Efficient Access to 1,5-Diketones from N-Sulfonyl Ketimines and 3-Chloropropiophenones

M.Sc. Thesis

by

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Efficient Access to 1,5-Diketones from N-Sulfonyl Ketimines and 3-Chloropropiophenones

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree
of
Master of Science

by
ARJUN KUMBHAKAR

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE
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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Efficient Access to 1,5-Diketones from N-Sulfonyl Ketimines and 3-Chloropropiophenones "** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from June 2022 to June 2023 under the supervision of **Prof. Sampak Samanta**, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Arjun Kumbhakar

Signature of the student
(Arjun Kumbhakar)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of Supervisor
(Prof. Sampak Samanta)

ARJUN KUMBHAKAR has successfully given his M.Sc. Oral Examination held on **16.05.2023**.

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Date: 16.05.2023

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Abstract

A series of 1,5-diketones were synthesized in good to high yields. This C-C bond-forming reaction proceeded between 4-alkyl N-sulfonyl ketimines and 3-chloropropiophenones in the presence of Cs_2CO_3 at heating conditions. Moreover, the current method is simple, has good substrate scope, and excellent tolerance of functionalities.

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ACRONYMS

ACN	Acetonitrile
$CDCl_3$	Chloroform-D
^{13}C NMR	Carbon-13 NMR Spectroscopy
DMSO	Dimethyl sulfoxide
DCM	Dichloromethane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DABCO	1,4-Diazabicyclo[2,2,2]octane
DBN	1.5-Diazabicyclo[4.3.0]non-5-ene
DMF	N, N-dimethyl formamide
EtOAc	Ethyl acetate
HRMS	High resolution mass spectroscopy
2-MeTHF	2-Methyltetrahydrofuran
M	Molar
NMR	Nuclear magnetic resonance
ppm	Parts per million
UV	Ultra visible spectroscopy

NOMENCLATURE

δ	Chemical shift
cm	Centimetre
°C	Degree Celsius
mmol	Millimole
mL	Millilitre
rt	Room temperature

Chapter 1

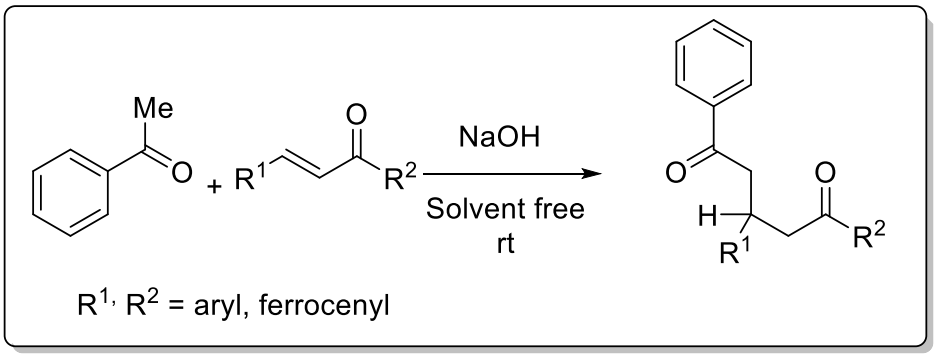
1 INTRODUCTION

1.1 General Introduction

Among the functional groups, ketones are the most important and valuable functional groups in organic molecules. Particularly, 1,5-diketones are the building blocks in the synthesis of a variety of heterocyclic molecules and other related skeletons which are essential subunits of many natural products. Particularly, they have promising applications in the synthesis of vital classes of aza-heterocyclic compounds such as pyridine [1], pyrazolo[1,5-a]pyrimidines [2], etc. Thus, many methods have been developed for synthesizing 1,5-diketones. Some of them methods are included in the next section.

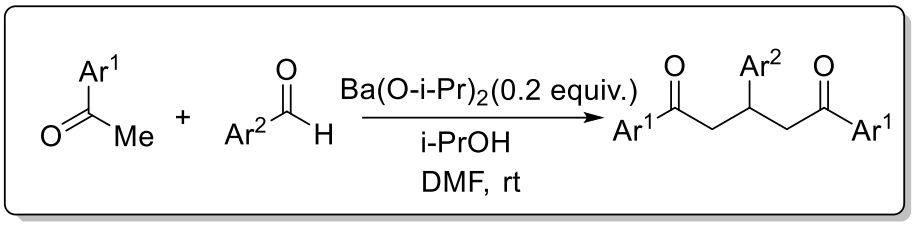
1.2. Review work

In 2001, Liu et al. established a very significant environmental-friendly method for the synthesis 1,5-diketone in good yields from acetophenones and α, β-unsaturated ketones using NaOH as a base under solvent-free conditions in Scheme 1**. [3]**



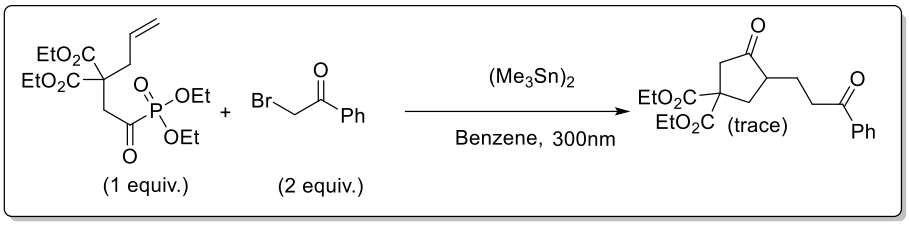
Scheme 1: Base-promoted access to 1,5-diketones

In 2007, Yanagisawa et al. developed an efficient way to synthesize 1,5-diketones, which has been achieved by a catalytic amount of barium isopropoxide in a mixture of acetophenone derivatives and benzaldehyde derivatives in DMF at room temperature (**Scheme 2**) [4]



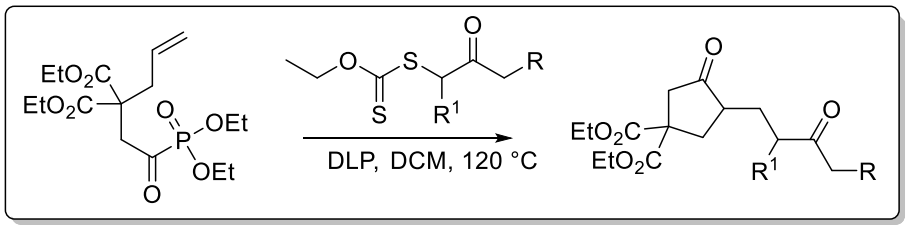
Scheme 2: One-pot synthesis of 1,5-diketones using barium isopropoxide catalyst.

In 2013, Zard et al. modified the methods to synthesize 1,5-diketones via aldol-Michael between α-halo ketones and alkenylacylphosphonate as a carbonyl group acceptor in the presence of hexamethylditin. (**Scheme: 3)** [5]



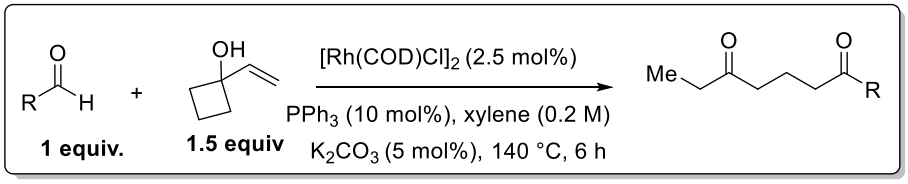
Scheme: 3 Intramolecular acylation in the presence of hexamethylditin.

Because of the toxicity of tin and low yield, they modified the method by using ketoxanthates instead of α-haloketone which proceeded through the radical pathway. (**Scheme: 4)** [5]



Scheme 4: Synthesis of 1,5-diketones from using ketoxenthane.

In 2017, Gua et al. developed rhodium catalyst hydroacylation using vinyl cyclobutanol and aldehyde that afforded 1,5-diketones. (**Scheme: 5)** [6]



Scheme 5: Synthesis of 1,5-diketones from vinyl cyclobutanols and aldehydes using rhodium-catalyst.

1.3 Conclusions

Literature study revealed that many efficient techniques have been established for accessing 1,5-diketones. However, they have their own drawbacks, including the use of toxic elements, the use of expensive metal catalysts, poor yields (few cases), limited structural scope, and the formation of by-products. Therefore, there is an ample scope to develop a new transition-metal-free protocol for assembling a diverse set of 1,5-diketones from simple reactants under mild conditions.

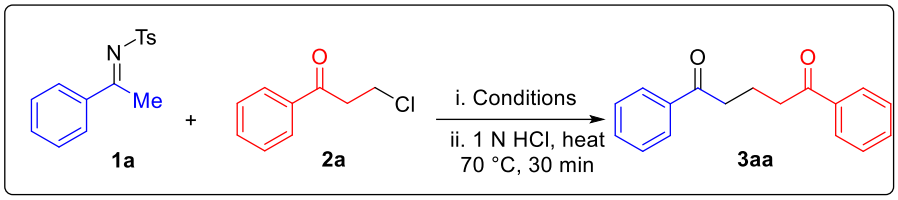
1.4 Objectives of the present work

The synthesis of 1,5-diketone derivatives is subject of growing interest in recent years due to their great importance in organic synthesis. For this purpose, here in we report a novel C-C bond forming reaction between 4-methyl-N-(1-arylethylidene)benzenesulfonamides and 3-chloropropiophenones promoted by Cs_2CO_3 in 2-MeTHF at heating conditions to deliver 1,5-diketones.

Chapter 2

2. RESULTS AND DISCUSSION:

2.1 Optimization of the reaction conditions[a]



Entry	Base	Solvent	Temperature(°C)	Time(h)	Yield[b] (3aa)(%)
1.	Cs_2CO_3	2-MeTHF	rt	12	0
2.	Cs_2CO_3	2-MeTHF	50	6	49
3.	**Cs_2CO_3**	**2-MeTHF**	**70**	**6**	**72**
4.	Cs_2CO_3	2-MeTHF	100	6	63
5.	Cs_2CO_3	THF	70	6	61
6.	Cs_2CO_3	MeCN	70	6	46
7.	Cs_2CO_3	DCE	70	6	47
8.	Cs_2CO_3	Toluene	70	6	57
9.	Cs_2CO_3	DMSO	70	6	31
10.	Cs_2CO_3	DMF	70	6	ND
11.	Cs_2CO_3	1,4-Dioxane	70	6	34
12.	Cs_2CO_3	EtOH	70	6	59
13.	DBU	2-MeTHF	70	6	61
14.	DBN	2-MeTHF	70	6	55
15.	DABCO	2-MeTHF	70	6	ND
16.	NEt_3	2-MeTHF	70	6	27
17.	DEIPA	2-MeTHF	70	6	41
18.	K_2CO_3	2-MeTHF	70	6	ND
19.	NaOH	2-MeTHF	70	6	ND
20.	KOH	2-MeTHF	70	6	57
21.	t-BuOK	2-MeTHF	70	6	15

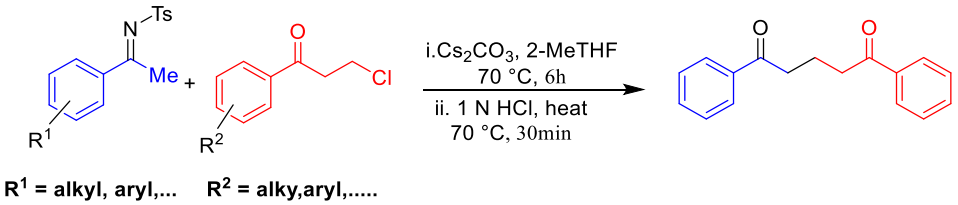
[a]All the reactions are carried out with **1a** (0.18 mmol, 1 equiv.), **2a** (0.18 mmol, 1 equiv.), and base (1.2 equiv.) in dry solvent (0.5 mL) at different temperatures. [b]Yield refers to isolated product **3aa** after column chromatography.

We did the model reaction between N-sulfonyl ketimine (**1a**) and 3-chloropropiophenone (**1b**) in 2-MeTHF using Cs_2CO_3 as a robust base at different temperatures and observed by TLC. After 6h, the reaction was completed and **3aa** was isolated in good yield at 70 °C. To improve the yield further, several common solvents such as THF, DCE, MeCN, 1,4-dioxane, toluene, DMF, DMSO, and EtOH were tested for this reaction. Most of the solvents gave moderate to good yields. Thus,

considering the yield, 2-MeTHF was best solvent for this reaction at 70 °C (entry 3). Further, we screened other bases such as DBU, DBN, DABCO, DEIPA, NEt_3, K_2CO_3, NaOH, KOH, and *t*-BuOK. Therefore, considering the yield of the desired product **3aa**, Cs_2CO_3 in 2-MeTHF at 70°C is the best-optimized condition for the reaction. It should be noted that using DABCO as a base, we isolated MBH adduct **4aa** instead of **3aa**.

2.2 Substrate Scope

Having optimal reaction parameters in hand, we demonstrated the substrate scope of the reaction by taking various N-sulfonyl ketimines and 3-chloropropiophenones in 2-MeTHF at 70 °C in the presence of Cs_2CO_3 under present conditions. The results are included in Table 2. It was found that a variety of aryl-substituted 3-chloropropiphenones have converted into vinyl ketones which were attacked by several 4-methyl-N-(1-arylethylidene)benzenesulfonamides as carbonucleophiles under present basic conditions, followed by hydrolysis of imine bonds. All of the reactions afforded the corresponding symmetrical and unsymmetrical 1,5-diarylpentane-1,5-diones in good to high yields. The current method tolerates a bunch of functionalities Me, MeO, Cl, Br, I, C=O, F, thiophene, cyclohexyl etc.



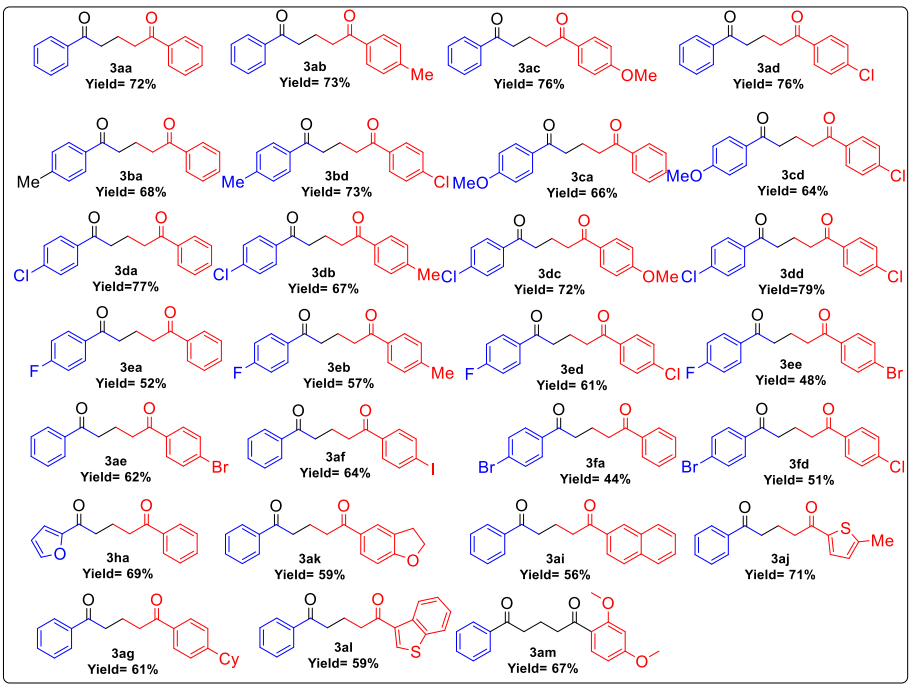
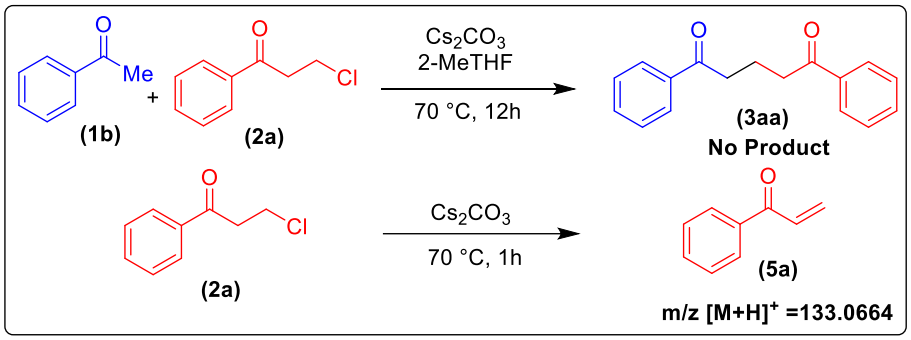


Table 2: Substrate Scope.

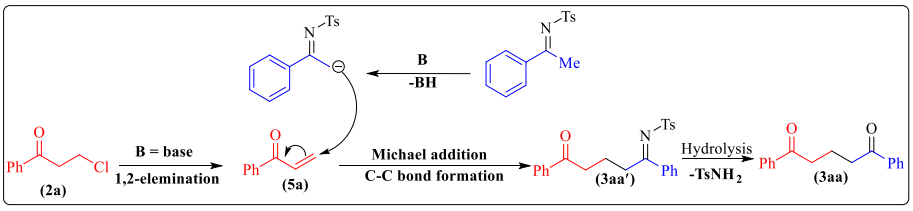
Control experiments were carried out to gain insight the pathway of the reaction (**Scheme 8**). Notably, the reaction between acetophenone (**1b**) and 3-chloropropiophenone (**2a**) was carried out under the best-optimized conditions, we didn't get any desired product **3aa**. Moreover, 3-chloropropiophenone (**2a**) was heated with Cs_2CO_3, at 70 °C, it led to vinyl ketone (**5a**).



Scheme 6: Control experiments

2.3 Plausible Reaction Mechanism

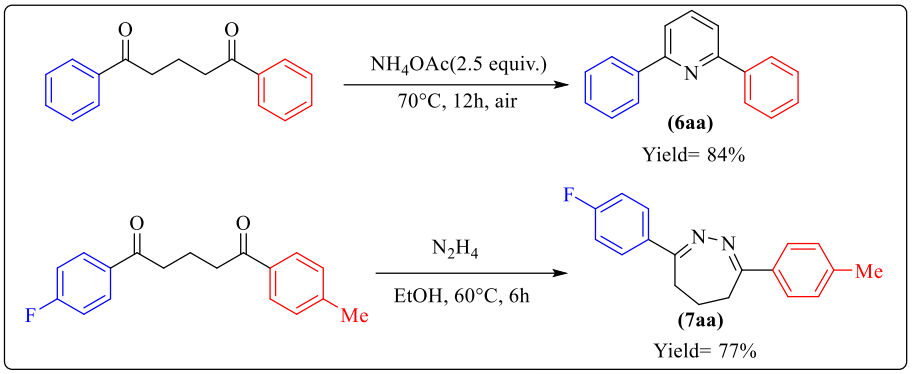
Based on the above control experimental data the plausible mechanism is drawn in **Scheme 9**. Initially, 3-chloropropiophenone undergoes elimination and thereby forms vinyl ketone (**5a**) which then undergoes Michael addition by the nucleophile **A**, generated from N-sulfonyl ketimine, and forms the intermediate **3aa´** (4-methyl-N-(5-oxo-1,5-diphenylpentylidene)benzenesulfonamide). Then intermediate **3aa´** undergoes hydrolysis to form the desired product **3aa** (1,5-diphenylpentane-1,5-dione).



Scheme 7: Reaction pathway for the synthesis of 1,5-diketone derivatives.

2.4 Applications:

Here we have shown some applications of 1,5-diketone derivatives which provide good yields.



Scheme 8: Application of 1,5-diketones.

Chapter 3

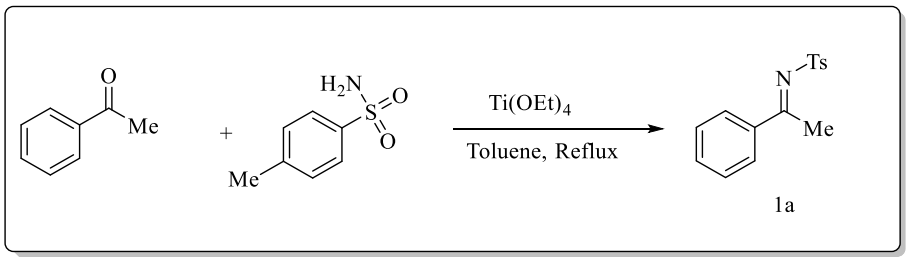
3. EXPERIMENTAL WORK

3.1 Required Materials and Instrumentation:

All the chemicals were bought from Sigma Aldrich and Spectrochem. All the reactions were in a closed tube and observed by TLC using Merck 60 F254 pre-coated silica gel plate and the product was apprehended by UV detection. Silica gel (60-120 mesh) was used for column chromatography. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) data were taken in $CDCl_3$ solvent using Bruker Advance 500. NMR data processed by MestReNova.

3.2 Standard procedure for the synthesis:

3.2.1 Synthesis of N-sulfonyl ketimines:

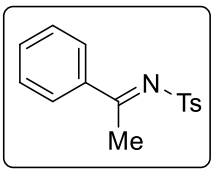


Scheme 9: Synthesis of N-Sulfonyl ketimines **(1a).**

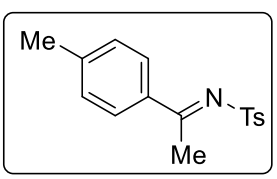
Firstly, a mixture of acetophenone (0.97 mL, 8.33 mmol) and p-toluene sulfonamide (1.71 gm, 10 mmol) were taken in a double-neck 250 mL round bottom flask and then brought together with a water-cooled reflux condenser. A balloon infused with argon was put over the top of the condenser. On the other side in a 50 mL beaker, toluene (10 mL) was taken and titanium ethoxide (1.9 gm, 8.33 mmol) dissolved in it. After that, the toluene-titanium solution was added to the mixture (inert condition) under rapid stirring at room temperature. Then the mixture is stirred and refluxed. After 6 hours, it was permitted to settle down to rt and then it was quenched with 5-10 mL of $NaHCO_3$ solution. The mixture was filtered and the workup of the filtrate was done by ethyl acetate. The organic layer was dried by Na_2SO_4. Column

chromatography (1:9; ethyl acetate/hexane) was used to purify the crude product. [7,8]

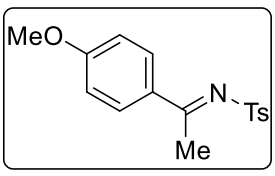
4-Methyl-N-(1-phenylethylidene)benzenesulfonamide (1aa): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.98 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 179.8, 143.5, 138.7, 137.5, 133.2, 129.5, 128.6, 128.3, 127.1, 21.6, 21.1 ppm.



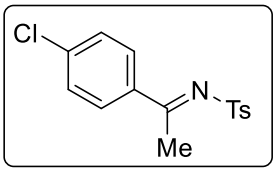
4-Methyl-N-(1-(4-methylphenyl)ethylidene)benzenesulfonamide (1ab): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.95 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 179.7, 144.2, 143.4, 138.9, 134.8, 129.4, 128.4, 129.3, 127.0, 21.61, 21.0 ppm.



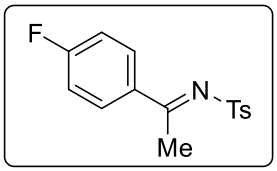
N-(-1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonamide (1ac) : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 3.84 (s, 3H), 2.93 (s, 3H), 2.43 (s, 3H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 178.7, 163.9, 143.3, 139.0, 130.6, 130.6, 129.4, 126.9, 113.9, 55.5, 21.5, 20.7 ppm.



N-(-1-(4-chlorophenyl)ethylidene)-4-methylbenzenesulfonamide (1ad): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.36 (m, 4H), 2.96 (s, 3H), 2.45 (s, 3H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 178.4, 143.7, 139.7, 138.4, 135.9, 129.6, 129.5, 128.9, 127.1, 21.6, 21.0 ppm.

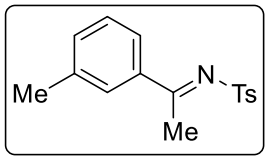


N-(-1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonamide



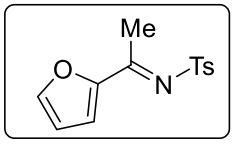
(1ae): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96-7.89 (m, 4H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.08 (m, 2H), 2.96 (s, 3H), 2.44 (s, 3H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$) δ** 178.2, 165.9 (d, *J* = 255.6 Hz), 143.6, 138.6, 133.7 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 9.2 Hz), 129.5, 127.1, 115.8 (d, *J* = 22.0 Hz), 21.6, 21.0 ppm.

4-Methyl-N-(1-(3-methylphenyl)ethylidene)benzenesulfonamide



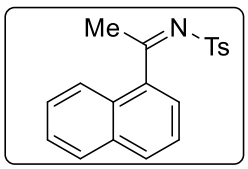
(1af): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 6.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 3H), 7.31-7.27 (m, 1H), 2.97 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 180.2, 143.5, 138.7, 138.4, 137.6, 134.0, 129.4, 128.7, 128.5, 127.1, 125.5, 21.6, 21.3 ppm.

N-(-1-(furan-2-yl)ethylidene)-4-methylbenzenesulfonamide (1ag): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.62 (s, 1H),



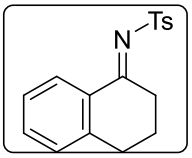
7.32 (d, *J* = 8.0 Hz, 2H), 7.26-7.23 (m, 1H), 6.56-6.53 (m, 1H), 2.85 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 168.2, 152.3, 147.9, 143.5, 138.5, 129.4, 127.1, 119.0, 113.1, 21.5, 19.7 ppm.

4-Methyl-N-(1-(naphthalen-1-yl)ethylidene)benzenesulfonamide



(1ah): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.88-7.85 (m, 1H), 7.63-7.59 (m, 1H), 7.54-7.45 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.12 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 184.0, 143.8, 138.3, 137.7, 133.8, 131.6, 129.5, 129.5, 128.6, 127.4, 127.2, 126.4, 126.3, 124.9, 124.7, 26.0, 21.6 ppm.

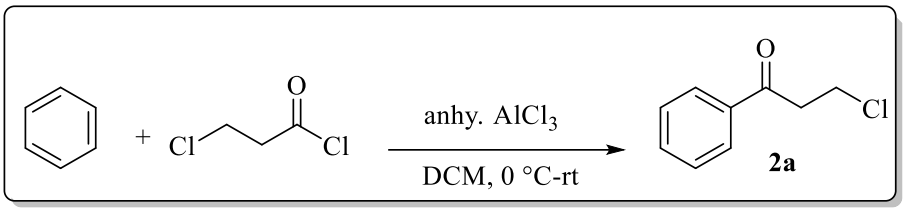
N-(3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-



methylbenzenesulfonamide (1ai): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.45-7.40 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 3.41 (s, 2H), 2.89 (s, 2H), 2.44 (s, 3H), 2.09-1.99 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 179.9, 144.3, 143.3, 139.0, 133.7, 131.9, 129.4, 129.0, 127.7, 126.9, 126.7, 33.0, 29.3, 22.4, 21.6 ppm.

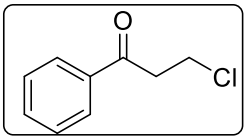
3.2.2 Synthesis of 3-chloropropiophenones (2a):

Firstly, in a 250 mL double-neck round bottom flask anhydrous $AlCl_3$ (6.14 gm, 46.15 mmol) was taken in DCM (10 mL) and connected to a balloon filled with argon. The atmosphere inside the flask made it inert. After that 3-chloropropionyl chloride (3.98 mL, 42.31 mmol) was added to anhydrous $AlCl_3$ in stirring condition at 0 °C and then benzene (3.43 mL, 46.15 mmol) was added to the mixture under stirring condition for 3 hours and allowed the reaction to come to rt. After 3 hours the reaction was checked using a TLC plate. Then the workup was done using DCM. The DCM layer was dried using Na_2SO_4 and filtered. The filtrate was concentrated using a rotary evaporator to yield crude and purified using column chromatography. (**Scheme: 12)** [9,10]



Scheme 10: Synthesis of 3-chloropropiophenone.

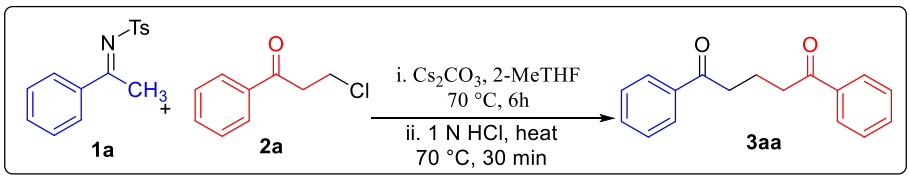
3-Chloro-1-phenylpropan-1-one (2aa): ^{1}H NMR (500 MHz, $CDCl_3$)



δ 7.99-7.92 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 196.72, 136.3, 133.5, 128.7, 128.0, 41.2, 38.7 ppm.

3.2.3 One-pot procedure for the synthesis of 1,5-diketones:

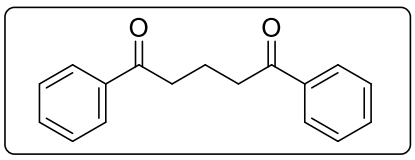
In a dry closed test tube, mixture of 4-methyl-N-(1-phenylethylidene) benzene sulfonamide (50 mg, 0.183 mmol, 1.0 equivalent), 3-chloropropiophenone (31 mg, 0.183 mmol, 1.0 equivalent), cesium carbonate (50 mg, 0.220 mmol) and 2-MeTHF (0.5 mL) taken and then it stirred under 70°C for 12h. The completion of the reaction judged by TLC, afterwards, the reaction was quenched by 1 N HCl and stirred for 30 min in 70°C. Then the reaction mixture was extracted with ethyl acetate (30 mL), washed with brine and dried using Na_2SO_4. After that, concentrated using a rotary evaporator under reduced pressure to yield the crude, which was purified using column chromatography over silica gel (60-120 mesh) with EtOAc/hexane (1:9, v/v). ^1H and ^{13}C data were use to characterize the product with MastReNova.



Scheme 11: Synthesis of 1,5-diketones **(3aa).**

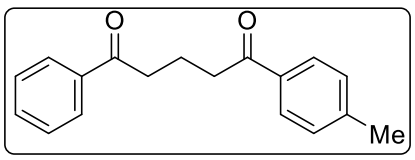
4.2. Data of all synthesized compounds

1,5-Diphenylpentane-1,5-dione (3aa): White solid; mp 58-60 °C; yield



= 72%; R_f = 0.69 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.98 (d, *J* = 7.6 Hz, 2H), 7.59-7.52 (t, J= 7.2Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 3.12 (t, *J* = 6.9 Hz, 4H), 2.24-2.18 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.8, 136.8, 133.0, 128.6, 128.0, 37.6, 18.7 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_2$ 253.1223, found 253.1210.

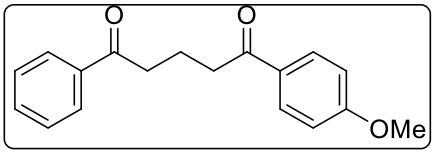
1-Phenyl-5-(4-methylphenyl)pentane-1,5-dione (3ab): White solid;



mp 64-66 °C; yield = 73%; R_f = 0.71 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.00-7.96 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.45 (t,

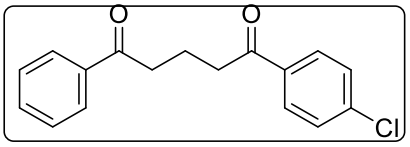
J = 7.7 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.13-3.06 (m, 2H), 2.40 (s, 3H), 2.22-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 199.5, 143.8, 136.8, 134.4, 133.0, 129.2, 128.6, 128.2, 128.0, 37.6, 37.5, 21.6, 18.8 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}O_2$ 267.1380, found 267.1380.

1-(4-Methoxyphenyl)-5-phenylpentane-1,5-dione (3ac): White solid;



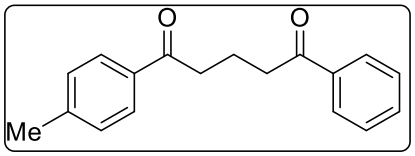
mp 78-80 °C; yield = 76%; R_f = 0.61 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.02-7.93 (m, 4H), 7.58-7.52 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 3H), 3.11 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.22-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 198.4, 163.4, 136.8, 133.0, 130.3, 129.9, 128.6, 128.0, 113.7, 55.4, 37.7, 37.2, 18.9 ppm; HRMS (ESI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{18}O_3$ 305.1148, found 305.1120.

1-(4-Chlorophenyl)-5-phenylpentane-1,5-dione (3ad): White solid;



mp 70-72 °C; yield = 76%; R_f = 0.67 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.97 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48-7.40 (m, 4H), 3.11 (t, *J* = 6.9 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.22-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 198.6, 139.4, 136.8, 135.1, 133.1, 129.5, 128.9, 128.6, 128.0, 37.6 37.4, 18.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}ClO_2$ 289.0833, found 289.0832.

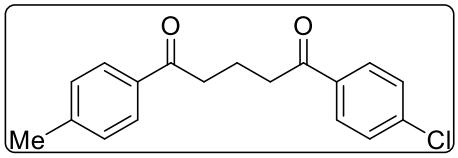
1-Phenyl-5-(4-methylphenyl)pentane-1,5-dione (3ba): White solid;



mp 64-66 °C; yield = 68%; R_f = 0.71 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.00-7.96 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.13-3.06 (m, 2H), 2.40 (s, 3H), 2.22-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 199.5, 143.8, 136.8, 134.4, 133.0, 129.2, 128.6, 128.2, 128.0, 37.6, 37.5,

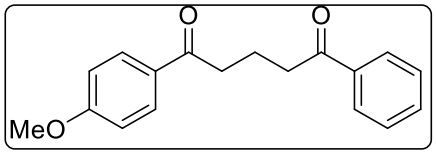
21.6, 18.8 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}O_2$ 267.1380, found 267.1378.

1-(4-Chlorophenyl)-5-(4-methylphenyl)pentane-1,5-dione (3bd):



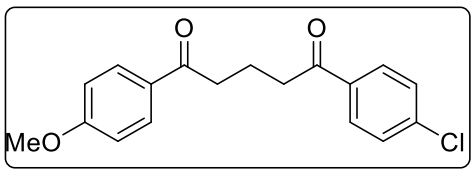
White solid; mp 74-76 °C; yield = 73%; R_f = 0.68 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.45-7.41 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.08 (m, 4H), 2.41 (s, 3H), 2.21-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.4, 198.7, 143.9, 139.4, 135.1, 134.3, 129.5, 129.3, 128.9, 128.1, 37.6, 37.3, 21.6, 18.7 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}ClO_2$ 301.0990, found 301.1010.

1-(4-Methoxyphenyl)-5-phenylpentane-1,5-dione (3ca): White solid;



mp 80-82 °C; yield = 66%; R_f = 0.61 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.01-7.93 (m, 4H), 7.57-7.52 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 3H), 3.11 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.24-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 198.4, 163.4, 136.8, 133.0, 130.3, 129.9, 128.6, 128.0, 113.7, 55.4, 37.7, 37.2, 18.9 ppm; HRMS (ESI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{18}O_3$ 305.1148, found 305.1120.

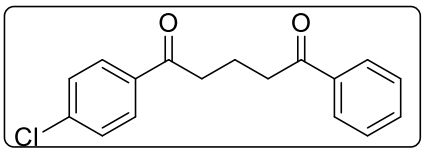
1-(4-Chlorophenyl)-5-(4-methoxyphenyl)pentane-1,5-dione (3cd):



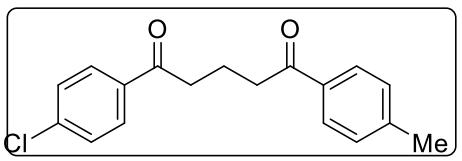
White solid; mp 86-87 °C; yield = 64%; R_f = 0.60 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.96 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.10-3.03 (m, 4H), 2.22-2.13 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.7, 198.3, 163.5, 139.4, 135.1, 130.3, 129.9, 129.5, 128.9, 113.7, 55.4, 37.6, 37.1, 18.8

ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}ClO_3$ 317.0939, found 317.0938.

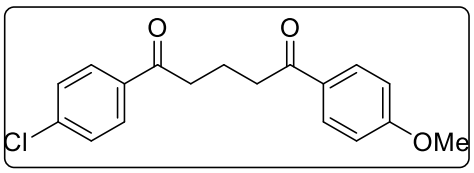
1-(4-Chlorophenyl)-5-phenylpentane-1,5-dione (3da): White solid; mp 70-72 °C; yield = 77%; R_f = 0.67 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.97 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48-7.40 (m, 4H), 3.11 (t, *J* = 6.9 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.21-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 198.6, 139.4, 136.8, 135.1, 133.1, 129.5, 128.9, 128.6, 128.0, 37.6 37.4, 18.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}ClO_2$ 289.0833, found 289.0832.



1-(4-Chlorophenyl)-5-(4-methylphenyl)pentane-1,5-dione(3db): White solid; mp 68-70 °C; yield = 67%; R_f = 0.68 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.45-7.41 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.11-3.05 (m, 4H), 2.41 (s, 3H), 2.21-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.4, 198.7, 143.9, 139.4, 135.1, 134.3, 129.5, 129.3, 128.9, 128.1, 37.6, 37.3, 21.6, 18.7 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}ClO_2$ 301.0990, found 301.1010.

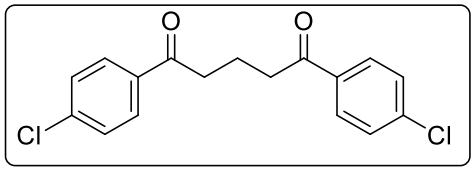


1-(4-Chlorophenyl)-5-(4-methoxyphenyl)pentane-1,5-dione (3dc): White solid; mp 86-88 °C; yield = 72%; R_f = 0.60 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.96 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.10-3.03 (m, 4H), 2.22-2.13 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.7, 198.3, 163.5, 139.4, 135.1, 130.3, 129.9, 129.5, 128.9, 113.7, 55.4, 37.6, 37.1, 18.8 ppm; HRMS



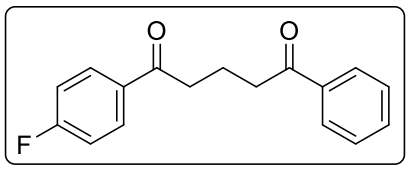
(ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}ClO_3$ 317.0939, found 317.09365.

1,5-Bis(4-chlorophenyl)pentane-1,5-dione (3dd): White solid; mp 76-78 °C; Yield = 79%; R_f = 0.65 (Ethyl acetate/ Hexane = 1:9); ^{1}H NMR



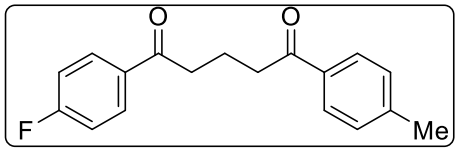
(500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 4H), 7.44 (d, *J* = 8.6 Hz, 4H), 3.09 (t, *J* = 6.9 Hz, 4H), 2.18 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.5, 139.6, 135.1, 129.4, 128.9, 37.4, 18.5 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}Cl_2O_2$ 321.0444; found 321.0440.

1-(4-Fluorophenyl)-5-phenylpentane-1,5-dione (3ea): White solid;



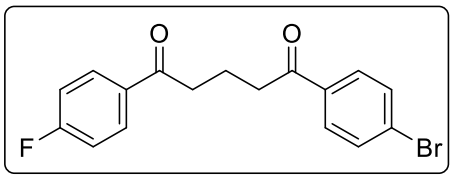
mp 60-62 °C; yield = 52%; R_f = 0.68 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.04-7.96 (m, 4H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 8.5 Hz, 2H), 3.15-3.06 (t, *J* = 6.9 Hz, 2H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.23-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 198.2, 165.7 (d, J_{C-F} = 254.6 Hz), 136.8, 133.2 (d, J_{C-F} = 3.2 Hz), 133.1 (s), 130.7 (d, J_{C-F} = 9.3 Hz), 128.6, 128.0, 115.6 (d, J_{C-F} = 21.7 Hz), 37.5, 37.5, 18.6 ppm; *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}FO_2$ 271.1129, found 271.1133.

1-(4-Fluorophenyl)-5-(4-methylphenyl)pentane-1,5-dione (3eb):



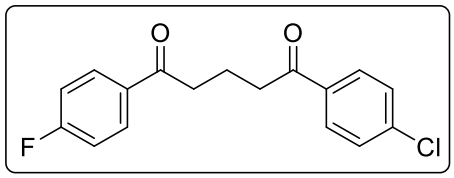
White solid; mp 66-68 °C; yield = 57%; R_f = 0.69 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.03-7.96 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.14-7.06 (m, 2H), 3.11-3.02 (m, 4H), 2.39 (s, 3H), 2.20-2.12 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.4, 198.2, 165.7 (d, *J* = 254.5 Hz), 143.8, 134.3, 133.3 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 9.3 Hz), 129.2, 128.1, 115.6 (d, *J* = 21.9 Hz), 37.5, 37.3, 21.6, 18.7 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}FO_2$ 285.1285, found 285.1287.

1-(4-Bromophenyl)-5-(4-fluorophenyl)pentane-1,5-dione (3ee):



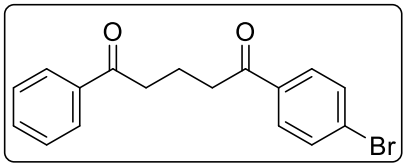
White solid; mp 70-72 °C; yield = 48%; R_f = 0.69 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.02-7.96 (m, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.14-7.07 (m, 2H), 3.10-3.03 (m, 4H), 2.20-2.11 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.7, 198.0, 165.7 (d, *J* = 254.8 Hz), 135.5, 133.2 (d, *J* = 3.0 Hz), 131.9, 130.6 (d, *J* = 9.3 Hz), 129.5, 128.2, 115.7 (d, *J* = 21.6 Hz), 37.4, 37.3, 18.5 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}{}^{79}BrO_2$ 349.0234, found 349.0236; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}{}^{81}BrO_2$ 351.0214, found 351.0201.

1-(4-chlorophenyl)-5-(4-fluorophenyl)pentane-1,5-dione (3ed):



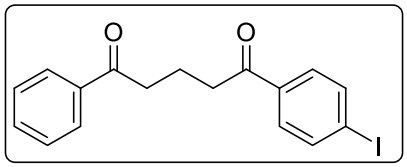
White solid; mp 74-76 °C; yield = 48%; R_f = 0.68 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.03-7.98 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 3.11-3.06 (m, 4H), 2.21-2.15 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.5, 198.1, 165.7 (d, *J* = 254.8 Hz), 139.5, 135.1, 133.2 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.2 Hz), 129.4, 128.9, 115.7 (d, *J* = 22.0 Hz), 37.5, 37.4, 18.5 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for 305.0739 found 305.0766.

1-(4-Bromophenyl)-5-phenylpentane-1,5-dione (3ae): White solid;



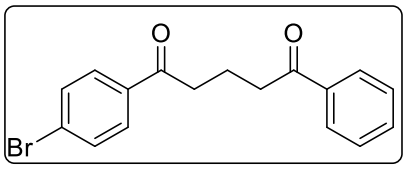
mp 68-70 °C; yield = 62%; R_f = 0.71 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.92-7.87 (m, 2H), 7.78-7.74 (m, 2H), 7.54-7.46 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.14-2.08 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 198.8, 136.8, 135.5, 133.1, 131.9, 129.6, 128.6, 128.2, 128.0, 37.5, 37.4, 18.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrO_2$ 331.0328, found 331.0324.

1-(4-Iodophenyl)-5-phenylpentane-1,5-dione (3af): White solid; mp



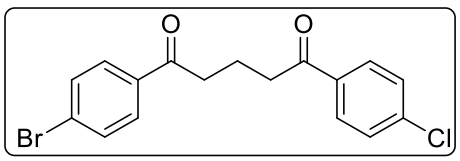
66-68 °C; yield = 64%; R_f = 0.73 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.99-7.96 (m, 2H), 7.83-7.80 (m, 2H), 7.70-7.66 (m, 2H), 7.58-7.53 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.11 (t, *J* = 6.9 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.22-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 199.1, 137.9, 136.8, 136.0, 133.1, 129.5, 128.6, 128.0, 101.0, 37.5, 37.4, 18.5 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}{}^{79}BrO_2$ 331.0328, found 331.0321; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}{}^{81}BrO_2$ 333.2287, found 333.2289.

1-(4-Bromophenyl)-5-phenylpentane-1,5-dione (3fa): White solid;



mp 68-70 °C; yield = 44%; R_f = 0.71 (Ethyl acetate/ Hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.92-7.87 (m, 2H), 7.78-7.74 (m, 2H), 7.54-7.46 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.14-2.07 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.7, 198.8, 136.8, 135.5, 133.1, 131.9, 129.6, 128.6, 128.2, 128.0, 37.5, 37.4, 18.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}{}^{79}BrO_2$ 331.0328, found 331.0321; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}{}^{81}BrO_2$ 333.2287, found 333.2289.

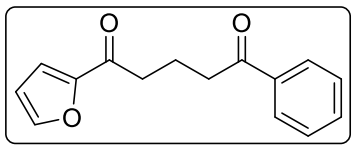
1-(4-Bromophenyl)-5-(4-chlorophenyl)pentane-1,5-dione (3fd):



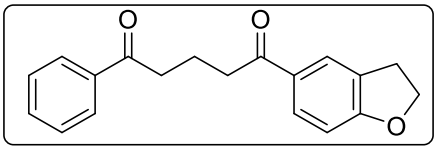
White solid; mp 72-74 °C; yield = 51%; R_f = 0.70 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.10-3.05 (m, 4H), 2.21-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 198.7, 198.5, 139.5, 135.5, 135.1, 131.9, 129.6, 129.4, 128.9, 128.3, 37.4, 18.4 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$

calcd for $C_{17}H_{14}{}^{79}BrClO_2$ 364.9938, found 368.9960; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}{}^{81}BrClO_2$ 365.9845, found 365.9821.

1-(Furan-2-yl)-5-phenylpentane-1,5-dione (3ha): White solid; mp 72-74 °C; yield = 69%; R_f = 0.65 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, CDCl$_3$) δ** 8.00-7.95 (m, 2H), 7.58-7.53 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 3.5 Hz, 1H), 6.54-6.51 (m, 1H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.1 Hz, 2H), 2.22-2.14 (m, 2H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$) δ** 199.7, 189.0, 152.6, 146.3, 136.8, 133.0, 128.6, 128.0, 117.1, 112.2, 37.5, 37.4, 18.6 ppm; *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}O_3$ 243.1016, found 213.1004.

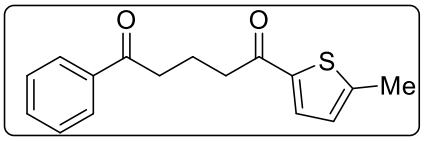


1-(2,3-Dihydrobenzofuran-5-yl)-5-phenylpentane-1,5-dione (3ak): White solid; mp 82-84 °C; yield = 59%; R_f = 0.66 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.94-7.85 (m, 2H), 7.78 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.51-7.43 (m, 1H), 7.40-7.34 (m, 2H), 6.73-6.69 (m, 1H), 4.60-4.53 (m, 2H), 3.18-3.11 (m, 2H), 3.05-2.99 (m, 2H), 2.98-2.93 (m, 2H), 2.14-2.06 (m, 2H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$) δ** 199.9, 198.3, 164.3, 136.8, 133.0, 130.3, 130.0, 128.6, 128.0, 127.6, 125.4, 72.1, 37.7, 37.3, 29.0, 19.0 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}O_3$ 295.1329, found 295.1314.

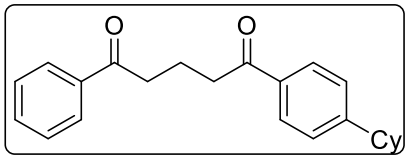


1-(Naphthalen-2-yl)-5-phenylpentane-1,5-dione (3ai): White solid; mp 72-73 °C; yield = 56%; R_f = 0.77 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, CDCl$_3$) δ** 8.41 (s, 1H), 7.98-7.83 (m, 4H), 7.81-7.74 (m, 2H), 7.47 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.21-2.13 (m, 2H) ppm; **^{13}C NMR (125 MHz, CDCl$_3$) δ** 199.9, 199.8, 136.8, 135.6, 134.1, 133.1, 132.5, 129.8, 129.6, 128.6, 128.4, 128.1, 127.7, 126.7, 123.8, 37.6, 37.6, 18.8 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}O_2$ 303.1080, found 303.1081.

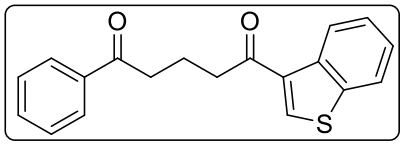
1-(5-Methylthiophen-2-yl)-5-phenylpentane-1,5-dione (3aj): White solid; mp 70-72 °C; yield = 71%; R_f = 0.69 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.89 (d, *J* = 7.3 Hz, 2H), 7.49-7.44 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.72-6.69 (m, 1H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 2.10 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.8, 192.5, 149.6, 142.0, 136.8, 133.0, 132.6, 128.6, 128.0, 126.8, 37.8, 37.5, 19.2, 16.0 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{16}H_{16}O_2S$ 273.0944, found 273.0941.



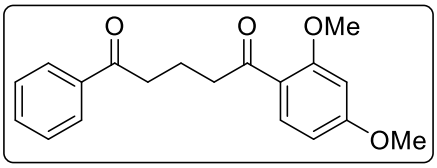
1-(4-Cyclohexylphenyl)-5-phenylpentane-1,5-dione (3ag): White solid; mp 62-64 °C; yield = 61%; R_f = 0.72 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.00-7.96 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.13-3.07 (m, 4H), 2.25-2.15 (m, 2H), 1.94-1.72 (m, 6H), 1.50-1.34 (m, 5H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 199.5, 153.7, 136.8, 134.7, 133.0, 128.6, 128.3, 128.0, 127.0, 44.6, 37.6, 37.5, 34.1, 26.7, 26.0, 18.8 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{23}H_{26}O_2$ 335.2006, found 335.2021.



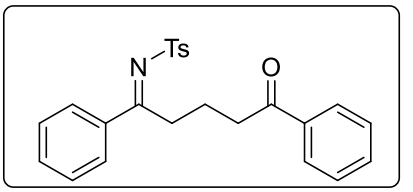
1-(Benzo[*b*]thiophen-3-yl)-5-phenylpentane-1,5-dione (3al): White solid; mp 76-78 °C; yield = 59%; R_f = 0.70 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.78 (d, *J* = 8.2 Hz, 1H), 8.40 (s, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.52-7.39 (m, 4H), 3.19-3.11 (m, 4H), 2.30-2.22 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.9, 195.2, 139.8, 137.0, 136.8, 136.6, 135.0, 133.1, 128.6, 128.0, 125.8, 125.6, 125.4, 122.2, 39.2, 37.5, 19.2 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{19}H_{16}O_2S$ 309.0944, found 309.0924.



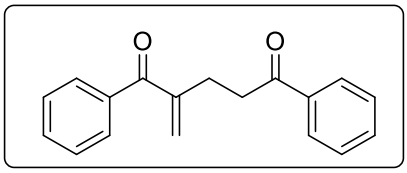
1-(2,4-Dimethoxyphenyl)-5-phenylpentane-1,5-dione (3am): White solid; mp 94-96 °C; yield = 67%; R_f = 0.41 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.98 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.54-6.50 (m, 1H), 6.45-6.43 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.10-3.04 (m, 4H), 2.17-2.10 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 200.3, 199.9, 164.4, 160.8, 136.9, 132.9, 132.6, 128.5, 128.1, 121.0, 105.1, 98.3, 55.5, 55.4, 42.6, 38.0 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}O_4$ 313.1434, found 313.1437.



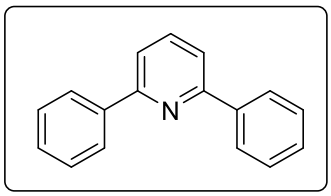
4-Methyl-N-(5-oxo-1,5-diphenylpentylidene (3aa´): White solid**;** yield = 23%; R_f = 0.63 (ethyl acetate/hexane = 1:9**); ^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.05 (d, *J* = 5.0 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.60-7.51 (m, 2H), 7.51-7.41 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.53 (s, 2H), 3.23 (t, *J* = 6.2 Hz, 2H), 2.45 (s, 3H), 2.27-2.18 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.4, 183.0, 143.5, 138.8, 136.7, 133.2, 129.4, 128.9, 128.8, 128.8, 128.5, 128.0, 127.1, 38.0, 33.5, 22.8, 21.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}NO_3S$ 406.1471, found 406.1468.



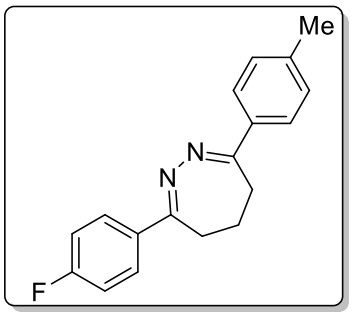
2-Methylene-1,5-diphenylpentane-1,5-dione (4aa): White solid; R_f = 0.74 (ethyl acetate/hexane = 1:9); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.00 – 7.96 (m, 2H), 7.76-7.72 (m, 2H), 7.59-7.51 (m, 2H), 7.45 (m, 4H), 5.97 (s, 1H), 5.68 (s, 1H), 3.25 (t, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 199.29, 198.1, 146.8, 137.7, 136.7, 133.1, 132.2, 129.5, 128.6, 128.2, 128.1, 127.3, 37.2, 27.4 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for C18H16O2 265.1223, found 263.1210.



2,6-Diphenylpyridine (6aa): Crystalline white solid; yield = 84%; mp 92-94 °C; R_f = 0.45 (ethyl acetate/hexane = 1:19); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.07 (d, *J* = 7.3 Hz, 4H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.37-7.32 (m, 2H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 156.8, 139.5, 137.5, 129.0, 128.7, 127.0, 118.6 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}N$ 232.1127, found 232.1133.



3-(4-Fluorophenyl)-7-(4-methylphenyl)-5,6-dihydro-4*H*-1,2-diazepine(7aa): White solid; Yield = 77%; mp 68-70 °C; R_f = 0.34 (ethyl acetate/hexane = 1:10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.87 (m, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.15-7.09 (m, 2H), 2.71-2.62 (m, 4H), 2.50-2.44 (m, 2H), 2.40 (s, 3H) ppm; **^{13}C NMR (125 MHz, $CDCl_3$) δ** 164.8, 162.8, 159.0 (d, *J* = 121.0 Hz), 140.2, 134.0, 133.2 (d, *J* = 3.1 Hz), 129.4, 128.7 (d, *J* = 8.4 Hz), 126.7, 115.6 (d, *J* = 21.8 Hz), 32.7, 26.5, 26.4, 21.3 ppm; HRMS (ESI-TOF): *m/z* $[M+H]^+$ calcd for 289.1449, found 289.1458.



Conclusion

Finally, we have developed a simple, one-pot synthesis of symmetrical and unsymmetrical 1,5-diarylpropane-1,5-diones from several N-sulfonyl ketimines and 3-chloropropiophenones in the presence of Cs_2CO_3. The method has many positive features such as good yields, transition metal-free and good substrate scope.

Appendix A

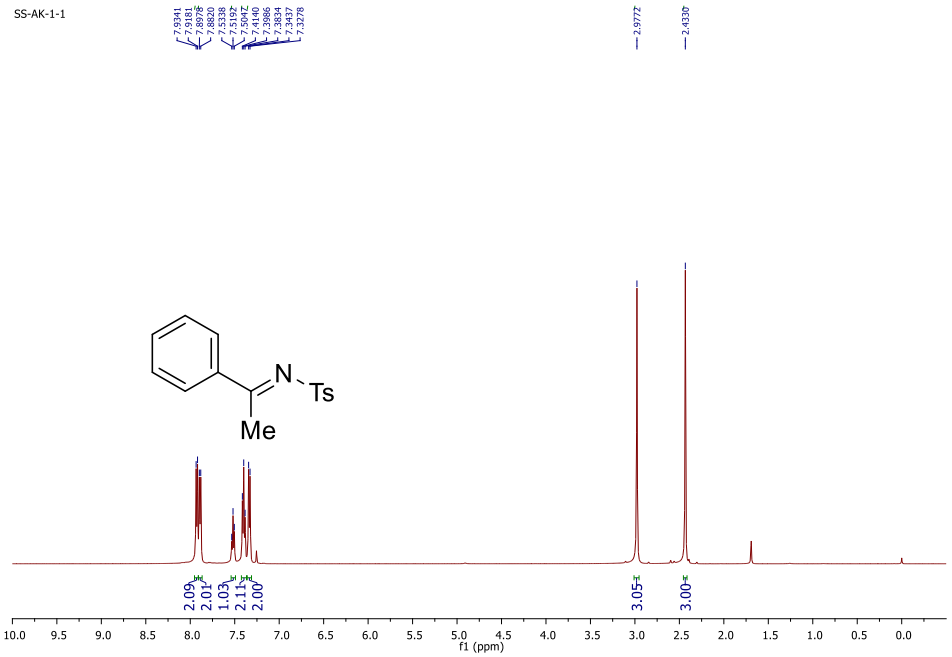


Figure 1: ^{1}H NMR spectrum (500MHz) of **1aa** in $CDCl_3$

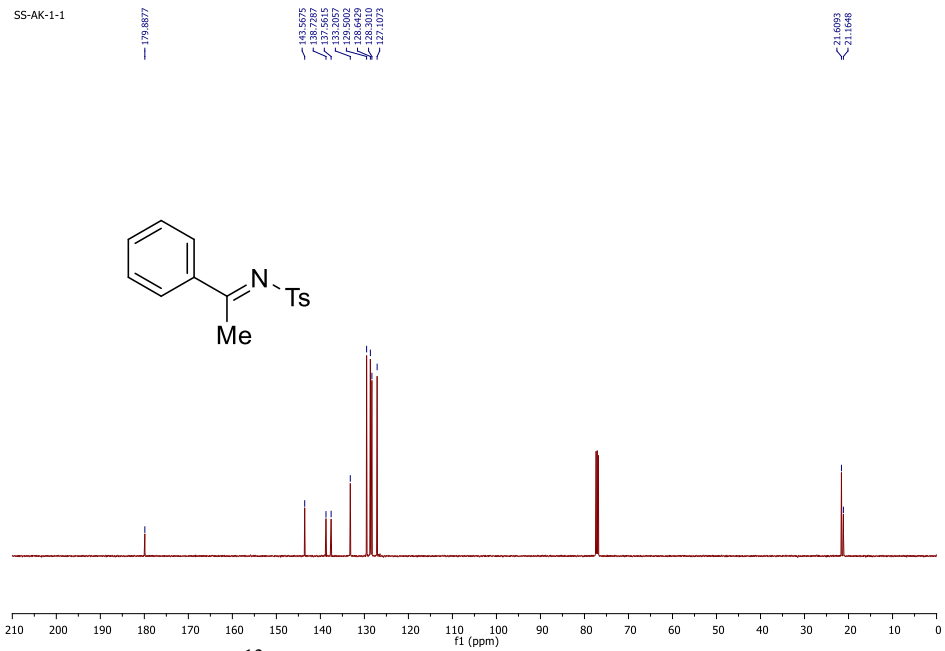


Figure 2: ^{13}C NMR spectrum (125MHz) of **1aa** in $CDCl_3$

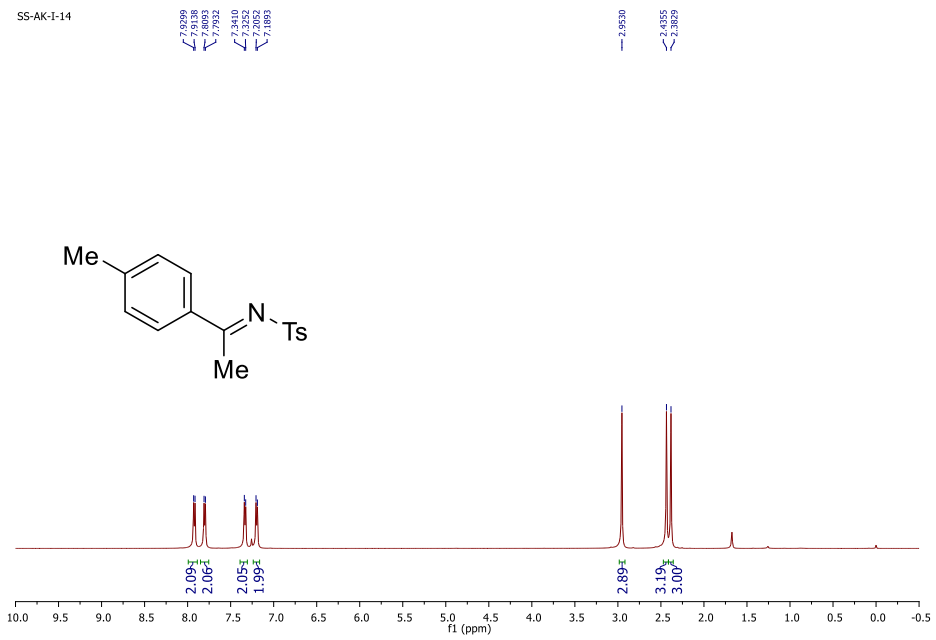


Figure 3: ^{1}H NMR spectrum (500MHz) of **1ab** in $CDCl_3$

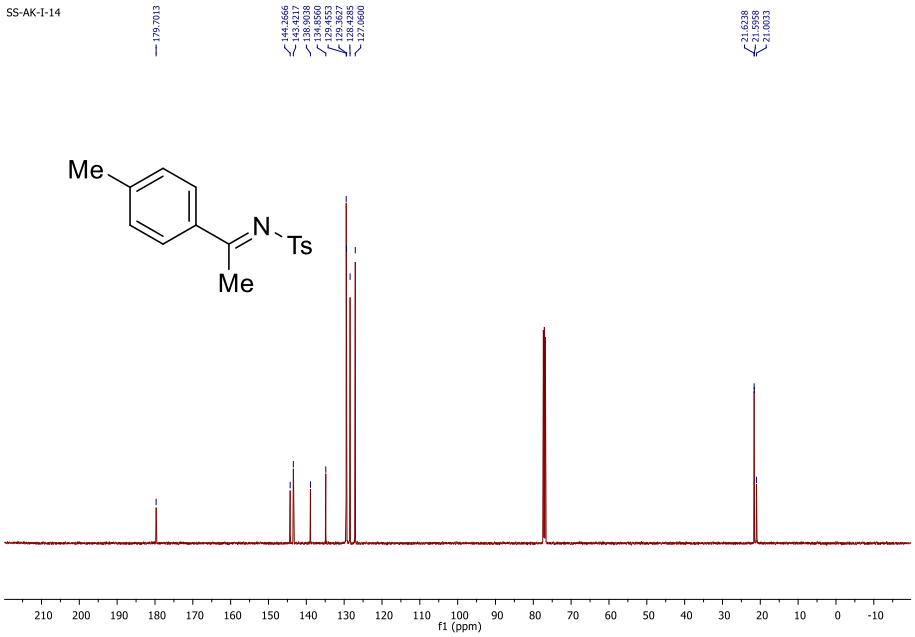


Figure 4: ^{13}C NMR spectrum (125MHz) of **1ab** in $CDCl_3$

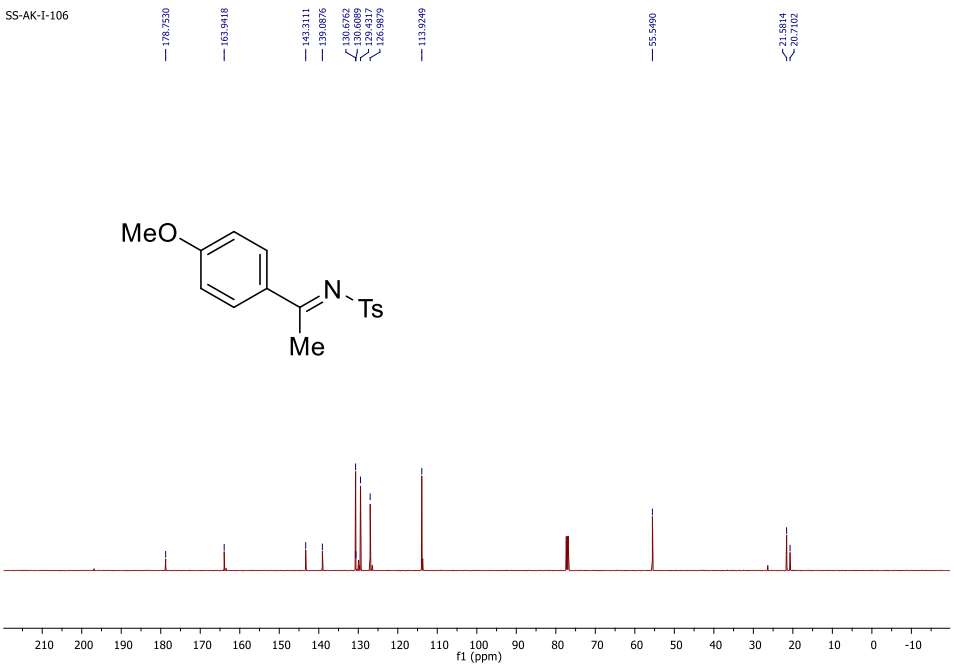


Figure 5: ^{1}H NMR spectrum (500MHz) of **1ac** in $CDCl_3$

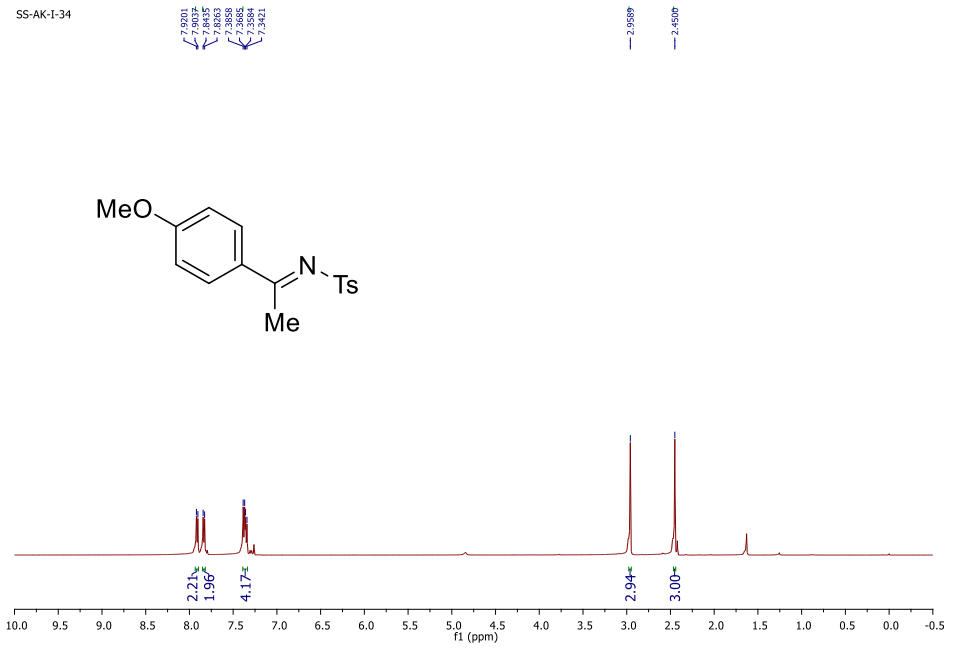


Figure 6: ^{13}C NMR spectrum (125MHz) of **1ac** in $CDCl_3$

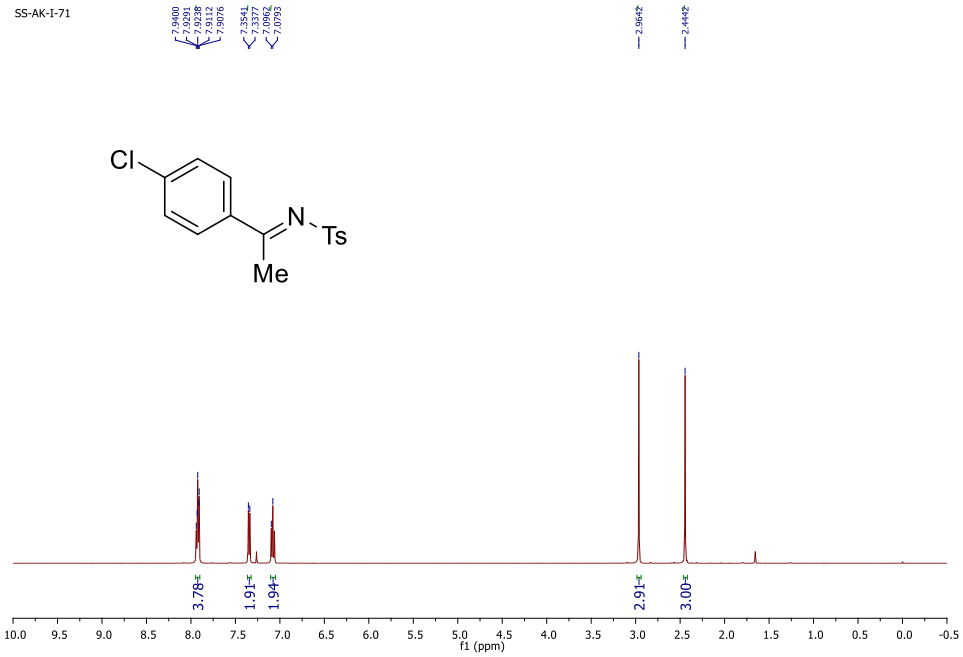


Figure 7: ^{1}H NMR spectrum (500MHz) of **1ad** in $CDCl_3$

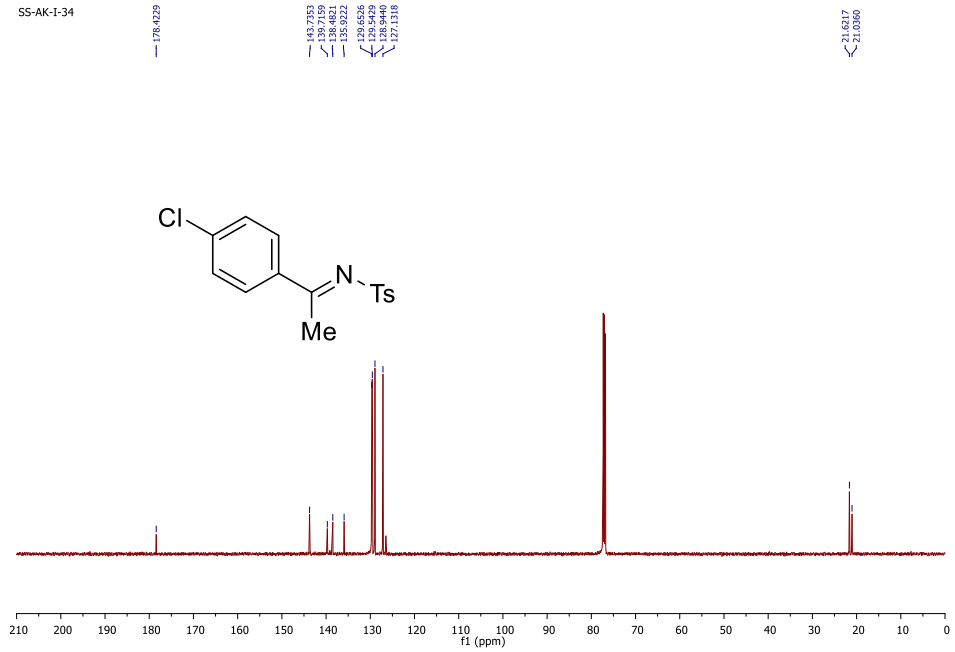


Figure 8: ^{13}C NMR spectrum (125MHz) of **1ad** in $CDCl_3$

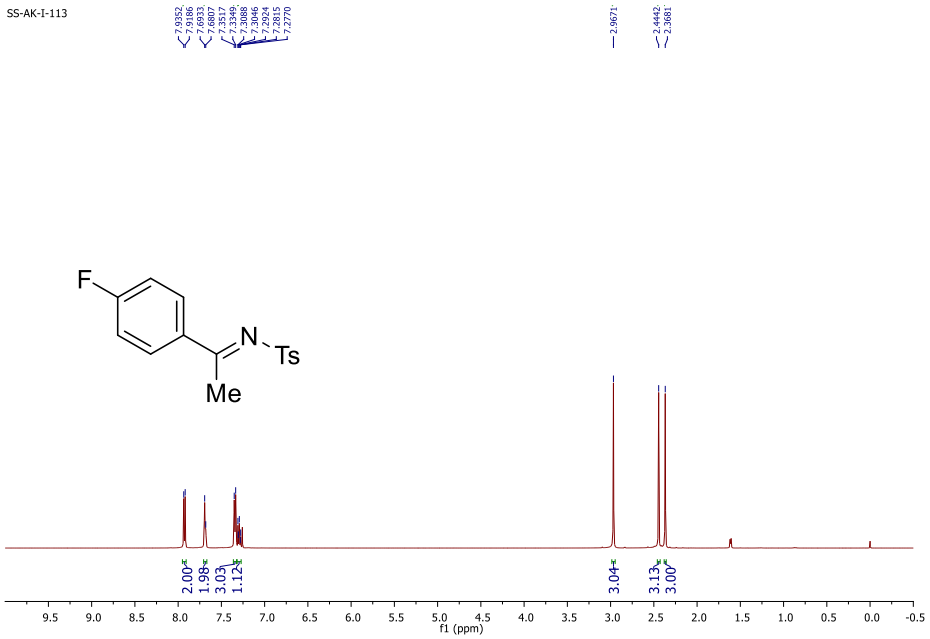


Figure 9: ^{1}H NMR spectrum (500MHz) of **1ae** in $CDCl_3$

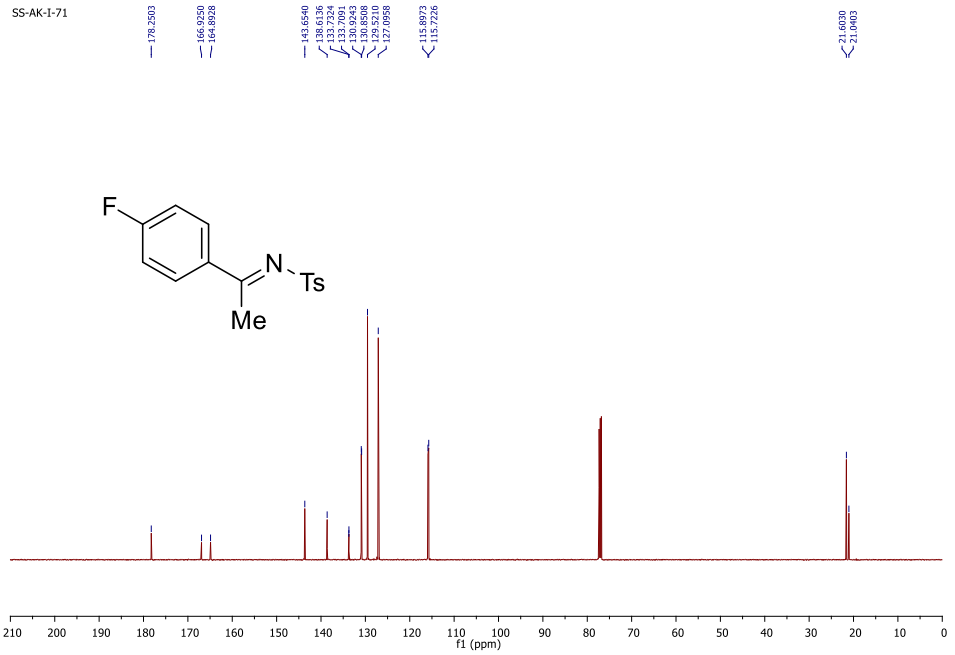


Figure 10: ^{13}C NMR spectrum (125MHz) of **1ae** in $CDCl_3$

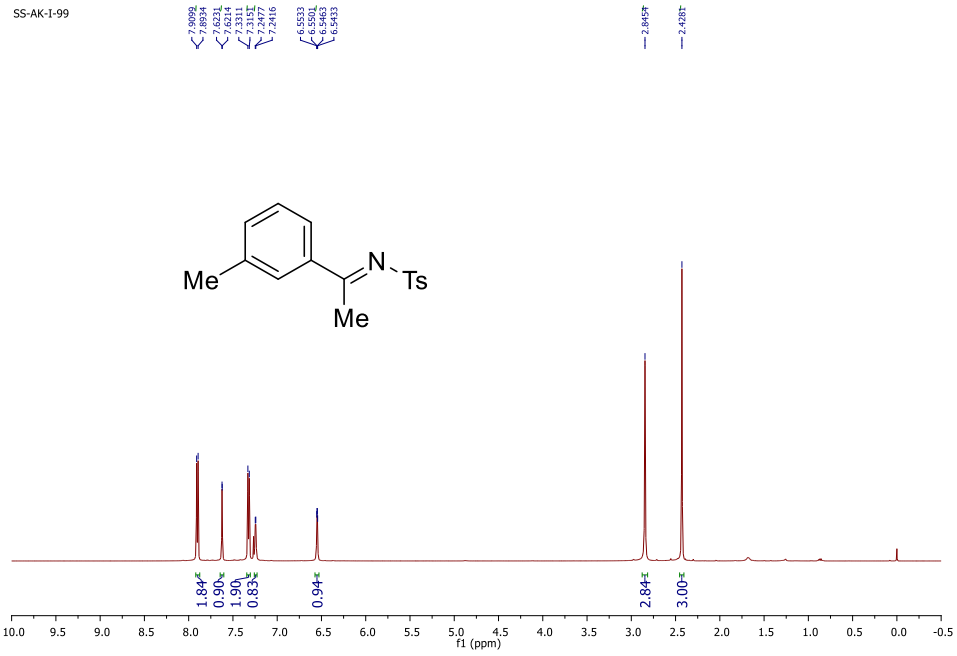


Figure 11: ^{1}H NMR spectrum (500MHz) of **1af** in $CDCl_3$

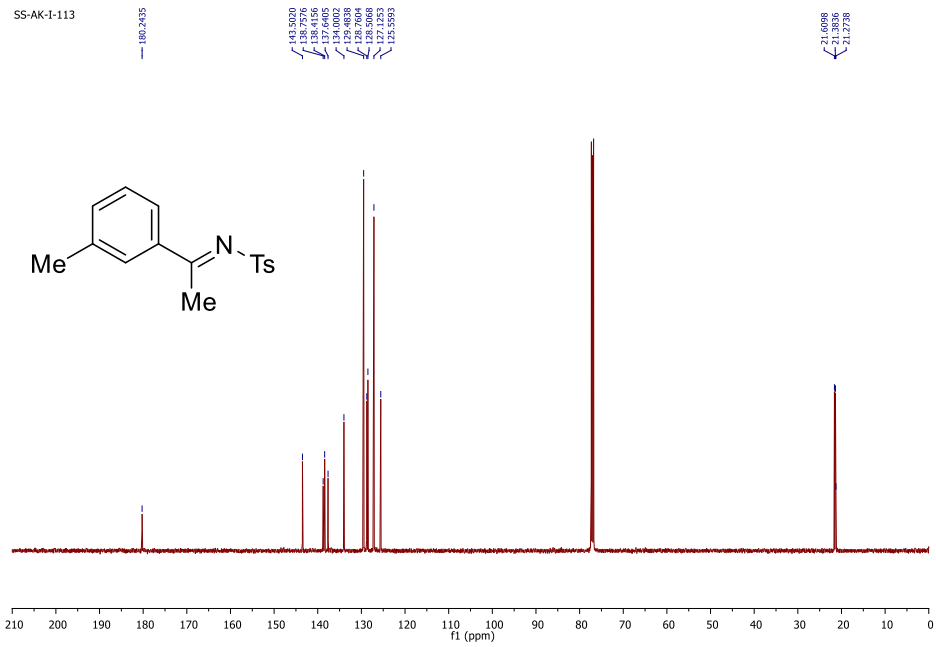


Figure 12: ^{13}C NMR spectrum (125MHz) of **1af** in $CDCl_3$

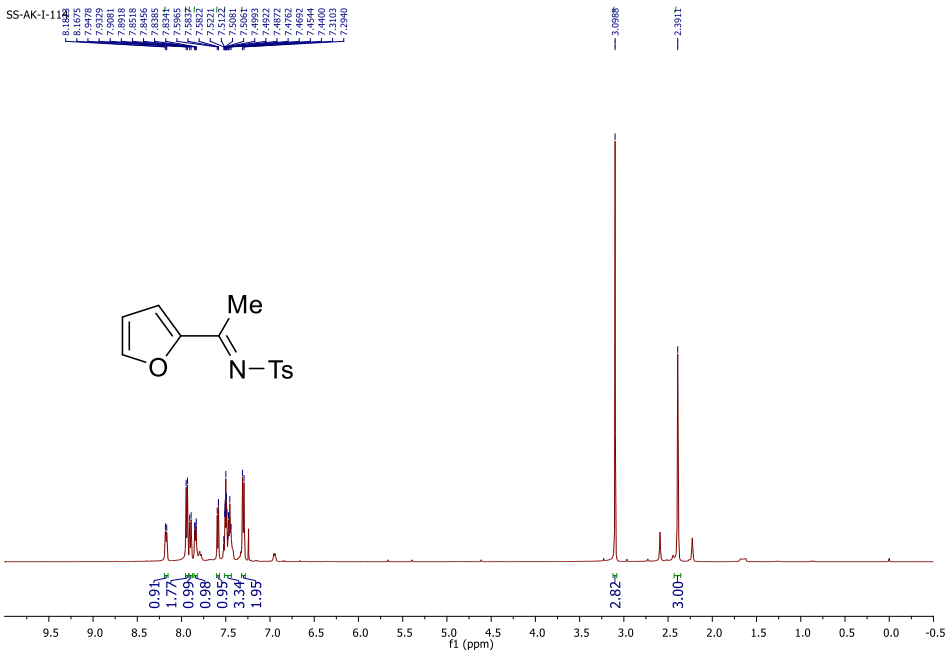


Figure 13: ^{1}H NMR spectrum (500MHz) of **1ag** in $CDCl_3$

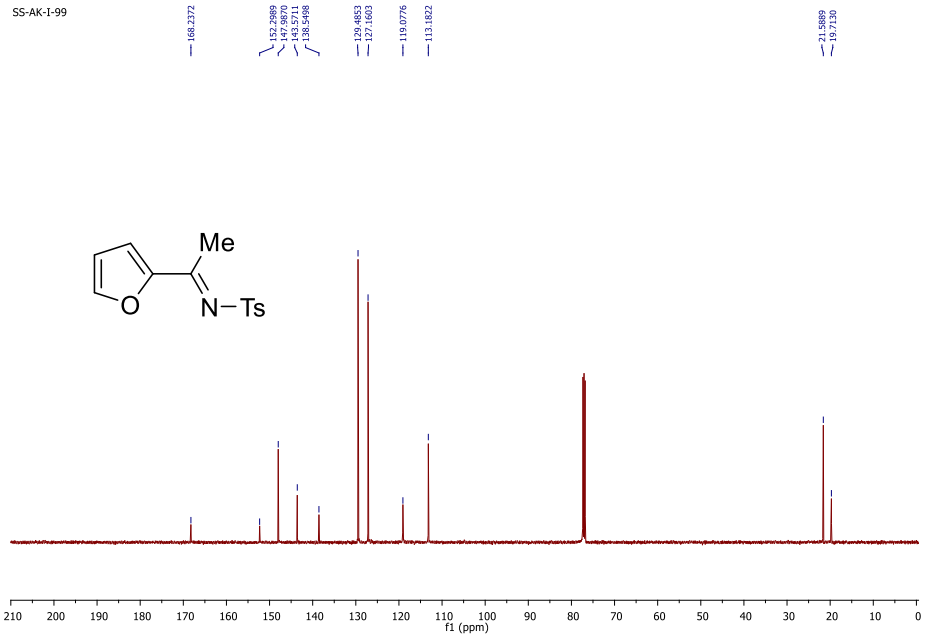


Figure 14: ^{13}C NMR spectrum (125MHz) of **1ag** in $CDCl_3$

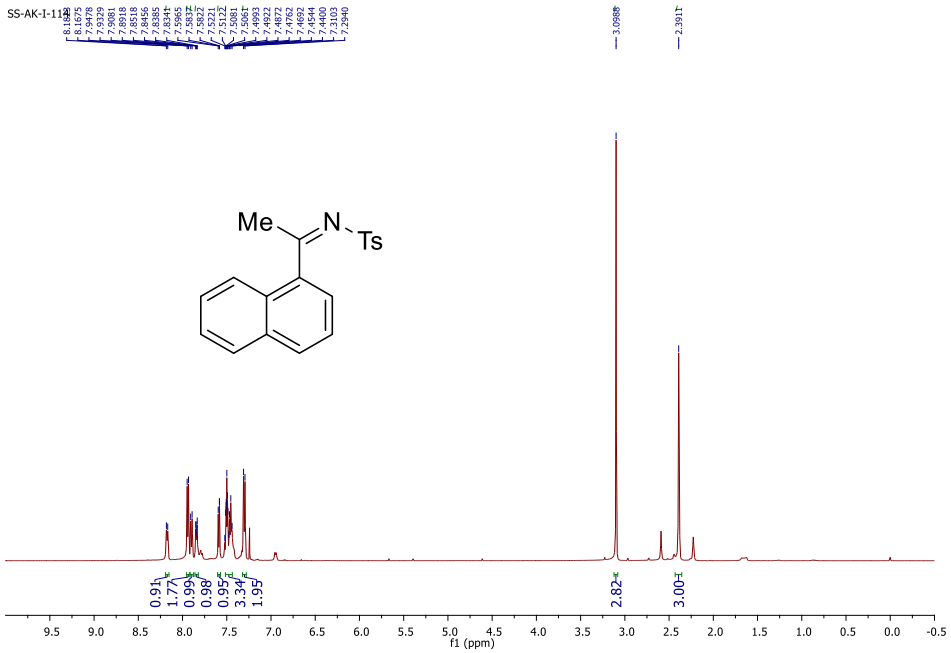


Figure 15: ^{1}H NMR spectrum (500MHz) of **1ah** in $CDCl_3$

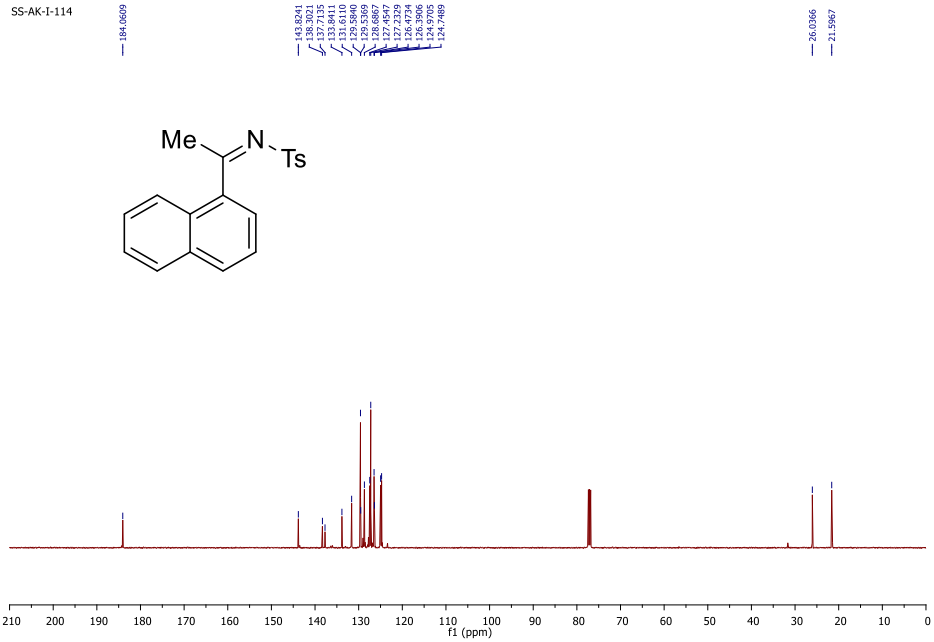


Figure 16: ^{13}C NMR spectrum (125MHz) of **1ah** in $CDCl_3$

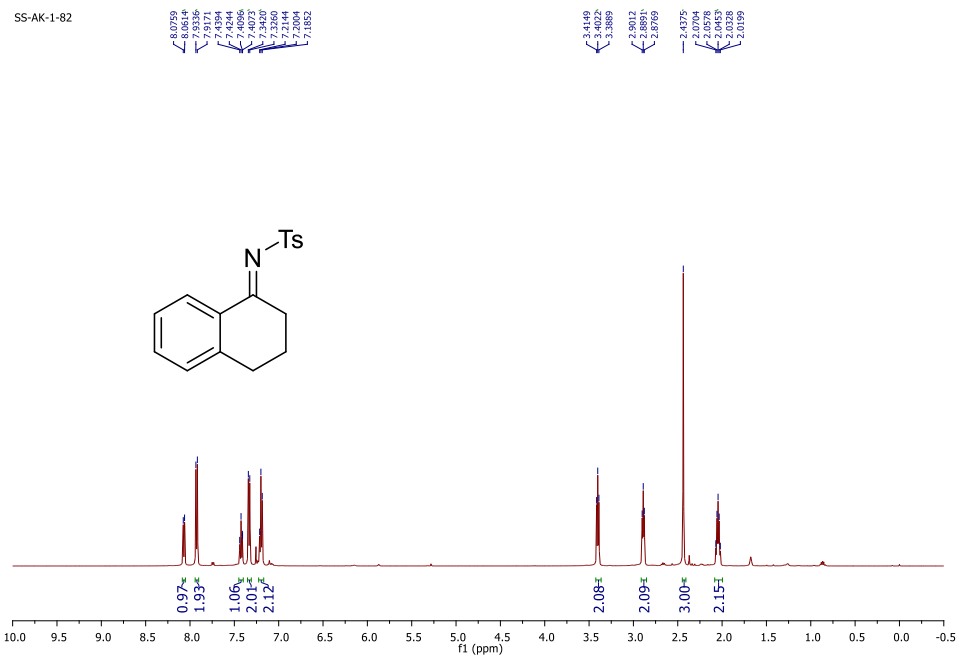


Figure 17: ^{1}H NMR spectrum (500MHz) of **1ai** in $CDCl_3$

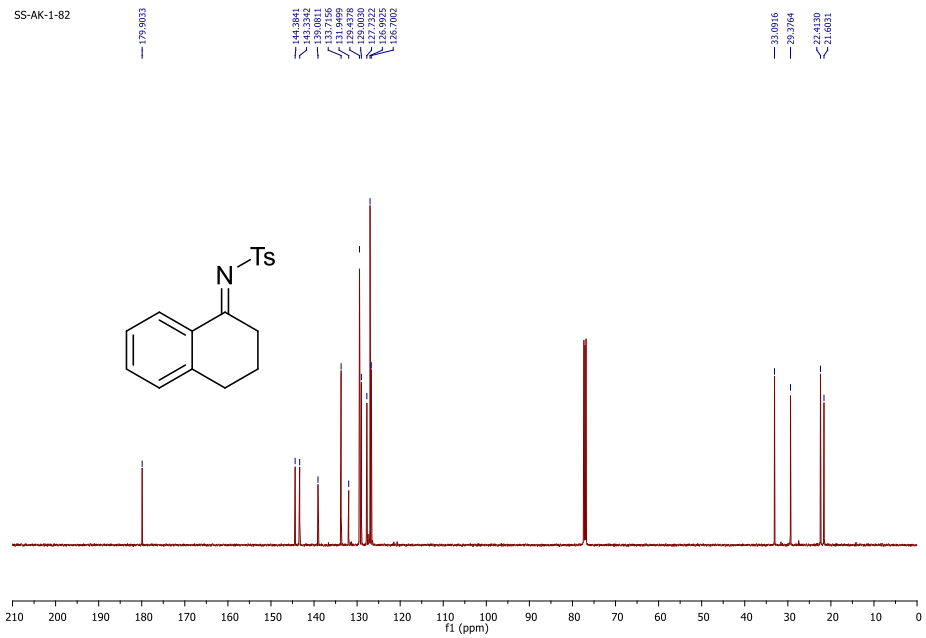


Figure 18: ^{13}C NMR spectrum (125MHz) of **1ai** in $CDCl_3$

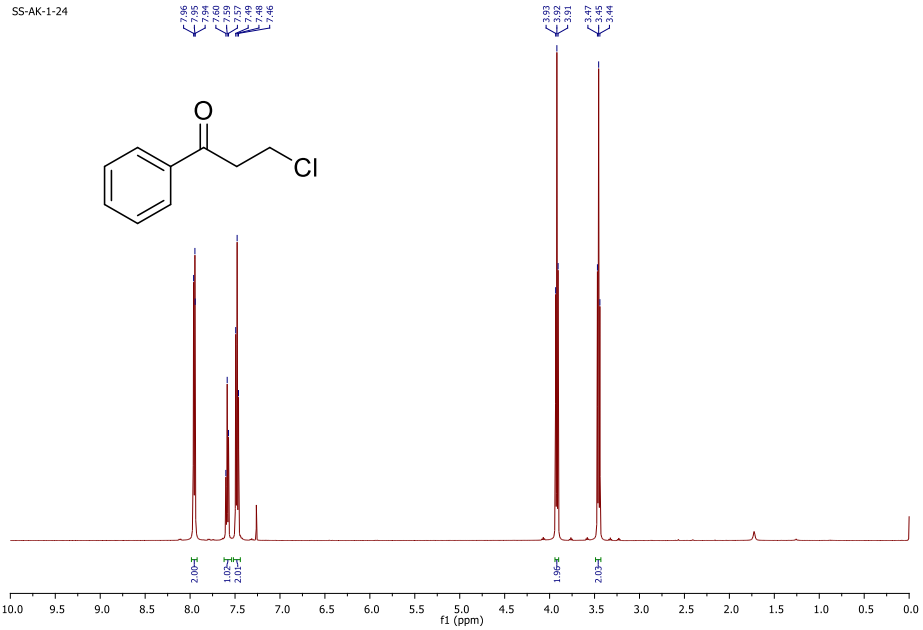


Figure 19: ^{1}H NMR spectrum (500MHz) of **2aa** in $CDCl_3$

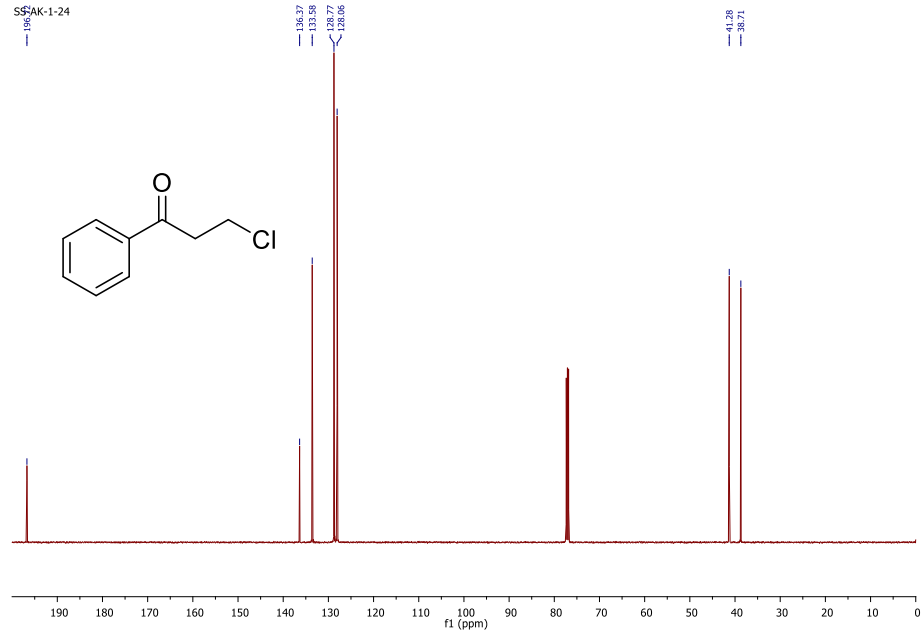


Figure 20: ^{13}C NMR spectrum (125MHz) of **2aa** in $CDCl_3$

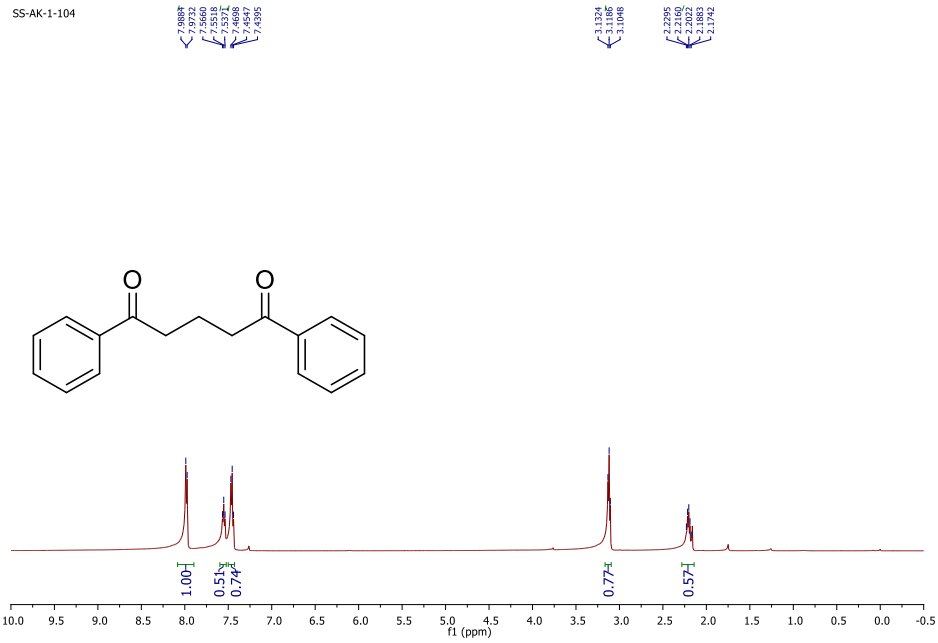


Figure 21: ^{1}H NMR spectrum (500MHz) of **3aa** in $CDCl_3$

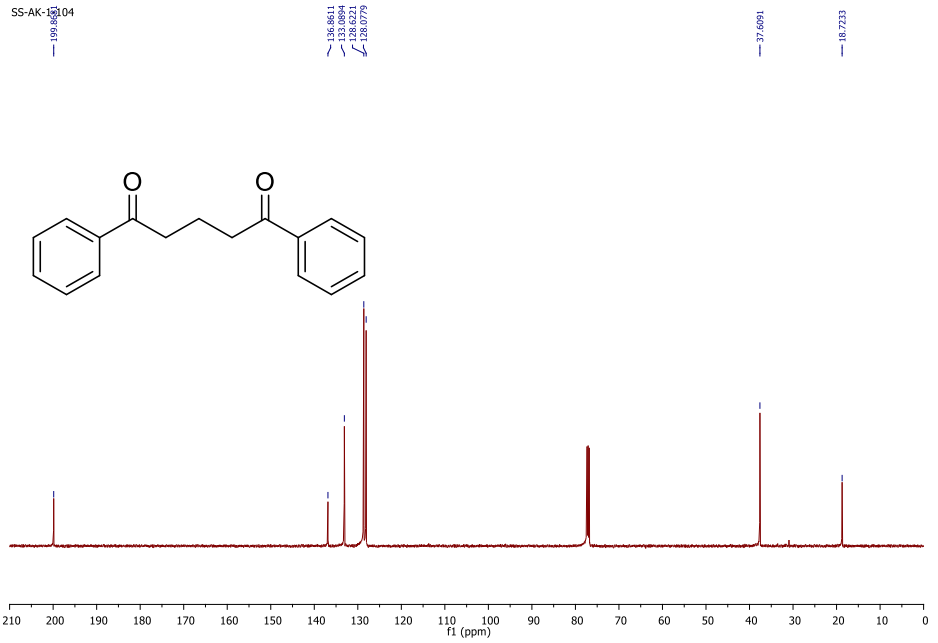


Figure 22: ^{13}C NMR spectrum (125MHz) of **3aa** in $CDCl_3$

.....

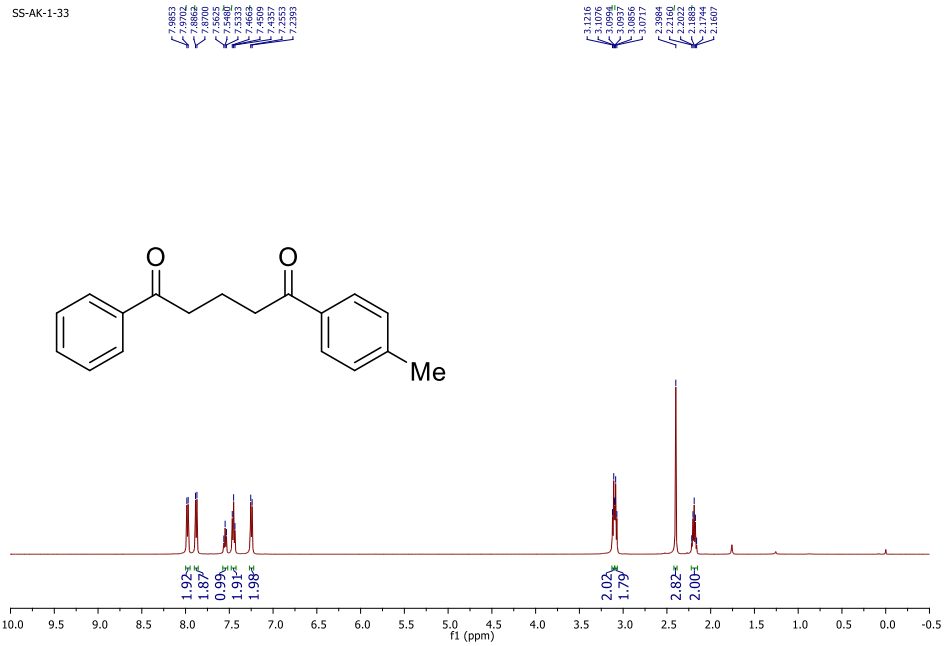


Figure 23: ^{1}H NMR spectrum (500MHz) of **3ab** in $CDCl_3$

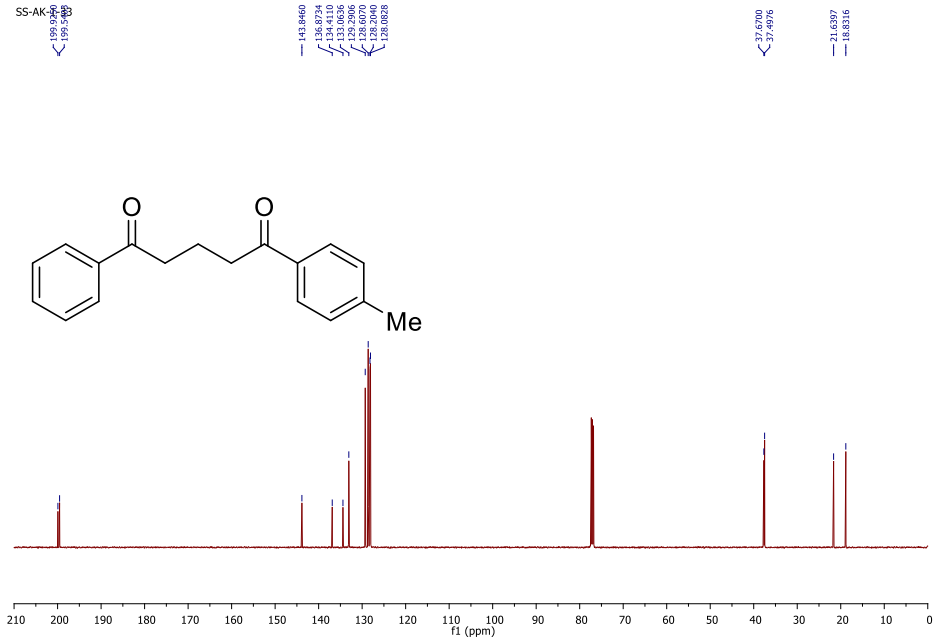


Figure 24: ^{13}C NMR spectrum (125MHz) of **3ab** in $CDCl_3$

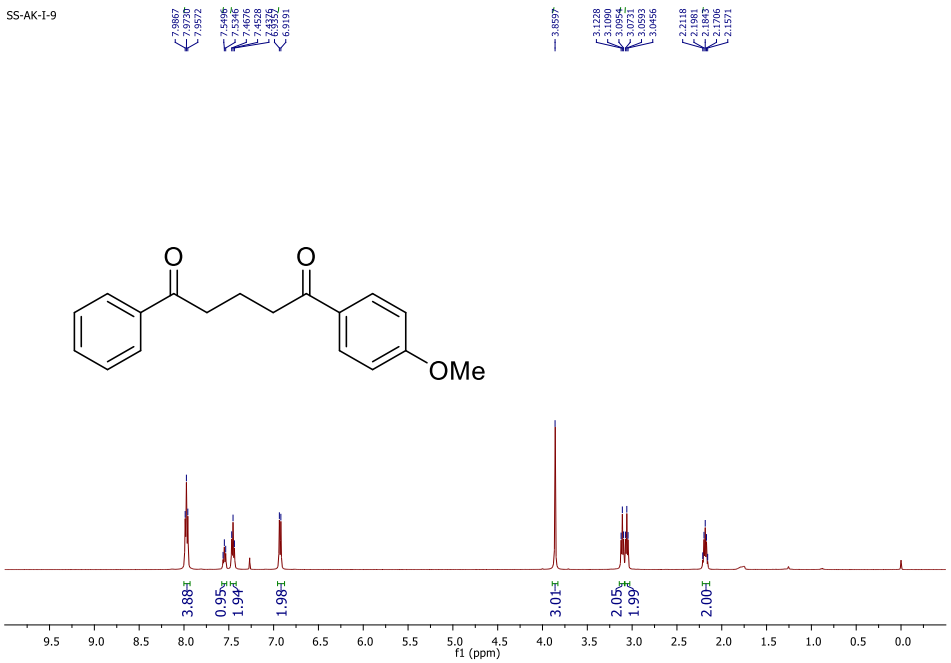


Figure 25: ^{1}H NMR spectrum (500MHz) of **3ac** in $CDCl_3$

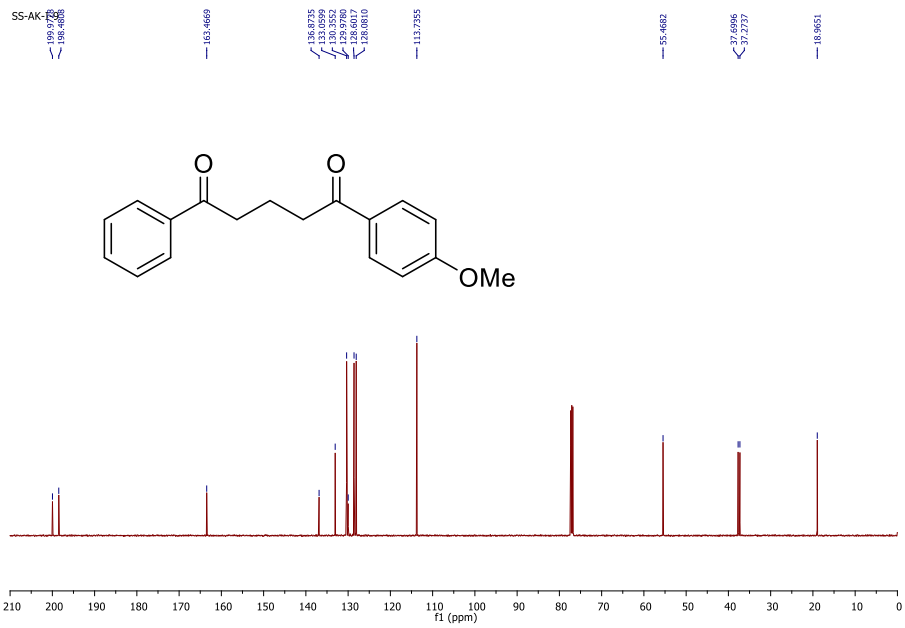


Figure 26: ^{13}C NMR spectrum (125MHz) of **3ac** in $CDCl_3$

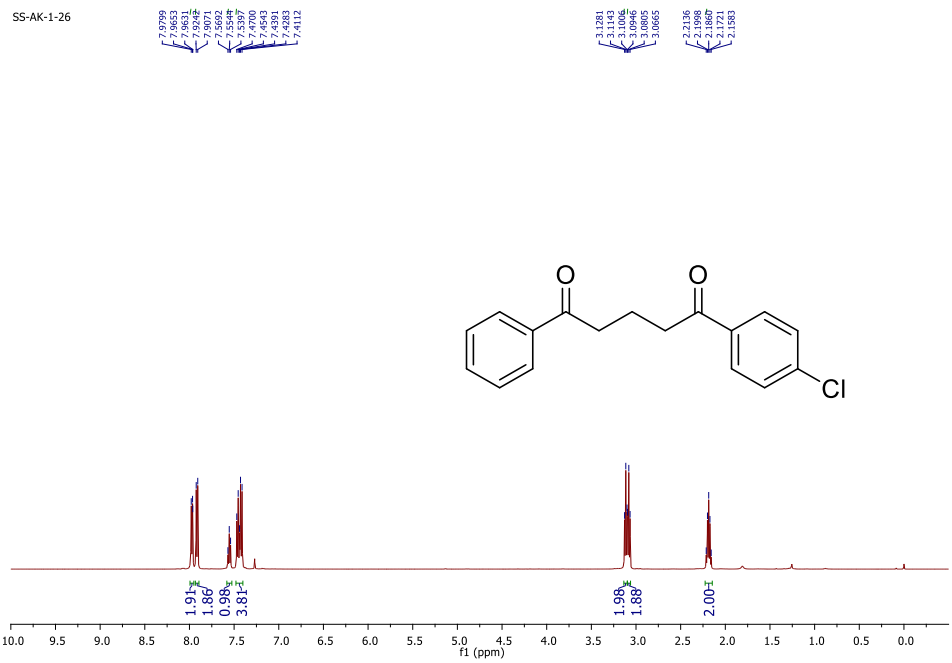


Figure 27: ^{1}H NMR spectrum (500MHz) of **3ad** in $CDCl_3$

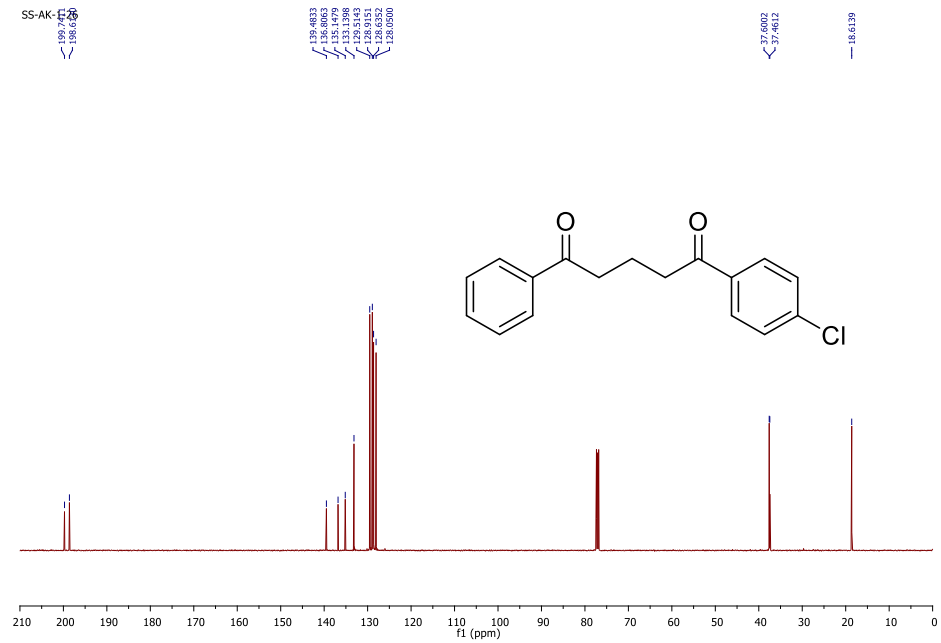


Figure 28: ^{13}C NMR spectrum (125MHz) of **3ad** in $CDCl_3$

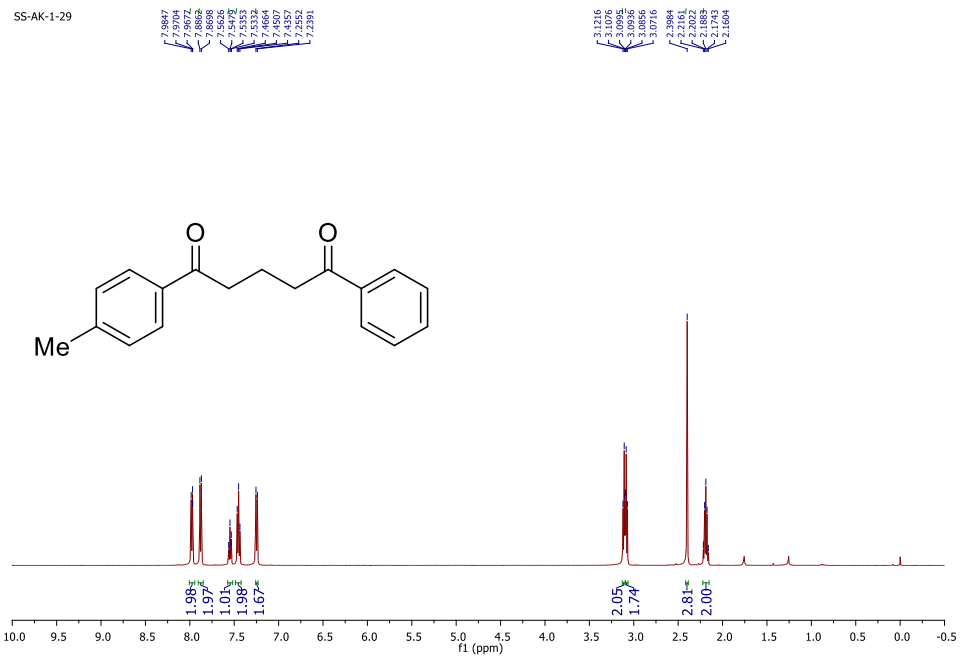


Figure 29: ^{1}H NMR spectrum (500MHz) of **3ba** in $CDCl_3$

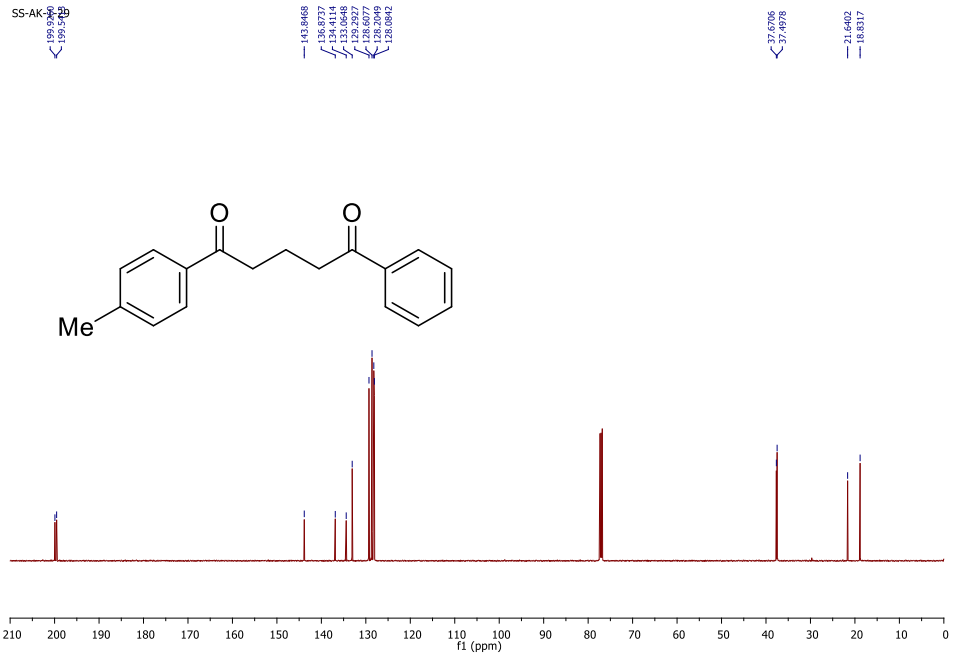


Figure 30: ^{13}C NMR spectrum (125MHz) of **3ba** in $CDCl_3$

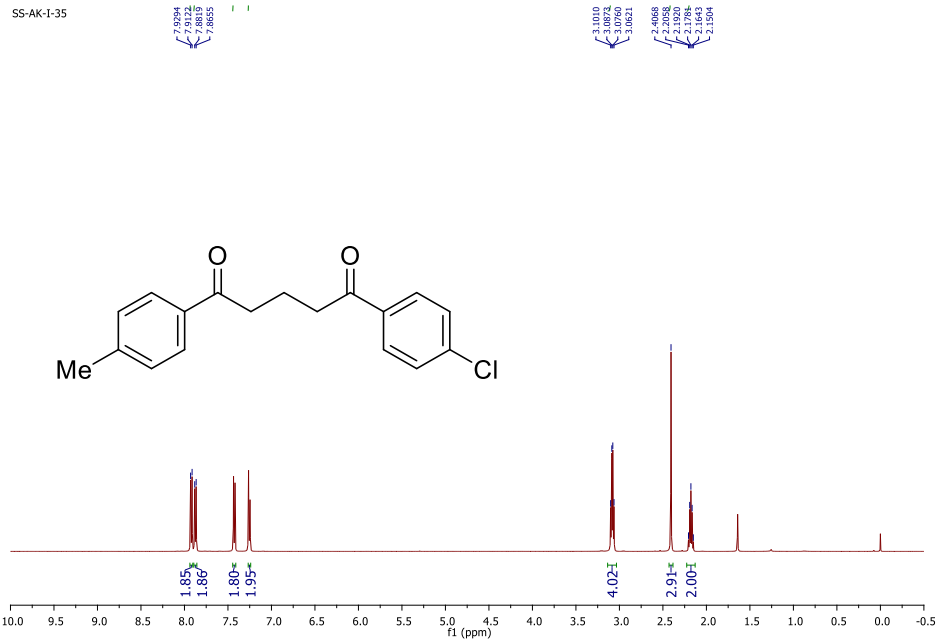


Figure 31: ^{1}H NMR spectrum (500MHz) of **3bd** in $CDCl_3$

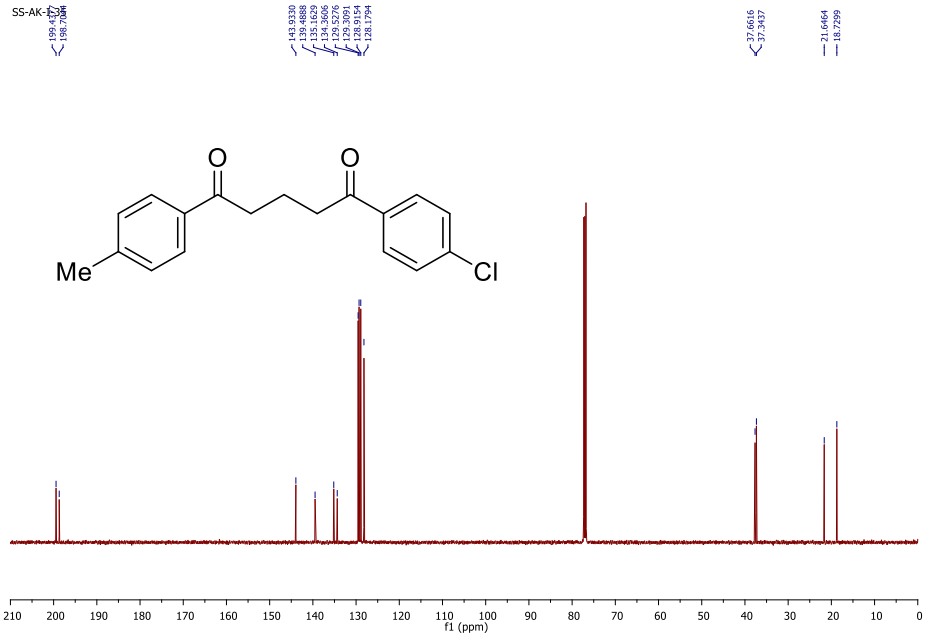


Figure 32: ^{13}C NMR spectrum (125MHz) of **3bd** in $CDCl_3$

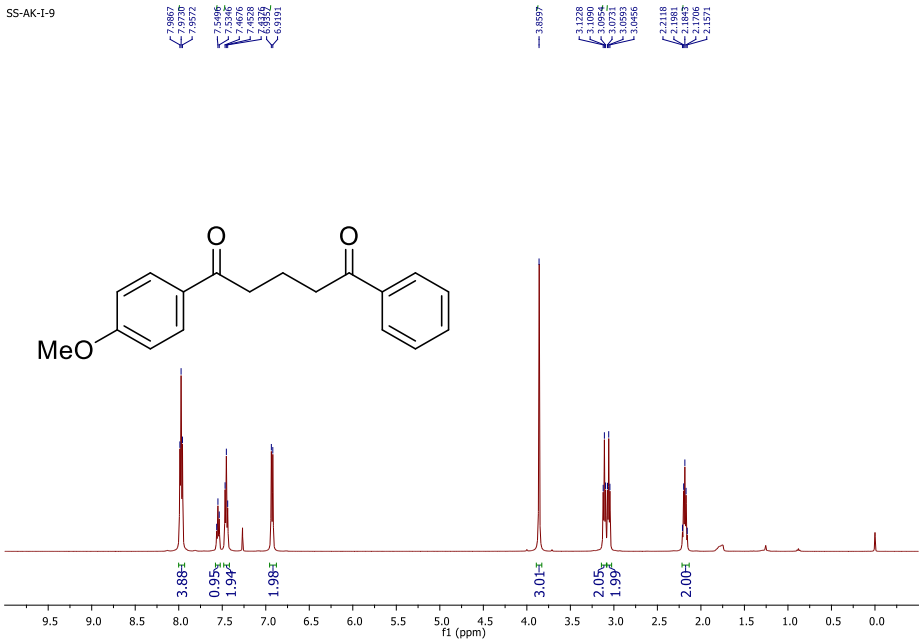


Figure 33: ^{1}H NMR spectrum (500MHz) of **3ca** in $CDCl_3$

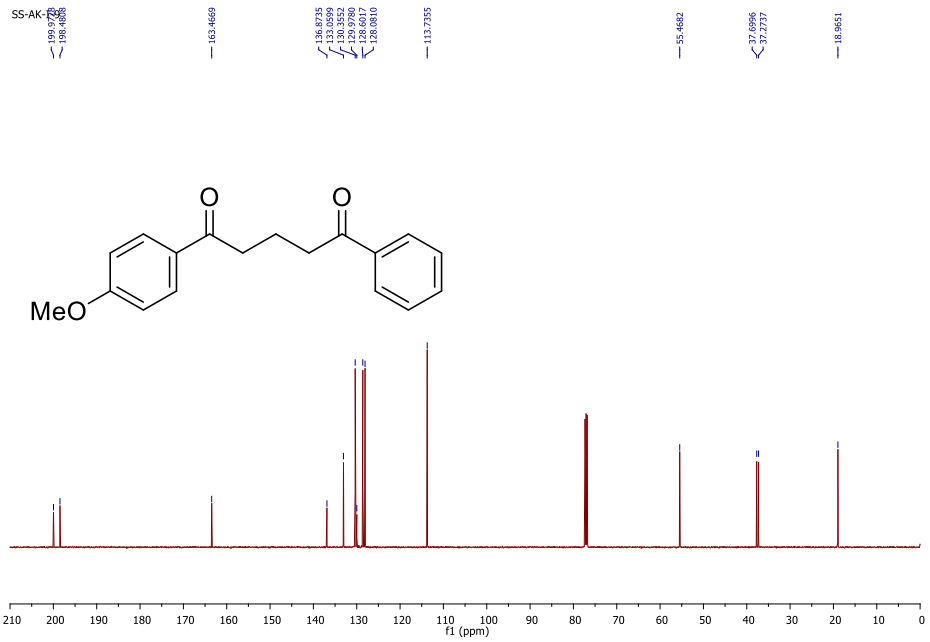


Figure 34: ^{13}C NMR spectrum (125MHz) of **3ca** in $CDCl_3$

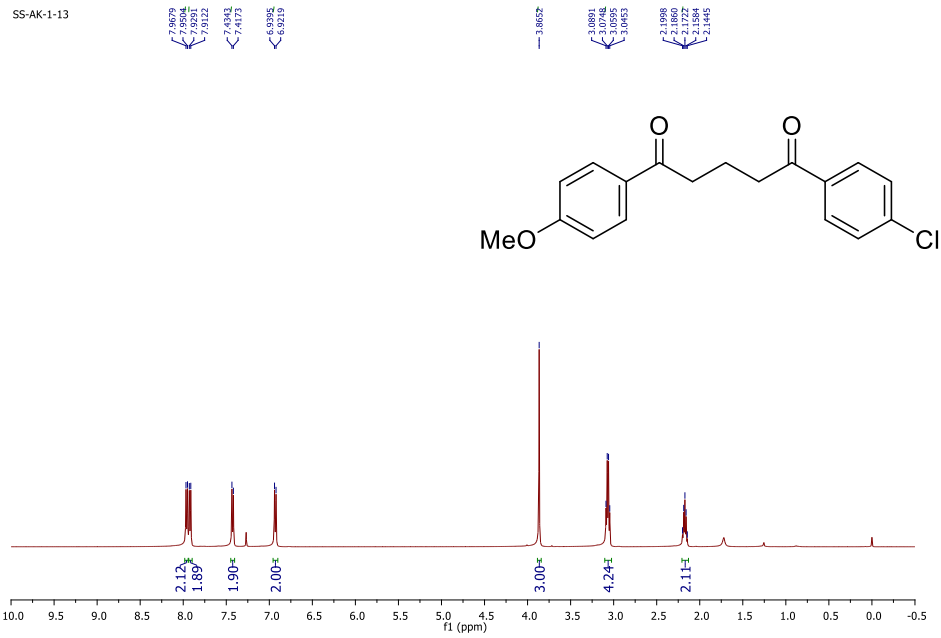


Figure 35: ^{1}H NMR spectrum (500MHz) of **3cd** in $CDCl_3$

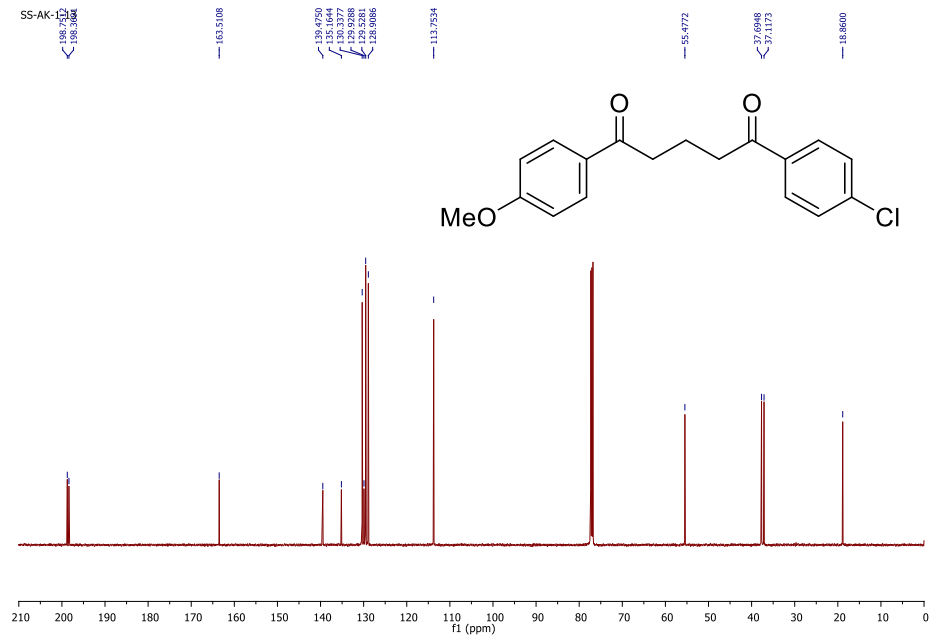


Figure 36: ^{13}C NMR spectrum (125MHz) of **3cd** in $CDCl_3$

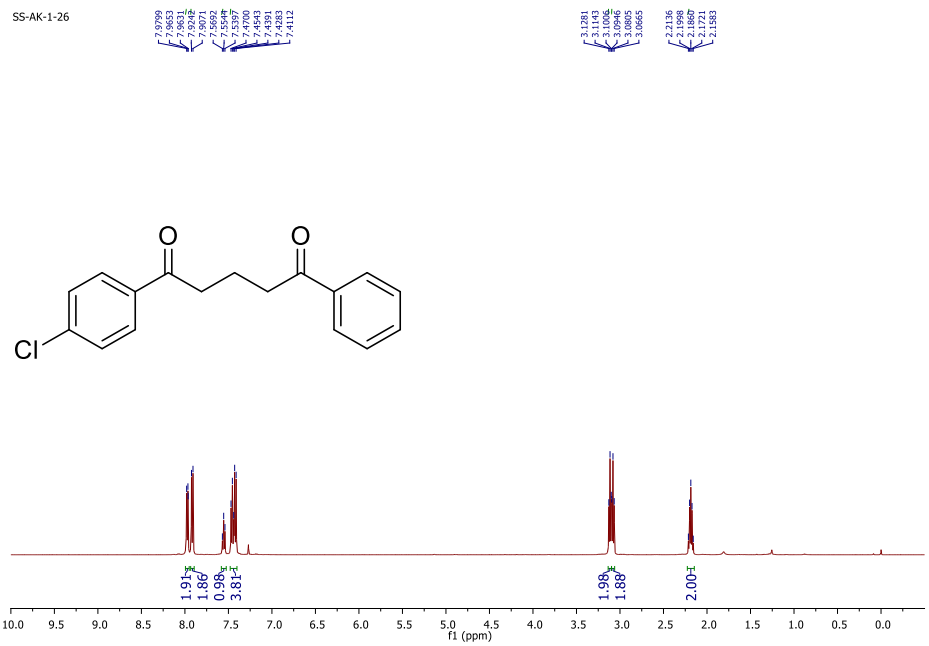


Figure 37: ^{1}H NMR spectrum (500MHz) of **3da** in $CDCl_3$

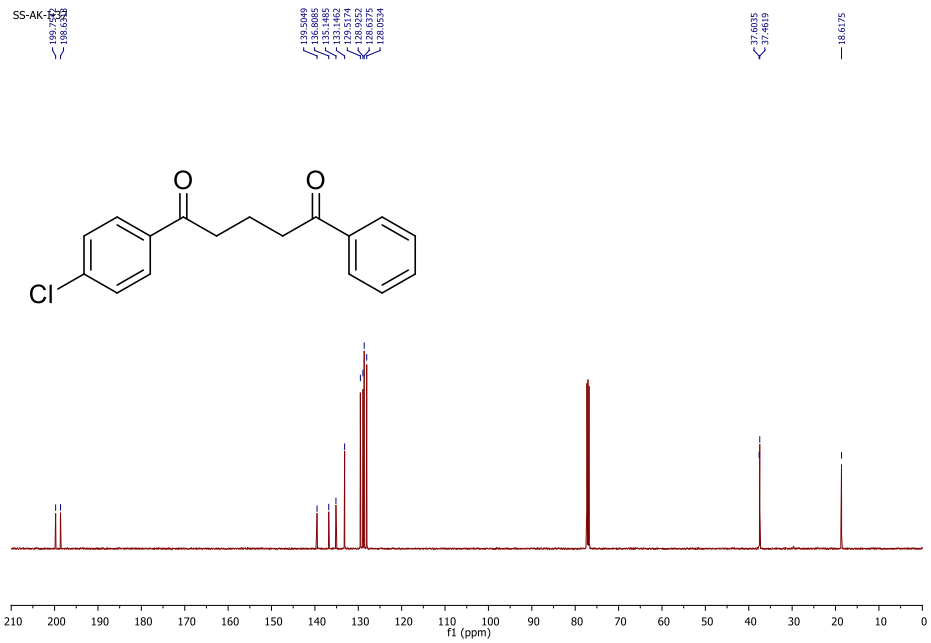


Figure 38: ^{13}C NMR spectrum (125MHz) of **3da** in $CDCl_3$

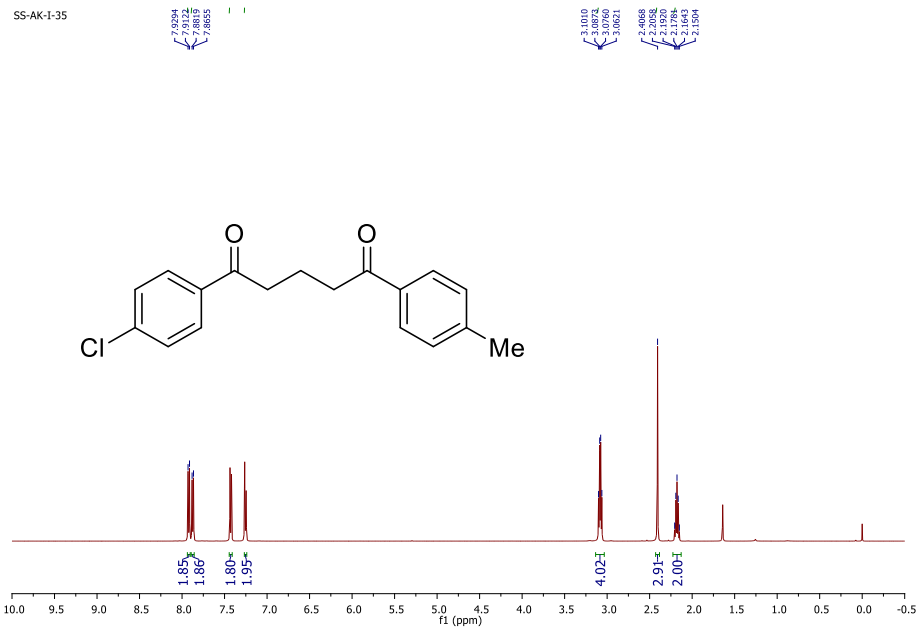


Figure 39: ^{1}H NMR spectrum (500MHz) of **3db** in $CDCl_3$

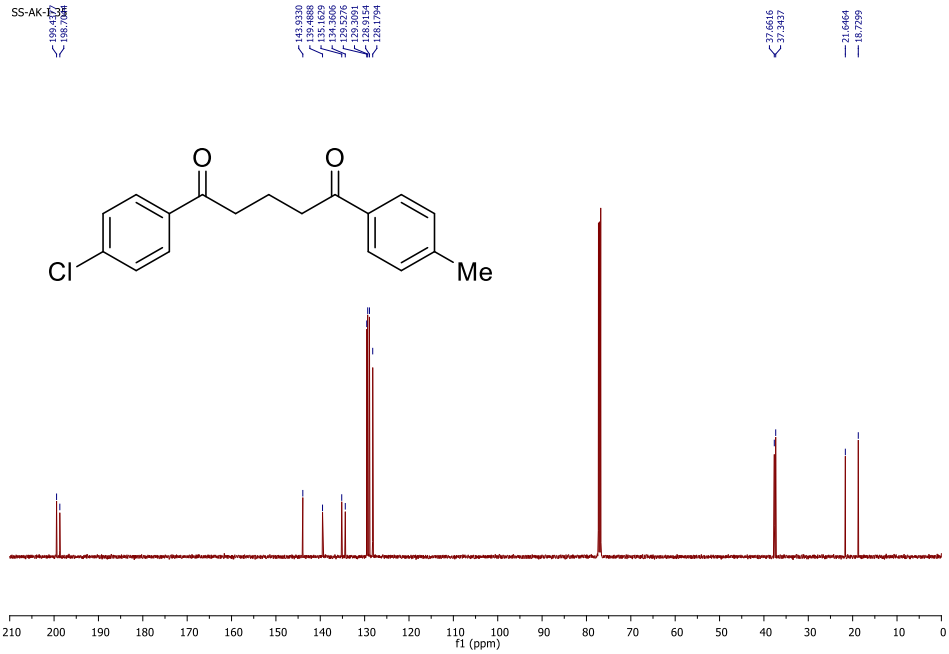


Figure 40: ^{13}C NMR spectrum (125MHz) of **3db** in $CDCl_3$

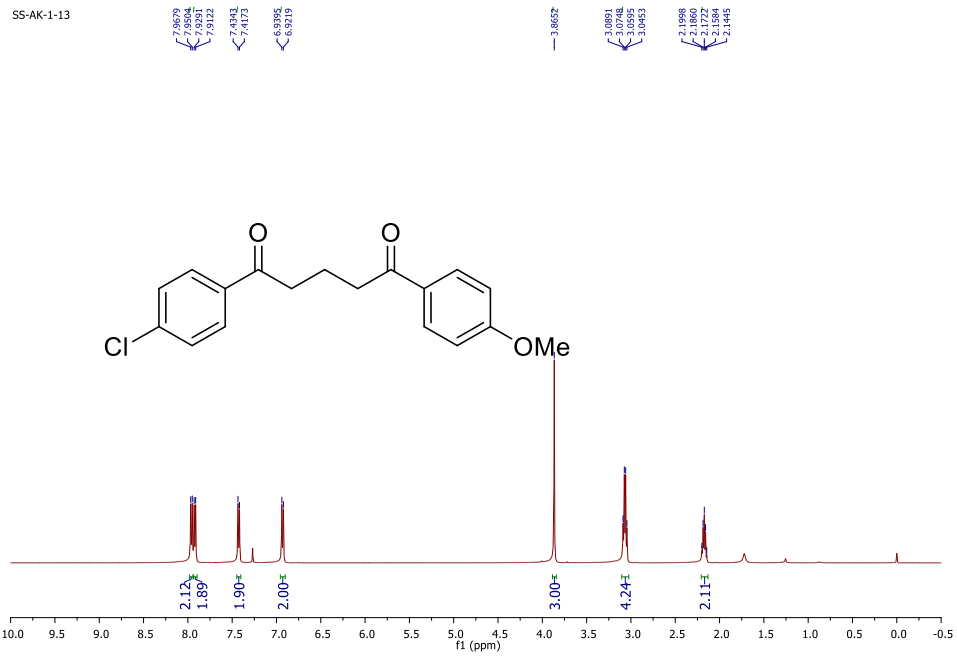


Figure 41: ^{1}H NMR spectrum (500MHz) of **3dc** in $CDCl_3$

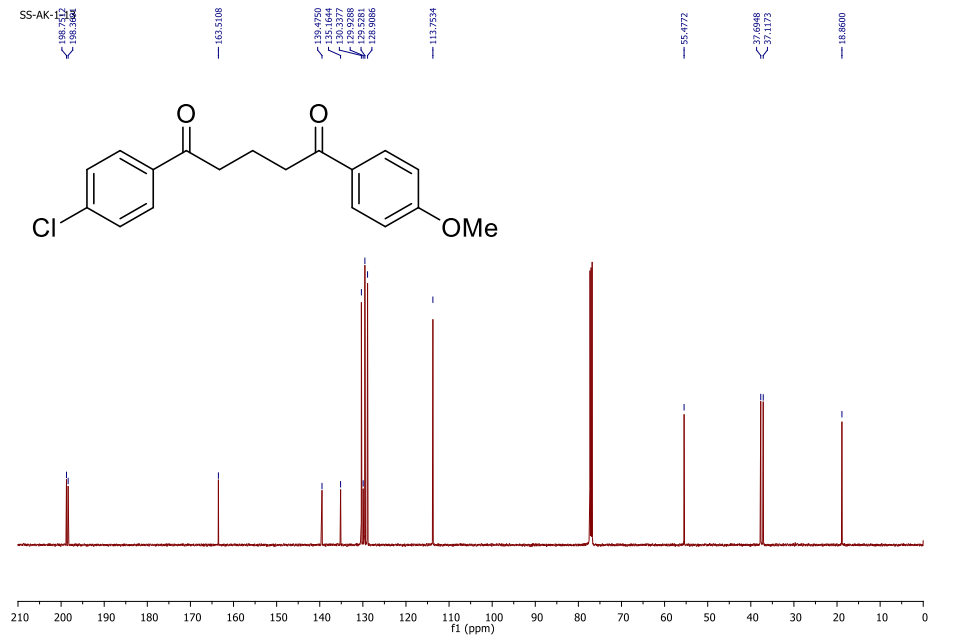


Figure 42: ^{13}C NMR spectrum (125MHz) of **3dc** in $CDCl_3$

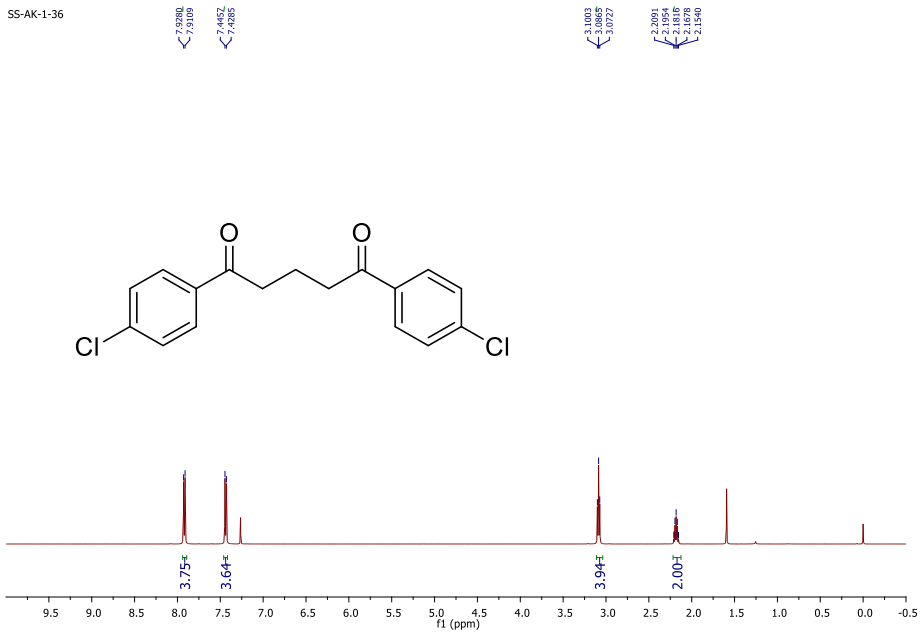


Figure 43: ^{1}H NMR spectrum (500MHz) of **3dd** in $CDCl_3$

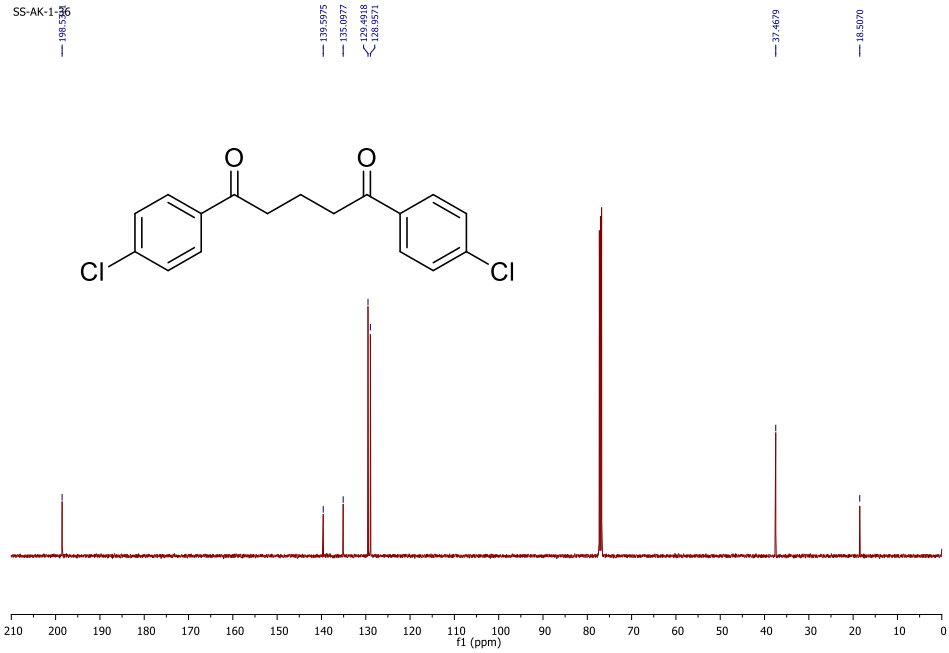


Figure 44: ^{13}C NMR spectrum (125MHz) of **3dd** in $CDCl_3$

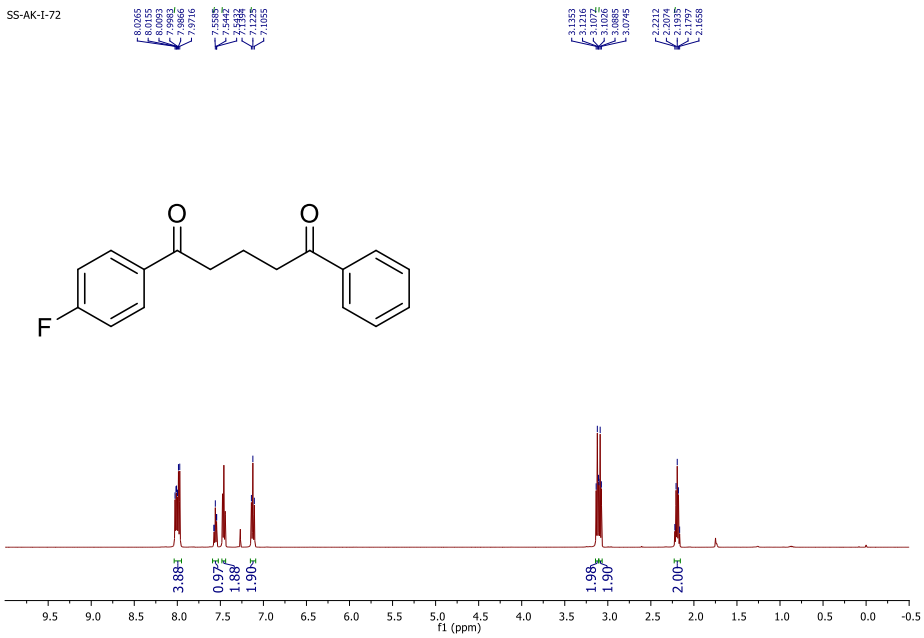


Figure 45: ^{1}H NMR spectrum (500MHz) of **3ea** in $CDCl_3$

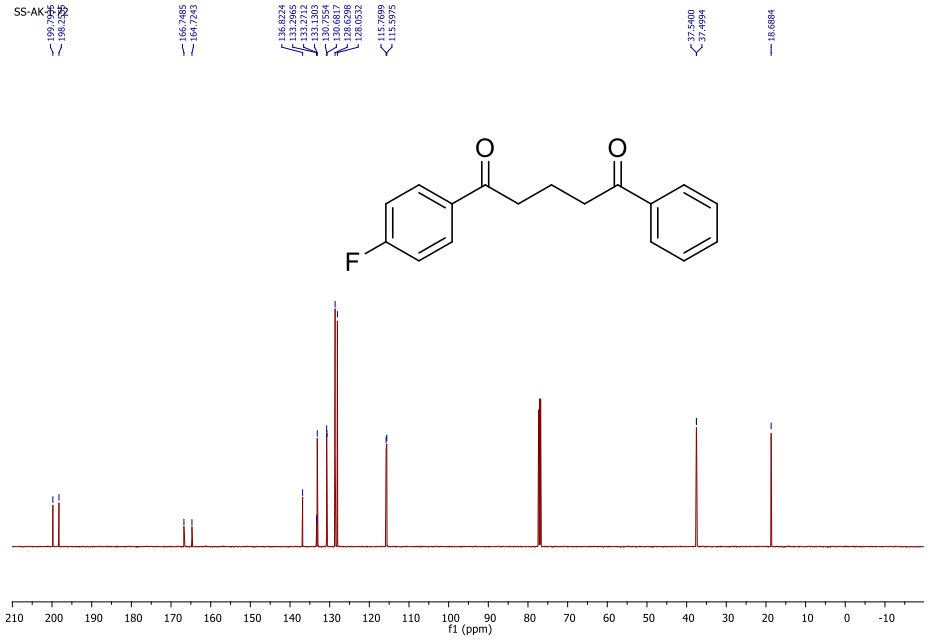


Figure 46: ^{13}C NMR spectrum (125MHz) of **3ea** in $CDCl_3$

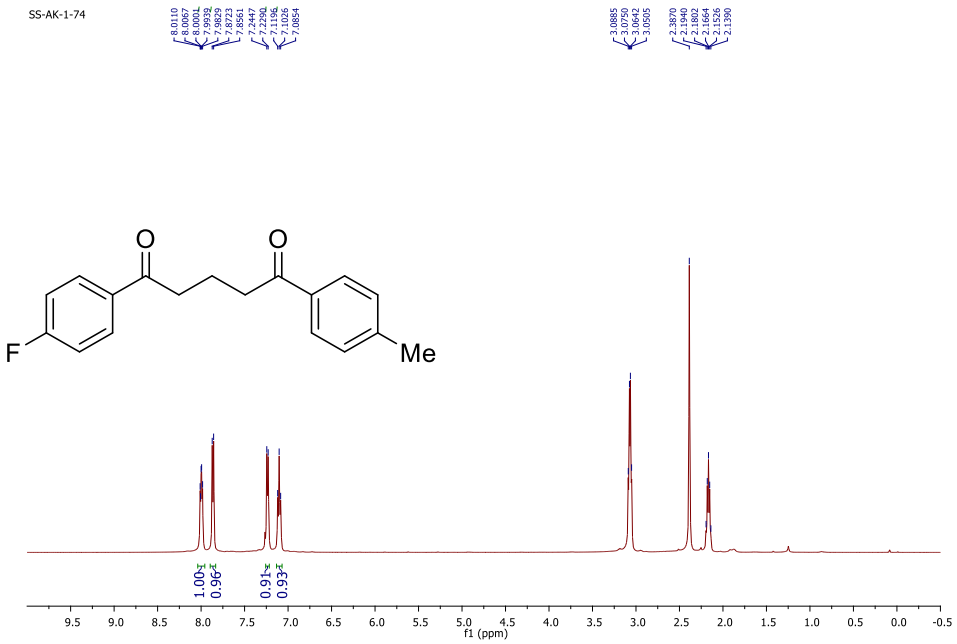


Figure 47: ^{1}H NMR spectrum (500MHz) of **3eb** in $CDCl_3$

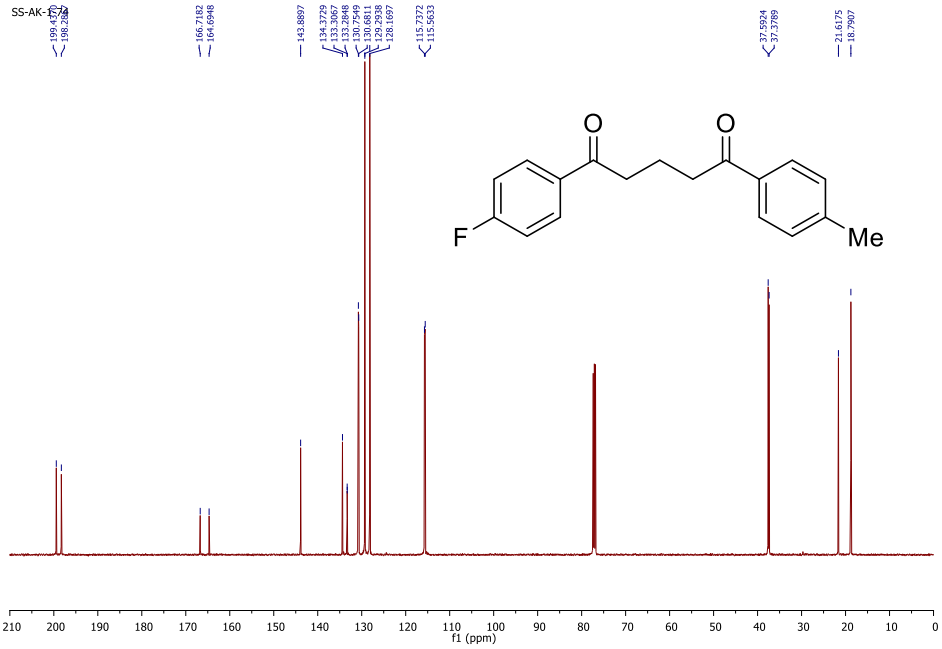


Figure 48: ^{13}C NMR spectrum (125MHz) of **3eb** in $CDCl_3$

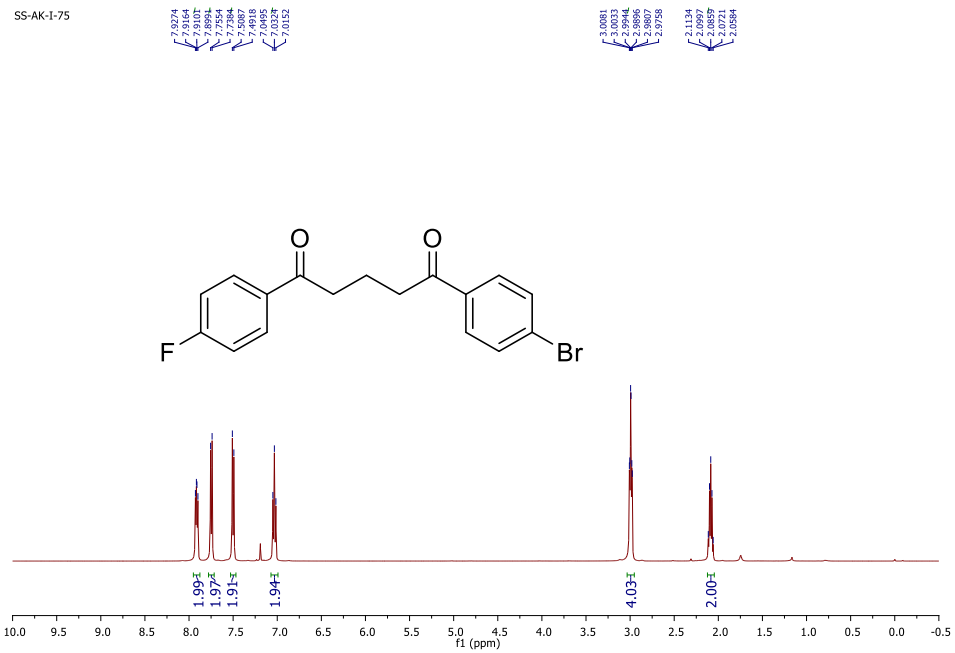


Figure 49: ^{1}H NMR spectrum (500MHz) of **3ee** in $CDCl_3$

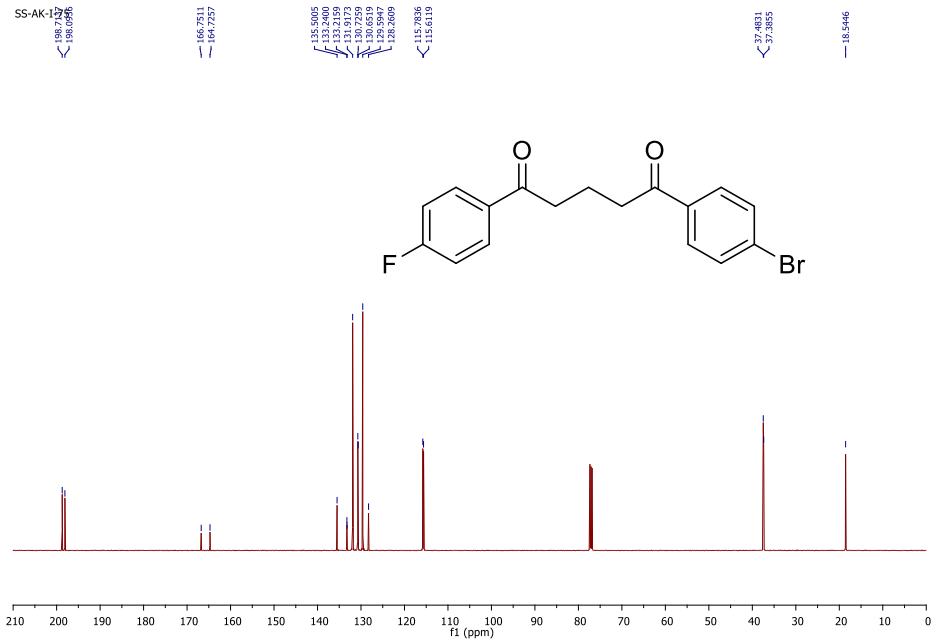


Figure 50: ^{13}C NMR spectrum (125MHz) of **3ee** in $CDCl_3$

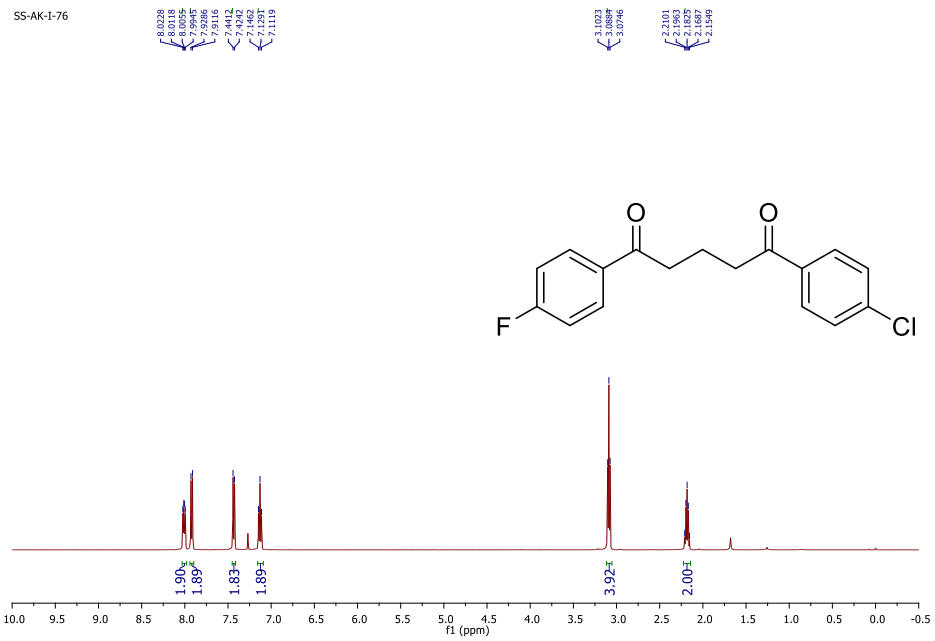


Figure 51: ^{1}H NMR spectrum (500MHz) of **3ed** in $CDCl_3$

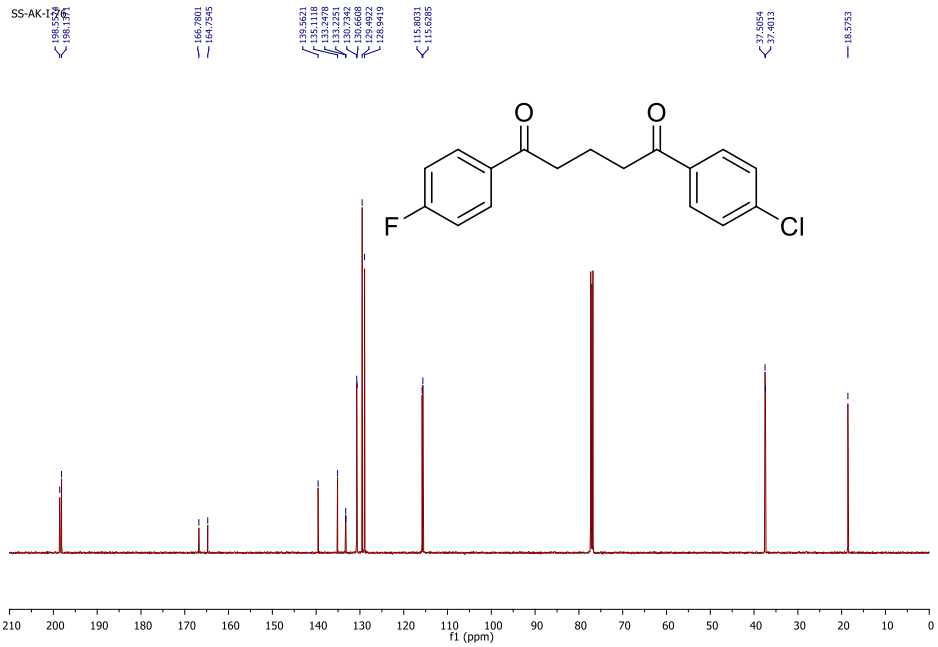


Figure 52: ^{13}C NMR spectrum (125MHz) of **3ed** in $CDCl_3$

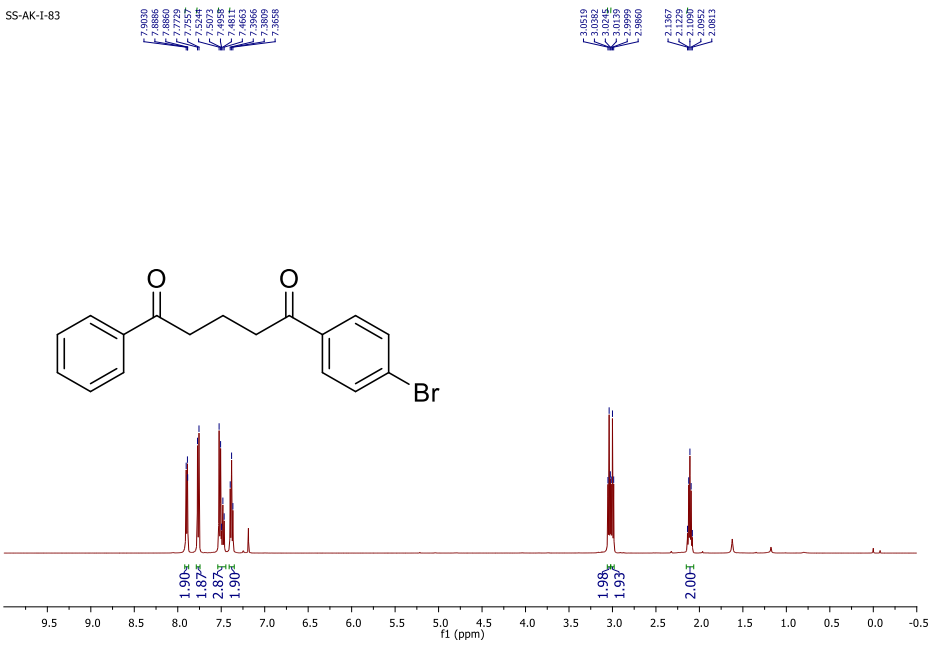


Figure 53: ^{1}H NMR spectrum (500MHz) of **3ae** in $CDCl_3$

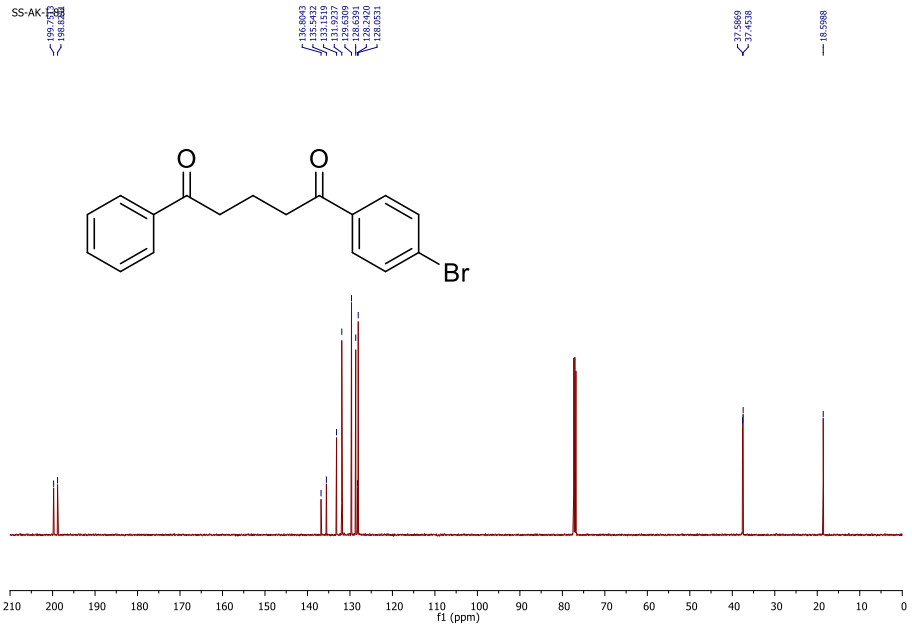


Figure 54: ^{13}C NMR spectrum (125MHz) of **3ae** in $CDCl_3$

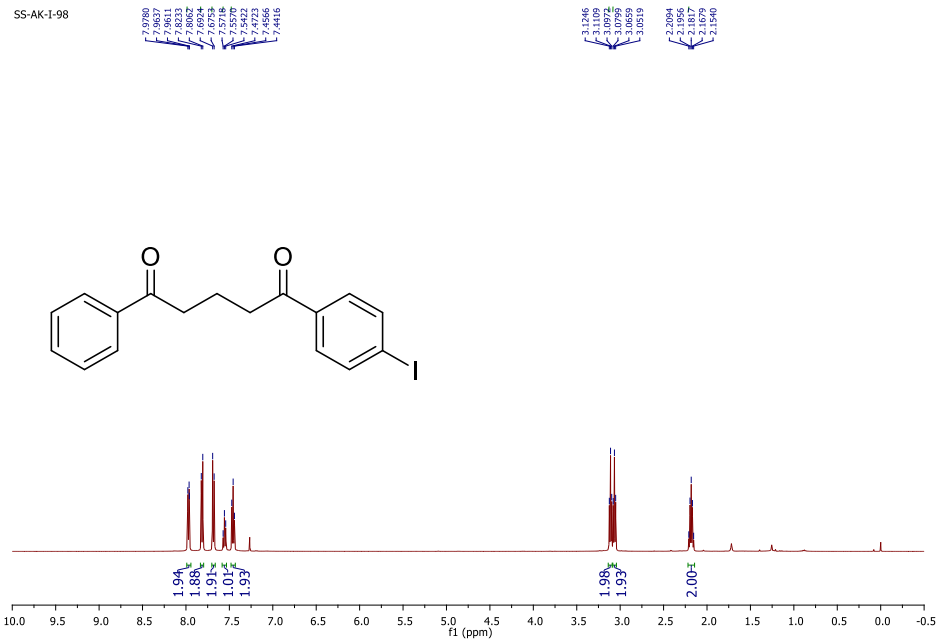


Figure 55: ^{1}H NMR spectrum (500MHz) of **3af** in $CDCl_3$

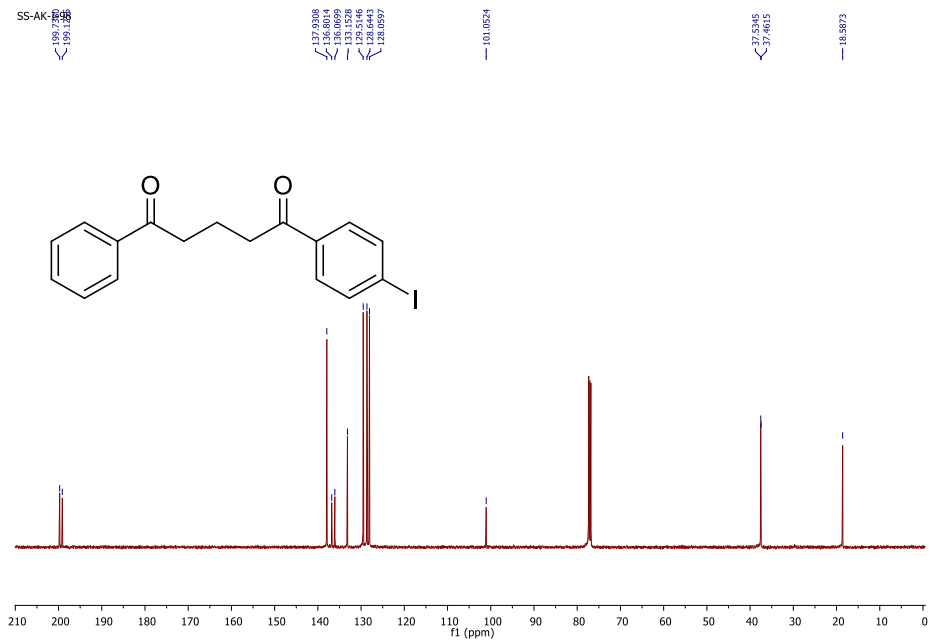


Figure 56: ^{13}C NMR spectrum (125MHz) of **3af** in $CDCl_3$

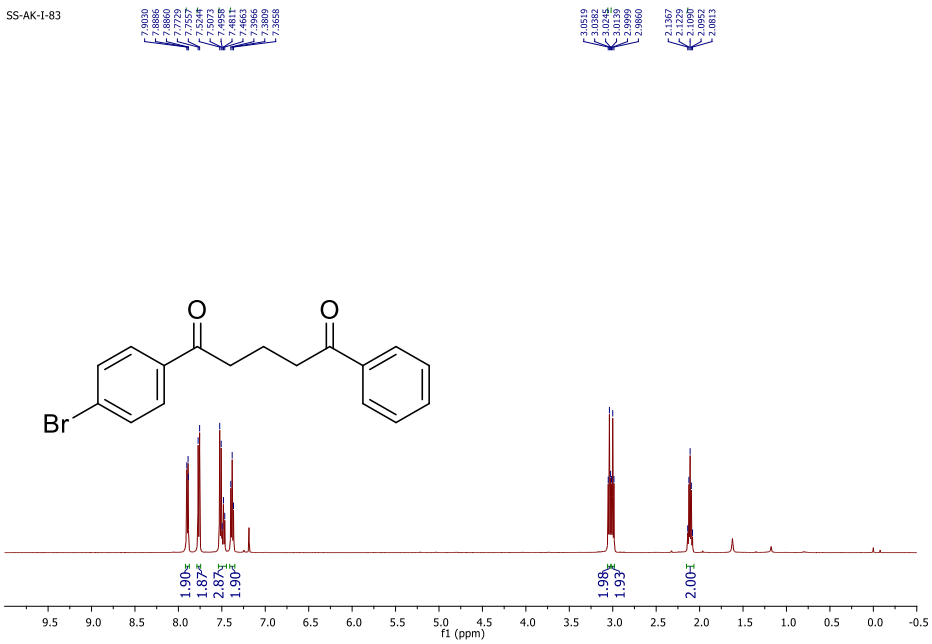


Figure 57: ^{1}H NMR spectrum (500MHz) of **3fa** in $CDCl_3$

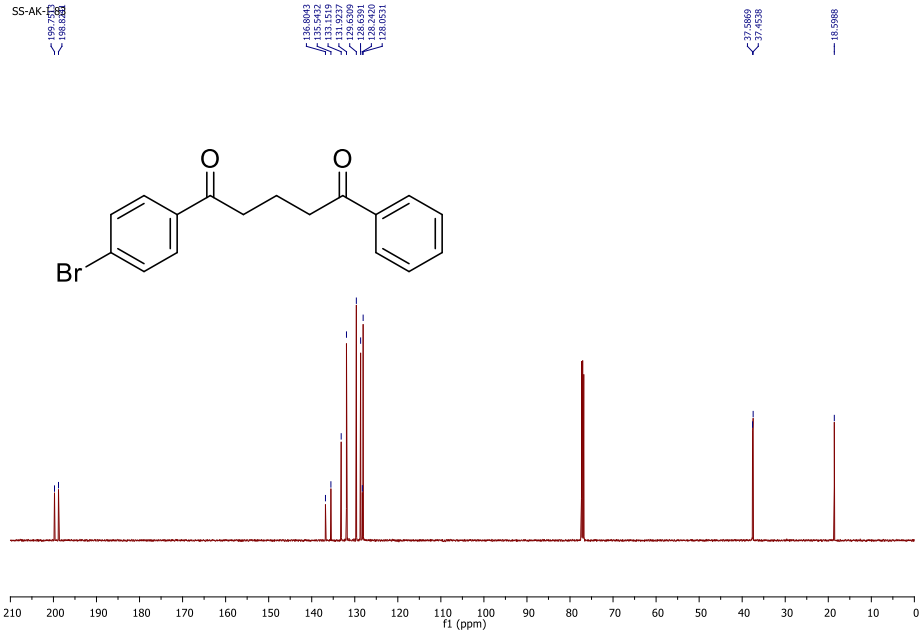


Figure 58: ^{13}C NMR spectrum (125MHz) of **3fa** in $CDCl_3$

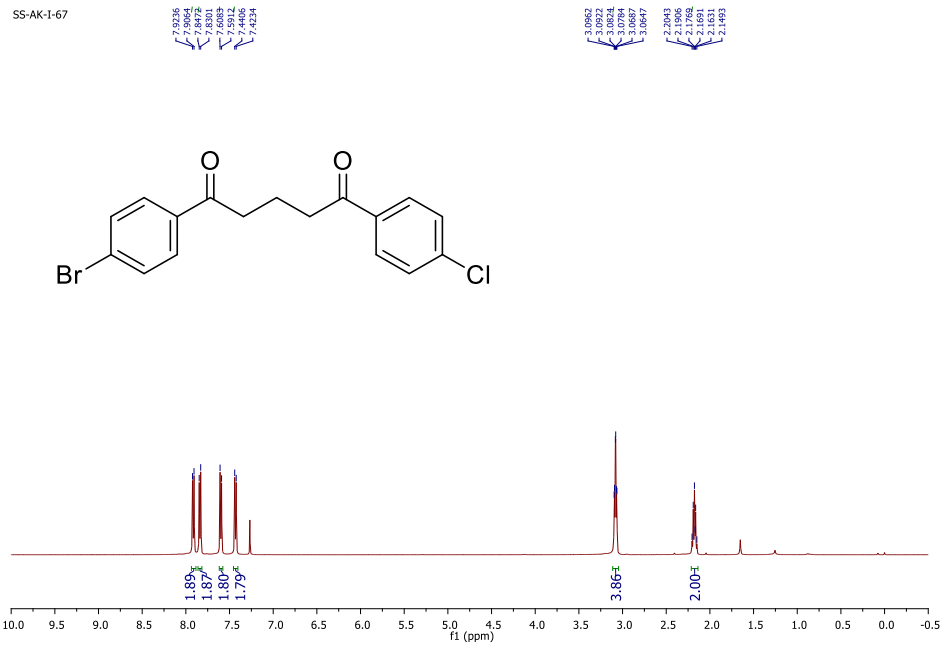


Figure 59: ^{1}H NMR spectrum (500MHz) of **3fd** in $CDCl_3$

Figure 60: ^{13}C NMR spectrum (125MHz) of **3fd** in $CDCl_{3\backslash}$

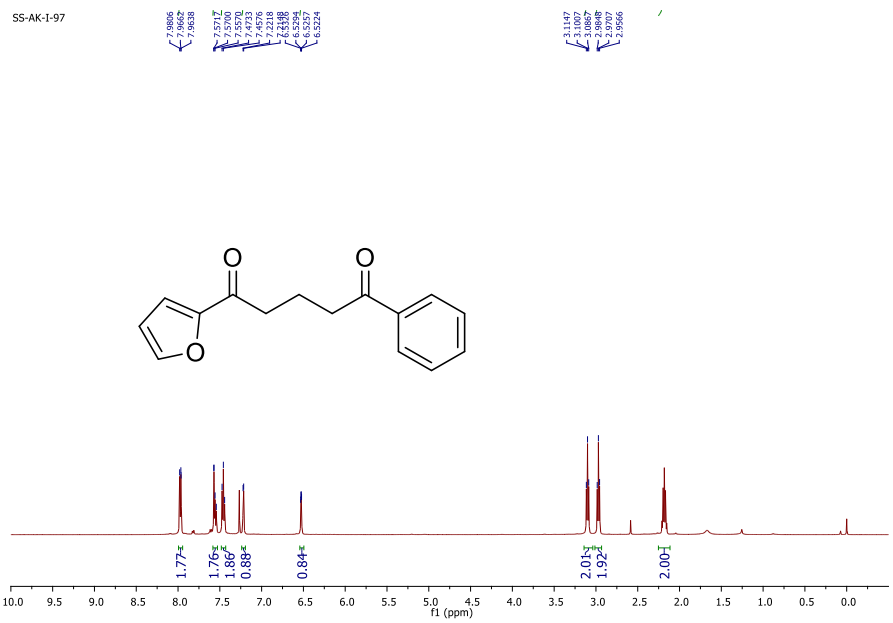


Figure 61: ^{1}H NMR spectrum (500MHz) of **3ha** in $CDCl_3$

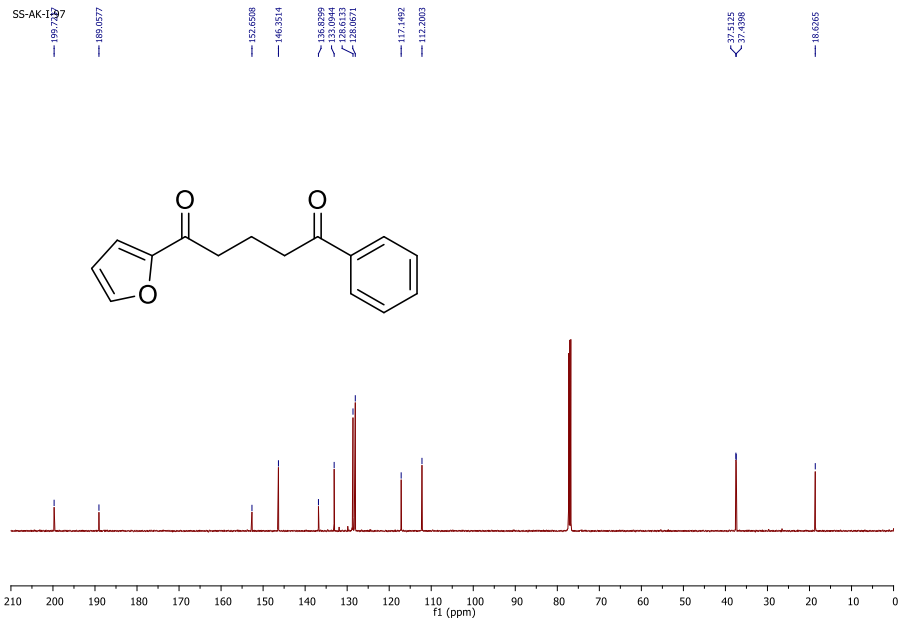


Figure 62: ^{13}C NMR spectrum (125MHz) of **3ha** in $CDCl_3$

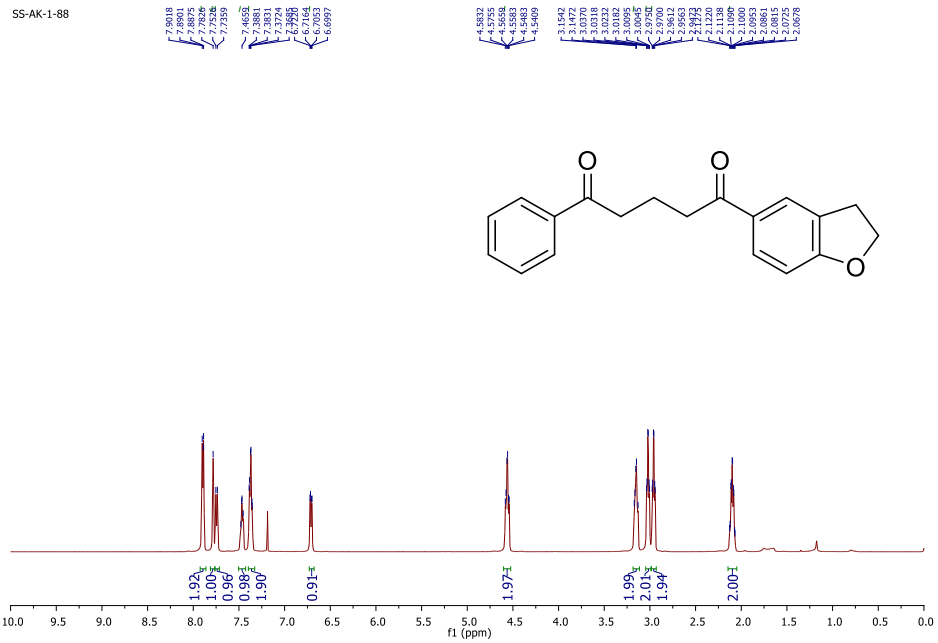


Figure 63: ^{1}H NMR spectrum (500MHz) of **3ak** in $CDCl_3$

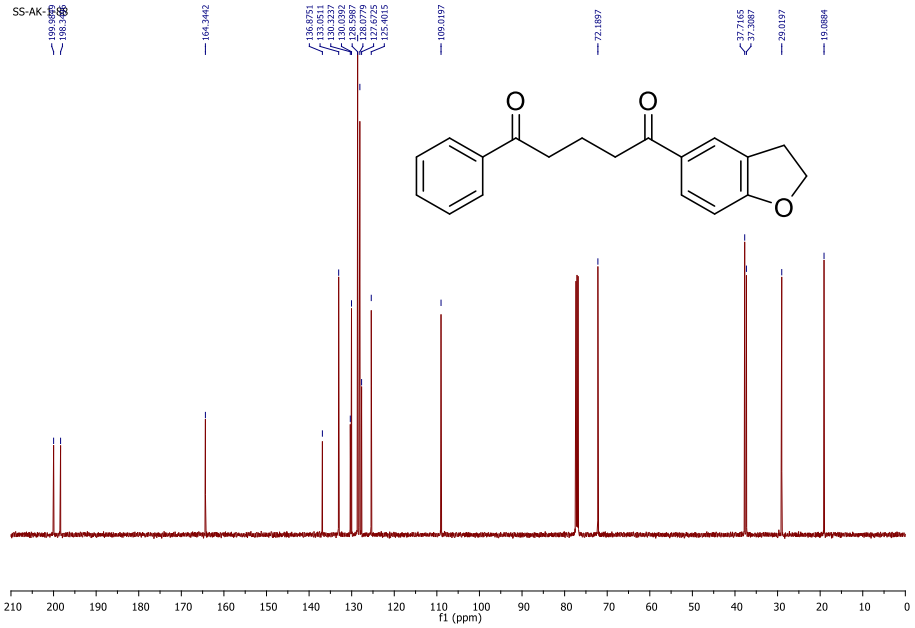


Figure 64: ^{13}C NMR spectrum (125MHz) of **3a**k in $CDCl_3$

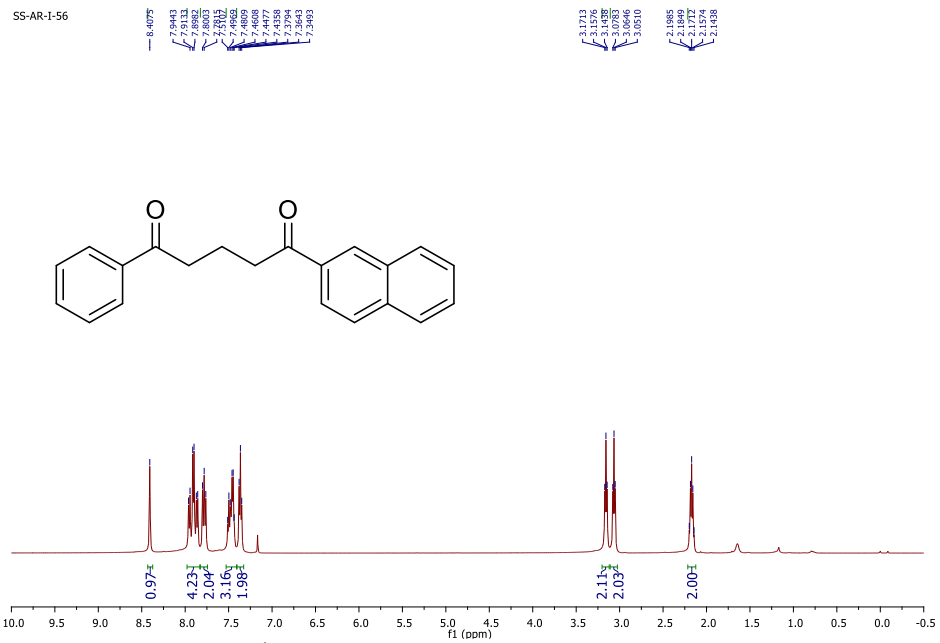


Figure 65: ^{1}H NMR spectrum (500MHz) of **3ai** in $CDCl_3$

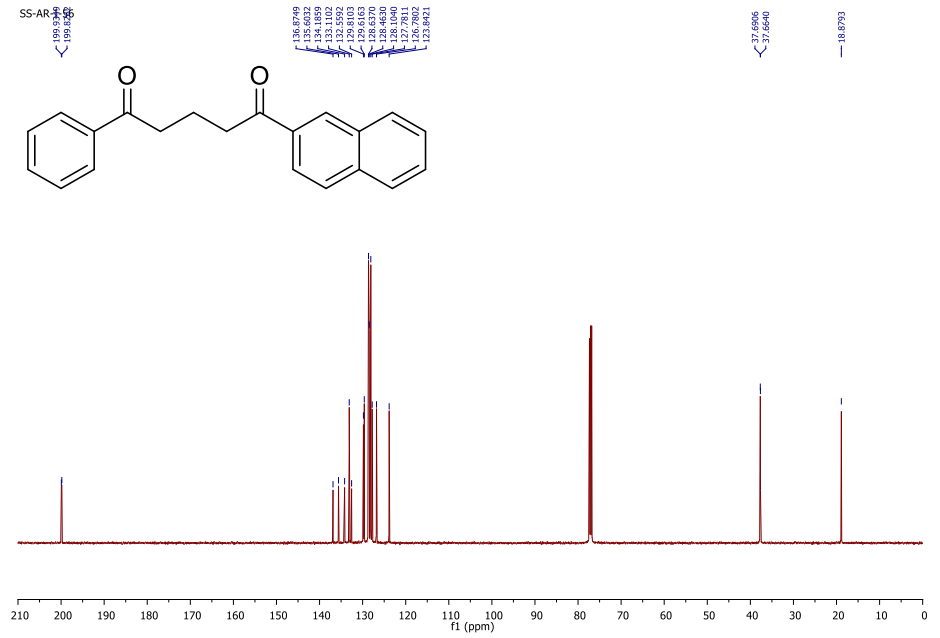


Figure 66: ^{13}C NMR spectrum (125MHz) of **3a**i in $CDCl_3$

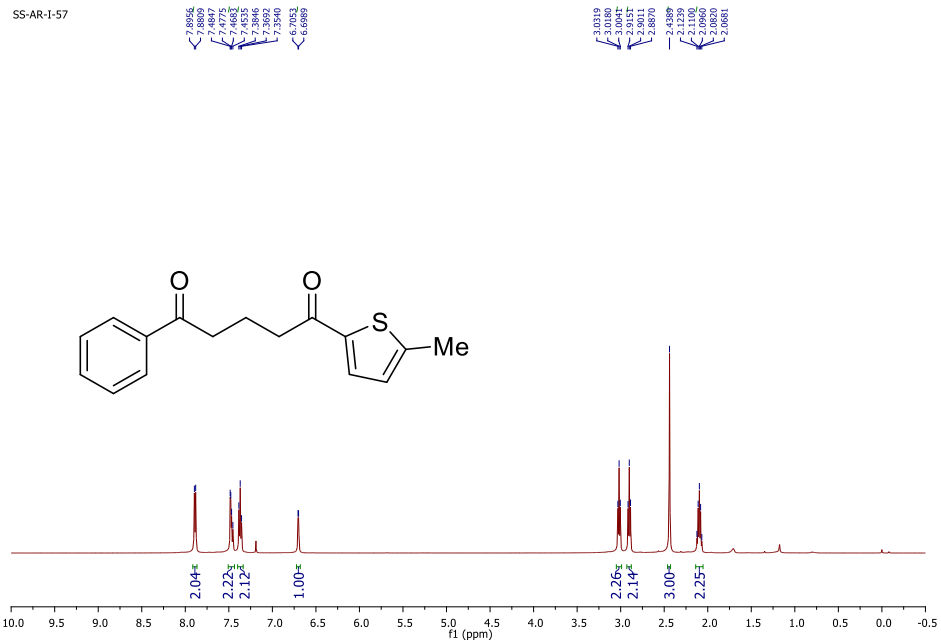


Figure 67: ^{1}H NMR spectrum (500MHz) of **3aj** in $CDCl_3$

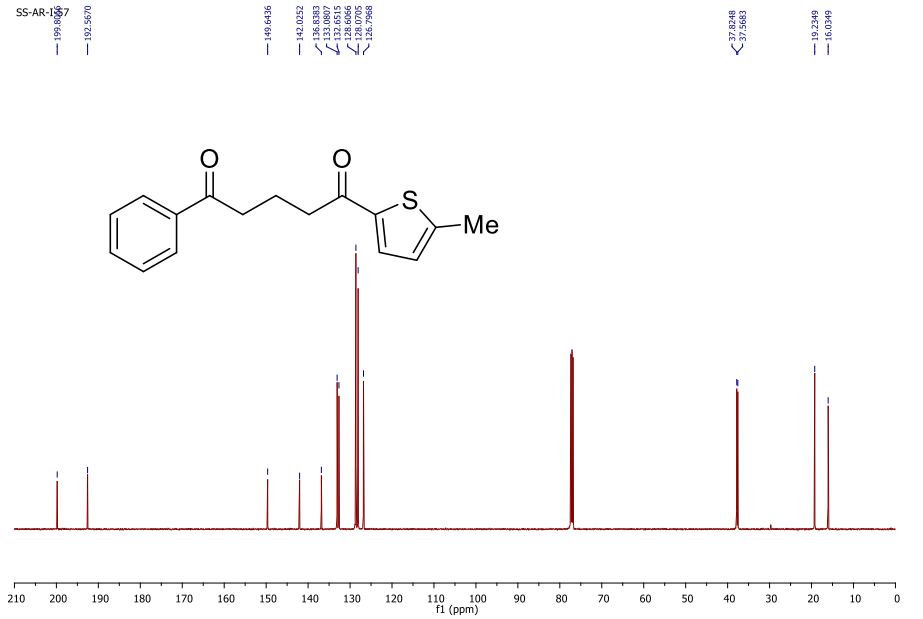


Figure 68: ^{13}C NMR spectrum (125MHz) of **3aj** in $CDCl_3$

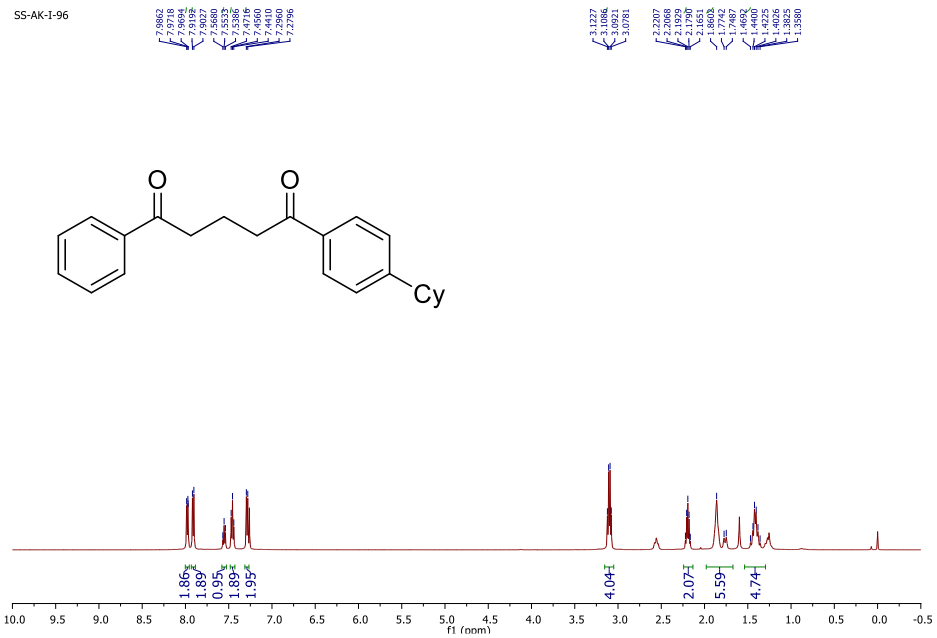


Figure 69: ^{1}H NMR spectrum (500MHz) of **3ag** in $CDCl_3$

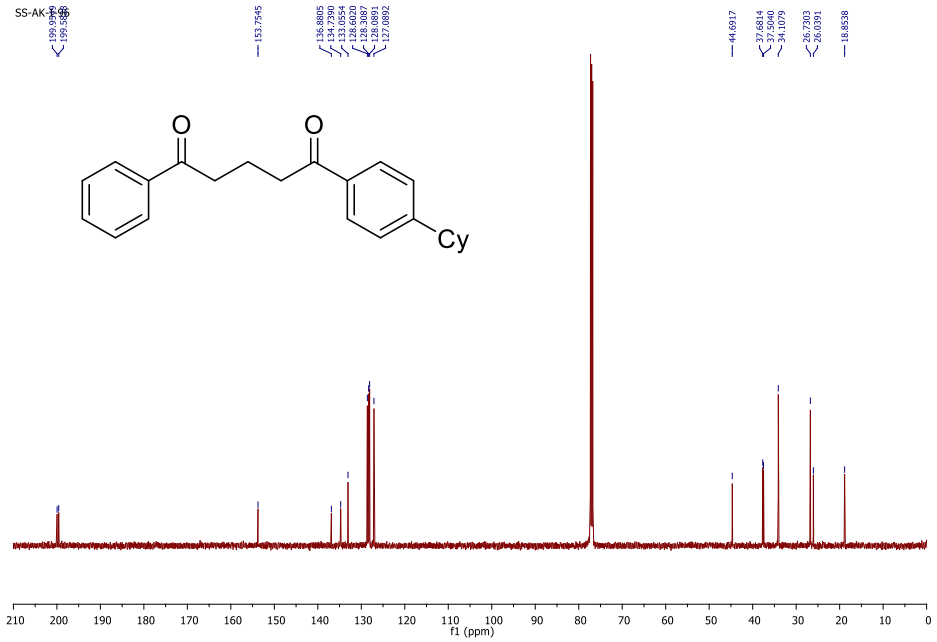


Figure 70: ^{13}C NMR spectrum (125MHz) of **3a**g in $CDCl_3$

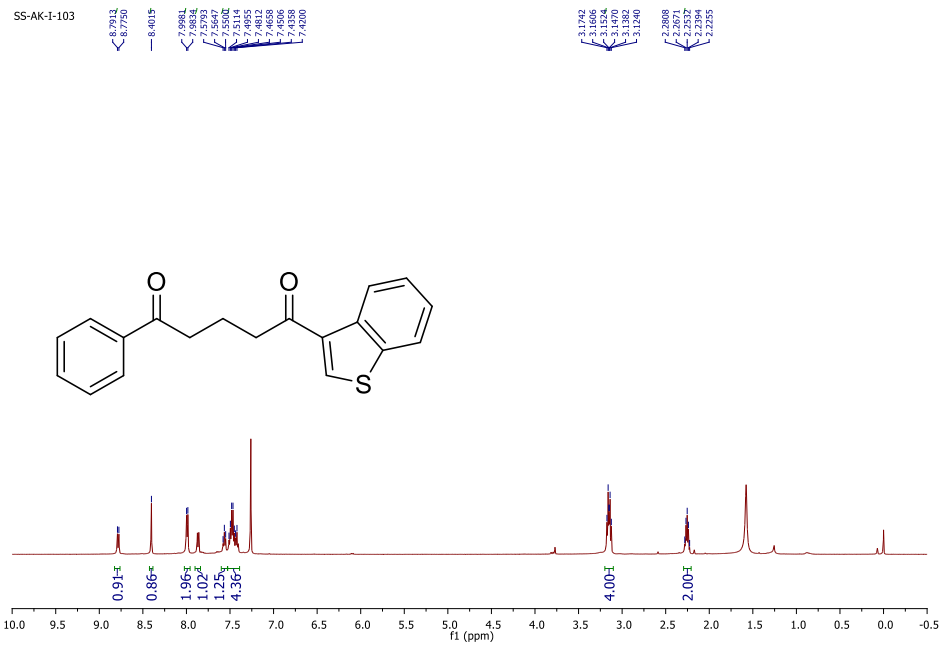


Figure 71: ^{1}H NMR spectrum (500MHz) of **3al** in $CDCl_3$

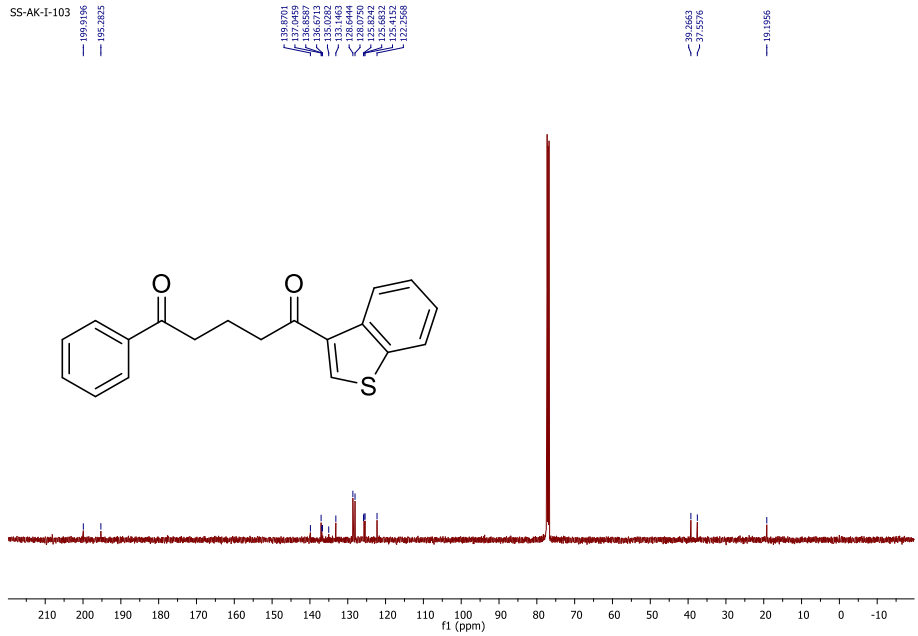


Figure 72: ^{13}C NMR spectrum (125MHz) of **3a**l in $CDCl_3$

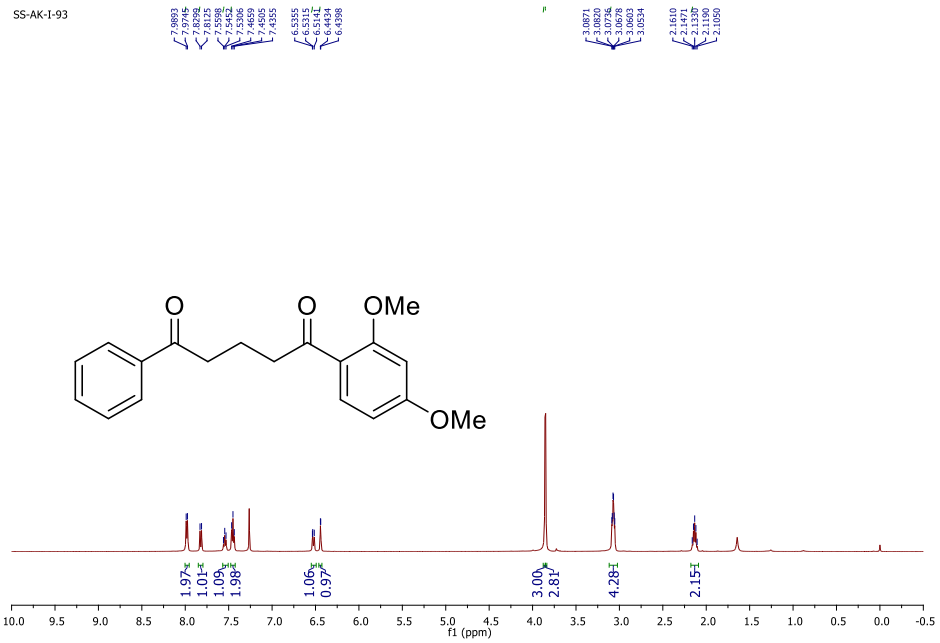


Figure 73: ^{1}H NMR spectrum (500MHz) of **3am** in $CDCl_3$

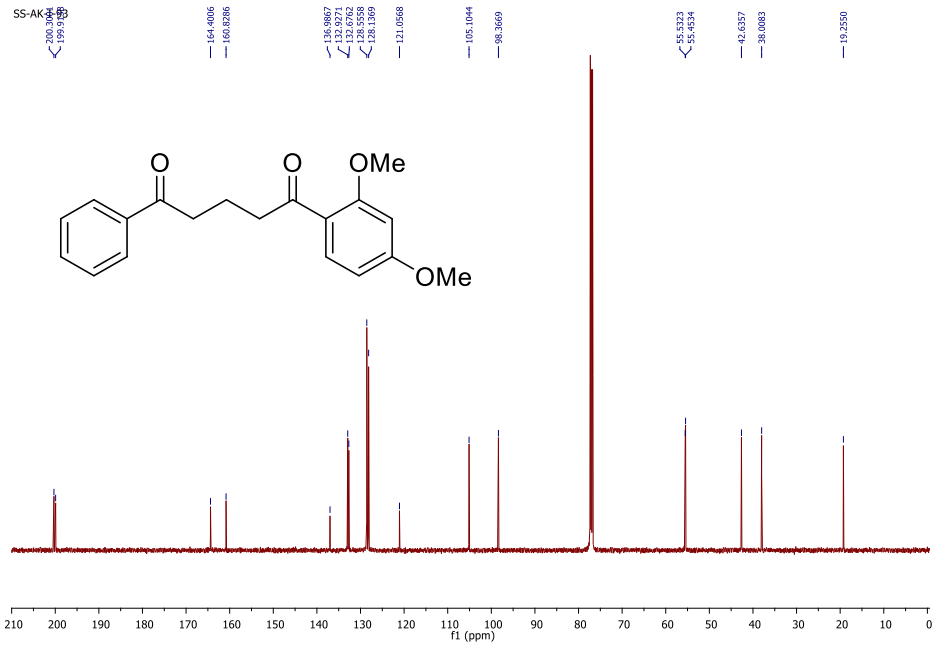


Figure 74: ^{13}C NMR spectrum (125MHz) of **3am** in $CDCl_3$

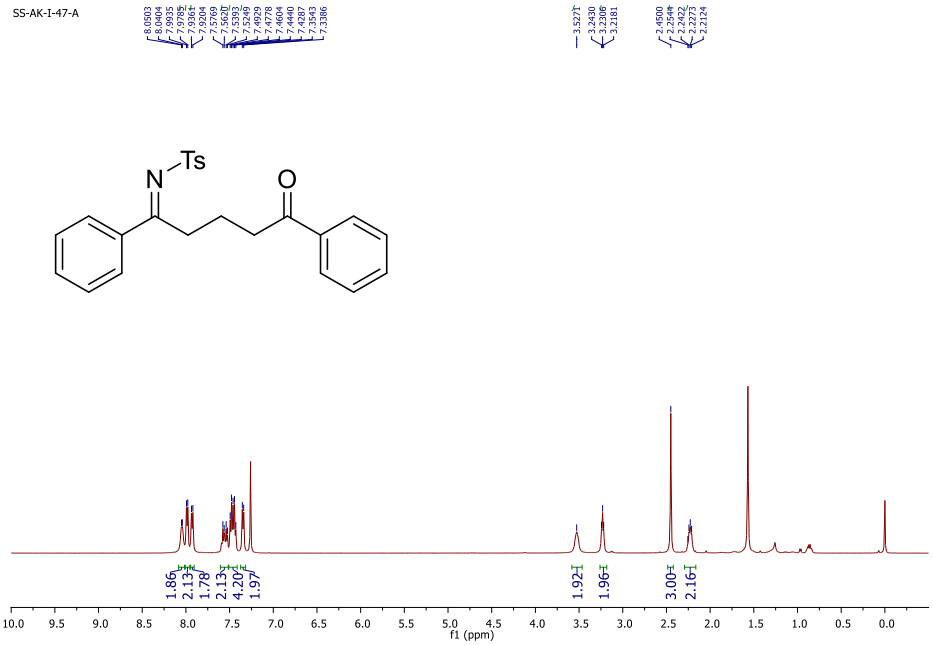


Figure 75: ^{1}H NMR spectrum (500MHz) of **3aa´** in $CDCl_3$

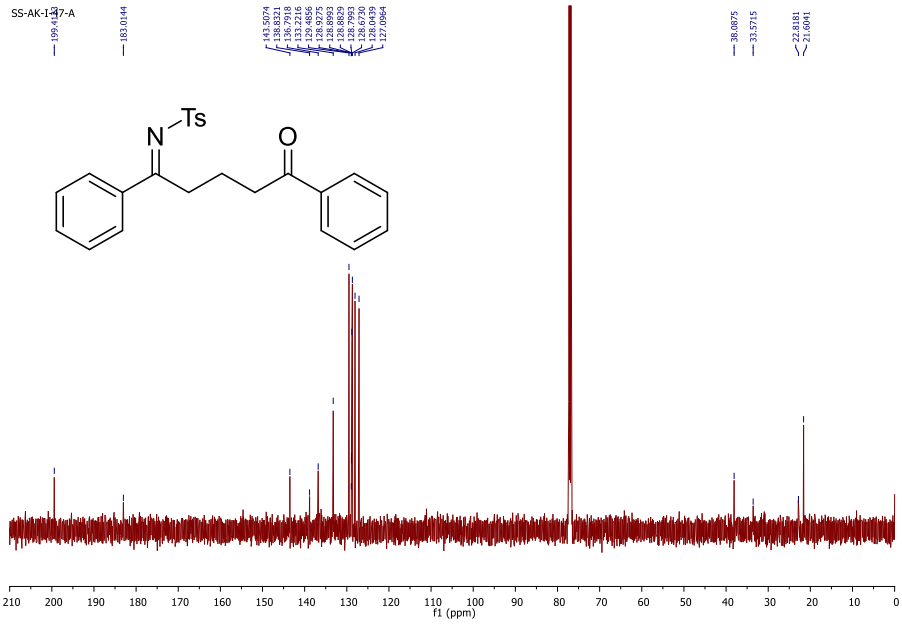


Figure 76: ^{13}C NMR spectrum (125MHz) of **3aa´** in $CDCl_3$

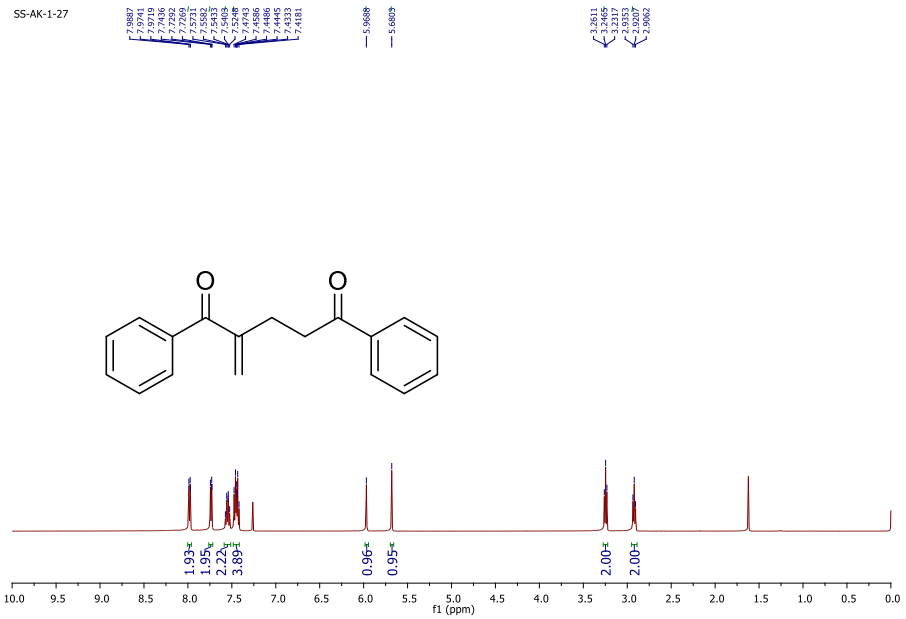


Figure 77: ^{1}H NMR spectrum (500MHz) of **4aa** in $CDCl_3$

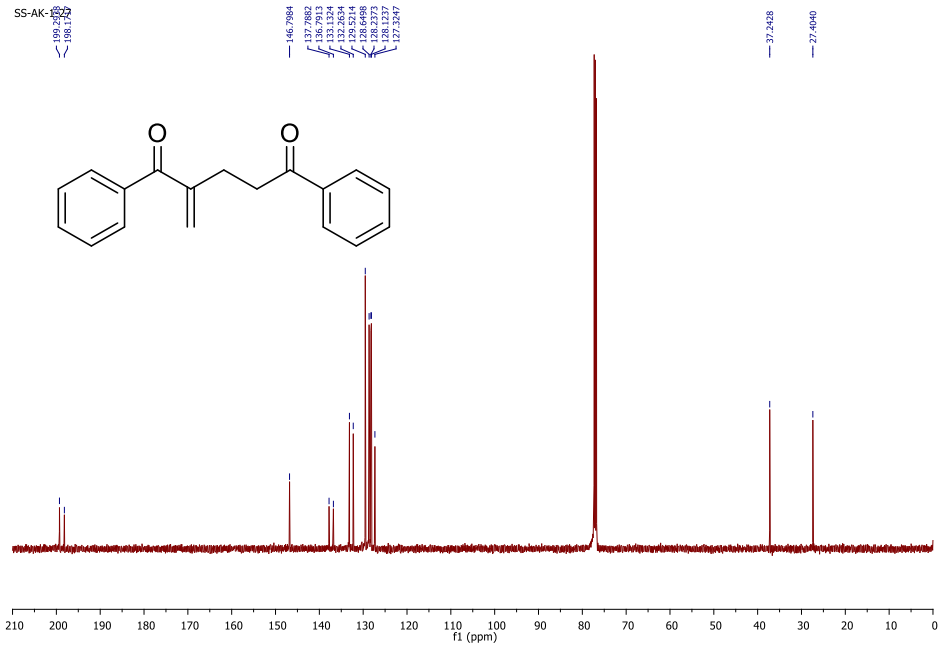


Figure 78: ^{13}C NMR spectrum (125MHz) of **4aa** in $CDCl_3$

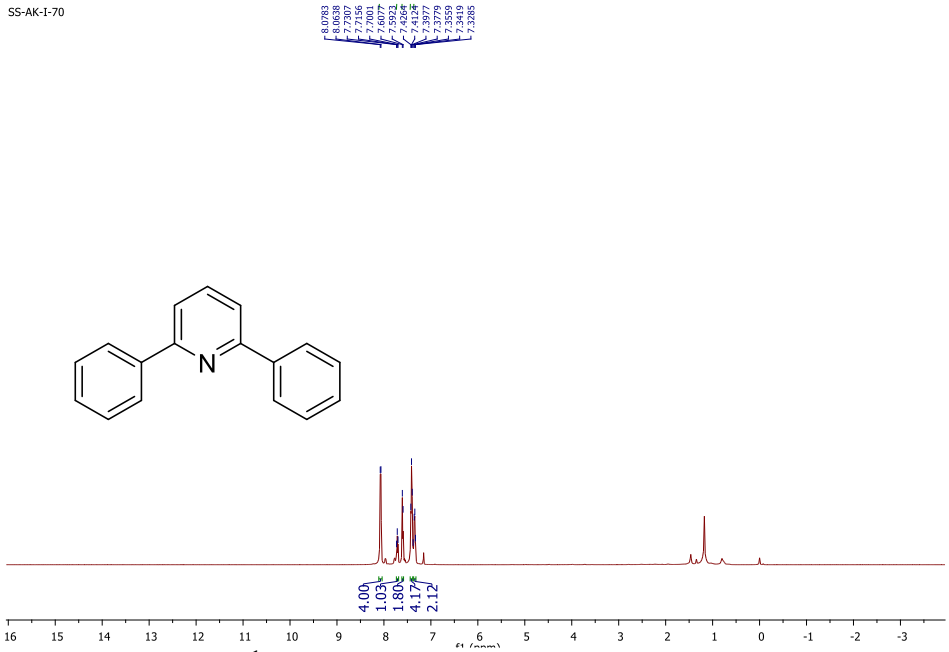


Figure 79: ^{1}H NMR spectrum (500MHz) of **6aa** in $CDCl_3$

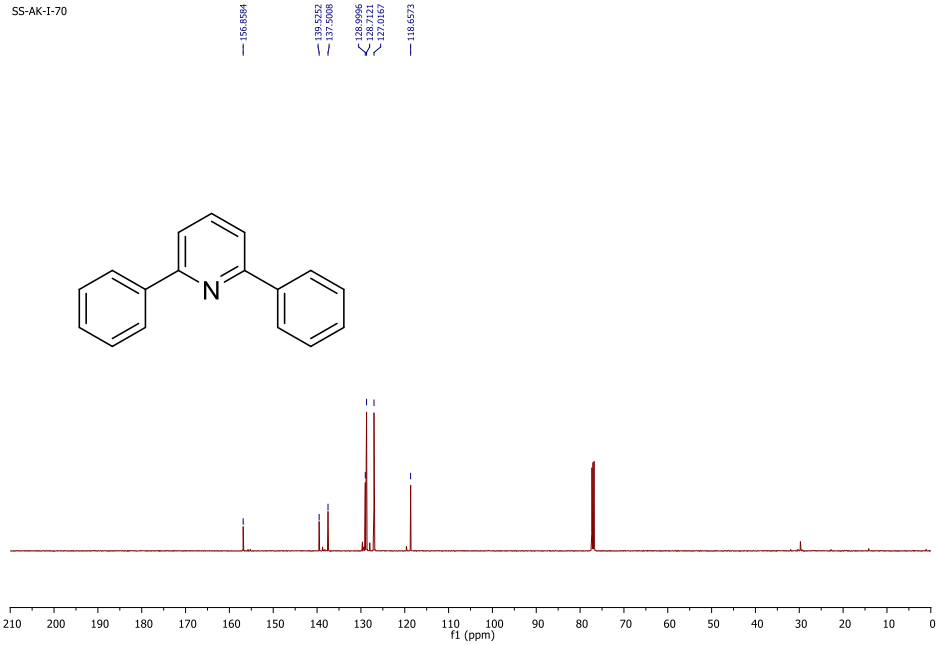


Figure 80: ^{13}C NMR spectrum (125MHz) of **6aa** in $CDCl_3$

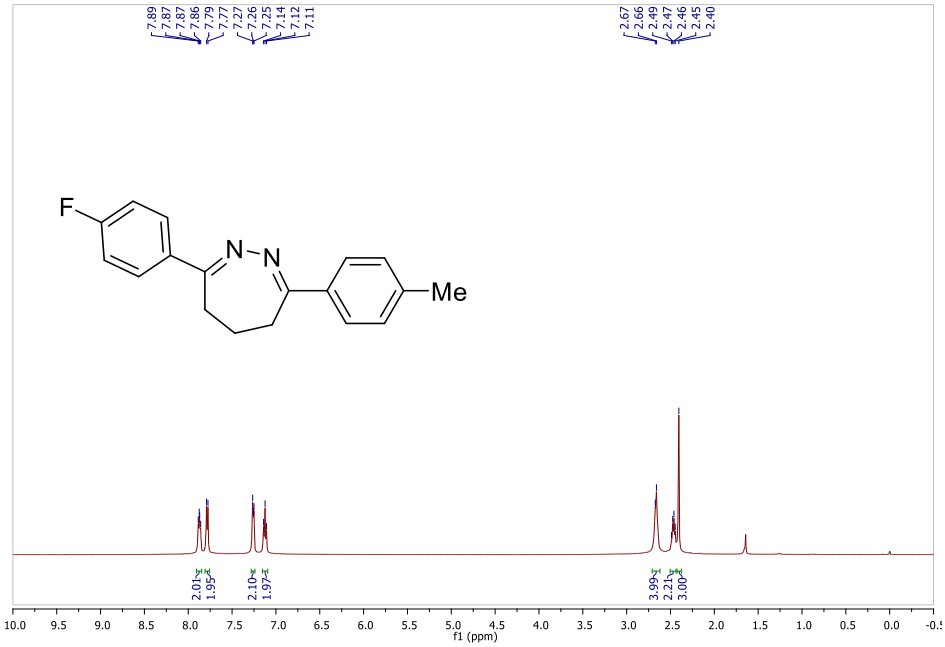


Figure 81: ^{1}H NMR spectrum (500MHz) of **7 aa** in $CDCl_3$

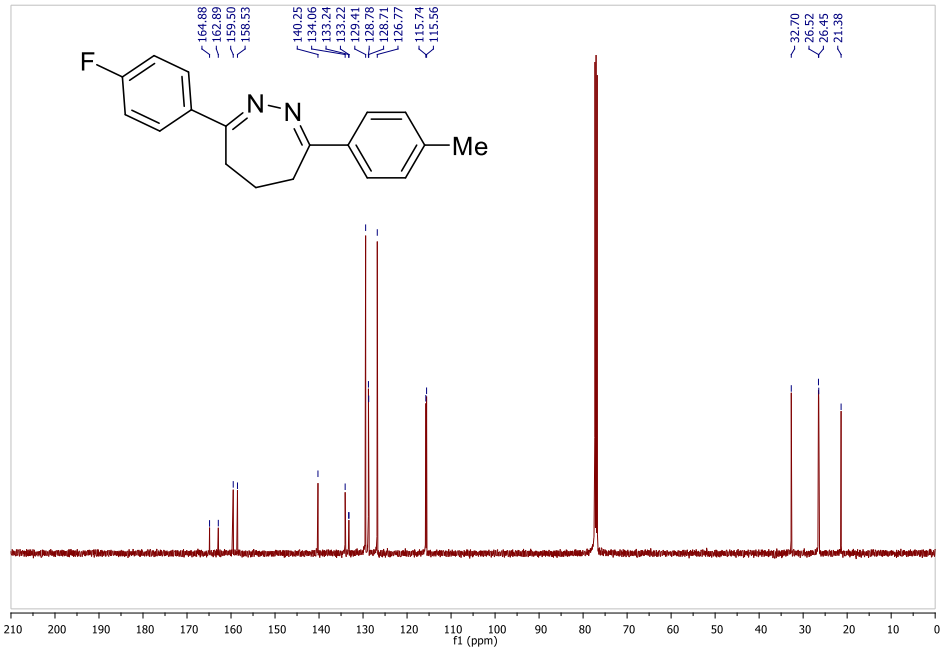


Figure 82: ^{13}C NMR spectrum (125MHz) of **7aa** in $CDCl_3$

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