Supporting Information for:

**Palladium–N-Heterocyclic Carbene (NHC)-Catalyzed Synthesis of 2-Ynamides via Oxidative Aminocarbonylation of Alkynes with Amines**

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1. General methods

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents were purchased from Alfa Aesar, and before use were dried and degassed by standard methods and stored under argon atmosphere. Aryl iodides were obtained from Alfa Aesar. Carbon monoxide (CO) with a purity of 99.99% was commercially available. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avance III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI) or Waters GCT Premier mass spectrometer (EI).
2. Synthesis of NHC palladium complexes

2.1 Synthesis of IPr-Pd-Peppsi-Cl$_2$ complex

IPr-Pd-Peppsi-Cl$_2$ was prepared according to the reported method $^1$.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.11 (d, $J = 6.88$, 12H), 1.47 (d, $J = 6.64$, 12H), 3.12-3.19 (m, 4H), 7.01-7.04 (m, 1H), 7.14 (s, 2H), 7.34-7.52 (m, 7H), 8.49-8.58 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 23.3, 26.4, 28.8, 124.1, 124.1, 124.4, 125.2, 130.4, 132.0, 135.0, 137.5, 146.7, 149.4, 150.4, 153.4.

![ORTEP drawing of IPr-Pd-Peppsi-Cl$_2$](image)

Figure S1. ORTEP drawing of IPr-Pd-Peppsi-Cl$_2$

2.2 Synthesis of IPr-Pd(allyl)Cl

IPr-Pd(allyl)Cl was prepared according to the reported method $^2$.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.08-1.18 (m, 12H), 1.32-1.40 (m, 12H), 1.56 (d, $J = 12$ Hz, 1H), 2.75-3.16 (m, 6H), 3.88-3.91 (m, 1H), 4.76-4.86 (m, 1H), 7.16-7.44 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.8, 22.9, 25.8, 26.5, 28.5, 28.6, 49.5, 72.5, 114.2, 123.8, 123.9, 124.1, 129.9, 135.8, 146.0, 146.2, 186.1.
2.3 Synthesis of IPr-Pd-dmba-Cl

IPr-Pd-dmba-Cl was prepared according to the reported method.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3 \] δ 0.80 (d, \( J = 2.68 \), 6H), 1.01 (d, \( J = 6.84 \), 6H), 1.17 (d, \( J = 6.8 \), 6H), 1.48 (d, \( J = 6.56 \), 6H), 2.38 (s, 6H), 3.12-3.19 (m, 2H), 3.32-3.39 (m, 2H), 3.45 (s, 2H), 6.52-6.79 (m, 4H), 7.14-7.20 (m, 4H), 7.29-7.41 (m, 4H).

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \] δ 23.2, 23.3, 26.2, 26.4, 28.3, 29.0, 49.8, 72.6, 121.5, 122.6, 123.7, 124.0, 124.5, 125.4, 129.7, 136.2, 144.7, 147.8, 147.8, 150.6, 177.6.

2.4 Synthesis of IMes-Pd-dmba-Cl

IMes-Pd-dmba-Cl was prepared according to the reported method.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3 \] δ 2.21 (s, 6H), 2.27 (s, 6H), 2.42 (d, \( J = 4.0 \), 6H), 3.51 (s, 2H), 6.56-6.58 (m, 1H), 6.67-6.71 (m, 1H), 6.75-6.83 (m, 4H), 6.97 (s, 2H), 7.08 (s, 2H).

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \] δ 19.8, 20.3, 21.1, 50.0, 72.3, 121.2, 122.9, 123.2, 123.9, 128.7, 129.4, 133.9, 136.2, 137.4, 138.3, 138.3, 147.6, 149.3, 175.7.

2.5 Synthesis of (IPr)PdCl\(_2\)(TEA) complex

(IPr)PdCl\(_2\)(TEA) was prepared according to the reported method.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3 \] δ 0.83 (t, \( J = 4.0 \), 9H), 1.05 (d, \( J = 8.0 \), 12H), 1.41 (d, \( J = 8.0 \), 12H), 2.50 (dd, \( J_1 = 4 \) Hz, \( J_2 = 8 \) Hz, 6H), 3.13-3.19 (m, 4H), 7.11 (s, 2H), 7.33 (d, \( J = 8.0 \) Hz, 4H), 7.48 (t, \( J = 8.0 \) Hz, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.7, 26.6, 28.7, 46.6, 123.6, 124.9, 130.0, 135.2, 147.1, 154.3.

References
3. General procedure for the carbonylation reaction

3.1 General procedure for the oxidative aminocarbonylation reaction

All carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, alkynes (1.0 mmol), amines (2.0 mmol), IPr-Pd-Peppsi-Cl$_2$ (1 mol%), K$_3$PO$_4$ (2.0 mmol), KI (10 mol%) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 °C, and the whole reaction mixture was stirred for 18 hours. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by GC-MS. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1-1/1) to afford the desired product 3 as a white solid.
4. Preliminary Mechanistic Studies

4.1 Preliminary Mechanistic Studies :HRMS

I: 2a + [Pd] + K$_3$PO$_4$

The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, 2a (2.0 mmol), IPr-Pd-Peppsi-Cl$_2$ (10 mol%), K$_3$PO$_4$ (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 °C, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.
II: 2a + [Pd] + K₃PO₄ + KI

The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, 2a (2.0 mmol), IPr-Pd-Peppsi-Cl₂ (10 mol%), KI (10 mol%), K₃PO₄ (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 °C, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.
III: 1a + 2a + [Pd] + K₃PO₄ + KI

The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, 1a (1.0 mmol), 2a (2.0 mmol), IPr-Pd-Peppsi-Cl₂ (10 mol%), KI (10 mol%), K₃PO₄ (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 °C, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.
4.2 Preliminary Mechanistic Studies :NMR

The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, 2a (2.0 mmol), IPr-Pd-Peppsi-Cl₂ (10 mol%), K₃PO₄ (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 °C, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. After evaporation of the solvents under reduced pressure, the residue was directly analyzed by NMR in DMSO-d₆.
5. NMR, HRMS and IR datas of 2-ynamides

N,N-diethyl-3-phenylpropiolamide (3aa):

The products 3aa were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.5 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.18 (t, $J = 8.0$ Hz, 3H), 1.28 (t, $J = 8.0$ Hz, 3H), 3.45 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 2H), 3.63 (dd, $J_1 = 12$ Hz, $J_2 = 8$ Hz, 2H), 7.34-7.43 (m, 2H), 7.53-7.55 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 12.8, 14.4, 39.3, 43.6, 81.9, 88.9, 120.7, 128.5, 129.9, 132.3, 153.9.

HRMS (ESI) calcd. for C$_{13}$H$_{15}$NO [M+H]: 202.1226, found: 202.1232.

IR (KBr, cm$^{-1}$) 2970, 2209, 1635, 1139, 765.

N,N-diethyl-3-(p-tolyl)propiolamide (3ba):

The products 3ba were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.45 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.18 (t, $J = 8.0$ Hz, 3H), 1.28 (t, $J = 8.0$ Hz, 3H), 3.45 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 2.38 (s, 3H), 3.64 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 12.9, 14.4, 21.6, 39.3, 43.6, 81.5, 89.4, 117.7, 129.3, 132.3, 140.3, 154.2.

HRMS (ESI) calcd. for C$_{14}$H$_{17}$NO [M+H]: 216.1019, found: 216.1019.
IR (KBr, cm$^{-1}$) 2954, 2215, 1619, 1419, 759.

3-(4-butylphenyl)-N,N-diethylpropiolamide (3ca):

![Structure](image)

The products 3ca were eluted with petroleum ether/ethyl acetate (20/1). R$_f$ = 0.4 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 92% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.84 (t, $J = 8.0$ Hz, 3H), 1.10 (t, $J = 8.0$ Hz, 3H), 1.18-1.21 (m, 3H), 1.25-1.15 (m, 2H), 2.54 (t, $J = 8.0$ Hz, 2H), 3.37 (dd, $J_1 = 12$ Hz, $J_2 = 8$ Hz, 2H), 3.55 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.9, 13.9, 14.4, 22.3, 33.3, 35.7, 39.3, 43.6, 81.5, 89.4, 117.8, 128.6, 132.3, 145.3, 154.2.

HRMS (ESI) calcd. for C$_{17}$H$_{23}$NO [M+H]: 280.1672, found: 280.1663.

IR (KBr, cm$^{-1}$) 2934, 2201, 1635, 1425, 1139, 715.

N,N-diethyl-3-(4-methoxyphenyl)propiolamide (3da):

![Structure](image)

The products 3da were eluted with petroleum ether/ethyl acetate (10/1). R$_f$ = 0.4 (petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.17 (t, $J = 8$ Hz, 3H), 1.28 (t, $J = 8$ Hz, 3H), 3.45 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 2H), 3.63 (dd, $J_1 = 12$ Hz, $J_2 = 4$ Hz, 2H), 3.83 (s, 3H), 6.86-6.90 (m, 2H), 7.47-7.50 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.9, 14.4, 39.2, 43.6, 55.7, 81.2, 89.5, 112.6,
HRMS (ESI) calcd. for C\textsubscript{14}H\textsubscript{17}NO\textsubscript{2} [M+H]: 232.1332, found: 232.1334.

IR (KBr, cm\textsuperscript{-1}) 2962, 2209, 1627, 1239, 1131, 823.

\textbf{N,N-diethyl-3-(4-(pentyloxy)phenyl)propiolamide (3ea):}

The products 3ea were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5 (petroleum ether/ethyl acetate = 5/1).

White solid, 94% yield, m. p. =48 °C.

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})} \delta 0.85 (t, J = 8 Hz, 3H), 1.07 (t, J = 8 Hz, 3H), 1.17 (t, J = 8 Hz, 3H), 1.28-1.33 (m, 4H), 1.64-1.71 (m, 2H), 3.34 (dd, J\textsubscript{1} = 16 Hz, J\textsubscript{2} = 4 Hz, 2H), 3.53 (dd, J\textsubscript{1} = 16 Hz, J\textsubscript{2} = 4 Hz, 2H), 3.84 (t, J = 8 Hz, 2H), 6.75 (dd, J\textsubscript{1} = 8 Hz, J\textsubscript{2} = 4 Hz, 2H), 7.36 (dd, J\textsubscript{1} = 8 Hz, J\textsubscript{2} = 4 Hz, 2H).

\textbf{13C NMR (100 MHz, CDCl\textsubscript{3})} \delta 12.9, 14.0, 14.4, 22.4, 28.1, 28.8, 39.2, 43.6, 68.1, 81.1, 89.6, 112.3, 114.6, 134.1, 154.3, 160.5.

HRMS (ESI) calcd. for C\textsubscript{18}H\textsubscript{25}NO\textsubscript{2} [M+H]: 288.1958, found: 288.1970.

IR (KBr, cm\textsuperscript{-1}) 3350, 2984, 2209, 1628, 1411, 1267, 787.

\textbf{N,N-diethyl-3-(3-fluorophenyl)propiolamide (3fa):}

The products 3fa were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.6 (petroleum ether/ethyl acetate = 5/1).

White solid, 87% yield, m. p. =48 °C.

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})} \delta 1.19 (t, J = 8 Hz, 3H), 1.29 (t, J = 8 Hz, 3H), 3.46 (dd, J\textsubscript{1} = 12 Hz, J\textsubscript{2} = 4 Hz, 2H), 3.63 (dd, J\textsubscript{1} = 12 Hz, J\textsubscript{2} = 4 Hz, 2H), 7.10-7.22 (m, 2H), 7.72 (m, 2H), 7.75 (m, 2H).
7.23-7.37 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 12.8, 14.4, 39.4, 43.6, 76.7, 77.1, 77.4, 82.5, 87.4, 87.4, 117.2, 117.4, 118.9, 119.1, 122.5, 122.6, 128.2, 128.2, 130.2, 130.3, 153.6, 161.0, 163.5.

HRMS (ESI) calcd. for C$_{13}$H$_{14}$FNO [M+H]: 242.0947, found: 242.0952.

IR (KBr, cm$^{-1}$) 2984, 2223, 1638, 1411, 1253, 1175, 787.

3-(4-chlorophenyl)-N,N-diethylpropionamide (3ga):

![3ga](image)

The products 3ga were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5 (petroleum ether/ethyl acetate = 5/1).

White solid, 93% yield, m. p. = 70 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.18 (t, $J$ = 8 Hz, 3H), 1.28 (t, $J$ = 8 Hz, 3H), 3.45 (dd, $J_1$ = 16 Hz, $J_2$ = 8 Hz, 2H), 3.63 (dd, $J_1$ = 16 Hz, $J_2$ = 8 Hz, 2H), 7.33-7.36 (m, 2H), 7.45-7.48 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.6, 191.4, 12.8, 14.4, 39.3, 43.6, 76.8, 77.1, 77.4, 82.8, 87.7, 119.2, 128.9, 133.5, 136.1, 153.7.

HRMS (ESI) calcd. for C$_{13}$H$_{14}$ClNO [M+H]: 236.0837, found: 236.0841.

IR (KBr, cm$^{-1}$) 2970, 2215, 1635, 1491, 1289, 1089, 845.

3-(4-bromophenyl)-N,N-diethylpropionamide (3ha):

![3ha](image)

The products 3ha were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.4 (petroleum ether/ethyl acetate = 5/1).

White solid, 91% yield, m. p. =82 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.10 (t, $J = 4$ Hz, 3H), 1.2 (t, $J = 4$ Hz, 3H), 3.37 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 3.55 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 7.30-7.33 (m, 2H), 7.41-7.45 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.8, 14.4, 39.4, 43.6, 76.8, 77.1, 77.4, 82.9, 87.8, 119.7, 124.5, 131.9, 133.7, 153.7.

HRMS (ESI) calcd. for C$_{13}$H$_{14}$BrNO [M+H]: 280.0322, found: 280.0324.

IR (KBr, cm$^{-1}$) 2934, 2202, 1618, 1413, 1297, 1055, 785.

3-(4-cyanophenyl)-N,N-diethylpropiolamide (3ia):

![3ia](attachment:image)

The products 3ia were eluted with petroleum ether/ethyl acetate (5/1). Rf = 0.4 (petroleum ether/ethyl acetate = 2/1).

Yellowish solid, 50% yield, m.p. =40°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.19 (t, $J = 4$ Hz, 3H), 1.29 (t, $J = 4$ Hz, 3H), 3.52 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 3.63 (dd, $J_1 = 16$ Hz, $J_2 = 8$ Hz, 2H), 7.62-7.69 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.8, 14.5, 39.4, 43.6, 76.8, 77.1, 77.4, 85.3, 86.6, 113.3, 118.0, 125.6, 132.2, 132.7, 153.2.

HRMS (ESI) calcd. for C$_{14}$H$_{14}$N$_2$O [M+H]: 227.1179, found: 227.1178.

IR (KBr, cm$^{-1}$) 2927, 2209, 1441, 1289, 851.

N,N-diethylhept-2-ynamide (3ja):

![3ja](attachment:image)

The products 3ja were eluted with petroleum ether/ethyl acetate (3/1). Rf = 0.4 (petroleum ether/ethyl acetate = 1/1).
Yellowish oil, 53% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (t, \(J = 8\) Hz, 3H), 1.11 (t, \(J = 8\) Hz, 3H), 1.19 (t, \(J = 8\) Hz, 3H), 1.45-1.55 (m, 2H), 1.56-1.57 (m, 2H), 3.38 (dd, \(J_1 = 16\) Hz, \(J_2 = 8\) Hz, 2H), 3.54 (dd, \(J_1 = 16\) Hz, \(J_2 = 8\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 12.8, 13.5, 14.3, 18.6, 21.9, 29.9, 39.1, 43.4, 74.3, 76.8, 77.1, 77.4, 91.8, 154.2.

HRMS (ESI) calcd. for C\(_{11}\)H\(_{20}\)NO [M+H]: 182.1537, found: 182.1539.

IR (KBr, cm\(^{-1}\)) 2962, 2212, 1628, 1283, 759.

3-phenyl-N,N-dipropylpropiolamide (3ab):

The products 3ab were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.4 (petroleum ether/ethyl acetate = 10/1)

Yellowish oil, 93% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91-1.00 (m, 6H), 1.59-1.70 (m, 4H), 3.35 (t, \(J = 8\) Hz, 2H), 3.55 (t, \(J = 8\) Hz, 2H), 7.33-7.41 (m, 3H), 7.51 (t, \(J = 4\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 11.0, 11.1, 20.5, 22.0, 46.3, 50.6, 76.7, 77.0, 77.3, 81.9, 89.0, 120.5, 128.3, 129.6, 132.0, 154.3.

HRMS (ESI) calcd. for C\(_{15}\)H\(_{20}\)NO [M+H]: 230.1539, found: 230.1540.

IR (KBr, cm\(^{-1}\)) 3306, 2970, 2209, 1618, 1419, 1139, 759.

N,N-dibenzyl-3-phenylpropiolamide (3ac):

The products 3ac were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.6
(petroleum ether/ethyl acetate = 10/1).

White solid, 91% yield, m.p. = 105 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.57 (s, 2H), 4.76 (s, 2H), 1.10 (t, $J$ = 4 Hz, 3H), 1.2 (t, $J$ = 4 Hz, 3H), 7.27-7.50 (m, 12H), 7.52 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 46.4, 51.5, 76.7, 77.0, 77.3, 81.7, 90.9, 120.4, 127.7, 127.8, 128.0, 128.5, 128.7, 28.9, 130.2, 132.5, 136.1, 136.3, 155.0.

HRMS (ESI) calcd. for C$_{23}$H$_{19}$NO [M+H]: 325.1467, found: 325.1469.

IR (KBr, cm$^{-1}$) 2962, 2352, 1655, 1455, 1267, 1023, 801.

3-ac X-ray

3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3ad):

The products 3ad were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5
1-(3,4-dihydroisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-one (3ae)

The products 3ae were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.3 (petroleum ether/ethyl acetate = 5/1).

1H NMR (400 MHz, CDCl₃) δ 2.90-2.99 (m, 2H), 3.91 (t, J = 4, 0.85H), 4.08 (t, J = 4, 1.25H), 4.82 (s, 1.23H), 4.98 (s, 0.83), 7.14-7.19 (m, 4H), 7.21-7.44 (m, 3H), 7.57-7.59 (m, 3H).

13C NMR (100 MHz, CDCl₃) δ 28.4, 29.6, 39.7, 44.1, 44.7, 48.7, 81.4, 81.5, 90.4, 91.1, 126.1, 126.5, 126.6, 126.7, 126.8, 127.0, 128.6, 128.6, 129.0, 130.1, 132.4, 132.4, 133.9, 153.4, 153.7.

HRMS (ESI) calcd. for C₁₈H₁₅NO [M+H]: 262.1226, found: 262.1224.

IR (KBr, cm⁻¹) 2934, 2202, 1618, 1413, 1297, 1055, 785.
N-benzyl-3-phenyl-N-propylpropiolamide (3af)

The products 3af were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.4 (petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 83% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87-0.97 (m, 3H), 1.56-1.68 (m, 3H), 3.33-3.55 (m, 2H), 4.68-4.87 (m, 2H), 7.28-7.56 (m, 10H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.3, 11.4, 20.3, 21.7, 45.9, 47.4, 50.0, 52.7, 81.8, 82.0, 90.0, 90.2, 127.5, 127.6, 128.1, 128.5, 128.6, 128.7, 128.8, 130.0, 132.4, 132.4, 154.8, 155.0.

HRMS (ESI) calcd. for C$_{19}$H$_{19}$NO [M+H]: 277.1467, found: 277.1462.

IR (KBr, cm$^{-1}$) 2934, 2202, 1618, 1413, 1297, 1055, 785.
6. Copies for $^1$H NMR and $^{13}$C NMR of the Compounds and 2-Ynamides products
B: IPr-Pd-NEt$_3$-Cl$_2$
3ba
n-Bu—\[\text{aryl} \equiv \text{O} \quad \text{NEt}_2\]

3ca
$3\text{ja}$
3ab

![Chemical Structure](image)
3ae