A New Synthetic Method for the Preparation of Indenones from Aromatic Imines. $Ru_3(CO)_{12}$-Catalyzed Carbonylation at an *ortho* C−H Bond in the Aromatic Imines

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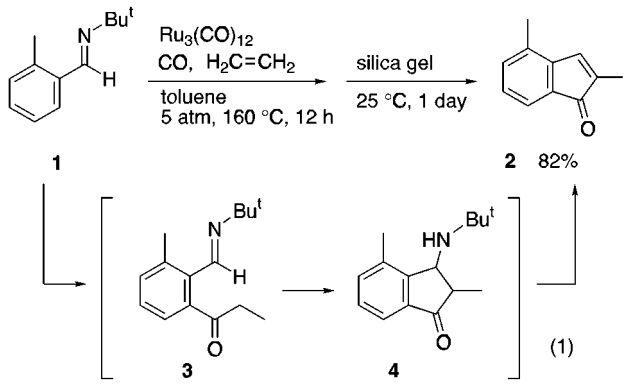
Indenones are important substructures in natural products and their related biologically active counterparts.[1] As a result, a variety of synthetic methods have been developed and remain the subject of study. The most straightforward synthetic method for the preparation of indenones is the α-bromination of 1-indanones, followed by dehydrobromination.[2] Other common methods include the $AlCl_3$-catalyzed addition of benzoyl chlorides to acetylenes[3] and the intramolecular Friedel−Crafts acylation of *β*-chloro-*β*-arylpropionyl chlorides[4] or variations of this approach.[5] A number of 2,3-disubstituted indenones have been prepared by the Pd-catalyzed reaction of *o*-bromo- or *o*-iodobenzaldehyde with various internal acetylenes,[6] as well as the Rh-catalyzed reaction of aroyl chlorides with internal acetylenes.[7] Although other methods for the preparation of indenones are known,[8] all have some drawbacks in terms of substrate limitation, yield, or reaction conditions. The present study was initiated in order to develop a more efficient method that would allow the preparation of some of indenones that cannot be prepared by previously reported methodology.

Recently, we reported the $Ru_3(CO)_{12}$-catalyzed reaction of pyridylbenzenes with CO and ethylene in which propionylation occurs selectively at an *ortho* position in the phenyl ring.[9] The reaction involves the effective carbonylation at a C−H bond[9,10] in the benzene ring. To explore some new aspects of this direct carbonylation reaction in organic synthesis, we have examined the $Ru_3(CO)_{12}$-catalyzed reaction of aromatic imines with CO and olefins. The initial concept was based on the regioselective propionylation of an aromatic imine. If the propionylation occurred *ortho* to an imino group in a manner similar to the reaction of pyridylbenzenes,[9] the product would possess an 1-imino-4-keto structure which should undergo intramolecular aldol cyclization to a five-membered ring.[11,12] Fortunately this took place readily. We now report a new, simple synthetic method for the preparation of indenones by the $Ru_3(CO)_{12}$-catalyzed reaction of aromatic imines with CO and olefins. Some of 2-substituted indenones, which were prepared by the present method, are new compounds and, thus, have not been reported thus far.

The reaction of *N*-(2-methylbenzylidene)-*tert*-butylamine (**1**) (2 mmol) with CO (5 atm at room temperature) and ethylene (7 atm at room temperature in a 50-mL stainless steel autoclave) in the presence of $Ru_3(CO)_{12}$ (0.1 mmol) was run in toluene (6 mL) at 160 °C for 12 h. After the solution was cooled to room temperature, silica gel (chromatography grade, 70−230 mesh, 5 g) (vide infra) was added to the solution and the mixture stirred at 25 °C for 1 d. The silica gel was filtered off and the residue subjected to column chromatography on silica gel (hexane/C_6H_6 = 1/1) to give 2,4-dimethyl-1*H*-inden-1-one (**2**) in 82% isolated yield based on **1** (eq 1). Increasing the



CO pressure (20 atm) resulted in a decreased product yield (50% yield), even after a 20 h reaction.[13] On the basis of studies of the $Ru_3(CO)_{12}$-catalyzed reaction of pyridylbenzenes with CO and ethylene,[9] a keto imine, such as **3**, would be expected as the primary product. However, **3** was not detected by GC. The keto imine **3** would readily undergo intramolecular aldol-type condensation to give **4** in situ. Although **4** could be isolated by bulb-to-bulb distillation, the formation of **2** was also observed, to a greater or lesser extent.[14] The elimination of *tert*-butylamine from **4** to give **2** proceeded smoothly on treatment of the crude reaction mixture with silica gel. No *ortho*-ethylation took place under CO, which is

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(11) To our knowledge, only two limited example of the intramolecular aldol condensation of a related compound, *o*-acylbenzophenone to 3-hydroxy-1-indanone or indenone, have been reported. Tada, M.; Maeda, T. *Chem. Ind. (London)* **1976**, *17*, 742. Baidossi, W.; Lahav, M.; Blum, J. *J. Org. Chem.* **1997**, *62*, 669.

(12) It was found that 2-acetyl-4,5-dimethoxybenzaldehyde decomposed during silica gel column chromatography to give 5,6-dimethoxy-3-methyl-3*H*-isobenzofuran-1-one but not the inden-1-one derivative. Van Broeck, P. I.; Vanderzande, D. J.; Kiekens, E. G.; Hoornaert, G. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 639.

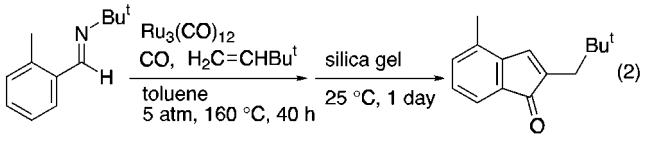
(13) Presumably because high pressure of CO inhibits the coordination of imine nitrogen to a metal center.

(14) Compounds similar to **3** and **4** can be isolated in a particular case (vide infra).

S0022-3263(97)00697-X CCC: $14.00

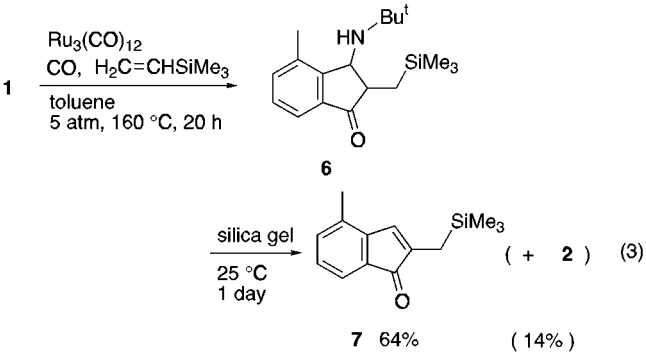
in contrast to the $Ru_3(CO)_{12}$-catalyzed *ortho*-ethylation of aromatic imines with ethylene under N_2.[15]

We examined the $Ru_3(CO)_{12}$-catalyzed reaction of **1** with a variety of olefins. It was found that **1** did not react with olefins such as 1-hexene, styrene, and methyl acrylate, but reaction with *tert*-butylethylene (4 equiv) gave the corresponding indenone **5** in 41% yield (eq 2). A similar limitation with respect to olefin reactivity was observed in the reaction of pyridylbenzenes.[9]



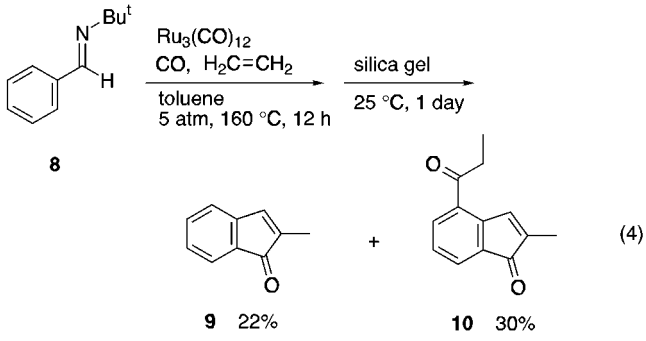
1 **5** 41% (2)

The reaction of **1** with trimethylvinylsilane (4 equiv) afforded 4-methyl-2-[(trimethylsilyl)methyl]-1*H*-inden-1-one (**7**) in 64% yield, along with **2** as a byproduct in 14% yield (eq 3). It is likely that byproduct **2** arises from ethylene, which is generated in situ from the vinylsilane.[16] Without treatment of the reaction mixture with silica gel, compound **6** was isolated in 60% yield in pure form, by bulb-to-bulb distillation.



(3)

The reaction of *N*-benzylidene-*tert*-butylamine (**8**) gave two products, 2-methyl-1*H*-inden-1-one (**9**) and 2-methyl-4-propionyl-1*H*-inden-1-one (**10**) (eq 4). The formation of **10** clearly indicates that the second acylation proceeds more rapidly than cyclization (aldol type condensation). Once cyclized, **9** does not undergo further acylation to **10** under the reaction conditions employed.

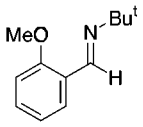
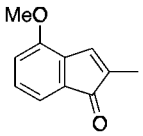
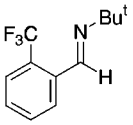
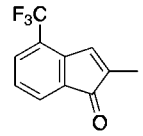
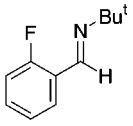
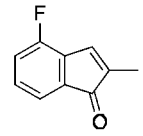
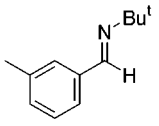
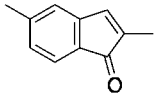
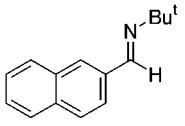
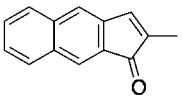


(4)

(15) Kakiuchi, F.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 111.

(16) The ruthenium-catalyzed conversion of vinylsilanes to ethylene and disilylethylene is known. Wakatuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. Marciniec, B.; Pietraszuk, C. *J. Organomet. Chem.* **1991**, *412*, C1. See also: Seki, Y.; Takeshita, K.; Kawamoto, K. *J. Organomet. Chem.* **1989**, *369*, 117.

Table 1. $Ru_3(CO)_{12}$-Catalyzed Reaction of Aromatic Imines with CO and Ethylene[a]

run	imine	time	products[b]
1	 **11**	8 h	 **12** 85%
2	 **13**	8 h	 **14** 58%
3	 **15**	12 h	 **16** 66%
4	 **17**	24 h	 **18** 69%
5[c]	 **19**	40 h	 **20** 68%

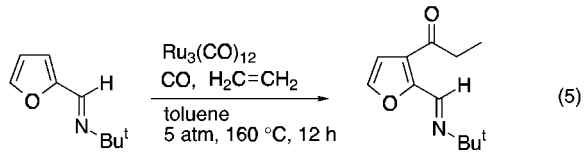
[a] Reaction conditions: imine (2 mmol), ethylene (initial pressure 7 atm at rt in a 50-mL stainless steel autoclave), CO (initial pressure 5 atm at rt in a 50-mL stainless steel autoclave), toluene (6 mL), 160 °C, and silica gel at rt for 1 day. [b] Isolated yields based on the imine. [c] Reaction run under 20 atm of CO.

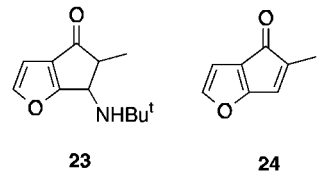
Some selected results of the reaction of aromatic imines with CO and ethylene are summarized in Table 1. The reaction of *o*-methoxy-substituted imine **11** gave, after deamination by treatment with silica gel, the corresponding indenone **12** in high yield (entry 1). A CF_3 group as in **13** resulted in a decrease in the product yield, and a small amount (3% yield) of *ortho*-ethylation product[15] (structure not shown) was obtained as a byproduct (entry 2). A high degree of regioselectivity was observed in the case of the *m*-methyl-substituted imine **17**. Carbonylation took place at a sterically less hindered C−H bond to selectively give **18** (entry 4), indicating the importance of steric factors. The present reaction provides an efficient method for the construction of a benz[*f*]indenone structure (entry 5).[17] Most of the synthetic methods for the preparation of indenones reported thus far involve electrophilic substitution as a key step (cyclization step).[3−7] In contrast, the present transformation involves a regioselective acylation and an intramolecular aldol-type reaction of the resulting keto imines, providing a comple-

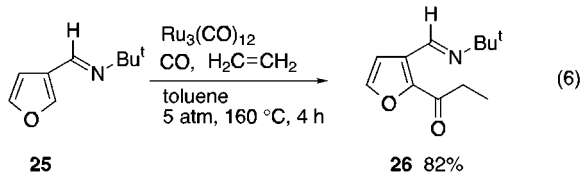
(17) Mal, D.; Hazra, N. K.; Murty, K. V. S. N.; Majumdar, G. *Synlett* **1995**, 1239.

mentary method to conventional electrophilic substituted methods. For example, indenones having an electron-withdrawing group at the 4-position, such as **14** and **16**, cannot be obtained by literature methods based on Friedel−Crafts acylation,[3−5] which are the most useful and reliable methods for the preparation of 2-methyl-1*H*-inden-1-one derivatives, but which involve electrophilic cyclization.[18] Indeed, prior to this report, these were unknown compounds. The present transformation is a synthetically useful method, as well as a new type of transformation.

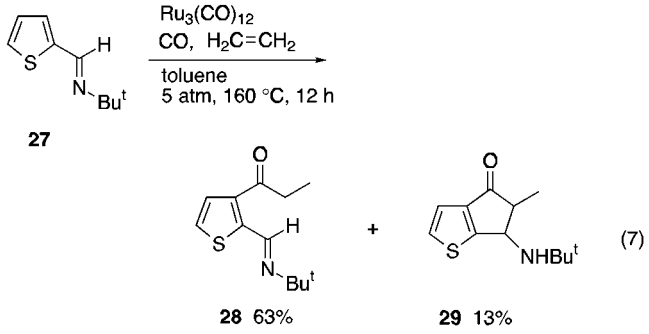
This protocol was applied to heteroaromaic compounds. Interestingly, the reaction of furfural imines **21** with CO and ethylene gave keto imine **22** in 63% GC yield (eq 5). GC analysis of the crude reaction mixture did not show the formation of further reaction products, such as 5,6-dihydro-6-amino-4*H*-cyclopenta[*b*]furan-4-one (**23**) and 4*H*-cyclopenta[*b*]furan-4-one derivative (**24**). In comparison with benzaldehyde imines, the two substituents, the keto and imino groups, in **22** are located too far from one another to undergo an intramolecular aldol-type reaction. The reaction of **25** also afforded keto imine **26** in high yield (eq 6).







On the other hand, the reaction of thiophenecarboxaldehyde imine **27** gave a mixture of keto imine **28** and aldol-type product **29** in favor of **28** (eq 7).



In summary, we have developed a two-step procedure (carbonylation at a C−H bond and intramolecular aldol condensation) for the synthesis of 2-substituted inden-1-ones from aromatic imines. The reaction involves carbonylation at an *ortho* C-H bond in the benzene ring. The isolation of keto imines, in some particular cases, clearly indicates that the transformation of aromatic imines to indenones involves keto imines as primary intermediate.

(18) 2-Methyl-4-nitro-1*H*-inden-1-one was prepared by the bromination−dehydrobromination of the corresponding indanone derivative. Murray, R. J.; Cromwell, N. H. *J. Org. Chem.* **1976**, *41*, 3540.

Experimental Section

General Procedures. In a 50-mL stainless autoclave were placed $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol), aromatic imine (2 mmol), and toluene (6 mL). The autoclave was charged with ethylene to 7 atm at 25 °C and carbon monoxide to 5 atm at 25 °C and then heated in an oil bath at 160 °C for 12 h. The autoclave was cooled to room temperature and the pressure released. To the reaction mixture was added ca. 5 g of SiO_2 (usual chromatography grade, 70−230 mesh), and the resulting mixture was stirred at room temperature for 1 day. After SiO_2 was filtered, the filtrate was evaporated in vacuo and the coupling product was isolated by column chromatography on silica gel with hexane/benzene as eluent. An analytical sample was obtained by bulb-to-bulb distillation or recrystallization.

2,3-Dihydro-2,4-dimethyl-3-[(1,1-dimethylethyl)amino]-1*H*-inden-1-one (4). After the reaction of **1** with CO and ethylene, bulb-to-bulb distillation gave a mixture of **2** and **4** (*trans* and *cis*). Spectral data were obtained from the mixture. **4-major:** ^{1}H NMR ($CDCl_3$) δ 1.17 (d, J = 7.6 Hz, 3H), 1.24 (s, 9H), 2.63 (s, 3H), 2.75−2.92 (m, 1H), 4.62 (d, J = 6.2 Hz, 1H), 7.18−7.60 (m, 3H); MS, m/z (rel intensity) 231 (M^+, 10), 216 (26), 58 (100). **4-minor:** ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H), 1.27 (d, J = 8.1 Hz), 2.48 (s, 3H), 2.56 (q, J = 8.1 Hz, 1H), 4.09 (s, 1H), 7.18−7.60 (m, 3H); MS, m/z (rel intensity) 231 (M^+, 8), 216 (16), 58 (100).

2-(2,2-Dimethylpropyl)-4-methyl-1*H*-inden-1-one (5): yellow oil; R_f = 0.23 (hexane/benzene = 2/1); ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9H), 2.17 (s, 2H), 2.28 (s, 3H), 7.03 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.9, 29.4, 31.6, 37.6, 120.3, 127.8, 130.3, 130.3, 135.5, 137.5, 142.6, 143.2, 199.0; IR (neat) 1709, 1604; MS, m/z (rel intensity) 214 (M^+, 3), 158 (100). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.01; H, 8.46.

2,3-Dihydro-3-[(1,1-dimethylethyl)amino]-4-methyl-2-[(trimethylsilyl)methyl]-1*H*-inden-1-one (6). The stereochemistry of **6** was not determined, but a single isomer was obtained: brown oil; bp 170 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.81 (dd, J = 14.9, 10.3 Hz, 1H), 1.03 (dd, J = 14.9, 4.6 Hz, 1H), 1.22 (s, 9H), 2.45 (s, 3H), 2.67 (dd, J = 10.3, 4.6 Hz, 1H), 4.10 (s, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.5, 17.9, 20.4, 30.1, 50.6, 55.2, 60.7, 121.3, 128.9, 135.8, 136.1, 136.3, 153.9, 209.8; IR (neat) 1711, 1645, 1607, 1591; MS, m/z (rel intensity) 303 (M^+, 0), 288 (M^+ − 15, 7), 73 (100); HRMS calcd for $C_{18}H_{29}NOSi$ (M^+) 303.2018, found 303.2005.

4-Methyl-2-[(trimethylsilyl)methyl]-1*H*-inden-1-one (7): brown oil; bp 150 °C (1 mmHg); R_f = 0.23 (hexane/benzene = 2/1); ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 1.74 (d, J = 1.4 Hz, 2H), 2.24 (s, 3H), 6.96 (t, J = 7.6 Hz, 1H), 6.97 (m, 1H), 7.06 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.7, 15.1, 16.9, 120.2, 126.9, 129.4, 130.2, 135.7, 138.2, 143.6, 137.3, 198.7; IR (neat) 1711, 1604; MS, m/z (rel intensity) 230 (M^+, 12), 215 (16), 73 (100); HRMS calcd for $C_{14}H_{18}OSi$ (M^+) 230.1127, found 230.1130.

2-Methyl-4-propionyl-1*H*-inden-1-one (10): yellow solid; mp 81−83 °C (hexane); R_f = 0.20 (benzene); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.3 Hz, 3H), 1.92 (d, J = 1.6 Hz, 3H), 2.96 (q, J = 7.3 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.98−8.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 8.0, 10.1, 33.3, 125.0, 127.8, 129.7, 131.7, 132.7, 138.4, 144.9, 143.7, 197.8, 201.5; IR (KBr) 1726, 1683, 1603, 1577; MS, m/z (rel intensity) 200 (M^+, 36), 171 (17), 143 (100). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.32; H, 6.07.

4-Methoxy-2-methyl-1*H*-inden-1-one (12): orange solid; mp 86−88 °C (EtOH); R_f = 0.23 (hexane/benzene = 1/2); ^{1}H NMR ($CDCl_3$) δ 1.85 (d, J = 1.6 Hz, 3H), 3.85 (s, 3H), 6.91 (d, J = 7.4 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.30−7.35 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 9.9, 55.7, 115.6, 118.3, 129.5,

131.0, 132.0, 133.8, 140.3, 151.6, 198.9; IR (Kbr) 1709, 1660, 1622, 1602; MS, *m/z* (rel intensity) 174 (M^+, 100), 159 (64). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.85; H, 5.79. Found: C, 75.59; H, 5.81.

2-Methyl-4-(trifluoromethyl)-1*H*-inden-1-one (14): yellow oil; bp 120 °C (1 mmHg); R_f = 0.26 (hexane/benzene = 3/1); ^{1}H NMR ($CDCl_3$) δ 1.94 (d, J = 1.6 Hz, 3H), 7.20−7.31 (m, 1H), 7.37−7.45 (m, 1H), 7.46−7.57 (m, 2H, 5-H); ^{13}C NMR ($CDCl_3$) δ 9.9, 122.8 (q, J = 32.7 Hz), 123.5 (q, J = 271.8 Hz), 124.9, 128.9, 129.5 (q, J = 3.6 Hz), 131.3, 138.3, 140.5, 142.6 (q, J = 2.4 Hz), 196.5; IR (neat) 1723, 1681, 1606; MS, *m/z* (rel intensity) 212 (M^+, 37), 115 (100). Anal. Calcd for $C_{11}H_7F_3O$: C, 62.27; H, 3.33. Found: C, 62.24; H, 3.39.

4-Fluoro-2-methyl-1*H*-inden-1-one (16): yellow solid; mp 64−65 °C (EtOH); R_f = 0.20 (hexane/benzene = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.90 (d, J = 1.6 Hz, 3H), 7.01 (t, J = 8.1 Hz, 1H), 7.12 (dt, J = 4.6, 8.1 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 7.28−7.35 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 10.0, 118.7 (d, J = 2.4 Hz), 122.2 (d, J = 21.8 Hz), 129.5 (d, J = 15.8 Hz), 123.0 (d, J = 6.1 Hz), 132.9 (d, J = 3.6 Hz), 136.2 (d, J = 2.4 Hz), 138.0, 154.5 (d, J = 251.56 Hz), 197.2; IR (KBr) 1710, 1627, 1614, 1596; MS, *m/z* (rel intensity) 162 (M^+, 56), 133 (100); HRMS calcd for $C_{10}H_7OF$ (M^+) 162.0481, found 162.0470.

2,5-Dimethyl-1*H*-inden-1-one (18): yellow oil; bp 130 °C (1 mmHg); R_f = 0.21 (hexane/benzene = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.86 (d, J = 1.6 Hz, 3H), 2.31 (s, 3H), 6.75 (s, 1H), 6.90 (d, J = 7.3 Hz, 1H), 7.02−7.08 (m, 1H), 7.26 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.9, 21.8, 122.3, 122.4, 127.6, 128.2, 136.4, 142.7, 144.5, 145.2, 142.7, 198.3; IR (neat) 1706, 1609; MS, *m/z* (rel intensity) 158 (M^+, 93), 129 (73), 115 (100). Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.43; H, 6.16.

2-Methyl-1*H*-benz[*f*]inden-1-one (20): yellow solid; mp 181−182 °C (EtOH); R_f = 0.26 (hexane/benzene = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.96 (d, J = 1.6 Hz, 3H), 7.24 (s, 1H), 7.32−7.36 (m, 1H), 7.37−7.52 (m, 2H), 7.70 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.4, 119.9, 123.9, 126.6, 128.6, 128.7, 130.3, 130.8, 133.1, 136.4, 139.4, 140.5, 144.6, 197.0; IR (KBr) 1719, 1695, 1626; MS, *m/z* (rel intensity) 194 (M^+, 72), 165 (100). Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.58; H, 5.25.

1-[2-[[(1,1-Dimethylethyl)imino]methyl]-3-furanyl]-1-propanone (22): brown oil; bp 100 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.3 Hz, 3H), 1.33 (s, 9H), 2.85 (q, J = 7.3 Hz, 2H), 6.74 (d, J = 2.0 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 7.4, 29.4, 34.7, 58.4, 110.7, 125.5, 143.6, 146.2, 153.2, 196.9; IR (neat) 1680, 1632; MS, *m/z* (rel intensity) 207 (M^+, 7), 151 (44), 57 (100); HRMS calcd for $C_{12}H_{17}NO_2$ (M^+) 207.1259, found 207.1258.

1-[3-[[(1,1-Dimethylethyl)imino]methyl]-2-furanyl]-1-propanone (26): yellow solid; mp 51−55 °C, bp 105 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.3 Hz, 3H), 1.29 (s, 9H), 2.94 (q, J = 7.3 Hz, 2H), 7.06 (brs, 1H), 7.42 (d, J = 1.7 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 7.4, 29.5, 32.5, 58.0, 110.8, 130.9, 144.3, 149.1, 149.9, 192.5; IR (KBr) 1675, 1639; MS, *m/z* (rel intensity) 207 (M^+, 1), 151 (56), 136 (100); HRMS calcd for $C_{12}H_{17}NO_2$ (M^+) 207.1259, found 207.1249.

1-[2-[[(1,1-Dimethylethyl)imino]methyl]-3-thienyl]-1-propanone (28) and 5,6-Dihydro-6-[(1,1-dimethylethyl)amino]-5-methyl-4*H*-cyclopenta[*b*]thiophen-4-one (29). Bulb-to-bulb distillation gave a **28**-enriched fraction and a **29**-enriched fraction. **28**: colorless oil; bp 135 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.3 Hz, 3H), 1.29 (s, 9H), 2.92 (q, J = 7.3 Hz, 2H), 7.28 (d, J = 5.6 Hz, 1H), 7.41 (d, J = 5.6 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 7.8, 29.5, 35.1, 57.9, 127.0, 128.4, 138.0, 149.5, 150.2, 197.0; MS, *m/z* (rel intensity) 223 (M^+, 8), 152 (100); HRMS calcd for $C_{12}H_{17}NOS$ (M^+) 223.1030, found 223.1019. **29**: colorless oil; bp 140 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.38 (d, J = 7.3 Hz, 3H), 2.60−2.75 (m, 1H), 4.07 (d, J = 3.3 Hz, 1H), 7.11 (d, J = 5.0 Hz, 1H), 7.35 (d, J = 5.0 Hz, 1H); MS, *m/z* (rel intensity) 223 (M^+, 12), 208 (15), 152 (100); HRMS calcd for $C_{12}H_{17}NOS$ (M^+) 223.1030, found 223.1035.

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