Carbonylative Cyclization of Biaryl Enones with Aldehydes and Oxamic Acids
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1. General information
All the reactions were performed in oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under inert atmosphere (nitrogen) using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100-200 mesh) using hexanes and ethyl acetate as eluent. 1H NMR was recorded in CDCl₃, DMSO on 500 MHz and 400 MHz and 13C NMR was recorded on 151 MHz, 126 MHz and 101 MHz. δ7.26 and δ77 and δ 2.5, δ 39.5 are corresponding to CDCl₃ and DMSO-d₆ in 1H NMR and 13C NMR respectively. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and J values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. FTIR spectra were recorded on Alpha (Bruker) Infrared Spectrophotometer. High resolution mass spectra (HRMS) [ESI+] were obtain using either a TOF or a double focusing spectrometer.
Structures of Bialy Enones:

All the biaryl enones were prepared following the literature procedures.1-3

Optimization of reaction conditions: The cyclic reaction of 1-(1,1'-biphenyl)-2-yl)-2-methylprop-2-en-1-one (1a) with 2 equiv. of oxoacetic acid as the carbamoylating agent was chosen as a model reaction.
**Table S1: Optimization of carbamoyl radical-promoted cyclization of biaryl enones:**

![Chemical structure](image)

<table>
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<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
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<td>AgOTf</td>
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<tr>
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<tr>
<td>6</td>
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<td>Ag₂CO₃</td>
<td>CH₂CN</td>
<td>80</td>
<td>-</td>
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</tbody>
</table>

Unless otherwise stated all the reactions were performed using **1a** (0.3 mmol) with **4a** (0.6 mmol), Ag₂CO₃ (20 mol%) oxidant (1.2 mmol) in 3 mL of solvent, bIsolated yield

**B. Radical trapping experiment:**

Control experiment was conducted by adding methyl(p-tolyl) carboxylic acid to biaryl enone in presence of 3.0 equiv of butylated hydroxytoluene (BHT; radical scavenger), and was found that the reaction was completely inhibited and no product (**5a**) formation, instead BHT-adduct **Y-4a** was isolated (confirmed by the reaction mass HRMS).

![Chemical structure](image)

**BHT-carbamoyl adduct**
confirmed by HRMS found for C₂₄H₃₄NO₂: 368.2577; Calculated: 368.2511

**Scheme S1**
Plausible mechanism:

A plausible mechanism is proposed based on the result of control experiment and literature survey (scheme 5). First, Ag(I) is oxidized to an Ag (II) species by S2O8\textsuperscript{2-}. Then, the Ag (II) species oxidizes oxamic acid to form carbamoyl radical E via decarboxylation. Regioselective addition of E on to olefin produces the tertiary radical F, which undergoes an intramolecular cyclization with the adjacent phenyl ring to give radical intermediate G. Then, a single electron transfer (SET) from G to oxidant, generates the cation H, which then rearomatizes through the loss of a proton producing the phenanthrenone 5a.
3. X-ray Crystallography:

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

A. Crystal structure determination of 3a:

Crystal Data for C_{23}H_{18}O_2 (M = 326.37 g/mol): monoclinic, space group P2_1/c (no. 14), a = 16.843(8) Å, b = 13.341(7) Å, c = 16.884(7) Å, β = 116.018(17)°, V = 3409(3) Å³, Z = 8, T = 294.15 K, μ(MoKα) = 0.080 mm⁻¹, Dcalc = 1.272 g/cm³, 29333 reflections measured (2.69° ≤ 2Θ ≤ 50°), 5915 unique (R_int = 0.1299, R_sigma = 0.1005) which were used in all calculations. The final R1 was 0.0599 (I > 2σ(I)) and wR2 was 0.1517 (all data). CCDC 2344358 deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/
**Figure S1:** ORTEP diagram of 3a compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

**B. Crystal structure determination of 7:**

**Crystal Data** for C$_{17}$H$_{14}$O$_2$ ($M = 250.28$ g/mol): orthorhombic, space group Pbca (no. 61), $a = 18.905(6)$ Å, $b = 7.073(2)$ Å, $c = 18.994(7)$ Å, $V = 2539.8(14)$ Å$^3$, $Z = 8$, $T = 294.15$ K, $\mu$(MoK$\alpha$) = 0.085 mm$^{-1}$, $D_{calc} = 1.309$ g/cm$^3$, 14223 reflections measured ($4.288^\circ \leq \theta \leq 57.834^\circ$), 3225 unique ($R_{int} = 0.0342$, $R_{sigma} = 0.0372$) which were used in all calculations. The final $R_1$ was 0.0471 (I > 2$\sigma$(I)) and $wR_2$ was 0.1500 (all data). **CCDC 2344359** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at [https://www.ccdc.cam.ac.uk/structures/](https://www.ccdc.cam.ac.uk/structures/)

**Figure S2:** ORTEP diagram of 7 compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

**4. References:**

$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz

3a
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{19}$F NMR, CDCl$_3$, 376MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{-13}C$ NMR, CDCl$_3$, 101MHz
$^{1}$H NMR, CDCl$_3$, 400 MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 126MHz

3I
$^{13}$C NMR, CDCl$_3$, 101MHz

3m
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{19}$F NMR, CDCl$_3$, 377MHz

3n
$\text{MeO}$

3o

$^1\text{H NMR, CDCl}_3, 400\text{MHz}$
\[ \text{MeO}\]

\[ \text{Ph} \]

3o

$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
3q
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}H$ NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^1$H NMR, CDCl$_3$, 500MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$H NMR, CDCl₃, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}H$ NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}H$ NMR, CDCl$_3$, 400MHz
$^1$H NMR, CDCl$_3$, 101MHz

3af

$^1$C NMR, CDCl$_3$, 101MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz

3ah
$^{1}H$ NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}$H NMR, CDCl$_3$, 500MHz

3aj
$^{13}$C NMR, CDCl$_3$, 126 MHz
$^1$H NMR, CDCl$_3$, 400MHz

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</tr>
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$^{13}$C NMR, CDCl$_3$, 101MHz
$^{13}$C NMR, CDCl$_3$, 126MHz
S71
$^{13}$C NMR, CDCl$_3$, 101MHz

$^{5}e$
$^{13}$C NMR, CDCl$_3$, 101MHz
$^{1}$H NMR, CDCl$_3$, 500MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$H NMR, CDCl$_3$, 377MHz
$^{13}$C NMR, CDCl$_3$, 101MHz

5i

S81
$^1$H NMR, CDCl$_3$, 400MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl₃, 101MHz
$^{1}$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 151MHz
$^{13}$C NMR, CDCl$_3$, 101MHz

5m
\[ ^1H \text{NMR, CDCl}_3, 500\text{MHz} \]
$^{13}$C NMR, CDCl$_3$, 101MHz
$^1$C NMR, DMSO, 101MHz
$^1$H NMR, CDCl$_3$, 400MHz
$^{13}$C NMR, CDCl$_3$, 101MHz
HRMS spectrum of TEMPO-benzoyl adduct X-2a