

Supporting Information

Reinventing the De Mayo Reaction: Synthesis of 1,5-Diketones via visible light [2+2] cycloaddition of β -diketones with Styrenes.

Rebeca Martinez-Haya^[b] Leyre Marzo^{*[a]} and Burkhard König^{*[a]}

[a] Institute of Organic Chemistry, University of Regensburg, D-93040 Regensburg, Germany.

[b] Instituto de Tecnología Química. Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas. Avda. de los Naranjos s/n, E-46022, Valencia, (Spain)

E-mail: Burkhard.Koenig@ur.de.

Table of Contents

1. General Methods and Materials	S2
2. Optimization of the reaction conditions	S3
3. Absorption and emission spectrum and luminescence quenching experiments	S5
3.1. Absorption and emission spectrum of 1a , 1d , 3a , and 2a	S5
3.2. Steady state and time resolved luminescence quenching experiments	S5
4. Cyclic voltammetry experiments, ΔG and comparative graphic	S7
5. NMR titration experiments	S10
6. Synthesis and characterization of starting materials	S13
7. Synthesis and characterization of compounds 4a-4y	S14
8. NMR spectra for starting materials and compounds 4a-4y	S24
9. References	S56

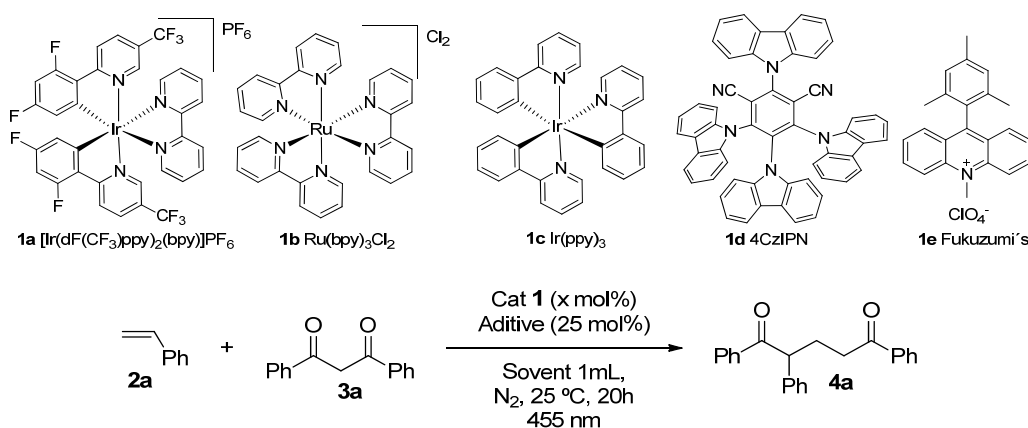
1. General Methods and Materials:

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for ^1H , 75 MHz for ^{13}C), or a Bruker Avance 400 (400 MHz for ^1H , 101 MHz for ^{13}C) NMR spectrometer. All chemical shifts are reported in δ -scale as parts per million [ppm] (multiplicity, coupling constant J , number of protons) relative to the solvent residual peaks as the internal standard.¹ Coupling constants J are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^1H -NMR: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. The mass spectrometric measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC/MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975MSD Detector. Data acquisition and evaluation was done with MSD ChemStationE.02.02.1431. A capillary column HP-5MS/30 m x 0.25 mm/0.25 μm film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 $^\circ\text{C}$, detection temperature 300 $^\circ\text{C}$ (FID). Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 μm , 230-440 mesh, Merck) on a Biotage® Isolera TM Spektra One device. Photocatalytic reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs ($\lambda = 455 \text{ nm} (\pm 15 \text{ nm})$, 3.5 V, 700 mA). Quartz cells of 1 cm optical pathlength were employed for all photophysical measurements, which were run at room temperature. UV-Vis measurements were carried out with a Varian Cary 50 UV/Vis spectrophotometer. Steady state and time resolved luminiscence measurements were performed with a FluoroMax-4 and HORIBA DeltaPro spectrofluorometer respectively. Phosphorescence spectra were performed in a Horiba Jobin Yvon Fluorolog 3 spectrometer in a liquid nitrogen dewar accessory at 77K. The samples were dissolved in ethanol ($\text{Abs}_{\lambda = 360 \text{ nm}} = 1$) introduced in a quartz tube of 5 mm of diameter and cooled at 77 K for the measurements. Electrochemical studies were performed in acetonitrile (CH_3CN) containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc^+) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed. Spectroelectrochemical studies were carried out in an optically transparent thin layer electrochemical cell (OTTLE). Quantum yield measurement were performed with the Quantum Yield Determination Setup, ag-Riedle.² Commercially available starting materials and solvents were used without further purification.

2. Optimization of the reaction conditions:

We began the optimization of the conditions in the reaction between **2a** and **3a** with 2 mol% of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})]\text{PF}_6$ **1a**, under nitrogen atmosphere, 25 °C and blue LED irradiation. Under these conditions, **4a** was isolated in 69% yield (entry 1, Table S1). Then, different photocatalysts were explored in this reaction (entries 2-5, Table S1). With $\text{Ru}(\text{bpy})_3^{2+}$ **1b**, ($E_T = 46.5 \text{ kcal mol}^{-1}$, or $\text{Ir}(\text{ppy})_3$ **1c** ($E_T = 55 \text{ Kcal mol}^{-1}$) the reaction did not work.³ However, 4CzIPN **1d** ($E_T = 60 \text{ kcal mol}^{-1}$) afforded the desired product in 44% yield.⁴ Fukuzumi's catalyst **1e**, with a higher oxidation power, did not react, thus discarding a photoredox pathway. In order to shift the keto-enol equilibria to the enol form and favour the [2+2] photocycloaddition step, we tried the reaction in the presence of different bases (entries 6-8, Table S1). The best result was obtained with tributylmethylammonium dibutyl phosphate, yielding **4a** in 79% isolated yield (entry 6, Table S1). Control experiments revealed that **1a** and blue LED irradiation are essential, and that the presence of air decrease the reactivity (entries 9-11, Table S1). Then different solvents were tested in the reaction (entry 12-17, Table S1), with EtOH showing the best result (**4a** 96% yield, entry 17, Table S1). Increasing or decreasing the reaction mixture concentration did not improve this result (entries 18-20, Table S1). Decreasing the amount of base (entries 21-22, Table S1), the number of equivalents of **2a** (entry 23 and 24, Table S1) or the catalyst loading (entry 25, Table S1) did not increase the product yield. Therefore, the optimized reaction conditions were 0.1 mmol of **3a**, 0.5 mmol of **2a**, 2 mol% **1a**, 25 mol% tributylmethylammonium dibutyl phosphate, 1 mL of EtOH, 25 °C, under nitrogen atmosphere and blue LED irradiation.

Table S1: Optimization of the reaction conditions in the visible light mediated De Mayo photocycloaddition.



Entry	Cat (mol%)	Additive	Solvent (1mL)	Yield ^b (%)
1	1a (2)	-	CH ₃ CN	69
2	1b (3)	-	CH ₃ CN	0
3	1c (2)	-	CH ₃ CN	0

4	1d (4)	-	CH ₃ CN	44
5	1e (4)	-	CH ₃ CN	0
6	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	79
7	1a (2)	DMAP	CH ₃ CN	69
8	1a (2)	BzOBF ₄	CH ₃ CN	71
9	1a (2) ^c	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	0
10	--	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	0
11	1a (2) ^d	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	65
12	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	DMSO	49
13	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	DMF	67
14	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	CH ₂ Cl ₂	86
15	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	THF	58
16	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	Et ₂ O	55
17	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH	96
18	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH (0.2 M)	71
19	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH (0.5 M)	87
20	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH (0.05 M)	85
21	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me (15 mol%)	EtOH	66
22	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me (5 mol%)	EtOH	88
23	1a (2) ^e	(BuO) ₂ P(O)ONBu ₃ Me	EtOH	65
24	1a (2) ^f	(BuO) ₂ P(O)ONBu ₃ Me	EtOH	34
25	1a (1)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH	75

^a All the reactions were performed using 0.1 mmol **3a**, 0.5 mmol **2a**, 25 mol% additive, under nitrogen atmosphere, 25 °C, blue LED irradiation, and stopped after 20h. ^b Isolated yield. ^c Without light. ^d In the presence of air. ^e 3 equiv. **2a**. ^f 1 equiv. **2a**.

3. Absorption and emission spectrum and luminescence quenching experiments:

3.1. Absorption and emission spectrum of 1a, 1d, 3a, and 2a:

The absorption spectrum of **1a**, **3a**, and **2a** were measured from a solution of EtOH, while **1c** was measured in ACN. The emission spectrum were measured from the solutions employed to measure the absorption spectrum.

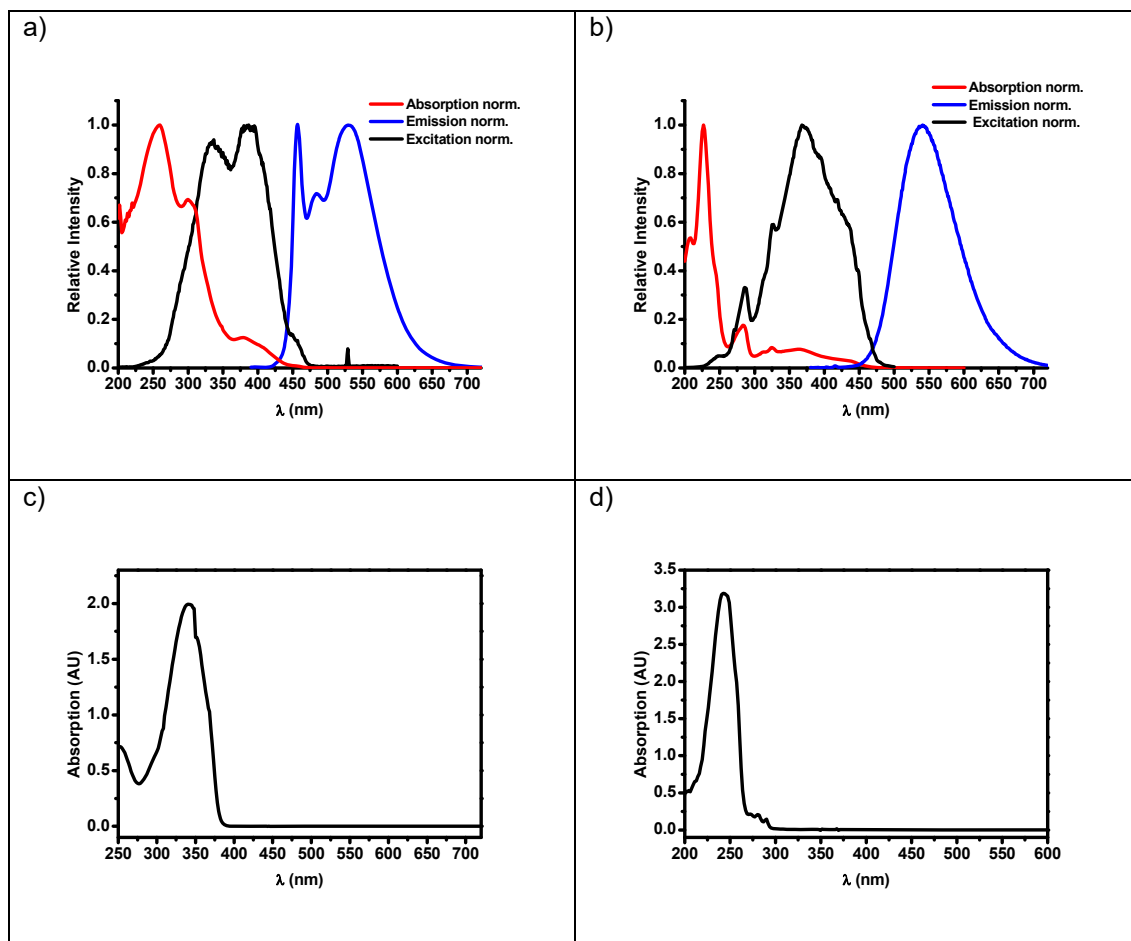
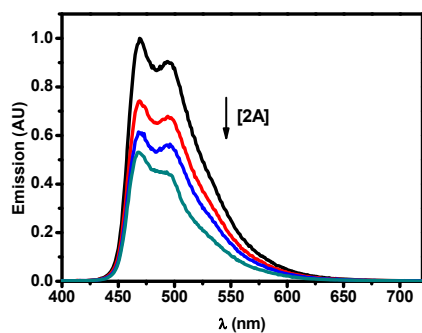


Figure S1: a) Normalized absorption, emission and excitation spectra of **1a**; b) Normalized absorption, emission and excitation spectra of **1d**; c) Absorption spectrum of **3a** in EtOH (10^{-4} M); d) Absorption spectrum of **2a** in EtOH (5.5×10^{-4} M);

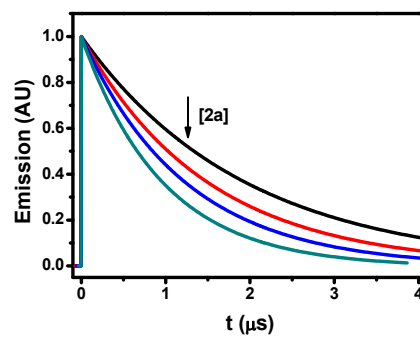
3.2. Steady-state and time resolved luminescence quenching experiments:

For the steady-state and time-resolved luminescence experiments, increasing concentrations of quencher (up to 5×10^{-5} M) were added to **1a** solutions in ethanol with absorbance 0.1-0.15 at the excitation wavelength ($\lambda_{exc} = 370$ nm) under N_2 atmosphere.

a)



b)



c)

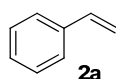
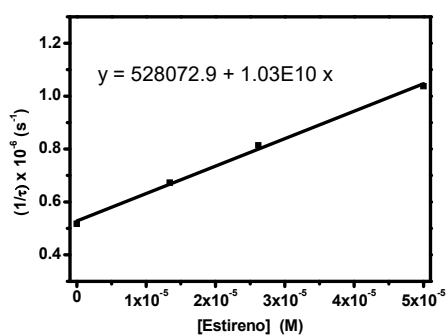
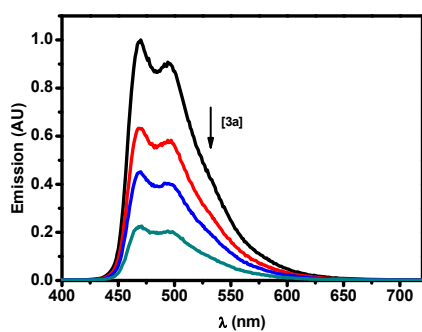
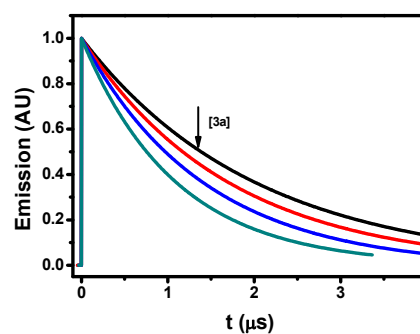


Figure S2: a) Steady state luminescence quenching of **1a*** with styrene **2a**; b) time resolved luminescence quenching of **1a*** with styrene **2a**; c) Stern-Volmer plot of the time resolved luminescence quenching.

a)



b)



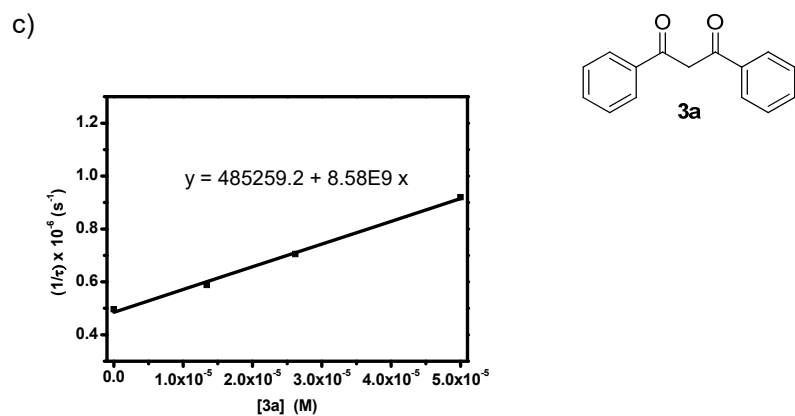


Figure S3: a) Steady state luminescence quenching of **1a*** with **3a**; b) time resolved luminescence quenching of **1a*** with **3a**; c) Stern-Volmer plot of the time resolved luminescence quenching.

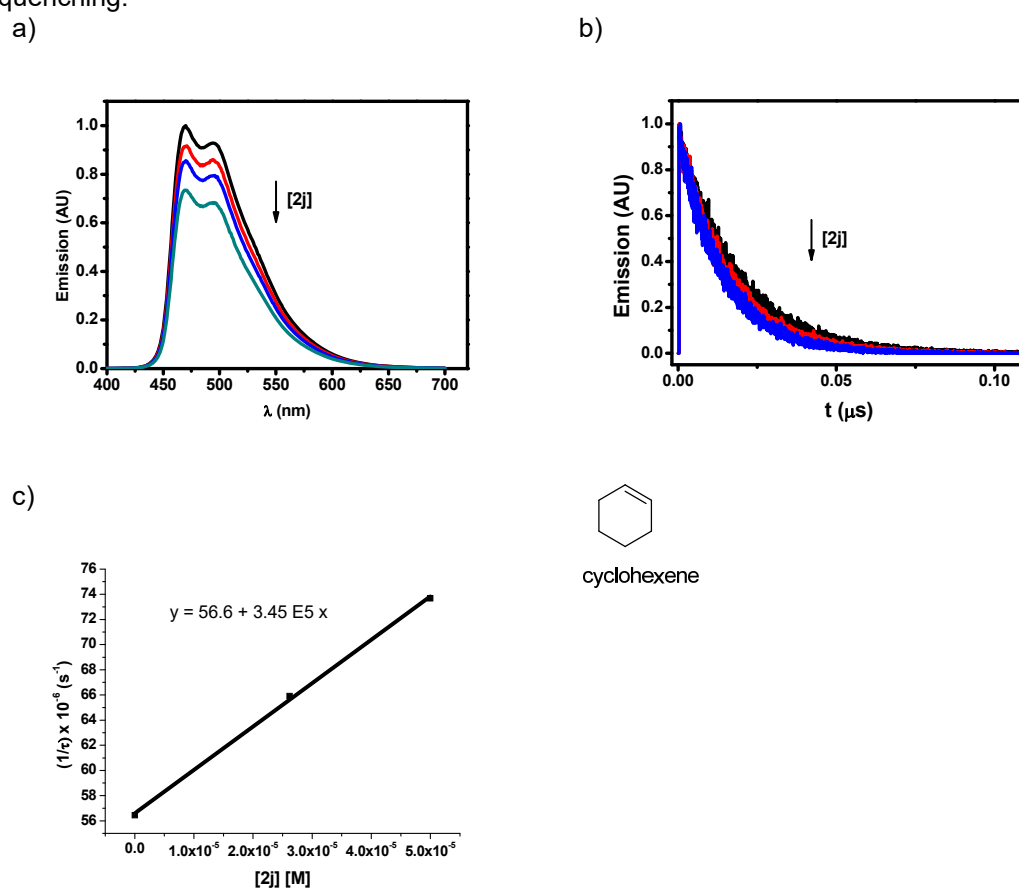
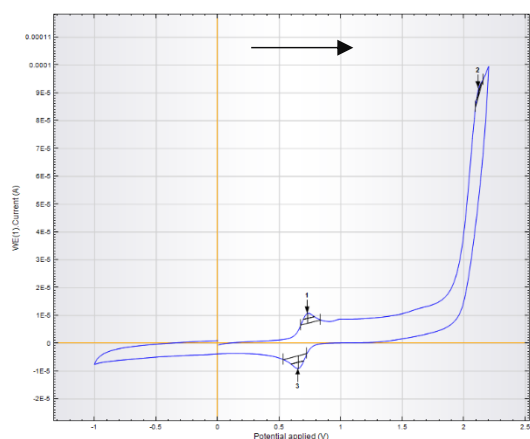


Figure S4: a) Steady state luminescence quenching of **1a*** with cyclohexene; b) time resolved luminescence quenching of **1a*** with cyclohexene; c) Stern-Volmer plot of the time resolved luminescence quenching.

4. Cyclic voltammetry experiments, ΔG and comparative graphic:

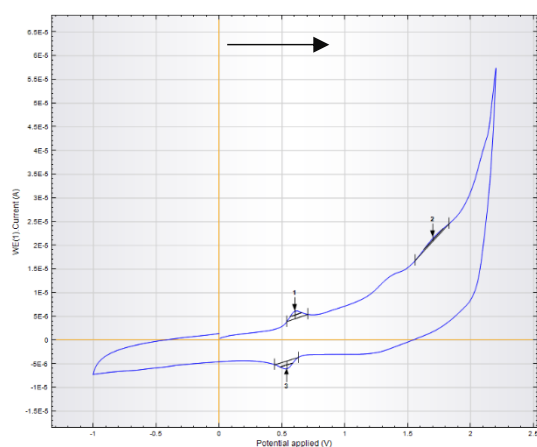
CV measurements were carried out under argon atmosphere. The measurement were performed in MeCN containing 0.1 M tetra *n*-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference. A glassy carbon electrode (working electrode), platinum wire

counter electrode, and Ag quasi-reference electrode was employed for the CV measurement. The scan rate was 50 mV/s, a step potential of 5.0 mV was applied.



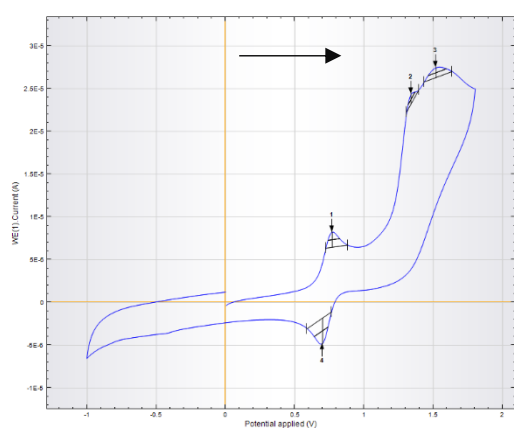
$E_{ox} = 1.43 \text{ eV vs SCE}$

Figure S5: Cyclic voltammetry of **3a**.



$E_{ox} = 1.13 \text{ eV vs SCE}$

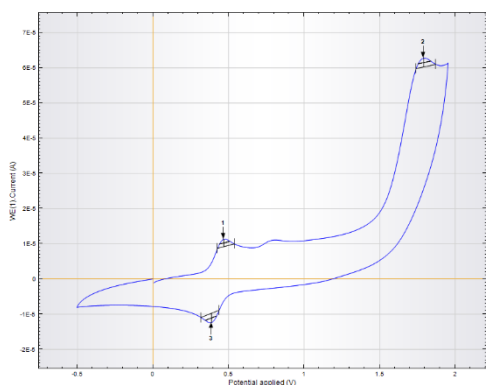
Figure S6: Cyclic voltammetry of **tributylmethylammonium dibutyl phosphate**



$E_{ox1} = 0.6 \text{ eV};$

$E_{ox2} = 0.79 \text{ eV vs SCE}$

Figure S7: Cyclic voltammetry of **3a** with **tributylmethylammonium dibutyl phosphate**



$E_{ox1} = 1.36 \text{ eV vs SCE}$

Figure S8: Cyclic voltammetry of (isopropenyloxy)trimethylsilane

$$\Delta G_{et}^0 (\text{eV}) = (E_{red}^0(PC^*/PC^{\cdot-}) - E_{red}^0(D^+/D))$$

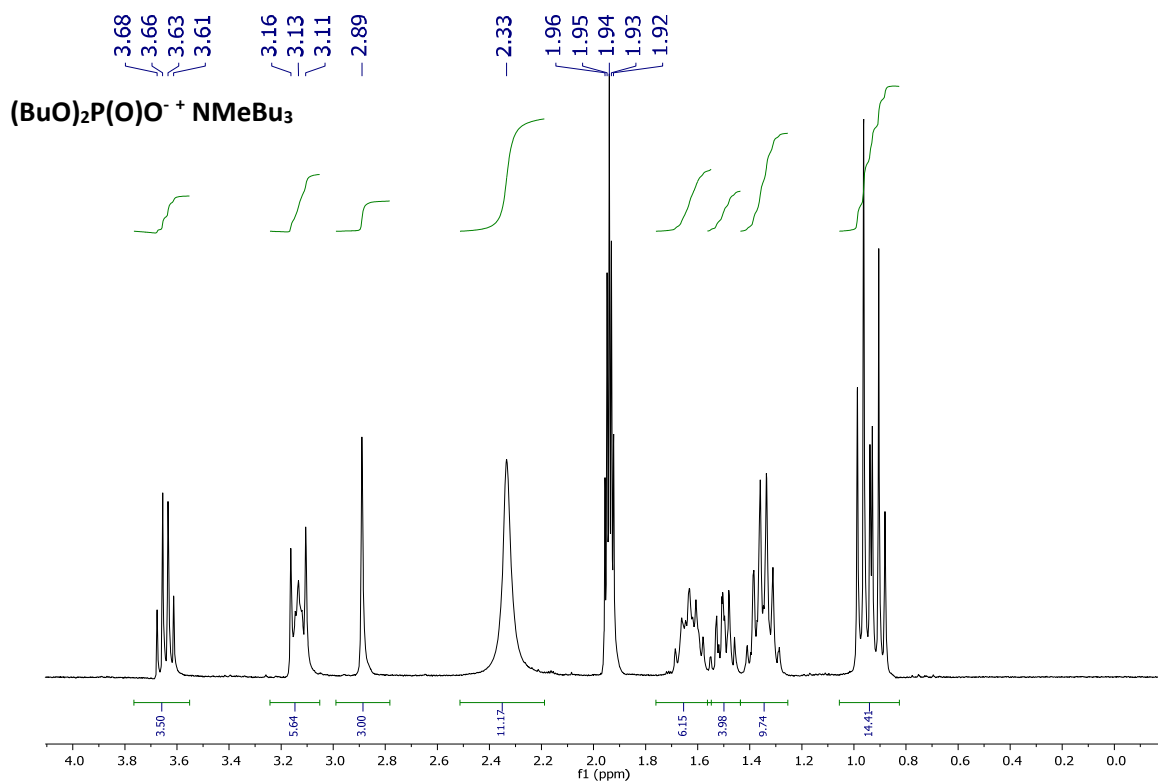
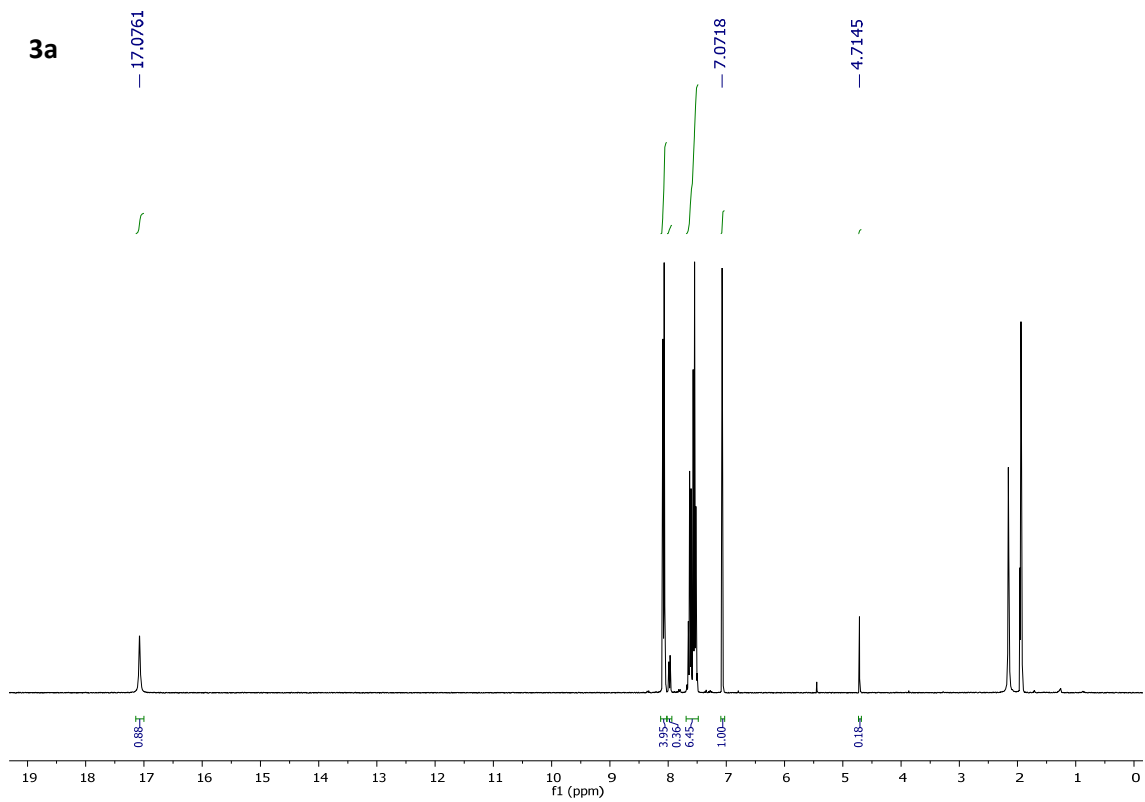
Table S2. Calculated ΔG for the possible oxidation pathways, and comparison between the redox potentials and the triplet energies.

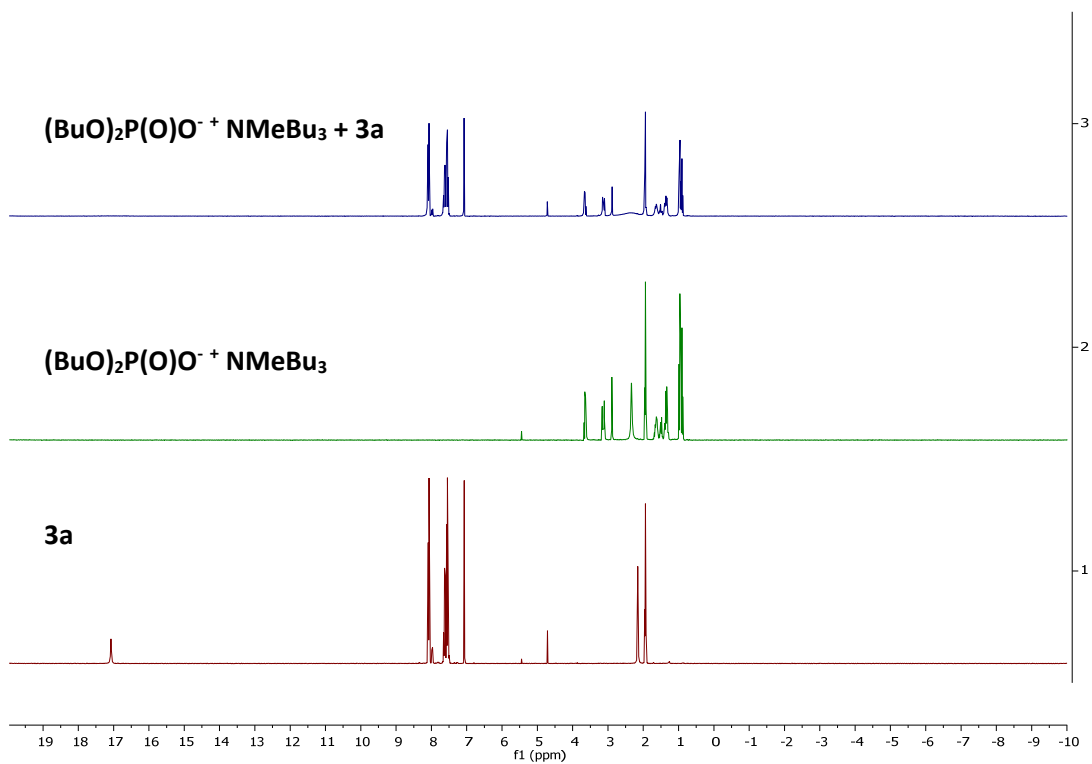
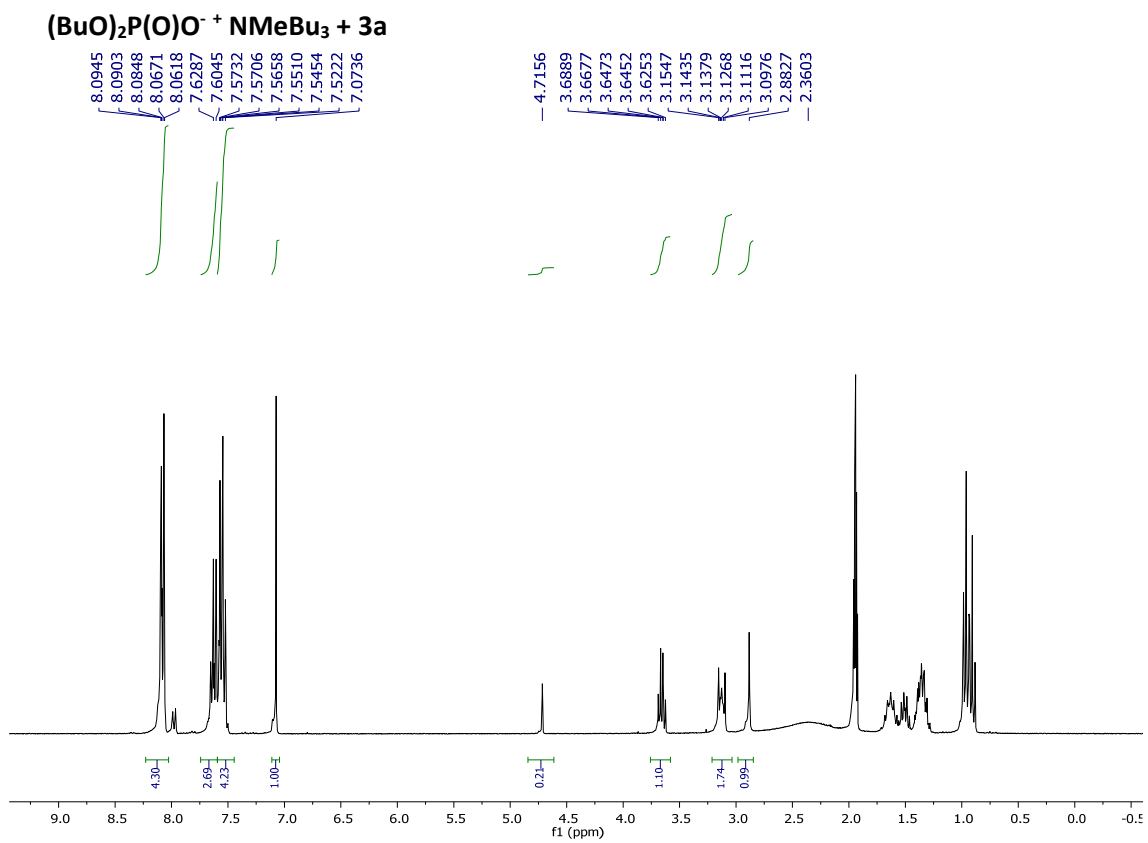
Photocatalyst		Substrate		ΔG (eV)	ΔG (Kcal/mole)
PC	E (PC ^{•+} /PC ^{•-}) (eV)	Substrate	E (D/D ^{•+})(eV)		
1a	1.32	3a	-1.43	0.11	2.5
		3a enolate	-0.6	-0.72	-16.6
		2a	-1.97	0.65	15.0
1b	1.33	3a	-1.43	0.10	2.3
		Enolate-3a	-0.6	-0.73	-16.8
		2a	-1.97	0.65	14.9
1c	0.31	3a	-1.43	1.12	25.8
		Enolate-3a	-0.6	0.29	6.7
		2a	-1.97	1.66	38.2
1d	1.35	3a	-1.43	0.08	1.8
		Enolate-3a	-0.6	-0.75	-17.3
		2a	-1.97	0.62	14.3
1e	2.18	3a	-1.43	-0.75	-17.3
		Enolate-3a	-0.6	-1.58	-36.4
		2a	-1.97	-0.21	-4.8

Redox potentials	Triplet energies
<u>1e</u> 2.18 V	
<u>2a</u> 1.97 V	
<u>3a</u> 1.43 V	
<u>1d</u> 1.35 V	
<u>1a</u> 1.32 V	
<u>3a enolate</u> 0.6 V	
	<u>3a enolate</u> 59 Kcal/mol
	<u>2a</u> 60 Kcal/mol
	<u>1d</u> 60 Kcal/mol
	<u>1a</u> 62 Kcal/mol
	<u>1c</u> 55 Kcal/mol
	<u>1e</u> 55 Kcal/mol
	<u>1b</u> 47 Kcal/mol

5. NMR titration experiments:

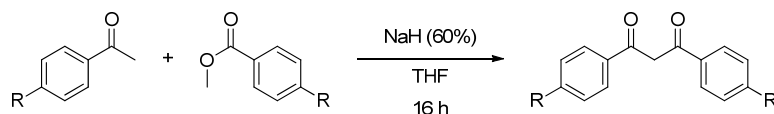
Evidences of the formation of enolate in the reaction. H-NMR experiments of **3a**, (BuO)₂P(O)ONBu₃Me and **3a**+25 mol% of (BuO)₂P(O)ONBu₃Me in CD₃CN were performed. The spectrum show disappearance of the proton corresponding to the OH of the enol in the presence of 25 mol% of the base, confirming the presence of enolate under the optimized reaction conditions.



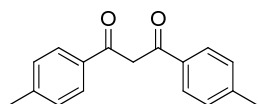


6. Synthesis and characterization of starting materials:

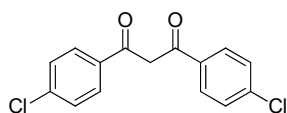
General procedure for the synthesis of 1,3-dyaryl-1,3-propanediones:



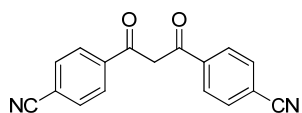
Acetophenone (1g, 7.5 mmol) was added dropwise to a dispersion of 60% NaH in mineral oil (906 mg, 22.6 mmol) in THF (21 mL) at 0 °C and under nitrogen atmosphere. Then, a solution of the methyl benzoate (1.2 mg, 8.2 mmol) in anhydrous THF (5.2 mL) was added dropwise over 15 min. The mixture was refluxed for 16 h under nitrogen and quenched with ice. Then a solution of HCl (0.1M) was added until a precipitate was formed. The solid was recovered by filtration and washed with distilled H₂O. The filtrate was extracted with AcOEt (3x20 mL); the organic phases were washed with brine (3 x 10 mL) and dried over anhydrous MgSO₄. The solvent is removed under reduced pressure, and the product purified by flash chromatography with the eluent indicated in each case.⁵



1,3-Bis(4'-methylphenyl)-1,3-propanedione: The compound was synthesized according to general procedure using 1 g (7.45 mmol) of starting material and obtained as a yellow solid in 97% yield (1.82 g) without further purification. **¹H-NMR** (400 MHz, acetone d₆) δ: 17.36 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.19 (s, 1H), 2.43 (s, 6H). **¹³C-NMR** (101 MHz, acetone d₆) δ: 185.6, 143.4, 132.7, 129.4, 127.3, 92.2, 20.7; **HMRS:** [M+H]⁺ calculated for C₁₇H₁₇O₂: 253.1223; found: 253.1225.

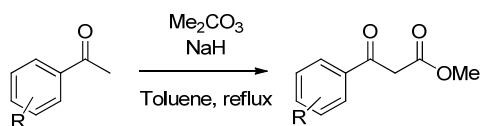


1,3-Bis(4-chlorophenyl)propane-1,3-dione: The compound was synthesized according to general procedure using 1 g (6.47 mmol) of starting material. After purification by flash chromatography (PE/EtOAc = 98/2), the product was obtained as a pale yellow solid in 16% yield (302.7 mg). The experimental data agree with the data previously described in the literature.⁶ **¹H NMR** (400 MHz, CDCl₃) δ: 16.75 (s, 1H), 7.92 (d, *J* = 8.64, 4H), 7.46 (d, *J* = 8.64, 4H), 6.76 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ: 184.6, 139.0, 133.8, 129.1, 128.6, 92.9.

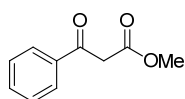


1,3-Bis(4'-cyanophenyl)-1,3-propanedione: The compound was synthesized according to general procedure using 1 g (6.89 mmol) of starting material. After purification by flash chromatography (PE/EtOAc = 80/20), the product was obtained as a yellow solid in 10% yield (176.3 mg). **¹H-NMR** (300 MHz, Acetone d₆) δ: 16.75 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 4H), 8.00 (d, *J* = 8.5 Hz, 4H), 7.50 (s, 1H). **¹³C-NMR** (101 MHz, acetone d₆) δ: 184.5, 138.7, 132.7, 128.1, 117.8, 115.9, 95.0. **HMRS:** [M]⁺ calculated for C₁₇H₁₀O₂N₂: 274.0742; found: 274.0727.

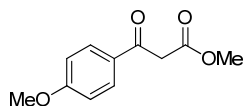
General procedure for the synthesis of β-keto esters:



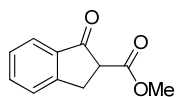
To a dried 25 mL flask containing a suspension of NaH (840 mg, 60% w/w, 21 mmol) in toluene (7.5 mL) under nitrogen atmosphere, dimethyl carbonate (1.3 μ L, 15 mmol) was added, and the mixture heated to reflux. Then a solution of acetophenone (7.5 mmol) in toluene (3.8 mL) was added dropwise over 30 minutes. After 2 hours, the reaction was cooled down to room temperature and glacial acetic acid (2.3 mL) was dropwise added while a heavy pasty solid was formed. Ice-cold water was slowly added until solvation of the solid. The solution was extracted with AcOEt (3 x 20 mL), washed with brine (3 x 10 mL) and dried over Na₂SO₄. After evaporating the solvent, the solid was purified by flash chromatography with the eluent indicated in each case.⁷



Methyl 3-oxo-3-phenylpropanoate: The compound was synthesized according to general procedure using 2 g (16.7 mmol) of starting material. After purification by flash chromatography (PE/EtOAc = 90/10), the product was obtained as a white oil in 63% yield (1.86 g). The experimental data agree with the data previously described in the literature.⁸ **¹H NMR** (400 MHz, CDCl₃) δ : 12.49 (s, 0.2H), 7.94 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 6.8 Hz, 0.4H), 7.60-7.55 (m, 1H), 7.49-7.40 (m, 1H), 7.43-7.36 (m, 0.4H), 5.68 (s, 0.2H), 4.01 (s, 2H), 3.81 (s, 0.7H), 3.76 (s, 3H).



Methyl 3-(4-methoxyphenyl)-3-oxopropanoate: The compound was synthesized according to general procedure using 1 g (6.66 mmol) of starting material. After purification by flash chromatography (PE/EtOAc = 85/15), the product was obtained as a yellow liquid in 76% yield (1.054 g). The experimental data agree with the data previously described in the literature.⁹ **¹H NMR** (400 MHz, CDCl₃) δ : 7.92 (dt, J = 2.88, 8.92 Hz, 2H), 6.95 (dt, J = 2.9, 8.9 Hz, 2H), 3.96 (s, 2H), 3.87 (s, 3H), 3.75 (s, 3H).



Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate: The compound was synthesized according to general procedure using 1 g (7.57 mmol) of starting material. After purification by flash chromatography (PE/EtOAc = 90/10), the product was obtained as a yellow solid 74% yield (1.055 g). The product was isolated as a mixture of keto and enol tautomer and the experimental data agree with the data previously described in the literature.¹⁰ **¹H NMR** (300 MHz, CDCl₃), keto tautomer: δ 7.74 (d, J = 7.7 Hz, 1H), 7.68 – 7.54 (m, 1H), 7.48 (dq, J = 7.8, 1.1 Hz, 1H), 7.42 – 7.29 (m, 1H), 3.77 (s, 3H), 3.72 (ddd, J = 8.3, 4.1, 1.1 Hz, 1H), 3.60 – 3.50 (m, 1H), 3.35 (dd, J = 17.3, 8.3 Hz, 1H); enol tautomer: 10.35 (bs, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.68 – 7.54 (m, 1H), 7.48 (dq, J = 7.8, 1.1 Hz, 1H), 7.42 – 7.29 (m, 1H), 3.83 (d, J = 1.2 Hz, 3H), 3.48 (m, 2H).

7. Synthesis and characterization of compounds 4a-4y:

General procedure A: In a 5 mL snap vial with magnetic stirring bar are weighted 0.1 mmol **3**, 0.5 mmol **2**, 0.002 mmol **1a**, 0.025 mmol tributylmethylammonium dibutyl phosphate and, under N₂ atmosphere, dissolved in 1 mL EtOH. The mixture was frozen with liquid N₂ and degassed under vacuum via syringe needle for two times. The snap capped vial containing the final reaction mixture was irradiated through the plane bottom side of the snap vial using a 455 nm LED. The reaction progress was monitored by TLC. The solvent of the reaction was removed under vacuum and the product purified by flash column chromatography using petrol ether/ethyl acetate as indicated in each case.

General procedure B: In a 5 mL snap vial with magnetic stirring bar are weighted 0.1 mmol **3**, 0.5 mmol **2**, 0.004 mmol **1c**, 0.025 mmol tributylmethylammonium dibutyl phosphate and, under N₂ atmosphere, dissolved in 1 mL ACN. The mixture was frozen with liquid N₂ and degassed under vacuum via syringe needle for two times. The snap capped vial containing the final reaction mixture was irradiated through the plane bottom side of the snap vial using a 455 nm LED. The reaction progress was monitored by TLC. The solvent of the reaction was removed under vacuum and the product purified by flash column chromatography using petrol ether/ethyl acetate as indicated in each case.

General procedure C: In a 5 mL snap vial with magnetic stirring bar are weighted 0.1 mmol **3**, 0.5 mmol **2**, 0.004 mmol **1c**, 0.1 mmol K₂CO₃ and, under N₂ atmosphere, dissolved in 1 mL ACN. The mixture was frozen with liquid N₂ and degassed under vacuum via syringe needle for two times. The snap capped vial containing the final reaction mixture was irradiated through the plane bottom side of the snap vial using a 455 nm LED. The reaction progress was monitored by TLC. The solvent of the reaction was removed under vacuum and the product purified by flash column chromatography using petrol ether/ethyl acetate as indicated in each case.

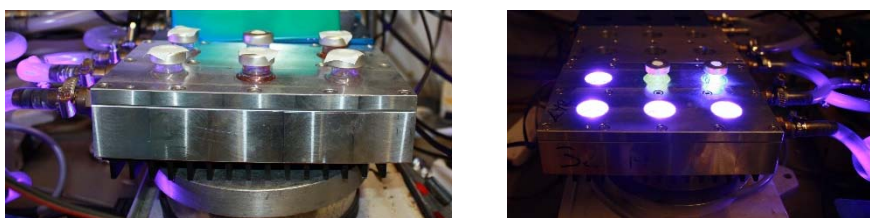
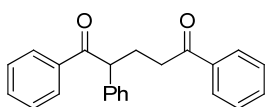


Figure S9. Set up for 0.1 mmol scale reactions



1,2,5-Triphenylpentane-1,5-dione (4a): The product was obtained following the general procedure A as a pale yellowish solid in 93% yield (30.4 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 94/6). The experimental data agree with the data previously described in the literature. ¹¹ **¹H-NMR** (300 MHz, CDCl₃) δ: 7.98 (d, *J* = 7.0 Hz, 2H), 7.90 (d, *J* =

7.0 Hz, 2H), 7.59 – 7.49 (m, 1H), 7.50 – 7.34 (m, 5H), 7.33 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 4.78 (t, $J = 7.3$ Hz, 1H), 3.14 – 2.84 (m, 2H), 2.59 (dq, $J = 14.3, 7.2$ Hz, 1H), 2.35 – 2.22 (m, 1H).

HMRS: $[M+H]^+$ calculated for $C_{23}H_{21}O_2$: 329.1542; found: 329.1543.

GC-MS of the reaction in the conditions of entry 9 Table 1 showed the formation of 5% of the dimerization of styrene at 14.845'.

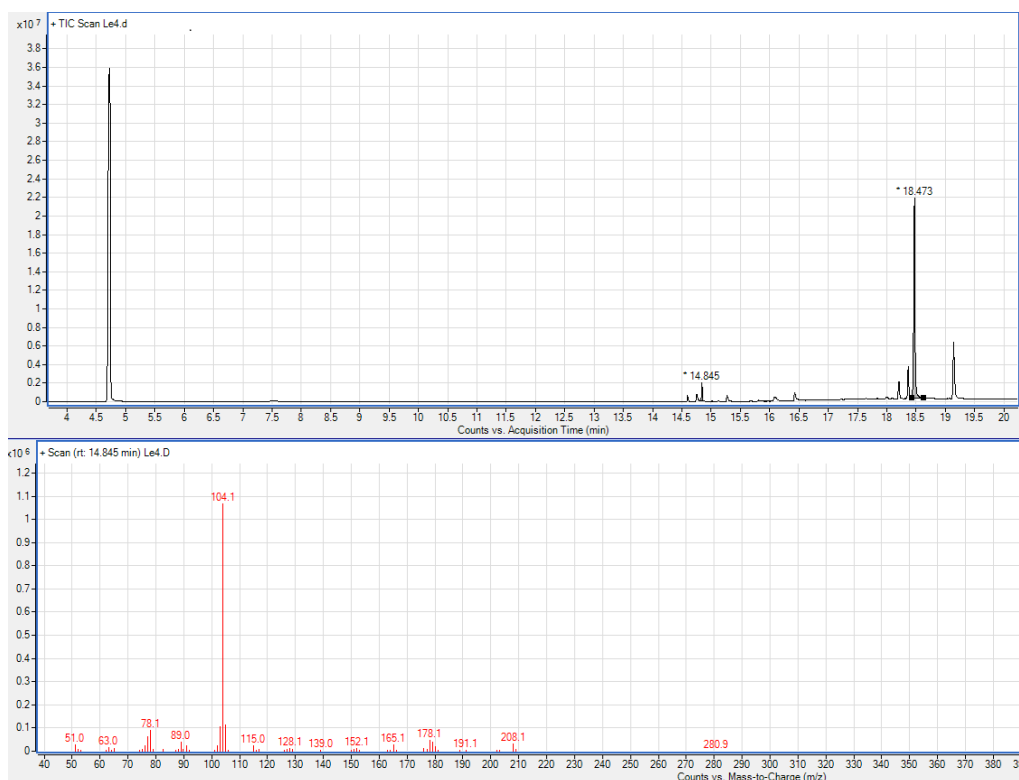


Figure S10. GC-MS of the reaction described in entry 9 Table 1.

Large scale reaction: In a 25 mL Schlenk with a stirring bar are weighted 1 mmol of **3a**, 0.02 mmol **1a**, 0.25 mmol tributylmethylammonium dibutyl phosphate and 5 mmol styrene **2a** and under N_2 atmosphere, dissolved in 10 mL ACN. The mixture was frozen with liquid N_2 and degassed under vacuum for two times. Then the schlenk was placed in a water bath at 25 °C, and the mixture irradiated with a 455 nm LED as indicated in the picture for 24h. Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 94/6). The product was obtained in 66% yield as a pale yellowish solid. **¹H-NMR** (300 MHz, $CDCl_3$) δ : 7.98 (d, $J = 7.0$ Hz, 2H), 7.90 (d, $J = 7.0$ Hz, 2H), 7.59 – 7.49 (m, 1H), 7.50 – 7.34 (m, 5H), 7.33 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 4.78 (t, $J = 7.3$ Hz, 1H), 3.14 – 2.84 (m, 2H), 2.59 (dq, $J = 14.3, 7.2$ Hz, 1H), 2.35 – 2.22 (m, 1H).

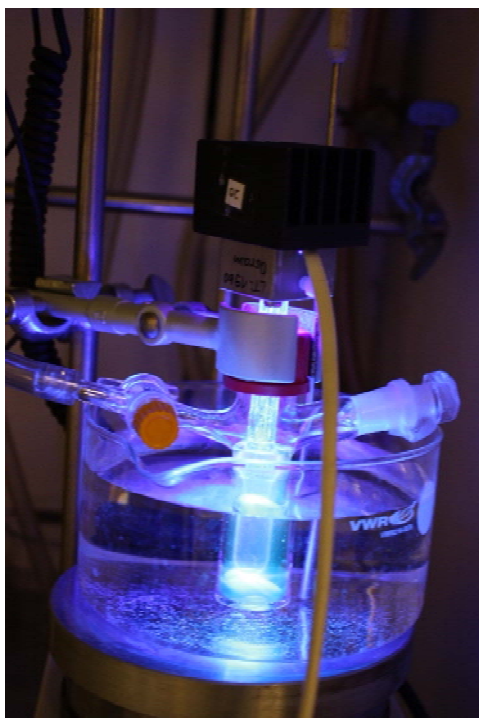
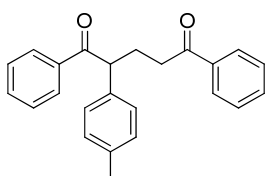
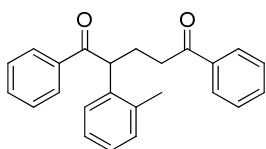


Figure S11. Set up for large scale reactions



1,5-Diphenyl-2-(p-tolyl)pentane-1,5-dione (4b): The product was obtained following the general procedure A as a yellow oil in 87% yield (29.8 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5). **¹H-NMR** (300 MHz, CDCl₃)

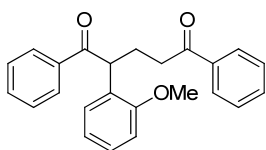
δ: 7.98 (d, *J* = 7.0 Hz, 2H), 7.91 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.48 (m, 1H), 7.48 – 7.33 (m, 5H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.74 (t, *J* = 7.3 Hz, 1H), 3.12 – 2.83 (m, 2H), 2.57 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.36 – 2.18 (m, 1H), 2.28 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ: 200.0, 199.8, 136.9, 136.8, 136.7, 136.1, 133.0, 132.9, 129.8, 128.8, 128.6, 128.5, 128.2, 128.1, 52.1, 36.0, 28.3, 21.1. **HMRS:** [M+H]⁺ calculated for C₂₄H₂₃O₂: 343.1692; found: 343.1693.



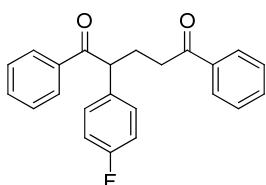
1,5-Diphenyl-2-(o-tolyl)pentane-1,5-dione (4c): The product was obtained following the general procedure A as a pale yellow solid in 79% yield (26.9 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the

product purified by flash chromatography (PE/EtOAc = 95/5). **¹H-NMR** (400 MHz, CDCl₃) δ: 7.93 (d, *J* = 7.1 Hz, 2H), 7.85 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.40 (m, 3H), 7.39 – 7.32 (m, 2H), 7.23 – 7.17 (m, 1H), 7.15 – 7.03 (m, 3H), 4.93 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.12 (dt, *J* = 17.3, 6.7 Hz, 1H), 3.01 (dt, *J* = 17.3, 7.0 Hz, 1H), 2.61 – 2.46 (m, 1H), 2.55 (s, 3H), 2.18 (dtd, *J* = 14.2, 7.1, 5.4 Hz, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.29 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ: 200.4, 200.1, 138.0, 137.0, 136.9, 135.4, 133.1,

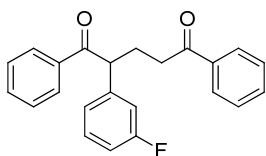
132.8, 131.2, 128.6, 128.5, 128.5, 128.1, 127.3, 127.1, 126.7, 48.7, 36.3, 27.7, 19.8. **HMRS:** $[M+H]^+$ calculated for $C_{24}H_{23}O_2$: 343.1693; found: 343.1693.



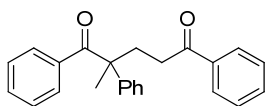
2-(2-Methoxyphenyl)-1,5-diphenylpentane-1,5-dione (4d): The product was obtained following the general procedure A as a yellow oil in 76% yield (27.2 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5). **1H -NMR** (400 MHz, $CDCl_3$) δ : 7.97 (d, $J = 7.1$ Hz, 2H), 7.91 (d, $J = 7.0$ Hz, 2H), 7.59 – 7.50 (m, 1H), 7.48 – 7.39 (m, 3H), 7.34 (dd, $J = 8.2, 6.9$ Hz, 2H), 7.22 – 7.11 (m, 2H), 6.90 – 6.82 (m, 2H), 5.19 (t, $J = 7.2$ Hz, 1H), 3.75 (s, 3H), 3.06 (dt, $J = 16.8, 7.6$ Hz, 1H), 2.85 (ddd, $J = 16.9, 7.9, 5.5$ Hz, 1H), 2.64 – 2.51 (m, 1H), 2.23 – 2.13 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ : 200.3, 199.9, 156.2, 137.0, 136.6, 132.9, 132.7, 128.6, 128.5, 128.4, 128.4 (2C), 128.1, 127.8, 121.2, 110.8, 55.4, 44.4, 36.0, 27.2. **HMRS:** $[M+H]^+$ calculated for $C_{24}H_{23}O_3$: 359.1644; found: 359.1642.



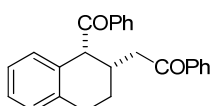
2-(4-Fluorophenyl)-1,5-diphenylpentane-1,5-dione (4e): The product was obtained following the general procedure A as a colorless oil in 98% yield (33.8 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5). **1H -NMR** (400 MHz, $CDCl_3$) δ : 7.97 (d, $J = 7.1$ Hz, 2H), 7.90 (d, $J = 7.1$ Hz, 2H), 7.58 – 7.50 (m, 1H), 7.50 – 7.47 (m, 1H), 7.45 – 7.37 (m, 4H), 7.32 – 7.24 (m, 2H), 7.02 – 6.93 (m, 2H), 4.79 (t, $J = 7.4$ Hz, 1H), 3.06 – 2.85 (m, 2H), 2.58 (dq, $J = 14.2, 7.1$ Hz, 1H), 2.25 (dq, $J = 13.9, 6.9$ Hz, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.29 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ : 199.8, 199.6, 162.0 (d, $J = 245.9$ Hz), 136.6 (d, $J = 29.2$ Hz), 134.9, 134.8, 133.2, 133.1, 129.9 (d, $J = 7.9$ Hz), 128.8, 128.6 (2C), 128.0, 116.0 (d, $J = 21.3$ Hz), 51.5, 35.8, 28.4. **HMRS:** $[M+H]^+$ calculated for $C_{23}H_{20}O_2F$: 347.1444; found: 347.1442.



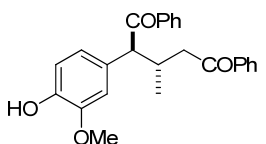
2-(3-Fluorophenyl)-1,5-diphenylpentane-1,5-dione (4f): The product was obtained following the general procedure A as a colorless oil in 80% yield (27.8 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5). **1H NMR** (300 MHz, $CDCl_3$) δ : 8.02 – 7.95 (m, 2H), 7.94 – 7.87 (m, 2H), 7.59 – 7.49 (m, 2H), 7.49 – 7.36 (m, 4H), 7.29 - 7.22 (m, 1H), 7.10 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.04 (ddd, $J = 9.8, 2.5, 1.6$ Hz, 1H), 6.91 (tdd, $J = 8.4, 2.6, 1.0$ Hz, 1H), 4.81 (t, $J = 7.4$ Hz, 1H), 3.12 – 2.85 (m, 2H), 2.59 (dq, $J = 14.1, 7.2$ Hz, 1H), 2.27 (tt, $J = 13.9, 6.7$ Hz, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.30 (s, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ : 199.7, 199.2, 163.1 (d, $J = 245$ Hz), 141.6, 141.5, 136.6 (d, $J = 24.7$ Hz), 133.2, 133.2, 130.5 (d, $J = 8.3$ Hz), 128.8, 128.7, 128.6, 128.0, 124.1 (d, $J = 2.8$ Hz), 115.2 (d, $J = 21.7$ Hz), 114.3 (d, $J = 21.0$ Hz), 51.9, 35.8, 28.2. **HMRS:** $[M+H]^+$ calculated for $C_{23}H_{20}O_2F$: 347.1444; found: 347.1449.



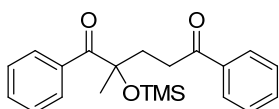
2-Methyl-1,2,5-triphenylpentane-1,5-dione (4g): The product was obtained following the general procedure A as a white solid in 56% yield (19.2 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5 to 90/10). **¹H NMR** (300 MHz, CDCl₃) δ: 7.85 – 7.78 (m, 2H), 7.56 – 7.47 (m, 3H), 7.44 – 7.27 (m, 8H), 7.26 – 7.19 (m, 2H), 2.95 – 2.72 (m, 2H), 2.58 – 2.40 (m, 2H), 1.66 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ: 203.1, 200.0, 143.7, 136.7, 136.3, 133.0, 131.9, 129.6, 129.1, 128.5, 128.1, 128.1, 127.2, 126.3, 54.2, 34.8, 34.1, 24.4. **HMRS:** [M+H]⁺ calculated for C₂₄H₂₃O₂: 343.1690; found: 343.1693.



(rac)-2-((1R,2S)-1-benzoyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1-phenylethanone ((rac)-((1R,2S)-4h): The product was obtained following the general procedure A as a yellow oil in 82% yield (29.2 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 90/10). **¹H NMR** (300 MHz, CDCl₃) δ 8.02 – 7.95 (m, 2H), 7.79 – 7.70 (m, 2H), 7.48 (dqt, *J* = 7.6, 3.1, 1.3 Hz, 2H), 7.44 – 7.29 (m, 4H), 7.22 – 7.12 (m, 2H), 7.03 (ddd, *J* = 7.8, 6.8, 1.9 Hz, 1H), 6.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.29 (d, *J* = 4.8 Hz, 1H), 3.18 – 2.84 (m, 3H), 2.50 – 2.28 (m, 1H), 1.86 – 1.77 (m, 1H). **¹³C NMR** (75 MHz, CDCl₃) δ 202.7, 199.2, 138.7, 137.2, 136.9, 134.5, 133.1, 133.0, 129.7, 129.2, 128.8, 128.7, 128.4, 127.8, 126.7, 125.7, 47.1, 41.7, 33.3, 28.5, 25.1. **HMRS:** [M+H]⁺ calculated for C₂₅H₂₃O₂: 355.1698; found: 355.1693.

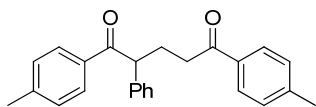


(rac)-(2S,3S)-2-(4-hydroxy-3-methoxyphenyl)-3-methyl-1,5-diphenylpentane-1,5-dione ((rac)-(2S,3S)-4i): The product was obtained following the general procedure A as a yellow oil in 77% yield (29.9 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 90/10 to 80/20). **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.96 (m, 4H), 7.58 – 7.37 (m, 6H), 6.85 – 6.79 (m, 3H), 5.60 (bs, 1H), 4.52 (d, *J* = 9.6 Hz, 1H), 3.82 (s, 3H), 3.22 (dd, *J* = 15.2, 3.7 Hz, 1H), 3.10 – 2.98 (m, 1H), 2.73 (dd, *J* = 15.2, 9.1 Hz, 1H), 0.84 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 200.3, 199.9, 146.9, 145.0, 137.2, 137.1, 133.0, 133.0, 129.3, 128.7, 128.6, 128.6, 128.4, 122.7, 114.5, 110.5, 58.7, 56.0, 44.4, 33.5, 17.5. **HMRS:** [M+H]⁺ calculated for C₂₅H₂₅O₄: 389.1752; found: 389.1747.

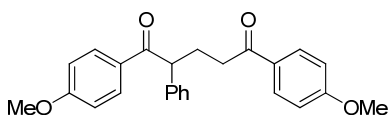


2-Methyl-1,5-diphenyl-2-((trimethylsilyl)oxy)pentane-1,5-dione (4l): The product was obtained following the general procedure A as a yellow oil in 52% yield (18.5 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 96/4 to 94/6). **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.1 Hz, 2H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.48 (m, 2H), 7.47 – 7.38 (m, 4H), 3.09 (ddd, *J* = 16.9, 10.4, 5.4 Hz, 1H), 2.98 (ddd, *J* = 16.9, 10.4, 5.2 Hz, 1H), 2.52 (ddd, *J* = 14.1, 10.4, 5.4

Hz, 1H), 2.26 – 2.15 (m, 1H), 1.61 (s, 3H), 0.05 (s, 9H).; **¹³C NMR** (101 MHz, CDCl₃) δ 204.0, 199.5, 136.8, 135.5, 133.0, 132.5, 130.2, 128.6, 128.1, 128.0, 82.8, 36.1, 33.4, 26.0, 2.01; **HMRS**: [M-OTMS]⁺ calculated for C₁₈H₁₇O₂: 265.1223; found: 265.1227.

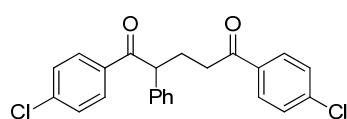


2-Phenyl-1,5-di-p-tolylpentane-1,5-dione (4m): The product was obtained following the general procedure A as a pale yellowish solid in 84% yield (30.1 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5). **¹H NMR** (400 MHz, CDCl₃) δ: 7.88 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.13 (m, 5H), 4.75 (t, *J* = 7.4 Hz, 1H), 3.08 – 2.81 (m, 2H), 2.58 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 2.31 – 2.21 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ: 199.7, 199.3, 143.8, 143.7, 139.5, 134.4, 134.2, 129.3, 129.2, 129.0, 128.9, 128.3, 128.2, 127.1, 52.4, 36.0, 28.5, 21.6, 21.6. **HMRS**: [M+H]⁺ calculated for C₂₅H₂₅O₂: 357.1855; found: 357.1856.



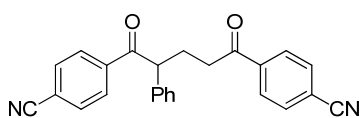
1,5-Bis(4-methoxyphenyl)-2-phenylpentane-1,5-dione (4n): The product was obtained following the general procedure A as a pale yellowish solid in 74% yield (28.8 mg).

Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 80/20). **¹H-NMR** (300 MHz, CDCl₃) δ: 7.97 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.26 (s, 4H), 7.24 – 7.15 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.72 (t, *J* = 7.3 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.02-2.80 (m, 2H), 2.57 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.24 (dq, *J* = 13.9, 7.0 Hz, 1H). **¹³C NMR** (75 MHz, CDCl₃) δ: 198.6, 198.2, 163.4, 163.3, 139.7, 131.1, 130.4, 129.9, 129.7, 129.0, 128.3, 127.1, 113.7, 113.7, 55.5, 55.4, 52.2, 35.8, 28.7). **HMRS**: [M+H]⁺ calculated for C₂₅H₂₅O₄: 389.1752; found: 389.1747.



1,5-Bis(4-chlorophenyl)-2-phenylpentane-1,5-dione (4o): The product was obtained following the general procedure A as a pale yellowish solid in 66% yield (26.2 mg). Once the reaction is

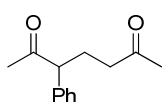
finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 90/10). **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.19 (m, 5H), 4.69 (t, *J* = 7.3 Hz, 1H), 3.03 – 2.83 (m, 2H), 2.56 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.26 (dq, *J* = 13.8, 6.6 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ: 198.6, 198.3, 139.6, 139.4, 138.8, 135.1, 134.8, 130.2, 129.5, 129.2, 128.9, 128.9, 128.3, 127.5, 52.5, 35.9, 28.1. **HMRS**: [M+H]⁺ calculated for C₂₃H₁₉Cl₂O₂: 397.0755; found: 397.0757.



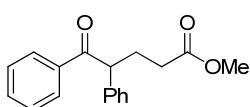
4,4'-(2-Phenylpentanedioyl)dibenzonitrile (4p): The product was obtained following the general procedure A as a pale yellowish solid in 71% yield (27.1 mg). Once the reaction is

finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and

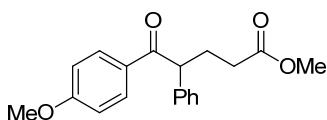
the product purified by flash chromatography (PE/EtOAc = 90/10). **¹H-NMR** (400 MHz, CDCl₃) δ: 8.36 (d, *J* = 8.5 Hz, 2H), 8.31 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.65 – 7.55 (m, 5H), 5.05 (t, *J* = 7.3 Hz, 1H), 3.38-3.25 (m, 2H), 2.91 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.63 (dq, *J* = 13.9, 6.6 Hz, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.29 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ: 198.3, 198.1, 139.6, 139.5, 137.9, 132.6, 132.4, 129.5, 129.2, 128.4, 128.3, 127.9, 117.9, 117.9, 116.5, 116.2, 52.8, 36.0, 27.7. **HMRS**: [M+H]⁺ calculated for C₂₅H₁₉N₂O₂: 379.1447; found: 379.1444.



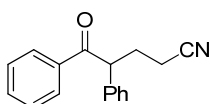
3-Phenylheptane-2,6-dione (4q): The product was obtained following the general procedure B as a colorless oil in 87% yield (17.8 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 96/4). **¹H-NMR** (400 MHz, CDCl₃) δ: 7.35 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 7.18 – 7.15 (m, 2H), 3.68 (dd, *J* = 8.2, 6.3 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.26 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 – 1.88 (m, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.29 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ: 208.4, 207.9, 138.3, 129.1, 128.3, 127.5, 58.3, 40.9, 30.0, 29.0, 25.7. **HMRS**: [M+H]⁺ calculated for C₁₃H₁₇O₂: 205.1229; found: 205.1223.



Methyl 5-oxo-4,5-diphenylpentanoate (4t): The product was obtained following the general procedure C as a pale yellowish oil in 78% yield (22.1 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5-90/10). The experimental data agree with the data previously described in the literature.¹² **¹H-NMR** (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 6 Hz, 1H), 7.38 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.31 - 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 4.67 (t, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 2.53 – 2.40 (m, 1H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.18 (ddd, *J* = 12.1, 7.8, 6.4 Hz, 1H); In the spectrum is possible to see the signal corresponding to the enol: 5.29 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 199.3, 173.7, 138.8, 136.6, 133.0, 129.1, 128.8, 128.5, 128.3, 127.3, 52.5, 51.6, 31.6, 28.8. **HMRS**: [M+H]⁺ calculated for C₁₈H₁₉O₃: 283.1327; found: 283.1329.

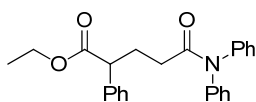


Methyl 5-(4-methoxyphenyl)-5-oxo-4-phenylpentanoate (4u): The product was obtained following the general procedure C as a pale yellow oil in 60% yield (18.8 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 90/10). The experimental data agree with the data previously described in the literature.¹³ **¹H-NMR** (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.29 - 7.26 (m, 5H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.62 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.64 (s, 3H), 2.49 – 2.40 (m, 1H), 2.30 (ddd, *J* = 7.9, 6.2, 1.4 Hz, 2H), 2.19 – 2.11 (m, 1H).



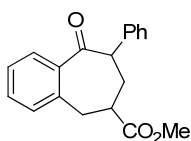
5-Oxo-4,5-diphenylpentanenitrile (4v): The product was obtained following the general procedure A as a pale yellowish oil in 46% yield (11.4 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the

solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 95/5-90/10). **¹H-NMR** (300 MHz, CDCl₃) δ 7.87 – 7.77 (m, 2H), 7.69 – 7.56 (m, 1H), 7.54 – 7.41 (m, 2H), 7.41 – 7.27 (m, 3H), 7.26 – 7.17 (m, 2H), 4.24 (dd, *J* = 7.8, 6.8 Hz, 1H), 2.98 (dt, *J* = 13.6, 6.7 Hz, 1H), 2.85 (dt, *J* = 14.0, 8.1 Hz, 1H), 2.32 (dt, *J* = 8.2, 7.0 Hz, 2H); In the spectrum is possible to see the signal corresponding to the enol: 5.30 (s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 190.5, 139.2, 134.5, 133.9, 129.1, 128.9, 128.7, 128.6, 126.9, 117.1, 38.9, 32.9, 31.4; **HMRS**: [M+H]⁺ calculated for C₁₇H₁₆NO: 250.1232; found: 250.1226.



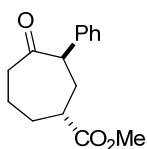
Ethyl 5-(diphenylamino)-5-oxo-2-phenylpentanoate (4w): The product was obtained following the general procedure C as a yellow oil in 78% yield (31.2 mg). Once the reaction is finished, the crude mixture was

absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 80/20). **¹H-NMR** (300 MHz, CDCl₃) δ 7.36 – 7.32 (m, 5H), 7.30 – 7.13 (m, 10H), 4.15 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.55 (dd, *J* = 7.9, 6.4 Hz, 1H), 2.68 (qdd, *J* = 13.7, 8.8, 6.5 Hz, 2H), 2.37 – 2.20 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 169.9, 169.0, 141.0, 129.8, 128.9, 128.4, 128.3, 128.3, 126.3, 126.1, 61.4, 49.4, 33.4, 30.8, 14.2; **HMRS**: [M+H]⁺ calculated for C₂₅H₂₆NO₃: 388.1910 found: 388.1907.



Methyl 9-oxo-8-phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (4x): The product was obtained following the general procedure B as a yellow oil in 65% yield as a separable mixture of two diastereoisomers in a relationship of 1.3/1 (10.7 mg and 8.5 mg respectively). Once the reaction

is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified by flash chromatography (PE/EtOAc = 90/10). (*rac*)-(6*S*,8*R*)-**4x**: **¹H NMR** (300 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.6 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.28 – 7.24 (m, 2H), 4.17 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.74 (s, 3H), 3.40 – 3.26 (m, 1H), 3.22 (dd, *J* = 15.3, 4.3 Hz, 1H), 2.95 (dtd, *J* = 10.8, 6.7, 4.2 Hz, 1H), 2.55 – 2.23 (m, 2H); In the spectrum is possible to see the signal corresponding to the enol: 5.30 (s, 1H); **¹³C NMR** (75 MHz, CDCl₃) δ 205.0, 175.0, 139.9, 139.3, 138.3, 132.2, 130.0, 128.8, 128.6, 128.6, 127.4, 127.1, 53.6, 52.2, 41.7, 34.7, 33.0; **HMRS**: [M+H]⁺ calculated for C₁₉H₁₉O₃: 295.1331; found: 295.1329. (*rac*)-(6*R*,8*R*)-**4x**: **¹H NMR** (300 MHz, , CDCl₃) δ 7.58 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 – 7.26 (m, 5H), 7.20 – 7.15 (m, 2H), 3.82 – 3.70 (m, 1H), 3.66 (s, 3H), 3.39 – 3.29 (m, 1H), 3.26 – 3.08 (m, 2H), 2.43 – 2.30 (m, 2H); In the spectrum is possible to see the signal corresponding to the enol: 5.30 (s, 1H); **¹³C NMR** (75 MHz, CDCl₃) δ 206.7, 174.3, 141.4, 139.5, 135.8, 132.2, 130.4, 128.6, 128.3, 128.1, 127.6, 127.0, 55.4, 52.0, 41.7, 33.7, 32.0; **HMRS**: [M+H]⁺ calculated for C₁₉H₁₉O₃: 295.1331; found: 295.1329.

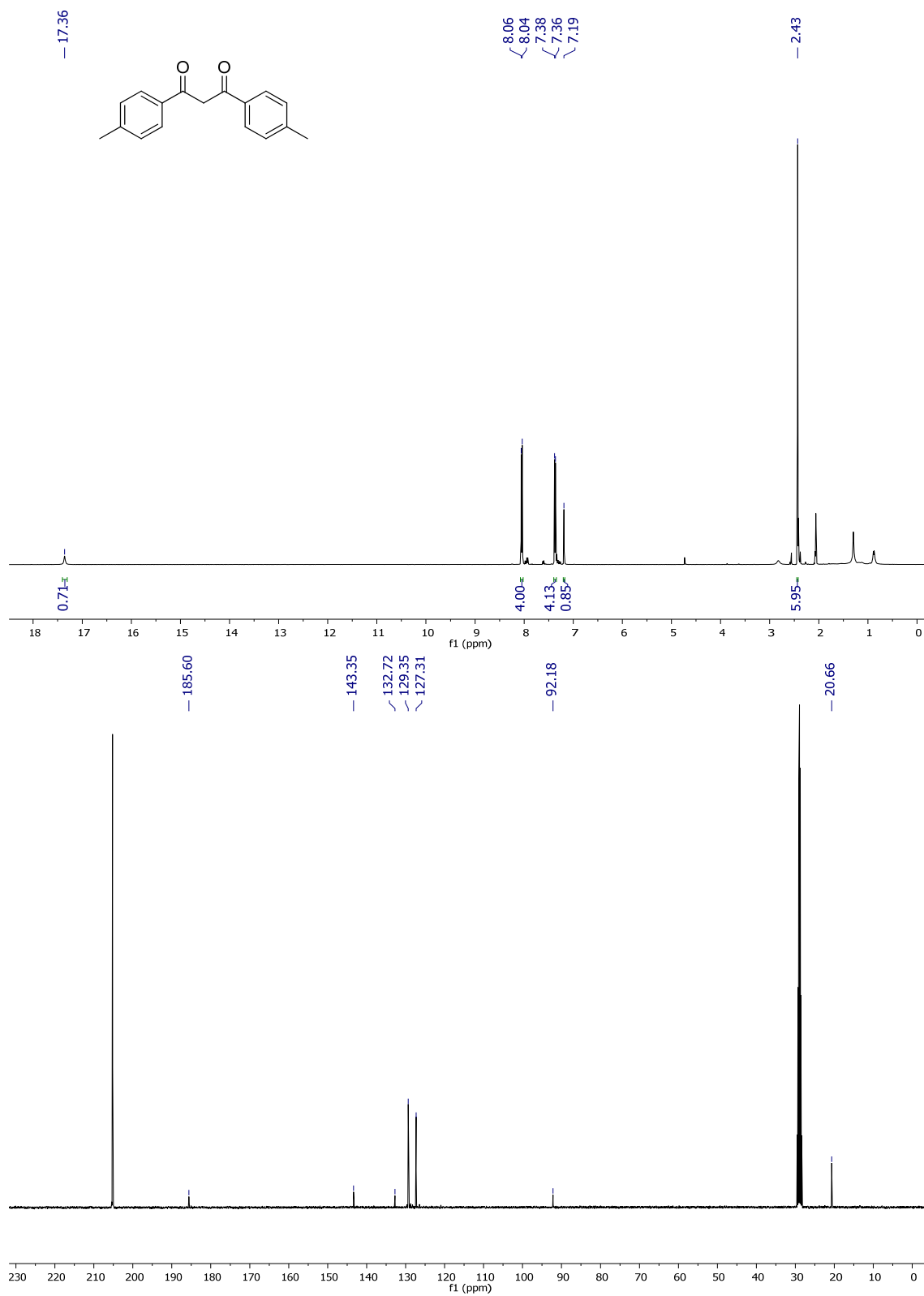


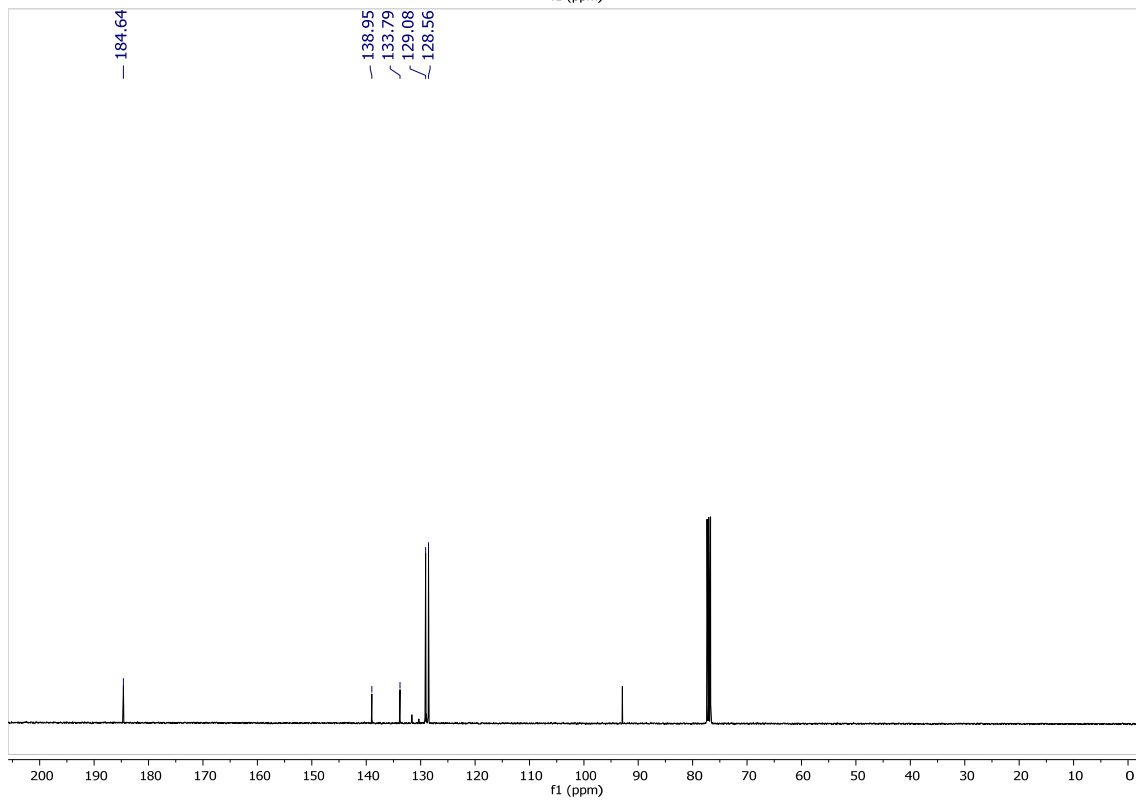
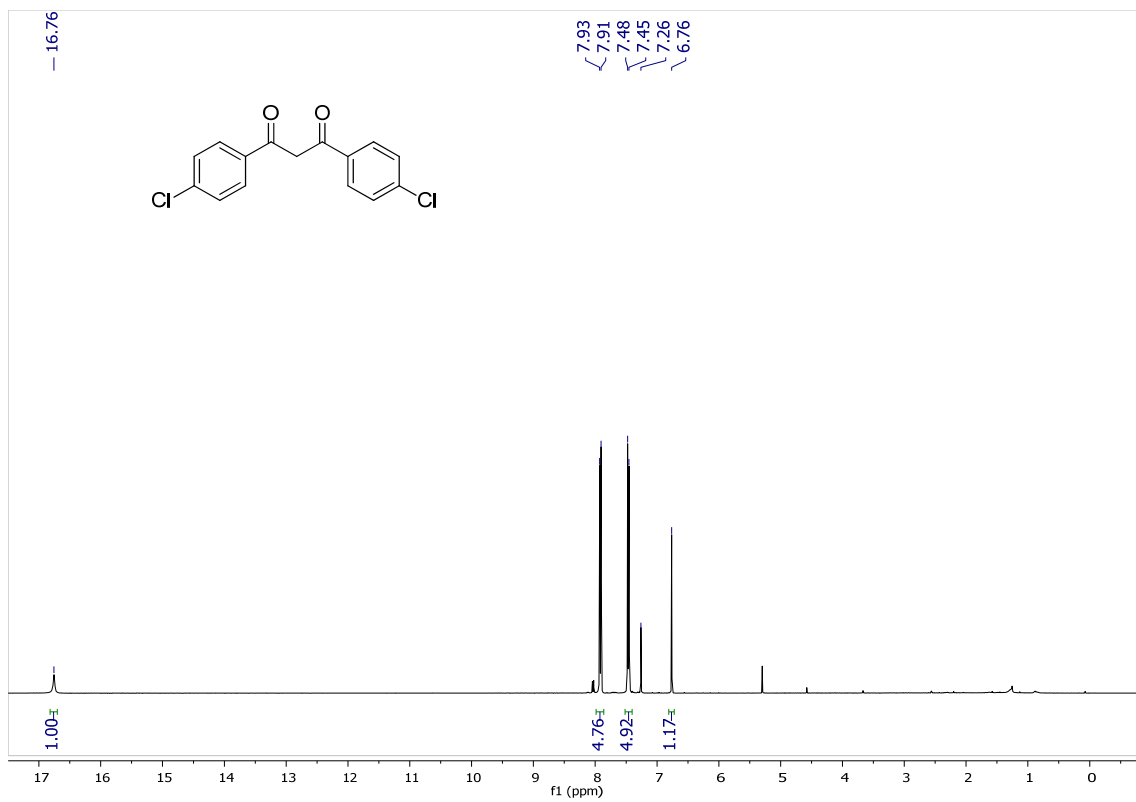
(rac)-(1*R*,3*R*)-Methyl 4-oxo-3-phenylcycloheptanecarboxylate ((rac)-(1*R*,3*R*)-4y): The product was obtained following the general procedure B as a colorless oil in 57% yield (13.6 mg). Once the reaction is finished, the crude mixture was absorbed on silica gel, the solvent removed under vacuum, and the product purified

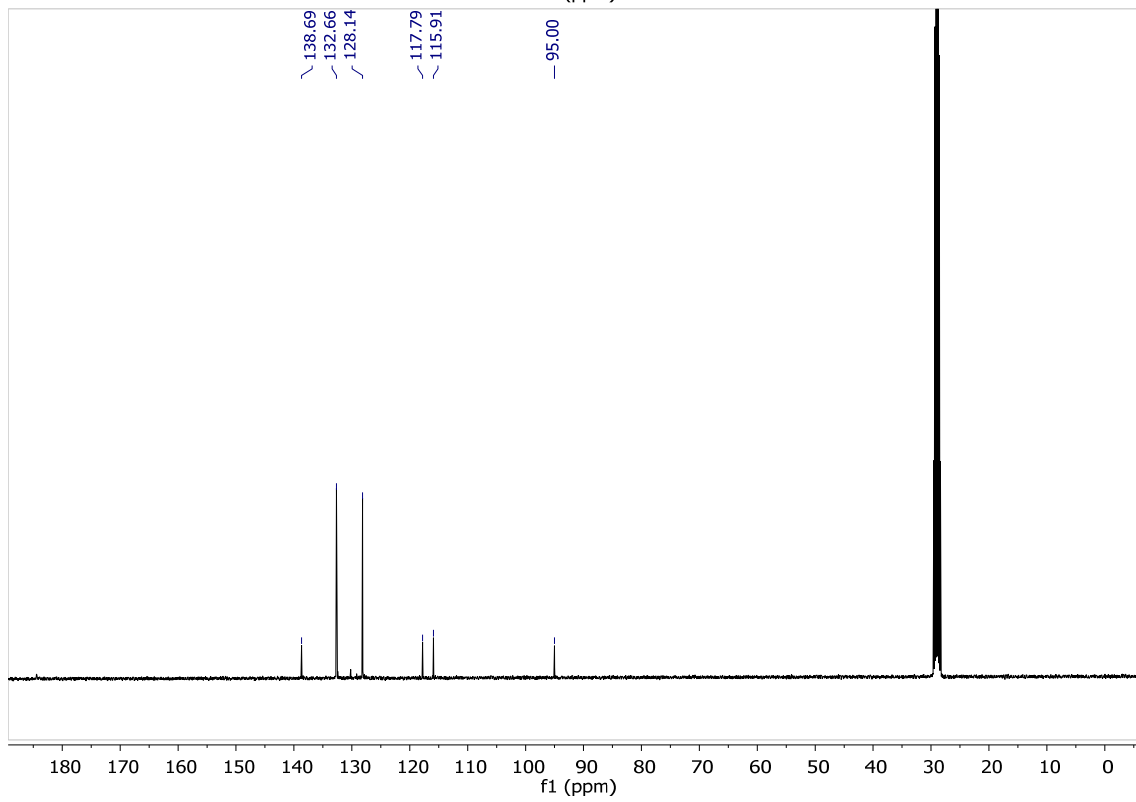
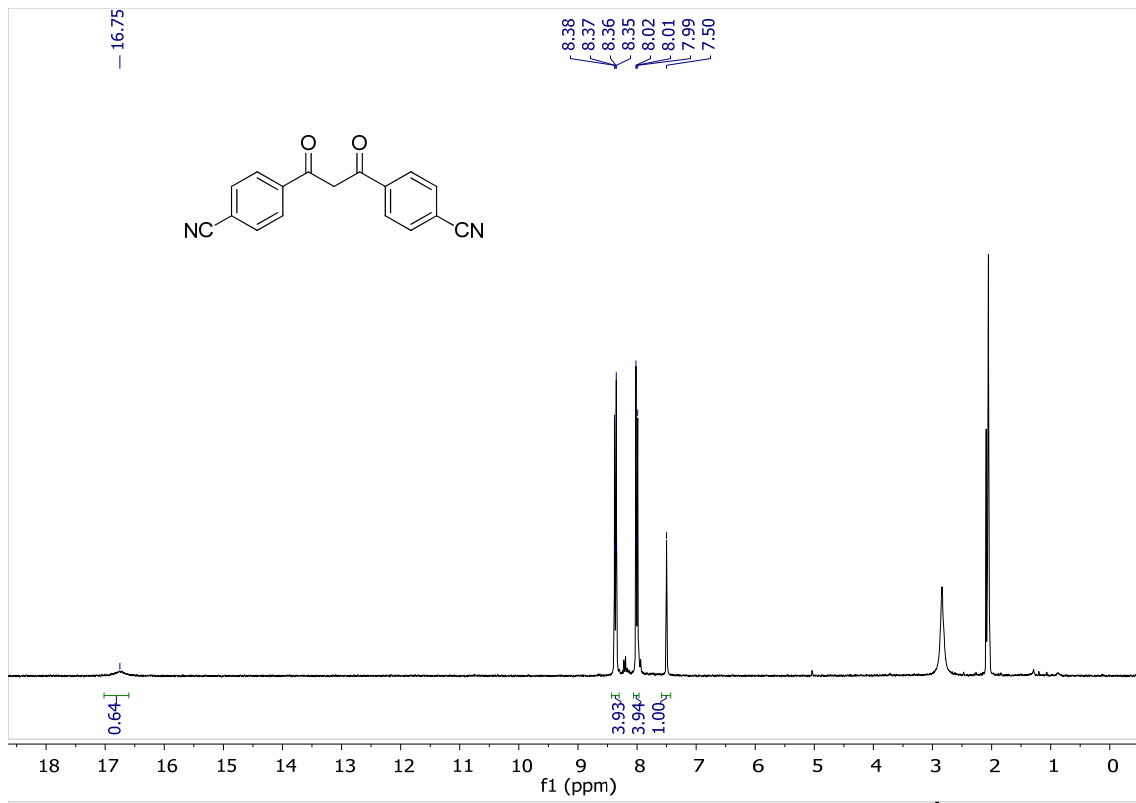
by flash chromatography (PE/EtOAc = 90/10). **¹H-NMR** (300 MHz, CDCl₃) δ 7.35 – 7.30 (m, 2H), 7.27– 7.18 (m, 3H), 4.03 (dd, *J* = 9.7, 3.9 Hz, 1H), 3.70 (s, 3H), 2.89 (tt, *J* = 7.0, 3.7 Hz, 1H), 2.64 (dd, *J* = 7.1, 5.6 Hz, 2H), 2.42 (ddd, *J* = 14.8, 6.5, 4.0 Hz, 1H), 2.27 (ddd, *J* = 14.8, 9.8, 3.7 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.05 – 1.92 (m, 1H), 1.90 – 1.78 (m, 2H); **¹³C NMR** (75 MHz, CDCl₃) δ 266.4, 212.1, 175.0, 128.5, 128.2, 126.9, 54.5, 51.9, 43.1, 42.0, 33.3, 30.8, 21.3; **HMRS**: [M]⁺ calculated for C₁₅H₁₈O₃: 246.1250; found: 246.1249.

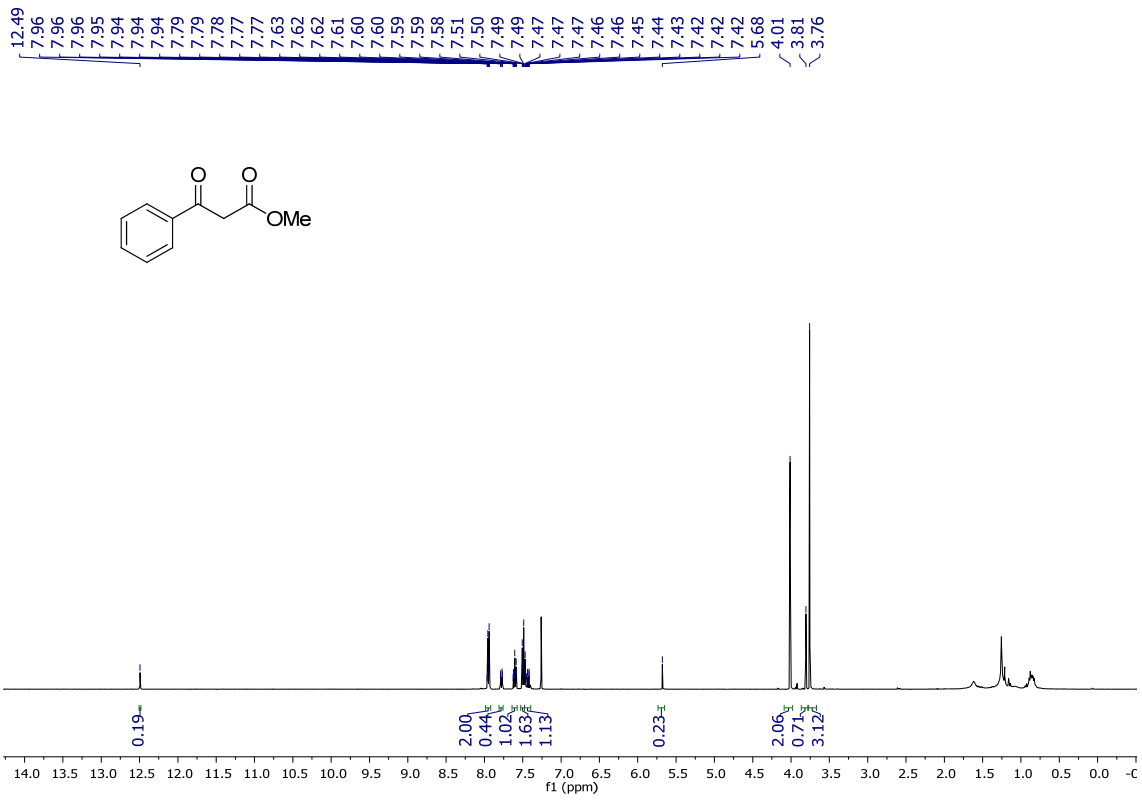
8. NMR spectra for starting materials and compounds 4a-4y:

(See experimental procedures for solvent and field of the NMR experiment.)

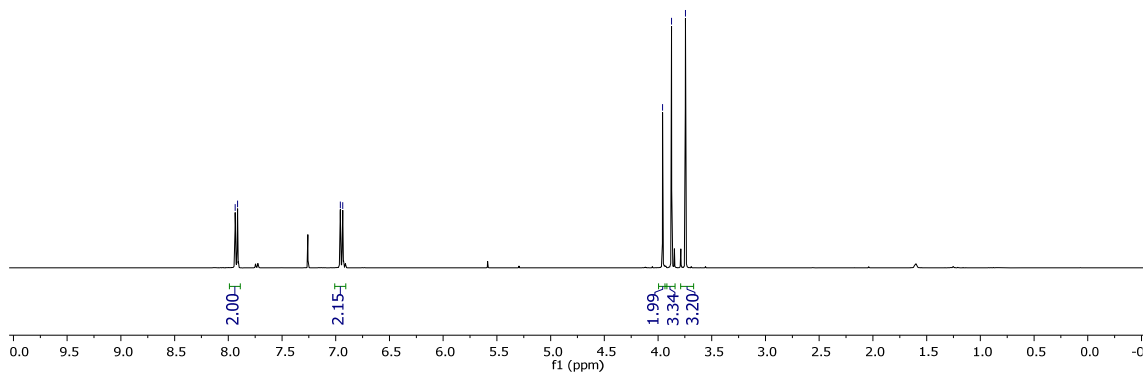
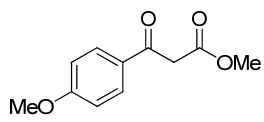


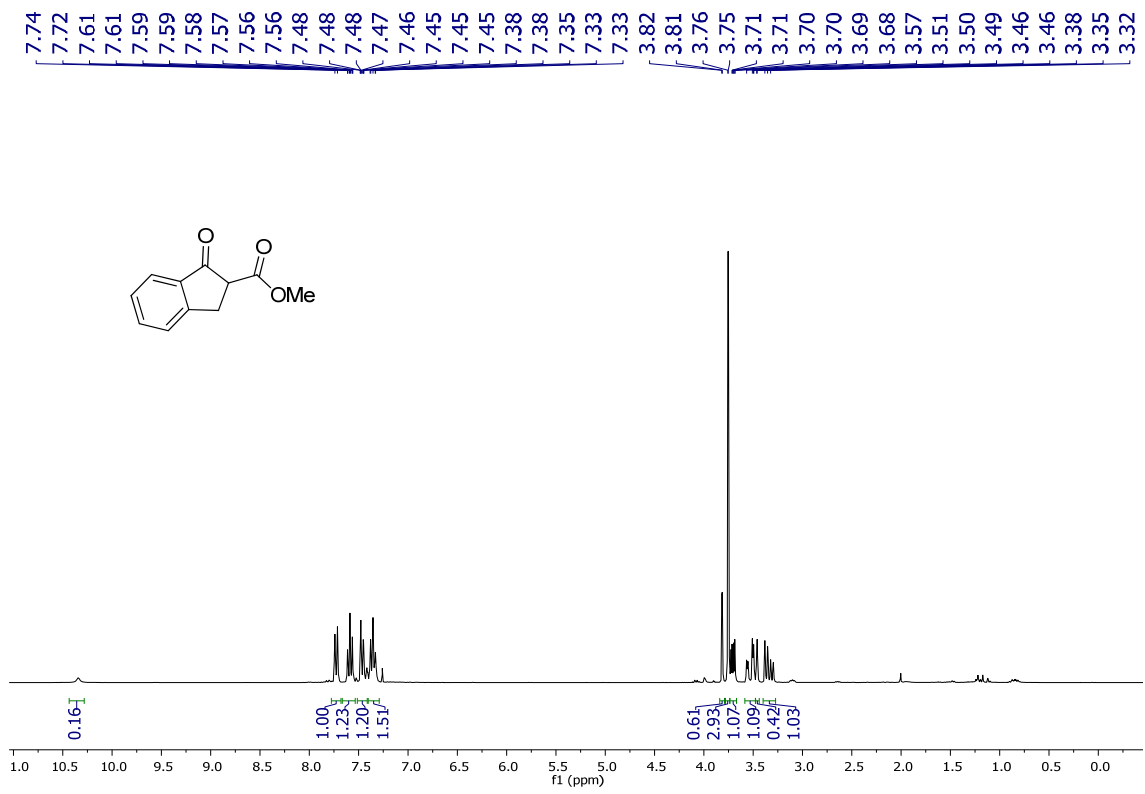




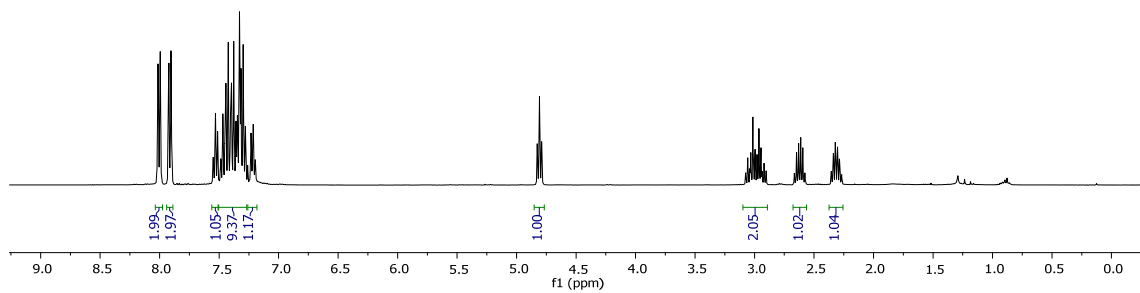
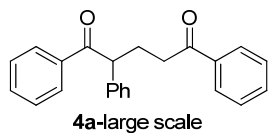
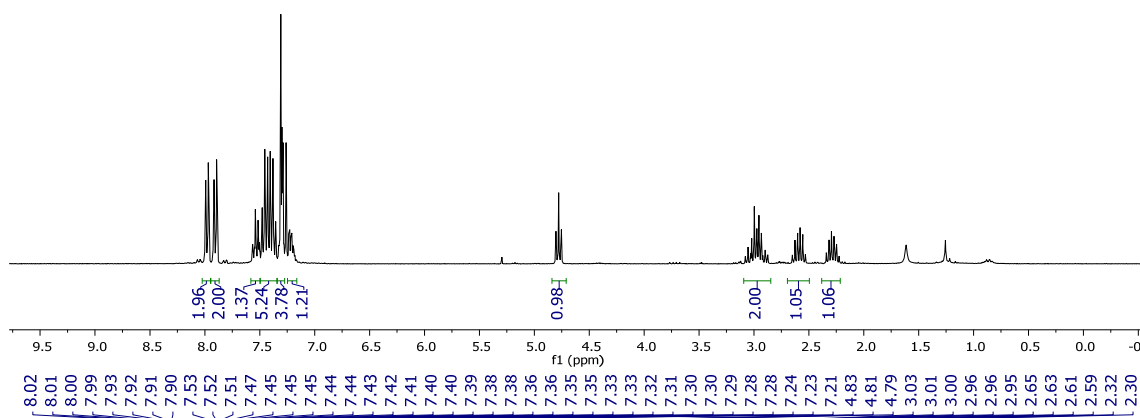
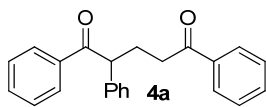


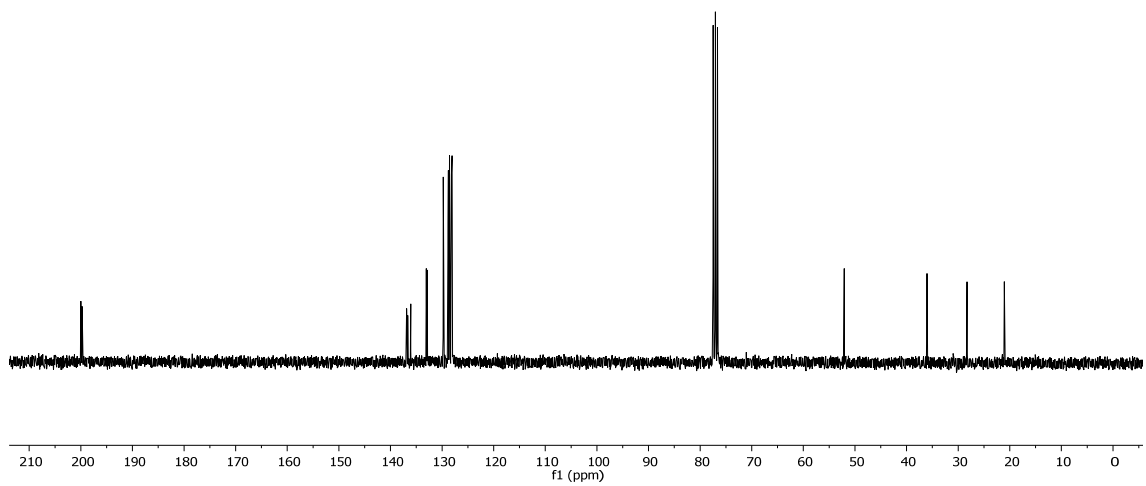
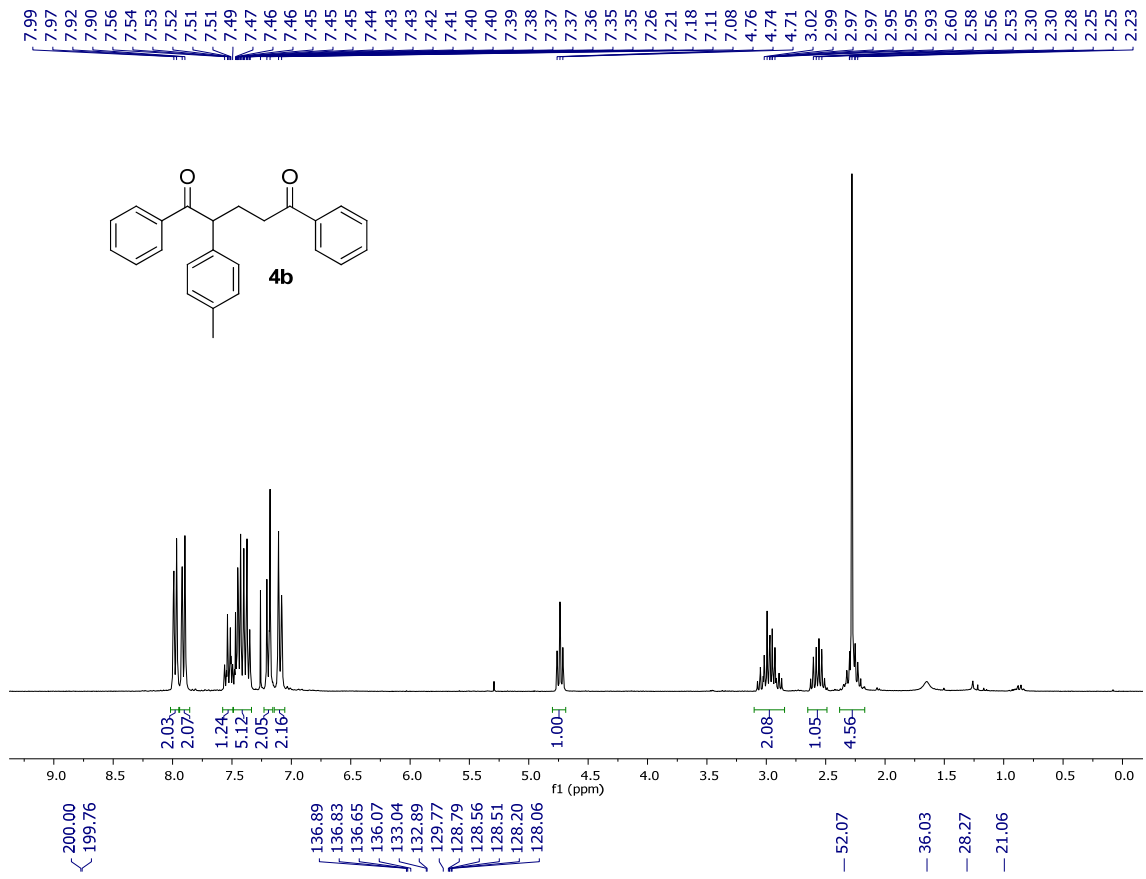
7.94 < 7.91
6.96 < 6.94
3.96 < 3.87
3.75

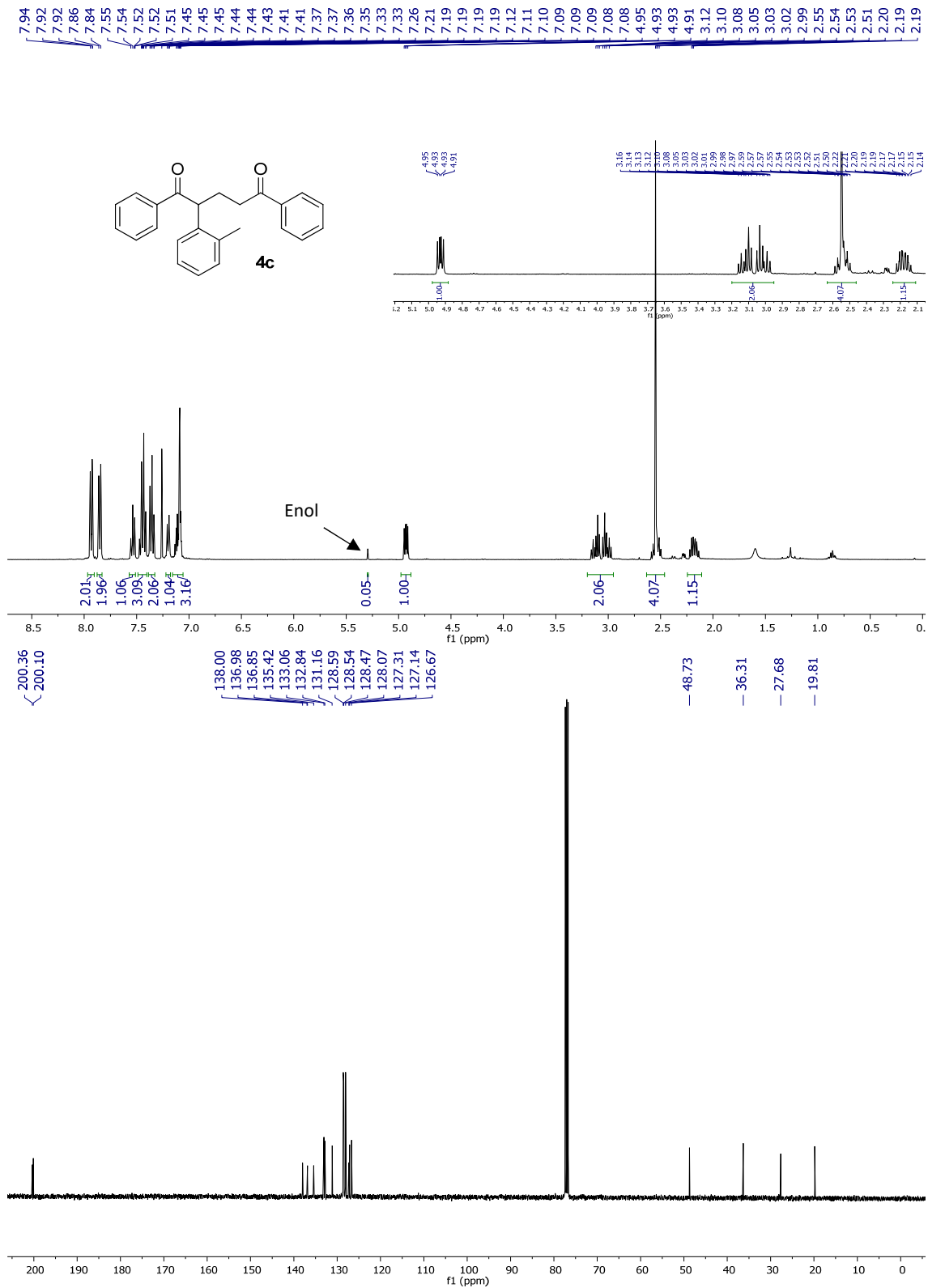


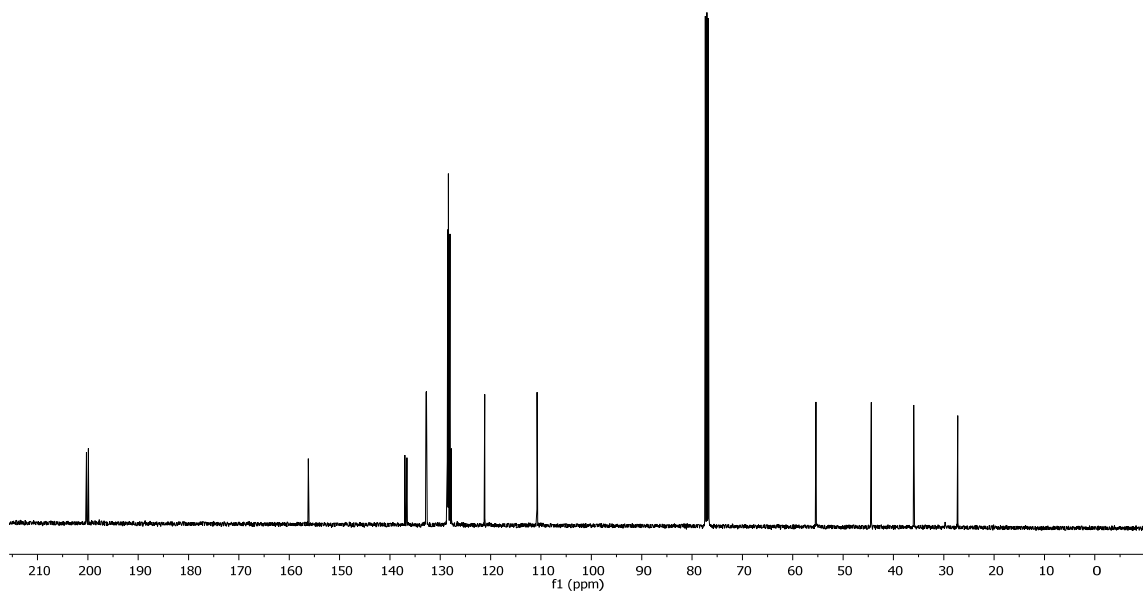
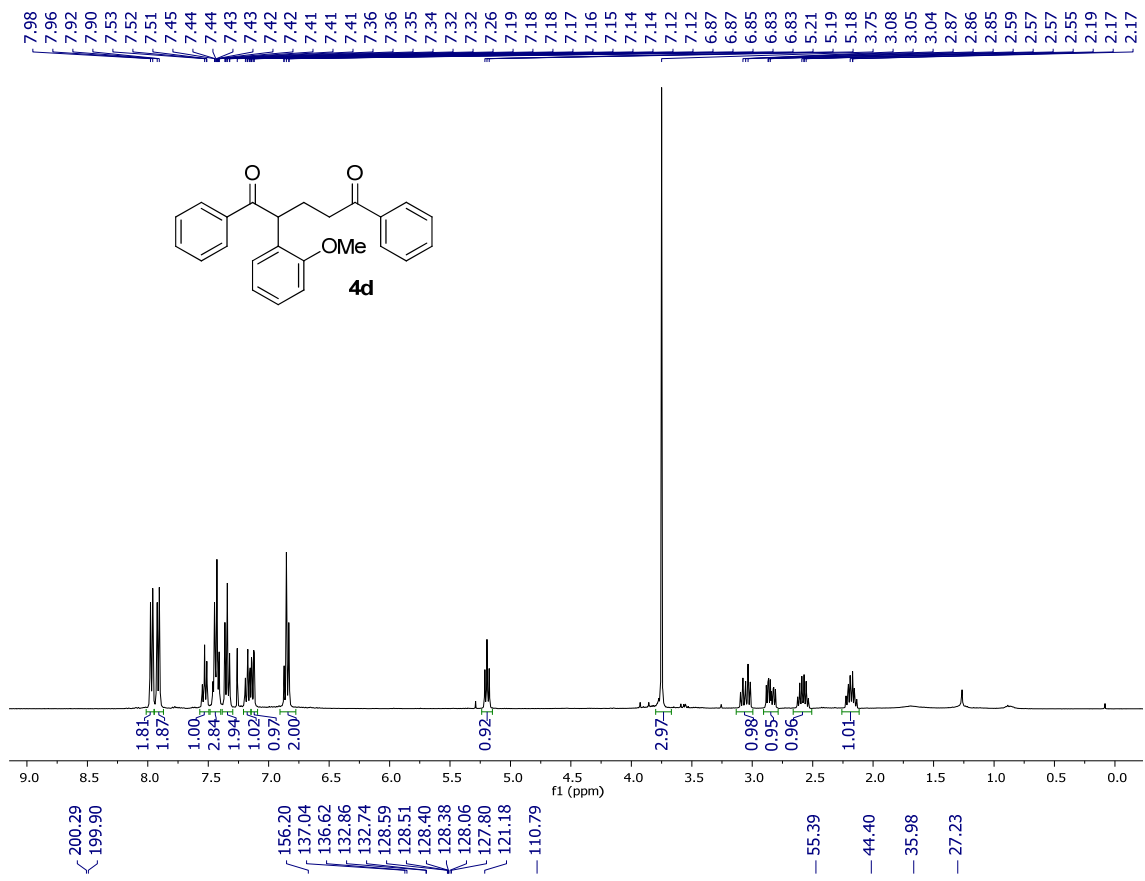


7.99
7.97
7.92
7.89
7.56
7.54
7.52
7.51
7.50
7.48
7.47
7.45
7.45
7.43
7.43
7.42
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.35
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.26
7.26
7.24
7.23
7.22
7.21
7.21
4.80
4.78
4.75
3.02
3.00
2.98
2.97
2.95
2.93
2.63
2.60
2.58
2.56
2.32
2.32
2.29
2.27
2.25

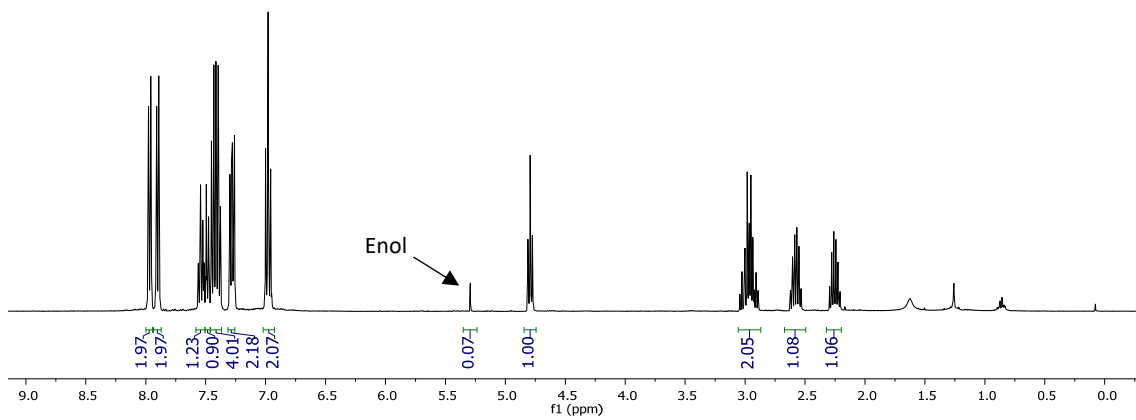
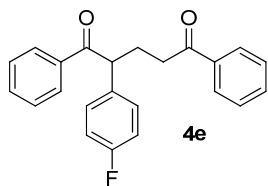




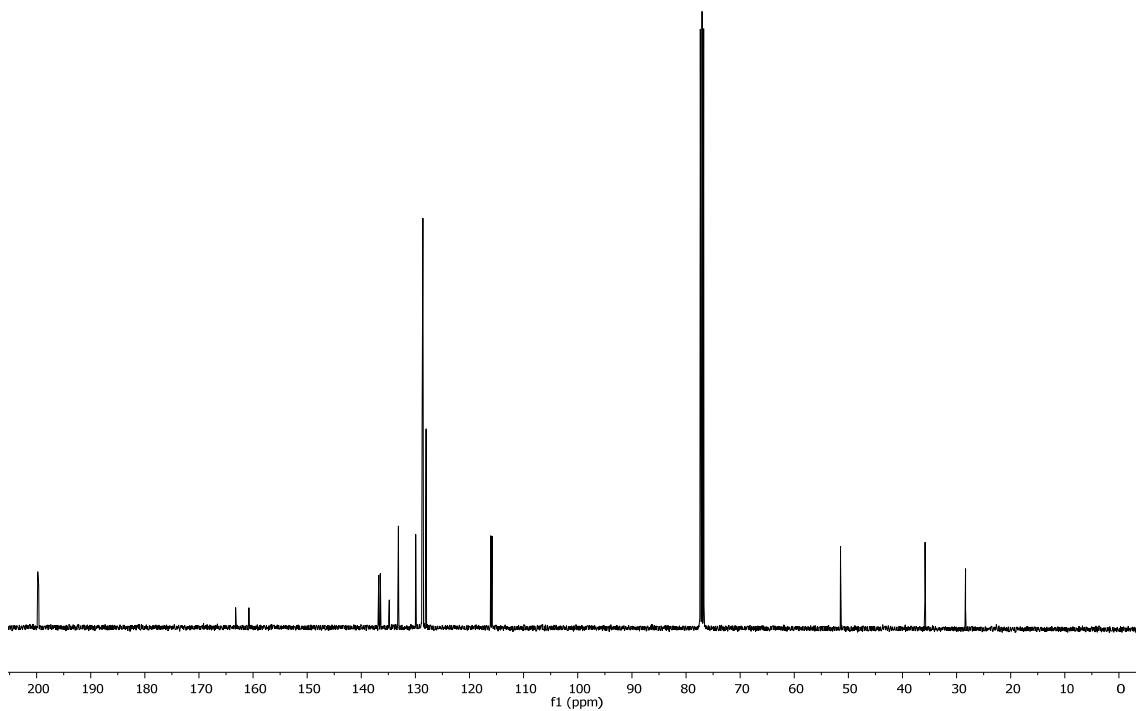


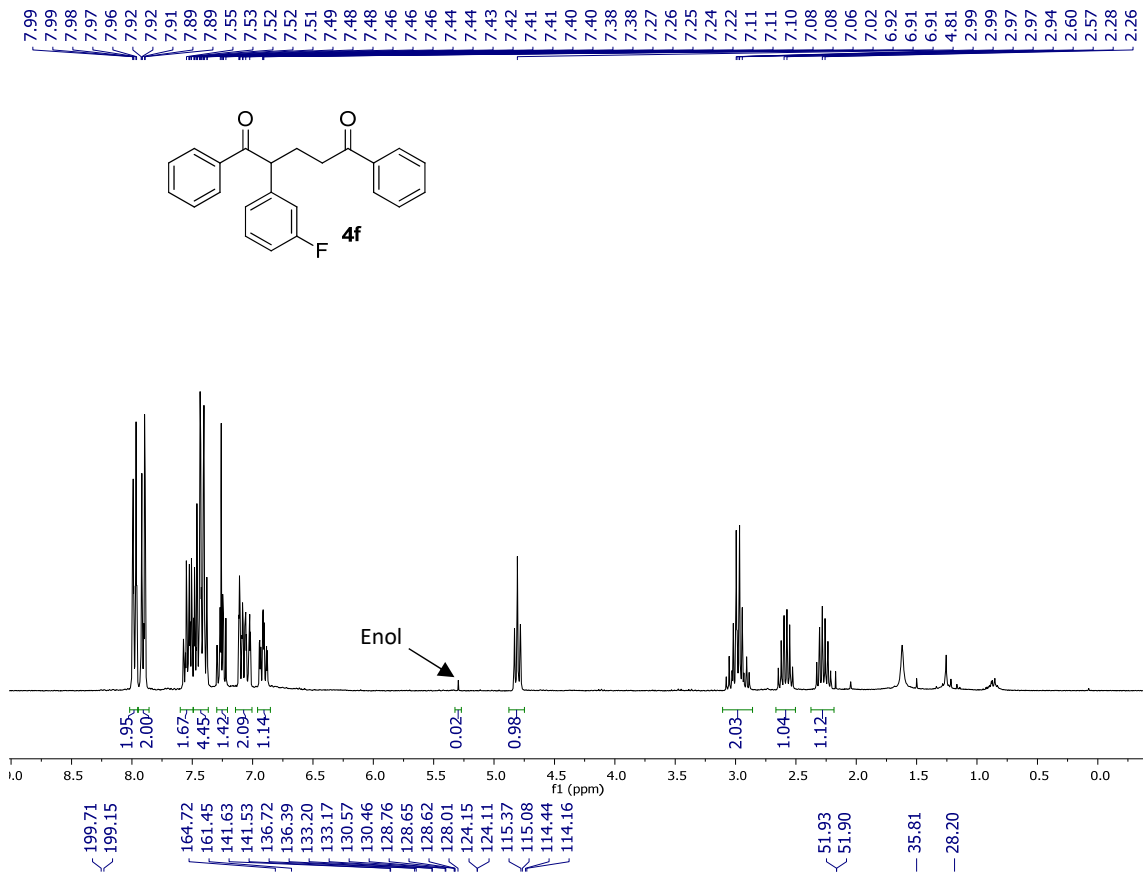


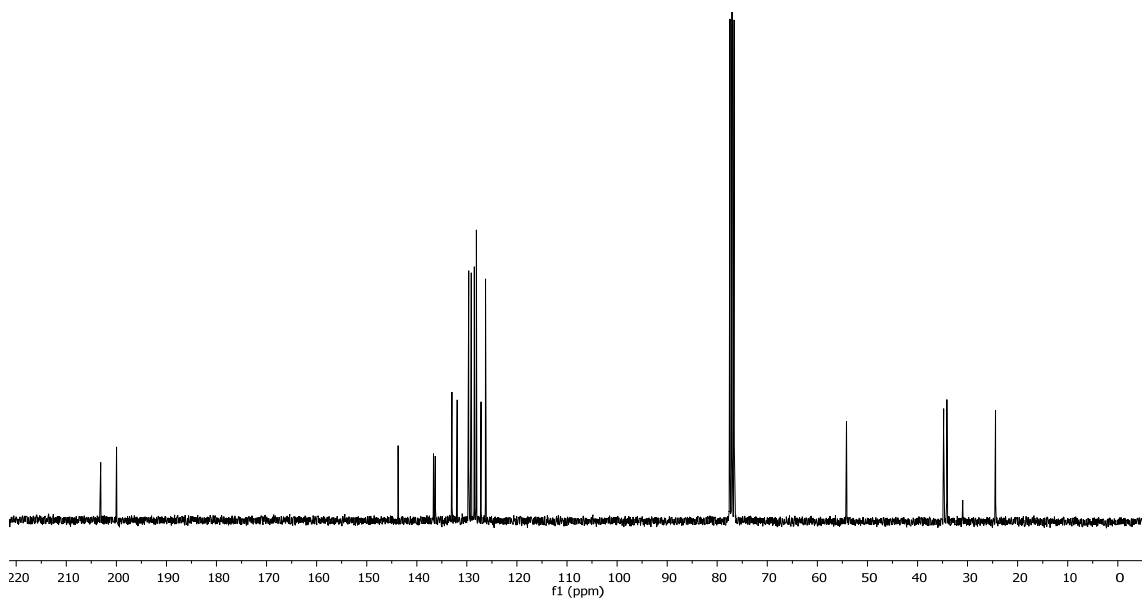
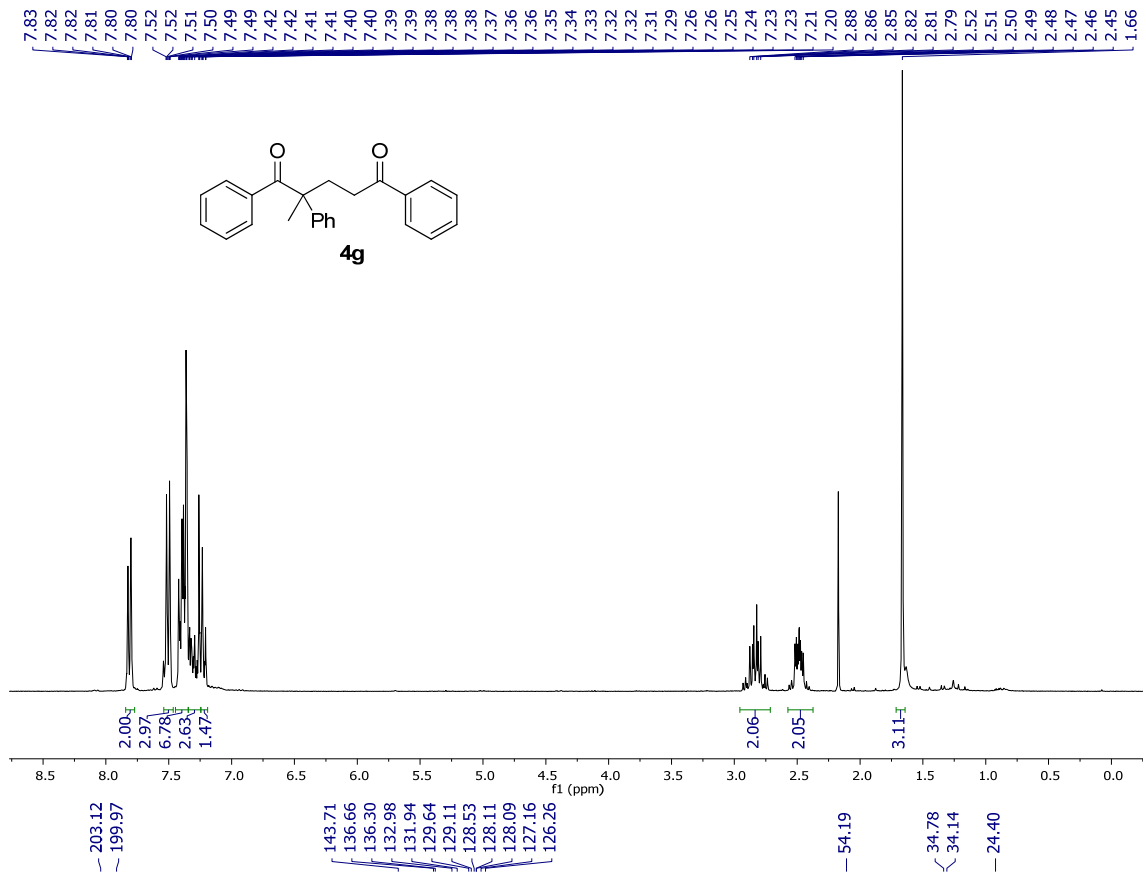
7.98
7.96
7.91
7.89
7.56
7.54
7.53
7.52
7.51
7.49
7.49
7.48
7.48
7.47
7.45
7.45
7.44
7.43
7.41
7.40
7.40
7.38
7.38
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.00
6.98
6.96
4.81
4.79
4.77
3.03
3.00
2.98
2.97
2.97
2.95
2.94
2.91
2.60
2.59
2.57
2.55
2.28
2.26
2.24
2.23

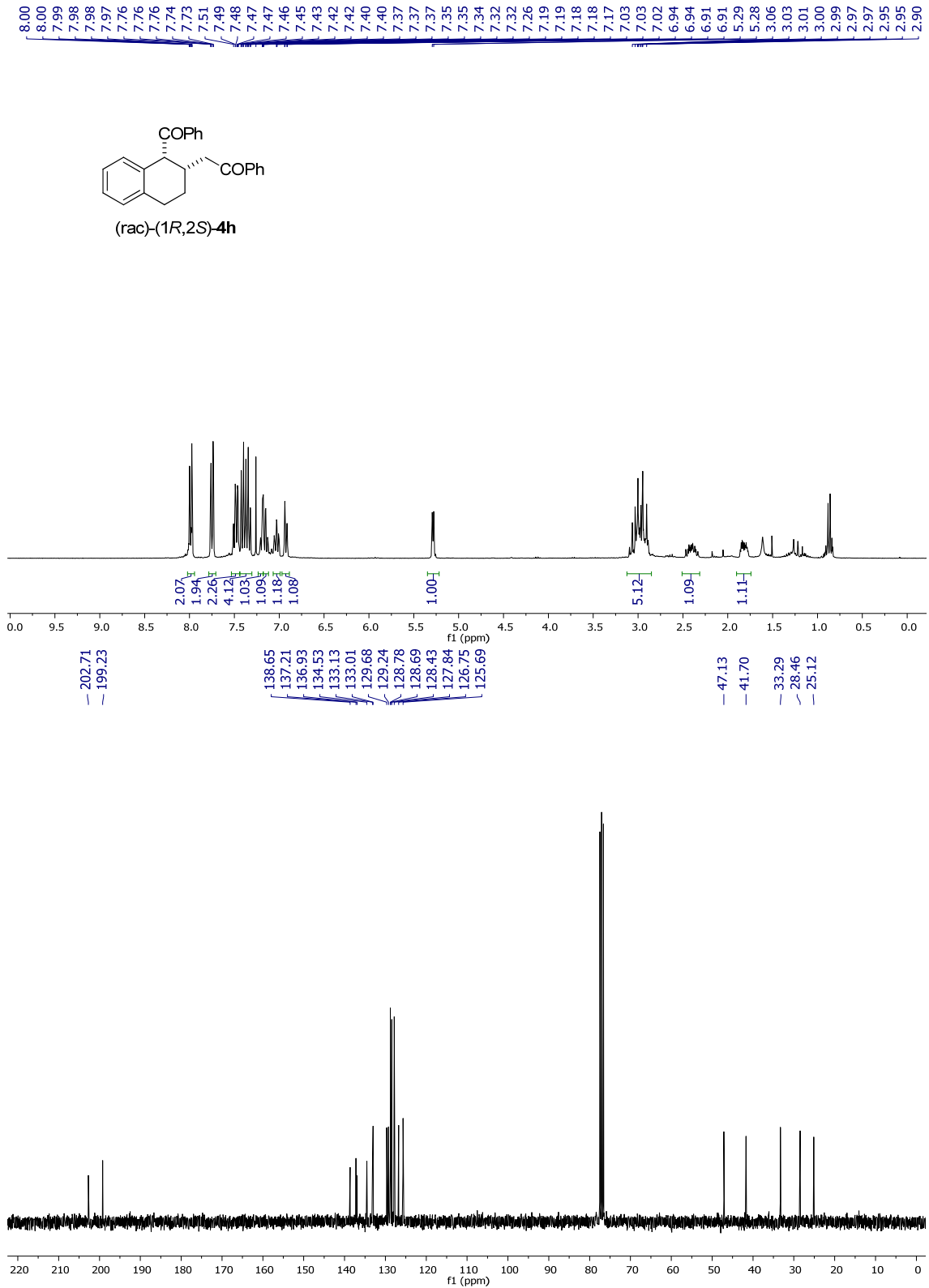


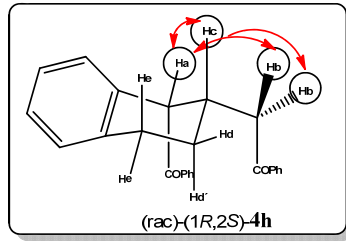
199.80
199.60
163.21
160.77
136.78
136.49
134.88
134.84
133.15
133.11
129.94
129.87
128.76
128.62
128.02
116.06
115.85
51.45
35.84
28.35



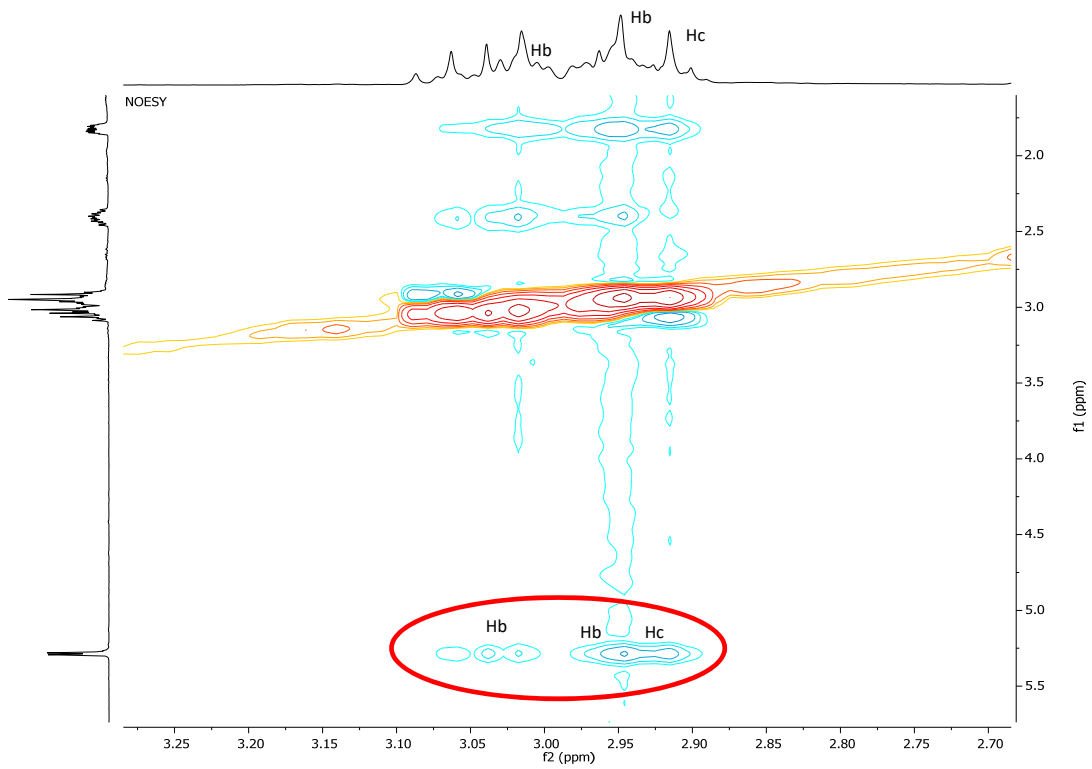
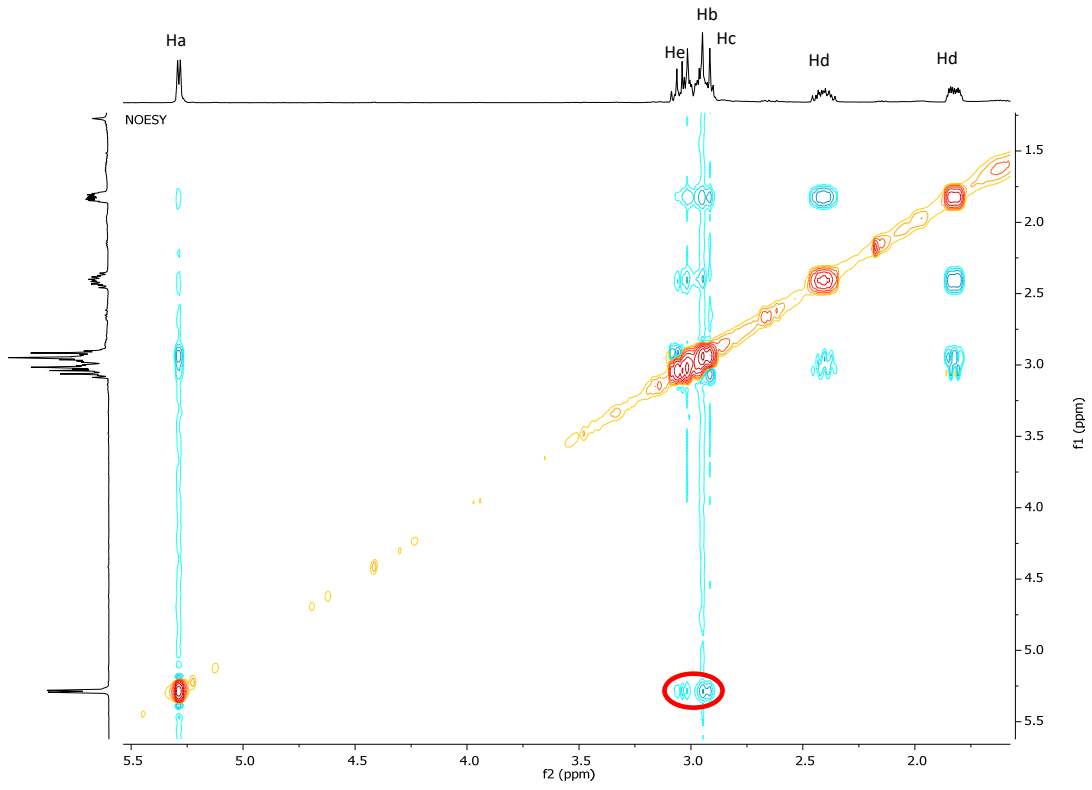
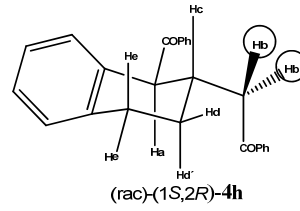


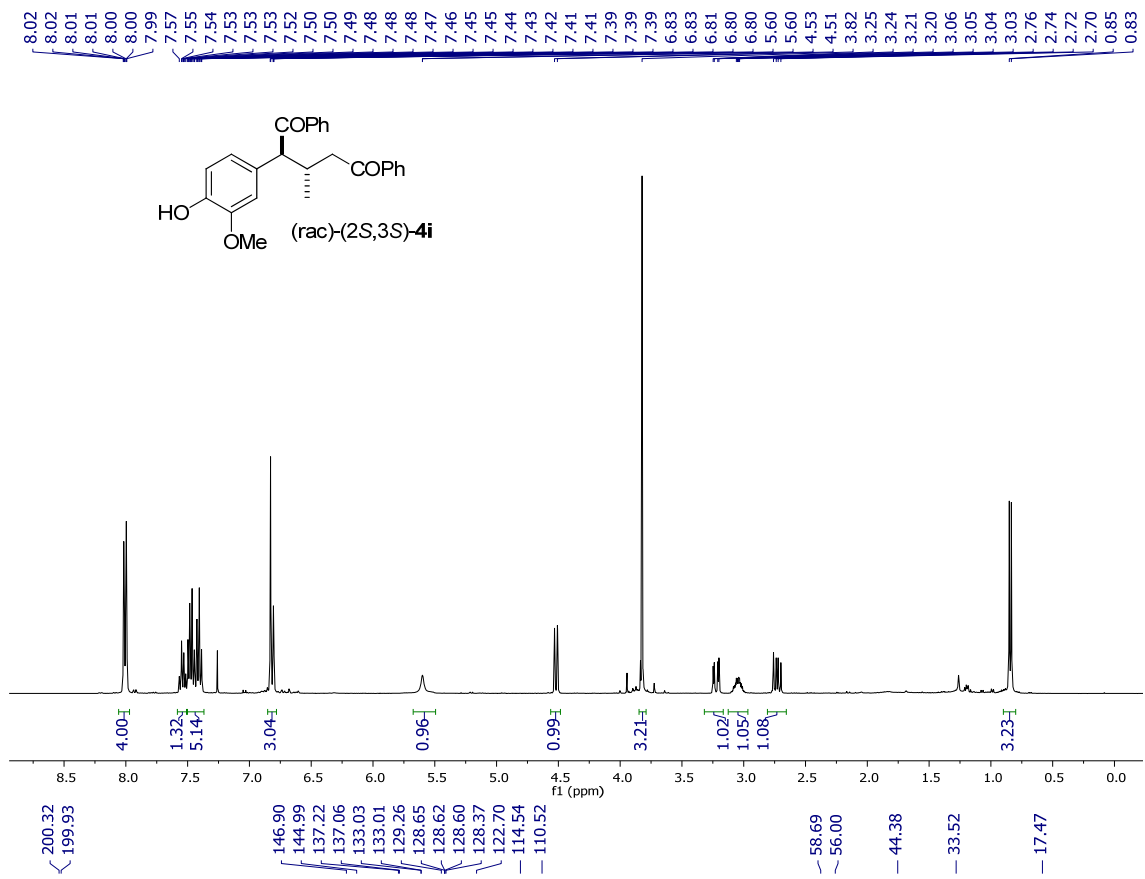


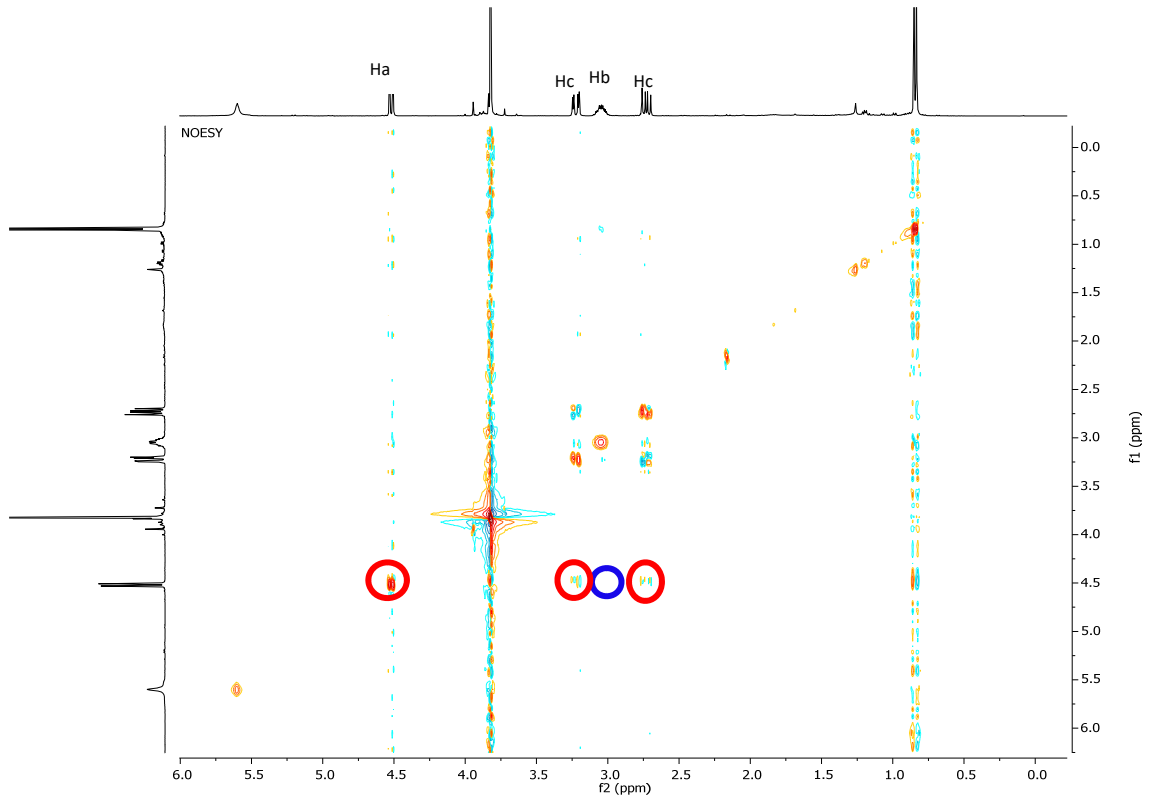
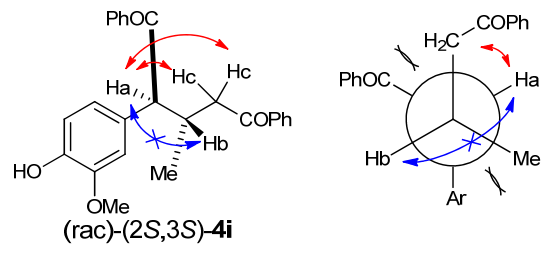


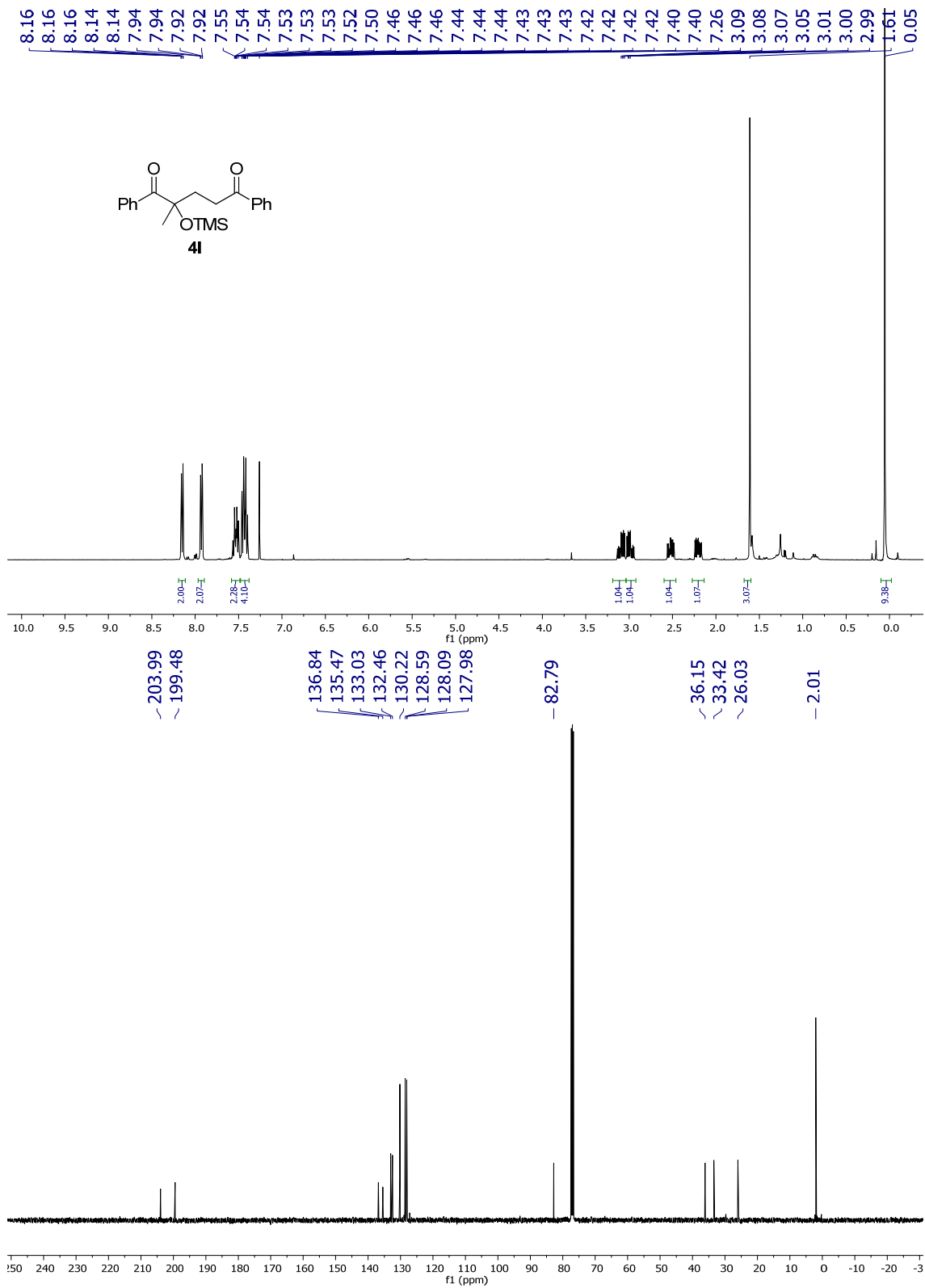


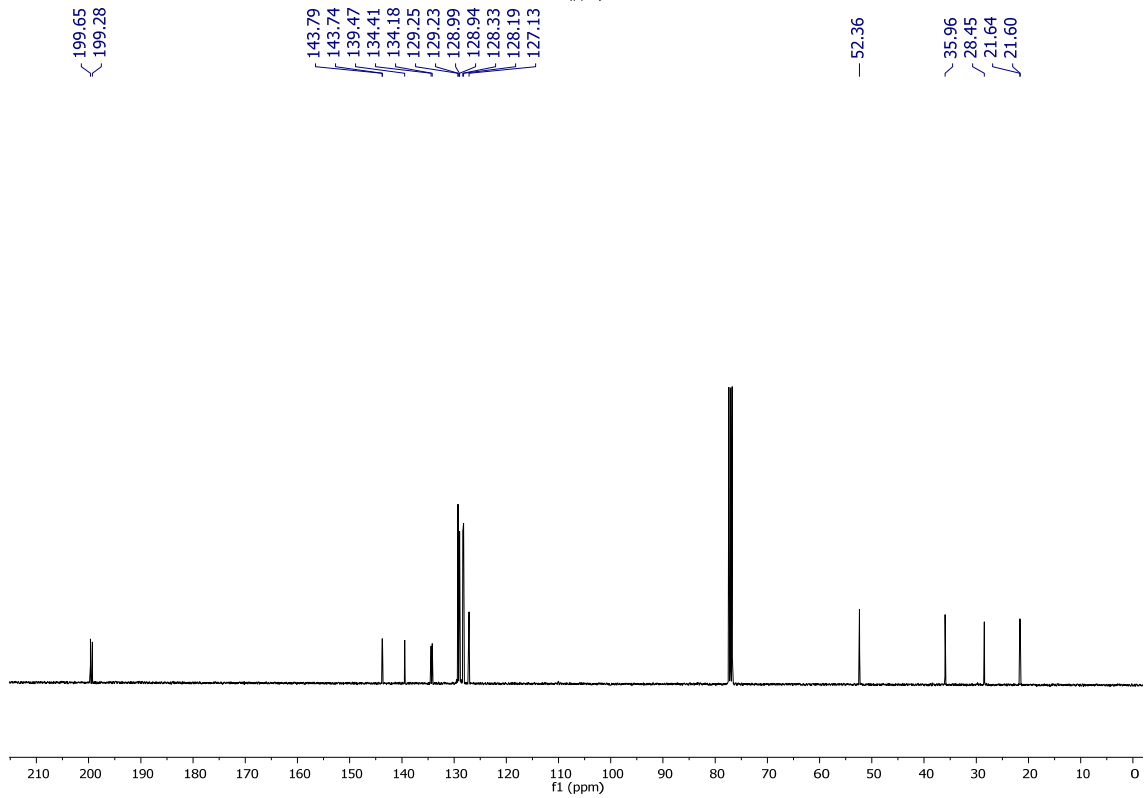
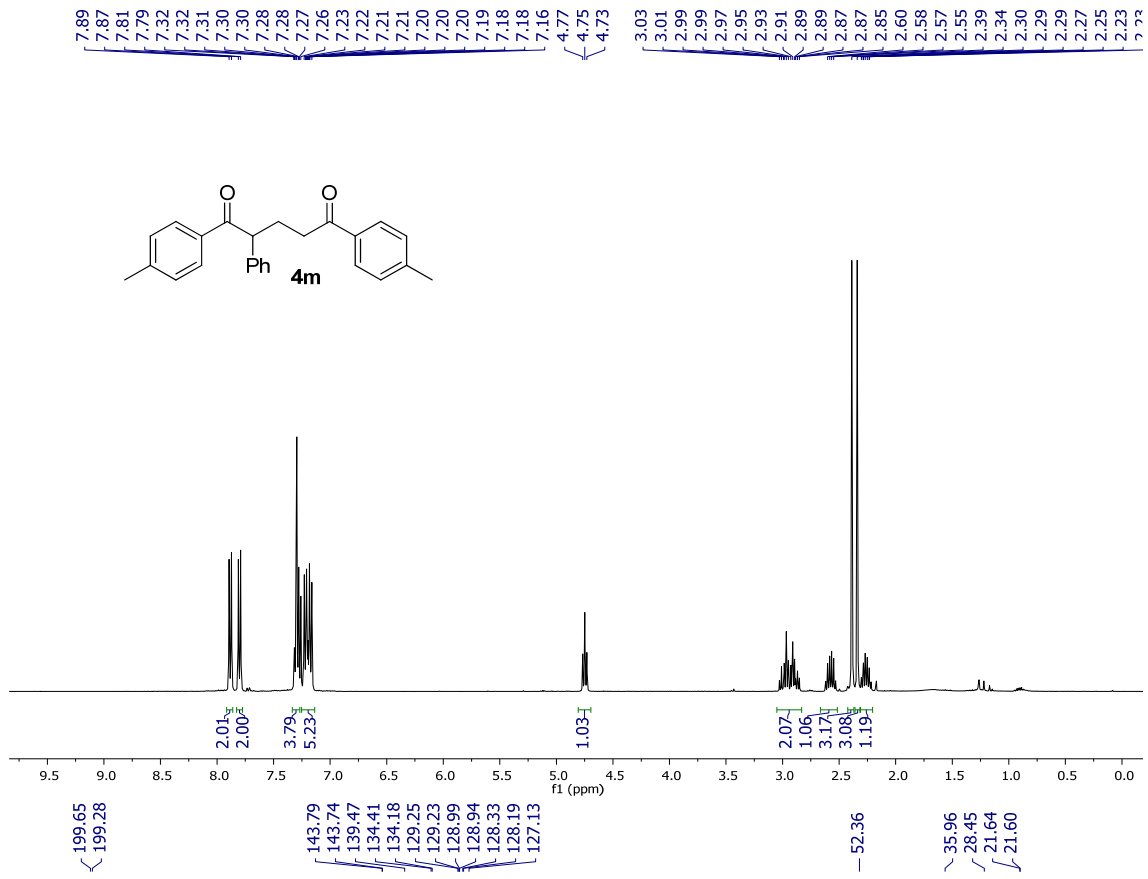
VS

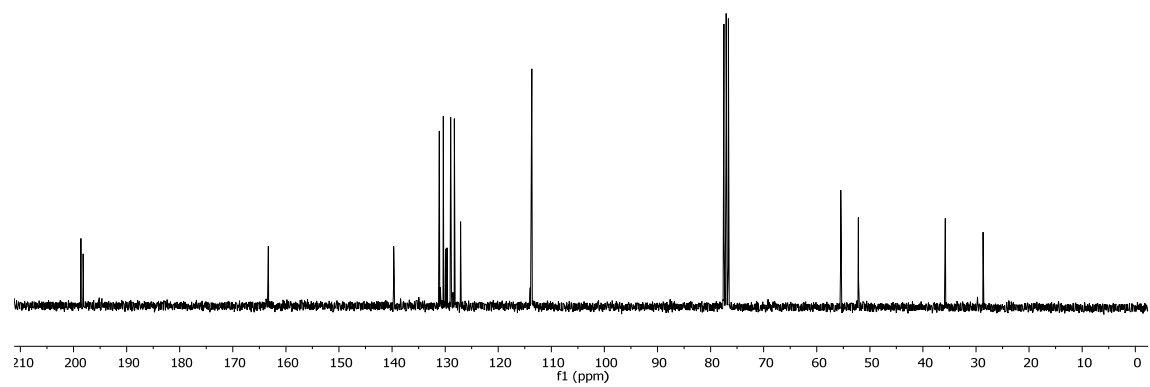
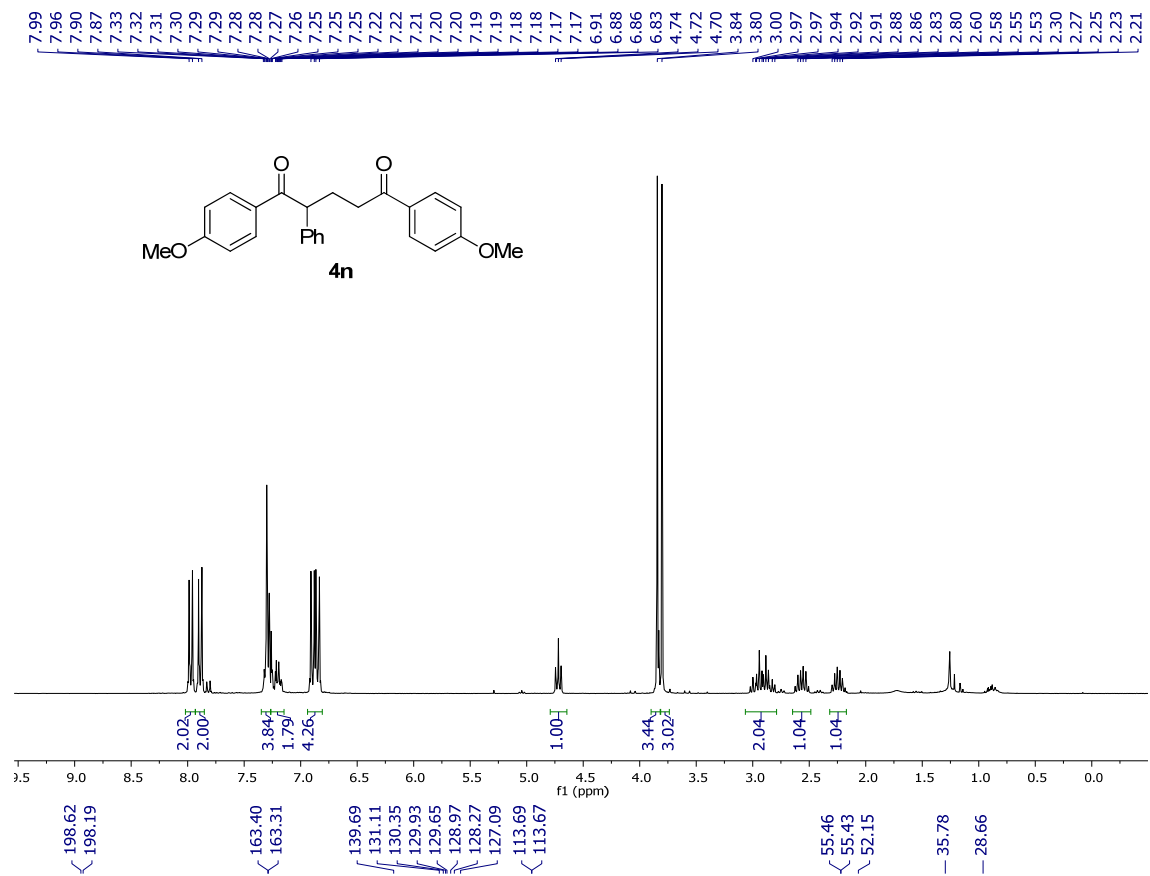


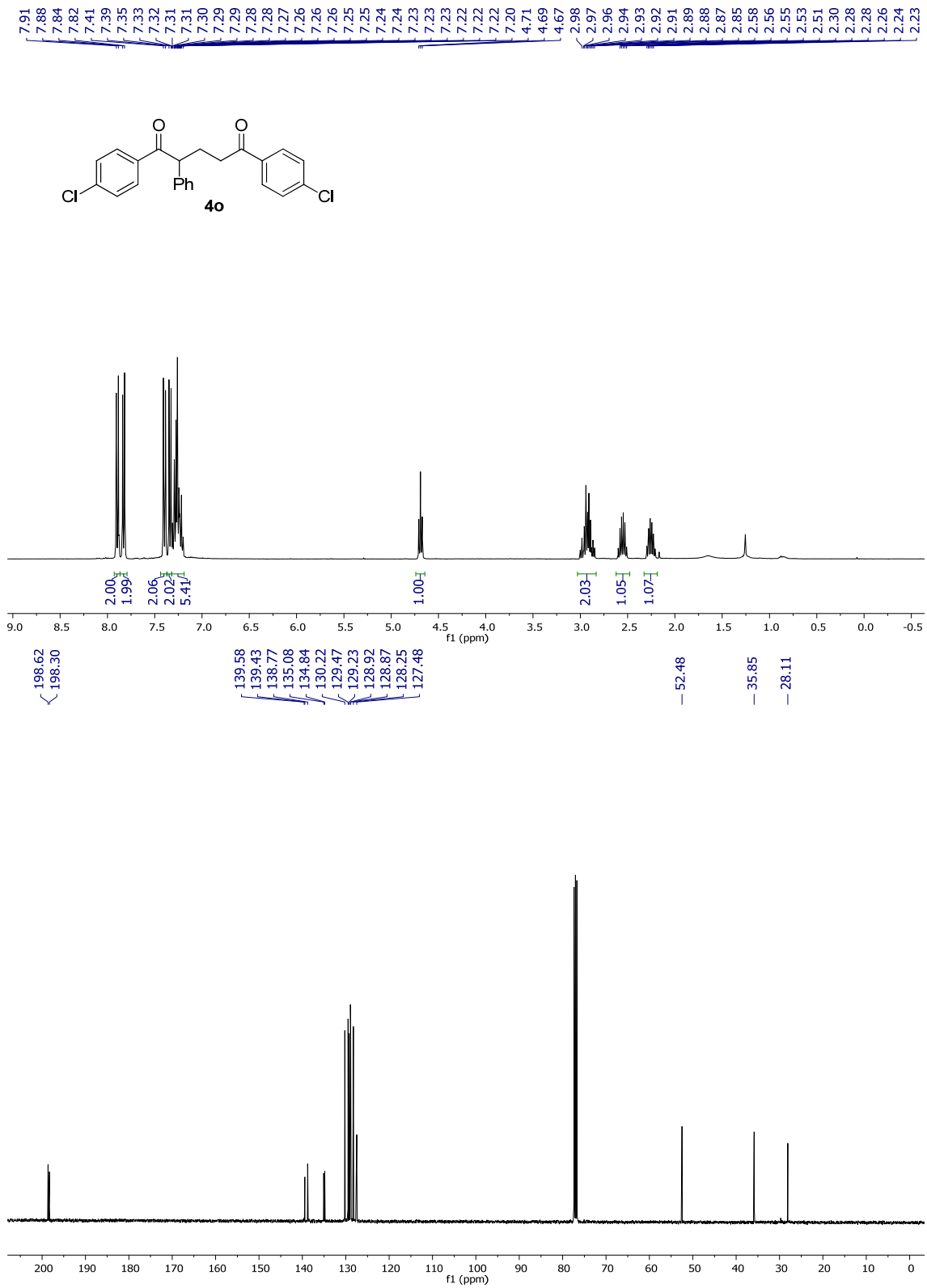




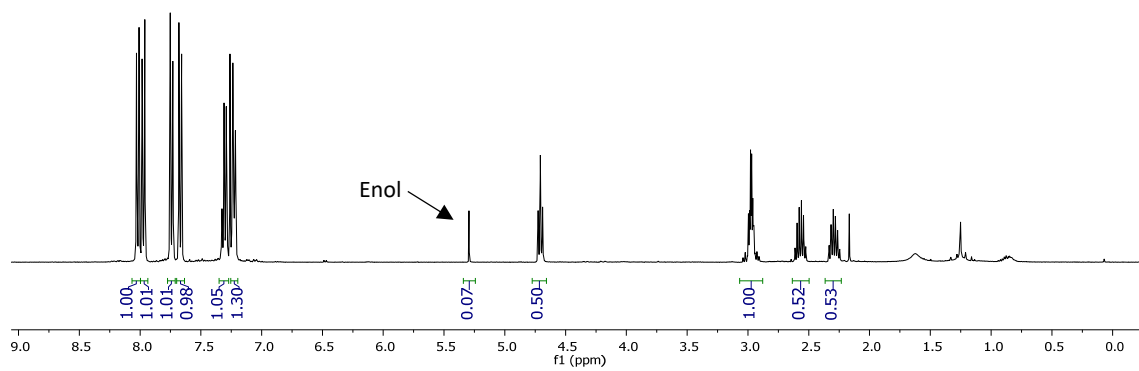
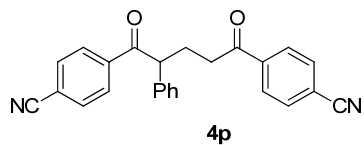






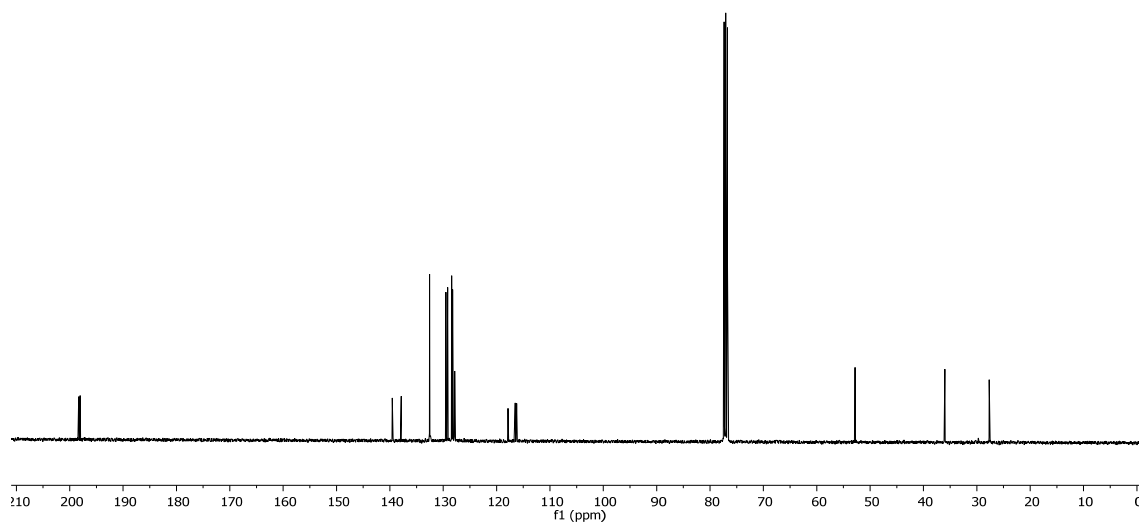


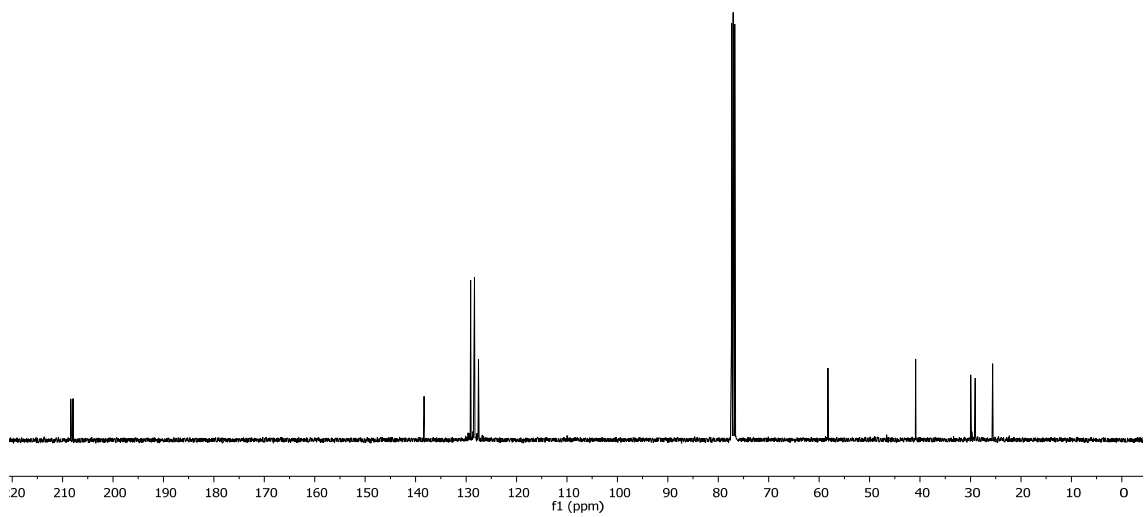
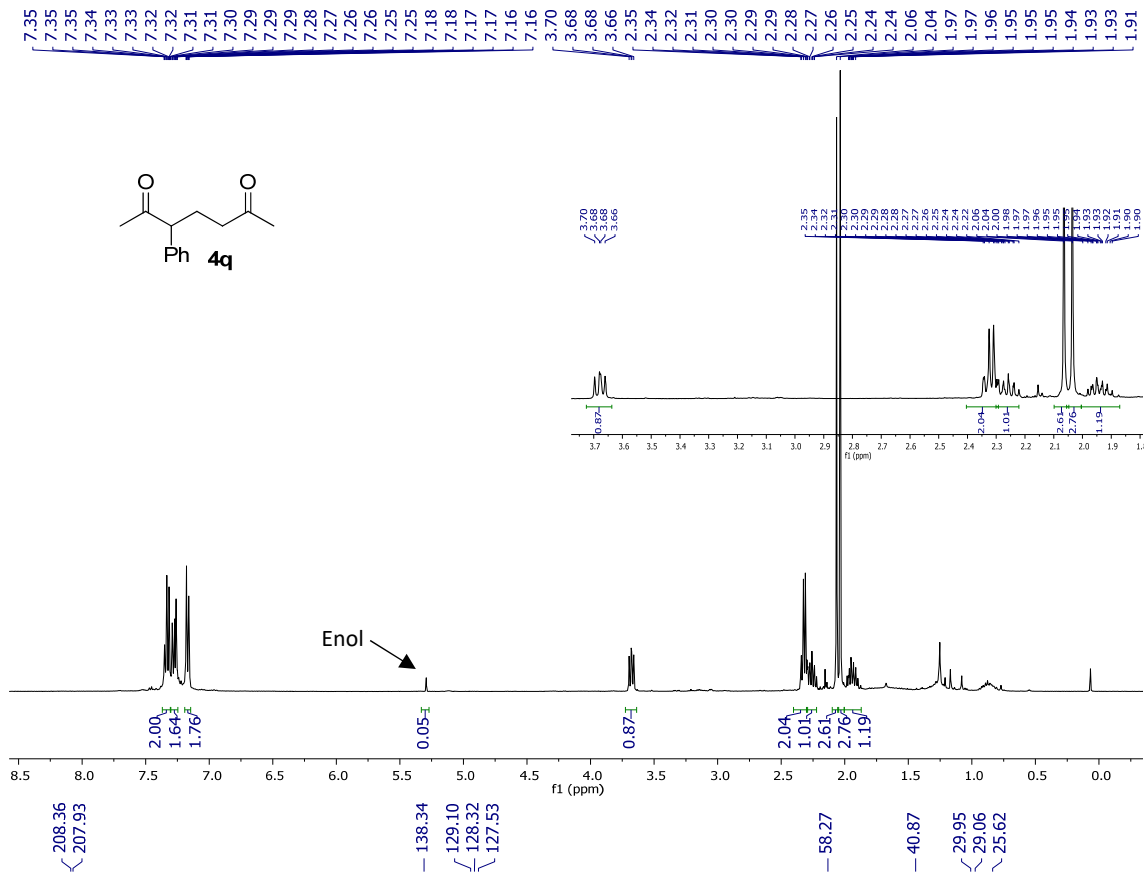
8.03
8.01
7.98
7.96
7.75
7.73
7.68
7.66
7.33
7.33
7.32
7.31
7.31
7.31
7.29
7.29
7.29
7.28
7.28
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
5.29
4.73
4.71
4.69
3.02
3.00
3.00
2.99
2.97
2.96
2.95
2.94
2.93
2.61
2.60
2.58
2.56
2.54
2.52
2.33
2.32
2.31
2.30
2.28
2.26
2.25



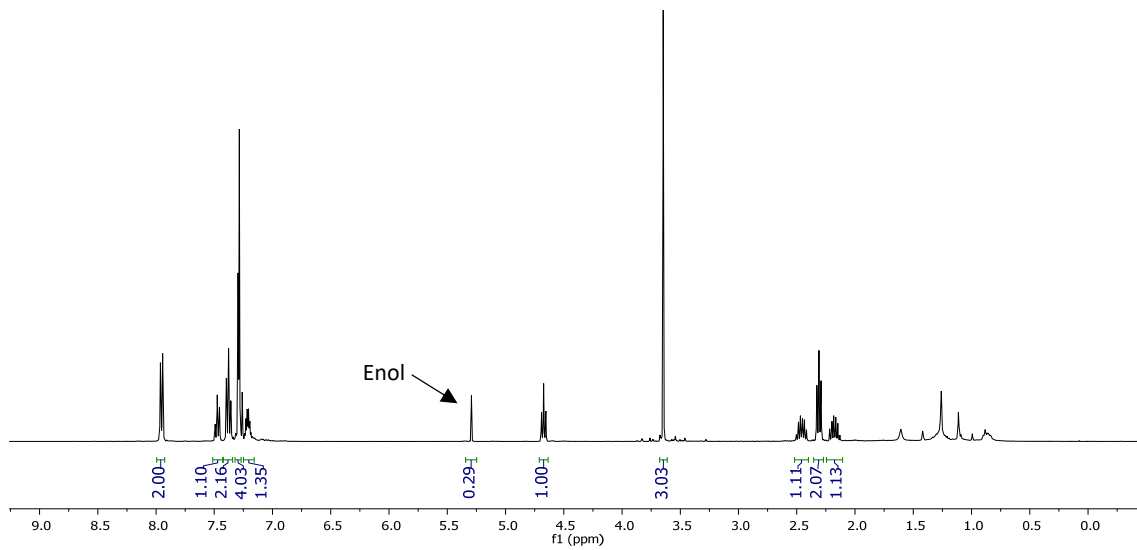
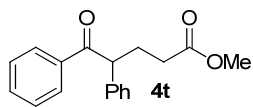
1.00
1.01
1.01
0.98
1.05
1.30
0.07
0.50
1.00
0.52
0.53
52.82
36.00
27.67

198.33
198.05
139.55
139.45
137.88
132.55
132.44
129.49
129.17
128.44
128.25
127.87
117.87
117.85
116.51
116.24
52.82
36.00
27.67





7.96
7.96
7.94
7.50
7.49
7.49
7.47
7.47
7.46
7.46
7.45
7.40
7.39
7.38
7.38
7.36
7.36
7.30
7.29
7.28
7.28
7.27
7.26
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.18
5.29
5.29
4.69
4.67
4.65
3.65
2.49
2.47
2.47
2.45
2.45
2.44
2.43
2.42
2.33
2.31
2.29
2.22
2.20
2.20
2.18
2.18
2.17
2.16
2.15



-199.25

-173.72

138.79

136.60

132.95

129.07

128.75

128.53

128.33

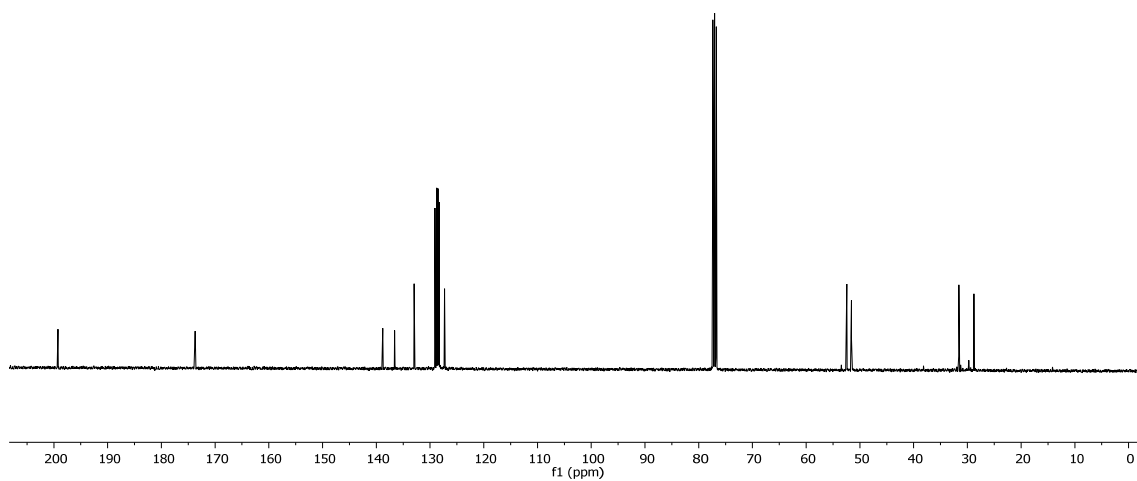
127.31

52.45

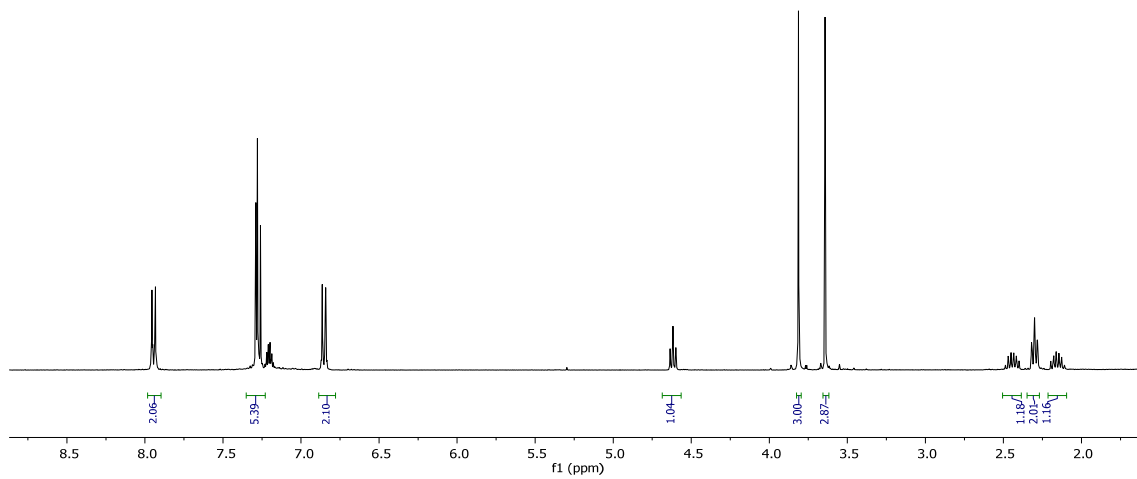
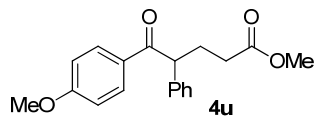
51.58

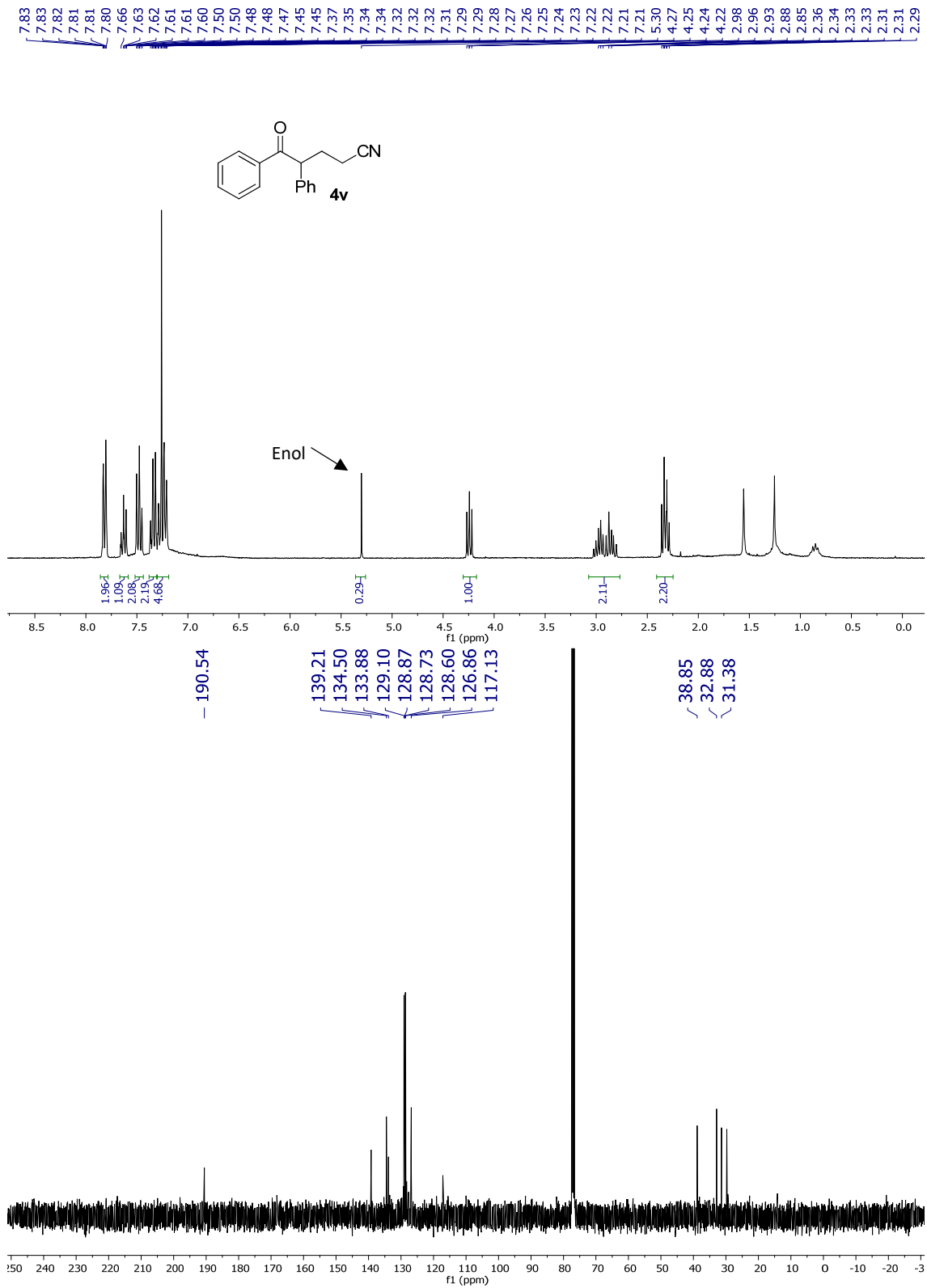
31.58

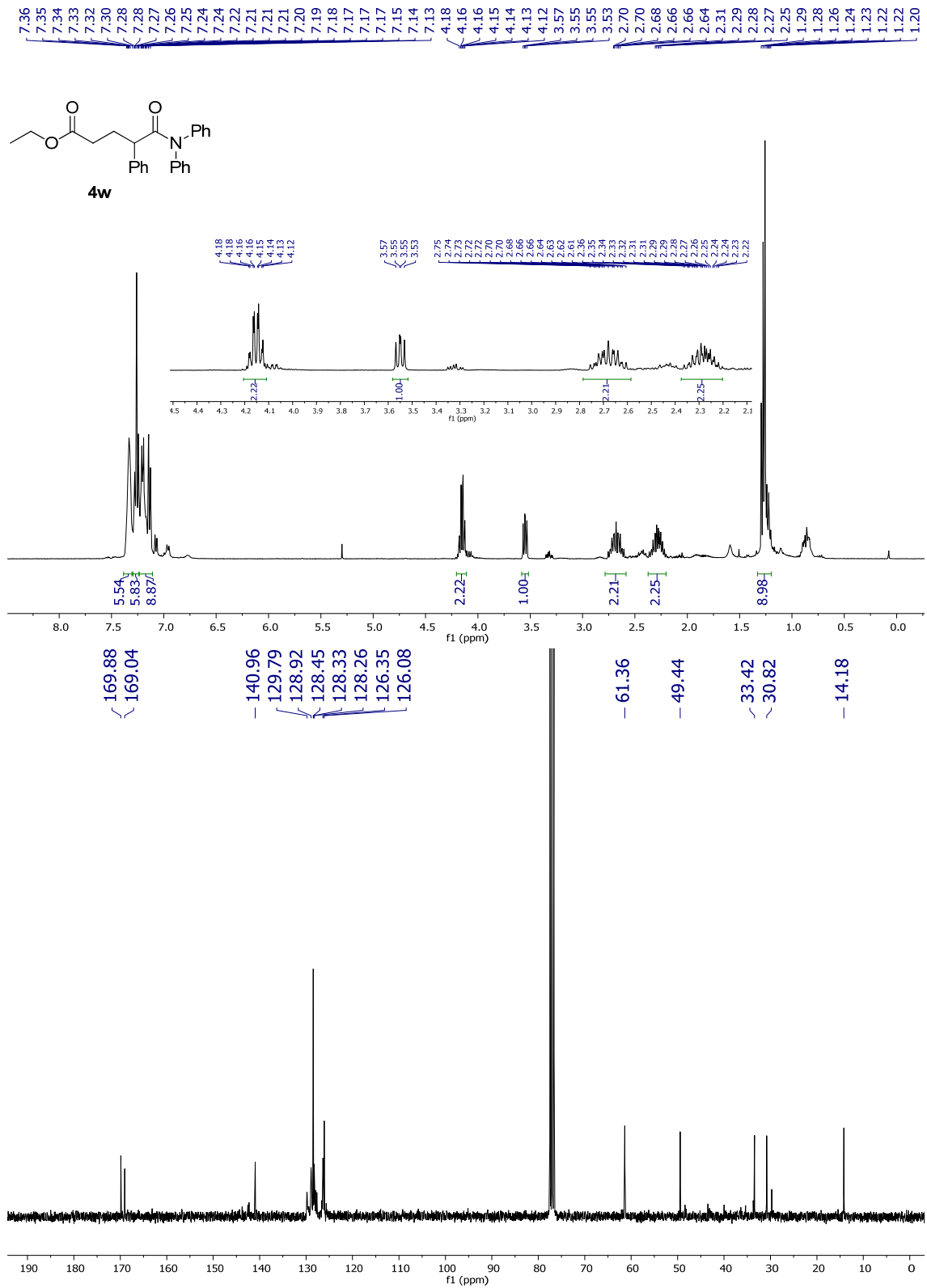
28.78

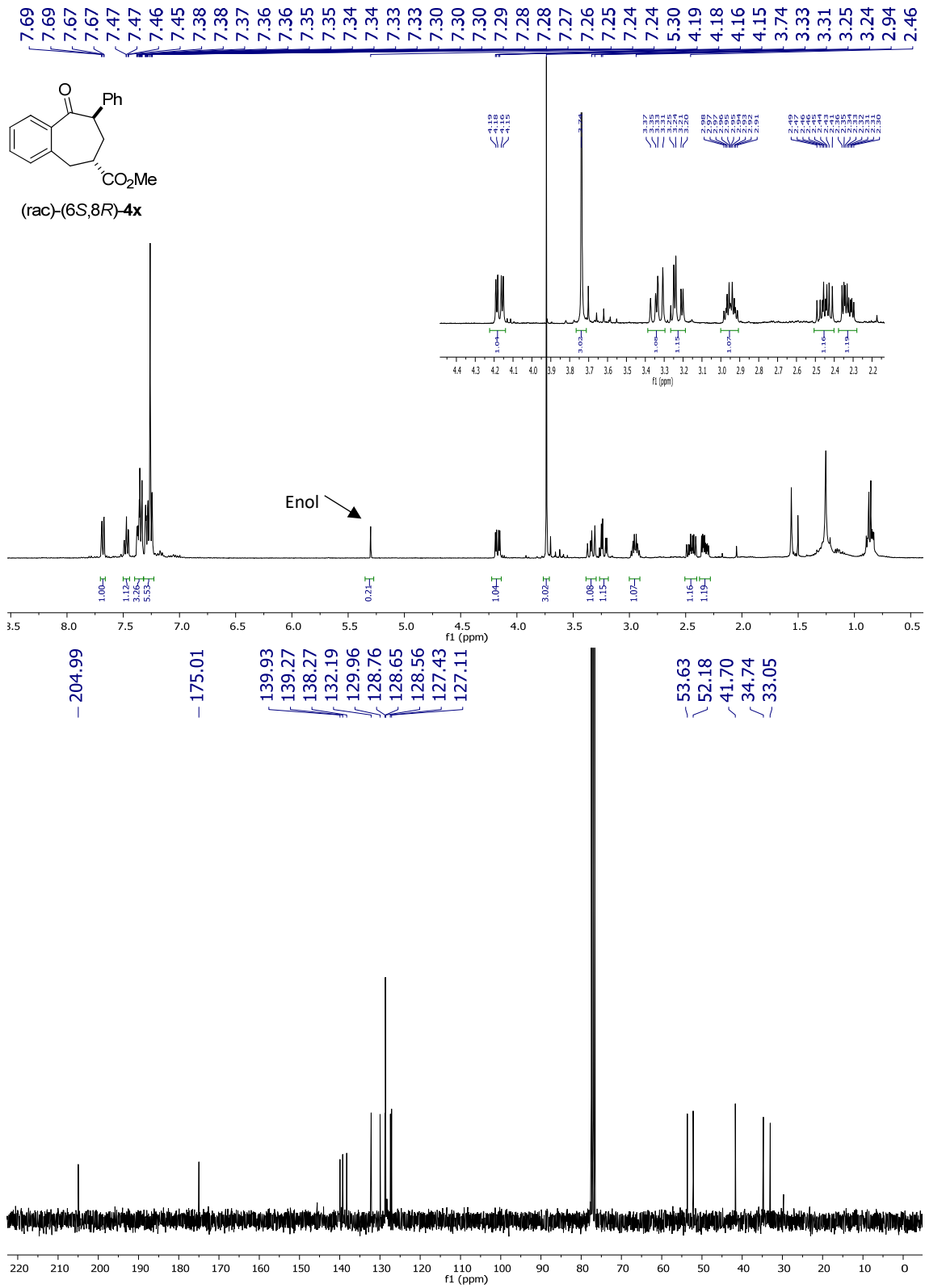


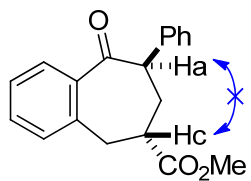
7.96
7.93
7.29
7.28
7.27
7.26
6.86
6.84
4.64
4.62
4.60
3.81
3.64
2.47
2.45
2.44
2.43
2.42
2.42
2.42
2.40
2.32
2.32
2.30
2.30
2.30
2.28
2.28
2.20
2.18
2.18
2.16
2.16
2.15
2.14
2.13
2.11



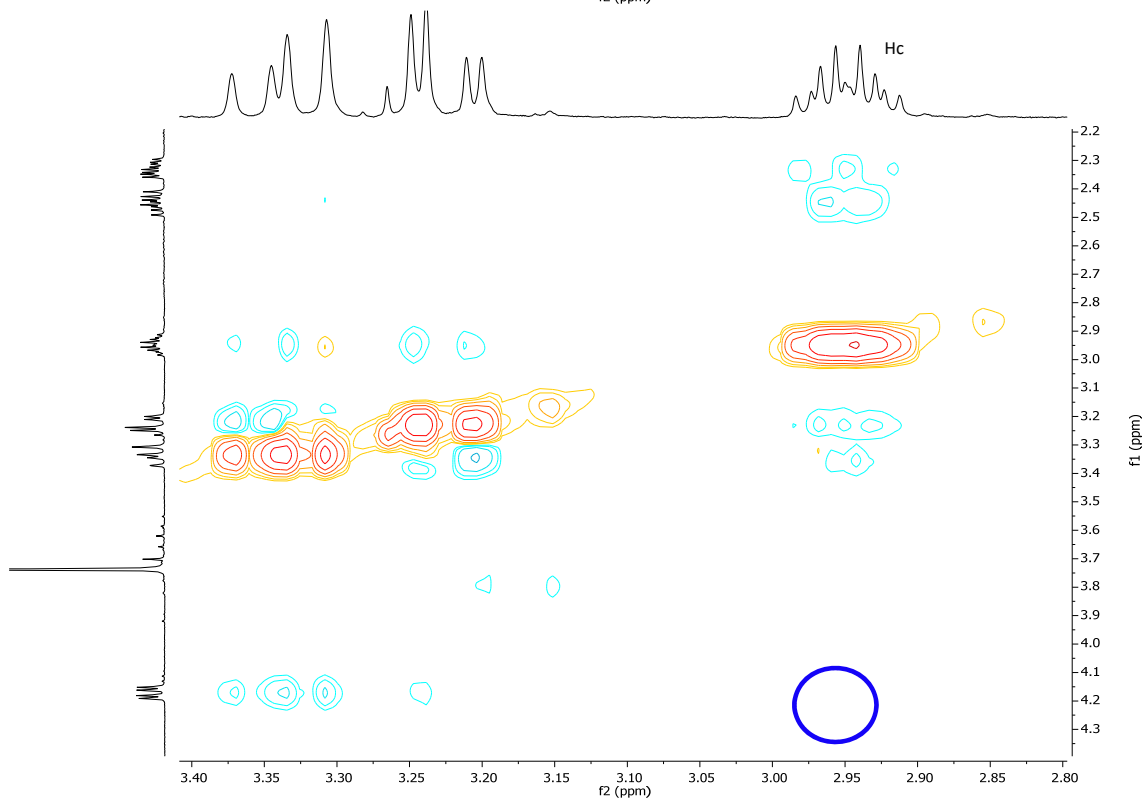
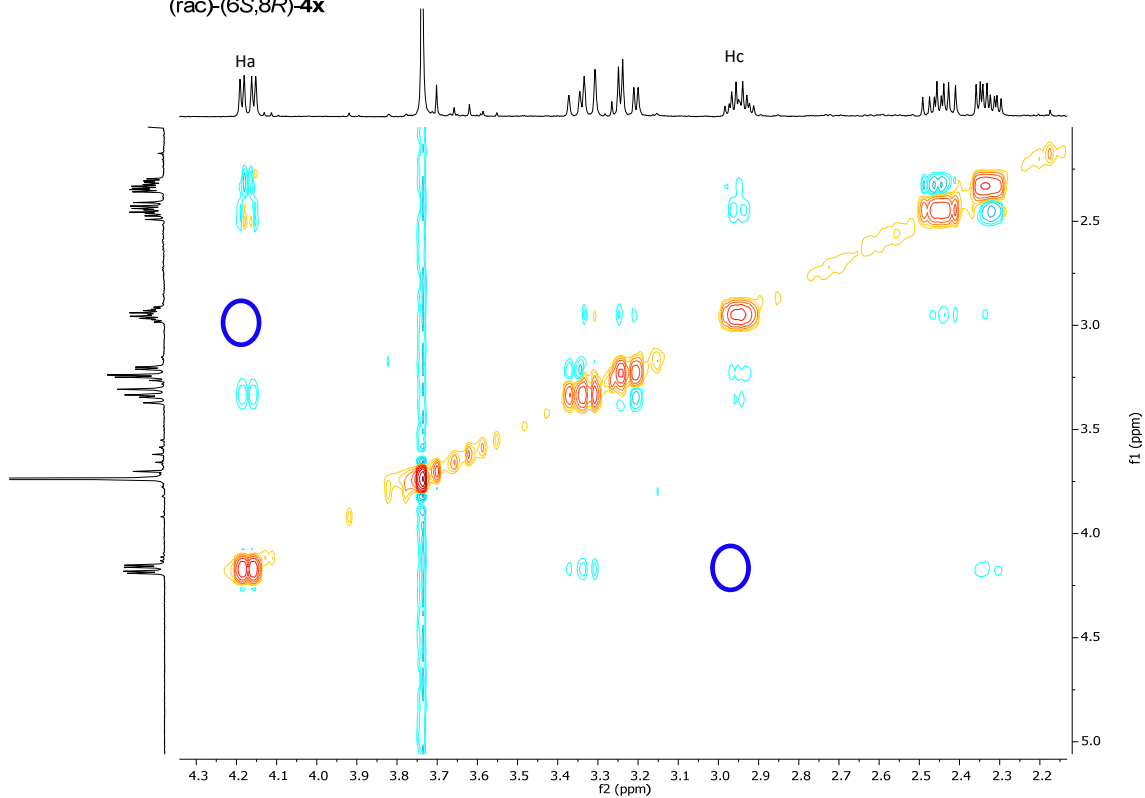


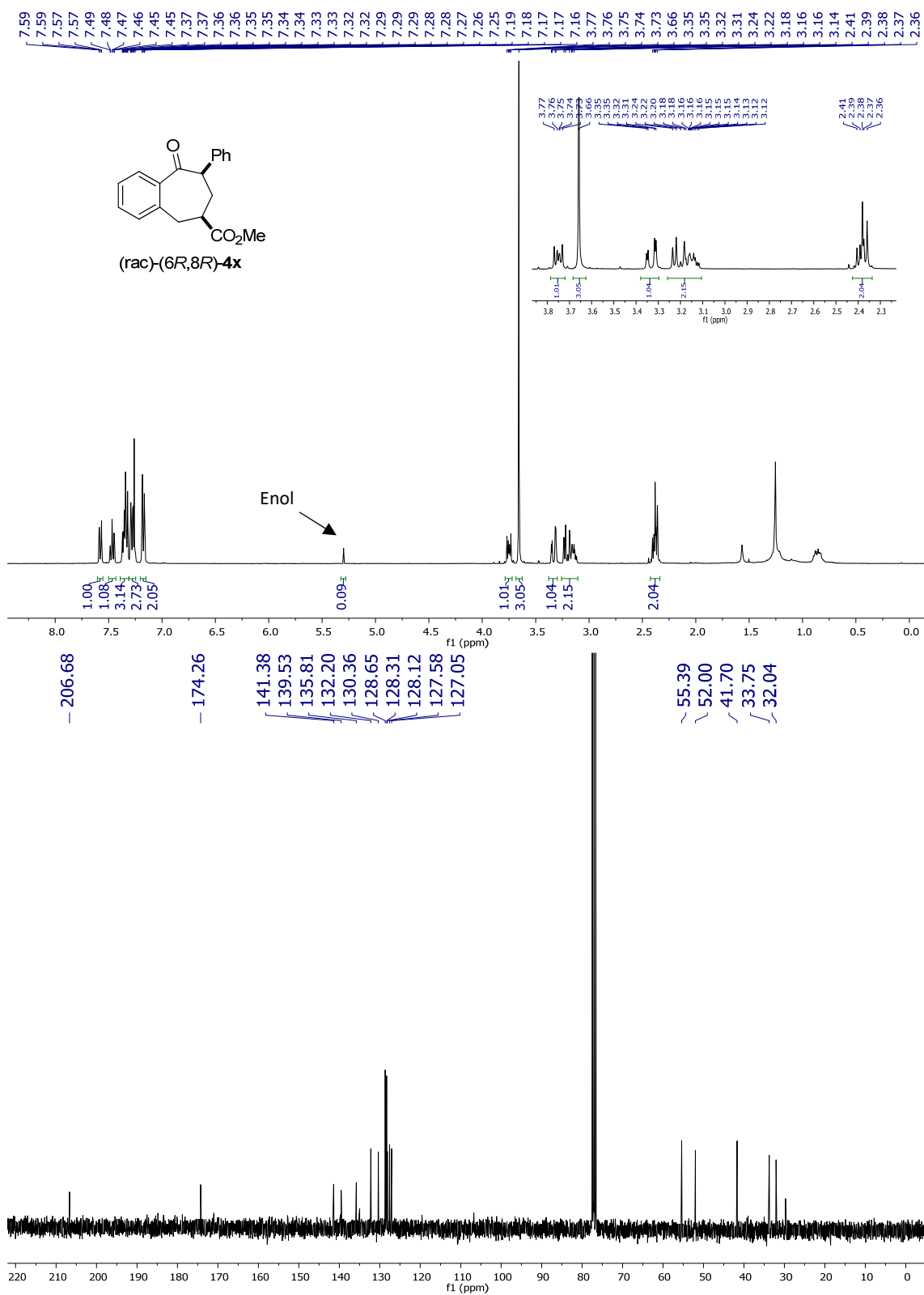


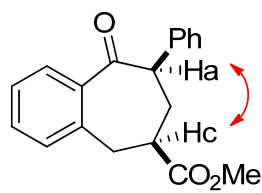




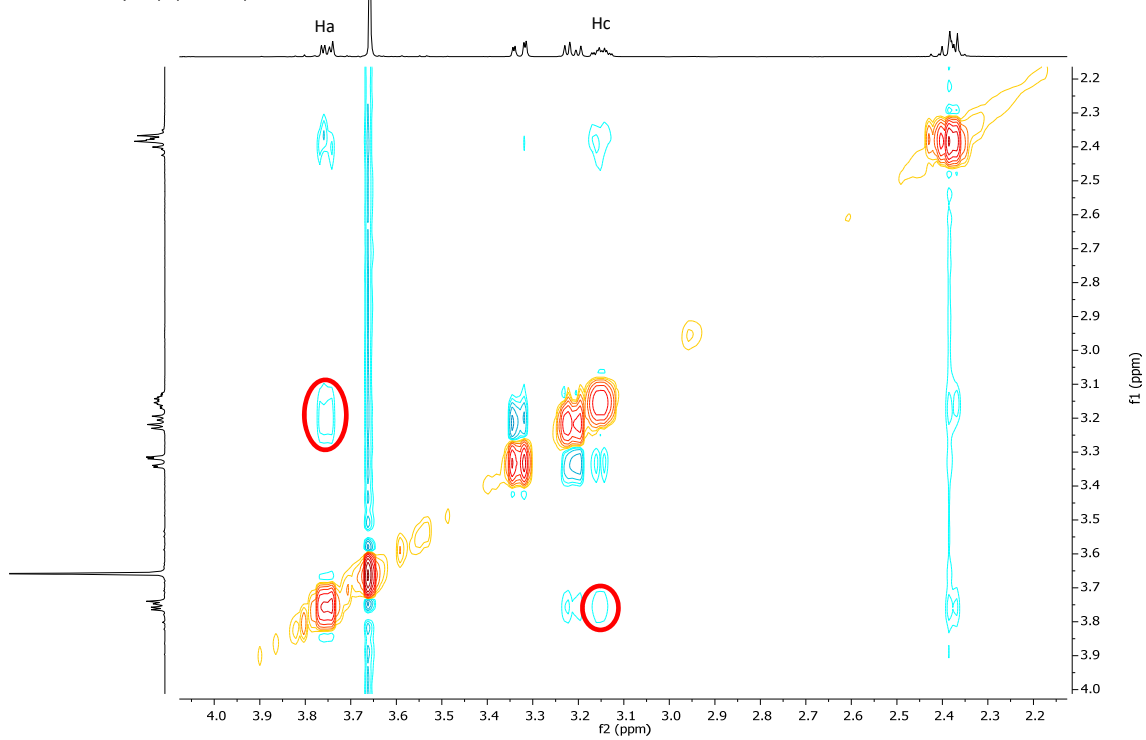
(rac)-(6S,8R)-4x

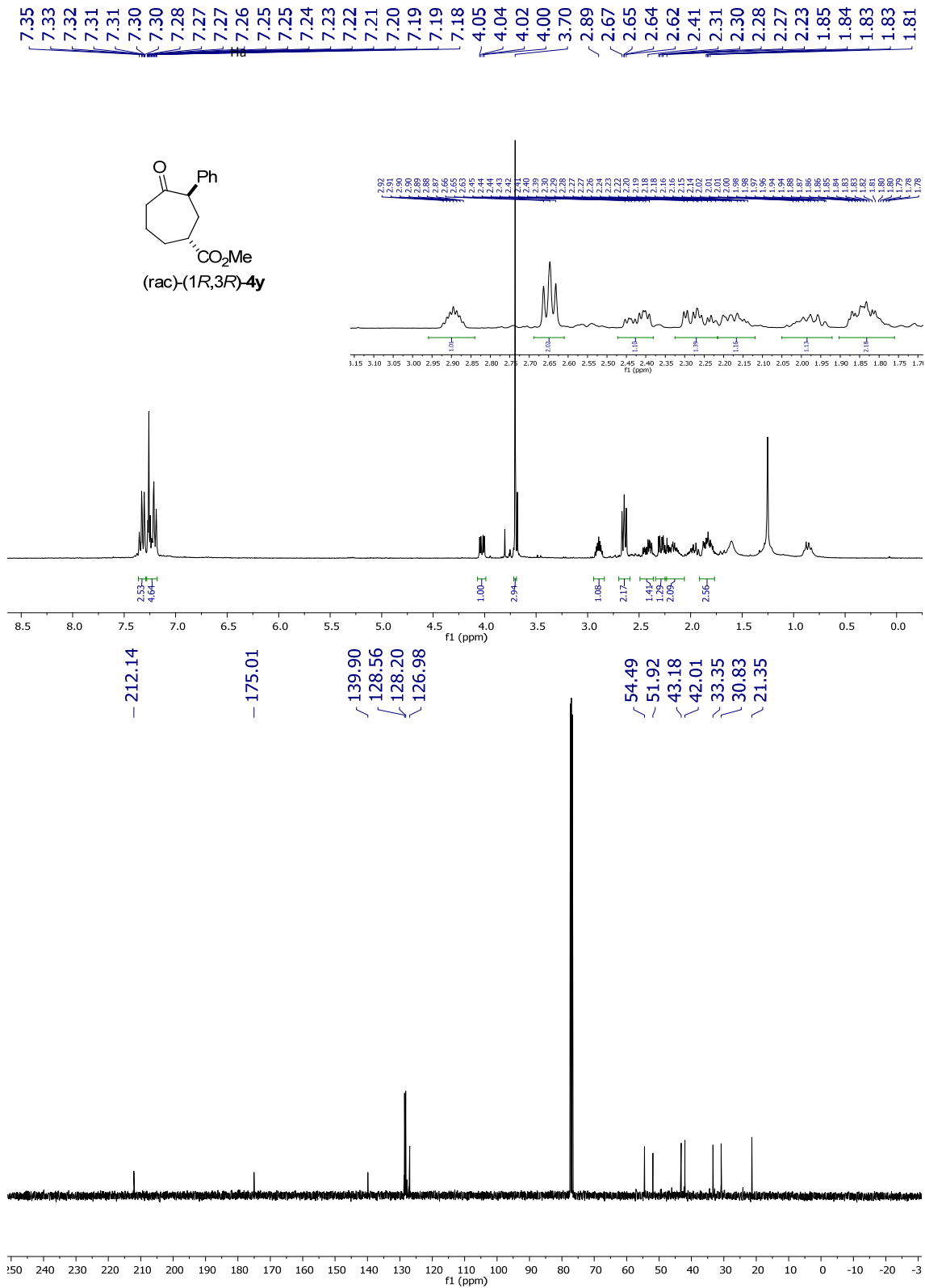


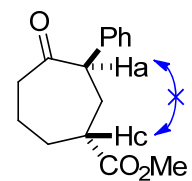




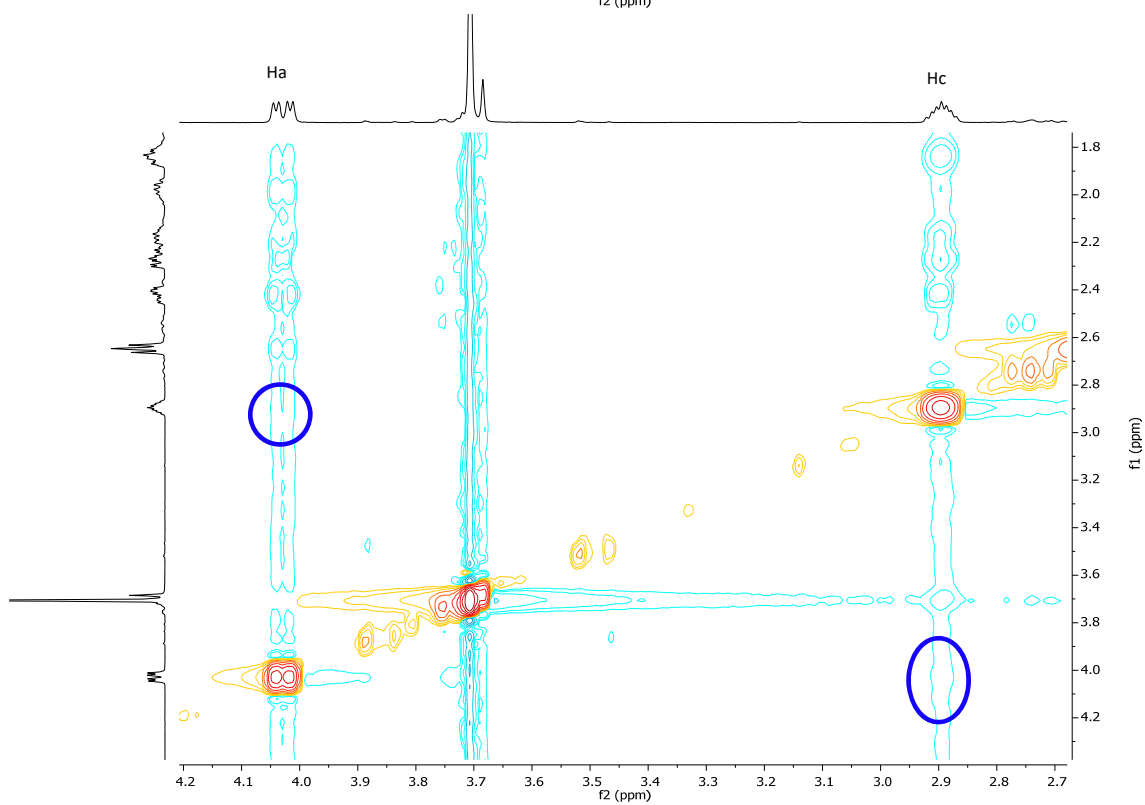
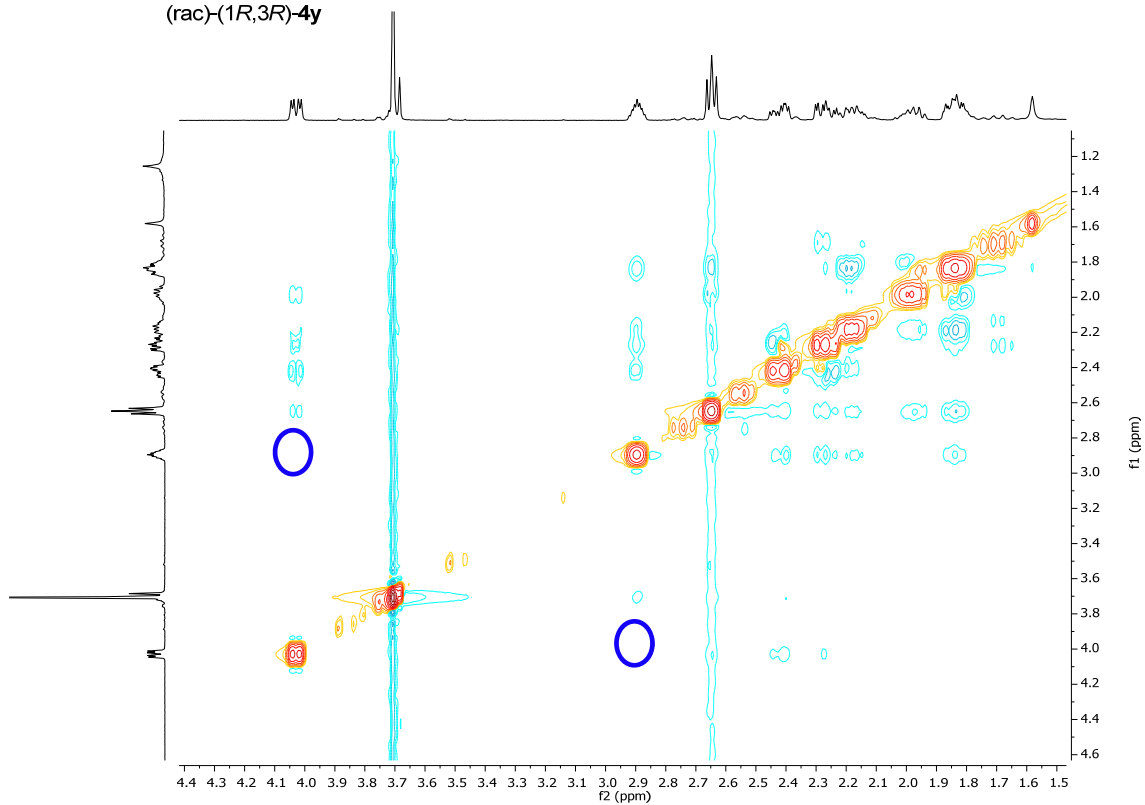
(rac)-(6R,8R)-4x







(rac)-(1*R*,3*R*)-4y



9. References:

1. (a) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* 1997, **62**, 7512; (b) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H.E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, **29**, 2176.
2. U. Megerle, R. Lechner, B. König, E. Riedle, *Photochem. Photobiol. Sci.*, 2010, **9**, 1400.
3. K. Teegardin, J. I. Day, J. Chan, J. Weaver, *Org. Process Res. Dev.* 2016, **20**, 1156.
4. J. Luo, J. Zhang, *ACS Catal.* 2016, **6**, 873.
5. L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, M. Visconti, *Chem. Eur. J.* 2012, **16**, 12328.
6. A. Hu, W. Lin, *Org. Lett.* 2005, **7**, 455.
7. P. Yang, H. Xu, J. Zhou, *Angew. Chem. Int. Ed.* 2014, **53**, 12210.
8. R. Balamurugan, S. Manojveer, *Chem. Commun.*, 2011, **47**, 11143.
9. H. Li, Z. He, X. Guo, W. Li, X. Zhao, Z. Li, *Org. Lett.*, 2009, **11**, 4176.
10. I. Geibel, J. Christoffers, *Eur. J. Org. Chem.* 2016, 918.
11. Y. Li, B. Liu, X.-H. Ouyang, R.-J. Song, J.-H. Li, *Org. Chem. Front.*, 2015, **2**, 1457.
12. M. Brown, R. Kumar, J. Rehbein, T. Wirth, *Chem. Eur. J.* 2016, **22**, 4030.
13. Y. Yu, U. K. Tambar, *Chem. Sci.*, 2015, **6**, 2777.