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Reaction of Methyl 1-Bromocyclopentane- and 1-Bromocyclohexanecarboxylates with Zinc and 2-Arylmethylidene-2,3-dihydro-1*H*-inden-1-ones or 2-Arylmethylidene-3,4-dihydronaphthalen-1(2*H*)-ones

N. F. Kirillov, A. G. Gavrilov, and M. I. Vakhrin

Perm State University, ul. Bukireva 15, Perm, 614990 Russia
e-mail: kirillov@psu.ru

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Abstract—Methyl 1-bromocyclopentanecarboxylate and methyl 1-bromocyclohexanecarboxylate reacted with zinc and 2-arylmethylidene-2,3-dihydro-1*H*-inden-1-ones or 2-arylmethylidene-3,4-dihydronaphthalen-1(2*H*)-ones to give 4′-aryl-4′,5′-dihydro-2′*H*-spiro[cyclopentane(cyclohexane)-1,3′-indeno[1,2-*b*]pyran]-2′-ones or 4-aryl-5,6-dihydrospiro[benzo[*h*]chromene-3,1′-cyclopentane(cyclohexane)]-2(4*H*)-ones, respectively.

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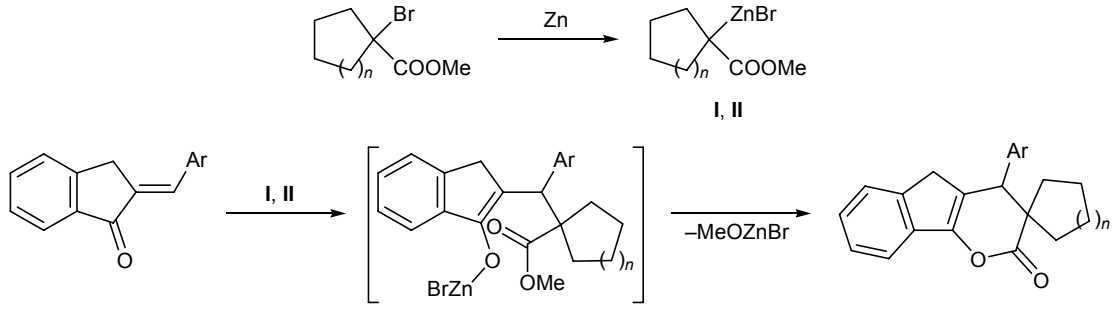
Reformatsky reactions with α,β-unsaturated ketones involve addition of organozinc compound at both 1,2- and 1,4-positions of the conjugated system, and 1,4-addition products undergo cyclization to unsaturated lactones that are derivatives of dihydropyran-2-one [1, 2]. Substituted spirodihydropyranones were isolated in reactions of alicyclic Reformatsky reagents with unsaturated ketones [3–6]. In continuation of these studies, we examined Reformatsky reactions of organozinc compounds **I** and **II** derived from methyl 1-bromocyclopentanecarboxylate and methyl 1-bromocyclohexanecarboxylate with 2-arylmethylidene-2,3-dihydro-1*H*-inden-1-ones **IIIa**–**IIIf**. The results showed that compounds **I** and **II** add to compounds **IIIa**–**IIIf** at positions *1*,*4* of the C=C–C=O fragment with formation of intermediates **IVa**–**IVf** or **Va**–**Vf**. Intramolecular attack by the oxygen atom in the bromozinc enolate fragment on the ester carbonyl carbon atom in intermediate **IV** or **V** resulted in cyclization with elimination of bromozinc methoxide and formation of 4′-aryl-4′,5′-dihydro-2′*H*-spiro[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-ones **VIa**–**VIf** or 4′-aryl-4′,5′-dihydro-2′*H*-spiro[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-ones **VIIa**–**VIIf** (Scheme 1).

Likewise, organozinc compounds **I** and **II** reacted with 2-arylmethylidene-3,4-dihydronaphthalen-1(2*H*)-ones **VIIIa**–**VIIIf** through intermediates **IXa**–**IXf** or **Xa**–**Xf** to produce 4-aryl-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclopentane]-2(4*H*)-ones **XIa**–**XIf** or 4-aryl-5,6-dihydrospiro[benzo[*h*]chromene-3,1′-cyclohexane]-2(4*H*)-ones **XIIa**–**XIIf** (Scheme 2).

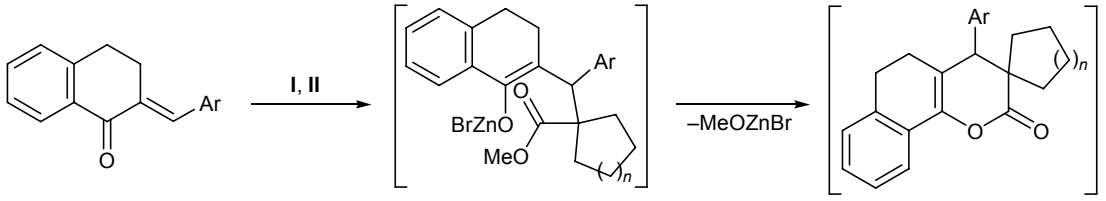
Scheme 1.



IIIa–IIIf **IVa–IVf**, **Va–Vf** **VIa–VIf**, **VIIa–VIIf**

Ar = Ph (**a**), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 2-FC_6H_4 (**e**), 3,4-$(MeO)_2C_6H_3$ (**f**); **I**, **IV**, **VI**, *n* = 1; **II**, **V**, **VII**, *n* = 2.

Scheme 2.



VIIIa–VIIIf **IXa–IXf**, **Xa–Xf** **XIa–XIf**, **XIIa–XIIf**

Ar = Ph (**a**), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 3-BrC_6H_4 (**e**), 3,4-$(MeO)_2C_6H_3$ (**f**); **IX**, **XI**, n = 1; **X**, **XII**, n = 2.

The structure of compounds **VIa**–**VIf**, **VIIa**–**VIIf**, **XIa**–**XIf**, and **XIIa**–**XIIf** was confirmed by their IR and ^{1}H NMR spectra and elemental analyses. The IR spectra contained absorption bands due to stretching vibrations of C=C bonds in the region 1655–1695 cm^{-1} and lactone carbonyl groups at 1745–1775 cm^{-1}. Compounds **VIa**–**VIf** and **VIIa**–**VIIf** characteristically displayed in the ^{1}H NMR spectra doublets from nonequivalent methylene protons in the indene fragment at δ 3.13–3.20 and 3.27–3.32 ppm, as well as singlets at δ 3.49–3.72 ppm from protons in the dihydropyran ring. Nonequivalent protons in the two methylene groups in the chromene fragment of **XIa**–**XIf** and **XIIa**–**XIIf** resonated in the ^{1}H NMR spectra as multiplets at δ 2.10–2.45 and 2.66–2.91 ppm, and singlets from 4-H were observed at δ 3.02–3.21 ppm.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were obtained on a Varian Mercury Plus-300 spectrometer at 300 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal reference.

General procedure for the synthesis of compounds VIa–VIf, VIIa–VIIf, XIa–XIf, and XIIa–XIIf. A mixture of 1.5 g of fine zinc turnings, a catalytic amount of mercury(II) chloride, 5 mmol of 2-arylmethylidene-2,3-dihydro-1*H*-inden-1-one **IIIa**–**IIIf** or 2-arylmethylidene-3,4-dihydronaphthalen-1(2*H*)-one, 5.1 mmol of methyl 1-bromocyclopentanecarboxylate or methyl 1-bromocyclohexanecarboxylate, 20 ml of benzene, 5 ml of ethyl acetate, and 1 ml of hexamethylphosphoramide was heated for 2 h under reflux. The mixture was cooled, the solution was separated from excess zinc by decanting and treated with 5% hydrochloric acid, the organic layer was separated, and the aqueous layer was extracted with two portions of ethyl acetate. The extracts were combined with the organic phase and dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was recrystallized from ethyl acetate.

4′-Phenyl-4′,5′-dihydro-2′*H*-spiro[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIa). Yield 1.03 g (65%), mp 132–133°C. IR spectrum, ν, cm^{-1}: 1770 (C=O), 1670 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.34–2.15 m (8H, CH_2), 3.17 d and 3.30 d (1H each, 5′-H, J = 22.2 Hz), 3.56 s (1H, 4′-H); 7.09 d (J = 7.2 Hz), 7.19–7.27 m, 7.34 t (J = 7.8 Hz), 7.49 d (J = 7.8 Hz) (9H, H_{arom}). Found, %: C 83.66; H 6.49. $C_{22}H_{20}O_2$. Calculated, %: C 83.51; H 6.37.

4′-(4-Bromophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIb). Yield 1.09 g (55%), mp 109–110°C. IR spectrum, ν, cm^{-1}: 1750 (C=O), 1660 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.30–2.16 m (8H, CH_2), 3.15 d and 3.30 d (1H each, 5′-H, J = 21.9 Hz), 3.53 s (1H, 4′-H), 6.97 d and 7.38 d (2H each, J = 8.1 Hz, BrC_6H_4); 7.24 t (J = 7.2 Hz), 7.31–7.41 m, 7.48 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 67.09; H 4.98; Br 20.02. $C_{22}H_{19}BrO_2$. Calculated, %: C 66.85; H 4.84; Br 20.21.

4′-(4-Chlorophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIc). Yield 1.25 g (71%), mp 114–115°C. IR spectrum, ν, cm^{-1}: 1750 (C=O), 1660 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.30–2.15 m (8H, CH_2), 3.16 d and 3.30 d (1H each, 5′-H, J = 22.2 Hz), 3.55 s (1H, 4′-H), 7.02 d and 7.23 d (2H each, J = 8.4 Hz, ClC_6H_4); 7.25 t (J = 7.8 Hz), 7.35 t (J = 7.8 Hz), 7.37 d (J = 7.8 Hz), 7.48 d (J = 7.8 Hz) (4H, C_6H_4). Found, %: C 75.53; H 5.29; Cl 9.95. $C_{22}H_{19}ClO_2$. Calculated, %: C 75.32; H 5.46; Cl 10.11.

4′-(4-Methoxyphenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VId). Yield 1.09 g (63%), mp 94–95°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1660 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.34–2.13 m (8H, CH_2), 3.18 d and 3.29 d (1H each, 5′-H, J = 21.9 Hz), 3.51 s (1H, 4′-H), 3.74 s (3H, MeO), 6.78 d and 7.00 d (2H each, J = 8.4 Hz,

$MeOC_6\mathbf{H}_4$); 7.22 t (J = 7.2 Hz), 7.34 t (J = 7.2 Hz), 7.36 d (J = 7.2 Hz), 7.48 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 79.55; H 6.51. $C_{23}H_{22}O_3$. Calculated, %: C 79.74; H 6.40.

4′-(2-Fluorophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIe). Yield 1.22 g (73%), mp 146–147°C. IR spectrum, ν, cm^{-1}: 1770 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.34–2.21 m (8H, CH_2), 3.17 d and 3.32 d (1H each, 5′-H, J = 21.9 Hz), 3.56 s (1H, 4′-H); 6.98–7.40 m, 7.48 d (J = 7.5 Hz) (8H, H_{arom}). Found, %: C 78.88; H 5.87. $C_{22}H_{19}FO_2$. Calculated, %: C 79.02; H 5.73.

4′-(3,4-Dimethoxyphenyl)-4′,5′-dihydro-2′*H*-spiro[cyclopentane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIf). Yield 1.24 g (66%), mp 156–157°C. IR spectrum, ν, cm^{-1}: 1775 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.38–2.14 m (8H, CH_2), 3.20 d and 3.29 d (1H each, 5′-H, J = 22.2 Hz), 3.49 s (1H, 4′-H), 3.79 s and 3.82 s (3H each, MeO); 6.58 s, 6.64 d (J = 8.4 Hz), 6.75 d (J = 8.4 Hz) (3H, C_6H_3); 7.22 t (J = 7.2 Hz), 7.33 t (J = 7.5 Hz), 7.36 d (J = 7.2 Hz), 7.47 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 76.74; H 6.30. $C_{24}H_{24}O_4$. Calculated, %: C 76.57; H 6.43.

4′-Phenyl-4′,5′-dihydro-2′*H*-spiro[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIIa). Yield 0.93 g (56%), mp 192–193°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1660 (C=C). ^1H NMR spectrum, δ, ppm: 1.14–2.14 m (10H, CH_2), 3.14 d and 3.27 d (1H each, 5′-H, J = 22.2 Hz), 3.72 s (1H, 4′-H); 7.08 d (J = 7.2 Hz), 7.18–7.28 m, 7.33 t (J = 7.8 Hz), 7.47 d (J = 7.8 Hz) (9H, H_{arom}). Found, %: C 83.81; H 6.79. $C_{23}H_{22}O_2$. Calculated, %: C 83.60; H 6.71.

4′-(4-Bromophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIIb). Yield 0.95 g (50%), mp 146–147°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 1.12–2.14 m (10H, CH_2), 3.13 d and 3.27 d (1H each, 5′-H, J = 22.2 Hz), 3.70 s (1H, 4′-H), 6.97 d and 7.37 d (2H each, J = 8.4 Hz, BrC_6H_4); 7.23 t (J = 7.5 Hz), 7.34 t (J = 7.5 Hz), 7.35 d (J = 7.5 Hz), 7.46 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 67.68; H 5.29; Br 19.31. $C_{23}H_{21}BrO_2$. Calculated, %: C 67.49; H 5.17; Br 19.52.

4′-(4-Chlorophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIIc). Yield 1.20 g (66%), mp 150–151°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 1.12–2.14 m (10H, CH_2), 3.13 d and 3.27 d (1H each, 5′-H, J = 22.2 Hz), 3.71 s (1H, 4′-H), 7.02 d and 7.28 d (2H each, J = 8.4 Hz, ClC_6H_4); 7.24 t (J = 7.2 Hz), 7.34 t (J = 7.2 Hz), 7.35 d (J = 7.2 Hz), 7.46 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 75.89; H 5.63; Cl 9.88. $C_{23}H_{21}ClO_2$. Calculated, %: C 75.71; H 5.80; Cl 9.72.

4′-(4-Methoxyphenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIId). Yield 0.99 g (55%), mp 132–133°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1660 (C=C). ^1H NMR spectrum, δ, ppm: 1.14–2.12 m (10H, CH_2), 3.15 d and 3.27 d (1H each, 5′-H, J = 21.9 Hz), 3.68 s (1H, 4′-H), 3.74 s (3H, MeO), 6.77 d and 7.00 d (2H each, J = 8.4 Hz, $MeOC_6\mathbf{H}_4$); 7.21 t (J = 7.2 Hz), 7.33 t (J = 7.2 Hz), 7.34 d (J = 7.2 Hz), 7.46 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 80.18; H 6.60. $C_{24}H_{24}O_3$. Calculated, %: C 79.97; H 6.71.

4′-(2-Fluorophenyl)-4′,5′-dihydro-2′*H*-spiro-[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIIe). Yield 1.18 g (68%), mp 128–129°C. IR spectrum, ν, cm^{-1}: 1775 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.12–2.20 m (10H, CH_2), 3.13 d and 3.27 d (1H each, 5′-H, J = 21.9 Hz), 3.72 s (1H, 4′-H); 6.92–7.38 m, 7.46 d (J = 7.5 Hz) (8H, H_{arom}). Found, %: C 79.48; H 6.23. $C_{23}H_{21}FO_2$. Calculated, %: C 79.29; H 6.08.

4′-(3,4-Dimethoxyphenyl)-4′,5′-dihydro-2′*H*-spiro[cyclohexane-1,3′-indeno[1,2-*b*]pyran]-2′-one (VIIf). Yield 1.24 g (66%), mp 115–116°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1655 (C=C). ^1H NMR spectrum, δ, ppm: 1.16–2.12 m (10H, CH_2), 3.17 d and 3.27 d (1H each, 5′-H, J = 22.2 Hz), 3.66 s (1H, 4′-H), 3.78 s and 3.81 s (3H each, MeO); 6.76 s, 6.64 d (J = 8.1 Hz), 6.74 d (J = 8.1 Hz) (3H, C_6H_3); 7.21 t (J = 7.5 Hz), 7.32 t (J = 7.5 Hz), 7.40 d (J = 7.5 Hz), 7.46 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 77.12; H 6.63. $C_{25}H_{26}O_4$. Calculated, %: C 76.90; H 6.71.

4-Phenyl-5,6-dihydrospiro[benzo[*h*]chromene-3,1′-cyclopentan]-2(4*H*)-one (XIa). Yield 1.19 g (72%), mp 161–162°C. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1660 (C=C). ^1H NMR spectrum, δ, ppm: 1.28–2.10 m (8H, CH_2), 2.19–2.45 m and 2.69–2.87 m (2H each, 5-H, 6-H), 3.08 s (1H, 4-H); 7.08–7.34 m, 7.62 d (J = 7.5 Hz) (9H, H_{arom}). Found, %: C 83.87; H 6.56. $C_{23}H_{22}O_2$. Calculated, %: C 83.60; H 6.71.

4-(4-Bromophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclopentan]-2(4*H*)-one (XIb). Yield 1.06 g (52%), mp 117–118°C. IR spectrum, ν, cm^{-1}: 1750 (C=O), 1680 (C=C). ^1H NMR spectrum, δ, ppm:

1.23–2.10 m (8H, CH_2), 2.15–2.44 m and 2.68–2.90 m (2H each, 5-H, 6-H), 3.05 s (1H, 4-H), 7.03 d and 7.40 d (2H each, J = 8.4 Hz, BrC_6H_4); 7.13 d (J = 7.2 Hz), 7.22 t (J = 7.2 Hz), 7.25 t (J = 7.2 Hz), 7.60 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 67.70; H 5.33; Br 19.27. $C_{23}H_{21}BrO_2$. Calculated, %: C 67.49; H 5.17; Br 19.52.

4-(4-Chlorophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclopentan]-2(4*H*)-one (XIc). Yield 1.06 g (58%), mp 107–108°C. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.24–2.10 m (8H, CH_2), 2.16–2.44 m and 2.68–2.90 m (2H each, 5-H, 6-H), 3.06 s (1H, 4-H), 7.09 d and 7.25 d (2H each, J = 8.7 Hz, ClC_6H_4); 7.12 d (J = 7.2 Hz), 7.22 t (J = 7.2 Hz), 7.25 t (J = 7.2 Hz), 7.61 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 75.94; H 5.66; Cl 9.56. $C_{23}H_{21}ClO_2$. Calculated, %: C 75.71; H 5.80; Cl 9.72.

4-(4-Methoxyphenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclopentan]-2(4*H*)-one (XId). Yield 0.72 g (40%), mp 153–154°C. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1660 (C=C). ^1H NMR spectrum, δ, ppm: 1.29–2.08 m (8H, CH_2), 2.18–2.44 m and 2.69–2.89 m (2H each, 5-H, 6-H), 3.02 s (1H, 4-H), 3.76 s (3H, MeO), 6.80 d and 7.07 d (2H each, J = 8.7 Hz, $MeOC_6\mathbf{H}_4$); 7.12 d (J = 7.5 Hz), 7.20 t (J = 7.2 Hz), 7.25 t (J = 7.5 Hz), 7.61 d (J = 7.2 Hz) (4H, C_6H_4), Found, %: C 80.21; H 6.54. $C_{24}H_{24}O_3$. Calculated, %: C 79.97; H 6.71.

4-(3-Bromophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclopentan]-2(4*H*)-one (XIe). Yield 0.90 g (44%), mp 122–123°C. IR spectrum, ν, cm^{-1}: 1750 (C=O), 1680 (C=C). ^1H NMR spectrum, δ, ppm: 1.26–2.10 m (8H, CH_2), 2.18–2.44 m and 2.70–2.91 m (2H each, 5-H, 6-H), 3.04 s (1H, 4-H); 7.09 d (J = 8.4 Hz), 7.18 t (J = 8.4 Hz), 7.29 s, 7.40 d (J = 8.4 Hz) (4H, BrC_6H_4); 7.11 d (J = 7.8 Hz), 7.22 t (J = 7.8 Hz), 7.25 t (J = 7.8 Hz), 7.60 d (J = 7.8 Hz) (4H, C_6H_4). Found, %: C 67.28; H 5.01; Br 19.73. $C_{23}H_{21}BrO_2$. Calculated, %: C 67.49; H 5.17; Br 19.52.

4-(3,4-Dimethoxyphenyl)-5,6-dihydrospiro-[benzo[*h*]chromene-3,1′-cyclopentan]-2(4*H*)-one (XIf). Yield 1.03 g (55%), mp 129–130°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1675 (C=C). ^1H NMR spectrum, δ, ppm: 1.08–2.09 m (8H, CH_2), 2.17–2.44 m and 2.68–2.89 m (2H each, 5-H, 6-H), 3.16 s (1H, 4-H), 3.80 s and 3.84 s (3H each, MeO); 6.64 s, 6.71 d (J = 8.4 Hz), 6.77 d (J = 8.4 Hz) (3H, C_6H_3); 7.11 d (J = 7.2 Hz), 7.20 t (J = 7.2 Hz), 7.26 t (J = 7.2 Hz), 7.56 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 77.03; H 6.64. $C_{25}H_{26}O_4$. Calculated, %: C 76.90; H 6.71.

4-Phenyl-5,6-dihydrospiro[benzo[*h*]chromene-3,1′-cyclohexan]-2(4*H*)-one (XIIa). Yield 1.29 g (75%), mp 169–170°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1695 (C=C). ^1H NMR spectrum, δ, ppm: 1.05–2.10 m (10H, CH_2), 2.14–2.43 m and 2.63–2.87 m (2H each, 5-H, 6-H), 3.19 s (1H, 4-H); 6.92–7.31 m, 7.53 d (J = 7.5 Hz) (9H, H_{arom}). Found, %: C 83.78; H 6.93. $C_{24}H_{24}O_2$. Calculated, %: C 83.69; H 7.02.

4-(4-Bromophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclohexan]-2(4*H*)-one (XIIb). Yield 1.44 g (68%), mp 133–135°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1695 (C=C). ^1H NMR spectrum, δ, ppm: 1.07–2.11 m (10H, CH_2), 2.16–2.42 m and 2.67–2.88 m (2H each, 5-H, 6-H), 3.18 s (1H, 4-H), 6.80 d and 7.07 d (2H each, J = 8.7 Hz, BrC_6H_4); 7.11 d (J = 7.5 Hz), 7.19 t (J = 7.5 Hz), 7.24 t (J = 7.5 Hz), 7.58 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 68.27; H 5.34; Br 19.09. $C_{24}H_{23}BrO_2$. Calculated, %: C 68.09; H 5.48; Br 18.87.

4-(4-Chlorophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclohexan]-2(4*H*)-one (XIIc). Yield 1.42 g (75%), mp 126–127°C. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1680 (C=C). ^1H NMR spectrum, δ, ppm: 1.05–2.12 m (10H, CH_2), 2.13–2.43 m and 2.66–2.89 m (2H each, 5-H, 6-H), 3.21 s (1H, 4-H), 7.09 d and 7.24 d (2H each, J = 8.4 Hz, ClC_6H_4); 7.11 d (J = 7.5 Hz), 7.20 t (J = 7.5 Hz), 7.25 t (J = 7.5 Hz), 7.58 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 75.86; H 6.25; Cl 9.19. $C_{24}H_{23}ClO_2$. Calculated, %: C 76.08; H 6.12; Cl 9.36.

4-(4-Methoxyphenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclohexan]-2(4*H*)-one (XIId). Yield 1.10 g (59%), mp 138–139°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1695 (C=C). ^1H NMR spectrum, δ, ppm: 1.07–2.10 m (10H, CH_2), 2.16–2.42 m and 2.67–2.88 m (2H each, 5-H, 6-H), 3.18 s (1H, 4-H), 3.76 s (3H, MeO), 6.80 d and 7.07 d (2H each, J = 8.7 Hz, $MeOC_6\mathbf{H}_4$); 7.11 d (J = 7.2 Hz), 7.19 t (J = 7.5 Hz), 7.23 t (J = 7.2 Hz), 7.61 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 80.42; H 7.13. $C_{25}H_{26}O_3$. Calculated, %: C 80.18; H 7.00.

4-(3-Bromophenyl)-5,6-dihydrospiro[benzo[*h*]-chromene-3,1′-cyclohexan]-2(4*H*)-one (XIIe). Yield 1.55 g (73%), mp 150–151°C. IR spectrum, ν, cm^{-1}: 1745 (C=O), 1685 (C=C). ^1H NMR spectrum, δ, ppm: 1.06–2.13 m (10H, CH_2), 2.15–2.42 m and 2.68–2.90 m (2H each, 5-H, 6-H), 3.18 s (1H, 4-H); 7.08 d

(J = 8.4 Hz), 7.15 t (J = 8.4 Hz), 7.30 s, 7.37 d (J = 8.4 Hz) (4H, BrC_6H_4); 7.12 d (J = 7.5 Hz), 7.23 t (J = 7.2 Hz), 7.24 t (J = 7.5 Hz), 7.59 d (J = 7.2 Hz) (4H, C_6H_4). Found, %: C 68.35; H 5.56; Br 19.11. $C_{24}H_{23}BrO_2$. Calculated, %: C 68.09; H 5.48; Br 18.87.

4-(3,4-Dimethoxyphenyl)-5,6-dihydrospiro-[benzo[*h*]chromene-3,1′-cyclohexan]-2(4*H*)-one (XIIf). Yield 1.17 g (58%), mp 118–119°C. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1695 (C=C). ^1H NMR spectrum, δ, ppm: 1.08–2.09 m (10H, CH_2), 2.18–2.44 m and 2.68–2.89 m (2H each, 5-H, 6-H), 3.17 s (1H, 4-H), 3.81 s and 3.84 s (3H each, MeO); 6.65 s, 6.71 d (J = 8.4 Hz), 6.76 d (J = 8.4 Hz) (3H, C_6H_3); 7.12 d (J = 7.2 Hz), 7.20 t (J = 7.2 Hz), 7.25 t (J = 7.5 Hz), 7.58 d (J = 7.5 Hz) (4H, C_6H_4). Found, %: C 77.44; H 7.09. $C_{26}H_{28}O_4$. Calculated, %: C 77.20; H 6.98.

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