Supporting Information

Where Does Au Coordinate to a N-(2-PyridiyI)benzotriazole: Gold-catalyzed Chemoselective Dehydrogenation and Borrowing Hydrogen Reaction

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I. General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. 1H NMR and 13C NMR spectra were recorded on Varian 400 or 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl₃ (δ 7.26 ppm) for 1H NMR and CDCl₃ (δ 77.0 ppm) for 13C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer. Substrates 8 and 11 were synthesized according to the literature as below:


1.1 Synthesis of Pyridyltriazole Gold Complex

1.1.1 Procedure for synthesis of 1-(pyridin-2-yl)-1H-benzo[d][1,2,3]triazole

\[
\text{N} \quad \text{N} \quad \text{Br} \quad + \quad 10\% \text{CuCl}, 20\% \text{L-proline} \quad 2\text{eq. K}_2\text{CO}_3, \text{DMSO}, 160 ^\circ\text{C} \quad \text{N} \quad \text{N} \quad \text{N}
\]

To 100 mL round-bottom flask was successively added N-H triazole (2.983 g, 25 mmol), bromopyridine (3.160 g, 20 mmol), copper (I) iodide (381 mg, 2 mmol), L-proline (0.461 mg, 4 mmol) and potassium carbonate (2.403 g, 40 mmol) under N₂, and then dimethylsulfoxide (30 mL) was added by syringes. The reaction mixture was stirred overnight at 160 °C and monitored by TLC until complete disappearance of the bromopyridine was confirmed. Then the reaction mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and flash silica gel chromatography gave the product (58% yield).

1.1.2 Preparation of Gold Complex
To a solution of $\text{PPh}_3\text{AuCl}$ (2.0 mmol) in 10 mL CH$_2$Cl$_2$ was added 1.1 equiv of AgOTf (2.2 mmol) at room temperature. The mixture was stirred for 5 min and was added the ligand (2.1 mmol). The resulting mixture was stirred for 4 h at room temperature. After this, the cloudy solution was filtered through a short pad of celite and washed with DCM (5 mL). Then petroleum ether was added very slowly on the top of the CH$_2$Cl$_2$ layer. The resultant white solid was collected and washed with petroleum ether and dried by vacuum pump, the pyridyltriazole Gold complexe ($1a$) was synthesized in 91% yield; CCDC number: 1490192.

**Figure S1.** Crystal structure of Pyridyltriazole Gold(I) Complex

**Table. S1** Crystallographic data for pyridyltriazole gold(I) complexe

<table>
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<th>Property</th>
<th>Value</th>
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<td>Empirical formula</td>
<td>C$<em>{30}$H$</em>{23}$AuF$_3$N$_4$O$_3$P$_S$</td>
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<tr>
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<td>Wavelength</td>
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<tr>
<td>Crystal system, space group</td>
<td>Triclinic $P-1$</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 11.706(5)$ Å  $\alpha = 90$ deg.</td>
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|                                | $b = 16.717(7)$ Å  $\beta = 96.390(7)$ deg.
1.2. Optimization of reaction conditions

Table S2. Optimization of reaction conditions$^a$

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<tr>
<th>Entry</th>
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<th>Base</th>
<th>Solvent</th>
<th>Yield[%]$^b$</th>
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<td>TA-Py-Au(1a) (1%)</td>
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<td>toluene</td>
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<td>KOH</td>
<td>MeOH</td>
<td>26</td>
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<td>TA-Py-Au(1a) (1%)</td>
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<td>DCM</td>
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<td>TA-Py-Au(1a) (1%)</td>
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<td>THF</td>
<td>83</td>
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<td>THF</td>
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<td>THF</td>
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<td>TA-Py-Au(1a) (1%)</td>
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<td>Ph$_3$PAuCl (1%)</td>
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</table>
1.3 Representative procedure for N-alkylation of aromatic amines with primary alcohols.

To 25 mL round-bottom flask was successively added aromatic amine (0.5 mmol), primary alcohol (0.6 mmol), potassium hydroxide (0.75 mmol), 1a (1 mol%), and THF (3 mL) at room temperature. The reaction mixture was stirred at reflux and monitored by TLC. After the reaction was completed (24 h), the mixture was cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (20:1) as eluent to give the desired product.

1.4 Representative procedure for the preparation of acetophenone

To 25 mL Schlenk tube was added 1a (1 mol%), toluene (3 mL), and alcohol (1 mmol) was added. Then the mixture was stirred at 110 °C for 10 h. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous MgSO₄. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 50:1) afforded the compound 9a as a colorless oil.

1.5 Representative procedure for the preparation of ketones

To 25 mL round-bottom flask was successively added 11 (0.5 mmol), primary alcohol (0.6 mmol), potassium hydroxide (0.75 mmol), 1a (1 mol%) and toluene (3 mL) at room temperature. The reaction mixture was stirred at reflux and monitored by TLC. After the reaction was completed (24 h), the mixture was cooled to room temperature. The resulting
solution was directly purified by column chromatography with petroleum ether/ethyl acetate (20:1) as eluent to give the desired product.

1.6 Representative procedure for the preparation of Allene 14a

![13a](image1) 1) [Au] (0.2 mol%), CH₂Cl₂, RT  2) NaBH₄, MeOH

To a solution of 13a (1 mmol) in wet CH₂Cl₂ (3.0 mL), was added Au(I) catalyst (0.2 mol%) at RT. The reaction mixture was kept at room temperature and monitored by TLC. After the reaction was completed (6-12 h), NaBH₄ (1.5 mmol) and MeOH (0.5 mL) was added to the mixture. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 80:1) afforded the title compound 14a as colorless oil.

1.7 Heat-stabilization experiments for gold complexes: 1a for TA-Py-Au (1a); 5 for pyridine gold. 7 for AuPPh₃OTf

![Figure S2. Heat stabilization test in toluene under reflux condition for 0.5 hour.](image2)

1.8 Run kinetics

![Run kinetics graph](image3)

Yield (%) vs Time (h)
Figure S3. The kinetics curve.
II. Compounds Characterization

1-(pyridin-2-yl)-1H-benzo[d][1,2,3]triazole

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 8.4$ Hz, 1H), 8.61 (d, $J = 4.0$ Hz, 1H), 8.31 (d, $J = 8.3$ Hz, 1H), 8.13 (d, $J = 8.3$ Hz, 1H), 7.94 (td, $J = 8.3$, 1.8 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.50 – 7.43 (m, 1H), 7.32 (dt, $J = 12.1$, 6.0 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.72, 148.33, 146.77, 138.81, 131.53, 128.76, 124.89, 122.27, 119.75, 114.83, 114.44.

HRMS (ESI) Calculated for C$_{11}$H$_9$N$_4$ (M+H)$^+$ 198.0827, found 198.0825.

(1a) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 – 8.81 (m, 1H), 8.74 (dd, $J = 4.8$, 1.2 Hz, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 8.30 (d, $J = 8.0$ Hz, 1H), 8.20 (td, $J = 7.6$, 1.6 Hz, 1H), 7.91 – 7.80 (m, 2H), 7.70 – 7.55 (m, 16H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 149.9, 149.0, 144.2, 140.5, 140.4, 134.3, 134.1, 132.9, 132.8, 132.2, 131.4, 129.9, 129.8, 129.3, 127.0, 126.4, 125.3, 117.1, 116.3, 116.2, 116.1, 116.0, 115.9. 31P NMR (162 MHz, CDCl$_3$) $\delta$ 29.4; Anal. Calcd for C$_{30}$H$_{23}$AuF$_4$N$_4$O$_3$: C, 44.79, H, 2.88, N, 6.96; Found: C, 44.63, H, 2.80, N, 6.89. CCDC number: 1490192. [M+H]$^+$ 805.0846

(1b) $^1$H NMR (400 MHz, DMSO) $\delta$ 8.74 (dd, $J = 4.8$, 0.8 Hz, 1H), 8.28 (dd, $J = 8.4$, 3.2 Hz, 2H), 8.19 (td, $J = 7.2$, 1.6 Hz, 1H), 7.76 (td, $J = 6.8$, 0.8 Hz, 1H), 7.72 – 7.57 (m, 17H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 151.0, 149.3, 146.2, 140.6, 134.7, 134.6, 135.5, 134.4, 134.3, 133.1, 133.0, 132.9, 131.5, 130.2, 130.1, 130.0, 128.1, 127.4, 126.3, 124.0, 119.8, 115.2, 115.0. 31P NMR (162 MHz, DMSO) $\delta$ 27.0; Anal. Calcd for C$_{29}$H$_{23}$AuF$_6$N$_4$PSb: C, 39.08, H, 2.60, N, 6.29; Found: C, 38.91, H, 2.52, N, 6.17. [M+H]$^+$ 891.0268

N-(4-chlorobenzyl)aniline (8a) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (s, 4H), 7.09 (t, $J = 7.6$ Hz, 2H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 2H), 4.23 (s, 2H), 4.04 – 3.91 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.8, 137.0, 131.9, 128.3, 127.7, 127.6, 116.8, 111.9, 46.6.

N-(4-methylbenzyl)aniline (8b) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 7.6$ Hz, 2H), 7.33 (dd, $J = 12.4$, 7.6 Hz, 4H), 6.68 (t, $J = 7.2$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 2H), 4.41 (s, 2H), 4.08 (s, 1H), 2.51 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.4, 137.0, 136.6, 129.5, 129.4, 127.7, 117.6, 113.0, 48.2, 21.3.
N-(4-methoxybenzyl)aniline (8c) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.41 (t, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 6.87 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.0 Hz, 2H), 4.36 (s, 2H), 4.17 – 3.96 (m, 1H), 3.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 148.4, 131.6, 129.4, 128.9, 117.6, 114.2, 113.0, 55.4, 47.9.

N-benzylaniline (8d) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.21 (m, 4H), 7.20-7.14 (m, 1H), 7.08 (t, J = 7.6 Hz, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.54 (d, J = 7.6 Hz, 2H), 4.23 (s, 2H), 4.05-3.80 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 139.4, 129.3, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3.

N-pentylaniline (8e) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.09 (t, J = 7.2 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.52 (d, J = 8.0 Hz, 2H), 3.72-3.43 (m, 1H), 3.02 (t, J = 7.2 Hz, 2H), 1.58-1.50 (m, 2H), 1.29 (d, J = 3.2 Hz, 4H), 0.84 (t, J = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.58, 129.25, 117.09, 112.71, 44.01, 29.36, 22.56, 14.09.

N-(2-ethylhexyl)aniline (8f) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.08 (t, J = 7.6 Hz, 2H), 6.58 (t, J = 7.2 Hz, 1H), 6.51 (d, J = 8.0 Hz, 2H), 3.50 (s, 1H), 3.01-2.78 (m, 2H), 1.63-1.28 (m, 1H), 1.37-1.29 (m, 2H), 1.24 (d, J = 8.0 Hz, 6H), 0.83 (t, J = 7.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.82, 129.28, 116.95, 112.66, 47.09, 39.17, 31.40, 29.07, 24.57, 23.20, 14.19, 11.01.

N-benzyl-3-chloroaniline (8g) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.23 (m, 4H), 7.20-7.14 (m, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.60 – 6.53 (m, 1H), 6.50 (t, J = 2.0 Hz, 1H), 6.39 (dd, J = 8.0, 2.0 Hz, 1H), 4.22 (s, 2H), 4.01 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 149.4, 135.2, 130.4, 128.9, 127.6, 127.5, 117.5, 112.7, 111.3, 48.2.

N-benzyl-4-chloroaniline (8h) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 4.4 Hz, 4H), 7.21 – 7.14 (m, 1H), 7.06 – 7.00 (m, 2H), 6.50 – 6.44 (m, 2H), 4.20 (s, 2H), 4.05 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 146.6, 138.9, 129.1, 128.7, 127.5, 122.1, 113.9, 48.4.

N-benzyl-2-chloroaniline (8i) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.25 (dd, J = 6.0, 4.0 Hz, 4H), 7.18 (t, J = 6.8 Hz, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.54 (t, J = 7.2 Hz, 2H), 4.64 (s, 1H), 4.30 (d, J = 5.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 143.9, 138.8, 129.2, 128.8, 127.9, 127.4, 127.3, 119.2, 117.5, 111.6, 47.9.

N-benzyl-4-fluoroaniline (8j) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.20 (m, 4H), 7.20-7.12 (m, 1H), 6.83-6.70 (m, 2H), 6.44 (dt, J = 6.4, 4.0 Hz, 2H), 4.18 (s, 2H), 4.11-3.59 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.1, 154.7, 144.5, 139.3, 128.7, 127.5, 115.7, 113.7, 48.9.
N-benzyl-4-methoxyaniline (8k) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (q, $J = 7.6$ Hz, 4H), 7.23 – 7.16 (m, 1H), 6.70 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 8.4$ Hz, 2H), 4.21 (s, 2H), 3.79 – 3.58 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.3.

3-chloro-N-(furan-2-ylmethyl)aniline (8l) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 – 7.18 (m, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.96 (t, $J = 8.0$ Hz, 1H), 6.58 (dd, $J = 7.6$, 1.2 Hz, 1H), 6.47 (t, $J = 2.0$ Hz, 1H), 6.35 (dd, $J = 8.4$, 1.6 Hz, 1H), 4.16 (s, 2H), 4.01 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.8, 142.2, 135.1, 130.3, 127.0, 125.3, 124.8, 118.0, 112.9, 111.5, 43.3.

4-chloro-N-(furan-2-ylmethyl)aniline (8m) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 1.2$ Hz, 1H), 7.10 – 6.99 (m, 2H), 6.56 – 6.44 (m, 2H), 6.25 (dd, $J = 3.2$, 2.0 Hz, 1H), 6.15 (dd, $J = 3.2$, 0.4 Hz, 1H), 4.21 (s, 2H), 3.99 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.3, 146.2, 142.1, 129.1, 122.7, 114.3, 110.4, 107.2, 41.5.

N-(furan-2-ylmethyl)aniline (8n) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, $J = 5.6$ Hz, 1H), 7.11 (t, $J = 8.0$ Hz, 2H), 6.66 (t, $J = 7.2$ Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 2H), 6.29 – 6.20 (m, 1H), 6.16 (t, $J = 5.2$ Hz, 1H), 4.24 (s, 2H), 4.00 – 3.85 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.7, 146.6, 140.9, 128.2, 117.0, 112.1, 109.3, 105.9, 40.4.

4-chloro-N-(4-chlorobenzyl)aniline (8o) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.24 (m, 4H), 7.19 – 7.00 (m, 2H), 6.51 (d, $J = 8.8$ Hz, 2H), 4.28 (s, 2H), 4.12 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.4, 137.5, 133.1, 129.1, 128.9, 128.6, 122.4, 114.0, 47.7.

4-chloro-N-(4-methylbenzyl)aniline (8p) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.14 (d, $J = 7.6$ Hz, 2H), 7.06 (d, $J = 7.6$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.44 (d, $J = 8.0$ Hz, 2H), 4.15 (s, 2H), 3.91 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.7, 137.1, 135.9, 129.4, 129.1, 127.5, 122.0, 113.9, 4.1, 21.1.

4-chloro-N-(4-methoxybenzyl)aniline (8q) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 (d, $J = 8.4$ Hz, 2H), 7.00 (d, $J = 8.4$ Hz, 2H), 6.78 (d, $J = 8.4$ Hz, 2H), 6.43 (d, $J = 8.4$ Hz, 2H), 4.11 (s, 2H), 3.86 (s, 1H), 3.70 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.0, 146.8, 131.0, 129.1, 128.8, 122.0, 114.1, 114.0, 55.3, 47.9.

3-chloro-N-(4-chlorobenzyl)aniline (8r) (Known compound, ref: F. Huang, Z. Liu, Z. Yu, Angew. Chem. Int. Ed. 2016, 55, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.96 (t, $J = 8.0$ Hz, 1H), 6.58 (dd, $J = 8.0$, 1.2 Hz, 1H), 6.47 (t, $J = 2.0$ Hz,
1H, 6.35 (dd, $J = 8.4, 1.6$ Hz, 1H), 4.16 (s, 2H), 4.01 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.0, 137.4, 135.1, 133.1, 130.3, 128.9, 128.7, 117.7, 112.7, 111.3, 47.4.

**N-(4-methoxybenzyl)naphthalen-1-amine (8s)** (Known compound, ref: F. Huang, Z. Liu, Z. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 – 7.61 (m, 2H), 7.35 – 7.26 (m, 2H), 7.13 (d, $J = 8.4$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 7.6$ Hz, 1H), 4.49 (s, 1H), 4.26 (s, 2H), 3.66 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.1, 143.3, 134.4, 131.1, 129.2, 128.8, 126.7, 125.8, 124.8, 123.5, 120.0, 117.8, 114.2, 104.9, 55.4, 48.2.

**N-(4-methoxybenzyl)pyridin-2-amine (8t)** (Known compound, ref: F. Huang, Z. Liu, Z. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 862) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, $J = 4.8$ Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.48 (t, $J = 6.0$ Hz, 1H), 6.27 (d, $J = 8.4$ Hz, 1H), 4.87 (s, 1H), 4.33 (d, $J = 5.6$ Hz, 2H), 3.70 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.9, 158.7, 148.2, 137.4, 131.2, 128.7, 114.0, 113.7, 106.8, 55.3, 45.8.

**1-(2-fluorophenyl)ethanone (9a)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (td, $J = 7.6, 2.0$ Hz, 1H), 7.52 (dddd, $J = 8.4, 7.2, 5.2, 2.0$ Hz, 1H), 7.25 – 7.20 (m, 1H), 7.14 (ddd, $J = 11.2, 8.4, 0.8$ Hz, 1H), 2.65 (d, $J = 4.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.9, 163.5 (d, $J = 255.8$ Hz), 134.7 (d, $J = 9.1$ Hz), 130.6 (d, $J = 2.4$ Hz), 125.8 (d, $J = 12.7$ Hz), 124.4 (d, $J = 3.4$ Hz), 116.8 (d, $J = 23.8$ Hz), 31.4.

**1-(o-tolyl)ethanone (9b)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.30 (dd, $J = 11.8, 7.6$ Hz, 2H), 2.62 (s, 3H), 2.57 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 201.6, 138.5, 137.8, 132.1, 131.4, 129.2, 125.6, 29.4, 21.6.

**1-(3-nitrophenyl)ethanone (9c)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.76 (s, 1H), 8.42 (d, $J = 7.6$ Hz, 1H), 8.29 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 1H), 2.70 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.7, 148.5, 138.3, 138.8, 129.9, 127.4, 123.2, 26.7.

**1-(3-methoxyphenyl)ethanone (9d)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, $J = 7.2$ Hz, 1H), 7.52 (s, 1H), 7.36 (t, $J = 8.4$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 3.85 (s, 3H), 2.63 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.8, 159.6, 138.4, 129.7, 121.3, 119.5, 112.3, 55.6, 26.8.

**1-(4-bromophenyl)ethanone (9e)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.75 – 8.72 (m, 2H), 7.65 – 7.59 (m, 2H), 2.60 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.0, 135.8, 131.9, 129.9, 128.3, 26.5.

**1-(4-nitrophenyl)ethanone (9f)** (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* **2016**, *358*, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 – 8.30 (m, 2H),
8.15 – 8.10 (m, 2H), 2.70 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.3, 150.4, 141.4, 129.3, 123.9, 27.0.

1-(4-chlorophenyl)ethanone (9g) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.88 (m, 2H), 7.46 – 7.42 (m, 2H), 2.59 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.8, 139.5, 135.4, 129.7, 128.9, 26.5.

1-(4-fluorophenyl)ethanone (9h) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 – 7.95 (m, 2H), 7.17 – 7.09 (m, 2H), 2.59 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 196.4, 167.0 (d, $^J$= 255.5 Hz), 133.6 (d, $^J$= 3.0 Hz), 131.0 (d, $^J$= 9.4 Hz), 115.7 (d, $^J$= 21.9 Hz), 26.5.

Acetophenone (9i) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $^J$= 7.2 Hz, 2H), 7.56 (t, $^J$= 7.2 Hz, 1H), 7.49 (t, $^J$= 7.2 Hz, 2H), 2.60 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.1, 137.2, 133.1, 128.6, 128.3, 26.6.

heptan-2-one (9j) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 2.41 (t, $^J$= 7.6 Hz, 2H), 2.12 (s, 3H), 1.61 – 1.51 (m, 2H), 1.35 – 1.21 (m, 4H), 0.88 (t, $^J$= 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 209.4, 43.8, 31.4, 29.8, 23.6, 22.5, 13.9.

1-(p-tolyl)ethanone (9k) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, $^J$= 7.2 Hz, 2H), 7.25 (d, $^J$= 7.2 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.6, 143.7, 134.7, 129.1, 128.3, 26.4, 21.5.

1-(2-methoxyphenyl)ethanone (9l) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (dd, $^J$= 7.6, 1.6 Hz, 1H), 7.46 (qd, $^J$= 8.4, 2.0 Hz, 1H), 7.92 – 6.05 (m, 2H), 3.91 (s, 3H), 2.61 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.9, 158.9, 133.6, 130.3, 128.3, 120.5, 111.6, 55.5, 31.8.

1-(2-chlorophenyl)ethanone (9m) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, $^J$= 7.2 Hz, 1H), 7.40 (q, $^J$= 8.0 Hz, 2H), 7.32 (t, $^J$= 7.2 Hz, 1H), 2.64 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 200.3, 139.1, 132.1, 131.2, 130.5, 129.3, 126.7, 30.5.

1-(2-nitrophenyl)ethanone (9n) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, Adv. Synth. Catal. 2016, 358, 1433.) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $^J$= 8.0 Hz, 1H), 7.76 (t, $^J$= 7.6 Hz, 1H), 7.60 (t, $^J$= 7.6 Hz, 1H), 7.43 (d, $^J$= 7.6 Hz, 1H), 2.55 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 199.5, 145.6, 137.7, 134.1, 130.5, 127.2, 124.1, 30.3.
1-(m-tolyl)ethanone (9o) (Known compound, ref: Y. Yang, A. Qin, K. Zhao, D. Wang, X. Shi, *Adv. Synth. Catal.* 2016, 358, 1433.) ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 10.4 Hz, 2H), 7.43-7.32 (m, 2H), 2.63 (s, 3H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 198.2, 138.1, 137.3, 133.7, 128.7, 128.5, 125.6, 26.7, 21.2.

1,3-diphenylpropan-1-one (12a) (Known compound, ref: Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *Tetrahedron Lett.* 2002, 43, 7987) ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 7.13 (t, J = 7.2 Hz, 1H), 3.23 (t, J = 7.2 Hz, 2H), 3.00 (t, J = 7.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 199.5, 141.5, 137.1, 133.2, 128.8, 128.7, 128.6, 128.2, 40.6, 30.3.

1-(4-fluorophenyl)-3-phenylpropan-1-one (12b) (Known compound, ref: Yan, F.-X.; Zhang, M.; Wang, X.-T.; Xie, F.; Chen, M.-M.; Jiang, H. *Tetrahedron* 2014, 70, 1193. and Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *Tetrahedron Lett.* 2002, 43, 7987.) ¹H NMR (400 MHz, CDCl₃) δ 8.01 (dd, J = 8.0, 5.6 Hz, 2H), 7.37 – 7.20 (m, 5H), 7.14 (t, J = 8.4 Hz, 2H), 3.30 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 197.6, 167.0 (d, J = 255.7 Hz), 141.1, 131.1 (d, J = 9.2 Hz), 130.7 (d, J = 9.3 Hz), 129.0, 128.6 (d, J = 15.0 Hz), 126.2, 115.8 (d, J = 21.9 Hz), 40.4, 30.1.

3-(2-chlorophenyl)-1-phenylpropan-1-one (12c) (Known compound, ref: Xu, Q.; Chen, J.; Tian, H.; Yuan, X.; Li, S.; Zhou, C.; Liu, J. *Angew. Chem. Int. Ed.* 2014, 53, 225.) ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.94 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.35 (dd, J = 7.6, 1.6 Hz, 1H), 7.31 (dd, J = 7.2, 2.0 Hz, 1H), 7.17 (pd, J = 7.2, 1.6 Hz, 2H), 3.34 – 3.28 (m, 2H), 3.21 – 3.15 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 198.9, 140.6, 136.8, 133.2, 132.9, 130.9, 128.6, 128.2, 128.1, 127.7, 124.4, 38.6, 30.8.

1,3-bis(4-chlorophenyl)propan-1-one (12d) (Known compound, ref: Yan, F.-X.; Zhang, M.; Wang, X.-T.; Xie, F.; Chen, M.-M.; Jiang, H. *Tetrahedron* 2014, 70, 1193. and Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *Tetrahedron Lett.* 2002, 43, 7987.) ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.88 (m, 2H), 7.49 – 7.42 (m, 2H), 7.28 (dd, J = 6.8, 1.6 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 197.5, 140.8, 139.7, 137.6, 135.1, 130.5, 129.3, 128.9, 91.3, 40.1, 29.5.

3-(4-chlorophenyl)-1-(4-fluorophenyl)propan-1-one (12e) (Known compound, ref: Yan, F.-X.; Zhang, M.; Wang, X.-T.; Xie, F.; Chen, M.-M.; Jiang, H. *Tetrahedron* 2014, 70, 1193. and Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *Tetrahedron Lett.* 2002, 43, 7987.) ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.96 (m, 2H), 7.31 – 7.26 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.15 (t, J = 8.4 Hz, 2H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 197.2, 167.1 (d, J = 255.8 Hz), 139.6, 133.3 (d, J = 2.9 Hz), 132.0, 130.7 (d, J = 9.3 Hz), 129.8, 128.6, 115.8 (d, J = 22.0 Hz), 40.0, 29.4.

(m, 2H), 7.47 – 7.43 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 2H), 3.33 – 3.27 (m, 2H), 3.11 – 3.07 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 198.00, 141.07, 139.52, 135.20, 129.47, 128.94, 128.58, 128.42, 126.24, 40.43, 30.12.

3-(4-methoxyphenyl)-1-phenylpropan-1-one (12g) (Known compound, ref: Xu, Q.; Chen, J.; Tian, H.; Yuan, X.; Li, S.; Zhou, C.; Liu, J. Angew. Chem. Int. Ed. 2014, 53, 225.) 1H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 3.26 (t, J = 7.6 Hz, 2H), 3.01 (t, J = 7.6 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 199.33, 138.23, 136.96, 135.64, 133.03, 129.23, 128.61, 128.32, 128.07, 40.62, 29.76, 21.02.

3-(furan-2-yl)-1-phenylpropan-1-one (12h) (Known compound, ref: Xu, Q.; Chen, J.; Tian, H.; Yuan, X.; Li, S.; Zhou, C.; Liu, J. Angew. Chem. Int. Ed. 2014, 53, 225.) 1H NMR (400 MHz, CDCl3) δ 8.00 (t, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 1.2 Hz, 1H), 6.31 (dd, J = 7.6, 3.6 Hz, 1H), 6.08 (d, J = 3.2 Hz, 1H), 3.36 (t, J = 7.2 Hz, 2H), 3.12 (t, J = 7.6 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 198.5, 143.9, 136.7, 133.1, 128.7, 128.1, 126.8, 124.6, 124.6, 24.2.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (12i). (Known compound, ref: Babu S. A.; Yasuda M.; Baba A. Org. Lett. 2007, 9, 405-408). 1H NMR (400 MHz, CDCl3) δ 7.95 – 7.90 (m, 2H), 7.31 – 7.15 (m, 5H), 6.94 – 6.87 (m, 2H), 3.83 (s, 3H), 3.23 (t, J = 7.2 Hz, 2H), 3.04 (t, J = 8.0 Hz, 2H); 13C NMR (101 MHz, CDCl3): δ 197.8 163.4, 141.5, 130.4, 130.1, 128.5, 128.4, 126.1, 113.7, 55.5, 40.2, 30.4.

1-(4-methoxyphenyl)-3-(o-tolyl)propan-1-one (12j) (Known compound, ref: Zhou X.; Li X.; Zhang W, Tetrahedron Lett. 2014, 55, 5137-5140). 1H NMR (400 MHz, CDCl3) δ 7.99 – 7.93 (m, 2H), 7.54 (dd, J = 8.0, 1.2 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.11 – 7.04 (m, 1H), 6.95 – 6.89 (m, 2H), 3.86 (s, 3H), 3.28 – 3.22 (m, 2H), 3.20 – 3.14 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 197.5, 163.4, 140.7, 132.8, 130.8, 130.4, 129.9, 127.9, 127.6, 124.4, 113.7, 55.4, 38.3, 27.7, 19.3.

1-phenyl-3-(o-tolyl)propan-1-one (12l). (Known compound, ref: Buil M. L.; Esteruelas M. A.; Herrero J. ACS Catal. 2013, 3, 2072-2075). 1H NMR (400 MHz, CDCl3) δ 7.96 – 7.91 (m, 2H), 7.20 – 7.09 (m, 4H), 6.94 – 6.88 (m, 2H), 3.84 (s, 3H), 3.21 – 3.13 (m, 2H), 3.08 – 2.99 (m, 2H), 2.34 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 199.4, 139.4, 136.9, 136.1, 133.1, 130.4, 128.7, 128.1, 126.3, 126.4, 126.2, 113.7, 55.5, 38.8, 27.7, 19.3.

3-(2-bromophenyl)-1-(4-methoxyphenyl)propan-1-one (12k). (Known compound, ref: Zhou X.; Li X.; Zhang W, Tetrahedron Lett. 2014, 55, 5137-5140). 1H NMR (400 MHz, CDCl3) δ 7.99 – 7.93 (m, 2H), 7.54 (dd, J = 8.0, 1.2 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.11 – 7.04 (m, 1H), 6.95 – 6.89 (m, 2H), 3.86 (s, 3H), 3.28 – 3.22 (m, 2H), 3.20 – 3.14 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 197.5, 163.4, 140.7, 132.8, 130.8, 130.4, 129.9, 127.9, 127.6, 124.4, 113.7, 55.4, 38.3, 27.7, 19.3.

3-(2-phenylvinylidene)heptan-1-ol (14a) (Known compound, see: D., Wang; Gautam, L. N. S.; Bollinger, C.; Harris, A.; M. Li; X. Shi. Org. Lett. 2011, J3, 2618-2621) 1H NMR (400 MHz, CDCl3): δ 7.28-7.31 (m, 4H), 7.17-7.20 (m, 1H), 6.20 (m, 1H), 3.78 (t, J = 6.4 Hz, 2H), 2.32-3.39
(m, 2H), 2.10-2.14 (m, 2H), 1.63 (s, 1H), 1.46-1.50 (m, 2H), 1.34-1.40 (m, 2H), 0.90 (t, J = 7.6 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 201.9, 135.4, 128.6, 126.7, 126.4, 105.8, 96.1, 60.9, 35.9, 32.7, 29.7, 22.4, 13.9.

3-(2-(2-fluorophenyl)vinylidene)heptan-1-ol (14b). 1H NMR (400 MHz, CDCl3): δ 7.38 (td, J = 7.6, 1.6 Hz, 1H), 7.20-7.13 (m, 1H), 7.12-7.00 (m, 2H), 6.47-6.39 (m, 1H), 3.80 (t, J = 6.4 Hz, 2H), 2.43-2.35 (m, 2H), 2.18-2.07 (m, 2H), 1.65 (s, 1H), 1.55-1.33 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 202.8 (d, J = 2.0 Hz), 161.0 (d, J = 249.8 Hz), 128.0 (d, J = 8.2 Hz), 127.9 (d, J = 3.6 Hz), 124.2 (d, J = 3.5 Hz), 115.8 (d, J = 21.6 Hz), 105.5, 88.5 (d, J = 6.4 Hz), 60.8, 35.9, 32.6, 29.7, 22.4, 13.9. HRMS (ESI) Calculated for C15H20FO2 [M+H]+ 235.1498, found 235.1495.

3-(2-(o-tolyl)vinylidene)heptan-1-ol (14c). 1H NMR (400 MHz, CDCl3): δ 7.39 (d, J = 7.6 Hz, 1H), 7.20-7.09 (m, 3H), 6.44-6.39 (m, 1H), 3.81 (dd, J = 11.2, 5.6 Hz, 2H), 2.47-2.31 (m, 5H), 2.21-2.08 (m, 2H), 1.67-1.33 (m, 5H), 0.93 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 202.6, 134.8, 133.4, 130.6, 126.7, 126.6, 126.2, 104.7, 93.2, 61.0, 35.9, 32.8, 29.8, 22.5, 19.8, 13.9. HRMS (ESI) Calculated for C16H22ONa [M+Na]+ 253.1568, found 253.1564.

3-(2-(2-methoxyphenyl)vinylidene)heptan-1-ol (14d). 1H NMR (400 MHz, CDCl3): δ 7.35 (dd, J = 7.6, 1.6 Hz, 1H), 7.23-7.15 (m, 1H), 6.99-6.84 (m, 2H), 6.62-6.53 (m, 1H), 3.87 (s, 3H), 3.80 (s, 2H), 2.36 (td, J = 6.4, 3.2 Hz, 2H), 2.16-2.08 (m, 2H), 2.04 (s, 1H), 1.55-1.45 (m, 2H), 1.44-1.33 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 202.4, 156.1, 127.8, 127.6, 123.7, 120.9, 111.1, 104.3, 90.3, 60.8, 55.6, 36.0, 32.8, 29.8, 22.5, 13.9. HRMS (ESI) Calculated for C16H23O2 [M+H]+ 247.1698, found 247.1696.

3-(2-(2-chlorophenyl)vinylidene)heptan-1-ol (14e). 1H NMR (400 MHz, CDCl3): δ 7.30-7.27 (m, 1H), 7.26-7.20 (m, 2H), 7.19-7.13 (m, 2H), 6.20-6.12 (m, 1H), 3.80 (t, J = 6.0 Hz, 2H), 2.45-2.31 (m, 2H), 2.18-2.10 (m, 2H), 1.60 (s, 1H), 1.53-1.43 (m, 2H), 1.43-1.33 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 202.3, 137.6, 134.6, 129.8, 126.7, 126.6, 124.6, 106.4, 95.1, 60.9, 35.8, 32.6, 29.7, 22.4, 13.9. HRMS (ESI) Calculated for C15H20OCl [M+H]+ 251.1203, found 251.1200.

3-(2-(3-Nitrophenyl)vinylidene)heptan-1-ol (14f). 1H NMR (400 MHz, CDCl3): δ 8.11-8.12 (m, 1H), 8.00-8.02 (m, 1H), 7.57-7.59 (m, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.24 (m, 1H), 3.79 (t, J = 6.4 Hz, 2H), 2.35-2.45 (m, 2H), 2.12-2.19 (m, 2H), 1.66 (s, 1H), 1.44-1.59 (m, 2H), 1.34-1.43 (m, 2H), 0.90 (t, J = 7.6 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 203.1, 148.7, 137.8, 132.1, 129.4, 121.3, 121.0, 107.1, 94.5, 60.7, 35.7, 32.4, 29.6, 22.4, 13.9. HRMS (ESI) Calculated for C15H20NO3 [M+H]+ 262.1443, found 262.1441.

3-(2-(3-Chlorophenyl)vinylidene)heptan-1-ol (14g). 1H NMR (400 MHz, CDCl3): δ 7.30-7.25 (m, 2H), 7.25-7.19 (m, 2H), 6.19-6.15 (m, 1H), 3.79 (t, J = 6.2 Hz, 2H), 2.45-2.30 (m, 2H), 2.13 (td, J = 7.2, 2.8 Hz, 2H), 1.61 (s, 1H), 1.53-1.43 (m, 2H), 1.43-1.32 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ 202.1, 134.0, 132.3, 128.8, 127.6, 106.2, 95.2, 60.9, 35.9, 32.7, 25.7, 22.4, 13.9. HRMS (ESI) Calculated for C15H20OCI [M+H]+ 251.1203, found 251.1202.
3-(2-(4-Fluorophenyl)vinylidene)heptan-1-ol (14h) (Known compound, see: D., Wang; Gautam, L. N. S.; Bollinger, C.; Harris, A.; M. Li; X. Shi. Org. Lett. 2011, 13, 2618-2621) ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.26 (m, 2H), 6.97-6.70 (m, 2H), 6.20 (quintet, J = 2.0 Hz, 1H), 3.76 (t, J = 6.0 Hz, 2H), 2.31-3.37 (m, 2H), 2.09-2.12 (m, 2H), 1.68 (s, 1H), 1.43-1.49 (m, 2H), 1.34-1.40 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 201.7, 162.6 (d, J = 244.4 Hz), 131.3 (d, J = 3.3 Hz), 127.8 (q, J = 8.4 Hz), 115.5, 105.9, 95.08 (t, J = 8.5 Hz), 60.9, 35.9, 32.7, 29.7, 22.4, 23.8.

Methyl 4-(3-(2-hydroxyethyl)hepta-1,2-dienyl)benzoate (14i) (Known compound, see: D., Wang; Gautam, L. N. S.; Bollinger, C.; Harris, A.; M. Li; X. Shi. Org. Lett. 2011, 13, 2618-2621) ¹H NMR (400 MHz, CDCl₃): δ 7.95-7.96 (m, 2H), 7.31-7.33 (m, 2H), 6.22 (quintet, J = 3.2 Hz, 1H), 3.90 (s, 3H), 3.77 (t, J = 6.4 Hz, 2H), 2.34-2.42 (m, 2H), 2.11-2.15 (m, 2H), 1.68 (s, 1H), 1.42-1.50 (m, 2H), 1.34-1.39 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 203.3, 166.9, 140.5, 129.9, 128.2, 126.2, 106.2, 95.5, 60.8, 51.9, 35.7, 32.5, 29.7, 22.4, 13.9.

3-(2-(2-Nitrophenyl)vinylidene)heptan-1-ol (14j). ¹H NMR (400 MHz, CDCl₃): δ 7.90 (dd, J = 8.4, 1.2 Hz, 1H), 7.64 (dd, J = 8.0, 1.2 Hz, 1H), 7.52 (td, J = 7.6, 1.2 Hz, 1H), 7.35-7.27 (m, 1H), 6.87-6.81 (m, 1H), 3.81 (t, J = 6.2 Hz, 2H), 2.45-2.37 (m, 2H), 2.45-2.16 (m, 2H), 1.66 (s, 1H), 1.54-1.34 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 204.5, 147.4, 132.7, 130.5, 129.1, 127.1, 124.8, 106.6, 91.0, 60.7, 35.6, 32.3, 29.6, 22.4, 13.9. HRMS (ESI) Calculated for C₁₅H₂₀NO₃ [M+H]⁺ 262.1443, found 262.1442.

1-methyl-2-(1-phenylhex-5-en-1-yn-3-yl)benzene (16) ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 7.6 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.39 – 7.33 (m, 3H), 7.33 – 7.27 (m, 1H), 7.24 (d, J = 4.0 Hz, 2H), 6.05 (m, 1H), 5.26 – 5.15 (m, 2H), 4.18 (t, J = 7.2 Hz, 1H), 2.63 (dd, J = 13.6, 7.2 Hz, 2H), 2.47 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.65, 135.73, 134.93, 131.70, 130.53, 128.31, 127.74, 126.84, 126.29, 123.84, 117.02, 91.42, 83.18, 41.32, 35.08, 19.37.
III. $^1$H NMR and $^{13}$C NMR Spectra
AuPPh₃OTf
8a

[Chemical structure image]

S21
8c
S25
$9f$