Manganese(III)-Based Facile Synthesis of 3-Cyano-4,5-dihydrofurans and 4-Cyano-1,2-dioxan-3-ols Using Alkenes and Acylacetonitrile Building Blocks[1]

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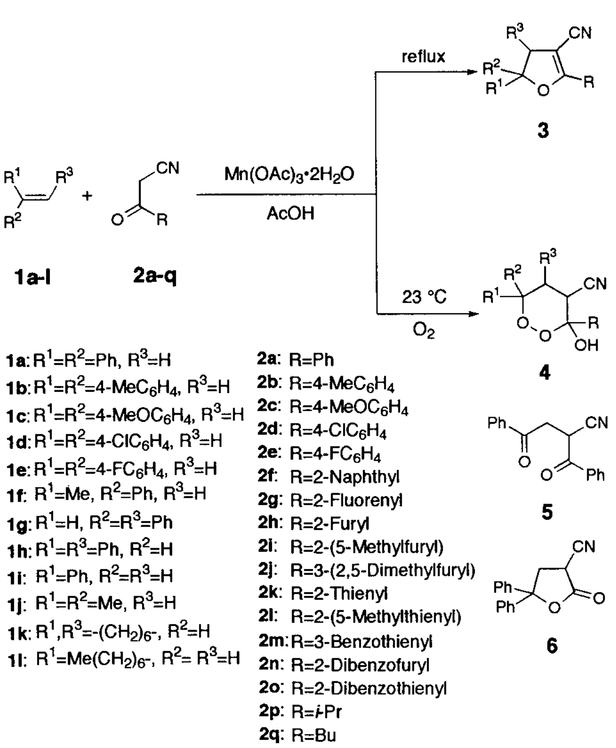
New 3-cyano-4,5-dihydrofurans and 4-cyano-1,2-dioxan-3-ols were alternatively synthesized in good yields by the oxidation of acylacetonitrile building blocks with manganese(III) acetate in the presence of alkenes without any byproducts. The reaction at reflux temperature gave 3-cyano-4,5-dihydrofurans under an argon atmosphere, while 4-cyano-1,2-dioxan-3-ols were obtained at 23 °C under an air atmosphere except for the reaction of styrene with benzoylacetonitrile which afforded 2-cyano-1,4-diphenylbutane-1,4-dione, and the reaction of 1,1-diphenylethene with 2-(2-cyano-1-oxoethyl)-5-methylfuran which yielded 2-cyano-4,4-diphenylbutanolide without any cyclic peroxides. The oxidation of benzoylacetonitrile itself at 23 °C under an air atmosphere in the absence of alkene gave benzoic acid. Easy conversion of the 1,2-dioxanes to furans was demonstrated, and mechanisms for the formation of dihydrofurans and dioxanes as well as the unusual transformation to butanedione and butanolide were also discussed.

One of the methodologies for the synthesis of 4*H*-pyran,[2] 2-pyridone,[3] and furan derivatives[4] is to use acylacetonitrile building blocks.[5] Since it is known that α-protons of the acylacetonitriles are more acidic than those of the methyl ketones, it is logical to use the acylacetonitrile building blocks at the first stage of the aldol-like condensation in the synthesis of these heterocyclic compounds.[2-5] In the course of manganese(III)-mediated oxidations, Fristad et al. reported that α-cyanoacetic acid was oxidized 3×10^5 times faster than acetic acid based on the α-hydrogen acidity.[6] It was expected that acylacetonitriles would be oxidized by manganese(III) acetate via the similar manner in the oxidation of α-cyanoacetic acid[6-8] and 1,3-dicarbonyl compounds[9] to give acylcyanomethyl radicals, •CH(COR)CN, which would attack alkenic double bonds to produce heterocyclic compounds in one step.[10-13] In our preliminary communication,[1] we showed that benzoylacetonitrile (**2a**) was oxidized with manganese(III) acetate in the presence of 1,1-diphenylethene (**1a**) to give 3-cyano-2,5,5-triphenyl-4,5-dihydrofuran (**3aa**) at reflux temperature and 4-cyano-3,6,6-triphenyl-1,2-dioxan-3-ol (**4aa**) at 23 °C, respectively. This was a very simple and convenient reaction for use in forming substituted dihydrofurans and 1,2-dioxanes without any byproducts with only simple temperature monitoring as a stipulation. We applied the reaction to many alkenes and acylacetonitriles, and obtained good results. Herein we report the results in detail and discuss the reaction mechanism.

Nineteen acylacetonitrile building blocks **2a–s**, prepared by cyanation of α-bromoacetyl derivatives, were allowed to react with alkenes **1a–l** in boiling acetic acid under argon to give the corresponding dihydrofurans **3** (Scheme 1 and Table 1).[1,10] The oxidation reaction was nearly finished within 1 min, and good results were obtained when 1,1-diarylethenes **1a–e** were used (Entries 1–5, 12–27). When a similar reaction was carried out at 23 °C under bubbling dry air, however, 1,2-dioxan-3-ols **4** were produced in high yields (Scheme 1 and Table 2). Although the formation of dioxane proceeded by the use of a catalytic amount of manganese(III) acetate,[13] the best results were obtained at the molar ratio of **1**:**2**:manganese(III) acetate = 1:2:0.5 (Entries 30–35, 41–47, 49–55). Use of *trans*-stilbene (**1g**), cyclooctene (**1k**), and non-1-ene (**1l**) did not react favorably under either set of conditions, affording the corresponding **4** in poor yields (Entries 36, 39, 40). In addition, the dioxane was not formed in the case of styrene (**1i**), but 2-cyano-1,4-diphenylbutane-1,4-dione (**5**) was obtained (Entry 37). Surprisingly, a similar reaction of **1a** with 2-(2-cyano-1-oxoethyl)-5-methylfuran (**2i**) gave 2-cyano-4,4-diphenylbutanolide (**6**) without any dioxanes (Entry 48).



Scheme 1

Using **2r** and **2s** which contain two acylacetonitrile functionalities led to the production of bis(dihydrofuryl)arenes **3ar** and **3as** at reflux temperature, while double dioxane ring formation occurred at 23 °C to yield **4ar** and **4as** as shown in Scheme 2 (Entries 28, 29, 56, 57).

It is possible to convert cyanodioxanes **4** to the corresponding cyanofurans by acid-catalyzed decomposition.[14] For example, dioxanes **4aa** and **4aj** were readily transformed by treatment with perchloric acid to 3-cyano-5-phenylfurans **7a** (61 %) and **7j** (46 %), respec-

Table 1. Reaction of Alkenes (**1a–l**) with Acylacetonitriles (**2a–s**) in the Presence of Manganese(III) Acetate at Reflux Temperature[a]

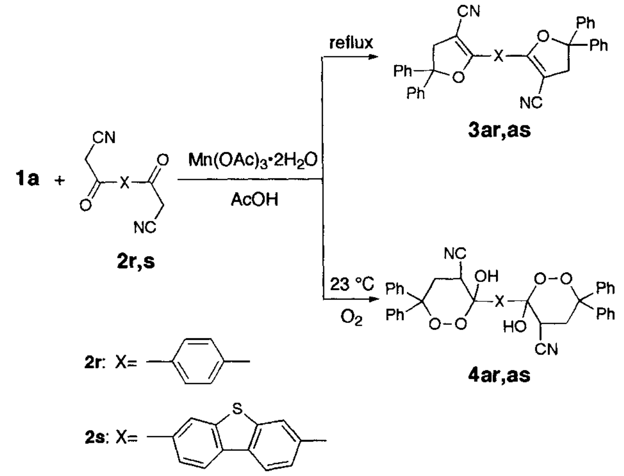
Entry	Alkene	Acylaceto-nitrile	Molar ratio[b]	Time (min)	Product Yield (%)[c]
1	**1a**	**2a**	1:2:3	1	**3aa** (65)
2	**1b**	**2a**	1:2:3	1	**3ba** (86)
3	**1c**	**2a**	1:2:3	1	**3ca** (80)
4	**1d**	**2a**	1:2:3	1	**3da** (59)
5	**1e**	**2a**	1:2:3	1	**3ea** (62)
6	**1f**	**2a**	1:2:3	1	**3fa** (25)
7	**1g**	**2a**	1:2:8	3	**3ga** (34)
8	**1h**	**2a**	1:2:8	3	**3ga** (24)[d]
9	**1i**	**2a**	1:2:3	1	**3ia** (12)
10	**1j**	**2a**	1:1.5:2	5	**3ja** (4)[e,f]
11	**1k**	**2a**	1:2:3	3	**3ka** (6)
12	**1a**	**2b**	1:2:3	1	**3ab** (67)
13	**1a**	**2c**	1:2:3	1	**3ac** (67)
14	**1a**	**2d**	1:2:3	1	**3ad** (74)
15	**1a**	**2e**	1:2:3	1	**3ae** (66)
16	**1a**	**2f**	1:2:3	1	**3af** (68)
17	**1a**	**2g**	1:2:3	1	**3ag** (66)
18	**1a**	**2h**	1:2:3	1	**3ah** (50)
19	**1a**	**2i**	1:2:3	1	**3ai** (64)
20	**1a**	**2j**	1:2:3	1	**3aj** (68)
21	**1a**	**2k**	1:2:3	1	**3ak** (88)
22	**1a**	**2l**	1:2:3	1	**3al** (60)
23	**1a**	**2m**	1:2:3	1	**3am** (63)
24	**1a**	**2n**	1:2:3	1	**3an** (70)
25	**1a**	**2o**	1:2:3	1	**3ao** (70)
26	**1a**	**2p**	1:2:3	1	**3ap** (62)
27	**1a**	**2q**	1:2:3	4 h	**3aq** (59)
28	**1a**	**2r**	2.4:1:6	3	**3ar** (36)[f]
29	**1a**	**2s**	2.4:1:6	3	**3as** (20)[f]

[a] The reaction was carried out under an argon atmosphere.
[b] **1**:**2**:manganese(III) acetate.
[c] Isolated yield based on the amount of **1** used.
[d] Alkene **1h** (51%) was recovered.
[e] The reaction was carried out at 80 °C.
[f] Yield based on the amount of **2** used.

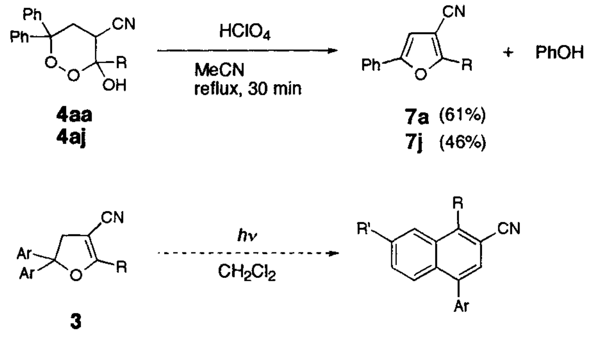
Table 2. Reaction of Alkenes (**1a–l**) with Acylacetonitriles (**2a–s**) in the Presence of Manganese(III) Acetate at 23 °C[a]

Entry	Alkene	Acylaceto-nitrile	Molar ratio[b]	Time (h)	Product Yield (%)[c]
30	**1a**	**2a**	1:2:0.5	3.0	**4aa** (86)
31	**1b**	**2a**	1:2:0.5	1.3	**4ba** (88)
32	**1c**	**2a**	1:2:0.5	1.2	**4ca** (92)
33	**1d**	**2a**	1:2:0.5	4.0	**4da** (80)
34	**1e**	**2a**	1:2:0.5	4.0	**4ea** (74)
35	**1f**	**2a**	1:2:0.5	1.3	**4fa** (61)
36	**1g**	**2a**	1:4:1	40.0	**4ga** (13)[d]
37	**1i**	**2a**	1:2:0.5	1.5	**5** (31)
38	**1j**	**2a**	1:1:2	3.0	**4ja** (41)[e]
39	**1k**	**2a**	1:2:1	16.0	**4ka** (25)
40	**1l**	**2a**	1:2:1	16.0	**4la** (7)
41	**1a**	**2b**	1:2:0.5	3.0	**4ab** (86)
42	**1a**	**2c**	1:2:0.5	3.0	**4ac** (85)
43	**1a**	**2d**	1:2:0.5	3.0	**4ad** (92)
44	**1a**	**2e**	1:2:0.5	3.0	**4ae** (86)
45	**1a**	**2f**	1:2:0.5	3.0	**4af** (91)
46	**1a**	**2g**	1:2:0.5	3.0	**4ag** (76)
47	**1a**	**2h**	1:2:0.5	1.5	**4ah** (70)
48	**1a**	**2i**	1:2:0.5	1.5	**6** (83)
49	**1a**	**2j**	1:2:0.5	1.5	**4aj** (61)
50	**1a**	**2k**	1:2:0.5	1.5	**4ak** (72)
51	**1a**	**2m**	1:2:0.5	3.0	**4am** (81)
52	**1a**	**2n**	1:2:0.5	3.0	**4an** (80)
53	**1a**	**2o**	1:2:0.5	3.0	**4ao** (70)
54	**1a**	**2p**	1:2:0.5	3.0	**4ap** (86)
55	**1a**	**2q**	1:2:0.5	3.0	**4aq** (92)
56	**1a**	**2r**	2.4:1:1	3.0	**4ar** (40)[e]
57	**1a**	**2s**	2.4:1:1	3.0	**4as** (24)[e]

[a] The reaction was carried out under bubbling dry air.
[b] **1**:**2**:manganese(III) acetate.
[c] Isolated yield based on the amount of **1** used.
[d] Alkene **1g** (40%) was recovered.
[e] Yield based on the amount of **2** used.



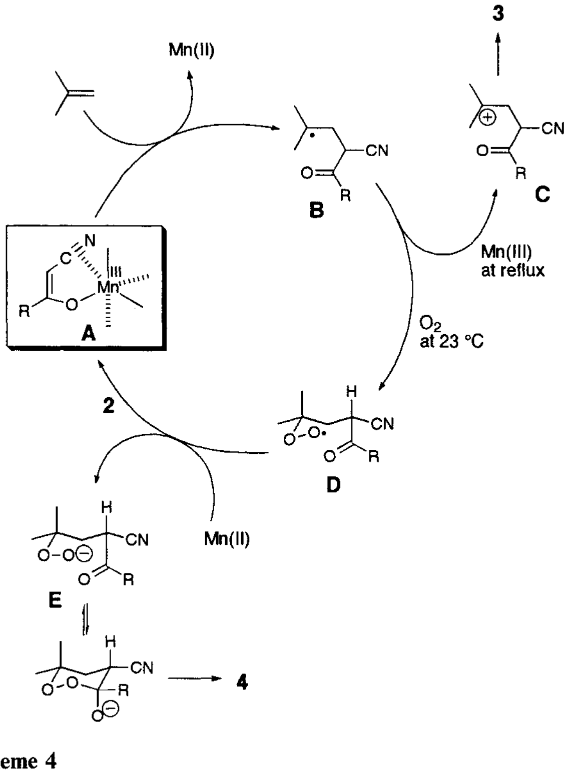
Scheme 2



Scheme 3

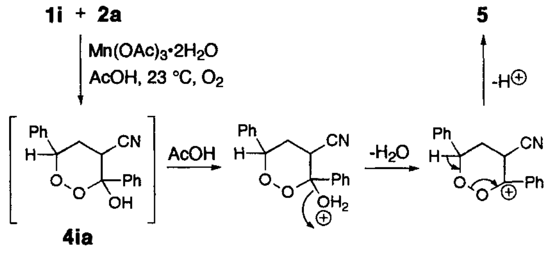
tively (Scheme 3).[14] In addition, the 5-aryl-3-cyano-4,5-dihydrofurans **3** will be excellent candidates for the photochemical synthesis of cyanonaphthalene derivatives.[15]

It seemed that the formation of new complex **A** initiated the present reaction according to a similar mechanism for the reaction with 1,3-dicarbonyl compounds (Scheme 4).[11,13] We failed to isolate the complex **A** from the solution; however, manganese(III) acetate readily reacted with 4,4,4-trifluoro-1-phenylbutane-1,3-dione to give tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)manganese(III) which was isolated and characterized. Several alkenes were oxidized with the complex at reflux temperature to give the corresponding 3-benzoyl-2-trifluoromethyl-4,5-dihydrofurans.[10] Based on the isolated products, it was strongly suggested that complex **A** should be formed at the first stage. The weak interaction of complex **A** and the alkene would induce a concerted one-electron transfer from the alkene to metal center via the coordinated acylacetonitrile ligand to form radical **B** at the second stage.[16] When the reaction was carried out at reflux temperature, further oxidation occurred and dihydrofuran **3** was obtained via cyclization of cation **C**. Therefore, in order to prepare **3**, more than two stoichiometric equivalents of manganese(III) acetate were needed. On the other hand, molecular oxygen should be trapped with radical **B** at 23 °C to yield peroxyl radical **D**, which is easily reduced with manganese(II) and cyclized to give 1,2-dioxan-3-ol **4**. The manganese(III) species which was generated by the reduction of **D** should react with another acylacetonitrile **2** again to give the complex **A**. That is, the catalytic cycle for the formation of 1,2-dioxane would be achieved in a similar way to the manganese(III)-1,3-dicarbonyl compound system.[13]



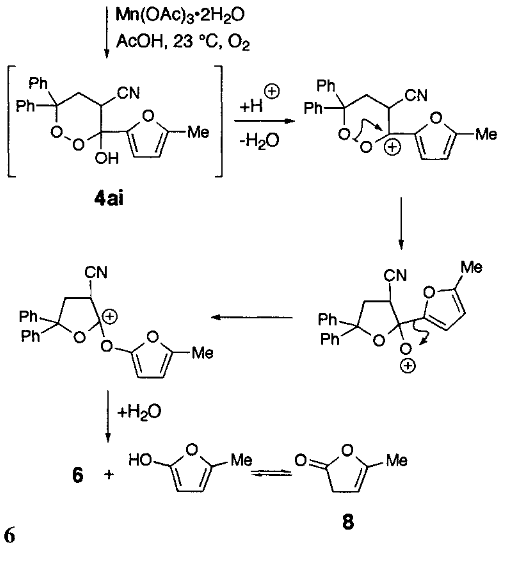
Scheme 4

The formation of butane-1,4-dione **5** deserves comment (Entry 37). Although it could be assumed that **5** might be formed by the manganese(III) oxidation in the absence of molecular oxygen, a similar experiment under argon gave only a trace amount of **5** and unreacted **2a**. It was suggested that molecular oxygen must be essential for the production of **5**. The reaction under air should give the corresponding 1,2-dioxane **4ia** followed by dehydration and subsequent deprotonation to afford **5** (Scheme 5). There were some precedents for the decomposition of the 1,2-dioxane ring to give butane-1,4-diones.[11,17,18] In addition, prolonged stirring in the reaction of **1c** with **2a** in acetic acid led to slight decomposition of dioxane **4ca** to form the corresponding butane-1,4-dione (23 %) and 4-methoxyphenol (20 %) after 14 h. The decomposition of **4ca** could be explained by the acid-catalyzed rearrangement of the 1,2-dioxane.[11,18]



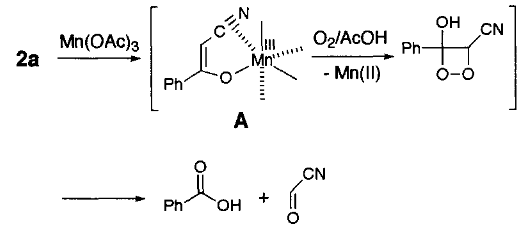
Scheme 5

The mechanism for the formation of lactone **6** has yet to be elucidated at this time (Entry 48). Corey and Gross reported that cyanoacetic acid reacted with manganese(III) acetate and alkenes at 23 °C for 15 min to form the corresponding α-cyano-γ-lactones in 77–85 % yields.[8] We repeated the reaction of **1a** with cyanoacetic acid according to their reaction conditions; however, **6** was obtained in only 5 % yields, and **1a** (77 %) was recovered. This experiment supports the assumption that the cyanoacetic acid radicals, $\cdot CH(CN)CO_2H$, might not be formed under our reaction conditions of **1a** and **2i**. We therefore postulated that the lactone **6** may be formed by degradation of the corresponding 1,2-dioxan-3-ol **4ai** under the reaction conditions (Scheme 6). In fact, the fragment lactone **8** was detected in the reaction mixture by GC/MS (*m*/*z* 98 M^+) and IR spectrometry (ν C=O 1790 cm^{-1}) after the oxidation. In addition, stirring 3-(2-furyl)-1,2-dioxan-3-ol **4ah** at 23 °C in acetic acid for 36 h in the presence of manganese(II) acetate afforded the same butanolide **6** in 14 % yield. Furthermore, normal acid-catalyzed decomposition of **4ah** in acetonitrile gave **6** (54 %) rather than 3-cyano-2-(2-furyl)-5-phenylfuran (16 %) (See Experimental Section). Consequently, the plausible mechanism via furyl migration is proposed as shown in Scheme 6.



Scheme 6

Surprisingly, the reaction of **2a** (1 mmol) with manganese(III) acetate (0.5 mmol) at 23 °C under air in the absence of alkene gave benzoic acid in 52 % yield. The same reaction under argon and the reaction with manganese(II) acetate gave only **2a** unchanged, respectively, and benzoic acid was not detected at all. It was suggested that molecular oxygen must be essential for the formation of benzoic acid. That is, molecular oxygen in the air must be reacted with the complex **A** which should be formed by the interaction of **2a** with manganese(III) acetate. Benzoic acid would than be produced via decomposition of the corresponding 1,2-dioxetane (Scheme 7).[19]



Scheme 7

In conclusion, a one-step synthesis of 3-cyano-4,5-dihydrofurans **3** and 4-cyano-1,2-dioxan-3-ols **4** was independently achieved by the thermodynamically controlled manganese(III)-based oxidation of alkenes with acylacetonitrile building blocks. The present reactions were very simple and clean, producing the desired compound without formation of any side products. This is in contrast to the formation of dihydrofurans and 1,2-dioxan-3-ols using 1,3-dicarbonyl compounds, which also produced benzophenones and/or 2-hydroxyethyl acetates.[10–13,18]

All of the ^1H and ^{13}C NMR spectra were taken with a JNM PMX-60SI (60 MHz), a JNM EX90 (90 MHz for ^1H and 22.5 MHz for ^{13}C), or JNM EX400 FT NMR (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer, respectively, with tetramethylsilane being used as the internal standard. The chemical shifts are shown in δ values (ppm). The IR spectra were measured on a JASCO A-102 IR spectrometer. The IR spectral data are expressed in cm^{-1}. Mass spectra were measured on either a SHIMADZU GCMS QP5000 or a JMS-LX1000 mass spectrometer. All of the melting points were determined with a Yanaco micromelting-point apparatus MP-J3 and were uncorrected. Elemental analyses were performed at the Elemental Analysis Center, Faculty of Pharmacy, Kumamoto University, Kumamoto, and Faculty of Science, Kyushu University, Fukuoka, Japan.

Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind. Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to the method described in literature.[11] 1,1-Diarylethenes were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides. Other alkenes were purchased from Wako Pure Chemical Ind. Ltd. and used as received. Benzoylacetonitrile was purchased from Tokyo Kasei Ind. Ltd. and was used as received. Other acylacetonitriles were prepared by bromination followed by cyanation of the corresponding methyl ketones.[20]

Manganese(III)-Based Reaction of Alkenes 1a–l with Acylacetonitriles 2a–s in Refluxing Acetic Acid; General Procedure:

Alkene **1** (1 mmol) was weighed into a 50 mL flask equipped with a magnetic stirrer. Glacial HOAc (15 mL) and acylacetonitrile **2** (2 mmol) were added. The mixture was heated in an oil-bath and $Mn(OAc)_3$ (3 mmol) was added just before refluxing. The mixture was then heated and stirred until the dark brown color of $Mn(OAc)_3$ disappeared (normally within 1 min). The solvent was removed in vacuo and the residue was triturated with H_2O (15 mL) followed by extraction with $CHCl_3$ (3 × 20 mL). The extract was dried (Na_2SO_4), filtered and concentrated to dryness. The products were separated on silica gel TLC (Wakogel B-10 or Whatman K6F silica gel 60A) with $CHCl_3$ as the developing solvent. The molar ratios, reaction times, and product yields are summarized in Table 1. Analytical samples were further purified by recrystallization from an appropriate solvent mentioned below except for liquid products. Specific details are given below.

3-Cyano-2,5,5-triphenyl-4,5-dihydrofuran (**3aa**): colorless prisms (from $CHCl_3$-hexane); mp 142 °C.

IR ($CHCl_3$): ν = 2196 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.3–7.3 (15H, m, arom H), 3.7 (2H, s, CH_2).

^{13}CNMR ($CDCl_3$): δ = 165.3 (C-2), 143.9, 127.9 (arom C), 131.5, 128.8, 128.6, 128.0, 127.2, 125.6 (arom CH), 117.3 (CN), 92.9 (C-5), 79.1 (C-3), 45.6 (CH_2).

MS: m/z (rel intensity): 323 (M$^+$, 47), 207 (10), 165 (18), 105 (100), 77 (84).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.64; H, 5.30; N, 4.33.

3-Cyano-2-(4-methylphenyl)-5,5-diphenyl-4,5-dihydrofuran (**3ab**): colorless needles (from $CHCl_3$-hexane); mp 110 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.1–7.2 (14H, m, arom H), 3.7 (2H, s, CH_2), 2.3 (3H, s, Me).

Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.67; N, 4.15. Found: C, 85.19; H, 5.62; N, 4.20.

3-Cyano-2-(4-methoxyphenyl)-5,5-diphenyl-4,5-dihydrofuran (**3ac**): colorless needles (from $CHCl_3$-hexane); mp 127 °C.

IR ($CHCl_3$): ν = 2196 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.2–6.8 (14H, m, arom H), 3.8 (3H, s, OMe), 3.7 (2H, s, CH_2).

Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.70; H, 5.57; N, 3.97.

2-(4-Chlorophenyl)-3-cyano-5,5-diphenyl-4,5-dihydrofuran (**3ad**): colorless needles (from $CHCl_3$-hexane); mp 114 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.1–7.2 (14H, m, arom H), 3.7 (2H, s, CH_2).

Anal. Calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91. Found: C, 77.07; H, 4.38; N, 3.98.

3-Cyano-2-(4-fluorophenyl)-5,5-diphenyl-4,5-dihydrofuran (**3ae**): colorless needles (from $CHCl_3$-hexane); mp 109 °C.

IR ($CHCl_3$): ν = 2204 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.2–7.0 (14H, m, arom H), 3.7 (2H, s, CH_2).

Anal. Calcd for $C_{23}H_{16}FNO$: C, 80.92; H, 4.72; N, 4.10. Found: C, 80.86; H, 4.86; N, 4.04.

3-Cyano-2-(2-naphthyl)-5,5-diphenyl-4,5-dihydrofuran (**3af**): colorless prisms (from $CHCl_3$-hexane); mp 138 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^1HNMR ($CDCl_3$): δ = 8.6–7.2 (17H, m, arom H), 3.7 (2H, s, CH_2).

^{13}CNMR ($CDCl_3$): δ = 165.1 (C-2), 143.8, 134.5, 132.6, 125.2 (arom C), 129.0, 128.5, 128.0, 127.9, 127.7, 126.8, 125.6, 123.3 (arom CH), 117.4 (CN), 92.8 (C-5), 79.5 (C-3), 45.7 (CH_2).

Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.75; H, 5.20; N, 3.81.

3-Cyano-2-(2-fluorenyl)-5,5-diphenyl-4,5-dihydrofuran (**3ag**): colorless needles (from $CHCl_3$); mp 209 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.3–7.2 (17 H, m, arom H), 3.9 (2 H, s, CH_2), 3.7 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 165.6 (C-2), 145.0, 144.1, 144.0, 143.6, 140.6, 126.1 (arom C), 128.6, 128.0, 127.8, 127.0, 126.3, 125.6, 125.2, 123.6, 120.6, 120.0 (arom CH), 117.7 (CN), 92.7 (C-5), 78.5 (C-3), 45.6, 36.9 (CH_2).

Anal. Calcd for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.40. Found: C, 87.42; H, 5.18; N, 3.39.

3-Cyano-2-(2-furyl)-5,5-diphenyl-4,5-dihydrofuran (**3ah**): colorless prisms (from $CHCl_3$-hexane); mp 108 °C.

IR ($CHCl_3$): ν = 2204 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.9–7.2 (11 H, m, H-5′, arom H), 7.15 (1 H, dd, J_a = 4 Hz, J_c = 0.6 Hz, H-3′), 6.55 (1 H, dd, J_a = 4 Hz, J_b = 2 Hz, H-4′), 3.7 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 156.7 (C-2), 145.4 (C-5′), 143.6, 143.5 (arom C), 130.0 (C-2′), 128.6, 128.1, 125.7 (arom CH), 116.3 (CN), 114.1, 111.9 (C-3′, C-4′), 94.0 (C-5), 78.1 (C-3), 45.0 (CH_2).

Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.79; H, 4.88; N, 4.50.

3-Cyano-2-[2-(5-methylfuryl)]-5,5-diphenyl-4,5-dihydrofuran (**3ai**): colorless needles (from $CHCl_3$-hexane); mp 112–113 °C.

IR ($CHCl_3$): ν = 2204 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.7–7.2 (10 H, m, arom H), 7.0 (1 H, d, J = 4 Hz, =CH), 6.55 (1 H, d, J = 4 Hz, =CH), 3.7 (2 H, s, CH_2), 2.4 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 156.3 (C-2), 143.6 (arom C), 142.3, 130.0 (C-2′, C-5′), 128.5, 128.0, 125.7 (arom CH), 117.1 (CN), 115.5, 108.4 (C-3′, C-4′), 93.7 (C-5), 76.5 (C-3), 45.0 (CH_2), 13.9 (Me).

MS: m/z (rel intensity) = 327 (M^+, 65), 284 (14), 217 (17), 165 (22), 109 (100), 53 (24), 43 (22).

Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.75; H, 5.22; N, 4.39.

3-Cyano-2-[3-(2,5-dimethylfuryl)]-5,5-diphenyl-4,5-dihydrofuran (**3aj**): colorless prisms (from $CHCl_3$-hexane); mp 116 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.4 (10 H, m, arom H), 6.7 (1 H, s, =CH), 3.7 (2 H, s, CH_2), 2.6 (3 H, s, Me), 2.4 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 162.1 (C-2), 152.8, 151.0 (C-2′, C-5′), 143.9 (arom C), 128.4, 127.8, 125.4 (arom CH), 117.4 (CN), 110.7 (C-3′), 105.0 (C-4′), 93.4 (C-5), 77.7 (C-3), 44.2 (CH_2), 14.4, 13.1 (Me).

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.81; H, 5.54; N, 4.20.

3-Cyano-2-(2-thienyl)-5,5-diphenyl-4,5-dihydrofuran (**3ak**): colorless needles (from $CHCl_3$-hexane); mp 124 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.0–7.0 (13 H, m, arom H), 3.7 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 160.7 (C-2), 143.6 (arom C), 130.2 (C-2′), 130.0, 129.8, 128.2 (C-3′, C-4′, C-5′), 128.6, 128.1, 125.6 (arom CH), 116.9 (CN), 93.7 (C-5), 77.5 (C-3), 45.3 (CH_2).

Anal. Calcd for $C_{21}H_{15}NOS$: C, 76.57; H, 4.59; N, 4.25. Found: C, 76.46; H, 4.68; N, 4.43.

3-Cyano-2-[2-(5-methylthienyl)]-5,5-diphenyl-4,5-dihydrofuran (**3al**): colorless needles (from $CHCl_3$-hexane); mp 126 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.0–7.0 (12 H, m, arom H), 3.7 (2 H, s, CH_2), 2.5 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 160.8 (C-2), 145.3 (C-5′), 143.6 (arom C), 130.3, 126.5 (C-3′, C-4′), 128.4, 127.9, 125.5 (arom CH), 127.6 (C-2′), 117.1 (CN), 93.4 (C-5), 76.2 (C-3), 45.1 (CH_2), 15.4 (Me).

Anal. Calcd for $C_{22}H_{17}NOS$: C, 76.94; H, 4.99; N, 4.08. Found: C, 76.91; H, 4.90; N, 4.31.

3-Cyano-2-(3-benzothienyl)-5,5-diphenyl-4,5-dihydrofuran (**3am**): colorless prisms (from $CHCl_3$); mp 204 °C.

IR ($CHCl_3$): ν = 2196 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.5–7.2 (15 H, m, arom H), 3.7 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 163.0 (C-2), 143.7, 139.8, 136.3, 124.1 (arom C), 131.7, 128.6, 128.1, 125.7, 125.2, 125.1, 124.5, 122.7 (arom CH), 117.6 (CN), 94.2 (C-5), 79.8 (C-3), 44.3 (CH_2).

Anal. Calcd for $C_{25}H_{17}NOS$: C, 79.13; H, 4.51; N, 3.69. Found: C, 79.50; H, 4.40; N, 3.72.

3-Cyano-2-(2-dibenzofuryl)-5,5-diphenyl-4,5-dihydrofuran (**3an**): colorless needles (from $CHCl_3$); mp 178 °C.

IR ($CHCl_3$): ν = 2196 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.7–7.2 (17 H, m, arom H), 3.7 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 165.3 (C-2), 157.6, 156.7, 143.9, 124.7, 123.5, 122.9 (arom C), 128.6, 128.1, 128.0, 126.5, 125.7, 123.4, 121.1, 120.0, 112.1, 111.9 (arom CH), 117.7 (CN), 92.9 (C-5), 78.5 (C-3), 45.7 (CH_2).

Anal. Calcd for $C_{29}H_{19}NO_2$: C, 84.24; H, 4.63; N, 3.39. Found: C, 84.37; H, 4.56; N, 3.66.

3-Cyano-2-(2-dibenzothienyl)-5,5-diphenyl-4,5-dihydrofuran (**3ao**): colorless needles (from $CHCl_3$); mp 203–204 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.9–7.2 (17 H, m, arom H), 3.8 (2 H, s, CH_2).

^{13}C NMR ($CDCl_3$): δ = 165.3 (C-2), 143.8, 142.8, 139.7, 135.8, 135.0, 124.3 (arom C), 128.6, 128.1, 127.5, 125.7, 124.9, 124.9, 123.1, 122.9, 122.1, 120.3 (arom CH), 117.6 (CN), 93.0 (C-5), 78.8 (C-3), 45.8 (CH_2).

Anal. Calcd for $C_{29}H_{19}NOS$: C, 81.09; H, 4.46; N, 3.26. Found: C, 80.74; H, 4.42; N, 2.91.

3-Cyano-2-isopropyl-5,5-diphenyl-4,5-dihydrofuran (**3ap**): colorless prisms (from $CHCl_3$-hexane); mp 90 °C.

IR ($CHCl_3$): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.3 (10 H, m, arom H), 3.5 (2 H, s, CH_2), 3.0 (1 H, q, J = 6.9 Hz, CH), 1.3 (6 H, d, J = 6.9 Hz, Me × 2).

Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.04; H, 6.69; N, 4.86.

2-Butyl-3-cyano-5,5-diphenyl-4,5-dihydrofuran (**3aq**): colorless liquid.

IR ($CHCl_3$): ν = 2204 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.3 (10 H, m, arom H), 3.5 (2 H, s, CH_2), 2.5 (2 H, t, J = 6.6 Hz, CH_2), 1.9–1.0 (4 H, m, CH_2 × 2), 0.9 (3 H, t, J = 6.6 Hz, Me).

MS: m/z (rel intensity) = 303 (M^+, 41), 261 (23), 246 (100), 191 (24), 165 (35), 85 (71), 77 (17), 57 (90), 41 (53).

1,4-Bis[2-(3-cyano-5,5-diphenyl-4,5-dihydrofuryl)]benzene (**3ar**): colorless plates (from $CHCl_3$; mp 298 °C (dec).

IR (KBr): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.2 (4 H, s, arom H), 7.5–7.2 (20 H, m, Ph × 4), 3.8 (4 H, s, CH_2 × 2).

Anal. Calcd for $C_{40}H_{28}N_2O_2$: C, 84.78; H, 4.62; N, 4.94. Found: C, 84.48; H, 4.90; N, 4.96.

3,8-Bis[2-(3-cyano-5,5-diphenyl-4,5-dihydrofuryl)]dibenzothiophene (**3as**): colorless needles (from $CHCl_3$-hexane); mp 257 °C.

IR (KBr): ν = 2200 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.9–7.2 (26 H, m, arom H), 3.8 (4 H, s, CH_2 × 2).

Anal. Calcd for $C_{46}H_{30}N_2O_2S$: C, 81.87; H, 4.48; N, 4.15. Found: C, 81.91; H, 4.60; N, 4.20.

3-Cyano-5,5-bis(4-methylphenyl)-2-phenyl-4,5-dihydrofuran (**3ba**): colorless liquid.

IR ($CHCl_3$): ν = 2196 (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.3–7.1 (13 H, m, arom H), 3.7 (2 H, s, CH_2), 2.3 (6 H, s, Me × 2).

^{13}C NMR ($CDCl_3$): δ = 165.1 (C-2), 141.0, 137.6, 127.9 (arom C), 131.2, 129.0, 128.6, 127.0, 125.9 (arom CH), 117.5 (CN), 92.8 (C-5), 78.9 (C-3), 45.4 (CH_2), 20.8 (Me × 2).

MS: *m*/*z* (rel intensity) = 351 (M^+, 35), 350 (36), 207 (18), 105 (100), 77 (38).

3-Cyano-5,5-bis(4-methoxyphenyl)-2-phenyl-4,5-dihydrofuran (**3ca**): yellow liquid.

IR ($CHCl_3$): $\nu = 2196$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.3–6.6$ (13H, m, arom H), 3.8 (6H, s, OMe × 2), 3.7 (2H, s, CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 165.1$ (C-2), 159.1, 136.0, 127.9 (arom C), 131.3, 127.0, 126.9, 113.7 (arom CH), 117.3 (CN), 92.7 (C-5), 78.8 (C-3), 55.1 (OMe × 2), 45.5 (CH_2).

MS: *m*/*z* (rel intensity) = 383 (M^+, 14), 278 (24), 170 (10), 105 (100), 77 (26).

Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.85. Found: C, 78.44; H, 5.48; N, 4.83.

5,5-Bis(4-chlorophenyl)-3-cyano-2-phenyl-4,5-dihydrofuran (**3da**): colorless microcrystals (from $CHCl_3$-hexane); mp 115 °C.

IR ($CHCl_3$): $\nu = 2200$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.2–7.3$ (13H, m, arom H), 3.7 (2H, s, CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 165.0$ (C-2), 141.8, 134.2, 127.5 (arom C), 131.7, 131.3, 128.8, 127.1, 127.0 (arom CH), 116.8 (CN), 91.8 (C-5), 79.2 (C-3), 45.3 (CH_2).

MS: *m*/*z* (rel intensity) = 391 (M^+, 20), 207 (26), 104 (100), 77 (64), 51 (19).

Anal. Calcd for $C_{23}H_{15}Cl_2NO$: C, 70.42; H, 3.85; N, 3.57. Found: C, 70.52; H, 3.95; N, 3.58.

3-Cyano-5,5-bis(4-fluorophenyl)-2-phenyl-4,5-dihydrofuran (**3ea**): yellow liquid.

IR ($CHCl_3$): $\nu = 2200$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.2–6.2$ (13H, m, arom H), 3.7 (2H, s, CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 167.8$, 156.8, 139.5, 139.4 (arom C), 165.0 (C-2), 131.6, 128.8, 127.6, 127.3, 127.0, 116.0, 114.0 (arom CH), 116.9 (CN), 92.0 (C-5), 79.1 (C-3), 45.6 (CH_2).

MS: *m*/*z* (rel intensity) = 359 (M^+, 33), 358 (30), 201 (14), 105 (100), 77 (61), 51 (19).

3-Cyano-5-methyl-2,5-diphenyl-4,5-dihydrofuran (**3fa**): colorless needles (from $CHCl_3$-hexane); mp 91 °C.

IR ($CHCl_3$): $\nu = 2204$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.1–7.2$ (10H, m, arom H), 3.2 (2H, s, CH_2), 1.8 (3H, s, Me).

^{13}C NMR ($CDCl_3$): $\delta = 165.4$ (C-2), 145.1, 128.2 (arom C), 131.3, 128.63, 128.58, 127.7, 127.1, 124.0 (arom CH), 117.0 (CN), 89.8 (C-5), 78.4 (C-3), 45.9 (CH_2), 29.0 (Me).

MS: *m*/*z* (rel intensity) = 261 (M^+, 12), 260 (97), 105 (100), 77 (97), 51 (36).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.78; N, 5.36. Found: C, 82.50; H, 5.72; N, 5.52.

(4R,5S*)-3-Cyano-2,4,5-triphenyl-4,5-dihydrofuran* (**3ga**): colorless liquid.

IR ($CHCl_3$): $\nu = 2204$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.2–7.3$ (15H, m, arom H), 5.6 (1H, d, $J = 7.3$ Hz, H-5), 4.4 (1H, d, $J = 7.3$ Hz, H-4).

^{13}C NMR ($CDCl_3$): $\delta = 166.6$ (C-2), 139.7, 139.6, 127.6 (arom C), 131.7, 129.2, 128.9, 128.8, 128.1, 127.6, 127.3, 125.3 (arom CH), 116.9 (CN), 92.1 (C-5), 84.3 (C-3), 59.0 (CH).

MS: *m*/*z* (rel intensity) = 323 (M^+, 76), 322 (76), 217 (27), 105 (100), 77 (62), 51 (16).

3-Cyano-2,5-diphenyl-4,5-dihydrofuran (**3ia**): colorless liquid.

IR ($CHCl_3$): $\nu = 2204$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.8$ (1H, dd, $J_1 = 8.79$ Hz, $J_3 = 10.74$ Hz, CH_2-C*H*), 8.1–7.1 (10H, m, arom H), 3.5 (1H, dd, $J_2 = 14.64$ Hz, $J_3 = 10.74$ Hz, CH-CH-H_b), 3.1 (1H, dd, $J_1 = 8.79$ Hz, $J_2 = 14.64$ Hz, CH-CH-H_a).

^{13}C NMR ($CDCl_3$): $\delta = 166.7$ (C-2), 140.3, 127.8 (arom C), 131.5, 128.9, 128.7, 127.2, 125.7 (arom CH), 117.5 (CN), 83.9 (C-5), 79.0 (C-3), 39.8 (C-4).

MS: *m*/*z* (rel intensity) = 247 (M^+, 76), 246 (68), 169 (16), 105 (100), 77 (91), 51 (33).

3-Cyano-5,5-dimethyl-2-phenyl-4,5-dihydrofuran (**3ja**): colorless liquid.

IR ($CHCl_3$): $\nu = 2204$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.1–7.3$ (5H, m, arom H), 2.8 (2H, s, CH_2), 1.5 (6H, s, Me × 2).

MS: *m*/*z* (rel intensity) = 199 (M^+, 76), 198 (54), 184 (28), 105 (100), 94 (33), 77 (77), 51 (44).

A Mixture of cis- and trans-4-Cyano-3-phenyl-2-oxabicyclo[6.3.0]undec-3-ene (**3ka**): colorless liquid.

IR ($CHCl_3$): $\nu = 2196$ (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.1–7.2$ (5H, m, arom H), 4.8 (1H, m, H-1), 3.2 (1H, m, H-5), 2.2–1.1 (12H, m, $-(CH_2)_6-$).

^{13}C NMR ($CDCl_3$): $\delta = 165.1$, 164.9 (C-3), 131.2, 128.6, 127.1 (arom CH), 127.0 (arom C), 118.2, 117.9 (CN), 89.5, 87.7 (C-1), 86.5, 85.7 (C-4), 48.7, 48.0 (C-5), 34.7, 33.9, 29.5, 27.4, 27.1, 27.0, 26.8, 26.2, 25.7, 25.3, 24.3, 22.5 (CH_2).

MS: *m*/*z* (rel intensity) = 253 (M^+, 32), 182 (100), 169 (17), 105 (68), 94 (33), 77 (43), 41 (25).

Manganese(III)-Based Reaction of Alkenes 1a–l with Acylacetonitriles 2a–s at 23 °C; General Procedure:

Alkene **1** (1 mmol) was weighed into a 50 mL three-necked flask equipped with a magnetic stirrer and a gas inlet tube. Glacial HOAc (15 mL), acylacetonitrile (2 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (0.5–1 mmol) were added to the flask, and the mixture was stirred at 23 °C under a dry air stream for the period of time shown in Table 2. The solvent was removed in vacuo and the residue was triturated with H_2O (15 mL) followed by extraction with $CHCl_3$ (3 x 20 mL). The extract was dried (Na_2SO_4), filtered, and concentrated to dryness. The products were separated on silica gel TLC (Wakogel B-10 or Whatman K6F silica gel 60A) developing with 1 % MeOH-CH_2Cl_2. The molar ratios, reaction times, and product yields are summarized in Table 2. Analytical samples were further purified by recrystallization from an appropriate solvent mentioned below except for liquid products. Specific details are given below.

4-Cyano-3,6,6-triphenyl-1,2-dioxan-3-ol (**4aa**): colorless prisms (from $CHCl_3$); mp 178 °C.

IR ($CHCl_3$): $\nu = 3600–3100$ (OH), 2253 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.8–7.3$ (15H, m, arom H), 4.0 (1H, br, OH), 3.3 (3H, s, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 141.5$, 139.2, 137.7 (arom C), 130.0, 128.9, 128.74, 128.68, 128.6, 128.1, 126.9, 126.2, 125.5 (arom CH), 117.8 (CN), 98.2 (C-3), 85.5 (C-6), 35.6 (CH), 33.0 (CH_2).

Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.58; H, 5.40; N, 3.90.

4-Cyano-3-(4-methylphenyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ab**): colorless needles (from $CHCl_3$); mp 165–166 °C.

IR ($CHCl_3$): $\nu = 3600–3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.6–7.1$ (14H, m, arom H), 3.7 (1H, br s, OH), 3.1 (3H, s, CH_2CH), 2.3 (3H, s, Me).

Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.28; H, 5.65; N, 3.78.

4-Cyano-3-(4-methoxyphenyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ac**): colorless prisms (from $CHCl_3$-hexane); mp 155–156 °C.

IR ($CHCl_3$): $\nu = 3600–3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.7–6.7$ (14H, m, arom H), 4.1 (1H, br s, OH), 3.7 (3H, s, OMe), 3.1 (3H, s, CH_2CH).

Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.61. Found: C, 74.51; H, 5.46; N, 3.64.

3-(4-Chlorophenyl)-4-cyano-6,6-diphenyl-1,2-dioxan-3-ol (**4ad**): colorless needles (from $CHCl_3$); mp 186°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.7-7.2$ (14 H, m, arom H), 4.2 (1 H, br s, OH), 3.1 (3 H, s, CH_2CH).

Anal. Calcd for $C_{23}H_{18}ClNO_3$: C, 70.50; H, 4.63; N, 3.57. Found: C, 70.28; H, 4.58; N, 3.60.

4-Cyano-3-(4-fluorophenyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ae**): colorless needles (from $CHCl_3$-hexane); mp 169°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.1-6.8$ (14 H, m, arom H), 4.1 (1 H, br s, OH), 3.1 (3 H, s, CH_2CH).

Anal. Calcd for $C_{23}H_{18}FNO_3$: C, 73.59; H, 4.83; N, 3.73. Found: C, 73.55; H, 4.86; N, 3.68.

4-Cyano-3-(2-naphthyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4af**): colorless needles (from $CHCl_3$); mp 184°C.

IR ($CHCl_3$) $\nu = 3600-3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.0-6.8$ (17 H, m, arom H), 4.1 (1 H, br s, OH), 3.1 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 141.4$, 139.2, 134.9, 133.6, 132.5 (arom C), 128.8, 128.6, 128.5, 128.0, 127.5, 127.0, 126.8, 126.4, 126.2, 125.8, 122.2 (arom CH), 117.8 (CN), 98.3 (C-3), 85.5 (C-6), 35.5 (CH), 32.9 (CH_2).

Anal. Calcd for $C_{27}H_{21}NO_3$: C, 79.59; H, 5.19; N, 3.44. Found: C, 79.92; H, 5.25; N, 3.28.

4-Cyano-3-(2-fluorenyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ag**): colorless needles (from $CHCl_3$); mp 195°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.8-7.1$ (17 H, m, arom H), 4.1 (1 H, br s, OH), 3.8 (2 H, s, CH_2), 3.15 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 143.7$, 143.6, 141.6, 140.7, 139.3, 135.9 (arom C), 128.9, 128.8, 128.7, 128.1, 127.4, 126.9, 126.2, 125.1, 124.3, 122.3, 120.3, 120.0 (arom CH), 117.9 (CN), 98.5 (C-3), 85.5 (C-6), 37.0, 33.2 (CH_2), 35.8 (CH).

Anal. Calcd for $C_{30}H_{23}NO_3$: C, 80.88; H, 5.20; N, 3.14. Found: C, 81.13; H, 5.36; N, 3.30.

4-Cyano-3-(2-furyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ah**): colorless prisms (from $CHCl_3$); mp 136°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 8.0-7.0$ (11 H, m, arom H, H-5′), 6.6 (1 H, dd, $J_1 = 4$ Hz, $J_3 = 0.6$ Hz, H-3′), 6.3 (1 H, dd, $J_1 = 4$ Hz, $J_2 = 2$ Hz, H-4′), 4.2 (1 H, br s, OH), 3.5–2.9 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 149.0$ (C-2′), 143.9 (C-5′), 141.7, 139.2 (arom C), 128.8, 128.6, 128.5, 128.2, 126.8, 126.3 (arom CH), 117.8 (CN), 110.9, 111.0 (C-3′, C-4′), 95.2 (C-3), 85.4 (C-6), 32.2 (CH and CH_2).

Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.49; H, 4.99; N, 4.23.

4-Cyano-3-[3-(2,5-dimethylfuryl)]-6,6-diphenyl-1,2-dioxan-3-ol (**4aj**): colorless needles (from $CHCl_3$-hexane); mp 142°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.7-7.0$ (10 H, m, arom H), 5.8 (1 H, s, =CH), 4.6 (1 H, br s, OH), 3.2–2.9 (3 H, m, CH_2CH), 2.0 (3 H, s, Me), 1.9 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): $\delta = 149.6$, 148.3, 141.6, 139.3, 118.4 (arom C), 128.6, 128.3, 127.8, 126.8, 125.9 (arom CH), 118.1 (CN), 105.0 (=CH), 96.4 (C-3), 85.0 (C-6), 34.8 (CH), 32.6 (CH_2), 13.0, 12.4 (Me).

Anal. Calcd for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.39; H, 5.62; N, 3.87.

4-Cyano-3-(2-thienyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ak**): colorless needles (from $CHCl_3$); mp 140°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.6-6.8$ (13 H, m, arom H), 4.4 (1 H, br s, OH), 3.2 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 141.3$, 140.1, 138.9 (arom C), 128.7, 128.5, 127.9, 127.7, 127.1, 126.9, 126.7, 126.2 (arom CH), 117.7 (CN), 97.2 (C-3), 85.6 (C-6), 36.2 (CH), 33.07 (CH_2).

Anal. Calcd for $C_{21}H_{17}NO_3S$: C, 69.40; H, 4.71; N, 3.85. Found: C, 69.17; H, 4.76; N, 3.78.

4-Cyano-3-(3-benzothienyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4am**): colorless needles (from $CHCl_3$); mp 180°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.9-6.5$ (15 H, m, arom H), 4.3 (1 H, br s, OH), 3.6–3.0 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): $\delta = 141.8$, 141.2, 139.6, 134.5, 132.8 (arom C), 129.3, 128.8, 128.7, 128.6, 128.4, 127.4, 126.1, 124.5, 124.4, 123.0, 122.8 (arom CH), 117.6 (CN), 98.2 (C-3), 85.5 (C-6), 33.6 (CH), 33.1 (CH_2).

Anal. Calcd for $C_{25}H_{19}NO_3S$: C, 72.62; H, 4.63; N, 3.39. Found: C, 72.52; H, 4.61; N, 3.13.

4-Cyano-3-(2-dibenzofuryl)-6,6-diphenyl-1,2-dioxan-3-ol (**4an**): colorless microcrystals (from $CHCl_3$); mp 199–200°C.

IR (KBr): $\nu = 3600-3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR (DMSO-d_6): $\delta = 8.6-7.1$ (17 H, m, arom H), 4.6 (1 H, br s, OH), 3.2 (3 H, m, CH_2CH).

^{13}C NMR (DMSO-d_6): $\delta = 155.9$, 155.7, 145.1, 142.5, 140.3, 134.1, 123.1 (arom C), 128.6, 128.4, 128.0, 127.6, 126.7, 126.2, 125.6, 125.2, 123.3, 120.9, 118.9, 111.7, 111.5 (arom CH), 118.7 (CN), 98.2 (C-3), 84.6 (C-6), 35.9 (CH), 31.6 (CH_2).

Anal. Calcd for $C_{29}H_{21}NO_4$: C, 77.84; H, 4.73; N, 3.13. Found: C, 77.58; H, 4.78; N, 3.15.

4-Cyano-3-(2-dibenzothienyl)-6,6-diphenyl-1,2-dioxan-3-ol (**4ao**): colorless microcrystals (from $CHCl_3$); mp 209°C.

IR (KBr): $\nu = 3600-3100$ (OH), 2248 (CN) cm^{-1}.

^1H NMR (DMSO-d_6): $\delta = 8.4$ (1 H, s, OH), 8.1–7.0 (17 H, m, arom H), 3.5 (1 H, dd, $J_1 = 13.19$ Hz, $J_2 = 3.91$ Hz, CHCH-H_a), 3.3 (1 H, dd, $J_1 = 13.19$ Hz, $J_2 = 3.91$ Hz, CHCH-H_b), 3.0 (1 H, t, $J = 13.19$ Hz, C*H*CH_2).

^{13}C NMR (DMSO-d_6): $\delta = 142.5$, 140.3, 139.8, 139.1, 135.8, 134.6, 134.4 (arom C), 128.6, 128.5, 128.1, 127.6, 127.4, 126.8, 125.6, 124.9, 124.3, 123.2, 123.0, 121.5, 119.3 (arom CH), 118.7 (CN), 98.2 (C-3), 84.6 (C-6), 35.7 (CH), 31.6 (CH_2).

Anal. Calcd for $C_{29}H_{21}NO_3S$: C, 75.14; H, 4.56; N, 3.02. Found: C, 74.92; H, 4.54; N, 3.03.

4-Cyano-3-isopropyl-6,6-diphenyl-1,2-dioxan-3-ol (**4ap**): colorless needles (from $CHCl_3$); mp 149°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.6-7.2$ (10 H, m, arom H), 3.6 (1 H, br s, OH), 3.1 (3 H, s, CH_2CH), 2.9 (1 H, heptet, $J = 6.3$ Hz, CH), 1.0 (3 H, d, $J = 6.3$ Hz, Me), 0.8 (3 H, d, $J = 6.3$ Hz, Me).

Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.54; N, 4.33. Found: C, 74.17; H, 6.44; N, 4.22.

3-Butyl-4-cyano-6,6-diphenyl-1,2-dioxan-3-ol (**4aq**): colorless needles (from $CHCl_3$-hexane); mp 133°C.

IR ($CHCl_3$): $\nu = 3600-3100$ (OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.6-7.2$ (10 H, m, arom H), 3.7 (1 H, br s, OH), 3.0 (3 H, s, CH_2CH), 2.0–0.9 (6 H, m, $CH_2CH_2CH_2$), 0.8 (3 H, t, $J = 5.7$ Hz, Me).

Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.66; H, 6.93; N, 4.07.

1,4-Bis[3-(4-cyano-3-hydroxy-6,6-diphenyl-1,2-dioxanyl)]benzene (**4ar**): colorless prisms (from $CHCl_3$); mp 212–213°C.

IR (KBr): $\nu = 3600-3200$ (OH), 2248 (CN) cm^{-1}.

^1H NMR (DMSO-d_6): $\delta = 8.0-7.7$ (24 H, m, arom H), 4.4 (2 H, br s, OH × 2), 3.8–2.9 (6 H, m, CH_2CH × 2).

^{13}C NMR (DMSO-d_6): $\delta = 142.5$, 140.1, 140.0 (arom C), 128.5, 128.4, 128.1, 127.6, 126.6, 125.8, 125.5 (arom CH), 118.5 (CN), 97.7 (C-3′), 84.5 (C-6′), 35.1 (CH_2), 31.0 (CH).

Anal. Calcd for $C_{40}H_{32}N_2O_6$: C, 75.47; H, 5.06; N, 4.40. Found: C, 75.14; H, 5.14; N, 4.36.

3,8-Bis[3-(4-cyano-3-hydroxy-6,6-diphenyl-1,2-dioxanyl)]dibenzothiophene (**4as**): colorless prisms (from $CHCl_3$); mp 197–198 °C.

IR (KBr): ν = 3600–3200 (OH), 2244 (CN) cm^{-1}.

^1H NMR (DMSO-d_6): δ = 8.5–7.0 (26 H, m, arom H), 4.2 (2 H, br s, OH × 2), 3.7–2.9 (6 H, m, CH_2CH × 2).

^{13}C NMR (DMSO-d_6): δ = 142.4, 140.2, 140.1, 136.1, 134.1 (arom C), 128.6, 128.5, 128.3, 128.0, 127.9, 126.7, 125.6, 123.3, 119.2 (arom CH), 118.5 (CN), 98.1 (C-3′), 84.6 (C-6′), 35.8 (CH_2), 31.8 (CH).

Anal. Calcd for $C_{46}H_{34}N_2O_6$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.50; H, 4.65; N, 3.72.

4-Cyano-6,6-bis(4-methylphenyl)-3-phenyl-1,2-dioxan-3-ol (**4ba**): colorless needles (from $CHCl_3$-hexane); mp 176 °C.

IR ($CHCl_3$): ν = 3600 – 3100 (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.6–7.3 (13 H, m, arom H), 4.3 (1 H, br s, OH), 3.1 (3 H, m, CH_2CH), 2.4 (3 H, s, Me), 2.2 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 138.8, 138.5, 137.8, 137.5, 136.3 (arom C), 129.7, 129.4, 129.1, 128.5, 126.7, 126.3, 125.6 (arom CH), 118.0 (CN), 98.0 (C-3), 85.3 (C-6), 35.6 (CH), 32.9 (CH_2), 21.0, 20.9 (Me).

Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.57; H, 5.95; N, 3.74.

4-Cyano-6,6-bis(4-methoxyphenyl)-3-phenyl-1,2-dioxan-3-ol (**4ca**): colorless needles (from $CHCl_3$-hexane); mp 144–145 °C.

IR ($CHCl_3$): ν = 3600–3100 (OH), 2240 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.5–6.7 (13 H, m, arom H), 4.4 (1 H, br s, OH), 3.9 (3 H, s, OMe), 3.7 (3 H, s, OMe), 3.2–2.8 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): δ = 159.6, 159.0, 137.8, 133.8, 132.2 (arom C), 129.7, 128.5, 128.14, 128.07, 125.5, 114.0, 113.8 (arom CH), 118.0 (CN), 98.0 (C-3), 85.1 (C-6), 55.2 (OMe × 2), 35.6 (CH), 32.97 (CH_2).

Anal. Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.53; N, 3.35. Found: C, 71.82; H, 5.61; N, 3.42.

6,6-Bis(4-chlorophenyl)-4-cyano-3-phenyl-1,2-dioxan-3-ol (**4da**): colorless cubes (from $CHCl_3$-hexane); mp 103–104 °C.

IR ($CHCl_3$): ν = 3600–3100 (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.5–7.1 (13 H, m, arom H), 4.1 (1 H, br s, OH), 3.3–3.0 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): δ = 139.5, 137.4, 137.3, 134.9, 134.2 (arom C), 130.0, 129.2, 128.8, 128.7, 128.2, 127.6, 125.4 (arom CH), 117.5 (CN), 98.2 (C-3), 84.6 (C-6), 35.5 (CH), 32.7 (CH_2).

Anal. Calcd for $C_{23}H_{17}Cl_2NO_3$: C, 64.80; H, 4.02; N, 3.29. Found: C, 64.76; H, 4.27; N, 3.25.

4-Cyano-6,6-bis(4-fluorophenyl)-3-phenyl-1,2-dioxan-3-ol (**4ea**): colorless needles (from Et_2O-hexane); mp 97–98 °C.

IR ($CHCl_3$): ν = 3600–3100 (OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.6–6.8 (13 H, m, arom H), 4.1 (1 H, br s, OH), 3.3–3.0 (3 H, m, CH_2CH).

^{13}C NMR ($CDCl_3$): δ = 168.2, 167.9, 157.1, 156.8, 137.5, 134.8, 134.6 (arom C), 130.0, 128.9, 128.7, 128.6, 128.2, 125.4, 116.4, 116.0, 115.4, 115.0 (arom CH), 117.6 (CN), 98.2 (C-3), 84.8 (C-6), 35.6 (CH), 33.1 (CH_2).

Anal. Calcd for $C_{23}H_{17}F_2NO_3$: C, 70.22; H, 4.35; N, 3.56. Found: C, 69.82; H, 5.15; H, 3.27.

4-Cyano-6-methyl-3,6-diphenyl-1,2-dioxan-3-ol (**4fa**): colorless needles (from Et_2O-hexane); mp 158–159 °C.

IR ($CHCl_3$): ν = 3600–3100 (OH), 2248 (CN).

^1H NMR ($CDCl_3$): δ = 7.6–7.1 (10 H, m, arom H), 4.2 (1 H, br s, OH), 3.1–2.6 (3 H, m, CH_2CH), 1.5 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 140.9, 137.6 (arom C), 129.7, 128.7, 128.4, 127.6, 125.4, 125.3 (arom CH), 117.9 (CN), 97.8 (C-3), 82.0 (C-6), 35.1 (CH), 32.9 (CH_2), 29.4 (Me).

Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N; 4.74. Found: C, 72.98; H, 5.99; N, 4.84.

(4R,5S*,6R*)-4-Cyano-3,5,6-triphenyl-1,2-dioxan-3-ol* (**4ga**): colorless needles (from $CHCl_3$); mp 192 °C.

IR (KBr): ν = 3452 (br, OH), 2244 (CN) cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.9–7.1 (15 H, m, arom H), 5.6 (1 H, d, J_2 = 10.2 Hz, H-6), 4.0 (1 H, br s, OH), 3.9 (1 H, dd, J_1 = 7.3 Hz, J_2 = 10.2 Hz, H-5), 3.2 (1 H, d, J_1 = 7.3 Hz, H-4).

^{13}C NMR (DMSO-d_6): δ = 138.4, 136.6, 134.7 (arom C), 129.4, 129.0, 128.6, 128.4, 128.3, 128.1, 127.5, 126.4 (arom CH), 117.6 (CN), 99.4 (C-3), 85.9 (C-6), 45.4, 44.5 (C-4 and C-5).

Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.23; H, 5.39; N, 4.13.

4-Cyano-6,6-dimethyl-3-phenyl-1,2-dioxan-3-ol (**4ja**): colorless needles (from CH_2Cl_2-hexane); mp 118 °C.

IR ($CHCl_3$): ν = 3580 (br, OH), 2248 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.6–7.3 (5 H, m, arom H), 3.9 (1 H, br s, OH), 3.4 (1 H, dd, J_1 = 6.1 Hz, J_3 = 12.4 Hz, C*H*CH_2), 2.2 (1 H, dd, J_2 = 14.6 Hz, J_3 = 12.4 Hz, CHCH-H_b), 2.0 (1 H, dd, J_1 = 6.1 Hz, J_2 = 14.6 Hz, CHCH-H_a), 1.5 (3 H, s, Me), 1.3 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): δ = 137.6 (arom C), 129.5, 128.3, 125.2 (arom CH), 117.8 (CN), 97.3 (C-3), 77.0 (C-6), 34.6 (CH), 34.2 (CH_2), 26.2, 21.7 (Me).

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 67.23; H, 6.08; N, 6.03. Found: C, 67.49; H, 6.59; N, 6.25.

5-Cyano-4-hydroxy-2,3-dioxa-4-phenylbicyclo[6.4.0]dodecane (**4ka**): colorless needles (from CH_2Cl_2-hexane); mp 74 °C.

IR ($CHCl_3$): ν = 3580–3200 (br, OH), 2252 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.6–7.2 (5 H, m, arom H), 4.2 (1 H, br s, OH), 4.0 (1 H, m, H-1), 2.8 (1 H, m, H-5), 2.3–1.2 (13 H, m, $(CH_2)_6$ and H-6).

^{13}C NMR ($CDCl_3$): δ = 137.7 (arom C), 129.9, 128.6, 125.7 (arom CH), 117.7 (CN), 99.2 (C-4), 85.0 (C-1), 45.5 (C-5), 39.0 (C-6), 29.5, 27.8, 26.0, 25.5, 25.0 23.9 (CH_2).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.36; N, 4.87. Found: C, 70.76; H, 7.25; N, 4.98.

A Diastereomixture of 4-Cyano-6-heptyl-3-phenyl-1,2-dioxan-3-ol (**4la**): colorless liquid.

IR ($CHCl_3$): ν = 3568 (br s, OH), 2244 (CN) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.7–7.2 (5 H, m, arom H), 4.4 (1 H, br s, OH), 3.9 (1 H, m, H-6), 2.7–2.0 (3 H, m, CH_2CH), 1.7–1.0 (12 H, m, $-(CH_2)_6-$), 0.9 (3 H, t, J_1 = 6 Hz, Me).

^{13}C NMR ($CDCl_3$): δ = 137.5, 134.6 (arom C), 130.5, 130.0, 128.9, 128.7, 126.9, 125.6 (arom CH), 119.2, 117.8 (CN), 99.3, 98.3 (C-3), 79.8, 75.4 (C-6), 37.6 (C-4), 37.2 (C-5), 32.8, 32.4, 31.7, 30.3, 29.4, 29.0, 25.1, 22.6 (CH_2), 14.1 (Me).

MS: m/z (rel intensity) = 286 (M^+ – OH, 4), 200 (100), 122 (14), 105 (91), 94 (33), 77 (35), 41 (19).

Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.30; N, 4.62. Found: C, 71.47; H, 8.47; N, 4.66.

2-Cyano-1,4-diphenylbutane-1,4-dione (**5**)[21]: colorless liquid.

IR ($CHCl_3$): ν = 2244 (CN), 1685 (br, CO) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 8.2–7.3 (10 H, m, arom H), 5.0 (1 H, dd, J_1 = 4.69 Hz, J_3 = 8.50 Hz, C*H*CH_2), 4.1 (1 H, dd, J_2 = 18.02 Hz, J_3 = 8.50 Hz, CHCH-H_b), 3.5 (1 H, dd, J_1 = 4.69 Hz, J_2 = 18.02 Hz, CHCH-H_a).

^{13}C NMR ($CDCl_3$): δ = 194.6, 189.0 (C=O), 135.2, 134.0 (arom C), 134.5, 133.9, 129.0, 128.9, 128.7, 128.1 (arom CH), 116.9 (CN), 37.5 (CH_2), 33.2 (CH).

Positive FAB MS: m/z (rel intensity) = 264 (M^+ + 1, 100), 246 (17), 115 (37), 105 (81), 79 (45), 77 (77), 55 (13).

2-Cyano-4,4-diphenylbutanolide (**6**): colorless needles (from $CHCl_3$-hexane); mp 123 °C (lit.[22] mp 123–124 °C).

IR ($CHCl_3$): ν = 2296 (CN), 1793 (C=O) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.4 (10 H, m, arom H), 3.8–3.0 (3 H, m, $CHCH_2$).

^{13}C NMR ($CDCl_3$): $\delta = 167.0$ (C=O), 141.3, 140.0 (arom C), 129.2, 128.9, 128.7, 125.3, 125.2 (arom CH), 114.3 (CN), 89.4 (C-4), 40.2 (C-3), 32.7 (C-2).

MS: m/z (rel intensity) = 263 (M^+, 58), 192 (15), 186 (36), 183 (35), 165 (14), 105 (100), 74 (54), 51 (30).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.54; H, 5.04; N, 5.42.

Acid-Catalyzed Decomposition of 4aa and 4aj

1,2-Dioxane **4aa** (1 mmol) was added to a solution of $HClO_4$ (3 mmol) in MeCN (15 mL) just before refluxing. The mixture was heated with stirring for 30 min. H_2O (20 mL) was added and the aqueous mixture obtained was extracted with Et_2O (3 × 20 mL). The ethereal extract was dried (Na_2SO_4) and then filtered. After removal of the solvent, the residue was separated by TLC using Et_2O/hexane (3 : 7 v/v) as the developing solvent, giving 3-cyano-2,5-diphenylfuran (**7a**, 61 %) and phenol (40 %). A similar reaction of **4aj** gave **7j** in 46 % yield.

3-Cyano-2,5-diphenylfuran (**7a**): Colorless needles (from CH_2Cl_2-hexane), mp 117 °C.

IR ($CHCl_3$): $\nu = 2248$ (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 8.1$–7.2 (10 H, m, arom H), 6.8 (1 H, s, H-4).

^{13}C NMR ($CDCl_3$): $\delta = 158.6$ (C-2), 153.5 (C-5), 130.0, 129.0, 128.92, 125.3, 124.2 (arom CH), 128.85, 128.6 (arom C), 114.9 (CN), 107.6 (C-4), 93.3 (C-3).

Anal. Calcd for $C_{17}H_{11}NO$: C, 83.25; H, 4.53; N, 5.71. Found: C, 83.35; H, 4.53; N, 5.69.

3-Cyano-2-[3-(2,5-dimethylfuryl)]-5-phenylfuran (**7j**): Colorless needles (from CH_2Cl_2-hexane), mp 135 °C.

IR ($CHCl_3$): $\nu = 2330$ (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 7.6$–7.3 (5 H, m, arom H), 6.8 (1 H, s, H-4), 6.6 (1 H, s, H-4′), 2.6 (3 H, s, Me), 2.3 (3 H, s, Me).

^{13}C NMR ($CDCl_3$): $\delta = 155.9$, 152.6, 151.3, 150.2 (C-2, 2′, 5, and 5′), 129.0, 128.5, 123.9 (arom CH), 128.0 (arom C), 114.9 (CN), 110.9 (C-3′), 106.5, 104.2 (C-4, 4′), 92.4 (C-3), 14.2, 13.3 (Me).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.29; H, 5.93; N, 5.52.

Reaction of Styrene (1i) with Benzoylacetonitrile (2a) under Argon:

A mixture of **1i** (105 mg), **2a** (290 mg), and $Mn(OAc)_3$ (124 mg) was stirred in HOAc (16 mL) at 23 °C under argon for 1.5 h. After usual workup mentioned above, **2a** (220 mg, 76 %) and **5** (8 mg, 3 %) were obtained.

Reactions of Benzoylacetonitrile (2a) with Manganese(III and II) Acetate:

A mixture of **2a** (290 mg) and $Mn(OAc)_3$ (248 mg) was stirred at 23 °C in HOAc (16 mL) under air for 16 h. After usual workup described above, benzoic acid (126 mg, 52 %) was obtained. The same reaction under Ar gave **2a** (191 mg, 66 %) and an intractable mixture; however, benzoic acid was not detected. A similar reaction of **2a** (145 mg) with $Mn(OAc)_3$ (248 mg) at reflux temperature for 3 min afforded **2a** (63 mg, 44 %) and an intractable mixture. A mixture of **2a** (145 mg) and $Mn(OAc)_2 \cdot 4H_2O$ (245 mg) was stirred at 23 °C under bubbling dry air for 20 h. After normal workup, **2a** (136 mg, 94 %) was recovered and no other products were obtained.

Reaction of Manganese(III) Acetate with 4,4,4-Trifluoro-1-phenylbutane-1,3-dione:

$Mn(OAc)_3 \cdot 2H_2O$ (55.1 mg) and 4,4,4,-trifluoro-1-phenylbutane-1,3-dione (134.8 mg) were stirred in HOAc (3 mL) at 23 °C under Ar for 1 h. The solvent was removed under high vacuum and the residual solid was recrystallized from CH_2Cl_2-hexane to give tris(4,4,4-trifluoro-1-phenylbutane-1,3-dionato)manganese(III) (52.5 mg), greenish dark brown solid, mp 128–130 °C.

Anal. Calcd for $C_{30}H_{18}O_6F_9Mn$: C, 51.45; H, 2.59. Found: C, 51.76; H, 2.83.

Reaction of 3-(2-Furyl)-1,2-dioxan-3-ol 4ah:

3-(2-Furyl)-1,2-dioxan-3-ol **4ah** (30 mg) was stirred in HOAc (12 mL) at 23 °C for 36 h in the presence of $Mn(OAc)_2 \cdot 4H_2O$ (12 mg). After normal workup, butanolide **6** (14 %), benzophenone (52 %), and **4ah** (12 % recovered) were obtained. On the other hand, **4ah** (30 mg) was heated under reflux in MeCN (16 mL) for 15 min in the presence of 3 drops of 60 % $HClO_4$. After the usual workup, 3-cyano-2-(2-furyl)-5-phenylfuran (16 %), butanolide **6** (54 %), and benzophenone (12 %) were obtained.

3-Cyano-2-(2-furyl)-5-phenylfuran:

Colorless needles (from CH_2Cl_2-hexane), mp 123 °C.

IR ($CHCl_3$): $\nu = 2244$ (CN) cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 7.7$–7.3 (5 H, m, arom H), 7.6 (1 H, d, $J = 1.96$ Hz, H-5′), 7.0 (1 H, d, $J = 3.42$ Hz, H-3′), 6.8 (1 H, s, H-4), 6.6 (1 H, dd, $J_1 = 3.42$ Hz, $J_2 = 1.96$ Hz, H-4′).

^{13}C NMR ($CDCl_3$): $\delta = 153.6$, 151.2, 143.6 (C-2, 2′, and 5), 144.3 (C-5′), 128.98, 128.97, 124.3 (arom CH), 128.5 (arom C), 113.9 (CN), 112.1, 110.6, 106.9 (C-3′, 4, and 4′), 92.5 (C-3).

MS: m/z (rel intensity) = 235 (M^+, 100), 206 (20), 178 (24), 118 (14), 77 (19), 51 (17).

Anal. Calcd for $C_{15}H_9NO_2$: C, 76.59; H, 3.84; N, 5.95. Found: C, 76.39; H, 3.89; N, 5.99.

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