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Chelation-Accelerated Sequential Decarbonylation of Formate and Alkoxycarbonylation of Aryl Halides Using a Combined Ru and Pd Catalyst

Sangwon Ko,[†] Chongmok Lee,[†] Moon-Gun Choi,[‡] Youngim Na,[§] and Sukbok Chang*[,§]

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea, Department of Chemistry, Yonsei University, Seoul 120-749, Korea, and Center for Molecular Design and Synthesis (CMDS), Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

sbchang@mail.kaist.ac.kr

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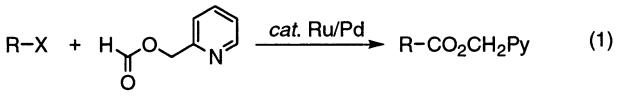
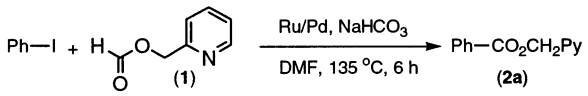
Abstract: An efficient cooperative catalyst system for the coupling of a wide range of organic electrophiles with chelated formate is reported to afford aryl and alkenyl esters by the simultaneous employment of Ru and Pd catalyst, in which ruthenium first promotes chelation-accelerated decarbonylation of formate to release CO and carbinol that are presumed to be transferred, still chelated to Ru, into Pd catalyst, which catalyzes alkoxycarbonylation of the organic electrophiles.

Transition-metal catalysis has made significant contributions to synthetic chemistry, especially in the past decades, and this trend will continue in the future.[1] Whereas a single metal species is employed to carry out a specified transformation in most cases, some recent examples have shown that one-pot tandem conversions could be achieved by the right combination of multiple catalysts, in which sequential catalytic processes are in action by the use of different metal species at the same time.[2] In the context of studies on metal catalyzed reactions,[3] we recently reported a novel chelation-assisted approach toward Ru-catalyzed hydroesterfication of olefins.[4] In this regard, we describe herein an efficient coupling protocol of a chelating formate with aryl and alkenyl (pseudo)halides on the basis of two sequential catalytic processes; decarbonylation of pyridylmethyl formate by Ru catalyst, and subsequent Pd-catalyzed alkoxycarbonylation of organic electrophiles (eq 1).[5]



In the hydroesterification reaction of alkenes with 2-pyridylmethyl formate (**1**) using $Ru_3(CO)_{12}$ catalyst,[4] we observed that, with bulky substrates such as tri- and tetrasubstituted olefins, decarbonylation of **1** was a major source of low product yields. The Ru-catalyzed decarbonylation of **1** became almost dominant, especially in the absence of organic acceptors such as alkenes and alkynes, which is believed to be accelerated presumably due to chelation.[6] For example, treatment of 2-pyridylmethyl formate (**1**) with $Ru_3(CO)_{12}$ complex (5 mol %) resulted in complete decarbonylation (DMF, 1 h, 135 °C), generating 2-pyridinemethanol and CO in quantitative yields. In contrast, benzyl formate was not affected by the same catalyst and was completely recovered unchanged, indicating that the facile decarbonylation of formate **1** is driven by chelation between ruthenium and the pyridyl group of **1** (vide infra).[7]

TABLE 1. Coupling of Iodobenzene with Formate 1[a]



entry	Ru (3 mol %)	Pd (2 mol %)	yield[b] (%)
1	$Ru_3(CO)_{12}$	–	<5
2	–	$PdCl_2$	<5
3	$Ru_3(CO)_{12}$	$PdCl_2$	94
4	$Ru_3(CO)_{12}$	$Pd(OAc)_2$	79
5	$Ru_3(CO)_{12}$	$Pd(PPh_3)_4$	88
6	$Ru_3(CO)_{12}$	$Pd_2(dba)_3$	93
7	$Ru_3(CO)_{12}$	Pd/C	86

[a] Iodobenzene (0.4 mmol), formate **1** (0.2 mmol), $NaHCO_3$ (0.3 mmol), and indicated catalysts in DMF (0.2 mL). [b] Refer to isolated yield.

This observation led us to test a possibility that the in situ generated carbinol and CO could be sequentially utilized to couple with organic electrophiles in the presence of a suitable second metal catalyst. As a test reaction, iodobenzene was allowed to react with 2-pyridylmethyl formate (**1**) under a variety of catalytic conditions (Table 1).[8] Whereas no coupled product was generated with the action of any single metal species alone (Ru, Rh, Pd, etc.), we were pleased to discover that *simultaneous employment of both Ru and Pd catalyst*, in

[†] Ewha Womans University.
[‡] Yonsei University.
[§] Korea Advanced Institute of Science and Technology.

(1) (a) *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998. (b) Tsuji, J. *Transition Metal Reagents and Catalysts*; John Wiley & Sons, Ltd.: London, 2000. (c) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002.

(2) For selected recent examples, see: (a) Barnhart, R. W.; Banzan, G. C.; Mourey, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (b) Jeong, N.; Seo, S. D.; Shin, J. Y. *J. Am. Chem. Soc.* **2000**, *122*, 10220. (c) Lee, P. H.; Sung, S.-y.; Lee, K. *Org. Lett.* **2001**, *3*, 3201. (d) Son, S. U.; Park, K. H.; Chung, Y. K. *J. Am. Chem. Soc.* **2002**, *124*, 6838.

(3) (a) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887. (b) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011. (c) Chang, S.; Lee, M.; Kim, S. *Synlett* **2001**, 1557. (d) Chang, S.; Na, Y.; Choi, E.; Kim, S. *Org. Lett.* **2001**, *3*, 2089. (e) Chang, S.; Yang, S. H.; Lee, P. H. *Tetrahedron Lett.* **2001**, *42*, 4833. (f) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209. (g) Choi, E.; Lee, C.; Na, Y.; Chang, S. *Org. Lett.* **2002**, *4*, 2369.

(4) Ko, S.; Na, Y.; Chang, S. *J. Am. Chem. Soc.* **2002**, *124*, 750.

(5) Although efficiency was generally low (<36% yield), a bimetallic catalytic system of Pd/Ru was previously utilized for the conversion of halobenzenes into aromatic acids with aqueous methyl formate under biphasic conditions at 160 °C, see: Jenner, G.; Taleb, A. B. *J. Organomet. Chem.* **1994**, *470*, 257.

(6) For recent examples of chelation-assisted strategy in metal catalyzed reactions, see: (a) Itami, K.; Mitsudo, K.; Kamei, T.; Koike, T.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 12013. (b) Ishiyama, T.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 12043. (c) Chatani, N.; Tatamidani, H.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 4849. (d) Jun, C.-H.; Lee, H.; Moon, C. W.; Hong, H.-S. *J. Am. Chem. Soc.* **2001**, *123*, 8600.

(7) $Ru_3(CO)_{12}$ has been known to catalyze decarbonylation of alkyl formates in the presence of phosphines or *N*-oxide ligands, see: (a) Kondo, T.; Tantayanon, S.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1989**, *30*, 4137. (b) Jenner, G.; Nahmed, E. M.; Leismann, H. *J. Organomet. Chem.* **1990**, *387*, 315.

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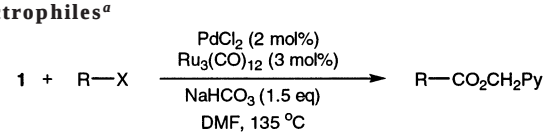
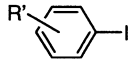
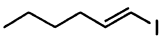
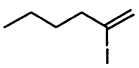
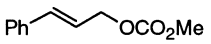
the presence of an inorganic base ($NaHCO_3$), afforded 2-pyridinemethyl benzoate (**2a**) in high yield. Whereas $Ru_3(CO)_{12}$ was the only effective Ru species among various complexes tested, choice of a Pd partner was more flexible. Although certain Pd catalysts exhibited rather similar efficiency on the coupling in the presence of $Ru_3(CO)_{12}$ catalyst (entries 3−6), $PdCl_2$ was chosen as the Pd catalyst for practical reasons. In addition to the homogeneous Pd catalysts, Pd/C (entry 7) turned out to be also effective for the reaction.[9] DMF (94%, entry 3) was the most effective medium for the reaction compared with other tested solvents such as toluene (72%), THF (61%), or dioxane (59%).[10] Although a bimetallic catalytic system of Rh/Pd was previously known to perform formate-halide carbonylation reactions,[11] the carbonylation did proceed only under pressurized CO atmosphere implying that *formate ester carbonyl is not the source of the generated carbonylated products*.

The sequential Ru/Pd bimetallic catalytic protocol could be successfully applied to a large array of aryl and alkenyl (pseudo)halides with formate **1** under the conditions established above (Table 2). In general, 2−5 mol % of each $PdCl_2$ and $Ru_3(CO)_{12}$ catalyst were sufficient to obtain satisfactory yields in DMF (135 °C) in the presence of $NaHCO_3$ (1.5 equiv). Whereas free hydroxyl group was tolerant to the reaction conditions (entry 4), steric hindrance near the reaction site slowed the conversion to some extent (entry 6). Chemoselective coupling on iodo group in the presence of bromo was observed (entry 7). However, with longer reaction times, bromobenzene itself was also reacted with higher loadings of both Pd (5 mol %) and Ru (5 mol %) catalyst (entry 8). For 1-iodonaphthalene, K_2CO_3 (73%) turned out to be a more effective base than $NaHCO_3$ (36%). An aryl triflate was smoothly reacted with **1** to afford benzoate in moderate yield (entry 10). Alkenyl iodides were also readily coupled with formate **1** under the standard conditions and conjugated esters were obtained in high yields (entries 11 and 12). In addition, allylic carbonate turned out to be another coupling partner to afford allylic ester (entry 13).[12] No isomerization of the olefinic geometry was observed with alkenyl substrates.

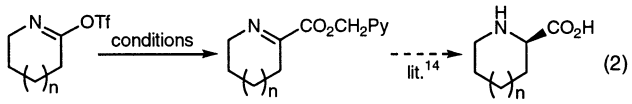
Notably, imidoyl triflates were also coupled with formate **1** under the employed conditions (DMF, 135 °C), and cyclic imidoyl carboxylates with variable ring sizes (**2l**−**2o**) were readily produced in 12−24 h (eq 2).[13] It should be mentioned that this could be potentially developed into an easy route for preparation of unnatural chiral amino acids upon stereoselective reduction of the imidoyl double bond.[14] *The conversion of imidoyl triflates into imidoyl carboxylates have not been reported using the conventional Pd-catalyzed carbonylation of iodobenzenes with alcohols even in the presence of high pressuric CO atmosphere*.[15] As shown in our previous paper,[4] the stable formate **1** is readily prepared with excellent yields (>95%) in large scales (>15 g) by a simple formylation of 2-pydidinemethanol. In addition, hydrolysis of the produced carboxylates under mild conditions gives pyridylcarbinol and the corresponding carboxylic acids in quantitative yields. Therefore, this protocol could be used as an attractive alternative to the Pd-catalyzed carbonylation reaction.

TABLE 2. Reaction of Formate 1 with Various Organic Electrophiles[a]



entry	R—X	t/h	yield (%)[b]
1	 (R' = H)	6	94 (**2a**)
2	(4-Me)	6	97 (**2b**)
3	(4-OMe)	6	95 (**2c**)
4	(4-OH)	6	67 (**2d**)
5	(4-$COCH_3$)	6	70 (**2e**)
6	(2,6-Me_2)	10	65 (**2f**)
7	(3-Br)	5	90 (**2g**)
8[c]	Ph—Br	24	92 (**2a**)
9[c,d]	1-Iodonaphthalene	12	73 (**2h**)
10	Ph—OTf	12	70 (**2a**)
11[c]		8	75 (**2i**)
12		6	90 (**2j**)
13[c]		12	65 (**2k**)

[a] Substrates (0.8 mmol), **1** (0.4 mmol), and $NaHCO_3$ (0.6 mmol) in DMF (0.4 mL). [b] Isolated yield after chromatography. [c] Pd and Ru were each used (5 mol %). [d] K_2CO_3 (1.5 equiv) was used instead of $NaHCO_3$.



(2)

n = 0 (**2l**, 24 h, 79%), 1 (**2m**, 12 h, 76%)
2 (**2n**, 24 h, 77%), 4 (**2o**, 24 h, 63%)

Although further studies have to be carried out to elucidate detailed aspects of this reaction, it is believed

(8) Pd-catalyzed alkoxycarbonylation of aryl halides with alkyl formates in the presence of sodium alkoxides was previously reported, in which sodium alkoxide decarbonylates stoichiometrically formates to provide carbon monoxide, see: Carpentier, J.-F.; Castanet, Y.; Brocard, J.; Mortreux, A.; Petit, F. *Tetrahedron Lett*. **1991**, *32*, 4705.

(9) Recently, it has been revealed that Pd/C is a source of soluble homogeneous catalyst in carbonylation reaction, see: Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139.

(10) On the basis of this result, a possibility that DMF acts as a CO source through decomposition of DMF could be ruled out, for reference; see: Wan, Y.; Altermann, M.; Larhed, M.; Hallberg, A. *J. Org. Chem*. **2002**, *67*, 6232.

(11) Buchan, C.; Hamel, N.; Woell, J. B.; Alper, H. *J. Chem. Soc., Chem. Commun*. **1986**, 167.

(12) However, chlorobenzene did not react under the present conditions.

(13) Imidoyl triflates were prepared in 70−90% yields starting from the corresponding lactams: Jacobi, P. A.; Liu, H. *J. Am. Chem. Soc.* **1999**, *121*, 1958.

(14) Blaser, H.-U.; Spindler, F. In *Comprehensive Asymmetric Catalysis I*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Heidelberg, 1999; Vol. 1, Chapter 6.2.

(15) *Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; Vol. 2, Part VI.

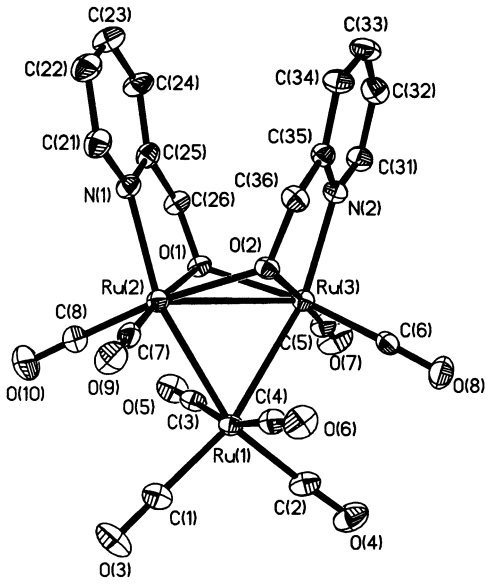
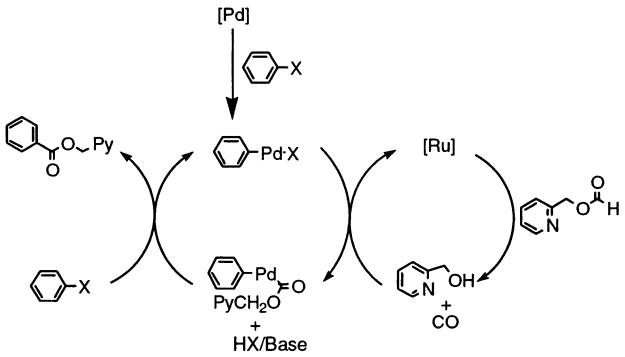


FIGURE 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) 2.7841(7), Ru(2)−Ru(3) 3.0197(9), Ru(1)−Ru(3) 2.7693(8), Ru(2)−O(1) 2.088(3), Ru(2)−O(2) 2.147(3), Ru(2)−N(1) 2.171(4); Ru(1)−Ru(2)−Ru(3) 56.825(18), Ru(2)−O(1)−Ru(3) 91.11(12), O(1)−Ru(2)−N(1) 77.81(13).

SCHEME 1. Proposed Mechanism for the Ru/Pd-Catalyzed Reaction



to proceed via two sequential catalytic executions (Scheme 1): decarbonylation of formate **1** by $Ru_3(CO)_{12}$ complex followed by Pd-catalyzed alkoxycarbonylation of organic electrophiles.

Treatment of 2-pyridylmethyl formate (**1**) with stoichiometric amounts of $Ru_3(CO)_{12}$ gave a brownish solid (**3**), the IR spectrum of which showed five detectable CO stretches: 2071, 2024, 1994, 1971, and 1932 cm^{-1}. Crystal structure of **3** reveals that it is a triruthenium cluster coordinated with eight carbon monoxides and two molecules of 2-pyridinemethanol which are generated via decarbonylation of formate **1** (Figure 1).[16] Whereas trinuclear Ru species were proposed previously as key intermediates in some organic transformations involving C−H activation,[17] to the best of our knowledge, this is the first example of a ruthenium cluster containing five-membered N,O-heteroatom chelation.[18] Under the atmospheric CO environment (1 atm), $PdCl_2$ (2 mol %) catalyst performed the stoichiometric coupling reaction between iodobenzene and **3** producing benzoate ester (**2a**) in 43% yield in the presence of $NaHCO_3$ (1.5 equiv) even at lower temperatures (80 °C, 2 h) compared with the catalytic conditions. Reaction of 2-pyridinemethanol with iodobenzene (2 equiv) under atmospheric CO was sluggish with Pd species alone in the absence of Ru catalyst and provided benzoate in low yield (33%) of benzoate with $PdCl_2$ catalyst (2 mol %) in DMF (80 °C, 2 h, 42% conversion). However, the same reaction proceeded much faster in the presence of $Ru_3(CO)_{12}$ (2 mol %), and resulted in complete conversion with 91% isolated yield under otherwise identical conditions. This implies that the transfer of 2-pyridinemethanol into the Pd-catalyzed alkoxycarbonylation cycles is greatly accelerated by chelation with Ru. Therefore, it is believed that the ruthenium catalyst has dual roles; it catalyzes decarbonylation of chelating formate **1** and facilitates chelation-assisting transfer of the in situ formed carbinol to Pd-catalyzed carbonylation pathways.

In summary, an efficient cooperative catalytic system for coupling a range of organic electrophiles with chelating formate has been achieved to afford aryl and alkenyl esters by the one-pot employment of Ru and Pd catalysts. In the processes, chelation plays a key role on the efficiency of both sequences of ruthenium-catalyzed decarbonylation of formate and palladium-catalyzed alkoxycarbonylation of aryl and alkenyl (pseudo)halides. Imidoyl carboxylates can be readily obtained from the corresponding imidoyl triflates. The merit of this protocol in comparison with Pd-catalyzed carbonylation is obvious such that it does not employ high pressuric CO atmosphere, which can potentially lead to an easy way of introducing a labeled carbonyl into products without need of using expensive labeled gaseous CO.[19]

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on a 250 and 62.5 MHz NMR spectrometer, respectively. Chemical shifts are reported in δ, parts per million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm of chloroform-*d* or to a center line of a pentet at 2.50 ppm of DMSO-d_6. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; td, triple of doublet; dd, double of doublet; b, broad. ^{13}C NMR data are reported in ppm relative to the center line of a triplet at 77.0 ppm of chlorofom-*d* or to a center line of a heptet at 39.5 ppm of DMSO-d_6. IR and mass spectra were obtained from the Center for Molecular Design and Synthesis (CMDS) at KAIST. Column chromatography was carried out using silica gel 60 (230−400 mesh, Merck). Solvents were purified by standard procedures. Commercially obtained chemicals including Ru and Pd complexes were purchased from a commercial supplier and used as obtained without further purification.

Representative Procedure for the Coupling Reaction. To a solution of 2-pyridylmethyl formate **1**[4] (54.8 mg, 0.4 mmol) in DMF (0.4 mL) was added iodobenzene (163.2 mg, 0.8 mmol)

(16) For full data of crystal **3**, see the Supporting Information. Selected data of crystal **3**: crystal dimension 0.28 × 0.26 × 0.16 mm, V = 2376.0(10) Å^3, monoclinic, space group $P2(1)/c$, a = 13.097(3) Å, b = 9.137(2) Å, c = 20.287(5) Å, measured 17585, R(int) = 0.0519, wR^2 (all data) = 0.0754, GOF = 1.180, Z = 11.

(17) Fukuyama, T.; Chatani, N.; Tatsumi, J.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 11522.

(18) For a previous report of a crystal structure of a ruthenium cluster with phenanthroline ligand, see: Fish, R. H.; Kim, T.-J.; Stewart, J. L.; Bushweller, J. H.; Rosen, R. K.; Dupon, J. W. *Organometallics* **1986**, *5*, 2193.

(19) Recently, the use of aldehyde as a CO source in catalytic Pauson−Khand reaction has been reported, see: (a) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **2002**, *124*, 3806. (b) Shibata, T.; Toshida, N.; Takagi, K. *Org. Lett.* **2002**, *4*, 1619.

followed by $Ru_3(CO)_{12}$ (7.7 mg, 3 mol %), $PdCl_2$ (1.4 mg, 2 mol %) and $NaHCO_3$ (50.4 mg, 0.6 mmol). The reaction mixture was stirred at 135 °C for 6 h in a sealed vial. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (15% EtOAc/hexane) to afford the 2-pyridylmethyl benzoate (**2a**) as a yellowish liquid: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.61 (d, 1H, J = 4.3 Hz), 8.12 (d, 2H, J = 8.3 Hz), 7.70 (td, 1H, J = 7.7, 1.7 Hz), 7.56 (dd, 1H, J = 7.7, 1.5 Hz), 7.43 (m, 3H), 7.24 (m, 1H), 5.49 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 166.6, 156.4, 149.9, 137.2, 133.6, 130.2, 128.9, 123.3, 122.1, 67.6; IR (neat) 3066, 3015, 2949, 1971, 1916, 1719, 1595, 1438 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{11}NO_2$ 213.0790 (M^+), found 213.0794.

2-Pyridylmethyl 4-methylbenzoate (2b): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.62 (d, 1H, J = 4.3 Hz), 8.00 (d, 2H, J = 8.2 Hz), 7.72 (td, 1H, J = 7.7, 1.7 Hz), 7.45 (d, 1H, J = 7.8 Hz), 7.26 (d, 3H, J = 7.3 Hz) 5.48 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 166.7, 156.5, 149.8, 144.4, 137.2, 130.2, 129.6, 127.5, 123.2, 122.0, 67.4, 22.1; IR (neat) 2948, 1930, 1720, 1612, 1438, 1276, 1108, 753 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{13}NO_2$ 227.0947 (M^+), found 227.0948.

2-Pyridylmethyl 4-methoxylbenzoate (2c): yellowish solid; mp 49−50 °C dec; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.61 (d, 1H, J = 4.4 Hz), 8.08 (d, 2H, J = 8.9 Hz), 7.72 (td, 1H, J = 7.7, 1.6 Hz), 7.44 (d, 1H, J = 7.8 Hz), 7.24 (m, 1H), 6.93 (d, 2H, J = 8.9 Hz), 5.46 (s, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 166.4, 164.0, 156.7, 149.9, 137.2, 132.3, 123.2, 122.6, 122.0, 114.1, 67.4, 55.9; IR (neat) 3387, 2977, 2938, 1705, 1608, 1295, 1104, 1020, 757 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{13}NO_3$ 243.0896 (M^+), found 243.0894.

2-Pyridylmethyl 4-hydroxylbenzoate (2d): yellowish solid; mp 167−170 °C dec; ^{1}H NMR (DMSO-d_6, 250 MHz) δ 10.47 (s, 1H), 8.57 (d, 1H, J = 4.3 Hz), 7.90 (d, 2H, J = 8.7 Hz), 7.84 (t, 1H, J = 7.7 Hz), 7.48 (d, 1H, J = 7.8 Hz), 7.35 (m, 1H), 6.88 (d, 2H, J = 8.6 Hz), 5.36 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 165.2, 162.2, 155.9, 149.0, 137.2, 131.7, 123.0, 121.5, 120.0, 115.4, 66.1; IR (neat) 3460, 2936, 1715, 1671, 1388, 1260, 1096, 771 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{11}NO_3$ 229.0739 (M^+), found 229.0740.

2-Pyridylmethyl 4-acetylbenzoate (2e): yellowish solid; mp 88−89 °C dec; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.63 (d, 1H, J = 4.6 Hz), 8.20 (d, 2H, J = 8.3 Hz), 8.02 (d, 2H, J = 8.3 Hz), 7.75 (t, 1H, J = 7.7 Hz), 7.46 (d, 1H, J = 7.8 Hz), 7.28 (m, 1H), 5.51 (s, 2H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 197.9, 165.8, 155.9, 150.0, 140.8, 137.3, 134.0, 130.5, 128.7, 123.5, 122.3, 68.1, 27.4; IR (neat) 3056, 2961, 1972, 1729, 1689, 1274 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}NO_3$ 255.0896 (M^+), found 255.0887.

2-Pyridylmethyl 2,6-dimethylbenzoate (2f): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.61 (d, 1H, J = 4.8 Hz), 7.71 (td, 1H, J = 7.7, 1.7 Hz), 7.45 (d, 1H, J = 7.8 Hz), 7.27−7.16 (m, 2H), 7.03 (d, 2H, J = 7.5 Hz), 5.48 (s, 2H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.0, 156.0, 150.0, 137.2, 135.6, 133.8, 130.0, 128.0, 123.4, 122.6, 67.8, 20.3; IR (neat) 3438, 3055, 2962, 1730, 1595, 1468, 1271, 1116, 1075, 736 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{15}NO_2$ 241.1104 (M^+), found 241.1103.

2-Pyridylmethyl 3-bromobenzoate (2g): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.63 (d, 1H, J = 4.7 Hz), 8.24 (s, 1H), 8.04 (dd, 1H, J = 7.8, 1.0 Hz), 7.73−7.68 (m, 2H), 7.43 (d, 1H, J = 7.8 Hz), 7.35 (d, 1H, J = 7.9 Hz), 7.26 (m, 1H), 5.48 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.3, 156.0, 150.0, 137.3, 136.6, 133.1, 132.1, 130.4, 128.8, 123.5, 122.9, 122.3, 68.0; IR (neat) 3432, 3069, 2950, 1720, 1572, 1425, 1252, 1122, 998, 747 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{10}NO_2Br$ 290.9895 (M^+), found 290.9885.

2-Pyridylmethyl 1-naphthalenecarboxylate (2h): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.99 (d, 1H, J = 8.6 Hz), 8.63 (d, 1H, J = 4.7 Hz), 8.31 (d, 1H, J = 7.3 Hz), 8.03 (d, 1H, J = 8.2 Hz), 7.88 (d, 1H, J = 8.2 Hz), 7.71 (td, 1H, J = 7.7, 1.6 Hz), 7.61−7.47 (m, 4H), 7.24 (m, 1H), 5.57 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 167.4, 156.5, 150.0, 137.3, 134.3, 134.2, 131.9, 131.0, 129.0, 128.4, 127.0, 126.7, 126.2, 125.0, 123.3, 122.2, 67.7; IR (neat) 3056, 2951, 1715, 1594, 1438, 1278, 1133, 1016, 783, 735 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}NO_2$ 263.0947 (M^+), found 263.0939.

2-Pyridylmethyl (*E*)-2-heptenoate (2i): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.60 (d, 1H, J = 4.7 Hz), 7.71 (td, 1H, J = 7.7, 1.6 Hz), 7.37 (d, 1H, J = 7.8 Hz), 7.23 (m, 1H), 7.07 (dt, 1H, J = 15.6, 7.8 Hz), 5.93 (d, 1H, J = 15.6 Hz), 5.30 (s, 2H), 2.24 (q, 1H, J = 6.6 Hz), 1.49−1.29 (m, 4H), 0.91 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 166.8, 156.5, 151.1, 149.9, 137.2, 123.2, 122.2, 121.0, 67.0, 32.4, 30.4, 22.6, 14.3; IR (neat) 2961, 1726, 1439, 1170, 1047, 732 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ 219.1260 (M^+), found 219.1260.

2-Pyridylmethyl 2-butylacrylate (2j): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.60 (d, 1H, J = 4.7 Hz), 7.71 (td, 1H, J = 7.7, 1.6 Hz), 7.37 (d, 1H, J = 7.8 Hz), 7.23 (m, 1H), 6.25 (s, 1H), 5.06 (s, 1H), 5.32 (s, 2H), 2.36 (t, 2H, J = 7.8 Hz), 1.51−1.30 (m, 4H), 0.91 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 167.3, 156.5, 149.8, 140.9, 137.2, 125.6, 123.2, 121.9, 67.3, 32.0, 30.9, 22.7, 14.3; IR (neat) 2959, 2871, 1722, 1595, 1438, 1282, 1155, 947, 757 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ 219.1260 (M^+), found 219.1262.

2-Pyridylmethyl (*E*)-4-phenyl-3-butenoate (2k): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.60 (d, 1H, J = 4.5 Hz), 7.73 (td, 1H, J = 7.6, 1.6 Hz), 7.51 (d, 1H, J = 7.8 Hz), 7.44−7.20 (m, 6H), 6.70 (d, 1H, J = 15.9 Hz), 6.40 (dt, 1H, J = 15.9, 6.1 Hz), 4.73 (s, 2H), 4.32 (dd, 2H, J = 6.0, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.5, 149.1, 136.6, 132.8, 128.5, 127.7, 126.5, 125.7, 122.3, 121.4, 73.1, 71.5; IR (neat) 3462, 2986, 1746, 1447, 1375, 1245, 1048, 918, 735 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{15}NO_2$ 253.1104 (M^+), found 253.1109.

2-Pyridylmethyl 1-pyrroline-2-carboxylate (2l): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.60 (d, 1H, J = 4.8 Hz), 8.40 (bs, 1H), 7.77 (td, 1H, J = 7.8, 1.6 Hz), 7.32 (d, 2H, J = 7.4 Hz), 5.31 (s, 2H), 3.47 (m, 2H), 2.62 (t, 2H, J = 6.5 Hz), 2.11−2.00 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 172.9, 155.3, 149.6, 137.8, 123.7, 122.8, 122.3, 117.7, 66.1, 43.8, 32.3, 25.6; IR (neat) 3058, 2887, 1741, 1599, 1441, 1375, 1191, 1080, 983, 743 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}N_2O_2$ 204.0899 (M^+), found 204.0878.

2-Pyridylmethyl-3,4,5,6-tetrahydropyridinecarboxylate (2m): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.60 (d, 1H, J = 4.8 Hz), 7.74 (td, 1H, J = 7.7, 1.6 Hz), 7.56 (bs, 1H), 7.35 (d, 1H, J = 7.8 Hz), 7.29−7.26 (m, 1H), 5.20 (s, 2H), 3.33 (m, 2H), 2.48 (t, 2H, J = 6.4 Hz), 1.83−1.65 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 173.5, 155.4, 149.7, 137.8, 123.8, 122.8, 117.7, 66.9, 43.8, 33.9, 29.9, 21.3; IR (neat) 3021, 2871, 1738, 1601, 1483, 1368, 1223, 1084, 762 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}N_2O_2$ 218.1056 (M^+), found 218.1056.

2-Pyridylmethyl 1-aza-1-cycloheptene-2-carboxylate (2n): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.58 (d, 1H, J = 4.9 Hz), 7.74 (td, 1H, J = 7.7, 1.6 Hz), 7.37 (d, 1H, J = 7.8 Hz), 7.29−7.26 (m, 1H), 7.15 (bs, 1H), 5.20 (s, 2H), 3.34 (m, 2H), 2.44 (t, 2H, J = 6.9 Hz), 1.73−1.59 (m, 4H), 1.50−1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 173.7, 155.6, 149.6, 137.7, 123.7, 123.1, 122.8, 117.7, 67.1, 44.2, 34.0, 29.8, 25.6. 24.2; IR (neat) 2949, 2868, 1746, 1600, 1440, 1372, 1183, 1046, 758 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{16}N_2O_2$ 232.1213 (M^+), found 232.1216.

2-Pyridylmethyl 1-aza-1-cyclononene-2-carboxylate (2o): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (d, 1H, J = 4.5 Hz), 7.69 (td, 1H, J = 7.7, 1.7 Hz), 7.34 (d, 1H, J = 7.8 Hz), 7.22 (m, 1H), 6.17 (bs, 1H), 5.19 (s, 2H), 3.26 (t, 2H, J = 7.1 Hz), 2.39 (t, 2H, J = 7.4 Hz), 1.67−1.53 (m, 4H), 1.31 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 173.4, 155.6, 149.6, 137.0, 123.0, 122.2, 66.6, 44.3, 34.0, 30.0, 28.6, 28.3, 25.8, 24.5; IR (neat) 2935, 1735, 1598, 1438, 1374, 1146, 763 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}N_2O_2$ 260.1526 (M^+), found 260.1531.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR of all 2-pyridylmethyl carboxylates prepared (**2a**−**o**) and crystal/refinement data of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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