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SUPPLEMENTARY MATERIAL TO

Camphor-10-sulfonic acid catalyzed condensation of 2-naphthol with aromatic/aliphatic aldehydes to 14-aryl/alkyl-14*H*-dibenzo[*a,j*]xanthenes

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PHYSICAL AND SPECTRAL DATA OF THE PRODUCTS (**3a**, **4a**–**m** AND **5**)

*Bis-(2-hydroxy-1-naphthyl)phenylmethane (**3a**)*.[1] Pink solid; m.p.: 195––196 °C; IR ($CHCl_3$, cm^{-1}): 3471, 3423, 3019, 1618, 1597, 1513, 1491, 1468, 1390, 1253, 1046, 877; ^{1}H-NMR (200 MHz, CD_3COCD_3, δ / ppm): 7.13–7.38 (12H, *m*, ArCHAr, ArH), 7.74–7.84 (4H, *m*, ArH), 8.12 (2H, *d*, *J* = 8.3 Hz, ArH); ^{13}C-NMR (50 MHz, CD_3COCD_3, δ / ppm): 43.0, 120.1, 120.4, 123.6, 123.7, 126.8, 127.5, 128.8, 129.1, 129.7, 130.0, 130.5, 135.2, 143.3, 154.0; ESI-MS (*m*/*z*, (relative abundance, %)): 376 (M, 25), 375 (M−H, 95), 353 (8), 349 (11), 339 (16), 337 (10), 325 (10), 321 (100), 311 (11), 309 (16), 293 (22), 283 (9), 265 (16), 231 (58), 143 (39); HRMS: *m*/*z* calcd. for $C_{27}H_{20}O_2Na$ (M+Na): 399.1361; found: 399.1365.

*14-Phenyl-14*H*-dibenzo[*a,j*]xanthene (**4a**)*.[2] Colorless solid; m.p.: 187–188 °C (lit. 186–187 °C); IR ($CHCl_3$, cm^{-1}): 3061, 3017, 2924, 1592, 1456, 1401, 1251, 1215, 962, 808; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.50 (1H, *s*, ArCHAr), 6.96–7.03 (1H, *m*, ArH), 7.16 (2H, *t*, *J* = 7.5 Hz, ArH), 7.38–7.63 (8H, *m*, ArH), 7.82 (4H, *t*, *J* = 7.8 Hz, ArH), 8.41 (2H, *d*, *J* = 8.5 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 38.0, 117.3, 117.9, 122.6, 124.1, 126.3, 126.6, 128.2, 128.4, 128.6, 128.7, 131.0, 131.4, 145.0, 148.7; EI-MS (*m*/*z*, (relative abundance, %)) = 358 (M, 20), 281 (100), 252 (13), 250 (8).

*14-(4-Bromophenyl)-14*H*-dibenzo[*a,j*]xanthene (**4b**)*.[3] Colorless solid; m.p.: 293–294 °C (lit. 295–296 °C); IR ($CHCl_3$, cm^{-1}): 3019, 2906, 1633, 1482, 1214; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.45 (1H, *s*, ArCHAr), 7.23–7.27 (2H, *m*, ArH), 7.37–7.50 (6H, *m*, ArH), 7.54–7.62 (2H, *m*, ArH), 7.82 (4H, *t*, *J* = 7.7 Hz, ArH), 8.31 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.4, 116.7, 118.0, 120.2, 122.4, 124.3, 126.9, 128.9, 129.1, 129.8, 131.1, 131.2,

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131.5, 143.9, 148.7; HRMS: *m*/*z* calcd. for $C_{27}H_{18}BrO$ (M+H): 437.0536; Found: 437.0533.

*14-(3-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthene* (***4c***).[2] Colorless solid; m.p.: 177–178 °C (lit. 179–180 °C); IR ($CHCl_3$, cm^{-1}): 3018, 2938, 1593, 1486, 1457, 1432, 1400, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 3.63 (3H, *s*, OCH_3), 6.46 (1H, *s*, ArCHAr), 6.50–6.56 (1H, *m*, ArH), 7.03–7.19 (3H, *m*, ArH), 7.37–7.50 (4H, *m*, ArH), 7.59 (2H, *td*, *J* = 7.7, 1.3 Hz, ArH), 7.81 (4H, *t*, *J* = 8.3 Hz, ArH), 8.40 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.9, 54.9, 110.9, 114.9, 117.1, 117.9, 120.7, 122.7, 124.1, 126.7, 128.7, 128.8, 129.2, 131.0, 131.4, 146.5, 148.7, 159.6; ESI-MS (*m*/*z*, (relative abundance, %)): 389 (M+H, 13), 388 (M, 14), 387 (M−H, 10), 363 (8), 297 (9), 282 (40), 281 (100).

*14-(2-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthene* (***4d***).[3] Colorless solid; m.p.: 258–259 °C (lit. 258–260 °C); IR ($CHCl_3$, cm^{-1}): 3019, 1641, 1459, 1404, 1243, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 4.27 (3H, *s*, OCH_3), 6.60––6.67 (1H, *m*, ArCHAr), 6.84–7.00 (3H, *m*, ArH), 7.19 (1H, *dd*, *J* = 7.6, 1.6 Hz, ArH), 7.35–7.57 (6H, *m*, ArH), 7.78 (4H, *t*, *J* = 8.0 Hz, ArH), 8.58 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 30.3, 55.6, 110.6, 117.9, 118.5, 121.7, 123.3, 124.1, 126.6, 127.5, 128.4, 130.7, 130.8, 132.1, 134.6, 148.8, 153.8; APCI-MS (*m*/*z*, (relative abundance, %)): 389 (M+H, 100), 388 (M, 9), 282 (32), 281 (79), 246 (12).

*14-(4-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthene* (***4e***).[2] Colorless solid; m.p.: 207–208 °C (lit. 205–206 °C); IR ($CHCl_3$, cm^{-1}): 3017, 2955, 2399, 1607, 1509, 1432, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 3.61 (3H, *s*, OCH_3), 6.45 (1H, *s*, ArCHAr), 6.67 (2H, *d*, *J* = 8.7 Hz, ArH), 7.37–7.62 (8H, *m*, ArH), 7.80 (4H, *t*, *J* = 8.8 Hz, ArH), 8.38 (2H, *d*, *J* = 8.5 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.1, 55.0, 113.8, 117.5, 117.9, 122.7, 124.1, 126.7, 128.6, 128.7, 129.1, 131.1, 131.4, 137.3, 148.7, 157.9; EI-MS (*m*/*z*, (relative abundance, %)): 388 (M, 22), 281 (100), 252 (20), 250 (11), 92 (13), 77 (14), 64 (6).

*4-(14*H*-Dibenzo[*a,j*]xanthen-14-yl)phenol* (***4f***).[4] Pink solid; m.p.: 138–139 °C (lit. 138–140 °C); IR ($CHCl_3$, cm^{-1}): 3535, 3402, 3070, 3019, 2926, 1609, 1592, 1509, 1458, 1431, 1401, 1241, 1214, 1173; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.43 (1H, *s*, ArCHAr), 6.58 (2H, *d*, *J* = 8.5 Hz, ArH), 7.34––7.49 (6H, *m*, ArH), 7.58 (2H, *td*, *J* = 7.6, 1.2 Hz, ArH), 7.80 (4H, *t*, *J* = 8.6 Hz, ArH), 8.36 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.1, 115.3, 117.5, 117.9, 122.7, 124.1, 126.7, 128.6, 128.7, 129.3, 131.1, 131.4, 148.7, 153.9; EI-MS (*m*/*z*, (relative abundance, %)): 374 (M, 20), 281 (100), 252 (15), 250 (6), 178 (6).

N-*[4-(14*H*-Dibenzo[*a,j*]xanthen-14-yl)phenyl]acetamide* (***4g***). Colorless solid; m.p.: 153–154 °C; Anal. Calcd. for $C_{29}H_{21}NO_2$: C, 83.83; H, 5.09; N, 3.37 %. Found: C, 83.58; H, 5.44; N 3.08 %; IR ($CHCl_3$, cm^{-1}): 3436, 3019, 1634,

1513, 1410, 1320, 1240, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.99 (3H, *s*, NHCOC**H**$_3$), 6.45 (1H, *s*, ArCHAr), 7.02 (1H, *br*, NH), 7.21–7.26 (3H, *m*, ArH), 7.36–7.49 (5H, *m*, ArH), 7.56 (2H, *t*, *J* = 7.6 Hz, ArH), 7.80 (4H, *t*, *J* = 7.9 Hz, ArH), 8.34 (2H, *d*, *J* = 8.5 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 24.0, 37.3, 117.0, 117.8, 119.9, 122.5, 124.2, 126.7, 128.6, 128.7, 128.8, 130.9, 131.3, 136.0, 141.0, 148.5, 168.4; ESI-MS (*m*/*z*, (relative abundance, %)): 438 (M+Na, 100), 416 (M+H, 60), 281 (10), 175 (19), 164 (8), 151 (16), 139 (26), 131 (18), 122 (26); HRMS: *m*/*z* calcd. for $C_{29}H_{22}NO_2$ (M+H): 416.1651. Found: 416.1653.

*4-(14*H*-Dibenzo[*a,j*]xanthen-14-yl)benzonitrile (**4h**)*.[17] Colorless solid; m.p.: 294–295 °C (lit. 291–292 °C); IR ($CHCl_3$, cm^{-1}): 3019, 2930, 2400, 2225, 1633, 1414, 1237, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.55 (1H, *s*, ArCHAr), 7.40–7.51 (6H, *m*, ArH), 7.55–7.64 (4H, *m*, ArH), 7.81–7.87 (4H, *m*, ArH), 8.27 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 38.0, 115.9, 118.0, 118.6, 122.1, 124.6, 127.1, 128.9, 129.0, 129.5, 131.0, 131.1, 132.1, 132.4, 148.8, 150.0; EI-MS (*m*/*z*, (relative abundance, %)): 383 (M, 18), 281 (100), 252 (17), 250 (10), 192 (9), 141 (10), 126 (6), 102 (13), 75 (8).

*4-(14*H*-Dibenzo[*a,j*]xanthen-14-yl)benzoic acid (**4i**)*. Colorless solid; m.p.: >300 °C; Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51 %. Found: C, 83.36; H, 4.73 %; IR ($CHCl_3$, cm^{-1}): 3428, 3019, 1679, 1604, 1421, 1214, 1080, 1018; ^{1}H--NMR (200 MHz, $CDCl_3$, δ / ppm): 6.55 (1H, *s*, ArCHAr), 7.37–7.53 (4H, *m*, ArH), 7.58–7.62 (4H, *m*, ArH), 7.78–7.86 (6H, *m*, ArH), 8.32 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 38.1, 116.3, 118.0, 122.3, 124.4, 127.0, 128.4, 128.9, 129.3, 130.5, 130.7, 131.0, 131.3, 148.7, 150.8, 170.9; ESI--MS (*m*/*z*, (relative abundance, %)): 403 (M+H, 9), 402 (M, 25), 401 (M−H, 100), 397 (25), 369 (13), 358 (7), 340 (8), 326 (5), 281 (5), 277 (19), 259 (8), 215 (9); HRMS: *m*/*z* calcd, for $C_{28}H_{19}O_3$ (M+H): 403.1334. Found: 403.1352.

*14-(4-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene (**4j**)*.[3] Yellow solid; m.p.: >300 °C (lit. 310–311 °C); IR ($CHCl_3$, cm^{-1}): 3019, 1634, 1516, 1340, 1250, 1239, 1106, 1014; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.60 (1H, *s*, ArCHAr), 7.40–7.69 (8H, *m*, ArH), 7.81–7.86 (4H, *m*, ArH), 7.97–8.01 (2H, *m*, ArH), 8.28 (2H, *d*, *J* = 8.5 Hz, Ar); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.8, 115.8, 118.0, 122.0, 123.8, 124.6, 127.2, 128.9, 129.0, 129.6, 131.1, 146.3, 148.8, 151.9; HRMS: *m*/*z* calcd. for $C_{27}H_{17}NNaO_3$ (M+Na): 426.1101. Found: 426.1100.

*14-(3-Flurophenyl)-14*H*-dibenzo[*a,j*]xanthene (**4k**)*.[5] Colorless solid; m.p.: 256–257 °C (lit. 259 °C); IR ($CHCl_3$, cm^{-1}): 3019, 2926, 2854, 2399, 2347, 1592, 1458, 1401, 1249, 1215; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.48 (1H, *s*, ArCHAr), 6.65–6.73 (1H, *m*, ArH), 7.05–7.18 (2H, *m*, ArH), 7.33–7.51 (5H, *m*, ArH), 7.59 (2H, *t*, *J* = 7.3 Hz, ArH), 7.82 (4H, *t*, *J* = 7.7 Hz, ArH), 8.34 (2H, *d*, *J* = 8.5 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 37.6, 113.2, 113.6, 115.0, 115.5, 116.7, 118.0, 122.4, 123.7, 123.8, 124.3, 126.9, 128.8, 129.1,

129.6, 129.8, 131.0, 131.3, 147.3, 147.4, 148.8, 160.5, 165.4; EI-MS (*m*/*z*, (relative abundance, %)): 376 (M, 8), 281 (100), 252 (14), 250 (8), 141 (6).

*14-Pentyl-14*H-*dibenzo[*a,j*]xanthene* (***4l***). Colorless solid; m.p.: 94–95 °C; Anal. Calcd. for $C_{26}H_{24}O$: C, 88.60; H, 6.86 %. Found: C, 88.28; H, 6.63 %; IR ($CHCl_3$, cm^{-1}): 3070, 2956, 2932, 2857, 1622, 1591, 1516, 1457, 1435, 1400, 1254, 1240, 956, 907, 815; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 0.63 (3H, *t*, *J* = 6.5 Hz, $C_4H_8C\mathbf{H}_3$), 0.97 (6H, *m*, $CH_2C_3\mathbf{H}_6CH_3$), 2.05 (2H, *m*, ArCHC$\mathbf{H}_2$), 5.57 (1H, *t*, *J* = 4.3 Hz, ArCHAr), 7.39 (2H, *d*, *J* = 9.0 Hz, ArH), 7.47 (2H, *t*, *J* = = 7.7 Hz, ArH), 7.63 (2H, *dd*, *J* = 7.5, 1.2 Hz, ArH), 7.78 (2H, *d*, *J* = 8.7 Hz, ArH), 7.89 (2H, *d*, *J* = 8.1 Hz, ArH), 8.27 (2H, *d*, *J* = 8.4 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 13.9, 22.4, 24.4, 30.9, 31.9, 35.8, 116.5, 117.5, 122.4, 124.0, 126.5, 128.1, 128.8, 130.9, 131.4, 149.9; EI-MS (*m*/*z*, (relative abundance, %)): 352 (M, 2), 281 (100), 140 (14), 126 (4); HRMS: *m*/*z* calcd. for $C_{26}H_{25}O$ (M+H): 353.1905. Found: 353.1912.

*14-Heptyl-14*H-*dibenzo[*a,j*]xanthene* (***4m***). Viscous liquid; Anal. Calcd. for $C_{28}H_{28}O$: C, 88.38; H, 7.42 %. Found: C, 87.95; H, 7.87 %; IR ($CHCl_3$, cm^{-1}): 3067, 2928, 2854, 1622, 1591, 1515, 1457, 1434, 1400, 1240, 1157, 1140, 960, 861, 813; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 0.77 (3H, *t*, *J* = 7.1 Hz, $C_6H_{12}C\mathbf{H}_3$), 1.02–1.36 (10H, *m*, $C_5\mathbf{H}_{10}CH_3$), 2.10–2.11 (2H, *m*, ArCHC$\mathbf{H}_2$), 5.59 (1H, *t*, *J* = 4.3 Hz, ArCHAr), 7.36–7.53 (4H, *m*, ArH), 7.66 (2H, *t*, *J* = 7.7 Hz, ArH), 7.80 (2H, *d*, *J* = 8.9 Hz, ArH), 7.91 (2H, *d*, *J* = 8.1 Hz, ArH), 8.30 (2H, *d*, *J* = 8.5 Hz, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 13.9, 22.4, 24.8, 28.9, 29.6, 30.9, 31.6, 35.9, 116.6, 117.4, 122.3, 123.9, 126.4, 128.0, 128.7, 131.0, 131.4, 149.9; HRMS: *m*/*z* calcd. for $C_{28}H_{29}O$ (M+H): 381.2218. Found: 381.2212.

*2,3,5,6,8,9,11,12,14,15-Decahydro-23-phenyl-23*H-*dinaphtho[2,1,*q*:1′2′-*t*]- -1,4,7,10,13,16-hexaoxacycloheneicosin* (***5***). Light yellow solid; m.p.: 155–156 °C; Anal. Calcd. for $C_{37}H_{38}O_6$: C, 76.79; H, 6.62 %. Found: C, 76.96; H, 6.51 %; IR ($CHCl_3$, cm^{-1}): 3058, 3016, 2874, 1622, 1598, 1511, 1492, 1451, 1451, 1295, 1259, 1243, 1215, 1176, 928, 806, 697; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.88–2.98 (2H, *m*, OC$\mathbf{H}_2CH_2O$), 3.10–3.21 (2H, *m*, OC$\mathbf{H}_2CH_2O$), 3.31–3.35 (4H, *m*, 2×OC$\mathbf{H}_2CH_2O$), 3.45–3.48 (8H, *m*, 4×OC$\mathbf{H}_2CH_2O$), 3.69–3.71 (2H, *m*, OC$\mathbf{H}_2CH_2O$), 3.77–3.83 (2H, *m*, OC$\mathbf{H}_2CH_2O$), 7.03–7.14 (6H, *m*, ArCHAr, ArH), 7.23–7.30 (6H, *m*, ArH), 7.73–7.81 (6H, *m*, ArH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 43.9, 68.4, 68.9, 70.3, 116.1, 122.7, 124.0, 124.8, 125.2, 125.8, 127.5, 128.1, 128.2, 128.7, 129.4, 133.4, 144.9, 155.2; APCI-MS (*m*/*z*, (relative abundance, %)): 579 (M+H, 70), 578 (M, 100), 577 (M−H, 43), 259 (35), 171 (31), 169 (25); HRMS: *m*/*z* calcd. for $C_{37}H_{39}O_6$ (M+H): 579.2747. Found: 579.2731.

^{1}H- AND ^{13}C-NMR SPECTRA FOR COMPOUNDS **3a**, **4a**–**4m** AND **5**

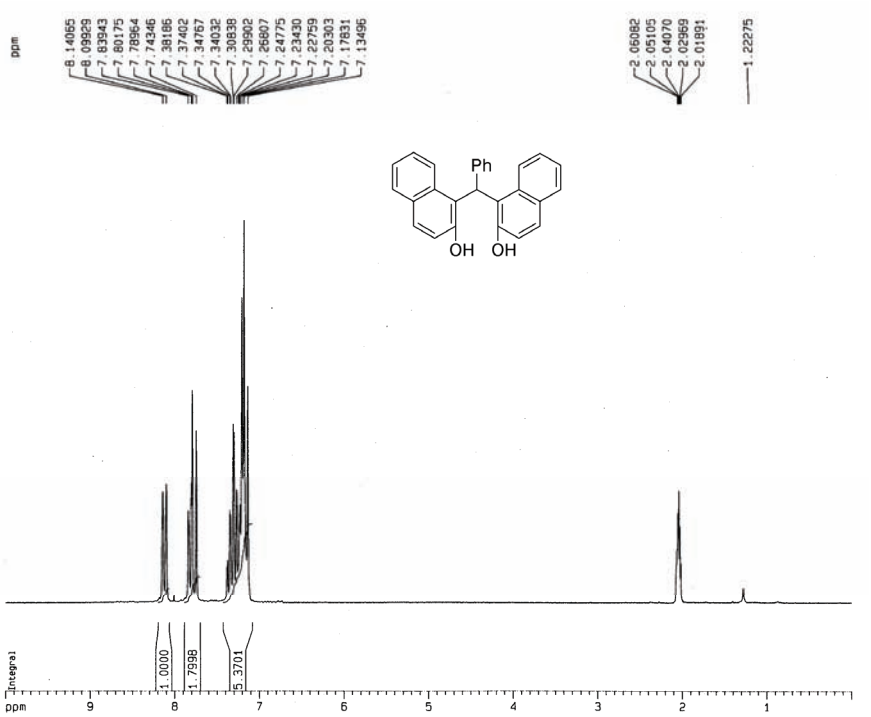

Fig. S-1. ^{1}H-NMR spectrum of **3a**.

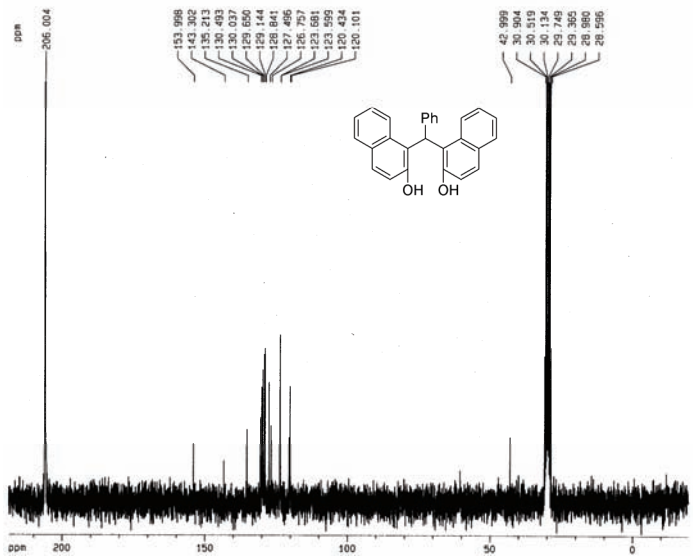

Fig. S-2. ^{13}C-NMR spectrum of **3a**.

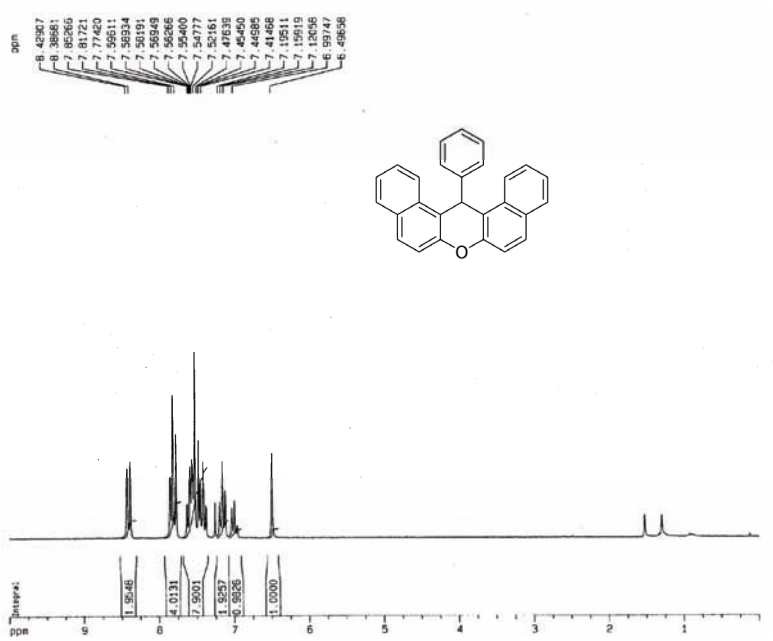

Fig. S-3. ^{1}H-NMR spectrum of **4a**.

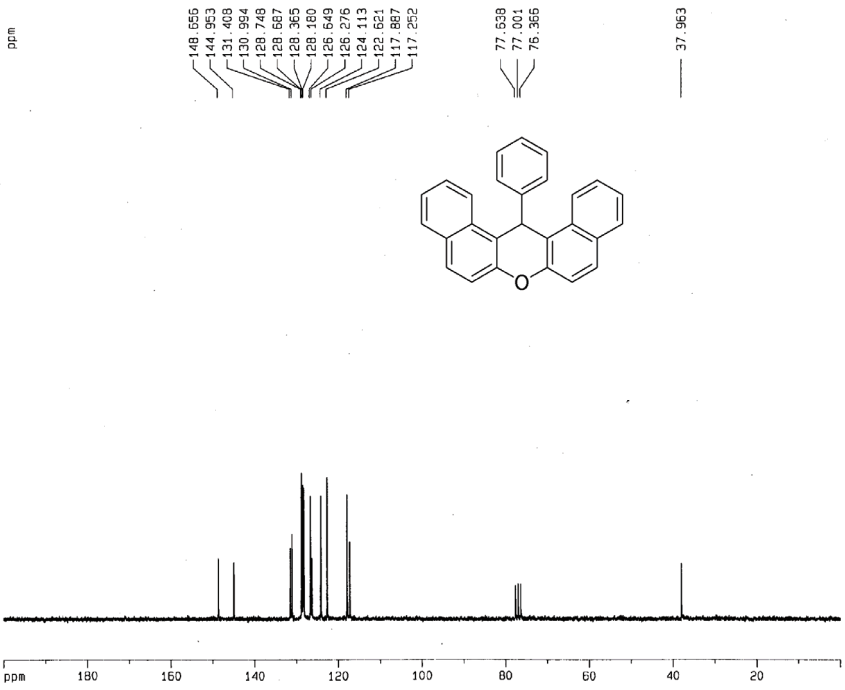

Fig. S-4. ^{13}C-NMR spectrum of **4a**.

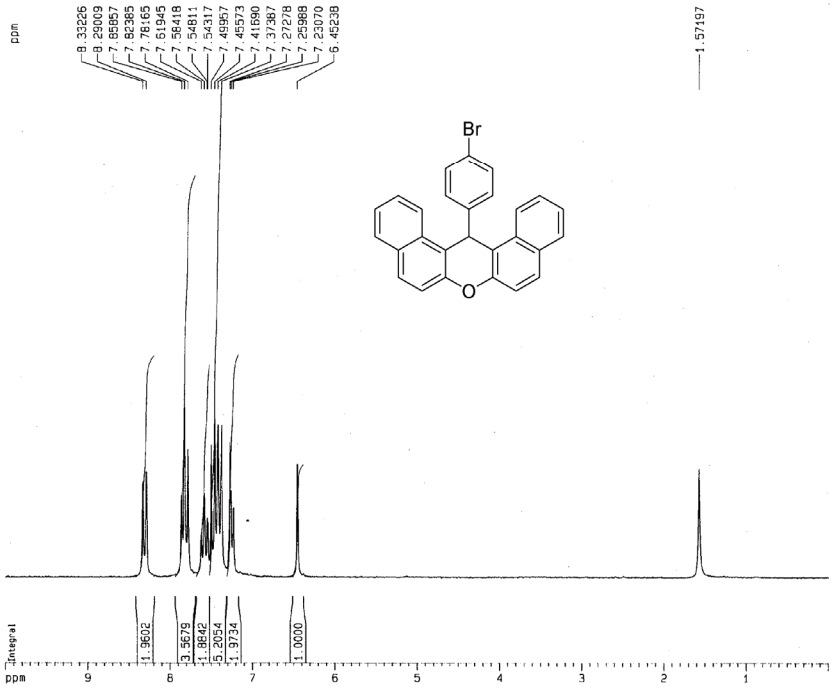

Fig. S-5. ^{1}H-NMR spectrum of **4b**.

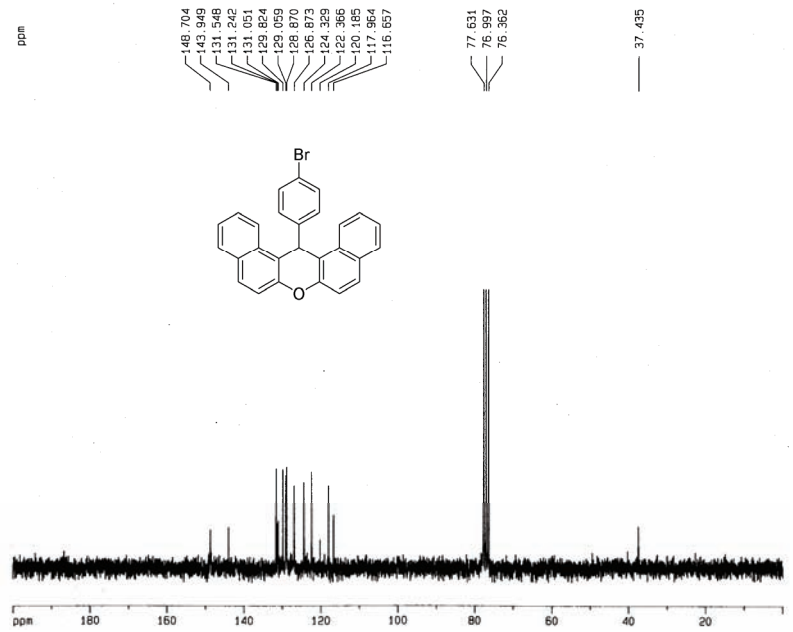

Fig. S-6. ^{13}C-NMR spectrum of **4b**.

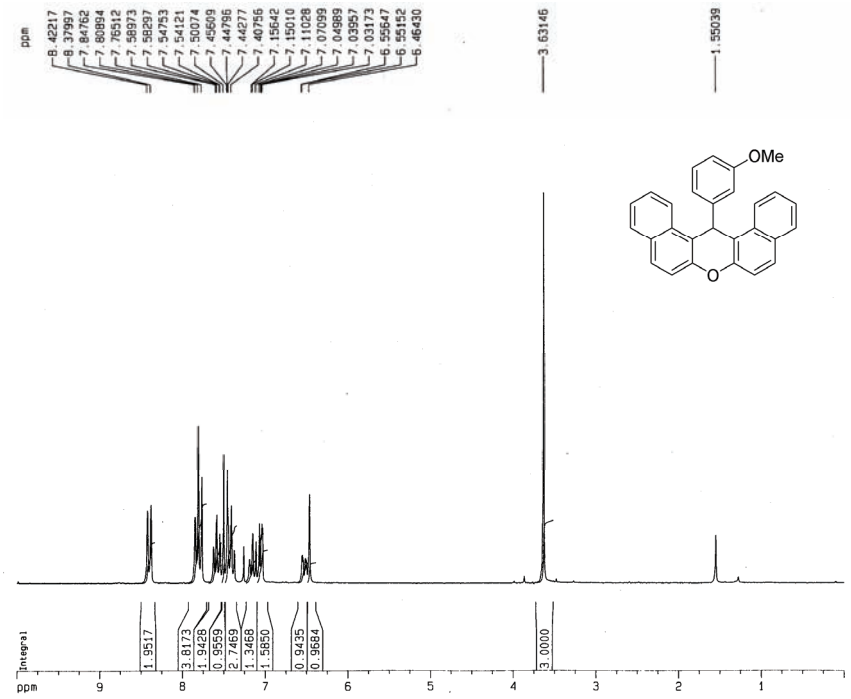

Fig. S-7. ^{1}H-NMR spectrum of **4c**.

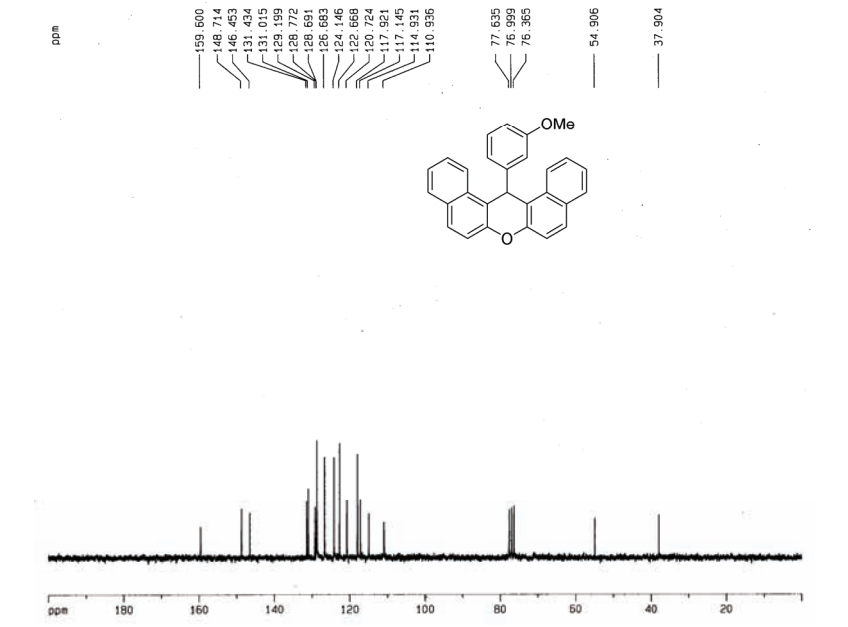

Fig. S-8. ^{13}C-NMR spectrum of **4c**.

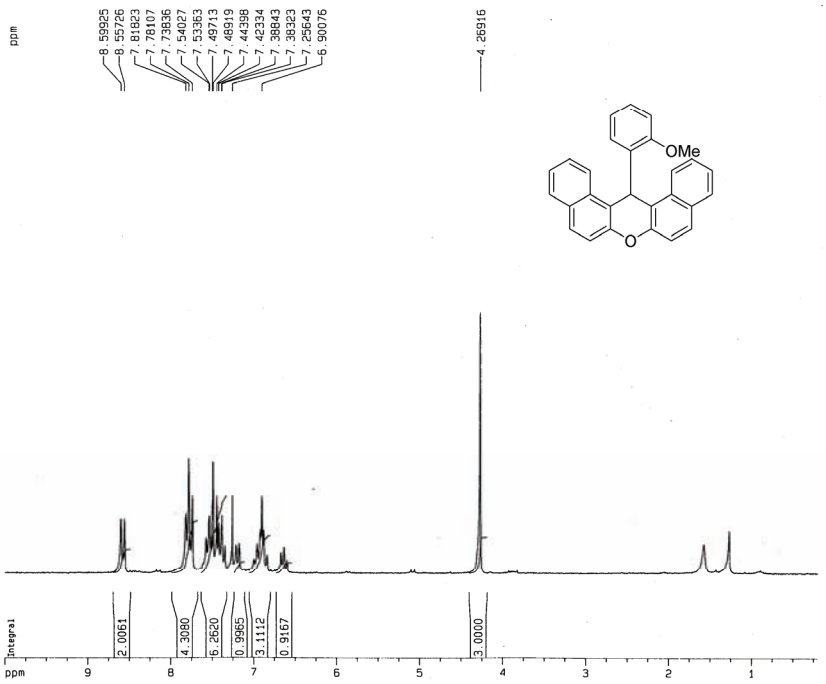

Fig. S-9. ^{1}H-NMR spectrum of **4d**.

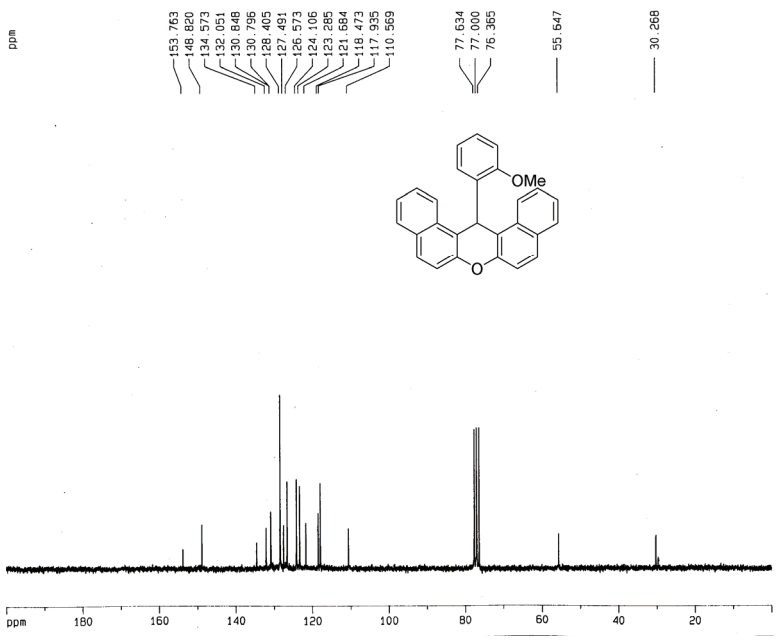

Fig. S-10. ^{13}C-NMR spectrum of **4d**.

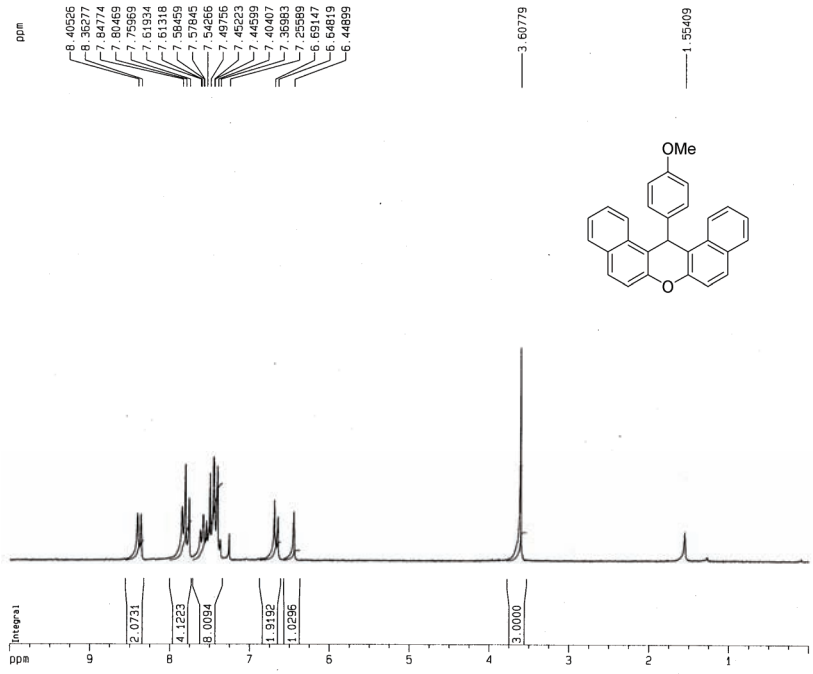

Fig. S-11. ^{1}H-NMR spectrum of **4e**.

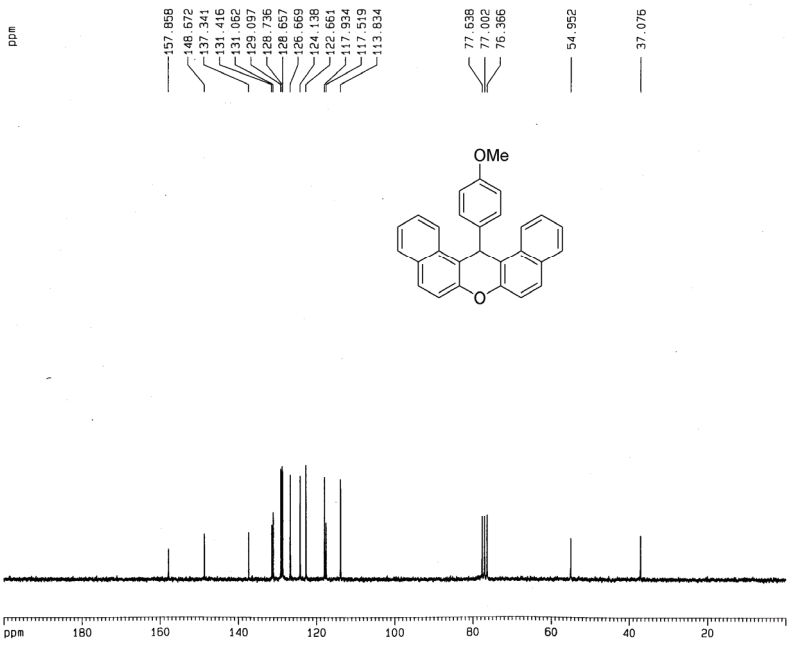

Fig. S-12. ^{13}C-NMR spectrum of **4e**.

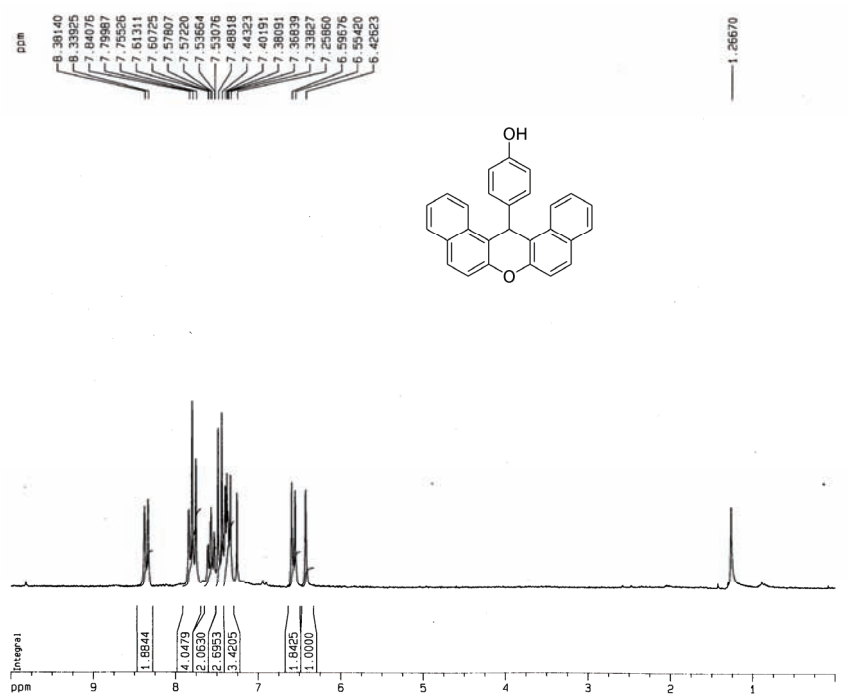

Fig. S-13. ^{1}H-NMR spectrum of **4f**.

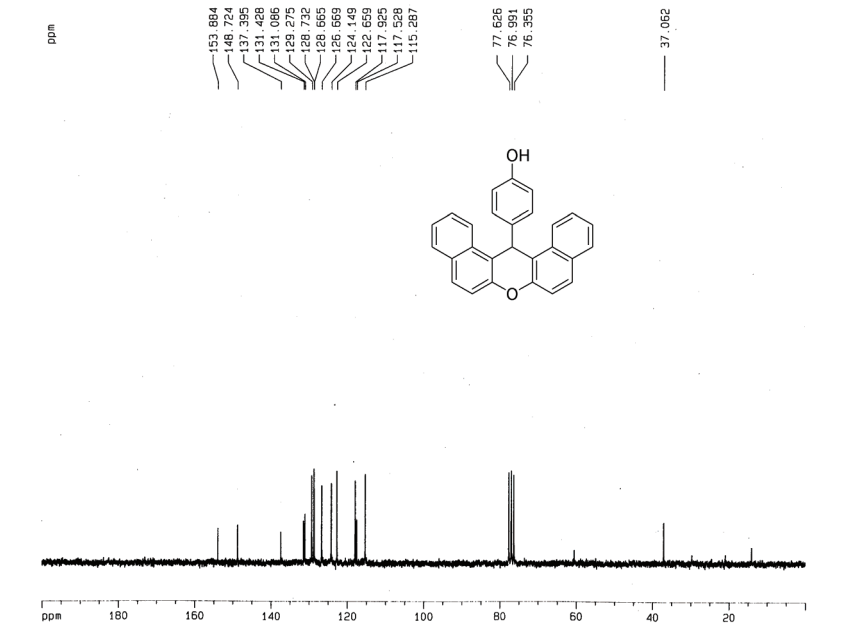

Fig. S-14. ^{13}C-NMR spectrum of 4f.

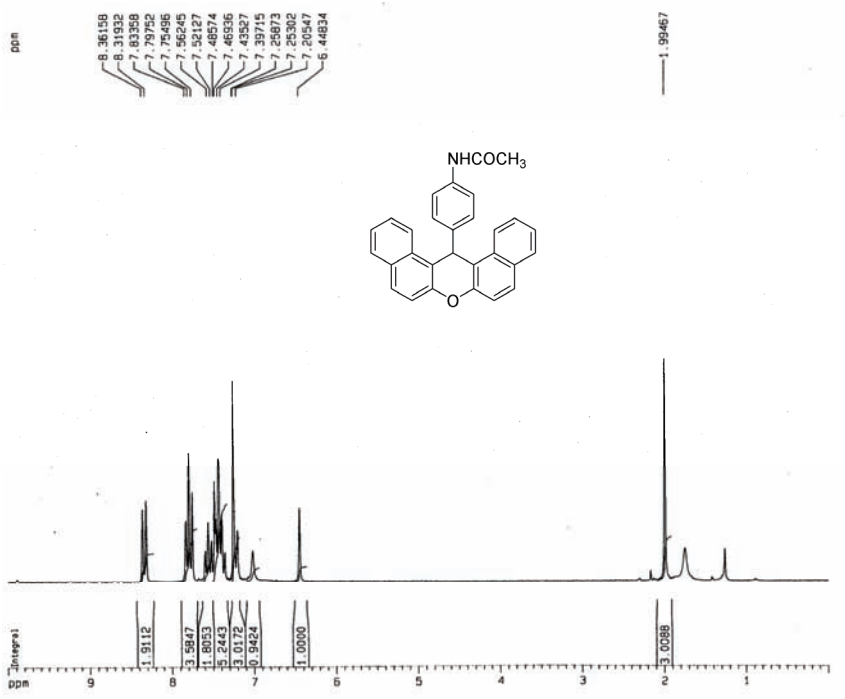

Fig. S-15. ^{1}H-NMR spectrum of **4g**.

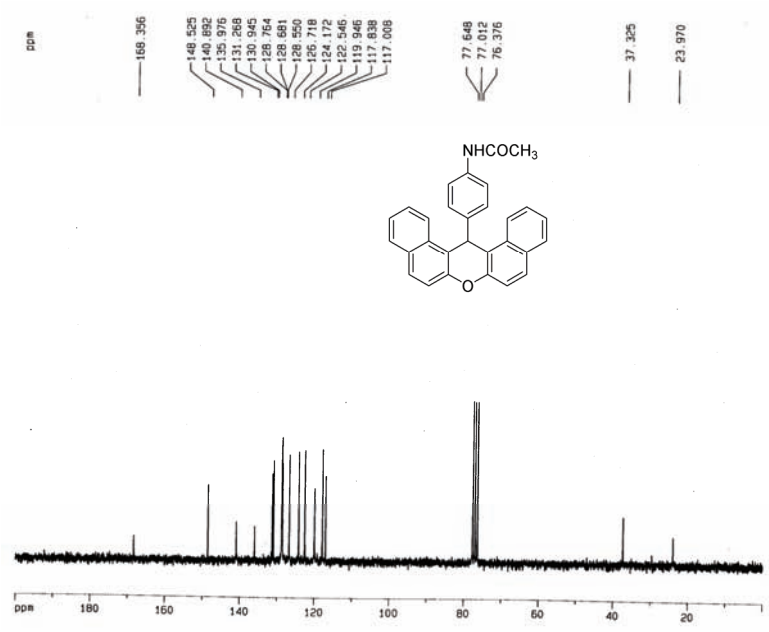

Fig. S-16. ^{13}C-NMR spectrum of **4g**.

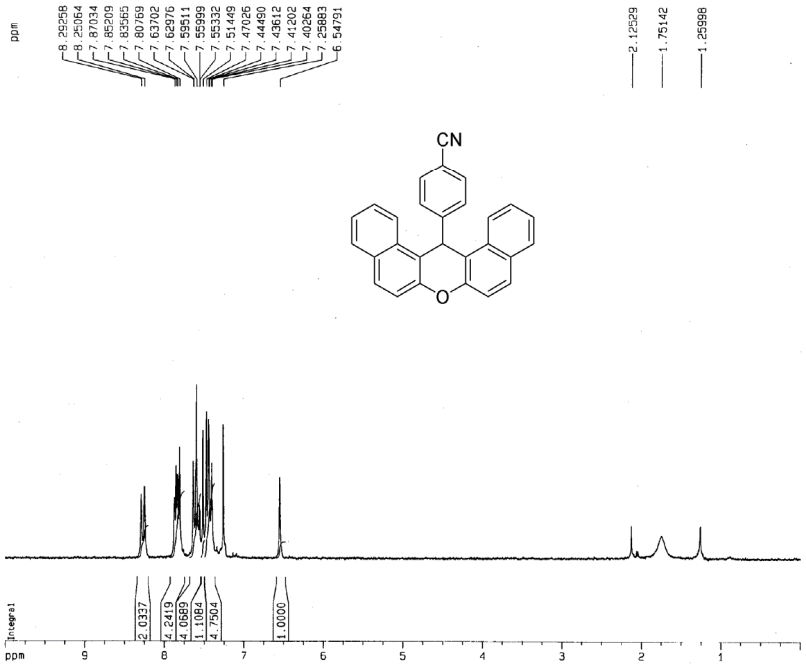

Fig. S-17. ^{1}H-NMR spectrum of **4h**.

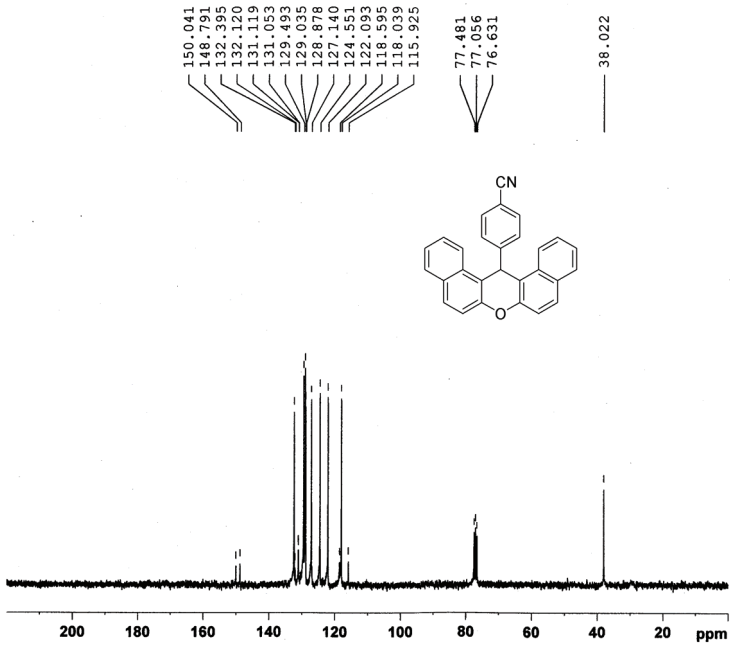

Fig. S-18. ^{13}C-NMR spectrum of **4h**.

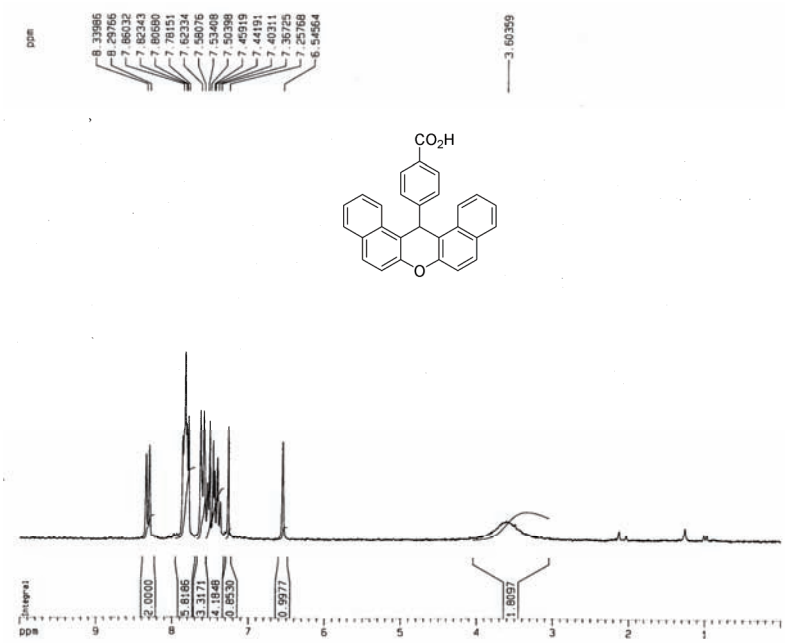

Fig. S-19. ^{1}H-NMR spectrum of **4i**.

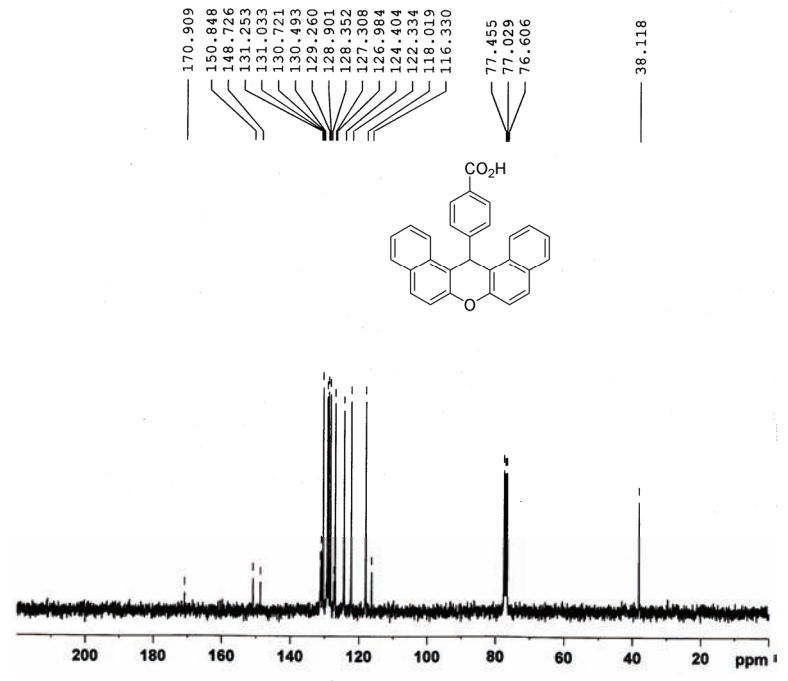

Fig. S-20. ^{13}C-NMR spectrum of **4i**.

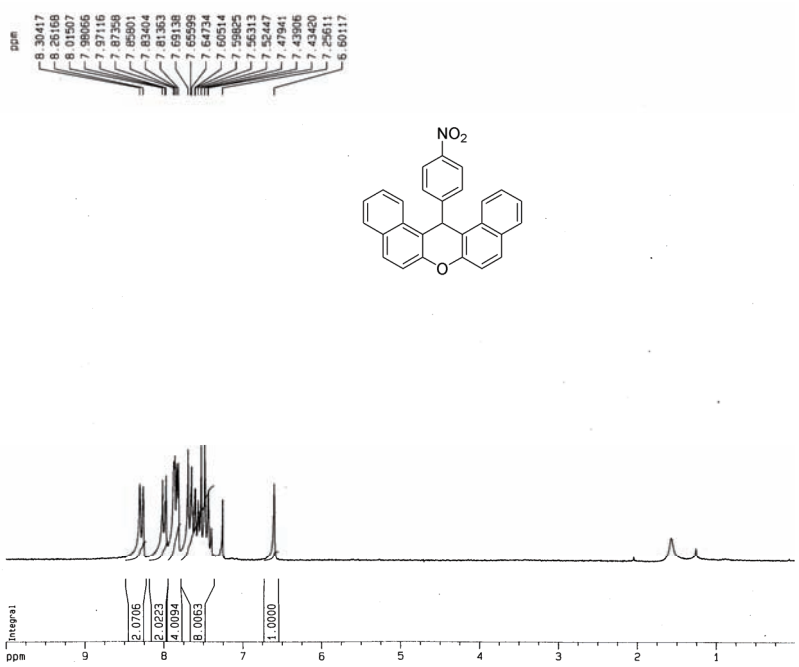

Fig. S-21. ^{1}H-NMR spectrum of **4j**.

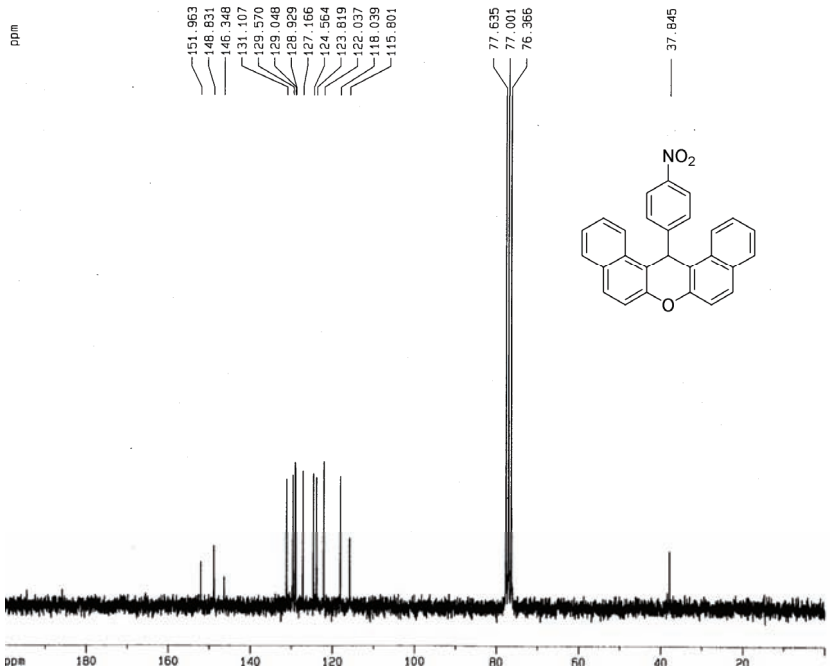

Fig. S-22. ^{13}C-NMR spectrum of **4j**.

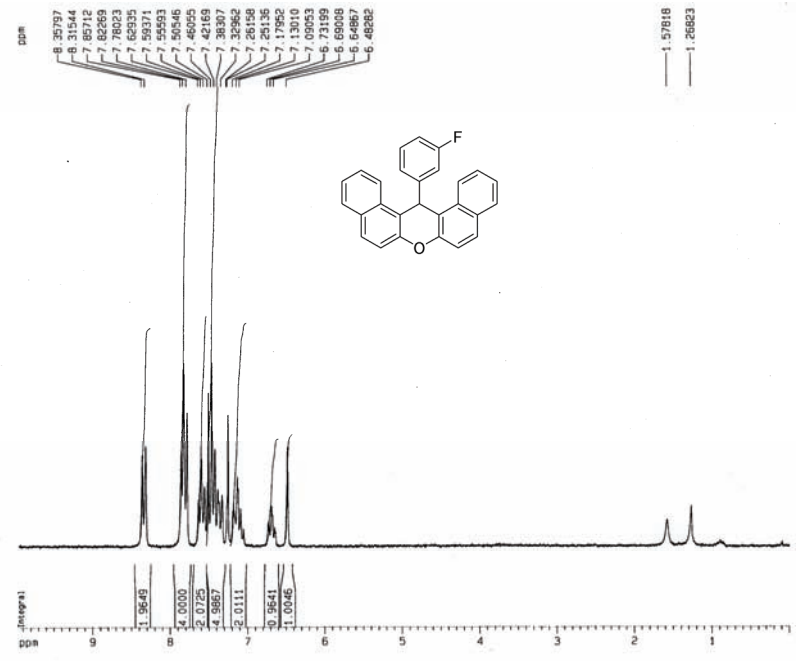

Fig. S-23. ^{1}H-NMR spectrum of **4k**.

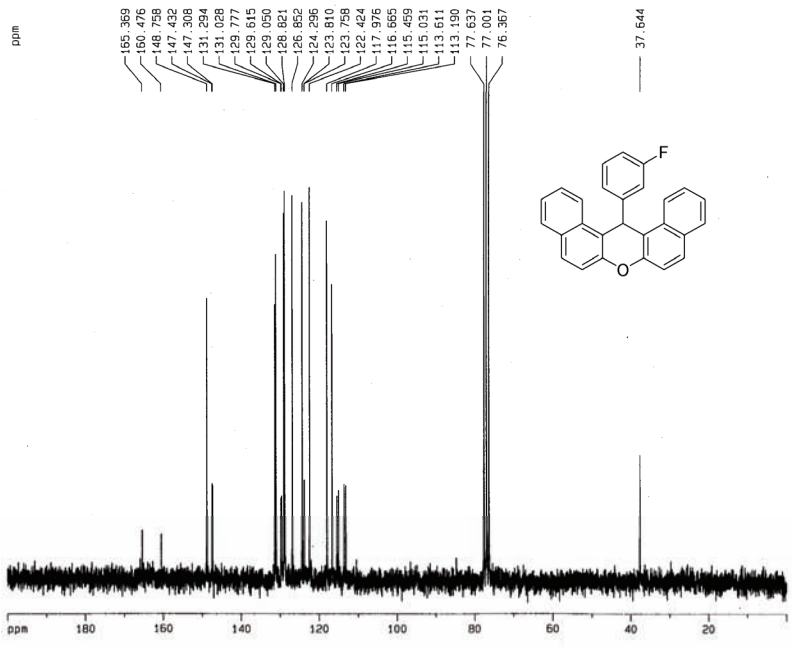

Fig. S-24. ^{13}C-NMR spectrum of **4k**.

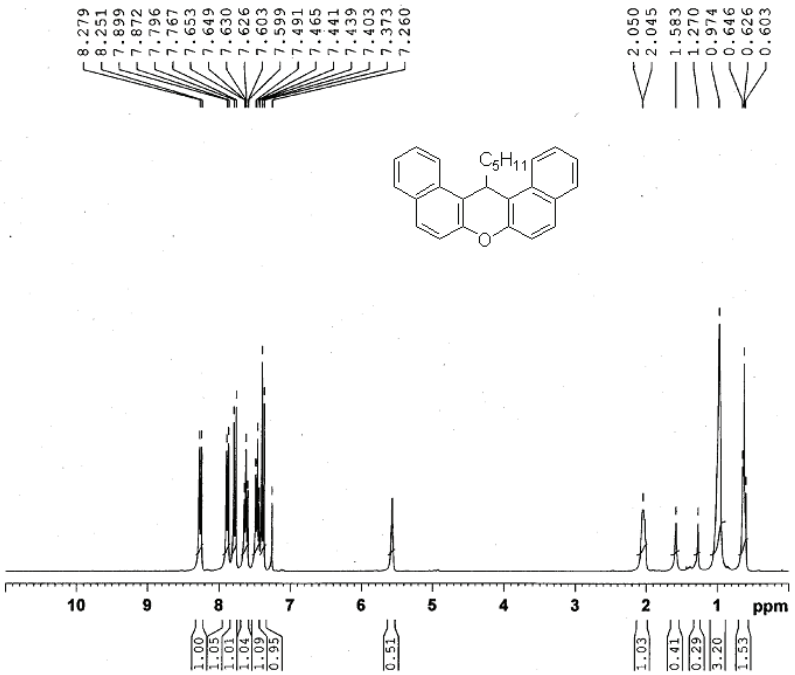

Fig. S-25. ^{1}H-NMR spectrum of **4l**.

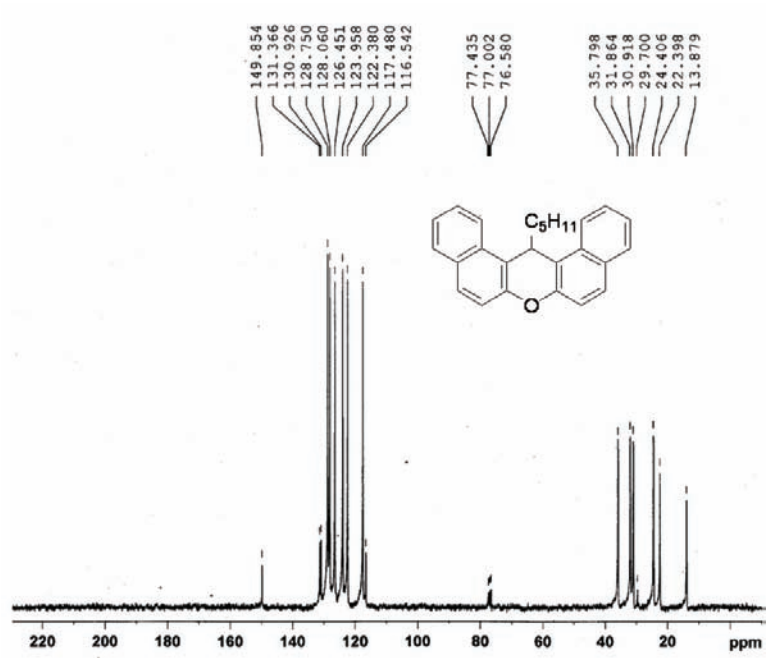

Fig. S-26. ^{13}C-NMR spectrum of **4l**.

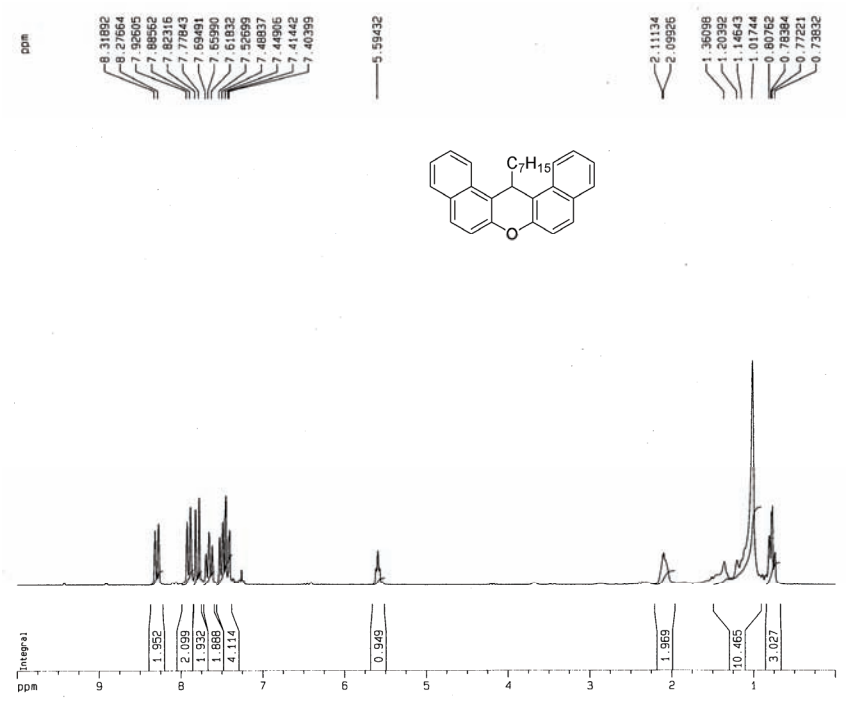

Fig. S-27. ^{1}H-NMR spectrum of **4m**.

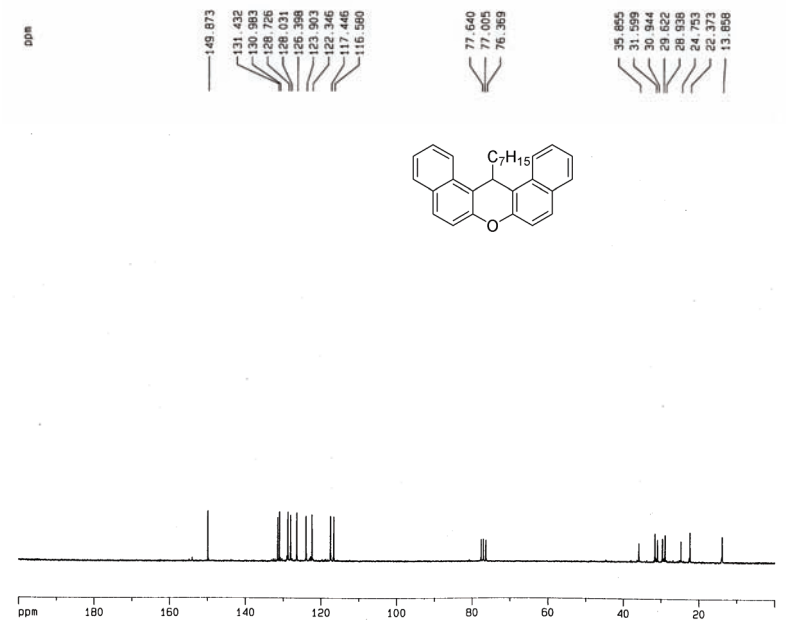

Fig. S-28. ^{13}C-NMR spectrum of **4m**.

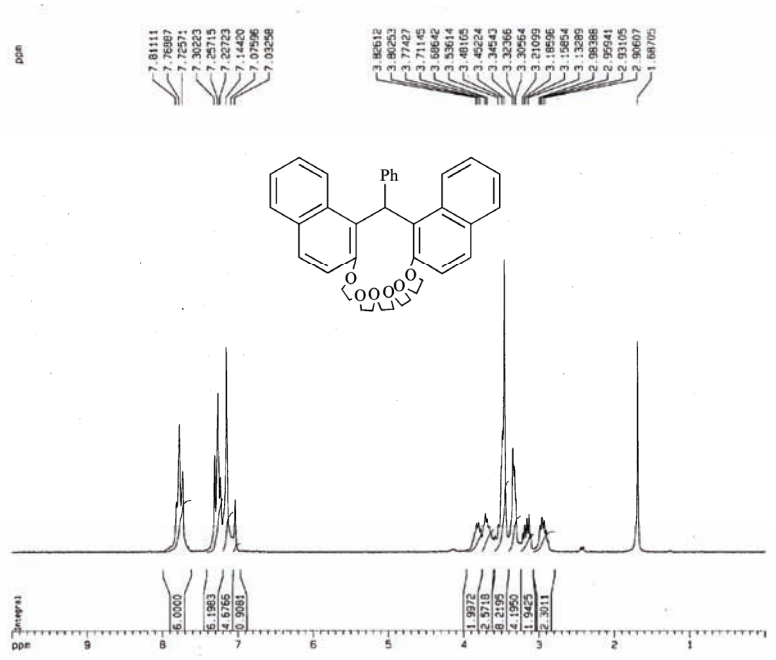

Fig. S-29. ^{1}H-NMR spectrum of **5**.

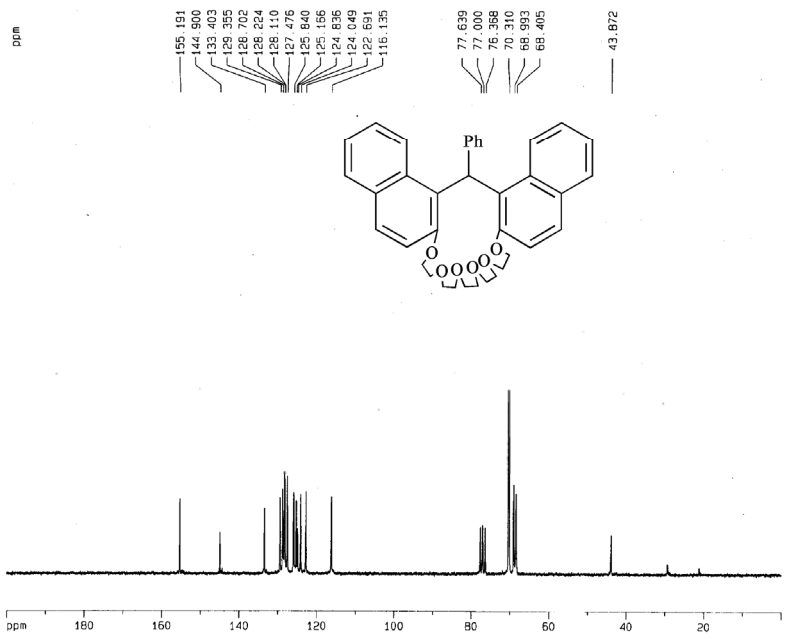

Fig. S-30. ^{13}C-NMR spectrum of **5**.

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