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Novel Ruthenium- and Platinum-Catalyzed Sequential Reactions: Synthesis of Tri- and Tetra-Substituted Furans and Pyrroles from Propargylic Alcohols and Ketones

Yoshiaki Nishibayashi,† Masato Yoshikawa,† Youichi Inada,† Marilyn Daisy Milton,† Masanobu Hidai,*†† and Sakae Uemura*†

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

General Method. ^{1}H NMR (400, 300, and 270 MHz) and ^{13}C NMR (100, 75, and 67.8 MHz) spectra were recorded using $CDCl_3$ as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m x 0.25 mm CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

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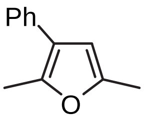
† Kyoto University

†† Tokyo University of Science

Ruthenium- and Platinum-Catalyzed Sequential Reactions: Synthesis of Substituted Furans from Propargylic Alcohols and Ketones. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with acetone catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**) and PtCl$_2$ is described below. In a 50 mL flask were placed **1a** (38 mg, 0.06 mmol), NH$_4$BF$_4$ (12 mg, 0.12 mmol), and PtCl$_2$ (31 mg, 0.12 mmol) under N$_2$. Anhydrous acetone (30 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol), the reaction flask was kept at reflux temperature for 36 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO$_2$) with EtOAc-hexane (1/9) to give 2,5-dimethyl-3-phenylfuran[S1] (**3a**) as a colorless oil (66.5 mg, 0.38 mmol, 64% yield).

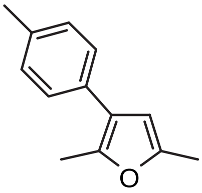


3a

2,5-Dimethyl-3-phenylfuran[S1] (3a): ^{1}H NMR δ 2.28 (s, 3H), 2.40 (s, 3H), 6.10 (s, 1H), 7.21-7.37 (m, 5H). ^{13}C NMR δ 12.9, 13.4, 106.9, 121.4, 126.0, 127.3, 128.5, 134.5, 145.8, 149.7.

[S1] T. S. Balaban, M. Hiegemann, *Tetrahedron* **1992**, *48*, 9827.

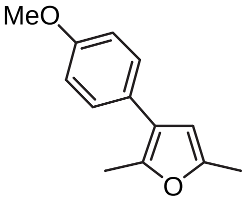
Spectroscopic data and isolated yield of other products are as follows.



3b

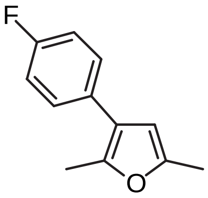
2,5-Dimethy-3-(4-methylphenyl)furan[S2] (3b): Yield 65%. A pale yellow oil. ^{1}H NMR δ 2.27 (s, 3H), 2.35 (s, 3H), 2.38 (s, 3H), 6.08 (s, 1H), 7.17 (d, 2H, *J* = 8 Hz), 7.25 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 13.0, 13.5, 21.1, 106.9, 121.2, 127.2, 129.1, 131.5, 135.6, 145.3, 149.5.

[S2] D. Mackay, E. G. Neeland, N. J. Taylor, *J. Org. Chem.* **1986**, *51*, 2351.



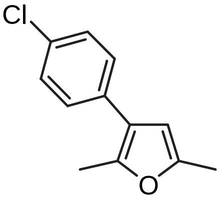
3c

3-(4-Methoxyphenyl)-2,5-dimethylfuran (3c): Yield 52%. Colorless crystals, 36.2-36.5 °C. ^{1}H NMR δ 2.27 (s, 3H), 2.37 (s, 3H), 3.80 (s, 3H), 6.05 (s, 1H), 6.90 (d, 2H, *J* = 9 Hz), 7.27 (d, 2H, *J* = 9 Hz). ^{13}C NMR δ 12.9, 13.5, 55.3, 106.9, 113.9, 120.9, 126.9, 128.3, 144.9, 149.4, 157.8. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.18; H, 7.05.



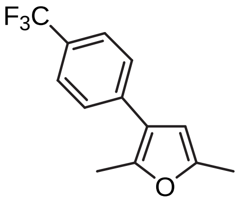
3d

3-(4-Fluorophenyl)-2,5-dimethylfuran (3d): Yield 57%. A pale yellow oil. ^{1}H NMR δ 2.19 (s, 3H), 2.28 (s, 3H), 5.96 (s, 1H), 6.93-6.98 (m, 2H), 7.19-7.23 (m, 2H). ^{13}C NMR δ 12.8, 13.3, 106.9, 115.3 (d, *J* = 21 Hz), 120.6, 128.8 (d, *J* = 8 Hz), 130.6 (d, *J* = 3 Hz), 145.6, 149.8, 161.4 (d, *J* = 245 Hz). HRMS Calcd for $C_{12}H_{11}FO$ [M] 190.0794. Found 190.0795. ^{1}H NMR spectrum is shown in the last page of supporting information.



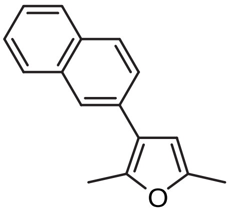
3e

3-(4-Chlorophenyl)-2,5-dimethylfuran (3e): Yield 74%. A yellow solid, 57.2-57.8 °C. ^{1}H NMR δ 2.27 (s, 3H), 2.37 (s, 3H), 6.06 (s, 1H), 7.26 (d, 2H, *J* = 8 Hz), 7.32 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 13.0, 13.4, 106.6, 120.4, 128.5, 128.6, 131.7, 132.9, 145.9, 149.9. Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36. Found: C, 69.65; H, 5.39.



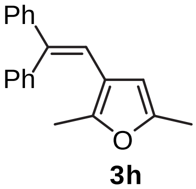
3f

2,5-Dimethyl-3-(4-trifluoromethylphenyl)furan (3f): Yield 54%. A colorless oil. ^{1}H NMR δ 2.29 (s, 3H), 2.41 (s, 3H), 6.11 (s, 1H), 7.44 (d, 2H, *J* = 8 Hz), 7.61 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 13.2, 13.5, 106.5, 120.4, 124.3 (d, *J* = 271 Hz), 125.3 (d, *J* = 4 Hz), 127.2, 127.9 (d, *J* = 32 Hz), 138.1, 146.7, 150.1. Anal. Calcd for $C_{13}H_{11}F_3O$: C, 65.00; H, 4.62. Found: C, 65.26; H, 4.69.



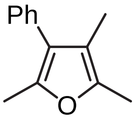
3g

2,5-Dimethyl-3-(2-naphthyl)furan (3g): Yield 64%. Colorless crystals, 42.0-42.2 °C. ^{1}H NMR δ 2.30 (s, 3H), 2.46 (s, 3H), 6.19 (s, 1H), 7.42-7.51 (m, 3H), 7.77-7.82 (m, 4H). ^{13}C NMR δ 13.2, 13.5, 107.0, 121.4, 125.3, 125.4, 126.0, 126.0, 127.5, 127.6, 127.9, 131.8, 131.9, 133.5, 146.0, 149.7. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.72; H, 6.37.



3h

3-(2,2-Diphenylvinyl)-2,5-dimethylfuran (3h): Yield 29%. Colorless crystals. ^{1}H NMR δ 2.04 (s, 3H), 2.31 (s, 3H), 4.85 (s, 1H), 6.74 (s, 1H), 7.22-7.41 (m, 10H). ^{13}C NMR δ 11.9, 13.2, 105.4, 118.5, 118.7, 126.8, 127.0, 127.3, 128.1, 128.5, 130.3, 138.7, 140.7, 143.2, 149.2, 150.2. HRMS Calcd for $C_{20}H_{18}O$ [M] 274.1358. Found 274.1349. ^{1}H NMR spectrum is shown in the last page of supporting information.

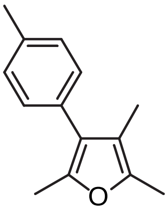


3j

2,3,5-Trimethyl-4-phenylfuran[S1] **(3j)**:

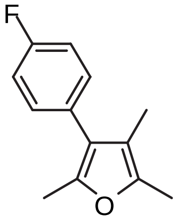
Yield 72%. A colorless oil. ^{1}H NMR δ 1.89 (s, 3H), 2.22 (s, 3H), 2.25 (s, 3H), 7.23-7.27 (m, 3H), 7.37 (t, 2H, *J* = 7 Hz). ^{13}C NMR δ 9.2, 11.5, 12.3, 113.8, 122.5, 126.1, 128.1, 129.1, 134.2, 144.9, 145.2.

[S1] T. S. Balaban, M. Hiegemann, *Tetrahedron* **1992**, *48*, 9827.



3k

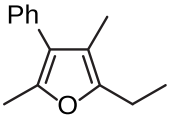
2,3,5-Trimethyl-4-(4-methylphenyl)furan (3k): Yield 78%. A pale yellow oil. ^{1}H NMR δ 1.88 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 2.36 (s, 3H), 7.14 (d, 2H, *J* = 8 Hz), 7.19 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 9.2, 11.5, 12.3, 21.2, 113.9, 129.0, 129.0, 131.2, 135.8, 144.9, 145.1. HRMS Calcd for $C_{14}H_{16}O$ [M] 200.1201. Found 200.1202.



3l

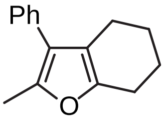
3-(4-Fluorophenyl)-2,4,5-trimethylfuran

(3l): Yield 65%. A colorless oil. ^{1}H NMR δ 1.86 (s, 3H), 2.21 (s, 3H), 2.23 (s, 3H), 7.06 (t, 2H, *J* = 9 Hz), 7.18-7.21 (m, 2H). ^{13}C NMR δ 9.0, 11.4, 12.2, 113.9, 115.2 (d, *J* = 21 Hz), 121.7, 130.2 (d, *J* = 3 Hz), 130.7 (d, *J* = 8 Hz), 145.0, 145.3, 161.6 (d, *J* = 244 Hz). Anal. Calcd for $C_{13}H_{13}FO$: C, 76.45; H, 6.42. Found: C, 76.59; H, 6.56.



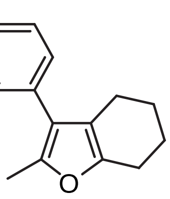
3m

2-Ethyl-3,5-dimethyl-4-phenylfuran (3m): Yield 75%. A colorless oil. ^{1}H NMR δ 1.22 (t, 3H, *J* = 8 Hz), 1.90 (s, 3H), 2.26 (s, 3H), 2.60 (q, 2H, *J* = 8 Hz), 7.24-7.28 (m, 3H), 7.38 (t, 2H, *J* = 8 Hz). ^{13}C NMR δ 9.1, 12.2, 13.2, 19.6, 112.9, 122.4, 126.1, 128.2, 129.2, 134.3, 145.3, 150.3. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.26; H, 8.21.



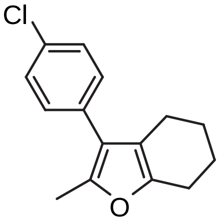
3n

2-Methyl-3-phenyl-4,5,6,7-tetrahydrobenzo[*b*]furan (3n): Yield 75%. A colorless oil. ^{1}H NMR δ 1.67-1.74 (m, 2H), 1.81-1.88 (m, 2H), 2.33 (s, 3H), 2.41 (t, 2H, *J* = 6 Hz), 2.59 (t, 2H, *J* = 6 Hz), 7.21-7.39 (m, 5H). ^{13}C NMR δ 12.5, 21.9, 23.0, 23.1, 23.3, 117.0, 120.9, 126.1, 128.3, 128.6, 134.1, 145.7, 148.5. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.12; H, 7.62.



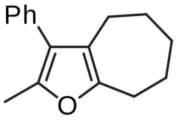
3o

3-(4-Fluorophenyl)-2-methyl-4,5,6,7-tetrahydrobenzo[*b*]furan (3o): Yield 75%. A white solid, 55.0-56.0 °C ^{1}H NMR δ 1.69-1.74 (m, 2H), 1.81-1.88 (m, 2H), 2.30 (s, 3H), 2.38 (t, 2H, *J* = 6 Hz), 2.59 (brt, 2H, *J* = 6 Hz), 7.05 (t, 2H, *J* = 9 Hz), 7.20-7.25 (m, 5H). ^{13}C NMR δ 12.4, 21.8, 23.0, 23.1, 23.2, 115.2 (d, *J* = 22 Hz), 116.9, 120.0, 130.1 (d, *J* = 8 Hz), 145.6, 148.6, 161.4 (d, *J* = 245 Hz). Anal. Calcd for $C_{15}H_{15}FO$: C, 78.24; H, 6.57. Found: C, 77.99; H, 6.61.



3p

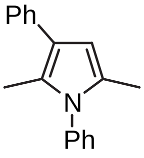
3-(4-Chlorophenyl)-2-methyl-4,5,6,7-tetrahydrobenzo[*b*]furan (3p): Yield 69%. A white solid, 74.5-75.0 °C. ^{1}H NMR δ 1.69-1.74 (m, 2H), 1.81-1.86 (m, 2H), 2.31 (s, 3H), 2.38 (t, 2H, *J* = 6 Hz), 2.58 (brt, 2H, *J* = 6 Hz), 7.20 (d, 2H, *J* = 8 Hz), 7.33 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 12.5, 21.8, 22.9, 23.1, 23.2, 116.8, 119.9, 128.5, 129.8, 131.9, 132.6, 145.9, 148.8. Anal. Calcd for $C_{15}H_{15}ClO$: C, 73.02; H, 6.13. Found: C, 72.88; H, 6.15.



3q

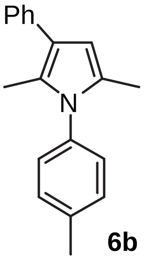
2-Methyl-3-phenyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]furan (3q): Yield 66%. A colorless oil. ^{1}H NMR δ 1.65-1.74 (m, 6H), 2.24 (s, 3H), 2.39 (t, 2H, *J* = 6 Hz), 2.77 (t, 2H, *J* = 6 Hz), 7.19-7.28 (m, 3H), 7.37 (t, 2H, *J* = 7 Hz). ^{13}C NMR δ 12.2, 24.5, 26.6, 28.7, 28.9, 31.0, 120.5, 122.8, 126.1, 128.1, 129.6, 134.0, 144.1, 151.0. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.16; H, 7.95.

Ruthenium- and Platinum-Catalyzed Sequential Reactions: Synthesis of Substituted Pyrroles from Propargylic Alcohols, Ketones, and Anilines. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with acetone and aniline catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**) and $PtCl_2$ is described below. In a 50 mL flask were placed **1a** (38 mg, 0.06 mmol), NH_4BF_4 (12 mg, 0.12 mmol), and $PtCl_2$ (31 mg, 0.12 mmol) under N_2. Anhydrous acetone (30 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol) and aniline (279 mg, 3.00 mmol), the reaction flask was kept at reflux temperature for 100 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc-hexane (2/98) to give 2,5-dimethyl-3,*N*-diphenylpyrrole (**6a**) as a colorless oil (74 mg, 0.30 mmol, 50% yield).



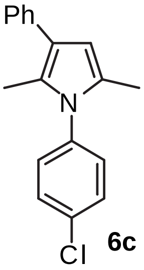
6a

6a: Yield 50%. A colorless oil. ^{1}H NMR δ 2.07 (s, 3H), 2.15 (s, 3H), 6.15 (s, 1H), 7.18-7.50 (m, 10H). ^{13}C NMR δ 12.2, 12.8, 106.5, 121.1, 125.0, 125.1, 127.8, 127.8, 128.3, 128.4, 128.6, 129.1, 137.3, 138.8. HRMS Calcd for $C_{18}H_{17}N$ [M] 247.1361. Found 247.1352.



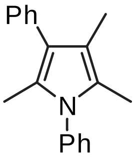
6b

2,5-Dimethyl-*N*-(4-methylphenyl)-3-phenylpyrrole (6b): Yield 44%. A colorless oil. ^{1}H NMR δ 2.06 (s, 3H), 2.14 (s, 3H), 2.41 (s, 3H), 6.14 (s, 1H), 7.12-7.22 (m, 3H), 7.26 (d, 2H, *J* = 8 Hz), 7.35 (t, 2H, *J* = 8 Hz), 7.44 (d, 2H, *J* = 7 Hz). ^{13}C NMR δ 12.3, 12.9, 21.2, 106.2, 120.8, 124.8, 125.1, 127.7, 128.0, 128.1, 128.5, 129.6, 136.1, 137.3, 137.5. Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.60; H, 7.40; N, 5.19.



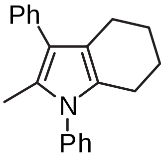
6c

***N*-(4-Chlorophenyl)-2,5-dimethyl-3-phenylpyrrole (6c)**: Yield 58%. A pale yellow solid, 64.5-65.2 °C. ^{1}H NMR δ 2.06 (s, 3H), 2.13 (s, 3H), 6.14 (s, 1H), 7.16-7.21 (m, 3H), 7.35 (m, 6H). ^{13}C NMR δ 12.3, 12.9, 106.9, 121.3, 124.8, 125.0, 127.7, 128.2, 128.4, 129.3, 129.5, 133.6, 136.9, 137.2. Anal. Calcd for $C_{18}H_{16}NCl$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.47; H, 5.59; N, 5.06.



6d

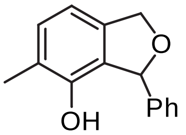
2,3,5-Trimethyl-4,*N*-diphenylpyrrole (6d): Yield 49%. A pale yellow oil. ^{1}H NMR δ 2.02 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 7.20-7.48 (m, 10H). ^{13}C NMR δ 10.3, 10.8, 11.7, 112.8, 121.6, 124.6, 125.2, 127.4, 127.9, 128.3, 128.9, 129.9, 136.7, 139.0. HRMS Calcd for $C_{19}H_{19}N$ [M] 261.1517. Found 261.1509.



6e

2-Methyl-3,*N*-diphenyl-4,5,6,7-tetrahydro-1*H*-indole (6e): Yield 56%. A pale yellow oil. ^{1}H NMR δ 1.77-1.81 (m, 4H), 2.12 (s, 3H), 2.38 (t, 2H, J = 5 Hz), 2.60 (t, 2H, J = 5 Hz), 7.17-7.46 (m, 10H). ^{13}C NMR δ 11.6, 22.8, 23.0, 23.5, 24.0, 115.8, 120.2, 124.7, 125.0, 127.2, 127.7, 128.9, 129.3, 136.4, 138.5. Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.36; N, 4.87. Found: C, 87.49; H, 7.49; N, 4.79.

Ruthenium- and Platinum-Catalyzed Sequential Reactions: Synthesis of Substituted Phenols from Propargylic Alcohols and 5-Methyl-2-furylmethanol. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with 5-methyl-2-furylmethanol catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**) and $PtCl_2$ is described below. In a 50 mL flask were placed **1a** (38 mg, 0.06 mmol), NH_4BF_4 (12 mg, 0.12 mmol), and $PtCl_2$ (31 mg, 0.12 mmol) under N_2. Anhydrous $ClCH_2CH_2Cl$ (36 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol) and 5-methyl-2-furylmethanol (338 mg, 3.00 mmol), the reaction flask was kept at 60 °C for 18 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc-hexane (1/9) to give 5-methyl-3-phenyl-1,3-dihydro-isobenzofuran-4-ol (**8a**) as white crystals (64 mg, 0.28 mmol, 47% yield).

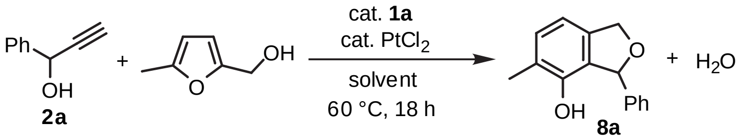


8a

5-Methyl-3-phenyl-1,3-dihydro-isobenzofuran-4-ol (8a): Yield 47%. White crystals, 113.0-114.0 °C. ^{1}H NMR δ 2.16 (s, 3H), 4.44 (br, 1H), 5.12 (d, 1H, *J* = 12 Hz), 5.27 (d, 1H, *J* = 12 Hz), 6.14 (s, 1H), 6.76 (d, 1H, *J* = 8 Hz), 7.08 (d, 1H, *J* = 8 Hz), 7.37-7.38 (m, 5H). ^{13}C NMR δ 15.0, 73.5, 84.7, 112.8, 123.2, 127.2, 127.5, 128.9, 129.0, 131.3, 139.2, 140.5, 148.7. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.72; H, 6.31.

For comparision, reactions of **2a** with 5-methyl-2-furylmethanol in the presence of **1a** and $PtCl_2$ were carried out under various reaction conditions. Typical results are shown in Table S1.

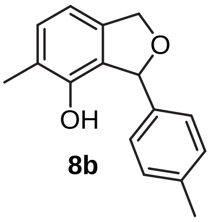
Table S1. Reaction of **2**a with 5-Methyl-2-furylmethanol in the Presence of [Cp*RuCl(μ-SMe)$_2$RuCp*Cl] (**1a**) and $PtCl_2$.[a]



run	solvent (mL)	**1a** (mol%)	$PtCl_2$ (mol%)	yield of **8a**, %[b]
1	$ClCH_2CH_2Cl$ (3)	5	10	38
2	$ClCH_2CH_2Cl$ (3)	10	10	38
3	toluene (3)	5	10	0
4	$ClCH_2CH_2Cl$ (3)	5	20	6
5	$ClCH_2CH_2Cl$ (6)	10	10	37
6	$ClCH_2CH_2Cl$ (6)	10	20	58
7[c]	$ClCH_2CH_2Cl$ (6)	10	20	25
8	$ClCH_2CH_2Cl$ (9)	10	20	28
9[d]	$ClCH_2CH_2Cl$ (6)	10	20	12

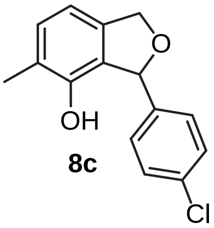
[a] All the reactions of **2a** (0.10 mmol) with 5-methyl-2-furylmethanol (0.50 mmol) were carried out in the presence of **1a** (0.01 mmol), NH_4BF_4 (0.02 mmol), and $PtCl_2$ (0.02 mmol) at 60 °C for 18 h. [b] GLC yield. [c] 5-Methyl-2-furylmethanol (1.00 mmol) was used. [d] At 80 °C.

Spectroscopic data and isolated yield of the following two products (**8b** and **8c**), which are not included in our manuscript, are described below.



8b

5-Methyl-3-(4-methylphenyl)-1,3-dihydro-isobenzofuran-4-ol (8b): Yield 30%. Yellow crystals, 103.5-104.0 °C. ^{1}H NMR δ 2.16 (s, 3H), 2.34 (s, 3H), 4.41 (br, 1H), 5.10 (d, 1H, *J* = 11 Hz), 5.26 (d, 1H, *J* = 11 Hz), 6.10 (s, 1H), 6.75 (d, 1H, *J* = 8 Hz), 7.07 (d, 1H, *J* = 8 Hz), 7.17 (d, 2H, *J* = 8 Hz), 7.26 (d, 2H, *J* = 8 Hz). ^{13}C NMR δ 15.0, 21.2, 73.4, 84.4, 112.7, 123.3, 127.2, 127.5, 129.8, 131.3, 137.3, 138.8, 139.2, 148.7. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.67; H, 6.80.



8c

3-(4-Chlorophenyl)-5-methyl-1,3-dihydro-isobenzofuran-4-ol (8c): Yield 29%. Yellow crystals; 137.2-138.0 °C. ^{1}H NMR δ 2.16 (s, 3H), 4.52 (br, 1H), 5.10 (d, 1H, *J* = 12 Hz), 5.25 (d, 1H, *J* = 12 Hz), 6.14 (s, 1H), 6.76 (d, 1H, *J* = 7 Hz), 7.08 (d, 1H, *J* = 7 Hz), 7.24-7.33 (m, 4H). ^{13}C NMR δ 15.1, 73.5, 84.0, 112.9, 122.8, 126.9, 128.8, 128.8, 131.4, 134.2, 139.1, 139.3, 148.5. Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03. Found: C, 68.74; H, 5.13.

X-ray Crystallographic Studies of 8a. Colorless crystals of **8a** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2–*n*-hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S2. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **8a** is shown in Figure S1.

Table S2. Crystallographic Data for **8a**.

formula	$C_{15}H_{14}O_2$
formula weigh	226.27
cryst size (mm^3)	0.20 x 0.20 x 0.50
cryst system	trigonal
space group	R-3(#148)
cryst color	colorless
a (Å)	24.634(2)
c (Å)	10.685(2)
V (Å^3)	5615.3(1)
Z	18
d_{calc} (g cm^{-1})	1.204
F (000)	2160.00
μ_{calc} (cm^{-1})	0.79
no. of unique data	3606
no. of data used ($I > 3\sigma(I)$)	1084
no. of params refined	171
R^{a}	0.060
R_{w}^{b}	0.059
goodness of fit indicator	1.38
maximum residuals (e Å^{-3})	0.29

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

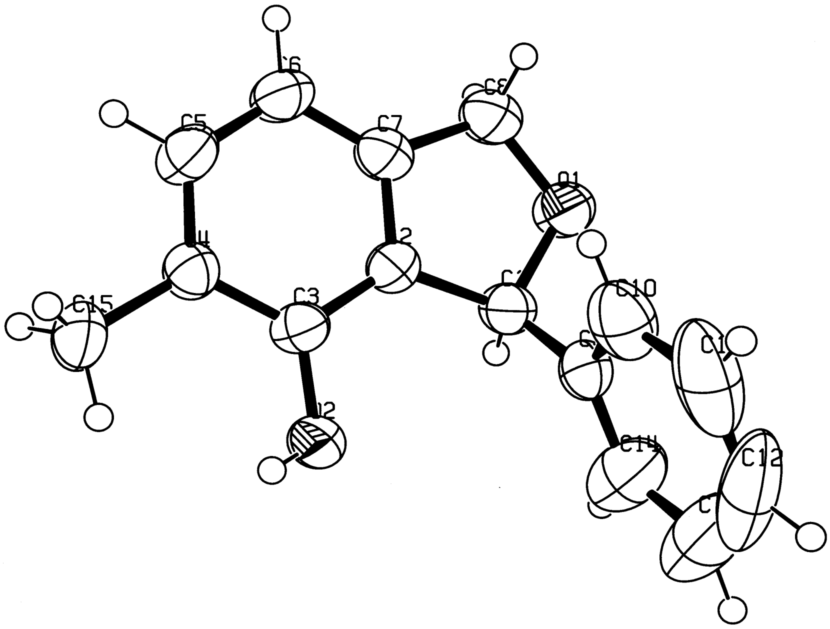
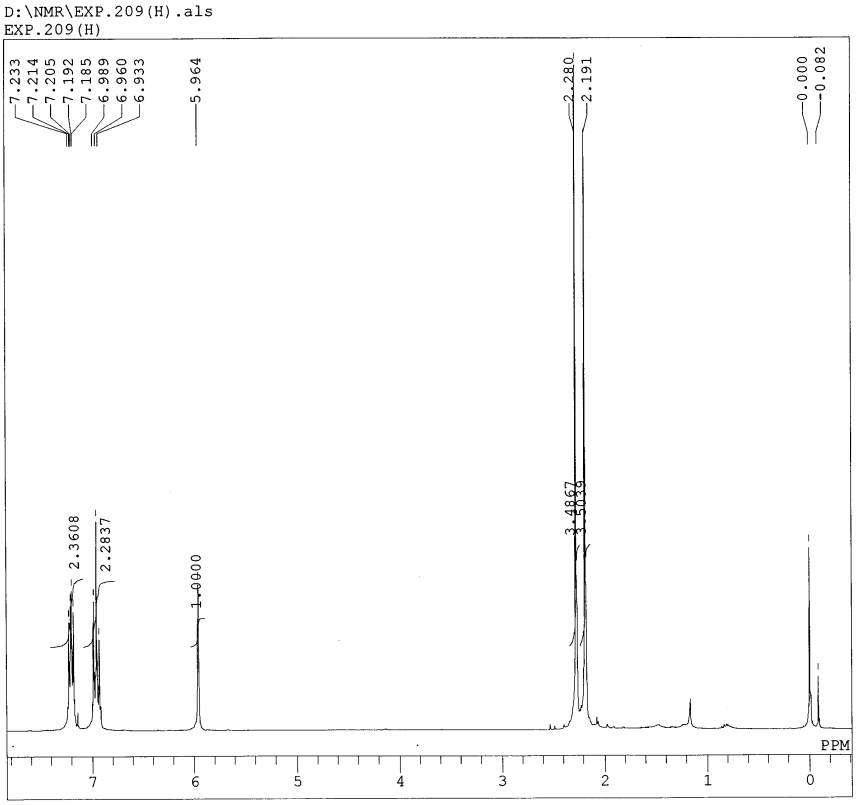
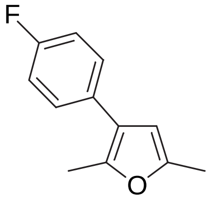


Figure S1. Crystal structure of **8a**.

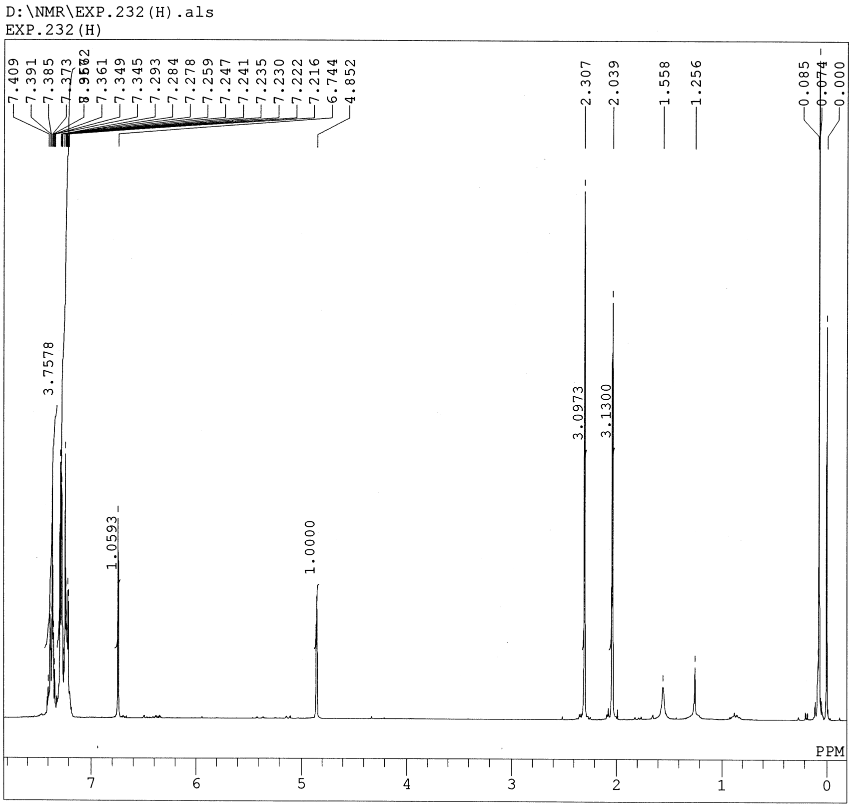
^{1}H NMR spectrum of **3d**.

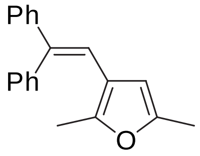




3d

^{1}H NMR spectrum of **3h**.





3h