Supporting Information

Synthesis of Enaminones via Palladium-Catalyzed Four-Component Carbonylative Addition Reaction

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1. General Information

Solvents were dried and degassed before use by standard procedures. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C); CDCl$_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield ($\delta$) from TMS, the coupling constants $J$ are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. TLC was carried out on SiO$_2$ (silica gel 60 F$_{254}$, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous KMnO$_4$. Flash chromatography was carried out on SiO$_2$ (silica gel 60, 200-300 mesh). All starting materials are commercially available.

2. Experimental Procedures and Spectral Data for products 4

A mixture of aryl bromides (0.5 mmol), alkynes (0.6 mmol), amines (0.75 mmol), PdCl$_2$(PPh$_3$)$_2$ (17.5 mg, 5 mol%), Et$_3$N (209 $\mu$L, 1.5 mmol), and DMF (4.0 mL) were placed in a 25 mL autoclave with a magnetic stir bar under a N$_2$ atmosphere. The autoclave was purged with CO three times, filled with CO to 5 atm pressure, and heated to 120 $^\circ$C for 20 h. The autoclave was cooled to room temperature and the remaining CO was vented. Then water (5 mL) was added to the resultant mixture. The product was extracted with ethyl acetate (5 mL $\times$ 3), and the combined organic layers were washed with brine (5mL $\times$ 2), dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1) to afford products 4.

1-(4-Acetylphenyl)-3-(diethylamino)-3-phenylprop-2-en-1-one (4a)

Pale yellow solid (138.2 mg, 86% yield). mp 96–98 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.45–7.23 (m, 5H), 5.93 (s, 1H), 3.51–2.90 (m, 4H), 2.59 (s, 3H), 1.47–0.94(m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.0, 185.9, 164.1, 146.2, 138.2, 137.0, 128.7, 128.5, 128.1, 127.8, 127.7, 93.1, 44.8, 26.9, 14.4. IR (neat): 3474, 3059, 2976, 1683, 1625, 1479, 1461, 1439, 1357, 1265, 1213, 775 cm$^{-1}$. HRMS (EI): calcd for C$_{21}$H$_{23}$NO$_2$: 321.1729 [M]$^+$; found: 321.1735.

1-(3-Acetylphenyl)-3-(diethylamino)-3-phenylprop-2-en-1-one (4b)
Pale yellow solid (125.3 mg, 78% yield). mp 72–74 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.42 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.46–7.24 (m, 6H), 5.97 (s, 1H), 3.65–2.98 (m, 4H), 2.59 (s, 3H), 1.35–1.08 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 198.2, 185.8, 163.9, 142.5, 137.0, 136.8, 132.0, 129.8, 128.5, 128.3, 128.2, 127.8, 127.6, 92.6, 44.4, 26.8, 14.0, 12.0. IR (neat): 3352, 3060, 3025, 2975, 2933, 2238, 1684, 1629, 1592, 1577, 1518, 1462, 1434, 1379, 1357, 1194, 1069, 1000, 778 cm⁻¹. HRMS (EI): calcd for C₂₁H₂₃NO₂: 321.1729 [M⁺]; found: 321.1729.

4-(3-(Diethylamo)3-phenylacryloyl)benzaldehyde (4d)

Pale yellow solid (110.7 mg, 72% yield). mp 100–102 °C; ¹H NMR (400 MHz, CDCl₃): δ 10.02 (s, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.45–7.23 (m, 5H), 5.93 (s, 1H), 3.52–3.03 (m, 4H), 1.35–1.06 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 192.2, 185.7, 164.2, 147.5, 137.2, 136.8, 129.5, 128.7, 128.5, 128.1, 127.6, 93.0, 45.0, 44.1, 16.4, 11.6. IR (neat): 3058, 2976, 2923, 2872, 2237, 1701, 1626, 1568, 1517, 1478, 1441, 1357, 1299, 1212, 1056, 1001, 918, 805 cm⁻¹. HRMS (EI): calcd for C₂₀H₂₁NO₂: 307.1572 [M⁺]; found: 307.1574.

3-(Diethylamo)1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (4e)

Pale yellow solid (105.6 mg, 71% yield). mp 44–46 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.44–7.22 (m, 5H), 7.00 (dd, J = 8.0, 8.0 Hz, 2H), 5.90 (s, 1H), 3.51–3.04 (m, 4H), 1.30–1.15 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 185.7, 164.4 (d, J₃,F = 248.0 Hz), 163.5, 138.4, 137.2, 132.4, 129.9 (d, J₃,F = 9.0 Hz), 128.6, 128.4, 127.8, 114.8 (d, J₃,F = 19.0 Hz), 92.8, 44.4, 43.7, 14.4, 13.0. IR (neat): 3059, 2976, 2933, 2873, 2221, 1628, 1597, 1522, 1500, 1479, 1441, 1379, 1357, 1211, 1001, 896, 767 cm⁻¹. HRMS (EI): calcd for C₁₉H₂₀NOF: 297.1529 [M⁺]; found: 297.1524.

3-(Diethylamo)-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (4f)

Pale yellow solid (149.4 mg, 86% yield). mp 70–72 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.45–7.24 (m, 5H), 5.92 (s, 1H), 3.52–3.11 (m, 4H), 1.34–1.09 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 185.6, 164.2,
145.4, 136.9, 131.5 (q, $J_{CF} = 32.0$ Hz), 128.7, 128.5, 127.9, 127.6, 124.3 (q, $J_{CF} = 270.0$ Hz), 125.0 (q, $J_{CF} = 3.0$ Hz), 92.7, 44.9, 44.0, 14.5, 11.5. IR (neat): 3060, 3027, 2978, 2935, 2223, 1630, 1575, 1519, 1462, 1439, 1358, 1213, 1164, 1124, 1067, 1015, 896, 778 cm$^{-1}$. HRMS (EI): calcld for C$_{20}$H$_{20}$NOF$_3$: 347.1497 [M]$^+$; found: 347.1487.

4-(3-(Diethylamino)-3-phenylacryloyl)benzonitrile (4g)

Pale yellow solid (127.8 mg, 84% yield). mp 118–120 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.45–7.21 (m, 5H), 5.87 (s, 1H), 3.54–3.04 (m, 4H), 1.37–0.95 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 184.9, 164.6, 146.1, 136.7, 131.9, 128.7, 128.6, 128.1, 127.5, 118.9, 113.4, 92.5, 45.2, 44.4, 14.5, 11.5. IR (neat): 3069, 2976, 2933, 2227, 1625, 1557, 1517, 1479, 1460, 1440, 1380, 1357, 1289, 1213, 1057, 895, 775 cm$^{-1}$. HRMS (EI): calcld for C$_{20}$H$_{20}$N$_2$O: 304.1576 [M]$^+$; found: 304.1569.

Methyl 4-(3-(diethylamino)-3-phenylacryloyl)benzoate (4h)

Pale yellow solid (140.0 mg, 83% yield). mp 88–90 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.43–7.23 (m, 5H), 5.93 (s, 1H), 3.90 (s, 3H), 3.50–3.11 (m, 4H), 1.37–0.89 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 186.0, 166.9, 164.0, 146.2, 137.0, 131.4, 129.3, 128.6, 128.4, 127.7, 127.5, 93.0, 52.2, 44.5, 14.5, 11.8. IR (neat): 3058, 2976, 2934, 2874, 2237, 1721, 1629, 1566, 1518, 1476, 1435, 1357, 1278, 1212, 1105, 896, 770 cm$^{-1}$. HRMS (EI): calcld for C$_{21}$H$_{23}$NO$_3$: 337.1678 [M]$^+$; found: 337.1672.

3-(Diethylamino)-1,3-diphenylprop-2-en-1-one (4i)$^1$

Pale yellow oil (81 mg, 58% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.0$ Hz, 2H), 7.44–7.32 (m, 6H), 7.25 (dd, $J = 8.0$, 4.0 Hz, 2H), 5.95 (s, 1H), 3.46–3.27 (m, 4H), 1.30–1.05 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 187.1, 163.3, 142.2, 137.3, 130.5, 128.6, 128.3, 128.0, 127.8, 127.7, 93.2, 44.4, 44.3, 13.6, 12.5. IR (neat): 3058, 3025, 2974, 2932, 2871, 2220, 1630, 1575, 1521, 1474, 1434, 1379, 1357, 1285, 1213, 1095, 1053, 917, 769 cm$^{-1}$. HRMS (EI): calcld for C$_{19}$H$_{21}$NO: 279.1623 [M]$^+$; found: 279.1626.

3-(Diethylamino)-1-(naphthalen-1-yl)-3-phenylprop-2-en-1-one (4j)
Pale yellow solid (74.1 mg, 45% yield). mp 100–102 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, $J$ = 8.0 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.67 (d, $J$ = 12.0 Hz, 1H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.41–7.37 (m, 2H), 7.29 (dd, $J$ = 8.0, 8.0 Hz, 1H), 7.27–7.11 (m, 5H), 5.71 (s, 1H), 3.52–2.87 (m, 4H), 1.36–0.88 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 192.8, 163.2, 142.2, 136.3, 133.6, 130.5, 129.0, 128.3, 128.2, 128.0, 126.5, 126.1, 125.7, 125.3, 124.8, 100.0, 44.4, 13.8. IR (neat): 3056, 2974, 2931, 1628, 1577, 1514, 1472, 1432, 1379, 1357, 1086, 896, 784 cm$^{-1}$. HRMS (EI): calcd for C$_{23}$H$_{23}$NO: 329.1780 [M]$^+$; found: 329.1779.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(p-tolyl)prop-2-en-1-one (4k)

Pale yellow solid (156.0 mg, 93 % yield). mp 116–118 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 5.91 (s, 1H), 3.57–3.02 (m, 4H), 2.59 (s, 3H), 2.37 (s, 3H), 1.35–1.05 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.9, 185.9, 164.2, 146.3, 138.1, 138.0, 136.8, 129.2, 128.4, 128.0, 127.7, 124.8, 93.0, 44.9, 43.7, 26.8, 21.6, 14.2, 11.8. IR (neat): 2974, 2931, 1683, 1626, 1562, 1511, 1462, 1435, 1356, 1263, 1212, 901 cm$^{-1}$. HRMS (EI): calcd for C$_{22}$H$_{23}$NO$_2$: 335.1885 [M]$^+$; found: 335.1882.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(m-tolyl)prop-2-en-1-one (4l)

Pale yellow solid (154.3 mg, 92% yield). mp 68–70 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93 (d, $J$ = 8.0 Hz, 2H), 7.89 (d, $J$ = 8.0 Hz, 2H), 7.33–7.25 (m, 3H), 7.08 (d, $J$ = 8.0 Hz, 1H), 5.98 (s, 1H), 3.67–2.98 (m, 4H), 2.60 (s, 3H), 2.22 (s, 3H), 1.40 (t, $J$ = 8.0 Hz, 3H), 1.00 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.0, 185.1, 162.8, 146.2, 138.0, 136.5, 134.9, 130.0, 128.4, 128.1, 127.6, 127.1, 126.1, 91.8, 44.7, 43.6, 26.9, 19.1, 14.3, 11.3. IR (neat): 3476, 3069, 2975, 2932, 2872, 1683, 1625, 1561, 1517, 1478, 1403, 1379, 1356, 1264, 1213, 1176, 1075, 1040, 901, 781 cm$^{-1}$. HRMS (EI): calcd for C$_{22}$H$_{25}$NO$_2$: 335.1885 [M]$^+$; found: 335.1876.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(o-tolyl)prop-2-en-1-one (4m)

Pale yellow oil (130.8 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.32 (dd, $J$ = 8.0, 8.0 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz,
1H), 7.04 (d, J = 8.0 Hz, 2H), 5.91 (s, 1H), 3.56–3.02 (m, 4H), 2.59 (s, 3H), 2.37 (s, 3H), 1.44–0.98 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 185.9, 164.2, 146.3, 138.1, 138.0, 136.8, 129.2, 128.4, 128.1, 128.0, 127.7, 124.8, 93.0, 44.9, 44.0, 26.8, 21.6, 14.2, 11.6. IR (neat): 2975, 2932, 2872, 2237, 1683, 1626, 1562, 1517, 1478, 1440, 1379, 1356, 1264, 1212, 1075, 1058, 1006, 914, 787 cm$^{-1}$. HRMS (EI): calcd for C$_{23}$H$_{25}$NO$_2$: 335.1885 [M$^+$]; found: 335.1877.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(4-(dimethylamino)phenyl)prop-2-en-1-one (4m)

[Diagram]

Pale yellow solid (173.1 mg, 95% yield). mp 114–115 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.89 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 5.98 (s, 1H), 3.54–3.14 (m, 4H), 2.95 (s, 6H), 2.59 (s, 3H), 1.32–1.08 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.1, 186.5, 165.5, 150.5, 146.8, 137.8, 129.2, 128.0, 127.8, 123.8, 111.9, 94.0, 47.2, 45.0, 43.0, 26.9, 13.7, 11.9. IR (neat): 2974, 2931, 2804, 2236, 1682, 1612, 1560, 1511, 1443, 1356, 1264, 1212, 1074, 1055, 899, 727 cm$^{-1}$. HRMS (EI): calcd for C$_{23}$H$_{25}$NO$_2$: 364.2151 [M$^+$]; found: 364.2141.

1-(4-Acetylphenyl)-3-(4-butyphenyl)-3-(diethylamino)prop-2-en-1-one (4o)

[Diagram]

Pale yellow solid 173.7 mg, 92% yield). mp 98–100 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.91 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.91 (s, 1H), 3.55–3.03 (m, 4H), 2.65 (t, J = 8.0 Hz, 2H), 2.59 (s, 3H), 1.64 (tt, J = 8.0, 8.0 Hz, 2H), 1.43–1.08 (m, 8H), 0.94 (t, J = 8.0, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.0, 186.2, 164.4, 146.5, 143.2, 138.0, 134.1, 128.7, 128.1, 127.8, 127.7, 93.4, 44.7, 44.2, 35.7, 33.4, 26.9, 22.7, 14.2, 11.8. IR (neat): 3351, 2958, 2930, 2871, 2236, 1683, 1627, 1563, 1512, 1463, 1378, 1356, 1302, 1264, 1212, 1074, 1054, 902, 788 cm$^{-1}$. HRMS (EI): calcd for C$_{23}$H$_{25}$NO$_2$: 377.2355 [M$^+$]; found: 377.2343.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(4-methoxyphenyl)prop-2-en-1-one (4p)

[Diagram]

Pale yellow solid (165.2 mg, 94% yield). mp 104–106 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 5.92 (s, 1H), 3.83 (s, 3H), 3.57–3.08 (m, 4H), 2.60 (s, 3H), 1.34–1.06 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.9, 186.0, 164.2, 159.6, 146.3, 138.0, 129.1, 128.8, 128.0, 127.7, 114.0, 93.3, 55.2, 44.7, 44.0, 26.8, 13.6, 11.6. IR
Pale yellow solid (95.1 mg, 56% yield). mp 124–126 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.22 (dd, $J = 8.0$, 4.0 Hz, 2H), 7.14 (dd, $J = 12.0$, 8.0 Hz, 2H), 5.94 (s, 1H), 3.58–2.61 (m, 4H), 2.61 (s, 3H), 1.45–1.00 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.0, 186.0, 163.1, 162.9 (d, $J_{C-F} = 245.0$ Hz), 146.1, 138.3, 132.8, 129.7 (d, $J_{C-F} = 9.8$ Hz), 128.2, 127.7, 115.9 (d, $J_{C-F} = 18.0$ Hz), 103.4, 93.3, 44.7, 26.9, 14.2, 11.9. IR (neat): 3049, 2977, 2923, 1681, 1619, 1604, 1564, 1521, 1475, 1355, 1266, 1217, 1005, 903 cm$^{-1}$. HRMS (EI): calcd for C$_{22}$H$_{25}$NO$_3$: 351.1834 [M]$^+$; found: 351.1829.

4-(3-(4-Acetylphe nyl)-1-(diethylamino)-3-oxoprop-1-en-1-yl)benzaldehyde (4r)

Pale yellow solid (92.6 mg, 53% yield). mp 124–126 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 10.07 (s, 1H), 7.98 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 5.97 (s, 1H), 3.74–2.91 (m, 4H), 2.61 (s, 3H), 1.45–1.03 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.0, 191.9, 185.9, 162.5, 145.6, 143.7, 138.5, 136.2, 130.2, 128.6, 128.3, 127.8, 92.9, 45.2, 27.0, 12.1. IR (neat): 2977, 2933, 2876, 2732, 1701, 1683, 1623, 1607, 1562, 1518, 1481, 1462, 1382, 1213, 903 cm$^{-1}$. HRMS (EI): calcd for C$_{22}$H$_{25}$NO$_3$: 349.1678 [M]$^+$; found: 349.1675.

4-(3-(Diethylamino)-3-(4-vinylphenyl)acryloyl)benzaldehyde (4s)

Pale yellow solid (147.7 mg, 85% yield). mp 138–140 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.75 (dd, $J = 16.0$, 12.0 Hz, 1H), 5.94 (s, 1H), 5.78 (d, $J = 16.0$ Hz, 1H), 5.27 (d, $J = 8.0$ Hz, 1H), 3.55–3.02 (m, 4H), 2.59 (s, 3H), 1.36–1.04 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.9, 185.7, 163.8, 146.0, 138.0, 137.5, 136.5, 136.3, 128.0, 127.8, 127.6, 126.5, 114.3, 92.9, 44.9, 44.0, 26.8, 14.4, 11.6. IR (neat): 3086, 2986, 2933, 2872, 1682, 1621, 1562, 1520, 1462, 1401, 1380, 1356, 1265, 1213,
1075, 1055, 1013, 903, 792 cm⁻¹. HRMS (EI): calcd for C_{23}H_{25}NO_{2}: 347.1885 [M]+; found: 347.1896.

1-(4-Acetylphenyl)-3-cyclohexyl-3-(diethylamino)prop-2-en-1-one (4t)

Pale yellow solid (137.5 mg, 84% yield). mp 34–36 ºC; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 5.62 (s, 1H), 3.51–3.45 (m, 4H), 2.63 (s, 3H), 1.92–1.73 (m, 6H), 1.40–1.17 (m, 11H). ¹³C NMR (100 MHz, CDCl₃): δ 198.1, 171.5, 138.0, 128.6, 128.3, 127.7, 127.2, 92.9, 47.9, 46.1, 29.7, 27.0, 26.96, 26.0, 25.9, 15.2, 13.7. IR (neat): 2977, 2928, 2853, 1684, 1612, 1561, 1523, 1491, 1449, 1351, 1264, 1215, 1074, 1028, 908, 792 cm⁻¹. HRMS (EI): calcd for C_{21}H_{29}NO_{2}: 327.2198 [M]+; found: 323.2196.

1-(4-Acetylphenyl)-3-(diethylamino)non-2-en-1-one (4u)

Pale yellow oil (135.1 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 5.66 (s, 1H), 3.40 (q, J = 8.0 Hz, 4H), 3.15–3.01 (m, 2H), 2.62 (s, 3H), 1.63–1.50 (m, 8H), 1.25 (t, J = 8.0 Hz, 6H), 0.9 (t, J = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.9, 185.7, 167.4, 147.7, 137.8, 128.1, 127.3, 90.8, 44.3, 31.7, 28.9, 26.8, 22.7, 14.1. IR (neat): 2956, 2929, 2856, 1684, 1614, 1562, 1529, 1473, 1355, 1264, 1216, 1097, 786 cm⁻¹. HRMS (EI): calcd for C_{21}H_{31}NO_{2}: 329.2355 [M]+; found: 329.2347.

1-(4-Acetylphenyl)-3-(diethylamino)-3-(pyridin-3-yl)prop-2-en-1-one (4v)

Pale yellow solid (146.0 mg, 91% yield). mp 108–110 ºC; ¹H NMR (400 MHz, CDCl₃): δ 8.68 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.39 (dd, J = 8.0, 4.0 Hz, 1H), 6.01 (s, 1H), 3.60–3.04 (m, 4H), 2.61 (s, 3H), 1.42–1.02 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 197.8, 185.9, 160.3, 149.4, 148.2, 145.6, 138.2, 135.5, 132.9, 128.1, 127.5, 123.3, 93.7, 44.6, 26.8, 14.1, 11.5. IR (neat): 3043, 2976, 2933, 2873, 2237, 1683, 1624, 1590, 1564, 1517, 1461, 1356, 1265, 1214, 1075, 900 cm⁻¹. HRMS (EI): calcd for C_{20}H_{22}N_{2}O_{2}: 322.1681 [M]+; found: 322.1683.

1-(4-Acetylphenyl)-3-(dimethylamino)-3-phenylprop-2-en-1-one (4w)
Pale yellow solid (127.7 mg, 87% yield). mp 90–92 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.89 (d, $J$ = 8.0 Hz, 2H), 7.44–7.23 (m, 5H), 5.87 (s, 1H), 2.97 (s, 6H), 2.59 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.9, 186.1, 165.5, 145.8, 138.2, 136.8, 128.7, 128.1, 127.9, 127.8, 93.9, 40.7, 26.9. IR (neat): 3059, 2927, 2865, 1682, 1625, 1524, 1438, 1406, 1265, 1221, 932 cm$^{-1}$. HRMS (EI): calcd for C$_{19}$H$_{19}$NO$_2$: 316.1313 [M]$^+$; found: 316.1316.

1-(4-Acetylphe nyl)-3-(dibutylamino)-3-phenylprop-2-en-1-one (4x)

![](image)

Pale yellow solid (171.0 mg, 91% yield). mp120–121 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.44–7.21 (m, 5H), 5.92 (s, 1H), 3.43–3.00 (m, 4H), 2.59 (s, 3H), 1.60–0.78 (m, 14H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 197.9, 185.7, 164.3, 146.2, 138.0, 136.9, 128.5, 128.3, 128.0, 127.7, 127.6, 93.3, 50.7, 49.8, 31.1, 28.1, 26.8, 20.3, 19.8, 13.7. IR (neat): 3058, 2958, 2931, 2871, 1684, 1628, 1518, 1459, 1432, 1368, 1264, 1205, 923, 777 cm$^{-1}$. HRMS (EI): calcd for C$_{25}$H$_{31}$NO$_2$: 377.2355 [M]$^+$; found: 377.2346.

1-(4-Acetylphe nyl)-3-(butylamino)-3-phenylprop-2-en-1-one (4y)

![](image)

Pale yellow solid (74 mg, 46% yield). mp 42–44 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 11.58 (s, 1H), 7.98 (d, $J$ = 8.0 Hz, 2H), 7.95 (d, $J$ = 8.0 Hz, 2H), 7.48–7.41 (m, 5H), 5.75 (s, 1H), 3.24 (t, $J$ = 8.0 Hz, 2H), 2.62 (s, 3H), 1.61–1.35 (m, 4H), 0.88 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 198.0, 186.7, 167.8, 144.4, 138.4, 135.5, 129.8, 128.7, 128.4, 127.7, 127.3, 93.6, 44.7, 32.8, 27.0, 20.0, 13.8. IR (neat): 3297, 3059, 2957, 2930, 2871, 1684, 1649, 1593, 1567, 1499, 1483, 1332, 1299, 1262, 783, 766 cm$^{-1}$. HRMS (EI): calcd for C$_{23}$H$_{23}$NO$_2$: 321.1729 [M]$^+$; found: 321.1727.

3. Experimental Procedures and Spectral Data of product 5a

A mixture of 1-(4-bromophenyl)ethanone (99.5 mg, 0.5 mmol), phenylacetylene (61.3 mg, 0.6 mmol), diethylamine (77.3 µL, 0.75 mmol), PdCl$_2$(PPh$_3$)$_2$ (17.5 mg, 5 mol%), and DMF (4.0 mL) were placed in a 25 mL autoclave with a magnetic stir bar under a N$_2$ atmosphere. The autoclave was purged with CO three times, filled with CO to 5 atm pressure, and heated to 120 °C for 20 h. The autoclave was cooled to room temperature and the remaining CO was vented. Then water (5 mL) was added to the resultant mixture. The product was extracted with ethyl acetate (5 mL × 3), and the combined organic layers were washed with brine (5mL × 2), dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue obtained was purified
via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford products 5.

**4-Acetyl-N,N-diethylbenzamide (5a)**

Pale yellow oil (100.9 mg, 92% yield). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 2H), 3.54 (q, $J$ = 6.4 Hz, 2H), 3.19 (q, $J$ = 6.8 Hz, 2H), 2.60 (s, 3H), 1.24 (t, $J$ = 6.4 Hz, 3H), 1.08 (t, $J$ = 6.8 Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 197.4, 170.1, 141.5, 137.3, 128.4, 126.4, 43.2, 39.3, 26.6, 14.1, 12.8.
4. Copies of $^1$H and $^{13}$C NMR Spectra
O\text{NEt}_2\text{COMe}
5. References