Supporting Information
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Superacid Mediated Intramolecular Cycliczation/Condensation:
Facile One-pot Synthesis of Spiro Tetracyclic Indanones and
Indenes
Bokka Venkat Ramulu, Devarapalli Ravi Kumar and Gedu Satyanarayana*
Indian institute of Technology Hyderabad, Kandi - 502 285, Sangareddy District, Telangana, India.
Fax: +91(40) 2301 6032
E-mail: gvsatya@iith.ac.in

Supporting Information

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compound (3a)\(^1\) is known in the literature.

compounds (9a, 9d, 9i)\(^2\) are known in the literature.

compounds (10j, 10l, 10o)\(^3\) are known in the literature.

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Experimental Section

General Considerations
IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. $^1$H-NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl$_3$; chemical shifts ($\delta$ ppm) and coupling constants (Hz) are reported in standard fashion with reference to internal standard tetramethyilsilane (TMS) ($\delta_H = 0.00$ ppm) or CHCl$_3$ ($\delta_H = 7.25$ ppm). $^{13}$C-NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl$_3$; chemical shifts ($\delta$ ppm) are reported relative to CHCl$_3$ ($\delta_C = 77.00$ ppm (central line of triplet)). In $^{13}$C-NMR spectra, the nature of carbons (C, CH, CH$_2$ and CH$_3$) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH$_2$) and q = quartet (for CH$_3$). In the $^1$H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by $^1$H, $^{13}$C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using micromass Q-TOF mass spectrometer using electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 $^\circ$C was used. Acme’s silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

GP-1 (General Procedure for Witting-Horner-Wadsworth-Emmons reaction of 1,3-diphenylpropan-1-ones):
To an oven dried round bottom flask under nitrogen atmosphere charged with 60% NaH (120 mg, 3.0 mmol), THF (10 mL) and cooled to ice temperature. Then TEPA (0.9 ml, 4.5 mmol) was added drop-wise until the solution becomes a clear solution. To the resulted yield, 1,3-diphenylpropan-1-ones 6 (315–399 mg, 1.5 mmol) was added, the reaction mixture was stirred at 0 $^\circ$C for 30 minutes and then heated at 60 $^\circ$C for 6 to 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NH$_4$Cl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the pendant $\beta$-aryl $\alpha,\beta$-unsaturated ester 3 (84–96 %).
**GP-2 (General Procedure for Spirotetracyclic indanones):**

To an oven dried Schlenk tube under nitrogen atmosphere, were added pendant β-aryl α,β-unsaturated ester 3 (70–84 mg, 0.25 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.1 mL, 1.5 mmol). The resultant reaction mixture was stirred at 50 °C for 30 to 36 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the Spirotetra cyclic indanone 9 (76–90%).

**GP-3 (General Procedure for indenes):**

To an oven dried Schlenk tube under nitrogen atmosphere, were added electron deactivating group pendant β-aryl α,β-unsaturated ester 3 (95–154 mg, 0.25 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.1 mL, 1.5 mmol). The resultant reaction mixture was stirred at 50 °C for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indenes 10 (68–78%).

**Ethyl (2E)-5-(4-methylphenyl)-3-phenylpent-2-enoate (3b):** GP-1 was followed to 6b (336 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester 3b (423 mg, 96%) as pale yellow viscous liquid. [TLC control Rᵣ(6b)=0.40, Rᵣ(3b)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (neat; MIR-ATR, 4000–600 cm⁻¹): ν_max= 2924, 2853, 1724, 1636, 1454, 1278, 1159, 1043, 748 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.53 (d, 2H, J=8.3 Hz, ArH), 7.33 (d, 2H, J=8.3 Hz, ArH), 7.20–6.98 (m, 5H, ArH), 6.05 (s, 1H, C=CH), 4.23 (q, 2H, J=7.3 Hz, OCH₂CH₃), 3.36 (t, 2H, J=7.8 Hz, CH₂), 2.69 (t, 2H, J=7.8 Hz, CH₂), 2.33 (s, 3H, ArCH₃), 1.32 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.0 (s, C=O), 158.0 (s, C=CH), 139.9 (s, ArC), 138.1 (s, ArC), 135.4 (s, ArC), 131.7 (d, 2C,
ArCH), 128.9 (d, 3C, ArCH), 128.3 (d, 3C, ArCH), 123.3 (d, ArCH), 118.1 (d, 1H, CH=C), 59.9 (t, OCH2CH3), 34.6 (t, CH2), 33.1 (t, CH2), 21.0 (q, ArCH3), 14.3 (q, CH3) ppm. HR-MS (APCI+): m/z calculated for [C20H23O2]+=[M+H]+: 295.1693; found: 295.1690.

**Ethyl (2E)-3-(2-methylphenyl)-5-phenylpent-2-enoate (3c):** GP-1 was followed to 6c (336 mg, 1.5 mmol) with 60% NaH (240 mg, 3.0 mmol), THF (10 mL), TEPA (1.8 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester 3c (397 mg, 90%) as pale yellow viscous liquid. [TLC control Rf(6c)=0.40, Rf(3c)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (neat; MIR-ATR, 4000–600 cm⁻¹): νmax= 2925, 1709, 1626, 1490, 1224, 1157, 1012, 808 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.48 (d, 1H, J=7.3 Hz, ArH), 7.44–7.30 (m, 3H, ArH), 7.21 (d, 2H, J=7.8 Hz, ArH), 7.10 (ddd, 3H, J=7.8 and 7.3 Hz, ArH), 6.08 (s, 1H, C=CH), 4.23 (q, 2H, J=7.3 Hz, OCH2CH3), 3.39 (t, 2H, J=7.3 Hz, CH2), 2.81–2.60 (m, 2H, CH2), 2.32 (s, 3H, ArCH3), 1.32 (t, 3H, J=7.3 Hz, OCH2C₂H₅) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.3 (s, C=O), 159.4 (s, C=CH), 141.4 (s, ArC), 138.5 (s, ArC), 135.6 (s, ArC), 129.1 (d, ArCH), 128.9 (d, ArCH), 128.6 (d, ArCH), 128.3 (d, ArCH), 128.1 (d, ArCH), 127.9 (d, ArCH), 127.7 (d, ArCH), 127.2 (d, ArCH), 126.7 (d, ArCH), 117.7 (d, 1H, CH=C), 59.8 (t, OCH3CH3), 42.2 (t, CH2), 34.7 (t, CH2), 21.0 (q, ArCH3), 14.3 (q, CH3) ppm. HR-MS (APCI+): m/z calculated for [C20H23O2]+=[M+H]+: 295.1693; found: 295.1712.

**Ethyl (2E)-3-(4-methylphenyl)-5-phenylpent-2-enoate (3d):** GP-1 was followed to 6d (336 mg, 1.5 mmol) with 60% NaH (240 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester 3d (423 mg, 96%) as pale yellow viscous liquid. [TLC control Rf(6d)=0.40, Rf(3d)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2922, 2930, 1707, 1584, 1446, 1244, 1121, 1004, 761 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.53 (dd, 1H, J=8.3 and 2.0 Hz, ArH), 7.34–7.01 (m, 8H, ArH), 6.07 (d, 1H, J=5.9 Hz, C=CH), 4.09–3.93 (m, 2H, OCH₂CH₃), 3.46–3.33 (m, 2H, CH₂), 2.83–2.64 (m, 2H, CH₂), 2.39 (s, 3H, ArCH₃), 1.38–1.24 (m, 3H, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.4 (s, ArCH).
C=O), 159.2 (s, C=CH), 141.7 (s, ArC), 139.1 (s, ArC), 137.5 (s, ArC), 129.3 (d, ArCH), 128.6 (d, ArCH), 128.4 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 127.2 (d, ArCH), 126.6 (d, ArCH), 126.0 (d, ArCH), 117.3 (d, 1H, CH=C), 59.8 (t, OCH₂CH₃), 42.1 (t, CH₂), 35.2 (t, CH₂), 21.3 (q, ArCH₃), 14.3 (q, CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₀H₂₃O₂]+=[M+H]+: 295.1693; found: 295.1691.

**Ethyl (2E)-3-(4-ethylphenyl)-5-phenylpent-2-enoate (3e):** GP-1 was followed to 6e (357 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester 3e (425 mg, 92%) as pale yellow viscous liquid. [TLC control Rf(6e)=0.40, Rf(3e)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (neat; MIR-ATR, 4000–600 cm⁻¹): νmax= 2965, 2930, 1707, 1622, 1454, 1224, 1155, 1033, 831, 698 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.42 (d, 2H, J=8.3 Hz, ArH), 7.34–7.05 (m, 7H, ArH), 6.08 (s, 1H, C=CH), 4.21 (q, 2H, J=6.8 Hz, OCH₂CH₃), 3.39 (q, 2H, J=7.8 Hz, CH₂), 2.81–2.56 (m, 4H, CH₂), 1.30 (t, 3H, J=7.8 Hz, CH₂CH₃), 1.07 (t, 3H, J=6.8 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.4 (s, C=O), 159.2 (s, C=CH), 145.4 (s, ArC), 141.7 (s, ArC), 138.2 (d, ArC), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 128.1 (d, ArCH), 127.4 (d, 2C, ArCH), 126.7 (d, ArCH), 126.0 (d, ArCH), 117.3 (d, 1H, CH=C), 59.8 (t, OCH₂CH₃), 42.1 (t, CH₂), 35.3 (t, CH₂), 33.9 (t, CH₂), 15.3 (q, CH₂CH₃), 14.3 (q, OCH₂CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₁H₂₅O₂]+=[M+H]+: 309.1849; found: 309.1861.

**Ethyl (2E)-3-(4-ethylphenyl)-5-(4-methylphenyl) pent-2-enoate (3f):** GP-1 was followed to 6f (378 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3f (444 mg, 92%) as pale yellow viscous liquid. [TLC control Rf(6f)=0.45, Rf(3f)=0.65, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2965, 2928, 1708, 1623, 1513, 1454, 1223, 1155, 1038, 808 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.44 (dd, 2H, J=8.3 and 2.0 Hz, ArH), 7.31–6.99 (m, 6H, ArH), 6.10 (s, 1H, C=CH), 4.23 (q, 2H, J=7.3 Hz, OCH₂CH₃), 3.39 (q, 2H, J=7.8 Hz, CH₂), 2.87–2.59 (m, 4H, CH₂), 2.33 (s, 3H, ArCH₃), 1.33 (t, 3H, J=7.8 Hz, CH₂CH₃), 1.10 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm.
$^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$=166.4 (s, C=O), 159.3 (s, C=CH), 145.4 (s, ArC), 138.6 (s, ArC), 137.8 (d, ArC), 135.4 (d, ArC), 129.0 (d, 2C, ArCH), 128.3 (d, ArCH), 128.1 (d, 2C, ArCH), 127.3 (d, 2C, ArCH), 126.6 (d, ArCH), 117.2 (d, 1H, CH=C), 59.7 (t, OCH$_2$CH$_3$), 42.2 (t, CH$_2$), 34.8 (t, CH$_2$), 28.6 (t, CH$_2$), 21.0 (q, ArCH$_3$), 15.3 (q, CH$_2$CH$_3$), 14.3 (q, CH$_3$) ppm. HR-MS (APCI+): m/z calculated for [C$_{22}$H$_{27}$O$_2$]$^+=[M+H]^+$: 323.2006; found: 323.2011.

Ethyl (2E)-3-(4-isopropylphenyl)-5-phenylpent-2-enoate (3g): GP-1 was followed to 6g (378 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3g (406 mg, 84%) as pale yellow viscous liquid. [TLC control $R_f$(6g)=0.40, $R_f$(3g)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{max}$= 2926, 2856, 1712, 1682, 1495, 1452, 1452, 1226, 1180, 744 cm$^{-1}$. $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$=7.42 (d, 2H, $J$=8.3 Hz, ArH), 7.32–7.07 (m, 7H, ArH), 6.08 (s, 1H, C=CH), 4.20 (q, 2H, $J$=6.8 Hz, OCH$_2$CH$_3$), 3.43–3.34 (m, 2H, CH$_2$), 2.99–2.85 (m, 1H, CH), 2.81–2.65 (m, 2H, CH$_2$), 1.30 (t, 3H, $J$=6.8 Hz, OCH$_2$CH$_3$), 1.28 (d, 6H, $J$=2.9 Hz, 2×CH$_3$) ppm. $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$=166.4 (s, C=O), 159.2 (s, C=CH), 150.0 (s, ArC), 141.7 (s, ArC), 138.3 (d, ArC), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 127.3 (d, ArCH), 126.7 (d, ArCH), 126.0 (d, ArCH), 125.9 (d, 2C, ArCH), 117.3 (d, 1H, CH=C), 59.8 (t, OCH$_2$CH$_3$), 42.0 (t, CH$_2$), 35.3 (t, CH$_2$), 33.8 (d, CH), 23.9 (q, 2×CH$_3$), 14.3 (q, CH$_3$) ppm. HR-MS (APCI+): m/z calculated for [C$_{22}$H$_{27}$O$_2$]$^+=[M+H]^+$: 323.2006; found: 323.2010.

Ethyl (2E)-3-(4-isopropylphenyl)-5-(4-methylphenyl)pent-2-enoate (3h): GP-1 was followed to 6h (399 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3h (430 mg, 85%) as pale yellow viscous liquid. [TLC control $R_f$(6h)=0.40, $R_f$(3h)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{max}$= 2960, 2869, 1710, 1621, 1456, 1264, 1158, 1036, 808 cm$^{-1}$. $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$=7.34–6.94 (m, 8H, ArH), 5.90 (s, 1H, C=CH),
3.99 (q, 2H, J=6.8 Hz, OCH₂CH₃), 3.42–3.31 (m, 2H, CH₂), 3.01–2.84 (m, 1H, CH), 2.78–2.61 (m, 2H, CH₂), 2.31 (s, 3H, ArCH₃), 1.27 (s, 6H, J=2.9 Hz, 2×CH₃), 1.05 (t, 3H, J=6.8 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.1 (s, C=O), 158.6 (s, C=CH), 148.3 (s, ArC), 138.6 (s, ArC), 137.9 (d, ArC), 135.4 (d, ArC), 129.0 (d, 2C, ArCH), 128.1 (d, 2C, ArCH), 127.2 (d, 2C, ArCH), 126.6 (d, ArCH), 125.9 (d, ArCH), 117.2 (d, 1H, CH=C), 59.7 (t, OCH₂CH₃), 42.2 (t, CH₂), 33.8 (d, CH), 33.5 (t, CH₂), 23.9 (q, 2×CH₃), 20.9 (q, CH₃), 14.3 (q, CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₃H₂₉O₂]+=[M+H]⁺: 337.2162; found: 337.2175.

Ethyl (2E)-3-(3-methoxyphenyl)-5-phenylpent-2-enoate (3i): GP-1 was followed to 6i (360 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethylicacetate 100:0 to 92:8) furnished the ester 3i (428 mg, 92%) as pale yellow viscous liquid. [TLC control Rₛ(6i)=0.40, Rₛ(3i)=0.60, (petroleum ether/ethyl acetate 92:8, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2924, 2855, 1718, 1681, 1456, 1233, 1180, 1077, 806 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.53 (dd, 2H, J=8.3 and 1.5 Hz, ArH), 7.42–7.34 (m, 3H, ArH), 7.15 (dd, 2H, J=8.8 and 2.0 Hz, ArH), 6.81 (dd, 2H, J=8.8 and 2.0 Hz, ArH), 6.05 (s, 1H, C=CH), 4.21 (q, 2H, J=6.8 Hz, OCH₂CH₃), 3.77 (s, 3H, ArOCH₃), 3.39–3.32 (m, 2H, CH₂), 2.70–2.63 (m, 2H, CH₂), 1.30 (t, 3H, J=6.8 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.4 (s, C=O), 159.4 (s, C=CH), 157.8 (s, ArC), 141.1 (s, ArC), 133.7 (s, ArC), 129.4 (d, 2C, ArCH), 128.9 (d, 2C, ArCH), 128.6 (d, 2C, ArCH), 126.7 (d, 2C, ArCH), 117.8 (d, ArCH), 113.7 (d, 1H, CH=C), 59.9 (t, OCH₂CH₃), 55.2 (q, ArOCH₃), 34.3 (t, CH₂), 33.4 (t, CH₂), 14.3 (q, OCH₂CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₀H₂₅O₃]+=[M+H]⁺: 311.1642; found: 311.1642.

Ethyl (2E)-3-(4-fluorophenyl)-5-phenylpent-2-enoate (3j): GP-1 was followed to 6j (342 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethylicacetate 100:0 to 96:4) furnished the ester 3j (420 mg, 94%) as pale yellow viscous liquid. [TLC control Rₛ(6j)=0.40, Rₛ(3j)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (neat; MIR-ATR, 4000–600 cm⁻¹): νmax= 2965, 2931, 1713, 1681, 1454, 1284, 1166, 1081,
834, 699 cm⁻¹. \(^1\)H-NMR (CDCl₃, 400 MHz): \(\delta=7.50\) (dd, 2H, \(J=8.8\) and 8.3 Hz, ArH), 7.35–7.22 (m, 3H, ArH), 7.22–7.15 (m, 2H, ArH), 7.12 (d, 1H, \(J=6.8\) Hz, ArH), 7.07 (d, 1H, \(J=8.3\) Hz, ArH), 6.03 (s, 1H, C=CH), 4.00 (q, 2H, \(J=7.3\) Hz, OCH₂CH₃), 3.40–3.31 (m, 1H, CH₂), 2.79–2.63 (m, 3H, CH₂), 1.10 (t, 3H, \(J=7.3\) Hz, OCH₂CH₃) ppm. \(^1\)C-NMR (CDCl₃, 100 MHz): \(\delta=166.1, 158.0, 141.2, 140.5, 138.6, 131.8, 131.1, 130.0, 128.5, 128.3, 126.2, 123.2, 121.9, 118.3, 60.0, 41.9, 35.0, 14.3\) ppm. HR-MS (APCI⁺): m/z calculated for [C₁₉H₂₀FO₂]+=[M+H]⁺: 299.1442; found: 299.1452.

Ethyl (2E)-3-(4-fluorophenyl)-5-(3-methylphenyl)pent-2-enoate (3k): GP-1 was followed to 6k (363.3 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3k (435 mg, 93%) as pale yellow viscous liquid. [TLC control \(R_f(6k)=0.40, R_f(3k)=0.60\), (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): \(\nu_{max}=2962, 2930, 1713, 1621, 1536, 1453, 1161, 1048, 986, 819\) cm⁻¹. \(^1\)H-NMR (CDCl₃, 400 MHz): \(\delta=7.47\) (dd, 2H, \(J=8.3\) and 6.8 Hz, ArH), 7.40 (dd, 1H, \(J=8.8\) and 2.0 Hz, ArH), 7.32–7.20 (m, 1H, CH₂), 7.19–7.08 (m, 1H, CH₂), 7.07–6.85 (m, 3H, CH₂), 6.00 (d, 1H, C=CH), 4.19 (q, 2H, \(J=7.3\) Hz, OCH₂CH₃), 3.36–3.24 (m, 2H, CH₂), 2.72–2.57 (m, 2H, CH₂), 2.28 (s, ArCH₃), 1.28 (t, 3H, \(J=7.3\) Hz, OCH₂CH₃) ppm. \(^1\)C-NMR (CDCl₃, 100 MHz): \(\delta=171.0\) (s, C=O), 166.1 (s, C=CH), 158.1 (s, ArC), 141.2 (s, ArC), 138.7 (s, ArC), 138.0 (s, ArC), 131.1 (d, ArCH), 128.9 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 126.9 (d, 2C, ArCH), 121.8 (d, ArCH), 118.1 (d, 1H, CH=C), 59.9 (t, OCH₂CH₃), 41.9 (t, CH₂), 34.9 (t, CH₂), 21.3 (q, ArCH₂), 14.3 (q, OCH₂CH₃) ppm.

Ethyl (2E)-3-(4-chlorophenyl)-5-phenylpent-2-enoate (3l): GP-1 was followed to 6l (366 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester 3l (424 mg, 90%) as pale yellow viscous liquid. [TLC control \(R_f(6l)=0.40, R_f(3l)=0.60\), (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (neat; MIR-ATR, 4000–600 cm⁻¹): \(\nu_{max}=2981, 2934, 1711, 1626, 1492, 1225, 1162, 1093, 828, 699\) cm⁻¹. \(^1\)H-NMR (CDCl₃, 400 MHz): \(\delta=7.40–7.30\) (m, 3H, ArH), 7.30–7.22 (m, 2H, ArH), 7.22–7.16 (m, 2H, ArH), 7.16–7.07 (m, 2H, ArH), 6.03 (s, 1H, C=CH), 4.21 (q, 2H, \(J=7.3\) Hz, OCH₂CH₃), 3.40–3.31 (m,
1H, CH₂), 2.78–2.63 (m, 3H, CH₂), 1.30 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.1 (s, C=O), 157.9 (s, C=CH), 141.2 (s, ArC), 139.5 (s, ArC), 133.7 (s, ArC), 128.8 (d, ArCH), 128.7 (d, ArCH), 128.5 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 128.2 (d, ArCH), 128.0 (d, ArCH), 126.2 (d, ArCH), 118.3 (d, 1H, CH=C), 59.9 (t, OCH₂CH₃), 41.9 (t, CH₂), 35.0 (t, CH₂), 14.3 (q, OCH₂CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₁₀H₁₉ClO₂]⁺=[M+H]⁺: 315.1146; found: 315.144.

Ethyl (2E)-3-(4-chlorophenyl)-5-(3-methylphenyl)pent-2-enoate (3m): GP-1 was followed to 6m (387 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3m (453 mg, 92%) as pale yellow viscous liquid. [TLC control Rₖ(6m)=0.40, Rₖ(3m)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2964, 2931, 1707, 1680, 1412, 1228, 1180, 1030, 986, 699 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.43–7.29 (m, 2H, ArH), 7.14 (dd, 2H, J=8.3 and 6.8 Hz, ArH), 7.02 (d, 2H, J=6.8 Hz, ArH), 6.93 (d, 2H, J=6.8 Hz, ArH), 6.04 (d, 1H, C=CH), 4.01 (q, 2H, J=7.3 Hz, OCH₂CH₃), 3.35 (t, 1H, J=7.8 Hz, CH₂), 2.77–2.60 (m, 3H, CH₂), 2.31 (s, ArCH₃), 1.11 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.1 (s, C=O), 158.0 (s, C=CH), 141.2 (s, ArC), 139.5 (s, ArC), 138.2 (s, ArC), 134.9 (s, ArC), 129.2 (d, ArCH), 128.8 (d, 2C, ArCH), 128.4 (d, ArCH), 128.2 (d, 2C, ArCH), 126.9 (d, ArCH), 125.2 (d, ArCH), 118.1 (d, 1H, CH=C), 59.4 (t, OCH₂CH₃), 42.0 (t, CH₂), 35.0 (t, CH₂), 21.3 (q, ArCH₃), 14.3 (q, OCH₂CH₃) ppm. HR-MS (APCI+) m/z calculated for [C₂₀H₂₂ClO₂]⁺=[M+H]⁺: 329.1303; found: 329.1299.

Ethyl (2E)-3-(4-chlorophenyl)-5-(4-methylphenyl)pent-2-enoate (3n): GP-1 was followed to 6n (387 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester 3n (453 mg, 92%) as pale yellow viscous liquid. [TLC control Rₖ(6n)=0.40, Rₖ(3n)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2924, 2853, 1714, 1624, 1454, 1281, 1165, 1045, 749, 698 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.43–7.27 (m, 2H, ArH), 7.17–7.04 (m, 4H, ArH), 7.04–6.96 (m, 2H, ArH), 6.02 (d, 1H, J=4.8 Hz, C=CH), 4.08–3.94 (m, 2H, ArH), 7.04–6.96 (m, 2H, ArH), 6.02 (d, 1H, J=4.8 Hz, C=CH), 4.08–3.94 (m, 2H, OCH₂CH₃), 3.39–3.28 (m,
1H, CH₂), 2.76–2.58 (m, 3H, CH₂), 2.30 (s, ArCH₃), 1.36–1.23 (m, 3H, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=166.1 (s, C=O), 158.0 (s, C=CH), 138.2 (s, ArC), 135.7 (s, 2C, ArC), 133.6 (s, ArC), 129.1 (d, ArCH), 129.0 (d, ArCH), 128.8 (d, ArCH), 128.7 (d, ArCH), 128.3 (d, ArCH), 128.2 (d, ArCH), 128.1 (d, 2C, ArCH), 118.2 (d, 1H, CH=CH), 60.0 (t, OCH₂CH₃), 42.1 (t, CH₂), 33.3 (t, CH₂), 21.0 (q, ArCH₃), 14.3 (q, OCH₂CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₀H₂₂ClO₂]+=[M+H]+: 329.1303; found: 329.1299.

Ethyl (2E)-3-(4-bromophenyl)-5-phenylpent-2-enoate (3o): GP-1 was followed to 6o (433 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the ester 3o (503 mg, 94%) as pale yellow viscous liquid. [TLC control Rf(6o)=0.40, Rf(3o)=0.60, (petroleum ether/ethyl acetate 98:2, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2964, 2930, 1713, 1681, 1607, 1413, 1227, 1180, 985, 818 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.46–7.31 (m, 2H, ArH), 7.31–6.89 (m, 7H, ArH), 5.98 (s, 1H, C=CH), 4.17 (q, 2H, J=7.3 Hz, OCH₂CH₃), 3.38–3.28 (m, 1H, CH₂), 2.75–2.60 (m, 3H, CH₂), 1.27 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=165.8 (s, C=O), 163.2 (s, C=CH), 157.1 (s, ArC), 141.0 (s, ArC), 136.8 (s, ArC), 135.2 (s, ArC), 128.8 (d, ArCH), 128.2 (d, ArCH), 128.1 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 125.8 (d, ArCH), 117.8 (d, ArCH), 115.3 (d, ArCH), 114.7 (d, 1H, CH=CH), 59.6 (t, OCH₂CH₃), 41.7 (t, CH₂), 34.7 (t, CH₂), 13.6 (q, OCH₂CH₃) ppm.

6'-Methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2H)-one (9b): GP-2 was carried out with ester 3b (74 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone 9b (54 mg, 87%) as brown color viscous liquid. [TLC control Rf(3b)=0.50, Rf(9b)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2922, 2851, 1710, 1601, 1461, 1287, 1236, 816, 763 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.79 (d, 1H, J=7.8 Hz, ArH), 7.57 (ddd, 1H, J=7.3, 7.3 and 1.0 Hz, ArH), 7.41 (ddd, 1H, J=7.3, 7.3 and 1.0 Hz, ArH), 7.27 (d, 1H, J=7.8 Hz, ArH), 7.21 (d, 1H, J=7.8 Hz, ArH), 7.08 (d, 1H, J=7.8 Hz, ArH), 6.57 (s, 1H, ArH), 3.19–3.00 (m, 2H, CH₂), 2.94 (d, 1H, J=18.6 Hz, CH₃H₆), 2.87 (d, 1H, J=18.6 Hz, CH₃H₆), 2.55–2.44 (m, 1H, CH₂), 2.40–2.30 (m, 1H, CH₂), 2.22 (s, 3H, ArCH₃) ppm. ¹³C-NMR
(CDCl₃, 100 MHz): δ=205.9 (s, C=O), 161.6 (s, ArC), 149.0 (s, ArC), 140.2 (s, ArC), 136.9 (d, ArC), 136.0 (s, ArC), 135.4 (d, ArCH), 128.1 (d, ArCH), 127.8 (d, ArCH), 125.1 (d, ArCH), 124.3 (d, ArCH), 123.3 (d, ArCH), 123.0 (d, ArCH), 54.4 [s, C(CH₂)₂], 52.4 (t, CH₂), 42.9 (t, CH₂), 30.8 (t, CH₂), 21.2 (q, ArCH₃) ppm. HR-MS (APCI+): m/z calculated for [C₁₈H₁₇O⁺]=[M+H⁺]: 249.1274; found: 249.1279.

7-Methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2H)-one (9c): GP-2 was carried out with ester 3c (74 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone 9c (49 mg, 78%) as brown color viscous liquid. [TLC control Rₗ(3c)=0.50, Rₗ(9c)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): 𝜈max= 2953, 2850, 1708, 1602, 1583, 1477, 1457, 1279, 1267, 1173, 1063, 909, 727 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.67 (dd, 1H, J=7.3 and 1.0 Hz, ArH), 7.41–7.26 (m, 3H, ArH), 7.21 (ddd, 1H, J=7.3, 7.3 and 1.0 Hz, ArH), 7.13 (dd, 1H, J=7.3 and 7.3 Hz, ArH), 6.82 (d, 1H, J=7.3 Hz, ArH), 3.24–3.06 (m, 2H, CH₂), 3.01 (d, 1H, J=19.1 Hz, CHaHb), 2.73 (d, 1H, J=19.1 Hz, CHaHb), 2.70–2.58 (m, 1H, CH₂), 2.23–2.13 (m, 1H, CH₂), 1.92 (s, 3H, ArCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=206.0 (s, C=O), 157.3 (s, ArC), 147.9 (s, ArC), 142.8 (s, ArC), 137.8 (d, ArCH), 137.2 (s, ArC), 136.2 (s, ArC), 128.3 (d, ArCH), 127.2 (d, ArCH), 127.1 (d, ArCH), 124.7 (d, ArCH), 122.6 (d, ArCH), 120.9 (d, ArCH), 55.0 [s, C(CH₂)₂], 53.9 (t, CH₂), 40.2 (t, CH₂), 31.1 (t, CH₂), 18.6 (q, ArCH₃) ppm. HR-MS (APCI+): m/z calculated for [C₁₈H₁₇O⁺]=[M+H⁺]: 248.1196; found: 248.1181.

5-Ethyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2H)-one (9e): GP-2 was carried out with ester 3e (77 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone 9e (59 mg, 90%) as brown color viscous liquid. [TLC control Rₗ(3e)=0.65, Rₗ(9e)=0.45, (petroleum ether/ethyl acetate 96:4, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): 𝜈max= 2962, 2929, 1708, 1613, 1577, 1485, 1456, 1241, 1159, 1020, 761 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.61 (s, 1H, ArH), 7.43 (dd, 1H, J=7.8 and 1.5 Hz, ArH), 7.32 (d, 1H, J=7.3 Hz, ArH), 7.24–7.07 (m, 3H, ArH), 6.79 (d, 1H, J=7.8 Hz, ArH), 3.16–3.07 (m, 2H, CH₂), 3.00
(d, 1H, J=18.6 Hz, CH3Hb), 2.86 (d, 1H, J=18.6 Hz, CH2Hb), 2.73 (q, 2H, J=7.8 Hz, CH2CH3), 2.55–2.43 (m, 1H, CH2), 2.40–2.28 (m, 1H, CH2), 1.27 (t, 3H, J=7.8 Hz, CH3CH2) ppm. 13C-NMR (CDCl3, 100 MHz): δ=205.9 (s, C=O), 159.2 (s, ArC), 149.0 (s, ArC), 144.2 (s, ArC), 143.2 (s, ArC), 136.3 (s, ArC), 135.8 (d, ArCH), 127.1 (d, 2C, ArCH), 124.8 (d, ArCH), 124.5 (d, ArCH), 122.8 (d, ArCH), 121.7 (d, ArCH), 54.1 [s, -C(CH3)], 52.7 (t, CH2), 42.8 (t, CH2), 31.2 (t, CH2), 28.4 (t, CH2), 15.4 (q, CH3) ppm. HR-MS (APCI+): m/z calculated for [C19H19O]+=[M+H]+: 263.1430; found: 263.1438.

5-Ethyl-6'-methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2H)-one(9f): GP-2 was carried out with ester 1f (81 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone 9f (58 mg, 84%) as brown color viscous liquid. [TLC control Rf(3f)=0.65, Rf(9f)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2961, 2922, 1713, 1614, 1487, 1456, 1284, 1241, 1159, 1032, 814 cm⁻¹. 1H-NMR (CDCl3, 400 MHz): δ=7.61 (s, 1H, ArH), 7.44 (dd, 1H, J=7.8 and 2.0 Hz, ArH), 7.18 (dd, 1H, J=7.3 and 7.8 Hz, ArH), 7.03 (d, 1H, J=7.8 Hz, ArH), 6.59 (s, 1H, ArH), 3.15–3.01 (m, 2H, CH2), 2.94 (d, 1H, J=18.6 Hz, CHHb), 2.86 (d, 1H, J=18.6 Hz, CH2Hb), 2.73 (q, 2H, J=7.8 Hz, CH2), 2.54–2.40 (m, 1H, CH2), 2.39–2.28 (m, 1H, CH2), 2.23 (s, 3H, ArCH3), 1.28 (t, 3H, J=7.8 Hz, CH3) ppm. 13C-NMR (CDCl3, 100 MHz): δ=206.0 (s, C=O), 159.3 (s, ArC), 149.1 (s, ArC), 144.1 (s, ArC), 140.1 (s, ArC), 136.8 (s, ArC), 136.3 (s, ArC), 135.7 (d, ArCH), 128.0 (d, ArCH), 124.9 (d, ArCH), 124.3 (d, ArCH), 123.4 (d, ArCH), 121.6 (d, ArCH), 54.1 [s, -C(CH3)], 52.7 (t, CH2), 43.0 (t, CH2), 30.8 (t, CH2), 28.4 (t, CH2), 21.2 (q, ArCH3), 15.3 (q, CH3) ppm. HR-MS (APCI+): m/z calculated for [C20H21O]+=[M+H]+: 277.1587; found: 277.1596.

5-Isopropyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2H)-one (9g): GP-2 was carried out with ester 3g (81 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone 9g (60 mg, 86%) as brown color viscous liquid. [TLC control Rf(3g)=0.65, Rf(9g)=0.50, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax= 2932, 2981, 1676, 1578, 1413, 1284, 1159, 1014 cm⁻¹. 1H-
NMR (CDCl₃, 400 MHz): δ=7.65 (s, 1H, ArH), 7.47 (dd, 1H, J=7.8 and 1.5 Hz, ArH), 7.32 (d, 1H, J=7.3 Hz, ArH), 7.24–7.08 (m, 3H, ArH), 6.80 (d, 1H, J=7.3 Hz, ArH), 3.21–3.05 (m, 2H, CH₂), 3.04–2.91 (m, 2H, CH₂), 2.86 (d, 1H, J=18.6 Hz, CH₃H₃), 2.56–2.43 (m, 1H, CH), 1.28 (d, 3H, J=1.5 Hz, CH₃), 1.27 (d, 3H, J=1.5 Hz, CH₃) ppm. 

13C-NMR (CDCl₃, 100 MHz): δ=206.0 (s, C=O), 159.3 (s, ArC), 149.0 (s, ArC), 148.9 (s, ArC), 143.2 (s, ArC), 136.2 (s, ArC), 127.1 (d, 2C, ArCH), 124.8 (d, ArCH), 124.5 (d, ArCH), 122.7 (d, ArCH), 120.1 (d, ArCH), 54.1 (s, -C-), 52.7 (t, CH₂), 42.8 (t, CH₂), 33.8 (d, CH), 31.2 (t, CH₂), 23.8 (q, 2 × CH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₀H₂₁O⁺]=[M+H]⁺: 277.1587; found: 277.1602.

5-Isopropyl-6′-methyl-2,3′-dihydro-1,1′-spirobi[inden]-3(2H)-one (9h): GP-2 was carried out with ester 3h (84 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone 9h (62 mg, 85%) as brown color viscous liquid. [TLC control Rf(3h)=0.60, Rf(9h)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax = 2930, 1710, 1674, 1586, 1456, 1412, 1127, 1014 cm⁻¹. 1H-NMR (CDCl₃, 400 MHz): δ=7.65 (s, 1H, ArH), 7.47 (dd, 1H, J=7.8 and 1.5 Hz, ArH), 7.19 (dd, 1H, J=7.8 Hz, ArH), 6.60 (s, 1H, ArH), 3.20–3.04 (m, 2H, CH₂), 3.03–2.92 (m, 2H, CH₂), 2.94 (d, 1H, J=18.6 Hz, CH₃H₃), 2.54–2.43 (m, 1H, CH), 2.38–2.27 (m, 2H, CH₂), 2.23 (s, 3H, ArCH₃), 1.30 (d, 3H, J=2.0 Hz, CH₃), 1.26 (d, 3H, J=2.0 Hz, CH₃) ppm. 13C-NMR (CDCl₃, 100 MHz): δ=206.1 (s, C=O), 159.4 (s, ArC), 149.1 (s, ArC), 148.8 (s, ArC), 140.2 (s, ArC), 136.8 (s, ArC), 136.2 (s, ArC), 134.6 (d, ArCH), 128.0 (d, ArCH), 124.8 (d, ArCH), 124.2 (d, ArCH), 123.4 (d, ArCH), 120.1 (d, ArCH), 54.0 (s, -C(CH₃)₂), 52.7 (t, CH₂), 43.0 (t, CH₂), 33.8 (d, CH), 30.8 (t, CH₂), 23.8 (q, 2 × CH₃), 21.2 (q, ArCH₃) ppm. HR-MS (APCI+): m/z calculated for [C₂₁H₂₃O⁺]=[M+H]⁺: 291.1743; found: 291.1731.

3-(4-fluorophenyl)-6-methyl-1H-indene (10k): GP-3 was carried out with ester 3k (78 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indene 10k (39 mg, 70%) as brown color viscous
liquid. [TLC control \(R_f(3k)=0.45\), \(R_f(10k)=0.65\), (petroleum ether/ethyl acetate 98:2, UV detection)]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \(\nu_{\text{max}}=2934, 1731, 1597, 1452, 1368, 1221, 1158, 747, 697\) cm\(^{-1}\). \(^{1}\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta=7.65–7.53\) (m, 2H, ArH), 7.46 (d, 1H, \(J=7.8\) Hz, ArH), 7.37 (s, 1H, ArH), 7.22–7.09 (m, 3H, ArH), 6.55 (t, 1H, \(J=2.0\) Hz, CH=C), 3.5 (s, 2H, CH\(_2\)), 2.44 (s, 3H, ArCH\(_3\)) ppm. \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta=163.5, 144.1, 141.7, 135.8, 132.3, 131.2, 129.3, 129.2, 125.8, 123.8, 120.8, 115.8, 115.3, 37.7, 21.6\) ppm. HR-MS (APCI+): m/z calculated for \([\text{C}_{16}\text{H}_{14}F]^+=[\text{M}+\text{H}]^+\): 225.1074; found: 225.1079.

3-(4-chlorophenyl)-6-methyl-1H-indene (10m): GP-3 was carried out with ester 3m (82 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished indene 10m (46 mg, 77%) as brown color viscous liquid. [TLC control \(R_f(3m)=0.45, R_f(10m)=0.60\), (petroleum ether/ethyl acetate 97:3, UV detection)]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \(\nu_{\text{max}}=2923, 1705, 1661, 1489, 1379, 1256, 1092, 1014, 818\) cm\(^{-1}\). \(^{1}\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta=7.56–7.50\) (m, 2H, ArH), 7.45–7.38 (m, 3H, ArH), 7.36 (s, 1H, ArH), 7.15 (d, 1H, \(J=7.8\) Hz, ArH), 6.50 (t, 1H, \(J=2.0\) Hz, CH=C), 2.47 (d, 1H, \(J=2.0\) Hz, CH\(_2\)), 2.43 (s, 3H, ArCH\(_3\)) ppm. \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta=145.0\) (s, ArC), 143.9 (s, ArC), 140.9 (s, ArC), 134.8 (d, ArC), 134.7 (s, ArC), 133.2 (s, ArC), 130.4 (d, ArCH), 128.9 (d, 2C, ArCH), 128.7 (d, 2C, ArCH), 126.9 (d, ArC), 125.1 (d, ArCH), 119.7 (d, CH=C), 38.0 (t, CH\(_2\)), 21.4 (q, ArCH\(_3\)) ppm. HR-MS (APCI+): m/z calculated for \([\text{C}_{16}\text{H}_{14}\text{Cl}]^+=[\text{M}+\text{H}]^+\): 241.0779; found: 241.0783.

3-(4-chlorophenyl)-5-methyl-1H-indene (10n): GP-3 was carried out with ester 3n (82 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished indene 10n (47 mg, 78%) as brown color viscous liquid. [TLC control \(R_f(3n)=0.45, R_f(10n)=0.60\), (petroleum ether/ethyl acetate 97:3, UV detection)]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \(\nu_{\text{max}}=2920, 1726, 1613, 1487, 1393, 1288, 1093, 1014, 885, 803, 731\) cm\(^{-1}\). \(^{1}\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta=7.57\) (dd, 2H, \(J=8.3\) and 2.0 Hz, ArH), 7.47 (dd, 3H, \(J=8.3\) and 2.0 Hz, ArH), 7.22–7.09 (m, 3H, ArH), 6.55 (t, 1H, \(J=2.0\) Hz, CH=C), 3.5 (s, 2H, CH\(_2\)), 2.44 (s, 3H, ArCH\(_3\)) ppm. HR-MS (APCI+): m/z calculated for \([\text{C}_{16}\text{H}_{14}\text{Cl}]^+=[\text{M}+\text{H}]^+\): 241.0779; found: 241.0783.
Hz, ArH), 7.38 (s, 1H, ArH), 7.14 (d, 1H, J=8.3 Hz, ArH), 6.58 (t, 1H, J=2.0 Hz, CH=C), 3.49 (d, 2H, J=2.0 Hz, CH₂), 2.45 (s, 3H, ArCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=144.0 (s, ArC), 143.7 (s, ArC), 141.7 (s, ArC), 135.8 (d, ArC), 134.6 (s, ArC), 133.3 (s, ArC), 131.7 (d, ArCH), 129.0 (d, 2C, ArCH), 128.7 (d, 2C, ArCH), 125.9 (d, ArCH), 123.9 (d, ArCH), 120.7 (d, CH=C), 37.8 (t, CH₂), 21.6 (q, ArCH₃) ppm. HR-MS (APCI⁺): m/z calculated for [C₁₆H₁₄Cl]⁺=[M+H]⁺: 241.0779; found: 241.0787.
$^1$H-NMR (400 MHz) spectrum of 3b in CDCl$_3$ 

$^{13}$C-NMR (100 MHz) spectrum of 3b in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3c in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3c in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3e in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3e in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3f in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3f in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3g in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3g in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3h in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3h in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3i in CDCl$_3$

$^1$C-NMR (100 MHz) spectrum of 3i in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3j in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3j in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of $3k$ in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of $3k$ in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3I in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3I in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3m in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 3m in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 3n in CDCl₃

$^{13}$C-NMR (100 MHz) spectrum of 3n in CDCl₃
1H-NMR (400 MHz) spectrum of 3o in CDCl₃

1³C-NMR (100 MHz) spectrum of 3o in CDCl₃
$^1$H-NMR (400 MHz) spectrum of 9a in CDCl₃

$^{13}$C-NMR (100 MHz) spectrum of 9a in CDCl₃
$^1$H-NMR (400 MHz) spectrum of $9b$ in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of $9b$ in CDCl$_3$
\[ ^1H\text{-NMR} (400 MHz) \text{ spectrum of } 9c \text{ in CDCl}_3 \]

\[ ^{13}C\text{-NMR} (100 MHz) \text{ spectrum of } 9c \text{ in CDCl}_3 \]
$^1$H-NMR (400 MHz) spectrum of 9d in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9d in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 9e in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9e in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 9f in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9f in CDCl$_3$
In addition to the $^1$H and $^{13}$C NMR studies, the chemical structures of spiro-tetracyclic ketones $9f$ were confirmed by 2D-NMR analysis such as COSY, HSQC, HMBC and NOESY spectra:

**Analysis Based on COSY:** COSY is a useful method for determining which signals arise from neighboring protons (usually up to four bonds). Correlations appear when there is spin-spin coupling between protons, but where there is no coupling, no correlation is expected to appear. The methylene signal at $\delta^H_{10}=2.72$ ppm is a quartet due to coupling with three protons of an adjacent methyl group with the coupling constant $J=7.6$ Hz. The methyl protons signal at $\delta^H_{11}=1.28$ ppm is a triplet indicating due to two neighboring vicinal protons with the coupling constant $J=7.6$ Hz. Based on the COSY spectrum, we can see that methylene protons at $\delta^H_{10}=2.73$ ppm are in correlation with aromatic protons ($\delta^H_8=7.62$ ppm, s; and $\delta^H_6=7.44$ ppm, dd). Also, it was observed that the methyl protons at $\delta^H_{20}=2.23$ ppm were in strong correlation between aromatic protons at ($\delta^H_{18}=6.60$ ppm, s; and $\delta^H_{16}=7.03$ ppm d).
HSQC-NMR (400 MHz) spectrum of 9f in CDCl₃

**Analysis Based on HSQC:** The HSQC (Heteronuclear Single-Quantum Correlation) experiment permits to obtain a 2D heteronuclear chemical shift correlation map between directly-bonded ¹H and X-heteronuclear (¹³C, ¹⁵N etc.). This method provides crucial information about which proton directly connected to which carbon atom of the present compound. The δC₂₀=21.3 ppm carbon correlates with protons δH₂₀=2.24 ppm. Whereas, δC₁₁=15.4 ppm carbon has strong correlation with protons δH₁₁=1.28 ppm. Also, δC₁₀=28.5 ppm carbon shows strong correlation with protons δH₁₁=2.74 ppm and δC₂=52.8 ppm correlates with the protons δH₂=2.95 ppm.
HMBC-NMR (400 MHz) spectrum of 9f in CDCl₃

**Analysis Based on HMBC:** The HMBC (Heteronuclear Multiple Bond Correlation) experiment gives correlations between carbons and protons that are separated by two, three and sometimes in conjugated systems distanced by four bonds. While direct one-bond correlations are suppressed. In HMBC spectrum, the H₂ protons (δH₂=2.95, d, J=18.9 Hz) exhibited cross peak with δC₁=206.1 ppm, which is suggestive that the H₂ protons connected C₂-carbon. Also, the same H₂ protons exhibited cross peaks with δC₄=159.4 and δC₉=149.2 carbons. The benzylic methylene protons (H₁₀) exhibited cross peaks with δC₇=144.2, δC₈=135.8 and δC₆=121.7 ppm of aromatic carbon atoms. The protons of H₂₀ exhibited cross peaks with δC₁₇=136.3, δC₁₈=128.1 and δC₁₆=123.4 ppm of aromatic carbons.
NOESY-NMR (400 MHz) spectrum of 9f in CDCl₃

**Based on NOESY:** This NOESY spectrum is useful for determining which signals arise from protons that are close to each other in space even if they are not bonded. From this spectrum, we can see that methyl protons (H₁₁) has correlation with aromatic protons (H₆ & H₄). Similarly, the methylene protons (H₁₀) shows the correlation with (H₈ & H₆). The methyl protons (H₂₀) have strong correlation with aromatic protons (H₁₈ & H₁₆). Also, the H₂ protons are strongly correlated with aromatic proton H₁₈. Therefore, based on all the above 2D-NMR analysis, the chemical structures of 9 were further unambiguously confirmed.
$^1$H-NMR (400 MHz) spectrum of 9g in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9g in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 9h in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9h in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 9i in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 9i in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 10j in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 10j in CDCl$_3$
$^{1}$H-NMR (400 MHz) spectrum of 10k in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 10k in CDCl$_3$
$^1$H-NMR (400 MHz) spectrum of 10l in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 10l in CDCl$_3$
In addition to the $^1$H, $^{13}$C NMR studies, the chemical structures of spiro-tetracyclic ketones 10l were confirmed by 2D-NMR analysis such as COSY, HSQC, HMBC and NOESY spectra:

Analysis Based on COSY: With $^1$H-NMR the methylene protons signal at $\delta_{H_1}=3.50$ ppm appears to be a doublet resulting from one proton on adjacent carbon with smaller coupling constant $J=2.2$ Hz. The olefin proton signal at $\delta_{H_2}=6.57$ ppm is a triplet indicating two neighboring proton with small coupling constant $J = 2.2$ Hz connected to the adjacent carbon atoms (i.e. both $H_1$ and $H_2$ are vicinal to each other). This is in very good agreement that in cyclopentenes the couplings of an adjacent CH$_2$ group to the vinyl hydrogens is typically around $^3J = 2.1$ Hz. Based on the COSY spectrum, we can see that methylene $H_1$ protons ($\delta_{H_1}=3.50$ ppm, d) showed strong correlation with one olefin proton ($\delta_{H_2}=6.56$ ppm, t). Also, the methylene protons at $\delta_{H_1}=3.50$ ppm have engaged in correlation with aromatic proton ($H_8$). Although, it is not very clear, there might be a correlation between $H_1$ protons and the aromatic protons ($H_5$ & $H_7$).
Analysis Based on HSQC: This spectral analysis gave crucial information about which proton connected which carbon atom of the compound. According to the HSQC analysis, the C$_2$-carbon ($\delta_{C2}=131.4$ ppm) correlated well with H$_2$ olefinic proton with chemical shift $\delta_{H2}=6.56$ ppm. Similarly, the C$_1$ carbon with chemical shift $\delta_{C1}=38.25$ ppm has strong correlation with H$_1$ methylene protons ($\delta_{H1}=3.50$ ppm).
HMBC-NMR (400 MHz) spectrum of 10l in CDCl₃

**Analysis Based on HMBC:** In this HMBC spectrum, the H₁ methylene protons (δH₁=3.50, d, J = 2.3 Hz) exhibits a cross peak with δC₂=131.4 ppm (olefinic CH-carbon). Also, the same H₁ methylene protons connected to C₁-carbon shows cross peaks with δC₃=143.6 ppm, δC₄=144.1 ppm (olefinic C-carbon) and δC₉=144.7 ppm (aromatic C-carbon).
Based on NOESY: This spectrum furnished some useful information about which signal arise from protons that are close to each other in space even if they are not bonded. It is noticed that methylene protons ($\delta H_1=3.50$ ppm) have strong correlation with olefin proton ($H_2$) with chemical shift $\delta H_2=6.56$ ppm. Also, the methylene protons at $\delta H_1=3.50$ ppm might have some correlation with aromatic protons ($H_8$), which is not very much clear due to overlapping aromatic protons. Therefore, based on all the above 2D-NMR analysis, the chemical structures of 10 were further unambiguously confirmed.
1H-NMR (400 MHz) spectrum of 10m in CDCl₃

13C-NMR (100 MHz) spectrum of 10m in CDCl₃
$^1$H-NMR (400 MHz) spectrum of 10n in CDCl$_3$

$^{13}$C-NMR (100 MHz) spectrum of 10n in CDCl$_3$