Supporting Information

Cleavage and Reassembly C≡C Bonds of Ynones to Access Highly Functionalized Ketones

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**General methods:**

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel (200 - 300 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at room temperature on 400 MHz Bruker spectrometers and 400 MHz JEOL spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for $^1$H NMR spectra and 77.0 ppm for $^{13}$C NMR spectra in CDCl$_3$). Chemical shift ($\delta$) is reported in ppm, coupling constants ($J$) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.
**General procedure for ynones 1 and their spectral data:**

![Chemical Diagram](image)

Ethynylmagnesium bromide (0.50 M solution in THF 12 mL, 1.2 equiv.) was added dropwise to a stirred solution of aldehyde 5 (5.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL) at -10 °C. The mixture was kept stirring at -10 °C for 20 minutes and warmed to room temperature for additional two hours. Then the reaction mixture was quenched with saturated ammonium chloride (20 mL) and extracted with ethyl acetate for three times. The organic layers was combined and dried with anhydrous MgSO₄. It was evaporated under reduced pressure to give intermediate alcohol 6, which was used in next step directly.

The crude alcohol 6 was dissolved in dichloromethane and treated with activated MnO₂ (10 equiv.). After completion of the reaction (monitored by TLC), the solid was removed by filtration of the reaction mixture through a pad of celite. Then it was extracted with ethyl acetate and dried with anhydrous Na₂SO₄. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired ynones 1.

**1-Phenylprop-2-yn-1-one (1a):**

![Chemical Structure](image)

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rₜ = 0.38). The product was obtained as yellow solid in 86% yield (559.0 mg), Mp. 44 - 45 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.18 - 8.16 (m, 2H), 7.66 - 7.62 (m, 1H), 7.52 - 7.49 (m, 2H), 3.50 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 136.1, 134.5, 129.7, 128.7, 80.8, 80.2; HRMS (ESI) m/z [M+H]^+: Calcd for C₉H₇O: 131.0497. Found: 131.0495.
1-(2-bromophenyl)prop-2-yn-1-one (1b):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.60). The product was obtained as yellow oil in 93% yield (967.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 - 8.11 (d, $J$ = 7.6 Hz, 1H), 7.70 - 7.68 (d, $J$ = 7.6 Hz, 1H), 7.48 - 7.38 (m, 2H), 3.54 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.3, 135.7, 135.1, 133.8, 133.7, 127.3, 121.2, 81.6, 80.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_6$BrO: 208.9602. Found: 208.9597.

1-(3-bromophenyl)prop-2-yn-1-one (1c):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.41). The product was obtained as yellow oil in 89% yield (925.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (s, 1H), 8.09 - 8.08 (d, $J$ = 7.6 Hz, 2H), 7.76 - 7.74 (d, $J$ = 8.0 Hz, 2H), 7.41 - 7.37 (m, 1H), 3.53 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.8, 137.7, 137.3, 132.4, 130.2, 128.1, 122.9, 81.7, 79.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_6$BrO: 208.9602. Found: 208.9599.

1-(4-Fluorophenyl)prop-2-yn-1-one (1d):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.55). The product was obtained as yellow solid in 70% yield (518.0 mg), Mp. 43 - 44 ºC. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 - 8.17 (m, 2H), 7.19 - 7.15 (t, $J$ = 8.4 Hz, 2H), 3.50 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.7, 166.6 (d, $J$ = 256.0 Hz), 132.6
(d, J = 2.9 Hz), 132.3 (d, J = 9.8 Hz), 115.9 (d, J = 22.2 Hz), 81.1, 79.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -102.2; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_6$FO: 149.0403. Found: 149.0403.

1-(4-Chlorophenyl)prop-2-yn-1-one (1e):

![Chemical structure of 1-(4-Chlorophenyl)prop-2-yn-1-one (1e)]

The title compound was prepared according to the general procedure (EA/PE = 1/9, R$_f$ = 0.58). The product was obtained as yellow solid in 75% yield (615.0 mg), Mp. 94 - 95 ºC. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 - 8.09 (d, J = 8.4 Hz, 2H), 7.49 - 7.47 (d, J = 8.4 Hz, 2H), 3.49 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.1, 141.2, 134.5, 130.1, 129.1, 81.3, 79.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_6$ClO: 165.0107. Found: 165.0109.

1-(4-Bromophenyl)prop-2-yn-1-one (1f):

![Chemical structure of 1-(4-Bromophenyl)prop-2-yn-1-one (1f)]

The title compound was prepared according to the general procedure (EA/PE = 1/9, R$_f$ = 0.73). The product was obtained as yellow solid in 98% yield (1019.2 mg), Mp. 109 - 110 ºC. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 - 8.00 (d, J = 7.6 Hz, 2H), 7.66 - 7.64 (d, J = 8.0 Hz, 2H), 3.49 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.3, 134.9, 132.1, 131.0, 130.1, 81.4, 79.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_9$H$_6$BrO: 208.9602. Found: 208.9607.

1-(4-Iodophenyl)prop-2-yn-1-one (1g):

![Chemical structure of 1-(4-Iodophenyl)prop-2-yn-1-one (1g)]
The title compound was prepared according to the general procedure (EA/PE = 1/9, R<sub>f</sub> = 0.68). The product was obtained as yellow solid in 58% yield (742.1 mg), Mp. 117 - 118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 - 7.82 (m, 4H), 3.48 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.6, 138.1, 135.4, 130.8, 103.2, 81.4, 79.9; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>9</sub>H<sub>6</sub>I O: 256.9463. Found: 256.6466.

1-(<i>p</i>-Tolyl)prop-2-yn-1-one (1h):

![1-(<i>p</i>-Tolyl)prop-2-yn-1-one](image)

The title compound was prepared according to the general procedure (EA/PE = 1/9, R<sub>f</sub> = 0.54). The product was obtained as yellow solid in 95% yield (684.5 mg), Mp. 35 - 36 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 - 7.95 (m, 2H), 7.21 - 7.19 (m, 2H), 3.34 (s, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.0, 145.7, 133.8, 129.8, 129.3, 80.4, 80.3, 21.8; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>10</sub>H<sub>9</sub>O: 145.0653. Found: 145.0655.

1-(2-methoxyphenyl)prop-2-yn-1-one (1i):

![1-(2-methoxyphenyl)prop-2-yn-1-one](image)

The title compound was prepared according to the general procedure (EA/PE = 1/9, R<sub>f</sub> = 0.58). The product was obtained as yellow oil in 91% yield (728.5 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 - 8.05 (m, 1H), 7.57 - 7.53 (m, 1H), 7.06 - 7.00 (m, 2H), 3.93 (s, 3H), 3.39 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.0, 160.0, 135.5, 133.2, 125.7, 120.2, 112.1, 82.1, 79.3, 55.8; HRMS (ESI) m/z [M+H]<sup>+</sup>: Calcd for C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>: 161.0603. Found: 161.0600.

1-(3-Methoxyphenyl)prop-2-yn-1-one (1j):

S6
The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.58). The product was obtained as yellow oil in 83% yield (664.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 - 7.79 (m, 1H), 7.64 - 7.63 (m, 1H), 7.43 - 7.39 (t, J = 8 Hz, 1H), 7.20 - 7.17 (m, 1H), 3.87 (s, 3H), 3.45 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 177.1, 159.7, 137.4, 129.7, 123.0, 121.4, 112.7, 80.7, 80.2, 55.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₀H₉O₂: 161.0603. Found: 161.0605.

1-(4-Methoxyphenyl)prop-2-yn-1-one (1k):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.45). The product was obtained as yellow solid in 80% yield (640.4 mg), Mp. 72 - 73 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 - 8.12 (m, 2H), 6.97 - 6.95 (m, 2H), 3.89 (s, 3H), 3.40 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 175.9, 164.7, 132.1 129.5, 113.9, 80.3, 80.1, 55.6; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₀H₇NO: 156.0449. Found: 156.0451.

4-Propioloylebenzonitrile (II):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.34). The product was obtained as yellow solid in 86% yield (666.5 mg), Mp. 99 - 100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28 - 8.26 (d, J = 8.8 Hz, 2H), 7.84 - 7.82 (d, J = 8.4 Hz, 2H), 3.62 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 175.7, 138.7, 132.5, 129.9, 117.6, 117.5, 82.7, 79.5; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₀H₆NO: 156.0449. Found: 156.0451.
1-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-one (1m):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.68). The product was obtained as yellow solid in 59% yield (584.1 mg), Mp. 65 - 66 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.28 - 8.26 (m, 2H), 7.78 - 7.76 (m, 2H), 3.57 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.2, 138.5, 135.5 (q, \(J = 32.5\) Hz), 129.9, 125.7 (q, \(J = 3.7\) Hz), 123.4 (q, \(J = 271.4\) Hz), 82.1, 79.7; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.2; HRMS (ESI) m/z [M+H]: Calcd for C\(_{10}\)H\(_6\)F\(_3\)O: 199.0375. Found: 199.0375.

1-(Thiophen-2-yl)prop-2-yn-1-one (1n):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.40). The product was obtained as yellow solid in 84% yield (571.2 mg), Mp. 39 - 40 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 - 7.98 (d, \(J = 3.2\) Hz, 1H), 7.77 - 7.76 (d, \(J = 4.8\) Hz, 1H), 7.20 - 7.18 (m, 1H), 3.40 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.1, 144.0, 136.2, 136.0, 128.4, 79.8, 79.4; HRMS (ESI) m/z [M+H]: Calcd for C\(_7\)H\(_5\)O\(_S\): 137.0061. Found: 137.0065.

1-(Furan-2-yl)prop-2-yn-1-one (1o):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.40). The product was obtained as yellow solid in 77% yield (462.0 mg), Mp. 44 - 45 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (s, 1H), 7.35 (m, 1H), 6.54 (m, 1H), 3.29 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.7, 152.6, 148.5, 122.1, 112.8, 79.5, 79.5;
HRMS (ESI) m/z [M+H]^+: Calcd for C_{7}H_{5}O_{2}: 121.0290. Found: 121.0287.

1-(Naphthalen-2-yl)prop-2-yn-1-one (1p):

![Naphthalen-2-yl]prop-2-yn-1-one (1p)

The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.63). The product was obtained as yellow solid in 90% yield (810.5 mg), Mp. 91 - 92 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.73 (s, 1H), 8.13 - 8.11 (m, 1H), 8.00 - 7.98 (m, 1H), 7.89 - 7.86 (m, 2H), 7.65 - 7.59 (m, 1H), 7.57 - 7.55 (m, 1H), 3.51 (s, 1H);
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 177.3, 136.2, 133.6, 133.3, 132.3, 129.8, 129.2, 128.6, 127.9, 127.0, 123.5, 80.7, 80.3; HRMS (ESI) m/z [M+H]^+: Calcd for C\(_{13}\)H\(_9\)O: 181.0653. Found: 181.0655.

1-(Phenanthren-9-yl)prop-2-yn-1-one (1q):

![Phenanthren-9-yl]prop-2-yn-1-one (1q)

The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.55). The product was obtained as yellow solid in 67% yield (770.8 mg), Mp. 89 - 90 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.80 - 9.15 (m, 1H), 8.83 (s, 1H), 8.63 - 8.57 (m, 2H), 7.96 - 7.94 (d, \(J = 8.0\) Hz, 1H), 7.74 - 7.70 (m, 1H), 7.64 - 7.56 (m, 3H), 3.42 (s, 1H);
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 178.7, 139.0, 133.0, 130.9, 130.7, 130.6, 130.3, 129.7, 128.3, 128.2, 127.5, 127.3, 126.7, 122.8, 122.7, 81.6, 79.5; HRMS (ESI) m/z [M+H]^+: Calcd for C\(_{17}\)H\(_{11}\)O: 231.0810. Found: 231.0805.

\((E)\)-2-Methyl-1-phenylpent-1-en-4-yn-3-one (1r):

![E-2-Methyl-1-phenylpent-1-en-4-yn-3-one (1r)]
The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.69). The product was obtained as yellow solid in 61% yield (518.8 mg), Mp. 43 - 44 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (s, 1H), 7.43 - 7.30 (m, 5H), 3.27 (s, 1H), 2.04 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 180.0, 146.6, 137.6, 135.2, 130.1, 129.4, 128.6, 80.0, 79.7, 12.0; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{12}\)H\(_{11}\)O: 171.0810. Found: 171.0811.

\((E)-4\text{-Methylhept-4-en-1-yn-3-one (1s)}:\)

![Structure of (E)-4-Methylhept-4-en-1-yn-3-one](image)

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.80). The product was obtained as yellow oil in 70% yield (427.4 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 - 7.17 (t, \(J = 7.2\) Hz, 1H), 3.24 (s, 1H), 2.38 - 2.30 (m, 2H), 1.80 (s, 3H), 1.15 - 1.11 (t, \(J = 7.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 179.6, 153.1, 137.5, 79.6, 79.0, 22.7, 12.7, 10.1; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_8\)H\(_{11}\)O: 123.0810. Found: 123.0811.

\(1\text{-}(4\text{-Ethynylphenyl})\text{prop-2-yn-1-one (1t)}:\)

![Structure of 1-(4-Ethynylphenyl)prop-2-yn-1-one](image)

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.60). The product was obtained as yellow solid in 54% yield (415.8 mg), Mp. 97 - 98 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 - 8.03 (d, \(J = 8.0\) Hz, 2H), 7.53 - 7.51 (d, \(J = 8.4\) Hz, 2H), 3.41 (s, 1H), 3.24 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.4, 135.7, 132.3, 129.5, 128.3, 82.6, 81.4, 81.3, 80.0; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{11}\)H\(_7\)O: 155.0497. Found: 155.0501.

\(\text{Hept-1-yn-3-one (1v)}:\)
The title compound was prepared according to the general procedure (EA/PE = 1/39, Rf = 0.55). The product was obtained as colorless oil in 35% yield (192.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.19 (s, 1H), 2.54 - 2.50 (t, $J = 7.2$ Hz, 2H), 1.63 - 1.55 (m, 2H), 1.33 - 1.24 (m, 2H), 0.87 - 0.83 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 187.5, 81.3, 78.3, 45.0, 25.7, 21.9, 13.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_7$H$_{11}$O: 111.0810. Found: 111.0814.

5-Phenylpent-1-yn-3-one (1w):

The title compound was prepared according to the general procedure (EA/PE = 1/9, Rf = 0.55). The product was obtained as colorless oil in 61% yield (582.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 - 7.25 (m, 2H), 7.21 - 7.16 (m, 3H), 3.22 (s, 1H), 2.98 - 2.95 (m, 2H), 2.91 - 2.87 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 186.1, 139.8, 128.4, 128.2, 126.2, 81.2, 78.9, 46.7, 29.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{11}$H$_{11}$O: 159.0810. Found: 159.0812.

Dec-1-yn-3-one (1x):

The title compound was prepared according to the general procedure (EA/PE = 1/39, Rf = 0.35). The product was obtained as colorless oil in 47% yield (357.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.20 (s, 1H), 2.60 - 2.57 (t, $J = 7.6$ Hz, 2H), 1.70 - 1.66 (m, 2H), 1.31 - 1.28 (m, 8H), 0.90 - 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 187.6, 81.4, 78.2, 45.4, 31.5, 28.9, 28.8, 23.7, 22.5, 14.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{10}$H$_{17}$O: 153.1279. Found: 153.1277.
5-Methylhex-4-en-1-yn-3-one (1z):

The title compound was prepared according to the general procedure (EA/PE = 1/9, \( R_f = 0.80 \)). The product was obtained as colorless oil in 83% yield (448.7 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.20 (m, 1H), 3.18 (s, 1H), 2.23 (d, \( J = 0.8 \) Hz, 3H), 1.96 (d, \( J = 1.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 175.5, 159.7, 125.2, 83.6, 76.7, 27.8, 21.2; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_7\)H\(_9\)O: 109.0653. Found: 109.0650.

**General procedure for synthesis of N-tosylhydrazones:**

![Diagram of reaction](image)

The carbonyl compound 7 (10 mmol, 1.0 equiv.) was added to a solution of TsNHNH\(_2\) 8 (10 mmol, 1.0 equiv.) in methanol (20 mL) at 60 °C. The reaction mixture was then stirred at 60 °C until 7 was consumed completely (monitor by TLC). The solution was cooled down to 0 °C, at which point the product precipitated out of solution in most cases (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane to give the pure N-tosylhydrazones 2.

**(E)-4-Methyl-N’-(1-phenylethylidene)benzenesulfonohydrazide (2a):**

![Diagram of reaction](image)

The title compound was prepared according to the general procedure. The product was obtained as white solid in 95% yield (2737.0 mg), Mp. 128 - 129 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.25 (s, 1H), 7.95 - 7.93 (m, 2H), 7.64 - 7.62 (m, 2H), 7.33 - 7.30 (m, 5H), 2.39 (s, 3H), 2.16 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 152.7, 144.1, 137.2, 135.3, 129.5, 129.4, 128.2, 128.0, 126.2, 21.5, 13.5; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{15}\)H\(_{17}\)N\(_2\)O\(_2\)S: 289.1011. Found: 289.1014.
(E)-4-Methyl-N’(1-(o-tolyl)ethylidene)benzenesulfonohydrazide (2b):

The title compound was prepared according to the general procedure. The product was obtained as white solid in 95% yield (2870.0 mg), Mp. 115 - 116 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.28 (s, 1H), 7.91 - 7.89 (m, 2H), 7.32 - 7.30 (m, 2H), 7.22 - 7.18 (m, 1H), 7.15 - 7.09 (m, 3H), 2.42 (s, 3H), 2.14 (s, 3H), 2.14 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.6, 144.1, 138.5, 135.7, 135.5, 130.8, 129.6, 128.5, 128.1, 128.0, 125.6, 21.6, 20.3, 17.4, 17.4; HRMS (ESI) m/z [M+H]^+: Calcd for C\(_{16}\)H\(_{19}\)N\(_2\)O\(_2\)S: 303.1167. Found: 303.1171.

(E)-4-Methyl-N’(1-(m-tolyl)ethylidene)benzenesulfonohydrazide (2c):

The title compound was prepared according to the general procedure. The product was obtained as white solid in 93% yield (2808.5 mg), Mp. 120 - 121 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (s, 1H), 7.96 - 7.94 (m, 2H), 7.42 (s, 2H), 7.28 - 7.27 (m, 2H), 7.19 - 7.13 (m, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 2.14 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.0, 143.9, 137.6, 137.1, 135.2, 130.1, 129.4, 128.0, 127.9, 126.8, 123.3, 21.4, 21.3, 13.6; HRMS (ESI) m/z [M+H]^+: Calcd for C\(_{16}\)H\(_{19}\)N\(_2\)O\(_2\)S: 303.1167. Found: 303.1168.

(E)-4-Methyl-N’(1-(p-tolyl)ethylidene)benzenesulfonohydrazide (2d):

The title compound was prepared according to the general procedure. The product was obtained as white solid in 91% yield (2749.1 mg), Mp. 157 - 158 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (s, 1H), 7.93 - 7.91 (m, 2H), 7.55 - 7.53 (m, 2H), 7.31 - 7.30 (m,
2H), 7.14 - 7.12 (m, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.8, 144.0, 139.6, 135.3, 134.4, 129.5, 128.9, 128.0, 126.1, 21.6, 21.2, 13.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{16}$H$_{19}$N$_2$O$_2$S: 303.1167. Found: 303.1168.

**(E)-N'-(1-(2,4-Dichlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2i):**

The title compound was prepared according to the general procedure. The product was obtained as white solid in 98% yield (3488.4 mg), Mp. 164 - 165 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 7.89 - 7.87 (m, 2H), 7.34 - 7.32 (m, 3H), 7.21 - 7.19 (m, 1H), 7.16 - 7.14 (m, 1H), 2.44 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 144.3, 136.6, 135.2, 132.9, 131.1, 129.6, 128.0, 127.1, 21.6, 17.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{15}$H$_{15}$Cl$_2$N$_2$O$_2$: 357.0231. Found: 357.0233.

**(E)-N'-(1-(4-Cyanophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2l):**

The title compound was prepared according to the general procedure. The product was obtained as white solid in 88% yield (2755.3 mg), Mp. 189 - 190 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.92 - 7.90 (m, 2H), 7.75 - 7.73 (m, 2H), 7.64 - 7.62 (m, 2H), 7.35 - 7.33 (m, 2H), 2.43 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.9, 144.6, 141.3, 135.0, 132.1, 129.7, 128.0, 126.7, 118.5, 112.8, 21.6, 13.2; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{16}$H$_{16}$N$_3$O$_2$: 314.0963. Found: 314.0961.

**(E)-N'-(1-(4-Methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2m):**
The title compound was prepared according to the general procedure. The product was obtained as white solid in 89% yield (2831.1 mg), Mp. 156 - 157 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (s, 1H), 7.94 - 7.92 (m, 2H), 7.60 - 7.58 (m, 2H), 7.32 - 7.30 (m, 2H), 6.85 - 6.83 (m, 2H), 3.80 (s, 3H), 2.40 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.7, 152.7, 144.0, 135.4, 129.8, 129.5, 128.1, 127.7, 113.6, 55.3, 21.6, 13.3; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{16}$H$_{19}$N$_2$O$_3$S: 319.1116. Found: 319.1118.

\[(E)-N'-(1-(4-(Dimethylamino)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2n):\]

The title compound was prepared according to the general procedure. The product was obtained as white solid in 85% yield (2814.4 mg), Mp. 158 - 159 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 - 7.91 (m, 2H), 7.57 - 7.55 (m, 2H), 7.53 (s, 1H), 7.31 - 7.29 (m, 2H), 6.64 - 6.62 (m, 2H), 2.97 (s, 6H), 2.40 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.6, 151.3, 143.8, 135.4, 129.8, 129.5, 128.1, 127.4, 124.8, 111.4, 40.1, 21.6, 13.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{22}$N$_3$O$_2$S: 332.1433. Found: 332.1433.

\[(E)-4-Methyl-N'-(1-(naphthalen-1-yl)ethylidene)benzenesulfonohydrazide (2o):\]

The title compound was prepared according to the general procedure. The product was obtained as white solid in 45% yield (1521.5 mg), Mp. 163 - 164 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 - 7.91 (m, 3H), 7.85 - 7.79 (m, 3H), 7.48 - 7.40 (m, 2H), 7.35 - 7.33 (m, 4H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.6, 144.2, 136.5, 135.5, 133.8, 130.3, 129.7, 129.5, 128.4, 128.3, 126.4, 126.2, 125.9, 125.4, 124.9, 21.6, 18.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{19}$H$_{19}$N$_2$O$_2$: 339.1167. Found: 339.1168.
\[N'(1-(\text{Furan-2-yl})\text{ethylidene})-4\text{-methylbenzenesulfonylhydrazide (2p)}:\]

The title compound was prepared according to the general procedure. The product was obtained as white solid in a *cis : trans* of 1:1 in 87% yield (2419.5 mg), Mp. 139 - 140 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.49 (s, 0.39H), 7.92 - 7.86 (m, 2H), 7.59 - 7.43 (m, 1H), 7.32 - 7.30 (m, 2H), 6.70 - 6.69 (m, 1H), 6.52 - 6.40 (m, 1H), 2.42 & 2.41 (s, 3H), 2.18 & 2.10 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.1, 148.7, 145.5, 144.1, 144.1, 144.0, 144.0, 138.2, 135.5, 135.2, 129.5, 129.5, 129.5, 128.0, 127.9, 114.7, 111.7, 111.5, 110.7, 21.6, 21.6, 20.9, 12.8; HRMS (ESI) m/z [M+H]: Calcd for C\(_{13}\)H\(_{15}\)N\(_2\)O\(_3\)S: 278.0803. Found: 278.0806.

\[(E)-4\text{-Methyl-}\text{N'-(1-phenylpropylidene)benzenesulfonylhydrazide (2r)}:\]

The title compound was prepared according to the general procedure. The product was obtained as white solid in 88% yield (2649.7 mg), Mp. 109 - 110 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 - 7.78 (m, 2H), 7.44 - 7.40 (m, 2H), 7.36 (s, 1H), 7.33 - 7.31 (m, 2H), 7.08 - 7.06 (m, 2H), 2.51 - 2.46 (q, \(J = 7.6\) Hz, 2H), 2.44 (s, 3H), 1.04 - 1.00 (t, \(J = 7.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.1, 143.9, 135.2, 135.2, 129.5, 129.5, 128.0, 127.9, 114.7, 111.7, 111.5, 110.7, 21.6, 21.6, 20.9, 12.8; HRMS (ESI) m/z [M+H]: Calcd for C\(_{16}\)H\(_{19}\)N\(_2\)O\(_2\)S: 302.1167. Found: 302.1169.

\[N'(\text{Diphenylmethylene})-4\text{-methylbenzenesulfonylhydrazide (2s)}:\]

The title compound was prepared according to the general procedure. The product was obtained as white solid in 88% yield (3080.9 mg), Mp. 134 - 135 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 - 7.85 (m, 2H), 7.56 - 7.51 (m, 4H), 7.45 - 7.43 (m, 2H), 7.34 -
7.28 (m, 5H), 7.13 - 7.11 (m, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.2, 144.1, 136.4, 135.4, 131.1, 130.1, 129.8, 129.7, 129.6, 128.2, 128.1, 127.9, 127.5, 21.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{20}$H$_{19}$N$_2$O$_2$S: 351.1167. Found: 351.1167.

(E)-N’-(2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonylhydrazide (2u):

![Image](image)

The title compound was prepared according to the general procedure. The product was obtained as white solid in 60% yield (1800.6 mg), Mp. 183 - 184 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 - 7.92 (m, 2H), 7.76 (s, 1H), 7.71 - 7.69 (m, 1H), 7.34 - 7.30 (m, 3H), 7.27 - 7.21 (m, 2H), 3.07 - 3.04 (m, 2H), 2.64 - 2.65 (m, 2H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.3, 148.3, 144.0, 137.0, 135.4, 130.9, 129.5, 128.0, 127.0, 125.3, 122.1, 28.4, 26.6, 21.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{16}$H$_{17}$N$_2$O$_2$: 301.1011. Found: 301.1011.

(E)-4-Methyl-N’-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)benzenesulfonylhydrazide (2w):

![Image](image)

The title compound was prepared according to the general procedure. The product was obtained as white solid in 68% yield (2231.1 mg), Mp. 139 - 140 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (s, 1H), 7.85 - 7.83 (m, 2H), 7.24 - 7.22 (m, 2H), 7.19 - 7.15 (m, 2H), 7.11 - 7.07 (m, 1H), 6.97 - 6.95 (m, 1H), 2.56 - 2.52 (t, $J$ = 6.8 Hz, 2H), 2.35 - 2.32 (m, 5H), 1.65 - 1.58 (m, 2H), 1.50 - 1.44 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.5, 144.0, 138.7, 137.2, 135.3, 129.5, 129.4, 128.4, 128.0, 127.9, 126.4, 31.1, 27.4, 25.3, 21.5, 20.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{21}$N$_2$O$_2$: 329.1324. Found: 329.1328.
General procedure for 1,4-ketoaldehydes and their spectral data:

A mixture of 1 (0.20 mmol, 1.0 equiv.), 2 (0.40 mmol, 2.0 equiv.), Cu(OH)$_2$ (0.02 mmol, 10 mol %), LiOCH$_3$ (0.40 mmol, 2.0 equiv.), H$_2$O (3.6 µL, 1.0 equiv.) and toluene (4.0 mL) was sealed in a Schlenk tube under argon protection at 100 °C and the mixture was stirred for 24 h or until the 1 was consumed completely. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography to give the desired product 3.

2-Methyl-4-oxo-2,4-diphenylbutanal (3aa):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f = 0.45$). The product was obtained as yellow oil in 94% yield (47.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.73 (s, 1H), 7.94 - 7.92 (m, 2H), 7.57 - 7.54 (m, 2H), 7.45 - 7.42 (m, 2H), 7.39 - 7.34 (m, 4H), 7.29 - 7.25 (m, 1 H), 3.75 (d, $J = 17.6$ Hz, 1H), 3.70 (d, $J = 17.6$ Hz, 1H), 1.68 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.6, 197.3, 139.9, 136.9, 133.5, 129.0, 128.7, 128.2, 127.5, 127.0, 51.9, 46.2, 20.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{17}$O$_2$: 253.1229. Found: 253.1228.

2-Methyl-4-oxo-4-phenyl-2-(o-tolyl)butanal (3ab):

The title compound was prepared according to the general procedure for reaction in 24
The product was obtained as yellow oil in yield: 68% (36.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.92 (s, 1H), 7.89 - 7.87 (m, 2H), 7.56 - 7.53 (m, 1H), 7.44 - 7.40 (m, 2H), 7.27 - 7.24 (m, 1H), 7.20 - 7.16 (m, 3H), 3.84 (d, $J$ = 17.2 Hz, 1H), 3.71 (d, $J$ = 17.2 Hz, 1H), 2.31 (s, 3H), 1.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.0, 197.6, 138.5, 136.9, 135.7, 133.2, 132.4, 128.6, 128.0, 127.6, 127.5, 126.3, 52.6, 45.8, 22.0, 21.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{19}$O$_2$: 267.1385. Found: 267.1387.

2-Methyl-4-oxo-4-phenyl-2-(m-tolyl)butanal (3ac):

![Structure 3ac]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f$ = 0.47). The product was obtained as yellow oil in 81% yield (43.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.71 (s, 1H), 7.95 - 7.93 (m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.43 (m, 2H), 7.28 - 7.24 (m, 1H), 7.14 - 7.12 (m, 2H), 7.10 - 7.08 (m, 1H), 3.74 (d, $J$ = 17.6 Hz, 1H), 3.39 (d, $J$ = 17.6 Hz, 1H), 2.34 (s, 3H), 1.67 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.4, 197.3, 139.5, 138.5, 136.7, 133.3, 128.7, 128.6, 128.1, 128.0, 127.6, 123.8, 51.6, 45.9, 21.6, 20.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{19}$O$_2$: 267.1385. Found: 267.1385.

2-Methyl-4-oxo-4-phenyl-2-(p-tolyl)butanal (3ad):

![Structure 3ad]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f$ = 0.39). The product was obtained as yellow oil in 91% yield (48.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.69 (s, 1H), 7.94 - 7.93 (m, 2H), 7.57 - 7.54 (m,
1H), 7.46 - 7.42 (m, 2H), 7.24 - 7.16 (m, 4H), 3.73 (d, J = 17.6 Hz, 1H), 3.68 (d, J = 17.6 Hz, 1H), 2.32 (s, 3H), 1.65 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 201.4, 197.2, 137.1, 136.8, 136.5, 133.3, 129.6, 128.5, 128.0, 126.7, 51.4, 45.9, 20.9, 20.6; HRMS (ESI) m/z [M+H]^+: Calcd for C18H16O2: 267.1385. Found: 267.1385.

2-(4-Fluorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ae):

![Chemical Structure]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.57). The product was obtained as yellow oil in 78% yield (42.2 mg). 1H NMR (400 MHz, CDCl3) δ 9.70 (s, 1H), 7.94 - 7.92 (m, 2H), 7.59 - 7.57 (m, 1H), 7.56 - 7.55 (m, 1H), 7.47 - 7.43 (m, 2H), 7.32 - 7.29 (m, 2H), 7.08 - 7.04 (m, 2H), 3.71 (s, 2H), 1.66 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 201.2, 197.0, 163.1, 160.7, 136.6, 135.3, 133.5, 128.6 (J = 8.0 Hz), 128.3 (J = 59.8 Hz), 115.7 (J = 21.1 Hz), 51.2, 46.1, 20.8; 19F NMR (376 MHz, CDCl3) δ -114.9; HRMS (ESI) m/z [M+H]^+: Calcd for C17H16FO2: 271.1134. Found: 271.1134.

2-(4-Chlorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3af):

![Chemical Structure]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.48). The product was obtained as yellow oil in 69% yield (34.5 mg). 1H NMR (400 MHz, CDCl3) δ 9.70 (s, 1H), 7.94 - 7.92 (m, 2H), 7.59 - 7.56 (m, 1H), 7.47 - 7.43 (m, 2H), 7.34 - 7.26 (m, 4H), 3.71 (s, 2H), 1.66 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 201.0, 196.8, 138.2, 136.5, 133.5, 133.4, 129.0, 128.6, 128.3, 128.0, 51.3, 46.0, 20.8; HRMS (ESI) m/z [M+H]^+: Calcd for C17H16ClO2: 287.0839. Found: 287.0840.
2-(4-Bromophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ag):

![Chemical structure](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.31). The product was obtained as yellow oil in 86% yield (56.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.71 (s, 1H), 7.94 - 7.92 (d, 2H), 7.59 - 7.55 (m, 1H), 7.50 - 7.43 (m, 4H), 7.22 - 7.20 (m, 2H), 3.71 (s, 2H), 1.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.0, 196.8, 138.8, 136.4, 133.5, 131.9, 128.6, 128.0, 121.5, 51.4, 46.0, 20.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$BrO$_2$: 331.0334. Found: 331.0332.

2-(4-Iodophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ah):

![Chemical structure](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.52). The product was obtained as yellow oil in 69% yield (52.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (s, 1H), 7.94 - 7.92 (d, 2H), 7.69 - 7.67 (m, 2H), 7.59 - 7.56 (m, 1H), 7.47 - 7.43 (m, 2H), 7.09 - 7.07 (m, 2H), 3.71 (s, 2H), 1.64 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.0, 196.8, 139.5, 137.9, 136.4, 133.5, 128.9, 128.6, 128.0, 51.4, 45.9, 20.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$I赵$_2$: 379.0195. Found: 379.0198.

2-(2,4-Dichlorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ai):

![Chemical structure](image)
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.58). The product was obtained as yellow oil in 99% yield (63.4 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.89 (s, 1H), 7.91 - 7.89 (m, 2H), 7.58 - 7.55 (m, 1H), 7.46 - 7.42 (m, 2H), 7.39 - 7.34 (m, 2H), 7.28 - 7.25 (m, 1H), 3.91 (d, \(J = 18.4\) Hz, 1H), 3.86 (d, \(J = 18.4\) Hz, 1H), 1.67 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.9, 197.3, 137.1, 136.6, 134.2, 133.5, 133.5, 130.7, 130.5, 128.7, 128.0, 127.4, 52.1, 44.4, 21.3; HRMS (ESI) m/z [M+H]: Calcd for C\(_{17}\)H\(_{15}\)Cl\(_2\)O\(_2\): 321.0449. Found: 321.0448.

**2-Methyl-4-oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanal (3aj):**

![Methyl-4-oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.48). The product was obtained as yellow oil in 53% yield (53.9 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.78 (s, 1H), 7.95 - 7.93 (m, 2H), 7.64 - 7.62 (m, 2H), 7.59 - 7.57 (m, 1H), 7.48 - 7.44 (m, 4H), 3.79 (d, \(J = 18.4\) Hz, 1H), 3.75 (d, \(J = 18.4\) Hz, 1H), 1.70 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.0, 196.7, 144.1, 136.4, 133.6, 129.4, 128.7, 128.1, 127.3, 125.8 (q, \(J = 42.6\) Hz), 51.8, 46.2, 21.2; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.7; HRMS (ESI) m/z [M+H]: Calcd for C\(_{18}\)H\(_{16}\)F\(_3\)O\(_2\): 321.1102. Found: 321.1101.

**2-Methyl-2-(4-nitrophenyl)-4-oxo-4-phenylbutanal (3ak):**

![Methyl-2-(4-nitrophenyl)-4-oxo-4-phenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.50). The product was obtained as yellow oil in 32% yield (19.0 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.80 (s, 1H), 8.24 - 8.22 (m, 2H), 7.95 - 7.93 (m, 2H), 7.62 - 7.56 (m, 1H), 7.54 - 7.52 (m, 2H), 7.49 - 7.45 (m, 2H), 3.80 (s, 2H), 1.72 (s,
3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.5, 196.3, 147.5, 136.2, 133.8, 128.8, 128.1, 128.0, 123.9, 52.0, 46.4, 21.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$NO$_4$: 298.1079. Found: 298.1077.

4-(2-Methyl-1,4-dioxo-4-phenylbutan-2-yl)benzonitrile (3al):

![Chemical structure of 4-(2-Methyl-1,4-dioxo-4-phenylbutan-2-yl)benzonitrile](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f$ = 0.15). The product was obtained as yellow oil in 56% yield (31.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.77 (s, 1H), 7.94 - 7.92 (m, 2H), 7.68 - 7.66 (m, 2H), 7.62 - 7.58 (m, 1H), 7.49 - 7.46 (m, 4H), 3.77 (s, 2H), 1.69 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.6, 196.4, 145.5, 136.2, 133.7, 132.5, 128.8, 128.1, 127.8, 118.4, 111.3, 52.0, 46.2, 21.2; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{16}$NO$_2$: 278.1181. Found: 278.1183.

2-(4-Methoxyphenyl)-2-methyl-4-oxo-4-phenylbutanal (3am):

![Chemical structure of 2-(4-Methoxyphenyl)-2-methyl-4-oxo-4-phenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f$ = 0.60). The product was obtained as yellow oil in 90% yield (50.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.65 (s, 1H), 7.94 - 7.92 (m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.44 (m, 2H), 7.26 - 7.24 (m, 2H), 6.91 - 7.89 (m, 2H), 3.77 (s, 2H), 3.69 (s, 2H), 1.66 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.2, 197.3, 158.7, 136.8, 133.3, 131.2, 128.6, 128.1, 114.3, 55.2, 51.1, 45.9, 20.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{19}$O$_3$: 283.1334. Found: 283.1332.

2-(4-(Dimethylamino)phenyl)-2-methyl-4-oxo-4-phenylbutanal (3an):
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.20). The product was obtained as yellow oil in 87% yield (51.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.54 (s, 1H), 7.88 - 7.86 (m, 2H), 7.52 - 7.47 (m, 1H), 7.40 - 7.36 (m, 2H), 7.16 - 7.14 (m, 2H), 6.73 (s, 2H), 3.63 (d, J = 17.6 Hz, 1H), 3.58 (d, J = 17.6 Hz, 1H), 2.89 (s, 6H), 1.58 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.1, 197.6, 137.0, 133.2, 130.5, 128.6, 128.1, 127.7, 112.8, 110.6, 51.0, 45.7, 40.5, 20.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{19}$H$_{22}$NO$_2$: 296.1651. Found: 296.1647.

2-Methyl-2-(napthalen-1-yl)-4-oxo-4-phenylbutanal (3ao):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.80). The product was obtained as yellow oil in 58% yield (35.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.07 (s, 1H), 7.89 - 7.87 (m, 1H), 7.81 - 7.77 (m, 4H), 7.52 - 7.39 (m, 5H), 7.35 - 7.32 (m, 2H), 4.07 (d, J = 16.8 Hz, 1H), 3.91 (d, J = 16.8 Hz, 1H), 1.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.8, 197.8, 136.8, 136.1, 134.7, 133.2, 130.9, 129.8, 128.9, 128.5, 128.0, 126.5, 125.8, 125.4, 125.3, 124.1, 52.8, 46.4, 22.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{21}$H$_{19}$O$_2$: 303.1385. Found: 303.1382.

2-(Furan-2-yl)-2-methyl-4-oxo-4-phenylbutanal (3ap):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.80). The product was obtained as yellow oil in 86% yield (51.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.07 (s, 1H), 7.89 - 7.87 (m, 1H), 7.81 - 7.77 (m, 4H), 7.52 - 7.39 (m, 5H), 7.35 - 7.32 (m, 2H), 4.07 (d, J = 16.8 Hz, 1H), 3.91 (d, J = 16.8 Hz, 1H), 1.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.8, 197.8, 136.8, 136.1, 134.7, 133.2, 130.9, 129.8, 128.9, 128.5, 128.0, 126.5, 125.8, 125.4, 125.3, 124.1, 52.8, 46.4, 22.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{21}$H$_{19}$O$_2$: 303.1385. Found: 303.1382.
2-(Ferrocenyl)-2-methyl-4-oxo-4-phenylbutanal (3aq):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.56). The product was obtained as yellow oil in 38% yield (27.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.86 (s, 1H), 7.92 - 7.90 (m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.43 (m, 2H), 4.22 (t, $J$ = 2.0 Hz, 2H), 4.21 (s, 5H), 4.10 - 4.08 (m, 1H), 4.07 - 4.05 (m, 1H), 3.60 (d, $J$ = 17.6 Hz, 1H), 3.46 (d, $J$ = 17.6 Hz, 1H), 1.59 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.0, 197.4, 136.6, 133.3, 128.6, 128.1, 133.6, 132.8, 110.6, 107.1, 49.1, 44.3, 19.2; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{21}$H$_{21}$FeO$_2$: 361.0891. Found: 361.0890.

2-Ethyl-4-oxo-2,4-diphenylbutanal (3ar):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.46). The product was obtained as yellow oil in 63% yield (33.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.85 (s, 1H), 7.97 - 7.95 (m, 2H), 7.60 - 7.56 (m, 1H), 7.50 - 7.44 (m, 2H), 7.39 - 7.35 (m, 2H), 7.31 - 7.27 (m, 4H), 3.79 (s, 2H), 2.36 - 2.26 (m, 1H), 2.11 - 2.01 (m, 1H), 0.79 - 0.75 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
202.8, 197.3, 158.5, 138.5, 136.5, 133.4, 128.8, 128.6, 128.1, 127.3, 127.2, 55.7, 42.2, 27.3, 8.6; HRMS (ESI) m/z [M+H]+: Calcd for C_{18}H_{19}O_2: 267.1385. Found: 267.1385.

4-oxo-2,2,4-Triphenylbutanal (3as):

![Triphenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.53). The product was obtained as yellow oil in 91% yield (57.2 mg). ^1H NMR (400 MHz, CDCl_3) δ 10.19 (s, 1H), 7.92 - 7.90 (m, 2H), 7.55 - 7.53 (m, 1H), 7.43 - 7.39 (m, 2H), 7.39 - 7.30 (m, 4H), 7.27 - 7.23 (m, 6H), 4.18 (s, 2H); ^13C NMR (100 MHz, CDCl_3) δ 199.6, 196.2, 140.4, 136.4, 133.3, 128.7, 128.6, 128.5, 128.1, 127.2, 60.7, 46.5; HRMS (ESI) m/z [M+H]^+: Calcd for C_{22}H_{19}O_2: 315.1385. Found: 315.1388.

4-oxo-2,4-Diphenylbutanal (3at):

![Diphenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.41). The product was obtained as yellow oil in 30% yield (14.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.81 (s, 1H), 7.99 - 7.97 (m, 2H), 7.59 - 7.55 (m, 1H), 7.48 - 7.44 (m, 2H), 7.41 - 7.39 (m, 2H), 7.38 - 7.34 (m, 1H), 7.32 - 7.29 (m, 2H), 4.48 - 4.45 (m, 1 H), 3.99 - 3.93 (m, 1H), 3.26 - 3.20 (m, 1H); ^13C NMR (100 MHz, CDCl_3) δ 199.0, 197.3, 136.3, 135.3, 133.3, 129.2, 129.1, 128.6, 128.1, 127.9, 53.6, 39.4; HRMS (ESI) m/z [M+H]^+: Calcd for C_{16}H_{15}O_2: 239.1072. Found: 239.1074.

1-(2-oxo-2-Phenylethyl)-2,3-dihydro-1H-indene-1-carbaldehyde (3au):
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.65). The product was obtained as yellow oil in 44% yield (23.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.71 (s, 1H), 7.88 - 7.86 (m, 2H), 7.51 - 7.47 (m, 1H), 7.39 - 7.36 (m, 2H), 7.24 - 7.15 (m, 4H), 3.90 (d, $J$ = 18.0 Hz, 1H), 3.36 (d, $J$ = 18.0 Hz, 1H), 3.08 - 2.98 (m, 2H), 2.88 - 2.81 (m, 1H), 2.20 - 2.13 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.2, 197.3, 144.8, 141.1, 136.4, 128.6, 128.4, 128.1, 127.0, 125.2, 124.5, 60.6, 46.2, 33.0, 30.9; HRMS (ESI) m/z [M+H]$^+$: Caled for C$_{18}$H$_{17}$O$_2$: 265.1229. Found: 265.1227.

1-(2-oxo-2-Phenylethyl)-1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (3av):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.56). The product was obtained as yellow oil in 45% yield (25.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.76 (s, 1H), 7.94 - 7.92 (m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.42 (m, 2H), 7.26 - 7.25 (m, 1H), 7.20 - 7.16 (m, 3H), 3.78 (d, $J$ = 18.0 Hz, 1H), 3.59 (d, $J$ = 18.0 Hz, 1H), 2.88 - 2.84 (m, 2H), 2.44 - 2.38 (m, 1H), 2.23 - 2.16 (m, 1H), 1.99 - 1.82 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.5, 197.1, 138.7, 136.9, 133.6, 133.2, 130.0, 128.6, 128.2, 128.0, 127.2, 126.5, 51.2, 47.1, 29.9, 28.7, 19.3; HRMS (ESI) m/z [M+H]$^+$: Caled for C$_{19}$H$_{19}$O$_2$: 279.1385. Found: 279.1383.

4-(2-Bromophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ba):
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, \( R_f = 0.44 \)). The product was obtained as yellow oil in 40% yield (26.5 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.57 (s, 1H), 7.51 - 7.48 (m, 1H), 7.27 - 7.23 (m, 2H), 7.22 - 7.21 (m, 3H), 7.20 - 7.17 (m, 3H), 3.60 (d, \( J = 17.6 \) Hz, 1H), 3.55 (d, \( J = 17.6 \) Hz, 1H), 1.66 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 201.5, 200.7, 141.5, 138.8, 133.6, 131.6, 128.9, 128.5, 127.5, 127.4, 126.9, 118.4, 52.4, 49.6, 19.9; HRMS (ESI) m/z [M+H]+: Calcd for C\(_{17}\)H\(_{16}\)BrO\(_2\): 331.0334. Found: 331.0331.

4-(3-Bromophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ca):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, \( R_f = 0.60 \)). The product was obtained as yellow oil in 66% yield (43.6 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.69 (s, 1H), 8.03 (s, 1H), 7.85 - 7.83 (m, 1H), 7.72 - 7.66 (m, 1H), 7.40 - 7.32 (m, 2H), 7.31 - 7.26 (m, 4H), 3.69 (d, \( J = 17.6 \) Hz, 1H), 3.64 (d, \( J = 17.6 \) Hz, 1H), 1.70 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 201.2, 195.8, 139.2, 138.4, 136.1, 131.1, 130.2, 128.9, 127.5, 126.8, 126.5, 122.9, 51.8, 45.9, 20.3; HRMS (ESI) m/z [M+H]+: Calcd for C\(_{17}\)H\(_{16}\)BrO\(_2\): 331.0334. Found: 331.0331.

4-(4-Fluorophenyl)-2-methyl-4-oxo-2-phenylbutanal (3da):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, \( R_f = 0.56 \)). The product was obtained as yellow oil in 91% yield (49.2 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.71 (s, 1H), 7.93 (m, 2H), 7.39 - 7.31 (m, 2H), 7.30 - 7.26 (m, 1H), 7.10 - 7.08 (m, 2H), 3.86 (s, 3H), 3.71 (d, \( J = 17.2 \) Hz, 1H), 3.66 (d, \( J = 17.2 \) Hz, 1H), 1.68 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 201.4, 195.6, 167.0, 164.5, 133.1 (\( J = 11.2 \)), 130.8, 130.7, 128.9, 127.4, 126.8, 115.8, 115.6, 51.8, 45.8, 20.5;
$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -104.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$FO: 271.1134. Found: 271.1140.

4-(4-Chlorophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ea):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f = 0.59$). The product was obtained as yellow solid in 68% yield (38.9 mg), Mp. 70 - 71 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (s, 1H), 7.87 - 7.85 (m, 2H), 7.43 - 7.36 (m, 4H), 7.33 - 7.28 (m, 3H), 3.70 (d, $J$ = 18.0 Hz, 1H), 3.64 (d, $J$ = 18.0 Hz, 1H), 1.69 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 196.0, 139.8, 139.4, 135.0, 129.5, 129.0, 128.9, 127.5, 126.8, 51.8, 45.9, 20.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$ClO: 287.0839. Found: 287.0837.

4-(4-Bromophenyl)-2-methyl-4-oxo-2-phenylbutanal (3fa):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, $R_f = 0.60$). The product was obtained as yellow solid in 89% yield (58.7 mg), Mp. 70 - 71 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.69 (s, 1H), 7.79 - 7.77 (m, 2H), 7.58 - 7.56 (m, 2H), 7.39 - 7.35 (m, 2H), 7.32 - 7.28 (m, 3H), 3.69 (d, $J$ = 18.0 Hz, 1H), 3.64 (d, $J$ = 18.0 Hz, 1H), 1.68 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.2, 196.2, 139.3, 135.4, 131.8, 129.5, 128.9, 128.5, 127.4, 126.8, 51.8, 45.8, 20.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{16}$BrO: 331.0334. Found: 331.0329.

4-(4-Iodophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ga):
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.61). The product was obtained as yellow solid in 77% yield (58.3 mg), Mp. 69 - 70 °C. 

^1^H NMR (400 MHz, CDCl$_3$) δ 9.62 (s, 1H), 7.74 - 7.72 (m, 2H), 7.56 - 7.54 (m, 2H), 7.32 - 7.30 (m, 2H), 7.25 - 7.18 (m, 3H), 3.61 (d, J = 18.0 Hz, 1H), 3.55 (d, J = 18.0 Hz, 1H), 1.61 (s, 3H); 

^13^C NMR (100 MHz, CDCl$_3$) δ 201.3, 196.5, 139.3, 137.9, 135.9, 129.4, 128.9, 127.5, 126.8, 101.4, 51.8, 45.8, 20.4; HRMS (ESI) m/z [M+H]^+:

Calcd for C$_{17}$H$_{16}$BrO$_2$: 379.0195. Found: 379.0199.

2-Methyl-4-oxo-2-phenyl-4-(p-tolyl)butanal (3ha):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.58). The product was obtained as yellow oil in 81% yield (43.1 mg). 

^1^H NMR (400 MHz, CDCl$_3$) δ 9.75 (s, 1H), 7.85 - 7.83 (m, 2H), 7.39 - 7.34 (m, 4H), 7.29 - 7.23 (m, 3H), 3.74 (d, J = 17.6 Hz, 1H), 3.68 (d, J = 17.6 Hz, 1H), 2.40 (s, 3H), 1.66 (s, 3H); 

^13^C NMR (100 MHz, CDCl$_3$) δ 201.6, 196.8, 144.3, 139.8, 134.3, 129.3, 128.9, 128.2, 127.3, 126.9, 51.8, 45.9, 21.6, 20.8; HRMS (ESI) m/z [M+H]^+:

Calcd for C$_{18}$H$_{19}$O$_2$: 267.1340. Found: 267.1343.

4-(2-Methoxyphenyl)-2-methyl-4-oxo-2-phenylbutanal (3ia):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R_f = 0.51). The product was obtained as yellow oil in 80% yield (45.1 mg). 

^1^H NMR (400 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.65 - 7.62 (m, 1H), 7.49 - 7.45 (m,
1H), 7.38 - 7.31 (m, 5H), 7.00 - 6.95 (m, 2H), 3.93 (s, 3H), 3.80 (s, 2H), 1.60 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.9, 199.6, 158.6, 140.2, 133.9, 130.4, 128.8, 127.9,
127.1, 126.9, 120.8, 111.4, 55.5, 52.1, 51.3, 21.4; HRMS (ESI) m/z [M+H]+: Calcd for
C$_{18}$H$_{19}$O$_3$: 283.1334. Found: 283.1336.

4-(3-Methoxyphenyl)-2-methyl-4-oxo-2-phenylbutanal (3ja):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R$_f$ = 0.49). The product was obtained as yellow oil in 83% yield (46.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.73 (s, 1H), 7.54 - 7.52 (m, 1H), 7.45 - 7.44 (m, 1H), 7.40 - 7.23 (m, 5H), 7.30 - 7.26 (m, 1H), 7.12 - 7.09 (m, 1H), 3.83 (s, 3H), 3.74 (d, J = 18.0 Hz, 1H), 3.69 (d, J = 18.0 Hz, 1H), 1.68 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.5, 197.0, 159.7, 139.6, 130.4, 129.6, 128.9, 127.4, 126.8, 120.7, 120.0, 112.0, 55.4, 51.8, 46.1, 20.7; HRMS (ESI) m/z [M+H]+: Calcd for C$_{18}$H$_{19}$O$_3$: 283.1334. Found: 283.1331.

4-(4-Methoxyphenyl)-2-methyl-4-oxo-2-phenylbutanal (3ka):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R$_f$ = 0.22). The product was obtained as yellow oil in 80% yield (45.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.75 (s, 1H), 7.93 - 7.91 (m, 2H), 7.39 - 7.32 (m, 4H), 7.29 - 7.26 (m, 1H), 6.93 - 6.90 (m, 2H), 3.86 (s, 3H), 3.71 (d, J = 17.6 Hz, 1H), 3.67 (d, J = 17.6 Hz, 1H), 1.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.6, 195.7, 163.7, 139.9, 130.4, 129.8, 128.9, 127.3, 126.8, 113.7, 55.5, 51.8, 45.8, 20.9; HRMS (ESI) m/z [M+H]+: Calcd for C$_{18}$H$_{19}$O$_3$: 283.1334. Found: 283.1331.
4-(4-Isocyanophenyl)-2-methyl-4-oxo-2-phenylbutanal (3la):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.27). The product was obtained as yellow solid in 64% yield (41.1 mg), Mp. 127 - 128 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.65 (s, 1H), 7.99 - 7.97 (m, 2H), 7.74 - 7.73 (m, 2H), 7.40 - 7.36 (m, 2H), 7.31 - 7.28 (m, 3H), 3.69 (d, J= 17.6 Hz, 1H), 3.64 (d, J= 17.6 Hz, 1H), 1.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 196.0, 139.7, 138.9, 132.4, 129.0, 128.4, 127.6, 126.8, 117.8, 116.4, 51.9, 46.0, 20.0; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₈H₁₆NO₂: 278.1181. Found: 278.1180.

2-Methyl-4-oxo-2-phenyl-4-(4-(trifluoromethyl)phenyl)butanal (3ma):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.67). The product was obtained as yellow oil in 70% yield (44.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.69 (s, 1H), 8.02 - 8.00 (m, 2H), 7.71 - 7.69 (m, 2H), 7.40 - 7.37 (m, 2H), 7.33 - 7.28 (m, 3H), 3.73 (d, J= 17.6 Hz, 1H), 3.67 (d, J= 17.6 Hz, 1H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.1, 196.4, 139.5, 139.2, 134.5 (q, J= 32.7, 129.0, 128.4, 127.6, 126.9, 125.7 (q, J= 4.0 Hz), 123.5 (d, J= 271.1 Hz), 51.9, 46.1, 20.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₈H₁₆F₃O₂: 321.1102. Found: 321.1104.

2-Methyl-4-oxo-2-phenyl-4-(thiophen-2-yl)butanal (3na):

The title compound was prepared according to the general procedure for reaction in 24
h (EA/PE = 1/9, Rf = 0.50). The product was obtained as yellow oil in 95% yield (49.1 mg). ^1H NMR (400 MHz, CDCl₃) δ 9.68 (s, 1H), 7.69 - 7.68 (m, 1H), 7.64 - 7.63 (d, J = 5.2, 1H), 7.40 - 7.36 (m, 2H), 7.33 - 7.26 (m, 3H), 7.12 - 7.09 (m, 1H), 3.65 (d, J = 16.8 Hz, 1H), 3.60 (d, J = 16.8 Hz, 1H), 1.68 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 201.0, 190.2, 144.1, 139.2, 134.2, 132.8, 128.9, 128.1, 127.5, 126.9, 52.0, 46.2, 20.2; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₅H₁₅O₂S: 259.0793. Found: 259.0794.

4-(Furan-2-yl)-2-methyl-4-oxo-2-phenylbutanal (3oa):

![Image of 4-(Furan-2-yl)-2-methyl-4-oxo-2-phenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.41). The product was obtained as yellow oil in 94% yield (45.6 mg). ^1H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1H), 7.54 (s, 1H), 7.38 - 7.35 (m, 2H), 7.32 - 7.25 (m, 3H), 7.14 - 7.13 (m, 1H), 6.51 - 6.50 (m, 1H), 3.57 (d, J = 16.8 Hz, 1H), 3.52 (d, J = 16.8 Hz, 1H), 1.66 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 200.9, 186.5, 152.7, 146.5, 139.2, 128.9, 127.5, 126.9, 117.3, 112.4, 52.0, 45.1, 20.2; HRMS (ESI) m/z [M+H]^+: Calcd for C₁₅H₁₅O₃: 253.1021. Found: 253.1021.

2-Methyl-4-(naphthalen-2-yl)-4-oxo-2-phenylbutanal (3pa):

![Image of 2-Methyl-4-(naphthalen-2-yl)-4-oxo-2-phenylbutanal](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.57). The product was obtained as yellow oil in 64% yield (38.7 mg). ^1H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 8.45 (s, 1H), 7.99 - 7.93 (m, 2), 7.88 - 7.86 (m, 2H), 7.65 - 7.55 (m, 2H), 7.39 - 7.38 (m, 4H), 7.28 - 7.27 (m, 1H), 3.87 (s, 2H), 1.72 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 201.5, 197.2, 139.7, 135.6, 134.1, 132.4, 129.9, 129.6, 128.9, 128.6, 128.5, 127.8, 127.4, 126.9, 126.8, 123.7, 51.9, 46.1, 20.7; HRMS (ESI) m/z [M+H]^+: Calcd for C₂₁H₁₉O₂: 303.1385. Found: 303.1383.
2-Methyl-4-oxo-4-(phenanthren-9-yl)-2-phenylbutanal (3qa):

![Chemical structure](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R₆ = 0.50). The product was obtained as yellow oil in 80% yield (56.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.73 (s, 1H), 8.61 - 8.56 (m, 2H), 8.31 - 8.29 (m, 1H), 7.97 (s, 1H), 7.83 - 7.81 (m, 1H), 7.67 - 7.64 (m, 1H), 7.61 - 7.50 (m, 3H), 7.29 - 7.28 (m, 4H), 7.21 - 7.18 (m, 1H), 3.79 (s, 2H), 1.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.0, 201.5, 139.6, 135.2, 131.9, 130.8, 129.9, 129.8, 129.5, 129.1, 129.0, 128.1, 127.6, 127.6, 127.3, 127.3, 127.3, 127.1, 126.6, 122.9, 122.8, 52.6, 49.6, 20.8; HRMS (ESI) m/z [M+H]+: Calcd for C₂₅H₂₁O₂: 353.1542. Found: 353.1540.

(E)-2,5-Dimethyl-4-oxo-2,6-diphenylhex-5-enal (3ra):

![Chemical structure](image)

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, R₆ = 0.60). The product was obtained as yellow oil in 79% yield (46.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.73 (s, 1H), 7.51 (s, 1H), 7.40 - 7.30 (m, 10H), 3.60 (d, J = 17.2 Hz, 1H), 3.55 (d, J = 17.2 Hz, 1H), 2.00 (s, 3H), 1.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.7, 199.4, 139.9, 139.4, 137.4, 135.6, 129.7, 128.9, 128.7, 128.4, 127.3, 126.9, 51.9, 45.3, 20.8, 13.0; HRMS (ESI) m/z [M+H]+: Calcd for C₂₀H₂₁O₂: 293.1542. Found: 293.1542.

(E)-2,5-Dimethyl-4-oxo-2-phenyloct-5-enal (3sa):

![Chemical structure](image)

The title compound was prepared according to the general procedure for reaction in 24
h (EA/PE = 1/9, Rf = 0.67). The product was obtained as colorless oil in 42% yield (20.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (s, 1H), 7.38 - 7.35 (m, 2H), 7.29 - 7.26 (m, 3H), 6.64 - 6.61 (m, 1H), 3.46 (d, $J$ = 17.2 Hz, 1H), 3.40 (d, $J$ = 17.2 Hz, 1H), 2.27 - 2.19 (m, 2H), 1.72 (s, 3H), 1.57 (s, 3H), 1.06 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.8, 198.9, 145.1, 140.1, 136.9, 128.8, 127.2, 126.8, 51.7, 44.9, 22.4, 20.8, 13.0, 11.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{16}$H$_{21}$O$_2$: 245.1542. Found: 245.1544.

4-(4-Ethynylphenyl)-2-methyl-4-oxo-2-phenylbutanal (3ta):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/9, Rf = 0.50). The product was obtained as yellow oil in 33% yield (18.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.63 (s, 1H), 7.81 - 7.79 (m, 2H), 7.48 - 7.46 (m, 2H), 7.32 - 7.28 (m, 2H), 7.25 - 7.21 (m, 3H), 3.64 (d, $J$ = 17.6 Hz, 1H), 3.59 (d, $J$ = 17.6 Hz, 1H), 3.18 (s, 1H), 1.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.3, 196.4, 139.4, 136.4, 132.3, 128.9, 127.9, 127.5, 127.1, 126.8, 82.6, 80.6, 51.8, 46.0, 20.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{19}$H$_{17}$O$_2$: 277.1229. Found: 277.1227.

**General procedure for cyclopentenones and their spectral data:**

![Cyclopentenone Reaction Scheme]

A mixture of 1 (0.20 mmol, 1.0 equiv.), 2 (0.40 mmol, 2.0 equiv.), Cu(OH)$_2$ (0.02 mmol, 10 mol %), LiOCH$_3$ (1.0 mmol, 5.0 equiv.), H$_2$O (5.4 µL, 1.5 equiv.) and toluene (4.0 mL) was sealed in a Schlenk tube under argon protection at 100 °C and the mixture was stirred for 24 h or until the 1 was consumed completely. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography to give the desired product 4.
4-Methyl-4-phenylcyclopent-2-en-1-one (4ua):

![Chemical structure]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, \( R_f = 0.50 \)). The product was obtained as yellow oil in 81% yield (27.9 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.70 - 7.68 (d, \( J = 5.6 \) Hz, 1H), 7.37 - 7.33 (m, 2H), 7.28 - 7.25 (m, 3H), 6.22 - 6.21 (d, \( J = 5.6 \) Hz, 1H), 2.66 (d, \( J = 18.8 \) Hz, 1H), 2.56 (d, \( J = 18.8 \) Hz, 1H), 1.64 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.8, 171.3, 145.2, 131.7, 128.7, 126.8, 125.7, 51.9, 48.2, 27.2; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{12}\)H\(_{13}\)O: 173.0966. Found: 173.0966.

4-Ethyl-4-phenylcyclopent-2-en-1-one (4ub):

![Chemical structure]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, \( R_f = 0.55 \)). The product was obtained as yellow oil in 64% yield (23.8 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 - 7.84 (d, \( J = 6.0 \) Hz, 1H), 7.37 - 7.33 (m, 2H), 7.26 - 7.23 (m, 3H), 6.27 (d, \( J = 5.6 \) Hz, 1H), 2.63 (d, \( J = 0.4 \) Hz, 2H), 2.04 - 1.91 (m, 2H), 0.83 (t, \( J = 7.6 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.2, 169.2, 144.7, 132.9, 128.7, 126.6, 126.2, 52.6, 49.2, 33.9, 9.4; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{13}\)H\(_{15}\)O: 187.1123. Found: 187.1120.

2',3'-Dihydrospiro[cyclopentane-1,1'-inden]-2-en-4-one (4uc):

![Chemical structure]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, \( R_f = 0.70 \)). The product was obtained as yellow oil in 51% yield (18.8 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 - 7.93 (d, \( J = 5.6 \) Hz, 1H), 7.37 - 7.33 (m, 2H), 7.28 - 7.25 (m, 3H), 6.22 - 6.21 (d, \( J = 5.6 \) Hz, 1H), 2.66 (d, \( J = 18.8 \) Hz, 1H), 2.56 (d, \( J = 18.8 \) Hz, 1H), 1.64 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.8, 171.3, 145.2, 131.7, 128.7, 126.8, 125.7, 51.9, 48.2, 27.2; HRMS (ESI) m/z [M+H]\(^+\): Calcd for C\(_{12}\)H\(_{13}\)O: 173.0966. Found: 173.0966.
mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 5.2$ Hz, 1H), 7.29 - 7.26 (m, 1H), 7.23 - 7.18 (m, 2H), 6.99 - 6.97 (m, 1H), 6.19 (d, $J = 5.6$ Hz, 1H), 3.07 - 3.03 (m, 2H), 2.65 (d, $J = 18.8$ Hz, 1H), 2.56 (d, $J = 18.8$ Hz, 1H), 2.40 - 2.32 (m, 1H), 2.22 - 2.16 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 209.9, 169.4, 146.1, 143.1, 131.9, 127.6, 127.1, 124.8, 122.5, 56.8, 49.3, 39.0, 30.9; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{13}$H$_{13}$O: 185.0966. Found: 185.0968.

$3',4'$-Dihydro-$2'H$-spiro[cyclopentane-1,1'-naphthalen]-2-en-4-one (4ud):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, $R_f = 0.55$). The product was obtained as yellow oil in 49% yield (19.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 5.6$ Hz, 1H), 7.15 - 7.13 (m, 3H), 7.00 - 6.98 (m, 1H), 6.26 - 6.25 (d, $J = 5.6$ Hz, 1H), 2.88 - 2.85 (m, 2H), 2.58 (d, $J = 16.0$ Hz, 1H), 2.51 (d, $J = 16.0$ Hz, 1H), 2.05 - 1.92 (m, 2H), 1.88 - 1.75 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.4, 172.0, 139.1, 136.4, 132.1, 129.5, 127.1, 126.8, 126.6, 52.7, 48.6, 36.1, 29.7, 20.6; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{14}$H$_{16}$O: 199.1123. Found: 199.1124.

$6,7,8,9$-Tetrahydrospiro[benzo[7]annulene-5,1'-cyclopentan]-2'-en-4'-one (4ue):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, $R_f = 0.40$). The product was obtained as yellow oil in 42% yield (17.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 6.0$ Hz, 1H), 7.13 - 7.11 (m, 2H), 7.08
- 7.07 (m, 1H), 6.99 - 6.97 (m, 1H), 6.21 (d, J = 5.6 Hz, 1H), 2.98 (d, J = 18.4 Hz, 1H), 2.44 (d, J = 18.4 Hz, 1H), 2.91 - 2.77 (m, 2H), 2.04 - 1.97 (m, 2H), 1.92 - 1.86 (m, 2H), 1.75 - 1.72 (m, 1H), 1.49 - 1.40 (m, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 209.4, 172.6, 145.5, 142.3, 131.1, 129.9, 127.0, 126.2, 125.9, 52.5, 46.1, 37.4, 36.6, 28.7, 27.4; HRMS (ESI) m/z [M+H]\(^{+}\): Calcd for C\(_{15}\)H\(_{17}\)O: 213.1279. Found: 213.1279.

4-Methyl-4-phenyl-2-propylcyclopent-2-en-1-one (4va):

\[
\text{Me} \quad \text{O} \quad \text{Ph} \\
\text{Me} 
\]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, \(R_f = 0.65\)). The product was obtained as yellow oil in 57\% yield (24.5 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 - 7.24 (m, 2H), 7.21 - 7.14 (m, 4H), 2.62 (d, \(J = 18.4\) Hz, 1H), 2.52 (d, \(J = 18.4\) Hz, 1H), 2.17 - 2.13 (m, 2H), 1.56 - 1.46 (m, 5H), 0.91 - 0.87 (t, \(J = 7.6\) Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 209.5, 164.5, 146.2, 143.7, 128.6, 126.5, 125.7, 52.5, 45.5, 27.6, 26.5, 21.0, 13.9; HRMS (ESI) m/z [M+H]\(^{+}\): Calcd for C\(_{15}\)H\(_{19}\)O: 215.1436. Found: 215.1437.

4-Methyl-2,4-diphenylcyclopent-2-en-1-one (4xa):

\[
\text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{Me} 
\]

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, \(R_f = 0.68\)). The product was obtained as yellow oil in 56\% yield (29.4 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 - 7.29 (m, 4H), 7.25 - 7.19 (m, 6H), 7.13 - 7.12 (m, 1H), 3.16 - 3.52 (m, 2H), 2.73 (d, \(J = 18.4\) Hz, 1H), 2.63 (d, \(J = 18.4\) Hz, 1H), 1.57 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 208.5, 165.5, 145.9, 143.5, 138.5, 128.9, 128.62, 128.59, 126.6, 126.4, 125.7; HRMS (ESI) m/z [M+H]\(^{+}\): Calcd for C\(_{19}\)H\(_{19}\)O: 263.1436. Found: 263.1439.
2-Hexyl-4-methyl-4-phenylcyclopent-2-en-1-one (4wa):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, Rf = 0.70). The product was obtained as yellow oil in 55% yield (28.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 - 7.32 (m, 2H), 7.27 - 7.21 (m, 4H), 2.69 (d, $J$ = 18.8 Hz, 1H), 2.59 (d, $J$ = 18.8 Hz, 1H), 2.26 - 2.22 (m, 2H), 1.60 (s, 3H), 1.56 - 1.50 (m, 2H), 1.37 - 1.26 (m, 6H), 0.90 - 0.87 (t, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 209.5, 164.3, 146.2, 144.0, 128.6, 126.5, 125.7, 52.5, 45.5, 31.5, 29.0, 27.7, 27.6, 24.5, 22.5, 14.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{25}$O: 257.1905. Found: 257.1901.

4-Methyl-2,4-diphenylcyclopent-2-en-1-one (4ya):

The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, Rf = 0.65). The product was obtained as yellow oil in 35% yield (17.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (s, 1H), 7.71 - 7.68 (m, 2H), 7.35 - 7.32 (m, 2H), 7.30 - 7.25 (m, 5H), 7.20 - 7.16 (m, 1H), 2.82 (d, $J$ = 18.8 Hz, 1H), 2.71 (d, $J$ = 18.8 Hz, 1H), 1.60 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.1, 165.3, 145.7, 140.7, 131.1, 128.8, 128.6, 128.5, 127.3, 126.8, 125.8, 53.4, 45.0, 27.3; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{18}$H$_{17}$O: 249.1729. Found: 249.1727.

4-Methyl-4-phenyl-2-(prop-1-en-2-yl)cyclopent-2-en-1-one (4za):
The title compound was prepared according to the general procedure for reaction in 24 h (EA/PE = 1/19, Rf = 0.65). The product was obtained as colorless oil in 52% yield (22.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (s, 1H), 7.36 - 7.32 (m, 2H), 7.29 - 7.22 (m, 3H), 6.16 (s, 1H), 5.25 (s, 1H), 2.79 (d, $J = 18.4$ Hz, 1H), 2.67 (d, $J = 18.4$ Hz, 1H), 1.98 (s, 3H), 1.63 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.3, 164.4, 145.9, 140.2, 134.1, 128.7, 126.7, 125.8, 117.8, 53.6, 44.3, 27.4, 22.0; HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{15}$H$_{17}$O: 213.1279. Found: 213.1281.

Spectral data of mechanistic investigations

3aa-I:

![Structure diagram]

The title compound was prepared under standard conditions with D$_2$O (1.0 equiv.) instead of H$_2$O. The product was obtained as yellow oil in 71% yield (35.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.66 (s, 0.65H), 7.87 - 7.85 (m, 2H), 7.51 - 7.47 (m, 1H), 7.32 - 7.35 (m, 2H), 7.32 - 7.26 (m, 4H), 7.22 - 7.18 (m, 1H), 3.71 - 3.62 (m, 1.12H), 1.60 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.5, 197.3, 197.2, 139.6, 136.7, 133.4, 128.9, 128.6, 128.1, 127.4, 126.8, 51.8, 51.7, 46.0, 20.7, 20.6. HRMS (ESI) m/z [M+H]$^+$: Calcd for C$_{17}$H$_{15}$D$_2$O$_2$: 255.1354. Found: 255.1350.

3aa-II:

![Structure diagram]

The title compound was prepared under standard conditions with 2a’ instead of 2a. The product was obtained as yellow oil in 69% yield (34.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.73 (m, 0.82H), 7.94 - 7.92 (m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.42 (m, 2H), 7.39 - 7.32 (m, 4H), 7.30 - 7.27 (m, 1H), 3.78 - 3.68 (m, 1.51H), 1.68 - 1.66 (d, $J = 6.8$ Hz, 2.39H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.5, 201.5, 201.5, 197.2, 139.6, 136.7, 136.7,
133.3, 128.9, 128.6, 128.1, 127.3, 126.8, 51.7, 51.7, 51.6, 46.0, 46.0, 20.7, 20.2. HRMS (ESI) m/z [M+H]^+: Calcd for C_{17}H_{15}D_{2}O_{2}: 255.1354. Found: 255.1350.

3aa-III:

The title compound was prepared under standard conditions with H$_{2}^{18}$O (5.0 equiv.) instead of H$_2$O. The product was obtained as yellow oil in 56% yield (28.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.66 (s, 0.90H), 7.87 - 7.85 (m, 2H), 7.51 - 7.47 (m, 1H), 7.39 - 7.35 (m, 2H), 7.32 - 7.25 (m, 4H), 7.22 -7.18 (m, 1 H), 3.68 (d, $J$ = 17.6 Hz, 1H), 3.63 (d, $J$ = 17.6 Hz, 1H), 1.61 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.5, 201.4, 197.2, 139.7, 136.7, 133.3, 128.9, 128.6, 128.1, 127.4, 126.8, 51.8, 46.0, 20.7. HRMS (ESI) m/z [M+H]^+: Calcd for C$_{17}$H$_{17}$O$_{18}$: 255.1271. Found: 255.1267; HRMS (ESI) m/z [M+Na]^+: Calcd for C$_{17}$H$_{16}$NaO$_{18}$: 277.1090. Found: 277.1086.

$^1$H and $^{13}$C NMR spectra of ynones
$^{13}$C NMR spectrum of compound 1c.
1p
$^1$H and $^{13}$C NMR spectra of N-tosylhydrazones

![NMR spectra of N-tosylhydrazones]
S72
$^1$H and $^{13}$C NMR spectra of 1,4-ketoaldehydes:
$3ak$
3ra

S125
$^1$H and $^{13}$C NMR spectra of cyclopentenones:
$^1$H and $^{13}$C NMR spectra of mechanistic investigations

3aa-l
3aa-II

3aa-II