## Supplementary Material

**Efficient Assembly of Ynones via Palladium-Catalyzed Sequential Carbonylation/Alkynylation**

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## Table of Contents

- Ligand screening of alkynylation ................................................................. S2
- Synthetic procedures and analytical data for the starting materials .......... S3
- The results of alkyl substituted alkynes in the carbonylation ............... S7
- NMR spectra for all the compounds ............................................................. S8
- HMBC spectra for 3k .............................................................................. S64

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Ligand screening of alkynylation

![Chemical structures and yields](image)

[a] Reaction conditions: 1a (0.3 mmol), 2a (0.36 mmol), Pd(OAc)$_2$ (5 mol %), L (15 mol %), Cs$_2$CO$_3$ (1 equiv), toluene (1.5 mL), 80 °C, under N$_2$, 8 h.

[b] Yield was determined by NMR analysis using dibromomethane as the internal standard.
Synthetic procedures and analytical data for the starting materials

**Typical Procedure for Synthesis of Aryl Iodides 1a-h.**

The starting phenol (5.0 mmol, 1 equiv) and K$_2$CO$_3$ (10.0 mmol, 2 equiv) were suspended in DMF (0.2 M). 3-Bromo-2-methylprop-1-ene (6.5 mmol, 1.3 equiv) was added by syringe, and the reaction was heated to 70 °C overnight. After cooling, the mixture was diluted with EtOAc and transferred to a separatory funnel. The organic phase was washed twice with H$_2$O and once with brine. Drying over MgSO$_4$, filtration, and rotary evaporation provided the crude material. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding aryl iodide products 1a-h in 88%, 70%, 90%, 82%, 83%, 80%, 75%, 73% yields respectively (yields of isolated products were given).

**Typical Procedure for Synthesis of Aryl Iodides 1i.**

NaH (4.0 mmol, 1.0 equiv) and THF (10 mL) were taken in an oven-dried flask under argon. o-iodoaniline (4.0 mmol, 1.0 equiv) was added to it at 0 °C and the mixture was stirred for 30 min. Iodomethane (6.0 mmol, 1.5 equiv) was added and the reaction mixture was warmed to room temperature and stirred overnight. After that, water was added and the resulting mixture was extracted with EtOAc (3 x 25 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (pentane: Et$_2$O = 95: 5) to afford o-(N-methylamino)iodobenzene as an orange liquid in 92% (3.67 mmol) yield. N-Allylation of o-(N-methylamino)iodobenzene (1.7 mmol, 1.0 equiv) was conducted with NaH (3.4 mmol, 2.0 equiv) and 3-bromo-2-methylprop-1-
ene (8.5 mmol, 5.0 equiv) in THF (5 mL). The crude mixture after aqueous work-up was purified by flash column chromatography to afford 1i as a colorless liquid in 56% yield (yields of isolated products were given).

**Typical Procedure for Synthesis of Aryl Iodides 1j.**

To a suspension of NaH (2.0 mmol, 1.0 equiv) in DMF (10 mL) was added of N-(2-iodophenyl)acetamide (2.0 mmol, 1.0 equiv) in DMF (5 mL). When the evolution of H₂ ceased, 3-bromo-2-methylprop-1-ene (4.0 mmol, 2.0 equiv) was added. The reaction mixture was heated to 80 °C overnight. The reaction mixture was quenched with water and extracted with Et₂O. The organic phase was dried over MgSO₄ and concentrated in vacuo. The residue was separated by column chromatography on a silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product in 67% yield (yields of isolated products were given).

**References**


**Compound Data of 1a-1j**

**1-Iodo-2-((2-methylallyl)oxy)benzene (1a):** ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, J = 7.8, 1.2 Hz, 1H), 7.26 (dd, J = 12.0, 4.8 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.69 (dd, J = 11.0, 4.1 Hz, 1H), 5.19 (s, 1H), 5.01 (s, 1H), 4.46 (s, 2H), 1.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.1, 140.2, 139.4, 129.3, 122.5, 112.9, 112.3, 86.5, 72.5, 19.4.

**2-Iodo-1-((2-methylallyl)oxy)-4-(trifluoromethyl)benzene (1b):** ¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5.19 (s, 1H), 5.05 (s, 1H), 4.54 (s,
2H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.6, 139.3, 136.4 (q, $J$ = 3.7 Hz), 126.7 (q, $J$ = 3.7 Hz), 124.4 (q, $J$ = 33.1 Hz), 123.2 (q, $J$ = 271.7 Hz), 113.3, 111.4, 86.1, 72.7, 19.2.

Methyl 3-iodo-4-((2-methylallyl)oxy)benzoate (1c): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J$ = 1.9 Hz, 1H), 7.98 (dd, $J$ = 8.6, 1.9 Hz, 1H), 6.79 (d, $J$ = 8.0 Hz, 1H), 5.19 (s, 1H), 5.04 (s, 1H), 4.54 (s, 2H), 3.88 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 160.7, 141.0, 139.5, 131.4, 124.4, 113.4, 111.1, 85.8, 72.8, 52.1, 19.4.

4-Fluoro-2-iodo-1-((2-methylallyl)oxy)benzene (1d): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (dd, $J$ = 7.6, 3.0 Hz, 1H), 7.16-6.81 (m, 1H), 6.65 (dd, $J$ = 9.0, 4.6 Hz, 1H), 5.15 (s, 1H), 4.98 (s, 1H), 4.36 (s, 2H), 1.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.5 (d, $J$ = 243.6 Hz), 153.6 (d, $J$ = 2.4 Hz), 139.8, 125.8 (d, $J$ = 25.0 Hz), 115.3 (d, $J$ = 22.6 Hz), 112.9, 112.1 (d, $J$ = 8.1 Hz, 8H), 85.8 (d, $J$ = 8.5 Hz), 73.0, 19.27.

4-(tert-Butyl)-2-iodo-1-((2-methylallyl)oxy)benzene (1e): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 2.1 Hz, 1H), 7.25 (dd, $J$ = 8.6, 2.1 Hz, 1H), 6.70 (d, $J$ = 8.0 Hz, 1H), 5.17 (s, 1H), 4.98 (s, 1H), 4.42 (s, 2H), 1.84 (s, 3H), 1.26 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.1, 145.7, 140.5, 136.6, 126.3, 112.9, 111.9, 86.6, 72.7, 34.1, 31.5, 19.6.

4-Chloro-1-iodo-2-((2-methylallyl)oxy)benzene (1f): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 1.9 Hz, 1H), 6.70 (dd, $J$ = 8.3, 2.0 Hz, 1H), 5.18 (s, 1H), 5.03 (s, 1H), 4.45 (s, 2H), 1.86 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.7, 139.7, 139.5, 135.0, 122.6, 113.6, 112.9, 83.8, 72.7, 19.4.

4-Bromo-1-iodo-2-((2-methylallyl)oxy)benzene (1g): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.0 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, $J$ = 8.3, 1.4 Hz, 1H), 5.18 (s, 1H), 5.03 (s, 1H), 4.44 (s, 2H), 1.85 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 140.1, 139.5, 125.5, 122.7, 115.7, 113.3, 84.7,
72.7, 19.4.

1-Iodo-2-((2-methylallyl)oxy)naphthalene (1h): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J$ = 8.0 Hz, 1H), 7.71 (dd, $J$ = 17.9, 8.5 Hz, 2H), 7.51 (t, $J$ = 7.6 Hz, 1H), 7.35 (t, $J$ = 7.4 Hz, 1H), 7.11 (d, $J$ = 8.0 Hz, 1H), 5.23 (s, 1H), 5.03 (s, 1H), 4.60 (s, 2H), 1.90 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.8, 140.3, 135.7, 131.2, 129.9, 128.1, 128.0, 124.3, 114.1, 113.2, 88.3, 73.4, 19.6.

2-Iodo-N-methyl-N-(2-methylallyl)aniline (1i): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J$ = 8.0 Hz, 1H), 7.34 (s, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 6.83 (s, 1H), 5.07 (s, 1H), 4.96 (s, 1H), 3.54 (s, 2H), 2.67 (s, 3H), 1.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.5, 142.7, 140.0, 128.9, 125.3, 122.1, 113.3, 98.6, 63.0, 42.1, 20.7.

N-(2-Iodophenyl)-N-(2-methylallyl)acetamide (1j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 8.0 Hz, 1H), 7.38 (t, $J$ = 7.6 Hz, 1H), 7.18 (d, $J$ = 7.8 Hz, 1H), 7.11-7.02 (m, 1H), 5.00 (d, $J$ = 12 Hz, 1H), 4.84 (s, 1H), 4.67 (s, 1H), 3.35 (d, $J$ = 16 Hz, 1H), 1.82 (s, 3H), 1.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.0, 144.7, 140.4, 140.2, 130.3, 129.7, 129.3, 114.1, 100.1, 53.9, 22.8, 20.7.
The results of alkyl substituted alkynes in the carbonylation

\[
\begin{align*}
\text{R}_1^1 & \quad \text{I} \quad \text{O} \quad \text{O} \quad \text{R}_2^1 & \quad + \quad \text{R}_2^2 & \quad + \quad \text{CO} & \quad \xrightarrow{\text{Pd(OAc)}_2 (5 \text{ mol } \%), \text{L}_2 (15 \text{ mol } \%), \text{CsF (1 equiv)}, 60^\circ \text{C}, 1,4\text{-dioxane (1.5 mL)}, 8 \text{ h}} & \quad \text{R}_1^1 & \quad \text{O} \quad \text{O} \quad \text{R}_2^1 \\
1 & \quad + \quad 2 & \quad + \quad \text{CO} & \quad \xrightarrow{\text{Standard conditions}} & \quad 3 \\
\end{align*}
\]

1a + 2q + CO → Standard conditions → 3q, 42%.

1a + 2r + CO → Standard conditions → 3r, 32%.

1a + 2s + CO → Standard conditions → 3s, N.D.

1a + 2t + CO → Standard conditions → 3t, N.D.

1a + 2u + CO → Standard conditions → 3u, N.D.

1a + 2v + CO → Standard conditions → 3v, N.D.

\* Reaction condition: 1 (0.3 mmol), 2 (0.45 mmol), Pd(OAc)$_2$ (5 mol%), L$_2$ (15 mol%), CsF (1 equiv), 1,4-dioxane (1.5 mL), 60°C, CO (1 atm), 8 h. \* Yields of isolated products were given. \* L$_2$ was tris(2,4-di-tert-butylphenyl) phosphite.
NMR spectra for all the compounds

$^1$H NMR, $^{13}$C NMR of (1a)
$^1$H NMR, $^{13}$C NMR of (1b)
$^1$H NMR, $^{13}$C NMR of (1c)
$^1$H NMR, $^{13}$C NMR of (1d)
$^1$H NMR, $^{13}$C NMR of (1e)
\(^1\)H NMR, \(^{13}\)C NMR of (I)}
$^1$H NMR, $^{13}$C NMR of (lg)
$^1$H NMR, $^{13}$C NMR of (1h)
$^1$H NMR, $^{13}$C NMR of (Ii)
$^1$H NMR, $^{13}$C NMR of (Ij)
$^1$H NMR, $^{13}$C NMR of (3a)
$^1$H NMR, $^{13}$C NMR of (3b)
$^{1}H$ NMR, $^{13}C$ NMR of (3c)
$^1$H NMR, $^{13}$C NMR of (3d)
$^1$H NMR, $^{13}$C NMR of (3e)
$^1$H NMR, $^{13}$C NMR of (3f)
$^1$H NMR, $^{13}$C NMR of (3g)
$^{1}H$ NMR, $^{13}C$ NMR of (3h)
$^1$H NMR, $^{13}$C NMR of (3i)
$^1$H NMR, $^{13}$C NMR of (3j)
$^1$H NMR, $^{13}$C NMR of (3k)
$^1$H NMR, $^{13}$C NMR of (3l)
$^1$H NMR, $^{13}$C NMR of (3m)
$^1$H NMR, $^{13}$C NMR of (3n)
$^1$H NMR, $^{13}$C NMR of (3o)
$^1$H NMR, $^{13}$C NMR of (3p)
$^1$H NMR, $^{13}$C NMR of (3q)

![NMR spectra](image)

![NMR spectra](image)
$^1$H NMR, $^{13}$C NMR of (3r)
$^{1}H$ NMR, $^{13}C$ NMR of (4a)
$^{1}H$ NMR, $^{13}C$ NMR of (4c)
$^1$H NMR, $^{13}$C NMR of (4d)
$^1$H NMR, $^{13}$C NMR of (4e)
$^1$H NMR, $^{13}$C NMR of (4f)
$\text{H NMR, C NMR of (dg)}$

![H NMR and C NMR spectra of (dg)](image-url)
$^1$H NMR, $^{13}$C NMR of (4i)
$^1$H NMR, $^{13}$C NMR of (4j)
$^1$H NMR, $^{13}$C NMR of (4k)
$^{1}$H NMR, $^{13}$C NMR of (4i)
$^1$H NMR, $^{13}$C NMR of (4m)
$^1$H NMR, $^{13}$C NMR of (4n)
$^1$H NMR, $^{13}$C NMR of (4o)
$^1$H NMR, $^{13}$C NMR of (4p)
$^1$H NMR, $^{13}$C NMR of (4q)
$^{1}H$ NMR, $^{13}C$ NMR of (4r)
$^1$H NMR, $^{13}$C NMR of (4s)
$^{1}H$ NMR, $^{13}C$ NMR of (4t)
$^1$H NMR, $^{13}$C NMR of (4u)
$^1$H NMR, $^{13}$C NMR of (dv)
$^1$H NMR, $^{13}$C NMR of (4w)
$^1$H NMR, $^{13}$C NMR of (4x)
$^1$H NMR, $^{13}$C NMR of (dy)
\[ \text{H NMR, }^{13}\text{C NMR of (4z)} \]

![NMR spectra image](image_url)
$^{1}$H NMR, $^{13}$C NMR of (4ab)
$^1$H NMR, $^{13}$C NMR of (5a)
HMBC spectra for 3k