Gold-Catalyzed Waste-Free Generation and Cycloaddition of Azomethine Ylides from Nitrone and Alkyne: 
Internal Redox-Dipolar Cycloaddition (IR-DC) Cascade

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General Remarks:
Anhydrous 1,2-dichloroethane and nitromethane (reagent grade) was purified by distillation over calcium hydride and anhydrous magnesium sulfate, respectively. All commercially available reagents were used without further purification. Flash column chromatography was performed on Kieselgel 60 (230-400 mesh). ¹H, ¹³C NMR spectra were recorded on a Varian (400 MHz) spectrometer with TMS as internal standard. Crude ¹H NMR spectra were obtained with mesitylene as internal standard. Multi-dimensional NMR experiments were conducted on Varian (600 MHz) at Seoul National University. Elemental analyses and HRMS experiments were conducted at Sogang University and Seoul National University.

All Au(I), Au(III), Pt(II), and Ag(I) complexes were used as purchased from Aldrich or Strem, except the following: Au(IMes)Cl and Au(IPr)Cl complexes were prepared following the literature method.[1] N-Alkylhydroxylamine hydrochloride and other starting materials for the preparation of enyne(or diyne)-nitrone substrates were purchased from Aldrich and used as received. The 1,6-enynes and 1,6-diynes[2] or β-halo-α,β-unsaturated aldehydes[3] were prepared adopting literature protocol.

References:
Representative procedure for the preparation of enyne(or Diyne)-Nitrone Substrates:

General Procedure A (Sonogashira reaction for the formation of o-1,6-enynyl benzaldehyde): To a solution of o-iodobenzaldehyde (0.500 g, 2.16 mmol) and 1,6-enyne (0.770 g, 3.23 mmol) in THF (20 mL) at rt, was added Pd(PPh₃)₂Cl₂ (30.2 mg, 0.0431 mmol), CuI (16.4 mg, 0.0.0862 mmol) and K₂CO₃ (0.894 g, 6.45 mmol). The mixture was stirred at 50 °C for 6 h and the volatiles were evaporated. The residue was purified by silica gel chromatography (EtOAc:Hex = 1:6) to give 0.682 g (92 %) of o-1,6-enynyl benzaldehyde as pale yellow oil.

General Procedure B (Condensation of o-1,6-enynyl benzaldehyde with N-benzyl hydroxylamine): The above prepared o-1,6-enynyl benzaldehyde (331 mg, 0.968 mmol) and N-benzylamine hydrochloride (278 mg, 1.75 mmol) in dichloromethane (10 mL) was added anhydrous magnesium sulfate (210 mg, 1.75 mmol) and 4 Å molecular sieves (210 mg). The resulting mixture was stirred at rt overnight. After filtration of insoluble materials and evaporation of solvent, the residue was purified by silica gel chromatography (EtOAc:Hex = 1:2) to give 413 mg (92 %) of enyne-nitrone 1 as colorless oil.

Characterization of Starting Materials

1H NMR (400 MHz, CDCl₃): δ 9.30 (d, J = 8.1 Hz, H), 8.22 (s, H), 7.62-7.55 (m, 2H), 7.45-7.25 (m, 6H), 5.70 (tdd, J = 7.4, 9.9, 17.2 Hz, H), 5.23 (s, 2H), 5.20 (d, J = 18.1 Hz, H), 5.17 (d, J = 9.9 Hz, H), 4.22 (q, J = 7.3 Hz, 4H), 3.05 (s, 2H), 2.90 (d, J = 7.4 Hz, 2H), 1.25 (t, J = 7.0 Hz, 6H);


1H NMR (400 MHz, CDCl₃): δ 9.31 (d, J = 8.6 Hz, H), 8.23 (s, H), 7.61 (d, J = 6.2 Hz, 2H), 7.52-7.18 (m, 6H), 5.24 (s, 2H), 4.94 (s, H), 4.86 (s, H), 3.09 (s, 2H), 2.94 (s, 2H), 1.70 (s, 3H), 1.26 (t, J = 7.2 Hz, 6H); 13C NMR (100 MHz, CDCl₃): δ 171.2, 140.3, 134.7, 133.3, 132.8, 132.2, 130.3, 129.8, 129.4, 129.3, 129.1, 128.2, 123.1, 117.2, 91.6, 82.0, 71.8, 62.5, 57.1, 40.6, 24.7, 24.0, 14.7; LRMS (EI+) calcd for C₂₈H₃₁NO₅ [M⁺]+ 461, found 461 [M⁺]+, 445 [M⁺]+-O, 416 [M⁺]+-OEt.

1H NMR (400 MHz, CDCl₃): (Inseparable E/Z mixture) δ 9.31 (d, J = 7.7 Hz, H), 8.25 (s, H), 7.70-7.56 (m, 2H), 7.48-7.20 (m, 6H), 5.80-5.55 (m, 2H), 5.38-5.15 (m, 3H), 3.04 (s, 2H), 2.93 (d, J = 7.7 Hz, 0.5H, minor) / 2.83 (d, J = 7.7 Hz, 1.5H, major), 1.66 (d, J = 6.3 Hz, 2.34 H, major) / 1.62 (d, J = 6.6 Hz, 0.85 H, minor), 1.25 (t, J = 7.3 Hz, 6 H); 13C NMR (100 MHz, CDCl₃): (E/Z mixture) δ 170.95, 170.89, 134.7, 133.3, 132.7, 132.2, 131.6, 130.3, 129.9, 129.8, 129.3, 129.1, 128.2, 123.3, 123.1, 91.54, 91.43, 81.66, 81.62, 71.8, 62.44, 62.37, 57.66, 57.56, 36.3, 24.5, 18.7, 14.78, 14.74, 13.7; LRMS (EI+) calcd for C₂₉H₃₃NO₅ [M⁺]+ 461, found 461 [M⁺]+, 445 [M⁺]+-O, 416 [M⁺]+-OEt. (The compound 6 was synthesized from previously commercially available crotlyl bromide with E/Z = 3:1 ratio).
$^{1}\text{H NMR}(400 \text{ MHz, CDCl}_3)$: $\delta$ 9.31 (d, $J = 7.7 \text{ Hz, H}$), 8.20 (s, H), 7.62-7.55 (m, 2H), 7.49-7.22 (m, 6H), 5.22 (s, 2H), 4.24 (q, $J = 7.0 \text{ Hz, H}$), 3.24 (s, 2H), 3.01 (q, $J = 2.2 \text{ Hz, H}$), 1.77 (s br, 3H), 1.26 (t, $J = 7.4 \text{ Hz, 6H}$); $^{13}\text{C NMR}(100 \text{ MHz, CDCl}_3)$: $\delta$ 170.0, 134.6, 133.2, 132.8, 132.1, 130.3, 129.8, 129.4, 129.3, 129.2, 128.9, 128.8, 128.2, 123.5, 122.9, 90.9, 84.7, 84.2, 82.0, 71.9, 62.8, 57.4, 24.8, 24.6, 14.7; LRMS (EI+) calcd for C$_{29}$H$_{32}$NO$_3$ [M$^+$] 459, found 459 [M$^+$].

$^{1}\text{H NMR}(400 \text{ MHz, CDCl}_3)$: $\delta$ 9.28 (d, $J = 7.7 \text{ Hz, H}$), 8.04 (s, H), 7.52-7.36 (m, 2H), 7.36-7.20 (m, 5H), 5.67 (dd, $J = 7.4, 9.9$, 17.7 Hz, H), 5.20 (d, $J = 16.9 \text{ Hz, H}$), 5.17 (d, $J = 10.3 \text{ Hz, H}$), 4.23 (q, $J = 7.0 \text{ Hz, H}$), 4.01 (s, 3H), 3.07 (s, 2H), 2.87 (d, $J = 7.7 \text{ Hz, 2H}$), 1.26 (t, $J = 7.3 \text{ Hz, 6H}$); $^{13}\text{C NMR}(100 \text{ MHz, CDCl}_3)$: $\delta$ 170.7, 134.1, 132.8, 132.2, 132.0, 130.3, 129.1, 128.1, 122.9, 120.8, 91.2, 81.7, 62.4, 57.4, 55.2, 37.4, 24.6, 14.7; LRMS (EI+) calcd for C$_{29}$H$_{32}$NO$_3$ [M$^+$] 371, found 371 [M$^+$], 355 [M$^+$-O], 326 [M$^+$-OEt]; LRMS (CI) calcd for C$_{29}$H$_{32}$NO$_3$ [M$^+$+H] 506, found 506 [M$^+$+H, Base peak].

$^{1}\text{H NMR}(400 \text{ MHz, CDCl}_3)$: $\delta$ 9.30 (d, $J = 7.7 \text{ Hz, H}$), 8.20 (s, H), 7.62-7.55 (m, 2H), 7.49-7.22 (m, 6H), 5.22 (s, 2H), 4.24 (q, $J = 7.0 \text{ Hz, 4H}$), 3.24 (s, 2H), 3.01 (q, $J = 2.2 \text{ Hz, 2H}$), 1.77 (s br, 3H), 1.26 (t, $J = 7.4 \text{ Hz, 6H}$); $^{13}\text{C NMR}(100 \text{ MHz, CDCl}_3)$: $\delta$ 170.0, 134.6, 133.2, 132.8, 132.1, 130.3, 129.8, 129.4, 129.3, 129.2, 128.9, 128.8, 128.2, 123.5, 122.9, 90.9, 84.7, 84.2, 82.0, 71.9, 62.8, 57.4, 24.8, 24.6, 14.7; LRMS (EI+) calcd for C$_{29}$H$_{32}$NO$_3$ [M$^+$] 459, found 459 [M$^+$], 443 [M$^+$-O], 428 [M$^+$-O-Me], 414 [M$^+$-OEt].

$^{1}\text{H NMR}(400 \text{ MHz, CDCl}_3)$: $\delta$ 9.31 (d, $J = 7.7 \text{ Hz, H}$), 8.20 (s, H), 7.70-7.52 (m, 2H), 7.52-7.16 (m, H), 5.21 (s, 2H), 4.38-4.16 (m, 4H), 3.32 (s, 2H), 3.29 (s, 2H), 1.27 (t, $J = 7.1 \text{ Hz, 6H}$); $^{13}\text{C NMR}(100 \text{ MHz, CDCl}_3)$: $\delta$ 169.8, 134.6, 133.1, 132.9, 132.3, 132.1, 130.3, 129.8, 129.4, 129.3, 129.2, 128.9, 128.8, 128.2, 123.5, 122.9, 90.9, 84.7, 84.2, 82.0, 71.9, 62.8, 57.4, 24.8, 24.6, 14.7; LRMS (EI+) calcd for C$_{33}$H$_{31}$NO$_3$ [M$^+$] 521, found 521 [M$^+$], 505 [M$^+$-O], 476 [M$^+$-OEt].

$^{1}\text{H NMR}(400 \text{ MHz, CDCl}_3)$: $\delta$ 9.26 (d, $J = 8.1 \text{ Hz, H}$), 7.88 (s, H), 7.71 (d, $J = 7.9 \text{ Hz, 2H}$), 7.60-7.48 (m, 2H), 7.48-7.40 (m, 2H), 7.36 (t, $J = 7.7 \text{ Hz, H}$), 7.30-7.22 (m, 2H), 7.22-7.15 (m, 2H), 7.06 (d, $J = 7.7 \text{ Hz, H}$), 5.88-5.64 (m, H), 5.28 (d, $J = 16.9 \text{ Hz, H}$), 5.26 (d, $J = 9.9 \text{ Hz, H}$), 5.10 (s, 2H), 4.21 (s, 2H), 3.85 (d, $J = 6.2 \text{ Hz, 2H}$), 2.30 (s, 3H); $^{13}\text{C NMR}(100 \text{ MHz, CDCl}_3)$: $\delta$ 144.6, 136.2, 133.9, 132.8, 132.7, 132.6, 132.1, 130.25, 130.18, 129.7, 129.64, 129.60, 128.4, 128.2, 122.1, 120.7, 89.0, 83.4, 72.2, 50.2, 37.3, 22.1.

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geometric isomers resulted presumably as a result of equilibration. In the Sonogashira reaction for the synthesis of aldehyde from hydroxylamine with the corresponding conjugated aldehyde (Z = 100 %) according to the General Procedure A. A mixture of 

\[
\text{C NMR (100 MHz, CDCl}_3\):} \ \delta 135.2, 133.9, 133.1, 133.0, 131.9, 130.5, 129.9, 129.7, 129.6, 129.4, 128.2, 122.8, 118.0, 94.7, 84.3, 74.9, 72.7, 70.6, 43.5, 29.9, 29.4, 27.1, 26.6, 26.59.
\]

\[1^1\text{H NMR (400 MHz, CDCl}_3\):} \ \delta 7.48 (d, J = 9.9 Hz, 0.5H, Z), 7.44-7.20 (m, 15 H, E/Z), 7.10-6.95 (m, 1.5H, E/Z), 6.08 (d br, J = 15.8 Hz, 0.5H, E) / 5.76 (d br, J = 10.3 Hz, 0.5H, Z), 5.81-5.69 (m, 1H, E/Z), 5.11-5.00 (m, 2H, E/Z), 4.91 (s, H, E) / 4.81 (s, H, Z), 4.49 (s, 2H, Z) / 4.48 (s, 2H, E), 3.36 (s, 2H, E) / 3.35 (s, 2H, Z), 2.48 (d, J = 2.2 Hz, H, Z) / 2.45 (d, J = 2.2 Hz, H, E), 2.20 (d, J = 7.3 Hz, H, E) / 2.19 (d, J = 6.6 Hz, H, Z); \[1^3\text{C NMR (100 MHz, CDCl}_3\):} \ \delta 139.3, 139.2, 135.8, 134.9, 134.33, 134.28, 133.53, 133.49, 130.0, 129.9, 129.74, 129.70, 129.67, 129.58, 129.55, 128.97, 128.91, 128.3, 128.1, 128.0, 127.9, 119.0, 118.91, 119.85, 116.8, 99.8, 97.2, 82.6, 79.8, 73.9, 72.53, 72.49, 70.3, 70.2, 43.3, 43.2, 24.4; LRMS (EI+) calced for C\textsubscript{33}H\textsubscript{35}NO\textsubscript{3} [M\textsuperscript{+}]+ 493, found 493 [M\textsuperscript{+}], 477 [M\textsuperscript{+}-O]. Substrate 21 (E/Z = ~1:1) was synthesized by condensation of N-aryl hydroxylamine with the corresponding conjugated aldehyde (Z = 100 %) according to the General Procedure A. A mixture of geometric isomers resulted presumably as a result of equilibration. In the Sonogashira reaction for the synthesis of aldehyde precursor of 21, Pd(PPh\textsubscript{3})\textsubscript{2} was used instead of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} under otherwise identical conditions.

\[1^1\text{H NMR (400 MHz, CDCl}_3\):} \ \delta 7.45-7.25 (m, 15 H), 7.10-6.96 (m, 2H), 6.08 (d br, J = 15.8 Hz, H), 5.75 (tdd, J = 7.7, 9.9, 16.3 Hz, H), 5.06 (d, J = 15.7 Hz, H), 5.03 (d, J = 7.7 Hz, H), 4.91 (s, 2H), 4.48 (s, 4H), 3.67 (s, 4H), 2.45 (d, J = 2.2 Hz, 2H), 2.20 (d, J = 7.3 Hz, H). (After IR-DC reaction, the E-isomer was recovered as a pure geometric isomer in 45 % yield)

\[1^1\text{H NMR (400 MHz, CDCl}_3\):} \ \delta 7.71 (d, J = 10.0 Hz, H), 7.62-7.46 (m, 2H), 7.46-7.30 (m, 3H), 6.88 (d, J = 10.0 Hz, H), 5.64 (tdd, J = 7.7, 9.9, 16.9 Hz, H), 5.17 (d, J = 17.6 Hz, H), 5.16 (d, J = 9.5 Hz, H), 4.98 (s, 2H), 4.21 (q, J = 6.9 Hz, 4H), 3.00 (s, 2H), 2.81 (d, J = 7.4 Hz, 2H), 2.21 (t, J = 7.3 Hz, 2H), 1.50 (quintet, J = 7.7 Hz, 2H), 1.36-1.20 (m, 2H), 1.25 (t, J = 7.3 Hz, 6H), 0.89 (t, J = 7.3 Hz, 3H); \[1^3\text{C NMR (100 MHz, CDCl}_3\):} \ \delta 170.5, 136.1, 134.4, 132.9, 132.1, 129.6, 129.3, 129.2, 125.5, 120.7, 95.5, 82.2, 69.9, 62.4, 57.4, 37.9, 37.4, 30.9, 24.6, 22.6, 14.7, 14.4. In the Sonorashira reaction for the synthesis of aldehyde precursor of 23, Pd(PPh\textsubscript{3})\textsubscript{2} was used instead of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} under otherwise identical conditions.

\[1^1\text{H NMR (400 MHz, CDCl}_3\):} \ \delta 7.75 (s, H), 7.62-7.48 (m, 2H), 7.46-7.28 (m, 3H), 5.64 (tdd, J = 7.4, 9.9, 17.2 Hz, H), 5.18 (d, J = 15.7 Hz, H), 5.15 (d, J = 8.8 Hz, H), 5.00 (s, 2H), 4.20 (q, J = 7.0 Hz, 4H), 2.96 (s, 2H), 2.86 (s br, J = 2H), 2.82 (d, J = 6.6 Hz, 2H), 2.22 (s br, 2H), 1.70-1.46 (m, 4H), 1.25 (t, J = 7.0 Hz, 6H); \[1^3\text{C NMR (100 MHz, CDCl}_3\):} \ \delta 170.6, 137.5, 136.4, 134.8, 132.1, 129.7, 129.2, 129.1, 125.3, 120.6, 92.7, 83.6, 71.2, 62.3, 57.4, 37.3, 31.9, 27.3, 24.6, 22.5, 22.1, 14.7; LRMS (EI+) calced for C\textsubscript{27}H\textsubscript{25}NO\textsubscript{3} [M\textsuperscript{+}]+ 451; found 451 [M\textsuperscript{+}], 435 [M\textsuperscript{+}-O], 406 [M\textsuperscript{+}-OEt]. In the Sonorashira reaction for the synthesis of aldehyde precursor of 25, Pd(PPh\textsubscript{3})\textsubscript{2} was used instead of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} under otherwise identical conditions.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.30 (d, $J = 8.0$ Hz, H), 8.05 (s, H), 7.68-7.48 (m, 3H), 7.48-7.26 (m, 5H), 5.10 (s, 2H), 3.32 (s, H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.8, 133.4, 132.8, 132.4, 130.4, 130.04, 129.98, 129.6, 128.2, 121.9, 83.9, 81.5, 72.5; LRMS (EI+) calcd for C$_{16}$H$_{13}$NO [M$^+$] 235, found 235 [M$^+$], 218 [M$^+$-OH].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.27 (d, $J = 7.7$ Hz, H), 7.91 (s, H), 7.55-7.46 (m, 2H), 7.46-7.35 (m, 4H), 7.35-7.25 (m, 2H), 5.09 (s, 2H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 133.6, 133.4, 132.7, 131.7, 130.4, 130.3, 129.6, 128.6, 128.1, 124.1, 92.8, 72.1, 5.0; LRMS (EI+) calcd for C$_{17}$H$_{15}$NO [M$^+$] 249, found 249 [M$^+$], 232 [M$^+$-OH]. In the Sonogashira reaction for the synthesis of 30 (General Procedure A), Pd(PPh$_3$)$_4$ (2 %), Cul (4 %), TBAF (3 eq.) and 1-(trimethylsilyl)-propyne was used, under otherwise similar conditions.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50-7.28 (m, 6H), 6.62 (s, 2H), 5.62 (ddd, $J = 7.4$, 9.9, 16.8 Hz, H), 5.14 (d, $J = 16.2$ Hz, H), 5.11 (d, $J = 8.8$ Hz, H), 4.90 (s, 2H), 4.28-4.12 (m, 4H), 2.86-2.68 (m, 4H), 2.51 (s, 2H), 1.30 (s, 6H), 1.24 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.6, 143.9, 134.3, 132.6, 129.5, 129.3, 129.2, 120.3, 81.3, 77.0, 71.2, 62.2, 57.6, 37.2, 37.1, 29.4, 24.0, 23.6, 14.8; LRMS (EI+) calcd for C$_{25}$H$_{34}$NO$_5$ [M$^+$+H] 428, found 428 [M$^+$+H], 412 [M$^+$-O+H], 396 [M$^+$-O-Me].
Table S1. Catalyst optimization using 1 as substrate \(^{[a]}\)

![Chemical structure](image)

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<th>Entry</th>
<th>catalyst</th>
<th>time (h)</th>
<th>temp (^{(\circ}C))</th>
<th>solvent</th>
<th>(2) (%)(^{[b]})</th>
<th>(3) (%)(^{[b]})</th>
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<td>70</td>
<td>DCE</td>
<td>62(^{e})</td>
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<tr>
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<td>Pt(OAc)(_2)</td>
<td>20</td>
<td>100(^{a})</td>
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<td>6</td>
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<td>PtCl(_2) (benzonitrile)(_2)</td>
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<td>100(^{a})</td>
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<td>59</td>
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<tr>
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<td>100(^{a})</td>
<td>DCE</td>
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<td>-</td>
<td>74</td>
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<td>5</td>
<td>PtCl(_4) (SMe(_2))</td>
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<td>100(^{b})</td>
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<td>-</td>
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<td>ND(^{f})</td>
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<td>DCM</td>
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<td>dec.(^{g})</td>
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<td>18</td>
<td>AuCl(_3)</td>
<td>2</td>
<td>r.t</td>
<td>CH(_2)NO(_2)</td>
<td>88</td>
<td>&lt;5</td>
<td>&lt;5</td>
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<tr>
<td>19</td>
<td>AuCl(_3)</td>
<td>18</td>
<td>r.t</td>
<td>CH(_3)CN</td>
<td>84</td>
<td>-</td>
<td>-</td>
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<tr>
<td>20</td>
<td>AuCl(_3)</td>
<td>18</td>
<td>r.t</td>
<td>n-Hex</td>
<td>16</td>
<td>-</td>
<td>63</td>
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</tbody>
</table>

\(^{[a]}\) 5 mol % Catalyst in solvents (0.1 M) unless otherwise noted; Data provided in the manuscript (Table 1) have been omitted.

\(^{[b]}\) Crude NMR yields unless otherwise indicated.

\(^{[c]}\) Isolated yield.

\(^{[d]}\) Reaction in a sealed vial.

\(^{[e]}\) Use of 10 mol% Rh cat.

\(^{[f]}\) Not determined.

\(^{[g]}\) Decomposed.
Characterization of Products (Products in Table 2 and Eq. 1-3)

Compound 2 (pale yellow crystals, m.p. 98 °C); IR (thin film): 1731, 1692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.3 Hz, H), 7.51 (dt, J = 1.1, 7.7 Hz, H), 7.37 (t, J = 7.3 Hz, H), 7.30-7.16 (m, 3H), 7.07 (d, J = 6.6 Hz, 2H), 7.00 (d, J = 7.7 Hz, H), 4.32-4.05 (m, 5H), 3.81 (d of ABq, J = 13.2 Hz, H), 3.28 (d of ABq, J = 13.2 Hz, H), 3.17 (d of ABq, J = 14.3 Hz, H), 2.75-2.65 (m, H), 2.63 (d of ABq, J = 13.2 Hz, H), 2.60 (dd, J = 5.1, 13.9 Hz, H), 2.47 (dd, J = 9.9, 13.2 Hz, H), 2.19 (ddd, J = 5.9, 6.2, 12.1 Hz, H), 1.97 (dd, J = 7.1, 11.3 Hz, H), 1.29 (t, J = 7.3 Hz, 3H), 1.16 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 197.6, 172.3, 171.8, 144.5, 139.3, 135.1, 130.8, 128.95, 128.88, 128.15, 127.6, 126.9, 82.0, 63.3, 63.2, 62.3, 62.1, 49.6, 45.5, 40.1, 38.6, 35.5, 14.7, 14.6. Anal Calcd for C₂₇H₂₉NO₅: C 72.46, H 6.53, N 3.13, found C 72.35, H 6.65, N 2.91; HRMS (ES+) Calcd for [M⁺+Na] 470.1943, found 470.1945.

Compound 3 (pale yellow liquid); Rᵣ = 0.25 (EtOAc:Hex = 1:2); IR (thin film): 1730, 1628, 1430, 1204, 989 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.8 Hz, H), 7.65 (d, J = 8.4 Hz, H), 7.43 (s, H), 7.36 (t, J = 8.1 Hz, H), 7.29-7.20 (m, 3H, Bn-Ar), 7.14 (t, J = 8.0 Hz, H), 7.11-7.06 (m, 2H, Bn-Ar), 5.92 (s, 2H, PhC=CH₂), 5.62 (ddd, J = 7.3, 10.3, 17.3 Hz, H, CH=CH₂), 4.94 (d, J = 10.3 Hz, H, CH=CH₂), 4.84 (d, J = 17.3 Hz, H, CH=CH₂), 4.25-4.09 (m, 4H, CO₂Et), 3.77 (s, 2H, CH₂C(CO₂Et)₂R), 2.86 (d, J = 7.7 Hz, 2H, CH₂CH=CH₂), 1.19 (t, J = 7.0 Hz, 6H, CO₂Et); ¹³C NMR (100 MHz, CDCl₃): δ 185.6 (ketone), 171.4 (CO₂Et), 137.8 (Bn, C-Ar), 133.6 (CH=CH₂), 129.9 (Q), 129.2 (Bn, C-Ar), 128.4 (Bn, C-Ar), 128.1 (Bn, C-Ar), 127.1 (CH), 125.4 (CHN), 125.0 (Q), 122.7 (CH), 121.8 (CH), 121.1 (CH), 120.8 (Q), 119.9 (CH=CH₂), 62.1 (OCH₂Me), 55.8 (C(CO₂Et)₂), 55.4 (NCH₂Ph), 44.9 (CH₂C(CO₂Et)₂R), 38.0 (CH₂CH=CH₂), 14.7 (OCH₂CH₂); HRMS (ES+) Calcd for C₂₇H₂₉NO₅Na [M⁺+Na] 470.1935, found 470.1935 (Assignment was inferred from HSQC as well as HMBC spectra).

The structure of isoindol 3 has been assigned based on the similarity of its ¹H and ¹³C NMR spectra with those of compound 31 prepared via alternative route.[⁴] For the synthesis of 31 via internal redox, see below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹H NMR</th>
<th>¹³C NMR</th>
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<td>185.6 (C=O)</td>
</tr>
<tr>
<td>3 (ref. 4)</td>
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<td>186.2</td>
</tr>
<tr>
<td>31</td>
<td>7.65 (d, J = 8.4 Hz, H)</td>
<td>55.4 (CH₂Bn)</td>
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<td></td>
<td>7.66 (dt, J = 8.4, 1 Hz)</td>
<td>54.7</td>
</tr>
<tr>
<td></td>
<td>7.43 (s, H)</td>
<td>5.94 (s, 2H)</td>
</tr>
<tr>
<td></td>
<td>5.92 (s, 2H, PhCH₂)</td>
<td>4.94 (d, J = 10.3 Hz, H, CH=CH₂), 4.84 (d, J = 17.3 Hz, H, CH=CH₂), 4.25-4.09 (m, 4H, CO₂Et), 3.77 (s, 2H, CH₂C(CO₂Et)₂R), 2.86 (d, J = 7.7 Hz, 2H, CH₂CH=CH₂), 1.19 (t, J = 7.0 Hz, 6H, CO₂Et);</td>
</tr>
</tbody>
</table>

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Compound 5 (red oil); IR (thin film): 1732, 1688 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, \(J = 7.7\) Hz, H), 7.50 (t, \(J = 7.4\) Hz, H), 7.37 (t, \(J = 7.7\) Hz, H), 7.28-7.16 (m, 3H), 7.03 (d, \(J = 7.0\) Hz, 2H), 6.95 (d, \(J = 7.7\) Hz, H), 4.26-4.15 (m, 3H), 4.08-3.99 (m, 2H), 3.90 (d of ABq, \(J = 13.2\) Hz, H), 3.25 (d of ABq, \(J = 12.9\) Hz, H), 3.14 (d of ABq, \(J = 15.0\) Hz, H), 3.10 (d of ABq, \(J = 15.4\) Hz, H), 2.83 (d of ABq, \(J = 14.7\) Hz, H), 2.54 (dd, \(J = 7.0, 12.1\) Hz, H), 2.23 (d of ABq, \(J = 13.9\) Hz, H), 1.62 (d, \(J = 12.1\) Hz, H), 1.27 (t, \(J = 7.3\) Hz, 3H), 1.11 (t, \(J = 7.0\) Hz, 3H), 0.90 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.8, 173.1, 172.0, 144.8, 139.0, 135.3, 131.1, 128.9, 128.8, 128.2, 127.6, 127.3, 126.5, 85.4, 62.4, 62.1, 61.6, 60.3, 51.5, 51.1, 49.5, 46.7, 34.4, 27.0, 14.7, 14.5; Anal Calcd for C\(_{28}\)H\(_{31}\)NO\(_5\): C 72.86, H 6.77, N 3.03; found C 72.98, H 6.71, N 3.04; HRMS (ES+) Calcd for [M\(^+\)+Na] 484.2100, found 484.2102.

Compound 7 (the major diastereomer, dark brown oil); IR (thin film): 1732, 1692 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.04 (d, \(J = 7.7\) Hz, H), 7.51 (t, \(J = 7.3\) Hz, H), 7.40 (t, \(J = 7.3\) Hz, H), 7.30-7.18 (m, 3H), 7.05 (d, \(J = 6.6\) Hz, 2H), 6.95 (d, \(J = 7.3\) Hz, H), 4.34-4.15 (m, 4H), 3.90 (d, \(J = 5.5\) Hz, H), 3.78 (d of ABq, \(J = 13.2\) Hz, H), 3.32 (d of ABq, \(J = 13.2\) Hz, H), 3.11 (d of ABq, \(J = 14.3\) Hz, H), 2.70-2.58 (m, 2H), 2.63 (d of ABq, \(J = 14.7\) Hz, H), 2.39 (dd, \(J = 102, 13.5\) Hz, H), 2.12 (ddd, \(J = 4.4, 6.6, 10.3\) Hz, H), 1.29 (t, \(J = 7.0\) Hz, 3H), 1.15 (t, \(J = 7.0\) Hz, 3H), 0.68 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.0, 172.3, 171.8, 141.1, 139.3, 134.5, 131.3, 129.3, 128.9, 128.8, 128.3, 127.6, 126.9, 82.5, 67.5, 63.2, 62.3, 61.3, 53.5, 49.7, 43.6, 38.5, 35.4, 17.0, 14.7, 14.6; HRMS (ES+) Calcd for C\(_{28}\)H\(_{31}\)NNaO\(_5\) [M\(^+\)+Na] 484.2100, found 484.2099.

Compound 9 (red oil); IR (thin film): 1731, 1692 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.03 (d, \(J = 7.3\) Hz, H), 7.51 (dt, \(J = 1.1, 7.3\) Hz, H), 7.39 (t, \(J = 7.3\) Hz, H), 7.30-7.19 (m, 3H), 7.12 (app d, \(J = 6.6\) Hz, 2H), 6.96 (d, \(J = 7.3\) Hz, H), 4.32-4.16 (m, 4H), 3.74 (d of ABq, \(J = 13.2\) Hz, H), 3.50 (s, 3H), 3.23 (d of ABq, \(J = 13.2\) Hz, H), 3.19 (d, \(J = 13.9\) Hz, H), 2.54-2.40 (m, 3H), 2.27 (dd, \(J = 8.8, 11.4\) Hz, H), 1.34 (t, \(J = 7.0\) Hz, 3H), 1.31 (s, 3H), 1.26 (t, \(J = 7.3\) Hz, 3H), 0.62 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.0, 172.2, 171.8, 142.5, 139.6, 134.5, 130.7, 129.3, 129.0, 128.9, 128.2, 127.7, 127.1, 83.0, 75.0, 64.8, 62.3, 62.2, 56.5, 50.2, 41.3, 37.2, 35.2, 28.3, 27.8, 14.74, 14.70; HRMS (ES+) Calcd for C\(_{28}\)H\(_{31}\)NNaO\(_5\) [M\(^+\)+Na] 498.2256, found 498.2253.

Compound 11 (yellow oil); IR (thin film): 1732, 1695 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.03 (d, \(J = 7.7\) Hz, H), 7.49 (t, \(J = 7.4\) Hz, H), 7.41 (t, \(J = 7.3\) Hz, H), 7.31-7.20 (m, 3H), 7.03 (d, \(J = 8.2\) Hz, 2H), 6.94 (d, \(J = 7.7\) Hz, H), 4.33 (d, \(J = 5.9\) Hz, H), 4.31-4.07 (m, 4H), 3.79 (d of ABq, \(J = 13.5\) Hz, H), 3.53 (t, \(J = 6.2\) Hz, H), 3.48 (s, 3H), 3.27 (d of ABq, \(J = 13.2\) Hz, H), 3.14 (d of ABq, \(J = 14.6\) Hz, H), 3.15-3.09 (m, 9H), 2.70 (dd, \(J = 3.0, 13.6\) Hz, H), 2.64 (d of ABq, \(J = 14.3\) Hz, H), 2.43 (dd, \(J = 10.3, 13.6\) Hz, H), 1.28 (t, \(J = 7.0\) Hz, 3H), 1.16 (t, \(J = 7.3\) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.7, 171.9, 171.8, 139.5, 138.5, 134.7, 131.4, 129.07, 129.00, 128.89, 128.75, 127.9, 127.0, 82.0, 64.9, 62.8, 62.5, 56.5, 52.4, 49.5, 47.1, 38.5, 35.1, 14.7, 14.5; HRMS (ES+) Calcd for C\(_{28}\)H\(_{31}\)NNaO\(_7\) [M\(^+\)+Na] 528.1998, found 528.1993.
Compound 13 (yellow oil); IR (thin film): 1731, 1692 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (d, J = 7.4 Hz, H), 7.54 (dt, J = 1.1, 7.7 Hz, H), 7.35 (t, J = 7.3 Hz, H), 7.16 (d, J = 7.4 Hz, H), 4.30-4.10 (m, 5H), 2.98 (d of ABq, J = 14.3 Hz, H), 2.67-2.55 (m, 2H), 2.51 (d of ABq, J = 14.3 Hz, H), 2.38 (dd, J = 9.9, 12.9 Hz, H), 2.30-2.21 (m, H), 2.20 (s, 3H), 1.98 (J = 11.0, 8.8 Hz, H), 1.284 (t, J = 6.9 Hz, 3H), 1.276 (t, J = 7.4 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.0, 172.2, 171.7, 144.6, 135.1, 130.3, 128.0, 127.2, 126.7, 81.4, 67.5, 62.8, 62.3, 61.9, 45.0, 40.1, 39.1, 35.3, 32.9, 14.71, 14.69; Anal Calcd for C\(_9\)H\(_9\)NO; C 67.91, H 6.78, N 3.77, found C 67.93, H 6.83, N 3.76; HRMS (ES+) Calcd for [M\(^{+}\)Na] 394.1630, found 394.1628.

Compound 15 (yellow oil); IR (thin film): 1734, 1690, 1558, 1598 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, J = 6.6 Hz, H), 7.45 (dt, J = 1.1, 7.3 Hz, H), 7.37 (t, J = 1.1, 7.7 Hz, H), 7.30-7.22 (m, 3H), 7.17-7.11 (m, 2H), 6.97 (d, J = 6.9 Hz, H), 4.28 (q, J = 6.9 Hz, 2H), 4.22 (q, J = 7.0 Hz, 2H), 4.11 (s, H), 3.78 (d of ABq, J = 12.8 Hz, H), 3.60 (d of ABq, J = 12.8 Hz, H), 3.07 (d of ABq, J = 14.3 Hz, H), 2.83 (s, 2H), 2.42 (d of ABq, J = 14.3 Hz, H), 1.75 (s, 3H), 1.31 (t, J = 7.3 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.6, 171.8, 171.5, 143.3, 142.8, 142.6, 138.6, 143.0, 130.5, 129.7, 128.9, 128.4, 128.1, 127.9, 125.6, 86.7, 75.4, 64.0, 62.6, 62.4, 52.2, 34.2, 30.9, 14.7, 13.6; Anal Calcd for C\(_2\)H\(_9\)NO; C 73.18, H 6.36, N 3.05, found C 73.21, H 6.13, N 2.71; HRMS (ES+) Calcd for [M\(^{+}\)Na] 482.1943, found 482.1943.

Compound 17 (yellow solid, m.p. 86 \(^\circ\)C); IR (thin film): 1733, 1691, 1599, 1555 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, J = 6.7 Hz, H), 7.45-7.16 (m, 12 H), 7.06 (d, J = 7.3 Hz, H), 4.94 (s, H), 4.40-4.28 (m, 2H), 4.28-4.13 (m, 2H), 3.85 (d of ABq, J = 12.9 Hz, H), 3.67 (d of ABq, J = 12.8 Hz, H), 3.41 (d of ABq, J = 18.0 Hz, H), 3.18-3.08 (m, 2H), 2.53 (d of ABq, J = 13.6 Hz, H), 1.35 (t, J = 7.3 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.2, 171.7, 171.5, 144.5, 144.0, 142.5, 138.4, 134.1, 133.5, 130.5, 129.7, 129.3, 129.1, 128.65, 128.60, 128.1, 127.4, 126.0, 88.3, 72.3, 65.0, 62.8, 62.69, 52.5, 34.5, 33.2, 14.8, 14.8; HRMS Calcd for C\(_{30}\)H\(_{21}\)N\(_3\)NaO\(_2\) [M\(^{+}\)Na] 544.2100, found 544.2103.

Compound 19 (brown solid, m.p. 146 \(^\circ\)C); IR (thin film): 1688 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.01 (d, J = 7.4 Hz, H), 7.77 (d, J = 8.1 Hz, 2H), 7.54 (dt, J = 1.1, 7.7 Hz, H), 7.40 (t, J = 7.0 Hz, H), 7.36 (d, J = 8.0 Hz, 2H), 7.26-7.16 (m, 3H), 7.04 (d, J = 7.3 Hz, H), 6.92-6.86 (m, 2H), 4.23 (d of ABq, J = 11.0 Hz, H), 4.09 (d, J = 6.2 Hz, H), 3.74 (t, J = 8.8 Hz, H), 3.60 (d, J = 13.2 Hz, H), 3.27 (d, J = 13.2 Hz, H), 3.26-3.30 (m, H), 3.23 (d, J = 10.6 Hz, H), 2.66-2.58 (m, H), 2.47 (s, 3H), 2.08 (dd, J = 5.9, 11.8 Hz, H), 1.88 (dd, J = 8.8, 12.1 Hz, H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.9, 145.1, 144.3, 138.9, 135.5, 133.3, 130.7, 130.4, 129.03, 129.00, 128.7, 128.5, 128.0, 127.5, 127.3; HRMS (ES+) Calcd for C\(_{37}\)H\(_{36}\)N\(_2\)NaO\(_3\)S [M\(^{+}\)Na], 481.1562, found 481.1563.

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Compound 22 (yellow oil); IR (thin film): 1681 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.09 (m, 15 H), 6.78 (dd, $J$ = 4.4, 9.6 Hz, H), 6.04 (d, $J$ = 9.5 Hz, H), 4.58-4.46 (m, 4H), 3.68 (d, $J$ = 5.5 Hz, H), 3.67 (d of ABq, $J$ = 13.7 Hz, H), 3.61 (d of ABq, $J$ = 8.8 Hz, H), 3.53 (d of ABq, $J$ = 8.8 Hz, H), 3.48 (d of ABq, $J$ = 13.9 Hz, H), 3.46 (d of ABq, $J$ = 10.3 Hz, H), 3.39 (d of ABq, $J$ = 10.3 Hz, H), 2.46 (d of ABq, $J$ = 13.9 Hz, H), 2.50-2.43 (m, H), 2.18 (dd, $J$ = 8.5, 12.9 Hz, H), 1.87 (dd, $J$ = 8.8, 11.8 Hz, H), 1.79 (dd, $J$ = 5.5, 11.4 Hz, H), 1.74 (dd, $J$ = 10.2, 12.8 Hz, H), 1.54 (d of ABq, $J$ = 14.0 Hz, H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.9, 149.3, 140.2, 139.64, 139.62, 129.01, 128.96, 128.91, 128.13, 128.02, 127.97, 127.8, 127.6, 86.7, 75.3, 73.9, 73.8, 73.2, 60.2, 53.6, 49.2, 45.8, 39.9, 35.7, 34.2; HRMS Calcd for C$_{33}$H$_{35}$NNaO$_3$ [M$^+$+Na], 516.2515, found 516.2515.

Compound 24 (yellow oil); IR (thin film): 1732, 1678 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36-7.15 (m, 5H), 6.38 (d, $J$ = 4.8 Hz, H), 4.28-4.00 (m, 4H), 3.73 (d of ABq, $J$ = 13.2 Hz, H), 3.63 (s br, H), 3.47 (d of ABq, $J$ = 13.6 Hz, H), 3.02 (d of ABq, $J$ = 14.3 Hz, H), 2.60-2.54 (m, 2H), 2.51 (d of ABq, $J$ = 14.3 Hz, H), 2.44 (dd, $J$ = 11.3, 14.3 Hz, H), 2.30-2.11 (m, 2H), 1.96-1.87 (m, 2H), 1.52-1.25 (m, 4H), 1.27 (t, $J$ = 7.0 Hz, 3H), 1.12 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.9, 172.4, 171.8, 142.2, 139.6, 138.8, 129.0, 128.7, 127.6, 82.1, 63.2, 62.3, 62.1, 59.1, 49.0, 45.4, 39.7, 36.1, 35.0, 31.4, 28.7, 23.1, 14.7, 14.6; Anal Calcd for C$_{27}$H$_{35}$NNaO$_5$ [M$^+$+Na], 476.2413, found 476.2416.

Compound 26 (pale yellow solid); IR (thin film): 1732, 1669 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32-7.20 (m, 3H), 7.20-7.15 (m, 2H), 4.28-4.05 (m, 4H), 3.72 (d of ABq, $J$ = 12.9 Hz, H), 3.40 (d of ABq, $J$ = 13.2 Hz, H), 3.29 (d of ABq, $J$ = 5.5 Hz, H), 3.03 (d of ABq, $J$ = 14.3 Hz, H), 2.62-2.42 (m, 4H), 2.42-2.32 (m, H), 2.12 (t, $J$ = 8.4 Hz, 3H), 1.96-1.87 (m, 3H), 1.82 (dd, $J$ = 8.4, 11.3 Hz, H), 1.78-1.67 (m, 2H), 1.60-1.40 (m, 2H), 1.27 (t, $J$ = 7.3 Hz, 3H), 1.15 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.6, 172.5, 171.9, 154.8, 139.8, 130.4, 129.0, 128.9, 127.6, 81.8, 63.9, 63.2, 62.3, 62.0, 49.3, 46.8, 40.1, 35.9, 35.0, 29.0, 22.7, 22.5, 21.4, 14.7, 14.6; Anal Calcd for C$_{27}$H$_{33}$NO$_5$: C 71.82, H 7.37, N 3.10, found C 71.85, H 7.32, N 3.17; HRMS (ES+) Calcd for [M$^+$+Na]$_2$C$_{27}$H$_{33}$NNaO$_5$, 474.2256, found 474.2255.

Compound 28 (yellow oil); IR (thin film): 1715, 1645 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J$ = 7.4 Hz, H), 7.48-7.23 (m, 7H), 7.18 (d, $J$ = 7.0 Hz, H), 4.76 (s, H), 4.46 (s, H), 4.36-4.16 (m, 4H), 3.91 (d of ABq, $J$ = 13.2 Hz, H), 3.84 (d of ABq, $J$ = 12.8 Hz, H), 1.30 (t, $J$ = 7.0 Hz, 3H), 1.28 (t, $J$ = 7.3 Hz, H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.0, 164.2, 163.6, 147.1, 143.4, 139.5, 137.2, 133.9, 129.7, 129.5, 129.3, 129.1, 129.4, 125.7, 79.3, 71.9, 62.5, 62.3, 56.8, 14.7, 14.6; HRMS Calcd for C$_{23}$H$_{23}$NNaO$_5$ [M$^+$+Na] 428.1374, found 428.1375.
**General Procedure C** (Synthesis of 29 and 31 from 27 via internal redox)

![Reaction Scheme]

To a solution of 30 (20 mg, 0.0802 mmol) in dichloromethane (0.8 mL) at rt was added Au(IPr)Cl (2.5 mg, 0.0040 mmol) and AgOTf (1.0 mg, 0.0040 mmol). After stirring 1 h at 70 °C, the mixture was evaporated to dryness and the residue was purified by silica gel chromatography (EtOAc:Hex = 1:6) to give 10.6 mg (53 %) of 31 as yellow oil.

**Compound 29** (yellow oil); IR (thin film): 3441 (OH, presumably from hydrate), 3085, 3031, 2829, 1644, 1450, 1336 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 10.08 (s, H), 7.95 (s br, H), 7.63 (d, J = 8.5 Hz, H), 7.48 (s, H), 7.38-7.13 (m, 7 H), 5.88 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 174.8, 136.4, 128.8, 128.2, 127.6, 124.9, 124.6, 123.0, 120.8, 53.6; LRMS (EI+) calcd for C₁₆H₁₃NO [M⁺] 235, found 235 [M⁺], 219 [M⁺-O]; HRMS (EI+) calcd for C₁₆H₁₃NO [M⁺] 235.0997, found 235.0998.

**Compound 31** (yellow oil); IR (thin film): 3105, 3058, 3025, 2997, 2911, 1715, 1625, 1421, 1331, 1213 cm⁻¹ (1713 cm⁻¹, lit.); ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.8 Hz, H), 7.65 (d, J = 8.4 Hz, H), 7.48 (s, H), 7.36-7.22 (m, 4H), 7.18-7.10 (m, 3H), 5.94 (s, 2H), 2.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 186.3, 137.3, 129.5, 128.7, 127.7, 127.4, 126.1, 124.3, 121.9, 121.1, 54.7, 30.7; LRMS (EI+) calcd for C₁₇H₁₅NO [M⁺] 249, found 249 [M⁺]; HRMS (EI+) calcd for C₁₇H₁₅NO [M⁺] 249.1154, found 249.1155. These spectral data (¹H, ¹³C, and IR spectra) exactly match those of compound 31 synthesized by a different route as reported in reference 4.

**Compound 33** (yellow oil); IR (thin film): 1729 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.20 (m, 5H), 4.24-4.05 (m, 5H), 3.63 (d of ABq, J = 14.3 Hz, H), 3.12 (d of ABq, J = 15.8 Hz, H), 3.08 (d, J = 6.3 Hz, H), 2.79-2.64 (m, 2H), 2.52 (d of ABq, J = 15.8 Hz, H), 2.29 (dd, J = 8.4, 13.5 Hz, H), 2.24 (d of ABq, J = 15.8 Hz, H), 2.09 (d of ABq, J = 15.8 Hz, H), 2.02 (dd, J = 8.8, 11.7 Hz, H), 1.86 (td, J = 6.2, 13.2 Hz, H), 1.24 (t, J = 7.0 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 0.94 (s, 3H), 0.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 205.4, 172.6, 171.7, 140.8, 128.9, 128.8, 127.5, 83.7, 73.7, 63.6, 62.2, 54.7, 49.2, 49.1, 43.6, 40.3, 31.9, 31.8, 29.9, 28.6, 14.65, 14.62; HRMS (ES+) Calcd for C₂₅H₃₅NNaO₅ [M⁺+Na] 450.2256, found 450.2253.
3

(E = CO₂Et)
7 (major)
17

$\text{Ph}$

$\text{BnN}$

$\text{CO}_2\text{Et}$

$\text{O}$

17

$\text{Ph}$

$\text{BnN}$

$\text{CO}_2\text{Et}$

$\text{O}$

17

$\text{Ph}$

$\text{BnN}$

$\text{CO}_2\text{Et}$

$\text{O}$

17