Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Copper-Catalyzed Oxidative Aromatization Reraction of 2-Cyclohexen-1-ones to Phenols in the Presence of Catalytic Hydrogen Bromide under Moleculer Oxygen

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General Experimental Information

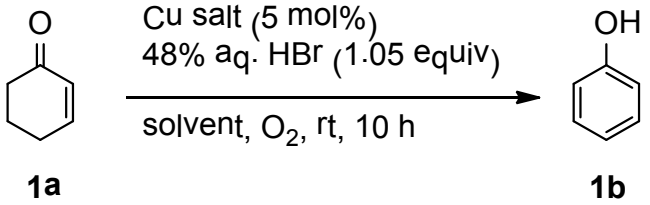
All commercially available compounds were purchased and used as received. Solvents 1,4-dioxane, MeCN, THF, Et_2O, toluene, dichloromethane, and cyclohexane were purchased from Wako Pure Chemical Industries and used as received. Diisopropylamine and chloro trimethylsilane were distilled over calcium hydride prior to use. Thin layer chromatography was performed using Merck TLC silica gel 60 F_{254} Aluminum sheets and visualized by UV irradiation, phosphomolybdic acid, and iodine staining. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical, 40-50 mesh). Gas chromatographic analysis was conducted with Shimadzu GC-2014 equipped with FID detector and the chemical yields were determined using dodecane as an internal standard. All ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to residual solvent peak $CDCl_3$ at δ 7.26 ppm. Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens).

General Procedure for the Copper-Catalyzed Oxidative Aromatization

A screw-capped test tube (20 mL) was charged with $CuBr_2$ (0.0125 mmol, 2.79 mg, 5 mol%), 1,4-dioxane (1.0 mL), 2-cyclohexen-1-one, and 48% HBr aq. (0.05 mmol, 6.0 μL, 20 mol%). The tube was filled with oxygen gas and then sealed. The reaction mixture was stirred at room temperature for 20 h and then the solvent was removed under vacuum. The residue was directly charged onto a chromatography column (SiO_2, 1 cm × 10 cm, AcOEt/hexane = 1:25), and the desired product was obtained.

Additional Screening

Table S1. Optimization of Reaction Conditions [a]



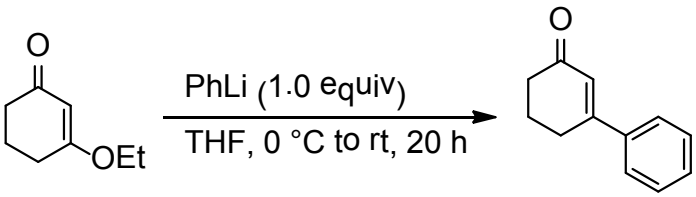
1a **1b**

Entry	Cu salt	solvent	Yield (%) [b]
1	$CuBr_2$	1,4-dioxane	80
2	$CuCl_2$	1,4-dioxane	53
3	$Cu(OAc)_2$	1,4-dioxane	73
4	$CuSO_4$	1,4-dioxane	69
5	CuO	1,4-dioxane	82
6	Cu_2O [c]	1,4-dioxane	71
7	CuI	1,4-dioxane	68
8	CuBr	1,4-dioxane	64
9	$CuBr_2$	MeCN	67
10	$CuBr_2$	THF	20
11	$CuBr_2$	Et_2O	35
12	$CuBr_2$	toluene	5
13	$CuBr_2$	CH_2Cl_2	3

[a] Conditions: 0.50 mmol of 2-cyclohexen-1-one, 0.025 mmol of copper salt, additive, 0.51 mmol of 48% aq. HBr, and olvent, rt. [b] Determined by GC analysis. [c] 0.0125 mmol of Cu_2O was used.

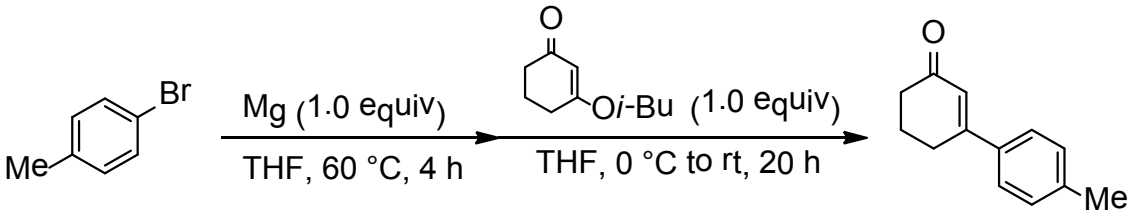
General Procedure for the Preparation of Cyclohexenones

5,6-Dihydro-[1,1′-biphenyl]-3(4H)-one (2a)



Title compound was prepared according to literature procedure [S1] (procedure A). In a well-dried 50 mL round-bottom flask, PhLi solution (5.0 mL, 9.5 mmol, 1.9 M in dibutylether, 1.9 equiv) was charged with THF (10 mL). To this, a solution of 3-ethoxy-2-cyclohexen-1-one (700 mg, 5.0 mmol) in THF (10 mL) was added dropwise at 0 ºC. After the mixture was stirred at room temperature for 20 h, saturated NH_4Cl aqueous solution (10 mL) was added to quench. The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. The characterization data matches previously reported data [S2]; ^{1}H NMR (300 MHz, CDCl3) δ 7.56-7.53 (m, 2H), 7.42-7.41 (m, 3H), 6.42 (s, 1H), 2.80-2.77 (m, 2H), 2.51-2.48 (m, 2H), 2.20-2.12 (m, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 199.89, 159.76, 138.78, 129.95, 128.73, 126.05, 125.43, 37.25, 28.08, 22.79.

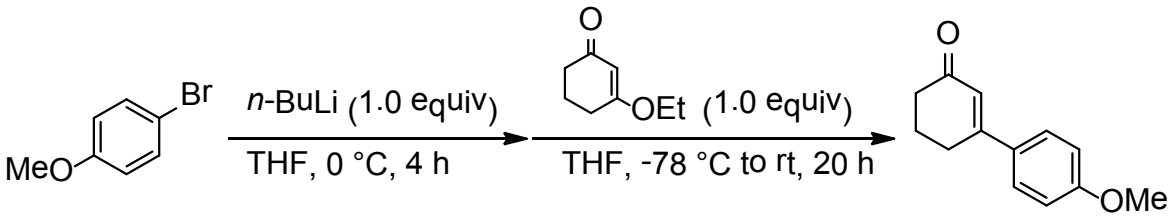
4′-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (3a)



Title compound was prepared according to literature procedure [S3] (procedure B). In a Schlenk flask, magnesium turnings (6.0 mmol, 1.2 equiv) was charged with a stirring bar and

heated under vacuum. After cooling to room temperature and backfilled with argon, ether (10 mL) was added. To this, *p*-bromotoluene (5.0 mmol) dissolved in THF (10 mL) was added dropwise and the reaction mixture was stirred at 40 °C for 4 h. Then, the reaction mixture was cooled to 0 °C and 3-butoxy-2-cyclohexen-1-one (3.0 mmol) dissolved in THF (10 mL) was added dropwise. After the mixture was stirred for 20 h, saturated NH_4Cl aqueous solution (10 mL) was added to quench. The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purication by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. The characterization data matches previously reported data [S4,5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 6.42 (t, J = 1.5 Hz, 1H), 2.78-2.75 (m, 2H), 2.50-2.46 (m, 2H), 2.18-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.93, 159.65, 140.32, 135.76, 129.43, 125.98, 124.61, 37.22, 27.94, 22.75, 21.26.

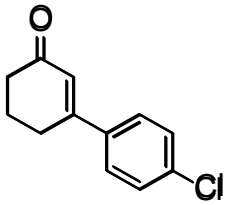
4′-Methoxyl-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (4a)



Title compound was prepared according to literature procedure [S1] (procedure C). In a well-dried 50 mL round-bottom flask, 4-bromoanisole (935 mg, 5.0 mmol) was dissolved in THF (10 mL). *n*-BuLi solution (3.0 mL, 5.0 mmol, 1.64 M in *n*-hexane, 1.0 equiv) was added dropwise at 0 ºC and the mixture was stirred for 4 h and the mixture was cooled to -78 ºC. To this, a solution of 3-ethoxy-2-cyclohexen-1-one (700 mg, 5.0 mmol) in THF (10 mL) was added dropwise. After the mixture was stirred for 20 h, saturated NH_4Cl aqueous solution (10

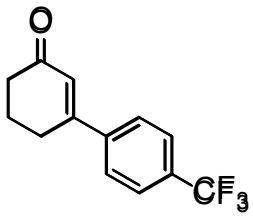
mL) was added to quench. The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purified by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow amorphous. The characterization data matches previously reported data [S4,6]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 9.1 Hz, 2H), 6.93 (d, J = 9.1 Hz, 2H), 6.40 (s, 1H), 3.85 (s, 3H), 2.77-2.74 (m, 2H), 2.48-2.45 (m, 2H), 2.17-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.91, 161.21, 159.09, 130.80, 127.61, 123.71, 114.12, 55.38, 17.19, 27.85, 22.76.

4′-Chloro-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (5a)



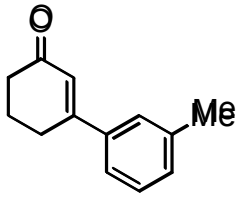
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4,5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 6.39 (t, J = 1.5 Hz, 1H), 2.76-2.72 (m, 2H), 2.50-2.47 (m, 2H), 2.19-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.63, 158.25, 137.15, 136.00, 128.97, 127.33, 125.61, 37.14, 27.96, 22.69.

4-chloro-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (6a)



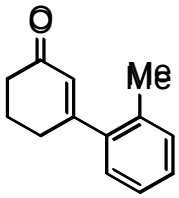
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4,5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 6.42 (s, 1H), 2.79-2.76 (m, 2H), 2.53-2.50 (m, 2H), 2.22-2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.39, 157.99, 142.36, 131.45 (J_{CF} = 33.7 Hz), 126.78, 126.33, 125.61 (J_{CF} = 3.73 Hz), 123.75 (J_{CF} = 270.9 Hz), 37.09, 28.02, 22.61.

3′-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (7a)



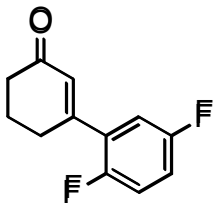
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4,5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 3H), 7.12-7.09 (m, 1H), 5.99 (t, *J* = 1.6 Hz, 1H), 2.61-2.57 (m, 2H), 2.52-2.49 (m, 2H), 2.31 (s, 3H), 2.19-2.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.56, 163.57, 140.67, 133.91, 130.63, 128.63, 128.30, 126.84, 125.87, 37.32, 31.20, 23.14, 19.97.

2′-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (8a)



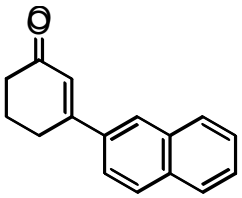
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4,5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 3H), 7.24-7.21 (m, 1H), 6.45 (t, *J* = 1.5 Hz, 1H), 2.79-2.75 (m, 2H), 2.50-2.47 (m, 2H), 2.39 (s, 3H), 2.18-2,13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.92, 160.02, 138.80, 138.36, 130.71, 128.61, 126.76, 125.31, 123.20, 37.26, 20.15, 22.81, 21.44.

2′,5′-Difluoro-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (9a)



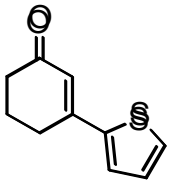
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.02 (m, 2H), 6.28 (s, 1H), 2.74-2.71 (m, 2H), 2.52-2.49 (m, 2H), 2.18-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.64, 158.14 (J_{CF} = 241.2 Hz), 155.39 (J_{CF} = 245.3 Hz), 154.95, 128.92 (J_{CF} = 1.2, 4.5 Hz), 128.49 (J_{CF} = 7.5 Hz), 117.18 (J_{CF} = 9.1, 25.3 Hz), 116.77 (J_{CF} = 7.2, 22.8 Hz), 114.77 (J_{CF} = 2.8, 24.7 Hz), 36.86 (J_{CF} = 1.2 Hz), 28.89 (J_{CF} = 1.5, 4.3 Hz), 22.58; HRMS (EI): m/z calcd for $C_{12}H_{10}OF_2$ ($[M]^+$) 208.0700, found 208.0694.

3-(Naphthalen-2-yl)cyclohex-2-enone (10a)



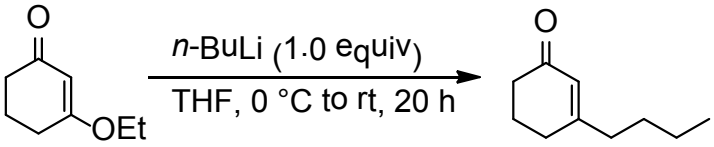
Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S7]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.6 Hz, 1H), 7.89-7.84 (m, 3H), 7.66 (dd, *J* = 1.9, 8.7 Hz, 1H), 7.55-7.51 (m, 2H), 6.58 (t, *J* = 0.7 Hz, 1H), 2.94-2.90 (m, 2H), 2.55-2.52 (m, 2H), 2.24-2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.83, 159.37, 135.90, 133.93, 133.05, 128.65, 128.45, 127.63, 127.15, 126.67, 126.09, 125.71, 123.26, 37.30, 28.05, 22.81.

3-(Thiophen-2-yl)cyclohex-2-enone (11a)



Title compound was prepared according to procedure B. Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 3.9 Hz, 1H), 7.10 (dd, *J* = 3.9, 5.1 Hz, 1H), 6.43 (s, 1H), 2.81-2.78 (m, 2H), 2.49-2.46 (m, 2H), 2.18-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.32, 152.34, 142.67, 128.69, 128.20, 127.26, 122.65, 37.17, 27.94, 22.37; HRMS (EI): m/z calcd for $C_{10}H_{10}OS$ ($[M]^+$) 178.0452, found 179.0453.

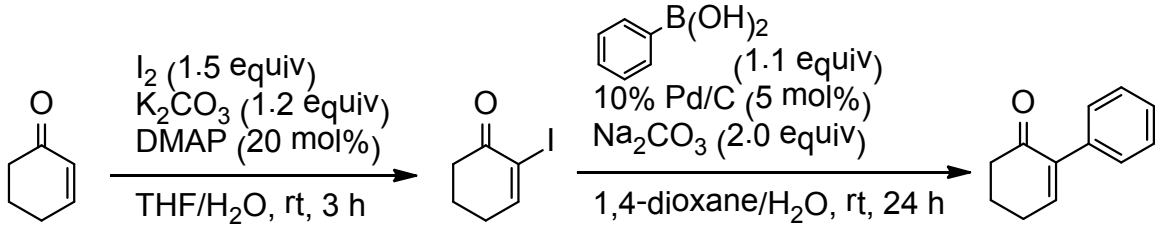
3-Butylcyclohex-2-enone (12a)



Title compound was prepared according to literature procedure [S8] (procedure D). In a well-dried 50 mL round-bottom flask, *n*-BuLi solution (5.0 mL, 8.0 mmol, 1.6 M in *n*-hexane, 1.6 equiv) was charged with THF (10 mL). To this, a solution of 3-ethoxy-2-cyclohexen-1-one (700 mg, 5.0 mmol) in THF (10 mL) was added dropwise at 0 ºC. After the mixture was stirred for 20 h, saturated NH_4Cl aqueous solution (10 mL) was

added to quench. The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. The characterization data matches previously reported data [S9]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (s, 1H), 2.35 (t, *J* = 6.7 Hz, 2H), 2.27 (t, *J* = 5.9 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.01-1.94 (m, 2 H), 1.51-1.44 (m, 2H), 1.37-1.28 (m, 2H), 0.91 (t, *J* = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.04, 166.85, 125.56, 37.73, 37.29, 29.62, 29.00, 22.68, 22.29, 13.78

4,5-Dihydro-[1,1′-biphenyl]-2(3*H*)-one (13a)

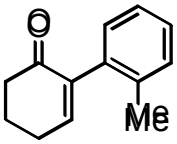


Title compound was prepared according to literature procedure [S10] (procedure E). 2-Cyclohexen-1-one (10.0 mmol) was dissolved in THF (10 mL) and H_2O (10 mL) in a 100 mL round-bottom flask. I_2 (15.0 mmol), K_2CO_3 (12.0 mmol, 1.2 equiv), and DMAP (5.0 mmol, 20 mol%) were added and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with AcOEt (10 mL) and H_2O (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 5 mL) and the combined organic phases was washed with saturated $Na_2S_2O_3$ aqueous solution and with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 10:1) afforded the iodide as a pale yellow solid.

2-Iodide-2-cyclohexen-1-one (222 mg, 1 mmol), phenyl boronic acid (134 mg, 1.1 mmol, 1.1 equiv), 10% Pd/C (10 wt%, 50 mg), and Na_2CO_3 (2.0 mmol, 2.0 equiv) were placed in test

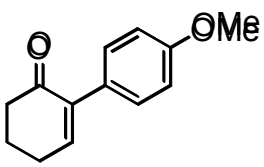
tube and 1,4-dioxane (2.0 mL) and H_2O (2.0 mL) were added. The mixture was stirred at room temperature for 24 h. The insoluble materials were filtered off and washed with AcOEt (10 mL). H_2O (10 mL) was added and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 5 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 10:1) afforded a pale yellow solid. The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 7.04 (t, *J* = 4.3 Hz, 1H), 2.62-2.58 (m, 2H), 2.57-2.53 (m, 2H), 2.15-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.87, 147.93, 140.33, 136.50, 128.56, 127.92, 127.48, 39.01, 26.54, 22.87.

2′-Methyl-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (14a)



Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.14 (m, 3H), 7.01 (d, *J* = 7.1 Hz, 1H), 6.89 (t, *J* = 4.3 Hz, 1H), 2.61-2.58 (m, 2H), 2.55-2.51 (m, 2H), 2.17-2.11 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.71, 148.56, 141.62, 136.92, 136.29, 129.70, 129.49, 127.73, 125.50, 38.65, 26.27, 23.07, 19.93.

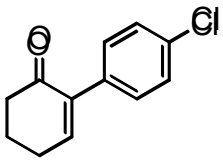
4′-Methoxy-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (15a)



Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.9 Hz, 2H), 6.85 (t, *J* = 4.3 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 2H), 3.67 (s, 3H), 2.47-2.43 (m, 2H), 2.41-2.36 (m, 2H), 1.99-1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.10, 158.93, 146.86, 139.51, 129.58, 128.84, 113.26, 55.07, 38.95, 26.42,

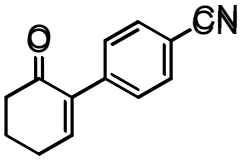
22.79.

4′-Chloro-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (16a)



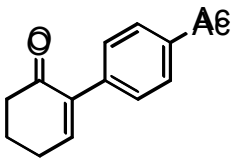
Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.02 (t, *J* = 4.3 Hz, 1H), 2.60-2.56 (m, 2H), 2.55-2.51 (m, 2H), 2.13-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.63, 148.26, 139.24, 134.85, 133.44, 129.91, 128.08, 38.89, 26.53, 22.77.

4′-Cyano-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (17a)



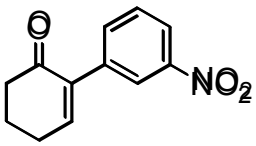
Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 4.3 Hz, 1H), 2.62-2.56 (m, 4H), 2.16-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.08, 149.78, 141.08, 139.00, 131.73, 129.33, 118.84, 111.17, 38.78, 26.61, 22.64; HRMS (EI): m/z calcd for $C_{13}H_{11}ON$ ($[M]^+$) 197.0841, found 197.0839.

4′-Acetyl-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (18a)



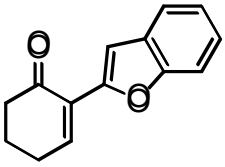
Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 4.3 Hz, 1H), 2.63-2.55 (m, 4H), 2.60 (s, 3H), 2.16-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.40, 197.07, 149.11, 141.05, 139.03, 135.63, 128.50, 127.64, 38.58, 26.27, 22.41.

3′-Nitro-4,5-dihydro-[1,1′-biphenyl]-2(3H)-one (19a)



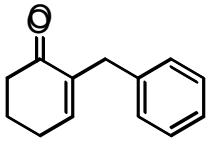
Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 10:1). The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.13 (m, 2H), 7.66 (ddd, *J* = 1.2, 1.6, 7.7 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 4.3 Hz, 1H), 2.64-2.57 (m, 4H), 2.17-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.09, 149.73, 147.99, 138.45, 137.97, 134.90, 128.78, 123.55, 122.39, 38.72, 26.58, 22.69.

2-(Benzofuran-2-yl)cyclohex-2-enone (20a)



Title compound was prepared according to procedure E. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S10]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 4.4 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.45-7.43 (m, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 2.61-2.58 (m, 4H), 2.12-2.06 (m, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 195.94, 153.59, 150.13, 146.40, 129.19, 29.15, 124.41, 122.61, 121.40, 110.51, 106.29, 106.28, 104.67, 38.97, 26.08, 22.33.

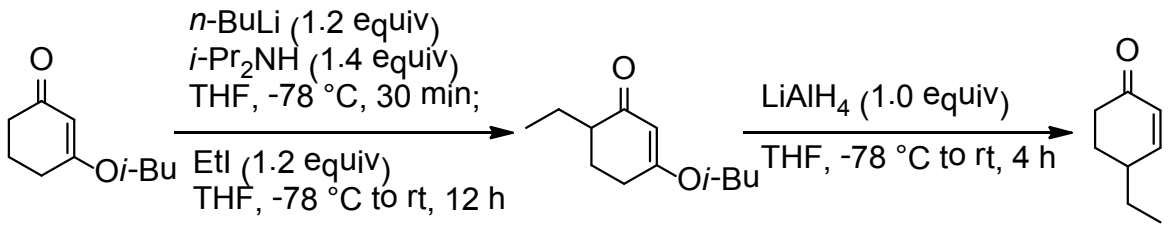
2-Benzylcyclohex-2-enone (21a)



Title compound was prepared according to literature procedure [S12] (procedure F). In a well-dried test tube, zinc dust (260 mg, 4 mmol, 1.6 equiv) was charged with THF (1 mL) and a drop of TMSCl. This suspension was stirred at 65 ºC for 30 min and then cooled to 0 ºC. A solution of benzyl bromide (360 µL, 3.0 mmol, 1.2 equiv) dissolved in THF (5 mL) was added dropwise and the mixture was stirred at 0 ºC for 3 h. The supernatant solution of this mixture was canulated to a 50 mL flask containing 2-iodo-2-cyclohexen-1-one (555 mg, 2.5 mmol) and $Pd(PPh_3)_2Cl_2$ (52.6mg, 0.075 mmol, 3

mol%) in DMF (10 mL), and the mixture was stirred at room temperature for 6 h. After quenching with saturated NH_4Cl aqueous solution (10 mL), the reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 10:1) afforded the title compound as a pale yellow oil. The characterization data matches previously reported data [S12]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.21-7.16 (m, 3H), 6.55 (dd, *J* = 4.0, 4.7 Hz, 1H), 3.52 (s, 2H), 2.47-2.43 (m, 2H), 2.35-2.31 (m, 2H), 2.01-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.96, 146.37, 139.62, 139.45, 129.13, 128.31, 126.01, 38.44, 35.37, 26.04, 23.00.

4-Ethylcyclohex-2-enone (22a)

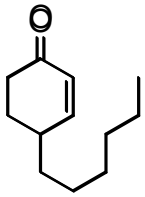


Title compound was prepared according to literature procedure [S13] (procedure G). To a solution of diisopropylamine (989 µL, 7 mmol, 1.4 equiv) dissolved in THF (5.0 mL) was added *n*-BuLi solution (5.0 mL, 8.0 mmol, 1.6 M in *n*-hexane, 1.6 equiv) dropwise. After stirring at -10 °C for 15 min, the reaction mixture was cooled to -78 °C. A solution of vinylogous ester (5.0 mmol) dissolved in THF (10 mL) was added dropwise using positive pressure cannulation. After an additional 30 min of stirring at -78 °C, a solution of ethyl iodide (5.0 mmol, 1.0 equiv) dissolved in THF (10 mL) was added dropwise using positive pressure cannulation. The reaction mixture was stirred for 12 h, and then quenched with saturated NH_4Cl aqueous solution (10 mL). The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10

mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil.

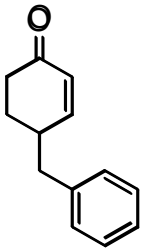
In a well-dried 50 mL round-bottom flask, $LiAlH_4$ (5.0 mmol, 1.0 equiv) was charged with THF (10 mL). To this, a solution of above prepared material in THF (10 mL) was added dropwise at -78 ºC and the reaction mixture was stirred for 4 h. After an addition of 1 N HCl aqueous solution (7.5 mL) at 0°C, the reaction mixture was stirred at room temperature for 4 h, and then neutralized by 1 N NaOH aqueous solution (12.5 mL). The phases were separated and the aqueous phase was extracted with AcOEt (2 x 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. The characterization data matches previously reported data [S14]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 10.1 Hz, 1H), 5.94 (dd, *J* = 2.3, 10.1 Hz, 1H), 2.48-2.42 (m, 1H), 2.36-2.25 (m, 2H), 2.10-2.03 (m, 1H), 1.69-1.59 (m, 1H), 1.54-1.47 (m, 1H), 1.47-1.38 (m, 1H), 0.96 (t, *J* = 7.6, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.00, 155.07, 128.87, 37.54, 36.85, 28.07, 27.37, 11.30.

4-Hexylcyclohex-2-enone (23a)



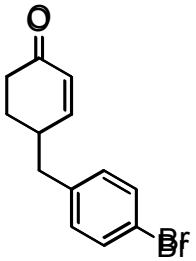
Title compound was prepared according procedure G. Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (300 MHz, CDCl3) δ 6.81 (d, *J* = 9.9 Hz, 1H), 5.91 (dd, *J* = 2.1, 9.9 Hz, 1H), 2.47-2.41 (m, 1H), 2.38-2.25 (m, 2H), 2.09-2.02 (m, 1H), 1.68-1.58 (m, 1H), 1.51-1.21 (m, 10H), 0.84 (t, *J* = 6.7, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.79, 155.21, 128.71, 36.81, 35.94, 34.46, 31.60, 29.16, 28.48, 26.75, 22.46, 13.93; HRMS (EI): m/z calcd for $C_{12}H_{20}O$ ($[M]^+$) 180.1514, found 180.1486.

4-Benzylcyclohex-2-enone (24a)



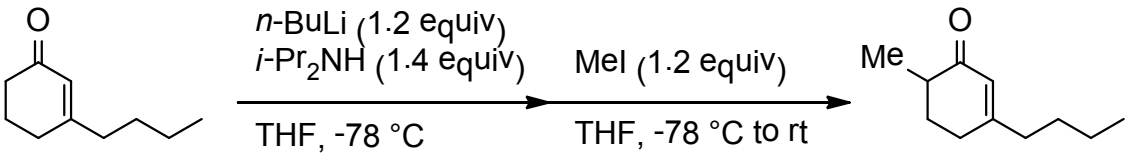
Title compound was prepared according procedure G. Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S15]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 9.7 Hz, 1H), 5.99 (d, *J* = 9.7 Hz, 1H), 2.81-2.72 (m, 3H), 2.53-2.47 (m, 1H), 2.39-2.31 (m, 1H), 2.09-2.04 (m, 1H), 1.78-1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.58, 153.72, 138.80, 129.11, 128.90, 128.44, 126.39, 40.74, 37.82, 36.65, 28.47

4-(4-Benzyl)cyclohex-2-enone (25a)



Title compound was prepared according procedure G. Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.80 (dd, *J* = 1.2, 10.4 Hz, 1H), 5.99 (d, *J* = 10.4 Hz, 1H), 2.77-2.65 (m, 3H), 2.53-2.45 (m, 1H), 2.39-2.30 (m, 1H), 2.07-2.04 (m, 1H), 1.76-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.38, 153.11, 137.86, 131.67, 130.72, 129.51, 120.39, 40.29, 37.76, 36.70, 28.52; HRMS (EI): m/z calcd for $C_{13}H_{13}OBr$ ($[M]^+$) 264.0150, found 265.0133.

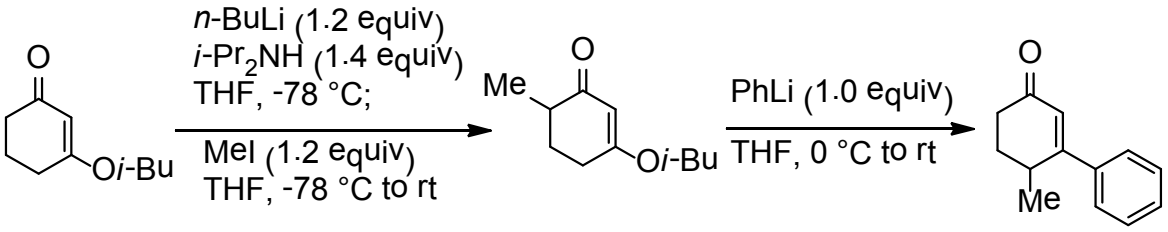
3-Butyl-6-methylcyclohex-2-enone (28a)



To a solution of diisopropylamine (989 μL, 7 mmol, 1.4 equiv) dissolved in THF (5.0 mL) was added *n*-BuLi solution (5.0 mL, 8.0 mmol, 1.6 M in *n*-hexane, 1.6 equiv) dropwise. After stirring at -10 °C for 15 min, the reaction mixture was cooled to -78 °C. A solution of 3-butyl-2-cyclohexen-1-one (5.0 mmol) dissolved in THF (10 mL) was added dropwise using

positive pressure cannulation. After an additional 30 min of stirring at -78 °C, a solution of methyl iodide (5.0 mmol, 1.0 equiv) dissolved in THF (10 mL) was added dropwise using positive pressure cannulation. The reaction mixture was stirred at room temperature, and then quenched with saturated NH_4Cl aqueous solution (10 mL). The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 2.36-2.21 (m, 3H), 2.15 (t, *J* = 7.5 Hz, 2H), 2.05-1.98 (m, 1H), 1.70-1.59 (m, 1H), 1.48-1.39 (m, 2H), 1.34-1.21 (m, 2H), 1.09 (d, *J* = 5.2 Hz, 3H), 0.87 (t, *J* = 7.7, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.24, 165.45, 124.96, 40.67, 37.39, 30.75, 29.14, 29.00, 22.23, 15.01, 13.74; HRMS (EI): m/z calcd for $C_{11}H_{18}O$ ($[M]^+$) 166.1358, found 167.1332.

6-Methyl-5,6-dihydro-[1,1′-biphenyl]-3(4H)-one (29a)

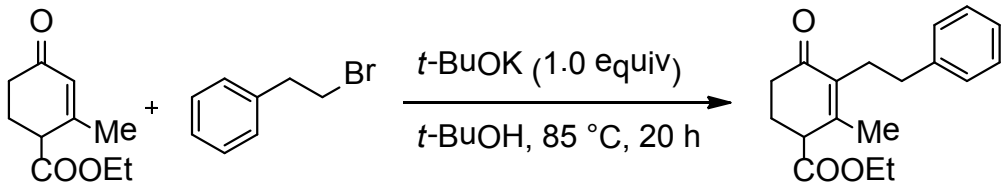


To a solution of diisopropylamine (989 μL, 7 mmol, 1.4 equiv) dissolved in THF (5.0 mL) was added *n*-BuLi solution (5.0 mL, 8.0 mmol, 1.6 M in , 1.6 equiv) dropwise. After stirring at -10 °C for 15 min, the reaction mixture was cooled to -78 °C. A solution of vinylogous ester (5.0 mmol) dissolved in THF (10 mL) was added dropwise using positive pressure cannulation. After an additional 30 min of stirring at -78 °C, a solution of methyl iodide (5.0 mmol, 1.0 equiv) was added dropwise using positive pressure cannulation. The reaction mixture was stirred at room temperature, and then quenched with saturated NH4Cl aqueous

solution (10 mL). The reaction mixture was diluted with diethylether (10 mL) and the phases were separated. The aqueous phase was extracted with diethylether (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. This compound was used for next step without purification.

In a well-dried 50 mL round-bottom flask, PhLi solution (5.0 mL, 9.5 mmol, 1.9 M in dibutylether, 1.9 equiv) was charged with THF (10 mL). To this, a solution of above crude material in THF (10 mL) was added dropwise at 0 ºC. After the mixture was stirred at room temperature for 20 h, saturated NH4Cl aqueous solution (10 mL) was added to quench. The reaction mixture was diluted with AcOEt (10 mL) and the phases were separated. The aqueous phase was extracted with AcOEt (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. The characterization data matches previously reported data [S16]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.42-7.38 (m, 3H), 6.24 (s, 1H), 3.19-3.12 (m, 1H), 2.64-2.55 (m, 1H), 2.47-2.41 (m, 1H), 2.35-2.26 (m, 1H), 2.01-1.94 (m, 1H), 1.17 (d, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.67, 165.22, 138.22, 129.73, 128.74, 126.59, 125.03, 33.11, 31.08, 29.47, 18.26.

Ethyl 2-methyl-4-oxo-3-phenethylcyclohex-2-enecarboxylate (30a)

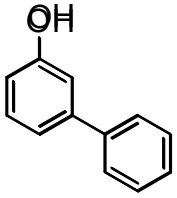


Title compound was prepared according to literature procedure [S17] (procedure H). To a solution of ethyl 2-methyl-4-oxo-2-cyclohexene-1-carboxylate (440 µL, 2.5 mmol) dissolved in *t*-BuOH (10 mL) was added *t*-BuOK (300 mg, 2.7 mmol, 1.1 equiv). After stirring at room

temperature for 30 min, (2-bromoethyl)benzene (343 μL, 2.5 mmol, 1.0 equiv). The reaction mixture was stirred at 85 °C for 16 h, and then poured into ice-water. The mixture was acidified with 1N HCl and diluted with AcOEt (10 mL), and then the phases were separated. The aqueous phase was extracted with diethylether (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.16 (m, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.24 (t, J = 4.8 Hz, 1H), 2.65-2.57 (m, 5H), 2.41-2.35 (m, 1H), 2.30-2.12 (m, 2H), 1.80 (s, 3H), 1.28 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.33, 172.15, 150.59, 141.90, 136.61, 128.63, 128.21, 125.81, 61.19, 47.66, 34.78, 34.72, 27.70, 25.58, 20.20, 14.18; HRMS (EI): m/z calcd for $C_{18}H_{22}O_3$ ($[M]^+$) 286.1569, found 286.1540.

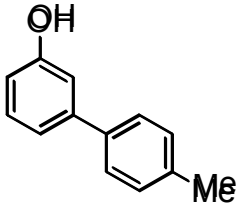
Spectral Data for Phenols

Biphenyl-3-ol (2b)



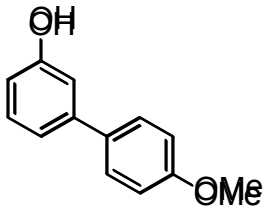
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4, 18]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 0.9, 7.7 Hz, 1H), 7.08 (dd, *J* = 1.6, 2.4 Hz, 1H), 6.84 (dd, *J* = 2.4, 8.0 Hz, 1H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.77, 142.98, 140.68, 129.97, 128.72, 127.46, 127.08, 119.76, 114.18, 114.08.

4′-Methylbiphenyl-3-ol (3b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4, 19]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.06 (t, *J* = 2.0 Hz, 1H) ,6.81 (dd, *J* = 2.5, 8.0 Hz, 1H), 5.09 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.71, 142.90, 137.77, 137.26, 129.92, 129.44, 126.90, 119.57, 113.88, 113.86, 21.06.

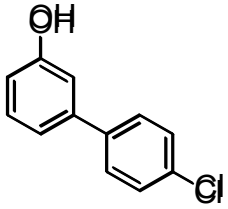
4′-Methoxylbiphenyl-3-ol (4b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4, 20]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 0.9, 7.9 Hz, 1H), 7.06 (dd, *J* = 1.9, 2.1 Hz, 1H), 6.82 (dd, *J* = 2.4, 8.0 Hz, 1H), 5.09 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.13, 155.79, 142.50, 133.25, 129.92, 128.08, 119.27, 114.17, 113.61,

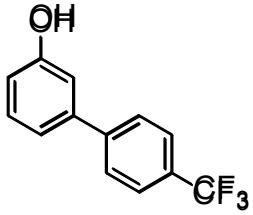
113.59, 112.73, 55.34.

4′-Chlorobiphenyl-3-ol (5b)



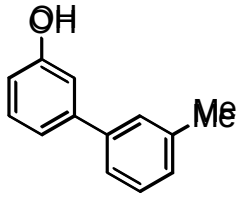
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.9 Hz, 1H), 7.13 (dd, J = 0.8, 7.7 Hz, 1H), 7.03 (dd, J = 1.7, 2.3 Hz, 1H), 6.84 (dd, J = 2.4, 7.9 Hz, 1H), 5.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.81, 141.71, 139.08, 133.53, 130.12, 128.86, 128.29, 119.59, 114.51, 113.91.

4′-(trifluoromethyl)biphenyl-3-ol (6b)



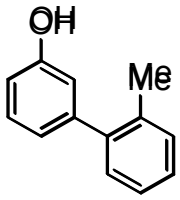
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 Hz, 2H) 7.65 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.18 (ddd, J = 0.7, 0.8, 7.7 Hz, 1H), 7.08 (dd, J = 1.7, 2.3 Hz, 1H), 6.89 (dd, J = 2.5, 8.0 Hz, 1H), 5.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.86, 144.15 (J_{CF} = 1.2 Hz), 141.51, 130.26, 129.52 (J_{CF} = 32.3 Hz), 127.35, 125.68 (J_{CF} = 3.7 Hz), 124.24 (J_{CF} = 270.5 Hz), 119.93, 115.11, 114.22.

3′-Methylbiphenyl-3-ol (7b)



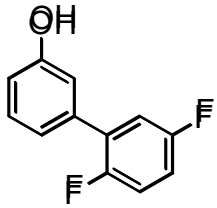
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.22 (m, 3H), 7.21-7.17 (m, 2H), 6.86 (ddd, J = 1.1, 1.5, 7.6 Hz, 1H), 6.80-6.76 (m, 2H), 5.09 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.09, 143.63, 141.43, 135.27, 130.27, 129.57, 129.26, 127.32, 125.69, 121.87, 116.16, 113.69, 20.37.

2′-Methylbiphenyl-3-ol (8b)



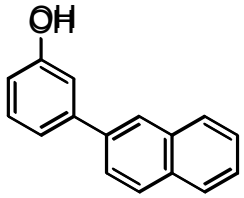
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S4]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.20-7.17 (m, 2H), 7.08 (dd, *J* = 1.9, 2.3 Hz, 1H), 6.83 (ddd, *J* = 0.9, 2.4, 8.0 Hz, 1H), 5.14 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.71, 143.10, 140.66, 138.30, 129.90, 128.62, 128.20, 127.88, 124.17, 119.77, 114.08, 21.48.

2′,5’-Difluorobiphenyl-3-ol (9b)



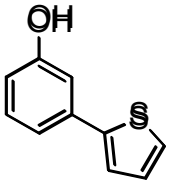
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 1H), 7.15-7.07 (m, 3H), 7.03-6.97 (m, 2H), 6.88 (ddd, *J* = 0.8, 2.7, 8.1 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ158.70 (J_{CF} = 2.5, 241.3 Hz), 155.65 (J_{CF} = 2.5, 241.3 Hz), 155.50, 136.30 (J_{CF} = 1.6 Hz), 129.84 (J_{CF} = 8.0 Hz), 129.83, 121.44 (J_{CF} = 3.1 Hz), 117.15 (J_{CF} = 8.8, 25.9 Hz), 116.80 (J_{CF} = 3.7, 24.3 Hz), 115.88 (J_{CF} = 3.5 Hz), 115.31 (J_{CF} = 8.8, 23.9 Hz), 115.19; HRMS (EI): m/z calcd for $C_{12}H_8OF_2$ ($[M]^+$) 206.0543, found 206.0551.

3-(Naphthalen-2-yl)phenol (10b)



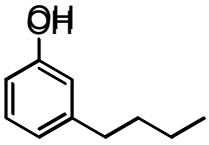
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.92-7.87 (m, 3H), 7.72 (dd, *J* = 1.9, 8.5 Hz, 1H), 7.55-7.49 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.33 (tt, *J* = 1.3, 7.7 Hz, 1H), 7.20 (dd, *J* = 1.6, 2.4 Hz, 1H), 6.88 (ddd, *J* = 2.4, 2.5, 7.9 Hz, 1H), 5.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.80, 142.86, 137.97, 133.55, 132.68, 130.07, 128.38, 128.19, 127.60, 126.29, 125.99, 125.80, 125.42, 120.05, 114.31, 114.28; HRMS (EI): m/z calcd for $C_{16}H_{12}O$ ($[M]^+$) 220.0888, found 220.0876.

3-(Thiophen-2-yl)phenol (11b)



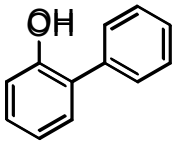
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S21]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 4H), 7.10 (t, *J* = 2.0 Hz, 1H), 7.07 (ddd, *J* = 0.5, 3.6, 5.1 Hz, 1H), 6.76 (ddd, *J* = 1.2, 2.3, 7.9 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.74, 143.82, 135.94, 130.14, 127.95, 124.95, 123.33, 118.65, 114.43, 112.78.

3-Butylphenol (12b)



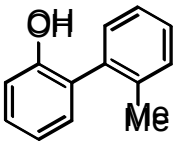
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S22]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.70-6.63 (m, 2H), 4.88 (s, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.59 (tt, *J* = 7.2, 7.7 Hz, 1H), 1.36 (qt, *J* = 7.2, 7.5 Hz, 2H), 0.93 (s, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.34, 144.91, 129.35, 120.99, 115.30, 112.45, 35.47, 33.40, 22.31, 13.92.

Biphenyl-2-ol (13b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S23, 24]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 4H), 7.44-7.40 (m, 1H), 7.31-7.27 (m, 2H), 7.05-7.01 (m, 2H), 5.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.37, 137.04, 130.21, 129.22, 129.11, 129.06, 128.09, 127.82, 120.81, 115.79.

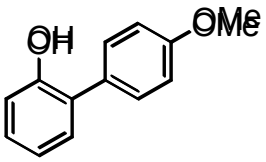
2′-Methylbiphenyl-2-ol (14b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S25]; ^{1}H NMR (400

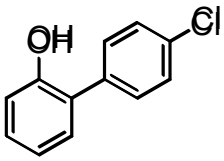
MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), 7.32-7.21 (m, 4H), 7.12 (dd, *J* = 1.6, 7.7 Hz, 1H), 7.01-6.96 (m, 2H), 4.74 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.46, 137.39, 135.67, 130.64, 130.45, 130.12, 129.09, 128.49, 127.67, 126.42, 120.42, 115.27, 19.72.

4′-Methoxybiphenyl-2-ol (15b)



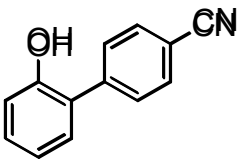
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S24]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.24-7.20 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.99-6.96 (m, 2H), 5.15 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22, 152.47, 130.22, 13021, 129.17, 128.72, 127.79, 120.71, 116.67, 115.63, 114.62, 55.29.

4′-Chlorobiphenyl-2-ol (16b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S26]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.29-7.22 (m, 2H), 7.00 (dt, *J* = 1.2, 3.5 Hz, 1H), 6.96 (dd, *J* = 1.1, 8.1 Hz, 1H), 5.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.27, 135.61, 133.79, 130.47, 130.24, 129.37, 129.23, 127.01, 121.05, 116.01.

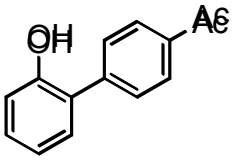
4′-Cyanobiphenyl-2-ol (17b)



Purified by silica gel column chromatography (hexane/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.32-7.26 (m, 2H), 7.04 (dt, *J* = 0.9, 7.7, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.35, 142.59, 132.41, 130.42, 130.07, 129.93, 126.49, 121.39, 118.82, 116.39, 110.95; HRMS (EI): m/z calcd for $C_{13}H_9ON$

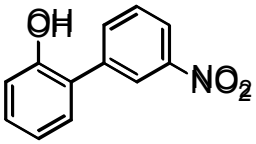
([M]$^+$) 195.0684, found 195.0703.

4′-Acethylbiphenyl-2-ol (18b)



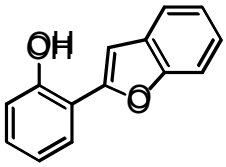
Purified by silica gel column chromatography (hexane/EtOAc = 25:1) The characterization data matches previously reported data [S27]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.31-7.27 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 5.45 (s, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.92, 152.51, 142.55, 135.97, 130.31, 129.74, 129.35, 128.93, 127.12, 121.10, 116.25, 26.64.

3′-Nitrobiphenyl-2-ol (19b)



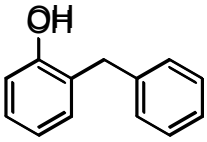
Purified by silica gel column chromatography (hexane/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (t, *J* = 1.9 Hz, 1H), 8.22 (ddd, *J* = 1.1, 2.3, 8.3 Hz, 1H), 7.89 (ddd, *J* = 1.2, 1.6, 7.7 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.34-7.29 (m, 2H), 7.06 (dt, *J* = 1.2, 7.2 Hz, 1H), 6.95 (dd, *J* = 1.1, 8.1 Hz, 1H), 4.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.31, 139.38, 135.32, 130.58, 129.98, 129.43, 125.98, 124.25, 122.16, 121.48, 116.36; HRMS (EI): m/z calcd for $C_{12}H_9O_3N$ ([M]$^+$) 215.0582, found 215.0561.

2-(Benzofuran-2-yl)phenol (20b)



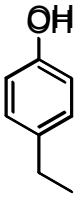
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S28]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.62 (dd, *J* = 1.6, 6.7 Hz, 1H), 7.55 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.35-7.27 (m, 3H), 7.18 (s, 1H), 7.11 (d, *J* = 0.9 Hz, 1H), 7.04-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.27, 153.95, 153.29, 130.26, 128.48, 127.14, 124.43, 123.41, 120.98, 120.76, 117.37, 116.05, 110.98, 103.31.

2-Benzylphenol (21b)



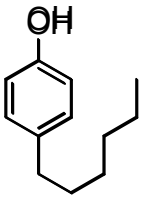
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.26-7.22 (m, 3H), 7.17-7.13 (m, 2H), 6.91 (m, 1H), 6.79 (d, J = 7.5 Hz, 1H), 4.82 (s, 1H), 4.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.66, 139.86, 130.94, 128.66, 128.59, 127.78, 126.97, 126.29, 120.90, 115.66, 36.27; HRMS (EI): m/z calcd for $C_{13}H_{12}O$ ($[M]^+$) 184.0888, found 184.0881.

4-Ethlyphenol (22b)



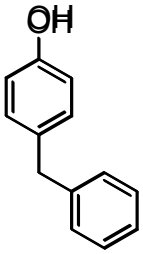
Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S29]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 4.85 (s, 1H), 2.59 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.29, 136.55, 128.88, 115.09, 27.93, 15.84.

4-Hexylphenol (23b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 2.53 (t, J = 7.9 Hz, 2H), 1.61-1.52 (m, 2H), 1.33-1.27 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.33, 135.20, 129.41, 115.02, 35.03, 31.71, 31.69, 28.90, 22.60, 14.08; HRMS (EI): m/z calcd for $C_{12}H_{18}O$ ($[M]^+$) 178.1358, found 178.1352

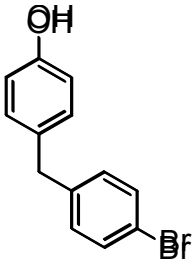
4-Benzylphenol (24b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1). The characterization data matches previously reported data [S30]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 7.1 Hz, 2H), 7.21-7.16 (m, 3H), 7.06 (d, J = 8.1 Hz, 2H),

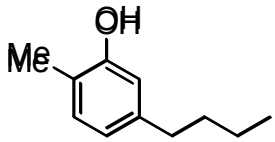
6.75 (s, J = 8.1 Hz, 2H), 4.58 (s, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 141.48, 130.05, 128.80, 128.42, 125.99, 115.25, 41.00.

4-(4-Bromobenzyl)phenol (25b)



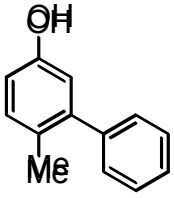
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 6.8 Hz, 1H), 7.03 (d, J = 6.8 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.98 (s, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.92, 140.47, 132.69, 131.44, 130.51, 129.99, 119.80, 115.37, 40.34; HRMS (EI): m/z calcd for $C_{13}H_{11}OBr$ ($[M]^+$) 261.9993, found 261.9966.

5-Butyl-2-methylphenol (28b)



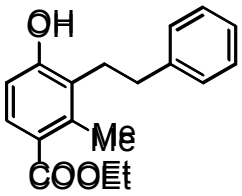
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); mp:°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 7.6 Hz, 1H), 6.69 (dd, J = 1.1, 7.6 Hz, 1H), 6.62 (d, J = 1.1 Hz, 1H), 4.72 (s, 1H), 2.54 (t, J = 7.7 Hz, 2H), 2.22 (s, 3H), 1.62-1.54 (m, 2H), 1.40-1.31 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.50, 142.23, 130.68, 120.73, 120.59, 114.92, 35.10, 33.53, 22.29, 15.26, 13.91; IR (ATR) ν cm-1; HRMS (EI): m/z calcd for $C_{11}H_{16}O$ ($[M]^+$) 164.1201, found 164.1175.

6-Methylbiphenyl-3-ol (29b)



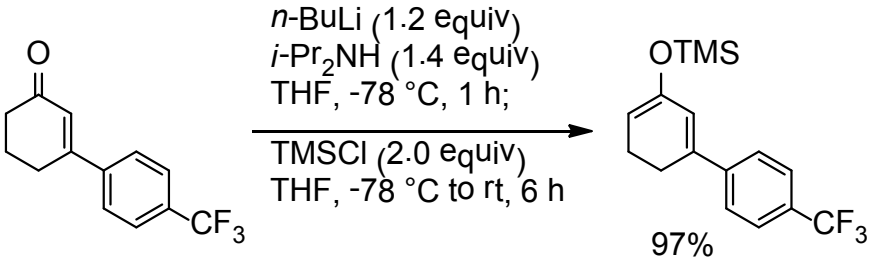
Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.37-7.34 (m, 1H), 7.33-7.31 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H), 6.78-6.74 (m, 2H), 4.83 (s, 1H), 2.20 (s, 3H; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.26, 143.03, 141.58, 131.34, 128.99, 128.04, 127.50, 126.85, 116.57, 114.06, 19.45; HRMS (EI): m/z calcd for $C_{13}H_{12}O$ ($[M]^+$) 184.0888, found 184.0872.

Ethyl 4-hydroxy-2-methyl-3-phenethylbenzoate (30b)



Purified by silica gel column chromatography (hexane/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 1H), 7.32-7.22 (m, 5H), 6.62 (d, *J* = 8.5 Hz, 1H), 4.85 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.01-2.97 (m, 2H), 2.81-2.77 (m, 2H), 2.54 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.60, 156.73, 142.01, 140.19, 129.86, 128.45, 128.35, 127.77, 126.03, 123.63, 112.39, 60.68, 35.12, 28.61, 16.50, 14.30; HRMS (EI): m/z calcd for $C_{18}H_{20}O_3$ ($[M]^+$) 284.1412, found 284.1411.

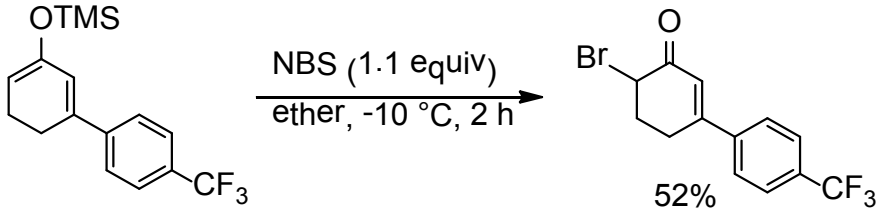
Preparation of 6-Bromo-3-(4-Trifluoromethylphenyl)-2-Cyclohexen-1-One



To a solution of diisopropylamine (141 µL, 1.0 mmol, 1.6 equiv) dissolved in THF (5.0 mL) was added *n*-BuLi solution (0.50 mL, 0.80 mmol, 1.6 M in *n*-hexane, 1.3 equiv) dropwise. After stirring at -10 °C for 15 min, the reaction mixture was cooled to -78 °C. A solution of 3-(4-trifluoromethylphenyl)-2-cyclohexen-1-one (150 mg, 0.624 mmol) dissolved in THF (5 mL) was added dropwise using positive pressure cannulation. After an additional 30 min of stirring at -78 °C, TMSCl (160 µL, 1.25 mmol, 2.0 equiv) was added dropwise. The reaction mixture was stirred for 6 h at -78 °C, and then quenched with ice cold 10% aqueous $NaHCO_3$ (10 mL). The reaction mixture was diluted with diethylether (10 mL) and the phases were separated. The aqueous phase was extracted with diethylether (2 x 10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. This compound was used for next step without purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.18 (s, 1H),

5.06-5.03 (m, 1H), 2.58-2.54 (m, 2H), 2.39-2.34 (m, 2H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.84, 143.93 (J_{CF} = 1.5 Hz), 137.55, 128.96 (J_{CF} = 32.1 Hz), 125.30 (J_{CF} = 3.7 Hz), 125.21, 124.50, 124.23 (J_{CF} = 270.5 Hz), 25.55, 22.30, 0.14.



In a well-dried 50 mL round-bottom flask, above silyl enol ether was charged with diethylether (5 mL) and the solution was cooled to -10 ºC. To this, NBS (122 mg, 0.686 mmol, 1.1 equiv) was added at one portion and the reaction mixture was stirred at this temperature for 2 h. After filtration to remove insoluble materials washed with diethylether, saturated $Na_2S_2O_3$ aqueous solution (10 mL) was added. The phases were separated and the aqueous phase was extracted with diethylehter (2 x 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 6.45 (s, 1H), 4.55 (t, J = 4.1 Hz, 1H), 3.11-3.02 (m, 1H), 2.76 (dt, J = 4.1, 17.9 Hz, 1H), 2.59-2.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.45, 157.86, 141.46, 132.00 (J_{CF} = 32.5 Hz), 126.52, 125.79 (J_{CF} = 3.7 Hz), 123.99, 123.67 (J_{CF} = 270.9 Hz), 48.13, 31.54, 25.32

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