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PAPER

N-heterocyclic carbene-mediated hydroacylation–Sonogashira/Heck/Suzuki coupling in a single pot: A new cascade reaction†

M. Sreenivasulu,[a,b] K. Siva Kumar,[a] P. Rajender Kumar,[a] K. B. Chandrasekhar[b] and Manojit Pal*[c]

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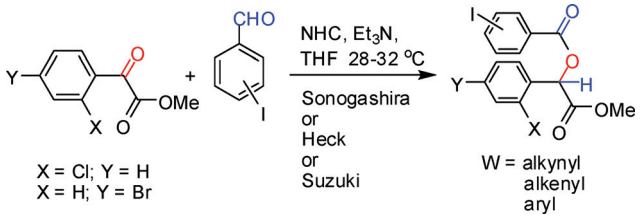
A dually NHC-catalyzed reaction cascade comprising an initial hydroacylation of an activated ketone and subsequent Sonogashira/Heck/Suzuki coupling in the same pot is reported. The reaction mechanism and scope of the methodology is presented.

Introduction

Although hydroacylation of alkenes using aldehydes as acyl donors is common in the literature[1], an analogous process involving aldehydes and carbonyl groups was not explored as a new synthetic tool until 2006.[2] Thus hydroacylation of α-keto esters (**2**) with aldehydes (**1**) was carried out using *N*-heterocyclic carbenes (NHCs) as organocatalysts and the methodology was further improved by using activated ketones as substrates.[3] Being environmentally benign and atom economical chemical transformations these methodologies are attractive and of particular interest. Palladium catalyzed C–C bond forming reactions such as Sonogashira, Heck or Suzuki reactions on the other hand have emerged as powerful tools in modern organic synthesis[4] especially in the synthesis of natural products, bioactive molecules and organic material. The use of NHCs as alternatives to phosphine ligands in these cross-coupling reactions[5–7] have been explored and studied with the major focus on the Suzuki reaction.[8,9] A variety of bulky NHC ligands have been reported to be effective for efficient Suzuki coupling involving chloroarenes at elevated and room temperature.[10–14] Intriguingly, the combination of NHC-mediated hydroacylation and subsequent Pd-catalyzed cross-coupling reactions in the same pot is not common in the literature. Herein, we report first NHC-organocatalyzed one-pot hydroacylation–Sonogashira/Heck/Suzuki coupling under mild conditions (Scheme 1). We envisioned that in addition to participating in the usual hydroacylation process the NHC ligand would facilitate the subsequent Pd-catalyzed cross-coupling reactions of the iodo derivative generated *in situ* in the same pot.



Scheme 1 NHC-mediated one-pot hydroacylation–Sonogashira/Heck/Suzuki coupling.

Results and discussion

While 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) in combination with triethylamine was identified as an efficient source of NHC in our previous study[3] it was however not clear if the same combination would be effective for subsequent Pd-catalyzed C–C bond forming reactions in the same pot. Our initial objective therefore was to identify appropriate *N*-heterocyclic salts suitable for one-pot hydroacylation–Sonogashira/Heck/Suzuki coupling under mild conditions. We choose to assess hydroacylation–Sonogashira coupling initially for this purpose. Accordingly, a few *N*-heterocyclic salts based on five-membered rings containing two hetero atoms (*e.g.* **A–D**, Fig. 1) were examined for their effect on the reaction of 4-iodobenzaldehyde (**1a**), methyl-2-(4-bromophenyl)-2-oxoacetate (**2a**) and phenyl acetylene (**3a**) in the presence of $Pd(OAc)_2$, CuI, Et_3N in THF (Table 1).

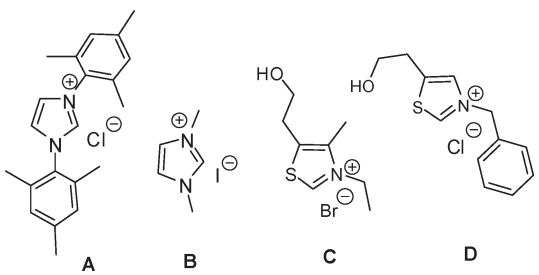
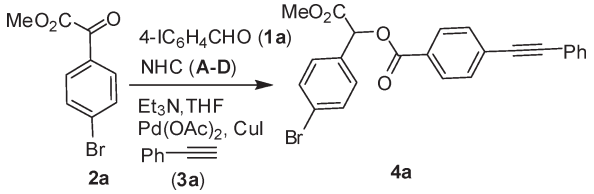


Fig. 1 *N*-heterocyclic salts as source of NHC.

[a]*Custom Pharmaceutical Services, Dr Reddy's Laboratories Limited, Bollaram Road, Miyapur, Hyderabad, 500 049, India*
[b]*Department of Chemistry, Jawaharlal Nehru Technological University of Anantapur, Anantapur, 515 002 Andhra Pradesh, India*
[c]*Institute of Life Sciences, University of Hyderabad Campus, Gachibowli, Hyderabad, 500 046 Andhra Pradesh, India. E-mail: manojitpal@rediffmail.com*

†Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR, MS and HRMS data of all new compounds. See DOI: 10.1039/c2ob06950d

Table 1 NHC-mediated hydroacylation–Sonogashira coupling of **1a** with **2a**[a]



Entry	NHC ligands (mol%)	Time (h)	Yield (%)[b]
1.	**A** (15)	5	58
2.	**A** (10)	5	61
3.	**A** (0.5)	10	12
4.	**B** (10)	10	38
5.	**C** (10)	15	16
6.	**D** (10)	15	22

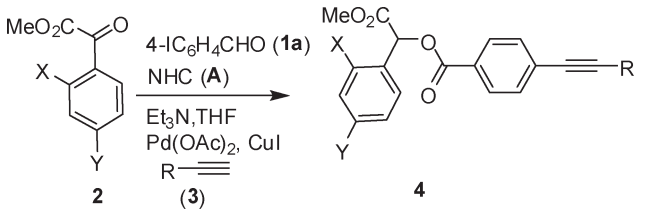
[a] The reaction was carried out using **1a** (0.43 mmol), **2a** (0.646 mmol), **3a** (0.646 mmol), NHC ligand (**A–D**), $Pd(OAc)_2$ (0.022 mmol), CuI (0.043 mmol) and Et_3N (1.08 mmol) in THF (5 mL) at 28–32 °C under nitrogen. [b] Isolated yield.

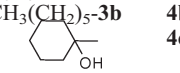
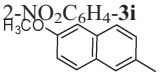
As evident from Table 1 the sterically encumbered 1,3-*bis* (2,4,6-trimethylphenyl)imidazolium chloride (**A**) facilitated the hydroacylation–Sonogashira coupling to afford the expected product **4a** (entry 1, Table 1). While the reaction was completed within 5 h when 15 mol% of **A** was used it was observed that a lower quantity of **A** *i.e.* 10 mol% was also effective providing the same yield of **4a** (entry 2, Table 1). However, further decrease of **A** decreased the product yield substantially (entry 3, Table 1). The other salts *e.g.* 1,3-dimethyl-1*H*-imidazol-3-ium iodide (**B**) afforded **4a** in low yield (entry 4, Table 1) whereas thiazolium salts **C** and **D** provided **4a** in poor yields even after 15 h (entries 5 & 6, Table 1). In all these reactions 0.022 mmol of $Pd(OAc)_2$ in combination with CuI (0.043 mmol) was used for the alkynylation step. The yield of **4a** was decreased when 0.011 mmol of $Pd(OAc)_2$ was used and **4a** was not formed in the absence of either of $Pd(OAc)_2$ or CuI indicating the need of Pd–Cu catalysts to facilitate the alkynylation step. In a separate study the hydroacylated product *i.e.* 1-(4-bromophenyl)-2-methoxy-2-oxoethyl-4-iodobenzoate isolated from the reaction of **1a** and **2a** was treated with **3a** in the presence of $Pd(OAc)_2$, CuI, Et_3N in THF at 28–32 °C when formation of **4a** was not observed even after 12 h. The formation of **4a** was also not observed when the reaction was carried out at refluxing temperature (65–67 °C) suggesting the additional role played by the NHC in the Sonogashira step.

Having established the optimum reaction conditions for the NHC-mediated hydroacylation–Sonogashira coupling we then examined the further scope and generality of this process.

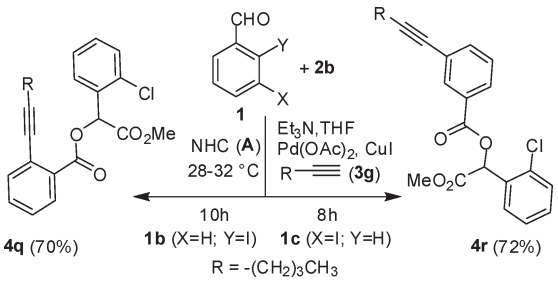
Thus a range of terminal alkynes (**3**) possessing different substituents were employed which provided the desired alkyne derivatives (**4**) in good yields (Table 2). The presence of a aryl, alkyl, cycloalkyl, pyridyl, hydroxyalkyl, chloroalkyl or naphthyl group in the alkyne **3** was well tolerated in the present one-pot reaction. The presence of bromo or chloro on the aromatic ring of **2** was also tolerated. In comparison to the earlier report[8] the present Sonogashira coupling proceeded under milder conditions. We also examined the use of *o*- and *m*-iodo

Table 2 NHC-mediated hydroacylation–Sonogashira coupling[a]



Entry	Ketone (**2**) X & Y =	Alkynes (**3**) R =	Products (**4**)	Time (h); yield[b] (%)
1.	H; Br **2a**	C_6H_5-**3a**	**4a**	4; 61
2.	**2a**	$CH_3(CH_2)_5$-**3b**	**4b**	5; 68
3.	**2a**	 **3c**	**4c**	6;58
4.	**2a**	 **3d**	**4d**	4; 71
5.	Cl; H **2b**	**3a**	**4e**	4; 66
6.	**2b**	$HOCH_2CH_2$-**3e**	**4f**	5; 58
7.	**2b**	$ClCH_2(CH_2)_2$-**3f**	**4g**	4; 78
8.	**2b**	$CH_3(CH_2)_3$-**3g**	**4h**	4; 75
9.	**2b**	$CH_3(OH)CH$-**3h**	**4i**	5; 61
10.	**2b**	**3c**	**4j**	4; 62
11.	**2b**	**3d**	**4k**	4; 62
12.	**2b**	2-$NO_2C_6H_4$-**3i**	**4l**	4; 70
13.	**2b**	 **3j**	**4m**	6; 59
14.	**2b**	$C_2H_5CH(OH)$- **3k**	**4n**	4; 63
15.	**2b**	$CH_3(CH_2)_4$-**3l**	**4o**	4; 79
16.	**2b**	**3b**	**4p**	4; 75

[a] All the reactions were carried out using **1a** (0.43 mmol), **2** (0.646 mmol), **3** (0.646 mmol), NHC ligand **A** (0.044 mmol), $Pd(OAc)_2$ (0.022 mmol), CuI (0.043 mmol) and Et_3N (1.08 mmol) in THF (5 mL) at 28–32 °C under nitrogen. [b] Isolated yield.

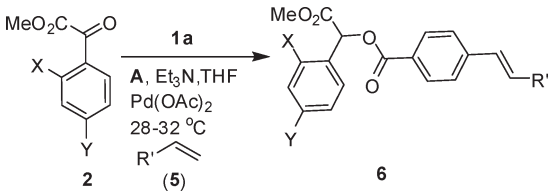


Scheme 2 The use of *o*- and *m*-iodo benzaldehyde (**1b** and **1c**) in NHC-mediated hydroacylation–Sonogashira coupling.

benzaldehyde (**1b** and **1c**, Scheme 2) in the present reaction and the corresponding products were isolated in good yields.

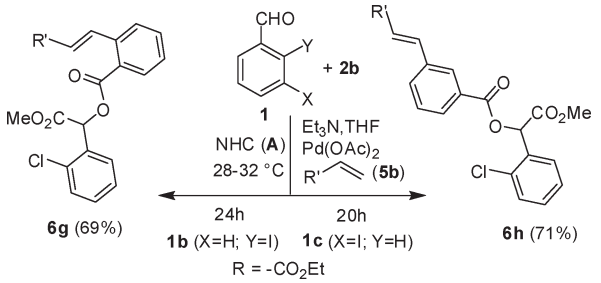
Encouraged by these results we then examined the posibility of conducting hydroacylation–Heck couplings in a single pot. Initially, a reaction was carried out using **1a**, **2a**, and methyl acrylate (R′ = CO_2Me, **5a**) in the presence of the Et_3N, NHC ligand **A**, $Pd(OAc)_2$ in THF at 28–32 °C. The reaction proceeded smoothly to give the corresponding product **6a** in 65% yield. Thus the use of other alkenes was examined and the results are summarised in Table 3. All these reactions required 10–15 h for

Table 3 NHC-mediated hydroacylation–Heck coupling[a]



Entry	Ketone (**2**)	Alkenes (**5**) R′ =	Products (**6**)	Time (h); yield[b] (%)
1.	**2a**	CH_3OCO-**5a**	**6a**	15; 65
2.	**2a**	C_2H_5OCO-**5b**	**6b**	14; 71
3.	**2a**	*t*-BuOCO-**5c**	**6c**	14; 64
4.	**2b**	**5a**	**6d**	14; 70
5.	**2b**	**5b**	**6e**	10; 65
6.	**2b**	**5c**	**6f**	12; 74

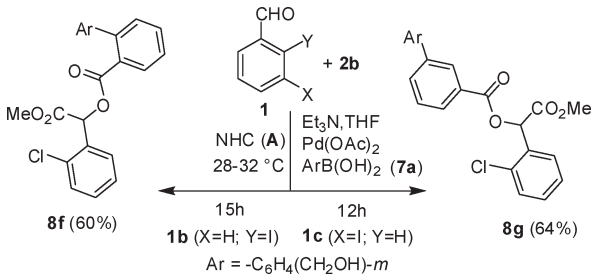
[a] All the reactions were carried out using **1a** (0.43 mmol), **2** (0.646 mmol), **5** (1.72 mmol), NHC ligand **A** (0.044 mmol), $Pd(OAc)_2$ (0.022 mmol), and Et_3N (1.08 mmol) in THF (5 mL) at 28–32 °C under nitrogen. [b] Isolated yield.



Scheme 3 The use of **1b** and **1c** in NHC-mediated hydroacylation–Heck coupling.

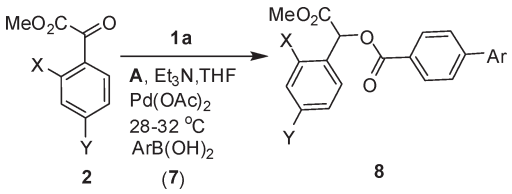
completion but remarkably did not require any heating to provide the desired alkene derivatives **6**. Both the benzaldehyde **1b** and **1c** participated well in the present reaction (Scheme 3). Based on ^{1}H NMR data all the alkenes prepared were characterized as the *E*-isomer (J = 15.6–16 Hz).†

We also examined the possibility of conducting hydroacylation–Suzuki coupling in a single pot and the results are presented in Table 4. Once again the process showed remarkable selectivity towards iodo over bromo and chloro, though NHC-mediated Suzuki reactions involving chloro or bromoarenes are known in the literature. While a number of functional groups present in the boronic acid **7** were tolerated the reactant **7c** however was added



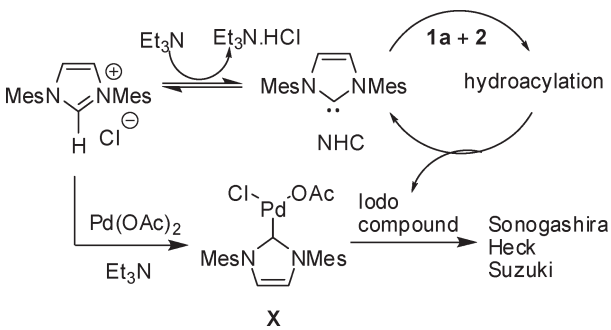
Scheme 4 The use of **1b** and **1c** in NHC-mediated hydroacylation–Suzuki couplings.

Table 4 NHC-mediated hydroacylation–Suzuki coupling[a]



Entry	Ketone (**2**)	Boronic acids (**7**) Ar =	Products (**8**)	Time (h); yield[b] (%)
1.	**2a**	**7a**	**8a**	8; 66
2.	**2a**	**7b**	**8b**	6; 69
3.	**2b**	**7a**	**8c**	8; 66
4.	**2b**	**7c**[c]	**8d**	7; 69
5.	**2b**	**7d**	**8e**	7; 71

[a] All the reactions were carried out using **1a** (0.43 mmol), **2** (0.646 mmol), **7** (0.646 mmol), NHC ligand **A** (0.044 mmol), $Pd(OAc)_2$ (0.022 mmol) and Et_3N (1.08 mmol) in THF (5 mL) at 28–32 °C under nitrogen. [b] Isolated yield. [c] The boronic acid **7c** was added after 3h.



Scheme 5 Generation of Pd(II)-NHC complex **X**.

to the reaction mixture 3 h later (entry 4, Table 4) to avoid its participation in the initial hydroacylation process. Like earlier reactions both the benzaldehyde **1b** and **1c** participated in the present process to give the desired products (Scheme 4).

To understand the role of NHC both in the Heck and Suzuki steps separate experiments were carried out in absence ligand **A**. Thus the hydroacylated product isolated from the reaction of **1a** and **2a** was treated separately with alkene **5a**, $Pd(OAc)_2$ and Et_3N in THF at 28–32 °C under nitrogen. No formation of desired product was observed after 15 h and only trace amount of the product **6a** was detected after 48h. Similarly, the same hydroacylated product was treated with boronic acid **7a**, $Pd(OAc)_2$ and Et_3N in THF at 28–32 °C under nitrogen. While the reaction proceeded in this case only 30% conversion was observed after 8 h. All these observations clearly suggest that the ligand **A** played a key role in step 2 of both the hydroacylation–Heck and hydroacylation–Suzuki reactions. Based on these

observations and the results presented in Table 1 a plausible mechanism can be proposed for the present one-pot hydroacylation–coupling reaction (Scheme 2). It is known that appropriate imidazolium salts react with $Pd(OAc)_2$ to generate the corresponding Pd(II)-NHC complexes[12] depending on the presence or absence of a base. However, it was still not clear if a diligated Pd-complex catalyzed the cross-coupling reactions.[15] Additionally, a monoligated Pd-complex generated from $Pd(OAc)_2$ has been used for the Suzuki reaction of aryl chlorides.[16] In the present reaction the ligand **A** (half equiv) initially participates in the organocatalyzed addition of aldehyde **1a**, converted to acyl anion equivalent by umpolung along with the regioselective reduction of the keto group of **2** and then acylation of the alcohol formed along with the regeneration of the NHC.[2,3] The regenerated NHC then reenters into the catalytic cycle of hydroacylation process.

The remaining half equivalent of **A** reacts with $Pd(OAc)_2$ to form the complex **X** (Scheme 5) that actually catalyzes the subsequent C–C bond forming reaction. Thus the iodoarene derivative generated *in situ* as a result of the hydroacylation process undergoes Sonogashira, Heck or Suzuki coupling depending on the reactants and reaction conditions employed. Various studies have suggested that steric bulk and the electronic nature of the NHC ligand play a key role in the overall performance of the Pd-NHC catalyst in the Suzuki reaction.[9] The reported mechanism for Pd-catalyzed cross-coupling reactions involve three important steps: oxidative addition, transmetallation and reductive elimination. While the electronic nature of the ligand may not be vital for facile oxidative insertion into the relatively labile C–I bond (towards Pd-catalyst) the steric bulk however seemed to aid the reductive elimination of the coupled product along with regeneration of the catalyst. Since the ligand possessing too much steric bulk can affect the rate of oxidative addition adversely, a balance between steric and electronic factors have been suggested to achieve optimum activity of the Pd-NHC catalyst generated *in situ*. The Pd center of complex **X** seemed to have a balanced electronic character and steric crowding necessary for facile oxidative addition as well as reductive elimination.

Overall, the present single step method *i.e.* hydroacylation–Sonogashira/Heck/Suzuki coupling in a single pot provided a series of O-acyl derivatives of analogues of mandelic acid ester. Notably mendelic acid has been used as an antibacterial agent particularly in the treatment of urinary tract infections.[17] 4-Substituted benzoic acids on the other hand have been explored for their inhibitory effect on the biosynthesis of fatty acids and sterols.[18] Due to our long standing interest in bioactive molecules[19,20] we thought that combining mandelic acid or its analogues with a variety of 4-substituted benzoic acids could provide a library of small molecules of potential pharmacological significance. The diversity based 2-aryloxy esters[21] presented here therefore may have medicinal value.

Conclusions

In conclusion, 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride has been identified as a single NHC ligand for facile one-pot hydroacylation–Sonogashira/Heck/Suzuki coupling under mild reaction conditions. The reaction involved the use of 2-, 3- or 4-iodobenzaldehyde as an acyl donor that allowed subsequent coupling reactions in the same pot facilitated by the NHC ligand. With its multiple bond-forming ability the present cascade reaction represents an attractive option for the rapid construction of compound library based on small organic molecules.

Experimental

General methods

Unless stated otherwise, reactions were performed under nitrogen atmosphere using oven dried glassware. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (230–400 mesh) using distilled hexane, ethyl acetate and THF. ^{1}H NMR and ^{13}C NMR spectra were determined in DMSO-d_6 or CD_3OD solution by using 400 and 100 (or 50) MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Coupling constants (J) are given in Hertz. Infrared spectra were recorded on a FT-IR spectrometer. Melting points were determined using melting point apparatus and are uncorrected. MS spectra were obtained on a mass spectrometer. High-resolution mass spectra (HRMS) were recorded using electron ionization (EI) mass spectrometry. The ketones *i.e.* methyl-2-(2-chlorophenyl)-2-oxoacetate and methyl 2-(4-bromophenyl)-2-oxoacetate were prepared according to known procedures.[22] The 4-iodo benzaldehyde, all alkynes and alkenes, palladium(II)acetate, boronic acids and imidazolium salt are purchased and used directly.

A typical procedure for one-pot NHC mediated hydroacylation and Sonogashira reactions

To a mixture of imidazolium salt **A** (14.8 mg, 0.044 mmol) and 4-iodobenzaldehyde (100 mg, 0.43 mmol) in THF (5.0 mL) triethylamine (109 mg, 1.08 mmol), methyl 2-(4-bromophenyl)-2-oxoacetate (157.1 mg, 0.646 mmol), palladium(II)acetate (4.84 mg, 0.022 mmol), copper iodide (8.2 mg, 0.043 mmol) were added, followed by phenyl acetylene (66.0 mg, 0.646 mmol) under a nitrogen atmosphere. The mixture was then stirred at 28–32 °C for 4 h (monitored by TLC). After completion of the reaction the mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (230–400 mesh) using 10–20% EtOAc-hexane.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(phenylethynyl) benzoate (4a)

This compound was purified by using 10% EtOAc/hexane to give the title compound (118.1 mg) as an off white solid; mp (DSC) 122.7 °C; R_f = (1 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 2950, 2214, 1755, 1716, 1260, 763; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (2H, d, J = 8.0 Hz, C_6H_4), 7.75 (2H, d, J = 8.0 Hz, C_6H_4), 7.70 (2H, d, J = 8.4 Hz, p-BrC_6H_4),7-62-7.60 (2H, m, C_6H_5), 7.59 (2H, d, J = 8.4 Hz, p-BrC_6H_4), 7.47–7.45

(3H, m, C_6H_5), 6.29 (1H, s, CH), 3.70 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.7, 73.9, 88.3, 92.7, 121.5, 122.8, 127.7, 128.1, 128.8 (2C), 129.4 (2C), 129.7, 129.8 (2C), 131.6 (2C), 131.8, 131.9 (2C), 133.0, 164.3, 168.6; mass (ES) *m/z* 449.1 (M + 1); HRMS (ESI) calculated for $C_{24}H_{18}O_4Br$ $(M + H)^+$ 449.0447; found 449.0388.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(oct-1-yn-1-yl) benzoate (4b)

This compound was purified by using 10% EtOAc/hexane to give the title compound (134.0 mg) as light yellow colour oil; R_f = (1 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 2954, 2226, 1760, 1727, 1255, 766; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (2H, d, J = 8.8 Hz, C_6H_4), 7.69 (2H, d, J = 8.4 Hz, C_6H_4), 7.57–7.53 (4H, m, p-BrC_6H_4), 6.27 (1H, s, CH), 3.69 (3H, s, OCH_3); 2.49–2.46 (2H, t, J = 7.6 Hz), 1.57–1.52 (2H, m, CH_2), 1.45–1.41 (2H, m, CH_2), 1.39–1.23 (4H, m, CH_2), 0.89–.85 (3H, m, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.8, 18.7, 21.9, 27.8, 27.9, 30.7, 52.7, 73.7, 79.8, 95.0, 122.7, 127.3, 128.9, 129.6 (2C), 129.8 (2C), 131.6 (2C), 131.9 (2C), 133.0, 164.4, 168.6. Mass (ES) *m/z* 457.2 (M + 1); HRMS (ESI) calculated for $C_{24}H_{26}O_4Br[M + H]^+$ 457.1023; found 457.1014.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(1-hydroxycyclohexyl)ethynyl) benzoate (4c)

This compound was purified by using 10% EtOAc/hexane to give the title compound (117.5 mg) as an off white solid; mp (DSC) 137.2 °C; R_f 0.37 (1 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 3517, 2933, 2222, 1718, 1695, 1303, 754; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (2H, d, J = 8.8 Hz, C_6H_4), 7.70 (2H, d, J = 8.4 Hz, C_6H_4), 7.58–7.55 (4H, m, p-BrC_6H_4), 6.28(1H, s, CH), 5.55 (1H, s, OH), 3.69 (3H, s, OCH_3), 1.8–1.23 (10H, m, CH_2 cyclohexanol); ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.5, 22.7, 24.6, 24.8, 52.7, 66.9, 73.8, 81.8, 122.8, 127.7 (2C), 128.1 (2C), 129.6 (2C), 129.8 (2C), 131.6 (2C), 131.9 (2C), 132.9, 164.3, 168.5; mass (ES) *m/z* 471.3 (M + 1); HRMS (ESI) calculated for $C_{24}H_{24}O_5Br$ $(M + H)^+$ 471.0808; found 471.0807.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(pyridin-2-ylethynyl) benzoate (4d)

This compound was purified by using 15% EtOAc/hexane to give the title compound (138.0 mg) as an off white solid; mp (DSC) 134.6 °C; R_f 0.20 (1 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 2951, 2219, 1757, 1730, 1276,770; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.65 (1H, m, C_5H_4N), 8.1 (2H, J = 7.6 Hz, C_6H_4),7.92 (1H, m, C_5H_4N), 7.81 (2H, J = 8.4 Hz, C_6H_4), 7.70 (1H, d, J = 8.4 Hz, C_5H_4N),7.68 (2H, d, J = 8.4 Hz, p-BrC_6H_4), 7.59 (2H, J = 8.0 Hz, p-BrC_6H_4), 7.48 (1H, m, C_6H_4), 6.30(1H, s, CH), , 3.69 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.7, 73.9, 87.0, 91.9, 122.8, 124.0, 126.7, 127.6, 128.7 (2C), 129.8 (2C), 129.9 (2C), 131.9 (2C), 132.2, 132.9, 136.9, 141.6, 150.3, 164.2, 168.5; mass (ES) *m/z* 450.0 (M + 1); HRMS (ESI) calculated for $C_{23}H_{17}NO_4Br$ $[M + H]^+$ 450.0338; found 450.0341.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(phenylethynyl) benzoate (4e)

This compound was purified by using 10% EtOAc/hexane to give the title compound (115.2 mg) as an off white solid; mp (DSC) 102.09 °C; R_f 0.63(1 : 3 EtOAc/hexane); IR (film) 2218, 1755, 1716, 1260, 763 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05 (2H, d, J = 7.60 Hz, C_6H_4), 7.74 (2H, d, J = 7.60 Hz, C_6H_4), 7.68 (2H, d, J = 7.6, O-ClC_6H_4), 7.60–7.62 (2H, m, O-ClC_6H_4), 7.50–7.53 (5H, m, C_6H_5), 6.63 (1H, s, CH), 3.74 (3H, s, OCH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 52.9, 71.4, 121.5 (2C), 127.9 (2C), 128.8 (2C), 129.3 (2C), 129.7 (2C), 130.0 (2C), 130.2 (2C), 131.5 (2C), 131.8 (2C), 133.0 (2C), 164.1, 167.9; mass (ES) *m/z* 405.20 (M + 1); HRMS (ESI) calculated for $C_{24}H_{18}O_4Cl[M + H]^+$ 405.0885; found 405.0894.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(4-hydroxybut-1-yn-1-yl) benzoate (4f)

This compound was purified by using 15% EtOAc/hexane to give the title compound (93.1 mg) as a light yellow oil; R_f 0.21 (1 : 3 EtOAc/hexane); IR (film) 3420, 2954, 2233, 1732, 1255, 766 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (2H, d, J = 8.4 Hz, C_6H_4), 7.59–7.64 (2H, m, O-ClC_6H_{4c}), 7.57 (2H, d, J = 8.4 Hz, C_6H_4), 7.46–7.50 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 5.75 (1H, b, OH), 3.73 (3H, s, OCH_3), 3.61 (2H, m, CH_2), 2.61 (2H, t, J = 6.8 Hz, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.4, 53.0, 59.5, 71.4, 80.4, 93.1, 127.4, 128.0, 128.9, 129.7 (2C), 130.1, 130.2 (2C), 131.4, 131.7, 131.9, 133.2, 164.3, 168.1; mass (ES) *m/z* 390.3 (M + 18); HRMS (ESI) calculated for $C_{20}H_{18}O_5Cl[M + H]^+$ 373.0839; found 373.0843.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(5-chloropent-1-yn-1-yl) benzoate (4g)

This compound was purified by using 15% EtOAc/hexane to give the title compound (136.2 mg) as a light yellow oil; R_f 0.59 (1 : 3 EtOAc/hexane); IR (film) 2955, 2229, 1759, 1255, 766 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (2H, d, J = 7.6 Hz, C_6H_4), 7.60–7.69 (4H, m, O-ClC_6H_{4c}), 7.46–7.59 (2H, m, C_6H_4), 6.60 (1H, s, CH), 3.75–3.79 (2H, t, J = 6.4 Hz, CH_2), 3.73 (3H, s, OCH_3), 2.61–2.65 (2H, t, J = 6.8 Hz, CH_2), 1.99–2.49 (2H, t, J = 6.8 Hz, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.2, 30.7, 44.1, 52.9, 71.4, 80.4, 93.2, 127.5, 127.9, 128.5, 129.6 (2C), 130.0, 130.2, 131.4, 131.6, 131.8, 133.1 (2C), 164.2, 168.0; mass (ES) *m/z* 405.20 (M + 1); HRMS (ESI) calculated for $C_{21}H_{19}O_4Cl_2$ $[M + H]^+$ 405.0600; found 405.0660.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(hex-1-yn-1-yl) benzoate (4h)

This compound was purified by using 10% EtOAc/hexane to give the title compound (124.5 mg) as a light yellow oil; R_f 0.77 (1 : 3 EtOAc/hexane); IR (film) 2932, 2229, 1732, 1255, 766 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (2H, d, J = 8.4 Hz, C_6H_4), 7.55 (2H, d, J = 8.4 Hz, C_6H_4), 7.48 (4H, m, O-ClC_6H_{4c}), 6.60 (1H, s, CH), 3.73 (3H, s, OCH_3), 2.45–2.49

(2H, m, CH_2), 1.51–1.58 (2H m, CH_2), 1.40–1.47 (2H, m, CH_2), 0.89–0.93 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.9, 18.8, 21.8, 30.4, 53.4, 71.8, 80.3, 95.4, 127.7, 128.4, 129.3, 130.1, 130.5, 130.6, 131.8 (2C), 132.1, 132.2 (2C), 133.6, 164.7, 168.5; mass (ES) m/z 385.20 (M + 1); HRMS (ESI) calculated for $C_{22}H_{22}O_4Cl$ $[M + H]^+$ 385.1216; found 385.1207.

1-(2-chlorophenyl)-2-methoxy-2-oxoethyl-4-(3-hydroxybut-1-yn-1-yl) benzoate (4i)

This compound was purified by using 15% EtOAc/hexane to give the title compound (98.0 mg) as a light yellow oil; R_f 0.26 (1 : 3 EtOAc/hexane); IR (film) 3467, 2954, 1741, 1222, 756 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (2H, d, J = 8.4 Hz, C_6H_4), 7.61–7.66 (2H, m, O-ClC_6H_4), 7.59 (2H, d, J = 8.4 Hz, C_6H_4), 7.45–7.53 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 5.56 (1H, b, OH), 4.60–4.65 (1H, q, J = 6.8 Hz, CHOH), 3.73 (3H, s, OCH_3), 1.40 (3H, d, J = 6.4 Hz, CH_3); ^{13}C NMR (50 MHz, CD_3OD): δ 25.0, 53.8, 59.4, 73.4, 83.6, 96.7, 129.1, 130.2, 130.3, 131.2 (2C), 131.4, 131.6, 132.5 (2C), 133.2, 133.9, 135.7, 166.7, 170.6; mass (ES) m/z 373.10 (M + 1); HRMS (ESI) calculated for $C_{20}H_{18}O_5Cl$ $[M + H]^+$ 373.0854; found 373.0843.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-((1-hydroxycyclohexyl)ethynyl) benzoate (4j)

This compound was purified by using 10% EtOAc/hexane to give the title compound (113.5 mg) as a light yellow oil; R_f 0.38 (1 : 3 EtOAc/hexane); IR (film) 3411, 2934, 1729, 1256, 754 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (2H, d, J = 8.4 Hz, C_6H_4), 7.59–7.65 (2H, m, O-ClC_6H_4), 7.58 (2H, d, J = 8.8 Hz, C_6H_4), 7.45–7.52 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 5.75 (1H, b, OH), 3.73 (3H, s, OCH_3), 1.47–1.66 (10H, m, $CH_{2\ cyclohexanol}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.5, 22.7, 24.6, 24.8, 52.9, 67.0, 71.4, 81.8, 98.8, 127.6, 127.9, 128.2, 129.7 (2C), 130.0 (2C), 130.2, 131.4 (2C), 131.6, 131.7, 133.1, 164.2, 168.0; mass (ES) m/z 427.3 (M + 1); HRMS (ESI) calculated for $C_{24}H_{24}O_5Cl$ $[M + H]^+$ 427.1310; found 427.1312.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(pyridin-2-ylethynyl) benzoate (4k)

This compound was purified by using 15% EtOAc/hexane to give the title compound (108.4 mg) as a light yellow oil; R_f 0.21 (1 : 3 EtOAc/hexane); IR (film) 3467, 2954, 1741, 1222, 756 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63–8.65 (1H, m, C_5H_4N), 8.07(2H, d, J = 8.0 Hz, C_6H_4), 7.91 (1H, m, C_5H_4N), 7.81 (2H, d, J = 8.0 Hz, C_6H_4), 7.72 (1H, d, J = 8.0 Hz, O-ClC_6H_4), 7.60–7.68 (2H, m, C_5H_4N), 7.44–7.53 (3H, m, O-ClC_6H_4), 6.63 (1H, s, CH), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 71.5, 87.0, 91.9, 124.0, 126.8, 127.6, 127.9, 128.6 (2C), 129.8, 130.0, 130.2, 131.3, 131.5, 132.2 (2C), 133.0, 136.9, 141.6, 150.2, 164.1, 167.9; mass (ES) m/z 406.10 (M + 1); HRMS (ESI) calculated for $C_{23}H_{17}NO_4Cl$ $[M + H]^+$ 406.0858; found 406.0846.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-((2-nitrophenyl) ethynyl) benzoate (4l)

This compound was purified by using 10% EtOAc/hexane to give the title compound (135.7 mg) as an orange colour solid; mp (DSC) 180.53 °C; R_f 0.37 (1 : 3 EtOAc/hexane); IR (film) 2954, 1752, 1718, 1490, 1390, 756 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (2H, d, J = 8.8 Hz, O-$NO_2C_6H_4$), 8.19 (2H, d, J = 8.4 Hz, C_6H_4), 7.82-7.84 (1H, m, O-$NO_2C_6H_4$), 7.71–7.76 (2H, m, C_6H_4), 7.68–7.70 (2H, m, O-ClC_6H_4), 7.60–7.62 (1H, m, O-$NO_2C_6H_4$), 7.46–7.54 (2H, m, O-ClC_6H_4), 6.64 (1H, s, CH), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 71.5, 114.2, 121.8, 122.7, 127.5, 127.9, 129.0 (2C), 129.5, 130.0 (2C), 130.2 (2C), 130.6, 131.0, 131.3, 131.5, 131.9, 133.0, 135.2, 147.3, 164.12, 168.0; mass (ES) m/z 450.20 (M + 1); HRMS (ESI) calculated for $C_{24}H_{17}NO_6Cl$ $[M + H]^+$ 450.0752; found 450.0744.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-((6-methoxynaphthalen-2-yl)ethynyl) benzoate (4m)

This compound was purified by using 10% EtOAc/hexane to give the title compound (123.3 mg) as a pale yellow colour solid; mp (DSC) 161.57 °C; R_f 0.53 (1 : 3 EtOAc/hexane); IR (film) 1741, 1719, 1268,, 1088, 767 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (1H, S, $CH_{naphthalene}$), 8.07 (2H, d, J = 8.4 Hz, C_6H_4), 7.85–7.88 (2H, m, $CH_{naphthalene}$), 7.74–7.76 (2H, d, J = 8.4 Hz, C_6H_4), 7.68 (1H, d, J = 9.2 Hz, $CH_{naphthalene}$), 7.59–7.62 (2H, m, O-ClC_6H_4), 7.48–7.59 (2H,m, O-ClC_6H_4),7.39 (1H, s, $CH_{(naphthalene)}$), 7.25 (1H, d, J = 8.8, $CH_{naphthalene}$), 6.63 (1H, s, CH), 3.9 (3H, s, $OCH_{3\ naphthalene}$), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 55.3, 71.4, 106.1, 119.5, 127.2 (2C), 127.3 (2C), 128.0 (2C), 128.4 (2C), 129.5 (2C), 129.8 (2C), 130.0, 130.2, 131.4 (2C), 131.6, 131.7, 133.1 (2C), 134.3 (2C), 168.03, 174.8; mass (ES) m/z 485.30 (M + 1); HRMS (ESI) calculated for $C_{29}H_{22}O_5Cl$ $[M + H]^+$ 485.1156; found 485.1156.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(3-hydroxypent-1-yn-1-yl) benzoate (4n)

This compound was purified by using 15% EtOAc/hexane to give the title compound (105.0 mg) as a light brown oil; R_f 0.33 (1 : 3 EtOAc/hexane); IR (film) 3416, 2932, 1732, 1254, 766 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.0 (2H, d, J = 8.4 Hz, C_6H_4), 7.61–7.65 (2H, m, ClC_6H_4), 7.52–7.59 (2H, m, O-ClC_6H_4), 7.46–7.50 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 5.75 (1H, b, OH), 4.43 (1H, t, J = 6.4 Hz, $CH_{aliphatic}$), 3.73 (3H, s, OCH_3), 1.65–1.69 (2H, m, CH_2), 0.95–0.99 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 9.6, 30.5, 53.0, 62.1, 71.4, 82.2, 96.2, 127.7, 128.0, 128.1, 129.7, 130.0, 130.2 (2C), 131.4(2C), 131.6, 131.8, 133.1, 164.2, 166.0; mass (ES) m/z 387.20 (M + 1); HRMS (ESI) calculated for $C_{21}H_{20}O_5Cl$ $[M + H]^+$ 387.1000; found 387.0999.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(hept-1-yn-1-yl) benzoate (4o)

This compound was purified by using 10% EtOAc/hexane to give the title compound (135.8 mg) as a light yellow colour oil;

R_f 0.74 (1 : 3 EtOAc/hexane);IR (film) 2955, 1760, 1727, 1254, 753 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (2H, d, J = 8.4 Hz, C_6H_4), 7.61–7.65 (2H, m, C_6H_4), 7.55 (2H, d, J = 8.4 Hz, O-ClC_6H_4), 7.44–7.52 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 3.72 (3H, s, OCH_3), 2.44–2.48 (2H, t, J = 6.8 Hz, CH_2), 1.52–1.59 (2H, m, CH_2), 1.28–1.40 (4H, m, CH_2), 0.90–0.87 (3H, t, J = 6.8 Hz, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 13.8, 18.6, 21.5, 27.6, 30.5, 52.9, 71.3, 79.8, 95.0, 127.2, 127.9, 128.8, 129.6, 129.9, 130.1 (2C), 131.3, 131.5, 131.6 (2C), 133.0, 164.1, 167.9; mass (ES) m/z 399.20 (M + 1); HRMS (ESI) calculated for $C_{23}H_{23}O_4Cl$ $[M + H]^+$ 399.1358; found 399.1363.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4-(oct-1-yn-1-yl) benzoate (4p)

This compound was purified by using 10% EtOAc/hexane to give the title compound (133.6 mg) as a light yellow colour oil; R_f 0.74 (1 : 3 EtOAc/hexane); IR (film) 2954, 2226, 1760, 1727, 1255, 766 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (2H, d, J = 8.4 Hz, C_6H_4), 7.61–7.65 (2H, m, C_6H_4), 7.55 (2H, d, J = 7.6 Hz, O-ClC_6H_4), 7.44–7.52 (2H, m, O-ClC_6H_4), 6.60 (1H, s, CH), 3.72 (3H, s, OCH_3), 2.44–2.48 (2H, t, J = 6.8 Hz, CH_2), 1.52–1.59 (2H, m, CH_2), 1.28–1.40 (6H, m, CH_2), 0.89–0.85 (3H, t, J = 6.8 Hz, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 13.8, 18.7, 21.9, 27.9, 30.7, 52.9, 71.3, 79.8, 95.0, 127.2, 127.9, 128.9 (2C), 129.6 (2C), 130.0 (2C), 130.2, 131.4, 131.6, 131.7, 133.0, 164.2, 168.0; mass (ES) m/z 413.0 (M + 1); HRMS (ESI) calculated for $C_{24}H_{26}O_4Cl$ $[M + H]^+$ 413.1515; found 413.1520.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl 2-(hex-1-yn-1-yl) benzoate (4q)

This compound was purified by using 10% EtOAc/hexane to give the title compound (116.2 mg) as a light yellow oil; R_f 0.76 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97–795 (2H, d, J = 8.0 Hz, C_6H_4), 7.55 (2H, d, J = 8.0 Hz, C_6H_4), 7.48–7.53 (4H, m, O-ClC_6H_{4c}), 6.60 (1H, s, CH), 3.72 (3H, s, OCH_3), 2.45–2.50 (2H, m, CH_2), 1.52–1.54 (2H m, CH_2), 1.28–1.44 (2H, m, CH_2), 0.89–0.93 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.9, 18.7, 21.9, 30.7, 52.9, 71.3, 79.8, 95.0, 127.2, 127.9, 128.9, 129.6(2C), 130.1, 130.2, 131.4(2C), 131.7 (2C), 133.0, 164.2, 168.0; mass (ES) m/z 385.20 (M + 1); HRMS (ESI) calculated for $C_{22}H_{22}O_4Cl$ $[M + H]^+$ 385.1207; found 385.1195.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl 3-(hex-1-yn-1-yl) benzoate (4r)

This compound was purified by using 10% EtOAc/hexane to give the title compound (119.5 mg) as light yellow oil; R_f 0.77 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (2H, d, J = 8.0 Hz, C_6H_4), 7.7 (2H, d, J = 8.0 Hz, C_6H_4), 7.67–7.5 (4H, m, O-ClC_6H_{4c}), 6.62 (1H, s, CH), 3.73 (3H, s, OCH_3), 2.46–2.42 (2H, t, J = 7.7 Hz, CH_2), 1.52–1.55 (2H m, CH_2), 1.44–1.46 (2H, m, CH_2), 0.88–0.93 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.4, 18.2, 21.4, 30.0, 52.9, 71.4, 79.2, 92.3, 127.9, 128.7, 128.8, 129.4, 130.0, 130.1, 130.2, 131.3, 131.5, 131.7, 133.0, 136.4, 164.0, 167.9; mass (ES) m/z 385.20 (M + 1); HRMS (ESI) calculated for $C_{22}H_{22}O_4Cl$ $[M + H]^+$ 385.1207; found 385.1190.

A typical procedure for one-pot NHC mediated hydroacylation and Heck reactions

To a mixture of imidazolium salt (14.8 mg, 0.044 mmol) and 4-iodobenzaldehyde (100 mg, 0.43 mmol) in THF (5.0 mL) triethylamine (109 mg, 1.08 mmol), methyl 2-(4-bromophenyl)-2-oxoacetate (157.1 mg, 0.646 mmol) palladium(II)acetate (4.84 mg, 0.022 mmol) were added, followed by methyl acrylate (148.4 mg, 1.72 mmol) under a nitrogen atmosphere. The mixture was then stirred at 28–32 °C for 15 h (monitored the reaction by TLC). After completion of the reaction the mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (230–400 mesh) using 10–20% EtOAc/hexane.

(*E*)-1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(3-methoxy-3-oxoprop-1-en-1-yl) benzoate (6a)

This compound was purified by using 10% EtOAc/hexane to give the title compound (121.0 mg) as a light yellow colour oil; R_f 0.36 (1 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05 (2H, d, J = 7.6 Hz, C_6H_4), 7.92 (2H, d, J = 8.4 Hz, C_6H_4), 7.76 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.71 (2H, d, J = 8.4 Hz p-BrC_6H_4), 7.58 (2H, d, J = 8.0 Hz, p-BrC_6H_4)); 6.83 (1H, d, J = 16 Hz, $CH_{ethylene}$), 6.29 (1H, s, CH), 3.75 (3H, s, OCH_3), 3.72 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 51.6, 52.7, 73.8, 120.8, 122.7, 128.7 (2C), 129.5 (2C), 129.8 (2C), 129..9, 131.8 (2C), 133.0, 139.1, 142.8, 164.4, 166.2, 168.5; mass (ES) m/z 433.2 (M + 1); HRMS (ESI) calculated for $C_{20}H_{18}O_6Br$ $[M + H]^+$ 433.0296; found 433.0287.

(*E*)-1-(4-bromophenyl)-2-methoxy-2-oxoethyl-4-(3-ethoxy-3-oxoprop-1-en-1-yl) benzoate (6b)

This compound was purified by using 10% EtOAc/hexane to give the title compound (136.5 mg) as a light yellow colour oil; R_f 0.44 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05 (2H, d, J = 8.4 Hz, C_6H_4), 7.92 (2H, d, J = 8.4 Hz, C_6H_4), 7.74 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.70 (2H, d, J = 8.8 Hz, p-BrC_6H_4), 7.58 (2H, d, J = 8.0 Hz, p-BrC_6H_4), 6.81 (1H, d, J = 16.0 Hz, $CH_{ethylene}$), 6.28 (1H, s, CH), 4.20–4.24 (2H, q, J = 7.6 Hz, CH_2), 3.69 (3H, s, OCH_3), 1.32–1.36 (3H, t, J = 7.6 Hz, $OCH_2\underline{CH_3}$);^{13}C NMR (100 MHz, DMSO-d_6): δ 14.1, 52.7, 60.2, 73.8, 121.2, 122.7, 128.7 (2C), 129.5 (2C), 129.7, 129.8 (2C), 131.8 (2C), 133.0, 139.2, 142.7, 164.4, 165.8, 168.5; mass (ES) m/z 447.2 (M + 1); HRMS (ESI) calculated for $C_{21}H_{20}O_6Br$ $[M + H]^+$ 447.0493; found 447.0443.

(*E*)-1-(4-bromophenyl)-2-methoxy-2-oxoethyl-4-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl) benzoate (6c)

This compound was purified by using 10% EtOAc/hexane to give the title compound (131.0 mg) as light yellow colour oil; R_f 0.53 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ

8.03 (2H, d, J = 8.4 Hz, C_6H_4), 7.89 (2H, d, J = 8.4 Hz, C_6H_4), 7.71 (2H, d, J = 8.4 Hz, p-BrC_6H_4), 7.64 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.58(2H, d, J = 8.8 Hz, p-BrC_6H_4), 6.70 (1H, d, J = 16.4 Hz, $CH_{ethylene}$), 6.28 (1H, s, CH), 3.69 (3H, s, OCH_3), 1.49 (9H, s, $O(CH_3)_3$);^{13}C NMR (100 MHz, DMSO-d_6): δ 27.7 (3C), 52.7, 73.8, 80.3, 122.7, 122.8, 128.6 (2C), 129.3 (2C), 129.8 (2C), 129.9, 131.9 (2C), 133.0, 139.3, 141.9, 164.4, 165.1, 168.5; mass (ES) m/z 497.2 (M+23); HRMS (ESI) calculated for $C_{23}H_{22}O_6Br$ $[M - H]^+$ 473.0619; found 473.0600.

(*E*)-1-(2-chlorophenyl)-2-methoxy-2-oxoethyl-4-(3-methoxy-3-oxoprop-1-en-1-yl) benzoate (6d)

This compound was purified by using 10% EtOAc/hexane to give the title compound (117.3 mg) as a light yellow colour oil; R_f 0.38 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (2H, d, J = 8.4 Hz, C_6H_4), 7.91 (2H, d, J = 8.8 Hz, C_6H_4), 7.73 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.59–7.68(2H, m, O-ClC_6H_4), 7.45–7.53 (2H, m, O-ClC_6H_4); 6.80 (1H, d, J = 16 Hz, $CH_{ethylene}$),6.60 (1H, s, CH), 3.75 (3H, s, OCH_3), 3.72 (3H, s, OCH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 51.6, 52.9, 71.4, 120.8, 127.9, 128.7 (2C), 129.4 (2C), 129.8, 130.0, 130.1, 131.3, 131.6, 133.0, 139.1, 142.8, 164.2, 166.2, 167.9; mass (ES) m/z 389.2 (M + 1); HRMS (ESI) calculated for $C_{20}H_{18}O_6Cl[M + H]^+$ 389.0783; found 389.0792.

(*E*)-1-(2-chlorophenyl)-2-methoxy-2-oxoethyl-4-(3-ethoxy-3-oxoprop-1-en-1-yl) benzoate (6e)

This compound was purified by using 10% EtOAc/hexane to give the title compound (112.8 mg) as a light yellow colour oil. R_f 0.46 (1 : 3 EtOAc/hexane);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (2H, d, J = 8.8 Hz, C_6H_4), 7.69 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.60 (2H, d, J = 8.4 Hz, C_6H_4), 7.45–7.57 (2H, m, O-ClC_6H_4), 7.32–7.38 (2H, m, O-ClC_6H_4); 6.70 (1H, s, CH), 6.51 (1H, d, J = 15.6 Hz, $CH_{ethylene}$), 4.25-4.30 (2H, q, J = 6.8 Hz, CH_2), 3.79 (3H, s, OCH_3), 1.32–1.36 (3H, t, J = 6.8 Hz, OCH_3); ^{13}C NMR (50 MHz, DMSO-d_6): δ 14.1, 52.9, 60.2, 71.4, 121.2, 127.9, 128.7 (2C), 129.4 (2C), 129.9, 130.0, 130.2, 131.3, 131.6, 133.0, 139.2, 142.7, 164.2, 165.8, 168.0; mass (ES) m/z 403.2 (M + 1); HRMS (ESI) calculated for $C_{21}H_{20}O_6Cl$ $[M + H]^+$ 403.0945; found 403.0948.

(*E*)-1-(2-chlorophenyl)-2-methoxy-2-oxoethyl-4-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl) benzoate (6f)

This compound was purified by using 10% EtOAc/hexane to give the title compound (137.4 mg) as a light yellow colour oil; R_f 0.56 (1 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (2H, d, J = 8.4 Hz, C_6H_4), 7.89 (2H, d, J = 8.4 Hz, C_6H_4), 7.65 (1H, d, J = 16 Hz, $CH_{ethylene}$),7.59–7.45 (4H, m, O-ClC_6H_4), 6.69 (1H, d, J = 15.6 Hz, $CH_{ethylene}$), 6.28 (1H, s, CH), 3.73 (3H, s, OCH_3), 1.49 (9H, s, $(CH_3)_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.6 (3C), 52.5, 71.1, 80.3, 122.7, 122.8, 128.6 (2C), 129.3 (2C), 129.7, 129.8 (2C), 131.9 (2C), 133.0, 139.3, 141.9, 164.1, 164.7, 167.8; mass (ES) m/z 431.3 (M + 1); HRMS (ESI) calculated for $C_{23}H_{24}O_6Cl$ $[M + H]^+$ 431.1263; found 431.1261.

(*E*)-1-(2-chlorophenyl)-2-methoxy-2-oxoethyl 2-(3-ethoxy-3-oxoprop-1-enyl) benzoate (6g)

This compound was purified by using 10% EtOAc/hexane to give the title compound (120.0 mg) as light yellow colour oil. R_f 0.46 (1 : 3 EtOAc/hexane);^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (2H, d, J = 8.4 Hz,C_6H_4), 7.92 (2H, d, J = 8.4 Hz, C_6H_4), 7.74 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.59–7.68(2H, m, O-ClC_6H_4), 7.49–7.53 (2H, m, O-ClC_6H_4); 6.80 (1H, d, J = 16 Hz, $CH_{ethylene}$),6.62 (1H, s, CH), 4.2–4.24(2H, m, CH_2), 3.73 (3H, s, OCH_3), 1.25–1.28(3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.1, 52.9, 60.2, 71.4, 121.2, 127.9, 128.7 (2C), 129.4 (2C), 129.9, 130.0, 130.2, 131.3, 131.6, 133.0, 139.2, 142.7, 164.2, 165.7, 168.0; mass (ES) m/z 403.2 (M + 1); HRMS (ESI) calculated for $C_{21}H_{20}O_6Cl$ $[M + H]^+$ 403.0948; found 403.0932.

(*E*)-1-(2-chlorophenyl)-2-methoxy-2-oxoethyl 3-(3-ethoxy-3-oxoprop-1-enyl) benzoate (6h)

This compound was purified by using 10% EtOAc/hexane to give the title compound (123.2 mg) as light yellow colour oil. R_f 0.47 (1 : 3 EtOAc/hexane);^{1}H NMR (400 MHz, DMSO-d_6): δ 8.26(1H, s, C_6H_4), 8.12 (2H, d, J = 8.0 Hz, C_6H_4), 7.78 (1H, d, J = 16 Hz, $CH_{ethylene}$), 7.52–7.58 (1H, m, C_6H_4), 7.60–7.70 (2H, m, O-ClC_6H_4, 7.48–7.51 (2H, m, O-ClC_6H_4); 6.75 (1H, d, J = 16 Hz, $CH_{ethylene}$), 6.64 (1H, s, CH), 4.18–4.23 (2H, m, CH_2), 3.73 (3H, s, OCH_3), 1.25–1.28 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.1, 52.9, 60.3, 71.4, 125.0, 125.4 126.6, 127.1, 128.0, 128.9, 130.0, 130.2, 131.3, 131.7, 133.1, 138.4, 143.5, 145.6, 164.4, 165.7, 168.1; mass (ES) m/z 403.2 (M + 1); HRMS (ESI) calculated for $C_{21}H_{20}O_6Cl$ $[M + H]^+$ 403.0948; found 403.0930.

A typical procedure for one-pot NHC mediated hydroacylation and Suzuki reaction

To a mixture of imidazolium salt (14.8 mg, 0.044 mmol) and 4-iodobenzaldehyde (100 mg, 0.43 mmol) in THF (5.0 mL) was added triethylamine (109 mg, 1.08 mmol), methyl 2-(4-bromophenyl)-2-oxoacetate (157.1 mg, 0.646 mmol), palladium(II) acetate (4.84 mg, 0.022 mmol) followed by 3-(hydroxyl methyl) phenyl boronic acid (98.2 mg, 0.646 mmol) under a nitrogen atmosphere. The mixture was then stirred at 28–32 °C for 8 h (monitored by TLC). After completion the reaction mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (230–400 mesh) using 10-20% EtOAc/hexane.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-3′-(hydroxymethyl)-[1,1′-biphenyl]-4-carboxylate (8a)

This compound was purified by using 15% EtOAc/hexane to give the title compound (130.0 mg) as a light brown color oil. R_f 0.38 (2 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (2H, d, J = 8.4 Hz, C_6H_4), 7.87 (2H, d, J = 8.4 Hz, C_6H_4), 7.71 (1H, d, J = 8.8 Hz, $C_6H_{4\,benzyl}$), 7.71(2H, d, J = 8.8 Hz, p-BrC_6H_4),7.63 (1H, s, $C_6H_{4\,benzyl}$), 7.6 (2H, d, J = 8.4 Hz,

p-BrC_6H_4), 7.47 (1H, d, J = 7.6 Hz, $C_6H_{4\ benzyl}$), 7.40 (1H, d, J = 8.0 Hz, $C_6H_{4\ benzyl}$), 6.30 (1H, s, CH), 5.30 (1H, b, OH), 4.59 (2H, s, CH_2), 3.70 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.7, 65.2, 73.7, 122.7, 125.0, 125.4, 126.6, 127.1, 127.2, 128.9 (2C), 129.8 (2C), 130.1 (2C), 131.9 (2C), 133.1, 138.5, 143.5, 145.6, 164.8, 168.7; mass (ES) m/z 476.9 (M+23); HRMS(ESI) calculated for $C_{23}H_{18}O_5Br$ $[M - H]^+$ 453.0378; found 453.0338.

1-(4-Bromophenyl)-2-methoxy-2-oxoethyl-4-(furan-2-yl) benzoate (8b)

This compound was purified by using 20% EtOAc/hexane to give the title compound (123.0 mg) as an off white solid; mp (DSC) 109.6 °C; R_f 0.40 (2 : 3 EtOAc/hexane);^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (2H, d, J = 8.8 Hz, C_6H_4), 7.88 (2H, d, J = 8.4 Hz, C_6H_4), 7.87 (1H, d, J = 1.6 Hz, CH_{furan}), 7.71 (2H, d, J = 8.8 Hz, *p*-BrC_6H_4), 7.6 (2H, d, J = 7.6 Hz, *p*-BrC_6H_4), 7.20 (1H, d, J = 3.6 Hz, CH_{furan}), 6.8 (1H, dd, J_1 = 1.6 Hz, J_2 = 2.0 Hz $_{\prime}$ CH_{furan}), 6.27 (1H, s, CH), 3.69 (3H, s, OCH_3);^{13}C NMR (100 MHz, DMSO-d_6): δ 52.7, 73.7, 108.9, 112.5, 122.7, 123.5, 126.7 (2C), 129.8 (2C), 130.2 (2C), 131.9 (2C), 133.1, 134.9, 144.4, 151.7, 164.5, 168.7; mass (ES) m/z 415.1 (M + 1); HRMS (ESI) calculated for $C_{20}H_{16}O_5Br$[M + H]$^+$ 415.0173; found 415.0181

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-3′-(hydroxymethyl)-[1,1′-biphenyl]-4-carboxylate (8c)

This compound was purified by using 15% EtOAc/hexane to give the title compound (116.8 mg) as a light brown color oil; R_f 0.40 (2 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 3543, 2949, 2344, 1749, 1709, 1260, 756; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (2H, d, J = 8.4 Hz, C_6H_4), 7.87 (2H, d, J = 8.0 Hz, C_6H_4), 7.68–7.60 (4H, m, $C_6H_{4\ benzyl}$), 7.54–7.50 (2H, m, *O*-ClC_6H_4), 7.49–7.38(2H, m, *O*-ClC_6H_4); 6.63 (1H, s, CH), 5.30–5.28 (1H, t, J = 6.0 Hz, OH), 4.59 (2H, d, J = 5.6 Hz, CH_2), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 62.7, 71.3, 125.0, 125.4, 126.6, 127.1, 128.0 (2C), 128.9 (2C), 130.0 (2C), 130.2 (2C), 131.3, 131.7, 133.1, 138.4, 143.5, 145.6, 164.6, 168.1; mass (ES) m/z 411.1 (M + 1); HRMS (ESI) calculated for $C_{23}H_{20}O_5Cl$ [M + H]$^+$ 411.1004; found 411.0999.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4′-formyl-[1,1′-biphenyl]-4-carboxylate (8d)

This compound was purified by using 20% EtOAc/hexane to give the title compound (121.5 mg) as a light brown color oil; R_f 0.35 (2 : 3 EtOAc/hexane); IR (cm^{-1}, KBr) 2955, 2150, 1753, 1766, 1262, 772; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (1H, s, CHO), 8.14 (2H, d, J = 8.4 Hz, C_6H_4), 8.00 (2H, d, J = 8.8 Hz, C_6H_4), 7.96–7.87 (4H, m, $C_6H_{4\ benzaldehyde}$), 7.69–7.60 (2H, m, *O*-ClC_6H_4), 7.54–7.46 (2H, m, *O*-ClC_6H_4); 6.65 (1H, s, CH), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 71.4, 127.7 (2C), 127.8 (2C), 128.0 (2C), 128.1 (2C), 130.0 (2C), 130.2 (2C), 131.3, 131.6, 133.1, 135.8, 144.0, 144.2, 164.4, 168.0, 192.7; mass (ES) m/z 409.2 (M + 1); HRMS(ESI) calculated for $C_{23}H_{18}O_5Cl$ [M + H]$^+$ 409.0842; found 409.0843.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-4′-fluoro-3′-methyl-[1,1′-biphenyl]-4-carboxylate (8e)

This compound was purified by using 20% EtOAc/hexane to give the title compound (126.3 mg) as a light brown color oil; R_f 0.6 (2 : 3 EtOAc/hexane);^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08 (2H, d, J = 8.4 Hz, C_6H_4), 7.85 (2H, d, J = 8.0 Hz, C_6H_4), 7.60–7.71 (4H, m, *O*-ClC_6H_4), 7.59–7.50 (2H, m, *p*-FC_6H_3), 7.29–7.25 (1H, m, *p*-FC_6H_3), 6.63 (1H, s, CH), 3.74 (3H, s, OCH_3), 2.32 (3H, s, CH_3^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3, 53.0, 71.3, 113.3, 115.3, 115.5, 115.7, 125.0, 125.1, 126.4, 126.5, 128.0, 130.1, 130.2, 130.4, 131.4, 131.7, 133.1, 134.8, 144.6, 164.6, 168.2; mass (ES) m/z 413.2 (M + 1); HRMS (ESI) calculated for $C_{23}H_{19}O_4FCl$ [M + H]$^+$ 413.0949; found 413.0956.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-3′-(hydroxymethyl) biphenyl-2-carboxylate (8f)

This compound was purified by using 15% EtOAc/hexane to give the title compound (106.2 mg) as light brown color oil. R_f 0.4 (2 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (2H,d,J = 8.4 Hz, C_6H_4), 7.86 (2H, d, J = 8.0 Hz, C_6H_4), 7.68–7.60 (4H, m, $C_6H_{4\ benzyl}$), 7.45–7.51(4H, m, *O*-ClC_6H_4); 6.63 (1H, s, CH), 5.30–5.28 (1H, t, J = 6.0 Hz, OH), 4.59 (2H, d, J = 5.6 Hz, CH_2), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 62.7, 71.3, 125.0, 125.4, 126.6, 127.1, 128.0 (2C), 128.9 (2C), 130.0 (2C), 130.2 (2C), 131.3, 131.7, 133.1, 138.4, 143.5, 145.6, 164.6, 168.1; mass (ES) m/z 428.2 (M + 18); HRMS (ESI) calculated for $C_{23}H_{20}O_5Cl$ [M + H]$^+$ 411.0999; found 411.0998.

1-(2-Chlorophenyl)-2-methoxy-2-oxoethyl-3′-(hydroxymethyl) biphenyl-3-carboxylate (8g)

This compound was purified by using 15% EtOAc/hexane to give the title compound (113 mg) as light brown color oil. R_f 0.4 (2 : 3 EtOAc/hexane); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.22 (1H, s, $C_6H_{4\ benzyl}$), 8.03 (2H, d, J = 8.4 Hz, C_6H_4), 7.93 (2H, d, J = 8.0 Hz, C_6H_4), 7.68–7.60 (3H, m, $C_6H_{4\ benzyl}$), 7.57–7.50 (2H, m, *O*-ClC_6H_4), 7.48–7.37(2H, m, *O*-ClC_6H_4); 6.65 (1H, s, CH), 5.28–5.25 (1H, t, J = 6.0 Hz, OH), 4.59 (2H, d, J = 5.6 Hz, CH_2), 3.74 (3H, s, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 62.7, 71.4, 124.8, 125.1, 126.1, 127.3, 127.9, 128.3, 128.9(2C), 129.7, 130.0, 130.2, 131.3, 131.7, 132.3, 133.1, 138.6, 141.0, 144.0, 164.7, 168.1; mass (ES) m/z 411.2 (M + 1); HRMS (ESI) calculated for $C_{23}H_{20}O_5Cl$ [M + H]$^+$ 411.0999; found 411.1001.

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