow oil (94 mg, 84%); e.r. 91:9*; d.r. 9.1:1; ^{1}H NMR (300 MHz, $CDCl_3$) 7.34 – 7.22 (m, 6H), 7.13 – 7.06 (m, 4H), 6.24 (brs, 1H), 4.48 (d, *J* = 12.5 Hz, 1H), 4.38 (d, *J* = 12.5 Hz, 1H), 3.79 (q, *J* = 1.3 Hz, 1H), 2.28 – 2.14 (m, 1H), 2.04 – 1.94 (m, 1H), 1.91 (d, *J* = 1.3 Hz, 3H), 1.49 – 1.09 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.8, 169.8, 149.6, 143.0, 136.9, 135.2, 129.3, 128.4, 128.3, 128.0, 127.9, 127.8, 66.4, 62.4, 56.1, 35.1, 25.8, 23.1, 13.9, 12.9; IR (neat, cm^{-1}) 3347, 3062, 3033, 2958, 2932, 2872, 1716, 1664, 1494, 1456, 1403, 1380, 1360, 1325, 1270, 1238; HRMS (ESI$^+$) *m*/*z* calcd for $C_{24}H_{26}O_4Na$ [M+Na]$^+$: 402.1723; found: 402.1728; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 90/10, flow 1 mL/min) t_R = 7.7 min (major), t_R = 10.4 min (minor).

*prepared using Δ-**11**

11. Modifications to the Cyclopentenone

Oxidative Cleavage of the Alkene

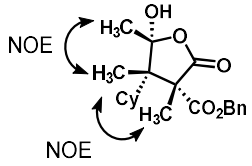


Benzyl (3*S*,4*S*,5*R*)-4-cyclohexyl-5-hydroxy-3,4,5-trimethyl-2-oxotetrahydrofuran-3-carboxylate (**37**)

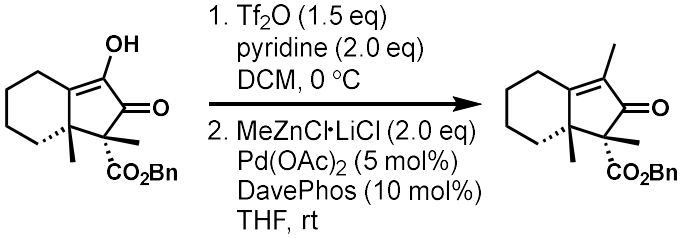
To a vigorously stirred suspension of cyclopentenone **20** (54 mg, 0.15 mmol, 1.0 equiv) in methanol (1 mL) was added an aqueous solution of $NaIO_4$ (160 mg, 0.75 mmol, 5.0 equiv, 5 mL H_2O). The heterogenous reaction mixture was allowed to stir vigorously for 5 days at which point the reaction was still incomplete. The reaction mixture was extracted with diethyl ether (x3). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* to provide a crude oil. Compound **37** was isolated by purification of the crude oil using silica gel column chromatography (load with PhMe, 0, 5, 7, 10, 15% ethyl acetate in hexane) as a colorless oil (26 mg, 48% yield, or 55% yield BRSM).

$[\alpha]_D^{20}$ +30.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 – 7.34 (m, 5H), 6.19 (q, *J* = 1.4 Hz, 1H), 5.28 (d, *J* = 12.0 Hz, 1H), 5.23 (d, *J* = 12.0 Hz, 1H), 1.85 – 1.81 (m, 1H), 1.72 – 1.14 (m, 5H), 1.58 (d, *J* = 1.4 Hz, 3H), 1.47 (s, 3H), 1.16 – 0.69 (m, 5H), 1.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.9, 173.3, 134.0, 129.1, 129.0, 128.9, 110.6, 69.1, 60.9, 54.2, 41.4, 28.1, 27.9, 26.4, 26.3, 26.0, 24.7, 18.0, 15.9; IR (neat, cm^{-1}) 3390, 2961, 2931, 2855, 1775, 1748, 1689, 1455, 1396, 1262, 1220, 1125, 1108, 1098, 1052; HRMS (ESI^+) *m*/*z* calcd for $C_{21}H_{28}O_5Na$ $[M+Na]^+$: 383.1829; found: 383.1834.

The relative stereochemistry of compound **37** was determined by NOESY experiments.



Negishi Cross Coupling



Benzyl (1*R*,7a*R*)-1,3,7a-trimethyl-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indene-1-carboxylate (**38**)

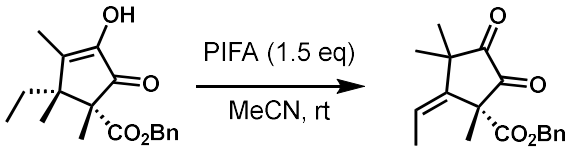
To a solution of cyclopentenone **14** (100 mg, 0.32 mmol, 1.0 equiv) and pyridine (50 mg, 0.64 mmol, 2.0 equiv) in DCM (10 mL) at 0 °C was added triflic anhydride (0.08 mL, 0.48 mmol, 1.5 equiv). The reaction mixture was stirred for 15 min before quenching with $NaHCO_3$ (sat. aq.). The

phases were separated and the aqueous phase was extracted with DCM (x2). The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed *in vacuo* and the crude enol triflate was used in the next step without further purification.

A stirred degassed solution of the crude enol triflate, $Pd(OAc)_2$ (3.5 mg, 0.016 mmol, 5 mol%), and DavePhos (13 mg, 0.032 mmol, 10 mol%) in THF (5 mL) was added a solution of MeZnCl·LiCl (0.64 mL, 0.64 mmol, 2.0 equiv, 1.0 M in THF) dropwise at room temperature. The reaction was allowed to stir at room temperature for 48 hours before being quenched by the addition of 1 M HCl and diethyl ether. The phases were separated and the aqueous phase extracted with diethyl (x2). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* to afford a crude oil. Compound **38** could be isolated from the crude using silica gel chromatography (eluent: load with PhMe, then 0, 5, 7, 10% ethyl acetate in hexanes) as a pale-yellow oil (40 mg, 40% yield).

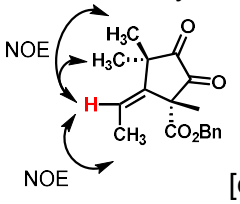
$[\alpha]_D^{20}$ −31.3 (*c* 0.96, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.36 – 7.26 (m, 5H), 5.14 (d, *J* = 12.6 Hz, 1H), 5.03 (d, *J* = 12.6 Hz, 1H), 2.70 (ddt, *J* = 14.2, 4.0, 1.8 Hz, 1H), 2.22 (tdd, *J* = 13.8, 5.4, 1.4 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.68 – 1.50 (m, 3H), 1.35 (s, 3H), 1.31 – 1.18 (m, 2H), 1.15 (s, 3H),
^{13}C NMR (75 MHz, $CDCl_3$) 206.1, 176.2, 172.3, 135.6, 131.1, 128.5, 128.1, 127.9, 66.4, 61.8, 48.2, 35.4, 26.6, 25.3, 21.9, 21.1, 16.5, 8.0; IR (neat, cm^{-1}) 3065, 3033, 2981, 2941, 2861, 1735, 1703, 1653, 1455, 1233, 1162; HRMS (ESI^+) *m*/*z* calcd for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798; found: 313.1804.

Oxidative Rearrangement



Benzyl (*R*,*Z*)-2-ethylidene-1,3,3-trimethyl-4,5-dioxocyclopentane-1-carboxylate (**39**)

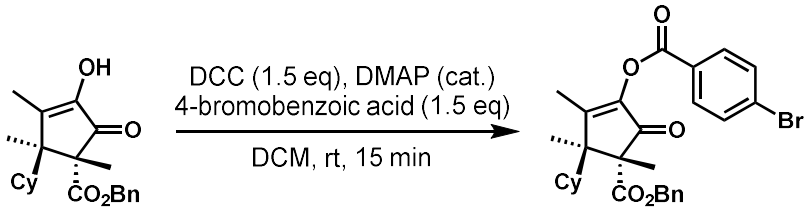
To a solution of cyclopentenone **22** (58 mg, 0.19 mmol, 1.0 equiv) in MeCN (3 mL) at room temperature is added PIFA (124 mg, 0.29 mmol, 1.5 equiv). After 5 minutes, the reaction mixture was diluted with diethyl ether and was quenched by the addition of saturated sodium bicarbonate. The phases were separated and the aqueous phase extracted with diethyl ether (x2). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed *in vacuo* to provide a crude oil. Compound **39** could be isolated from the crude oil using silica gel chromatography (eluent: load with PhMe, 0, 5, 7, 10% ethyl acetate in hexane gradient) as a yellow oil (23 mg, 40% yield).



$[\alpha]_D^{20}$ +6.1 (*c* 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 7.40 – 7.26 (m, 3H), 7.21 – 7.18 (m, 2H), 5.72 (q, *J* = 7.3 Hz, 1H), 5.22 (d, *J* = 12.3 Hz, 1H), 4.99 (d, *J* = 12.3 Hz, 1H), 1.63 (s, 3H), 1.59 (d, *J* = 7.3 Hz, 3H), 1.30 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 205.3, 201.6, 168.7, 143.0, 134.9, 128.5, 128.5, 128.1, 124.4, 67.7, 55.9, 47.5, 27.7, 25.4, 19.8, 13.6; IR

(neat, cm^{-1}) 3066, 3034, 2975, 2935, 2868, 1769, 1740, 1456, 1377, 1256, 1214, 1105, 1063; HRMS (EI^+) *m*/*z* calcd for $C_{18}H_{20}O_4$ $[M]^+$: 300.1356; found: 300.1362.

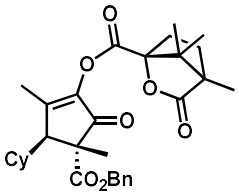
Esterification of α-hydroxycyclopentenone



(3*R*,4*S*)-4-((benzyloxy)carbonyl)-3-cyclohexyl-2,3,4-trimethyl-5-oxocyclopent-1-en-1-yl 4-bromobenzoate (**E1**)

To a solution of cyclopentenone **21** (46 mg, 0.13 mmol, 1.0 equiv) and 4-bromobenzoic acid (40 mg, 0.19 mmol, 1.5 equiv) in DCM (5 mL) was added DCC (40 mg, 0.19 mmol, 1.5 equiv) and DMAP (spatula tip) at once. The reaction mixture was allowed to stir at room temperature for 15 min before being diluted with diethyl ether and filtered through Celite. The organic phase was washed with 1M HCl and brine, and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed *in vacuo* and the crude oil dry loaded onto a silica gel column. 4-bromobenzoate **E1** could be isolated from silica gel chromatography (eluent: 2, 4% ethyl acetate in hexanes) as a white solid (55 mg, 77% yield).

er 97/3; ^{1}H NMR (300 MHz, $CDCl_3$) 8.00 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.31 (m, 5H), 5.15 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.5 Hz, 1H), 1.91 (s, 3H), 1.85 – 1.46 (m, 9H), 1.22 – 1.08 (m, 5H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, T = −20 °C) 197.6, 171.8, 163.0, 162.4, 146.0, 135.1, 129.1, 128.4, 128.2, 127.8, 127.1, 66.8, 62.6, 51.2, 43.6, 32.1, 29.7, 29.0, 27.5, 26.2, 26.0, 17.2, 14.6, 14.2, 13.5; IR (neat, cm^{-1}) 2927, 2852, 1743, 1717, 1661, 1589, 1485, 1455, 1398, 1382, 1327, 1256, 1175, 1089, 1031, 1011; HRMS (ESI^+) *m*/*z* calcd for $C_{42}H_{32}OBr$ $[M+H]^+$: 539.1428; found: 539.1436; HPLC (Chiralpak AD-H®, 4.6 mm x 250 mm, UV 261 nm, hexane/*i*-PrOH = 70/30, flow 1 mL/min) t_R = 6.3 min (major), t_R = 8.4 min (minor).

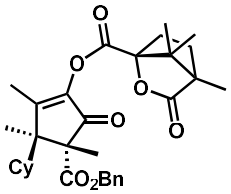


(3*S*,4*R*)-4-((benzyloxy)carbonyl)-3-cyclohexyl-2,4-dimethyl-5-oxocyclopent-1-en-1-yl (1*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (**E2**)

Compound **E2** was prepared in a similar way as **E1** using (*R*)-camphanic acid. Only a single diastereomer was detectable by analysis of the crude reaction mixture by ^{1}H NMR. Crystals suitable for single crystal analysis were grown by DCM/pentane vapor diffusion which provided colorless needles of **E2** (73 mg, quant.).

$[\alpha]_D^{20}$ +47.1 (*c* 0.32, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 7.34 – 7.27 (m, 5H), 5.13 (d, *J* = 12.5 Hz, 1H), 5.09 (d, *J* = 12.5 Hz, 1H), 3.06 (brs, 1H), 2.54 (ddd, *J* = 13.5, 10.8, 4.2 Hz, 1H), 2.15 (ddd, *J* = 13.7, 9.4, 4.6 Hz, 1H), 2.07 (s, 3H), 1.97 (ddd, *J* = 13.1, 10.8, 4.6 Hz, 1H), 1.79 – 1.51 (m, 8H), 1.45 (s, 3H), 1.42 – 1.37 (m, 1H), 1.19 – 1.06 (m, 3H), 1.15 (s, 3H), 1.12 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) 195.5, 178.0, 171.3, 164.3, 162.7, 144.5, 135.5, 128.5, 128.2, 127.8, 90.8, 67.4, 58.1, 54.9, 54.9, 53.7, 38.5, 33.4, 30.7, 29.8, 29.7, 28.8, 27.4, 26.2, 16.6, 16.5, 16.1, 15.6, 9.8; IR

(neat, cm^{-1}) 2928, 2854, 1793, 1762, 1721, 1664, 1455, 1379, 1312, 1260, 1226, 1194; HRMS (ESI^+) *m*/*z* calcd for $C_{31}H_{39}O_7$ $[M+H]^+$: 523.2690; found: 523.2696.



(3*S*,4*R*)-4-((benzyloxy)carbonyl)-3-cyclohexyl-2,3,4-trimethyl-5-oxocyclopent-1-en-1-yl (1R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (**E3**)

Compound **E3** was prepared in a similar way as **E1** using (*R*)-camphanic acid. Only a single diastereomer was detectable by analysis of the crude reaction mixture by ^1H NMR. Crystals suitable singly crystal analysis were grown by slow evaporation from an acetonitrile solution which provided needles of **E3** (27 mg, quant.)

$[\alpha]_D^{20}$ −6.3 (*c* 0.52, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 7.35 – 7.25 (m, 5H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H), 2.56 (ddd, *J* = 13.5, 10.8, 4.2 Hz, 1H), 2.15 (ddd, *J* = 13.7, 9.3, 4.6 Hz, 1H), 1.97 (ddd, *J* = 13.1, 10.8, 4.6 Hz, 1H), 1.90 (s, 3H), 1.84 – 1.79 (m, 1H), 1.76 – 1.71 (m, 2H), 1.67 – 1.63 (m, 1H), 1.56 (brs, 3H), 1.54 – 1.49 (m, 2H), 1.42 (brs, 3H), 2.94 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 1.21 – 1.05 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) 196.5, 178.1, 171.4, 164.2, 135.1, 128.4, 128.2, 127.9, 90.9, 66.9, 54.9, 54.8, 51.5, 30.6, 29.2, 28.8, 27.7, 26.2, 16.6, 16.5, 9.8; IR (neat, cm^{-1}) 2935, 2858, 1789, 1760, 1738, 1716, 1665, 1455, 1313, 1261; HRMS (ESI^+) *m*/*z* calcd for $C_{32}H_{41}O_7$ $[M+H]^+$: 537.2847; found: 537.2852.

12. X-Ray Crystallography

X-ray structural analysis for **Δ-C6a**, **E2**, and **E3**: Crystal data and refinement details are summarized in **Table S5**. Candidate crystals of **Δ-C6a**, **E2**, and **E3**, grown by slow evaporation in ethyl acetate/hexane, by vapor diffusion of pentane into dichloromethane, and, by slow evaporation of acetonitrile, respectively, were selected, mounted using viscous oil onto plastic loops and cooled to the data collection temperature. Data were collected on a D8 Venture Photon diffractometer with Cu-Kα radiation (λ = 1.54178 Å) focused with Goebel mirrors. Unit cell parameters were obtained from fast scan data frames, 1º/s ω, of an Ewald hemisphere. The unit-cell dimensions, equivalent reflections and systematic absences in the diffraction data were consistent with *C*2, *Cm* and *C*2/*m* for **Δ-C6a**, and, uniquely, for $P2_12_12_1$ for **E2** and **E3**. For **Δ-C6a**, after an exploration of the space group options, only *C*2 yielded chemically reasonable and computationally stable results of refinement consistent with the enantiomerically pure chiral compound. The anomalous dispersion factors refined to nil within experimental error in each case indicating the true hand of the data was determined. For **E2** and **E3**, the (*R*)-camphanic acid moiety of each ester, introduced by chirally retentive esterification, confirms the enantiomeric assignation. The data were treated with multi-scan absorption corrections.[14] Structures were solved using intrinsic phasing methods[15] and refined with full-matrix, least-squares procedures on F^2.[16]

The penultimate difference map in **Δ-C6a** showed features in a void that could not be modeled that were treated as diffused contributions, using Squeeze[17], arising from a severely disordered ethyl acetate molecule of solvation. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2 U_{eq} (1.5 U_{eq} for methyl) of the attached atom. Atomic scattering factors are contained in the SHELXTL program library.[15] The structures have been deposited at the Cambridge Structural Database under CCDC 2154234 - 2154236.

Table S5. Crystal data and structure refinement details.

Sum Formula	$C_{65}FH_{63}N_3O_6Rh$	$C_{31}H_{38}O_7$	$C_{32}H_{40}O_7$
Moiety Formula	$C_{61}H_{55}FN_3O_4Rh$, $[CH_3COOC_2H_5]$	$C_{31}H_{38}O_7$	$C_{32}H_{40}O_7$
Formula Weight, g/mol	1104.09	522.61	536.64
Temperature, K	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C*2	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions			
a, Å	28.8510(17)	6.4651(2)	6.7321(2)
b, Å	15.3005(9)	9.9755(3)	9.8995(3)
c, Å	12.0037(7)	41.8034(12)	41.9029(12)
α, °	90	90	90
β, °	96.747(2)	90	90
γ, °	90	90	90
Volume, Å^3	5262.2(5)	2696.01(14)	2792.59(14)
Z	4	4	4
ρ_{calc}, g/cm^3	1.394	1.288	1.276
μ/mm^{-1}	3.119	0.733	0.721
F(000)	2304.0	1120.0	1152.0
Reflections collected	29351	26912	27183
Independent reflections	8808	4722	4710
Data/restraints/parameters	8808/0/630	4722/0/348	4710/0/358
Goodness-of-fit	1.043	1.090	1.199
R [I>=2σ (I)] R1/wR2	0.0506/0.1296	0.0285/0.0694	0.0505/0.1025
R indexes [all data] R1/wR2	0.0483/0.1340	0.0300/0.0704	0.0622/0.1059
Absolute structure parameter	-0.007(8)	0.05(8)	-0.01(12)
CCDC	2154234	2154235	2154236

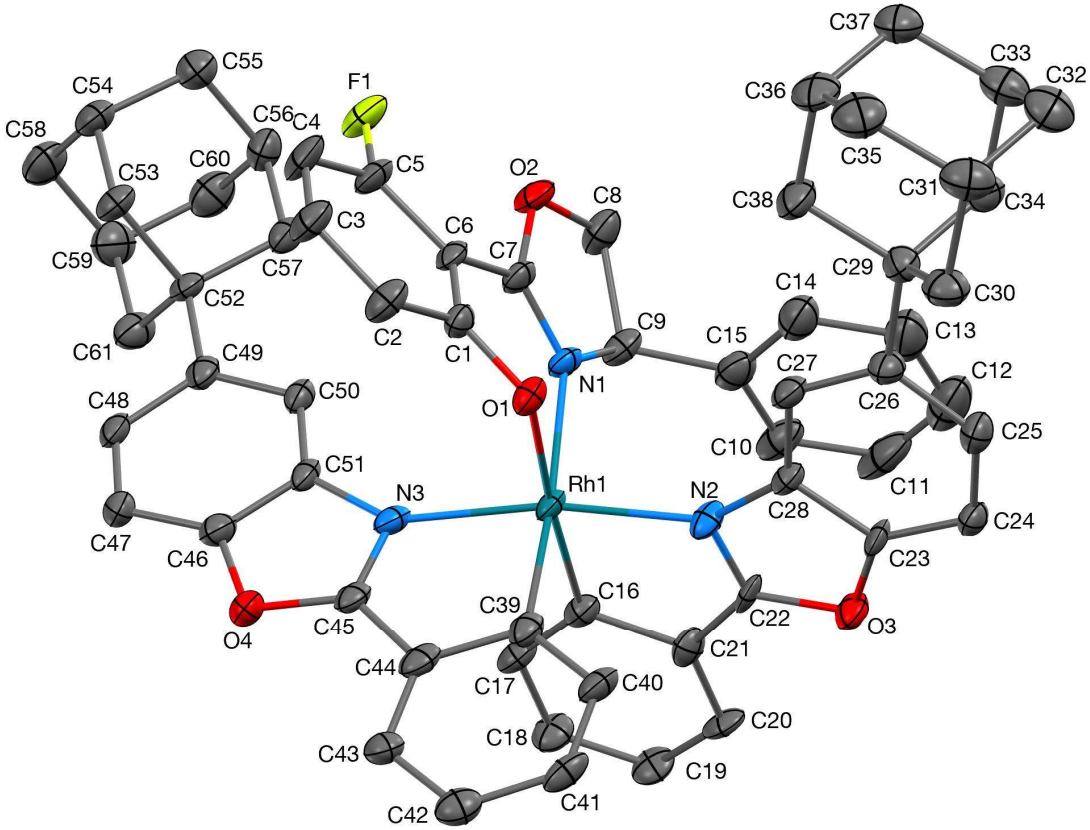


Figure S1. Molecular diagram and labelling scheme for **Δ-C6a** with ellipsoids at 30% probability. Ethyl acetate solvent molecule not depicted. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh1-N1 2.166(5); Rh1-N2 2.017(8); Rh1-N3 2.046(8); Rh1-O1 2.125(6); Rh1-C16 2.005(9); Rh1-C39 2.009(7); N1-Rh1-O1 81.9(3); N2-Rh1-C16 80.8(3); N3-Rh1-C39 81.0(4).

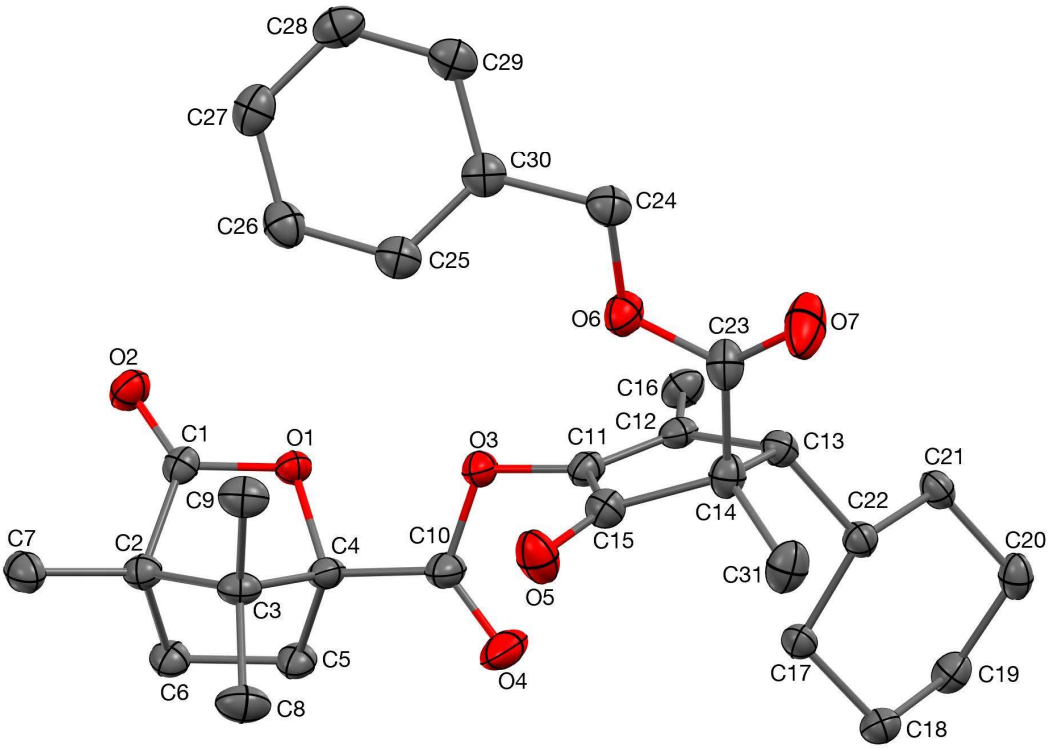


Figure S2. Molecular diagram and labelling scheme for **E2** with ellipsoids at 30% probability. H-atoms omitted for clarity.

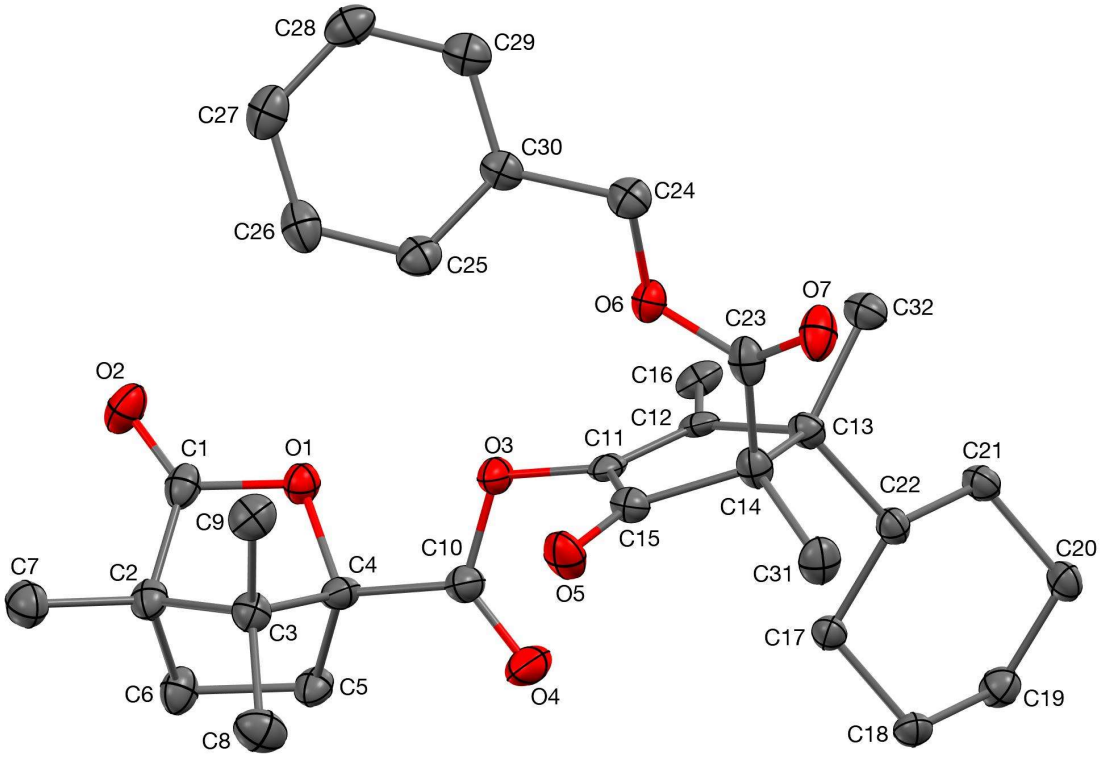


Figure S3. Molecular diagram and labelling scheme for **E3** with ellipsoids at 30% probability. H-atoms omitted for clarity.

13. References

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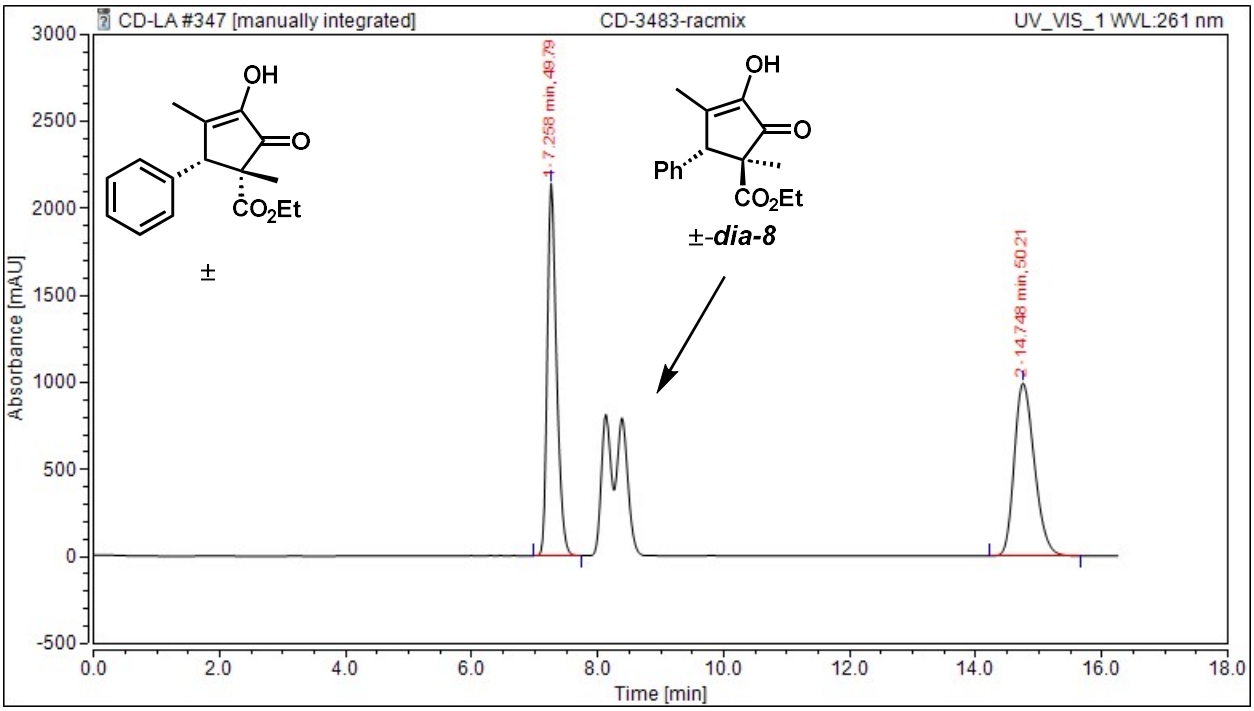
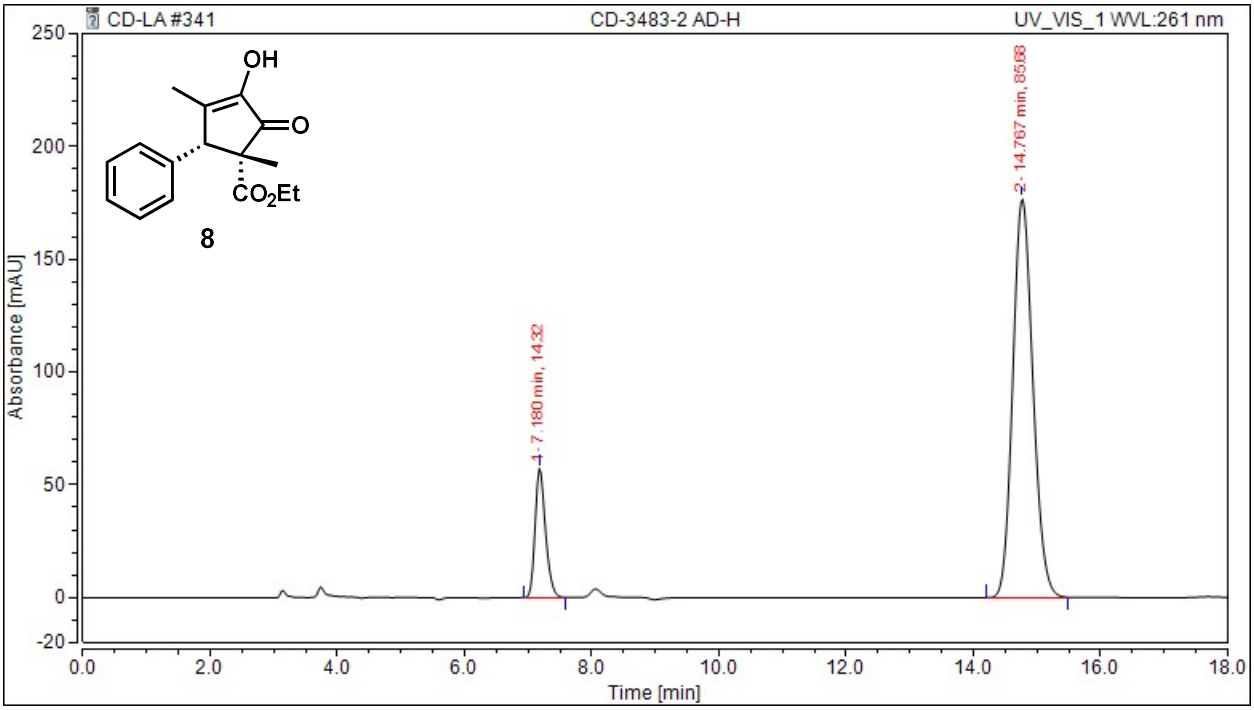
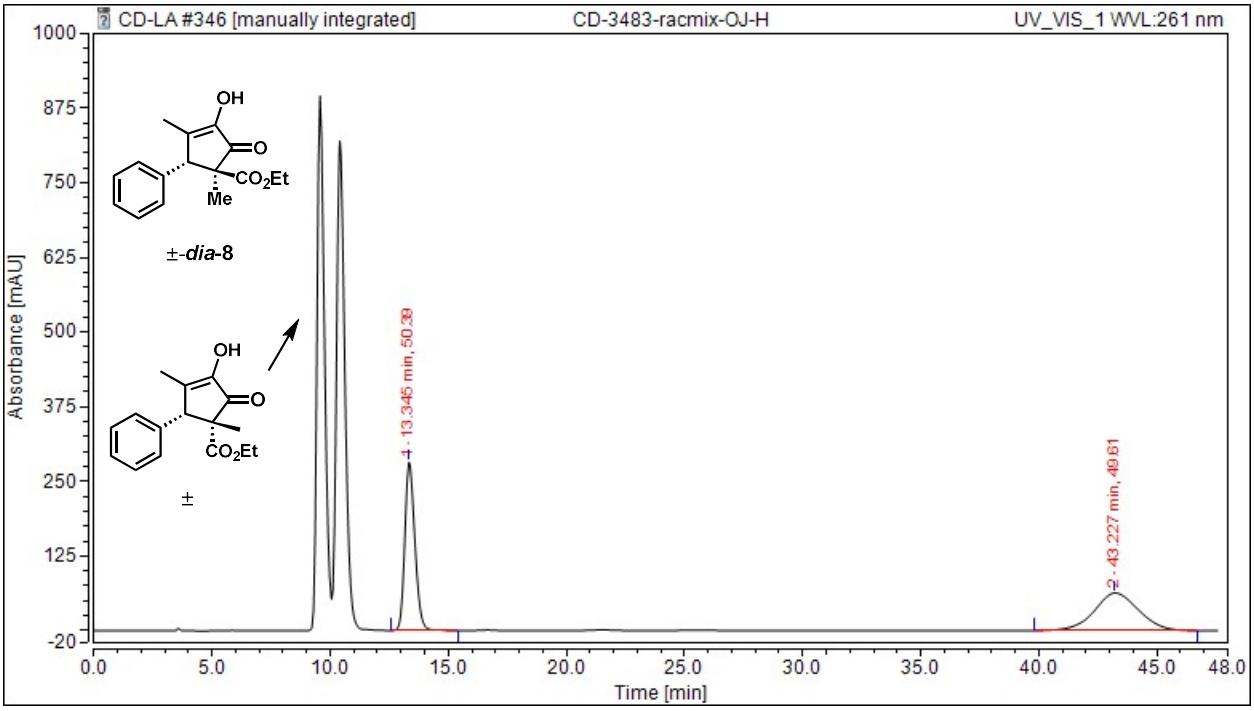
14. HPLC Traces



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±
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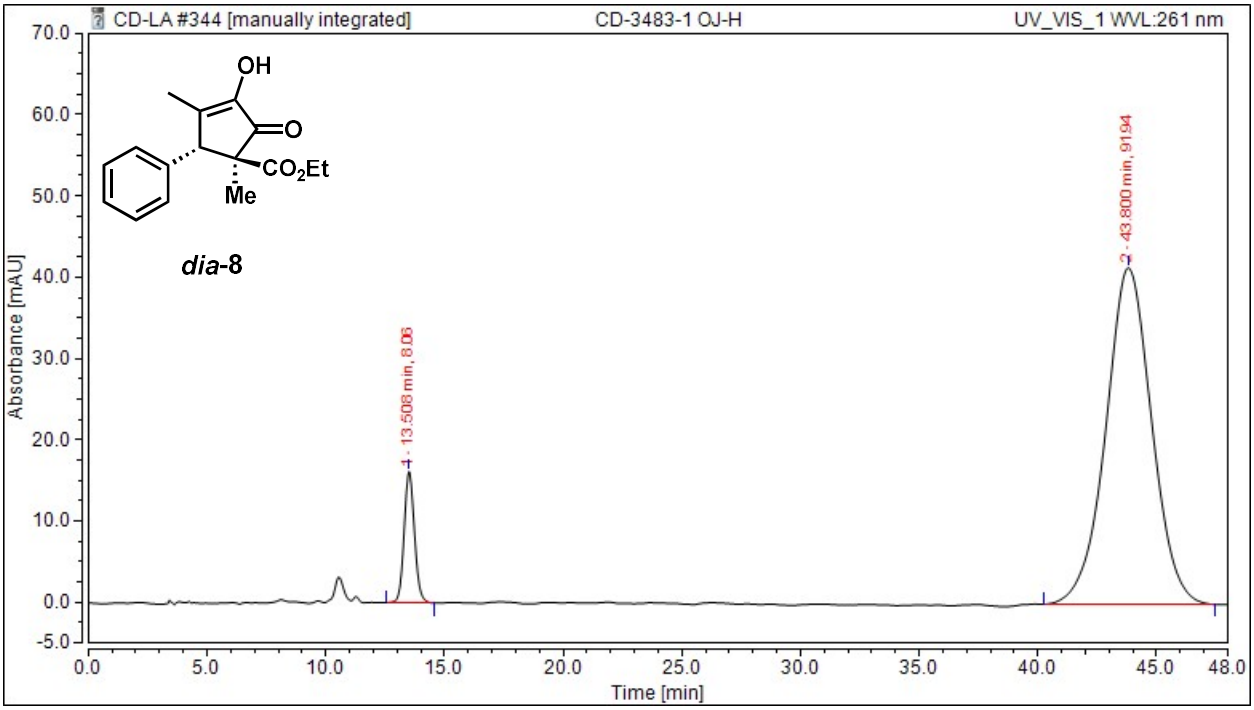
Time [min]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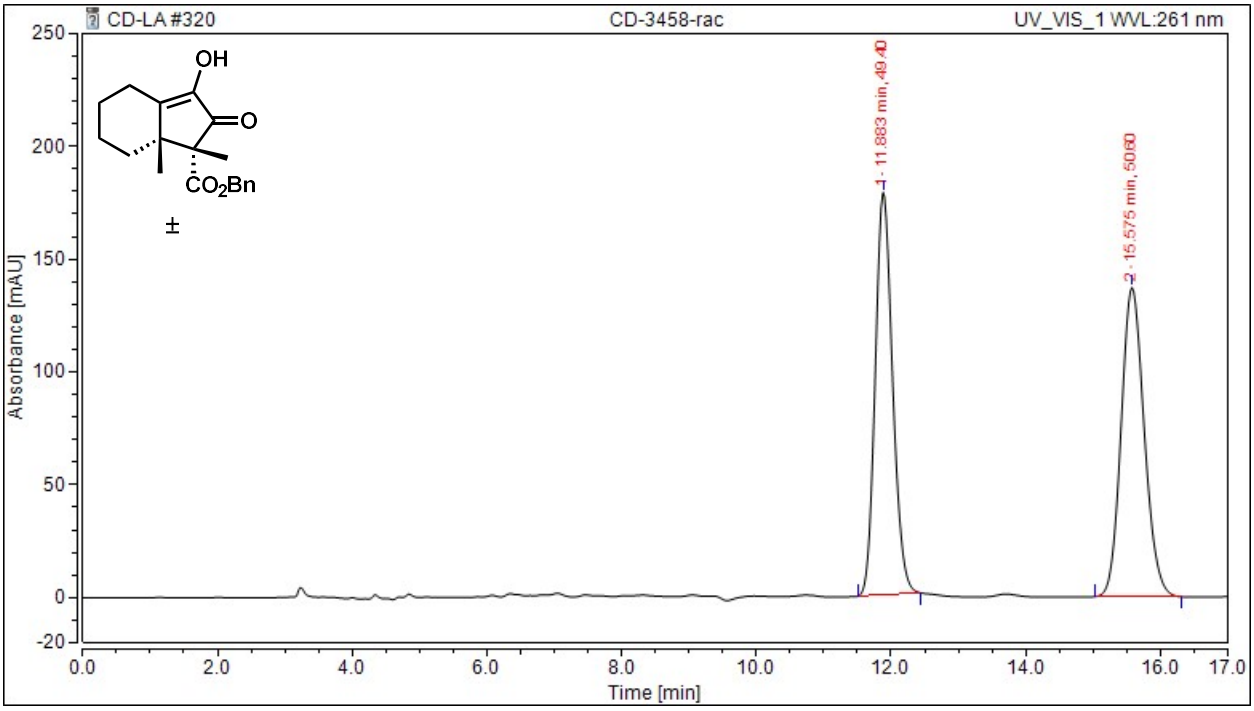
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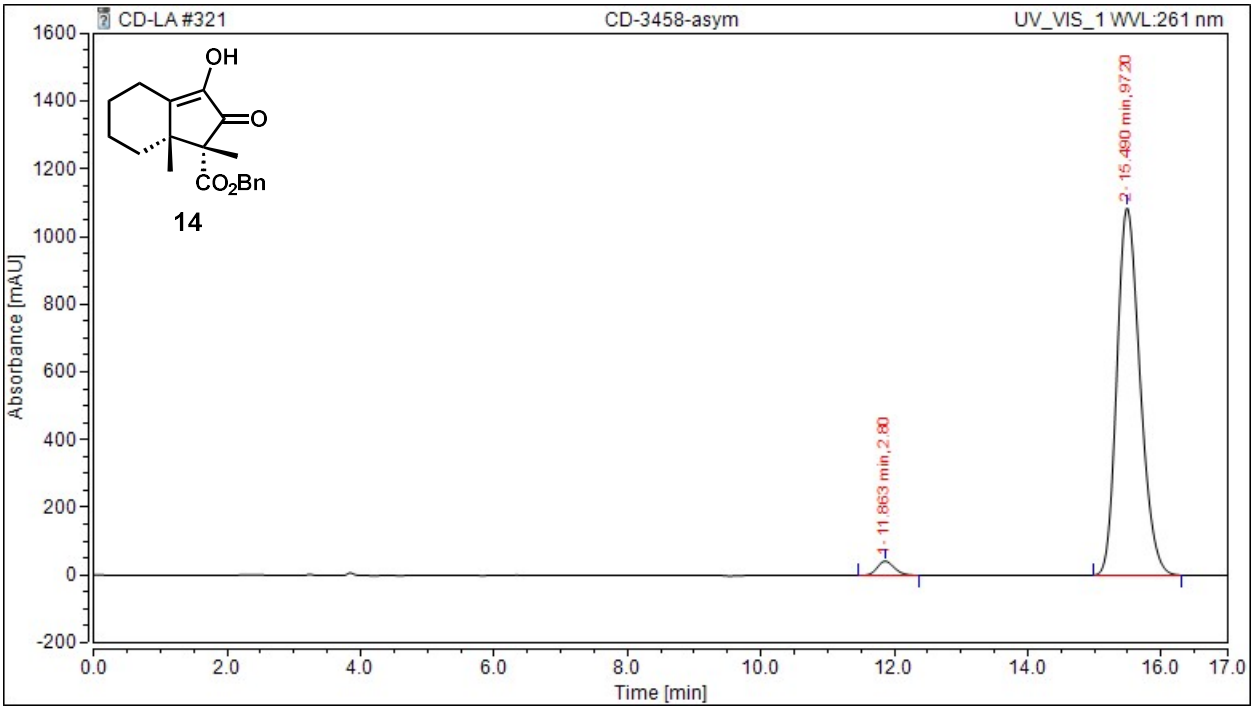
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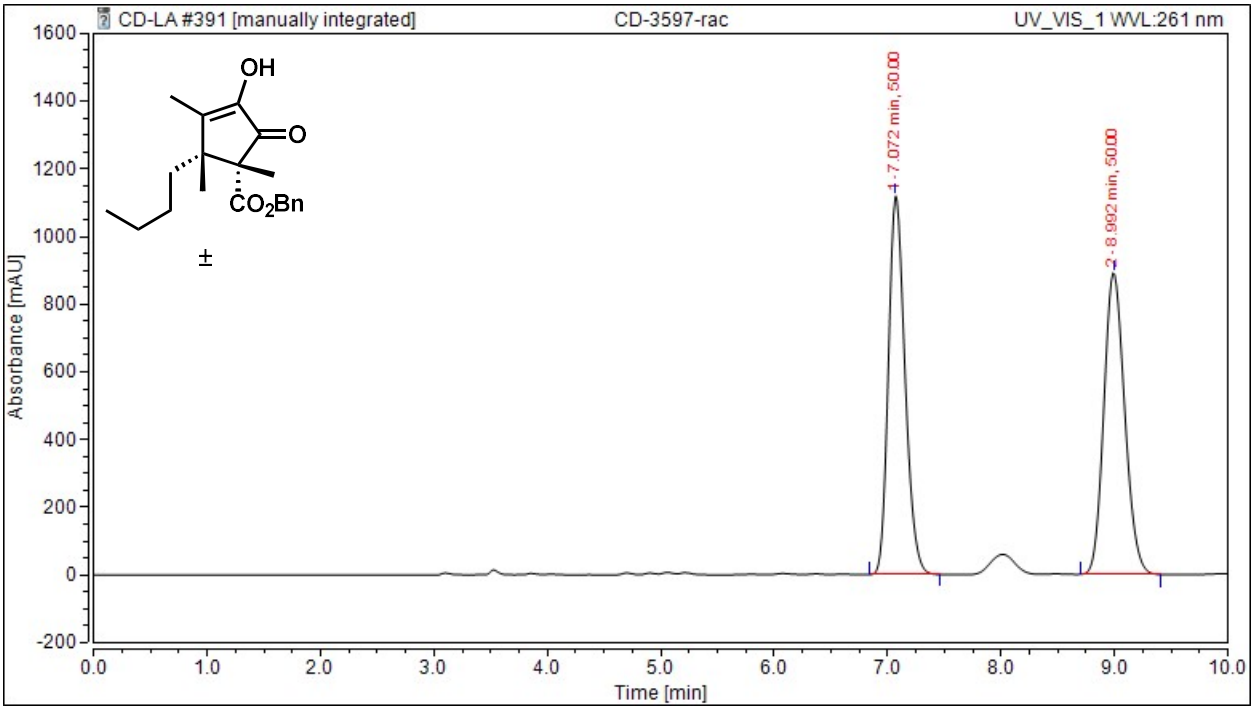
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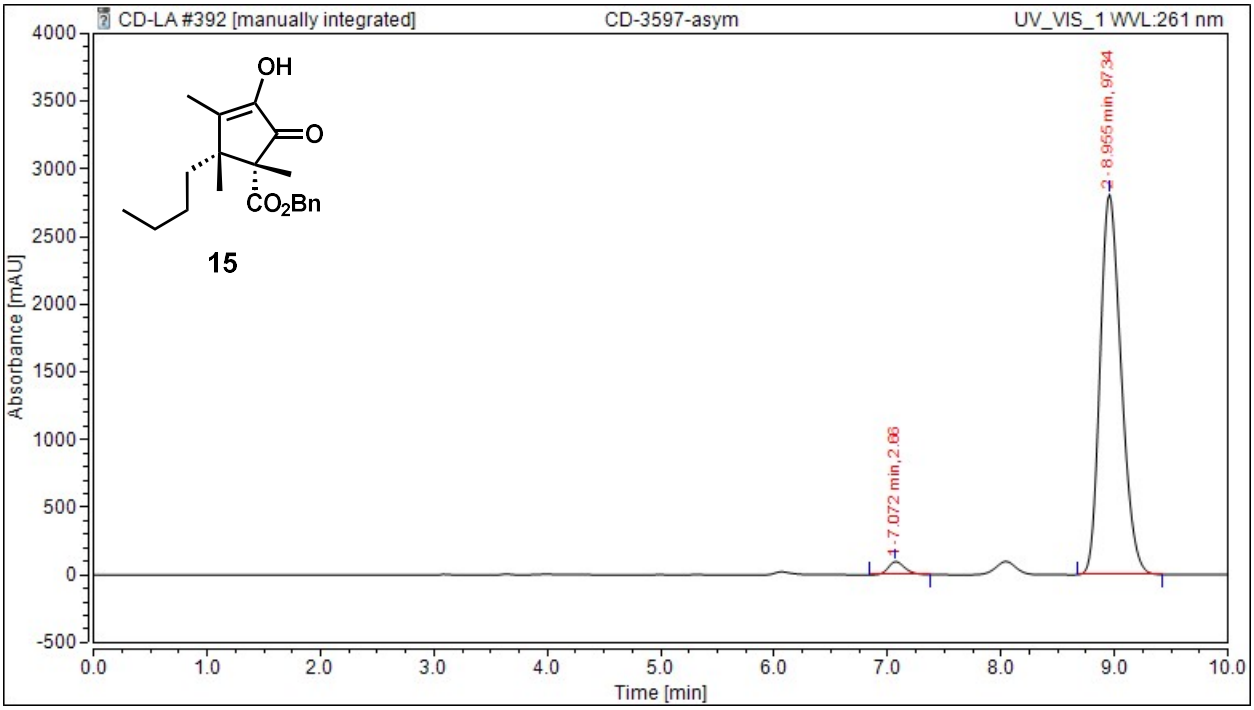
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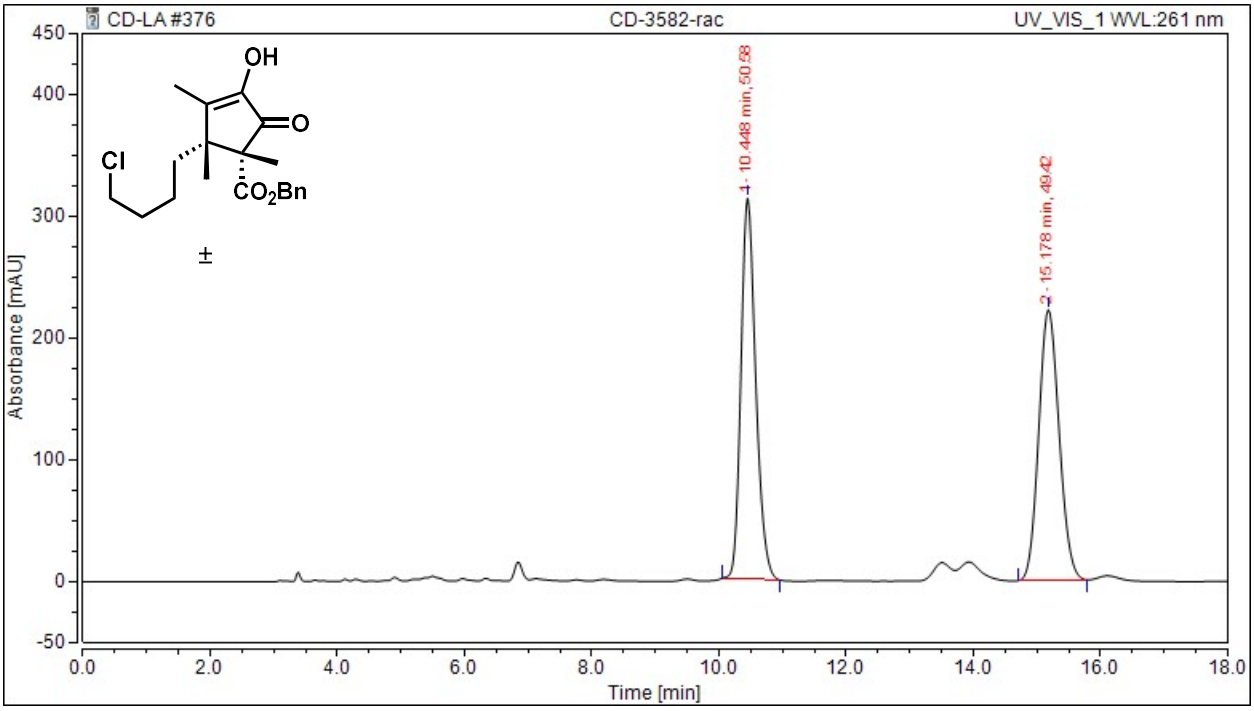
Time [min]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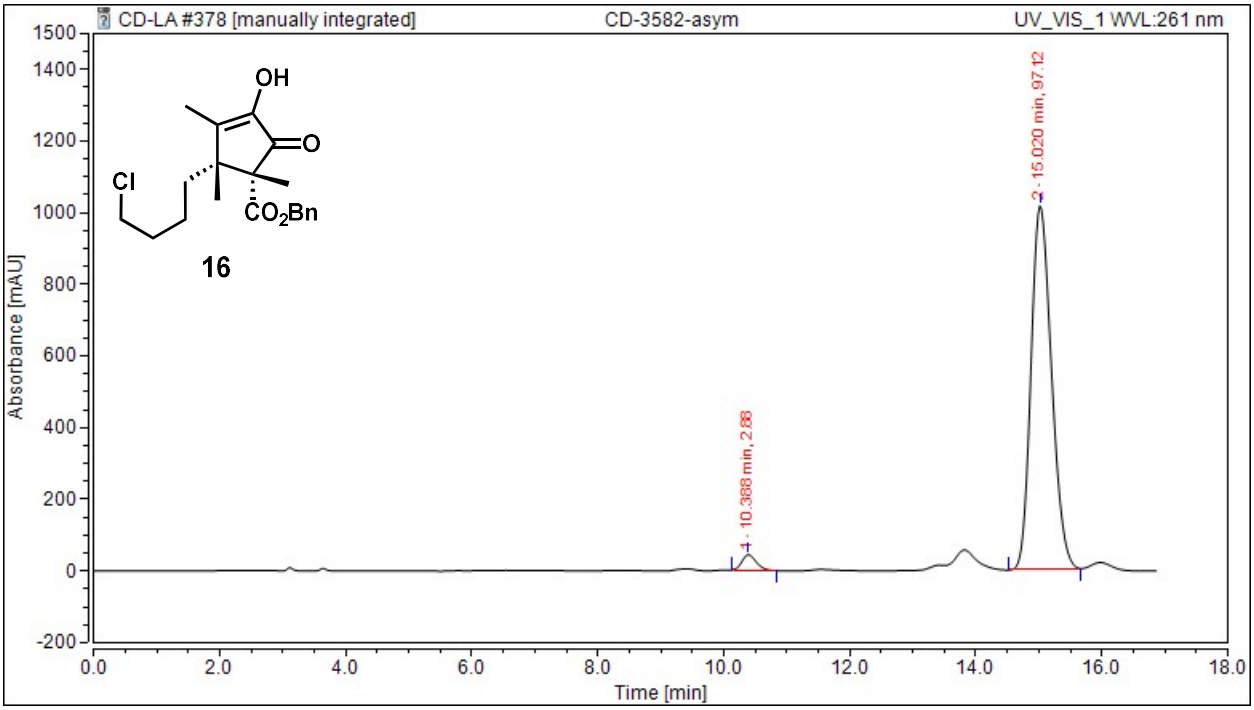
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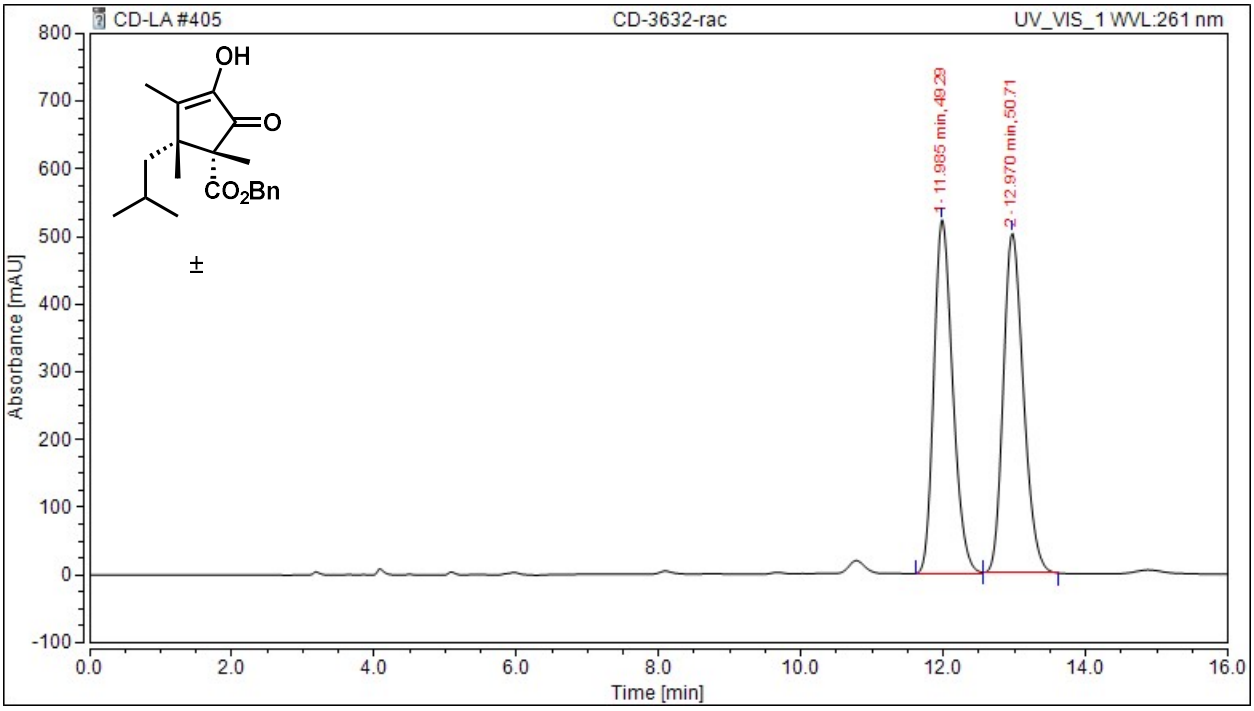
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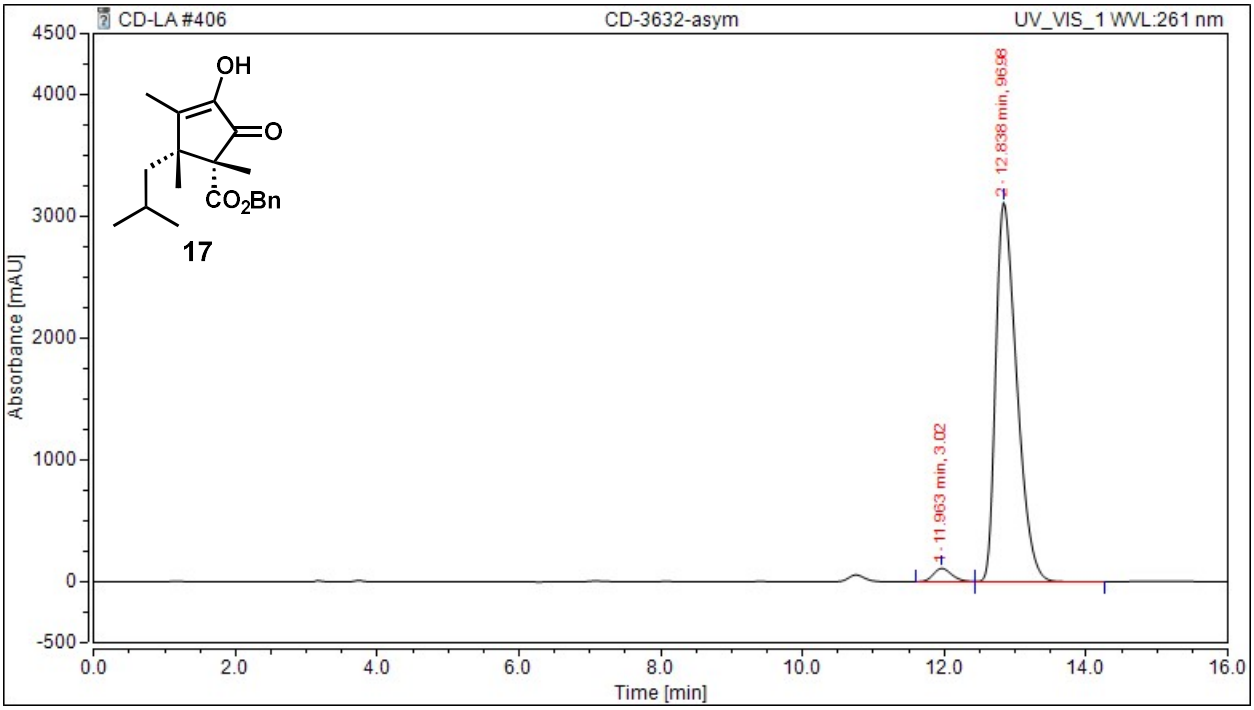
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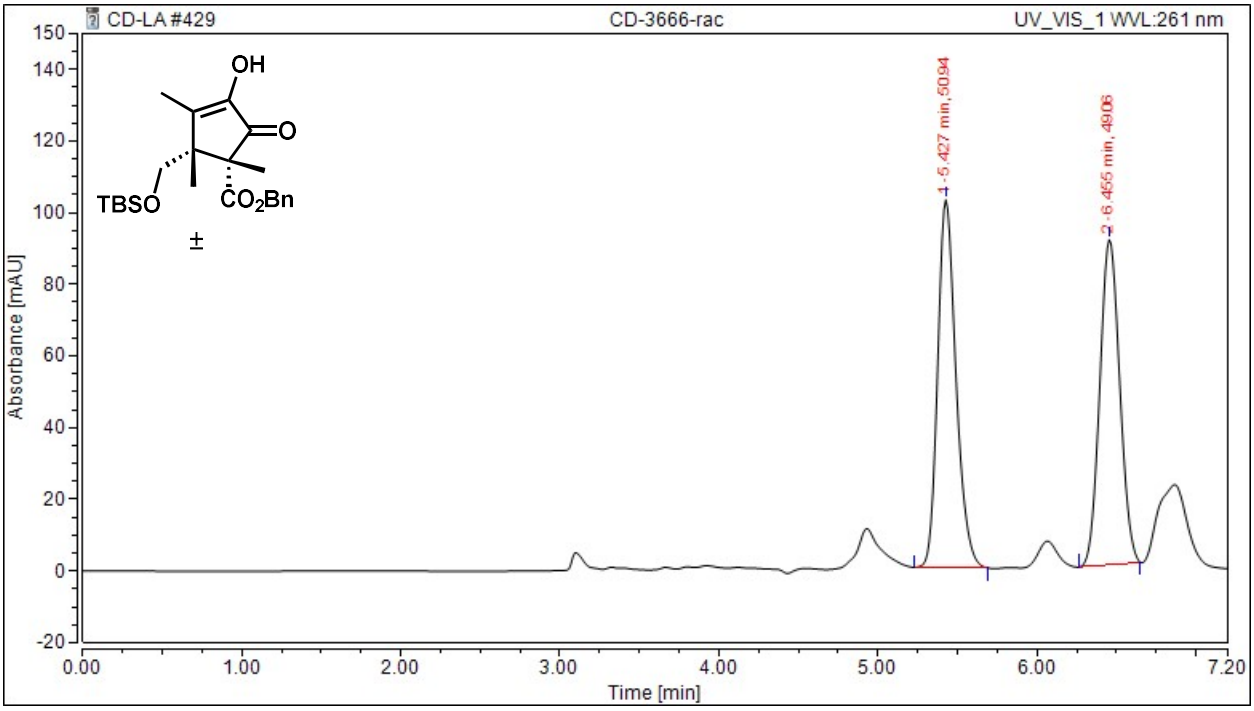
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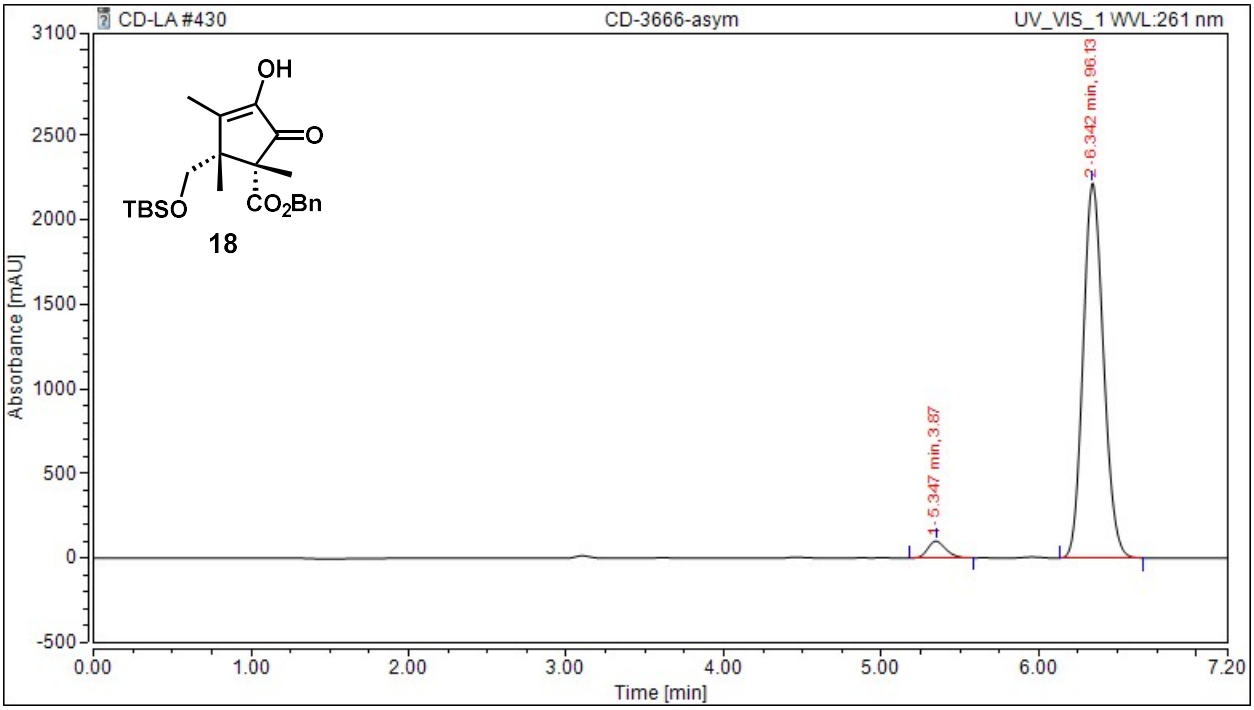
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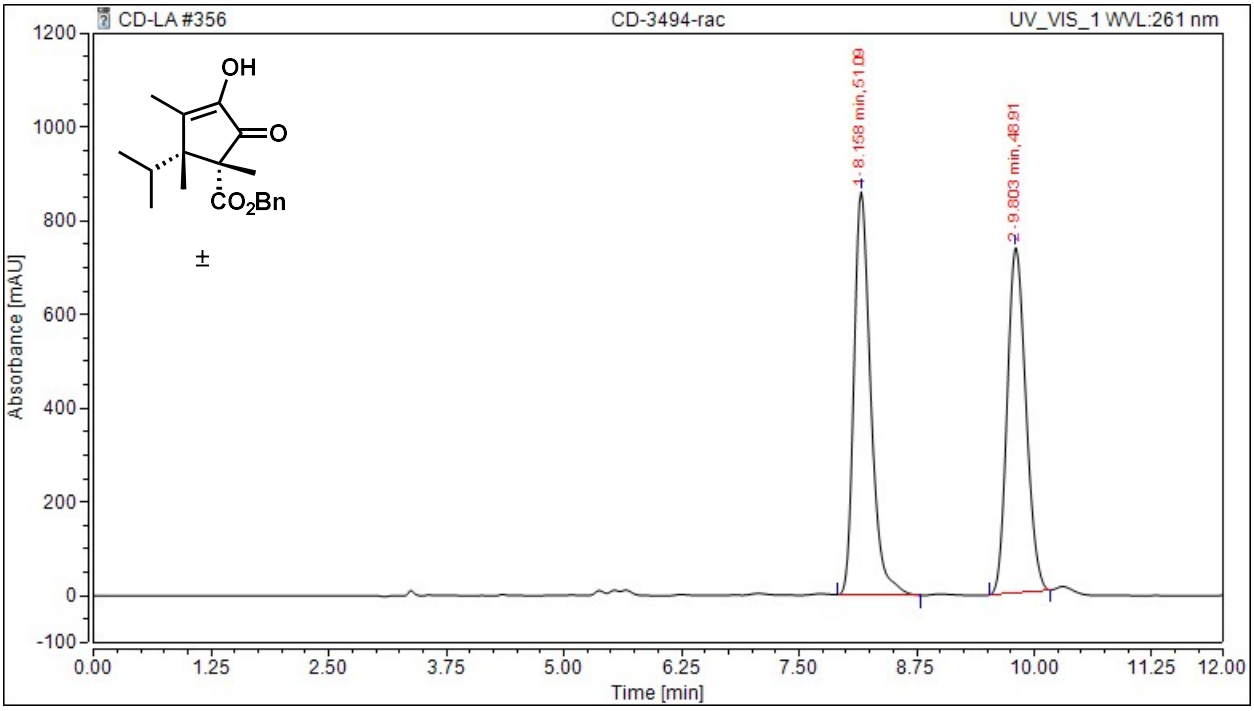
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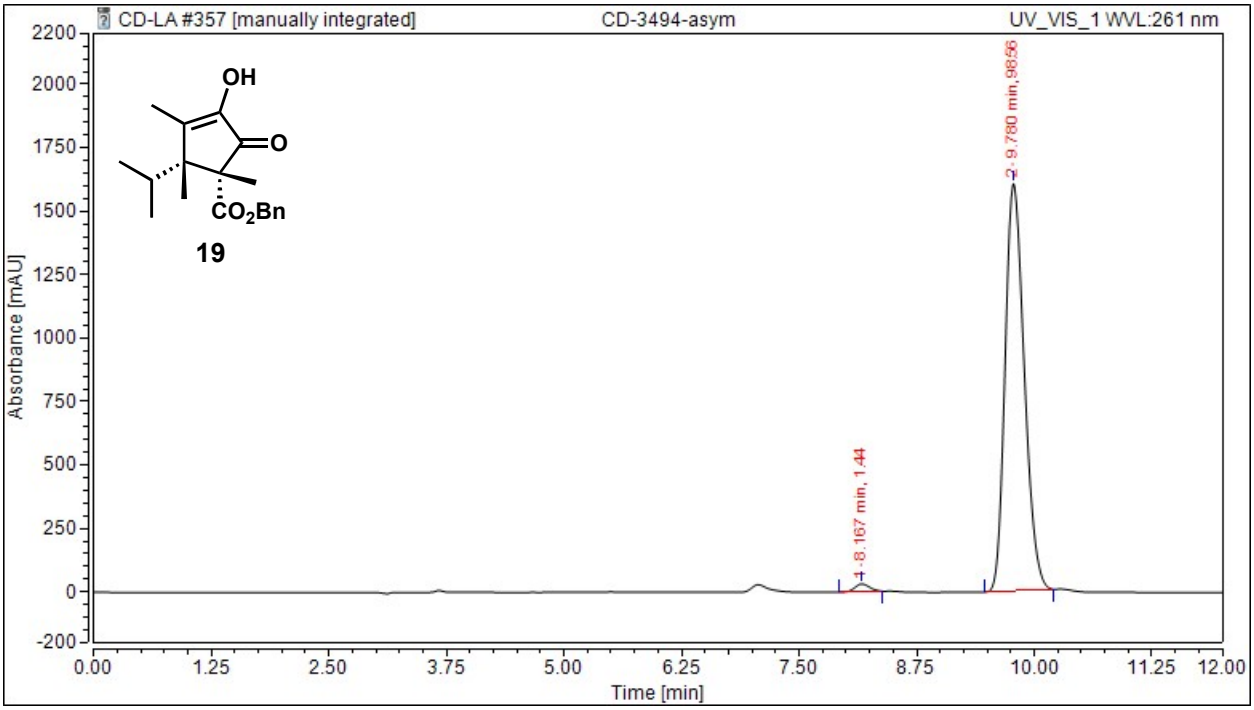
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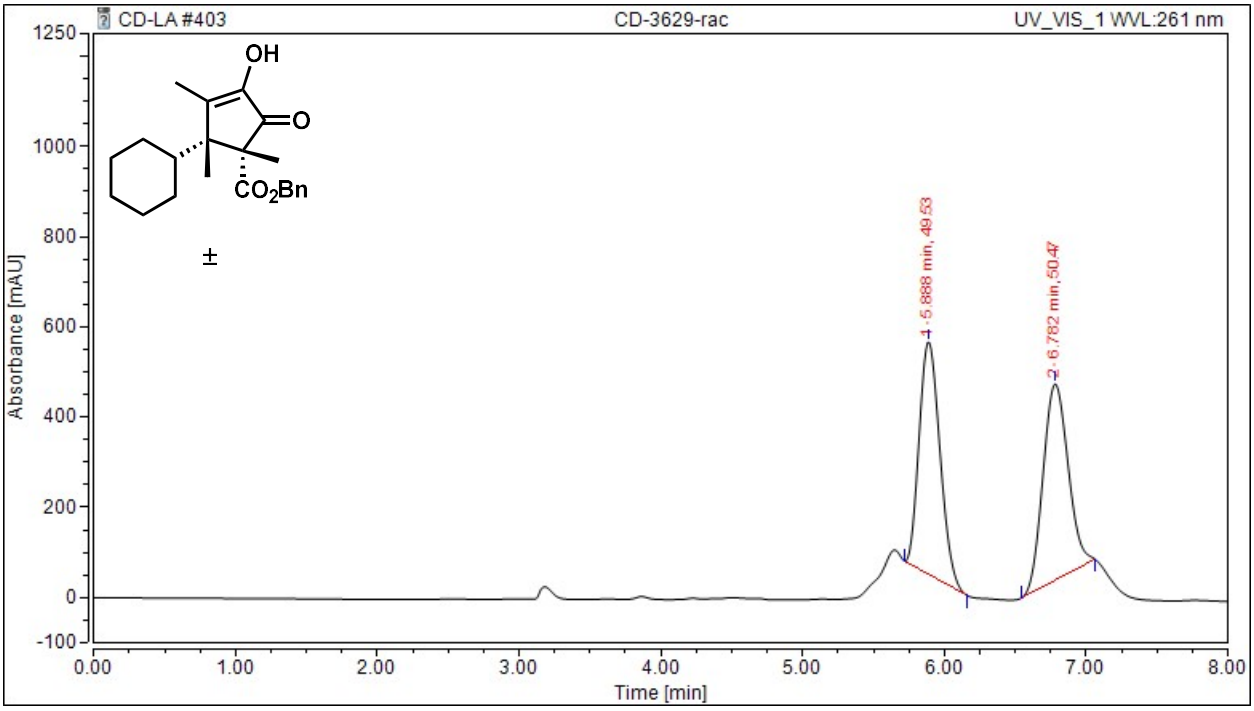
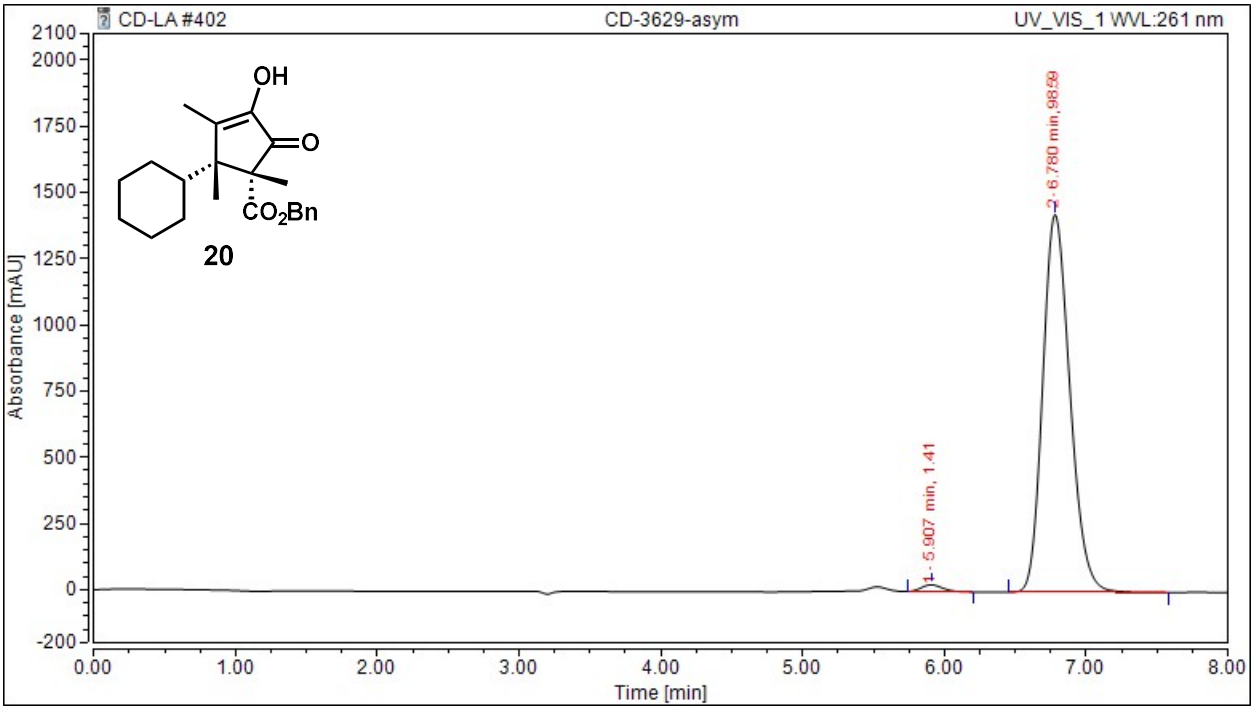
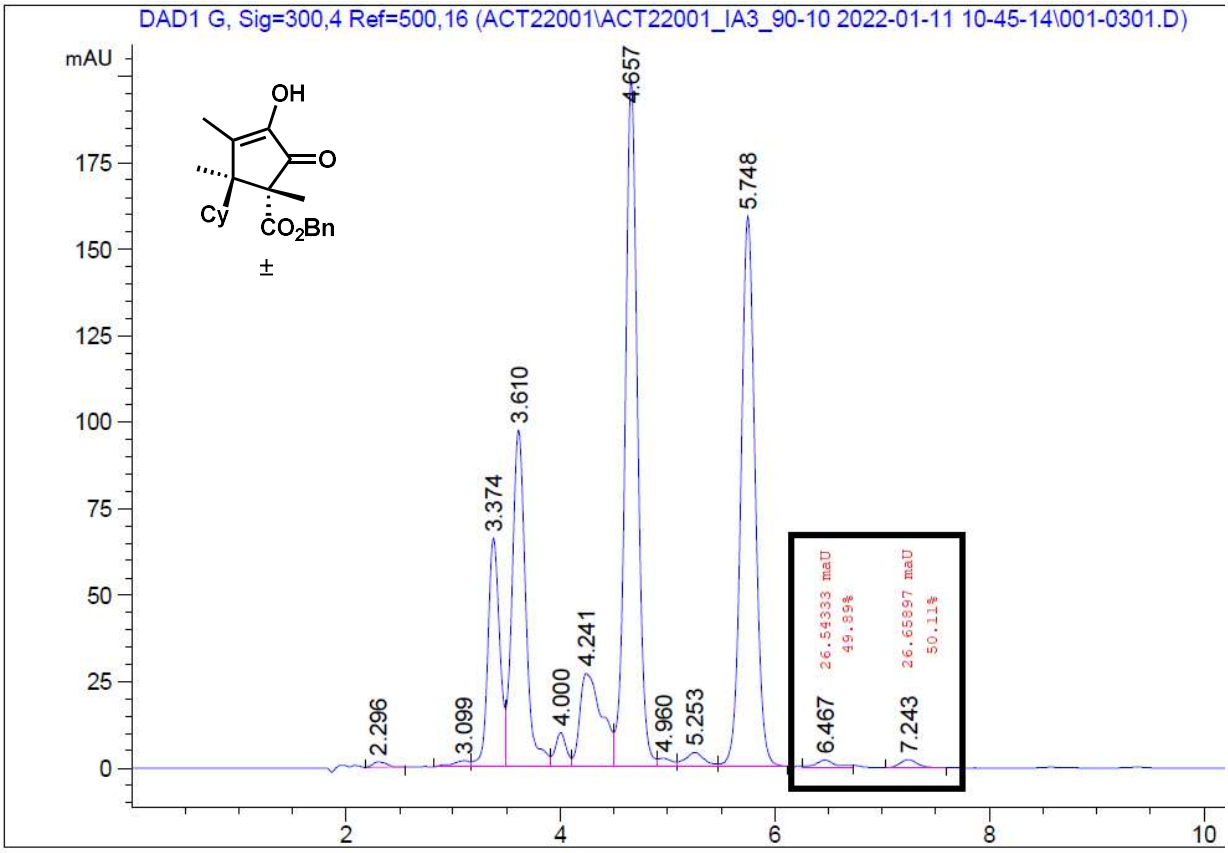
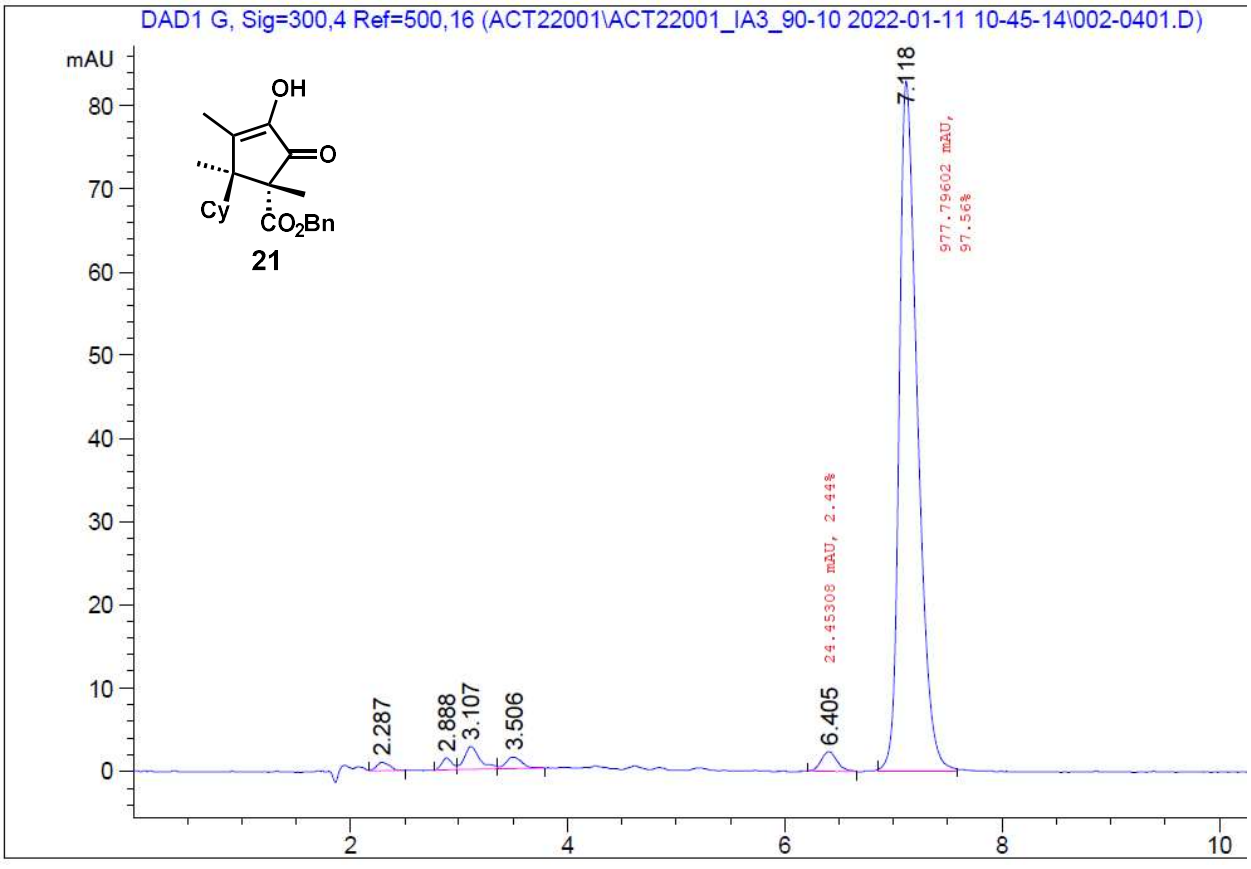
Absorbance [mAU]
Time [min]


CD-LA #403
CD-3629-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
Absorbance [mAU]
Time [min]
1 - 5.888 min, 49.53
2 - 6.782 min, 50.47


CD-LA #402
CD-3629-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
20
Absorbance [mAU]
Time [min]
1 - 5.907 min, 1.41
2 - 6.780 min, 98.59


DAD1 G, Sig=300,4 Ref=500,16 (ACT22001\ACT22001_IA3_90-10 2022-01-11 10-45-14\001-0301.D)
mAU
OH
O
Cy
CO2Bn
±
2.296
3.099
3.374
3.610
4.000
4.241
4.657
4.960
5.253
5.748
6.467
7.243
26.54333 mAU
49.89%
26.65897 mAU
50.11%


DAD1 G, Sig=300,4 Ref=500,16 (ACT22001\ACT22001_IA3_90-10 2022-01-11 10-45-14\002-0401.D)
mAU
OH
O
Cy
CO2Bn
21
2.287
2.888
3.107
3.506
6.405
7.118
24.45308 mAU, 2.44%
977.79602 mAU,
97.56%

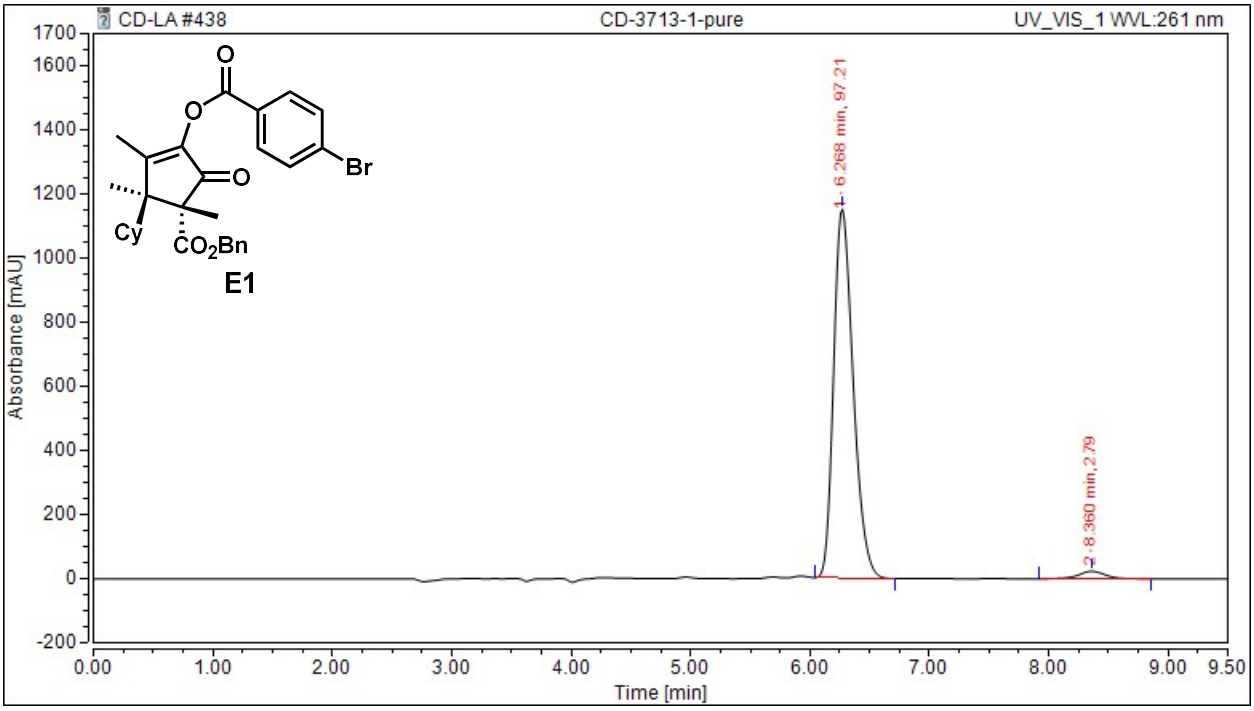
Racemate

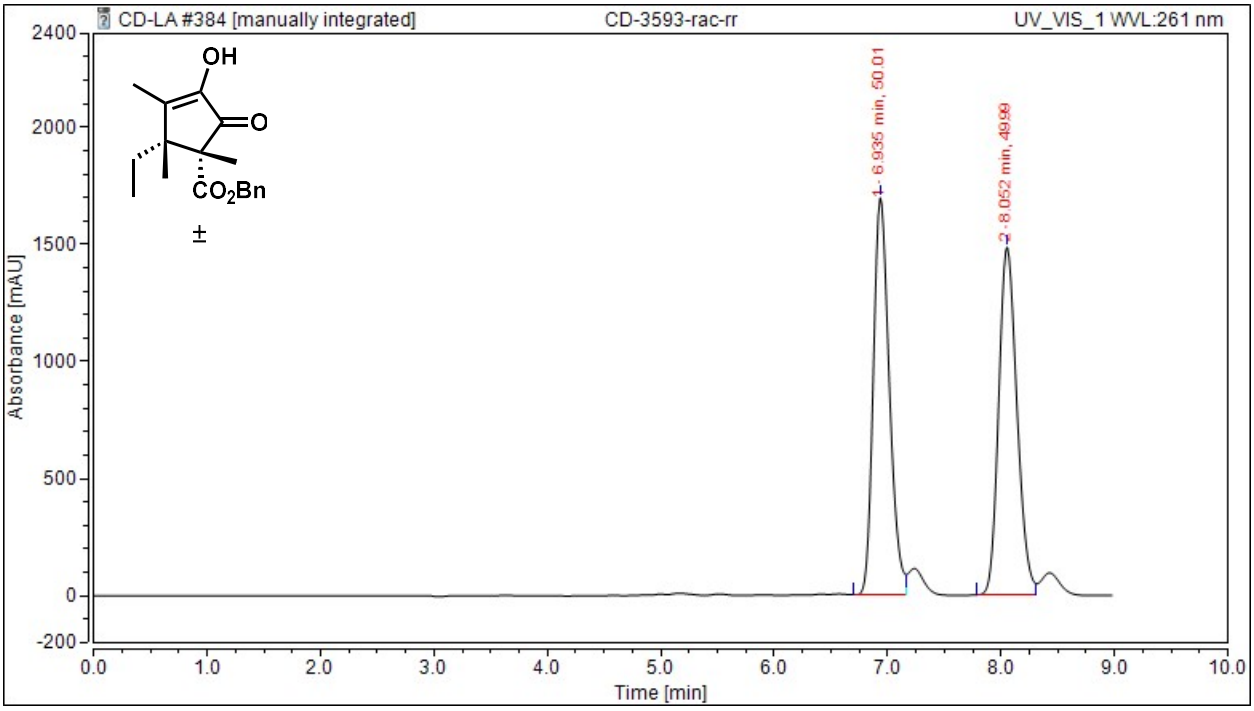
Peak #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	2.296	0.1165	13.77966	1.63174	0.2719	
2	3.099	0.1442	18.49623	1.71046	0.3650	
3	3.374	0.1197	507.48364	66.03960	10.0135	
4	3.610	0.1353	862.81726	97.43438	17.0248	
5	4.000	0.1085	71.81117	9.91276	1.4169	
6	4.241	0.2132	386.81549	26.98928	7.6325	
7	4.657	0.1222	1606.08691	199.00288	31.6907	
8	4.960	0.1251	22.82681	2.53419	0.4504	
9	5.253	0.1839	53.65327	4.17477	1.0587	
10	5.748	0.1418	1471.04150	159.16948	29.0260	
11	**6.467**	**0.1889**	**26.54333**	**2.07974**	**0.5237**	**=> rel. area % = 49.89**
12	**7.243**	**0.1737**	**26.65897**	**2.36128**	**0.5260**	**=> rel. area % = 50.11**

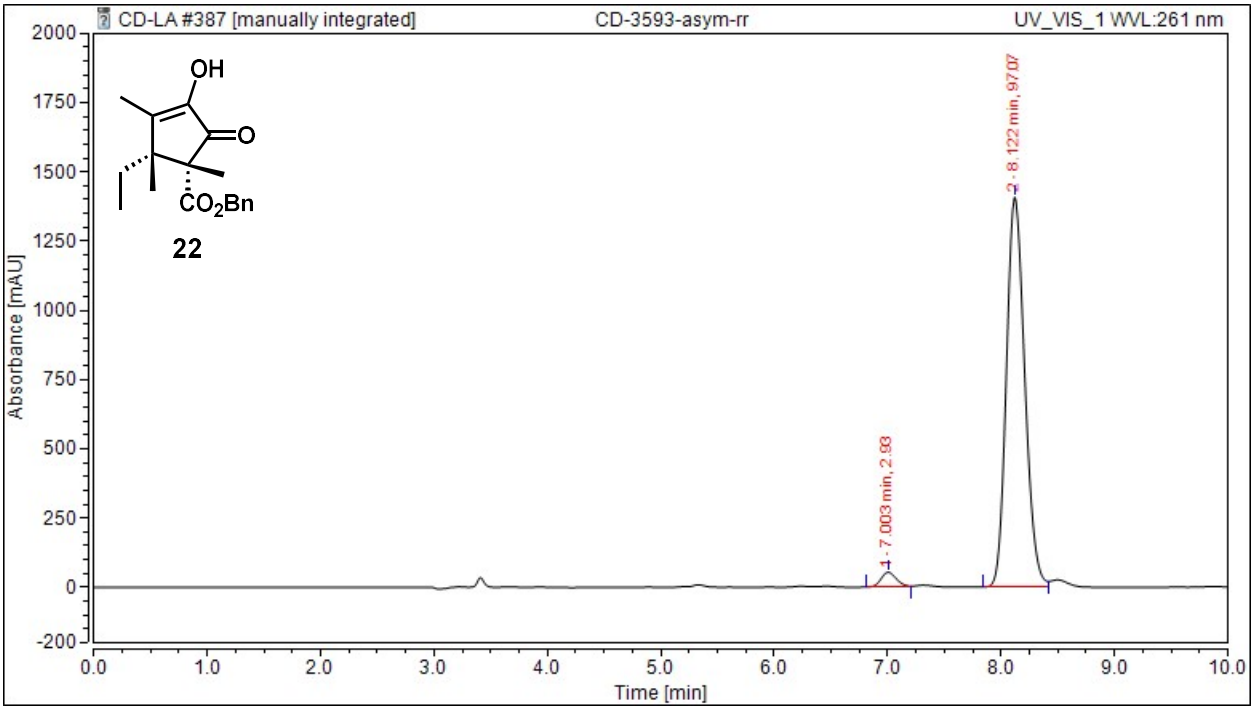
Asymmetric

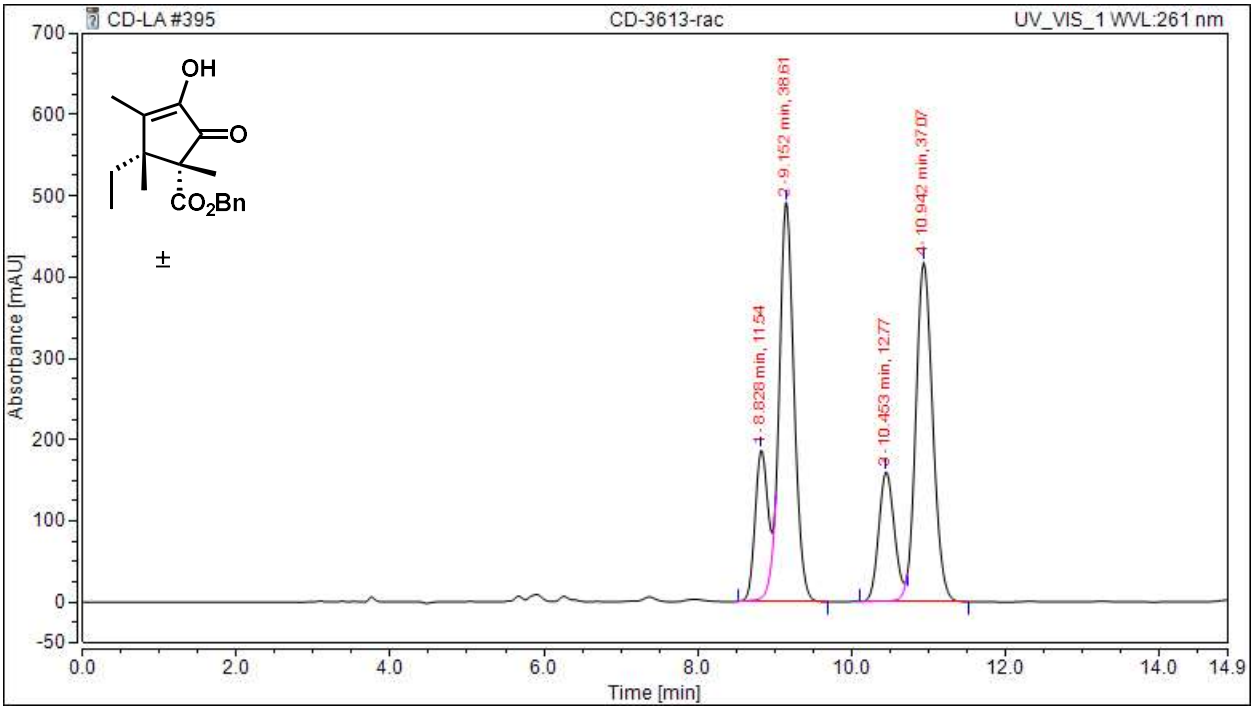
Peak #	RetTime [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %	
1	2.287	0.1096	8.23185	1.02570	0.7757	
2	2.888	0.0957	9.27655	1.42878	0.8742	
3	3.107	0.1458	27.07973	2.72710	2.5518	
4	3.506	0.1651	14.36393	1.36122	1.3536	
5	**6.405**	**0.1514**	**24.45308**	**2.38939**	**2.3043**	**=> rel. area % = 2.44**
6	**7.118**	**0.1775**	**977.79602**	**82.96968**	**92.1405**	**=> rel. area % = 97.56**

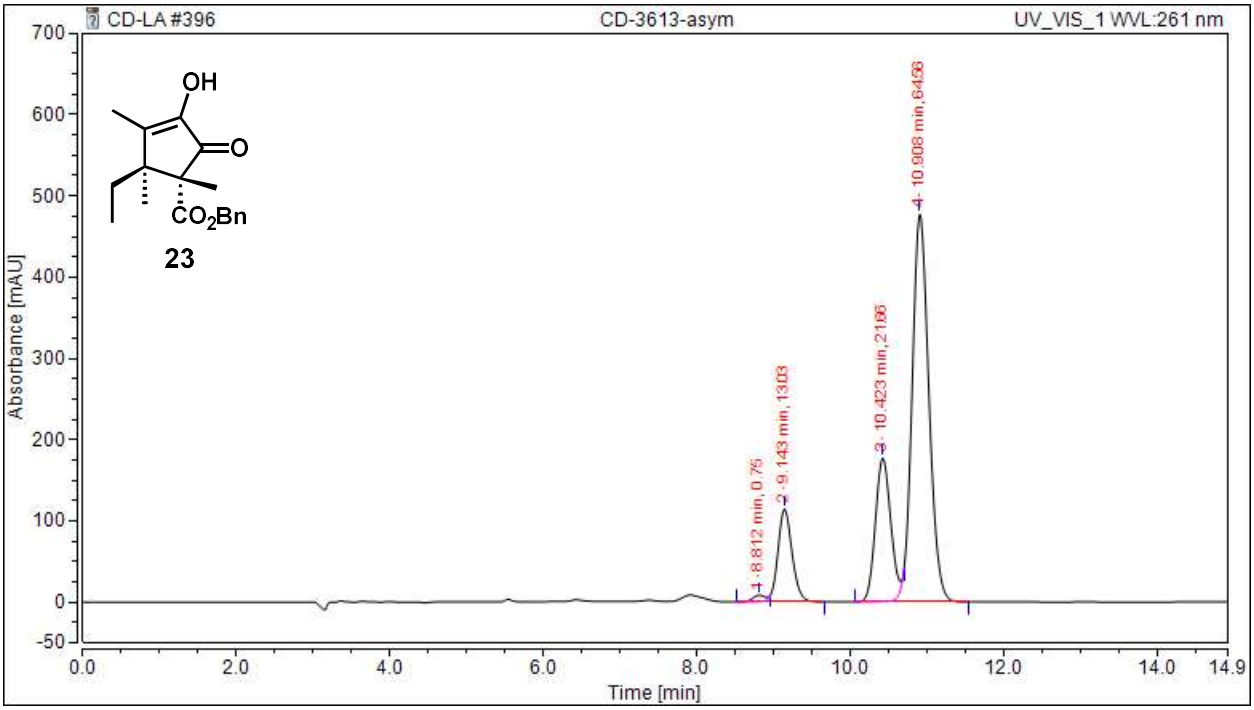
Note: HPLC data collection for compound **28** and its racemate was performed as a courtesy by Daicel (operator: Jay Ferraro).

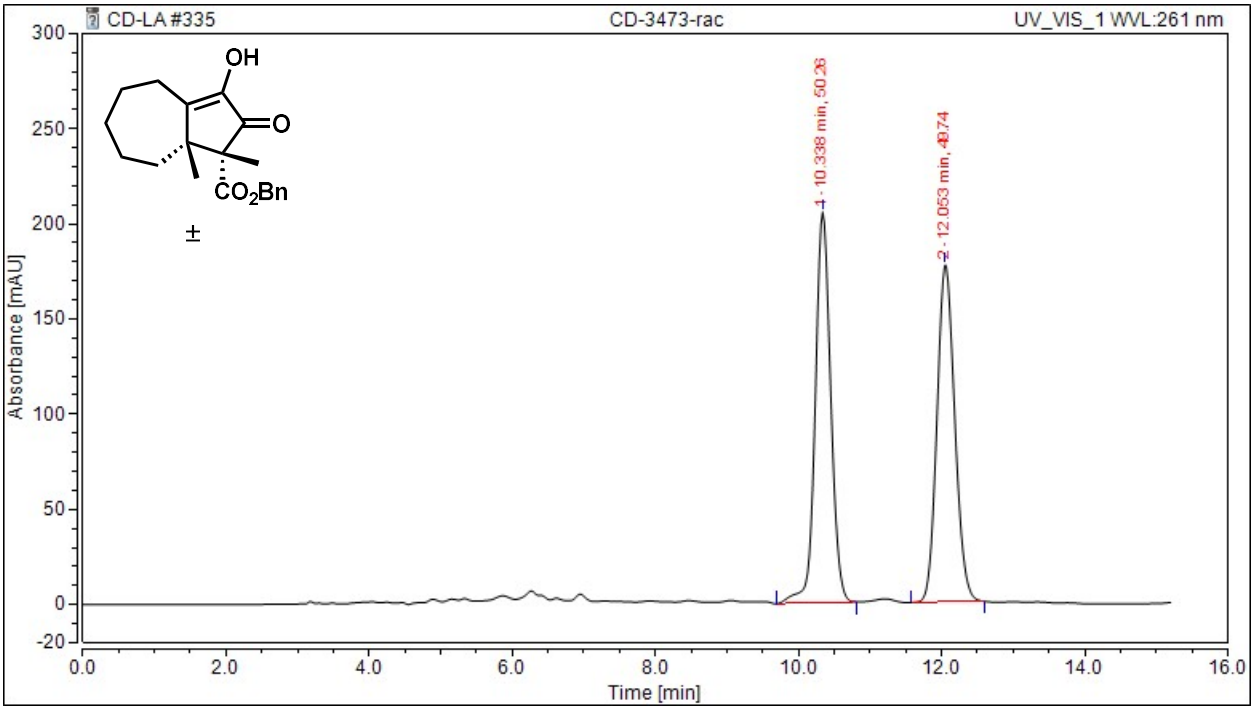

CD-LA #438
CD-3713-1-pure
UV_VIS_1 WVL:261 nm
1 - 6.268 min, 97.21
2 - 8.360 min, 2.79
Absorbance [mAU]
Time [min]
Cy
CO2Bn
Br
E1

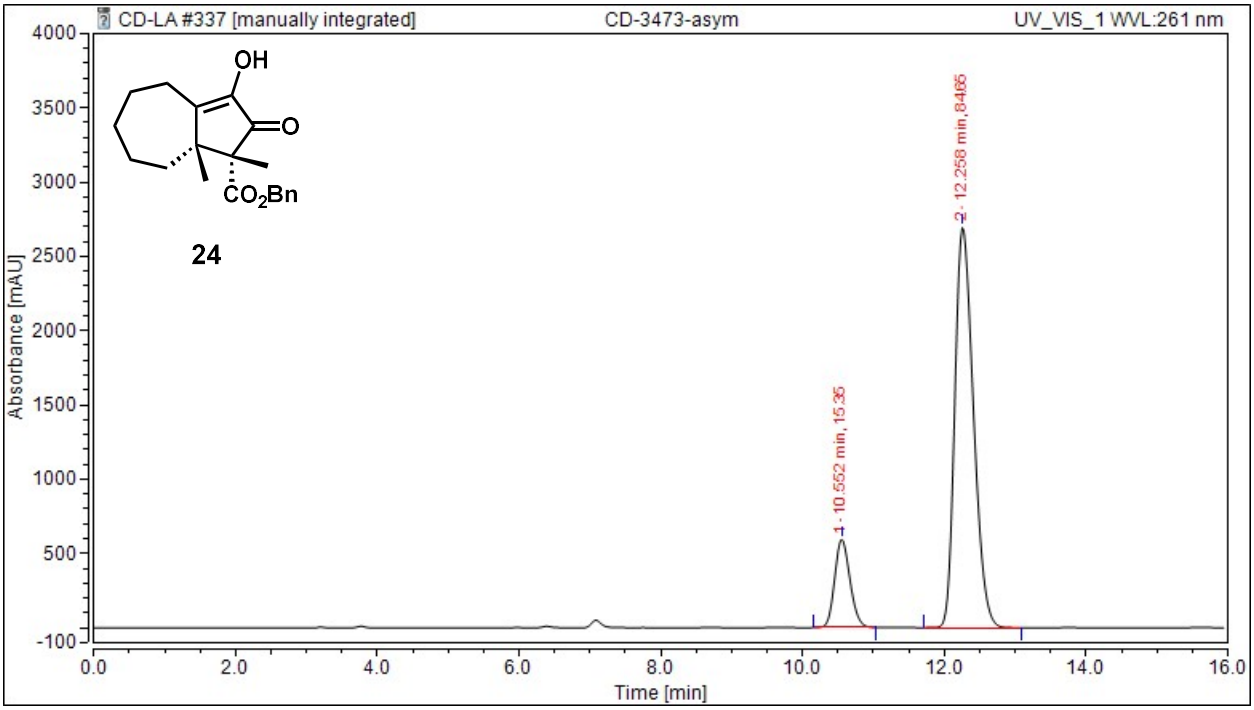

CD-LA #384 [manually integrated]
CD-3593-rac-rr
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 6.935 min, 50.01
2 - 8.052 min, 49.99
Absorbance [mAU]
Time [min]

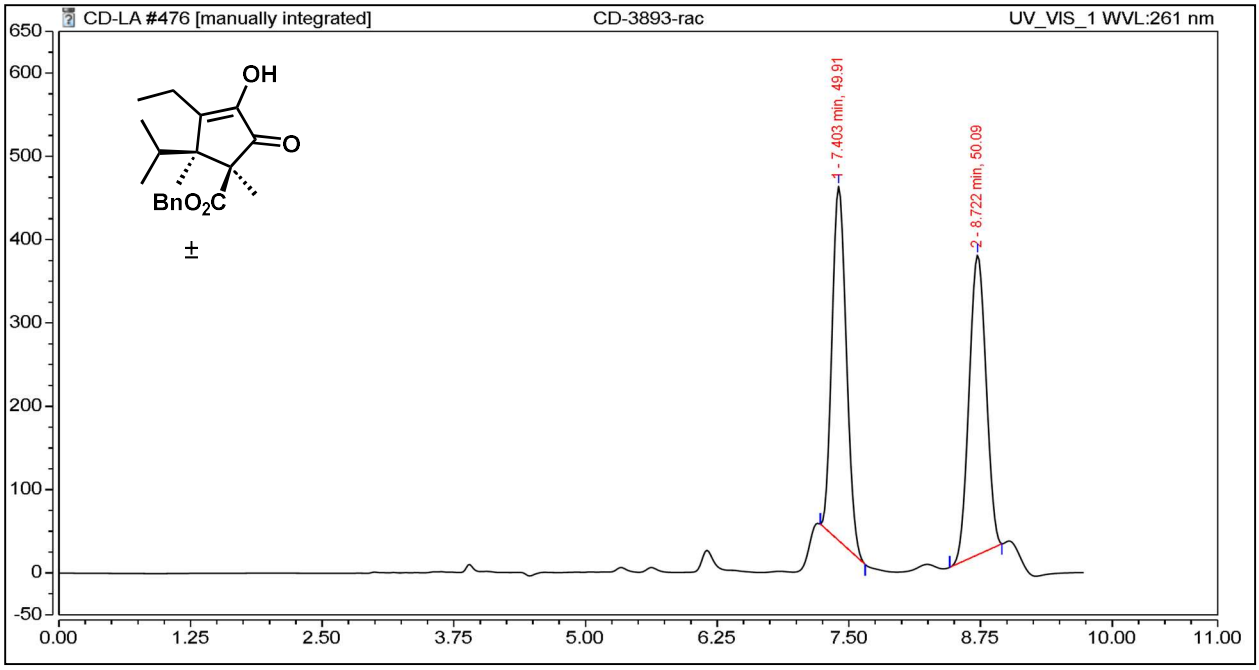

CD-LA #387 [manually integrated]
CD-3593-asym-rr
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
22
1 - 7.003 min, 2.93
2 - 8.122 min, 97.07
Absorbance [mAU]
Time [min]

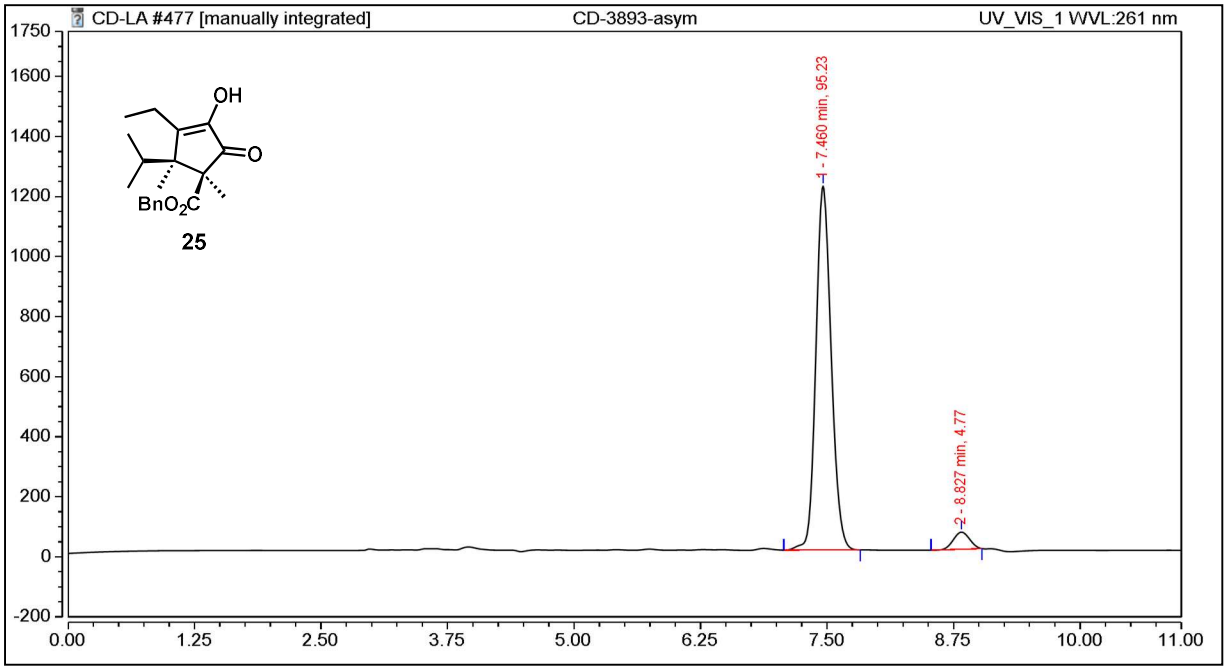

CD-LA #395
CD-3613-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 8.828 min, 11.54
2 - 9.152 min, 38.61
3 - 10.453 min, 12.77
4 - 10.942 min, 37.07
Absorbance [mAU]
Time [min]

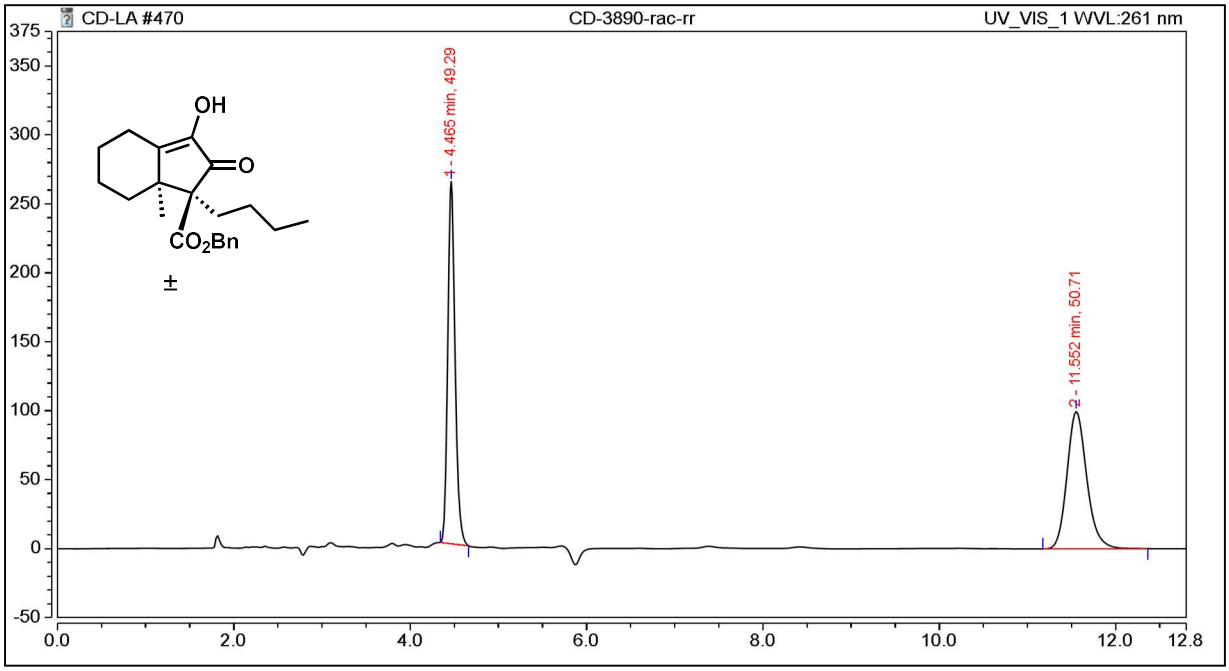

CD-LA #396
CD-3613-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
23
1 - 8.812 min, 0.75
2 - 9.143 min, 13.03
3 - 10.423 min, 21.86
4 - 10.908 min, 64.56
Absorbance [mAU]
Time [min]

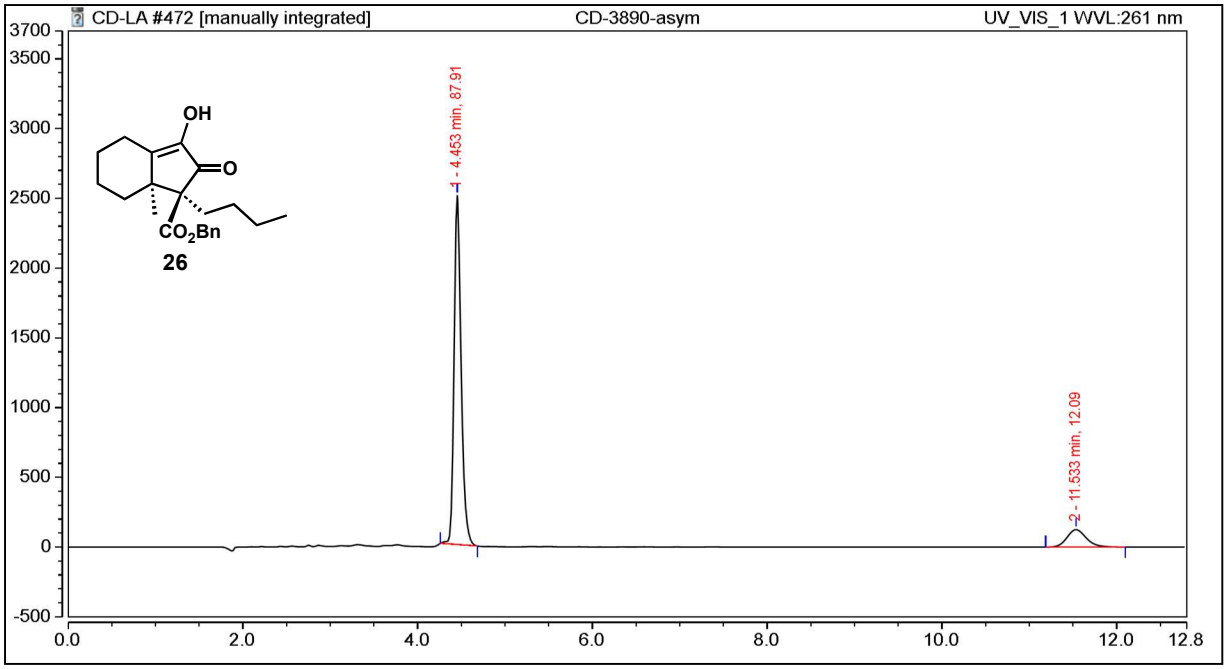

CD-LA #335
CD-3473-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 10.338 min, 50.26
2 - 12.053 min, 49.74
Absorbance [mAU]
Time [min]

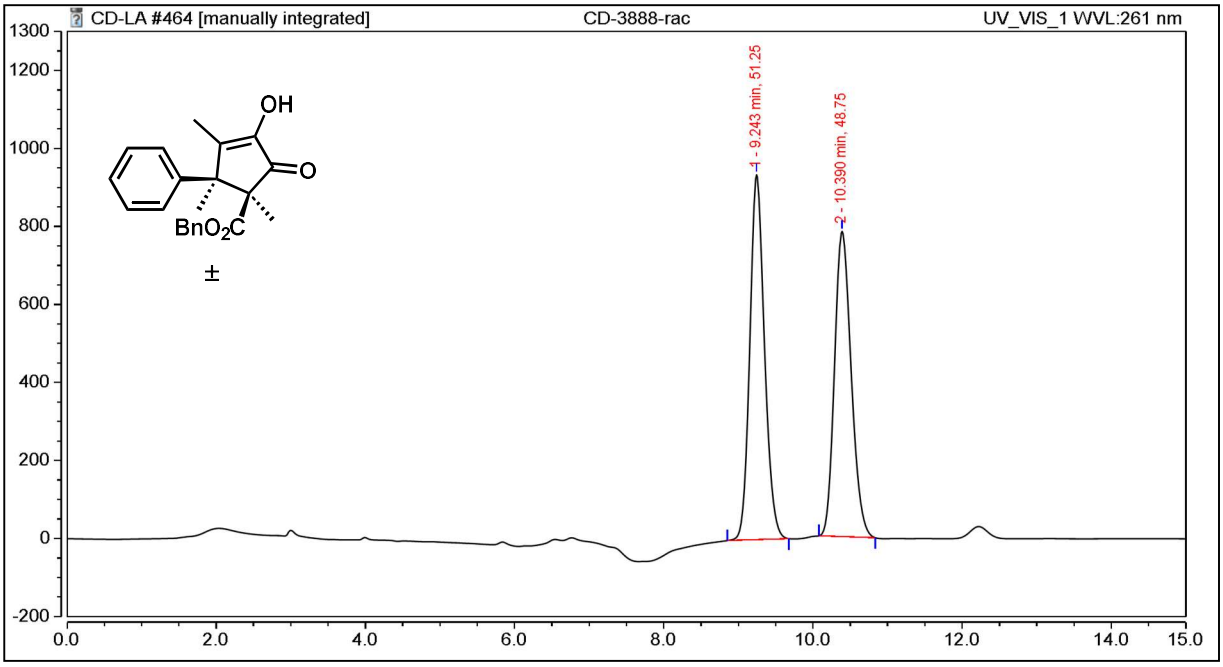

CD-LA #337 [manually integrated]
CD-3473-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
24
1 - 10.552 min, 15.35
2 - 12.258 min, 84.65
Absorbance [mAU]
Time [min]

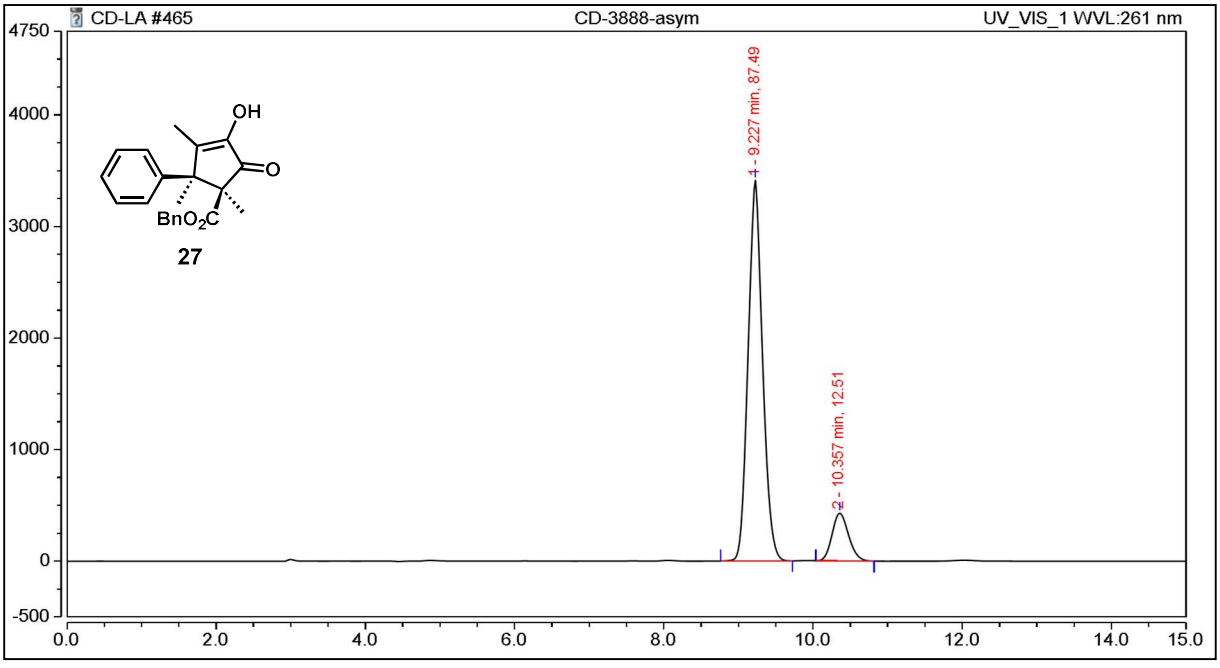

CD-LA #476 [manually integrated]
CD-3893-rac
UV_VIS_1 WVL:261 nm
OH
O
BnO2C
±
1 - 7.403 min, 49.91
2 - 8.722 min, 50.09
650
600
500
400
300
200
100
0
-50
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
11.00

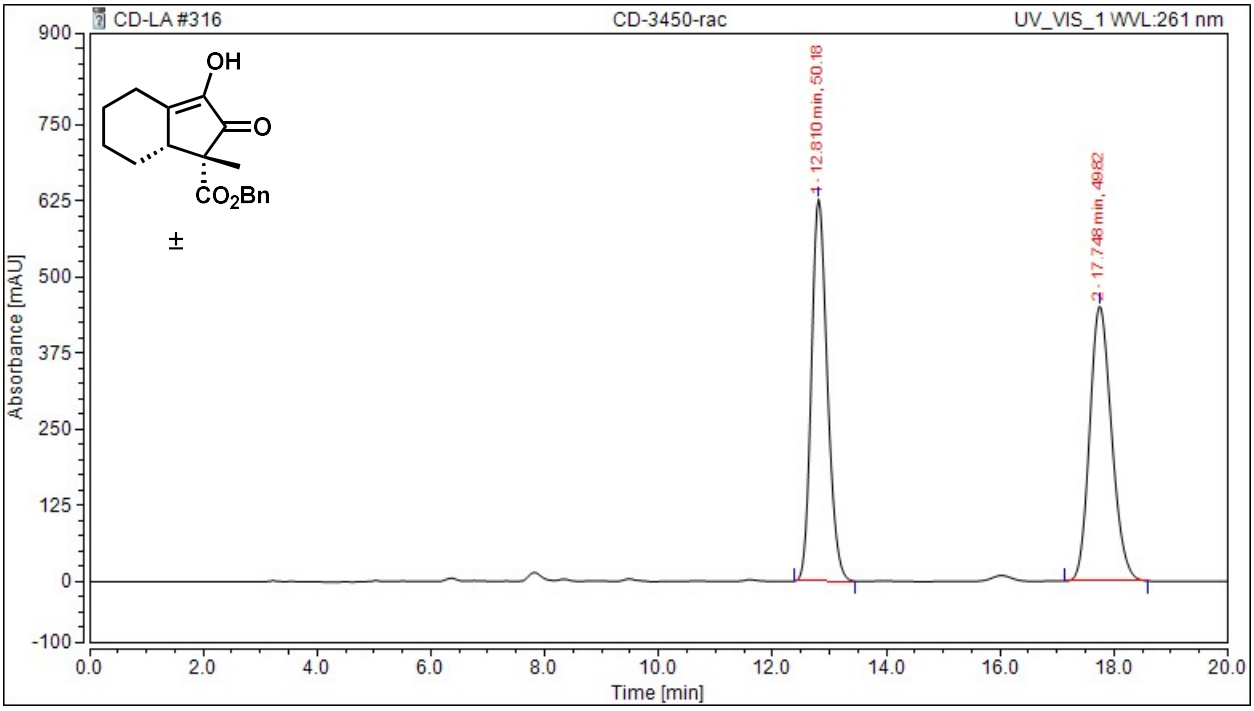

CD-LA #477 [manually integrated]
CD-3893-asym
UV_VIS_1 WVL:261 nm
OH
O
BnO2C
25
1 - 7.460 min, 95.23
2 - 8.827 min, 4.77
1750
1600
1400
1200
1000
800
600
400
200
0
-200
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
11.00

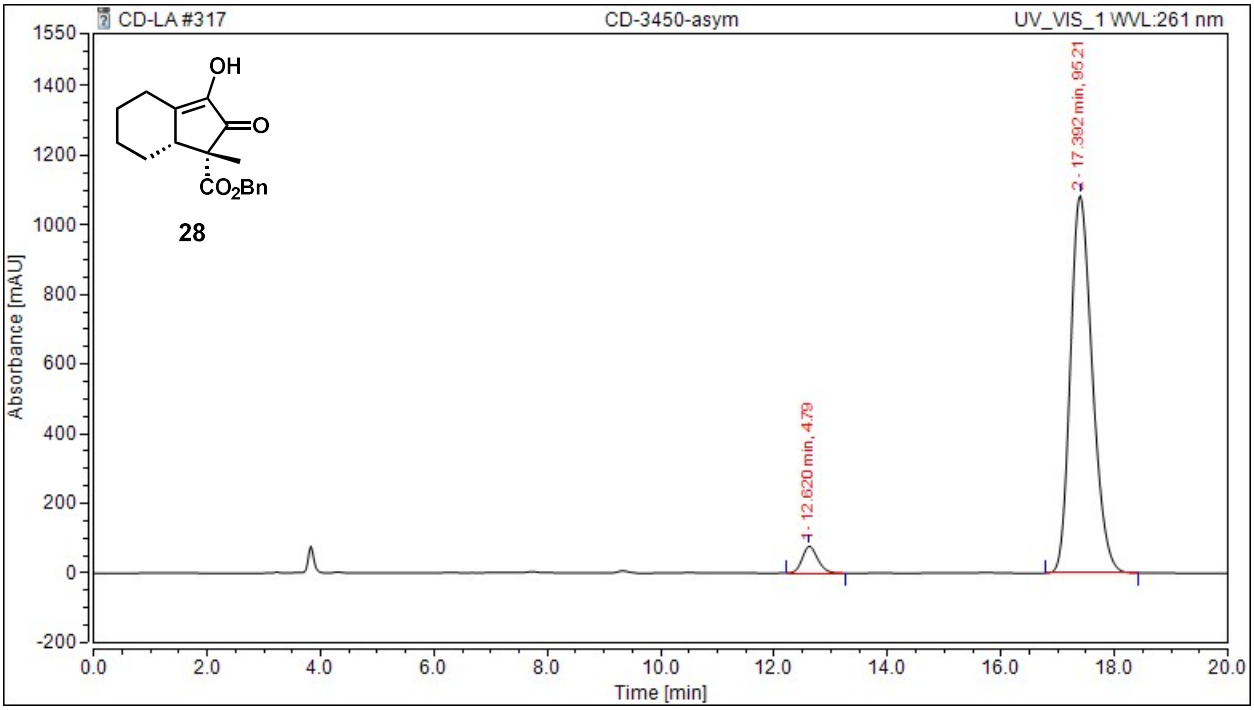

CD-LA #470
CD-3890-rac-rr
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 4.465 min, 49.29
2 - 11.552 min, 50.71
375
350
300
250
200
150
100
50
0
-50
0.0
2.0
4.0
6.0
8.0
10.0
12.0
12.8

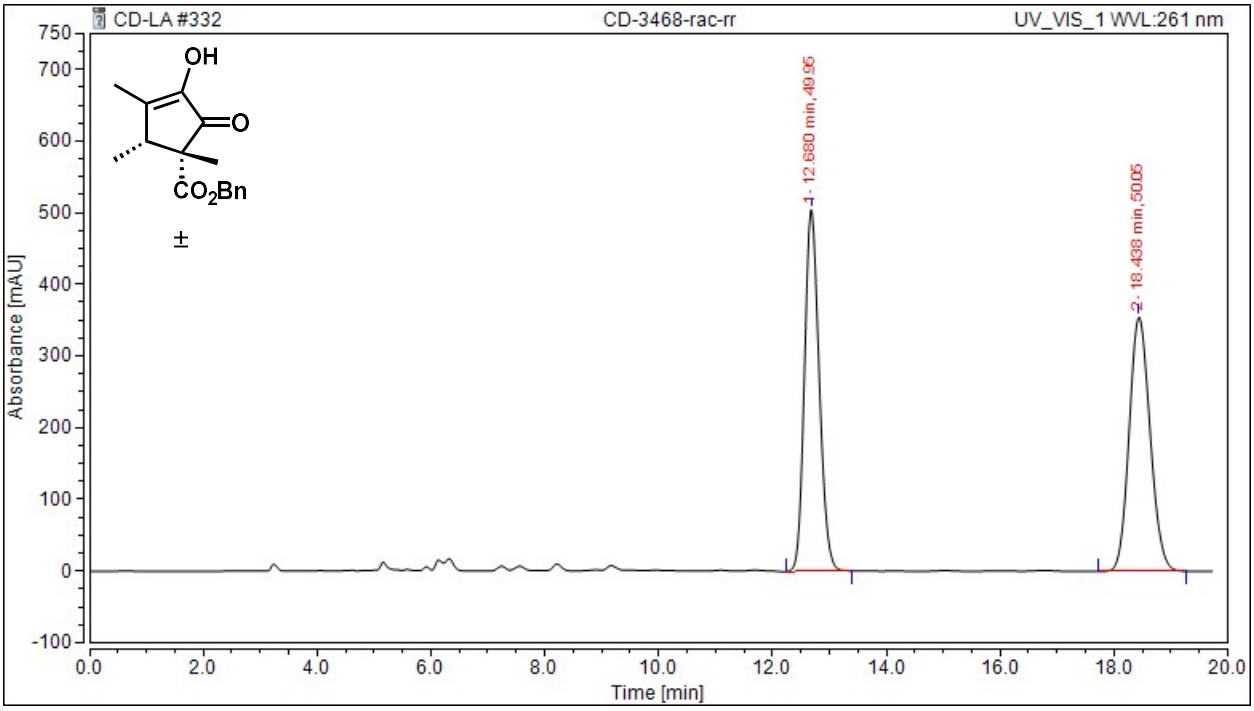

CD-LA #472 [manually integrated]
CD-3890-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
26
1 - 4.453 min, 87.91
2 - 11.533 min, 12.09
3700
3500
3000
2500
2000
1500
1000
500
0
-500
0.0
2.0
4.0
6.0
8.0
10.0
12.0
12.8

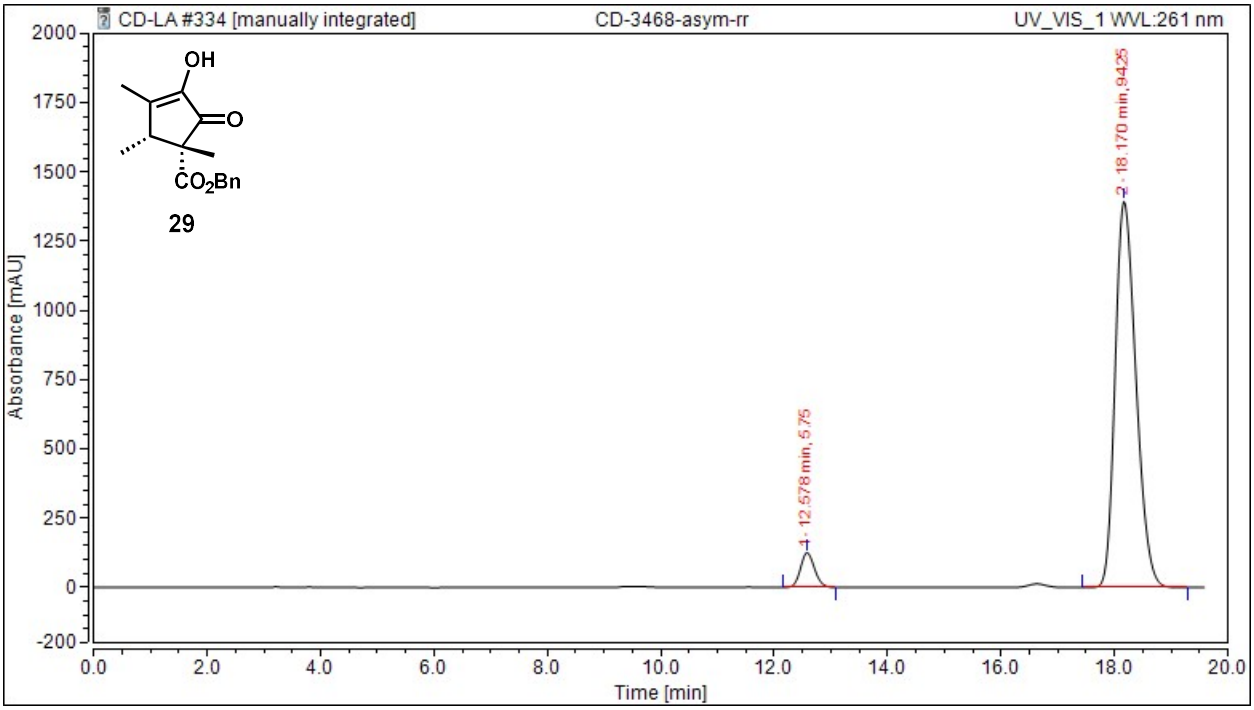

CD-LA #464 [manually integrated]
CD-3888-rac
UV_VIS_1 WVL:261 nm
1 - 9.243 min, 51.25
2 - 10.390 min, 48.75
OH
O
BnO2C
±

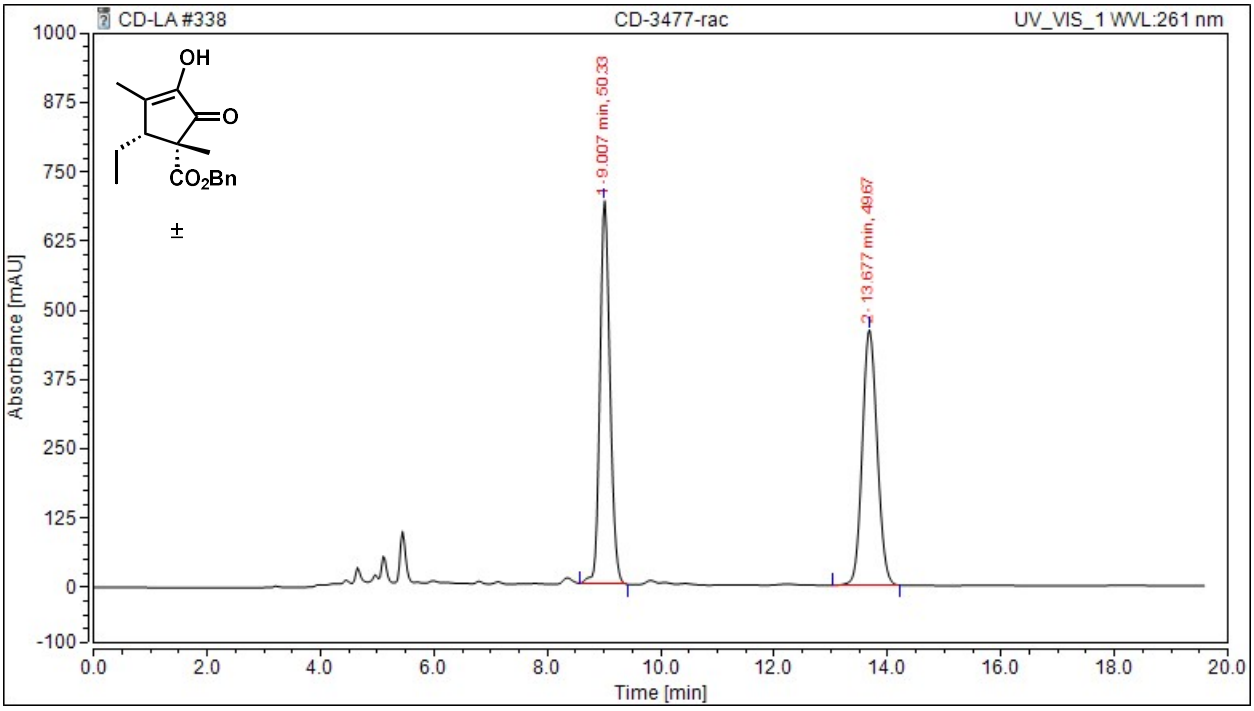

CD-LA #465
CD-3888-asym
UV_VIS_1 WVL:261 nm
1 - 9.227 min, 87.49
2 - 10.357 min, 12.51
OH
O
BnO2C
27

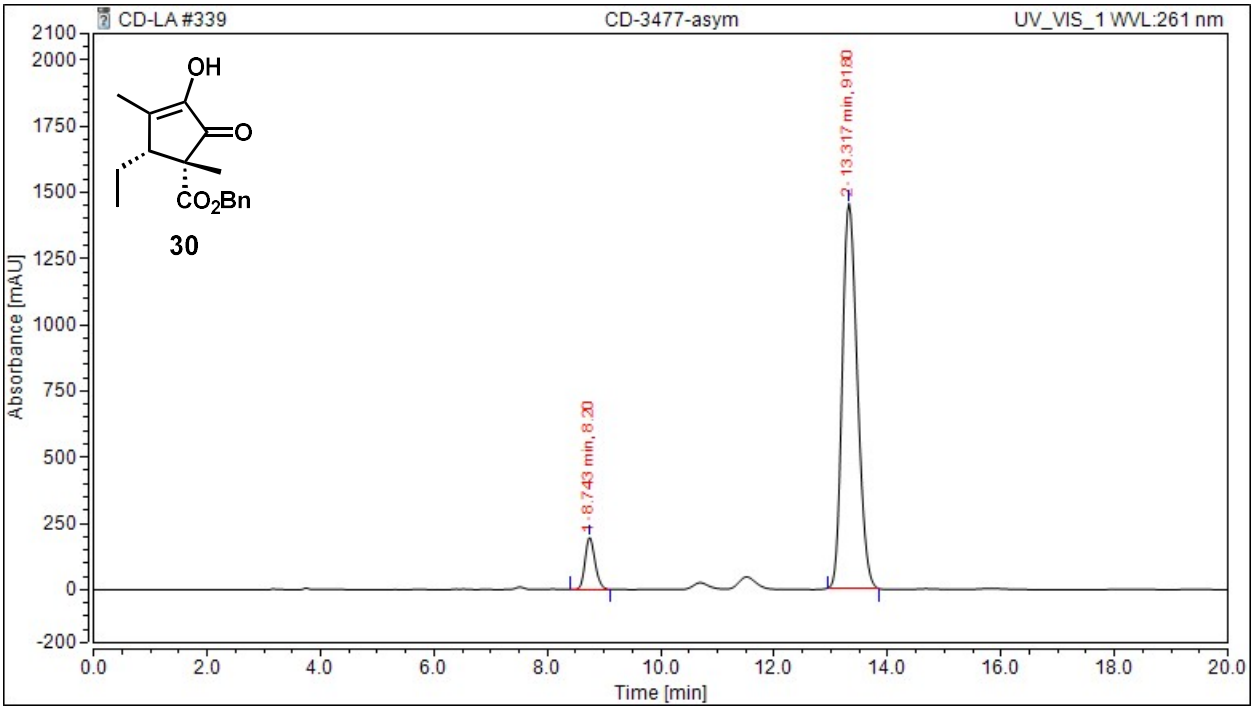

CD-LA #316
CD-3450-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 12.810 min, 50.18
2 - 17.748 min, 49.82
Absorbance [mAU]
Time [min]

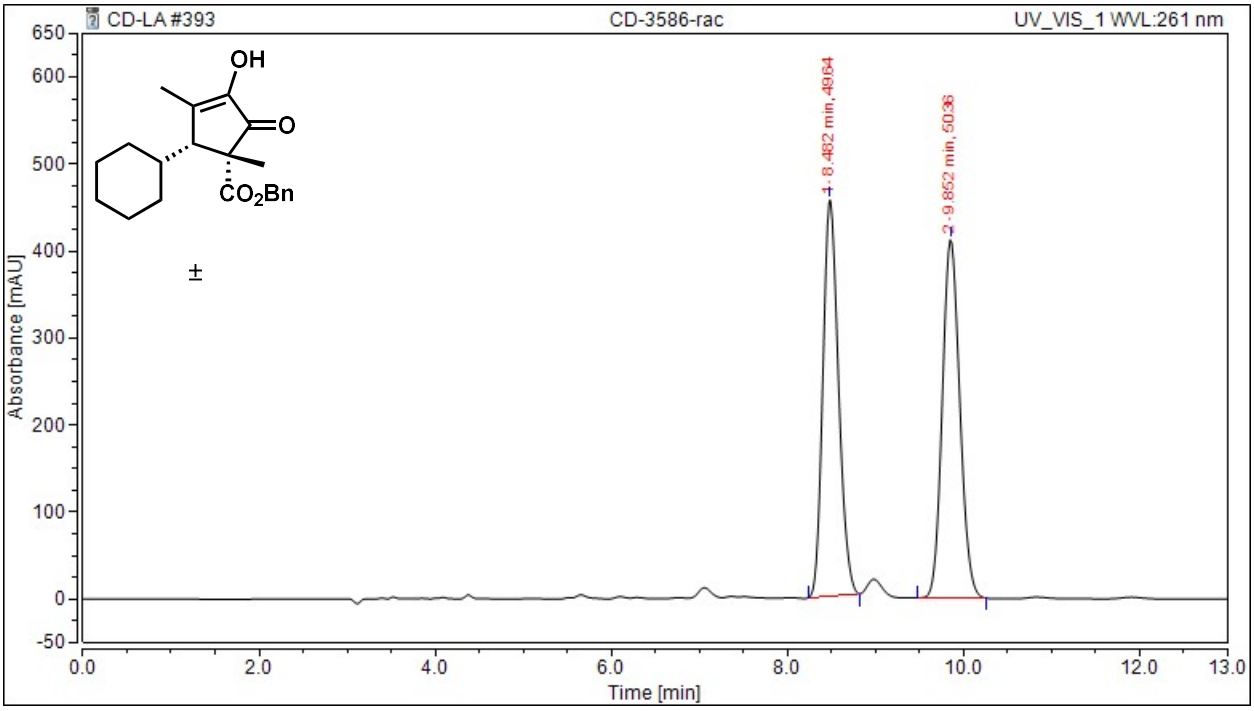

CD-LA #317
CD-3450-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
28
1 - 12.620 min, 4.79
2 - 17.392 min, 95.21
Absorbance [mAU]
Time [min]

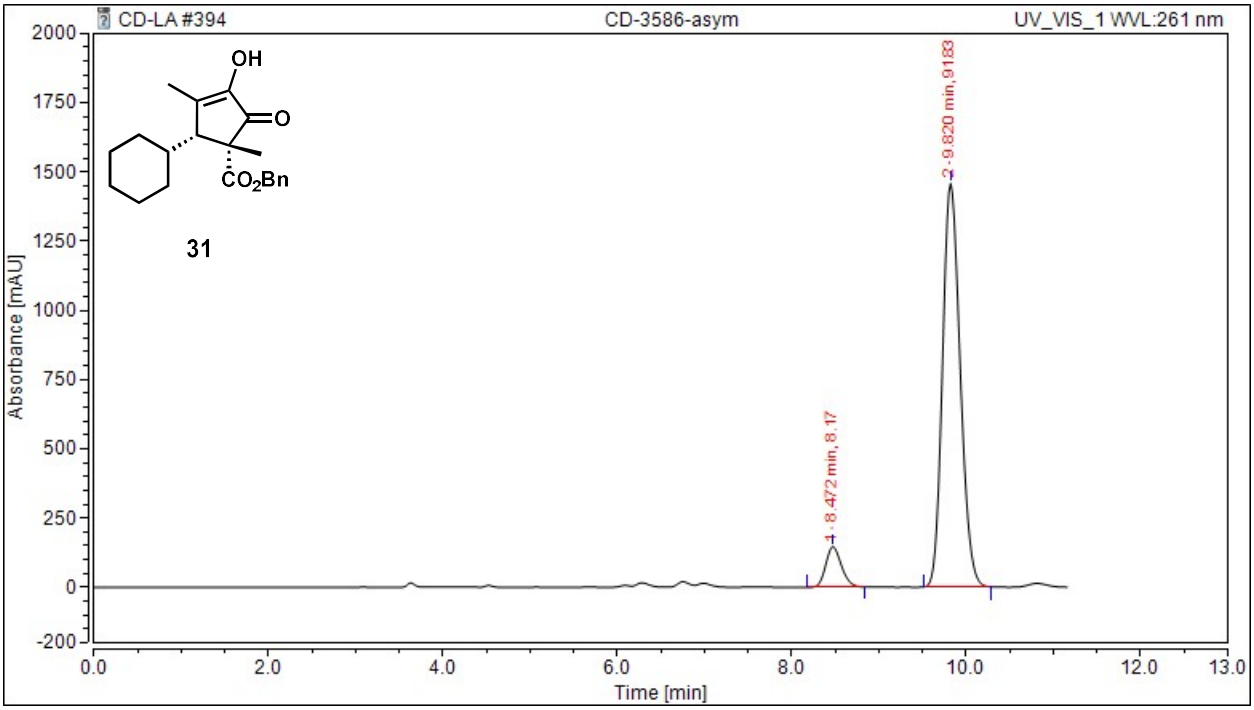

CD-LA #332
CD-3468-rac-rr
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 12.680 min,49.95
2 - 18.438 min,50.05
Absorbance [mAU]
Time [min]

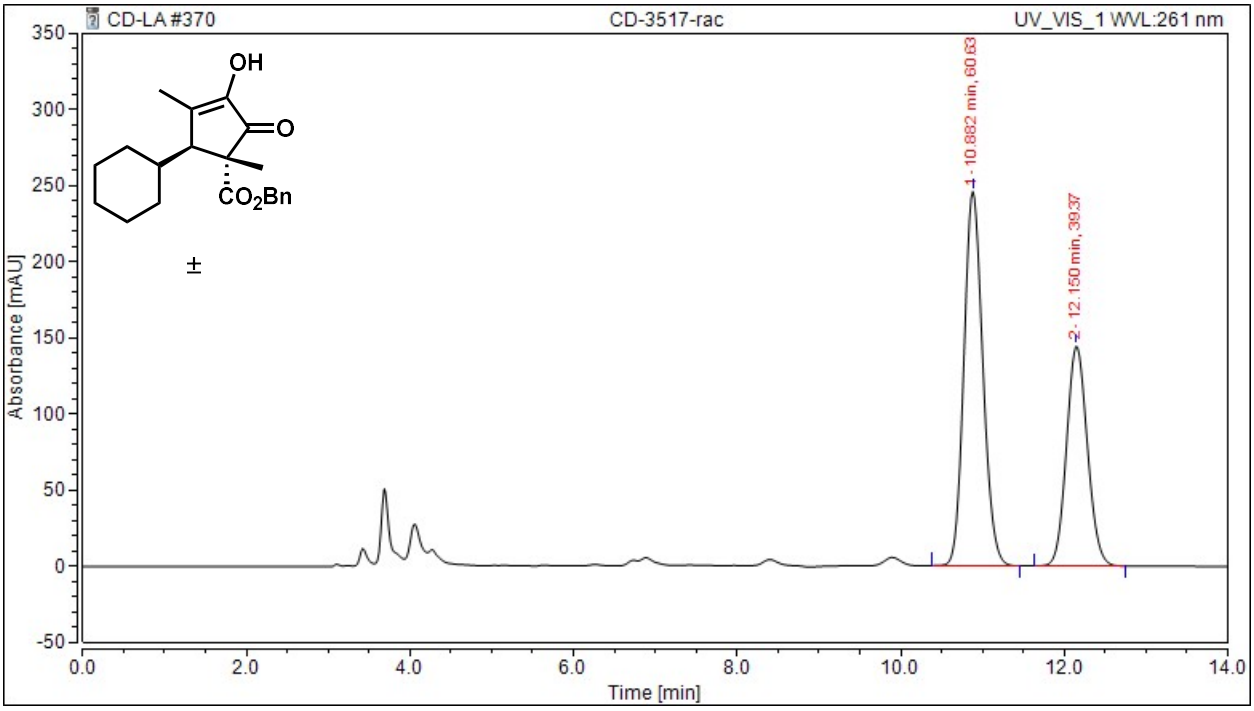

CD-LA #334 [manually integrated]
CD-3468-asym-rr
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
29
1 - 12.578 min, 5.75
2 - 18.170 min,94.25
Absorbance [mAU]
Time [min]

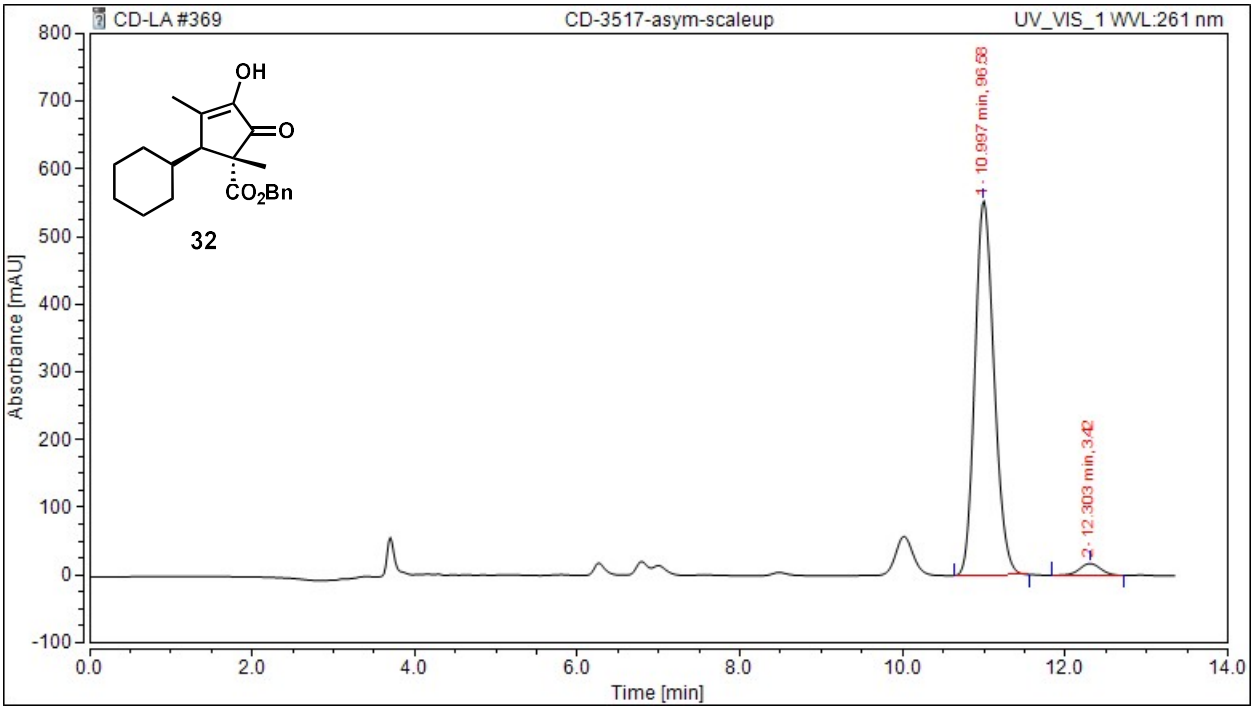

CD-LA #338
CD-3477-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 9.007 min, 50.33
2 - 13.677 min, 49.67
Absorbance [mAU]
Time [min]

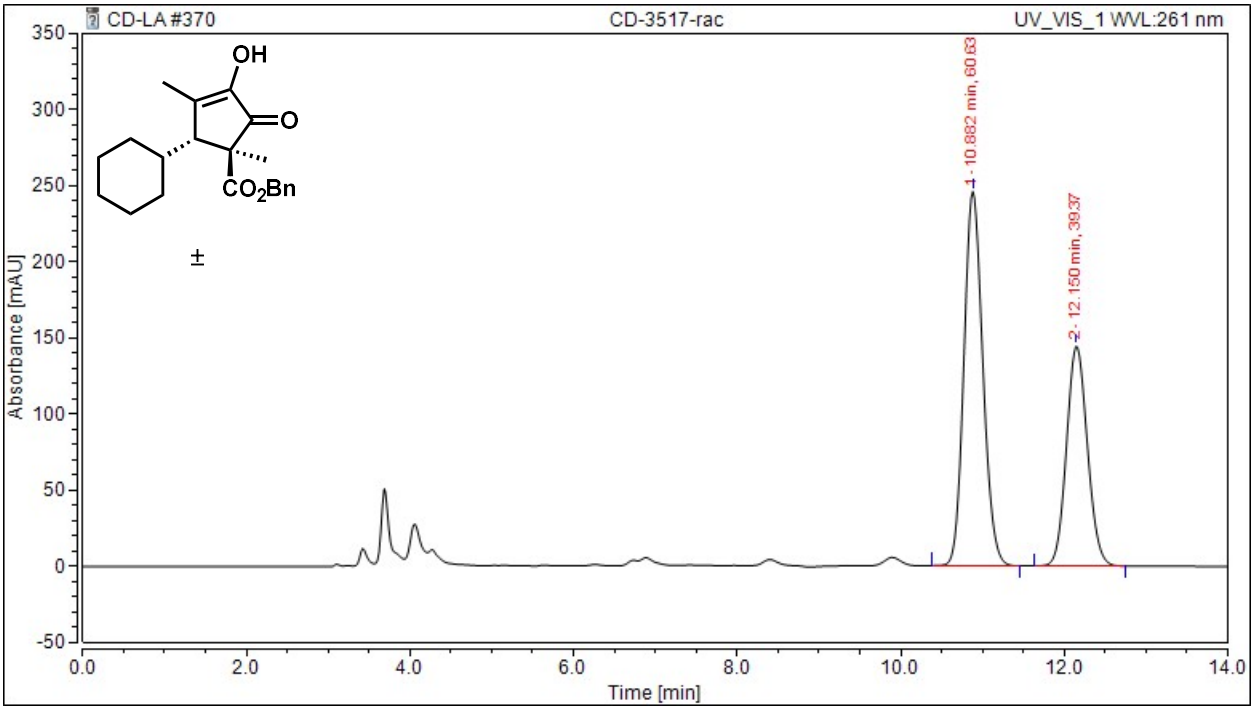

CD-LA #339
CD-3477-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
30
1 - 8.743 min, 8.20
2 - 13.317 min, 91.80
Absorbance [mAU]
Time [min]

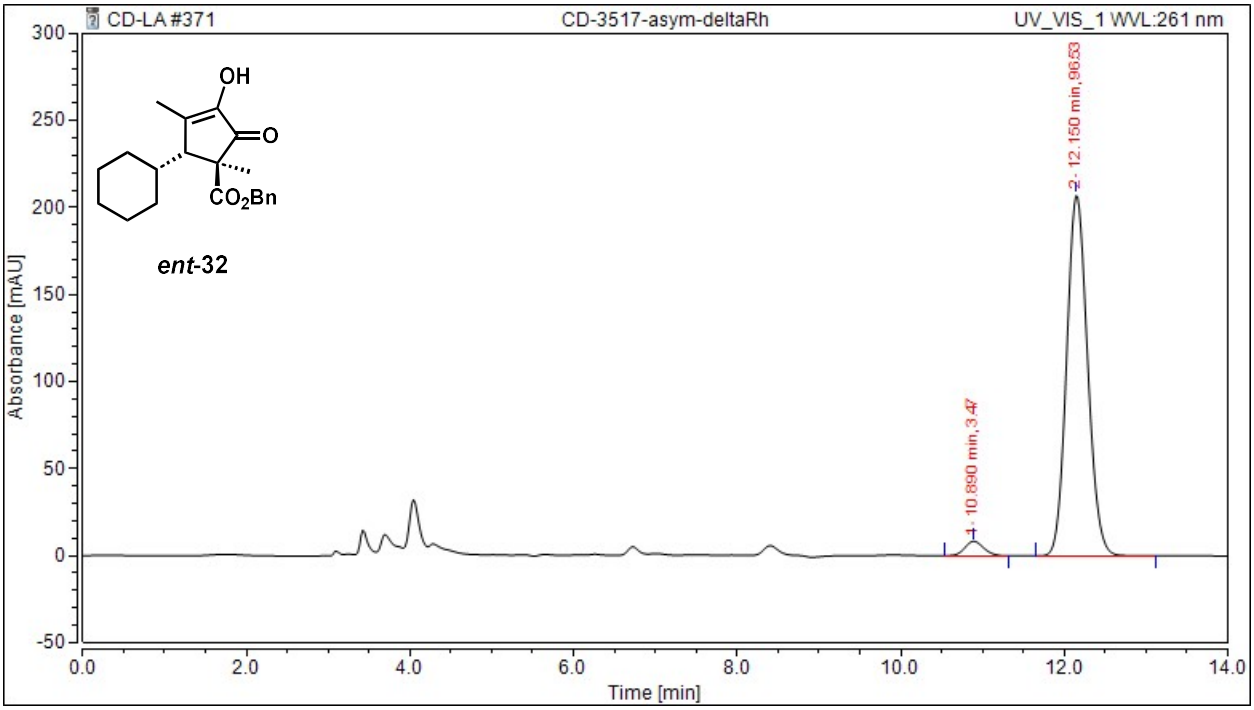

CD-LA #393
CD-3586-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 8.482 min, 4964
2 - 9.852 min, 5036
Absorbance [mAU]
Time [min]

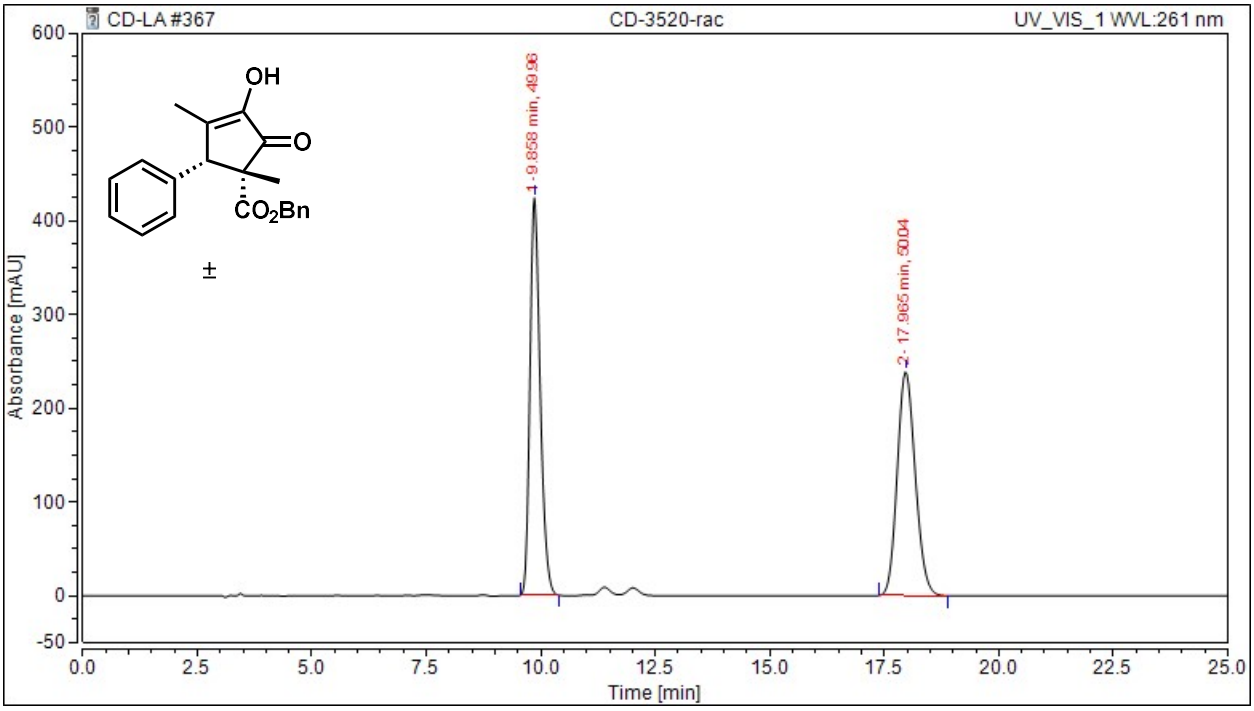

CD-LA #394
CD-3586-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
31
1 - 8.472 min, 8.17
2 - 9.820 min, 9183
Absorbance [mAU]
Time [min]

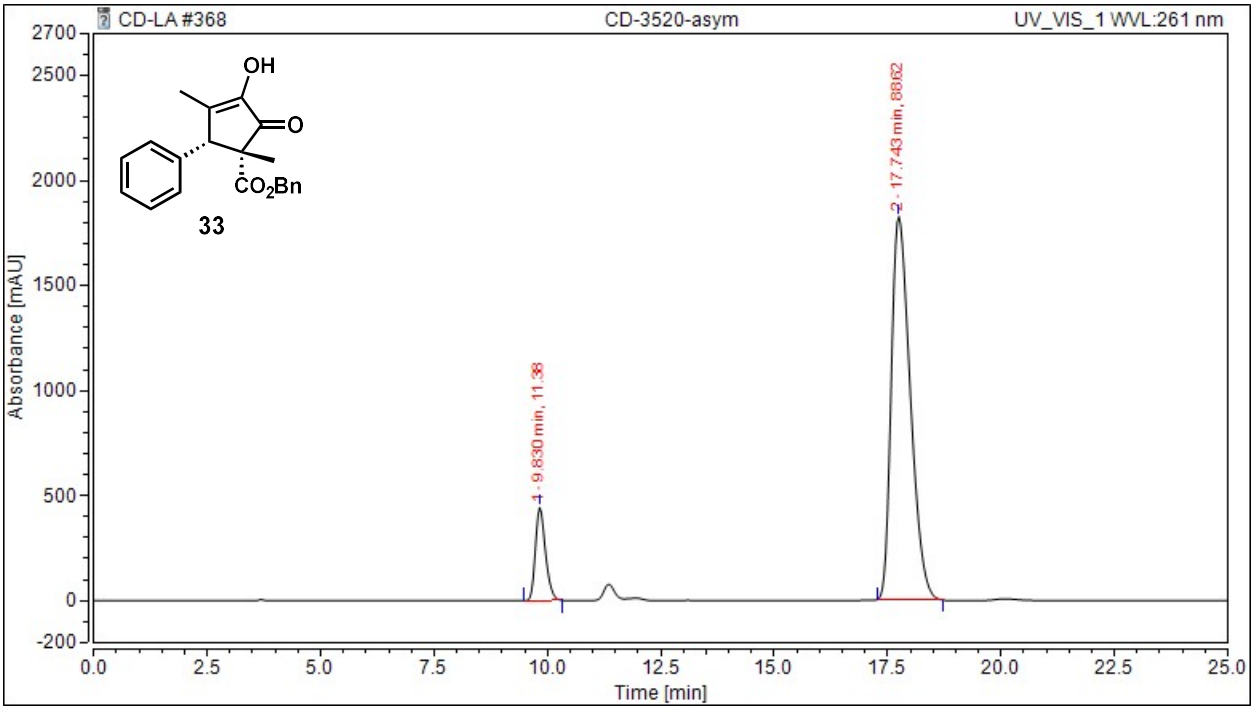

CD-LA #370
CD-3517-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 10.882 min, 60.63
2 - 12.150 min, 39.37
Absorbance [mAU]
Time [min]

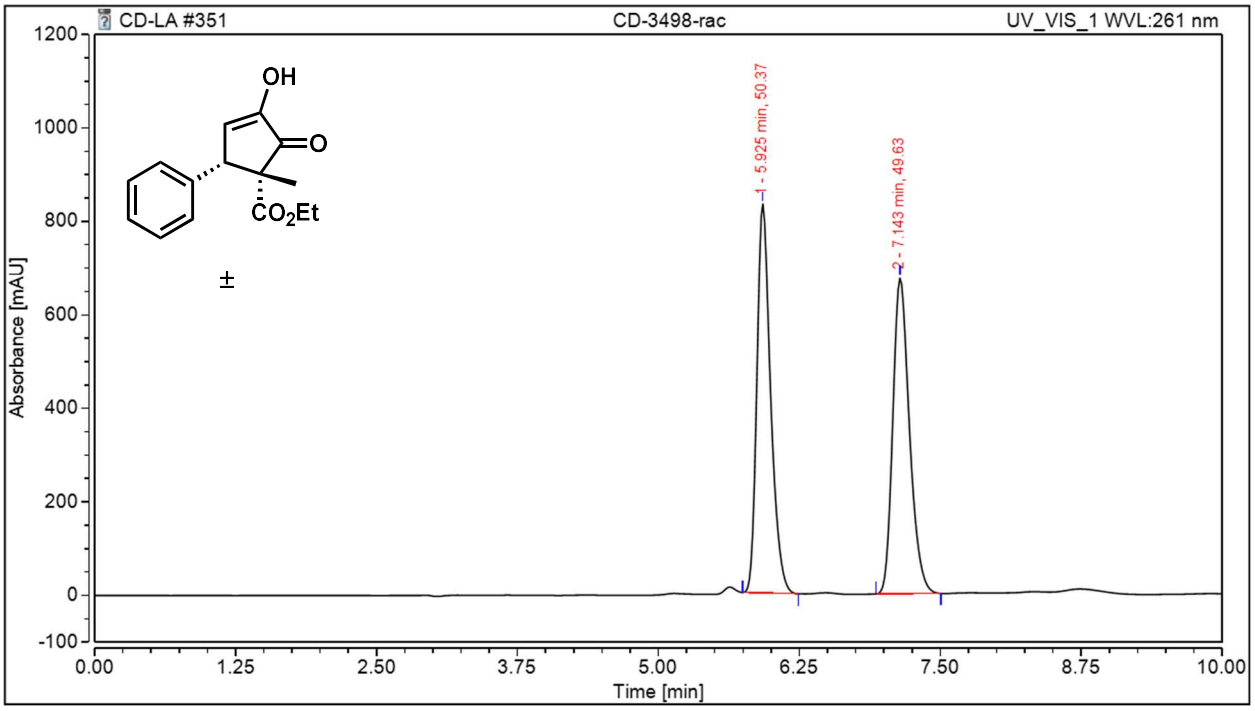

CD-LA #369
CD-3517-asym-scaleup
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
32
1 - 10.997 min, 96.58
2 - 12.303 min, 3.42
Absorbance [mAU]
Time [min]

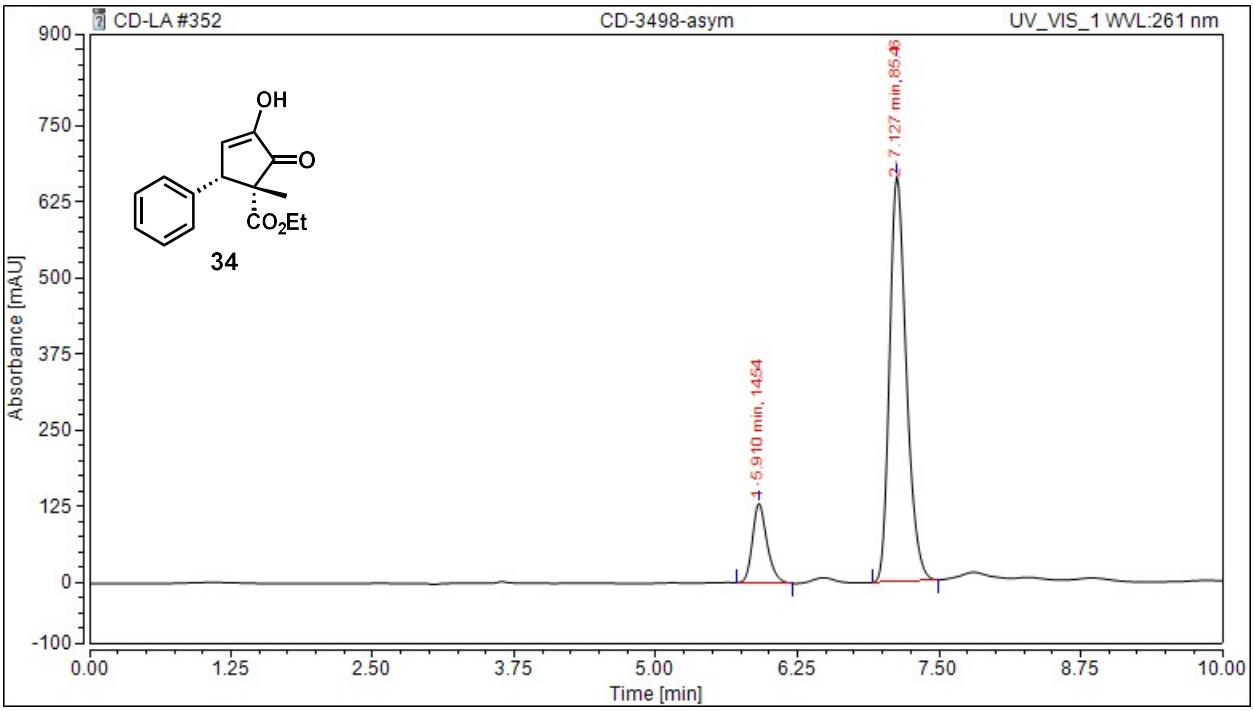

CD-LA #370
CD-3517-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 10.882 min, 60.63
2 - 12.150 min, 39.37
Absorbance [mAU]
Time [min]

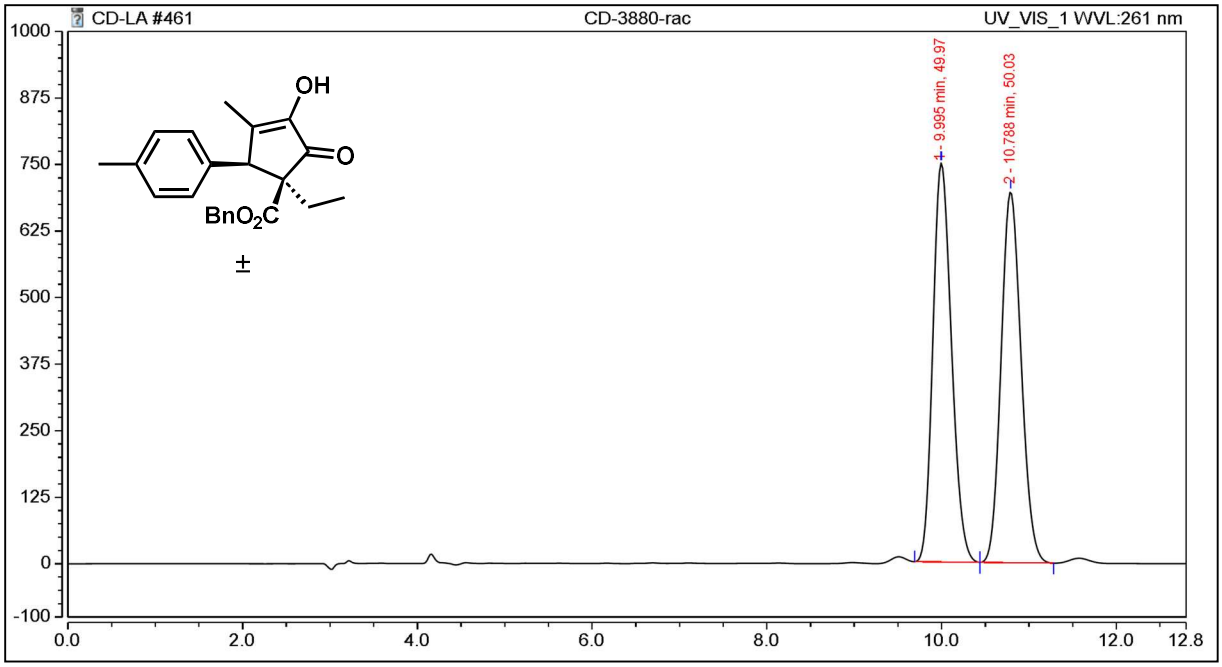

CD-LA #371
CD-3517-asym-deltaRh
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
ent-32
1 - 10.890 min, 3.47
2 - 12.150 min, 96.53
Absorbance [mAU]
Time [min]

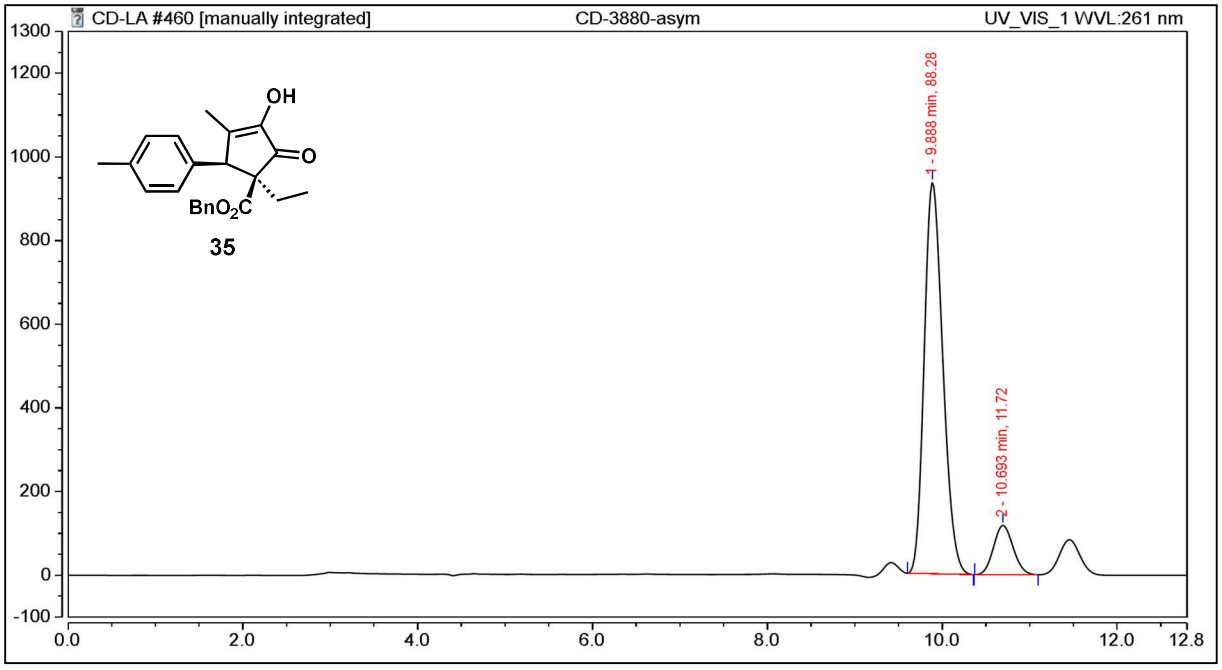

CD-LA #367
CD-3520-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
±
1 - 9.858 min, 49.96
2 - 17.965 min, 50.04
Absorbance [mAU]
Time [min]

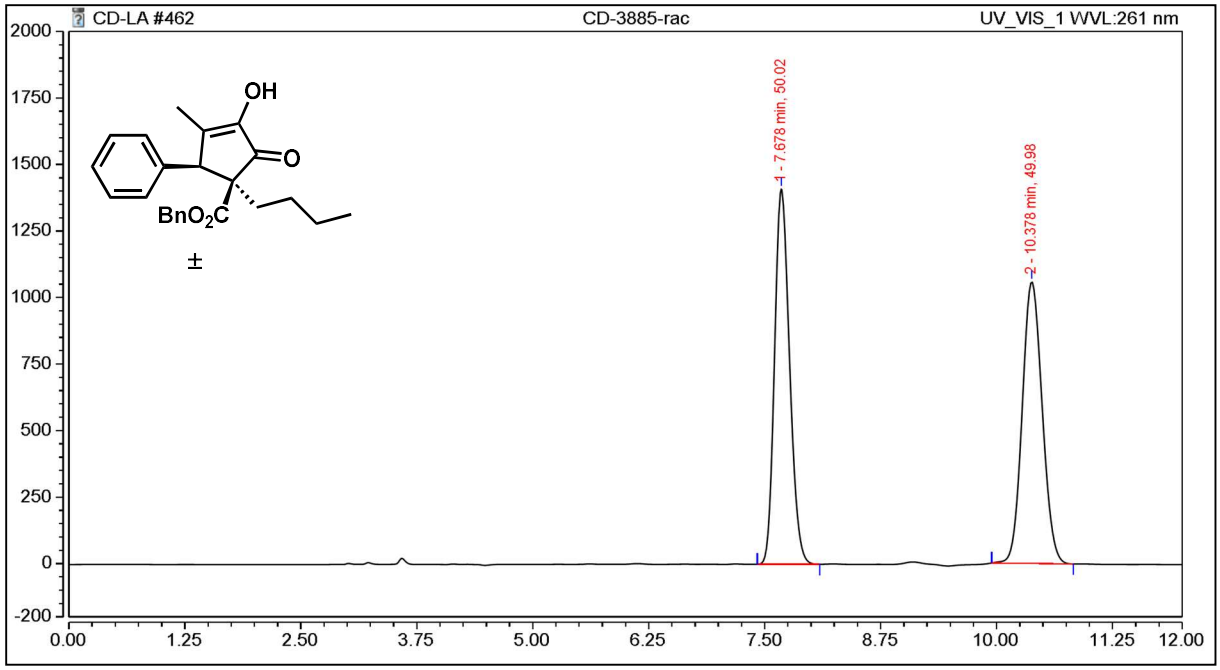

CD-LA #368
CD-3520-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Bn
33
1 - 9.830 min, 11.38
2 - 17.743 min, 88.62
Absorbance [mAU]
Time [min]

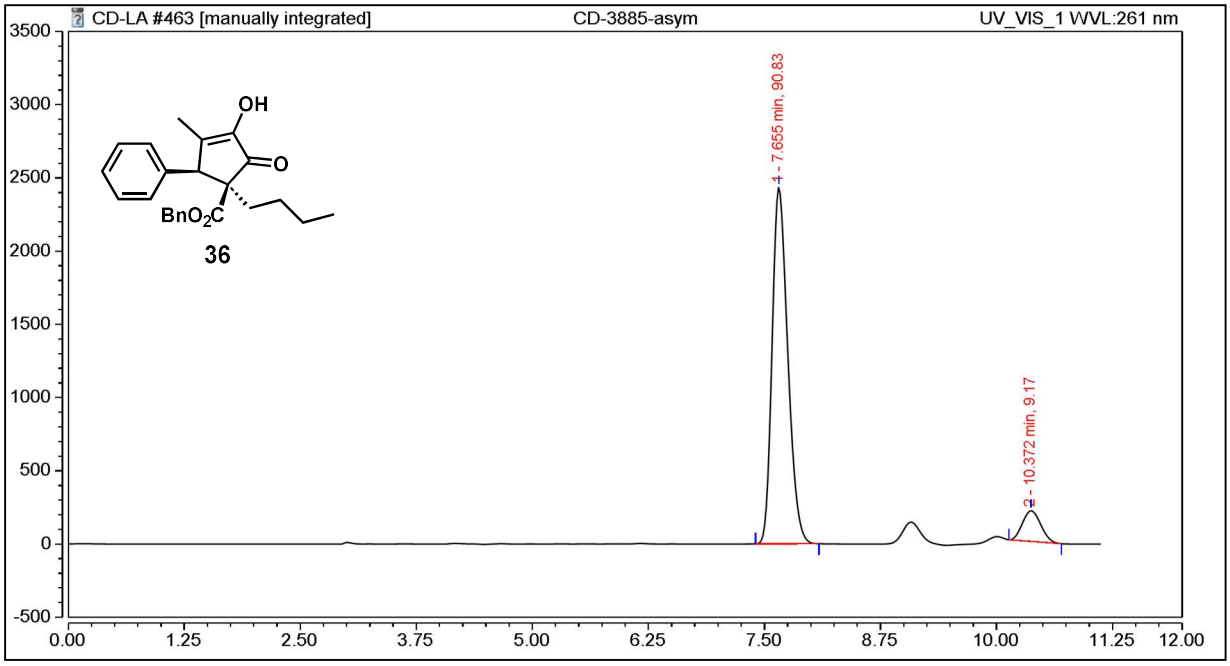

CD-LA #351
CD-3498-rac
UV_VIS_1 WVL:261 nm
OH
O
CO2Et
±
1 - 5.925 min, 50.37
2 - 7.143 min, 49.63
Absorbance [mAU]
Time [min]


CD-LA #352
CD-3498-asym
UV_VIS_1 WVL:261 nm
OH
O
CO2Et
34
1 - 5.910 min, 1454
2 - 7.127 min, 8546
Absorbance [mAU]
Time [min]

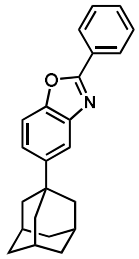

CD-LA #461
CD-3880-rac
UV_VIS_1 WVL:261 nm
1 - 9.995 min, 49.97
2 - 10.788 min, 50.03
OH
O
BnO2C
±
1000
875
750
625
500
375
250
125
0
-100
0.0
2.0
4.0
6.0
8.0
10.0
12.0
12.8


CD-LA #460 [manually integrated]
CD-3880-asym
UV_VIS_1 WVL:261 nm
1 - 9.888 min, 88.28
2 - 10.693 min, 11.72
OH
O
BnO2C
35
1300
1200
1000
800
600
400
200
0
-100
0.0
2.0
4.0
6.0
8.0
10.0
12.0
12.8


CD-LA #462
CD-3885-rac
UV_VIS_1 WVL:261 nm
OH
O
BnO2C
±
1 - 7.678 min, 50.02
2 - 10.378 min, 49.98
2000
1750
1500
1250
1000
750
500
250
0
-200
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
11.25
12.00

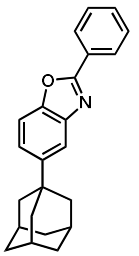

CD-LA #463 [manually integrated]
CD-3885-asym
UV_VIS_1 WVL:261 nm
OH
O
BnO2C
36
1 - 7.655 min, 90.83
2 - 10.372 min, 9.17
3500
3000
2500
2000
1500
1000
500
0
-500
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
11.25
12.00

15. NMR Spectra



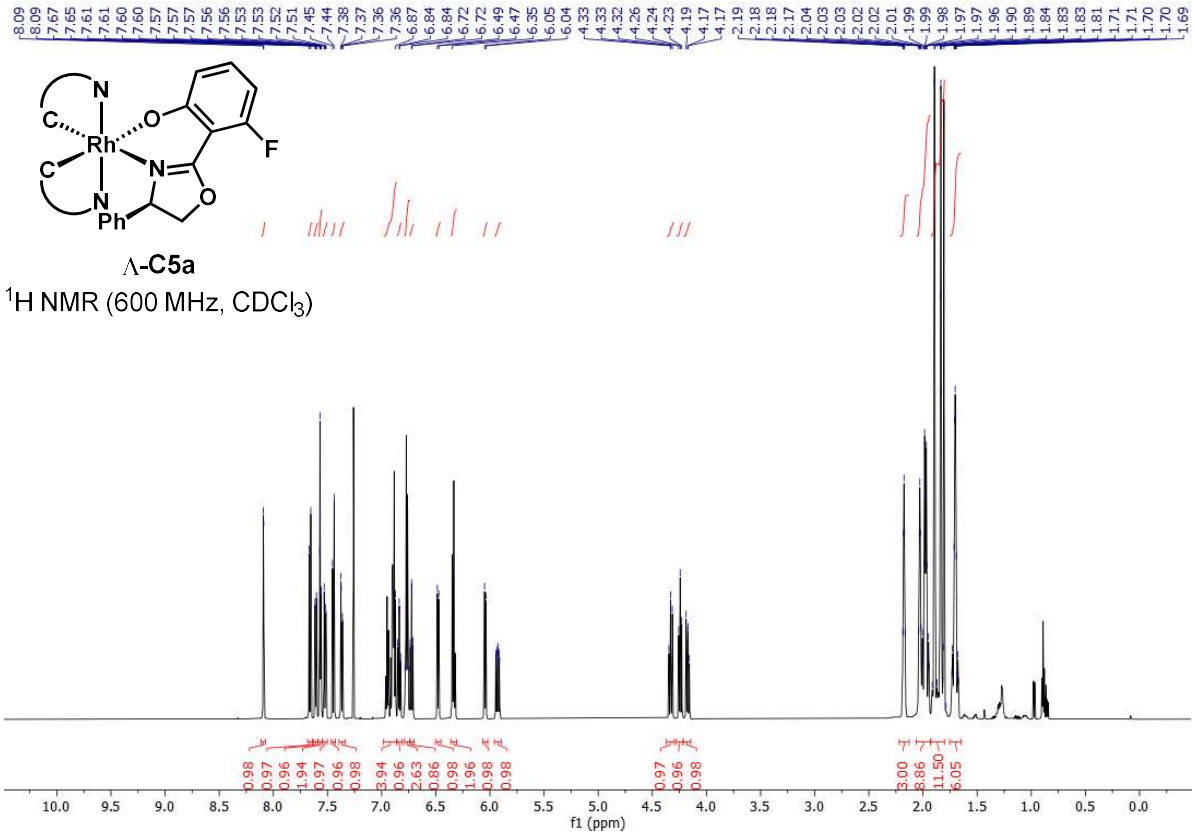
C2a

^{1}H NMR (300 MHz, $CDCl_3$)



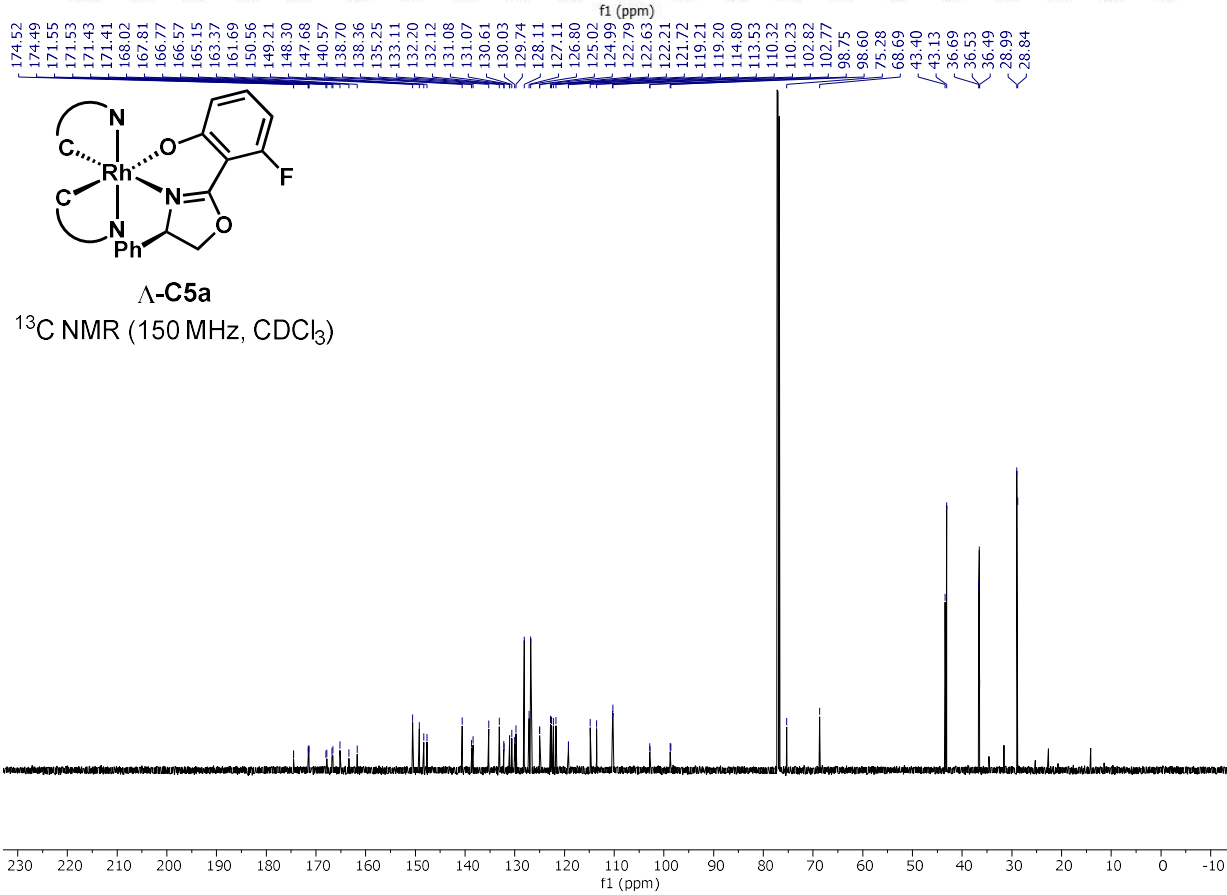
C2a

^{13}C NMR (75 MHz, $CDCl_3$)



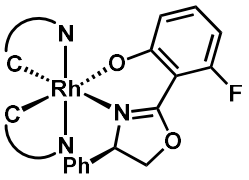
Λ-**C5a**

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



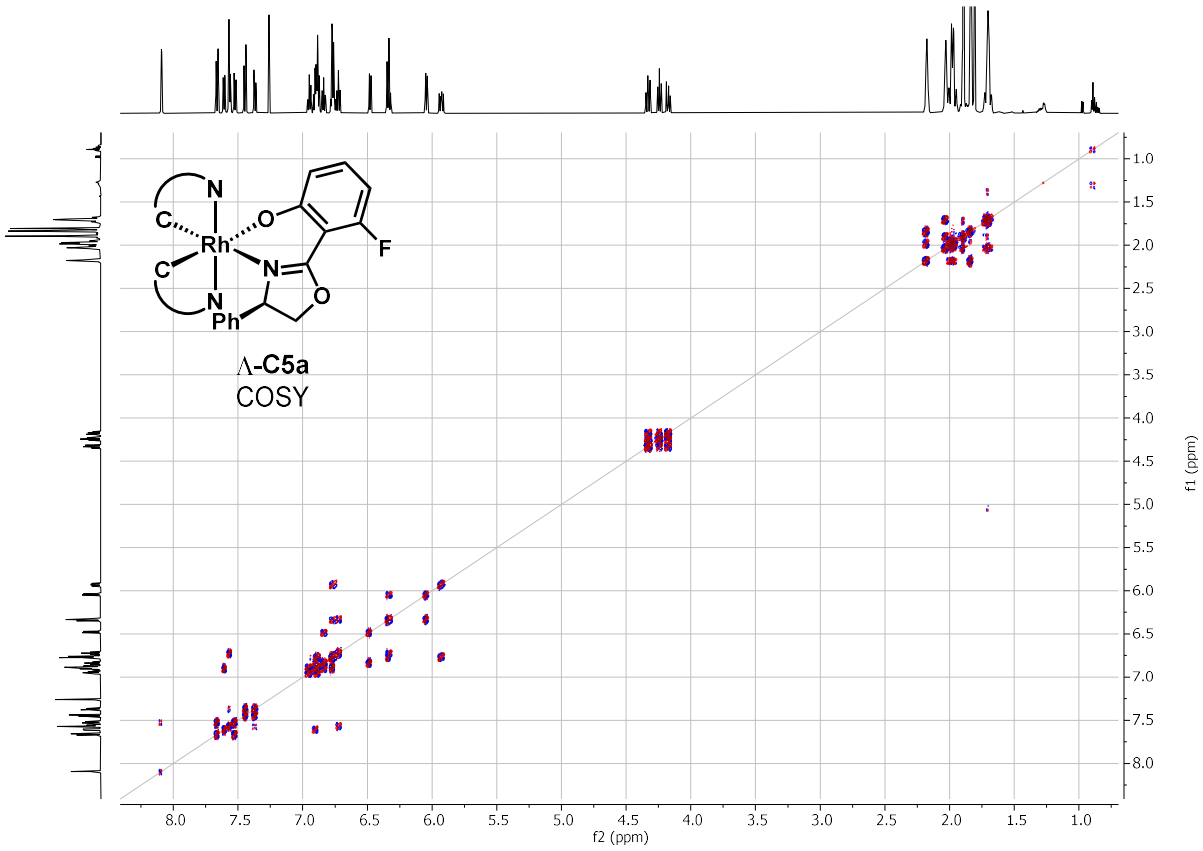
Λ-**C5a**

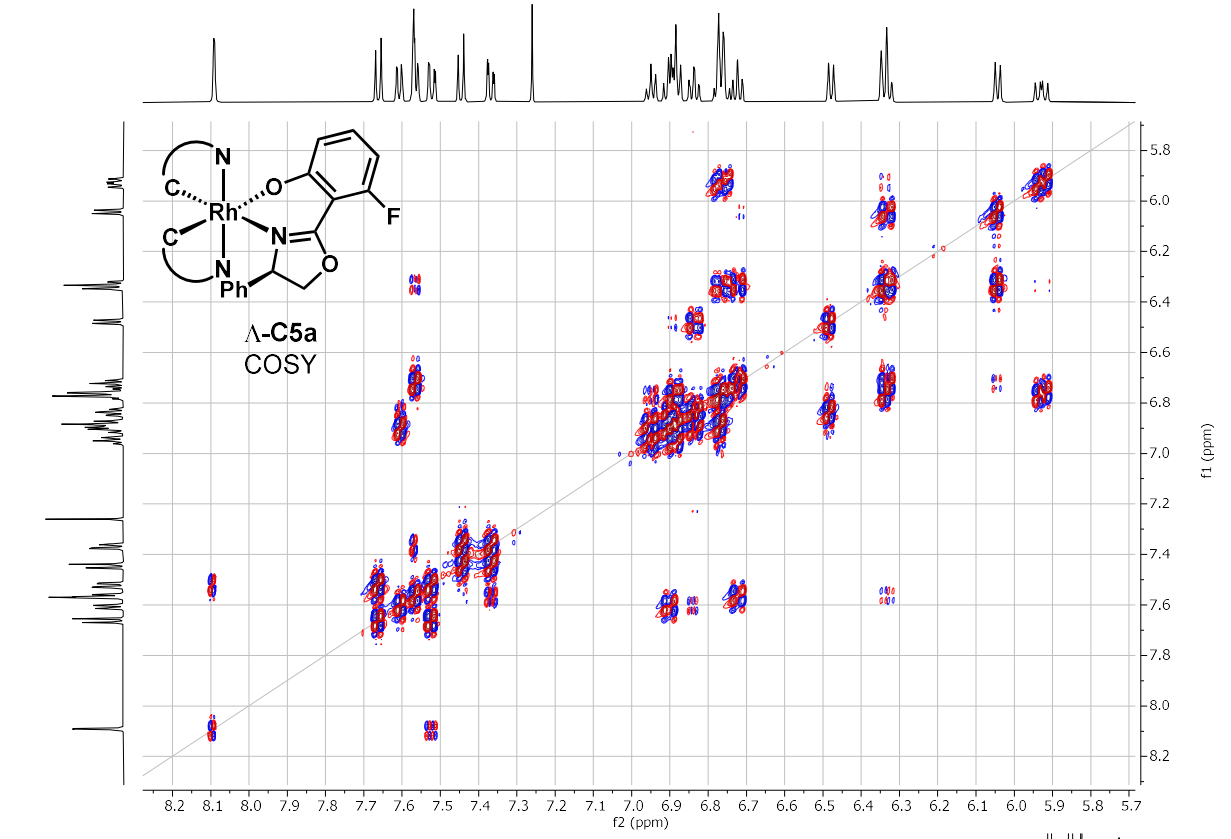
^{13}C NMR (150 MHz, $CDCl_3$)

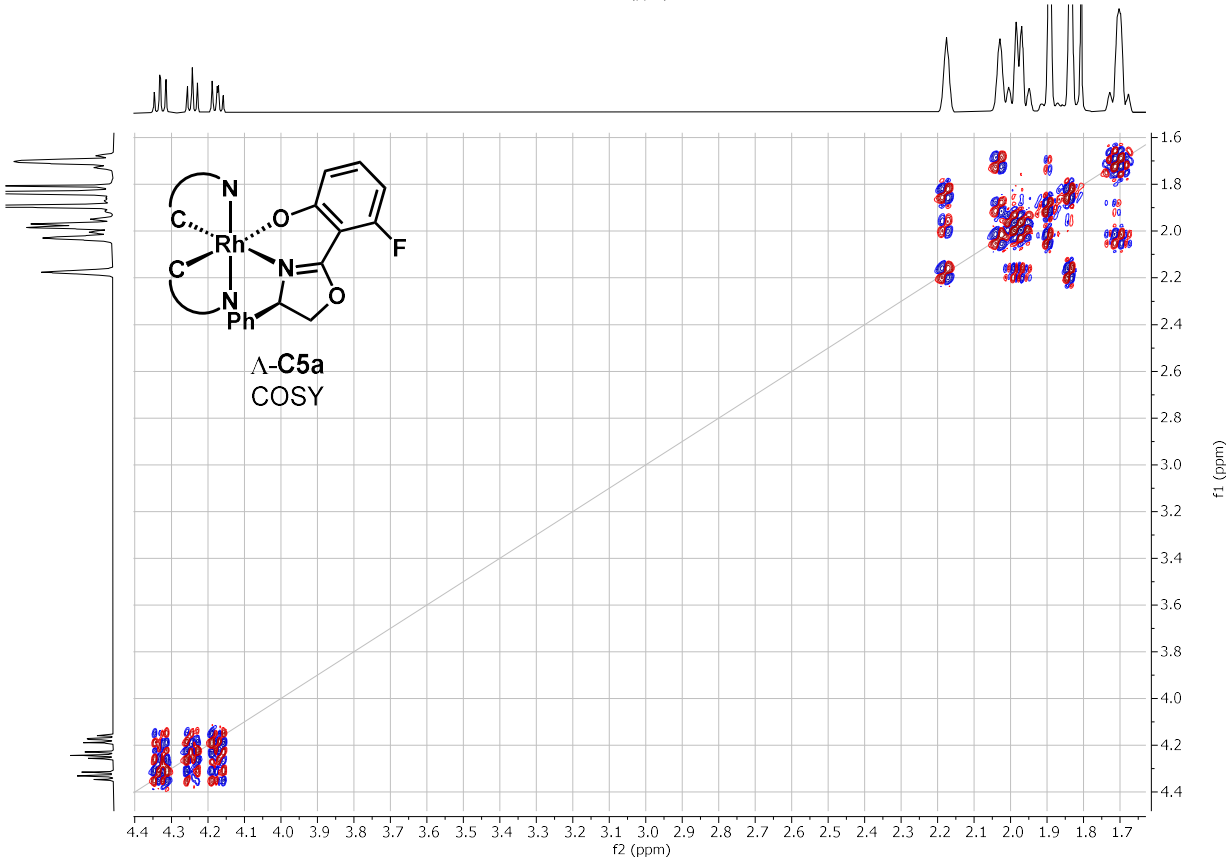


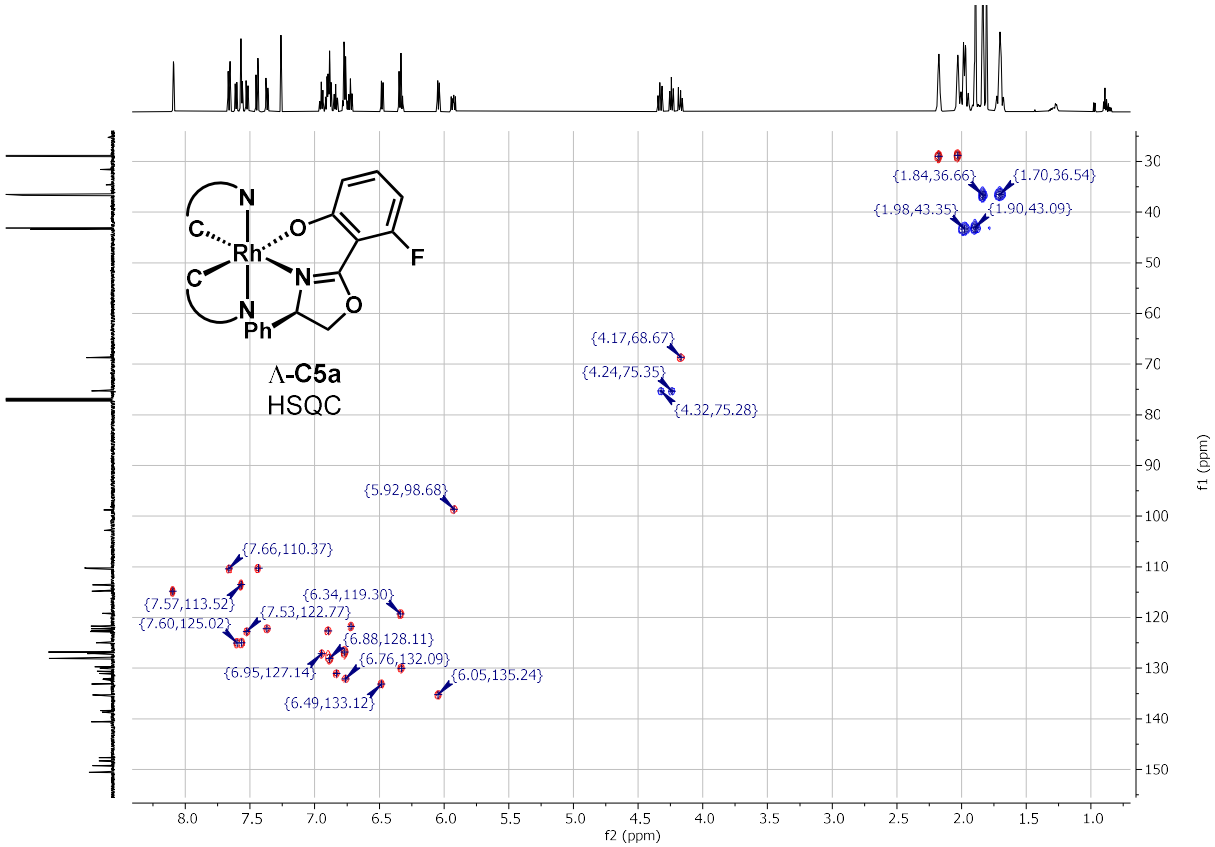
Λ-**C5a**

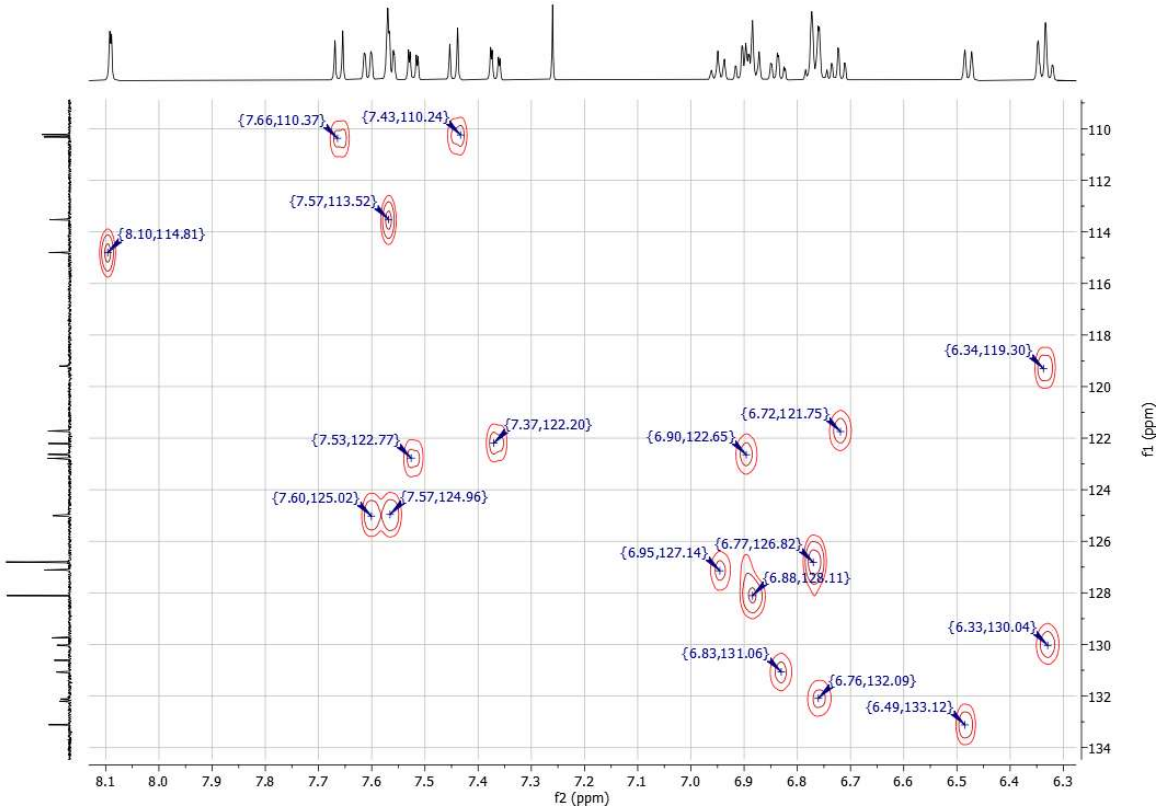
^{19}F NMR (564 MHz, $CDCl_3$)

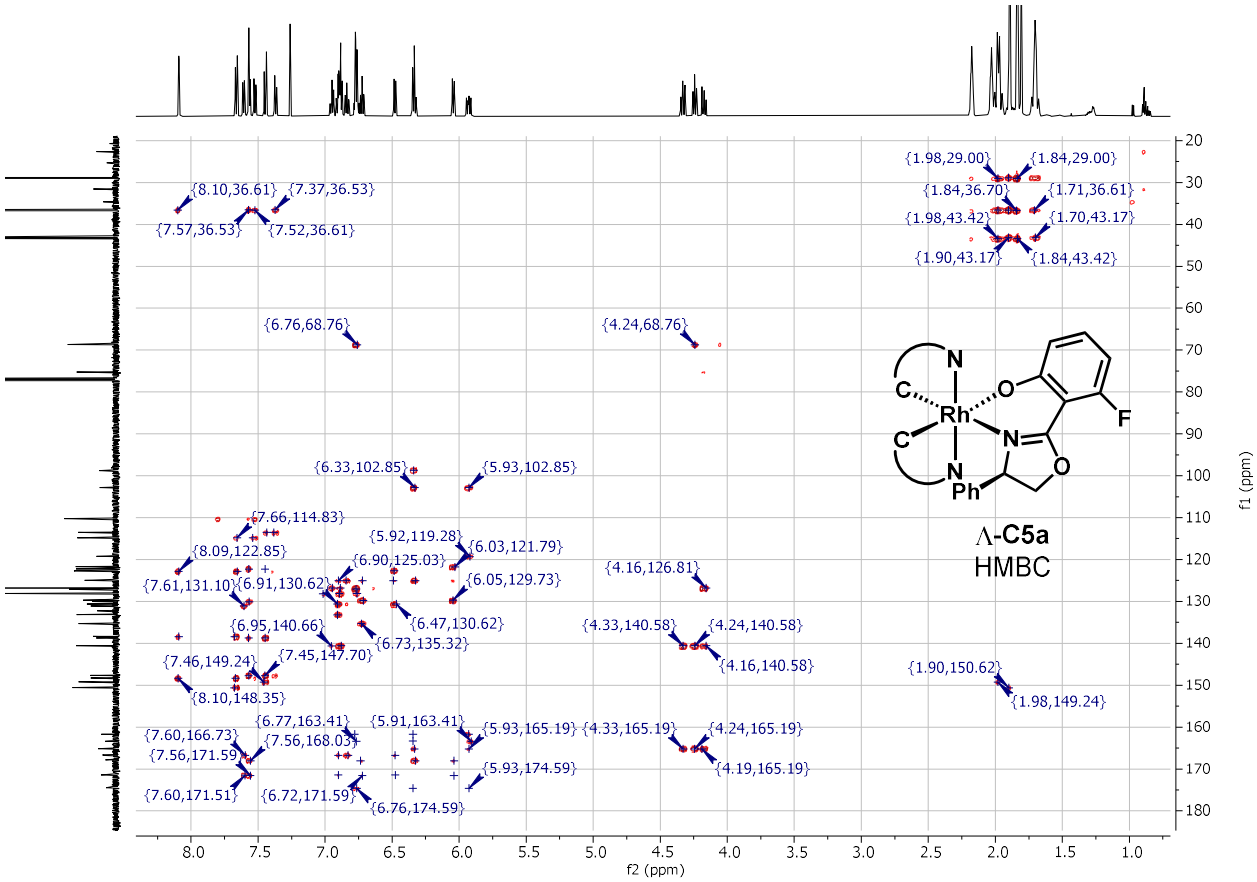


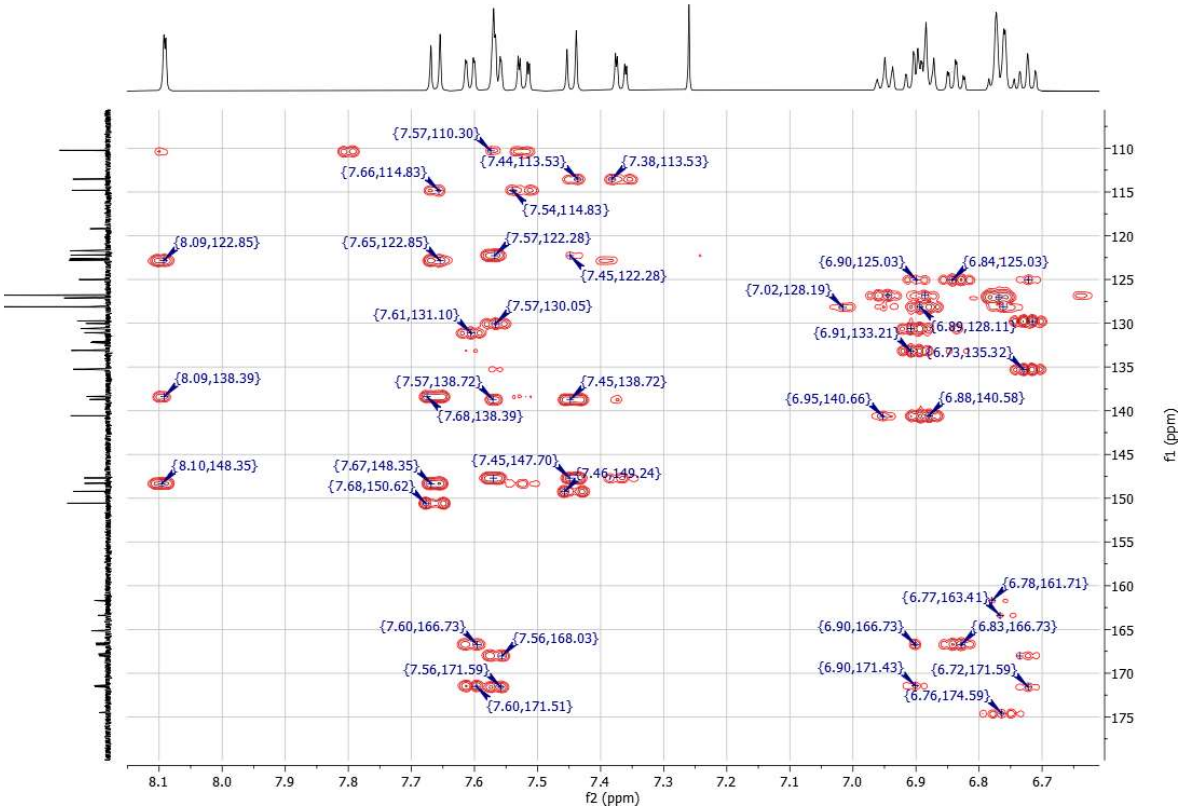

Λ-C5a
COSY
f2 (ppm)
f1 (ppm)

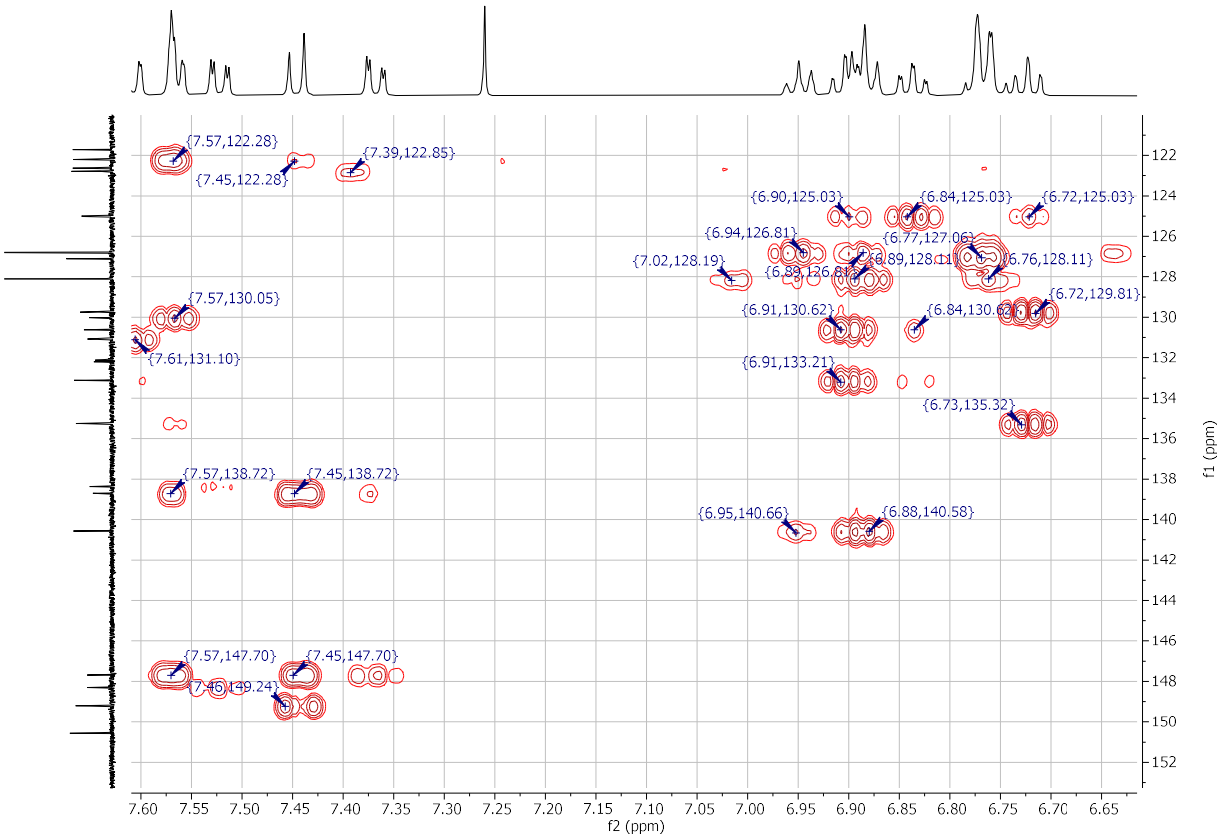

Λ-C5a
COSY
f2 (ppm)
f1 (ppm)

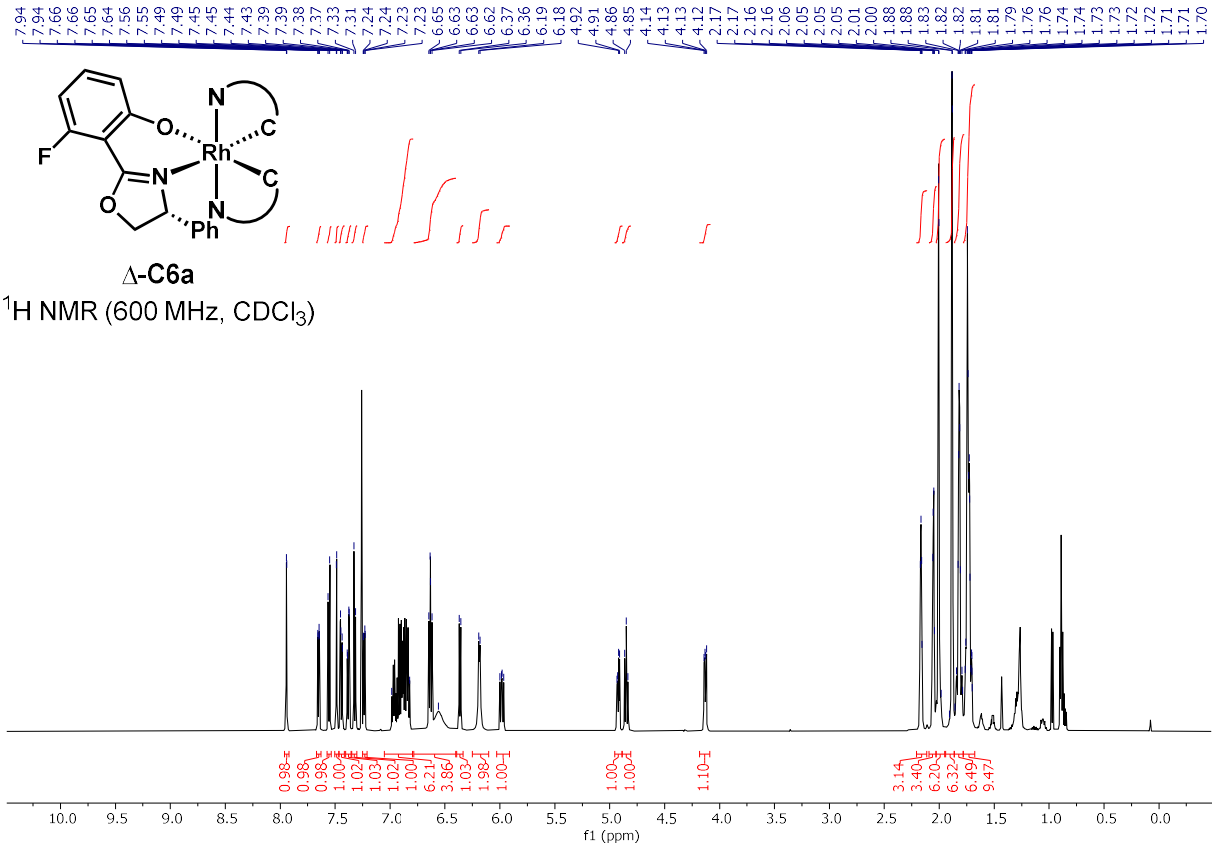

Λ-C5a
HSQC
{1.84,36.66}
{1.70,36.54}
{1.98,43.35}
{1.90,43.09}
{4.17,68.67}
{4.24,75.35}
{4.32,75.28}
{5.92,98.68}
{7.66,110.37}
{7.57,113.52}
{6.34,119.30}
{7.60,125.02}
{7.53,122.77}
{6.88,128.11}
{6.95,127.14}
{6.76,132.09}
{6.05,135.24}
{6.49,133.12}
f2 (ppm)
f1 (ppm)


{7.66,110.37}
{7.43,110.24}
{7.57,113.52}
{8.10,114.81}
{6.34,119.30}
{6.72,121.75}
{7.37,122.20}
{6.90,122.65}
{7.53,122.77}
{7.60,125.02}
{7.57,124.96}
{6.95,127.14}
{6.77,126.82}
{6.88,128.11}
{6.33,130.04}
{6.83,131.06}
{6.76,132.09}
{6.49,133.12}
f2 (ppm)
f1 (ppm)


{8.10,36.61} {7.37,36.53}
{7.57,36.53} {7.52,36.61}
{1.98,29.00} {1.84,29.00}
{1.84,36.70} {1.71,36.61}
{1.98,43.42} {1.70,43.17}
{1.90,43.17} {1.84,43.42}
{6.76,68.76}
{4.24,68.76}
{6.33,102.85} {5.93,102.85}
{7.66,114.83}
{8.09,122.85}
{5.92,119.28} {6.03,121.79}
{6.90,125.03}
{7.61,131.10} {6.91,130.62} {6.05,129.73}
{4.16,126.81}
{6.95,140.66} {6.47,130.62}
{6.73,135.32}
{4.33,140.58} {4.24,140.58}
{7.46,149.24} {7.45,147.70}
{4.16,140.58}
{8.10,148.35}
{1.90,150.62}
{1.98,149.24}
{6.77,163.41} {5.91,163.41} {5.93,165.19}
{4.33,165.19} {4.24,165.19}
{7.60,166.73} {7.56,168.03}
{7.56,171.59}
{4.19,165.19}
{5.93,174.59}
{7.60,171.51} {6.72,171.59}
{6.76,174.59}
N
C
Rh
O
F
C
N
N
O
Ph
Λ-C5a
HMBC
f2 (ppm)
f1 (ppm)

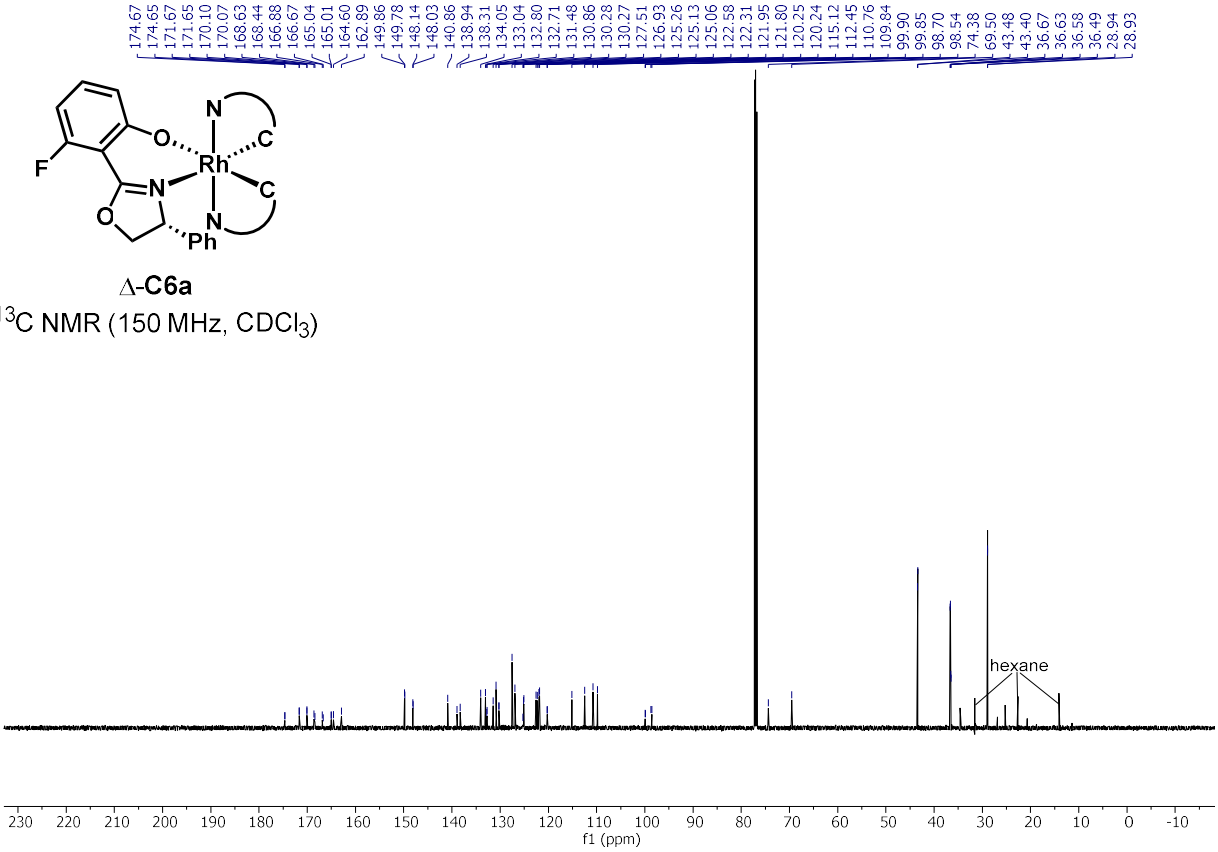

{7.57,110.30}
{7.44,113.53} {7.38,113.53}
{7.66,114.83}
{7.54,114.83}
{8.09,122.85}
{7.65,122.85} {7.57,122.28}
{7.45,122.28}
{6.90,125.03} {6.84,125.03}
{7.02,128.19}
{7.61,131.10} {7.57,130.05}
{6.91,133.21} {6.89,128.11}
{6.73,135.32}
{8.09,138.39}
{7.57,138.72} {7.45,138.72}
{6.95,140.66} {6.88,140.58}
{7.68,138.39}
{8.10,148.35}
{7.67,148.35} {7.45,147.70} {7.46,149.24}
{7.68,150.62}
{6.78,161.71}
{6.77,163.41}
{7.60,166.73} {7.56,168.03}
{6.90,166.73} {6.83,166.73}
{7.56,171.59}
{6.90,171.43} {6.72,171.59}
{7.60,171.51}
{6.76,174.59}
f2 (ppm)
f1 (ppm)


{7.57,122.28}
{7.45,122.28}
{7.39,122.85}
{6.90,125.03}
{6.84,125.03}
{6.72,125.03}
{6.94,126.81}
{6.77,127.06}
{7.02,128.19}
{6.89,128.11}
{6.76,128.11}
{6.89,136.81}
{7.57,130.05}
{6.72,129.81}
{6.91,130.62}
{6.84,130.62}
{7.61,131.10}
{6.91,133.21}
{6.73,135.32}
{7.57,138.72}
{7.45,138.72}
{6.95,140.66}
{6.88,140.58}
{7.57,147.70}
{7.45,147.70}
{7.46,149.24}
f2 (ppm)
f1 (ppm)



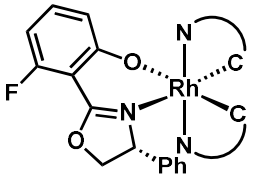
Δ-C6a

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



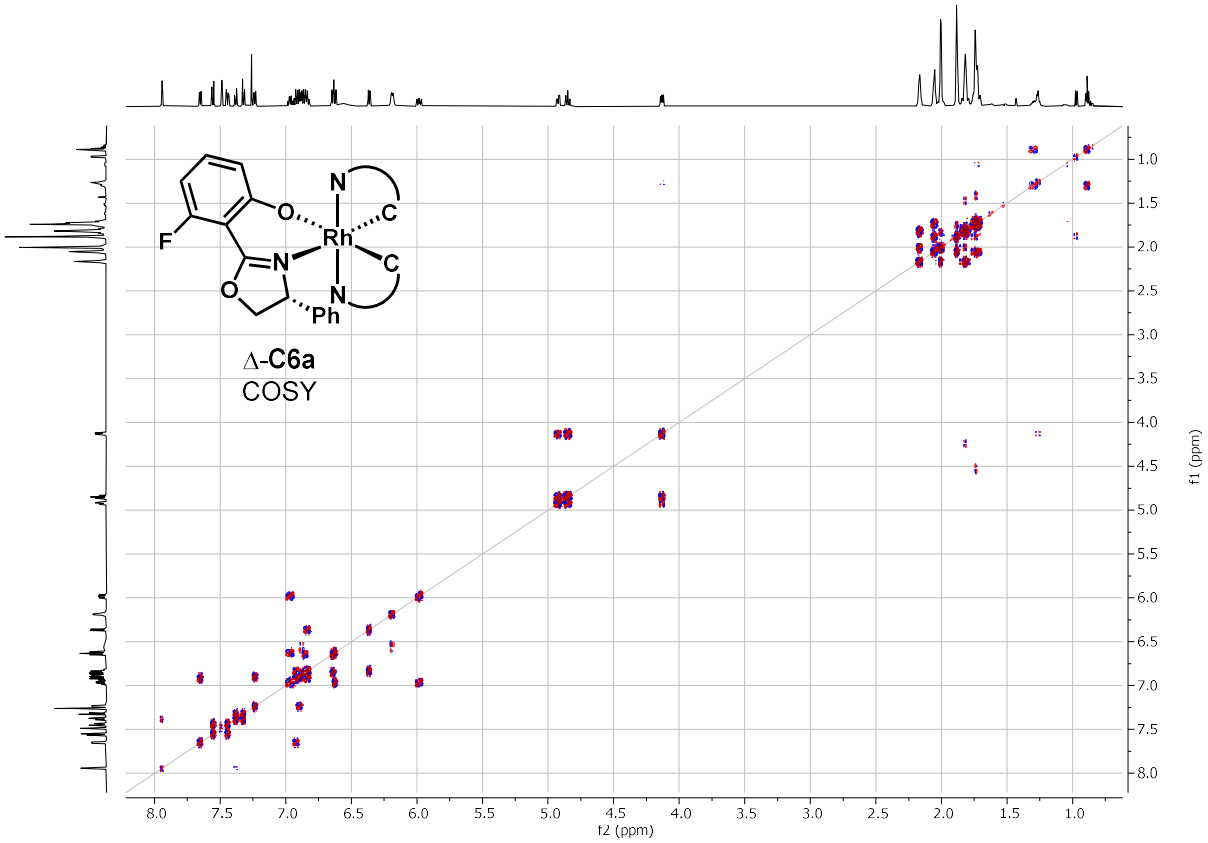
Δ-C6a

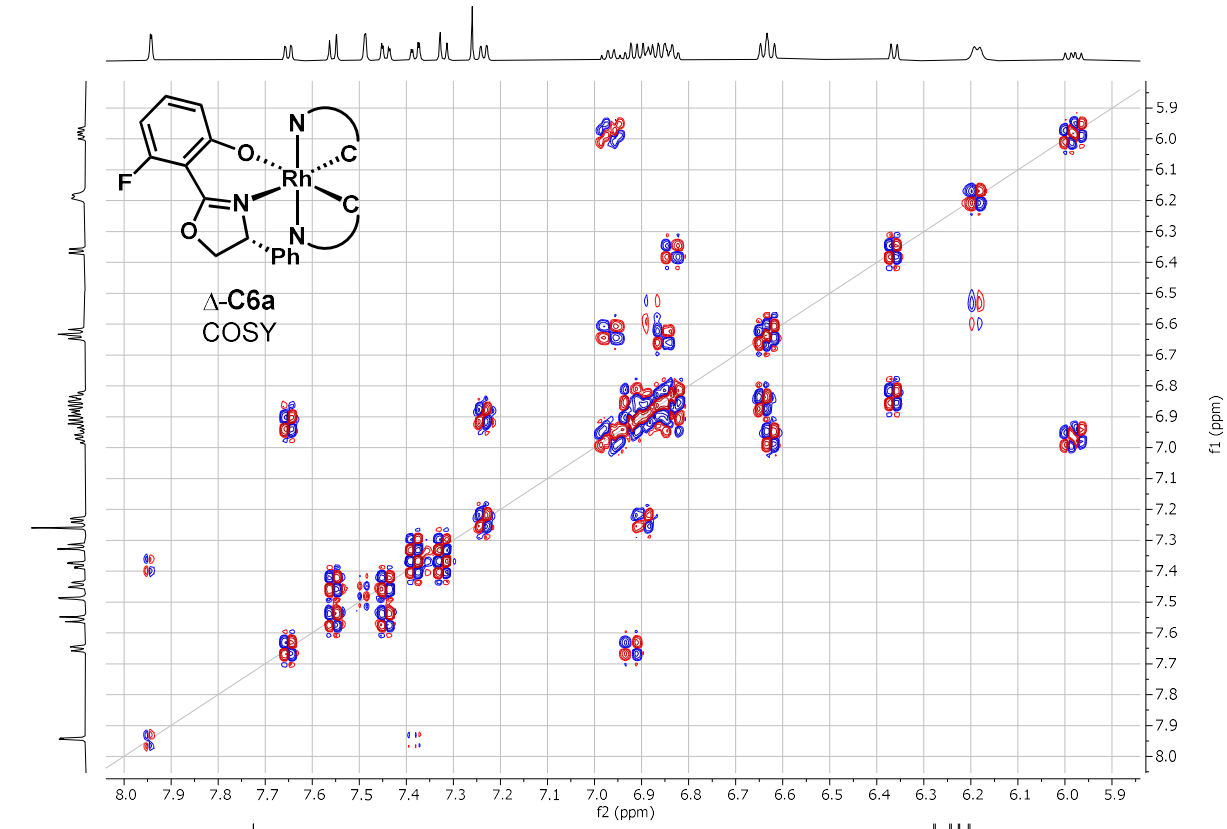
^{13}C NMR (150 MHz, $CDCl_3$)

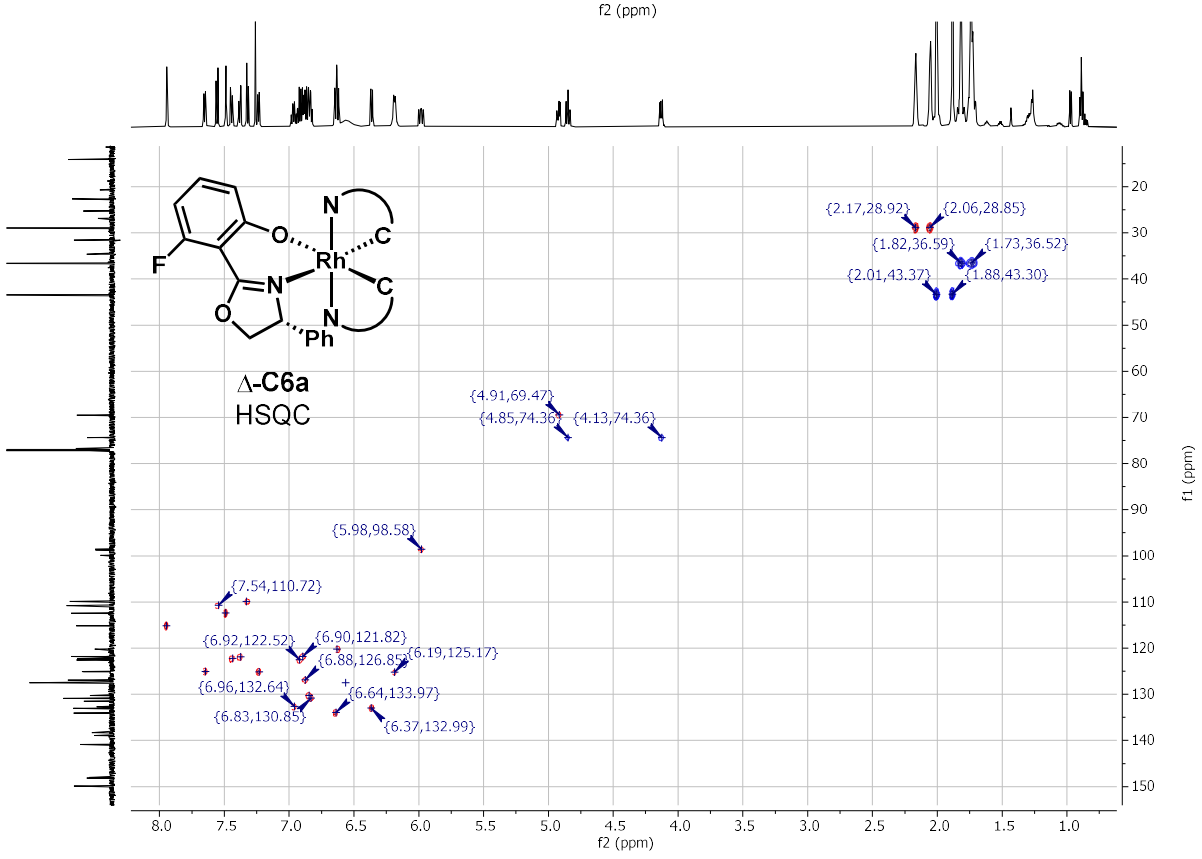


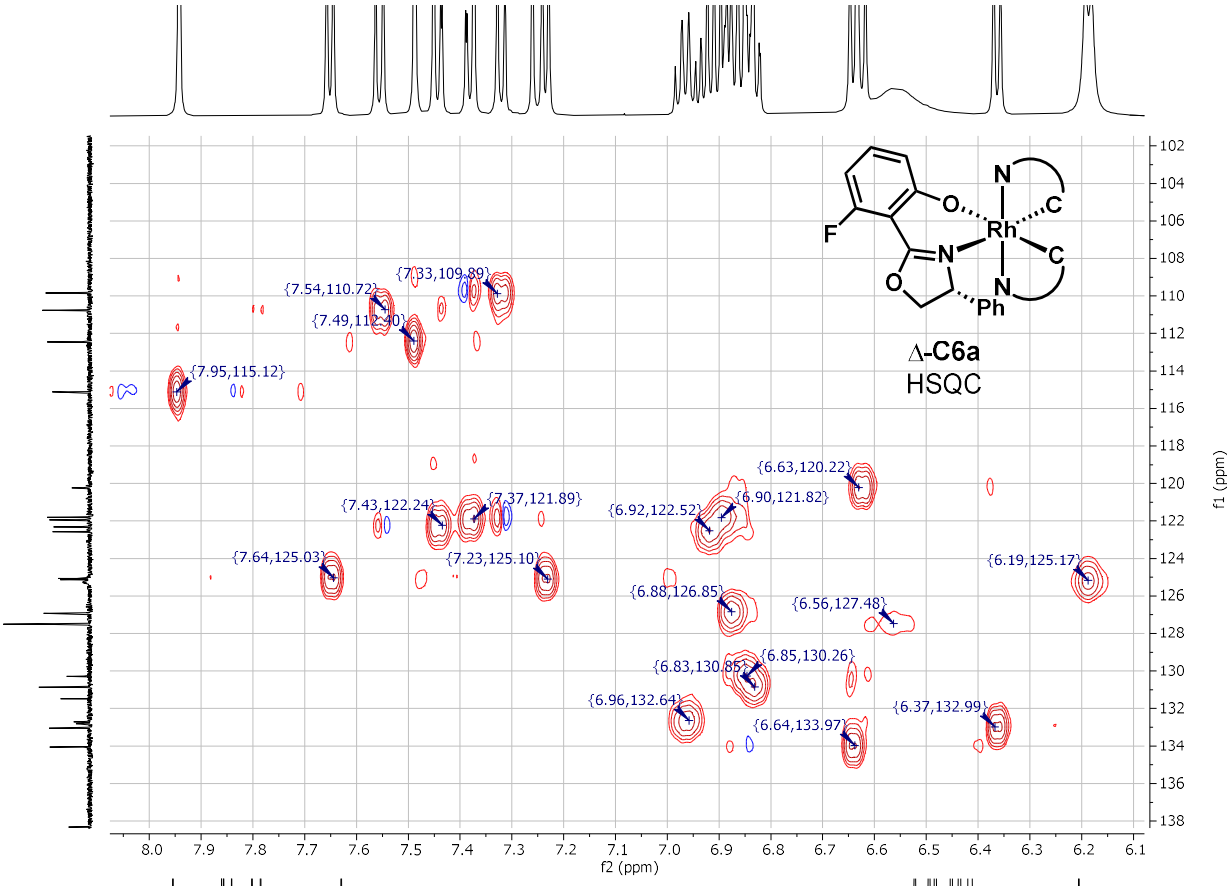
Δ-**C6a**

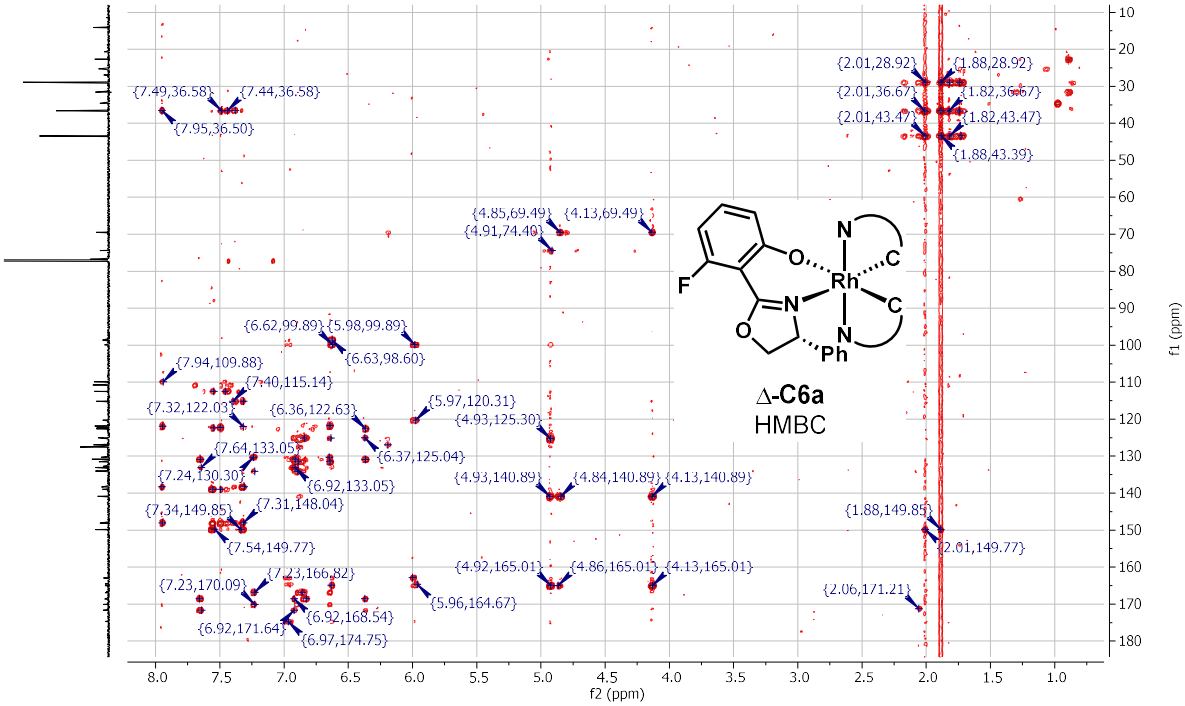
^{19}F NMR (564 MHz, $CDCl_3$)

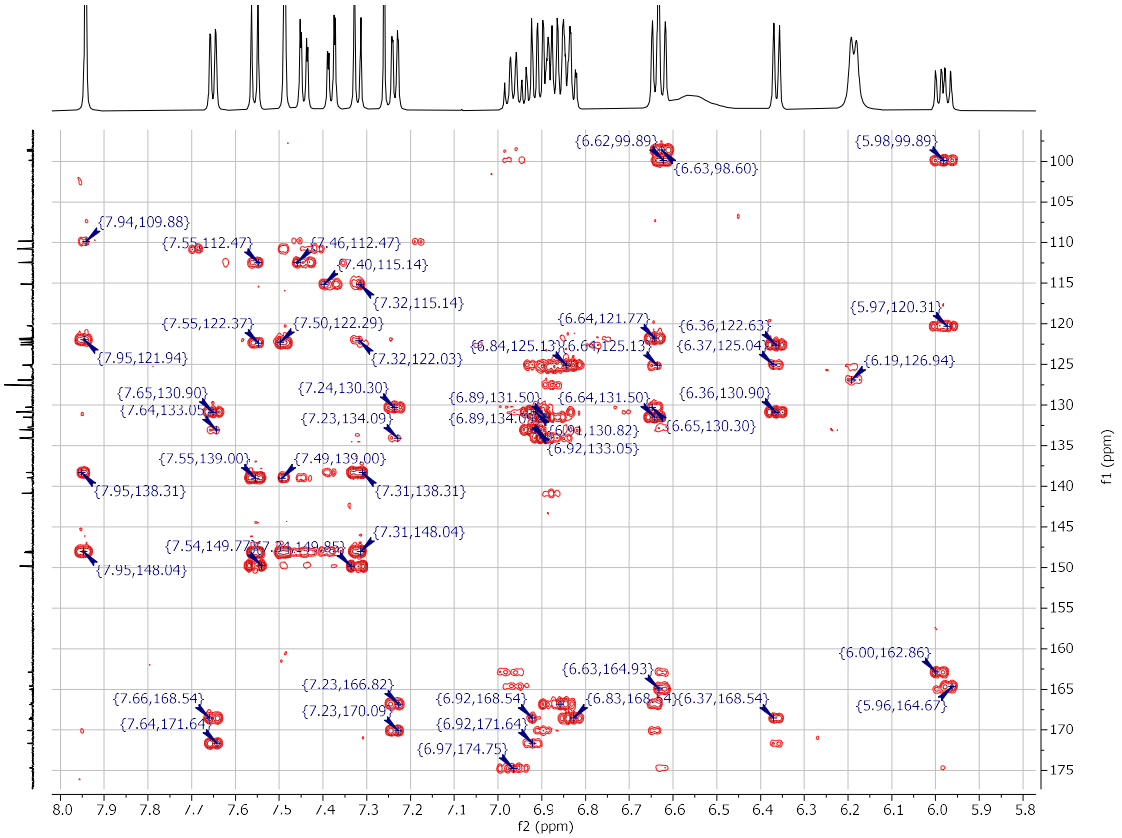


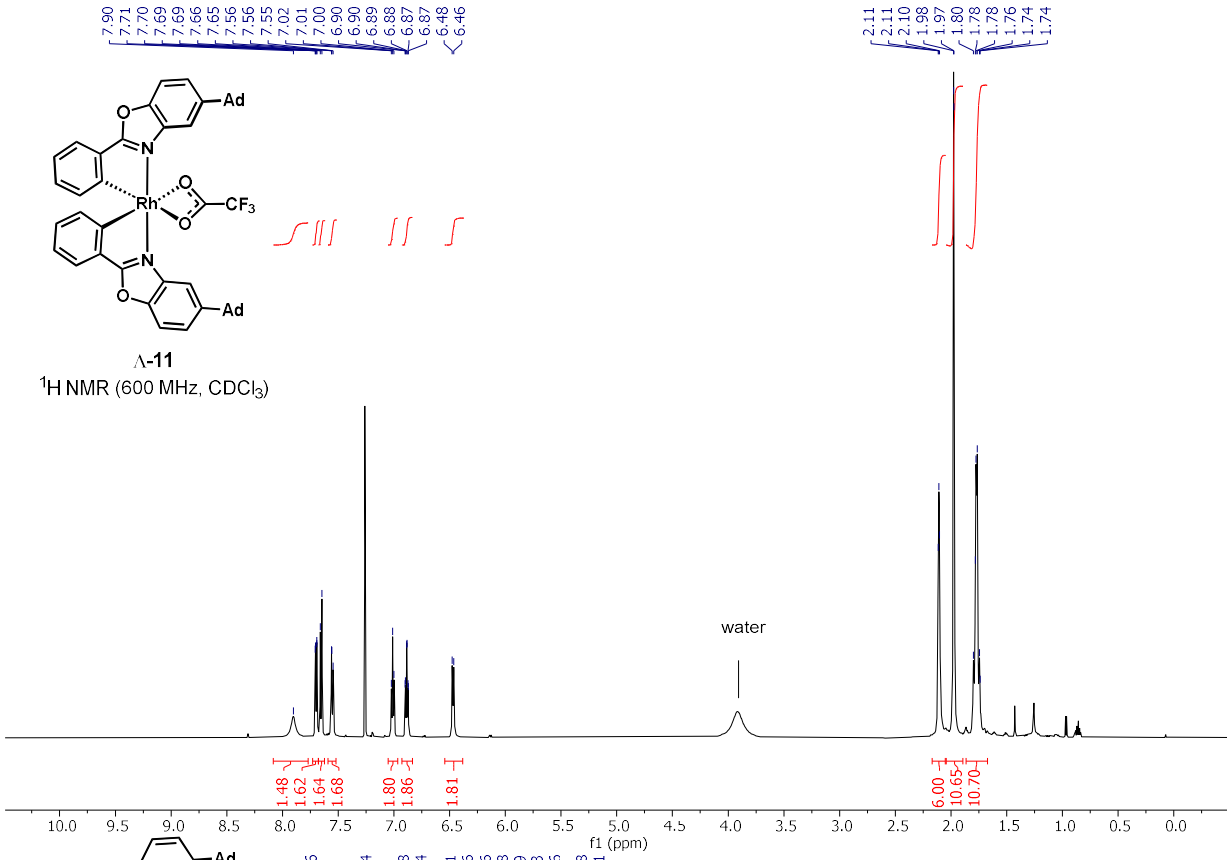

Δ-C6a
COSY
f2 (ppm)
f1 (ppm)


Δ-C6a
HSQC
{2.17,28.92}
{2.06,28.85}
{1.82,36.59}
{1.73,36.52}
{2.01,43.37}
{1.88,43.30}
{4.91,69.47}
{4.85,74.36}
{4.13,74.36}
{5.98,98.58}
{7.54,110.72}
{6.92,122.52}
{6.90,121.82}
{6.88,126.85}
{6.19,125.17}
{6.96,132.64}
{6.64,133.97}
{6.83,130.85}
{6.37,132.99}
f2 (ppm)
f1 (ppm)


Δ-C6a
HSQC
f2 (ppm)
f1 (ppm)

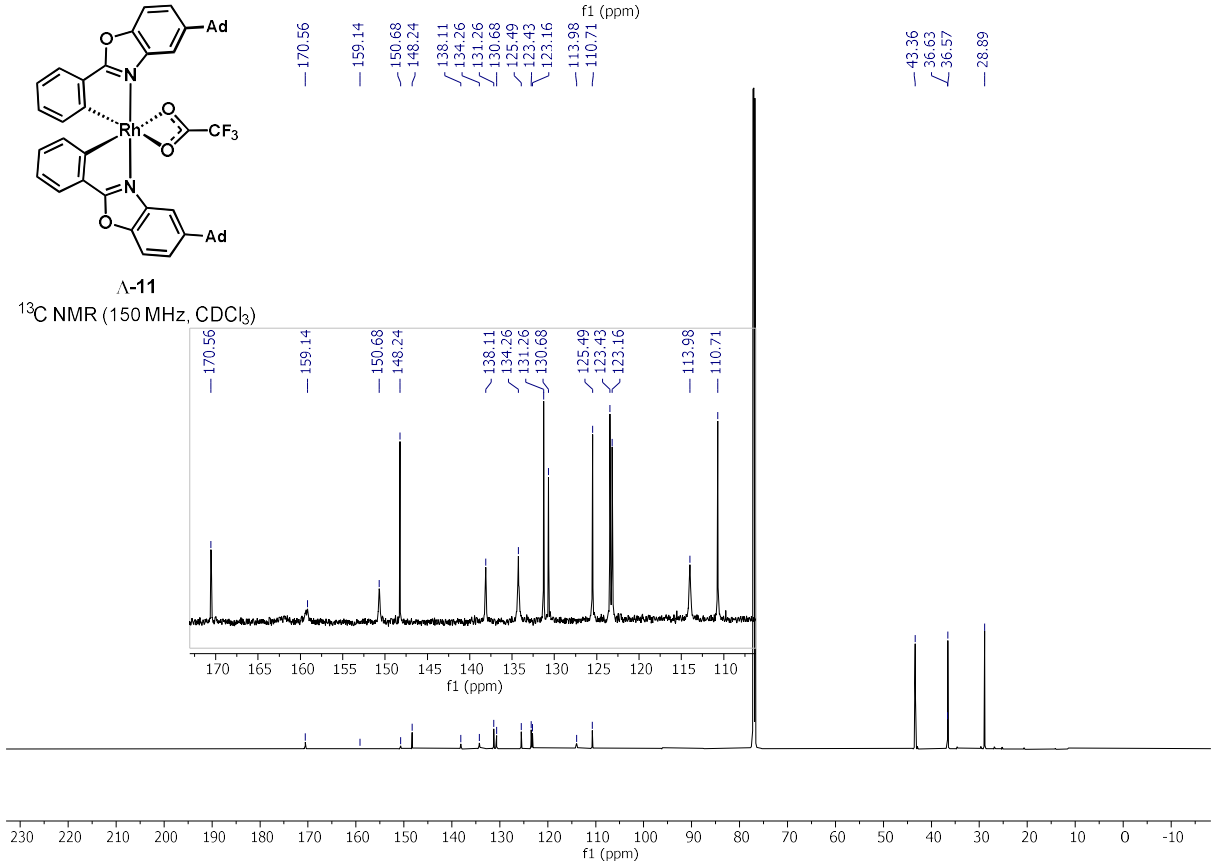

Δ-C6a
HMBC
f2 (ppm)
f1 (ppm)


{6.62,99.89}
{6.63,98.60}
{5.98,99.89}
{7.94,109.88}
{7.55,112.47}
{7.46,112.47}
{7.40,115.14}
{7.32,115.14}
{5.97,120.31}
{7.55,122.37}
{7.50,122.29}
{6.64,121.77}
{6.36,122.63}
{7.95,121.94}
{7.32,122.03}
{6.84,125.13}
{6.64,125.13}
{6.37,125.04}
{6.19,126.94}
{7.65,130.90}
{7.64,133.05}
{7.24,130.30}
{7.23,134.09}
{6.89,131.50}
{6.64,131.50}
{6.36,130.90}
{6.89,134.09}
{6.84,130.82}
{6.65,130.30}
{6.92,133.05}
{7.55,139.00}
{7.49,139.00}
{7.95,138.31}
{7.31,138.31}
{7.31,148.04}
{7.54,149.77}
{7.95,148.04}
{6.00,162.86}
{6.63,164.93}
{7.23,166.82}
{7.66,168.54}
{6.92,168.54}
{6.83,168.54}
{6.37,168.54}
{5.96,164.67}
{7.23,170.09}
{7.64,171.64}
{6.92,171.64}
{6.97,174.75}
f2 (ppm)
f1 (ppm)



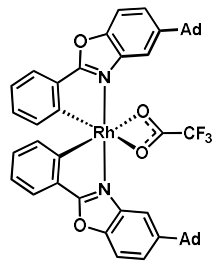
Λ-11

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



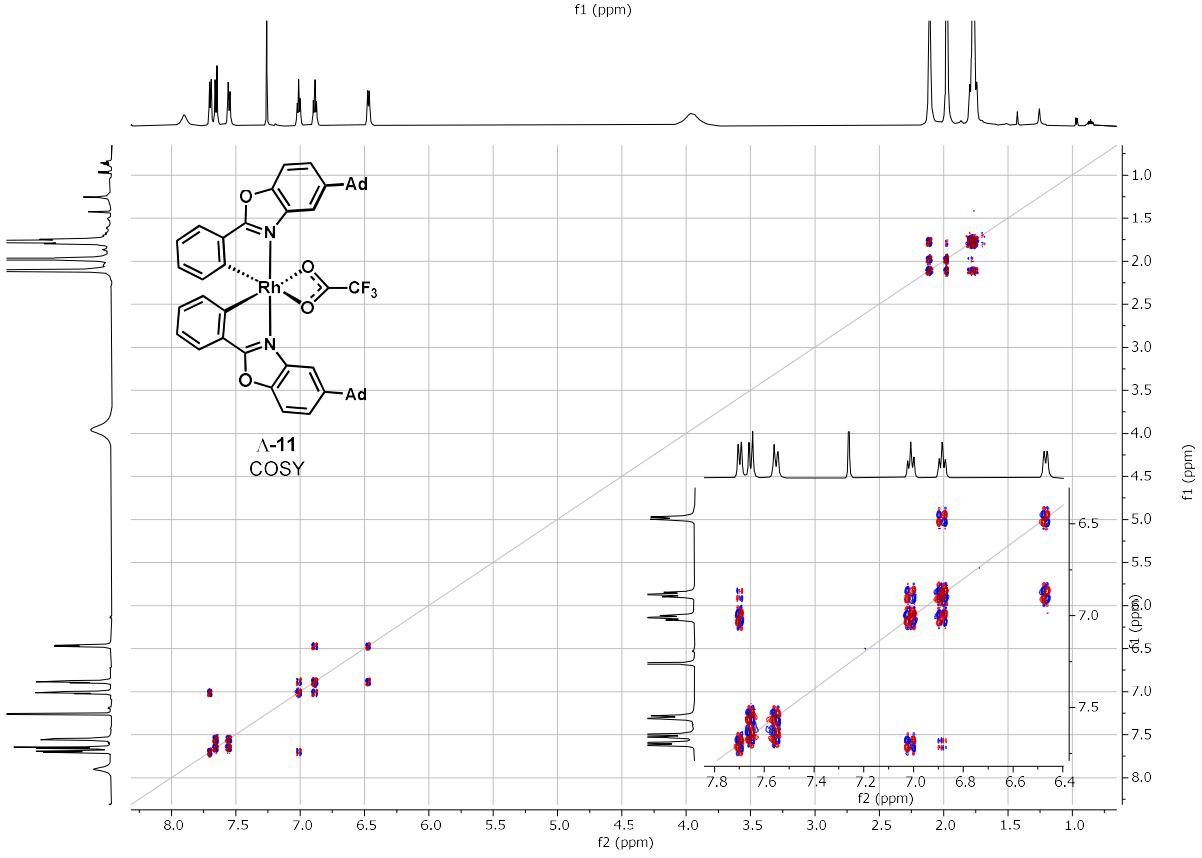
Λ-11

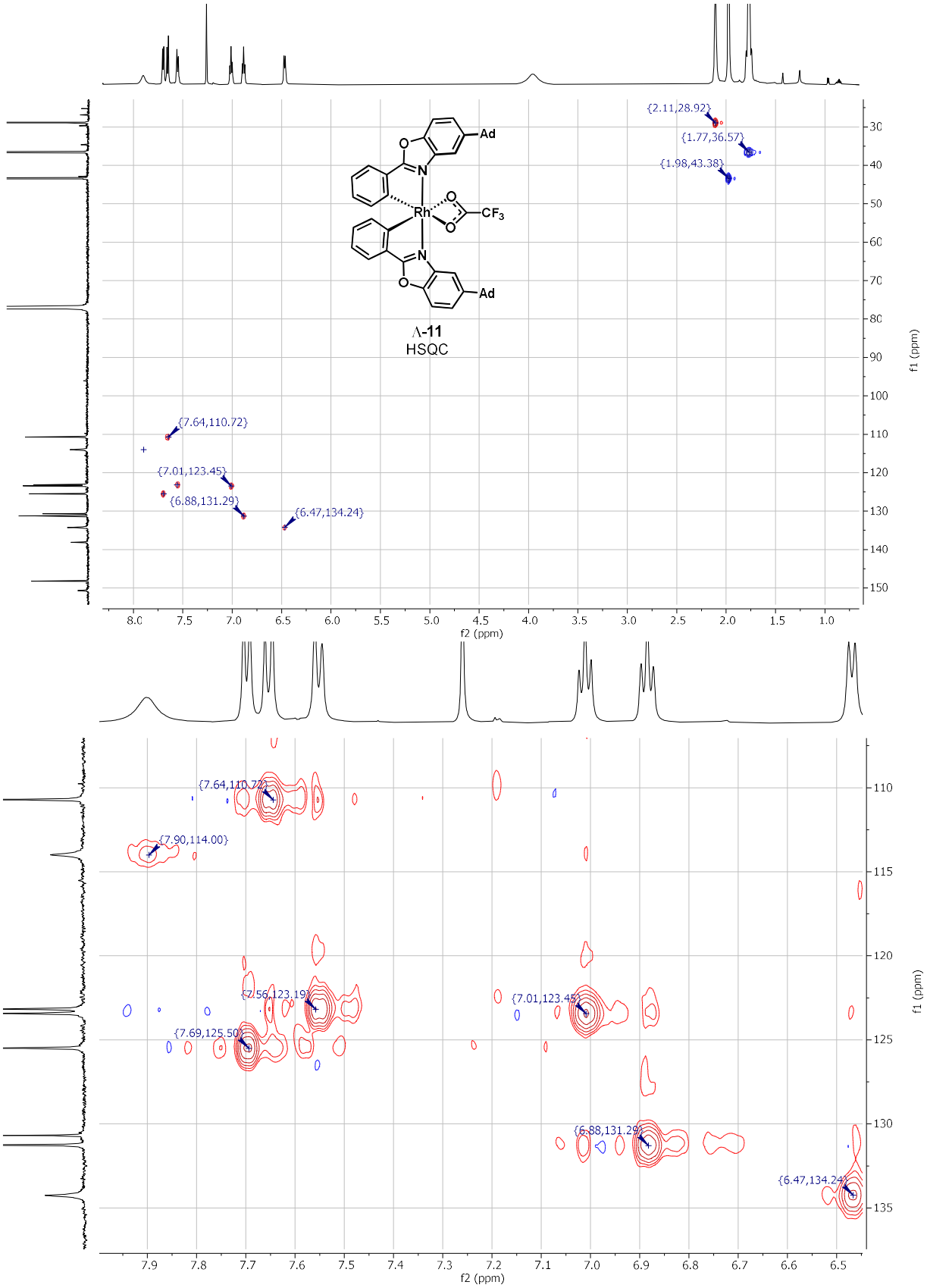
^{13}C NMR (150 MHz, $CDCl_3$)

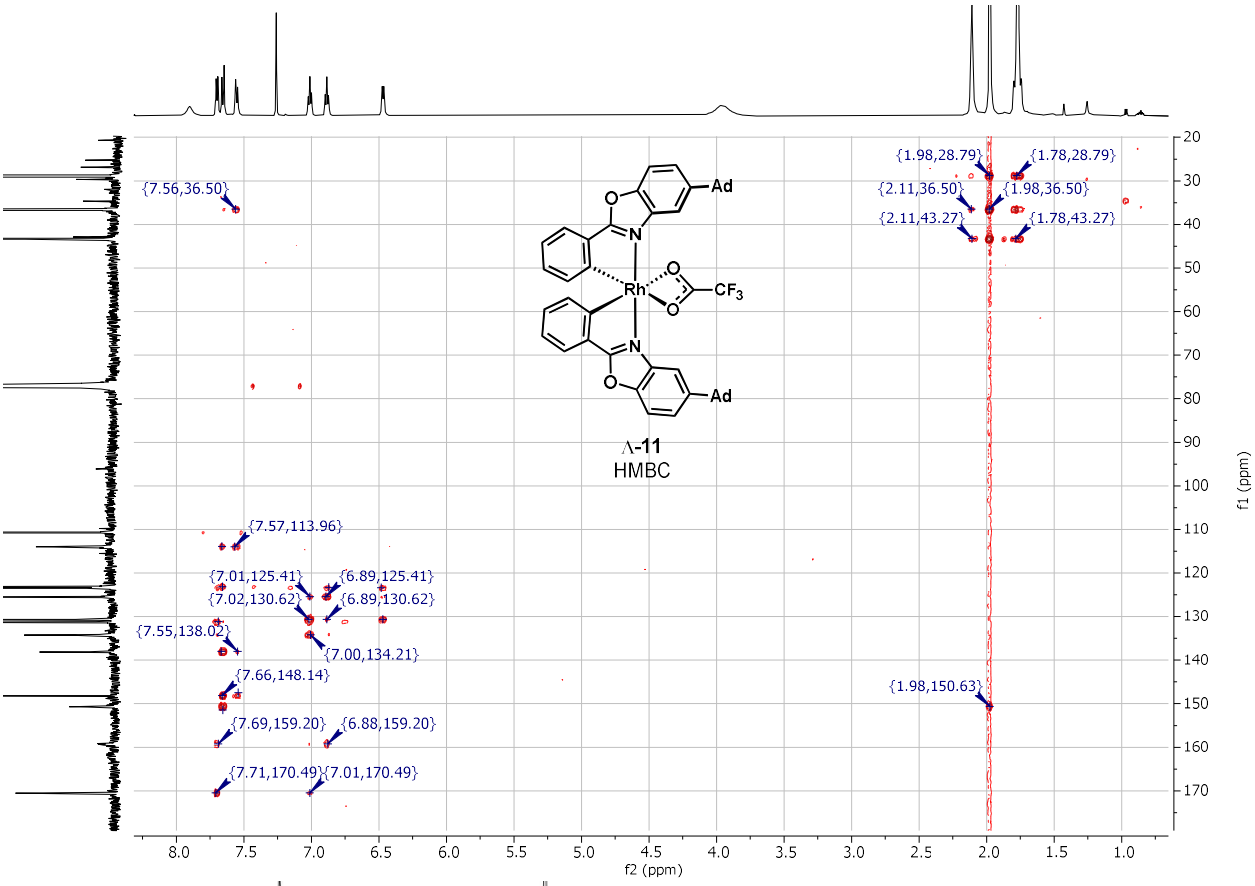


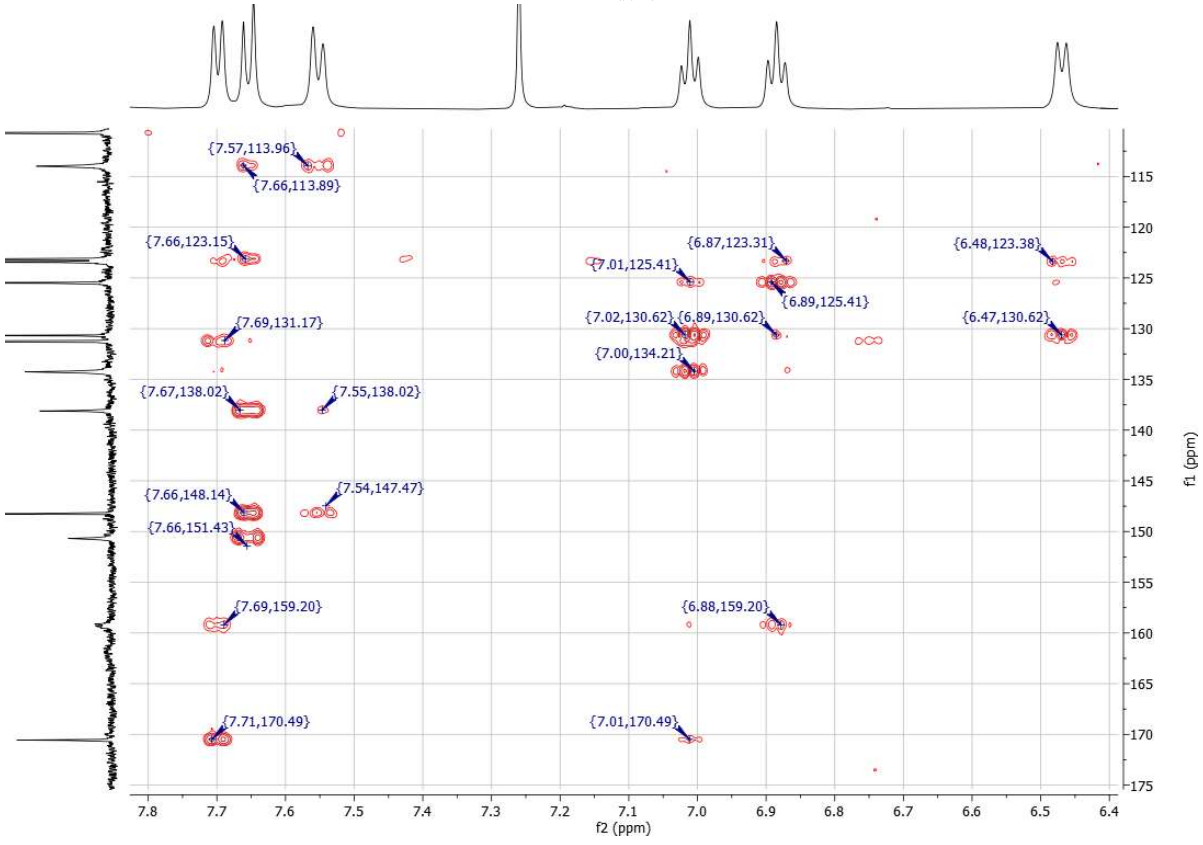
Λ-11

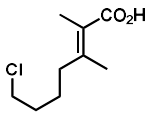
^{19}F NMR (564 MHz, $CDCl_3$)




Ad
Rh
CF3
Ad
Λ-11
HSQC
{2.11,28.92}
{1.77,36.57}
{1.98,43.38}
{7.64,110.72}
{7.01,123.45}
{6.88,131.29}
{6.47,134.24}
f2 (ppm)
f1 (ppm)
{7.64,110.72}
{7.90,114.00}
{7.56,123.19}
{7.69,125.50}
{7.01,123.45}
{6.88,131.29}
{6.47,134.24}
f2 (ppm)
f1 (ppm)

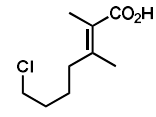

{7.56,36.50}
{1.98,28.79}
{1.78,28.79}
{2.11,36.50}
{1.98,36.50}
{2.11,43.27}
{1.78,43.27}
Ad
Rh
CF3
Ad
Λ-11
HMBC
{7.57,113.96}
{7.01,125.41}
{6.89,125.41}
{7.02,130.62}
{6.89,130.62}
{7.55,138.02}
{7.00,134.21}
{7.66,148.14}
{1.98,150.63}
{7.69,159.20}
{6.88,159.20}
{7.71,170.49}
{7.01,170.49}
f2 (ppm)
f1 (ppm)


{7.57,113.96}
{7.66,113.89}
{7.66,123.15}
{6.87,123.31}
{6.48,123.38}
{7.01,125.41}
{6.89,125.41}
{7.69,131.17}
{7.02,130.62}
{6.89,130.62}
{6.47,130.62}
{7.00,134.21}
{7.67,138.02}
{7.55,138.02}
{7.66,148.14}
{7.54,147.47}
{7.66,151.43}
{7.69,159.20}
{6.88,159.20}
{7.71,170.49}
{7.01,170.49}
f2 (ppm)
f1 (ppm)



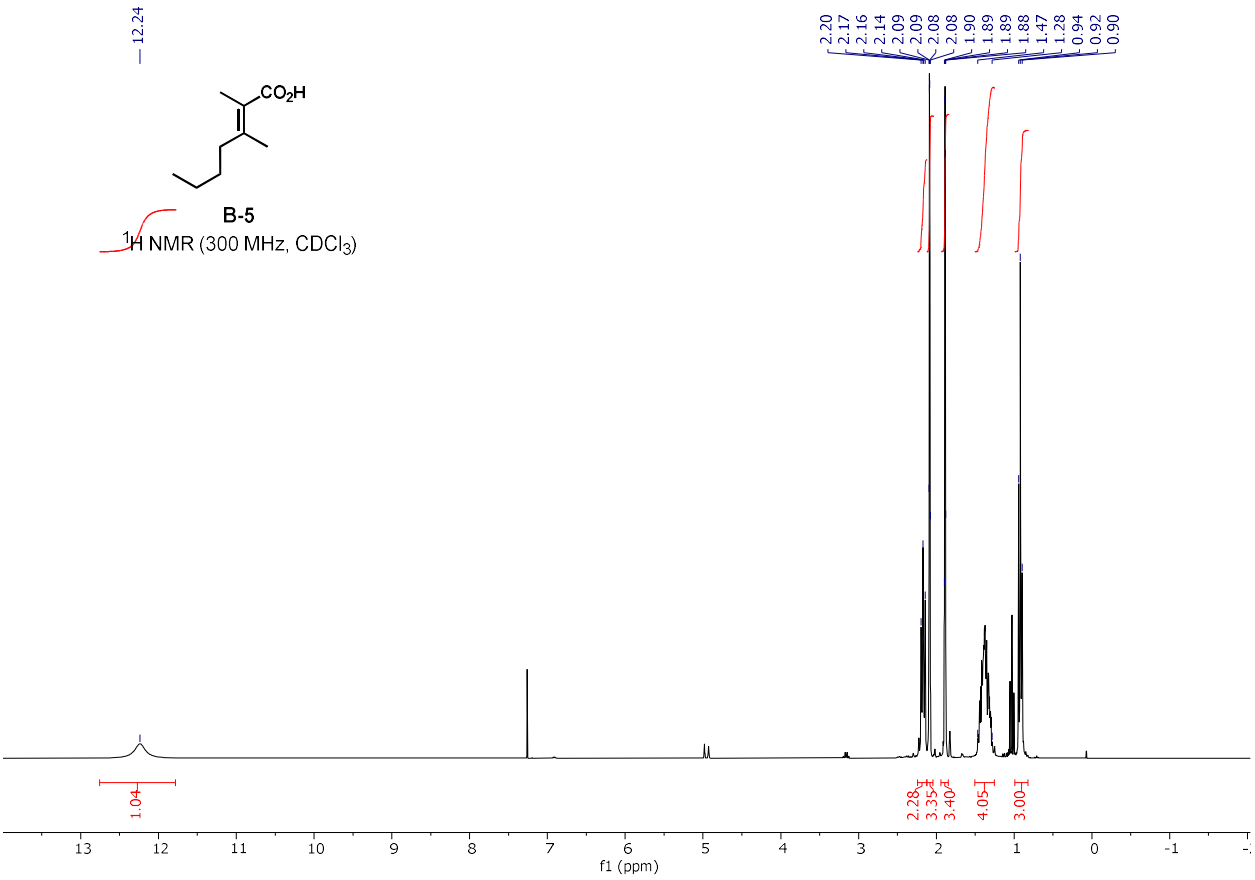
B-4

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



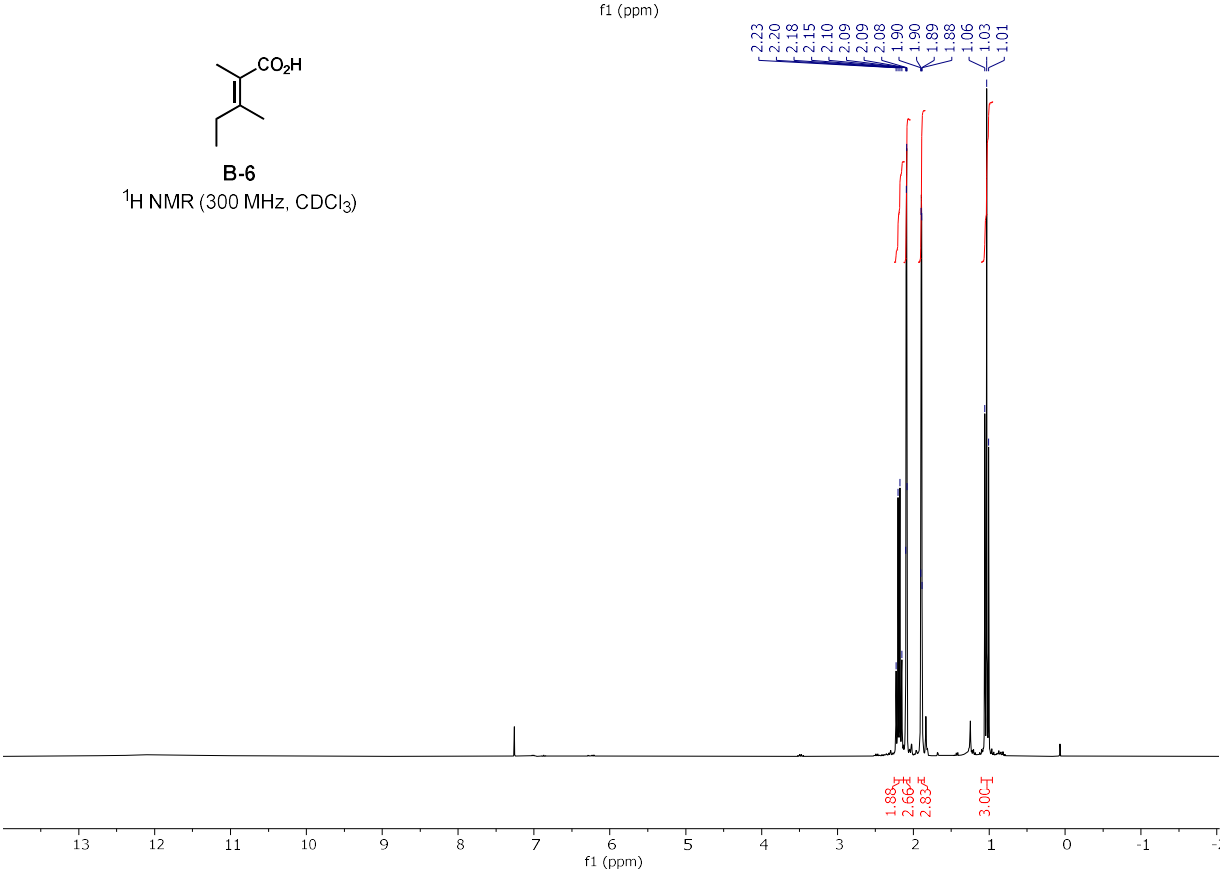
B-4

^{13}C NMR (150 MHz, $CDCl_3$)



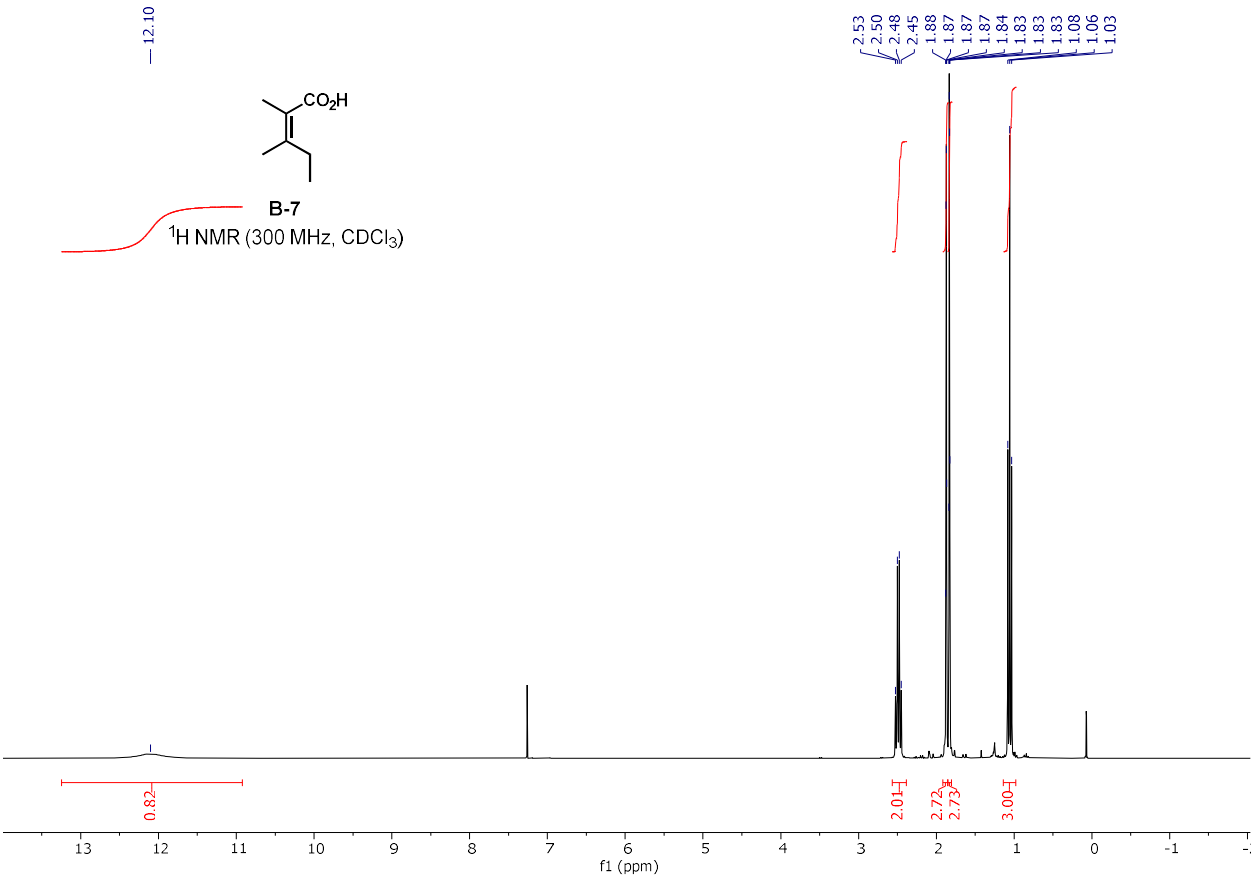
B-5

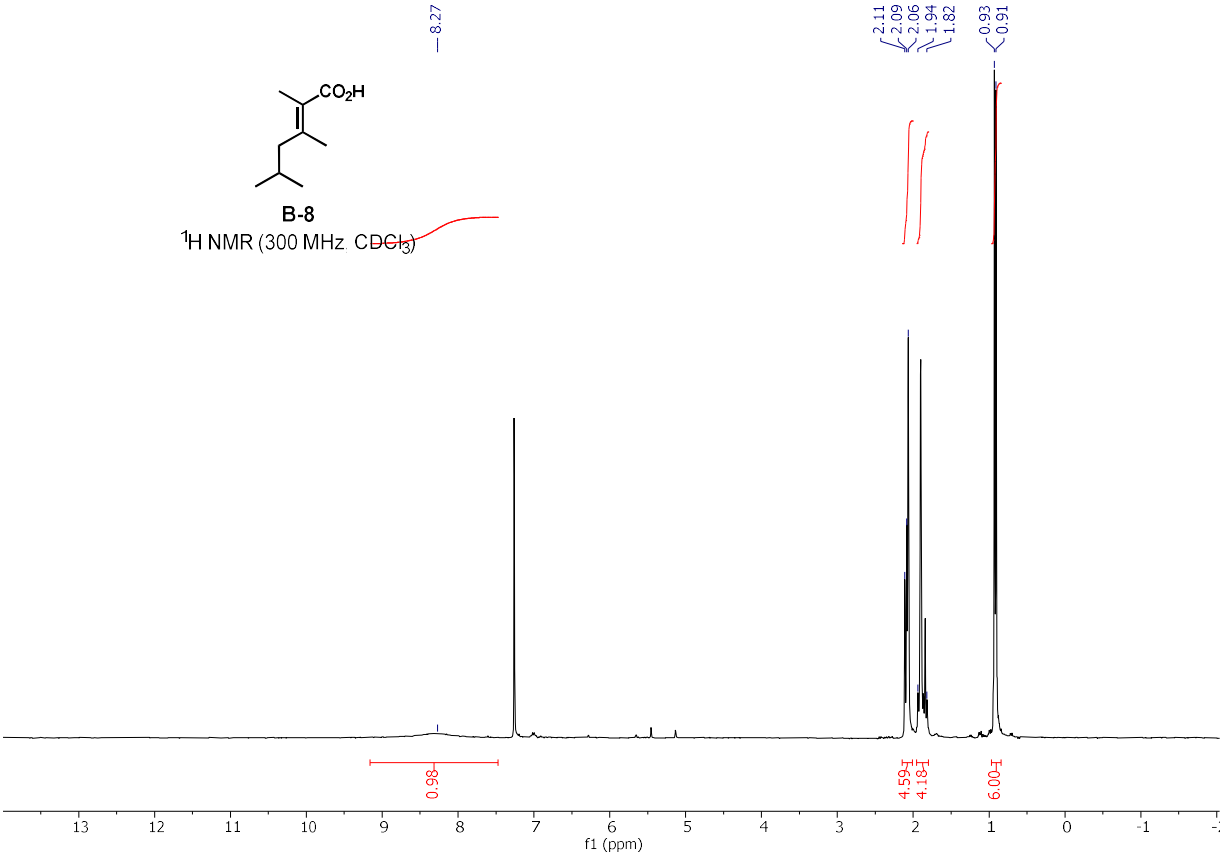
^{1}H NMR (300 MHz, $CDCl_3$)

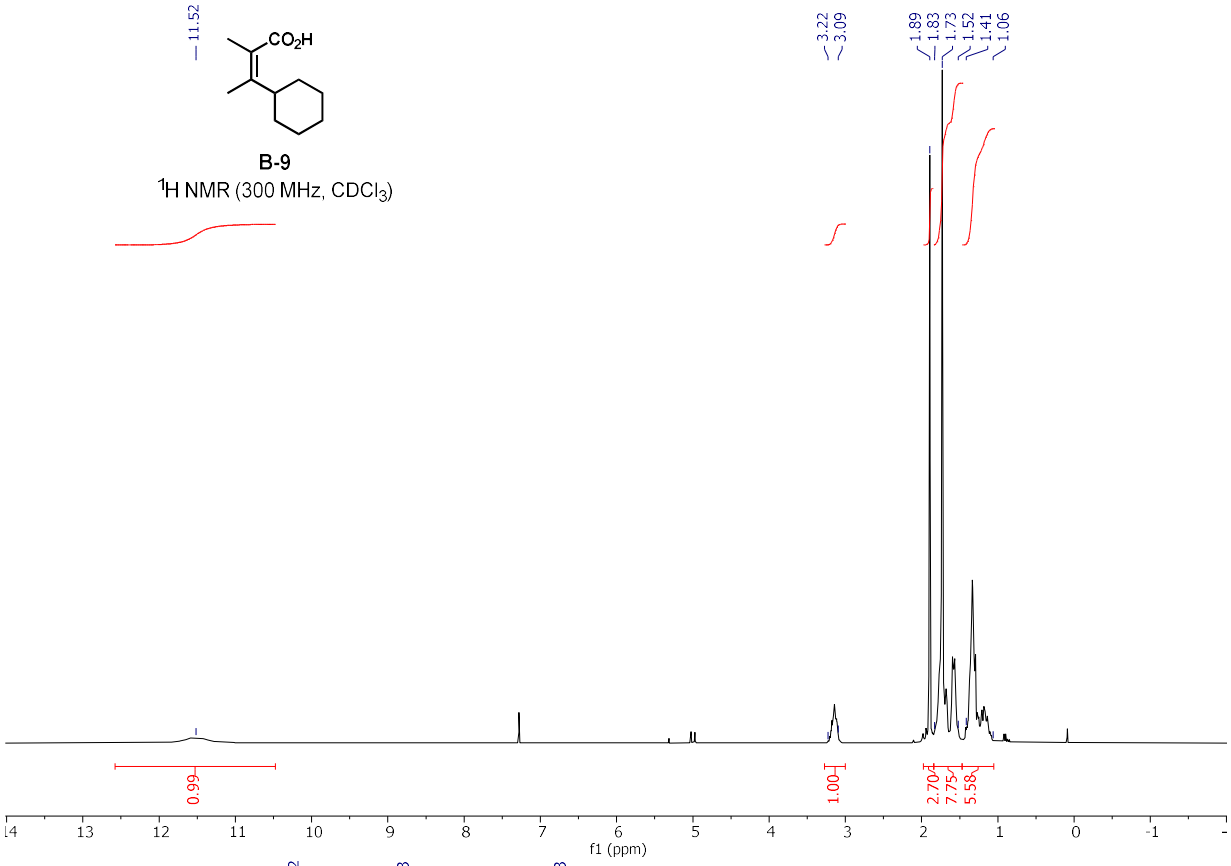


B-6

^{1}H NMR (300 MHz, $CDCl_3$)

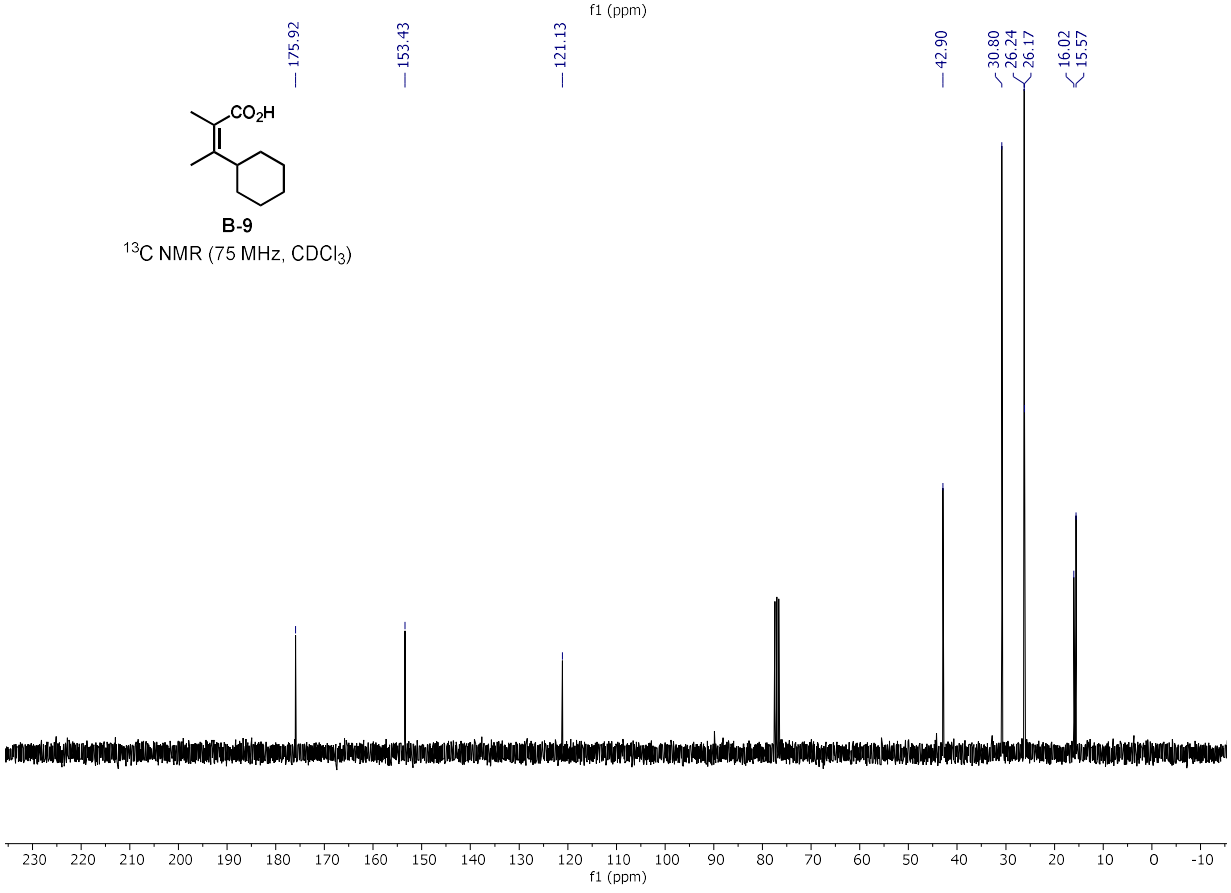

12.10
2.53
2.50
2.48
2.45
1.88
1.87
1.87
1.87
1.84
1.83
1.83
1.83
1.08
1.06
1.03
CO2H
B-7
1H NMR (300 MHz, CDCl3)
0.82
2.01
2.72
2.73
3.00
f1 (ppm)


8.27
2.11
2.09
2.06
1.94
1.82
0.93
0.91
CO2H
B-8
1H NMR (300 MHz, CDCl3)
0.98
4.59
4.18
6.00
f1 (ppm)



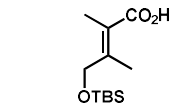
B-9

^{1}H NMR (300 MHz, $CDCl_3$)



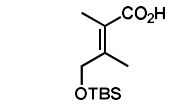
B-9

^{13}C NMR (75 MHz, $CDCl_3$)



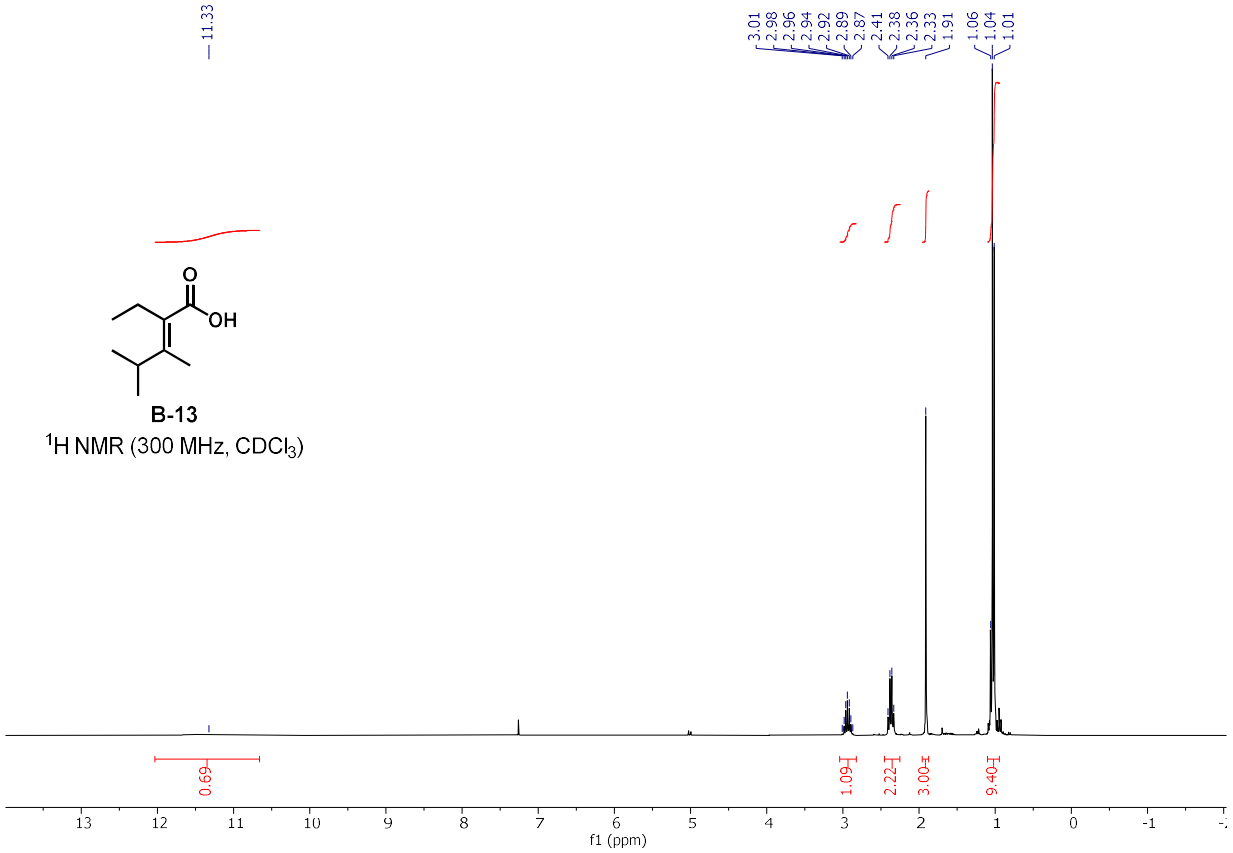
B-10

^{1}H NMR (300 MHz, $CDCl_3$)



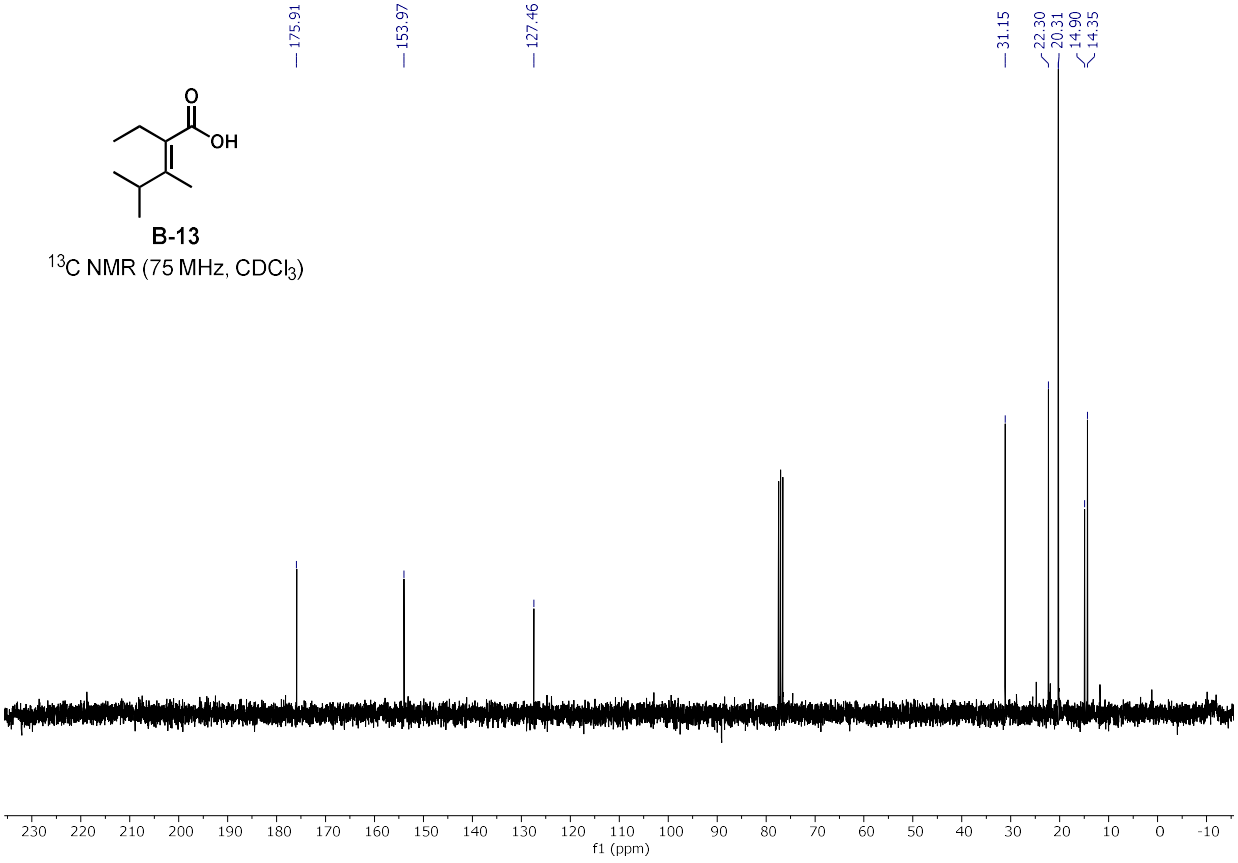
B-10

^{13}C NMR (75 MHz, $CDCl_3$)



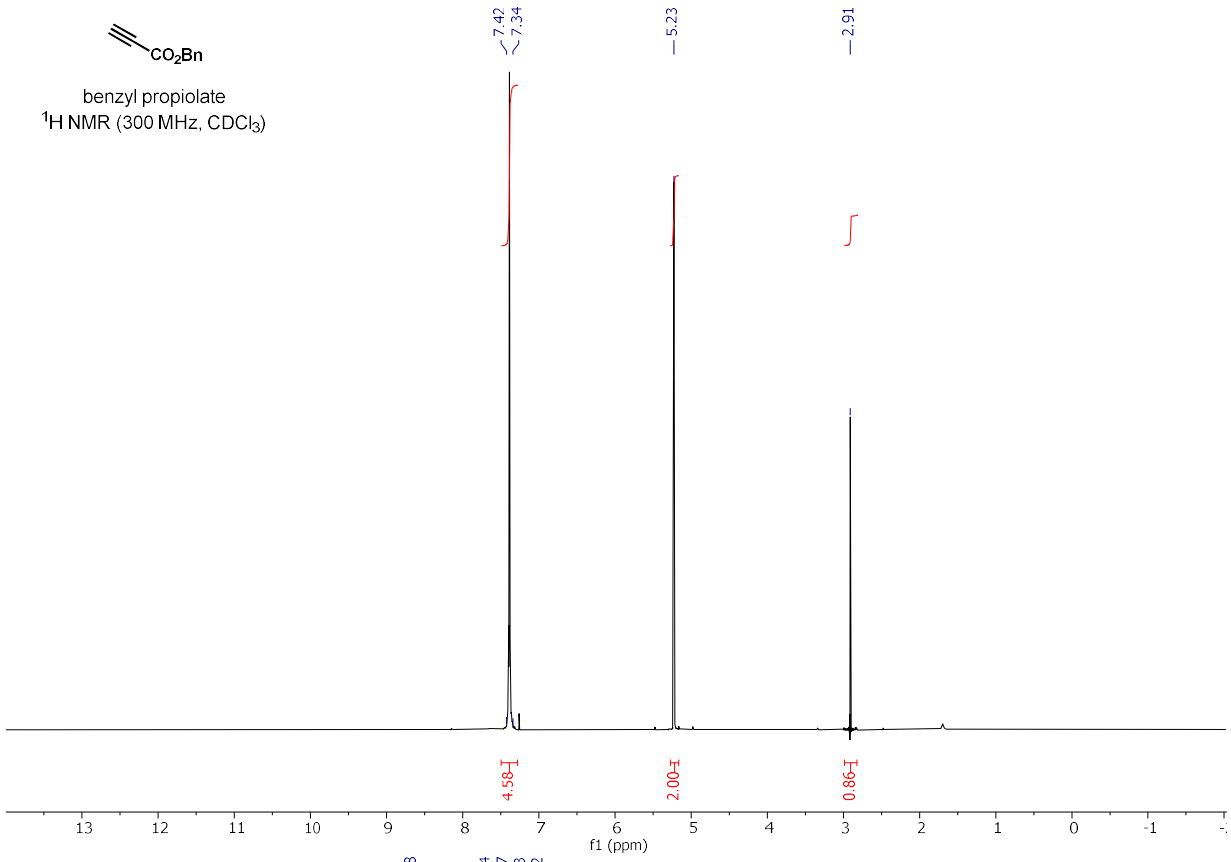
B-13

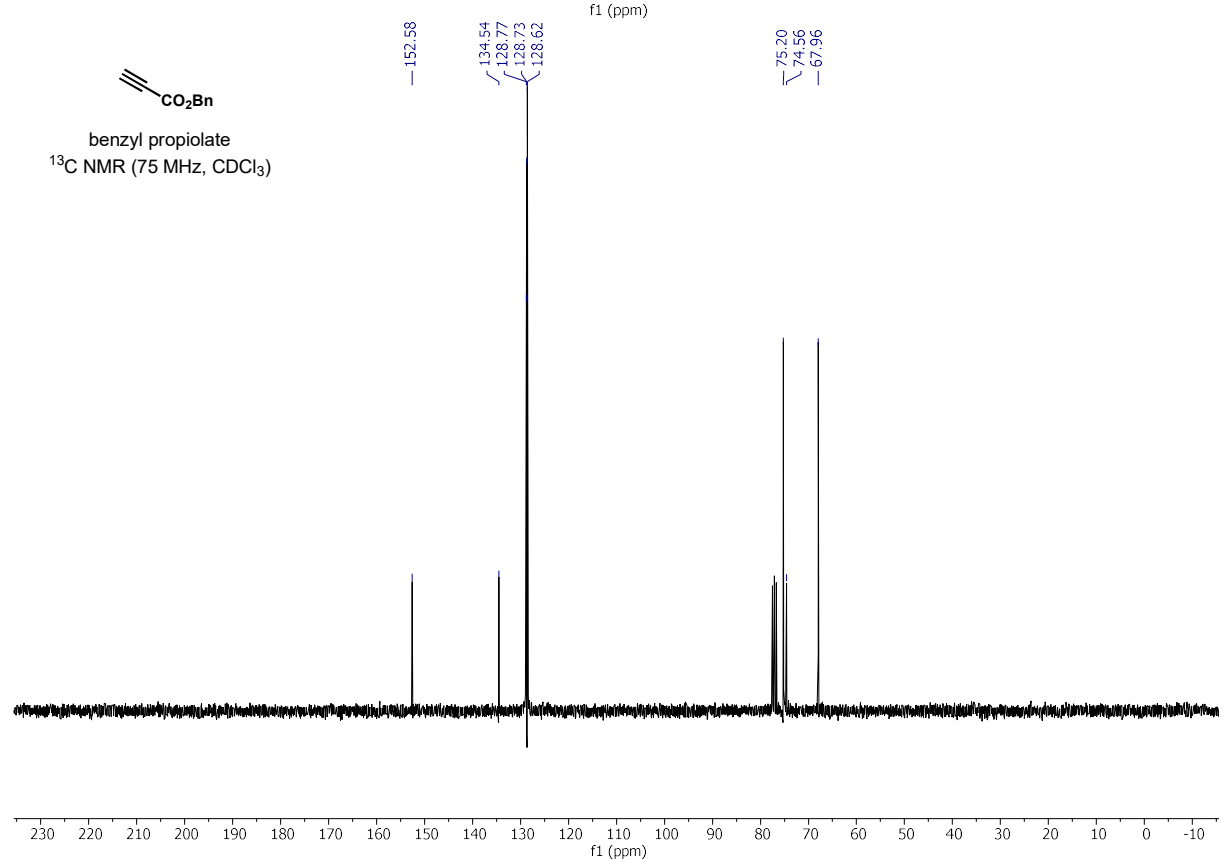
^{1}H NMR (300 MHz, $CDCl_3$)

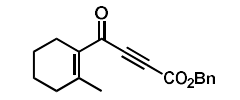


B-13

^{13}C NMR (75 MHz, $CDCl_3$)

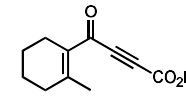

CO2Bn
benzyl propiolate
1H NMR (300 MHz, CDCl3)
7.42
7.34
5.23
2.91
4.58
2.00
0.86
f1 (ppm)


CO2Bn
benzyl propiolate
13C NMR (75 MHz, CDCl3)
152.58
134.54
128.77
128.73
128.62
75.20
74.56
67.96
f1 (ppm)



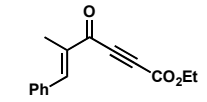
5

^{1}H NMR (300 MHz, $CDCl_3$)



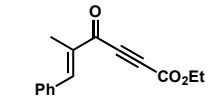
5

^{13}C NMR (75 MHz, $CDCl_3$)



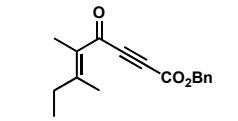
A2

^{1}H NMR (300 MHz, $CDCl_3$)



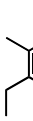
A2

^{13}C NMR (75 MHz, $CDCl_3$)



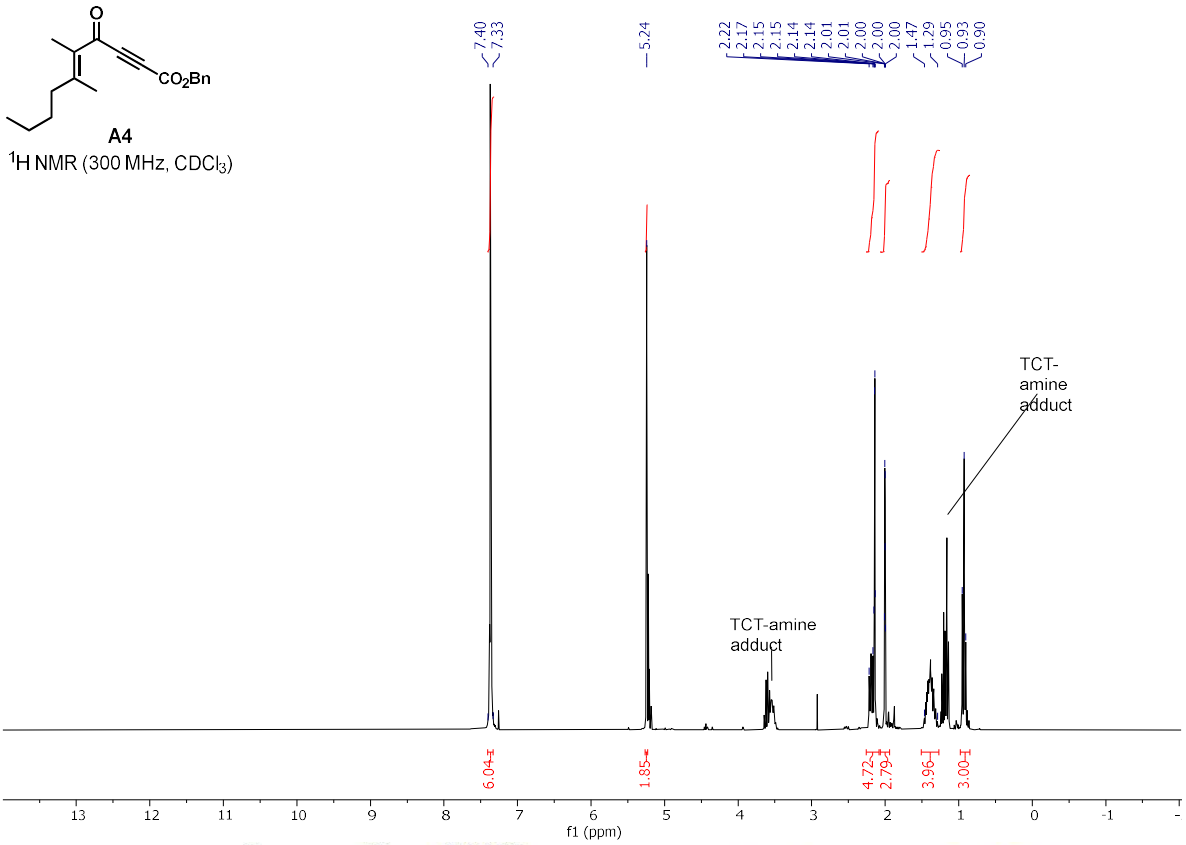
A3

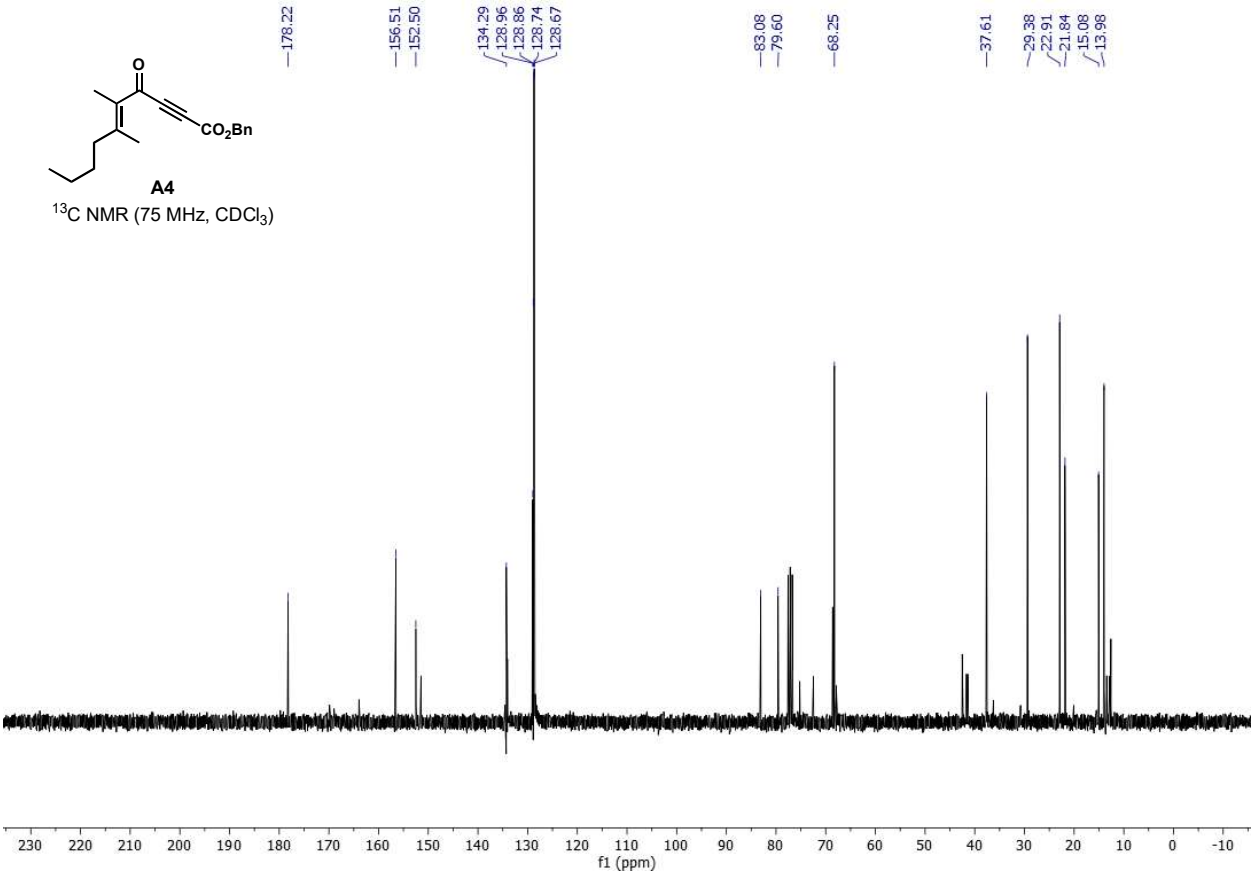
^{1}H NMR (300 MHz, $CDCl_3$)

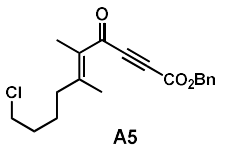


A3

^{13}C NMR (75 MHz, $CDCl_3$)

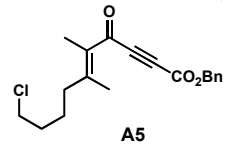

A4
^{1}H NMR (300 MHz, $CDCl_3$)
7.40
7.33
5.24
2.22
2.17
2.15
2.15
2.14
2.14
2.01
2.01
2.00
2.00
2.00
1.47
1.29
0.95
0.93
0.90
TCT-amine adduct
TCT-amine adduct
6.04
1.85
4.72
2.79
3.96
3.00
f1 (ppm)


A4
^{13}C NMR (75 MHz, $CDCl_3$)
178.22
156.51
152.50
134.29
128.96
128.86
128.74
128.67
83.08
79.60
68.25
37.61
29.38
22.91
21.84
15.08
13.98
f1 (ppm)



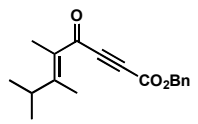
A5

^{1}H NMR (300 MHz, $CDCl_3$)



A5

^{13}C NMR (75 MHz, $CDCl_3$)

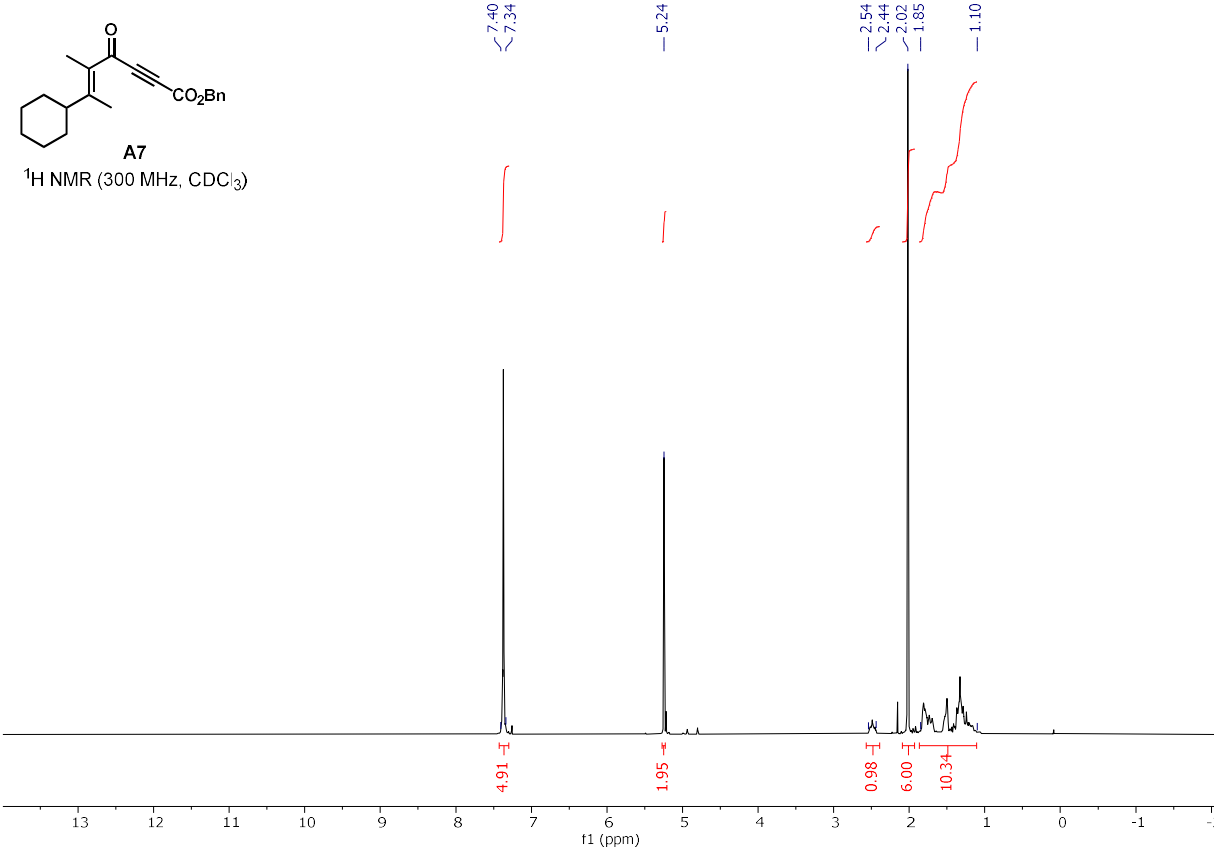


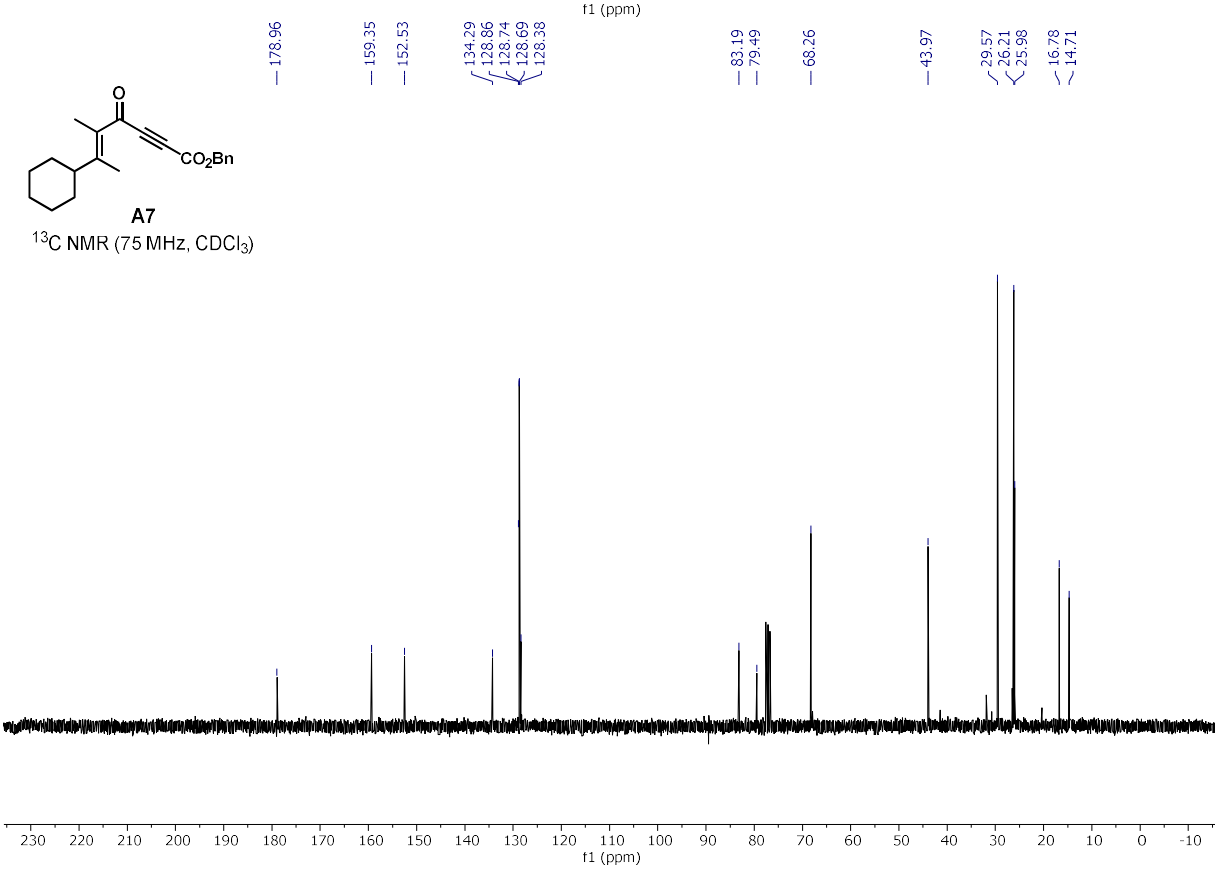
A6

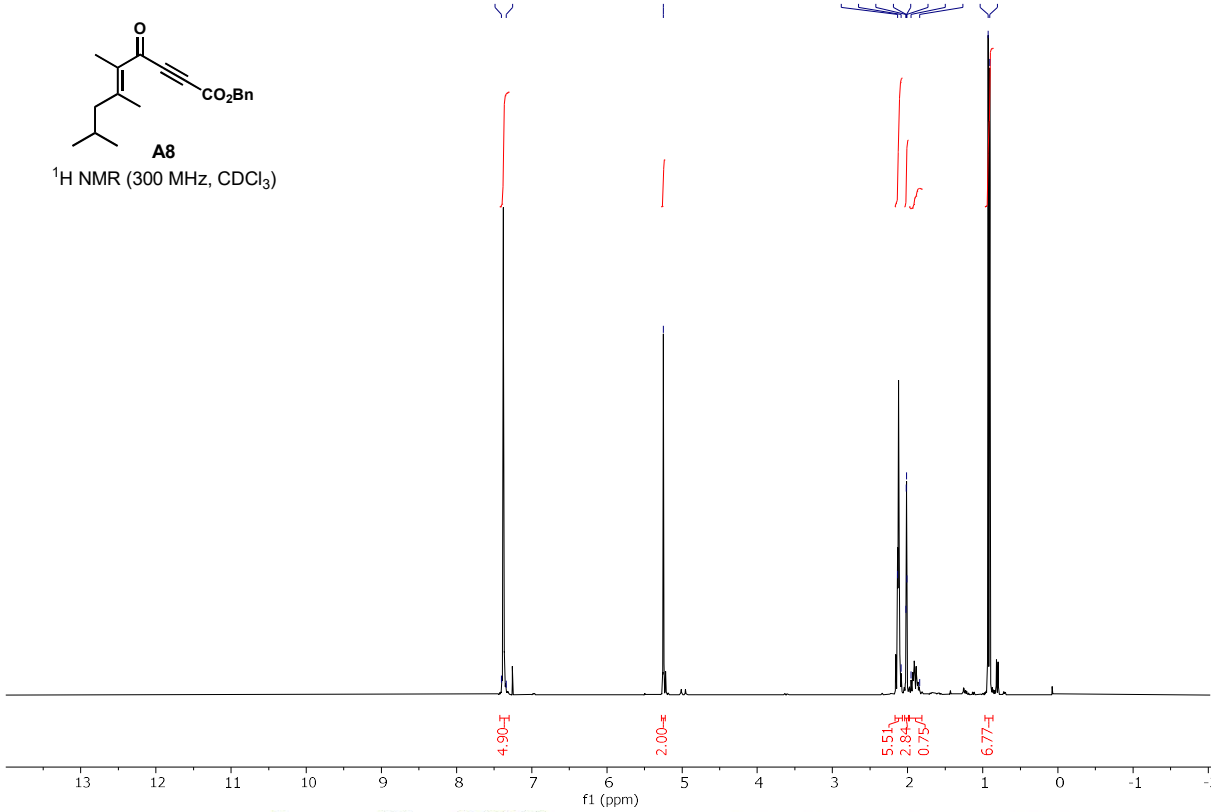
^{1}H NMR (300 MHz, $CDCl_3$)

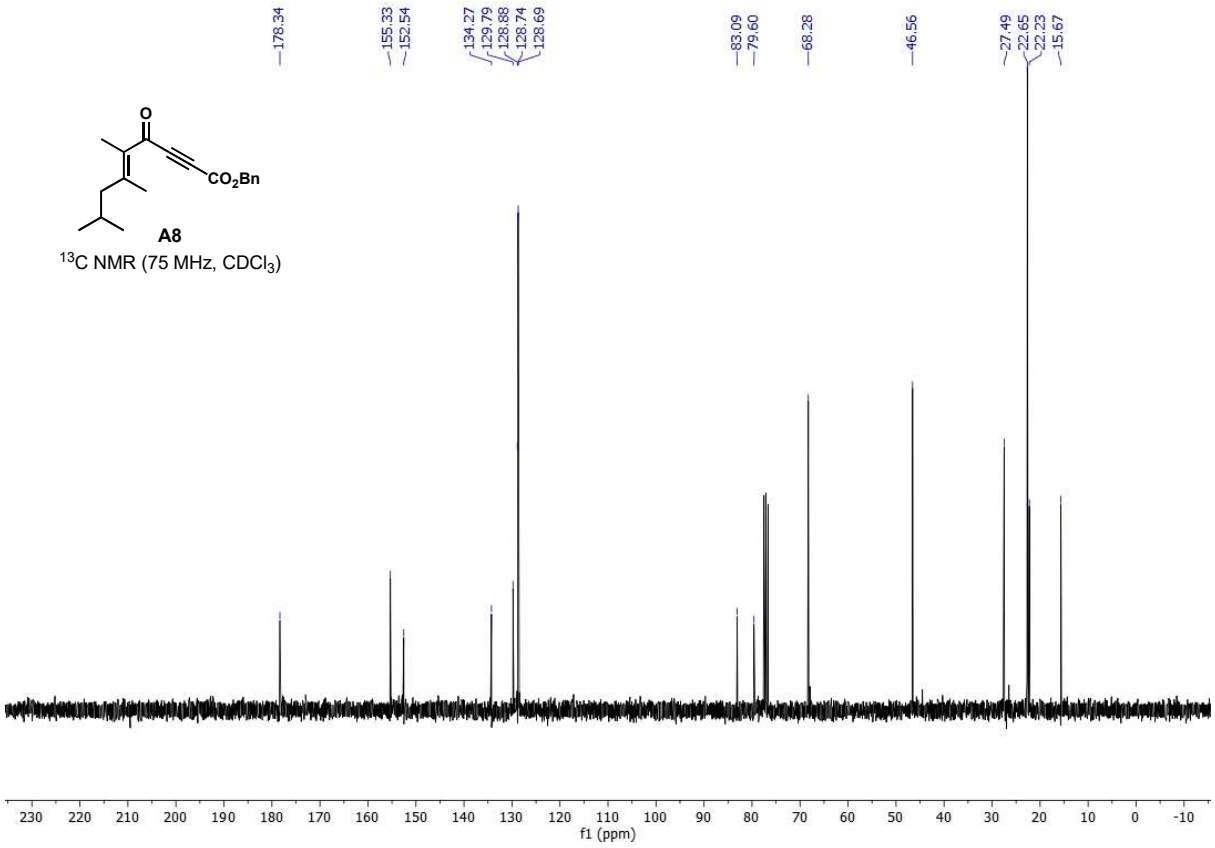
A6

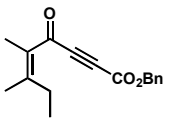
^{13}C NMR (75 MHz, $CDCl_3$)


A7
^{1}H NMR (300 MHz, CDCl$_3$)
7.40
7.34
5.24
2.54
2.44
2.02
1.85
1.10
4.91
1.95
0.98
6.00
10.34
f1 (ppm)


A7
^{13}C NMR (75 MHz, CDCl$_3$)
178.96
159.35
152.53
134.29
128.86
128.74
128.69
128.38
83.19
79.49
68.26
43.97
29.57
26.21
25.98
16.78
14.71
f1 (ppm)

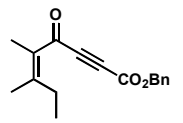

O
CO2Bn
A8
1H NMR (300 MHz, CDCl3)
7.40
7.34
5.25
2.13
2.08
2.02
2.02
2.01
2.01
1.95
1.84
0.93
0.91
4.90
2.00
5.51
2.84
0.75
6.77
f1 (ppm)


178.34
155.33
152.54
134.27
129.79
128.88
128.74
128.69
83.09
79.60
68.28
46.56
27.49
22.65
22.23
15.67
O
CO2Bn
A8
13C NMR (75 MHz, CDCl3)
f1 (ppm)



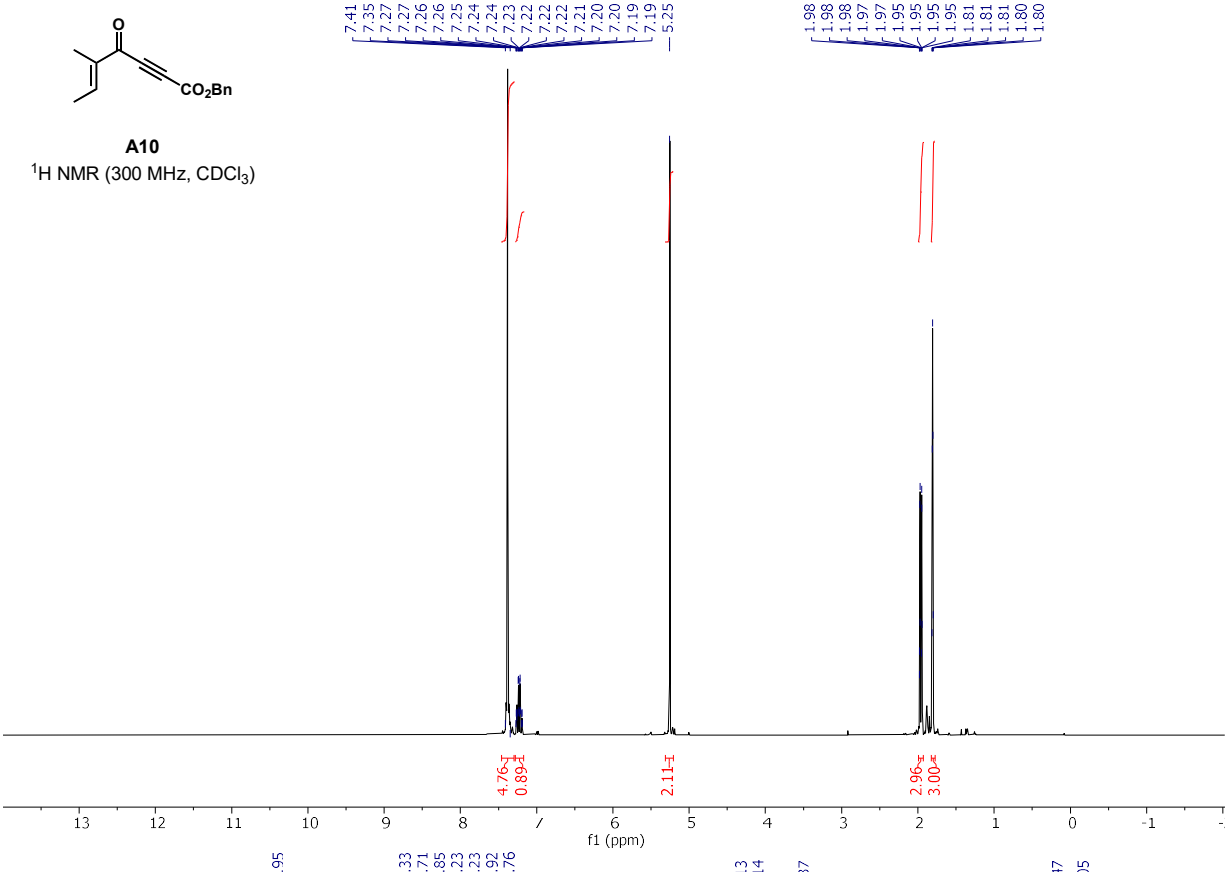
A9

^{1}H NMR (300 MHz, $CDCl_3$)



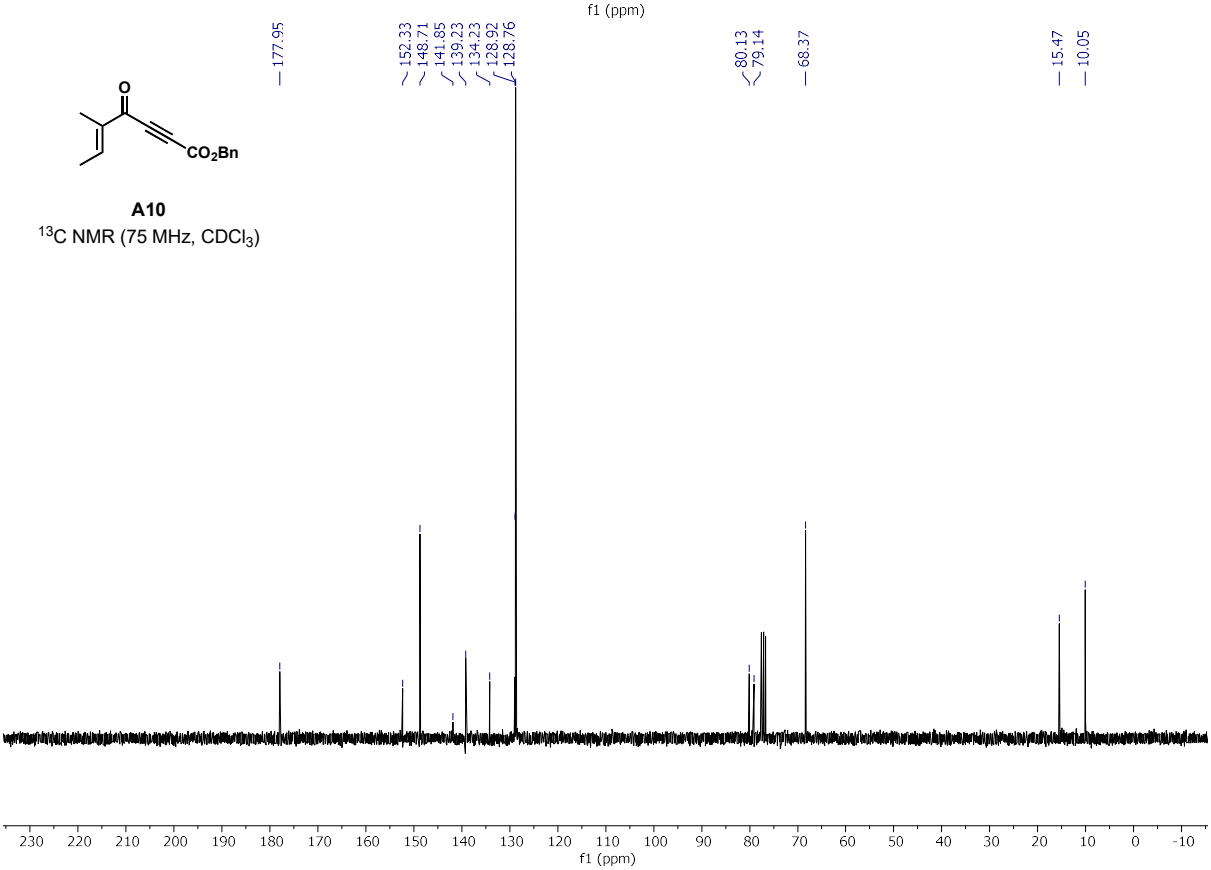
A9

^{13}C NMR (75 MHz, $CDCl_3$)



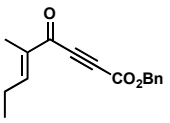
A10

^{1}H NMR (300 MHz, $CDCl_3$)



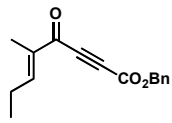
A10

^{13}C NMR (75 MHz, $CDCl_3$)



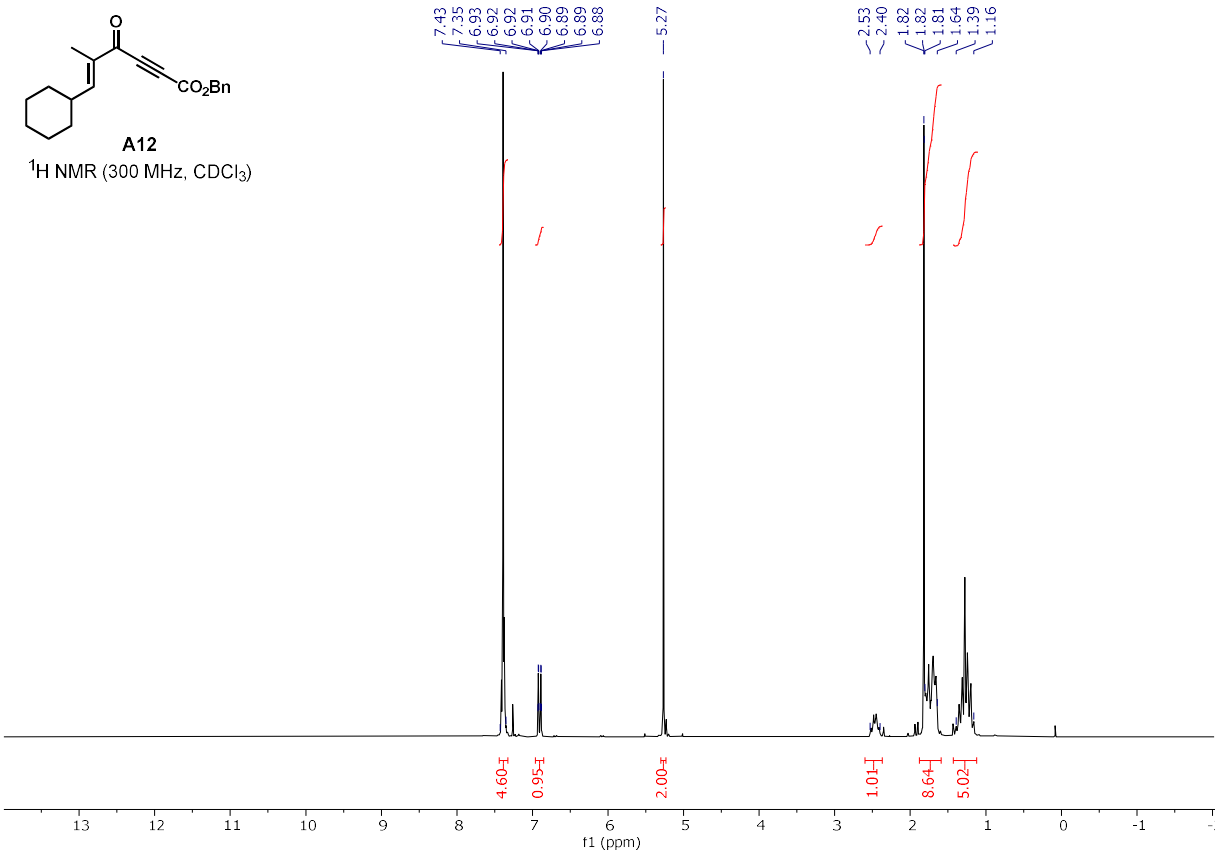
A11

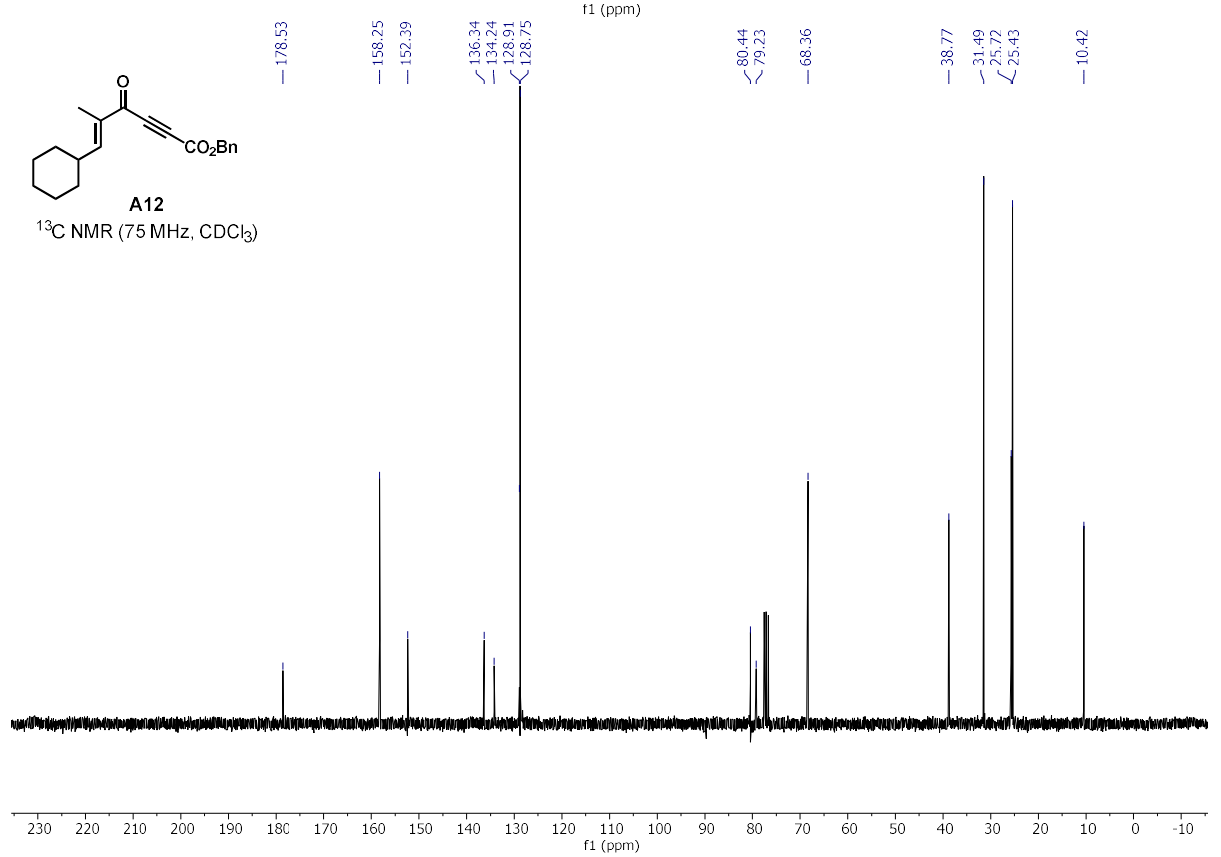
^{1}H NMR (300 MHz, $CDCl_3$)

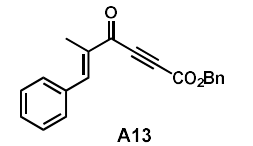


A11

^{13}C NMR (75 MHz, $CDCl_3$)

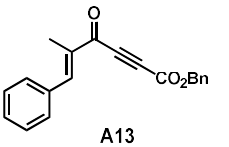

A12
^{1}H NMR (300 MHz, $CDCl_3$)
7.43
7.35
6.93
6.92
6.92
6.91
6.90
6.89
6.89
6.88
5.27
2.53
2.40
1.82
1.82
1.81
1.64
1.39
1.16
4.60
0.95
2.00
1.01
8.64
5.02
f1 (ppm)


A12
^{13}C NMR (75 MHz, $CDCl_3$)
178.53
158.25
152.39
136.34
134.24
128.91
128.75
80.44
79.23
68.36
38.77
31.49
25.72
25.43
10.42
f1 (ppm)



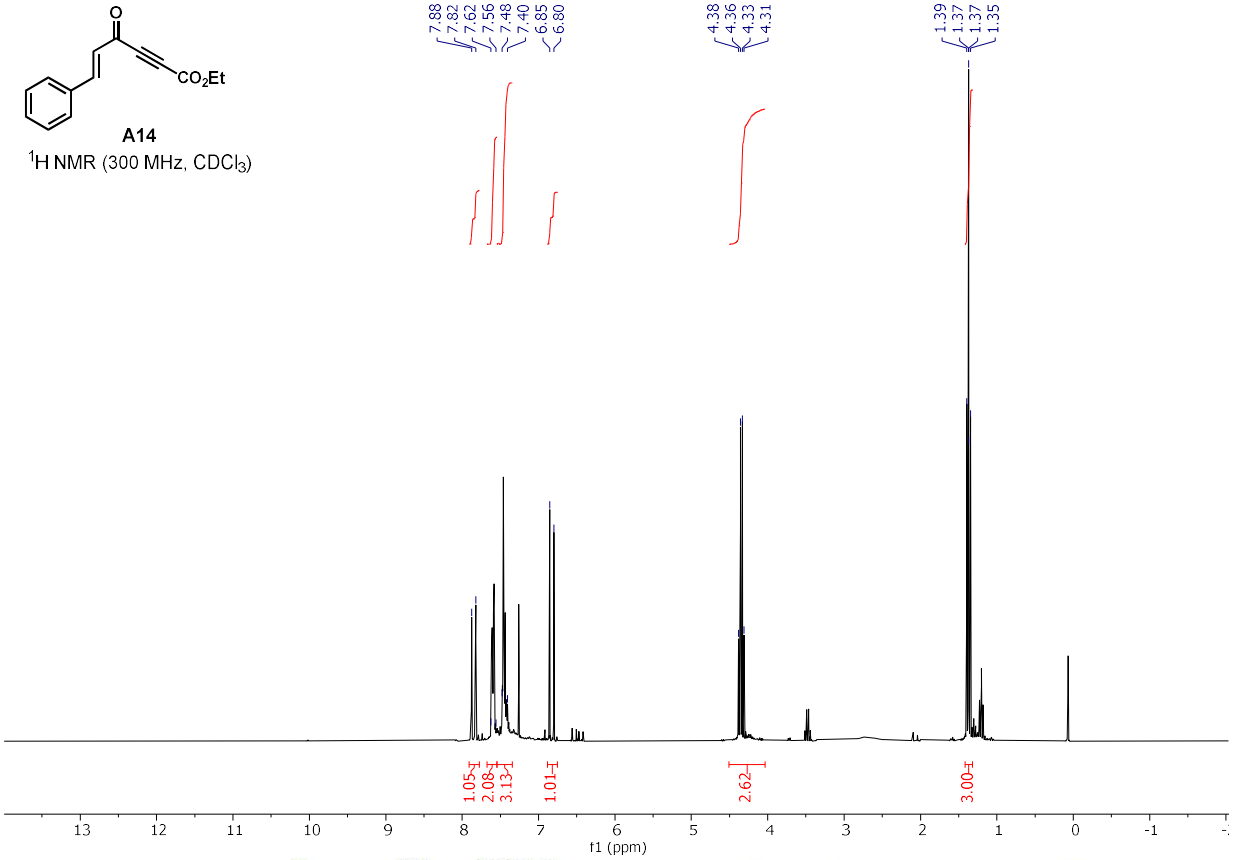
A13

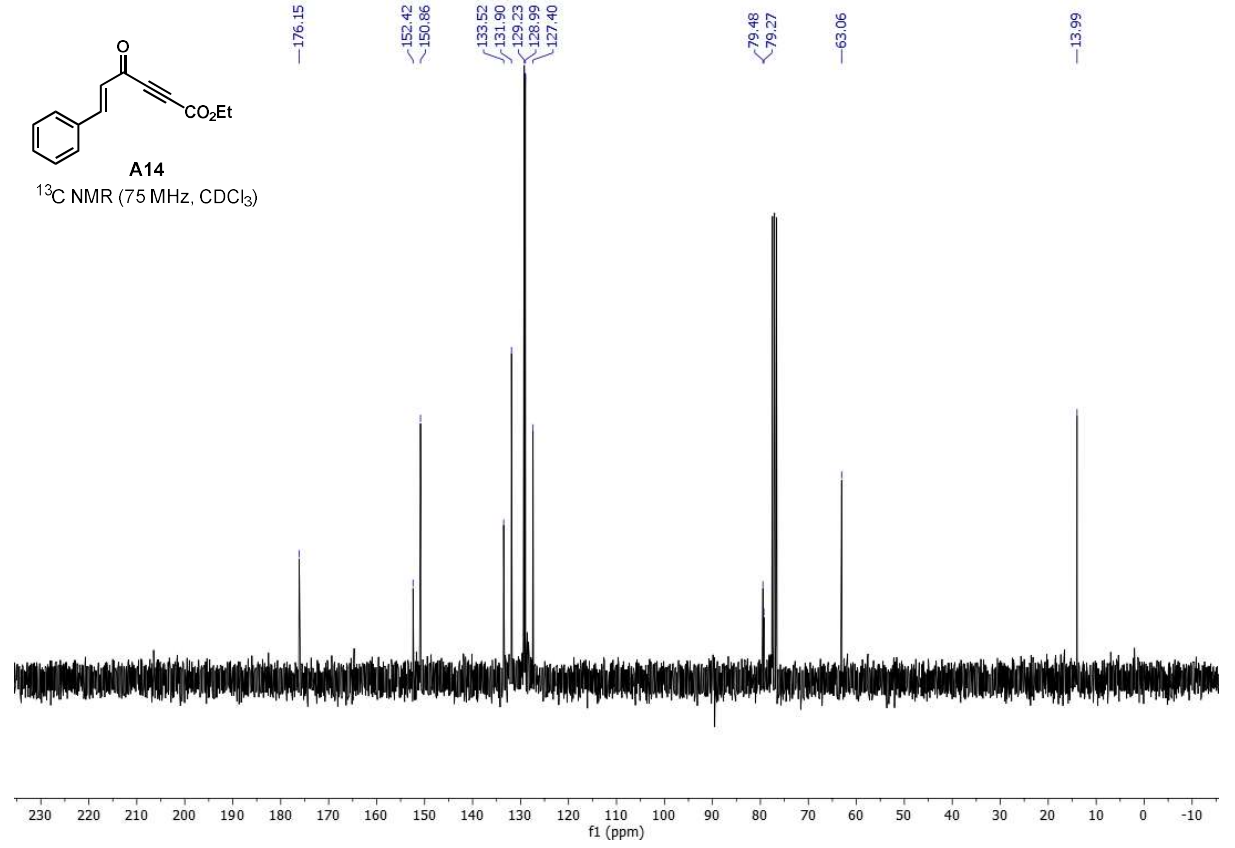
^{1}H NMR (300 MHz, $CDCl_3$)

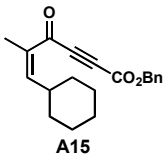


A13

^{13}C NMR (75 MHz, $CDCl_3$)

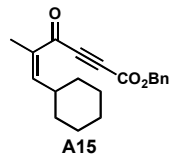

A14
1H NMR (300 MHz, CDCl3)
7.88
7.82
7.62
7.56
7.48
7.40
6.85
6.80
4.38
4.36
4.33
4.31
1.39
1.37
1.37
1.35
1.05
2.08
3.13
1.01
2.62
3.00
f1 (ppm)


A14
13C NMR (75 MHz, CDCl3)
176.15
152.42
150.86
133.52
131.90
129.23
128.99
127.40
79.48
79.27
63.06
13.99
f1 (ppm)



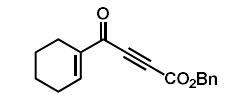
A15

^{1}H NMR (300 MHz, $CDCl_3$)



A15

^{13}C NMR (75 MHz, $CDCl_3$)

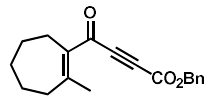


A16

^{1}H NMR (300 MHz, $CDCl_3$)

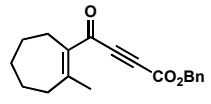
A16

^{13}C NMR (75 MHz, $CDCl_3$)



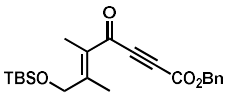
A17

^{1}H NMR (300 MHz, $CDCl_3$)



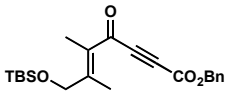
A17

^{13}C NMR (75 MHz, $CDCl_3$)



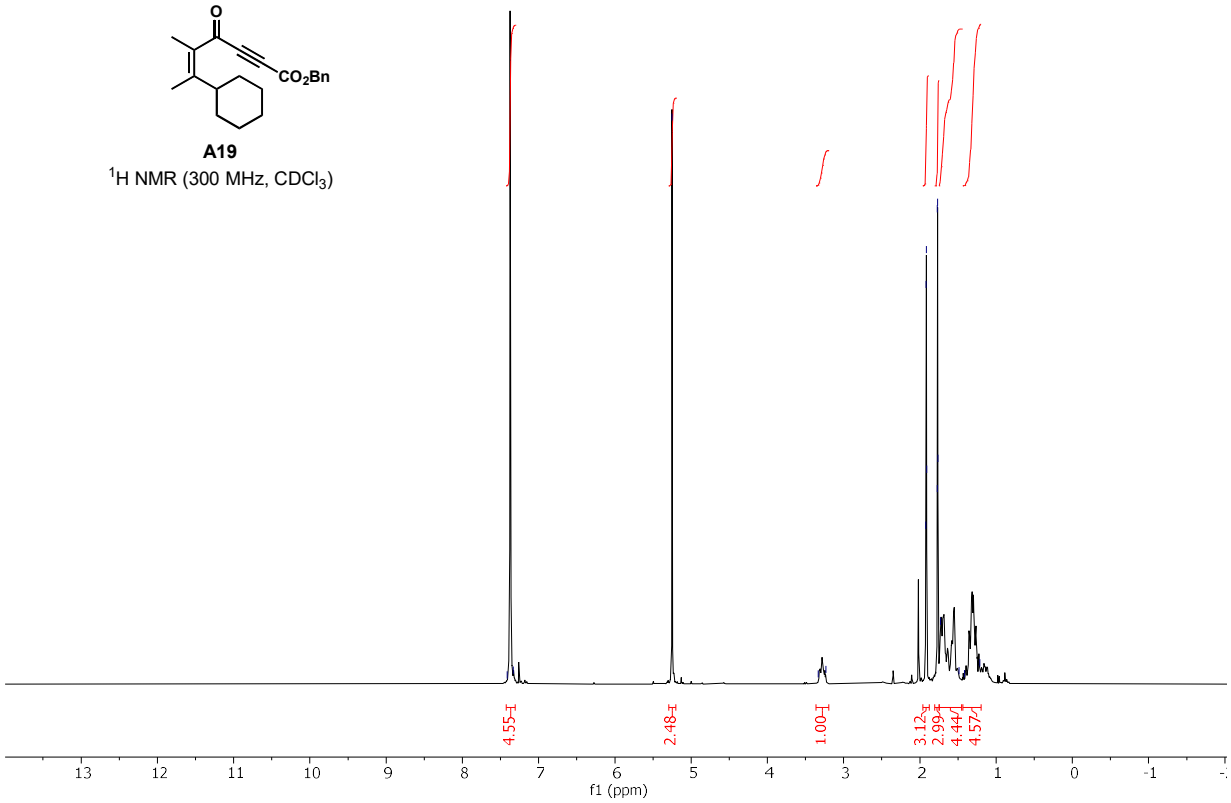
A18

^{1}H NMR (300 MHz, $CDCl_3$)



A18

^{13}C NMR (75 MHz, $CDCl_3$)

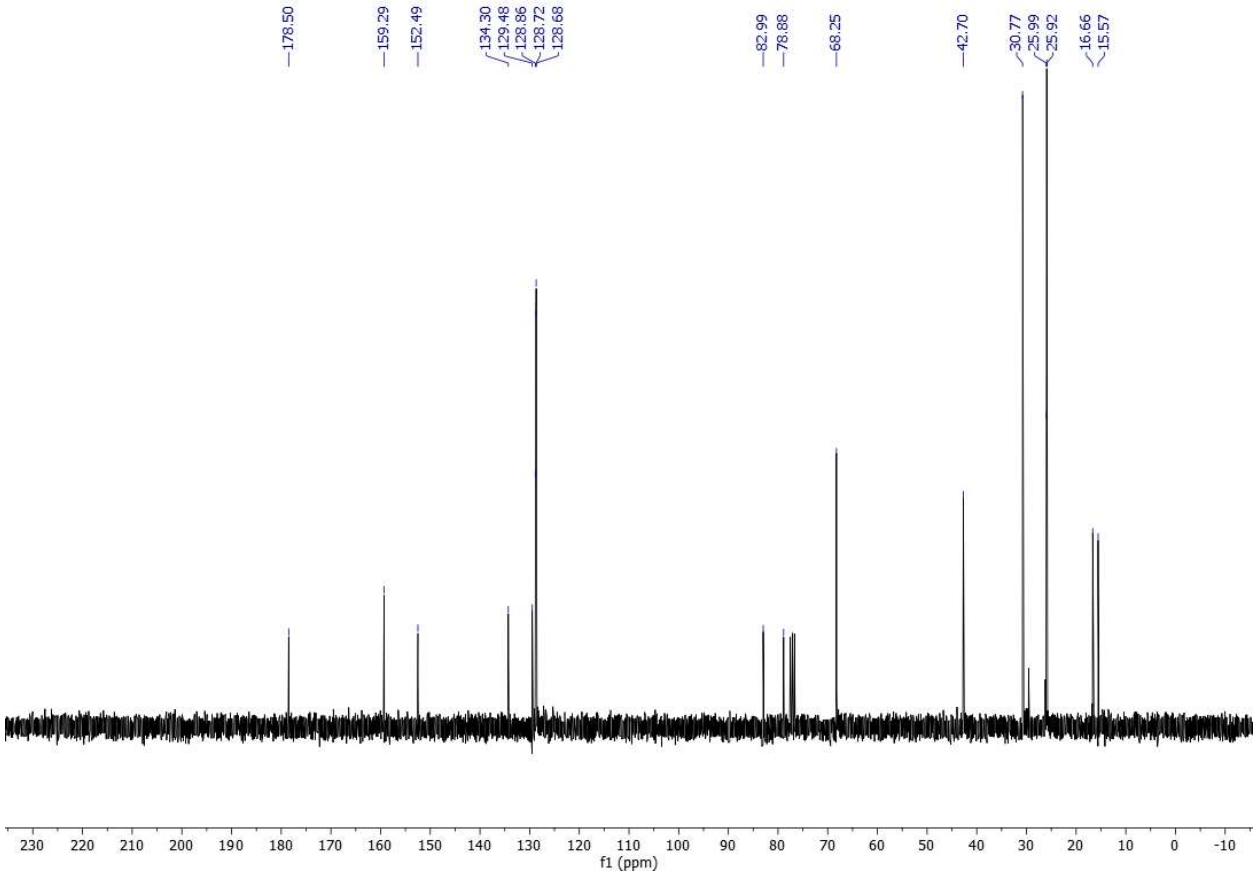


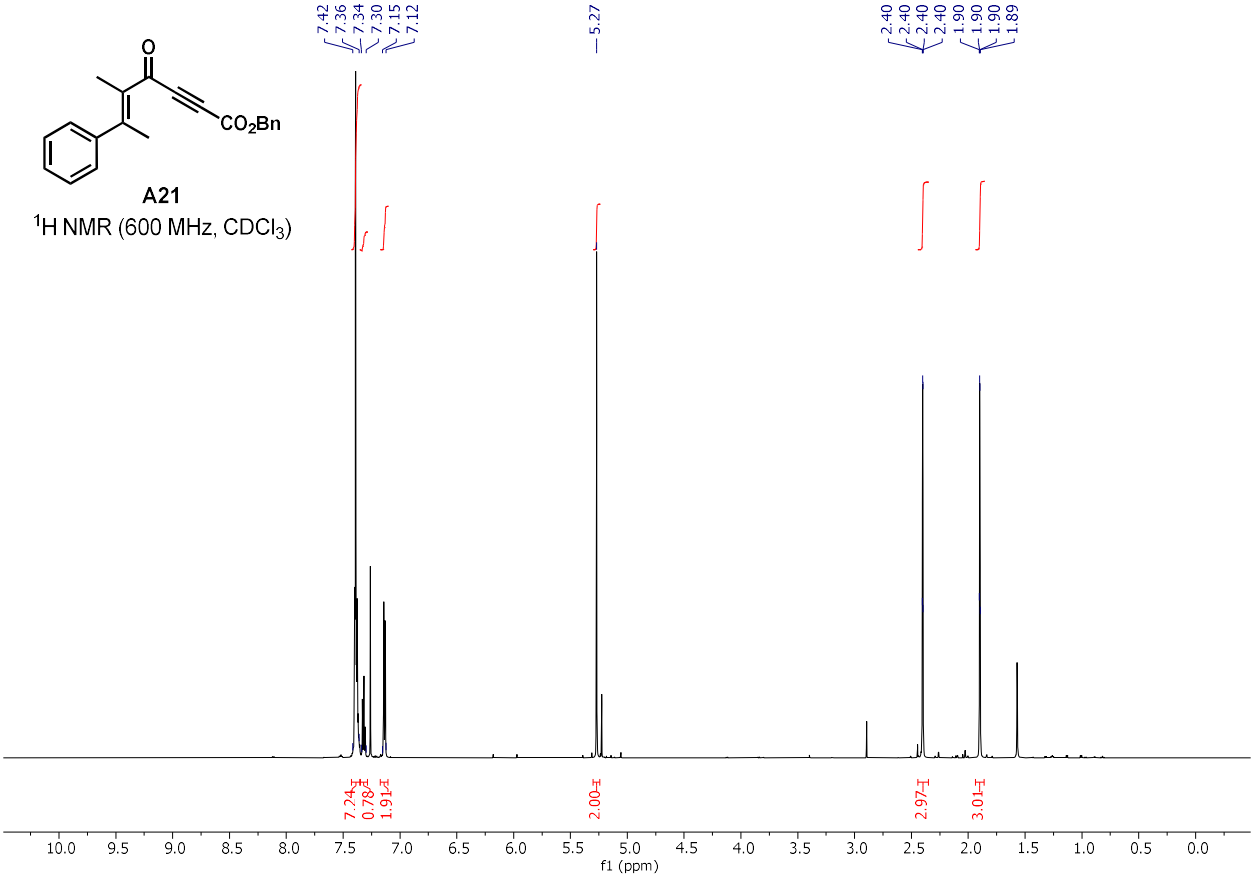
A19

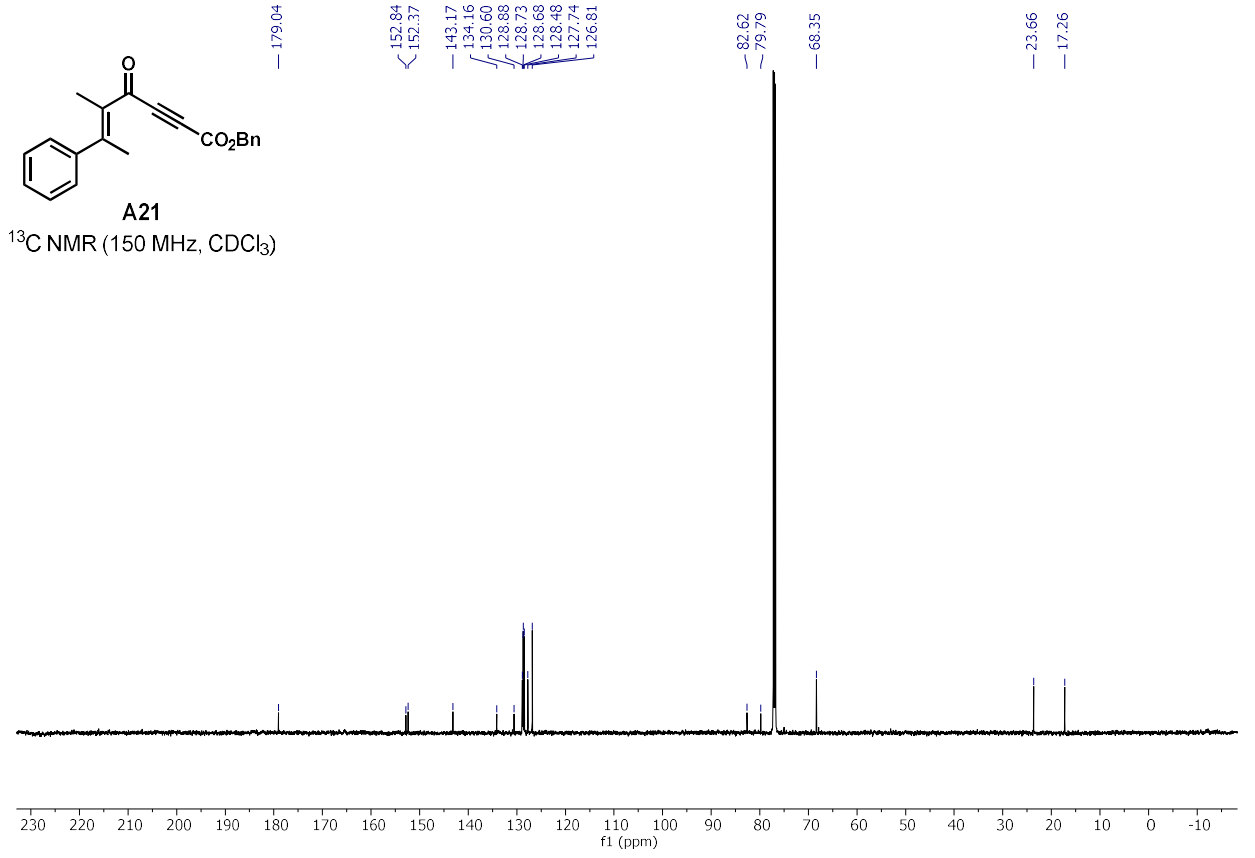
^{1}H NMR (300 MHz, $CDCl_3$)

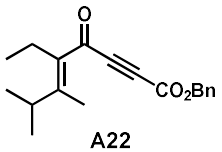
A19

^{13}C NMR (75 MHz, $CDCl_3$)


178.50
159.29
152.49
134.30
129.48
128.86
128.72
128.68
82.99
78.88
68.25
42.70
30.77
25.99
25.92
16.66
15.57
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

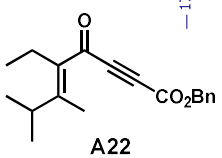

A21
1H NMR (600 MHz, CDCl3)
7.42
7.36
7.34
7.30
7.15
7.12
5.27
2.40
2.40
2.40
2.40
1.90
1.90
1.90
1.89
7.24
0.78
1.91
2.00
2.97
3.01
f1 (ppm)


A21
13C NMR (150 MHz, CDCl3)
179.04
152.84
152.37
143.17
134.16
130.60
128.88
128.73
128.68
128.48
127.74
126.81
82.62
79.79
68.35
23.66
17.26
f1 (ppm)



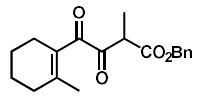
A22

^{1}H NMR (300 MHz, $CDCl_3$)
contaminated with benzyl propiolate



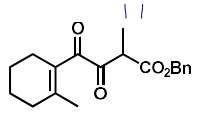
A22

^{13}C NMR (300 MHz, $CDCl_3$)
contaminated with benzyl propiolate



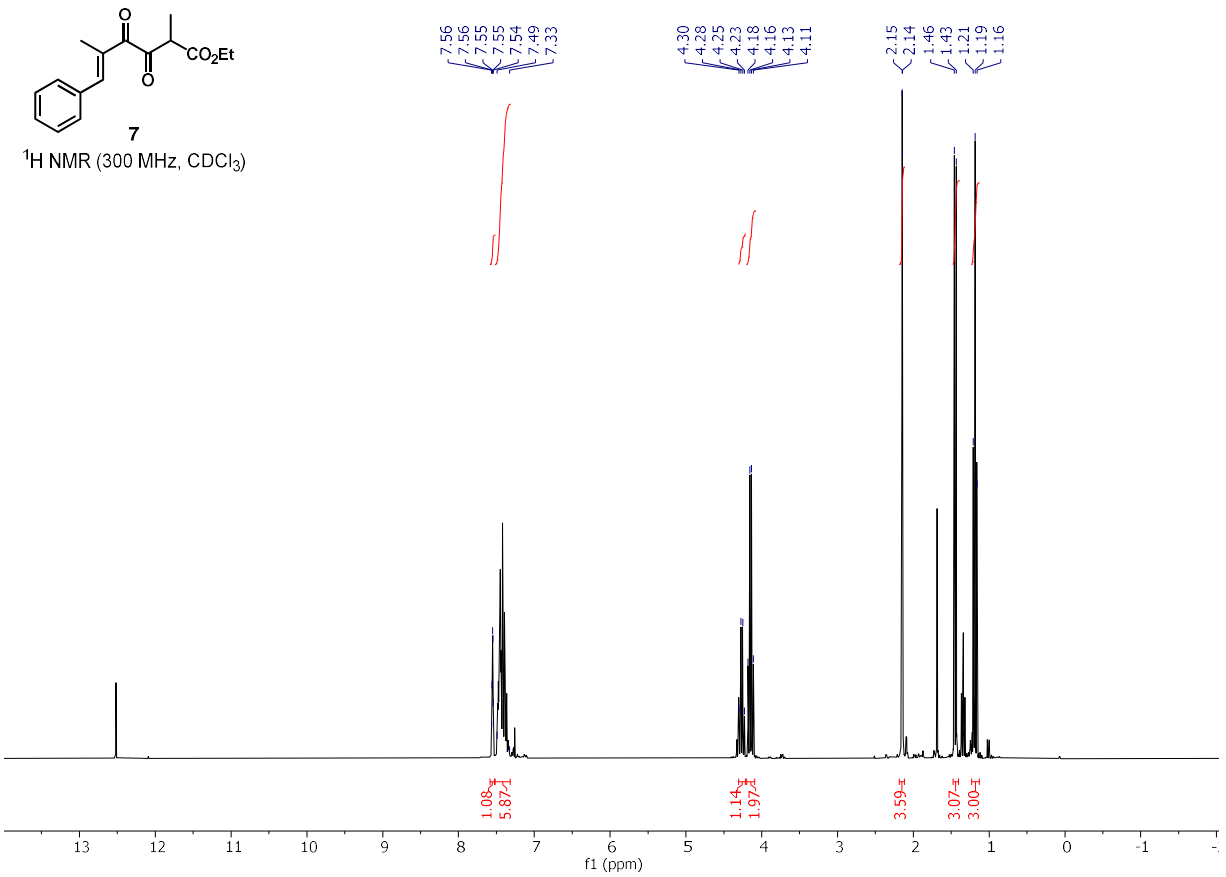
6

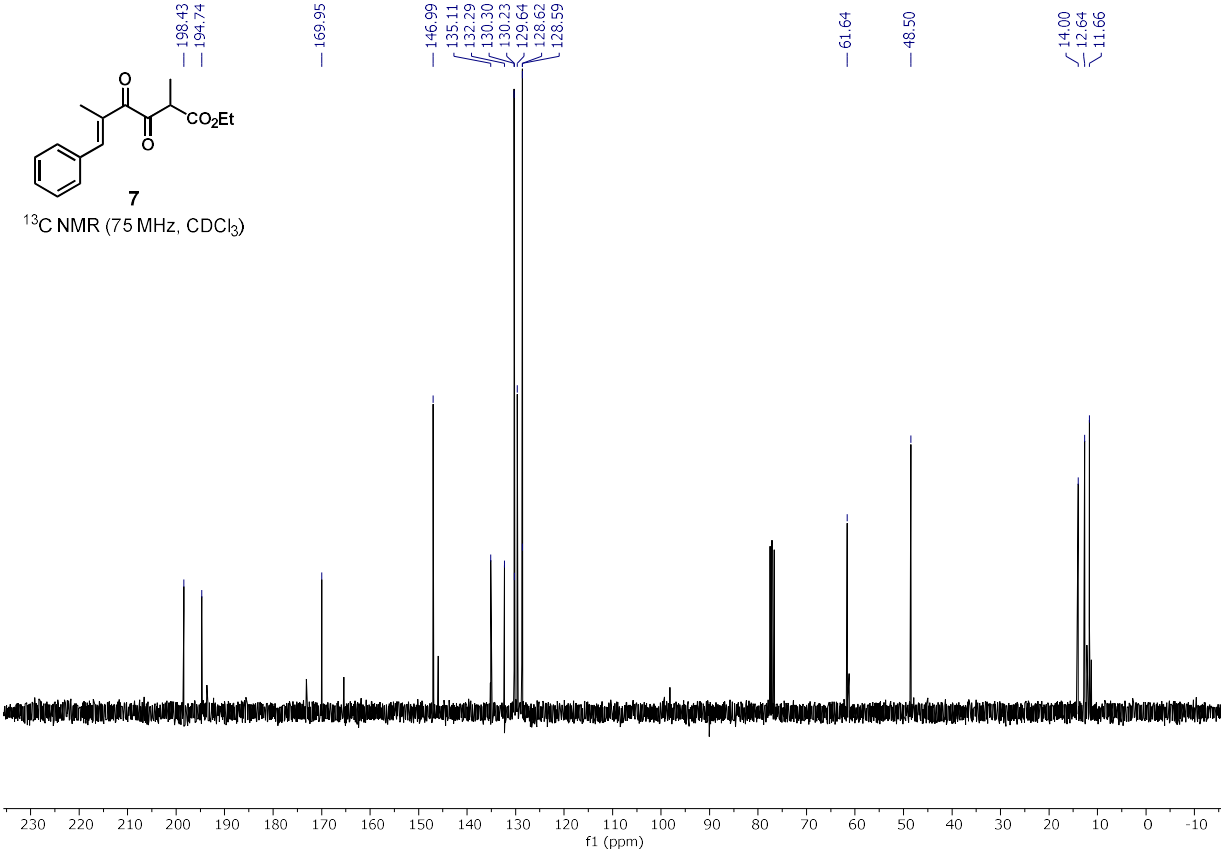
^{1}H NMR (300 MHz, $CDCl_3$)

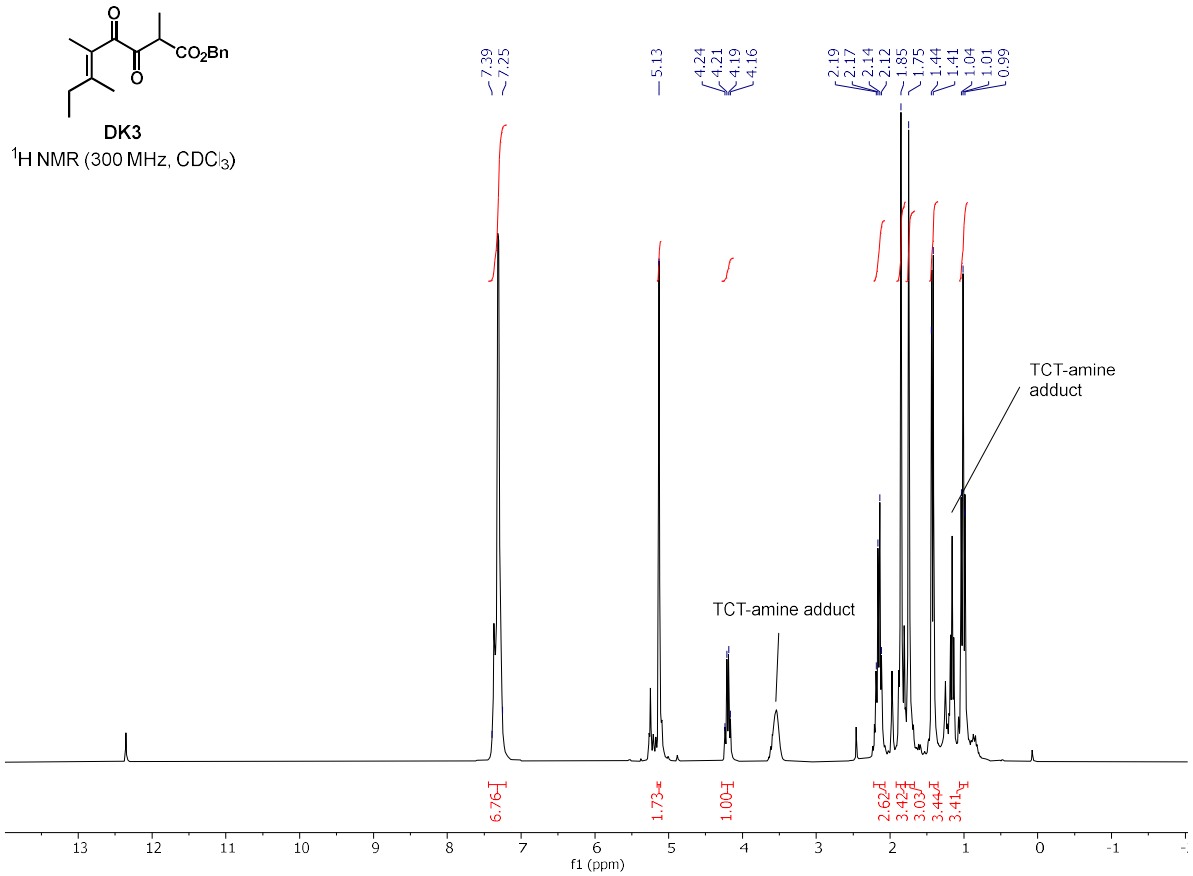


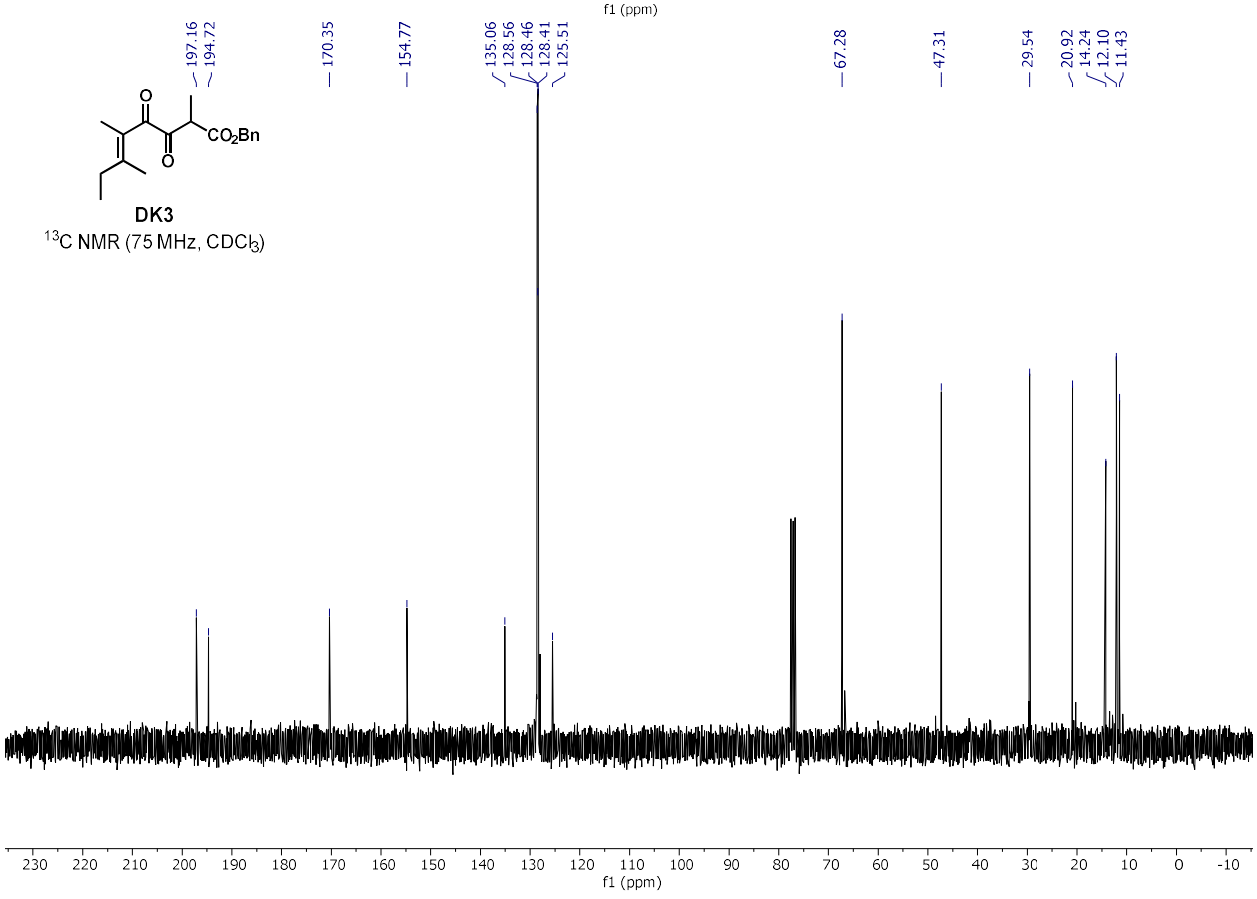
6

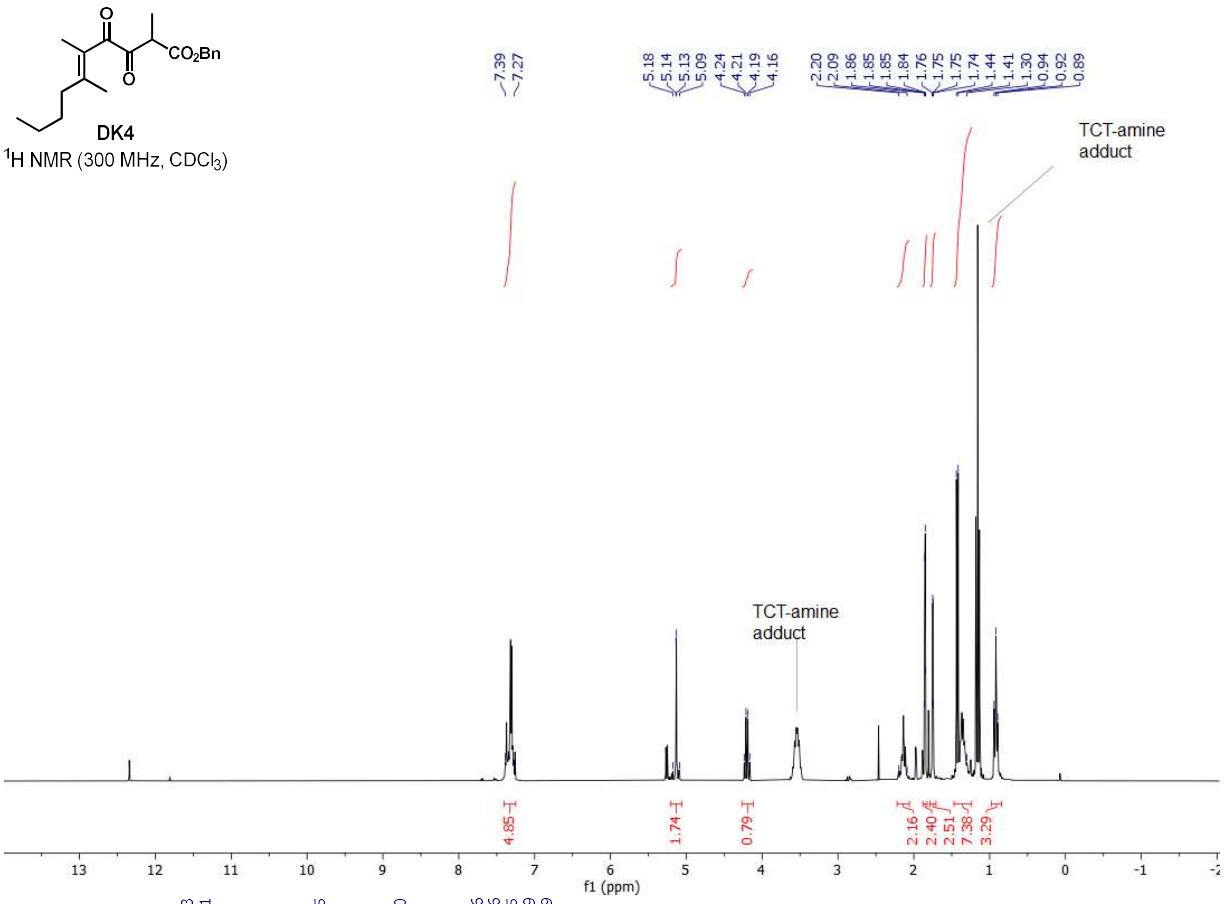
^{13}C NMR (75 MHz, $CDCl_3$)

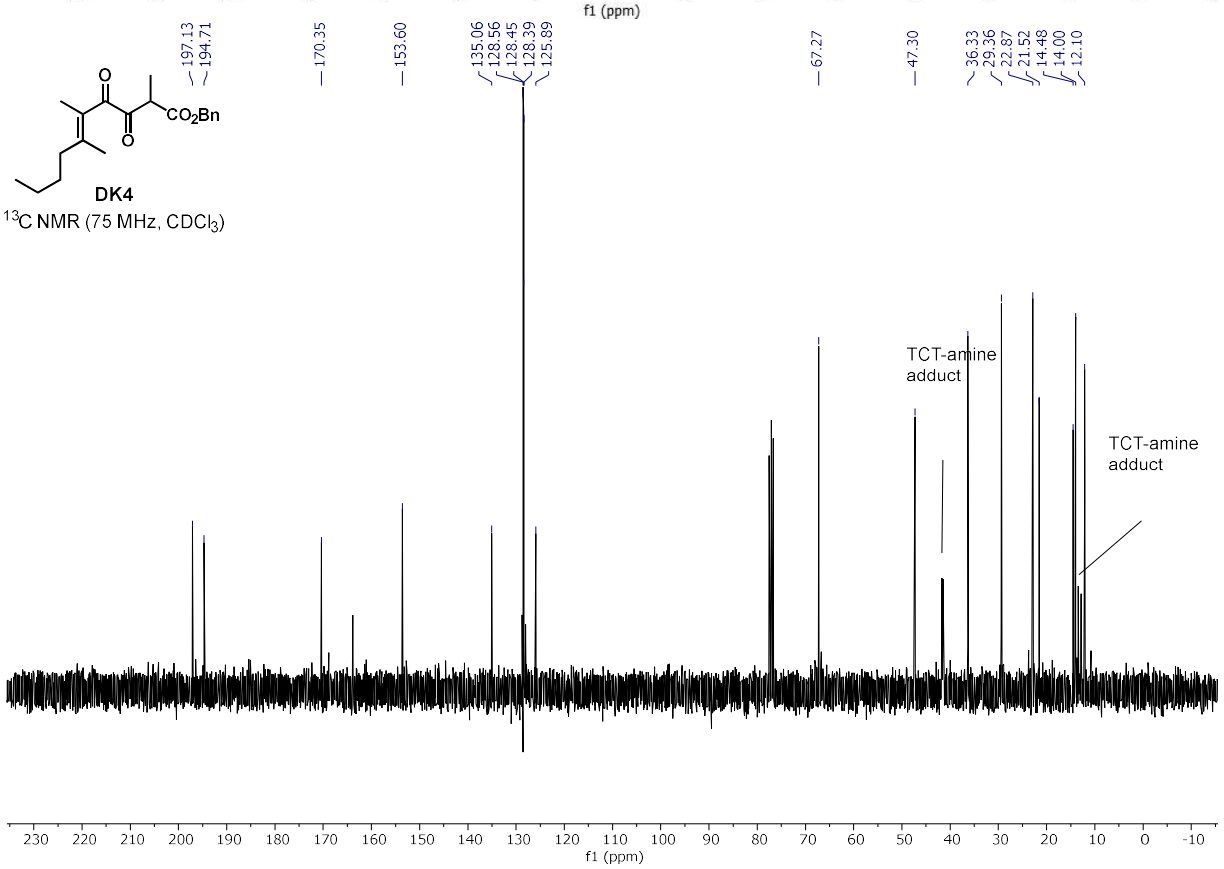

7
^{1}H NMR (300 MHz, $CDCl_3$)
7.56
7.56
7.55
7.55
7.54
7.49
7.33
4.30
4.28
4.25
4.23
4.18
4.16
4.13
4.11
2.15
2.14
1.46
1.43
1.21
1.19
1.16
1.08
5.87
1.14
1.97
3.59
3.07
3.00
f1 (ppm)

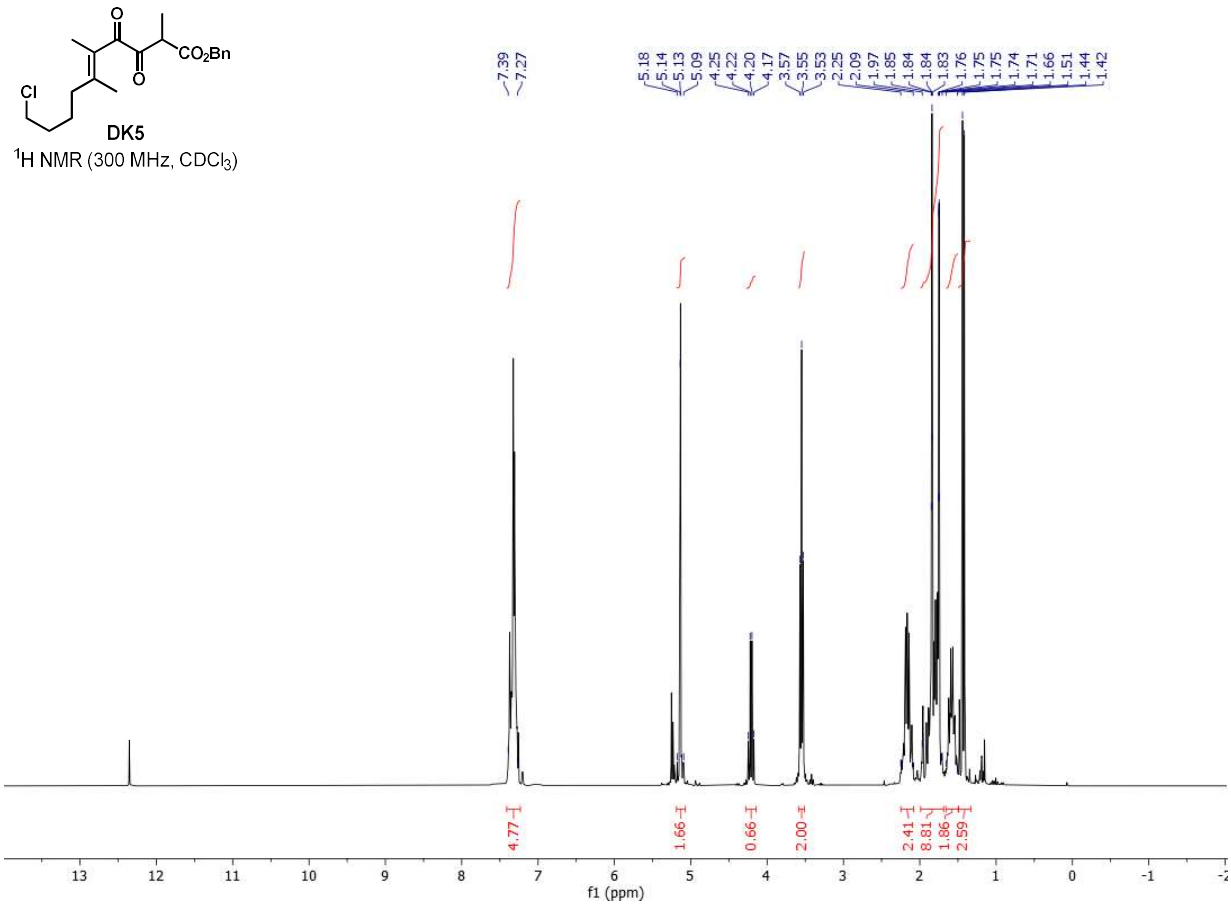

7
^{13}C NMR (75 MHz, $CDCl_3$)
198.43
194.74
169.95
146.99
135.11
132.29
130.30
130.23
129.64
128.62
128.59
61.64
48.50
14.00
12.64
11.66
f1 (ppm)

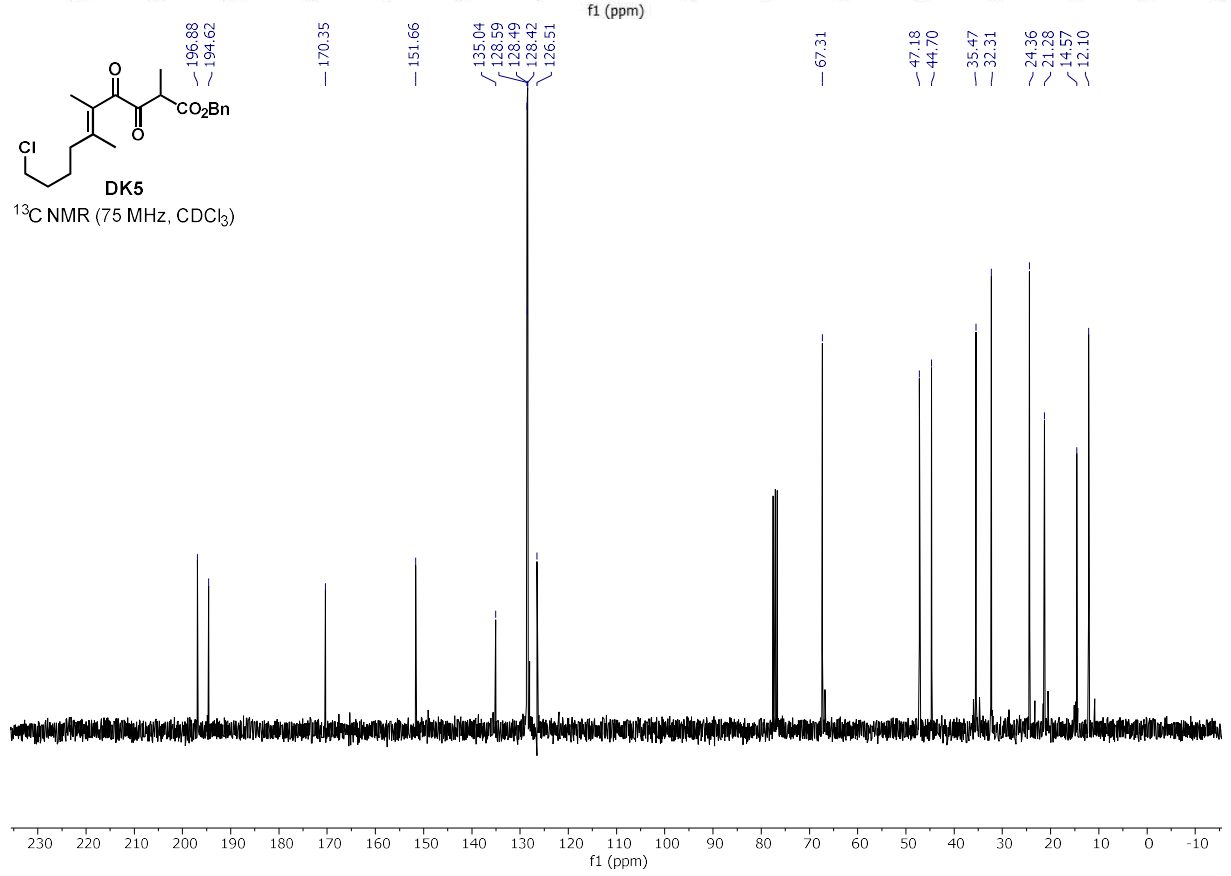

DK3
^{1}H NMR (300 MHz, $CDCl_3$)
7.39
7.25
5.13
4.24
4.21
4.19
4.16
2.19
2.17
2.14
2.12
1.85
1.75
1.44
1.41
1.04
1.01
0.99
TCT-amine adduct
TCT-amine adduct
6.76
1.73
1.00
2.62
3.42
3.03
3.44
3.41
f1 (ppm)

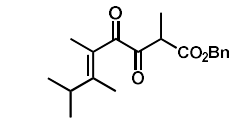

DK3
^{13}C NMR (75 MHz, $CDCl_3$)
197.16
194.72
170.35
154.77
135.06
128.56
128.46
128.41
125.51
67.28
47.31
29.54
20.92
14.24
12.10
11.43
f1 (ppm)


DK4
^{1}H NMR (300 MHz, $CDCl_3$)
TCT-amine adduct
TCT-amine adduct
f1 (ppm)


DK4
^{13}C NMR (75 MHz, $CDCl_3$)
TCT-amine adduct
TCT-amine adduct
f1 (ppm)

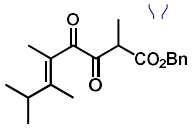

DK5
^{1}H NMR (300 MHz, $CDCl_3$)
7.39
7.27
5.18
5.14
5.13
5.09
4.25
4.22
4.20
4.17
3.57
3.55
3.53
2.25
2.09
1.97
1.85
1.84
1.84
1.83
1.76
1.75
1.75
1.74
1.71
1.66
1.51
1.44
1.42
4.77
1.66
0.66
2.00
2.41
8.81
1.86
2.59
f1 (ppm)


DK5
^{13}C NMR (75 MHz, $CDCl_3$)
196.88
194.62
170.35
151.66
135.04
128.59
128.49
128.42
126.51
67.31
47.18
44.70
35.47
32.31
24.36
21.28
14.57
12.10
f1 (ppm)



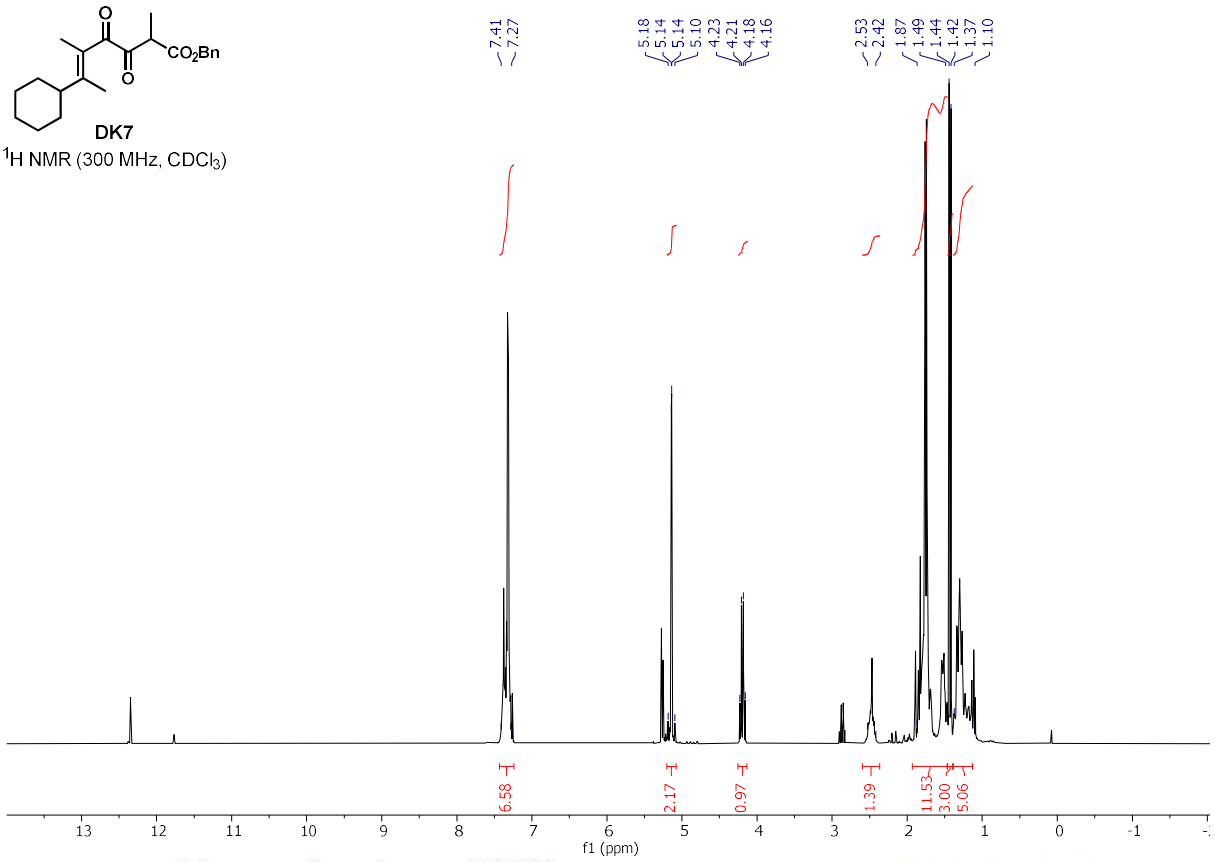
DK6

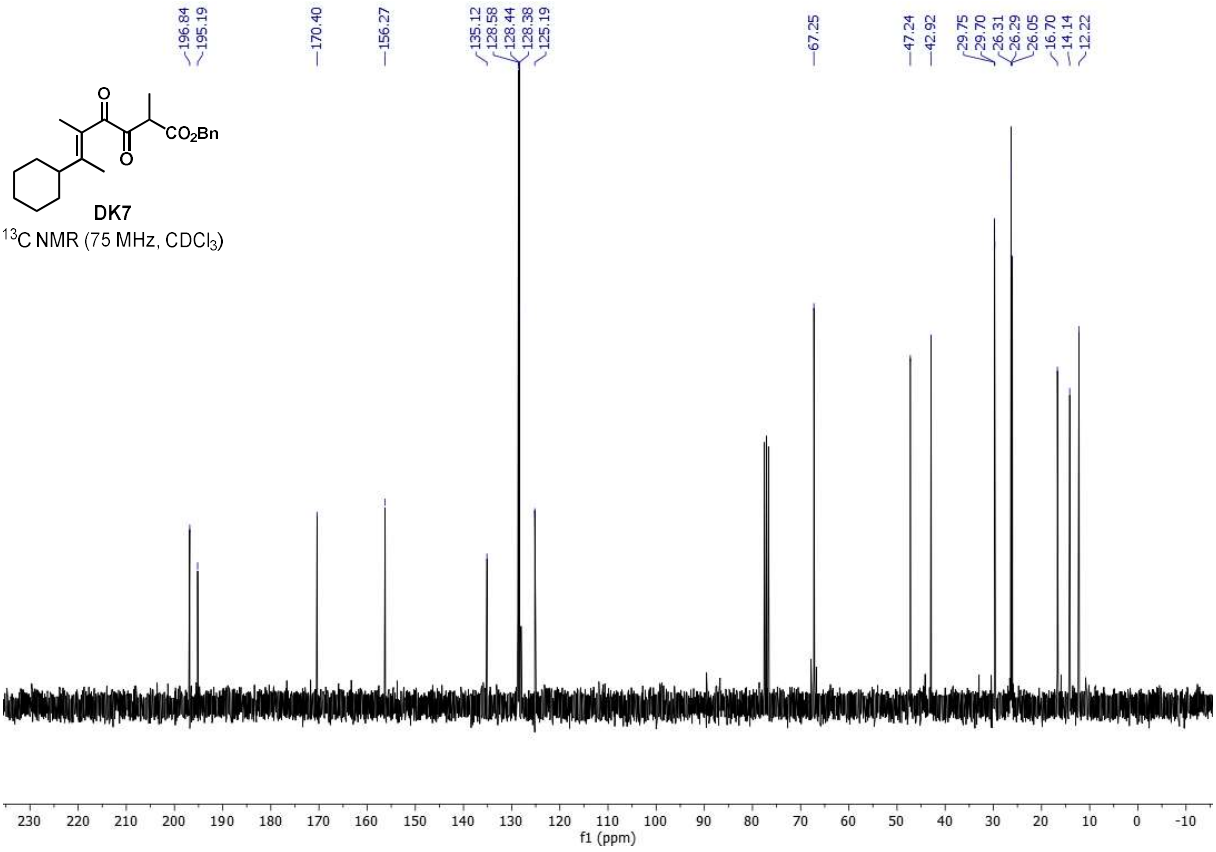
^{1}H NMR (300 MHz, $CDCl_3$)

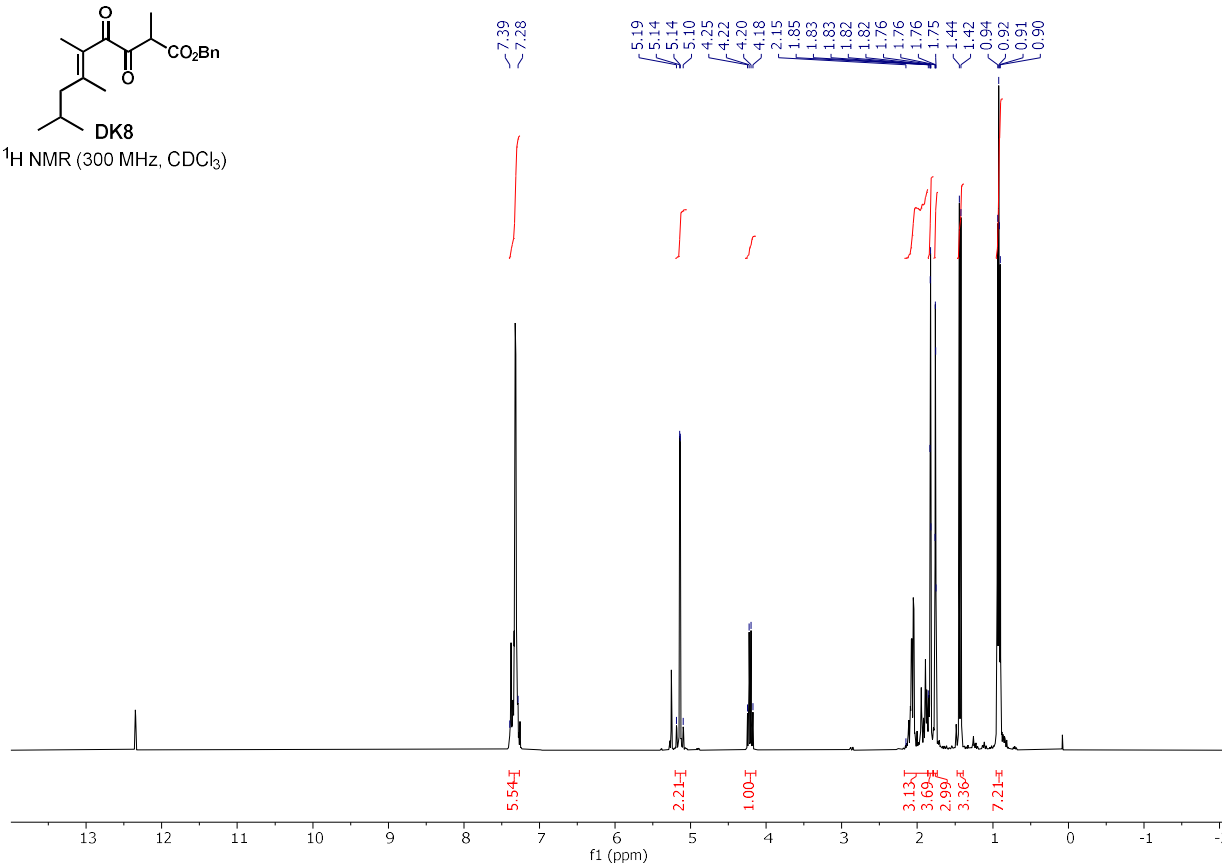


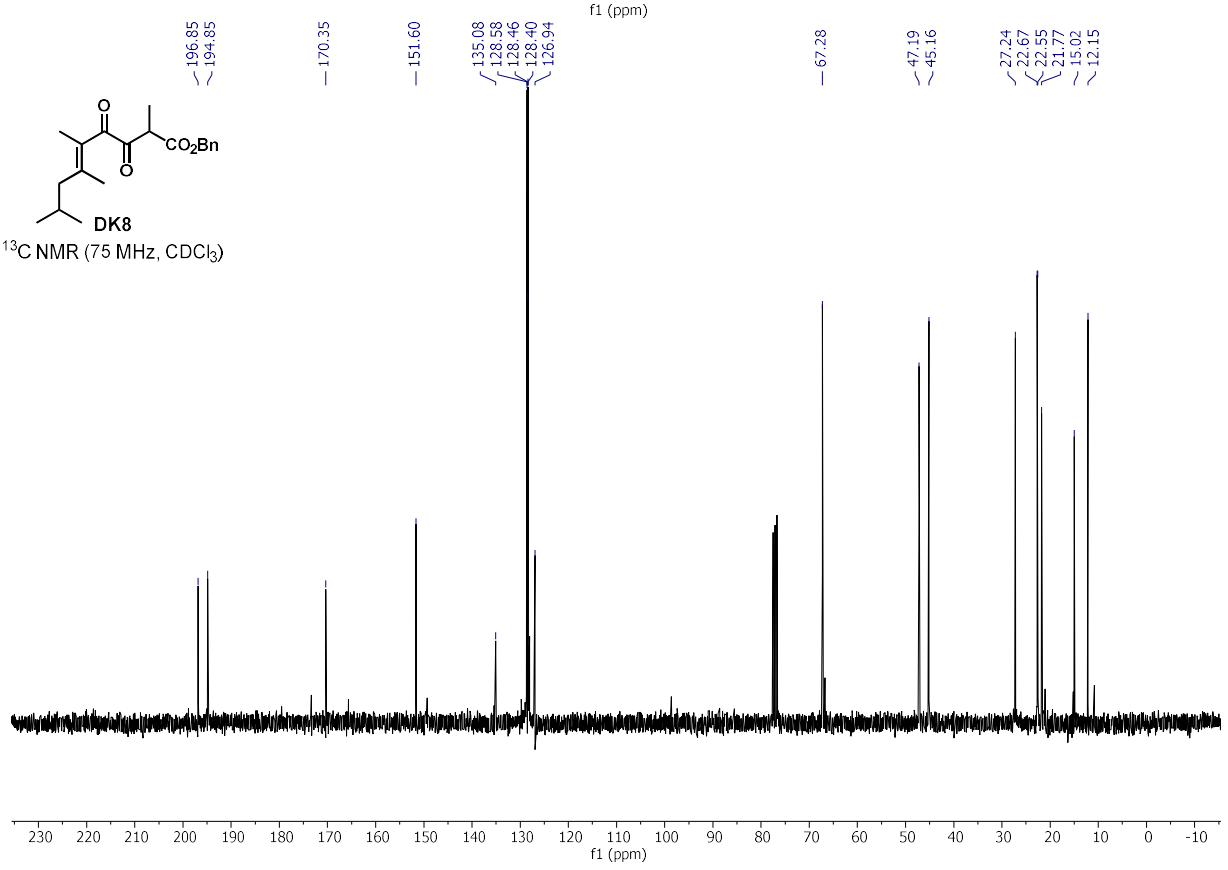
DK6

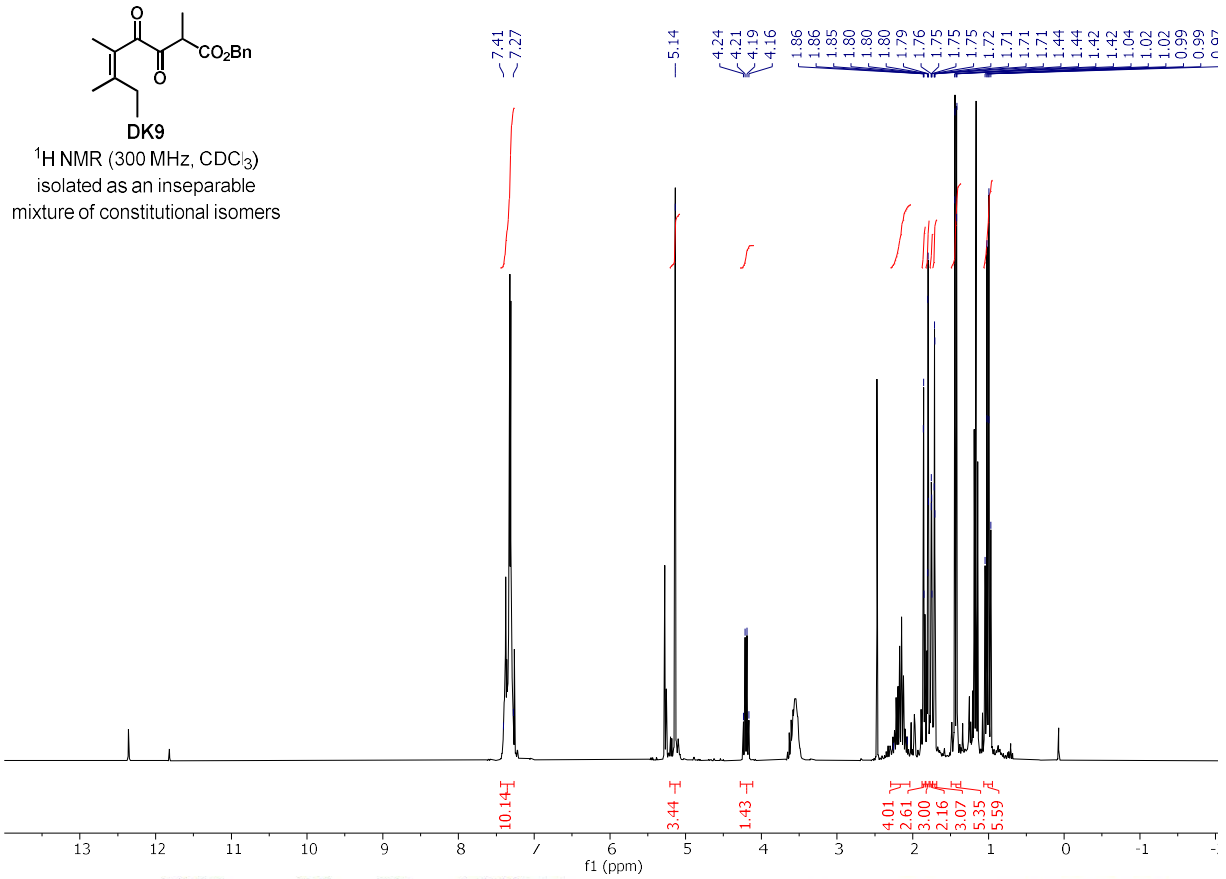
^{13}C NMR (75 MHz, $CDCl_3$)

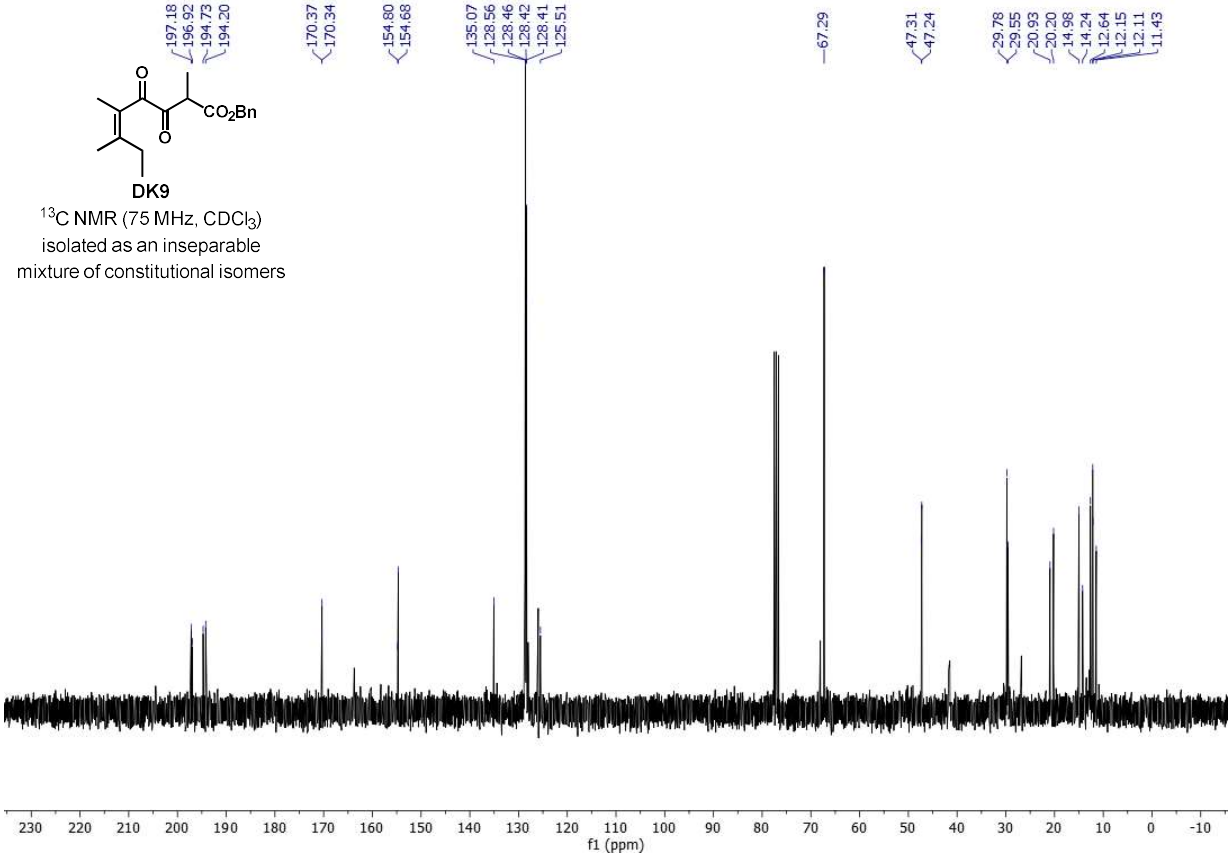

DK7
1H NMR (300 MHz, CDCl3)
7.41
7.27
5.18
5.14
5.14
5.10
4.23
4.21
4.18
4.16
2.53
2.42
1.87
1.49
1.44
1.42
1.37
1.10
6.58
2.17
0.97
1.39
11.53
3.00
5.06
f1 (ppm)

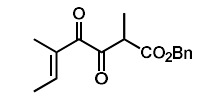

DK7
13C NMR (75 MHz, CDCl3)
196.84
195.19
170.40
156.27
135.12
128.58
128.44
128.38
125.19
67.25
47.24
42.92
29.75
29.70
26.31
26.29
26.05
16.70
14.14
12.22
f1 (ppm)


DK8
^{1}H NMR (300 MHz, $CDCl_3$)
7.39
7.28
5.19
5.14
5.14
5.10
4.25
4.22
4.20
4.18
2.15
1.85
1.83
1.83
1.82
1.82
1.76
1.76
1.76
1.75
1.44
1.42
0.94
0.92
0.91
0.90
5.54
2.21
1.00
3.13
3.69
2.99
3.36
7.21
f1 (ppm)


DK8
^{13}C NMR (75 MHz, $CDCl_3$)
196.85
194.85
170.35
151.60
135.08
128.58
128.46
128.40
126.94
67.28
47.19
45.16
27.24
22.67
22.55
21.77
15.02
12.15
f1 (ppm)

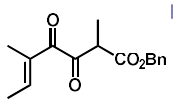

DK9
^{1}H NMR (300 MHz, $CDCl_3$)
isolated as an inseparable
mixture of constitutional isomers
f1 (ppm)


DK9
^{13}C NMR (75 MHz, $CDCl_3$)
isolated as an inseparable
mixture of constitutional isomers
f1 (ppm)



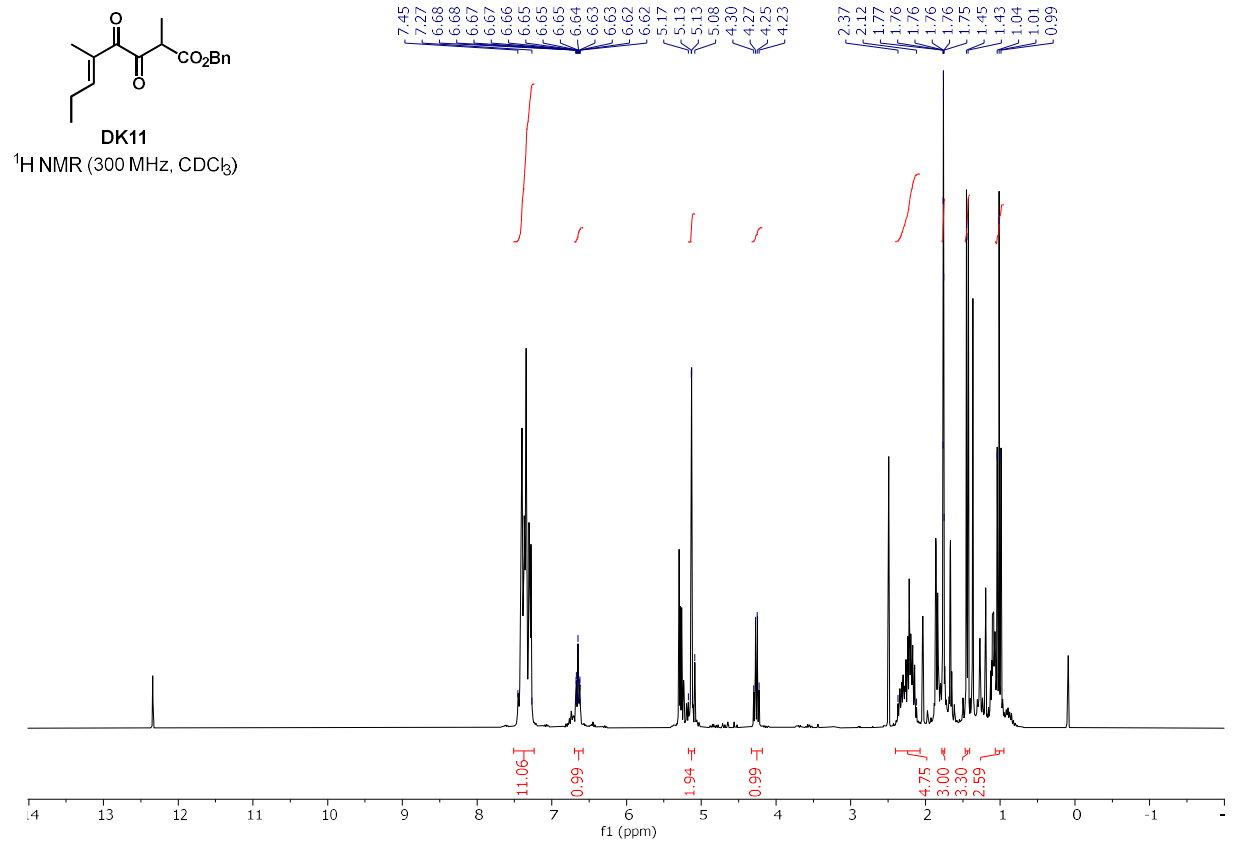
DK10

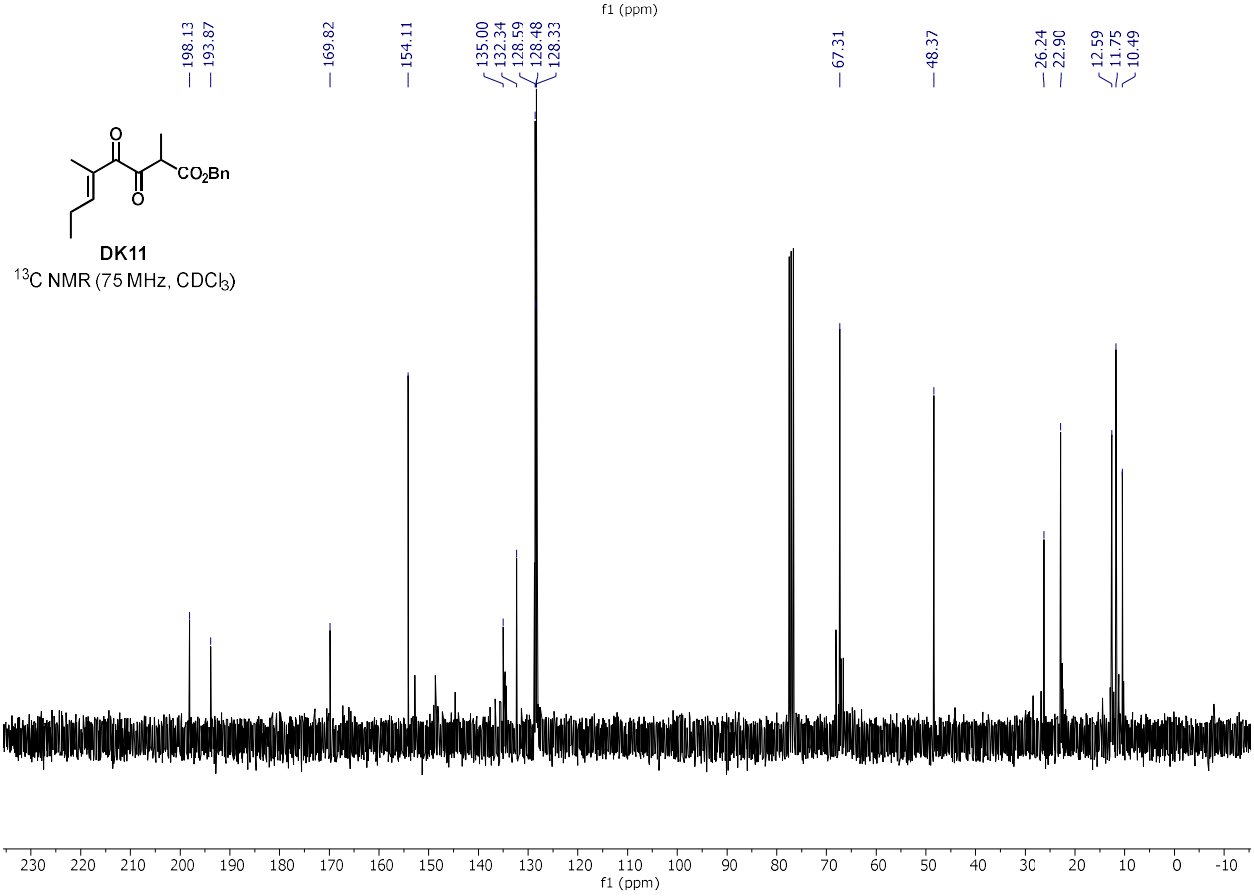
^{1}H NMR (300 MHz, $CDCl_3$)

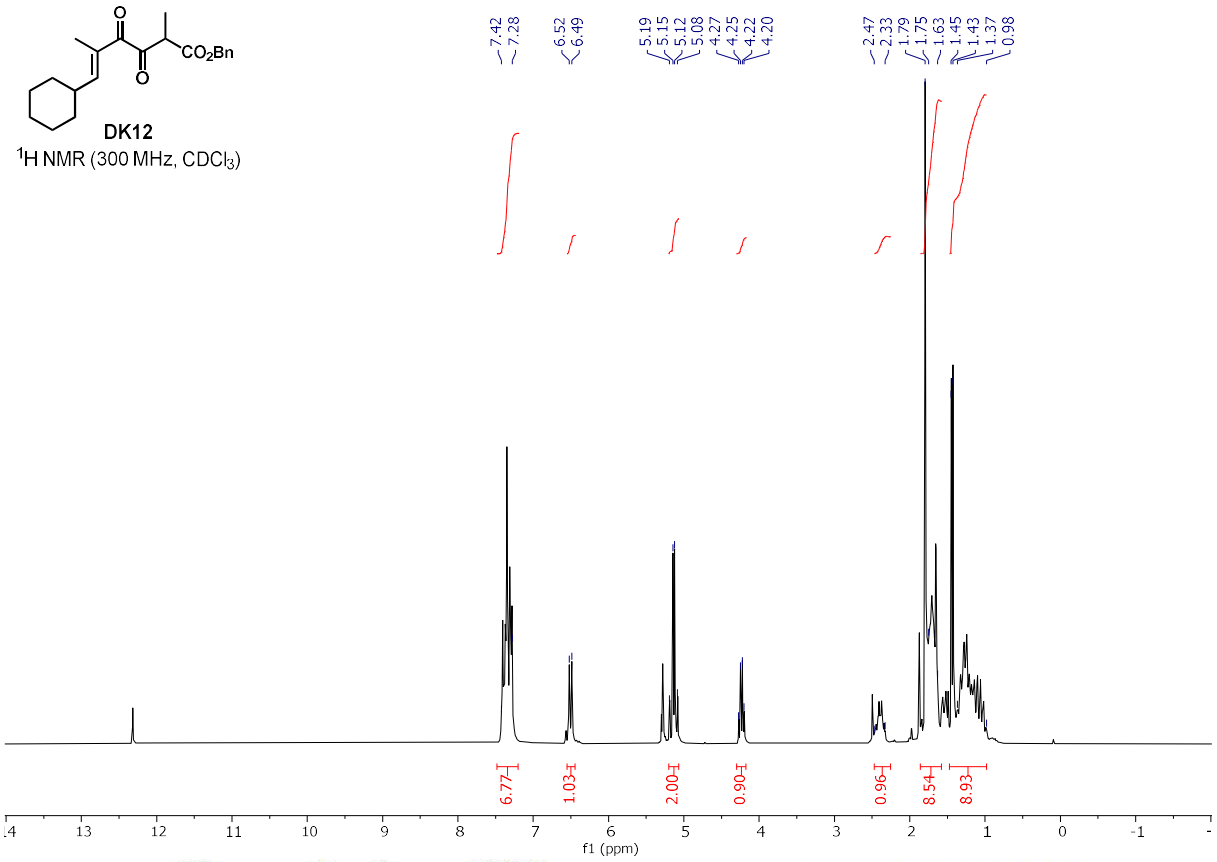


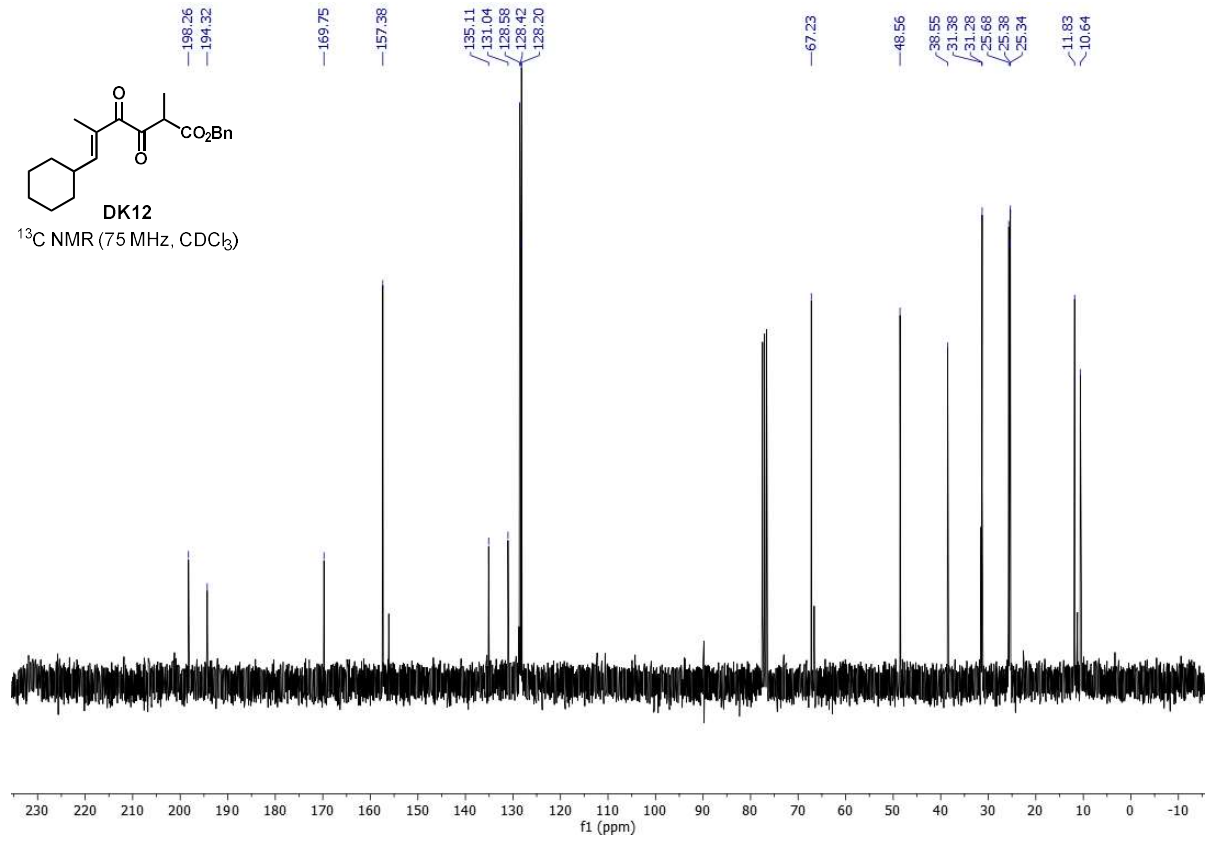
DK10

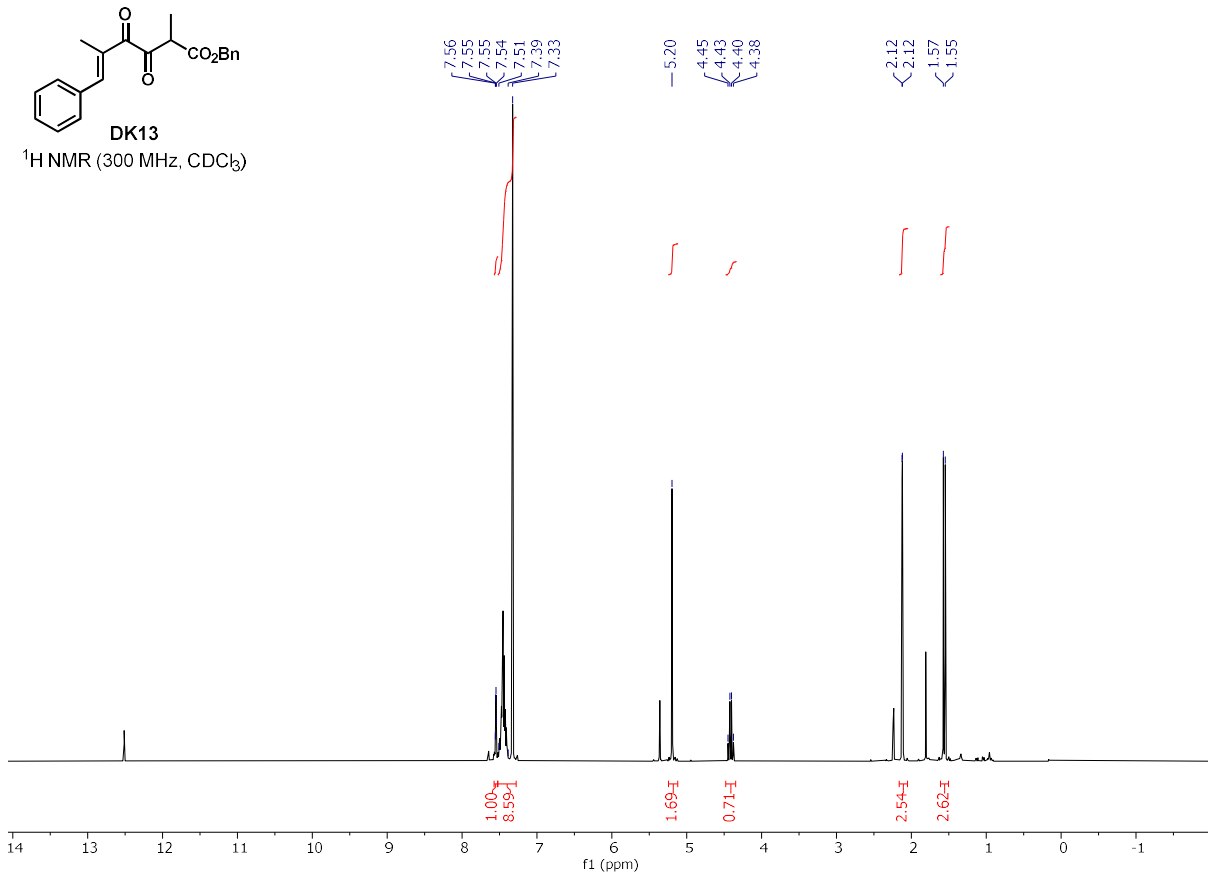
^{13}C NMR (75 MHz, $CDCl_3$)

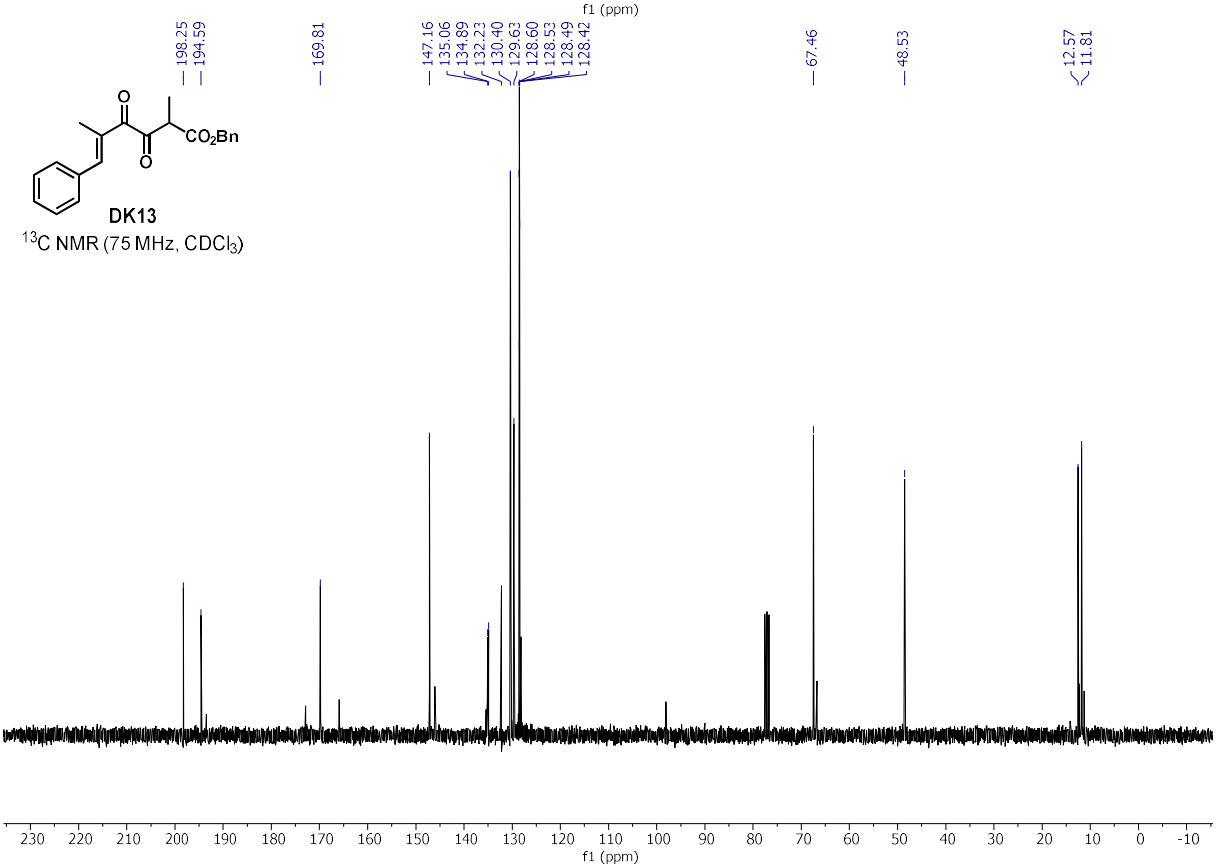

DK11
1H NMR (300 MHz, CDCl3)
7.45
7.27
6.68
6.68
6.67
6.67
6.66
6.65
6.65
6.65
6.64
6.63
6.63
6.62
6.62
5.17
5.13
5.13
5.08
4.30
4.27
4.25
4.23
2.37
2.12
1.77
1.76
1.76
1.76
1.76
1.75
1.45
1.43
1.04
1.01
0.99
11.06
0.99
1.94
0.99
4.75
3.00
3.30
2.59
f1 (ppm)

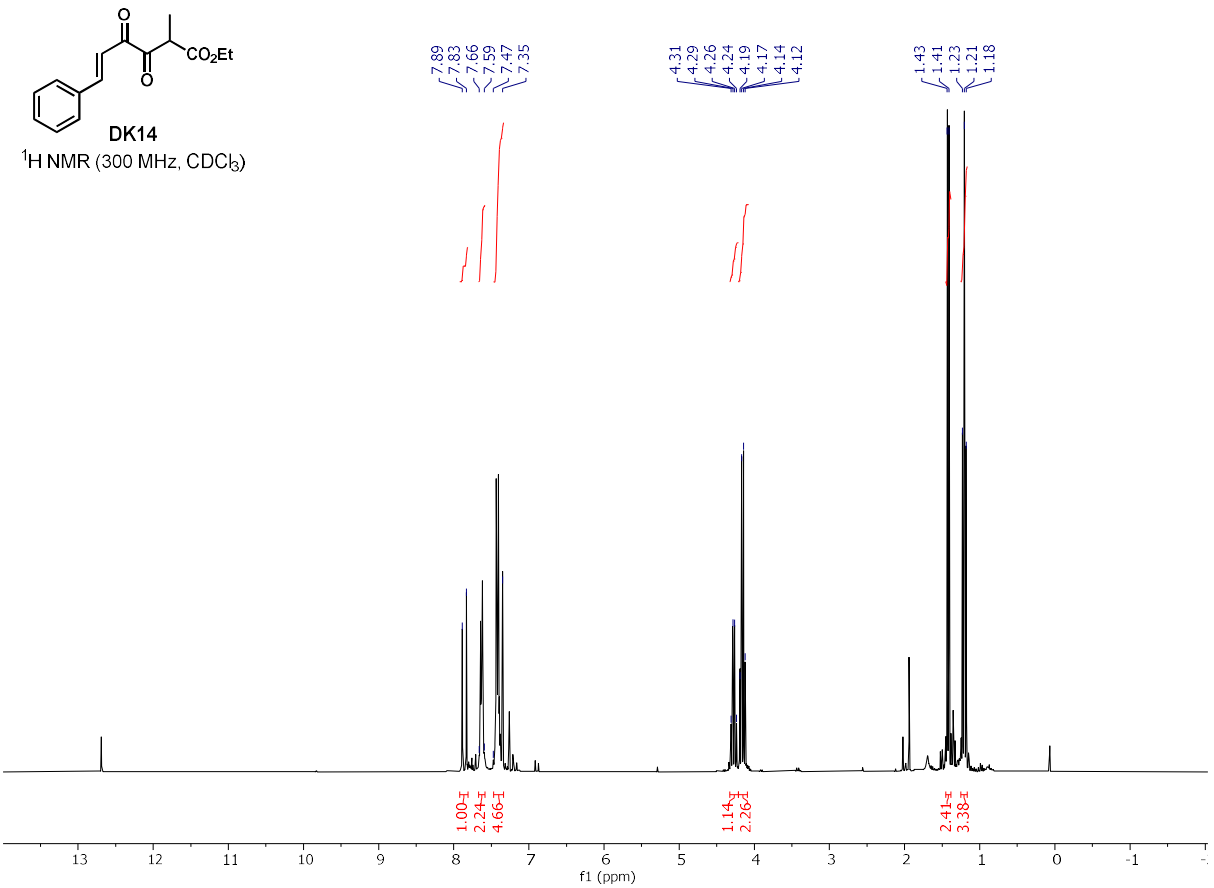

DK11
13C NMR (75 MHz, CDCl3)
198.13
193.87
169.82
154.11
135.00
132.34
128.59
128.48
128.33
67.31
48.37
26.24
22.90
12.59
11.75
10.49
f1 (ppm)

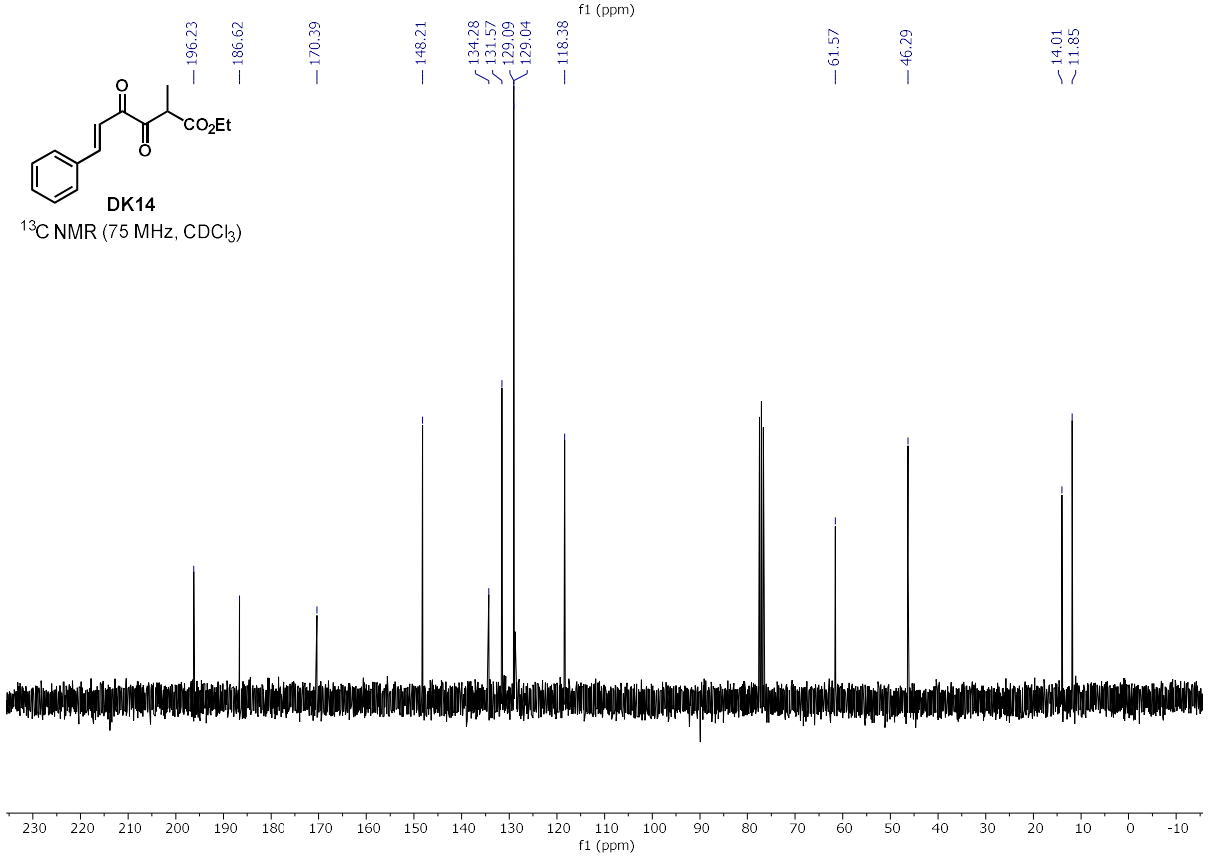

DK12
1H NMR (300 MHz, CDCl3)
7.42
7.28
6.52
6.49
5.19
5.15
5.12
5.08
4.27
4.25
4.22
4.20
2.47
2.33
1.79
1.75
1.63
1.45
1.43
1.37
0.98
6.77
1.03
2.00
0.90
0.96
8.54
8.93
f1 (ppm)

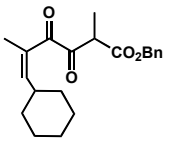

DK12
13C NMR (75 MHz, CDCl3)
198.26
194.32
169.75
157.38
135.11
131.04
128.58
128.42
128.20
67.23
48.56
38.55
31.38
31.28
25.68
25.38
25.34
11.83
10.64
f1 (ppm)


DK13
^{1}H NMR (300 MHz, $CDCl_3$)
7.56
7.55
7.55
7.54
7.51
7.39
7.33
5.20
4.45
4.43
4.40
4.38
2.12
2.12
1.57
1.55
1.00
8.59
1.69
0.71
2.54
2.62
f1 (ppm)


DK13
^{13}C NMR (75 MHz, $CDCl_3$)
198.25
194.59
169.81
147.16
135.06
134.89
132.23
130.40
129.63
128.60
128.53
128.49
128.42
67.46
48.53
12.57
11.81
f1 (ppm)


DK14
^{1}H NMR (300 MHz, $CDCl_3$)
7.89
7.83
7.66
7.59
7.47
7.35
4.31
4.29
4.26
4.24
4.19
4.17
4.14
4.12
1.43
1.41
1.23
1.21
1.18
1.00
2.24
4.66
1.14
2.26
2.41
3.38
f1 (ppm)


DK14
^{13}C NMR (75 MHz, $CDCl_3$)
196.23
186.62
170.39
148.21
134.28
131.57
129.09
129.04
118.38
61.57
46.29
14.01
11.85
f1 (ppm)

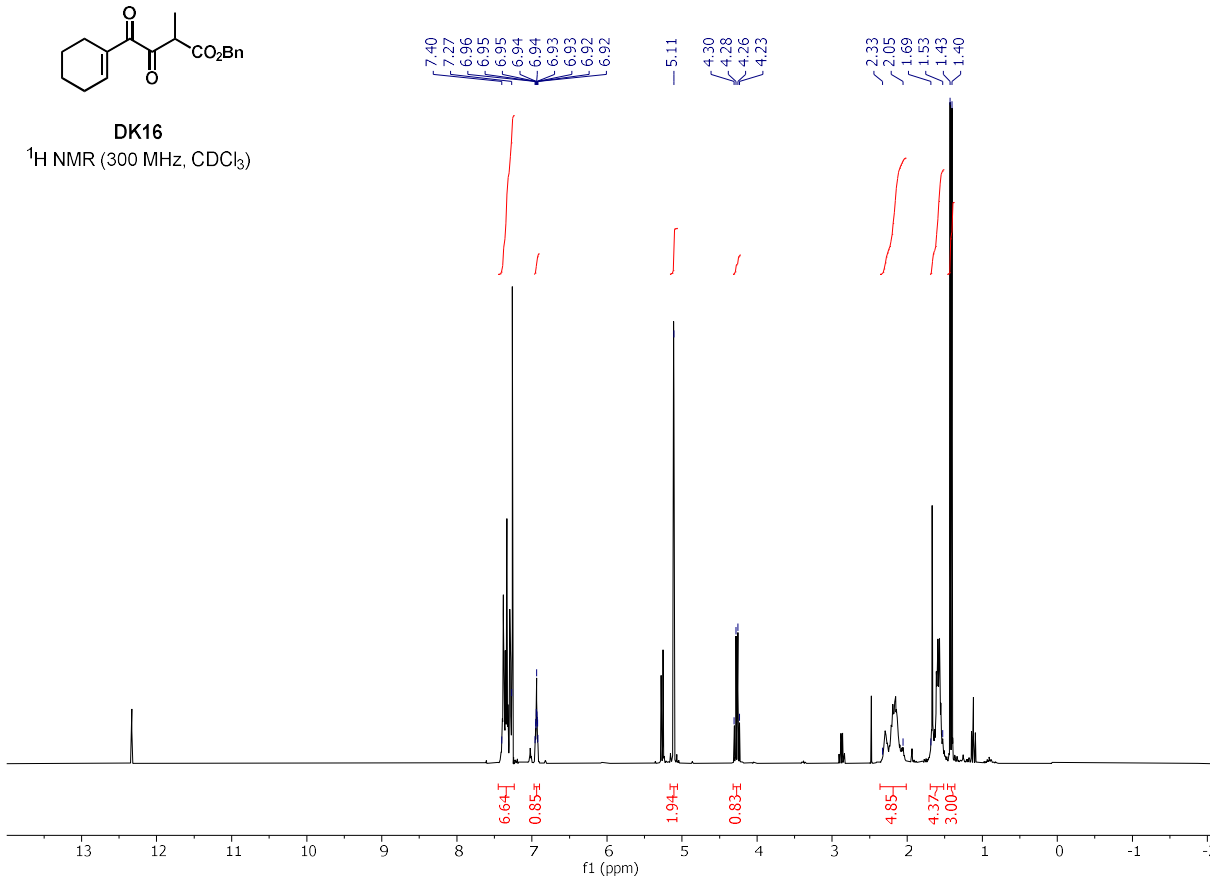


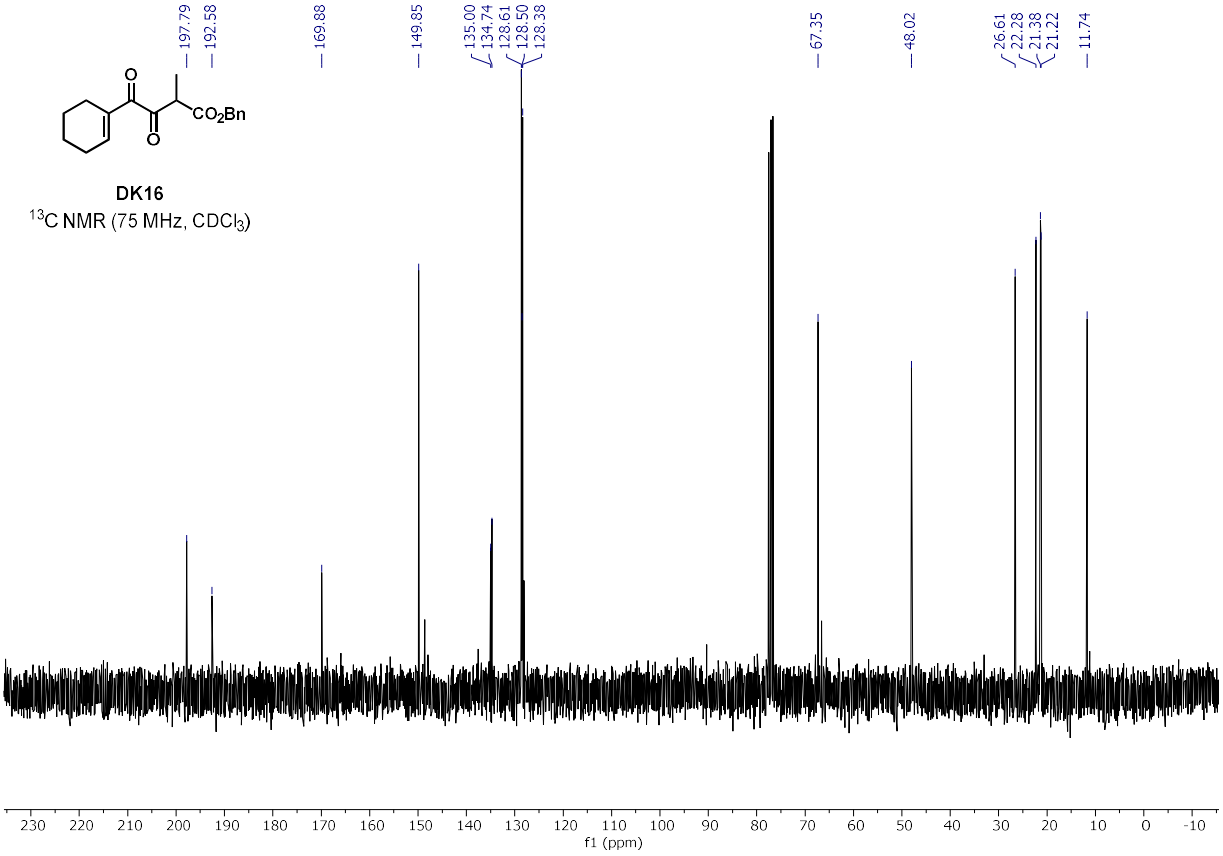
DK15

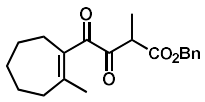
^{1}H NMR (300 MHz, $CDCl_3$)

3-80

^{13}C NMR (75 MHz, $CDCl_3$)

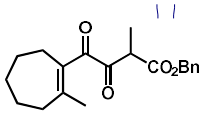

DK16
1H NMR (300 MHz, CDCl3)
7.40
7.27
6.96
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.92
5.11
4.30
4.28
4.26
4.23
2.33
2.05
1.69
1.53
1.43
1.40
6.64
0.85
1.94
0.83
4.85
4.37
3.00
f1 (ppm)


DK16
13C NMR (75 MHz, CDCl3)
197.79
192.58
169.88
149.85
135.00
134.74
128.61
128.50
128.38
67.35
48.02
26.61
22.28
21.38
21.22
11.74
f1 (ppm)



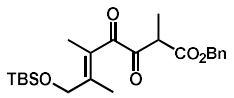
DK17

^{1}H NMR (300 MHz, $CDCl_3$)



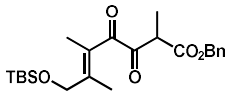
DK17

^{13}C NMR (75 MHz, $CDCl_3$)



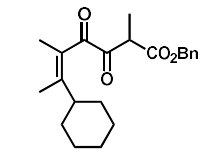
DK18

^{1}H NMR (300 MHz, $CDCl_3$)



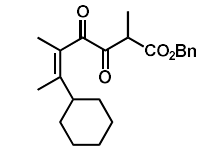
DK18

^{13}C NMR (75 MHz, $CDCl_3$)



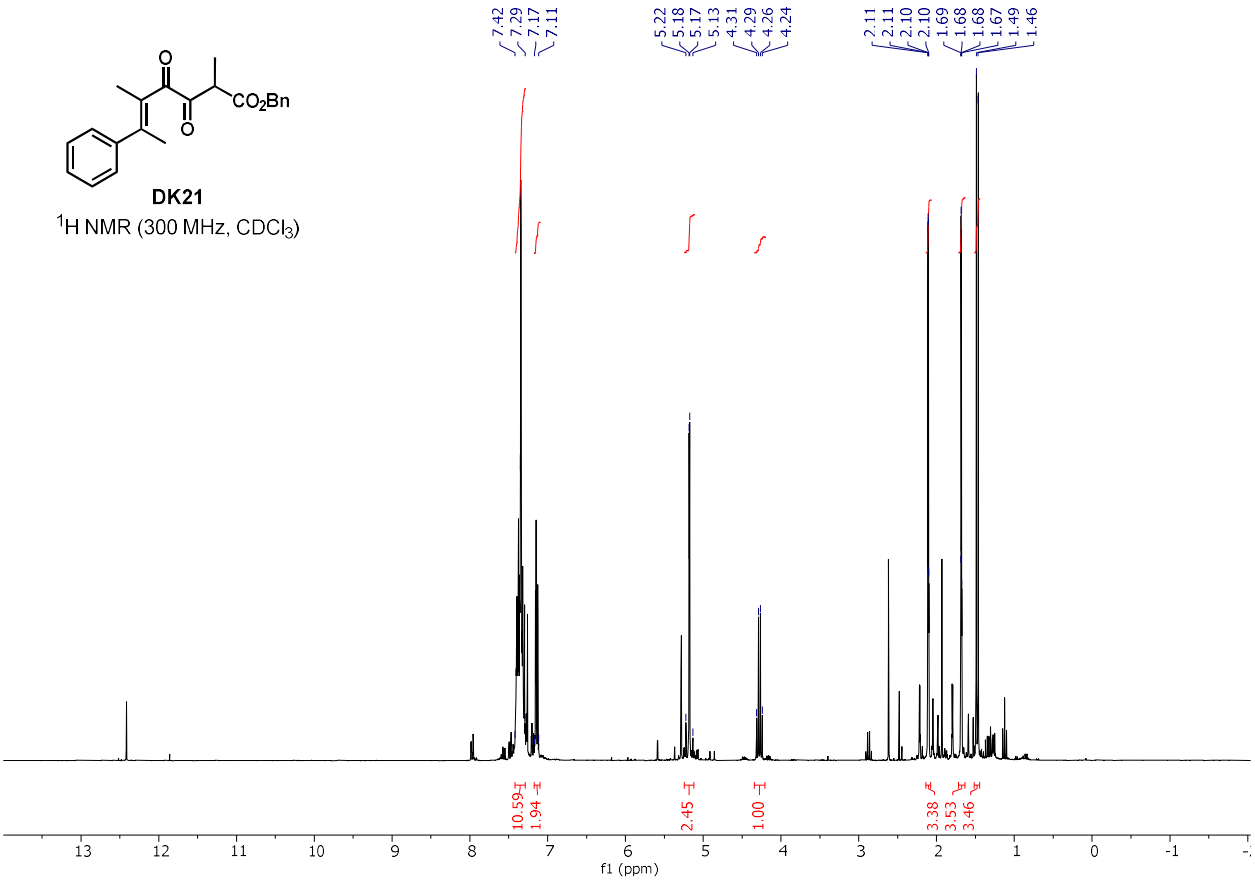
DK19

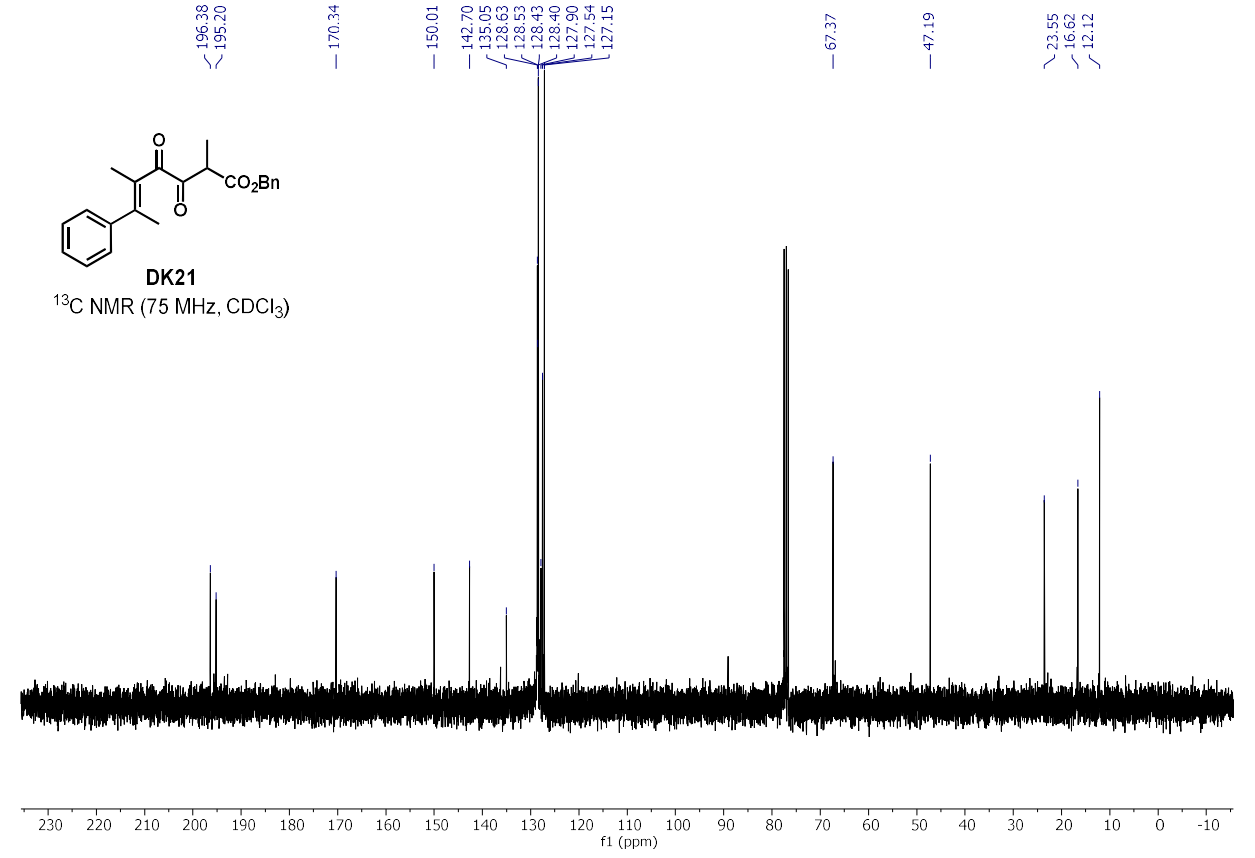
^{1}H NMR (300 MHz, $CDCl_3$)

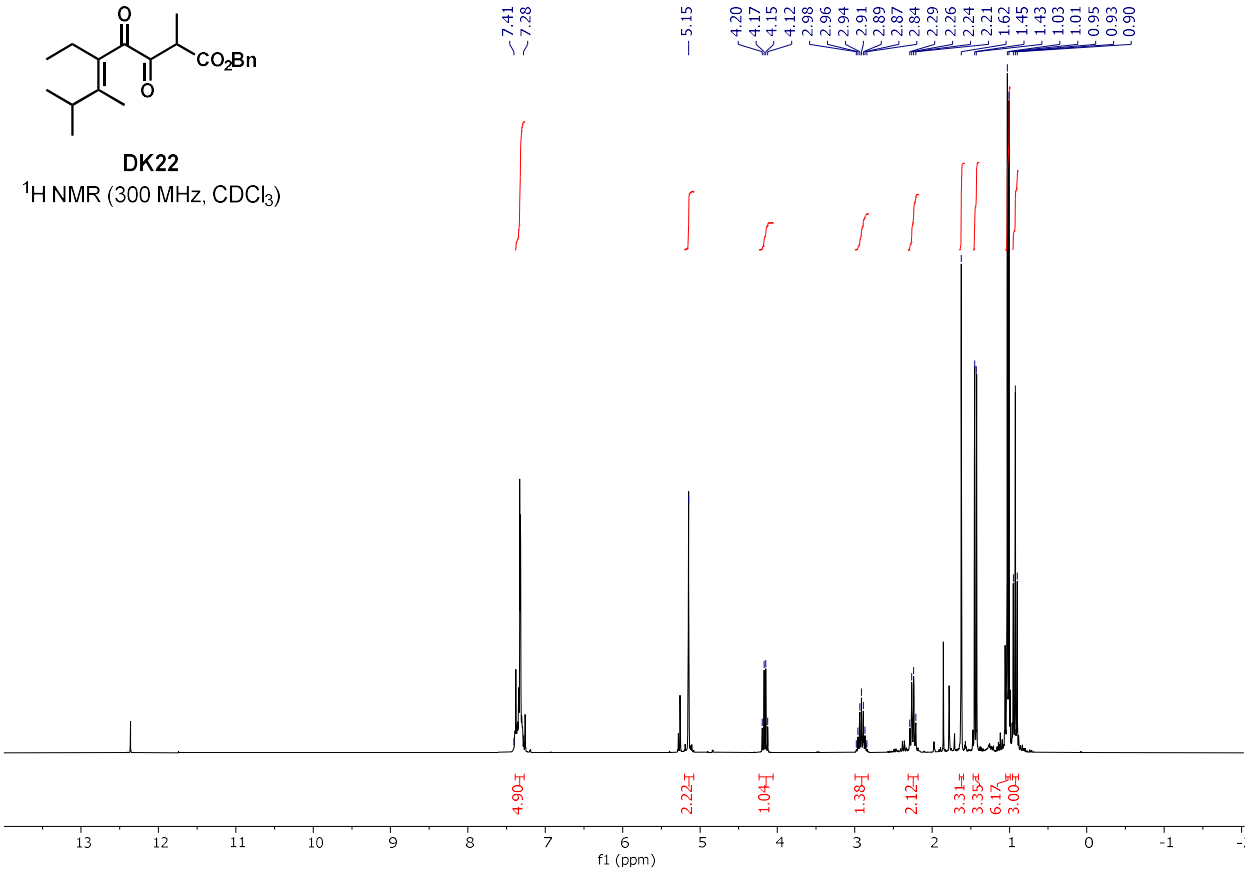


DK19

^{13}C NMR (75 MHz, $CDCl_3$)

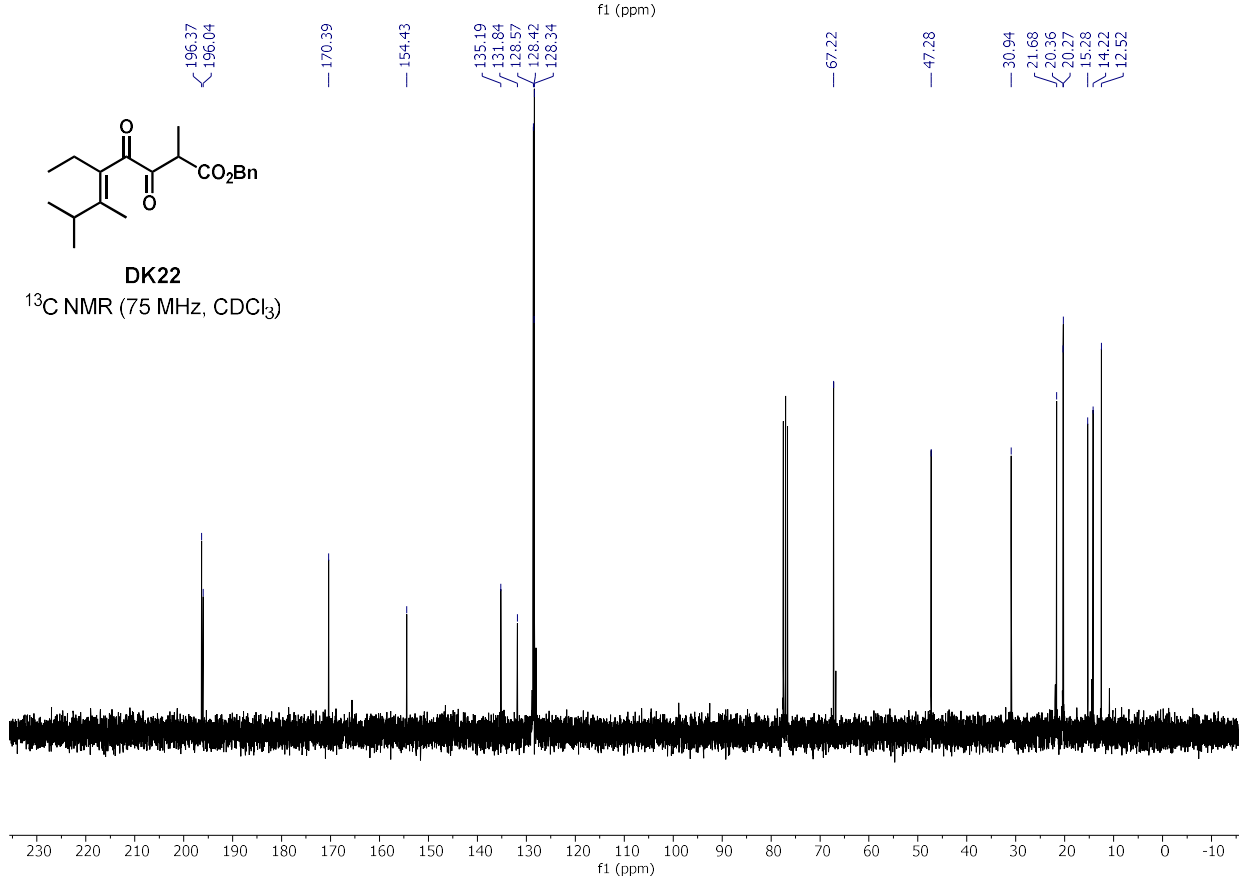

DK21
^{1}H NMR (300 MHz, $CDCl_3$)
7.42
7.29
7.17
7.11
5.22
5.18
5.17
5.13
4.31
4.29
4.26
4.24
2.11
2.11
2.10
2.10
1.69
1.68
1.68
1.67
1.49
1.46
10.59
1.94
2.45
1.00
3.38
3.53
3.46
f1 (ppm)


DK21
^{13}C NMR (75 MHz, $CDCl_3$)
196.38
195.20
170.34
150.01
142.70
135.05
128.63
128.53
128.43
128.40
127.90
127.54
127.15
67.37
47.19
23.55
16.62
12.12
f1 (ppm)



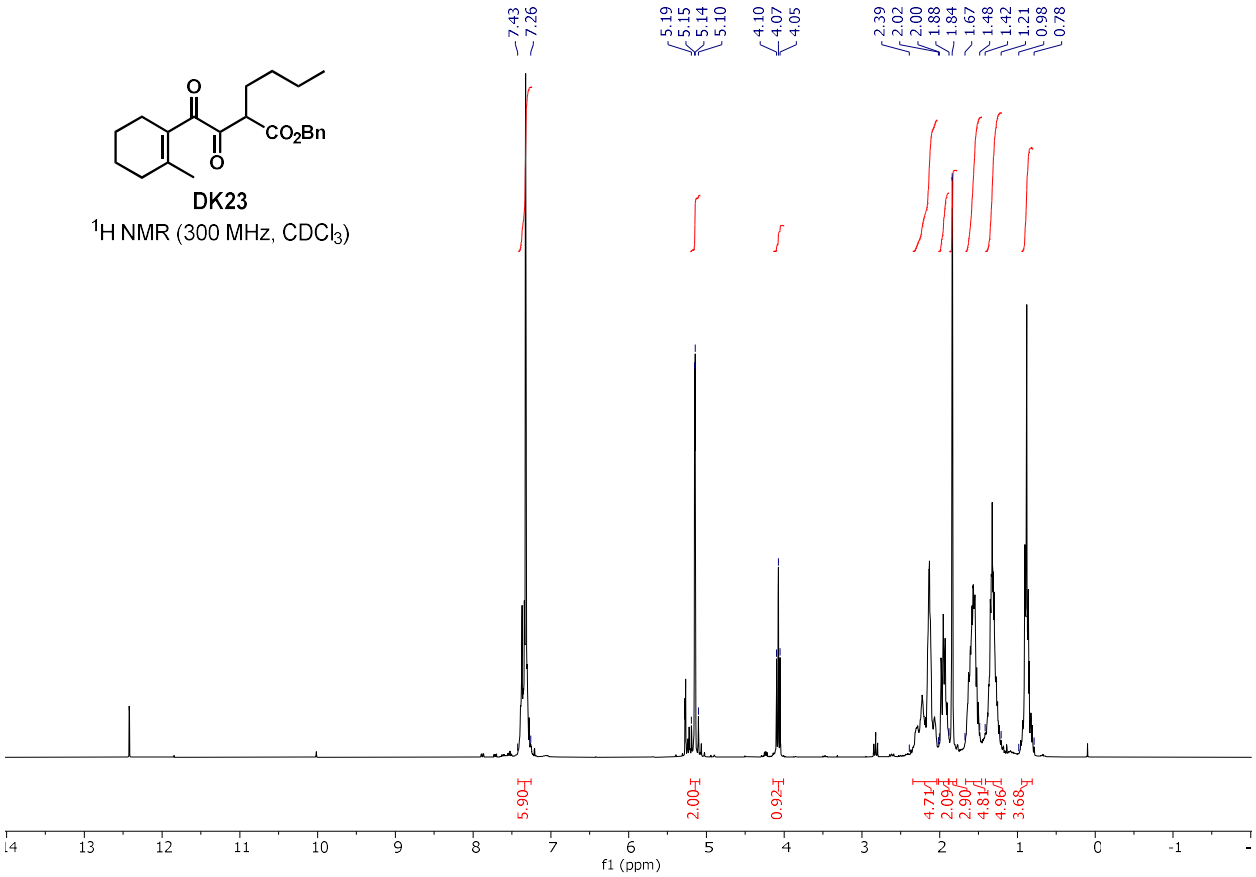
DK22

^{1}H NMR (300 MHz, $CDCl_3$)



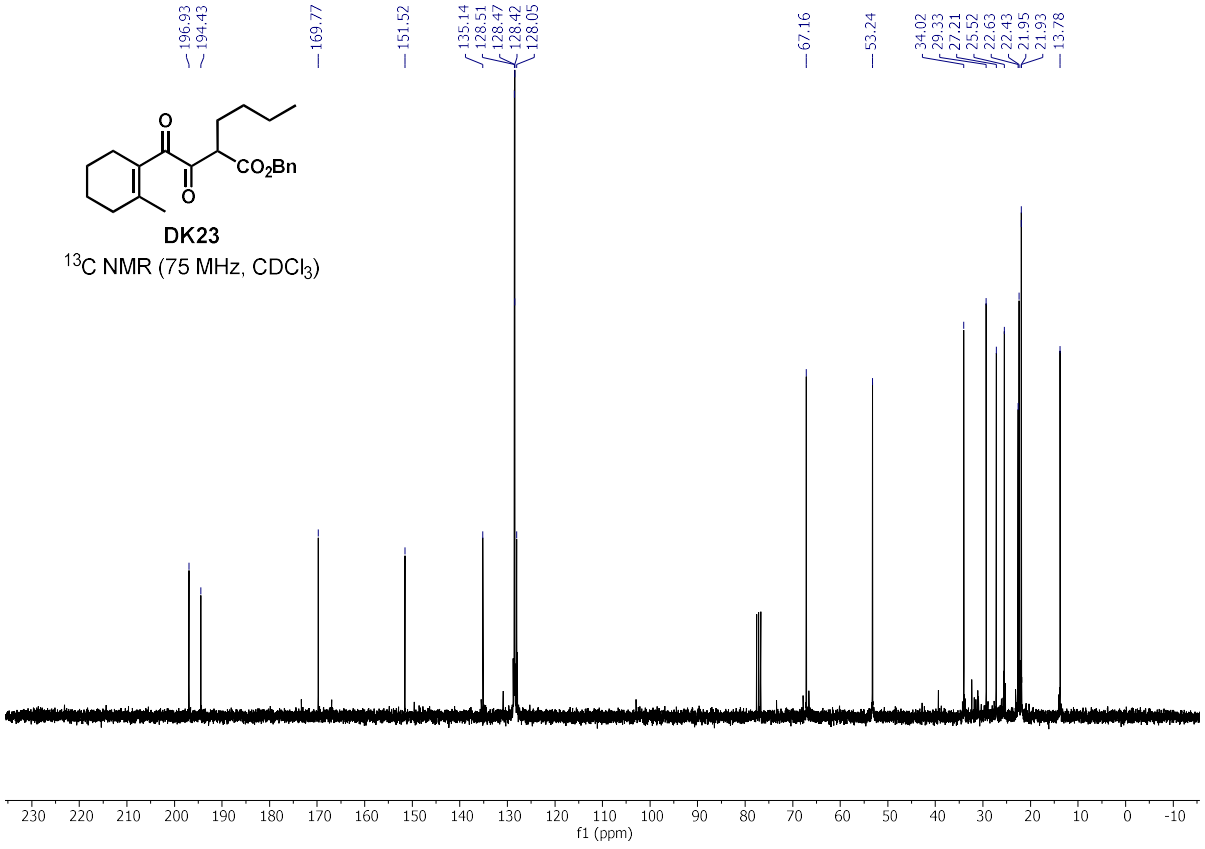
DK22

^{13}C NMR (75 MHz, $CDCl_3$)



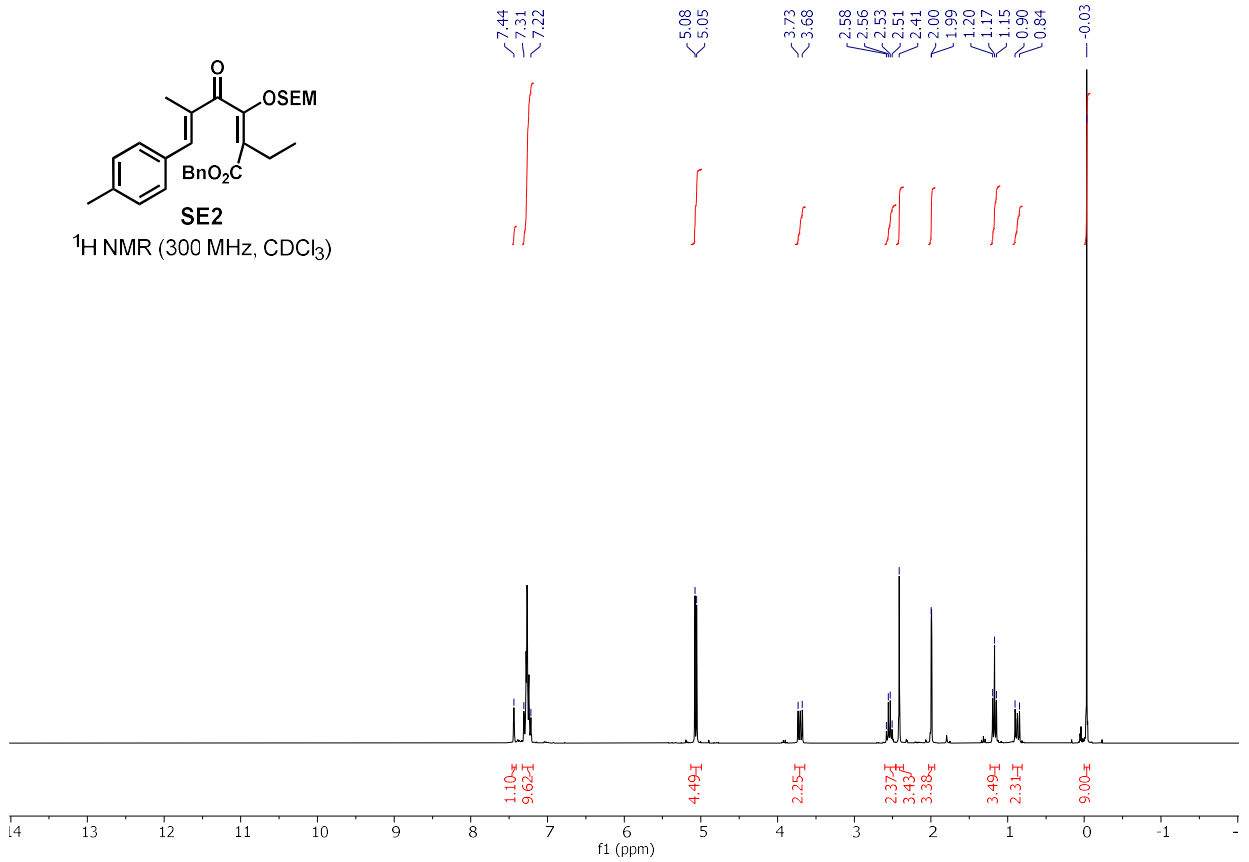
DK23

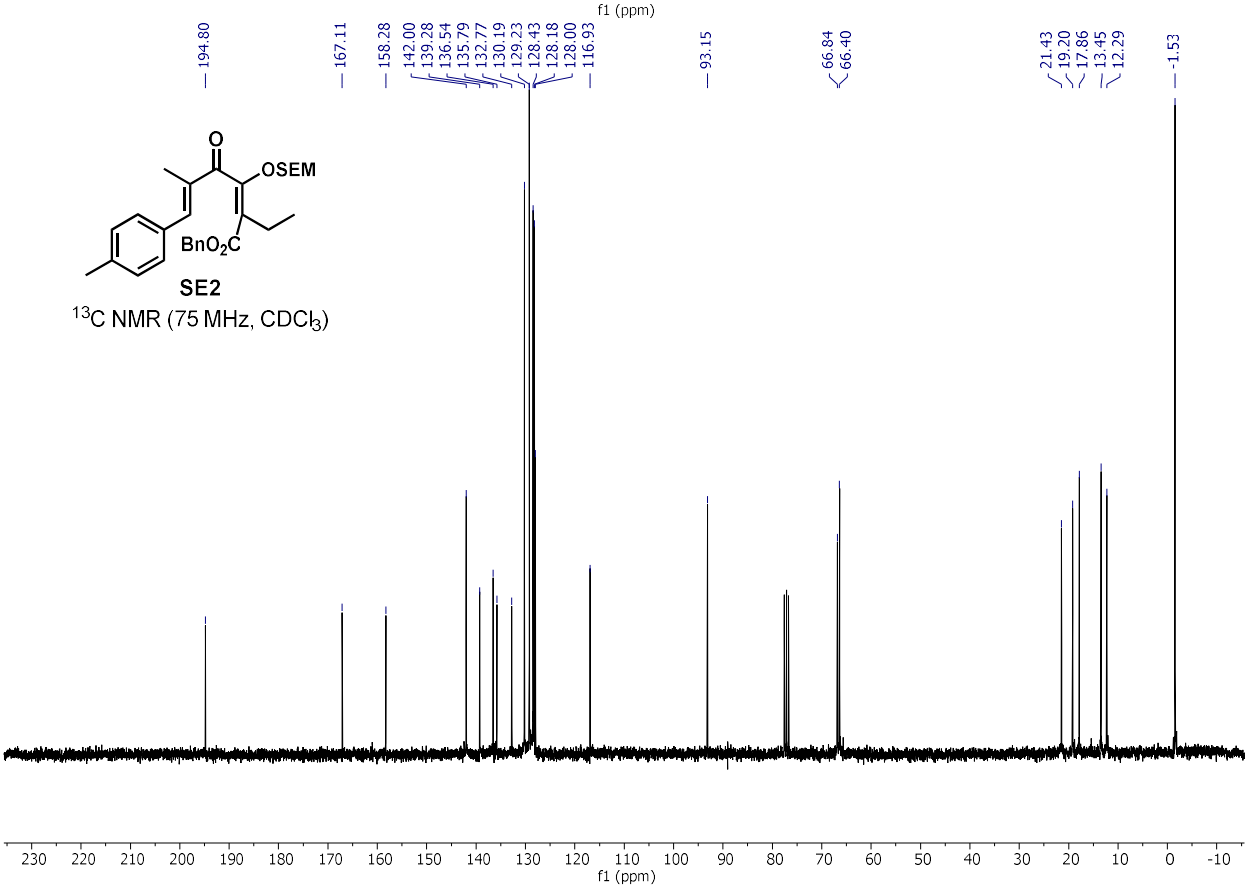
^{1}H NMR (300 MHz, $CDCl_3$)

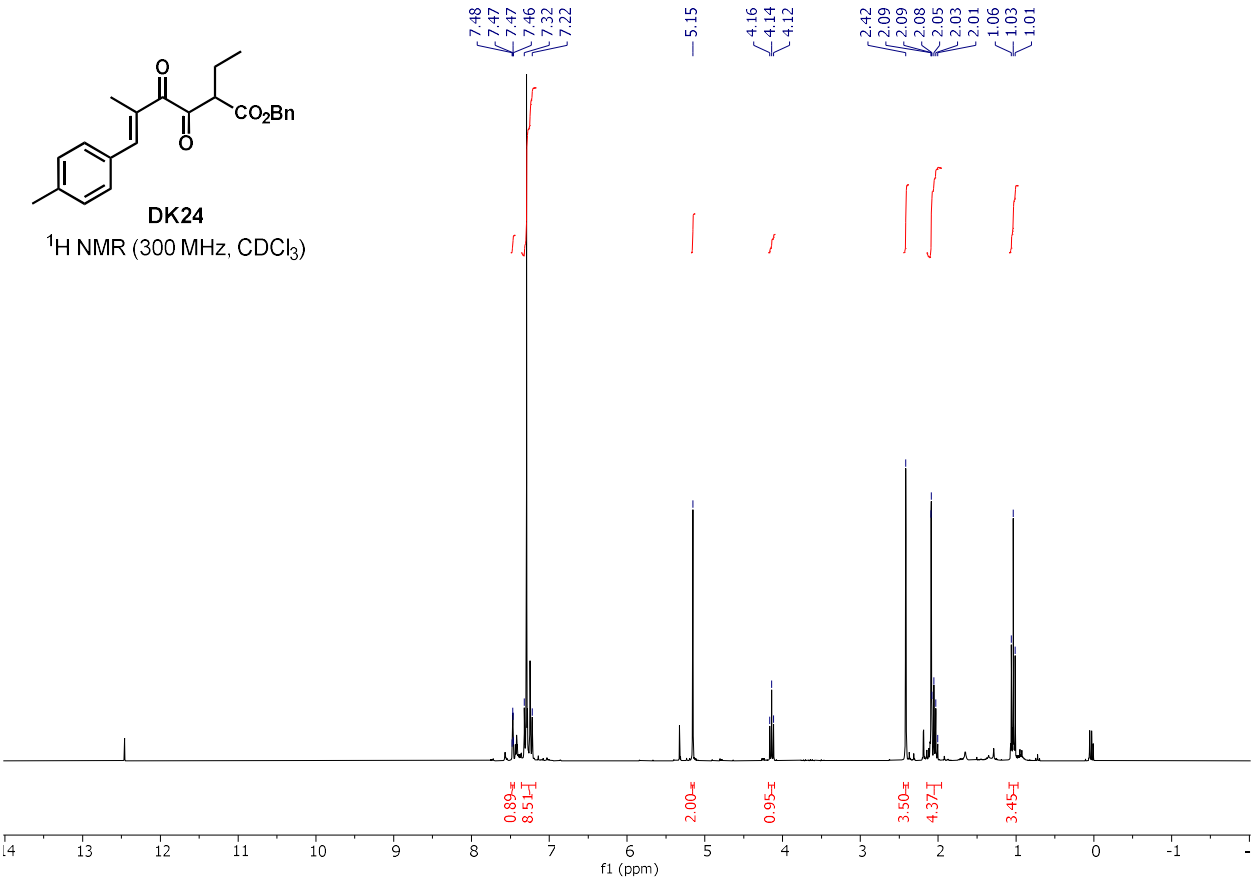


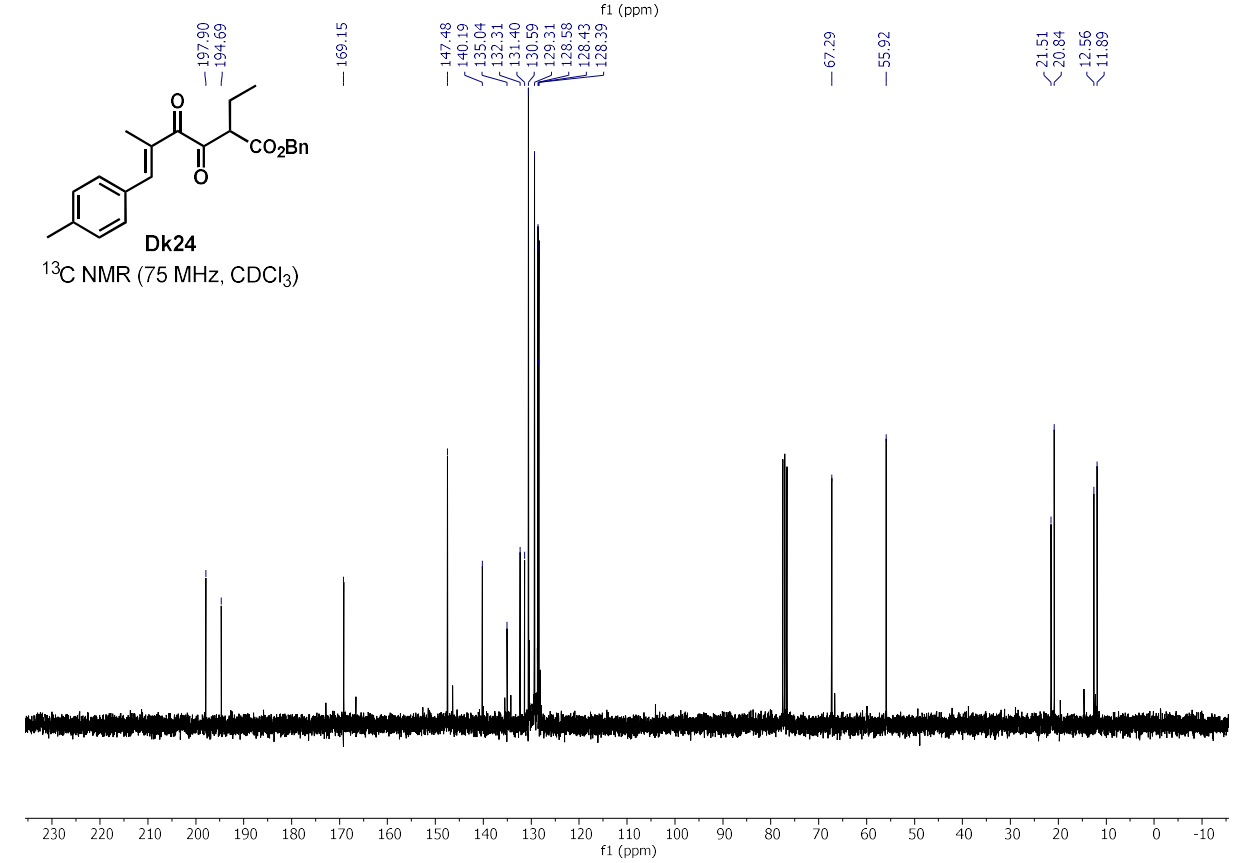
DK23

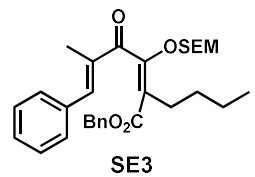
^{13}C NMR (75 MHz, $CDCl_3$)


OSEM
BnO2C
SE2
1H NMR (300 MHz, CDCl3)
7.44
7.31
7.22
5.08
5.05
3.73
3.68
2.58
2.56
2.53
2.51
2.41
2.00
1.99
1.20
1.17
1.15
0.90
0.84
-0.03
1.10
9.62
4.49
2.25
2.37
3.43
3.38
3.49
2.31
9.00
f1 (ppm)


OSEM
BnO2C
SE2
13C NMR (75 MHz, CDCl3)
194.80
167.11
158.28
142.00
139.28
136.54
135.79
132.77
130.19
129.23
128.43
128.18
128.00
116.93
93.15
66.84
66.40
21.43
19.20
17.86
13.45
12.29
-1.53
f1 (ppm)

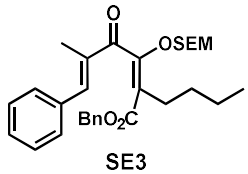

DK24
1H NMR (300 MHz, CDCl3)
7.48
7.47
7.47
7.46
7.32
7.22
5.15
4.16
4.14
4.12
2.42
2.09
2.09
2.08
2.05
2.03
2.01
1.06
1.03
1.01
0.89
8.51
2.00
0.95
3.50
4.37
3.45
f1 (ppm)


Dk24
13C NMR (75 MHz, CDCl3)
197.90
194.69
169.15
147.48
140.19
135.04
132.31
131.40
130.59
129.31
128.58
128.43
128.39
67.29
55.92
21.51
20.84
12.56
11.89
f1 (ppm)



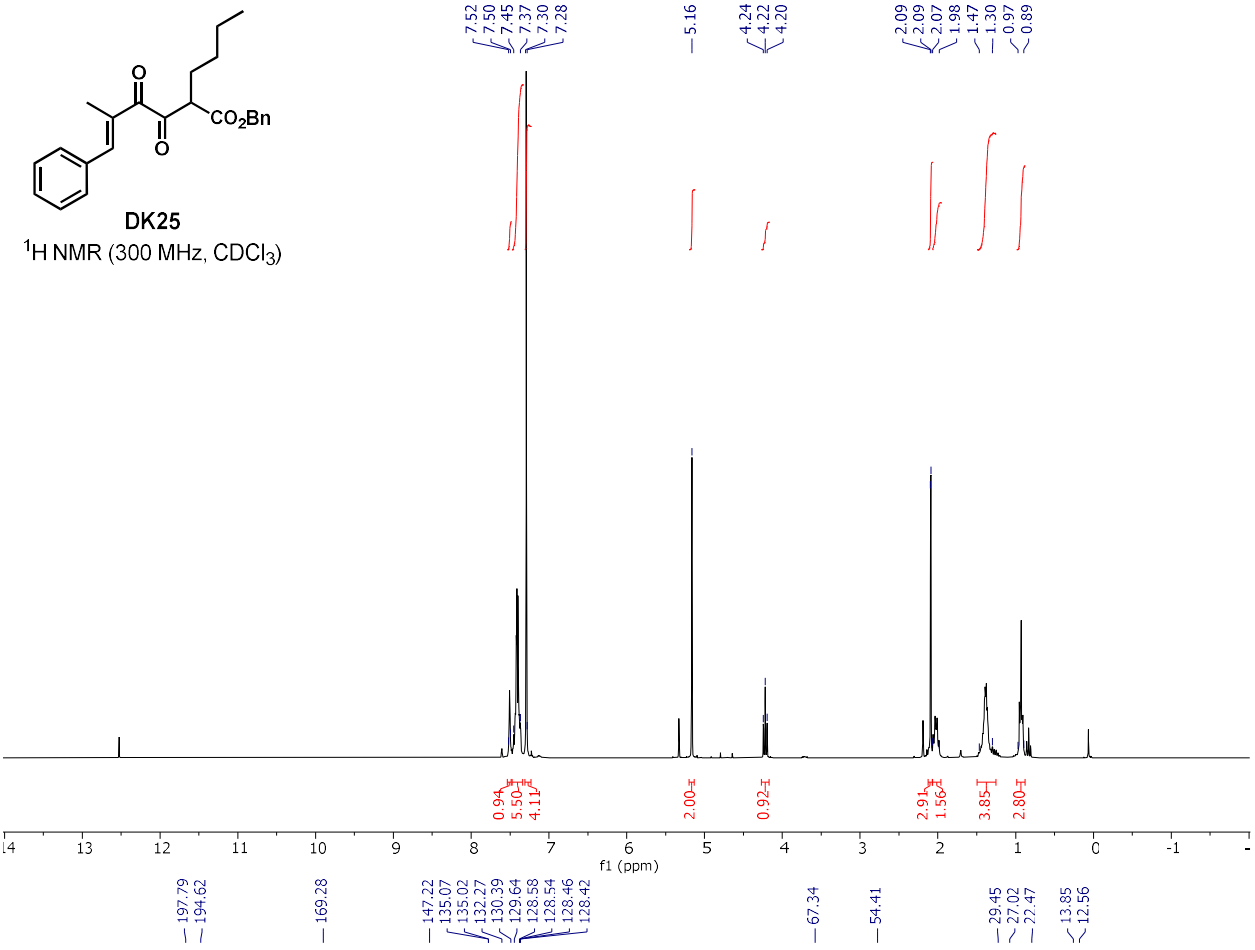
SE3

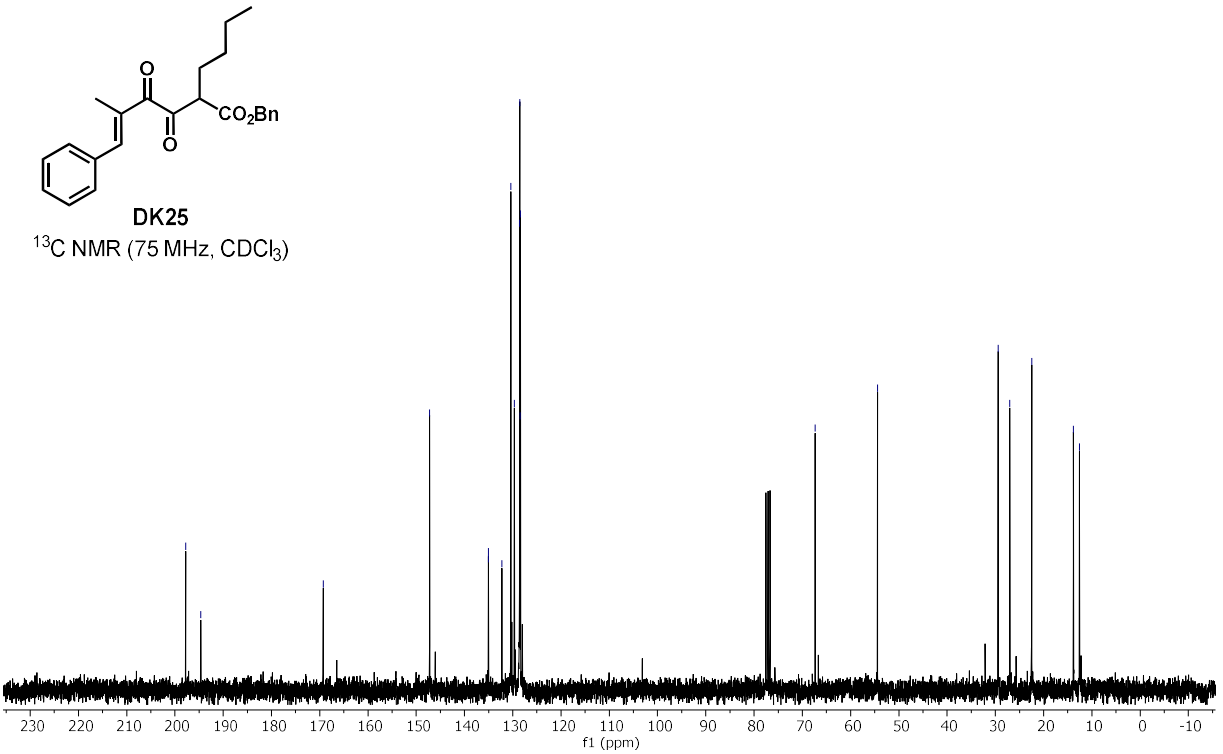
^{1}H NMR (300 MHz, $CDCl_3$)

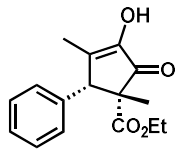


SE3

^{13}C NMR (75 MHz, $CDCl_3$)

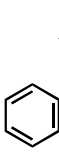

DK25
1H NMR (300 MHz, CDCl3)
7.52
7.50
7.45
7.37
7.30
7.28
5.16
4.24
4.22
4.20
2.09
2.09
2.07
1.98
1.47
1.30
0.97
0.89
0.94
5.50
4.11
2.00
0.92
2.91
1.56
3.85
2.80
f1 (ppm)


DK25
13C NMR (75 MHz, CDCl3)
197.79
194.62
169.28
147.22
135.07
135.02
132.27
130.39
129.64
128.58
128.54
128.46
128.42
67.34
54.41
29.45
27.02
22.47
13.85
12.56
f1 (ppm)



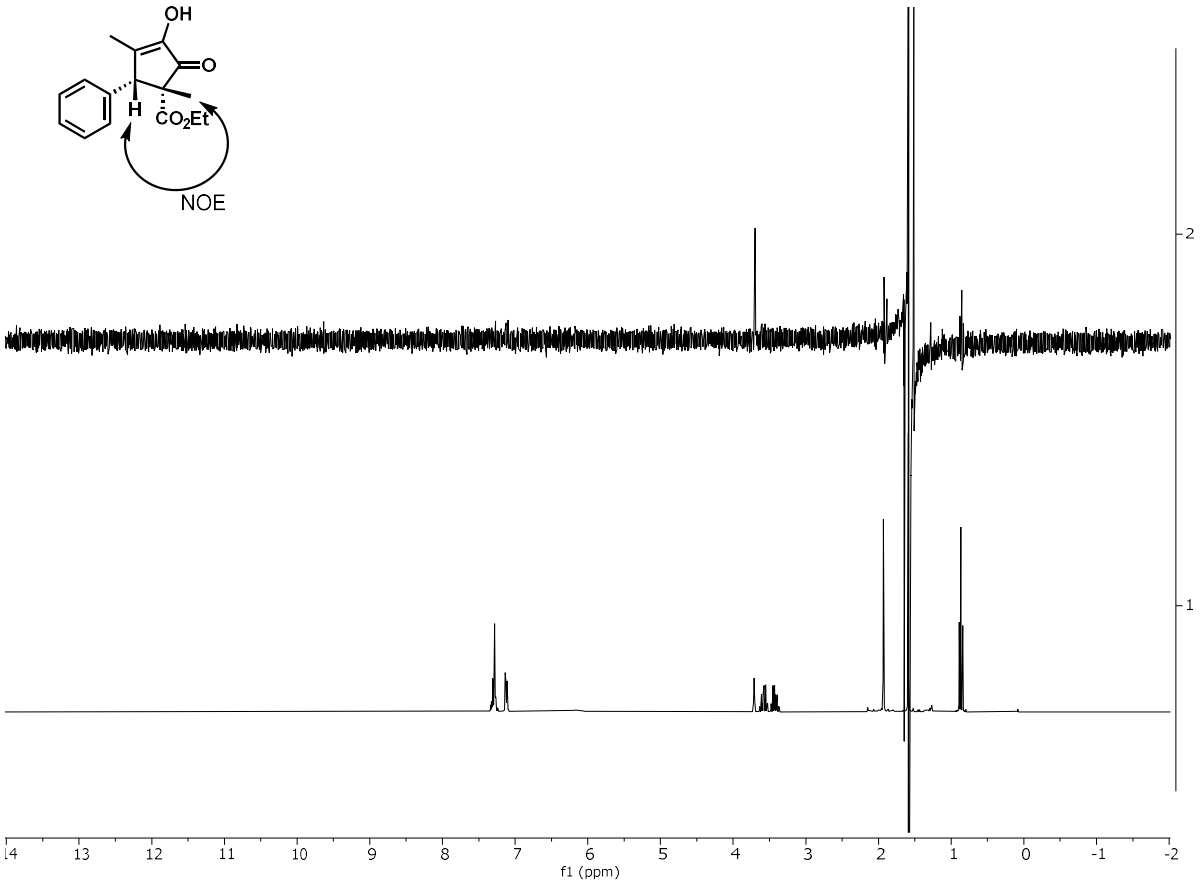
8

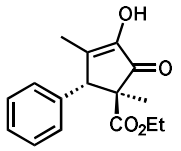
^{1}H NMR (300 MHz, $CDCl_3$)



8

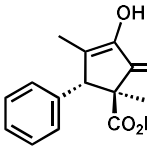
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
H
CO2Et
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



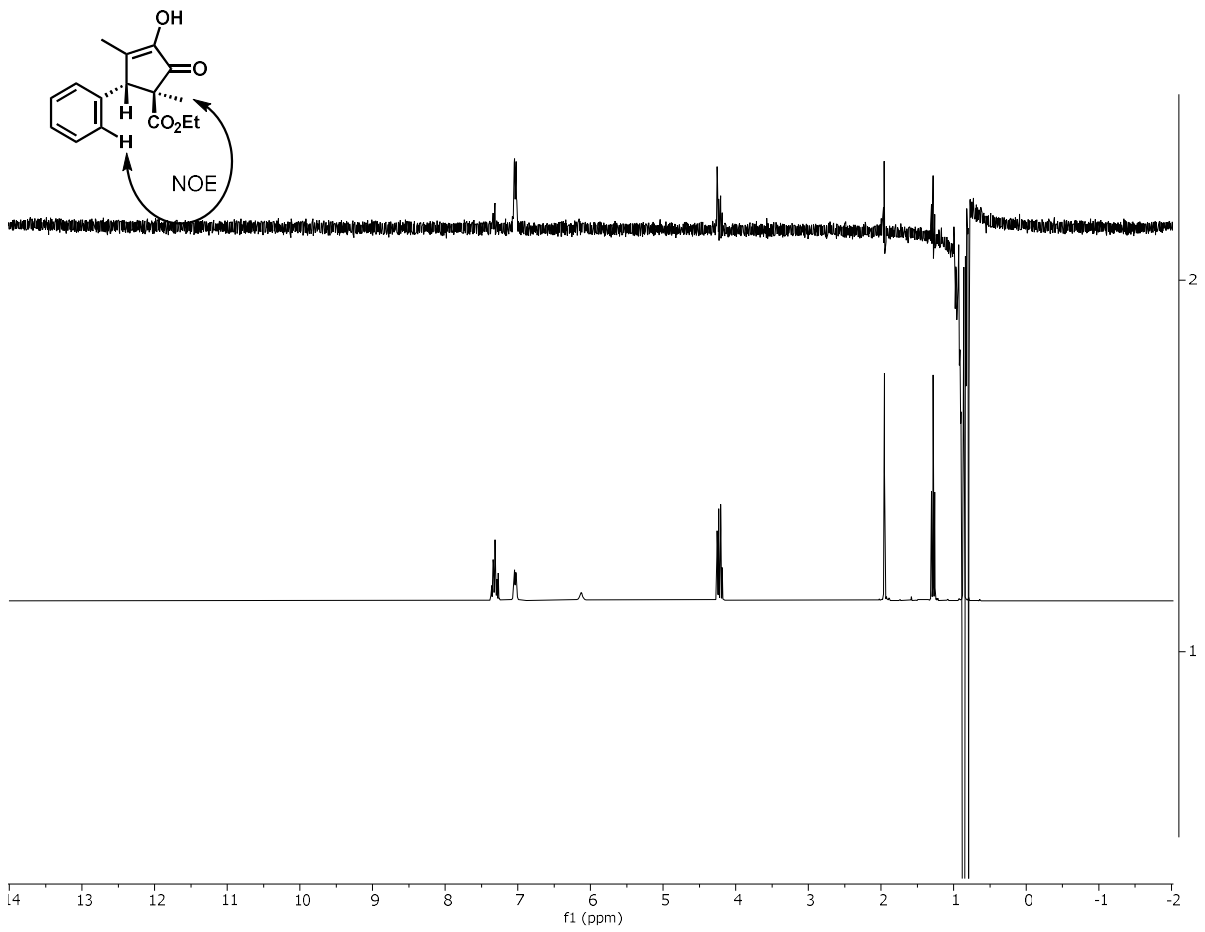
***dia*-8**

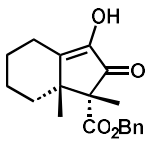
^{1}H NMR (300 MHz, $CDCl_3$)



***dia*-8**

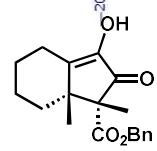
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
H
CO2Et
H
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



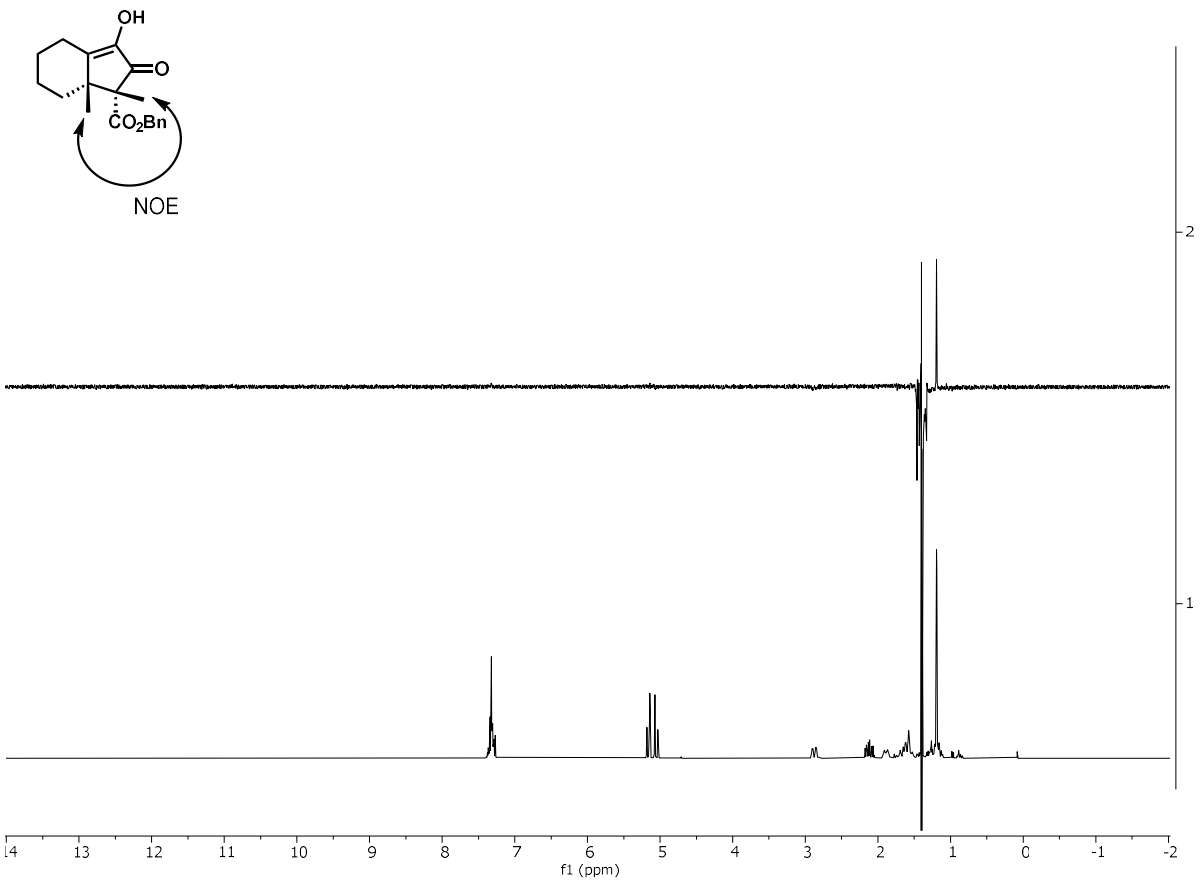
14

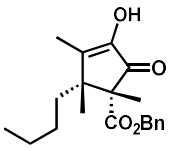
^{1}H NMR (300 MHz, $CDCl_3$)



14

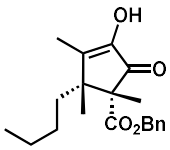
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
CO2Bn
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



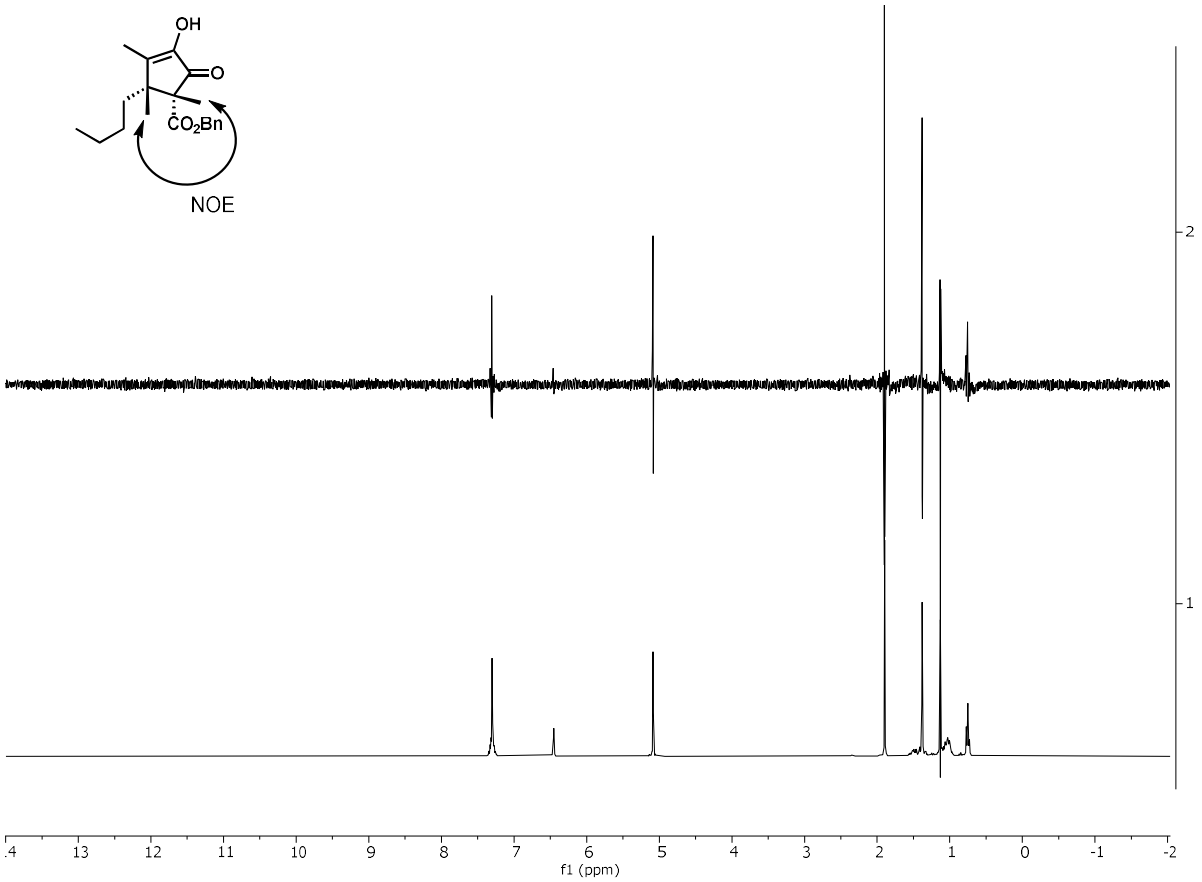
15

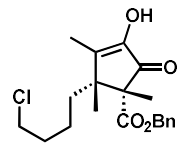
^{1}H NMR (300 MHz, $CDCl_3$)



15

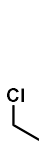
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
CO2Bn
NOE
2
1
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



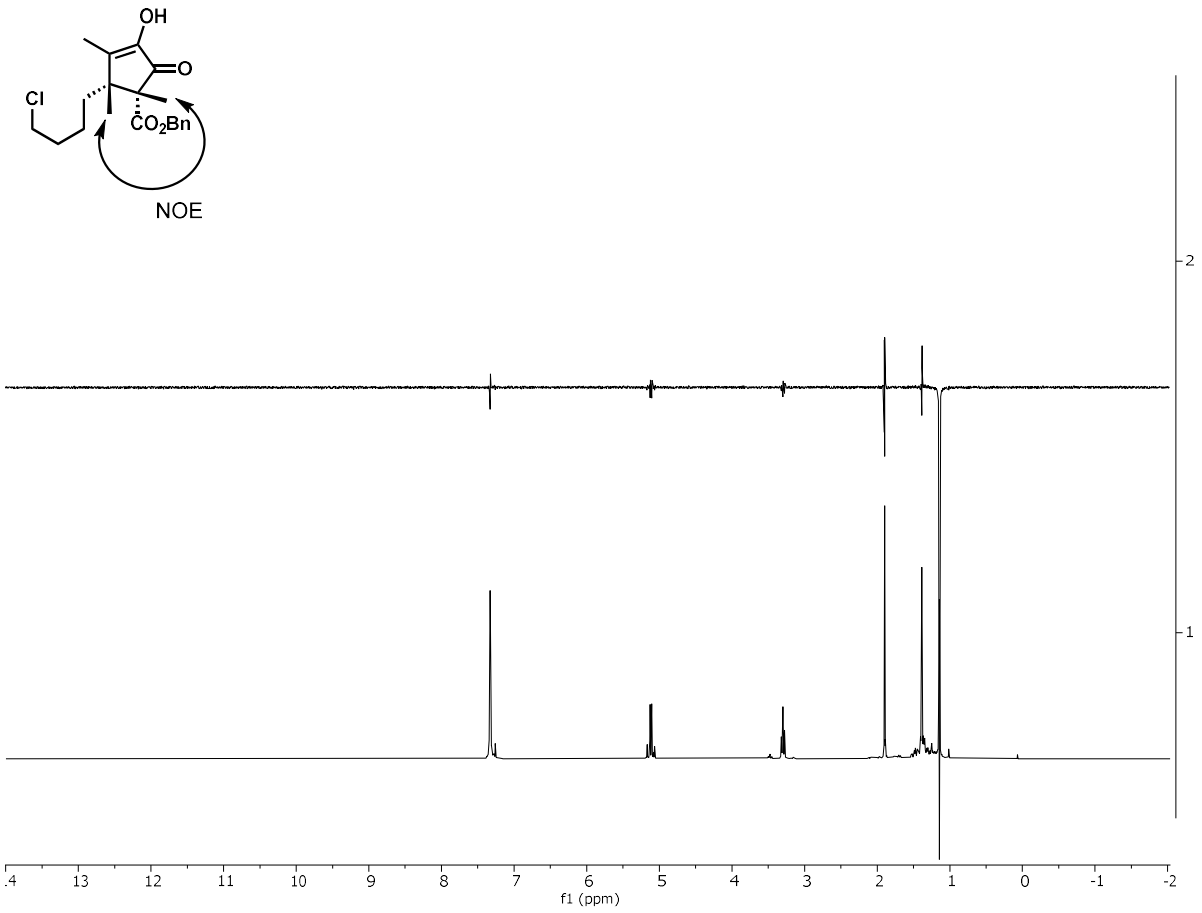
16

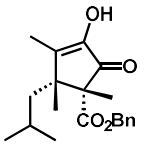
^{1}H NMR (300 MHz, $CDCl_3$)



16

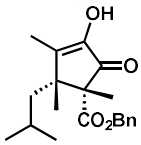
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
Cl
CO2Bn
NOE
2
1
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



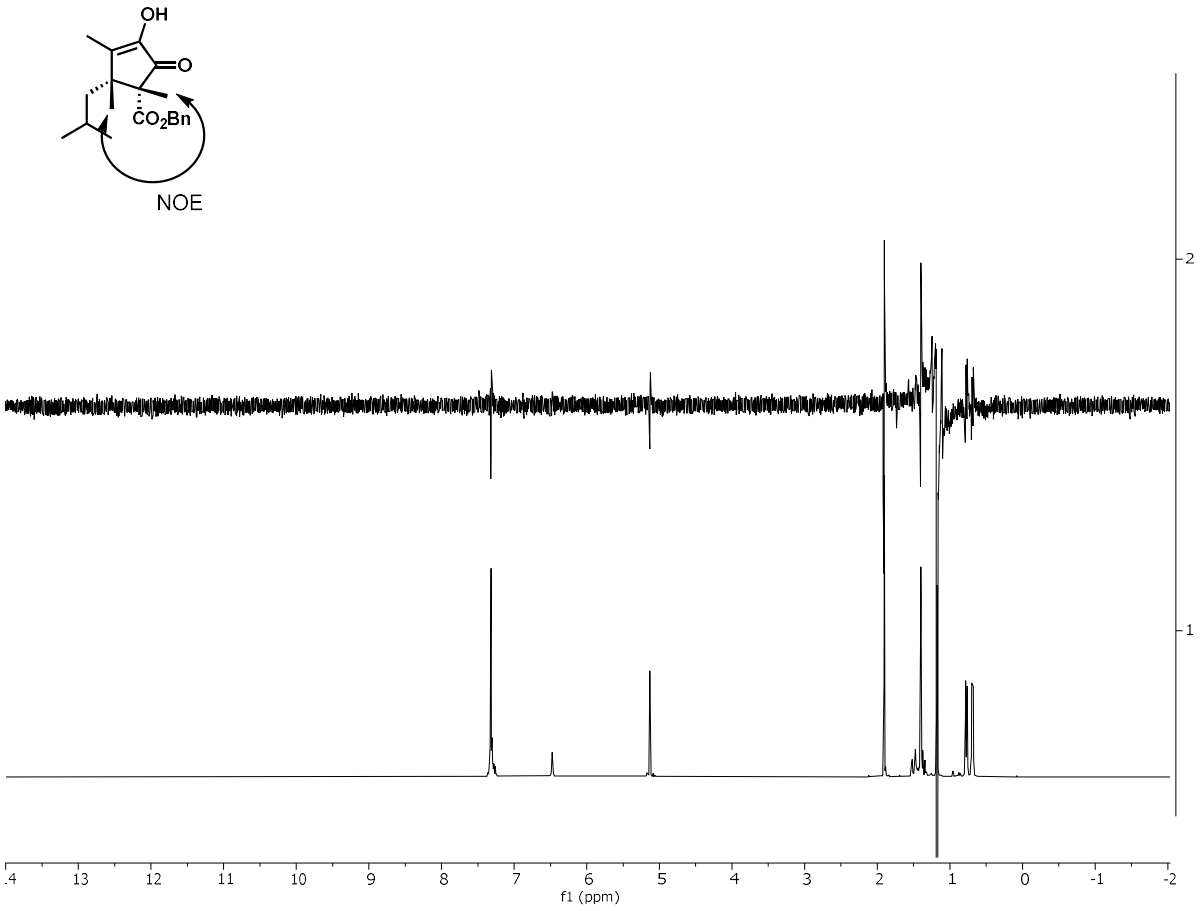
17

^{1}H NMR (300 MHz, $CDCl_3$)



17

^{13}C NMR (75 MHz, $CDCl_3$)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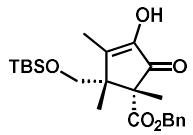
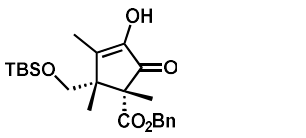
O
CO2Bn
NOE
2
1
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



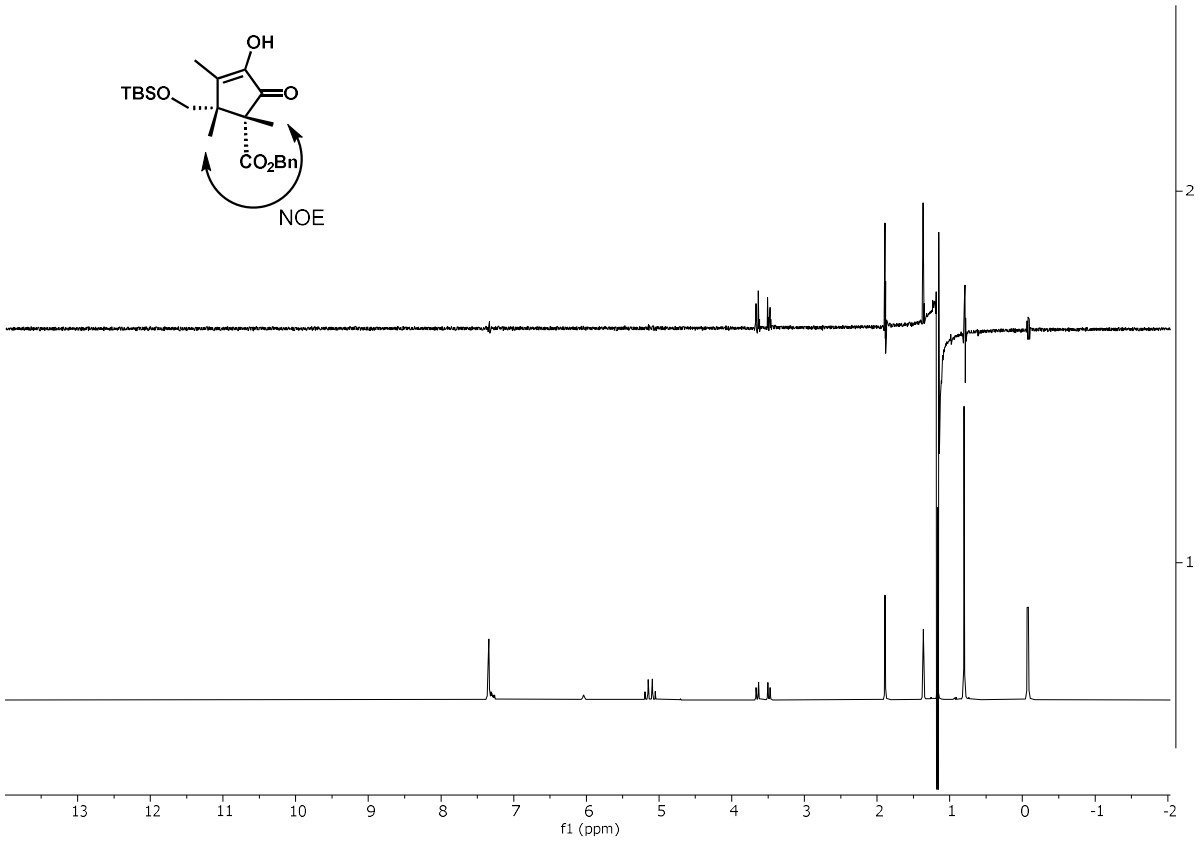
18

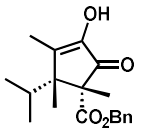
^{1}H NMR (300 MHz, $CDCl_3$)



18

^{13}C NMR (75 MHz, $CDCl_3$)


OH
TBSO
O
CO2Bn
NOE
2
1
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

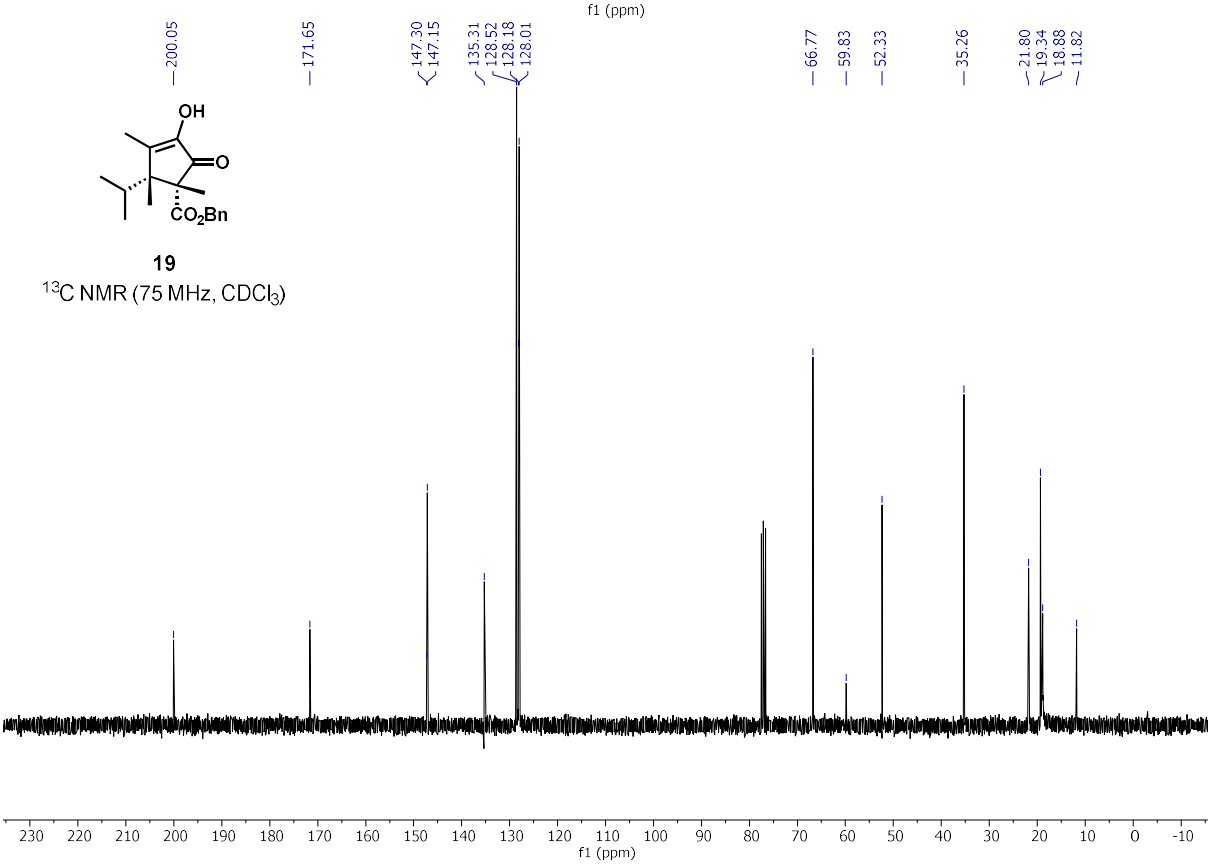


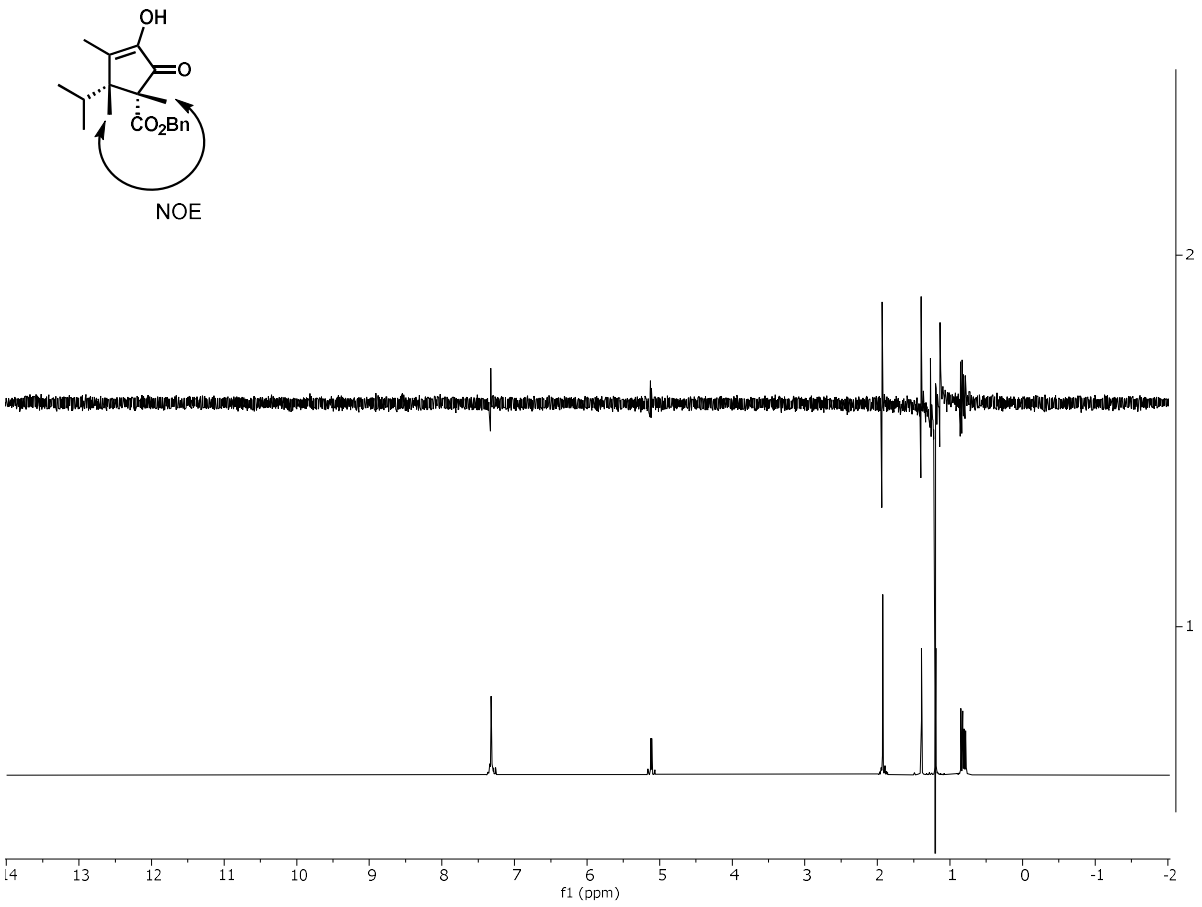
19

^{1}H NMR (300 MHz, $CDCl_3$)

19

^{13}C NMR (75 MHz, $CDCl_3$)




OH
O
CO2Bn
NOE
2
1
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13
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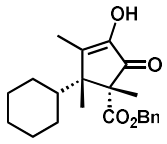
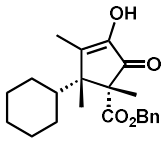
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



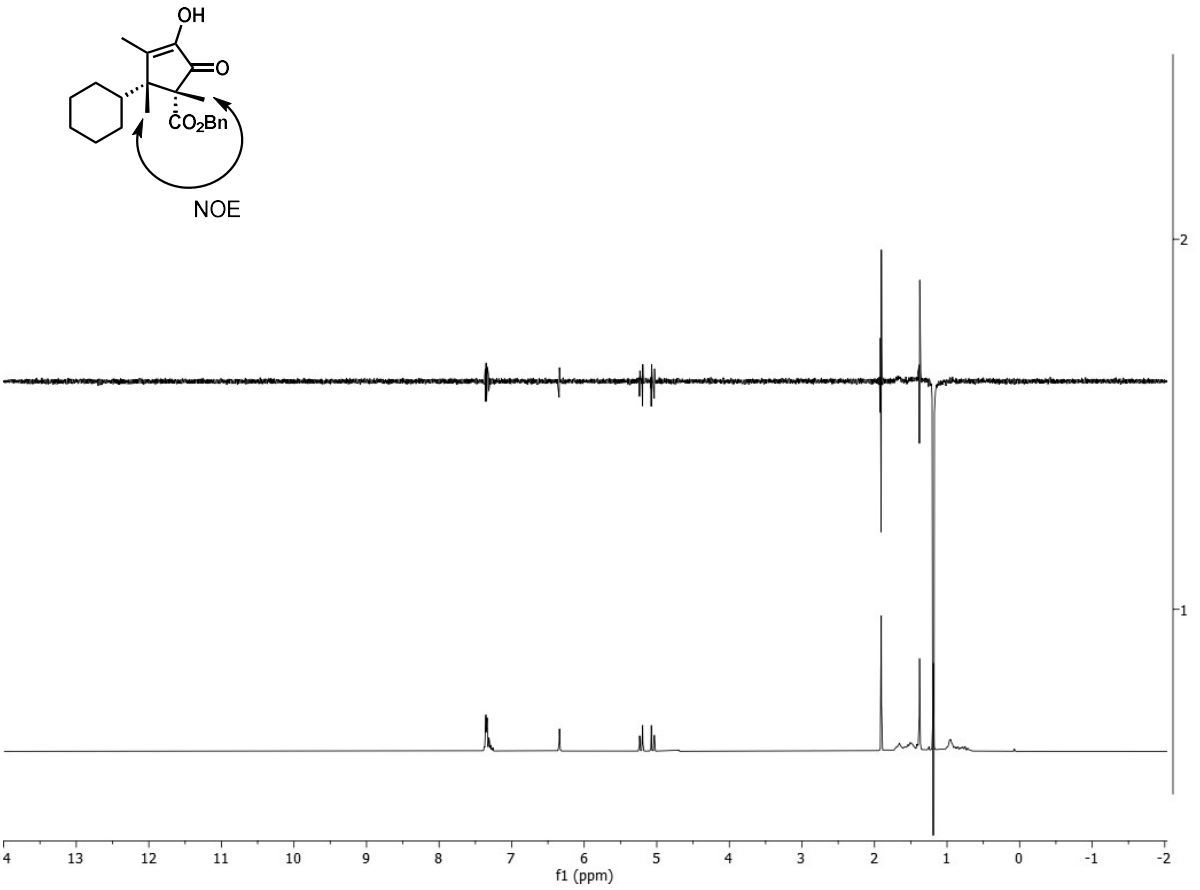
20

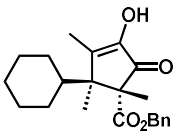
^{1}H NMR (300 MHz, $CDCl_3$)



20

^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
CO2Bn
NOE
2
1
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

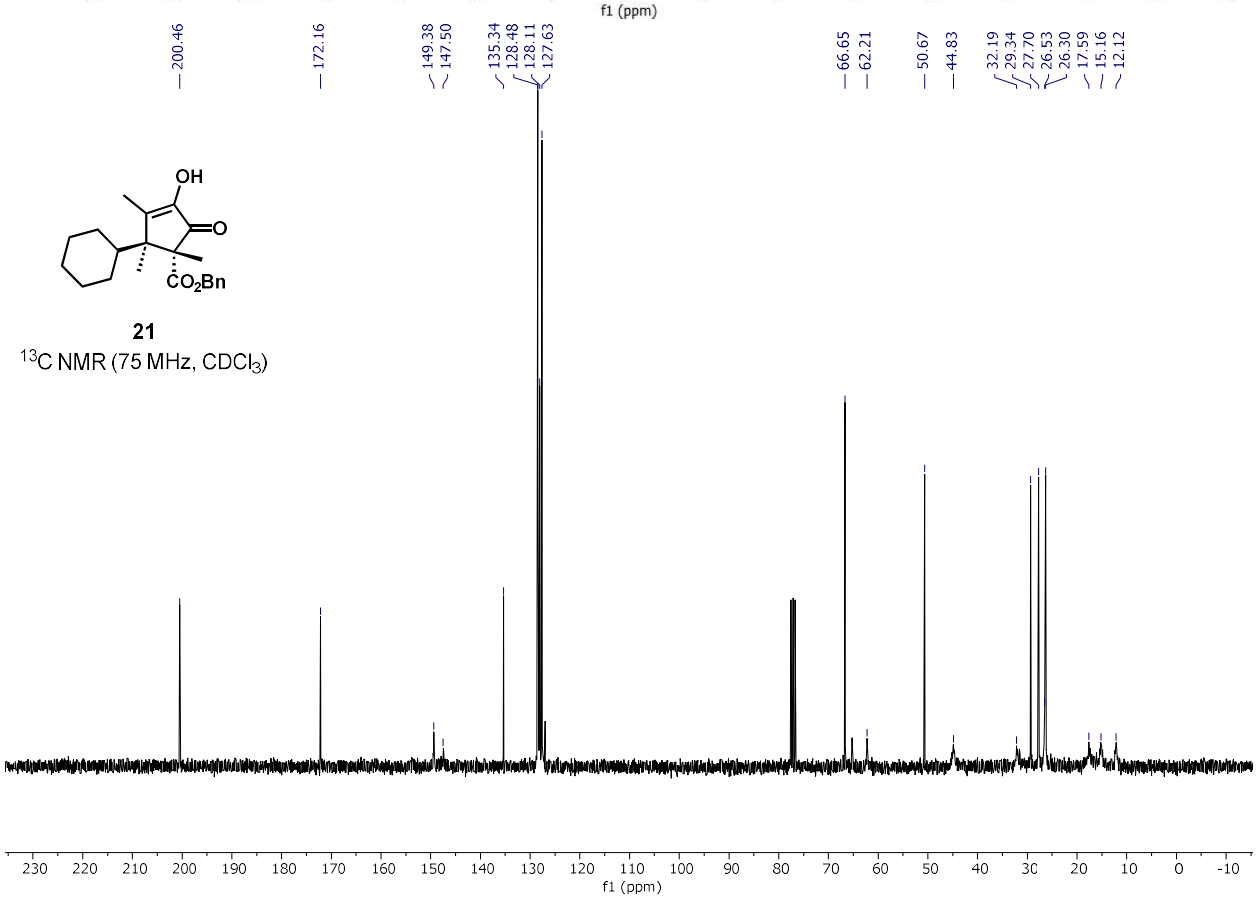


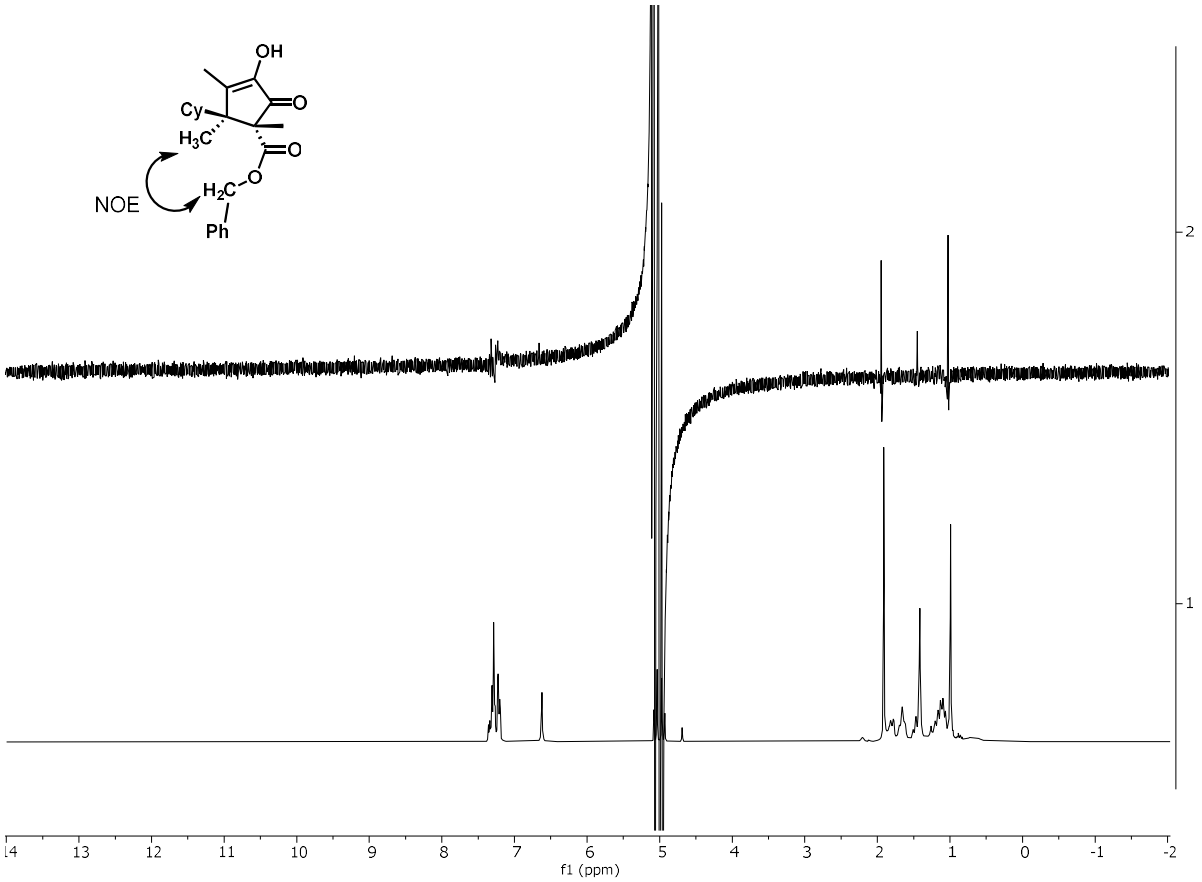
21

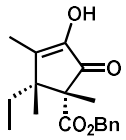
^{1}H NMR (300 MHz, $CDCl_3$)

21

^{13}C NMR (75 MHz, $CDCl_3$)

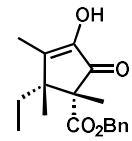



OH
Cy
H3C
O
O
O
H2C
Ph
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



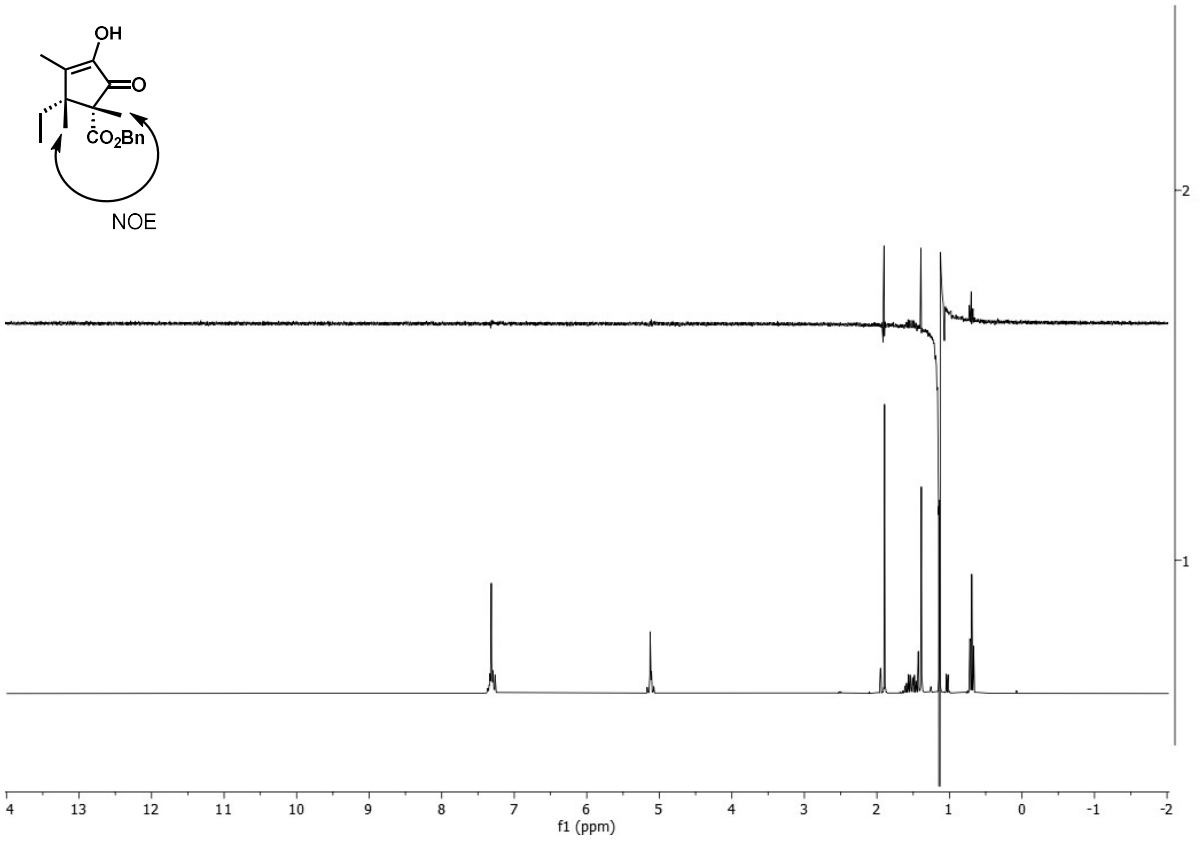
22

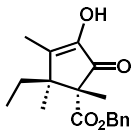
^{1}H NMR (300 MHz, $CDCl_3$)



22

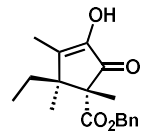
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
CO2Bn
NOE
2
1
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



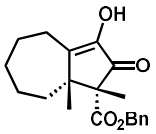
23

^{1}H NMR (300 MHz, $CDCl_3$)



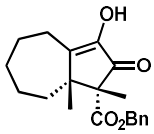
23

^{13}C NMR (75 MHz, $CDCl_3$)



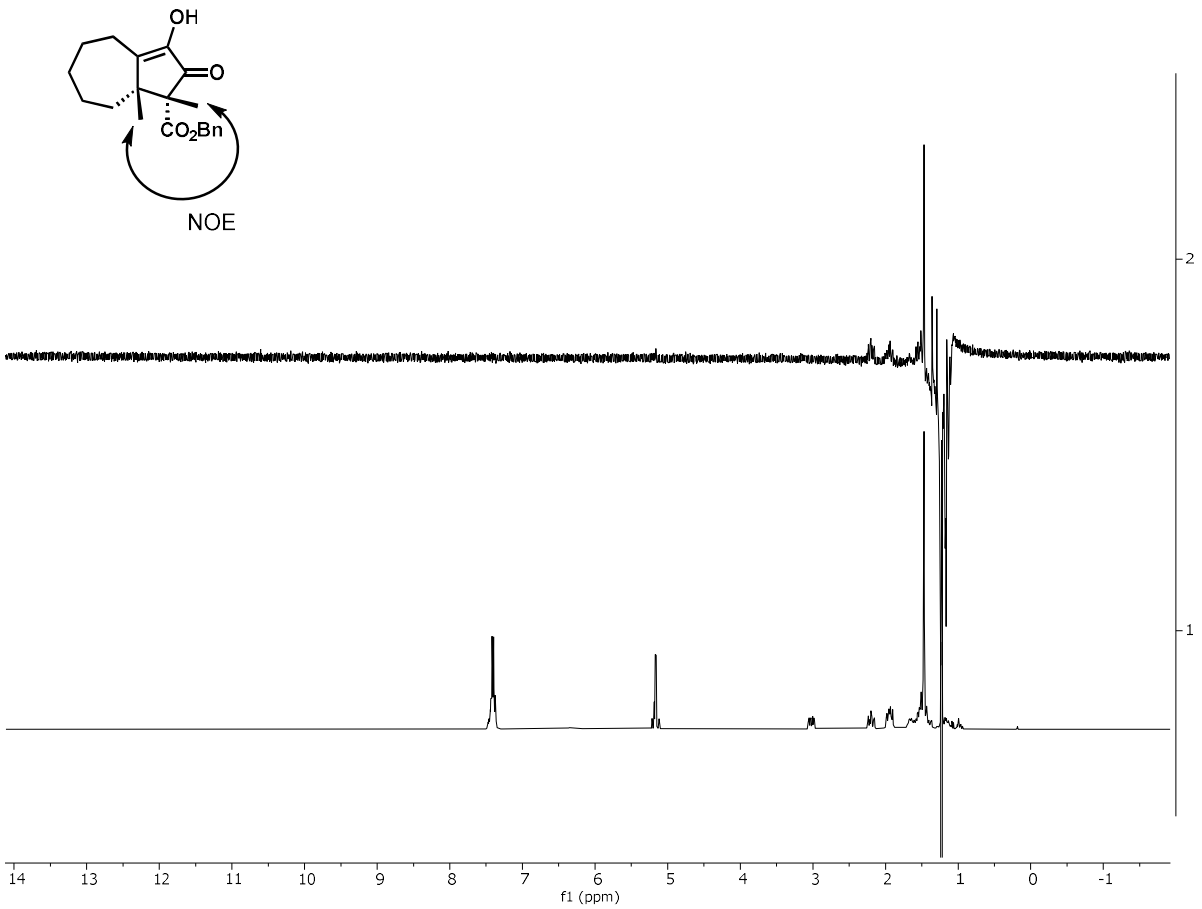
24

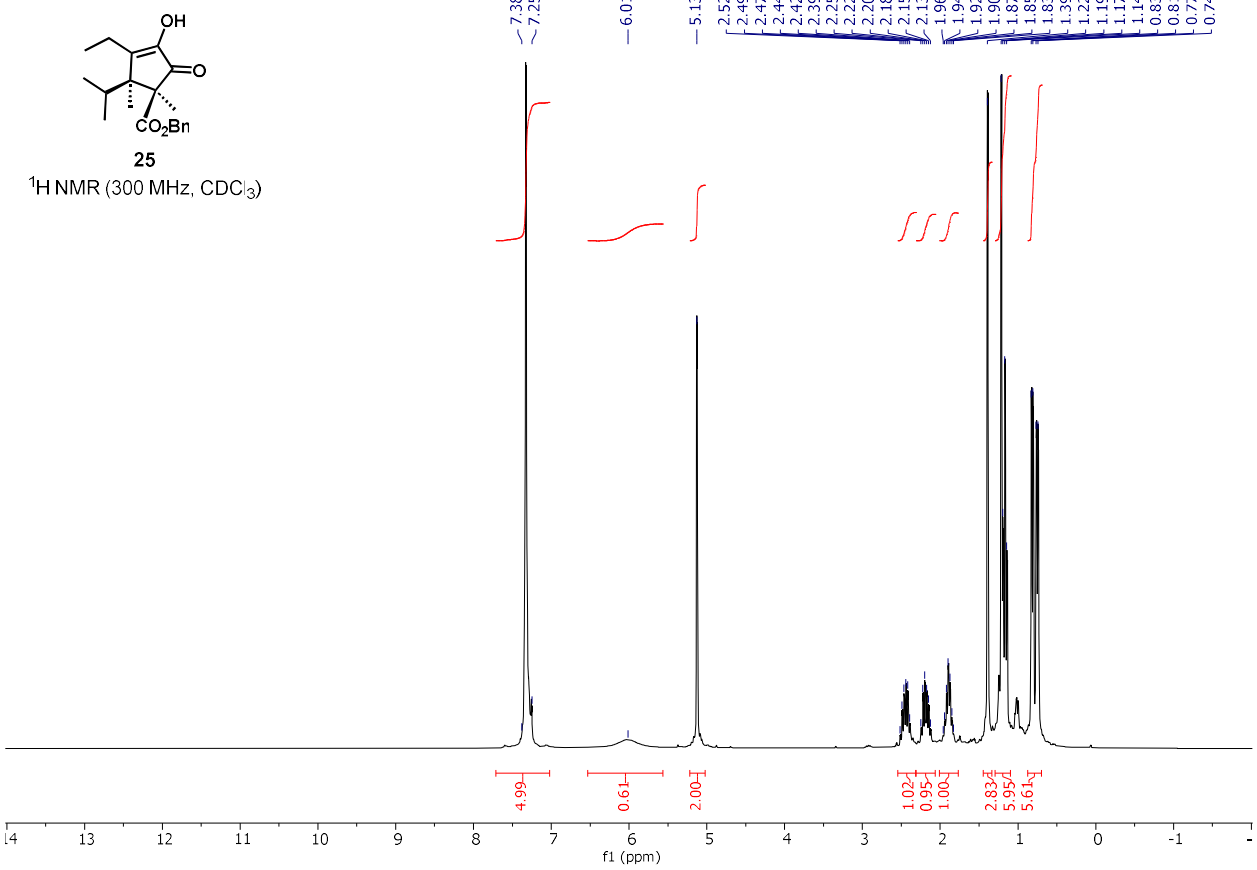
^{1}H NMR (300 MHz, $CDCl_3$)



24

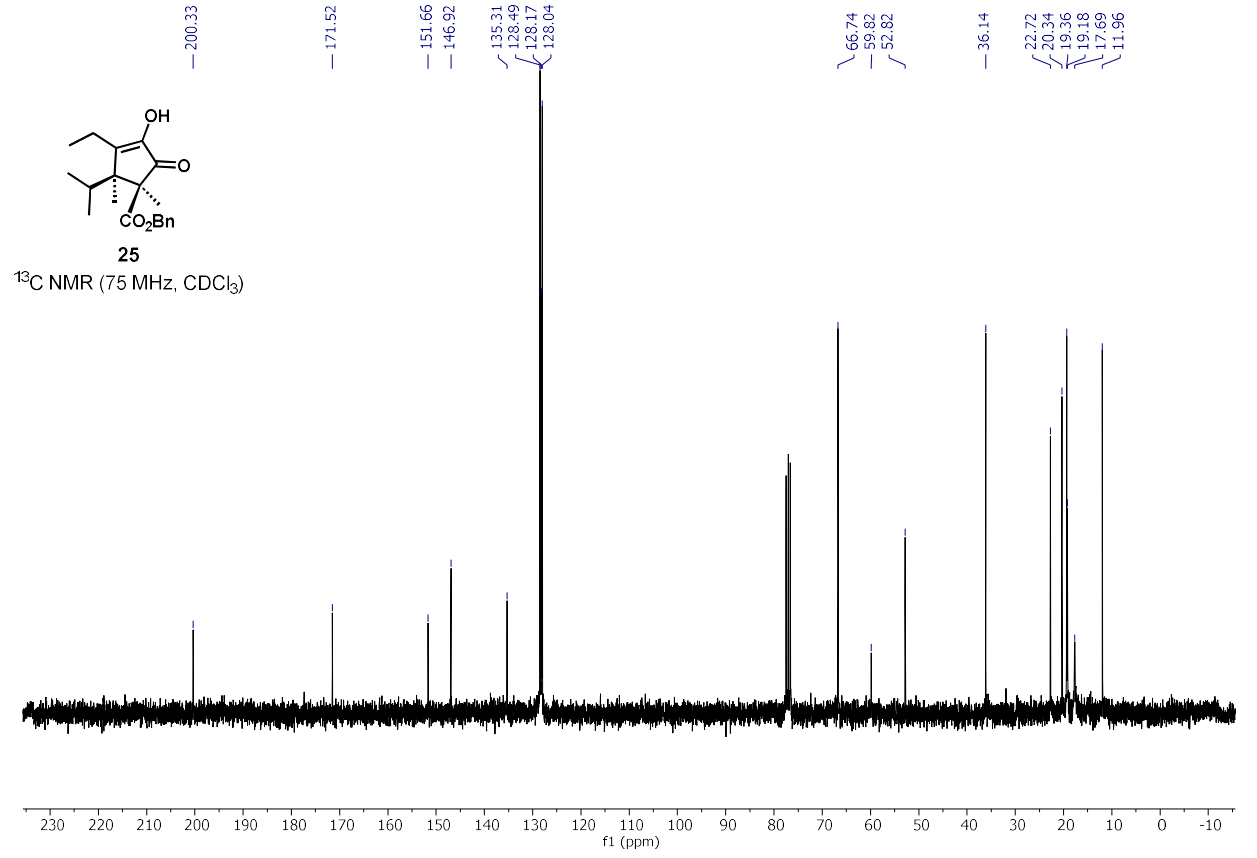
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
CO2Bn
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



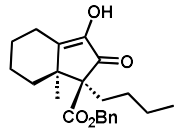
25

^{1}H NMR (300 MHz, $CDCl_3$)



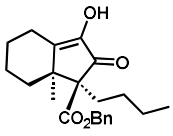
25

^{13}C NMR (75 MHz, $CDCl_3$)



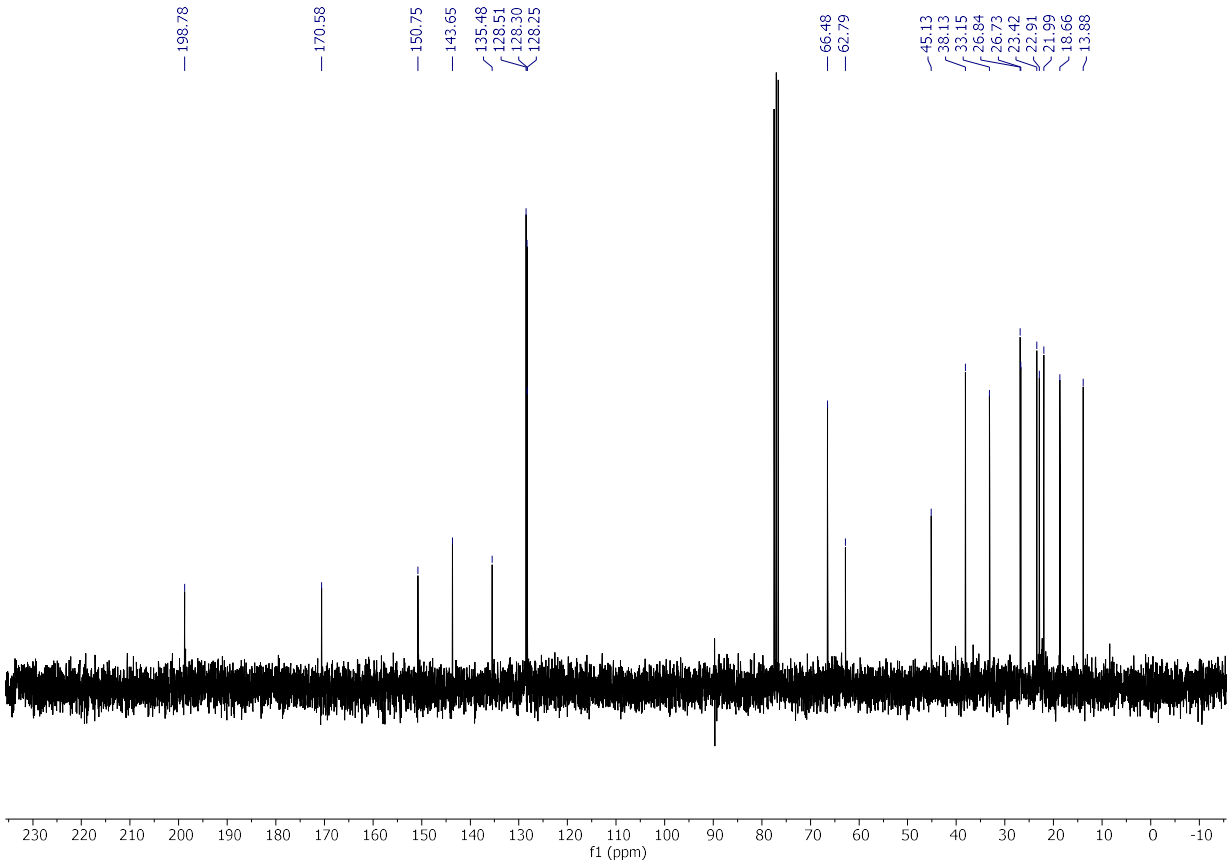
26

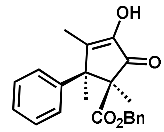
^{1}H NMR (300 MHz, $CDCl_3$)



26

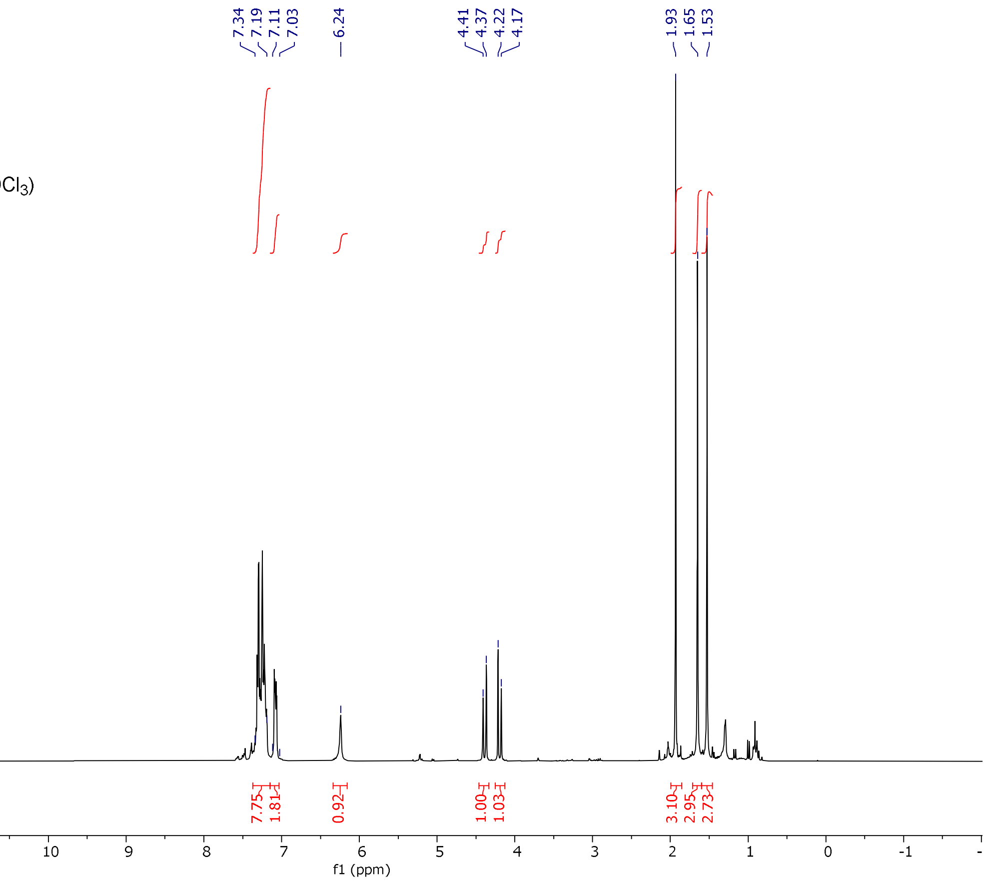
^{13}C NMR (75 MHz, $CDCl_3$)

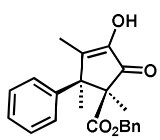

198.78
170.58
150.75
143.65
135.48
128.51
128.30
128.25
66.48
62.79
45.13
38.13
33.15
26.84
26.73
23.42
22.91
21.99
18.66
13.88
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



27

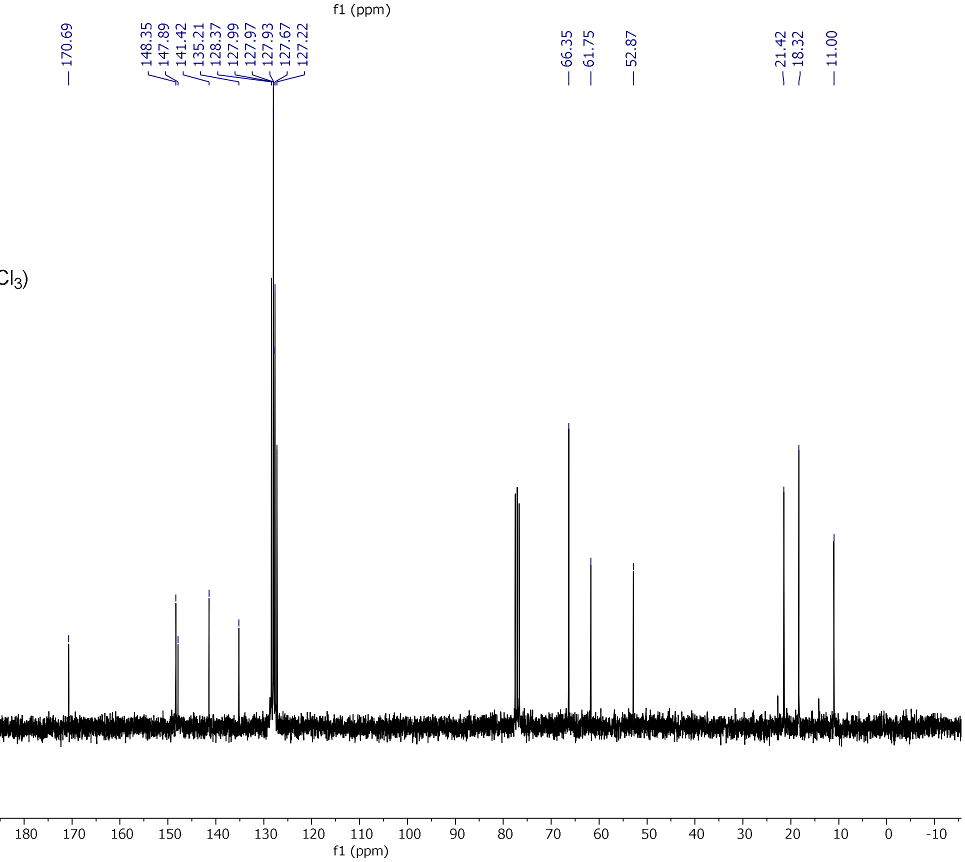
^{1}H NMR (300 MHz, $CDCl_3$)

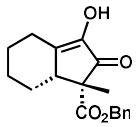




27

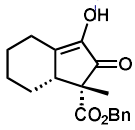
^{13}C NMR (75 MHz, $CDCl_3$)





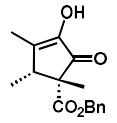
28

^{1}H NMR (300 MHz, $CDCl_3$)



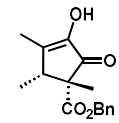
28

^{13}C NMR (75 MHz, $CDCl_3$)



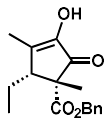
29

^{1}H NMR (300 MHz, $CDCl_3$)



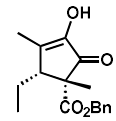
29

^{13}C NMR (75 MHz, $CDCl_3$)



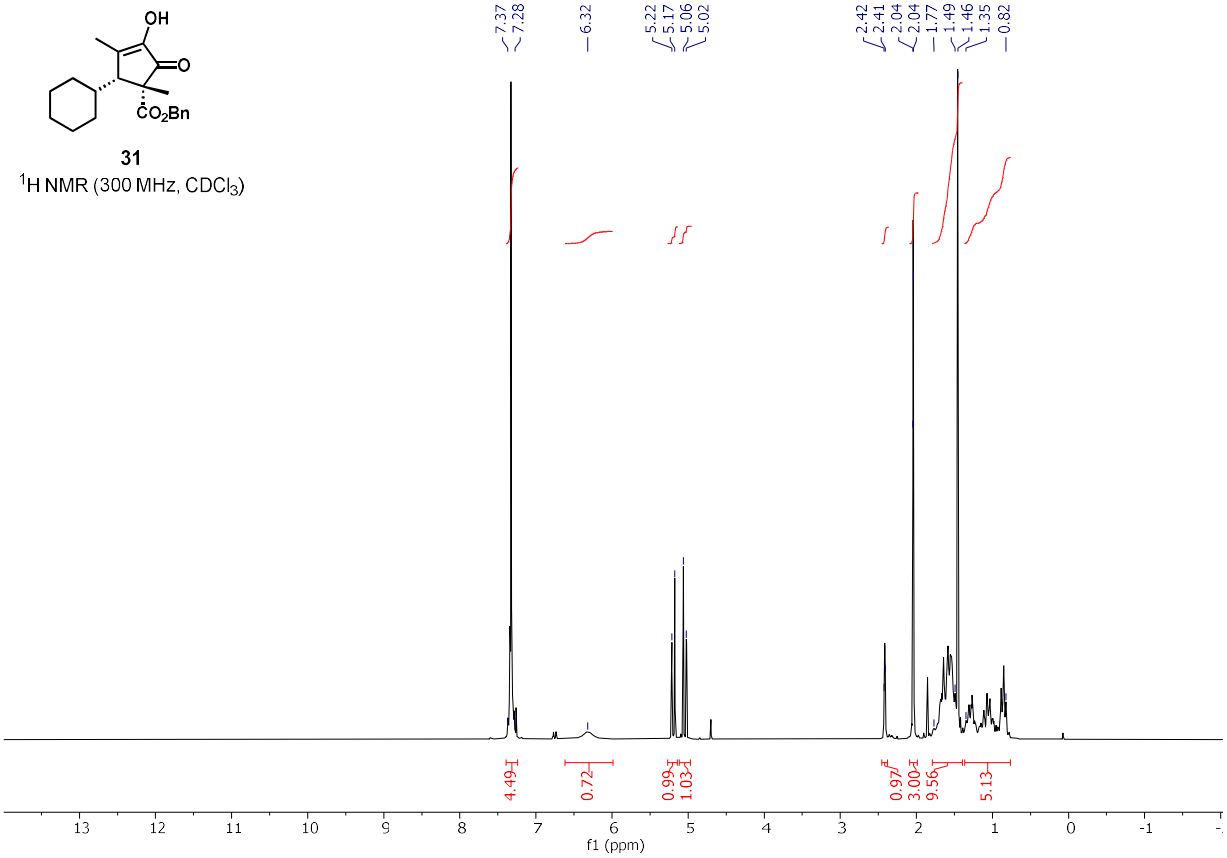
30

^{1}H NMR (300 MHz, $CDCl_3$)



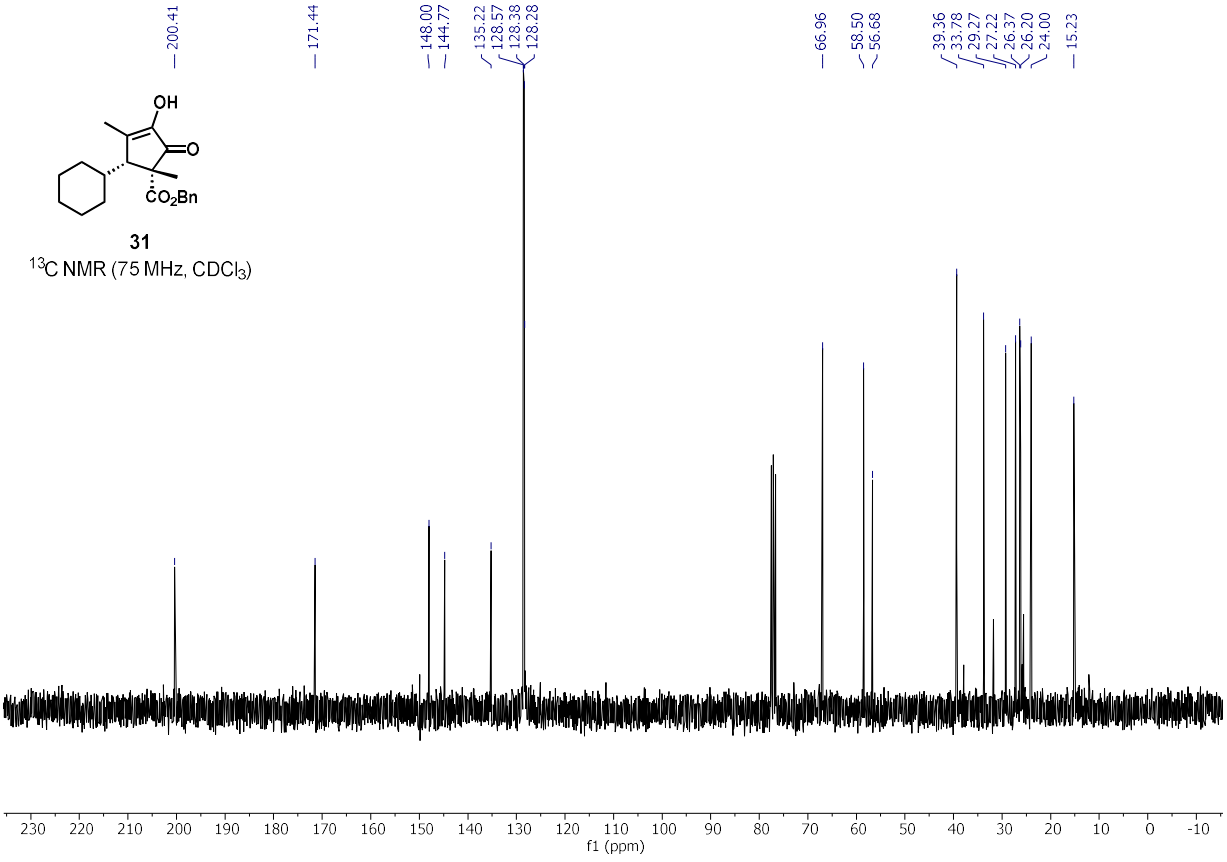
30

^{13}C NMR (75 MHz, $CDCl_3$)



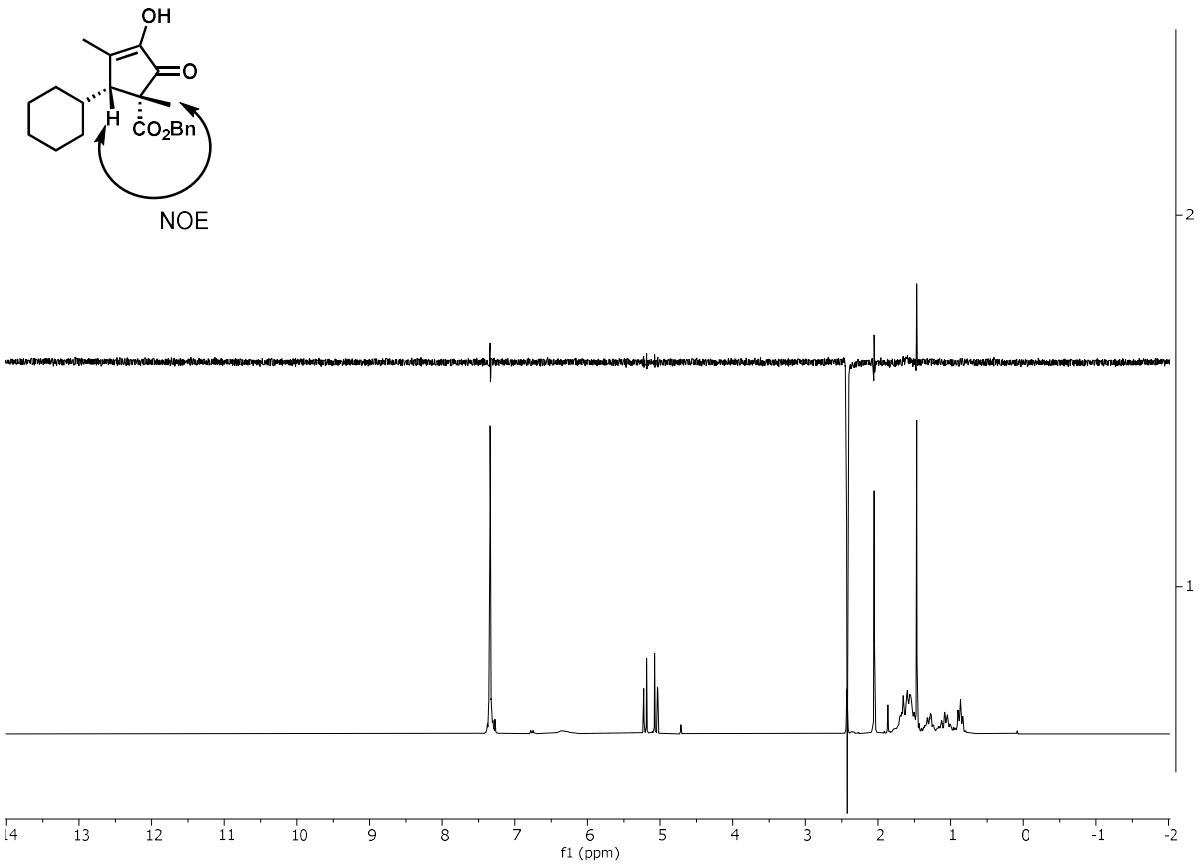
31

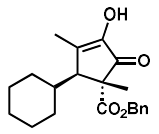
^{1}H NMR (300 MHz, $CDCl_3$)



31

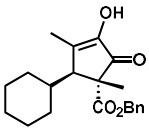
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
H
CO2Bn
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



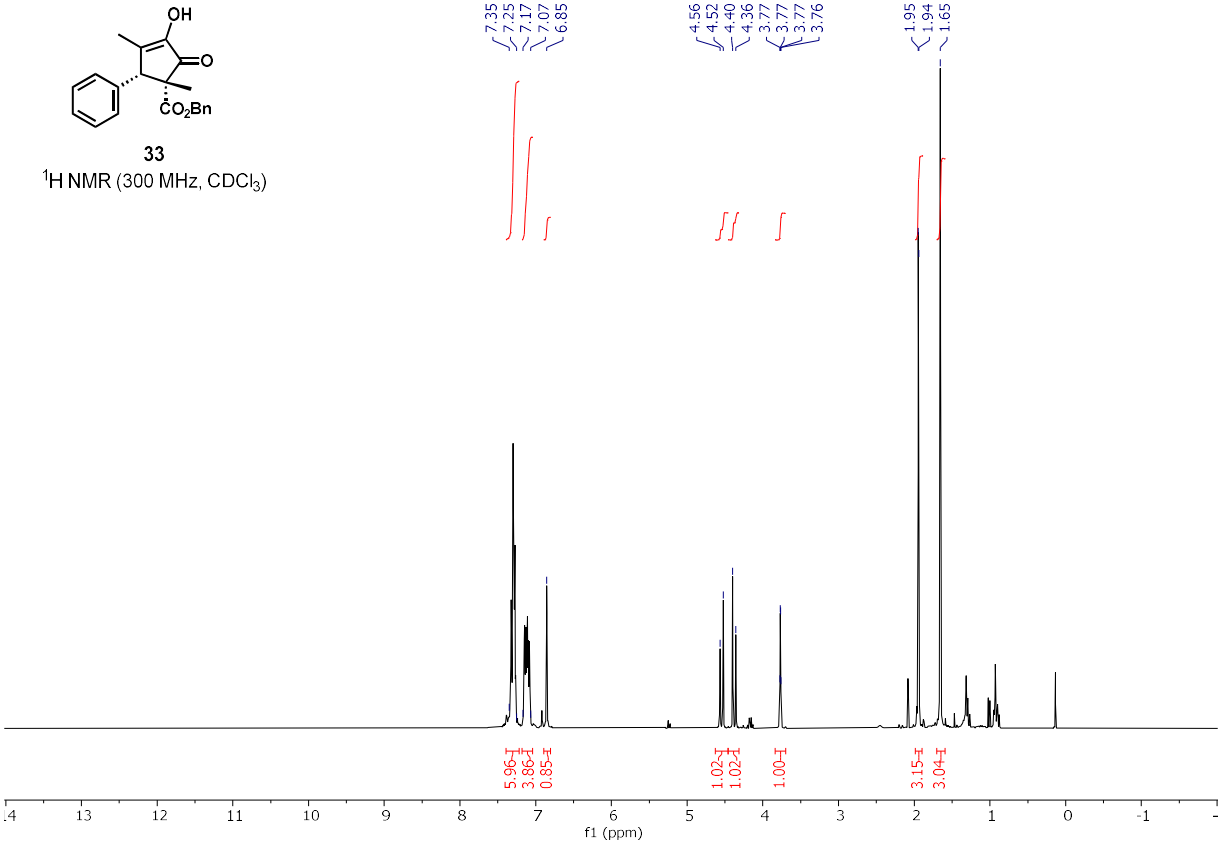
32

^{1}H NMR (300 MHz, $CDCl_3$)



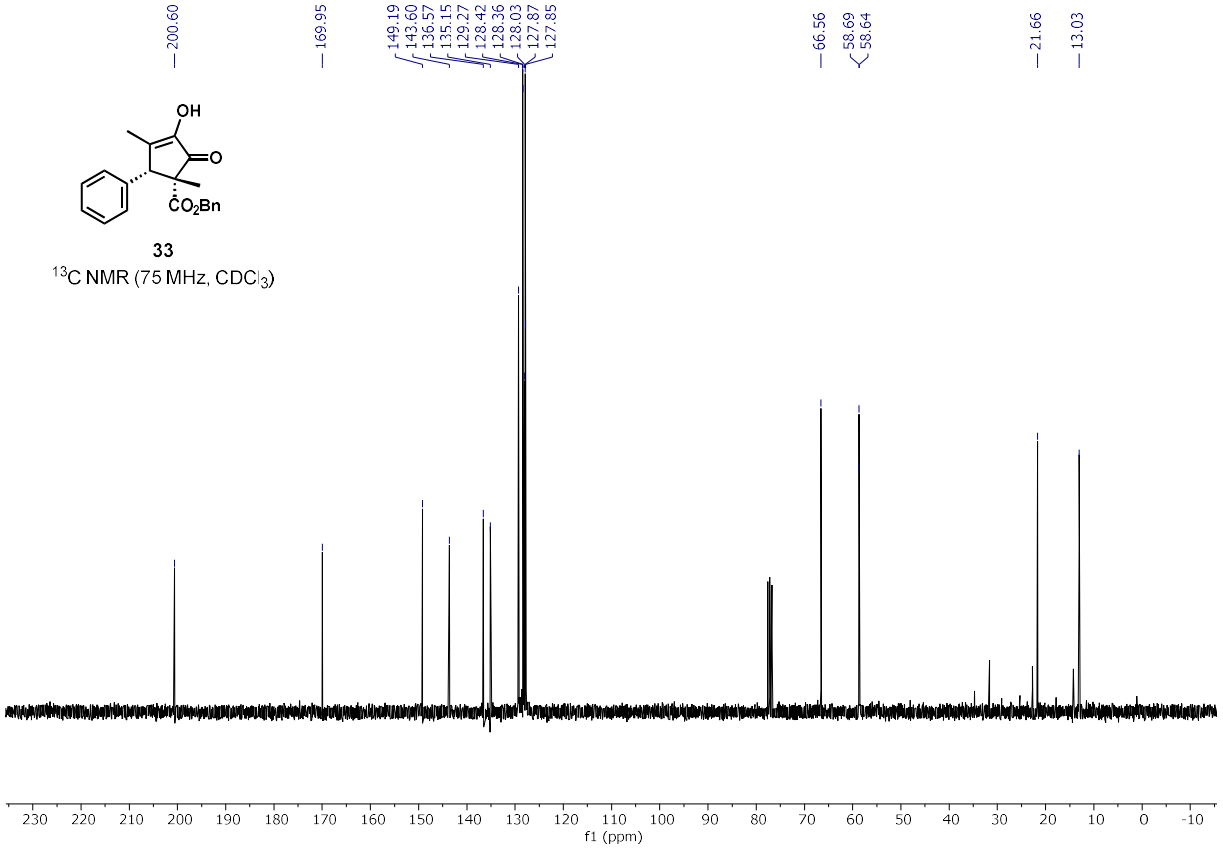
32

^{13}C NMR (75 MHz, $CDCl_3$)



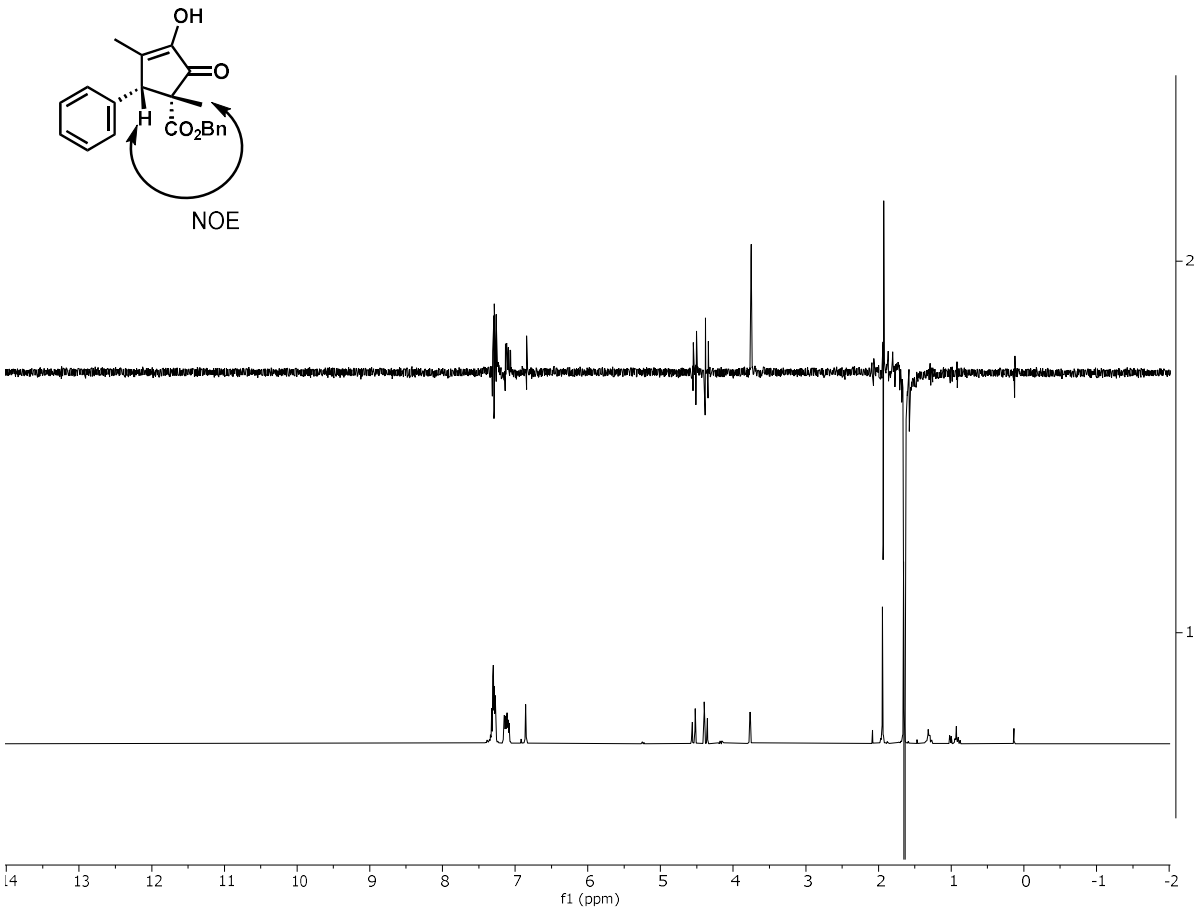
33

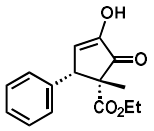
^{1}H NMR (300 MHz, $CDCl_3$)



33

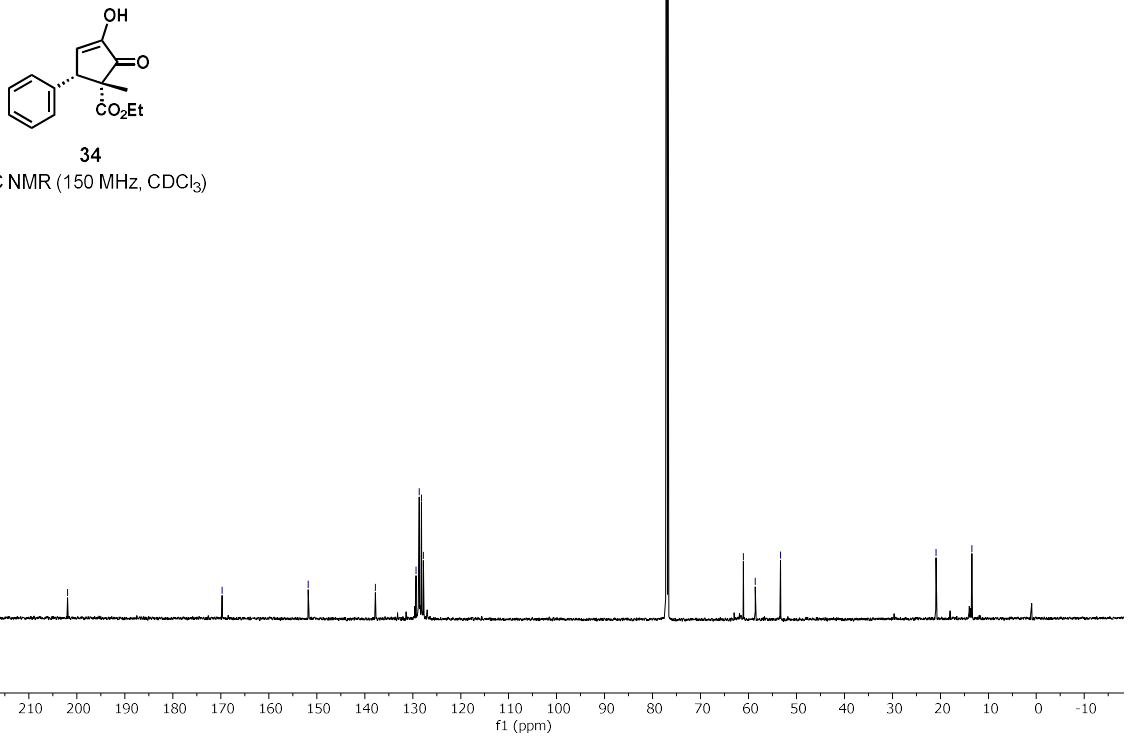
^{13}C NMR (75 MHz, $CDCl_3$)


OH
O
H
CO2Bn
NOE
2
1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



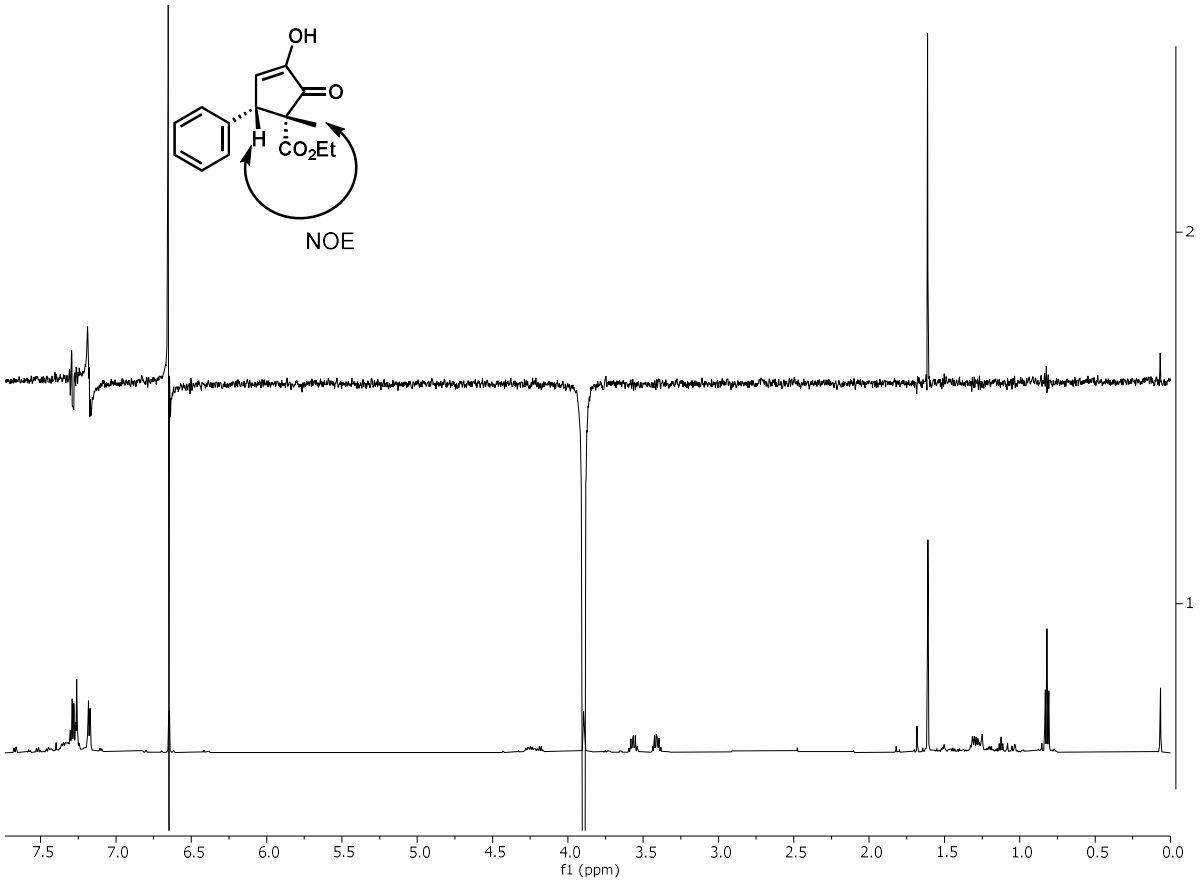
34

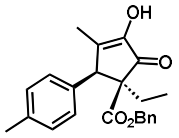
^{1}H NMR (300 MHz, $CDCl_3$)



34

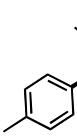
^{13}C NMR (150 MHz, $CDCl_3$)


OH
O
H
CO2Et
NOE
2
1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



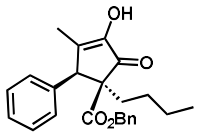
35

^{1}H NMR (300 MHz, $CDCl_3$)



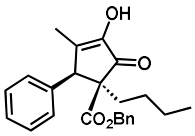
35

^{13}C NMR (75 MHz, $CDCl_3$)



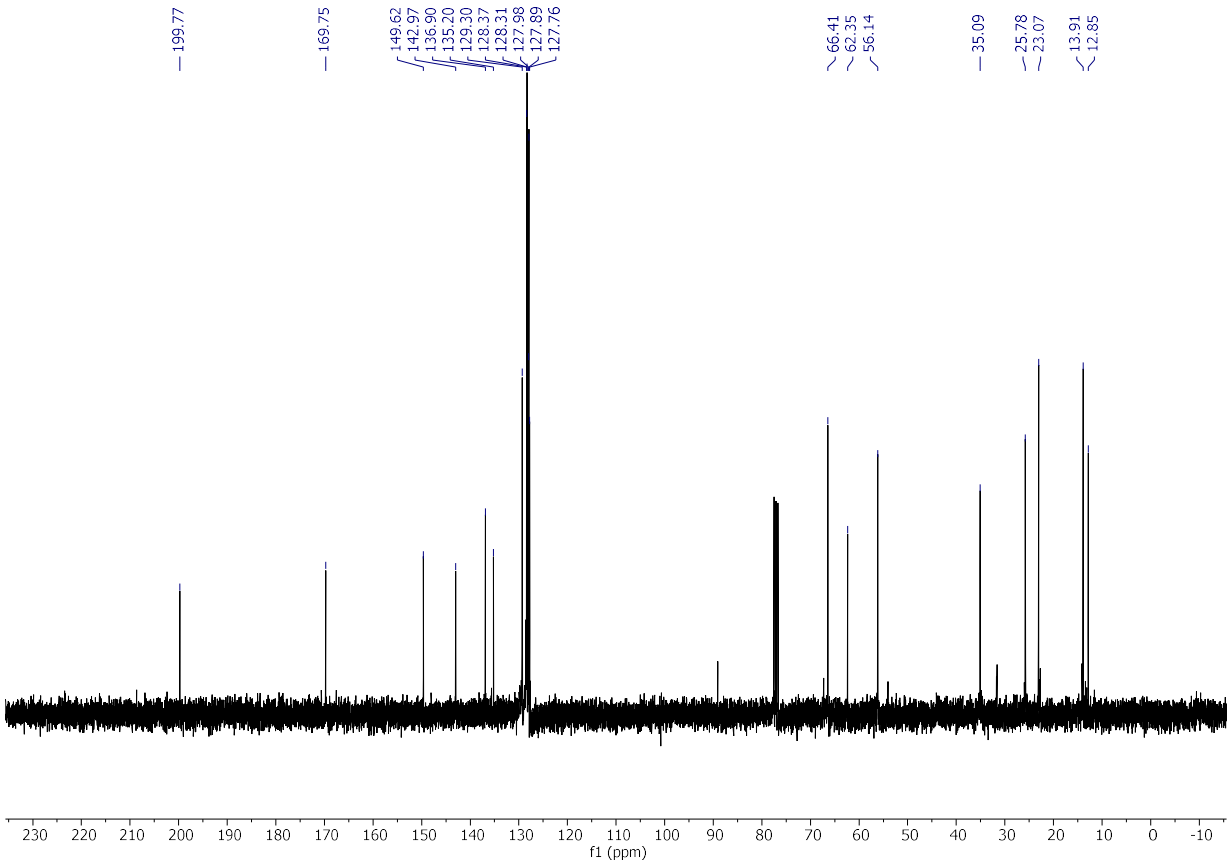
36

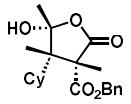
^{1}H NMR (300 MHz, $CDCl_3$)



36

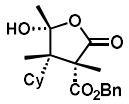
^{13}C NMR (75 MHz, $CDCl_3$)


199.77
169.75
149.62
142.97
136.90
135.20
129.30
128.37
128.31
127.98
127.89
127.76
66.41
62.35
56.14
35.09
25.78
23.07
13.91
12.85
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



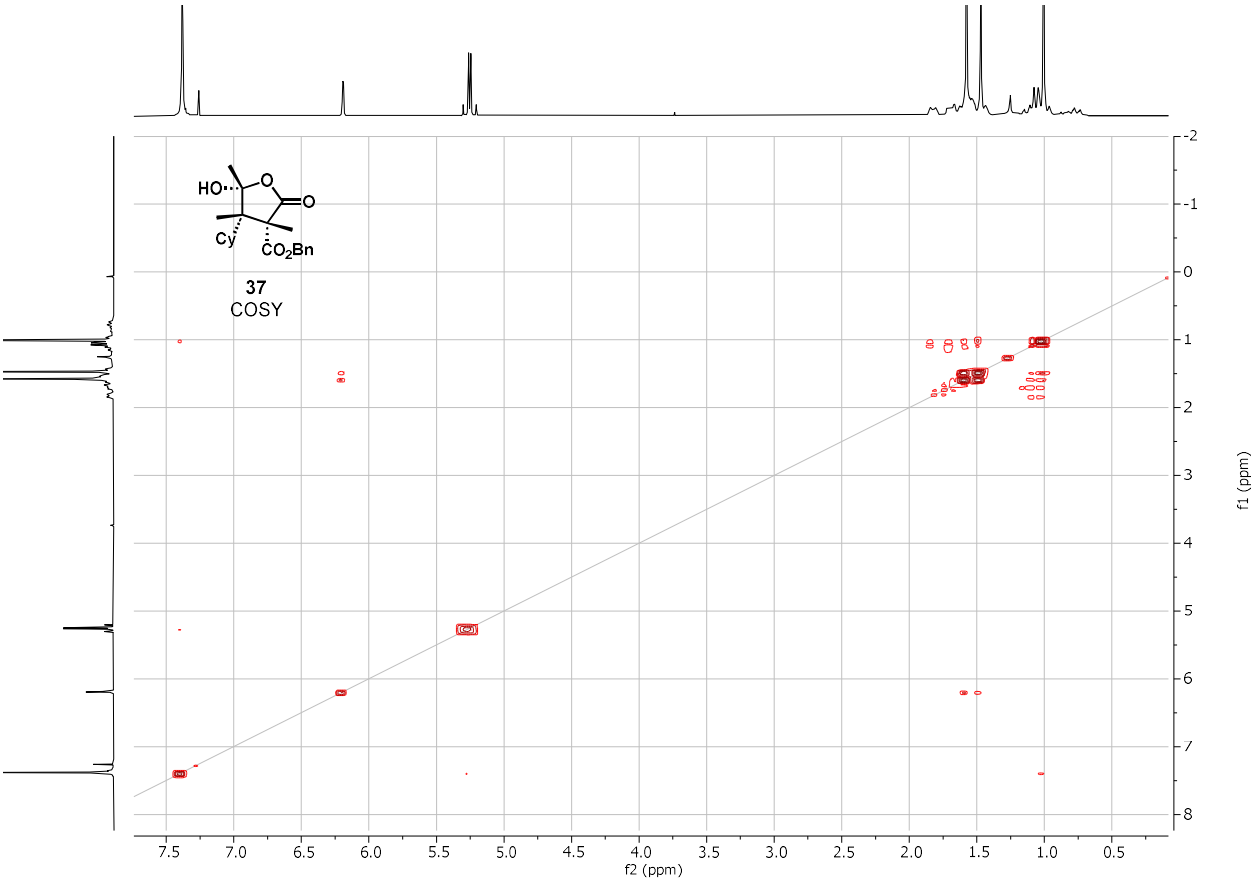
37

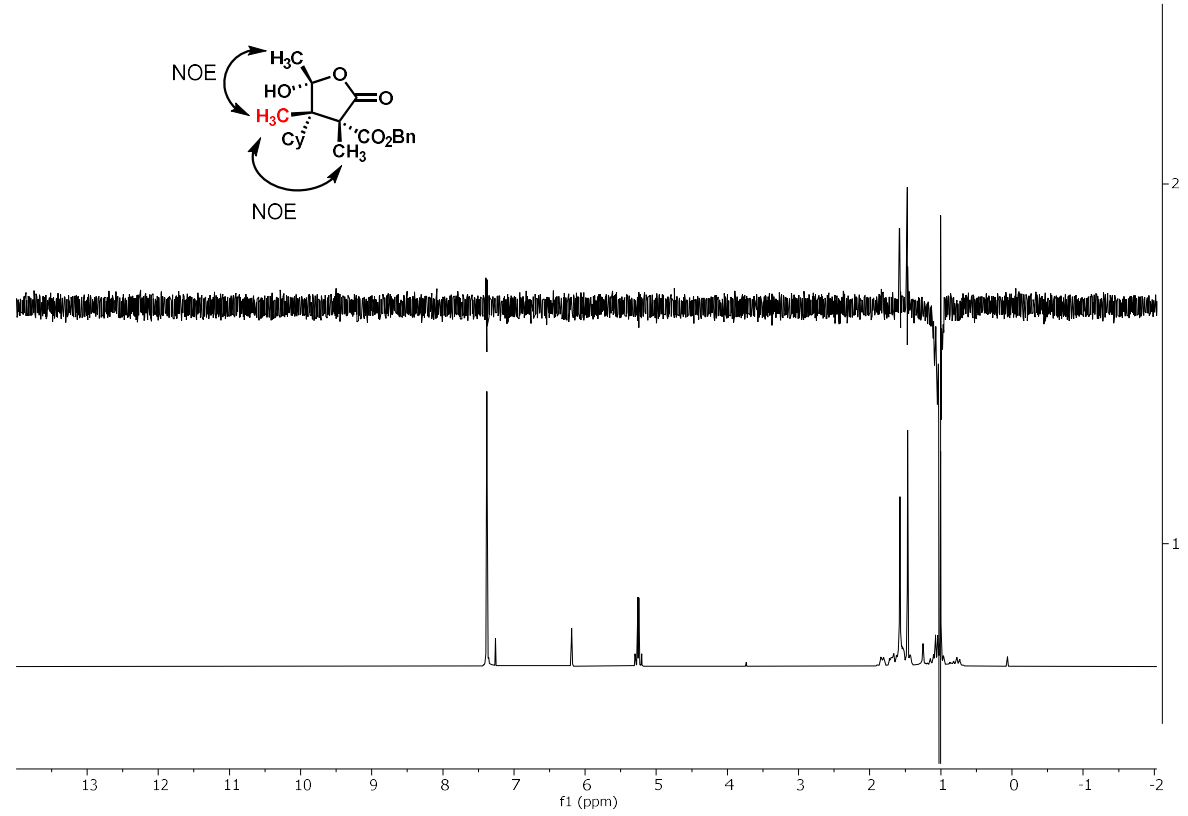
^{1}H NMR (300 MHz, $CDCl_3$)

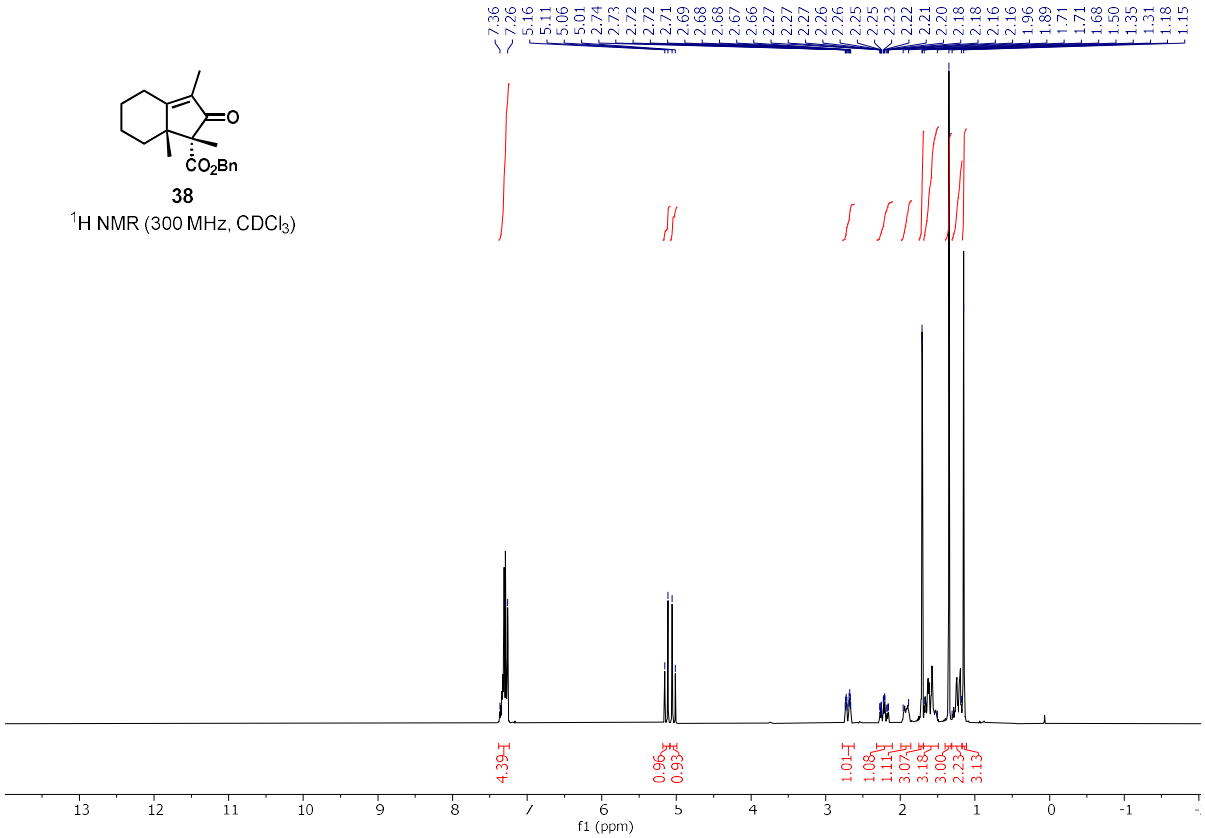


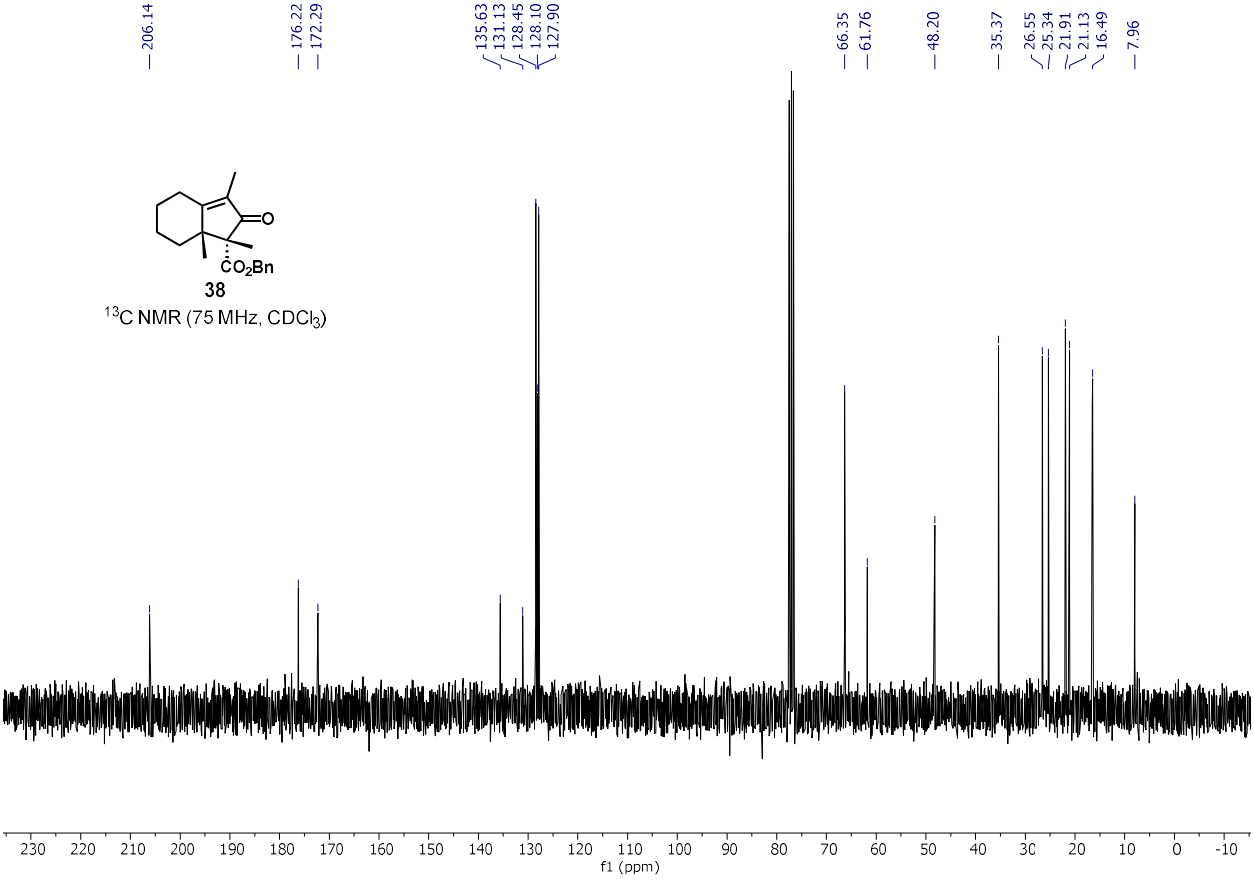
37

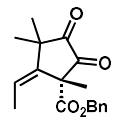
^{13}C NMR (75 MHz, $CDCl_3$)


HO
O
O
Cy
CO2Bn
37
COSY
f2 (ppm)
f1 (ppm)


NOE
H3C
HO
O
O
H3C
Cy
CO2Bn
CH3
NOE
f1 (ppm)

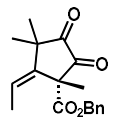

38
1H NMR (300 MHz, CDCl3)
f1 (ppm)


38
13C NMR (75 MHz, CDCl3)
f1 (ppm)



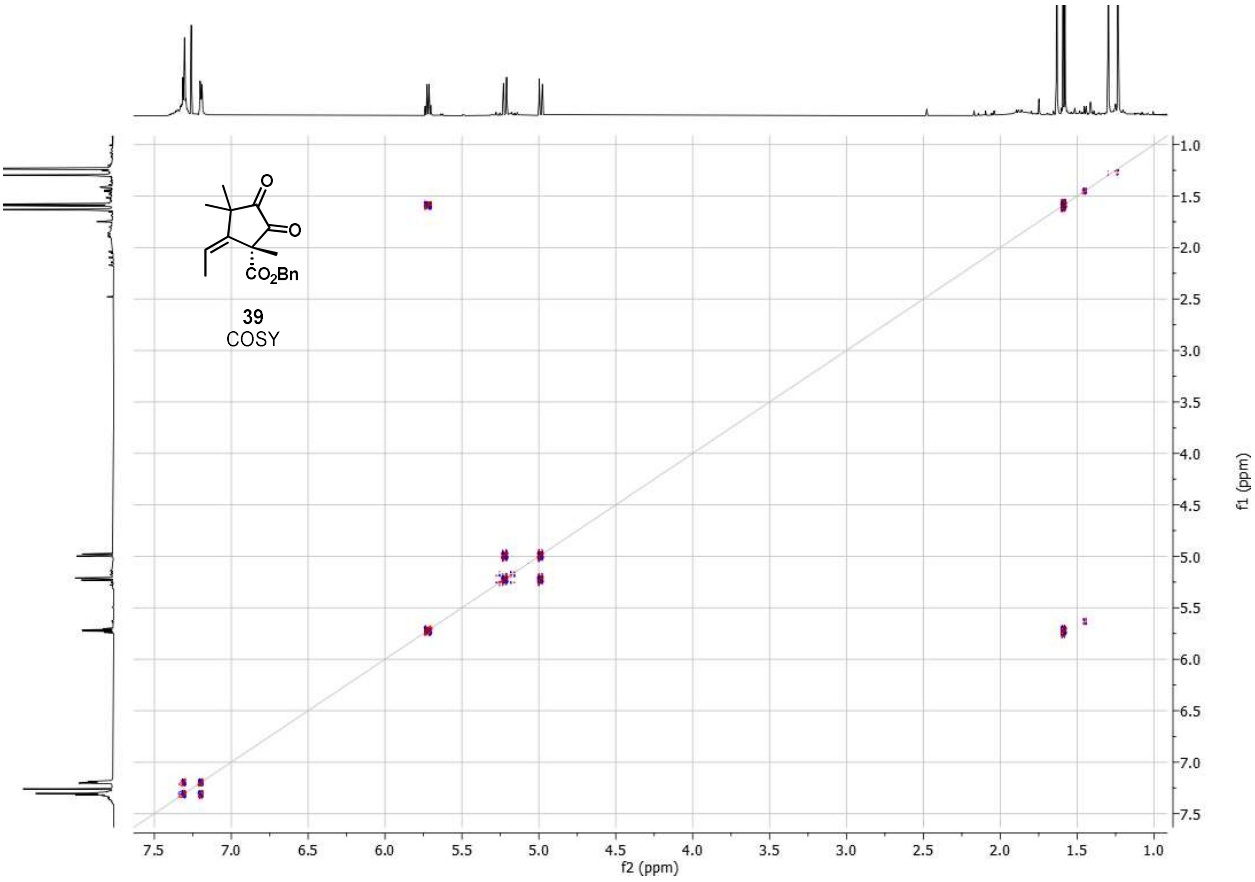
39

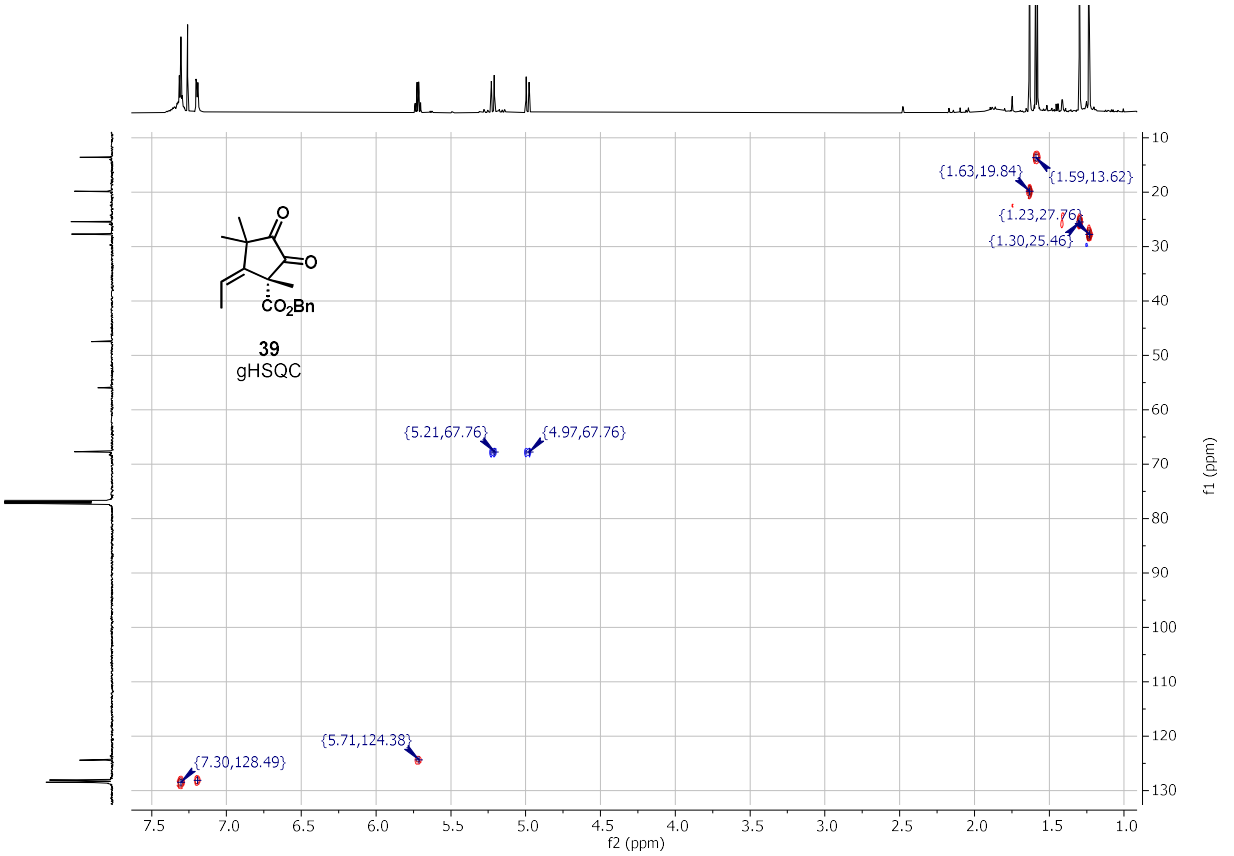
^{1}H NMR (600 MHz, $CDCl_3$)

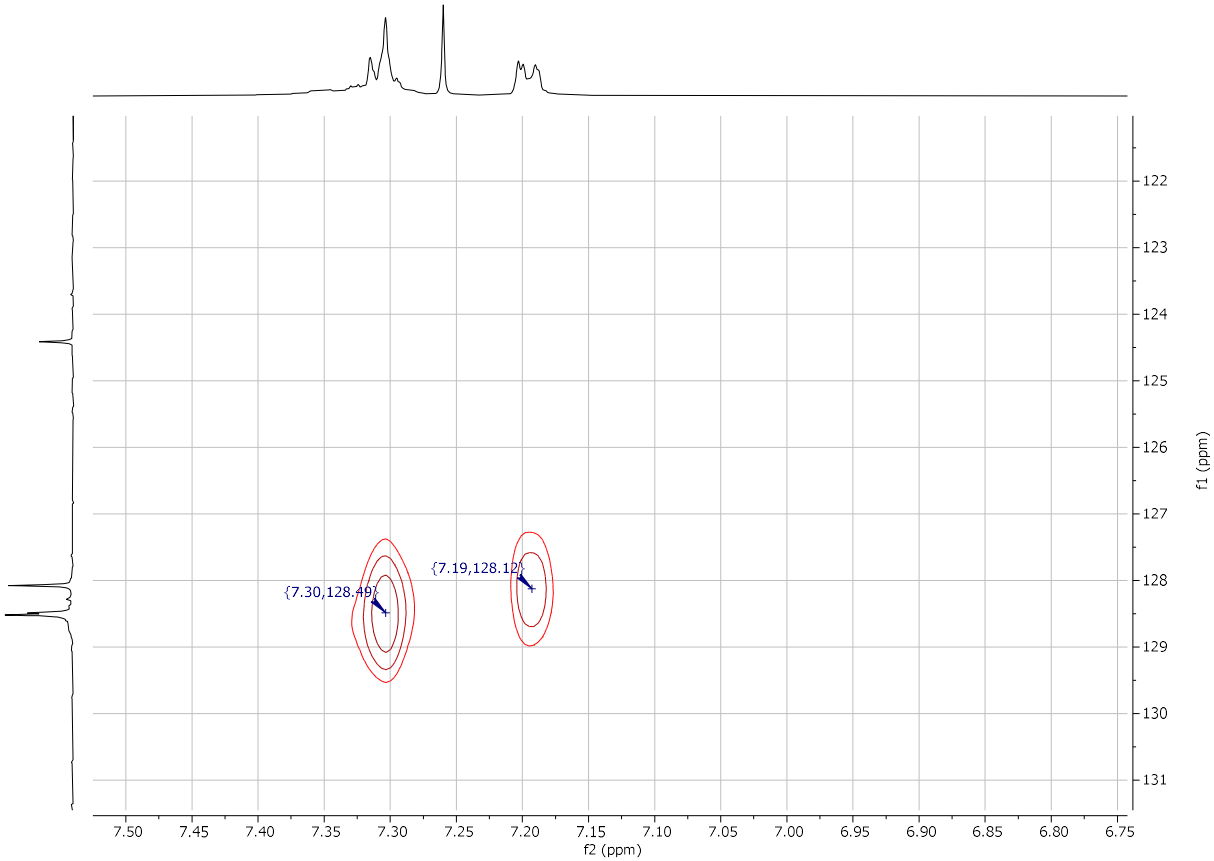


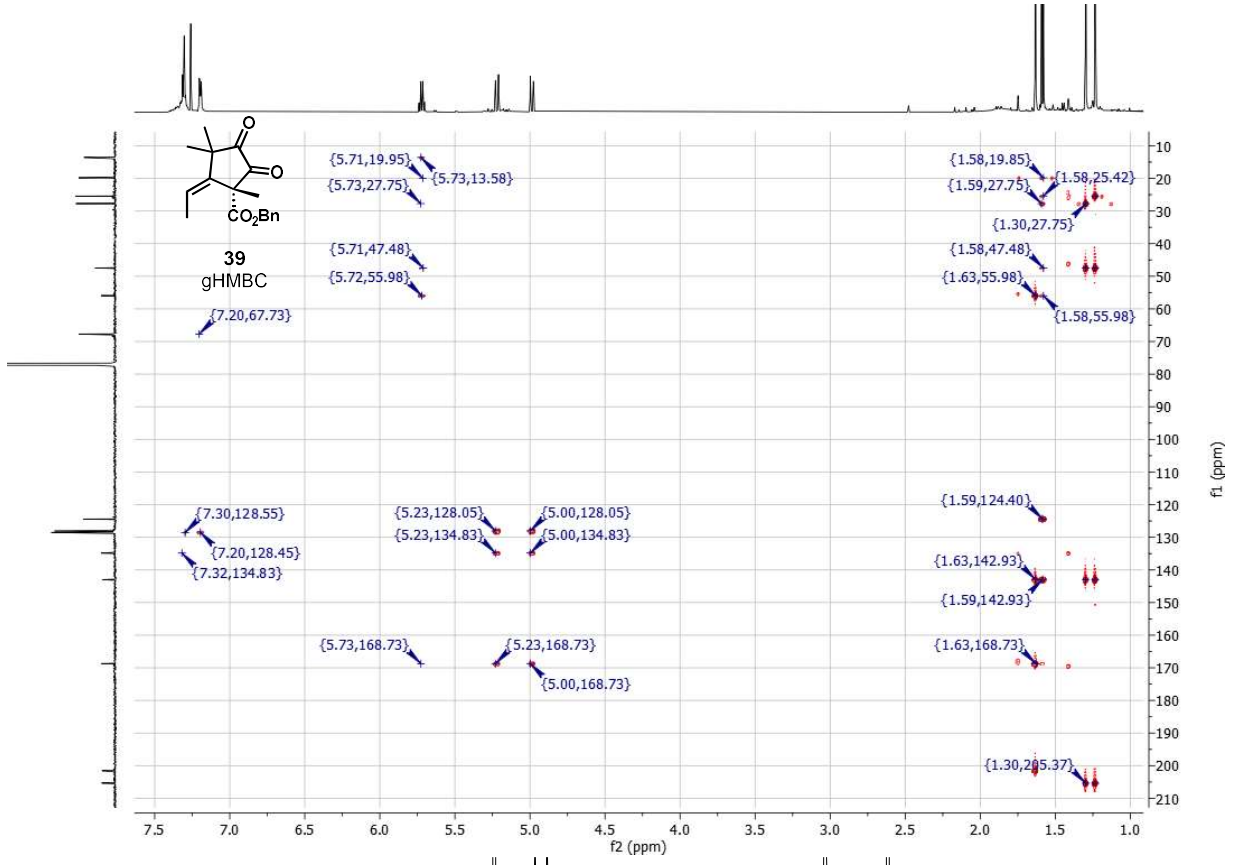
39

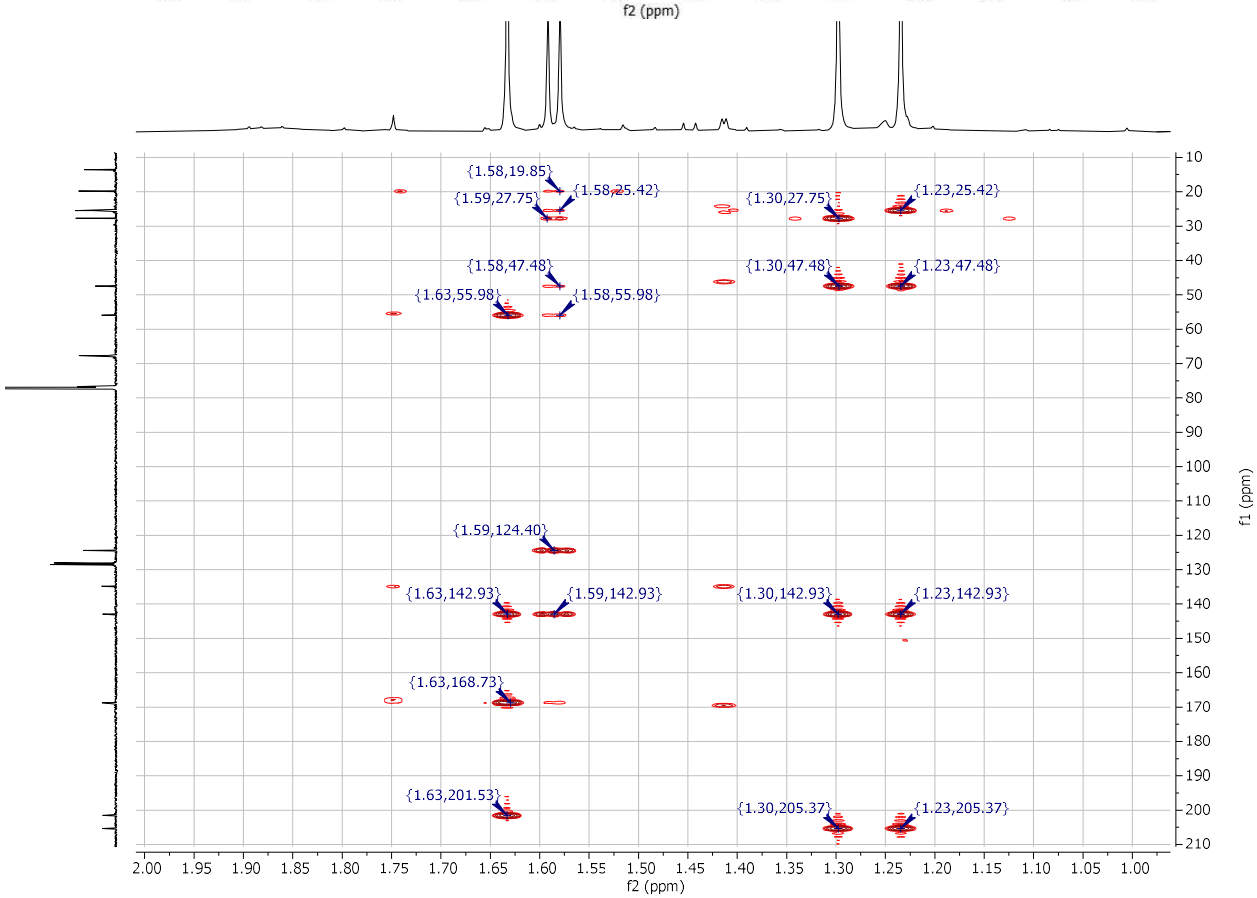
^{13}C NMR (150 MHz, $CDCl_3$)

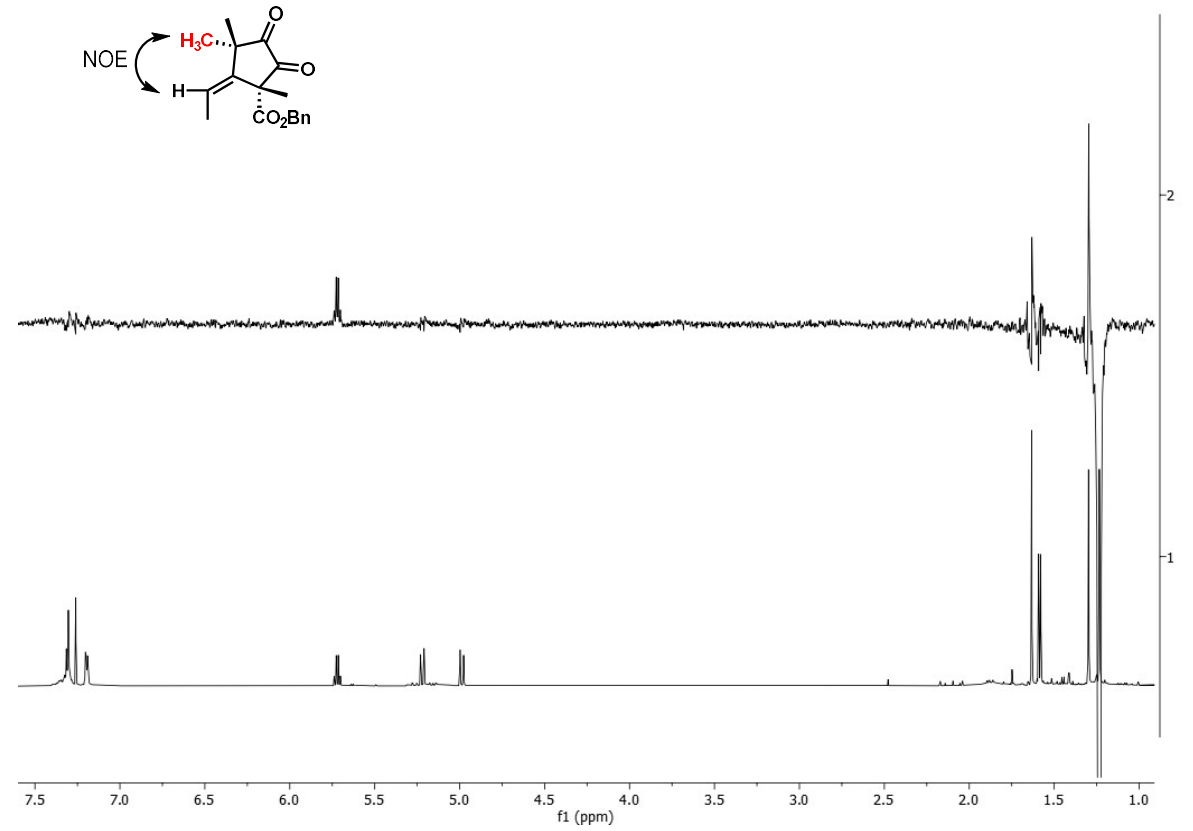

O
O
CO2Bn
39
COSY
f2 (ppm)
f1 (ppm)

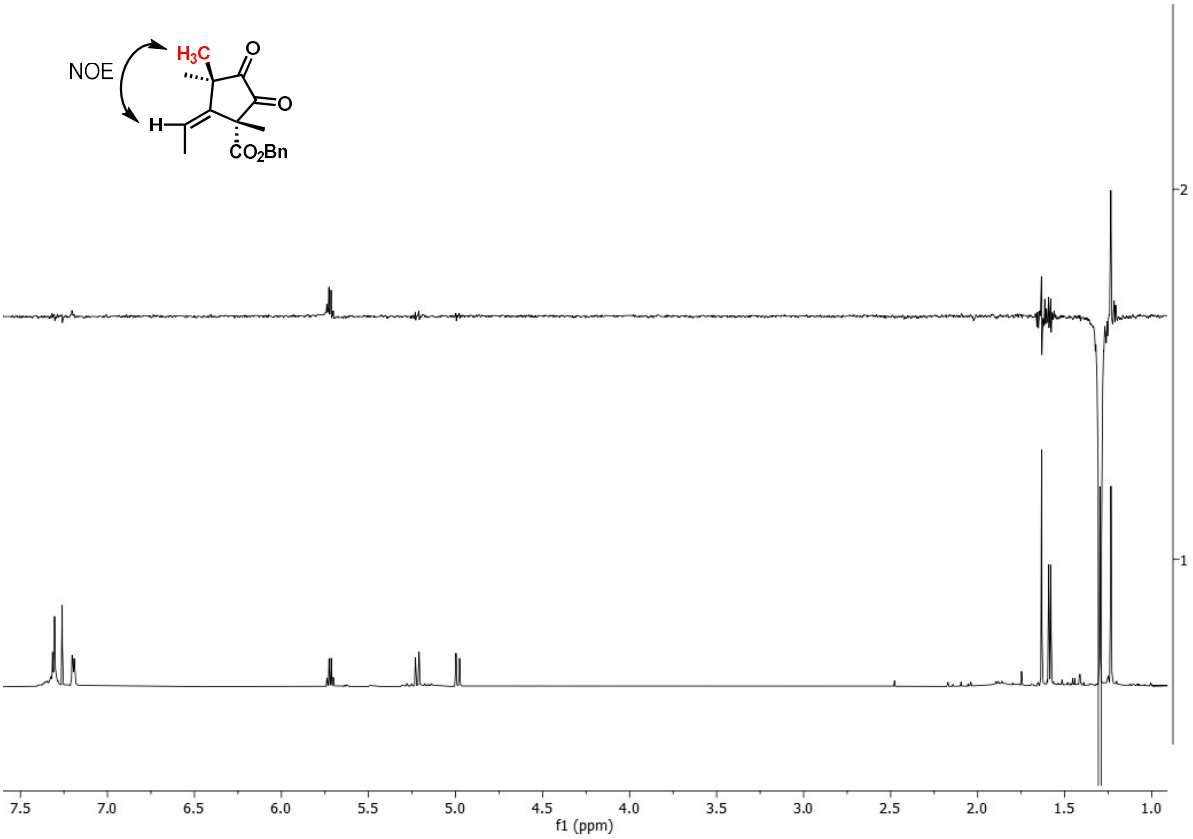

{1.63,19.84}
{1.59,13.62}
{1.23,27.76}
{1.30,25.46}
{5.21,67.76}
{4.97,67.76}
{5.71,124.38}
{7.30,128.49}
39
gHSQC
f2 (ppm)
f1 (ppm)

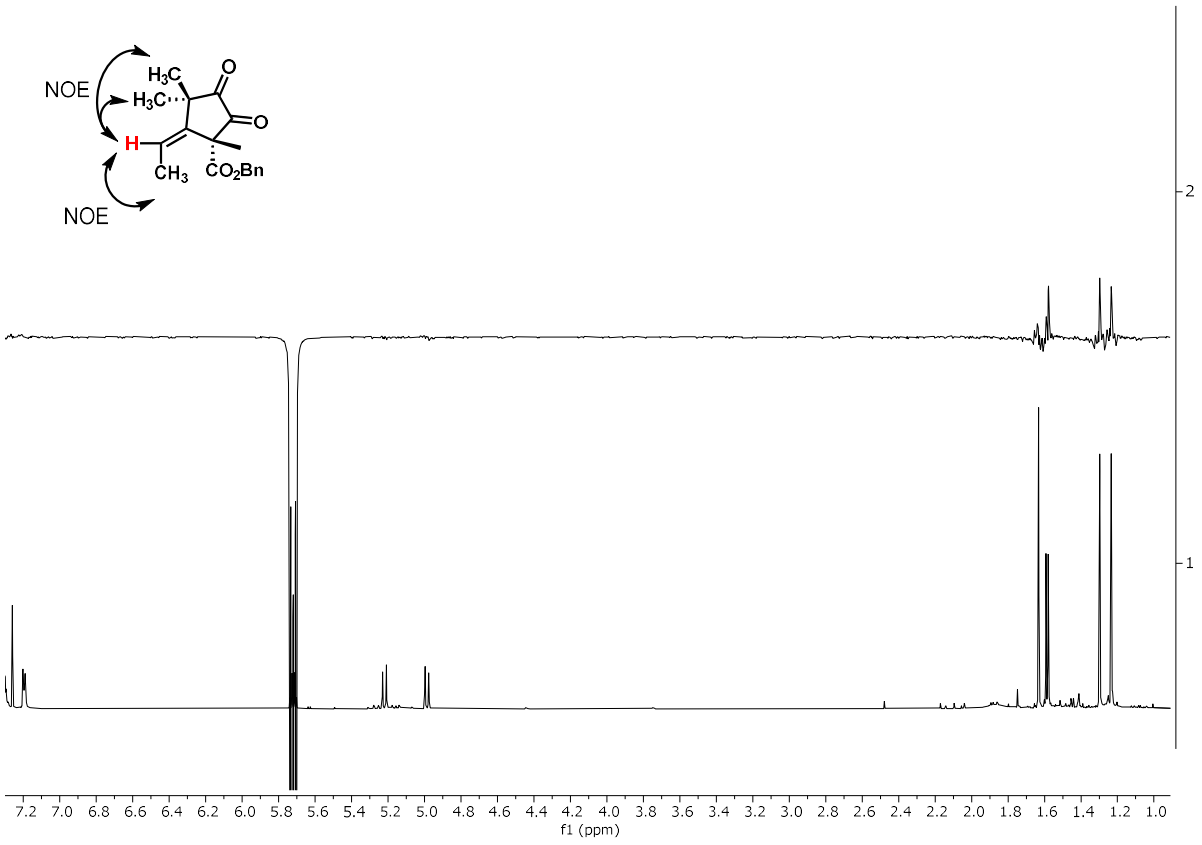

{7.30,128.49}
{7.19,128.12}
f2 (ppm)
f1 (ppm)

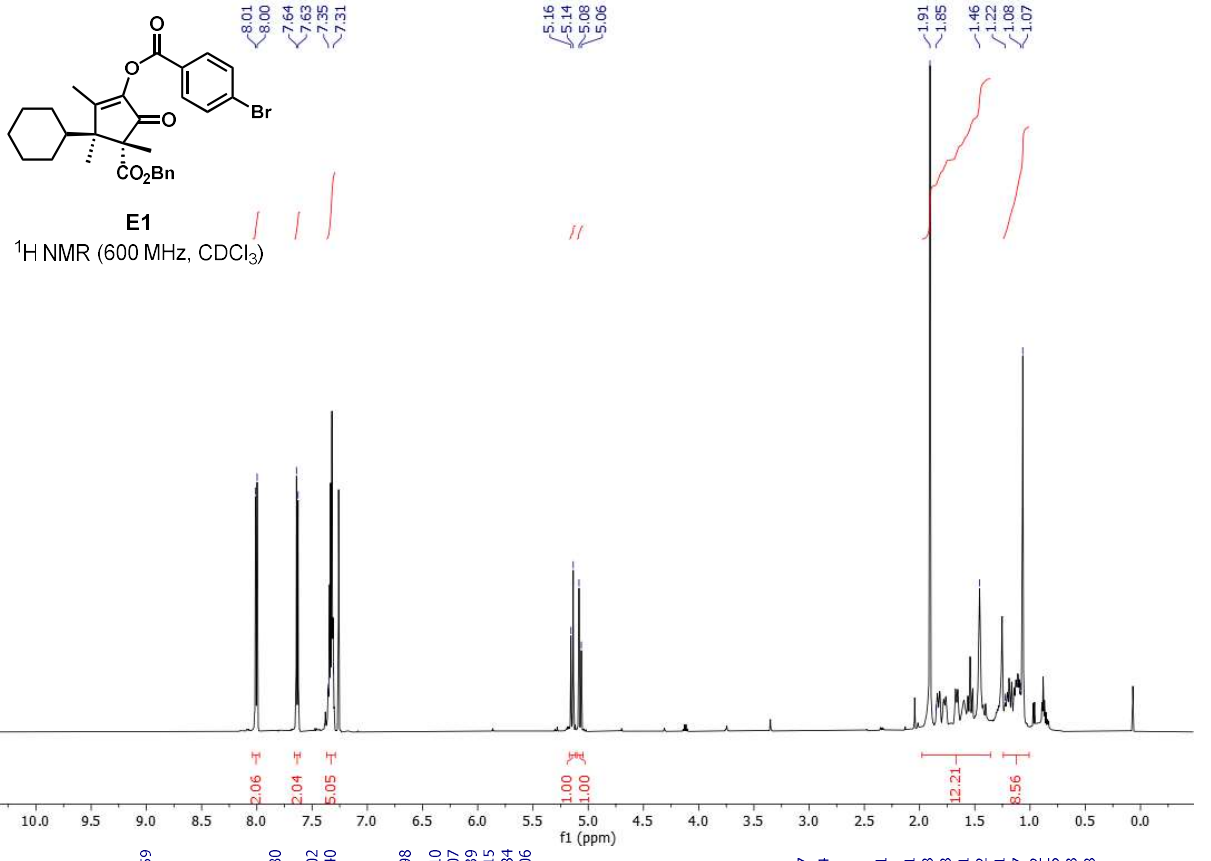

39
gHMBC
{5.71,19.95}
{5.73,13.58}
{5.73,27.75}
{5.71,47.48}
{5.72,55.98}
{7.20,67.73}
{1.58,19.85}
{1.58,25.42}
{1.59,27.75}
{1.30,27.75}
{1.58,47.48}
{1.63,55.98}
{1.58,55.98}
{7.30,128.55}
{7.20,128.45}
{7.32,134.83}
{5.23,128.05}
{5.23,134.83}
{5.00,128.05}
{5.00,134.83}
{1.59,124.40}
{1.63,142.93}
{1.59,142.93}
{5.73,168.73}
{5.23,168.73}
{5.00,168.73}
{1.63,168.73}
{1.30,205.37}
f2 (ppm)
f1 (ppm)


{1.58,19.85}
{1.59,27.75}
{1.58,25.42}
{1.30,27.75}
{1.23,25.42}
{1.58,47.48}
{1.63,55.98}
{1.58,55.98}
{1.30,47.48}
{1.23,47.48}
{1.59,124.40}
{1.63,142.93}
{1.59,142.93}
{1.30,142.93}
{1.23,142.93}
{1.63,168.73}
{1.63,201.53}
{1.30,205.37}
{1.23,205.37}
f2 (ppm)
f1 (ppm)


NOE
H3C
O
O
H
CO2Bn
2
1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

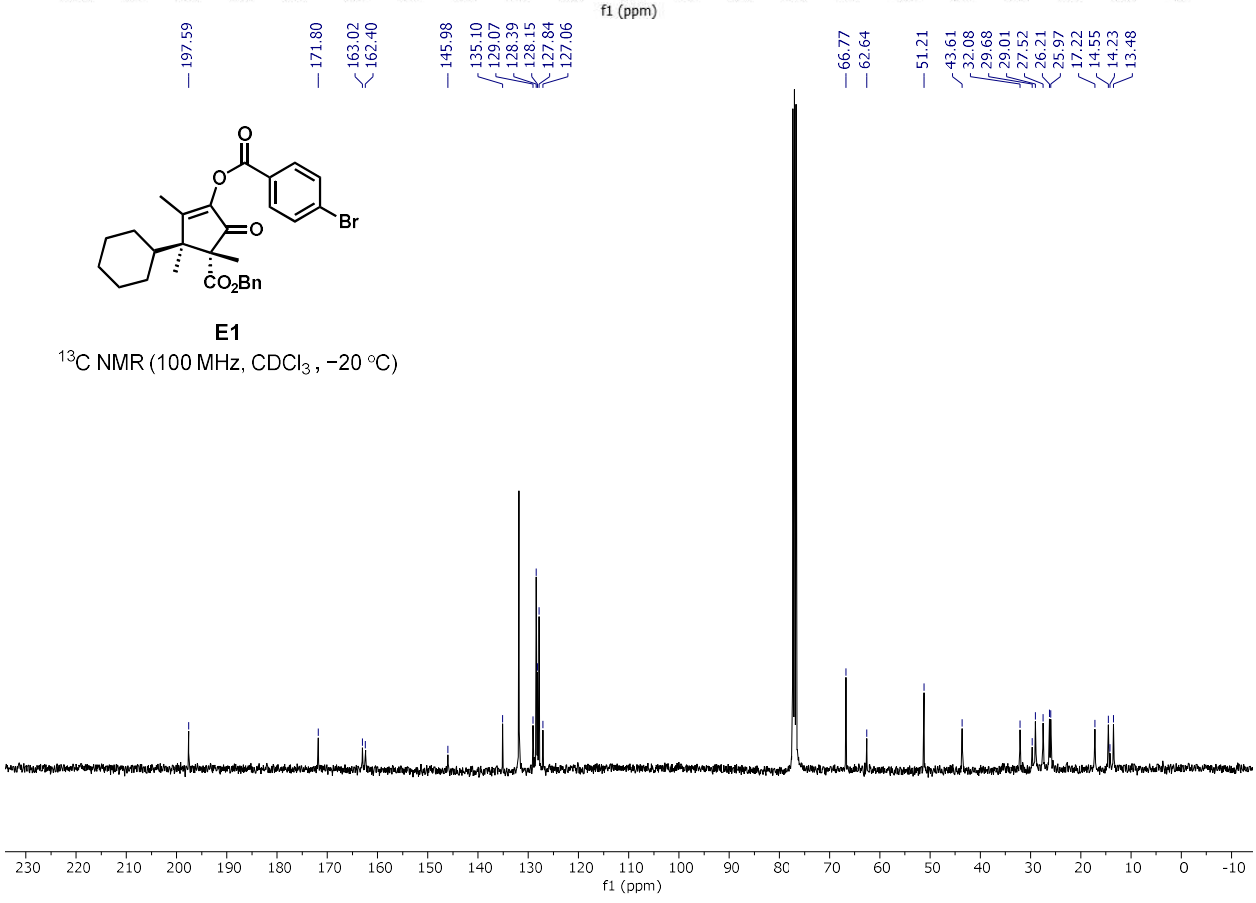

NOE
H3C
O
O
H
CO2Bn
2
1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


NOE
H3C
H3C
O
O
H
CH3
CO2Bn
NOE
2
1
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)



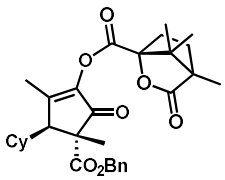
E1

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



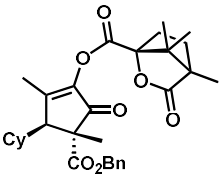
E1

^{13}C NMR (100 MHz, $CDCl_3$, −20 °C)



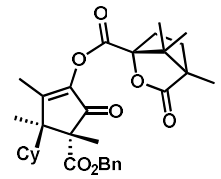
E2

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



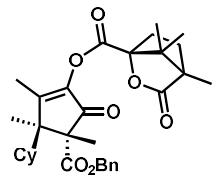
E2

^{13}C NMR (150 MHz, $CDCl_3$)



E3

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



E3

^{13}C NMR (150 MHz, $CDCl_3$)