

Supporting Information

Rh-Catalyzed Synthesis of Helically Chiral and Ladder-Type Molecules via [2 + 2 + 2] and Formal [2 + 1 + 2 + 1] Cycloadditions Involving C–C Triple Bond Cleavage

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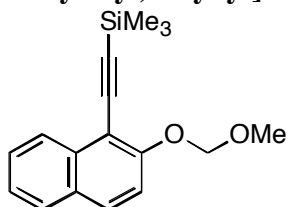
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I. General

Anhydrous CH_2Cl_2 (No. 27,099-7), $(\text{CH}_2\text{Cl})_2$ (No. 28,450-5), and THF (No. 18,656-2) were obtained from Aldrich and used as received. Tol-BINAP and xyl-Segphos [(4,4'-bi-1,3-benzodioxole)-5,5'-diylbis{di(3,5-dimethylphenyl)phosphine}] were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

II. Synthesis of Triynes

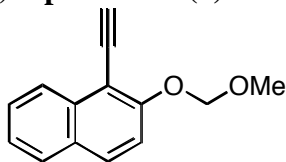
2-Methoxymethoxy-1-[2-(trimethylsilyl)ethynyl]naphthalene (**2**).



To a solution of 1-iodo-2-methoxymethoxynaphthalene¹ (**1**, 8.84 g, 28.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (325 mg, 0.281 mmol) in *i*-Pr₂NH (200 mL) was added trimethylsilyl acetylene (5.6 mL, 139 mmol) at rt. The mixture was then stirred at rt for 5 min, and CuI (107 mg, 0.562 mmol) was added. The resulting mixture was stirred at rt for 23 h. The reaction mixture was filtered and concentrated. The crude alkyne **2** (10.89 g) was used in the next step without purification.

¹H NMR (CDCl_3 , 300 MHz) δ 8.32–8.23 (m, 1H), 7.85–7.72 (m, 2H), 7.62–7.51 (m, 1H), 7.46–7.36 (m, 1H), 7.35 (d, $J = 9.3$ Hz, 1H), 5.37 (s, 2H), 3.60 (s, 3H), 0.35 (s, 9H).

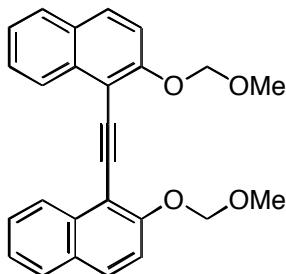
1-Ethynyl-2-(methoxymethoxy)naphthalene (**3**).¹



A solution of KOH (1.89 g, 33.7 mmol) in distilled water (7.4 mL) was added to a solution of the crude alkyne **2** (10.89 g) in MeOH (147 mL) and THF (37 mL). The mixture was stirred at rt for 45 min. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified on a silica gel column chromatography (hexane/EtOAc = 10:1) to afford **3** (5.90 g, 27.8 mmol, 99% yield from **1**) as a pale red oil.

¹H NMR (CDCl₃, 300 MHz) δ 8.34–8.25 (m, 1H), 7.87–7.75 (m, 2H), 7.62–7.50 (m, 1H), 7.48–7.36 (m, 2H), 5.40 (s, 2H), 3.74 (s, 1H), 3.58 (s, 3H).

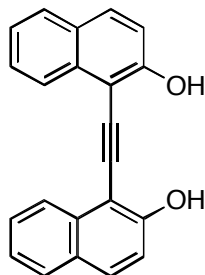
Bis[2-(methoxymethoxy)naphthalen-1-yl]acetylene (4**).**



To a solution of **1** (1.57 g, 5.01 mmol) in *i*-Pr₂NH (10 mL) were added Pd(PPh₃)₄ (115.3 mg, 0.100 mmol) and CuI (38.0 mg, 0.200 mmol) and washed remaining materials away by using *i*-Pr₂NH (10 mL). To the mixture was slowly added a solution of **3** (1.06 g, 5.00 mmol) in *i*-Pr₂NH (30 mL). The resulting mixture was stirred at rt overnight. The reaction was quenched by the addition of water and extracted with CH₂Cl₂. The organic layer was washed with saturated aqueous NH₄Cl, and the water layer was extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified on a silica gel column chromatography (hexane/CH₂Cl₂ = 1:1), which furnished **4** (1.88 g, 4.72 mmol, 95% yield from **3**) as a pale yellow solid.

¹H NMR (CDCl₃, 300 MHz) δ 8.69–8.59 (m, 2H), 7.91–7.78 (m, 4H), 7.66–7.54 (m, 2H), 7.51–7.40 (m, 4H), 5.51 (s, 4H), 3.63 (s, 6H).

Bis(2-hydroxynaphthalen-1-yl)acetylene (5**).**

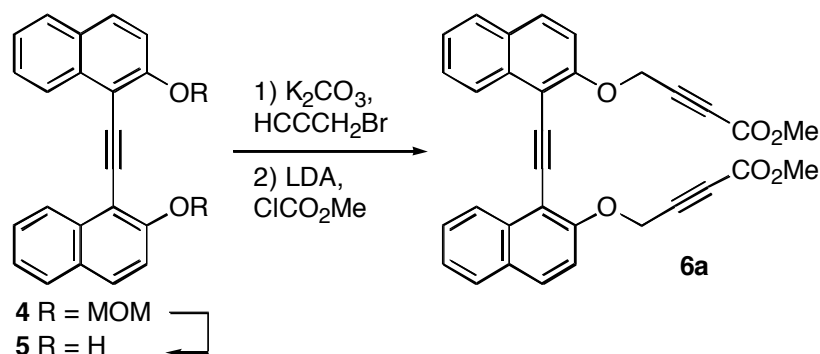


A solution of **4** (0.207 g, 0.520 mmol) in THF/H₂O/conc HCl (6:2:1, 9 mL) was stirred at rt for 16 h. The reaction was quenched by the addition of water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated.

The residue was purified on a silica gel column chromatography (hexane/EtOAc = 10:1) to afford **5** (0.145 g, 0.466 mmol, 89% yield) as a pale yellow solid.

Mp 191.5–192.5 °C; IR (KBr) 3303, 3052, 1621, 1587, 1510, 1349, 1273, 1205, 955, 810, 742 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.32–8.19 (m, 2H), 7.90–7.75 (m, 4H), 7.66–7.54 (m, 2H), 7.48–7.37 (m, 2H), 7.32–7.20 (m, 2H), 6.36 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 156.3, 133.5, 131.2, 128.6, 128.4, 127.8, 124.9, 124.3, 116.6, 102.8, 93.3; HRMS (FAB) calcd for C₂₂H₁₄O₂ [M]⁺ 310.0994, found 310.0995.

Bis[2-(4-methoxy-4-oxobut-2-ynyloxy)naphthalen-1-yl]acetylene (6a).



A solution of **4** (1.04 g, 2.60 mmol) in THF/H₂O/conc HCl (6:2:1, 18 mL) was stirred at rt for 21 h. The reaction was quenched by the addition of water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated to afford crude alkyne **5** (0.732 g). To a stirred suspension of K₂CO₃ (0.461 g, 3.34 mmol) in acetone (5 mL) was added the crude alkyne **5** (0.206 g) and propargyl bromide (0.242 g, 2.03 mmol) in acetone (10 mL), and the resulting mixture was stirred at rt for 88 h. The reaction mixture was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated to afford crude bis[2-(prop-2-ynyloxy)naphthalen-1-yl]acetylene (0.244 g) as a pale yellow solid, a portion of which (0.115 g) was used in the next step without further purification.

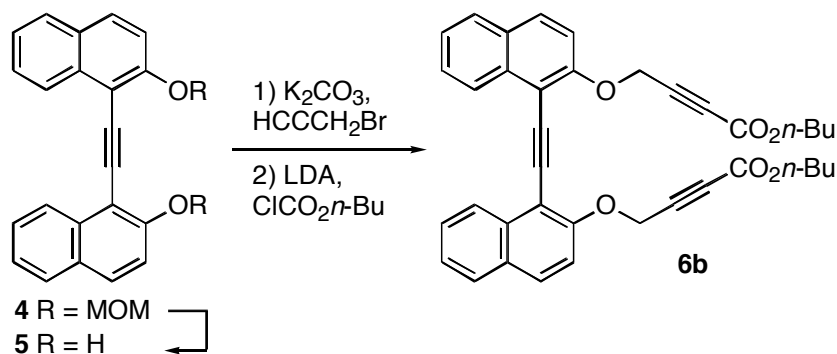
¹H NMR (CDCl₃, 300 MHz) δ 8.71–8.61 (m, 2H), 7.90–7.77 (m, 4H), 7.68–7.56 (m, 2H), 7.50–7.35 (m, 4H), 5.06 (d, *J* = 2.4 Hz, 4H), 2.60 (t, *J* = 2.4 Hz, 2H).

A solution of LDA, prepared from *i*-Pr₂NH (0.10 mL, 0.708 mmol), *n*-BuLi (0.45 mL, 1.52 M in hexane, 0.68 mmol), and THF (10 mL), was added dropwise to a stirred solution of the crude bis[2-(prop-2-ynyloxy)naphthalen-1-yl]acetylene (0.115 g) in THF (10 mL) at –78 °C, and the resulting mixture was stirred at –78 °C for 30 min. To the resulting solution was slowly added a solution of methyl chloroformate (0.096 mL, 1.24 mmol) in THF (10 mL) at –78 °C, and the resulting mixture was stirred at rt for 3 h. The reaction was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified on a silica gel column chromatography (hexane/EtOAc = 10:1), which furnished **6a** (0.087 g, 0.173 mmol, 50% yield from **4**) as a pale yellow solid.

Mp 197.0–198.5 °C; IR (KBr) 3038, 2954, 2906, 2854, 2246, 1711, 1510, 1434, 1262, 1044 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.68–8.55 (m, 2H), 7.95–7.78 (m, 4H), 7.73–7.60

(m, 2H), 7.53–7.41 (m, 2H), 7.37 (d, $J = 9.3$ Hz, 2H), 5.19 (s, 4H), 3.77 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 156.7, 153.3, 134.3, 130.2, 129.5, 128.1, 127.7, 125.9, 125.1, 115.2, 109.2, 93.7, 82.2, 78.7, 57.7, 52.9; HRMS (FAB) calcd for $\text{C}_{32}\text{H}_{22}\text{O}_6$ $[\text{M}]^+$ 502.1416, found 502.1329.

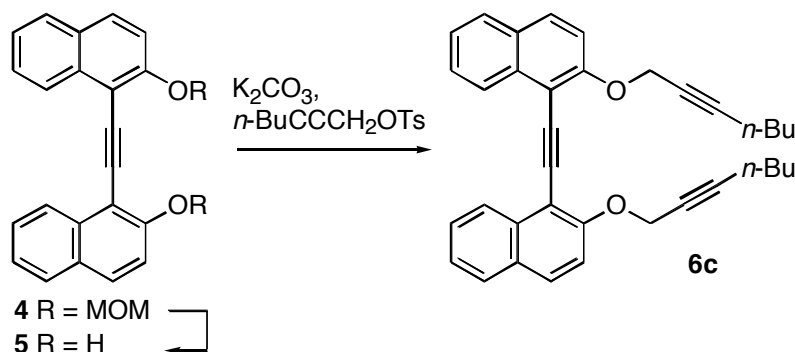
Bis[2-(4-*n*-butoxy-4-oxobut-2-ynyloxy)naphthalen-1-yl]acetylene (6b**).**



A solution of **4** (0.250 g, 0.627 mmol) in THF/ H_2O /conc HCl (6:2:1, 9 mL) was stirred at rt for 15 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated to afford crude alkyne **5** (0.205 g). To a stirred suspension of K_2CO_3 (0.467 g, 3.38 mmol) in acetone (5 mL) was added the crude alkyne **5** (0.205 g) and propargyl bromide (0.246 g, 2.06 mmol) in acetone (15 mL), and the resulting mixture was stirred at rt for 22 h. The reaction mixture was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated to afford crude bis[2-(prop-2-ynyloxy)naphthalen-1-yl]acetylene (0.250 g). A solution of LDA, prepared from *i*- Pr_2NH (0.22 mL, 1.56 mmol), *n*-BuLi (0.9 mL, 1.59 M in hexane, 1.43 mmol), and THF (10 mL), was added dropwise to a stirred solution of the crude bis[2-(prop-2-ynyloxy)naphthalen-1-yl]acetylene (0.250 g) in THF (20 mL) at -78°C , and the resulting mixture was stirred at -78°C for 20 min. To the resulting solution was slowly added with stirring a solution of *n*-butyl chloroformate (0.33 mL, 2.59 mmol) in THF (10 mL) at -78°C , and the resulting mixture was stirred at rt for 18 h. The reaction was quenched by the addition of water and extracted with EtOAc three times. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The residue was purified on a silica gel column chromatography (hexane/ CH_2Cl_2 = 2:1), which furnished **6b** (0.178 g, 0.303 mmol, 48% yield from **4**) as a pale yellow solid.

Mp 129.5 – 131.0°C ; IR (KBr) 3050, 2957, 2247, 1706, 1257, 1053 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.63–8.58 (m, 2H), 7.93–7.80 (m, 4H), 7.72–7.63 (m, 2H), 7.52–7.42 (m, 2H), 7.37 (d, $J = 9.3$ Hz, 2H), 5.18 (s, 4H), 4.18 (t, $J = 6.6$ Hz, 4H), 1.64–1.57 (m, 4H), 1.44–1.29 (m, 4H), 0.91 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 156.7, 153.1, 134.3, 130.1, 129.5, 128.1, 127.7, 125.9, 125.1, 115.2, 109.2, 93.7, 81.8, 79.1, 66.1, 57.7, 30.3, 19.0, 13.6; HRMS (FAB) calcd for $\text{C}_{38}\text{H}_{34}\text{O}_6$ $[\text{M}]^+$ 586.2355, found 586.2376.

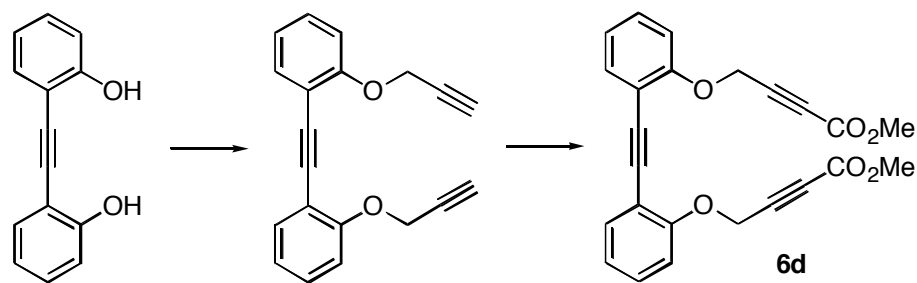
Bis[2-(hept-2-ynyloxy)naphthalen-1-yl]acetylene (6c**).**



A solution of **4** (0.398 g, 1.00 mmol) in THF/H₂O/conc HCl (6:2:1, 6 mL) was stirred at rt for 5 h. The reaction was quenched by the addition of water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated to afford crude alkyne **5** (0.394 g). To a stirred suspension of K₂CO₃ (0.691 g, 5.00 mmol) in acetone (5 mL) was added the crude alkyne **5** (0.394 g) and 2-heptynyl tosylate² (0.666 g, 2.50 mmol) in acetone (25 mL), and the resulting mixture was stirred at rt for 21 h. The reaction mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified on a silica gel column chromatography (hexane/CH₂Cl₂ = 4:1) to afford **6c** (0.147 g, 0.295 mmol, 30% yield from **4**) as a pale yellow solid.

Mp 86.5–87.5 °C; IR (KBr) 3055, 2955, 2925, 1587, 1507, 1278, 1255, 1219, 1043 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.71–8.63 (m, 2H), 7.88–7.75 (m, 4H), 7.65–7.55 (m, 2H), 7.48–7.36 (m, 4H), 5.04 (t, J = 2.1 Hz, 4H), 2.23 (tt, J = 6.9 and 2.1 Hz, 4H), 1.58–1.25 (m, 8H), 0.85 (t, J = 7.5 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 157.4, 134.4, 129.5, 129.1, 127.9, 127.2, 126.1, 124.5, 115.6, 109.0, 93.8, 88.7, 75.2, 58.6, 30.5, 21.9, 18.6, 13.5; HRMS (FAB) calcd for C₃₆H₃₅O₂ [M+H]⁺ 499.2637, found 499.2633.

Bis[2-(4-methoxy-4-oxobut-2-ynyloxy)phenyl]acetylene (6d).



To a stirred suspension of NaH (55% in paraffin liquid, 0.124 g, 2.85 mmol) in DMF (5 mL) was added a solution of 2,2'-(1,2-ethynediyl)bisphenol³ (0.270 g, 1.28 mmol) and propargyl bromide (0.460 g, 3.87 mmol) in DMF (20 mL) at 0 °C, and the resulting mixture was stirred at rt for 17 h. The reaction mixture was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified on a silica gel column chromatography

(hexane/EtOAc = 10:1), which furnished bis[2-(prop-2-ynyloxy)phenyl]acetylene (0.202 g, 0.705 mmol, 55% yield) as a pale yellow solid.

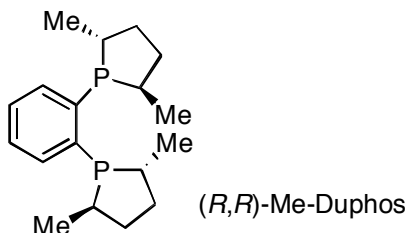
^1H NMR (CDCl_3 , 300 MHz) δ 7.61–7.47 (m, 2H), 7.39–7.20 (m, 2H), 7.16–6.91 (m, 4H), 4.86 (d, J = 2.1 Hz, 4H), 2.54 (t, J = 2.1 Hz, 2H).

A solution of LDA, prepared from *i*-Pr₂NH (0.12 mL, 0.845 mmol), *n*-BuLi (0.49 mL, 1.58 M in hexane, 0.77 mmol), and THF (5 mL), was added dropwise to a stirred solution of bis[2-(prop-2-ynyloxy)phenyl]acetylene (0.100 g, 0.349 mmol) in THF (12 mL) at -78°C , and the resulting mixture was stirred at -78°C for 20 min. To the resulting solution was added a solution of methyl chloroformate (0.108 mL, 1.24 mmol) in THF (4 mL) at -78°C , and the resulting mixture was gradually warmed to rt. The reaction was quenched by the addition of water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified on a silica gel column chromatography (hexane/EtOAc = 4:1), which furnished **6d** (0.077 g, 0.191 mmol, 55% yield) as a pale yellow solid.

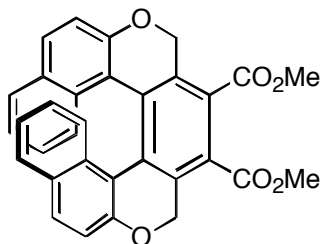
Mp 120.0–121.0 $^\circ\text{C}$; IR (KBr) 3059, 3001, 2953, 2925, 2850, 2252, 1715, 1504, 1442, 1380, 1263, 1230, 1017 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.59–7.48 (m, 2H), 7.38–7.24 (m, 2H), 7.10–6.94 (m, 4H), 4.99 (s, 4H), 3.77 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 157.6, 153.3, 133.7, 129.7, 122.2, 113.85, 113.78, 89.8, 82.2, 78.6, 56.6, 52.8; HRMS (FAB) calcd for C₂₄H₁₈O₆ [M]⁺ 402.1103, found 402.1115; HRMS (ESI) calcd for C₂₄H₁₈O₆Na [M+Na]⁺ 425.1001, found 425.0994.

III. Rh-Catalyzed Cycloadditions of Triynes

General Procedure for Rh(I)⁺/(*R,R*)-Me-Duphos-Catalyzed Cycloaddition of Triynes (Tbele 1, entry 1, **6a).** Under an Ar atmosphere, (*R,R*)-MeDuphos (6.1 mg, 0.02 mmol) and [Rh(cod)₂]BF₄ (8.1 mg, 0.02 mmol) were dissolved in CH₂Cl₂ (1.0 mL) and the mixture was stirred for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting mixture was concentrated to dryness. To a CH₂Cl₂ (1.0 mL) solution of the residue was added a CH₂Cl₂ (3.0 mL) solution of **6a** (50.3 mg, 0.10 mmol) and washed the remaining substrate away by using CH₂Cl₂ (1.0 mL). The mixture was stirred at rt for 15 h. The resulting mixture was concentrated and purified on a preparative TLC (hexane/EtOAc/CH₂Cl₂ = 10:1:1), which furnished **7a** (40.3 mg, 0.0802 mmol, 80% yield, 71% ee) as a yellow solid.

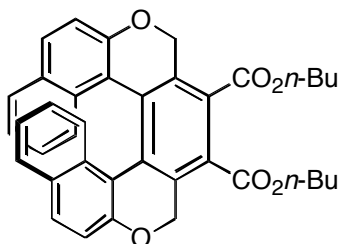


(*M*)-(-)-Dimethyl 8*H*,11*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]-benzo[*d*]pyran-9,10-dicarboxylate [(*M*)-(-)-7a**].**



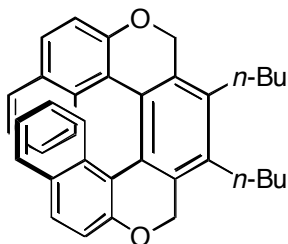
Mp 191.0–192.0 °C; $[\alpha]_D^{25} -908.6^\circ$ (CHCl₃, *c*1.49, 71% ee); IR (KBr) 3060, 2952, 2924, 2851, 1720, 1230, 1207, 1000 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.45 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.23–7.14 (m, 2H), 6.87–6.71 (m, 4H), 6.64–6.53 (m, 2H), 5.54 (d, *J* = 14.1 Hz, 2H), 4.89 (d, *J* = 14.1 Hz, 2H), 3.98 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.3, 156.1, 137.9, 131.3, 129.6, 129.3, 128.6, 127.1, 126.3, 125.1, 123.2, 121.9, 118.4, 117.6, 67.9, 52.8; HRMS (FAB) calcd for C₃₂H₂₃O₆ [M+H]⁺ 503.1495, found 503.1472; CHIRALPAK AD, Hexane/*i*-PrOH = 80:20, 1.0 mL/min, retention times: 9.7 min (minor isomer) and 15.2 min (major isomer).

(–)-Di-*n*-butyl 8*H*,11*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]benzo[*d*]pyran-9,10-dicarboxylate [(–)-7b].



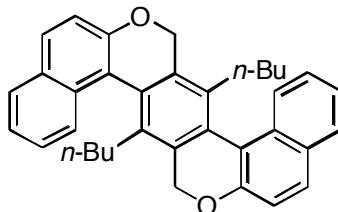
Yellow solid; Mp 50.0–51.0 °C; $[\alpha]_D^{25} -845.8^\circ$ (CHCl₃, *c*1.31, 77% ee); IR (KBr) 2957, 2926, 2853, 1722, 1231, 1195 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.30–7.22 (m, 2H), 7.22–7.14 (m, 2H), 6.86–6.71 (m, 4H), 6.63–6.52 (m, 2H), 5.54 (d, *J* = 14.1 Hz, 2H), 4.89 (d, *J* = 14.1 Hz, 2H), 4.46 (dt, *J* = 10.8 and 6.6 Hz, 2H), 4.30 (dt, *J* = 10.8 and 6.6 Hz, 2H), 1.84–1.69 (m, 4H), 1.57–1.40 (m, 4H), 0.99 (t, *J* = 7.5 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.0, 156.0, 137.7, 131.2, 129.4, 129.3, 128.6, 127.0, 126.7, 125.1, 123.2, 122.0, 118.4, 117.5, 68.0, 66.0, 30.6, 19.3, 13.7; HRMS (FAB) calcd for C₃₈H₃₄O₆ [M]⁺ 586.2355, found 586.2386; CHIRALPAK AD, Hexane/*i*-PrOH 80:20, 1.0 mL/min, retention times: 8.1 min (minor isomer) and 25.2 min (major isomer).

(–)-8*H*,11*H*-9,10-Di-*n*-butylnaphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]-benzo[*d*]pyran [(–)-7c].



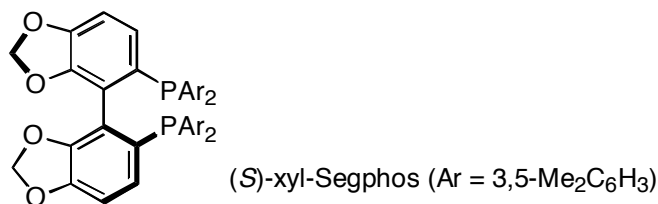
Pale yellow solid; Mp 135.5–136.1 °C; $[\alpha]_D^{25} -604.0^\circ$ (CHCl_3 , c 1.73, 85% ee); IR (KBr) 3056, 2956, 2925, 2852, 1227, 809 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.22–7.14 (m, 2H), 6.95–6.87 (m, 2H), 6.82–6.72 (m, 2H), 6.58–6.47 (m, 2H), 5.52 (d, J = 12.9 Hz, 2H), 4.71 (d, J = 12.9 Hz, 2H), 2.77 (t, J = 7.8 Hz, 4H), 1.75–1.46 (m, 8H), 1.04 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 154.9, 136.1, 134.5, 129.40, 129.37, 129.2, 126.7, 125.0, 124.3, 122.73, 122.71, 119.9, 117.5, 67.7, 33.5, 28.7, 23.2, 14.0; HRMS (FAB) calcd for $\text{C}_{36}\text{H}_{34}\text{O}_2$ $[\text{M}]^+$ 498.2559, found 498.2527; CHIRALPAK AD-H, Hexane/*i*-PrOH = 98:2, 1.0 mL/min, retention times: 6.0 min (major isomer) and 6.8 min (minor isomer).

8*H*,17*H*-9,18-Di-*n*-butyl-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo[*d*]pyran (8c).

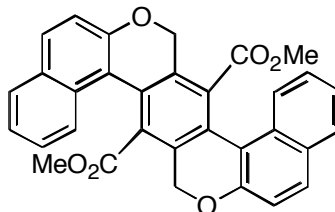


Pale yellow greasy solid; IR (KBr) 3059, 2925, 2854, 1464, 1377, 1230, 1011, 816 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.87–7.75 (m, 6H), 7.46–7.33 (m, 6H), 5.47 (d, J = 12.9 Hz, 2H), 4.76 (d, J = 12.9 Hz, 2H), 2.79–2.54 (m, 4H), 1.22–0.60 (m, 8H), 0.49 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.8, 136.1, 132.6, 130.4, 130.0, 129.2, 128.32, 128.30, 125.9, 125.7, 123.7, 119.9, 117.9, 68.4, 32.9, 29.9, 22.0, 13.5; HRMS (FAB) calcd for $\text{C}_{36}\text{H}_{34}\text{O}_2$ $[\text{M}]^+$ 498.2559, found 498.2538.

General Procedure for Rh(I)⁺/(*S*)-xyl-Segphos-Catalyzed Cycloaddition of Triynes (Table 1, entry 4, 6a). Under an Ar atmosphere, (*S*)-xyl-Segphos (14.5 mg, 0.02 mmol) and $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (8.1 mg, 0.02 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting mixture was concentrated to dryness. To the (CH_2Cl_2)₂ (1.0 mL) solution of the residue was added a (CH_2Cl_2)₂ (3.0 mL) solution of **6a** (50.3 mg, 0.10 mmol) and washed the remaining substrate away by using (CH_2Cl_2)₂ (1.0 mL). The mixture was stirred at 80 °C for 15 h. The resulting mixture was concentrated and purified on a preparative TLC (hexane/EtOAc = 5:1), which furnished **7a** (19.4 mg, 0.0386 mmol, 39% yield) as a pale yellow solid and **8a** (17.1 mg, 0.0340 mmol, 34% yield) as a yellow solid.

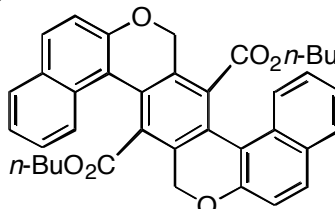


Dimethyl 8*H*,17*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo-[*d*]pyran-9,18-dicarboxylate (8a).



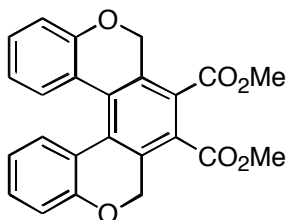
Mp 250.0–251.2 °C; IR (KBr) 2947, 2925, 2851, 1717, 1305, 1169 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.95–7.74 (m, 6H), 7.53–7.27 (m, 6H), 5.49 (d, *J* = 13.8 Hz, 2H), 4.96 (d, *J* = 13.8 Hz, 2H), 2.99 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.5, 155.4, 137.0, 130.9, 130.8, 129.7, 129.0, 128.6, 128.3, 126.9, 124.2, 123.3, 117.9, 117.7, 68.1, 52.0; HRMS (FAB) calcd for C₃₂H₂₂O₆ [M]⁺ 502.1416, found 502.1432; HRMS (ESI) calcd for C₃₂H₂₂O₆Na [M+Na]⁺ 525.1314, found 525.1314.

Di-*n*-butyl 8*H*,17*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo-[*d*]pyran-9,18-dicarboxylate (8b).



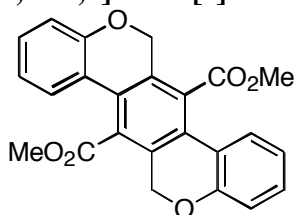
Small amount of pure ladder-type molecule **8b** (4.4 mg) could be separated from helicen-like molecule **7b** by silica gel column chromatography (hexane/EtOAc = 10:1) as the first fraction. Yellow solid; Mp 54.3–55.8 °C; IR (KBr) 3060, 2956, 2925, 2854, 1712, 1302, 1248, 1176, 1124, 1020 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.96–7.89 (m, 2H), 7.87–7.77 (m, 4H), 7.50–7.43 (m, 2H), 7.43–7.36 (m, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 5.51 (d, *J* = 13.8 Hz, 2H), 4.97 (d, *J* = 13.8 Hz, 2H), 3.71 (dt, *J* = 10.8 and 6.3 Hz, 2H), 3.04 (dt, *J* = 10.8 and 6.3 Hz, 2H), 0.98–0.70 (m, 8H), 0.64 (t, *J* = 6.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.3, 155.4, 137.0, 130.9, 130.6, 129.9, 129.4, 128.5, 128.2, 126.9, 124.2, 123.5, 118.0, 117.8, 68.2, 65.5, 29.6, 18.7, 13.6; HRMS (FAB) calcd for C₃₈H₃₄O₆ [M]⁺ 586.2355, found 586.2360.

Dimethyl 6*H*,9*H*-chromeno[3',4':4,3]benzo[*c*]chromene-7,8-dicarboxylate (7d).



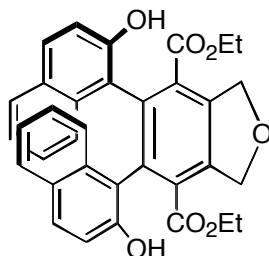
The reaction was conducted in CH_2Cl_2 at 40 °C for 14 h. Pale yellow solid; Mp 227.5–228.1 °C; IR (KBr) 2949, 1726, 1229, 1202, cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.35–7.28 (m, 2H), 7.28–7.18 (m, 2H), 7.14–7.04 (m, 2H), 6.83–6.72 (m, 2H), 5.64–4.50 (br, 4H), 3.90 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 167.0, 156.5, 137.2, 130.34, 130.28, 129.0, 126.9, 122.8, 121.6, 117.9, 67.7, 52.7; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_6$ $[\text{M}+\text{H}]^+$ 403.1182, found 403.1210; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 425.1001, found 425.0987.

Dimethyl 6H,13H-chromeno[3',4':4,5]benzo[c]chromene-7,14-dicarboxylate (8d).



The reaction was conducted in CH_2Cl_2 at 40 °C for 14 h. Pale yellow solid; Mp 186.0–187.5 °C; IR (neat) 2953, 2925, 2852, 1726, 1261, 1227, 1043, 1018 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40–7.19 (m, 4H), 7.13–6.99 (m, 4H), 5.02 (s, 4H), 3.85 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.2, 155.9, 133.2, 130.4, 127.7, 127.5, 125.7, 122.3, 122.1, 117.7, 66.8, 52.7; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_6$ $[\text{M}+\text{H}]^+$ 403.1182, found 403.1153; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 425.1001, found 425.1005.

(+)-5,6-Bis(2-hydroxynaphthalen-1-yl)-1,3-dihydroisobenzofuran-4,7-dicarboxylic acid diethyl ester [(+)-10]. Under an Ar atmosphere, (*R*)-tol-BINAP (4.7 mg, 0.0075 mmol) and $[\text{Rh}(\text{cod})_2]\text{BF}_4$ (3.0 mg, 0.0075 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 1 h, the resulting solution was concentrated and dissolved in THF (0.3 mL). To this solution was added a THF (0.4 mL) solution of **5** (93.0 mg, 0.30 mmol) at rt, and then a THF (1.3 mL) solution of bis[3-(ethoxycarbonyl)propargyl] ether⁴ (**9**, 35.7 mg, 0.15 mmol) dropwise over 30 min at rt. After stirring at rt for 1 h, the resulting solution was concentrated and purified on a preparative TLC (hexane/EtOAc = 2:1), which furnished **10** (18.9 mg, 0.034 mmol, 23% yield, 69% ee) as a pale yellow solid.

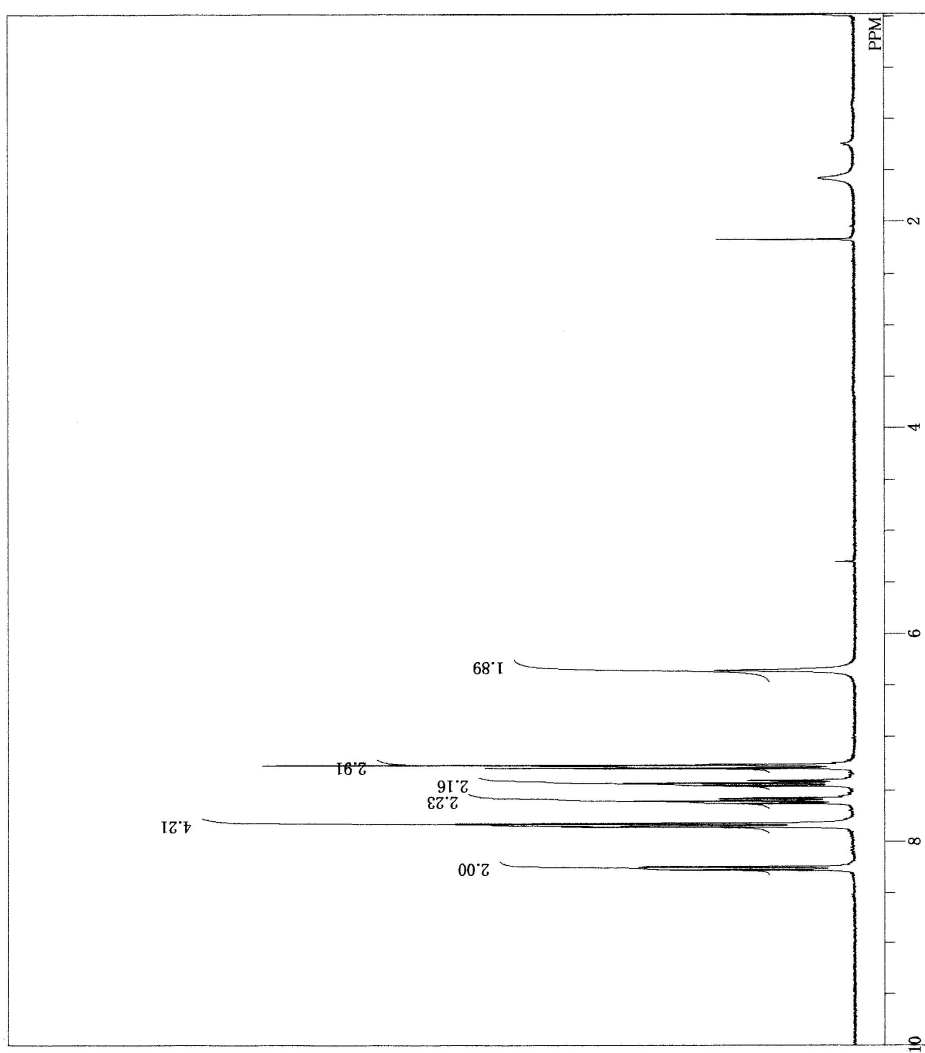
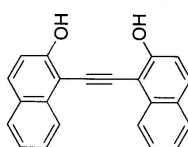


Mp 219.0–220.0 °C; $[\alpha]_D^{25} +121.8^\circ$ (CHCl_3 , c 0.280, 69% ee); IR (KBr) 3435, 3057, 2979, 2961, 2926, 2856, 1704, 1257, 1184–1092(br), 1023 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.66–7.55 (m, 2H), 7.48–7.35 (m, 4H), 7.35–7.17 (m, 4H), 6.58 (d, J = 8.7 Hz, 2H), 5.63–5.47 (m, 2H), 5.47–5.33 (m, 2H), 4.64 (s, 2H), 3.78 (q, J = 7.2 Hz, 4H), 0.53 (t, J = 7.2 Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.3, 150.5, 142.1 137.0, 133.5, 131.5, 129.3, 128.4, 127.8, 126.1, 124.4, 123.1, 118.5, 117.3, 74.1, 61.2, 13.0; HRMS (FAB) calcd for $\text{C}_{34}\text{H}_{28}\text{O}_7$ $[\text{M}]^+$ 548.1835, found 548.1785; CHIRALCEL OD-H (Connected two columns were employed.), Hexane/*i*-PrOH = 85:15, 0.5 mL/min, retention times: 27.3 min (minor isomer) and 31.4 min (major isomer).

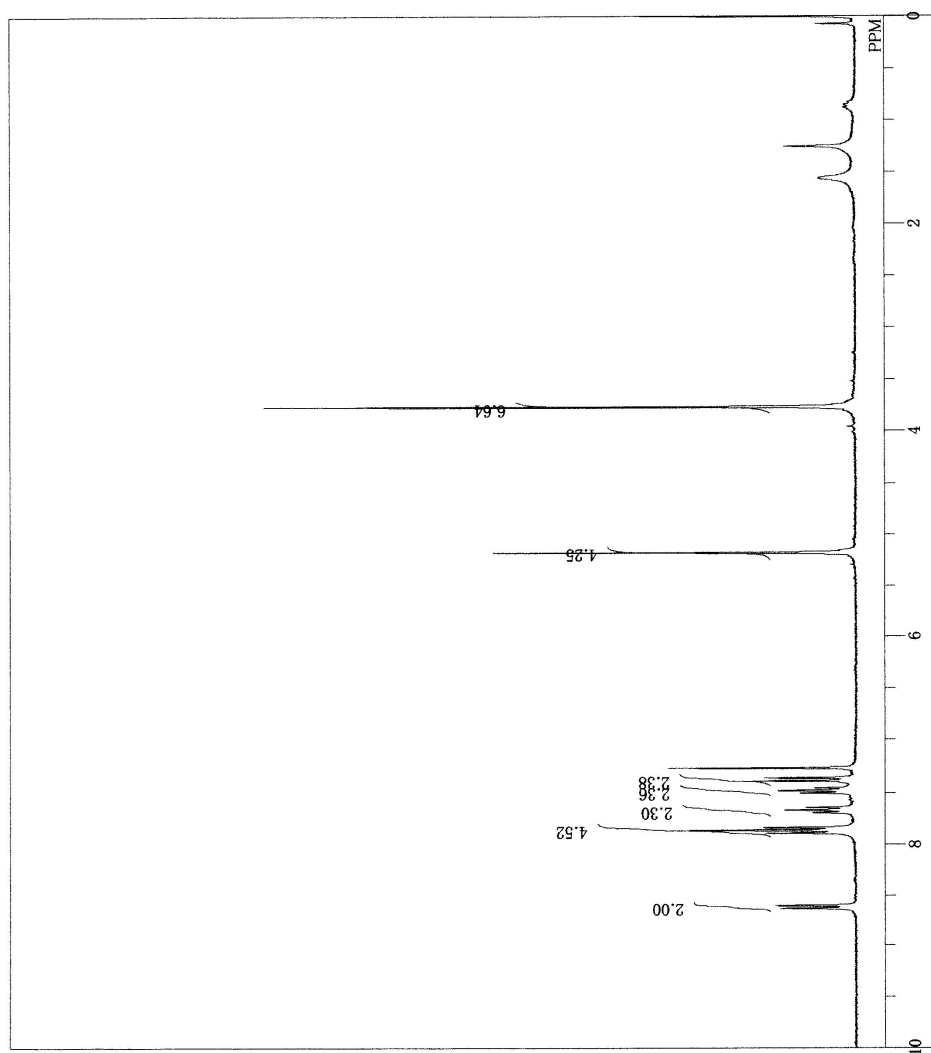
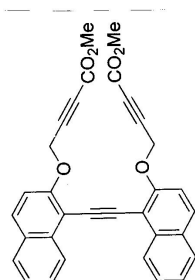
IV. References

- (1) Cironi, P.; Albericio, F.; Alvarez, M. *Tetrahedron Lett.* **2004**, *45*, 7311.
- (2) Baldwin, J. E.; Adlington, R. M.; Crouch, N. P.; Hill, R. L.; Laffey, T. G. *Tetrahedron Lett.* **1995**, *36*, 7925.
- (3) Hiroya, K.; Suzuki, N.; Yasuhara, A.; Egawa, Y.; Kasano, A.; Sakamoto, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4339.
- (4) Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem.–Eur. J.* **2003**, *9*, 2469.

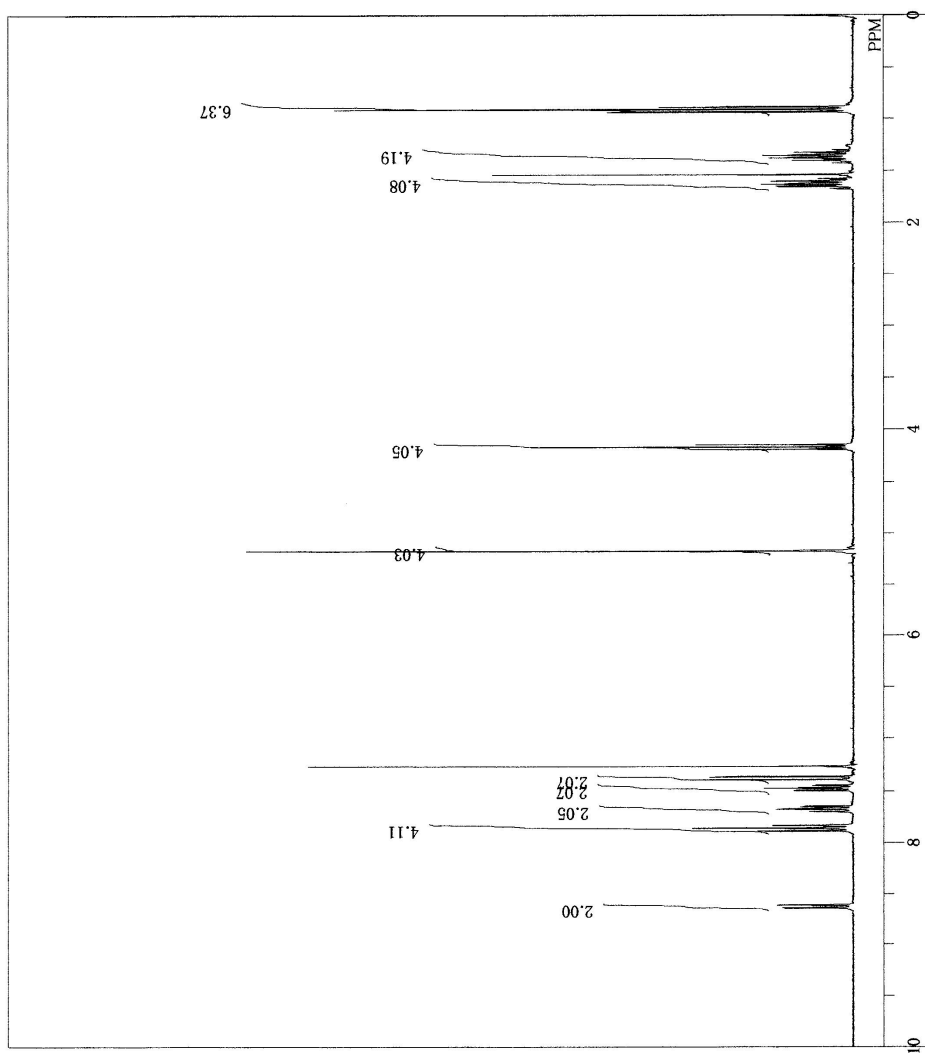
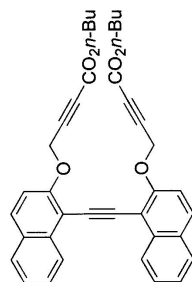
Bis(2-hydroxynaphthalen-1-yl)acetylene (**5**)



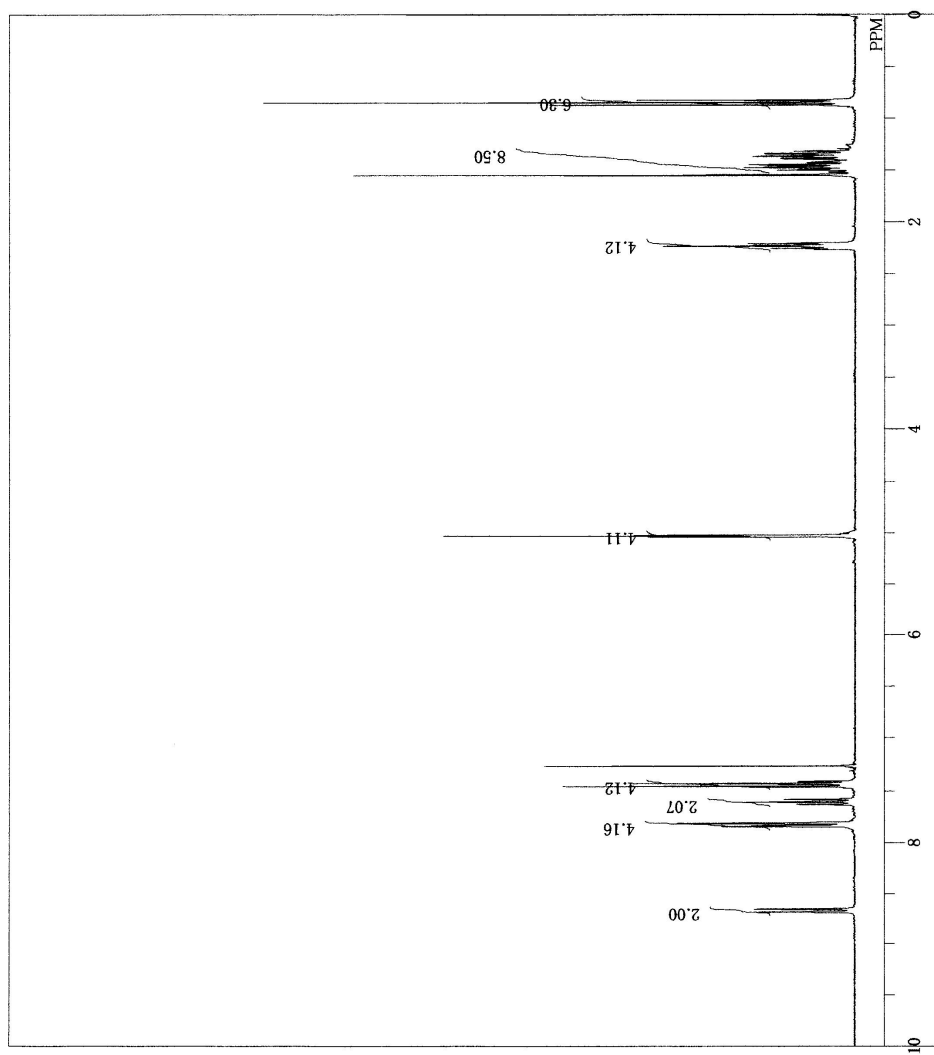
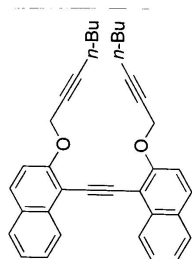
Bis[2-(4-methoxy-4-oxobut-2-ynyloxy)naphthalen-1-yl]acetylene (**6a**)

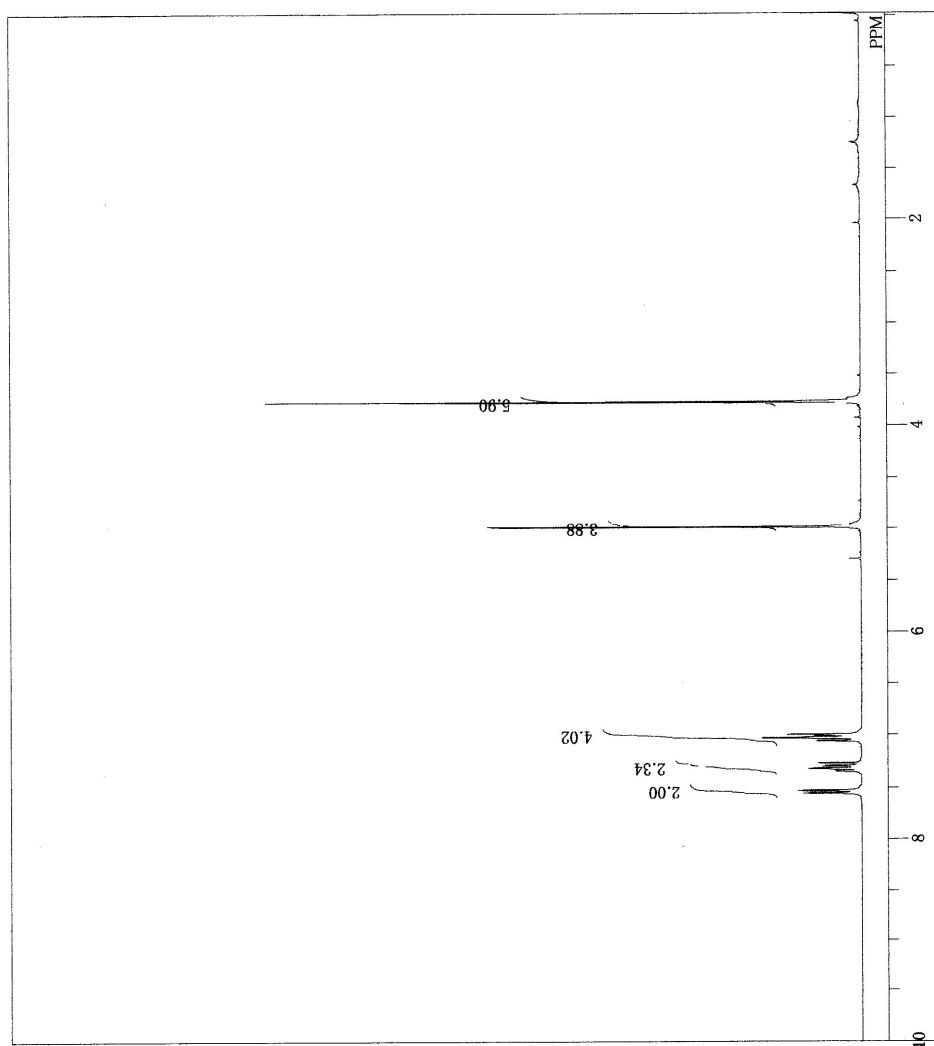
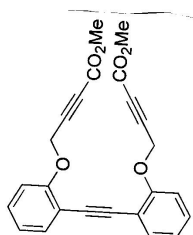


Bis[2-(4-*n*-butoxy-4-oxobut-2-ynyloxy)naphthalen-1-yl]acetylene (**6b**)

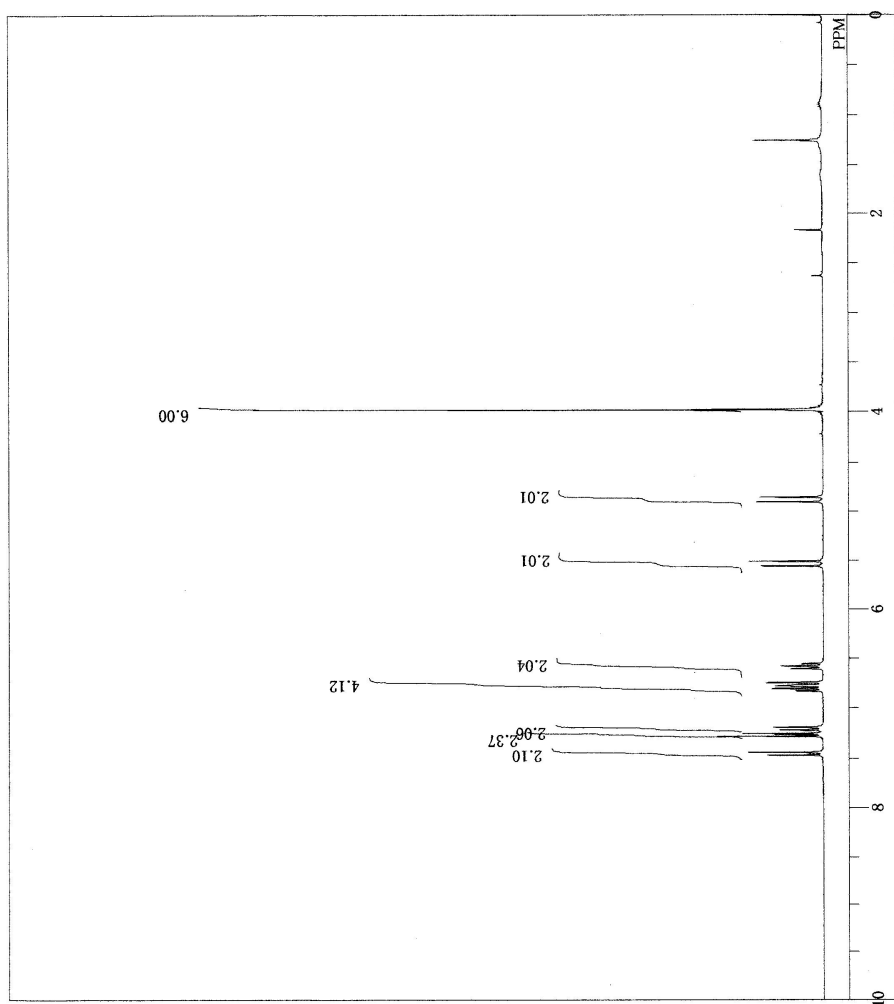
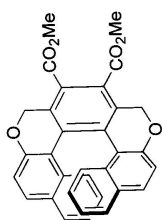


Bis[2-(hept-2-ynyloxy)naphthalen-1-yl]acetylene (**6c**)

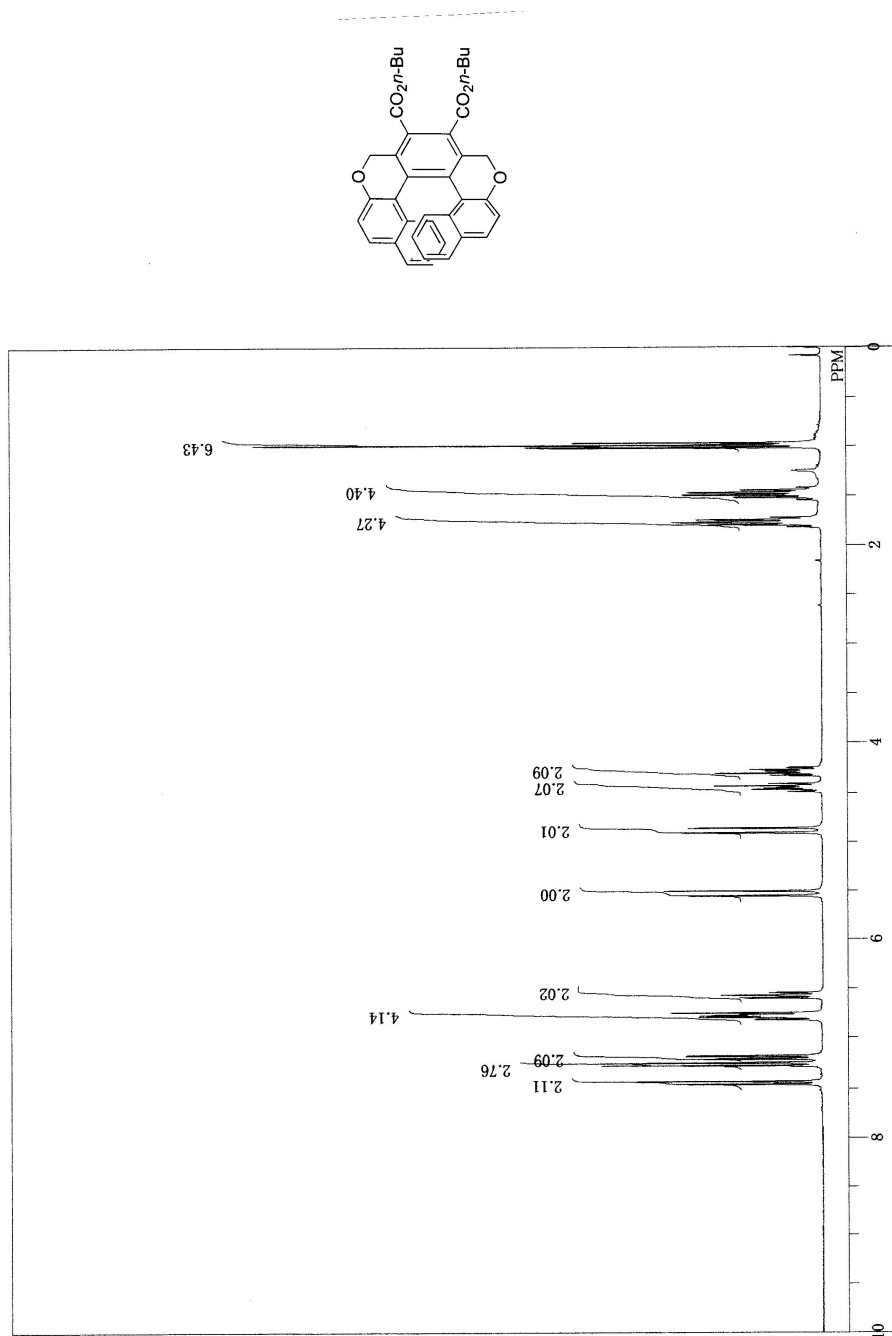


Bis[2-(4-methoxy-4-oxobut-2-ynyloxy)phenyl]acetylene (**6d**)

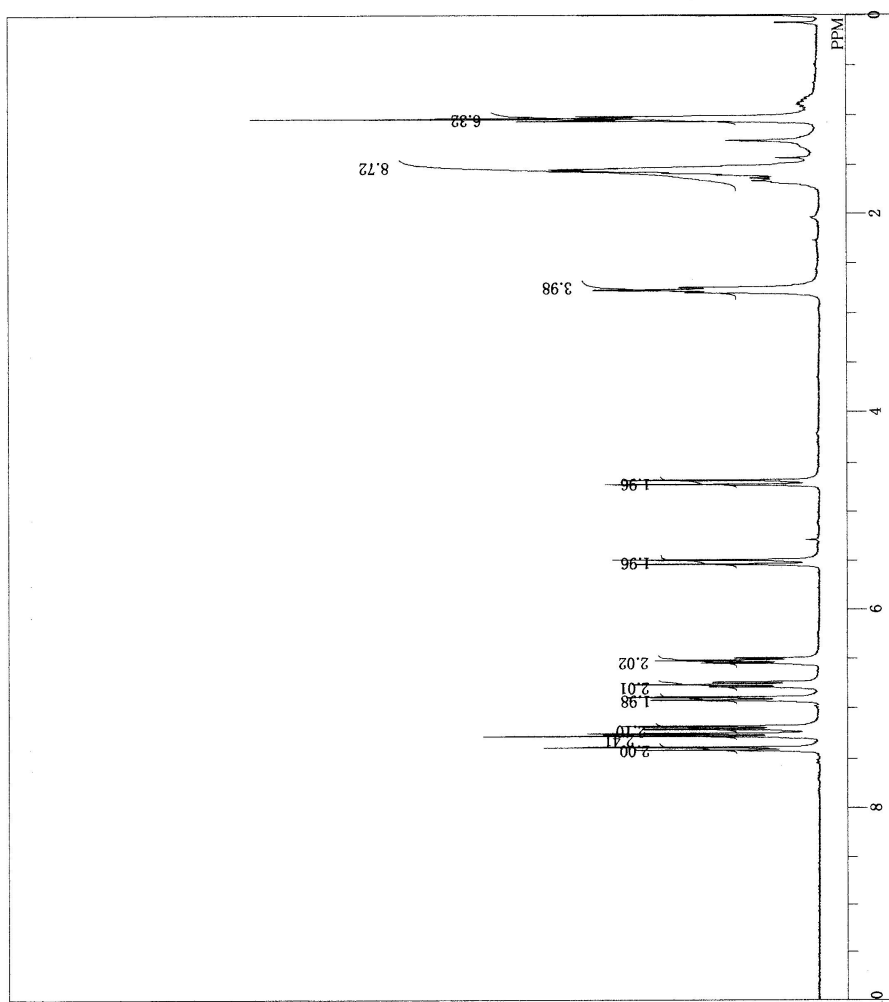
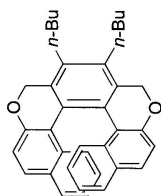
Dimethyl 8*H*,11*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]benzo[*d*]pyran-9,10-dicarboxylate (**7a**)



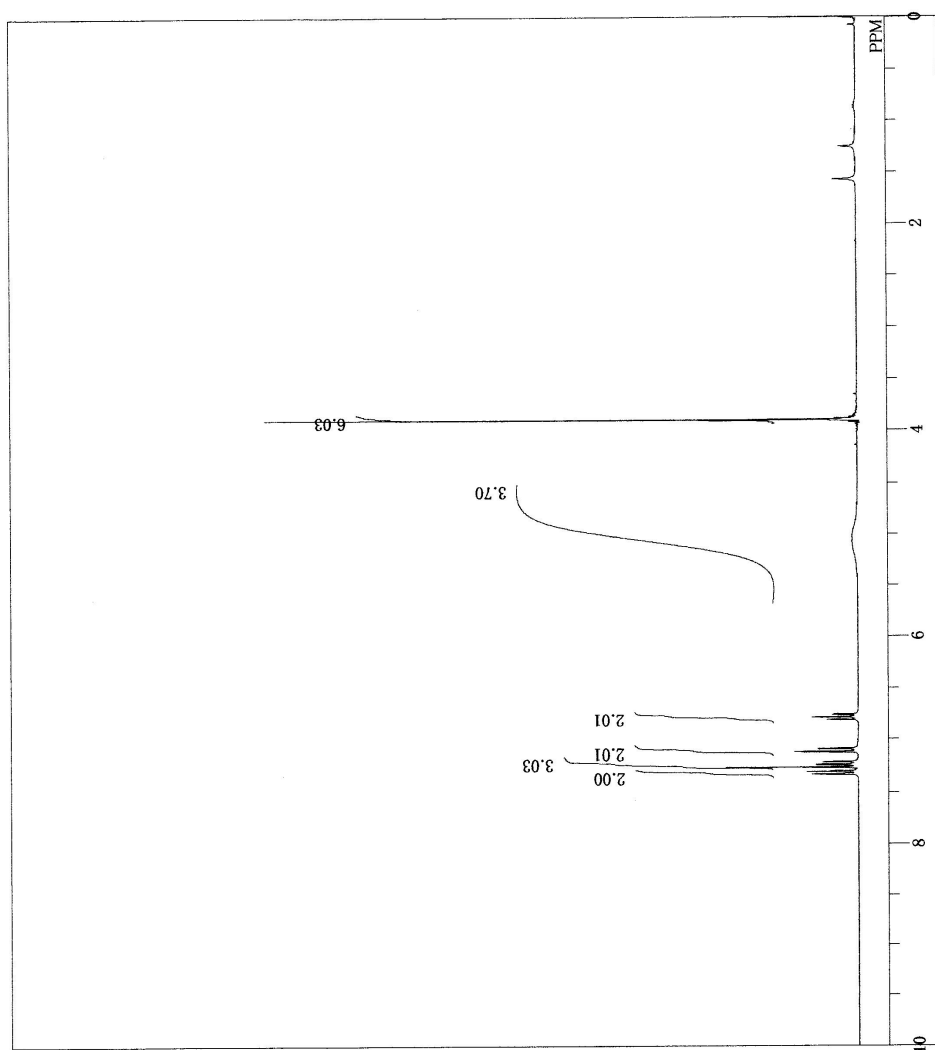
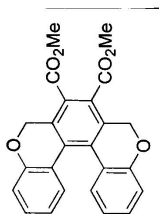
Di-*n*-butyl 8*H*,11*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]benzo[*d*]pyran-9,10-dicarboxylate (**7b**)



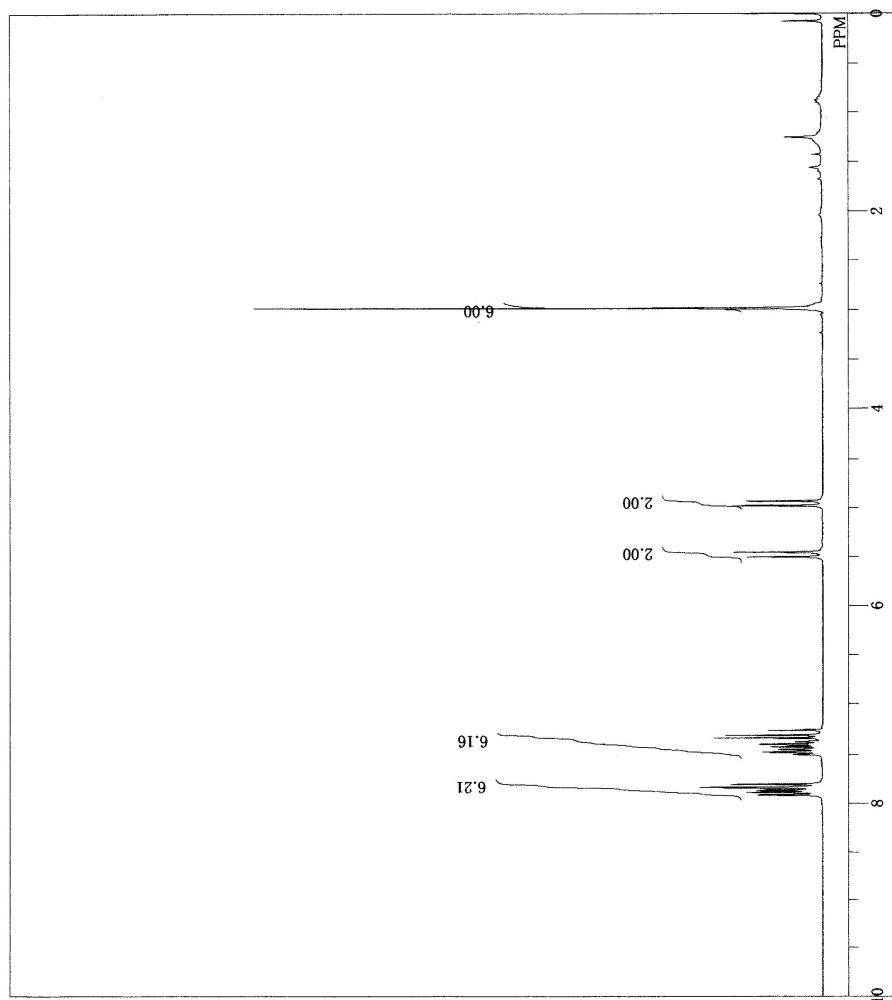
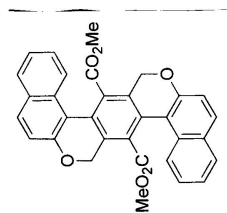
8*H*,11*H*-9,10-Di-*n*-butylnaphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,6]benzo[*d*]pyran
(7c)



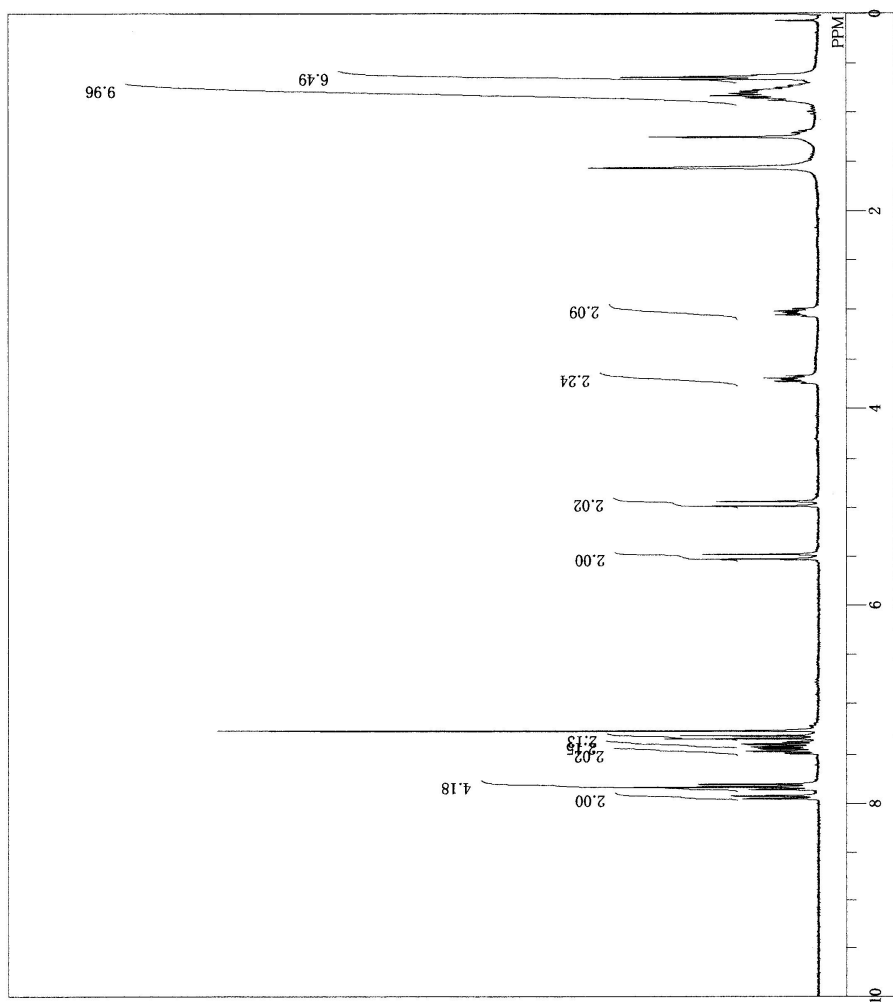
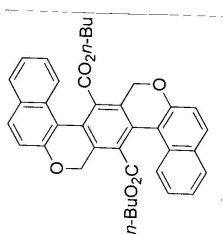
Dimethyl 6*H*,9*H*-chromeno[3',4':4,3]benzo[*c*]chromene-7,8-dicarboxylate (**7d**)



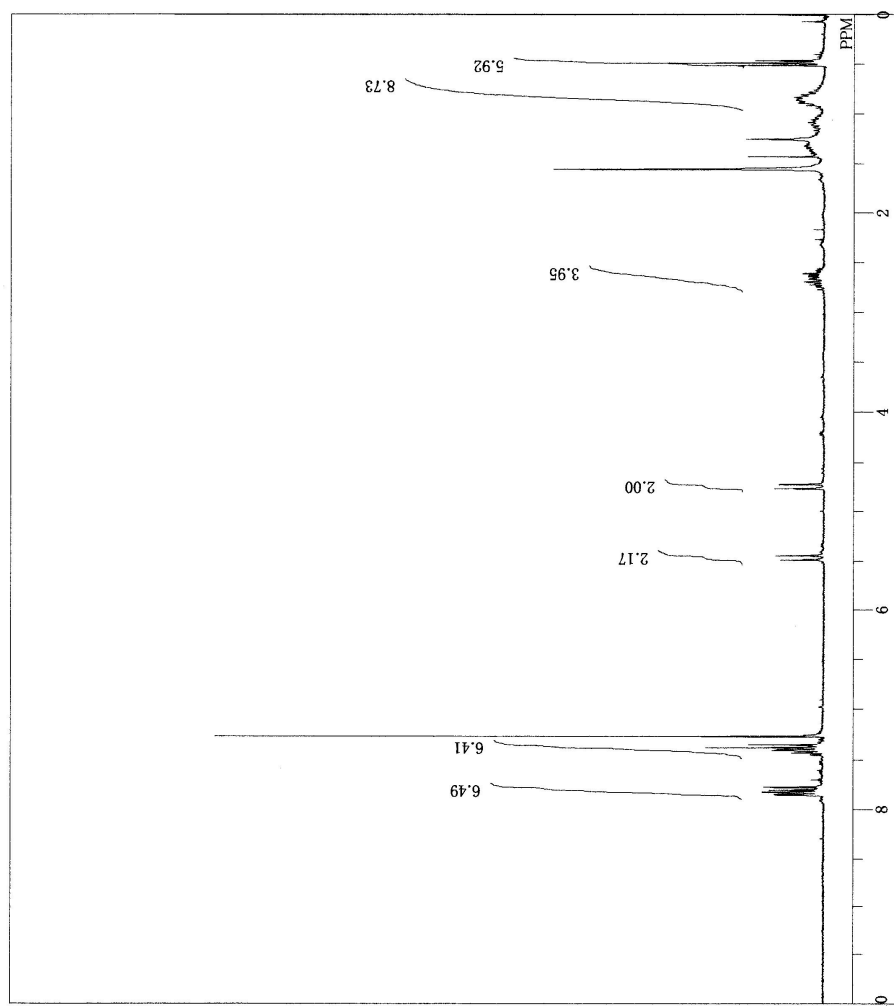
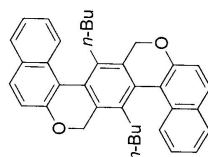
Dimethyl 8*H*,17*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo[*d*]pyran-9,18-dicarboxylate (**8a**)



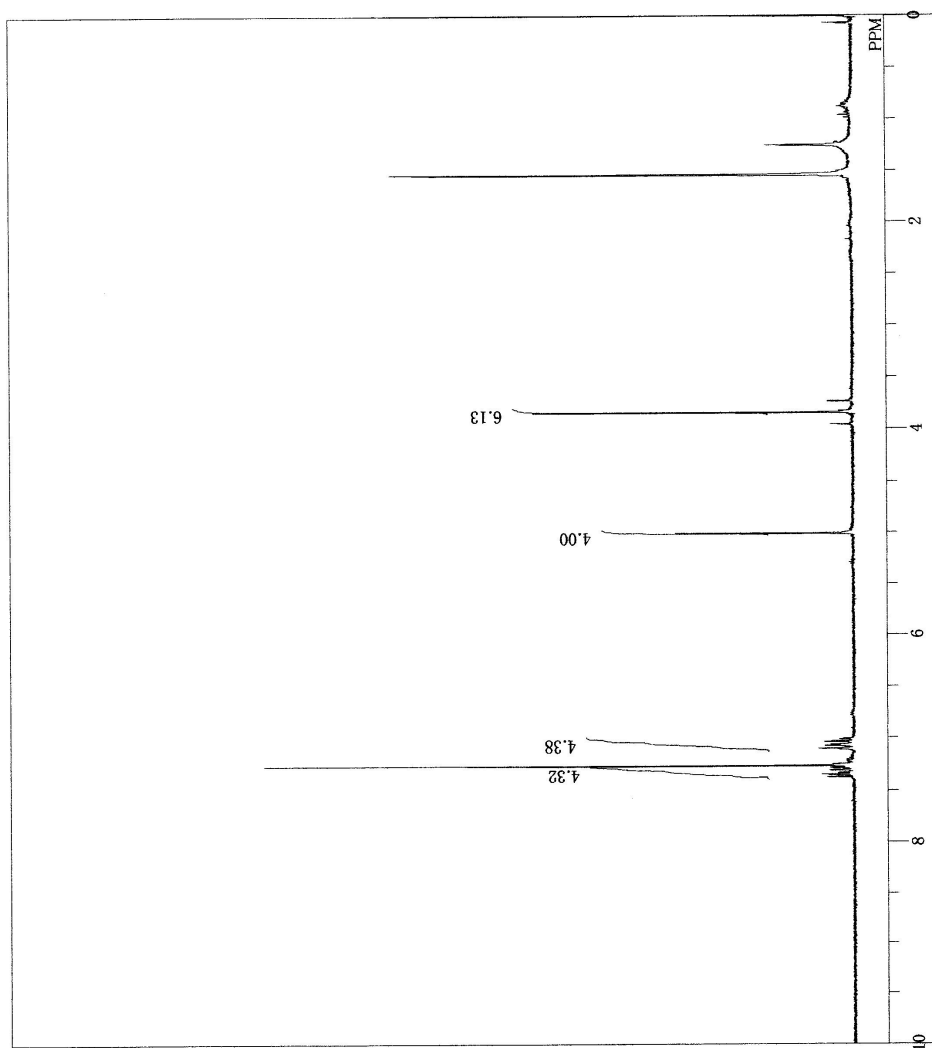
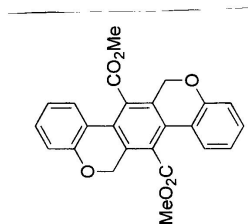
Di-*n*-butyl 8*H*,17*H*-naphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo[*d*]pyran-9,18-dicarboxylate (**8b**).



8*H*,17*H*-9,18-Di-*n*-butylnaphtho[2,1-*b*]naphtho[1'',2'':5',6']pyrano[3',4':5,4]benzo[*d*]pyran
(8c)



Dimethyl 6*H*,13*H*-chromeno[3',4':4,5]benzo[*c*]chromene-7,14-dicarboxylate (**8d**)



5,6-Bis-(2-hydroxynaphthalen-1-yl)-1,3-dihydroisobenzofuran-4,7-dicarboxylic acid
diethyl ester (**10**)

