

Supporting Information

Reactions of Cyclopropyl Aryl Ketones with α -ketoacetic acids Catalyzed by $C_8F_{17}SO_3H$ in Fluorous Phase

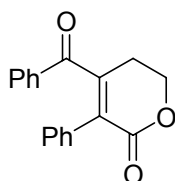
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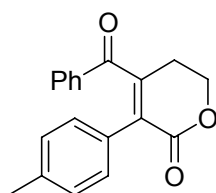
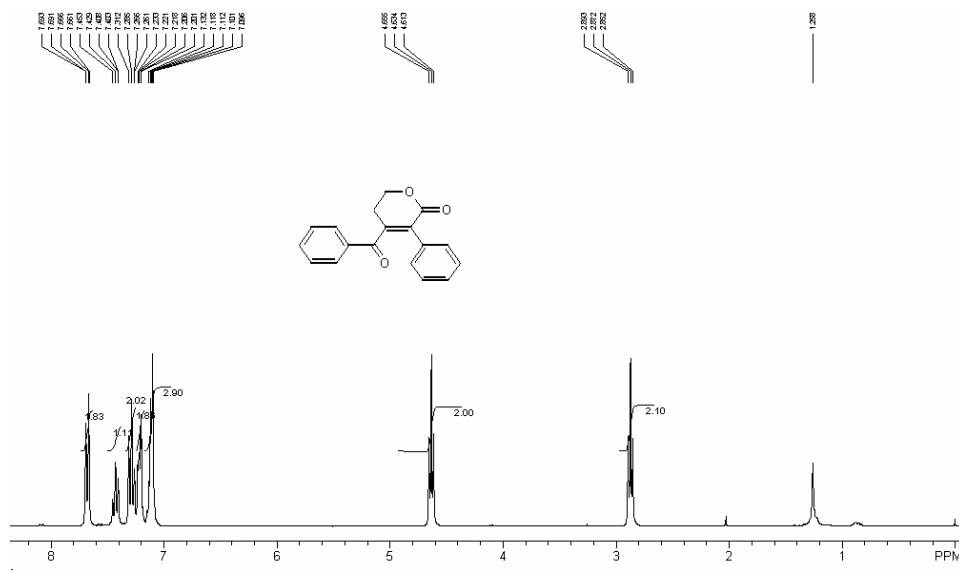
Typical reaction procedure for Reaction of Cyclopropyl Aryl Ketone with α -ketoacetic acid Catalyzed by $C_8F_{17}SO_3H$ in Fluorous Phase.

To a solution of $C_8F_{17}SO_3H$ (45 mg, 0.006 mmol) in perfluorodecalin ($C_{10}F_{18}$, *cis*- and *trans*-mixture) (solvent, 1.0 mL) was added cyclopropyl aryl ketone (**1**, 0.3 mmol), α -ketoacetic acid (**2**, 0.3 mmol) and DCE (solvent, 1.0 mL). Then, the mixture was stirred at 60 °C for the necessary time. The fluorous layer was separated for the next reaction. The reaction mixture (organic layer) was washed by water (5 mL) and extracted with dichloromethane (2 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 4) to give the corresponding product **3**.



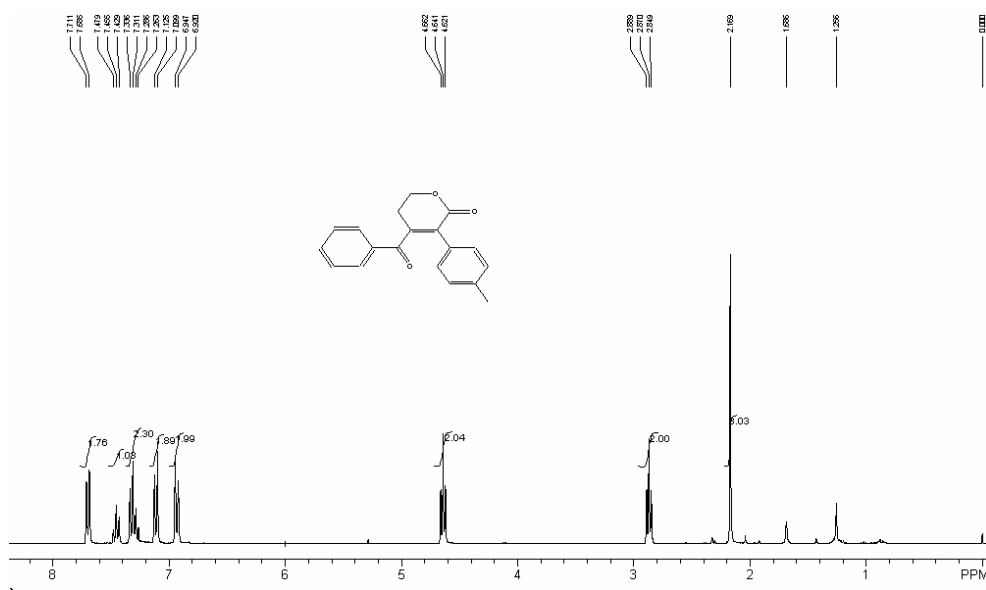
4-Benzoyl-3-phenyl-5,6-dihydropyran-2-one (**3a**):

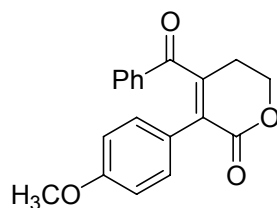
This compound was obtained as a white solid, yield: 77 mg, 92%. This is a known compound. Its 1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ 1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.87 (t, J = 6.3 Hz, 2H, CH_2), 4.63 (t, J = 6.3 Hz, 2H, OCH_2), 7.10-7.13 (m, 3H, Ar), 7.20-7.23 (m, 2H, Ar), 7.26-7.31 (m, 2H, Ar), 7.40-7.45 (m, 1H, Ar), 7.66-7.69 (m, 2H, Ar).



4-Benzoyl-3-p-tolyl-5,6-dihydropyran-2-one (3b):

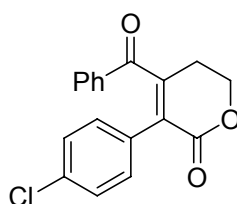
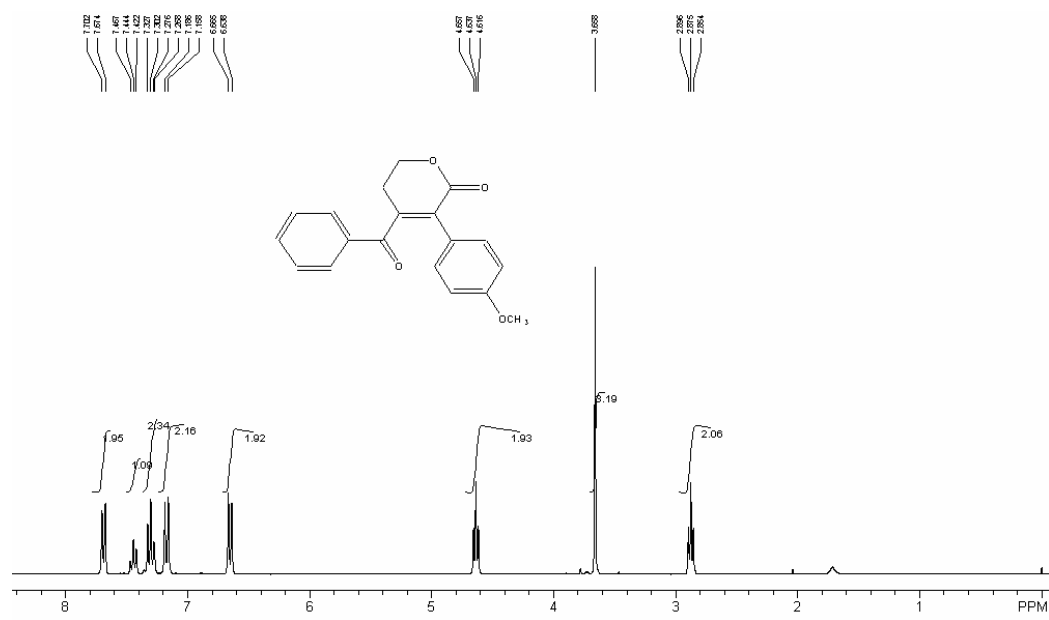
This compound was obtained as a red oil, yield: 70 mg, 80%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 2.17 (s, 3H, CH_3), 2.87 (t, $J = 6.3$ Hz, 2H, CH_2), 4.64 (t, $J = 6.3$ Hz, 2H, OCH_2), 6.93 (d, $J = 8.1$ Hz, 2H, Ar), 7.11 (d, $J = 8.1$ Hz, 2H, Ar), 7.31 (t, $J = 7.5$ Hz, 2H, Ar), 7.46 (t, $J = 7.5$ Hz, 1H, Ar), 7.70 (d, $J = 7.8$ Hz, 2H, Ar).





4-Benzoyl-3-(4-methoxy-phenyl)-5,6-dihydropyran-2-one (3c):

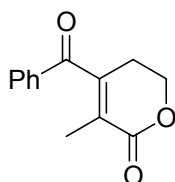
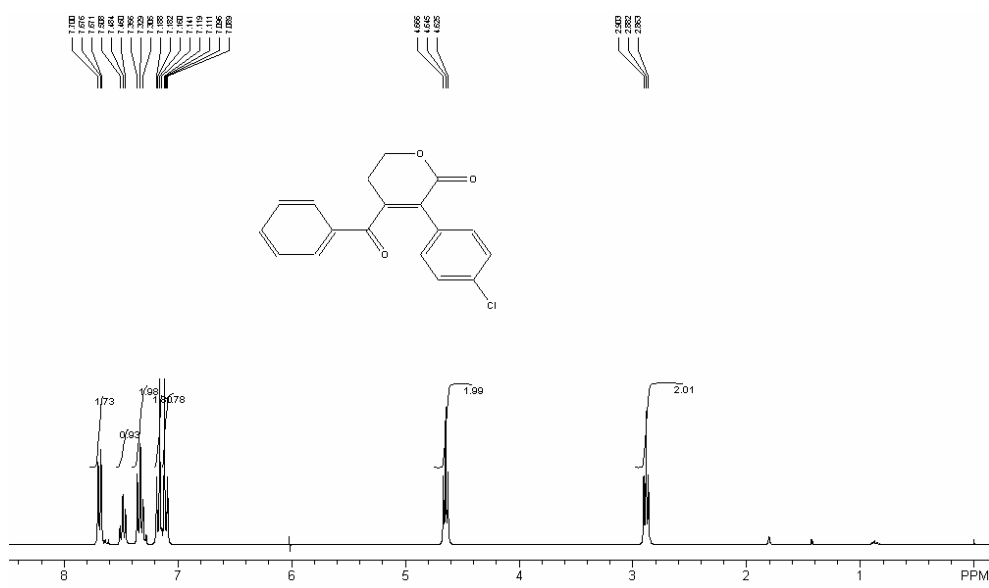
This compound was obtained as a pale-red oil, yield: 66 mg, 71%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 2.88 (t, $J = 6.0$ Hz, 2H, CH_2), 3.66 (s, 3H, OCH_3), 4.64 (t, $J = 6.0$ Hz, 2H, OCH_2), 6.65 (d, $J = 8.1$ Hz, 2H, Ar), 7.17 (d, $J = 8.1$ Hz, 2H, Ar), 7.30 (t, $J = 7.5$ Hz, 2H, Ar), 7.42 (t, $J = 6.9$ Hz, 1H, Ar), 7.69 (d, $J = 7.4$ Hz, 2H, Ar).



4-Benzoyl-3-(4-chloro-phenyl)-5,6-dihydropyran-2-one (3d):

This compound was obtained as a white solid, yield: 86 mg, 92%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 2.88 (t, $J = 6.0$ Hz, 2H, CH_2), 4.65 (t, $J = 6.0$ Hz, 2H, OCH_2), 7.10 (dd, $J = 9.0$ Hz, $J = 2.1$ Hz, 2H, Ar), 7.17 (dd, $J = 9.0$ Hz, $J = 2.1$ Hz, 2H, Ar),

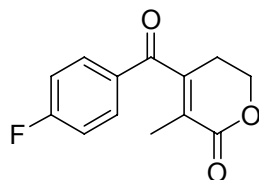
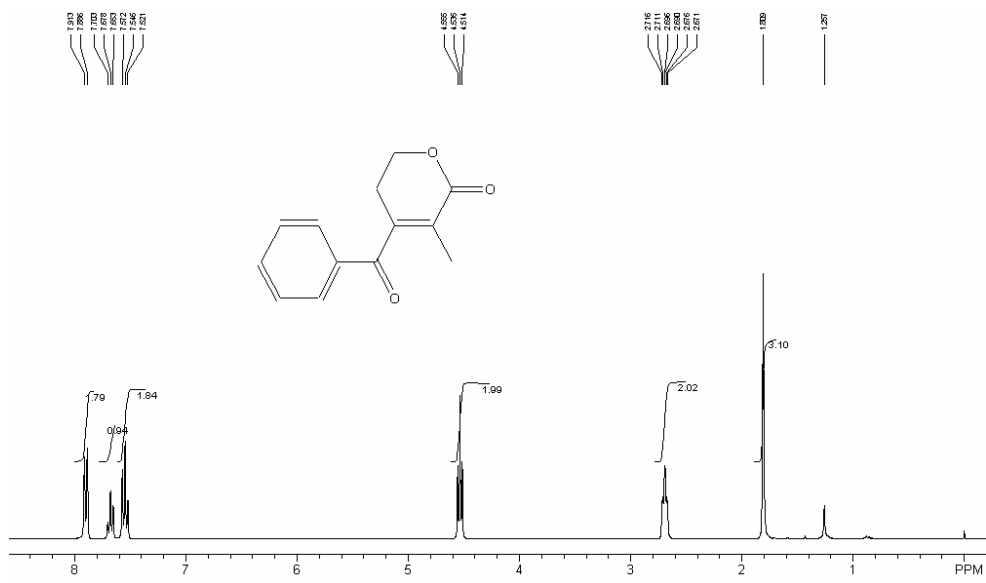
7.33 (t, $J = 7.2$ Hz, 2H, Ar), 7.48 (t, $J = 7.2$ Hz, 1H, Ar), 7.67-7.70 (m, 2H, Ar).



4-Benzoyl-3-methyl-5,6-dihydro-2H-pyran-2-one (3e):

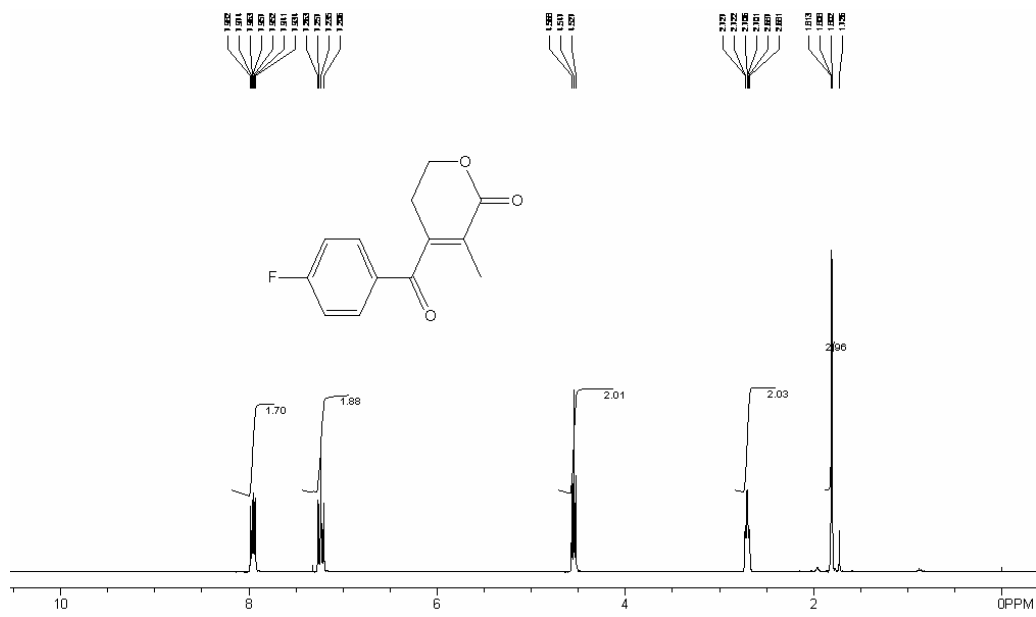
This compound was obtained as a yellow oil, yield: 61 mg, 94%. This is a known compound.

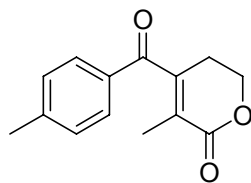
Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.81 (s, 3H, CH_3), 2.70 (t, $J = 6.6$ Hz, 2H, CH_2), 4.54 (t, $J = 6.6$ Hz, 2H, OCH_2), 7.53-7.58 (m, 2H, Ar), 7.67-7.70 (m, 1H, Ar), 7.89-7.93 (m, 2H, Ar).



4-(4-Fluoro-benzoyl)-3-methyl-5,6-dihydropyran-2-one (3f):

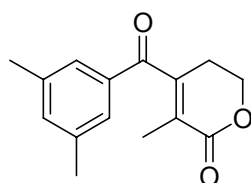
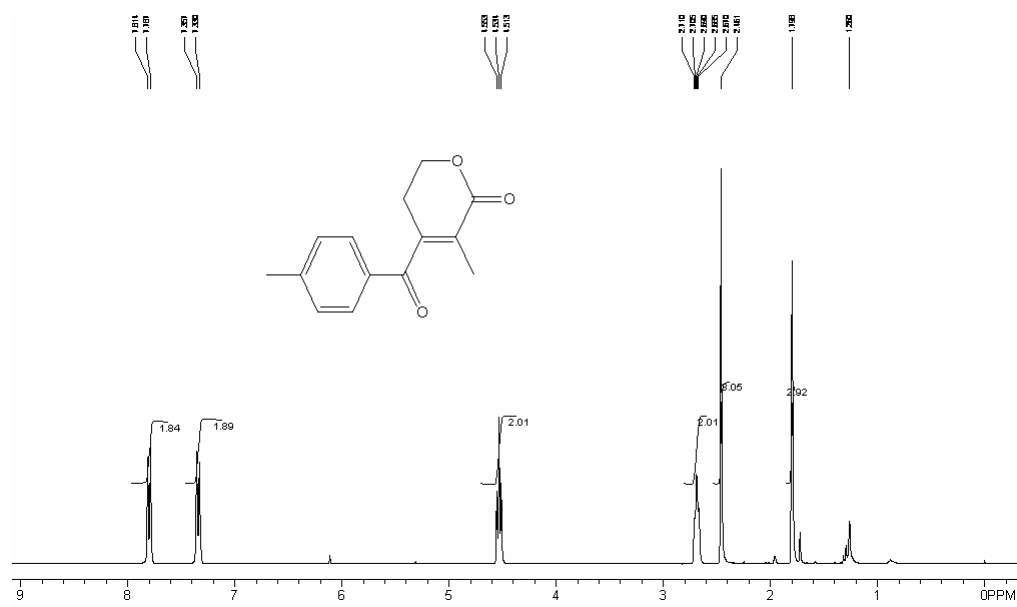
This compound was obtained as a white solid, yield: 50 mg, 71%. This is a known compound. Its ¹H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.81 (t, *J* = 1.5 Hz, 3H, CH₃), 2.70 (dt, *J* = 1.5 Hz, *J* = 6.0 Hz, 2H, CH₂), 4.55 (t, *J* = 6.0 Hz, 2H, OCH₂), 7.21-7.26 (m, 2H, Ar), 7.93-7.98 (m, 2H, Ar).





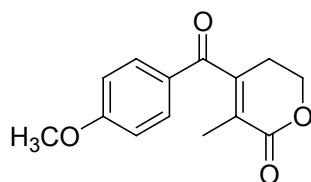
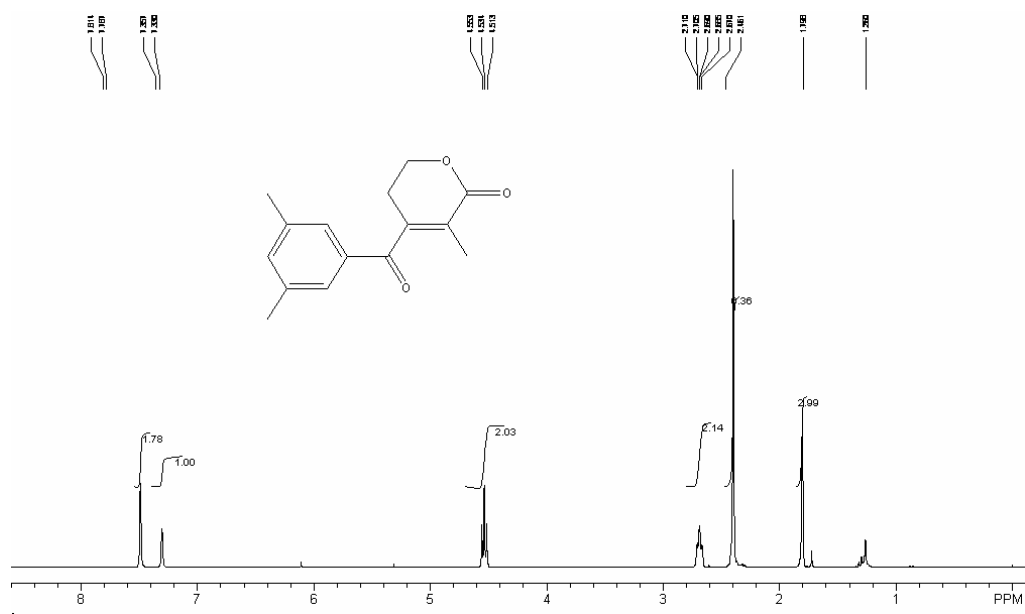
3-Methyl-4-(4-methyl-benzoyl)-5,6-dihydropyran-2-one (3g):

This compound was obtained as a white solid, yield: 64 mg, 93%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.80 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 2.69 (dt, $J = 1.2$ Hz, $J = 6.0$ Hz, 2H, CH_2), 4.53 (t, $J = 6.0$ Hz, 2H, OCH_2), 7.34 (d, $J = 7.8$ Hz, 2H, Ar), 7.80 (t, $J = 7.8$ Hz, 2H, Ar).



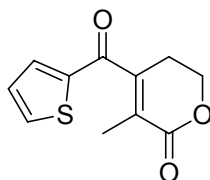
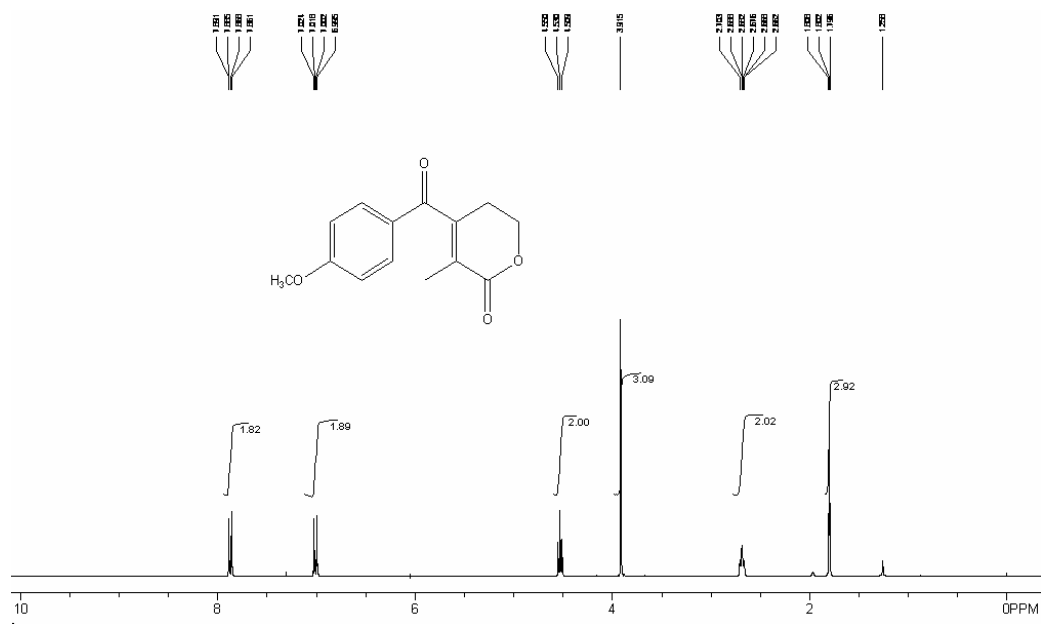
4-(3,5-Dimethyl-benzoyl)-3-methyl-5,6-dihydropyran-2-one (3h):

This compound was obtained as a white solid, yield: 63 mg, 86%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.80 (s, 3H, CH_3), 2.40 (s, 6H, CH_3), 2.69 (dt, $J = 1.8$ Hz, $J = 6.0$ Hz, 2H, CH_2), 4.54 (t, $J = 6.0$ Hz, 2H, OCH_2), 7.30 (s, 1H, Ar), 7.49 (s, 2H, Ar).



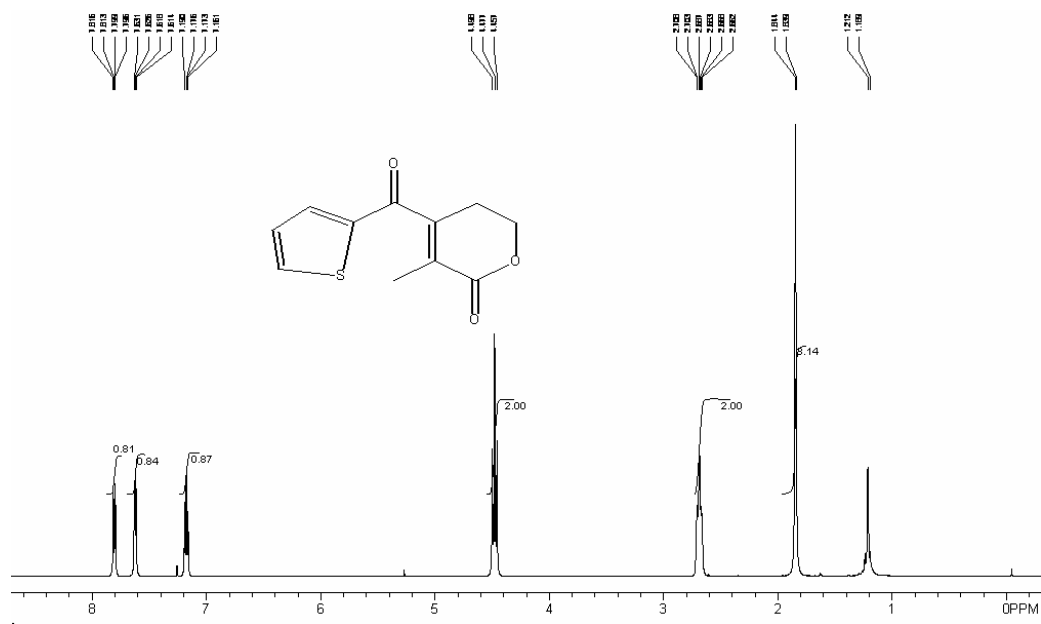
4-(4-Methoxy-benzoyl)-3-methyl-5,6-dihydropyran-2-one (3i):

This compound was obtained as a pale oil, yield: 66 mg, 89%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.80 (t, $J = 1.8$ Hz, 3H, CH_3), 2.69 (dt, $J = 1.8$ Hz, $J = 6.3$ Hz, 2H, CH_2), 3.92 (s, 3H, OCH_3), 4.53 (t, $J = 6.3$ Hz, 2H, OCH_2), 7.01 (dd, $J = 7.2$ Hz, $J = 2.1$ Hz, 2H, Ar), 7.88 (dd, $J = 7.2$ Hz, $J = 2.1$ Hz, 2H, Ar).



3-Methyl-4-(thiophene-2-carbonyl)-5,6-dihydropyran-2-one (3j):

This compound was obtained as a white solid, yield: 37 mg, 56%. This is a known compound. Its ^1H NMR spectroscopic data are consistent with those reported in our previous paper.¹ ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.89 (d, $J = 1.8$ Hz, 3H, CH_3), 2.73 (dt, $J = 1.8$ Hz, $J = 6.0$ Hz, 2H, CH_2), 4.53 (t, $J = 6.0$ Hz, 2H, OCH_2), 7.22 (dd, $J = 5.1$ Hz, $J = 3.9$ Hz, 1H, Ar), 7.67 (dd, $J = 3.9$ Hz, $J = 1.2$ Hz, 1H, Ar), 7.67 (dd, $J = 5.1$ Hz, $J = 1.2$ Hz, 1H, Ar).



References and Notes

1. Yang, Y.-H.; Shi, M. *J. Org. Chem.* **2006**, *70*, 10082-10085.