# An Efficient Synthesis of Highly Substituted Indanones and Chalcones Promoted By Superacid

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The Degree of Master of Science


Department of Chemistry

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## Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of **Dr. G. Satyanarayana**.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Student's Roll no.– **CY12M1003**

**Approval Sheet**

This thesis entitled **"An Efficient Synthesis of Highly Substituted Indanones and Chalcones Promoted By Superacid"** by Amrita Das is approved for the degree of Master of Science from IIT Hyderabad.

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Dedicated to

*My Family*

# Abstract

Superacid promoted one-pot method was developed for the efficient synthesis of indanones. This process enabled the formation of dual C-C bond between aryl isopropyl ketones and benzaldehydes. Interestingly, when the reaction was performed between acetophenones and benzaldehydes, it was impeded after the aldol condensation and furnished the corresponding chalcones.

# Contents

# An Efficient Synthesis of Highly Substituted Indanones and Chalcones Promoted By Superacid

## 1.1 Introduction:

A synthetic chemist is always challenged with the need to discover methods that emphasise on the environmental and limiting resources aspects. This led to focus more keenly on designing more accelerated and competent strategies in the organic synthesis. The growing demand for the preparation of the basic moieties of many natural products has still further strengthened this focus. Thus, as a result of these demands, the accelerated synthetic procedures (like sonochemical and microwave techniques) that can reduce the number of reactions and purification steps, are highly approving.

These approaches improve the efficiency of a chemical reaction wherein a reactant is subjected to sequential chemical reactions in one reactor, thus, saving time and resources along with increasing the chemical yield. Therefore, one-pot synthetic methods have become indispensible in synthesis of organic compounds as they permit the construction of more than one bond. An illustration of a one-pot synthesis is demonstrated in the total synthesis of tropinone and Gassman indole synthesis. Highly complex molecules have also been generated with multiple stereo centres, such as, oseltamivir, with significantly shortened number of steps and commercial implications. Similarly, among the classical C-C bond forming reactions, Friedel-Crafts reaction is one of the best classical methods for either alkylation or acylation discovered by Friedel and Crafts in 1877.[1] Remarkably, in past few decades this reaction has been extensively applied in the field of organic synthesis under Brønsted/Lewis acidic conditions.[2,3,4] Significantly, Friedel-Crafts cyclization became useful method for the synthesis of cyclic systems via single or multiple C-C bonds formation.[5]

Therefore, the development of such methods that facilitates C-C bonds formation in a single step, for the synthesis of carbocyclic compounds, are of particular interest since many cyclic systems are present as core structures in many natural products of biological relevance. Notably, the concept of superelectrophiles has been brought by Olah et al in the seventies.[6] Of late, this concept of superelectrophiles has been applied to construct ring systems efficiently[3b] as they are more reactive species.

In continuation of our research interests on domino/sequential domino one-pot transformations,[7] and based on recently reported work on the synthesis of indanones using simple cinnamate esters via dual C-C bond formation promoted by superacid.[8] Also, very recently, we have developed a mild method for the controlled formation of β-diaryl esters without the subsequent intramolecular acylation to give the indanones, via Freidel-Crafts Michael addition on cinnamate esters as key step for the synthesis of chromans.[9] With this background, we became interested to design a novel methodology towards indanone synthesis promoted by acid.

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## 1.2 Biological activity:

Indanones are ubiquitous systems that are present in many natural products of biological relevance as well as in a variety of drug candidates. Representative examples of such compounds include neo-lignin,[10] pauciflorol F,[11] alcyopterosin N,[12] and indacrinone[13] (Fig 1). Because of the importance of indanone core, various acid mediated approaches have been reported on their synthesis.[14]

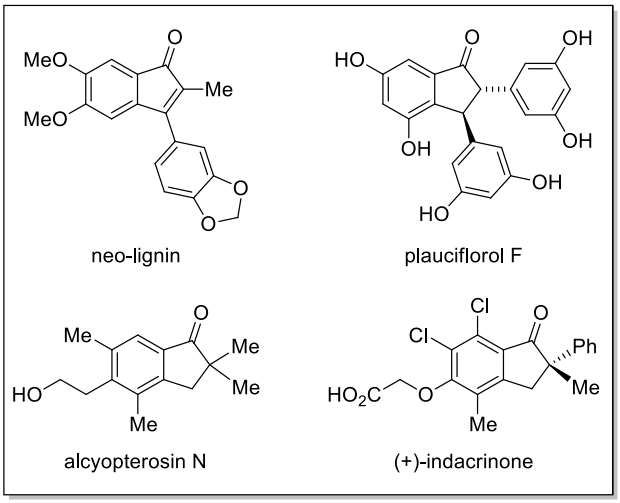



Figure 1. Representative examples for indanone based drugs and natural products.

Interestingly, chalcones form a very important and abundant subclass of flavonoids; especially the prenyl or geranyl groups are found to display a variety of biological and pharmacological activities. For example, isobavachalcone showed antibacterial, antitubercular, anticancer, antifungal, anti-reverse transcriptase, and antioxidant activities.[15,16,17] Bavachalcone showed a significant inhibitor effect on baculovirus as well as inhibition on osteoclast differentiation. This also exhibits high α-glucosidase inhibitory activity.[18] Xanthoangelol demonstrated antibacterial activity against Gram-positive pathogenic bacteria,[19] antitumor-promoting activity and cytotoxicity against neuroblastoma cells.[20] Also it was found that isoxanthoangelol shows potent anticancer activity in some specialized cells like, SW 872 human liposarcoma cells (Fig 2).[21]

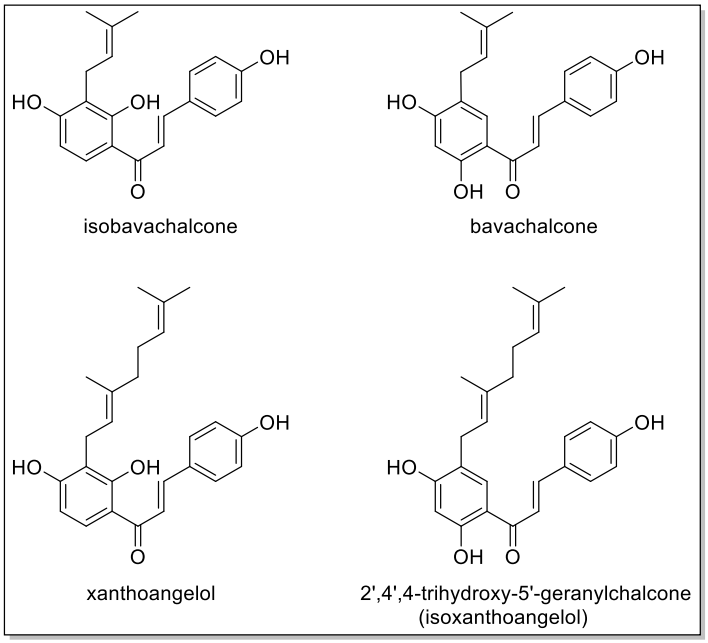



Figure 2. Representative examples for chalcone based drugs.

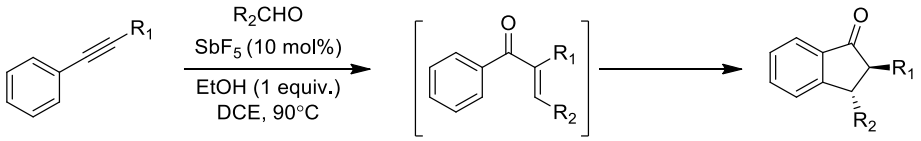
### 1.3 Background:

The wide occurrence of indanone moiety in several natural products has attracted the attention of chemists. They show a range of biological activities by just varying the substituents of its core structure. Out of many methods used for the synthesis of indanones, some reports were based on the use of transition metal catalysts (e.g. Pd, Ru) for the enantioselective synthesis of indanones, while, other reports used Lewis acid promoted

reaction pathways. Herein, we disclose the superacid (triflic acid) promoted dual C-C bond formation for the synthesis of indanones.

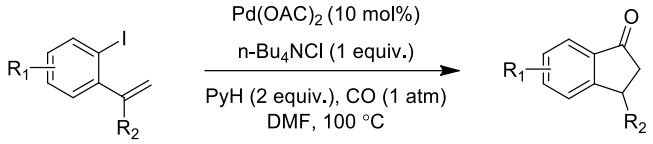
**Some methodologies for indanone synthesis:**

To begin with long history of the synthesis of indanones, a catalytic Lewis acid ($SbF_5$) was used to convert a mixture of phenylalkynes and aldehydes to indanones in one-pot in the presence of EtOH as an additive, yielding the corresponding 2,3-disubstituted indanones as a single *anti*-isomer (Scheme 1).[22]



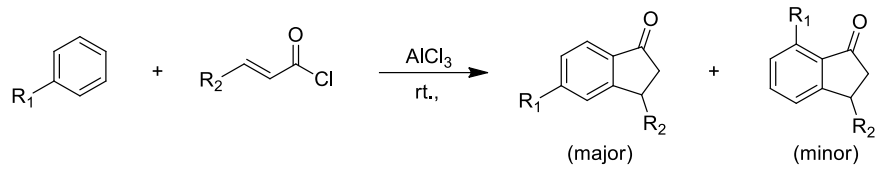

**Scheme 1.** Synthesis of the 2,3-disubstituted indanones from phenylalkynes and aldehydes by using a catalytic Lewis acid ($SbF_5$).

Indanones and 2-cyclopentenones have also been successfully prepared in good to excellent yields by the palladium-catalyzed carbonylative cyclization of unsaturated aryl iodides and dienyl triflates, iodides, and bromides, respectively (Scheme 2).[23]




**Scheme 2:** Synthesis of indanones through palladium-catalyzed carbonylative cyclization of unsaturated aryl iodides.

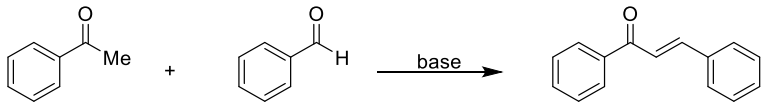
A series of 1-indanones were also synthesized in good yields via tandem Friedel−Crafts acylation and Nazarov cyclization of arenes and α,β-unsaturated acyl chlorides in the presence of $AlCl_3$ under microwave irradiation, these systems are known to be important synthetic intermediates for pharmaceuticals and ligands of olefin polymerization catalysts (Scheme 3).[24]



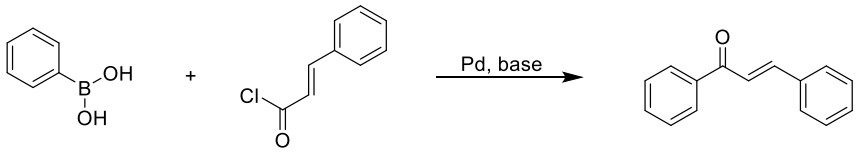

**Scheme 3**. Formation of indanones via tandem Friedel−Crafts acylation and Nazarov cyclization of arenes and α,β-unsaturated acyl chlorides.

**Some methodologies for chalcone synthesis**:

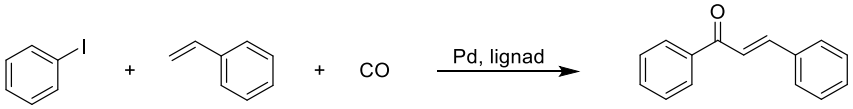
In addition, some other synthetic protocols, such as involving Claisen-Schimdt condensation of acetophenones and benzaldehyde, in the presence of a base in polar solvent,[25,26,27] (Scheme 4), Pd-mediated Suzuki coupling between cinnamoyl chloride and phenyl boronic acid (Scheme 5) and palladium mediated carbonylative Heck coupling with aryl halides and styrenes in the presence of carbon monoxide (Scheme 6).[28,29]




**Scheme 4.** Claisen-Schimdt condensation of acetophenones and benzaldehyde.




**Scheme 5.** Pd-mediated Suzuki coupling between cinnamoyl chloride and phenyl boronic acid.

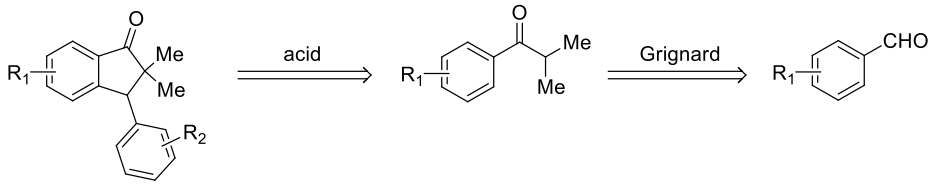



**Scheme 6.** palladium mediated carbonylative Heck coupling with aryl halides and styrenes in the presence of carbon monoxide.

## 1.4 Results and Discussion:

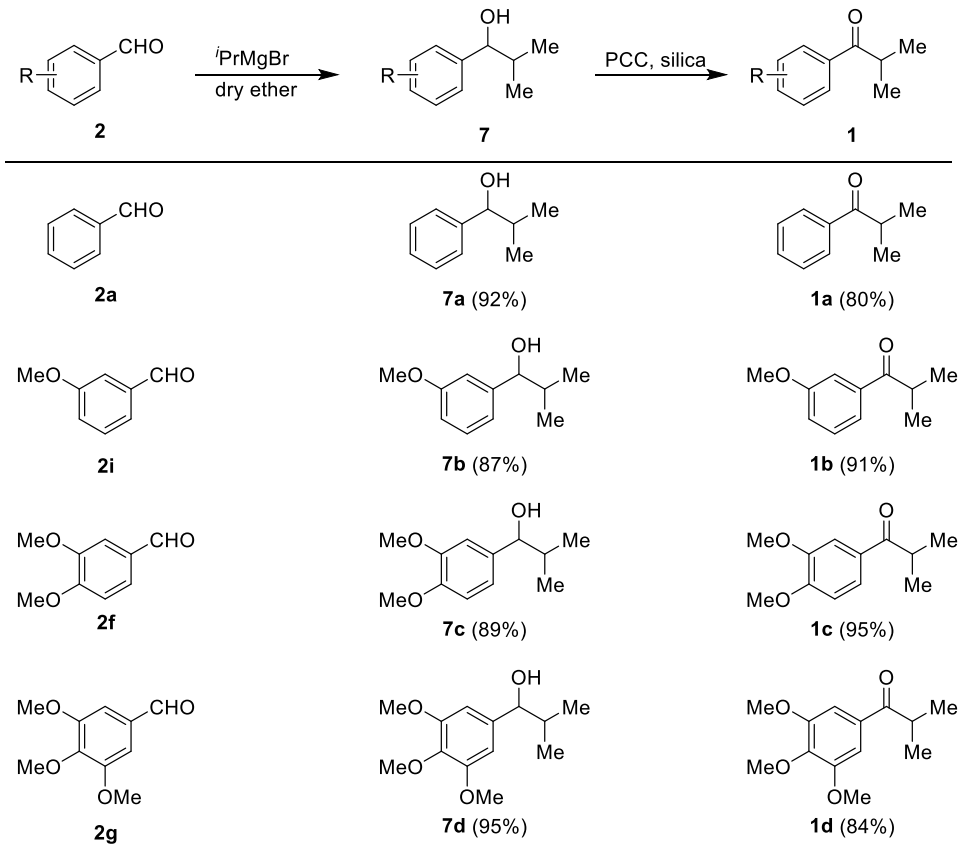
The general strategy for the synthesis of indanones is as shown in the retro synthetic approach (Scheme 7). We envisaged that it would be feasible to generate enol selectively from aryl alkyl ketone under strong acidic conditions. Thus the so formed enol of the ketone

would act as a nucleophile and attack the aldehyde in intermolecular fashion to give the β-hydroxy ketone intermediate which in turn liable for subsequent intramolecular Friedel-Crafts alkylation to furnish the target indanones.

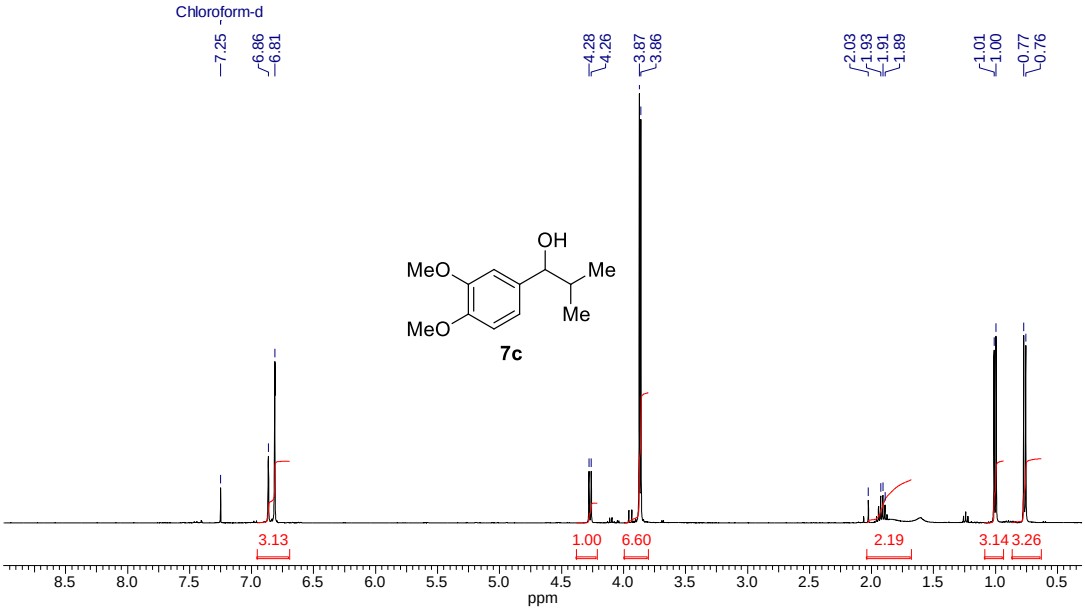



**Scheme 7**. Retro synthetic approach of indanones.

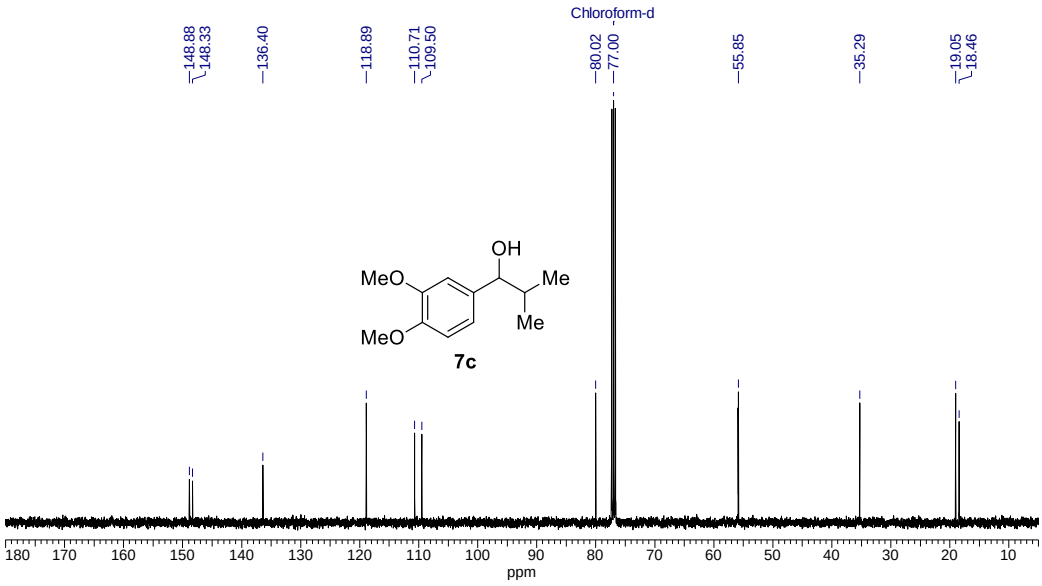
Though, it can be realized that the intramolecular Friedel-Crafts alkylation would be difficult with an aromatic ring connected to a deactivating group (carbonyl), the idea behind of this aim is based on the use of superacid that may overcome such hurdles. The required aryl isopropyl ketones for this study were synthesized from the corresponding benzaldehydes using standard isopropyl Grignard addition and oxidation protocol (Scheme 8). To a cold (−10 °C), magnetically stirred benzaldehydes **2a**, **2i**, **2f**, **2g** (6 mmol), was added isopropylmagnesium bromide (48 mmol) [prepared from magnesium (8 equiv) and isopropyl bromide (12 equiv) and a catalytic amount of iodine in 70 mL of dry ether]. The reaction mixture was stirred at −10 °C to room temperature for 4 h. It was then poured into a cold saturated aqueous $NH_4Cl$ solution and the aqueous layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried ($Na_2SO_4$) and concentrated. The crude secondary alcohol **7a-d** was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent. The structure of the compound was confirmed based on the IR and NMR spectroscopic technique. As an illustration, the dimethoxyisopropyl alcohol **7c** has been exemplified in the spectrum below. The carbonyl peak seen in IR of the starting material was seen to have disappeared and the presence of O-H peak suggested the alcohol formation. It was further confirmed by the proton NMR that clearly showed the presence of two methyl groups at 0.6 and 1.0 ppm that the secondary alcohol was formed.




**Scheme 8**. Synthesis of aryl isopropyl alcohols **7** and ketones **1**.

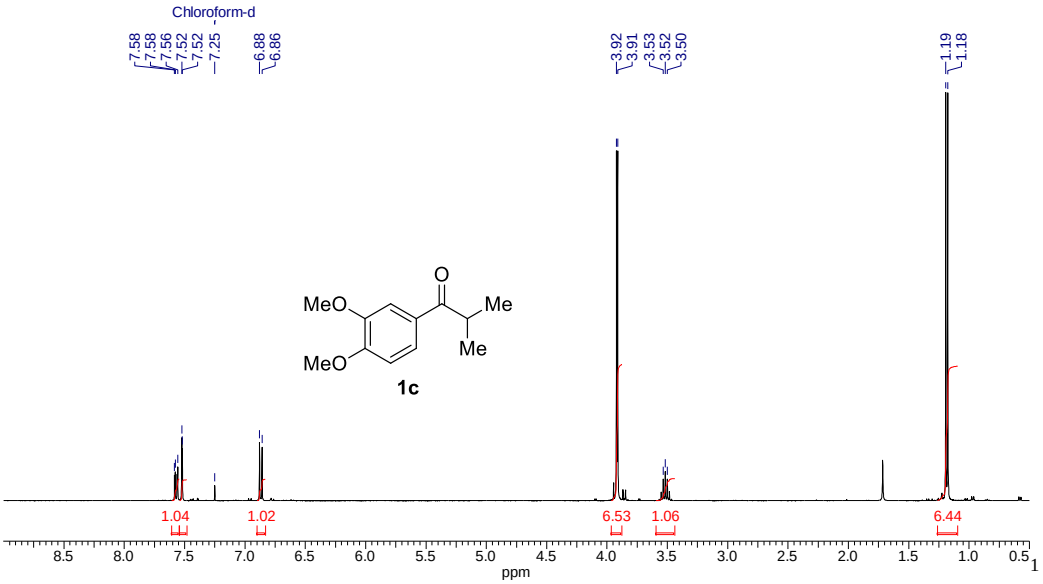



$^{1}$H NMR (400 MHz) spectrum of **7c** in $CDCl_3$

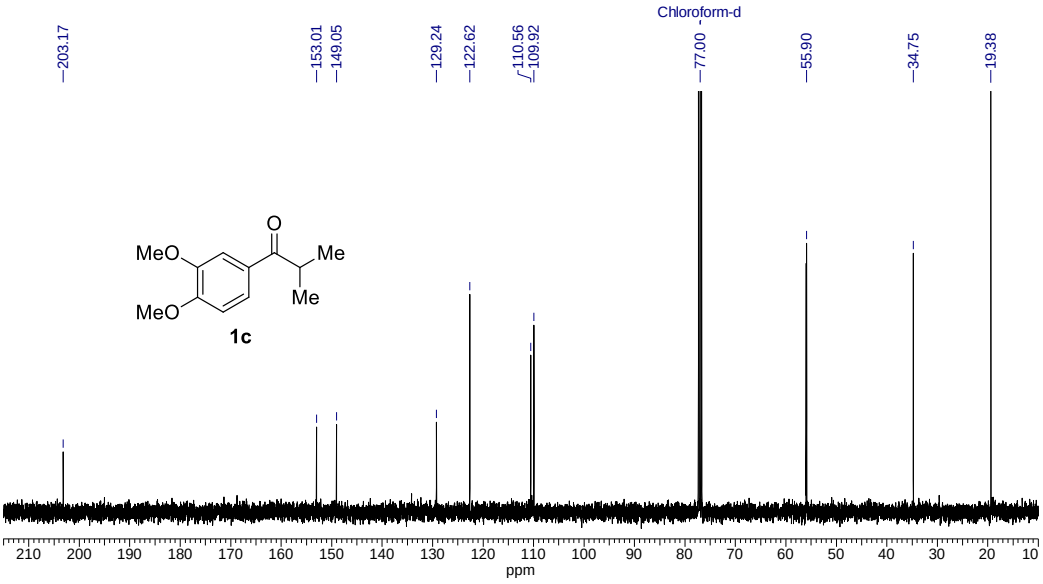



$^{13}$C NMR (100 MHz) spectrum of **7c** in $CDCl_3$

To prepare the ketone, the secondary alcohol, **7a-d** (6 mmol), was magnetically stirred in a solution in dry $CH_2Cl_2$ and a homogeneous mixture of PCC (12 mmol) and equivalent amount of silica gel at room temperature for 2 h. Filtration of the reaction mixture through a short silica column with excess $CH_2Cl_2$ furnished the pure ketones **1a-d**. The structure of the compound was confirmed based on the IR and NMR spectroscopic technique. The disappearance of the O-H stretching frequency and the presence of carbonyl peak in IR spectrum showed the formation of the aryl isopropylketone. The change in the integration of the tertiary protons from 2 to 1 at δ=3.52 ppm in $^{1}H$ NMR and the peak at δ=203 ppm in $^{13}C$, has allowed the confirmation of carbonyl group.



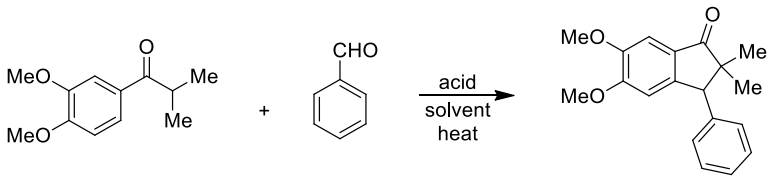

$^{1}$H NMR (400 MHz) spectrum of **1c** in $CDCl_3$




$^{13}$C NMR (100 MHz) spectrum of **1c** in $CDCl_3$

The aryl isopropyl ketones were prepared using Grignard reagent. After that, to find out the best optimized reaction conditions, the ketone **1c** was chosen as model and reacted with the benzaldehyde **2a** under different reaction conditions in the presence of acid as promoting agent and the results are summarized in Table 1. The initial attempts with TFA either as reagent or as the reaction medium at 50 °C were unclear (Table 1, entries 1 & 2). These results led to the requirement of using relatively strong acid than TFA so that, it may be good enough to drive the reaction. Therefore, the reaction was conducted in the presence of 5 equivalents of superacid (triflic acid) in DCE at ambient temperature (Table 1, entry 3). Interestingly, as expected, the product indanone **3c** was obtained albeit in poor yield, 30% along with the recovery of the starting material **1c** (Table 1, entry 3). However, the reaction was not clean when it was carried out with benzene as the solvent (Table 1, entry 4). On the other hand, $CHCl_3$ was employed as medium and heated the reaction mixture at 50 °C, increased the product **3b** yield (50%, Table 1, entry 5). Gratifyingly, the reaction in DCE at 50 °C found to be the best and furnished **3b** as an exclusive product in very good yield (85%, Table 1 entry 6). The compound **3b** is confirmed based on the IR and NMR spectroscopic technique. In $^{1}$ H-NMR presence of two singlets at 1.32 [s, 3H, $C(CH_3)_{2a}$], 0.66 [s, 3H, $C(CH_3)_{2b}$] ppm, and in $^{13}$C NMR, peaks at $\delta$ = 25.8 [q, $C(CH_3)_{2a}$], 22.8 [q, $C(CH_3)_{2b}$] ppm established the structure of **3b**.

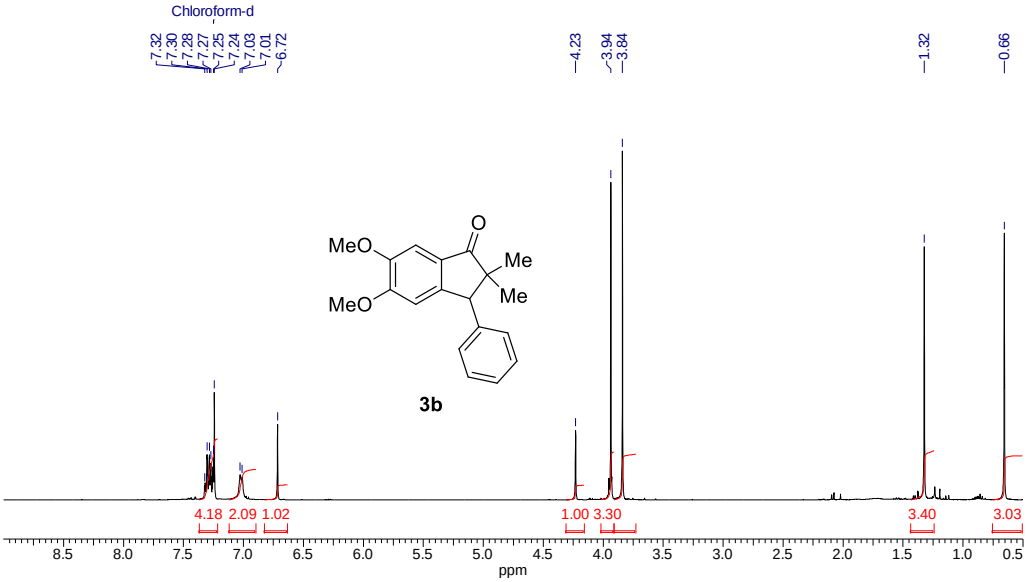
Table 1: Reaction conditions for preparation of indanone **3b**.[a]



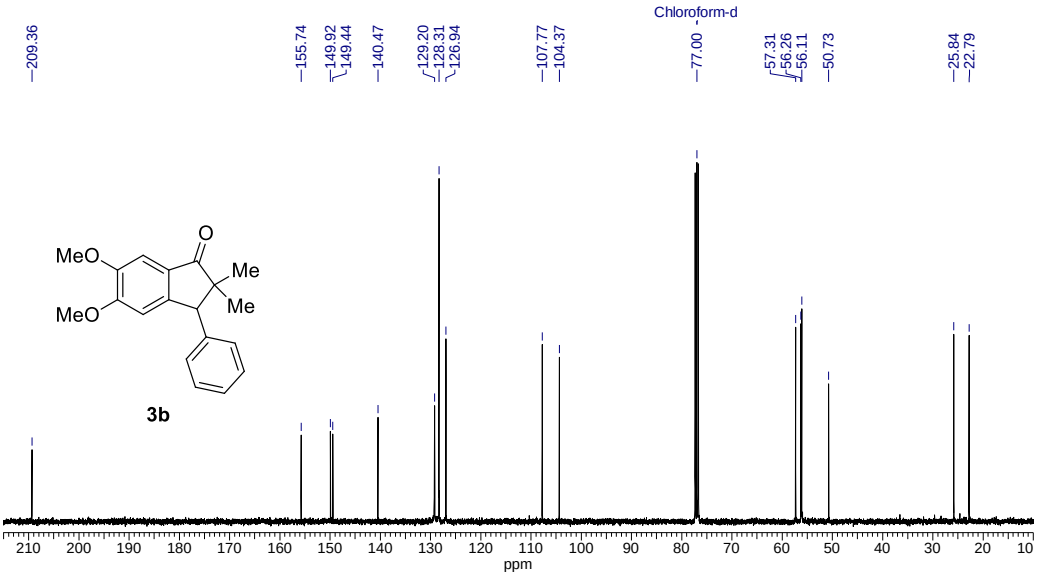

**1c** **2a** **3b**

| Entry | Acid (equiv) | Solvent (mL) | Temp (oC) | Time (h) | Yield (%)a |
|---|---|---|---|---|---|
| 1 | TFA (5) | DCE (2) | 50 | 12 | - |
| 2 | TFA | TFA (2) | 50 | 12 | - |
| 3 | TfOH (5) | DCE (2) | r.t. | 24 | 30 |
| 4 | TfOH (5) | benzene (2) | r.t. | 24 | - |
| 5 | TfOH (5) | $CHCl_3$ (2) | 50 | 24 | 50 |
| 6 | TfOH(5) | DCE (2) | 50 | 24 | 85 |

**[a]** Isolated yields of the pure products.

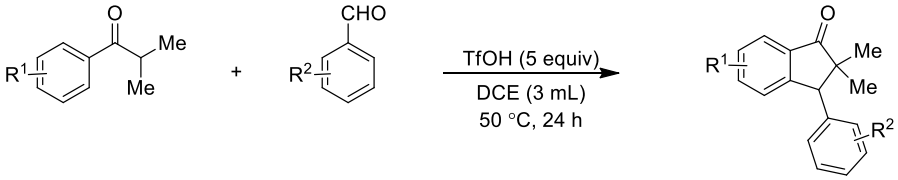



$^{1}$H NMR (400 MHz) spectrum of **3b** in $CDCl_3$

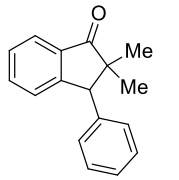



$^{13}$C NMR (100 MHz) spectrum of **3b** in $CDCl_3$

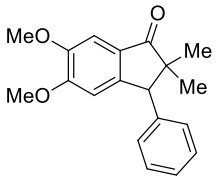
Table 2. Scope of superacid mediated one-pot formation of indanones **3** from various ketones **1**.



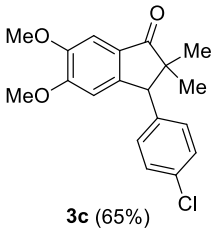

**1** **2** **3**



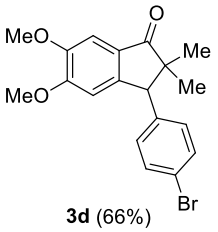
**3a** (50%)[a]



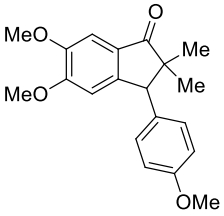
**3b**(85%)



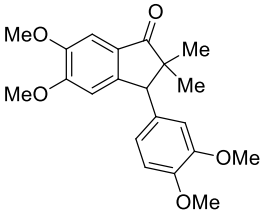
**3c** (65%)



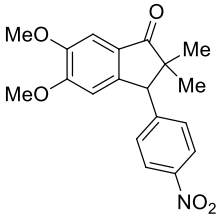
**3d** (66%)



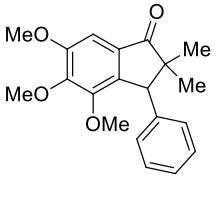
**3e** (83%)



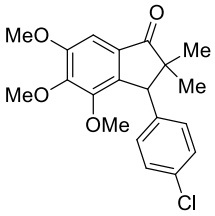
**3f** (78%)



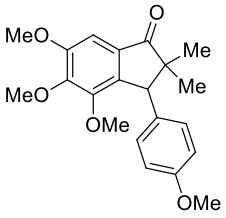
**3g** (---)[b]



**3h** (86%)



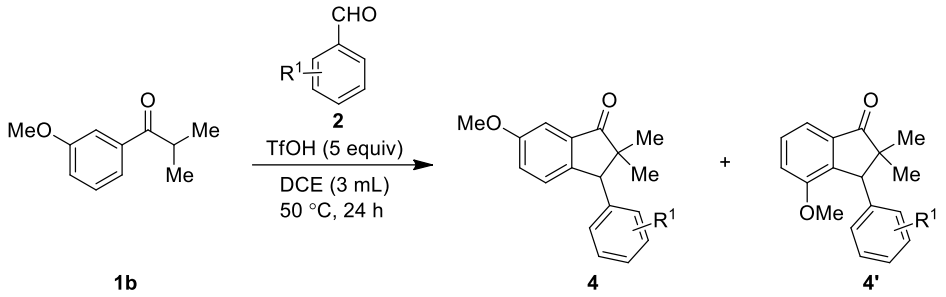
**3i** (64%)



**3j** (76%)

While, the reaction with 3-anisyl isopropyl ketone **1b** furnished the regioisomeric mixture of indanones **4** & **4'** in almost 4:1 ratios, in which, as expected, the major isomer was the one where cyclization occurred at *para* position to the electron donating methoxy group and the results are as summarized in the Table 3.

Table 3. Superacid mediated formation of indanones **4 & 4'** from ketone **1b**.



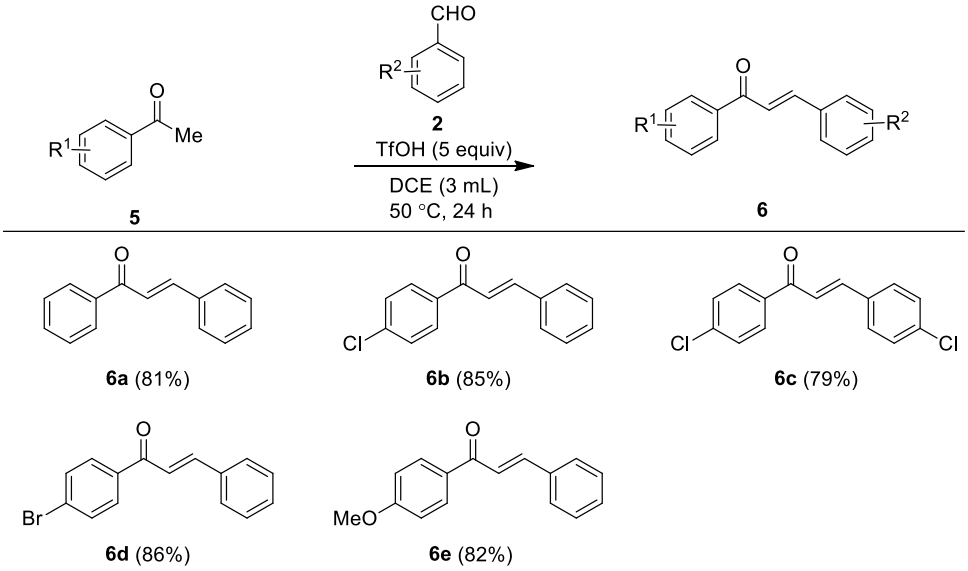

**1b** **4** **4'**

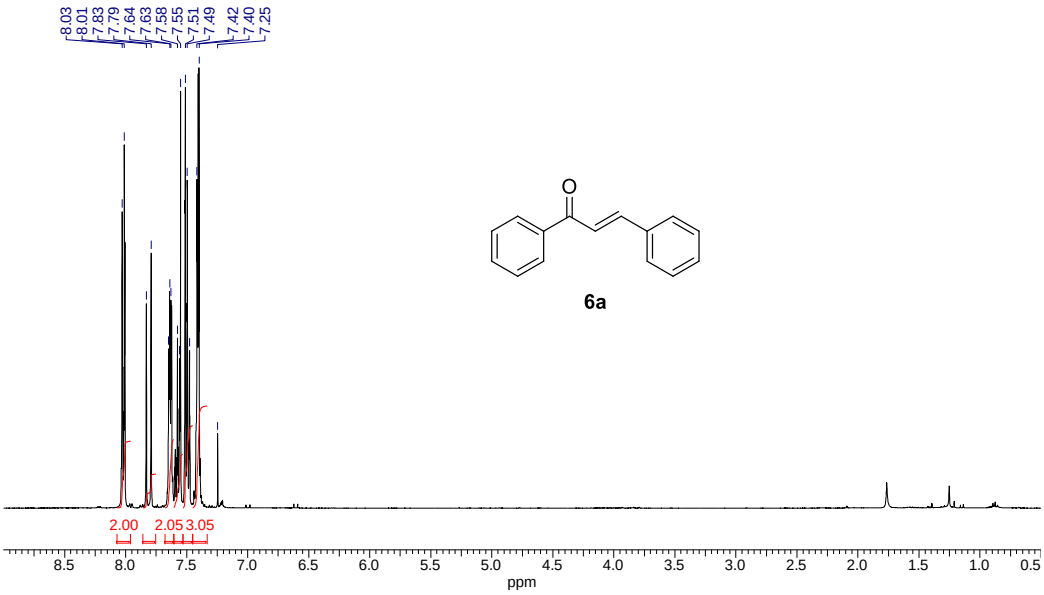
| | | |
|---|---|---|
| **4a** (64%) | **4:1** | **4a'** (16%) |
| **4b** (68%) | **4:1** | **4b'** (17%) |
| **4c** (68%) | **4:1** | **4c'** (17%) |

To further check the scope and generality of the method, the reaction has been tried between acetophenones **5** and benzaldehydes **2** as well. Surprisingly, the reaction was impeded after the aldol condensation without subsequent cyclization (Table 4). This can be justified based on the inert nature of enones as well as the aromatic ring of ketone as it is directly in conjugation to the electron withdrawing carbonyl group. Moreover, to check the generality of the reaction, several trials has been done between different acetophenones **5** and benzaldehydes **2**. Gratifyingly, the reaction was found to be quite successful and furnished

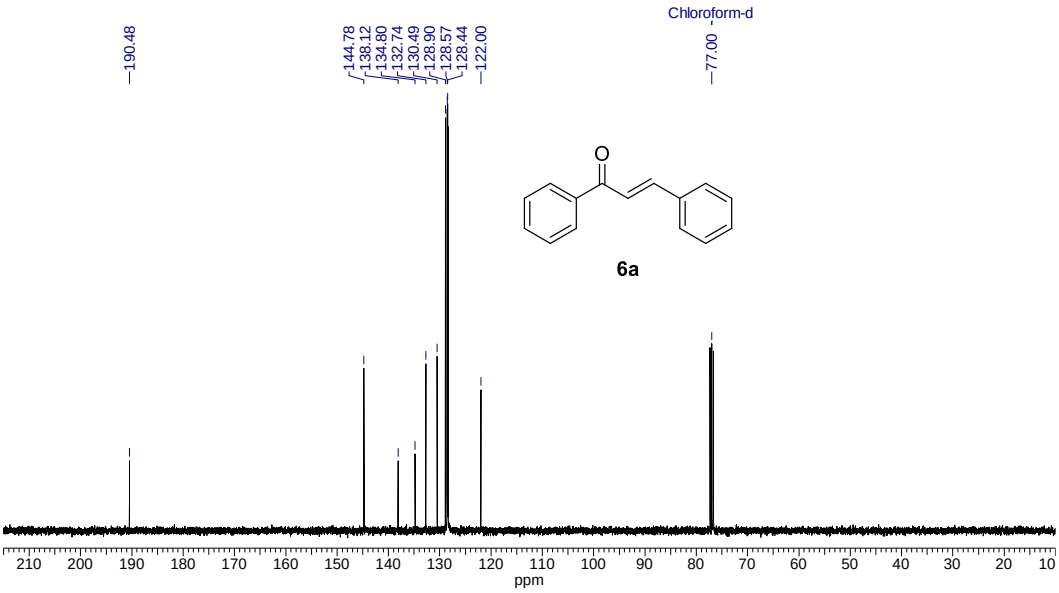
the chalcone products **6** in very good to excellent yields as summarized in Table 4. The structure of chalcone **6a** is confirmed based on the IR and NMR spectroscopic techniques. In $^{1}$H-NMR, the presence of peaks at δ=7.81 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.53 (d, 1H, *J*=15.6 Hz, CH=C*H*COPh), and in $^{13}$C-NMR peaks at δ=144.8 (d, *C*H=CHCOPh), 122.0 (d, CH=*C*HCOPh) ppm established the structure of chalcone **6a.**

Table 4. Scope of the formation of chalcone **6** products.



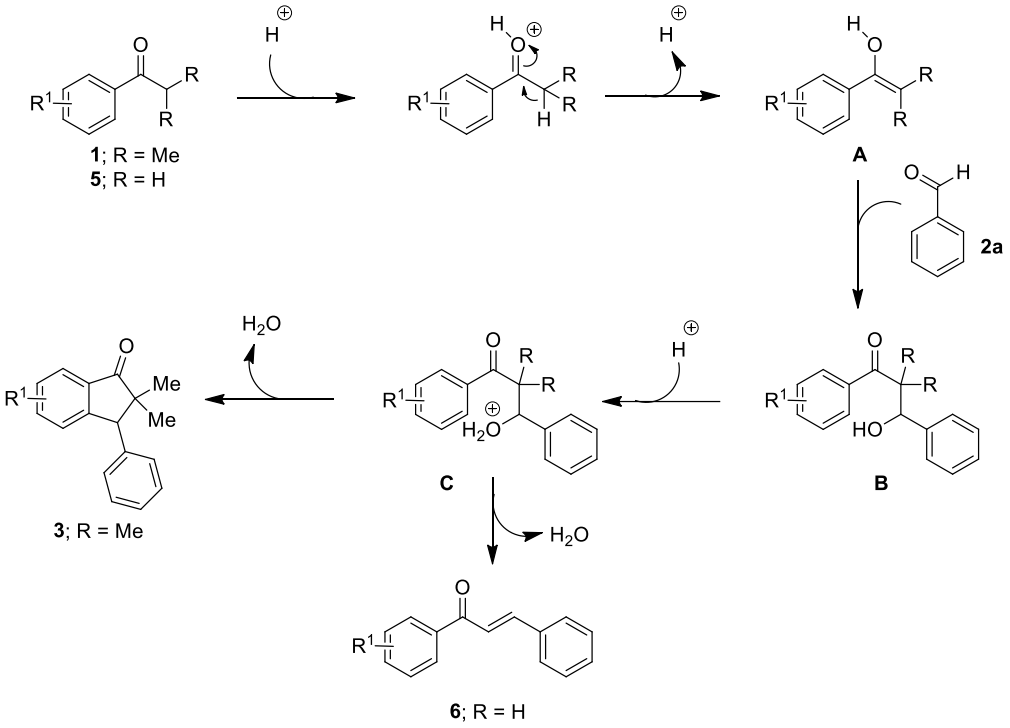



$^{1}$H NMR (400 MHz) spectrum of **6a** in $CDCl_3$




$^{13}$C NMR (100 MHz) spectrum of **6a** in $CDCl_3$

The possible reaction mechanism for the formation of indanones **3** and chalcones **6** is outlined in Scheme 9. Initially, the ketone is activated by the protonation of the carbonyl oxygen by using the superacid and yielded the corresponding enol **A**. Nucleophilic attack of the enol **A** to the aldehyde carbon result into the formation of β-hydroxy ketone intermediate **B**. Since the β-hydroxy ketone intermediate **B** is liable for intramolecular Friedel-Crafts alkylation in the presence of acid, triggers to the cyclization through **C** and generated the final indanone product **3**. Similarly, acetophenones yielded the corresponding β-hydroxy ketone intermediate **B**. However, because of the availability of β-hydrogen for hydroxyl group, it prefers dehydration than cyclization and furnished the chalcone **6** products.




**Scheme 9.** Possible reaction mechanism for the formation of indanones **3** and chalcones **6**.

## 1.5 Conclusion:

In summary, we have developed an efficient one-pot method for the synthesis of highly substituted indanones via dual C–C bond formation promoted by superacid. Significantly, these indanone systems are ubiquitous units that are present in drugs and many biologically active natural products. Interestingly, when acetophenones were treated with benzaldehydes

in the presence of superacid, the reaction was impeded after aldol condensation and furnished the chalcones.

### 1.6 Experimental Section:

**General:**

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. $^{1}$H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts ($\delta$ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_H$ =0.00 ppm) or $CHCl_3$ ($\delta_H$ = 7.25 ppm). $^{13}$C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts ($\delta$ ppm) are reported relative to $CHCl_3$ [$\delta_C$ = 77.00 ppm (central line of triplet)]. In the $^{13}$C NMR, the nature of carbons (C, CH, $CH_2$ and $CH_3$) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for $CH_2$) and q = quartet (for $CH_3$). In the $^{1}$H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by $^{1}$H, $^{13}$C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using Schlenk tubes under inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Dichloroethane (DCE) was dried over $CaH_2$ and absolute ethanol was purchased from local sources, used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

**GP-1 (General procedure for preparation of 2,2-dimethyl-3-phenylindan-1-ones 3):**

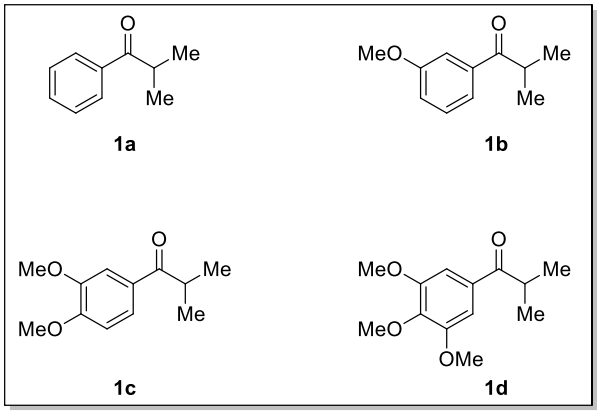
In an oven dried Schlenk tube, were added ketone **1** (37.0–59.6 mg, 0.25 mmol), benzaldehyde **2** (53.0–92.5 mg, 0.50 mmol) and dichloroethane (1.5 mL) followed by triflic acid (0.11 mL, 1.25 mmol) at room temperature under nitrogen atmosphere. The reaction mixture stirred at room temperature and was then heated in an oil bath at 50 °C for 24 h (80 °C for 48 h in case of phenyl isopropyl ketone) and monitored by TLC. Then, the reaction

mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 15 mL). The organic layers was washed with saturated NaCl solution, dried ($Na_2SO_4$), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanones **3** (50–86%).

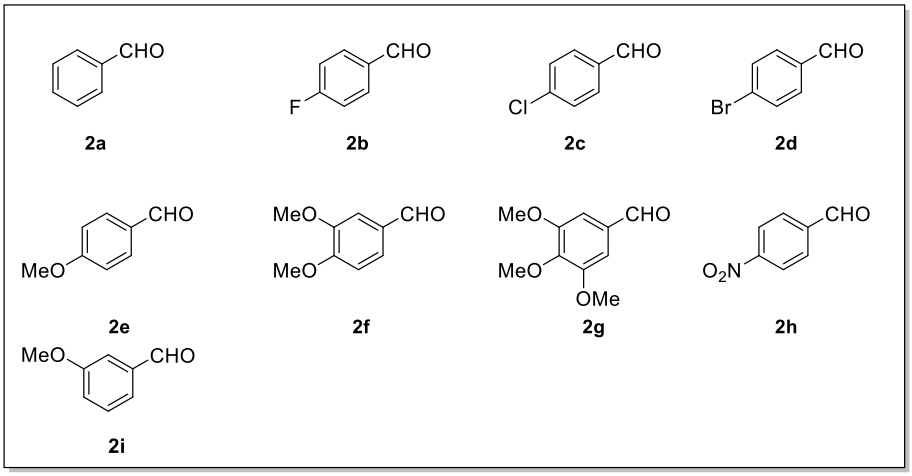
**GP-2 [General procedure for preparation of (2*E*)-1,3-diphenylprop-2-en-1-ones (chalcones) 6]:**

In an oven dried Schlenk tube, were added ketone **5** (60.0–99.5 mg, 0.50 mmol), benzaldehyde **2** (106.0–185.0 mg, 1.00 mmol) and dichloroethane (3.0 mL) followed by triflic acid (0.22 mL, 2.5 mmol) at room temperature under nitrogen atmosphere. The reaction mixture stirred at room temperature and was then heated in an oil bath at 50 °C for 24 h and monitored by TLC. Then, the reaction mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 15 mL). The organic layers was washed with saturated NaCl solution, dried ($Na_2SO_4$), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the chalcones **6** (79–94%).

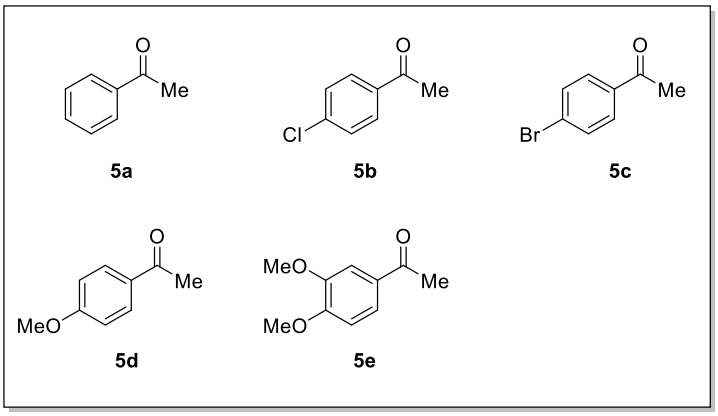
The following isopropyl ketones **1a–1d**, which have been used as starting materials are reported in literature.



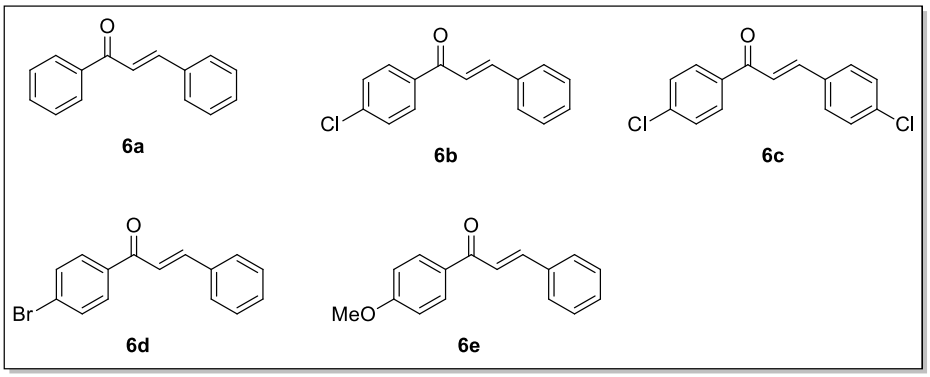

The following benzaldehydes **2a–2h**, which are used as starting materials, are commercially available.

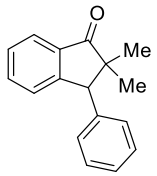



All acetophenones, which have been used as starting materials are commercially available




The following isopropyl ketones **6a–6i**, which have been prepared are reported in literature.[1]

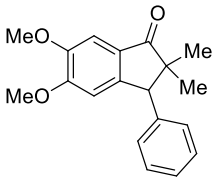





**3a**

**2,2-dimethyl-3-phenylindan-1-one (3a):**

**GP-1** was carried out with ketone **1a** (37.0 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 80 °C for 48 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 99:1 to 95:5) furnished the indanone **1a** (15.2 mg, 50%) as a pale yellow viscous liquid along with the recovery of starting material **1a** (18 mg, 49%). [TLC control (petroleum ether/ethyl acetate 97:3), $R_f$(**1a**)=0.49, $R_f$(**3a**)=0.27, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2922, 1713, 1602, 1494, 1452, 1240, 1212, 1035, 753, 699 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=7.83 (d, 1H, $J$=7.8 Hz, Ar-H), 7.67 (ddd, 1H, $J$=8.3, 7.8 and 1.5 Hz, Ar-H), 7.54 (d, 1H, $J$=7.8 Hz, Ar-H), 7.42 (ddd, 1H, $J$=8.3, 7.8 and 1.5 Hz, Ar-H), 7.35 (dd, 2H, $J$=8.3 and 7.8 Hz, Ar-H), 7.29 (tt, 1H, $J$=7.8 and 1.5 Hz, Ar-H), 7.13 (dd, 2H, $J$=8.3 and 1.5 Hz, Ar-H), 3.78 (s, 1H, CH), 1.58 [s, 3H, $C(CH_3)_{2a}$], 0.90 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=205.5 (s, C=O), 162.2 (s, Ar-C), 136.7 (s, Ar-C), 135.2 (d, Ar-CH), 135.0 (s, Ar-C), 130.1 (d, 2C, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 127.6 (d, Ar-CH), 127.1 (d, Ar-CH), 123.8 (d, Ar-CH), 123.6 (d, Ar-CH), 67.0 (d, CH), 43.8 [s, $C(CH_3)_2$], 28.5 [q, $C(CH_3)_{2a}$], 28.4 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{17}O]^+$=$[M+H]^+$: 237.1274; found 237.1272.

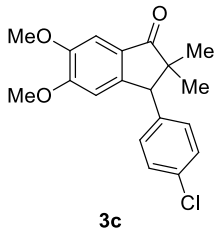



**3b**

**5,6-dimethoxy-2,2-dimethyl-3-phenylindan-1-one (3b):**

**GP-1** was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3b** (62.9 mg, 85%) as yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15), $R_f$(**1c**)=0.45, $R_f$(**3b**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$):

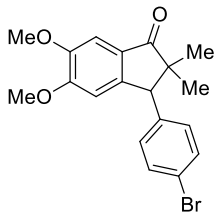
$\nu_{max}$=2964, 2928, 1697, 1591, 1498, 1465, 1453, 1303, 1264, 1220, 1109, 1018, 911, 866, 728, 702 $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.37–7.21 (m, 3H, Ar-H), 7.24 (s, 1H, Ar-H), 7.02 (d, 2H, *J*=7.3 Hz, Ar-H), 6.72 (s, 1H, Ar-H), 4.23 (s, 1H, CH), 3.94 (s, 3H, Ar-$OCH_3$), 3.84 (s, 3H, Ar-$OCH_3$), 1.32 [s, 3H, $C(CH_3)_{2a}$], 0.66 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=209.4 (s, C=O), 155.7 (s, Ar-C), 149.9 (s, Ar-C), 149.4 (s, Ar-C), 140.5 (s, Ar-C), 129.2 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 126.9 (d, Ar-CH), 107.8 (d, Ar-CH), 104.4 (d, Ar-CH), 57.3 (d, CH), 56.3 (q, Ar-$OCH_3$), 56.1 (q, Ar-$OCH_3$), 50.7 [s, $C(CH_3)_2$], 25.8 [q, $C(CH_3)_{2a}$], 22.8 [q, $C(CH_3)_{2b}$] ppm.




**3c**

**3-(4-chlorophenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3c):**

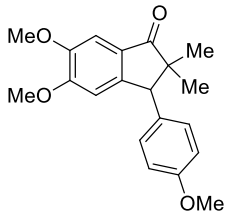
**GP-1** was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2c** (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3c** (53.7 mg, 65%) as a palebrown solid, recrystallized the solid with dichloromethane/hexane, m. p. 110–112 °C. [TLC control (petroleum ether/ethyl acetate 80:20), $R_f$(**1c**)=0.45, $R_f$(**3c**)=0.41, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2964, 2928, 1697, 1590, 1500, 1491, 1464, 1301, 1264, 1219, 1112, 1015, 913, 866, 845, 770, 728 $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.27 (d, 2H, *J*=8.3 Hz, Ar-H), 7.23 (s, 1H, Ar-H), 6.95 (d, 2H, *J*=8.3 Hz, Ar-H), 6.66 (s, 1H, Ar-H), 4.20 (s, 1H, CH), 3.93 (s, 3H, Ar-$OCH_3$), 3.84 (s, 3H, Ar-$OCH_3$), 1.31 [s, 3H, $C(CH_3)_{2a}$], 0.66 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=208.8 (s, C=O), 155.9 (s, Ar-C), 150.1 (s, Ar-C), 148.9 (s, Ar-C), 139.1 (s, Ar-C), 132.8 (s, Ar-C), 130.5 (d, 2C, 2 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 107.6 (d, Ar-CH), 104.5 (d, Ar-CH), 56.7 (d, CH), 56.3 (q, Ar-$OCH_3$), 56.1 (q, Ar-$OCH_3$), 50.6 [s, $C(CH_3)_2$], 25.9 [q, $C(CH_3)_{2a}$], 22.8 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}ClO_3]^+$=$[M+H]^+$: 331.1095; found 331.1095.




**3d**

**3-(4-bromophenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3d):**

**GP-1** was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2d** (92.5 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3d** (61.9 mg, 66%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 114–116 °C. [TLC control (petroleum ether/ethyl acetate 80:20), $R_f$(**1c**)=0.45, $R_f$(**3d**)=0.42, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2964, 2926, 2867, 1697, 1590, 1500, 1300, 1219, 1112, 1010, 729 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=7.42 (d, 2H, *J*=8.8 Hz, Ar-H), 7.23 (s, 1H, Ar-H), 6.89 (d, 2H, *J*=8.8 Hz, Ar-H), 6.66 (s, 1H, Ar-H), 4.18 (s, 1H, CH), 3.93 (s, 3H, Ar-$OCH_3$), 3.84 (s, 3H, Ar-$OCH_3$), 1.31 [s, 3H, C$(CH_3)_{2a}$], 0.66 [s, 3H, C$(CH_3)_{2b}$] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=208.8 (s, C=O), 155.9 (s, Ar-C), 150.1 (s, Ar-C), 148.8 (s, Ar-C), 139.6 (s, Ar-C), 131.5 (d, 2C, Ar-CH), 130.8 (d, 2C, Ar-CH), 128.2 (s, Ar-C), 120.9 (s, Ar-C), 107.5 (d, Ar-CH), 104.5 (d, Ar-CH), 56.8 (d, CH), 56.3 (q, Ar-$OCH_3$), 56.1 (q, Ar-$OCH_3$), 50.6 [s, *C*$(CH_3)_2$], 25.9 [q, C(*C*$H_3)_{2a}$], 22.8 [q, C(*C*$H_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}BrO_3]^+$=$[M+H]^+$: 375.0590; found 375.0594.

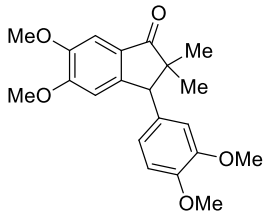



**3e**

**5,6-dimethoxy-3-(4-methoxyphenyl)-2,2-dimethylindan-1-one (3e):**

**GP-1** was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2e** (68.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 92:8 to 80:20) furnished the indanone **3e** (67.7 mg, 83%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20), $R_f$(**1c**)=0.45, $R_f$(**3e**)=0.34, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$):

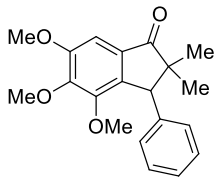
$\nu_{max}$=2963, 2930, 2836, 1695, 1591, 1499, 1464, 1301, 1264, 1218, 1176, 1106, 1018, 911, 726 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.21 (s, 1H, Ar-H), 6.92 (d, 2H, *J*=8.8 Hz, Ar-H), 6.82 (d, 2H, *J*=8.8 Hz, Ar-H), 6.70 (s, 1H, Ar-H), 4.16 (s, 1H, CH), 3.92 (s, 3H, Ar-$OCH_3$), 3.83 (s, 3H, Ar-$OCH_3$), 3.77 (s, 3H, Ar-$OCH_3$), 1.28 [s, 3H, $C(CH_3)_{2a}$], 0.65 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=209.5 (s, C=O), 158.5 (s, Ar-C), 155.7 (s, Ar-C), 149.8 (s, Ar-C), 149.7 (s, Ar-C), 132.4 (s, Ar-C), 130.1 (d, 2C, Ar-CH), 128.1 (s, Ar-C), 113.6 (d, 2C, Ar-CH), 107.7 (d, Ar-CH), 104.3 (d, Ar-CH), 56.5 (d, CH), 56.2 (q, Ar-$OCH_3$), 56.1 (q, Ar-$OCH_3$), 55.1 (q, Ar-$OCH_3$), 50.7 [s, $C(CH_3)_2$], 25.6 [q, $C(CH_3)_{2a}$], 22.8 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{23}O_4]^+$=$[M+H]^+$: 327.1591; found 327.1591.




**3f**

**3-(3,4-dimethoxyphenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3f):**

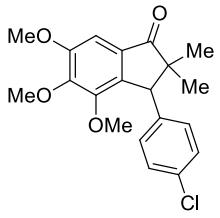
**GP-1** was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2f** (83.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3f** (69.5 mg, 78%) as a brown solid, recrystallized the solid with dichloromethane/hexane, m. p. 96–98 °C. [TLC control (petroleum ether/ethyl acetate 70:30), $R_f$(**1c**)=0.53, $R_f$(**3f**)=0.20, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2962, 2931, 2867, 2836, 1695, 1590, 1513, 1499, 1463, 1416, 1305, 1265, 1108, 1018, 866, 730, 699 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.19 (s, 1H, Ar-H), 6.77 (d, 1H, *J*=8.3 Hz, Ar-H), 6.69 (s, 1H, Ar-H), 6.55 (br. s, 1H, Ar-H), 6.45 (br. s, 1H, Ar-H), 4.13 (s, 1H, CH), 3.89 (s, 3H, Ar-$OCH_3$), 3.81 (s, 3H, Ar-$OCH_3$), 3.80 (s, 3H, Ar-$OCH_3$), 3.73 (s, 3H, Ar-$OCH_3$), 1.26 [s, 3H, $C(CH_3)_{2a}$], 0.64 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=209.3 (s, C=O), 155.6 (s, Ar-C), 149.7 (s, Ar-C), 149.4 (s, Ar-C), 148.6 (s, Ar-C), 147.9 (s, Ar-C), 132.7 (s, Ar-C), 128.0 (s, Ar-C), 121.3 (d, Ar-CH), 112.2 (d, Ar-CH), 110.8 (d, Ar-CH), 107.6 (d, Ar-CH), 104.2 (d, Ar-CH), 56.8 (d, CH), 56.1 (q, Ar-$OCH_3$), 55.9 (q, Ar-$OCH_3$), 55.7 (q, Ar-$OCH_3$), 55.6 (q, Ar-$OCH_3$), 50.6 [s, $C(CH_3)_2$], 25.6 [q, $C(CH_3)_{2a}$], 22.6 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{25}O_5]^+$=$[M+H]^+$: 357.1697; found 357.1696.




**3h**

**4,5,6-trimethoxy-2,2-dimethyl-3-phenylindan-1-one (3h):**

**GP-1** was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3h** (70.2 mg, 86%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1d**)=0.47, $R_f$(**3h**)=0.38, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2966, 2935, 1703, 1602, 1469, 1342, 1313, 1123, 1087, 906, 726 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=7.50–7.20 (m, 6H, Ar-H), 4.41 (s, 1H, CH), 4.07 (s, 3H, Ar-$OCH_3$), 4.05 (s, 3H, Ar-$OCH_3$), 3.52 (s, 3H, Ar-$OCH_3$), 1.45 [s, 3H, $C(CH_3)_{2a}$], 0.87 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=210.1 (s, C=O), 154.8 (d, Ar-CH), 150.5 (d, Ar-CH), 148.7 (d, Ar-CH), 141.6 (d, Ar-CH), 141.3 (d, Ar-CH), 130.6 (d, Ar-CH), 128.1 (d, 3C, Ar-CH), 126.6 (d, 2C, Ar-CH), 100.8 (d, Ar-CH), 60.8 (q, Ar-$OCH_3$), 60.0 (q, Ar-$OCH_3$), 56.2 (q, Ar-$OCH_3$), 55.1 (d, CH), 50.7 [s, $C(CH_3)_2$], 28.3 [q, $C(CH_3)_{2a}$], 21.6 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{23}O_4]^+$=$[M+H]^+$: 327.1591; found 327.1590.

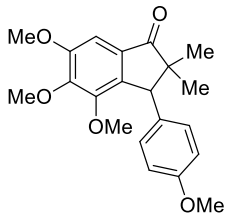



**3i**

**3-(4-chlorophenyl)-4,5,6-trimethoxy-2,2-dimethylindan-1-one (3i):**

**GP-1** was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2c** (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the indanone **3i** (57.7 mg, 64%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1d**)=0.47, $R_f$(**3i**)=0.41, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$):

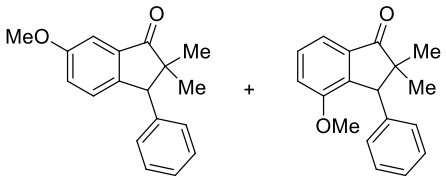
$\nu_{max}$=2967, 2935, 1705, 1600, 1469, 1417, 1343, 1311, 1121, 1013, 912, 848, 770, 728 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.50–6.10 (m, 5H, Ar-H), 4.22 (s, 1H, CH), 3.91 (s, 3H, Ar-$OCH_3$), 3.89 (s, 3H, Ar-$OCH_3$), 3.43 (s, 3H, Ar-$OCH_3$), 1.28 [s, 3H, $C(CH_3)_{2a}$], 0.70 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=209.6 (s, C=O), 155.0 (s, Ar-C), 150.4 (s, Ar-C), 148.7 (s, Ar-C), 140.6 (s, Ar-C), 140.2 (s, Ar-C), 132.3 (s, Ar-C), 130.5 (s, Ar-C), 128.3 (d, 4C, Ar-CH), 100.9 (d, Ar-CH), 60.9 (q, Ar-$OCH_3$), 60.1 (q, Ar-$OCH_3$), 56.2 (q, Ar-$OCH_3$), 54.4 (d, CH), 50.5 [s, $C(CH_3)_2$], 28.1 [q, $C(CH_3)_{2a}$], 21.7 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{22}ClO_4]^+$=$[M+H]^+$: 361.1201; found 361.1196.




**3j**

**4,5,6-trimethoxy-3-(4-methoxyphenyl)-2,2-dimethylindan-1-one (3j):**

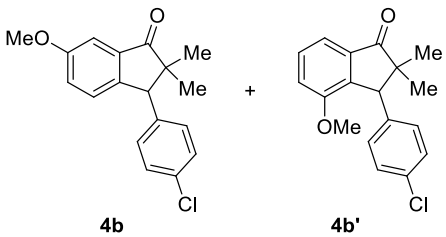
**GP-1** was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2e** (68.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3j** (67.7 mg, 76%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1d**)=0.47, $R_f$(**3j**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2964, 2933, 2837, 1704, 1600, 1511, 1467, 1417, 1342, 1310, 1244, 1121, 1033, 731 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.20–6.50 (m, 5H, Ar-H), 4.20 (s, 1H, CH), 3.91 (s, 3H, Ar-$OCH_3$), 3.89 (s, 3H, Ar-$OCH_3$), 3.74 (s, 3H, Ar-$OCH_3$), 3.39 (s, 3H, Ar-$OCH_3$), 1.27 [s, 3H, $C(CH_3)_{2a}$], 0.71 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=210.2 (s, C=O), 158.2 (s, 2C, Ar-C), 154.8 (s, Ar-C), 150.5 (s, Ar-C), 148.7 (s, Ar-C), 141.5 (s, Ar-C), 133.7 (s, Ar-C), 130.5 (s, Ar-C), 129.3 (d, Ar-CH), 125.0 (d, Ar-CH), 113.4 (d, Ar-CH), 100.8 (d, Ar-CH), 60.8 (q, Ar-$OCH_3$), 60.1 (q, Ar-$OCH_3$), 56.2 (q, Ar-$OCH_3$), 55.1 (q, Ar-$OCH_3$), 54.4 (d, CH), 50.7 [s, $C(CH_3)_2$], 28.2 [q, $C(CH_3)_{2a}$], 21.7 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{25}O_5]^+$=$[M+H]^+$: 357.1697; found 357.1694.




**4a** **4a'**

**6-methoxy-2,2-dimethyl-3-phenylindan-1-one (4a) & 4-methoxy-2,2-dimethyl-3-phenylindan-1-one (4a'):**

**GP-1** was carried out with ketone **1b** (44.5 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the inseparable regioisomeric mixture of indanones **4a** (42.6 mg, 64%) and **4a'** (10.6 mg, 16%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1b**)=0.50, $R_f$(**4a** & **4a'**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2965, 2927, 1711, 1602, 1488, 1465, 1291, 1270, 1241, 1027, 757, 702 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz, peaks due to major isomer **4a**): $\delta$=7.35–7.10 (m, 6H, Ar-H), 7.02 (d, 2H, $J$=7.3 Hz, Ar-H), 4.26 (s, 1H, CH), 3.88 (s, 3H, Ar-$OCH_3$), 1.35 [s, 3H, $C(CH_3)_{2a}$], 0.69 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz, peaks due to major isomer **4a**): $\delta$=210.7 (s, C=O), 159.8 (s, Ar-C), 147.1 (s, Ar-C), 140.4 (s, Ar-C), 136.7 (s, Ar-C), 129.2 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 127.8 (d, Ar-CH), 126.9 (d, Ar-CH), 124.3 (d, Ar-CH), 105.1 (d, Ar-CH), 56.8 (d, CH), 55.6 (q, Ar-$OCH_3$), 51.4 [s, $C(CH_3)_2$], 25.5 [q, $C(CH_3)_{2a}$], 22.8 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{19}O_2]^+$=$[M+H]^+$: 267.1380; found 267.1380.

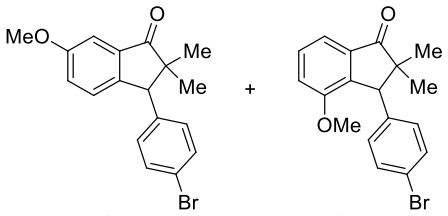



**4b** **4b'**

**3-(4-chlorophenyl)-6-methoxy-2,2-dimethylindan-1-one (4b) & 3-(4-chlorophenyl)-4-methoxy-2,2-dimethylindan-1-one (4b'):**

**GP-1** was carried out with ketone **1b** (44.5 mg, 0.25 mmol), aldehyde **2c** (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the inseparable

regioisomeric mixture of indanones **4b** (56.2 mg, 68%) and **4b'** (14.0 mg, 17%) as a paleyellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 78–81 °C. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1b**)=0.50, $R_f$(**4b** & **4b'**)=0.42, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2963, 2926, 1707, 1599, 1488, 1465, 1270, 1241, 1089, 1013, 796 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz, peaks due to major isomer **4b**): $\delta$=7.32–7.17 (m, 5H, Ar-H), 6.96 (d, 2H, *J*=8.3 Hz, Ar-H), 4.23 (s, 1H, CH), 3.88 (s, 3H, Ar-$OCH_3$), 1.34 [s, 3H, $C(CH_3)_{2a}$], 0.69 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz, peaks due to major isomer **4b**): $\delta$=210.2 (s, C=O), 160.0 (s, Ar-C), 146.5 (s, Ar-C), 139.0 (s, Ar-C), 136.6 (s, Ar-C), 132.8 (s, Ar-C), 130.4 (d, 2C, 2 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 127.6 (d, Ar-CH), 124.4 (d, Ar-CH), 105.3 (d, Ar-CH), 56.1 (d, CH), 55.6 (q, Ar-$OCH_3$), 51.2 [s, $C(CH_3)_2$], 25.5 [q, $C(CH_3)_{2a}$], 22.7 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}ClO_2]^+$=$[M+H]^+$: 301.0990; found 301.0988.

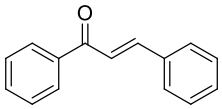



**4c** **4c'**

**3-(4-bromophenyl)-6-methoxy-2,2-dimethylindan-1-one (4c) & 3-(4-bromophenyl)-4-methoxy-2,2-dimethylindan-1-one (4c'):**

**GP-1** was carried out with ketone **1b** (44.5 mg, 0.25 mmol), aldehyde **2d** (92.5 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the inseparable regioisomeric mixture of indanones **4c** (58.7 mg, 68%) and **4c'** (14.7 mg, 17%) as a paleyellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f$(**1b**)=0.50, $R_f$(**4c** & **4c'**)=0.43, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2964, 2925, 1710, 1602, 1488, 1465, 1270, 1242, 1011, 796 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz, peaks due to major isomer **4c**): $\delta$=7.43 (d, 2H, *J*=8.3 Hz, Ar-H), 7.26 (d, 1H, *J*=1.9 Hz, Ar-H), 7.21 (dd, 1H, *J*=8.3 and 1.9 Hz, Ar-H), 7.20 (d, 1H, *J*=8.3 Hz, Ar-H), 6.91 (d, 2H, *J*=8.3 Hz, Ar-H), 4.22 (s, 1H, CH), 3.87 (s, 3H, Ar-$OCH_3$), 1.34 [s, 3H, $C(CH_3)_{2a}$], 0.69 [s, 3H, $C(CH_3)_{2b}$] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz, peaks due to major isomer **4c**): $\delta$=210.1 (s, C=O), 160.0 (s, Ar-C), 146.4 (s, Ar-C), 139.5 (s, Ar-C), 136.6 (s, Ar-C), 131.4 (d, 2C, 2 × Ar-CH), 131.0 (s, Ar-C), 130.8 (d, 2C, 2 × Ar-CH), 127.5 (d, Ar-CH), 124.4 (d, Ar-CH), 105.3 (d, Ar-CH),

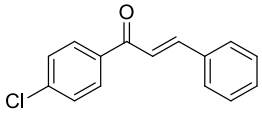
56.2 (d, CH), 55.6 (q, Ar-$OCH_3$), 51.2 [s, $C(CH_3)_2$], 25.5 [q, $C(CH_3)_{2a}$], 22.7 [q, $C(CH_3)_{2b}$] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}BrO_2]^+$=$[M+H]^+$: 345.0485; found 345.0484.



**6a**

**(2E)-1,3-diphenylprop-2-en-1-one (6a):**

**GP-2** was carried out with acetophenone **5a** (60 mg, 0.5 mmol), aldehyde **2a** (106 mg, 1.0 mmol), triflic acid (0.22 mL, 2.5 mmol), dichloroethane (1.5 mL) for the formation of chalcone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 97:3 to 95:5) furnished the chalcone **6a** (48.6, 81%) as yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f$(**5a**)=0.32, $R_f$(**6a**)=0.42, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=3059, 2921, 1661, 1601, 1574, 1448, 1334, 1285, 1212, 1015, 976, 743, 686 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.02 (d, 2H, *J*=8.3 Hz, Ar-H), 7.81 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.64 (d, 1H, *J*=7.3 Hz, Ar-H), 7.63 (d, 1H, *J*=7.3 Hz, Ar-H), 7.58 (t, 1H, *J*=7.8 Hz, Ar-H), 7.53 (d, 1H, *J*=15.6 Hz, CH=C*H*COPh), 7.49 (dd, 2H, *J*=7.3 and 7.3 Hz, Ar-H), 7.45–7.35 (m, 3H, Ar-H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=190.5 (s, C=O), 144.8 (d, *C*H=CHCOPh), 138.1 (s, Ar-C), 134.8 (s, Ar-C), 132.7 (d, Ar-CH), 130.5 (d, Ar-CH), 128.9 (d, 2C, 2 × Ar-CH), 128.6 (d, 2C, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 122.0 (d, CH=*C*HCOPh) ppm.

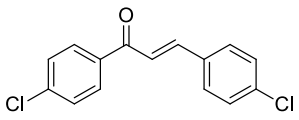


**6b**

**(2*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (6b):**

**GP-2** was carried out with p-chloroacetophenone **5b** (77.2 mg, 0.5 mmol), aldehyde **2a** (106 mg, 1.0 mmol), triflic acid (0.22 mL, 2.5 mmol), dichloroethane (1.5 mL) for the formation of chalcone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 98:2 to 97:3) furnished the chalcone **6b** (65.6 mg, 85%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 90–92 °C. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f$(**5b**)=0..35, $R_f$(**6b**)=0.44, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=3052, 2923, 1659, 1599, 1448, 1332, 1215, 1087, 1035, 1010, 982, 828, 761, 692,

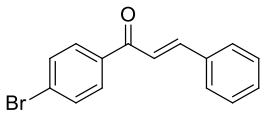
543 $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.96 (d, 2H, *J*=8.3 Hz, Ar-H), 7.81 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.67–7.58 (m, 2H, Ar-H), 7.52–7.32 (m, 6H, Ar-H and CH=C*H*COPh) ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=189.1 (s, C=O), 145.3 (d, *C*H=CHCOPh), 139.2 (s, Ar-C), 136.4 (s, Ar-C), 134.6 (s, Ar-CH), 130.7 (d, Ar-CH), 129.9 (d, 2C, 2 × Ar-CH), 129.0 (d, 2C, 2 × Ar-CH), 128.9 (d, 2C, 2 × Ar-CH) 128.5 (d, 2C, 2 × Ar-CH), 121.4 (d, CH=*C*HCOPh) ppm.




**6c**

**(2*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (6c):**

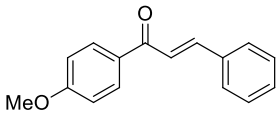
**GP-2** was carried out with p-chloroacetophenone **5b** (77.2, 0.5 mmol), aldehyde **2c** (140.5 mg, 1.0 mmol), triflic acid (0.22 mL, 2.5 mmol), dichloroethane (1.5 mL) for the formation of chalcone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 98:2 to 97:3) furnished the chalcone **6c** (60.9 mg, 79%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 140–142°C. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f$(**5b**)=0.35, $R_f$(**6c**)=0.45, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2921, 1660, 1586, 1487, 1328, 1216, 1088, 1010, 983, 834, 814, 742, 670 $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 400 MHz): $\delta$=7.94 (d, 2H, *J*=8.3 Hz, Ar-H), 7.74 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.56 (d, 2H, *J*=8.3 Hz, Ar-H), 7.46 (d, 2H, *J*=8.3 Hz, Ar-H), 7.44 (d, 1H, *J*=15.6 Hz, CH=C*H*COPh), 7.38 (d, 2H, *J*=8.3 Hz, Ar-H) ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$=188.8 (s, C=O), 143.8 (d, *C*H=CHCOPh), 139.4 (s, Ar-C), 136.6 (s, Ar-C), 136.3 (s, Ar-C), 133.1 (s, Ar-C), 129.9 (d, 2C, 2 × Ar-CH), 129.6 (d, 2C, 2 × Ar-CH), 129.3 (d, 2C, 2 × Ar-CH), 129.0 (d, 2C, 2 × Ar-CH), 121.8 (d, CH=*C*HCOPh) ppm.




**6d**

**(2*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (6d):**

**GP-2** was carried out with p-bromoacetophenone **5c** (99 mg, 0.5 mmol), aldehyde **2a** (106 mg, 1.0 mmol), triflic acid (0.22 mL, 2.5 mmol), dichloroethane (1.5 mL) for the formation of chalcone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 98:2 to 97:3) furnished the chalcone **6d** (85.1 mg, 86%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 92–94°C. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f$(**5c**)=0.47, $R_f$(**6d**)=0.52, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2922, 1657, 1599, 1582, 1447, 1332, 1214, 1067, 981, 759, 690 $cm^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=7.87 (d, 2H, *J*=8.3 Hz, Ar-H), 7.80 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.70–7.55 (m, 4H, Ar-H), 7.46 (d, 1H, *J*=15.6 Hz, CH=C*H*COPh), 7.43–7.35 (m, 3H, Ar-H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=189.2 (s, C=O), 145.3 (d, *C*H=CHCOPh), 136.8 (s, Ar-C), 134.6 (s, Ar-C), 131.8 (d, 2C, 2 × Ar-CH), 130.7 (d, Ar-CH), 129.9 (d, 2C, 2 × Ar-CH), 128.9 (d, 2C, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 127.8 (s, Ar-C), 121.3 (d, CH=*C*HCOPh) ppm.

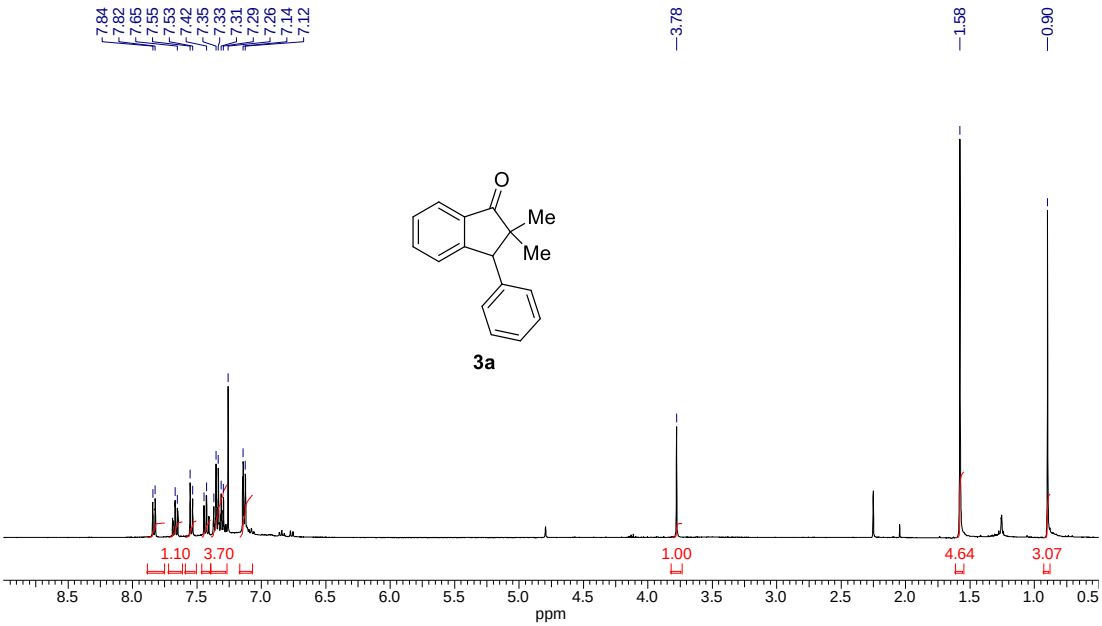



**6e**

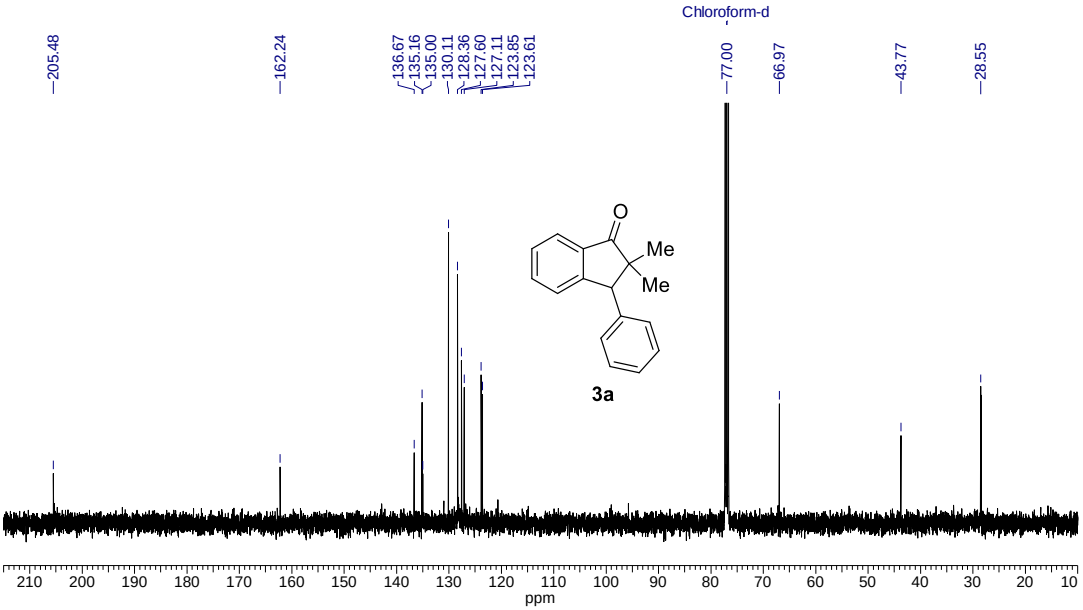
**(2*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (6e):**

**GP-2** was carried out with p-methoxyacetophenone **5d** (75 mg, 0.5 mmol), aldehyde **2a** (106 mg, 1.0 mmol), triflic acid (0.22 mL, 2.5 mmol), dichloroethane (1.5 mL) for the formation of chalcone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 97:3 to 95:5) furnished the chalcone **6e** (61.5 mg, 82%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 92–94 °C. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f$(**5d**)=0.26, $R_f$(**6e**)=0.31, UV detection]. IR (MIR-ATR, 4000–600 $cm^{-1}$): IR (MIR-ATR, 4000–600 $cm^{-1}$): $\nu_{max}$=2922, 2851, 1658, 1605, 1336, 1260, 1220, 1170, 834, 767, 695 $cm^{-1}$.$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.04 (d, 2H, *J*=8.8 Hz, Ar-H), 7.80 (d, 1H, *J*=15.6 Hz, C*H*=CHCOPh), 7.68–7.58 (m, 2H, Ar-H), 7.54 (d, 1H, *J*=15.6 Hz, CH=C*H*COPh), 7.45–7.32 (m, 3H, Ar-H), 6.97 (d, 2H, *J*=8.8 Hz, Ar-H), 3.88 (s, 3H, Ar-$OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=188.7 (s, C=O), 163.4 (s, Ar-C), 143.9 (d, *C*H=CHCOPh), 135.0 (s, Ar-C), 131.0 (s, Ar-C), 130.8 (d, 2C, 2 × Ar-CH), 130.3 (d, Ar-CH), 128.9 (d, 2C, 2 × Ar-

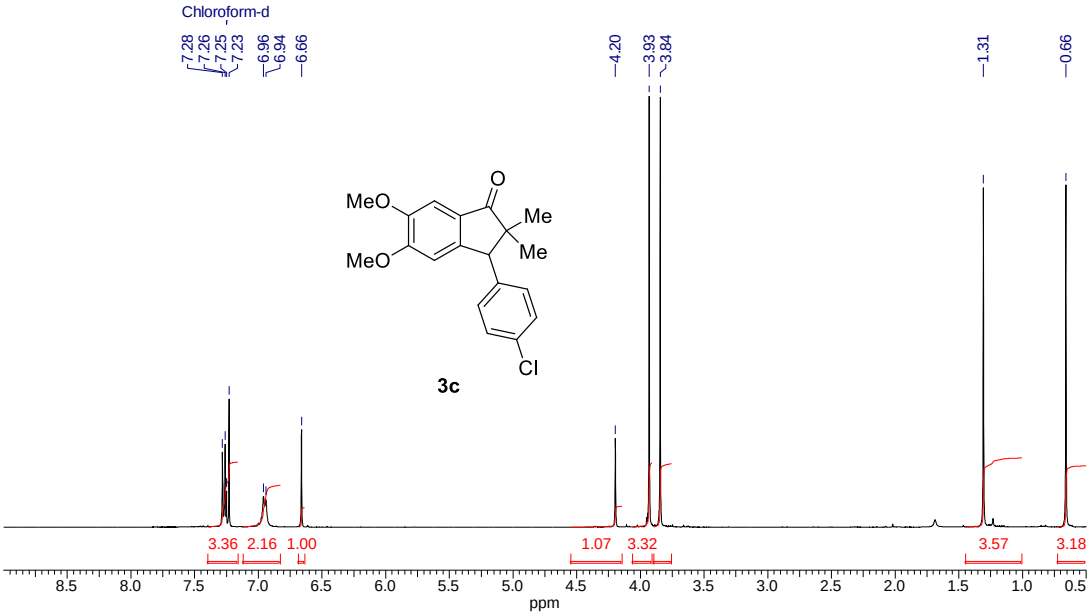
CH), 128.3 (d, 2C, 2 × Ar-CH), 121.8 (d, CH=*C*HCOPh), 113.8 (d, 2C, 2 × Ar-CH), 55.4 (q, Ar-$OCH_3$) ppm.



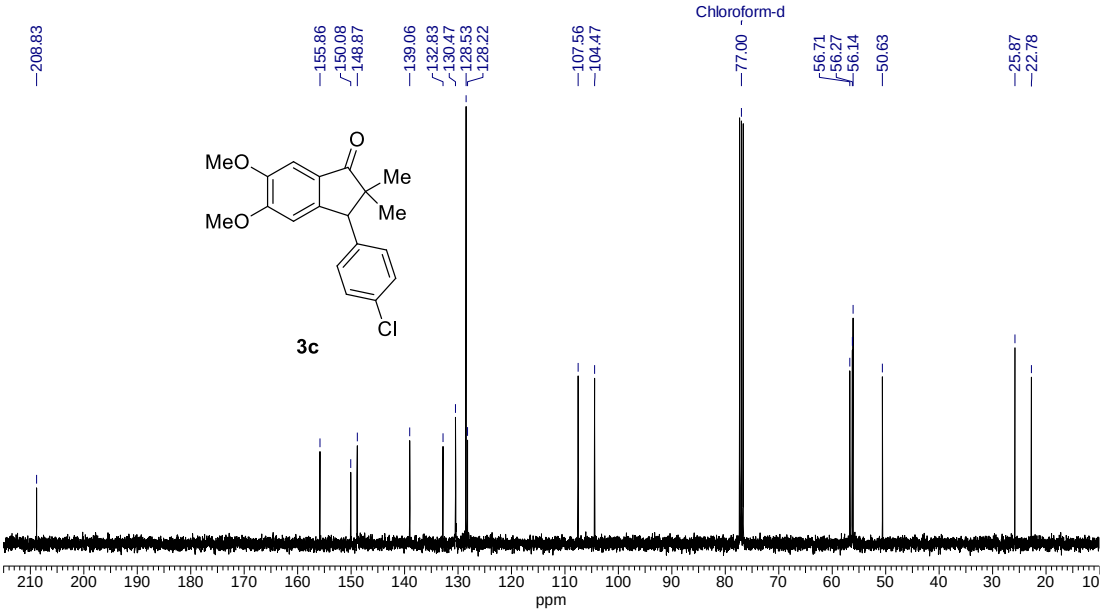

$^1$H NMR (400 MHz) spectrum of **3a** in $CDCl_3$



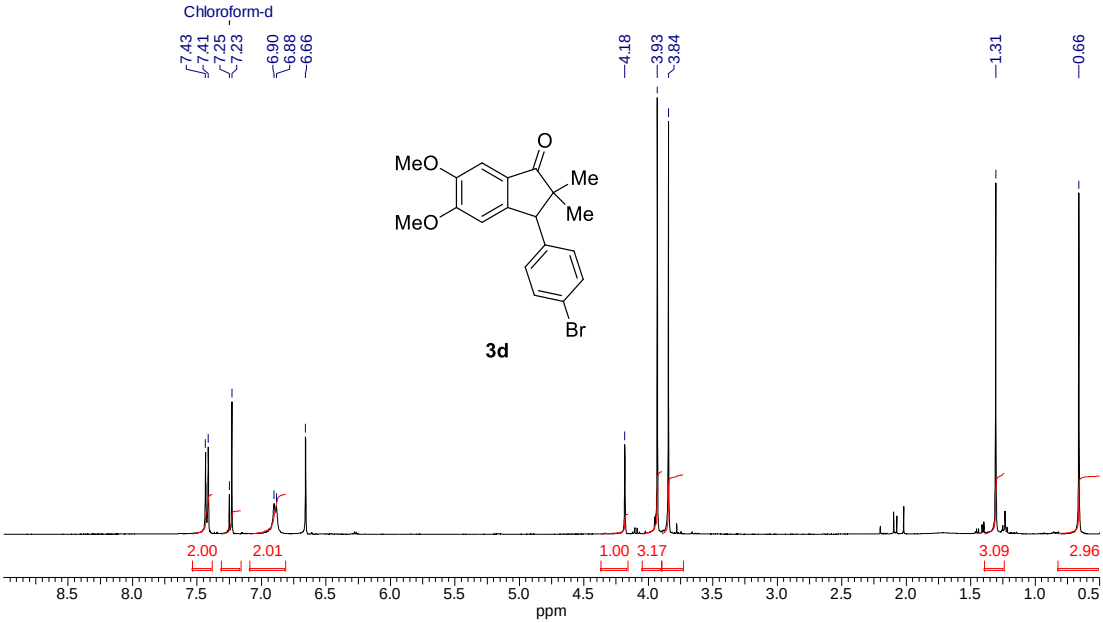

$^{13}$C NMR (100 MHz) spectrum of **3a** in $CDCl_3$



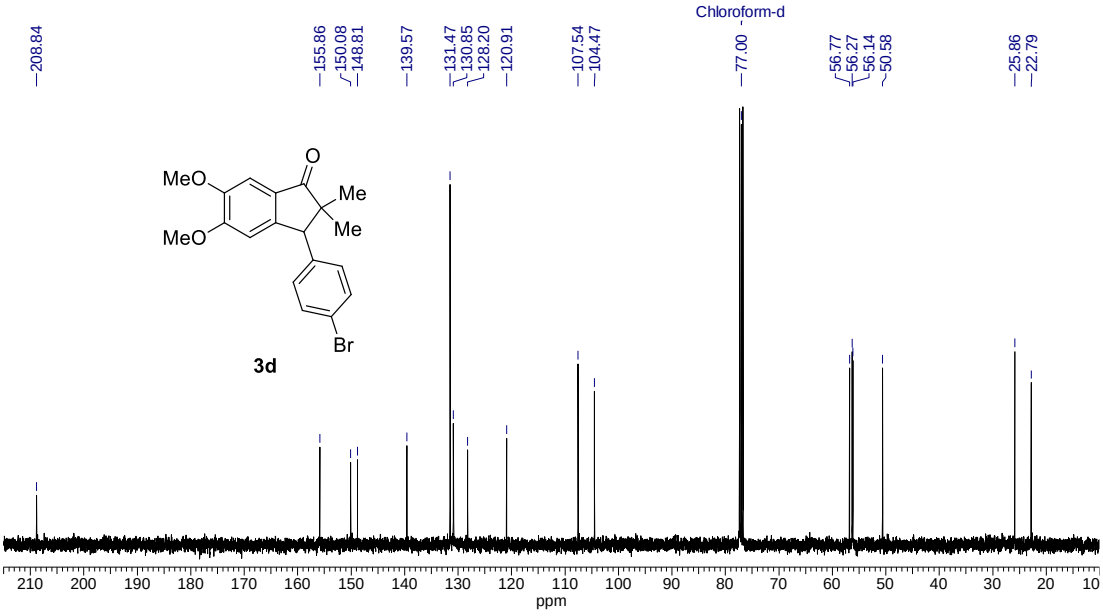

$^{1}$H NMR (400 MHz) spectrum of **3c** in $CDCl_3$



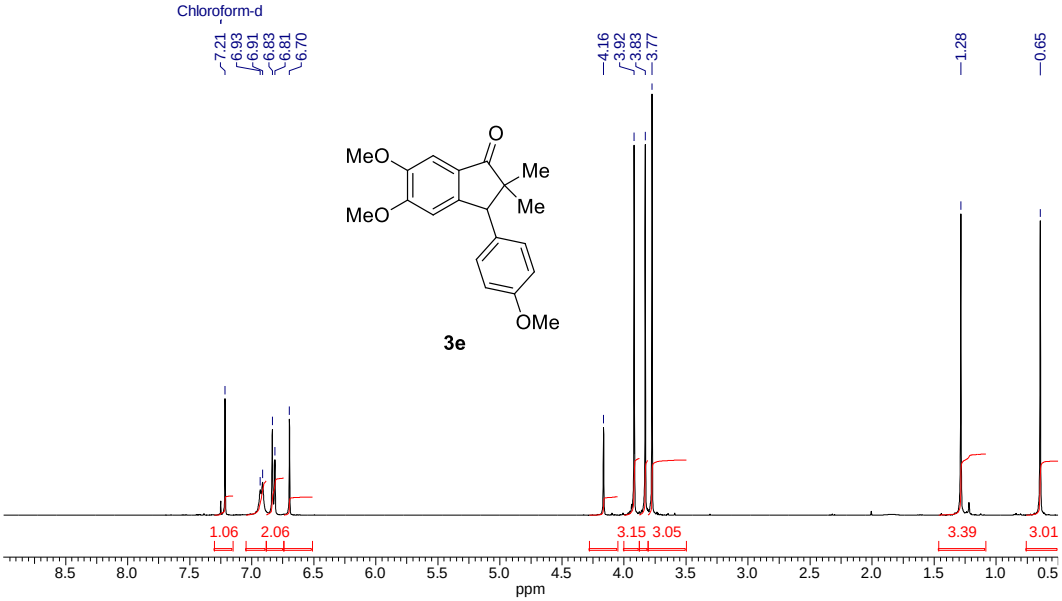

$^{13}$C NMR (100 MHz) spectrum of **3c** in $CDCl_3$



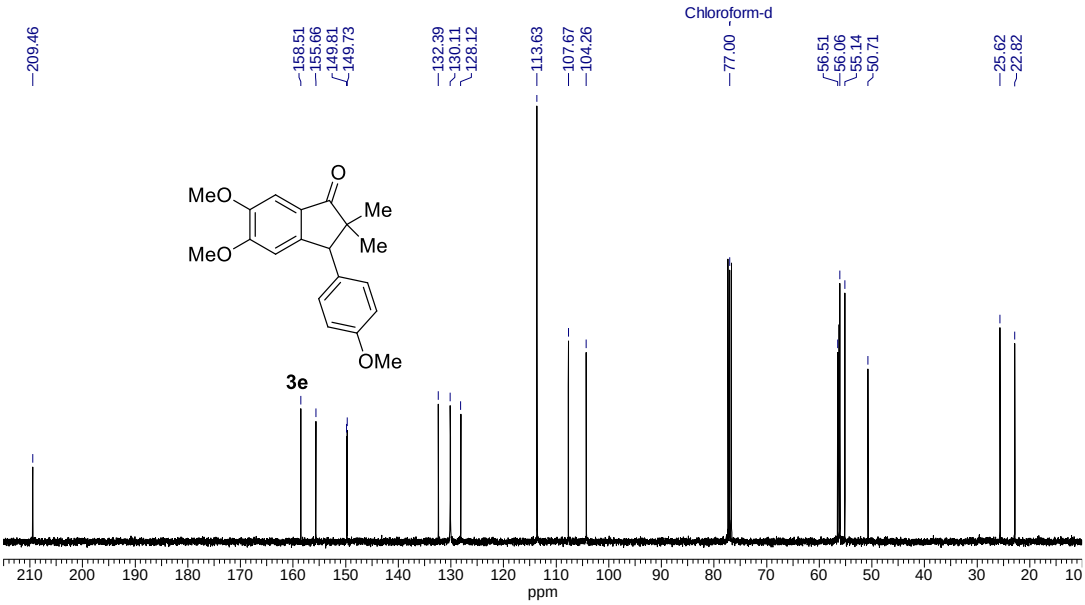

$^{1}$H NMR (400 MHz) spectrum of **3d** in $CDCl_3$



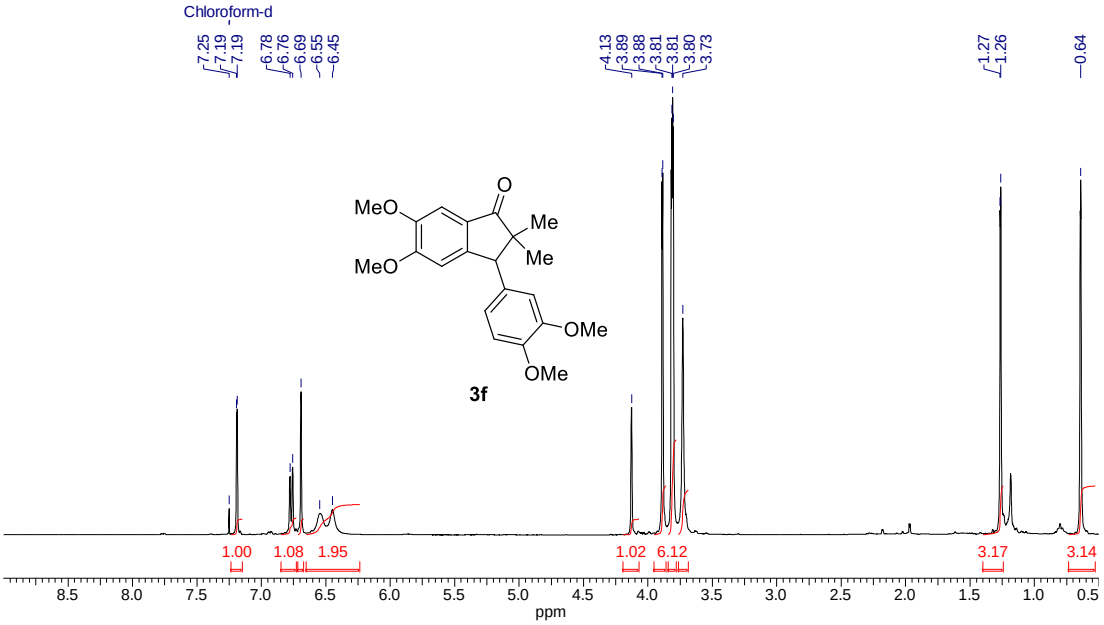

$^{13}$C NMR (100 MHz) spectrum of **3d** in $CDCl_3$



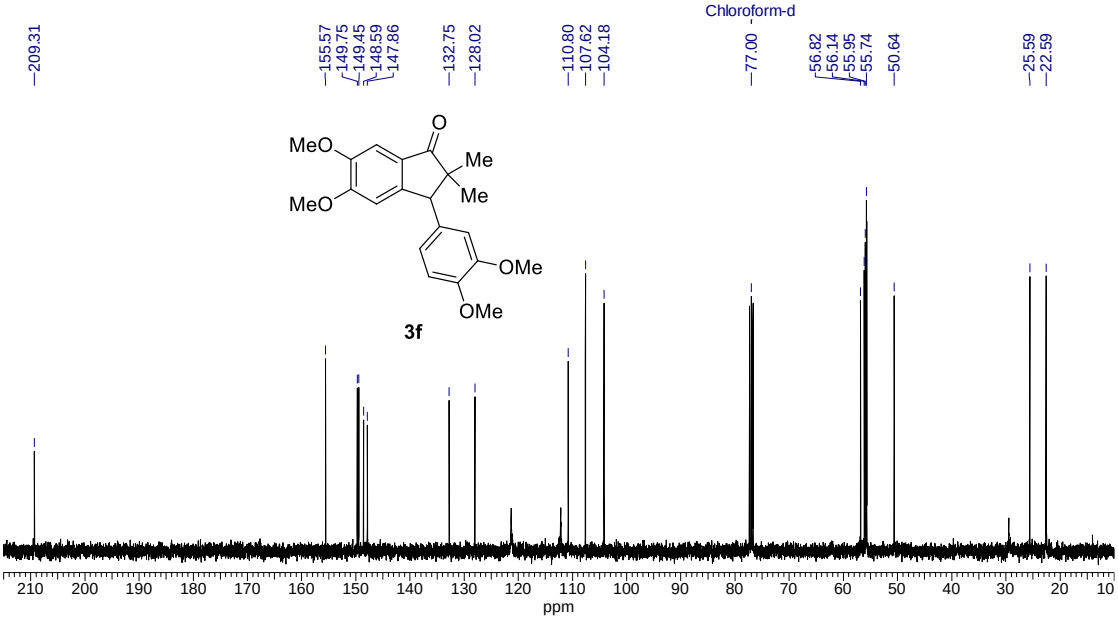

$^{1}$H NMR (400 MHz) spectrum of **3e** in $CDCl_3$



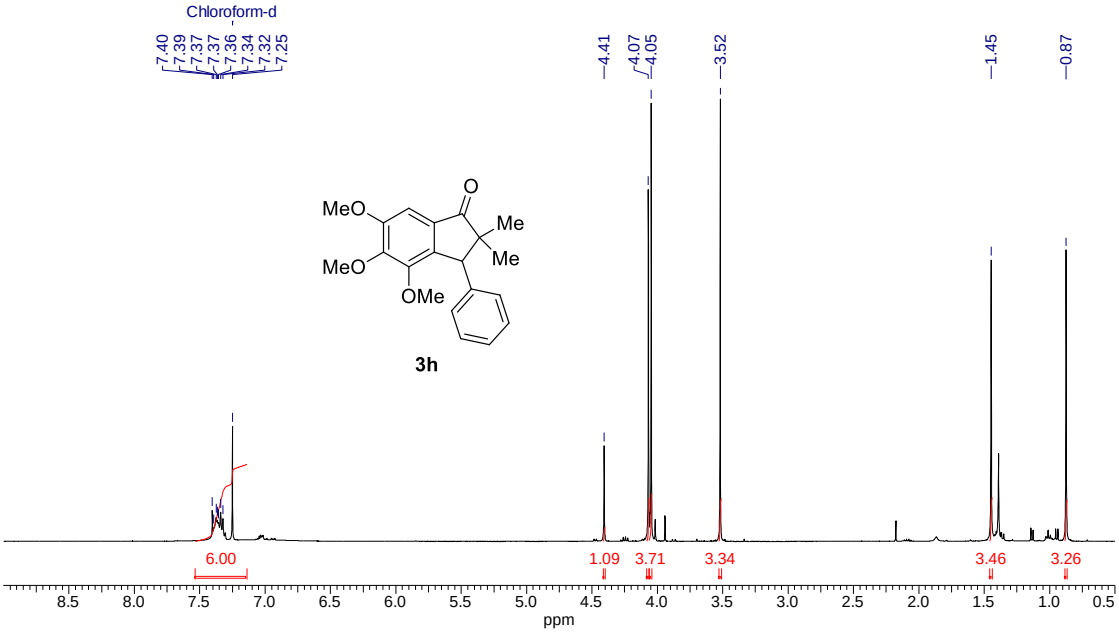

$^{13}$C NMR (100 MHz) spectrum of **3e** in $CDCl_3$



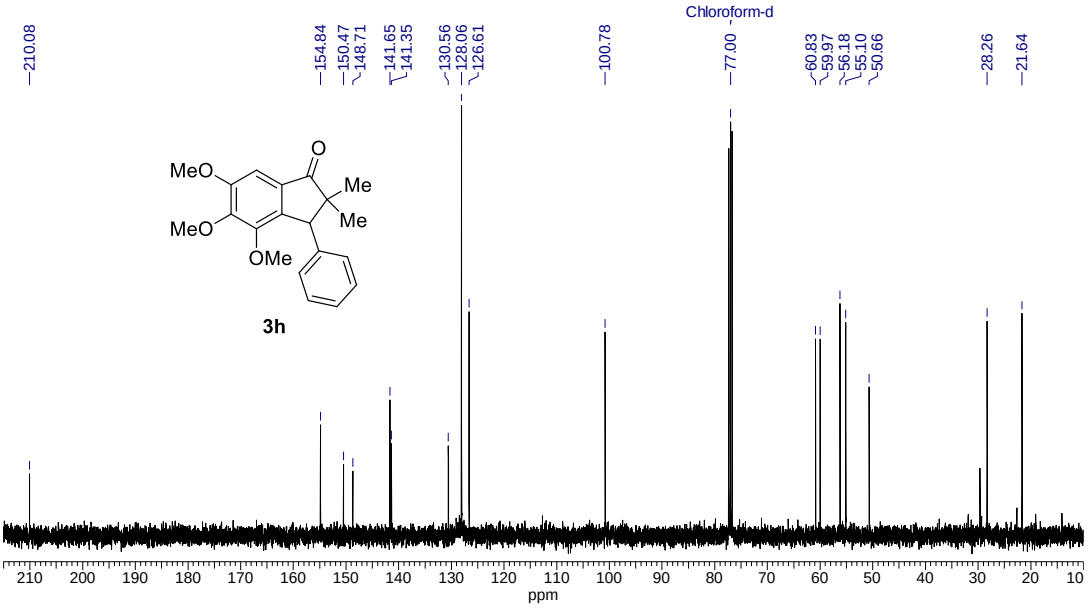

$^{1}$H NMR (400 MHz) spectrum of **3f** in $CDCl_3$



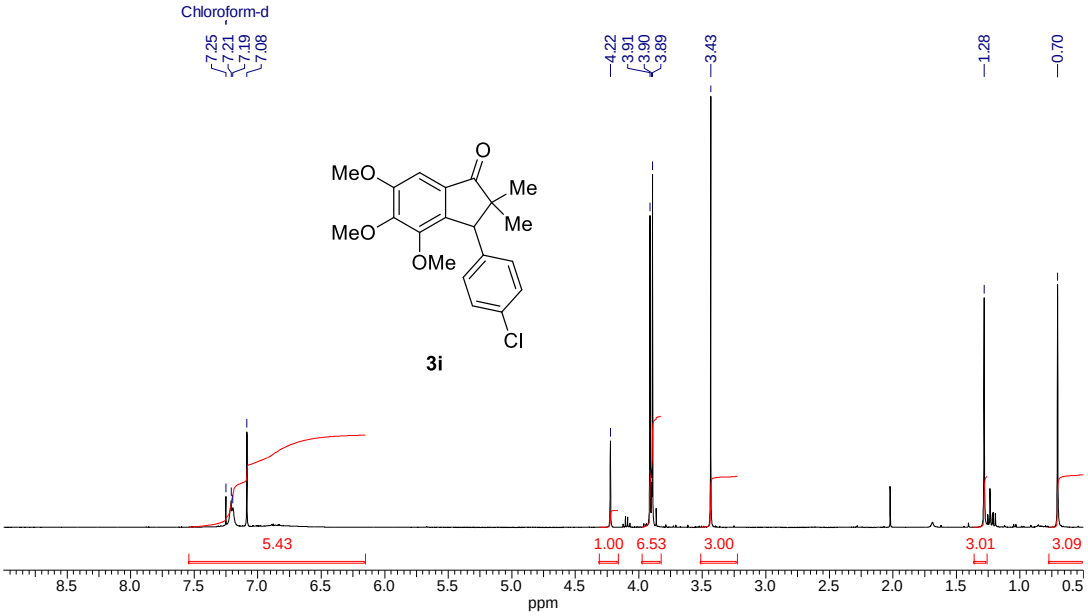

$^{13}$C NMR (100 MHz) spectrum of **3f** in $CDCl_3$



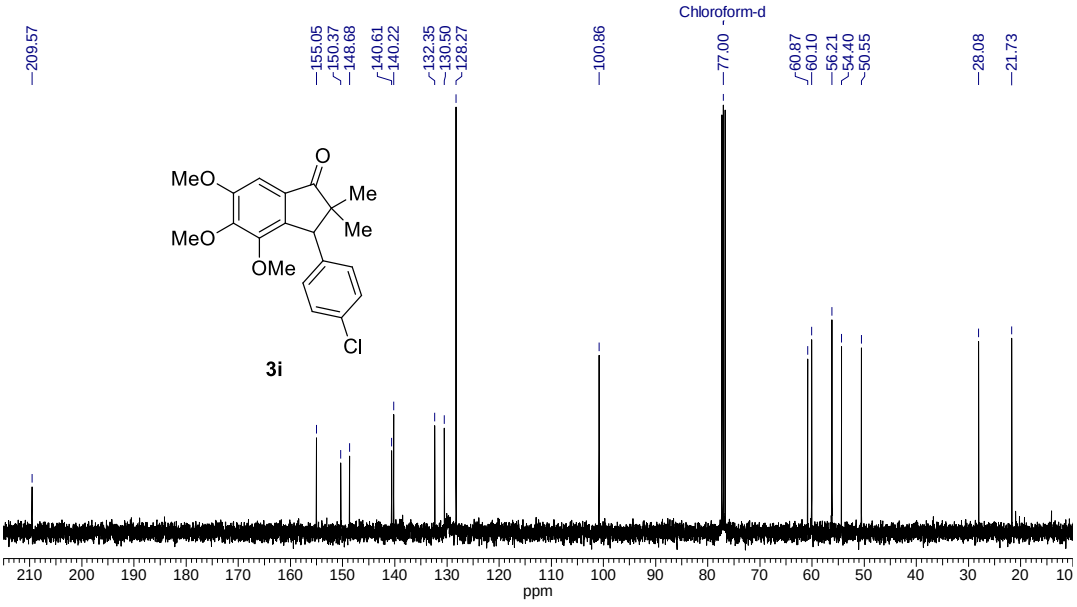

$^{1}$H NMR (400 MHz) spectrum of **3h** in $CDCl_3$



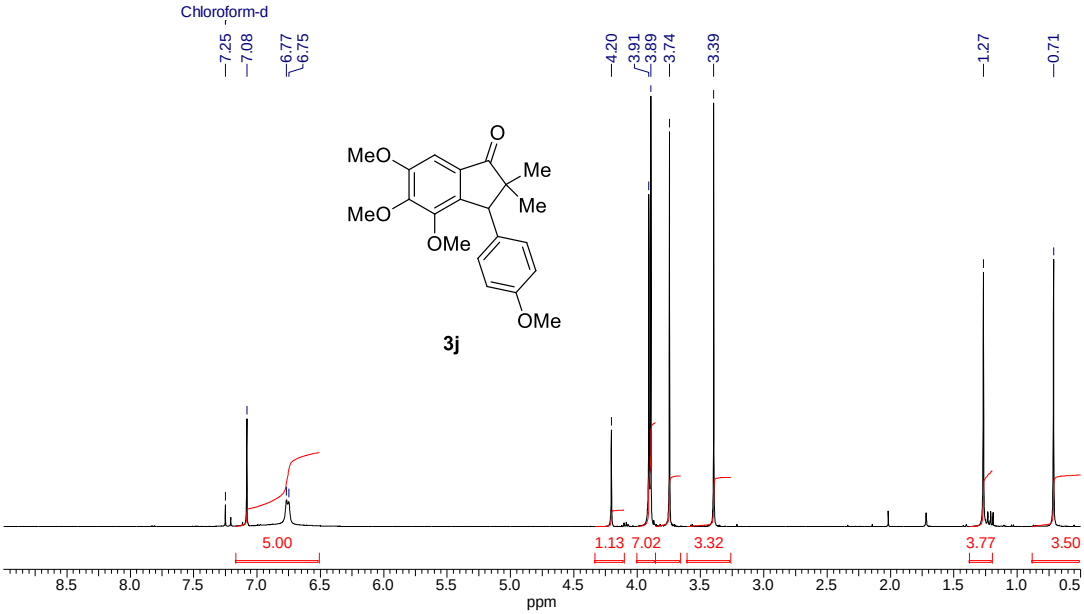

$^{13}$C NMR (100 MHz) spectrum of **3h** in $CDCl_3$



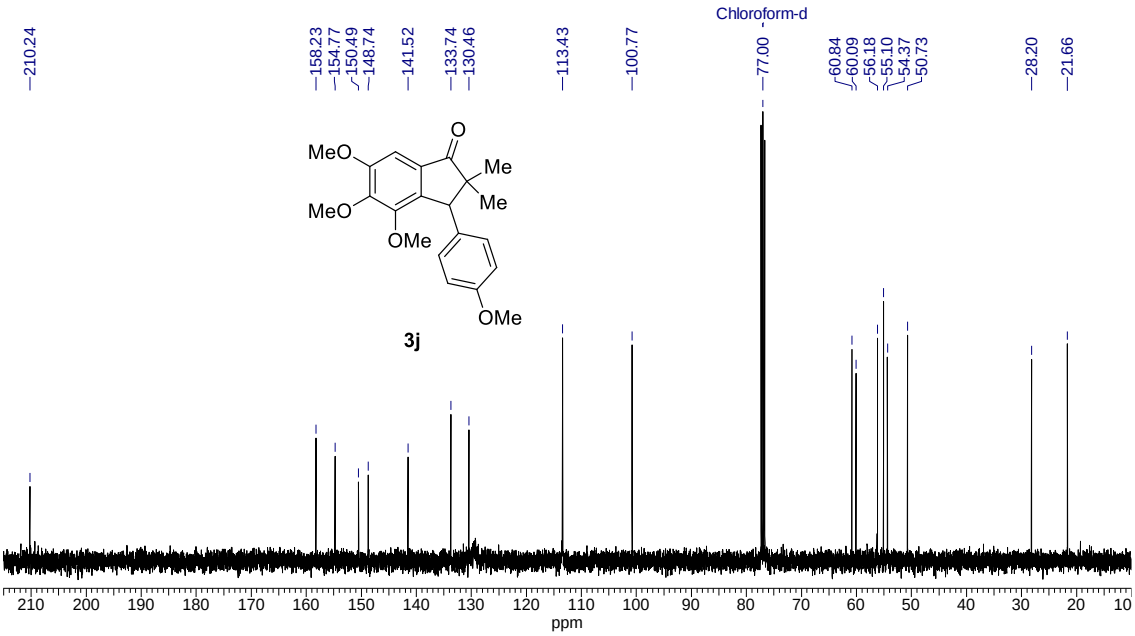

$^{1}$H NMR (400 MHz) spectrum of **3i** in $CDCl_3$



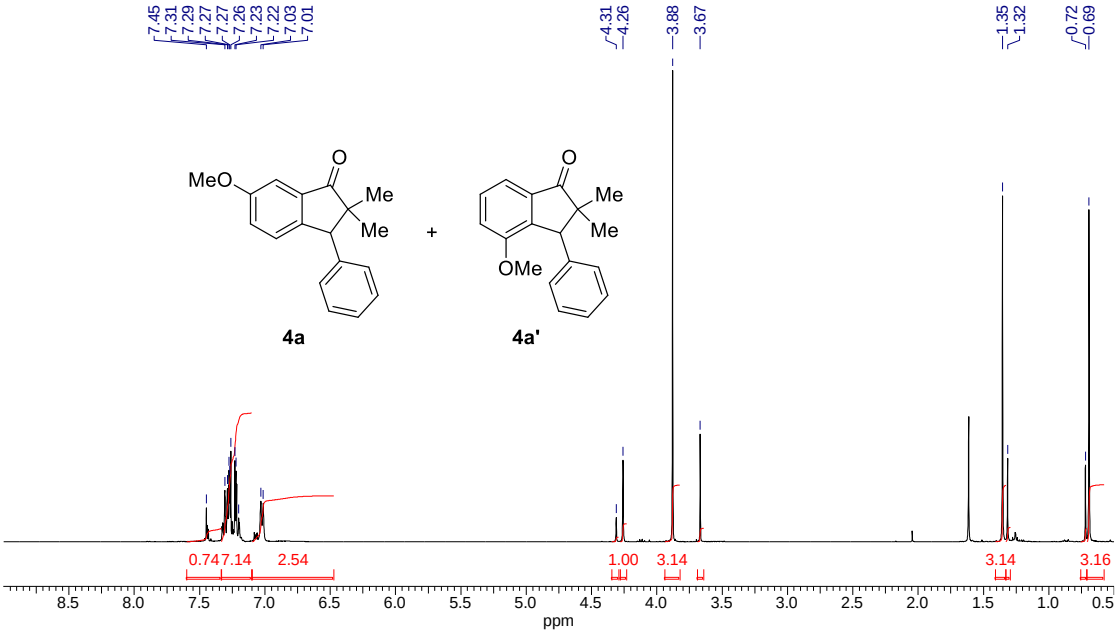

$^{13}$C NMR (100 MHz) spectrum of **3i** in $CDCl_3$



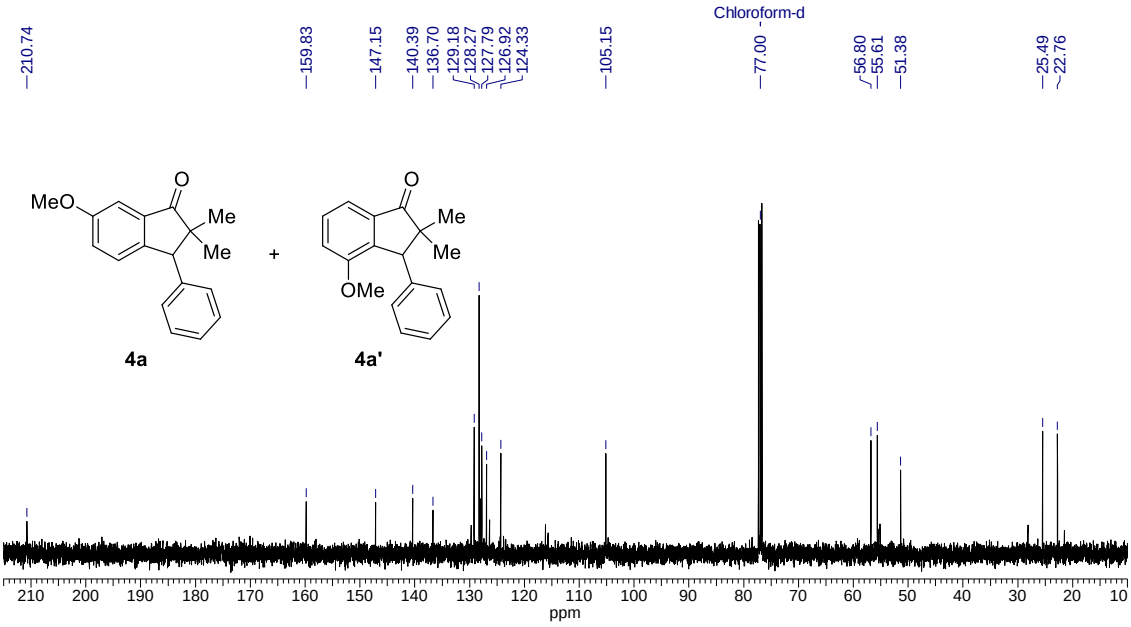

$^{1}$H NMR (400 MHz) spectrum of **3j** in $CDCl_3$



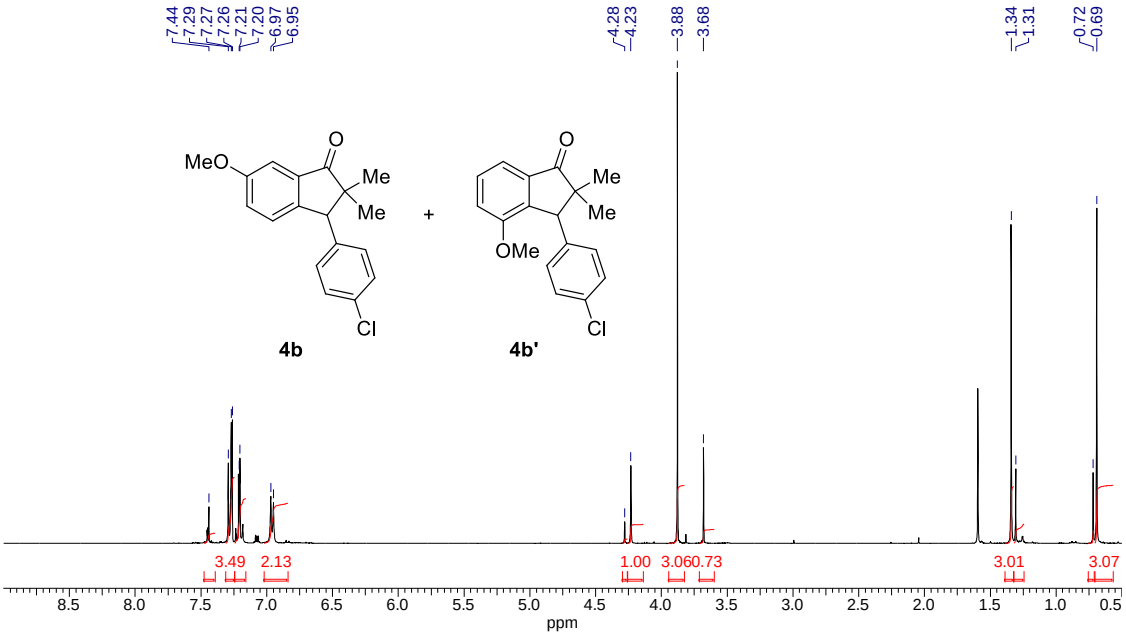

$^{13}$C NMR (100 MHz) spectrum of **3j** in $CDCl_3$



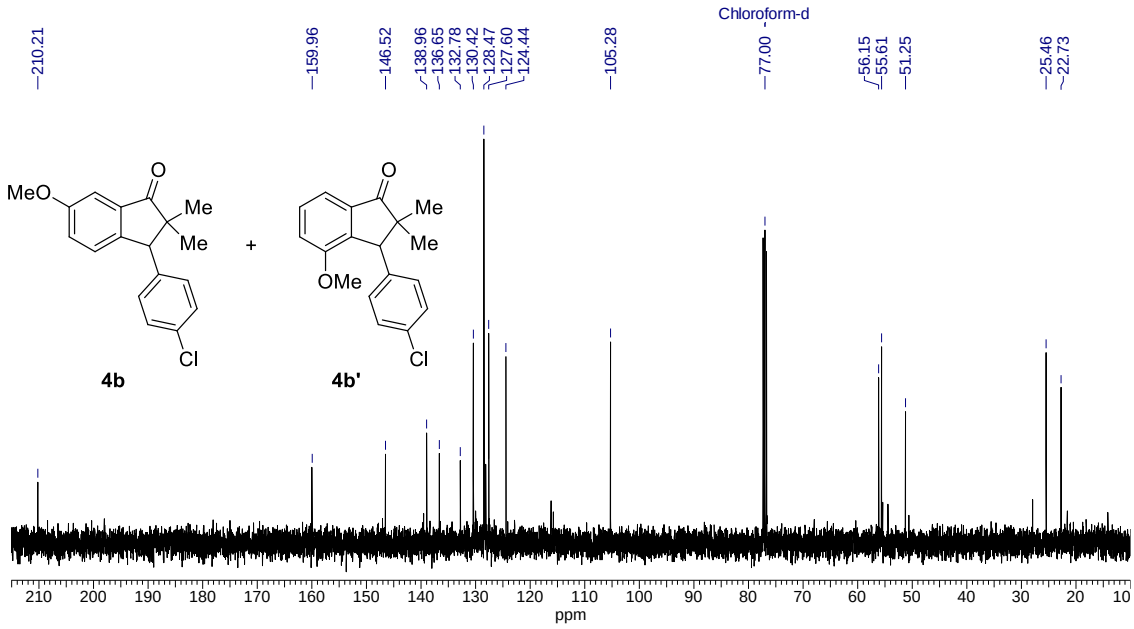

$^{1}$H NMR (400 MHz) spectrum of **4a** & **4a'** in $CDCl_3$



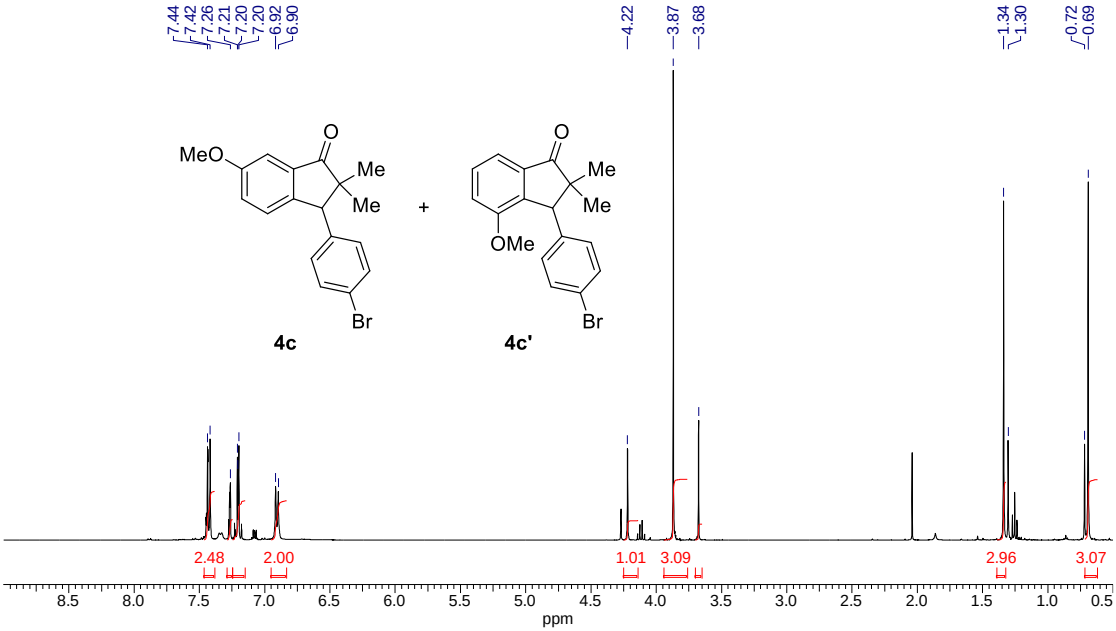

$^{13}$C NMR (100 MHz) spectrum of **4a** & **4a'** in $CDCl_3$



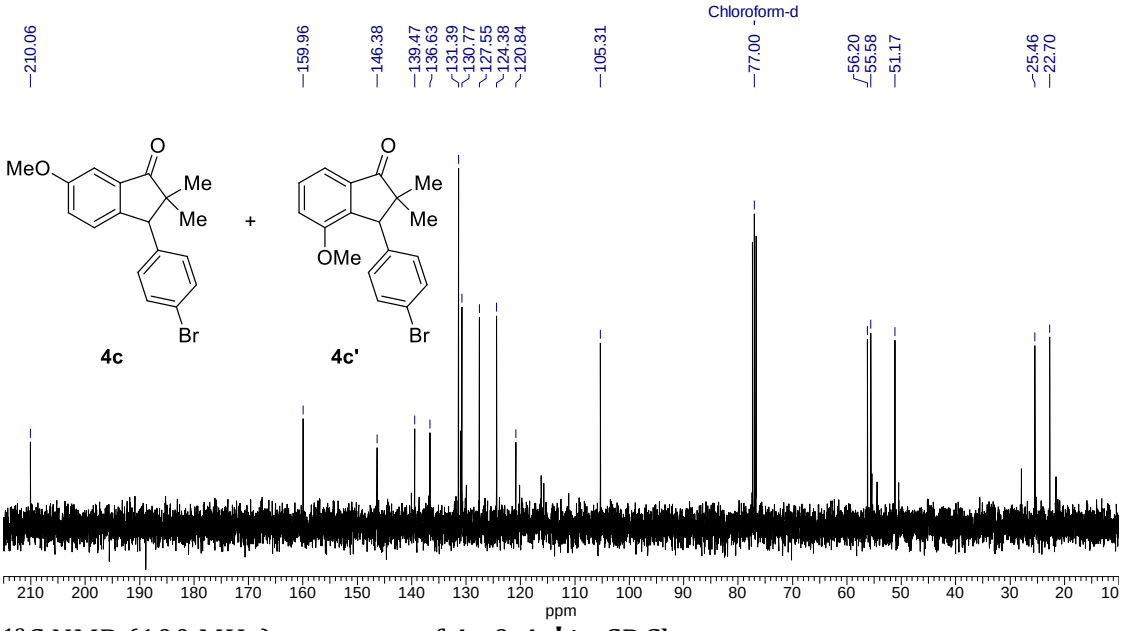

$^{1}$H NMR (400 MHz) spectrum of **4b** & **4b'** in $CDCl_3$



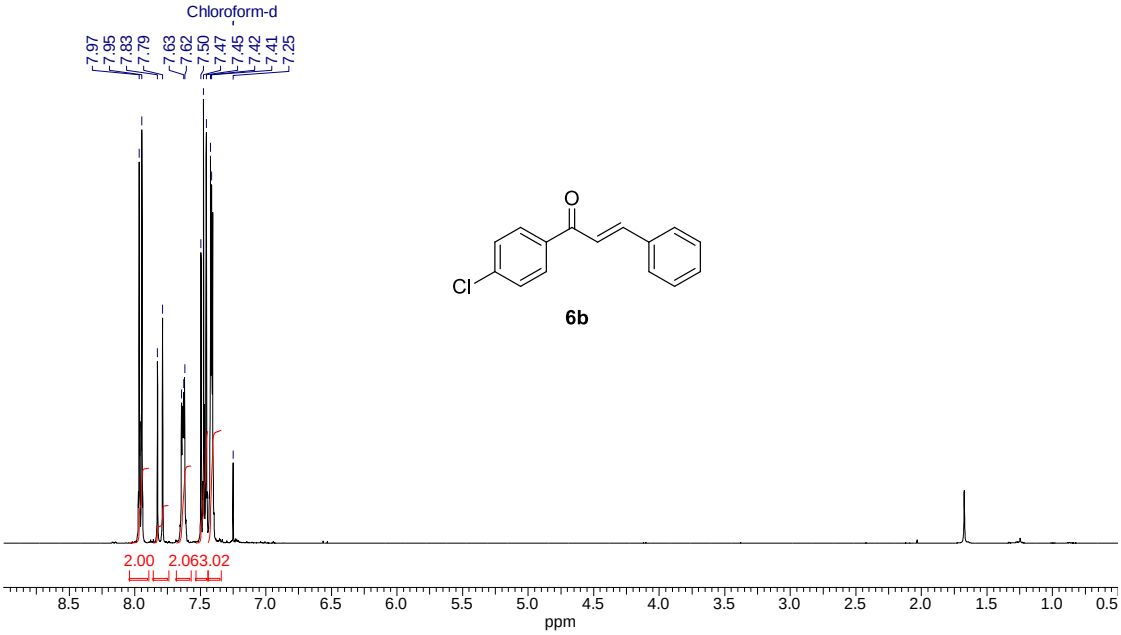

$^{13}$C NMR (100 MHz) spectrum of **4b** & **4b'** $CDCl_3$



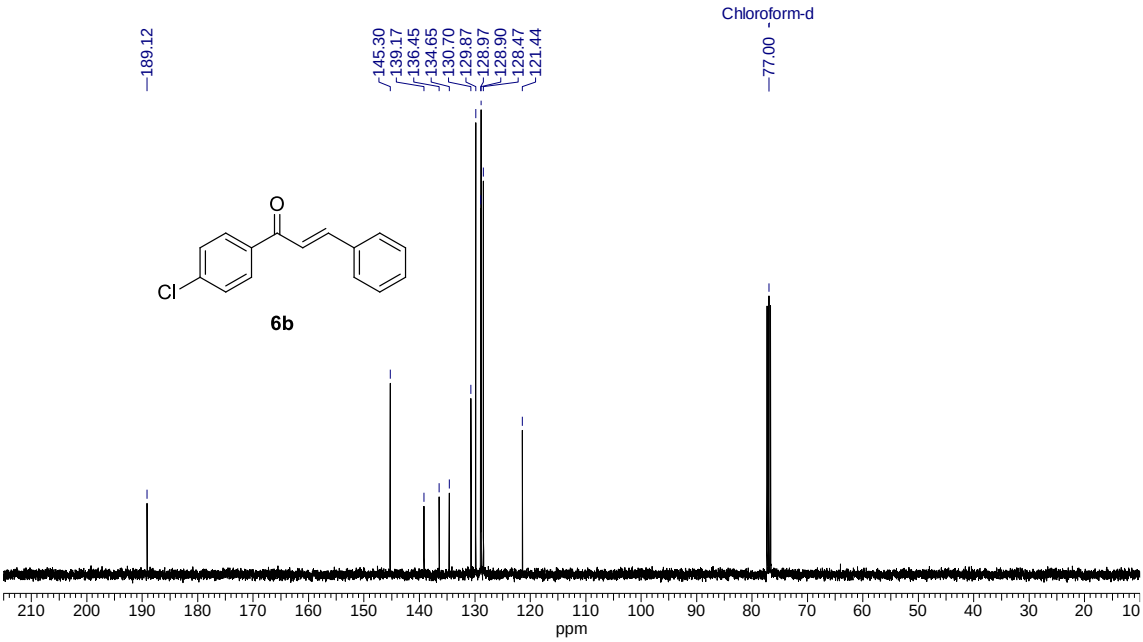

$^{1}$H NMR (400 MHz) spectrum of **4c** & **4c'** in $CDCl_3$



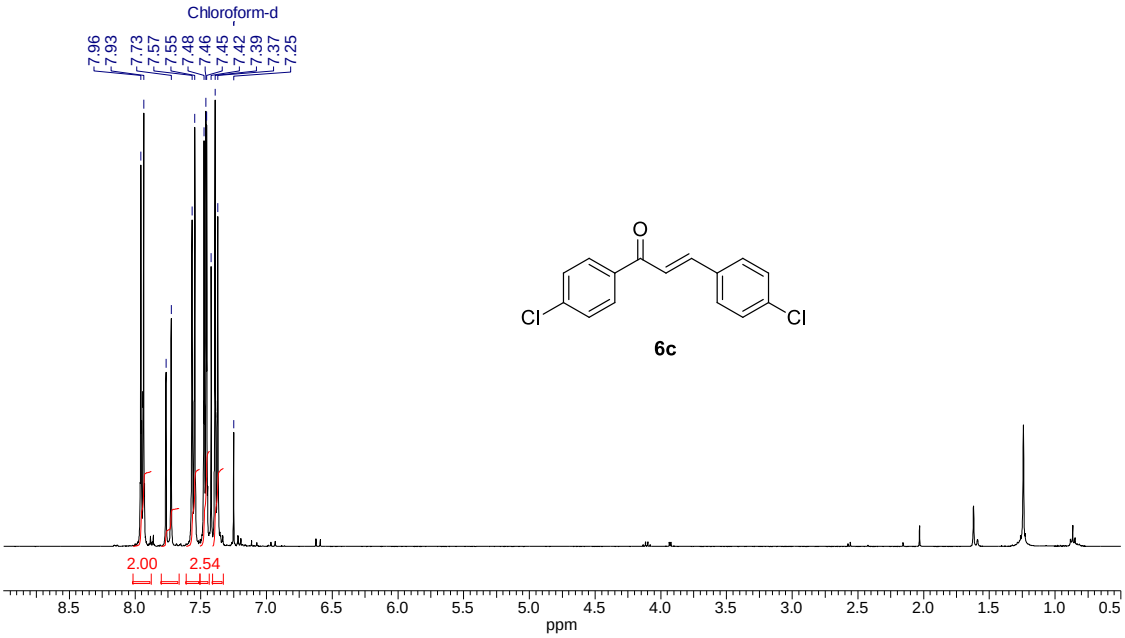

$^{13}$C NMR (100 MHz) spectrum of **4c** & **4c'** in $CDCl_3$



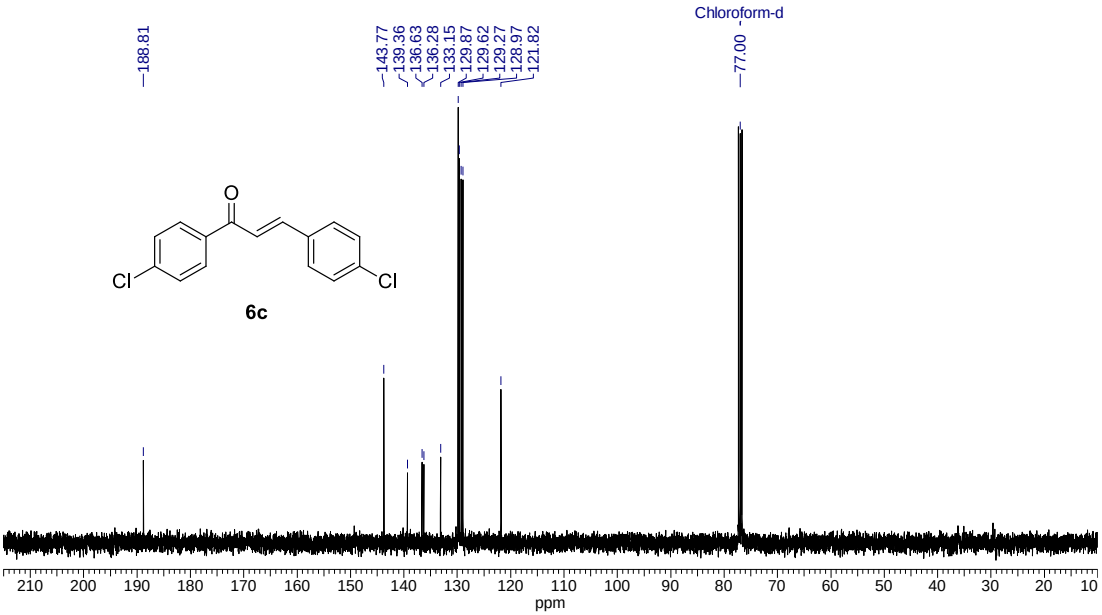

$^{1}$H NMR (400 MHz) spectrum of **6b** in $CDCl_3$



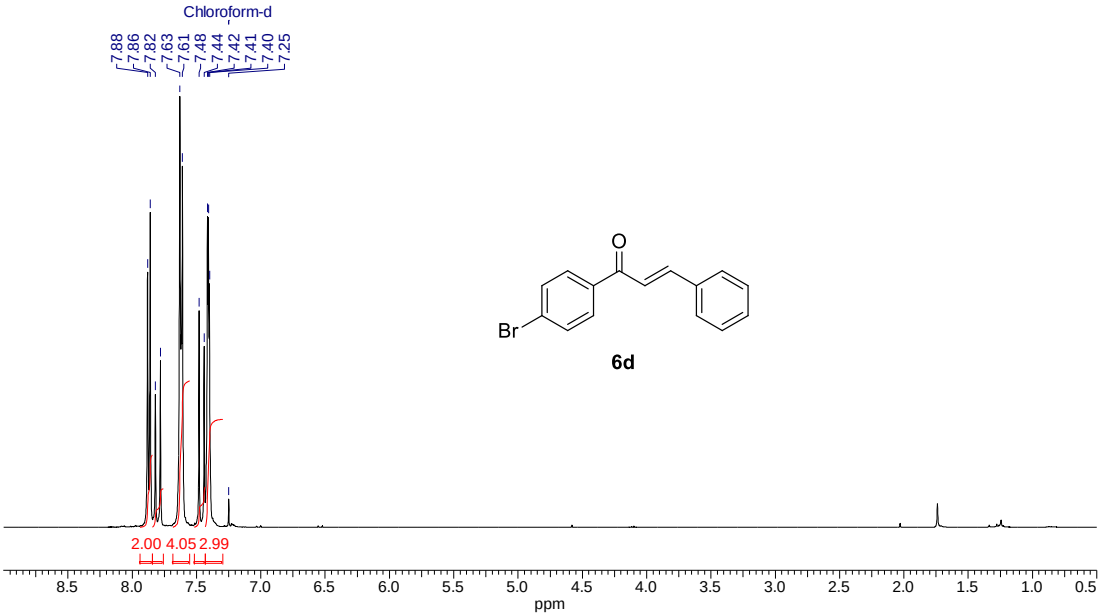

$^{13}$C NMR (100 MHz) spectrum of **6b** in $CDCl_3$



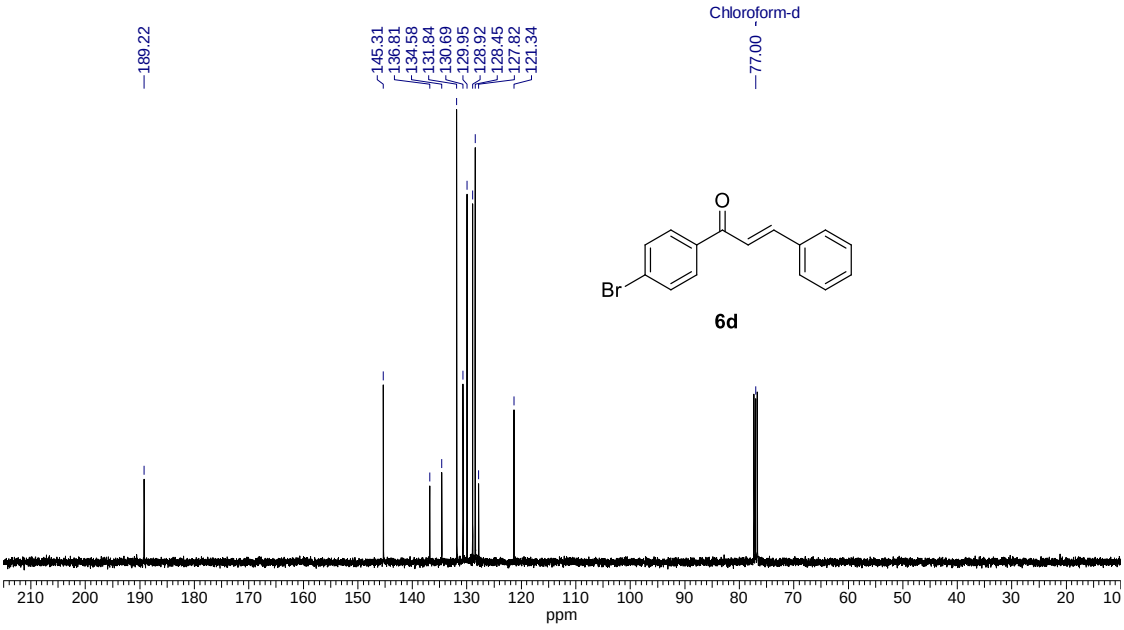

$^{1}$H NMR (400 MHz) spectrum of **6c** in $CDCl_3$



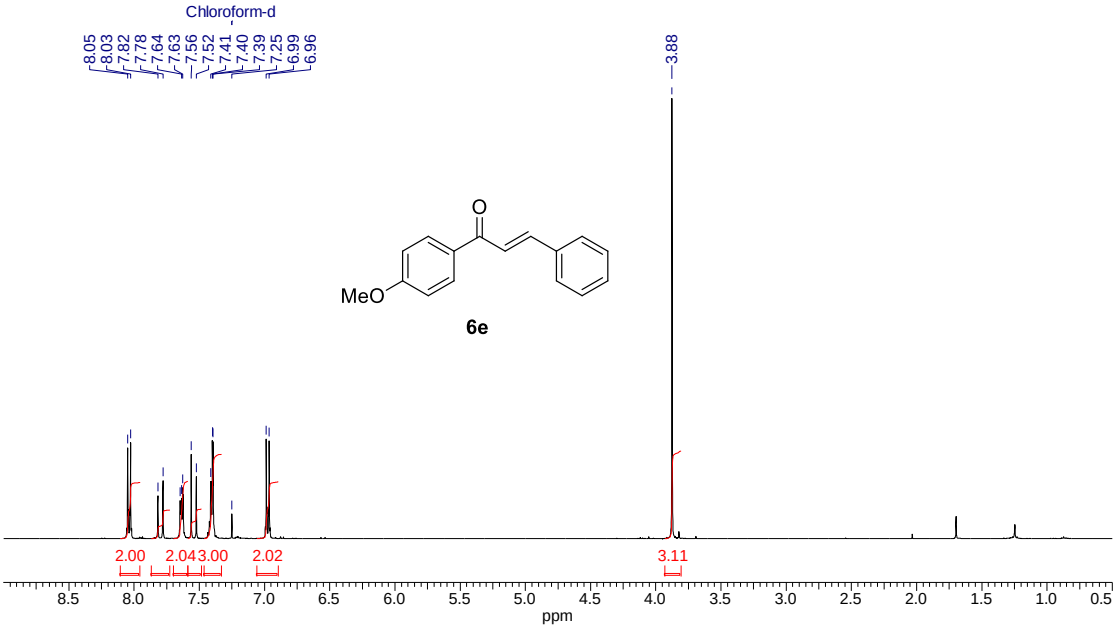

$^{13}$C NMR (100 MHz) spectrum of **6c** in $CDCl_3$



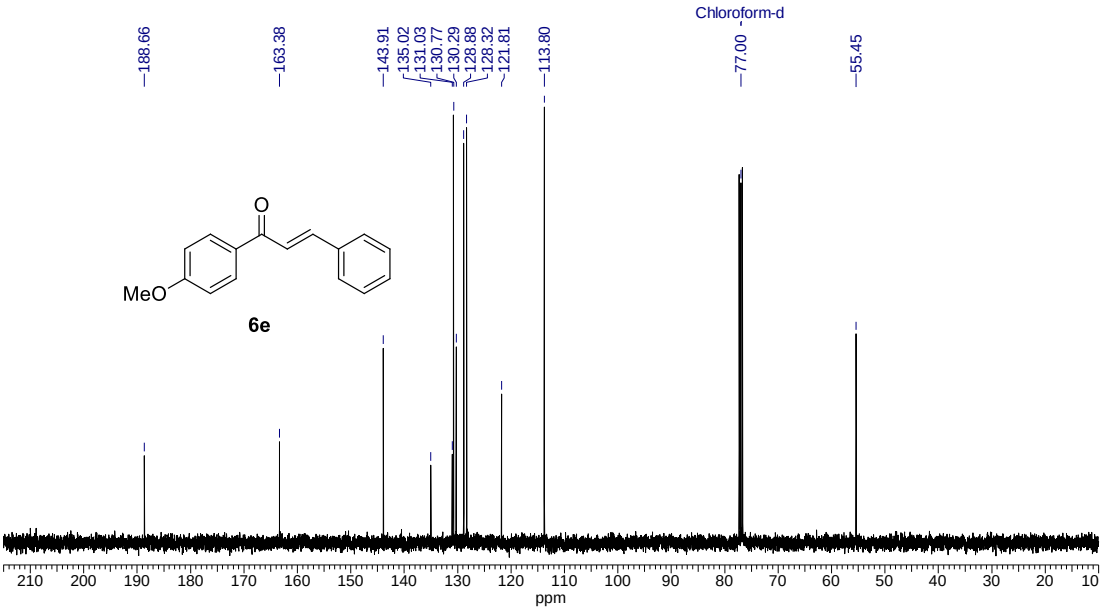

$^{1}$H NMR (400 MHz) spectrum of **6d** in $CDCl_3$




$^{13}$C NMR (100 MHz) spectrum of **6d** in $CDCl_3$




$^{1}$H NMR (400 MHz) spectrum of **6e** in $CDCl_3$




$^{13}$C NMR (100 MHz) spectrum of **6e** in $CDCl_3$

## 1.7 References and Notes

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