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The radical reactions of imine radicals produced from the metal salts oxidation of 2-amino-1,4-benzoquinones

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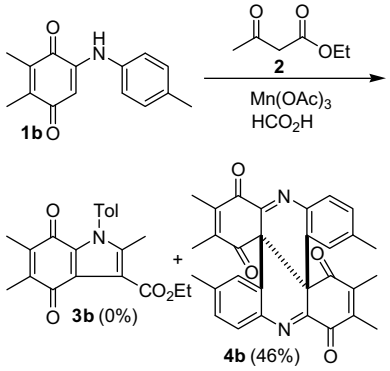
ABSTRACT

The metal salts mediated oxidative free radical reaction of 2-amino-1,4-benzoquinones is described. Imine radicals can be generated by the oxidation of 2-amino-1,4-benzoquinones with Mn(III) and Ag(II). The dimeric products **4** and **14** were formed via the intermolecular radical coupling reaction of the corresponding radical intermediates **5** and **15**. In the presence of styrene, twistane **17** was afforded from 2-phenylamino-1,4-benzoquinone **1** via a radical annulation reaction of imine radical **5**.

1. Introduction

Carbon–carbon bond forming reactions mediated by radical have received considerable attention in organic synthesis during the last two decades.[1] The oxidative free radical reaction mediated by metal salts has been developed into a versatile protocol for the formation of highly functionalized products from simple precursors.[2–5] Among these, manganese(III) acetate, cerium(IV) ammonium nitrate, and silver(I) carbonate have been used most efficiently. Previously, we found that oxidative free radical reactions of 2-phenylamino-1,4-naphthoquinones with β-dicarbonyl compounds produced benzo[*f*]indole-4,9-diones and benzo[*b*]acridine-6,11-diones effectively.[3f,j,k] The solvent effects play an important role in this free radical reaction.[3k] We have continued to study this manganese(III) mediated reaction with 2-phenylamino-1,4-benzoquinone **1**. When 2,3-dimethyl-5-(4-methylphenylamino)-1,4-benzoquinone (**1b**) was treated with ethyl acetoacetate (**2**) and manganese(III) acetate in formic acid, dimer **4b** was obtained exclusively in 46% yield and no trace of the expected indole-4,9-dione **3b** could be isolated (Eq. 1).[6] Dimer **4b** was formed presumably via the intermolecular coupling reaction of imine radical **5b** produced by the manganese(III) oxidation of **1b** (Scheme 1).[7] This different behavior of **1b** can be explained by the higher the electron density of **1b**, owing to electron donating of the two methyl groups, therefore it was oxidized in a much faster rate than that of the corresponding 2-phenylamino-1,4-naphthoquinone derivative. The formation of this dimeric product **4b** is interesting. Although it has been known that imine radical **8** can be generated by the oxidation of enamine **6** with metal salts (Eq. 2) and it undergoes efficient addition to the C–C double bond.[8] The generation of imine radial **5** has not yet been reported. In this report, we wish to describe our results on the free radical reaction of imine radical produced from the metal salts oxidation of 2-amino-1,4-benzoquinones.



(1)

2. Results and discussion

We began our studies of the manganese(III) mediated dimerization reaction with 2-phenylamino substituted 1,4-benzoquinones **1** (Eq. 3). When 2,3-dimethyl-5-(3,5-dimethylphenylamino)-1,4-benzoquinone (**1a**) was treated with manganese(III)

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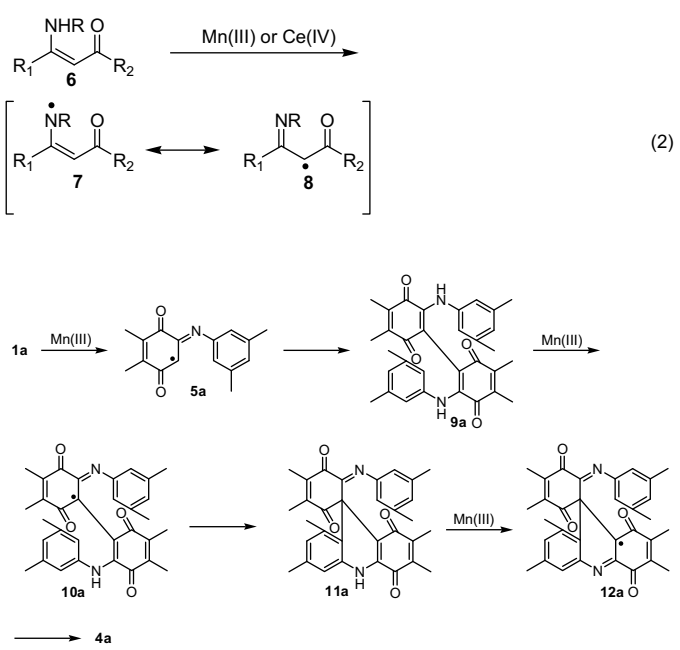
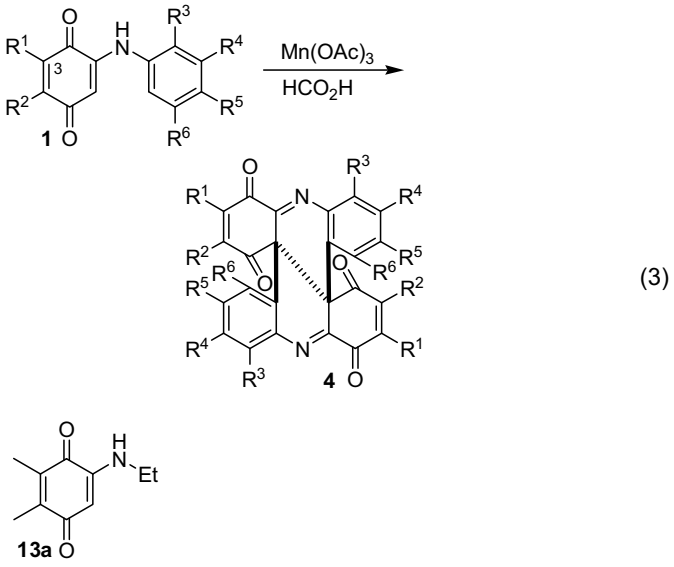


Scheme 1.



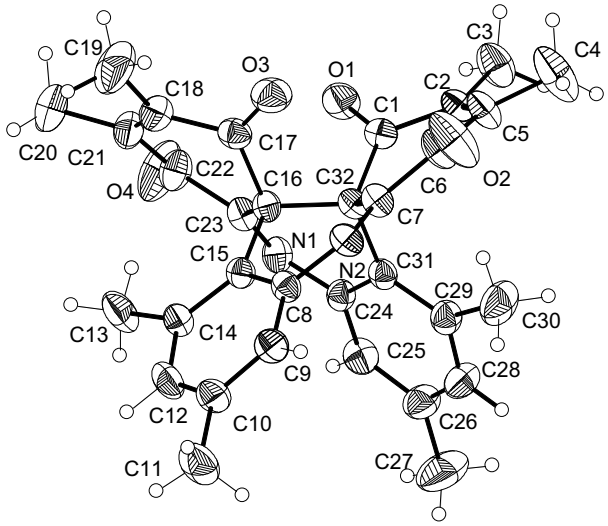


Figure 1. The molecular structure of **4a**.

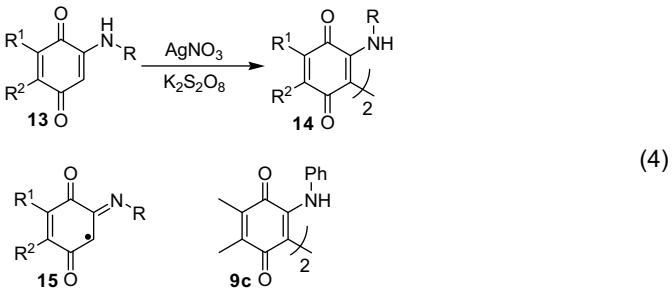
acetate in formic acid at 0 °C, **4a** was obtained in 56% yield (Table 1, entry 1). The structure of **4a** was revealed by ^{1}H NMR and ^{13}C NMR analyses. In addition, the NMR-based structure was confirmed by single crystal X-ray crystallographic analysis (Figure 1).[9] By using acetic acid as solvent, this reaction only resulted in the deterioration of **1a** and no desired product **4a** can be found after stirred at room temperature for 16 h (entry 2). Although the mechanistic details of this reaction are unclear, dimer **4a** may be formed by the reaction mechanism presented in Scheme 1. Initiation occurs with the manganese(III) oxidation of **1a** to produce imine radical **5a**. Intermolecular coupling[7] of **5a** generates **9a**, which is then oxidized by manganese(III) to produce imine radical **10a**. Six-membered-ring radical cyclization of **10a** gives **11a** after aromatization. Oxidation of **11a** by manganese(III) produces imine radical **12a** and then it undergoes another six-membered-ring radical cyclization and subsequent aromatization to give dimer **4a**. The generalities of this reaction were examined with other 2-phenylamino-1,4-benzoquinones **1** and the results are summarized in Table 1. This reaction worked well and dimers **4** were formed in 21–60% yields. It shows that the reaction yields for this reaction are highly dependent on the effect of substituent on the benzene ring. The reactions of **1d** and **1e** bearing an *ortho*-methyl group gave the corresponding dimers **4d** and **4e** in lower yields (entries 5 and 6). This can be attributed to the steric effect of the *ortho* substituent, which retards the free radical cyclization of **10** and **12** onto the benzene ring. When the electron-withdrawing halogeno groups were substituted on the benzene ring, the yields of **4f** and **4g** are reduced substantially (entries 7 and 8). These results can be rationalized by consideration that the electron deficiency of radical intermediates **10** and **12** makes the rate of free radical cyclization to the halogeno group substituted benzene ring much slower. To test the regioselectivity of this reaction, the oxidative radical reaction of 2-methyl-5-phenylamino-1,4-benzoquinones **1h** and **1i** was next studied. Treatment of **1h** with manganese(III) acetate under the same conditions afforded dimer **4h** exclusively in 51% yield (entry 9). No product derived from the addition of radical **5h** to the C_3 of another **1h** can be found. It indicates that the intermolecular radical coupling reaction of **5h** proceeds in a much faster reaction rate than that of the intermolecular addition of it to C_3 of another **1h**. Reaction of **1i** with manganese(III) acetate gave result similar to **1h**, with the corresponding dimer **4i** as the sole product in 37% yield (entry 10). This reaction was also examined with 2-alkylamino substituted 1,4-benzoquinone. In contrast to the results shown above, the reaction of 5-ethylamino-2,3-dimethyl-1,4-benzoquinone (**13a**) with manganese(III) acetate gave no distinguishable product (entry 11).

Table 1
Oxidative dimerization mediated by manganese(III) acetate

Entry	1,4-Benzoquinone							Product (yield (%))
		R^1	R^2	R^3	R^4	R^5	R^6	
1	**1a**	Me	Me	H	Me	H	Me	**4a** (56)[a]
2	**1a**							**4a** (0)[b]
3	**1b**	Me	Me	H	H	Me	H	**4b** (60)[a]
4	**1c**	Me	Me	H	H	H	H	**4c** (49)[a]
5	**1d**	Me	Me	Me	H	H	H	**4d** (31)[a]
6	**1e**	Me	Me	Me	H	Me	H	**4e** (46)[a]
7	**1f**	Me	Me	H	H	Br	H	**4f** (24)[a]
8	**1g**	Me	Me	H	H	Cl	H	**4g** (21)[a]
9	**1h**	H	Me	H	H	Me	H	**4h** (51)[a]
10	**1i**	H	Me	H	H	H	H	**4i** (37)[a]
11	**13a**							—

[a] These reactions were carried with **1** (0.71 mmol), manganese(III) acetate (2.94 mmol) in formic acid (10 mL) at 0 °C for 30 min.
[b] The reaction mixture was stirred at rt in HOAc for 16 h.

Carbon radical is produced by the Ag(I)/$S_2O_8^{-2}$ redox system and it undergoes efficient addition to the C–C double bond.[10] In this reaction, Ag(II) was generated in situ from Ag(I) by the action of $S_2O_8^{-2}$ and catalytical amount of silver(I) was used. Today's environmental concerns encourage the development of greener reaction conditions. We have continued to study the radical



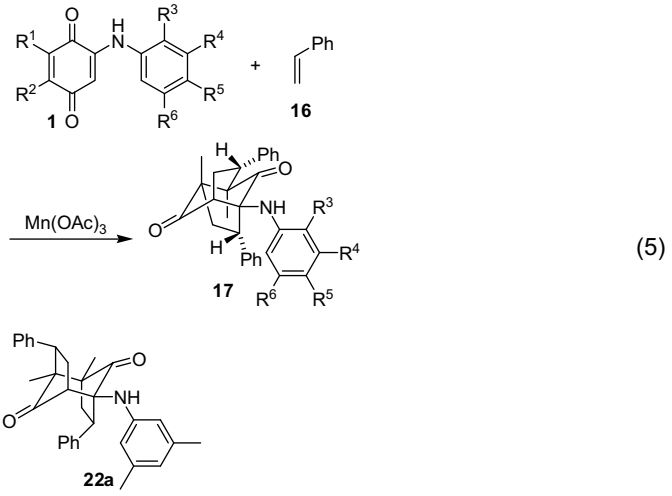
(4)

dimerization reaction of 2-alkylamino substituted 1,4-benzoquinones under Ag(I)/$S_2O_8^{-2}$ conditions (Eq. 4). When 5-ethylamino-2,3-dimethyl-1,4-benzoquinone (**13a**) was treated with silver(I) nitrate and potassium persulfate in acetonitrile–H_2O at 70 °C, **14a** was obtained in 66% yield (Table 1, entry 1). Similar result was obtained when ammonium persulfate was employed in place of potassium persulfate (entry 2). In the absence of silver(I) nitrate, the yield of **14a** decreased to 37% (entry 3). The formation of **14a** occurs from the intermolecular coupling reaction of imine radical **15a**, which was produced by the manganese(III) oxidation of **13a**. To find the optimum reaction conditions, a solvent-screening for this dimerization reaction of **13a** was then undertaken. The change of solvent to DMA, acetone, and dioxane gave **14a** in much poor yields (entries 6–8). In ethanol, **14a** was afforded in 69% yield (entry 4). Encouraged by these initial results, by choosing acetonitrile and ethanol as solvent, we applied these reaction conditions to other 5-ethylamino-1,4-benzoquinones **13b–f**. The reaction of **13b** worked well and **14b** was produced in good yield (entry 9 and 10). Reaction of **13c** under these reaction conditions afforded dimer **14c** in 63% yield (entry 11). Similar to the results shown in Table 1, dimer **14c** was formed in high regioselectivity, no product derived from the addition of radical **15c** to the C_3 of another **13c** can be found. Again, it can be concluded that radical **15c** is preferred to undergo intermolecular coupling reaction. Analogous results were obtained with **13d–f** and are also listed in Table 2 (entries 12–14). We also studied this silver(II) mediated reaction with 2-phenylamino substituted 1,4-benzoquinone **1**. Under Ag(I)/$S_2O_8^{-2}$ conditions, **1c** was converted to the corresponding dimeric product **9c** in 48% yield (entry 15). Contrary to the results shown in Table 1, **9c** is the only product and no trace of **4c** can be found. This can be ascribed to the poor solubility of **9c** in acetonitrile–H_2O. It precipitated as the reaction proceeded and could not undergo further oxidation reaction (**9c**→**4c**).

Table 2
Oxidative dimerization mediated by silver(I) nitrate and potassium persulfate

Entry	1,4-Benzoquinone				Solvent	Product (yield (%))
		R^1	R^2	R		
1	**13a**	Me	Me	Et	CH_3CN–H_2O	**14a** (66)[a]
2	**13a**				CH_3CN–H_2O	**14a** (64)[b]
3	**13a**				CH_3CN–H_2O	**14a** (37)[c]
4	**13a**				EtOH–H_2O	**14a** (69)[a]
5	**13a**				EtOH–H_2O	**14a** (69)[b]
6	**13a**				DMA–H_2O	**14a** (51)[a]
7	**13a**				Acetone–H_2O	**14a** (35)[a]
8	**13a**				Dioxane–H_2O	**14a** (37)[a]
9	**13b**	Me	Me	Bn	CH_3CN–H_2O	**14b** (62)[a]
10	**13b**				EtOH–H_2O	**14b** (67)[d]
11	**13c**	H	Me	Et	EtOH–H_2O	**14c** (63)[a]
12	**13d**	H	Me	Bn	EtOH–H_2O	**14d** (58)[a]
13	**13e**	*t*-Bu	H	Me	EtOH–H_2O	**14e** (70)[a]
14	**13f**	*t*-Bu	H	Bn	CH_3CN–H_2O	**14f** (63)[e]
15	**1c**				CH_3CN–H_2O	**9c** (48)[f]

[a] These reactions were carried with **13** (0.84 mmol), potassium persulfate (1.67 mmol), and silver(I) nitrate (0.25 mmol) at 70 °C for 1 h.
[b] The reaction was performed with silver(I) nitrate and ammonium persulfate under similar reaction conditions.
[c] The reaction was performed with ammonium persulfate under similar reaction conditions.
[d] The reaction yield was based on 89% conversion of **13b**.
[e] The reaction yield was based on 93% conversion of **13f**.
[f] The reaction was carried with **1c**, potassium persulfate, and silver(I) nitrate under similar reaction conditions.



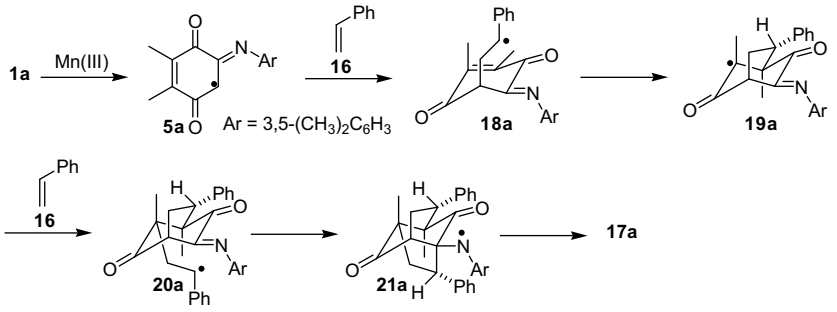
(5)

Radical annulation—the combination of addition and cyclization reaction mediated by manganese(III) acetate has been used for the synthesis of cyclic systems.[11] Since imine radical **5** can be generated effectively from the manganese(III) acetate oxidation of 2-phenylamino-1,4-benzoquinone **1**, we next investigated the manganese(III) mediated radical annulation reaction between **1** and styrene (**16**) (Eq. 5). Treatment of 2,3-dimethyl-5-(3,5-dimethylphenylamino)-1,4-benzoquinone (**1a**), styrene (**16**) with manganese(III) acetate in acetonitrile at 70 °C led to the formation of **17a** in 24% yield (Table 3, entry 1). The structure of **17a** was characterized by ^{1}H NMR and ^{13}C NMR spectra. Furthermore, the exact configuration of **17a** was determined by X-ray crystallographic analysis.[12] Twistane **17a** may be formed by the reaction

Table 3
Radical annulation reaction mediated by manganese(III) acetate

Entry	1,4-Benzoquinone						Product (yield (%))
		R^1	R^2	R^3	R^4		
1	**1a**	H	Me	H	Me	—	**17a** (24)
2	**1a**					*i*-PrOH	**17a** (38)[a]
3	**1a**					*i*-PrOH	**17a** (25)[b]
4	**1a**					Et_3SiH	**17a** (33)[c]
5	**1a**					Ph_3SiH	**17a** (30)[c]
6	**1b**	H	H	Me	H	*i*-PrOH	**17b** (30)[a]
7	**1b**					Et_3SiH	**17b** (25)[a]
8	**1c**	H	H	H	H	*i*-PrOH	**17c** (33)[a]
9	**1d**	Me	H	H	H	*i*-PrOH	**17d** (20)[a]
10	**1e**	Me	H	Me	H	*i*-PrOH	**17e** (21)[a]
11	**1f**	H	H	Br	H	*i*-PrOH	**17f** (31)[a]
12	**1g**	H	H	Cl	H	*i*-PrOH	**17g** (30)[a]
13	**1j**	H	OMe	H	H	*i*-PrOH	**17j** (30)[a]

[a] These reactions were carried with **1** (0.59 mmol), styrene (12.4 mmol), isopropanol (2 mL), and manganese(III) acetate (2.98 mmol) in acetonitrile (8 mL) at 70 °C for 7 h.
[b] The reaction was performed in *i*-PrOH.
[c] These reactions were carried with **1** (0.59 mmol), styrene (12.4 mmol), silane (1.18 mmol), and manganese(III) acetate (2.94 mmol) in acetonitrile (10 mL) at 70 °C for 7 h.



Scheme 2.

mechanism presented in Scheme 2. Manganese(III) oxidation of **1a** produces imine radical **5a**. Intermolecular addition of **5a** to the C–C double bond of styrene generates radical **18a**, which undergoes 6-*exo* radical cyclization to produce radical **19a**. This radical intermediate **19a** undergoes intermolecular addition to another styrene to generate **20a**. Free radical cyclization of **20a** to the imine group followed by hydrogen atom abstraction from the reaction mixture gives **17a**. There is no trace of another expected product **22a**, derived from the 5-*exo* radical cyclization of **18a**, can be found. To improve the reaction yield of **17a**, we next conducted this annulation reaction of **1a** with isopropanol, triethylsilane, and triphenylsilane as hydrogen atom sources (entries 2–5). As shown in Table 3, in the presence of isopropanol, **17a** was produced in best reaction yield (entry 4). Other examples with isopropanol as hydrogen atom source are also listed in Table 3 (entries 7–13). In all cases, **1** was converted to **17** effectively in fair yield. Due to the steric effect of the *ortho*-methyl group, **1d** and **1e** gave the corresponding **17d** and **17e** in lower yields (entries 9 and 10) (Fig. 2).

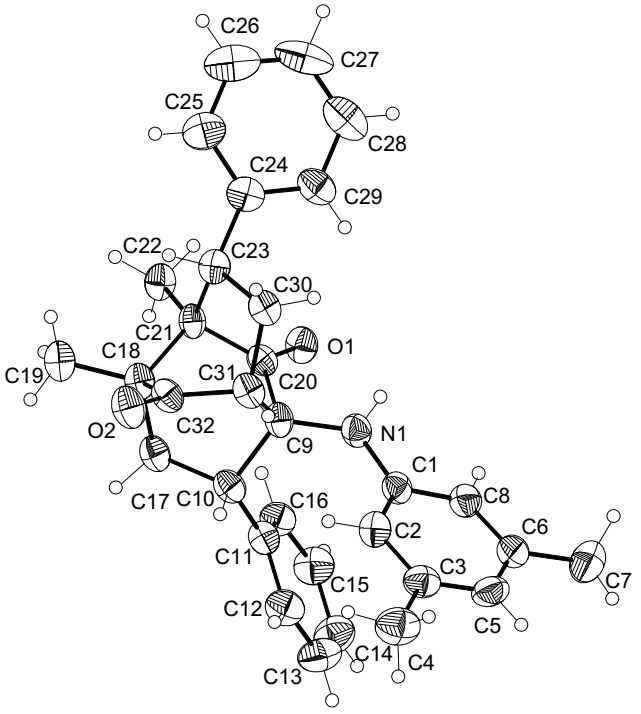


Figure 2. The molecular structure of **17a**.

In conclusion, imine radicals **5** and **15** can be generated from the manganese(III), silver(II) oxidation of 2-amino-1,4-benzoquinones. These free radical reactions provide efficient methods for the generation of the dimeric products **4** and **14**. In the presence of styrene, twistane **17** was afforded from 2-phenylamino-1,4-benzoquinone **1** via a radical annulation reaction of imine radical **5**.

3. Experimental

3.1. General

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260–30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400, AVANCE 500 or AVANCE 300 spectrometer. Chemical shifts are reported in parts per million relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded with Finnigan MAT-95XL mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F_{254} plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh). The starting 2-amino-1,4-benzoquinones **1** and **13** were synthesized according to literature procedure.[13]

3.2. Typical experimental procedure for the manganese(III) mediated dimerization reaction

A mixture of 2,3-dimethyl-5-(3,5-dimethylphenylamino)-1,4-benzoquinone (**1a**, 182 mg, 0.71 mmol) and manganese(III) acetate (788 mg, 2.94 mmol) in formic acid (10 mL) was stirred at 0 °C for 30 min. The reaction mixture was diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bisulfite (50 mL), water (2×50 mL), saturated aqueous sodium bicarbonate (50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel (20 g) using dichloromethane–ethyl acetate (30:1) as eluent, followed by crystallization (chloroform–hexane) to give **4a** (100 mg, 56%).

3.2.1. Dimer *4a*

Yellow powders; mp 271–272 °C (dec); IR (KBr) 1680, 1600, 1255, 1065, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H, 2×CH_3), 2.12 (s, 6H, 2×CH_3), 2.19 (s, 6H, 2×CH_3), 2.25 (s, 6H, 2×CH_3), 6.74 (s, 2H, 2×ArH), 7.31 (s, 2H, 2×ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.4, 14.7, 20.4, 23.0, 56.2, 116.4, 129.6, 135.6, 136.2, 139.9, 144.4, 147.5, 147.8, 157.2, 181.5, 191.7; HRMS calcd for $C_{32}H_{28}N_2O_4$: *m*/*z* 504.2051, found *m*/*z* 504.2050.

3.2.2. Dimer *4b*

Yellow crystals; mp 253–254 °C (dec); IR (KBr) 1680, 1665, 1615, 1375, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H, 2×CH_3), 2.21 (s, 6H, 2×CH_3), 2.34 (s, 6H, 2×CH_3), 6.68 (s, 2H, ArH), 7.11 (d, *J*=7.9 Hz, 2H, ArH), 7.53 (d, *J*=7.9 Hz, 2H, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.7, 14.5, 21.6, 54.9, 122.6, 126.9, 131.0, 131.2,

140.0, 141.3, 146.2, 148.4, 155.8, 181.6, 191.4. Anal. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.63; H, 5.05; N, 5.88.

3.2.3. Dimer ***4c***

Yellow powders; mp 275–276 °C (dec); IR (KBr) 1665, 1610, 1375, 1260, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 6H, 2×CH_3), 2.34 (s, 6H, 2×CH_3), 6.93 (d, J=7.6 Hz, 2H, ArH), 7.18 (t, J=7.6 Hz, 2H, ArH), 7.32 (t, J=7.6 Hz, 2H, ArH), 7.64 (d, J=7.6 Hz, 2H, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.8, 14.5, 54.9, 122.6, 126.4, 130.6, 131.1, 142.0, 146.3, 148.6, 156.6, 181.4, 191.2; HRMS calcd for $C_{28}H_{20}N_2O_4$: m/z 448.1431, found m/z 448.1427.

3.2.4. Dimer ***4d***

Yellow powders; mp 348–349 °C (dec); IR (KBr) 1665, 1610, 1370, 1260, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H, 2×CH_3), 2.32 (s, 6H, 2×CH_3), 2.50 (s, 6H, 2×CH_3), 6.75 (d, J=7.6 Hz, 2H, ArH), 7.04 (t, J=7.6 Hz, 2H, ArH), 7.14 (d, J=7.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 14.4, 17.7, 54.7, 122.6, 124.1, 129.9, 132.2, 139.8, 140.4, 146.1, 148.4, 155.4, 181.4, 191.6; HRMS calcd for $C_{30}H_{24}N_2O_4$: m/z 476.1752, found m/z 476.1744.

3.2.5. Dimer ***4e***

Yellow powders; mp 327–328 °C (dec); IR (KBr) 2920, 1665, 1610, 1260, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 6H, 2×CH_3), 2.17 (s, 6H, 2×CH_3), 2.31 (s, 6H, 2×CH_3), 2.47 (s, 6H, 2×CH_3), 6.51 (s, 2H, ArH), 6.94 (s, 2H, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.7, 14.5, 17.6, 21.5, 54.7, 122.7, 124.7, 133.0, 138.5, 139.6, 140.4, 146.1, 148.2, 154.5, 181.7, 191.8; HRMS calcd for $C_{32}H_{28}N_2O_4$: m/z 504.2043, found m/z 504.2046.

3.2.6. Dimer ***4f***

Yellow crystals; mp 314–315 °C (dec); IR (KBr) 1675, 1610, 1370, 1260, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 6H, 2×CH_3), 2.36 (s, 6H, 2×CH_3), 7.00 (d, J=1.8 Hz, 2H, ArH), 7.48 (dd, J=8.4, 1.8 Hz, 2H, ArH), 7.55 (d, J=8.4 Hz, 2H, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.9, 14.6, 54.5, 124.1, 124.6, 129.2, 132.4, 134.1, 140.8, 146.2, 149.1, 156.0, 180.7, 190.5; HRMS calcd for $C_{28}H_{18}Br_2N_2O_4$: m/z 603.9641, found m/z 603.9637.

3.2.7. Dimer ***4g***

Yellow crystals; mp 315–316 °C; IR (KBr) 2920, 1675, 1550, 1330, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 6H, 2×CH_3), 2.36 (s, 6H, 2×CH_3), 6.86 (d, J=2.0 Hz, 2H, ArH), 7.32 (dd, J=8.5, 2.0 Hz, 2H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.8, 14.5, 54.5, 123.9, 126.4, 131.0, 132.2, 136.3, 140.4, 146.2, 149.1, 156.0, 180.7, 190.5; HRMS calcd for $C_{28}H_{18}Cl_2N_2O_4$: m/z 516.0649, found: m/z 516.0646.

3.2.8. Dimer ***4h***

Yellow powders; mp 209–210 °C (dec); IR (KBr) 1685, 1615, 1565, 1310, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02 (d, J=1.4 Hz, 6H, 2×CH_3), 2.24 (s, 6H, 2×CH_3), 6.79 (d, J=0.8 Hz, 2H, ArH), 7.14 (dd, J=7.9, 0.8 Hz, 2H, ArH), 7.27 (q, J=1.4 Hz, 2H, 2×CH), 7.55 (d, J=7.9 Hz, 2H, ArH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 17.4, 21.6, 55.1, 121.8, 127.2, 131.3, 131.5, 139.5, 139.7, 141.8, 150.9, 155.8, 181.4, 191.8; HRMS calcd for $C_{28}H_{20}N_2O_4$: m/z 448.1417, found m/z 448.1420.

3.2.9. Dimer ***4i***

Yellow powders; mp 235–236 °C (dec); IR (KBr) 1680, 1625, 1565, 1310, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02 (d, J=1.3 Hz, 6H, 2×CH_3), 7.05 (dd, J=7.8, 1.1 Hz, 2H, ArH), 7.23 (td, J=7.8, 1.1 Hz, 2H, ArH), 7.29 (q, J=1.3 Hz, 2H, 2×CH), 7.36 (td, J=7.8, 1.1 Hz, 2H, ArH), 7.67 (dd, J=7.8, 1.1 Hz, 2H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 17.4, 55.1, 121.7, 126.6, 130.88, 130.91, 131.4, 139.7, 141.4, 150.9, 156.5, 181.2, 191.5; HRMS calcd for $C_{26}H_{16}N_2O_4$: m/z 420.1100, found m/z 420.1105.

3.3. Typical experimental procedure for the silver(II) mediated dimerization reaction

A solution of 5-ethylamino-2,3-dimethyl-1,4-benzoquinone (**13a**, 150 mg, 0.84 mmol), potassium persulfate (452 mg, 1.67 mmol), and silver(I) nitrate (43 mg, 0.25 mmol) in ethanol–water (8 mL, 1:3) was heated at 70 °C for 1 h. The reaction mixture was diluted with ethyl acetate (100 mL), washed with water (3×50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel (20 g) using dichloromethane as eluent, followed by crystallization (chloroform–hexane) to give **14a** (104 mg, 69%).

3.3.1. 2,2′-Bi(3-ethylamino-5,6-dimethyl-1,4-benzoquinone) ***14a***

Dark violet crystals; mp 174–175 °C; IR (KBr) 3305, 3265, 1660, 1575, 1300 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, J=7.0 Hz, 6H, 2×CH_3), 2.01 (s, 6H, 2×CH_3), 2.04 (s, 6H, 2×CH_3), 3.13 (dq, J=11.0, 7.0 Hz, 2H, CH_2), 3.25 (dq, J=11.0, 7.0 Hz, 2H, CH_2), 5.61 (br s, 2H, 2×NH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.9, 13.1, 15.2, 37.7, 104.7, 136.1, 143.8, 144.4, 184.06, 184.11. Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.32; H, 6.82; N, 7.85.

3.3.2. 2,2′-Bi(3-benzylamino-5,6-dimethyl-1,4-benzoquinone) ***14b***

Pink crystals; mp 197–198 °C; IR (KBr) 3330, 1650, 1580, 1500, 1300 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 6H, 2×CH_3), 1.97 (s, 6H, 2×CH_3), 4.29 (dd, J=13.6, 5.2 Hz, 2H, CH_2), 4.33 (dd, J=13.6, 5.2 Hz, 2H, CH_2), 5.99 (t, J=5.2 Hz, 2H, 2×NH), 7.06–7.12 (m, 4H, ArH), 7.21–7.31 (m, 6H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.0, 13.2, 47.2, 105.5, 127.1, 127.5, 128.7, 136.4, 137.9, 144.0, 144.3, 183.9, 184.2. Anal. Calcd for $C_{30}H_{28}N_2O_4$: C, 74.98; H, 5.87; N, 5.83. Found: C, 74.98; H, 5.92; N, 5.84.

3.3.3. 2,2′-Bi(3-ethylamino-6-methyl-1,4-benzoquinone) ***14c***

Dark violet crystals; mp 164–165 °C (dec); IR (KBr) 3330, 1670, 1560, 1515, 1290 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J=7.2 Hz, 6H, 2×CH_3), 2.08 (d, J=1.5 Hz, 6H, 2×CH_3), 3.05–3.35 (m, 4H, 2×CH), 5.59 (br s, 2H, 2×NH), 6.52 (q, J=1.5 Hz, 2H, 2×CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.3, 16.9, 37.8, 105.1, 129.1, 144.2, 150.3, 183.7, 184.3. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.77; H, 6.18; N, 8.50.

3.3.4. 2,2′-Bi(3-benzylamino-6-methyl-1,4-benzoquinone) ***14d***

Dark violet crystals; mp 174–175 °C; IR (KBr) 3315, 3290, 1670, 1565, 1335 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (d, J=1.3 Hz, 6H, 2×CH_3), 4.31 (d, J=6.1 Hz, 4H, 2×CH_2), 5.97 (t, J=6.1 Hz, 2H, 2×NH), 6.48 (q, J=1.3 Hz, 2H, 2×CH), 7.06–7.11 (m, 4H, ArH), 7.22–7.32 (m, 6H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 16.8, 47.0, 105.7, 127.1, 127.7, 128.8, 129.2, 137.6, 144.2, 150.1, 183.5, 184.2. Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.17; H, 5.33; N, 6.16.

3.3.5. 2,2′-Bi(5-tert-butyl-3-methylamino-1,4-benzoquinone) ***14e***

Dark red crystals; mp 194–195 °C; IR (KBr) 3310, 1670, 1580, 1510, 1335 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, 6×CH_3), 2.89 (s, 6H, 2×CH_3), 6.56 (s, 2H, 2×CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.9, 30.3, 34.7, 103.5, 135.3, 146.3, 150.9, 183.5, 184.7. Anal. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.83; H, 7.36; N, 7.23.

3.3.6. 2,2′-Bi(3-benzylamino-5-tert-butyl-1,4-benzoquinone) ***14f***

Dark red crystals; mp 164–165 °C (dec); IR (KBr) 3280, 1665, 1575, 1505, 1330 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 18H, 6×CH_3), 4.29 (d, J=5.9 Hz, 4H, 2×CH_2), 6.04 (t, J=5.9 Hz, 2H, 2×NH), 6.49 (s,

2H, 2×CH), 7.07–7.13 (m, 4H, ArH), 7.23–7.32 (m, 6H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.0, 34.8, 47.3, 104.0, 127.2, 127.8, 128.9, 135.3, 137.8, 145.3, 151.1, 183.3, 184.9. Anal. Calcd for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22. Found: C, 75.76; H, 6.75; N, 5.11.

3.3.7. 2,2′-Bi(5,6-dimethyl-3-phenylamino-1,4-benzoquinone) ***9c***

Dark red powder; mp 235–236 °C; IR (KBr) 3360, 3305, 1635, 1580, 1310 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 6H, 2×CH_3), 2.01 (s, 6H, 2×CH_3), 6.84 (d, J=7.5 Hz, 4H, ArH), 6.96 (t, J=7.5 Hz, 2H, ArH), 7.01 (br s, 2H, 2×NH), 7.05 (t, J=7.5 Hz, 4H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.9, 108.4, 123.9, 124.9, 127.8, 135.9, 137.8, 139.2, 144.0, 183.2, 184.1. Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.12; H, 5.33; N, 6.17.

3.4. Typical experimental procedure for the radical annulation reaction

A mixture of 2,3-dimethyl-5-(3,5-dimethylphenylamino)-1,4-benzoquinone (**1a**, 151 mg, 0.59 mmol), styrene (1.29 g, 12.4 mmol), isopropanol (2 mL), and manganese(III) acetate (395 mg, 1.47 mmol) in acetonitrile (8 mL) was heated at 70 °C. After heated for 3 h, the color of manganese(III) acetate disappeared, another manganese(III) acetate (405 mg, 1.51 mmol) was added. The reaction mixture was heated for another 4 h and then diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bisulfite (50 mL), water (2×50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel (20 g) using ethyl acetate–hexane (1:20) as eluent, followed by crystallization (ethyl acetate–hexane) to give **17a** (105 mg, 38%).

3.4.1. rel-(1R,3S,4S,6S,8S,10R)-1,6-Dimethyl-3-(3,5-dimethylphenylamino)-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17a***

White crystals; mp 222–223 °C; IR (KBr) 3375, 2950, 1725, 1605, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.89 (dd, J=13.5, 11.1 Hz, 1H, CH), 1.98 (dd, J=13.5, 9.2 Hz, 1H, CH), 2.08–2.23 (m, 2H, 2×CH), 2.17 (s, 6H, 2×CH_3), 3.08 (dd, J=11.7, 8.5 Hz, 1H, CH), 3.72 (dd, J=4.4, 1.2 Hz, 1H, CH), 3.95 (dd, J=11.1, 9.2 Hz, 1H, CH), 4.77 (s, 1H, NH), 6.23 (s, 2H, ArH), 6.34 (s, 1H, ArH), 6.82 (dd, J=7.6, 1.7 Hz, 2H, ArH), 7.00–7.13 (m, 5H, ArH), 7.27–7.34 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 21.4, 31.1, 37.6, 47.1, 48.1, 51.8, 53.8, 57.2, 70.2, 113.5, 120.3, 127.0, 127.7, 127.8, 128.3, 128.7, 138.5, 138.6, 139.0, 144.1, 214.6, 216.4. Anal. Calcd for $C_{32}H_{33}NO_2$: C, 82.90; H, 7.17; N, 3.02. Found: C, 82.81; H, 7.21; N, 3.00.

3.4.2. rel-(1R,3S,4S,6S,10R)-1,6-Dimethyl-3-(4-methylphenylamino)-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17b***

White powder; mp 201–202 °C; IR (KBr) 3390, 2935, 1730, 1615, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.89 (dd, J=13.5, 11.1 Hz, 1H, CH), 1.98 (dd, J=13.5, 9.1 Hz, 1H, CH), 2.09–2.24 (m, 2H, 2×CH), 2.20 (s, 3H, CH_3), 3.08 (dd, J=11.6, 8.6 Hz, 1H, CH), 3.70 (dd, J=4.5, 1.6 Hz, 1H, CH), 3.94 (dd, J=11.1, 9.1 Hz, 1H, CH), 6.52 (d, J=8.4 Hz, 2H, ArH), 6.82 (dd, J=7.8, 1.4 Hz, 2H, ArH), 6.86 (d, J=8.4 Hz, 2H, ArH), 6.99–7.12 (m, 5H, ArH), 7.24–7.34 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.5, 12.7, 20.3, 30.9, 37.6, 46.9, 48.0, 51.8, 53.7, 57.2, 70.2, 115.4, 127.0, 127.4, 127.6, 127.8, 128.2, 128.7, 129.4, 138.5, 139.0, 141.6, 214.6, 216.2. Anal. Calcd for $C_{31}H_{31}NO_2$: C, 82.82; H, 6.95; N, 3.12. Found: C, 82.80; H, 6.98; N, 3.06.

3.4.3. rel-(1R,3S,4S,6S,10R)-1,6-Dimethyl-3-phenylamino-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17c***

White crystals; mp 204–205 °C; IR (KBr) 3380, 2970, 1730, 1600, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.90 (dd, J=13.5, 11.1 Hz, 1H, CH), 1.99 (dd, J=13.5, 9.1 Hz, 1H, CH), 2.10–2.25 (m, 2H, 2×CH), 3.09 (dd, J=11.6, 8.6 Hz, 1H, CH), 3.72 (dd, J=4.5, 1.6 Hz, 1H, CH), 3.98 (dd, J=11.1, 9.1 Hz, 1H, CH), 4.89 (br s, 1H, NH), 6.61 (dd, J=7.7, 1.2 Hz, 2H, ArH), 6.68 (t, J=7.7 Hz, 1H, ArH), 6.81 (dd, J=7.7, 1.2 Hz, 2H, ArH), 6.98–7.11 (m, 7H, ArH), 7.27–7.34 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 31.0, 37.6, 46.8, 48.1, 51.9, 53.8, 57.2, 70.1, 115.2, 118.2, 127.1, 127.7, 127.8, 128.3, 128.72, 128.74, 128.9, 138.4, 139.0, 144.2, 214.6, 216.1. Anal. Calcd for $C_{30}H_{29}NO_2$: C, 82.73; H, 6.71; N, 3.22. Found: C, 82.81; H, 6.82; N, 3.15.

3.4.4. rel-(1R,3S,4S,6S,10R)-1,6-Dimethyl-3-(2-methylphenylamino)-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17d***

White crystals; mp 249–250 °C; IR (KBr) 3400, 2945, 1725, 1605, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.91 (dd, J=13.5, 11.1 Hz, 1H, CH), 2.00 (dd, J=13.5, 9.2 Hz, 1H, CH), 2.13–2.28 (m, 2H, 2×CH), 3.11 (dd, J=11.5, 8.7 Hz, 1H, CH), 3.78 (dd, J=4.3, 1.4 Hz, 1H, CH), 4.02 (dd, J=11.1, 9.2 Hz, 1H, CH), 4.87 (br s, 1H, NH), 6.63 (t, J=7.5 Hz, 1H, ArH), 6.73 (d, J=7.5 Hz, 2H, ArH), 6.84 (d, J=7.5 Hz, 1H, ArH), 6.94 (d, J=8.0 Hz, 1H, ArH), 6.97–7.03 (m, 2H, ArH), 7.03–7.11 (m, 4H, ArH), 7.27–7.37 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 17.2, 31.0, 37.6, 46.3, 48.1, 52.5, 53.8, 57.1, 70.4, 113.0, 118.1, 124.3, 126.3, 127.0, 127.6, 127.7, 128.3, 128.68, 128.71, 130.4, 138.2, 139.0, 142.5, 215.0, 216.3. Anal. Calcd for $C_{31}H_{31}NO_2$: C, 82.82; H, 6.95; N, 3.12. Found: C, 83.05; H, 7.10; N, 3.07.

3.4.5. rel-(1R,3S,4S,6S,10R)-1,6-Dimethyl-3-(2,4-dimethylphenylamino)-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17e***

White crystals; mp 257–258 °C; IR (KBr) 3390, 2925, 1730, 1515, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.90 (dd, J=13.5, 11.1 Hz, 1H, CH), 1.99 (dd, J=13.5, 9.2 Hz, 1H, CH), 2.12–2.25 (m, 2H, 2×CH), 2.19 (s, 3H, CH_3), 3.09 (dd, J=11.4, 8.8 Hz, 1H, CH), 3.75 (dd, J=4.2, 1.9 Hz, 1H, CH), 3.99 (dd, J=11.1, 9.2 Hz, 1H, CH), 4.72 (s, 1H, NH), 6.67 (s, 1H, ArH), 6.73 (d, J=7.2 Hz, 2H, ArH), 6.80–6.88 (m, 2H, ArH), 6.97–7.10 (m, 5H, ArH), 7.25–7.35 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 17.2, 20.3, 31.0, 37.6, 46.5, 48.1, 52.5, 53.8, 57.1, 70.5, 113.1, 124.4, 126.5, 127.0, 127.2, 127.6, 127.7, 128.3, 128.7, 131.2, 138.3, 139.1, 139.9, 215.1, 216.4. Anal. Calcd for $C_{32}H_{33}NO_2$: C, 82.90; H, 7.17; N, 3.02. Found: C, 82.73; H, 7.18; N, 2.95.

3.4.6. rel-(1R,3S,4S,6S,10R)-3-(4-Bromophenylamino)-1,6-dimethyl-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17f***

White crystals; mp 251–252 °C; IR (KBr) 3385, 2970, 1730, 1595, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.89 (dd, J=13.4, 11.2 Hz, 1H, CH), 1.98 (dd, J=13.4, 9.2 Hz, 1H, CH), 2.06–2.24 (m, 2H, 2×CH), 3.09 (dd, J=11.7, 8.4 Hz, 1H, CH), 3.63 (d, J=3.8 Hz, 1H, CH), 3.92 (dd, J=11.2, 9.2 Hz, 1H, CH), 4.94 (br s, 1H, NH), 6.48 (d, J=7.9 Hz, 2H, ArH), 6.80 (d, J=7.9 Hz, 2H, ArH), 6.99–7.16 (m, 7H, ArH), 7.23–7.34 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 30.9, 37.6, 46.8, 48.0, 51.7, 53.7, 57.2, 69.9, 110.1, 116.7, 127.3, 127.8, 128.0, 128.3, 128.6, 128.7, 131.7, 138.2, 138.8, 143.3, 214.3, 215.7. Anal. Calcd for $C_{30}H_{28}BrNO_2$: C, 70.04; H, 5.49; N, 2.72. Found: C, 69.89; H, 5.42; N, 2.63.

3.4.7. rel-(1R,3S,4S,6S,10R)-3-(4-Chlorophenylamino)-1,6-dimethyl-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17g***

White crystals; mp 241–242 °C; IR (KBr) 3395, 2975, 1730, 1600, 1500 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.88 (dd, J=13.5, 11.2 Hz, 1H, CH), 1.99 (dd, J=13.5, 9.1 Hz, 1H, CH), 2.03–2.26 (m, 2H, 2×CH), 3.09 (dd, J=11.7, 8.4 Hz, 1H, CH), 3.63 (dd, J=4.0, 1.2 Hz, 1H, CH), 3.91 (dd, J=11.2, 9.1 Hz, 1H, CH), 4.93 (br s, 1H, NH), 6.52 (d, J=8.8 Hz, 2H, ArH), 6.79 (dd, J=7.7, 1.4 Hz, 2H, ArH), 6.97–7.15 (m, 7H, ArH), 7.28–7.36 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 30.9, 37.6, 46.8, 48.0, 51.8, 53.7, 57.2,

70.0, 116.2, 123.0, 127.2, 127.7, 127.9, 128.3, 128.6, 128.7, 128.8, 138.2, 138.8, 142.9, 214.3, 215.8. Anal. Calcd for $C_{30}H_{28}ClNO_2$: C, 76.66; H, 6.00; N, 2.98. Found: C, 76.64; H, 6.03; N, 2.92.

3.4.8. rel-(1R,3S,4S,6S,10R)-1,6-Dimethyl-3-(3-methoxyphenyl-amino)-4,10-diphenyl-tricyclo[4,4,0,0^{3,8}]decane-2,7-dione ***17j***

White crystals; mp 197–198 °C; IR (KBr) 3390, 2935, 1730, 1600, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.90 (dd, J=13.5, 11.1 Hz, 1H, CH), 1.99 (dd, J=13.5, 9.2 Hz, 1H, CH), 2.08–2.25 (m, 2H, CH), 3.09 (dd, J=12.5, 8.5 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.71–3.76 (m, 1H, CH), 3.98 (dd, J=11.1, 9.2 Hz, 1H, CH), 6.13 (t, J=2.2 Hz, 1H, ArH), 6.26 (d, J=7.9 Hz, 2H, ArH), 6.84 (dd, J=7.9, 2.2 Hz, 2H, ArH), 6.98 (t, J=7.9 Hz, 1H, ArH), 7.00–7.13 (m, 5H, ArH), 7.27–7.32 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.6, 12.7, 31.0, 37.6, 46.8, 48.0, 51.7, 53.7, 55.0, 57.2, 70.1, 101.6, 103.5, 108.1, 127.1, 127.7, 127.8, 128.3, 128.7, 129.6, 138.4, 138.9, 145.4, 160.4, 214.5, 215.9. Anal. Calcd for $C_{31}H_{31}NO_3$: C, 79.97; H, 6.71; N, 3.01. Found: C, 79.98; H, 6.79; N, 2.93.

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6. Reaction of 2-phenylamino-1,4-naphthoquinones with β-dicarbonyl compounds and manganese(III) acetate in formic acid produced corresponding benzo[*f*]indole-4,7-diones exclusively. See: Ref. 3k.
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9. Crystal data for **4a**: $C_{32}H_{28}N_2O_3$, M=504.21, T=296(2) K, λ=0.71073 Å, Monoclinic, space group $P21/c$, a=12.9982(7) Å, b=13.4719(8) Å, c=18.1372(9) Å, α=90°, β=108.346(2)°, γ=90°, V=3014.6(3) $Å^3$, Z=4, D_c=1.240 mg/m^3, μ=0.083 mm^{-1}, $F(000)$=1192, crystal size 0.65×0.40×0.14 mm^3, reflections collected 24,647, independent reflections 5241 [R(int)=0.0489], refinement method, full-matrix least-squares on F^2, goodness-of-fit on F^2 1.059, final R indices [$I>2\sigma(I)$] R_1=0.0854, wR_2=0.2568, R indices (all data) R_1=0.1158, wR_2=0.2850, largest diff. peak and hole 1.002 and −0.567 e $Å^{-3}$. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 658188. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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12. Crystal data for **17a**: $C_{32}H_{33}NO_2$, M=463.59, T=200(2) K, λ=0.71073 Å, Orthorhombic, space group $Pcab$, a=12.1928(4) Å, b=15.2127(5) Å, c=27.2743(9) Å, α=90°, β=90°, γ=90°, V=5059.0(3) $Å^3$, Z=8, D_c=1.217 mg/m^3, μ=0.075 mm^{-1}, $F(000)$=1984, crystal size 0.42×0.28×3 mm^3, reflections collected 30,151, independent reflections 4627 [R(int)=0.1528], refinement method, full-matrix least-squares on F^2, goodness-of-fit on F^2 1.133, final R indices [$I>2\sigma(I)$] R_1=0.0982, wR_2=0.2173, R indices (all data) R_1=0.1764, wR_2=0.2563, largest diff. peak and hole 0.420 and −0.440 e $Å^{-3}$. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 727230. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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