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A highly efficient synthesis of 1-trimethylsilyl-2-arylcyclopentenes using two consecutive stages of aqueous and anhydrous reactions

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Dedicated to Prof. G. Nagendrappa, on the occasion of his 75th birthday

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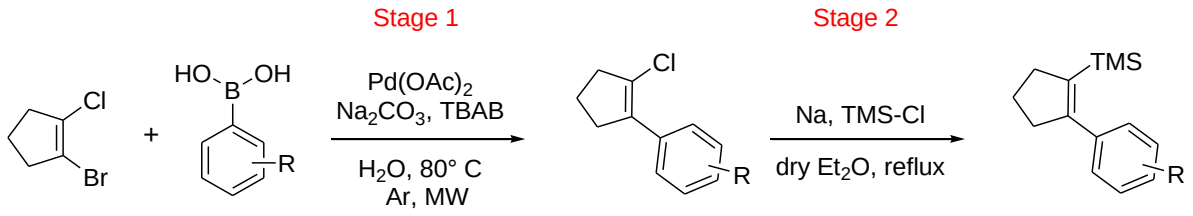
Abstract

A consecutive sequential two stage synthetic strategy for the preparation of eleven novel 1-trimethylsilyl-2-arylcyclopentenes is reported. In the first stage, the Suzuki reaction of 1-bromo-2-chlorocyclopentene with eleven arylboronic acids in aqueous conditions yielded the novel 1-chloro-2-arylcyclopentenes in 91-96% yields. The single crystal XRD structures of two representative 1-chloro-2-arylcyclopentenes are highlighted. In the second stage, the Wurtz–Fittig coupling reaction of the 1-chloro-2-arylcyclopentenes with metallic sodium and chlorotrimethylsilane in anhydrous ether afforded the anionic synthons: 1-trimethylsilyl-2-arylcyclopentenes in 62-82% yields. A library of twenty-two novel compounds from the two stages is reported.



Keywords: Anionic synthons, arylcyclopentenes, cross-coupling reactions, cyclic vinylsilanes, microwaves

Introduction

Microwave assisted organic synthesis (MWAOS) has gained significant importance in recent years. Use of aqueous conditions has rendered the technique more advantageous due to green chemistry protocol principles.[1]

Sequential transformations have come of age in recent years. The strategy has been used in the synthesis of complex organic molecules.[2] Simultaneously, cross coupling reactions involving C-C bond formations are employed in the synthesis of wide array of organic molecules.[3-7]

Among the many reactions, the Suzuki cross-coupling reaction of aryl/vinyl halides or triflates with boronic acids has gained importance for the synthesis of novel aryl/vinyl molecules.[8-12] One of the recent areas of interest among scientists worldwide is to employ the green chemistry strategies which aim at reducing reaction times.

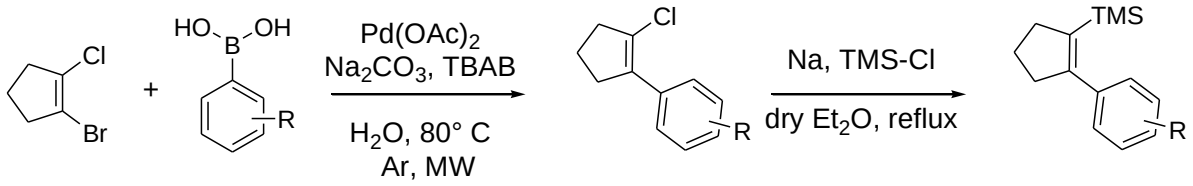
One of the protocols advocates the use of water as solvent.[13-15] In order to increase the solubility of organic compounds in water, the use of phase transfer catalysts such as tetraalkylammonium salts/crown ethers has been employed.[16,17] In this regard, literature reports also suggest the use of additives in the Suzuki coupling reactions of aryl halides with arylboronic acids in aqueous media.[18-24] Therefore, a combination of water as solvent and microwave conditions act as the best methodology, which reduces the reaction time and increases the yields of the products.[25-33]

Since the first use of microwave conditions for Suzuki couplings by Larhed and Hallberg, using $Pd(PPh_3)_4$ as the catalyst,[29] to our knowledge, there exist no reports in the literature for the use of microwaves for the coupling of vinylhalides/triflates with arylboronic acid under palladium catalyzed conditions in aqueous conditions.

In continuation of our previous work,[34] we now wish to report the microwave assisted sequential regiospecific conversion of 1-bromo-2-chlorocyclopentene (**1**) with eleven arylboronic acids **2a-k** to 1-chloro-2-arylcyclopentenes **3a-k**, under aqueous conditions employing the Suzuki coupling reaction and their subsequent transformation into the vinylsilanes: 1-trimethylsilyl-2-arylcyclopentenes **4a-k** as depicted in Scheme 1, employing the Wurtz-Fittig coupling reaction. The first stage employs aqueous reaction conditions, whereas the second stage involves total anhydrous conditions and metallic sodium in ether solvent.

Results and Discussion

The work presented in this article is summarized in Scheme 1, which consecutively and sequentially employs the Suzuki coupling reaction in aqueous conditions in the first stage; and the Wurtz-Fittig coupling reaction in completely anhydrous conditions in the second stage.



1 **2a-k** **3a-k** **Y= 91-96%** **4a-k** **Y= 62-82%**

Scheme 1. Synthesis of 1-trimethylsilyl-2-arylcyclopentenes.

Stage 1. The Suzuki-Miyaura cross-coupling reactions

Two routes for the syntheses of 1-chloro-2-arylcyclopentenes **3a-k** from **1** were envisaged. The Suzuki-Miyaura cross coupling reactions were carried out by:

(i) **The conventional method:** which involved the reaction of 1-bromo-2-chlorocyclopentene (**1**) with eleven arylboronic acids **2a-k** in the presence of $Pd(dppf)_2Cl_2$ catalyst, inert argon atmosphere and K_2CO_3 in 1,4-dioxane solvent under the sealed tube conditions at 110 °C. The *o*- substituted arylboronic acids **2a** and **2b** required 6 hours for the formation of products **3a** and **3b** respectively. The coupling was found to proceed faster in the case of *p*- substituted reagents **2c-g** requiring 3 hours. The *m*- substituted reactant **2h** and the di-substituted reactant **2i** were converted in 4.5 hours. The arylboronic acids **2j** and**2k** were converted into the corresponding products in 5 hours. The yields of the products were in the range of 55-65%. The absence of the inert argon atmosphere decreased the yields of **3a-k** to 41-45%.

(ii) **The microwave assisted organic synthesis (MWAOS) method:** In an effort to obtain better yields and employing green chemistry protocols, a preliminary trial Suzuki-Miyaura coupling reaction of **1** with **2f** was performed under microwave conditions. The use of $Pd(dppf)_2Cl_2$ catalyst in 1,4-dioxane, as in the conventional method, under microwave irradiation gave the undesired symmetrical bis-arylated compounds after replacement of both the halogens in more than 50% yields.[36] Use of the solvents: THF, DMF or toluene individually, or the solvent mixtures: THF/water, DMF/water, or toluene/water in 1:1 ratios had no considerable effect of increase in the yields under microwave conditions. The use of water exclusively as solvent under microwave conditions using $Pd(OAc)_2$, $Pd(dppf)_2$ Cl_2, $Pd(dba)_3$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$ and Na_2CO_3 base were found to furnish the product **3f** in less than 35% yields.

Survey of literature indicated the use of phase transfer catalysts tetra-n-butylammonium iodide and tetra-*n*-butylammonium bromide (TBAB) for the Suzuki-Miyaura coupling reaction in aqueous media.[16,17]

We employed the phase transfer catalyst TBAB in 0.4 mmol equiv. and found increase in the yields of the product **3f** to 55% in the aqueous media. The increase to 1 mmol equiv. of TBAB gave better yields of **3f** under microwave irradiation for 10 minutes. Further increase in the amount of TBAB led to no considerable increase in the product yields.

After several trials for optimization of conditions, we found that 1-bromo-2-chloro-cyclopentene (**1**, 250mg, 1.37 mmol equiv) when reacted with 4-thioethylphenylboronic acid (**2f,** 350mg, 1.4 mmol equiv) in the presence of $Pd(OAc)_2$cat. (0.03 mol%), Na_2CO_3 (556mg, 3.82 mmol equiv) and tetra-n-butylammonium bromide (442mg, 1 mmol equiv) in 2.5mL water solvent under microwave irradiation for 10 minutes, including rt to 80 °C ramp time gave best results. The reactions were monitored both by GC and TLC, and the chromatograms indicated the complete conversion of the starting material **1** to form only **3f**. The mixture was cooled under a jet of compressed a*IR* to ambient temperature and subjected to extraction using ethyl acetate. Work up as given in the experimental gave **3f** exclusively in 96% isolated yield.

A comparative study of the conditions employed by us indicated that even though **3f** was formed in 65% yield through the conventional method, the best conditions we have found is to employ MWAOS in aqueous media, in terms of both time and yield.

With these trial results of **1** with **2f**, further Suzuki-Miyaura cross-coupling reactions under microwave conditions were carried for eleven differently substituted phenylboronic acids **2a-e** and **2g-k** to obtain the 1-chloro-2-arylcyclopentenes **3a-e** and **3g-k**. To the best of our knowledge, there exists no other reports for the synthesis of **3a-k** in the literature.

Each microwave reaction was carried out for a minimum of three trials and the optimum yields, in greater than 91% are given in **Table 1**. The compounds were isolated as high boiling/low melting, off white to yellow colored solids. Distillation under reduced pressure under 0.01 mm Hg gave tarry material indicating the

decomposition of the compounds. The compounds **3a-k** were finally isolated in pure form after column chromatography over silica gel (100-200 mesh) using ethyl acetate – petroleum benzine (60 – 74 °C) as eluent. The products were completely characterized spectroscopically.

The recrystallization of the compounds **3a-k** was further carried out in petroleum benzine (60 – 74 °C) solvent. We found that the compounds 1-chloro-2-biphenylcyclopentene (**3j**) and 1-chloro-2-naphthylcyclopentene (**3k**) gave best crystals when recrystallized from petroleum ether (60-74 °C) solvent. The compounds **3j** and **3k** were subjected to single crystal XRD studies and the ORTEP view of the representative molecule 1-chloro-2-biphenylcyclopentene **3j** with atomic labeling (thermal ellipsoids drawn at 50% probability) is given in **Figure 1**. The ORTEP diagram unambiguously confirms the regiospecific formation of the product **3j** and 1-chloro-2-arylcyclopentenes in general.

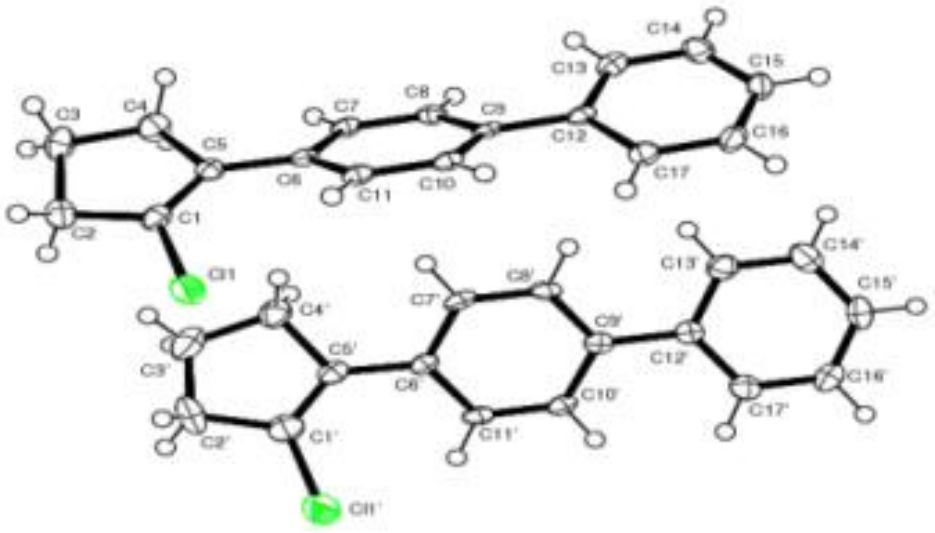


Figure 1.ORTEP view of compound **3j.**

The ORTEP view of compound 1-chloro-2-napthylcyclopentene (**3k**) along with other crystallographic details is furnished in supplementary data.

The mechanism for the Suzuki-Miyaura cross coupling reaction is postulated to proceed through established routes.[37] We postulate the regiospecific formation of 1-chloro-2-arylcyclopentenes **3a-k** due to the different bond strengths of C-Br and C-Cl of **1**. The C-Cl bond energy is 335 kJ mol^{-1} whereas C-Br bond strength is 268 kJ mol^{-1}.[38] Due to the lesser C-Br bond strength, the regioselective oxidative addition of the carbon-bromine bond to the palladium catalyst preferentially occurs, followed by trans-metalation and reductive elimination of the products **3a-k**.

Stage 2. The Wurtz-Fittig cross-coupling reaction

Our laboratory is primarily involved in the synthesis and reactions of cyclic vinylsilanes[39] employing the Wurtz-Fittig coupling reaction. A wide range of simple and substituted cyclic vinylsilanes, which are anionic synthons, have been synthesized in our laboratory. Some of our molecules have found utility as starting materials for the total synthesis of natural products. The reaction involves the cross-coupling of cyclic vinyl halides with sodium and chlorotrimethylsilane in suitable solvent. The Wurtz-Fittig coupling reaction in contrast to the Suzuki-Miyaura coupling reaction, as performed in stage 1 above, requires completely anhydrous conditions.

In further extension of our previous work of the preparation of the 1-trimethylsilyl-2-arylcyclohexenes,[34] the 1-chloro-2-arylcyclopentenes **3a-k** obtained through the Suzuki cross-coupling reaction under aqueous microwave conditions, were next subjected to the Wurtz–Fittig cross-coupling reaction to obtain the novel aryl substituted cyclic vinylsilanes **4a-k**. Individually refluxing **3a-k** with chlorotrimethylsilane and sodium in dry ether solvent afforded the products **4a-k** in 62-82% yields (**Table 1**).

Table 1. Optimized yields of 1-chloro-2-arylcyclopentenes **3a-k** and 1-trimethylsilyl-2-arylcyclopentenes **4a-k**

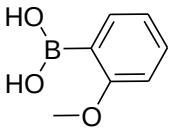
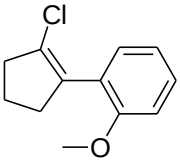
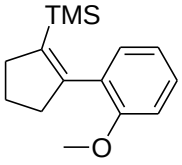
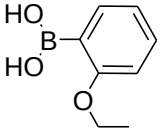
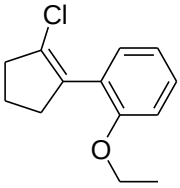
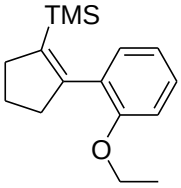
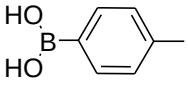
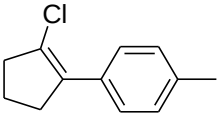
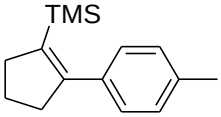
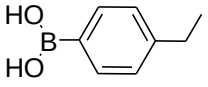
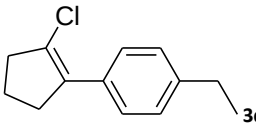
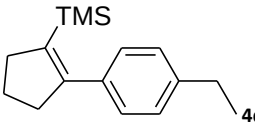
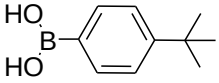
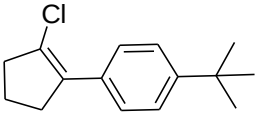
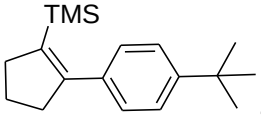
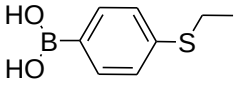
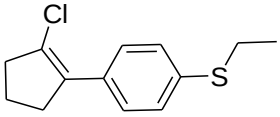
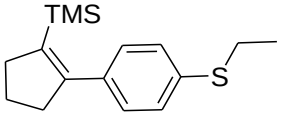
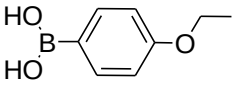
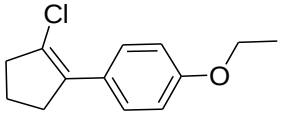
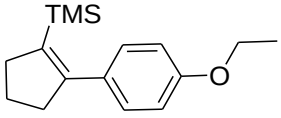
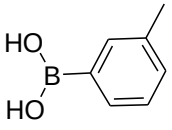
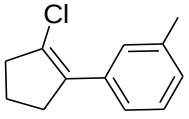
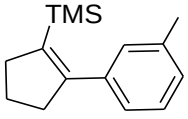
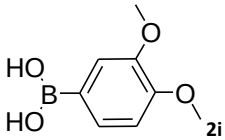
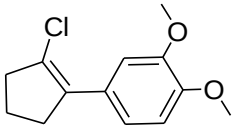
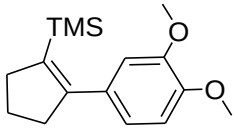
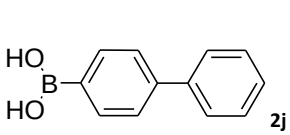
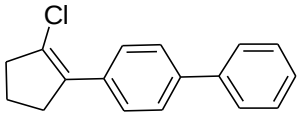
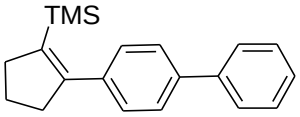
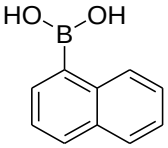
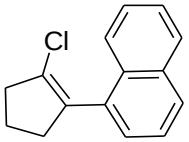
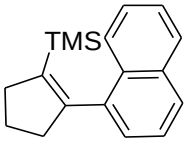
Entry	Boronic acids	1-chloro-2-arylcyclopentenes	1-trimethylsilyl-2-arylcyclopentenes
1	 **2a**	 **3a**[40] (91%)	 **4a**[41] (71%)
2	 **2b**	 **3b**(92%)	 **4b**(69%)
3	 **2c**	 **3c** (95%)	 **4c** (79%)
4	 **2d**	 **3d** (94%)	 **4d** (79%)
5	 **2e**	 **3e** (95%)	 **4e** (62%)
6	 **2f**	 **3f** (96%)	 **4f** (82%)
7	 **2g**	 **3g**(93%)	 **4g** (71%)
8	 **2h**	 **3h** (91%)	 **4h** (71%)
9	 **2i**	 **3i** (91%)	 **4i** (65%)

Table 1. Continued

Entry	Boronic acids	1-chloro-2-arylcyclopentenes	1-trimethylsilyl-2-arylcyclopentenes
10	 **2j**	 **3j** (94%)	 **4j** (69%)
11	 **2k**	 **3k**(92%)	 **4k** (74%)

We postulate the mechanism for the formation of the five-membered anionic synthons **4a-k** from **3a-k** to traverse the mechanistic pathway as reported by us earlier.[34]

In this article, we would wish to report that in our experience over the years, it is found that the synthesis of the six-membered cyclic vinylsilanes is most favorable and requires less reaction time.[34] In comparison, the synthesis of other medium sized rings, including the five membered rings **4a-k**, requires more time and the overall yields are comparatively lesser. We reason that due to ring strain, the isolated yields of the products **4a-k**, have been reduced and the time for formation increased.

Conclusions

1-Bromo-2-chlorocyclopentene (**1**) which possesses differing carbon-halogen bond strengths was exploited for the regioselective synthesis of 1-chloro-2-arylcyclopentenes **3a-k** by the Suzuki-Miyaura cross coupling reaction. Aqueous conditions and microwave assisted organic synthesis methodology yielded the best results. The compounds **3a-k** were converted to the anionic synthons: the five membered 1-trimethylsilyl-2-arylcyclopentenes **4a-k** employing the Wurtz-Fittig coupling reaction under completely anhydrous conditions.

Experimental Section

General. All reactions were performed in oven dried glass apparatus. The fine chemicals and solvents were purchased from Sigma-Aldrich, Merck and Spectrochem, Bangalore. Palladium catalysts were procured from Avra, Alfa – Aesar, Spectrochem and SD Fine Chemicals, Bangalore. Chlorotrimethylsilane was freshly distilled over Na before use. Anhydrous diethylether was distilled over Na/benzophenone ketyl radical before use. All reactions were monitored by Mayura 9800 GC instrument; and Merck F-254 pre-coated TLC plastic sheets using petroleum benzine (60 – 74 °C) as mobile phase using iodine crystals as TLC visualization charring agent. Preliminary gas chromatograms were recorded using a Mayura 9800 gas chromatograph with OV-101 SS 2m x 1/8" column, using the temperature program 80 ^{o}C (2 mins. hold, 5 ^{o}C/min. riseto 180 ^{o}C,12 mins. hold); injector temperature 200 ^{o}C, detector temperature 220 ^{o}C. IR spectra were recorded on Shimadzu FT-IR 8400S (KBr die method); Cary 630 FT-IR, Bruker ALPHA-P spectrometers (ATR) and the values are reported in wave number (cm^{-1}).^{1}H NMR and ^{13}C NMR were obtained on a Bruker AMX 400 spectrometer using $CDCl_3$ with tetramethylsilane as internal standard. Chemical shifts are reported in δ (ppm downfield) with reference to tetramethylsilane for non trimethylsilyl- containing compounds **3a-k** and $CDCl_3$ with δ 7.26 for compounds **4a-**

k possessing the trimethylsilyl- group. EI-MS spectra were obtained using Perkin Elmer Clarus 680 C, employing a fused silica column, packed with Elite-5MS (5% biphenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm ID × 250µm df). The components were separated using Helium as carrier gas at a constant flow of 1 ml/min. The injector temperature was set at 260°C during the chromatographic run. The 1µL of extract sample injected into the instrument the oven temperature was as follows: 60 °C (2 mins. hold, 10 °C/min. rise to 300 °C, 6 mins. hold). The mass detector conditions were: transfer line temperature 240 °C; ion source temperature 240 °C; and ionization mode electron impact at 70 eV, a scan time 0.2 sec and scan interval of 0.1 sec. The fragments were from 40 to 600 Da. Elemental analyses were obtained with a VarioMicro Cube V1.9.7 CHNS mode elemental analyzer. Microwave reactions were performed using CEM DISCOVER-SP W/ACTIVENT (Matthews NC, USA) microwave reactor model no 909155, in a 5 mL reactor vials using Teflon caps, under completely sealed environment with reactor specifications: Voltage - 180/240 V AC; Max Cur. - 6.3 A; Freq. - 50/60 Hz; Mag. Freq.-2455 MHz; Max Microwave power - 300W; Max power output option – 1100Hz. The microwave reactor, provided with a stirring option, was used for all the reactions. The reaction temperature, 80 °C, was reached in a ramp time of 2 minutes and hold time was set for 13 minutes. After the completion of the reaction, the reactor vials were cooled with a jet of compressed air for 3 – 6 minutes. The reactor utilizes automatic pressure control, monitoring the pressure of the reaction and avoiding the loss of reaction mixture.

General procedure for the preparation of 1-chloro-2-arylcyclopentenes 3a-k

Method 1. Conventional Suzuki coupling. To 250 mg of 1-bromo-2-chlorocyclopentene (**1**) taken in a pressure tube was added arylboronic acids **2a-k** (1.4 mmol equiv), $Pd(dppf)_2Cl_2$ (0.03 mol %) catalyst, K_2CO_3 (3.82 mmol equiv) and anhydrous 1,4-dioxane (2.5 mL). The pressure tube was purged with Argon gas, capped and then introduced to a preheated oil bath at 110 ºC. The reaction mixture was heated for 4-6 hours under magnetic stirring. The reaction mixture was cooled, diluted with 30 mL ethyl acetate and filtered through a Celite bed. The excess solvent was removed on a rotary evaporator and crude residue purified by column chromatography using silica gel (100-200 mesh) and 1: 5 ethyl acetate – petroleum benzine (60 – 74 °C).

Method 2. MWAOS-Suzuki couplingin aqueous media using phase transfer catalyst. To 250 mg of 1-bromo-2-chlorocyclopentene (**1,** 1 mmol equiv) taken in a 5 mL microwave vessel equipped with a stirring bar was added arylboronic acids **2a - k** (1.4 mmol equiv), $Pd(OAc)_2$ catalyst (0.03 mol %), Na_2CO_3 (556mg, 3.82 mmol equiv), TBAB (442mg, 1 mmol equiv) in water. The microwave vessel was purged with argon gas and stirred for 2 minutes before introducing into the microwave reactor. The temperature was ramped from room temperature to 80 °C in 2 minutes and held at same temperature for 13 min. The microwave reaction vessel was allowed to cool for 6 minutes. Confirming the completion of the reaction by GC analysis of aliquots, the reaction mixture was extracted with 10 mL ethyl acetate, separated and organic layer was filtered through a Celite bed. The excess solvent was removed on a rotary evaporator and crude residue purified by column chromatography using silica gel (100-200 mesh) using 1: 5 ethyl acetate – petroleum ether (60 – 74 °C) as eluent. The pure compounds **3a-k**, which appeared as single spot on TLC under UV lamp, were isolated and characterized completely. The optimized yields are given in **Table 1.**

General procedure for the preparation of 1-trimethylsilyl-2-arylcyclopentenes 4a-k. To a suspension of finely cut sodium metal (3 g atom equiv), pre-sonicated for 10 minutes in petroleum ether (60 – 74 °C) and chlorotrimethylsilane (4 mmol equiv) in 3 mL dry ether was added the individual 1-chloro-2-arylcyclopentene (1 mmol equiv) 3a-k, in 5 mL anhydrous ether. The mixture was heated on an oil bath to reflux temperature employing a Graham water-cooled condenser with $CaCl_2$ guard tube. The reflux was continued until the appearance of deep navy-blue coloration, and then the reactions were monitored by TLC and GC through micro work-up of aliquots. After completion of the reaction as indicated by the chromatograms, the reaction

mixture was cooled to ambient temperature, the precipitated solid and remaining sodium were removed by filtering on a plug of glass wool and washed with ether (2 × 5 mL). The combined organic extract was washed with saturated sodium bicarbonate (15 mL), saturated brine (15 mL), water (3 × 10 mL), and dried over anhydrous K_2CO_3. The combined extract was concentrated on a rotary evaporator and purified by column chromatography, using silica gel (230–400 mesh) and petroleum benzine (60 – 74 °C) as mobile phase, to obtain the pure compounds **4a-k**. The spectral characterization is summarized in experimental. The optimized yields are tabulated in **Table 1**.

Spectral details of compounds **3a-k**and **4a-k**.

1-Chloro-2-(2′ -methoxyphenyl)cyclopentene(**3a**). Light yellow solid (91%yield); IR (cm^{-1}) 3058, 3004, 2954, 2901, 2850, 2831, 2366, 1654, 1488, 1319, 1263, 1161, 1114, 1053, 1029, 894, 879, 786, 752, 667, 632; ^{1}H NMR (400 MHz, $CDCl_3$,*δ*/ppm) 2.07 (q, *J* 7.6 Hz, 2H), 2.81-2.73 (m, *J* 4.8 Hz, 4H), 3.83 (s, 3H), 6.91- 6.94 (m, *J* 9.6 Hz, 1H), 6.96 - 7 (m, *J* 7.2Hz, 1H), 7.30 - 7.31 (m, *J* 7.2Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 21.6, 35.6, 38.7, 55.5, 111.1, 120.4, 125.1, 128.2, 128.9, 130.5, 135.2, 157.2; MS *m/z* Calculated for $C_{12}H_{13}ClO$ 208.07, Found 210.2554 (M+2 **=** 34%), 208.2378 (97%), 131.2351 (100%); CHNS anal.calcd C,69.07%; H, 6.28%**.** Found C,69.27%; H,6.26%.

1-Chloro-2-(2′ -ethoxyphenyl)cyclopentene(**3b**). Off white solid (92%yield); IR (cm^{-1}) 2923, 2852, 1596, 1578, 1474, 1446, 1391, 1318, 1232, 1161, 1121, 1046, 1004, 926, 874, 749, 700, 668, 602, 561, 508, 443; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 1.27 (t, *J* 6.8 Hz, 3H), 1.41 (t, *J* 6.5 Hz, 3H), 2.01 - 2.08 (m, *J* 8 Hz, 2H), 2.72 (q, *J* 7.2 Hz, 2H), 2.786 - 2.823 (m, *J* 4.8 Hz, 2H), 3.99 - 4.076.66 (m, *J* 6.8Hz, 4H), 6.89 (d, *J* 8 Hz, 1H), 6.94 - 6.99 (m, *J* 8 Hz, 2H), 7.24 – 7.32 (m, *J* 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 14.9, 15, 21.8, 29.9, 35.6, 38.7, 63.9, 112.2, 112.3, 120.2, 125.3, 128, 128.4, 128.5, 128.9, 130.6, 131.7, 135.4, 156.6; MS *m/z* Calculated for $C_{13}H_{15}ClO$ 222.08, Found 224.1572 (M+2 = 30%), 222.1402 (M = 90%); CHNS anal.calcd C,70.11%; H,6.79%**.**Found C,69.83%; H,6.77%.

1-Chloro-2-(4′ -methylphenyl)cyclopentene(**3c**). Light yellow solid (95%yield); IR (cm^{-1}) 3024, 2954, 2920, 2850, 2765, 1901, 1620, 1508, 1438, 1407, 1299, 1276, 1230, 1207, 1188, 1107, 802, 769; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 2.048 (q, *J* 7.6Hz, 2H), 2.391 (s, 3H), 2.71 - 2.85 (m, *J* 7.2 Hz, 4H), 7.21 (d, *J* 8Hz, 2H), 7.57 (d, *J* 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 20.8, 21.3, 21.4, 23.5, 29.9, 33.4, 35.3, 40.2, 125.2, 125.6, 126.4, 126.9, 127.4, 128.1, 128.9, 129.1, 129.6, 132.4, 134.7, 136.6, 136.8, 137.3, 138.4, 142; MS *m/z* Calculated for $C_{12}H_{13}Cl$192.07, Found 194.3223 (M+2 = 28%), 192.3044 (M = 81%), 142.2450 (100%); CHNS anal.calcd C,74.80%; H,6.80%**.**Found C,74.64%; H,6.78%.

1-Chloro-2-(4′ -ethylphenyl)cyclopentene(**3d**). Light yellow solid (94%yield); IR (cm^{-1}) 2924, 1715, 1214, 1080, 967, 751, 667; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 1.25 (t, *J* 7.6 Hz, 3H), 1.98 - 2.05 (m, 2H), 2.62 – 2.68 (m, 2H), 2.78 - 2.81 (m, 2H), 7.2 (d, *J* 8.4 Hz, 2H), 7.56 (d, *J* 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 15.6, 20.82, 28.8, 35.3, 40.2, 126.4, 127.4, 127.7, 132.7, 134.2, 143.6; MS *m/z* Calculated for $C_{13}H_{15}Cl$ 206.7112, Found 208.0968 (M+2 = 34%), 206.0792 (100%); CHNS anal.calcd C,75.53%; H,7.31%**.**Found C, 75.39%; H, 7.29%.

1-Chloro-2-(4′ -tertiatybutylphenyl)cyclopentene(**3e**). Light yellow solid (95%yield); IR (cm^{-1}) 2921, 2868, 1712, 1605, 1509, 1461, 1407, 1364, 1269, 1191, 1109, 1017, 963, 834, 756, 707, 665, 577, 546; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 1.36 (s, 9H), 2.02 (q, *J* 7.6 Hz, 2H), 2.88 (t, *J* 7.6 Hz, 4H), 7.15 (d, *J* 8.4 Hz, 1H), 7.23 (d, *J* 8.4 Hz, 1H), 7.45 (d, *J* 8.4 Hz, 1H) , 7.52 (d, *J* 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 29.9, 31.4, 31.5, 31.53, 34.7, 125, 125.8, 126.8, 126.8, 127, 150.1; MS *m/z* Calculated for $C_{15}H_{19}Cl$ 234.12, Found 240.3053 (M+2 = 3%), 238.2187 (M = 10%), 43.0908 (100%); CHNS anal.calcd C,76.74%; H,8.16%**.** Found C,76.55%; H,8.14%.

1-Chloro-2-(4′ -ethylsulfanephenyl)cyclopentene(**3f**). Off white solid (96%yield); IR (cm^{-1}) 2959, 2924, 2850, 1680, 1620, 1593, 1492, 1443, 1401, 1375, 1261, 1095, 1013, 968, 878, 819, 761, 726, 634, 572, 529, 474;^{1}H

NMR (400 MHz, $CDCl_3$, *δ*/ppm) 1.33 (t, *J* 7.2 Hz, 4H), 2.02 (q, *J* 7.6Hz, 3H), 2.75 - 2.81 (m, *J* 5.6 Hz, 4H), 2.96 (q, *J* 7.6 Hz, 2H), 7.3 (d, *J* 8.4 Hz, 2H), 7.57 (d, *J* 8.4Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 14.5, 20.8, 23.5, 27.5, 28, 29.8, 33.3, 33.5, 35.2, 40.3, 126.1, 127.1, 127.9, 128.4, 129.3, 132.7, 133.6, 134.7, 134.9, 136; MS *m/z* Calculated for $C_{13}H_{15}ClS$ 238.06, Found 240.2357 (M+2 = 40%), 238.2187 (M = 100%); CHNS anal.calcd C,65.39%; H,6.33%**;** S,13.43. Found C,65.24%; H,6.29%; S,13.39%.

1-Chloro-2-(4′ -ethoxyphenyl)cyclopentene(**3g**). Light yellow solid (93%yield); IR (cm^{-1}) 2959, 2925, 2851, 1749, 1700, 1607, 1574, 1559, 1510, 1287, 1247, 1181, 1122, 1049, 923, 826, 802, 572; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 1.42 (t, *J*7.2 Hz, 4H), 2.01 (q, *J* 7.6Hz, 2H), 2.78 (m, *J* 4.4Hz, 4H), 4.05 (q, *J* 6.8Hz, 2H), 6.89 (d, *J* 8Hz, 2H), 7.59 (d, *J* 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 14.9, 20.8, 29.8, 35.3, 40.2, 63.5, 114.1, 125.3, 127.7, 128.7, 133.6. MS *m/z* Calculated for $C_{13}H_{15}ClO$ 222.08, Found 224.3074 (M+2 **=** 32%), 222.2901 (M **=** 94%), 159.3097 (100%); CHNS anal.calcd C, 70.11%; H, 6.79%**.** Found C, 69.95%; H, 6.76%.

1-Chloro-2-(3′ -methylphenyl)cyclopentene(**3h**). Light yellow solid (91%yield); IR (cm^{-1}) 3025, 2955, 2924, 2853, 1603, 1490, 1456, 1377, 772, 754, 698;^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 2.03 (t, *J* 7.2 Hz, 2H), 2.38 (s, 3H), 2.76 – 2.83 (m, *J* 5.2Hz, 3H), 3.82 (s, 3H), 7.09 – 7.20 (m, *J*7.6Hz, 2H), 7.24 - 7.33 (m, *J* 7.2Hz, 1H), 7.42 (q, *J* 8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 20.9, 22.8, 30.5, 34.6, 124.2, 126.7, 132.7, 139.1, 148.9; MS *m/z* Calculated for $C_{12}H_{13}Cl$ 192.07, Found 194.3223 (M+2 = 25%), 192.3044 (M = 75%), 157.2902 (100%); CHNS anal.calcd C, 74.80%; H, 6.80%. Found C, 74.72%; H, 6.75%.

1-Chloro-2-(3′ ,4′ -dimethoxyphenyl)cyclopentene(**3i**). Light yellow solid (91%yield); IR (cm^{-1}) 2997, 2931, 2846, 2333, 1793, 1654, 1515, 1458, 1253, 1210, 1165, 1145, 1110, 1026, 806, 763; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 2.01 (q, *J* 8 Hz, 2H), 2.50 - 2.81 (m, *J* 6.4 Hz, 4H), 3.88 (s, 3H), 3.89 (s, 3H), 6.8 - 6.86 (m, *J* 8.4 Hz, 1H), 7.11-7.14 (dd, *J* 8.4 Hz, 1H), 7.34 (d, *J* 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 20.6, 23.4, 29.7, 33.4, 35.2, 40.2, 55.9, 108.8, 110.6, 118.2, 120.2, 142.4, 125.6, 128, 130.1, 133.6, 142.1, 148.4; MS *m/z* Calculated for $C_{13}H_{15}ClO_2$ 238.08, Found 240.2357 (M+2 = 37%), 238.2187 (100%); CHNS anal.calcd C, 65.41%; H, 6.33%**.**Found C, 65.29%; H, 6.31%.

1-Chloro-2-(4′ -biphenyl)cyclopentene(**3j**). White crystalline solid (94%yield); IR (cm^{-1}) 3029, 2923, 2849, 1683, 1600, 1486, 1445, 1402, 1124, 1106, 1005, 878, 839, 764, 726, 694, 580; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 2.09 (q, *J* 6 Hz,2H), 2.82 - 2.88 (m, *J* 3.5 Hz, 4H), 7.37 (d, *J* 5.2 Hz, 1H), 7.46 (d, *J* 6 Hz, 2H), 7.63 (d, *J* 5.2 Hz, 4H), 7.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) 20.8, 23.5, 29.8, 33.3, 33.6, 35.5, 40.4, 126.1, 126.5, 126.9, 127.1, 127.4, 127.5, 127.9, 128.9, 133.8, 134.3, 136, 140.2, 140.9; MS *m/z* Calculated for $C_{17}H_{15}Cl$ 254.09, Found 256.2325 (M+2 = 35%), 254.2850 (M = 100%); CHNS anal.calcd C, 80.15%; H, 5.93%**.** Found C, 79.94%; H, 5.89%.CCDC number **:** 1553574.

1-Chloro-2-(napthyl)cyclopentene(**3k**). White solid (92%yield); IR (cm^{-1}) 3047, 2923, 2900, 2843, 2557, 2490, 2410, 2384, 2329, 1793, 1603, 1505, 1396, 1315, 1288, 1245, 1199, 1126, 1096, 1056, 715; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) 2.21 (t, *J*7.2Hz, 2H), 2.87 (q, *J* 4 Hz, 4H), 7.34 (s, 1H), 7.5 (d, *J 9.*6 Hz, 3H), 7.83 (d, *J* 4Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ/*ppm) 21.9, 38.1, 38.9, 125.5, 125.7, 125.8, 125.9, 126, 128, 128.6, 127.9, 128.6, 129.8, 130.8, 133.8, 134.5, 136.5; MS m/z Calculated for $C_{15}H_{13}Cl$ 228.07, Found 230.2198 (M+2 = 15%), 228.2027 (M = 45%); CHNS anal.calcd C, 78.77%; H, 5.73%**.**Found C, 78.69%; H, 5.69%.CCDC number: 1553573.

1-Trimethylsilyl-2-(2′ -methoxyphenyl)cyclopentene(**4a**). Light yellow high boiling liquid (71%yield); IR (cm^{-1}) 30.17, 2958, 1598, 1490, 1464, 1437, 1252, 1245, 1052, 544, 746, 667, 466; ^{1}H NMR (400 MHz, $CDCl_3$,*δ*/ppm) -0.28 (s, 9H), 1.99 - 2.04 (m, *J* 7.6Hz, 3H), 2.44 - 2.48 (m, *J* 4.8Hz, 2H), 2.66 - 2.72 (m, *J* 8.8 Hz, 2H), 3.881 (s, 3H), 7.14 (m, *J* 7.2 Hz, 1H), 7.18 (m, *J* 6.8 Hz, 2H), 7.39 (m, *J* 8.8 Hz, 1H), 7.57 (m, *J* 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) -0.14, 21.47, 31.52, 35.84, 55.87, 111.09, 119.10, 125.06, 128.05, 130.13, 135.16, 139.22; MS *m/z* Calculated for $C_{15}H_{22}SiO$ 246.4201, Found 246.3862 (M), 91.2141 (100%), 73.1200 (10%); CHNS anal.calcd C, 73.11%; H, 9%**.** Found C, 73.09%; H, 8.92%.

1-Trimethylsilyl-2-(2′ -ethoxyphenyl)cyclopentene (**4b**). Light yellow high boiling liquid (69%yield); IR (cm^{-1}) 2958, 2925, 2852, 2335, 21614, 2026, 1963, 1596, 1491, 1445, 1391, 1252, 1123, 1048, 749, 665, 482; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) - 0.27 (s, 9H), 1.23 (t, *J* 7.6 Hz, 2H), 1.75 (t, *J* 4Hz, 2H), 2.18 - 2.21 (m, *J* 3.6 Hz, 2H), 2.37 (q, *J* 4 Hz, 2H), 2.89 (q, *J* 7.6Hz, 3H), 6.83 - 6.95 (m, *J* 8.4 Hz, 3H), 7.37 – 7.39 (m, *J* 8.8 Hz, 1H), 7.45 - 7.47 (m, *J* 6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.3, 14, 22.7, 31.5, 31.6, 63.2, 112.5, 125.2, 129.6, 131.3, 131.4, 134.9; MS *m/z* Calculated for $C_{16}H_{24}SiO$ 260.1596, Found 260.2188 (M), 91.1443 (100%), 73.12 (15%); CHNS anal.calcd C, 73.79%; H, 9.29%**.** Found C, 73.53%; H, 9.27%.

1-Trimethylsilyl-2-(4′ -methylphenyl)cyclopentene(**4c**). Light yellow high boiling liquid (79%yield); IR (cm^{-1}) 2952, 2923, 2852, 1510, 1458, 1405, 1377, 1247, 1214, 1003, 905, 835, 751, 668; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) -0.24 (s, 8H), 1.928 (m, *J* 7.2 Hz, 2H), 2.37 (s, 3H), 2.59 (m, *J* 8.4Hz, 2H), 2.71 - 2.75 (m, *J* 8 Hz, 2H), 6.99 (s, 2H), 7.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.165, 20.87, 22.86, 29.93, 31.73, 124.33, 125.42, 132.65, 138.97, 142.72; MS *m/z* Calculated for $C_{15}H_{22}Si$ 230.1491, Found 230.2113 (M), 73.1041 (100%); CHNS anal.calcd C, 78.19%; H, 9.62%**.** Found C, 77.96%; H, 9.60%.

1-Trimethylsilyl-2-(4′ -ethylphenyl)cyclopentene(**4d**). Light yellow high boiling liquid (79%yield); IR (cm^{-1}) 2924, 2852, 1671, 1605, 1474, 1240, 1114, 1845, 922, 808, 754; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) -0.221(s, 8H), 1.09 (t, *J* 7.2 Hz, 4H), 1.88–1.89 (m, *J* 5.2 Hz, 4H), 2.24 – 2.29 (m, *J* 7.2Hz, 2H), 2.32 – 2.35 (t, *J* 6.8 Hz, 2H), 2.60 – 2.65 (m, *J* 8 Hz, 1H), 7.11 (d, *J* 6.8 Hz, 2H), 7.48 (d, *J* 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.23, 17.82, 21.18, 29.84, 30.52, 32.17, 126.21, 127.42, 129.58, 133.82, 134.8**;** MS *m/z* Calculated for $C_{16}H_{24}Si$ 244.1647, Found 244.1299 (M = 40%); CHNS anal.calcd C, 78.61%; H, 9.90%**.**Found C, 78.52%; H, 9.85%.

1-Trimethylsilyl-2-(4′ -tertiatybutylphenyl)cyclopentene(**4e**). Light yellow high boiling liquid (62%yield); IR (cm^{-1}) 2958, 2866, 1624, 1463, 1409, 1394, 1363, 1333, 1267, 1247, 1188, 1110, 1081, 1037, 1020, 968, 833, 755, 736, 698, 561; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) -0.25 (s, 9H), 1.36 (s, 9H), 1.99 - 2.04 (m, *J* 8 Hz, 3H), 2.49 - 2.54 (m, *J* 2.4 Hz, 2H), 2.68 - 2.72 (m, *J* 2.8 Hz, 2H), 7.12 - 7.19 (m, *J* 8.4 Hz, 2H) , 7.32 - 7.39 (m, *J* 8.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.14, 25.5, 29.73, 30.57, 31.2234.46, 125.01, 125.64, 126.78, 127.74, 141.01, 143.23; MS *m/z* Calculated for $C_{18}H_{28}Si$ 272.1960, Found 272.2142 (M), 91.0804 (100%); CHNS anal.calcd C, 79.34%; H, 10.36%**.** Found C, 79.25%;H, 10.25%.

1-Trimethylsilyl-2-(4′ -ethylsulfanephenyl)cyclopentene(**4f**). Light yellow high boiling liquid (82% yield); IR (cm^{-1}) 2955, 2924, 2853, 1731, 1670, 1454, 1377, 1346, 1270, 1247, 1214, 1093, 978, 840, 754, 665; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) -0.26 (s, 9H), 1.24 (q, *J* 8 Hz, 5H), 1.93 - 1.98 (m, *J* 8 Hz, 2H), 2.49 - 2.52 (m, *J* 3.2 Hz, 2H), 2.60 - 2.63 (m, *J* 3.6 Hz, 2H), 2.91 - 2.97 (q, *J* 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.155, 14.41, 21.57, 27.43, 29.43, 33.20, 126.08, 129.16, 131.57, 132.94, 134.54; MS *m/z* Calculated for $C_{16}H_{24}SiS$ 276.1368, Found 277.1714 (M+1), 73.1498 (100%); CHNS anal.calcd C, 69.50%; H, 8.75%**;** S, 11.60. Found C, 68.42%; H, 8.73%; S, 11.57%.

1-Trimethylsilyl-2-(4′ -ethoxyphenyl)cyclopentene(**4g**). Light yellow high boiling liquid (71%yield); IR (cm^{-1}) 3027, 2956, 2924, 2854, 1604, 1493, 1453, 1391, 1377, 1244, 1215, 1177, 1117, 1058, 1030, 757, 699; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) -0.25 (s, 9H), 1.41(t, *J* 6.8Hz, 3H), 1.39 - 2.05 (3, *J* 3.2Hz, 2H), 2.43 - 2.5 (m, *J* 4.4Hz, 2H), 2.64 - 2.69 (m, *J* 7.2Hz, 1H), 2.90 - 2.95 (m, *J* 7.2Hz, 1H),3.98 - 4.04 (m, *J* 6.8 Hz, 2H), 6.82 (d, *J* 8.8Hz, 1H), 7.6 (d, *J* 10 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.14, 14.8, 20.7, 29.9, 31.6, 63.4, 114.2, 125.8, 127.8, 128.3, 131.9, 134.1; MS *m/z* Calculated for $C_{16}H_{24}SiO$ 260.1596, Found 260.3898, 91.2375 (100%), 73.1205 (8.6%); CHNS anal.calcd C, 73.79%; H, 9.29%**.** Found C, 73.65%; H, 9.27%.

1-Trimethylsilyl-2-(3′ -methylphenyl)cyclopentene(**4h**). Light yellow high boiling liquid (71%yield); IR (cm^{-1}) 2924, 1594, 1532, 1368, 1247, 1217, 1182, 1080, 1055, 836, 755, 699, 514; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) - 0.213 (s, 9H), 2.02 - 2.05 (m, *J* 3.2 Hz, 3H), 2.42 (s, 3H), 2.58 - 2.64 (m, *J* 8.8Hz, 4H), 6.87 –6.92 (m, *J*8.4 Hz, 1H), 7.10 -7.12 (d, *J* 8 Hz, 2H),7.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm) -0.18, 20.90, 22.74, 29.44, 30.47,

124.33, 126.49, 132.55, 135.63, 138.97; MS *m/z* Calculated for $C_{15}H_{22}Si$ 230.1491, Found 231.3353 (M+1), 91.2141 (100%), 73.1200 (11%); CHNS anal.calcd C, 78.19%; H, 9.62%. Found C, 78.14%; H, 9.57%.

1-Trimethylsilyl-2-(3′ ,4′ -dimethoxyphenyl)cyclopentene(**4i**). Light yellow high boiling liquid (65%yield); IR (cm^{-1}) 2923, 2853, 1710, 1604, 1581, 1492, 1463, 1376, 1364, 1286, 1251, 1214, 1081, 1049, 967, 749, 668; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) -0.29 (s, 9H), 1.79 - 1.87 (m, *J* 12Hz, 2H), 2.49 - 2.54 (m, *J* 11.2Hz, 2H), 2.672 (m, *J* 4Hz, 2H), 3.799 (s, 7H), 6.68 - 6.721 (m, *J* 8 Hz, 3H), 7.194 (t, *J* 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) -0.17, 20.43, 23.34, 28.52, 29.44, 55.66, 107.63, 110.87, 122.23, 131.58, 139.2; MS *m/z* Calculated for $C_{16}H_{24}SiO_2$ 276.4461, Found 276.1351 (M), 41.0226 (100%), 73.1321 (33%); CHNS anal.calcd C, 69.51%; H, 8.75%**.** Found C, 69.19%; H, 8.72%.

1-Trimethylsilyl-2-(4′ -biphenyl)cyclopentene(**4j**). Light yellow solid (69%yield); IR (cm^{-1}) 2953, 2854, 2160, 2043, 1599, 1487, 1247, 1113, 1061, 1006, 834, 758, 696; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) -0.30 (s, 10H), 1.69 - 1.74 (m, *J* 4.8 Hz, 2H), 1.82 – 1.84 (m, *J* 3.2 Hz, 2H), 2.09 - 2.12 (m, *J* 4 Hz, 2H), 3 - 3.09 (m, *J* 8 Hz, 1H), 7.325 (d, *J* 8.4 Hz, 3H) , 7.41 - 7.45 (m, *J* 8 Hz, 2H) , 7.53 (d, *J* 8 Hz, 2H) , 7.58 - 7.6 (m, *J* 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm) -0.3, 22.7, 29.6, 29.8, 30.3, 31.5, 126.1, 126.4, 127.3, 127.9, 129.6, 131.3, 131.4, 134.9, 137.8; MS *m/z* Calculated for $C_{20}H_{24}Si$ 292.1647, Found 294.1919 (M+2), 72.9924 (100%). CHNS anal.calcd C, 82.13%; H, 8.27%**.** Found C, 82.02%; H, 8.25%.

1-Trimethylsilyl-2-(naphthyl)cyclopentene(**4k**). Light yellow solid (74%yield); IR (cm^{-1}): 2954, 2924, 2853, 1599, 1493, 1454, 1376, 1247, 214, 966, 835, 753, 699, 668, 626; ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm) -0.061 (s, 10H), 2.02 - 2.05 (m, *J* 4 Hz, 2H), 2.45 - 2.5 (m, *J* 4.8 Hz, 3H), 7.28 - 7.44 (m, *J* 3.6 Hz, 2H), 7.46 - 7.51 (m, *J* 6.8 Hz, 3H), 7.85 (m, *J* 8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ/*ppm) -0.2, 21.9, 34.5, 38.2, 124.5, 125.7, 125.8, 127.8, 128.2, 130.8, 131.7, 132.8; MS *m/z* Calculated for $C_{18}H_{22}Si$ 266.1491, Found 266.2792 (M), 73.12 (100%); CHNS anal.calcd C, 81.14%; H, 8.32%**.** Found C, 81.05%; H, 8.29%.

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Supplementary Material

Supporting information features spectral details: FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra of compounds **3a-k, 4a-k** and X-ray structure analysis of two representative compounds **3j** and **3k.**

References and Notes

1. Kappe, O. C.; Dallinger, D.; Murphree, S. S. *Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments and Protocols*; Wiley- VCH: Weinheim, 2009.
2. Szudkowska-Fratczak, J.; Hreczycho, G.; Pawluc, P. *Org. Chem. Front.* **2015,** 2, 730-738. https://doi.org/10.1039/C5QO00018A
3. Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011,** *111,* 1417-1492. https://doi.org/10.1021/cr100327p
4. Molnár, A. *Chem. Rev.* **2011**, *111,* 2251-2320. https://doi.org/10.1021/cr100355b
5. Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780-1824. https://doi.org/10.1021/cr100379j
6. Theeramunkong, S.; Caldarelli, A.; Massarotti, A.;Aprile, S.; Caprioglio, D.; Zaninetti, R.; Teruggi, A.; P*IR*ali, T.; Grosa, G.; Tron, G. C.; Genazzani, A. A. *J. Med. Chem.* **2011**, 54, 4977-4986. https://doi.org/10.1021/jm200555r
7. Christian, G.; Hartung.; Klaus Kohler.; Beller, M. *Org. Lett.* **1999**, *1*, 709-711. https://doi.org/10.1021/ol9901063
8. Hazari, N.; Melvin, P. R.; Beromi, M. M. *Nature Rev.* **2017**, *1*, 1-16. https://doi.org/10.1038/s41570-017-0025
9. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483. https://doi.org/10.1021/cr00039a007
10. Hajipour, A. R.; Rezaei, F.; Khorsandi, Z**.** *Green Chem***. 2017***, 19,*1353-1361. https://doi.org/10.1039/C6GC03377F
11. Fris, S. D.; P*IR*not, M. T.; Dupuis, L. N.; Buchwald, S. L. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 7242-7246. https://doi.org/10.1002/anie.201703400
12. Suzuki, A. Nobel lecture December 8, 2010.. https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2010/suzuki_lecture.pdf
13. Anamitra Chatterjee. Ward, T. R. *Catal. Lett.* **2016**, *146*, 820-840. https://doi.org/10.1007/s10562-016-1707-8
14. Li, C.-J.; Chen, T.-H. *Organic Reactions in Aqueous Media*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
15. Cornils, B., Herrmann, W. A., Eds.; *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*; Wiley- VCH: Weinheim, 1998.
16. Leadbeater, N. E.; Marco, M. *Angew. Chem.* **2003**, *115*, 1445-1447. https://doi.org/10.1002/ange.200390334
17. Botella, L.; Najera, C. *Angew.Chem. Int. Ed.* **2002**, *41*, 179-181. https://doi.org/10.1002/1521-3773(20020104)41:1<179:AID-ANIE179>3.0.CO;2-O
18. Badone, D.; Baroni, M.; Cardamone, R.; Ielmini, A.; Guzzi, U. *J. Org. Chem.* **1997**, *62*, 7170-7173. https://doi.org/10.1021/jo970439i
19. Genet, J.; Savignac, M. J. *Organomet. Chem.* **1999**, *576*, 305-317. https://doi.org/10.1016/s0022-328x(98)01088-2.
20. Bumagin, N A.; Bykov, V. V. *Tetrahedron* **1997**, *53*, 14437-14450. https://doi.org/10.1016/S0040-4020(97)00936-8

21. Sakurai, H.; Tsukuda, T.; H*IR*ao, T. J. Org. *Chem*. **2002**, *67*, 2721-2722. https://doi.org/10.1021/jo016342k
22. Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem.* **1999**, *64*, 3384-3388. https://doi.org/10.1021/jo982438b
23. Shaughnessy, K. H.; Booth, R. S. *Org. Lett.* **2001**, *3*, 2757-2759. https://doi.org/10.1021/ol0163629
24. Dupuis, C.; Adiey, K.; Charruault, L.; Michelet, V.; Savignac, M.; Genet, J.-P. *Tetrahedron Lett.* **2001**, *42*, 6523-6526. https://doi.org/10.1016/S0040-4039(01)01301-6
25. Westman, J. *Org. Lett.* **2001**, *3*, 3745-3747. https://doi.org/10.1021/ol0167053
26. Kuhnert, N.; Danks, T. N. *Green Chem.* **2001**, *3*, 68-70. https://doi.org/10.1039/B008866H
27. Loupy, A.; Regnier, S. *Tetrahedron Lett.* **1999**, *40*, 6221-6224. https://doi.org/10.1016/S0040-4039(99)01159-4
28. Stadler, A.; Kappe, A. C. *Eur. J. Org. Chem.* **2001**, 919-925. https://doi.org/10.1002/1099-0690(200103)2001:5<919::AID-EJOC919>3.0.CO;2-V
29. Hallberg, A.; Larhed, M. *J. Org. Chem.* **1996**, *61*, 9582-9584. https://doi.org/10.1021/jo9612990
30. Hallberg, A.; Lindeberg, G.; Larhed, M. *Tetrahedron Lett.* **1996**, *37*, 8219-8222. https://doi.org/10.1016/0040-4039(96)01872-2
31. Blettner, C. G.; Konig, W. A.; Stenzel, W.; Schotten, T. *J. Org. Chem.* **1999**, *64*, 3885-3890. https://doi.org/10.1021/jo982135h
32. Leadbeater, N. E.; Marco, M. *J. Org. Chem.* **2003**, *68*, 888-892. https://doi.org/10.1021/jo0264022
33. Leadbeater, N. E.; Marco, M. *Org. Lett.* **2002**, *4*, 2973-2976. https://doi.org/10.1021/ol0263907
34. Jeevan Chakravarthy, A. S.; Krishnamurthy, M. S.; Begum, N. S.; HariPrasad, S. *Tetrahedron Lett.* **2016**, *57*, 3231-3234. https://doi.org/10.1016/j.tetlet.2016.06.051
35. In our previous work, we had reported bromination of cyclohexanone using NBS/PTSA to isolate α-bromocyclohexanone in good yields. However, when the protocol was repeated for cyclopentanone, the formation of *α*-bromocyclopentanone was found to be only in traces. Adopting molecular bromine in $CHCl_3$ solvent yielded *α*-bromocyclopentanone in greater than 80% yield.
36. Both the bromo- and chloro- groups were replaced to form the bis-1,2-(4′ -thioethylphenyl)cyclopentene greater than 50% yield.
37. Fernández, E.; Whiting, A. In Synthesis and Application of Organoboron compounds, Topics in Organometallic Chemistry - 49; Springer: London, 2015.
38. O'Neil, M. J., Ed. *The Merck Index an Encyclopedia of Chemicals, Drugs and Biologicals*, 14th Ed.; Merck and Co., Inc.: N.J., USA, 2006; ONR – 104, 443. https://doi.org/10.1108/09504120710775534
39. For the most recent review on vinylsilanes see: Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983-1010. https://doi.org/10.1055/s-0031-1289729

40. Refers to the isolated yields obtained by reacting 250 mg of 1 (1 mmol equiv.), **2a-k** (1.40 mmol equiv.), 556 mg of Na_2CO_3 (3.82 mmol equiv.), $Pd(OAc)_2$ cat. (0.03 mol%), 442 mg of TBAB (1 mmol equiv.) in 2.5 mL water solvent under microwave irradiation, with ramp time of 2 minutes (ambient to 80 °C) and hold time of 13 minutes.
41. Refers to the isolated yields obtained on reacting **3a-k** (1 mmol equiv.) individually with finely cut sodium metal (3 g atom equiv), chlorotrimethylsilane (4 mmol equiv.) in 3 mL dry ether under reflux, employing a Graham water-cooled condenser.