Bis-(dialkylamino)-cyclopropenylidene (BAC) catalyzed Conjugate Addition of Nuleophiles to *para*-Quinone Methides and Chalcones

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A dissertation submitted for the partial fulfilment of

MS degree in Science

Department of Chemical Sciences

Indian Institute of Science Education and Research Mohali

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Dedicated

To

My Parents

who have been my inspiration to lead a successful life.

Certificate of Examination

This is to certify that the dissertation titled **"Bis-(dialkylamino)-cyclopropenylidene (BAC) catalyzed Conjugate Addition of Nuleophiles to *para*-Quinone Methides and Chalcones"** submitted by Mr. Gurdeep Singh (Reg. No. MP14012) for the partial fulfilment of MS degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Declaration

The work presented in this dissertation has been carried out by me under the guidance of **Dr. R. Vijaya Anand** at the Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Acknowledgement

Without acquiring any help from others, nobody succeeds in any field. I would like to acknowledge all people, who directly or indirectly contributed to my MS thesis. I am very lucky to have **Dr. R. Vijaya Anand** as my MS thesis supervisor. In many occasions, he has given valuable suggestions that directed me towards right path and motivated me for learning new entity. His understanding about people, positive approach towards problems, his enormous conviction and intellectual ideas make him best human being. I am feeling blessed for submitting my thesis under his supervision.

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Notations and Abbreviations

cm	Centimeter
δ	Chemical shift
CDCl3	Chloroform-D
J	Coupling constant
Cy	Cyclohexyl
DCE	Dichloroethane
DCM	Dichloromethane
Et2O	Diethyl ether
DME	Dimethoxyethane
DMF	*N*,*N*'-Dimethyl formamide
DMSO	Dimethyl sulfoxide
d	Doublet
dd	Doublet of doublet
ddd	Doublet of doublet of doublet
dt	Doublet of triplets
EWG	Electron withdrawing group
°C	Degree celsius
dr	Diastereomeric ratio
EtOAc	Ethylacetate
equiv	Equivalents
FT-IR	Fourier transform infrared spectroscopy
Hz	Hertz
h	Hour(s)

i-Pr	*iso*-Propyl
m.p.	Melting point
mg	Milligram(s)
mL	Milliliter(s)
mmol	Millimole(s)
min	Minute(s)
m	Multiplet
NHC	*N*-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
Q	Quartet
R*f*	Retention factor
rt	Room temperature
s	Singlet
sept	Septet
tert	Tertiary
*t*Bu	*tert*-Butyl
TMS	Tetramethylsilane
t	Triplet
td	Triplet of doublets
tt	Triplet of triplet

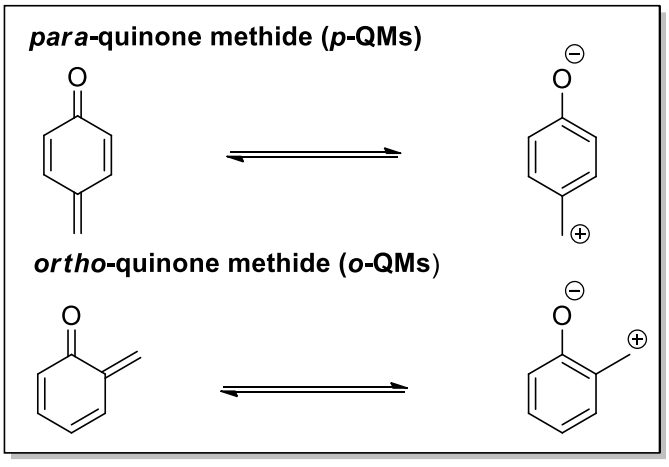
Abstract

Bis-(dialkylamino)-cyclopropenylidene (BAC) has been utilized as a Brønsted base for the conjugate addition of C-nucleophiles to *para*-quinone methides and chalcones. This transformation occurs at mild conditions and is tolerant to a variety of functional groups. This protocol provides an easy and straightforward access to a set of diaryl and triarylmethanes in good to excellent yields.

Chapter 1

1.1 General introduction to *para*-Quinone methides

The *ortho*-quinone methides (*o*-QMs) and *para*-quinone methides (*p*-QMs) are structural isomers. In these compounds, structurally, carbonyl and olefinic moieties are in conjugation, and chemically these are neutral and zwitterionic entities (scheme **1.1**). *p*-QM units widely exist in variety of natural products such as metabolites, terpenes and plant pigments.[1] Due to the intrinsic electrophilicity of benzylic carbon centre, these compound act as Michael acceptors in organic synthesis to generate new C-C and C-hetero bonds through 1,6-conjugate addition reactions.[2] The driving force for this reactivity is the aromatization of cyclohexadiene ring .



Scheme **1.1**

1.2 General Introduction on bis(dialkylamino)cyclopropenylidene (BAC)

In recent years, NHCs are dominating in organocatalysis due to their unmatched nucleophilicity[3] as well as high stability.[4] The unique reactivity of heterocyclic based carbenes for the umpolung type activation of carbonyl compound is very well known and this concept has applied in many organic transformations, especially in carbon-carbon and carbon-heteroatom bond forming reactions. Apart from umpolung activity, NHCs have been utilized as a Brønsted base in some transformations. Bis(amino)cyclopropenylidenes (BACs), are another type of nucleophilic carbenes derived from cyclopropenium salts, are found to be a non-heterocyclic based candidates in terms of reactivity towards metals as well as carbonyl compounds. The stability of these cyclopropenyidenes could be attributed to push-pull effect of the two amino subsituents that are attached to the ring and also the σ-aromaticity of the cyclopropene ring.[6] Although the synthesis and structural properties of bis(amino)cyclopropenylidene salts have been exploited a way back in 1970s by weiss and yoshida groups[7] independently, their application have been realized very recently, particularly in organometallic chemistry. [8] Fig. **1.1** illustrates the general structures of *N*-heterocyclic carbene (**1a)** and bis(amino)cyclopropenylidene (**1b)**.

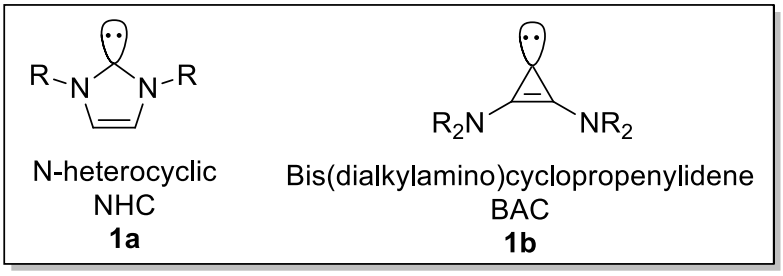


Figure 1.1

1.3 Literature reports on BAC

Bertrand and co-workers demonstrated the first isolation of bis(diisopropylamino)cyclopropenylidene (**2a**).[9] This particular BAC (**2a**) was found to be highly air-senstive. BAC **2a** was thoroughly characterized by NMR techniques and X-ray analysis. The structral comparison between BAC (**2a**) and NHC (**2b**) is shown in Fig. **1.2**

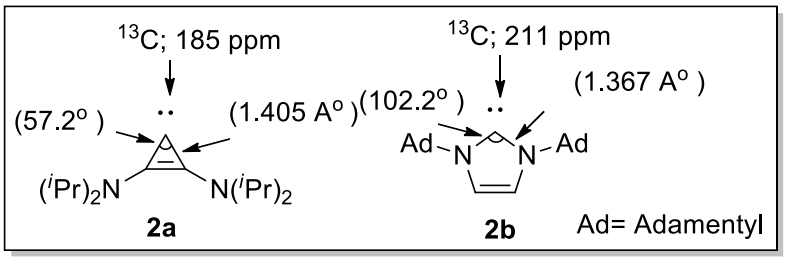
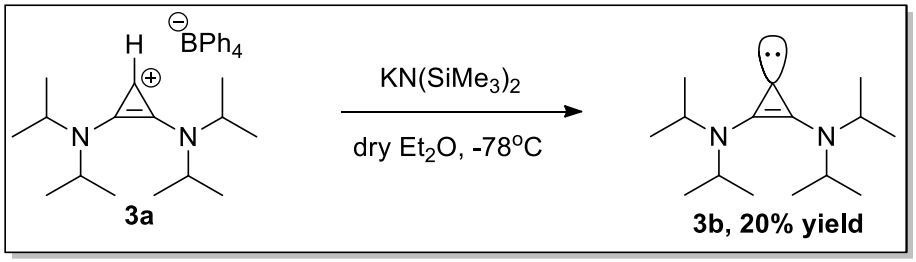


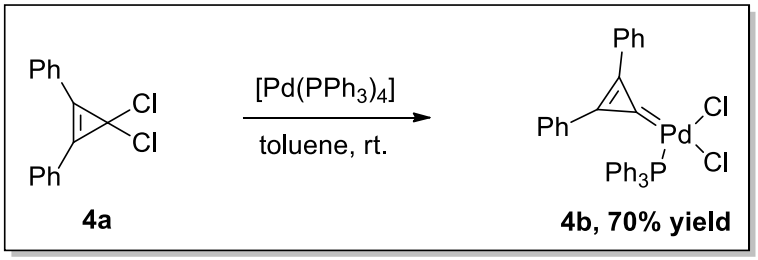
Figure 1.2

Bis(diisopropylamino)cyclopropenylidenecarbene (**3b**) was isolated in 20% yield when bis(diisopropylamino)cyclopropnylidenetetraphenylborate salt (**3a**) was treated with same equivalent of $KN(SiMe_3)_2$ in dry diethyl ether at -78 °C (Scheme **1.2**) .



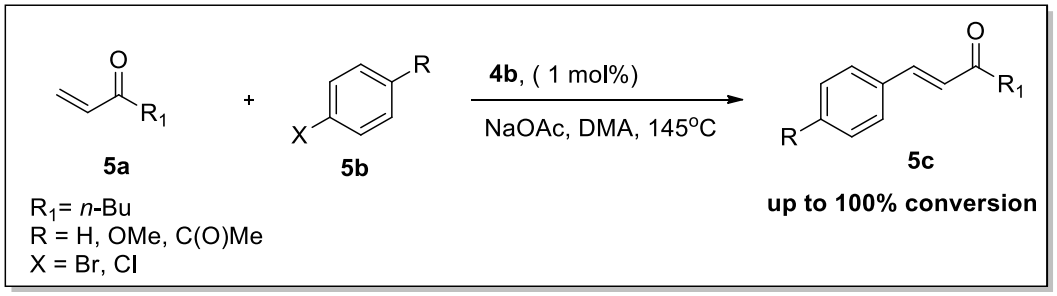
Scheme 1.2

After the successful isolation of BAC, several reports appeared in the literature on the application of BAC as a ligand in organometallic chemistry. Wass and co-wokers reported the synthesis of 2,3-diphenylcyclopropenylidene supported palladium complex (**4b),** and its application in Heck and Suzuki coupling reactions.[10] This Pd complex was easily prepared by the reaction of 1,1-dichloro-2,3-diphenylcyclopropene (**4a**) and $[Pd(PPh_3)_4]$ in toluene at room temperature (Scheme **1.3**) .



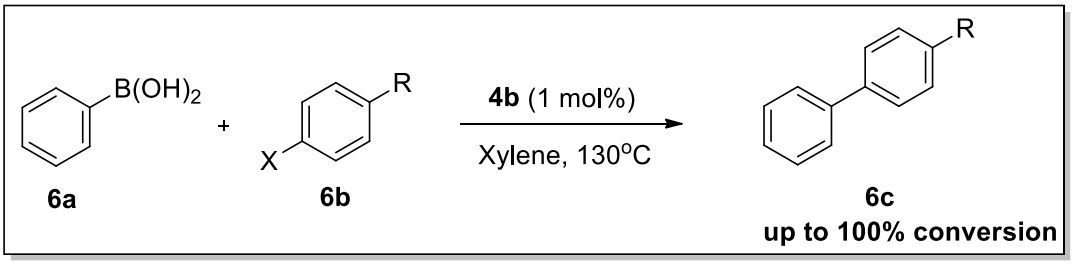
Scheme 1.3

The catalytic activity of Pd-BAC complex (**4b**) was evaluated in Heck coupling reaction of *n*-butyl acrylate (**5a**) with various aryl halides (**5b**) in the presence of NaOAc at high temperature (145 °C), and desired Heck products (**5c**) were obtained in good yields (scheme **1.4**) .



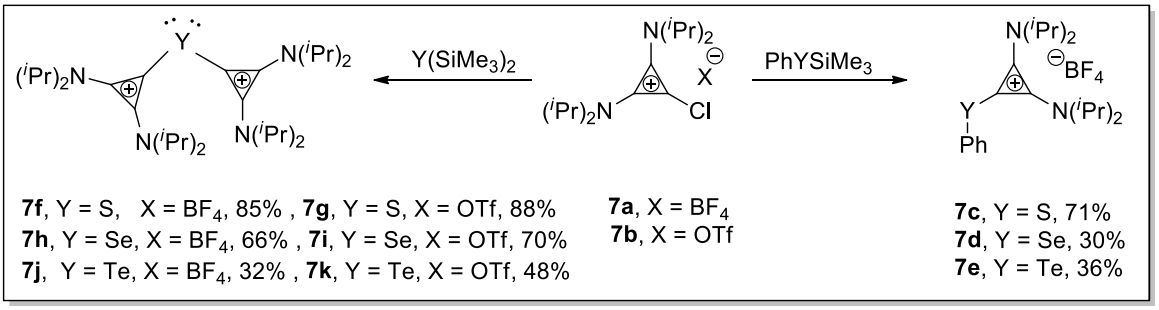
Scheme 1.4

The catalytic activity of Pd-BAC complex (**4b**) was also observed in Suzuki coupling reaction of phenyl boronic acid (**6a**) with aryl halides (**6b**) in the presence base K_2CO_3 at high temperature (130 °C) (scheme **1.5**) .



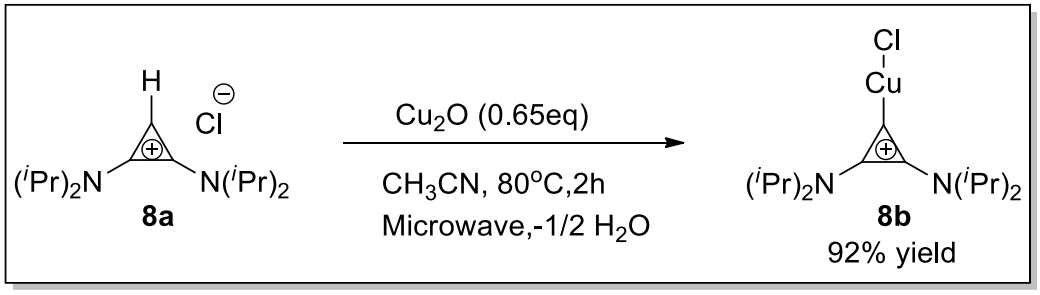
Scheme 1.5

Recently, Alcarazo and co-workers reported the synthesis and structural characterization of cyclopropenylidene stabilized S(II), Se (II), Te(II) mono (**7c-7e**) and dications (**7f-7k**), by gentle heating of suspension containing 1-chloro-2,3-bis(diisopropylamino)cyclopropenium salts (**7a** or **7b**) with $PhYMe_3$ and $Y(SiMe_3)_2$ (Y = S, Se, Te) respectively (Scheme **1.6**) .[11]



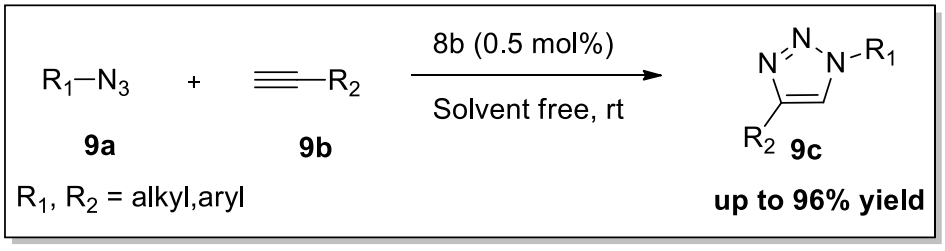
Scheme 1.6

Cazin and co-workers reported the first example of CuCl(BAC) (**8b**) complex.[12] The BAC-Cu^I complex (**8b**) was obtained by the reaction of cyclopropenium chloride (**8a**) with Cu_2O in MeCN under microwave heating (80 °C) (Scheme **1.7**) .



Scheme 1.7

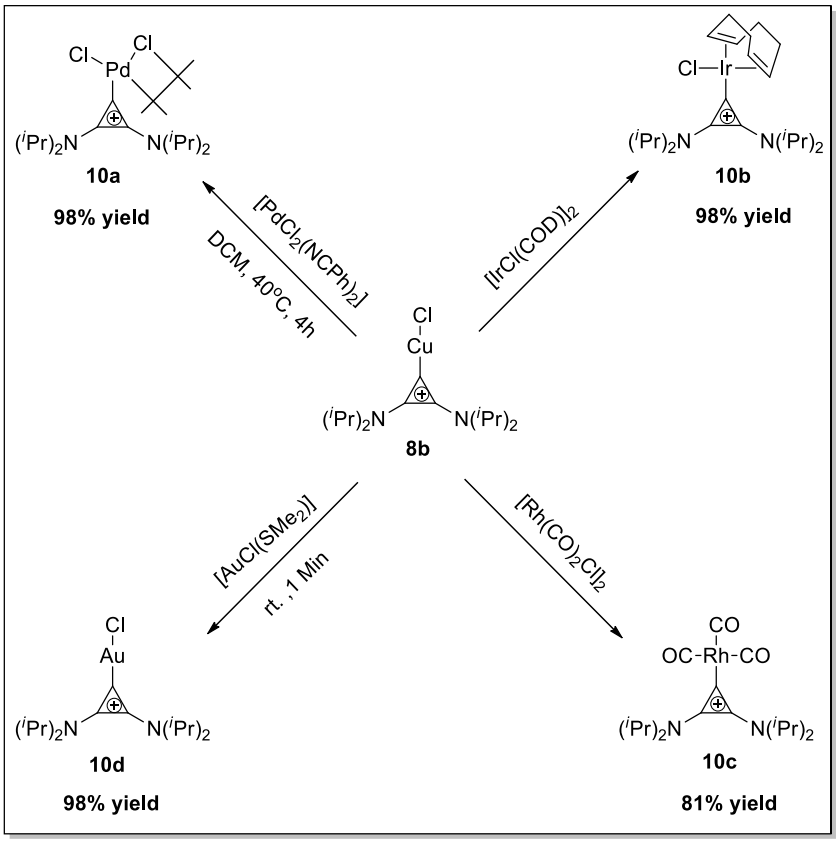
This complex (**8b**) has been used as a catalyst in the formation of 1,2,3-triazole (**9c**) *via*



Scheme 1.8

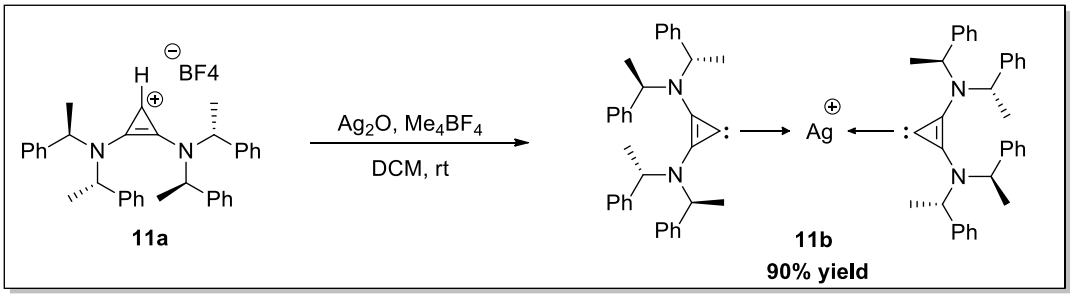
[3+2]-cycloaddition of azides with alkynes. A variety of 1,2,3-triazole derivatives were prepared from various azides (**9a**) and alkynes (**9b**) using catalytic amount of BAC-Cu^{I} complex under solvent free condition (Scheme **1.8**) .

This complex has also been used for the synthesis of other metal-cyclopropenylidene complexes such as Au, Pd, Ir, and Rh-BAC complexes (**10a**-**10d**) *via* transmetallation reaction (scheme **1.9**) .



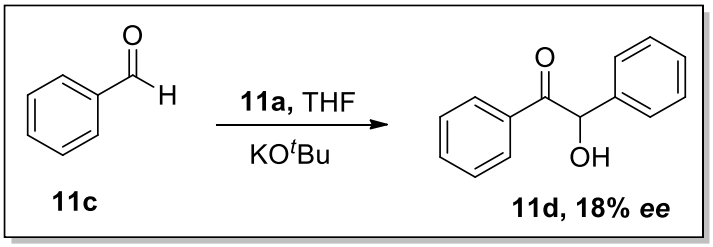
Scheme 1.9

Tamm and co-workers reported the synthesis and isolation of chiral bis[bis(R-1-phenyl)amino]cyclopropenylidene and its dicarbene complex with Ag (**11b**). This complex was synthesized by the reaction of chiral cyclopropenylium salt (**11a**) with Ag_2O in the presence of catalytic amount of Me_4BF_4 in DCM (Scheme **1.10**)[13].



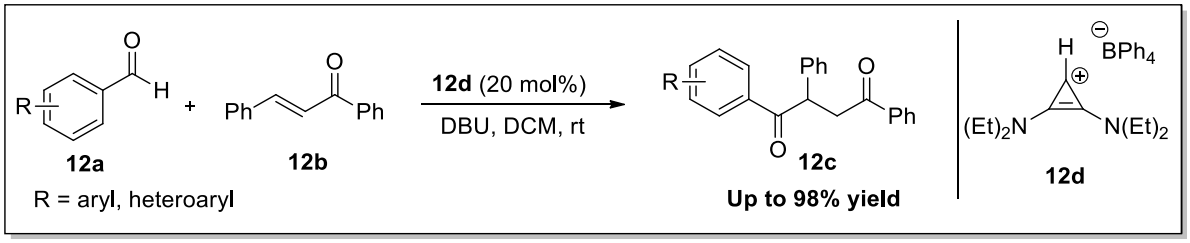
Scheme 1.10

.This chiral catalyst (**11a**) has also been used as an organocatalyst in an enantioselective benzoin reaction. However, the product was obtained only in 18% *ee* (Scheme **1.11**). It was speculated that the low enantioselectivity of product was due to rapid rotation of chiral amino groups.



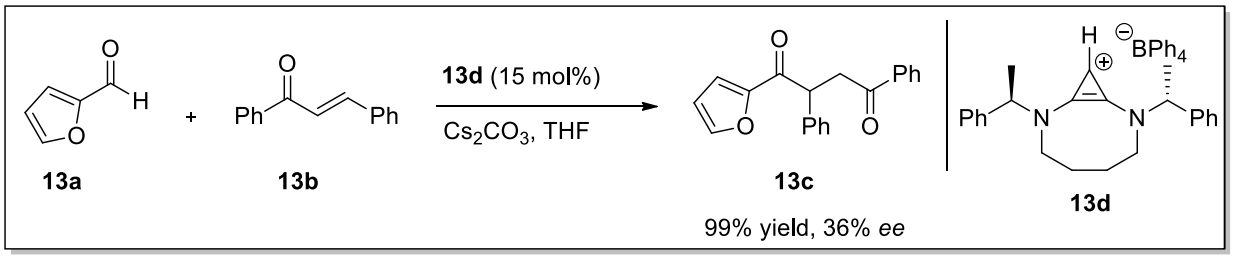
Scheme 1.11

Gravel and co-workers described a highly chemo-selective intermolecular Stetter reaction with bis(amino)cyclopropenylidene salt (**12d**) as a precatalyst.[14] In this reaction, benzoin product was not observed during the course of reaction, which was contradictory to the reactions using thiazolium and triazolium salts as precatalyst (Scheme **1.12**) .



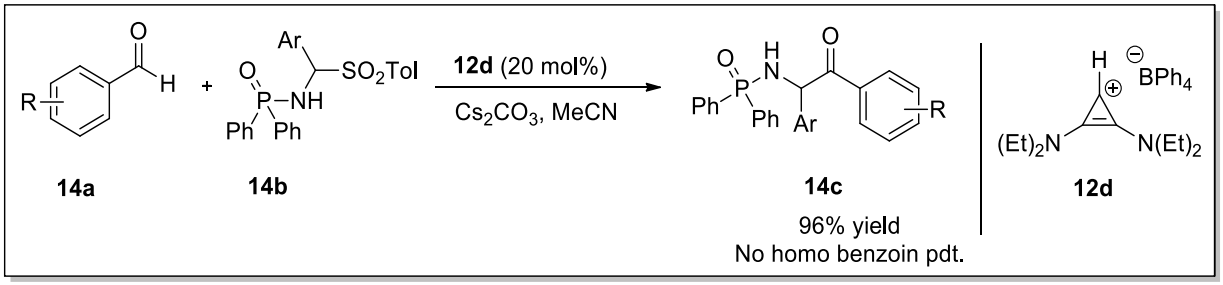
Scheme 1.12

Same group also reported an enantioselective Stetter reaction between furfural (**13a**) and chalcone (**13b**) using a chiral BAC precursor (**13d**). Although the yield of the Stetter reaction was excellent, the enatioselectivity of the product was low (36%) (Scheme **1.13**) .



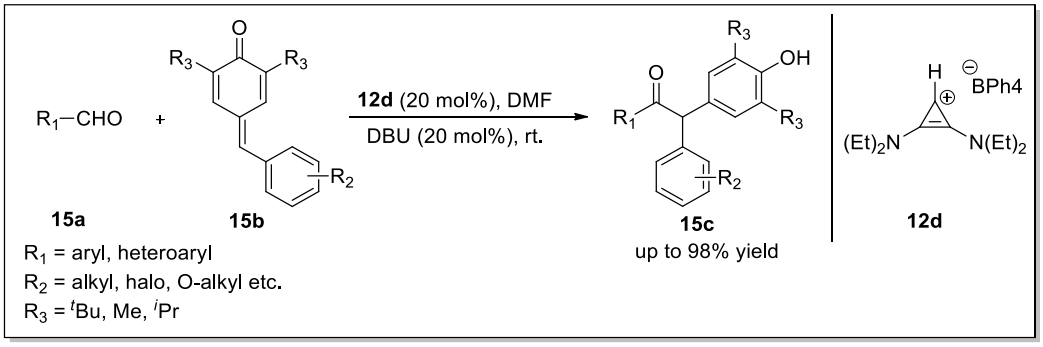
Scheme 1.13

Gravel and co-workers also demonstrated a highly chemoselective aza-benzoin reaction between aldehydes and imines using bis(amino)cyclopropenylidene as a catalyst.[15] In this method, a variety of aldehydes (**14a**) and phosphinoyl imines (**14b**) were treated using **12d** as a precatalyst. No homobenzoin product was observed during the reaction (Scheme **1.14**) .



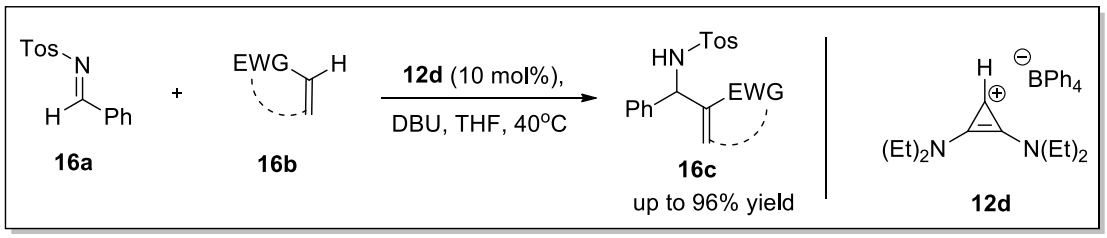
Scheme 1.14

Very recently, our research group described the synthesis of *α,α′*-diarylated ketones(**15c**) using bis(amino)cyclopropenylidene salt (**12d**) as a precatalyst.[16] A variety of aromatic as well as hetero-aromatic aldehydes (**15a**) were treated with various *para*-quinone methides (**15b**) using a catalytic amount of BAC (**12d**) under mild conditions, and the corresponding products (**15c**) obtained in moderate to excellent yield (Scheme **1.15**) .



Scheme 1.15

Recently, Schneider and co-workers reported BAC catalyzed Aza-Mortia-Baylis-Hillman reactions between aromatic, heteroaromatic or aliphatic imines (**16a**) and acyclic or cyclic α,β-unsaturated ketones and carboxyclic acid derivatives (**16b**).[17] Interestingly, the important functionalities such as unprotected amino and hydroxy groups were tolerated under the reaction conditions (Scheme **1.16**).

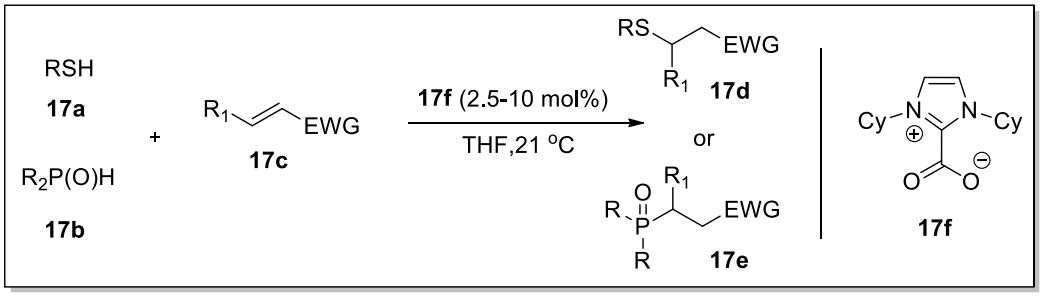


Scheme 1.16

Chapter 2

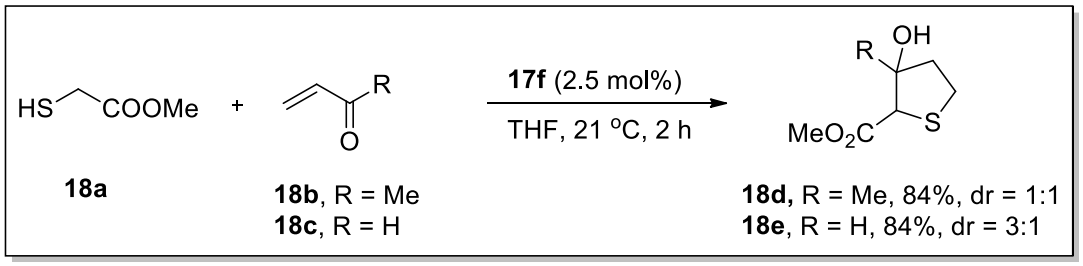
Results and discussion

Recently, Coquerel and co-wokers described the *N*-heterocyclic carbene catalyzed carba-, sulfa, and phospha- Micheal additions.[5] This NHC-catalyzed Michael additions are among the most effective methods to synthesize organo-sulfur (**17d**) and organo-phosphorus compounds (**17e**). In this type of reactions, NHC is actually acting as a Brønsted base (Scheme **2.17**) .



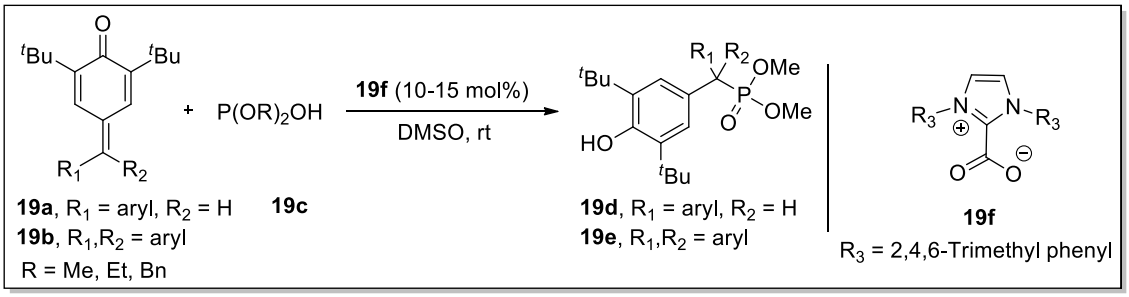
Scheme 2.17

The same group also reported the synthesis of tetrahydrothiophenes (**18d**) by NHC-catalyzed sulfa-Michael-initiated organocascade reaction (Scheme **2.18**) .



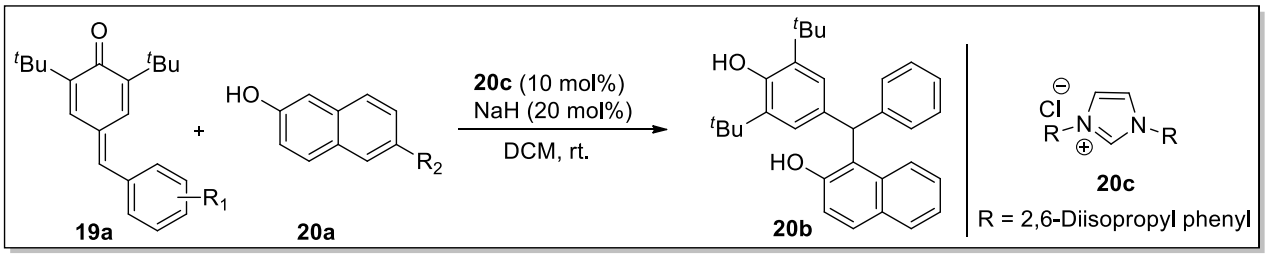
Scheme **2.18**

Recently, our research group described the synthesis of unsymmetrical diaryl- and triarylmethylphosphonates using NHC as a Brønsted base catalyst.[18] The synthesis of diaryl and triarylmethylphosphonates were achieved by the reaction of dialkylphosphites to *p*-QMs (**19a)** and fuchsones (**19b**) through a 1,6-conjugate addition of dialkylphosphites (**19c**) (Scheme **2.19**) .



Scheme **2.19**

Our group also reported the synthesis of unsymmetrical triarylmethanes (**20b**) by activating the 2-naphthol (**20a**) using NHC as a Brønsted base catalyst (**20c**).[19] Triarylmethanes (**20b**) were obtained in good to excellent yields through 1,6-conjugate addition of 2-naphthol to *p*-QMs (**19a**) (Scheme **2.20**).

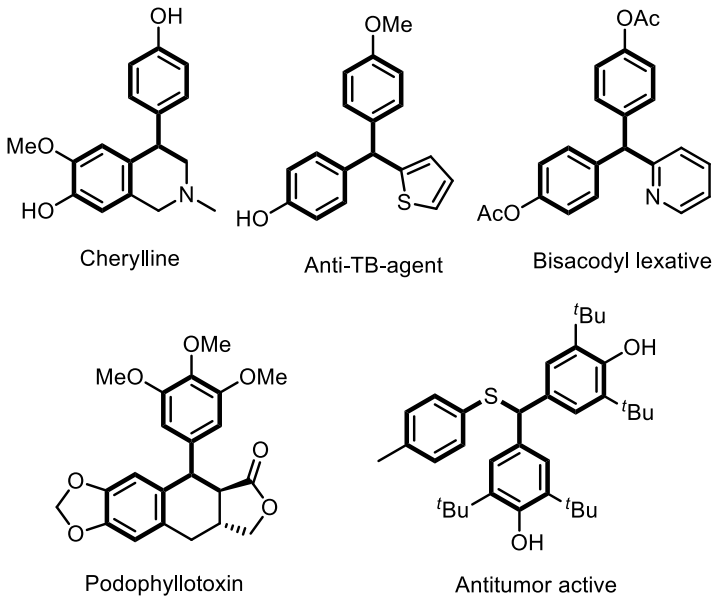


Scheme **2.20**

Although there are many reports available in the literature for the application of NHC as a Brønsted base, BAC has not been utilized as a Brønsted base so far. Here in, we disclose a BAC catalyzed conjugate addition of malonate to *p*-QMs and chalcones. To the best of our knowledge, this conjugate addition catalyzed by BAC is not reported in the literature, which prompted to investigate this reaction.

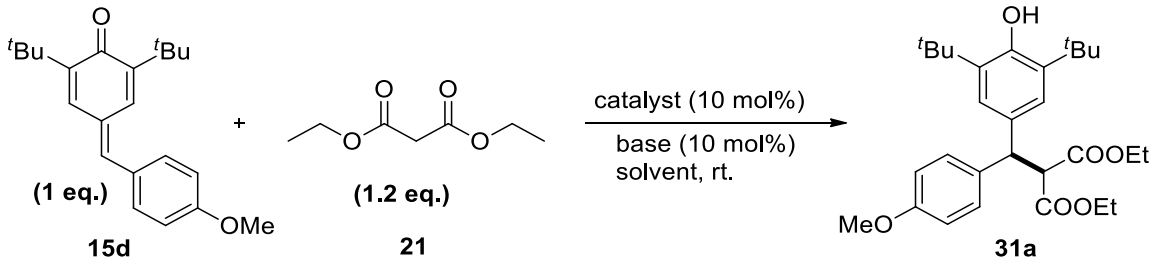
Diaryl and triarylmethanes are very important not only in the dye industries but also in medicinal chemistry and drug discovery. These have emerged as one of the essential architectural motifs, often found in many pharmaceuticals and biologically active natural molecules (Fig. **2.1)**. Some of their analogues exhibit interesting therapeutic activities such as anti-TB, anti-malarial and anti-tumour activities.[20]

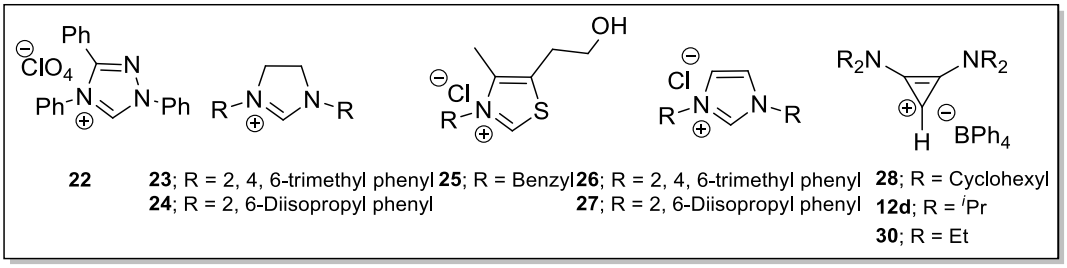
Figure 2.1 Biologically active compounds



Optimization studies were carried out using *para*-quinone methide (**15d**) and diethyl malonate (**21**) using a wide range of bis(dialkylamino)cyclopropenylidene (BAC) and *N*-heterocycle (NHC) salts as pre-catalysts under various conditions. A base is required for this reaction to generate active carbene catalyst.

Table 2.1 Catalyst screen and optimization[a].





Entry	Catalyst	Base	Solvent	Time [h]	Yield [%]
1	22	Cs_2CO_3	THF	5	50
2	23	$Cs2CO_3$	THF	5	54
3	24	Cs_2CO_3	THF	5	57
4	25	Cs_2CO_3	THF	5	61
5	26	Cs_2CO_3	THF	4	63
6	27	Cs_2CO_3	THF	4	65
7	28	Cs_2CO_3	THF	1	75
8	**12d**	**Cs_2CO_3**	**THF**	**1**	**94**
9	30	Cs_2CO_3	THF	1	77
10	29	K_2CO_3	THF	1	81
11	29	Cs_2CO_3	DCM	2	79
12	29	Cs_2CO_3	Et_2O	2	72
13	29	Cs_2CO_3	DCE	2	75
14	29	Cs_2CO_3	DMSO	1.5	77
15	-	Cs_2CO_3	THF	8	7

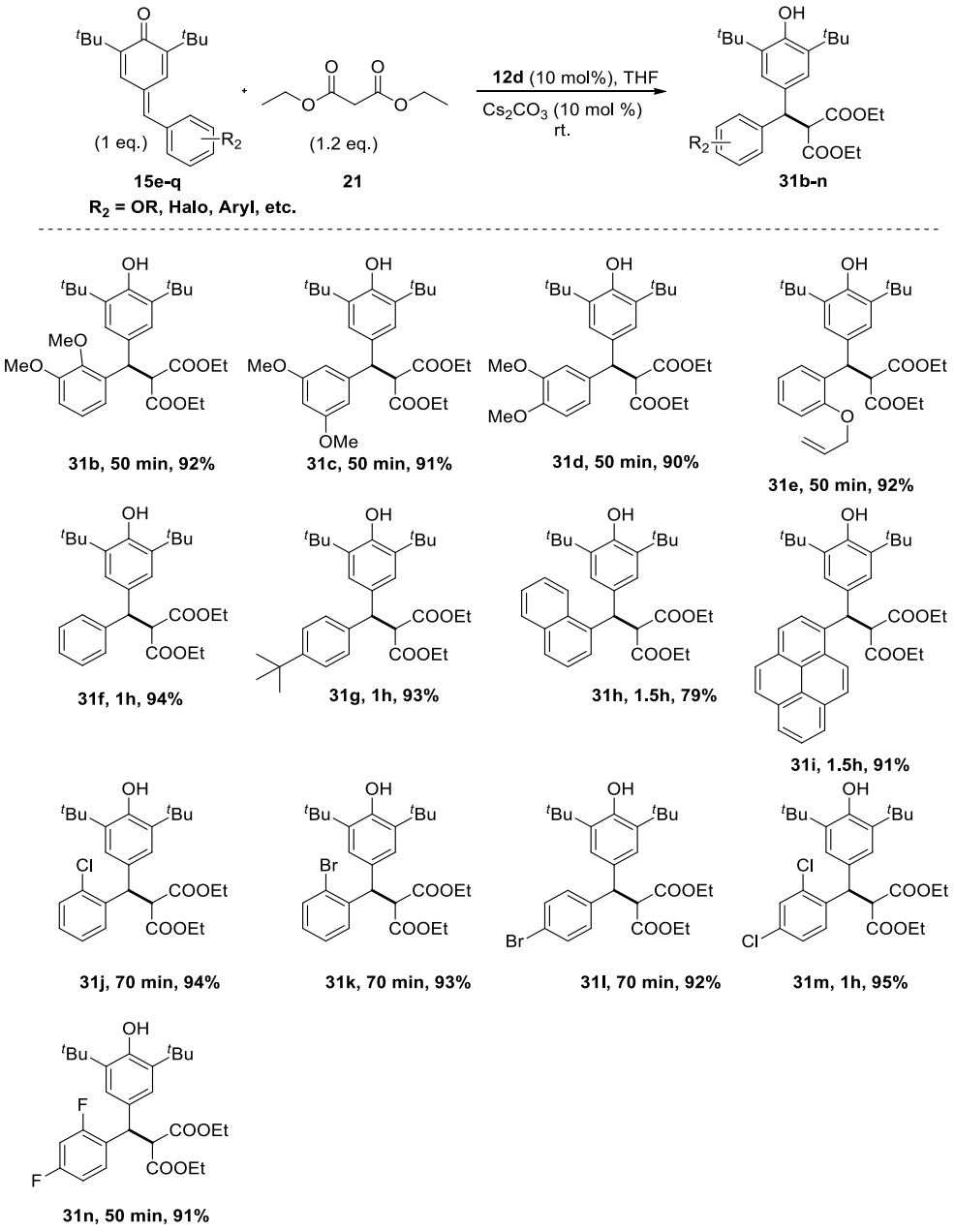
[a] Reaction Conditions: All reactions were carried out with **15b** (0.062 mmol), **17** (0.074 mmol) in solvent (1 ml). Isolated yield is reported.

The results of optimization studies are shown in Table **2.1**. Surprisingly, our initial attempt itself using the triazolium (**22**) based NHC pre-catalyst and Cs_2CO_3 as a base in THF, gave positive result within 5 h, however, the yield of the isolated product **31a** was very low (entry **1**). Changing the NHC based pre-catalysts (**23-27**) improved the yield of product up to 65% (entries **2-6**). Interestingly, when **28** was used as a precatalyst in THF, product (**31a**) was obtained in 75% yield in 1h (entry **7**). Encouraged by this result, further optimization studies were carried out using other BAC pre-catalyst (**12d**) in THF. In this case, the expected product **31a** was isolated in 94% yield within 1 h (entry **8**). Further screening was performed in variety of solvents (entries **11-14**), but yield of product was found to be inferior.

In the absence of BAC pre-catalyst, only 7% of expected product **31a** was isolated (entry **15**), which clearly indicates that BAC is actually acting as a catalyst for this transformation.

With the optimized conditions in hand, the scope of reaction was investigated with a variety of *p*-QMs and active methylene compounds. The results are summarized in Table **2.2** and **2.3**. It is evident from Table **2.2** that irrespective of the electronic nature of the aryl group present in *p*-QMs, the required products were obtained in excellent yield within a short reaction time. This methodology worked very well in the cases of *p*-QMs (**15e-h**) derived from electron rich aldehydes and in all those cases the desired product (**31b-e**) was obtained in excellent yields (90-92%). In the cases of *p*-QMs derived from a simple benzaldehyde (**15i**) and 4-*tert*-butyl substituted benzaldehyde (**15j**), the corresponding products (**31f & 31g**) were obtained in 94% and 93% yield respectively. Surprisingly, the *p*-QMs derived from aryl-fused benzaldehydes **15k**, gave less yield (77%), but the *p*-QM derived from pyrenecarboxaldehyde **15l** gave excellent yield of the desired product **31i** (91%). The *p*-QMs (**15m–q**) derived from halo-substituted benzaldehydes also underwent smooth conversion to their respective products (**31j–n**) in very high yields (91-95%).

Table 2.2 Substrate scope with different *para*-quinone methides[a].

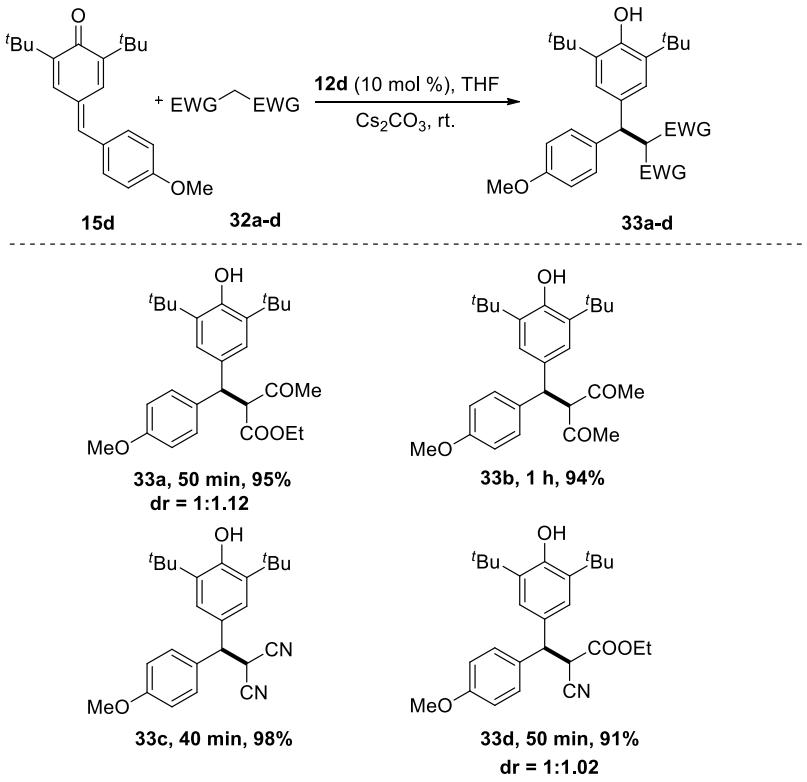


[a]Reactions conditions: All reactions were carried out with 20 mg scale of **15e-q** in 1ml of THF. Yields reported are isolated yields.

Then, we turned our attention to the scope of different carbon nucleophiles under same reaction conditions and the results are summarized in Table **2.3**. This methodology worked very well with different carbon nucleophiles and the desired products (**33a-d**) were obtained

within short reaction time. Reaction of **15d** with malononitrile provided the desired product **33c** in 98% yield in 40 min.

Table 2.3 Substrate scope with different carbon nucleophiles[a]

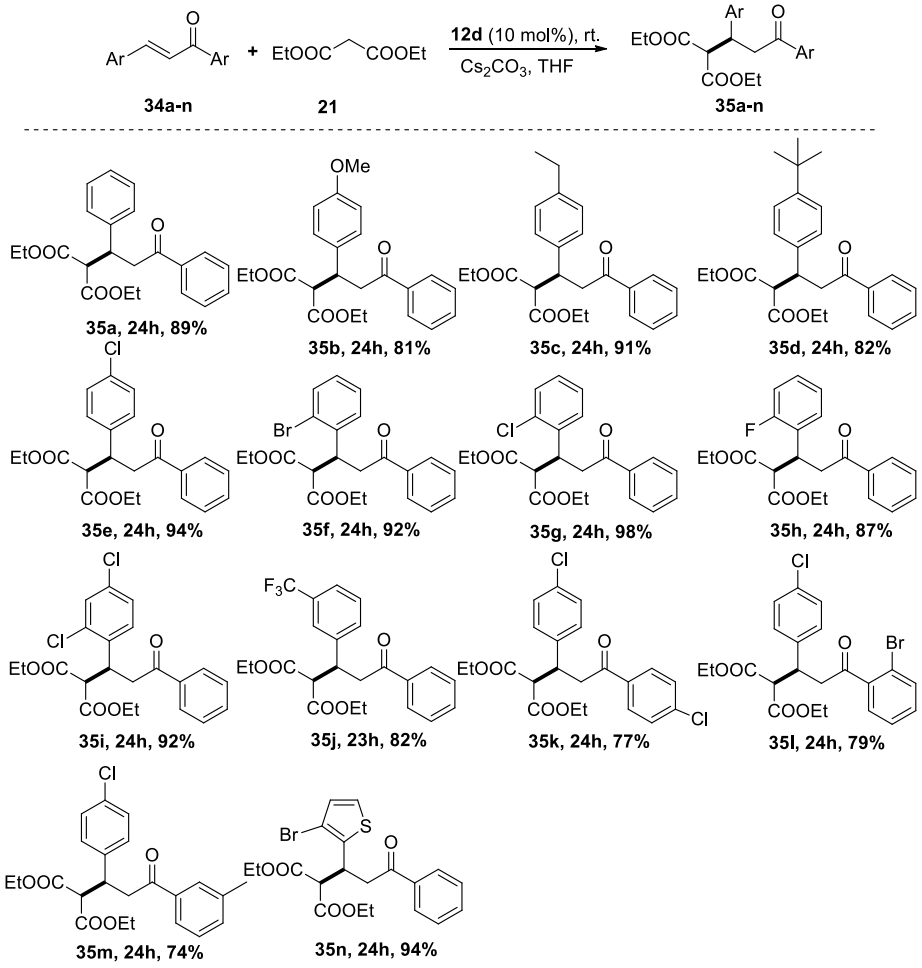


[a]Reactions conditions: All reactions were carried out with 20 mg scale of **15d** in 1ml of THF. Yields reported are isolated yields.

This methodology was also extended for the 1,4-conjugate addition of malonates to enone systems (**8**). The reaction was carried out with a variety of substituted chalcones (Table **2.4**) and in all these, the yield of the isolated products were good to excellent. It is evident from Table **2.4** that the chalcone derived from a simple benzaldehyde (**34a**) and 4-substituted benzaldehydes (**34b-d**), the corresponding products (**35a**) and (**35b-d**) were obtained in 81-91% isolated yields. In the case of chalcones derived from substituted halo-benzaldehydes (**34e-i**) also underwent smooth conversion to their respective products (**35e-i**) in very good yield (85-98%). The generality of this method was also examined with chalcone derived from electron-poor aromatic aldehydes such as 3-triflouromethyl benzaldehyde (**34j**) and in

this case, the corresponding product **34j** was obtained in 81% yield. The chalcones (**34k-m**) derived from different substituted acetophenone also giving good yield of isolated products (**35k-m**). The chalcone (**34n**) derived from heterocycle benzaldehyde was gave very good yield (94%) under the same reaction conditions.

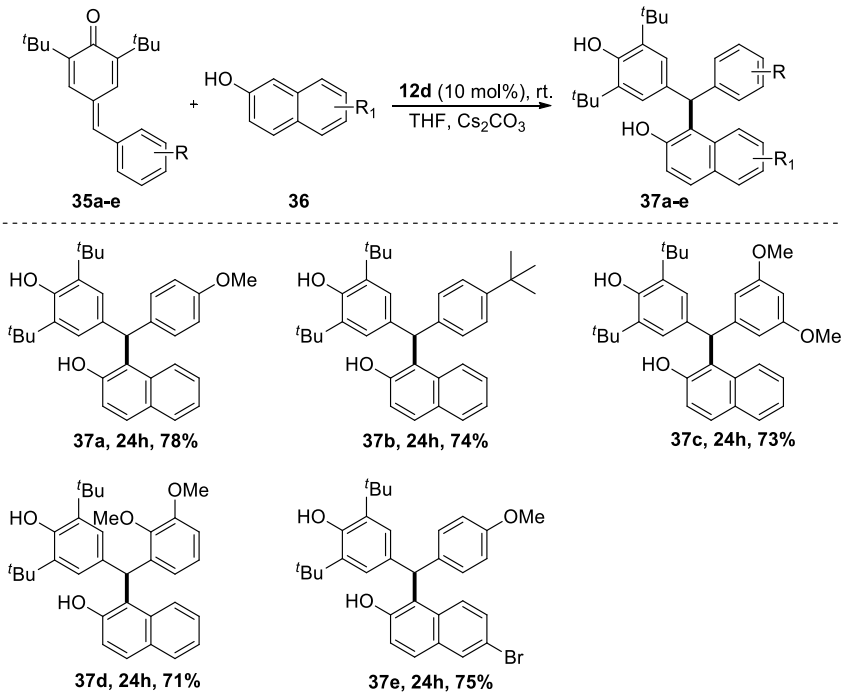
Table 2.4 Substrate scope of BAC-catalyzed malonate-Micheal adducts[a]



[a]Reactions conditions: All reactions were carried out with 20 mg scale of **34a-n** in 1ml of THF. Yields reported are isolated yields.

We also elaborated this methodology for 1,6-conjugate addition of 2-naphthol to *p*-QMs. From Table **2.5**, it was evident that, steric effects of the aryl substituents in *p*-QMs were found to have minimal influence in the reaction. All the *p*-QMs underwent smooth conversion to their corresponding triarylmethanes (**37a-e**) in good yields.

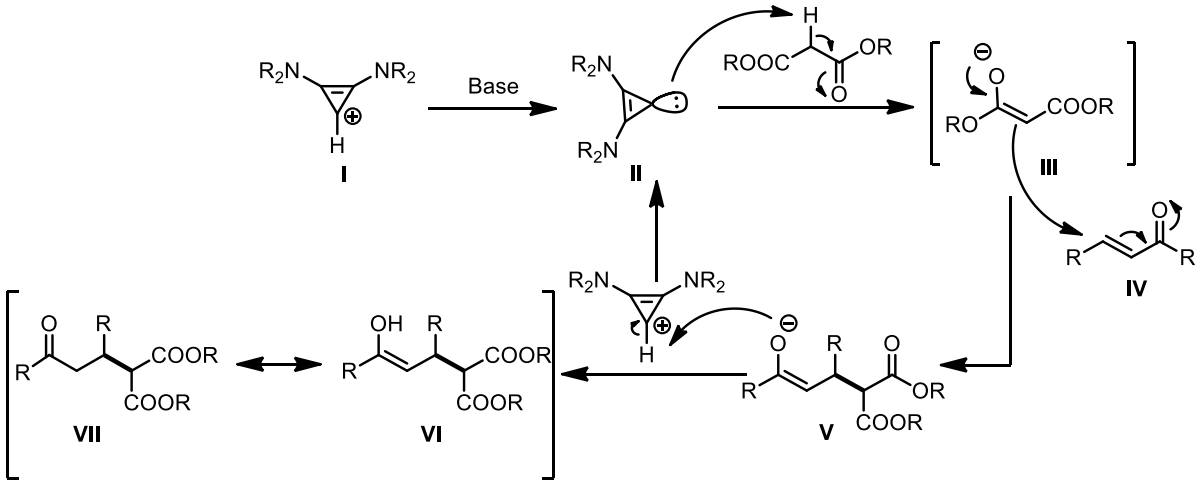
Table 2.5 Substrate scope of BAC-catalyzed 2-Naphthol addition to *para*-quinone methides[a]



[a]Reaction conditions: All reactions were carried out with 20 mg scale of **35a-e** in 1ml of THF. Yields reported are isolated yield.

Based on the outcome of the reaction, we proposed a plausible mechanism for this transformation (Scheme **2.21**). Initially, the base abstracts the proton of BAC salt (**I**) to generate free BAC (**II**), which abstracts the acidic proton of the malonate and generates an enolate anion and BAC salt (**III**). The enolate anion then immediately reacts with enone or dienone (**IV**) to generate intermediate (**V**), which then abstracts the acidic proton of the BAC salt (**I**) to produce the enol (**VI**) with regeneration of free BAC (**II**). Then the enol (**VI**) immediately tautomerise to the product (**VII**).

Plausible Mechanism:



Scheme **2.21**

Chapter 3

Experimental Section

3.1 *General methods*

All reactions were carried out under an argon atmosphere in an oven dried vial. Solvents were dried over calcium hydride and was used without further distillation. Melting points were recorded on SMP20 melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F spectra were recorded in $CDCl_3$ (400, 100 and 376 MHz respectively) on Bruker FT - NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS (for ^{1}H and ^{13}C) and coupling constant (*J*) are reported in Hz . FT-IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Most of the reagents and starting materials were purchased from commercial sources and used as such. All *p*-quinone methides were prepared by following a literature procedure[21] and also chalcones by following the literature procedure.[22] BAC precursors were prepared according to the literature procedure.[9] Thin layer chromatography was performed on Merck silica gel 60 F254 TLC pellets and visualized by UV irradiation, $KMnO_4$ stain. Column chromatography was carried out through silica gel (100–200 mesh) using EtOAc/hexane as an eluent.

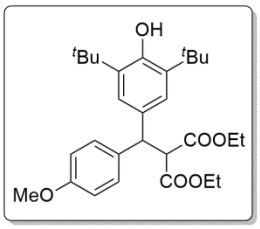
3.2 *General procedure for the conjugate addition of nucleophiles to p–quinone methides and chalcones :*

Anhydrous THF (1.0 mL) was added to the mixture of *p*-quinone methide or chalcones (20 mg), catalyst **12d** (10 mol%) and Cs_2CO_3 (10 mol%) under argon atmosphere, and the resulting suspension was stirred at room temperature until *p*-quinone methide or chalcone

was completely consumed. The reaction mixture was concentrated under reduced pressure and purified through silica gel column without further workup, using EtOAc/Hexane mixture as an eluent to get the pure product.

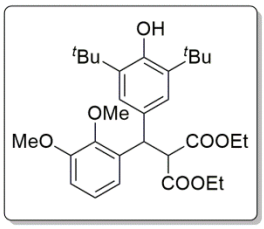
3.3 *Supporting Information*

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)malonate (31a)



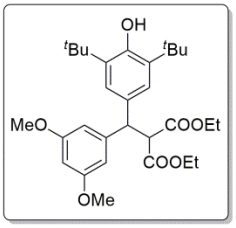
The reaction was performed at 0.062mmol scale of *p*-quinone methide**(15d)**; R_f = 0.5 (10% EtOAc in hexane); pale yellow gummy solid (28.1 mg, 94% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 7.05 (s, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.03 (s, 1H), 4.59 (d, J = 12.2 Hz, 1H), 4.22 (d, J = 12.2 Hz, 1H), 4.04 – 3.92 (m, 4H), 3.75 (s, 3H), 1.38 (s, 18H), 1.04 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 158.3, 152.6, 135.7, 132.1, 134.3, 128.9, 124.4, 114.0, 61.5, 61.4, 58.5, 55.3, 50.8, 34.4, 30.4, 14.0, 13.9; FT-IR (thin film, neat): 3442, 2958, 1758, 1732, 1612, 1513, 1436, 1303, 1250, 1179, 1036, 838, 637 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,3-dimethoxyphenyl)methyl)malonate (31b)



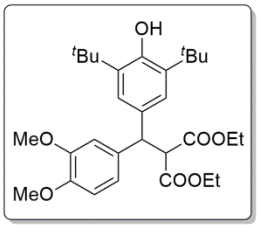
The reaction was performed at 0.0565 mmol scale of *p*-quinone methide**(15e)**; R_f = 0.5 (20% EtOAc in hexane); brown solid (26.7 mg, 92% yield); m. p. = 100 – 104 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.01 – 6.94 (m, 2H), 6.75 (d, J = 7.8 Hz, 1H), 5.07 (d, J = 12.5 Hz, 1H), 4.99 (s, 1H), 4.35 (d, J = 12.5 Hz, 1H), 3.98 (dq, J = 18.4, 7.1 Hz, 4H), 3.80 (s, 3H), 3.74 (s, 3H), 1.37 (s, 18H), 1.03 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.0, 153.1, 152.4, 147.0, 136.2, 135.4, 131.6, 125.0, 123.8, 119.0, 110.9, 61.4, 61.3, 60.4, 57.4, 55.7, 44.6, 34.4, 30.4, 13.93, 13.90; FT-IR (thin film, neat): 3417, 2959, 1758, 1732, 1586, 1479, 1435, 1368, 1274, 1155, 1094, 1037, 862, 746 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl)malonate (31c)



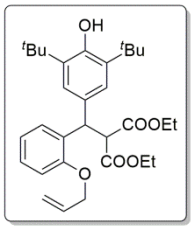
The reaction was performed at 0.0564 mmol scale of *p*-quinone methide **(15f)**; R_f = 0.5 (20% EtOAc in hexane); pale yellow solid (26.4 mg, 91% yield); m. p. = 110-114 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 6.66 (s, 2H), 6.45 (s, 1H), 5.23 (s, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.41 (d, *J* = 12.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.93 (s, 6H), 1.57 (s, 18H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.96, 167.92, 160.8, 152.8, 144.4, 135.8, 131.4, 124.5, 125.0, 106.1, 98.7, 61.6, 61.4, 58.2, 55.4, 51.7, 34.5, 30.4, 14.00, 13.9; FT-IR (thin film, neat): 3616, 3443, 2959, 1758, 1732, 1597, 1463, 1435, 1368, 1204, 1156, 1065, 1036, 847, 698 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dimethoxyphenyl)methyl)malonate (31d)



The reaction was performed at 0.0564 mmol scale of *p*-quinone methide **(15g)**; R_f = 0.5 (20% EtOAc in hexane); orange gummy solid (26.1 mg, 90% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 6.86 (d, *J* = 12.5 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.04 (s, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.21 (d, *J* = 12.1 Hz, 1H), 4.04 – 3.93 (m, 4H), 3.85 (s, 3H), 3.82 (s, 3H), 1.39 (s, 18H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.01, 168.03, 152.7, 148.8, 147.8, 135.8, 134.7, 131.9, 124.5, 119.8, 111.4, 111.3, 61.5, 61.4, 58.7, 56.0, 55.9, 51.2, 34.5, 30.4, 14.0, 13.9; FT-IR (thin film, neat): 3458, 2959, 1758, 1732, 1592, 1515, 1464, 1436, 1367, 1262, 1143, 1030, 858, 663 cm^{-1} .

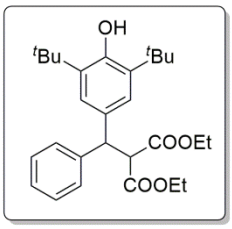
Diethyl 2-((3-(allyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)malonate (31e)



The reaction was performed at 0.0571 mmol scale of *p*-quinone methide **(15h)**; R_f = 0.5 (20% EtOAc in hexane); pale yellow gummy solid (26.8 mg, 92% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 1H), 7.13 (s, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* =

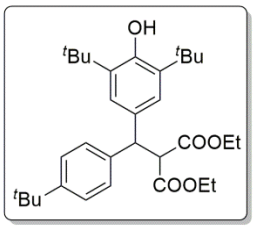
8.2 Hz, 1H), 6.08-5.99 (m, 1H), 5.37 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.06 (d, *J* = 12.5 Hz, 1H), 4.99 (s, 1H), 4.56 (dd, *J* = 12.9, 4.7 Hz, 1H), 4.51 (d, *J* = 4.4 Hz, 1H), 4.48 (s, 1H), 4.05 – 3.93 (m, 4H), 1.37 (s, 18H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.1, 156.0, 152.4, 135.3, 133.6, 131.5, 130.9, 127.67, 127.60, 125.1, 120.7, 117.3, 112.3, 69.0, 61.31, 61.27, 56.9, 45.4, 34.4, 30.4, 13.9; FT-IR (thin film, neat): 3638, 3446, 2959, 1758, 1732, 1599, 1492, 1436, 1368, 1242, 1120, 1035, 929, 868, 752, 645 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)malonate (31f)



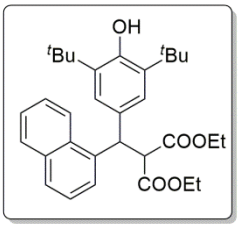
The reaction was performed at 0.0679 mmol scale of *p*-quinone methide**(15i)**; R_f = 0.5 (10% EtOAc in hexane); white solid (29.02 mg, 94% yield); m. p. = 110-113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.28 (s, 2H), 7.18 (dd, *J* = 10.1, 4.3 Hz, 1H), 7.09 (s, 2H), 5.06 (s, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 12.2 Hz, 1H), 4.05 – 3.95 (m, 4H), 1.40 (s, 18H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.05, 167.99, 152.7, 142.1, 135.8, 131.7, 128.6, 127.9, 126.8, 124.5, 61.5, 61.4, 58.3, 51.6, 34.5, 30.4, 13.92, 13.90; FT-IR (thin film, neat): 3638, 3440, 2959, 1759, 1732, 1601, 1436, 1368, 1316, 1259, 1177, 1156,1036, 865, 700, 645 cm^{-1} .

Diethyl 2-((4-(tert-butyl)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)malonate (31g)



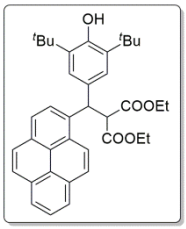
The reaction was performed at 0.0571 mmol scale of *p*-quinone methide **(15j)**; R_f = 0.5 (10% EtOAc in hexane); pale yellow gummy solid (27.1 mg, 93% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.09 (m, 4H), 7.09 (s, 2H), 5.03 (s, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 4.01 – 3.93 (m, 4H), 1.39 (s, 18H), 1.26 (s, 9H), 0.98 – 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.11, 168.07, 152.6, 149.5, 138.9, 135.7, 131.9, 127.5, 125.5, 124.6, 61.42, 61.35, 58.5, 51.4, 34.48, 34.45, 31.5, 30.4, 13.88, 13.84; FT-IR (thin film, neat): 3443, 2961, 1760, 1732, 1596, 1436, 1367, 1314, 1257, 1176, 1156, 1037, 842, 630 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methyl)malonate (31h)



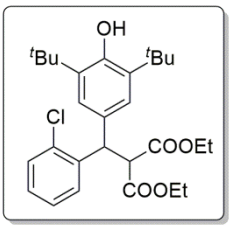
The reaction was performed at 0.0581 mmol scale of *p*-quinone methide **(15k)**; R_f = 0.5 (20% EtOAc in hexane); pale yellow gummy solid (23.2 mg, 79% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 13.5, 7.1 Hz, 2H), 7.45 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.17 (s, 2H), 5.54 (d, *J* = 12.1 Hz, 1H), 5.02 (s, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.93 – 3.82 (m, 2H), 1.36 (s, 18H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 167.8, 152.7, 138.1, 135.6, 134.3, 131.9, 131.1, 128.8, 127.5, 126.2, 125.6, 125.3, 124.9, 124.0, 123.1, 61.48, 61.46, 58.9, 46.0, 34.4, 30.4, 13.9, 13.8. FT-IR (thin film, neat): 3441, 2959, 1758, 1732, 1599, 1435, 1368, 1254, 1155, 1036, 872, 777, 733 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(4,6-dihydropyren-1-yl)methyl)malonate (31i)



The reaction was performed at 0.0478 mmol scale of *p*-quinone methide**(15l)**; R_f = 0.4 (20% EtOAc in hexane); orange gummy solid (25.2 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J*= 9.5 Hz, 1H), 8.19 – 8.16 (m, 3H), 8.09 (d, *J* = 8.1 Hz, 1H), 8.03 – 7.98 (m, 3H), 7.27 (d, *J* = 7.9 Hz, 3H), 5.90 (d, *J* = 12.0 Hz, 1H), 5.02 (s, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.37 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.8, 152.6, 136.0, 135.8, 131.7, 131.5, 130.9,130.1, 128.9, 127.7, 127.5, 127.2, 126.0, 125.4, 125.2, 125.04, 124.96 , 124.7, 123.9, 123.4, 61.6, 61.5, 58.9, 46.1, 34.4, 30.4, 14.0, 13.7; FT-IR (thin film, neat): 3388, 2961, 2924, 1760, 1731, 1598, 1436, 1120, 848, 799, 723 cm^{-1} .

Diethyl 2-((2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)malonate (31j)

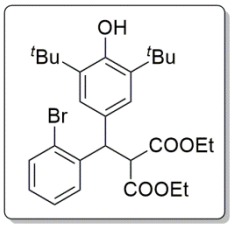


The reaction was performed at 0.061 mmol scale of *p*-quinone methide**(15m)**; R_f = 0.5 (10% EtOAc in hexane); pale yellow gummy solid (28.0 mg, 94% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.08 (m, 3H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.06 (s, 1H), 4.34 (d, *J* = 12.4 Hz, 1H), 4.00 (dq, *J* = 21.5, 7.1 Hz, 4H), 1.38 (s, 18H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* =

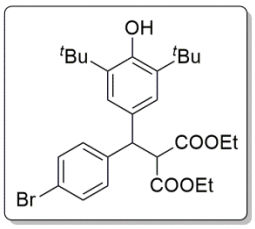
7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.6, 152.8, 139.8, 135.7, 134.4, 130.2, 130.1, 127.8, 127.4, 127.0, 125.0, 61.7, 61.5, 57.9, 46.7, 34.4, 30.4, 13.89, 13.86; FT-IR (thin film, neat): 3638, 3451, 2960, 2927, 1758, 1732, 1592, 1436, 1368, 1257, 1157, 1037, 867, 753, 730, 643, 600 cm^{-1} .

Diethyl 2-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)malonate (31k)

The reaction was performed at 0.0537 mmol scale of *p*-quinone methide**(15n)**; R_f = 0.5 (10% EtOAc in hexane); white solid (26.6 mg, 93% yield); m. p. = 143-146 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.18 (s, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 5.25 (d, *J* = 12.3 Hz, 1H), 5.07 (s, 1H), 4.35 (d, *J* = 12.3 Hz, 1H), 4.06 – 3.96 (m, 4H), 1.40 (s, 18H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.6, 152.8, 141.4, 135.7, 133.6, 130.1, 128.1, 127.7, 127.5, 125.4, 125.0, 61.7, 61.5, 58.1, 49.1, 34.4, 30.4, 13.9; FT-IR (thin film, neat): 3635, 2959, 1758, 1732, 1590, 1468, 1436, 1368, 1255, 1156, 1035, 808, 753, 725, 642 cm^{-1} . In this case, Methyl peaks of malonate merges.

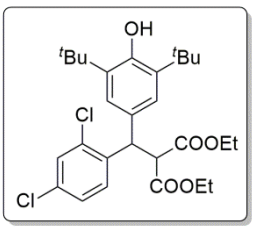


Diethyl 2-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)malonate (31l)



The reaction was performed at 0.0537 mmol scale of *p*-quinone methide**(150)**; R_f = 0.5 (10% EtOAc in hexane); pale yellow gummy solid (26.3 mg, 92% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 2H), 5.07 (s, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.22 (d, *J* = 12.1 Hz, 1H), 4.04 – 3.93 (m, 4H), 1.38 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H;^{13}C NMR (100 MHz, $CDCl_3$) δ 167.80, 167.78, 152.8, 141.3, 136.0, 131.7, 131.2, 129.6, 124.4, 120.6, 61.7, 61.5, 58.0, 50.9, 34.5, 30.4, 14.0,13.9; FT-IR (thin film, neat): 3407, 2959, 1758, 1732, 1592, 1489, 1436, 1468, 1239, 1155, 1036, 1011, 811 cm^{-1} .

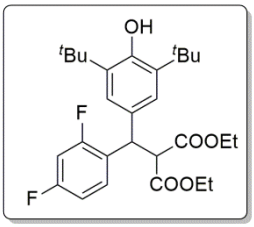
Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,4-dichlorophenyl)methyl)malonate (31m)



The reaction was performed at 0.055 mmol scale of *p*-quinone methide**(15p)**; R_f = 0.4 (10% EtOAc in hexane); pale yellow gummy

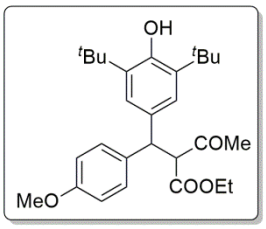
solid (27.4 mg, 95% yield);[1]H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.3, 5.2 Hz, 2H), 7.21 (dd, J = 8.4, 1.9 Hz, 1H), 7.09 (s, 2H), 5.18 (d, J = 12.4 Hz, 1H), 5.09 (s, 1H), 4.30 (d, J = 12.4 Hz, 1H), 4.08 – 3.94 (m, 4H), 1.38 (s, 18H), 1.07 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.4, 152.9, 138.6, 135.8, 135.1, 132.8, 130.0, 129.6, 128.2, 127.3, 124.8, 61.8, 61.6, 57.6, 46.2, 34.4, 30.4, 13.94, 13.88; FT-IR (thin film, neat): 3385, 2960, 2922, 1756, 1732, 1588, 1471, 1436, 1368, 1239, 1155, 1106, 1036, 867, 771 cm^{-1} .

Diethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,4-difluorophenyl)methyl)malonate (31n)



The reaction was performed at 0.0606 mmol scale of *p*-quinone methide**(15q)**; R_f = 0.6 (10% EtOAc in hexane); white solid (27.0 mg, 91% yield); m. p. = 110-114 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 1H), 7.13 (s, 2H), 7.06 (t, J = 7.4 Hz, 1H), 6.98 (t, 1H), 5.07 (s, 1H), 4.95 (d, J = 12.6 Hz, 1H), 4.41 (d, J = 12.4 Hz, 1H), 4.05 – 3.96 (m, 4H), 1.39 (s, 18H), 1.02 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.8, 160.6 (d, $J_{C\text{-}F}$ = 244.7 Hz), 152.8, 135.7, 130.6, 129.4 (d, $J_{C\text{-}F}$ = 14.0 Hz), 128.7 (d, $J_{C\text{-}F}$ = 4.3 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 124.8 (d, $J_{C\text{-}F}$ = 1 Hz), 124.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.7 Hz), 61.6, 61.5, 56.9 (d, $J_{C\text{-}F}$ =1.9 Hz), 45.1 (d, $J_{C\text{-}F}$ = 0.6 Hz), 34.4, 30.4, 13.90, 13.87 ; ^{19}F NMR (376 MHz, CDCl3) δ –116.05; 3387, 2960, 1760, 1732, 1595, 1436, 1371, 1236, 1121, 871, 757 cm^{-1} .

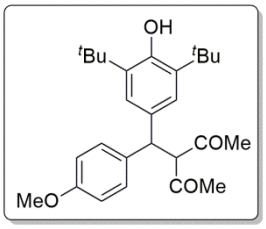
Ethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-3-oxobutanoate(33a)



The reaction was performed at 0.062 mmol scale of *p*-quinone methide**(15d)**; R_f = 0.5 (10% EtOAc in hexane); orange gummy solid (26.6 mg, 95% yield); The product was obtained as 1:1.2 diasteromeric ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 8.6 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.05 (d, J = 9.6 Hz, 1H), 4.60 (d, J = 12.2 Hz, 1H), 4.41 (dd, J = 12.1, 7.8 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.75 (s, 3H), 2.06 (d, J = 19.8 Hz, 3H), 1.38 (d, J = 1.0 Hz, 18H), 0.98 (dt, J = 35.3, 7.1 Hz, 3H)v; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 202.5, 168.09, 168.06, 158.4, 158.3, 152.6, 152.5,136.1, 135.8,

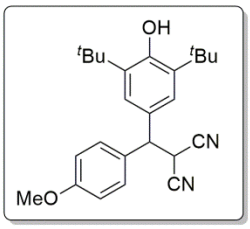
134.5, 134.1, 132.3,132, 128.9, 128.8, 124.4, 124.3, 114.2, 114.0, 66.4, 66.1, 61.5, 61.4, 55.32, 55.30, 50.7, 34.5, 34.5, 30.4, 30.2, 30.0, 14.0, 13.9; FT-IR (thin film, neat): 3626, 2959, 1747, 1715, 1612, 1513, 1436, 1303, 1250, 1180, 1036, 889, 837, 737, 640 cm^{-1} .

3-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)pentane-2,4-dione (33b)



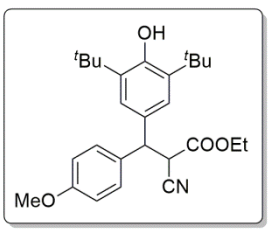
The reaction was performed at 0.062 mmol scale of *p*-quinone methide**(15d)**; R_f = 0.5 (10% EtOAc in hexane); brown solid (24.6 mg, 95% yield); m. p. = 114-117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 7.00 (s, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.07 (s, 1H), 4.64 (s, 2H), 3.75 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 203.7, 158.4, 152.6, 136.2, 134.2, 132.1, 128.8, 124.2, 114.3, 75.4, 55.3, 51.0, 34.5, 30.4, 30.0, 29.9; FT-IR (thin film, neat): 3636, 2958, 1698, 1611, 1513, 1436, 1357, 1252, 1180, 1154, 1120, 1035, 889, 835, 770, 738, 642, 539 cm^{-1} .

2-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)malononitrile (33c)



The reaction was performed at 0.062 mmol scale of *p*-quinone methide**(15d)**; R_f = 0.4 (10% EtOAc in hexane); yellow solid (23.6 mg, 98% yield); m. p. = 130-134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.11 (s, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.27 (s, 1H), 4.50 (d, *J* = 7.5 Hz, 1H), 4.30 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 153.9, 136.5, 129.8, 129.2, 128.1, 124.7, 114.6, 112.5,55.4, 51.2, 34.6, 30.3, 30.1; FT-IR (thin film, neat): 3626, 2961, 2255, 2203, 1710, 1612, 1515, 1437, 1363, 1307, 1254, 1182, 1157, 1121, 1034, 836, 773, 738, 635 cm^{-1} .

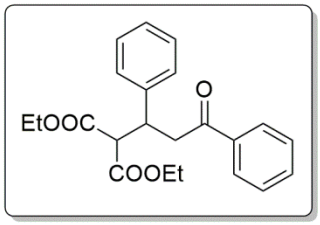
Ethyl 2-cyano-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(4-methoxyphenyl)propanoate (33d)



The reaction was performed at 0.062 mmol scale of *p*-quinone methide**(15d)**; R_f = 0.4 (10% EtOAc in hexane); orange gummy solid(24.5 mg, 91% yield); The product was obtained as 1:1.02

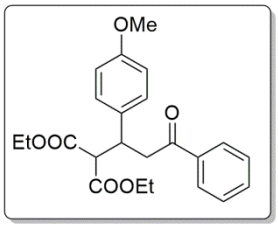
diasteromeric ratio.^{1}H NMR (400 MHz, $CDCl_3$)δ7.33 (d, J = 8.5 Hz, 1H), 7.26 (t, 1H), 7.16 (s, 1H), 7.10 (s, 1H), 6.89 (t, J = 8.3 Hz, 2H), 5.19 (d, J = 3.8 Hz, 1H), 4.61 (dd, J = 8.2, 3.1 Hz, 1H), 4.16 – 4.07 (m, 3H), 3.81 (d, J = 3.2 Hz, 3H), 1.43 (d, J= 4.5 Hz, 18H), 1.09 (dd, J = 11.9, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 159.0, 158.9, 153.3, 153.2, 136.1, 136.0, 132.1, 131.6, 130.2, 129.43, 129.37, 129.1, 125.0, 124.5, 116.33, 116.29, 114.22, 114.17, 62.8,55.36, 55.34, 50.8, 50.7, 44.8, 44.7, 34.5, 30.4, 30.3, 13.89, 13.87; FT-IR (thin film, neat): 3627, 3458, 2960, 2249, 1745, 1612, 1514, 1437, 1368, 1305, 1251, 1181, 1034, 836, 738, 771, 636 cm^{-1} .

Diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate (35a)



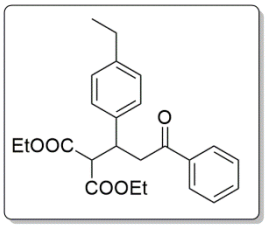
The reaction was performed at 0.096 mmol scale of chalcones **(34a)**; R_f = 0.5 (20% EtOAc in hexane); pale yellow solid (31.5 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 1H), 7.88 (t, 1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 7.28 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 4.25 – 4.14 (m, 3H), 3.95 (q, J = 7.1 Hz, 2H), 3.82 (d, J = 9.7 Hz, 1H), 3.50 (qd, J = 16.7, 6.9 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 168.5, 167.9, 140.5, 136.9, 133.2, 128.7, 128.5, 128.4, 128.2, 127.3, 61.8, 61.5, 547.7, 42.8, 40.9, 14.2, 13.9; FT-IR (thin film, neat): 2981, 1752, 1732, 1688, 1598, 1496, 1449, 1369, 1258, 1154, 1033, 861, 751, 700, 559 cm^{-1} .

Diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (35b)



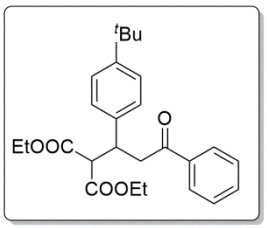
The reaction was performed at 0.084 mmol scale of chalcones **(34b)**; R_f = 0.5 (20% EtOAc in hexane); yellow gummy solid (27.01 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.26 – 4.10 (m, 3H), 3.96 (q, J = 7.1 Hz, 2H), 3.77 (d, J = 9.8 Hz, 1H), 3.73 (s, 3H), 3.46 (ddd, J = 26.0, 16.5, 7.0 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 168.5, 167.9, 158.0, 136.9, 133.1, 132.4, 129.4, 128.7, 128.2, 113.8, 61.8, 61.5, 57.9, 55.3, 42.9, 40.3, 14.2, 13.9; FT-IR (thin film, neat): 2961, 2929, 2839, 1751, 1732, 1688, 1612, 1598, 1583, 1515, 1449, 1369, 1251, 1180, 1154, 1114, 1035, 832, 737, 692, 560 cm^{-1} .

Diethyl 2-(1-(4-ethylphenyl)-3-oxo-3-phenylpropyl)malonate (35c)



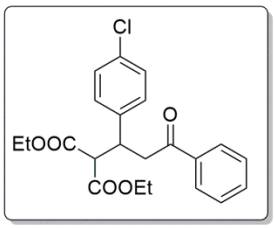
The reaction was performed at 0.085 mmol scale of chalcones **(34c)**; R_f = 0.5 (20% EtOAc in hexane); orange gummy solid (30.5 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 4.25 – 4.12 (m, 3H), 3.95 (q, J = 7.1 Hz, 2H), 3.80 (d, J = 9.6 Hz, 1H), 3.48 (qd, J = 16.7, 6.9 Hz, 2H), 2.56 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 168.6, 168.0, 143.1, 137.7, 137.0, 133.1, 128.6, 128.23, 128.22, 128.0, 61.7, 61.4, 57.8, 42.8, 40.6, 28.5, 15.5, 14.1, 13.9; FT-IR (thin film, neat): 2965, 2929, 1748, 1732, 1688, 1598, 1515, 1449, 1368, 1258, 1154, 1097, 1034, 831, 756, 691, 572 cm^{-1} .

Diethyl 2-(1-(4-(tert-butyl)phenyl)-3-oxo-3-phenylpropyl)malonate (35d)



The reaction was performed at 0.076 mmol scale of chalcones **(34d)**; R_f = 0.6(20% EtOAc in hexane); yellow solid (26.3 mg, 82% yield); m. p. = 102-105 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.18 (d, J = 7.9 Hz, 2H), 4.18 (dd, J = 14.2, 7.3 Hz, 3H), 3.94 (q, J = 6.8 Hz, 2H), 3.80 (d, J = 9.5 Hz, 1H), 3.55 – 3.42 (m, 2H), 1.24 – 1.21 (m, 12H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 168.6, 168.0, 149.9, 137.5, 137.0, 133.1, 128.6, 128.2, 127.9, 125.4, 61.7, 61.4, 57.7, 42.8, 40.4, 34.5, 31.4, 14.1, 13.8; FT-IR (thin film, neat): 2964, 2929, 2871, 1748, 1732, 1689, 1598, 1582, 1513, 1464, 1449, 1368, 1257, 1154, 1097, 837, 755, 691, 586 cm^{-1} .

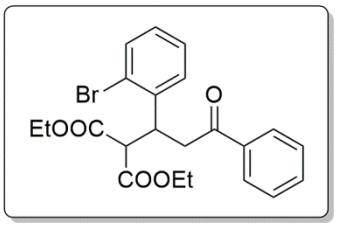
Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (35e)



The reaction was performed at 0.082 mmol scale of chalcones **(34e)**; R_f = 0.5 (20% EtOAc in hexane); orange solid (31.2 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.26 (s, 1H), 7.21 (s, 3H), 4.26 – 4.13 (m, 3H), 3.98 (q, J = 7.1 Hz, 2H), 3.78 (d, J = 9.6 Hz, 1H), 3.48 (ddd, J = 26.3, 16.9, 6.9 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 168.2, 167.7, 139.1, 136.7, 133.3, 133.0, 129.8, 128.8,

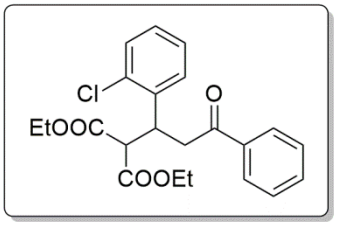
128.6, 128.2, 61.9, 61.6, 57.4, 42.5, 40.2, 14.1, 13.9; FT-IR (thin film, neat): 2982, 2937, 1750, 1732, 1688, 1598, 1581, 1492, 1449, 1369, 1256, 1155, 1094, 1032, 1015, 861, 829, 754, 691, 552 cm^{-1} .

Diethyl 2-(1-(2-bromophenyl)-3-oxo-3-phenylpropyl)malonate (35f)



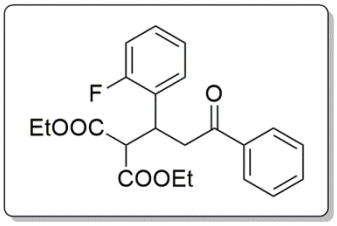
The reaction was performed at 0.070 mmol scale of chalcones **(34f)**; R_f = 0.5 (20% EtOAc in hexane); orange solid (28.7 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.54 (dd, *J* = 7.6, 4.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.65 (dd, *J* = 13.7, 8.0 Hz, 1H), 4.20 – 4.10 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 3H), 3.72 – 3.60 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 168.4, 167.9, 139.6, 136.8, 133.5, 133.2, 128.68, 128.66, 128.3, 127.6, 127.5, 125.1, 61.7, 55.4, 40.6, 39.6, 14.1, 14.0; FT-IR (thin film, neat): 2981, 1751, 1732, 1688, 1598, 1473, 1448, 1369, 1229, 1154, 1096, 1025, 861, 752, 691 cm^{-1} .

Diethyl 2-(1-(2-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (35g)



The reaction was performed at 0.082 mmol scale of chalcones **(34g)**; R_f = 0.5 (20% EtOAc in hexane); orange gummy solid (32.5 mg, 98% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.13 (p, *J* = 7.2 Hz, 2H), 4.65 (td, *J* = 8.6, 5.0 Hz, 1H), 4.22 – 4.11 (m, 2H), 4.08 – 4.00 (m, 3H), 3.65 (qd, *J* = 17.1, 6.7 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 168.4, 167.9, 137.9, 136.8, 134.2, 133.2, 130.2, 129.5, 128.7, 128.4, 128.2, 126.9, 61.7, 61.6, 55.3, 40.6, 37.5, 14.1, 13.9; FT-IR (thin film, neat): 2982, 2930, 1750, 1732, 1689, 1598, 1582, 1477, 1448, 1369, 1229, 1155, 1036, 861, 692, 566 cm^{-1} .

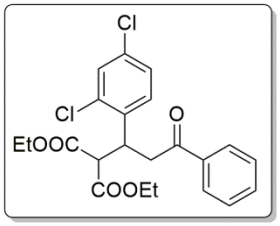
Diethyl 2-(1-(2-fluorophenyl)-3-oxo-3-phenylpropyl)malonate (35h)



The reaction was performed at 0.088 mmol scale of chalcones **(34f)**; R_f = 0.6 (20% EtOAc in hexane); orange gummy solid

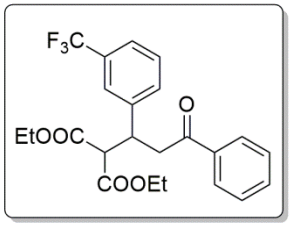
(29.7 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.28 (dd, J = 7.8, 6.4 Hz, 1H), 7.20 – 7.12 (m, 1H), 6.98 (dt, J = 10.2, 8.0 Hz, 2H), 4.34 (td, J = 9.8, 4.3 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.97 (dt, J = 14.2, 8.7 Hz, 3H), 3.55 (qd, J = 17.0, 6.9 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 168.3, 167.8, 161.3 (d, $J_{C\text{-}F}$ = 244.8 Hz), 136.8, 133.2, 131.3 (d, $J_{C\text{-}F}$ = 4.9 Hz), 129.04 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.7, 128.2, 127.2 (d, $J_{C\text{-}F}$ = 13 Hz), 124.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 61.9, 61.5, 55.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 41.2 (d, $J_{C\text{-}F}$ = 1.9 Hz), 36.7, 14.1, 13.9 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.6; FT-IR (thin film, neat): 2925, 1751, 1732, 1688, 1598, 1493, 1449, 1369, 1255, 1155, 1105, 1033, 758, 691 cm^{-1} .

Diethyl 2-(1-(2,4-dichlorophenyl)-3-oxo-3-phenylpropyl)malonate (35i)



The reaction was performed at 0.072 mmol scale of chalcones **(34i)**; R_f = 0.5 (20% EtOAc in hexane); orange gummy solid (29.0 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 4.62 – 4.57 (m, 1H), 4.24 – 4.12 (m, 2H), 4.07 (td, J = 12.5, 7.0 Hz, 3H), 3.65 (qd, J = 17.3, 6.8 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.2, 167.7, 136.7, 136.6, 135.0, 133.44, 133.38, 130.4, 129.9, 128.7, 128.2, 127.2, 61.84, 61.80, 55.1, 40.4, 37.0, 14.1, 14.0; FT-IR (thin film, neat): 3066, 2982, 2929, 1751, 1732, 1689, 1560, 1475, 1449, 1369, 1302, 1230, 1155, 1106, 1033, 864, 823, 734, 691, 579 cm^{-1} .

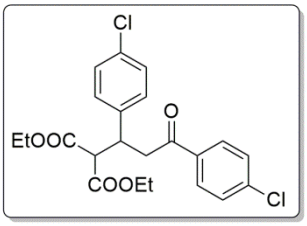
Diethyl 2-(3-oxo-3-phenyl-1-(3-(trifluoromethyl)phenyl)propyl)malonate (35j)



The reaction was performed at 0.072 mmol scale of chalcones **(34l)**; R_f = 0.6 (20% EtOAc in hexane); pale yellow gummy solid (25.9 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.7 Hz, 2H), 7.56 – 7.52 (m, 3H), 7.40 (dt, J = 22.5, 7.7 Hz, 4H), 4.28 – 4.16 (m, 3H), 3.96 (q, J = 7.1 Hz, 2H), 3.83 (d, J = 9.4 Hz, 1H), 3.54 (ddd, J = 26.3, 17.1, 6.7 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 168.2, 167.6, 141.8, 136.7, 133.4, 132.2, 130.6 (q, $J_{C\text{-}F}$ = 32 Hz), 129.0, 128.8, 128.2, 125.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.2 (q, $J_{C\text{-}F}$ = 37 Hz), 124.1 (q, $J_{C\text{-}F}$

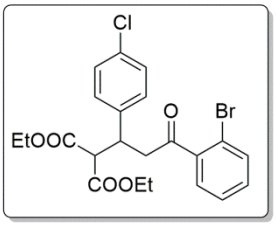
= 271 Hz), 62.0, 61.7, 57.2, 42.4, 40.5, 14.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; FT-IR (thin film, neat): 2924, 1751, 1732, 1598, 1449, 1329, 1260, 1123, 1031, 868, 803, 745, 691 cm^{-1} .

Diethyl 2-(1,3-bis(4-chlorophenyl)-3-oxopropyl)malonate (35k)



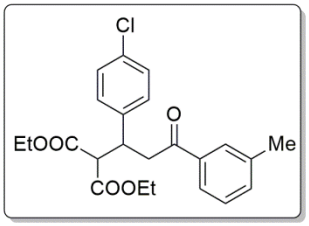
The reaction was performed at 0.070 mmol scale of chalcones **(34m)**; R_f = 0.5 (20% EtOAc in hexane); pale yellow gummy solid (23.9 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.26 – 7.18 (m, 4H), 4.26 – 4.09 (m, 3H), 3.97 (q, J = 7.1 Hz, 2H), 3.76 (d, J = 9.6 Hz, 1H), 3.51 (dd, J = 16.7, 4.2 Hz, 1H), 3.37 (dd, J = 16.8, 9.6 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 168.2, 167.6, 139.8, 138.9, 135.0, 133.1, 129.7, 129.6, 129.1, 128.7, 61.9, 61.7, 57.4, 42.5, 40.3, 14.1, 13.9; FT-IR (thin film, neat): 2983, 2937, 1751, 1732, 1689, 1590, 1491, 1446, 1401, 1369, 1256, 1155, 1093, 1032, 1014, 832, 724, 650, 530 cm^{-1} .

Diethyl 2-(3-(2-bromophenyl)-1-(4-chlorophenyl)-3-oxopropyl)malonate (35l)



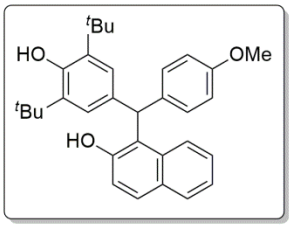
The reaction was performed at 0.062 mmol scale of chalcones **(34n)**; R_f = 0.5 (20% EtOAc in hexane); white solid (23.7 mg, 79% yield); m. p. = 77-81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.31 – 7.18 (m, 6H), 7.13 (dd, J = 7.2, 1.4 Hz, 1H), 4.26 – 4.15 (m, 2H), 4.06 (td, J = 9.7, 4.3 Hz, 1H), 3.97 (q, J = 7.1 Hz, 2H), 3.73 (d, J = 9.7 Hz, 1H), 3.50 (dd, J = 17.3, 4.3 Hz, 1H), 3.39 (dd, J = 17.2, 9.8 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 168.1, 167.6, 141.2, 138.6, 133.8, 133.2, 131.8, 130.0, 128.7, 128.6, 127.5, 118.7, 62.0, 61.7, 57.3, 46.4, 40.2, 14.2, 13.9; FT-IR (thin film, neat): 2982, 2927, 1751, 1732, 1588, 1492, 1466, 1429, 1369, 1254, 1156, 1094, 1030, 860, 829, 759, 573 cm^{-1} .

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-(m-tolyl)propyl)malonate (35m)

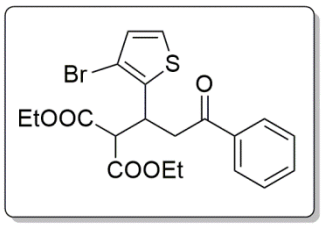


The reaction was performed at 0.078 mmol scale of chalcones **(34o)**; R_f = 0.5 (20% EtOAc in hexane); white solid (24.1 mg, 74%

yield); m. p. = 80-83 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 4H), 4.24 – 4.13 (m, 3H), 3.98 (q, J = 7.1 Hz, 2H), 3.78 (d, J = 9.6 Hz, 1H), 3.46 (qd, J = 16.9, 6.8 Hz, 2H), 2.37 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 168.2, 167.7, 139.2, 138.5, 136.7, 134.1, 132.9, 129.8, 128.7, 128.63, 128.59, 125.4, 61.9, 61.6, 57.4, 42.5, 40.2, 21.5, 14.2, 13.9; FT-IR (thin film, neat): 2983, 2928, 1751, 1732, 1683, 1604, 1587, 1492, 1369, 1260, 1155, 1094, 1036, 1015, 859, 827, 783, 558 cm^{-1} .



Diethyl 2-(1-(3-bromothiophen-2-yl)-3-oxo-3-phenylpropyl)malonate (35n)

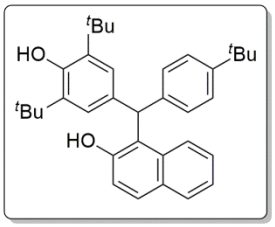


The reaction was performed at 0.068 mmol scale of chalcones **(34p)**; R_f = 0.5 (10% EtOAc in hexane); pale yellow gummy solid (29.1 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 5.3 Hz, 1H), 6.86 (d, J = 5.3 Hz, 1H), 4.64 (td, J = 8.5, 4.7 Hz, 1H), 4.25 – 4.03 (m, 5H), 3.62 (qd, J = 17.3, 6.6 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.0, 167.5, 138.1, 136.7, 133.4, 130.1, 128.7, 128.3, 124.8, 110.3, 61.9, 61.8, 56.0, 42.0, 35.5, 14.1, 14.0; FT-IR (thin film, neat): 3111, 2982, 2937, 1751, 1732, 1689, 1516, 1449, 1369, 1256, 1156, 1096, 1031, 861, 757, 691, 539 cm^{-1} .

1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl]naphthalen-2-ol (37a)

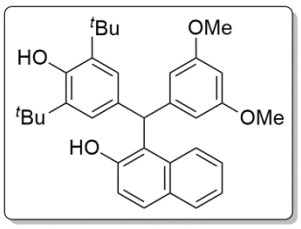
The reaction was performed at 0.062 mmol scale of *p*-quinone methide (**15d**); pale yellow solid; yield 78% (22.53 mg); R_f = 0.5 (20%EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.02 (d, J = 8.6 Hz, 1H), 7.78 (dd, J = 7.9, 1.0 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.43 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.34–7.30 (m, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 7.02 (s, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.23 (s, 1H), 5.44 (s, 1H), 5.20 (s, 1H), 3.78 (s, 3H), 1.33 (s, 18H);^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.14, 153.13, 136.8, 134.1, 133.5, 132.2, 130.1, 129.6, 129.5, 128.8, 126.8, 125.7, 123.1, 123.0, 120.6, 120.1, 114.4, 55.4, 47.9, 34.5, 30.3 .

1-{[4-(*tert*-butyl)phenyl](3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl}naphthalen-2-ol (37b)



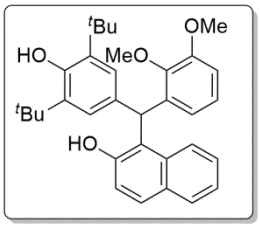
The reaction was performed at 0.057 mmol scale of *p*-quinone methide (**15j**); pale yellow solid; yield 74% (20.9 mg);R_f = 0.7 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.08 (d, J = 8.6 Hz, 1H), 7.80 (dd, J = 8.0, 1.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.46 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.36–7.32 (m, 3H), 7.18 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.8 Hz, 1H), 7.03 (s, 2H), 6.28 (s, 1H), 5.42 (s, 1H), 5.20 (s, 1H), 1.35 (s, 18H), 1.31 (s, 9H);^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 153.0, 150.0, 139.1, 136.6, 133.6, 131.9, 129.7, 129.4, 128.8, 128.6, 126.8, 126.0, 125.8, 123.1, 123.0, 120.7, 120.1, 48.1, 34.6, 34.5, 31.5, 30.3 .

1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl]naphthalen-2-ol (37c)



The reaction was performed at 0.056 mmol scale of *p*-quinone methide(**15f**) ; pale yellow solid; yield 73% (20.5 mg); R_f = 0.5 (20%EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.04 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 8.0, 1.0 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.45 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.35–7.31 (m, 1H), 7.08 (d, J = 8.8 Hz, 1H), 7.07 (s, 2H), 6.41 (d, J = 2.2 Hz, 2H), 6.36 (t, J = 2.2 Hz, 1H), 6.21 (s, 1H), 5.50 (s, 1H), 5.20 (s, 1H), 3.70 (s, 6H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.3, 153.1, 145.2, 136.7, 133.6, 131.2, 129.63, 129.56, 128.8, 126.8, 125.7, 123.1, 123.0, 120.3, 120.1, 107.3, 98.9, 55.4, 48.9, 34.5, 30.4 .

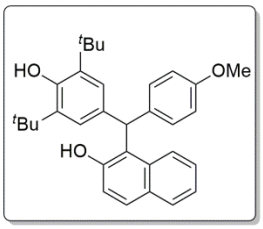
1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,3-dimethoxyphenyl)methyl]naphthalen-2-ol(37d)



The reaction was performed at 0.28mmol scale of *p*-quinone methide (**15e**); yellow solid; yield 71% (20 mg); R_f = 0.6 (20%EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.08 δ 8.08 (d, J = 8.6 Hz, 1H), 7.75 (dd, J = 8.1, 1.0 Hz, 1H), 7.70 (d, J = 8.9 Hz, 1H), 7.42 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.32–7.28 (m, 1H), 7.06 (d, J, = 8.9 Hz,

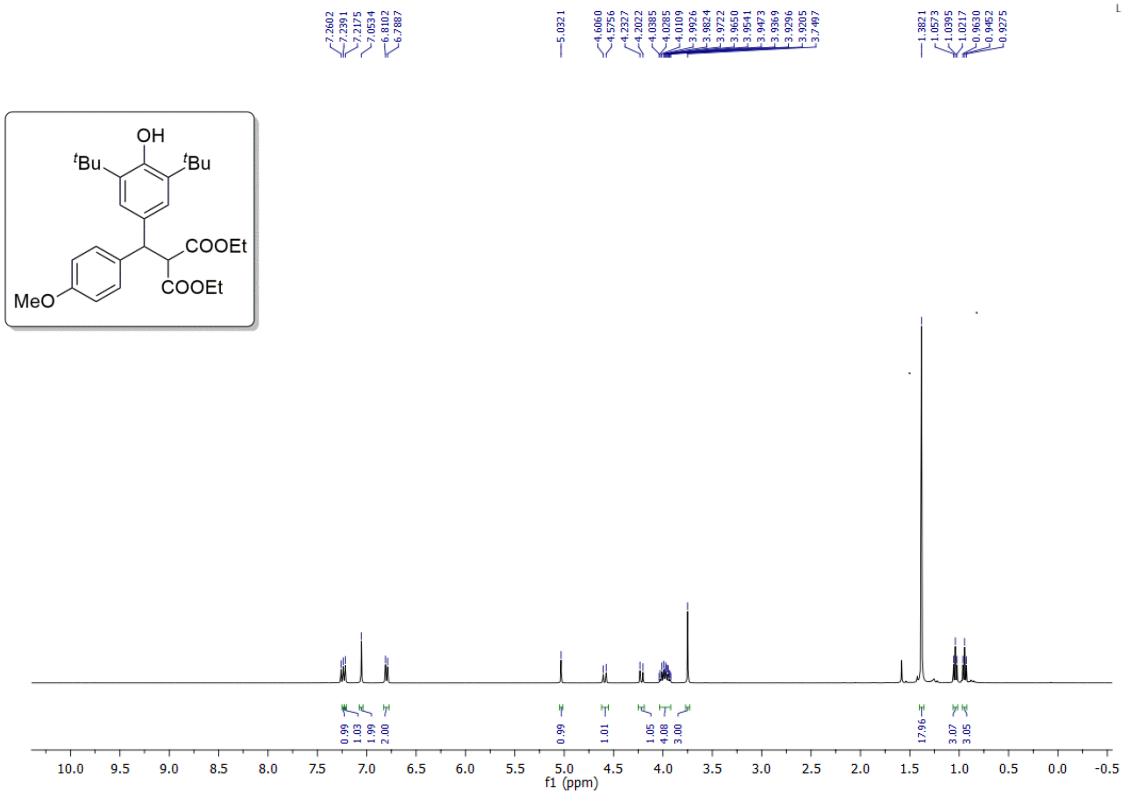
1H), 7.03 (s, 2H), 6.99–6.95 (m, 1H), 6.84 (dd, J = 8.2, 1.4 Hz, 1H), 6.76 (dd, J = 7.8, 1.4 Hz, 1H), 6.67 (s, 1H), 5.78 (s, 1H), 5.20 (s, 1H), 3.88 (s, 3H), 3.49 (s, 3H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 153.1, 152.9, 146.8, 136.8, 136.6, 133.7, 131.8, 129.6, 129.3, 128.6, 126.8, 125.6, 124.5, 123.3, 123.1, 121.7, 120.4, 120.0, 111.4, 60.6, 55.9, 42.7, 34.6, 30.4 .

6-bromo-1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl]naphthalen-2-ol (37e)

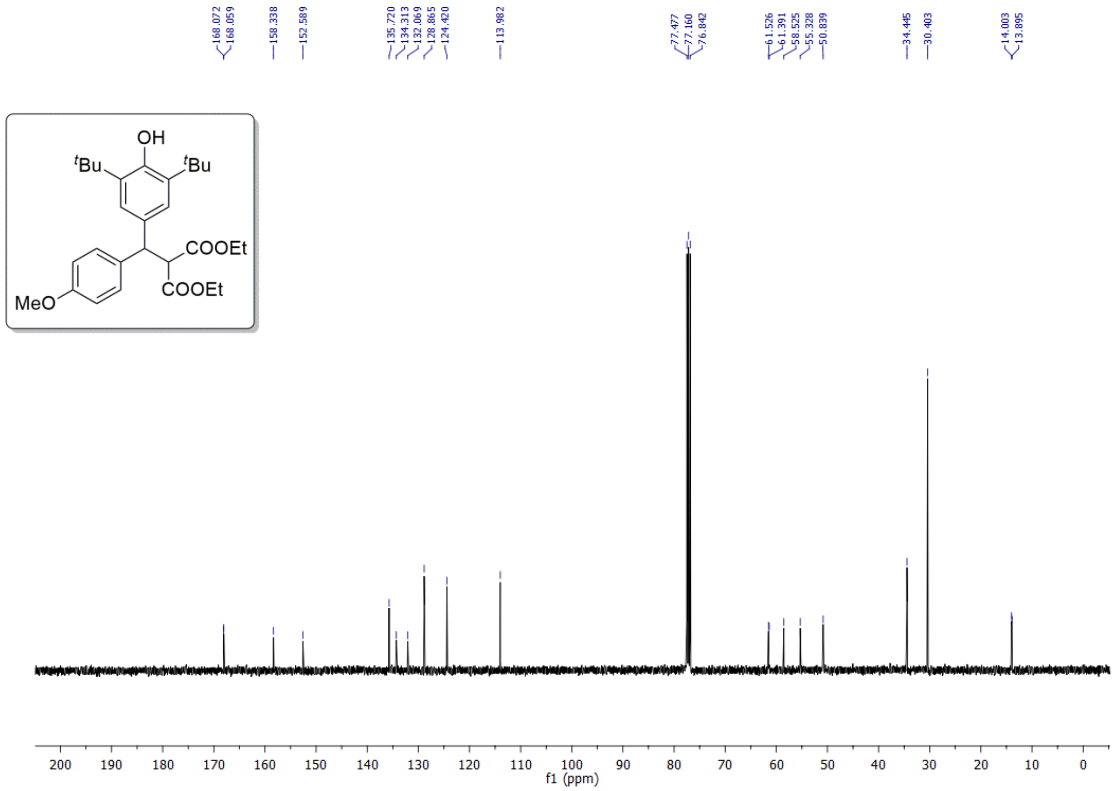


The reaction was performed at 0.062 mmol scale of *p*-quinone methide (**15d**); pale yellow solid; yield 75% (25.3 mg); R_f = 0.4 (20%EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.92 (d, J = 2.1 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.63 (d, J = 8.9 Hz, 1H), 7.47 (dd, J = 9.2,2.1Hz, 1H), 7.13 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.9 Hz, 1H), 6.99 (s, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.16 (s, 1H), 5.47 (s, 1H), 5.22 (s, 1H), 3.78 (s, 3H), 1.33 (s, 18H);^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 153.4, 153.2, 136.9, 133.7, 132.1, 131.7, 130.9, 130.6, 130.1, 129.9, 128.6, 125.6, 124.9, 121.2, 120.9, 116.9, 114.5, 55.4, 47.9, 34.6, 30.3 .

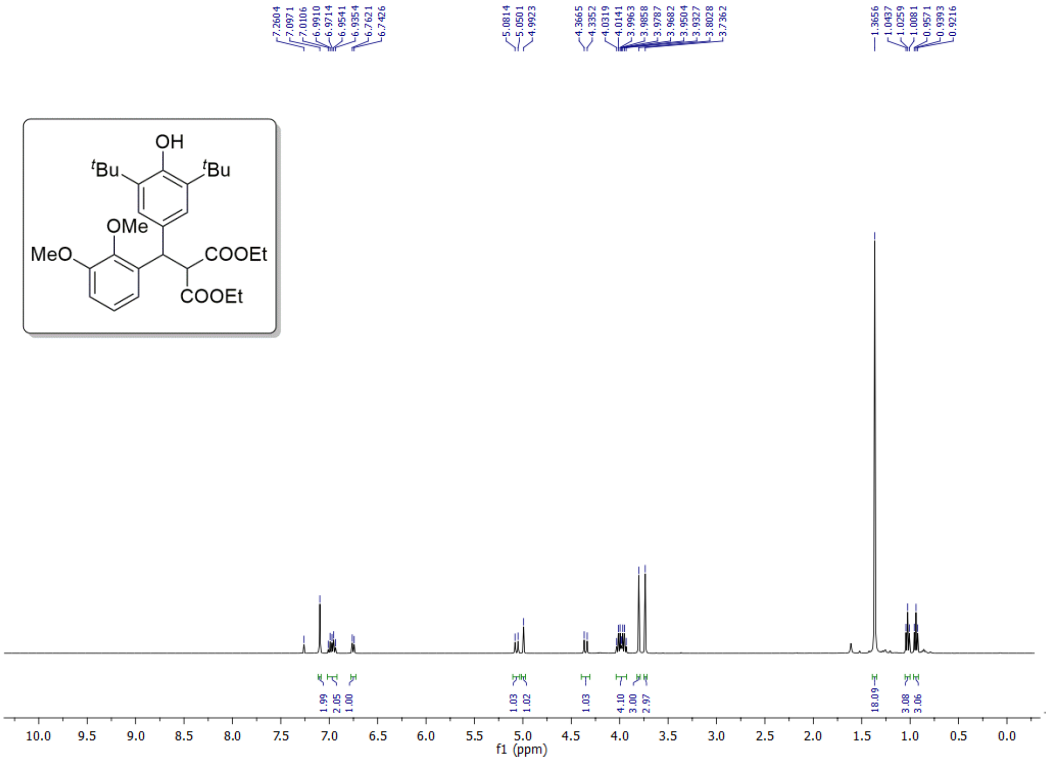
^{1}H NMR spectrum of 31a



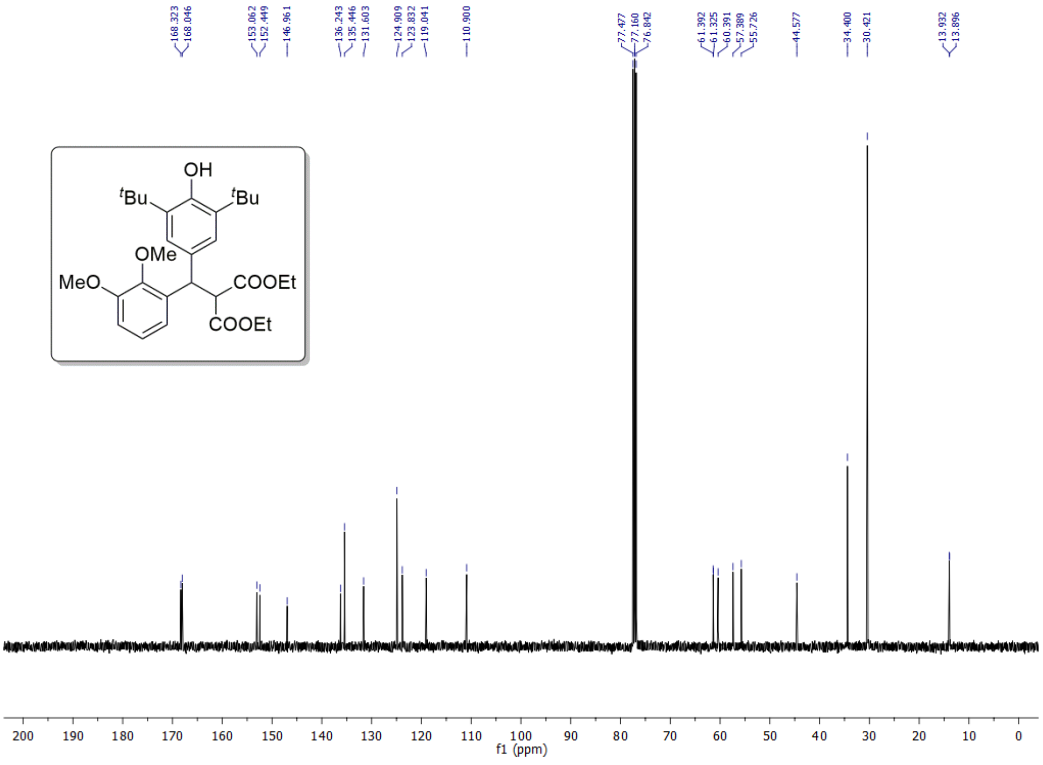
^{13}C NMR spectrum of 31a



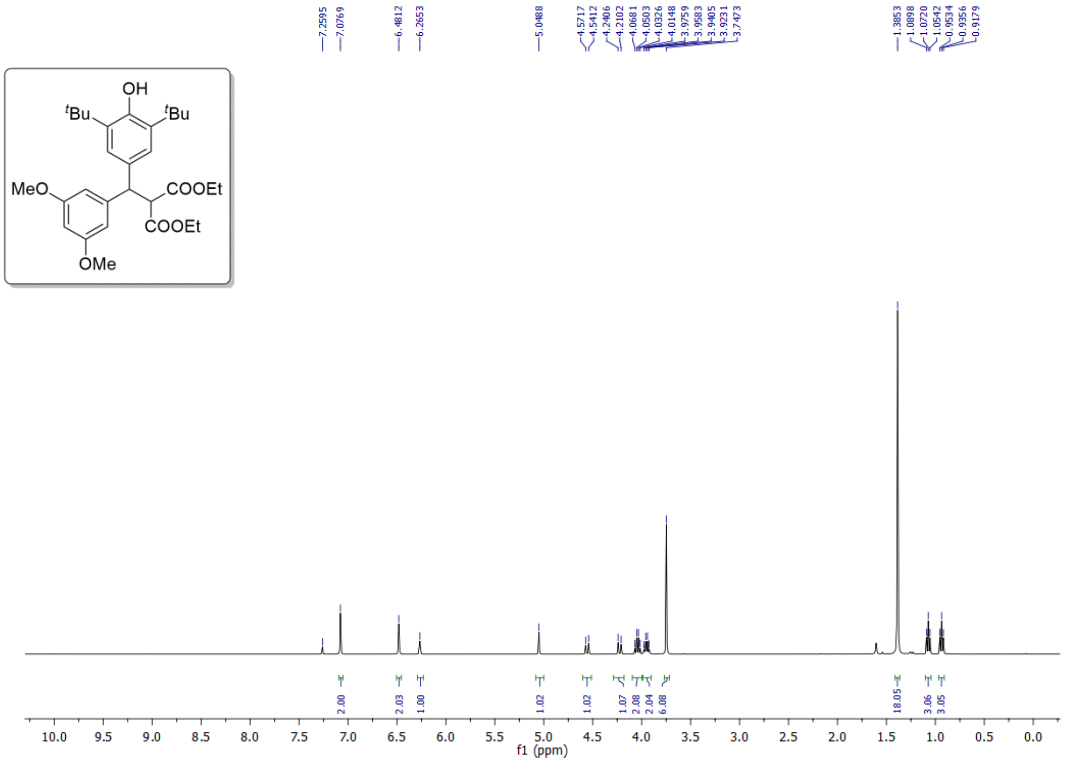
^{1}H NMR spectrum of 31b



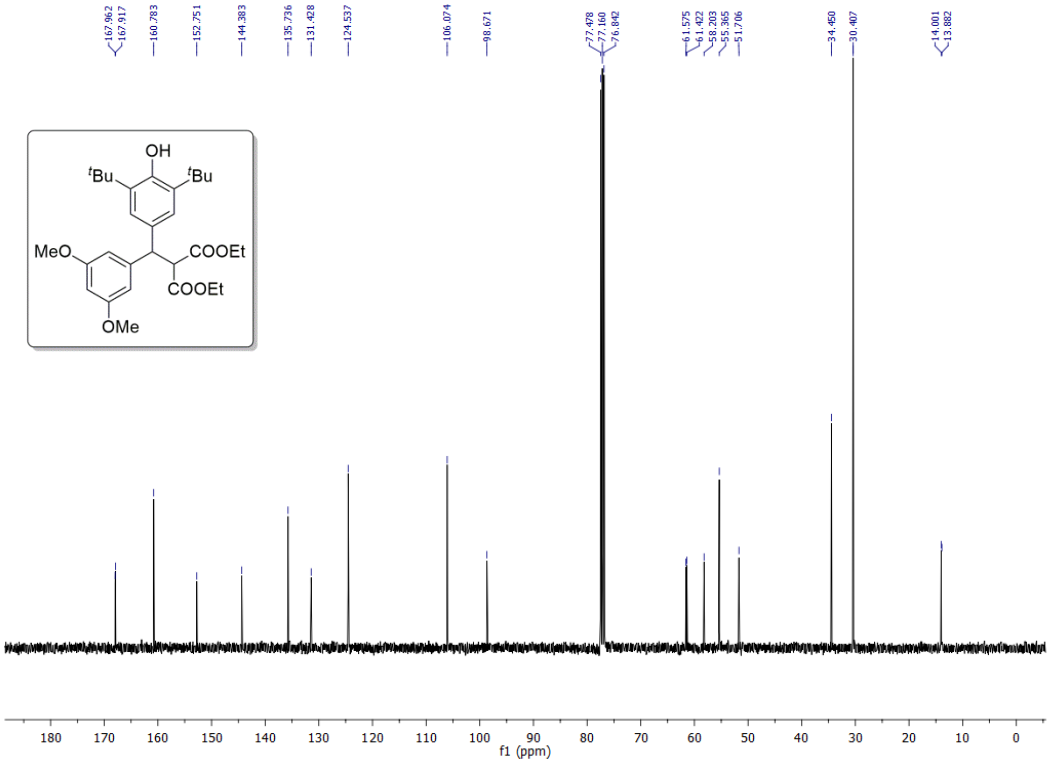
^{13}C NMR spectrum of 31b



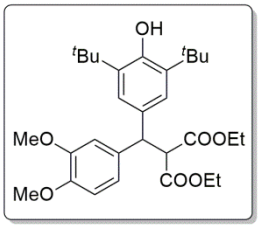
^{1}H NMR of 31c



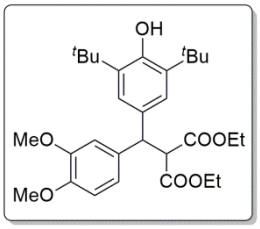
^{13}C NMR of 31c



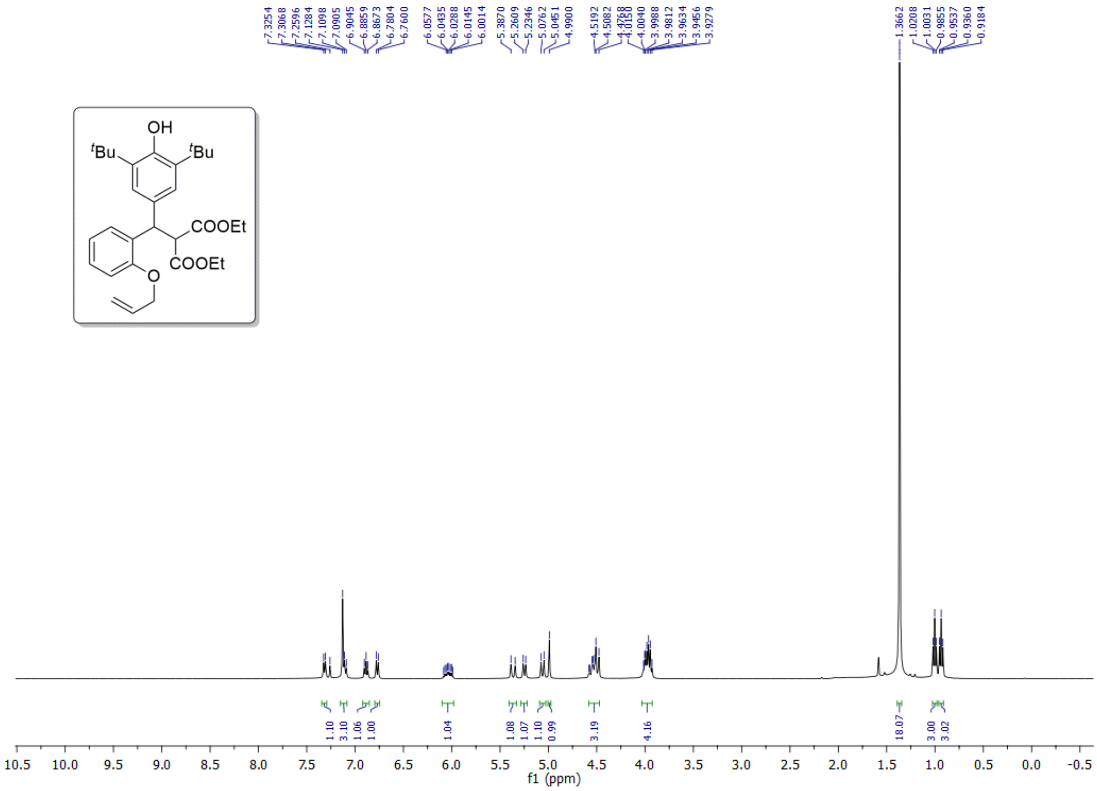
^{1}H NMR spectrum of 31d



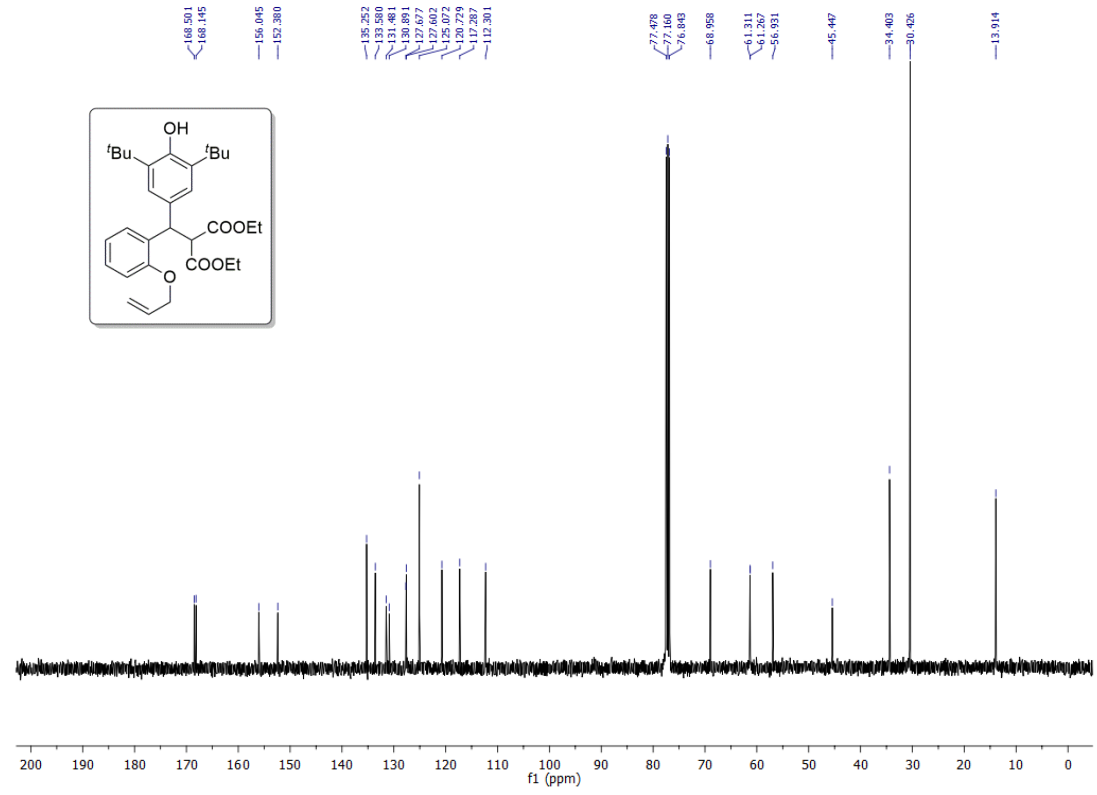
^{13}C NMR spectrum of 31d



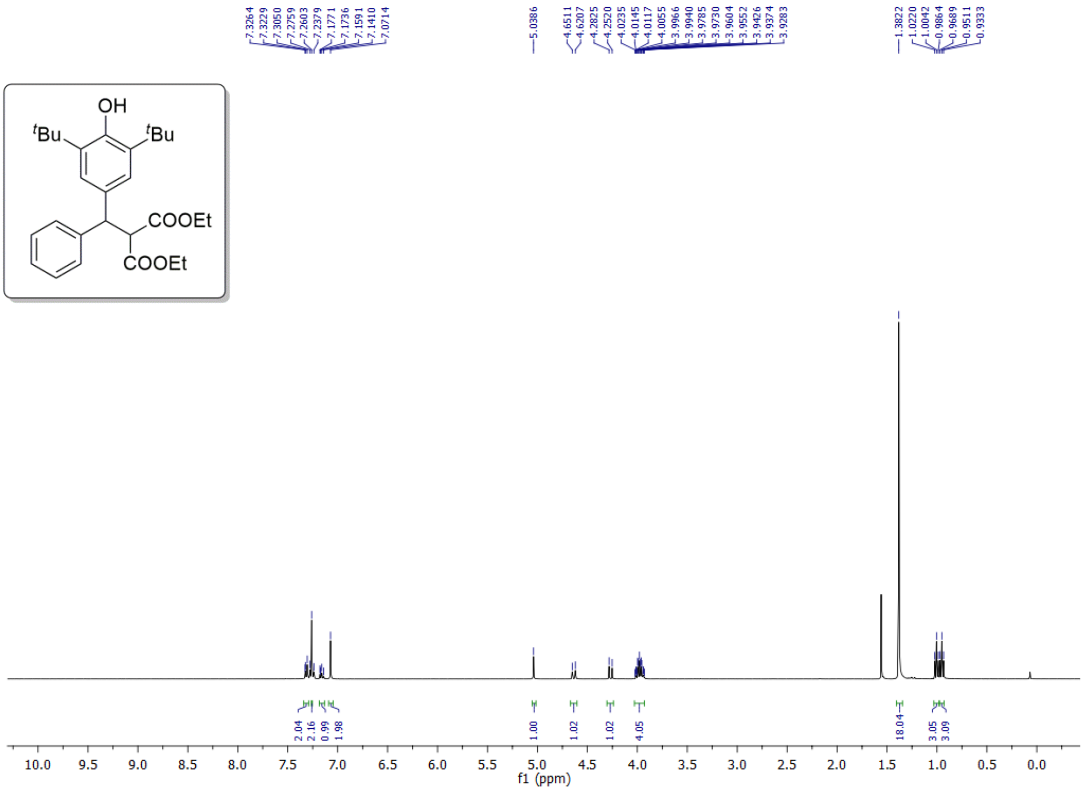
^{1}H NMR of 31e



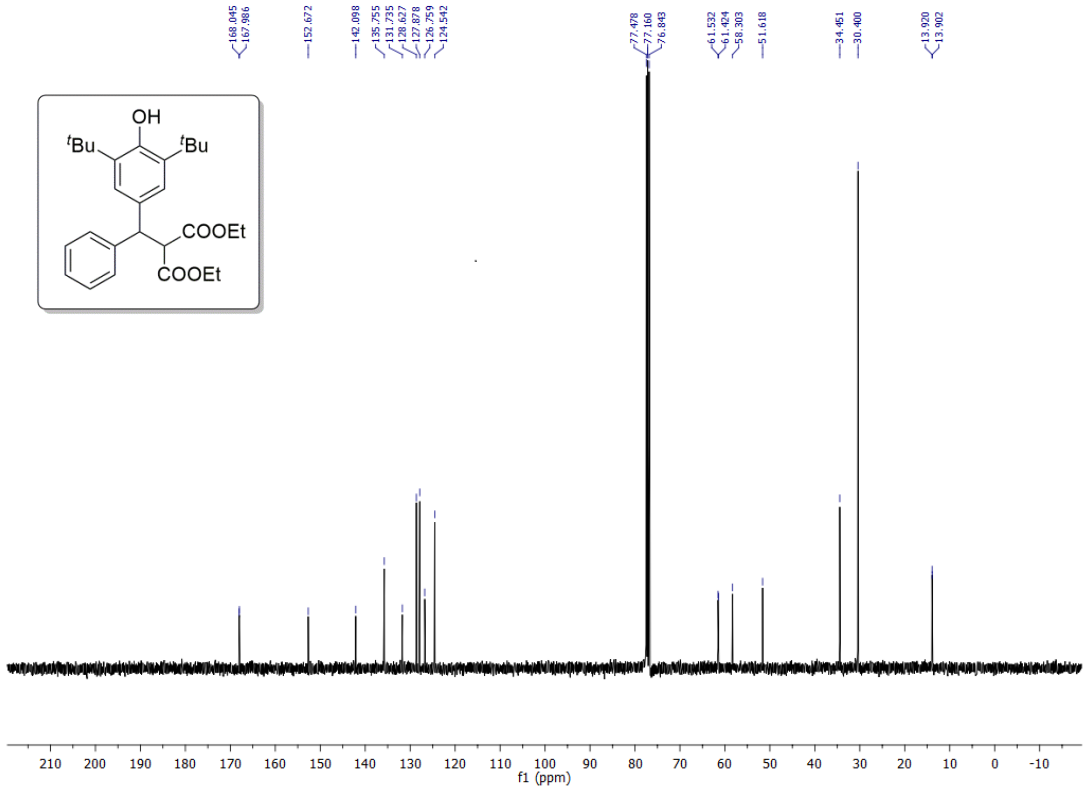
^{13}C NMR of 31e



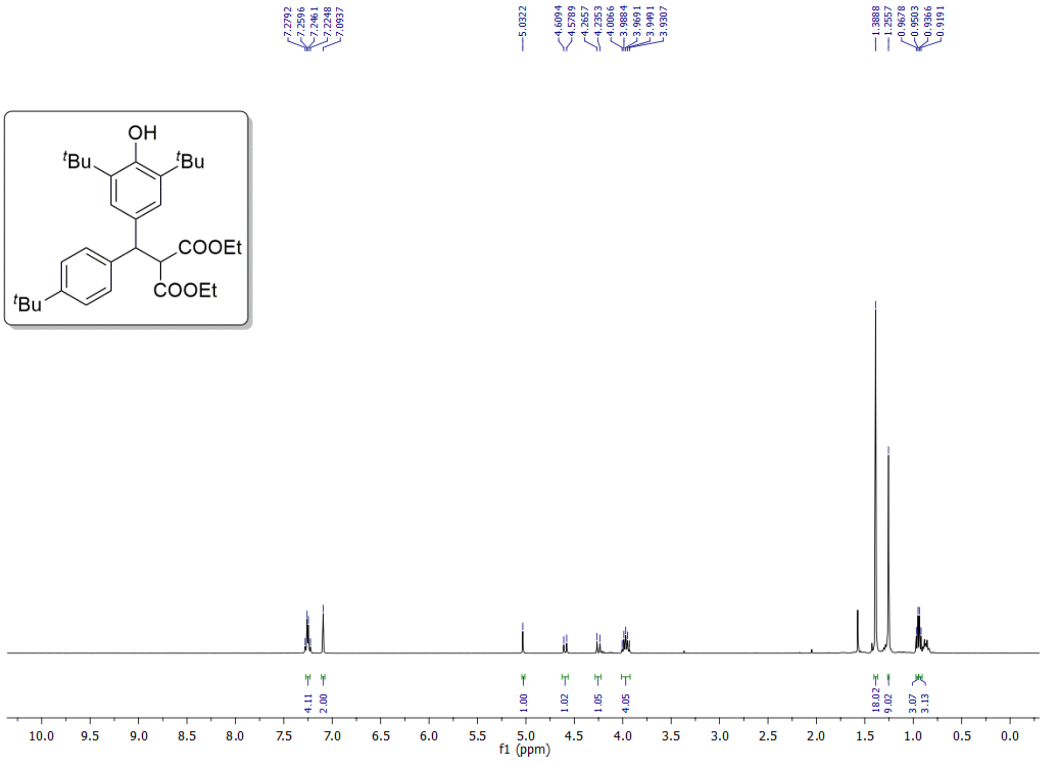
^{1}H NMR of 31f



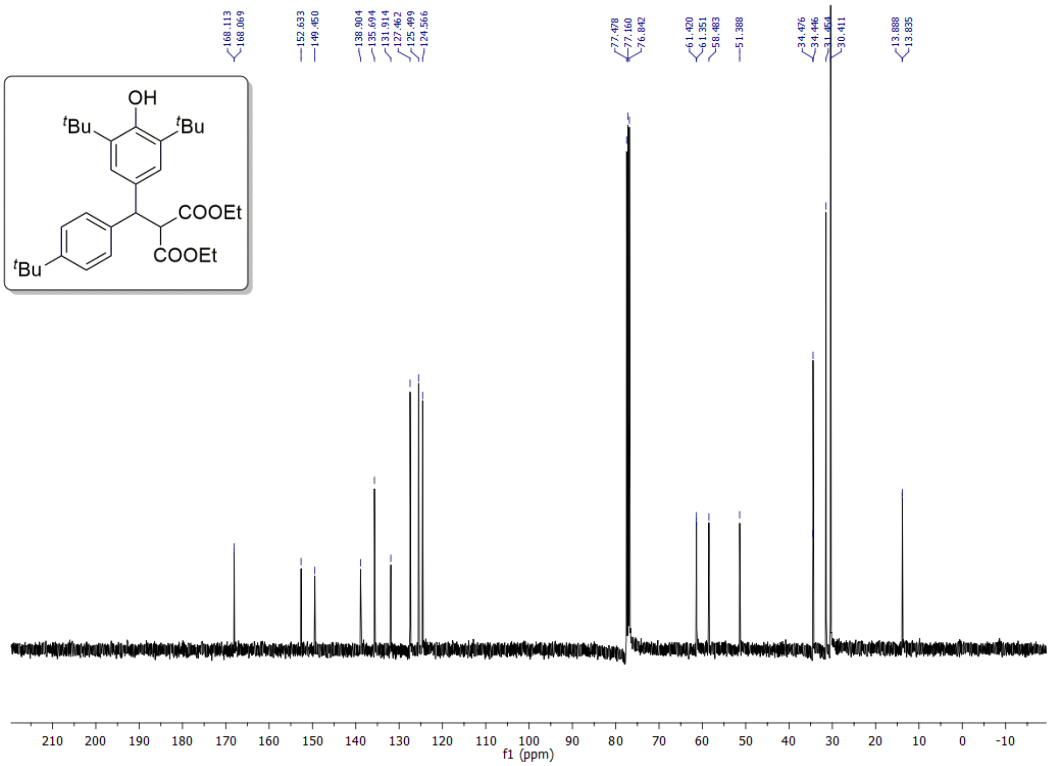
^{13}C NMR of 31f



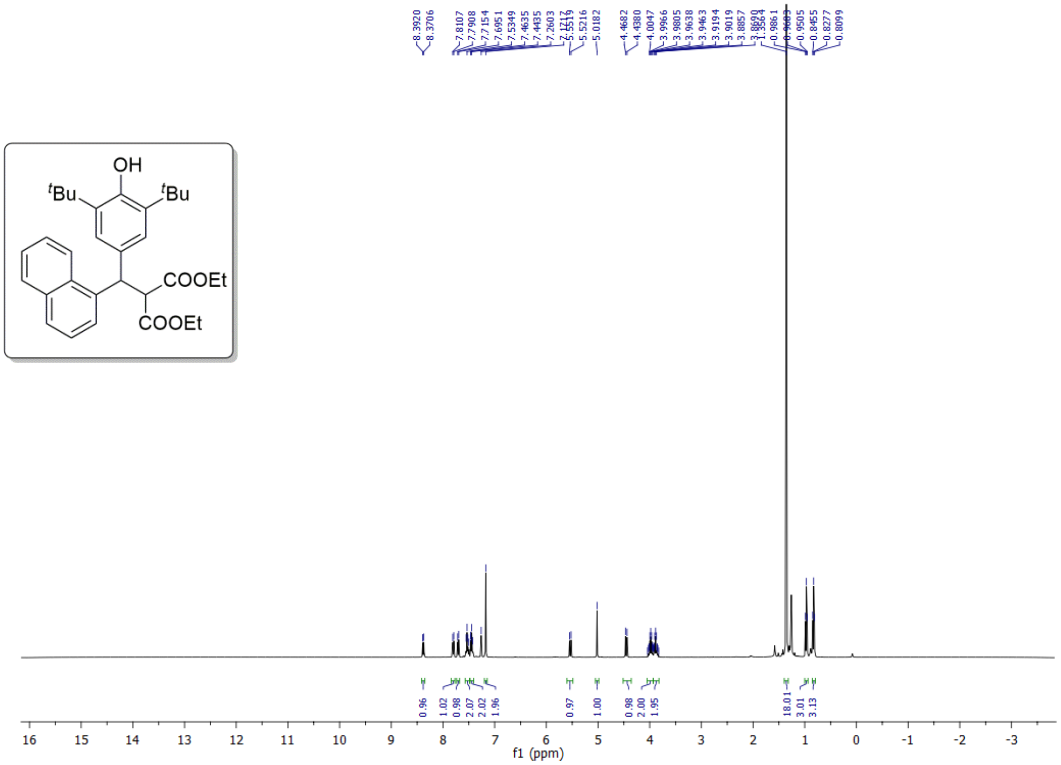
^{1}H NMR of 31g



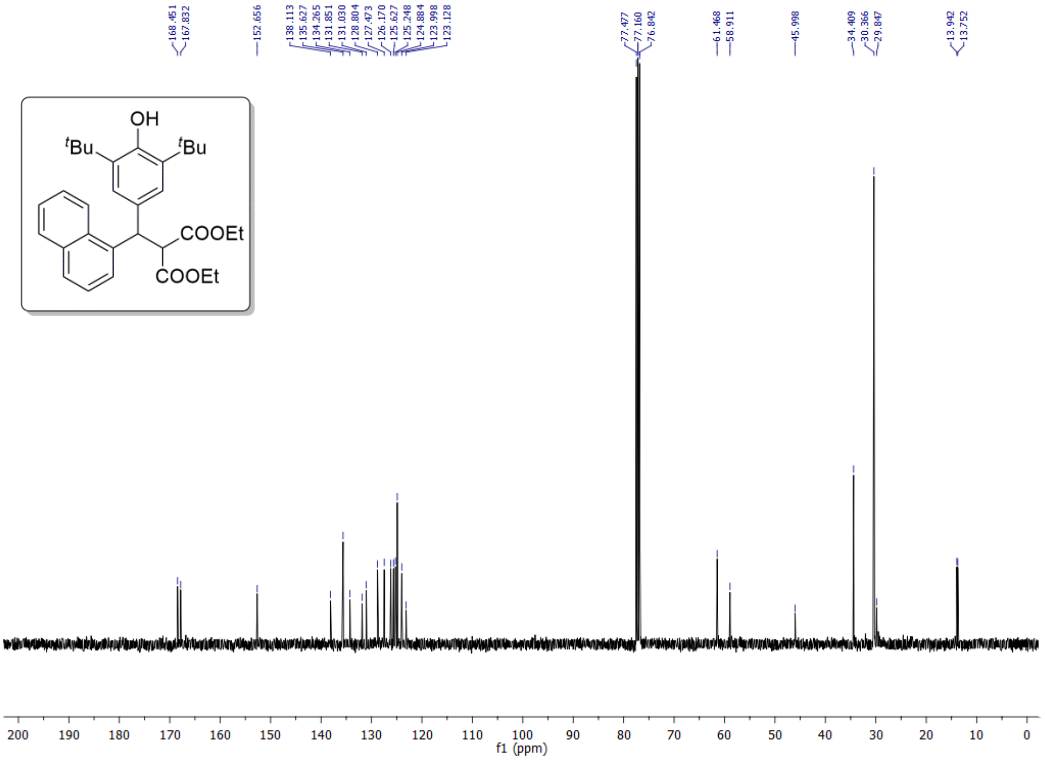
^{13}C NMR of 31g



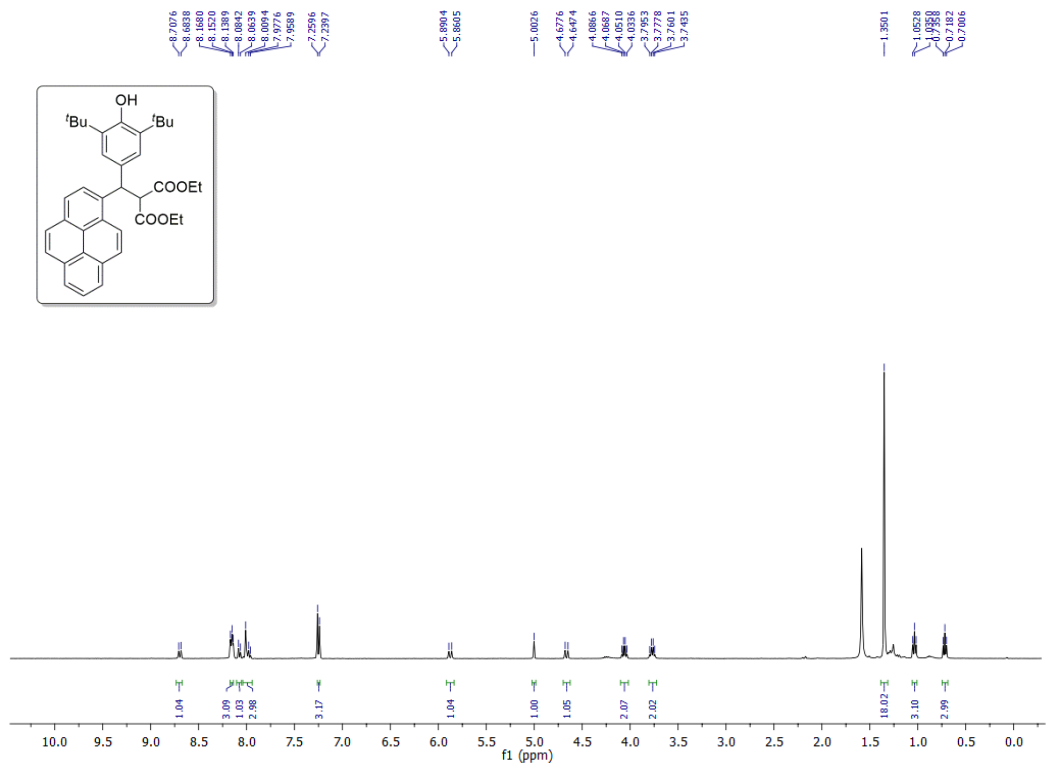
1H NMR of 31h



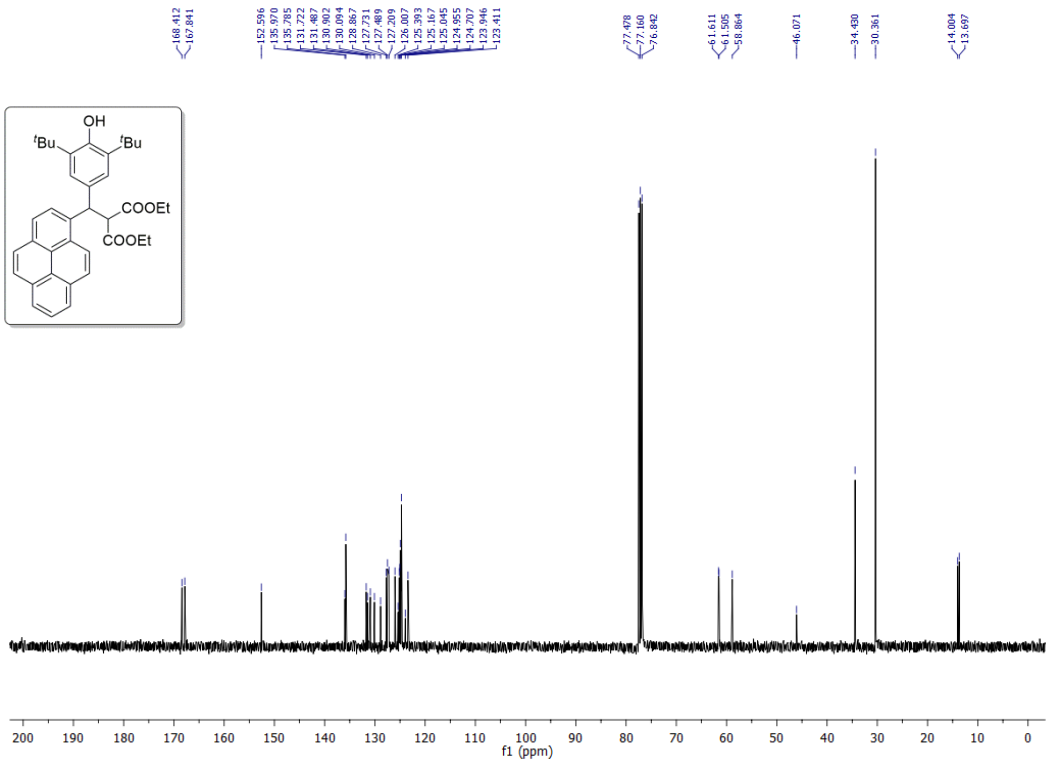
^{13}C NMR of 31h



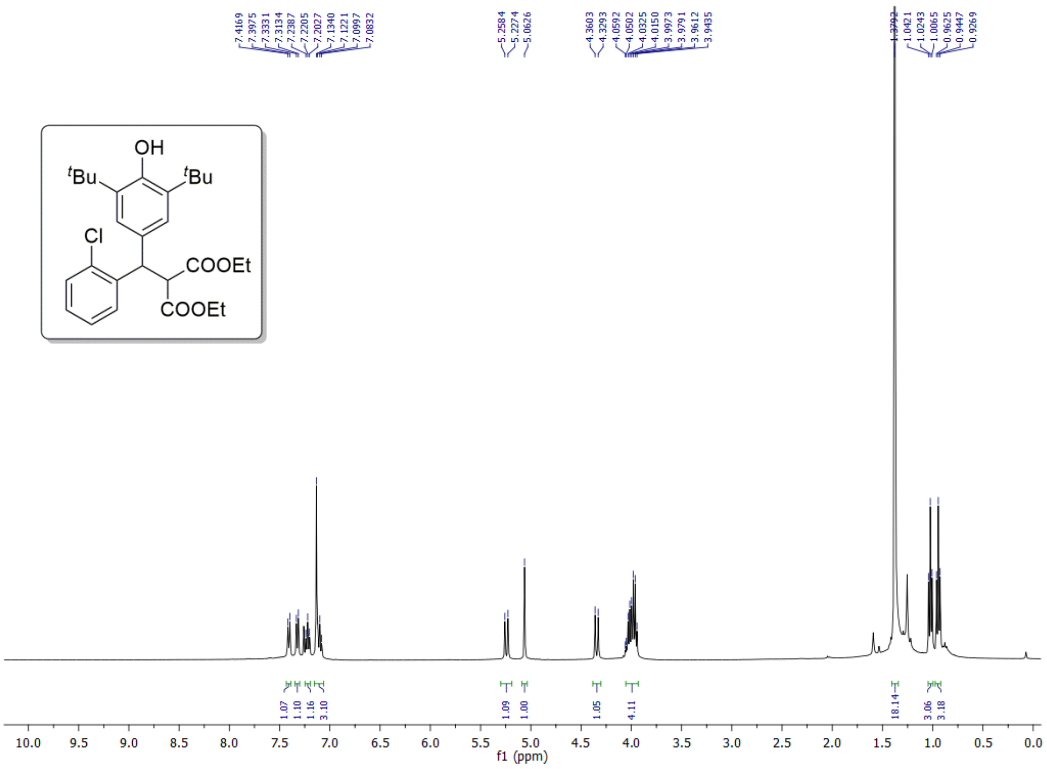
^{1}H NMR of 31i



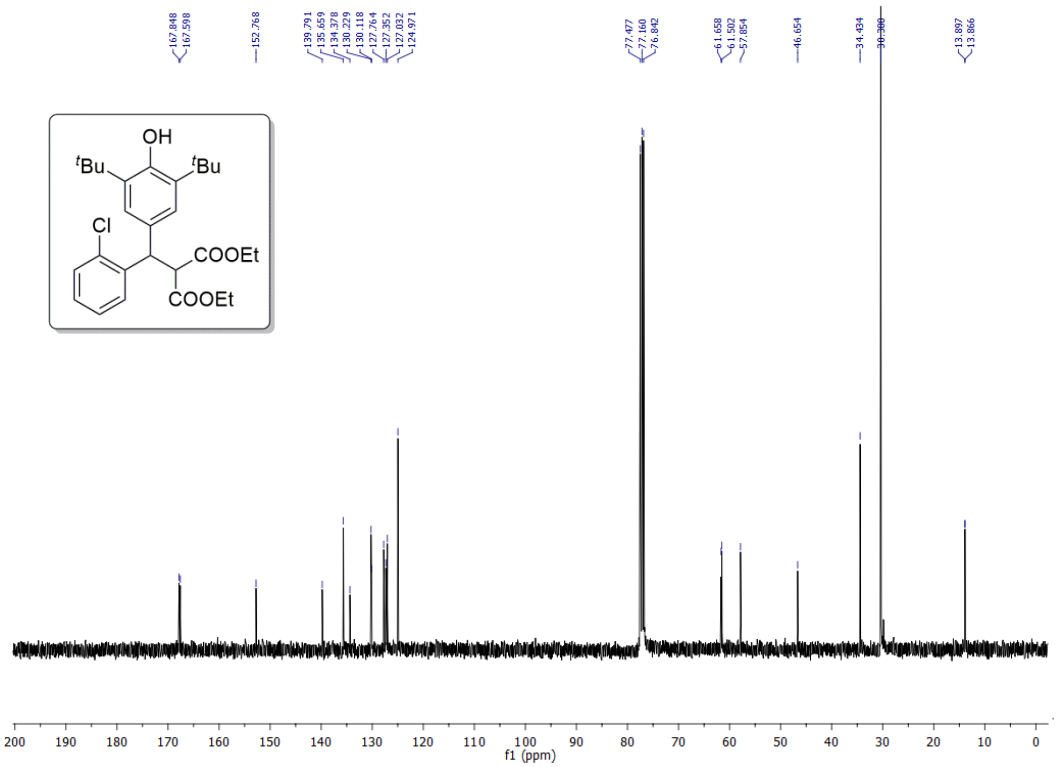
^{13}C NMR of 31i



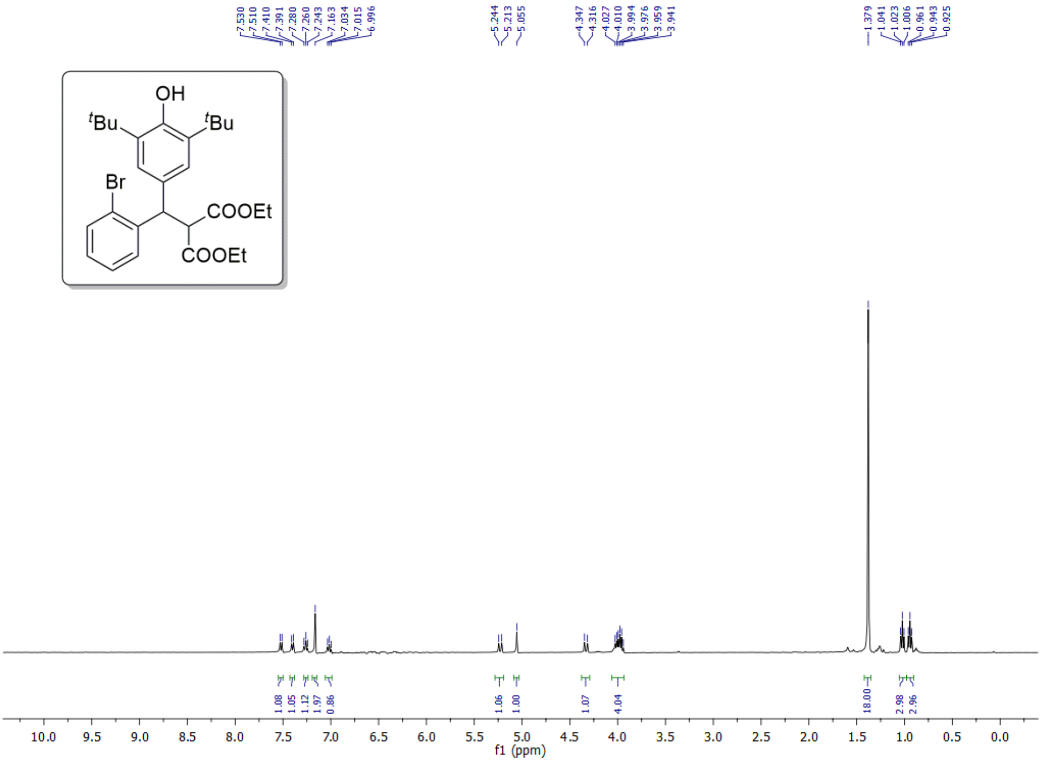
^{1}H NMR of 31j



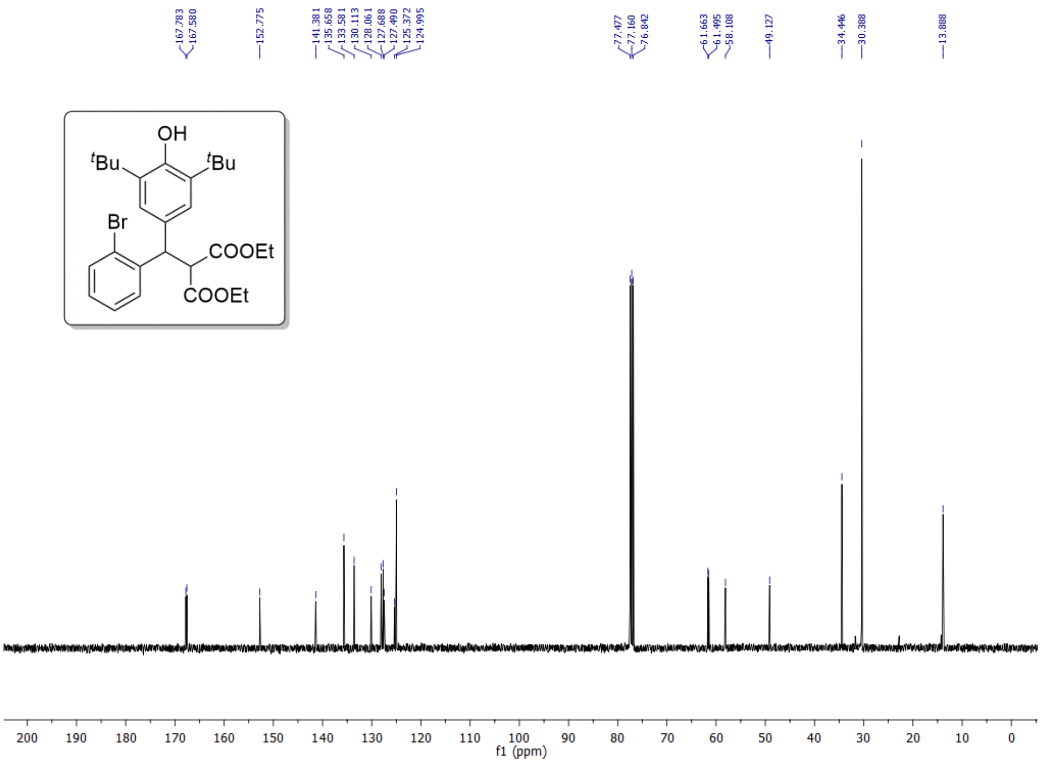
^{13}C NMR of 31j



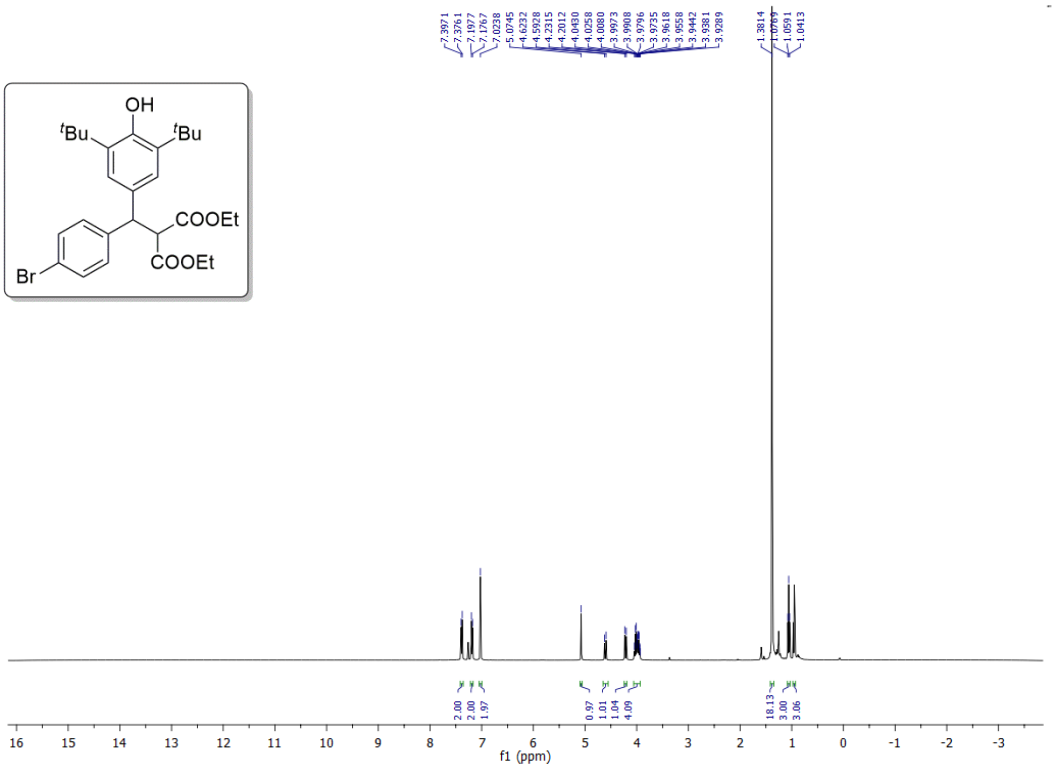
^{1}H NMR of 31k



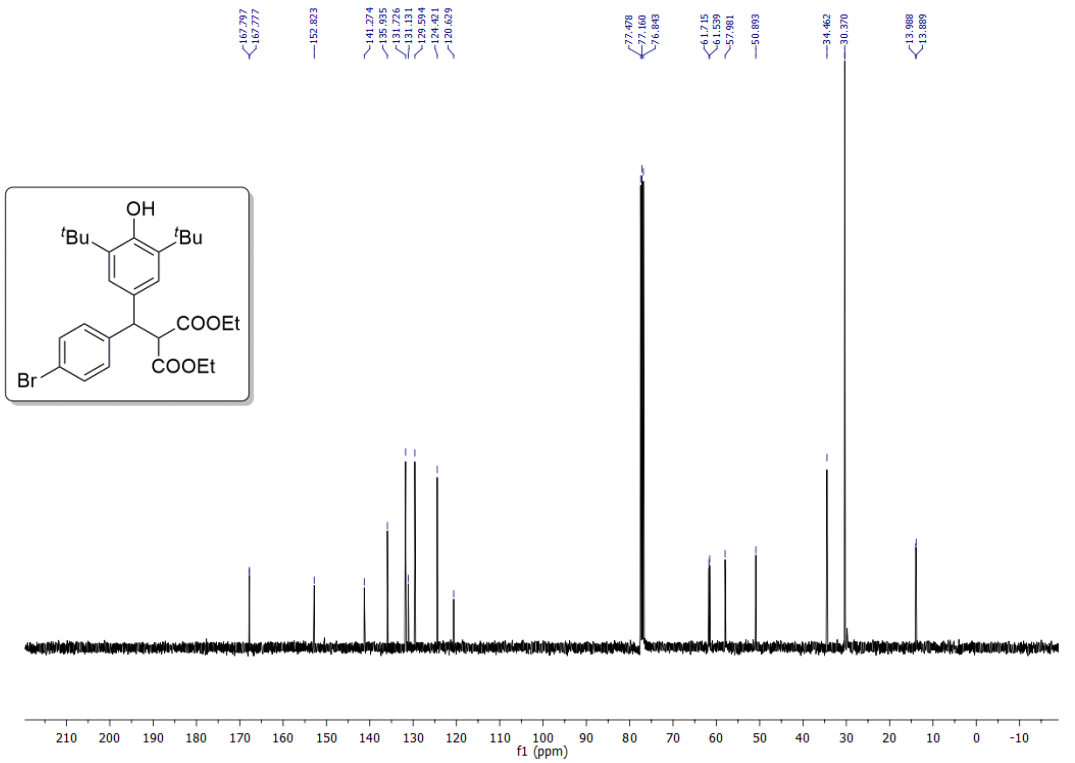
13C NMR of 31k



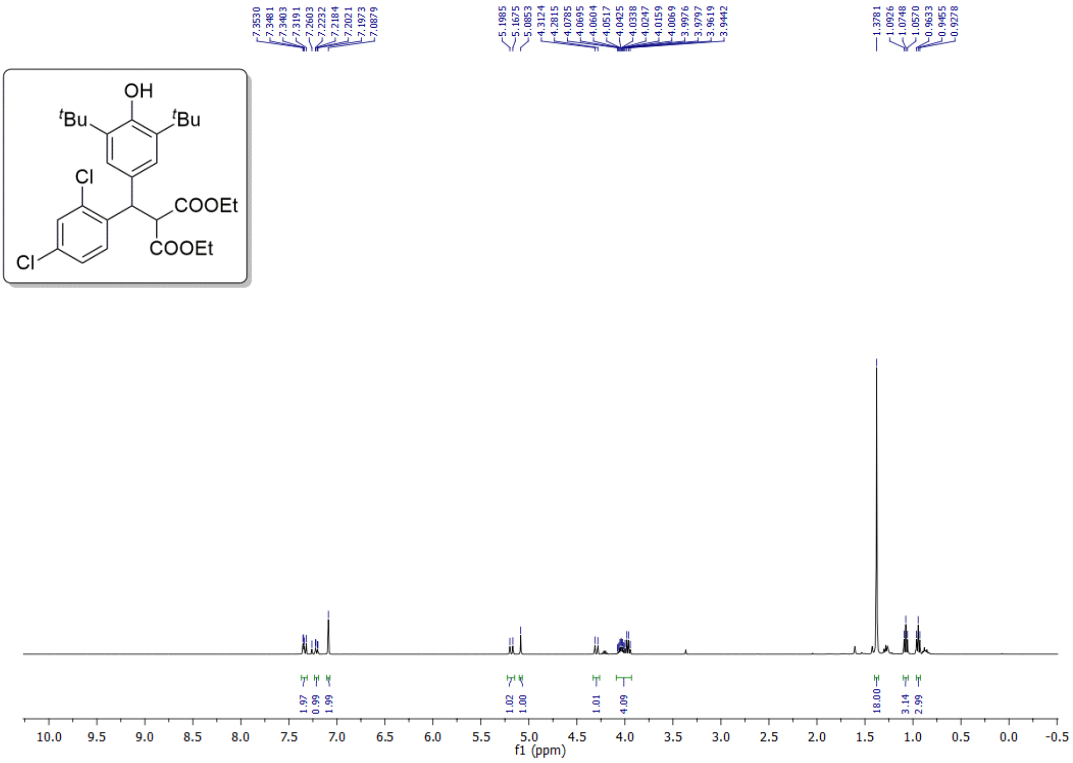
^{1}H NMR of 31l



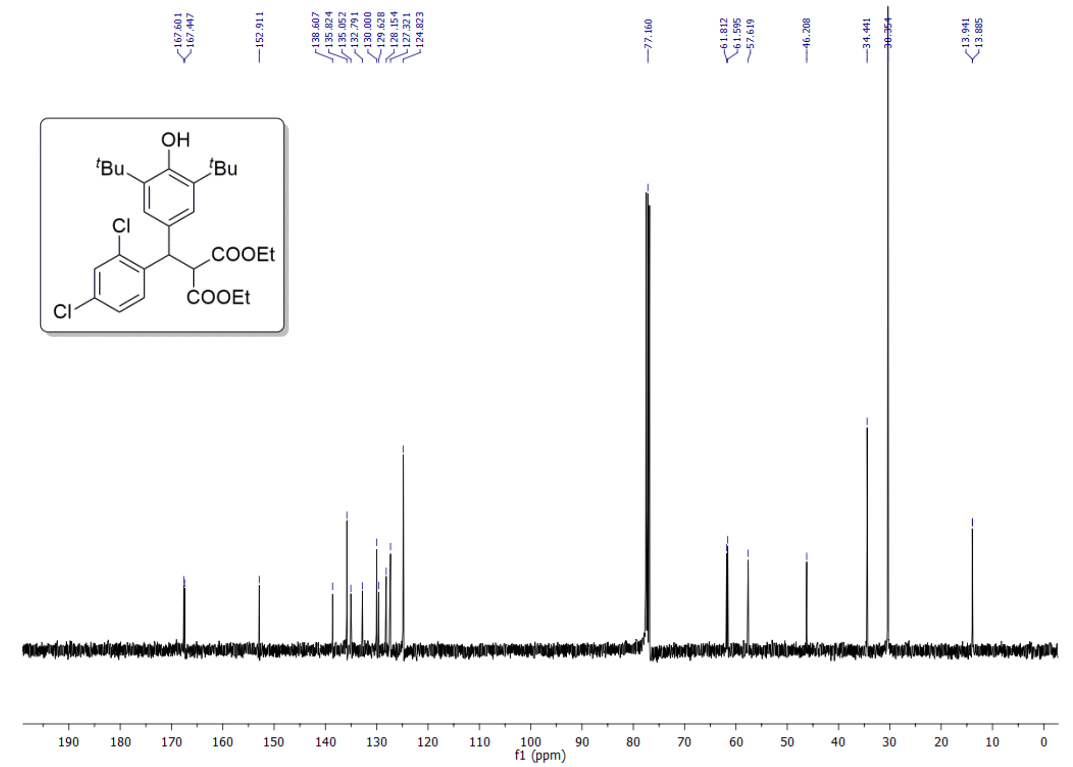
^{13}C NMR of 31l



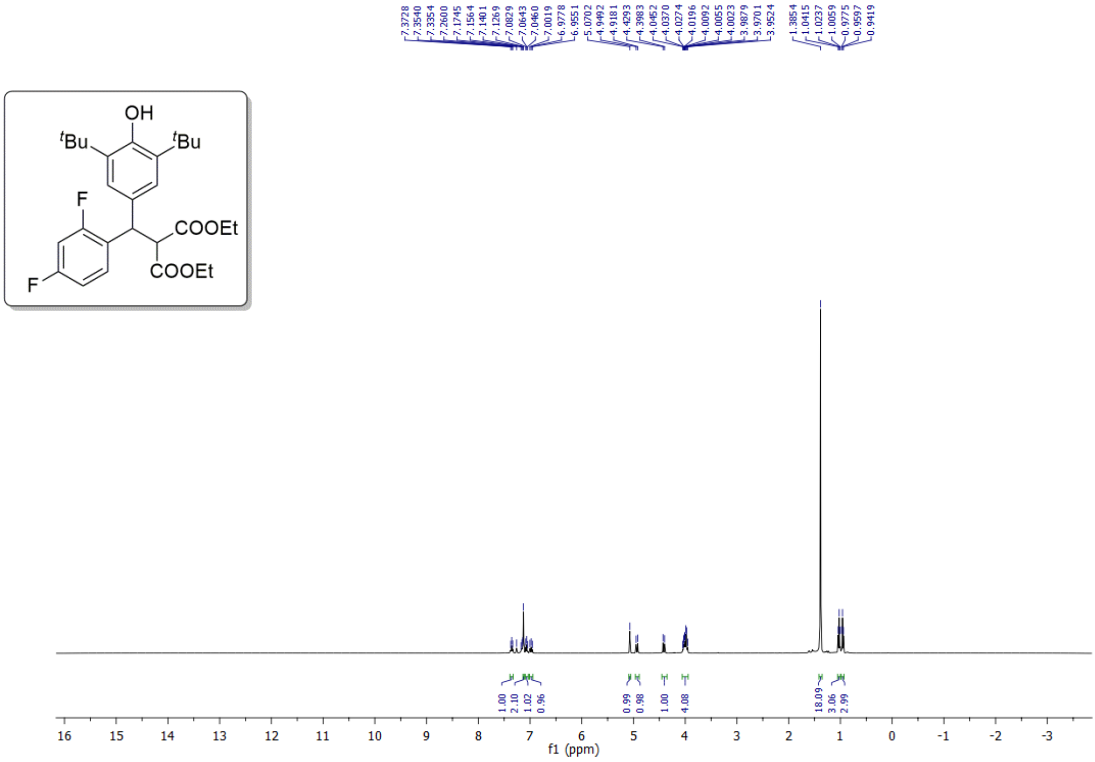
1H NMR of 31m



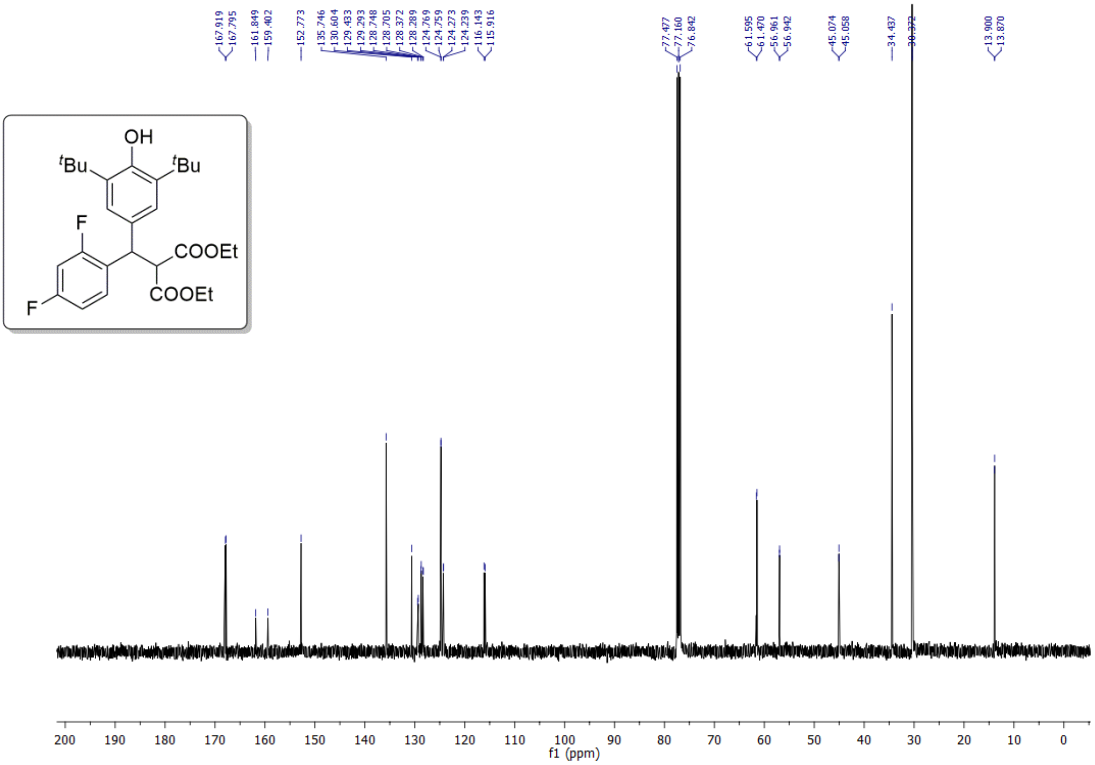
^{13}C NMR of 31m



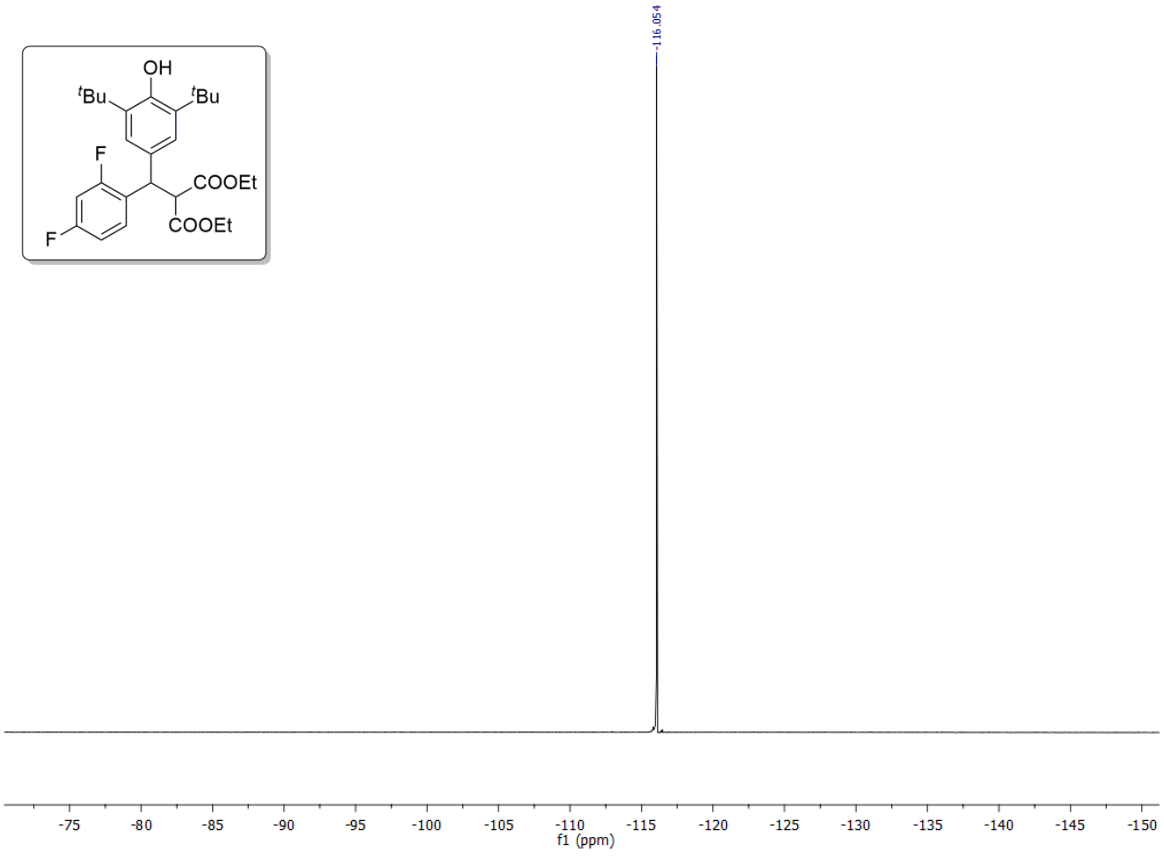
^{1}HNMR of 31n



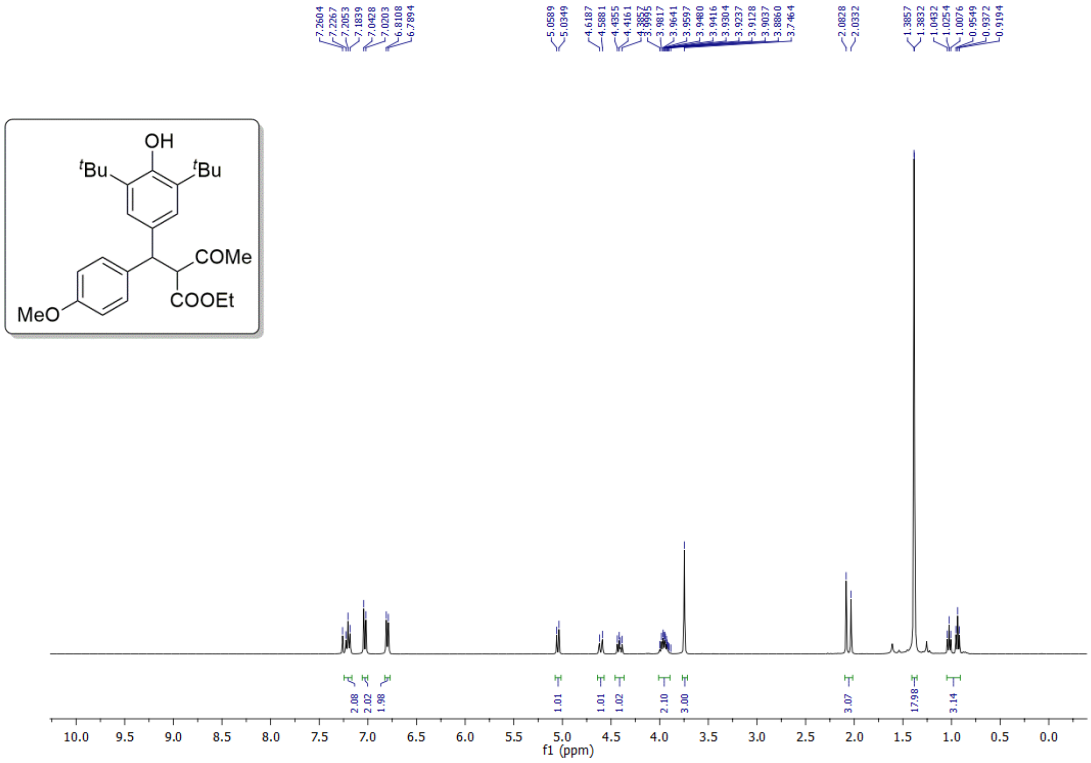
^{13}C NMR of 31n



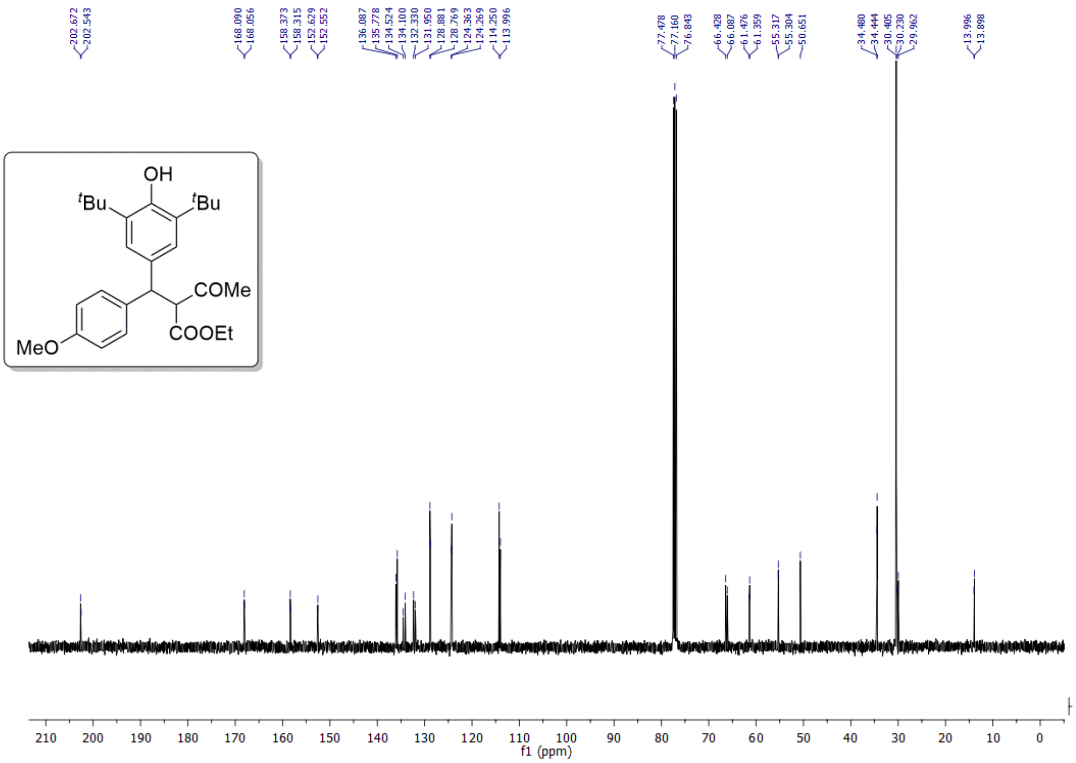
^{19}F NMR of 31n



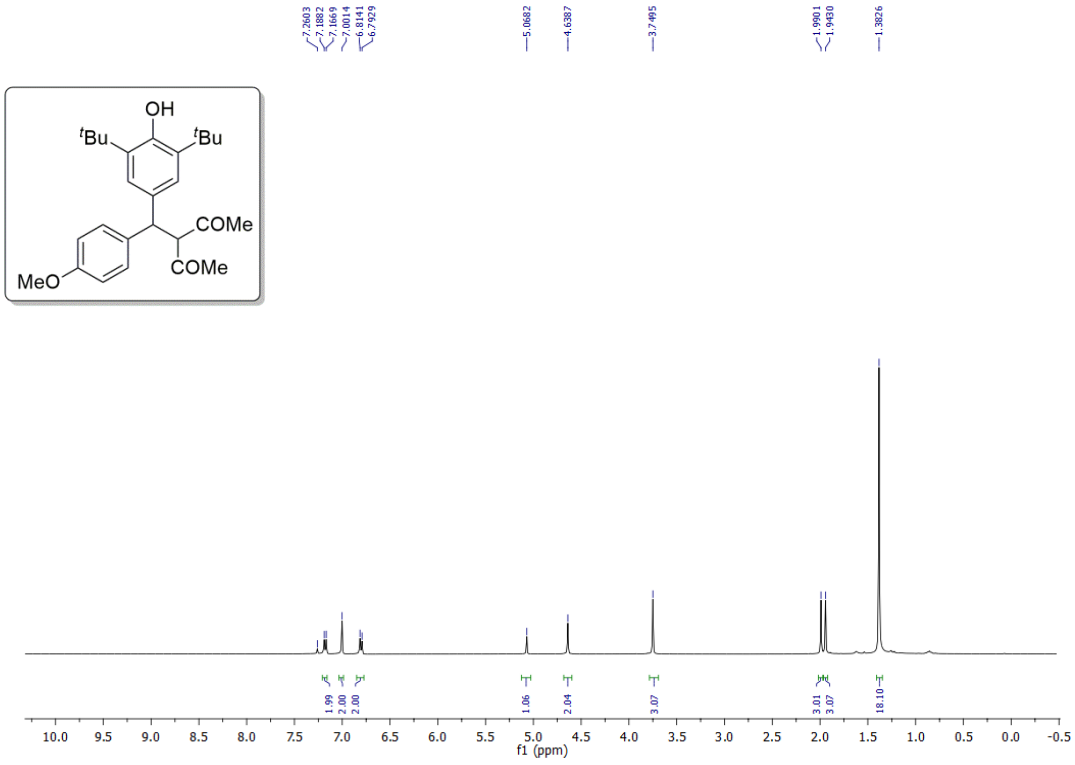
^{1}H NMR of 33a



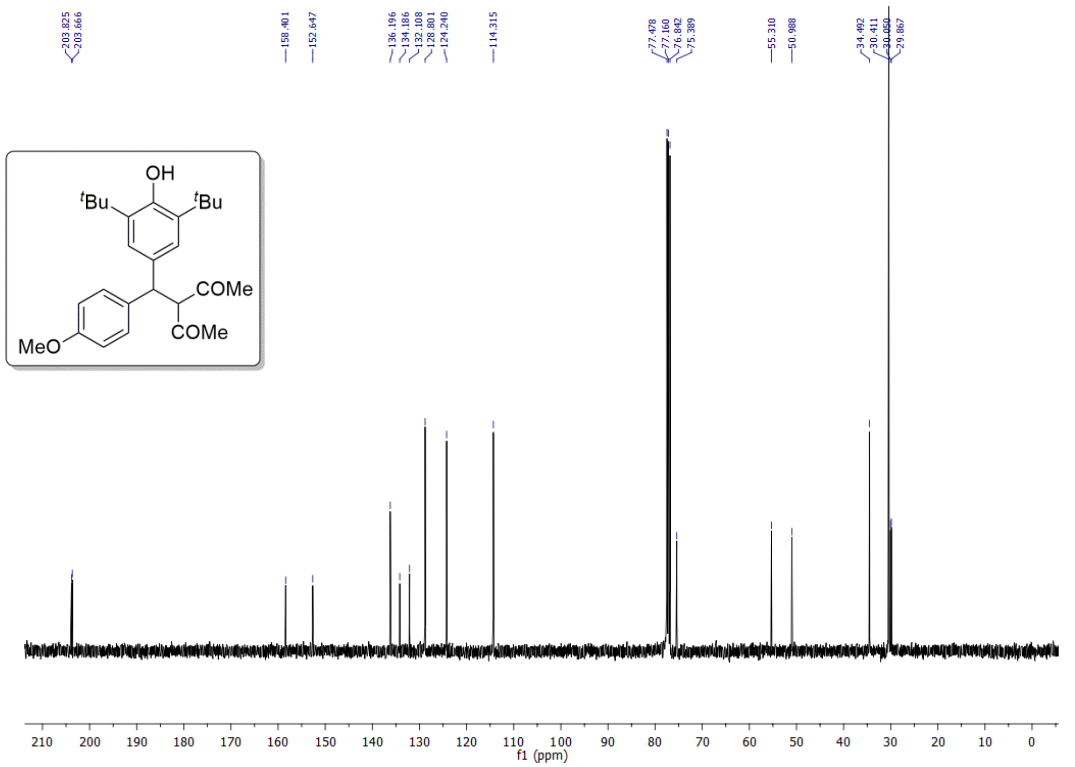
13C NMR of 33a



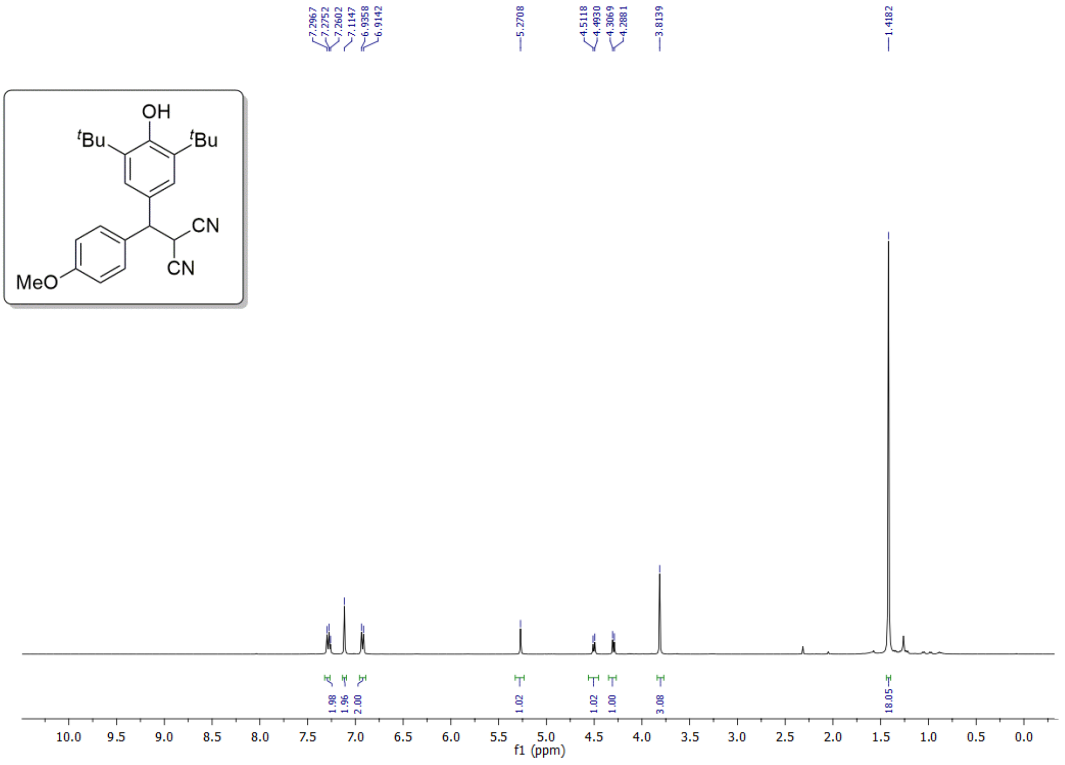
1H NMR of 33b



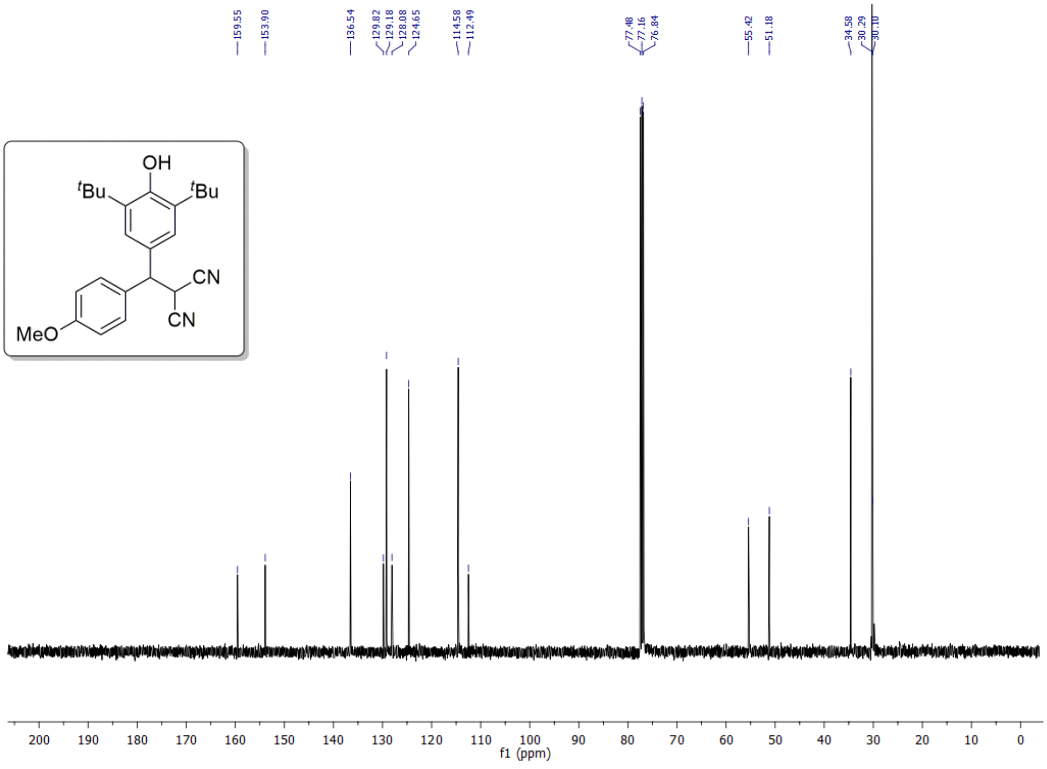
13C NMR of 33b



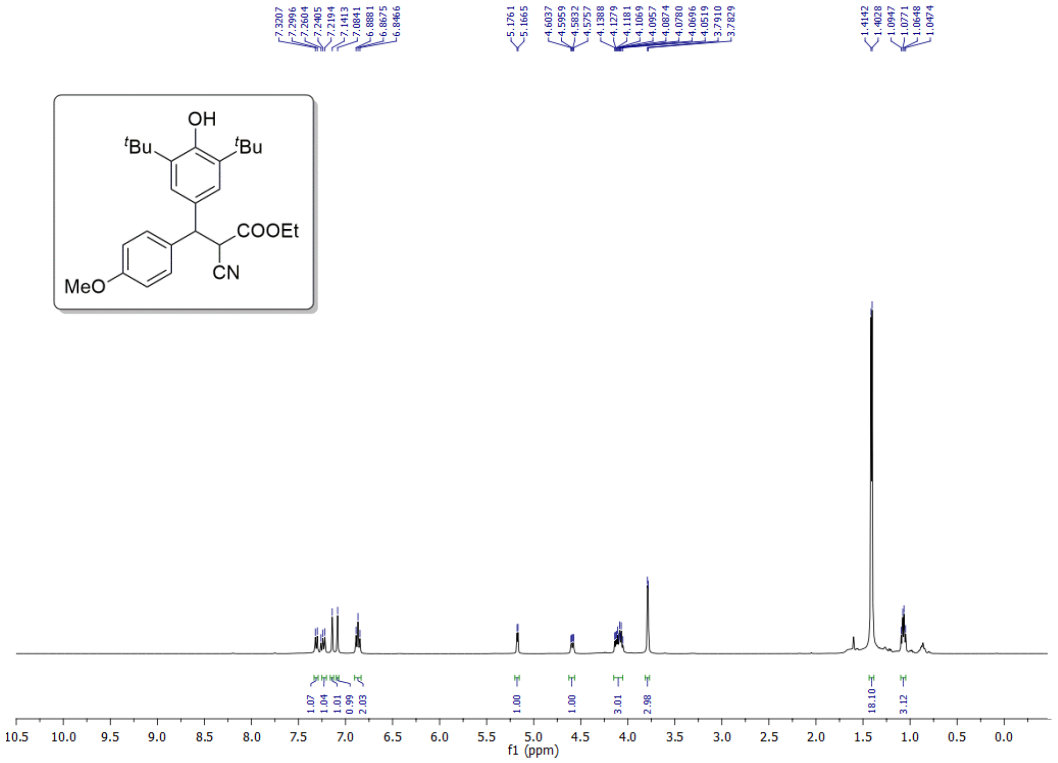
^{1}HNMR of 33c



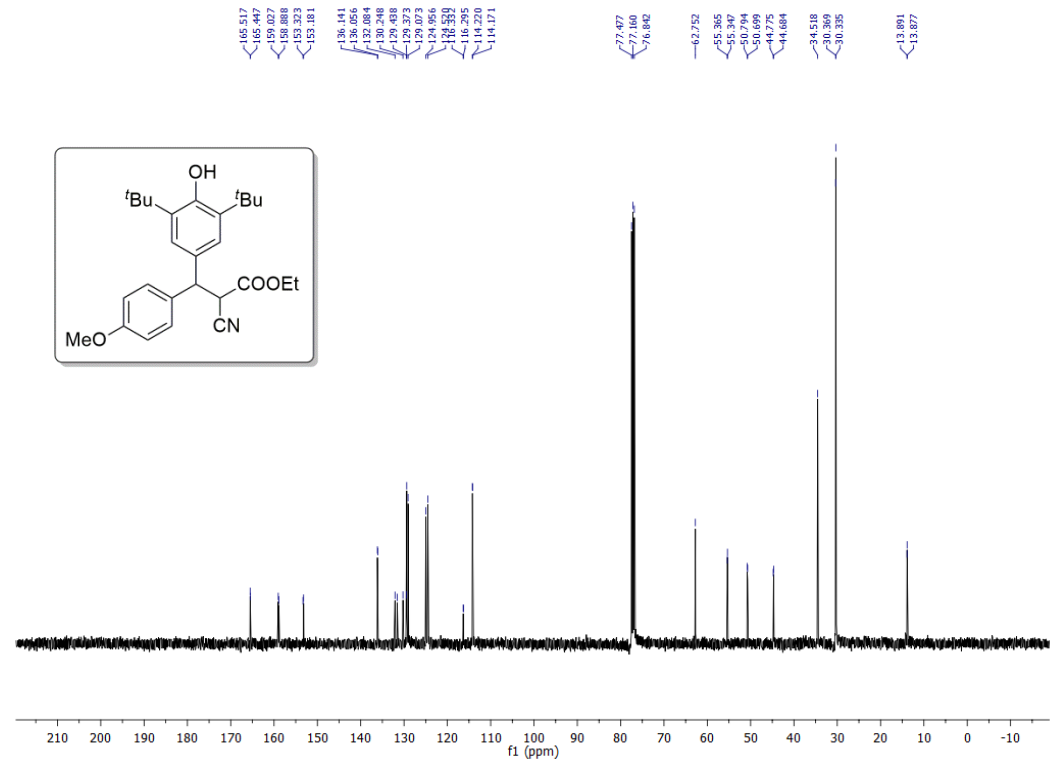
^{13}C NMR of 33c



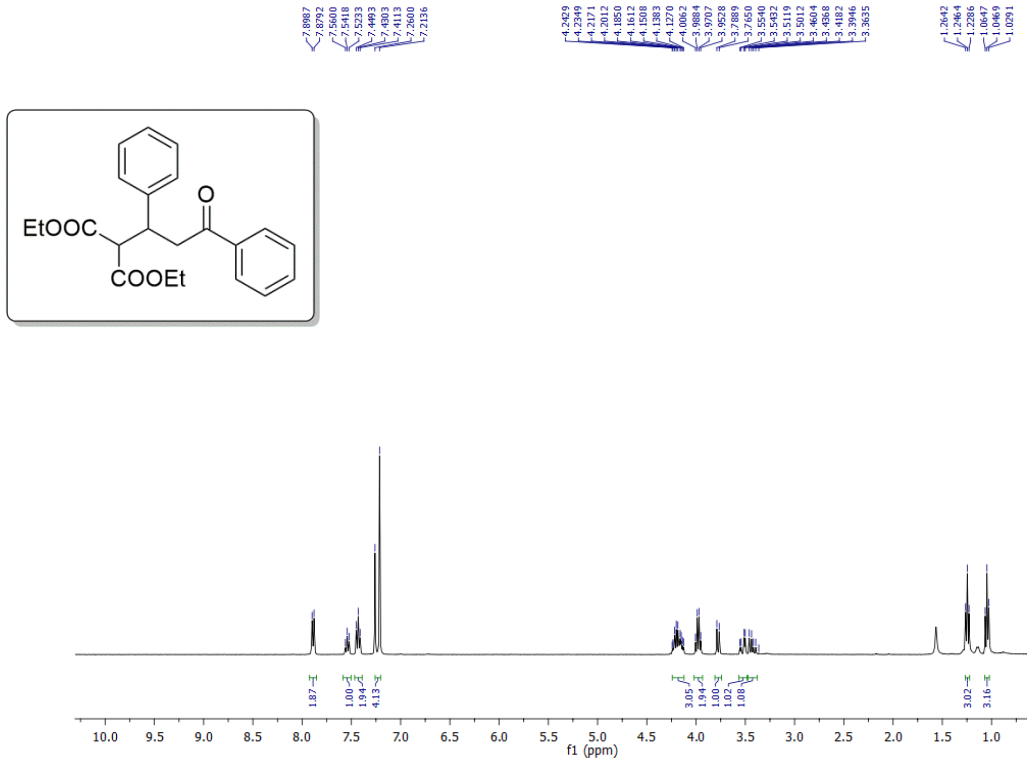
^{1}H NMR of 33d



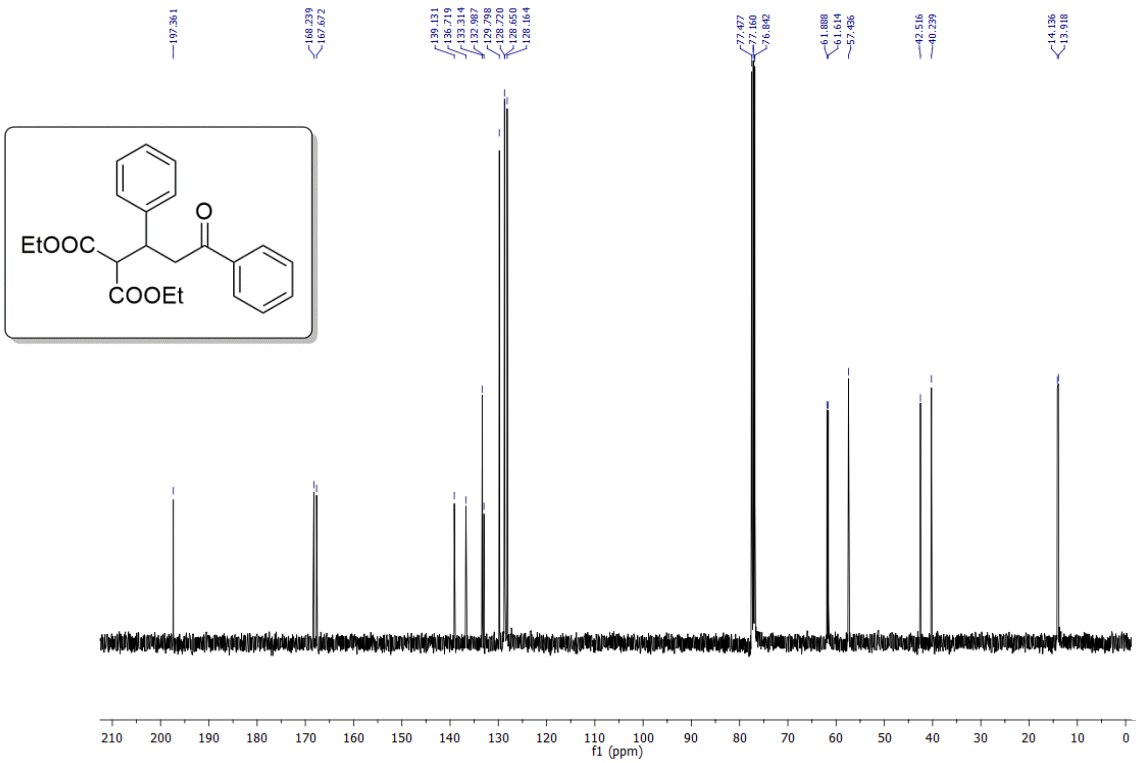
^{13}C NMR of 33d



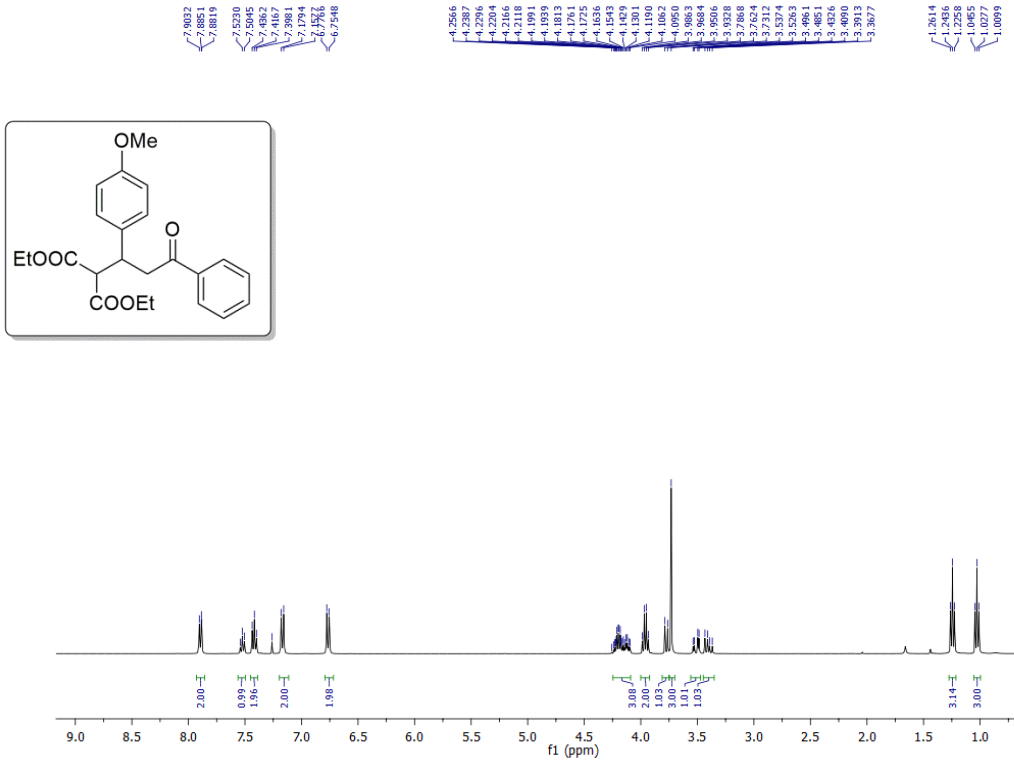
^{1}H NMR of 35a



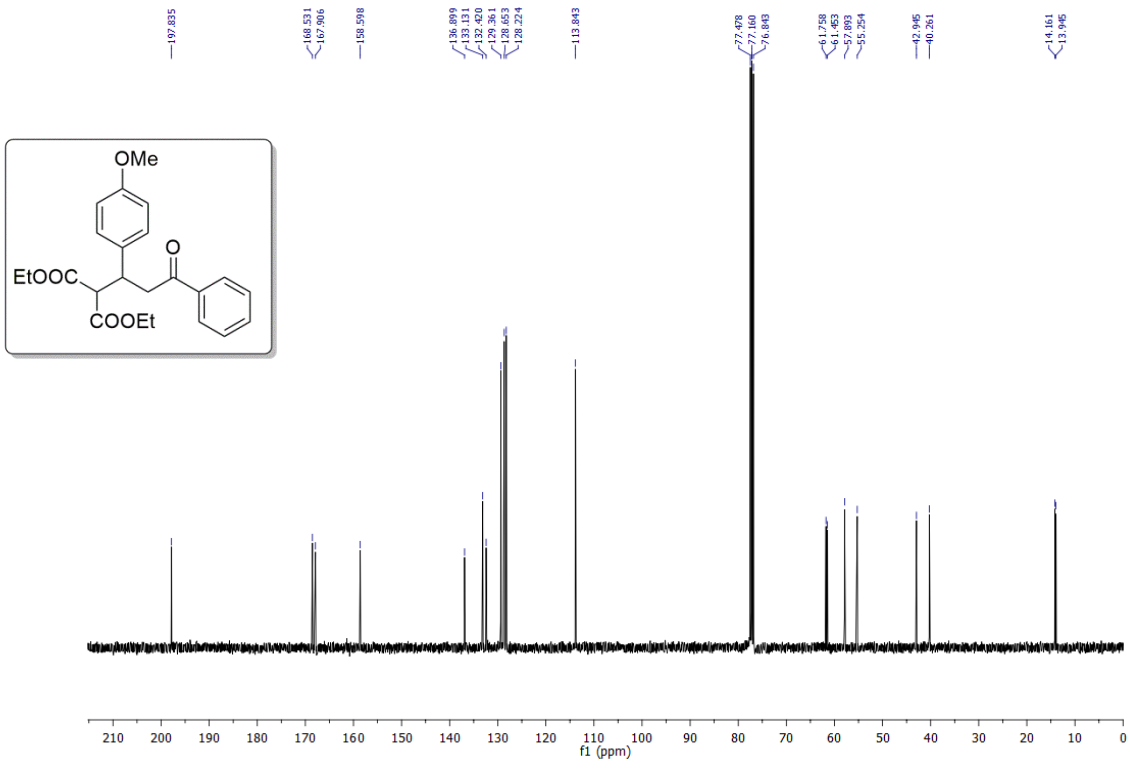
^{13}C NMR of 35a



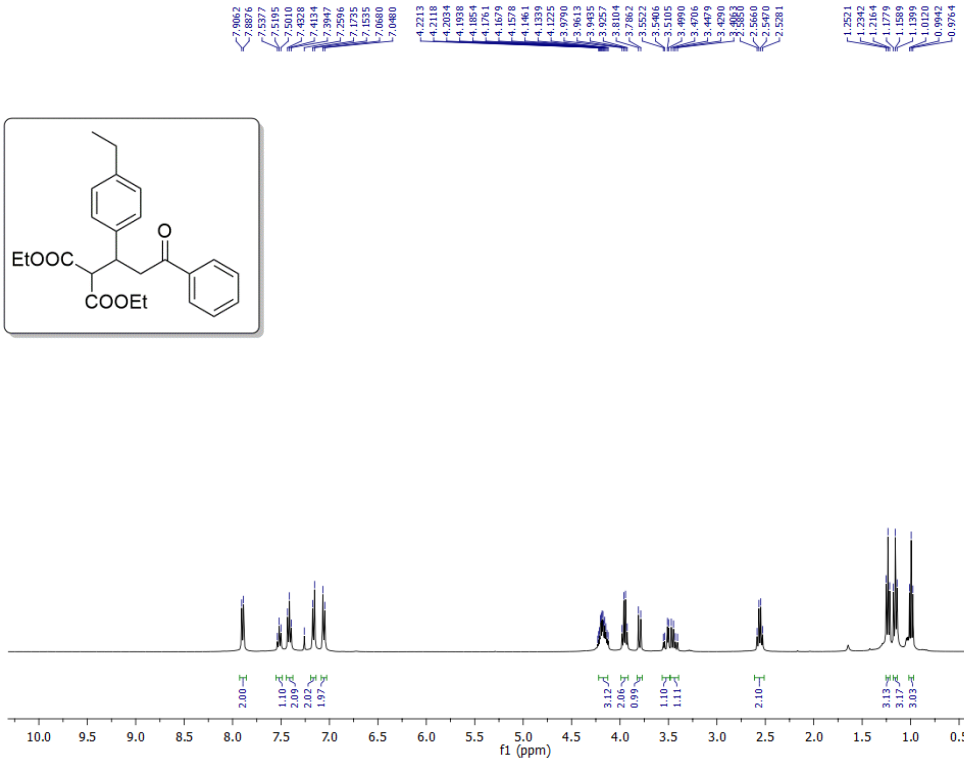
^{1}H NMR of 35b



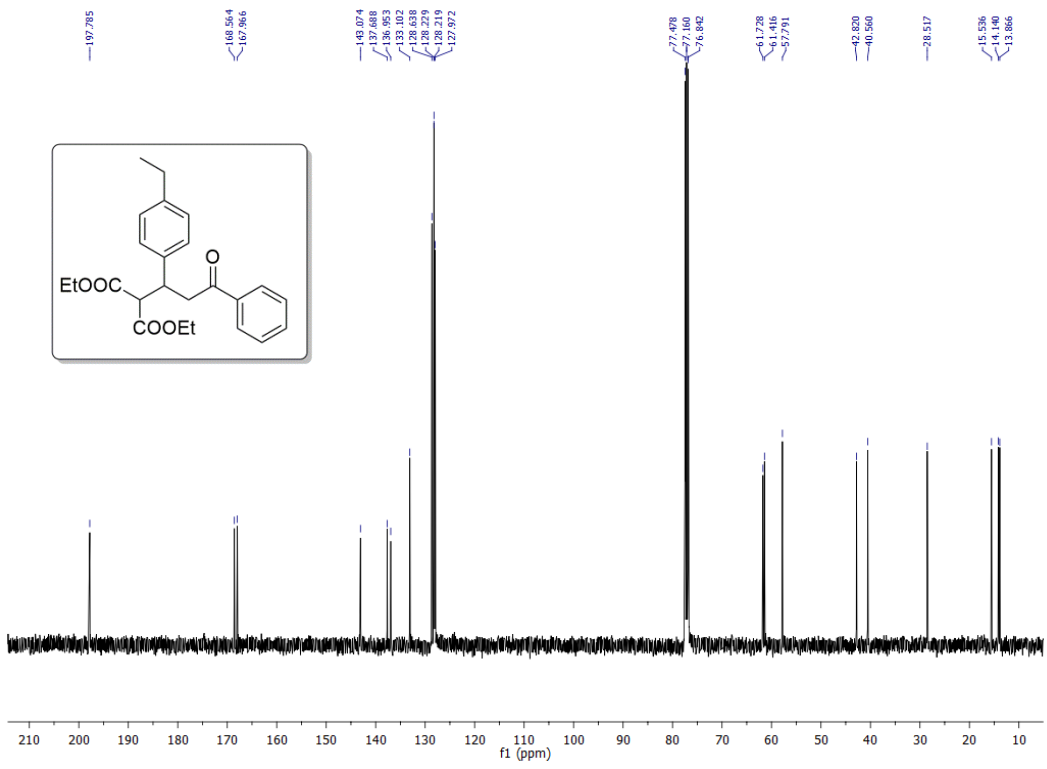
^{13}C NMR of 35b



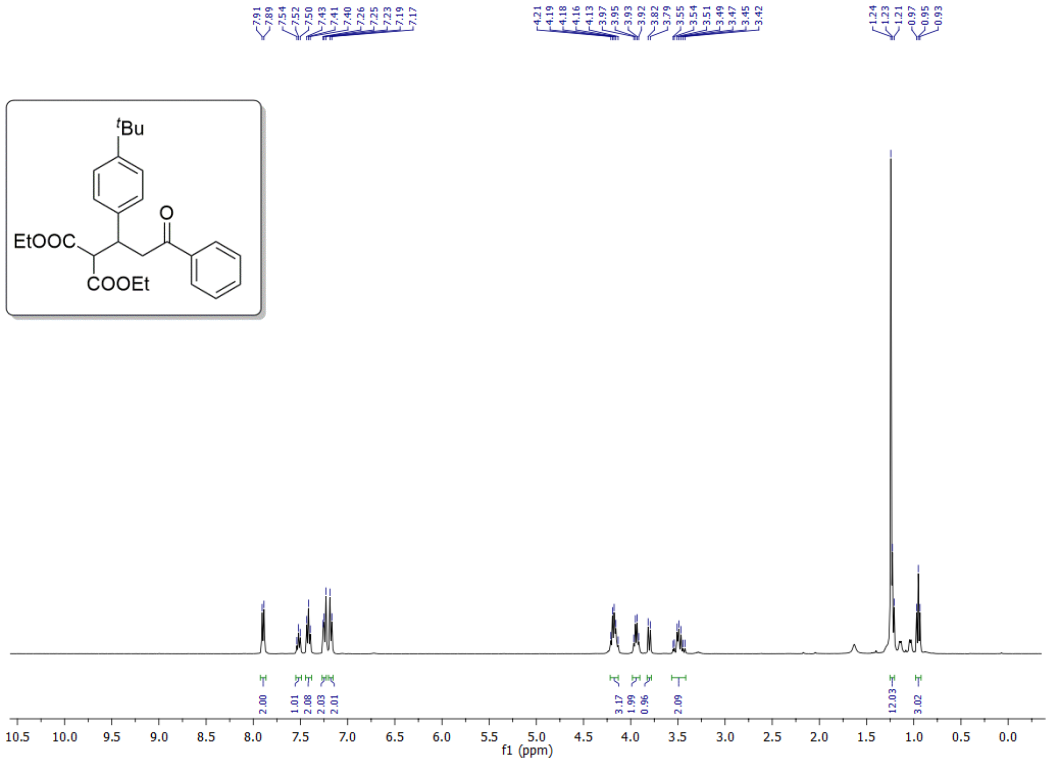
^{1}H NMR of 35c



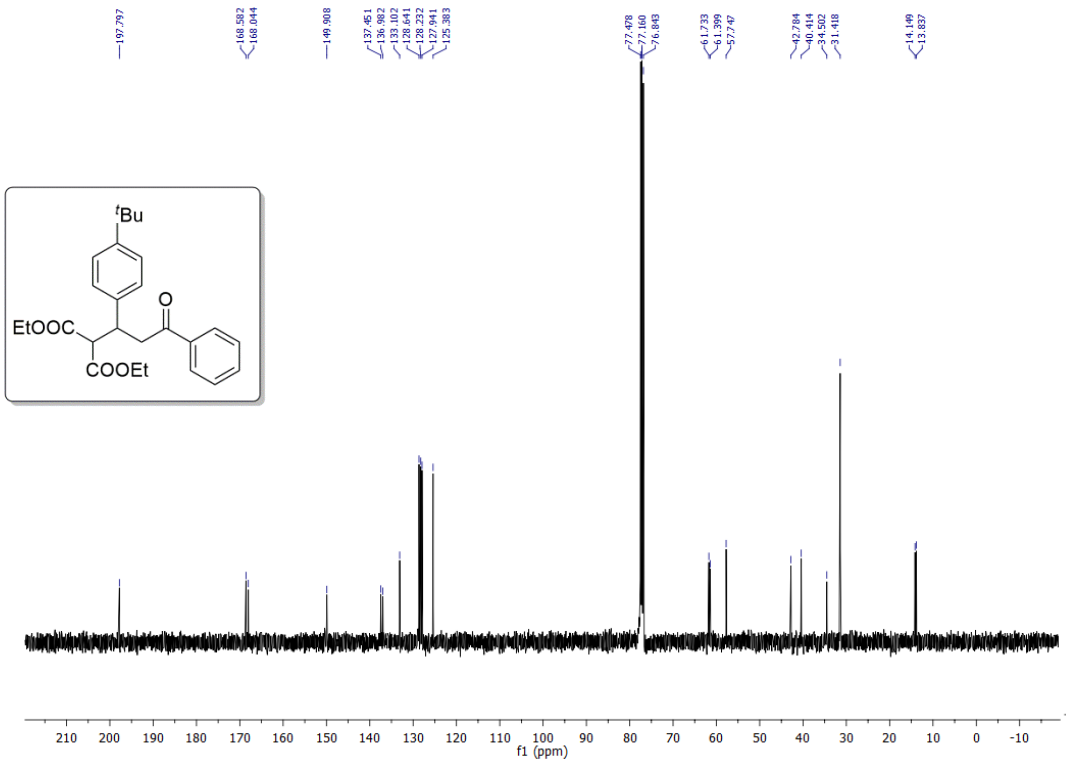
^{13}C NMR of 35c



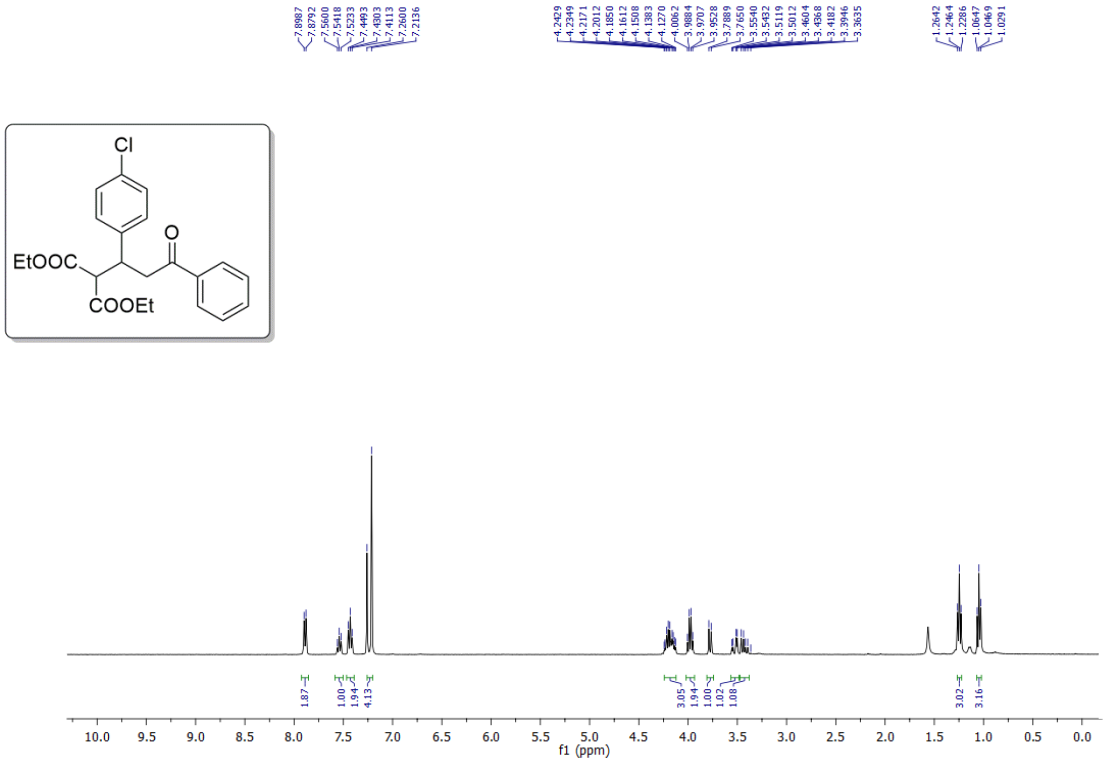
^{1}H NMR of 35d



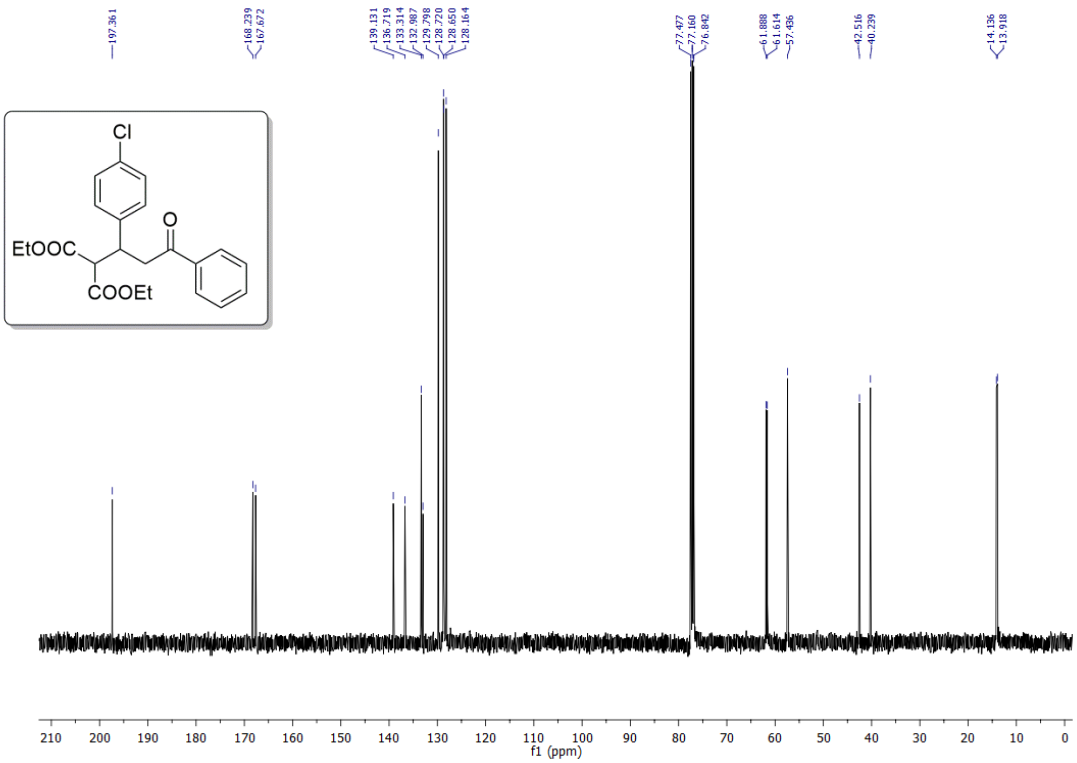
^{13}C NMR of 35d



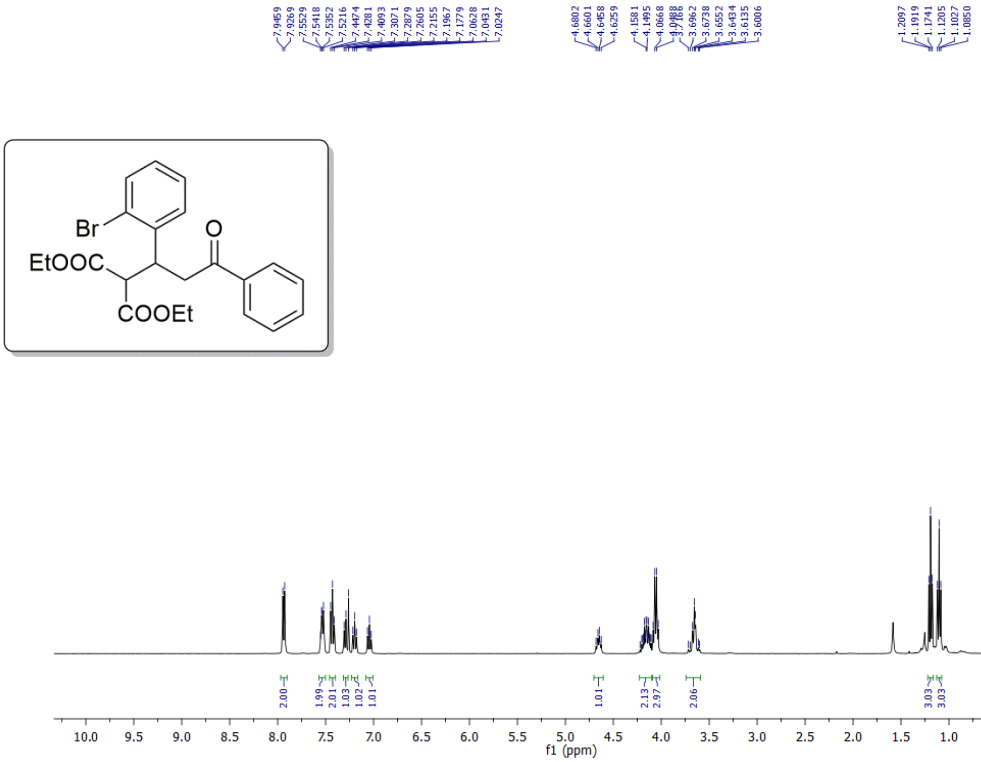
^{1}H NMR of 35e



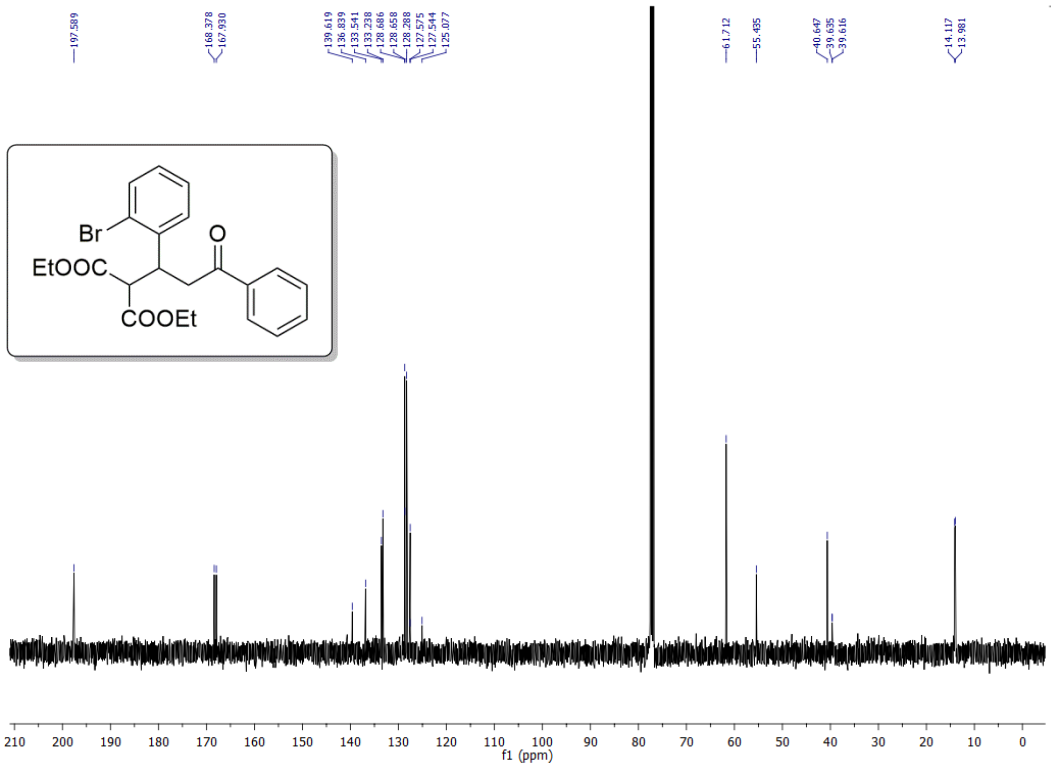
^{13}C NMR of 35e



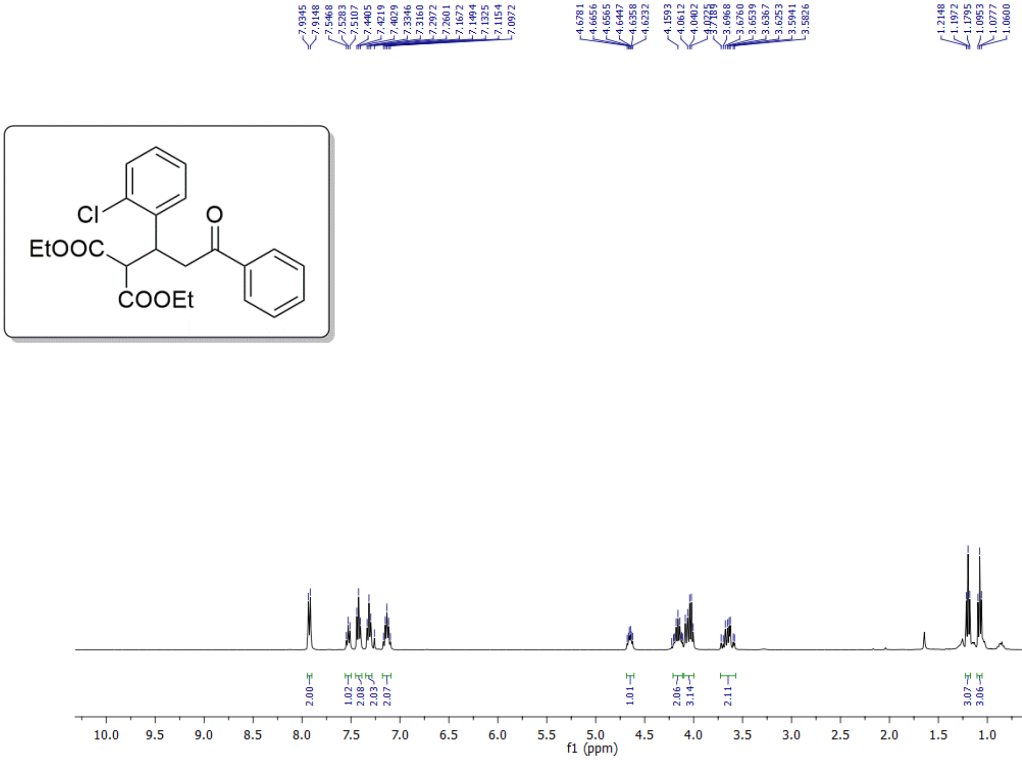
^{1}H NMR of 35f



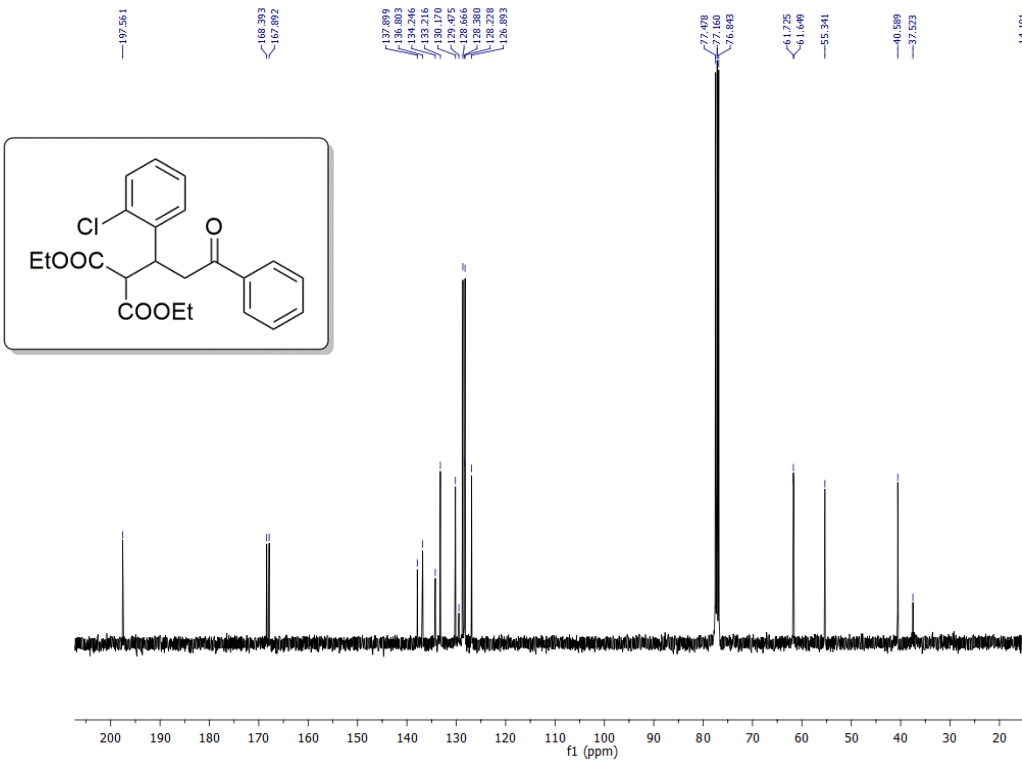
^{13}C NMR of 35f



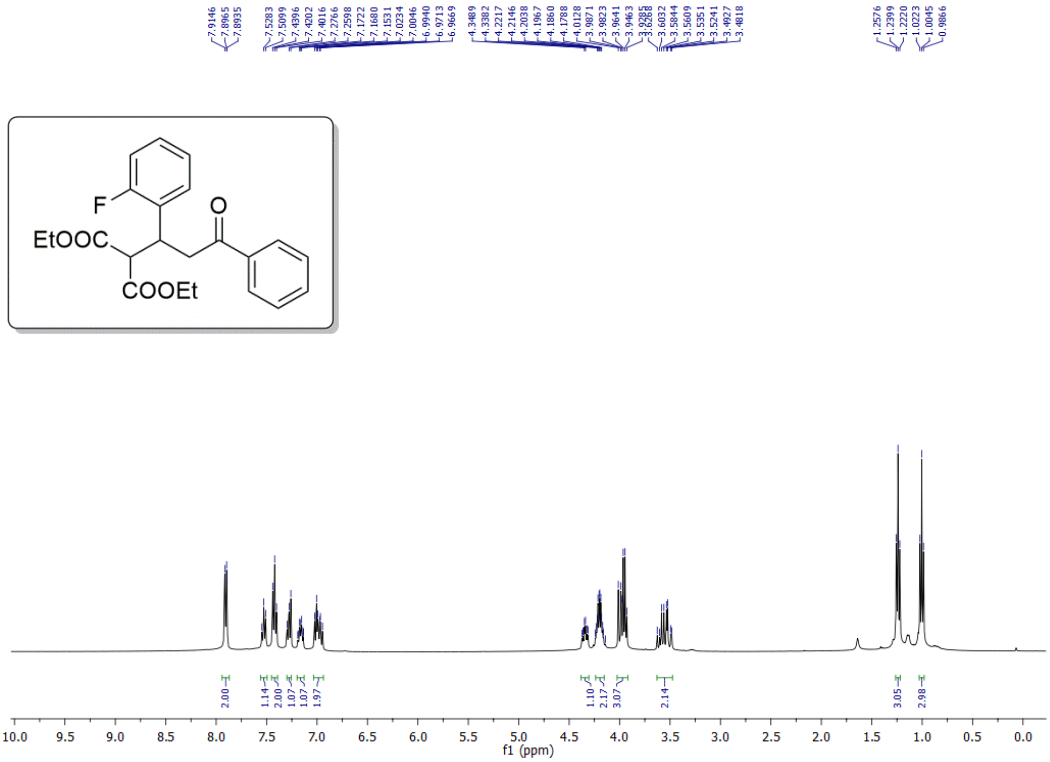
^{1}H NMR of 35g



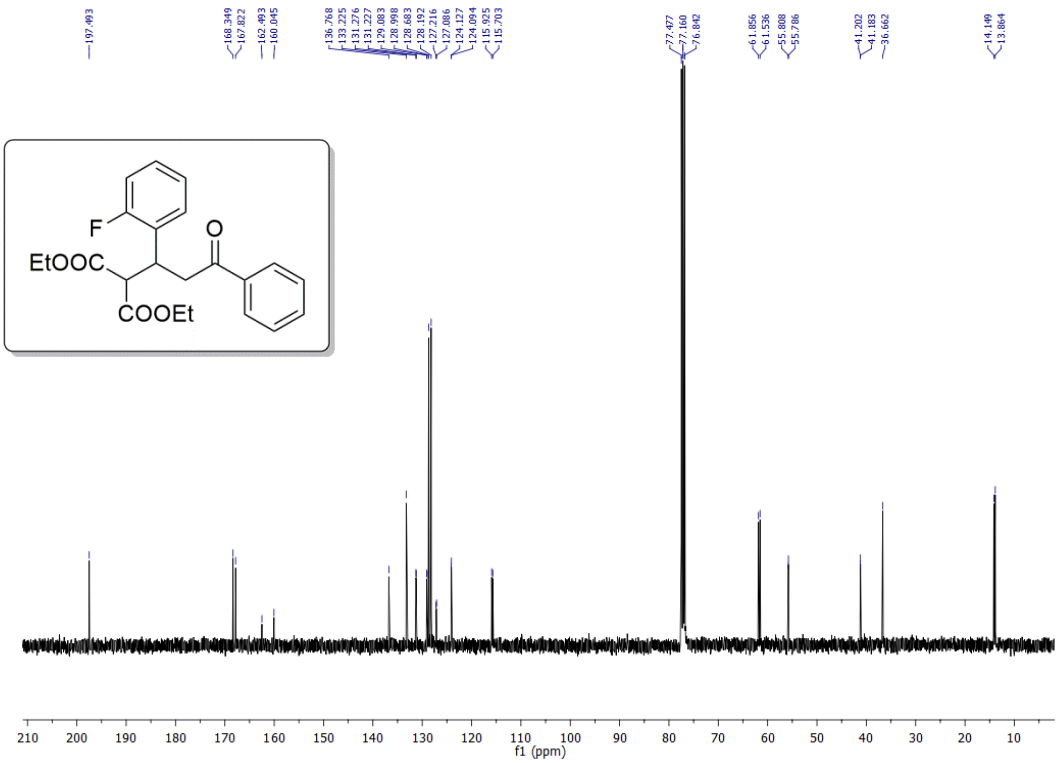
^{13}C NMR of 35g



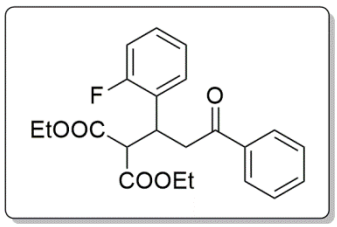
^{1}H NMR of 35h



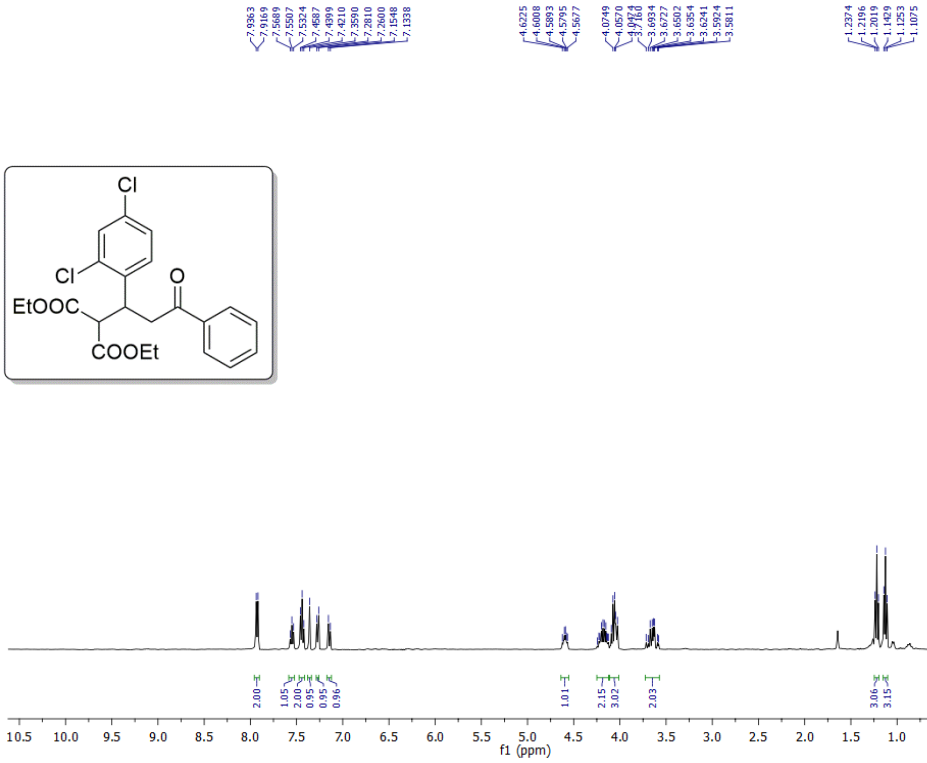
^{13}C NMR of 35h



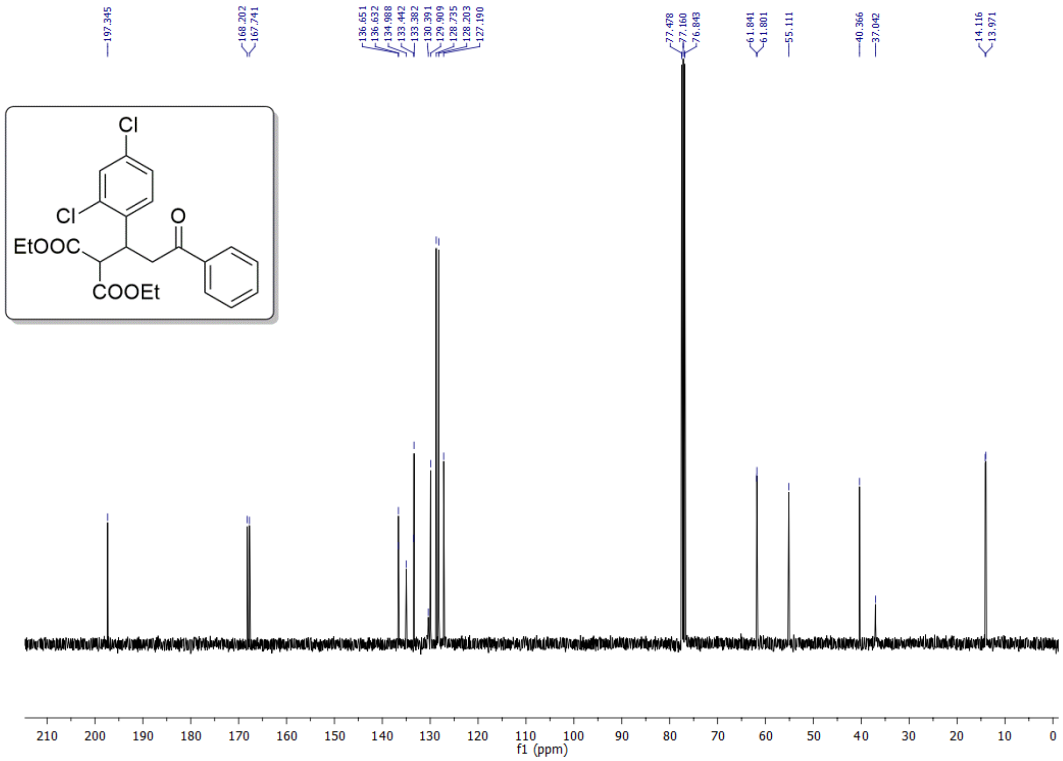
^{19}F NMR of 35h



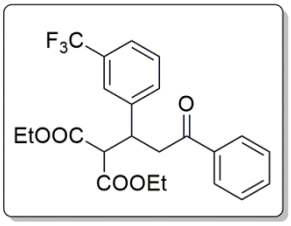
1H NMR of 35i

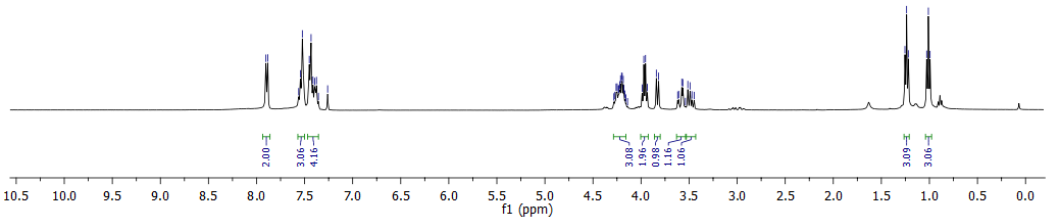


^{13}C NMR of 35i



^{1}H NMR of 35j





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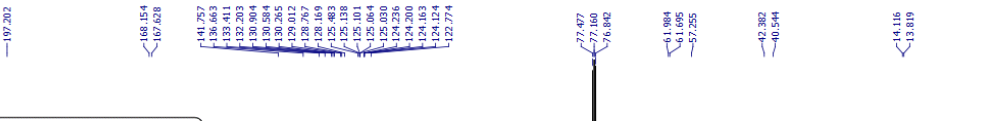
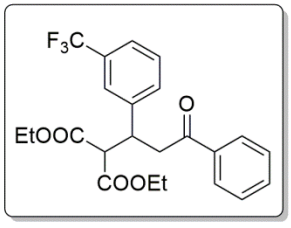
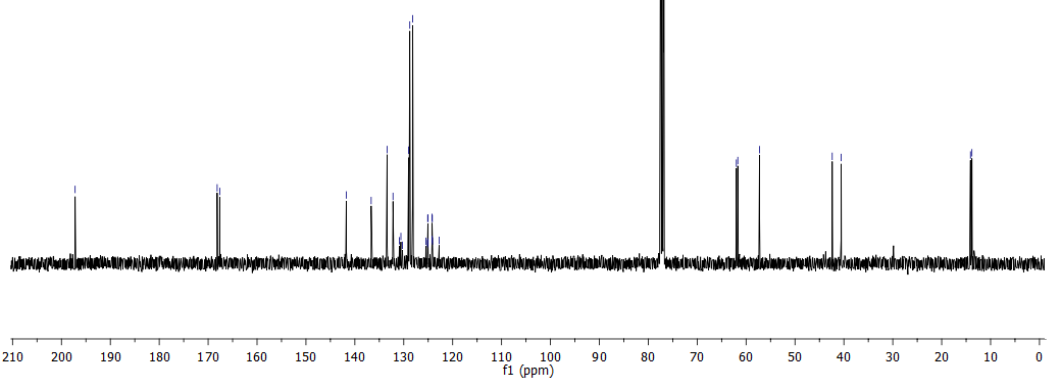
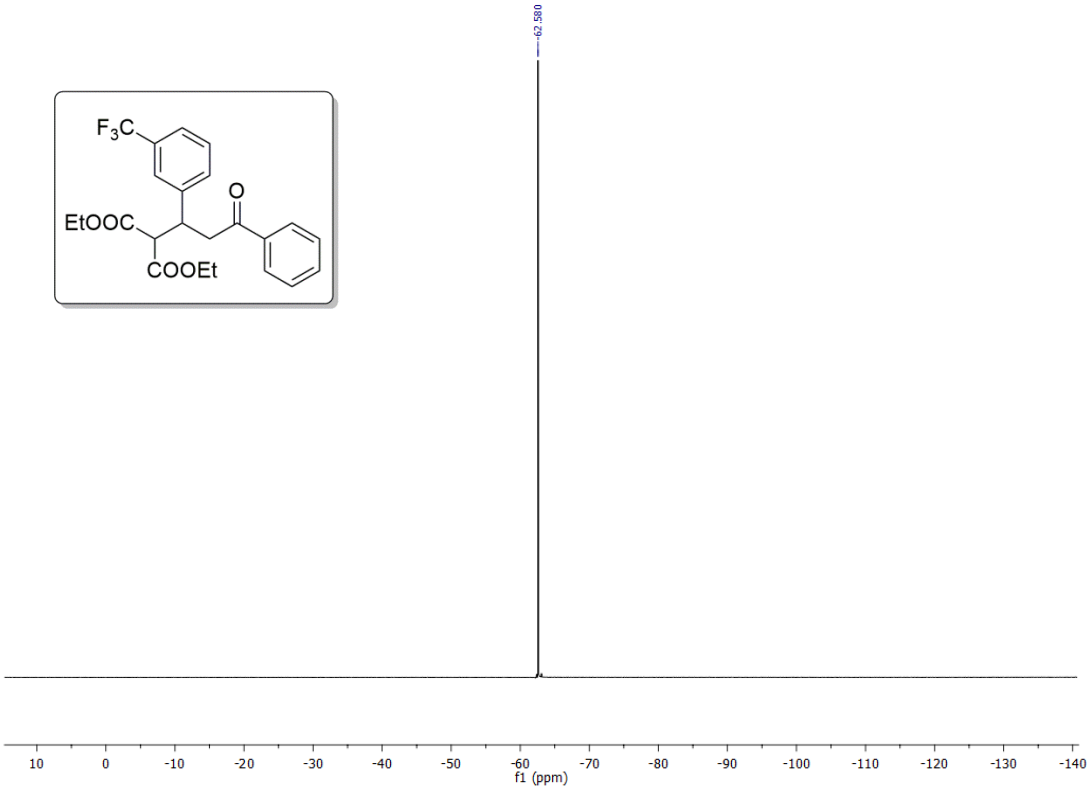


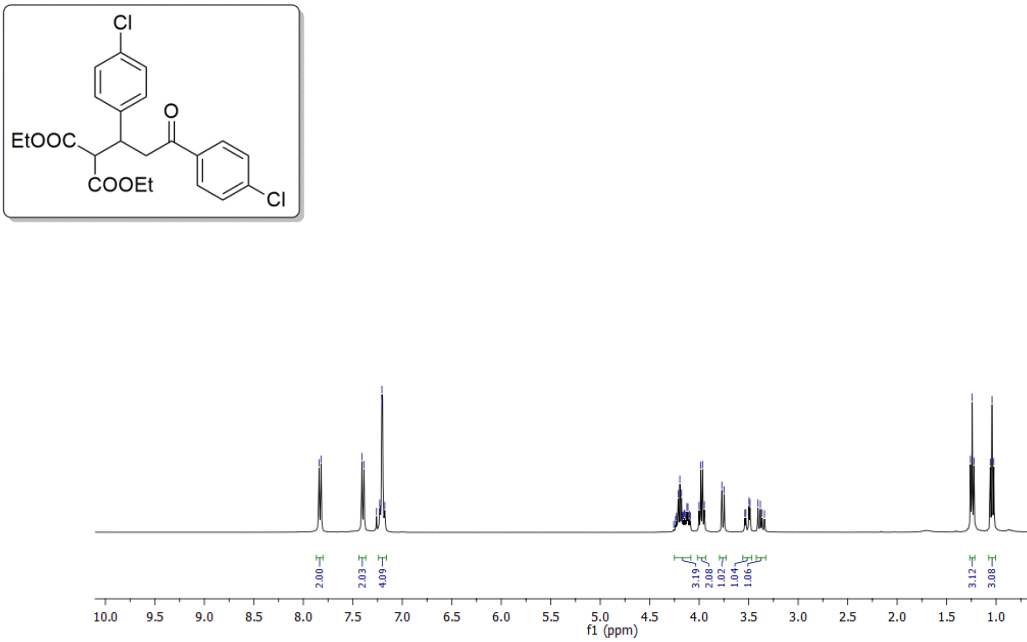




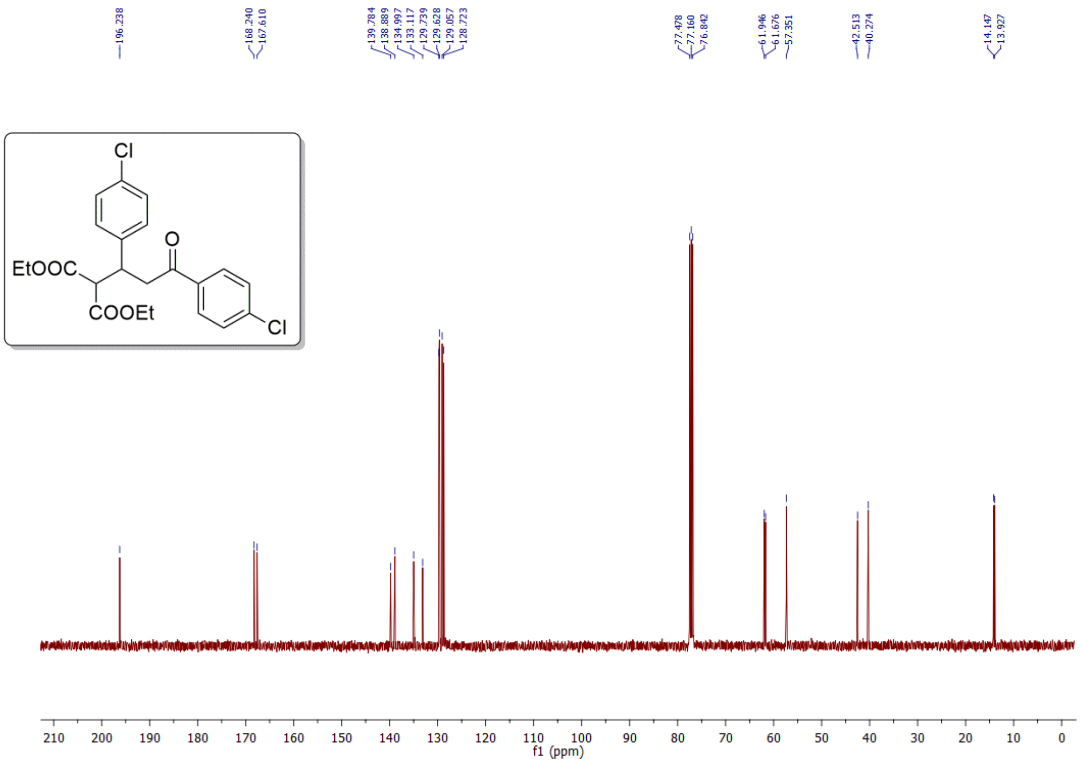
^{19}F NMR of 35j



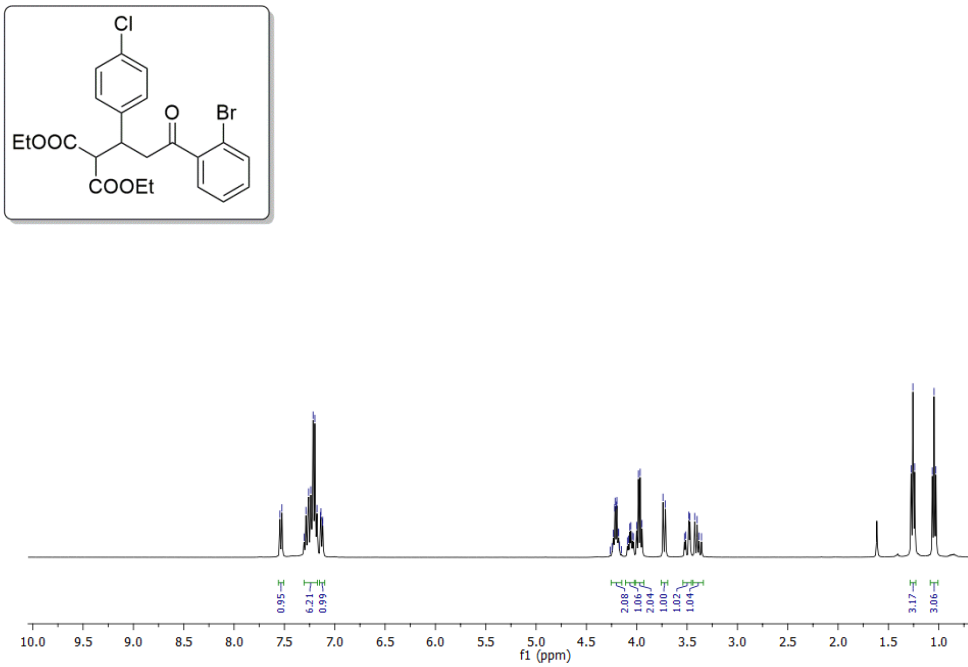
^{1}H NMR of 35k



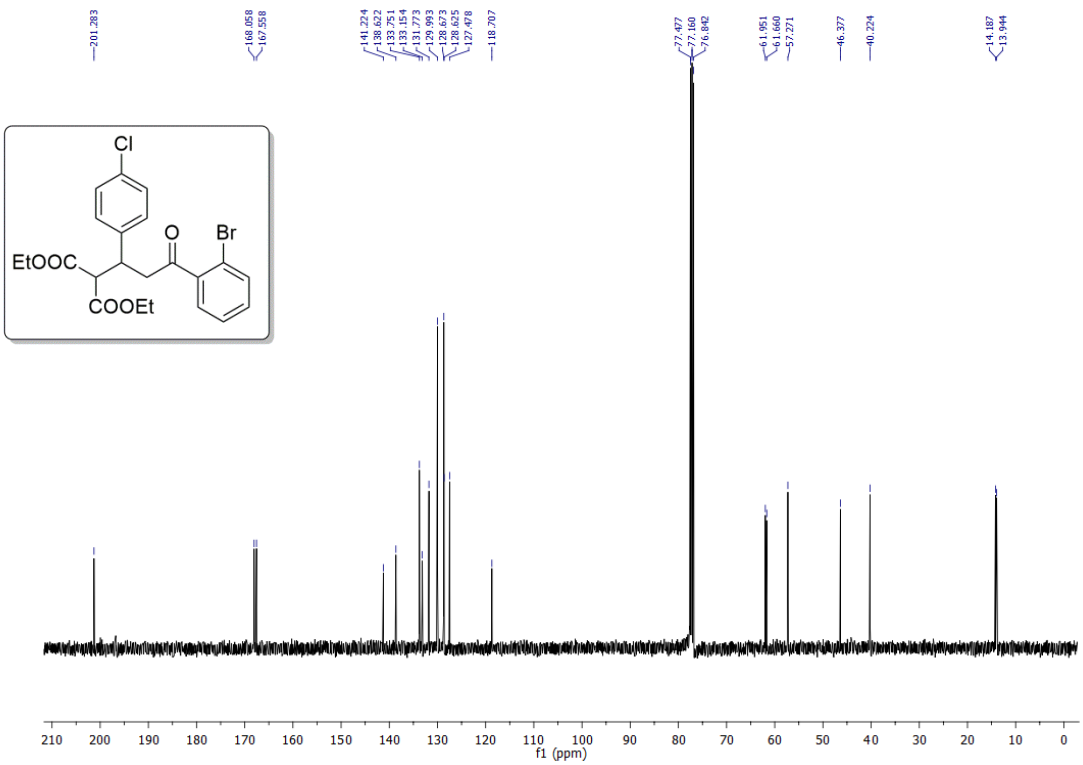
^{13}C NMR of 35k



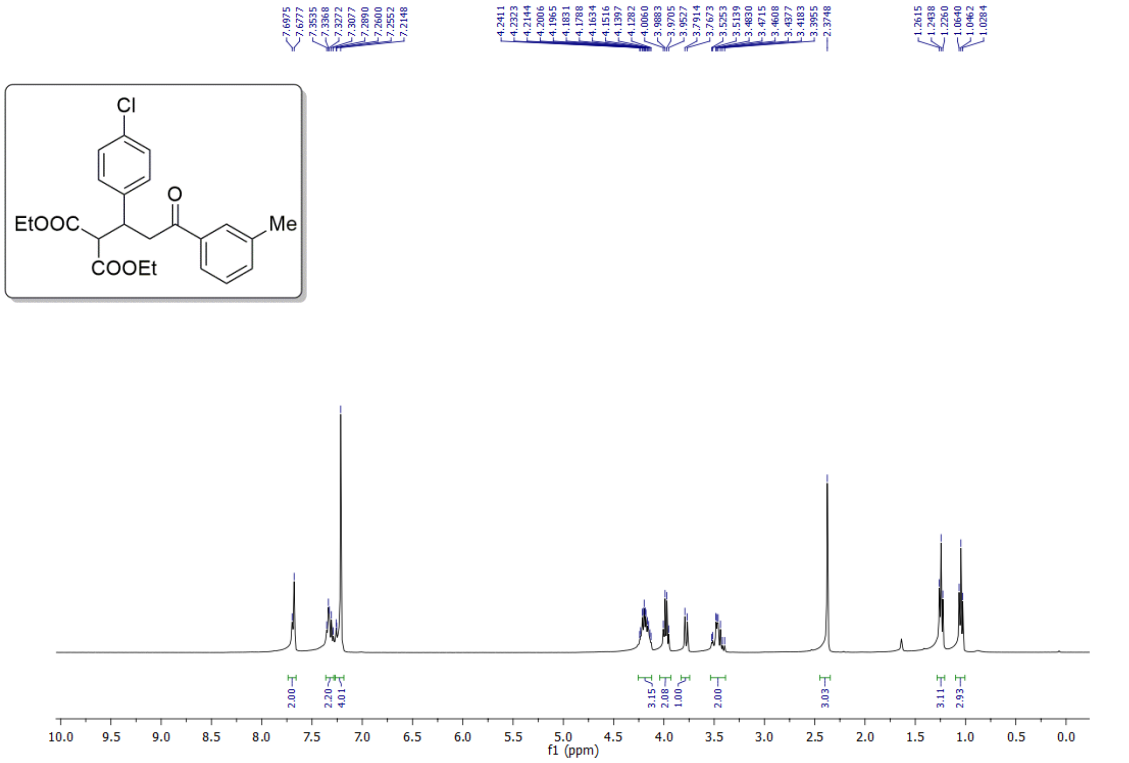
1H NMR of 35l



^{13}C NMR of 35l



1H NMR of 35m



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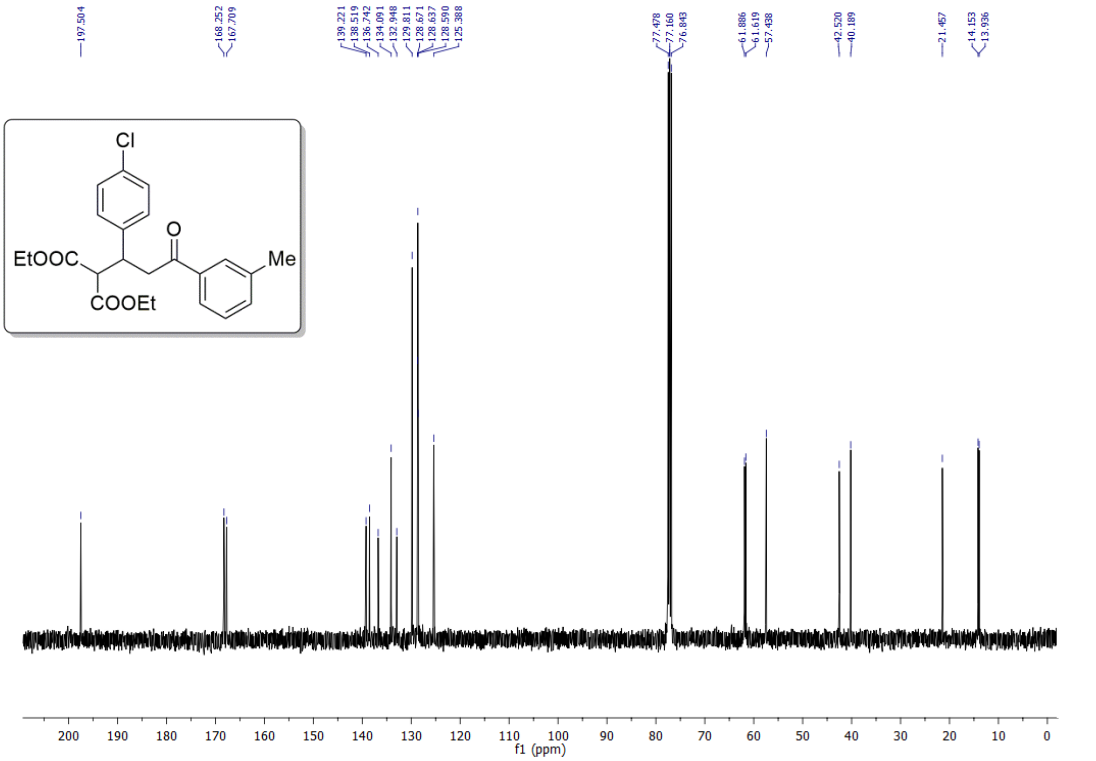

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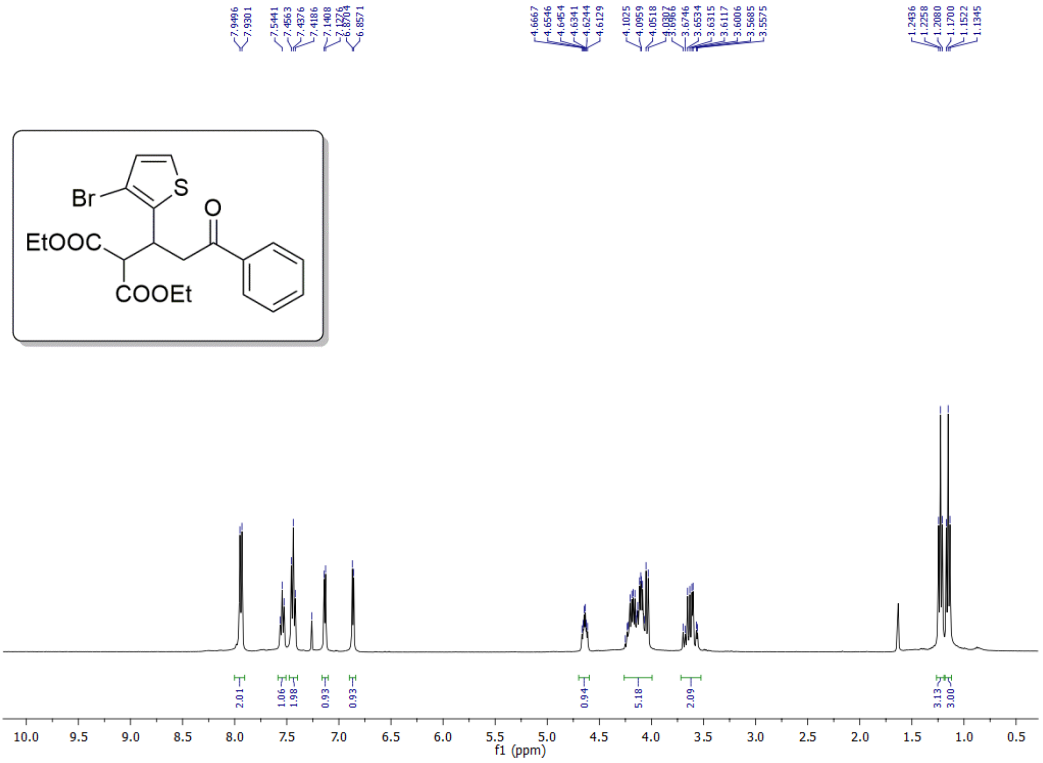

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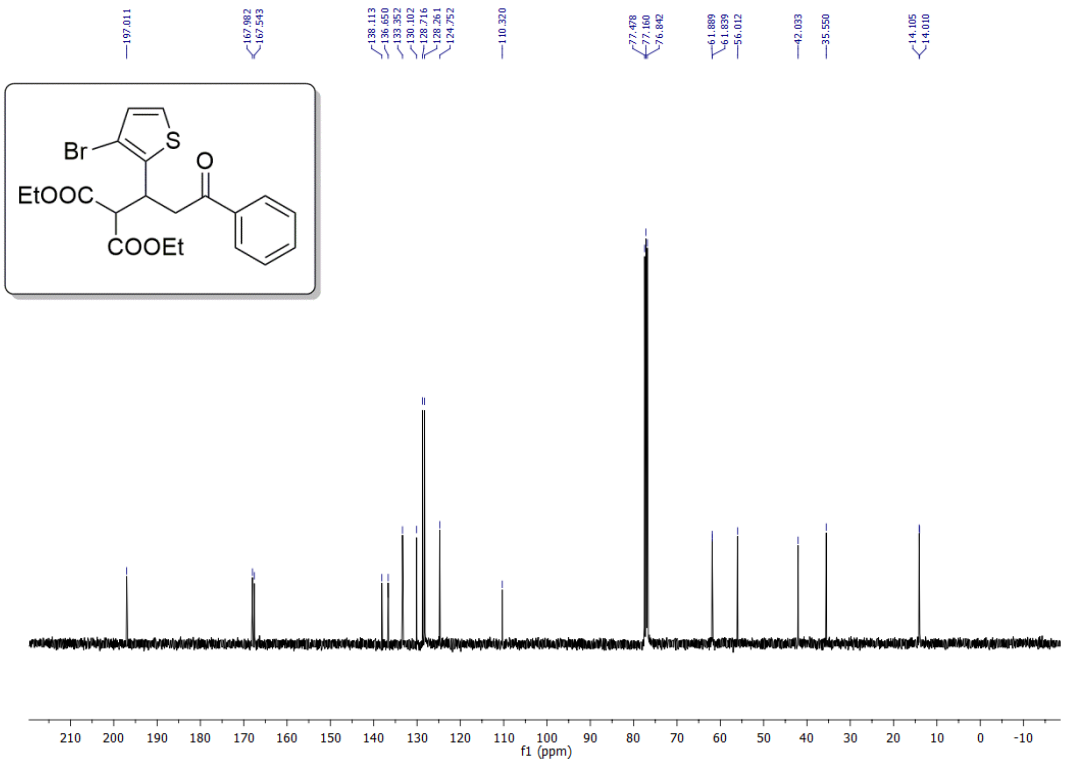
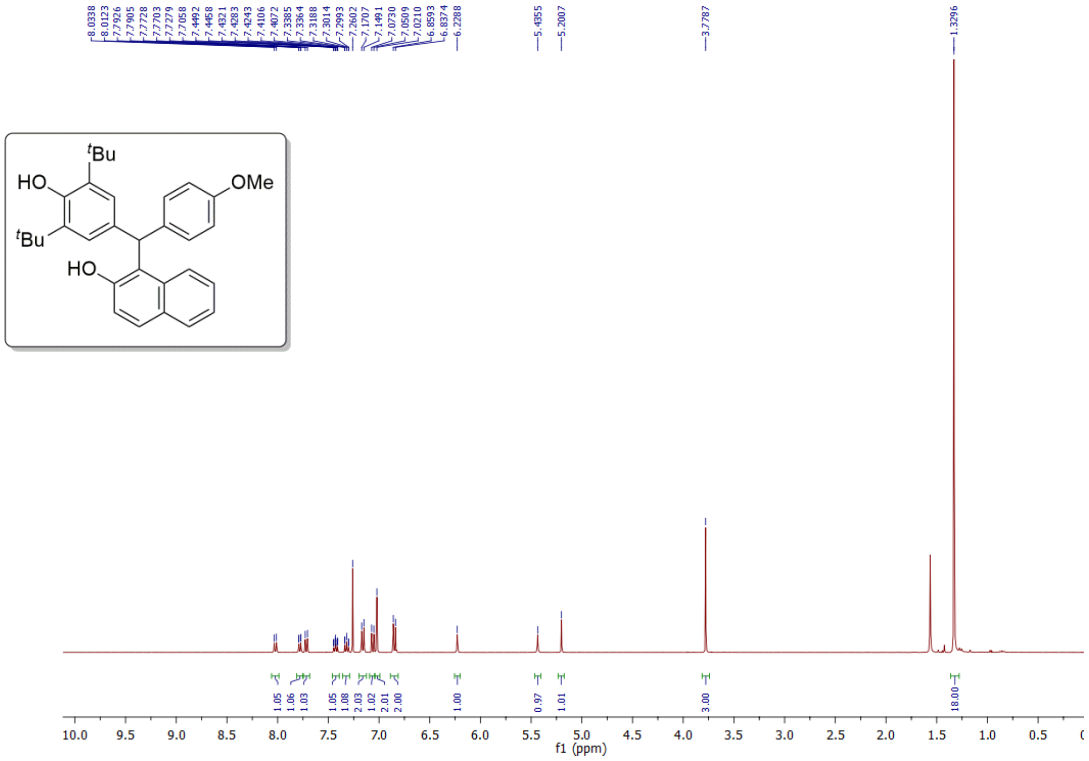


^{1}H NMR of 37a



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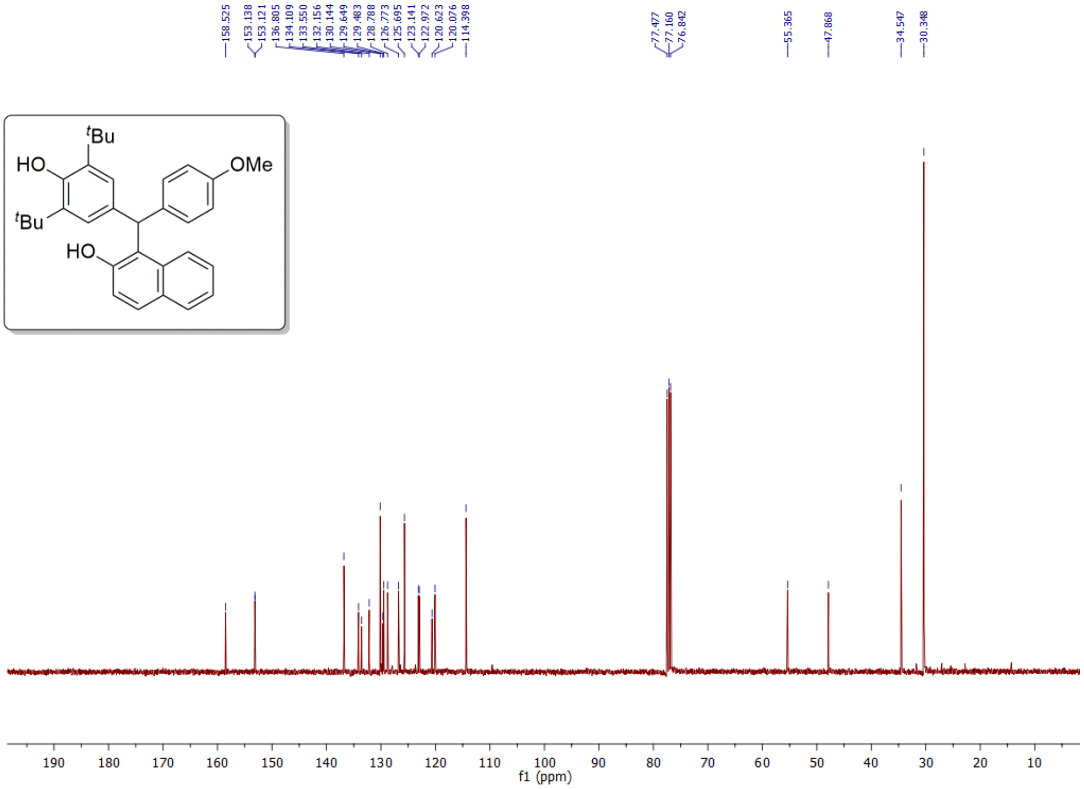

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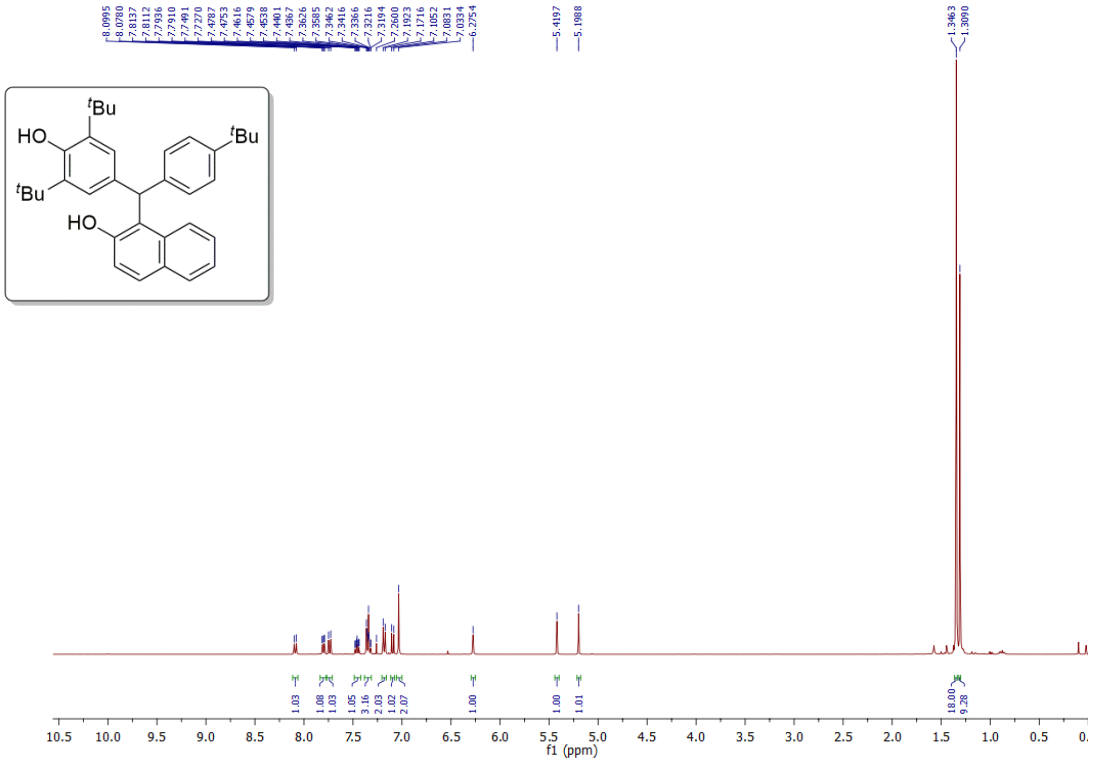

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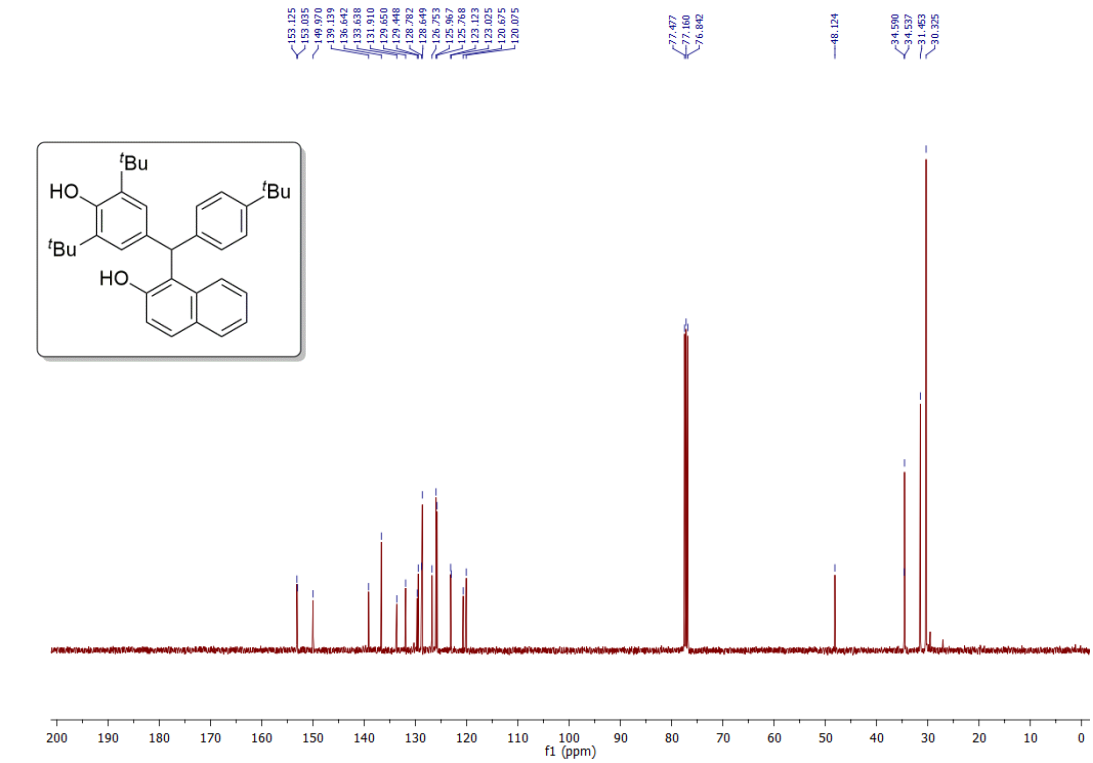

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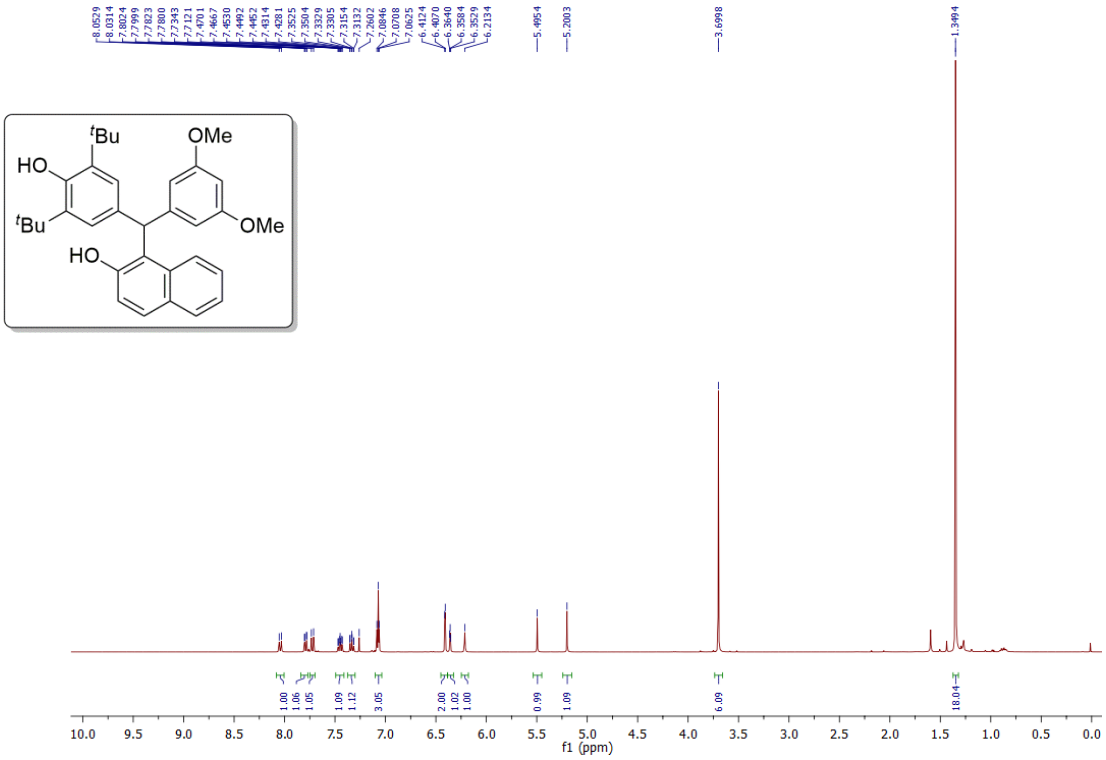

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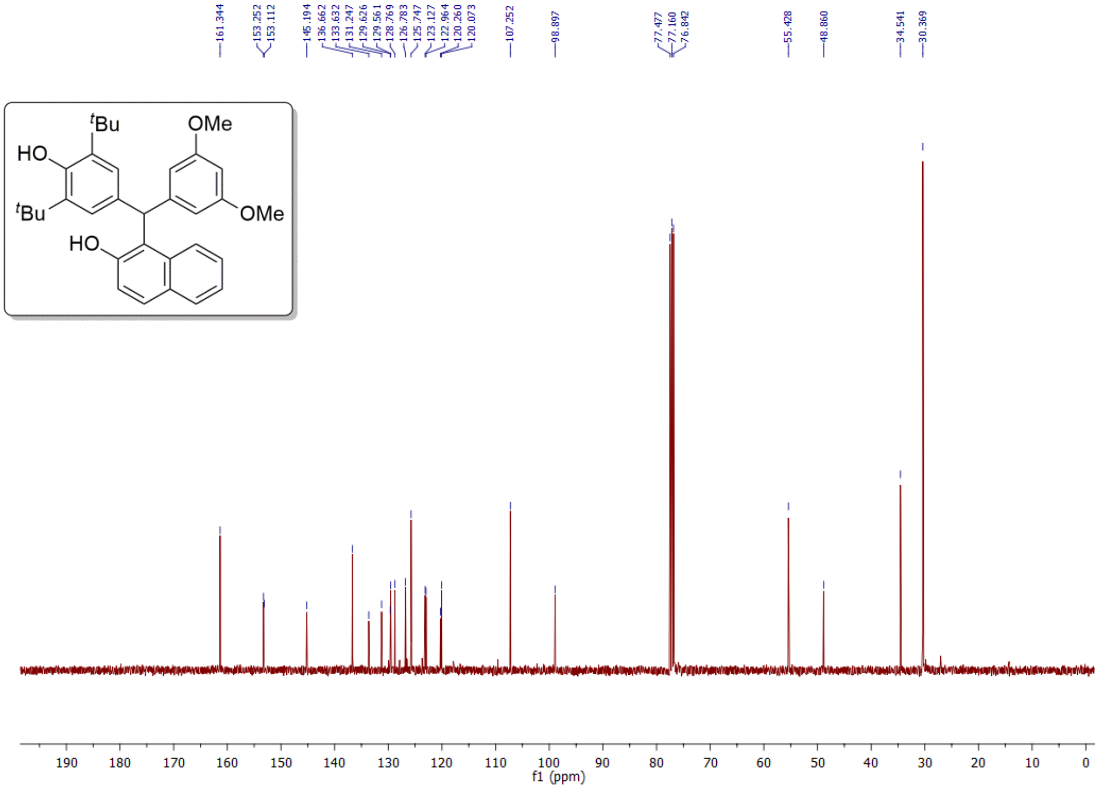

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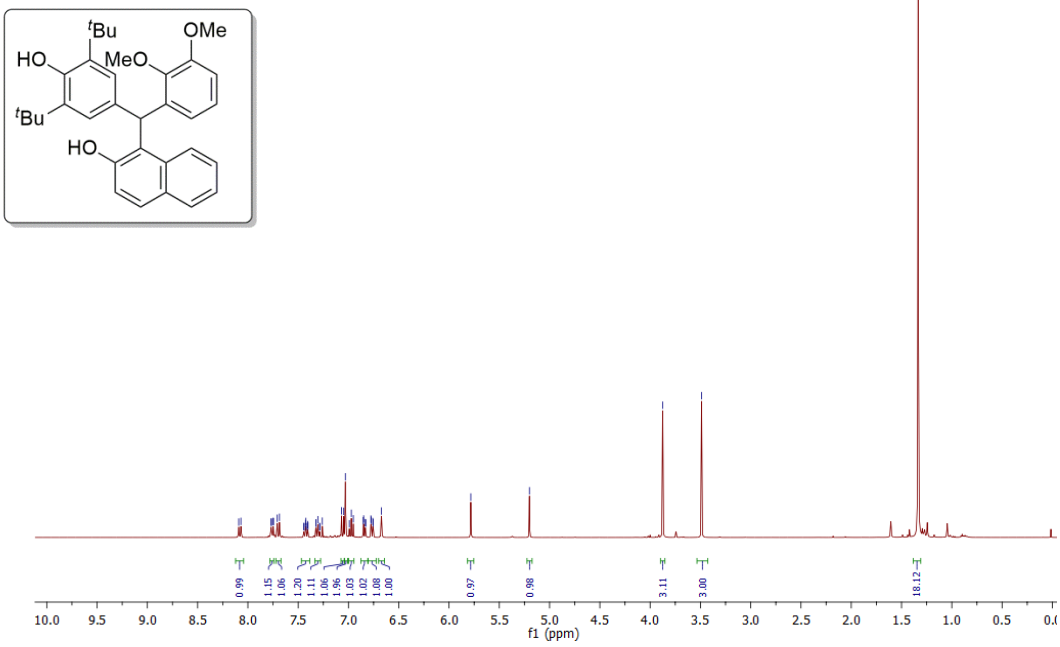

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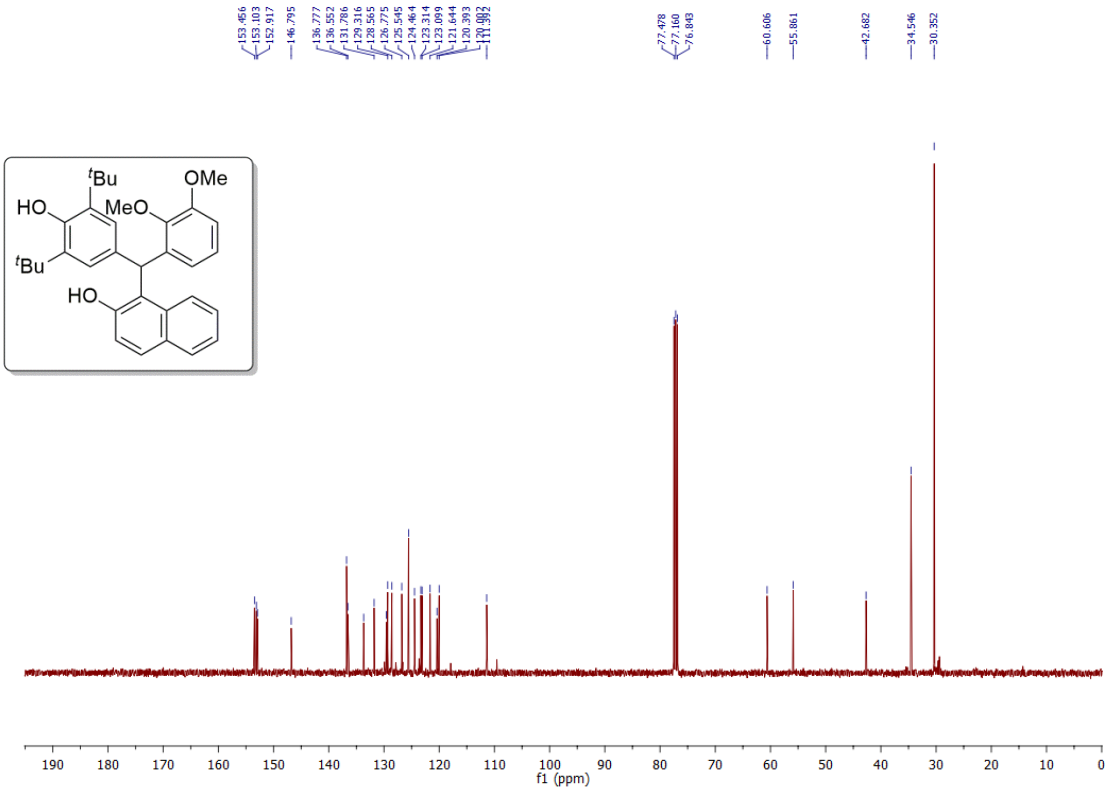

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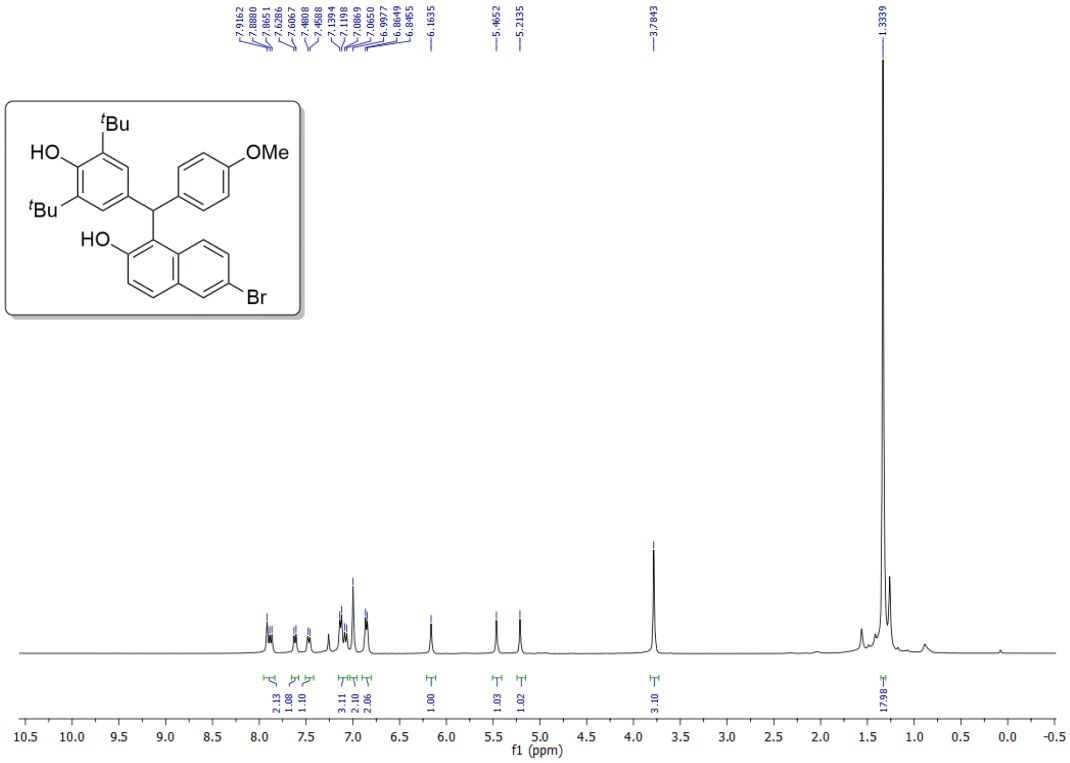

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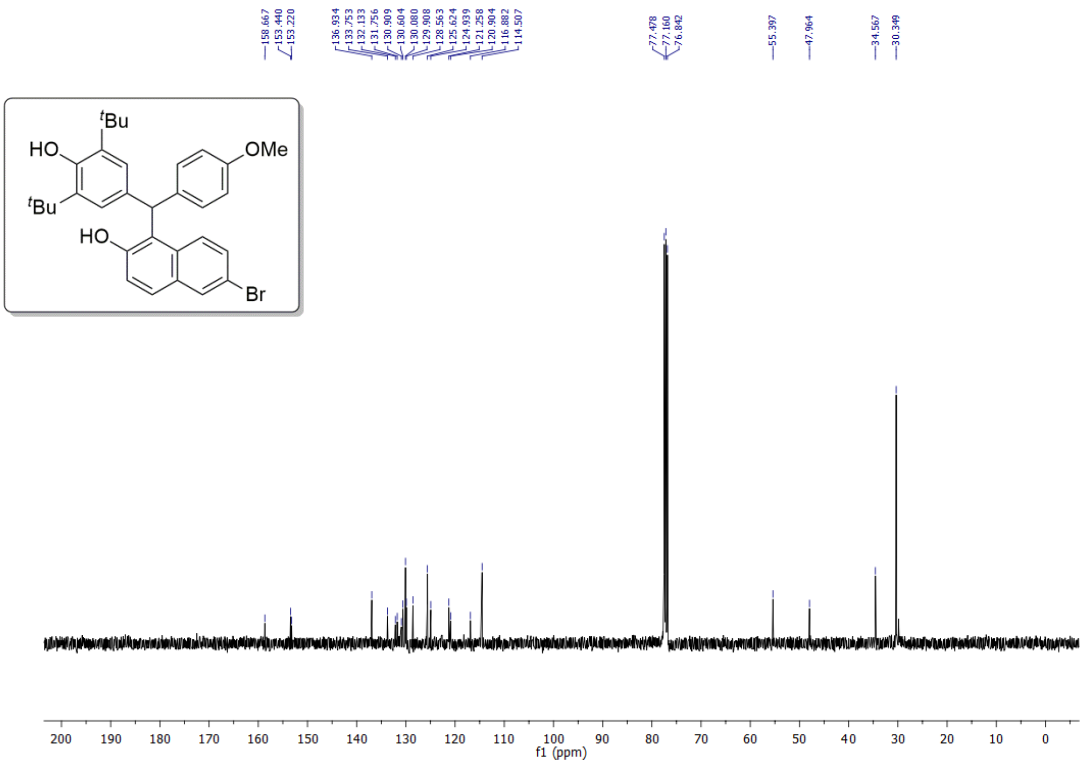

Conclusion

We have demonstrated BAC as a Brønsted Base in conjugate addition reactions of a variety of nucleophiles to enone and dienone systems. To the best of our knowledge, this is the first report of BAC acting as a Brønsted base. This transformation occurs at mild conditions and is tolerant to a variety of functional groups. Further, this protocol provides an easy and straight forward access to a set of triarylmethanes and micheal adducts in good to excellent yields.

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