

Decarboxylative Allylation of Amino Alkanoic Acids and Esters via Dual Catalysis.

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General Information:

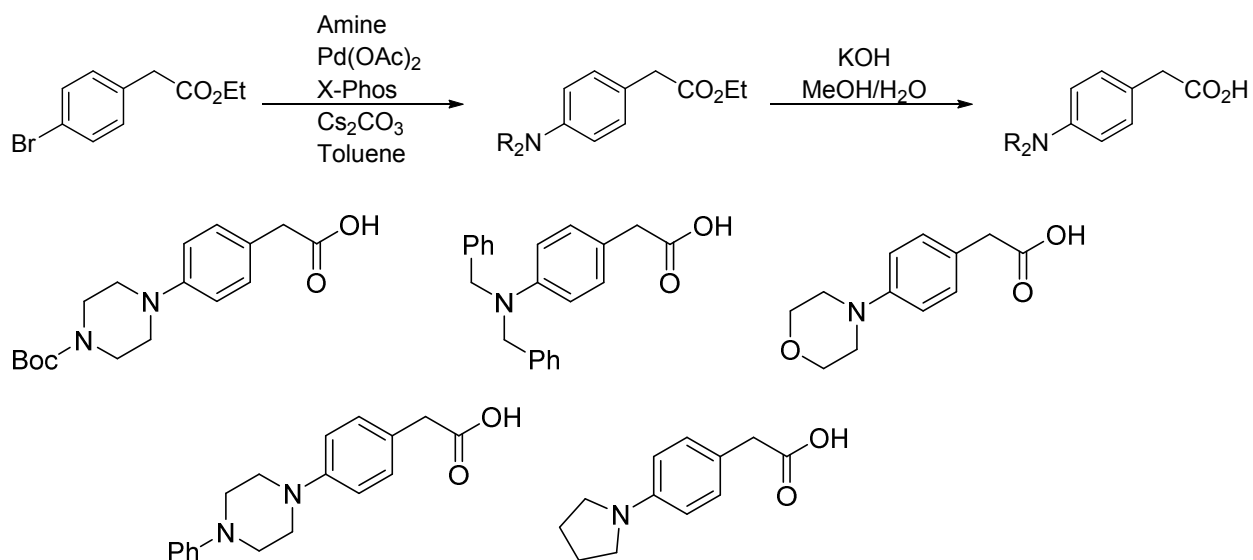
TLC analysis was performed with silica gel HL TLC plates w/UV254 from Sorbent Technologies. 60 Å porosity, 230 x 400 mesh standard grade silica gel from Sorbent Technologies was used for column chromatography. GC/MS data was obtained using a Shimadzu GCMS-QP2010 SE. ¹H and ¹³C spectra were obtained on a Bruker Advance 500 DRX equipped with a QNP cryoprobe or a Bruker Advance 400. ¹H and ¹³C NMR spectra were referenced to residual protio solvent signals.

All final reactions were run in oven dried 2.0 – 5.0 mL microwave vials from Biotage using a TCP 14W white LED bulb (LED14E26P3027KFL). Acetonitrile, allyl methyl carbonate and palladium tetrakis were purchased from Sigma Aldrich. The photocatalyst Ir(ppy)₂(bpy)[BF₄] was synthesized according to a literature procedure.¹ Compound **3a** is a known compound. The ¹H NMR was identical to literature values.²

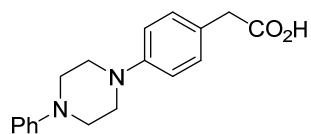
Synthesis of Starting Materials:

4-(Dimethylamino)phenylacetic acid was purchased from Sigma Aldrich.

The following carboxylic acids were prepared according to a literature procedure³:



The characterization data for the novel phenylpiperazine analog is presented below:



1H NMR Spectra (500 MHz, $CDCl_3$):

δ 7.30 (dd, $J = 8.70, 7.25$ Hz, 2H), 7.21 (d, $J = 8.60$ Hz, 2H), 6.96 (m, 5H), 3.59 (s, 2H), 3.34 (s, 8H).

^{13}C NMR (126 MHz, $CDCl_3$):

δ 175.81, 151.18, 150.43, 130.11, 129.20, 124.65, 120.18, 116.47, 116.42, 49.43, 49.36, 39.86.

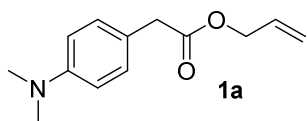
HRMS:

M+H calc: 297.1603, M+H found: 297.1599.

Synthesis of para amino substituted phenyl acetic allyl esters

Reactions were typically run on a 1 to 5 mmol scale.

General procedure: To a cooled (0 °C) stirred solution under argon of the para amino phenylacetic acid (1.0 eq) in DCM (20 mL) was added base (Et₃N or Hunig's base, 2.5 eq), followed by allyl alcohol (1.3 eq), and then coupling reagent (1.3 eq). The solution was allowed to warm to rt and stirred overnight. The solvent was evaporated and the crude product purified by flash chromatography.



DCC and catalytic DMAP (no base) were used. 72% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

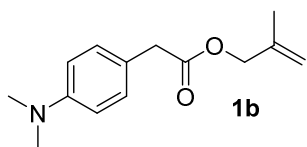
δ 7.16 (d, *J* = 8.62 Hz, 2H), 6.70 (d, *J* = 8.67 Hz, 2H), 5.90 (m, 1H), 5.25 (m, 2H), 4.58 (dt, *J* = 5.64, 1.40 Hz, 2H), 3.55 (s, 2H), 2.93 (s, 6H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.96, 149.76, 132.21, 129.89, 121.73, 118.09, 112.78, 65.32, 40.70, 40.36.

HRMS:

M+H calc: 220.1338, M+H found: 220.1332.



PyBOP and β-methallyl alcohol were used. 44% yield.

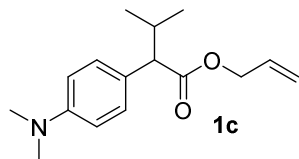
¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.16 (d, *J* = 8.64 Hz, 2H), 6.70 (d, *J* = 8.67 Hz, 2H), 4.91 (d, *J* = 15.70 Hz, 2H), 4.50 (s, 2H), 3.56 (s, 2H), 2.93 (s, 6H), 1.72 (s, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 171.97, 149.76, 139.96, 129.90, 121.79, 112.78, 112.74, 67.84, 40.70, 40.42, 19.50.

HRMS:

M+H calc: 234.1494, M+H found: 234.1490.



10 mL of DMF was added to 4-dimethylamino phenylacetic acid allyl ester (0.91 mmol) in a Schlenk flask under argon. The solution was cooled to 0 °C and KO^tBu (0.91 mmol) was added followed by 2-bromopropane (0.91 mmol). After stirring overnight at room temperature, the reaction mixture was taken up in EtOAc, washed with water, dried, concentrated, and purified by flash column chromatography to give the desired product in a 70% yield.

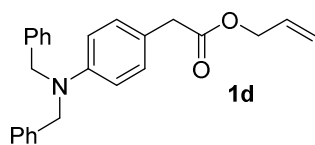
¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.19 (d, *J* = 8.71 Hz, 2H), 6.68 (d, *J* = 8.72 Hz, 2H), 5.87 (m, 1H), 5.21 (m, 2H), 4.59 (ddt, *J* = 13.41, 5.67, 1.45 Hz, 1H), 4.49 (ddt, *J* = 13.42, 5.61, 1.46 Hz, 1H), 3.07 (d, *J* = 10.62 Hz, 1H), 2.93 (s, 6H), 2.30 (m, 1H), 1.02 (d, *J* = 6.51 Hz, 3H), 0.72 (d, *J* = 6.69 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃):

δ 174.21, 149.75, 132.34, 129.10, 126.17, 117.90, 112.50, 64.95, 59.14, 40.62, 31.83, 21.50, 20.26.

HRMS: M+H calc: 262.1807, M+H found: 262.1809.



EDCI HCl was used as the coupling reagent, 61% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

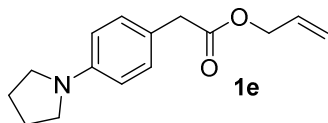
δ 7.32 (m, 4H), 7.25 (m, 6H), 7.08 (d, *J* = 6.86 Hz, 2H), 6.69 (d, *J* = 8.11 Hz, 2H), 5.90 (m, 1H), 5.24 (m, 2H), 4.64 (s, 4H), 4.58 (d, *J* = 4.50 Hz, 2H), 3.53 (s, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.96, 148.24, 138.53, 132.19, 130.06, 128.65, 126.90, 126.63, 121.79, 118.12, 112.50, 65.33, 54.23, 40.24.

HRMS:

M+H calc: 372.1964, M+H found: 372.1976.



EDCI HCl was used. 32% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

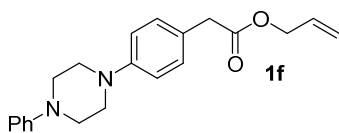
δ 7.14 (d, *J* = 8.56 Hz, 2H), 6.52 (d, *J* = 8.59 Hz, 2H), 5.90 (m, 1H), 5.24 (m, 2H), 4.58 (dt, *J* = 5.67, 1.42 Hz, 2H), 3.54 (s, 2H), 3.26 (m, 4H), 1.99 (m, 4H).

¹³C NMR (126 MHz, CDCl₃):

δ 172.11, 147.08, 132.25, 129.95, 120.37, 118.04, 111.70, 65.27, 47.64, 40.46, 25.47.

HRMS:

M+H calc: 246.1494, M+H found: 246.1489.



EDCI HCl was used. 88% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

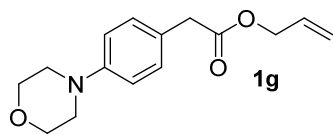
δ 7.31 (m, 2H), 7.24 (m, 2H), 7.01 (m, 2H), 6.97 (m, 2H), 6.92 (tt, *J* = 7.35, 1.06 Hz, 1H), 5.93 (m, 1H), 5.27 (m, 2H), 4.61 (dt, *J* = 5.66, 1.43 Hz, 2H), 3.61 (s, 2H), 3.35 (s, 8H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.68, 151.25, 150.34, 132.15, 130.06, 129.22, 125.31, 120.12, 118.23, 116.47, 116.39, 65.43, 49.46, 49.43, 40.46.

HRMS:

M+H calc: 337.1916, M+H found: 337.1913.



PyBOP was used, 55% yield over two steps from the ethyl ester which was hydrolyzed according to the procedure in ref 3.

¹H NMR Spectra (500 MHz, CDCl₃):

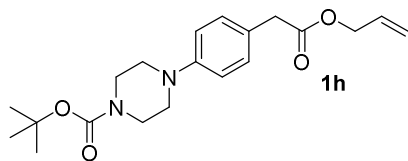
δ 7.20 (d, *J* = 8.61 Hz, 2H), 6.87 (d, *J* = 8.65 Hz, 2H), 5.90 (m, 1H), 5.24 (m, 2H), 4.58 (dt, *J* = 5.72, 1.46 Hz, 2H), 3.85 (m, 4H), 3.57 (s, 2H), 3.14 (m, 4H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.64, 150.36, 132.10, 130.03, 125.29, 118.20, 115.82, 66.91, 65.41, 49.37, 40.40.

HRMS:

M+H calc: 262.1443, M+H found: 262.1448.



EDCI HCl was used. 55% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.19 (d, *J* = 8.59 Hz, 2H), 6.88 (d, *J* = 8.61 Hz, 2H), 5.90 (m, 1H), 5.24 (m, 2H), 4.58 (dt, *J* = 5.68, 1.42 Hz, 2H), 3.57 (m, 6H), 3.11 (t, *J* = 5.12 Hz, 4H), 1.48 (s, 9H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.61, 154.73, 150.36, 132.09, 130.04, 125.53, 118.21, 116.73, 79.90, 65.41, 49.44, 40.40, 28.44.

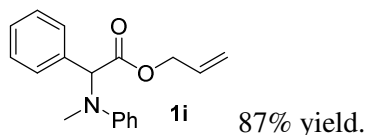
HRMS:

M+H calc: 361.2127, M+H found: 361.2133.

General procedure for the synthesis of α -amino allyl esters:

Reactions were typically run on the 4 mmol scale.

α -bromo phenylacetic acid allyl ester (1.0 eq) in DMF (20 mL) was cooled to 0 °C under argon. The secondary amine (1.0 eq), K_2CO_3 (1.0 eq), and tetrabutyl ammonium iodide (0.25 eq) were added and the reaction stirred at room temperature overnight. The solution was taken up in EtOAc, washed with water, dried, concentrated, and purified by flash column chromatography.



1H NMR Spectra (500 MHz, $CDCl_3$):

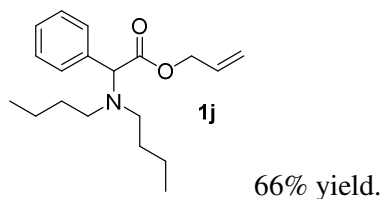
δ 7.34 (m, 7H), 6.89 (m, 2H), 6.82 (m, 1H), 5.90 (m, 1H), 5.70 (s, 1H), 5.26 (m, 2H), 4.71 (m, 2H), 2.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$):

δ 171.56, 149.86, 135.81, 131.71, 129.29, 128.67, 128.45, 128.11, 118.87, 118.08, 113.48, 65.74, 65.62, 34.55.

HRMS:

M+H calc: 282.1494, M+H found: 282.1498.



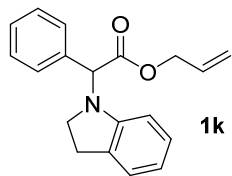
1H NMR Spectra (500 MHz, $CDCl_3$):

δ 7.38 (m, 2H), 7.31 (m, 3H), 5.90 (m, 1H), 5.24 (m, 2H), 4.64 (m, 2H), 4.59 (s, 1H), 2.54 (t, $J = 7.44$ Hz, 4H), 1.39 (m, 4H), 1.21 (m, 4H), 0.83 (t, $J = 7.35$ Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$):

δ 172.15, 137.37, 132.06, 128.78, 128.19, 127.70, 118.42, 68.85, 65.01, 50.39, 29.69, 20.36, 14.01.

HRMS: M+H calc: 304.2277, M+H found: 304.2269.



1k
53% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

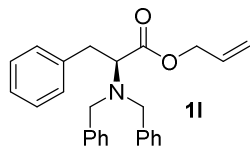
δ 7.38 (m, 5H), 7.06 (m, 2H), 6.69 (td, *J* = 7.41, 0.93 Hz, 1H), 6.46 (d, *J* = 7.98 Hz, 1H), 5.86 (m, 1H), 5.31 (s, 1H), 5.22 (m, 2H), 4.67 (m, 2H), 3.65 (q, *J* = 9.42, 8.60 Hz, 1H), 3.14 (ddd, *J* = 9.71, 8.52, 5.63, 1H), 2.93 (m, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 170.94, 150.86, 135.10, 131.68, 130.28, 128.71, 128.68, 128.35, 127.16, 124.67, 118.75, 118.35, 106.80, 65.56, 63.79, 49.81, 28.17.

HRMS:

M+H calc: 294.1494, M+H found: 294.1487.



1l
Boc-Phe-OH (7.54 mmol) was dissolved in DMF (20 mL) and cooled to 0 °C under argon. K₂CO₃ (10 mmol) and tetrabutyl ammonium bromide (1 mmol) were added followed by allyl bromide (8.5 mmol). The reaction was stirred at room temperature overnight. The mixture was taken up in EtOAc and washed with water, dried, and concentrated. The residue was purified by column chromatography and then treated with 30% by volume of TFA/DCM until TLC indicated complete conversion to the free amine. The mixture was washed with aq K₂CO₃ to provide the phenyl alanine allyl ester in a 81% yield over two steps.

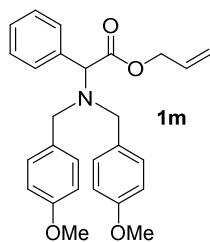
The ester (6.09 mmol) was dissolved in MeCN (25 mL) under argon and benzyl bromide (13.4 mmol) was added followed by Hunig's base (15 mmol). The mixture was refluxed overnight, concentrated, and purified by column chromatography to provide the desired dibenzyl allyl ester in 62% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.26 (m, 9H), 7.19 (m, 4H) 7.03 (m, 2H), 5.95 (m, 1H), 5.30 (m, 2H), 4.65 (m, 2H), 3.97 (d, *J* = 13.99 Hz, 2H), 3.71 (t, *J* = 7.73 Hz, 1H), 3.58 (d, *J* = 13.91 Hz, 2H), 3.14 (dd, *J* = 13.96, 7.20 Hz, 1H), 3.02 (dd, *J* = 13.98, 8.31 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 171.99, 139.25, 138.09, 132.17, 129.47, 128.71, 128.17, 126.93, 126.28, 118.53, 64.97, 62.33, 54.41, 35.76.

HRMS: M+H calc: 386.2120, M+H found: 386.2121.



Prepared according to the general procedure. 40% yield.

¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.34 (d, *J* = 4.35 Hz, 4H), 7.29 (m, 1H), 7.24 (d, *J* = 8.62 Hz, 4H), 6.85 (m, 4H), 5.95 (m, 1H), 5.29 (m, 2H), 4.71 (m, 2H), 4.62 (m, 1H), 3.79 (s, 6H), 3.66 (q, *J* = 13.75, 10.5 Hz, 4H).

¹³C NMR (126 MHz, CDCl₃):

δ 171.87, 158.63, 136.79, 132.045, 131.55, 129.91, 128.80, 128.31, 127.75, 118.65, 113.63, 65.59, 65.00, 55.25, 53.29.

HRMS:

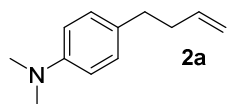
M+H calc: 432.2175, M+H found: 432.2165.

Example experimental procedure for allyl esters:

An oven dried 2.0 – 5.0 mL Biotage microwave vial charged with a stirbar was taken into the glovebox. Pd(PPh₃)₄ and Ir(ppy)₂(bpy)[BF₄] (2.5 mol% and 0.5 mol%, respectively) were added to the vial followed by 2.5 mL MeCN. The vial was capped with a Biotage cap using a crimper and removed from the glovebox. Allyl ester (0.25 mmol) was added via syringe and the vial was placed into a 25 °C water bath directly in front of a white LED. After stirring for 2 hours, the reaction mixture was analyzed by GC/MS and loaded directly onto a flash column.

Example experimental procedure for carboxylic acids:

An oven dried 2.0 – 5.0 mL Biotage microwave vial charged with a stirbar was taken into the glovebox. Pd(PPh₃)₄ and Ir(ppy)₂(bpy)[BF₄] (2.5 mol% and 0.5 mol%, respectively) were added to the vial followed by the carboxylic acid (0.25 mmol), and 2.5 mL MeCN. The vial was capped with a Biotage cap using a crimper and removed from the glovebox. Allyl methyl carbonate (0.25 mmol) was added via syringe and the vial was placed into a 25 °C water bath directly in front of a white LED. After stirring for 2 hours the reaction mixture was analyzed by GC/MS and loaded directly onto a flash column.



¹H NMR Spectra (500 MHz, CDCl₃):

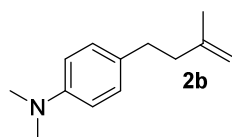
δ 7.08 (d, *J* = 8.23 Hz, 2H), 6.71 (d, *J* = 8.63 Hz, 2H), 5.88 (m, 1H), 5.01 (m, 2H), 2.92 (s, 6H), 2.63 (m, 2H), 2.34 (m, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 149.04, 138.57, 130.12, 128.98, 114.60, 112.96, 40.94, 35.91, 34.38.

HRMS:

M+H calc: 176.1439, M+H found: 176.1433.



¹H NMR Spectra (500 MHz, CDCl₃):

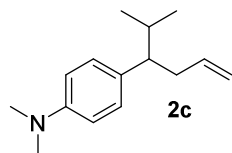
δ 7.09 (d, *J* = 8.51 Hz, 2H), 6.71 (d, *J* = 8.53 Hz, 2H), 4.73 (d, *J* = 5.83 Hz, 2H), 2.92 (s, 6H), 2.67 (m, 2H), 2.29 (dd, *J* = 9.82, 6.53 Hz, 2H), 1.77 (s, 3H).

¹³C NMR (126 MHz, CDCl₃):

δ 149.01, 145.86, 130.49, 128.86, 113.01, 109.91, 40.96, 39.99, 33.23, 22.68.

HRMS:

M+H calc: 190.1596, M+H found: 190.1522.



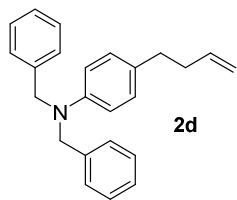
¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.00 (d, *J* = 8.67 Hz, 2H), 6.70 (d, *J* = 8.68 Hz, 2H), 5.64 (m, 1H), 4.92 (m, 2H), 2.93 (s, 6H), 2.49 (m, 1H), 2.36 (m, 2H), 1.83 (m, 1H), 0.94 (d, *J* = 6.68 Hz, 3H), 0.76 (d, *J* = 6.77 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃):

δ 147.82, 137.10, 130.63, 128.18, 114.04, 111.28, 50.59, 39.75, 36.35, 31.82, 19.95, 18.97.

HRMS: M+H calc: 218.1909, M+H found: 218.1892.



¹H NMR Spectra (500 MHz, CDCl₃):

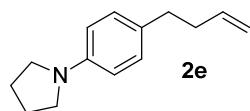
δ 7.33 (m, 4H), 7.25 (m, 6H), 7.00 (d, *J* = 8.46 Hz, 2H), 6.68 (d, *J* = 8.53 Hz, 2H), 5.88 (m, 1H), 5.01 (m, 2H), 4.63 (s, 4H), 2.60 (dd, *J* = 9.29, 6.57 Hz, 2H), 2.32 (q, *J* = 7.13, 6.94 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 146.37, 137.78, 137.55, 128.96, 128.02, 127.55, 125.77, 125.65, 113.51, 111.46, 53.28, 34.74, 33.29.

HRMS:

M+H calc: 328.2065, M+H found: 328.2055



¹H NMR Spectra (500 MHz, CDCl₃):

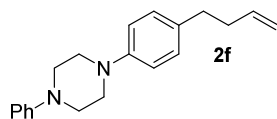
δ 7.07 (d, *J* = 8.10 Hz, 2H), 6.54 (s, 2H), 5.88 (m, 1H), 5.01 (m, 2H), 3.27 (s, 4H), 2.62 (dd, *J* = 9.07, 6.68 Hz, 2H), 2.34 (m, 2H), 2.00 (s, 4H).

¹³C NMR (126 MHz, CDCl₃):

δ 146.25, 138.63, 129.10, 114.56, 111.62, 47.76, 36.06, 34.48, 25.42.

HRMS:

M+H calc: 202.1596, M+H found: 202.1586.



¹H NMR Spectra (500 MHz, CDCl₃):

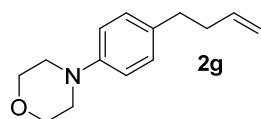
δ 7.30 (dd, *J* = 8.76, 7.27 Hz, 2H), 7.12 (d, *J* = 8.56 Hz, 2H), 7.00 (m, 2H), 6.92 (m, 3H), 5.87 (m, 1H), 5.01 (m, 2H), 3.32 (m, 8H), 2.65 (dd, *J* = 8.97, 6.70 Hz, 2H), 2.36 (m, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 151.27, 149.40, 138.32, 133.62, 129.18, 129.10, 120.03, 116.51, 116.33, 114.79, 49.80, 49.47, 35.71, 34.49.

HRMS:

M+H calc: 293.2018, M+H found: 293.2012.



¹H NMR Spectra (500 MHz, CDCl₃):

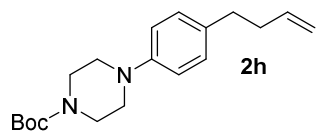
δ 7.11 (d, *J* = 8.55 Hz, 2H), 6.86 (d, *J* = 8.52 Hz, 2H), 5.86 (m, 1H), 5.00 (m, 2H), 3.86 (m, 4H), 3.13 (m, 4H), 2.64 (m, 2H), 2.34 (m, 2H).

¹³C NMR (126 MHz, CDCl₃):

δ 149.43, 138.29, 133.57, 129.11, 115.85, 114.79, 67.00, 49.72, 35.69, 34.45.

HRMS:

M+H calc: 218.1545, M+H found: 218.1541.



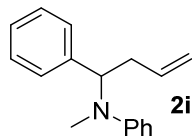
¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.10 (d, *J* = 8.68 Hz, 2H), 6.87 (d, *J* = 8.58 Hz, 2H), 5.85 (m, 1H), 4.99 (m, 2H), 3.57 (t, *J* = 6.25 Hz, 4H), 3.09 (t, *J* = 5.47 Hz, 4H), 2.64 (dd, *J* = 8.95, 6.70 Hz, 2H), 2.34 (m, 2H), 1.48 (s, 9H).

¹³C NMR (126 MHz, CDCl₃):

δ 154.76, 149.43, 138.26, 133.88, 129.11, 116.81, 114.80, 79.86, 49.82, 35.67, 34.46, 28.45.

HRMS: M+H calc: 317.2229, M+H found: 317.2223.



¹H NMR Spectra (500 MHz, CDCl₃):

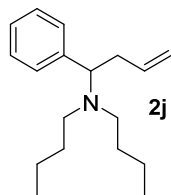
δ 7.30 (m, 4H), 7.24 (m, 3H), 6.83 (d, $J = 8.13$ Hz, 2H), 6.73 (t, $J = 7.24$ Hz, 1H), 5.84 (m, 1H), 5.16 (dq, $J = 17.06, 1.63$ Hz, 1H), 5.05 (m, 2H), 2.81 (m, 2H), 2.72 (s, 3H).

¹³C NMR (126 MHz, CDCl₃):

δ 150.55, 141.08, 135.81, 129.17, 128.40, 127.22, 127.04, 116.85, 116.63, 113.02, 61.37, 36.13, 31.87.

HRMS:

M+H calc: 238.1596, M+H found: 238.1591.



¹H NMR Spectra (500 MHz, CDCl₃):

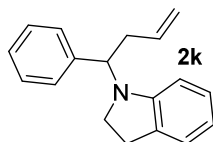
δ 7.29 (m, 2H), 7.24 (m, 3H), 5.71 (m, 1H), 4.96 (m, 2H), 3.72 (dd, $J = 8.80, 5.79$ Hz, 1H), 2.64 (dt, $J = 13.85, 6.78$ Hz, 1H), 2.50 (dt, $J = 12.30, 7.60$ Hz, 3H), 2.23 (m, 2H), 1.39 (m, 4H), 1.26 (m, 4H), 0.87 (t, $J = 7.32$ Hz, 6H).

¹³C NMR (126 MHz, CDCl₃):

δ 140.69, 136.72, 128.56, 127.56, 126.47, 115.60, 64.11, 49.49, 36.05, 30.03, 20.38, 13.94.

HRMS:

M+H calc: 260.2378, M+H found: 260.2377.



This material is ~95% pure by ^1H NMR spectroscopy. The suspected contaminant is thought to be *N*-benzylindoline (singlet at 4.26 ppm).

^1H NMR Spectra (500 MHz, CDCl_3):

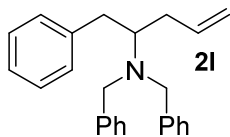
δ 7.33 (m, 4H), 7.26 (m, 1H), 7.02 (m, 2H), 6.58 (t, $J = 7.32$ Hz, 1H), 6.47 (d, $J = 7.75$ Hz, 1H), 5.83 (m, 1H), 5.08 (m, 2H), 4.69 (t, $J = 7.60$ Hz, 1H), 3.49 (m, 1H), 3.30 (m, 1H), 2.93 (m, 2H), 2.77 (ddt, $J = 8.00, 6.76, 1.41$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3):

δ 151.32, 140.15, 135.73, 129.63, 128.34, 127.87, 127.22, 127.19, 124.46, 116.84, 116.67, 106.57, 58.91, 47.17, 35.55, 28.15.

HRMS:

M+H calc: 250.1596, M+H found: 250.1596.



^1H NMR Spectra (500 MHz, CDCl_3):

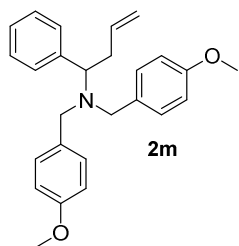
δ 7.25 (m, 10H), 7.20 (m, 3H), 7.03 (m, 2H), 5.75 (m, 1H), 5.01 (m, 2H), 3.71 (d, $J = 13.83$ Hz, 2H), 3.63 (d, $J = 13.78$ Hz, 2H), 2.96 (m, 2H), 2.57 (m, 1H), 2.45 (m, 1H), 2.08 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3):

δ 139.57, 139.07, 136.37, 128.37, 127.68, 127.07, 127.04, 125.65, 124.68, 114.78, 58.37, 52.18, 34.78, 33.37.

HRMS:

M+H calc: 342.2222, M+H found: 342.2215.



¹H NMR Spectra (500 MHz, CDCl₃):

δ 7.38 (t, $J = 7.62$ Hz, 2H), 7.30 (d, $J = 8.44$ Hz, 5H), 7.24 (d, $J = 7.72$ Hz, 2H), 6.87 (d, $J = 8.24$ Hz, 4H), 5.80 (m, 1H), 5.04 (m, 2H), 3.81 (m, 7H), 3.74 (d, $J = 13.59$ Hz, 2H), 3.13 (d, $J = 13.54$ Hz, 2H), 2.85 (m, 1H), 2.57 (m, 1H).

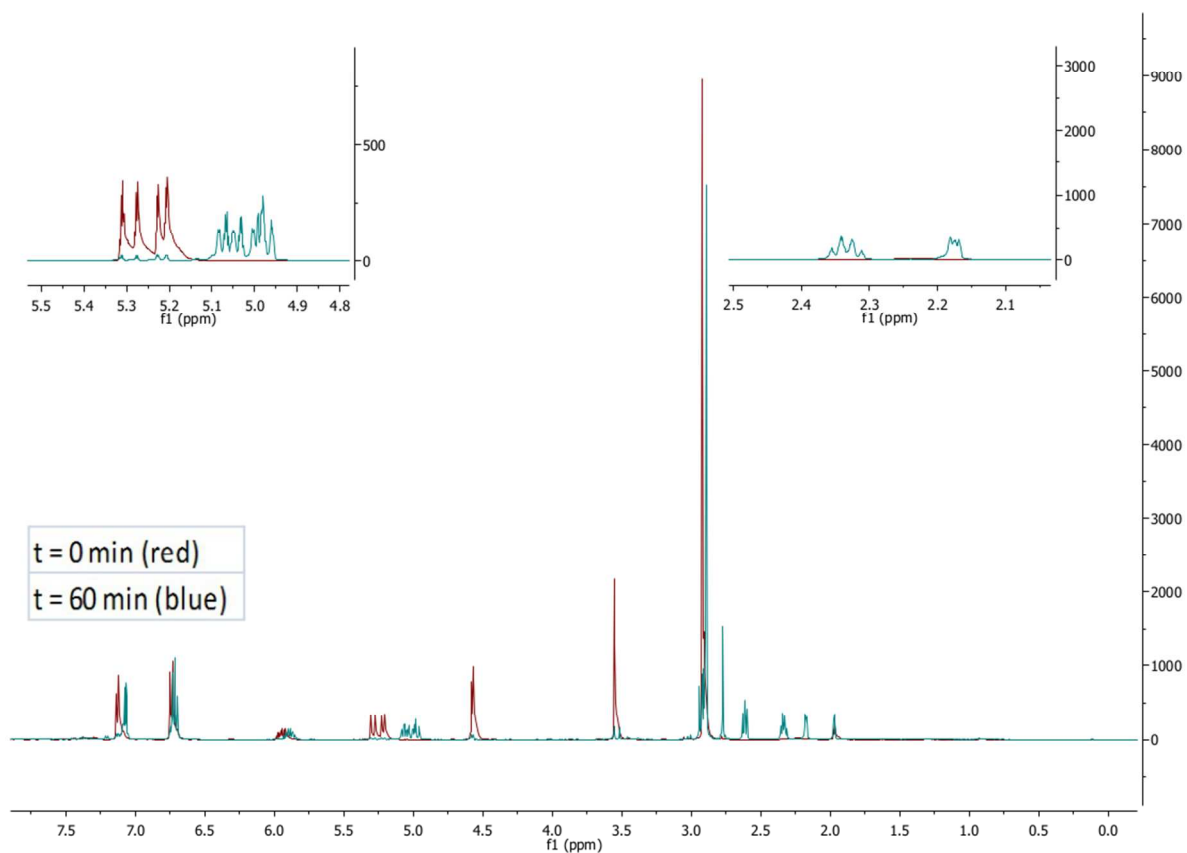
¹³C NMR (126 MHz, CDCl₃):

δ 158.48, 138.79, 136.85, 132.28, 129.82, 128.97, 127.90, 127.00, 116.00, 113.58, 61.17, 55.26, 52.60, 35.21.

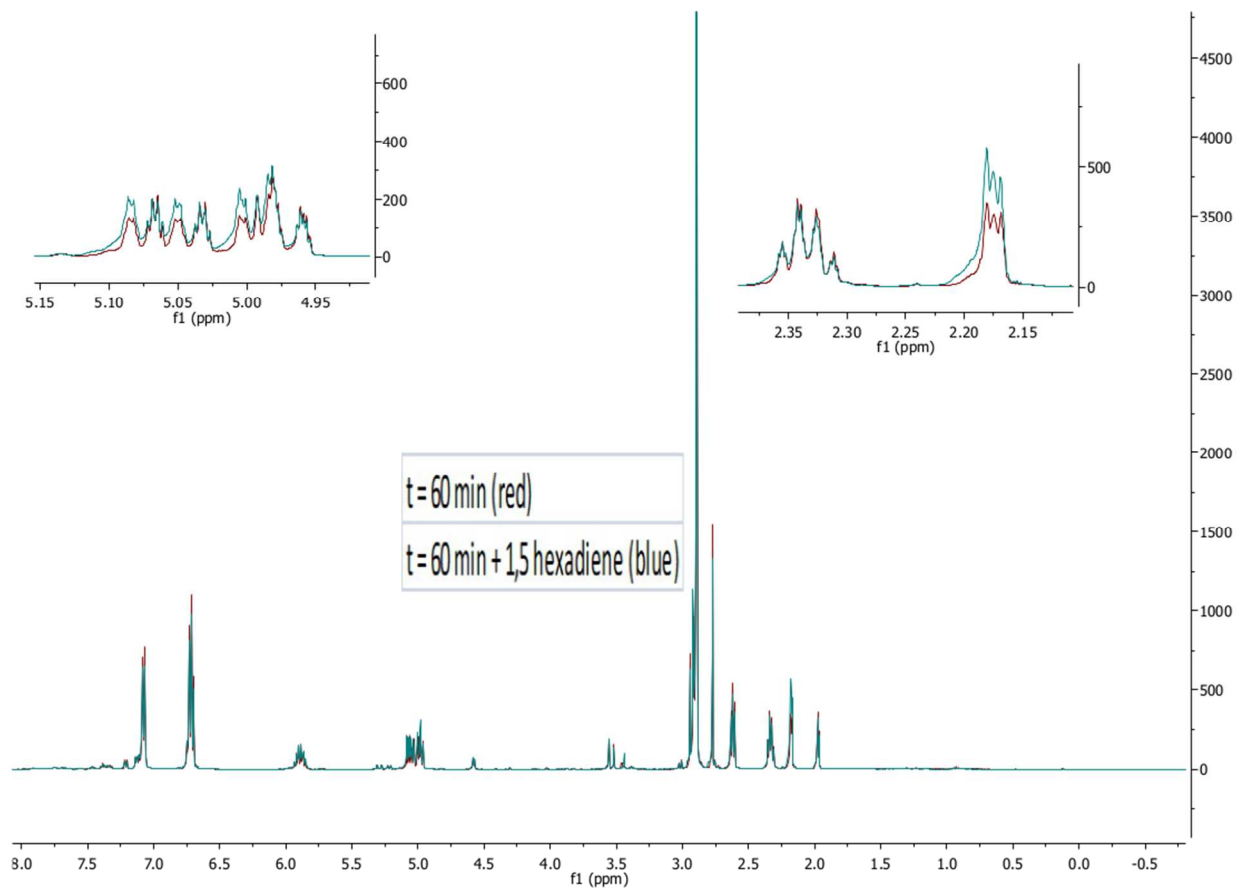
HRMS:

M+H calc: 388.2277, M+H found: 388.2262.

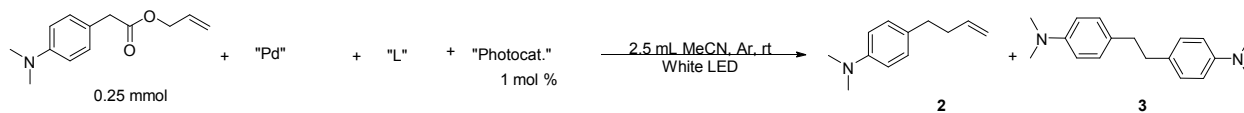
¹H NMR Experimental Procedure: An oven dried flask was charged with 0.25 mmol **1a**, 2.5 mol % Pd(PPh₃)₄, 0.5 mol % Ir(ppy)₂(bpy)[BF₄], and 2.5 mL CD₃CN in a glovebox. 1.0 mL of the reaction mixture was added to an NMR tube which was then capped and removed from the glovebox. A time = 0 mins ¹H NMR spectrum was recorded. The NMR tube was placed in a 25 °C water bath directly in front of a white LED for 1h. A time = 60 mins ¹H NMR spectrum was recorded. Immediately after, 30 μL of 1,5 hexadiene was added to the NMR tube and an additional ¹H NMR was obtained.



After the addition of 1,5 hexadiene the peak intensity at 5.08, 5.05, 5.01, 4.98, and 2.17 ppm selectively increased which confirms the presence of allyl dimer in the reaction mixture



Selected Pd/L Screening Results:



<u>Pd Source</u>	<u>Ligand</u>	<u>photocat.</u>	<u>2:3</u>
2.5 mol % Pd(PPh ₃) ₄	-	Ru(bpy) ₃ [BF ₄] ₂	70:30
5 mol % Pd(PPh ₃) ₄	-	Ir(ppy) ₂ (bpy)[BF ₄]	63:37
5 mol % CpPdallyl	6 mol % bpy	Ir(ppy) ₂ (bpy)[BF ₄]	low conv.
5 mol % CpPdCinnamyl	6 mol % bpy	Ir(ppy) ₂ (bpy)[BF ₄]	low conv.
5 mol % Pd(II)OAc ₂	11 mol % TFP	Ir(ppy) ₂ (bpy)[BF ₄]	68:32
5 mol % Pd(II)OAc ₂	11 mol % PCy ₃	Ir(ppy) ₂ (bpy)[BF ₄]	66:34
5 mol % Pd(II)OAc ₂	6 mol % (S,S)-Anden Phenyl Trost	Ir(ppy) ₂ (bpy)[BF ₄]	66:33
2.5 mol % Pd ₂ dba ₃	6 mol % (S,S)-Anden Phenyl Trost	Ir(ppy) ₂ (bpy)[BF ₄]	58:42
2.5 mol % Pd(II)OAc ₂	4 mol % dppf	Ru(bpy) ₃ [BF ₄] ₂	62:38
2.5 mol % Pd(II)OAc ₂	4 mol % xantphos	Ru(bpy) ₃ [BF ₄] ₂	71:29
2.5 mol % Pd(II)OAc ₂	6 mol % <i>p</i> - ^t Bu-triphenyl phosphite	Ru(bpy) ₃ [BF ₄] ₂	70:30

Additionally, the following Pd/L combinations produced poor to no conversion even with extended reaction times:

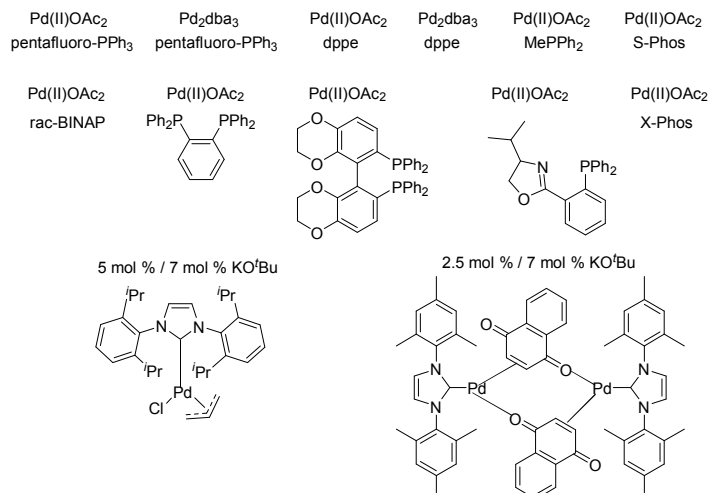
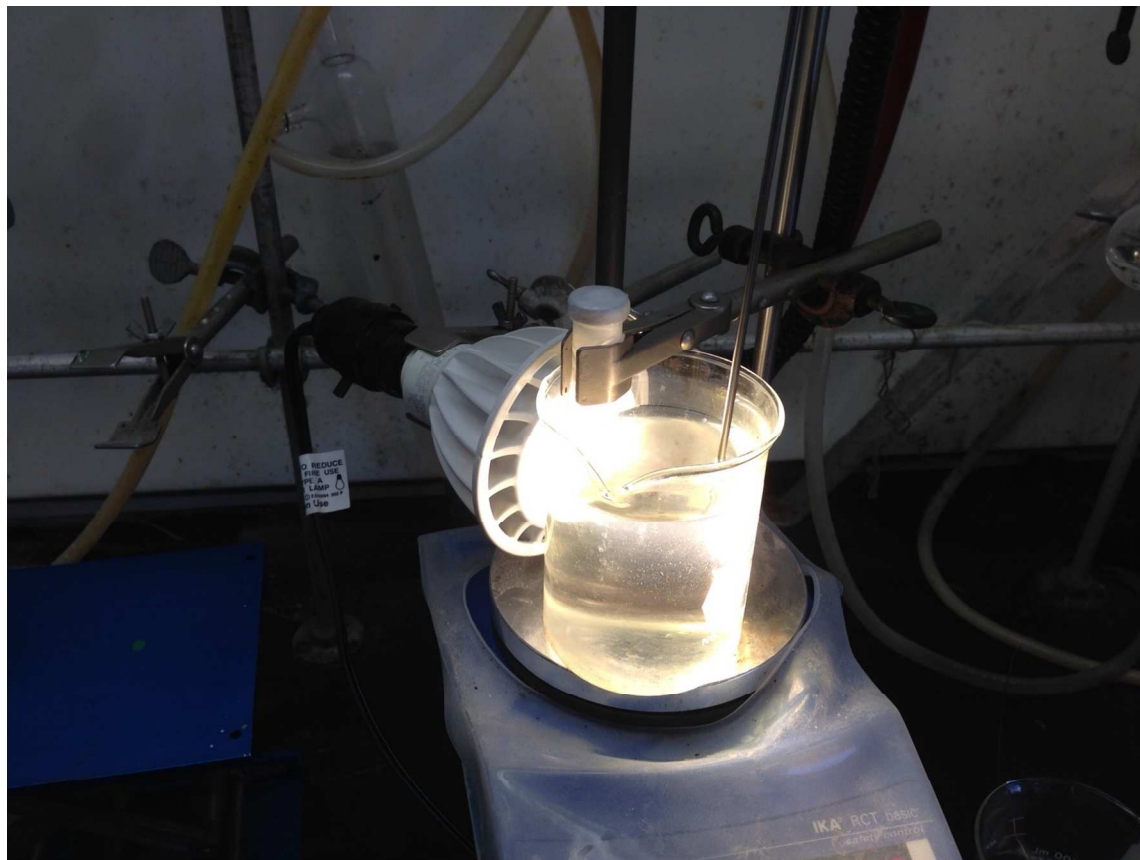


Photo of Experimental Setup:



References:

- 1: Miyake, Y.; Nakajima, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2012**, 3338.
- 2: Katritzky, A. R.; Lang, H.; Lan, X. *Tetrahedron* **1993**, 7445.
- 2: Miyake, Y.; Nakajima, K.; Nishibayashi, Y. *Chem. Commun.* **2013**, 7854.

