

Synthesis of oligo(phenyleneethynylene)s containing central pyromellitdiimide or naphthalenediimide groups and bearing terminal isocyanide groups: molecular components for single-electron transistors

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Abstract—Oligo(phenyleneethynylene)s that are of variable length, contain a central arenediimide unit, either a pyromellitdiimide or a naphthalenediimide group, and are terminated by isocyanide groups have been prepared. The extended frameworks were assembled from appropriately functionalized arenediimide and areneformamide units whose lengths were adjusted by adding phenyleneethynylene units. Final transformation of the formamide groups into isocyanide groups gave the title compounds. Several isocyanide-terminated oligo(phenyleneethynylene)s without an arenediimide unit have also been prepared.

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1. Introduction

The basic devices of single electronics, e.g., the single-electron box, the single-electron trap, or the single-electron transistor, consist of simple arrangements of single-electron islands that are separated from each other and from solid electrodes by tunnel barriers.¹ Single-electron theory specifies the sizes of the islands and the tunnel barriers as well as the geometry of their arrangement, but leaves open the choice of material from which they are made. One possible means of implementation involves molecular components. We are developing a building block system for suitable molecules. Toward this goal, we are using strong electron acceptor units as the single-electron islands and linear unsaturated units as the tunnel junctions. The molecular single-electron device components also bear terminal surface-binding groups for the attachment to solid electrode surfaces.

For initial investigations we are preparing molecules that allow the placement of just one single-electron island between two solid electrodes. Such entities may be used as the molecular components in hybrid single-electron transistors. The general design consists of a linear molecular rod featuring

a central electron acceptor group and terminal surface attachment groups. The title compounds **1–8**, shown in **Figure 1**, are molecules of this type. In these compounds, the central electron acceptor is either a pyromellitdiimide or a naphthalenediimide unit. These arenediimides readily undergo reversible reduction.² Oligo(phenyleneethynylene)s (OPEs) are used as moderately conducting tunnel barriers. OPEs have already been tested as conductors in a variety of molecular electronic devices.³ Isocyanide groups are attached to the ends of the molecules as surface attachment groups.⁴ The length of these molecular single-electron device components can be adjusted by inserting the appropriate number of phenyleneethynylene units into the linear chains. In the present series the distance between the terminal isocyanide carbon atoms varies from about 3–9 nm. We also report the synthesis of several diisocyanides without a central diimide group and the preparation of corresponding molecules with only one terminal isocyanide group. The first molecular electronic devices based on some of the new diisocyanides have recently been reported.⁵

The chemical synthesis of the title compounds was not expected to pose any significant challenges, since all molecular components and chemical transformations involved are well established. We anticipated that the unusual length of some of the molecules might give rise to problems concerning their solubility in common solvents. However, with the introduction of hexyl and isopropyl side chains these potential

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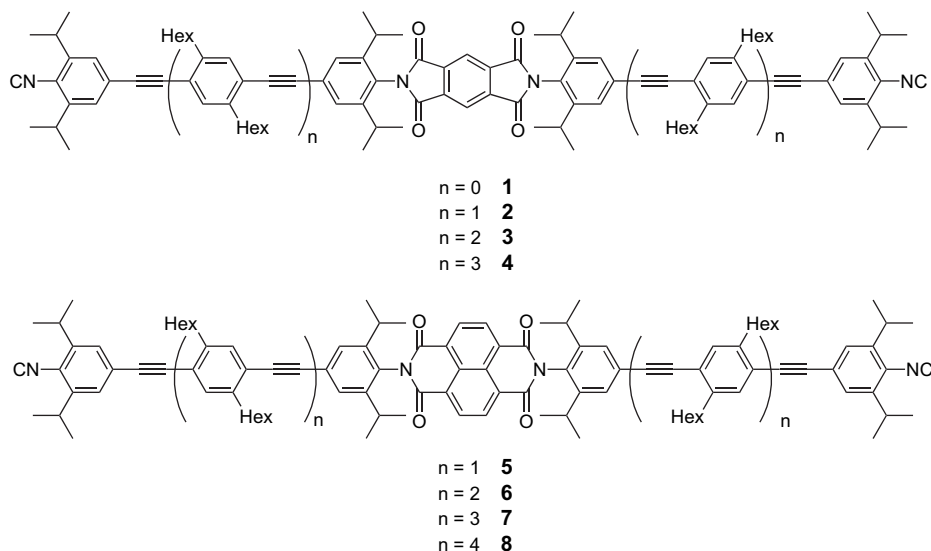


Figure 1. The title compounds.

problems were effectively eliminated.⁶ The isopropyl groups at the arenediimide linkages have the added effect of preventing the coplanar arrangement of the diimide unit and the OPE chains. This feature adds to the tunnel barrier between these units. Even the longest products are soluble in relatively nonpolar solvents or solvent mixtures such as the toluene/triethylamine mixtures used in the chemical syntheses or the hexane/dichloromethane or hexane/ethyl acetate mixtures used in the chromatographic purification procedures. The isopropyl substituents on the terminal arylisocyanide groups also increase the stability of the final products. In contrast, unsubstituted arylisocyanides are known to exhibit a strong tendency toward polymerization.⁷

2. Results and discussion

The arenediimide cores **11** and **20** were prepared from 4-iodo-2,6-diisopropylaniline, **9**, and 1,2,4,5-benzenetetracarboxylic dianhydride, **10** (Scheme 1a), and from 4-bromo-2,6-diisopropylaniline, **18**, and 1,4,5,8-naphthalenetetracarboxylic dianhydride, **19** (Scheme 1b). The reaction between **9** and **10** proceeded in hot acetic acid, while the reaction between **18** and **19** required more forceful conditions. A moderate yield of **20** was obtained by heating a mixture of **18** and **19** in *m*-cresol in the presence of a small amount of isoquinoline to about 210 °C for 20 h.⁸ Attempts to prepare the iodo-analogue of **20** were not successful. Only trace amounts, if any, of the desired compound were obtained when **9** and **19** were allowed to react under the conditions of the synthesis of **20**.

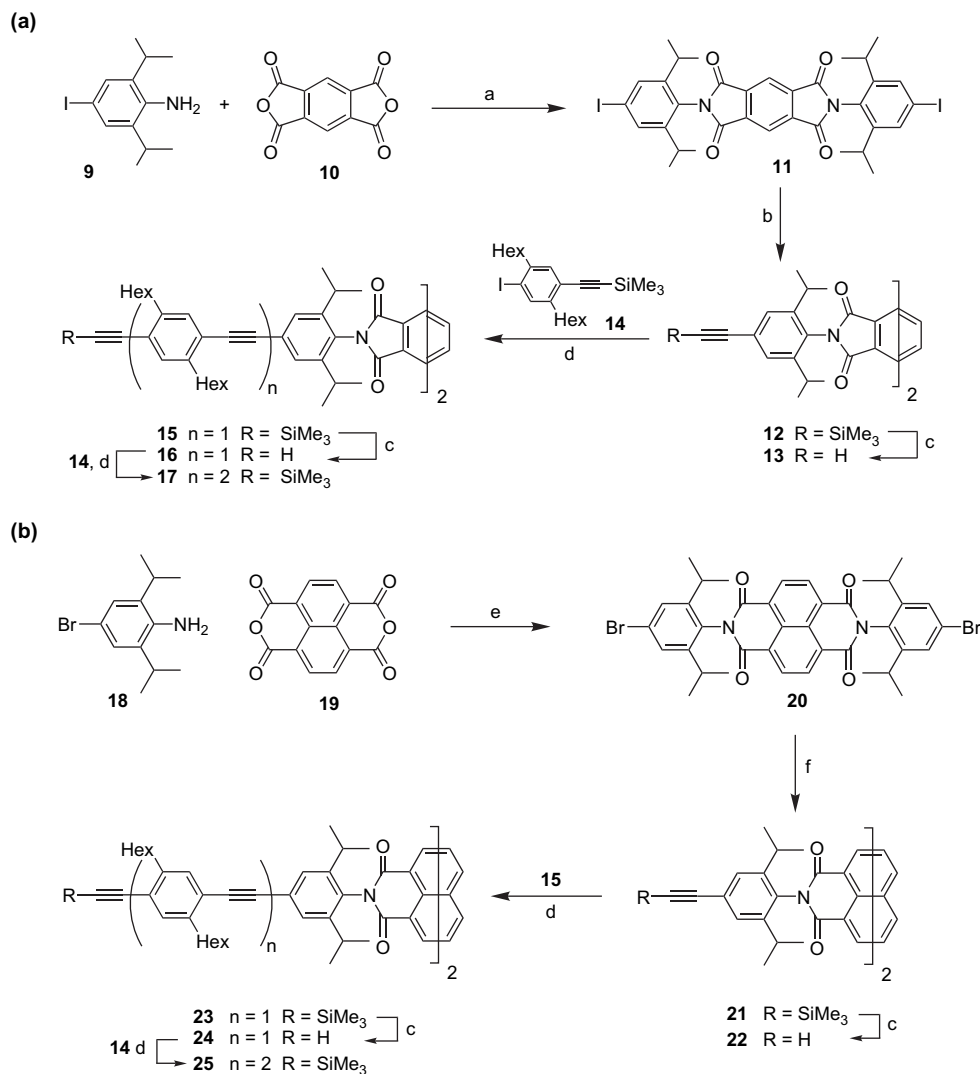
Compounds **11** and **20** were then transformed into the corresponding trimethylsilylethynyl derivatives **12** and **21** by means of palladium-catalyzed coupling with trimethylsilylacetylene.⁹ The behavior of compound **20** in this reaction proved to be somewhat erratic. In some attempts of the synthesis of **21**, the formation of a palladium mirror was observed. In those cases only low yields of **21** were obtained after the addition of further increments of catalyst and alkyne. The ethynyl derivatives **13** and **22** were obtained

in good yields by treatment of **12** and **21** with tetrabutylammonium fluoride adsorbed on silica gel. These particular desilylation procedures did not proceed satisfactorily with K₂CO₃ or KOH in methanol. The parent compounds of **13** and **22**, bis(4-ethynylphenyl)pyromellitdiimide and bis(4-ethynylphenyl)naphthalenediimide, have previously been prepared by the reaction of **10** and **19** with 4-ethynylaniline.¹⁰

The core units **13** and **22** were extended by one or two phenyleneethynylene units. The terminal acetylenes **16** and **24** were obtained by palladium-catalyzed coupling of **13** and **22**, respectively, with 4-iodo-2,5-dihexyl-trimethylsilylethynylbenzene, **14**, followed by a desilylation step. Compounds **17** and **25** were then obtained by renewed coupling of **16** and **24** with **14**.

3,5-Diisopropyl-4-formamido-1-ethynylbenzene, **26**, was chosen as the precursor for the terminal isocyanide groups. This compound was extended by up to three phenyleneethynylene groups to afford compounds **28**, **30**, and **32** (Scheme 2a). This was accomplished by repeated palladium-catalyzed coupling with **14** and desilylation of the respective intermediates **27**, **29**, and **31** with KOH in CH₃OH. The terminal acetylenes **28**, **30**, and **32** have a tendency to turn gradually pink or even brown during storage. For this reason, they were generated just prior to use. The iodo-terminated derivatives **34–37** were then obtained from compounds **26**, **28**, **30**, and **32**, respectively, by treatment with excess 1,4-diiodo-2,6-dihexylbenzene, **33**, under established coupling conditions (Scheme 2b). Unused **33** was readily recovered. These reactions were accompanied by the formation of small amounts of the extended diformamides **38**, **40**, **41**, and **42**. These compounds as well as diformamide **39**, which contains an even number of phenyleneethynylene groups, can be prepared straightforwardly as shown in Scheme 2c.

As an alternative route to the iodo-terminated compounds **34–37** we also tested the procedure shown in Scheme 3. It involves the triazene reagent **45**, which was prepared from the diiodobenzene **33** in two steps via the intermediates **43**



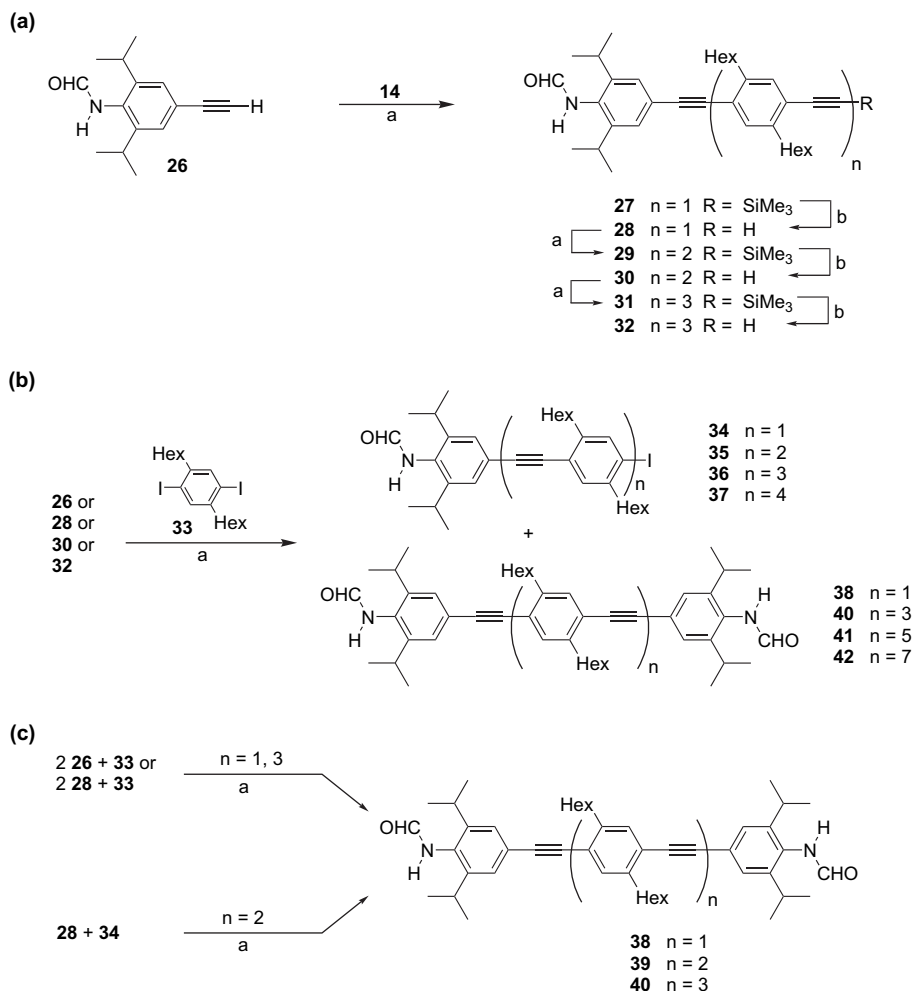
Scheme 1. Reagents and conditions: (a) acetic acid, 120 °C, 1 h; (b) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, toluene, NEt₃, 2 h, rt; (c) TBAF/THF, silica gel, CHCl₃, rt, 30 min; (d) Pd(PPh₃)₄, CuI, toluene, Et₃N, 12 h, rt; (e) quinoline, *m*-cresol, 210 °C, 20 h; (f) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, toluene, NEt₃, 65 °C, 7 days.

and **44**.^{11,12} Palladium-catalyzed coupling of **45** with **28** afforded the triazene compound **46**, which was subsequently converted into **35** by treatment with methyl iodide at elevated temperatures. While this triazene route affords the iodo-terminated compound **35** without the byproduct **40**, the shorter procedure shown in Scheme 2a and b is overall more efficient.

The diformamide precursors **47–53** of the isocyanides **1–8** were obtained by palladium-catalyzed coupling of appropriate combinations of the halo- or ethynyl-terminated core units **11**, **13**, **16**, **22**, and **24** and the ethynyl- or iodo-terminated formamide units **26**, **34**, **35**, and **36** (Scheme 4a). Finally, treatment of these compounds with COCl₂ in the presence of triethylamine¹³ afforded the isocyanides **1–8**. Furthermore, the monoisocyanides **54–56** and the diisocyanides **57–59** were prepared from the monoformamides **27**, **29**, and **31** and the diformamides **38–40**, respectively, under similar conditions (Scheme 4b).

The IR spectra of all isocyanide compounds exhibit a characteristic absorption at about 2110 cm⁻¹. The IR spectra of all compounds bearing the 2,6-diisopropyl-formamidobenzene

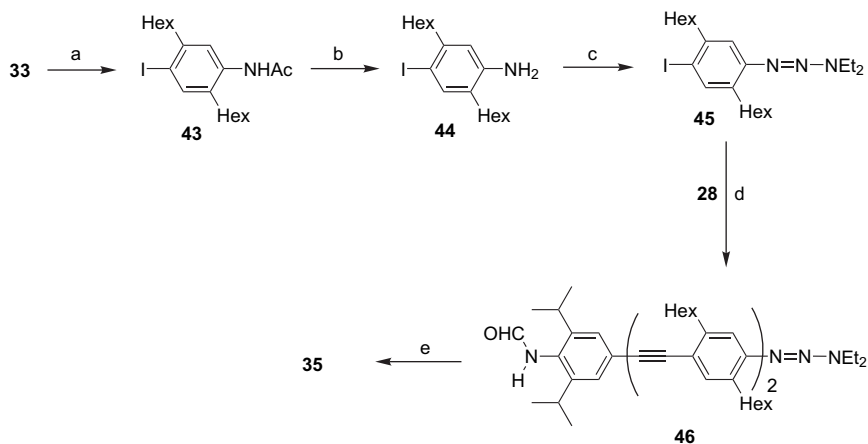
group show absorptions in the 3200–3230 cm⁻¹ and 1660–1690 cm⁻¹ regions for the formamide group. The latter band is resolved into two peaks in several cases. All compounds containing the pyromellitdiimide group give rise to an IR band of medium intensity near 1778 cm⁻¹ and a band of strong intensity near 1730 cm⁻¹. A band of medium intensity at about 1715 cm⁻¹ and one of strong intensity at about 1680 cm⁻¹ are characteristic for the naphthalenediimide unit. The trimethylsilylethynyl groups give rise to a band of medium intensity near 2150 cm⁻¹, the terminal ethynyl groups to a band of very low intensity near 2110 cm⁻¹, and the internal ethynylene groups to an even weaker band near 2210 cm⁻¹. The NMR spectra of all compounds containing a formamide group exhibit two sets of signals for the two conformers that arise due to slow rotation about the OHC–NH bond. The isocyanides **1–8** exhibit only the number of signals expected for the symmetry indicated by the structural formulas. The ¹³C NMR signals for the isocyanide carbon atoms were found at about δ 170 for compounds **54–59**. The corresponding signals were not found for compounds **1–8** since only very small amounts of these materials were available. The isocyanides **54–59** gave rise



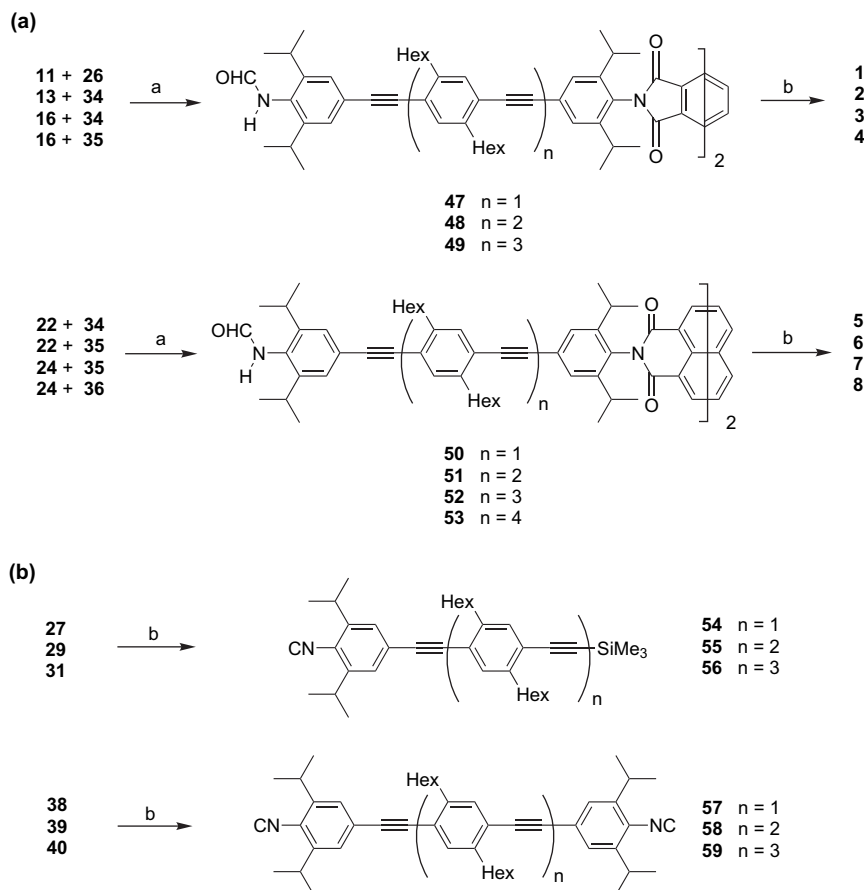
Scheme 2. Reagents and conditions: (a) Pd(PPh₃)₄, CuI, toluene, Et₃N, rt, 12 h; (b) KOH/CH₃OH, 2 h.

to strong molecular ion peaks in the mass spectra. Attempts to observe the molecular ion peaks for compounds **1–8** were not successful. A number of other compounds containing arenediimide groups, especially those with longer OPE chains also failed to give rise to molecular ion peaks.

The elemental analyses of the longer molecules consistently gave lower carbon mass percentages than calculated, while the hydrogen and nitrogen values stayed within the expected range. We were not able to identify any impurity, which might have caused this discrepancy.



Scheme 3. Reagents and conditions: (a) *N,N'*-dimethylethylenediamine, K₃PO₄, CuI, DMF, 80 °C, 24 h; (b) HCl, EtOH, reflux, 5 h; aq KOH, rt, 1 h; (c) BF₃·Et₂O, *t*-BuNO, CH₂Cl₂, K₂CO₃, HNEt₂, 0 °C; (d) Pd(PPh₃)₄, CuI, NEt₃, toluene, rt; (e) MeI, 110 °C.



Scheme 4. Reagents and conditions: (a) Pd(PPh₃)₄, CuI, toluene, Et₃N, rt, 12 h; (b) COCl₂, Et₃N, CH₂Cl₂, -78 °C to rt.

Compounds **1–8** are readily soluble in methylene chloride and toluene or other moderately polar solvents or solvent mixtures. The solubility of these compounds in highly polar solvents such as dimethylformamide or dimethylsulfoxide decreases strongly with increasing length of the OPE chain.

3. Summary

A building block system for the synthesis of unsaturated linear molecules containing a central pyromellitimide and naphthalenediimide units as electron acceptors and terminal isocyanide groups as surface-binding groups has been developed. The individual building blocks for the central and terminal portions of the molecules can be prepared from readily available starting materials. The lengths of these molecules can be adjusted by attaching phenyleneethynylene units to the basic building blocks prior to the assembly of the complete extended structures.

4. Experimental

4.1. General information

The compounds **9**,¹⁴ **14**,¹⁵ **18**,¹⁴ **26**,^{14b} and **33**¹⁶ were prepared as described in the literature. The solvents toluene, triethylamine, CH₂Cl₂, and THF were dried using appropriate drying agents under an atmosphere of nitrogen. All other

solvents and reagents were used as received from commercial sources. All coupling reactions were performed under an atmosphere of nitrogen gas. The IR spectra were recorded on a Mattson Galaxy FTIR 3000 instrument. The ¹H NMR spectra (CDCl₃) were recorded using a Varian Gemini 2300 spectrometer at 300 MHz and ¹³C NMR spectra (CDCl₃) were recorded using Varian Inova 400 spectrometer at 100 MHz. Mass spectrometric measurements were performed by the Stony Brook Mass Spectrometry Facility. Column chromatographies were performed using silica gel (45–60 μm). Elemental analyses were obtained from QTI laboratories.

4.2. Synthetic procedures

4.2.1. Typical procedure for the preparation of compounds 1–8 and 55–59. *Compound 2:* compound **47** (50 mg, 0.033 mmol) was dissolved in CH₂Cl₂ (10 mL) and NEt₃ (0.3 mL). The stirred mixture was cooled to -78 °C and a 1.9 M solution of COCl₂ in toluene (0.3 mL) was added. After 30 min, the reaction mixture was allowed to warm to room temperature. A solution of KHCO₃ (10%, 50 mL) was introduced into the mixture and stirred for a further 30 min. The mixture was then extracted with CH₂Cl₂ (50 mL), washed with water (2 × 50 mL), and dried over anhydrous MgSO₄. Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography on silica gel (hexane/CH₂Cl₂ 5:1). Pale yellow solid. Yield: 46 mg, 94%.

4.2.2. Typical procedure for the preparation of compounds 15, 17, 23, 25, 27, 29, and 31. *Compound 15*: a mixture of **13** (0.200 g, 0.34 mmol), **14** (0.400 g, 0.85 mmol), and Pd(PPh₃)₄ (0.050 g) in toluene (30 mL) and NEt₃ (15 mL) was stirred for 10 min. Then CuI (0.025 g) was added and the mixture was stirred for a further 2 h. The salt formed was filtered off. Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography (silica gel, hexane/CH₂Cl₂ 4:1). Pale yellow solid. Yield: 0.35 g, 81%.

4.2.3. Typical procedure for the preparation of compounds 13, 16, 22, and 24. *Compound 13*: tetrabutylammonium fluoride (TBAF, 1.05 g, 4 mmol) and silica gel (5 g) were added to THF (10 mL). The mixture was stirred for 10 min and then dried. A solution of **12** (0.730 g, 1 mmol) in CHCl₃ (20 mL) was added to a stirred suspension of TBAF adsorbed on silica gel in CHCl₃ (20 mL). The mixture was stirred for 30 min. The silica gel was filtered off and washed with CHCl₃ (5×5 mL). The combined solutions were washed with a saturated aqueous solution of KHCO₃ (50 mL) and water (2×50 mL) and then dried over anhydrous MgSO₄. Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography on silica gel (hexane/CH₂Cl₂ 3:1). Colorless solid. Yield: 0.510 g, 85%.

4.2.4. Typical procedure for the preparation of compounds 28, 30, and 32. *Compound 28*: potassium hydroxide (1 M, 15 mL) was added to a methanol solution of **27** (1.3 g, 2.28 mmol). The mixture was stirred for 2 h. Then the solvent was removed under vacuum and the residue was extracted with CH₂Cl₂ (2×50 mL). The combined extracts were washed with water (2×50 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was used as such for further reactions. Off-white solid.

4.2.5. Typical procedure for the preparation of compounds 34–37. *Compound 34*: a mixture of **26** (1.15 g, 5 mmol), **33** (20.0 g, 32 mmol), and Pd(PPh₃)₄ (0.100 g) in NEt₃ (70 mL) was stirred for 10 min. Then CuI (0.050 g) was added and the mixture was stirred for a further 16 h. The salt formed was removed by filtration. The solvent was removed from the filtered solution under vacuum. The residue was redissolved in CH₂Cl₂ and 50 g of silica gel was added with stirring. The solvent was slowly removed under vacuum and the residue dried. The solid residue was added to the top of a silica gel column (5×30 cm), which had been prepared with hexane. Excess **33** was eluted with hexane. Compound **34** was eluted with hexane/EtOAc (1:1). The product thus obtained was contaminated with a small amount of compound **38**. Compounds **34** (2.24 g, 75%) and **38** (0.274 g, 8%) were separated by a second chromatography on silica gel (hexane/EtOAc 1:1). Both compounds were obtained as off-white solids.

4.2.6. Typical procedure for the preparation of compounds 38–40, 46, and 47–53. *Compound 52*: a mixture of **24** (0.377 g, 0.32 mmol), **35** (0.608 g, 0.70 mmol), Pd(PPh₃)₄ (0.025 g) in NEt₃ (40 mL) was stirred for 10 min. Then CuI (0.012 g) was added and the mixture

was stirred for a further 16 h. The salt formed was removed by filtration. The solvent was removed from the filtered solution under vacuum. Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography on silica gel (hexane/EtOAc 2:1). Pale yellow solid. Yield: 0.537 g, 63%.

4.2.7. Compound 1. Yield: 0.110 g, 86%; IR (KBr, cm⁻¹): 2965, 2934, 2872, 2111, 1778, 1730, 1602, 1468, 1366, 1116; ¹H NMR: δ 8.56 (s, 2H), 7.50 (s, 4H), 7.38 (s, 4H), 3.39 (septet, *J*=6.9 Hz, 4H), 2.67 (septet, *J*=6.9 Hz, 4H), 1.32 (d, *J*=6.9 Hz, 24H), 1.20 (d, *J*=6.9 Hz, 24H); ¹³C NMR (75 MHz): δ 170.1, 165.8, 147.5, 145.3, 137.3, 127.6, 126.8, 126.6, 125.2, 124.0, 119.8, 90.6, 89.6, 31.6, 29.8, 23.8, 22.5.

4.2.8. Compound 2. IR (KBr, cm⁻¹): 2957, 2922, 2854, 2112, 1779, 1732, 1597, 1462, 1367; ¹H NMR: δ 8.57 (s, 2H), 7.48 (s, 4H), 7.44 (s, 2H), 7.42 (s, 2H), 7.33 (s, 4H), 3.40 (septet, 4H), 2.88–2.81 (m, 8H), 2.70 (septet, 4H), 1.76–1.70 (m, 8H), 1.46–1.26 (m, 24H), 1.32 (d, *J*=6.9 Hz, 24H), 1.22 (d, *J*=6.9 Hz, 24H), 0.92–0.89 (m, 12H); ¹³C NMR (75 MHz): δ 170.0, 165.8, 147.4, 145.3, 142.5, 137.3, 132.4, 127.4, 126.5, 126.3, 125.9, 124.6, 124.0, 122.7, 122.3, 119.8, 93.8, 93.4, 90.1, 89.1, 34.4, 34.3, 31.8, 31.7, 30.8, 29.8, 29.5, 29.4, 23.8, 22.7, 22.7, 22.5, 14.1.

4.2.9. Compound 3. Yield: 0.112 g, 83%; IR (KBr, cm⁻¹): 2961, 2926, 2855, 2109, 1778, 1730, 1596, 1460, 1365; ¹H NMR: δ 8.57 (s, 2H), 7.47 (s, 4H), 7.43 (s, 2H), 7.40 (s, 2H), 7.39 (s, 2H), 7.38 (s, 2H), 7.32 (s, 4H), 3.39 (septet, *J*=6.9 Hz, 4H), 2.87–2.80 (m, 16H), 2.68 (septet, *J*=6.9 Hz, 4H), 1.78–1.68 (m, 16H), 1.48–1.28 (m, 48H), 1.31 (d, *J*=6.9 Hz, 24H), 1.21 (d, *J*=6.9 Hz, 24H), 0.91–0.86 (m, 24H); ¹³C NMR: δ 165.8, 147.4, 145.3, 142.5, 142.0, 137.3, 132.5, 132.4, 127.4, 126.5, 124.6, 123.0, 119.8, 93.8, 93.3, 90.2, 85.9, 34.2, 31.8, 31.8, 31.7, 30.8, 30.7, 29.8, 29.5, 29.4, 29.3, 23.9, 22.7, 22.5, 14.1.

4.2.10. Compound 4. Yield: 0.044 g, 98%; IR (KBr, cm⁻¹): 2959, 2924, 2855, 2108, 1778, 1729, 1596, 1463, 1366; ¹H NMR (300 MHz): δ 8.57 (s, 2H), 7.48 (s, 4H), 7.43–7.39 (m, 12H), 7.32 (s, 4H), 3.39 (septet, *J*=9.6 Hz, 4H), 2.85–2.80 (m, 24H), 2.69 (septet, *J*=6.9 Hz, 4H), 1.78–1.69 (m, 24H), 1.47–1.31 (m, 96H), 1.22 (d, *J*=6.9 Hz, 24H), 0.90–0.89 (m, 36H); ¹³C NMR (75 MHz): δ 170.0, 165.8, 147.4, 145.3, 142.5, 142.0, 141.9, 137.3, 132.5, 132.5, 132.3, 127.4, 126.5, 126.3, 126.0, 124.6, 123.3, 123.1, 122.8, 122.7, 122.2, 121.9, 119.8, 93.6, 93.3, 93.1, 93.0, 92.9, 90.2, 89.3, 34.4, 34.3, 31.8, 31.8, 31.7, 30.8, 30.7, 29.8, 29.7, 29.5, 29.4, 29.3, 23.8, 22.7, 22.5, 14.1.

4.2.11. Compound 5. Yield: 0.029 g, 60%; IR (cm⁻¹): 2964, 2929, 2858, 2111, 1718, 1682, 1599, 1581, 1460, 1448, 1337, 1249; ¹H NMR (300 MHz): δ 8.91 (s, 4H), 7.51 (s, 4H), 7.44 (s, 2H), 7.41 (s, 2H), 7.32 (s, 4H), 3.39 (septet, 4H), 2.88–2.81 (m, 8H), 2.72 (septet, 4H), 1.78–1.68 (m, 8H), 1.48–1.26 (m, 24H), 1.31 (d, 24H), 1.20 (d, 24H), 0.92–0.87 (m, 12H); ¹³C NMR (100 MHz): δ 162.8, 146.0, 145.3, 141.8, 140.2, 139.4, 135.9, 132.2, 131.7, 127.6, 126.8, 126.5, 34.4, 31.7, 30.7, 29.5, 25.1, 23.8, 22.6, 22.5, 14.1.

4.2.12. Compound 6. Yield: 0.016, 72%; IR (cm⁻¹): 2961, 2928, 2856, 2111, 1717, 1682, 1598, 1581, 1460, 1446, 1337, 1248; ¹H NMR (400 MHz): δ 8.92 (s, 4H), 7.52 (s, 4H), 7.44–7.39 (m, 8H), 7.32 (s, 4H), 3.39 (septet, 4H), 2.88–2.81 (m, 16H), 2.72 (septet, 4H), 1.78–1.68 (m, 16H), 1.46–1.26 (m, 48H), 1.32 (d, 24H), 1.20 (d, 24H), 0.96–0.84 (m, 24H); ¹³C NMR (100 MHz): δ 169.7, 162.8, 146.0, 145.3, 143.7, 142.4, 142.0, 133.3, 132.5, 132.4, 131.7, 130.3, 127.7, 126.9, 126.5, 125.2, 124.6, 123.3, 122.8, 122.5, 121.9, 93.9, 93.3, 92.9, 90.2, 88.7, 34.4, 34.3, 34.1, 33.9, 31.8, 31.8, 31.7, 30.8, 30.7, 30.7, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 23.8, 22.7, 22.6, 22.5, 21.9, 14.1.

4.2.13. Compound 7. Yield: 0.034 g, 76%; IR (cm⁻¹): 2958, 2926, 2856, 2110, 1716, 1681, 1597, 1581; ¹H NMR: δ 8.93 (s, 4H), 7.53 (s, 4H), 7.45 (s, 2H), 7.41–7.39 (m, 10H), 7.32 (s, 4H), 3.39 (septet, $J=6.9$ Hz, 4H), 2.90–2.81 (m, 24H), 2.72 (septet, $J=6.9$ Hz, 4H), 1.78–1.68 (m, 24H), 1.44–1.30 (m, 96H), 1.21 (d, $J=6.9$ Hz, 24H), 0.91–0.89 (m, 36H); ¹³C NMR: δ 169.8, 162.8, 146.0, 145.3, 142.5, 142.0, 132.5, 132.4, 131.7, 130.2, 128.8, 127.7, 126.9, 126.5, 125.2, 124.6, 123.3, 122.9, 122.7, 122.5, 121.9, 94.0, 93.3, 93.1, 92.9, 90.2, 88.8, 34.4, 34.3, 34.2, 31.8, 31.8, 31.7, 30.8, 30.7, 29.8, 29.5, 29.4, 29.3, 23.8, 22.9, 22.7, 22.6, 22.5, 14.1, 14.1.

4.2.14. Compound 8. Yield: 0.043 g, 84%; IR (cm⁻¹): 2111, 1718, 1681; ¹H NMR: δ 8.92 (s, 4H), 7.52 (s, 4H), 7.44–7.32 (m, 20H), 3.39 (septet, 4H), 2.90–2.80 (m, 24H), 2.72 (septet, 4H), 1.77–1.20 (m, 144H), 0.91–0.88 (m, 48H); ¹³C NMR: δ 171.1, 164.8, 146.9, 146.5, 143.7, 142.8, 142.4, 141.9, 141.9, 139.4, 132.4, 132.3, 132.3, 130.0, 129.8, 127.0, 126.8, 124.0, 123.8, 123.0, 122.9, 122.8, 122.7, 122.6, 122.4, 122.2, 94.0, 93.6, 93.1, 93.0, 92.5, 92.3, 88.9, 88.4, 34.3, 34.2, 33.8, 31.8, 31.7, 31.7, 31.6, 30.8, 30.7, 30.2, 29.4, 29.4, 29.3, 29.2, 29.0, 28.4, 23.5, 22.6, 22.6, 14.0.

4.2.15. Compound 11. To a suspension of 1,2,4,5-benzenetetracarboxylic dianhydride, **10** (1.30 g, 6 mmol), in acetic acid (30 mL) at 100 °C was added **9** (3.20 g, 9.6 mmol) in acetic acid (30 mL). The reaction mixture was heated to 120 °C for 1 h and then allowed to cool gradually to room temperature. The precipitate formed was filtered off, washed with acetic acid (2×50 mL) and water (2×50 mL), and then dried under vacuum. The crude product was redissolved in CH₂Cl₂ and filtered through a short bed of silica gel (hexane/CH₂Cl₂ 1:1) to give **11** as a colorless solid. Yield: 4.7 g, 50%; IR (KBr, cm⁻¹): 2960, 2929, 2870, 1778, 1727, 1567, 1455, 1364, 1244, 861, 847, 730; ¹H NMR (400 MHz): δ 8.53 (s, 2H), 7.62 (s, 4H), 2.59 (septet, $J=9.2$ Hz, 1H), 1.15 (d, $J=9.2$ Hz, 24H); ¹³C NMR (100 MHz): δ 165.2, 149.0, 136.8, 133.3, 125.9, 119.5, 97.2, 29.0, 23.4; FABMS: m/z 789.26 ((M+1)⁺). Analysis: C₃₄H₃₄I₂N₂O₄ requires C, 51.79; H, 4.35; N, 3.55. Found: C, 51.89; H, 4.16; N, 3.47.

4.2.16. Compound 12. A mixture of **11** (1.60 g, 2 mmol), trimethylsilylacetylene (1.28 mL, 9 mmol), Pd(PPh₃)₄ (0.075 g) in toluene (10 mL) and Et₃N (25 mL) was stirred for 10 min. Then CuI (0.030 g) was added and the reaction mixture was stirred at room temperature for a further 2 h and then at 50 °C for 15 min. The salt formed was filtered

off. Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography on silica gel (hexane/CH₂Cl₂ 1:3). Yield: 0.73 g, 50%; IR (KBr, cm⁻¹): 2964, 2159, 1778, 1729; ¹H NMR (300 MHz): δ 8.52 (s, 2H), 7.40 (s, 4H), 2.62 (septet, $J=6.9$ Hz, 4H), 1.17 (d, $J=6.9$ Hz, 24H), 0.29 (s, 18H); ¹³C NMR (100 MHz): δ 165.7, 147.2, 137.2, 127.9, 126.5, 125.5, 119.7, 104.7, 95.2, 29.5, 23.8, -0.1; FABMS: m/z 729.42 ((M+1)⁺).

4.2.17. Compound 13. IR (KBr, cm⁻¹): 3270, 2965, 2120, 1778, 1725; ¹H NMR (400 MHz): δ 8.54 (s, 2H), 7.44 (s, 4H), 3.16 (s, 2H), 2.64 (septet, 4H), 1.17 (d, $J=9.2$ Hz, 24H); ¹³C NMR (100 MHz): δ 165.7, 147.4, 137.3, 128.1, 126.8, 124.6, 119.8, 83.3, 78.0, 29.5, 23.8; FABMS: m/z 585.16 ((M+1)⁺). Analysis: C₃₈H₃₆N₂O₄ requires C, 78.06; H, 6.21; N, 4.79. Found: C, 76.68; H, 6.11; N, 4.69.

4.2.18. Compound 15. IR (KBr, cm⁻¹): 2959, 2926, 2148, 1779, 1729; ¹H NMR (300 MHz): δ 8.56 (s, 2H), 7.44 (s, 4H), 7.36 (s, 2H), 7.32 (s, 2H), 2.78–2.64 (m, 12H), 1.65–1.60 (m, 8H), 1.42–1.30 (m, 24H), 1.19 (d, $J=6.9$ Hz, 24H), 0.89 (m, 12H), 0.27 (s, 18H); ¹³C NMR (75 MHz): δ 165.8, 147.4, 142.8, 142.3, 137.3, 132.6, 132.3, 127.4, 126.3, 126.0, 122.7, 122.4, 119.8, 103.9, 99.1, 93.5, 89.2, 34.3, 34.2, 31.7, 30.8, 30.6, 29.5, 29.4, 29.3, 23.8, 22.7, 22.6, 14.1, 14.0, 0.0; FABMS: m/z 1265.60 ((M+1)⁺).

4.2.19. Compound 16. Yield: 0.158 g, 94%; IR (KBr, cm⁻¹): 3274, 2961, 2926, 2855, 2215, 2108, 1777, 1728; ¹H NMR (400 MHz): δ 8.56 (s, 2H), 7.45 (s, 4H), 7.38 (s, 2H), 7.35 (s, 2H), 3.31 (s, 2H), 2.80–2.60 (m, 12H), 1.71–1.64 (m, 8H), 1.44–1.32 (m, 24H), 1.20 (d, $J=8$ Hz, 24H), 0.93–0.85 (m, 12H); ¹³C NMR (100 MHz): δ 165.8, 147.4, 142.8, 142.3, 137.2, 133.0, 132.3, 127.4, 126.3, 125.8, 122.7, 121.7, 119.7, 93.5, 89.0, 82.4, 81.5, 34.2, 33.8, 31.7, 31.6, 30.7, 30.5, 29.5, 29.4, 29.1, 23.8, 22.6, 22.6, 14.1; FABMS: m/z 1121.64 ((M+1)⁺).

4.2.20. Compound 17. Yield: 0.120 g, 61%; IR (KBr, cm⁻¹): 2959, 2926, 2856, 2148, 1779, 1729; ¹H NMR (400 MHz): δ 8.59 (s, 2H), 7.50 (s, 4H), 7.45 (s, 2H), 7.41 (s, 2H), 7.35 (s, 2H), 7.34 (s, 2H), 2.90–2.62 (m, 20H), 1.82–1.62 (m, 16H), 1.44–1.34 (m, 48H), 1.23 (d, $J=7.2$ Hz, 24H), 0.94–0.89 (m, 24H), 0.29 (s, 18H); ¹³C NMR (100 MHz): δ 165.8, 147.4, 142.8, 142.4, 141.9, 141.8, 137.3, 132.5, 132.4, 127.4, 126.3, 126.0, 123.1, 123.0, 122.4, 122.2, 119.7, 104.0, 98.9, 93.5, 93.1, 93.0, 89.3, 34.4, 34.2, 34.2, 34.1, 31.8, 31.7, 31.7, 30.8, 30.7, 30.6, 29.5, 29.4, 29.3, 29.2, 23.8, 22.7, 22.6, 14.1, 0.0.

4.2.21. Compound 20. A mixture of **18** (5.9 g, 22 mmol), **19** (2.7 g, 10 mmol), *m*-cresol (50 mL), and isoquinoline (1 mL) was heated to 210 °C for 20 h. Then the mixture was poured into a solution of MeOH/water (1:1, 200 mL) and allowed to settle for 1 h. The precipitate was filtered off, washed with MeOH/water (1:1, 2×100 mL), and dried. The residue was purified by column chromatography over silica gel (hexane/CH₂Cl₂ 1:1) to give **20** as a pale yellow solid. Pure samples are colorless. Yield: 1.7 g, 23%; IR (KBr, cm⁻¹): 3021, 2932, 2872, 2968, 1714, 1677, 1581, 1467, 1445, 1343, 1250, 1222, 856, 788, 736; ¹H NMR (300 MHz): δ 8.89 (s, 4H), 7.47 (s, 4H), 2.66 (septet,

$J=6.9$ Hz, 4H), 1.15 (d, $J=6.9$ Hz, 24H); ^{13}C NMR (100 MHz): δ 162.7, 147.9, 131.7, 129.1, 127.8, 127.6, 126.8, 124.4, 29.4, 23.7; ES-MS (m/z): 743.40 (($M+1$) $^+$).

4.2.22. Compound 21. A mixture of **20** (0.500 g, 0.67 mmol), trimethylsilylacetylene (0.6 mL, 4 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.050 g) in toluene (40 mL) and Et_3N (10 mL) was stirred for 10 min. Then CuI (0.025 g) was added and the reaction mixture was stirred for a further 4 days at 65 °C. Then, additional amounts of $\text{Pd}(\text{PPh}_3)_4$ (0.050 g), trimethylsilylacetylene (0.5 mL), and CuI (0.025 g) were added to the reaction mixture, which was stirred for a further 2 days at 75 °C. The salt formed was filtered off and washed with toluene (2×20 mL). Evaporation of the solvent under vacuum gave a residue, which was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 1:3). Yield: 0.40 g, 77%, pale yellow solid; IR (KBr, cm^{-1}): 2964, 2935, 2873, 2155, 1716, 1678, 1580; ^1H NMR (400 MHz): δ 8.90 (s, 4H), 7.49 (s, 4H), 7.37 (s, 2H), 7.32 (s, 2H), 2.84–2.64 (m, 12H), 1.74–1.60 (m, 8H), 1.45–1.29 (m, 24H), 1.18 (d, $J=6.9$ Hz, 24H), 0.93–0.87 (m, 12H), 0.27 (s, 18H); ^{13}C NMR (100 MHz): δ 162.7, 145.8, 131.6, 130.4, 128.0, 127.6, 126.8, 124.7, 105.1, 94.5, 29.3, 23.8, 0.02.

4.2.23. Compound 22. Yield: 0.230 g, 71%; ^1H NMR (400 MHz): δ 8.89 (s, 4H), 7.49 (s, 4H), 3.15 (s, 2H), 2.68 (septet, $J=6.9$ Hz, 4H), 1.58 (d, $J=6.9$ Hz, 24H); ^{13}C NMR (100 MHz): δ 162.7, 146.0, 131.7, 130.7, 128.4, 127.6, 126.8, 123.8, 83.6, 29.2, 23.8.

4.2.24. Compound 23. Yield: 0.478 g, 73%; IR (KBr, cm^{-1}): 2959, 2926, 2856, 2148, 1716, 1680, 1580; ^1H NMR (400 MHz): δ 8.90 (s, 4H), 7.34 (s, 2H), 7.32 (s, 1H), 7.33 (s, 2H), 2.81 (m, 4H), 2.72 (m, 8H), 1.64 (m, 8H), 1.42–1.32 (m, 24H), 1.19 (d, $J=6.9$ Hz, 24H), 0.91 (m, 12H), 0.28 (s, 18H); ^{13}C NMR (100 MHz): δ 162.8, 146.0, 142.8, 142.3, 134.3, 134.2, 132.5, 132.3, 131.7, 130.2, 129.5, 128.4, 128.3, 127.7, 127.6, 126.9, 125.2, 122.6, 122.5, 104.0, 99.0, 93.8, 88.7, 34.3, 34.2, 31.8, 31.7, 30.8, 30.6, 29.4, 29.3, 23.8, 22.7, 22.6, 14.1, 14.0, 0.0.

4.2.25. Compound 24. Yield: 0.377 g, 87%; IR (KBr, cm^{-1}): 3266, 2958, 2926, 2855, 2108, 1715, 1679, 1580; ^1H NMR (400 MHz): δ 8.91 (s, 4H), 7.51 (s, 4H), 7.40 (s, 2H), 7.36 (s, 2H), 3.32 (s, 2H), 2.86–2.67 (m, 12H), 1.77–1.62 (m, 8H), 1.48–1.32 (m, 24H), 1.20 (d, $J=6.9$ Hz, 24H), 0.91 (m, 12H); ^{13}C NMR (100 MHz): δ 162.8, 146.0, 142.8, 142.3, 134.3, 134.2, 132.5, 132.3, 131.7, 130.2, 129.5, 127.7, 127.6, 126.9, 125.2, 122.6, 122.5, 104.0, 99.0, 93.8, 88.7, 34.3, 33.9, 31.7, 30.7, 30.5, 29.4, 29.3, 23.8, 22.7, 22.6, 14.1.

4.2.26. Compound 25. Yield: 0.286 g, 76%; IR (KBr, cm^{-1}): 2959, 2926, 2856, 2149, 1716, 1679, 1580; ^1H NMR (400 MHz): δ 8.90 (s, 4H), 7.49–7.29 (m, 12H), 2.80–2.68 (m, 12H), 1.72–1.64 (m, 16H), 1.41–1.33 (m, 48H), 1.18 (d, $J=12$ Hz, 24H), 0.93–0.87 (m, 24H), 0.27 (s, 18H); ^{13}C NMR (100 MHz): δ 162.8, 146.0, 142.8, 142.3, 134.3, 134.2, 132.5, 132.3, 131.7, 130.2, 129.5, 128.4, 128.3, 127.7, 127.6, 126.9, 125.2, 122.6, 104.0, 98.9, 93.8, 88.8, 34.3, 34.2, 31.8, 31.7, 30.8, 30.6, 29.4, 29.3, 23.8, 22.7, 22.6, 14.1, 14.1, 0.0.

4.2.27. Compound 27. Yield: 2.24 g, 75%; IR (KBr, cm^{-1}): 3249, 3009, 2962, 2929, 2859, 2147, 1690, 1490, 1467; ^1H NMR (300 MHz): δ 8.45 (s) and 8.03 (d) (1H), 7.64 and 7.04 (1H), 7.40–7.30 (4H), 3.21 (m) and 3.10 (m, 2H), 2.74 (m, 4H), 1.57 (m, 4H), 1.22 (m, 4H), 1.17 (d) and 1.12 (d) (6H), 0.88 (m, 6H), 0.26 (s, 9H); ^{13}C NMR (100 MHz): δ 165.1, 160.5, 146.9, 146.4, 142.9, 142.8, 142.2, 132.6, 132.5, 132.2, 130.2, 129.8, 127.0, 126.8, 124.0, 123.8, 122.6, 122.4, 104.0, 103.9, 99.1, 98.9, 94.0, 93.5, 88.8, 88.3, 34.3, 34.2, 34.1, 31.7, 30.7, 30.6, 29.4, 29.3, 29.2, 28.8, 28.4, 23.5, 23.4, 22.6, 14.1, 0.1; FABMS: m/z 570.88 (($M+1$) $^+$).

4.2.28. Compound 28. Yield: 2.49 g, 93%; IR (KBr, cm^{-1}): 3302, 3019, 2964, 2929, 2870, 2859, 2108, 1691; ^1H NMR (300 MHz): δ 8.49 (s) and 8.03 (d, $J=11.7$ Hz) (1H), 7.36–7.34 (4H), 7.12 (d, $J=11.7$ Hz) and 6.76 (s) (1H), 3.30 and 3.29 (1H), 3.29–3.17 (m, 2H), 2.82–2.72 (m, 4H), 1.72–1.60 (m, 4H), 1.44–1.29 (m, 12H), 1.24 (d, 12H), 0.92–0.87 (m, 6H); FABMS: m/z 498.65 (($M+1$) $^+$). Analysis: $\text{C}_{35}\text{H}_{47}\text{NO}$ requires C, 84.45; H, 9.52; N, 2.81. Found: C, 84.11; H, 9.36; N, 2.84.

4.2.29. Compound 29. Yield: 1.53 g, 89%; IR (KBr, cm^{-1}): 3250, 2962, 2929, 2859, 2157, 1690, 1490, 1467; ^1H NMR (250 MHz): δ 8.46 (d, $J=1$ Hz) and 8.04 (d, $J=11$ Hz) (1H), 7.42–7.32 (m, 6H), 7.73 (d, $J=11$ Hz) and 7.06 (s) (1H), 3.24 (m) and 3.11 (m) (2H), 2.84–2.70 (m, 8H), 1.78–1.22 (m, 36H), 0.89 (m, 12H), 0.27 (s, 9H); ^{13}C NMR (100 MHz): δ 165.2, 160.6, 146.9, 146.4, 142.7, 142.3, 141.9, 141.9, 141.7, 132.4, 132.3, 132.2, 130.2, 129.9, 127.0, 126.8, 124.0, 123.8, 123.0, 122.9, 122.9, 122.8, 122.4, 122.4, 122.3, 122.2, 104.0, 104.0, 99.0, 98.9, 94.0, 93.6, 93.1, 93.0, 92.9, 88.8, 88.4, 34.3, 34.2, 34.1, 31.8, 31.7, 30.7, 30.6, 30.5, 29.4, 29.4, 29.3, 29.2, 28.8, 28.4, 23.5, 23.4, 22.6, 14.1, -0.1 ; FABMS: m/z 837.11 (M^+).

4.2.30. Compound 30. Yield: 1.32 g, 98%; ^1H NMR (300 MHz): δ 8.50 (d, $J=1$ Hz) and 8.04 (d, $J=11$ Hz) (1H), 7.39–7.33 (6H), 6.90 (d, $J=11$ Hz) and 6.70 (s) (1H), 3.30 (s, 1H), 3.24–3.09 (m, 2H), 2.84–2.72 (m, 8H), 1.70–1.59 (m, 8H), 1.40–1.30 (m, 24H), 1.24 (d, 12H), 0.90–0.85 (m, 12H).

4.2.31. Compound 31. Yield: 0.130 g, 73%; ^1H NMR (400 MHz): δ 8.49 (s) and 8.04 (d, $J=11$ Hz) (1H), 7.41–7.30 (8H), 7.17 (d, $J=11$ Hz) and 6.79 (s) (1H), 3.28–3.08 (m, 2H), 2.88–2.71 (m, 12H), 1.78–1.60 (m, 12H), 1.48–1.30 (m, 36H), 1.26–1.24 (m, 12H), 0.9 (m, 18H), 0.24 (s, 9H); ^{13}C NMR (100 MHz): δ 164.9, 160.5, 146.9, 146.5, 142.8, 142.4, 142.0, 141.9, 141.8, 132.5, 132.4, 132.4, 132.3, 130.1, 129.8, 127.1, 126.9, 124.0, 123.9, 123.1, 123.0, 122.9, 122.8, 122.7, 122.4, 122.3, 122.2, 104.0, 99.0, 94.1, 93.6, 93.2, 93.0, 92.9, 88.9, 88.4, 34.3, 34.2, 34.1, 31.8, 31.7, 30.8, 30.7, 30.7, 30.6, 29.4, 29.3, 28.8, 28.4, 23.5, 23.5, 22.6, 14.1, 0.0; FABMS: m/z 1106.37 (($M+1$) $^+$).

4.2.32. Compound 32. Yield: 0.045 g, 89%; ^1H NMR (300 MHz): δ 8.67 (d, $J=1$ Hz) and 8.22 (d, $J=11$ Hz) (1H), 7.58–7.43 (8H), 7.19 (d, $J=11$ Hz) and 6.94 (1H), 3.48 (s, 1H), 3.44–3.24 (m, 2H), 3.03–2.71 (m, 12H),

1.91–1.72 (m, 12H), 1.51–1.48 (m, 36H), 1.43–1.41 (m, 12H), 1.10–1.03 (m, 18H).

4.2.33. Compound 34. IR (KBr, cm^{-1}): 3201, 2962, 2925, 2860, 1687, 1669, 1524, 1459, 1387, 879; ^1H NMR (300 MHz): δ 8.48 (s) and 8.03 (d, $J=11$ Hz) (1H), 7.68 (s) and 7.67 (s) (1H), 7.38–7.33 (3H), 7.11 (d, $J=11$ Hz) and 6.80 (s) (1H), 3.23–3.10 (m, 2H), 2.77–2.63 (m, 4H), 1.72–1.54 (m, 4H), 1.41–1.28 (m, 12), 1.23 (d, $J=6.9$ Hz, 12H), 0.88 (m, 6H); ^{13}C NMR (100 MHz): δ 164.9, 160.4, 146.9, 146.5, 144.2, 142.8, 142.7, 139.5, 139.4, 132.2, 130.1, 129.8, 127.0, 126.8, 123.9, 123.8, 123.7, 122.6, 122.4, 101.1, 100.9, 93.5, 93.1, 88.2, 87.6, 40.2, 34.0, 33.9, 31.6, 30.7, 30.2, 29.4, 29.3, 29.0, 28.8, 28.4, 23.6, 23.4, 23.5, 22.6, 22.5, 14.1, 14.0; FABMS: m/z 600.54 ((M+1) $^+$). Analysis: $\text{C}_{33}\text{H}_{46}\text{INO}$ requires C, 66.10; H, 7.73; N, 2.34. Found: C, 66.41; H, 7.94; N, 2.27.

4.2.34. Compound 35. Yield: 3.85 g, 65%; IR (KBr, cm^{-1}): 3200, 2960, 2924, 2856, 1685, 1597, 1524, 1464, 1385, 879; ^1H NMR (300 MHz): δ 8.50 (s) and 8.04 (d) (1H), 7.69 (s, 1H), 7.39–7.30 (5H), 6.98 (d) and 6.75 (s) (1H), 3.30–3.08 (m, 2H), 2.84–2.63 (m, 8H), 1.74–1.55 (m, 8H), 1.44–1.25 (m, 24H), 1.23 (d, 12H), 0.88 (m, 12H); ^{13}C NMR (100 MHz): δ 164.8, 160.4, 146.9, 146.5, 143.7, 142.8, 142.4, 142.0, 139.5, 132.4, 132.3, 132.3, 130.0, 129.7, 127.1, 126.9, 124.1, 123.9, 123.0, 122.9, 122.9, 122.8, 122.7, 122.6, 122.5, 122.2, 100.8, 94.1, 93.6, 93.1, 93.0, 92.5, 92.3, 88.9, 88.4, 40.2, 34.4, 34.2, 33.9, 31.7, 31.7, 30.8, 30.7, 30.2, 29.4, 29.3, 29.2, 28.8, 28.4, 23.5, 22.6, 22.6, 14.1; FABMS: m/z 867.0 (M $^+$). Analysis: $\text{C}_{53}\text{H}_{74}\text{INO}$ requires C, 73.33; H, 8.59; N, 1.61. Found: C, 74.16; H, 8.88; N, 1.80.

4.2.35. Compound 36. Yield: 1.75 g, 88%; IR (KBr, cm^{-1}): 3329, 2954, 2922, 2852, 1658, 1595, 1497, 1458, 1381, 878; ^1H NMR (250 MHz): δ 8.47 (s) and 8.07 (d) (1H), 7.70 (s, 1H), 7.42–7.33 (7H), 7.65 (d) and 7.02 (s) (1H), 3.25–3.22 (m, 2H), 2.90–2.62 (m, 12H), 1.80–1.55 (m, 12H), 1.50–1.20 (m, 48H), 0.90 (m, 18H); ^{13}C NMR (75 MHz): δ 165.2, 146.9, 146.4, 143.7, 142.8, 142.4, 141.9, 139.4, 132.4, 130.2, 129.8, 127.0, 126.8, 124.0, 123.8, 123.0, 122.9, 122.8, 122.7, 122.6, 122.2, 100.8, 94.1, 93.6, 93.1, 93.0, 92.5, 92.3, 88.9, 88.4, 40.2, 34.3, 34.2, 33.9, 31.8, 31.7, 31.6, 30.8, 30.6, 30.2, 29.4, 29.3, 29.0, 28.8, 28.4, 23.5, 22.6, 14.1; ES-MS: m/z 1135.05 (M $^+$). Analysis: $\text{C}_{73}\text{H}_{102}\text{INO}$ requires C, 77.15; H, 9.05; N, 1.23. Found: C, 76.46; H, 8.99; N, 1.24.

4.2.36. Compound 37. Yield: 0.042 g, 72%; IR (KBr, cm^{-1}): 2954, 2925, 2852, 1685, 1669, 1498, 1460, 1384, 879; ^1H NMR (300 MHz): δ 8.50 (d, $J=1$ Hz) and 8.04 (d, $J=11$ Hz) (1H), 7.69 (s, 1H), 7.41–7.32 (9H), 6.94 (d, $J=11$ Hz) and 6.73 (d, $J=1$ Hz) (1H), 3.29–3.02 (m, 2H), 2.87–2.64 (m, 16H), 1.76–1.62 (m, 16H), 1.45–1.30 (m, 48H), 1.25 (d, 12H), 0.94–0.87 (m, 24H); ^{13}C NMR (100 MHz): δ 162.8, 148.6, 146.0, 145.2, 142.4, 141.9, 132.4, 132.3, 131.7, 130.2, 129.0, 128.2, 127.5, 126.8, 126.4, 125.2, 125.2, 124.6, 123.3, 122.8, 122.6, 121.9, 93.9, 93.3, 93.0, 90.2, 88.7, 45.7, 44.4, 34.4, 34.3, 34.2, 31.8, 31.8, 31.7, 31.6, 30.8, 30.7, 29.8, 29.4, 29.3, 29.2, 23.8, 22.7, 22.6, 22.4, 14.1, 13.7, 13.2, 12.7. Analysis: $\text{C}_{93}\text{H}_{130}\text{INO}$ requires C, 79.50; H, 9.33; N, 1.00. Found: C, 81.23; H, 8.79; N, 2.65.

4.2.37. Compound 38. IR (KBr, cm^{-1}): 3228, 2960, 2926, 2857, 1679, 1666, 1597, 1511; ^1H NMR (300 MHz): δ 8.49 (s) and 8.04 (d, $J=11$ Hz) (1H), 7.40–7.35 (6H), 7.11 (d, $J=11$ Hz) and 6.78 (s) (1H), 3.26–3.07 (m, 4H), 2.82 (m, 4H), 1.72–1.64 (m, 4H), 1.44–1.23 (m, 36H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz): δ 165.0, 160.5, 146.9, 146.5, 142.4, 132.3, 130.1, 129.8, 127.1, 126.9, 124.0, 122.45, 94.1, 93.7, 88.8, 88.3, 34.3, 31.7, 30.7, 29.4, 28.8, 28.4, 23.5, 22.6, 14.1; Analysis: $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_2$ requires C, 82.24; N, 9.20; N, 4.00. Found: C, 81.20; H, 9.11; N, 3.85.

4.2.38. Compound 39. Yield: 0.720 g, 77%; IR (KBr, cm^{-1}): 3233, 2959, 2926, 2855, 1688, 1667, 1597, 1499, 1464; ^1H NMR (300 MHz): δ 8.45 (d, $J=1$ Hz) and 8.04 (d, $J=11$ Hz) (1H), 7.41–7.36 (8H), 7.71 (d, $J=11$ Hz) and 7.03 (s) (1H), 3.27–3.08 (m, 4H), 2.86–2.81 (m, 8H), 1.77–1.69 (m, 8H), 1.44–1.20 (m, 48H), 0.91–0.86 (m, 12H); ^{13}C NMR (100 MHz): δ 165.2, 160.6, 146.9, 146.4, 142.4, 141.9, 141.9, 132.5, 132.3, 130.2, 129.8, 127.0, 126.8, 123.9, 123.8, 123.8, 123.0, 122.9, 122.8, 122.7, 122.5, 122.4, 122.2, 122.2, 94.1, 94.0, 93.6, 93.6, 93.1, 93.0, 93.0, 92.9, 88.9, 88.8, 88.4, 88.3, 34.4, 34.3, 31.8, 31.7, 30.8, 30.7, 29.4, 29.2, 23.5, 22.3, 14.1, 14.0.

4.2.39. Compound 40. Yield: 0.176 g, 11% (Scheme 2b); IR (KBr, cm^{-1}): 3233, 2957, 2924, 2854, 1687, 1666, 1596, 1499, 1464, 1383, 1363, 1244, 892, 879, 723; ^1H NMR (300 MHz): δ 8.50 (d, $J=1$ Hz) and 8.04 (d, $J=11$ Hz) (1H), 7.40–7.35 (10H), 6.98 (d, $J=11$ Hz) and 6.76 (s) (1H), 3.26–3.07 (m, 4H), 2.86–2.78 (m, 12H), 1.76–1.65 (m, 12H), 1.44–1.20 (m, 60H), 0.91–0.86 (m, 18H); ^{13}C NMR (100 MHz): δ 164.9, 160.5, 146.9, 146.5, 142.4, 142.0, 141.9, 133.3, 132.4, 132.3, 131.1, 132.0, 130.0, 129.8, 128.9, 128.6, 128.4, 127.1, 126.9, 124.0, 123.8, 123.6, 123.0, 122.8, 122.2, 94.1, 93.6, 93.0, 88.9, 88.4, 34.3, 34.2, 31.8, 31.7, 31.7, 30.8, 30.7, 29.4, 29.3, 29.0, 28.9, 28.4, 23.6, 23.5, 22.6, 14.1. Analysis: $\text{C}_{88}\text{H}_{120}\text{N}_2\text{O}_2$ requires C, 85.38; N, 9.77; N, 2.26. Found: C, 82.99; H, 9.44; N, 2.53.

4.2.40. Compound 41. Yield: 0.098 g, 9%; ^1H NMR (300 MHz): δ 8.51 and 8.04 (2H), 7.40–7.26 (14H), 7.03 and 6.78 (2H), 3.25–3.01 (m, 4H), 2.86–2.84 (m, 20H), 1.74–1.72 (m, 20H), 1.43–1.24 (m, 84H), 0.91–0.89 (m, 30H); ^{13}C NMR (100 MHz): δ 164.8, 160.4, 146.9, 146.5, 142.4, 141.9, 132.4, 132.3, 130.0, 129.7, 128.4, 127.1, 126.9, 124.1, 123.1, 122.8, 122.4, 122.2, 94.0, 93.6, 93.1, 88.9, 88.4, 34.3, 34.2, 31.8, 31.7, 30.8, 30.7, 29.4, 29.3, 28.8, 28.4, 23.5, 22.7, 14.1. Analysis: $\text{C}_{128}\text{H}_{176}\text{N}_2\text{O}_2$ requires C, 86.62; N, 10.00; N, 1.58. Found: C, 84.64; H, 9.86; N, 1.53.

4.2.41. Compound 42. Yield: 0.009 g, 15%; ^1H NMR (300 MHz): δ 8.50 and 8.40 (2H), 7.55–7.28 (18H), 6.78 and 6.69 (2H), 3.23–3.10 (m, 4H), 2.86–2.82 (m, 28H), 1.74–1.66 (m, 28H), 1.43–1.24 (m, 108H), 0.89–0.87 (m, 42H); MALDI-TOF (in DTH): 2311.65 ((M+1) $^+$).

4.2.42. Compound 43. A mixture of **33** (4.98 g, 10 mmol), acetamide (750 mg, 15 mmol), K_3PO_4 (5 g), CuI (110 mg), and *N,N'*-dimethylethylenediamine (110 mg) was heated to 80 °C for 24 h and then cooled to room temperature. After

addition of 40 mL ethyl acetate, the resulting mixture was filtered through a plug of silica gel and rinsed with several portions of ethyl acetate. The solvent was removed and the residue dried under vacuum. The residue was redissolved in a 1:1 mixture of ethanol and dichloromethane (100 mL). To this solution was added 25 g of silica gel with stirring. The solvent was removed and the residue dried slowly under vacuum. The silica with the adsorbed product mixture was added to the top of a silica gel column (4×20 cm), which had been prepared with a 99:1 mixture of hexane/ethyl acetate. Remaining **33** (1.1 g, 2.2 mmol) was eluted with the same solvent mixture. The product was eluted with a 10:1 mixture of hexane/ethyl acetate. Yield: 1.99 g, 59% based on consumed starting material; IR (KBr, cm^{-1}): 3020, 2957, 2929, 2858, 1688, 1501, 1465; ^1H NMR (300 MHz): 7.68 (s, 1H), 7.59 (s, 1H), 6.91 (br s, 1H), 2.64 (m, 2H), 2.45 (m, 2H), 2.18 (s, 3H), 1.59–1.52 (m, 4H), 1.40–1.26 (m, 12H), 0.91–0.87 (m, 6H); ^{13}C NMR (100 MHz): δ 168.3, 143.8, 139.7, 135.3, 133.4, 124.4, 96.1, 40.5, 31.6, 31.6, 30.5, 30.2, 29.6, 29.1, 29.0, 24.3, 22.6, 22.5, 14.1, 14.0; FABMS: m/z 430.36 (M^+). Analysis: $\text{C}_{20}\text{H}_{32}\text{INO}$ requires C, 55.94; H, 7.51; N, 3.26. Found: C, 55.53; H, 7.40; N, 3.18.

4.2.43. Compound 44. A mixture of **43** (2 g), 10 mL concd HCl, and 5 mL ethanol was heated to 85 °C for 5 h. After cooling to room temperature, 40 mL of water was added. Then a 40% KOH solution was added until the solution became basic. The product was extracted with ether to give the product as a light brown oil, which partly crystallized after solvent removal. (This raw product was sufficiently pure for the next stage.) A sample was further purified by chromatography on silica gel using a 10:1 mixture of hexane/ethyl acetate as the eluent. The purified product partly crystallized in the form of colorless crystals. ^1H NMR (400 MHz): δ 7.42 (s, 1H), 6.56 (s, 1H), 3.57 (s, 2H), 2.57 (m, 2H), 2.39 (m, 2H), 1.60–1.54 (m, 4H), 1.40–1.33 (m, 12H), 0.91 (m, 6H); ^{13}C NMR (100 MHz): δ 144.2, 143.4, 139.3, 127.1, 116.3, 86.5, 40.3, 31.7, 30.5, 30.3, 29.4, 29.3, 29.1, 28.6, 22.6, 14.1.

4.2.44. Compound 45. To a stirred mixture of **44** (0.774 g, 2 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.37 mL, 3 mmol) in 10 mL CH_2Cl_2 at 0 °C was added *t*-BuNO (0.3 mL, 2.5 mmol) and stirring was continued for 30 min at the same temperature. Then K_2CO_3 (1 g) and HNET_2 (1 mL) were added sequentially. After stirring for 1 h at room temperature, the mixture was poured into water. The organic product was extracted with ethyl acetate. The combined extracts were dried with MgSO_4 and filtered, and then the solvent was removed under vacuum. The product was purified by chromatography on silica gel, using hexane/ethyl acetate (98:2) as the eluent. Yellow-orange oil. Yield: 0.869 g, 92%; IR (toluene, cm^{-1}): 2957, 2930, 2857, 1467, 1379, 1394, 1237, 1100, 755; ^1H NMR (300 MHz): δ 7.59 (s, 1H), 7.19 (s, 1H), 3.75 (q, $J=7.2$ Hz, 4H), 2.73–2.62 (m, 4H), 1.63–1.52 (m, 4H), 1.42–1.25 (m, 18H), 0.93–0.86 (m, 6H); ^{13}C NMR (100 MHz): δ 148.7, 142.9, 140.0, 137.0, 117.1, 95.7, 40.6, 31.7, 31.7, 31.1, 31.0, 30.4, 29.3, 29.1, 22.6, 22.6, 14.1; FABMS: m/z 472.41 ($(\text{M}+1)^+$).

4.2.45. Compound 46. Yield: 0.302 g, 90%; IR (KBr, cm^{-1}): 2959, 2929, 2857, 1691, 1466; ^1H NMR

(300 MHz): δ 8.47 (d, $J=1$ Hz) and 8.07 (d, $J=12$ Hz) (1H), 7.40–7.34 (6H), 7.28 (d, $J=12$ Hz) and 6.83 (s) (1H), 3.79 (q, $J=7.2$ Hz, 4H), 3.27–3.07 (m, 2H), 2.84–2.76 (m, 8H), 1.73–1.57 (m, 8H), 1.45–1.23 (m, 42H), 0.96–0.87 (m, 12H); ^{13}C NMR (100 MHz): δ 165.0, 160.5, 148.5, 146.9, 146.4, 143.7, 142.9, 142.3, 141.7, 134.9, 134.7, 133.8, 133.8, 132.3, 132.2, 130.0, 129.7, 127.1, 126.9, 124.2, 124.0, 123.8, 123.5, 121.8, 121.6, 119.0, 118.9, 118.6, 116.4, 116.3, 94.3, 94.1, 93.7, 93.3, 91.2, 91.1, 89.1, 88.6, 34.7, 34.4, 34.2, 31.8, 31.8, 31.4, 31.3, 31.2, 31.0, 30.9, 30.8, 29.7, 29.4, 29.3, 28.8, 28.4, 23.5, 22.6, 14.1; FABMS: m/z 842.07 ($(\text{M}+1)^+$); Analysis: $\text{C}_{57}\text{H}_{84}\text{N}_4\text{O}$ requires C, 81.37; H, 10.06; N, 6.66. Found: C, 80.35; H, 10.36; N, 5.79.

4.2.46. Alternative route to 35. A mixture of **46** (0.035 g, 0.04 mmol) and methyl iodide (0.29 g, 2.0 mmol) was heated to 110 °C in a sealed tube for 10 h. Then, the mixture was cooled to room temperature, diluted with hexanes, and purified over silica gel using hexanes/ethyl acetate (1:1). Yield: 0.025 g, 72%.

4.2.47. Compound 47. Yield: 0.240 g, 37%; IR (KBr, cm^{-1}): 3380, 3234, 2961, 2927, 2856, 1779, 1732, 1679; ^1H NMR (300 MHz): δ 8.56 (s, 2H), 8.51 (d, $J=1$ Hz) and 8.04 (d, $J=12$ Hz) (2H), 7.46 (s), 7.42 (s), 7.41 (s), 7.36 (s) (12H), 6.82 (d, $J=12$ Hz) and 6.64 (s, $J=1$ Hz) (2H), 3.22 (septet) and 3.12 (septet) (4H), 2.86–2.81 (m, 8H), 2.68 (septet, 4H), 1.74–1.68 (m, 8H), 1.45–1.33 (m, 24H), 1.25 (d, $J=7$ Hz, 24H), 1.21 (d, $J=7$ Hz, 24H), 0.92–0.87 (m, 12H); ^{13}C NMR (75 MHz): δ 165.8, 165.0, 147.4, 146.9, 146.5, 142.5, 142.4, 137.2, 132.4, 130.2, 127.4, 127.1, 126.9, 126.2, 125.9, 124.0, 122.7, 122.2, 119.8, 94.2, 93.6, 88.8, 88.3, 85.7, 34.3, 31.7, 30.7, 29.4, 28.8, 28.4, 23.8, 23.5, 22.7, 14.1. Analysis: $\text{C}_{104}\text{H}_{126}\text{N}_4\text{O}_6$ requires: C, 81.74; H, 8.31; N, 3.67. Found: C, 80.32; H, 8.22; N, 3.66.

4.2.48. Compound 48. Yield: 0.192 g, 56%; IR (KBr, cm^{-1}): 3386, 3245, 2959, 2926, 2855, 1779, 1730, 1691; ^1H NMR (300 MHz): δ 8.57 (s, 2H), 8.49 (d, $J=1$ Hz) and 8.05 (d, $J=12$ Hz) (2H), 7.48 (s, 4H), 7.43–7.36 (12H), 7.14 (d, $J=12$ Hz) and 6.81 (s) (2H), 3.27–3.08 (m, 4H), 2.88–2.83 (m, 16H), 2.74–2.64 (m, 4H), 1.74–1.71 (m, 16H), 1.45–1.27 (m, 48H), 1.27–1.21 (m, 48H), 0.92–0.88 (m, 24H); ^{13}C NMR (75 MHz): δ 165.7, 164.9, 147.4, 146.9, 146.5, 142.5, 142.4, 142.0, 137.3, 132.6, 132.4, 132.3, 130.1, 129.7, 127.4, 127.1, 126.9, 126.3, 126.0, 124.0, 123.9, 123.0, 122.8, 122.5, 122.2, 119.8, 93.6, 93.0, 89.3, 88.9, 88.4, 85.8, 34.4, 34.2, 31.8, 31.7, 30.8, 30.7, 29.5, 29.3, 28.8, 28.4, 23.8, 23.5, 22.7, 14.1; MALDI-TOF (in DTH): 2065.38 (M^+); Analysis: $\text{C}_{144}\text{H}_{182}\text{N}_4\text{O}_6$ requires C, 83.75; H, 8.88; N, 2.71. Found: C, 80.24; H, 8.59; N, 2.73.

4.2.49. Compound 49. Yield: 0.200 g, 95%; IR (KBr, cm^{-1}): 3400, 3300, 2958, 2925, 2855, 1730, 1690; ^1H NMR (300 MHz): δ 8.57 (s, 2H), 8.50 (s) and 8.05 (d, $J=12$ Hz) (2H), 7.47 (s, 4H), 7.43–7.36 (20H), 6.90 (d) and 6.72 (s) (2H), 3.22 (septet) and 3.12 (septet) (4H), 2.90–2.80 (m, 24H), 2.69 (septet, 4H), 1.78–1.68 (m, 24H), 1.48–1.21 (m, 120H), 0.90–0.88 (m, 36H); ^{13}C NMR (75 MHz): δ 165.9, 164.8, 147.4, 147.0, 146.5, 142.5, 142.4, 141.9, 137.3, 132.5, 132.5, 132.4, 130.0,

127.4, 127.1, 126.9, 126.3, 123.9, 122.8, 122.2, 119.8, 93.6, 93.1, 93.0, 89.3, 88.6, 34.4, 34.2, 31.8, 31.8, 30.8, 30.7, 29.5, 29.3, 23.8, 23.5, 22.7, 14.1; MALDI-TOF (in DTH): 2604.08 ((M+2)⁺); Analysis: C₁₈₄H₂₃₈N₄O₆ requires C, 84.94; H, 9.22; N, 2.15. Found: C, 83.11; H, 9.14; N, 2.08.

4.2.50. Compound 50. Yield: 0.128 g, 91%; IR (cm⁻¹): 2958, 2927, 2856, 1717, 1684; ¹H NMR (400 MHz): δ 8.93 (s, 4H), 8.57 (s) and 8.05 (d, *J*=11 Hz) (2H), 7.52–7.47 (12H), 7.37 (d, *J*=11 Hz) and 6.78 (s) (2H), 3.12 (m, 4H), 2.83 (m, 8H), 2.71 (m, 4H), 1.82–1.35 (m, 32H), 1.18–1.26 (m, 48H), 0.92–0.88 (m, 12H); ¹³C NMR (100 MHz): δ 164.7, 162.9, 162.8, 146.9, 146.5, 146.0, 142.4, 132.5, 132.4, 131.7, 127.6, 127.1, 126.9, 125.2, 124.1, 94.0, 91.3, 85.9, 39.4, 34.4, 31.8, 31.7, 30.8, 29.5, 29.4, 28.4, 23.8, 23.5, 22.7, 14.1. Analysis: C₁₀₈H₁₂₈N₄O₆ requires: C, 82.19; H, 8.17; N, 3.55. Found: C, 80.16; H, 8.17; N, 3.40.

4.2.51. Compound 51. Yield: 0.210 g, 58%; IR (cm⁻¹): 2957, 2926, 2856, 1718, 1683, 1598, 1580, 1499, 1466, 1459, 1338, 1248; ¹H NMR (300 MHz): δ 8.92 (s, 4H), 8.50 (s) and 8.05 (d, *J*=12 Hz) (2H), 7.53 (s, 4H), 7.44–7.37 (12H), 7.06 (d, *J*=12 Hz) and 6.78 (s) (2H), 3.27–3.08 (m, 4H), 2.86–2.68 (m, 20H), 1.78–1.70 (m, 16H), 1.44–1.20 (m, 96H), 0.94–0.84 (m, 24H); ¹³C NMR (75 MHz): δ 165.0, 162.8, 146.9, 146.4, 146.0, 142.4, 141.9, 132.5, 132.4, 131.7, 130.3, 127.6, 127.0, 126.8, 125.2, 122.8, 122.4, 94.1, 93.0, 88.6, 88.0, 85.8, 34.4, 34.2, 31.8, 31.8, 30.8, 30.7, 29.5, 29.3, 29.1, 28.4, 23.8, 23.5, 22.7, 14.1; Analysis: C₁₄₈H₁₈₄N₄O₆ requires C, 84.04; H, 8.77; N, 2.65. Found: C, 81.84; H, 8.73; N, 2.15.

4.2.52. Compound 52. IR (cm⁻¹): 2959, 2927, 2857, 1718, 1683; ¹H NMR (400 MHz): δ 8.92 (s, 4H), 8.48 (s) and 8.05 (d) (2H), 7.53 (s, 4H), 7.41–7.36 (16H), 7.49 (d) and 6.85 (s) (2H), 3.25–3.12 (m, 4H), 2.85 (m, 24H), 2.77–2.70 (m, 4H), 1.74 (m, 24H), 1.45–1.26 (m, 72H), 1.25 (m, 24H), 1.21 (d, *J*=6.9 Hz, 24H), 0.94–0.89 (m, 36H); ¹³C NMR (75 MHz): δ 164.8, 162.8, 146.9, 146.5, 146.0, 142.4, 141.9, 132.4, 131.7, 130.2, 127.6, 127.1, 126.9, 125.2, 124.1, 122.8, 122.4, 94.0, 93.0, 88.8, 85.8, 34.4, 34.2, 31.8, 31.8, 31.7, 30.8, 30.7, 29.5, 29.4, 29.3, 23.8, 23.5, 22.7, 22.7, 14.1; Analysis: C₁₈₈H₂₄₀N₄O₆ requires C, 85.15; H, 9.12; N, 2.11. Found: C, 81.50; H, 8.84; N, 2.04.

4.2.53. Compound 53. Yield: 0.256 g, 93%; IR (cm⁻¹): 3380, 2960, 2926, 2856, 1717, 1682, 1599, 1581, 1499, 1467, 1459, 1336, 1250; ¹H NMR (400 MHz): δ 8.93 (s, 4H), 8.50 (s) and 8.01 (d) (2H), 7.55 (s, 4H), 7.46–7.35 (20H), 7.50 (d) and 6.90 (s) (2H), 3.18 (m, 4H), 2.81 (m, 32H), 2.79–2.71 (m, 4H), 1.75–1.22 (m, 176H), 0.91 (m, 48H); ¹³C NMR (100 MHz): δ 165.1, 162.8, 146.9, 146.4, 146.0, 142.4, 141.9, 132.4, 131.7, 127.7, 127.6, 127.0, 126.8, 122.8, 93.1, 34.2, 31.8, 30.7, 29.3, 23.8, 23.5, 22.6, 14.1.

4.2.54. Compound 54. Yield: 0.412 g, 83%; IR (KBr, cm⁻¹): 2959, 2922, 2854, 2152, 2118, 1597, 1567, 1491, 1464; ¹H NMR (300 MHz): δ 7.34 (s, 1H), 7.31 (s, 1H), 7.30 (s, 2H), 3.39 (septet, 2H), 2.80–2.71 (m, 4H), 1.71–1.59 (m, 4H), 1.43–1.27 (m, 24H), 0.90 (m, 6H), 0.27 (s, 9H); ¹³C NMR (75 MHz): δ 170.2, 145.2, 142.8, 142.2, 132.6, 132.2, 126.4, 124.5, 123.9, 122.8, 122.1, 103.8,

99.1, 93.2, 90.1, 34.2, 34.1, 31.7, 31.6, 30.7, 30.5, 29.7, 29.3, 29.2, 22.6, 22.4, 14.1, 14.0, –0.1. MS: *m/z* 551.41 (M⁺).

4.2.55. Compound 55. Yield: 0.240 g, 98%; IR (KBr, cm⁻¹): 2961, 2928, 2856, 2151, 2112, 1597, 1496, 1464; ¹H NMR (300 MHz): δ 7.39 (s, 1H), 7.37 (s, 1H), 7.33–7.31 (4H), 3.02 (septet, 2H), 2.78–2.64 (m, 8H), 1.69–1.55 (m, 8H), 1.37–1.23 (m, 36H), 0.86–0.79 (m, 12H), 0.20 (s, 9H); ¹³C NMR (100 MHz): δ 170.1, 145.2, 142.8, 142.4, 142.0, 141.8, 132.5, 132.4, 132.3, 126.5, 124.6, 123.9, 123.3, 122.9, 122.5, 121.9, 104.0, 99.0, 93.3, 93.2, 92.8, 90.2, 34.3, 34.2, 34.1, 34.1, 31.8, 31.7, 31.7, 30.8, 30.7, 30.6, 30.6, 29.8, 29.4, 29.3, 29.2, 22.6, 22.4, 14.1, 14.0, 0.0; MS: *m/z* 819.61 (M⁺).

4.2.56. Compound 56. Yield: 0.212 g, 94%; IR (KBr, cm⁻¹): 2959, 2926, 2855, 2150, 2111, 1599, 1500, 1466, 1461; ¹H NMR (300 MHz): δ 7.40 (s, 1H), 7.39 (s, 1H), 7.38 (s, 2H), 7.34–7.32 (4H), 3.40 (septet, 2H), 2.87–2.72 (m, 12H), 1.71–1.61 (m, 12H), 1.45–1.28 (m, 84H), 0.90 (m, 18H), 0.28 (s, 9H); ¹³C NMR (75 MHz): δ 170.1, 145.3, 142.8, 142.5, 142.0, 141.9, 141.8, 132.5, 132.4, 132.4, 126.5, 124.6, 123.9, 123.3, 122.9, 122.9, 122.7, 122.4, 121.9, 104.0, 99.0, 93.3, 93.3, 93.0, 93.0, 92.9, 90.2, 34.3, 34.2, 34.1, 31.8, 31.7, 31.7, 30.8, 30.7, 30.6, 29.8, 29.4, 29.3, 22.6, 22.5, 14.1, 14.1, 0.0; MS: *m/z* 1087.77 (M⁺).

4.2.57. Compound 57. Yield: 0.764 g, 62%; IR (KBr, cm⁻¹): 2965, 2928, 2856, 2207, 2114, 1598, 1494, 1465; ¹H NMR (300 MHz): δ 7.40 (s, 2H), 7.31 (s, 4H), 3.88 (septet, 4H), 2.81 (m, 4H), 1.71 (m, 4H), 1.43 (m, 4H), 1.40–1.30 (m, 8H), 1.31 (d, 24H), 0.88 (m, 6H); ¹³C NMR (100 MHz): δ 170.1, 145.3, 142.5, 132.4, 126.5, 124.5, 122.4, 93.5, 90.0, 34.3, 31.7, 30.8, 29.8, 29.4, 22.6, 22.5, 14.0, 34.3, 31.7, 30.7, 29.8, 29.3, 22.6, 22.5, 14.0; MS: *m/z* 664.58 (M⁺).

4.2.58. Compound 58. Yield: 0.090 g, 72%; IR (KBr, cm⁻¹): 2961, 2926, 2856, 2205, 2111, 1598, 1500, 1465; ¹H NMR (300 MHz): δ 7.41 (s, 2H), 7.39 (s, 2H), 7.32 (s, 4H), 3.39 (septet, 4H), 2.87–2.79 (m, 8H), 1.78–1.65 (m, 8H), 1.44–1.26 (m, 72H), 0.88 (m, 12H); ¹³C NMR (75 MHz): δ 170.1, 145.3, 142.5, 142.0, 132.5, 132.4, 126.5, 124.6, 123.9, 123.2, 122.1, 93.3, 93.1, 90.1, 34.3, 34.2, 31.8, 31.7, 30.8, 30.7, 29.8, 29.4, 29.3, 22.6, 22.5, 14.1, 14.0. MS: *m/z* 932.78 (M⁺).

4.2.59. Compound 59. Yield: 0.142 g, 98%; IR (KBr, cm⁻¹): 2960, 2926, 2855, 2204, 2111, 1597, 1501, 1464; ¹H NMR (300 MHz): δ 7.40 (s, 2H), 7.39–7.37 (4H), 7.32–7.30 (4H), 3.39 (septet, 4H), 2.87–2.75 (m, 12H), 1.77–1.68 (m, 12H), 1.45–1.26 (m, 84H), 0.89 (m, 18H); ¹³C NMR (75 MHz): δ 170.1, 145.3, 145.2, 142.4, 142.0, 141.9, 132.5, 132.4, 132.3, 126.5, 126.4, 124.6, 123.2, 122.8, 121.9, 93.3, 93.2, 92.9, 90.2, 45.8, 34.3, 34.2, 31.8, 31.7, 30.8, 30.7, 30.6, 29.8, 29.4, 29.3, 22.6, 22.4, 14.1, 14.0; MS: *m/z* 1200.66 (M⁺).

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