Supporting information for

Synthesis and structural analysis of a novel iodinated cyclopentadienone via ring-contraction iodination
and its application in synthesis of alkyne-functionlized cyclopentadienones

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1. Tables

Table 1 Spectral characteristics of cyclopentadienones in chloroform

<table>
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<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (cm$^{-1}$M$^{-1}$)</th>
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Table 2 UV-Visible absorption maxima of substituted cyclopentadienone in different solvents (nm)

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<th>Compound</th>
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2. Figures

![Figure 1](image1.png)

**Fig. 1** Packing of 3 in its single crystal and the short O···H contact of 2b in its crystal lattice
Fig. 2. The visible absorption maxima shift ($\Delta \lambda_{\text{max}}$) of substituted cyclopentadienones in solvents with different polarities. ($\Delta \lambda_{\text{max}} = \lambda_{\text{max}}_{\text{solvent}} - \lambda_{\text{max}}_{\text{hexane}}$); (A) in non-halogenated solvent, (B) in chlorinated solvents; Solvent polarity index values from Phenomenex technical resources.

3. Experiment Section

- Materials:
  All the chemicals and reagents were purchased from Acros Organics. Tetrahydrofuran was freshly distilled from sodium-potassium alloy. Triethylamine was freshly distilled from sodium hydride. $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, using a Varian ANOVA spectrometer. X-ray data were collected on an Bruker SMART 1000 CCD diffractometer. UV–vis absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. GCMS analyses were performed with an Agilent 6890 gas chromatograph and Agilent 5937 mass-spectrometer instrument equipped with an Agilent HP-5MS column (30 m x 0.25 mm), using helium (99.9995 %) as a carrier gas, a split ratio of 30:1, and an injection volume of 1-3 µL. In the standard GC program, the oven temperature was kept at 50 °C for 2 min, then raised to 200 °C at a rate of 25 °C per minute, and kept at 200 for 20 min. The solvent delay for MS acquisition was 5 min.
General procedures:

Compound 2a and compound 3

(1) Oxygen free conditions: 50 mL of a degased aqueous solution of 0.840 g sodium bicarbonate (10 mmol) were slowly added, with stirring, to 50 mL of a degased methanol solution of 2.223 g compound 1 and 2.538 g iodine (10 mmol). Reaction mixtures were allowed to react for 1 hour under nitrogen protection, followed by extraction of products with methylene chloride. The resulting red methylene chloride solution was washed 3 times with 10 mL saturated sodium thiosulfate solution and 3 times with water. This solution was dried overnight over anhydrous sodium sulfate. A mixture of compound 2 and compound 3 were obtained by vacuum evaporation, following which 2.611g pure compound 2 and 0.637g pure compound 3 were obtained by column chromatography using hexanes/ethyl acetate solvent pair as eluent.

(2) Oxygen rich conditions: 50 mL of an aqueous solution of 0.840 g sodium bicarbonate (10 mmol) were slowly added, with stirring, to a 50 mL methanol solution of 2.223 g compound 1 and 2.538 g iodine (10 mmol) in the presence of bubbled oxygen. Reaction mixtures were allowed to react for 1 hour, followed by same work up procedures as above. 2.437g pure compound 2 and 0.254g pure compound 3 were obtained.

Compound 2b

0.75 mL of acetyl chloride was slowly added to a 20 mL THF solution of 1.74 g compound 2a at -5°C with rapid stirring, followed by dropwise addition of 5.6 mL triethylamine. The reaction mixture was then allowed to warm to room temperature and to stir for 30 minutes. Following quenching of the reaction by addition of ice, the product was extracted into ether which was then dried overnight over anhydrous sodium sulfate. After evaporation of solvent from the crude product, 2.118 g pure compound 2b were obtained by column chromatography using hexanes/ethyl acetate solvent pair as eluent.

Compound 4a-m, 4s

Detailed procedures are described in our previous work [10]

Physical properties of products:

4,6-di-tert-butyl-2-iodo-1,3-phenylene diacetate (2b): \( ^1H \) NMR (400MHz, CDCl\(_3\)) \( \delta \) 7.46 (s, 1H), 2.376 (s, 6H), 1.329 (s, 18H); \( ^13C \) NMR (100MHz, CDCl\(_3\)) \( \delta \) 168.8 (2C), 148.7 (2C), 139.7 (2C), 126.8 (1C), 95.8 (1C), 35.1 (2C), 30.5 (6C), 22.4 (2C).

3,5-di-tert-butyl-2-iodocyclopenta-2,4-dienone (3): \( ^1H \) NMR (400MHz, CDCl\(_3\)) \( \delta \) 6.74 (s, 1H), 1.317 (s, 9H), 1.165 (s, 9H); \( ^13C \) NMR (100MHz, CDCl\(_3\)) \( \delta \) 196.3 (1C), 167.3 (1C), 142.1 (1C), 139.9 (1C), 80.0 (1C), 32.3 (1C), 29.7 (1C), 28.9 (3C), 28.1 (3C). HRMS (ESI) Calcd for C\(_{13}\)H\(_{19}\)IO [MNa\(^+\)] 341.0378, found 341.0376.
3,5-di-tert-butyl-2-((trimethylsilyl)ethynyl)cyclopenta-2,4-dienone (4a): ¹H NMR (400MHz, CDCl₃) δ 6.64 (s, 1H), 1.29 (s, 9H), 1.16 (s, 9H), 0.20 (s, 9H); ¹³C NMR (100MHz, CDCl₃) δ 198.6 (1C), 170.4 (1C), 142.4 (1C), 137.7 (1C), 107.6 (1C), 104.7 (1C), 97.9 (1C), 34.8(1C), 32.1(1C), 29.0 (3C), 28.0 (3C), 0.2(3C). HRMS (ESI) Calcd for C₁₈H₂₈O₅Si [MNa⁺] 311.1807, found 311.1785.

3,5-di-tert-butyl-2-(hex-1-yn-1-yl)cyclopenta-2,4-dienone (4b): ¹H NMR (400MHz, CDCl₃) δ 6.63 (s, 1H), 2.42 (t, 2H, J=7.0 Hz), 1.55 (m, 2H), 1.45 (m, 2H), 0.91 (t, 3H, J=7.2 Hz); ¹³C NMR (100MHz, CDCl₃) δ 199.4 (1C), 166.9 (1C), 141.5 (1C), 138.1 (1C), 108.1 (1C), 100.3 (1C), 73.5 (1C), 34.4 (1C), 31.9 (1C), 30.7 (1C), 29.1 (3C), 28.1 (3C), 22.1 (1C), 19.7 (1C), 13.6 (1C). HRMS (ESI) Calcd for C₁₉H₂₈O [MNa⁺] 295.2038, found 295.2013.

3,5-di-tert-butyl-2-(3,3-dimethylbut-1-yn-1-yl)cyclopenta-2,4-dienone (4c): ¹H NMR (400MHz, CDCl₃) δ 6.59 (s, 1H), 1.25 (s, 18H), 1.12 (s, 9H); ¹³C NMR (100MHz, CDCl₃) δ 199.5 (1C), 167.0 (1C), 141.5 (1C), 138.0 (1C), 109.8 (1C), 108.0 (1C), 72.1 (1C), 34.4 (1C), 31.9 (1C), 30.7 (3C), 29.1 (3C), 28.5 (1C), 28.1 (3C). HRMS (ESI) Calcd for C₁₉H₂₈O [MNa⁺] 295.2038, found 295.2023.

3,5-di-tert-butyl-2-(cyclohexylethynyl)cyclopenta-2,4-dienone (4d): ¹H NMR (400MHz, CDCl₃) δ 6.63 (s, 1H), 2.61 (m, 1H), 1.81 (m, 2H), 1.72 (m, 2H), 1.50 (m, 3H), 1.31 (m, 3H), 1.27 (s, 9H), 1.16 (s, 9H); ¹³C NMR (100MHz, CDCl₃) δ 199.5 (1C), 167.0 (1C), 141.5 (1C), 138.1 (1C), 108.1 (1C), 104.3 (1C), 73.5 (1C), 34.4 (1C), 32.5 (2C), 31.9 (1C), 30.1 (1C), 29.1 (3C), 28.1 (3C), 25.9 (2C), 24.8 (1C). HRMS (ESI) Calcd for C₂₁H₃₀O [MNa⁺] 321.2194, found 321.2174.

3,5-di-tert-butyl-2-(3-cyclopentylprop-1-yn-1-yl)cyclopenta-2,4-dienone (4e): ¹H NMR (400MHz, CDCl₃) δ 6.63 (s, 1H), 2.42 (d, 2H, J=6.8), 1.82-2.27 (m, 2H), 1.78 (m, 2H), 1.45-1.67 (m, 4H), 1.43 (s, 1H), 1.29 (s, 9H), 1.17 (s, 9H); ¹³C NMR (100MHz, CDCl₃) δ 199.5 (1C), 166.8 (1C), 141.5 (1C), 138.1 (1C), 108.2 (1C), 99.9 (1C), 73.5 (1C), 39.2 (1C), 34.3 (1C), 31.8 (2C), 29.1 (3C), 25.9 (1C), 24.8 (2C). HRMS (ESI) Calcd for C₂₁H₃₀O [MNa⁺] 321.2194, found 321.2187.

3,5-di-tert-butyl-2-(cyclopropylethynyl)cyclopenta-2,4-dienone (4f): ¹H NMR (400MHz, CDCl₃) δ 6.62 (s, 1H), 1.46 (m, 1H), 1.25 (s, 9H), 1.15 (s, 9H), 0.83 (m, 2H), 0.76 (m, 2H); ¹³C NMR (100MHz, CDCl₃) δ 199.4 (1C), 167.0 (1C), 141.5 (1C), 138.1 (1C), 108.0 (1C), 103.3 (1C), 68.8 (1C), 34.3 (1C), 31.9 (1C), 29.1 (3C), 28.1 (3C), 8.8 (2C), 0.85 (1C). HRMS (ESI) Calcd for C₁₈H₂₄O [MNa⁺] 279.1725, found 279.1715.
3,5-di-tert-butyl-2-(phenylethynyl)cyclopenta-2,4-dienone (4g): $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.47 (m, 2H), 7.30 (m, 3H), 6.63 (s, 1H), 1.35 (s, 9H), 1.20 (s, 9H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 198.8(1C), 168.8 (1C), 142.4 (1C), 138.3 (1C), 131.2 (2C), 128.2 (3C), 123.6 (1C) 107.6 (1C), 98.7 (1C), 82.9 (1C), 34.8 (1C), 32.1 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for C$_{21}$H$_{24}$O [MNa$^+$] 315.1725, found 315.1718.

3,5-di-tert-butyl-2-((6-methoxynaphthalen-2-yl)ethynyl)-cyclopenta-2,4-dienone (4h): $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.88 (s, 1H), 7.65 (dd, 2H, $J_1$=9.2Hz, 8.0 Hz), 7.45 (d, 1H, $J$=9.2), 7.11 (dd, 1H, $J$=8.8, 1.2 Hz), 7.07 (s, 1H), 6.63 (s, 1H), 3.89 (s, 3H), 1.35 (s, 9H), 1.18 (s, 9H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 198.8(1C), 168.8 (1C), 158.3 (1C), 142.4 (1C), 138.3 (1C), 134.1 (1C), 130.9 (1C), 129.3 (1C), 128.7 (1C), 128.5 (1C), 126.7 (1C), 119.3 (1C), 118.6 (1C), 107.8 (1C), 105.8 (1C), 99.4 (1C), 82.7 (1C), 55.3 (1C), 34.8 (1C), 32.1 (1C), 29.1 (3C), 28.3 (3C). HRMS (ESI) Calcd for C$_{26}$H$_{29}$O$_2$ [MNa$^+$] 395.1987, found 395.1988.

3,5-di-tert-butyl-2-(phenanthren-9-yethynyl)cyclopenta-2,4-dienone (4i) $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 8.58-8.70 (m, 3H), 8.00 (s, 1H), 7.85 (dd, 2H, $J$=7.8, 1.2Hz), 7.58-7.74 (m, 4H), 6.78 (s, 1H), 1.44 (s, 9H), 1.24 (s, 9H); 13C NMR (100MHz, CDCl$_3$) $\delta$ 198.8(1C), 168.8 (1C), 142.8 (1C), 138.3 (1C), 131.4 (1C), 131.3 (1C), 131.1 (1C), 130.2 (1C), 130.0 (1C), 128.5 (1C), 127.4 (2C), 127.3(1C), 127.0 (1C), 126.9 (1C), 122.6 (2C), 120.2 (1C), 107.8 (1C), 97.3 (1C), 87.5 (1C), 34.8 (1C), 32.2 (1C), 29.1 (3C), 28.4 (3C). HRMS (ESI) Calcd for C$_{29}$H$_{28}$O [MH$^+$] 415.2038, found 415.2031.

3,5-di-tert-butyl-2-((4-(dimethylamino)phenyl)ethynyl)-cyclopenta-2,4-dienone (4j): $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.31 (d, 2H, $J$=9.2 Hz), 6.66 (s, 1H), 6.60 (d, 2H, $J$=8.4 Hz), 2.95 (s, 6H, ), 1.31 (s, 9H), 1.16 (s, 9H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 199.3 (1C), 168.8 (1C), 142.8 (1C), 138.3 (1C), 131.4 (1C), 131.3 (1C), 130.2 (1C), 130.0 (1C), 128.5 (1C), 97.3 (1C), 87.5 (1C), 40.1 (2C), 34.6 (1C), 32.0 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for C$_{23}$H$_{29}$NO [MH$^+$] 336.2327, found 336.2316.

3,5-di-tert-butyl-2-((3,5-di-tert-butyl-4-methoxyphenyl)ethynyl)-cyclopenta-2,4-dienone (4k): $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.33 (s, 2H), 6.68 (s, 1H), 3.65 (s, 3H), 1.39 (s, 18H), 1.33 (s, 9H), 1.17 (s, 9H); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 199.1 (1C), 167.9 (1C), 160.1 (1C), 143.9 (2C), 142.1 (1C), 138.4 (1C), 129.7 (2C), 117.9 (1C), 107.8 (1C), 99.5 (1C), 81.3 (1C), 64.3 (1C), 35.7 (1C), 34.6 (1C), 32.0 (1C), 31.9 (6C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for C$_{30}$H$_{43}$O$_2$ [MH$^+$] 435.3263, found 435.3259.
3,5-di-tert-butyl-2-(α-tolylethynyl)cyclopenta-2,4-dienone (4l): \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta\) 7.44 (d, 1H, J=7.6Hz), 7.20 (m, 2H), 7.14 (m, 1H), 6.71 (s, 1H), 2.50 (s, 3H), 1.34 (s, 9H), 1.19 (s, 9H) \(^{13}\)C NMR (100MHz, CDCl\(_3\)); \(\delta\) 199.1 (1C), 167.1 (1C), 141.7 (1C), 140.1 (1C), 138.4 (1C), 131.7 (1C), 129.4 (1C) 128.2 (1C), 125.4 (1C), 123.4 (1C), 107.8 (1C), 97.9 (1C), 86.5 (1C), 34.7 (1C), 32.1 (1C), 29.1 (3C), 28.2 (3C), 20.9 (1C). HRMS (ESI) Calcd for C\(_{22}\)H\(_{26}\)O [MNa\(^+\)] 329.1881, found 329.1885.

3,5-di-tert-butyl-2-(ferrocenyl)cyclopenta-2,4-dienone (4m): \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta\) 6.68 (s, 1H), 4.64 (t, 2H, J=1.6 Hz), 4.24 (s, 5H), 4.22 (t, 2H, J=1.6Hz) 1.35 (s, 9H), 1.20 (s, 9H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta\) 198.8 (1C), 167.1 (1C), 141.7 (1C), 138.5 (1C), 108.3 (1C), 98.1 (1C), 79.0 (1C), 71.3 (2C), 69.9 (5C), 68.8 (2C) 65.6 (1C), 34.6 (1C), 32.0 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for C\(_{25}\)H\(_{28}\)FeO [MNa\(^+\)] 423.1387, found 423.1389.

3,5-di-tert-butyl-2-(5-hydroxypent-1-yn-1-yl)cyclopenta-2,4-dienone (4s): \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta\) 6.63 (s, 1H), 3.81 (t, 2H, J=6.4 Hz), 2.55 (t, 2H, J=6.8 Hz), 1.83 (p, 2H, 6.4Hz), 1.27 (s, 9H), 1.16 (s, 9H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta\) 199.6 (1C), 167.1 (1C), 141.8 (1C), 138.1 (1C), 107.8 (1C), 99.1 (1C), 74.2 (1C), 62.0 (1C), 34.4 (1C), 32.0 (1C), 31.2 (1C), 29.0 (3C), 28.1 (3C), 16.8 (1C). HRMS (ESI) Calcd for C\(_{18}\)H\(_{26}\)O\(_2\) [MH\(^+\)] 275.2011, found 275.1999.
$^{1}H$ NMR for compound 2b
$^{13}$C NMR for compound 2b
$^1$H NMR for compound 3
$^{13}$C NMR for compound 3
$^1$H NMR for compound 4a
$^{13}$C NMR for compound 4a
$^1$H NMR for compound 4b
$^{13}$C NMR for compound 4b
$^1$H NMR for compound 4c
$^{13}$C NMR for compound 4c
$^1$H NMR for compound 4d
$^{13}$C NMR for compound 4d
$^1$H NMR for compound 4e
$^{13}$C NMR for compound 4e
\(^1\text{H NMR for compound 4f}\)
$^{13}$C NMR for compound 4f
$^1$H NMR for compound 4g
$^{13}$C NMR for compound 4g
$^{13}$C NMR for compound 4h
$^1$H NMR for compound 4i
$^{13}$C NMR for compound 4i
$^1$H NMR for compound 4j
\textsuperscript{13}C NMR for compound 4j
$^1$H NMR for compound 4k
$^{13}$C NMR for compound 4k
$^1$H NMR for compound 41
$^{13}$C NMR for compound 4l
$^1$H NMR for compound 4m
$^{13}$C NMR for compound 4m
$^1$H NMR for compound 4s
$^{13}$C NMR for compound 4s
GC-MS for compound 4g
The $^{13}$C NMR spectrum (page 11) suggests that compound 3 contains 5 sp$^2$ carbons and two tert-butyl groups. Among the five sp$^2$ carbons, a typical ketone shift at low field ($\delta=196.32$) is observed (Figure 1). In contrast to the literature value for non-iodine substituted cyclopentadienone derivatives,[13] the introduction of iodine substituent results in a ~30ppm upfield shift of the corresponding carbon to $\delta=80.1$ ppm, whereas the introduction of tert-butyl groups results in a ~20 to 30ppm downfield shift of corresponding carbons to $\delta=167.3$ ppm and 143.9 ppm. Thus these assignments are consistent with literature values.[13] The inferred cyclic structure is further confirmed by X-ray diffraction analysis which indicates that this product has a cyclopentadienone backbone with one iodine and two tert-butyl substituents.

![Figure 1. Chemical shifts of five membered ring carbons.](image)

Consistent with literature values,[14] introduction of the iodine substituent onto compound 1, does not significantly affect the shifts of the other 4 carbons on the ring (Figure 2), which suggests that there is only an inductive effect from iodine substitution and no clear resonance effect. This furthermore indicates that there is minimal conjugation on the five membered ring, although all five carbons are sp$^2$ carbons.

![Figure 2. Chemical shift differences of the ring carbon atoms caused by the introduction of iodine to compound 0.](image)
