Supplementary Information

Palladium mediated one-pot synthesis of 3-aryl-cyclohexenones and 1,5-diketones from allyl alcohols and aryl ketones

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Reaction set up for hydrogen evolution

In one of the two-neck RB (**RB 1**), $Pd(OAc)_2$ (0.3 mmol), and BINOL phosphoric acid (0.3 mmol) were taken. In the other RB (**RB 2**) Palladium on charcoal (0.1 mmol) was taken. The whole system was subjected to vacuum and then nitrogen was purged into it (repeated 3 times). Then 1-penten-3-ol (3 mmol) and DCE (2 mL) were added to the **RB 1** and phenylacetylene (1 mmol) and methanol (1 mL) were added to the **RB 2.** The system was closed and both the RBs were allowed to stir at room temperature. After 48 h, the reaction mixture from **RB 2** was filtered through celite and crude proton NMR was recorded. It was found that the phenylacetylene in the presence of hydrogen gas (evolved from **RB 1)** was reduced to styrene and ethyl benzene.

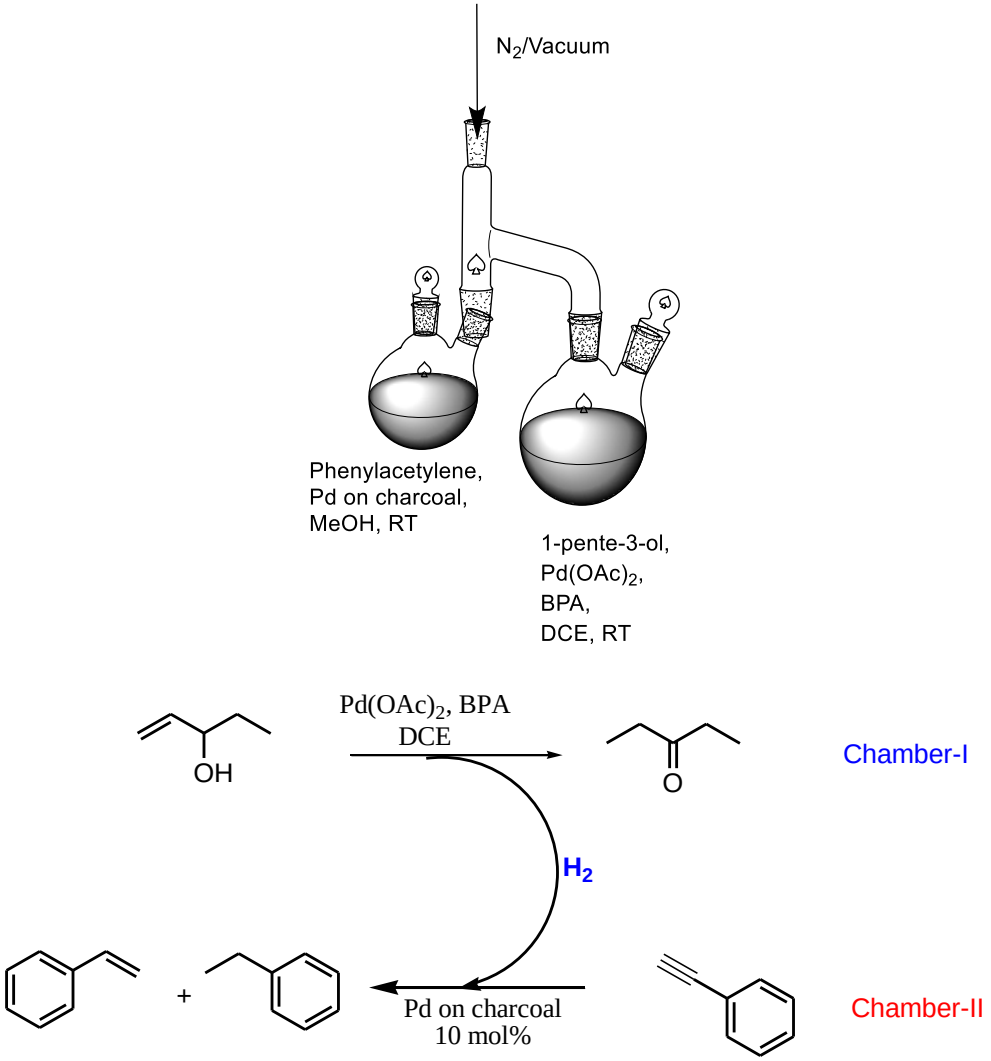


Table S1: Crystal data and structure refinement parameters for compound **22.**

Empirical formula	$C_{15}H_{16}O$
Formula weight	212.28
Temperature/K	114.5(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.9714(15)
b/Å	6.6608(7)
c/Å	19.405(3)
α/°	90
β/°	98.551(15)
γ/°	90
Volume/Å^3	1146.7(3)
Z	4
ρcalcg/cm^3	1.230
μ/mm^{-1}	0.580
F(000)	456.0
Radiation	CuKα (λ = 1.54184)
2 θ range for data collection/°	9.218 to 133.184
Index ranges	$-10 \leq h \leq 10$, $-7 \leq k \leq 6$, $-23 \leq l \leq 23$
Reflections collected	13865
Independent reflections	1899 [R_{int} = 0.1362, R_{sigma} = 0.0616]
Data/restraints/parameters	1899/0/146
Goodness-of-fit on F^2	1.280
Final R indexes [I>=2σ (I)]	R_1 = 0.1022, wR_2 = 0.2919
Final R indexes [all data]	R_1 = 0.1201, wR_2 = 0.3190
Largest diff. peak/hole / e Å^{-3}	0.44 and -0.34

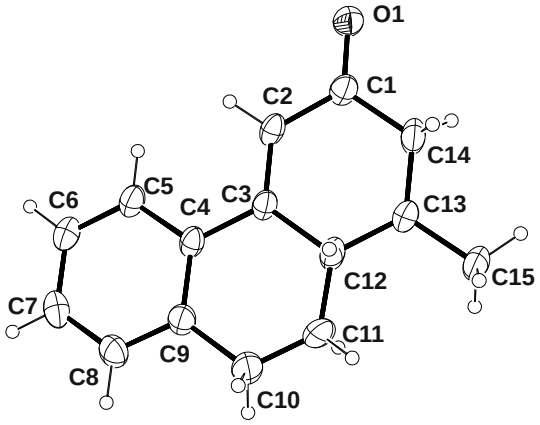


Figure S1: Molecular structure of compound **22**(thermal ellipsoids at the 30 % probability).

NMR spectra of all new compounds:

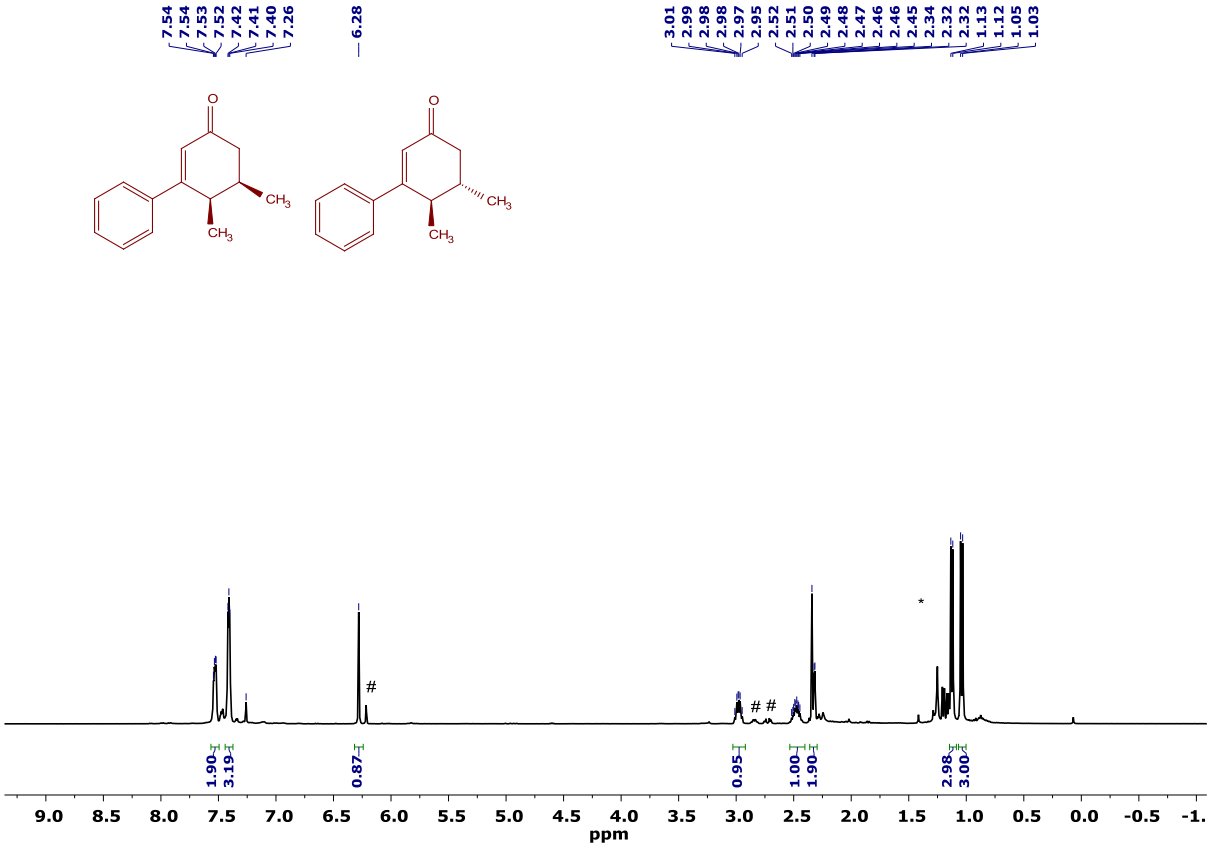


Figure S2: ^{1}H NMR spectrum of compound **2 (# belong to second isomer)**

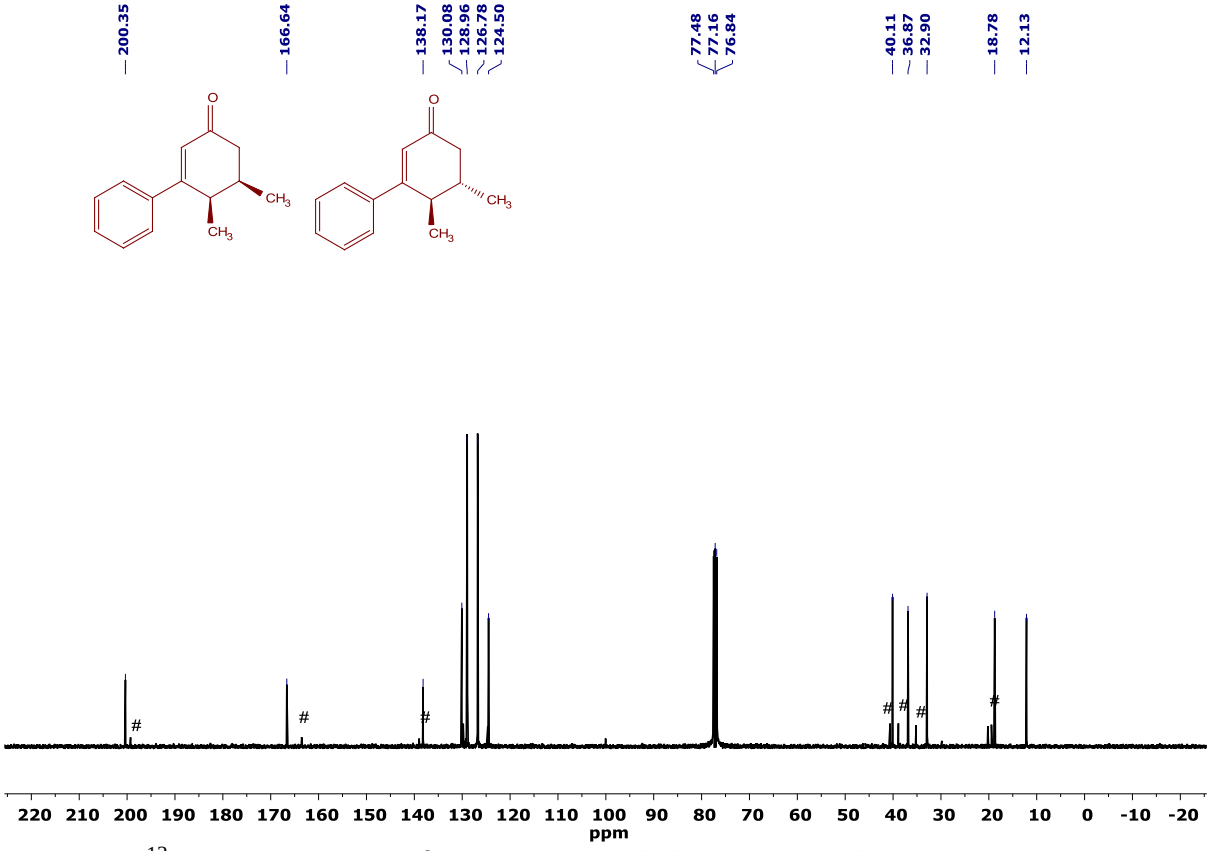


Figure S3: ^{13}C NMR spectrum of compound **2 (# belong to second isomer)**

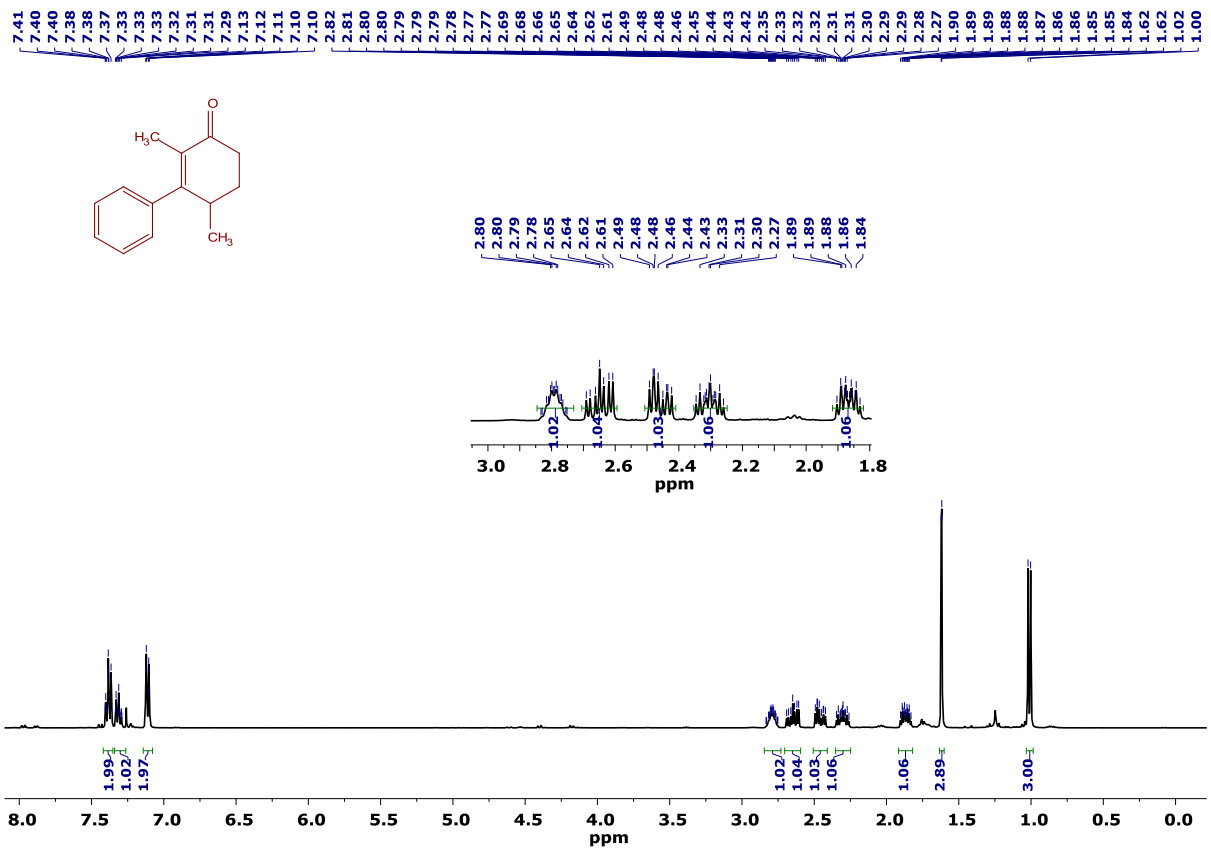


Figure S4: [1]H NMR spectrum of compound **3**

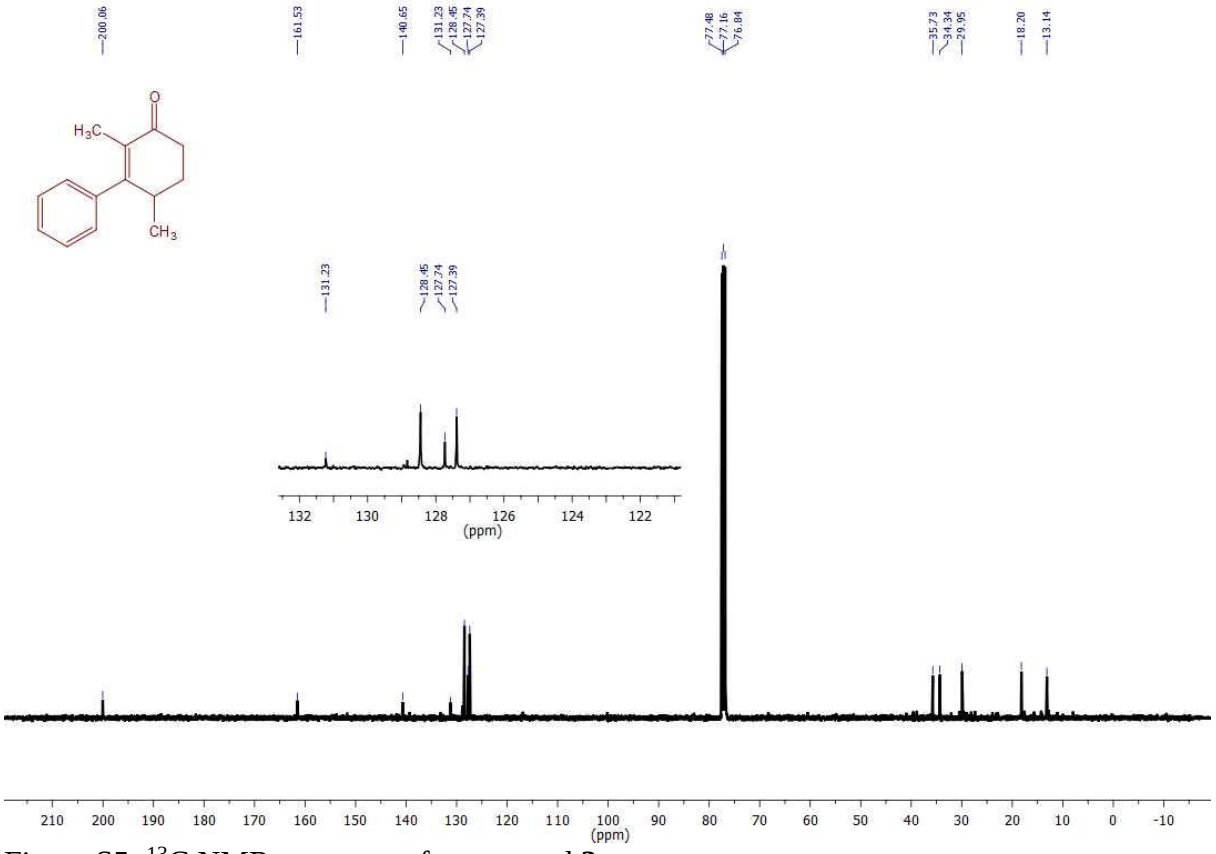


Figure S5: [13]C NMR spectrum of compound **3**

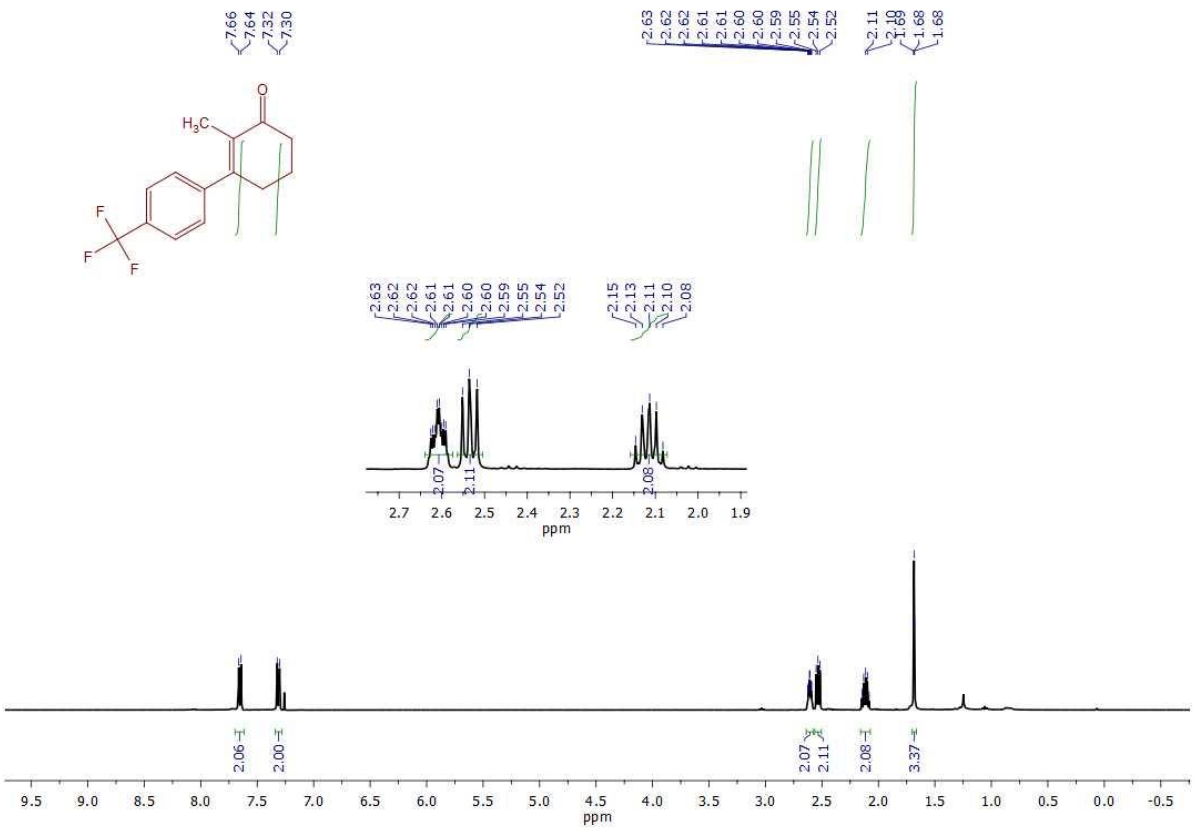


Figure S6: ^{1}H NMR spectrum of compound **12**

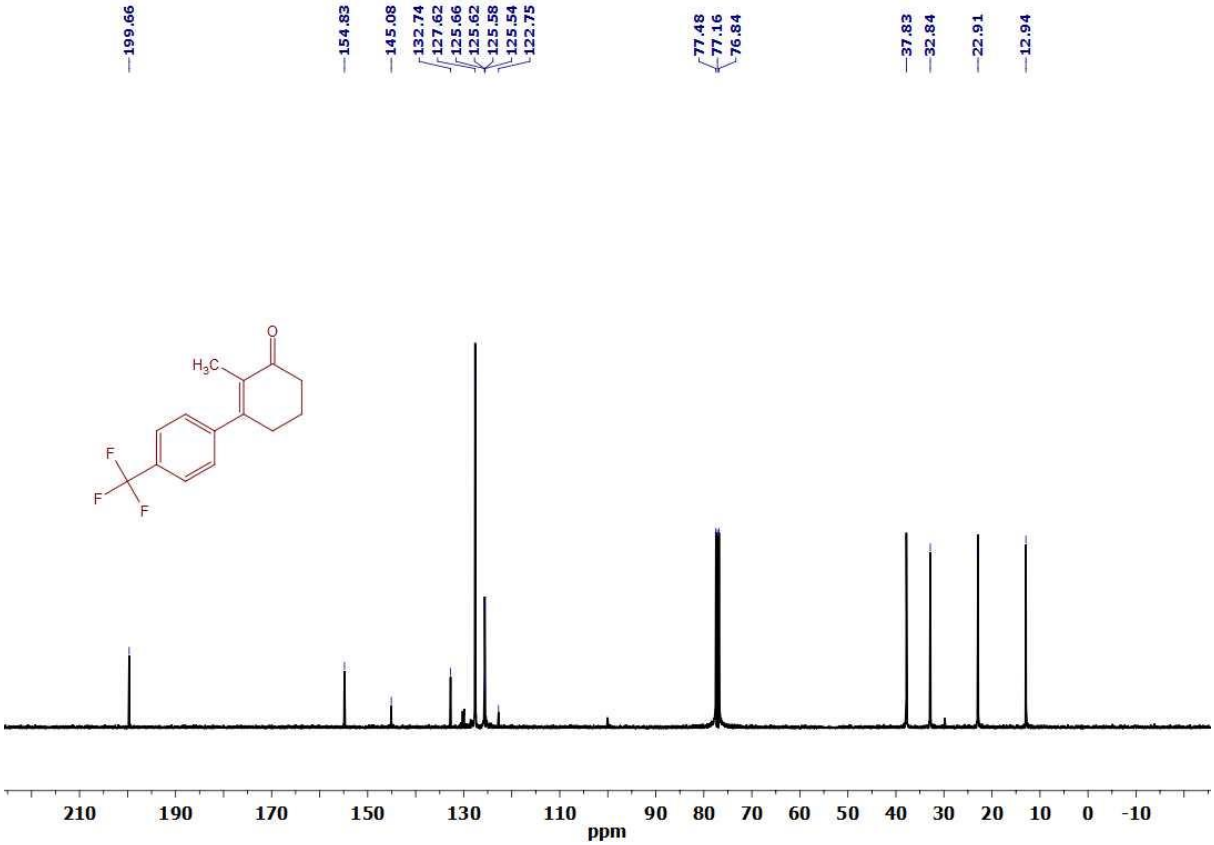


Figure S7:^{13}C NMR spectrum of compound **12**

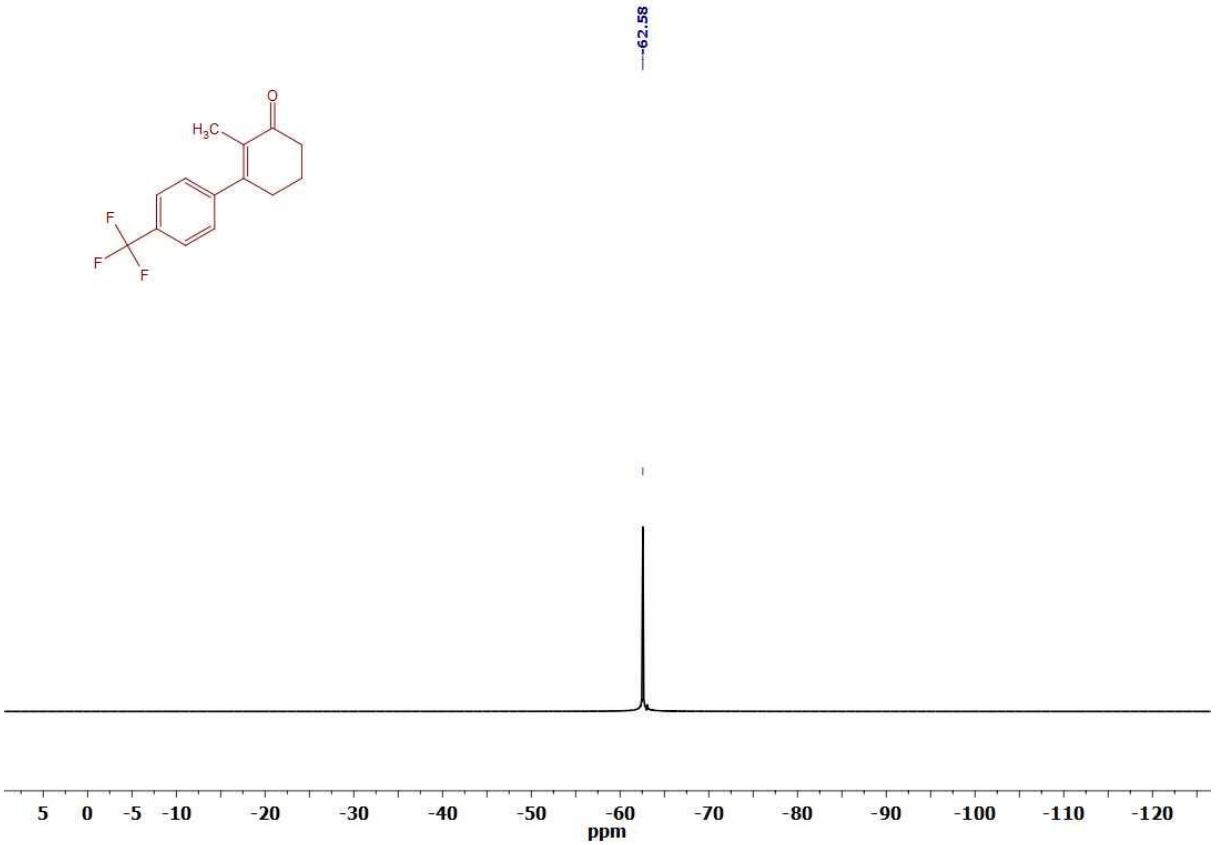


Figure S8: ^{19}F NMR spectrum of compound **12**

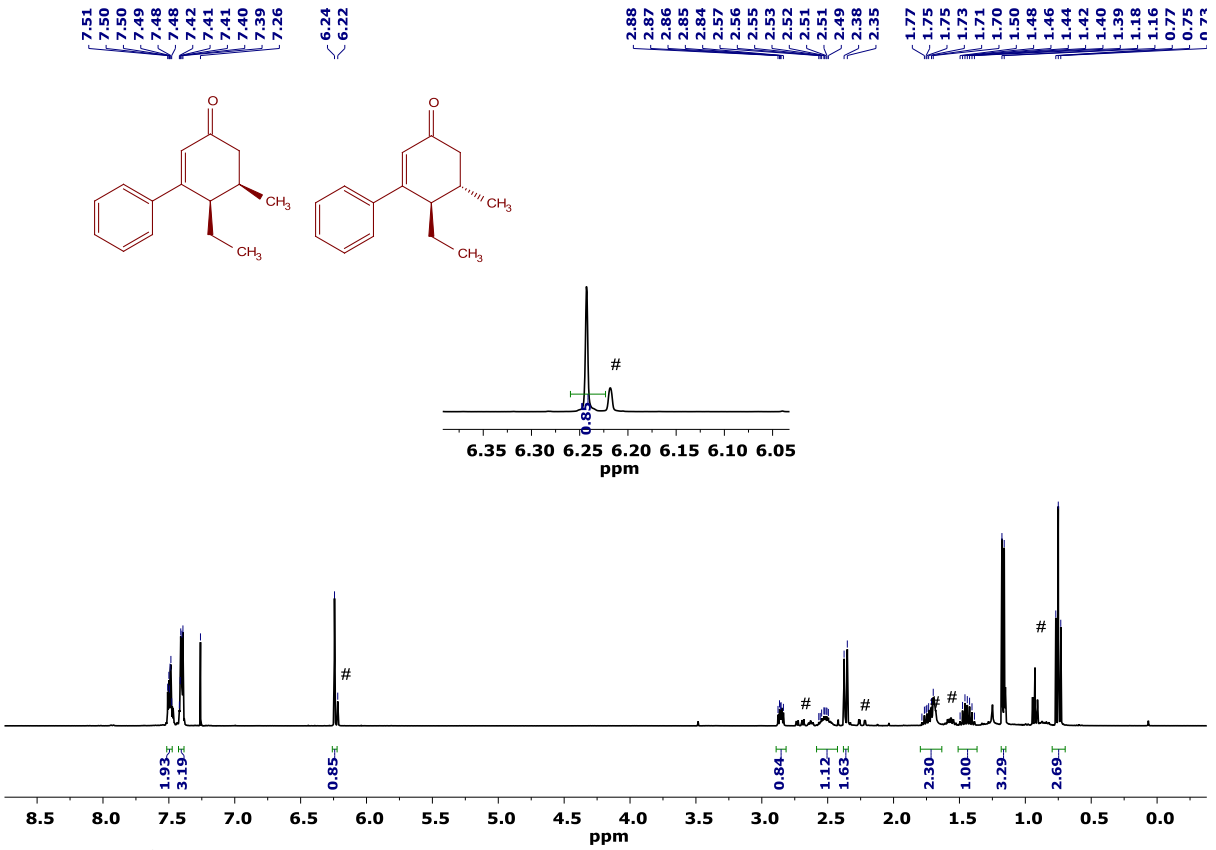


Figure S9: ^{1}H NMR spectrum of compound **17(# belongs to second isomer)**

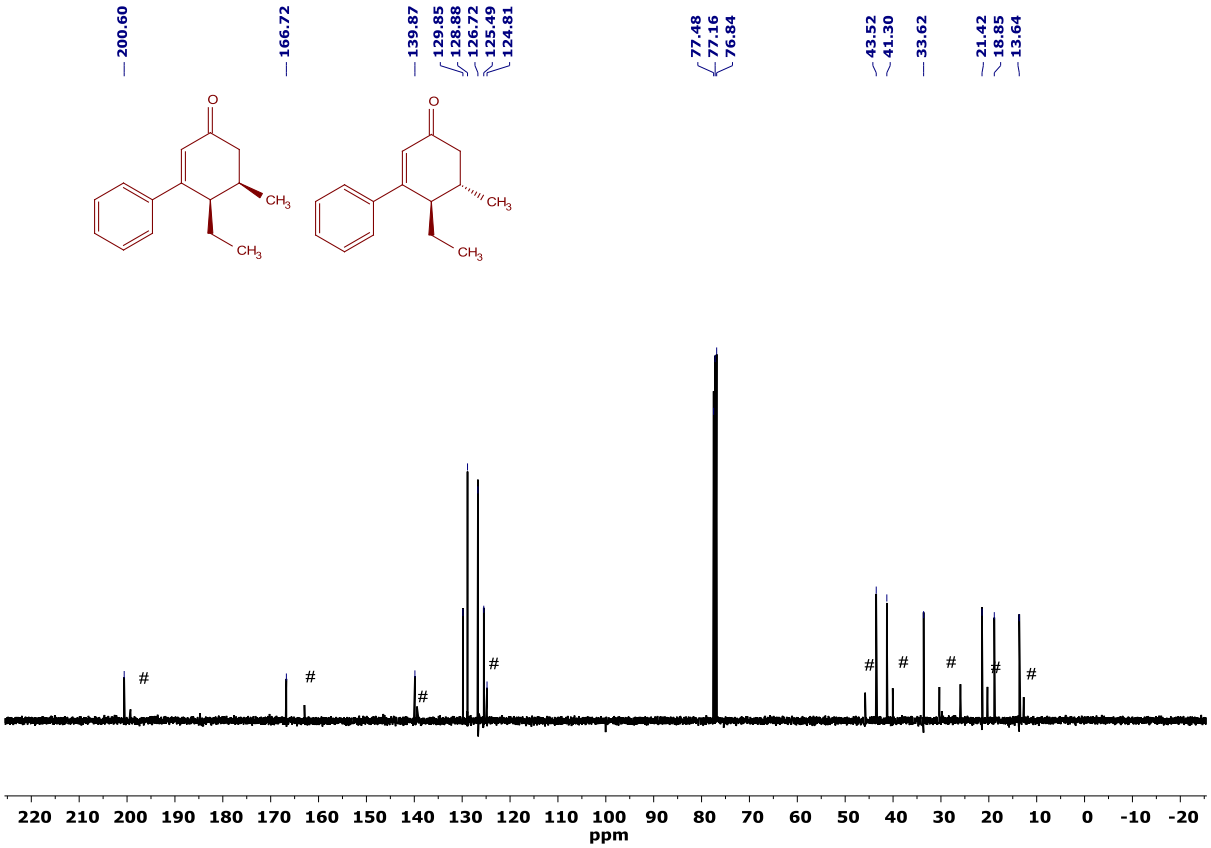


Figure S10: ^{13}C NMR spectrum of compound **17 (# belongs to second isomer)**

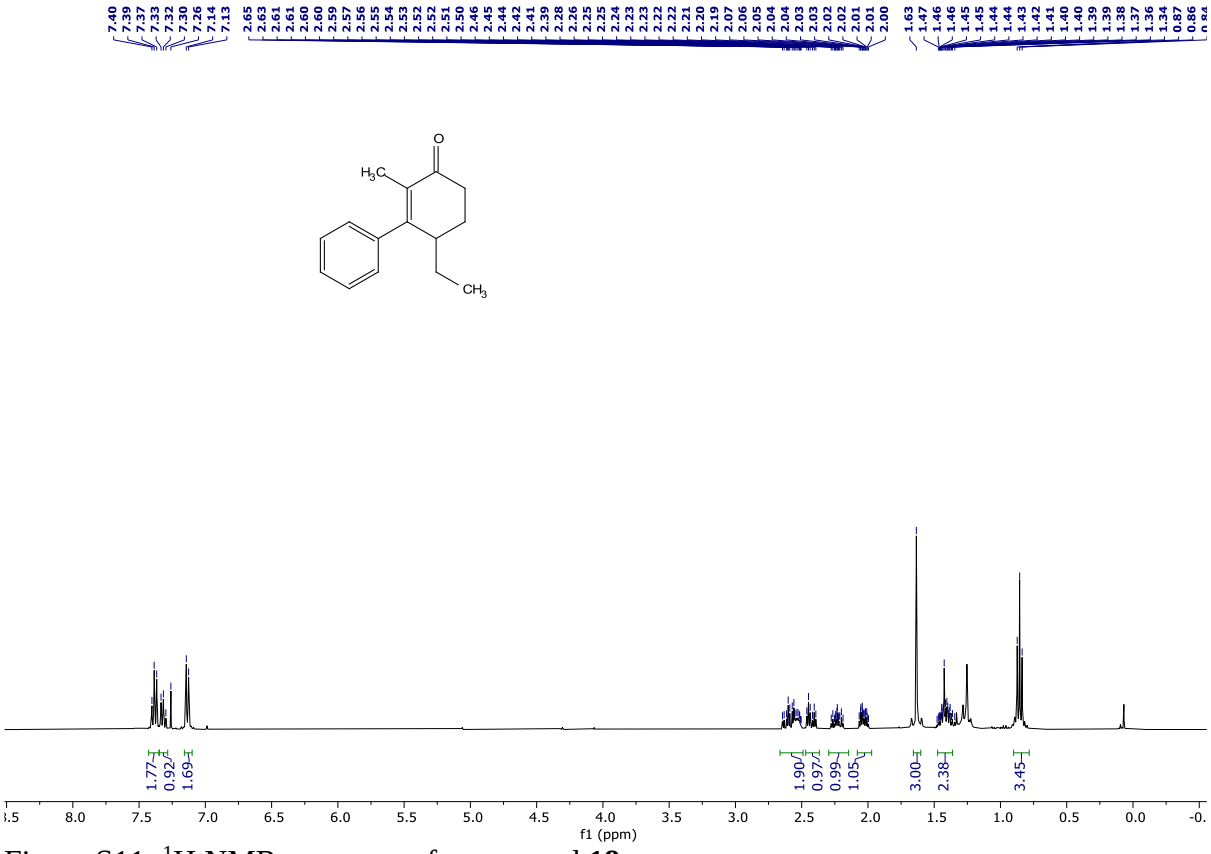


Figure S11: ^{1}H NMR spectrum of compound **18**

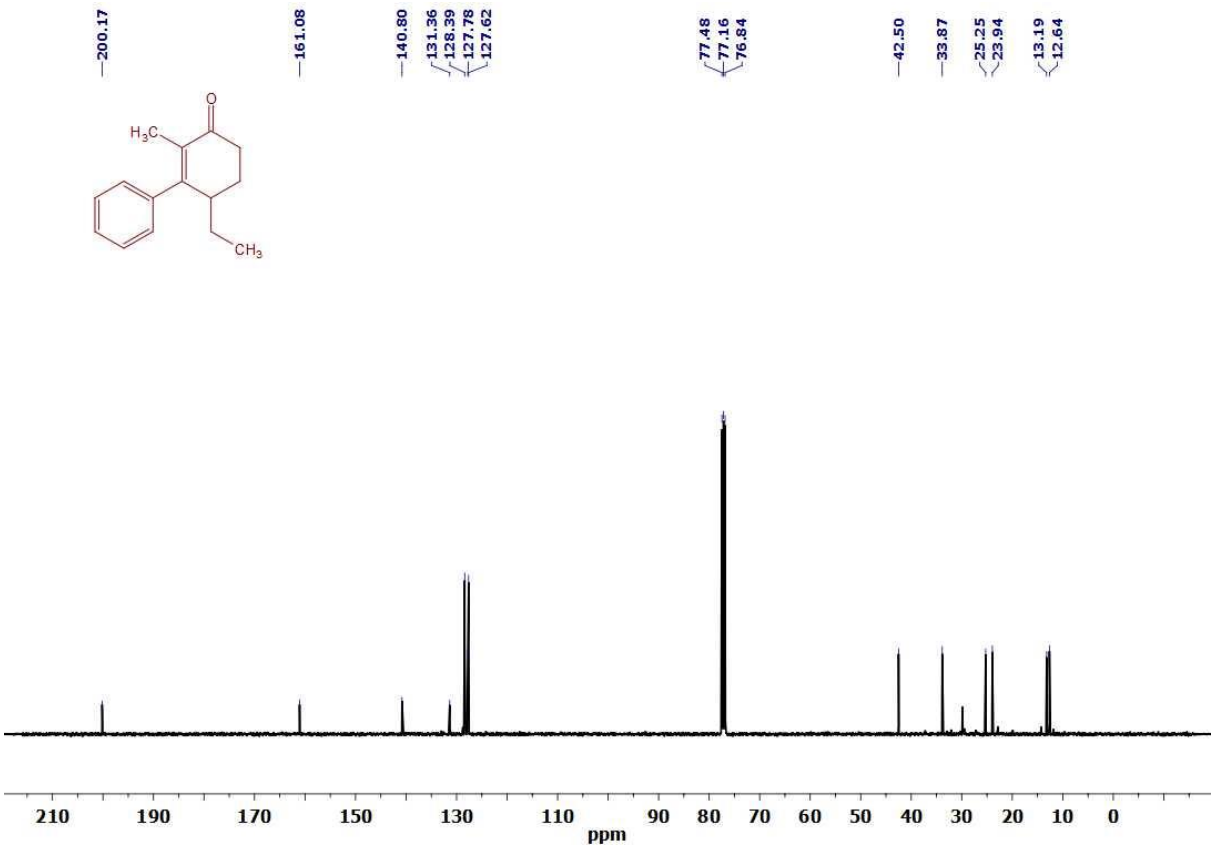


Figure S12: ^{13}C NMR spectrum of compound **18**

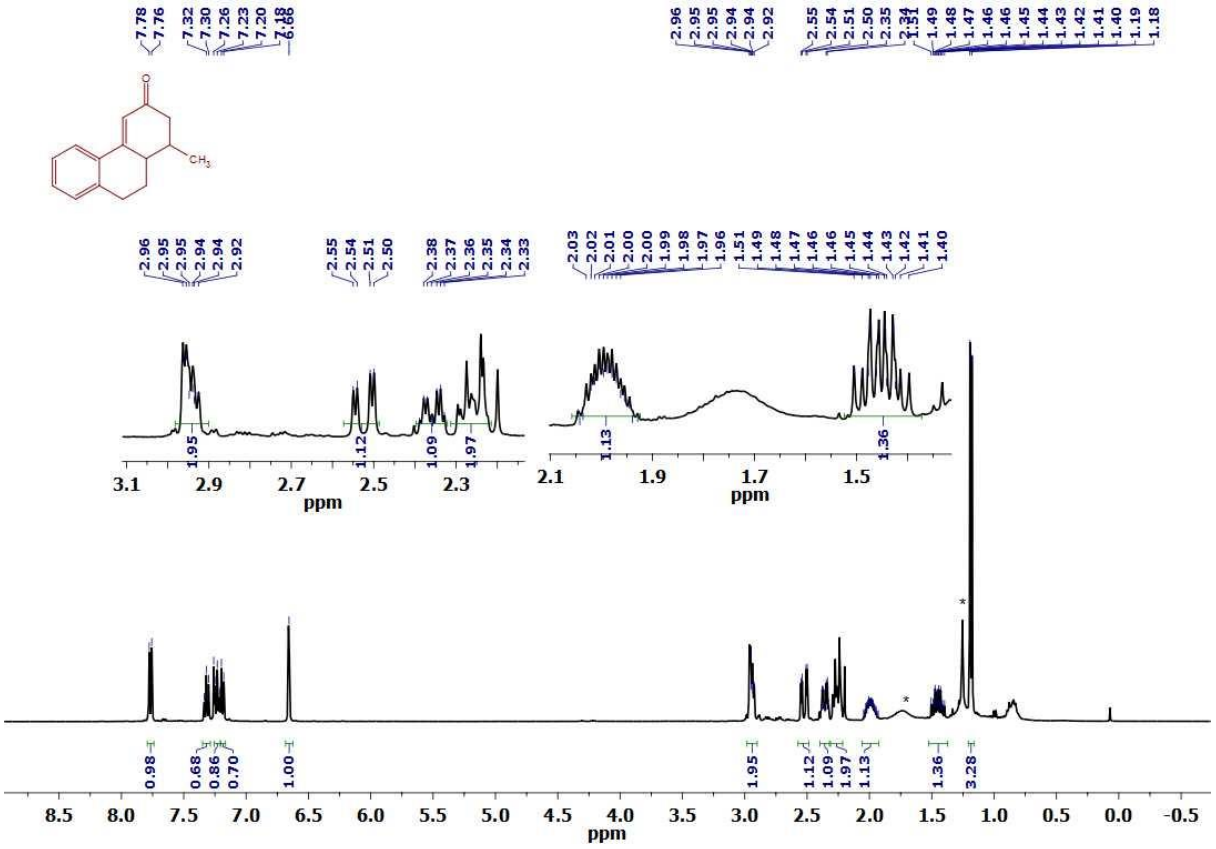


Figure S13: ^{1}H NMR spectrum of compound **22 (* solvent residues)**

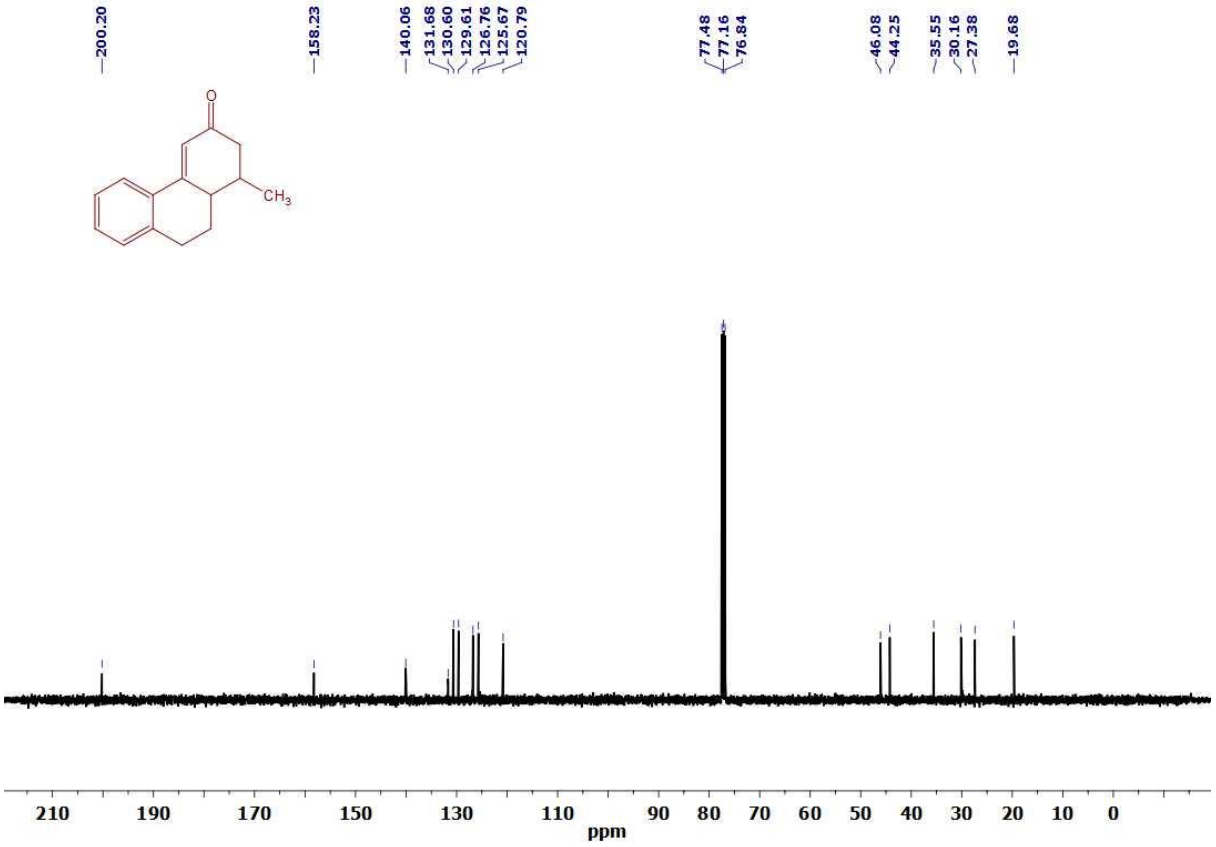


Figure S14:[13]C NMR spectrum of compound **22**

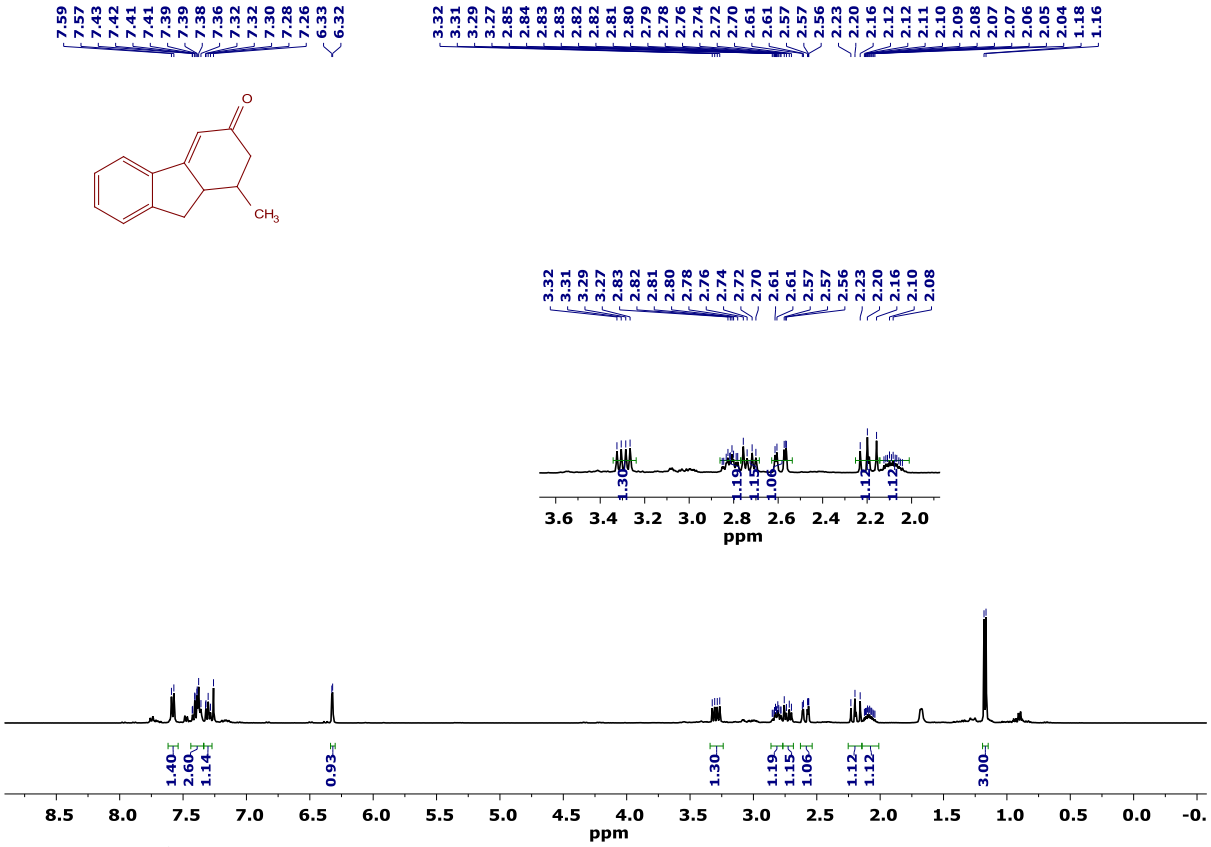


Figure S15: [1]H NMR spectrum of compound **23**

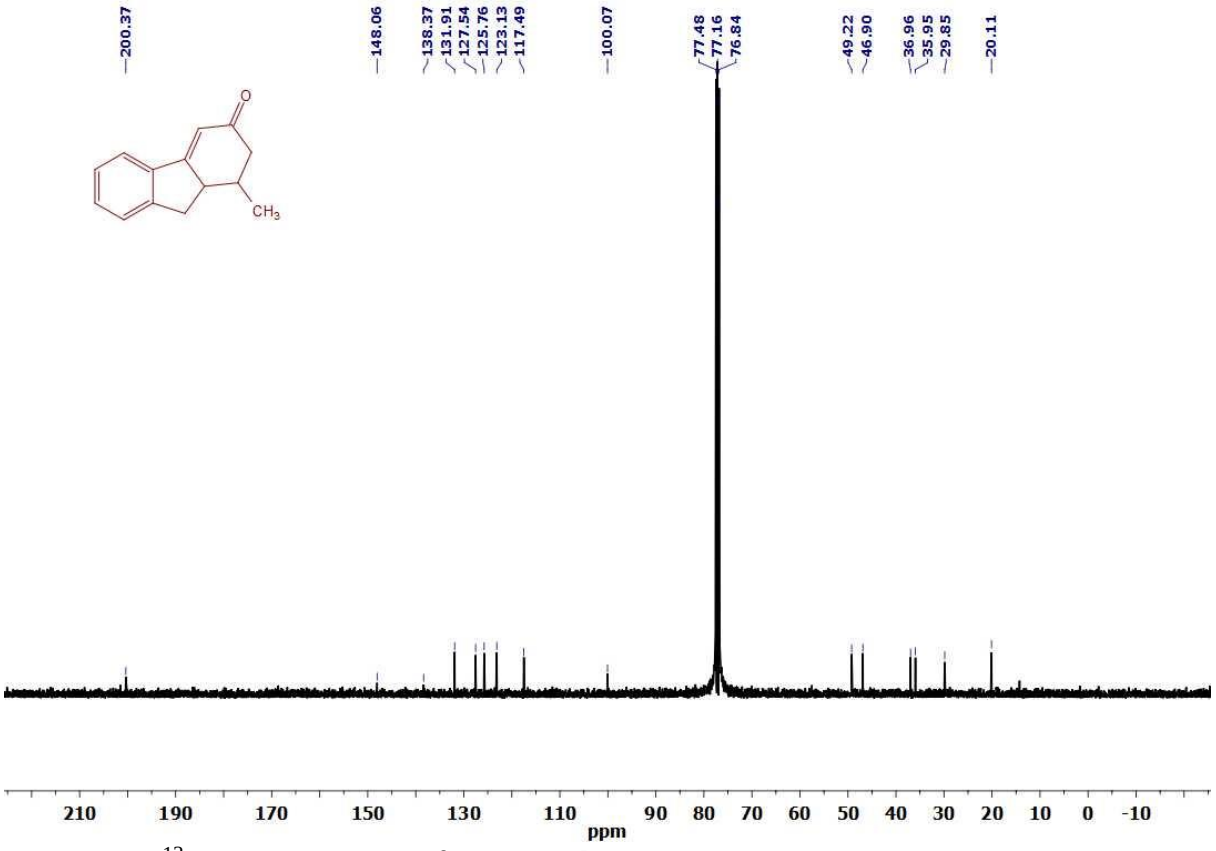


Figure S16: ^{13}C NMR spectrum of compound **23**

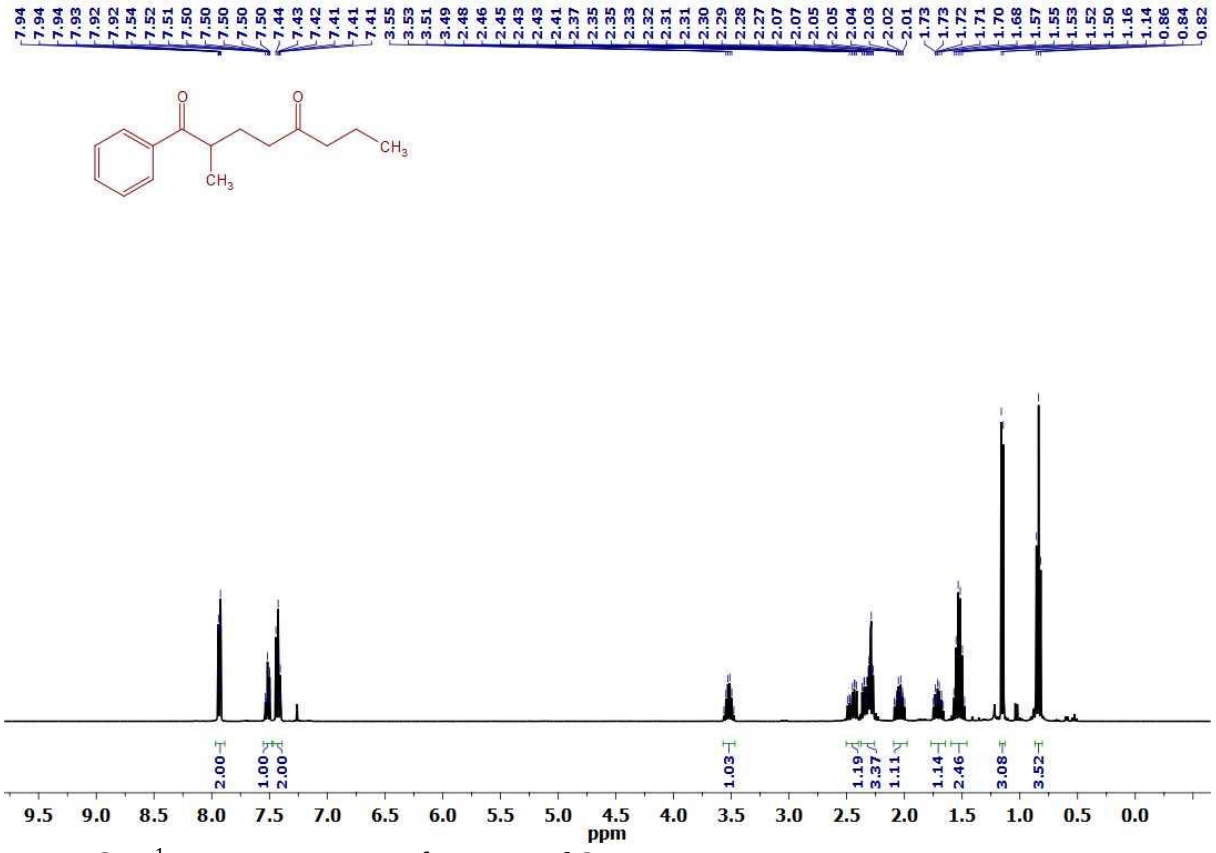


Figure S17:^{1}H NMR spectrum of compound **24**

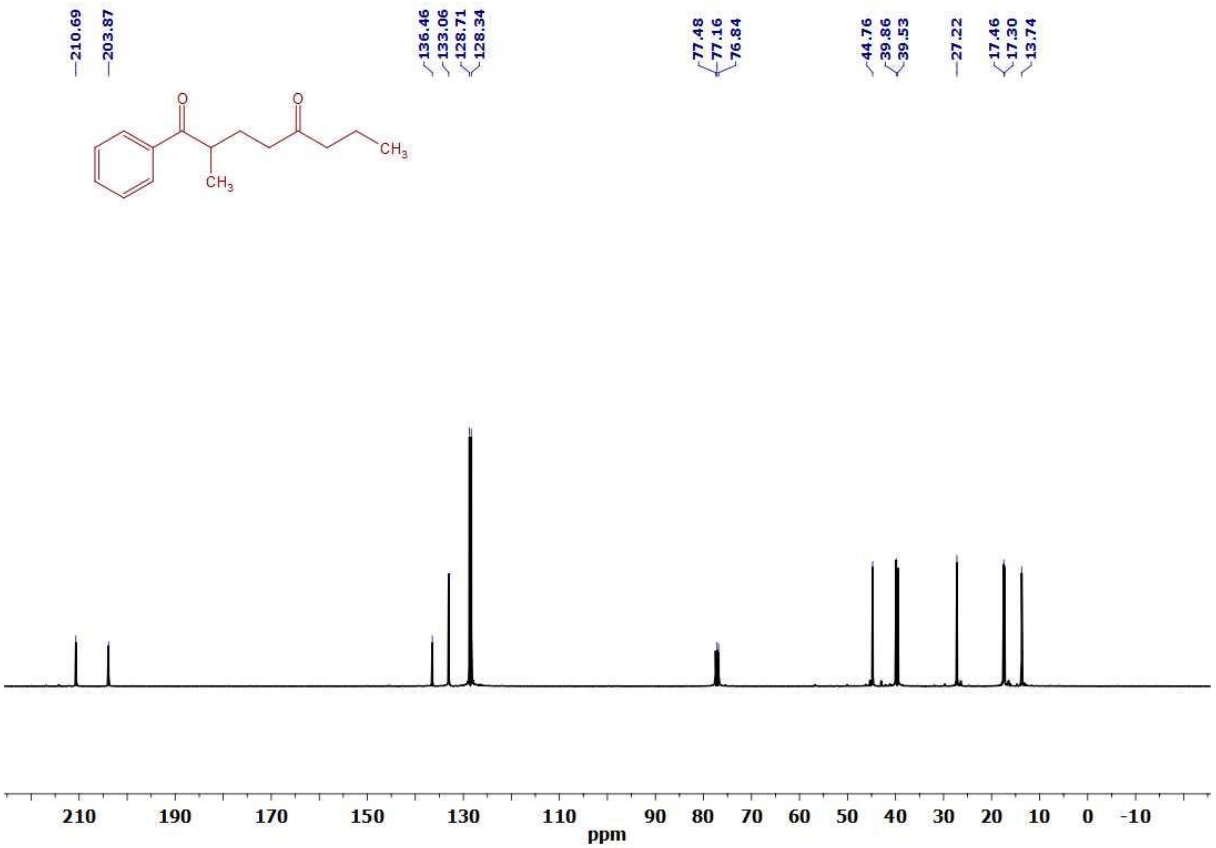


Figure S18: ^{13}C NMR spectrum of compound **24**

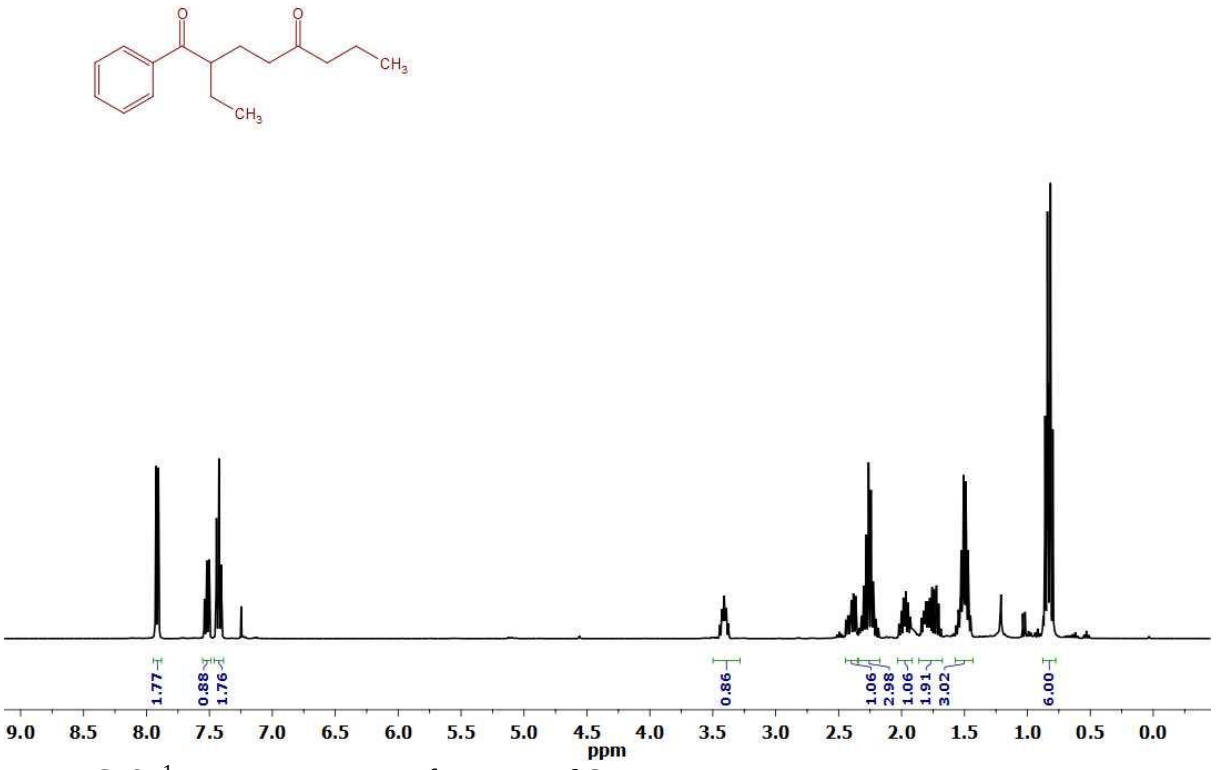


Figure S19: ^{1}H NMR spectrum of compound **25**

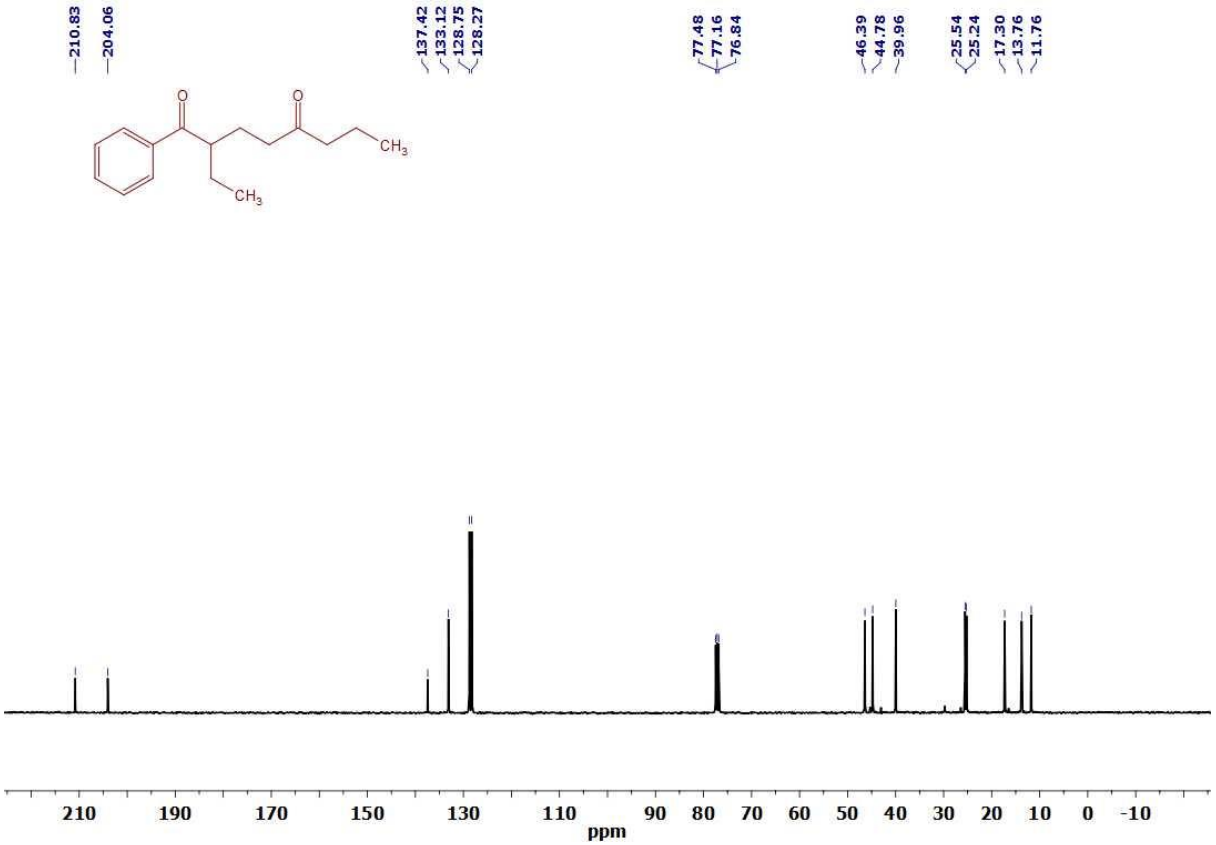


Figure S20: ^{13}C NMR spectrum of compound **25**

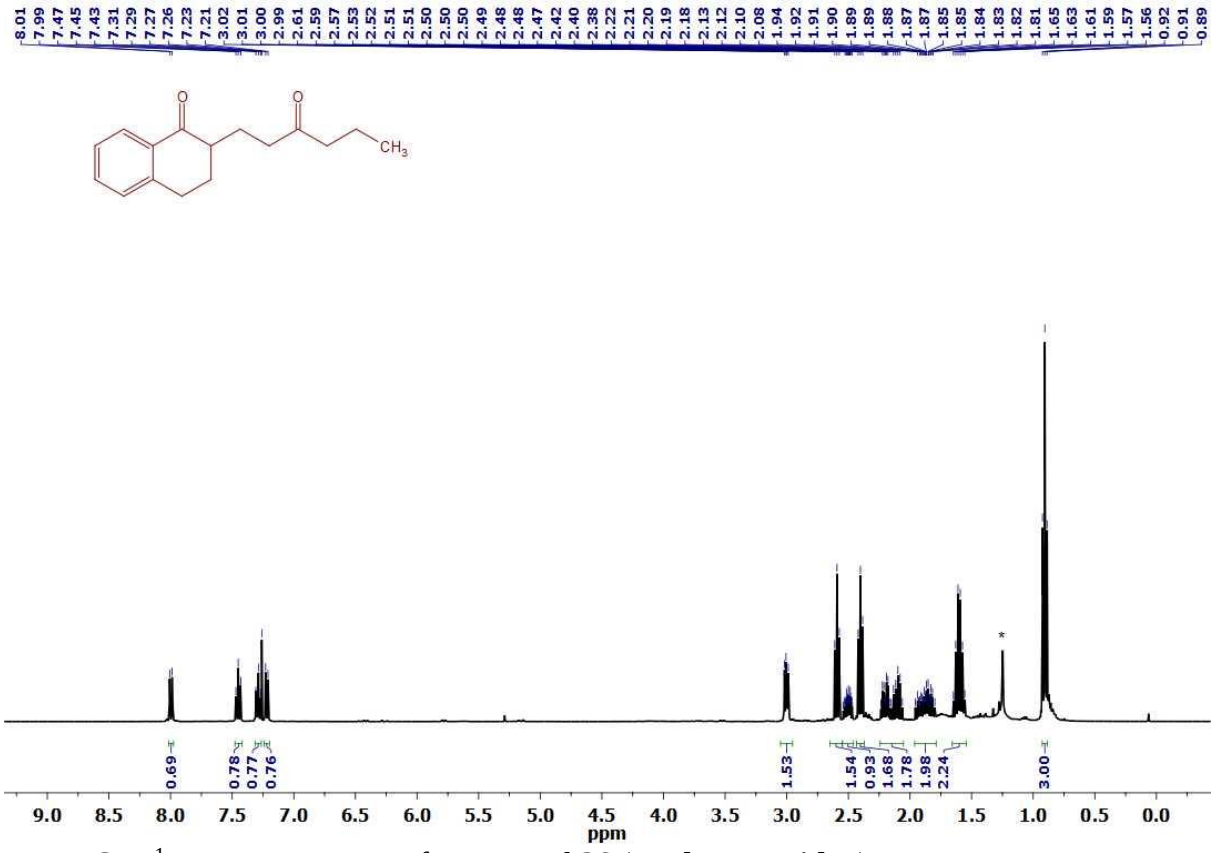


Figure S21:^{1}H NMR spectrum of compound **26 (* solvent residue)**

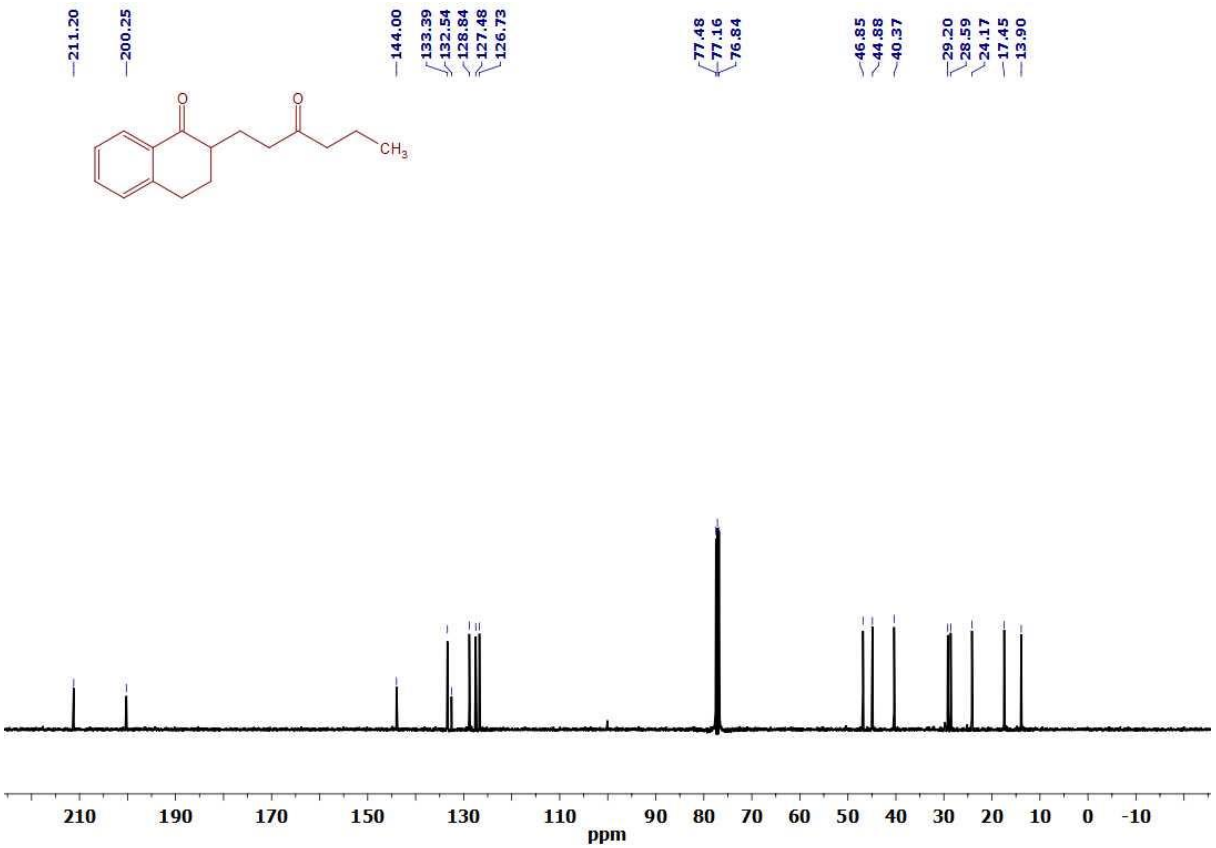


Figure S22: ^{13}C NMR spectrum of compound **26**

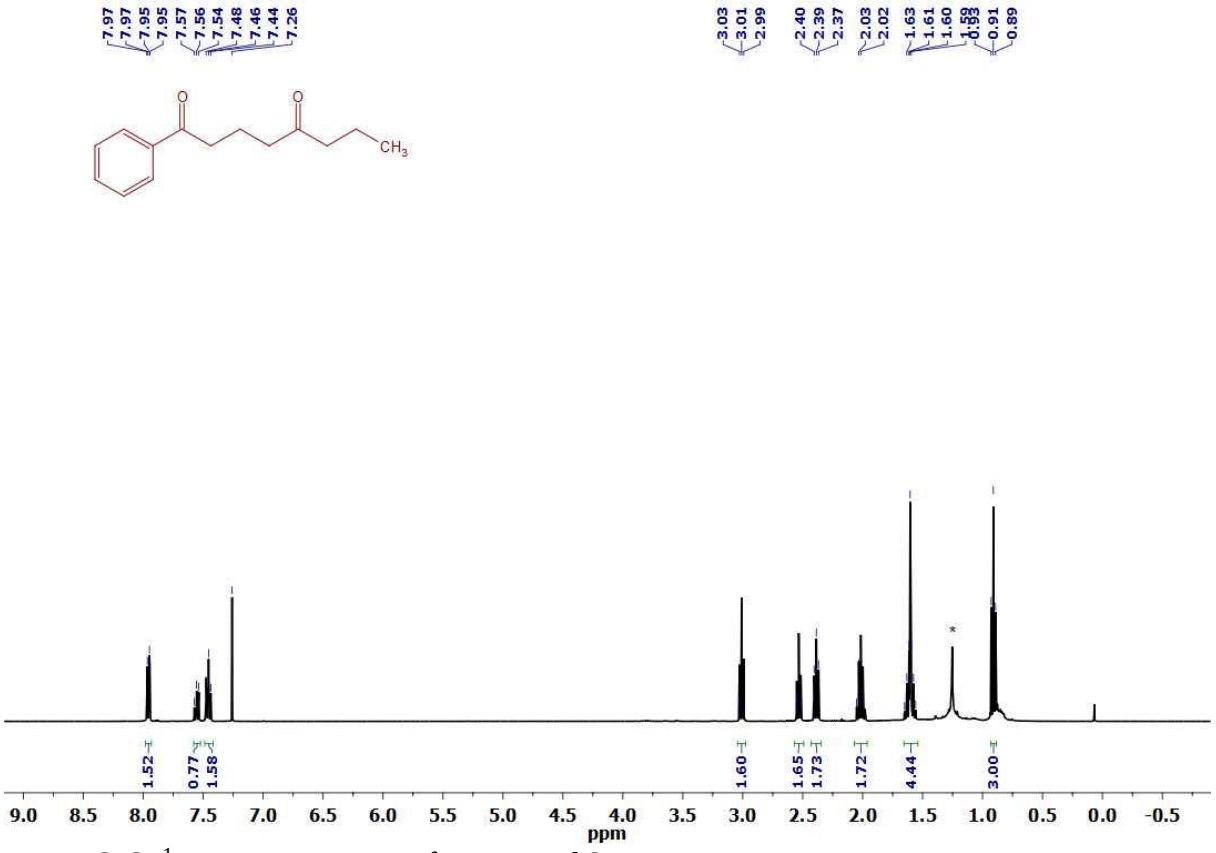


Figure S23: ^{1}H NMR spectrum of compound **27**

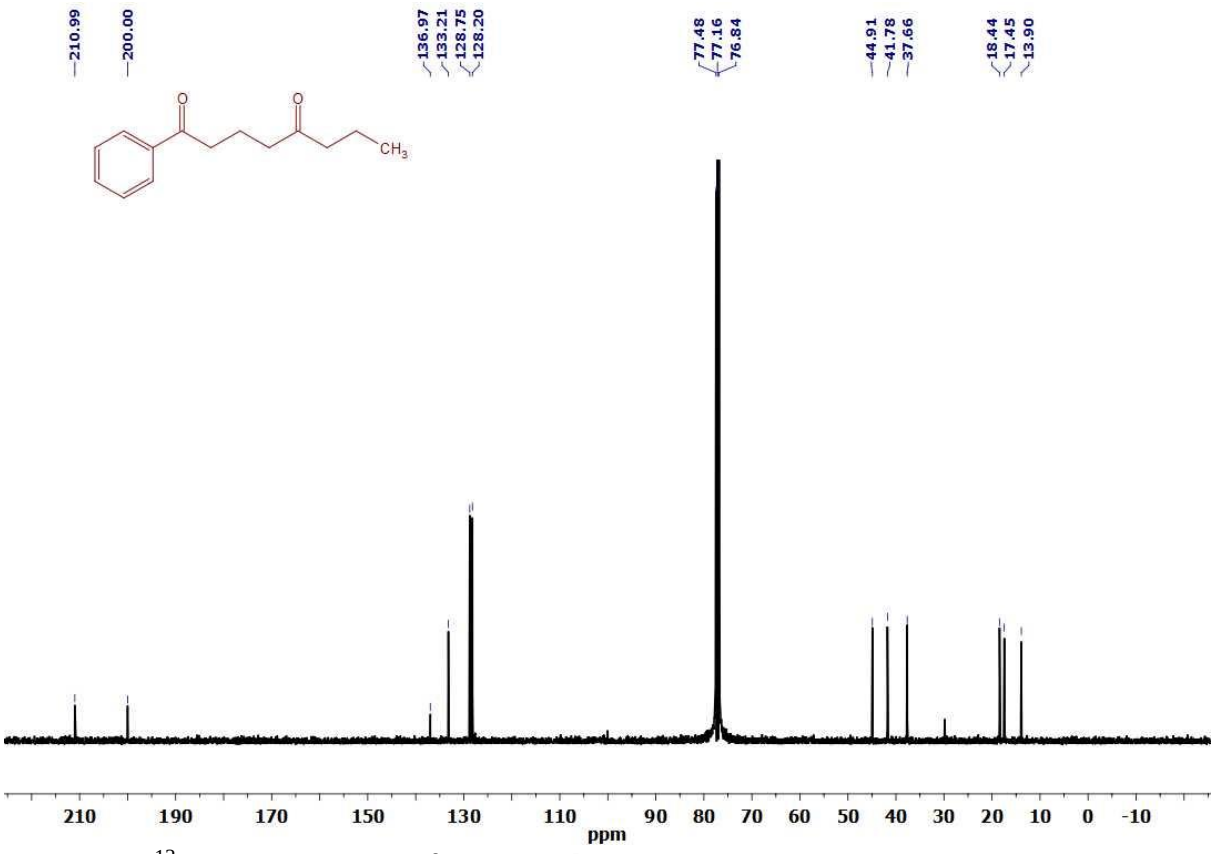


Figure S24:[13]C NMR spectrum of compound **27**

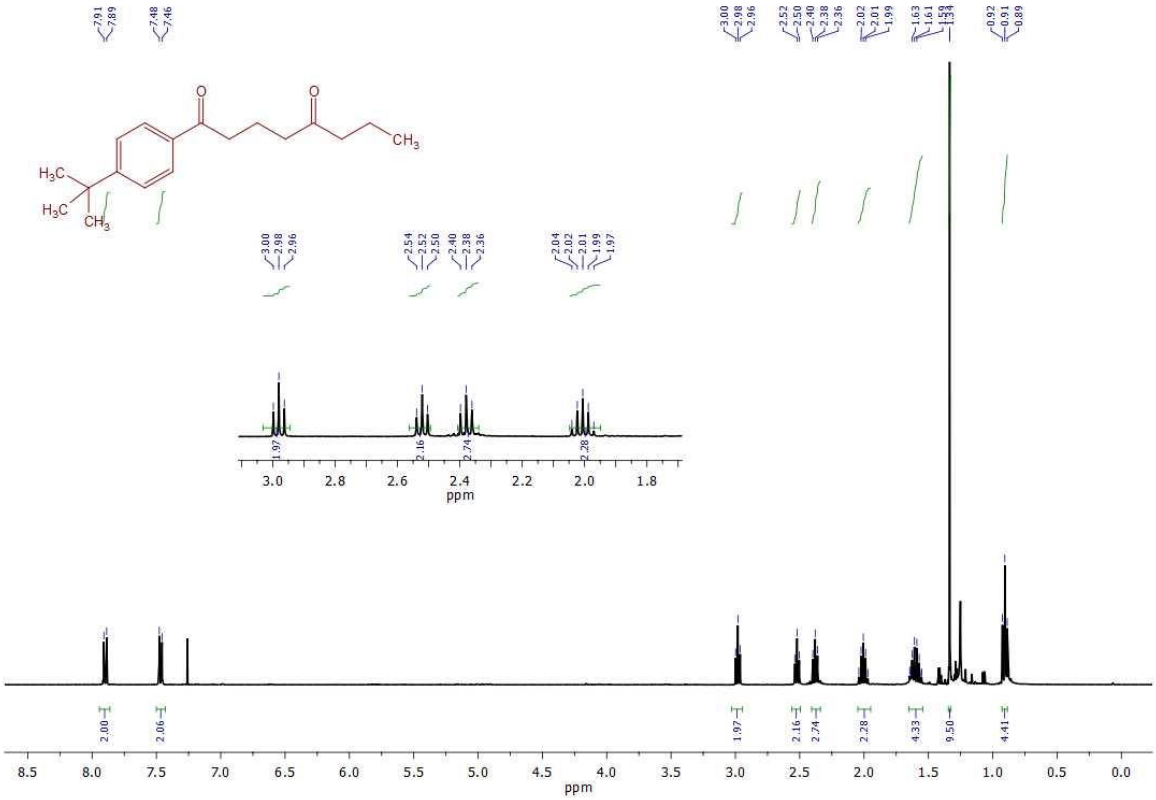


Figure S25: [1]H NMR spectrum of compound **28**

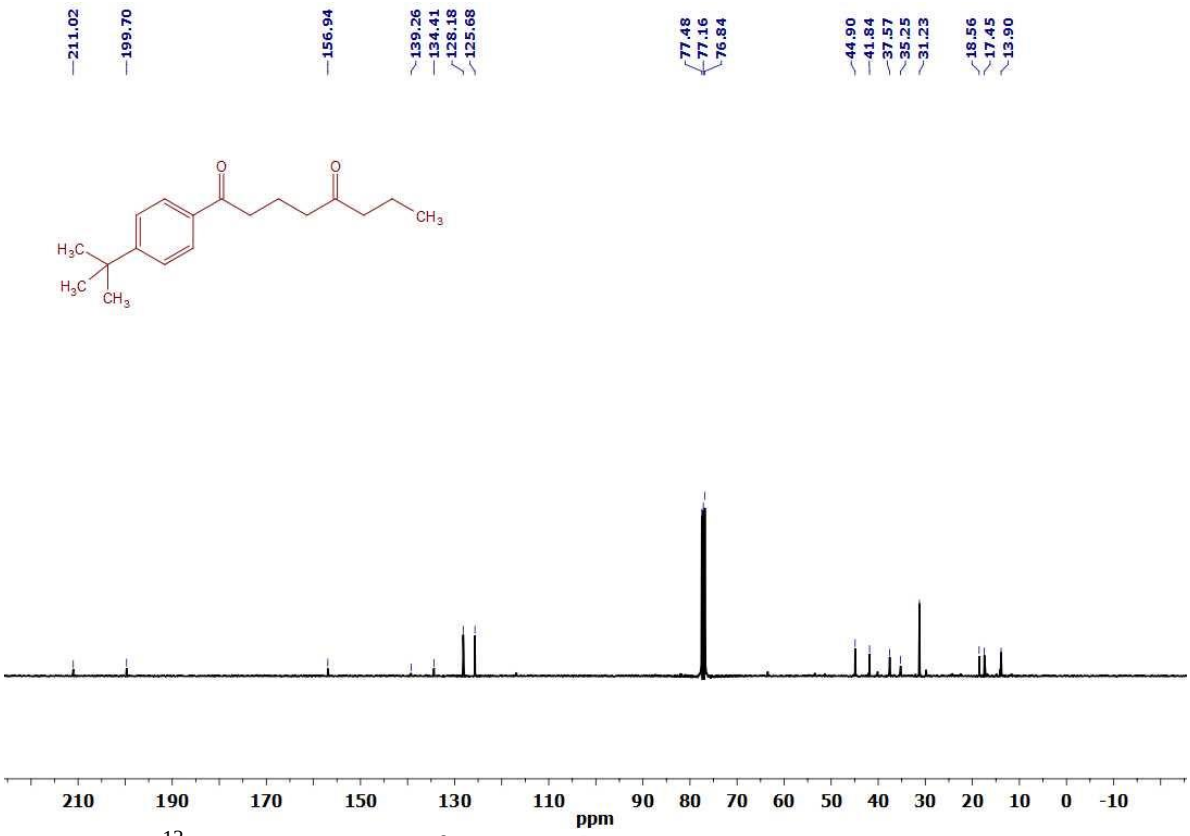


Figure S26: ^{13}C NMR spectrum of compound **28**

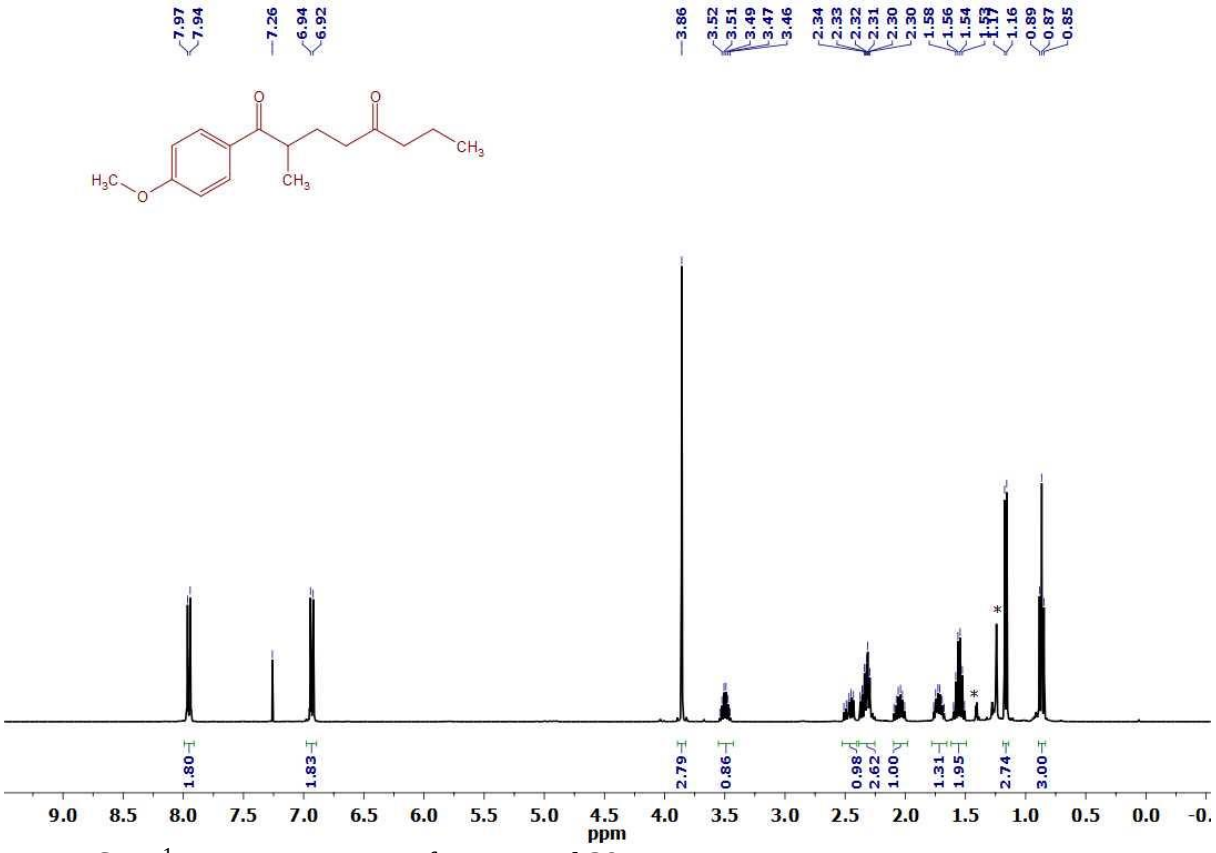


Figure S27: ^{1}H NMR spectrum of compound **29**

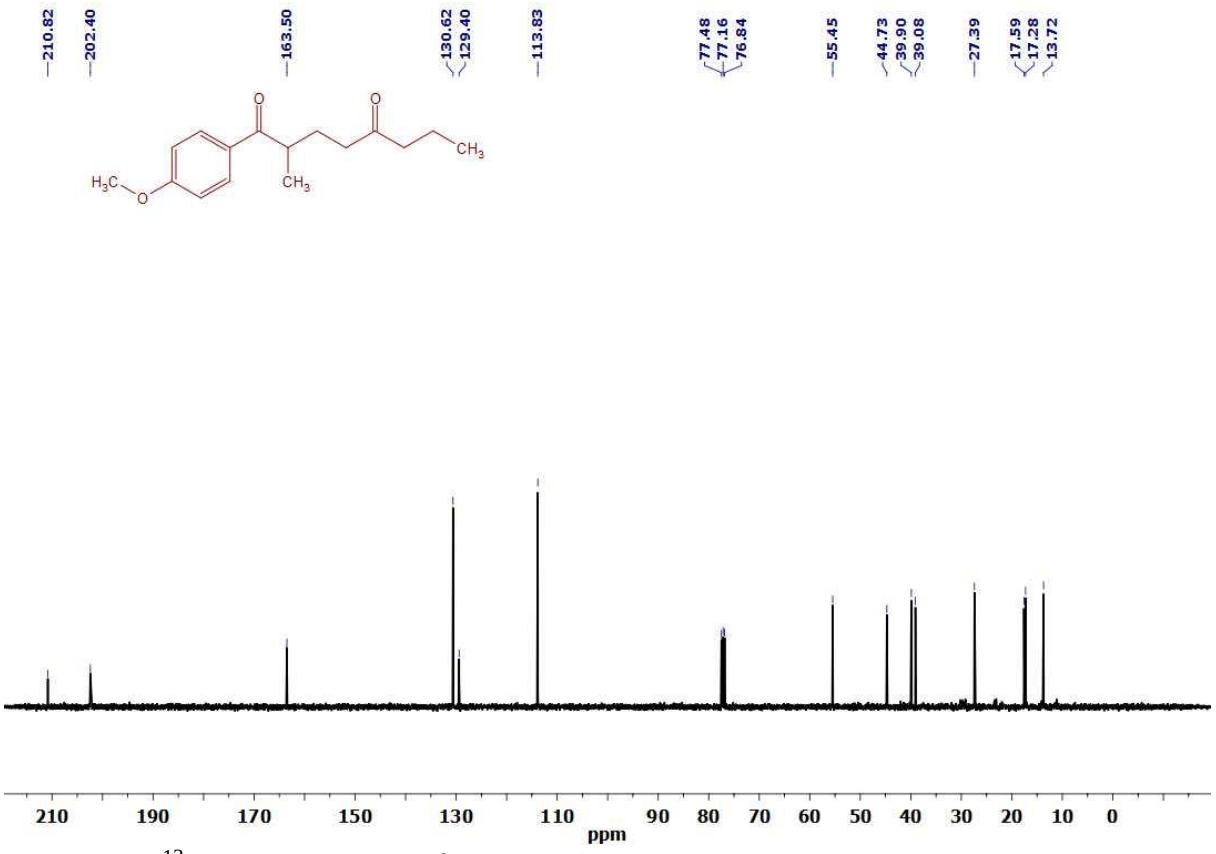


Figure S28: ^{13}C NMR spectrum of compound **29**

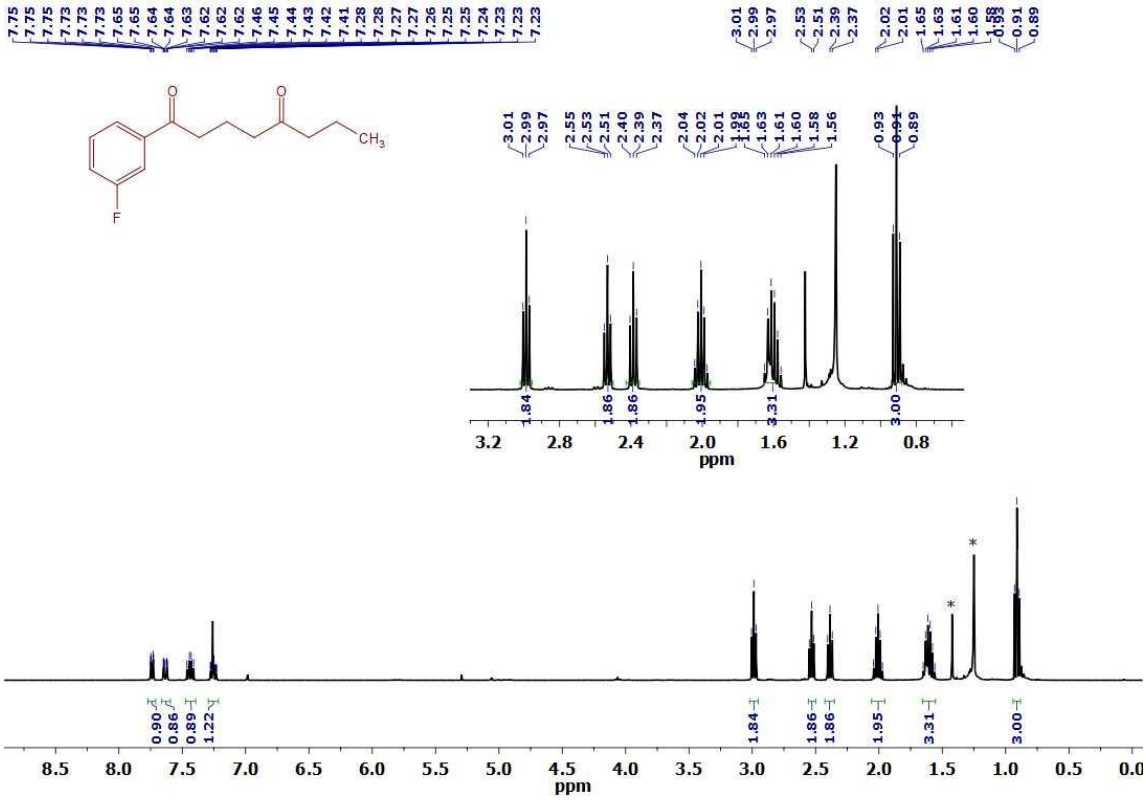


Figure S29: ^{1}H NMR spectrum of compound **30 (* solvent residues)**

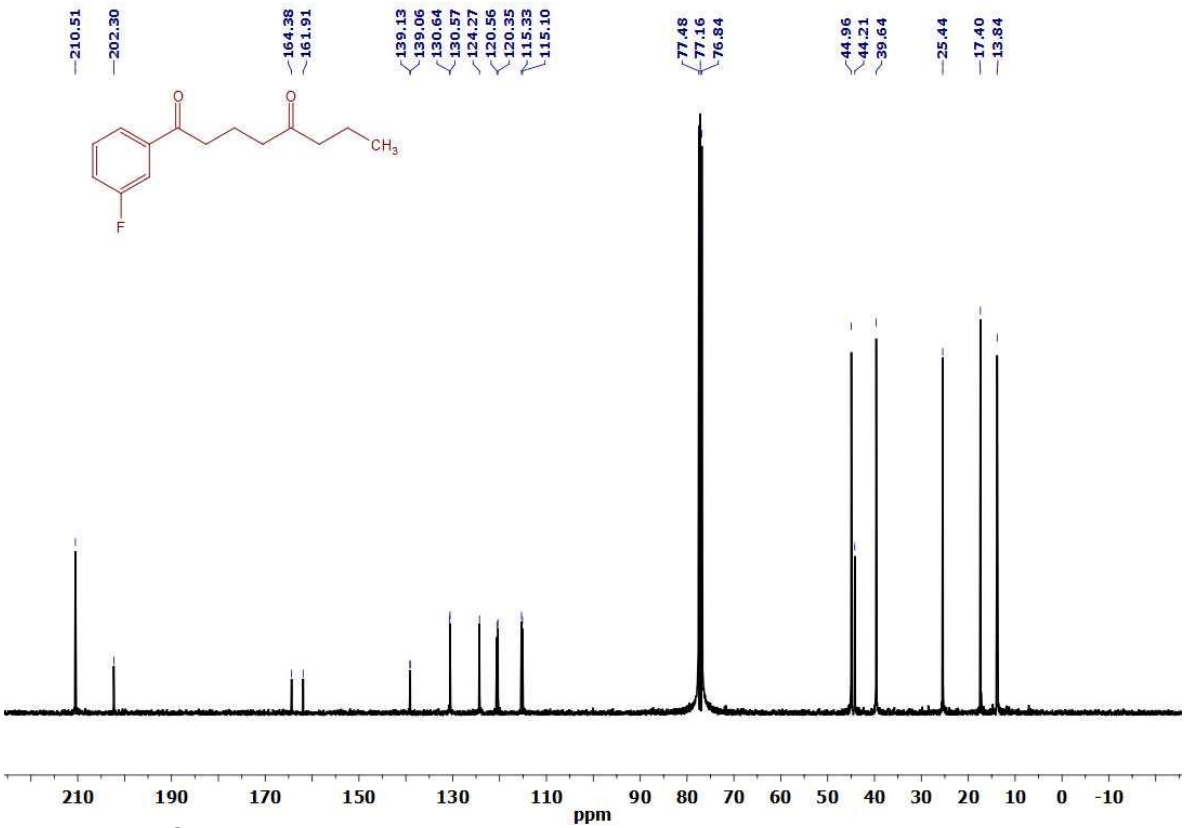


Figure S30: ^{13}C NMR spectrum of compound **30**

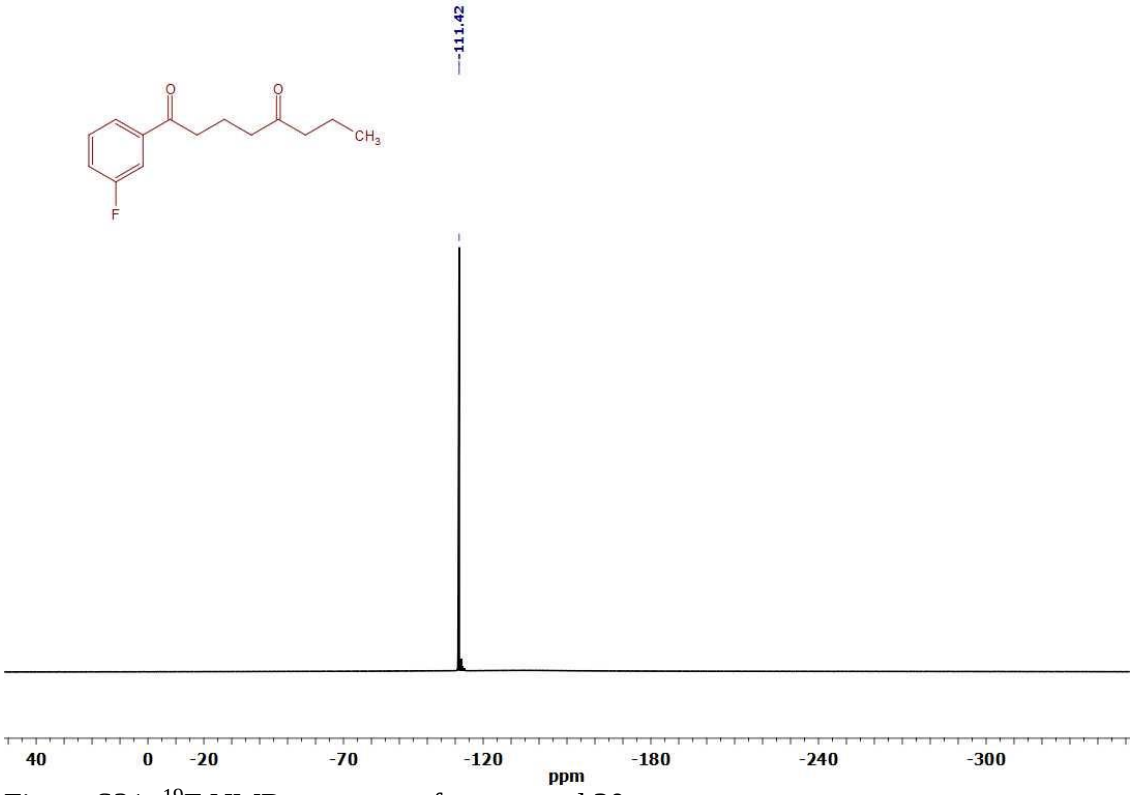


Figure S31: ^{19}F NMR spectrum of compound **30**

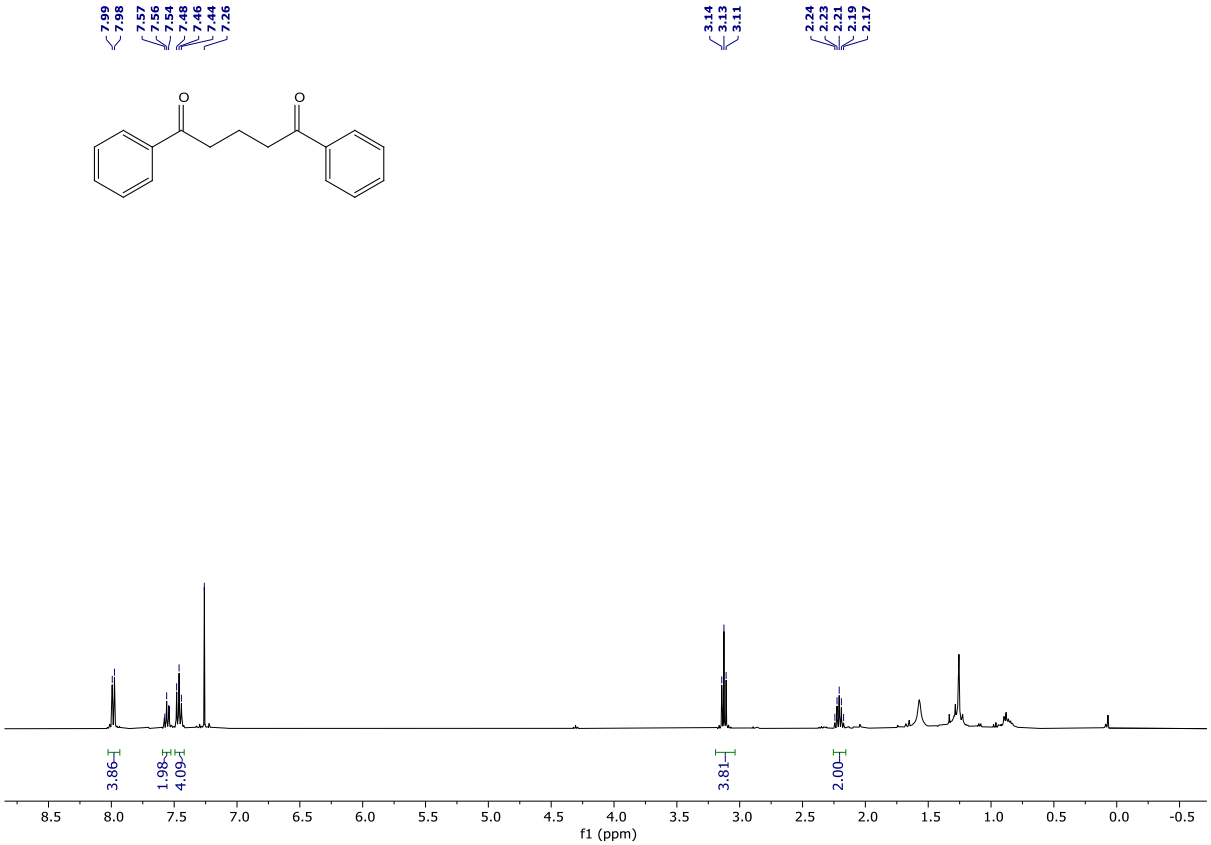


Figure S32: ^{1}H NMR of compound **35**

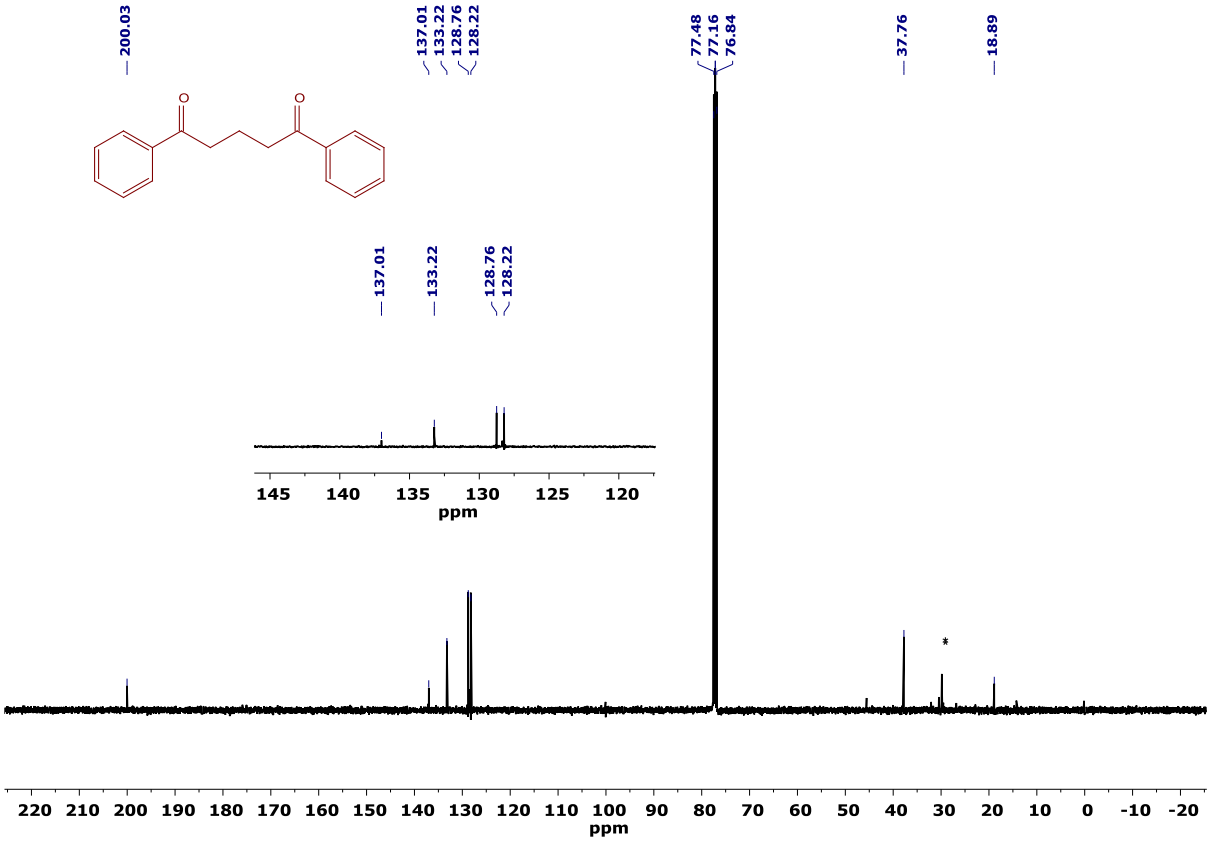


Figure S33: ^{13}C NMR of compound **35**

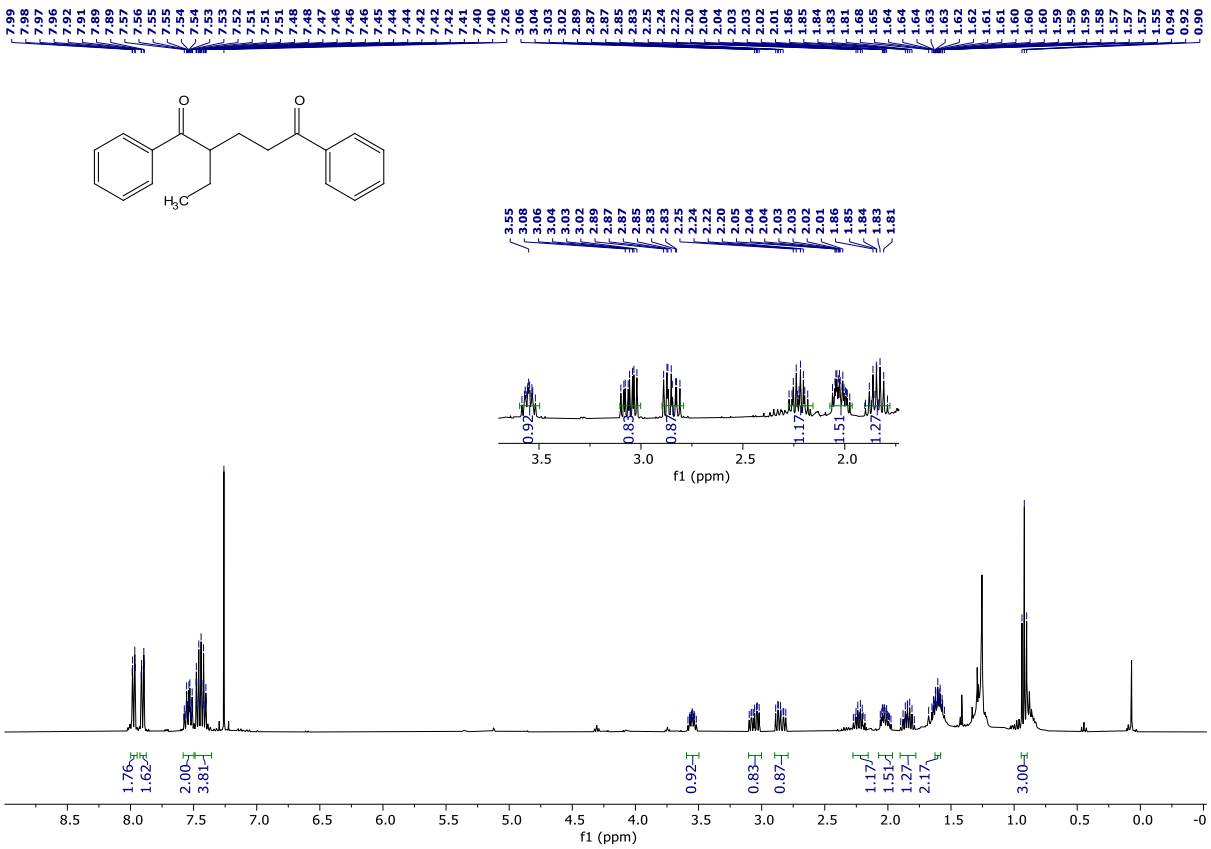


Figure S34: ^{1}H NMR of compound **36**

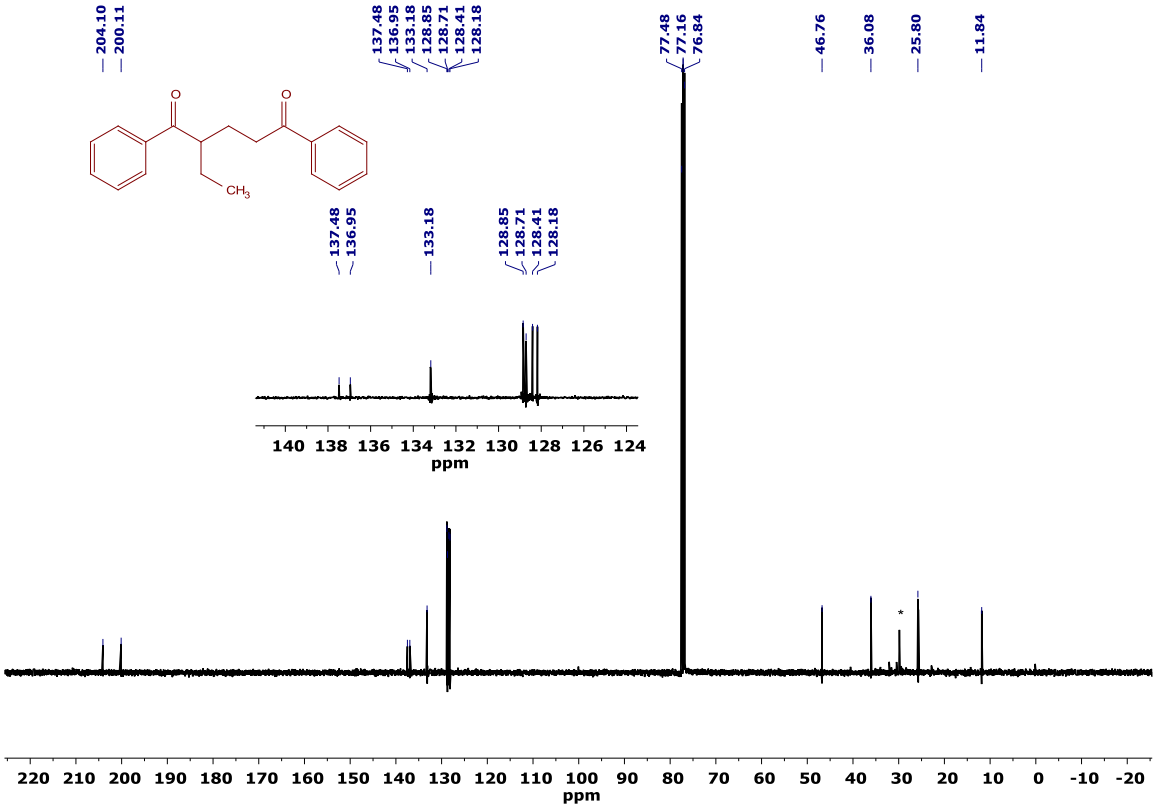


Figure S35: ^{13}C NMR of compound **36**

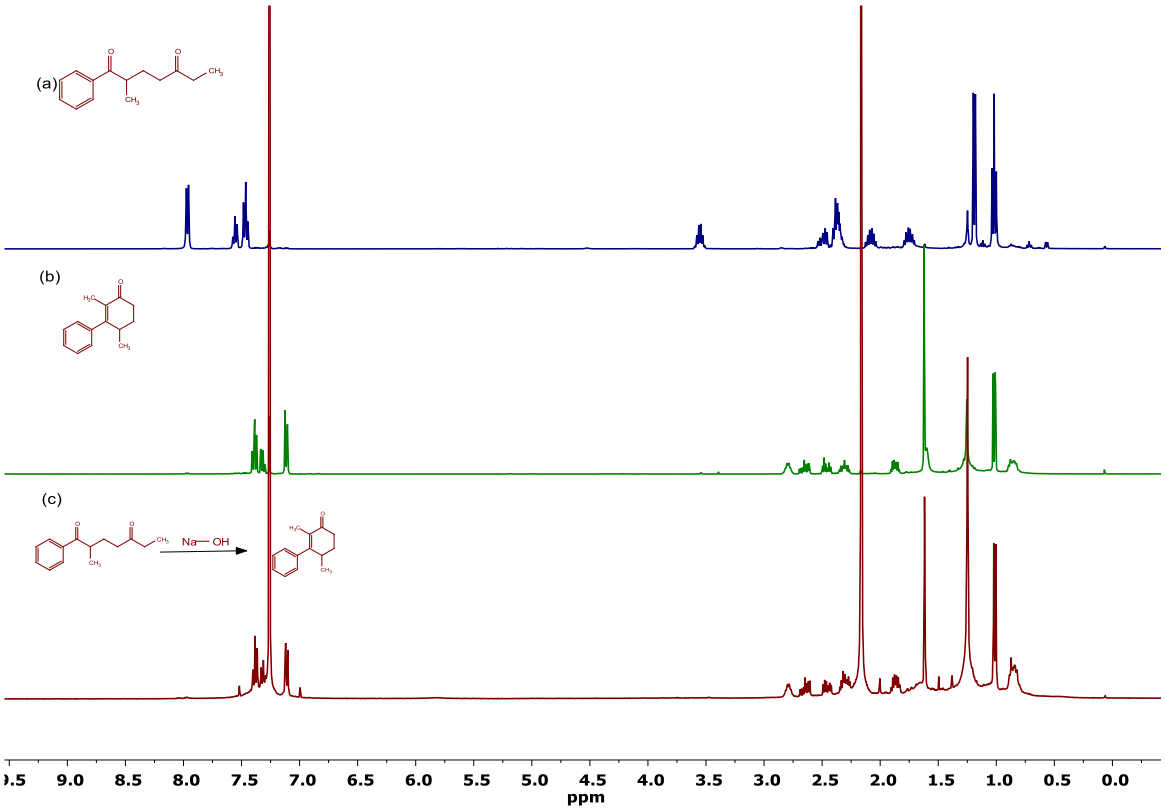


Figure S36: Stacked ^{1}H NMR spectrum of (a) diketone-**33** (b) compound **3** and (c) crude reaction mixture of diketone after stirring with NaOH for 12 h **(control experiment)**.

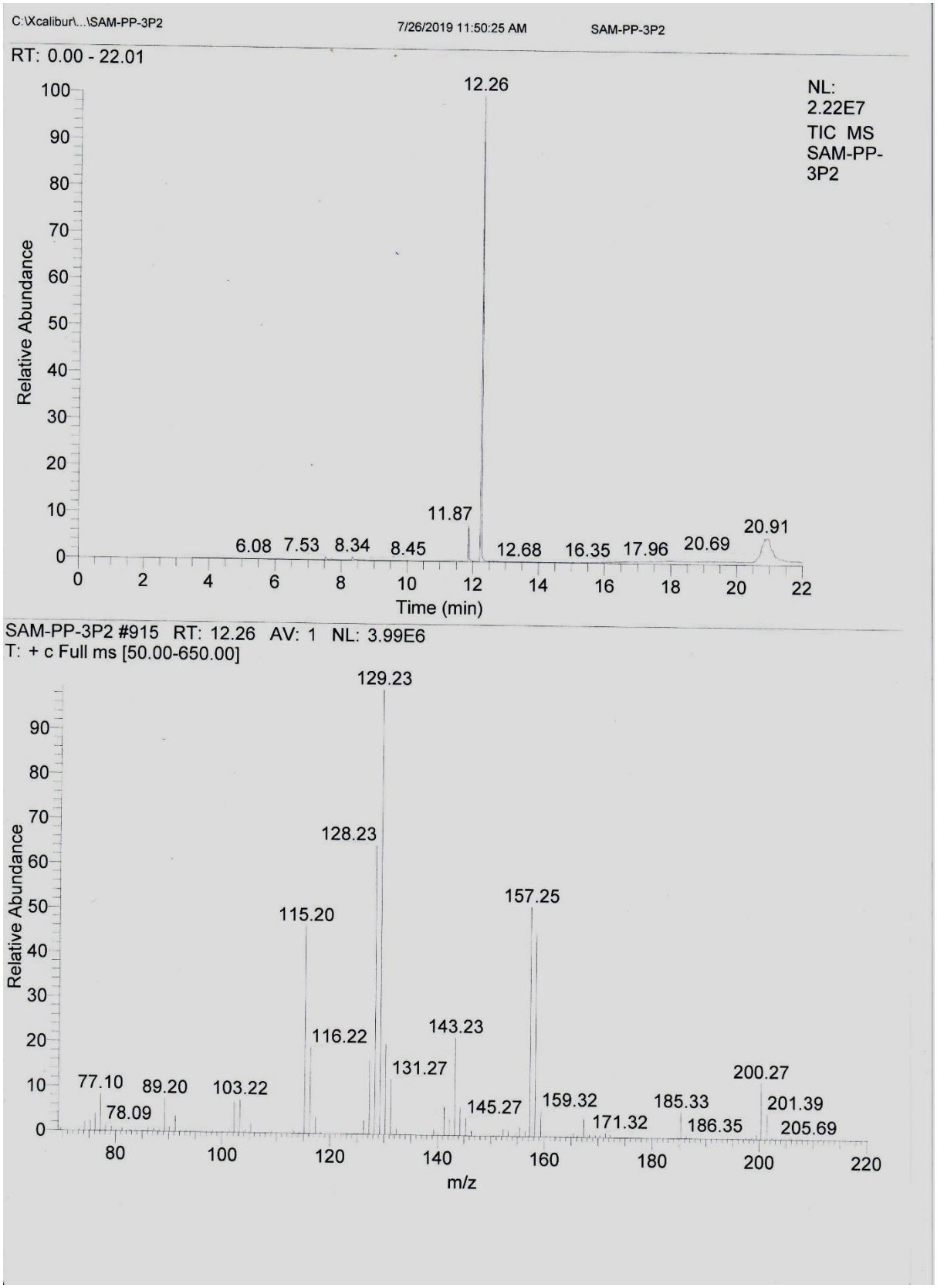


Figure S37: GC-MS of compound **2** at RT 12.26

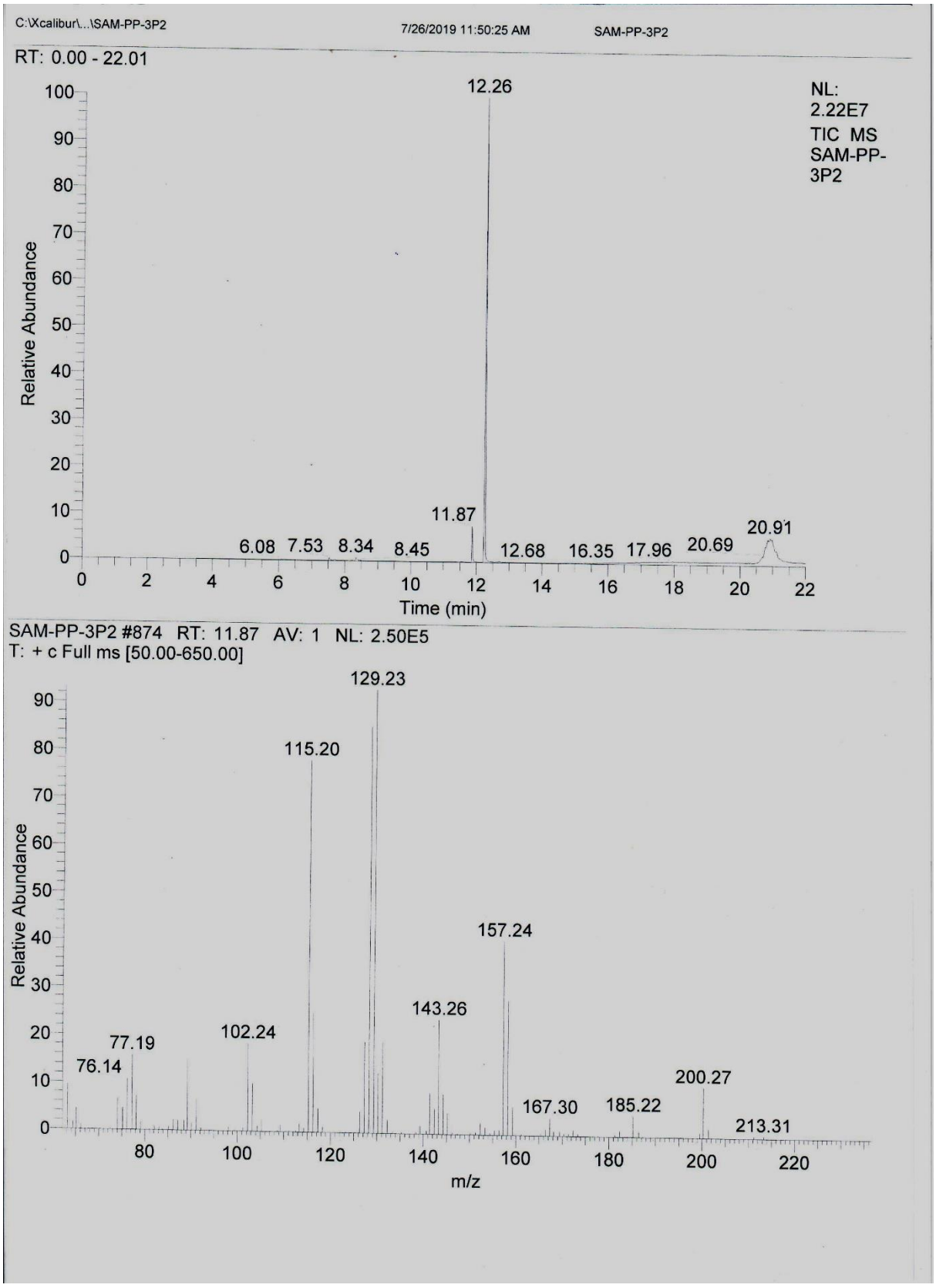
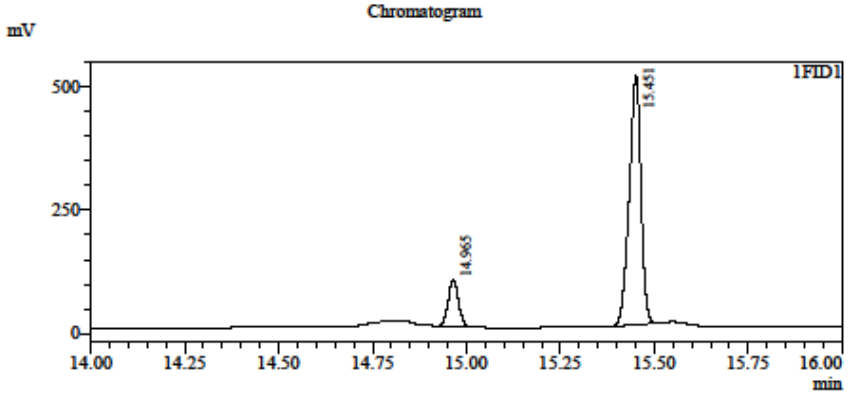


Figure S38: GC-MS of compound **2** at RT 11.87

Sample Information

Acquired by	: HP
Sample Name	: sam-pp-3p2
Sample ID	: sam-pp-3p2
Vial#	: 1
Injection Volume	: 1
Data File	: sam-pp-3p2.gcd
Method File	: relay sam.gcm
Batch File	:
Report Format File	: DEFAULT.lsr
Date Acquired	: 8/1/2019 9:07:37 PM
Date Processed	: 8/10/2019 11:29:21 AM

Chromatogram



Peak Table

FID1

Peak#	Ret. Time	Area	Area%	Height	Name
1	14.965	179470	14.096	93137	
2	15.451	1093715	85.904	498102	
Total		1273185	100.000	591239	

Figure S39: GC trace of compound **2**

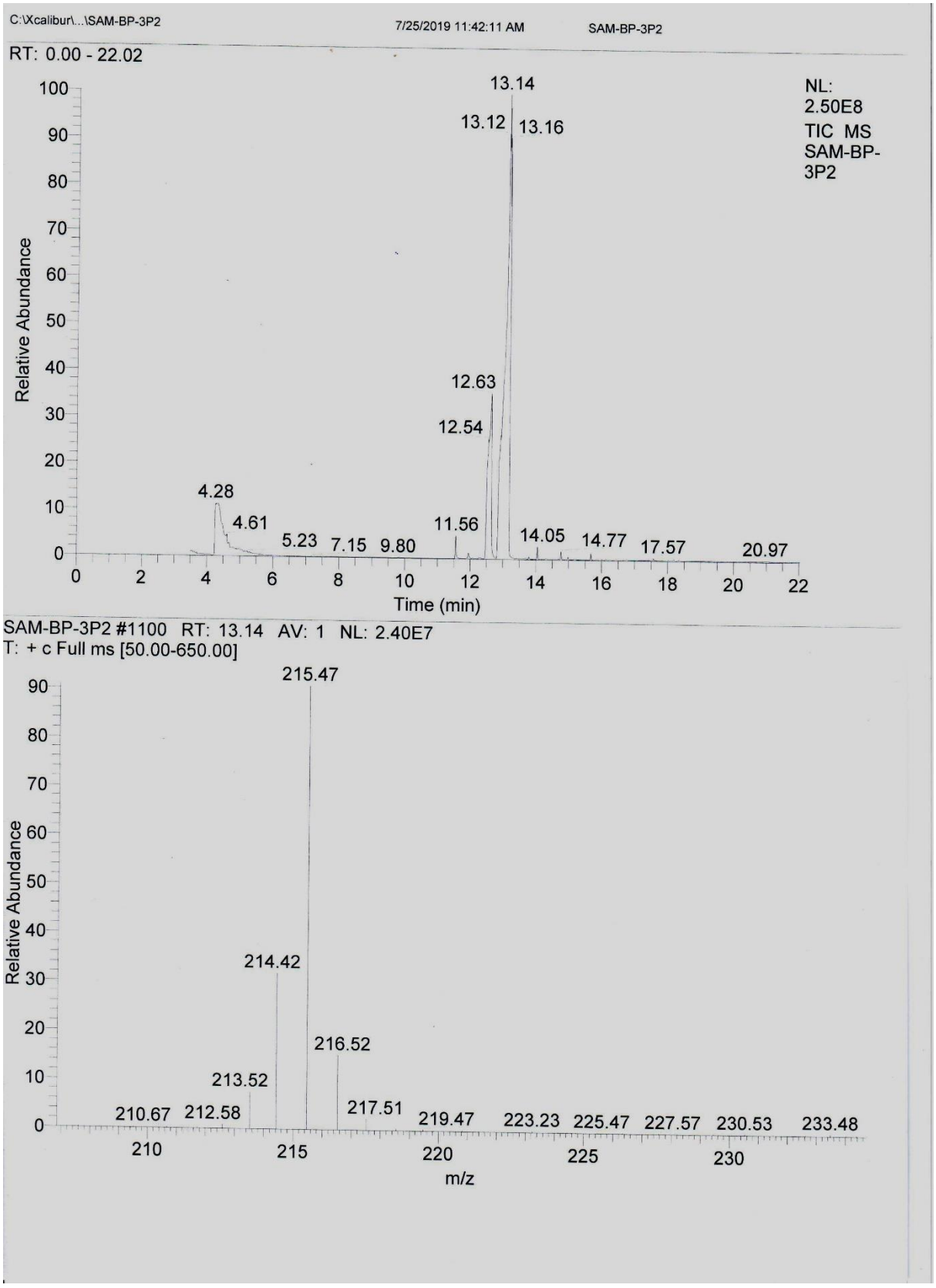


Figure S40: GC-MS of compound **17** at RT 13.14

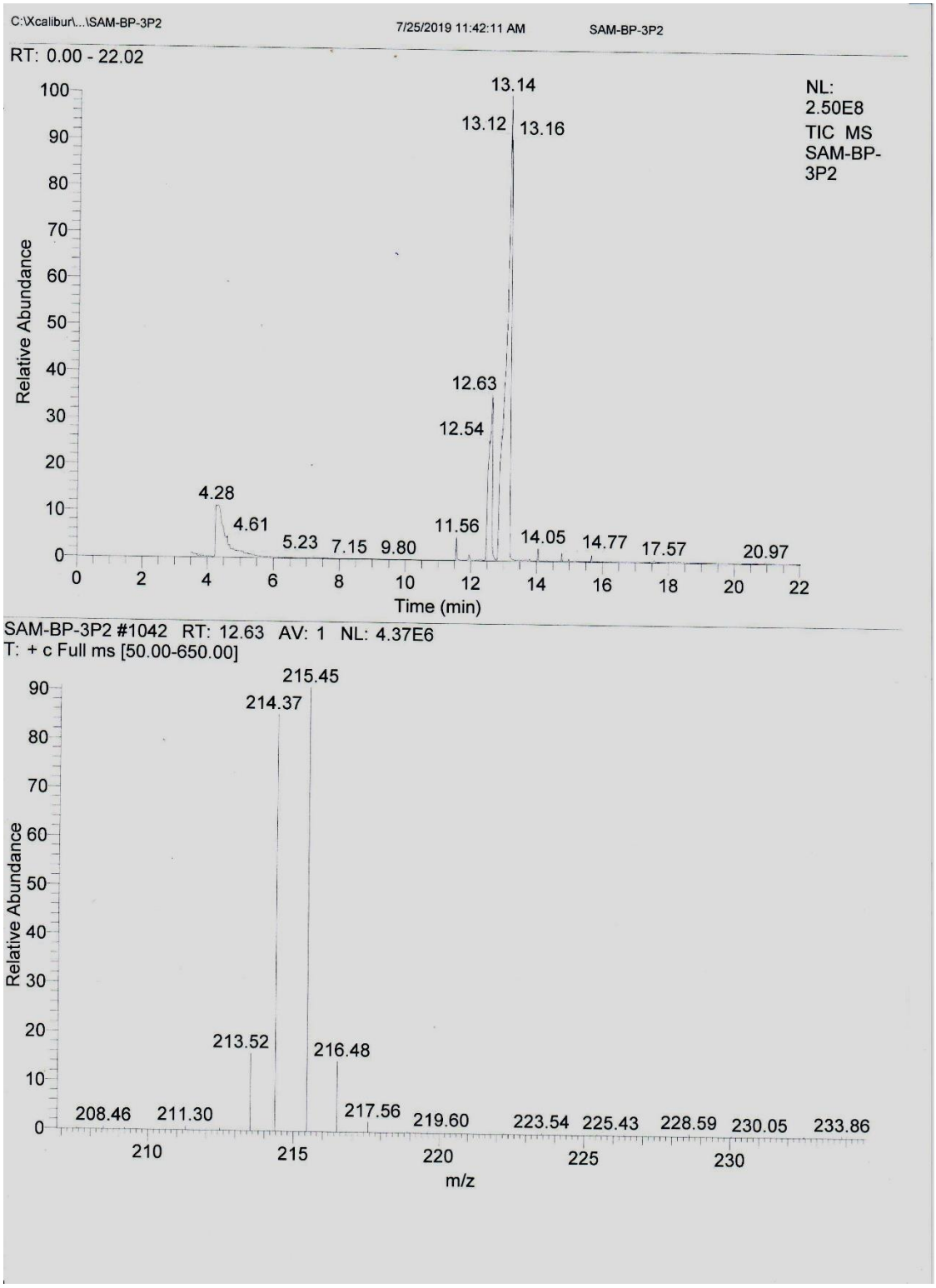


Figure S41: GC-MS of compound **17** at RT 12.63

Sample Information

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Sample ID	: sam-bp-3p2_re
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Injection Volume	: 1
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Method File	: relay sam.gcm
Batch File	:
Report Format File	: DEFAULT.lsr
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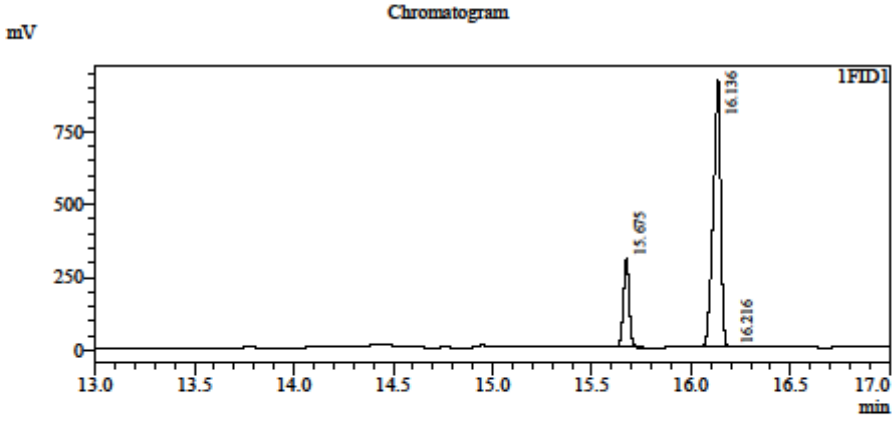
Chromatogram



Peak Table

FID1

Peak#	Ret. Time	Area	Area%	Height	Name
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2	16.136	2429079	79.584	907586	
3	16.216	3731	0.122	2010	
Total		3052204	100.000	1211203	

Figure S42: GC trace of compound **17**

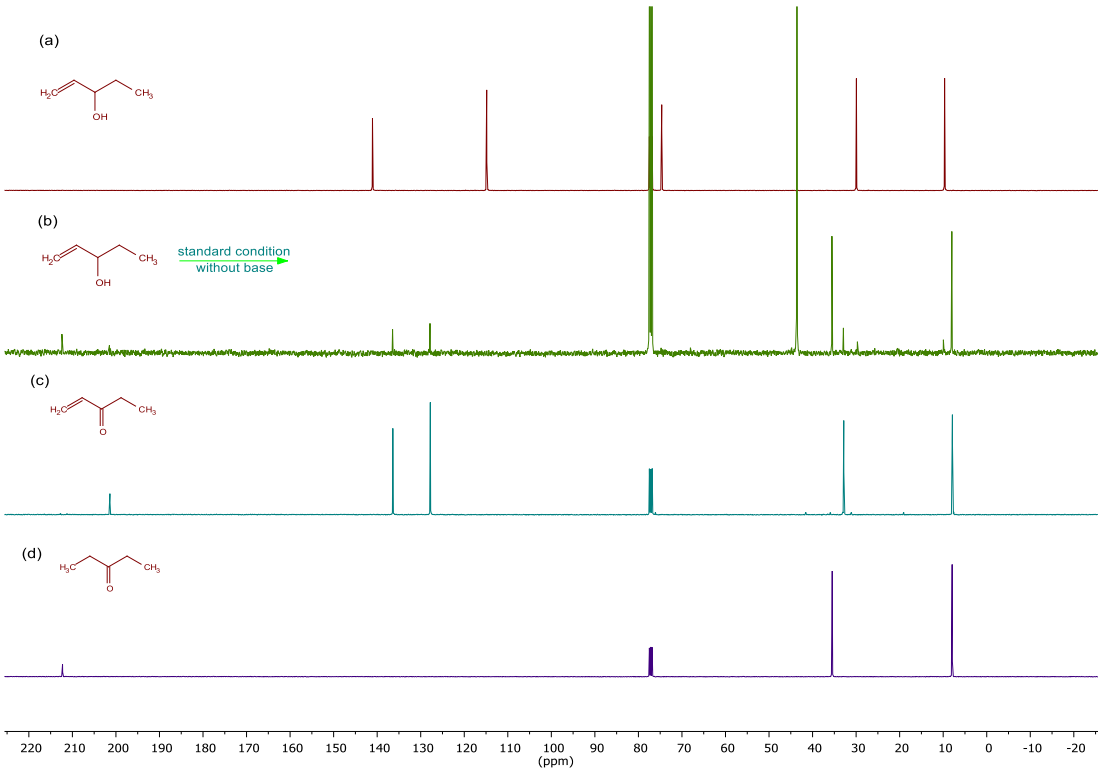


Figure S43: Stacking of crude ^{13}C NMR of control experiment (Scheme 1a). ^{13}C NMR spectrum of (a) pure 1-penten-3-ol. (b) Reaction mixture of Scheme 1a(without base). (c)Pure 1-penten-3-one and (d) pure 3-pentanone.

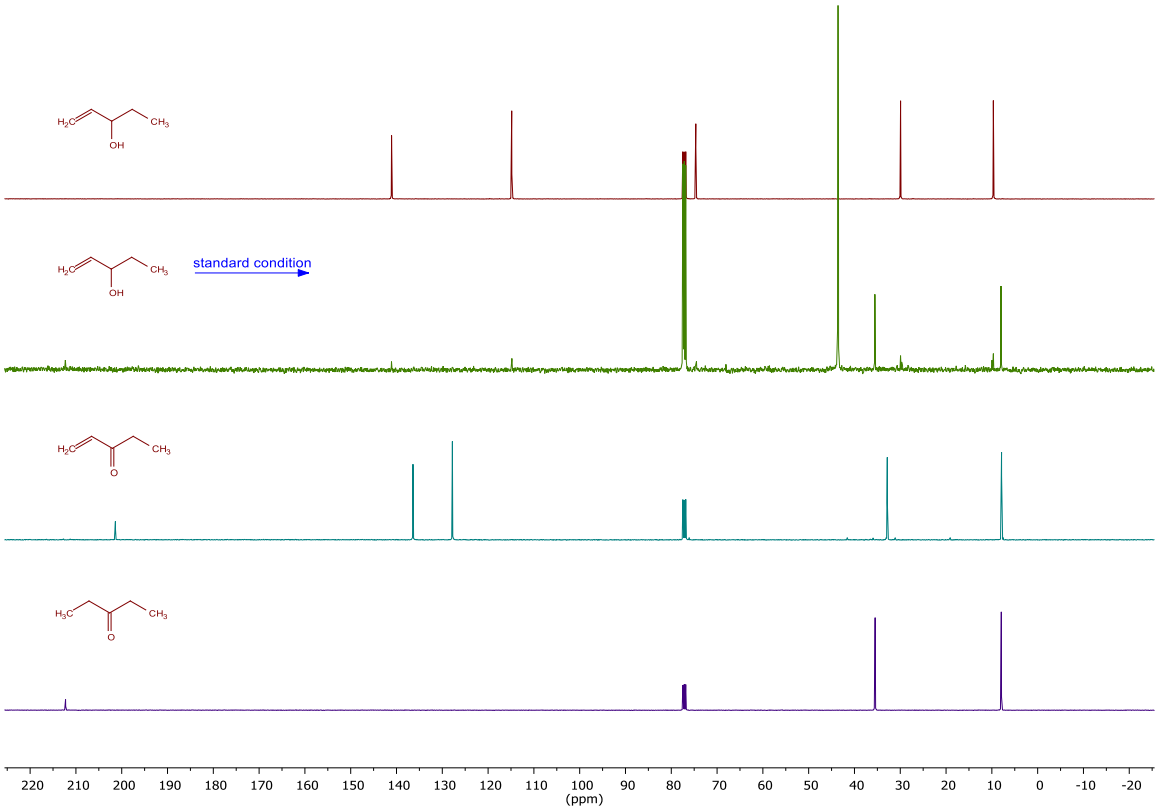


Figure S43: Stacking of crude ^{13}C NMR of control experiment (Scheme 1a). ^{13}C NMR spectrum of (a) pure 1-penten-3-ol. (b) Reaction mixture of Scheme 1a(with base). (c)Pure 1-penten-3-one and (d) pure 3-pentanone.

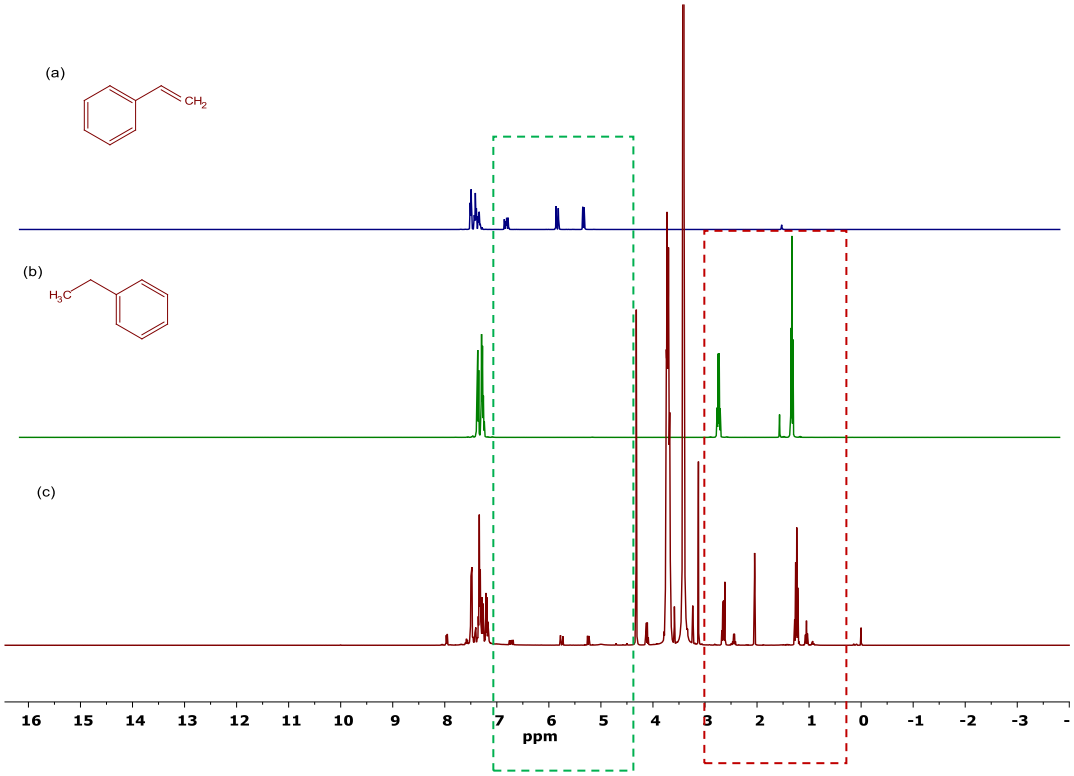
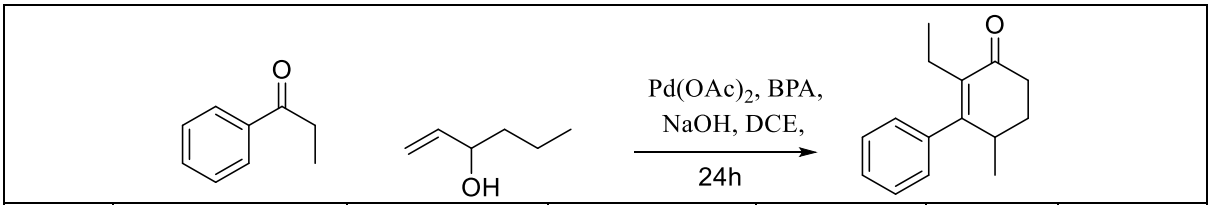


Figure S44: ^{1}H NMR stacking of (a) styrene (b) ethyl benzene and (c) crude reaction mixture of reduction of phenylacetylene by palladium charcoal

Procedure for Attempted annulation with 1-hexen-3-ol

In a Schlenk tube, $Pd(OAc)_2$, base and ligand were added followed by 1-hexen-3-ol. Ketone, 4Å molecular sieves and solvent were added to it. The reaction was sealed and heated. After 24h, the reaction mixture was evaporated under vacuum and was purified by column chromatography.

Table S2: Attempt for annulation with 1-hexen-3-ol[#]



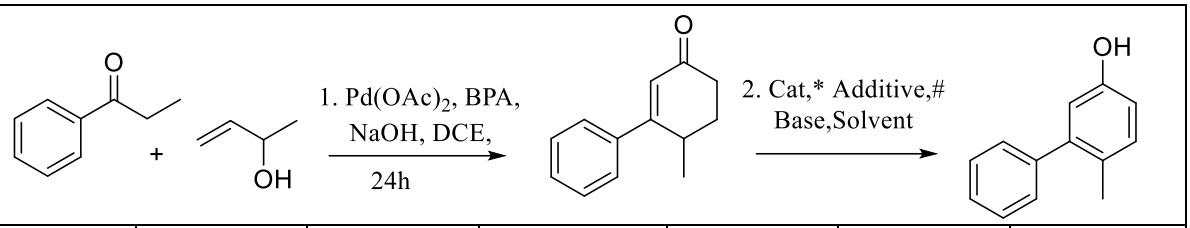
S No.	Catalyst (mol%)	Base(equiv)	Ligand(mol%)	Solvent	T (^{o} C)	yield
1[a]	$Pd(OAc)_2$(10)	NaOH(1)	BPA (10)	DCE	RT	N.D[c]
2	$Pd(OAc)_2$(10)	NaOH(1)	BPA (10)	DCE	80	N.D[c]
3[a]	$Pd(OAc)_2$(10)	Cs_2CO_3(1)	BPA (10)	DCE	80	N.D[c]
4[a]	$Pd(OAc)_2$(10)	Cs_2CO_3(1)	BPA (10)	DCE	100	N.D[c]
5[b]	$Pd(OAc)_2$(10)	NaOAc(1)	--	Toluene	80	N.D[d]
6[b]	$Pd(TFA)_2$(10)	NaOAc(1)	--	Toluene	80	N.D[d]

[#]Reaction conditions: 1 mmol ketone, 6 mmol allyl alcohol, 1 mL solvent, molecular sieves 4 Å, [a]3 mL DCE used, [b]2 equivalent acetic acid, O_2 balloon, [c]1,5-diketone product observed, [d]trace amount of 1,5-diketone observed, N.D = annulated product not detected

Procedure for attempted aromatization of cyclohexanone product

Palladium acetate (0.022 g, 0.10 mmol), BINOL phosphoric acid (0.035 g, 0.10 mmol) and sodium hydroxide (0.039 g, 1.00 mmol) were taken in a Schlenk tube. Aryl ketone (1.00 mmol), allyl alcohol (2.00 mmol) and 0.8 mL of dichloroethane (DCE) were added to it. Finally, 4Å molecular sieves was added to the reaction mixture and stirred at room temperature for 24 hours. Then, the reaction was evaporated under vacuum, additional catalyst, additive and base were added to it (Table S3, entries 1-4). Solvent was added to it and the reaction was heated at the specified temperature for further 24h, the reaction mixture was evaporated under vacuum and the reaction mixture was purified by column chromatography. For entry 5, we used Pd/C as the catalyst for both steps.

Table S3: Attempt for one pot-sequential synthesis of phenol



S No	Catalyst* (mol%)	Additive# (mol%)	Base	Solvent	T (^{o} C)	Yield
1	Pd/C (5)	-	K_2CO_3(20)	DMA	100	ND[d]
2[a]	Pd/C (5)	-	K_2CO_3(20)	DMA	100	ND[d]
3	I_2(20)	DMSO (100)	--	CH_3NO_2	100	ND[d]
4[b]	$CuBr_2$(5)	48% HBr	--	Dioxane	RT	ND[d]
5[c]	Pd/C (5)		K_2CO_3(100)	DMA	100	No Conversion

Reaction was carried out in one pot sequential method starting from propiophenone and 3-buten-2-ol. [a]Cs_2CO_3 was used instead of NaOH for annulation in the first step, [b] O_2 Balloon used for aromatisation, [c]reaction was carried out in one pot starting from propiophenone, Pd/C used instead of $Pd(OAc)_2$ for the annulation reaction. [d]annulated product recovered, ND=phenol formation not detected.