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Palladium(II)-catalyzed intramolecular carboxypalladation-olefin insertion cascade: direct access to indeno[1,2-*b*]furan-2-ones

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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A catalytic, atom-economical, domino 5-*endo-dig* cyclization-intramolecular olefin insertion sequence was developed under mild conditions. Aryl alkynoic acids bearing a tethered enone partner afforded the indeno[1,2-*b*]furan-2-ones, the core skeleton present in a number of biologically significant molecules including the natural product solanacol, under ligand-free, palladium-catalyzed reaction conditions in high yields. The competitive β-hydride elimination in the final step leading to the conjugated analogs was avoided by the addition of lithium bromide. A plausible mechanism for this domino sequence is proposed involving intramolecular carboxypalladation and olefin insertion steps.

Introduction

Indeno[1,2-*b*]furan-2-one and its hydrogenated counterparts are significant structural motifs present in a large number of biologically pertinent synthetic and natural compounds. This tricyclic moiety is the core structure of the family of plant hormones, strigolactones, responsible for cambium activity stimulation, growth regulation, nodule formation, root architecture and inhibition of shoot branching.[1,2] Solanacol **1** was the first example of natural strigolactones possessing indeno[1,2-*b*]furan-2-one skeleton which was isolated from the root exudates of tobacco and tomato.[3] The related synthetic derivative GR24, **2** was also known for its role as the reference compound in seed germination bioassay of parasitic weeds[4] (Fig. 1).

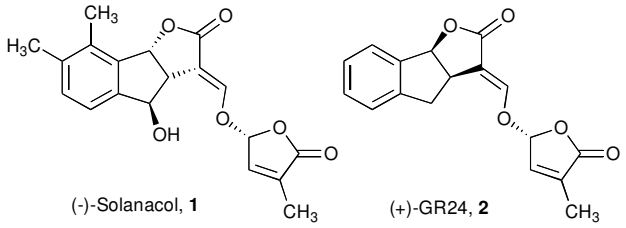

Fig. 1. Representative examples of natural and synthetic indeno[1,2-*b*]furan-2-ones.

Despite the prominence of the indeno[1,2-*b*]furan-2-one moiety only few protocols have been developed for its synthesis. For example, Boyer, Beau and co-workers synthesized the tricyclic compound **4**, a key intermediate for the total synthesis of solanacol, starting from the aryl precursor **3**, involving a ring-closing metathesis/atom-transfer ring closure strategy.[5] Other significant approaches to access indeno[1,2-*b*]furan-2-ones include lactonization of 2-substituted indenone **5**,[2e,6] [2+2] cycloaddition-oxidation sequence of compound **7**[7], cobalt-catalyzed domino reaction between 2-bromoarylaldehyde and dimethyl itaconate[8] and acid catalyzed double cyclization (Scheme 1).[9] Although some of these methods are effective to construct this tricyclic core, they suffer with some limitations including the multistep synthetic route to access the precursors and lower yields. In this connection, we envisioned to design a domino sequence comprising an intramolecular carboxypalladation of alkynoic acids **9** followed by intramolecular olefin insertion to access the indeno[1,2-*b*]furan-2-one derivatives **10** in a single operation (Scheme 1e).

The intramolecular cyclization of alkynoic acids leading to unsaturated lactones and the related nucleophilic cyclization reactions have been conveniently achieved in the presence of transition metal catalysts including copper, gold, palladium, rhodium, ruthenium and iridium.[10,11] Especially gold and palladium catalysts are significant since they allowed a wide variety of interesting alkynoic acid cyclization-initiated domino reaction sequences to access complex molecules in a single operation.[12] Furthermore in the past two decades a large number of palladium catalyzed cascade cyclization reactions have been developed to access compounds that could not be obtained by means of conventional methods.[13]

Results and Discussion

At the outset of this study we synthesized the designed aryl alkynoic acids **9a** and **9b** bearing an enone moiety starting from 2-bromobenzaldehyde involving sequential Sonogashira, Wittig (or aldol) and periodic acid oxidation reactions in high overall yields. The envisioned domino 5-*endo-dig* cyclization-intramolecular olefin insertion sequence was investigated in the presence of palladium acetate under various reaction conditions to achieve indeno[1,2-*b*]furan-2-ones **10** (Table 1). Treatment of alkynoic acid **9a** with the *in situ* generated Pd-SPRIX complex (10 mol%) from palladium acetate and spiro bis(isoxazoline) ligand **13**[14] in toluene at 15 °C afforded a mixture of the expected product **10a** (41% isolated yield), furan-2(3*H*)-one **11a** and small amount of compound **12a** (Table 1, entry 1). The formation of compounds **11a** and **12a** could be

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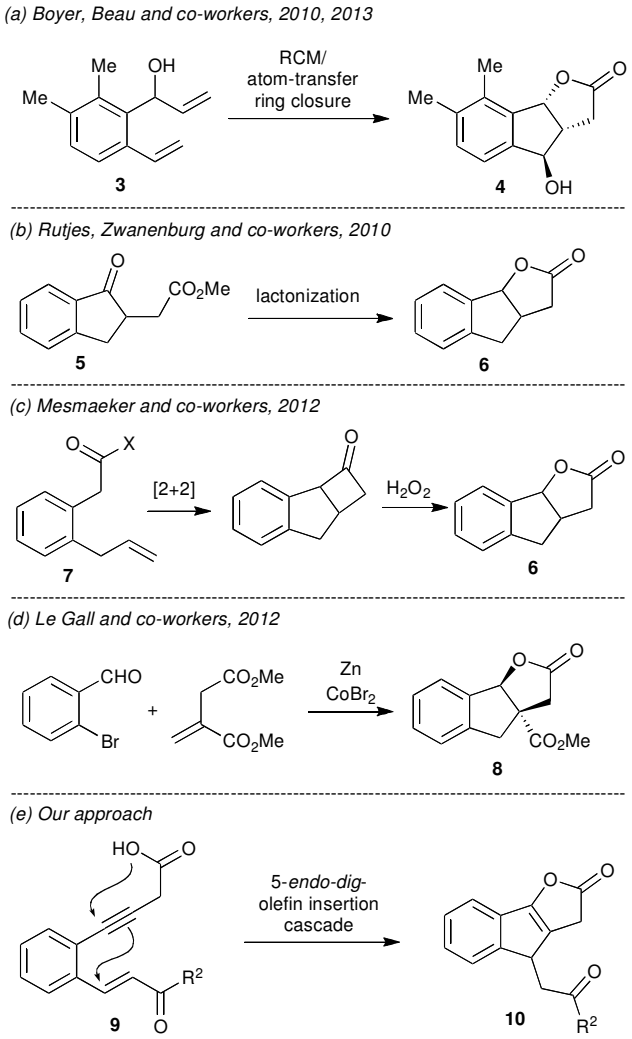
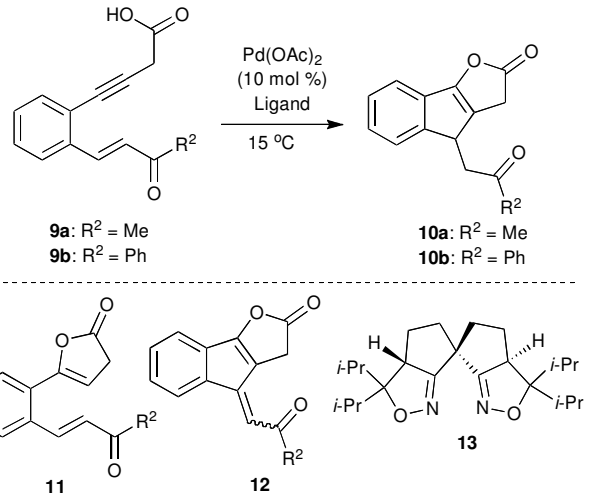


Scheme 1. Synthesis of indeno[1,2-*b*]furan-2-ones from aryl precursors.

explained, respectively, by 5-*endo-dig* cyclization/protonation and 5-*endo-dig* cyclization/intramolecular olefin insertion/β-hydride elimination sequences. Although change of solvent to dioxane completely suppressed the formation of compound **11a**, the β-hydride elimination product **12a** was the major one (entry 2). It has already been proved that lithium bromide reduces the undesirable β-hydride elimination in palladium-catalyzed transformations.[15] Expectedly, addition of two equivalents of LiBr furnished the product **10a** in 72% yield with negligible quantity of the side product **12a** (entry 3). For our surprise, the reaction also smoothly proceeded to afford the product in the absence of any ligand in shorter reaction time with improved yield (entry 4). Use of toluene as solvent under similar experimental conditions further increased the yield to 93% (entry 5). The relatively longer reaction time with Pd-SPRIX complex compared to the ligand-free conditions can be attributed to the steric retardation owing to the bulkiness of the catalytic system and the lower Lewis acidity of the Pd-SPRIX complex. A similar trend in yield was observed for substrate **9b** derived from acetophenone in the presence of $Pd(OAc)_2$, both in dioxane and toluene (entries 6 and 7). But only traces of **10b** was obtained in the presence of 10 mol% $Pd(OAc)_2$-Bpy complex even after 7 h under optimized conditions. Furthermore, use of $PdCl_2$ as catalyst afforded only 12% of **10b** and $PdCl_2(MeCN)_2$ furnished the product in 61% yield (entries 8 and 9).

Table 1. Optimization of reaction conditions[a]



Entry	9	Solvent	Time (h)	10:11:12 ratio	Yield of 10 (%)[d]
1[b]	**9a**	Toluene	12	54:33:13	41
2[b]	**9a**	Dioxane	12	43:0:57	29
3[b]	**9a**	Dioxane	12	92:0:8	72
4	**9a**	Dioxane	2	95:0:5	83
5	**9a**	**Toluene**	**2**	**-[c]**	**93**
6	**9b**	Dioxane	2	-[c]	72
7[e]	**9b**	Toluene	2	-[c]	78
8[f]	**9b**	Toluene	7	-	12
9[g]	**9b**	Toluene	7	-	61

[a] Unless otherwise noted, 1 equiv of **9** and 10 mol% of $Pd(OAc)_2$ were used; In entries 3-9, 2 equiv of LiBr was used. [b] 12 mol% of (*rac*)-*i*-Pr-SPRIX ligand **13** was used. [c] Traces of compound **12** was observed in the crude ^{1}H-NMR spectra. [d] Isolated yield. [e] Only traces of product was observed with 10 mol% of $Pd(OAc)_2$-Bpy complex after 7 h. [f] 10 mol% of $PdCl_2$ was used as catalyst. [g] 10 mol% $PdCl_2(MeCN)_2$ was used as catalyst.

With the optimal conditions for the 5-*endo-dig* cyclization-intramolecular olefin insertion cascade in hand ($Pd(OAc)_2$, LiBr, Toluene, 15 °C), the scope and limitations of the protocol were then examined (Scheme 2). The ligand-free, palladium-catalyzed synthesis of indeno[1,2-*b*]furan-2-ones **10** was shown to tolerate a number of substituents in the tethered enone coupling partner as well as on the aryl moiety. Similar to the optimized substrates **9a** and **9b**, the alkynoic acid **9c** derived from 2-bromobenzaldehyde and pentan-2-one afforded the corresponding cyclized product **10c** in good yield despite its relatively poor stability under ambient conditions. The substrates derived from aryl methyl ketones (**9d**-**9j**) underwent the cascade transformation smoothly to afford the products in high yields (up to 90%). The enone partner tolerated a variety of aryl substituents bearing both electron-donating (OBn, OMe, Me) and electron-withdrawing (Cl) substituents. The 2-naphthyl-derived substrate **9k** was also found to be equally effective. The compounds obtained from heteroaryl ketones (**9l**-**9n**) also furnished the products in reasonably good yields under optimized conditions. Contrarily, ester **9o** failed to afford the domino product; instead, the 5-*endo-dig* cyclization-protonation product **11o** was the only isolated product. Further optimization to achieve the corresponding indeno[1,2-*b*]furan-2-one derivative **10o** under different experimental conditions were ineffective.

Attempts were also made to develop the enantioselective version of the domino sequence combining the palladium catalyst with chiral

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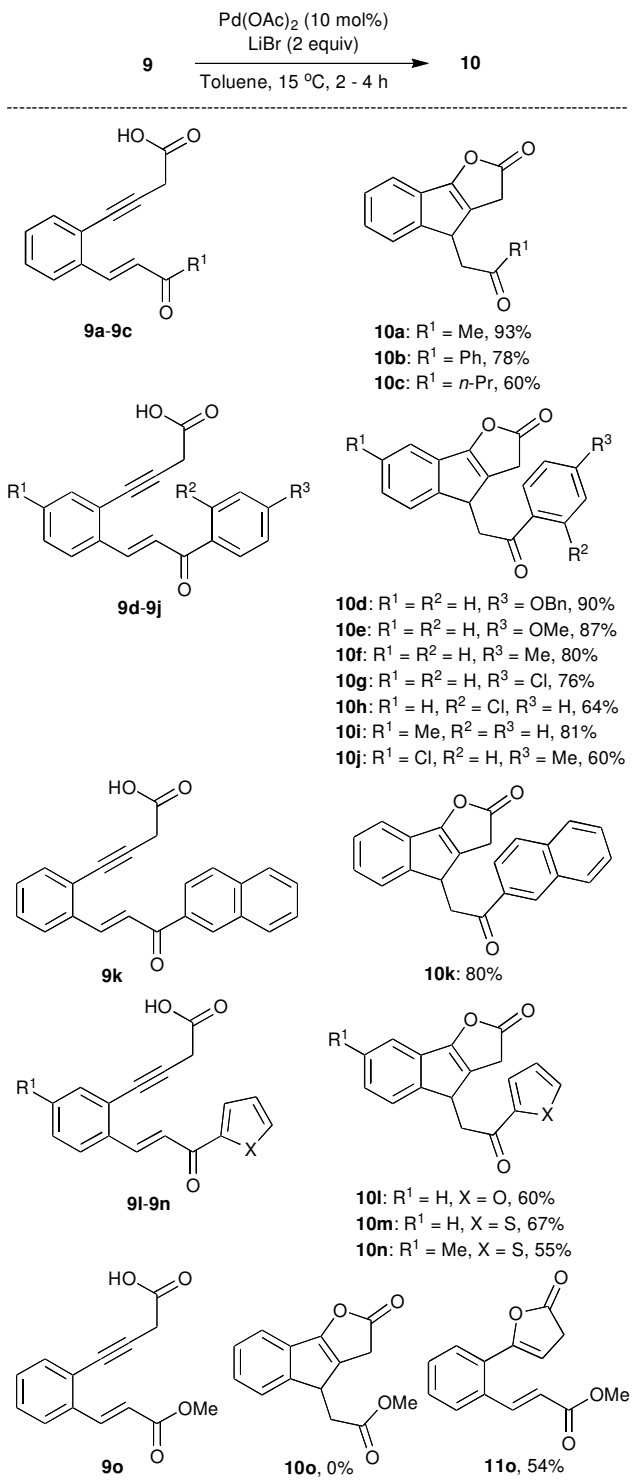
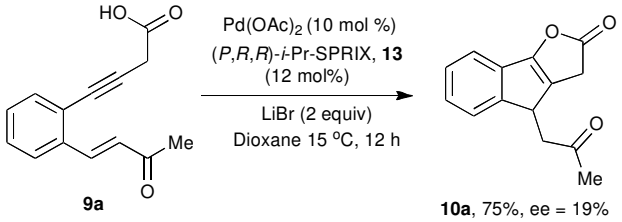


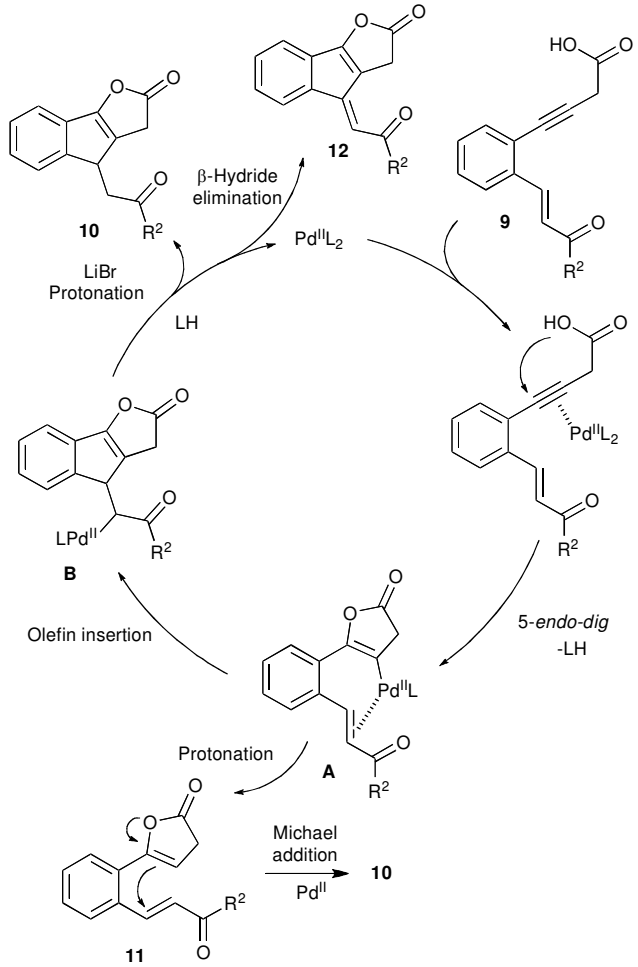
Scheme 2. Scope and limitations of 5-*endo-dig* cyclization/intramolecular olefin insertion cascade. Unless otherwise noted, 1 equiv of **9**, 10 mol% of $Pd(OAc)_2$ and 2 equiv of LiBr were used; reaction conditions: toluene, 15 °C, 2 h. Reaction times for **9c**,**g**,**h**,**i**,**j**,**n** were 4 h and for **9o** was 10 h.

bidentate nitrogen ligands such as (*P,R,R*)-*i*-Pr-SPRIX **13** and (*S,S*)-*t*-BuBOX. Although the latter ligand did not afford any enantioselectivity, chiral Pd-SPRIX complex[16] furnished the product in 75% yield with 19% enantiomeric excess (Scheme 3). Increase of the amount of SPRIX ligand to 20 mol% to avoid the background reaction did not improve the enantioselectivity. The detailed optimization studies to identify a suitable chiral catalytic system to allow high enantioselectivity is under progress in our laboratory.



Scheme 3. Preliminary studies towards the enantioselective version.

A plausible mechanism for the ligand-free palladium-catalyzed synthesis of indeno[1,2-*b*]furan-2-one derivatives is depicted in Scheme 4. Initial coordination of the palladium catalyst to the alkyne moiety trigger the intramolecular nucleophilic cyclization (5-*endo-dig*) to afford the palladium(II) intermediate **A** involving carboxypalladation.[17] Subsequent domino intramolecular olefin insertion followed by protonation afforded product **10** regenerating the catalyst through the intermediacy of species **B**. In the absence of LiBr, a part of intermediate **B** furnished the side product **12** *via* β-hydride elimination. In a separate experiment, treatment of compound **10b** with $Pd(OAc)_2$ and LiBr under optimized conditions



Scheme 4. Plausible mechanism.

for two hours afforded traces of compound **12**. Thus the reverse reaction involving the formation of intermediate **B** and the

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subsequent β-hydride elimination cannot be completely ruled out.[18] Alternatively, protonation of intermediate **A** to afford intermediate **11** followed by palladium triggered intramolecular Michael addition could furnish indeno[1,2-*b*]furan-2-one **10**.[19] The cascade reaction of **9b** failed to occur in the presence of Lewis acids including $InCl_3$ and $Sc(OTf)_3$ without palladium catalyst ever after 10 h under optimized reaction conditions. This observation supports the carboxypalladation-initiated mechanism rather than a simple Lewis acid catalyzed transformation.

Conclusions

In conclusion, we have developed an efficient ligand-free palladium catalyzed 5-*endo-dig* cyclization-intramolecular olefin insertion cascade of alkynoic acids bearing tethered enone moiety under mild conditions. This 100% atom-economical route allowed access to indeno[1,2-*b*]furan-2-ones, an important skeleton present in a family of plant hormones, strigolactones. A plausible mechanism is proposed involving palladium triggered intramolecular carboxypalladation followed by intramolecular olefin insertion and final protonation steps. Addition of lithium bromide avoided the undesirable β-hydride elimination. A preliminary study for the enantioselective version of this domino route was also investigated.

Experimental

General

All reagents and solvents were purchased from commercial suppliers (Avra, Alfa Aesar, Sigma-Aldrich, CDH) and used without further purification. All reactions were carried out in oven-dried glassware under nitrogen atmosphere. The reactions were monitored by thin-layer chromatography using Merck silica gel 60 F_{254} and visualized by UV detection or using *p*-anisaldehyde stain or molecular iodine. Silica gel (230-400 mesh) was used for flash column chromatography. Melting points were recorded on a Royal melting point apparatus in capillaries and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts (δ) are expressed in ppm using TMS as internal standard and coupling constants (*J*) are given in Hz. Infrared (IR) spectra were obtained in an Agilent Cary630 FTIR spectrometer with a diamond ATR accessory for solid and liquid samples, requiring no sample preparation and the major frequencies were reported in cm^{-1}. Elemental analyses were determined at the CAI de Microanálisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer. ESI-MS spectra were obtained with a JMS-T100LC (JEOL) instrument. HPLC analyses were performed using a JASCO HPLC system (a JASCO PU 980 pump and a UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as eluents.

General procedure for the palladium-catalyzed 5-*endo-dig* cyclization-intramolecular olefin insertion cascade: Synthesis of compounds 10a-n and 11o

To a stirred solution of acid **9** (0.5 mmol, 1 equiv) in toluene (3 mL) at 0 °C under nitrogen atmosphere were added $Pd(OAc)_2$ (0.05 mmol, 10 mol%) and LiBr (1 mmol, 2 equiv). The reaction mixture was stirred at 15 °C for 2-4 h. After completion of the reaction, as indicated by TLC, the reaction mixture was directly poured onto silica column and purified using petroleum ether-ethyl acetate mixture (95:5, v/v) as eluent to afford the pure products.

Characterization data of compounds 10 and 11o

4-(2-Oxopropyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10a): Colorless solid; mp 104 °C, yield: 93%; IR (neat) 3066, 2910, 1801, 1640, 1596, 1421, 1230, 1061 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.50 (dd, *J* = 18.3, 9.6 Hz, 1H), 3.12 (dd, *J* = 18.3, 4.8 Hz, 1H), 3.41 (d, *J* = 24.6 Hz, 1H), 3.63 (dd, *J* = 24.6, 1.5 Hz, 1H), 3.91 (dd, *J* = 9.6, 4.8 Hz, 1H), 7.27- 7.41 (m, 4H); ^{13}C NMR (75MHz, $CDCl_3$): δ 30.1, 35.1, 39.7, 44.8, 117.9, 122.1, 123.7, 126.3, 127.3, 132.2, 147.6, 157.2, 177.8, 206.5 Anal Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.39; H, 5.21.

4-(2-Oxo-2-phenylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10b): Colorless solid; mp 124-125 °C, yield: 78%; IR (neat) 3086, 2887, 1805, 1679, 1596, 1398, 1227, 1064 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (dd, *J* = 18.0, 10.5 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.64 -3.73 (m, 2H), 4.13 (dd, J = 10.5, 4.8 Hz, 1H), 7.29-7.41 (m, 3H), 7.47-7.52 (m, 3H), 7.58-7.63 (m, 1H) 7.95-7.98 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 40.1, 40.3, 118.0, 122.5, 123.9, 126.4, 127.4, 128.1, 128.8, 132.4, 133.7, 136.4, 147.9, 157.2, 177.9, 198.1. HRMS (ESI): calcd for $C_{19}H_{14}NaO_3$, m/z 313.0841 ([M+Na]$^+$); found, m/z 313.0835.

4-(2-Oxopentyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10c): Yellow liquid; yield: 60%; IR (neat) 3043, 2918, 1810, 1672, 1426, 1131, 1051 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.69-1.74 (m, 2H), 2.34-2.50 (m, 3H), 3.10 (dd, *J* = 18.0, 5.4 Hz, 1H), 3.38 (d, *J* = 24.6 Hz, 1H), 3.61 (dd, *J* = 24.6, 1.8 Hz, 1H), 3.93 (dd, *J* = 9.9, 5.4 Hz, 1H), 7.24-7.40 (m, 4H); ^{13}C NMR (75MHz, $CDCl_3$): 13.7, 17.3, 35.1, 38.7, 43.8, 44.8, 117.9, 122.2, 123.8, 126.3, 127.3, 128.8, 132.3, 147.8, 157.1, 177.9, 209.0. HRMS (ESI): calcd for $C_{16}H_{16}NaO_3$, m/z 279.0997 ([M+Na]$^+$); found, m/z 279.0992.

4-(2-(4-(Benzyloxy)phenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10d): Colorless solid; mp 166-167 °C, yield: 90%; IR (neat) 3062, 2900, 1808, 1682, 1396, 1122, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.95 (dd, *J* = 17.4, 10.2 Hz, 1H), 3.38 (d, *J* = 24.9 Hz, 1H), 3.56 -3.71 (m, 2H), 4.12 (dd, *J* = 10.2, 4.5 Hz, 1H), 5.14 (S, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.28-7.48 (m, 9H), 7.94 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 33.8, 38.4, 38.7, 68.7, 113.3, 116.5, 121.2, 122.4, 124.8, 125.9, 126.0, 126.8, 127.2, 128.2, 128.9, 130.9, 134.5, 146.5, 155.6, 161.5, 176.4, 195.0 HRMS (ESI): calcd for $C_{26}H_{20}NaO_4$, m/z 419.1259 ([M+Na]$^+$); found, m/z 419.1252.

4-(2-(4-Methoxyphenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10e): Colorless solid; mp 137-138 °C, yield: 87%; IR (neat) 3060, 2899, 1797, 1677, 1596, 1392, 1225, 1167, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.96 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.39 (d, *J* = 24.9 Hz, 1H), 3.57-3.71 (m, 2H), 3.88 (s, 3H), 4.12 (dd, *J* = 10.5, 4.5 Hz, 1H) 6.95 (d, *J* = 8.7 Hz, 2H), 7.29-7.40 (m, 3H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.95(d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 39.9, 40.2, 55.6, 114.0, 117.9, 122.7, 123.9, 126.3, 127.4, 129.5, 130.4, 132.4, 148.0, 157.1, 163.9, 178.0, 196.5. HRMS (ESI): calcd for $C_{20}H_{16}NaO_4$, m/z 343.0946 ([M+Na]$^+$); found, m/z 343.0942.

4-(2-Oxo-2-*p*-tolylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10f): Colorless solid; mp 113-114 °C, yield: 80%; IR (neat) 3048, 1788, 1669, 1606, 1389, 1341, 1229, 1182, 1069 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.98 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.39 (d, *J* = 25.2 Hz, 1H), 3.60-3.72 (m, 2H), 4.13 (dd, *J* = 10.5, 4.5 Hz, 1H) 7.29-7.33 (m, 3H), 7.35-7.41 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.86(d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 21.7, 35.3, 40.1, 40.2, 117.8, 122.6, 123.9, 126.3, 127.4, 128.2, 129.5, 132.4, 133.9, 144.6, 148.0, 157.1, 177.9, 197.7. Anal Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.63; H, 5.30.

4-(2-(4-Chlorophenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10g): Colorless solid; mp 167-168 °C,

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yield: 76%; IR (neat) 2935, 1801, 1665, 1465, 1232, 1165 cm-1; 1H NMR (300 MHz, $CDCl_3$): δ 2.98 (dd, *J* = 17.7, 10.2 Hz, 1H), 3.39 (d, *J* = 24.6 Hz, 1H), 3.64 (dd, *J* = 17.7, 4.8 Hz, 1H), 3.68 (dd, *J* = 24.6, 1.8 Hz, 1H), 4.12 (dd, *J* = 10.2, 4.8 Hz, 1H) 7.29-7.41 (m, 3H), 7.45-7.48 (m, 3H), 7.89-7.92 (d, *J* = 8.7Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.3, 39.9, 40.3, 118.1, 122.3, 123.9, 126.4, 127.5, 129.2, 129.5, 132.3, 134.7, 140.2, 147.7, 157.3, 177.8, 196.8. Anal Calcd for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 69.98; H, 3.93.

4-(2-(2-Chlorophenyl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10h): Yellow gummy solid; yield: 64%; IR (neat) 2919, 1796, 1704, 1587, 1467, 1431, 1258 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.03 (dd, *J* = 18.0, 10.2 Hz, 1H), 3.49 (d, *J* = 24.3 Hz, 1H), 3.60 -3.73 (m, 2H), 4.11 (dd, *J* = 10.2, 4.5 Hz, 1H), 7.28-7.50 (m, 8H); ^{13}C NMR (75MHz, $CDCl_3$)*: δ 34.2, 39.2, 43.3, 117.0, 120.9, 122.8, 125.4, 126.1, 126.4, 128.0, 129.8, 130.1, 131.3, 137.5, 146.4, 156.3, 176.8, 200.2. Anal Calcd for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 69.99; H, 3.92. *One aromatic carbon is merged with others.

7-Methyl-4-(2-oxo-2-phenylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10i): Colorless solid; mp 144-145 °C, yield: 81%; IR (neat) 2917, 1811, 1676, 1446, 1375, 1222, 1185 cm-1; 1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H) 2.99 (dd, *J* = 18.0, 10.5 Hz, 1H), 3.38 (d, *J* = 24.6 Hz, 1H), 3.60 -3.71 (m, 2H), 4.09 (dd, *J* = 10.5, 4.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.21 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 1H) 7.46-7.51 (m, 2H) 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 21.4, 35.3, 39.8, 40.4, 118.7, 122.6, 123.5, 127.0, 128.0, 128.8, 132.5, 133.6, 136.4, 137.3, 145.0, 157.1, 178.0, 198.2. Anal Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.72; H, 5.21.

7-Chloro-4-(2-oxo-2-*p*-tolylethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10j): Yellow solid; mp 89-90 °C, yield: 60%; IR (neat) 2922, 1802, 1694, 1572, 1455, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.99 (dd, *J* = 18.0, 10.2 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.58 (dd, *J* = 18.0, 5.1 Hz, 1H), 3.68 (d, *J* = 24.6 Hz, 1H), 4.12 (dd, *J* = 10.2, 5.1 Hz, 1H), 7.25- 7.30 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 21.7, 35.3, 39.9, 40.0, 118.4, 124.5, 124.8, 126.1, 128.2, 129.5, 133.5, 133.8, 133.9, 144.7, 146.2, 156.1, 177.3, 197.3. Anal Calcd for $C_{20}H_{15}ClO_3$: C, 70.90; H, 4.46. Found: C, 70.61; H, 4.35.

4-(2-(Naphthalen-2-yl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10k): Colorless solid; mp 114-115 °C, yield: 80%; IR (neat) 2917, 1792, 1663, 1602, 1391, 1267, 1172, 1036 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$): δ 3.17 (dd, *J* = 17.7, 10.5 Hz, 1H), 3.43 (d, *J* = 24.6 Hz, 1H), 3.71 (d, *J* = 24.6 Hz, 1H), 3.80 (dd, *J* = 17.7, 4.5 Hz, 1H), 4.20 (dd, *J* = 10.5, 4.5 Hz, 1H), 7.29-7.43 (m, 3H), 7.52-7.65 (m, 3H), 7.89-7.95 (m, 3H) 8.05 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.4, 40.3, 40.5, 118.2, 122.7, 123.7, 124.1, 126.5, 127.2, 127.6, 128.0, 128.9, 129.0, 129.7, 130.1, 132.5, 132.6, 133.8, 135.9, 148.1, 157.4, 178.1, 198.2. HRMS (ESI): calcd for $C_{23}H_{16}NaO_3$, m/z 363.0997 ([M+Na]$^+$); found, m/z 363.0992.

4-(2-(Furan-2-yl)-2-oxoethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10l): Colorless solid; mp 111-112 °C, yield: 60%; IR (neat) 3011, 1810, 1701, 1633, 1341, 1177, 1043 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.89 (dd, *J* = 17.4, 10.2 Hz, 1H), 3.42 (d, *J* = 24.9 Hz, 1H), 3.52 (dd, *J* = 17.4, 5.1 Hz, 1H), 3.64 (dd, *J* = 24.9, 1.8 Hz, 1H), 4.09 (dd, *J* = 10.2, 5.1 Hz, 1H) 6.57 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.29-7.40 (m, 3H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$): δ 35.1, 39.8, 39.9, 112.5, 117.6, 118.0, 122.1, 123.9, 126.4, 127.4, 132.3, 146.8, 147.7, 152.3, 157.3, 177.8, 187.2. Anal Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.32. Found: C, 72.52; H, 4.21.

4-(2-Oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10m): Colorless solid; mp 145-146 °C, yield: 67%; IR (neat) 3106, 2921, 1792, 1722, 1657, 1414, 1387, 1229 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.95 (dd, *J* = 17.1, 10.2 Hz, 1H), 3.42 (d, *J* = 24.0 Hz, 1H), 3.55-3.70 (m, 2H), 4.12 (dd, *J* = 10.2, 5.1 Hz, 1H), 7.15 (t, *J* = 4.5, 1H), 7.30-7.41 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.69-7.71 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 34.2, 39.2, 39.8, 117.1, 121.3, 123.0, 125.5, 126.6, 127.5, 131.3, 131.4, 133.4, 142.6, 146.7, 156.3, 176.9, 190.0. Anal Calcd for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08; S, 10.82. Found: C, 68.62; H, 4.04; S, 10.65.

7-Methyl-4-(2-oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydro-2*H*-indeno[1,2-*b*]furan-2-one (10n): Brown solid; mp 119-120 °C, yield: 55%; IR (neat) 3093, 2918, 1794, 1718, 1660, 1413, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H) 2.93 (dd, *J* = 17.1, 10.2 Hz, 1H), 3.40 (d, *J* = 24.6 Hz, 1H), 3.52 -3.67 (m, 2H), 4.07 (dd, *J* = 10.2, 4.8 Hz, 1H), 7.09-7.16 (m, 2H), 7.21 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H) 7.68-7.70 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 19.7, 33.4, 38.1, 39.2, 117.0, 120.6, 121.8, 125.3, 126.6, 130.5, 132.5, 135.7, 141.8, 143.0, 155.5, 176.2, 189.3. Anal Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55; S, 10.33. Found: C, 69.34; H, 4.42; S, 10.09.

(*E*)-Methyl 3-(2-(5-oxo-4,5-dihydrofuran-2-yl)phenyl)acrylate (11o): Off-white solid; mp 94-95°C, yield: 54%; IR (neat) 2914, 2117, 1782, 1706, 1634, 1433, 1321, 1170 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (d, *J* = 2.4 Hz, 2H), 3.83 (s, 3H), 5.56 (t, *J* = 2.4 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.43-7.49 (m, 2H), 7.58-7.67 (m, 2H), 8.04 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.1, 51.9, 105.1, 120.6, 127.7, 127.9, 128.5, 129.8, 129.9, 133.3, 142.9, 152.0, 167.0, 175.3. Anal Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.66; H, 5.06.

Acknowledgements

Financial support from the Department of Science and Technology, DST (No. SB/FT/CS-006/2013) and the Council of Scientific and Industrial Research, CSIR (No. 02(0219)/14/EMR-II) is gratefully acknowledged.

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