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Efficient synthesis of esters containing tertiary amine functionalities via active cyanomethyl ester intermediates

Camille Bouillon, Gilles Quéléver *, Ling Peng

Centre Interdisciplinaire de Nanoscience de Marseille, CNRS UPR 3118, Department of Chemistry, Faculty of Sciences of Luminy, Aix-Marseille Université, 13288 Marseille Cedex 9, France

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ABSTRACT

Esters containing tertiary amine functionalities were successfully synthesized under mild conditions and in good yields, using a three-step process involving the activation of acids into their corresponding cyanomethyl esters, followed by transesterification with the alcohol counterparts, and subsequent scavenging of the excess of alcohol to facilitate purification.

The formation of an ester bond is frequently required in organic synthesis and a large variety of methods are available to achieve this reaction.[1] One of the simplest and most popular procedures involves the activation of the acid using activating agents such as DCC, EDC and BOP, followed by coupling with the corresponding alcohol under mild conditions. However, according to a recent report on the preparation of esters of EDTA[2] and our own experience,[3] it is not the method of choice for the synthesis of esters bearing tertiary amine functionalities. Indeed, the presence of these tertiary amines in acids or alcohols was often associated with the reaction not going to completion. Purification of the product also proved difficult and the yields were rather poor.[2,3] The fact that tertiary amines are protonated to form zwitterions or H-bonds in the reaction medium may explain why the presence of the tertiary amine functionalities reduces the reactivity for ester formation and enhances the difficulty of purification.

To overcome this, we explored the possibility of synthesizing tertiary amine-bearing esters via active cyanomethyl ester intermediates.[4] The process involved firstly the conversion of the acid into its corresponding cyanomethyl ester by the action of chloroacetonitrile. This was followed by a transesterification step with the alcohol counterpart to achieve the corresponding ester. This whole reaction sequence could be performed under mild conditions, leading to the desired esters in good to excellent yields. This method has previously been reported for the synthesis of amino acid esters of peptides[5] and nucleotides,[6] as well as natural products.[7] However, it has not yet been widely explored and generally applied for the synthesis of esters. Here, we report the use of this method in the synthesis of tertiary amine-containing esters. The method developed for the synthesis of this particular family of esters involves the activation of the acid to its cyanomethyl ester, followed by its transesterification and subsequent solution-phase scavenging of the excess of alcohol (Scheme 1). In this way and in contrast to previously reported methods of synthesis, tertiary amine-bearing esters can be readily synthesized and easily purified.

Scheme 2 shows the synthesis of the tertiary amine containing alcohols (**1–3**) and acids (**4–6**) used in this study. Alcohols **1–3** were obtained quantitatively via double Michael additions starting with commercially available amino alcohols and *t*-butylacrylate.[8,9] Subsequent acylation with benzoic anhydride led to **1′-3′**[10] which were further treated with TFA to remove the *t*-butyl group, giving the corresponding acids **4–6** in excellent yields.[11]

Starting with the amine containing alcohol **1** and acid **4**, we first attempted to synthesize ester **7** using the conventional coupling system DCC/DMAP in CH_2Cl_2 (Scheme 3). Under these conditions, **7** could neither be isolated nor identified since the

* Corresponding author. Tel.: +33 491 82 91 54; fax: +33 491 82 93 01.
E-mail address: gilles.quelever@univmed.fr (G. Quéléver).

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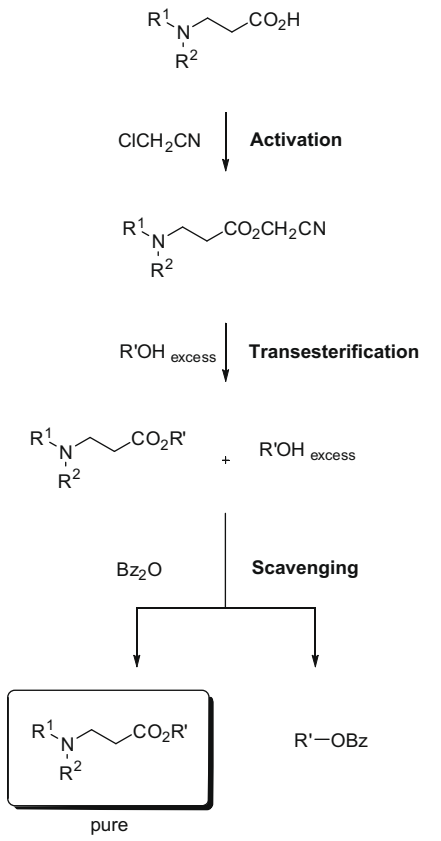
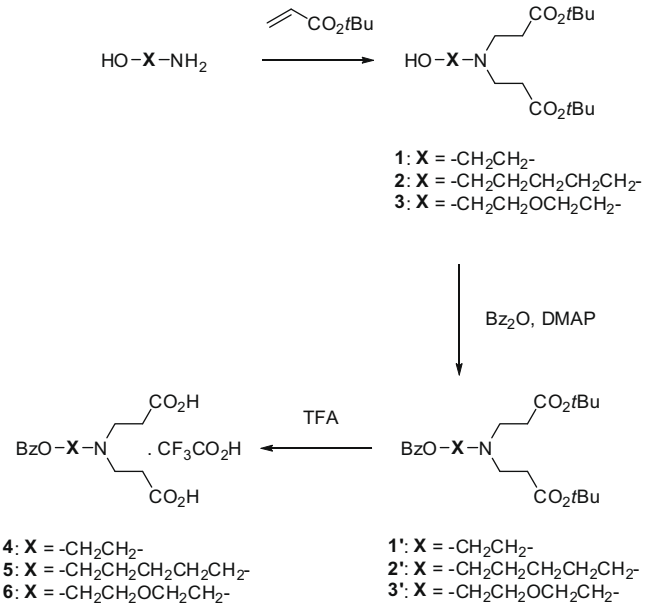


Scheme 1. Three-step sequence involving activation, transesterification and scavenging for synthesizing esters containing tertiary amines.



Scheme 2. Preparation of alcohols (**1**–**3**) and acids (**4**–**6**).

coupling reaction did not go to completion, leaving both **1** and **4** in the reaction mixture. It was impossible for us to separate **7** from **1**, with both **7** and **1** migrating very closely on silica gel. We then carried out a scavenging process to remove the excess of **1** by treating the crude reaction mixture with benzoic anhydride in the presence of DMAP. In this way, **1** could be quantitatively transformed into the less polar benzoate ester **1′** leading to its ease of separation from **7**. However, the yield of the desired ester **7** was a mere 40% with contamination of dicyclohexylurea, DCU.[12]

We then focused our attention on using the active cyanomethyl ester to synthesize **7** (Scheme 3). Treating acid **4** with chloroacetonitrile in the presence of Et_3N, we were able to obtain the cyanomethyl ester **4′** (Scheme 3), almost quantitatively[13] using a procedure previously described by Wong et al.[5] This cyanomethyl ester **4′** was stable enough to be isolated and characterized and was also sufficiently reactive to undergo a transesterification with **1** in the presence of DBU in CH_3CN to give **7** (Scheme 3).[14] After scavenging of the excess of alcohol **1** with benzoic anhydride, **7** could be easily purified on silica gel and isolated in 75% yield in pure form.[15] Collectively, the three-step procedure involving the activation of the acid into its cyanomethyl ester, followed by a transesterification step and subsequent scavenging of the excess of alcohol appeared to be the method of choice to synthesize the tertiary amine bearing ester **7**.

We further applied this three-step sequence to synthesize esters, starting with acid **4** and alcohols **2** and **3** (Scheme 4). Compared to **1**, both **2** and **3** are characterized by longer linkers between the terminal hydroxyl group and the tertiary amine function, with the former having a non-polar linker ($-CH_2CH_2CH_2CH_2CH_2-$) and the latter having a polar one ($-CH_2CH_2OCH_2CH_2-$). Using the above-described three-step synthesis, the two esters **8** and **9** (Scheme 4) were obtained in yields of 63% and 70%, respectively.[15] Similarly, starting with acids **5** and **6**, we quantitatively obtained the corresponding cyanomethyl esters **5′** and **6′**,[13] which were further coupled with alcohols **2** and **3** to give the corresponding esters **10** and **11** (Scheme 4) with yields of 68% and 70%, respectively.[15] It is noteworthy that the esters containing $-CH_2CH_2OCH_2CH_2-$ linkers (**9** and **11**) are more polar than those with $-CH_2CH_2CH_2CH_2CH_2-$ linkers (**7**, **8** and **10**), and consequently required more effort for their purification.

In summary, we have developed a three-step sequence for the preparation of esters containing tertiary amine functions. The synthesis involves activation of the acid into its cyanomethyl ester, subsequent transesterification with the alcohol counterpart, and a final solution-phase scavenging of the excess of alcohol. This procedure is particularly suitable and efficient for the synthesis of esters containing tertiary amine functionalities in both acid and alcohol components. The synthesis can be performed under very mild conditions, giving the desired esters in good yields following an easy purification. Further work is underway to validate this method for the synthesis of various tertiary amine-bearing esters and other esters which are otherwise difficult to obtain using conventional coupling methods.

Acknowledgements

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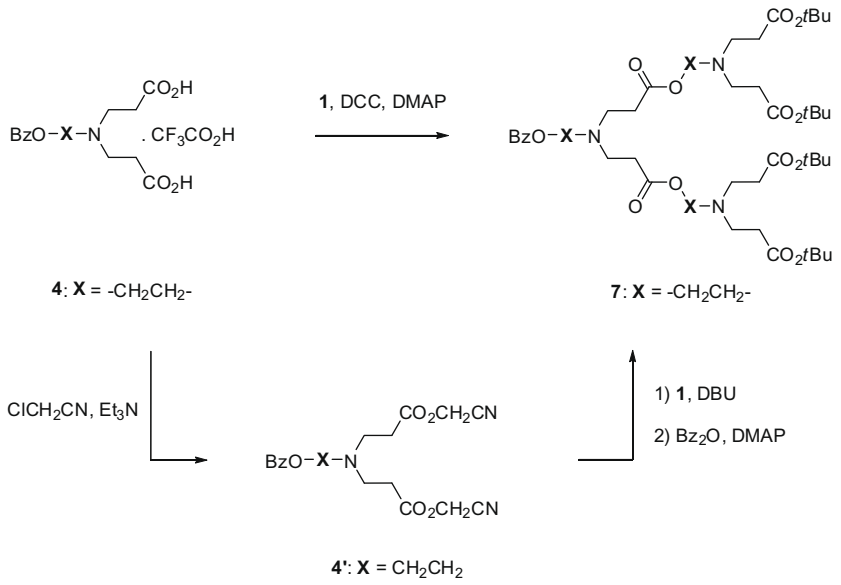
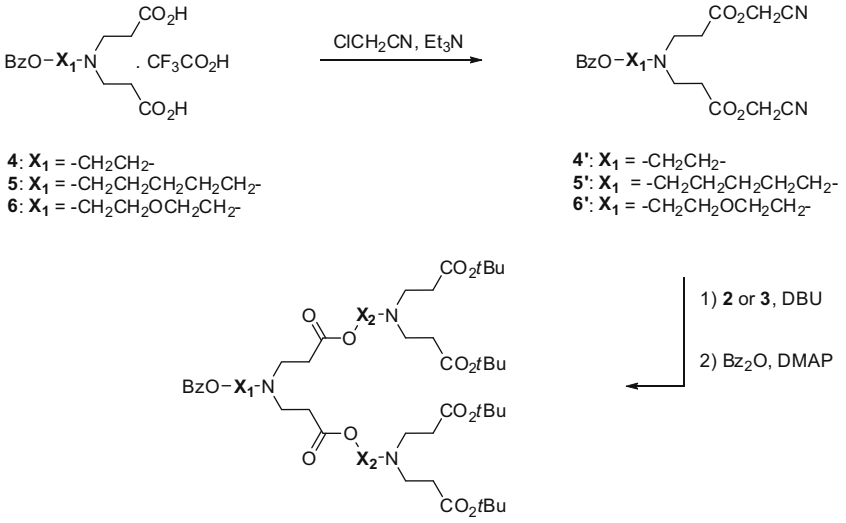


Scheme 3. Synthesis of tertiary amine-containing ester **7** starting with **1** and **4**.



Scheme 4. Synthesis of tertiary amine-containing esters using the three-step sequence.

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9. General procedure for the synthesis of alcohols **1**–**3**: A mixture of an amino alcohol and *tert*-butyl acrylate (2.6 equiv) in MeOH was stirred at room temperature for 4 days. Then, excess of *tert*-butyl acrylate and solvent were removed in vacuo. The crude material was purified by flash chromatography on silica gel (eluent cyclohexane–EtOAc) to afford the product.
Compound **1** (98%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.45 (s, 18H), 2.35 (t, 4H, ^3J = 6.8 Hz), 2.56 (t, 2H, ^3J = 5.2 Hz), 2.74 (t, 4H, ^3J = 6.8 Hz), 3.55 (t, 2H, ^3J = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 27.8 (6C), 33.5 (2C), 49.0 (2C), 55.5, 58.8, 80.3 (2C), 171.8 (2C).
Compound **2** (97%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.26–1.65 (m, 24H), 2.28–2.39 (m, 6H), 2.68 (t, 4H, ^3J = 7.2 Hz), 3.54–3.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 23.3, 26.8, 28.0 (6C), 32.4, 33.5 (2C), 49.2 (2C), 53.4, 62.5, 80.2 (2C), 172.1 (2C); HMRS *m*/*z* calcd for $C_{19}H_{37}NO_5$ $[M+H]^+$ 360.2748, found 360.2738.
Compound **3** (78%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.43 (s, 18H), 2.39 (t, 4H, ^3J = 6.1 Hz), 2.65 (t, 2H, ^3J = 4.5 Hz), 2.81 (t, 4H, ^3J = 6.1 Hz), 3.54–3.59 (m,

4H), 3.68–3.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 28.1 (6C), 33.4 (2C), 49.9 (2C), 53.6, 61.9, 69.5, 72.6, 80.5 (2C), 171.9 (2C); HMRS *m*/*z* calcd for $C_{18}H_{35}NO_6$ $[M+H]^+$ 362.2537, found 362.2529.

10. General procedure for the synthesis of esters **1′**–**3′**: The corresponding alcohol, benzoic anhydride (2.0 equiv) and DMAP (4.0 equiv) in CH_2Cl_2 were stirred at room temperature for 1 h. Solvent was then removed in vacuo, and the residue was diluted with EtOAc (20 mL), washed successively with aqueous saturated $NaHCO_3$ (2 × 10 mL) and brine (10 mL), dried and concentrated. The resulting crude material was purified by flash chromatography (eluent cyclohexane–EtOAc) to afford the desired product.
Compound **1′** (98%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.42 (s, 18H), 2.39 (t, 4H, ^3J = 7.1 Hz), 2.82–2.88 (m, 6H), 4.36 (t, 2H, ^3J = 6.1 Hz), 7.43 (t, 2H, ^3J = 7.5 Hz), 7.55 (t, 1H, ^3J = 7.5 Hz), 8.03 (d, 2H, ^3J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 28.1 (6C), 34.1 (2C), 50.0 (2C), 52.1, 63.3, 80.4 (2C), 128.3 (2C), 129.6 (2C), 131.2, 132.9, 166.5, 171.8 (2C).
Compound **2′** (98%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.24–1.60 (m, 22H), 1.71–1.82 (m, 2H), 2.31–2.44 (m, 6H), 2.72 (t, 4H, ^3J = 7.3 Hz), 4.30 (t, 2H, ^3J = 6.6 Hz), 7.42 (t, 2H, ^3J = 6.8 Hz), 7.54 (t, 1H, ^3J = 7.3 Hz), 8.03 (d, 2H, ^3J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 23.8, 27.0, 28.0 (6C), 28.6, 33.6 (2C), 49.3 (2C), 53.5, 64.9, 80.2 (2C), 128.2 (2C), 129.5 (2C), 130.4, 132.7, 166.6, 172.0 (2C).
Compound **3′** (90%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.42 (s, 18H), 2.35–2.39 (m, 4H), 2.62–2.83 (m, 6H), 3.52–3.61 (m, 2H), 3.78 (t, 2H, ^3J = 4.8 Hz), 4.45 (t, 2H, ^3J = 5.0 Hz), 7.44 (t, 2H, ^3J = 7.3 Hz), 7.56 (t, 1H, ^3J = 7.4 Hz), 8.06 (d, 2H, ^3J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 28.1 (6C), 33.8 (2C), 50.0 (2C), 53.1, 64.1, 69.1, 69.7, 80.3 (2C), 128.3 (2C), 129.7 (2C), 130.1, 133.0, 166.5, 171.9 (2C).

11. General procedure for the synthesis of acids **4**–**6**: To a CH_2Cl_2 solution of the corresponding *tert*-butyl ester was added TFA (20 equiv). The solution was stirred at room temperature for 48 h. Solvent and TFA were removed in vacuo, and the resulting residue was triturated into Et_2O to afford the desired product.
Compound **4** (quantitative): ^{13}C NMR (CD_3OD, 62.9 MHz) δ_C 29.0 (2C), 51.7 (2C), 54.0, 60.1, 129.7 (2C), 130.5, 130.9 (2C), 134.7, 167.3, 174.3 (2C); HMRS *m*/*z* calcd for $C_{15}H_{19}NO_6$ $[M+H]^+$ 310.1285, found 310.1284.
Compound **5** (70%): ^{13}C NMR (CD_3OD, 62.9 MHz) δ_C 24.2, 24.4, 29.3 (3C), 50.6 (2C), 54.5, 65.7, 129.6 (2C), 130.5 (2C), 131.4, 134.3, 168.0, 173.6 (2C); HMRS *m*/*z* calcd for $C_{18}H_{25}NO_6$ $[M+H]^+$ 352.1755, found 352.1746.
Compound **6** (93%): ^{13}C NMR (CD_3OD, 62.9 MHz) δ_C 29.2 (2C), 51.6 (2C), 54.8, 65.0, 65.6, 70.3, 129.6 (2C), 130.6 (2C), 131.1, 134.4, 167.9, 174.1 (2C).

12. Unfortunately, DCU could not be completely removed from **7** in our hands. Further attempts to replace DCC/DMAP by BOP or Mukaiyama's reagent were unsuccessful, since no desired product could be identified.

13. General procedure for the synthesis of activated cyanomethyl esters **4′**–**6′**: To a solution of acid in CH_2Cl_2, were added slowly Et_3N (4.0 equiv) and chloroacetonitrile (6.0 equiv). The solution was stirred overnight at room temperature. Solvents were removed in vacuo, and the residue was diluted with EtOAc (20 mL), washed successively with water (2 × 10 mL) and brine (10 mL), dried and concentrated. The resulting crude material was purified by flash chromatography (eluent cyclohexane–EtOAc) to afford the corresponding activated cyanomethyl ester.
Compound **4′** (84%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 2.50 (t, 4H, ^3J = 6.7 Hz), 2.77–2.85 (m, 6H), 4.30 (t, 2H, ^3J = 5.8 Hz), 4.59 (s, 4H), 7.40 (t, 2H, ^3J = 7.5 Hz), 7.52 (t, 1H, ^3J = 7.3 Hz), 7.96 (d, 2H, ^3J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 32.2 (2C), 48.0 (2C), 49.2 (2C), 51.8, 62.3, 114.4 (2C), 128.1 (2C), 129.2 (2C), 129.7, 132.8, 166.0, 170.4 (2C); HMRS *m*/*z* calcd for $C_{19}H_{21}N_3O_6$ $[M+H]^+$ 388.1503, found 388.1502.
Compound **5′** (crude material): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.31–1.58 (m, 4H), 1.74 (q, 2H, ^3J = 6.7 Hz), 2.38–2.53 (m, 6H), 2.74 (t, 4H, ^3J = 6.6 Hz), 4.28 (t, 2H, ^3J = 6.5 Hz), 4.67 (s, 4H), 7.41 (t, 2H, ^3J = 7.5 Hz), 7.53 (t, 1H, ^3J = 7.8 Hz), 8.00 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 23.4, 26.3, 28.4, 32.0 (2C), 48.1 (2C), 48.8 (2C), 53.3, 64.7, 114.4 (2C), 128.1 (2C), 129.3 (2C), 130.1, 132.7, 166.4, 170.7 (2C); HMRS *m*/*z* calcd for $C_{22}H_{27}N_3O_6$ $[M+H]^+$ 430.1973, found 430.1964.
Compound **6′** (60%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 2.50 (t, 4H, ^3J = 6.6 Hz), 2.67 (t, 2H, ^3J = 5.8 Hz), 2.82 (t, 4H, ^3J = 6.6 Hz), 3.56 (t, 2H, ^3J = 5.6 Hz), 3.75 (t, 2H, ^3J = 5.0 Hz), 4.44 (t, 2H, ^3J = 4.7 Hz), 4.67 (s, 4H), 7.43 (t, 2H, ^3J = 7.5 Hz), 7.55 (t, 1H, ^3J = 7.4 Hz), 8.03 (d, 2H, ^3J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 32.3 (2C), 48.1 (2C), 49.6 (2C), 53.0, 63.9, 68.9, 69.5, 114.5 (2C), 128.3 (2C), 129.5 (2C), 129.9, 133.0, 166.4, 170.7 (2C); HMRS *m*/*z* calcd for $C_{21}H_{25}N_3O_7$ $[M+H]^+$ 432.1765, found 432.1746.

14. We tried to optimize this transesterification step by varying organic bases (DMAP, Et_3N or DBU) and solvents (CH_2Cl_2 and CH_3CN). The best results were obtained in the presence of DBU in CH_3CN, with complete consumption of the activated ester overnight at room temperature. It is to note that no trace of the desired ester could be detected by using either weaker bases such as DMAP and Et_3N, or in the absence of any base, whereas transesterification in CH_2Cl_2 required a much longer reaction time (48 h) than in CH_3CN.

15. General procedure for the synthesis of esters **7**–**11**: The corresponding cyanomethyl ester, alcohol (2.6 equiv) and DBU (2.6 equiv) in CH_3CN were stirred at room temperature for 48 h. Solvent was then removed in vacuo, and the residue was diluted with EtOAc (20 mL), washed successively with water (2 × 10 mL) and brine (10 mL), dried and concentrated. The resulting crude material, benzoic anhydride (2.0 equiv) and DMAP (4.0 equiv) in CH_2Cl_2 were stirred at room temperature for 1 h. Solvent was then removed in vacuo, and the residue was diluted with EtOAc (20 mL), washed successively with aqueous saturated $NaHCO_3$ (2 × 10 mL) and brine (10 mL), dried and concentrated. The desired *tert*-butyl ester was obtained by flash chromatography (eluent cyclohexane–EtOAc).
Compound **7** (75%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.35 (s, 36H), 2.27 (t, 8H, ^3J = 7.2 Hz), 2.40 (t, 4H, ^3J = 7.1 Hz), 2.60 (t, 4H, ^3J = 6.2 Hz), 2.70 (t, 8H, ^3J = 7.2 Hz), 2.76–2.84 (m, 6H), 4.01 (t, 4H, ^3J = 6.3 Hz), 4.28 (t, 2H, ^3J = 6.0 Hz), 7.35 (t, 2H, ^3J = 7.4 Hz), 7.47 (t, 1H, ^3J = 7.3 Hz), 7.94 (d, 2H, ^3J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 27.8 (12C), 32.6 (2C), 33.7 (4C), 49.5 (2C), 49.7 (4C), 51.8 (2C), 53.3, 62.3 (2C), 62.7, 80.1 (4C), 128.1 (2C), 129.3 (2C), 129.9, 132.7, 166.1, 171.4 (4C), 171.9 (2C); HMRS *m*/*z* calcd for $C_{47}H_{77}N_3O_{14}$ $[M+H]^+$ 908.5478, found 908.5476.
Compound **8** (63%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.15–1.33 (m, 8H), 1.41 (s, 36H), 1.55–1.66 (m, 4H), 2.29–2.48 (m, 16H), 2.67–2.73 (m, 8H), 2.82–2.90 (m, 6H), 3.99 (t, 4H, ^3J = 6.6 Hz), 4.34 (t, 2H, ^3J = 6.0 Hz), 7.41 (t, 2H, ^3J = 7.5 Hz), 7.53 (t, 1H, ^3J = 7.3 Hz), 8.00 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 23.6 (2C), 26.8 (2C), 28.0 (12C), 28.4 (2C), 32.9 (2C), 33.5 (4C), 49.2 (4C), 49.7 (2C), 52.1, 53.4 (2C), 63.0, 64.4 (2C), 80.2 (4C), 128.3 (2C), 129.5 (2C), 130.1, 132.8, 166.4, 171.9 (4C), 172.3 (2C); HMRS *m*/*z* calcd for $C_{53}H_{89}N_3O_{14}$ $[M+H]^+$ 992.6417, found 992.6436.
Compound **9** (70%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.38 (s, 36H), 2.33 (t, 8H, ^3J = 7.3 Hz), 2.47 (t, 4H, ^3J = 7.1 Hz), 2.63 (t, 4H, ^3J = 6.3 Hz), 2.76 (t, 8H, ^3J = 7.3 Hz), 2.82–2.88 (m, 6H), 3.49 (t, 4H, ^3J = 6.1 Hz), 3.57 (t, 4H, ^3J = 4.9 Hz), 4.13 (t, 4H, ^3J = 4.8 Hz), 4.32 (t, 2H, ^3J = 6.0 Hz), 7.39 (t, 2H, ^3J = 7.4 Hz), 7.51 (t, 1H, ^3J = 7.4 Hz), 7.98 (d, 2H, ^3J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 27.9 (12C), 32.6 (2C), 33.4 (4C), 49.6 (2C), 49.7 (4C), 51.9, 52.9 (2C), 62.8, 63.4 (2C), 68.7 (2C), 69.3 (2C), 80.2 (4C), 128.2 (2C), 129.4 (2C), 130.0, 132.8, 166.3, 171.7 (4C), 172.1 (2C).
Compound **10** (68%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.13–1.71 (m, 54H), 2.22–2.37 (m, 18H), 2.59–2.71 (m, 12H), 3.92–4.02 (m, 4H), 4.22 (t, 2H, ^3J = 6.4 Hz), 7.35 (t, 2H, ^3J = 7.0 Hz), 7.46 (t, 1H, ^3J = 6.6 Hz), 7.95 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 23.4 (2C), 23.5, 26.7 (2C), 27.8 (12C), 28.3, 28.4 (2C), 29.9, 32.3 (2C), 33.4 (4C), 48.9 (2C), 49.0 (4C), 53.3 (3C), 64.2 (2C), 64.7, 79.9 (4C), 128.1 (2C), 129.3 (2C), 130.1, 132.6, 166.3, 171.7 (4C), 172.4 (2C); HMRS *m*/*z* calcd for $C_{56}H_{95}N_3O_{14}$ $[M+H]^+$ 1034.6887, found 1034.6853.
Compound **11** (70%): ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H 1.42 (s, 36H), 2.35 (t, 8H, ^3J = 7.2 Hz), 2.47 (t, 4H, ^3J = 7.2 Hz), 2.62–2.70 (m, 6H), 2.74–2.86 (m, 12H), 3.51 (t, 4H, ^3J = 6.2 Hz), 3.55–3.62 (m, 6H), 3.76 (t, 2H, ^3J = 4.7 Hz), 4.16 (t, 4H, ^3J = 4.9 Hz), 4.44 (t, 2H, ^3J = 4.9 Hz), 7.43 (t, 2H, ^3J = 7.4 Hz), 7.55 (t, 1H, ^3J = 7.4 Hz), 8.04 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ_C 27.9 (12C), 32.3 (2C), 33.6 (4C), 49.5 (2C), 49.8 (4C), 52.9 (3C), 63.3 (2C), 63.9, 68.7 (2C), 68.8, 69.4 (2C), 69.5, 80.1 (4C), 128.2 (2C), 129.5 (2C), 129.9, 132.8, 166.3, 171.7 (4C), 172.3 (2C); HMRS *m*/*z* calcd for $C_{53}H_{89}N_3O_{17}$ $[M+H]^+$ 1040.6265, found 1040.6269.