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



To 20 mL colorimetric tube was added **2** (0.5 mmol), **3** (0.75 mmol), $Mn(OAc)_3 H_2O$ (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 °C 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



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 (2.0 eq.), DCE (2.0 mL).

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), $Mn(OAc)_3 2H_2O$ (2.5 mol%), Fc-TA-1 (3.0 mol%), K₂CO₃ (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), $Mn(OAc)_3 H_2O$ (2.5 mol%), Fc-TA-3 (3.0 mol%), Cs_2CO_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



Entry	Catalyst	Base	Solvent	Yield[%]
1	Mn(OAc) ₃ ·2H ₂ O (20%)	-	DCE	<5
2	Mn(OAc) ₃ ·2H ₂ O(2.5%)	NaOAc (1.5 eq)	DCE	<5
3	Mn(OAc) ₃ ·2H ₂ O(2.5%)	-	DCE	31
3	/Fc-TA-3(3.0%)			
4	Mn(OAc) ₃ ·2H ₂ O(2.5%)	NaOAc (1.5 eq) DCE	34	
	/Fc-TA-3(3.0%)		DCL	54
5	Mn(OAc) ₃ ·2H ₂ O(2.5%)	KOAc (1.5 eq) D	DCE	37
	/Fc-TA-3(3.0%)		DCE	52
6	Mn(OAc) ₃ ·2H ₂ O(20%)	NaOAc (1.5 eq)	DCE	83
	/Fc-TA-3(20%)			
7	Mn(OAc) ₃ ·2H ₂ O(20%)	-	DCE	8 2
	/Fc-TA-3(20%)		DCE	82
8	Mn(OAc) ₃ ·2H ₂ O(2.5%)	NaOAc (1.5 eq)	TBA	38
	/Fc-TA-3(3.0%)			
9	Mn(OAc) ₃ ·2H ₂ O(2.5%)	NaOAc (1.5 eq)	FtOH	41
	/Fc-TA-3(3.0%)		LIOII	71

^{*a*}Reagents and conditions: **7a** (0.2 mmol), **11a** (0.3 mmol, 1.5 eq), $Mn(OAc)_3 2H_2O$ (2.5-20 mol%), L (3.0-20 mol%), base (0.3 mmol), solvent (3.0 mL), reflux, 10 h. ^{*b*}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), $Mn(OAc)_3 2H_2O$ (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.

[1] (a) W. D. Chu, L. F. Zhang, X. Bao, X. H. Zhao, C. Zeng, J. Y. Du, G. B. Zhang,
F. X. Wang, X. Y. Ma, C. A. Fan, *Angew. Chem. Int. Ed.* 2013, *52*, 9229–9233; (b) V.
Reddy, R. V. Anand, *Org. Lett.* 2015, *17*, 3390–3393.

II. Compounds Characterization



Fc-TA-1. Khaki solid. Mp: 174–177 °C. ¹H NMR (400 MHz, DMSO) δ 7.89 (s, 1H), 4.75 (s, 2H), 4.33 (s, 2H), 4.04 (s, 5H). ¹³C NMR (101 MHz, DMSO) δ 69.20 (s), 66.56 (s), 30.64 (s).¹³C NMR (101 MHz, DMSO) δ 69.74 (s), 68.92 (s), 67.06 (s). HRMS (ESI) Calculated for C₁₂H₁₁FeN₃+H (M+H)⁺ 254.0381, found 254.0382.



Fc-TA-2

Fc-TA-2. Yellow solid. Mp: 79–80 °C. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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 C₁₉H₁₇FeN₃+H (M+H)⁺ 344.0845, found 344.0843.



Fc-TA-3. Yellow solid. Mp: 149–151 °C. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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 C₁₉H₁₇FeN₃+H (M+H)⁺ 344.0845, found 344.0842.



Fc-TA-4

Fc-TA-4. Dark red solid. Mp: 122–123 °C.¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₅FeN₃+H (M+H)⁺ 330.0694, found 330.0692.



Fc-TA-5. Yellow solid. Mp: 168–170 °C. ¹H 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); ¹³C 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 C₁₈H₁₅FeN₃+H (M+H)⁺ 330.0694, 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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 C₁₄H₁₂O₂+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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR (400 MHz, CDCl₃) 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. ¹H NMR and ¹³C NMR Spectra







¹³C NMR Spectrum of Fc-TA-2





¹³C NMR Spectrum of Fc-TA-3





¹³C NMR Spectrum of Fc-TA-4











¹H NMR Spectrum of 4b





¹H NMR Spectrum of 4d





¹H NMR Spectrum of 4f





¹H NMR Spectrum of 4h





¹H NMR Spectrum of 4j





¹H NMR Spectrum of 41





¹³C NMR Spectrum of 6













¹³C NMR Spectrum of 8d





¹⁹F NMR Spectrum of 8e



¹H NMR Spectrum of 8f













¹⁹F NMR Spectrum of 8j





¹³C NMR Spectrum of 8k



S32



¹³C NMR Spectrum of 8l





¹³C NMR Spectrum of 10a



³¹P NMR Spectrum of 10a



¹H NMR Spectrum of 10b





³¹P NMR Spectrum of 10b





¹³C NMR Spectrum of 10c



³¹P NMR Spectrum of 10c



¹H NMR Spectrum of 10d





³¹P NMR Spectrum of 10d





¹³C NMR Spectrum of 10e



¹⁹F NMR Spectrum of 10e



³¹P NMR Spectrum of 10e





³¹P NMR Spectrum of 10f -27.33 4000 -3500 QН *t*Bu *∙t*Bu -3000 -2500 PO(OEt)₂ -2000 10f -1500 -1000 -500 -0 110 70 60 fl (ppm) 50 40 30 20 10 -10 140 130 120 100 90 80 0 -20 ¹H NMR Spectrum of 10g 77.24 77.24 77.24 77.24 6.97 6.97 6.87 6.87 1.143 1.12 1.108 40000 RR V 777 -35000







³¹P NMR Spectrum of 10h











³¹P NMR Spectrum of 10j





¹³C NMR Spectrum of 10k

S50

100 90 fl (ppm)

 -0

-1000



¹H NMR Spectrum of 10l

³¹P NMR Spectrum of 101













¹³C NMR Spectrum of 12e







110 100 fl (ppm)



¹³C NMR Spectrum of 12h





¹³C NMR Spectrum of 12i

