Supporting Information

Magnetically recoverable silica catalysed solvent-free domino Knoevenagel-hetero-Diels-Alder reaction to access divergent chromenones

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Experimental
Materials and apparatus

All the chemicals were purchased from Sigma Aldrich, Merck, SRL, and Spectrochem and used without further purification. The powder XRD measurements were carried out using a 2-80° 2θ on a Rigaku Ultima IV X-ray diffractometer with CuKα source ($\lambda = 1.54056$ Å). In built program ‘XG operation RINT 2200’ associated with the XRD was used to process the data and ‘Rigaku PDXL 1.2.0.1’ library database was used for identification of the peaks. IR spectra (4000-400 cm$^{-1}$) were recorded in a Perkin Elmer Spectrum 100 machine using KBr pellet. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were recorded on a JEOL JEM-2011 electron microscope functioned at an accelerating voltage of 200 kV. All NMR spectra of the products were recorded by using Bruker AV500 Avance-III 500 MHz FTNMR spectrometer. Thermogravimetric analysis (TGA) was carried out on a SDT Q600 V20.9 Build 20 instrument at a heating rate of 10 °C/min under N$_2$ atmosphere. HRMS data were recorded in a Waters XEVO G2-Xs QTof apparatus.

General procedure for the synthesis of silica-supported iron oxide catalyst

Iron (III) chloride hexahydrate {FeCl$_3$.6H$_2$O} (1.2 g) and iron (II) chloride tetrahydrate {FeCl$_2$.4H$_2$O} (0.47 g) was dissolved in 100 mL of Milli-Q water under N$_2$ atmosphere to form a homogeneous solution. This was followed by the dropwise addition of 10 mL of 10 N NaOH solutions into the mixture under vigorous stirring and the resulting solution was heated at 80 °C for 1 h when a black precipitate of Fe$_3$O$_4$ appeared. Silicic acid (2 g) was also homogeneously dispersed separately in 40 mL of Milli-Q water under N$_2$ atmosphere in another flask. The silicic acid solution was then added dropwise into the iron oxide solution with stirring. The mixture was further allowed to stir at room temperature under N$_2$ atmosphere for 16 h. The precipitate obtained was separated by magnetic decantation and washed with Milli-Q water and ethanol until neutral and then dehydrated at 200 °C for 4 h in a vacuum oven. A brownish-black powder of Fe$_3$O$_4$@SiO$_2$ was obtained.

General procedure for the synthesis of chromenone / spirochromenone

To a mixture of 1,3-cyclohexanediione (0.9 mmol), benzaldehyde (0.9 mmol) and phenylacetylene (0.9 mmol), Fe$_3$O$_4$@SiO$_2$ (10 wt%) was added and the mixture was heated at 100 °C for 2 h under solvent-free condition. The progress of the reaction was followed using thin layer chromatography (TLC). After the completion of the reaction, 5 mL ethyl acetate
was added to the reaction mixture and the catalyst was removed by magnetic filtration. Organics were extracted with ethyl acetate (2 x 20 mL) and the combined organic fraction was washed with water (2 x 10 mL) and brine (10 mL). Drying over Na₂SO₄ and removal of the solvent under reduced pressure, produced the crude mixture which was purified by column chromatography using ethyl acetate /hexane as eluent. For further recyclability experiments, the recovered catalyst was oven-dried (at 100 °C for 2 h) under vacuum before the next run.

**Characterization of Fe₃O₄@SiO₂ nanoparticle**

Initially, the crystalline structure of the synthesized material was monitored by powder XRD analysis (Figure S1). The diffraction peaks at 2θ = 35.7°, 53.2° and 65.8° could be ascribed to the (311), (422) and (440) planes of cubic spinel phase of Fe₃O₄ crystal. These values are in good agreement with the JCPDS card no. 19-629 for magnetite, respectively. The broad, low intensity diffraction peaks observed at 2θ from 20° to 27° can be ascribed to the silica surrounding the Fe₃O₄ core. The crystallite size of the prepared material was calculated from XRD pattern at 2θ value of 35.7° by means of Scherer equation and found to be in the range of 3.5 nm.

![Figure S1. Powder XRD pattern of Fe₃O₄@SiO₂ nanoparticle](image)

The functional groups present and the mode of bonding in the Fe₃O₄@SiO₂ nanoparticles were examined through FTIR spectroscopy recorded in the 4000-400 cm⁻¹ range (Figure S2).
The bands observed in the regions of 3391 and 1631 cm\(^{-1}\) could be assigned to the –OH stretching and H-O-H bond vibrations of the surface adsorbed water molecules, respectively. The absorption peaks at 583 and 619 cm\(^{-1}\) is due to Fe-O stretching vibration. The absorption peaks at 795 and 1054 cm\(^{-1}\) may be attributed to stretching vibration of Si–O–Si (symmetrical), and Si–O–Si (asymmetrical), respectively. These peaks confirm the coating of silica over Fe\(_3\)O\(_4\).

![Figure S2. IR spectrum of Fe\(_3\)O\(_4\)@SiO\(_2\) nanoparticle](image)

The particle size and microstructure of the prepared Fe\(_3\)O\(_4\)@SiO\(_2\) catalyst was characterized by TEM and HRTEM analysis (Figure S3). The low resolution TEM image revealed homogeneous distribution of the particles with nearly spherical shape. The particle size distribution was found to be in the range 2-3 nm with number-average diameter of 2.5 nm (standard deviation (SD) = 0.22). The close relation between surface-weighted diameter (Ds = 2.58 nm) and volume-weighted diameter (Dv = 2.59 nm) revealed narrow-size distribution of the prepared nanoparticle. The HRTEM image indicated that silica shell was successfully coated on the surface of Fe\(_3\)O\(_4\) nanoparticle and the inter-planar lattice-fringe spacing of the Fe\(_3\)O\(_4\) core was found to be 0.25 nm, corresponding to the (311) spinel phase.
of Fe₃O₄ crystal (Figure S3b). The selected area electron diffraction (SAED) pattern further confirmed the crystalline nature of the sample as indicated by the (311) and (422) crystalline planes (Figure S3c). Energy Dispersive X-ray (EDX) analysis of the prepared nanoparticle indicates the presence of Fe, Si and O signals, devoid of the presence of any other metal or impurity (Figure S3d).

![Image of particle size distribution histogram, TEM image of Fe₃O₄@SiO₂ (inset a), HRTEM image with fringe spacing, SAED pattern of Fe₃O₄@SiO₂ nanoparticles, and EDX spectra of Fe₃O₄@SiO₂ nanoparticles showing the presence of Fe, O and Si.]

**Figure S3.** (a) Particle size distribution histogram, TEM image of Fe₃O₄@SiO₂ (inset a), (b) HRTEM image with fringe spacing (c) SAED pattern of Fe₃O₄@SiO₂ nanoparticles (d) and EDX spectra of Fe₃O₄@SiO₂ nanoparticles showing the presence of Fe, O and Si.

The magnetic properties of the synthesized Fe₃O₄@SiO₂ nanoparticles were studied by Vibrating Sample Magnetometer at room temperature (Figure S4). Saturation magnetization value of 13.24 emu/g was obtained for the synthesized nanoparticle, which was quite lower than that reported for bare Fe₃O₄ nanoparticle.² This reduction in saturation magnetization value can be attributed to the coating of Fe₃O₄ nanoparticles by an amorphous silica shell.²
However, the decrease in saturation magnetization value did not affect the magnetic properties of the nanoparticles and they could be magnetically separated by the application of an external magnetic field.

![Magnetisation curve of Fe₃O₄@SiO₂ nanoparticles](image)

**Figure S4.** Magnetisation curve of Fe₃O₄@SiO₂ nanoparticles

The thermal stability of the magnetic Fe₃O₄@SiO₂ nanoparticles was analysed by thermogravimetric analysis (TGA) as shown in Figure S5. The TGA curve of Fe₃O₄@SiO₂ nanoparticles showed a weight loss of 12.49% at 800 °C. The initial weight loss of 9.73% below 200 °C can be attributed to the release of adsorbed water molecules from the catalyst surface. This confirms high thermal stability of the prepared Fe₃O₄@SiO₂ nanoparticle.
To study the recyclability of the catalyst, after the completion of the reaction, the solid catalyst was recovered by using an external magnet followed by washing with Milli-Q water and drying at 100 °C. It was observed that the catalyst could be reused up to five consecutive catalytic cycles without any significant loss in the activity (Figure S6). However, after the 5th run, the catalytic activity of the recovered catalyst decreased gradually.

Figure S5. TGA curve of Fe$_3$O$_4$@SiO$_2$ nanoparticles

Figure S6. Study of recyclability of the catalyst
Characterization data of the product

2,4-diphenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4a)

Orange solid compound. Mp: 169-171 °C (Lit.\textsuperscript{4} 171-173 °C); Yield: 86%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.60-7.58 (m, 2H), 7.38 – 7.31 (m, 5H), 7.30 -7.25 (m, 2H), 7.20 -7.15 (m, 1H), 5.71 (d, 1H, \(J = 5.0\) Hz), 4.52 (d, 1H, \(J = 5.0\) Hz), 2.75 – 2.64 (m, 2H), 2.40 – 2.35 (m, 2H), 2.08 – 2.02 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 197.7 (C), 166.6 (C), 147.0 (C), 145.4 (C), 133.1 (C), 128.9 (CH), 128.6 (CH), 128.4 (CH), 126.8 (CH), 124.7 (CH), 114.0 (C), 104.7 (CH), 37.3 (CH2), 35.5 (CH), 27.9 (CH2), 20.6 (CH2); HRMS (ESI) \textit{m/z} 303.1394 ([M+H]\textsuperscript{+} C\textsubscript{21}H\textsubscript{19}O\textsubscript{2} requires 303.1385).

4-(4-bromophenyl)-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4b)\textsuperscript{5}

White solid compound. Mp: 110-112 °C. Yield: 79%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.60 -7.56 (m, 2H), 7.41 – 7.35 (m, 5H), 7.21 (d, 2H, \(J = 8.5\) Hz), 5.66 (d, 1H, \(J = 5.0\) Hz), 4.49 (d, 1H, \(J = 5.0\) Hz), 2.71 – 2.64 (m, 2H), 2.41 – 2.35 (m, 2H), 2.09 – 2.01 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 197.3 (C), 166.4 (C), 147.0 (C), 144.1 (C), 132.6 (C), 131.3 (CH), 129.9 (CH), 128.8 (CH), 128.4 (CH), 124.4 (CH), 120.3 (C), 113.3 (C), 103.7 (CH), 36.9
(CH2), 34.7 (CH), 27.6 (CH2), 20.3 (CH2); HRMS (ESI) m/z 381.0497 ([M+H]^+ C_{21}H_{18}O_2Br requires 381.0490).

4-(2-nitrophenyl)-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4c)

Yellow solid compound. Mp: 160-162 °C. Yield: 77%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, 1H, \(J = 8.0\) Hz), 7.62 – 7.58 (dd, 2H, \(J = 8.0\) Hz, 1.5 Hz), 7.49 (t, 1H, \(J = 7.5\) Hz), 7.40 – 7.33 (m, 4H), 7.29 (t, 1H, \(J = 7.5\) Hz), 5.88 (d, 1H, \(J = 4.5\) Hz), 5.09 (d, 1H, \(J = 4.5\) Hz), 2.76 – 2.68 (m, 2H), 2.38 – 2.34 (m, 2H), 2.11 – 2.04 (m, 2H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 197.1 (C), 167.5 (C), 149.4 (C), 147.7 (C), 139.9 (C), 133.1 (CH), 132.8 (C), 130.7 (CH), 129.2 (CH), 128.7 (CH), 127.4 (CH), 124.7 (CH), 124.3 (CH), 112.9 (C), 102.9 (CH), 36.9 (CH2), 31.1 (CH), 27.8 (CH2), 20.7 (CH2); HRMS (ESI) m/z 348.1238 ([M+H]^+ C_{21}H_{18}NO_4 requires 348.1236).

4-(2,4-dichlorophenyl)-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4d)

Pale yellow solid compound. Mp: 85-87 °C. Yield: 80 %. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.57 – 7.54 (m, 2H), 7.38 – 7.33 (m, 4H), 7.15 (dd, 1H, \(J = 8.5\) Hz, 2.5 Hz), 7.09 (d, 1H, \(J = 8.5\) Hz), 5.68 (d, 1H, \(J = 4.5\) Hz), 4.93 (d, 1H, \(J = 4.5\) Hz), 2.80 – 2.69 (m, 2H), 2.46 – 2.40
(m, 2H), 2.18 – 2.07 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 197.2 (C), 168.1 (C), 147.3 (C), 140.9 (C), 133.7 (C), 132.8 (CH), 130.4 (C), 129.6 (CH), 129.2 (CH), 128.8 (C), 128.6 (CH), 127.7 (CH), 124.7 (CH), 112.1 (C), 102.4 (CH), 37.2 (CH2), 32.5 (CH), 28.0 (CH2), 20.7 (CH2); HRMS (ESI) $m/z$ 371.0591 ([M+H]$^+$ C$_{21}$H$_{17}$O$_2$Cl$_2$ requires 371.0606).

![4e](image)

4-(4-chlorophenyl)-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4e)

White solid compound. Mp: 117-119 °C (Lit.$^4$ 117-118 °C). Yield: 79%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.61 – 7.57 (m, 2H), 7.40 – 7.34 (m, 3H), 7.29 – 7.22 (m, 4H), 5.66 (d, 1H, $J$ = 5.0 Hz), 4.50 (d, 1H, $J$ = 5.0 Hz), 2.74 – 2.64 (m, 2H), 2.42 – 2.36 (m, 2H), 2.09 – 2.00 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 197.6 (C), 166.7 (C), 147.3 (C), 143.9 (C), 132.9 (C), 132.5 (C), 129.8 (CH), 129.1 (CH), 128.7 (CH), 128.7 (CH), 124.7 (CH), 113.7 (C), 104.1 (CH), 37.2 (CH2), 34.9 (CH), 27.9 (CH2), 20.6 (CH2); HRMS (ESI) $m/z$ 337.0996 ([M+H]$^+$ C$_{21}$H$_{18}$O$_2$Cl requires 337.0995).

![4f](image)

4-phenyl-2-(p-tolyl)-4,6,7,8-tetrahydro-5H-chromen-5-one (4f)

White solid compound. Mp: 130-132 °C (lit.$^6$ 130-131 °C). Yield: 83%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46 (d, 2H, $J$ = 8.0 Hz), 7.33 – 7.29 (m, 2H), 7.26 (d, 2H, $J$ = 8.0 Hz), 7.17 – 7.13 (m, 3H), 5.64 (d, 1H, $J$ = 5.0 Hz), 4.49 (d, 1H, $J$ = 5.0 Hz), 2.72 – 2.61 (m, 2H), 2.39 - 2.35
(m, 2H), 2.34 (s, 2H), 2.07 – 1.97 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 197.7 (C), 166.6 (C), 147.1 (C), 145.6 (C), 138.9 (C), 130.2 (C), 129.3 (CH), 128.6 (CH), 128.4 (CH), 126.7 (CH), 124.6 (CH), 114.1 (C), 103.8 (CH), 37.3 (CH2), 35.4 (CH), 28.0 (CH2), 21.4 (CH2), 20.6 (CH3); HRMS (ESI) m/z 317.1554 ([M+H]$^+$ C$_{22}$H$_{21}$O$_2$ requires 317.1542).

4-(4-nitrophenyl)-2-(p-tolyl)-4,6,7,8-tetrahydro-5H-chromen-5-one (4g)

Pale yellow solid compound. Mp: 144-145 °C. Yield: 80%. $^1$H NMR (500 MHz, CDCl$_3$): δ 8.11 (d, 2H, $J = 8.5$ Hz), 7.49 - 7.43 (m, 4H), 7.17 (d, 2H, $J = 8.5$ Hz), 5.57 (d, 1H, $J = 4.5$ Hz), 4.60 (d, 1H, $J = 4.5$ Hz), 2.74 – 2.65 (m, 2H), 2.39 – 2.35 (m, 2H), 2.35 (s, 3H), 2.11 – 2.00 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 196.9 (C), 167.3 (C), 152.8 (C), 148.0 (C), 146.8 (C), 139.5 (C), 129.8 (C), 129.4 (CH), 129.3 (CH), 124.7 (CH), 123.9 (CH), 113.0 (C), 102.1 (CH), 37.1 (CH2), 35.7 (CH), 28.0 (CH2), 21.5 (CH2), 20.6 (CH3); HRMS (ESI) m/z 362.1390 ([M+H]$^+$ C$_{22}$H$_{20}$NO$_4$ requires 362.1392).

2-(4-fluorophenyl)-4-(4-nitrophenyl)-4,6,7,8-tetrahydro-5H-chromen-5-one (4h)

Yellow solid compound. Mp: 55-57 °C. Yield: 74%. $^1$H NMR (500 MHz, CDCl$_3$): δ 8.12 (d, 2H, $J = 8.5$ Hz), 7.57 - 7.52 (m, 2H), 7.47 (d, 2H, $J = 8.5$ Hz), 7.08 - 7.02 (m, 2H), 5.56 (d,
1H, J = 4.5 Hz), 4.61 (d, 1H, J = 4.5 Hz), 2.72 - 2.64 (m, 2H), 2.40 -2.36 (m, 2H), 2.12-1.90 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 197.4 (C), 167.1 (C), 163.4 (C, d, J = 247.5 Hz), 152.5 (C), 147.1 (C), 146.9 (C), 129.3 (CH), 128.8 (C), 126.7 (CH, d, J = 8.7 Hz), 124.0 (CH), 115.8 (CH, d, J = 21.2 Hz), 113.0 (C), 102.7 (CH), 37.1 (CH2), 35.7 (CH), 27.9 (CH2), 20.5 (CH2); HRMS (ESI) m/z 366.1136 ([M+H]+ C₂₁H₁₇NO₄F requires 366.1142).

4-benzyl-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4i)

Yellow solid compound. Mp: 55-57 °C. Yield: 84%. ¹H NMR (500 MHz, CDCl₃): δ 7.49 - 7.45 (m, 2H), 7.35 – 7.30 (m, 4H), 7.28 – 7.23 (m, 4H), 5.47 (d, 1H, J = 5.0 Hz), 3.71 – 3.63 (m, 1H), 3.06 – 3.01 (m, 1H), 2.69 – 2.63 (m, 1H), 2.51 – 2.40 (m, 4H), 2.06 – 2.01 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 198.4 (C), 167.9 (C), 147.9 (C), 139.1 (C), 133.4 (C), 129.9 (CH), 128.8 (CH), 128.6 (CH), 128.1 (CH), 126.3 (CH), 124.6 (CH), 113.4 (C), 103.9 (CH), 42.9 (CH2), 37.4 (CH2), 31.2 (CH), 27.8 (CH2), 20.7 (CH2); HRMS (ESI) m/z 317.1554 ([M+H]+ C₂₂H₂₁O₂ requires 317.1542).

4-(4-(allyloxy)phenyl)-2-phenyl-4,6,7,8-tetrahydro-5H-chromen-5-one (4j)
Yellow solid compound. Mp: 92-94 °C. Yield: 85%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.63 – 7.59 (m, 2H), 7.41 – 7.32 (m, 3H), 7.26 (d, 2H, $J = 9.0$ Hz), 6.85 (d, 2H, $J = 9.0$ Hz), 6.10 – 6.0 (m, 1H), 5.72 (d, 1H, $J = 5.0$ Hz), 5.42 (dd, 1H, $J = 17.0$, 1.5 Hz), 5.39 (dd, 1H, $J = 11.0$, 1.5 Hz), 4.52 – 4.48 (m, 3H), 2.75 – 2.65 (m, 2H), 2.43 – 2.37 (m, 2H), 2.09 – 2.02 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 197.8 (C), 166.3 (C), 157.5 (C), 146.9 (C), 137.9 (C), 133.6 (CH), 133.2 (C), 129.4 (CH), 128.9 (CH), 128.6 (CH), 124.6 (CH), 117.8 (CH2), 114.8 (CH), 114.3 (C), 104.8 (CH), 69.0 (CH2), 37.3 (CH2), 34.5 (CH), 27.9 (CH2), 20.6 (CH2); HRMS (ESI) m/z 359.1665 ([M+H]$^+$ C$_{24}$H$_{23}$O$_3$ requires 359.1647).

Brown solid compound. Mp: 60-62 °C. Yield: 84%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.66 (d, 2H, $J = 7.0$ Hz), 7.44 – 7.38 (m, 3H), 7.29 – 7.27 (m, 2H), 6.87 (d, 2H, $J = 8.5$ Hz), 5.68 (d, 1H, $J = 4.5$ Hz), 4.44 (d, 1H, $J = 3.5$ Hz), 3.80 (s, 3H), 2.83 -2.78 (m, 2H), 2.52 – 2.48 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 203.4 (C), 178.7 (C), 158.7 (C), 148.5 (C), 135.6 (C), 133.0 (C), 129.4 (CH), 129.2 (CH), 128.7 (CH), 124.9 (CH), 117.5 (C), 114.1 (CH), 104.3 (CH), 55.5 (CH3), 35.0 (CH), 33.6 (CH2), 25.8 (CH2); HRMS (ESI) m/z 319.1346 ([M+H]$^+$ C$_{21}$H$_{19}$O$_3$ requires 319.1334).

4-(4-methoxyphenyl)-2-phenyl-6,7-dihydrocyclopenta[b]pyran-5(4H)-one (4k)
4-benzyl-2-phenyl-6,7-dihydrocyclopenta[b]pyran-5(4H)-one (4l)

Orange solid compound. Mp: 88-90 °C. Yield: 83%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.52 – 7.48 (m, 2H), 7.41 – 7.33 (m, 3H), 7.30 – 7.16 (m, 5H), 5.42 (d, 1H, \(J = 4.0\) Hz), 3.62 – 3.58 (m, 1H), 3.33 – 3.28 (m, 1H), 2.75 – 2.63 (m, 3H), 2.54 – 2.50 (m, 2H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 204.3 (C), 180.2 (C), 149.0 (C), 138.6 (C), 133.2 (C), 129.8 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 126.4 (CH), 124.9 (CH), 117.0 (CH), 103.6 (CH), 41.2 (CH2), 33.6 (CH), 31.8 (CH2), 25.7 (CH2); HRMS (ESI) \(m/z\) 303.1394 ([M+H]\(^+\) C\(_{21}\)H\(_{19}\)O\(_2\) requires 303.1385).

7,7-dimethyl-2,4-diphenyl-4,6,7,8-tetrahydro-5\(H\)-chromen-5-one (4m)

Yellow solid compound. Mp: 141-143 °C (lit.\(^6\) 142-143 °C). Yield: 81%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.63 – 7.59 (m, 2H), 7.40 – 7.27 (m, 7H), 7.19 (t, 1H, \(J = 7\) Hz), 5.74 (d, 1H, \(J = 5.0\) Hz), 4.52 (d, 1H, \(J = 5.0\) Hz), 2.58 (s, 2H), 2.27 (ABq, 2H, \(J = 16.5\) Hz), 1.16 (s, 3H), 1.09 (s, 3H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 197.5 (C), 164.8 (C), 146.9 (C), 145.4 (C), 133.2 (C), 128.9 (CH), 128.6 (CH), 128.4 (CH), 126.8 (CH), 124.7 (CH), 112.7 (C), 104.7 (CH), 51.1 (CH2), 41.7 (CH), 35.6 (CH2), 32.3 (C), 29.4 (CH3), 27.9 (CH3); HRMS (ESI) \(m/z\) 331.1716 ([M+H]\(^+\) C\(_{23}\)H\(_{23}\)O\(_2\) requires 331.1698).
4-(4-bromophenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydro-5\textit{H}-chromen-5-one (4n)

Pale yellow solid compound. Mp: 93-94 °C. Yield: 72%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.62 – 7.58 (m, 2H), 7.43 – 7.35 (m, 5H), 7.23 (d, 2H, $J = 8.5$ Hz), 5.68 (d, 1H, $J = 5.0$ Hz), 4.49 (d, 1H, $J = 5.0$ Hz), 2.57 (s, 2H), 2.26 (ABq, 2H, $J = 16.0$ Hz), 1.15 (s, 3H), 1.07 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 197.4 (C), 164.9 (C), 147.3 (C), 144.5 (C), 132.9 (C), 131.7 (CH), 130.2 (CH), 129.1 (CH), 128.7 (CH), 124.7 (CH), 120.6 (C), 112.4 (C), 103.9 (CH), 51.1 (CH2), 41.6 (CH2), 35.2 (CH), 32.4 (C), 29.4 (CH3), 27.8 (CH3); HRMS (ESI) $m/z$ 425.0768 ([M+H]$^+$ C$_{23}$H$_{22}$O$_3$Br requires 425.0752)

4-benzyl-2-(p-tolyl)-6,7-dihydrocyclopenta[b]pyran-5(4\textit{H})-one (4o)

Yellow solid compound. Mp: 125-126 °C. Yield: 80%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.39 (d, 2H, $J = 8.5$ Hz), 7.30 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 7.20 – 7.15 (m, 4H), 5.37 (d, 1H, $J = 4.0$ Hz), 3.62 – 3.55 (m, 1H), 3.30 (dd, 1H, $J = 13.0$, 3.5 Hz), 2.71 (dd, 1H, $J = 13.0$, 9.0 Hz), 2.67 - 2.63 (m, 2H), 2.54 – 2.50 (m, 2H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 204.3 (C), 180.2 (C), 149.0 (C), 139.1 (C), 138.6 (C), 130.3 (C), 129.8 (CH), 129.3 (CH), 128.3 (CH), 126.4 (CH), 124.8 (CH), 117.0 (C), 102.7 (CH), 41.2 (CH$_2$), 33.6 (CH), 31.8
(CH₂), 25.7 (CH₂), 21.4 (CH₃); HRMS (ESI) m/z 317.1554 ([M+H]+ C₂₂H₂₁O₂ requires 317.1542)

2,4-diphenyl-4H,5H-pyran[2,3-b]chromen-5-one (4p)

Yellow solid compound. Mp: 158-159 °C. Yield: 84%. ¹H NMR (500 MHz, CDCl₃): δ 8.07 – 8.03 (m, 1H), 7.79 – 7.74 (m, 2H), 7.62 – 7.57 (m, 1H), 7.50 – 7.41 (m, 5H), 7.40 -7.32 (m, 4H), 7.28 – 7.23 (m, 1H), 5.87 (d, 1H, J = 4.5 Hz), 4.74 (d, 1H, J = 4.5 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 161.7 (C), 156.0 (C), 153.0 (C), 147.1 (C), 143.7 (C), 132.8 (C), 132.2 (CH), 129.5 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.4 (CH), 124.9 (CH), 124.0 (CH), 123.0 (CH), 117.1 (CH), 114.8 (C), 104.0 (CH), 103.9 (C), 36.8 (CH); HRMS (ESI) m/z 353.1198 ([M+H]+ C₂₄H₁₇O₃ requires 353.1178)

2,4-diphenyl-2,3,4,6,7,8-hexahydro-5H-chromen-5-one (4q)

White solid compound. Mp: 127-129 °C (lit. 129-130 °C). Yield: 81%. ¹H NMR (500 MHz, CDCl₃): δ 7.37-7.36 (m, 4H), 7.34-7.31 (m, 1H),  7.26-7.23 (m, 2H), 7.19-7.13 (m, 3H), 4.97 (dd, 1H, J = 11.5, 1.5 Hz), 3.97-3.93 (m, 1H), 2.64-2.24 (m, 5H), 2.05-1.96 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 196.8 (C), 173.1 (C), 145.0 (C), 139.3 (C), 128.6 (CH), 128.3 (CH), 128.3 (CH), 126.4 (CH), 126.0 (CH), 125.9 (CH), 115.6 (C), 79.0 (CH), 41.7 (CH₂),
37.1 (CH₂), 36.9 (CH), 29.2 (CH₂), 20.2 (CH₂); HRMS (ESI) m/z 305.1555 ([M+H]⁺ C₂₁H₂₁O₂ requires 305.1542)

2-(3-chlorophenyl)-4-phenyl-2,3,4,6,7,8-hexahydro-5H-chromen-5-one (4r)

White solid compound. Mp: 150-151 °C. Yield: 71%. ¹H NMR (500 MHz, CDCl₃): δ 7.38 (s, 1H), 7.30-7.28 (m, 2H), 7.26-7.23 (m, 3H), 7.17-7.13 (m, 3H), 4.96 (dd, 1H, J = 11.5, 1.5 Hz), 3.96-3.92 (m, 1H), 2.67-2.36 (m, 5H), 2.07-1.91 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 196.4 (C), 172.8 (C), 144.6 (C), 141.5 (C), 134.4 (C), 130.0 (CH), 128.5 (CH), 128.5 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 124.1 (CH), 115.6 (C), 78.1 (CH), 41.7 (CH₂), 37.7 (CH₂), 36.8 (CH), 29.0 (CH₂), 20.1 (CH₂); HRMS (ESI) m/z 339.1162 ([M+H]⁺ C₂₁H₂₀O₂Cl requires 339.1152).

4-phenyl-2-(p-tolyl)-2,3,4,6,7,8-hexahydro-5H-chromen-5-one (4s)

White solid compound. Mp: 121-123 °C. Yield: 75%. ¹H NMR (500 MHz, CDCl₃): δ 7.28 – 7.23 (m, 5H), 7.21 – 7.14 (m, 4H), 4.94 (d, 1H, J = 10.5 Hz), 3.96 – 3.91 (m, 1H), 2.64 – 2.39 (m, 3H), 2.35 (s, 3H), 2.36 – 2.17 (m, 2H), 2.05-1.97 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 196.7 (C), 173.2 (C), 145.0 (C), 138.2 (C), 136.3 (C), 129.2 (CH), 128.3 (CH), 126.3 (CH), 126.1 (CH), 125.8 (CH), 115.5 (C), 79.0 (CH), 41.6 (CH₂), 38.0 (CH₂), 36.9 (CH), 29.1
2-phenyl-7,8-dihydrospiro[chromene-4,1'-cyclobutan]-5(6H)-one (6a)

Yellow solid compound. Mp: 77-78 °C. Yield: 79%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.61 (d, 2H, $J$ = 7.0 Hz), 7.40 (t, 1H, $J$ = 7.0 Hz), 7.37 (d, 2H, $J$ = 7.0 Hz), 5.87 (s, 1H), 3.16 - 3.07 (m, 2H), 2.56 (t, 2H, $J$ = 6.5 Hz), 2.47 (t, 2H, $J$ = 6.5 Hz), 2.14 - 2.0 (m, 4H), 1.88 - 1.82 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 199.2 (C), 166.3 (C), 143.8 (C), 133.3 (C), 128.6 (CH), 128.6 (CH), 124.4 (CH), 115.7 (C), 111.3 (CH), 39.0 (CH$_2$), 36.6 (CH$_2$), 35.9 (CH$_2$), 29.9 (C), 28.4 (CH$_2$), 20.7 (CH$_2$), 14.2 (CH$_2$); HRMS (ESI) $m/z$ 319.1708 ([M+H]$^+$ C$_{22}$H$_{23}$O$_2$ requires 319.1698)
2’-phenyl-6’,7’-dihydro-5’H-spiro[cyclobutane-1,4’-cyclopenta[b]pyran]-5’-one (6c)

White solid compound. Mp: 100-101 °C. Yield: 82%. ¹H NMR (500 MHz, CDCl₃): δ 7.57 – 7.53 (m, 2H), 7.35 – 7.27 (m, 3H), 5.79 (s, 1H), 2.85 – 2.77 (m, 2H), 2.61 – 2.57 (m, 2H), 2.45 – 2.41 (m, 2H), 2.09 - 1.82 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 204.4 (C), 178.3 (C), 146.5 (C), 133.1 (C), 129.0 (CH), 128.7 (CH), 124.8 (CH), 119.7 (C), 110.5 (CH), 35.8 (CH₂), 35.6 (CH₂), 34.0 (CH₂), 29.9 (C), 25.2 (CH₂), 15.2 (CH₂); HRMS (ESI) m/z 253.1218 ([M+H]⁺ C₁₇H₁₇O₂ requires 253.1229).

2-(4-fluorophenyl)-7,7-dimethyl-7,8-dihydrospiro[chromene-4,1’-cyclobutan]-5(6H)-one (6d)

White solid compound. Mp: 124-125 °C. Yield: 73%. ¹H NMR (500 MHz, CDCl₃): δ 7.58 – 7.53 (m, 2H), 7.10-7.03 (m, 2H), 5.78 (s, 1H), 3.11 – 3.03 (m, 2H), 2.40 (s, 2H), 2.31 (s, 2H), 2.12 – 2.01 (m, 2H), 1.87 – 1.79 (m, 2H), 1.11 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 199.0 (C), 164.3 (C), 162.9 (d, C, J = 246.5 Hz), 143.1 (C), 129.4 (C), 126.3 (d, CH, J = 8.75 Hz), 115.5 (d, CH, J = 21.25 Hz), 114.5 (C), 111.0 (CH), 52.7 (CH₂), 42.0 (CH₂), 36.6 (CH₂), 35.7 (CH₂), 31.8 (C), 29.9 (C), 28.4 (CH₃), 28.4 (CH₃), 14.2 (CH₂); HRMS (ESI) m/z 313.1599 ([M+H]⁺ C₂₀H₂₂O₂F requires 313.1604).
7,7-dimethyl-2-(o-tolyl)-2,3,7,8-tetrahydrospiro[chromene-4,1'-cyclobutane]-5(6H)-one (6e)

White solid compound. Mp: 110-111 °C. Yield: 80%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31 (d, 1H, $J = 7.5$ Hz), 7.16 – 7.02 (m, 3H), 4.83 (d, 1H, $J = 10.5$ Hz), 3.10 (q, 1H, $J = 10.5$ Hz), 2.6 (q, 1H, $J = 10.5$ Hz), 2.24 (s, 3H), 2.19-2.15 (m, 4H), 2.02 - 1.79 (m, 4H), 1.75 –1.51 (m, 2H), 0.95 (s, 3H), 0.94 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 197.9 (C), 169.4 (C), 137.8 (C), 134.4 (C), 130.4 (CH), 127.8 (CH), 126.2 (CH), 125.4 (CH), 115.9 (C), 73.7 (CH), 51.9 (CH$_2$), 44.0 (CH$_2$), 42.6 (CH$_2$), 36.2 (CH$_2$), 33.4 (C), 31.2 (CH$_2$), 30.3 (C), 29.1 (CH$_3$), 27.1 (CH$_3$), 18.8 (CH$_3$), 14.3 (CH$_2$); HRMS (ESI) $m/z$ 311.2017 ([M+H]$^+$ C$_{21}$H$_{27}$O$_2$ requires 311.2011).

2-(4-methoxyphenyl)-7,8-dihydrospiro[chromene-4,1'-cyclopentane]-5(6H)-one (6f)

Yellow semi-solid compound. Yield: 83%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.41 (d, 2H, $J = 9.0$ Hz), 6.82 (d, 2H, $J = 9.0$ Hz), 5.24 (s, 1H), 3.76 (s, 3H), 2.49 (t, 2H, $J = 6.5$ Hz), 2.34 (t, 2H, $J = 6.5$ Hz), 2.25 – 2.17 (m, 2H), 1.99 – 1.92 (m, 4H), 1.89 – 1.84 (m, 2H), 1.66 – 1.63 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 198.4 (C), 166.4 (C), 159.6 (C), 141.8 (C), 135.1 (C), 125.5 (CH), 116.2 (C), 113.6 (CH), 109.6 (C), 55.2 (CH$_3$), 42.2 (CH$_2$), 38.8 (CH$_2$), 38.8
2'-phenyl-6',7'-dihydro-5'H-spirocyclopentane-1,4'-cyclopenta[b]pyran-5'-one (6g)

Yellow solid compound. Mp: 191-192 °C. Yield: 85%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.62 – 7.58 (m, 2H), 7.41 – 7.33 (m, 3H), 5.49 (s, 1H), 2.70 – 2.66 (m, 2H), 2.50 – 2.46 (m, 2H), 2.25 – 2.13 (m, 2H), 1.94 – 1.88 (m, 2H), 1.78 – 1.73 (m, 2H), 1.58-1.51 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 203.7 (C), 178.4 (C), 145.1 (C), 133.0 (C), 128.5 (CH$_2$), 128.3 (CH$_2$), 124.5 (CH$_2$), 120.1 (C), 110.2 (CH), 40.8 (CH$_2$), 39.7 (CH$_2$), 33.6 (CH$_2$), 29.6 (C), 25.3 (CH$_2$), 25.0 (CH$_2$), 14.0 (CH$_2$); HRMS (ESI) $m/z$ 267.1630 ([M+H]$^+$ C$_{18}$H$_{19}$O$_2$ requires 267.1385).

References:

Spectra