

Supporting Information

Transition-Metal-Free Catalytic Formal Hydroacylation of Terminal Alkynes

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Supporting Methods

Instrumental and Reagents: GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-5 capillary column using calibration-curve method or effective carbon number approach. GC-MS spectra were recorded on Shimadzu GCMS-QP2010 equipped with an InertCap5 capillary column at an ionization voltage of 70 eV. Liquid-state ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA 500. ^1H and ^{13}C NMR were measured at 500 and 125 MHz, respectively, with TMS as an internal standard ($\delta = 0$ ppm). ^{19}F NMR was measured at 470 MHz with benzotrifluoride as an external standard ($\delta = -63.72$ ppm). Several hydroacylated products were isolated using Biotage Isolera. ICP-AES analyses were performed on Shimadzu ICPS-8100. DR UV-Vis spectra were recorded on a Jasco V-570DS. XRD patterns were recorded using a Rigaku SmartLab instrument under Cu K α radiation (45 kV, 200 mA). IR spectra were measured on Jasco FT/IR-4100 using KBr disks. BET surface areas were measured on micromeritics ASAP 2010 and calculated from the N_2 adsorption isotherm with the BET equation. Elemental analyses for C, H, and N were performed on Elementar vario MICRO cube. Elemental analysis for Cl was performed on Thermo Fisher Scientific ICS-1600. $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$ ($47 \text{ m}^2 \text{ g}^{-1}$, Cat. No. Tomita-AD 500, Tomita Pharmaceutical), hydroxyapatite ($11 \text{ m}^2 \text{ g}^{-1}$, Cat. No. 011-14882, FUJIFILM Wako), MgO ($38 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. 137-10831, FUJIFILM Wako), CaO ($15 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. 036-19655, FUJIFILM Wako), ZnO ($7 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. 265-00971, FUJIFILM Wako), CeO_2 ($45 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. 544841-25G, Aldrich), ZrO_2 ($48 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. JRC-ZRO-6, Catalysis Society of Japan), Al_2O_3 ($183 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. KHS-24, Sumitomo Chemical), TiO_2 ($66 \text{ m}^2 \text{ g}^{-1}$ after calcination at 600°C for 3 h, Cat. No. ST-01, Ishihara Sangyo Kaisha), and $\text{Ca}(\text{OH})_2$ (Cat. No. 07069-00, Kanto Chemical) were commercially available. Solvents, substrates, and metal sources were obtained from Kanto Chemical, TCI, Wako, Nacalai Tesque, or Aldrich (reagent grade). Several substrates were purified by kugelrohr distillation just before the use for reactions.

Preparation of $\text{Mg}_2\text{Al}-\text{CO}_3$ LDH: The $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot n\text{H}_2\text{O}$ ($\text{Mg}_2\text{Al}-\text{CO}_3$ LDH) was prepared as follows according to the previous report.¹ An aqueous solution (60 mL) of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (4.06 g) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (2.42 g) was gradually added into an aqueous solution of Na_2CO_3 (0.1 M, 100 mL) while the pH of the solution was retained *ca.* 10.0 using an aqueous solution of NaOH (2 M). After completing the addition, the mixture was stirred at 80°C for 14 h. The obtained slurry was filtrated, washed with deionized water (1 L), and dried at 80°C for 6 h, affording the desired $\text{Mg}_2\text{Al}-\text{CO}_3$ LDH (2.2 g, Mg/Al molar ratio determined by ICP-AES = 2.1). The $\text{Mg}_8\text{Al}_4(\text{OH})_{20}(\text{CO}_3) \cdot n\text{H}_2\text{O}$ ($\text{Mg}_4\text{Al}-\text{CO}_3$ LDH) was prepared in the same method (1.6 g, Mg/Al

molar ratio determined by ICP-AES = 4.0) using an aqueous solution (30 mL) of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (4.06 g) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1.21 g), and an aqueous solution of Na_2CO_3 (0.1 M, 50 mL).

Preparation of $\text{Mg}_3\text{Al}-\text{Cl}$ LDH: The $\text{Mg}_6\text{Al}_2(\text{OH})_{12}\text{Cl}_{1.6}(\text{CO}_3)_{0.2} \cdot n\text{H}_2\text{O}$ ($\text{Mg}_3\text{Al}-\text{Cl}$ LDH) was prepared as follows according to the previous report.² $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (15.2 g) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (6.04 g) were dissolved into decarbonated water (100 mL). Into the solution was gradually added an aqueous solution of NaOH (2 M, 100 mL) under an Ar flow while the pH of the solution was retained *ca.* 10.0 using an aqueous solution of HCl . After adding all of the NaOH solution, the mixture was stirred at 70 °C for 18 h with an Ar balloon (1 atm). The slurry was filtrated, washed with decarbonated water (500 mL), and dried at overnight, affording the desired $\text{Mg}_3\text{Al}-\text{Cl}$ LDH (6.2 g, Mg/Al molar ratio determined by ICP-AES = 2.9, Mg : 22.1wt%, Al : 8.36wt%, Cl : 8.90wt%). When NaCl remained in the obtained LDH, the LDH was dispersed into decarbonated water (200 mL) and stirred for 15 min, and then the white powder was retrieved in the above-mentioned manner, giving the pure $\text{Mg}_3\text{Al}-\text{Cl}$ LDH.

Preparation of $\text{Mg}(\text{OH})_2$: The $\text{Mg}(\text{OH})_2$ was prepared as follows. An aqueous solution (60 mL) of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (3.1 g) was gradually added into an aqueous solution of NaOH (50 mL, pH = *ca.* 10) while the pH of the solution was retained *ca.* 11 using an aqueous solution of NaOH (2 M). After completing the addition, the mixture was stirred at 80 °C for 24 h. The obtained slurry was filtrated, washed with deionized water (1 L), and dried at 80 °C overnight, affording the desired $\text{Mg}(\text{OH})_2$ (0.62 g).

Catalytic Reaction: The catalytic reaction was typically carried out according to the following procedure. Into a glass schlenk tube (volume: *ca.* 20 mL) were successively added $\text{Mg}_3\text{Al}-\text{CO}_3$ LDH (130 mg), biphenyl (0.1 mmol, internal standard), *p*-anisaldehyde (**1a**, 0.5 mmol), phenylacetylene (**2a**, 0.5 mmol), toluene (2 mL), and a Teflon-coated magnetic stir bar. Through freeze-pump-thaw cycling, the dissolved gases were removed from the solution, and the atmosphere was replaced into an Ar atmosphere; the mixture was then stirred at 120 °C for 15 h under an Ar atmosphere with a balloon. The yields of products were determined by GC analysis using biphenyl as an internal standard. With respect to the isolation of products, after the reaction, the catalyst was removed by simple filtration and the filtrate was then concentrated by evaporation of toluene. The crude product was subjected to column chromatography on silica gel (typically using $\text{EtOAc}/\text{hexane} = 1/9$ as an eluent), giving the pure hydroacylated products.

Leaching Test: To verify whether the catalytic reaction occurred on solid $\text{Mg}_3\text{Al}-\text{CO}_3$ LDH or not, the catalyst was removed by hot filtration 20 min after the reaction started under the optimized

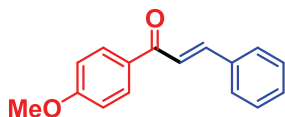
conditions and the reaction was again carried out with the filtrate under the same conditions. When the amount of leached metals was measured, the filtrate after the reaction for 15 h was evaporated *in vacuo*, treated with concentrated HNO₃ (1 mL), and sonicated. Then, Mg and Al species in the filtrate were analyzed by ICP-AES after the filtrate was moved into a 10 mL volumetric flask.

Reuse Test: Four runs under the optimized conditions were performed for three reuses not to change the amount of catalysts used for the respective reuses. After the reaction, Mg₃Al–CO₃ LDH was retrieved from the reaction mixture by simple filtration using a PTFE membrane filter. The retrieved Mg₃Al–CO₃ LDH catalyst after the reaction was washed with acetone (25 mL/run) and dried *in vacuo*. Then, 4–N runs were performed for the Nth reuse, *e.g.*, three runs under the optimized conditions were performed for the first reuse using the retrieved catalyst. These reuse experiments were repeated until the third reuse.

Synthesis of benzaldehyde- α -d₁ (D-1d): Benzaldehyde- α -d₁ (**D-1d**) was synthesized in the following method.³ Benzylalcohol- α,α -d₂ (2.7 mmol) and Ru(OH)_x/Al₂O₃ (0.2 g, prepared referring to the previous report)³ were added to toluene (10 mL), and stirred for 4 h at 80 °C under an O₂ atmosphere with a balloon. After filtrating Ru(OH)_x/Al₂O₃, washing with toluene, and drying with Na₂SO₄, the solution was condensed till *ca.* 1 mL under reduced pressure. Benzaldehyde- α -d₁ was obtained as the mixture with toluene to inhibit the auto-oxidation (deuterated ratio: >99%, molar ratio: benzaldehyde- α -d₁/toluene = 1/0.32).

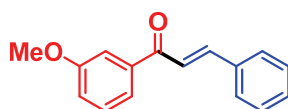
¹H NMR (500 MHz, CDCl₃, TMS): δ 7.51–7.56 (m, 2H), 7.63 (tdd, *J* = 7.0, 1.5 and 1.5 Hz, 1H), 7.87–7.91 (m, 2H).

Spectral Data of Synthesized Chalcones, Its Derivatives (3), and Propargylic Alcohol (4)



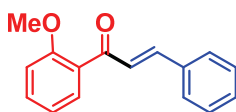
3aa (Eluent: EtOAc/hexane = 2/8)

(E)-4'-methoxychalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.88 (s, 3H), 6.97–7.00 (m, 2H), 7.38–7.43 (m, 3H), 7.55 (d, $J = 15.5$ Hz, 1H), 7.62–7.66 (m, 2H), 7.80 (d, $J = 15.5$ Hz, 1H), 8.03–8.06 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 55.6, 114.0, 122.0, 128.5, 129.0, 130.4, 130.9, 131.2, 135.2, 144.1, 163.5, 188.8. MS (EI): m/z (%): 239 (16), 238 (100), 237 (80), 223 (18), 210 (13), 195 (15), 167 (13), 165 (12), 135 (67), 131 (16), 107 (16), 103 (29), 92 (24), 77 (62), 64 (13), 63 (11), 51 (14).



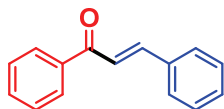
3ba (Eluent: EtOAc/hexane = 2/8)

(E)-3'-methoxychalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.85 (s, 3H), 7.11 (ddd, $J = 8.5$, 3.0, and 1.0 Hz, 1H), 7.37–7.41 (m, 4H), 7.50 (d, $J = 15.5$ Hz, 1H), 7.54–7.55 (m, 1H), 7.59 (ddd, $J = 7.5$, 1.0, and 1.0 Hz, 1H), 7.61–7.64 (m, 2H), 7.80 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 55.5, 112.9, 119.3, 121.1, 122.1, 128.5, 129.0, 129.6, 130.6, 134.9, 139.6, 144.9, 159.9, 190.2. MS (EI): m/z (%): 239 (16), 238 (96), 237 (100), 223 (12), 135 (24), 131 (49), 107 (21), 103 (55), 102 (10), 92 (19), 77 (63), 64 (14), 63 (12), 51 (15).



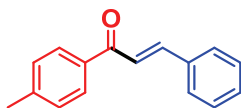
3ca (Eluent: EtOAc/hexane = 2/8)

(E)-2'-methoxychalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.86 (s, 3H), 6.96–6.99 (m, 1H), 7.02 (td, $J = 7.5$ and 1.0 Hz, 1H), 7.35–7.39 (m, 4H), 7.43–7.47 (m, 1H), 7.55–7.59 (m, 2H), 7.62 (dd, $J = 7.5$ and 2.0 Hz, 1H), 7.62 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 55.8, 111.7, 120.8, 127.1, 128.4, 128.9, 129.2, 130.28, 130.35, 132.9, 135.1, 143.2, 158.1, 193.0. MS (EI): m/z (%): 238 (50), 237 (54), 223 (19), 221 (10), 219 (11), 179 (16), 178 (11), 167 (13), 165 (14), 160 (12), 152 (10), 147 (22), 135 (64), 131 (36), 121 (22), 120 (26), 119 (13), 105 (13), 104 (15), 103 (54), 102 (15), 92 (34), 91 (47), 78 (10), 77 (100), 76 (16), 64 (12), 63 (14), 51 (27).



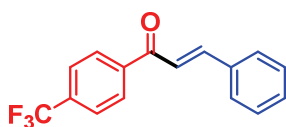
3da (Eluent: EtOAc/hexane = 1/9)

(E)-chalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.38–7.42 (m, 3H), 7.47–7.51 (m, 2H), 7.53 (d, J = 15.5 Hz, 1H), 7.57 (tdd, J = 7.5, 1.5 and 1.5 Hz, 1H), 7.61–7.65 (m, 2H), 7.81 (d, J = 15.5 Hz, 1H), 8.01–8.03 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 122.1, 128.5, 128.6, 128.7, 129.0, 130.6, 132.9, 134.9, 138.2, 144.9, 190.6. MS (EI): m/z (%): 209 (12), 208 (79), 207 (100), 179 (23), 178 (12), 165 (12), 131 (43), 130 (16), 105 (35), 103 (46), 102 (16), 89 (11), 77 (97), 76 (13), 51 (36), 50 (10). This MS spectral data accords with that in the previous report.⁴



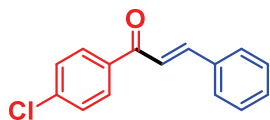
3ea (Eluent: EtOAc/hexane = 1/9)

(E)-4'-methylchalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.41 (s, 3H), 7.27–7.29 (m, 2H), 7.36–7.42 (m, 3H), 7.52 (d, J = 15.5 Hz, 1H), 7.59–7.64 (m, 2H), 7.79 (d, J = 15.5 Hz, 1H), 7.92–7.94 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 21.7, 122.1, 128.5, 128.7, 129.0, 129.4, 130.5, 135.0, 135.6, 143.7, 144.4, 190.0. MS (EI): m/z (%): 223 (15), 222 (88), 221 (100), 207 (26), 179 (28), 178 (19), 144 (10), 131 (28), 119 (49), 103 (35), 102 (10), 96 (11), 91 (55), 77 (35), 65 (30), 51 (16). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



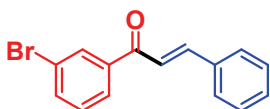
3fa (Eluent: CHCl_3 /hexane = 2/8)

(E)-4'-(trifluoromethyl)chalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.41–7.45 (m, 3H), 7.49 (d, J = 15.5 Hz, 1H), 7.62–7.66 (m, 2H), 7.74–7.77 (m, 2H), 7.82 (d, J = 15.5 Hz, 1H), 8.08–8.11 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 121.6, 123.8 (q, J = 270.6 Hz), 125.8, 128.7, 128.9, 129.2, 131.1, 134.1 (q, J = 32.3 Hz), 134.6, 141.1, 146.2, 189.7. ^{19}F NMR (470 MHz, CDCl_3 , benzonitrile): δ -64.2. MS (EI): m/z (%): 277 (10), 276 (69), 275 (100), 207 (14), 179 (12), 178 (11), 173 (13), 145 (39), 131 (37), 103 (44), 77 (35), 51 (14). This MS spectral data accords with that in the previous report.⁴



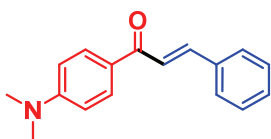
3ga (Eluent: EtOAc/hexane = 1/9)

(E)-4'-chlorochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.38–7.41 (m, 3H), 7.43–7.45 (m, 2H), 7.47 (d, J = 15.5 Hz, 1H), 7.60–7.63 (m, 2H), 7.79 (d, J = 15.5 Hz, 1H), 7.92–7.96 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 121.4, 128.6, 128.96, 129.04, 130.0, 130.8, 134.7, 136.5, 139.2, 145.3, 189.1. MS (EI): m/z (%): 244 (23), 243 (41), 242 (67), 241 (100), 207 (46), 179 (19), 178 (24), 141 (11), 139 (32), 131 (36), 113 (13), 111 (41), 103 (48), 102 (13), 89 (21), 77 (45), 76 (21), 75 (28), 51 (22), 50 (12). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



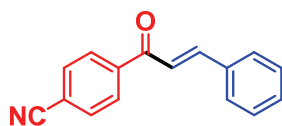
3ha (Eluent: CHCl_3 /hexane = 4/6)

(E)-3'-bromochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.35 (t, J = 8.0 Hz, 1H), 7.38–7.42 (m, 3H), 7.44 (d, J = 16.0 Hz, 1H), 7.60–7.64 (m, 2H), 7.67 (ddd, J = 8.0, 2.0, and 1.0 Hz, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.91 (ddd, J = 8.0, 1.5, and 1.0 Hz, 1H), 8.12 (t, J = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 121.3, 123.0, 127.0, 128.6, 129.0, 130.2, 130.9, 131.5, 134.6, 135.6, 140.0, 145.7, 188.9. MS (EI): m/z (%): 289 (10), 288 (64), 287 (100), 286 (65), 285 (92), 207 (44), 185 (13), 183 (13), 179 (25), 178 (38), 157 (22), 155 (23), 131 (85), 104 (11), 103 (97), 102 (25), 89 (29), 77 (79), 76 (54), 75 (30), 74 (12), 51 (32), 50 (26).



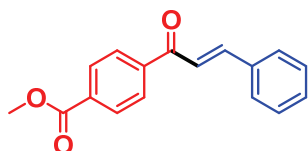
3ia (Eluent: EtOAc/hexane = 2/8)

(E)-4'-(dimethylamino)chalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.02 (s, 6H), 6.64–6.67 (m, 2H), 7.33–7.40 (m, 2H), 7.58 (d, J = 15.5 Hz, 1H), 7.60–7.63 (m, 2H), 7.78 (d, J = 15.5 Hz, 1H), 7.98–8.01 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 40.0, 110.8, 122.2, 125.9, 128.3, 128.9, 129.9, 130.8, 135.5, 142.4, 153.4, 187.7. MS (EI): m/z (%): 252 (18), 251 (100), 250 (28), 223 (49), 222 (24), 207 (16), 148 (61), 125 (15), 105 (12), 104 (15), 103 (21), 78 (10), 77 (34), 51 (11). This MS spectral data accords with that in the previous report.⁴



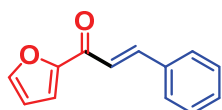
3ja (Eluent: EtOAc/hexane = 2/8)

(E)-4'-cyanochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.41–7.47 (m, 3H), 7.47 (d, J = 15.5 Hz, 1H), 7.63–7.67 (m, 2H), 7.79–7.82 (m, 2H), 7.83 (d, J = 15.5 Hz, 1H), 8.07–8.10 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 116.0, 118.2, 121.2, 128.8, 129.0, 129.2, 131.3, 132.6, 134.4, 141.5, 146.7, 189.3. MS (EI): m/z (%): 233 (60), 232 (100), 204 (12), 131 (33), 130 (15), 103 (44), 102 (44), 78 (11), 77 (40), 76 (12), 75 (12), 51 (22).



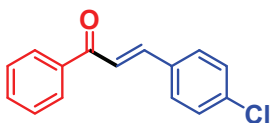
3ka (Eluent: CHCl_3 /hexane = 4/6, isolated concomitant with methyl 4-formylbenzoate (**1k**))

(E)-4'-(methoxycarbonyl)chalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.97 (s, 3H), 7.42–7.45 (m, 3H), 7.52 (d, J = 15.5 Hz, 1H), 7.64–7.67 (m, 2H), 7.83 (d, J = 15.5 Hz, 1H), 8.05–8.07 (m, 2H), 8.16–8.18 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 52.7, 121.9, 128.5, 128.7, 129.2, 130.0, 131.0, 133.7, 134.7, 141.8, 145.9, 166.4, 190.2. MS (EI): m/z (%): 267 (12), 266 (71), 265 (100), 235 (10), 207 (33), 179 (13), 178 (18), 163 (15), 135 (11), 131 (38), 117 (16), 103 (58), 77 (36), 76 (18), 51 (11). This MS spectral data accords with that in the previous report.⁴



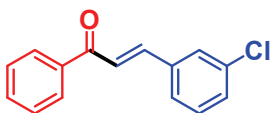
3la (Eluent: EtOAc/hexane = 1/9)

(E)-1-(furan-2-yl)-3-phenylprop-2-en-1-one: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 6.58 (dd, J = 4.0 and 2.0 Hz, 1H), 7.34 (dd, J = 3.5 and 1.0 Hz, 1H), 7.38–7.42 (m, 3H), 7.45 (d, J = 15.5 Hz, 1H), 7.62–7.66 (m, 3H), 7.87 (d, J = 15.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 112.6, 117.6, 121.2, 128.6, 129.0, 130.7, 134.7, 144.0, 146.6, 153.7, 178.0. MS (EI): m/z (%): 199 (9), 198 (67), 197 (100), 170 (6), 169 (17), 142 (10), 141 (52), 131 (12), 115 (18), 103 (36), 102 (15), 95 (24), 77 (39), 76 (7), 63 (6), 51 (19), 50 (7). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



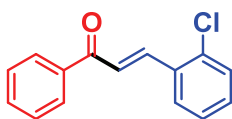
3db (Eluent: EtOAc/hexane = 1/9)

(E)-4-chlorochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.36–7.39 (m, 2H), 7.48–7.61 (m, 6H), 7.75 (d, J = 16.0 Hz, 1H), 8.00–8.03 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 122.5, 128.6, 128.8, 129.3, 129.7, 133.0, 133.4, 136.5, 138.1, 143.4, 190.3. MS (EI): m/z (%): 244 (31), 243 (33), 242 (93), 241 (60), 208 (12), 207 (72), 179 (51), 178 (32), 167 (14), 165 (46), 139 (11), 137 (31), 130 (27), 105 (62), 102 (54), 101 (44), 89 (25), 77 (100), 76 (25), 75 (32), 74 (10), 51 (47), 50 (18). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



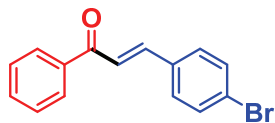
3dc (Eluent: EtOAc/hexane = 1/9)

(E)-3-chlorochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.31–7.37 (m, 2H), 7.46–7.51 (m, 3H), 7.51 (d, J = 16.0 Hz, 1H), 7.56–7.61 (m, 2H), 7.71 (d, J = 16.0 Hz, 1H), 8.00–8.03 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 123.2, 126.9, 128.0, 128.6, 128.8, 130.3, 130.4, 133.1, 135.0, 136.8, 137.9, 143.1, 190.1. MS (EI): m/z (%): 244 (26), 243 (29), 242 (76), 241 (55), 208 (14), 207 (87), 179 (47), 178 (30), 167 (11), 165 (37), 137 (25), 130 (10), 105 (71), 102 (50), 101 (36), 89 (20), 77 (100), 76 (23), 75 (30), 51 (46), 50 (16).



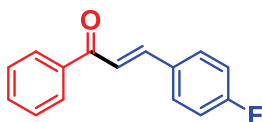
3dd (Eluent: EtOAc/hexane = 1/9)

(E)-2-chlorochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.27–7.32 (m, 2H), 7.39–7.42 (m, 1H), 7.46–7.51 (m, 3H), 7.57 (tdd, J = 7.5, 1.5 and 1.5 Hz, 1H), 7.71–7.75 (m, 1H), 8.00–8.02 (m, 2H), 8.17 (d, J = 16.0 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 124.7, 127.2, 127.8, 128.6, 128.7, 130.3, 131.3, 133.0, 133.2, 135.5, 137.9, 140.6, 190.4. MS (EI): m/z (%): 242 (13), 208 (16), 207 (100), 179 (9), 178 (11), 165 (6), 137 (8), 105 (17), 102 (12), 101 (17), 89 (7), 77 (35), 76 (8), 75 (13), 51 (17), 50 (6). This MS spectral data accords with that in the previous report.⁵



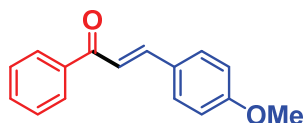
3de (Eluent: EtOAc/hexane = 1/9)

(E)-4-bromochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.46–7.53 (m, 7H), 7.57 (tdd, J = 7.5, 1.5 and 1.5 Hz, 1H), 7.72 (d, J = 15.5 Hz, 1H), 7.99–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 122.5, 124.8, 128.6, 128.7, 129.9, 132.2, 133.0, 133.8, 138.0, 143.4, 190.2. MS (EI): m/z (%): 288 (56), 287 (42), 286 (57), 285 (36), 211 (21), 209 (23), 208 (16), 207 (94), 183 (11), 181 (12), 179 (52), 178 (42), 130 (31), 105 (62), 103 (12), 102 (100), 101 (20), 89 (27), 77 (96), 76 (38), 75 (28), 74 (12), 51 (45). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



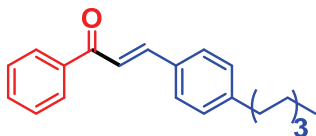
3df (Eluent: EtOAc/hexane = 1/9)

(E)-4-fluorochalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.06–7.10 (m, 2H), 7.47–7.50 (m, 3H), 7.56 (tdd, J = 7.5, 1.5 and 1.5 Hz, 1H), 7.58–7.62 (m, 2H), 7.76 (d, J = 15.5 Hz, 1H), 8.00–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 116.0, 116.2, 121.7, 128.5, 128.7, 130.37, 130.43, 131.1, 131.2, 132.9, 138.1, 143.5, 163.1, 165.1, 190.2. ^{19}F NMR (470 MHz, CDCl_3 , benzotrifluoride): δ –110.2. MS (EI): m/z (%): 226 (100), 225 (61), 197 (24), 183 (11), 149 (54), 130 (30), 121 (39), 120 (12), 105 (47), 102 (12), 101 (47), 95 (10), 77 (70), 75 (21), 51 (30), 50 (10). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



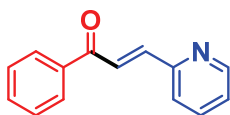
3dg (Eluent: EtOAc/hexane = 1/9)

(E)-4-methoxychalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.81 (s, 3H), 6.90–6.92 (m, 2H), 7.40 (d, J = 15.5 Hz, 1H), 7.46–7.49 (m, 2H), 7.53–7.59 (m, 3H), 7.78 (d, J = 15.5 Hz, 1H), 7.99–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 55.4, 114.4, 119.7, 127.6, 128.4, 128.6, 130.3, 132.6, 138.5, 144.7, 161.7, 190.5. MS (EI): m/z (%): 239 (17), 238 (100), 237 (50), 223 (24), 207 (21), 195 (15), 167 (12), 165 (13), 161 (49), 133 (32), 118 (14), 108 (51), 105 (29), 90 (16), 89 (19), 77 (67), 63 (11), 51 (21). This MS spectral data accords with that obtained from Wiley Subscription Services, Inc.



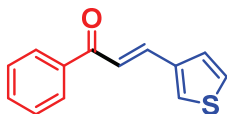
3dh (Eluent: toluene)

(E)-4-pentylchalcone: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.28–1.37 (m, 4H), 1.62 (quin, $J = 7.5$ Hz, 2H), 2.62 (t, $J = 7.5$ Hz, 2H), 7.20–7.22 (m, 2H), 7.46–7.50 (m, 2H), 7.49 (d, $J = 15.5$ Hz, 1H), 7.54–7.56 (m, 3H), 7.80 (d, $J = 15.5$ Hz, 1H), 8.00–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 14.1, 22.6, 31.0, 31.5, 36.0, 121.1, 128.59, 128.65, 128.7, 129.1, 132.4, 132.7, 138.4, 145.1, 146.2, 190.7. MS (EI): m/z (%): 278 (14), 277 (17), 222 (5), 221 (24), 208 (17), 207 (100), 193 (10), 179 (5), 178 (15), 131 (7), 116 (5), 115 (17), 105 (13), 91 (6), 77 (21).



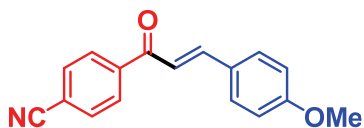
3di (Eluent: EtOAc/hexane = 2/8)

(E)-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.28 (ddd, $J = 7.5$, 4.5 and 1.0 Hz, 1H), 7.46–7.52 (m, 3H), 7.58 (tdd, $J = 7.5$, 1.5 and 1.5 Hz, 1H), 7.72 (td, $J = 7.5$ and 2.0 Hz, 1H), 7.78 (d, $J = 15.5$ Hz, 1H), 8.09–8.11 (m, 2H), 8.12 (d, $J = 15.5$ Hz, 1H), 8.67–8.69 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 124.5, 125.5, 128.7, 128.8, 133.2, 137.0, 137.8, 142.8, 150.1, 153.2, 190.5. MS (EI): m/z (%): 210 (5), 209 (34), 208 (5), 182 (5), 181 (41), 180 (100), 132 (39), 105 (25), 104 (34), 78 (33), 77 (55), 76 (7), 52 (7), 51 (35), 50 (10). This MS spectral data accords with that in the previous report.⁶



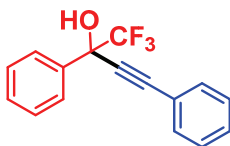
3dj (Eluent: EtOAc/hexane = 2/8)

(E)-1-phenyl-3-(thiophen-3-yl)prop-2-en-1-one: ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.34 (d, $J = 15.5$ Hz, 1H), 7.34–7.36 (m, 1H), 7.41 (dd, $J = 5.0$ and 1.5 Hz, 1H), 7.47–7.50 (m, 2H), 7.54–7.59 (m, 2H), 7.79 (d, $J = 15.5$ Hz, 1H), 7.98–8.01 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 121.8, 125.3, 127.1, 128.5, 128.7, 129.3, 132.8, 138.2, 138.26, 138.32, 190.8. MS (EI): m/z (%): 215 (16), 214 (100), 213 (27), 186 (22), 185 (77), 184 (11), 141 (11), 137 (74), 130 (22), 109 (55), 105 (45), 77 (86), 65 (35), 51 (41), 50 (12).



3jg (Eluent: toluene, Gradient eluent: CHCl₃, EtOAc)

4'-cyano-4-methoxychalcone: ¹H NMR (500 MHz, CDCl₃, TMS): δ 3.86 (s, 3H), 6.93–6.96 (m, 2H), 7.34 (d, J = 15.5 Hz, 1H), 7.59–7.62 (m, 2H), 7.77–7.80 (m, 2H), 7.80 (d, J = 15.5 Hz, 1H), 8.05–8.08 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, TMS): δ 55.5, 114.6, 115.7, 118.2, 118.8, 127.1, 128.8, 130.6, 132.5, 141.9, 146.5, 162.2, 189.1. MS (EI): m/z (%): 264 (18), 263 (100), 262 (69), 248 (26), 233 (10), 232 (53), 220 (15), 190 (10), 165 (10), 161 (56), 133 (39), 130 (15), 118 (20), 108 (52), 103 (13), 102 (50), 90 (21), 89 (23), 77 (19), 76 (10), 75 (14), 63 (14), 51 (13).

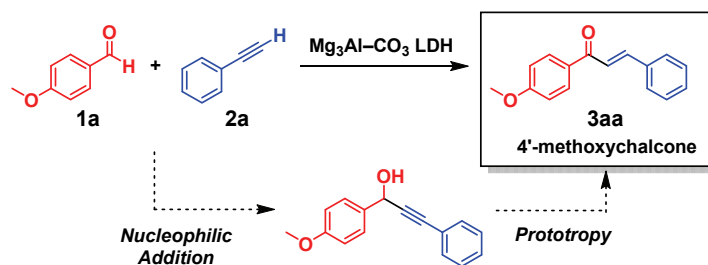


4na

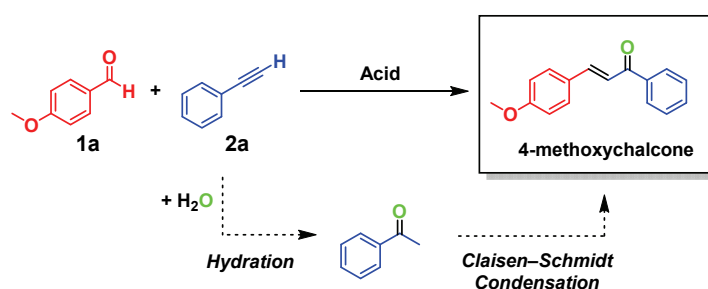
1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol: ¹H NMR (500 MHz, CDCl₃, TMS, the crude product referring to the previous report⁷): δ 3.21 (s, 1H), 7.35–7.46 (m, 6H), 7.49–7.53 (m, 2H), 7.79–7.84 (m, 2H). MS (EI): m/z (%): 276 (5), 209 (5), 208 (17), 207 (100), 179 (8), 178 (10), 130 (8), 129 (80), 105 (28), 101 (6), 78 (6), 77 (29), 76 (6), 75 (8), 51 (11).

Supporting Figures

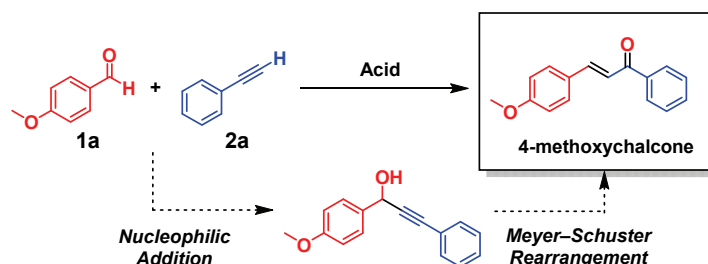
a) This Work: Very Rare "Formal Hydroacylation"



b) Hydration/Aldol Condensation: NOT "Formal Hydroacylation" (ref. 4a–c)



c) Addition/Meyer–Schuster Rearrangement: NOT "Formal Hydroacylation" (ref. 4d,e)



d) Aldehyde–Alkyne Metathesis: NOT "Formal Hydroacylation" (ref. 4f–i)

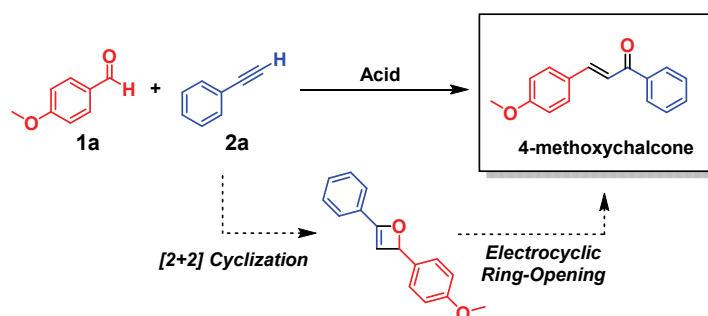
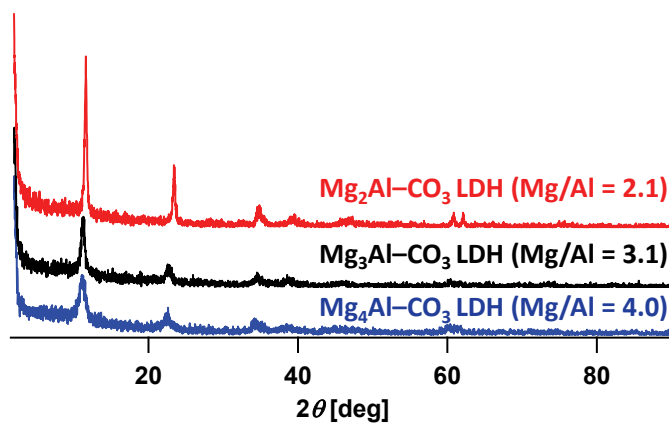
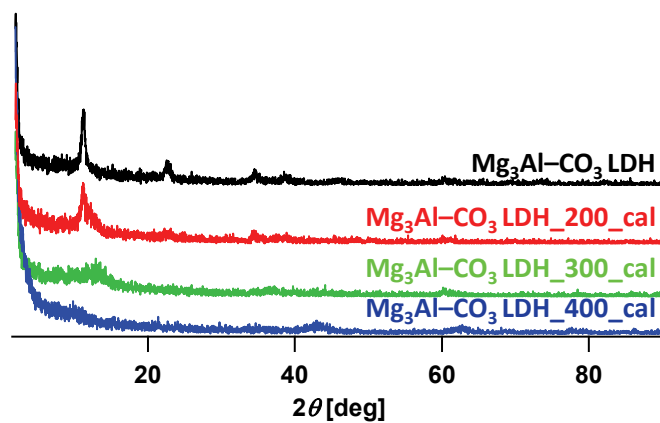


Figure S1. Difference among aldehyde–alkyne couplings; a) This work: Formal hydroacylation through nucleophilic addition/prototropy retaining the skeletons of substrates, b) enone synthesis through hydration/aldol condensation, c) enone synthesis through nucleophilic addition/Meyer–Schuster rearrangement, and d) enone synthesis through aldehyde–alkyne metathesis.

(a)



(b)



(c)

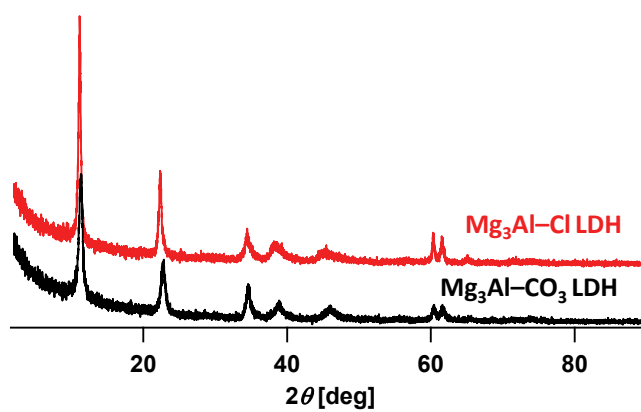


Figure S2. XRD patterns of LDH (a) when changing the ratio of Mg/Al ratio, (b) when calcined at various temperatures, and (c) when changing the interlayer anion. $\text{Mg}_3\text{Al}-\text{CO}_3$ LDH_xx_cal: $\text{Mg}_3\text{Al}-\text{CO}_3$ LDH calcined at xx °C for 3 h.

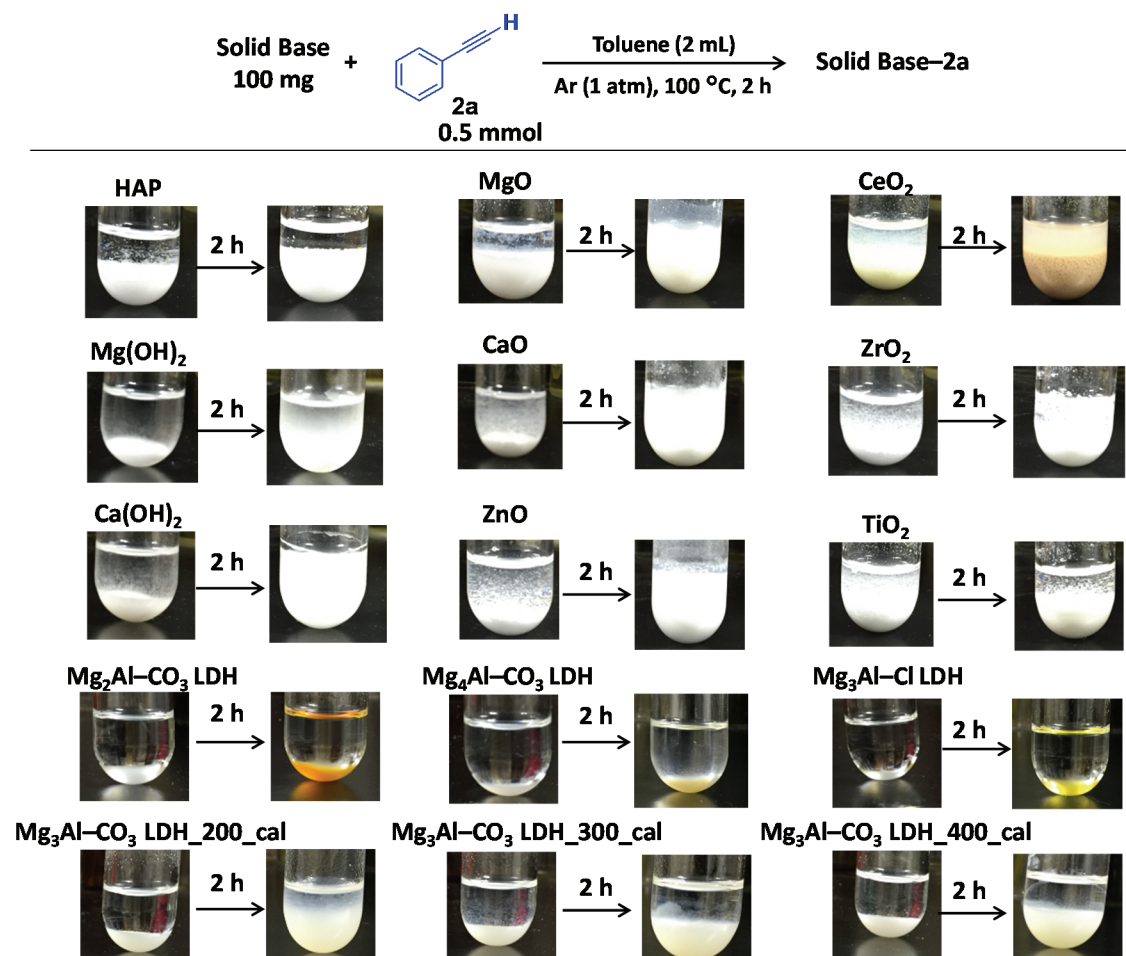


Figure S3. Photo images of solid catalysts before/after stirring with **2a**. Reaction conditions: **2a** (0.5 mmol), base catalyst (100 mg), toluene (2 mL), Ar (1 atm), 100 °C, 2 h.

Mg₃Al-CO₃ LDH

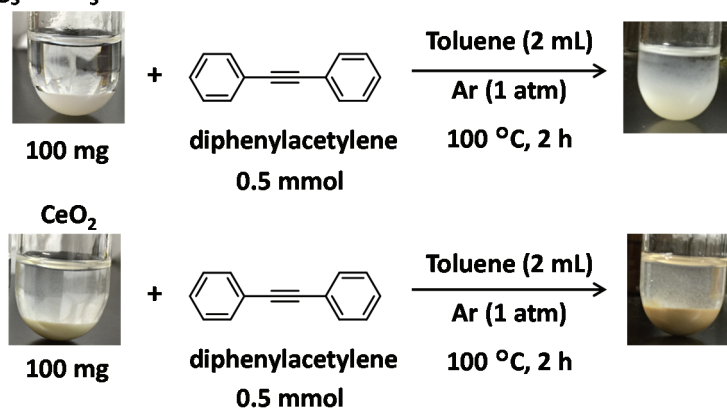


Figure S4. Photo images of solid catalysts before/after stirring with diphenylacetylene. Reaction conditions: diphenylacetylene (0.5 mmol), base catalyst (100 mg), toluene (2 mL), Ar (1 atm), 100 °C, 2 h.

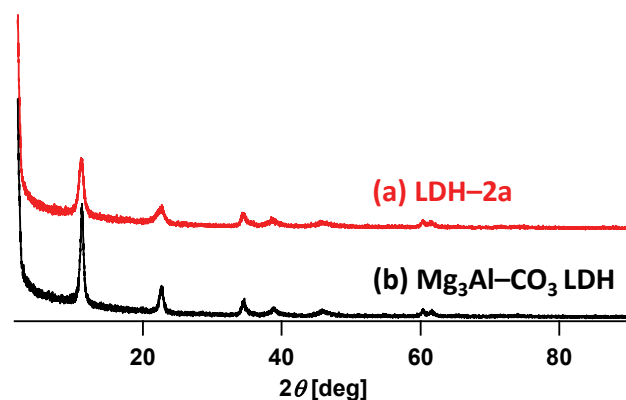


Figure S5. XRD patterns of (a) retrieved $\text{Mg}_3\text{Al-CO}_3$ LDH after stirring with **2a** and (b) fresh $\text{Mg}_3\text{Al-CO}_3$ LDH.

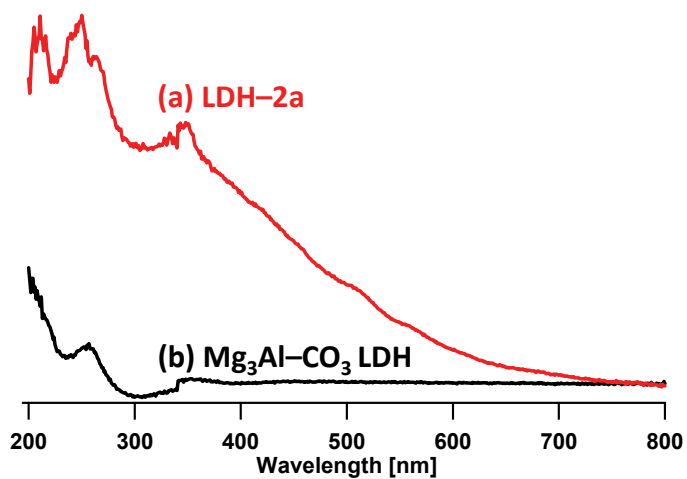


Figure S6. DR UV-Vis spectra of (a) retrieved $\text{Mg}_3\text{Al-CO}_3$ LDH after stirring with **2a** and (b) fresh $\text{Mg}_3\text{Al-CO}_3$ LDH.

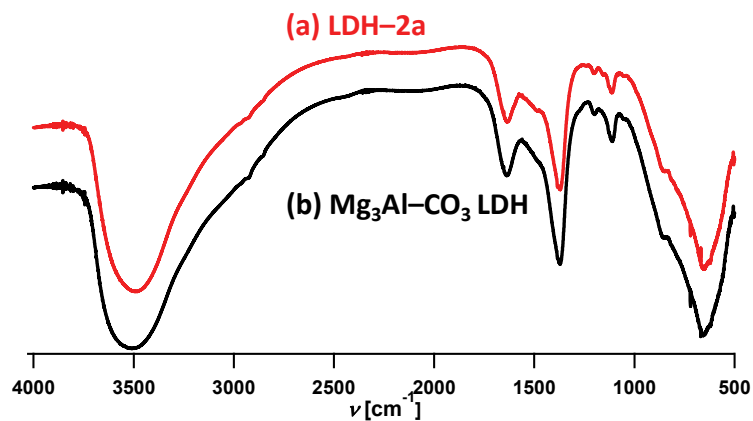


Figure S7. FT-IR spectra of (a) retrieved $\text{Mg}_3\text{Al-CO}_3$ LDH after stirring with **2a** and (b) fresh $\text{Mg}_3\text{Al-CO}_3$ LDH.

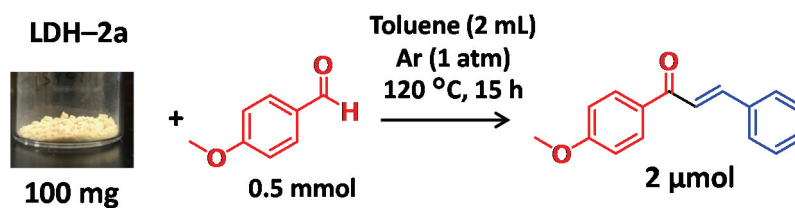


Figure S8. Synthesis of 4'-methoxychalcone (**3aa**) using LDH-**2a**. Reaction conditions: **1a** (0.5 mmol), LDH-**2a** (100 mg), toluene (2 mL), 120 °C, Ar balloon (1 atm), 15 h. Yields were determined by GC analysis using biphenyl as an internal standard.

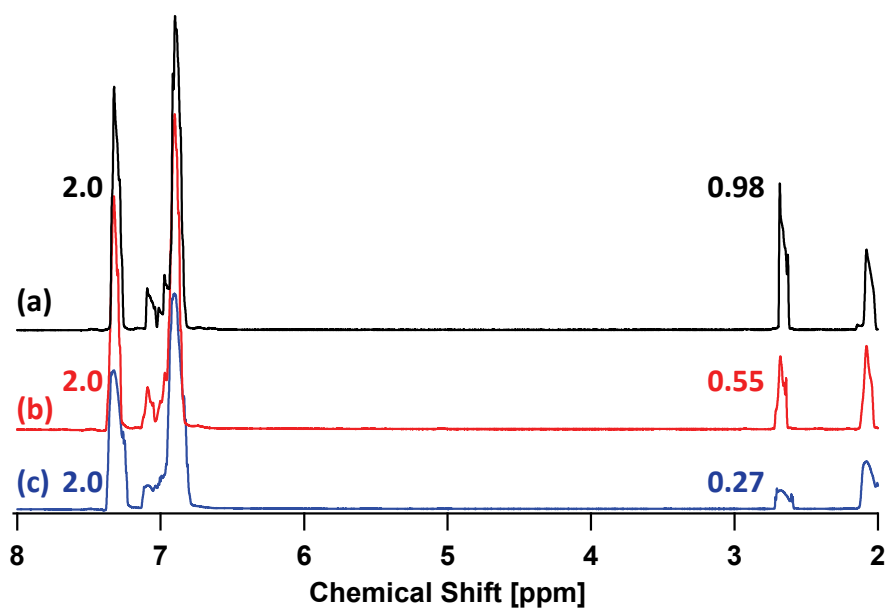


Figure S9. ^1H NMR (in toluene- d_8) spectra after the reaction of phenylacetylene (**2a**) with D_2O (50 μL) under the conditions shown in Scheme 1 using (a) no catalysts, (b) $\text{Mg}_3\text{Al-CO}_3$ LDH, and (c) Al_2O_3 . The numbers next to peaks represent areas of the peaks.

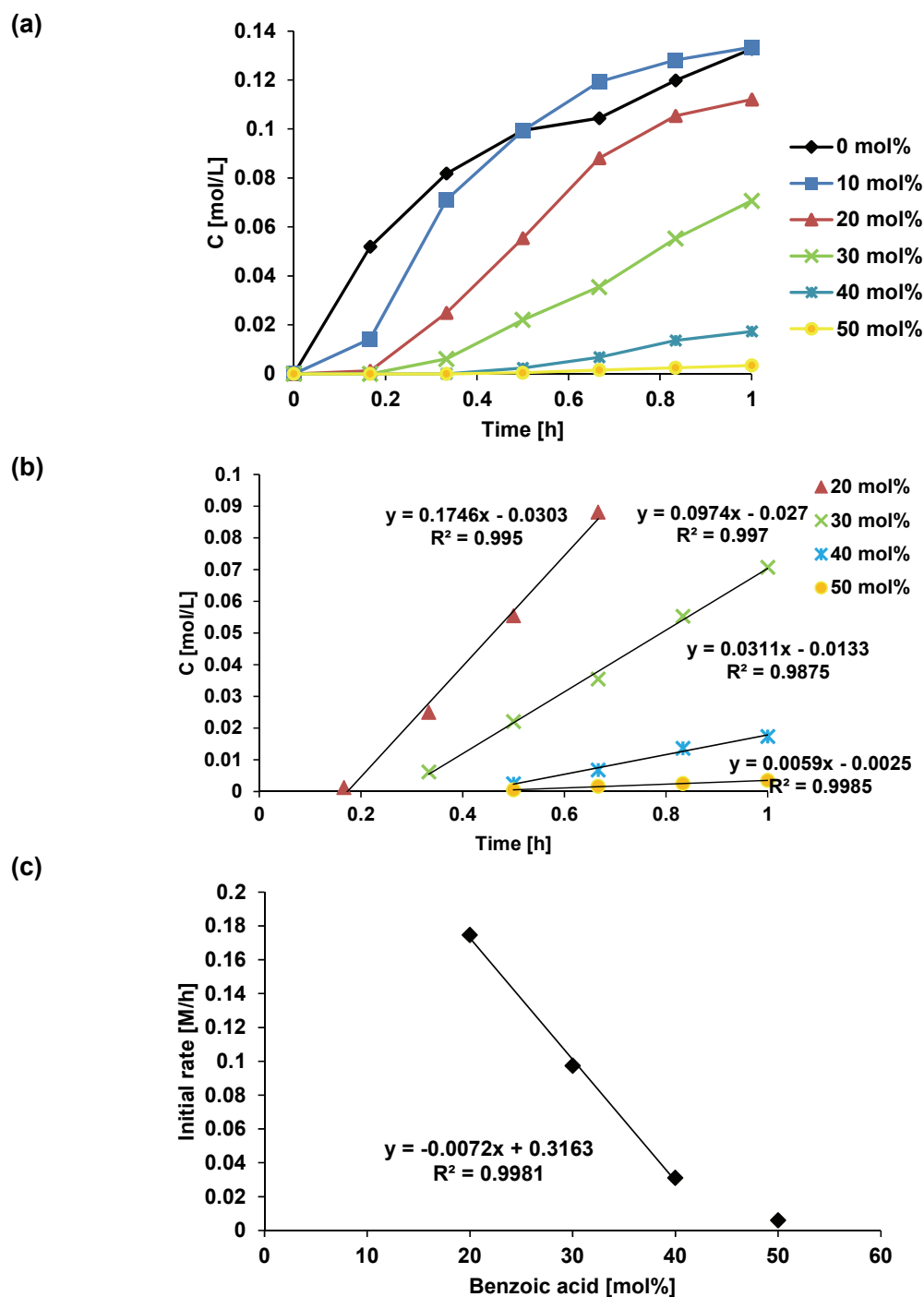


Figure S10. Reactions in the presence of benzoic acid. (a) The reaction profiles affected by changing the amount of benzoic acid from 0 mol% to 50 mol% by 10 mol%. (b) Calculation of initial rates after induction periods. (c) Relation between initial rate and the amount of benzoic acid. Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), Mg₃Al-CO₃ LDH (100 mg), toluene (2 mL), 110 °C, Ar balloon (1 atm). Yields were determined by GC analysis using biphenyl as an internal standard.

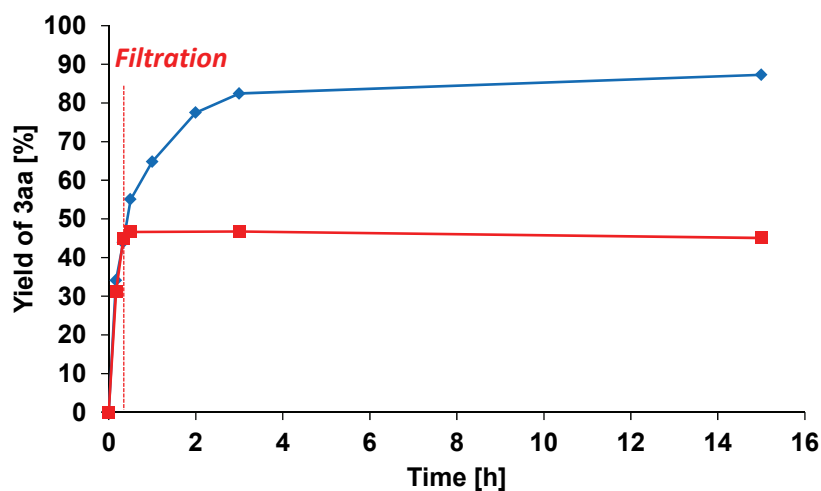


Figure S11. The reaction profile affected by removing $\text{Mg}_3\text{Al-CO}_3$ LDH in the middle of the reaction starting from **1a** and **2a** (verification of heterogeneous catalysis). Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), $\text{Mg}_3\text{Al-CO}_3$ LDH (130 mg), toluene (2 mL), 120 °C, Ar balloon (1 atm). Yields were determined by GC analysis using biphenyl as an internal standard.

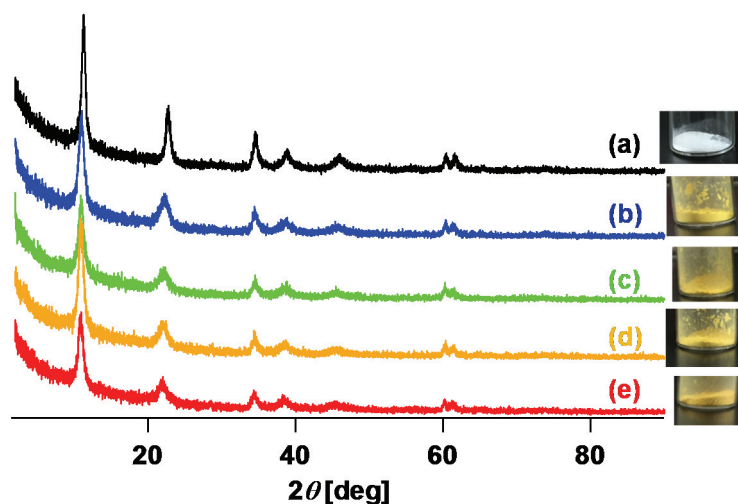


Figure S12. XRD patterns and images of (a) $\text{Mg}_3\text{Al-CO}_3$ LDH before use, (b) $\text{Mg}_3\text{Al-CO}_3$ LDH after the first use, (c) $\text{Mg}_3\text{Al-CO}_3$ LDH after the second use, (d) $\text{Mg}_3\text{Al-CO}_3$ LDH after the third use, and (e) $\text{Mg}_3\text{Al-CO}_3$ LDH after the fourth use.

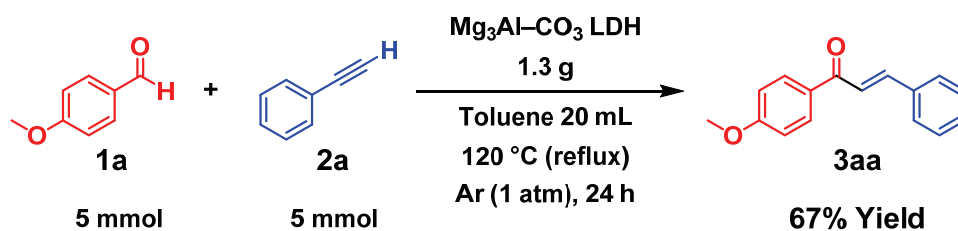


Figure S13. Large-scale synthesis of **3aa** from **1a** and **2a**. Reaction conditions: **1a** (5 mmol), **2a** (5 mmol), $\text{Mg}_3\text{Al-CO}_3$ LDH (1.3 g), toluene (20 mL), 120 °C (reflux), Ar (1 atm), 24 h. Yield was determined by gas chromatography analysis using biphenyl as an internal standard.

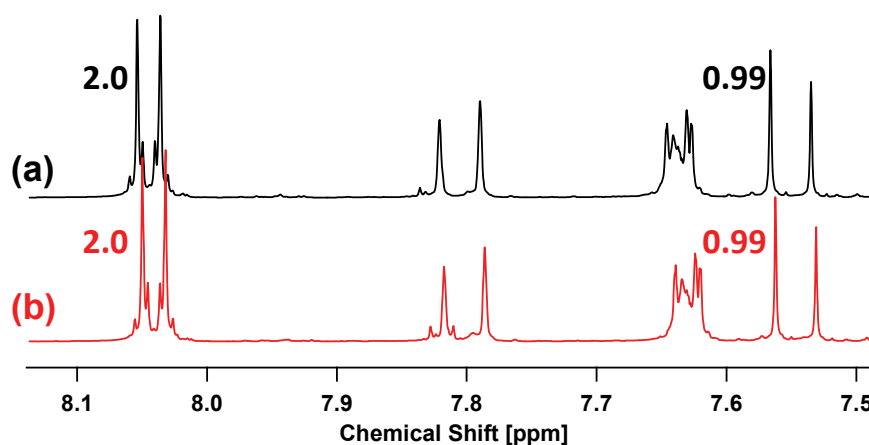


Figure S14. ^1H NMR (in CDCl_3) spectra of crude solution after the reaction under the optimized conditions using (a) *p*-anisaldehyde (**1a**) and phenylacetylene (**2a**), and (b) *p*-anisaldehyde (**1a**) and phenylacetylene- d_1 (**D-2a**) as substrates respectively. The numbers next to peaks represent areas of the peaks.

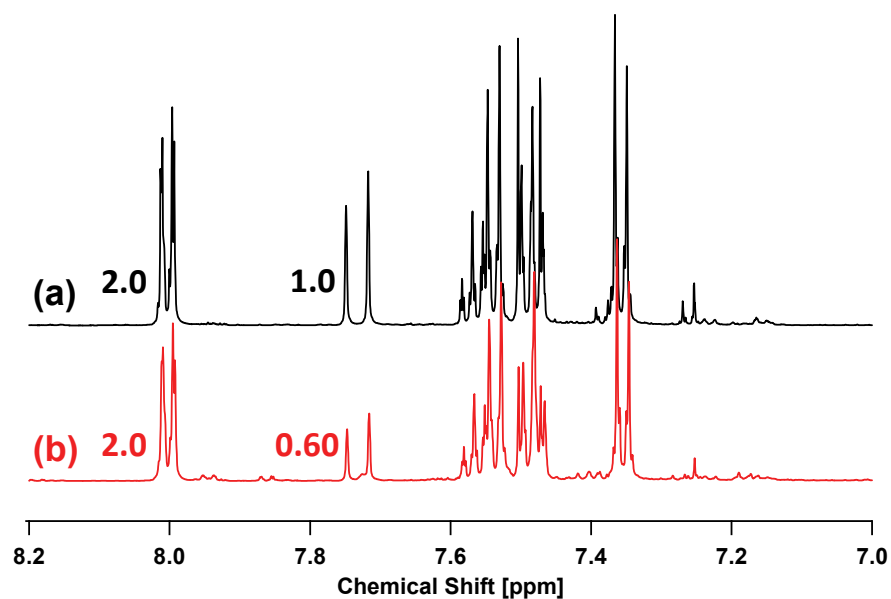


Figure S15. ^1H NMR (in CDCl_3) spectra of crude solution after the reaction under the optimized conditions using (a) benzaldehyde (**1d**) and 4-chlorophenylacetylene (**2b**), and (b) benzaldehyde- α - d_1 (**D-1d**) and 4-chlorophenylacetylene (**2b**) as substrates respectively. The numbers next to peaks represent areas of the peaks.

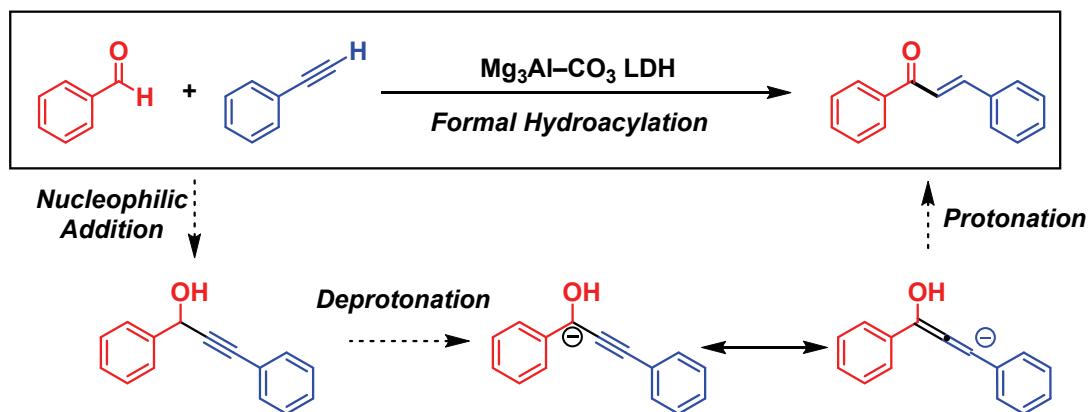


Figure S16. Proposed mechanism of $\text{Mg}_3\text{Al-CO}_3$ LDH-catalyzed formal hydroacylation.

Supporting Tables

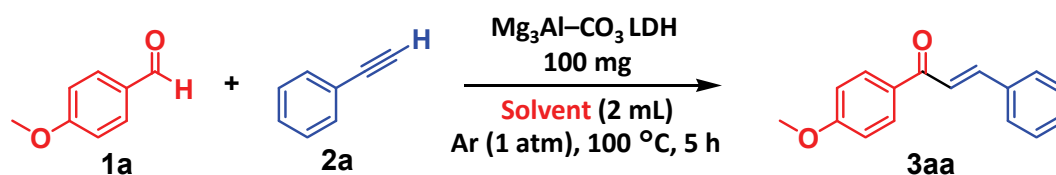
Table S1. Effect of base catalysts on the synthesis of 4'-methoxychalcone (**3aa**)^a

COc1ccc(C=O)cc1 (**1a**) + c1ccccc1C#C (**2a**) $\xrightarrow[\text{Ar (1 atm), 100 }^\circ\text{C, 5 h}]{\text{Base 100 mg, Toluene (2 mL)}}$ COc1ccc(C(=O)C=Cc2ccccc2)cc1 (**3aa**)

entry	catalyst	conv. (%)		yield (%)
		1a	2a	3aa
1	Mg ₂ Al–CO ₃ LDH	52	48	39
2	Mg ₄ Al–CO ₃ LDH	<1	<1	<1
3	Mg ₃ Al–CO ₃ LDH_200_cal	5	10	3
4	Mg ₃ Al–CO ₃ LDH_300_cal	2	2	<1
5	Mg ₃ Al–CO ₃ LDH_400_cal	6	6	<1
6	Mg ₃ Al–Cl LDH	28	30	19
7	K ₂ CO ₃	2	3	<1
8	Na ₂ CO ₃	2	16	<1
9 ^b	<i>i</i> Pr ₂ EtN	2	7	<1
10	None	<1	2	<1

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), base (100 mg), toluene (2 mL), 100 °C, 5 h, Ar balloon (1 atm). Conversions and yields were determined by GC analysis using biphenyl as an internal standard. Mg₃Al–CO₃ LDH_xx_cal: Mg₃Al–CO₃ LDH calcined at xx °C for 3 h. ^b**1a** (1 mmol), base (10 mol%).

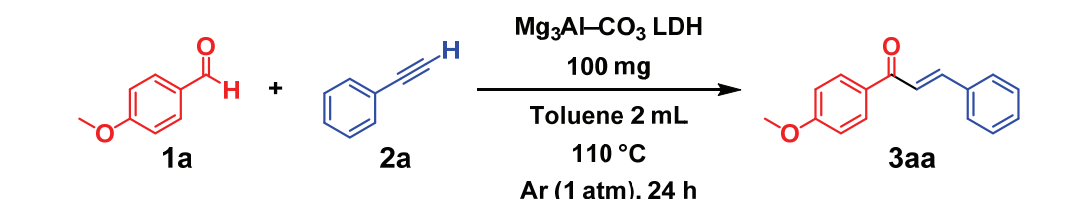
Table S2. Effect of solvents on the synthesis of **3aa**^a



entry	solvent	conv. (%)		yield (%)
		1a	2a	3aa
1	CPME	67	65	51
2	PhCF ₃	59	57	46
3	toluene	55	52	42
4	<i>n</i> -octane	29	29	13
5	<i>p</i> -xylene	23	—	13
6	<i>m</i> -xylene	21	—	13
7	mesitylene	21	22	10
8	DMSO	10	12	8
9	<i>o</i> -xylene	13	13	7
10	DMA	22	7	2
11	NMP	<1	11	<1
12	BuOAc	<1	<1	<1
13	1,4-dioxane	9	<1	<1
14	diglyme	7	24	<1
15	1-BuOH	11	4	<1
16 ^b	CPME	77	75	62
17 ^b	PhCF ₃	79	77	59
18 ^b	toluene	92	87	69

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), $\text{Mg}_3\text{Al-CO}_3\text{ LDH}$ (100 mg), solvent (2 mL), 100 °C, 5 h, Ar balloon (1 atm). Conversions and yields were determined by GC analysis using biphenyl as an internal standard. —: **2a** peak was not detected because of the solvent peak whose retention time is almost the same as that of **2a**. ^b120 °C. CPME = methoxycyclopentane. DMSO = dimethyl sulfoxide. DMA = *N,N*-dimethylacetamide. NMP = *N*-methylpyrrolidone.

Table S3. Effect of benzoic acid on the yield of **3aa**^a

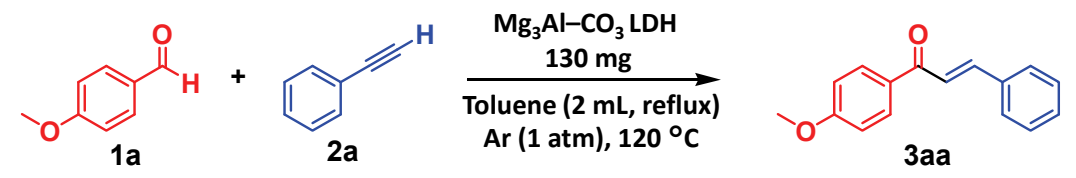


COc1ccc(C=O)cc1 (**1a**) + c1ccccc1C#C (**2a**) $\xrightarrow[\text{Ar (1 atm), 24 h}]{\text{Mg}_3\text{Al-CO}_3\text{ LDH 100 mg, Toluene 2 mL, 110 }^\circ\text{C}}$ COc1ccc(C(=O)/C=C/c2ccccc2)cc1 (**3aa**)

Entry	Amount of benzoic acid (mol%)	Conv. (%)		Yield (%)
		1a	2a	3aa
1	0	94	94	87
2	10	98	98	91
3	20	>99	98	76
4	30	94	93	81
5	40	39	46	25
6	50	10	11	5

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), Mg₃Al–CO₃ LDH (100 mg), toluene (2 mL), 110 °C, 24 h, Ar balloon (1 atm). Conversions and yields were determined by GC analysis using biphenyl as an internal standard.

Table S4. Reuse of Mg₃Al–CO₃ LDH for the synthesis of **3aa**^a



COc1ccc(C=O)cc1 (**1a**) + c1ccccc1C#C (**2a**) $\xrightarrow[\text{Ar (1 atm), 120 }^\circ\text{C}]{\text{Mg}_3\text{Al-CO}_3\text{ LDH 130 mg, Toluene (2 mL, reflux)}}$ COc1ccc(C(=O)/C=C/c2ccccc2)cc1 (**3aa**)

Entry	Mg ₃ Al–CO ₃ LDH	Conv. (%)		Yield (%)
		1a	2a	3aa
1 ^b	fresh	>99	87	91
2 ^c	1st reuse	92	77	80
3	2nd reuse	83	71	79
4	3rd reuse	84	71	73

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), Mg₃Al–CO₃ LDH (130 mg), toluene (2 mL), 120 °C, 15 h, Ar balloon (1 atm). Conversions and yields were determined by GC analysis using biphenyl as an internal standard. LDH was washed with acetone (25 mL/run) after respective reactions. ^bAverage value of three runs. ^cAverage value of two runs.

Supporting References

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NMR Spectra

