

Supporting Information

In(III)-TMSBr-Catalyzed Cascade Reaction of Diarylalkynes with Acrylates for The Synthesis of Aryldihydronaphthalene Derivatives

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1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. The TMSBr and InBr₃ used was purchased from Sigma-Aldrich.

Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating.

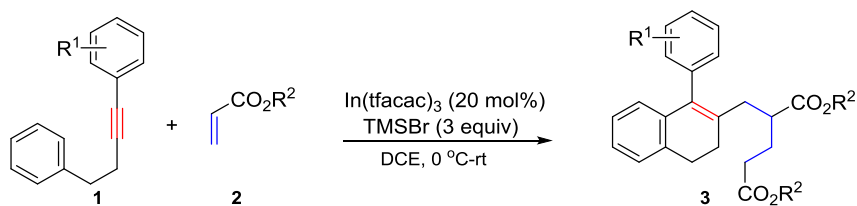
Flash column chromatography was performed using Merck silica gel 60 with analytical grade solvents as eluents.

¹H NMR, ¹³C NMR and 2D NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Corresponding chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d (δ=7.26, singlet). Multiplicities were given as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, dd = doublet of doublets, td = triplet of doublets. Values of coupling constant are reported as *J* in Hz.

HRMS spectra were recorded on a Waters Q-Tof Premier Spectrometer.

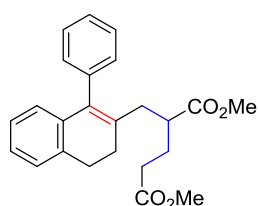
2. Experimental Sections

2.1 General procedure of In(III)-TMSBr-catalyzed Cascade Reaction of **1** with **2**



A dry reaction tube was charged with aryl alkyne **1** (0.4 mmol), acrylate **2** (1.2 mmol), indium (III) trifluoroacetylacetonate (In(tfacac)₃, 20 mol%, 0.08 mmol, 45.9 mg) and DCE (2 mL) under N₂ atmosphere at 0 °C. Bromotrimethylsilane (TMSBr, 3 equiv, 1.2 mmol, 183.6 mg) was added and the reaction mixture was stirred at room temperature for 2 h. Upon completion of the reaction as indicated by TLC analysis, the residue was directly purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate 10:1) to afford the desired product

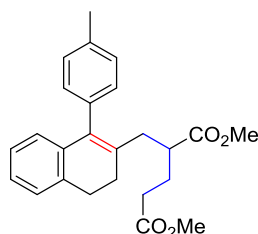
3.



Dimethyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (**3aa**)

Colorless oil, 106.2 mg, 0.281 mmol, 70% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.45 - 7.41 (m, 2H), 7.38 - 7.34 (m, 1H), 7.18 - 7.10 (m, 4H), 7.05 - 7.02 (m, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.66 - 2.61 (m, 1H), 2.44 - 2.31 (m, 4H), 2.22 - 2.18 (m, 2H), 1.79 - 1.76 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 175.4, 173.3, 139.2, 136.7, 136.3, 135.2, 134.3, 130.2, 128.4, 127.0, 126.9, 126.4, 126.2, 125.8, 51.6, 51.5, 43.5, 37.0, 31.6, 28.4, 27.4, 26.7.

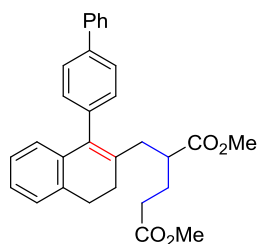


Dimethyl 2-((1-(*p*-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (**3ba**)

Colorless oil, 114.5 mg, 0.292 mmol, 73% yield.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.24 - 7.22 (m, 2H), 7.17 - 7.12 (m, 1H), 7.11 - 7.08 (m, 1H), 7.05 - 7.01 (m, 3H), 6.60 (d, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.66 - 2.62 (m, 1H), 2.44 (s, 3H), 2.43 - 2.35 (m, 4H), 2.22 - 2.18 (m, 2H), 1.79 - 1.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 175.5,

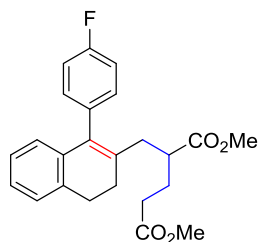
173.3, 136.8, 136.4, 136.2, 136.0, 135.2, 134.2, 130.1, 129.1, 127.0, 126.3, 126.2, 125.9, 51.6, 51.5, 43.4, 37.0, 31.6, 28.4, 27.4, 26.6, 21.2.



Dimethyl 2-((1-([1,1'-biphenyl]-4-yl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ca)

Colorless oil, 116.3 mg, 0.256 mmol, 64% yield.

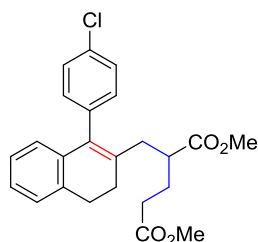
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.71 - 7.66 (m, 4H), 7.51 - 7.47 (m, 2H), 7.44 - 7.37 (m, 2H), 7.23 (br, 2H), 7.15 - 7.11 (m, 1H), 7.08 - 7.04 (m, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.94 - 2.90 (m, 2H), 2.70 - 2.66 (m, 1H), 2.50 - 2.41 (m, 4H), 2.25 - 2.19 (m, 2H), 1.83 - 1.77 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.5, 173.3, 140.9, 139.6, 138.2, 136.7, 135.9, 135.2, 134.5, 130.7 \times 2, 128.8, 127.3, 127.1 \times 2, 126.4, 126.2, 125.9, 51.7, 51.6, 43.5, 37.0, 31.6, 28.4, 27.4, 26.6.



Dimethyl 2-((1-(4-fluorophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3da)

Colorless oil, 90.3 mg, 0.228 mmol, 57% yield.

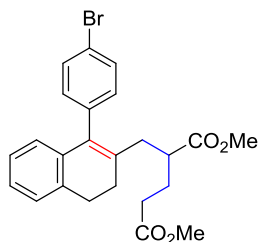
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.18 - 7.16 (m, 1H), 7.14 - 7.10 (m, 5H), 7.07 - 7.03 (m, 1H), 6.56 - 6.54 (d, $J = 7.5$ Hz, 1H), 3.68 (s, 3H), 3.65 (s, 3H), 2.90 (t, $J = 7.9$ Hz, 2H), 2.66 - 2.61 (m, 1H), 2.44 - 2.29 (m, 4H), 2.24 - 2.19 (m, 2H), 1.80 - 1.73 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.3, 161.9 (d, $J_{\text{C-F}} = 243.7$ Hz), 136.5, 135.3, 135.2, 134.9 (d, $J_{\text{C-F}} = 4.0$ Hz), 134.8, 131.8 (d, $J_{\text{C-F}} = 7.8$ Hz), 127.1, 126.5, 126.2, 125.7, 115.3 (d, $J_{\text{C-F}} = 21.1$ Hz), 51.7, 51.6, 43.4, 37.0, 31.5, 28.3, 27.4, 26.7.



Dimethyl 2-((1-(4-chlorophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ea)

Colorless oil, 107.1 mg, 0.260 mmol, 65% yield.

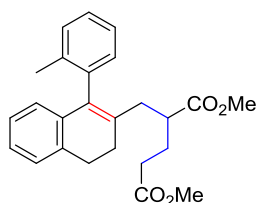
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.61 - 7.59 (m, 2H), 7.22 - 7.14 (m, 3H), 7.10 - 7.06 (m, 2H), 6.58 (d, $J = 7.6$ Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 2.93 (t, $J = 7.8$ Hz, 2H), 2.71 - 2.67 (m, 1H), 2.48 - 2.41 (m, 4H), 2.37 - 2.32 (m, 2H), 1.83 - 1.77 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.2, 138.1, 136.2, 135.2, 135.1, 134.8, 132.0, 131.6, 127.1, 126.6, 126.3, 125.7, 121.0, 51.7, 51.6, 43.3, 37.0, 31.5, 28.3, 27.3, 26.7.



Dimethyl 2-((1-(4-bromophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3fa)

Colorless oil, 122.2 mg, 0.268 mmol, 67% yield.

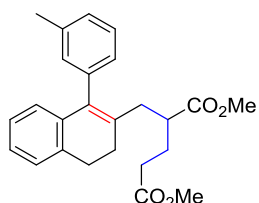
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.41 - 7.39 (m, 2H), 7.17 - 7.02 (m, 5H), 6.54 (d, $J = 7.6$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.89 (t, $J = 7.9$ Hz, 2H), 2.68 - 2.61 (m, 1H), 2.43 - 2.26 (m, 4H), 2.24 - 2.19 (m, 2H), 1.79 - 1.75 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.2, 137.6, 136.3, 135.1, 134.9, 132.9, 131.7, 128.7 \times 2, 127.1, 126.6, 126.3, 125.7, 51.7, 51.6, 43.3, 37.0, 31.5, 28.3, 27.3, 26.7.



Dimethyl 2-((1-(*o*-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ga)

Colorless oil, 73.7 mg, 0.188 mmol, 47% yield.

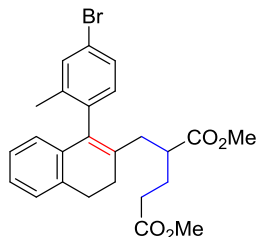
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.28 - 7.22 (m, 3H), 7.18 - 7.17 (m, 1H), 7.12 - 7.08 (m, 2H), 7.03 - 7.00 (m, 1H), 6.49 (d, $J = 7.4$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.92 - 2.90 (m, 2H), 2.64 - 2.61 (m, 1H), 2.46 - 2.29 (m, 4H), 2.19 - 2.15 (m, 2H), 2.05 (s, 3H), 1.79 - 1.72 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.7, 173.3, 138.3, 136.8, 135.8, 135.4, 135.1, 134.2, 130.6, 130.4, 130.1, 127.3, 127.0, 126.4, 125.8, 125.1, 51.6, 51.5, 43.3, 36.8, 31.5, 28.4, 27.1, 26.5, 19.3.



Dimethyl 2-((1-(*m*-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ha)

Colorless oil, 90.9 mg, 0.232 mmol, 58% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.32 - 7.30 (m, 1H), 7.17 - 7.15 (m, 2H), 7.12 - 7.08 (m, 1H), 7.05 - 7.01 (m, 1H), 6.97 - 6.93 (m, 2H), 6.59 (d, $J = 7.5$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.91 - 2.87 (m, 2H), 2.65 - 2.62 (m, 1H), 2.43 - 2.34 (m, 4H), 2.39 (s, 3H), 2.22 - 2.17 (m, 2H), 1.79 - 1.76 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.6, 173.3, 139.0, 136.7, 136.3, 135.1, 134.1, 130.8, 128.2, 127.6 \times 2, 127.2, 127.0, 126.3, 126.2, 125.9, 51.6, 51.5, 43.4, 36.9, 31.6, 28.4, 27.3, 26.6, 21.5.



Dimethyl 2-((1-(4-bromo-2-methylphenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ia)

Colorless oil, 97.8 mg, 0.208 mmol, 52% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.44 (s, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.17 (d, $J = 7.1$ Hz, 1H), 7.13 - 7.10 (m, 1H), 7.04 - 7.00 (m, 1H),

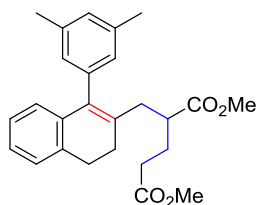
6.97 (d, $J = 8.1$ Hz, 1H), 6.45 (d, $J = 7.4$ Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.92 - 2.88 (m, 2H),

2.64 - 2.62 (m, 1H), 2.46 - 2.34 (m, 4H), 2.22 - 2.11 (m, 2H), 2.03 (s, 3H), 1.80 - 1.70 (m, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.5, 173.2, 139.4, 137.3, 135.3, 135.1, 134.8, 134.3,

133.0, 132.1, 129.0, 127.2, 126.6, 126.4, 124.9, 121.1, 51.7, 51.6, 43.2, 36.9, 31.5, 28.3 \times 2,

27.0, 26.5.



Dimethyl 2-((1-(3,5-dimethylphenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ja)

Colorless oil, 89.4 mg, 0.220 mmol, 55% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.17 - 7.15 (m, 1H), 7.12 - 7.08

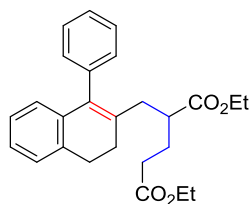
(m, 1H), 7.06 - 7.02 (m, 1H), 6.98 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 6.62 (d, $J = 7.5$ Hz, 1H),

3.67 (s, 3H), 3.66 (s, 3H), 2.91 - 2.86 (m, 2H), 2.66 - 2.61 (m, 1H), 2.44 - 2.37 (m, 4H), 2.35 (s,

6H), 2.24 - 2.14 (m, 2H), 1.81 - 1.75 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.7,

173.3, 139.0, 137.7, 136.8, 136.4, 135.1, 133.9, 128.4, 127.9, 126.9, 126.2, 126.1, 125.9, 51.6,

51.5, 43.5, 37.0, 31.6, 28.4, 27.3, 26.6, 21.3.



Diethyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ab).

Colorless oil, 97.5 mg, 0.240 mmol, 60% yield. $^1\text{H-NMR}$ (400 MHz,

CDCl_3): δ (ppm) 7.44 - 7.40 (m, 2H), 7.37 - 7.33 (m 1H), 7.18 - 7.16 (m,

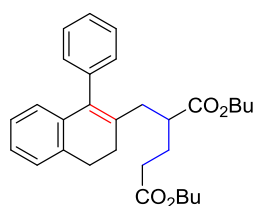
3H), 7.12 - 7.09 (m, 1H), 7.05 - 7.01 (m, 1H), 6.58 (d, $J = 7.6$ Hz, 1H), 4.17 - 4.08 (m, 4H), 2.90

(t, $J = 8.3$ Hz, 2H), 2.65 - 2.58 (m, 1H), 2.43 - 2.30 (m, 4H), 2.21 - 2.14 (m, 2H), 1.79 - 1.74 (m,

2H), 1.29 - 1.27 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.1, 172.9, 139.2, 136.7,

136.2, 135.2, 134.5, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 60.4, 60.3, 43.5, 37.0,

31.8, 28.4, 27.4, 26.8, 14.2.

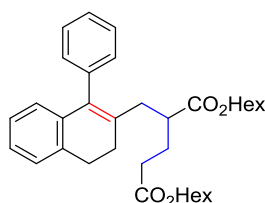


Dibutyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)

methyl) pentanedioate (3ac).

Colorless oil, 96.2 mg, 0.208 mmol, 52% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.44 - 7.40 (m, 2H), 7.37 - 7.33 (m, 1H), 7.17 - 7.09 (m, 4H), 7.05 - 7.01 (m, 1H), 6.58 (d, $J = 7.0$ Hz, 1H), 4.07 - 4.03 (m, 4H), 2.91 (t, $J = 8.1$ Hz, 2H), 2.66 - 2.57 (m, 1H), 2.47 - 2.30 (m, 4H), 2.21 - 2.12 (m, 2H), 1.81 - 1.73 (m, 2H), 1.65 - 1.54 (m, 4H), 1.42 - 1.29 (m, 4H), 0.97 - 0.89 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.1, 173.0, 139.2, 136.7, 136.2, 135.1, 134.4, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 64.4, 64.3, 43.5, 37.0, 31.9, 30.7, 30.6, 28.4, 27.4, 26.8, 19.1 \times 2, 13.7, 13.6.

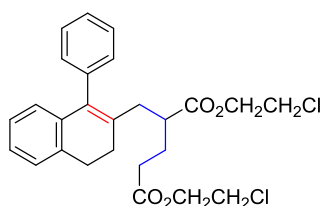


Dihexyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)

methyl) pentanedioate (3ad).

Colorless oil, 66.1 mg, 0.148 mmol, 37% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.44 - 7.40 (m, 2H), 7.37 - 7.35 (m, 1H), 7.17 - 7.16 (m, 3H), 7.12 - 7.08 (m, 1H), 7.05 - 7.01 (m, 1H), 6.57 (d, $J = 7.5$ Hz, 1H), 4.09 - 4.02 (m, 4H), 2.92 - 2.88 (m, 2H), 2.64 - 2.62 (m, 1H), 2.45 - 2.32 (m, 4H), 2.22 - 2.16 (m, 2H), 1.79 - 1.71 (m, 2H), 1.65 - 1.56 (m, 6H), 1.32 - 1.28 (m, 10H), 0.93 - 0.87 (m, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.1, 173.0, 139.2, 136.7, 136.2, 135.1, 134.4, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 64.7, 64.6, 43.5, 37.0, 31.8, 31.4, 31.3, 28.6, 28.5, 28.4, 27.4, 26.7, 25.6 \times 2, 22.5, 22.4, 14.0 \times 2.



Bis(2-chloroethyl) 2-((1-phenyl-3,4-dihydronaphthalen

-2-yl) methyl)pentanedioate (3ae).

Colorless oil, 89.2 mg, 0.200 mmol, 50.0% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.45 - 7.43 (m, 2H), 7.38 - 7.36 (m, 1H), 7.18 - 7.10 (m, 4H), 7.06 - 7.02 (m, 1H), 6.58 (d, $J = 7.6$ Hz, 1H), 4.35 - 4.29 (m, 4H), 3.70 - 3.63 (m, 4H), 2.94 - 2.89 (m, 2H), 2.73 - 2.67 (m, 1H), 2.50 - 2.33 (m, 4H), 2.31 - 2.26 (m, 2H), 1.84 - 1.79 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) 174.6, 172.4, 139.1, 136.6, 136.4, 135.1, 134.0, 130.2, 128.4, 127.0, 126.9, 126.4, 126.2, 125.9, 64.0, 63.9, 43.2, 41.5, 41.4, 36.9, 31.5, 28.4, 27.4, 26.4.

3. NMR Spectra

