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One Pot Syntheses of Indenes

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ABSTRACT

One pot syntheses of indene derivatives was achieved in high yields. Indenes were prepared from 1, 3 di phenyl propane-1-ones by the $AlCl_3$ promoted Friedel crafts benzoylation followed by intra molecular cyclisation reaction.

Keywords: Indenes, Aluminum chloride, 1,3-diphenyl propane-1-ones, Benzoyl chlorides

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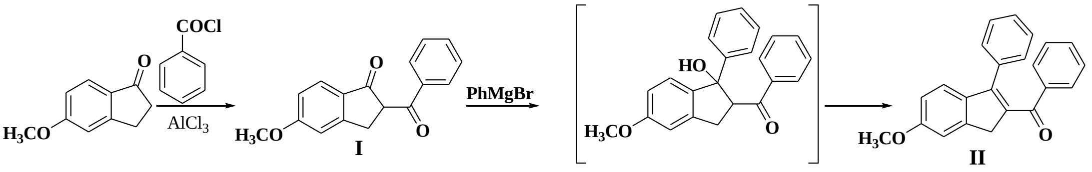
INTRODUCTION

Indene derivatives are important cyclic compounds that serve as building blocks for natural products [1,2] and pharmaceutical compounds possessing interesting biological activities [3-6], as well as many functional materials [7,8]. They can also be used as valuable ligands for indenyl metal complexes, which are widely utilized in various catalytic reactions [9-13]. Consequently, much effort has been devoted to the construction of indene frameworks [14-28]. Chemical transformations via transition-metal-catalyzed C–H bond activation are an important and challenging theme because the introduction of functional groups can be achieved more directly and byproducts such as metal halides are not formed [29-34]. Meanwhile, transition metal-catalyzed carbocyclization is a powerful method for the construction of indene derivatives in organic synthesis. As a result, various methods to construct indene ring systems have been reported, such as iron-catalyzed annulation of N-benzylic sulfonamides with disubstituted alkynes [35], palladium-catalyzed carboannulation of 2-(2-(1-alkynyl)phenyl)malonate with arylhalides [36], BF_3–Et_2O-mediated cycloaddition of methylenecyclopropanes with aldehydes [37], copper-catalyzed [3+2] cycloaddition of α-aryl diazoesters with terminal alkynes [38], $Cu(OTf)_2$-catalyzed rearrangement of vinylcyclopropenes [39], $FeCl_3$-catalyzed Friedel-Crafts reaction of arylated allylic alcohols [40], gold (I)-catalyzed intramolecular carboalkoxylation [41], ruthenium-mediated ring-closing metathesis [42], iodonium-promoted 5-endo-dig carbocyclization of 2-(2-ethynylphenyl) malonates [43] and photochemical cyclization of Tetrafluoropyridinyl (TFP)-substituted enediynes [44], Polyphosphoric Acid (PPA)-mediated cyclocondensation reaction of4-arylbutan-2-ones [45-47].

The earlier procedures for the synthesis of 2-benzoyl 3-aryl indene derivatives are reported in several ways. One synthesis is based on Grignard reaction of phenyl magnesium bromide on 2-benzoyl 1-indanoneI to give the required product II [48-50] (Scheme 1).



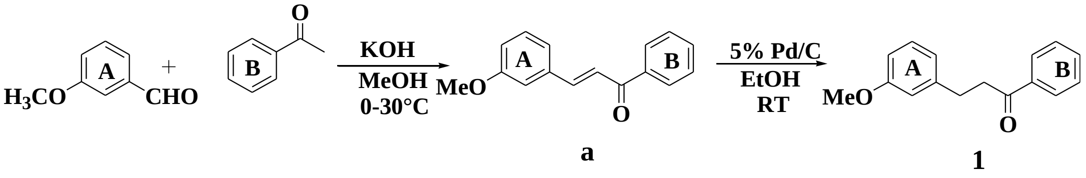
Scheme 1: Preparation of 3-Aryl-2-benzoyl indene

EXPERIMENTAL SECTION

Materials and methods

Most of the reagents used in this work were obtained from commercial suppliers and were of LR/AR grade. Solvents were purified before use by standard procedures. Melting points were determined using open capillary tubes on Polmon melting points apparatus (Model-96) and are uncorrected. Proton Nuclear Magnetic Resonance (^{1}H-NMR) (400 MHz) and Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) (100 MHz) spectra were recorded by using a Bruker 400 Spectrometer with Tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier Transform Infra-Red (FTIR) spectrophotometer as KBr pellets or with the neat products. Mass spectra were recorded on an API 2000 Liquid (LC-MS/MS) Applied Bio Systems MDS Sciex spectrometer. Microanalysis was performed on a Perkin-Elmer 240, C, H, N elemental analyzer. Analytical Thin Layer Chromatography (TLC) was conducted on E-Merck 60F254 aluminium-packed plates of silica gel (0.2 mm). Developed plates were visualized by using UV light or in an iodine chamber. High Performance Liquid Chromatography (HPLC) was performed by using a Shimadzu 2010 instrument.

General procedure for the syntheses of 3-(3-Methoxy-phenyl)-1-phenyl-propan-1-one (1)



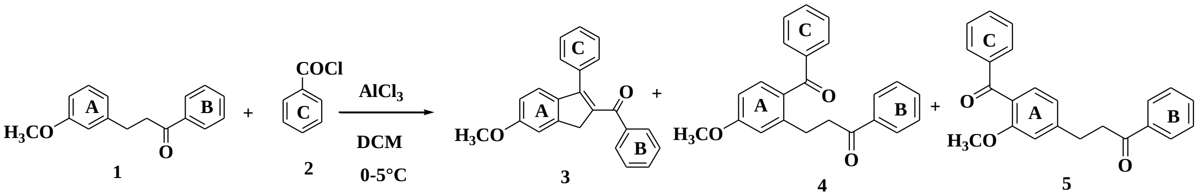
To a stirred solution of 3-methoxy benzaldehyde (20 g 0.14 mol) and acetophenone (21.1 g 0.17 mol) in methanol (80 ml), 6 M KOH solution (35 ml) was added slowly at 5-10°C and then stirred for another 4 h at 5-10°C. After completion of the reaction (monitored by TLC) solvent (methanol) was evaporated completely and the residue was extracted with ethyl acetate (2 × 200 ml), combined extracts were washed with 5% brine solution (100 ml) and DM water (100 ml). The organic layer was dried over sodium sulfate and concentrated under vacuum gave the crude product. Crude product was purified on silica gel column (eluting solvent 10% ethyl acetate in hexane) to afford a yellow color desired product.

3-(3-Methoxy-phenyl)-1-phenyl-propan-1-one (a): Yield: 30 g (88%); Description: Yellow solid; M.p: 56-58°C; IR (in KBr, cm^{-1}): 2832, 1960, 1656, 1578, 1492, 1267, 770;^1H-NMR (400 MHz, $CDCl_3$), (δ ppm)=8.17 (d, *J*=7.74 Hz, 2H), 7.96 (d, *J*=7.80 Hz, 1H), 7.64-7.75 (m, 2H), 7.57 (t, *J*=7.45 Hz, 2H), 7.49 (s, 1H), 7.43 (d, *J*=7.58 Hz, 1H), 7.34 (t, *J*=7.66 Hz, 1H), 7.02 (d, *J*=7.87 Hz, 1H), 3.82 (s, 3H, OCH_3);^{13}C-NMR (100 MHz, $CDCl_3$), (δ ppm)=187.0, 161.9, 142.8, 136.7, 135.9, 134.3, 129.7, 129.4, 129.0, 123.3, 118.5, 113.3, 111.8, 56.0.

To a solution of a (3-(3-Methoxy-phenyl)-1-phenyl-propan-1-one) (25 g) and ethanol (500 ml) 5% Pd/C (1.2 g) was added at RT, after 15 min H_2 gas was passed slowly at RT for 3 h. After completion of the reaction (monitored by TLC) Pd/C was filtered through celite bed and washed with ethanol (50 ml), total reaction mass was concentrated under vacuum to get the desired product.

3-(3-Methoxy-phenyl)-1-phenyl-propan-1-one (1): Yield: 24 g (95%); Description: White solid; M.p: 65-67.5°C; IR (in KBr, cm^{-1}): 2931, 1916, 1679, 1593, 1448, 1256, 746; ^1H-NMR (400 MHz, $CDCl_3$), (δ ppm)=7.97 (d, *J*=7.55 Hz, 2H), 7.56 (t, *J*=7.34 Hz, 1H), 7.46 (t, *J*=7.6 Hz, 2H), 7.26-7.21 (m, 1H), 6.88-6.75 (m, 3H), 3.80 (s, 3H, OCH_3), 3.30 (t, *J*=4.2 Hz, 2H), 3.06 (t, *J*=7.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$), (δ ppm)=197.6, 161.9, 141.2, 137.4, 132.9, 129.4, 128.6, 128.4, 120.2, 113.5, 111.3, 56.0, 41.2, 30.2;

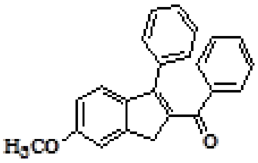
General procedure for the syntheses of 6-methoxy-3-aryl-2-benzoyl indenes (3)



To a stirred solution of aluminum chloride (4.23 g, 0.031 mol) and Dichloromethane (DCM) (30 ml) at 0-5°C substituted benzoyl chloride ((5.5 g, 0.031 mol in DCM) was added over 20 min, after 10 min 1 (5 g, 0.020 mol in 20 ml DCM) was added at 20-25°C, Stirred at RT. After completion of the reaction (monitored by TLC) the reaction mixture was quenched in to 10% aq HCl solution (100 ml) and extracted with DCM (2 × 100 ml). Organic layer were washed with DM water (200 ml) and dried over sodium sulfate and concentrated under vacuum, to get the crude product. Crude product was purified on silica gel column (eluting solvent 10% ethyl acetate in hexane) to afford a desired product3, 4 and 5.

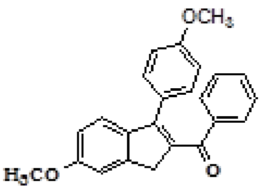
Characterization data

(6-Methoxy-3-phenyl-1H-inden-2-yl)-phenyl-methanone(3a)



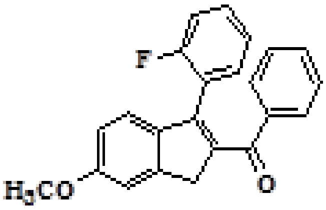
M.p: 96.1-99.8°C; IR (in KBr, cm^{-1}) 2832, 1610, 1343, 1244, 1025, 697; ^1H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.51 (d, *J*=7.48 Hz, 2H), 7.38 (d, *J*=4.48 Hz, 1H), 7.26-7.13 (m, 7H), 7.07 (t, *J*=7.26 Hz, 2H), 6.92 (dd, *J*=1.6, 1.76 Hz, 1H), 4.02 (s, 2H), 3.88 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm)=195.19, 160.27, 150.87, 146.03, 138.39, 138.15, 137.43, 134.31, 131.45, 129.37, 129.17, 128.01, 127.56, 123.61, 113.42, 109.91, 55.64, 40.38.

[6-Methoxy-3-(4-methoxy-phenyl)-1H-inden-2-yl]-phenyl-methanone(3b)



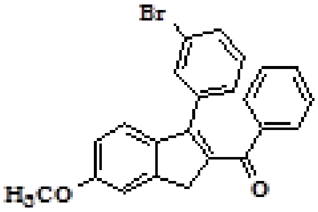
M.p: 102.1-104.9°C; IR (in KBr, cm^{-1}); 2836, 1604, 1243, 1030, 714; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.51 (d, *J*=7.48 Hz, 2H), 7.39 (d, *J*=8.52 Hz, 1H), 7.23 (t, *J*=7.52 Hz, 1H), 7.16-7.07 (m, 5H), 6.93-6.90 (q, 1H), 6.67 (d, *J*=8.44 Hz, 2H), 3.99 (s, 2H), 3.87 (s, 3H), 3.71 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm)=195.30, 160.23, 159.43, 150.62, 146.09, 138.47, 137.54, 137.47, 131.38, 130.72, 129.19, 127.59, 126.68, 123.60, 113.55, 113.38, 109.91, 55.62, 55.23, 40.30.

[3-(2-Fluoro-phenyl)-6-methoxy-1H-inden-2-yl]-phenyl-methanone(3c)



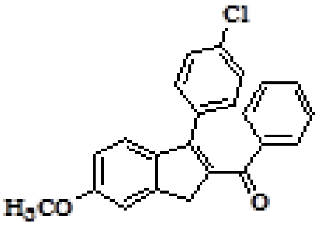
M.p: 93.7-97.8°C; IR (in KBr, cm^{-1}); 2839, 1613, 1354, 1243, 1030, 696; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.53 (d, *J*=7.2 Hz, 2H), 7.23 (t, *J*=7.56 Hz, 2H), 7.15-7.10 (m, 5H), 6.94 (d, *J*=7.52 Hz, 1H), 6.91 (d, *J*=7.84 Hz, 1H), 6.85 (t, *J*=8.9 Hz, 1H), 4.05 (s, 2H), 3.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm)=194.61, 160.54, 160.41, 158.08, 145.77, 145.14, 139.78, 138.51, 137.04, 131.52, 131.13, 131.09, 130.18, 130.10, 128.84, 127.54, 123.82, 123.79, 123.62, 122.60, 122.44, 115.56, 115.35, 113.56, 109.82, 55.64, 40.31.

[3-(3-Bromo-phenyl)-6-methoxy-1H-inden-2-yl]-phenyl-methanone(3d)



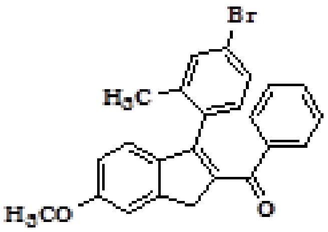
IR (neat, cm^{-1}) 2936, 1733, 1614, 1354, 1242, 1031, 696; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.53-7.45 (q, 2H), 7.32 (t, *J*=6.08 Hz, 2H), 7.25 9d, *J*=7.12 Hz, 2H), 7.16-7.03 (m, 4H), 6.99 (t, *J*=7.7 Hz, 1H), 6.93 (d, *J*=7.7 Hz, 1H), 4.01 (s, 2H), 3.87 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm)=194.88, 160.46, 149.39, 145.94, 138.95, 138.41, 136.85, 136.30, 132.32, 131.70, 130.99, 129.57, 129.10, 129.03, 128.92, 128.43, 128.17, 127.84, 127.73, 123.40, 122.10, 113.57, 110.02, 55.65, 4.034.

[3-(4-Chloro-phenyl)-6-methoxy-1H-inden-2-yl]-phenyl-methanone (3e)



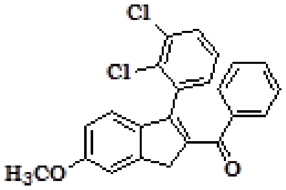
M.p: 124.1-128.2°C; IR (in KBr, cm^{-1}) 2836, 1599, 1356, 1241, 1086, 712; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.50 (d, *J*=7.44 Hz, 2H), 7.32-7.26 (m, 2H), 7.16-7.09 (m, 7H), 6.91 (d, *J*=10.48 Hz, 1H), 4.0 (s, 2H), 3.87 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 194.90, 160.39, 149.53, 145.97, 138.59, 138.30, 137.0, 133.98, 132.80, 131.71, 130.62, 129.13, 128.28, 127.77, 123.34, 113.51, 110.01, 55.65, 40.44.

[3-(4-Chloro-phenyl)-6-methoxy-1H-inden-2-yl]-phenyl-methanone(3f)



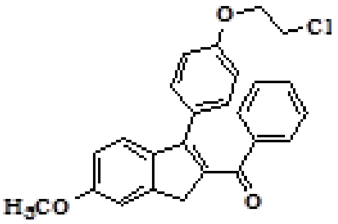
M.p: 116.2-120.3°C; IR (in KBr, cm^{-1}) 2919, 1622, 1356, 1248, 1098, 718; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm)=7.45 (d, *J*=7.48 Hz, 2H), 7.31-7.26 (m, 1H), 7.16-7.11 (m, 5H), 7.02 (d, *J*=8.52 Hz, 1H), 6.86 (dd, *J*=3.44, 3.88 Hz, 2H), 4.04 (s, 2H), 3.89 (s, 3H, OCH_3), 2.08 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 194.73, 160.56, 150.46, 145.91, 139.22, 138.85, 138.10, 137.48, 133.26, 132.80, 131.43, 131.08, 128.45, 127.54, 123.79, 121.83, 113.56, 109.90, 55.65, 40.13, 19.93.

[3-(2,3-Dichloro-phenyl)-6-methoxy-1H-inden-2-yl]-phenyl-methanone(3g)



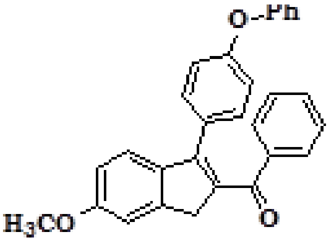
M.p: 142.1-146.8°C; IR (in KBr, cm^{-1}) 2833, 1613, 1244, 1031, 708; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm): 7.52 (d, *J*=7.48 Hz, 2H), 7.20-7.21 (m, 2H), 7.15 (t, *J*= 8.05 Hz, 3H), 7.10 (d, *J*=9.88 Hz, 1H), 9.97-9.94 (m, 2H), 6.88 (dd, *J*=1.62, 1.2 Hz, 1H), 4.08 (s, 2H), 3.87 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 194.32, 160.56, 148.69, 145.62, 140.05, 138.96, 136.52, 136.13, 133.32, 131.58, 131.27, 129.97, 129.52, 128.38, 127.47, 126.99, 123.97, 113.58, 109.89, 55.63, 40.04.

{3-[4-(2-Chloro-ethoxy)-phenyl]-6-methoxy-1H-inden-2-yl}-phenyl-methanone(3h)



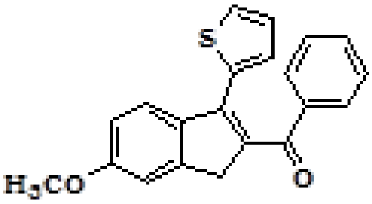
mp: 98.6-102.2 °C; IR (in KBr, cm^{-1}) 2835, 1603, 1359, 1244, 1027, 711; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm): 7.50 (d, *J*=7.48 Hz, 2H), 7.37 (d, *J*=8.56 Hz, 1H), 7.26 (t, *J*=6.99 Hz, 1H), 7.16-7.07 (m, 5H), 6.93-6.90 (m, 1H), 6.69 (d, *J*=8.6 Hz, 2H), 4.12 (t, *J*=5.85 Hz, 2H), 3.99 (s, 2H), 3.88 (s, 3H), 3.73 (t, *J*=5.85 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 195.23, 160.26, 157.94, 150.46, 146.07, 138.47, 137.67, 137.41, 131.41, 130.82, 129.20, 127.63, 127.48, 123.55, 114.46, 113.42, 109.92, 67.99, 55.64, 41.74, 40.31.

[6-Methoxy-3-(4-phenoxy-phenyl)-1H-inden-2-yl]-phenyl-methanone(3i)



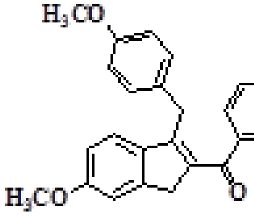
M.p: 137.8-141.6°C; IR (in KBr, cm^{-1}) 2835, 1632, 1355, 1242, 1098, 711; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm): 7.51 (d, *J*=7.48 Hz, 2H), 7.41 (d, *J*=8.5 Hz, 1H), 7.33 (t, *J*=7.55 Hz, 3H), 7.18-7.16 (m, 4H), 7.15-7.13 (m, 2H), 7.10 (d, *J*=7.2 Hz, 1H), 6.84-6.78 (m, 4H), 4.03 (s, 2H), 3.89 (s, 3H, OCH3); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 195.21, 160.36, 157.22, 156.96, 150.60, 146.12, 138.75, 138.13, 137.30, 131.28, 130.94, 129.68, 129.48, 129.30, 127.65.

(6-Methoxy-3-thiophen-2-yl-1H-inden-2-yl)-phenyl-methanone (3j)



M.p: 79.3-82.4°C; IR (in KBr, cm^{-1}): 2934, 2166, 1606, 1245, 1025, 811, 711; ^{1}H-NMR (400 MHz, $CDCl_3$) (δ ppm): 7.64 (d, *J*=8.27 Hz, 3H), 7.33-7.22 (m, 1H), 7.21-7.15 (m, 4H), 6.97-6.81 (m, 2H), 6.80 (d, *J*=3.82 Hz, 3H), 3.99 (s, 2H), 3.90 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 195.15, 160.22, 145.59, 142.10, 139.0, 138.14, 136.76, 134.71, 131.95, 129.19, 129.0, 127.87, 127.11, 127.0, 123.51, 113.42, 109.97, 55.65, 40.71.

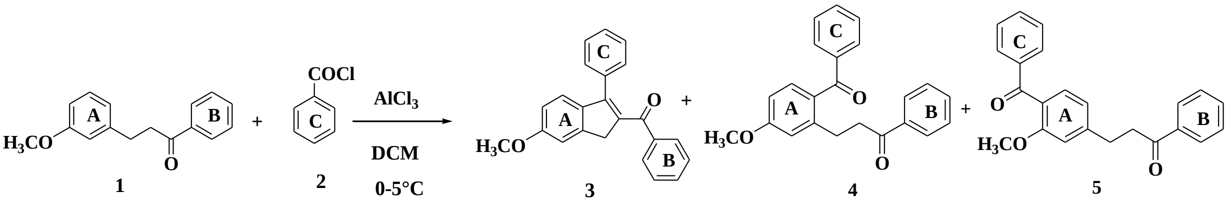
[6-Methoxy-3-(4-methoxy-benzyl)-1H-inden-2-yl]-phenyl-methanone (3k)



M.p: 101.22-104.12°C; IR (in KBr, cm^{-1}): 2842, 1685, 1353, 1255, 1075; ^1H-NMR (400 MHz, $CDCl_3$) (δ ppm): 7.73 (d, *J*=7.40 Hz, 2H), 7.50 (d, *J*=7.46 Hz, 1H), 7.40 (t, *J*=7.52 Hz, 2H), 7.25 (s, 1H), 7.05-7.04 (m, 3H), 6.82 (dd, *J*1=2.0 Hz, *J*2=2.0 Hz, 1H), 6.74 (d, *J*=8.44 Hz, 2H), 3.97 (s, 2H), 3.86 (s, 2H), 3.84 (s, 3H), 3.73 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) (δ ppm): 195.14, 160.08, 157.97, 150.88, 146.17, 140.39, 137.77, 137.57, 131.94, 130.78, 129.46, 128.62, 128.37, 123.34, 113.84, 113.20, 109.66, 55.55, 55.21, 40.66, 32.35.

RESULTS AND DISCUSSION

In our attempts to benzoylate 3-(3-Methoxy-phenyl)-1-phenyl-propan-1-one to obtain 4 was unsuccessful under normal Friedel-crafts reaction conditions, instead we obtained major compound 3, 4, and 5 are minor products, which were characterized by spectral means. To obtain these indene derivatives (3) in good yields the reaction conditions were optimized (Scheme 2).



Scheme 2: Synthesis of indenes 3 from 1 and 2

Firstly the mole ratios of aluminum chloride, reaction temperature and time were studied (Table 1) and found that at RT (25-30°C) and in 2 h compound 3 is formed in 60% yield.

Table 1: Optimization of moles of aluminum chloride, reaction temperature and time

Entry	$AlCl_3$ Equivalent	Solvent	Temperature (°C)	Time (h)	Yield %[a]		
					3	4	5
a	1.0	MDC	0-5	1.0	23	15	40
b	1.0	MDC	5-15	1.5	40	20	22
c	1.5	MDC	15-20	1.5	58	18	8
d	2.0	MDC	25-30	2.0	60	16	5

Later to improve the yields we studied other Lewis acids like $FeCl_3$ and BF_3-Et_2O and found that the product 3 is obtained only with $AlCl_3$ (2.0 equivalent) (Table 2).

Table 2: Reagent optimization study

Entry	Reagent	Solvent	Temperature (°C)	Time in (h)	Product
a	$AlCl_3$	MDC	30-35	2-4	60%
b	$FeCl_3$	MDC	30-35	5.0	ND
c	BF_3.OEt	MDC	30-35	8.0	ND

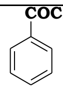
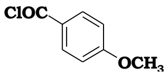
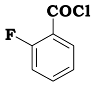
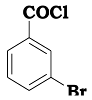
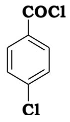
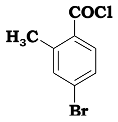
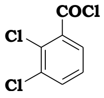
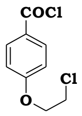
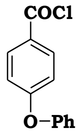
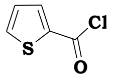
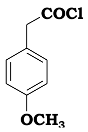
A screening of different solvents revealed that, apart from methylene chloride, ethylene dichloride and chloroform were also effective solvents, but yields are low compared with methylene chloride. Reactions were tried in 1,4-dioxane, THF, 2-Methyl THF, toluene, DMSO, DMF and acetonitrile but the target product was not obtained (Table 3).

Table 3: Solvent optimization study

Entry	$AlCl_3$equivalent	Solvent	Temperature (°C)	Product %		
				3	4	5
a	2.0	MDC	RT	60	21.22	2.38
b	2.0	EDC	RT	50	18.21	3.20
c	2.0	$CHCl_3$	RT	48	20.21	8.25
d	2.0	THF	RT	Traces		
e	2.0	2-Me THF	RT	Traces		
f	2.0	Toluene	40-45	ND		
g	2.0	Hexane	40-45	ND		
h	2.0	Dioxane	55	ND		
i	2.0	DMF	60	ND		
j	2.0	DMSO	60	ND		

To study the generality of the reaction we examined different substitutions on a ring and found that cyclisation occur only with 3-methoxy compounds. Later we studied the effect of substituents on C ring (benzoylchloride). The results are tabulated in Table 4.

Table 4: Synthesis of indene derivatives from 1 and 2 (only C ring variation)

S. No.	Substrate	Reaction time	Yield %		
			3	4	5
a		2.0 h	60	21.22	2.38
b		2.5 h	80.63	12.24	2.22
c		1.5 h	40.32	19.22	2.15
d		1.0 h	30.15	21.9	4.22
e		2.0 h	67.12	22.14	2.56
f		4.0 h	21.22	17.37	8.65
g		4.0 h	60.8	21.22	2.88
h		3.5 h	56.6	18.78	2.24
i		8.0 h	55.5	20.1	3.86
j		6.0 h	48.22	17.54	11.28
k		3.0 h	65.8	13.55	22.2

CONCLUSION

We have successfully developed a simple methodology for the syntheses of 2,3-disubstituted indene derivatives via $AlCl_3$ Friedel-crafts acylation followed by intra molecular cyclisation reactions.

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