Supporting Information

Mn-Catalyzed 1,6-Conjugate Addition/Aromatization of para-Quinone Methides

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I. General Methods and materials:

All of the reactions were carried out under the air atmosphere in an 20 mL colorimetric tube. Most of the reagents and starting materials were purchased from commercial sources and used as such. All p-quinone methides were prepared by following a literature procedure.[1] ¹H, ¹³C and ³¹P spectra were recorded on Varian 400, 101 or 162 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl₃ (δ 7.26 ppm) for ¹H NMR, CDCl₃ (δ 77.16 ppm) for ¹³C NMR, and H₃PO₄ [85%] (δ 0.00 ppm) for ³¹P NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with visualized by fluorescence and by charring after treatment with potassium permanganate stain.

1.1 Representative procedure for the preparation of 4

![Chemical structure](image)

To 20 mL colorimetric tube was added 2 (0.5 mmol), 3 (0.75 mmol), Mn(OAc)₃·2H₂O (2.5 mol%), Fc-TA-2 (3.0 mol%), K₂S₂O₈ (3.0 eq.), DCM:H₂O =2:1 (3.0 mL). The mixture was stirred at 80 ºC in air for 10 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

1.2 Representative procedure for the preparation of 6

![Chemical structure](image)

To 20 mL colorimetric tube was added 2b (0.5 mmol), 5a (1.0 mmol), Mn(OAc)₃·2H₂O (2.5 mol%), Fc-TA-2 (3.0 mol%), K₂CO₃, DCE reflux. The mixture was refluxed for several hours and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.
The mixture was refluxed for 8 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

1.3 Representative procedure for the preparation of 8

To 20 mL colorimetric tube was added 7 (0.2 mmol), 5b (0.3 mmol), Mn(OAc)$_3$·2H$_2$O (2.5 mol%), Fc-TA-2 (3.0 mol%), K$_2$CO$_3$ (2.0 eq.), THF (2.0 mL). The mixture was refluxed for 5 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

1.4 Representative procedure for the preparation of 11

To 20 mL colorimetric tube was added 7 (0.2 mmol), 9 (0.3 mmol), Mn(OAc)$_3$·2H$_2$O (2.5 mol%), Fc-TA-3 (3.0 mol%), Cs$_2$CO$_3$ (2.0 eq.), DCE (2.0 mL). The mixture was refluxed for 3 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

1.5 Representative procedure for the preparation of 12

Table S1. Screening of reaction conditions$^a$

S3
### Table

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield [%]</th>
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<tr>
<td>1</td>
<td>Mn(OAc)$_3$·2H$_2$O (20%)</td>
<td>-</td>
<td>DCE</td>
<td>&lt;5</td>
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<tr>
<td>2</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%)</td>
<td>NaOAc (1.5 eq)</td>
<td>DCE</td>
<td>&lt;5</td>
</tr>
<tr>
<td>3</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%) /Fc-TA-3 (3.0%)</td>
<td>-</td>
<td>DCE</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%) /Fc-TA-3 (3.0%)</td>
<td>NaOAc (1.5 eq)</td>
<td>DCE</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%) /Fc-TA-3 (3.0%)</td>
<td>KOAc (1.5 eq)</td>
<td>DCE</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>Mn(OAc)$_3$·2H$_2$O (20%) /Fc-TA-3 (20%)</td>
<td>NaOAc (1.5 eq)</td>
<td>DCE</td>
<td>83</td>
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<tr>
<td>7</td>
<td>Mn(OAc)$_3$·2H$_2$O (20%) /Fc-TA-3 (20%)</td>
<td>-</td>
<td>DCE</td>
<td>82</td>
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<tr>
<td>8</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%) /Fc-TA-3 (3.0%)</td>
<td>NaOAc (1.5 eq)</td>
<td>TBA</td>
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</tr>
<tr>
<td>9</td>
<td>Mn(OAc)$_3$·2H$_2$O (2.5%) /Fc-TA-3 (3.0%)</td>
<td>NaOAc (1.5 eq)</td>
<td>EtOH</td>
<td>41</td>
</tr>
</tbody>
</table>

*Reagents and conditions: 7a (0.2 mmol), 11a (0.3 mmol, 1.5 eq), Mn(OAc)$_3$·2H$_2$O (2.5-20 mol%), L (3.0-20 mol%), base (0.3 mmol), solvent (3.0 mL), reflux, 10 h. *Isolated yield.

#### 1.6 Representative procedure for the preparation of 12

To 20 mL colorimetric tube was added 7 (0.2 mmol), 11 (0.3 mmol), Mn(OAc)$_3$·2H$_2$O (20 mol%), Fc-TA-3 (20 mol%), DCE (2.0 mL). The mixture was refluxed for 10 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as...
eluent to give the desired product.

II. Compounds Characterization

Fc-TA-1. Khaki solid. Mp: 174–177 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 7.89 (s, 1H), 4.75 (s, 2H), 4.33 (s, 2H), 4.04 (s, 5H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 69.20 (s), 66.56 (s), 30.64 (s). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 69.74 (s), 68.92 (s), 67.06 (s). HRMS (ESI) Calculated for C$_{12}$H$_{11}$FeN$_3$+$\text{H}$(M+H)$^+$ 254.0381, found 254.0382.

Fc-TA-2. Yellow solid. Mp: 79–80 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (s, 1H), 7.36 – 7.28 (m, 5H), 5.58 (s, 2H), 4.72 – 4.65 (m, 2H), 4.33 – 4.27 (m, 2H), 4.05 (s, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.59 (s), 135.78 (s), 131.73 (s), 128.87 (s), 128.31 (s), 127.84 (s), 74.95 (s), 69.71 (s), 69.01 (s), 66.96 (s), 58.58 (s). HRMS (ESI) Calculated for C$_{19}$H$_{17}$FeN$_3$+$\text{H}$(M+H)$^+$ 344.0845, found 344.0843.

Fc-TA-3. Yellow solid. Mp: 149–151 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.33 (m, 4H), 7.29 (d, $J$ = 7.3 Hz, 2H), 5.55 (s, 2H), 4.76 (s, 2H), 4.34 (s, 2H), 4.11 (s, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.37 (s), 158.36 (s), 152.54 (s), 135.82 (s), 134.09 (s), 131.94 (s), 128.83 (s), 124.33 (s), 114.01 (s), 58.26 (s), 55.22 (s), 52.56 (s), 52.43 (s), 50.60 (s), 34.42 (s), 30.40 (s). HRMS (ESI) Calculated for C$_{19}$H$_{17}$FeN$_3$+$\text{H}$(M+H)$^+$ 344.0845, found 344.0842.

Fc-TA-4. Dark red solid. Mp: 122–123 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (dd, $J$ = 8.6, 1.0 Hz, 2H), 7.78 (s, 1H), 7.50 (t, $J$ = 8.0 Hz, 2H), 7.34 (t, $J$ = 7.4 Hz, 1H), 4.79
(t, J = 1.8 Hz, 2H), 4.7 (t, J = 2 Hz, 2H), 4.11 (s, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.76 (s), 140.05 (s), 132.94 (s), 129.36 (s), 127.16 (s), 118.75 (s), 74.51 (s), 69.78 (s), 69.27 (s), 67.19 (s), 31.03 (s). HRMS (ESI) Calculated for C$_{18}$H$_{15}$FeN$_3$+H (M+H)$^+$ 330.0694, found 330.0692.

**Fc-TA-5.** Yellow solid. Mp: 168−170 °C. $^1$H NMR (400 MHz, DMSO) δ 8.91 (s, 1H), 7.95 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 4.81 (d, J = 1.5 Hz, 2H), 4.36 (d, J = 1.5 Hz, 2H), 4.09 (s, 5H); $^{13}$C NMR (101 MHz, DMSO) δ 206.99 (s), 147.13 (s), 137.16 (s), 130.36 (s), 128.93 (s), 120.23 (s), 118.92 (s), 75.78 (s), 69.83 (s), 68.99 (s), 66.97 (s), 31.16 (s). HRMS (ESI) Calculated for C$_{18}$H$_{15}$FeN$_3$+H (M+H)$^+$ 330.0695, found 330.0695.

**[1,1'-Biphenyl]-2,5-dione (4a)** (Known compound, see: Y. Fujiwara, V. Domingo, I. B. Seiple, R. Gianatassio, M. D. Bel, P. S. Baran, J. Am. Chem. Soc. 2011, 133, 3292.). Faint yellow solid. 173.0 mg. Mp: 117−118 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.45 (m, 5H), 6.90-6.84 (m, 3H).

**3'-Methyl-[1,1'-biphenyl]-2,5-dione (4b)** (Known compound, see: Y. Fujiwara, V. Domingo, I. B. Seiple, R. Gianatassio, M. D. Bel, P. S. Baran, J. Am. Chem. Soc. 2011, 133, 3292.). Yellow solid. 164.5mg. Mp: 76–78 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 1H), 7.29 (d, J = 7.6 Hz, 3H), 6.93 – 6.80 (m, 3H), 2.42 (s, 3H).

**4'-Isopropyl-[1,1'-biphenyl]-2,5-dione (4c)** (Known compound, see: D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, J. Org. Chem. 2014, 79, 8607.). Light yellow solid. 192.2 mg. Mp: 48–50°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.91 – 6.77 (m, 3H), 2.95 (dt, J = 13.8, 6.9 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H).

**3',5'-Dimethyl-[1,1'-biphenyl]-2,5-dione (4d)** (Known compound, see: K. Komeyama, T. Kashihara, K. Takaki, Tetrahedron Lett. 2013, 54, 1084.). Pale yellow solid. 165.5 mg. Mp: 101–102 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.10 (s, 1H), 7.08 (s, 2H), 6.88 – 6.79 (m, 3H), 2.36 (s, 6H).

**4'-Ethyl-[1,1'-biphenyl]-2,5-dione (4e)** (Known compound, see: D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, J. Org. Chem. 2014, 79, 8607.). Yellow oil. 169.8 mg. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.89 – 6.79 (m, 3H), 2.71 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). HRMS (ESI) Calculated for C$_{14}$H$_{12}$O$_2$+H (M+H)$^+$ 213.0916, found 213.0918.
2'-Methyl-[1,1'-biphenyl]-2,5-dione (4f) (Known compound, see: D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, *J. Org. Chem.* 2014, 79, 8607.). Yellow oil. 160.5 mg. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.34 (m, 1H), 7.31 – 7.28 (m, 2H), 7.12 (d, $J$ = 7.2 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.74 (d, $J$ = 2.2 Hz, 1H), 2.21 (s, 3H).

3'-Methoxy-[1,1'-biphenyl]-2,5-dione (4g) (Known compound, see: D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, *J. Org. Chem.* 2014, 79, 8607.). Yellow solid. 162.8 mg. Mp: 113–115 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.30 (m, 1H), 7.09 – 6.95 (m, 3H), 6.89 – 6.74 (m, 3H), 3.83 (s, 3H).

4'-Bromo-[1,1'-biphenyl]-2,5-dione (4h) (Known compound, see: A. Honraedt, F. L. Callonnec, E. L. Grognec, V. Fernandez, F. Felpin, *J. Org. Chem.* 2013, 78, 4604.). Yellow solid. 231.5 mg. Mp: 100–102 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J$ = 8.5 Hz, 2H), 7.36 (d, $J$ = 8.5 Hz, 2H), 6.91 – 6.78 (m, 3H).

4'-Iodo-[1,1'-biphenyl]-2,5-dione (4i) (Known compound, see: Y. Fujiwara, V. Domingo, I. B. Seiple, R. Gianatassio, M. D. Bel, P. S. Baran, *J. Am. Chem. Soc.* 2011, 133, 3292.). Light yellow solid. 257.4 mg. Mp: 133–136 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 8.2 Hz, 2H), 7.22 (d, $J$ = 8.2 Hz, 2H), 6.90 – 6.81 (m, 3H).

2-(Naphthalen-2-yl)cyclohexa-2,5-diene-1,4-dione (4j) (Known compound, see: Wang, J.; Wang, S.; Wang, G.; Zhang, J.; Yu, X. Yu. *Chem. Commun.* 2012, 48, 11769). Pale yellow solid. 156.8 mg. Mp: 172–174 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (s, 1H), 7.94 – 7.85 (m, 3H), 7.59 – 7.51 (m, 3H), 6.99 (d, $J$ = 2.2 Hz, 1H), 6.94 – 6.84 (m, 2H).

2-Methylcyclohexa-2,5-diene-1,4-dione (4k) (Known compound, see: D. Wang, B. Ge, L. Du, H. Miao, Y. Ding, *Synlett*, 2014, 25, 2895). Yellow solid. 67.2 mg. Mp: 65-67 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.78 – 6.68 (m, 2H), 6.61 (s, 1H), 2.06 (s, 3H).

[2,2'-Binaphthalene]-1,4-dione (4l) (Known compound, see: G. S. Sidhu, M. Pardhasaradhi, M. H. Babu, *Indian J. Chem.* 1976, 14, 218.). Light yellow solid. 176.3 mg. Mp: 168–170 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 – 8.20 (m, 1H), 8.16 – 8.11 (m, 2H), 7.93 (d, $J$ = 8.5 Hz, 2H), 7.88 (d, $J$ = 7.0 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.65 (d, $J$ = 7.5 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.21 (s, 1H).
III. $^1$H NMR and $^{13}$C NMR Spectra

$^1$H NMR Spectrum of Fc-TA-1

$^{13}$C NMR Spectrum of Fc-TA-1
$^{1}$H NMR Spectrum of Fc-TA-2

$^{13}$C NMR Spectrum of Fc-TA-2
$^{1}H$ NMR Spectrum of Fc-TA-3

$^{13}C$ NMR Spectrum of Fc-TA-3
$^{1}\text{H NMR Spectrum of Fc-TA-4}$

$^{13}\text{C NMR Spectrum of Fc-TA-4}$
$^1$H NMR Spectrum of Fc-TA-5

$^{13}$C NMR Spectrum of Fc-TA-5
$^1$H NMR Spectrum of 4a

4a

$^1$H NMR Spectrum of 4b

4b
$^1$H NMR Spectrum of 4c

$^1$H NMR Spectrum of 4d
$^1$H NMR Spectrum of 4e

$^1$H NMR Spectrum of 4f
$^1$H NMR Spectrum of 4g

![H NMR Spectrum of 4g](image1)

$^1$H NMR Spectrum of 4h

![H NMR Spectrum of 4h](image2)
$^1$H NMR Spectrum of 4i

$^1$H NMR Spectrum of 4j
$^1$H NMR Spectrum of 4k

$^1$H NMR Spectrum of 4l
$^1$H NMR Spectrum of 6

$^{13}$C NMR Spectrum of 6
$^1$H NMR Spectrum of 8a

$^{13}$C NMR Spectrum of 8a
$^1$H NMR Spectrum of 8b

$^{13}$C NMR Spectrum of 8b
$^1$H NMR Spectrum of 8c

$^{13}$C NMR Spectrum of 8c
$^{1}H$ NMR Spectrum of 8d

$^{13}C$ NMR Spectrum of 8d
$^1$H NMR Spectrum of 8e

$^{13}$C NMR Spectrum of 8e
$^{19}$F NMR Spectrum of 8e

$^1$H NMR Spectrum of 8f
$^{13}$C NMR Spectrum of 8f

$^1$H NMR Spectrum of 8g
$^{13}$C NMR Spectrum of 8h

$^1$H NMR Spectrum of 8i
$^{13}$C NMR Spectrum of 8i

$^1$H NMR Spectrum of 8j
\[ ^{13}\text{C} \text{ NMR Spectrum of 8j} \]

\[ ^{19}\text{F} \text{ NMR Spectrum of 8j} \]
$^1$H NMR Spectrum of 8k

$^{13}$C NMR Spectrum of 8k
$^1$H NMR Spectrum of 8l

$^{13}$C NMR Spectrum of 8l
$^1$H NMR Spectrum of 10a

$^{13}$C NMR Spectrum of 10a
$^{31}$P NMR Spectrum of 10a

10a

$^{1}$H NMR Spectrum of 10b

10b
$^{13}$C NMR Spectrum of 10b

$^{31}$P NMR Spectrum of 10b
$^{1}H$ NMR Spectrum of 10c

$^{13}C$ NMR Spectrum of 10c
$^{31}$P NMR Spectrum of 10c

$^{1}$H NMR Spectrum of 10d


**$^{13}$C NMR Spectrum of 10d**

![13C NMR Spectrum of 10d](image)

**$^{31}$P NMR Spectrum of 10d**

![$^{31}$P NMR Spectrum of 10d](image)
$^{1}H$ NMR Spectrum of 10e

$^{13}C$ NMR Spectrum of 10e
$^{19}$F NMR Spectrum of 10e

$^{31}$P NMR Spectrum of 10e
$^{1}{}$H NMR Spectrum of 10f

$^{13}{}$C NMR Spectrum of 10f
$^{31}$P NMR Spectrum of 10f

$^{1}$H NMR Spectrum of 10g
$^{13}$C NMR Spectrum of 10g

$^{31}$P NMR Spectrum of 10g
$^{1}H$ NMR Spectrum of 10h

$^{13}C$ NMR Spectrum of 10h
$^{31}$P NMR Spectrum of 10h

$^{1}$H NMR Spectrum of 10i
$^{13}$C NMR Spectrum of 10i

$^{31}$P NMR Spectrum of 10i
\[^1\text{H}\text{ NMR Spectrum of 10j}\]

\[^{13}\text{C}\text{ NMR Spectrum of 10j}\]
$^{31}$P NMR Spectrum of 10j

$^1$H NMR Spectrum of 10k
$^{13}$C NMR Spectrum of 10k

$^{31}$P NMR Spectrum of 10k
$^{1}H$ NMR Spectrum of 10l

$^{13}C$ NMR Spectrum of 10l
$^{31}$P NMR Spectrum of 10l

10l

$^{1}$H NMR Spectrum of 12a

12a
$^{13}$C NMR Spectrum of 12a

$^{1}$H NMR Spectrum of 12b
$^{13}$C NMR Spectrum of 12b

![13C NMR Spectrum of 12b](image1)

$^1$H NMR Spectrum of 12c

![$^1$H NMR Spectrum of 12c](image2)
**$^{13}$C NMR Spectrum of 12c**

![13C NMR Spectrum of 12c](image)

**$^1$H NMR Spectrum of 12d**

![$^1$H NMR Spectrum of 12d](image)
$^{13}$C NMR Spectrum of 12d

$^{19}$F NMR Spectrum of 12d
$^1$H NMR Spectrum of 12f

$^{13}$C NMR Spectrum of 12f
$^{1}H$ NMR Spectrum of 12g

$^{13}C$ NMR Spectrum of 12g
$^{1}H$ NMR Spectrum of 12h

$^{13}C$ NMR Spectrum of 12h
$^1$H NMR Spectrum of 12i

$^{13}$C NMR Spectrum of 12i