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A Transition-Metal Mediated Regioselective Synthesis of Phenyl Quinones via Sequential Benzannulation and Cross Coupling Reactions

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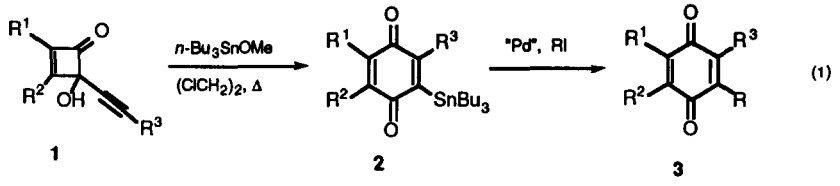
Abstract: A synthetic route for the regioselective synthesis of polysubstituted quinones by the benzannulation and subsequent cross coupling reactions has been developed. Alkenyl chromium carbene complexes undergo regioselective benzannulation with 2-(trimethylsilyl)-1-phenylethyne with oxidative workup to yield silyl quinones which upon iodination with ICl produce iodoquinones. Subsequent Stille's and Suzuki's cross coupling reactions of these iodoquinones yield polysubstituted quinones.

Introduction

The search for new synthetic approaches for the quinone functionality is a continuously growing area of investigation.[1] In fact, many polysubstituted quinones are incorporated in the structures of a variety of biologically natural products and some naturally occurring quinones[2] are widely found in both plants and animals. However, the conventional synthetic approach to these highly substituted compounds involves the elaboration of the quinone precursors *via* electrophilic substitution and metalation-alkylation reaction which may subject to regiochemical problems. Therefore the regiocontrolled synthesis of highly substituted aromatic skeletons present a great synthetic challenge which is best met by the application of regioselective annulation strategies.



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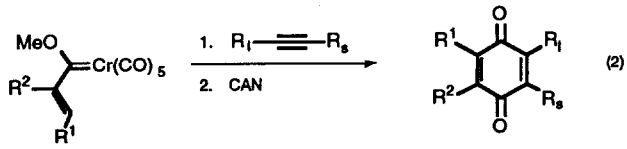
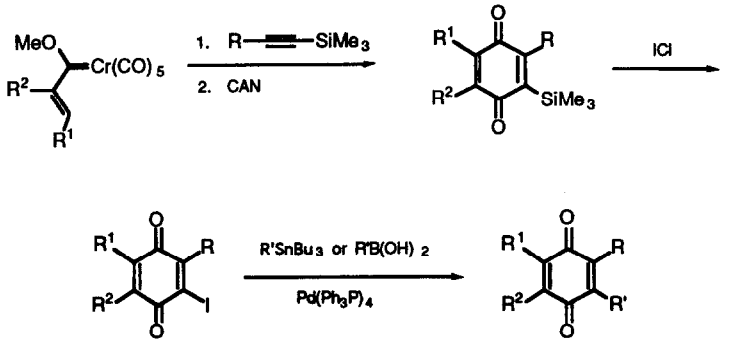
The regioselective construction of quinones *via* the cyclobutenones-vinyl ketenes annulation stratergy has been investigated mainly by Danheiser[3], Moore[4] and Liebeskind[5]. Liebeskind further takes advantage of thermolysis of 4-alkyl-4-hydroxy-cyclobutenones in the presence of n-Bu_3SnOMe to produce stannylquinones which undergo Stille's cross coupling reactions to yield polysubstituted quinones (eq 1). Dötz[6], Semmelheck[7] and Wulff[8] have employed the benzannulation of Fischer chromium carbene complexes with alkynes to synthesize quinones and the benzannulation, indeed, is a facile and regioselective entry to polysubstituted 1,4-quinones (eq 2).[9] However, limitation exists. The substitutents of alkynes have to be symmetrical or substantially different in size otherwise regio-isomeric mixtures are obtained.[9]



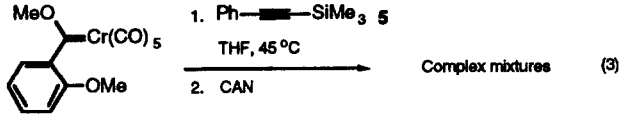
(2)

Furthermore, highly functionalized and sterically bulky alkynes have met with limited success.[10,11] We envisoned that if silylated phenols could be obtained in good yields from silylated alkynes *via* the benzannulation, they could serve as precursors for haloquinones. Employing the palladium-catalyzed cross-coupling reactions developed by Stille[12] and Suzuki,[13] these haloquinones, utilized as the electrophilic coupling partners, could be converted into polysubstituted quinones. In this paper, we report our success in this benzannulation-cross coupling reaction sequence for the regioselective synthesis of polysubstituted quinones (Scheme 1).

Scheme 1



Results and Discussion

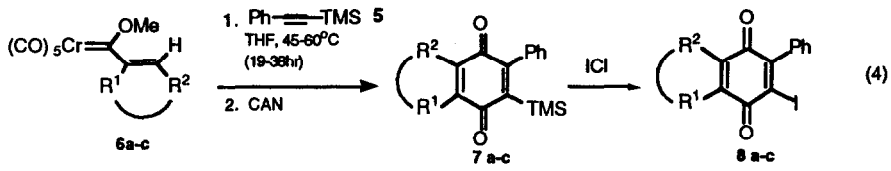


(3)

4

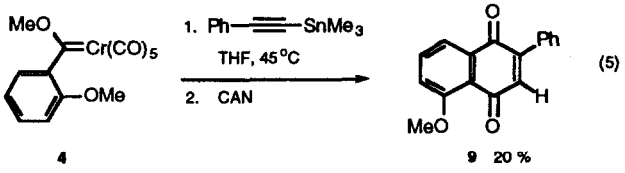
Our initial attempt to react the aryl carbene complex, (2-methoxyl)phenyl-methoxyl-pentacarbonyl chromium carbene complex **4** with 2-(trimethylsilyl)-1-phenylethyne **5** gave complex mixtures upon oxidative workup with ceric ammonium nitrate [CAN][eq 3]. Indeed, Dötz has reported silyl alkynes reacted with aryl carbene complexes to give a mixture of silyl ketenes and annulated products.[14] However, the more reactive alkenyl complex, dihydropyranyl carbene complex **6a**, did react smoothly with silyl alkyne 5 to give the silylated quinone **7a** in 66 % yield after oxidative workup with CAN. The benzannulation also proceeded smoothly for the alkyl substituted alkenyl complexes **6b** and **6c** to produce the quinones **7b** and **7c** (Table 1). The choice of HNO_3 in making up the CAN solution is important. If HCl was used instead, lower yield of **7a** was obtained presumably due to proto-desilyation.

Table 1 Synthesis of silyl quinones and iodoquinones



(4)

Complex	R^1	R^2	% yield of 7a-c	% yield of 8a-c
6a	$-O(CH_2)_3-$		66	70
6b	H	Me	70	80
6c	H	Ph	60	60



(5)

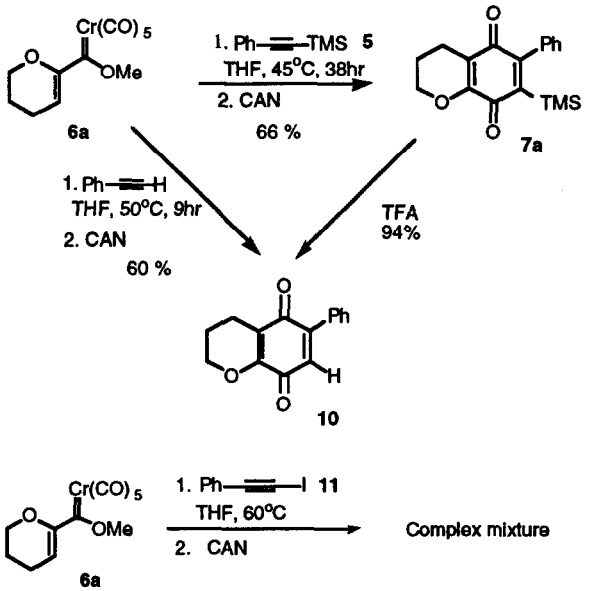
We have also studied the reaction of the aryl carbene complex **4** with the 1-phenyl-2-(trimethylstannyl)ethyne (eq 5). However, low yield of destannylated quinone **9** was isolated in 20 % yield and the reaction with stannyl alkyne was not pursued.

The structures of the silyl quinones were established spectroscopically. In the ^1H NMR spectra, silyl-quinones **7a-c** exhibit the characteristic resonances of Me_3Si protons at δ -0.11, -0.12, -0.07 ppm respectively. Furthermore, the appearance of δ 6.64 and 6.90 ppm in silyl-quinones **7b** and **7c** respectively confirm the presence of quinonic protons in the benzannulation products. The enone functionalities were supported by the wavenumber in the range of 1659-1632 cm^{-1} in the IR spectra of these silyl quinones.

The regiochemistry of this reaction was elucidated by comparing the spectroscopic properties of the desilyated quinones **10** with those of authentic sample. Upon *ipso*-desilylation with trifluoroacetic acid (TFA) in refluxing dichloromethane (Scheme 2), the silyl-quinone **7a** was converted into the quinone **10** which was also independently prepared from the benzannulation reaction of phenylacetylene with carbene complex **6a**. Since the products from both routes are identical in their ^1H and ^{13}C NMR (both broad-band and gated-decoupled) spectra and the regiochemistry of the reaction of carbene complex 6a with terminal alkyne has been well established,[9] the structure of the silyl-quinone 7a and so as the others, **7b** and **7c**, are established as shown in Table 1.

The cross-coupling partners, iodoquinones 8a-c were successfully prepared *via ipso*-iodination of the silyl-quinones **7a-c** by ICl[15] (Table 1). The structures of these iodoquinones were confirmed by the disappearance of the trimethylsilyl group as indicated in the ^1H NMR spectra. Furthermore, the chemical shifts of the olefinic proton resonance in the iodoquinones **8b** and **8c**, respectively are down-field shifted; 6.64 to 6.78, 6.90 to 7.08 ppm, consistent with the replacement of the Me_3Si groups by the more electron-withdrawing iodide atoms.

Scheme 2

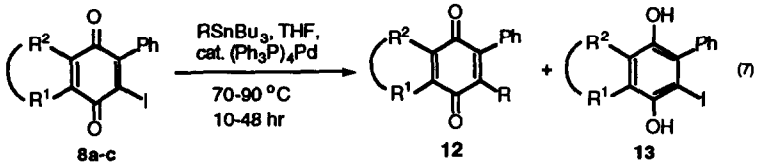


It is worthwhile mentioning that iodoquinones **8a** could not be synthesized directly from the benzannulation of alkenyl carbene complexes with 1-iodo-2-phenylethyne **11** as a complex reaction mixture formed (eq 6). Hence such tandem annulation and *ipso*-iodination reaction is an unique entry to these iodoquinones.

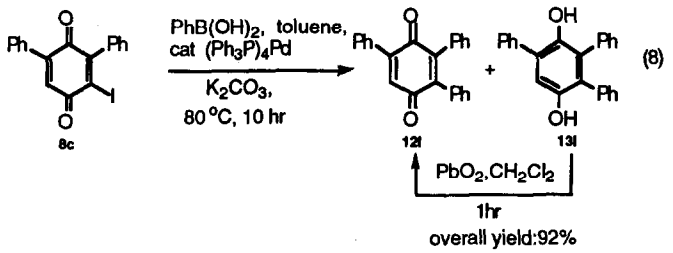
Iodoquinones 8a-c were cross-coupled with alkynyl, alkenyl, aryl and allyl tributylstannanes in order to achieve the highly-substituted quinones (Table 2). For the more electron rich iodoquinone 8a, the coupling reactions proceeded smoothly giving the desired products (**12a-e**, entry 1-5). On the other hand, for the less electron rich iodoquinone **8b** and **8c**, a noticeable amount ring-reduced *p*-hydroxy-iodophenols **13h** or **13i** were obtaind together with the coupled products (entry 8-11). The amount of reduced phenols increased with more electron deficient quinones (**8c** > **8b** > **8a**) when reacted with the same organostannane (entry 2, 6, and 9). The ratio or yield of the reduction products did not depend on the amount of organotin reagent used and even in the presence of copper(I) iodide.[16] Fortunately, all the iodoquinones **8b** and **8c** could be recovered from the phenols **13h** or **13i** simply by oxidation with PbO_2 in dichloromethane at room temperature for an hour. In contrast, even the electron poor iodoquinone 8c underwent facile coupling reaction with phenyltributyltin without any *ring reduction (entry 12). We are, however, unclear about the mechanism for the formation of the* ring-reduced phenols and might likely due to the reaction of Bu_3SnCl with Pd(O).[16c]

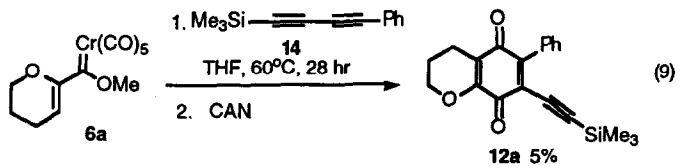
Apart from Stille's cross-coupling reaction, Suzuki coupling reaction[13] were also successfully applied in these quinones. The electron poor iodoquinone **8c** underwent coupling reaction with phenylboronic acid to produce the coupling products without any reduction of the iodoquinone **8c** although reduction of the coupled quinone **12l** was observed. However, phenol **13l** was oxidized easily by PbO_2 to quinone **12l** (eq 8). The successful Suzuki cross coupling reaction with iodoquinone with phenylboronic acid is direct contrast with the unsuccessful attempt of bromonapthoquinone with phenylboronic acid which decomposed in the reaction.[16a]

Table 2 Cross coupling reaction of iodoquinones with organostannanes



entry	Iodoquinone:	R	%yield of 12	%yield of 13
1	8a	—≡—TMS	a:65	
2		—≡—Ph	b:92	
3		—≡—Bu	c:50	
4			d:60	
5			e:66	
6	8b	—≡—Ph	f:62	
7		—≡—Bu	g:64	
8			h:32	h:28
9	8c	—≡—Ph	i:30	i:40
10		—≡—Bu	j:19	j:70
11			k:21	k:61
12		Ph	l:86	





Direct benzannulation of carbene complex **6a** with 2-(trimethylsilyl)-1-phenyl-buta-1,3-diyne **14** in order to target the highly-substituted quinone in a one-pot manner led only to a complex mixture with the desired product **12a** isolated in 5% (eq 9). Even the yield of the reaction was low, the structure of **12a** supports that phenyl group rather than trimethylsilylethynyl group dictated the regioselectivity. In fact, the reactions of diyne with carbene complexes have been known to give alknylquinones and cyclobutenones.[17] Therefore this benzannulation-cross coupling reactions constitute an unique route to these highly-substituted quinones.

Conclusion

In conclusion, alkenyl Fischer carbene complexes 6a-c undergo benzannulation with silyl alkyne 5 and subsequent cross coupling reactions to give polysubstituted quinones **12a-l** in mild and neutral conditions regioselectively. This is an unique entry to these highly substituted quinones unavailable from the direct benzannulation.

Experimental Section

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Phenylethynyltributylstannane and vinyltributylstannane were purchased from Aldrich. Allyltributylstannane[18], phenyltrimetylstanne,[19] phenyltributylstannane[19] (trimethylsilylethynyl)tributylstannane[20] 1-Hexynyltributylstannane,[21] 1-phenyl-2-trimethylsilylacetylene **5**,[22] phenylethynyliodide **11**[23] and 4-(trimethylsily)-1-phenyl-1,3-butadiyne **14**[24] were prepared according to the literature. The carbene complex **6a**[10] carbene complex **6b**[25] and carbene complex **6c**[26] were known compounds and were prepared according to the literature methods. THF and diethyl ether were freshly distilled from sodium benzophenone ketyl before use. Hexane was distilled over calcium chloride and toluene was distilled from sodium. For reactions involving carbene complexes the reaction mixtures were deoxygenated by the freeze-thaw-pump method (-196 to 25 °C, three cycles). All column chromatography was carried out under air even for the various carbene complexes by using the 'flash' method as described by Still[27] with silica-gel (230-400 mesh). All reactions were monitored by thin layer chromatography (TLC) performed on Merck precoated silica gel $60F_{254}$ plates, and compounds were visualized under UV light or with a spray of 5% w/v dodecamolybdophosphoric acid. All melting points were incorrected.

Routine proton NMR spectra were recorded on a Jeol 60-MHz or Bruker 250-MHz spectrometer in $CDCl_3$ (residual $CHCl_3$ δ 7.24 ppm) with tetramethylsilane as internal standard. Chemical shifts are reported as part per million (ppm) in δ scale down-field from TMS. Coupling constants (J) are reported in hertz (Hz). ^{13}C NMR spectra were obtained on a Bruker 250 spectrometer at 62.9 MHz. Infrared spectra were recorded on a Nicolet (205) FT-IR spectrophotometer as neat film on KBr. Low and high resolution mass spectra were obtained from the VG 70-70 system. Elemental analysis were carried out by Medac Ltd, UK or Shanghai Institute of Organic Chemistry, China.

Benzannulation of chromium alkenylmethoxy carbene complex with Phenylacetylene or 2-trimethylsilyl-1-phenylethyne (5). The reaction of 2-dihydro-pyranylmethoxymethylene pentacarbonyl chromium **(6a)** with phenylacetylene was described as a typical example. A solution of 6a (70 mg, 0.22 mmol) and phenylacetylene (45 mg, 0.44 mmol) in 5 mL of THF was deoxygenated by the freeze-thaw-pump method for 3 cycles. The mixture was stirred under a N_2 atmosphere at 50 °C for 9 hr. The mixture was opened to air and oxidised by vigorously stirring with 4 mL of 0.5 M of ceric ammonium nitrate (7.5 equiv.) in 0.1 N HNO_3 for 1 hr. The mixture was extracted with ether, washed with H_2O and saturated brine and dried ($MgSO_4$). The crude product was flash-chromatographed on silica gel using hexane/ethyl acetate (4:1) as the solvent mixture (R_f = 0.26), affording the quinone 10 as yellow solids (30 mg, 60 %). mp 51-53 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.98 (m, 2 H), 2.49 (t, 2 H, J = 6.4 Hz), 4.27 (t, 2 H, J = 5.2 Hz), 6.69 (s, 1 H), 7.40 (br. s, 5 H); ^{13}C NMR ($CDCl_3$, gated decoupled, 62.9 MHz) δ 18.07 (t, $^1J_{C-H}$ = 133.0 Hz), 20.56 (t, $^1J_{C-H}$ = 133.0 Hz), 67.39 (t, $^1J_{C-H}$ = 147.2 Hz), 119.14 (m), 128.21 (dd, ^1J = 161.3 Hz, $^2J_{C-H}$ = 6.6 Hz), 129.32 (dt, ^1J = 159.1Hz, $^2J_{C-H}$ = 6.9 Hz), 129.74 ((dd, ^1J = 161.0 Hz, $^2J_{C-H}$ = 7.6 Hz) 130.23 (d, $^1J_{C-H}$ = 166.7 Hz), 133.20 (br s), 146.13 (s), 153.60 (m), 181.69 (s), 185.73 (d, $^2J_{C-H}$ = 12.6 Hz); IR (neat) 1651, 1697 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 240 (M^+, 47), 211 (13), 184 (33), 156 (32), 128 (29), 102 (65), 76 (22), 55 (100). Anal. Calcd for $C_{14}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.98; H, 5.14.

Benzannulation of metal carbene complex 6a with 2-trimethylsilyl-1-phenylethyne (5). A mixture of carbene complex **6a** (0.26 g, 0.82 mmol) and silylalkyne 5 (0.29 g, 1.67 mmol) was stirred at 55°C for 38 hr. After oxidation, the mixture was purified by column chromatography using hexane/ethyl acetate (4:1) as the solvent mixture (R_f = 0.37) to afford the silyl-quinone **7a** (0.17 g, 66 %) as yellow prism-like crystals (methanol/hexane): mp 125-126 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ -0.11 (s, 9 H), 1.96 (m, 2 H), 2.42 (t, 2 H, J = 6.4 Hz), 4.26 (t, 2 H, J = 5.2 Hz), 7.08-7.12 (m, 2 H), 7.33-7.37 (m, 3 H); IR (neat) 1632, 1638, 1651, 1657 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 312 (M^+, 21), 297 (58), 269 (100), 159 (21), 129 (27), 73 (47); calcd for $C_{18}H_{20}O_3Si$ *m/z* 312.1177, measured *m/z* 312.1182. Anal. Calcd for $C_{18}H_{20}O_3Si$: C, 69.23; H, 6.41. Found: C, 69.10; H, 6.45.

Benzannulation of metal carbene complex 6b with 2-trimethylsilyl-1-phenylethyne (5). A mixture of carbene complex **6b** (0.6 g, 2.16 mmol) and silylalkyne 5 (0.76 g, 4.37 mmol) was stirred at 60 °C for 19 hr. After oxidation, the mixture was purified by column chromatography using hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.37) to afford the silyl-quinone **7b** (0.35 g, 60%) as yellown solid: mp 36-38 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ -0.12 (s, 9 H), 2.03 (d, 3 H, J = 1.7 Hz), 6.64 (q, 1 H, J = 1.4 Hz), 7.09-7.13 (m, 2 H), 7.36-7.38 (m, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 0.40, 15.75, 127.75, 128.75, 129.61, 134.87, 135.55, 145.13, 148.25, 155.01, 186.83, 192.04; IR (neat) 1648 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 270 (M^+, 0.4), 256 (100), 228 (12), 181 (18), 159 (14), 129 (9), 73 (23); calcd for $C_{16}H_{18}O_2Si$ *m/z* 270.1071, measured *m/z* 270.1113. Anal. Calcd for $C_{16}H_{18}O_2Si$: C, 71.11; H, 6.66. Found: C, 70.95; H, 6.69.

Benzannulation of metal carbene complex 6c with 2-trimethylsilyl-1-phenylacetylene (5). A mixture of carbene complex **6c** (0.16 g, 0.47 mmol) and silylalkyne **5** (0.16 g, 0.92 mmol) was stirred at 60 °C for 30 hr. After oxidation, the mixture was purified by column chromatography using hexane /ethyl acetate (20:1) as the solvent mixture (R_f = 0.26) to afford the silyl-quinone **7c** (0.21 g, 70%) as orange solids (methanol/hexane): mp 83-86 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ -0.07 (s, 9 H), 6.90 (s, 1 H), 7.18-7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 0.40, 127.77, 128.37, 128.84, 129.25, 129.76, 133.19, 133.87, 135.64, 145.35, 148.07, 155.31, 185.85, 192.15; IR (neat) 1634, 1659 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 332 (M^+, 17), 317 (100), 301 (33), 215 (11), 159 (21), 102 (45), 73 (36); calcd for $C_{21}H_{20}O_2Si$ *m/z* 332.1227, measured *m/z* 332.1283.

Benzannulation of metal carbene complex 6a with 4-(Trimethylsilyl)-1-phenyl-1,3-butadiyne (14). A mixture of carbene complex **6a** (0.20 g, 0.63 mmol) and diyne **14** (0.20 g, 0.96 mmol) was stirred at 60 °C for 28 hr. After oxidation, the mixture was purified by column chromatography using hexane/ethyl acetate (4:1) as the solvent mixture (R_f = 0.33) to afford the quinone **12a** as yellow solids (10 mg, 5 %). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.07 (s, 9 H), 1.98 (m, 2 H), 2.47 (t, 2 H, *J* = 6.4 Hz), 4.27 (t, 2 H, *J* = 5.2 Hz), 7.35-7.45 (br s, 5 H); IR (neat) 1635, 1676 cm^{-1}. The spectroscopic data were consistent with the one derived from the coupling reaction of the iodoquinone **8a** and (trimethylsilylethynyl)-tributylstannane.

***ipso*-Iodination of silyl-quinones.**[15] General procedure. The reaction of silyl-quinone **7a** with ICl was described as a typical example. A solution of **7a** (80 mg, 0.26 mmol) in CCl_4 (10 mL) was stirred in an ice bath while ICl (90 mg, 0.53 mmol) in CCl_4 (10 mL) was added over a period of 10 min. After the mixture was stirred for an additional 5 min, the ice bath was removed. The mixture was then stirred for 2 hr at room temperature and poured into saturated aqueous sodium bisulfite. Normal aqueous workup followed by column chromatography with hexane/ethyl acetate (4:1) as the solvent mixture (R_f = 0.21) gave the iodoquinone **8a** (70 mg, 70 %) as yellow needle-shaped crystals (methanol/hexane): mp 148-149 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.01(m, 2 H), 2.51 (t, 2 H, *J* = 6.3 Hz), 4.32 (t, 2 H, *J* = 5.2 Hz), 7.26-7.50 (m, 5 H); IR (neat) 1589, 1634, 1687 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 366 (M^+, 2), 274 (54), 239 (100), 211 (10), 183 (15), 129 (64); calcd for $C_{15}H_{11}O_3I$ *m/z* 365.9750, measured *m/z* 365.9757. The compound was insufficiently stable to allow for an acceptable elemental analysis as three batches of purified sample still gave unsatisfactory analysis.

***ipso*-Iodination of silyl-quinone 7b.** A mixture of silyl-quinone **7b** (0.35 g, 1.30 mmol) and ICl (0.42 g, 2.59 mmol) was stirred for 3 hr at room temperature and poured into saturated aqueous sodium bisulfite. Normal aqueous workup followed by column chromatography with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.31) gave the iodoquinone **8b** (0.25 g, 60%) as yellow prism-like crystals (methanol/hexane): mp 105-107 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.07 (s, 3 H), 6.78 (s, 1 H), 7.20-7.24 (m, 2 H), 7.37-7.43 (m, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 15.83, 127.88, 129.20, 129.46, 131.34, 132.60, 140.27, 143.78, 146.17, 179.45, 184.49; IR (neat) 1656, 1668 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 324 (M^+, 0.2), 232 (56), 197 (100), 169 (55), 129 (40), 115 (21), 101 (21), 77 (7). calcd for $C_{13}H_9O_2$ (M^+-I) *m/z* 197.0600,

measured *m/z* 197.0650. The compound was insufficiently stable to allow for an acceptable elemental analysis as three batches of purified sample still gave unsatisfactory analysis.

***ipso*-Iodination of silyl-quinone 7c.** A mixture of silyl-quinone **7c** (0.12 g, 0.36 mmol) and ICl (0.12 g, 0.74 mmol) was stirred for 3 hr at room temperature and poured into saturated aqueous sodium bisulfite. Normal aqueous workup followed by column chromatography with hexane/ethyl acetate (6:1) as the solvent mixture (R_f = 0.24) gave the iodoquinone **8c** (0.11 g, 80%) as red solids (methanol/hexane): mp 121-123 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.08 (s, 1 H), 7.29-7.51 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 128.05, 128.51, 129.45, 129.70, 130.35, 131.55, 131.99, 132.54, 140.46, 144.07, 146.34, 179.80, 183.74; IR (neat) 1662 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 386 (M^+, 0.7), 294 (100), 259 (85), 231 (90), 202 (40), 129 (73), 102 (55), 77 (9). Calcd for $C_{18}H_{11}O_2$ (M^+-I) *m/z* 259.0756, measured *m/z* 259.0787. The compound was insufficiently stable to allow for an acceptable elemental analysis as three batches of purified sample still gave unsatisfactory analysis.

Desilylation of quinone 7a. To the yellow solution of quinone **7a** (13 mg, 40 mmol) in 4 mL of CH_2Cl_2 was added TFA (0.06 mL, 0.8 mmol). The mixture was refluxed for 4 hr and saturated sodium bicarbonate solution (10 mL) was added. The mixture was extracted with CH_2Cl_2, washed with brine and dried (anhyd $MgSO_4$). The extracts were concentrated and flash- chromatographed on silica gel using hexane/ethyl acetate (3:1) as the solvent mixture (R_f = 0.28) to afford the yellow solids (15 mg, 94%) identical in spectroscopic data with quinone **10** obtained from the reaction of **6a** with phenylacetylene.

Palladium-catalyzed cross-coupling reactions of iodoquinones and organostannanes: General procedure. Reaction of iodoquinone **8a** and (trimethylsilylethynyl)tributyltin was described as a typical example. To the solution of iodoquinone **8a** (55 mg, 0.16 mmol) and (trimethylsilylethynyl)-tributyltin (0.18 g, 0.47 mmol) in 8 mL of THF was added $Pd(Ph_3P)_4$ (10 mg, 5 mol %). The mixture was degassed by the freeze-thaw-pump method for three cycles and then it was heated to 80 °C in a Teflon stoppered flask and allowed to stir under N_2 for 2 day. The dark mixture was filtered and the filtrate was concentrated and flash-chromatographed on silica gel with hexane/ethyl acetate (3:1) as the solvent mixture (R_f = 0.46) to give the quinone **12a** (30 mg, 65 %) as orange prism-like crystals (methanol/hexane): mp 114-115 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.08 (s, 9 H), 1.97 (m, 2 H), 2.47 (t, 2 H, *J* = 6.3 Hz), 4.27 (t, 2 H, *J* = 5.2 Hz), 7.36-7.43 (br. s, 5 H); IR (neat) 1635, 1676, 2375 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 366 (M^+, 91), 293 (100), 265 (47), 183 (43), 129 (30), 73 (78); calcd for $C_{20}H_{20}O_3Si$ *m/z* 336.1177, measured *m/z* 336.1182. Anal. Calcd for $C_{20}H_{20}O_3Si$: C, 71.43; H, 5.95. Found: C, 71.62; H, 5.88.

Quinone 12b. A mixture of iodoquinone **8a** (20 mg, 0.06 mmol), phenylethynyltributyltin (40 mg, 0.10 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 36 hr. Final purification utilized chromatography with hexane/ethyl acetate (3:1) as the solvent mixture (R_f = 0.23) afforded the red prism-like crystals (17 mg, 92%): mp 214-215 °C (methanol/ hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.99 (m, 2 H), 2.50 (t, 2 H, *J* = 6.3 Hz), 4.30 (t, 2 H, *J* = 5.2 Hz), 7.26-7.34 (m, 5 H), 7.42-7.50 (m, 5 H); IR(neat) 1627, 1637, 1677, 2359 cm^{-1}; mass

spectrum, *m/z* (% rel intensity) 340 (M^+, 11), 342 (100), 314 (15), 286 (14), 257 (7), 231 (8), 202 (14), 105 (7), 77 (5); calcd for $C_{23}H_{16}O_3$ *m/z* 340.1095, measured *m/z* 340.1059. Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.18; H, 4.71. Found: C, 80.79; H, 4.78.

Quinone 12c. A mixture of iodoquinone **8a** (40 mg, 0.11 mmol), 1-hexynyltributyltin (80 mg, 0.22 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 43 hr. Purification by utilizing chromatography on silica gel with hexane/ethyl acetate (4:1) (R_f = 0.34) gave the prism-like orange crystals (18 mg, 50 %): mp 119-120 °C (ethanol/hexane); ^1H NMR($CDCl_3$, 250 MHz) δ 0.79 (t, *J* = 7.2 Hz, 3 H), 1.14-1.44 (m, 4 H), 1.97 (m, 2 H), 2.33 (t, 2 H, *J* = 6.9 Hz), 2.47 (t, 2 H, *J* = 6.3 Hz), 4.27 (t, 2 H, *J* = 5.2 Hz), 7.38-7.47 (br. s, 5 H); IR(neat) 1633,1676, 2225 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 320 (M^+, 20), 277 (21), 249 (11), 165 (17), 139 (10), 91 (100), 65 (8); calcd for $C_{21}H_{20}O_3$ *m/z* 320.1407, measured *m/z* 320.1397. Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.75; H, 6.25. Found: C, 78.62; H, 6.38.

Quinone 12d. A mixture of iodoquinone **8a** (0.12 g, 0.33 mmol), vinyltributyltin (0.21 g, 0.66 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 40 hr. Final purification was achieved by chromatography on silica gel with hexane/ethyl acetate (8:1) (R_f = 0.37) to give the needle-shaped red crystals (58 mg, 60 %): mp 123-124 °C (ethanol/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.98 (m, 2 H), 2.46 (t, 2 H, *J* = 6.3 Hz), 4.29 (t, 2 H, *J* = 5.3 Hz), 5.49 (dd, 1 H, *J* = 2.3, 11.6 Hz), 6.07 (dd, 1 H, *J* = 2.3, 17.8 Hz), 6.24 (dd,1 H, *J* = 11.5, 17.8 Hz), 7.12-7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 17.98, 20.66, 67.65, 118.46, 126.55, 127.90, 128.58, 128.73, 130.04, 132.92, 135.26, 142.54, 153.55, 181.77, 186.01; IR (neat) 1627, 1637, 1677 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 266 (M^+, 100), 237 (23), 210 (41), 181 (36), 155 (27), 128 (50), 102 (24), 77 (21), 55 (42); calcd for $C_{17}H_{14}O_3$ *m/z* 266.0939, measured *m/z* 266.0950. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 76.35; H, 5.56.

Quinone 12e. A mixture of iodoquinone **8a** (60 mg, 0.16 mmol), allyltributyltin (0.11 g, 0.33 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 77 °C and was stirred under a N_2 atmosphere for 40 hr. Purification by chromatography on silica gel with hexane/ethyl acetate (3:1) (R_f = 0.39) gave the yellow solids (30 mg, 66 %): mp 62-64 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.98 (m, 2 H), 2.45 (t, 2 H, *J* = 6.3 Hz), 3.06-3.09 (dt, 2 H, *J* = 1.5, 6.4 Hz), 4.28 (t, 2H, *J* = 3 Hz), 4.86-4.93 (ddt, 1 H, *J* = 1.6, 1.6, 17.1 Hz), 4.95-5.00 (ddt, 1 H, *J* = 1.4, 1.4, 10.1 Hz), 5.68-5.84 (ddt, 1 H , *J* = 6.3, 10.3, 17.1 Hz), 7.11-7.16 (m, 2 H), 7.37-7.66 (m, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.04, 20.75, 31.48, 67.62, 116.84, 118.66, 127.91, 128.52, 129.27, 133.11, 134.58, 140.40, 144.38, 153.60, 181.90, 186.24; IR (neat) 1609, 1640, 1644, 1667 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 280 (M^+, 100), 252 (19), 224 (13), 181 (11), 149 (90), 115 (21), 77 (10), 55 (23); calcd for $C_{18}H_{16}O_3$ *m/z* 280.1095, measured *m/z* 280.1082. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 76.98; H, 5.72.

Palladium-catalyzed cross-couplig reactions of iodoquinone 8b or 8c and organostannanes: General procedure. Reaction of iodoquinone **8b** and phenylethynyltributyltin was described as a typical example. To the solution of iodoquinone **8b** (72 mg, 0.22 mmol) and

(phenylethynyl)-tributyltin (0.12 g, 0.44 mmol) in THF (8 mL) was added $Pd(Ph_3P)_4$ (10 mg, 5 mol %). The mixture was degassed by the freeze-thaw-pump method for three cycles and then it was heated to 80 °C and allowed to stir under a N_2 atmosphere for 30 hr. The dark mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was redissolved in CH_2Cl_2 (20 mL) and to it was added PbO_2 (4 equiv.). The mixture was stirred at room temperature for an hour and then it was filtered and concentrated again. The residue was finally purified by flash-chromatography on silica gel with hexane/ethyl acetate (4:1) as the solvent mixture (R_f = 0.29) to give the quinone **12f** (30 mg, 62 %) as yellow prism-like crystals ($CHCl_3$/hexane): mp 164-166°C; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.29 (s, 3 H), 6.81 (s, 1 H), 7.17-7.28 (m, 5 H), 7.41-7.52 (m, 5 H); IR (neat) 1631, 1637, 1641, 2300 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 298 (M^+, 100), 270 (31), 255 (30), 241 (25), 202 (50), 165 (10), 126 (12), 101 (10), 69 (15). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.56; H, 4.70. Found: C, 84.69; H, 4.72.

Quinone 12g. A mixture of iodoquinone **8b** (0.13 g, 0.40 mmol), 1-hexynyltributyltin (0.30 g, 0.81 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 90 °C and was stirred under a N_2 atmosphere for 12 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (8:1) as the solvent mixture (R_f = 0.40) gave the quinone **12g** (70 mg, 64%) as yellownish-orange low melting solids: ^1H NMR ($CDCl_3$, 250 MHz) δ 0.76 (t, 3 H, J = 7.2 Hz), 1.10-1.24 (m, 2 H), 1.29-1.41 (m, 2 H), 2.30 (t, 2 H, J = 6.8 Hz), 6.62 (br. s, 1 H), 7.34 (br. s, 5 H); IR (neat) 1639, 1650, 1656, 1663, 2217 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 278 (M^+, 27), 250 (11), 235 (100), 207 (8), 193 (18), 178 (18), 165 (14), 152 (10), 139 (19), 115 (5), 68 (16). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.80; H, 6.50.

Quinone 12h. A mixture of iodoquinone **8b** (70 mg, 0.22 mmol), vinyltributyltin (0.13 g, 0.41 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 12 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.29) gave the quinone **12h** (30 mg, 32 %) as yellownish-orange solids: mp 63-65 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.06 (s, 3 H), 5.52 (dd, J = 2.1, 11.4 Hz, 1 H), 6.07 (dd, J = 2.3, 18.0 Hz, 1 H), 6.25 (dd, 1 H, J = 11.5, 18.0 Hz), 6.64 (br s, 1 H), 7.13-7.19 (m, 2 H); 7.32-7.43 (m, 3 H); IR (neat) 1653 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 224 (M^+, 100), 195 (38), 181 (47), 167 (14), 153 (16), 128 (24), 102 (14), 68 (27), 51 (13). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 79.91; H, 5.35. Apart from the coupled quinone **12h**, *para*-hydroxyiodophenol **13h** was also obtained in 28% yield: R_f = 0.2 (hexane/ethyl acetate=10:1)which was not characterized but confirmed for compound indirectly *via* oxidation to the iodoquinone **8b** by PbO_2 (2 equiv.) in CH_2Cl_2 (20 mL) at room temperature within 1 h.

Quinone 12i. A mixture of iodoquinone **8c** (0.21 g, 0.54 mmol), phenylethynyltributyltin (0.43 g, 1.10 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 17 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.27) gave the quinone **12i** (60 mg, 30%) as red prism-like crystals (ethyl acetate/hexane): mp 191-193 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.99 (s, 1 H), 7.30-7.56 (m, 15 H); IR(neat) 1655, 2200 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 360 (M^+, 100), 331 (47), 303 (44), 255 (17), 230 (16), 202 (75), 178 (12), 150 (21), 126 (9), 102

(92), 76 (14), 51 (13); calcd for $C_{26}H_{16}O_2$ *m/z* 360.1146, measured *m/z* 360.1123. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.44; H, 4.44. Found: C, 85.57; H, 4.48. *para*-Hydroxyiodophenol **13i** was also obtained in 40% yield: R_f = 0.17 (hexane/ethyl acetate=10:1); ^1H NMR ($CDCl_3$, 250 MHz) δ 4.80 (s, 1 H), 5.31 (s, 1 H), 7.03 (s, 1 H), 7.35-7.70 (m, 10 H). Compound **13i** was also converted back to the iodoquinone **8c** by stirring the compound dissolved in CH_2Cl_2 (30 mL) in the presence of PbO_2 (2 equiv.) at room temperature for 1 h.

Quinone 12j. A mixture of iodoquinone **8c** (0.12 g, 0.31 mmol), 1-hexynyltributyltin (0.23 g, 0.62 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 70 °C and was stirred under a N_2 atmosphere for 16 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.30) gave the quinone **12j** (20 mg, 19%) as yellownish-orange liquid: ^1H NMR ($CDCl_3$, 250 MHz) δ 0.82 (t, 3 H, *J* = 7.3 Hz), 1.16-1.24 (m, 2 H), 1.28-1.44 (m, 2 H), 2.38 (t, 2 H, *J* = 6.9 Hz), 6.93 (s, 1 H), 7.39-7.51 (m, 10 H); IR (neat) 1658, 2221 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 340 (M^+, 46), 255 (24), 239 (25), 228 (11), 149 (14), 139 (29), 102 (58), 77 (15), 57 (7). Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.67; H, 5.93. *para*-Hydroxyiodophenol **13j** was also obtained in 70% yield and the spectroscpoic data and its conversion to the iodoquinone **8c** can be referred to compound **13i** described above.

Quinone 12k. A mixture of iodoquinone **8c** (0.13 g, 0.34 mmol), vinyltributyltin (0.21 g, 0.66 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 90 °C and was stirred under a N_2 atmosphere for 16 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.41) gave the quinone **12k** (20 mg, 21%) as deep red solids: mp 104-106 °C (ether/hexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 5.58 (dd, 1 H, *J* = 2.3, 11.3 Hz), 6.17 (dd, 1 H, *J* = 2.6, 18.0 Hz), 6.31 (dd, 1 H, *J* = 11.4, 17.6 Hz), 6.92 (s, 1 H), 7.20-7.53 (m, 10 H); IR (neat) 1658, 1610 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 286 (M^+, 100), 257 (37), 229 (20), 202 (5), 181 (8), 155 (15), 128 (31), 102 (67), 77 (10), 51 (11); calcd for $C_{20}H_{14}O_2$ *m/z* 286.0990, measured *m/z* 286.0908. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.92; H, 4.90. Found: C, 83.50; H, 5.31. *para*-Hydroxyiodophenol **13k** was also obtained in 61% yield and the spectroscpoic data and its conversion to the iodoquinone **8c** can be referred to compound **13i** described above.

Quinone 12l. A mixture of iodoquinone **8c** (80 mg, 0.21 mmol), phenyltributyltin (0.15 g, 0.41 mmol) and $Pd(Ph_3P)_4$ (5 mol %) was heated to 80 °C and was stirred under a N_2 atmosphere for 24 hr. Oxidation and purification by flash-chromatography on silica gel with hexane/ethyl acetate (10:1) as the solvent mixture (R_f = 0.29) gave the quinone **12l** (60 mg, 86%) as yellow solids. The spectroscopic data were identical to the one derived from cross-coupling reaction between phenylboronic acid and iodoquinone **8c** described below.

Palladium-catalyzed cross-coupling reaction of iodoquinone 8c and phenylboronic acid. To the solution of iodoquinone **8c** (60 mg, 0.16 mmol) and phenylboronic acid (20 mg, 0.17 mmol) in 5 mL of toluene was added tetrakis-(triphenylphosphine) palladium(0) (9 mg, 5 mol%) and potassium carbonate (25 mg, 0.23mmol). The mixture was degassed by the freeze-thaw-pump method for three cycles and then it was heated to 85 °C and was stirred under a N_2 atmosphere for 12 hr. The orange mixture was concentrated and flash-chromatographed on silica gel with hexane/ethyl acetate (4:1) as

the solvent mixture (R_f = 0.42) to give the quinone **12l** (23 mg, 44%) as yellow solids (methanol/hexane): mp 160-162 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.06-7.61 (m, 16 H); IR(neat) 1646, 1656 cm^{-1}; mass spectrum, *m/z* (% rel intensity) 336 (M^+, 100), 308 (16), 279 (6), 231 (9), 178 (41), 102 (52). Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.71; H, 4.76. Found: C, 85.68; H, 4.52. Apart from quinone **12l**, hydroquinone **13l**[28] was also obtained in 57% yield: R_f = 0.06 (hexane/ethyl acetate=10:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.76 (s, 1 H), 4.90 (s, 1 H), 7.05 (s, 1 H), 7.14-7.68 (m, 15 H). The hydroquinone **13l** can be converted into quinone **12l** by stirring **13l** dissolved in CH_2Cl_2 (20 mL) in the presence of PbO_2 (2 equiv.) at room temperature for 1 hr. Hence quinone **12l** can be obtained in 92% overall yield.

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