

Facile One-pot Synthesis of Photochromic Pyrans

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Supplementary Material

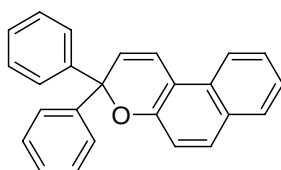
General Information: All reactions were performed using oven dried glassware. 1,2-dichloroethane was dried over molecular sieves. Naphthols, 2-hydroxydibenzofuran, 1,1-diphenyl-2-propyn-1-ol were purchased from either Aldrich or Fluka chemical companies and used without prior purification. 4-hydroxy-1-phenyl-naphthoic acid ethyl ester and propargyl alcohols were prepared by the known procedure.^{1, 2} Chromatographic purification of products was accomplished using forced flow chromatography on Fluka Silica Gel 60. NMR spectra were recorded on a Varian Mercury 300 operating at 300 MHz and 75 MHz for ¹H and ¹³C, respectively, and referenced to the internal solvent signals. The data is reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constant(s), integration). IR spectra were recorded on a Perkin Elmer Spectrum RX I FT-IR spectrometer and data was reported in unit of cm⁻¹. Mass and high resolution mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ. Combustion analysis was performed by the Mikroelementaranalytisches Laboratorium at the ETHZ.

¹ Heller, H.G.; Levell, J. R. U.S. Patent 5955520, 1999.

² Moustrou, C.; Rebiere, N.; Samat, A.; Guglielmetti, R.; Yassar, A. E.; Dubest, R.; Aubard, J. *Helv. Chim. Acta*, **1998**, *81*, 1293

General Procedure:

Naphthol or phenol (1 mmol) and propargyl alcohol (1.05-1.1 mmol) in the presence of PPTS (0.05 mmol) and trimethyl orthoformate (2 mmol) in 1,2-dichloroethane (5 ml) were refluxed for 1.5-3.5 hr. Solvent was removed in vacuo, the residue was purified by chromatography and recrystallization.



3a. 3,3-diphenyl-[3H]-naphtho-[2,1b]pyran.

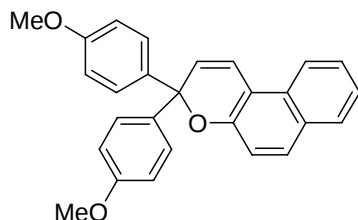
IR (KBr): 3060, 1635, 1588, 1490, 1460, 1445, 1241, 1215, 1008, 945, 804, 751, 731, 699.

¹H-NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.4Hz, 1H), 7.72 (d, J = 8.1Hz, 1H), 7.66 (d, J = 8.7Hz, 1H), 7.52-7.22 (m, 5H), 7.36-7.23 (m, 8H), 7.21 (d, J = 9.0Hz, 1H), 6.28 (d, J = 10.0Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ 150.7, 145.0, 129.8, 129.9, 128.6, 128.2, 127.8, 127.6, 127.1, 126.7, 123.7, 121.4, 119.6, 118.4, 82.5.

MS: 334.2(M⁺).

Anal. Calcd for C₂₅H₁₈O: C, 89.79; H, 5.43. Found: C, 89.51; H, 5.63.



3b. 3,3-di-(*p*-methoxyphenylphenyl)-[3H]-naphtho[2,1-b]pyran.

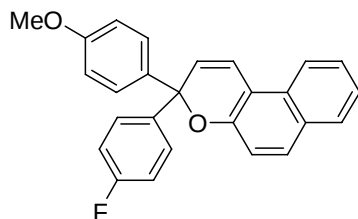
IR (KBr): 3055, 2960, 2838, 1628, 1608, 1581 1509, 1460, 1439, 1300, 1249, 1229, 1175, 1081, 1030, 1000, 954, 829, 814, 746, 724.

¹H-NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.1Hz, 1H), 7.72 (d, J = 8.1Hz, 1H), 7.66 (d, J = 8.7Hz, 1H), 7.46 (ddd, J = 8.1, 6.8, 1.3Hz, 1H), 7.42-7.35 (m, 4H), 7.30 (ddd, J = 8.1, 6.8, 0.9Hz, 1H), 7.29 (d, J = 10.0Hz, 1H), 7.17 (d, J = 8.7Hz, 1H), 6.88-6.80 (m, 4H), 6.21 (d, J = 10.0Hz, 1H), 3.77 (s, 6H).

¹³C-NMR (75 MHz, CDCl₃): δ 158.8, 150.5, 137.2, 129.8, 129.7, 129.2, 128.5, 128.3, 128.0, 126.5, 123.5, 121.3, 119.1, 118.3, 113.9, 113.3, 82.2, 55.2.

MS: 394.2(M⁺).

Anal. Calcd for C₂₇H₂₂O₃: C, 82.21; H, 5.62. Found: C, 82.10; H, 5.63.



3c. 3-(*p*-fulorophenyl)-3-(*p*-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran.

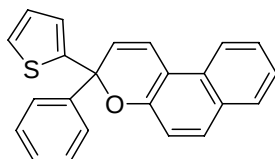
IR (KBr): 3052, 2966, 2932, 2840, 1632, 1600, 1583, 1509, 1458, 1300, 1255, 1230, 1177, 1157, 1080, 1000, 953, 835, 817, 752.

¹H-NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.1Hz, 1H), 7.72 (dd, J = 8.1, 0.6Hz, 1H), 7.68 (d, J = 8.7Hz, 1H), 7.51-7.41 (m, 3H), 7.40-7.36 (m, 2H), 7.33 (ddd, J = 7.8, 6.8, 0.9Hz, 1H), 7.31 (d, J = 10.0Hz, 1H), 7.17 (d, J = 8.7Hz, 1H), 7.05-6.94 (m, 2H), 6.89-6.80 (m, 2H), 6.20 (d, J = 10.0Hz, 1H), 3.77 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 162.0 (¹J = 246.6Hz), 159.0, 150.3, 140.9, 136.7, 129.9, 129.7, 129.3, 128.7 (³J = 7.3Hz), 128.5, 128.3, 127.6, 126.6, 123.6, 121.3, 119.5, 118.2, 114.8 (²J = 22.0Hz), 113.4, 81.9, 55.2.

MS: 382.2(M⁺).

Anal. Calcd for C₂₆H₁₉FO₂: C, 81.66; H, 5.01; F, 4.97. Found: C, 81.55; H, 5.13; F, 5.06.



3d. 3-phenyl-3-(thiophene-2-yl)-[3H]-naphtho[2,1-b]pyran.

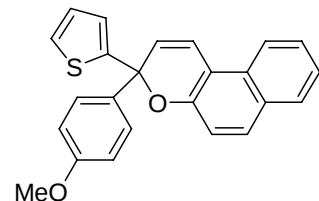
IR (KBr): 3064, 1632, 1492, 1446, 1229, 1205, 1006, 813, 752, 709, 693.

¹H-NMR (300 MHz, CDCl₃): δ 7.97 (d, J = 8.4Hz, 1H), 7.73 (d, J = 8.1Hz, 1H), 7.68 (d, J = 9.0Hz, 1H), 7.62-7.54 (m, 2H), 7.48 (ddd, J = 8.3, 6.8, 1.3Hz, 1H), 7.40-7.27 (m, 5H), 7.22 (d, J = 8.7Hz, 1H), 6.98-6.88 (m, 2H), 6.30 (d, J = 10.0Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ 150.3, 149.3, 144.4, 130.0, 129.7, 129.4, 128.5, 128.1, 127.8, 127.2, 126.7, 126.4, 126.3, 123.7, 121.3, 119.7, 118.3, 113.8, 80.3.

MS: 340.1(M⁺).

Anal. Calcd for C₂₃H₁₆OS: C, 81.14; H, 4.74; S, 9.42. Found: C, 81.14; H, 4.94; S, 9.39.



3e. 3-(*p*-methoxyphenyl)-3-(thiophene-2-yl)-[3H]-naphtho[2,1-b]pyran.

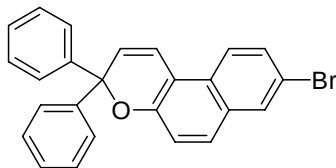
IR (KBr): 3061, 3009, 2962, 2833, 1628, 1609, 1584 1510, 1459, 1436, 1304, 1250, 1234, 1174, 1033, 1000, 825, 804, 753, 700.

¹H-NMR (300 MHz, CDCl₃): δ 7.97 (d, J = 8.4Hz, 1H), 7.73 (d, J = 8.4Hz, 1H), 7.67 (d, J = 8.7Hz, 1H), 7.54-7.42 (m, 3H), 7.37-7.26 (m, 3H), 7.19 (d, J = 8.7Hz, 1H), 6.98-6.90 (m, 2H), 6.90-6.80 (m, 2H), 6.26 (d, J = 10.0Hz, 1H), 3.78 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 159.3, 150.4, 149.8, 136.7, 130.0, 129.9, 129.5, 128.6, 127.9, 127.5, 126.7, 126.4, 126.3, 126.2, 123.8, 121.4, 119.6, 118.4, 113.9, 113.5, 80.2, 55.2.

MS: 370.2 (M⁺)

Anal. Calcd for C₂₄H₁₈O₂S: C, 77.81; H, 4.90; S, 8.66. Found: C, 77.74; H, 4.95; S, 8.62.



4a. 8-bromo-3,3-diphenyl-[3H]-naphtho-[2,1b]pyran.

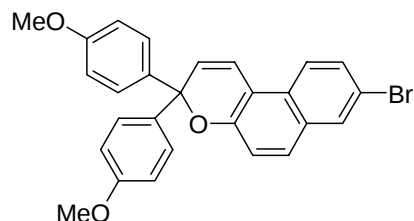
IR (KBr): 3056, 1628, 1580, 1491, 1446, 1210, 1184, 1007, 960, 877, 806, 767, 742, 728, 706, 694.

¹H-NMR (300 MHz, CDCl₃): δ 7.86 (d, J = 1.9Hz, 1H), 7.81 (d, J = 9.0Hz, 1H), 7.56 (d, J = 9.0Hz, 1H), 7.56-7.40 (m, 5H), 7.38-7.14 (m, 8H), 6.29 (d, J = 10.0Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ 150.9, 144.7, 130.6, 130.5, 129.9, 128.9, 128.3, 128.2, 127.7, 127.1, 123.2, 119.5, 119.1, 117.3, 114.2, 82.7.

MS: 412.1 (M⁺).

Anal. Calcd for C₂₅H₁₇OBr: C, 72.65; H, 4.15; Br, 19.33. Found: C, 72.65; H, 4.32; Br, 19.43.



4b. 8-bromo-3,3-di-(*p*-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran.

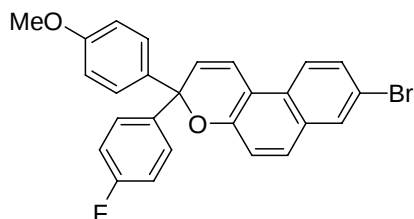
IR (KBr): 3055, 3010, 2951, 2832, 1628, 1607, 1579 1507, 1462, 1439, 1300, 1249, 1176, 1033, 1002, 954, 833, 814, 753, 700.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.85 (d, $J = 1.9\text{Hz}$, 1H), 7.81 (d, $J = 8.7\text{Hz}$, 1H), 7.54 (d, $J = 9.0\text{Hz}$, 1H), 7.51 (dd, $J = 9.0, 1.9\text{Hz}$, 1H), 7.42-7.33 (m, 4H), 7.21 (d, $J = 10.2\text{Hz}$, 1H), 7.17 (d, $J = 9.0\text{Hz}$, 1H), 6.88-6.80 (m, 4H), 6.22 (d, 1H, $J = 9.6\text{Hz}$), 3.77 (s, 6H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 150.9, 137.1, 130.5, 129.8, 128.8, 128.7, 128.4, 123.3, 119.5, 118.8, 117.3, 114.1, 113.5, 82.4, 55.2.

Anal. Calcd for $\text{C}_{27}\text{H}_{21}\text{BrO}_3$: C, 68.51; H, 4.47; Br, 16.88. Found: C, 68.31; H, 4.66; Br, 16.86.

HRMS (MALDI) Calcd. for $\text{C}_{27}\text{H}_{21}\text{BrO}_3$: 473.0747 (MH^+). Found: 473.0752 (93%).



4c. 8-bromo-3-(*p*-fulorophenyl)-3-*p*-methoxyphenyl-[3H]-naphtho[2,1-*b*]pyran.

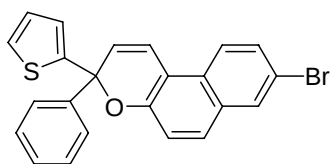
IR (KBr): 3051, 2928, 2835, 1627, 1600, 1581, 1508, 1464, 1300, 1249, 1218, 1176, 1159, 1004, 961, 837, 727.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.85 (d, $J = 1.9\text{Hz}$, 1H), 7.81 (d, $J = 8.7\text{Hz}$, 1H), 7.54 (d, $J = 9.0\text{Hz}$, 1H), 7.51 (dd, $J = 9.0, 2.2\text{Hz}$, 1H), 7.46-7.39 (m, 2H), 7.38-7.31 (m, 2H), 7.24 (d, $J = 10.2\text{Hz}$, 1H), 7.17 (d, $J = 9.0\text{Hz}$, 1H), 7.04-6.95 (m, 2H), 6.88-6.80 (m, 2H), 6.20 (d, $J = 10.0\text{Hz}$, 1H), 3.77 (s, 3H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 162.2 ($^1J = 246.6\text{Hz}$), 159.2, 150.7, 140.7, 136.6, 130.6, 130.5, 129.9, 129.0, 128.9 ($^3J = 7.3\text{Hz}$), 128.4, 128.3, 128.3, 123.2, 119.4, 119.1, 117.4, 115.0 ($^2J = 22.0\text{Hz}$), 114.2, 113.6, 82.1, 55.2.

MS: 460.0 (M^+).

Anal. Calcd for $\text{C}_{27}\text{H}_{21}\text{BrFO}_2$: C, 67.69; H, 3.93; Br, 17.32; F, 4.12. Found: C, 67.48; H, 4.08; Br, 17.23; F, 4.15.



4d. 8-bromo-3-phenyl-3-(thiophene-2-yl)-[3H]-naphtho[2,1-*b*]pyran.

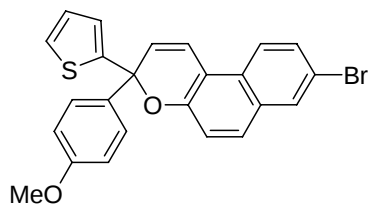
IR (KBr): 3051, 3020, 1628, 1583, 1497, 1446, 1228, 1213, 1170, 1093, 1066, 996, 948, 876, 809, 703, 692.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.87 (d, $J = 1.9\text{Hz}$, 1H), 7.82 (d, $J = 9.0\text{Hz}$, 1H), 7.64-7.48 (m, 4H), 7.40-7.22 (m, 5H), 7.22 (d, $J = 8.7\text{Hz}$, 1H), 6.98-6.87 (m, 2H), 6.30 (d, $J = 9.7\text{Hz}$, 1H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 150.6, 149.2, 144.3, 130.7, 130.5, 130.0, 129.1, 128.4, 128.3, 128.0, 127.9, 126.6, 126.5, 126.5, 126.4, 123.2, 119.5, 119.4, 117.5, 114.0, 80.5.

MS: 418.0 (M^+).

Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{BrOS}$: C, 65.88; H, 3.61; Br, 19.05; S, 7.65. Found: C, 65.65; H, 3.80; Br, 18.93; S, 7.61.



4e. 8-bromo-3-(*p*-methoxyphenyl)-3-(thiophene-2-yl)-[3H]-naphtho[2,1-b]pyran.

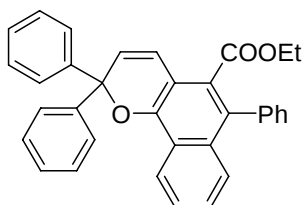
IR (KBr): 3066, 2950, 2837, 1636, 1607, 1580, 1508, 1460, 1304, 1255, 1215, 1164, 1067, 1030, 995, 942, 892, 814, 703.

¹H-NMR (300 MHz, CDCl₃): δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.52 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.50-7.44 (m, 2H), 7.31-7.27 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.96-6.82 (m, 4H), 6.27 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 159.4, 150.6, 149.5, 136.4, 130.7, 130.5, 129.9, 129.0, 128.3, 128.0, 127.8, 126.5, 126.3, 123.2, 119.5, 119.1, 117.4, 114.0, 113.5, 80.3, 55.2.

MS: 447.1 (M⁺).

Anal. Calcd for C₂₄H₁₇BrO₂S: C, 64.15; H, 3.81; Br, 17.78; S, 7.14. Found: C, 64.11; H, 3.95; Br, 17.81; S, 7.12.



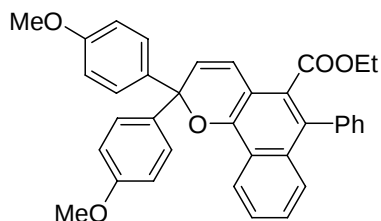
5a. 2,2,6-triphenyl-5-ethoxycarbonyl-[2H]naphtho[1,2-b]pyran.

IR (KBr): 3056, 2980, 2920, 2865, 1716, 1642, 1490, 1448, 1398, 1366, 1230, 1165, 1041, 1000, 938, 763, 700.

¹H-NMR (200 MHz, CDCl₃): δ 8.47-8.38 (m, 1H), 7.60-7.46 (m, 6H), 7.46-7.20 (m, 10H), 6.83 (d, *J* = 10.0 Hz, 1H), 6.24 (d, *J* = 10.0 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 168.6, 147.6, 145.0, 138.3, 133.0, 131.0, 130.6, 128.9, 128.3, 128.1, 128.0, 127.7, 127.4, 127.0, 126.6, 125.1, 122.1, 121.1, 112.1, 83.2, 61.0, 13.4.

HRMS (MALDI) Calcd for C₃₄H₂₆O₃: 505.1774 (MNa⁺). Found: 505.1776 (67%).



5b. 2,2-di-(*p*-methoxyphenyl)-5-ethoxycarbonyl-6-phenyl[2H]naphtho[1,2-b]pyran.

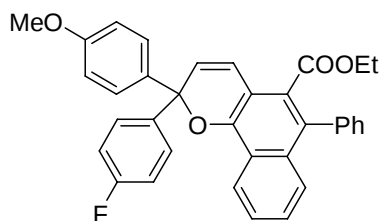
IR (KBr): 3062, 2933, 2902, 2835, 1721, 1607, 1509, 1463, 1444, 1373, 1292, 1252, 1230, 1173, 1038.

¹H-NMR (300 MHz, CDCl₃): δ 8.41-8.36 (m, 1H), 7.56-7.28 (m, 12H), 6.90-6.83 (m, 4H), 6.79 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 6H), 0.87 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 168.5, 159.0, 147.5, 138.3, 137.3, 132.8, 130.7, 130.6, 128.8, 128.4, 128.3, 128.0, 127.4, 126.9, 126.4, 125.1, 122.1, 120.6, 113.5, 112.1, 110.0, 82.8, 61.0, 55.3, 13.6.

MS: 542.1 (M⁺).

Anal. Calcd for C₃₆H₃₀O₅: C, 79.69; H, 5.57. Found: C, 79.47; H, 5.84.



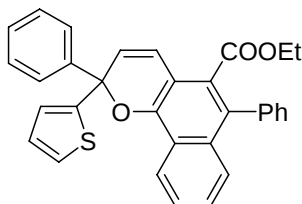
5c. 5-ethoxycarbonyl-2-(*p*-fluorophenyl)-2-(*p*-methoxyphenyl)-6-phenyl[2H]naphtho[1,2-b]pyran.

IR (KBr): 3057, 2979, 2835, 1719, 1605, 1506, 1444, 1372, 1291, 1253, 1227, 1175, 1158, 1040, 997.

$^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 8.43-8.35 (m, 1H), 7.60-7.28 (m, 12H), 7.10-6.96 (m, 2H), 6.92-6.83 (m, 2H), 6.83 (d, $J = 10.0\text{Hz}$, 1H), 6.17 (d, $J = 10.0\text{Hz}$, 1H), 4.00 (q, $J = 7.1\text{Hz}$, 2H), 3.79 (s, 3H), 0.88 (t, $J = 7.1\text{Hz}$, 3H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 168.6, 162.2 ($^1J = 247.8\text{Hz}$), 147.4, 141.1, 138.3, 136.9, 133.0, 131.1, 130.6, 128.8 ($^3J = 7.3\text{Hz}$), 128.4, 128.0, 127.5, 127.1, 127.0, 126.7, 125.1, 122.0, 121.1, 115.1 ($^2J = 22.0\text{Hz}$), 113.7, 112.1, 111.0, 82.6, 61.0, 55.2, 13.4.

HRMS (MALDI) Calcd for $\text{C}_{35}\text{H}_{27}\text{FO}_4$: 553.1786 (MNa^+). Found: 553.1784 (12%).



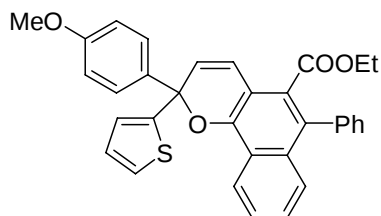
5d. 2,6-diphenyl-5-ethoxycarbonyl-2-(thiophene-2-yl)-[2H]naphtho[1,2-b]pyran.

IR (KBr): 3056, 2977, 2933, 1717, 1650, 1599, 1503, 1444, 1393, 1372, 1293, 1258, 1230, 1169, 1145, 1114, 1041, 990.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.47-8.38 (m, 1H), 7.65-7.56 (m, 2H), 7.55-7.47 (m, 2H), 7.46-7.27 (m, 10H), 7.04 (dd, $J = 3.4, 1.2\text{Hz}$, 1H), 6.94 (dd, $J = 5.0, 3.4\text{Hz}$, 1H), 6.82 (d, $J = 9.7\text{Hz}$, 1H), 6.25 (d, $J = 9.7\text{Hz}$, 1H), 3.98 (q, 2H, $J = 7.1\text{Hz}$), 0.87 (t, 3H, $J = 7.1\text{Hz}$).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 168.5, 149.5, 147.4, 144.6, 138.3, 133.0, 131.3, 130.6, 128.8, 128.3, 128.0, 127.7, 127.5, 127.2, 127.0, 126.7, 126.5, 126.4, 126.3, 125.2, 122.3, 121.3, 112.0, 80.9, 61.0, 13.4.

HRMS (MALDI) Calcd for $\text{C}_{32}\text{H}_{24}\text{O}_3\text{S}$: 511.1338 (MNa^+). Found: 511.1335 (15%).



5e. 5-ethoxycarbonyl-2-(*p*-methoxyphenyl)-2-(thiophene-2-yl)-6-phenyl[2H]naphtho[1,2-b]pyran.

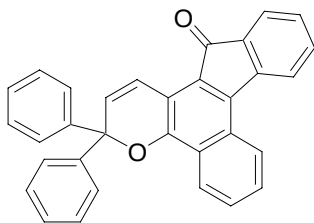
IR (KBr): 3056, 2985, 2950, 2832, 1727, 1606, 1508, 1442, 1368, 1249, 1224, 1164, 1038, 946, 816, 770, 702.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.44-8.38 (m, 1H), 7.56-7.47 (m, 4H), 7.46-7.36 (m, 4H), 7.35-7.28 (m, 3H), 7.01 (dd, $J = 3.4, 1.2\text{Hz}$, 1H), 6.95 (dd, $J = 5.0, 3.5\text{Hz}$, 1H), 6.92-6.85 (m, 2H), 6.80 (d, $J = 10.0\text{Hz}$, 1H), 6.22 (d, 1H, $J = 10.0\text{Hz}$), 3.98 (q, $J = 7.1\text{Hz}$, 2H), 3.80 (s, 3H), 0.87 (t, $J = 7.1\text{Hz}$, 3H).

^{13}C -NMR (75 MHz, CDCl_3): δ 168.6, 159.4, 149.8, 147.3, 138.3, 136.7, 133.0, 131.2, 130.6, 128.8, 128.0, 127.8, 127.8, 127.5, 127.1, 127.0, 126.6, 126.5, 126.4, 126.1, 125.2, 122.3, 121.1, 113.6, 112.0, 80.8, 61.0, 55.2, 13.4.

MS: 518.1 (M^+).

Anal. Calcd for $\text{C}_{33}\text{H}_{26}\text{O}_4\text{S}$: C, 76.42; H, 5.05; S, 6.18. Found: C, 76.22; H, 5.09; S, 6.12.



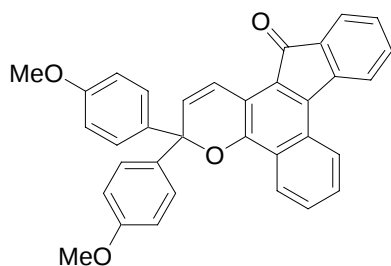
6a. 3,3-diphenyl-13-oxo-3H, 13H-indeno[2,1-f]naphtho[1,2-b] pyran.

IR (KBr): 3055, 1701, 1601, 1558, 1490, 1463, 1450, 1398, 1369, 1338, 1274, 1195, 1133, 1112, 1076, 955, 770, 755, 699, 674.

^1H NMR (300 MHz, CDCl_3): δ 8.43-8.36 (m, 1H), 8.36-8.28 (m, 1H), 7.91(d, J = 10.0Hz, 1H), 7.82 (d, J = 7.8Hz, 1H), 7.60-7.48 (m, 7H), 7.41 (td, J = 7.4, 1.3Hz, 1H), 7.37-7.22 (m, 6H), 7.18 (t, J = 7.4Hz, 1H), 6.29 (d, J = 10.0Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3): δ 195.6, 149.0, 144.7, 144.4, 135.4, 134.4, 134.2, 129.8, 129.2, 128.1, 127.8, 127.7, 127.6, 127.4, 126.8, 126.1, 124.6, 123.5, 123.4, 122.2, 119.6, 113.3, 108.8, 83.3.

HRMS (MALDI) Calcd. for $\text{C}_{32}\text{H}_{20}\text{O}_2$: 437.1536 (MH^+). Found: 437.1532 (100%).



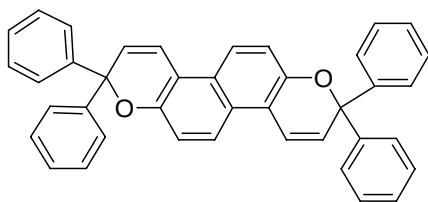
6b. 3,3-di(*p*-methoxyphenyl)-13-oxo-3H, 13H-indeno[2,1-f]naphtho[1,2-b] pyran.

IR (KBr): 3063, 2932, 2836, 1705, 1605, 1583, 1507, 1463, 1401, 1368, 1278, 1246, 1175, 1079, 1031, 831, 778, 716, 664.

^1H NMR (300 MHz, CDCl_3): δ 8.40-8.30 (m, 2H), 7.88(d, J = 10.0Hz, 1H), 7.86 (d, J = 7.4Hz, 1H), 7.58 (d, J = 7.8Hz, 1H), 7.57-7.48 (m, 2H), 7.47-7.34 (m, 5H), 7.19 (t, J = 7.4Hz, 1H), 7.00-6.78 (m, 4H), 6.29 (d, J = 10.0Hz, 1H), 3.77 (s, 6H).

^{13}C NMR (75 MHz, CDCl_3): δ 196.1, 159.2, 149.4, 145.1, 137.1, 135.4, 134.7, 134.4, 130.4, 129.4, 128.4, 128.0, 127.8, 127.6, 124.8, 123.7, 122.4, 119.4, 113.6, 113.5, 83.3, 55.2.

HRMS (MALDI) Calcd. for $\text{C}_{34}\text{H}_{24}\text{O}_4$: 497.1747 (MH^+). Found: 497.1742 (100%).



7a. 3,3,9,9-tetraphenyl-3H,9H-naphtho[2,1-b:6,5b']dipyran

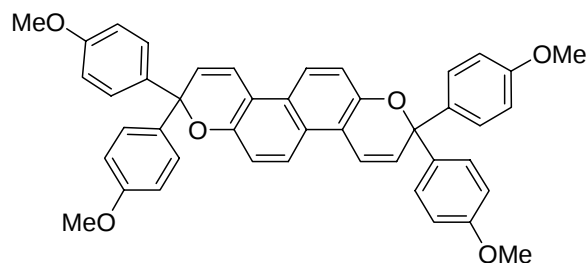
IR (KBr): 3058, 1626, 1520, 1490, 1447, 1380, 1253, 1068, 749, 700.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.79 (d, J = 9.0Hz, 2H), 7.52-7.44 (m, 8H), 7.36-7.14 (m, 16H), 6.27 (d, J = 10.0Hz, 2H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 148.9, 144.7, 128.3, 128.0, 127.5, 126.9, 125.5, 123.0, 119.6, 118.8, 114.7, 82.2.

MS: 540.3.

Anal. Calcd for $\text{C}_{40}\text{H}_{28}\text{O}_2$: C, 88.86; H, 5.22. Found: C, 88.68; H, 5.42.



7b. 3,3,9,9-tetra-(*p*-methoxyphenyl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

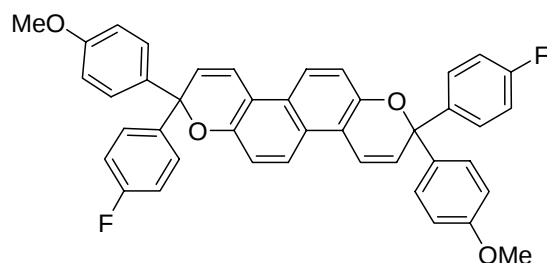
IR (KBr): 3068, 3000, 2860, 1607, 1578, 1509, 1463, 1299, 1252, 1175, 1062, 1033, 838.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.77 (d, J = 9.0Hz, 2H), 7.39-7.32 (m, 4H), 7.19 (d, J = 10.0Hz, 2H), 7.15 (d, J = 9.0Hz, 2H), 6.86-6.78 (m, 4H), 6.18 (d, J = 10.0Hz, 2H), 3.76 (s, 12H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 158.8, 148.9, 137.1, 128.6, 128.3, 125.4, 122.9, 119.3, 118.8, 114.7, 113.3, 81.8, 55.2.

HRMS (MALDI) Calcd for $\text{C}_{44}\text{H}_{36}\text{O}_6$: 660.2506 (M^+). Found: 660.2505 (100%).

Anal. Calcd for $\text{C}_{44}\text{H}_{36}\text{O}_6$: C, 79.98; H, 5.49. Found: C, 80.00; H, 5.61.



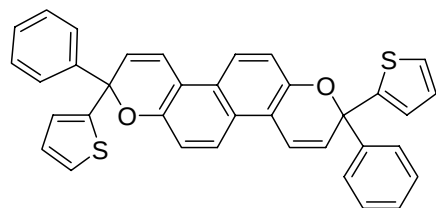
7c. 3,9-di-(*p*-fluorophenyl)-3,9-di-(*p*-methoxyphenyl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3056, 2967, 2932, 2838, 1603, 1509, 1299, 1254, 1229, 1178, 1159, 1060, 1030, 835.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.78 (d, J = 9.1Hz, 2H), 7.50-7.28 (m, 8H), 7.21 (d, J = 10.3Hz, 2H), 7.15 (d, J = 9.1Hz, 2H), 7.06-6.91 (m, 4H), 6.88-6.76 (m, 4H), 6.17 (d, J = 10.0Hz, 2H), 3.76 (s, 6H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 161.9 (1J = 246.0Hz), 158.8, 148.7, 140.6, 136.5, 128.6 (3J = 7.9Hz), 128.2, 125.4, 123.0, 119.5, 118.7, 114.8 (2J = 21.4Hz), 113.4, 81.7, 55.3.

HRMS (MALDI) Calcd. for $\text{C}_{42}\text{H}_{30}\text{F}_2\text{O}_4$: 636.2106 (M^+). Found: 636.2105 (100%).



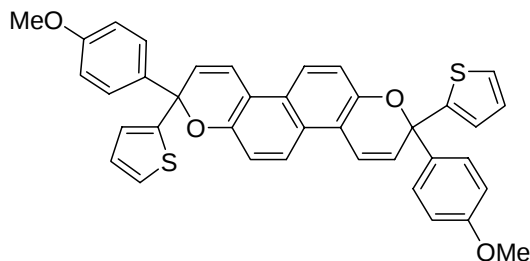
7d. 3,9-di-phenyl-3,9-di-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3088, 1618, 1516, 1490, 1448, 1376, 1252, 1062.

¹H-NMR (300 MHz, CDCl₃): δ 7.82 (d, J = 9.0Hz, 2H), 7.59-7.52 (m, 4H), 7.38-7.24 (m, 8H), 7.23 (d, J = 9.7Hz, 2H), 7.21 (d, J = 9.0Hz, 2H), 6.95-6.87 (m, 4H), 6.27 (d, J = 10.0Hz, 2H).

¹³C-NMR (75 MHz, CDCl₃): δ 149.2, 148.8, 144.3, 128.0, 127.8, 127.8, 126.4, 126.3, 126.2, 125.6, 123.1, 119.8, 118.8, 114.6, 80.0.

HRMS (MALDI) Calcd. for C₃₆H₂₄O₂S₂: 552.1211 (M⁺). Found: 55.1208 (100%).



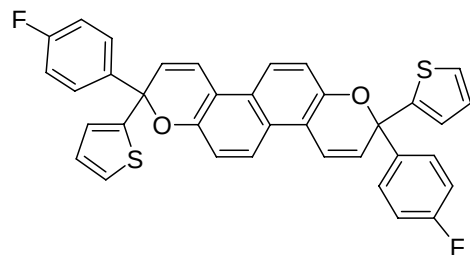
7e. 3,9-di-(p-methoxyphenyl)-3,9-di-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3070, 2930, 2834, 1608, 1509, 1461, 1377, 1302, 1251, 1176, 1061, 1031, 830.

¹H-NMR (300MHz, CDCl₃): δ 7.80 (d, J = 9.1Hz, 2H), 7.54-7.41 (m, 4H), 7.32-7.23 (m, 2H), 7.21 (d, J = 10.0Hz, 2H), 7.19 (d, J = 9.1Hz, 2H), 6.96-6.78 (m, 8H), 6.25 (d, J = 10.0Hz, 2H), 3.78 (s, 6H).

¹³C-NMR (75MHz, CDCl₃): δ 159.1, 149.5, 148.8, 136.4, 128.0, 127.7, 126.2, 126.1, 125.6, 123.1, 119.6, 118.8, 114.6, 113.4, 80.0, 55.2.

HRMS (MALDI) Calcd. for C₃₈H₂₈O₄S₂: 612.1424 (M⁺). Found: 612.14218 (100%).



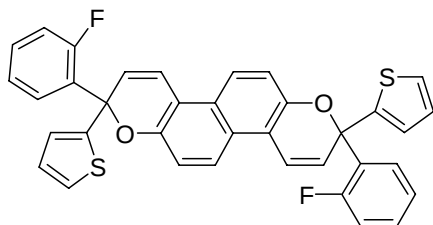
7f. 3,9-di-(p-fluorophenyl)-3,9-di-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3072, 1627, 1600, 1519, 1504, 1416, 1379, 1250, 1232, 1221, 1159, 1062, 963, 827, 817, 750, 715.

¹H-NMR (300MHz, CDCl₃): δ 7.82 (d, J = 9.0Hz, 2H), 7.58-7.46 (m, 4H), 7.30-7.25 (m, 2H), 7.23 (d, J = 10.0Hz, 2H), 7.19 (d, J = 9.0Hz, 2H), 7.07-6.95 (m, 4H), 6.94-6.86 (m, 4H), 6.24 (d, J = 10.0Hz, 2H).

¹³C-NMR (75MHz, CDCl₃): δ 162.1 (¹J = 245.6Hz), 148.8, 148.6, 140.0, 128.1 (³J = 8.6Hz), 127.5, 126.3, 125.5, 123.1, 119.9, 118.8, 114.9 (²J = 22.0Hz), 114.5, 79.8.

HRMS (MALDI) Calcd. for C₃₆H₂₂F₂O₂S₂: 589.1102 (MH⁺). Found: 598.1097 (58%).



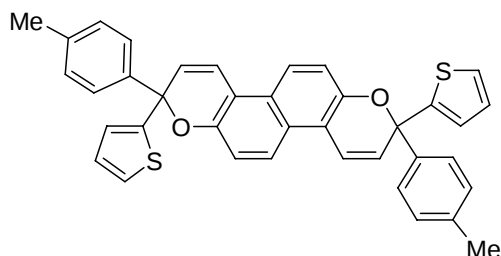
7g. 3,9-di-(o-fluorophenyl)-3,9-di-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3070, 1626, 1583, 1518, 1483, 1454, 1379, 1322, 1272, 1238, 1200, 1106, 1063, 960, 897, 838, 754, 710.

¹H-NMR (300MHz, CDCl₃): δ 7.84 (d, J = 9.3Hz, 2H), 7.85-7.70 (m, 2H), 7.33-7.19 (m, 8H), 7.18-7.08 (m, 2H), 7.08-6.98 (m, 2H), 6.98-6.86 (m, 4H), 6.50 (dd, J = 10.0, 5.0Hz, 2H).

¹³C-NMR (75MHz, CDCl₃): δ 159.2 (¹J = 247.2Hz), 148.4, 147.8, 130.9 (²J = 11.0Hz), 129.7 (³J = 8.6Hz), 127.4, 126.3, 126.0, 125.6, 123.7, 123.1, 119.7, 118.6, 116.3 (²J = 22.0Hz), 114.4, 78.0.

HRMS (MALDI) Calcd. for C₃₆H₂₂F₂O₂S₂: 611.0922 (MNa⁺). Found: 611.0917 (87%).



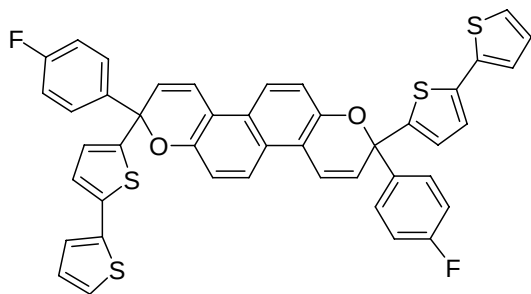
7h. 3,9-di-(*p*-methylphenyl)-3,9-di-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3088, 3022, 2918, 1625, 1519, 1510, 1382, 1254, 1236, 1219, 1185, 1071, 959, 816, 804, 704.

¹H-NMR (300MHz, CDCl₃): δ 7.80 (d, J = 9.0Hz, 2H), 7.44 (d, J = 7.8 Hz, 4H), 7.30-7.24 (m, 2H), 7.21 (d, J = 10.0Hz, 2H), 7.19 (d, J = 9.0Hz, 2H), 7.14 (dd, J = 7.8, 0.6Hz, 4H), 6.95-6.85 (m, 4H), 6.27 (d, J = 10.0Hz, 2H), 2.32 (s, 6H).

¹³C-NMR (75MHz, CDCl₃): δ 149.3, 148.7, 141.3, 137.4, 128.7, 127.9, 126.2, 125.5, 123.0, 119.6, 118.8, 114.5, 80.0, 21.2.

HRMS (MALDI) Calcd. for C₃₈H₂₈O₂S₂: 603.1243 (MNa⁺). Found: 603.1429 (51%).



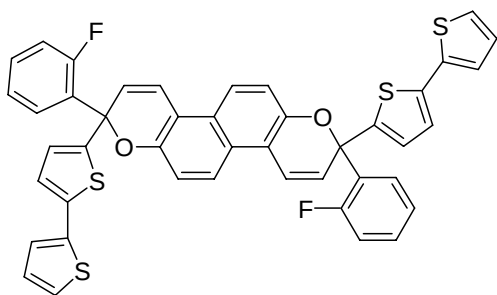
7i. 3,9-di-(2,2'-bithiophene-5-yl)-3,9-di-(*p*-fluorophenyl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans

IR (KBr): 3069, 1626, 1601, 1506, 1415, 1379, 1324, 1228, 1158, 1062, 1014, 954, 837, 800, 745, 695.

¹H-NMR (300MHz, CDCl₃): δ 7.84 (d, J = 9.0Hz, 2H), 7.62-7.52 (m, 4H), 7.25 (d, J = 10.0Hz, 2H), 7.22 (d, J = 9.0Hz, 2H), 7.17 (d, J = 4.0Hz, 2H), 7.09 (dd, J = 3.7, 1.3Hz, 2H), 7.08-6.99 (m, 4H), 6.97 (d, J = 4.0Hz, 2H), 6.95 (d, J = 3.7Hz, 2H), 6.82 (d, J = 3.7Hz, 2H), 6.22 (d, J = 10.0Hz, 2H).

¹³C-NMR (75MHz, CDCl₃): δ 162.1 (¹J = 246.6Hz), 148.5, 147.5, 139.7, 138.4, 136.9, 128.1 (³J = 8.5Hz), 127.6, 127.2, 127.1, 127.1, 125.7, 124.5, 123.7, 123.3, 122.7, 120.1, 118.8, 115.0 (²J = 21.4Hz), 114.5, 79.8.

HRMS (MALDI) Calcd. for C₄₄H₂₆F₂O₂S₄: 753.0857 (MH⁺). Found: 753.0851 (100%).

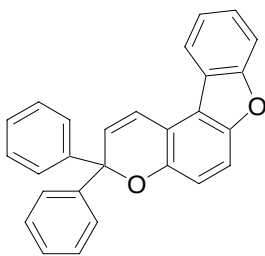


7j. 3,9-di-(2,2'-bithiophene-5-yl)-3,9-di-(*o*-fluorophenyl)-3H,9H-naphtho[2,1-b:6,5b']dipyrans
IR (KBr): 3070, 1629, 1610, 1580, 1518, 1482, 1452, 1416, 1380, 1324, 1271, 1242, 1203, 1105, 1063, 954, 904, 839, 821, 799, 752, 697.

¹H-NMR (300MHz, CDCl₃): δ 7.86 (d, J = 9.0Hz, 2H), 7.82-7.73 (m, 2H), 7.35-7.26 (m, 2H), 7.27 (d, J = 9.0Hz, 2H), 7.25 (d, J = 9.7Hz, 2H), 7.20-7.10 (m, 4H), 7.10-7.04 (m, 3H), 7.03 (dd, J = 8.1Hz, 0.9 Hz, 1H), 6.99-6.90 (m, 4H), 6.86 (d, J = 4.0Hz, 2H), 6.48 (dd, J = 10.0, 4.7Hz, 2H).

¹³C-NMR (75MHz, CDCl₃): δ 159.1 (¹J = 248.4Hz), 148.4, 146.4, 138.2, 137.1, 130.5 (²J = 19.0Hz), 129.8 (³J = 7.9Hz), 127.6, 127.4, 126.7, 125.8 (³J = 4.3Hz), 125.6, 124.4, 123.7, 123.2, 122.9, 120.0, 118.7, 116.4 (²J = 22.0Hz), 114.5, 78.0.

HRMS (MALDI) Calcd. for C₄₄H₂₆F₂O₂S₄: 753.0857 (MH⁺). Found: 753.0856 (100%).



8. 3,3-diphenyl-[3H]-benzofuro[3,2-f]chromene.

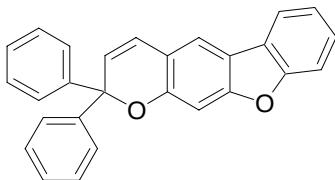
IR (KBr): 3056, 3032, 1487, 1472, 1446, 1427, 1244, 1187, 1148, 1092, 988, 745, 698.

¹H-NMR (300 MHz, CDCl₃): δ 8.10 (dd, J = 7.8, 0.6Hz, 1H), 7.57-7.40 (m, 6H), 7.38 (d, J = 10.0Hz, 1H), 7.37-7.20 (m, 8H), 7.06 (d, J = 8.7Hz, 1H), 6.40 (d, J = 9.7Hz, 1H).

¹³C-NMR (75 MHz, CDCl₃): δ 157.1, 151.4, 148.2, 144.7, 130.6, 128.2, 127.7, 127.2, 127.0, 124.3, 122.6, 122.2, 120.6, 116.3, 115.7, 111.8, 111.7, 82.2.

MS: 374.2(M⁺).

Anal. Calcd for C₂₇H₁₈O₂: C, 86.61; H, 4.85. Found: C, 86.67; H, 5.05.



9. 7,7-diphenyl-[7H]-benzofuro[2,3-g]chromene.

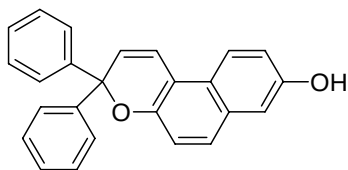
IR (KBr): 3025, 1631, 1487, 1459, 1436, 1318, 1241, 1220, 1196, 1165, 992, 944, 870, 700.

¹H-NMR (300 MHz, CDCl₃): δ 7.84 (d, J = 9.0Hz, 1H), 7.54-7.45 (m, 6H), 7.40 (ddd, J = 8.4, 7.2, 1.2Hz, 1H), 7.37-7.22 (m, 7H), 7.20 (s, 1H), 6.76 (d, J = 9.9Hz, 1H), 6.30 (d, 1H, J = 9.7Hz).

¹³C-NMR (75 MHz, CDCl₃): δ 157.1, 148.7, 144.8, 130.4, 128.3, 127.6, 127.2, 124.4, 124.1, 122.6, 121.2, 120.7, 111.6, 111.0, 108.9, 107.9, 82.7.

MS: 374.2 (M^+).

Anal. Calcd for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.47; H, 5.08.



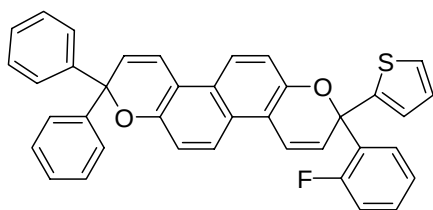
10. 3,3-diphenyl-8-hydroxy-[3H][2,1-b]naphthopyran.

IR (KBr): 3616, 3059, 1618, 1593, 1518, 1490, 1446, 1380, 1250, 1220, 1189, 1083, 1009, 860, 749, 728, 696.

1H -NMR (300MHz, $CDCl_3$): δ 7.86 (d, J = 9.0Hz, 1H), 7.52-7.45 (m, 5H), 7.36-7.20 (m, 7H), 7.17 (d, J = 8.7Hz, 1H), 7.09 (dd, J = 9.0, 2.5Hz, 1H), 7.04 (d, J = 2.5Hz, 1H), 6.27 (d, J = 10.0Hz, 1H), 4.75 (s, 1H).

^{13}C -NMR ($CDCl_3$): δ 151.6, 148.9, 144.8, 130.3, 128.0, 128.0, 127.0, 125.0, 123.2, 119.5, 119.0, 118.1, 114.2, 110.3, 82.3.

MS: 350.2 (M^+).



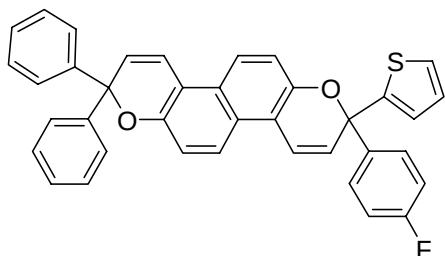
11. 3,3-di-phenyl-9-(*o*-fluorophenyl)-9-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyran

IR (KBr): 3059, 1627, 1517, 1483, 1448, 1379, 1322, 1240, 1222, 1193, 1166, 1060, 959, 838, 822, 750, 701.

1H -NMR (300MHz, CD_2Cl_2): δ 7.88 (d, J = 7.8Hz, 1H), 7.83 (d, J = 7.8Hz, 1H), 7.75 (dt, J = 7.8, 1.6Hz, 1H), 7.51-7.43 (m, 4H), 7.36-7.19 (m, 12H), 7.14 (dt, J = 7.8, 1.2Hz, 1H), 7.02 (ddd, J = 11.8, 8.1, 1.2Hz, 1H), 6.95 (dd, J = 3.7, 0.9Hz, 1H), 6.91 (dd, J = 5.0, 3.7Hz, 1H), 6.48 (d, J = 10.0, 5.0Hz, 1H), 6.34 (d, J = 10.0Hz, 1H).

^{13}C -NMR (75MHz, $CDCl_3$): δ 159.2 (1J = 248.4Hz), 149.0, 148.2, 147.8, 144.6, 130.9 (2J = 11.0Hz), 129.7 (3J = 7.9Hz), 128.2, 128.0, 127.4, 126.9, 126.8, 126.3, 126.2, 126.1, 126.0, 125.6, 125.3, 123.7, 123.1, 122.9, 119.7, 119.4, 118.9, 118.5, 116.4, 116.2, 114.5 (2J = 18.3Hz), 82.3, 77.9.

HRMS (MALDI) Calcd. for $C_{38}H_{25}FO_2S$: 564.1554 (M^+). Found: 564.1560 (94%).



12. 3,3-di-phenyl-9-(*p*-fluorophenyl)-9-(thiophene-2-yl)-3H,9H-naphtho[2,1-b:6,5b']dipyran

IR (KBr): 3057, 1622, 1601, 1519, 1506, 1492, 1446, 1378, 1324, 1224, 1187, 1157, 1065, 969, 828, 810, 750, 698.

1H -NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 9.0Hz, 1H), 7.79 (d, J = 9.0Hz, 1H), 7.56-7.48 (m, 2H), 7.48-7.42 (m, 4H), 7.34-7.29 (m, 3H), 7.39-7.19 (m, 7H), 7.18 (d, J = 9.7Hz, 1H), 7.05-6.95 (m, 2H), 6.92-6.87 (m, 2H), 6.26 (d, J = 10.0Hz, 1H), 6.23 (d, J = 9.7Hz, 1H).

^{13}C -NMR (75 MHz, CDCl_3): δ 162.0 ($^1J = 246.0\text{Hz}$), 149.0, 148.9, 148.4, 144.6, 140.0, 128.3, 128.1 ($^3J = 7.9\text{Hz}$), 128.0, 127.9, 127.4, 126.8, 126.3, 125.6, 125.3, 123.2, 122.9, 119.9, 119.4, 118.9, 118.6, 114.8 ($^2J = 22.0\text{Hz}$), 114.4, 82.3, 79.7.
HRMS (MALDI) Calcd. for $\text{C}_{38}\text{H}_{25}\text{FO}_2\text{S}$: 564.1554 (M^+). Found: 564.1561 (87%).