Cobalt(III)-Catalyzed Efficient Synthesis of Indenones through Carboannulation of Benzoates and Alkynes

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I. General

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Diphenylacetylenes\(^1\) and \([\text{CoCp}^*(\text{CO})\text{I}_2]\)\(^2\) were prepared by following literature reports. All reactions were carried out using Schlenk techniques or in an \(\text{N}_2\)-filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless \(\delta\) values and is frequency referenced relative to TMS in \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300–400 mesh) using dichloromethane (DCM)/petroleum ether (PE).

II. General procedures for the synthesis of compound 3

Benzoates (0.2 mmol), alkynes (0.24 mmol), \([\text{Cp}^*\text{Co(\text{CO})I}_2]\) (10 mol %), \(\text{AgNTf}_2\) (20 mol %), \(\text{Zn(OAc)}_2\) (2.0 equiv), and HFIP (2.0 mL) were charged into the pressure tube. The reaction mixture was stirred under \(\text{N}_2\) at 120 \(^\circ\text{C}\) for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/DCM to afford the product 3.

2,3-Diphenyl-1H-inden-1-one (3aa)

3aa was obtained according to the general procedure in 86\% yield (48.5 mg). red solid;
\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 6.8\) Hz, 1H), 7.44 – 7.32 (m, 6H), 7.29 – 7.25 (m, 6H), 7.14 (d, \(J = 7.1\) Hz, 1H). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.5, 155.4, 145.3, 133.5, 132.8, 132.4, 130.8, 130.7, 130.0, 129.3, 129.0, 128.8, 128.5, 128.1, 127.8, 123.0, 121.3. The NMR data agree with those in a literature report.\(^3\)

5-Methyl-2,3-diphenyl-1H-inden-1-one (3ba)

3ba was obtained according to the general procedure in 91\% yield (53.9 mg). red solid;
\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, \(J = 7.2\) Hz, 1H), 7.30 – 7.35 (m, 5H), 7.27 – 7.23 (m, 5H), 7.06 (d, \(J = 7.1\) Hz, 1H), 6.93 (s, 1H), 2.33 (s, 3H). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.2, 154.9, 145.6, 144.4, 132.8, 132.7, 130.8, 129.9, 129.1, 128.9, 128.7, 128.5, 128.3, 128.0, 127.6, 123.0, 122.5, 22.1. The NMR data agree with those in a literature report.\(^3\)
5-Methoxy-2,3-diphenyl-1H-inden-1-one (3ca)

3ca was obtained according to the general procedure in 77% yield (47.8 mg). Red solid; 
1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 7.9 Hz, 1H), 7.40 – 7.34 (m, 5H), 7.30 – 7.20 (m, 5H), 6.73 – 6.63 (m, 2H), 3.82 (s, 3H). 
13C NMR (100 MHz, CDCl3) δ 195.1, 164.5, 153.2, 147.9, 133.9, 132.7, 130.9, 130.0, 129.2, 128.8, 128.6, 128.1, 127.8, 124.9, 123.5, 110.5, 110.3, 55.8. The NMR data agree with those in a literature report. 

5-Fluoro-2,3-diphenyl-1H-inden-1-one (3da)

3da was obtained according to the general procedure in 51% yield (30.3 mg). Red solid;
1H NMR (400 MHz, CDCl3) δ 7.57 (dd, J = 7.8, 5.2 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.34 (m, 2H), 7.26 – 7.24 (m, 5H), 6.96 – 6.89 (m, 1H), 6.86 (dd, J = 8.5, 1.9 Hz, 1H). 
13C NMR (100 MHz, CDCl3) δ 194.8, 166.5 (d, JCF = 252.9 Hz), 153.2 (d, JCF = 2.4 Hz), 148.6 (d, JCF = 9.3Hz), 133.7 (d, JCF = 1.0 Hz), 132.2, 130.4, 120.0, 129.5, 129.0, 128.4, 128.2, 128.1, 126.5 (d, JCF = 3.2 Hz), 124.8 (d, JCF = 9.7 Hz), 114.4 (d, JCF = 23.0 Hz), 110.2 (d, JCF = 25.7 Hz). The NMR data agree with those in a literature report. 

5-Chloro-2,3-diphenyl-1H-inden-1-one (3ea)

3ea was obtained according to the general procedure in 58% yield (36.6 mg). Red solid; 
1H NMR (400 MHz, CDCl3) δ 7.51 (d, J = 7.6 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.38 – 7.34 (m, 2H), 7.28 – 7.24 (m, 6H), 7.11 (d, J = 1.6 Hz, 1H). 
13C NMR (100 MHz, CDCl3) δ 195.0, 154.0, 147.3, 139.8, 133.5, 132.2, 130.3, 130.0, 129.6, 129.0, 128.9, 128.5, 128.4, 128.2, 128.1, 123.9, 122.0. The NMR data agree with those in a literature report. 

5-Bromo-2,3-diphenyl-1H-inden-1-one (3fa)

3fa was obtained according to the general procedure in 54% yield (39.1 mg). Red solid; 
1H NMR (400 MHz, CDCl3) δ 7.47 – 7.40 (m, 5H), 7.36 – 7.34 (m, 2H), 7.27 – 7.24 (m, 6H). 13C NMR
(100 MHz, CDCl$_3$) $\delta$ 195.3, 154.3, 147.4, 133.5, 132.3, 131.8, 130.4, 130.1, 129.7, 129.5, 129.1, 128.5, 128.44, 128.3, 128.2, 124.8, 124.2. The NMR data agree with those in a literature report.$^5$

5-Iodo-2,3-diphenyl-1H-inden-1-one (3ga)

3ga was obtained according to the general procedure in 55% yield (44.5 mg). red solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (dd, $J$ = 7.5, 1.1 Hz, 1H), 7.46 (d, $J$ = 0.8 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.36 – 7.33 (m, 2H), 7.30 (d, $J$ = 7.5 Hz, 1H), 7.27 – 7.24 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.6, 154.4, 146.9, 138.0, 133.1, 132.2, 130.2, 130.0, 129.6, 129.0, 128.4, 128.2, 128.1, 124.2, 100.9. HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{14}$IO$^+$: 409.0084, found: 409.0084.

6-Methoxy-2,3-diphenyl-1H-inden-1-one (3ha), major : minor = 1.2:1

3ha was obtained according to the general procedure in 87% yield (54.6 mg). red solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.12 (m, 3H), 7.03 (d, $J$ = 8.0 Hz, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.2, 161.1, 154.0, 136.9, 131.1, 130.1, 129.9, 129.4, 128.8, 128.5, 128.1, 127.9, 127.6, 122.3, 119.7, 116.1, 110.7, 55.7. HRMS: [M + H]$^+$ calculated for C$_{22}$H$_{17}$O$_2$$^+$: 313.1223, found: 313.1222.

6-Fluoro-2,3-diphenyl-1H-inden-1-one (3ia), major : minor = 15:1

3ia was obtained according to the general procedure in 90% yield (54.0 mg). red solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.32 (m, 6H), 7.30 – 7.15 (m, 6H), 7.06 (t, $J$ = 9.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.2, 156.1 (d, $J_{C,F}$ = 255.9 Hz), 154.4 (d, $J_{C,F}$ = 3.4 Hz), 133.7 (d, $J_{C,F}$ = 2.6 Hz), 133.5 (d, $J_{C,F}$ = 3.8 Hz), 133.46, 133.4, 131.4 (d, $J_{C,F}$ = 6.8 Hz), 130.3, 130.1, 129.3, 128.54 (d, $J_{C,F}$ = 2.7 Hz), 128.3, 128.1, 127.9, 123.4 (d, $J_{C,F}$ = 23.1 Hz), 119.2 (d, $J_{C,F}$ = 2.6 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.2. HRMS: [M + H]$^+$ calculated for C$_{22}$H$_{17}$FO$^+$: 301.1023, found: 301.1027.

6-Chloro-2,3-diphenyl-1H-inden-1-one (3ja), major : minor = 3.2:1

3ja was obtained according to the general procedure in 47% yield (30.0 mg). red solid;
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J$ = 1.8 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.39 – 7.34 (m, 3H), 7.27 – 7.24 (m, 5H), 7.08 (d, $J$ = 7.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.1, 155.1, 143.3, 135.0, 132.6, 132.4, 130.4, 129.9, 129.6, 128.9, 128.4, 128.2, 127.9, 123.6, 122.2. HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{14}$ClO$: 317.0728$, found: 317.0730.  

7-Methyl-2,3-diphenyl-1H-inden-1-one (3ka)  
3ka was obtained according to the general procedure in 85% yield (50.3 mg). red solid;  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.32 (m, 5H), 7.28 – 7.17 (m, 6H), 7.04 (d, $J$ = 7.8 Hz, 1H), 6.95 (d, $J$ = 7.2 Hz, 1H), 2.61 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.7, 154.3, 145.7, 138.0, 133.0, 132.6, 132.4, 132.2, 131.0, 130.1, 129.1, 128.8, 128.6, 128.0, 127.6, 127.1, 119.3, 17.4. The NMR data agree with those in a literature report.  

7-Fluoro-2,3-diphenyl-1H-inden-1-one (3la)  
3la was obtained according to the general procedure in 29% yield (17.4 mg). red solid;  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.31 (m, 3H), 7.30 – 7.24 (m, 3H), 7.20 – 7.15 (m, 5H), 6.88 (t, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.6 (d, $J_{CF}$ = 1.4 Hz), 157.9 (d, $J_{CF}$ = 262.3 Hz), 154.5 (d, $J_{CF}$ = 4.7 Hz), 147.4 (d, $J_{CF}$ = 3.5 Hz), 135.8 (d, $J_{CF}$ = 8.3 Hz), 133.0 (d, $J_{CF}$ = 1.3 Hz), 132.5, 130.2, 130.1, 129.4, 128.9, 128.5, 128.1, 128.0, 118.3 (d, $J_{CF}$ = 21.5 Hz), 117.7 (d, $J_{CF}$ = 2.4 Hz), 115.6 (d, $J_{CF}$ = 12.4 Hz). HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{14}$FO$: 301.1023$, found: 301.1021.  

7-Bromo-2,3-diphenyl-1H-inden-1-one (3ma)  
3ma was obtained according to the general procedure in 42% yield (30.3 mg). red solid;  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.32 (m, 6H), 7.30 – 7.18 (m, 6H), 7.09 (d, $J$ = 7.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.7, 153.4, 148.2, 134.1, 134.0, 132.9, 132.2, 130.1, 129.4, 128.9, 128.5, 128.1, 128.0, 127.6, 120.5, 119.1. HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{14}$BrO$: 361.0223$, found:
2,3-Diphenyl-1H-cyclopenta[a]napthalen-1-one (3na)

3na was obtained according to the general procedure in 70% yield (46.8 mg). red solid;
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.73 (d, $J = 8.3$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.47 – 7.41 (m, 5H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.33 – 7.23 (m, 6H) $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.6, 153.8, 146.7, 134.2, 132.8, 131.2, 130.8, 130.1, 129.4, 129.3, 129.2, 128.9, 128.6, 128.4, 128.1, 127.7, 126.0, 123.9, 122.4, 119.3. HRMS: [M + H]$^+$ calculated for C$_{25}$H$_{17}$O$: 333.1274, found: 333.1277.

2,3-Di-p-tolyl-1H-inden-1-one (3ab)

3ab was obtained according to the general procedure in 38% yield (23.6 mg). red solid;
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 6.9$ Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.18 (m, 6H), 7.17 – 7.13 (m, 2H), 7.09 – 7.07 (m, 2H), 2.40 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.8, 154.8, 145.5, 139.4, 137.5, 133.3, 132.1, 130.9, 129.9, 129.8, 129.5, 128.9, 128.7, 128.5, 128.0, 122.8, 121.1, 21.5, 21.4. The NMR data agree with those in a literature report.$^5$

2,3-Bis(4-(tert-butyl)phenyl)-1H-inden-1-one (3ac)

3ac was obtained according to the general procedure in 45% yield (35.5 mg). red solid;
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 6.9$ Hz, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.33 (m, 3H), 7.30 – 7.22 (m, 5H), 7.16 (d, $J = 7.2$ Hz, 1H), 1.36 (s, 9H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.0, 154.7, 152.5, 150.6, 145.6, 133.3, 131.8, 130.9, 129.9, 129.6, 128.7, 128.3, 127.9, 125.6, 125.0, 122.8, 121.3, 34.9, 34.6, 31.3. The NMR data agree with those in a literature report.$^5$
2,3-Bis(4-fluorophenyl)-1H-inden-1-one (3ad)

3ad was obtained according to the general procedure in 90% yield (57.6 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.0$ Hz, 1H), 7.40 – 7.35 (m, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.10 (m, 3H), 7.00 – 6.94 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.2, 163.2 (d, $J_{CF} = 248.7$ Hz), 162.4 (d, $J_{CF} = 247.0$ Hz), 154.2, 144.9, 133.6, 131.8 (d, $J_{CF} = 8.0$ Hz), 131.5, 130.6, 130.5 (d, $J_{CF} = 8.2$ Hz), 129.2, 128.5 (d, $J_{CF} = 3.4$ Hz), 126.6 (d, $J_{CF} = 3.4$ Hz), 123.2, 121.1, 116.2 (d, $J_{CF} = 21.6$ Hz), 115.4 (d, $J_{CF} = 21.4$ Hz). HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{13}$F$_2$O$: 319.0929, found: 319.0929.

2,3-Bis(4-chlorophenyl)-1H-inden-1-one (3ae)

3ae was obtained according to the general procedure in 86% yield (60.4 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 6.9$ Hz, 1H), 7.42 – 7.36 (m, 3H), 7.33 – 7.27 (m, 3H), 7.27 – 7.23 (m, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 7.2$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.8, 154.3, 144.6, 135.6, 134.1, 133.7, 131.5, 131.2, 130.9, 130.5, 129.9, 129.4, 129.3, 128.9, 128.6 123.3, 121.2. The NMR data agree with those in a literature report.4

2,3-Bis(4-bromophenyl)-1H-inden-1-one (3af)

3af was obtained according to the general procedure in 73% yield (64.4 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 – 7.54 (m, 3H), 7.41 – 7.38 (m, 3H), 7.33 – 7.22 (m, 3H), 7.13 – 7.09 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.7, 154.4, 144.6, 133.7, 132.3, 131.5, 131.4, 131.3, 130.5, 130.1, 129.4, 129.3, 123.9, 123.3, 122.4, 121.2. The NMR data agree with those in a literature report.5
2,3-Di-m-tolyl-1H-inden-1-one (3ag)

3ag was obtained according to the general procedure in 56% yield (35.0 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 7.0$ Hz, 1H), 7.36 (t, $J = 7.0$ Hz, 1H), 7.29 – 7.24 (m, $J = 8.2$, 4.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.09 (m, 4H), 7.05 (d, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.7, 155.4, 145.4, 138.4, 137.5, 133.4, 132.8, 132.4, 130.8, 130.7, 130.6, 130.0, 128.9, 128.7, 128.5, 127.9, 127.1, 125.7, 122.9, 121.3, 21.5, 21.4. The NMR data agree with those in a literature report.³

2,3-Bis(3-fluorophenyl)-1H-inden-1-one (3ah)

3ah was obtained according to the general procedure in 88% yield (56.0 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 6.8$ Hz, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 – 7.12 (m, 1H), 7.09 – 6.97 (m, 4H), 6.97 – 6.85 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.6, 162.9 (d, $J_{C,F} = 246.4$ Hz), 162.5 (d, $J_{C,F} = 243.9$ Hz), 154.7 (d, $J_{C,F} = 1.9$ Hz), 144.6, 134.5 (d, $J_{C,F} = 8.0$ Hz), 133.8, 132.4 (d, $J_{C,F} = 8.4$ Hz), 131.7 (d, $J_{C,F} = 2.1$ Hz), 130.8 (d, $J_{C,F} = 8.2$ Hz), 130.4, 129.7 (d, $J_{C,F} = 8.3$ Hz), 129.5, 125.7 (d, $J_{C,F} = 2.7$ Hz), 124.2 (d, $J_{C,F} = 2.9$ Hz), 123.4, 121.4, 116.8 (d, $J_{C,F} = 22.2$ Hz), 116.6 (d, $J_{C,F} = 21.0$ Hz), 115.4 (d, $J_{C,F} = 22.3$ Hz), 115.0 (d, $J_{C,F} = 20.8$ Hz). The NMR data agree with those in a literature report.⁶

2,3-Bis(3-chlorophenyl)-1H-inden-1-one (3ai)

3ai was obtained according to the general procedure in 84% yield (59.1 mg). red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 6.4$ Hz, 1H), 7.32 – 7.22 (m, 6H), 7.18 – 7.08 (m, 3H), 7.04 – 6.99 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.5, 154.5, 144.5, 154.5, 135.0, 134.1, 134.12, 133.8, 132.08, 131.6, 130.4, 130.3, 129.9, 129.7, 129.5, 129.4, 128.2, 128.19, 128.1, 126.8, 123.4, 121.4. The NMR data agree with those in a literature report.³
2,3-Bis(3-bromophenyl)-1H-inden-1-one (3aj)

3aj was obtained according to the general procedure in 83% yield (73.0 mg), red solid;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.53 (m, 3H), 7.46 (s, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.22 (m, 3H), 7.16 – 7.08 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.5, 154.4, 144.4, 134.4, 133.8, 132.7, 132.6, 132.3, 131.5, 131.1, 131.0, 130.6, 130.3, 129.7, 129.6, 128.5, 127.2, 123.4, 123.0, 122.3, 121.4.

HRMS: [M + H]$^+$ calculated for C$_{21}$H$_{13}$Br$_2$O$: 438.9328$, found: 438.9326.

III. Mechanistic Studies

1. KIE measurements of reaction for indenones

A mixture of ethyl benzoate 1a (0.2 mmol, 30.0 mg), diphenylacetylene 2a (0.24 mmol, 42.8 mg), [Cp*Co(CO)$_2$I$_2$] (10 mol %, 9.5 mg), AgNTf$_2$ (20 mol %, 16.0 mg), Zn(OAc)$_2$ (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N$_2$. In another tube were added a mixture of ethyl benzoate-d$_5$ 1a$'$ (0.2 mmol, 31.0 mg), diphenylacetylene 2a (0.24 mmol, 42.8 mg), [Cp*Co(CO)$_2$I$_2$] (10 mol %, 9.5 mg), AgNTf$_2$ (20 mol %, 16.0 mg), Zn(OAc)$_2$ (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N$_2$. These two reaction mixtures were stirred side-by-side in the same oil bath at 100 °C for 20 min. These two mixtures were rapidly combined and all the volatiles were rapidly removed under reduced pressure. The residue was purified by silica gel chromatography using PE/DCM to afford the mixed product. KIE value ($k_{\text{H}}/k_{\text{D}} = 4.5$) was estimated on the basis of $^1$H NMR analysis. No H/D exchanged in the reaction product was observed. If the relative amount of D is x and $1*14 + 10*x = 16.23$, then $x = 0.223$. KIE = $1/x = 4.5$. 

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2. Competitive Experiment

An equimolar mixture of acetanilide 1b (0.2 mmol, 32.0 mg) and 1e (0.2 mmol, 37.0 mg), diphenylacetylene 2a (0.2 mmol, 36.0 mg), [Cp*Co(CO)]_2 (10 mol %, 9.5 mg), AgNTf_2 (20 mol %, 16.0 mg), Zn(OAc)_2 (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N_2. The reaction mixture was stirred at 120 °C for 6 h. The solvent was rapidly removed under reduced pressure and the residue was purified by silica gel chromatography using PE/DCM to afford the mixed product. The yield ratio (3ba/3ea = 2.3:1) was determined on the basis of ^1H NMR analysis.
IV. References


V. NMR Spectra

3aa

3ba
3da
3ga
3ka
3ma