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TRIPOD-LIKE COMPOUNDS: SYNTHESES OF TRIS(p- OR o-AMINO PHENOXYMETHYL)-PROPANE, TRIS(p- OR o-AMINO PHENOXYETHYL)AMINE, AND THEIR SCHIFF BASE OR SALICYL DERIVATIVES

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ABSTRACT

Tris(nitrophenoxymethyl)propane and tris(nitrophenoxy ethyl)amine, prepared by the reaction of trimethylol propane or triethanol amine with p- or o-chloronitrobenzene, were reduced to give the corresponding amines. The amines condensed with 2-pyridinecarboxaldehyde, 2-quinoline-carboxaldehyde, or salicylaldehyde to give the tripod Schiff bases. The tripodal salicylamides were obtained by condensation of salicylic acid with the amines in the presence of phosphorus trichloride.

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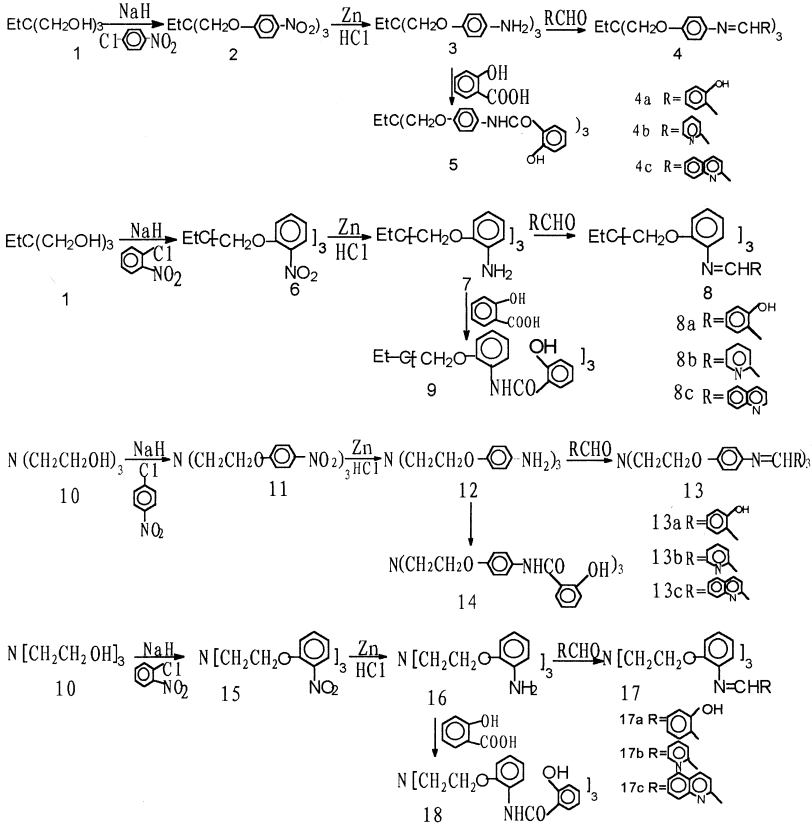
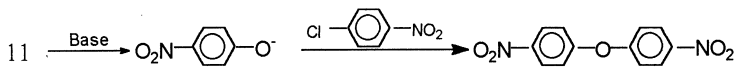
Tripodal ionophores are attracting considerable attention in the area of coordination chemistry.[1–4] The attachment of three flexible, donor-atom-containing chains to a framework leads to tripodal ligands, which can form complexes with many cations, such as alkali metal, alkaline earth metal, and transition metal cations. The ligands can be used for the analysis and separation of metal ions,[5–7] as well as for many catalytical or biological applications.[8–14] Our interest in the effective coordination between transition metal ions and organic ligands, and in understanding the mechanism of molecular transportation in organisms, prompted us to design and synthesize a series of new tripod-like compounds containing phenyl, pyridyl, salicyl, or quinolyl groups, which are usually biologically active. The preliminary experiments indicated that these tripod-like



Scheme 1.

compounds had excellent coordination ability with alkali metal, alkaline earth metal, and transition metal. In this paper, we report the syntheses of these new tripod-like compounds. The basic tripodal structure was constructed from trimethylol propane and triethanol amine. The synthetic routes are shown in Scheme 1.

The reaction of trimethylol propane **1** with o- or p-chloronitrobenzene in the presence of sodium hydride gave the corresponding nitro compounds **2** or **6**. This nucleophilic substitution reaction took place easily and occurred with an exotherm in a suitable solvent such as DMSO, DMF, or THF. However, when the procedure was applied to triethanol amine **10** and p-chloronitrobenzene, a side reaction occurred, and 4,4′-dinitrophenyl ether was isolated. This might result from the reaction of p-chloronitrobenzene with p-nitrophenolate, which was possibly generated from the decomposition of the desired product **11** (see Scheme 2). To prevent this side reaction, the reaction of riethanol amine **10** with p-chloronitrobenzene had to be carried out under mild conditions, and only DMSO could be used as solvent. The reaction of triethanol amine **10** with o-chloronitrobenzene was carried out analogous to the reaction with p-chloronitrobenzene. All the nitro compounds were readily reduced by zinc powder or iron powder in acid, giving the corresponding triamines 3, 7, 12, and 16. The triamines reacted with salicylaldehyde, 2-pyridinecarboxaldehyde, or 2-quinolinecarboxaldehyde to give the corresponding Schiff bases 4, 8, 13, and 17. Also, when the triamines were treated with salicylic acid in the presence of phosphorus trichloride, the corresponding salicylamides 5, 9, 14, and 18 were isolated.



Scheme 2.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer FTIR1750 spectrophotometer.^{1}H NMR spectra were recorded on a Bruke-DPX400 spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. DMSO was dried (CaH_2) and distilled at reduced pressure. All other reagents were used as commercial grade.

Preparation of the Nitro Compounds: General Procedure

A mixture of 0.1 mol (13.4 g) of trimethylol propane **1** (or triethanol amine **10**) and 0.3 mol (11.5 g) of sodium hydride (60% suspension in paraffin oil) in 30 mL of petroleum ether was stirred and refluxed for about 20 m. The mixture was cooled and petroleum ether was decanted. Dry DMSO (50 mL) was added to the residue solid. The suspension was stirred for another 10 m. A solution of 0.4 mol (63 g) of p-chloronitrobenzene (or o-chloronitrobenzene) in 40 mL of dry DMSO was added dropwise to the suspension with stirring and cooling. The temperature was kept below 30°C throughout the addition process. The resulting dark-brown solution was stirred at 30°C for about 20 h, and poured into 2 L of cold water. The oil separated was treated with steam distillation to separate the excess chloronitrobenzene. The residues were purified by recrystallization (for a solid) or by chromatography (for an oil).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}p)\text{-}NO_2]_3$ (**2**)

Yield 85%. Yellow solid, m.p. 177°–179°C (acetone). Anal. found (%): C, 58.18; H, 4.73; N, 8.35. Calc. for $C_{24}H_{23}N_3O_9$: C, 57.95; H, 4.63; N, 8.45. IR (cm^{-1}), 1595, 1508, 1337, 1300, 1253, 1110, 1032, 850. ^1H NMR: δ (ppm)1.07(t, 3H, CH_3), 1.92 (q, 2H, CH_2C), 4.44 (s, 6H, $3CH_2O$), 7.22 ~ 8.19 (d, 12H, Ar-H).

$CH_3CH_2[CH_2O\text{-}(C_6H_4\text{-}o)\text{-}NO_2]_3$ (**6**)

Yield 78%. Yellow solid, m.p. 97°C (ethanol) Anal. found (%): C, 57.99; H, 4.68; N, 8.33. Calc. for $C_{24}H_{23}N_3O_9$: C, 57.95; H, 4.63; N, 8.45. IR (cm^{-1}): 1608, 1523, 1352, 1283, 1160, 1012, 857, 741. ^1H NMR: δ (ppm) 0.97 (t, 3H, CH_3), 1.91 (q, 2H, CH_2C), 4.34(s, 6H, $3CH_2O$), 7.07 ~ 7.88 (m, 12H, Ar-H).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}p)\text{-}NO_2]_3$ (**11**)

Yield 73%. Yellow Solid, m.p. 96°C (acetone). Anal. found (%): C, 56.34; H, 4.69; N, 10.81. Calc. for $C_{24}H_{24}N_4O_9$: C, 56.25; H, 4.69; N, 10.94. IR(cm^{-1}, KBr pellet): 3120, 1510, 1340, 1260, 1020, 1170, 840. ^1H NMR: δ (ppm) 3.24 (t, 6H, $3NCH_2$), 4.20 (t, 6H, $3CH_2O$), 6.94(d, 6H, Ar-H), 8.19 (d, 6H, Ar-H).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}NO_2]_3$ (**15**)

Yield 69%. Brown oil (chloroform as eluent). Anal. found (%): C, 56.39; H, 4.73; N, 10.88. Calc. for $C_{24}H_{24}N_4O_9$: C, 56.25; H, 4.69; N, 10.94. IR (cm^{-1}): 1607, 1583, 1521, 1354, 1275, 1160, 1037, 851, 744. ^1H NMR: δ (ppm) 3.29 (t, 6H, 3 NCH_2), 4.24 (t, 6H, $3CH_2O$), 6.97 ~ 7.82 (m, 12H, Ar-H).

Preparation of the Amines: General Procedure

To the mixture of 0.02 mol of the above prepared nitro compounds and 0.1 mol of zinc powder in 50 mL of ethanol was added 50 mL of 15% hydrochloric acid in 1 h at about 80°C with stirring. After this addition, the mixture was stirred for another hour at about 80°C. Ethanol was distilled off, and the mixture was cooled. A solution of 20% of sodium hydroxide was added to neutralize the system. The system was extracted with methylene chloride. The organic mixture was washed with an equal volume of dilute hydrochloric acid. The water layer was basified with dilute sodium hydroxide to separate the product. The crude product was further purified by recrystallization or by chromatography.

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}p)\text{-}NH_2]_3$ (**3**)

Yield, 60%. gray solid, m.p. 87°C (methanol). Anal. found (%): C, 70.97; H, 7.16; N, 9.98. Calc. for $C_{24}H_{29}N_3O_3$: C, 70.76; H, 7.13; N, 10.32. IR (cm^{-1}): 3411, 3397, 1620, 1512, 1230, 825. ^1H NMR: δ (ppm) 0.92 (t, 3H, CH_3), 1.66 (q, 2H, CH_2C), 3.86 (s, 6H, $3CH_2O$), 4.80 (s, b, 6H, $3NH_2$), 6.51 ~ 6.67(m, 12H, Ar-H).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}o)\text{-}NH_2]_3$ (**7**)

Yield, 57%. Dark-brown solid, m.p. 75°C (methanol). Anal. found (%): C, 70.81; H, 7.13; N, 10.21. Calc. for $C_{24}H_{29}N_3O_3$: C, 70.76; H, 7.13; N, 10.32. IR (cm^{-1}): 3402, 3379, 3020, 1609, 1501, 1451, 1269, 1204, 849, 730. ^1H NMR: δ (ppm) 1.06 (t, 3H, CH_3), 1.90 (q, 2H, CH_2C), 3.58 (s, b, 6H, $3NH_2$), 4.20 (s, 6H, $3CH_2O$), 6.64–6.87 (m, 12H, Ar-H).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}p)\text{-}NH_2]_3$ (**12**)

Yield, 55%. Dark-brown solid, m.p. 68°C (ethanol). Anal. found (%): C, 68.33; H, 7.38; N, 13.19. Calc. for $C_{24}H_{30}N_4O_3$: C, 68.25; H, 7.11; N,

13.27. IR (cm^{-1}): 3399, 3289, 1610, 1508, 1233, 827. ^1H NMR: δ (ppm) 3.13 (t, 6H, $3NCH_2$), 4.03 (t, 6H, $3CH_2O$), 3.40 (b, overlap with $3NH_2$, 6H, $3NH_2$), 6.65–6.74 (m, 12H, Ar-H).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}NH_2]_3$ (**16**)

Yield 58%. Brown oil (methylene chloride as eluent). Anal. found (%): C, 68.50; H, 7.41; N, 13.22. Calc. for $C_{24}H_{30}N_4O_3$: C, 68.25; H, 7.11; N, 13.27. IR (cm^{-1}): 3421, 3374, 1607, 1500, 1257, 1218, 1039, 843, 735. ^1H NMR: δ (ppm) 3.11 (t, 6H, $3NH_2$), 4.12 (t, 6H, $3CH_2O$), 3.86 (s, b, 6H, $3NH_2$), 6.68 ~ 6.80 (m, 12H, Ar-H).

Preparation of the Schiff Bases: General Procedure

Fifteen mmol of one of the above prepared amines and 45 mmol of a suitable aldehyde were dissolved in 20 mL of ethanol. The mixture was refluxed for 3 h. After cooling, the solid product was filtered and washed with ethanol. Further purification could be performed by recrystallization from ethanol.

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N=CH\text{-}(C_6H_4\text{-}o)\text{-}OH]_3$ (**4a**)

Yield 96%. Yellow solid, m.p. 118°C (ethanol). Anal. found (%): C, 75.55; H, 5.83; N, 5.81. Calc. for $C_{45}H_{41}N_3O_6$: C, 75.51; H, 5.70; N, 5.84. IR (cm^{-1}): 3361, 1618, 1577, 1502, 1231, 1022, 821, 747. ^1H NMR: δ (ppm) 1.06 (t, 3H, CH_3), 1.90 (q, 2H, CH_2C), 4.16 (s, 6H, $3CH_2O$), 6.90~7.37 (m, 24H, Ar-H), 8.59 (s, 3H, 3N = CH-). 13.38 (s, 3H, 3ArOH).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N=CH\text{-}Py\text{-}2]_3$ (**4b**)

Yield 99%. Gray solid, m.p. 108°C (ethanol). Anal. found (%): C, 74.91; H, 5.93; N, 12.47. Calc. for $C_{42}H_{38}N_6O_3$: C, 74.78; H, 5.64; N, 12.46. IR (cm^{-1}): 1692, 1603, 1573, 1502, 1218, 1017, 745. ^1H NMR: δ (ppm) 1.04 (t, 3H, CH_3), 1.91 (q, 2H, CH_2C), 4.01 (s, 6H, $3CH_2O$), 6.95 ~ 8.17 (m, 24H, Ar-H and Py-H), 9.03 (s, 3H, 3N = CH).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N{=}CH\text{-}Qui\text{-}2]_3$ (**4c**)

Yield 98%. Gray solid, m.p. 135°C (ethanol). Anal. found (%): C, 78.63; H, 5.37; N, 10.07. Calc. for $C_{54}H_{44}N_6O_3$: C, 78.64; H, 5.34; N, 10.19. IR (cm^{-1}): 1620, 1590, 1575, 1501, 1237, 1010, 831, 743. ^1H NMR: δ (ppm) 1.08 (t, 3H, CH_3), 1.92 (q, 2H, CH_2C), 4.20 (s, 6H, $3CH_2O$), 7.01 ~ 8.38 (m, 30H, Ar-H and Qui-H), 8.85 (s, 3H, 3N = CH).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}(C_6H_4\text{-}o)\text{-}OH]_3$ (**8a**)

Yield 98%. Brown solid, m.p. 117°C(ethanol). Anal. found (%): C, 75.54; H, 5.81; N, 5.81. Calc. for $C_{45}H_{41}N_3O_6$: C, 75.51; H, 5.70; N, 5.84. IR (cm^{-1}): 3340, 1608, 1483, 1455, 1378, 1340, 1008, 742. ^1H NMR: δ (ppm) 0.90 (t, 3H, CH_3), 1.71 (q, 2H, CH_2C), 4.06 (s, 6H, $3CH_2O$), 6.86 ~ 7.65 (m, 24H, Ar-H), 8.91 (s, 3H, 3N = CH), 14.10 (s, b, 3H, 3ArOH).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}Py\text{-}2]_3$ (**8b**)

Yield 97%. Brown solid, m.p. 95°C (ethanol). Anal. found (%): C, 74.89; H, 5.88; N, 12.41. Calc. for $C_{42}H_{38}N_6O_3$: C 74.78; H, 5.64; N, 12.46. IR (cm^{-1}): 1617, 1598, 1572, 1224, 1010, 821, 740. ^1H NMR: δ (ppm): 1.06 (t, 3H, CH_3), 1.93 (q, 2H, CH_2C), 4.17 (s, 6H, $3CH_2O$), 6.98 ~ 8.16 (m, 24H, Ar-H and Py-H), 9.18 (s, 3H, 3N = CH).

$CH_3CH_2C[CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}Qui\text{-}2]_3$ (**8c**)

Yield 98%. Brown solid, m.p. 111°C (ethanol). Anal. found (%): C, 78.61; H, 5.35; N, 10.11. Calc. for $C_{54}H_{44}N_6O_3$: C, 78.64; H, 5.34; N, 10.19. IR (cm^{-1}): 1621, 1589, 1574, 1506, 1224, 1021, 830, 741. ^1H NMR: δ (ppm) 1.04 (t, 3H, CH_3), 1.93 (q, 2H, CH_2C), 4.11 (s, 6H, $3CH_2O$), 7.01 ~ 8.31 (m, 30H, Ar-H and Qui-H), 9.01 (s, 3H, 3N = CH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N=CH\text{-}(C_6H_4\text{-}o)\text{-}OH]_3$ (**13a**)

Yield 92%. Brown solid, m.p. 112°C (ethanol). Anal. found (%): C, 73.81; H, 5.73; N, 7.55. Calc. for $C_{45}H_{42}N_4O_6$: C, 73.57; H, 5.72; N, 7,63. IR(cm^{-1}): 3289, 1620, 1601, 1574, 1234, 1020, 822, 745. ^1H NMR: δ (ppm)

3.10 (t, 6H, $3NCH_2$), 4.13 (t, 6H, $3CH_2O$), 6.50 ~ 7.60 (m, 24H, Ar-H), 8.91 (s, 3H, 3N=CH), 13.24 (s, 3H, 3Ar-OH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N=CH\text{-}Py\text{-}2]_3$ (**13b**)

Yield 95%. Brown solid, m.p. 108°C (ethanol). Anal. found (%): C, 73.15; H, 5.69; N, 12.01. Calc. for $C_{42}H_{39}N_7O_3$: C, 73.15; H, 5.66; N, 12.19. IR (cm^{-1}): 1621, 1608, 1574, 1506, 1220, 1014, 739. ^1H NMR: δ (ppm) 3.13 (t, 6H, $3NCH_2$), 4.15 (t, 6H, $3CH_2O$), 6.79 ~ 8.03 (m, 24H, Ar-H and Py-H), 9.11(s, 3H, 3N = CH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}p)\text{-}N=CH\text{-}Qui\text{-}2]_3$ (**13c**)

Yield 98%. Brown solid, m.p. 100°C (ethanol). Anal. found (%): C, 77.47; H, 5.38; N, 11.54. Calc. for $C_{54}H_{45}N_7O_3$: C, 77.23; H, 5.36; 11.68. IR (cm^{-1}): 1618, 1597, 1569, 1504, 1220, 1011, 834, 743. ^1H NMR: δ (ppm) 3.11(t, 6H, $3NCH_2$), 4.17(t, 6H, $3CH_2O$), 6.98 ~ 8.31 (m, 30H, Ar-H and Qui-H), 9.05(s, 3H, 3N = CH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}(C_6H_4\text{-}o)\text{-}OH]_3$ (**17a**)

Yield 88%. Brown solid, m.p. 106°C (ethanol). Anal. found (%): C, 73.43; H, 5.96; N, 7.58. Calc. for $C_{45}H_{42}N_4O_6$: C, 73.57; H, 5.72, N, 7.63. IR (cm^{-1}): 3338, 1610, 1507, 1485, 1378, 1340, 1010, 740. ^1H NMR: δ (ppm) 3.14 (t, 6H, $3NCH_2$), 4.13 (t, 6H, $3CH_2O$), 6.97 ~ 7.41 (m, 24H, Ar-H), 8.71 (s, 3h, 3N = CH), 13.52 (s, 3H, 3Ar-OH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}Py\text{-}2]_3$ (**17b**)

Yield 90%. Brown solid, m.p. 101°C (ethanol). Anal. found (%): C, 73.29; H, 5.65; N, 12.11. Calc. for $C_{42}H_{39}N_7O_3$: C, 73.15; H, 5.66; N, 12.19. IR (cm^{-1}): 1620, 1602, 1573, 1223, 1021, 822, 744. ^1H NMR: δ (ppm) 3.13 (t, 6H, $3NCH_2$), 4.08 (t, 3H, $3CH_2O$), 7.01 ~ 8.10 (m, 24H, Ar-H and Py-H), 9.35 (s, 3H, 3N = CH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}N=CH\text{-}Qui\text{-}2]_3$ (**17c**)

Yield 93%. Brown solid, m.p. 118°C (ethanol). Anal. found (%): C, 77.31; H, 5.35; N, 11.70. Calc. for $C_{54}H_{45}N_7O_3$: C, 77.23; H, 5.36; N,

11.68. IR (cm^{-1}): 1618, 1579, 1562, 1501, 1242, 1020, 833, 743. ^1H NMR: δ (ppm) 3.12 (t, 6H, $3NCH_2$), 4.16 (t, 6H, $3CH_2O$), 6.90 ~ 8.41 (m, 30H, Ar-H and Qui-2H), 9.17 (s, 3H, 3N = CH).

Preparation of Salicyl Amide: General Procedure

To a solution of 4 mmol of salicylic acid in 20 mL of chlorobenzene was added successively 1.5 mmol of phosphorus trichloride and 1 mmol of the above prepared amine. The mixture was heated to reflux for 5 h with stirring. Chlorobenzene was distilled off. The residue was washed with a hot dilute solution of sodium hydrocarbonate and water. The resulting solid was recrystallized from ethanol. Further purification was carried out through chromatography with chloroform as eluent.

CH_3CH_2C [CH_2O-(C_6H_4-p)-NHCO-(C_6H_4-o)-OH]$_3$ (**5**)

Yield 78%. Gray solid, m.p. 90°C. Anal. found (%): C, 70.41; H, 5.69; N, 5.47. Calc. for $C_{45}H_{41}N_3O_9$: C, 70.40; H, 5.35; N, 5.48. IR (cm^{-1}): 3401, 1638, 1600, 1507, 1220, 1022, 820, 743. ^1H NMR: δ (ppm) 1.07(t, 3H, CH_3), 1.90(q, 2H, CH_2C), 4.19(s, 6H, $3CH_2O$), 7.00 ~ 8.00(m, 24H, Ar-H), 10.45 (s, 3H, 3NH), 12.11(s, 3H, 3Ar-OH).

CH_3CH_2C[CH_2O-(C_6H_4-o)-NHCO-(C_6H_4-o)-OH]$_3$ (**9**)

Yield 79%. Gray solid, m.p. 93°C. Anal. found (%):C, 70.42; H, 5.67; N, 5.44. Calc. for $C_{45}H_{41}N_3O_9$: C, 70.40; H, 5.35; N, 5.48. IR (cm^{-1}): 3403, 1647, 1602, 1511, 1220, 1023, 822, 741. ^1H NMR: δ (ppm) 0.89 (t, 3H, CH_3), 1.88 (q, 2H,CH_2C), 4.21 (s, 6H, $3CH_2O$), 6.98 ~ 7.88 (m, 24H, Ar-H), 10.39 (s, 3H, 3NH), 13.87 (s, 3H, 3Ar-OH).

N[CH_2CH_2O-(C_6H_4-p)-NHCO-(C_6H_4-o)-OH]$_3$ (**14**)

Yield 70%. Gray solid, m.p. 101°C. Anal. found (%): C, 69.11; H, 5.40; N, 7.12. Calc. for $C_{45}H_{42}N_4O_9$: C, 69.05; H, 5.37; N, 7.16. IR (cm^{-1}): 3396, 1641, 1601, 1507,1222, 1020, 831, 742. ^1H NMR: δ (ppm) 3.80 (t, 6H, $3NCH_2$), 4.48 (t, 6H, $3CH_2O$), 6.93 ~ 8.01 (m, 24H, Ar-H), 10.37 (s, 3H, 3NH), 11.99 (s, 3H, 3Ar-OH).

$N[CH_2CH_2O\text{-}(C_6H_4\text{-}o)\text{-}NHCO\text{-}(C_6H_4\text{-}o)\text{-}OH]_3$ (**18**)

Yield 70%. Gray solid, m.p. 96°C. Anal. found (%): C, 68.99; H, 5.39; N, 7.17. Calc. for $C_{45}H_{42}N_4O_9$: C, 69.05; H, 5.37; N, 7.16. IR (cm^{-1}): 3400, 1638, 1605, 1521, 1224, 1022, 822, 739. ^1H NMR: δ (ppm) 3.11 (t, 6H, $3NCH_2$), 4.10 (t, 6H, $3CH_2O$), 6.97 ~ 7.91 (m, 24H, Ar-H), 10.12 (s, 3H, 3NH), 13.57 (s, 3H, 3Ar-OH).

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