Electronic supplementary information

Self-assembly of chiral oligo(methylene-*p*-phenyleneethynylene)s into vesicle-like particles independent on hydrophilicity/hydrophobicity of side chains and solvents

Zhiqiang Zhao, Zheng Bian, Yu Chen, Chuanqing Kang, Lianxun Gao and Guangshan Zhu

Table of Contents

1. Characterization of foldamers **6a**-**k**

2. Chiral HPLC spectra of intermediates **5a**-**k**

3. [1]H and [13]C NMR spectra of the intermediates

4. Characterization of M*p*-PE tetramer **8h**

5. Characterization of foldamers **9**-**10** with disordered *R*/*S* chiral units

6. Dynamic light scattering diagrams of vesicular assemblies

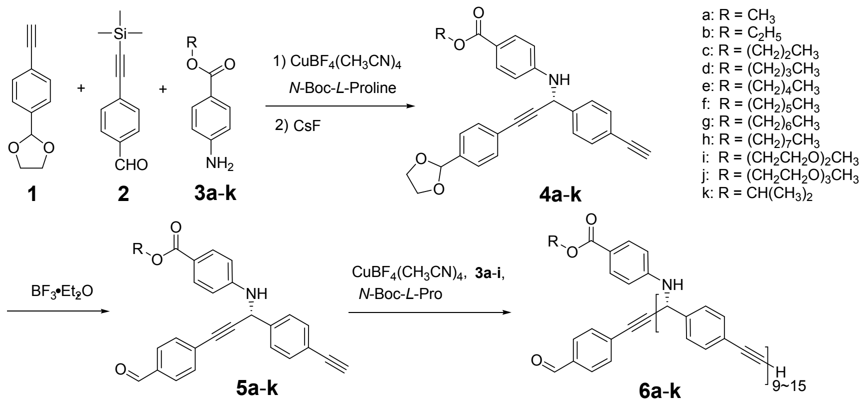
7. SEM images of vesicular assembly **6c** in CH_2Cl_2/*n*-C_6H_{14} at different storage time

8. Fluorescence spectra of foldamers **6a-j** in different solvent systems

9. The statistical data of shell thicknesses of vesicle-like particles[a]

10. Reference

1. Characterization of foldamers **6a**-**k**



4a: yield 86%. $[\alpha]_D^{20}$ = 60.5 (0.20, THF). M. p.: 83-85 ^oC. IR (KBr; cm^{-1}): υ_{max} 3334, 3288, 2950, 2877, 2111, 1915, 1686, 1602, 1581, 1564, 1469, 1462, 1439, 1418, 1391, 1339, 1324, 1286, 1221, 1193, 1114, 1077, 1018, 981, 939, 853, 771, 698, 666. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46-7.40 (m, 4H), 6.81 (d, *J* = 8.8 Hz,2H), 5.91 (d, *J* = 7.9 Hz, 1H), 5.73 (s, 1H), 4.21 (s, 1H), 4.06-3.98 (m, 2H), 3.99-3.91 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.69, 151.42, 140.70, 139.10, 132.52, 131.84, 131.23, 127.97, 127.3, 123.01, 121.73, 117.80, 112.86, 102.68, 89.57, 84.34, 83.64, 81.58, 65.34, 51.80, 48.28. ESI-HRMS: m/z 460.1613 ([$C_{29}H_{25}NO_4$+Na^+] calcd. 460.1625).

4b: yield 88%. $[\alpha]_D^{20}$ = 28 (0.20, THF). M. p.: 84-86 ^oC. IR (KBr; cm^{-1}): υ_{max} 3375, 3278, 2984, 2956, 2887, 2107, 1921, 1682, 1602, 1521, 1463, 1417, 1389, 1367, 1323, 1275, 1221, 1179, 1112, 1083, 1019, 972, 943, 841, 824, 772, 701, 654, 639. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.46-7.40 (m, 4H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 8.0 Hz, 1H), 5.78-5.69 (m, 1H), 4.25-4.17 (m, 2H), 4.06-3.99 (m, 2H), 3.98-3.90 (m, 2H), 1.26 (td, *J* = 7.1, 1.5 Hz, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 166.20, 151.36, 140.71, 139.09, 132.51, 131.84, 131.18, 127.97, 127.37, 123.02, 121.72, 118.10, 112.85, 102.68, 89.58, 84.33, 83.64, 81.58, 65.34, 60.16, 55.39, 48.29, 14.80. ESI-HRMS: m/z 474.1664 ([$C_{29}H_{25}NO_4$+Na^+] calcd. 474.1681).

4c：yield 87%. $[\alpha]_D^{20}$ = 85.5 (0.20, THF). M. p.: 85-87 ^oC. IR (KBr; cm^{-1}); υ_{max} 3376, 3280, 2966, 2882, 2104, 1916, 1682, 1603, 1521, 1470, 1417, 1389, 1313, 1274, 1220, 1202, 1177, 1109, 1082, 1019, 972, 942, 885, 832, 772, 699, 637. ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.47-7.37 (m, 4H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 7.9 Hz, 1H), 5.73 (s, 1H), 4.21 (s, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 4.07-3.99 (m, 2H), 3.99-3.89 (m, 2H), 1.70-1.64 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.25, 151.37, 140.74, 139.12, 132.51, 131.84, 131.17, 127.96, 127.36, 123.02, 121.71, 118.12 , 112.88, 102.69, 89.38, 84.35, 81.54 , 65.64, 65.35 , 48.31 , 22.23 , 10.87 . ESI-HRMS: m/z 488.1823 ([$C_{30}H_{27}NO_4$+Na^+] calcd. 488.1838).

4d: yield 85%. $[\alpha]_D^{20}$ = 85.5 (0.20, THF); M. p.: 85-87 °C. IR (KBr; cm^{-1}): υ_{max} 3373, 3280, 2955, 2925, 2872, 1917, 1681, 1603, 1521, 1469, 1417, 1385, 1325, 1274, 1220, 1177, 1110, 1083, 1019, 973, 943, 832, 771, 699, 637. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.51-7.38 (m, 5H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.91 (d, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 4.07-4.00 (m, 2H), 3.98-3.90 (m, 2H), 1.67-1.60 (m, 2H), 1.42-1.36 (m, 2H), 0.91 (t, *J* = 7.4, 1.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.24, 151.36, 140.73, 139.10, 132.51, 131.84, 131.17, 127.96, 127.37, 123.01, 121.71, 118.09, 112.86, 102.68, 89.58, 84.33, 83.64, 81.58, 65.34, 63.88, 48.28, 30.88, 19.26, 14.11. ESI-HRMS: m/z 502.1979 ([$C_{31}H_{29}NO_4$+Na^+] calcd. 502.1994).

4e: yield 88%. $[\alpha]_D^{20}$ = 90.5 (0.20, THF). M. p.: 84-86 °C. IR (KBr; cm^{-1}); υ_{max} 3374, 3279, 2958, 2927, 2875, 1915, 1681, 1603, 1521, 1469, 1417, 1384, 1326, 1275, 1220,1177, 1110, 1082, 1019, 972, 943, 832, 771, 699, 637. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J*= 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46-7.40 (m, 4H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H), 4.22 (s, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 4.06-3.98 (m, 2H), 3.98-3.91 (m, 2H), 1.71-1.78 (m, 2H), 1.40-1.28 (m, 4H), 0.91-0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.89, 167.22, 139.07, 133.37, 133.28, 132.95, 132.37, 131.96, 130.09, 127.83, 127.04, 113.60, 103.76, 83.68, 78.65, 78.46, 77.85, 65.91, 65.20, 64.31, 50.64, 29.13, 28.84, 22.98, 14.61. ESI-HRMS: m/z 516.2137 ([$C_{32}H_{31}NO_4$+Na^+] calcd. 516.2151).

4f: yield 86%. $[\alpha]_D^{20}$ = 92.9 (0.17, THF). M. p.: 84-86 °C. IR (KBr; cm^{-1}): υ_{max} 3371, 3277, 2953, 2926, 2853, 1915, 1677, 1602, 1514, 1466, 1417, 1383, 1324, 1272, 1217, 1176, 1110, 1083, 1017, 973, 941, 928, 769, 699, 637, 568. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42 (m, 4H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.79 (s, 1H), 5.57 (s, 1H), 4.60 (s, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 4.13-4.06 (m, 2H), 4.06-3.98 (m, 2H), 3.10 (s, 1H), 1.76-1.69 (m, 2H), 1.44-1.39 (m, 2H), 1.33 (m, 4H), 0.94-0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 150.41, 140.10, 139.02, 133.28, 132.37, 131.96, 127.76, 127.05, 123.62, 122.84, 120.95, 113.39, 103.76, 88.04, 86.07, 83.72, 78.45, 65.90, 65.16, 50.43, 32.10, 29.40, 26.35, 23.17, 14.63. ESI-HRMS: m/z 530.2293 ([$C_{33}H_{33}NO_4$+Na^+] calcd. 530.2307).

4g: yield 87%. $[\alpha]_D^{20}$ = 63.8 (0.40, THF). M. p.: 86-88 °C. IR (KBr; cm^{-1}): υ_{max} 3371, 3277, 2950, 2926, 2857, 1915, 1677, 1597, 1518, 1466, 1414, 1386, 1324, 1272, 1217, 1176, 1110, 1083, 1017, 973, 941, 828, 769, 699, 637, 571. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 11.6 Hz, 2H), 7.61 (d, *J* = 11.2 Hz, 2H), 7.55 (d, *J* = 11.2 Hz, 2H), 7.44 (m, 4H), 6.73 (d,*J* = 11.6 Hz, 2H), 5.81 (s, 1H), 5.59 (s, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 4.12

(m, 2H), 4.05 (m, 2H), 3.13 (s, 1H), 1.81-1.69 (m, 2H), 1.41-1.25 (m, 8H), 0.91 (t, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.31, 150.39, 140.10, 139.02, 133.28, 132.36, 131.96, 127.75, 127.04, 123.60, 122.84, 120.97, 113.38, 103.75, 88.02, 86.07, 83.70, 78.43, 65.90, 65.16, 50.43, 32.35, 29.59, 29.44, 26.64, 23.20, 14.67. ESI-HRMS: m/z 544.2443 ([$C_{34}H_{35}NO_4$+Na^+] calcd. 544.2464).

4h: yield 84%. $[\alpha]_D^{20}$ = 100 (0.33, THF). M. p.: 85-87 °C. IR (KBr; cm^{-1}): υ_{max} 3374, 3280, 2954, 2926, 2855, 2105, 1917, 1679, 1602, 1521, 1468, 1417, 1391, 1325, 1274, 1220, 1176, 1112, 1084, 1018, 973, 944, 832, 771, 700, 639. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 11.6 Hz 2H), 7.61 (d, *J* = 11.2 Hz, 2H), 7.55 (d, *J* = 11.2 Hz, 2H), 7.44 (m, 4H), 6.73 (d, *J* = 11.6 Hz, 2H), 5.81 (s, 1H), 5.59 (s, 1H), 4.62 (s, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 4.18-4.08 (m, 2H), 4.08-3.94 (m, 2H), 3.12 (s, 1H), 1.73 (m, 2H), 1.49-1.20 (m, 10H), 0.96-0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 149.78, 139.53, 138.51, 132.61, 131.68, 131.30, 127.07, 126.35, 122.96, 122.24, 120.47, 112.78, 103.11, 87.43, 85.48, 83.07, 77.72, 65.21, 64.47, 49.86, 31.72, 29.19, 29.11, 28.79, 26.01, 22.54, 13.96. ESI-HRMS: m/z 558.2605 ([$C_{35}H_{37}NO_4Na^+$] calcd. 558.2620).

4i: yield 90%. $[\alpha]_D^{20}$ = 86 (0.36, THF). M. p.: 106-108 °C. IR (KBr; cm^{-1}): υ_{max} 3346, 3288, 2979, 2883, 2109, 1929, 1676, 1599, 1517, 1442, 1408, 1378, 1361, 1279, 1250, 1177, 1128, 1111, 1068, 1022, 972, 821, 774, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.62-7.52 (m, 4H), 7.43 (s, 4H), 6.75-6.69 (m, 2H), 5.80 (s, 1H), 5.58 (s, 1H), 4.68 (s, 1H), 4.44 (t, *J* = 9.6 Hz, 2H), 4.16-3.98 (m, 4H), 3.82 (t, *J* = 9.6 Hz, 2H), 3.74-3.66(m, 2H), 3.61-3.54 (m, 2H), 3.39 (s, 3H), 3.12 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.48, 149.98, 139.44, 138.40, 132.60, 131.70, 131.49, 127.11, 126.41, 122.96, 122.17, 119.69, 112.71, 103.08, 87.41, 85.39, 83.08, 77.87, 71.86, 70.62, 70.50, 69.34, 65.23, 63.55, 58.93, 49.69, 29.63. ESI-HRMS: m/z 524.2048 ([$C_{32}H_{30}NO_6$-H^+] calcd. 524.2073).

4j: yield 83%. $[\alpha]_D^{20}$ = 68.5 (0.35, THF). IR (KBr; cm^{-1}): υ_{max} 3366, 3288, 2981, 2883, 2109, 1929, 1676, 1600, 1517, 1442, 1408, 1378, 1361, 1279, 1250, 1177, 1128, 1111, 1068, 1022, 972, 821, 774, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.59-7.50 (m, 4H), 7.44-7.38 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.77 (s, 1H), 5.56 (s, 1H), 4.78 (s, 1H), 4.40 (t, *J* = 4.6 Hz, 2H), 4.15-3.96 (m, 4H), 3.79 (t, *J* = 4.8 Hz, 2H), 3.72-3.59 (m, 6H), 3.54-3.50 (m, 2H), 3.35 (s, 3H), 3.11 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 149.98, 139.44, 138.40, 132.60, 131.70, 131.49, 127.11, 126.41, 122.96, 122.17, 119.69, 112.71, 103.08, 87.41, 85.39, 83.08, 77.87, 71.86, 70.62, 70.57, 69.34, 65.23, 63.55, 58.93, 49.69, 29.63. ESI-HRMS: m/z 592.2299 ([$C_{34}H_{35}NO_7$+Na^+] calcd. 592.2311).

4k: yield 88%. $[\alpha]_D^{20}$ = 67 (0.36, THF). IR (KBr; cm^{-1}): υ_{max}3375, 3285, 2974, 2936, 2887, 2107, 1918, 1673, 1601, 1521, 1452, 1417, 1383, 1373, 1344, 1324, 1275, 1221, 1179, 1138, 1096, 1079, 1020, 973, 941, 920, 834, 772, 696, 699, 634. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.5 Hz, 4H), 6.80 (d, J = 8.5 Hz, 2H), 5.91 (d, J = 7.9 Hz, 1H), 5.73 (s, 1H), 5.04 (m, 1H), 4.23 (s, 1H), 4.08 – 3.99 (m, 2H), 3.99 – 3.85 (m, 2H), 1.26 (d, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 149.78, 139.58, 138.47, 132.70, 131.80, 131.36, 127.18, 126.47, 123.07, 122.27, 120.81, 112.81, 103.19, 87.51, 85.50, 83.16, 77.85, 67.57, 65.32, 49.88, 22.07. ESI-HRMS: m/z 488.1829 ([$C_{29}H_{25}NO_4$+Na^+] calcd. 488.1838)

5a：yield 94%. $[\alpha]_D^{20}$ = 146 (0.23, THF). M. p.: 80-82 ^oC. IR (KBr; cm^{-1}): υ_{max} 3329, 3286, 2951, 2838, 2735, 2108, 1924, 1691, 1602, 1563, 1527, 1497, 1438, 1422, 1407, 1340, 1320, 1284, 1208, 1192, 1176, 1112, 1083, 1017, 964, 841, 827, 770, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.92 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.60-7.54 (m, 6H), 6.82 (d, J = 8.8 Hz, 2H), 5.62 (s, 1H), 4.62 (s, 1H), 3.87 (s, 3H), 3.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.70, 171.43, 156.10, 145.09, 140.84, 137.34, 135.99, 134.86, 132.94, 132.77, 126.59, 122.70, 117.67, 97.61, 88.74, 88.36, 86.38, 56.56, 53.11, 45.39. ESI-HRMS: m/z 416.1246 ([$C_{26}H_{19}NO_3$+Na^+] calcd. 416.1263).

5b：yield 95%. $[\alpha]_D^{20}$ = 74.4 (0.25, THF). M. p.: 81-83 ^oC. IR (KBr; cm^{-1}): υ_{max} 3342, 3286, 2979, 2843, 2737, 2107, 1919, 1702, 1602, 1562, 1521, 1414, 1389, 1367, 1276, 1206, 1177, 1107, 1018, 974, 829, 771, 733, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.95 (d, J = 10.8 Hz, 2H), 7.84 (d, J = 10.8 Hz, 2H), 7.63-7.55 (m, 6H), 6.77 (d, J = 10.8 Hz, 2H), 5.62 (s, 1H), 4.33 (d, J = 7.2 Hz, 2H), 3.13 (s, 1H), 1.37 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.30, 166.60, 149.64, 138.95, 135.81, 132.79, 132.36, 131.42, 129.51, 128.42, 127.19, 122.53, 120.64, 112.86, 90.95, 84.88, 82.99, 78.04, 60.40, 49.90, 14.44. ESI-HRMS: m/z 430.1406 ([$C_{27}H_{21}NO_3$+Na^+] calcd. 430.1419).

5c: yield 94%. $[\alpha]_D^{20}$ = 104 (0.23, THF). M. p.: 81-83 ^oC. IR (KBr; cm^{-1}): υ_{max} 3388, 3286, 2964, 2848, 2743, 2107, 1913, 1704, 1600, 1563, 1524, 1495, 1388, 1345, 1325, 1304, 1272, 1261, 1209, 1173, 1104, 1074, 1016, 937, 848, 931, 768, 750, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.95 (d, J = 11.6 Hz, 2H), 7.84 (d, J = 10.8 Hz, 2H), 7.63-7.56 (m, 6H), 6.75 (d, J = 11.6 Hz, 2H), 5.61 (s, 1H), 4.62 (s, 1H), 4.37-4.18 (m, 2H), 3.12 (s, 1H), 1.76 (m, 2H), 1.12-0.91 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.30, 166.64, 149.76, 138.91, 135.81, 132.79, 132.37, 131.42, 129.50, 128.41, 127.21, 122.55, 112.92, 90.90, 84.92, 82.99, 78.05, 77.26, 66.04, 49.94, 22.22, 10.56. ESI-HRMS: m/z 444.1565 ([$C_{28}H_{23}NO_3$+Na^+] calcd. 444.1576).

5d：yield 93%. $[\alpha]_D^{20}$ = 115 (0.22, THF). M. p.: 81-83 ^oC. IR (KBr; cm^{-1}): υ_{max} 3355, 3291, 2954, 2932, 2865, 2743, 2107, 1929, 1701, 1677, 1602, 1564, 1517, 1471, 1414, 1390, 1335, 1324, 1304, 1281, 1261, 1208, 1177, 1115, 1077, 1021, 969, 833, 772, 738, 696. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H),7.63 - 7.56 (m, 6H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 1H), 4.67 (s, 1H), 4.28 (t, *J* = 6.6 Hz, 2H), 3.14 (s, 1H), 1.72 (m, 2H), 1.48 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.30, 166.67, 149.67, 138.98, 135.80, 132.78, 132.36, 131.42, 129.50, 128.43, 127.19, 122.52, 120.63, 112.86, 90.99, 84.88, 83.01, 78.06, 64.31, 49.89, 30.91, 19.33, 13.80. ESI-HRMS: m/z 458.1720 ([$C_{29}H_{25}NO_3$+Na^+] calcd. 458.1732).

5e：yield 96%. $[\alpha]_D^{20}$ = 75.3 (0.30, THF). M. p.: 81-83 °C. IR (KBr; cm^{-1}): υ_{max} 3352, 3290, 2963, 2927, 2863, 2737, 2107, 1929, 1699, 1677, 1603, 1517, 1463, 1415, 1326, 1309, 1273, 1207, 1178, 1167, 1125, 1079, 1011, 969, 833, 774, 735, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.64-7.52 (m, 6H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 4.61 (s, 1H), 4.27 (t, *J* = 6.8Hz, 2H), 3.13 (s, 1H), 1.76 (m 2H), 1.41 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.28, 166.80, 149.62, 138.96, 135.94, 132.78, 132.36, 131.41, 129.50, 128.42, 127.17, 122.44, 120.63, 112.85, 84.67, 82.95, 78.03, 64.60, 49.89, 34.49, 28.54, 28.25, 22.38, 14.00. ESI-HRMS: m/z 472.1873 ([$C_{30}H_{27}NO_3$+Na^+] calcd. 472.1889).

5f：yield 96%. $[\alpha]_D^{20}$ = 133.3 (0.30, THF). M.p.: 82-84 °C. IR (KBr; cm^{-1}): υ_{max} 3346, 3294, 2969, 2927, 2889, 2738, 2107, 1919, 1704, 1598, 1562, 1525, 1504, 1468, 1415, 1389, 1279, 1211, 1173, 1106, 1073, 1016, 974, 832, 770, 728, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.61-7.53 (m, 6H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 3.12 (s, 1H), 1.76 – 1.70 (m, 2H), 1.47-1.36 (m, 2H), 1.33 (m, 4H), 0.96-0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.87, 167.25, 150.20, 139.54, 136.39, 133.37, 132.95, 132.00, 130.09, 129.01, 127.77, 123.12, 121.27, 113.45, 91.54, 85.47, 83.58, 78.62, 65.21, 50.49, 32.10, 29.39, 26.35, 23.16, 14.61. ESI-HRMS: m/z 464.2207 ([$C_{28}H_{23}NO_3$+H^+] calcd. 464.2226).

5g：yield 94%. $[\alpha]_D^{20}$ = 98.7 (0.30, THF). M.p.: 82-84 °C. IR (KBr; cm^{-1}): υ_{max} 3355, 3291, 2948, 2928, 2855, 2735, 2107, 1925, 1704, 1685, 1602, 1564, 1522, 1505, 1466, 1459, 1445, 1420, 1409, 1389, 1337, 1312, 1302, 1282, 1205, 1178, 1163, 1113, 1083, 1013, 972, 886, 841, 830, 771, 735, 700. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.63-7.51 (m, 6H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.60 (s, 1H), 4.61 (s, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 3.12 (s, 1H), 1.80-1.65 (m, 2H), 1.47-1.22 (m, 8H), 0.93-0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.89, 167.26, 150.21, 139.53, 136.38, 133.36, 132.94, 131.99, 130.09, 127.78, 123.10, 121.23, 113.47, 91.54, 85.47, 83.59, 78.64, 65.21, 60.98, 50.48, 32.35, 29.58, 29.44, 26.64, 23.20, 14.67. ESI-HRMS: m/z 478.2371 ([$C_{32}H_{31}NO_3$+H^+] calcd. 478.2382).

5h: yield 94%. $[\alpha]_D^{20}$ = 99.1 (0.27, THF). M. p.: 82-84 °C. IR (KBr; cm^{-1}): υ_{max} 3360, 3328, 3289, 2954, 2922, 2856, 2743, 2107, 1913, 1705, 1678, 1602, 1562, 1524, 1504, 1466, 1409, 1386, 1342, 1320, 1283, 1204, 1178, 1127, 1080, 1018, 973, 880, 831, 770, 736, 697. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.94 (d, *J* = 8.7 Hz 2H), 7.84 (d, *J* = 8.4 Hz 2H), 7.73-7.49 (m, 6H), 6.78 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.14 (s, 1H), 1.75 (m, 2H), 1.54-1.24 (m, 10H), 1.02-0.76 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.36, 166.70, 149.62, 138.95, 135.80, 132.81, 132.38, 131.44, 129.54, 128.43, 127.21, 122.53, 120.66, 112.86, 90.94, 83.00, 78.06, 64.65, 49.88, 31.82, 29.29, 29.23, 28.84, 26.10, 22.67, 14.12. ESI-HRMS: m/z 491.2345 ($[C_{31}H_{29}NO_4+Na^+]$ calcd. 491.2360).

5i: yield 88%. $[\alpha]_D^{20}$ = 104 (0.45, THF). IR (KBr; cm^{-1}): υ_{max} 3363, 3279, 2980, 2883, 2733, 2110, 1925, 1670, 1597, 1520, 1440, 1411, 1376, 1364, 1278, 1263, 1177, 1130, 1106, 1068, 1021, 972, 821, 770, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.98-7.85 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.64-7.46 (m, 6H), 6.80-6.60 (m, 2H), 5.60 (s, 1H), 4.69 (s, 1H), 4.42 (d, *J* = 4.8 Hz, 2H), 3.80 (d, 4.8 Hz, 2H), 3.76-3.64 (m, 2H), 3.61-3.54 (m, 2H), 3.37 (s, 3H), 3.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.35, 166.52, 149.87, 138.94, 135.76, 132.75, 132.35, 131.60, 129.51, 128.42, 127.21, 122.48, 119.99, 112.84, 90.99, 84.85, 83.03, 78.15, 71.93, 70.54, 69.45, 63.64, 59.05, 49.80. ESI-HRMS: m/z 504.1783 ($[C_{30}H_{27}NO_5+Na^+]$ calcd. 504.1781).

5j: yield 83%. $[\alpha]_D^{20}$ = 119 (0.60, THF). IR (KBr; cm^{-1}): υ_{max} 3366, 3288, 2981, 2883, 2739, 2109, 1928, 1677, 1600, 1517, 1442, 1408, 1378, 1361, 1277, 1260, 1177, 1128, 1111, 1068, 1022, 972, 821, 777, 699. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.64-7.53 (m, 6H), 6.73 (d, *J* = 8.7 Hz, 2H), 5.62 (d, *J* = 6.9 Hz, 1H), 4.70 (d, *J* = 6.9 Hz, 1H), 4.43 (t, *J* = 4.8 Hz, 3H), 3.82 (t, *J* = 4.8 Hz, 2H), 3.74-3.63 (m, 6H), 3.58-3.53 (m, 2H), 3.37 (s, 3H), 3.14 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.37, 166.51, 149.81, 138.90, 135.75, 132.77, 132.36, 131.60, 129.52, 128.40, 127.21, 122.49, 120.03, 112.82, 90.92, 84.86, 83.00, 78.12, 71.92, 70.59, 69.41, 63.68, 59.04, 49.81, 21.08, 14.22. ESI-HRMS: m/z 548.2040 ($[C_{32}H_{31}NO_6+Na^+]$ calcd. 548.2049).

5k: yield 92%. $[\alpha]_D^{20}$ = 101 (0.24, THF). IR (KBr; cm^{-1}): υ_{max}3358, 3291,2979, 2942, 2743, 2107, 1914, 1703, 1679, 1601, 1580, 1563, 1523, 1507, 1498, 1467, 1421, 1408, 1386, 1373, 1347, 1337, 1313, 1302, 1277, 1206, 1178, 1165, 1145, 1101, 1085, 1020, 973, 919, 842, 829, 773, 734, 700. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.64-7.52 (m, 6H), 6.73 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 1H), 5.22 (m, 1H), 4.59 (s, 1H), 3.13 (s, 1H), 1.34 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

191.32, 149.45, 138.53, 132.60, 132.37,131.37, 129.52, 127.08, 123.53, 112.85, 104.14, 99.99, 67.62, 49.93, 22.07. ESI-HRMS: m/z 444.1561 ($[C_{28}H_{23}NO_3+Na^+]$ calcd. 444.1576).

6a: yield 60%. $[\alpha]_D^{20}$ = 103 (0.15, THF). M_n = 3123 g/mol, M_w = 3818 g/mol, PDI = 1.16. IR (KBr; cm^{-1}): υ_{max} 3357, 2948 , 2217, 1915, 1709, 1605, 1563, 1520, 1506, 1482, 1434, 1412, 1334, 1314, 1279, 1171, 1110, 1082, 1017, 969, 838, 770, 698. ^1H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.98-7.88 (m, 34H), 7.55-7.46 (m, 80H), 6.75-6.67 (m, 34H), 5.58 (s, 18H), 3.90-3.81 (m, 54H), 3.14 (s, 1H).

6b: yield 55%. $[\alpha]_D^{20}$ = 124 (0.23, THF). M_n = 4923 g/mol, M_w = 5655 g/mol, PDI = 1.15. IR (KBr; cm^{-1}): υ_{max} 3357, 2979, 2221, 1912, 1704, 1605, 1520, 1506, 1477, 1411, 1391, 1367, 1314, 1276, 1176, 1107, 1019, 972, 839, 770, 698. ^1H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.96-7.88 (m, 22H), 7.66-7.40 (m, 48H), 6.77-6.72 (m, 22H), 5.58 (s, 12H), 4.37-4.11 (m, 24H), 3.14 (s, 1H).

6c: yield 60%. $[\alpha]_D^{20}$ = 111 (0.16, THF). M_n = 4719 g/mol, M_w = 5410 g/mol, PDI = 1.15. IR (KBr; cm^{-1}): υ_{max} 3355, 2966, 2204, 1912, 1704, 1605, 1519, 1507, 1473, 1411, 1389, 1376, 1313, 1273, 1176, 1107, 1083, 1018, 971, 940, 839, 770, 698. ^1H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.01-7.80 (m, 18H), 7.66-7.39 (m, 40H), 6.77-7.71 (m, 18H), 5.60 (s, 10H), 4.65-4.58 (m, 10H), 4.27-4.09 (m, 18H), 3.15 (s, 1H), 1.86-1.72 (m, 18H), 1.14-0.98 (m, 27H).

6d: yield 61%. $[\alpha]_D^{20}$ = 85 (0.15, THF). M_n = 3824 g/mol, M_w = 4461 g/mol, PDI = 1.17. IR (KBr; cm^{-1}): υ_{max} 3354, 2958, 2872, 2204, 1915, 1705, 1605, 1520, 1467, 1411, 1486, 1311, 1276, 1176, 1106, 1016, 967, 838, 770, 698. ^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.96-7.83 (m, 22H), 7.62-7.39 (m, 48H), 6.75-6.62 (m, 22H), 5.64-5.51 (s, 11H), 4.58-4.44 (m, 11H), 4.34-4.10 (m, 22H), 3.10 (s, 1H), 1.89-1.62 (m, 22H), 1.45 (m, 22H), 0.96 (t, *J* = 7.4 Hz, 33H).

6e: yield 53%. $[\alpha]_D^{20}$ = 124 (0.15, THF). M_n = 4668 g/mol, M_w = 5483 g/mol, PDI = 1.17. IR (KBr; cm^{-1}): υ_{max} 3347, 2955, 2930, 2204, 1913, 1705, 1604, 1520, 1467, 1411, 1386, 1316, 1272, 1175, 1106, 1017, 968, 887, 837, 769, 697. ^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.94-7.86 (b, 22H), 7.61-7.37 (b, 48H), 6.74-6.64 (b, 22H), 5.59 (s, 11H), 4.59 (s, 11H), 4.30-4.17 (m, 22H), 3.12 (s, 1H), 1.77-1.68 (m, 22H), 1.44-1.29 (m, 32H), 1.05-0.77 (m, 33H).

6f: yield 62%. $[\alpha]_D^{20}$ = 81 (0.42, THF). M_n = 4090 g/mol, M_w = 4883 g/mol, PDI = 1.19. IR (KBr; cm^{-1}): υ_{max} 3358, 2954, 2930, 2204, 1915, 1704, 1605, 1520, 1468, 1412, 1386, 1314, 1273, 1176, 1107, 1018, 975, 838, 770, 698. ^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.93-7.86 (m, 22H), 7.60-7.40 (m, 48H), 6.74-6.66 (m, 22H), 5.61-5.53 (s, 11H), 4.29-4.22 (m, 22H), 3.11 (s, 1H), 1.76-1.67 (m, 22H), 1.46-1.27 (m, 66H), 0.93-0.85 (s, 33H).

6g: yield 55%. $[\alpha]_D^{20}$ = 93 (0.22, THF). M_n = 5299 g/mol, M_w = 6249 g/mol, PDI = 1.18. IR (KBr; cm^{-1}): υ_{max} 3355, 2953, 2928, 2204, 1915, 1705, 1605, 1520, 1506, 1467, 1412, 1386, 1315, 1274, 1176, 1107, 1082, 1018, 970, 838, 770, 6976.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.95-7.83 (m, 22H), 7.60-7.42 (m, 48H), 6.84-6.57 (m, 22H), 5.75-5.51 (m, 11H), 4.64 (s, 11H), 4.32-4.17 (m, 22H), 3.10 (s, 1H), 1.71 (m, 22H), 1.52-1.27 (m, 88H), 0.90 (m, 33H).

6h: yield 57%. $[\alpha]_D^{20}$ = 65 (0.19, THF). M_n = 6040 g/mol, M_w = 8714 g/mol, PDI = 1.44. IR (KBr; cm^{-1}): υ_{max} 3361, 2953, 2927, 2214, 1915, 1706, 1605, 1520, 1467, 1412, 1387, 1314, 1273, 1176, 1108, 1019, 839, 770, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.92-7.83 (m, 26H), 7.58-7.39 (m, 96H), 6.73-6.64 (m, 26H), 5.59-5.51 (s, 13H), 4.60 (m, 13H), 4.28-4.16 (m, 26H), 3.15 (s, 1H), 1.78-1.61 (m, 26H), 1.46-1.18 (m, 130H), 0.91-0.80 (m, 39H).

6i: yield 57%. $[\alpha]_D^{20}$ = 73 (0.22, THF). M_n = 3233 g/mol, M_w = 3981 g/mol, PDI = 1.23. IR (KBr; cm^{-1}): υ_{max} 3346, 2927, 2877, 2821, 2583, 2204, 1916, 1701, 1603, 1520, 1504, 1452, 1411, 1356, 1272, 1173, 1101, 1016, 972, 883, 836, 768, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.98-7.78 (m, 20H), 7.64-7.39 (m, 40H), 6.76-6.63 (s, 20H), 5.4-5.51 (m, 10H), 4.53-4.36 (m, 20H), 3.89-3.77 (m, 20H), 3.73-3.62 (m, 20H), 3.60-3.48 (m, 20H), 3.41-3.28 (m, 30H), 3.12 (m, 1H).

6j: yield 50%. $[\alpha]_D^{20}$ = 69 (0.14, THF). M_n = 3988 g/mol, M_w = 6055 g/mol, PDI = 1.52. IR (KBr; cm^{-1}): υ_{max} 3360, 2947, 2877, 2597, 2223, 1923, 1705, 1606, 1524, 1455, 1411, 1336, 1272, 1177, 1101, 1019, 840, 768, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.07-7.76 (m, 22H), 7.72-7.36 (m, 48H), 6.89-6.61 (m, 22H), 5.64-5.67 (m, 11H), 4.58-4.32 (m, 11H), 4.01-3.42 (m, 154H), 3.40-3.20 (m, 33H), 3.11 (s, 1H).

6k: yield 58%. $[\alpha]_D^{20}$ = 122 (0.20, THF). M_n = 3011 g/mol, M_w = 3632 g/mol, PDI = 1.20. IR (KBr; cm^{-1}): υ_{max} 3355, 2978, 2210, 1915, 1703, 1606, 1519, 1469, 1411, 1386, 1373, 1353, 1334, 1314, 1276, 1176, 1144, 1103, 1018, 972, 920, 840, 771, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.00-7.78 (m, 20H), 7.66-7.38 (m, 40H), 6.77-6.55 (m, 20H), 5.61-5.50 (m, 9H), 5.25-5.07 (m, 9H), 3.11 (s, 1H), 1.42-1.20 (m, 54H).

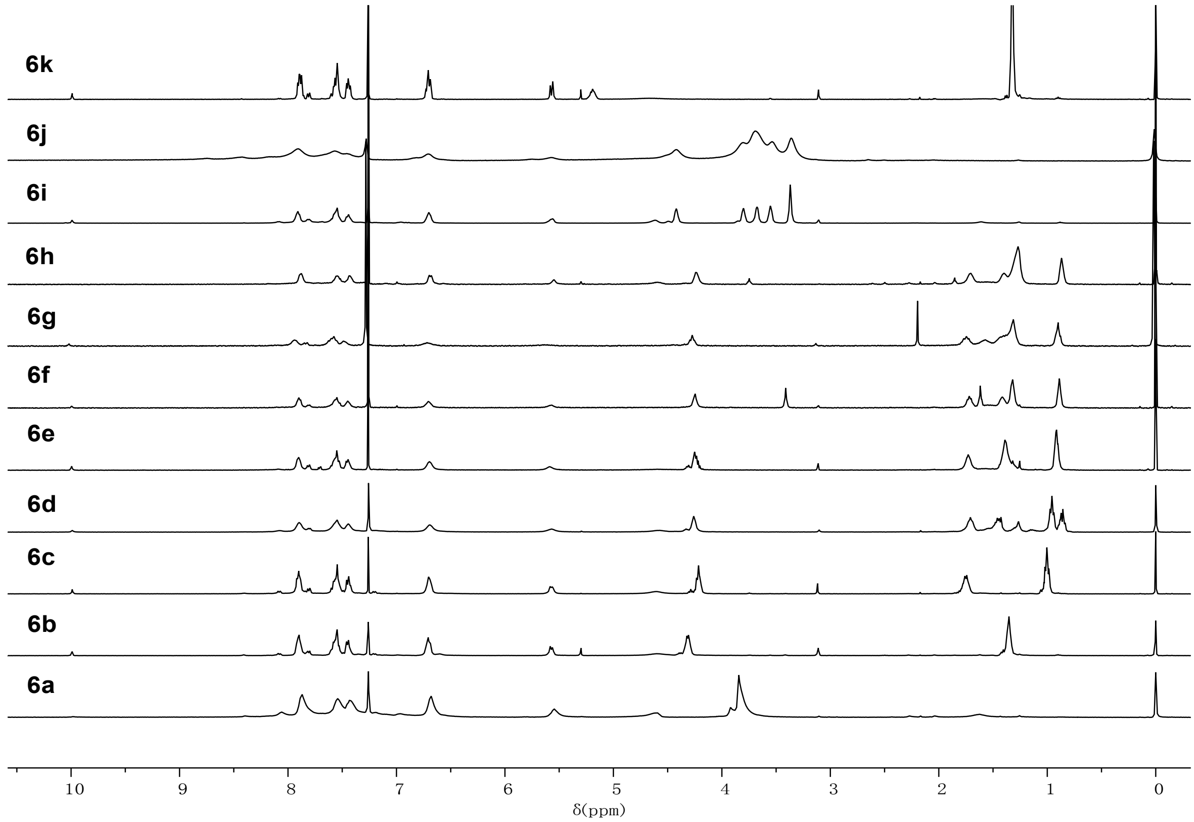


Fig. S1 The ^{1}H NMR spectra of foldamers **6a-k** in $CDCl_3$

The weak signal peaks at 8.04 ppm may be ascribed to N-H of imines formed by condensation of terminal aldehyde of foldamer and amino group of 4-aminobenzoate ester.

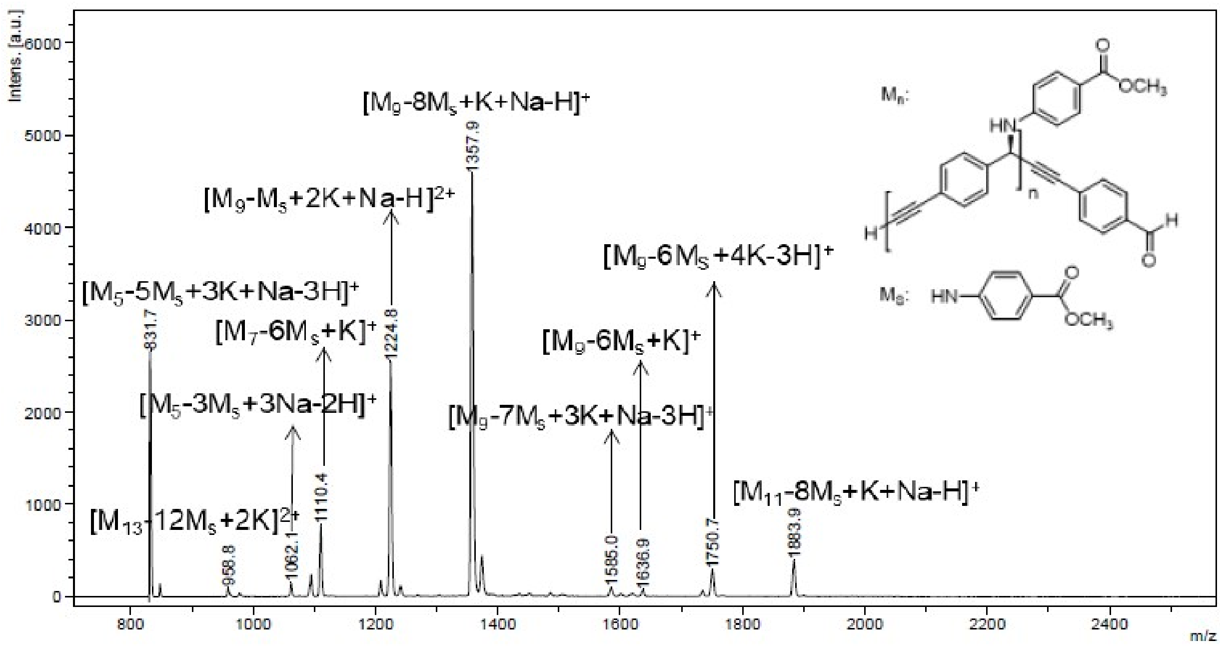


Fig. S2 Mass spectra of foldamer **6a**[1]

M_n: molecular formula of **6a**; M_s: 4-methyloxycarbonylanilino segment; n, number of repeat unit.

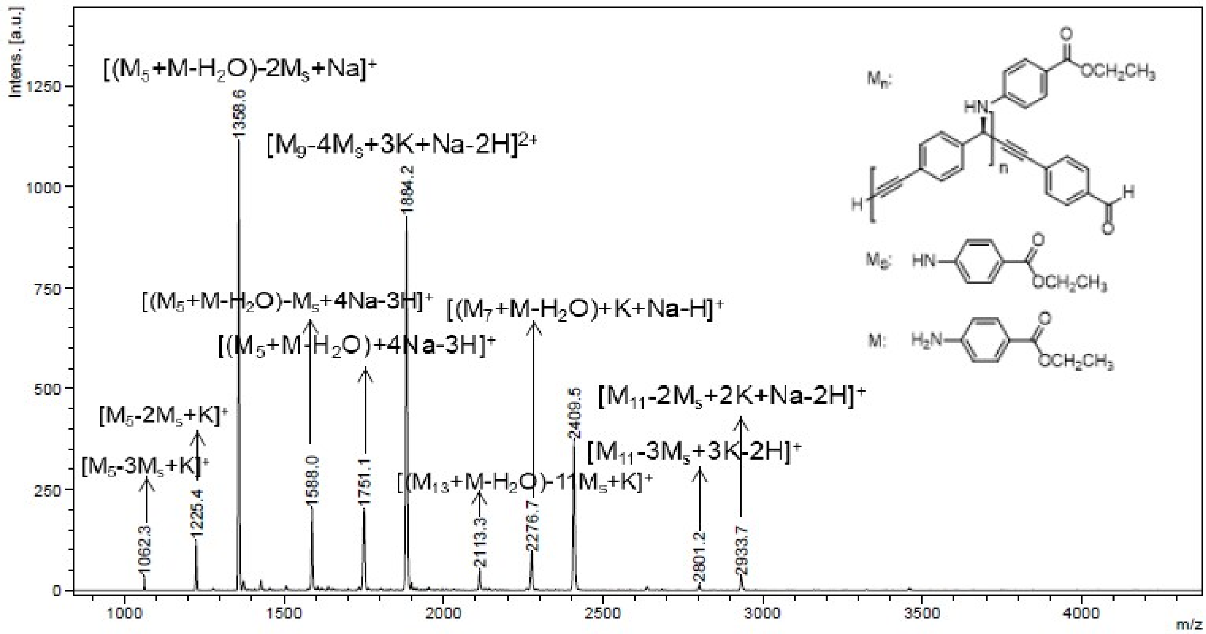


Fig. S3 Mass spectra of foldamer **6b**[1]

M_n: molecular formula of **6b**; Ms: 4-ethyloxycarbonylanilino segment; M: ethyl 4-aminobenzoate; n, number of repeat unit.

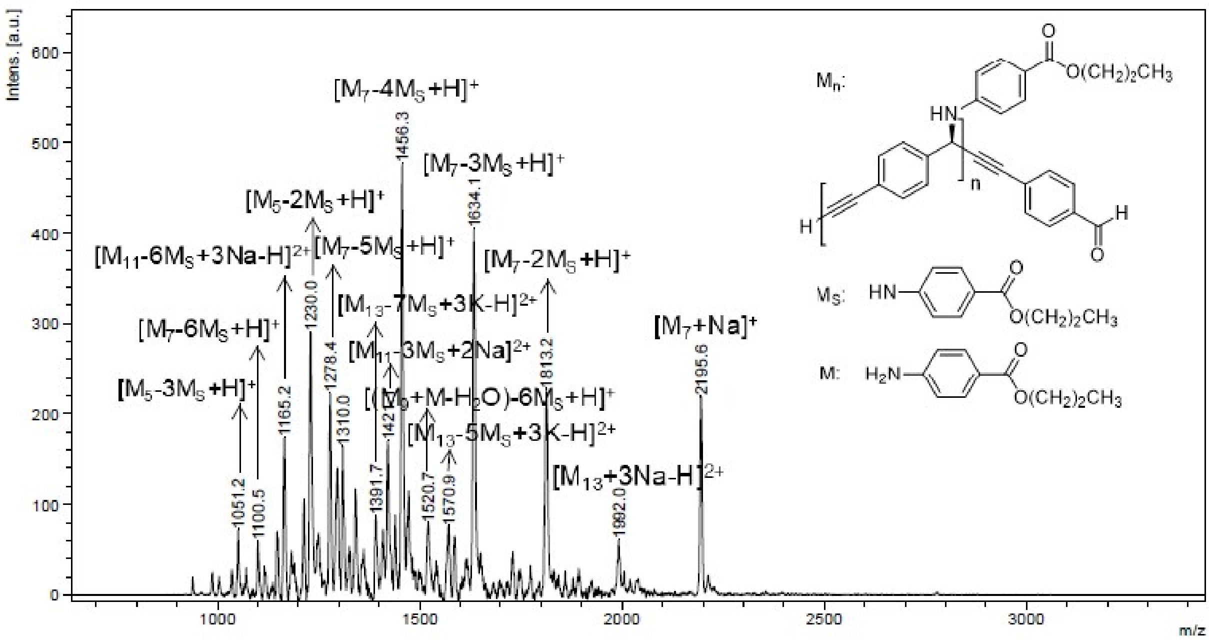


Fig. S4 Mass spectra of foldamer **6c**[1]

M_n: molecular formula of **6c**; Ms: 4-*n*-propyloxycarbonylanilino segment; M: *n*-propyl 4-aminobenzoate; n, number of repeat unit.

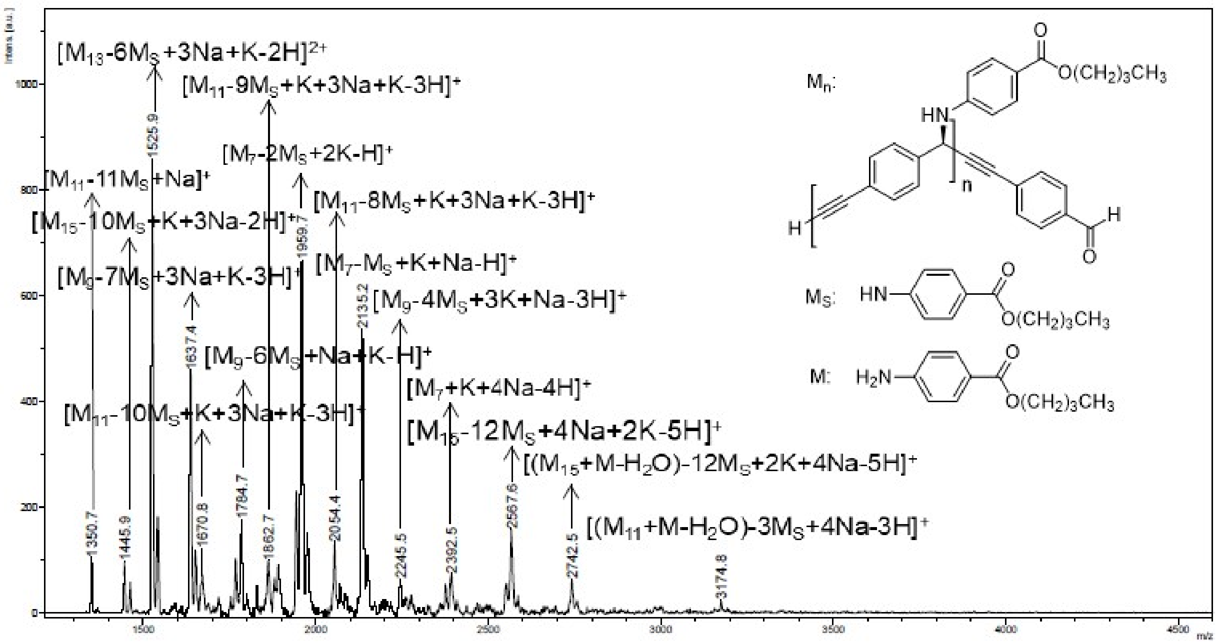


Fig. S5 Mass spectra of foldamer **6d**[1]

M_n: molecular formula of **6d**; M_s: 4-*n*-butyloxycarbonylanilino segment; M: *n*-butyl 4-aminobenzoate; n, number of repeat unit.

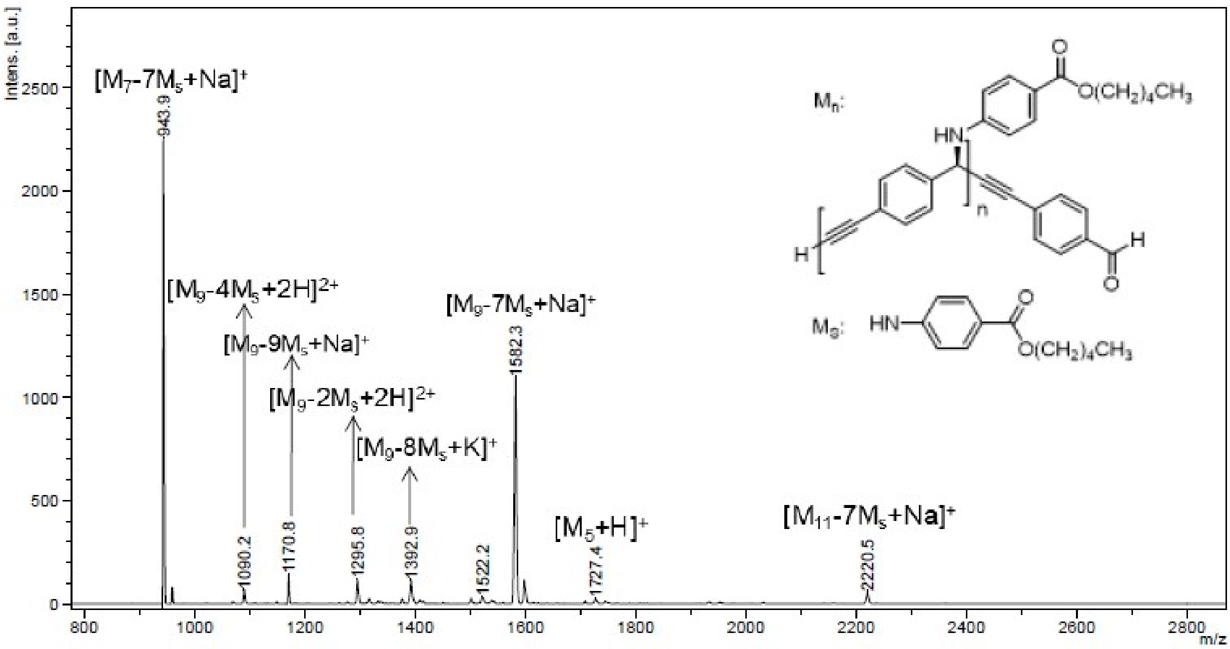


Fig. S6 Mass spectra of foldamer **6e**[1]

M_n: molecular formula of **6e**; Ms: 4-*n*-pentyloxycarbonylanilino segment; n, number of repeat unit.

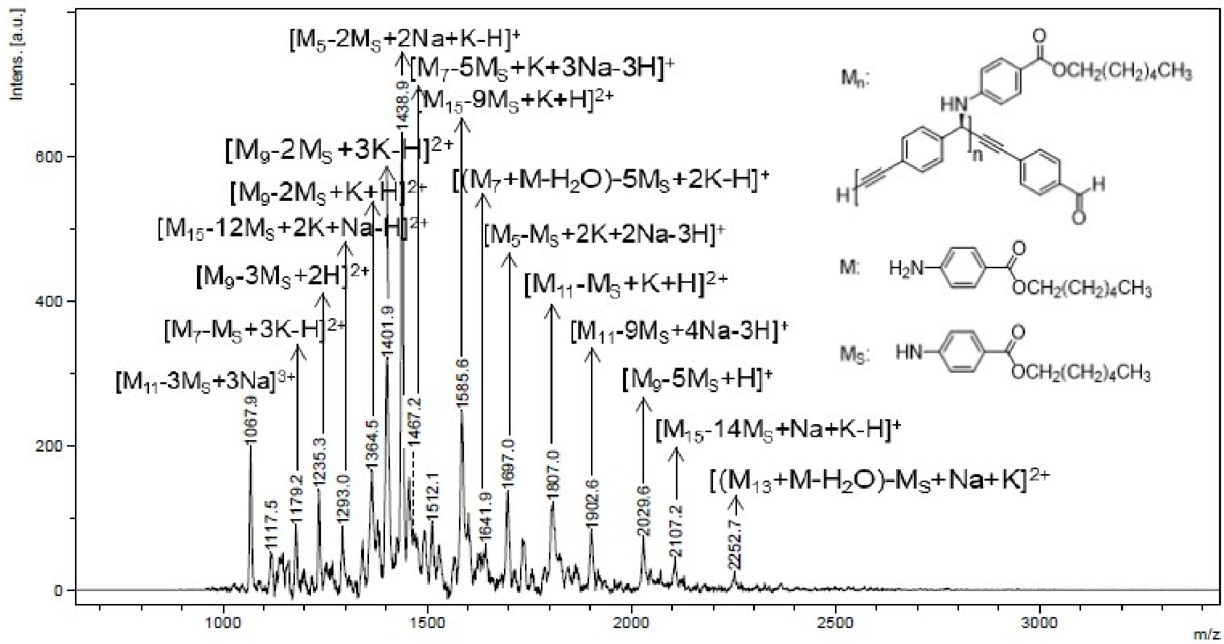


Fig. S7 Mass spectra of foldamer **6f**[1]

M_n: molecular formula of **6f**; M_s: 4-*n*-hexyloxycarbonylanilino segment; M: *n*-hexyl 4-aminobenzoate; n, number of repeat unit.

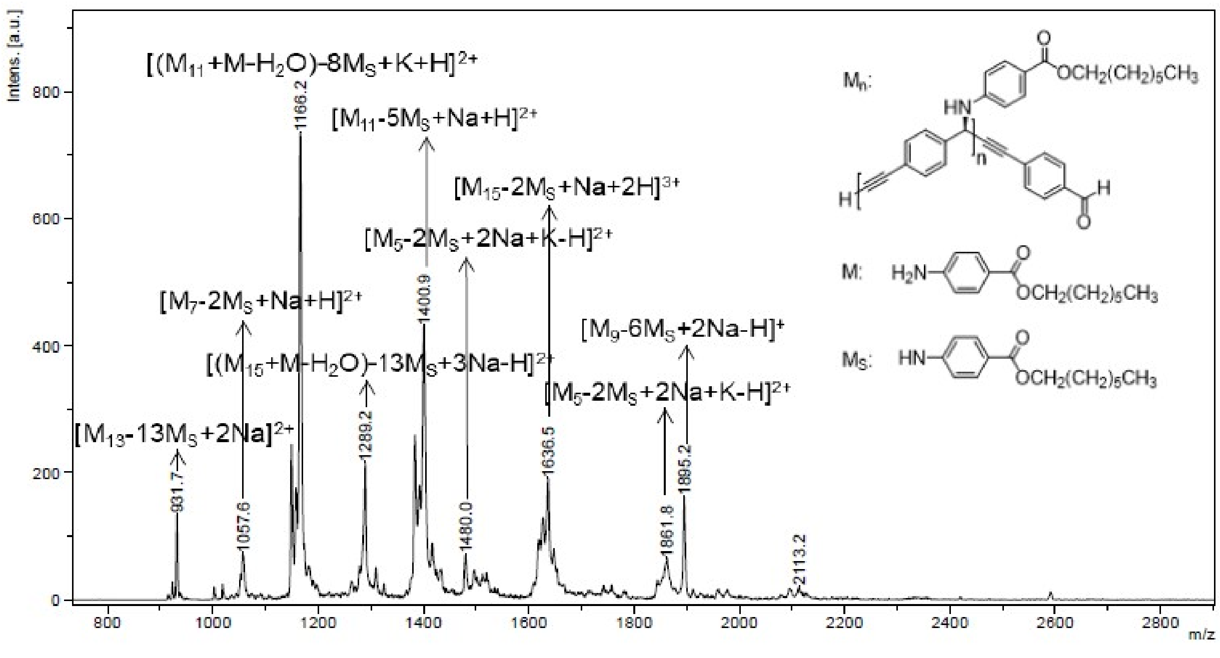


Fig. S8 Mass spectra of foldamer **6g**[1]

M_n: molecular formula of **6g**; M_s: 4-*n*-heptyloxycarbonylanilino segment; M: *n*-heptyl 4-aminobenzoate; n, number of repeat unit.

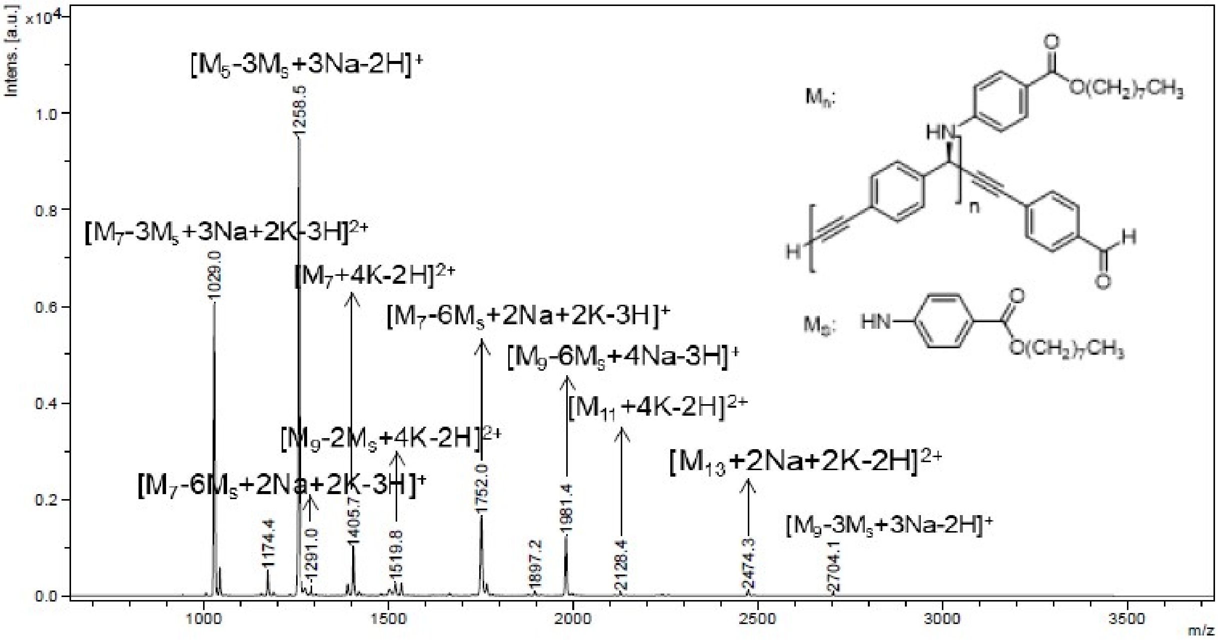


Fig. S9 Mass spectra of foldamer **6h**[1]

M_n: molecular formula of **6h**; M_s: 4-*n*-octyloxycarbonylanilino segment; n, number of repeat unit.

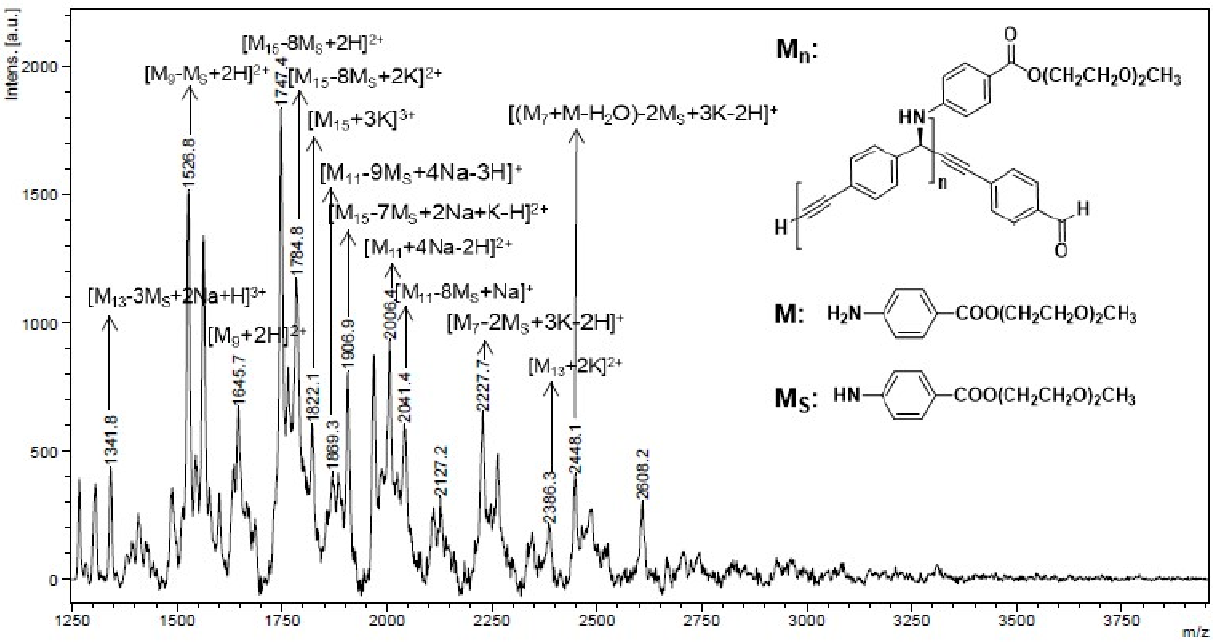


Fig. S10 Mass spectra of foldamer **6i**[1]

M_n: molecular formula of **6i**; M_s: 4-(2,5,8-trioxanonanoyl)anilino segment; n, number of repeat unit.

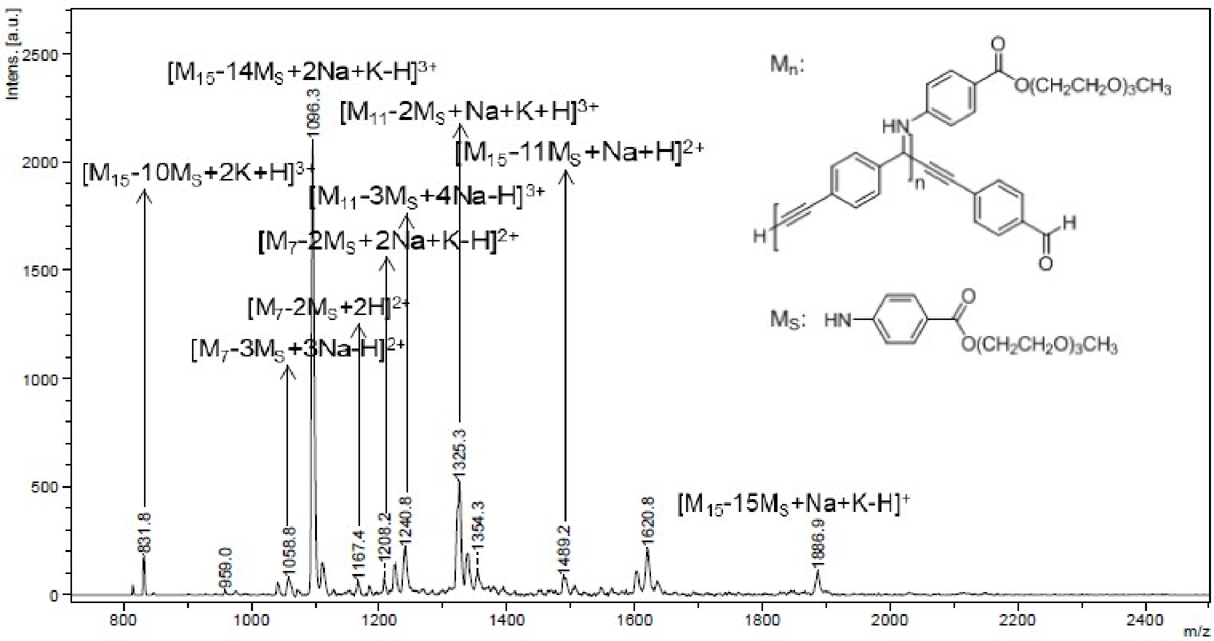


Fig. S11 Mass spectra of foldamer **6j**[1]

M_n: molecular formula of **6j**; M_s: 4-(2,5,8,11-tetraoxadodecanoyl)anilino segment; n, number of repeat unit.

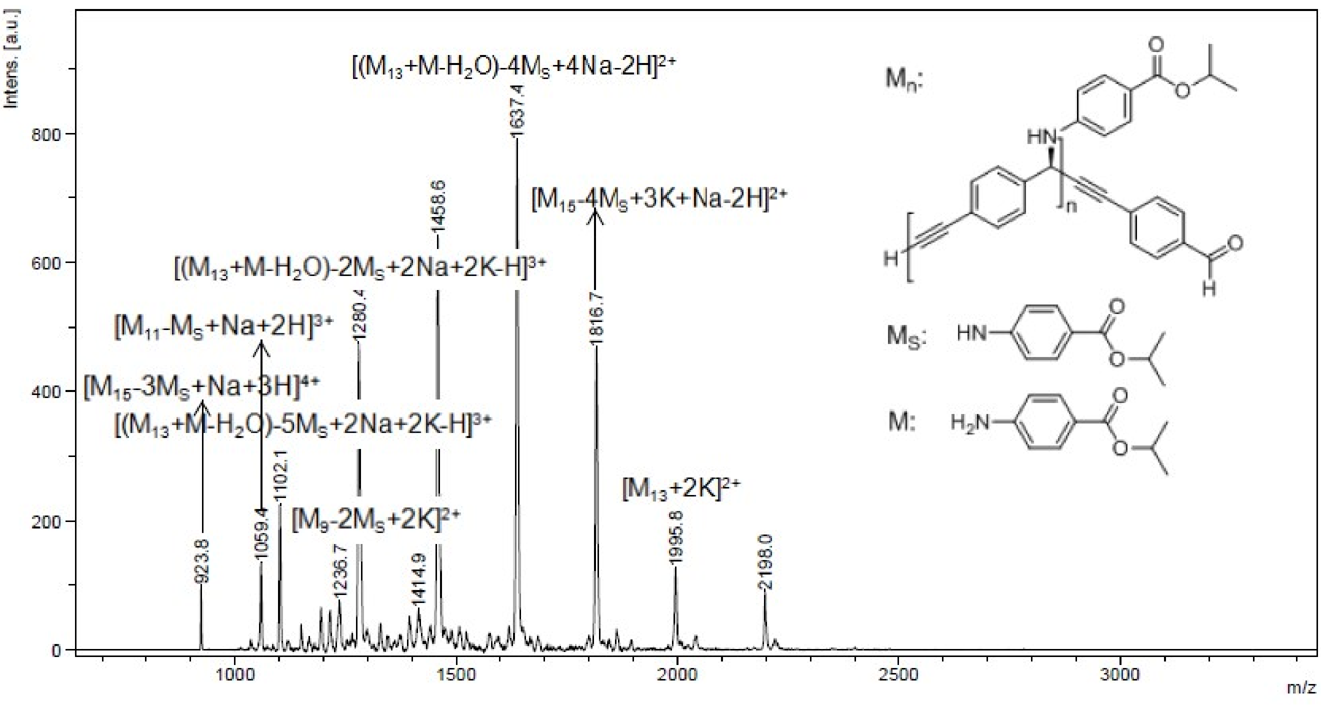


Fig. S12 Mass spectra of foldamer **6k**[1]

M_n: molecular formula of **6k**; M_s: 4-(*i*-propoxycarbonyl)anilino segment; n, number of repeat unit.

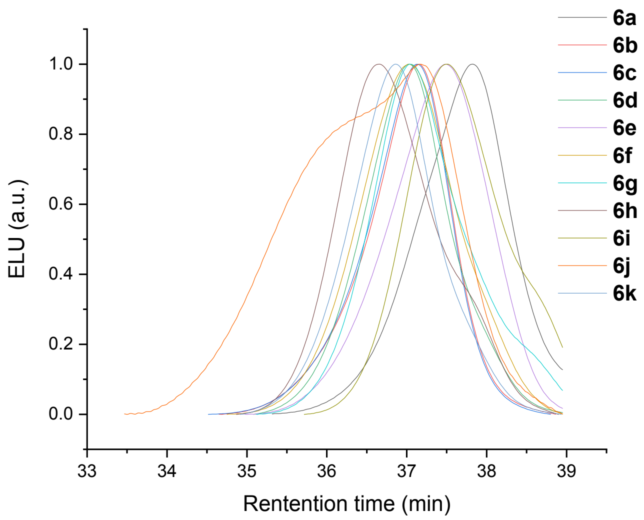
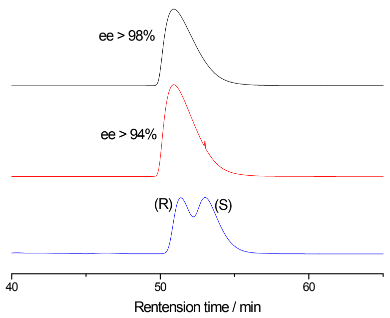


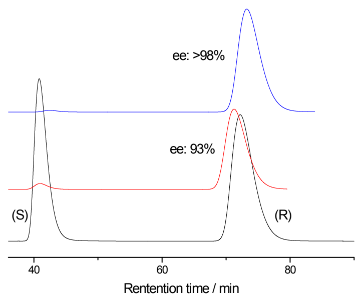
Fig. S13 The GPC curves of foldamers **6a-k**

THF was used as the eluent at a flow rate of 1.0 ml/min.

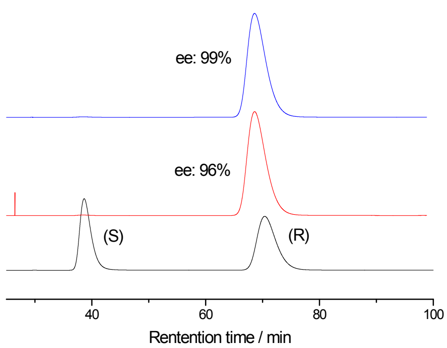
2. Chiral HPLC spectra of intermediates **5a-k**



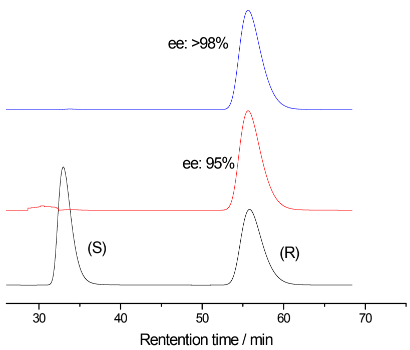
HPLC spectra of racemic standard substance (blue) and compound **5a** before (red) and after (black) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 87/13, v/v, 1 ml/min



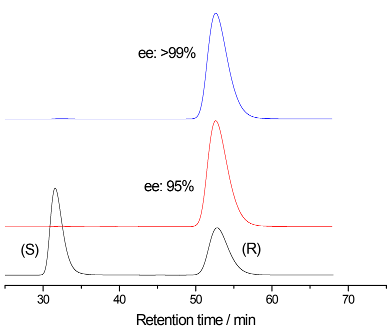
HPLC spectra of racemic standard substance (black) and compound **5b** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



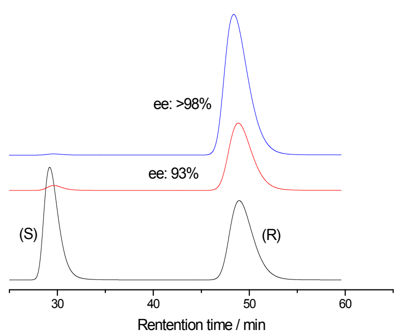
HPLC spectra of racemic standard substance (black) and compound **5c** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



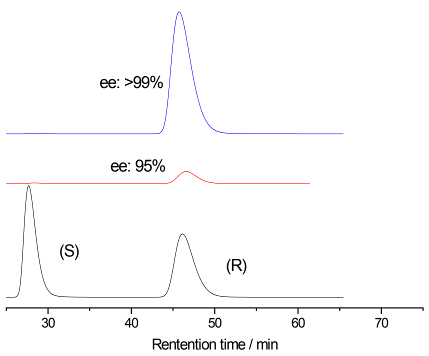
HPLC spectra of racemic standard substance (black) and compound **5d** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



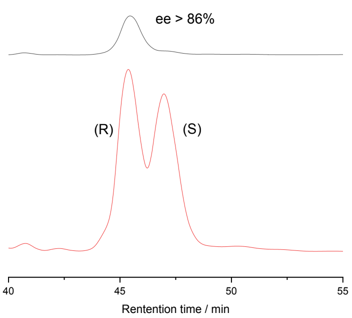
HPLC spectra of racemic standard substance (black) and compound **5e** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



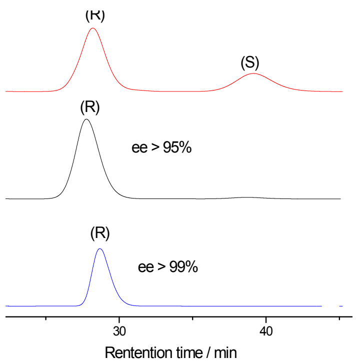
HPLC spectra of racemic standard substance (black) and compound **5f** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



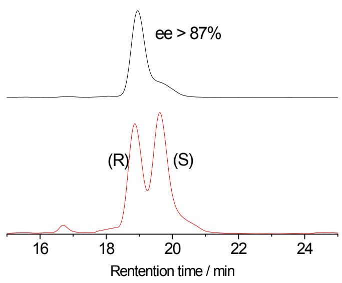
HPLC spectra of racemic standard substance (black) and compound **5g** before (red) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min



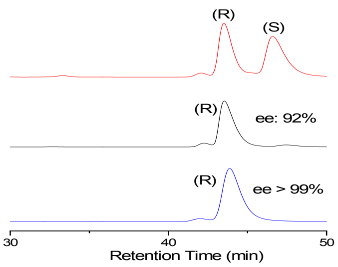
HPLC spectra of racemic standard substance (red) and compound **5i** before (black) using CHIRALPAK ID. Eluent: *n*-hexane/CH_2Cl_2/*i*-propanol = 32.5/32.5/25, v/v/v, 0.15 ml/min



HPLC spectra of racemic standard substance (red) and compound **5h** before (black) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min

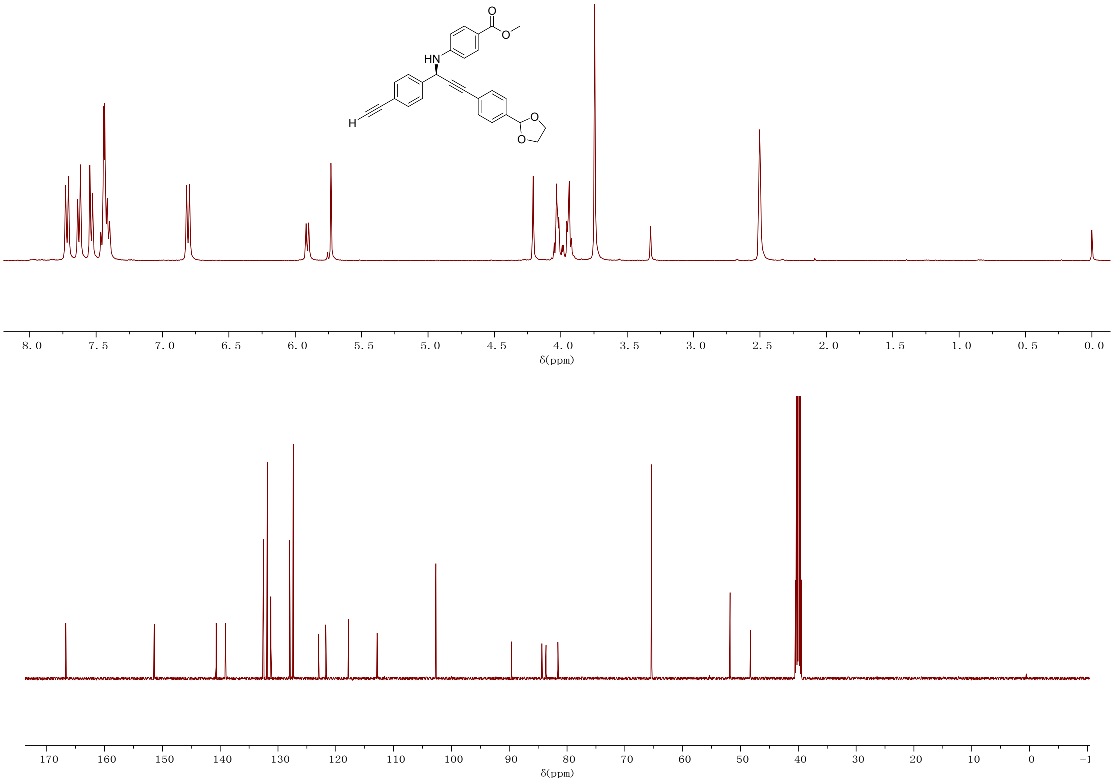


HPLC spectra of racemic standard substance (red) and compound **5j** before (black) using CHIRALPAK ID. Eluent: *n*-hexane/CH_2Cl_2/*i*-propanol = 34.5/34.5/31, v/v/v, 0.2 ml/min

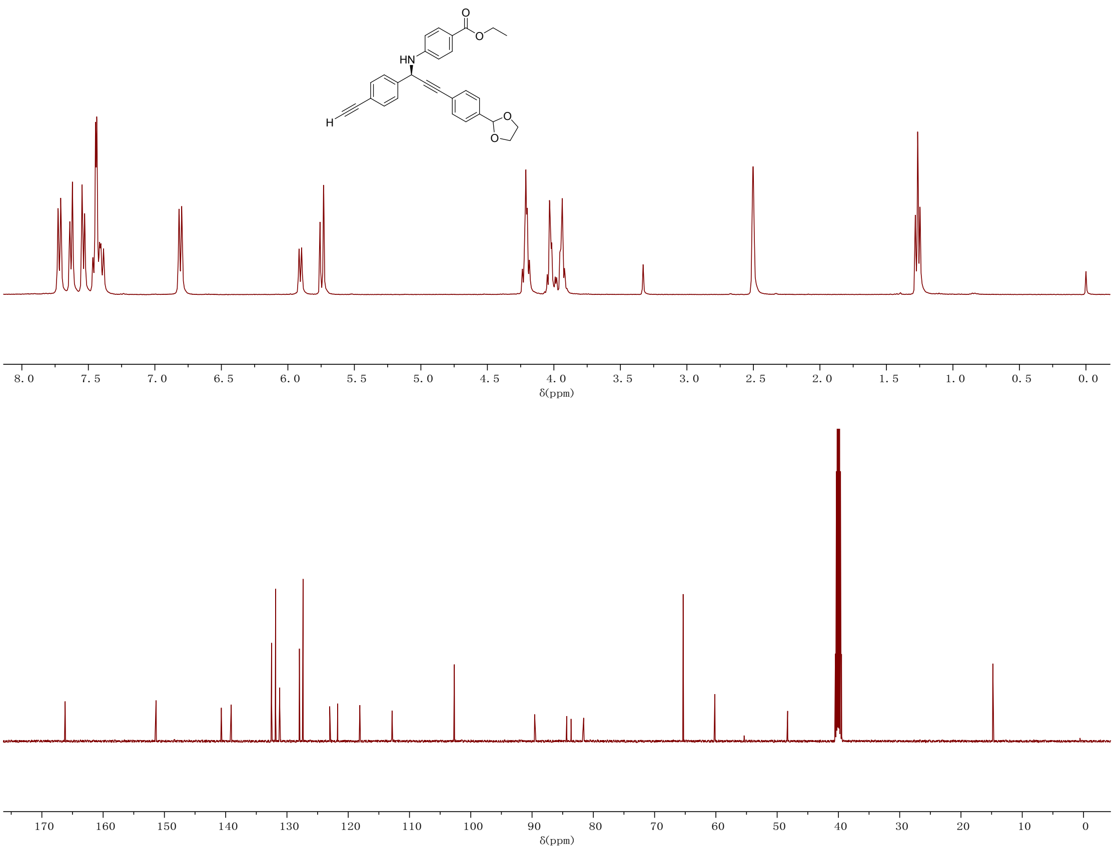


HPLC spectra of racemic standard substance (red) and compound **5k** before (black) and after (blue) recrystallization using CHIRALPAK ID. Eluent: *n*-hexane/*i*-propanol = 85/15, v/v, 1 ml/min

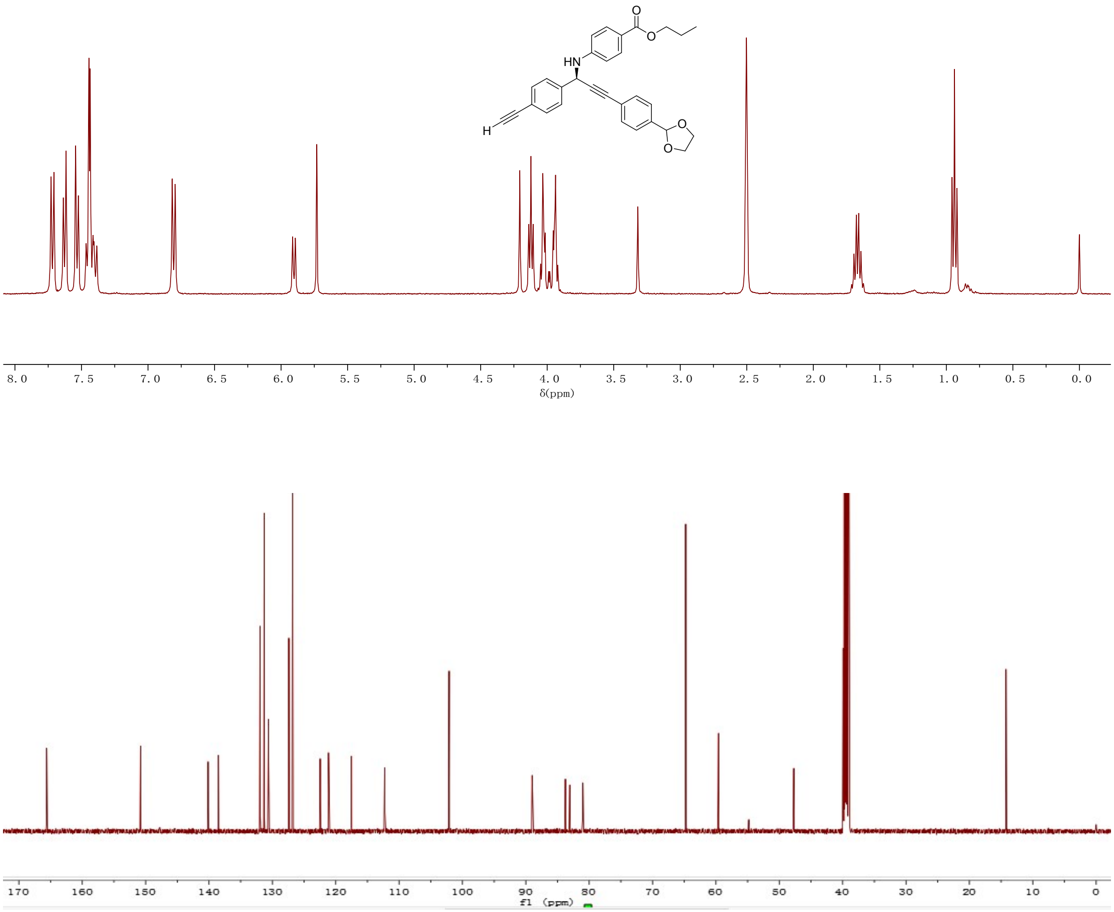
3. ^{1}H and ^{13}C NMR spectra of the intermediates



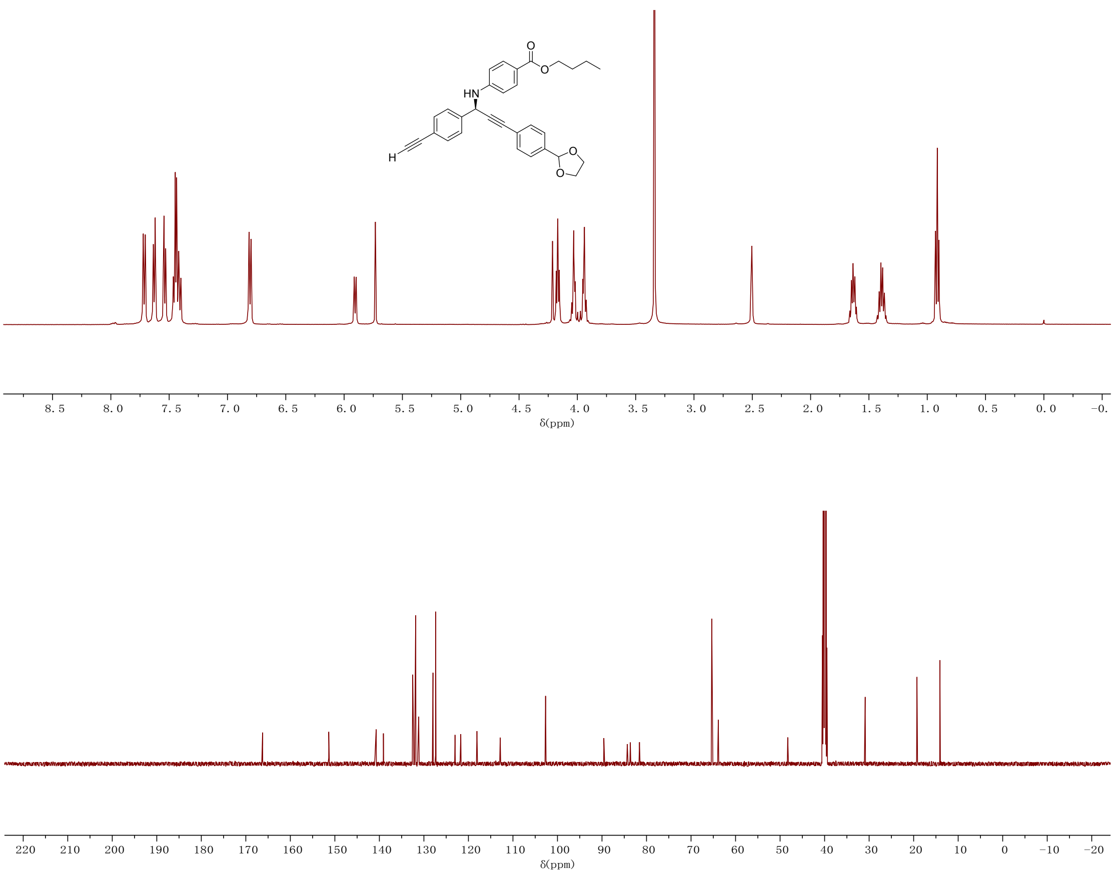
The ^{1}H(top) and ^{13}C NMR (bottom) spectra of **4a** in d_6-DMSO



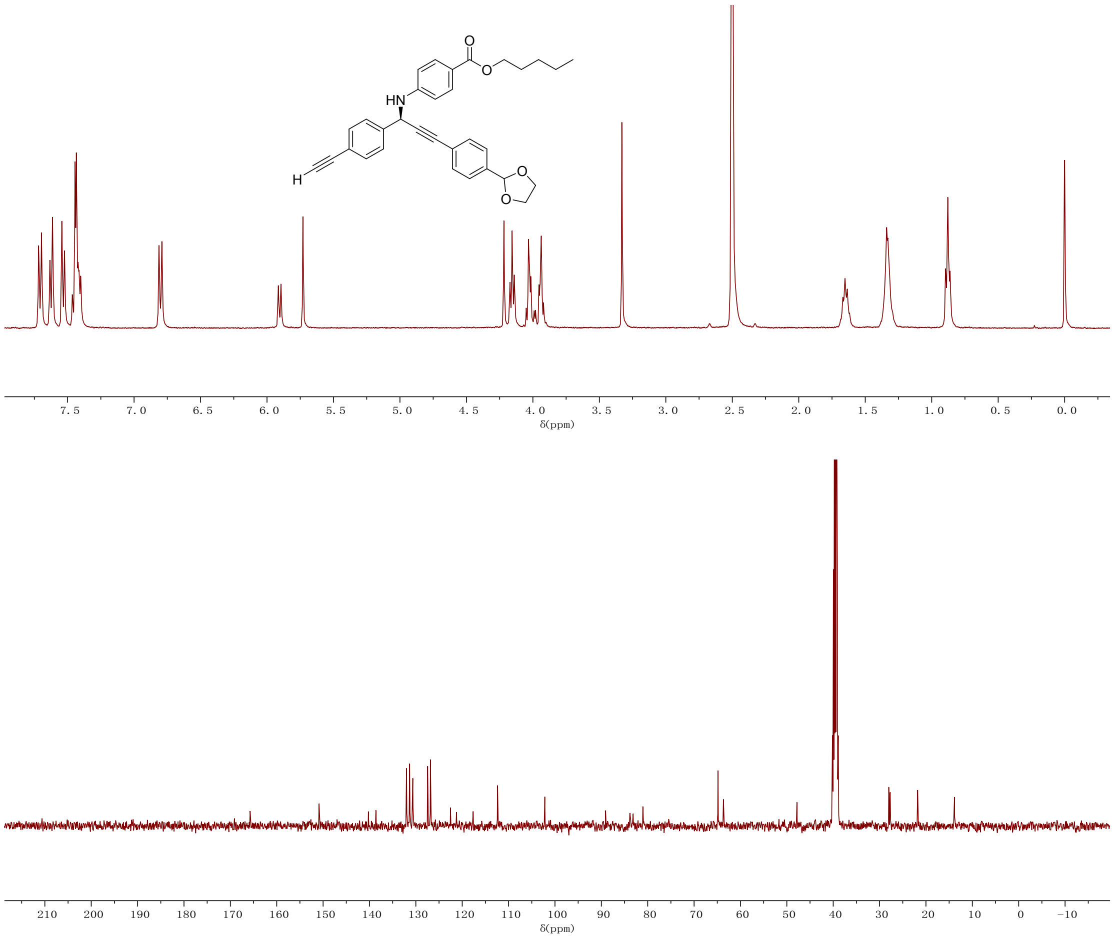
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4b** in d_6-DMSO



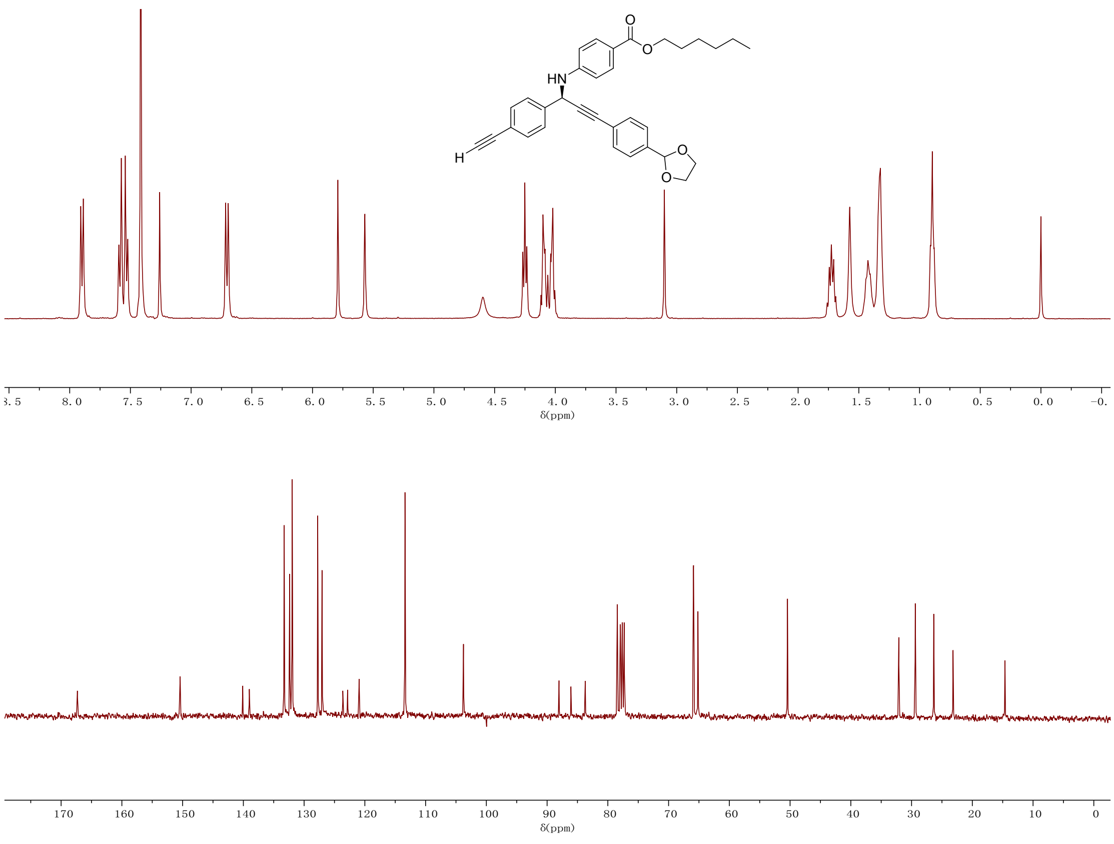
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4c** in *d*$_6$-DMSO



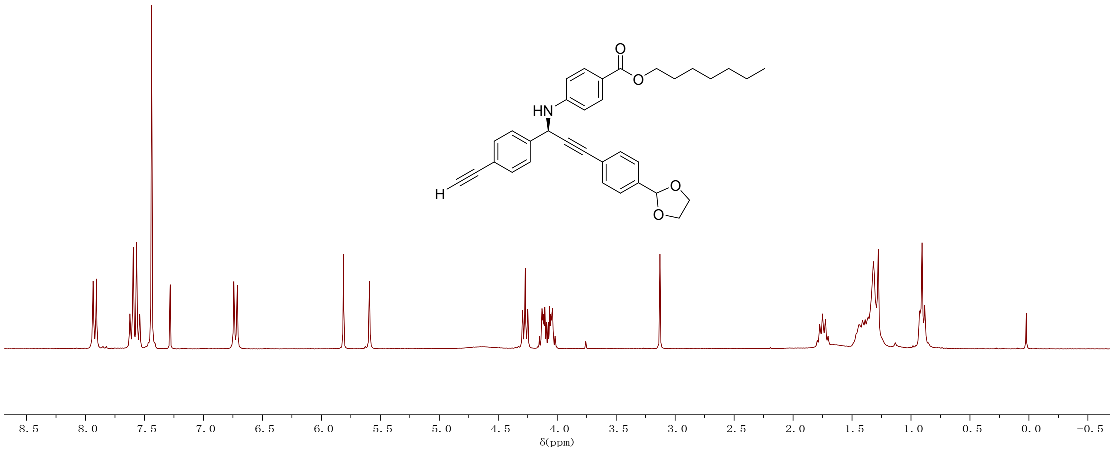
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4d** in *d*$_6$-DMSO

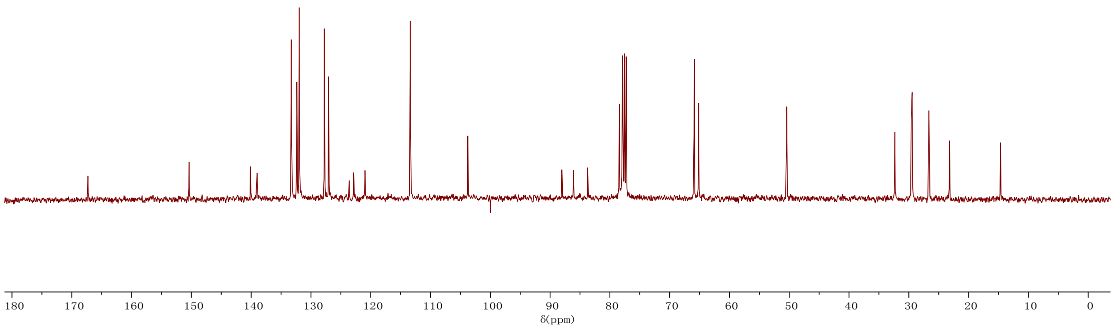


The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4e** in d_6-DMSO

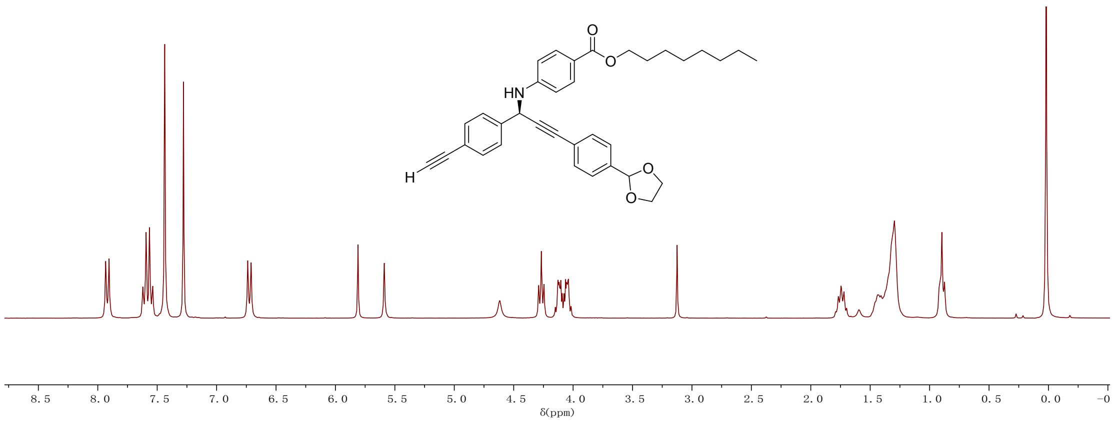


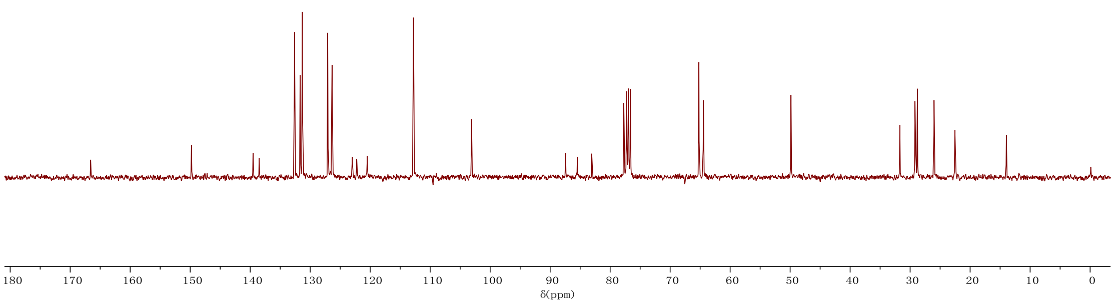
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4f** in $CDCl_3$



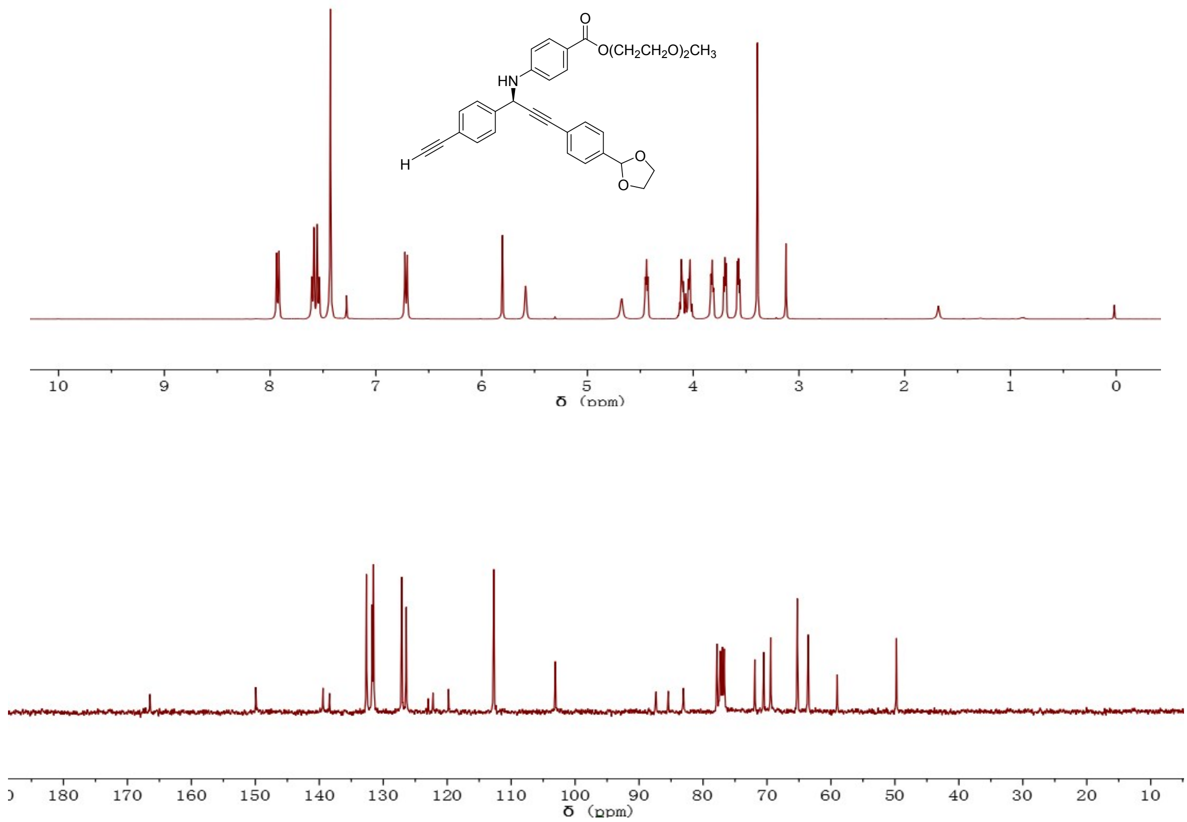


The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4g** in $CDCl_3$

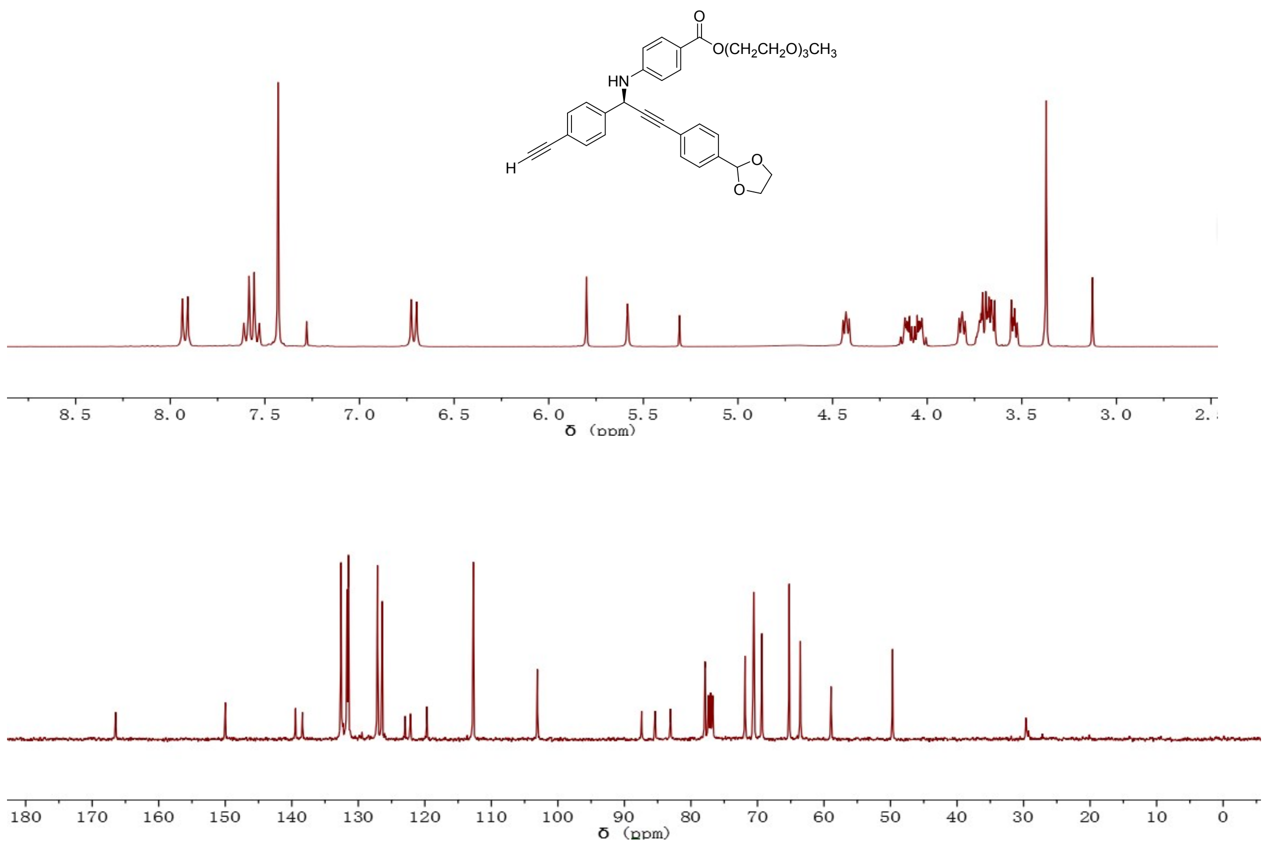




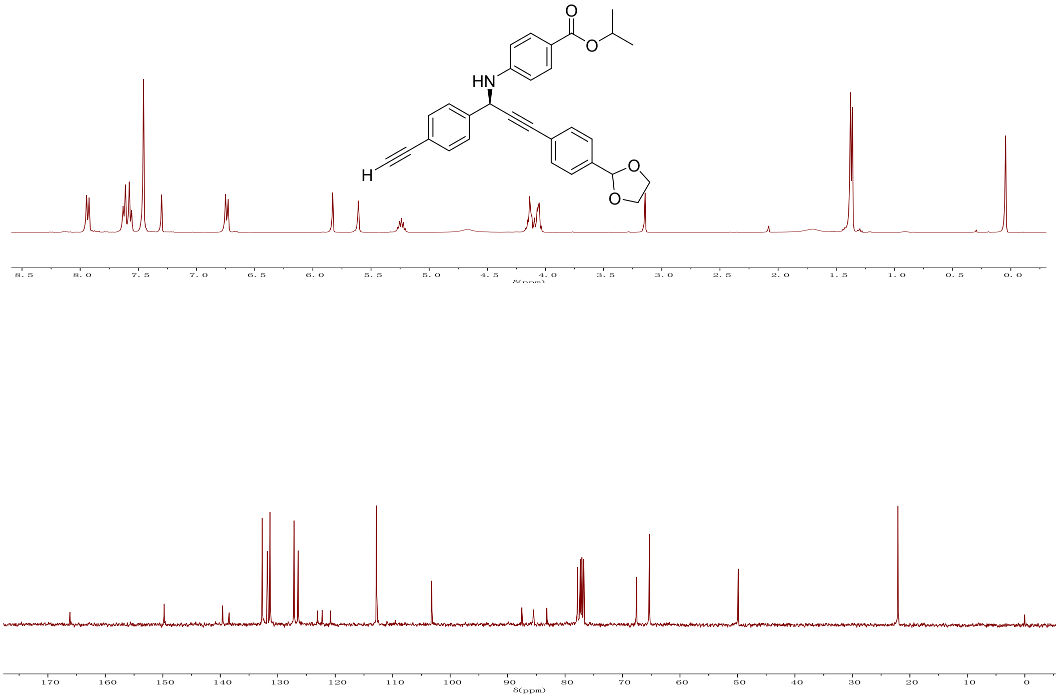
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4h** in d_6-DMSO



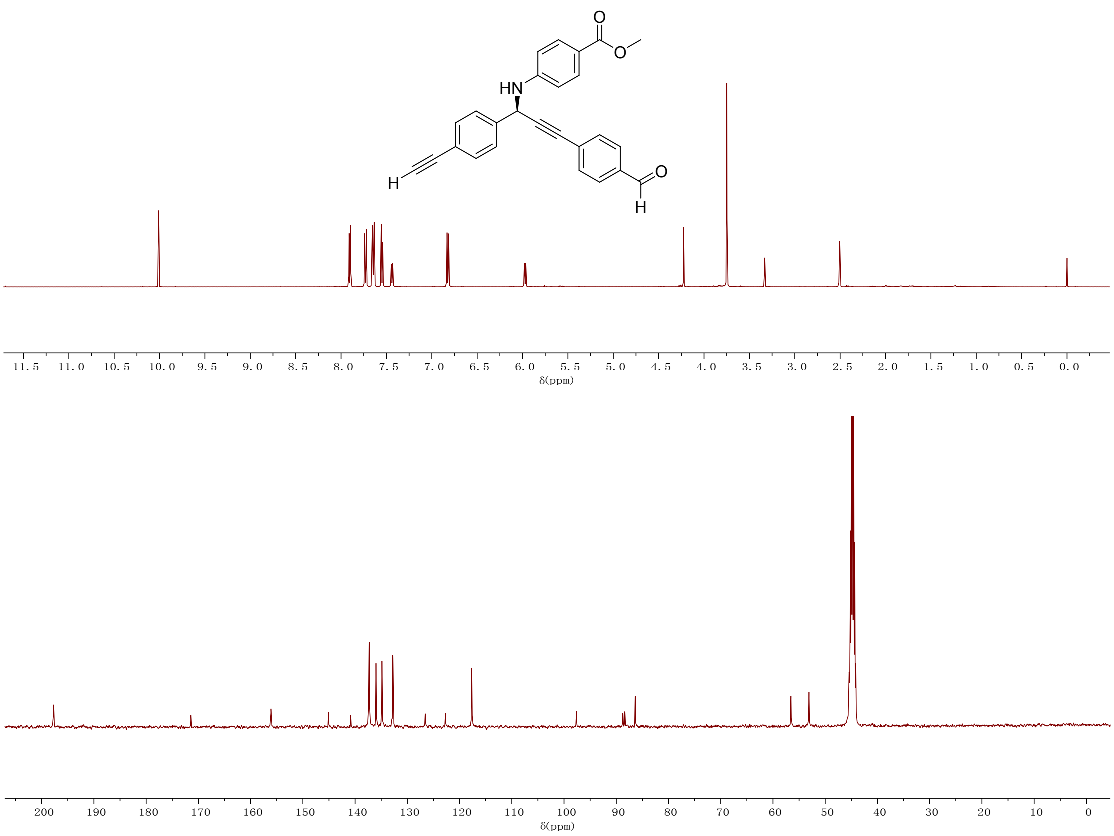
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4i** in $CDCl_3$



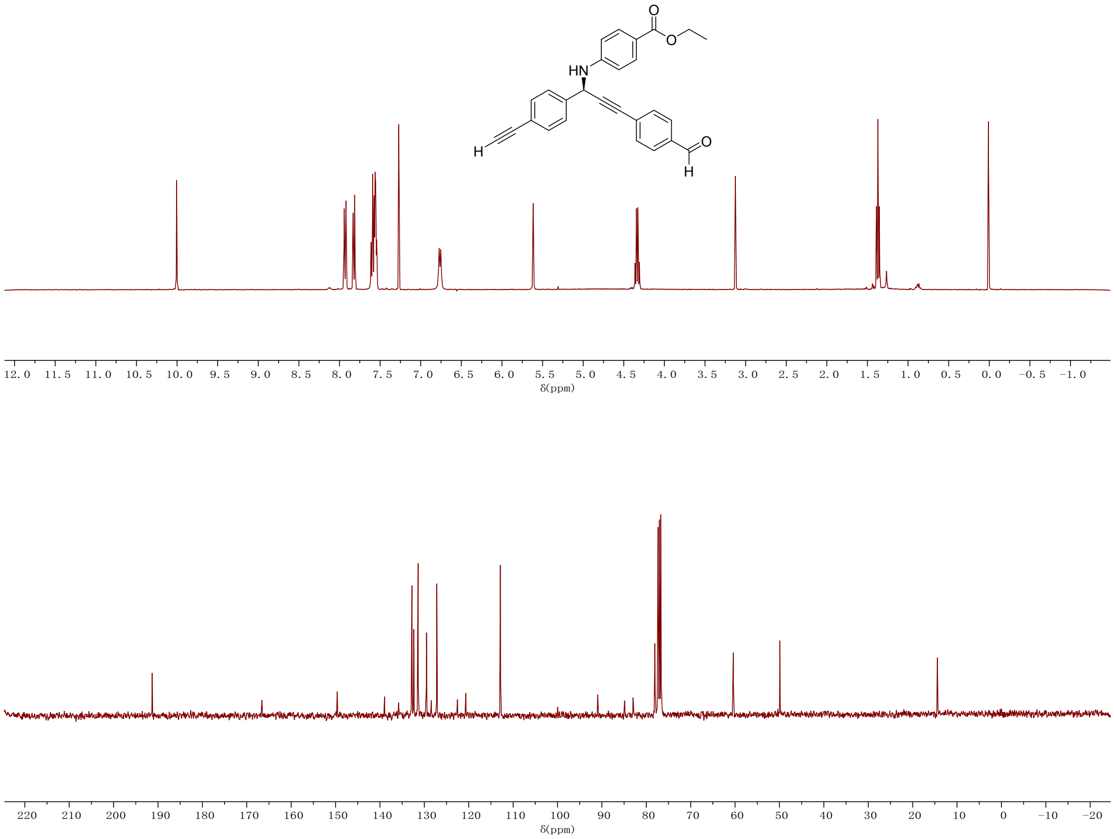
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4j** in $CDCl_3$



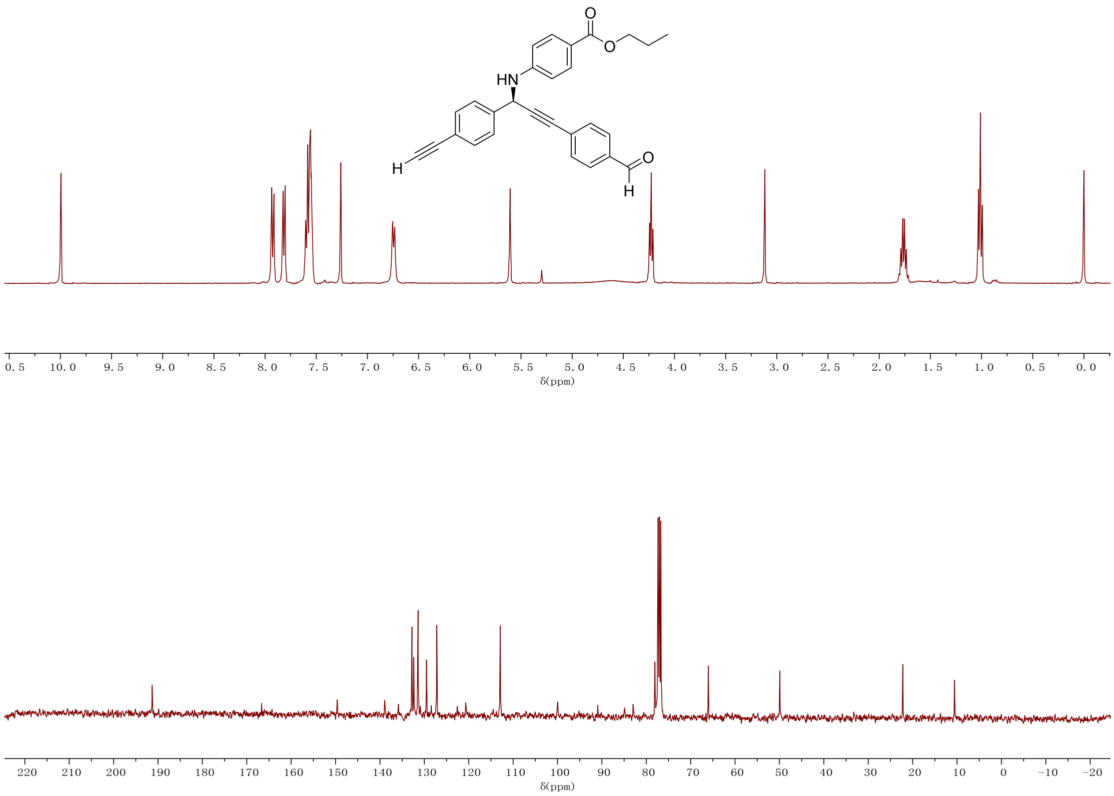
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **4k** in $CDCl_3$



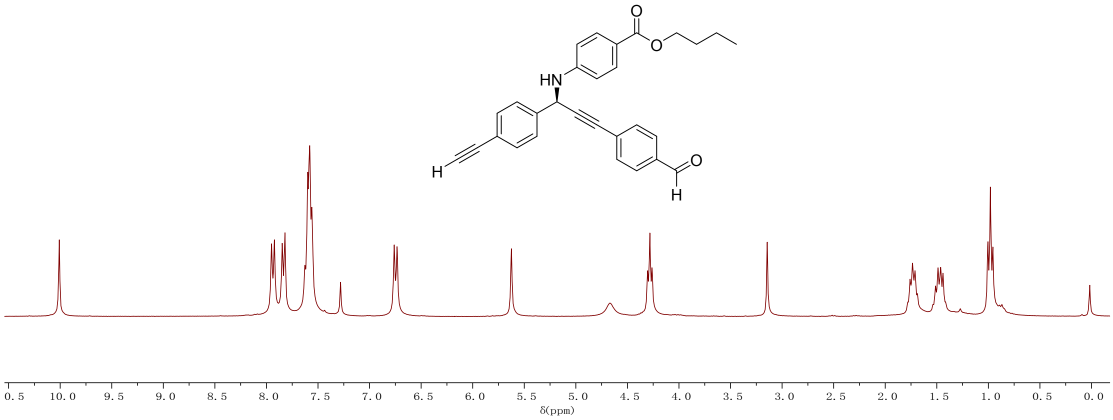
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5a** in d_6-DMSO

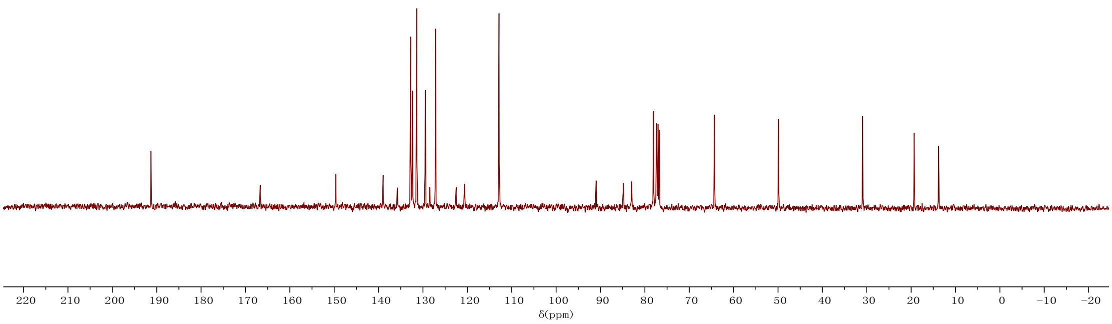


The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5b** in $CDCl_3$

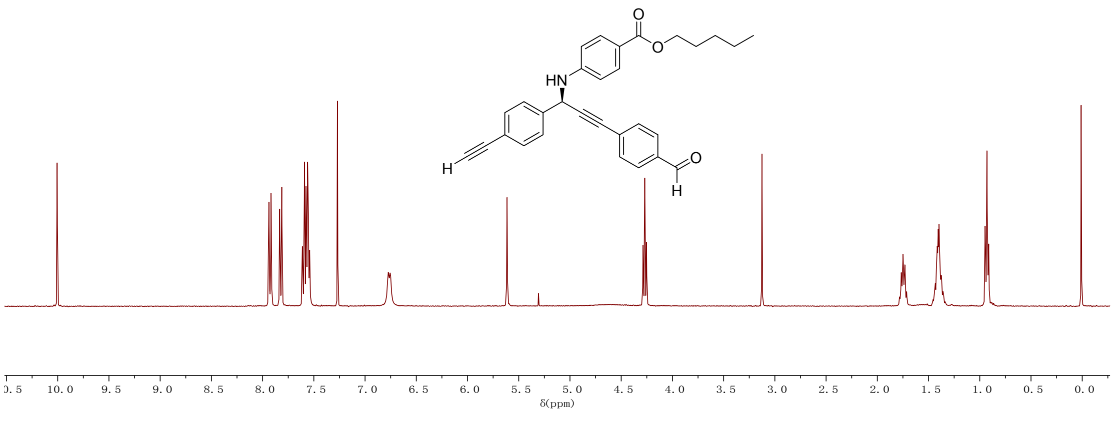


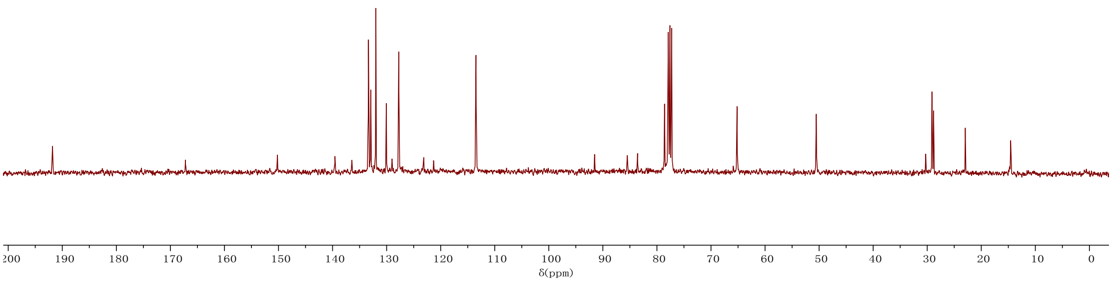
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5c** in $CDCl_3$



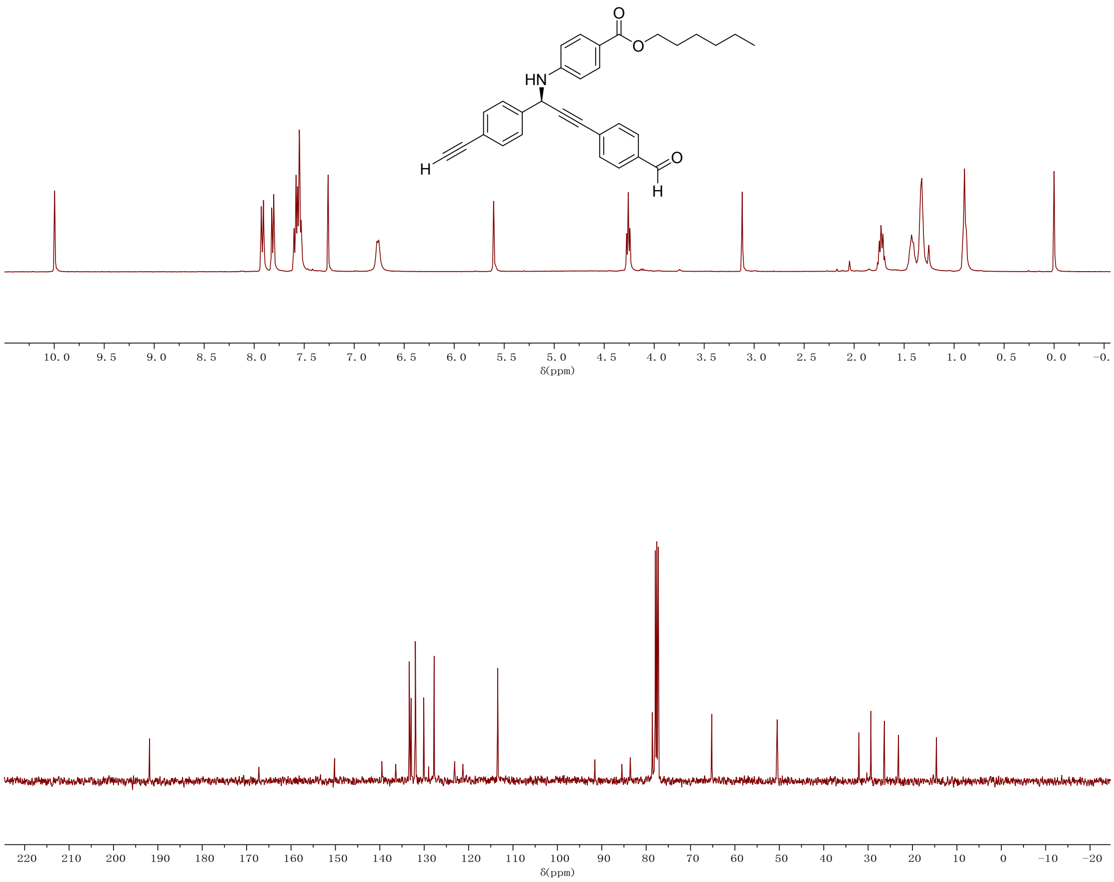


The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5d** in $CDCl_3$

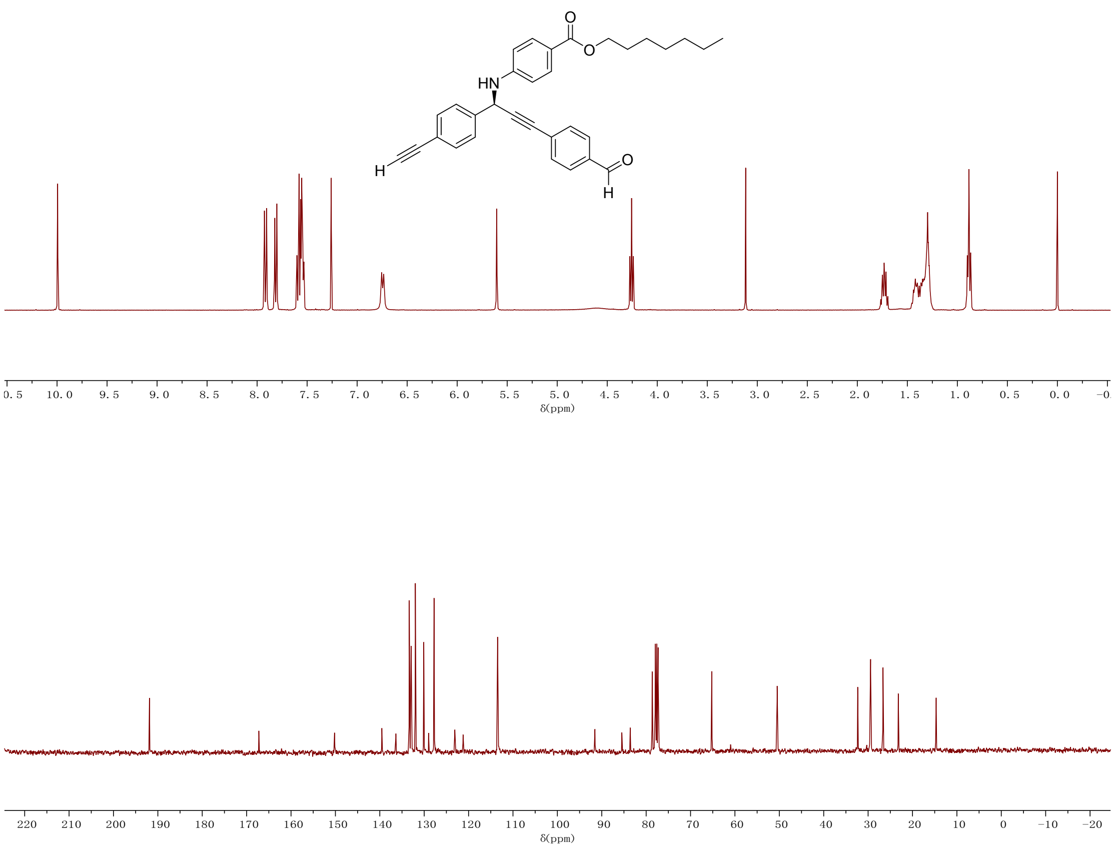




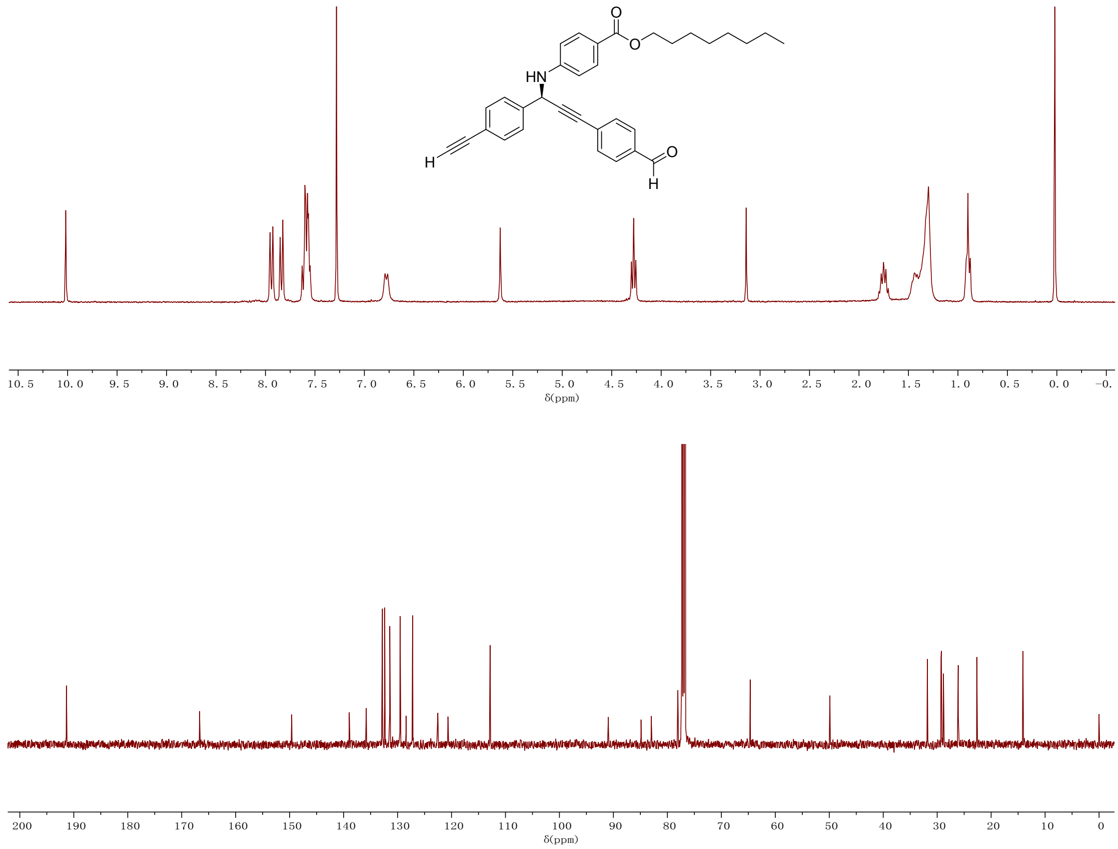
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5e** in $CDCl_3$



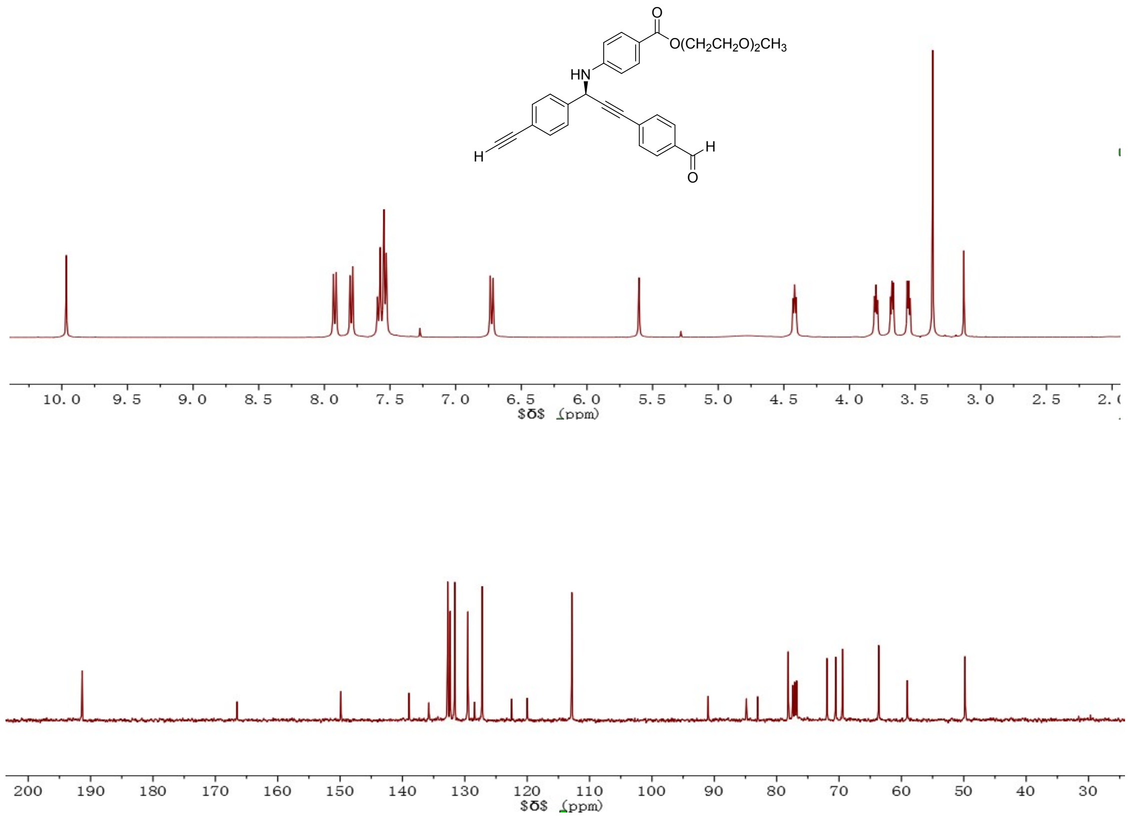
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5f** in $CDCl_3$



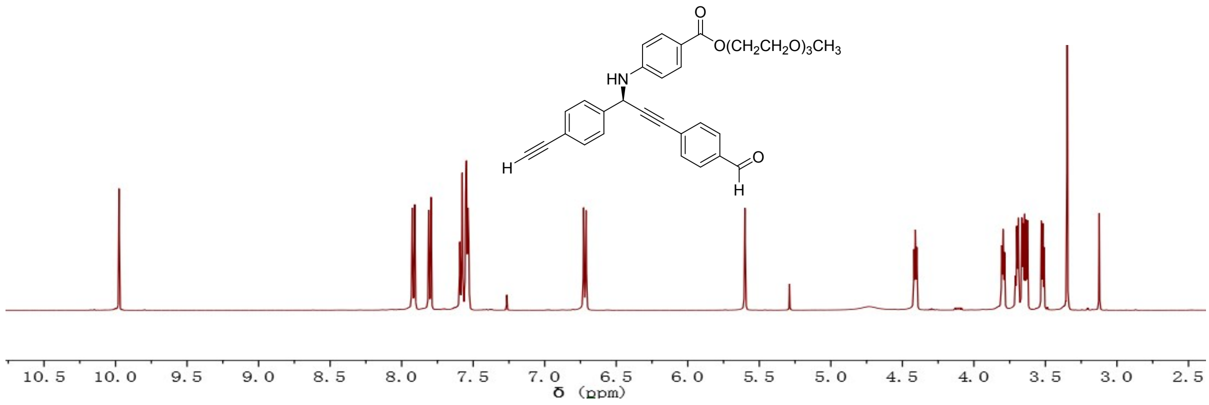
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5g** in $CDCl_3$

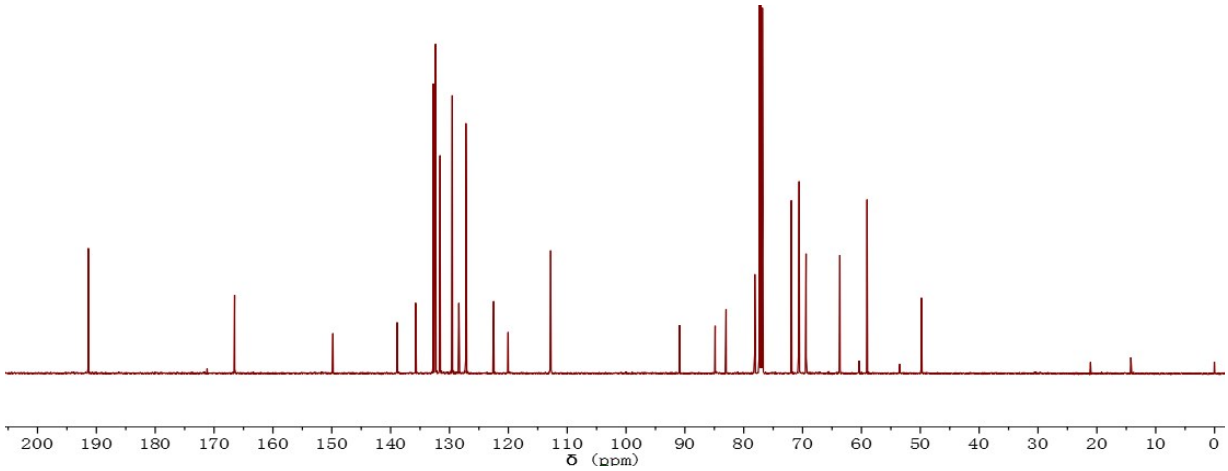


The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5h** in $CDCl_3$

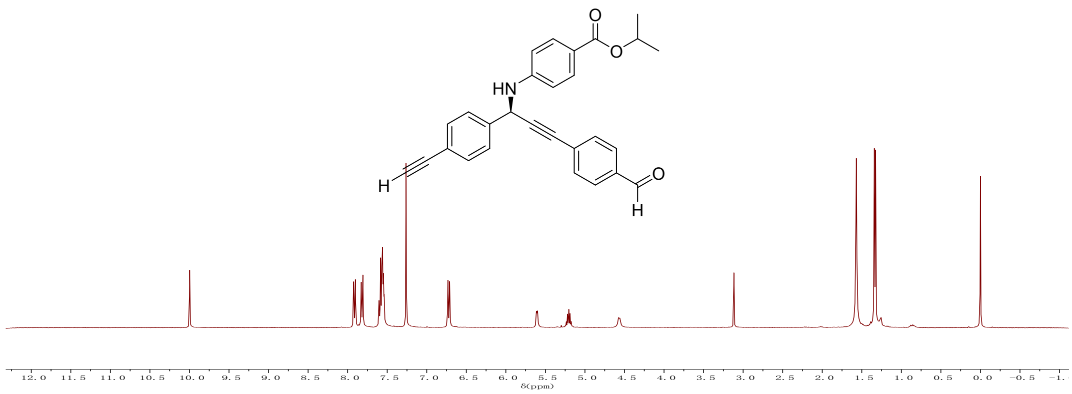


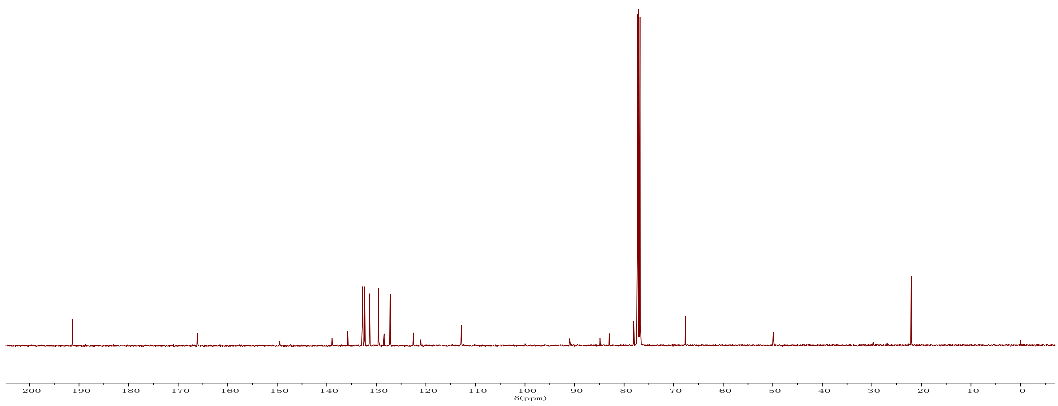
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5i** in $CDCl_3$





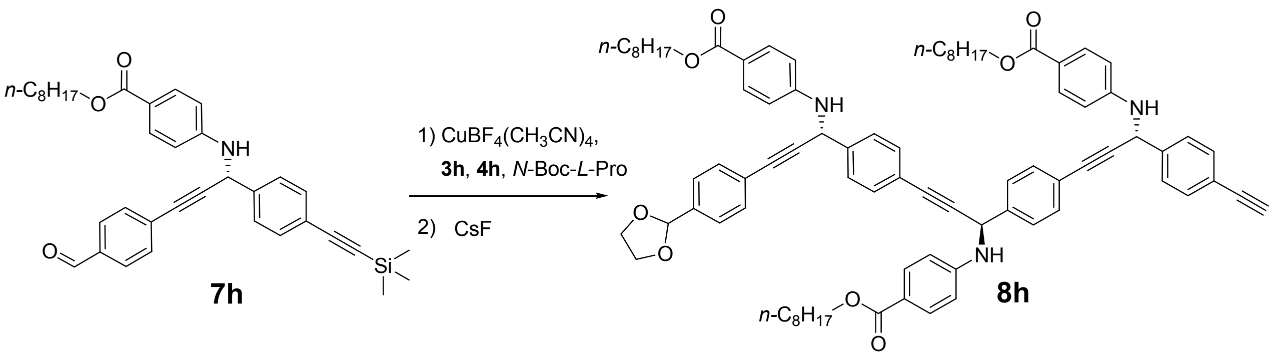
The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5j** in $CDCl_3$





The ^{1}H (top) and ^{13}C NMR (bottom) spectra of **5k** in $CDCl_3$

4. Characterization of M*p*-PE tetramer **8h**.



8h (Yield, 70% for two steps): $[\alpha]_D^{20}$ = 97.3 (0.25, THF). IR (KBr; cm^{-1}): υ_{max} 3363, 2927, 2855, 2219, 1706, 1605, 1521, 1468, 1411, 1273, 1176, 1107, 839, 770. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.85 (m, 6H), 7.65-7.39 (m, 16H), 6.72-6.69 (m, 6H), 5.63-5.53 (m, 3H), 4.60 (s, 3H), 4.26 (t, *J* = 6.6 Hz, 6H), 4.12-4.03 (m, 4H), 3.12 (s, 1H), 1.78-1.69 (m, 6H), 1.46-1.29 (m, 30H), 0.89 (t, *J* = 4.8 Hz, 9H). HRMS (MALDI-TOF) *m/z* 1280.6671. ([$C_{68}H_{61}N_3O_8$+Na^+] Calcd 1280.6704).

The diastereomer (*R*,*S*,*R*)-**8h** was prepared using similar methods by *N*-Boc-*D*-proline as catalyst (Yield, 61% for two steps). $[\alpha]_D^{20}$ = 68.1 (0.36, THF). IR (KBr; cm^{-1}): υ_{max} 3365, 2930, 2850, 2220, 1705, 1602, 1520, 1467, 1410, 1272, 1175, 1110, 839, 769, 698. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.84 (m, 6H), 7.63-7.54 (m, 10H), 7.49-7.43 (m, 8H), 6.81-6.64 (m, 6H), 5.63-5.54 (m, 3H), 4.63-4.59 (m, 3H), 4.27 (t, *J* = 6.6 Hz, 6H), 4.18-3.94 (m, 4H), 3.13 (s, 1H), 1.79-1.70 (m, 6H), 1.41-1.19 (m, 24H), 0.96-0.83 (m, 9H). HRMS (MALDI-TOF) *m/z* 1280.6670. ([$C_{68}H_{61}N_3O_8$+Na^+] Calcd 1280.6704).

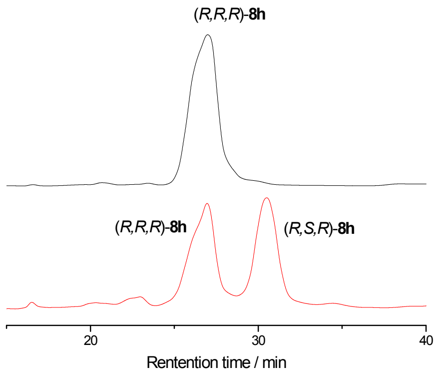
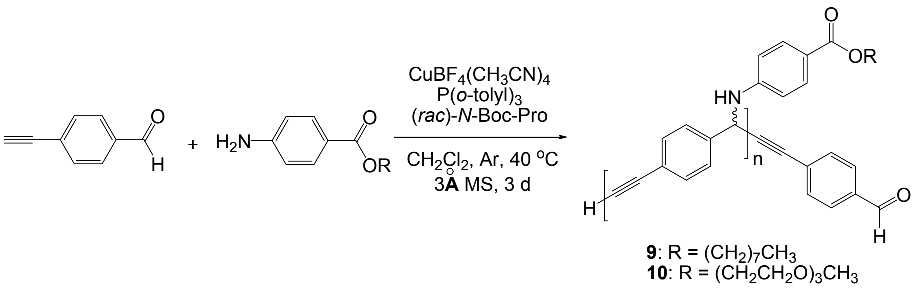


Fig. S14 HPLC analysis of (*R,R,R*)-**8h** using CHIRALPAK ID.

Eluent: *n*-hexane/dichloromethane/*i*-propanol (v/v/v) = 40.63/24.37/35, 0.3 ml/min.

The diastereomer (*R*,*S*,*R*)-**8h** was hardly detected by HPLC in the product of (*R*,*R*,*R*)-**8h**. This suggested that the polymerization method to all-*R* product was reliable.

5. Characterization of foldamers **9-10** with disordered *R*/*S* chiral units



9: yield 60%. M_n = 2451 g/mol, M_w = 3311 g/mol, PDI = 1.35. IR (KBr; cm^{-1}): υ_{max} 3360, 2954, 2924, 2852, 2733, 2106, 1923, 1705, 1666, 1606, 1520, 1465, 1272, 1214, 1173, 1105, 1012, 975, 840, 768, 699. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.05-7.72 (m, 14H), 7.72-7.35 (m, 54H), 6.84-6.49 (m, 14H), 5.66-5.51 (m, 7H), 4.69-4.54 (m, 7H), 4.48-4.01 (m, 14H), 3.13 (s, 1H), 1.86-1.59 (m, 14H), 1.53-1.12 (m, 70H), 0.96-0.77 (m, 21H).

10: yield 60%. M_n = 2761 g/mol, M_w = 3547 g/mol, PDI = 1.29. IR (KBr; cm^{-1}): υ_{max} 3360, 2877, 2733, 2102, 1701, 1663, 1599, 1524, 1452, 1411, 1272, 1214, 1167, 1098, 1012, 982, 843, 768, 699. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.01-7.74 (m, 14H), 7.70-7.33 (m, 54), 6.90-6.53 (m, 14H), 5.58 (s,7H), 4.67 (s,7H), 4.60-4.26 (m, 14H), 3.90-3.78 (m, 14H), 3.76-3.59 (m, 42H), 3.60-3.45 (m, 28H), 3.44-3.25 (m, 21H), 3.14 (s, 1H).

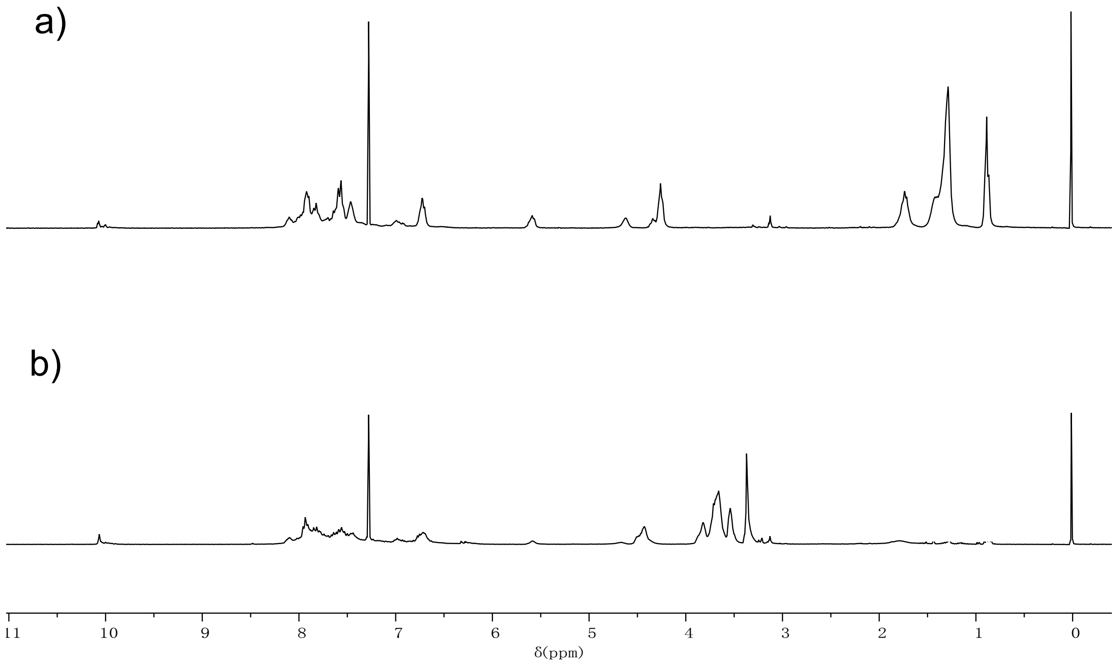


Fig. S15 The ^{1}H NMR spectra of foldamers **9** (a) and **10** (b) in $CDCl_3$

6. Dynamic light scattering diagrams of vesicular assemblies

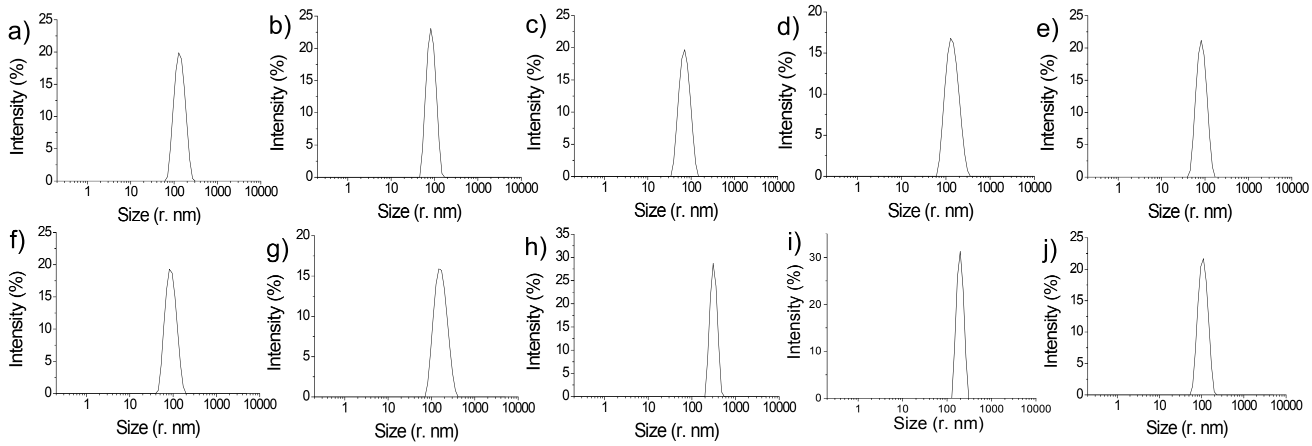


Fig. S16 Dynamic light scattering diagrams of as-synthesized vesicular assemblies **6a-j** (a-j) of 0.02 mg/mL in CH_2Cl_2/*n*-C_6H_{14} (1/5, v/v) at room temperature.

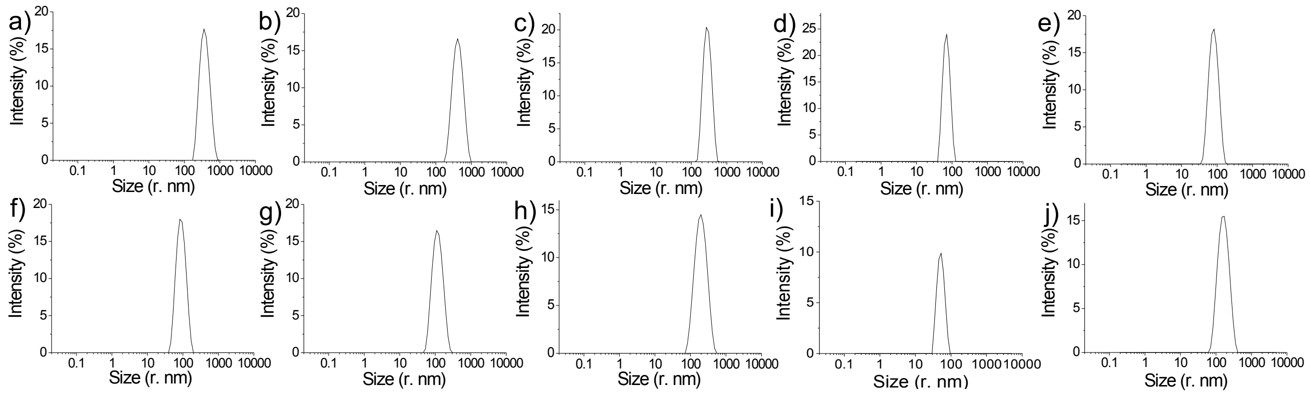


Fig. S17 Dynamic light scattering diagrams of as-synthesized vesicular assemblies **6a-j** (a-j) of 0.02 mg/mL in CH_2Cl_2/CH_3OH (1/5, v/v) at room temperature.

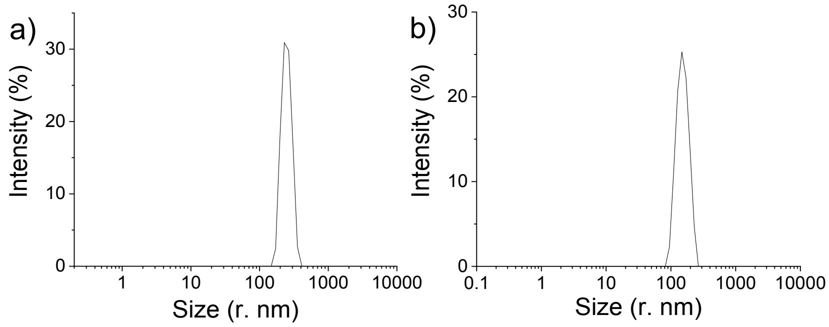


Fig. S18 Dynamic light scattering diagrams of as-synthesized vesicular assemblies **6h** (a) and **6j** (b) of 0.02 mg/mL in THF/H_2O (1/5, v/v) at room temperature.

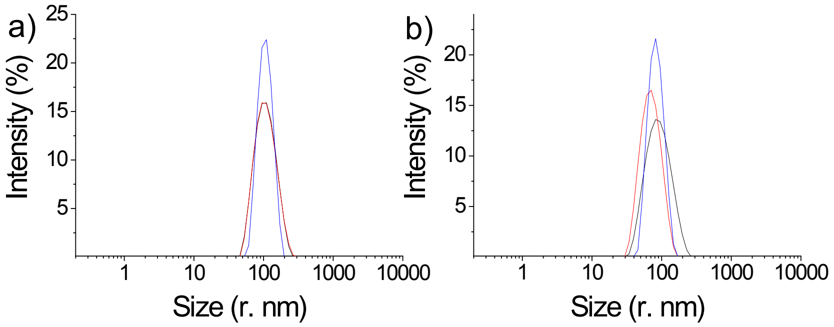


Fig. S19 Dynamic light scattering diagrams of as-synthesized vesicular assemblies **6b** (a) and **6f** (b) in $CH_2Cl_2/n\text{-}C_6H_{14}$ with the volumetric ratio of 1/3 (black), 1/4 (red) and 1/5 (blue), respectively.

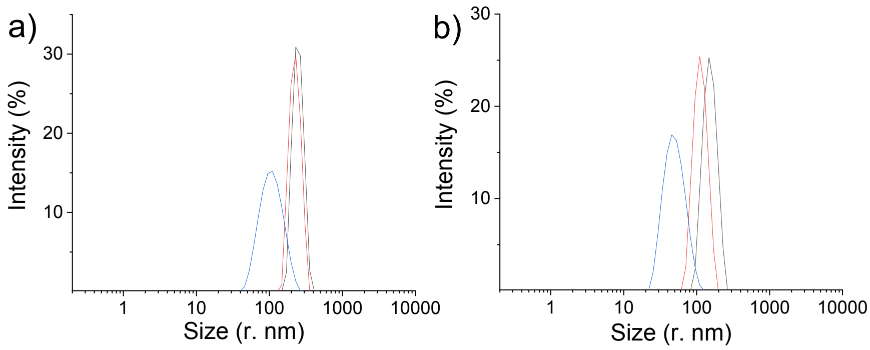


Fig. S20 Dynamic light scattering diagrams of vesicular assemblies **6h** (a) and **6j** (b) of 0.02 mg/mL in THF/H_2O (1/5, v/v) at room temperature. Black line, as prepared; red line, after kept for two weeks; blue line, after dialysis in H_2O.

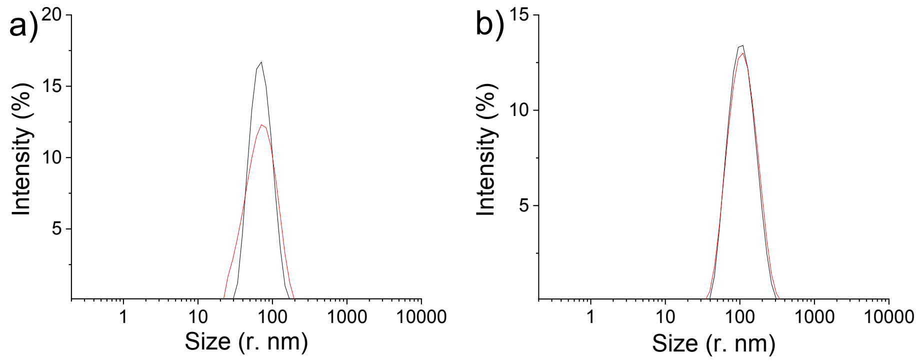


Fig. S21 Dynamic light scattering diagrams of vesicular assemblies **6h** (a) and **6j** (b) of 0.02 mg/mL in H_2O (1/5, v/v) at room temperature. Black line, after dialysis in H_2O; red line, after kept for two weeks.

7. SEM images of vesicular assembly **6c** in CH_2Cl_2/*n*-C_6H_{14} at different storage time

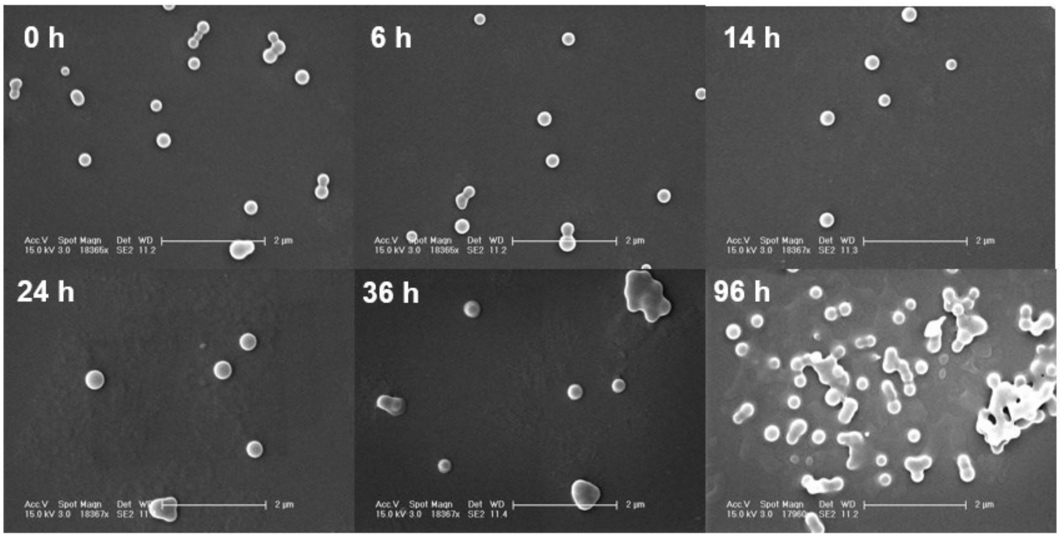


Fig. S22 SEM images of vesicular assembly **6c** of different storage time (0, 6, 14, 24, 36 and 96 h) in CH_2Cl_2/*n*-C_6H_{14} (1/5, v/v) at room temperature. Concentration, 0.02 mg/mL.

8. Fluorescence spectra of foldamers **6a-j** in different solvent systems

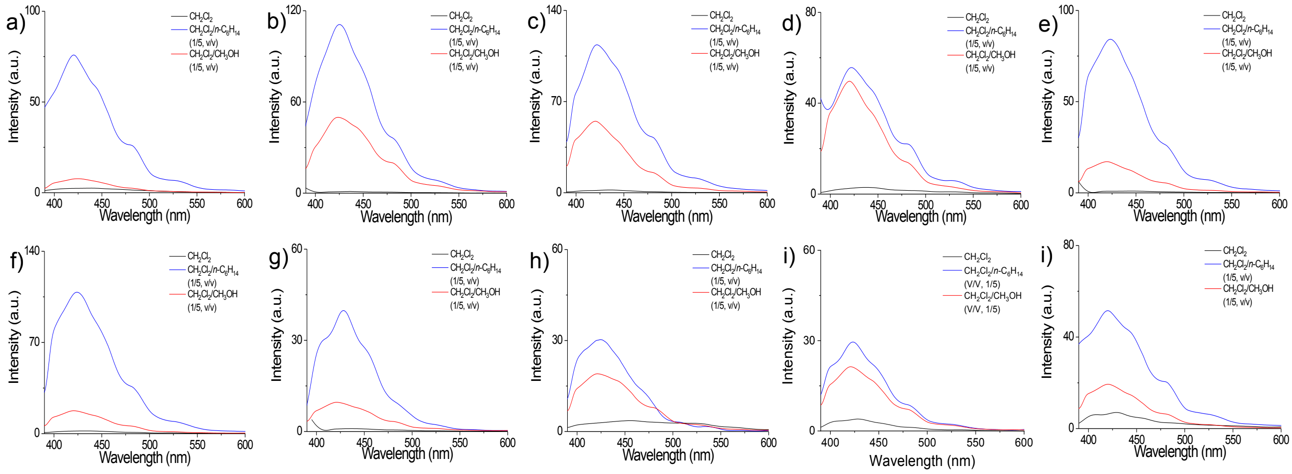


Fig. S23 Fluorescence spectra of foldamers **6a** (a), **6b** (b), **6c** (c), **6d** (d), **6e** (e), **6f** (f), **6g** (g), **6h** (h), **6i** (i) and **6j** (j) of 0.02 mg/ml in different solvent systems. λ_{ex}, 370 nm.

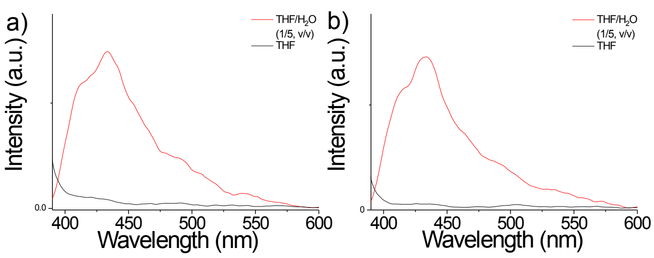


Fig. S24 Fluorescence spectra of foldamers **6h** (a) and **6j** (b) of 0.02 mg/ml in THF and THF/H_2O. λ_{ex}, 370 nm

9. The statistical data of shell thicknesses of vesicle-like particles in different solvent systems

Table S1 The statistical data of shell thicknesses of vesicle-like particles in different solvent systems[a]

Foldamer	CH_2Cl_2/*n*-C_6H_{14}	CH_2Cl_2/CH_3OH	THF/H_2O
6a	4.4-6.1 nm	8.1-11.6 nm	-
6b	4.3-5.6 nm	6.7-9.8 nm	-
6c	4.3-5.8 nm	6.5-8.3 nm	-
6d	4.7-7.1 nm	5.2-7.8 nm	-
6e	4.2-6.3 nm	7.3-10.0 nm	-
6f	3.9-5.9 nm	1.9-11.0 nm	-
6g	4.3-6.1 nm	7.1-9.7 nm	-
6h	4.9-7.2 nm	8.2-11.4 nm	8.6-10.9 nm
6i	3.9-5.5 nm	8.6-10.2 nm	
6j	4.5-7.3 nm	7.9-10.6 nm	8.3-10.4 nm

[a] The shell thicknesses of vesicular assemblies of each foldamer were measured ten times using TEM images.

The shell thicknesses of these vesicular assemblies are not evidently relative to side chain length of foldamers, possibly due to the roughness of uranyl acetate staining method.

10. Reference

1. X. Li, L. Guo, M. Casiano-Maldonado, D. Zhang, C. Wesdeminotis, *Macromolecules*, 2011, **44**, 4555-4564