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Selective Heck reaction of aryl bromides with cyclopent-2-en-1-one or cyclohex-2-en-1-one

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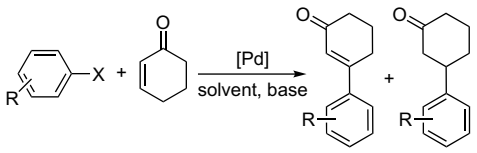
ABSTRACT

The selective Heck reaction of cyclopent-2-en-1-one or cyclohex-2-en-1-one with aryl bromides gives a simple access to the corresponding 3-arylcycloalk-2-en-1-ones. The choice of the base was found to be crucial to avoid the formation of 3-arylcyclopentanones or 3-arylcyclohexanones as side-products. Using KF as base, DMF as solvent and $Pd(OAc)_2$ as catalyst, the target products were obtained in moderate to good yields with a variety of aryl bromides. Substituents such as fluoro, trifluoromethyl, acetyl, benzoyl, formyl, ester or nitrile on the aryl bromide are tolerated. Sterically congested aryl bromides or bromopyridines can also be employed.

1. Introduction

3-Arylcycloalk-2-en-1-ones bearing various substituents on the aromatic ring are useful building blocks in organic synthesis. The Heck palladium catalyzed reaction of aryl and heteroaryl halides with cycloalk-2-en-1-one should be a powerful method for the synthesis of these compounds.[1] However, if the Heck reaction of aryl halides with linear alk-1-en-3-ones has been largely described,[2–4] on the other hand, only a few examples of coupling of cyclopent-2-en-1-one or cyclohex-2-en-1-one with aryl halides have been reported.[2n,3i,5,6–10] Moreover, most of the results employ aryl iodides, which are generally more expensive than aryl bromides.[2n,9,10] In most cases, the reaction of cycloalk-2-en-1-one with aryl bromides led to moderate yields or to mixtures.[3i,5] For example, 2-bromo-6-dimethylaminonaphthalene reacted with cyclopent-2-en-1-one or cyclohex-2-ene-1-one in the presence of $PdCl_2(PPh_3)_2$ as catalyst gave the desired products in 50 and 38% yields, respectively.[3i] A similar yield was observed for the coupling of 4-bromoanisole with cyclopent-2-en-1-one using $Pd(OAc)_2$/DABCO as catalyst and K_2CO_3 as base.[5] In some cases, the formation of the double bond hydrogenated by-product was obtained in relatively large amount (Scheme 1). Negishi and co-workers had observed the formation of this unexpected side-product in 30% selectivity in the course of the intramolecular arylation of a 4-substituted cyclohex-2-en-1-one.[6] Genet and co-workers also studied this reaction. They observed that for the coupling of iodobenzene with cyclohex-2-en-1-one using $Pd(OAc)_2$/TPPTS as catalyst, the ratio of desired Heck product and hydrogenated product was 40:60.[7] In a few other cases, expensive aryl iodides were also employed for this reaction.[2n,8–10] Myers and Tanaka have recently reported the influence of some reaction conditions for the vinylation of 2,4-dimethoxyiodobenzene using cyclohex-2-en-1-one.[8] The best yield was obtained using $Pd(OAc)_2$ as catalyst, $NaHCO_3$ as base in the presence of a stoichiometric amount of Bu_4NCl.



Scheme 1.

Therefore, the discovery of reaction conditions leading selectively and in high yields to the 3-arylcycloalk-2-en-1-ones, especially in the presence of aryl bromides, which are more easily available than iodides, and in absence of additives such as ammonium salts, which are an important source of wastes, is desirable. Here, in order to establish the requirements for a successful 3-arylation of cyclopent-2-en-1-one or cyclohex-2-en-1-one, we

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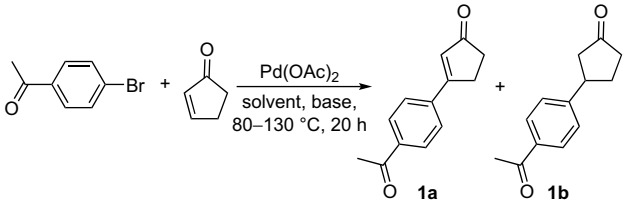
wish to report on the influence of several reaction parameters and also on the aryl bromide substitution, on the yields and selectivities.

2. Results and discussion

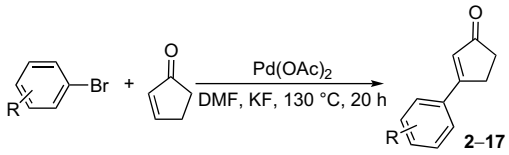
For this study, based on previous results,[4,11–13] DMF was initially chosen as the solvent. The reactions were performed at 130 °C under argon in the presence $Pd(OAc)_2$ as catalyst. First, we examined the influence of the base for the coupling of 4-bromoacetophenone with cyclopent-2-en-1-one. Surprisingly, a very important effect of the base was observed. In all cases, a complete conversion of the aryl bromide was observed. However, the yield in target product **1a** strongly depends on the base. Using Cs_2CO_3 or *t*-BuOK, no formation of **1a** was detected by gas chromatography (Scheme 2, Table 1, entries 1 and 2). A clean reaction was observed using Na_2CO_3, but, in the presence of this base, the hydrogenated side-product **1b** was obtained in 81% selectivity (Table 1, entry 3). A suitable conformation of the Pd intermediate is necessary for the β-elimination step of the catalytic cycle. With cyclopent-2-en-1-one, the conformation of the palladium intermediate is probably not suitable for a fast β-elimination, and side-reactions occur. A similar phenomenon had been observed for Heck reactions using cyclopentene or cyclohexene. With these substrates, the partial migration of the double bond of the cycloalkene was observed.[13] Therefore, the formation of **1b** using cyclopent-2-en-1-one was not surprising. Then, we studied this reaction using other bases, and we observed more selective reactions in favour of **1a** in the presence of K_2CO_3 or NaOAc (Table 1, entries 4 and 5). However, the best selectivity in **1a** was obtained employing KF as base with a ratio **1a**/**1b** of 88:12 (Table 1, entry 6). Using these conditions, **1a** was isolated in 62% yield.



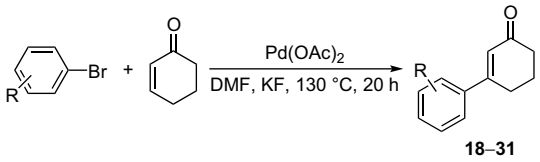
Scheme 2.

Next, we examined the influence of the solvent on the conversion and selectivity. Very low conversions of 4-bromoacetophenone were observed in the presence of acetonitrile or 1,2-dimethoxyethane (Table 1, entries 7 and 8). On the other hand, NMP or DMAc led to complete conversion of the aryl bromide, but no improvement of the selectivity in **1a** was observed (Table 1, entries 9 and 10). A lower reaction temperature (80 °C) also led to a very low conversion of the aryl bromide (Table 1, entry 11).

Then, using the most selective reaction condition (DMF, KF, $Pd(OAc)_2$, 130 °C), we explored the scope and limitations of this reaction using *para*-, *meta*- and *ortho*-substituted aryl bromides and also a few heteroaryl bromides employing cyclopent-2-en-1-one or cyclohex-2-en-1-one as vinylation partners (Schemes 3 and 4, Tables 2–5).



Scheme 3.



Scheme 4.

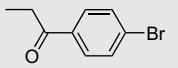
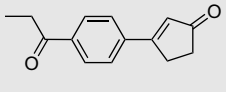
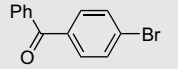
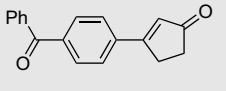
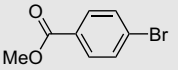
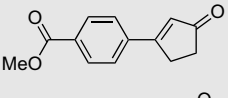
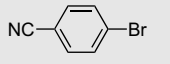
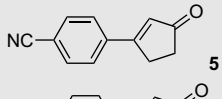
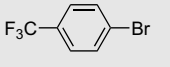
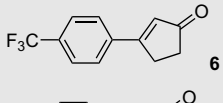
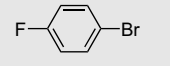
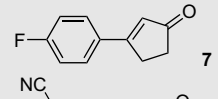
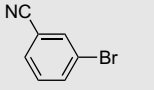
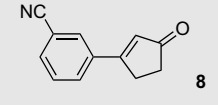
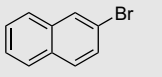
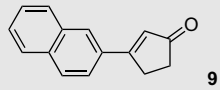
First, we have investigated the reaction of cyclopent-2-en-1-one with several *para*-substituted aryl bromides (Scheme 3, Table 2). In most cases, the reaction proceeds very smoothly in the

Table 1
Influence of the reaction conditions for palladium catalyzed arylation of cyclopent-2-en-1-one using 4-bromoacetophenone (Scheme 2)

Entry	Base	Solvent	Temperature (°C)	Conversion of 4-bromoacetophenone (%)	Ratio of products **1a**/**1b**	Yield in **1a** (%)
1	Cs_2CO_3	DMF	130	100	—	0
2	*t*-BuOK	DMF	130	100	—	0
3	Na_2CO_3	DMF	130	100	19/81	12
4	K_2CO_3	DMF	130	100	50/50	4
5	NaOAc	DMF	130	100	64/36	41
6	KF	DMF	130	100	88/12	66 (62)
7	NaOAc	MeCN	130	0	—	0
8	NaOAc	DME	130	5	—	3
9	KF	NMP	130	100	72/28	34
10	KF	DMAc	130	100	72/28	24
11	KF	DMF	80	2	—	0

Conditions: $Pd(OAc)_2$ (0.02 equiv), 4-bromoacetophenone (1 equiv), cyclopent-2-en-1-one (2 equiv), KF (2 equiv), DMF, 20 h, GC and NMR yields, yield in parenthesis is isolated.

Table 2
Palladium catalyzed reaction of cyclopent-2-en-1-one with *para*- or *meta*-substituted aryl bromides (Scheme 3)

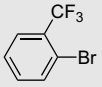
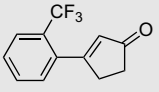
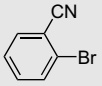
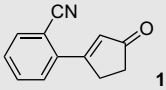
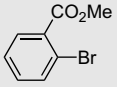
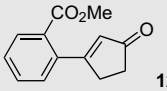
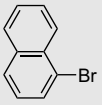
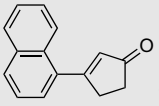
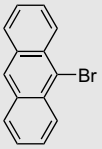
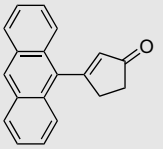
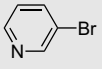
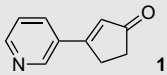
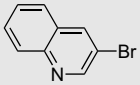
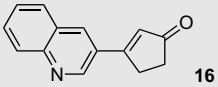
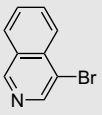
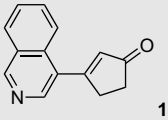
Entry	Aryl bromide	Product	Yield (%)
1		 **2**	69
2		 **3**	71
3		 **4**	61
4		 **5**	73
5		 **6**	67
6		 **7**	68
7		 **8**	58
8		 **9**	70

Conditions: $Pd(OAc)_2$ (0.02 equiv), ArBr (1 equiv), cyclopent-2-en-1-one (2 equiv), KF (2 equiv), DMF, 130 °C, 20 h, isolated yields.

presence of 2 mol % catalyst. We observed that yields of 61–71% can be obtained for activated substrates such as 4-bromopropiophenone, 4-bromobenzophenone, 4-bromobenzonitrile, 4-trifluoromethylbromobenzene or 4-fluorobromobenzene (Table 2, entries 1–6). The influence of the presence of *meta*-substituents on the aryl bromide is also reported in Table 2. As expected a relatively similar yield than in the presence of the *para*-substituted substrates was observed with 3-bromobenzonitrile (Table 2, entry 7). With the non-activated 2-bromonaphthalene, a yield of 70% in **9** was obtained (Table 2, entry 8).

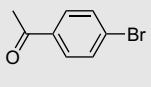
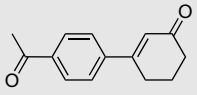
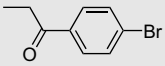
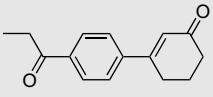
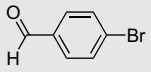
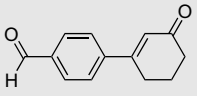
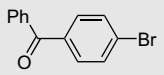
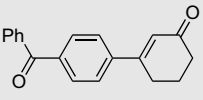
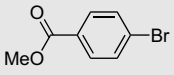
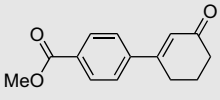
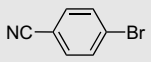
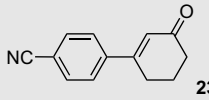
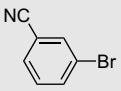
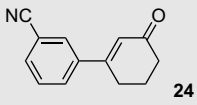
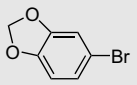
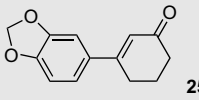
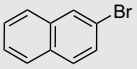
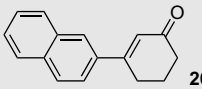
ortho-Substituents on the aryl bromides generally have a more important effect on the reaction rates of Heck reactions due to their steric or coordination properties. With cyclopent-2-en-1-one, in some cases, similar yields than in the presence of the *para*-substituted aryl bromides were obtained. We observed that the coupling of 2-trifluoromethylbromobenzene or 1-bromonaphthalene proceeds nicely to give **10** and **13** in 64 and 77% yields, respectively (Table 3, entries 1 and 4). On the other hand, 2-bromobenzonitrile and methyl 2-bromobenzoate gave **11** and **12** in lower yields of 48 and 46%, respectively, due to the formation of unidentified side-products (Table 3, entries 2 and 3). Next, we tried to evaluate the difference of reactivity between mono- and di-*ortho*-substituted aryl bromides, and we observed that even the highly hindered aryl bromide, 9-bromoanthracene, could be employed successfully (Table 3, entry 5).

Table 3
Palladium catalyzed reaction of cyclopent-2-en-1-one with *ortho*-substituted aryl bromides and heteroaryl bromides (Scheme 3)

Entry	Aryl bromide	Product	Yield (%)
1		 **10**	64
2		 **11**	48
3		 **12**	46
4		 **13**	77
5		 **14**	57
6		 **15**	68
7		 **16**	60
8		 **17**	51

Conditions: $Pd(OAc)_2$ (0.02 equiv), ArBr (1 equiv), cyclopent-2-en-1-one (2 equiv), KF (2 equiv), DMF, 130 °C, 20 h, isolated yields.

Table 4
Palladium catalyzed reaction of cyclohex-2-en-1-one with *para*- or *meta*-substituted aryl bromides (Scheme 4)

Entry	Aryl bromide	Product	Yield (%)
1		 **18**	55
2		 **19**	57
3		 **20**	50
4		 **21**	53
5		 **22**	48
6		 **23**	64
7		 **24**	51
8		 **25**	46
9		 **26**	55

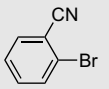
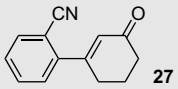
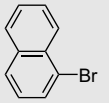
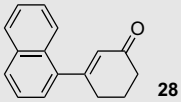
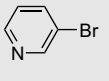
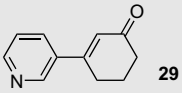
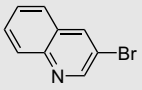
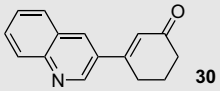
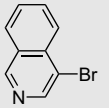
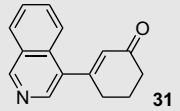
Conditions: $Pd(OAc)_2$ (0.02 equiv), ArBr (1 equiv), cyclohex-2-en-1-one (2 equiv), KF (2 equiv), DMF, 130 °C, 20 h, isolated yields.

Then, we examined the reactivity of cyclohex-2-en-1-one with a set of aryl bromides using the same reaction conditions (Scheme 4, Tables 4 and 5). The expected 3-arylcyclohex-2-en-1-ones **18**–**31** were obtained in moderate to good yields. In the presence of *para*-substituted aryl bromides, compounds **18**–**23** have been isolated in 48–64% yields (Table 4, entries 1–6). The highest yield was obtained using 4-bromobenzonitrile (Table 4, entry 6).

In all cases, the formation of the hydrogenated compounds and also of several other minor side-products was observed. 3-Bromobenzonitrile led to **24** in 51% yield (Table 4, entry 7). Non-activated aryl bromides, 4-bromo-1,2-(methylenedioxy)benzene and 2-bromonaphthalene also gave the target products **25** and **26** in moderate yields (Table 4, entries 8 and 9). The two *ortho*-substituted aryl bromides 2-bromobenzonitrile and 1-bromonaphthalene were found to give **27** and **28** in 39 and 51% yields, respectively (Table 5, entries 1 and 2). Finally, three heteroaryl bromides have been employed. 3-Bromopyridine, 3-bromoquinoline or 4-bromoisoquinoline gave **29**–**31** in 56–60% yields (Table 5, entries 3–5).

In summary, we have established that, using appropriate reaction conditions, $Pd(OAc)_2$ provides an efficient catalyst for the coupling of aryl bromides with cyclopent-2-en-1-one or cyclohex-2-en-1-one. The nature of the base has a determining influence on the reaction yields and selectivities. In the presence of KF as base,

Table 5
Palladium catalyzed reaction of cyclohex-2-en-1-one with *ortho*-substituted aryl bromides and heteroaryl bromides (Scheme 4)

Entry	Aryl bromide	Product	Yield (%)
1		 **27**	39
2		 **28**	51
3		 **29**	56
4		 **30**	59
5		 **31**	60

Conditions: $Pd(OAc)_2$ (0.02 equiv), ArBr (1 equiv), cyclohex-2-en-1-one (2 equiv), KF (2 equiv), DMF, 130 °C, 20 h, isolated yields.

the 3-arylcycloalk-2-en-1-ones were generally obtained in moderate to high yields. A wide range of functions such as fluoro, acetyl, formyl, benzoyl, carboxylate or nitrile on the aryl bromide are tolerated. Sterically hindered aryl bromides and some heteroaromatic substrates such as bromopyridines have also been employed successfully. It should be noted that, despite their interest, most of the products prepared by this method are new, indicating a relatively limited access to such compounds using more traditional cross-coupling procedures. A very wide variety of aryl bromides, cyclopent-2-en-1-one or cyclohex-2-en-1-one and also the catalyst are commercially available. This is a practical advantage of this reaction.

3. Experimental

3.1. General remarks

All reactions were run under argon in Schlenk tubes using vacuum lines. DMF analytical grade was not distilled before use. KF (99%) was used. Commercial aryl bromides were used without purification. The reactions were followed by GC and NMR. ^1H and ^{13}C spectra were recorded with a Bruker 200 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in parts per million relative to $CDCl_3$ (7.25 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

3.2. General procedure

In a typical experiment, the aryl halide (1 mmol), cyclopent-2-en-1-one (0.164 g, 2 mmol) or cyclohex-2-en-1-one (0.192 g, 2 mmol), KF (0.116 g, 2 mmol), $Pd(OAc)_2$ (0.005 g, 0.02 mmol), were dissolved in DMF (5 mL) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 18 h. Then, the product was extracted three times with Et_2O or CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography.

3.3. 3-(4-Acetylphenyl)-cyclopent-2-enone (1a)

From 4-bromoacetophenone (0.199 g, 1 mmol) and cyclopent-2-en-1-one, product **1** was obtained in 62% (0.124 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 8.02 (d, J=8.4 Hz, 2H), 7.73 (d, J=8.4 Hz, 2H), 6.64 (s, 1H), 3.07 (m, 2H), 2.63 (s, 3H), 2.58 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.9, 197.2, 172.1, 138.6, 138.1, 129.4, 128.8, 126.9, 35.3, 28.6, 26.7; $C_{13}H_{12}O_2$: calcd C 77.98, H 6.04; found C 77.90, H 6.15. Product **1b** was also isolated in low yield: ^1H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, J=8.4 Hz, 2H), 7.34 (d, J=8.4 Hz, 2H), 3.50 (m, 1H), 2.80–1.97 (m, 9H).

3.4. 3-(4-Propionylphenyl)-cyclopent-2-enone (2)

From 4-bromopropiophenone (0.213 g, 1 mmol) and cyclopent-2-en-1-one, product **2** was obtained in 69% (0.148 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 8.01 (d, J=8.4 Hz, 2H), 7.71 (d, J=8.4 Hz, 2H), 6.62 (s, 1H), 3.05 (m, 2H), 2.99 (q, J=7.5 Hz, 2H), 2.60 (m, 2H), 1.22 (t, J=7.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.8, 199.8, 172.1, 138.4, 137.9, 129.1, 128.4, 126.9, 35.2, 32.0, 28.6, 8.04; $C_{14}H_{14}O_2$: calcd C 78.48, H 6.59; found C 78.61, H 6.39.

3.5. 3-(4-Benzoylphenyl)-cyclopent-2-enone (3)

From 4-bromobenzophenone (0.261 g, 1 mmol) and cyclopent-2-en-1-one, product **3** was obtained in 71% (0.186 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 7.95–7.60 (m, 9H), 6.67 (s, 1H), 3.09 (m, 2H), 2.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.9, 195.8, 172.3, 139.5, 137.5, 137.0, 132.8, 130.4, 130.0, 129.2, 128.4, 126.6, 35.3, 28.7; $C_{18}H_{14}O_2$: calcd C 82.42, H 5.38; found C 82.47, H 5.20.

3.6. 4-(3-Oxocyclopent-1-enyl)-benzoic acid methyl ester (4)

From methyl 4-bromobenzoate (0.215 g, 1 mmol) and cyclopent-2-en-1-one, product **4** was obtained in 61% (0.132 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 8.09 (d, J=8.3 Hz, 2H), 7.70 (d, J=8.3 Hz, 2H), 6.63 (s, 1H), 3.94 (s, 3H), 3.06 (m, 2H), 2.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.9, 172.3, 166.2, 138.0, 132.1, 130.0, 129.2, 126.7, 52.3, 35.3, 28.7; $C_{13}H_{12}O_3$: calcd C 72.21, H 5.59; found C 72.30, H 5.48.

3.7. 4-(3-Oxocyclopent-1-enyl)-benzonitrile (5)

From 4-bromobenzonitrile (0.182 g, 1 mmol) and cyclopent-2-en-1-one, product **5** was obtained in 73% (0.134 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (m, 4H), 6.65 (s, 1H), 3.05 (m, 2H), 2.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.5, 170.9, 138.1, 132.6, 130.1, 127.2, 118.1, 114.3, 35.3, 28.5; $C_{12}H_9NO$: calcd C 78.67, H 4.95; found C 78.51, H 5.07.

3.8. 3-(4-Trifluoromethylphenyl)-cyclopent-2-enone (6)

From 4-bromobenzotrifluoride (0.225 g, 1 mmol) and cyclopent-2-en-1-one, product **6** was obtained in 67% (0.152 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 7.90 (m, 4H), 6.65 (s, 1H), 3.05 (m, 2H), 2.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.8, 171.8, 132.7 (q, J=31.7 Hz), 129.3, 127.3, 126.0, 125.8 (q, J=3.7 Hz), 124.6 (q, J=271.6 Hz), 35.3, 28.7; $C_{12}H_9F_3O$: calcd C 63.72, H 4.01; found C 63.59, H 4.19.

3.9. 3-(4-Fluorophenyl)-cyclopent-2-enone (7)

From 4-bromofluorobenzene (0.175 g, 1 mmol) and cyclopent-2-en-1-one, product **7** was obtained in 68% (0.120 g) yield.

^1H NMR (200 MHz, $CDCl_3$) δ 7.70 (dd, J=5.3 and 8.7 Hz, 2H), 7.70 (t, J=8.7 Hz, 2H), 3.06 (m, 2H), 2.62 (m, 2H).

3.10. 3-(3-Oxocyclopent-1-enyl)-benzonitrile (8)

From 3-bromobenzonitrile (0.182 g, 1 mmol) and cyclopent-2-en-1-one, product **8** was obtained in 58% (0.106 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.88 (d, J=8.5 Hz, 1H), 7.75 (d, J=8.5 Hz, 1H), 7.59 (t, J=8.5 Hz, 1H), 3.04 (m, 2H), 2.62 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.5, 170.6, 135.3, 134.0, 130.8, 130.0, 129.8, 129.3, 118.0, 113.4, 35.2, 28.5; $C_{12}H_9NO$: calcd C 78.67, H 4.95; found C 78.39, H 4.87.

3.11. 3-(Naphthalen-2-yl)cyclopent-2-enone (9)

From 2-bromonaphthalene (0.207 g, 1 mmol) and cyclopent-2-en-1-one, product **9** was obtained in 70% (0.146 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.00–7.88 (m, 3H), 7.70 (d, J=8.0 Hz, 1H), 7.26 (m, 2H), 6.65 (s, 1H), 3.10 (m, 2H), 2.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.2, 173.4, 134.4, 132.8, 131.2, 128.8, 128.5, 127.7 (2C), 127.6, 126.8 126.7, 123.8, 35.1, 28.4; $C_{15}H_{12}O$: calcd C 86.51, H 5.81; found C 86.59, H 5.69.

3.12. 3-(2-Trifluoromethylphenyl)-cyclopent-2-enone (10)

From 2-bromobenzotrifluoride (0.225 g, 1 mmol) and cyclopent-2-en-1-one, product **10** was obtained in 64% (0.145 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, J=8.0 Hz, 1H), 7.64–7.46 (m, 2H), 7.32 (d, J=8.0 Hz, 1H), 6.24 (s, 1H), 2.97 (m, 2H), 2.61 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.8, 174.4, 133.7, 131.7, 128.8, 128.2, 127.5 (q, J=30.5 Hz), 126.4 (q, J=5.2 Hz), 124.2 (q, J=273.5 Hz), 35.5, 33.5; $C_{12}H_9F_3O$: calcd C 63.72, H 4.01; found C 63.80, H 3.98.

3.13. 2-(3-Oxocyclopent-1-enyl)-benzonitrile (11)

From 2-bromobenzonitrile (0.182 g, 1 mmol) and cyclopent-2-en-1-one, product **11** was obtained in 48% (0.088 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80 (d, J=8.4 Hz, 1H), 7.85–7.30 (m, 3H), 6.83 (s, 1H), 3.16 (m, 2H), 2.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.4, 170.0, 137.9, 134.6, 133.2, 133.1, 130.2, 128.0, 118.0, 110.4, 35.2, 30.4; $C_{12}H_9NO$: calcd C 78.67, H 4.95; found C 78.79, H 4.96.

3.14. Methyl 2-(3-oxocyclopent-1-enyl)-benzoate (12)

From methyl 2-bromobenzoate (0.215 g, 1 mmol) and cyclopent-2-en-1-one, product **12** was obtained in 46% (0.099 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96 (d, J=8.2 Hz, 1H), 7.57 (t, J=7.6 Hz, 1H), 7.46 (t, J=7.6 Hz, 1H), 7.28 (d, J=8.2 Hz, 1H), 6.11 (s, 1H), 3.85 (s, 3H), 2.94 (m, 2H), 2.59 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.3, 178.4, 167.1, 138.2, 132.1, 131.0, 130.4, 129.0, 128.6, 127.9, 52.4, 35.8, 32.6; $C_{13}H_{12}O_3$: calcd C 72.21, H 5.59; found C 72.36, H 5.38.

3.15. 3-(Naphthalen-1-yl)-cyclopent-2-enone (13)

From 1-bromonaphthalene (0.207 g, 1 mmol) and cyclopent-2-en-1-one, product **13** was obtained in 77% (0.160 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.08 (m, 1H), 7.98–7.88 (m, 2H), 7.60–7.40 (m, 4H), 6.50 (s, 1H), 3.12 (m, 2H), 2.66 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.1, 174.9, 134.0, 133.7, 133.4, 130.0, 129.9, 128.6, 126.8, 126.2, 124.9, 124.6, 124.4, 35.1, 32.6; $C_{15}H_{12}O$: calcd C 86.51, H 5.81; found C 86.40, H 5.94.

3.16. 3-(Anthracen-9-yl)-cyclopent-2-enone (14)

From 9-bromoanthracene (0.257 g, 1 mmol) and cyclopent-2-en-1-one, product **14** was obtained in 57% (0.147 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.10–7.95 (m, 2H), 7.95–7.85 (m, 2H), 7.60–7.40 (m, 4H), 6.49 (s, 1H), 3.13 (m, 2H), 2.83 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.4, 177.2, 136.0, 131.2, 131.0, 128.7, 127.6, 127.3, 126.3, 125.4, 124.8, 35.7, 34.5; $C_{19}H_{14}O$: calcd C 88.34, H 5.46; found C 88.49, H 5.31.

3.17. 3-(Pyridin-3-yl)-cyclopent-2-enone (15)

From 3-bromopyridine (0.158 g, 1 mmol) and cyclopent-2-en-1-one, product **15** was obtained in 68% (0.108 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.68 (d, J=4.2 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.40 (dd, J=8.1 and 4.2 Hz, 1H), 6.63 (s, 1H), 3.07 (m, 2H), 2.62 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.6, 170.4, 151.8, 147.8, 133.8, 129.7, 128.7, 123.7, 35.0, 28.4; $C_{10}H_9NO$: calcd C 75.45, H 5.70; found C 75.50, H 5.56.

3.18. 3-(Quinolin-3-yl)-cyclopent-2-enone (16)

From 3-bromoquinoline (0.208 g, 1 mmol) and cyclopent-2-en-1-one, product **16** was obtained in 60% (0.126 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.32 (s, 1H), 8.14 (d, J=8.2 Hz, 1H), 7.89 (d, J=8.2 Hz, 1H), 7.80 (t, J=7.5 Hz, 1H), 7.60 (t, J=7.5 Hz, 1H), 6.76 (s, 1H), 3.16 (m, 2H), 2.62 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.6, 170.2, 149.4, 148.5, 133.6, 131.1, 129.4, 128.6, 128.5, 127.6, 127.3, 126.9, 34.9, 28.4; $C_{14}H_{11}NO$: calcd C 80.36, H 5.30; found C 80.52, H 5.27.

3.19. 3-(Isoquinolin-4-yl)-cyclopent-2-enone (17)

From 4-bromoisoquinoline (0.208 g, 1 mmol) and cyclopent-2-en-1-one, product **17** was obtained in 51% (0.107 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.60 (s, 1H), 8.05–7.90 (m, 2H), 7.80–7.55 (m, 2H), 6.58 (s, 1H), 3.19 (m, 2H), 2.68 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.6, 171.5, 154.2, 153.0, 144.0, 140.8, 134.5, 131.5, 130.8, 128.4, 127.7, 123.6, 35.1, 32.3; $C_{14}H_{11}NO$: calcd C 80.36, H 5.30; found C 80.21, H 5.24.

3.20. 3-(4-Acetylphenyl)-cyclohex-2-enone (18)

From 4-bromoacetophenone (0.199 g, 1 mmol) and cyclohex-2-en-1-one, product **18** was obtained in 55% (0.118 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.99 (d, J=8.4 Hz, 2H), 7.61 (d, J=8.4 Hz, 2H), 6.44 (s, 1H), 2.81 (t, J=7.6 Hz, 2H), 2.62 (s, 3H), 2.53 (t, J=7.6 Hz, 2H), 2.24 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.5, 197.3, 158.2, 143.2, 137.7, 128.7, 126.8, 126.2, 37.2, 28.0, 26.7, 22.7; $C_{14}H_{14}O_2$: calcd C 78.48, H 6.59; found C 78.60, H 6.68.

3.21. 3-(4-Propionylphenyl)-cyclohex-2-enone (19)

From 4-bromopropiophenone (0.213 g, 1 mmol) and cyclohex-2-en-1-one, product **19** was obtained in 57% (0.130 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 6.43 (s, 1H), 3.02 (q, J=7.6 Hz, 2H), 2.77 (t, J=7.6 Hz, 2H), 2.49 (t, J=7.6 Hz, 2H), 2.19 (m, 2H), 1.22 (t, J=7.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.0, 199.6, 158.3, 142.9, 137.5, 128.3, 126.6, 126.2, 37.1, 31.9, 28.0, 22.7, 8.1; $C_{15}H_{16}O_2$: calcd C 78.92, H 7.06; found C 78.71, H 7.14.

3.22. 4-(3-Oxocyclohex-1-enyl)-benzaldehyde (20)

From 4-bromobenzaldehyde (0.185 g, 1 mmol) and cyclohex-2-en-1-one, product **20** was obtained in 50% (0.100 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.92 (d, J=8.4 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 6.45 (s, 1H), 2.82 (t, J=7.6 Hz, 2H), 2.51 (t, J=7.6 Hz, 2H), 2.18 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.5, 191.5,

158.1, 144.6, 136.9, 129.9, 127.2, 126.6, 37.1, 28.1, 22.7; $C_{13}H_{12}O_2$: calcd C 77.98, H 6.04; found C 77.79, H 6.00.

3.23. 3-(4-Benzoylphenyl)-cyclohex-2-enone (21)

From 4-bromobenzophenone (0.261 g, 1 mmol) and cyclohex-2-en-1-one, product **21** was obtained in 53% (0.146 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00–7.30 (m, 9H), 6.47 (s, 1H), 2.83 (t, J=7.6 Hz, 2H), 2.51 (t, J=7.6 Hz, 2H), 2.18 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.5, 195.8, 158.4, 142.5, 138.4, 137.1, 132.6, 130.3, 129.9, 128.3, 126.7, 125.9, 37.2, 28.0, 22.7; $C_{19}H_{16}O_2$: calcd C 82.58, H 5.84; found C 82.47, H 6.02.

3.24. 4-(3-Oxocyclohex-1-enyl)-benzoic acid methyl ester (22)

From methyl 4-bromobenzoate (0.215 g, 1 mmol) and cyclohex-2-en-1-one, product **22** was obtained in 48% (0.111 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.09 (d, J=8.2 Hz, 2H), 7.58 (d, J=8.2 Hz, 2H), 6.44 (s, 1H), 3.93 (s, 3H), 2.78 (t, J=7.6 Hz, 2H), 2.50 (t, J=7.6 Hz, 2H), 2.20 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.6, 166.4, 158.4, 143.1, 130.2, 129.9, 126.7, 126.0, 52.3, 37.2, 28.0, 22.7; $C_{14}H_{14}O_3$: calcd C 73.03, H 6.13; found C 73.14, H 6.00.

3.25. 4-(3-Oxocyclohex-1-enyl)-benzonitrile (23)

From 4-bromobenzonitrile (0.182 g, 1 mmol) and cyclohex-2-en-1-one, product **23** was obtained in 64% (0.126 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71 (d, J=8.2 Hz, 2H), 7.60 (d, J=8.2 Hz, 2H), 6.41 (s, 1H), 2.78 (t, J=7.6 Hz, 2H), 2.51 (t, J=7.6 Hz, 2H), 2.20 (m, 2H).

3.26. 3-(3-Oxocyclohex-1-enyl)-benzonitrile (24)

From 3-bromobenzonitrile (0.182 g, 1 mmol) and cyclohex-2-en-1-one, product **24** was obtained in 51% (0.101 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.95–7.40 (m, 4H), 6.34 (s, 1H), 2.74 (t, J=7.6 Hz, 2H), 2.50 (t, J=7.6 Hz, 2H), 2.17 (m, 2H).

3.27. 3-(Benzo[1,3]dioxol-5-yl)-cyclohex-2-enone (25)

From 4-bromo-1,2-(methylenedioxy)benzene (0.201 g, 1 mmol) and cyclohex-2-en-1-one, product **25** was obtained in 46% (0.100 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.10 (d, J=8.0 Hz, 1H), 6.83 (d, J=8.0 Hz, 1H), 6.34 (s, 1H), 6.01 (s, 1H), 2.71 (t, J=7.6 Hz, 2H), 2.48 (t, J=7.6 Hz, 2H), 2.14 (m, 2H).

3.28. 3-(Naphthalen-2-yl)-cyclohex-2-enone (26)

From 2-bromonaphthalene (0.207 g, 1 mmol) and cyclohex-2-en-1-one, product **26** was obtained in 55% (0.122 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.95–7.85 (m, 3H), 7.60 (d, J=8.0 Hz, 1H), 7.60–7.40 (m, 2H), 6.57 (s, 1H), 2.90 (t, J=7.6 Hz, 2H), 2.53 (t, J=7.6 Hz, 2H), 2.20 (m, 2H).

3.29. 2-(3-Oxocyclohex-1-enyl)-benzonitrile (27)

From 2-bromobenzonitrile (0.182 g, 1 mmol) and cyclohex-2-en-1-one, product **27** was obtained in 39% (0.077 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (d, J=8.2 Hz, 1H), 7.64 (t, J=7.6 Hz, 1H), 7.51 (t, J=7.6 Hz, 1H), 7.38 (d, J=8.2 Hz, 1H), 6.20 (s, 1H), 2.82 (t, J=7.6 Hz, 2H), 2.54 (t, J=7.6 Hz, 2H), 2.21 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.8, 158.5, 144.3, 133.7, 133.0, 129.8, 129.0, 127.9, 117.7, 110.0, 37.2, 30.1, 23.1; $C_{13}H_{11}NO$: calcd C 79.16, H 5.62; found C 79.07, H 5.45.

3.30. 3-(Naphthalen-1-yl)-cyclohex-2-enone (28)

From 1-bromonaphthalene (0.207 g, 1 mmol) and cyclohex-2-en-1-one, product **28** was obtained in 51% (0.113 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00–7.90 (m, 3H), 7.60–7.40 (m, 3H), 7.32 (d, J=8.0 Hz, 1H), 6.21 (s, 1H), 2.77 (t, J=7.6 Hz, 2H), 2.60 (t, J=7.6 Hz, 2H), 2.26 (m, 2H).

3.31. 3-(Pyridin-3-yl)-cyclohex-2-enone (29)

From 3-bromopyridine (0.158 g, 1 mmol) and cyclohex-2-en-1-one, product **29** was obtained in 56% (0.098 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.64 (d, J=4.0 Hz, 1H), 7.79 (d, J=7.7 Hz, 1H), 7.35 (dd, J=7.7 and 4.0 Hz, 1H), 6.42 (s, 1H), 2.80 (t, J=7.6 Hz, 2H), 2.54 (t, J=7.6 Hz, 2H), 2.25 (m, 2H).

3.32. 3-(Quinolin-3-yl)-cyclohex-2-enone (30)

From 3-bromoquinoline (0.208 g, 1 mmol) and cyclohex-2-en-1-one, product **30** was obtained in 59% (0.132 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.24 (s, 1H), 8.09 (d, J=8.3 Hz, 1H), 7.84 (d, J=8.3 Hz, 1H), 7.71 (t, J=7.7 Hz, 1H), 7.57 (t, J=7.7 Hz, 1H), 6.58 (s, 1H), 2.87 (t, J=7.6 Hz, 2H), 2.54 (t, J=7.6 Hz, 2H), 2.23 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.1, 156.3, 148.3, 147.8, 133.3, 131.2, 130.5, 129.2, 128.3, 127.4, 127.2, 126.4, 37.1, 27.7, 22.6; $C_{15}H_{13}NO$: calcd C 80.69, H 5.87; found C 80.47, H 5.79.

3.33. 3-(Isoquinolin-4-yl)-cyclohex-2-enone (31)

From 4-bromoisoquinoline (0.208 g, 1 mmol) and cyclohex-2-en-1-one, product **31** was obtained in 60% (0.134 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.24 (s, 1H), 8.00 (d, J=8.3 Hz, 1H), 7.85 (d, J=8.3 Hz, 1H), 7.67 (t, J=7.7 Hz, 1H), 7.59 (t, J=7.7 Hz, 1H), 6.21 (s, 1H), 2.79 (t, J=7.6 Hz, 2H), 2.59 (t, J=7.6 Hz, 2H), 2.25 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.9, 158.5, 153.1, 143.8, 140.3, 132.4, 132.0, 131.0, 130.5, 128.2, 127.5, 123.7, 37.3, 31.5, 23.1; $C_{15}H_{13}NO$: calcd C 80.69, H 5.87; found C 80.42, H 5.98.

Registry No.: **7**, 111945-91-6; **23**, 123732-13-8; **24**, 130339-70-7; **25**, 77545-60-9; **26**, 42160-93-0; **28**, 42160-94-1; **29**, 63843-14-1.

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