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Palladium catalyzed ring opening of meso bicyclic hydrazines with catechol and resorcinol

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ABSTRACT

A novel method for the synthesis of disubstituted cyclopentenes with phenolic hydroxyl group has been investigated. This methodology involves the palladium catalyzed ring opening of azabicyclichydrazines with catechols and resorcinolthatlead to the formation of 1,4-disubstituted cyclopentenes with potent phenolic hydroxyl group. This method is useful for synthesis of benzoquinone appended cyclopentenes, which are known to be highly bioactive molecules.

Key words: azabicycilc olefin, palladium, 1,4-disubstituted cyclopentene,catechol, resorcinol.

INTRODUCTION

Transition metal catalyzed reactions of azabicyclic alkenes have been successfully employed in the synthesis of many biologically active molecules in modern drug research.[1-4] Palladium metal catalyzed desymmetrization of meso azabicyclic alkenes with nucleophiles is a facile route through which cyclic compounds with multiple stereocenters can be synthesized in single step.[5-8]Azabicyclic alkenesare more efficient starting material in the synthesis of cyclic compound derivatives.[9]

In recent years, substituted cyclopentenes havegot more importance in the drug discovery, because of their high biological activity.[10-13] In addition, they are the key intermediates for the synthesis of a variety of building blocks.[14-15] Micouin and co-workers studied the synthesis of bisubstitutedcyclopentenes by palladium-catalyzed allylic substitution.[16] Copper catalysed ring opening reactions of bicyclic olefin[17],Ligand Control Desymmetrization of Bicyclic Hydrazines using RhodiumCatalyzed Ring-Opening[18-19], Rh Catalyzed Ring Opening of Diazabicycles with Boronic acids.[20]

MATERIALS AND METHODS

All the reactions were conducted in oven-dried glassware. Solvents used for the experiments were distilled or dried as specified. All reactions were monitored by TLC (silica gel 60 F254,.25mm,Merck) until conversion was complete; visualization was effected with UV and /or by staining with McGill or Enholm Yellow solution.Column chromatography was performed by using 100-200 mesh silica gel and appropriate mixture of hexane and ethyl acetate for elution. The solvents were removed using a buchi E.L rotary evaporator. HPLC analyses were conducted with a LC Recycling preparative chromatograph.IR spectra were taken on FT-IR spectrophotometer.NMR spectra were recorded at **300** and **500** MHz (^{1}H) and **75** and **125** (^{13}**C)** MHz, respectively on abruker DPX-**300** and -**500MHz** FT-NMR spectrometer. NMR spectra were obtained using $CDCl_3$ as a solvent with TMS as internal standard. Mass spectra were recorded by FAB ionization technique using a jeol JMS 600H mass spectrometer.

$Pd_2(dba)_3CHCl_3$ (10.7mg, 0.010mmol) PPh3 (5.4mg, 0.020mmol), and $K2CO_3$ (27.7mg, 0.208mmol) were added to a Schlenk tube and placed under vacuum for 15 min. Freshly distilled toluene(2ml) was degassed and then added to the mixture at 60^0C.;the solution was stirred for 15 min. To the schlenk tube was added **2a** (22.9mg, 0.202 mmol), and **1a** (50.0 mg, 0.208mmol) dissolved in toluene (2ml) and the solution was stirred at 60^0C (TLC monitoring). The solvent was removed under reduced pressure and the residue was subjected chromatography (silica gel, EtOAc-hexane,) to afford **3a** as a white solid.

RESULTS AND DISCUSSION

In this paper, our main objective was to perform desymmetrization of azabicyclic olefin by catechol and resorcinol, which lead to the formation of bisubstitutedcyclopentenes.Our studies started with diethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate**(1a)** with catechol (**2a)** in the presence of$Pd_2(dba)_3CHCl_3$ (5mol %), triphenylphosphine (PPh_3, 10mol %), potassium carbonate (K_2CO_3, 1.0 equiv) and lithium chloride in toluene at 60^oC and the reaction produced diethyl 1-(4-(2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate **(3a)** (Table 1, entry 1).

Detailed optimization studies were carried out to find out the best condition for this transformation. Potassium carbonate was found to be more efficient than barium carbonate. Different catalysts were screened for the reaction that included $Pd_2(dba)_3CHCl_3$, $[Pd(allyl)Cl]_2$ and $PdCl_2$. Among those, only $Pd_2(dba)_3CHCl_3$afforded the desired product with 81% of yield (entry 3) but rest of the two were found the ineffective (entries 5-6).

In the ligand optimization studies, BINAP, PPh_3 and dppf were evaluated for the desired reaction. PPh_3 was found to be best ligand (entry 3) when compared to the other two ligands (entry 1, 4).LiCl was utilized as additive for the reaction which gave 81% yield (entry 3) and in its absence; the yield was only 66% (entry 2).It also has been founded that prolonged reaction duration, reaction yield was poor. In solvent optimization, toluene (81% yield, entry 3) was proved to be best solvent compared to acetonitrile (71% yield, entry 8) and tetrahydrofuran (yielded trace, entry 7). After the optimization studies, the best condition for the transformation was $Pd_2(dba)_3CHCl_3$ (5mol %), triphenylphosphine (PPh_3, 10mol %), potassium carbonate (K_2CO_3, 1.0 equiv) and lithium chloride in toluene at 60^oC.Using this condition corresponding bisubstitutedcyclopentenes by desymmetrization of azabicyclic olefin withsubstituted catechol and resorcinol carried out.

The IR spectrum of the compound **3a** showed the characteristic ester carbonyl absorption at 1705 cm^{-1}. In the ^{1}HNMR spectrum, peaks in the region δ 6.88-6.78 ppm were assigned to the aromatic protons. -NH and –OH protons resonated in the region δ 6.40 and δ 5.88 respectively. The peak at δ 5.32 ppm corresponded to the proton on the carbon attached to the oxygen. The proton on the carbon bearing the hydrazine moiety resonated in the region δ 5.32 – 5.21 ppm. The methylene protons of the cyclopentene ring appeared as two separate peaks at δ 2.76-2.70 and 2.17 ppm. In the ^{13}C NMR spectrum ester carbonyl carbons resonated at δ 156.8 and 155.64 ppm. The carbon attached to oxygen resonated at δ 81.44 ppm. All other signals in ^{13}C NMR spectra were in agreement with the proposed structure. The structure assigned was further confirmed by low resolution mass spectral analysis which showed a molecular ion peak at m/z =373.73.

From, the above all analysis the structure of the compound (3a) is confirmed. Similarly the structures of the corresponding synthesized compounds are also assigned by the spectral analysis and the spectra of compound 3a shown below.

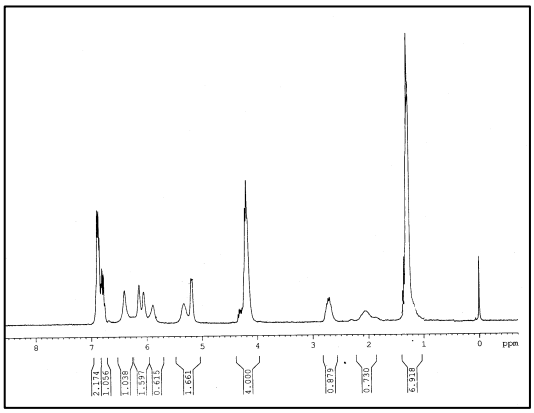


Fig. (1).^{1}H NMR spectrum of 3a

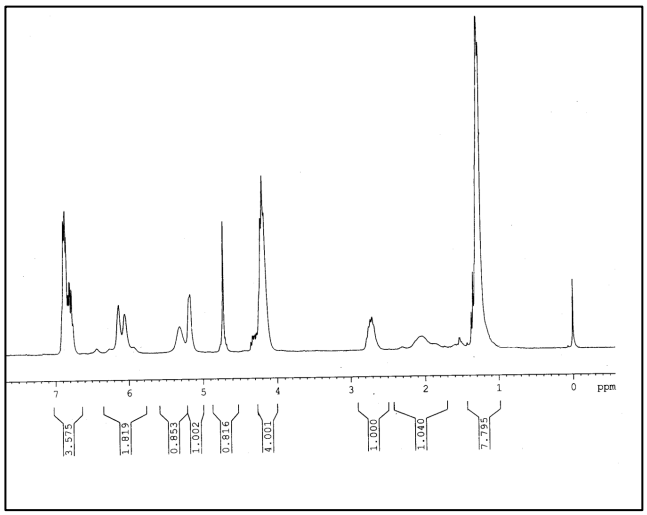


Fig. (2).^{1}H NMR spectrum of 3a in D_2O

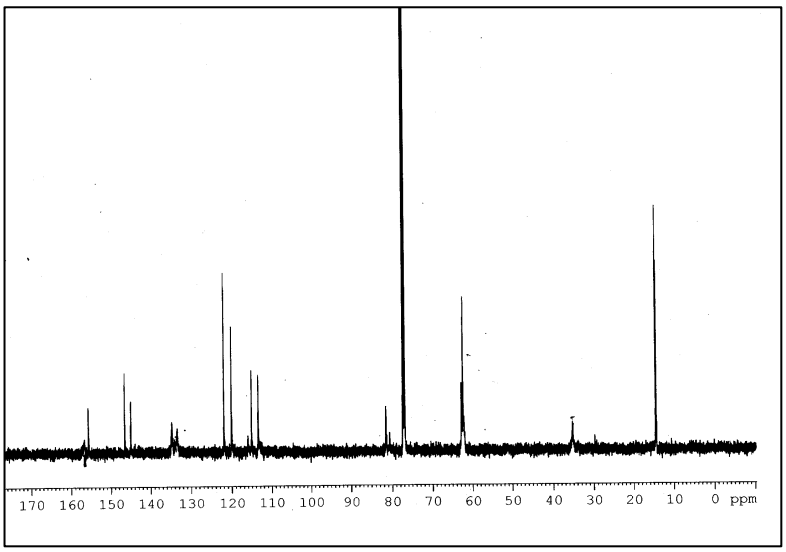
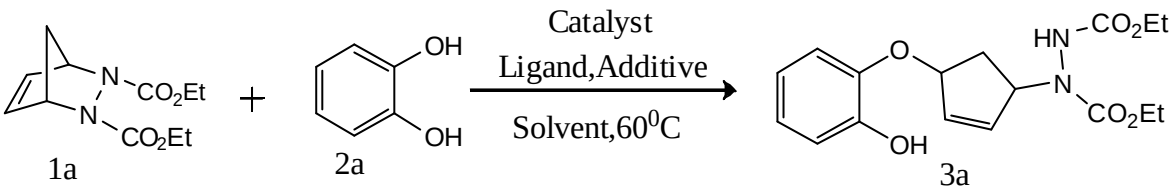


Fig. (3).^{13}C NMR spectrum of 3a

Table 1 Optimization Studies

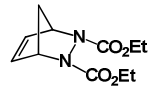
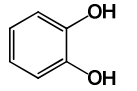
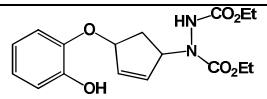
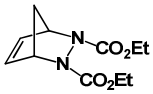
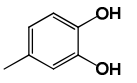
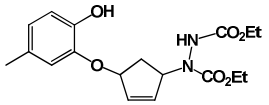
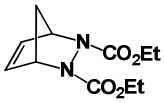
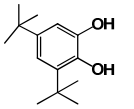
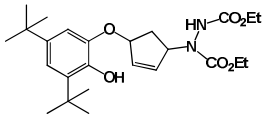
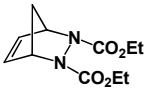
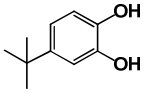
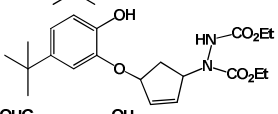
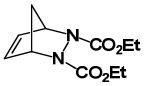
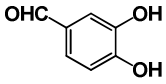
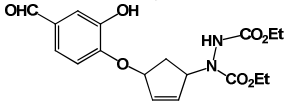
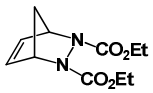
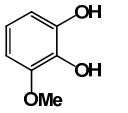
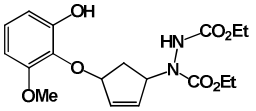
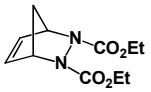
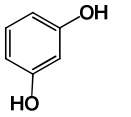
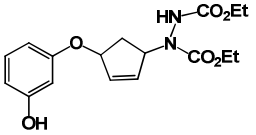
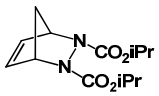
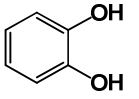
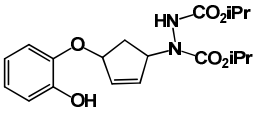
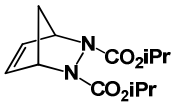
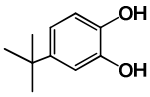
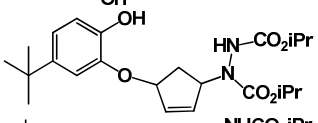
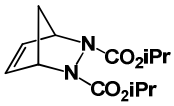
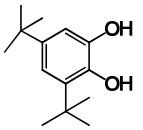
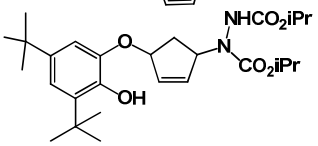
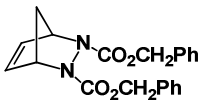
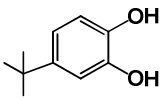
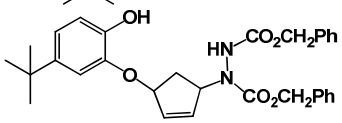
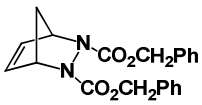
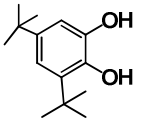
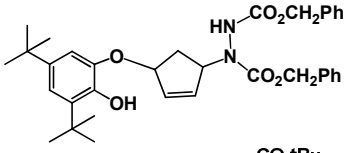
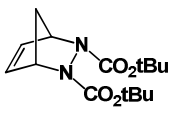
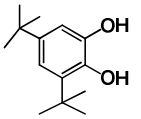
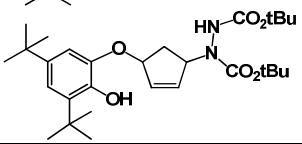


Entry	Catalyst	Ligand	Additive	Base	Solvent	Yield%
1	$Pd_2(dba)_3CHCl_3$	BINAP	__	K_2CO_3	Toluene	10
2	$Pd_2(dba)_3CHCl_3$	PPh_3	__	K_2CO_3	Toluene	66
3	$Pd_2(dba)_3CHCl_3$	PPh_3	LiCl	K_2CO_3	Toluene	81
4	$Pd_2(dba)_3CHCl_3$	dppf	__	K_2CO_3	Toluene	43
5	$[Pd(allyl)Cl]_2$	PPh_3	LiCl	K_2CO_3	Toluene	No Reaction
6	$PdCl_2$	PPh_3	LiCl	K_2CO_3	Toluene	No Reaction
7	$Pd_2(dba)_3CHCl_3$	PPh_3	LiCl	K_2CO_3	THF	Trace
8	$Pd_2(dba)_3CHCl_3$	PPh_3	LiCl	K_2CO_3	MeCN	71
9	$Pd_2(dba)_3CHCl_3$	PPh_3	LiCl	K_2CO_3	MeCN	No Reaction
10	$Pd_2(dba)_3CHCl_3$	_	Bu_4Cl	Ba_2CO_3	MeCN	No Reaction

Reaction Conditions: alkene (1.0 equiv.), nucleophile (1.0 equiv.), catalyst (5 mol %), base (1.0 equiv.), ligand (10 mol%), solvent (2 ml), 60 °C, 24 hr.

The generality of the ring opening reaction was proved under the optimized condition with resorcinol and various substituted catechols. The results are summarized in Table 2.

Table 2

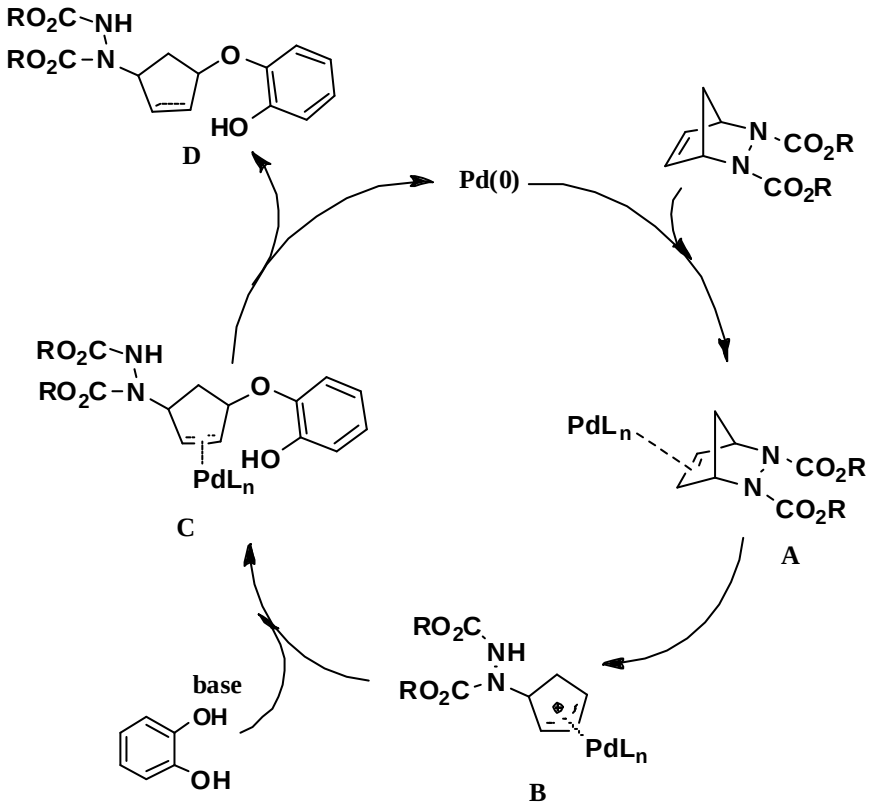
Entry	Alkene	Catechol	Product	Yield
1				**81**
2				**83**
3				**59**
4				**64**
5				**67**
6				**21**
7				**44**
8				**54**
9				**92**
10				**59**
11				**77**
12				**63**
13				**48**

Reaction Conditions: alkene (1.0 equiv.), nucleophile (1.0 equiv.), catalyst (5 mol %), base (1.0 equiv.), ligand (10mol%), solvent (2 mL), 60 °C, 24 h.

Mechanistic Rationale

A plausible mechanism is illustrated for the reaction of catechol and resorcinol with bicyclic alkenes involves two stages, the initial being the ring opening of the bicyclic alkene.The first step of catalytic cycle involves the formation

of π–allyl palladium intermediate **B** by the attack of Pd(O)the coordination of the phenolic oxygen atom to Pd(0) on the double bond (allylic species), and subsequent oxidative addition to C-N bond leading to the ring opening .In the second stage, the nucleophile attacks the of π –allylpalladium species B there by forming the intermediate **C** .



Proposed mechanism of the reaction

Diethyl-1-(4-(2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate;
IR(KBr): 3517, 3300, 3050, 2983, 2936, 1705, 1595, 1500, 1067, 943, 746 $cm^{-1;}$ **^{1}H NMR (500MHz,CDCl3):** δ = 6.89 – 6.76 (m, 4H), 6.40 (1H), 5.19 – 5.17 (m, 1H), 4.35 – 4.19 (m, 4H), 2.73 – 2.71 (m, 1H), 2.07 – 2.03 (m, 1H), 1.26 – 1.24 (m, 6H).; **^{13}C NMR (125MHz, CDCl3):** δ = 156.7, 155.64, 146.47, 144.92, 134.68, 133.35, 121.92, 120.02, 115.98, 115.04, 113.40, 81.44, 62.70, 62.32, 62.10, 35.15, 14.17, 14.41.; **MS(FAB**): m/z $[M]^{+}$calcd for $C_{17}H_{22}N_2O_6$: 350.15; found 350.73.

diisopropyl 1-(4-(3,5-di-tert-butyl-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3517, 3321, 2961, 2869, 1705, 1593, 1485, 1395, 1252, 1162, 1072, 910, 734 $cm^{-1;}$ **^{1}H NMR (500MHz, CDCl3):** δ = 6.98 (S, 1H), 6.83 (S, 1H), 6.20 (S, 1H), 6.08 – 5.94 (m, 2H), 5.9 (S, 1H), 5.36 (S, 1H), 5.17 (S, 1H), 2. 79 – 2.72 (m, 1H), 2.15(s,1H), 1.40 (s,9H), 1.3 (s,9H),; **^{13}C NMR (125MHz, CDCl3):** δ =154.63, 153.82, 144.44, 142.52, 141.29, 134.81, 133.01,116.09, 108.44, 81.40, 60.9, 34.52, 31.66, 29.49, 28.22,28.10.; **MS(FAB**): m/z $[M]^{+}$calcd for $C_{17}H_{22}N_2O_6$: 378.14; found 378.73.

diethyl 1-(4-(3-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3302, 2983, 2937, 1696, 1595, 1489, 1419, 1148, 1068, 912, 762, 688.; **^{1}H NMR (500MHz, CDCl3):** 7.10-7.07 (m, 1 H), 6.67 (s, 1H), 6.64-6.43 (m, 4 H), 6.18-5.10(m, 2 H), 5.32- 5.30 (m, 1 H), 5.07 (m, 1 H), 4.20-4.18 (m, 4 H), 2.74-2.70 (m, 1 H), 2.03 (m, 1 H), 1.25-1.21 (m, 6 H),; **^{13}C NMR (125MHz, CDCl3):** 159.20,157.24, 156.66, 155.80, 133.94, 130.02, 108.28, 107.76, 103.42, 80.09, 62.63, 62.08, 35.32, 14.35, 14.23.
MS(FAB): m/z $[M]^{+}$calcd for $C_{27}H_{42}N_2O_6$: 490.30; found 490.14.

diisopropyl 1-(4-(5-(tert-butyl)-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3525, 3304, 2966, 2871, 2871, 1708, 1589, 1507, 1412, 1279, 1109, 1063, 761, 734.; **^{1}H NMR (500MHz, CDCl3):** 7.98-6.93 (m, 1 H), 6.87-6.82 (m, 2 H), 6.38 (S, 1 H), 6.11-6.04 (m, 2 H), 5.90 (S, 1 H), 5.35 (S, 1 H), 5.20-5.16 (m, 2 H), 4.94-4. (m, m H), 2.76-2.70 (m, 1 H), 2.10- 2.08 (m, 1 H), 1.29-1.25 (m, 21 H),; **^{13}C NMR (125MHz, CDCl3):** δ = 156.26, 155.20, 145.86, 145.27, 144.16, 134.77, 133.37, 118.49, 116.48, 112.90, 112.53,

81.53, 70.32, 70.07, 61.79, 34.31, 34.22, 31.58,31.43, 22.05. ; **MS(FAB)**: m/z $[M]^+$calcd for $C_{23}H_{34}N_2O_6$: 434.24; found 434.37

diethyl 1-(4-(3,5-di-tert-butyl-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3515, 3298, 2957, 2908, 286, 1712 1593, 1419, 1299, 1229, 1069, 911, 761, 733.; **^{1}H NMR (500MHz, CDCl3):** δ = 6.92 (S, 1 H), 6.82 (S, 1 H), 6.43 (S, 1 H), 6.13-6.01 (m, 3 H), 5.34 (S, 1 H), 5.17 (S, 1 H), 4.20 (S, 4 H), 2.79-2.76 (m, 1 H), 2.073-2.02 (m, 1 H), 1.40 (S, 9 H), 1.29-1.26 (S, 14 H),; **^{13}C NMR (125MHz, CDCl3):** δ = 156.63, 155.61, 144.49, 142.50, 141.32, 134.97, 134.47, 133.79,; **MS(FAB)**: m/z $[M]^+$calcd for $C_{25}H_{38}N_2O_6$: 462.27; found 462.4.

diethyl1-(4-(5-(tert-butyl)-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3521, 3301, 2962, 2869, 1708, 1590, 1508, 1279, 1067, 1021, 761**. ; ^{1}H NMR (500MHz, CDCl3):** δ = 6.98-6.79 (m, 3 H), 6.45 (s, 1 H), 6.25-6.13 (m, 2 H), 5.90 (s, 1 H), 5.34-5.29 (m, 1 H), 5.20-5.16 (m, 1 H), 4.20-4.18 (m, 4 H), 2.75-2.7 (m, 1 H), 2.08-2 (m, 1 H), 1.29-1.25 (m, 14 H),; **^{13}C NMR (125MHz, CDCl3):** δ = 156.67, 155.60, 145.79, 145.33, 134.55, 133.65, 118.54, 116.50, 112.57, 81.50, 62.70, 62.35, 62.07, 35.24, 34.32, 31.50, 31.42, 14.48, 14.32.; **MS(FAB)**: m/z $[M]^+$calcd for $C_{23}H_{34}N_2O_6$: 434.24; found 434.37

diisopropyl 1-(4-(3,5-di-tert-butyl-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3517, 3301, 2957, 2907, 2870, 1709, 1593, 1486, 1418, 1300, 1109, 1033, 911, 761, 734.; **^{1}H NMR (500MHz,CDCl3):** δ = 6.92 (S, 1 H), 6.82 (S, 1 H), 6.11-6.01 (m, 3 H), 5.34 (S, 1 H), 5.17 (S, 1 H), 4.98-4.94 (q, 2 H), 2.80-2.74 (m, 1 H), 2.09 (S, 1 H), 1.40 (S, 1 H), 1.29 (S, 1 H), 1.27-1.26 (q, 2 H),; **^{13}C NMR (125MHz, CDCl3):** δ =156.31, 155.18, 144.55, 142.16, 141.32, 134.60, 133.53, 116.19, 108.44, 81.73, 70.32, 70.02, 61.92, 61.92, 34.90, 34.48, 31.62, 32.51, 21.98, 21.79. ; **MS(FAB)**: m/z $[M]^+$calcd for $C_{27}H_{42}N_2O_6$: 490.30; found 490.14.

dibenzyl 1-(4-(5-(tert-butyl)-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3524, 3301, 3065, 3034, 2960, 2867, 1710, 1507, 1416, 1279, 1065, 783, 697. ; **^{1}H NMR (500MHz, CDCl3):** δ = 7.29-7.25 (m, 10 H), 6.97-6.79 (m, 3 H), 6.65 (S, 1 H), 6.21-6.04 (m, 2 H), 5.88 (S, 1 H), 5.35 (S, 1 H), 5.15-5.10 (M, 5 H),2.74-2.71 (m, 1 H), 2 (S, 1 H). ; **^{13}C NMR (125MHz, CDCl3):** δ = 155.43, 145.80, 145.36, 135.76, 134.43, 134.10, 128.55, ,128.52, 128.36, 128.23, 127.96, 118.56, 116.51, 111.07, 81.49, 68.20, 67.93, 62.18, 35.28, 34.33, 34.24, 31.45, 29.27. ; **MS(FAB)**: m/z $[M]^+$calcd for $C_{31}H_{34}N_2O_6$: 530.24; found 529.92.

Diethyl-1-(4-(5-formyl-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3505,3303, 2983, 2935, 2729, 1734, 1717, 1686, 1590, 1508, 1273, 1067, 1014, 871, 732. ; **^{1}H NMR (500MHz, CDCl3):** 9.80(S, 1 H), 7.46-7.40 (m, 2 H), 7.03-6.10 (m, 1 H), 6.82 (S, 1 H), 6.67 (S, 1 H), 6.26-5.10 (m, 2 H), 5.30 (S, 2 H), 4.20 (S, 1 H), 2.80-2.79 (m, 1 H), 2.15-2.12 (m, 1 H), 1.27-1.24 (m, 6 H).; **^{1}H NMR (500MHz, CDCl3):** δ = 190.66, 155.52,152.63, 152.63,145.63, 134.77, 133.37, 129.72,127.49,114.94,112.02,81.71,62.39; **MS(FAB)**: m/z $[M]^+$calcd for $C_{17}H_{22}N_2O_6$: 378.14; found 378.73.

Diethyl-1-(4-(2-hydroxy-3-methoxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 33.95, 3315, 2981, 2936, 2850, 1712, 1629, 1477, 1232, 1090, 763, 695. ; **^{1}H NMR (500MHz, CDCl3):** δ = 6.78-6.72 (m, 1 H), 6.61-6.56 (m, 3 H), 6.15-6.04 (m, 2 H), 5.17 (S, 1 H), 4.18 (S, 4 H), 3.89 (S, 3 H), 2.67-2.64 (m, 1 H), 1.74 (S, 1 H), 1.28-1.26 (m, 6 H), ; **^{13}C NMR (125MHz, CDCl3):** δ = 156.44, 155.62, 146.41, 145.57, 135.05, 133.83, 128.94, 127.97,118.99, 105.98, 82.04, 62.09, 61.50, 35.66, 14.40, 14.29. ; **MS(FAB)**: m/z $[M]^+$calcd for $C_{18}H_{24}N_2O_7$: 380.16; found 380.40.

diethyl1-(4-(2-hydroxy-5-methylphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3522,3301, 2982, 2931, 1707, 1591, 1509, 1274, 1236, 1067, 802, 761.; **^{1}H NMR (500MHz, CDCl3):** δ = 6.81-6.65 (m, 3 H), 6.65 (s, 1 H), 6.13-6.04 (m, 2 H), 5.91 (s, 1 H), 5.33 (s, 1 H), 5.15-5.13 (m, 1 H), 4.19-4.16 (m, 4 H), 2.74-2.69 (m, 1 H), 2.63 (m, 3 H), 1.80 (m, 1 H), 1.26-1.25 (m, 6 H),; **^{13}C NMR (125MHz, CDCl3):** δ = 156.61, 155.63, 146.26, 142.71, 134.58, 133.60, 122.11, 120.26, 115.82, 113.58, 81.78, 62.72, 62.32, 35.16, 21.01, 14.48, 14.31.; **MS(FAB)**: m/z $[M]^+$calcd for $C_{18}H_{24}N_2O_6$: 364.16; found 364.63.**IR(KBr):** 3514, 3296, 3034, 2956, 2906, 2868, 1714, 1592, 1486, 1419, 1299, 1223, 1067, 737, 697.

dibenzyl 1-(4-(3,5-di-tert-butyl-2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3514, 3296, 3034, 2956, 2906, 2868, 1714, 1592, 1486, 1419, 1299, 1223, 1067,737,697.; **^{1}H NMR (500MHz, CDCl3):** δ = 7.28-7.24 (m, 10 H), 6.92-6.92 (m, 1 H), 6.80 (s, 1 H), 6.59 (s, 1 H), 6.09 (s, 1 H), 6.01 (s, 1 H), 5.86 (s, 1 H), 5.14 (s, 4 H), 2.78-2.77 (m, 1 H), 1.28 (s, 9 H).; **^{13}C NMR (125MHz, CDCl3):** δ = 156.48, 155.40, 144.59, 142.58, 141.40, 135.87, 135.59, 134.21, 128.49, 128.46, 128.25, 128.18, 128.13, 127.89, 116.28,108.42, 81.77,62.27, 67.94, 62.36, 35.47, 34.92, 34.50, 31.63,29.55.; **MS(FAB** m/z $[M]^+$calcd for $C_{35}H_{42}N_2O_6$: 586.30; found 585.88.

diisopropyl 1-(4-(2-hydroxyphenoxy)cyclopent-2-en-1-yl)hydrazine-1,2-dicarboxylate
IR(KBr): 3306, 3049, 2981, 2939, 2876, 1712, 1595, 1499, 1258, 1108, 901, 746.; **^{1}H NMR (500MHz, CDCl3):** δ = 6.93-6.79 (m, 1 H), 6.34 (S, 1 H), 6.12-6.06 (m, 2 H), 5.93 (S, 1 H), 5.34 (S, 1 H), 5.19 (S, 1 H), 5.03-4.95 (m, 2 H), 2.63 (S, 1 H), 2.14-2.13 (m, 1 H),; **^{13}C NMR (125MHz, CDCl3):** δ = 156.33, 155.12, 146.74, 145.03, 134.87, 133.83, 121.99, 120.65, 119.93, 113.41, 81.72, 70.12, 69.91, 62.05, 38.40, 38.29, 35.40, 21.91, 21.84.; **MS(FAB** m/z $[M]^{+}$calcd for $C_{19}H_{26}N_2O_6$: 378.18; found 378.71.

CONCLUSION

In conclusion we have unraveled a facile method towards the synthesis of a new class of disubstituted cyclopentenes with potent phenolic hydroxyl group. The widespread occurrence and interesting biological activities of substituted cyclopentane derivatives in nature make them important targets for synthesis. The product can also act as useful intermediates in the modulation of heterocyclic substituents by multicomponent hydrazine–based chemistry.

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