Electronic Supplementary Material (ESI) for Green Chemistry.

A new route to α,ω-diamines from hydrogenation of dicarboxylic acids and their derivatives in the presence of amines

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1. General Method

All the commercially available reagents were used without further purification unless specified. 1,4-Dinitrobenzene, 4-nitroaniline, benzylamine, dodecanedioic acid, dodecanediol, decanedioic acid, heptanedioic acid and 1,4-dioxane were purchased from Alfa Aesar; dodecane, *tris*(2,4-pentanedionato)ruthenium(III) ([$Ru(acac)_3$], 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) and *N*-methylaniline were purchased from Sigma Aldrich; tris(dibenzylideneacetone)dipalladium(0) ([$Pd_2(dba)_3$]), 4-fluoroaniline was purchased from Fluorochem. Aniline was distilled over zinc powder and KOH under vacuum. Air sensitive or moisture sensitive reactions were carried out under argon in a fume hood using standard Schlenk techniques with oven-dried glassware. Flash column chromatography was performed manually using silica gel (pore size 60 Å, 70-230 mesh particle size, 40-63 μm particle size). Analytical TLC was performed on pre-coated polyester sheets of silica (60 F254 nm) and visualised by short-wave UV light at 254nm. Permanganate TLC stain was used for compounds with no UV visible chromophore. Ninhydrin stain was also used for primary and secondary amines, giving a dark purple spot for primary amines, and a yellow/orange spot for secondary amines. Mass spectra were recorded on a Micromass LCT with a TOF mass spectrometer coupled to a Waters 2795 HPLC and a Waters 2996 detector. NMR spectra were recorded on Bruker Avance II 400 and Bruker Avance II 500 spectrometers, ^{13}C spectra were measured with ^{1}H decoupling. Residual protio peaks from deuterated solvents were used as reference with TMS at 0 ppm. GCMS was carried out using a Thermo electron Corporaton DSQ II for the GC, and Trace GC ULTRA Thermo Electron Corporation mass spectrometer for the

MS with a THERMO TR-5 (5% Phenyl Methylpolysiloxane) column. Method: 50-300 °C, ramp rate 15 °C/min, hold for 20 mins.

2. Experimental Procedures

2.1. Synthesis of esters from carboxylic acids[1]

General procedure 1: To a solution of carboxylic acid (20 g, 1.0 equiv.) in alcohol (50 mL) was slowly added concentrated sulfuric acid (0.3 equiv.). The resulting mixture was stirred at reflux for 2 h until TLC analysis indicated complete consumption of the starting material. The excess alcohol was removed under vacuum to give the crude product, which was poured into crushed ice and then extracted with dichloromethane (DCM, 5 x 50 mL). The organic layers were washed with 5 % aq. $NaHCO_3$ solution (50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure.

2.2. Synthesis of primary or secondary amides from carboxylic acid.[2]

General procedure 2: Oxalyl chloride (4.6 mL, 53 mmol, 4 equiv.) was added dropwise into a suspension of carboxylic acid (13 mmol) in anhydrous DCM (65 mL) in a Schlenk flask. The reaction mixture was stirred overnight under Ar. The reaction mixture was concentrated under reduced pressure to afford the carboxylic acid chloride. For the synthesis of primary amides, anhydrous THF (30 mL) was then added into the flask and the solution of the carboxylic acid chloride was slowly added to aqueous ammonia (6 mL, 53 mmol, 4 equiv.) at 0 °C. A white solid appeared immediately after addition, and the reaction mixture was stirred for 2 h at room temperature. The white solid was filtered and washed with THF (50 mL) to afford the primary amide. For the synthesis of secondary amides, distilled aniline (2.4 mL, 26 mmol, 2 equiv.) in pyridine (16 mL) was prepared under Ar. Acid chloride was then added into the solution of aniline in pyridine dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then poured into distilled water (100 mL). Filtration afforded and drying the crude product.

2.3. Hydrogenation of difunctional carboxylic acids and their derivatives in the presence of amine source.[3]

General procedure 3: $[Ru(acac)_3]$ (0.010-0.020 g, 0.025-0.05 mmol, 1-2 mol%), triphos (0.031-0.062 g, 0.05-0.1 mmol, 2-4 mol%) and substrate (2.5 mmol) were weighed in air and introduced into a 250 mL Hastelloy autoclave fitted with a stirrer bar. The autoclave was sealed and purged by three vacuum/Ar cycles. Methanesulfonic acid (1.62-3.24 μL, 0.025-0.05 mmol, 1-2 mol%) in degassed 1,4-dioxane or 2-methyl tetrahydrofuran (15 mL) was introduced into the autoclave through a septum using a syringe. Amine (3-5 equiv.) was also introduced into the autoclave. The autoclave was sealed again, connected to the high pressure system, and purged six times with 10 bar of H_2. The autoclave was charged with 10 bar of H_2, and heated to 220 °C for the required amount of time. The autoclave was cooled, vented and opened. The crude mixtures were analysed using GC-MS, GC-FID, NMR spectroscopy, or mass spectrometry, examples of spectra are shown below. Quantitative calculations were based on the analysis of ^1H NMR spectra with 1,4-dinitrobenzene as an internal standard.

2.4. Reduction of dicarboxylic acids and diesters using $LiAlH_4$.[4]

General procedure 4: Carboxylic acid (30 mmol) in anhydrous THF (100 mL) was added slowly into a solution of lithium aluminum hydride (92 mmol, 3 equiv.) in anhydrous THF (250 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight. Excess lithium aluminium hydride was quenched with ethyl acetate. Saturated potassium sodium tartrate solution (Rochelle solution) was slowly added to the reaction mixture. The mixture was stirred for 3 hours and the two layers were separated using a separating funnel. The organic layer was dried over magnesium sulfate. Filtration and concentration under reduced pressure afforded the product.

2.5. Amination of diols

General procedure 5: For the synthesis of *N*-substituted diamines

$[Ru(acac)_3]$ (0.010 g, 0.025 mmol, 1 mol%), triphos (0.031 g, 0.05 mmol, 2 mol%) and substrate (2.5 mmol) were weighed in air and introduced into a 250 mL Hastelloy autoclave fitted with a stirrer bar. The autoclave was sealed and

purged by three vacuum/Ar cycles. Methanesulfonic acid (1.62 μL, 0.025 mmol, 1 mol%) in degassed 1,4-dioxane (15 mL) was introduced into the autoclave through a septum using a syringe. For the synthesis of *N*-substituted diamines, amine (3 equiv.) was also introduced into the autoclave. The autoclave was sealed again. Depending on the reaction conditions, the autoclave was charged with Ar (1 bar or 10 bar), or H_2 (10 bar), and heated to 220 °C for 20 h. The autoclave was cooled, vented and opened. The crude mixtures were analysed using GC-MS, GC-FID, NMR spectroscopy, or mass spectrometry, examples of spectra are shown below. Quantitative calculations were based on the analysis of ^{1}H NMR spectra with 1,4-dinitrobenzene as an internal standard.

General procedure 6: For the synthesis of primary diamines

[$Ru(acac)_3$] (0.010 g, 0.025 mmol, 2 mol%), triphos (0.031 g, 0.05 mmol, 4 mol%) and substrate (1.25 mmol) were weighed in air and introduced into a 250 mL Hastelloy autoclave fitted with a stirrer bar. The autoclave was sealed and purged by three vacuum/Ar cycles. Methanesulfonic acid (1.62 μL, 0.025 mmol, 2 mol%) in degassed 1,4-dioxane (20 mL) or ammonia in dioxane (0.5 M, 20 mL) was introduced into the autoclave through a septum using a syringe. Aqueous ammonia (35 %, 30 mL) was added into the autoclave. The autoclave was sealed again, connected to the high pressure system, and purged six times with 10 bar of H_2. The autoclave was charged with 10 bar of H_2, and heated to 220 °C or 165 °C for the required for the required amount of time. The autoclave was cooled, vented and opened. The crude mixtures were analysed using GC-MS, GC-FID, NMR spectroscopy, or mass spectrometry, examples of spectra are shown below. Quantitative calculations were based on the analysis of ^{1}H NMR spectra with 1,4-dinitrobenzene as an internal standard if the product was soluble in deuterated chloroform or methanol, if not, isolated yields were obtained.

2.6. Sequential reactions

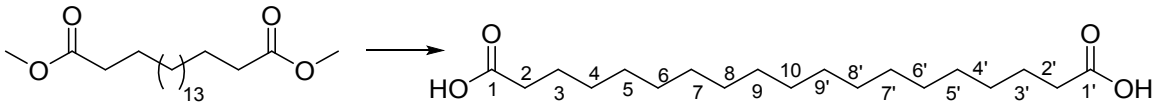
[$Ru(acac)_3$] (0.010 g, 0.025 mmol, 2 mol%), triphos (0.031 g, 0.05 mmol, 4 mol%) and substrate (1.25 mmol) were weighed in air and introduced into a 250 mL Hastelloy autoclave fitted with a stirrer bar. The autoclave was sealed and

purged by three vacuum/Ar cycles. Methanesulfonic acid (1.62 μL, 0.025 mmol, 2 mol%) in degassed 1,4-dioxane (7.5 mL) and degassed distilled water (5 mL) were introduced into the autoclave through a septum using a syringe. The autoclave was sealed, and purged 6 times with H_2 (~10 bar). The autoclave was charged with H_2 (10 bar), and heated at 220 °C (internal temperature) for 20 hours. The autoclave was cooled, and hydrogen gas was slowly vented before the autoclave was reconnected to a Schlenk line. Under a flow of Ar, degassed 1,4-dioxane (12.5 mL) and aqueous ammonia (30 mL) were added into the autoclave by a long needle. The autoclave was purged again with H_2 (~10 bar), and charged with 10 bar of H_2. The autoclave was heated at 220 °C for another 20 hours. The autoclave was then cooled, vented and opened. The crude mixtures were concentrated under reduced pressure to yellowish solids. Quantitative calculations were based on the analysis of ^{1}H NMR spectra with 1,4-dinitrobenzene as an internal standard.

2.7. Synthesis and characterization of substrates

2.7.1. Dicarboxylic acids

Nonadecanedioic acid

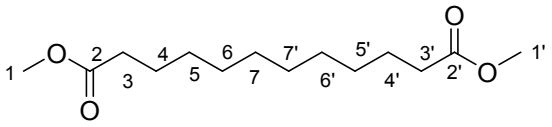


Reaction conditions adopted from the literature.[5] 1,19-Dimethyl nonadecanedioate (1.0 g, 2.8mmol, 1 equiv.) was introduced into a round bottom flask. Dioxane (80 mL), distilled water (50 mL) and hydrochloric acid (36 % in water, 3 drops) were added and the mixture was heated under reflux overnight. After cooling, the solvent was removed on a rotary evaporator. DCM (100 mL) was added and the heterogeneous mixture was stirred fast before being filtered through a Buchner funnel. The white solid was washed with DCM (50 mL) and dried under reduced pressure to afford the crude material which was then recrystallised from THF and DCM (1:1) to afford 1,19-nonadecanedioic acid as a white powder (0.75 g, 82 %); δ_H (400 MHz, *d*^{8}-DMSO) 1.23 (26H, s, $H_{4,4'\text{-}9,9',10}$), 1.43-1.51 (4H, m, $H_{3,3'}$), 2.18 (4H, t, *J* = 7.2 Hz, $H_{2,2'}$), 11.96 (2H, s, OH); δ_H (400 MHz, $CDCl_3$/ d^4-MeOD) 1.21-1.36 (26H, s,

$H_{4,4'\text{-}9,9',10}$), 1.54-1.63 (4H, m, $H_{3,3'}$), 2.26 (4H, t, *J* = 7.5 Hz, $H_{2,2'}$), 11.96 (2H, s, OH); δ_C (101MHz, $CDCl_3$/ d^4-MeOD) 25.7 ($C_{3,3'}$), 29.8, 30.0, 30.2, 30.3 ($C_{4,4'\text{-}9,9',10}$), 34.8 ($C_{2,2'}$), 177.5 ($C_{1,1'}$). *The spectroscopic properties of this compound were consistent with literature data.*[5]

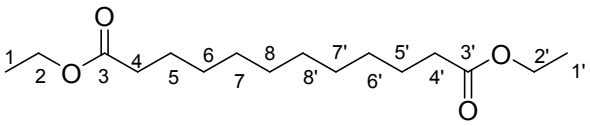
2.7.2. Diesters

1,12-dimethyl dodecandioate 3



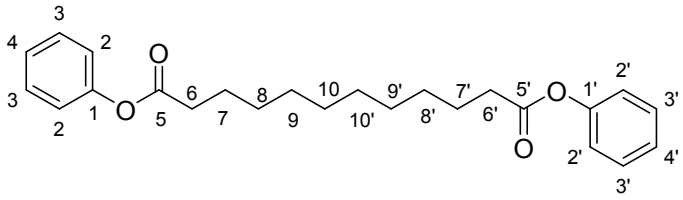
General procedure 1 was applied using dodecanedioic acid (20 g). Dimethyl dodecanedioate was obtained as a white solid (22 g, 98 %); δ_H (400 MHz, $CDCl_3$) 1.21-1.36 (12H, s, $H_{5,5'\text{-}7,7'}$), 1.61 (4H, qui, *J* = 7.4 Hz, $H_{4,4'}$), 2.29 (4H, t, *J* = 7.6 Hz, $H_{3,3'}$), 3.66 (6H, s, $H_{1,1'}$); δ_C (101 MHz, $CDCl_3$) 25.1 ($C_{4,4'}$), 29.3, 29.4, 29.5 ($C_{5,5'\text{-}7,7'}$), 34.3 ($C_{3,3'}$), 51.6 ($C_{1,1'}$), 174.5 ($C_{2,2'}$). *The spectroscopic properties of this compound were consistent with literature data.*[6]

Diethyl dodecanedioate 5



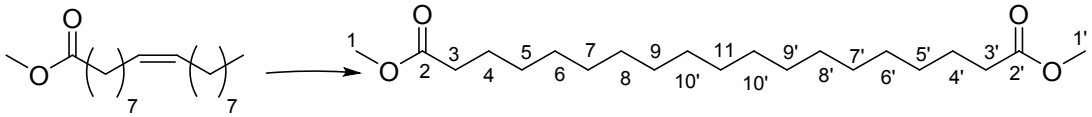
General procedure 1 was applied using dodecanedioic acid (10 g) and ethanol. Diethyl dodecanedioate was obtained as a colourless oil (12.2 g, 98 %); δ_H (400 MHz, $CDCl_3$) 1.20-1.34 (18H, m, $H_{1,1',\ 6,6'\text{-}8,8'}$), 1.46-1.71 (4H, m, $H_{5,5'}$), 2.27 (4H, t, *J* = 7.6 Hz, $H_{4,4'}$), 4.11 (4H, q, *J* = 7.1 Hz, $H_{2,2'}$); δ_C (101 MHz, $CDCl_3$) 14.4 ($C_{1,1'}$), 25.1 ($C_{5,5'}$), 29.3, 29.4, 29.5 ($C_{6,6'\text{-}8,8'}$), 34.5 ($C_{4,4'}$), 60.3 ($C_{2,2'}$), 174.1 ($C_{3,3'}$). Micro Anal. Found: C, 66.93; H, 10.42. Calc'd for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. HRMS: (NSI$^+$) Found: $[M+H]^+$ 287.2215, $C_{16}H_{31}O_4$ requires 287.2217.

Diphenyl dodecanedioate 4



Reaction conditions adopted from the literature.[7] Dodecanedioic acid (23.7 g, 103 mmol, 1 equiv.), diphenyl carbonate (44 g, 205.4 mmol, 2 equiv.), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.56 g, 10.3 mmol, 10 mol%) were added into a flask and heated at 160 °C for 24 h. The by-product, phenol, was removed under vacuum. The crude product was filtered through active charcoal and recrystalised from ethyl acetate/ hexane (1:3) to afford diphenyl dodecanedioate as a white solid (25 g, 64 %). δ_H (400 MHz, $CDCl_3$) 1.31-1.47 (12H, m, $H_{8,8'\text{-}10,10'}$), 1.71-1.82 (4H, m, $H_{7,7'}$), 2.56 (4H, t, *J* = 7.5 Hz, $H_{6,6'}$), 7.03-7.13 (4H, m, $H_{2,2'}$), 7.18-7.26 (2H, m, $H_{4,4'}$), 7.34-7.43 (4H, m, $H_{3,3'}$); δ_C (101 MHz, $CDCl_3$) 25.1 ($C_{7,7'}$), 29.2, 29.4, 29.5 ($C_{8,8'\text{-}10,10'}$), 34.5 ($C_{6,6'}$), 121.7 ($C_{2,2'}$), 125.8 ($C_{4,4'}$), 129.5 ($C_{3,3'}$), 150.9 ($C_{1,1'}$), 172.5 ($C_{5,5'}$). mp 59-61°C. Micro Anal. Found: C, 75.29; H, 7.86. Calc'd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. HRMS: (NSI$^+$) Found: $[M+H]^+$ 383.2217, $C_{24}H_{31}O_4$ requires 383.2219.

1,19-Dimethylnonadecanedioate 7

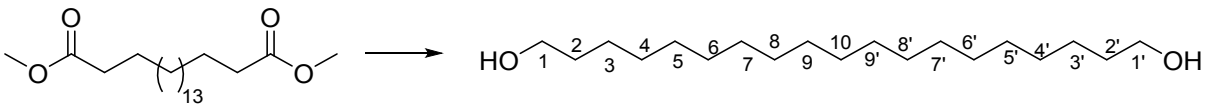


Reaction conditions adopted from literature.[5] 1,2-(Bis(ditertbutylphosphinomethyl)-benzene (2.37 g, 6 mmol, 0.2 equiv.) was weighed in a glove box and introduced into a Hastelloy autoclave together with [$Pd_2(dba)_3$] (0.54 g, 0.6 mmol, 0.02 equiv.) under a flow of Ar. The autoclave was sealed and purged with Ar. A mixture of degassed methanol (30 mL), methyl oleate (10 mL) (or sunflower oil, 10 mL) and methanesulfonic acid (0.78 mL, 12 mmol, 0.4 equiv.) was prepared in a Schlenk flask and added to the autoclave by syringe. The autoclave was sealed again, purged with carbon monoxide gas (CO), and the CO pressure was set to 30 bar. The autoclave was heated to 80°C for 22 h. After cooling, venting and opening, the yellow

solid was dissolved in dichloromethane (20 mL) and the yellow solution was filtered through celite. The solvent was removed on a rotary evaporator until a white precipitate appeared. Ice cold methanol was added and the mixture was stirred in an ice bath for 20 min before filtration. The remaining yellow solvent was again evaporated on a rotary evaporator until a precipitate appeared, cooled in an ice bath for 20 min, and filtered. 1,19-Dimethyl nonadecanedioate was obtained as a white powder (methyl oleate: 5.02 g, 95 %; sunflower oil: 3.2 g, 80 % based on oleate); δ_H (400 MHz, $CDCl_3$) 1.19-1.34 (26H, m, $H_{5,5'\text{-}10,10',11}$), 1.55-1.67 (4H, m, $H_{4,4'}$), 2.29 (4H, t, *J* = 7.6 Hz, $H_{3,3'}$), 3.66 (6H, s, $H_{1,1'}$); δ_C (101 MHz, $CDCl_3$) 25.1 ($C_{4,4'}$), 29.8 ($C_{5,5'\text{-}10,10',11}$), 34.3 ($C_{3,3'}$), 51.6 ($C_{1,1'}$), 174.5 ($C_{2,2'}$).*The spectroscopic properties of this compound were consistent with literature data.*[8]

2.7.3. Diols

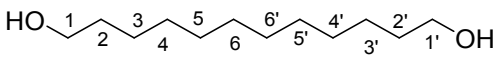
1,19-Nonadecanediol



[$Ru(acac)_3$] (4.5 mg, 0.011 mmol, 1 mol%), triphos (14 mg, 0.022 mmol, 2 mol%) and 1,19-dimethyl nonadecanedioate (393 mg, 1.103 mmol) were weighed in air and introduced into a Hastelloy autoclave fitted with a stirrer bar. The autoclave was sealed and purged by three vacuum/ Ar cycles Degassed dioxane (15 mL) and water (10 mL) were introduced into the autoclave through a septum. The autoclave was sealed again, connected to the high pressure system, and purged six times with H_2. The autoclave was charged with 40 bar of H_2, and heated to 220 °C for 16 h. The autoclave was cooled, vented and opened. After opening, the yellow suspension containing a white solid was transferred into a round bottomed flask. The reaction mixture was concentrated under reduced pressure. The solid was recrystallised from THF and DCM. Filtration gave the product as a white solid (265 mg, 80 % yield). δ_H (400 MHz, $CDCl_3$/ d^4-MeOD) 1.26 (30H, s, $H_{3,3'\text{-}9,9',10}$), 1.45-1.56 (4H, m, $H_{2,2'}$), 3.55 (4H, t, *J* = 7.2 Hz, $H_{1,1'}$); δ_C (101 MHz, $CDCl_3$/ d^4-MeOD) 26.3, 30.0, 30.2, 33.0 ($C_{2,2'\text{-}}$

$_{9,9',10}$), 62.7 ($C_{1,1'}$). *The spectroscopic properties of this compound were consistent with literature data*[5,8]

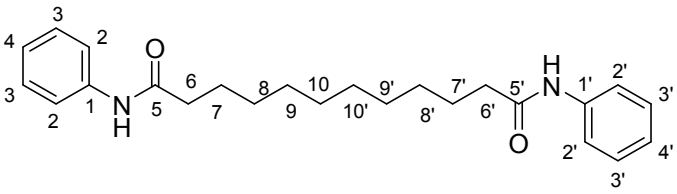
1,12-Dodecanediol



General procedure 4 was applied using dodecanedioic acid (7.0 g). 1,12-Dodecanediol was obtained as a white solid (5.6 g, 91 %). δ_H (500 MHz, $CDCl_3$/ d^4-MeOD) 1.25-1.36 (16H, m, $H_{3,3'-6,6'}$), 1.47-1.56 (4H, m, $H_{2,2'}$), 3.53 (4H, t, *J* = 6.7 Hz, $H_{1,1'}$), 4.80 (2H, s, OH); δ_C (126 MHz, $CDCl_3$/ d^4-MeOD) 26.6, 30.3, 30.4 ($C_{3,3'-6,6'}$), 33.3 ($C_{2,2'}$), 62.8 ($C_{1,1'}$). *The spectroscopic properties of this compound were consistent with literature data.*[9]

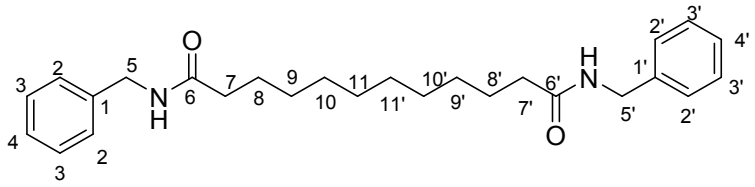
2.7.4. Diamides

***N*$_1$,*N*$_{12}$-diphenyldodecanediamide 9**



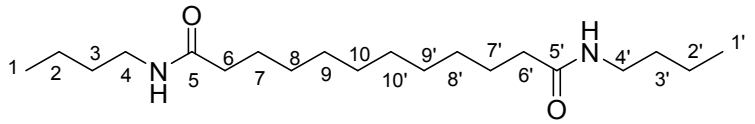
General prodecure 2 was applied using dodecanedioic acid (10 g). Recrystallisation from hot DCM/MeOH afforded *N*$_1$,*N*$_{12}$-diphenyldodecanediamide as a white solid (15 g, 90 % yield). δ_H (400 MHz, $CDCl_3$/ d^4-MeOD) 1.26-1.36 (12H, m, $H_{8,8'-10,10'}$), 1.67 (4H, quint, *J* = 7.4 Hz, $H_{7,7'}$), 2.33 (4H, t, *J* = 7.5 Hz, $H_{6,6'}$), 7.00-7.10 (2H, m, $H_{4,4'}$), 7.21-7.31 (4H, m, $H_{3,3'}$), 7.47-7.55 (4H, m, $H_{2,2'}$); δ_C (101 MHz, $CDCl_3$/ d^4-MeOD) 26.5 ($C_{7,7'}$), 29.9, 30.0, 30.1 ($C_{8,8'-10,10'}$), 37.7 ($C_{6,6'}$), 120.9 ($C_{2,2'}$), 124.7 ($C_{4,4'}$), 129.4 ($C_{3,3'}$), 139.2 ($C_{1,1'}$), 174.3 ($C_{5,5'}$). Micro Anal. Found: C, 75.61; H, 8.32; N, 7.49. Calc'd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. m.p. 152-154 °C. HRMS: (NSI$^+$) Found: $[M+H]^+$ 381.2534, $C_{24}H_{33}N_2O_2$ requires 381.2537.

N_1,N_{12}-dibenzyldodecanediamide



General procedure 3 was applied using dodecanedioic acid and benzylamine. The diamide was a side product of this reaction. Dibenzylamide was collected by filtration and washed with DCM (42 % yield). δ_H (500 MHz, $CDCl_3$/ d^4-MeOD) 1.21-1.34 (14H, m, $H_{9,9'\text{-}11,11'}$, OH), 1.55-1.66 (4H, m, $H_{8,8'}$), 2.20 (4H, t, J = 7.6 Hz, $H_{7,7'}$), 4.34 (4H, s, $H_{5,5'}$), 7.17-7.32 (10H, m, $H_{2,2'\text{-}4,4'}$); δ_C (101 MHz, $CDCl_3$/ d^4-MeOD) 26.6, 29.8, 29.9, 30.0 ($C_{8,8'\text{-}11,11'}$), 36.8 ($C_{7,7'}$), 43.8 ($C_{5,5'}$), 127.8, 128.1, 129.1 ($C_{2,2'\text{-}4,4'}$), 139.3 ($C_{1,1'}$), 175.6 ($C_{6,6'}$). m.p. 144-146 °C. HRMS: (ESI$^+$) Found: $[M+H]^+$ 409.2842, $C_{26}H_{37}N_2O_2$ requires 409.2855.

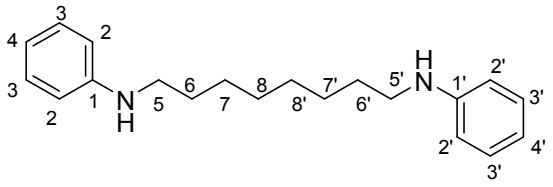
N_1,N_{12}-dibutyldodecanediamide



General prodecure 3 was applied using decanedioic acid and butylamine. N_1,N_{12}-dibutyldodecanediamide was obtained as a side product (58 % yield). δ_H (400 MHz, $CDCl_3$) 0.92 (6H, t, J = 7.3 Hz, $H_{1,1'}$), 1.25-1.39 (16H, m, $H_{2,2';\ 8,8'\text{-}10,10'}$), 1.43-1.52 (4H, m, $H_{3,3'}$), 1.56-1.66 (4H, m, $H_{7,7'}$), 2.27 (4H, t, J = 7.6 Hz, $H_{6,6'}$), 3.24 (4H, td, J = 5.7, 7.1 Hz, $H_{4,4'}$), 5.41 (2H, s, NH); δ_C (101 MHz, $CDCl_3$) 13.9 ($C_{1,1'}$), 20.2 ($C_{2,2'}$), 25.9 ($C_{7,7'}$), 29.4 ($C_{8,8'\text{-}10,10'}$), 31.9 ($C_{3,3'}$), 37.1 ($C_{6,6'}$), 39.3 ($C_{4,4'}$), 173.2 ($C_{5,5'}$). HRMS: (NSI$^+$) Found: $[M+H]^+$ 341.3164, $C_{20}H_{41}N_2O_4$ requires 341.3163.

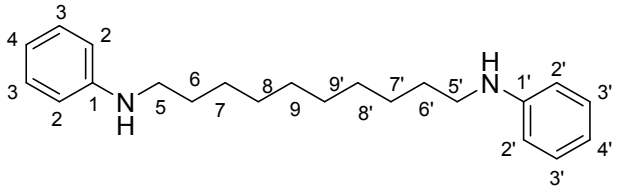
2.7.5. Synthesis and characterisation of diamine products

***N*$_1$,*N*$_8$-diphenyloctane-1,8-diamine**



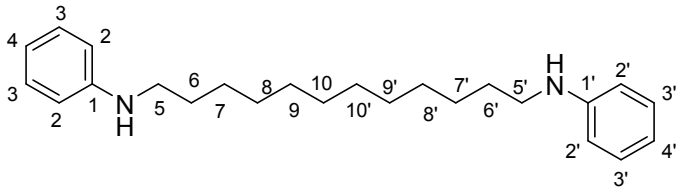
General prodecure 3 was applied using octanedioic acid and aniline. A sample for analysis was purified by flash column chromatography (10 % ethyl acetate/ petroleum ether). δ_H (400 MHz, $CDCl_3$) 1.30-1.52 (8H, m, $H_{7,7',8,8'}$), 1.63 (4H, quint, *J* = 7.5 Hz, $H_{6,6'}$), 3.13 (4H, t, *J* = 7.1 Hz, $H_{5,5'}$), 3.61 (2H, br s, NH), 6.59-6.66 (4H, m, $H_{2,2'}$), 6.72 (2H, tt, *J* = 1.1, 7.3 Hz, $H_{4,4'}$), 7.16-7.24 (4H, m, $H_{3,3'}$); δ_C (101 MHz, $CDCl_3$) 27.2, 29.5, 29.7 ($C_{6,6'-8,8'}$), 44.1 ($C_{5,5'}$), 112.8 ($C_{2,2'}$), 117.2 (C_4), 129.3 ($C_{3,3'}$), 148.6 ($C_{1,1'}$). Micro Anal. Found: C, 80.94; H, 9.42; N, 9.25. Calc'd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. HRMS: (ESI$^+$) Found: $[M+H]^+$ 297.2317, $C_{20}H_{29}N_2$ requires 297.2331.

***N*$_1$,*N*$_{10}$-diphenyldecane-1,10-diamine**



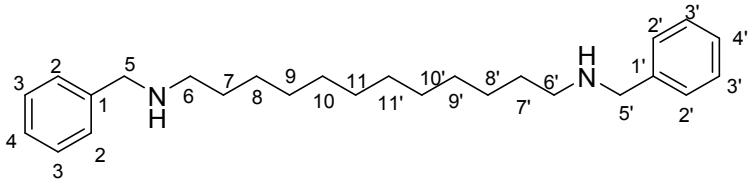
General procedure 3 was applied using decanedioic acid and aniline. A sample for analysis was purified by flash column chromatography (10 % ethyl acetate/ petroleum ether). δ_H (400 MHz, $CDCl_3$) 1.28-1.44 (12H, m, $H_{7,7'-9,9'}$), 1.57-1.67 (4H, m, $H_{6,6'}$), 3.10 (4H, t, *J* = 7.1 Hz, $H_{5,5'}$), 3.59 (2H, br s, NH), 6.56-6.67 (4H, m, $H_{2,2'}$), 6.69 (2H, tt, *J* = 1.1, 7.3 Hz, $H_{4,4'}$), 7.12-7.22 (4H, m, $H_{3,3'}$); δ_C (101 MHz, $CDCl_3$) 27.3, 29.6, 29.7 ($C_{6,6'-9,9'}$), 44.1 ($C_{5,5'}$), 112.8 ($C_{2,2'}$), 117.2 (C_4), 129.4 ($C_{3,3'}$), 148.7 ($C_{1,1'}$). Micro Anal. Found: C, 81.61; H, 9.82; N, 8.57. Calc'd for $C_{21}H_{26}N_2O_2$: C, 81.43; H, 9.94; N, 8.63. m.p. 58-59 °C. HRMS: (ESI$^+$) Found: $[M+H]^+$ 325.2628, $C_{22}H_{33}N_2$ requires 325.2644.

N_1,N_{12}-diphenyldodecane-1,12-diamine 1



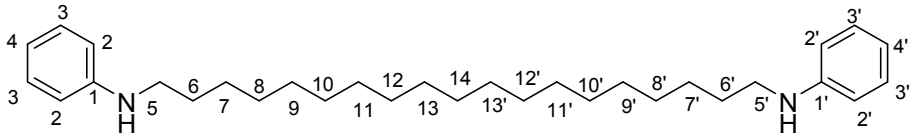
General prodecure 3 was applied using dodecanedioic acid and aniline. A sample for analysis was purified by preparative TLC (pre-coated polyester sheets of silica (60 F254 nm)) (10 % ethyl acetate/ petroleum ether). δ_H (400 MHz, $CDCl_3$) 1.19-1.47 (16H, m, $H_{7,7'\text{-}10,10'}$), 1.52-1.69 (4H, m, $H_{6,6'}$), 3.11 (4H, t, J = 7.1 Hz, $H_{5,5'}$), 3.57 (2H, br s, NH), 6.56-6.64 (4H, m, $H_{2,2'}$), 6.70 (2H, tt, J = 1.1, 7.3 Hz, $H_{4,4'}$), 7.12-7.23 (4H, m, $H_{3,3'}$); δ_C (101 MHz, $CDCl_3$) 27.3, 29.6, 29.7, 29.8 ($C_{6,6'\text{-}10,10'}$), 44.1 ($C_{5,5'}$), 112.8 ($C_{2,2'}$), 117.2 ($C_{4,4'}$), 129.3 ($C_{3,3'}$), 148.7 ($C_{1,1'}$). HRMS: (ESI^+) Found: $[M+H]^+$ 353.2940, $C_{24}H_{37}N_2$ requires 353.2957. *The spectroscopic properties of this compound were consistent with literature data.*[10]

N_1,N_{12}-dibenzyldodecane-1,12-diamine 11



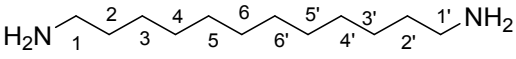
General prodecure 5 was applied using 1,12-dodecanediol and benzylamine. A sample for analysis was purified by preparative TLC (pre-coated polyester sheets of silica (60 F254 nm)) (30 % ethyl acetate/ petroleum ether+ 1 % aqueous ammonia). δ_H (400 MHz, $CDCl_3$) 1.21-1.35 (16H, m, $H_{8,8'\text{-}11,11'}$), 1.51 (4H, quint, J = 7.2 Hz, $H_{7,7'}$), 2.00 (2H, br s, NH), 2.62 (4H, t, J = 7.2 Hz, $H_{6,6'}$), 3.79 (4H, s, $H_{5,5'}$), 7.22-7.28 (2H, m, $H_{4,4'}$), 7.32 (8H, d, J = 4.4 Hz, $H_{2,2',3,3'}$); δ_C (101 MHz, $CDCl_3$) 27.5, 29.7 ($C_{8,8'\text{-}11,11'}$), 30.1 ($C_{7,7'}$), 49.5 ($C_{6,6'}$), 54.1 ($C_{5,5'}$), 127.1 ($C_{4,4'}$), 128.3, 128.5 ($C_{2,2',3,3'}$), 140.3 ($C_{1,1'}$). HRMS: (NSI^+) Found: $[M+H]^+$ 381.3265, $C_{26}H_{41}N_2$ requires 381.3264. *The spectroscopic properties of this compound were similar to those of* ***11.****2HCl.*[11]

N_1,N_{19}-diphenylnonadecane-1,19-diamine 8



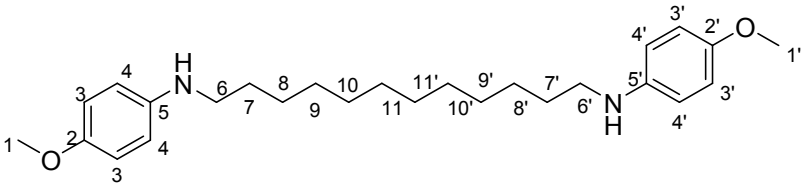
General prodecure 3 was applied using nonadecanedioic acid and aniline. A sample for analysis was purified by recrystallization with DCM and Et_2O. The product was obtained as white crystals. δ_H (400 MHz, $CDCl_3$) 1.25-1.45 (30H, m, $H_{7,7'\text{-}13,13',14}$), 1.62 (4H, quint, J = 6.9 Hz, $H_{6,6'}$), 3.11 (4H, t, J = 7.1 Hz, $H_{5,5'}$), 3.60 (2H, br s, NH), 6.57-6.65 (4H, m, $H_{2,2'}$), 6.70 (2H, tt, J = 1.1, 7.3 Hz, $H_{4,4'}$), 7.07-7.23 (4H, m, $H_{3,3'}$); δ_C (101 MHz, $CDCl_3$) 27.3, 29.6, 29.7, 29.8 ($C_{6,6'\text{-}13,13',14}$), 44.1 ($C_{5,5'}$), 112.8 ($C_{2,2'}$), 117.2 ($C_4$), 129.3 ($C_{3,3'}$), 148.7 ($C_{1,1'}$). Micro Anal. Found: C, 82.42; H, 11.33; N, 6.09. Calc'd for $C_{21}H_{26}N_2O_2$: C, 82.60; H, 11.18; N, 6.21. m.p. 66-68 °C. HRMS: (ESI^+) Found: $[M+H]^+$ 451.4034, $C_{31}H_{51}N_2$ requires 451.4052.

1,12-Diaminododecane 13



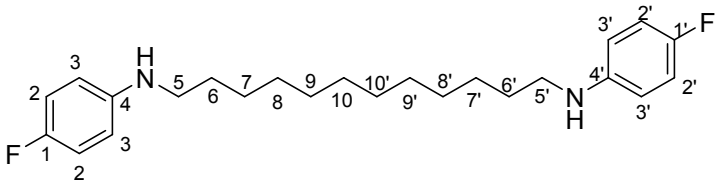
General prodecure 6 was applied using decanediol and aqueous ammonia. A sample for analysis was purified by recrystallization with DCM/MeOH and petroleum ether. δ_H (500 MHz, $CDCl_3$/ d^4-MeOD) 1.19-1.33 (20H, m, $H_{3,3'\text{-}6,6'}$, NH), 1.46 (4H, quint, J = 7.3 Hz, $H_{2,2'}$), 2.65 (4H, t, J = 7.3 Hz, $H_{1,1'}$); δ_C (126 MHz, $CDCl_3$/ d^4-MeOD) 27.2 ($C_{3,3'}$), 29.8, 29.9 ($C_{4,4'\text{-}6,6'}$), 32.4 ($C_{2,2'}$), 41.6 ($C_{1,1'}$). *The spectroscopic properties of this compound were consistent with literature data.*[12]

N_1,N_{12}-bis(4-methoxyphenyl)dodecane-1,12-diamine



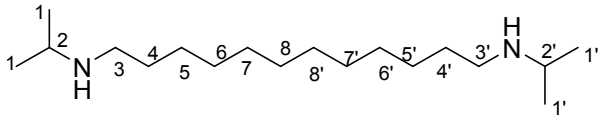
General prodecure 3 was applied using dodecanedioic acid and 4-methoxyaniline. A sample for analysis was purified by flash column chromatography (30 % ethyl acetate/ petroleum ether). δ_H (400 MHz, $CDCl_3$) 1.24-1.43 (16H, m, $H_{8,8'\text{-}11,11'}$), 1.60 (4H, quit, J = 7.6 Hz, $H_{7,7'}$), 3.05 (4H, t, J = 7.1 Hz, $H_{6,6'}$), 3.75 (6H, s, $H_{1,1'}$), 6.54-6.62 (4H, m, $H_{3,3'}$), 6.74-6.82 (4H, m, $H_{4,4'}$); δ_C (101 MHz, $CDCl_3$) 27.3 ($C_{8,8'}$), 29.6, 29.7, 29.8 ($C_{9,9'\text{-}11,11'}$), 45.2 ($C_{6,6'}$), 56.0 ($C_{1,1'}$), 114.2 ($C_{4,4'}$), 115.0 ($C_{3,3'}$), 143.0 ($C_{5,5'}$), 152.1 ($C_{2,2'}$). Micro Anal. Found: C, 75.47; H, 9.55; N, 6.88. Calc'd for $C_{26}H_{40}N_2O_2$: C, 75.68; H, 9.77; N, 6.79. HRMS: (NSI$^+$) Found: $[M+H]^+$ 413.3156, $C_{26}H_{41}N_2O_2$ requires 413.3163. mp. 80-81 °C.

N_1,N_{12}-bis(4-fluorophenyl)dodecane-1,12-diamine



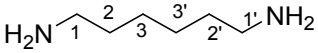
General prodecure 3 was applied using dodecanedioic acid and 4-fluoro aniline. A sample for analysis was purified by preparative TLC (pre-coated polyester sheets of silica (60 F254 nm)) (10 % ethyl acetate/ petroleum ether). δ_H (400 MHz, $CDCl_3$) 1.20-1.45 (16H, m, $H_{7,7'\text{-}10,10'}$), 1.60 (4H, quit, J = 6.2 Hz, $H_{6,6'}$), 3.05 (4H, t, J = 7.1 Hz, $H_{5,5'}$), 6.49-6.57 (4H, m, $H_{3,3'}$), 6.83-6.93 (4H, m, $H_{2,2'}$); δ_C (101 MHz, $CDCl_3$) 27.3, 29.6, 29.7 ($C_{6,6'\text{-}11,11'}$), 44.9 ($C_{5,5'}$), 113.6 (d, J = 7.4 Hz, $C_{3,3'}$), 115.7 (d, J = 7.4 Hz, $C_{2,2'}$), 143.0 ($C_{4,4'}$), 155.8 (d, J = 234.4 Hz, $C_{1,1'}$). δ_F (376 MHz, $CDCl_3$) -128.6. Micro Anal. Found: C, 74.33; H, 8.53; N, 7.40. Calc'd for $C_{24}H_{34}F_2N_2$: C, 74.19; H, 8.82; N, 7.21. HRMS: (APCI) Found: $[M+H]^+$ 389.2754, $C_{24}H_{35}F_2N_2$ requires 389.2763. mp. 58-60 °C.

N_1,N_{12}-diisopropyldodecane-1,12-diamine 12



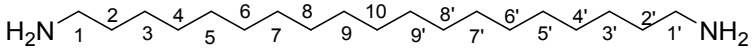
General prodecure 5 was applied using dodecanediol and isopropylamine. A sample for analysis was purified by preparative TLC (pre-coated glass with basic alumina (60 F254 nm)) (5 % MeOH/ DCM). δ_H (400 MHz, $CDCl_3$) 1.04 (12H, d, *J* = 6.6 Hz, $H_{1,1'}$), 1.20-1.32 (16H, m, $H_{5,5'\text{-}8,8'}$), 1.40-1.50 (4H, m, $H_{4,4'}$), 2.56 (4H, t, *J* = 7.6 Hz, $H_{3,3'}$), 2.78 (2H, hept, $H_{2,2'}$); δ_C (101 MHz, $CDCl_3$) 23.1 ($C_{1,1'}$), 27.6 ($C_{5,5'}$), 29.7, 29.8 ($C_{6,6'\text{-}8,8'}$), 30.5 ($C_{4,4'}$), 47.8 ($C_{3,3'}$), 50.5 ($C_{2,2'}$). HRMS: (NSI$^+$) Found: $[M+H]^+$ 285.3265, $C_{18}H_{41}N_2$ requires 285.3264.

Hexane-1,6-diamine 14



General prodecure 6 was applied using 1,6-hexanediol and aqueous ammonia. A sample for analysis was purified by sublimation. δ_H (400 MHz, d^4-MeOD) 1.29-1.41 (4H, m, $H_{3,3'}$), 1.43-1.51 (4H, m, $H_{2,2'}$), 2.62 (4H, t, *J* = 7.2 Hz, $H_{1,1'}$); δ_C (101 MHz, $CDCl_3$) 27.9 ($C_{3,3'}$), 34.0 ($C_{2,2'}$), 42.6 ($C_{1,1'}$). *The spectroscopic properties of this compound were consistent with literature data.*[13]

1,19-nonadecanediamine 15



General prodecure 6 was applied using nonadecanediol and aqueous ammonia. δ_H (500 MHz, d^6-DMSO) 1.20-1.28 (30H, m, $H_{3,3'\text{-}10}$), 1.33-1.47 (4H, m, $H_{2,2'}$), 2.60 (4H, t, *J* = 7.2 Hz, $H_{1,1'}$); δ_C (126 MHz, d^6-DMSO)* 26.6 ($C_{3,3'}$), 29.4 ($C_{4,4'\text{-}10}$), 31.0 ($C_{2,2'}$), 41.0 ($C_{1,1'}$). HRMS: (NSI$^+$) Found: $[M+H]^+$ 299.3422, $C_{19}H_{43}N_2$ requires 299.3421. *The spectroscopic properties of this compound were consistent with literature data.*[14]

*Peaks observed and assigned based on 2D HSQC NMR spectra, see Figure 46

3. NMR spectra of pure samples

3.1. Diacids

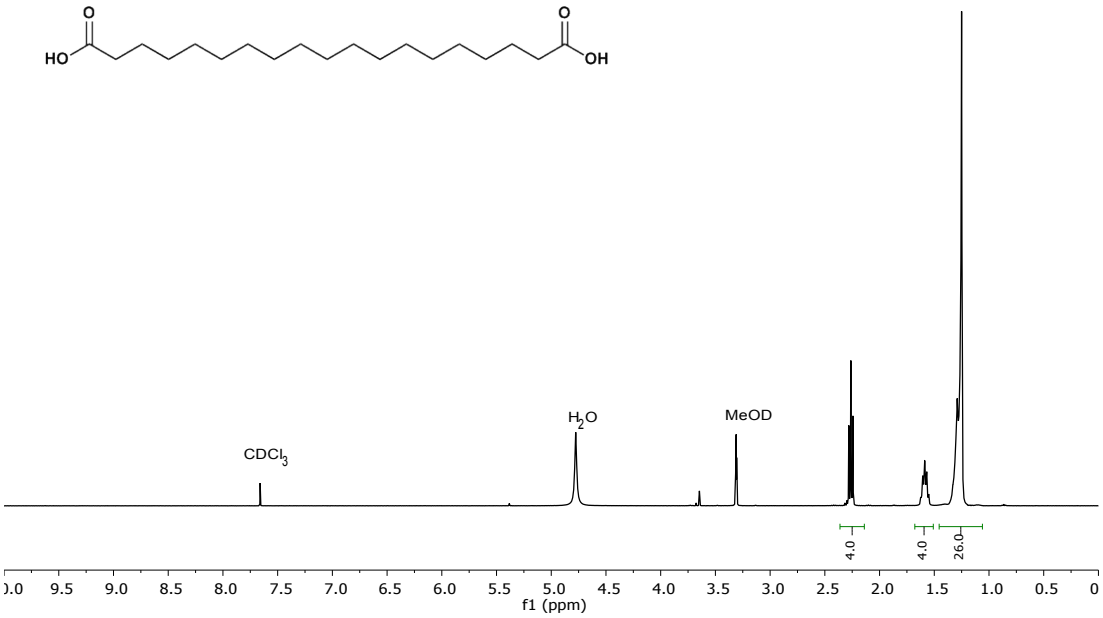


Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$/ d^4-MeOD) of 1,19-nonadecanedioic acid. Spectrum referenced to MeOD.

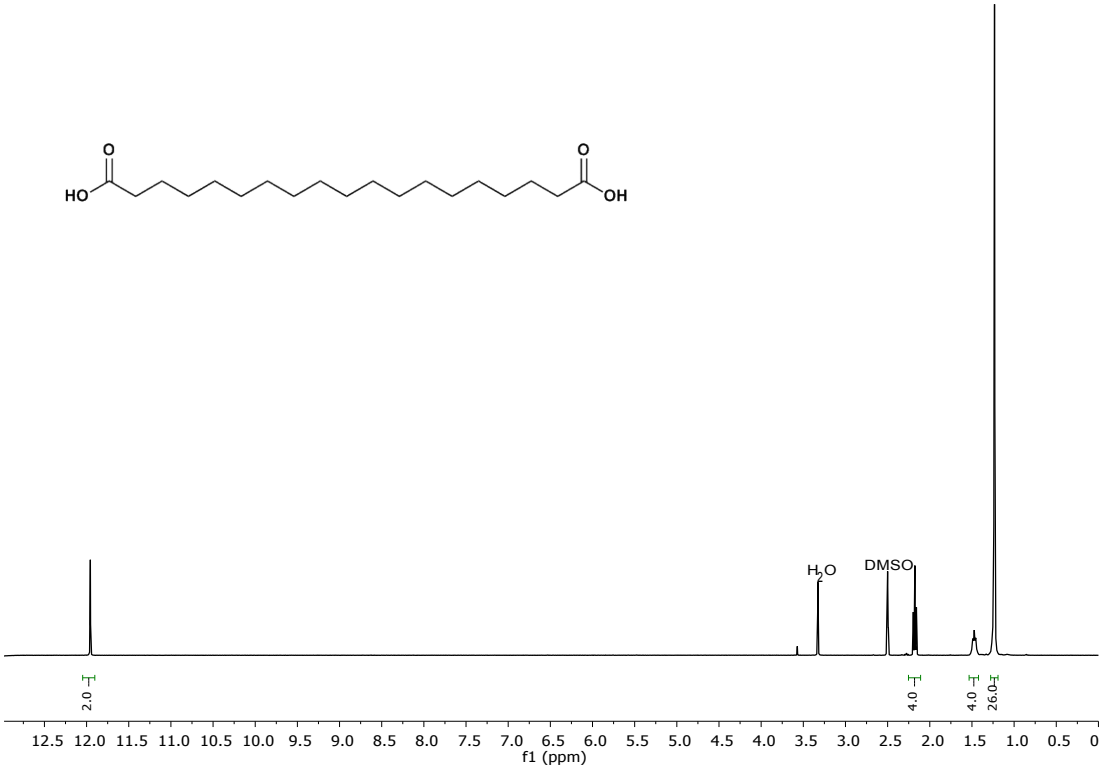


Figure 2. ^{1}H NMR (400 MHz, d^6-DMSO) of 1,19-nonadecanedioic acid.

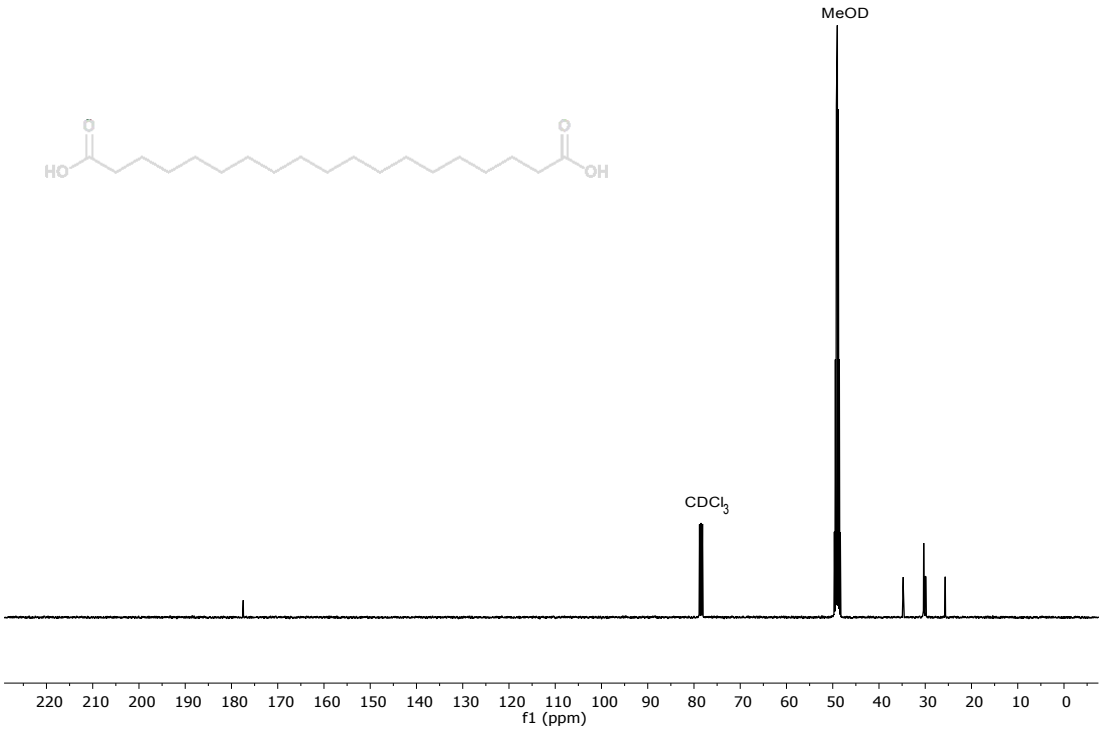


Figure 3. ^{13}C NMR (101 MHz, $CDCl_3$/ d^4-MeOD) of 1,19-nonadecanedioic acid. Spectrum referenced to MeOD.

3.2. Diesters

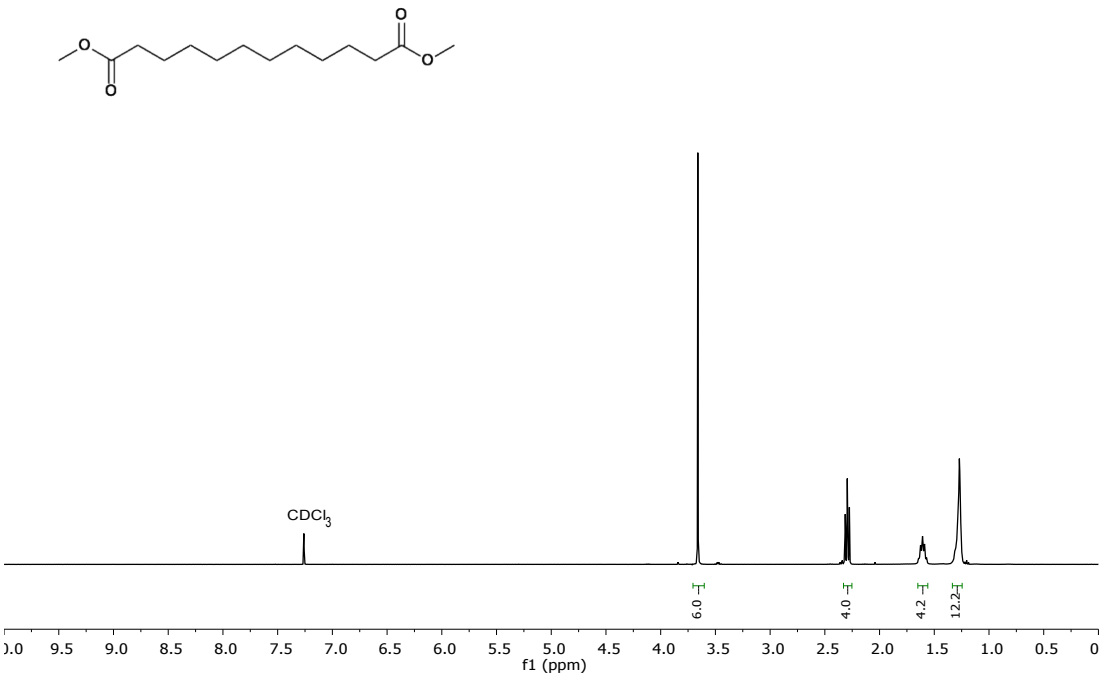


Figure 4. ^1H NMR (400 MHz, $CDCl_3$) of dimethyl 1,12-dodecanedioate **3**.

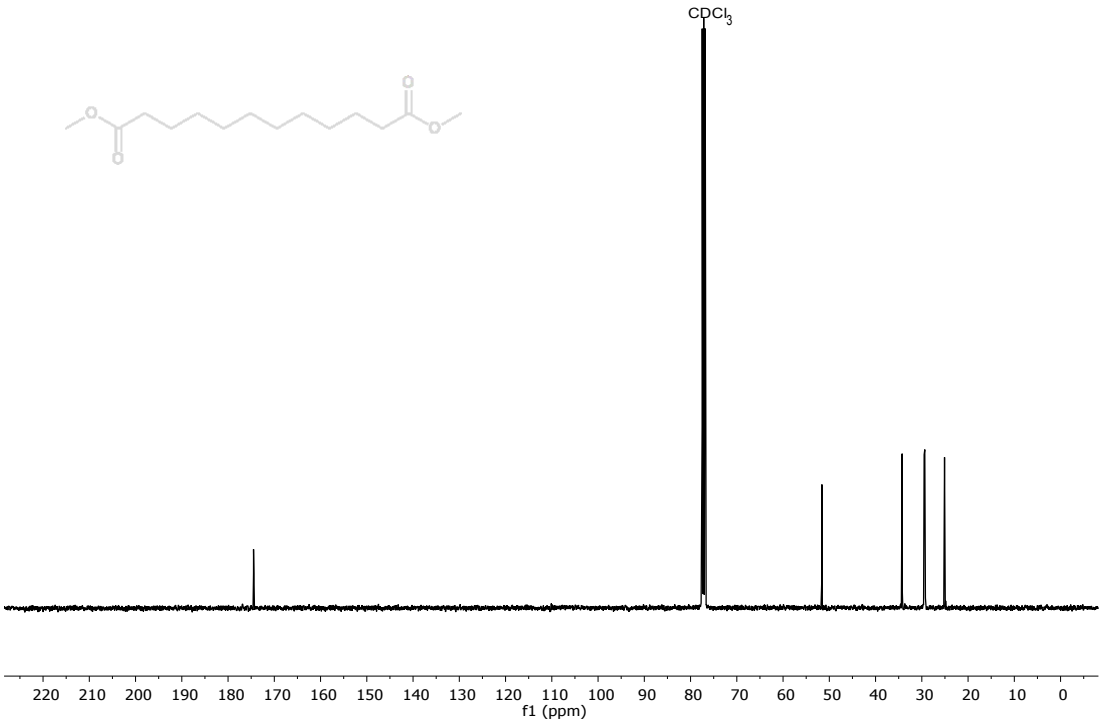


Figure 5. ^{13}C NMR (101 MHz, $CDCl_3$) of 1,12-dimethyl dodecanedioate **3**.

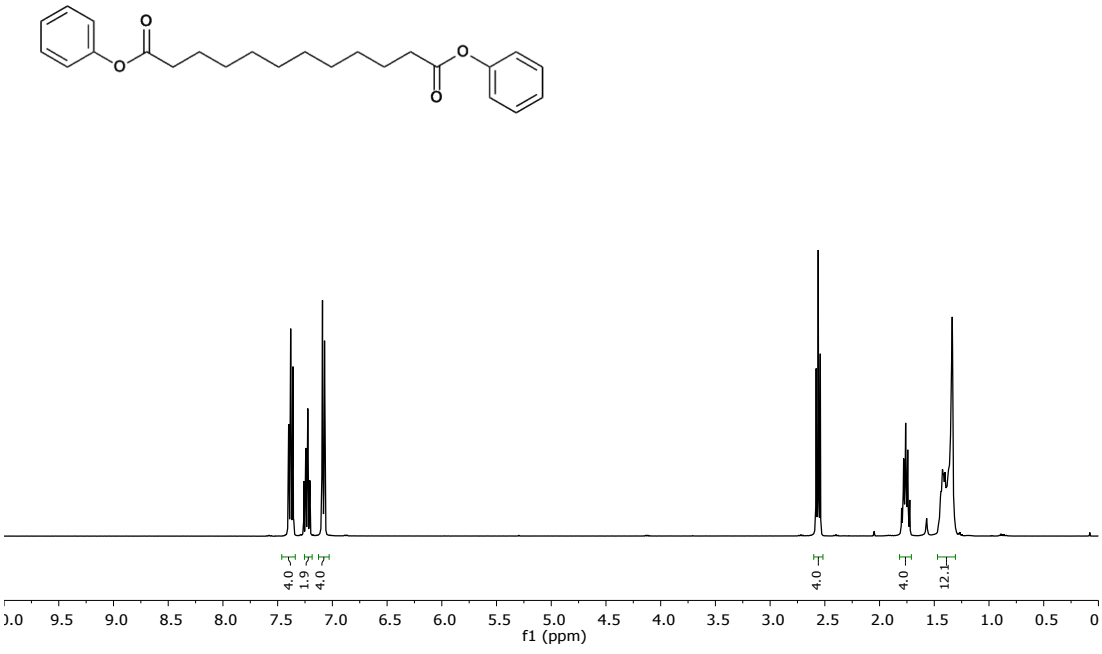


Figure 6. ^{1}H NMR (400 MHz, $CDCl_3$) of diphenyl 1,12-dodecanedioate **4**.

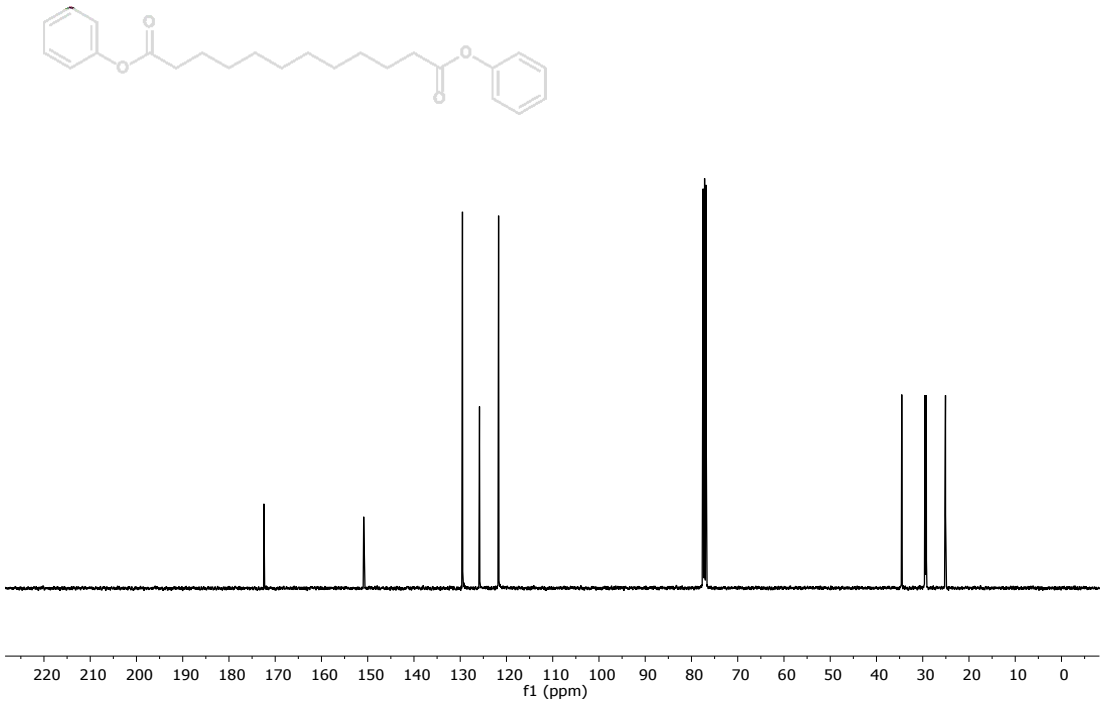


Figure 7. ^{13}C NMR (101 MHz, $CDCl_3$) of diphenyl 1,12-dodecanedioate **4**.

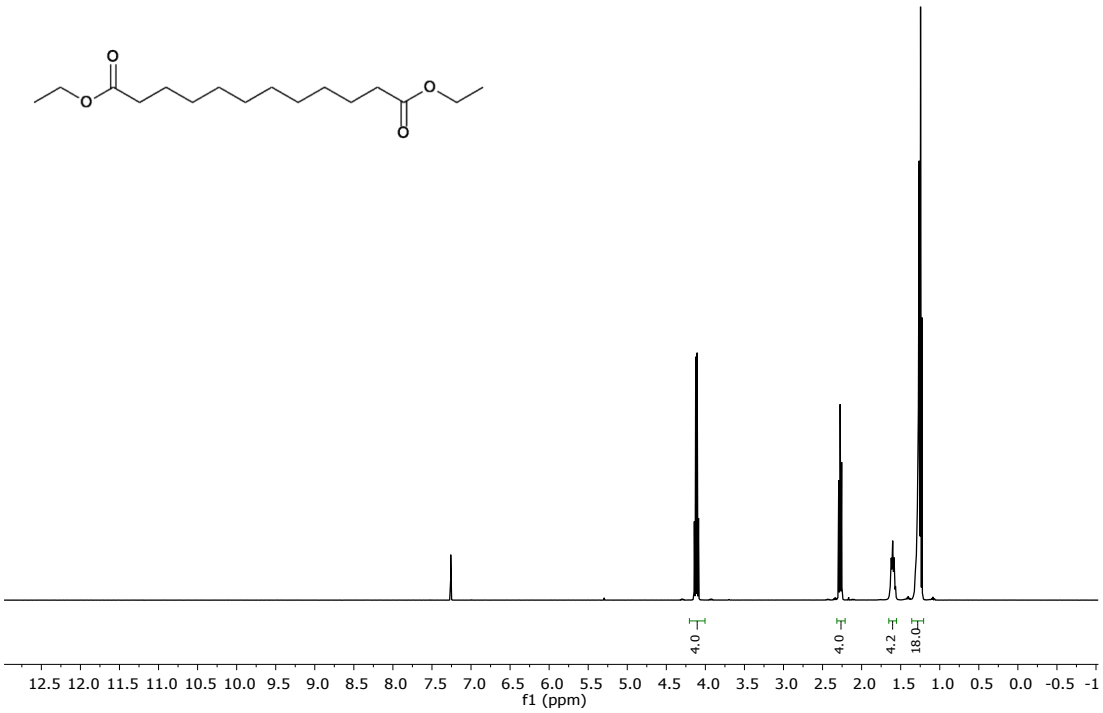


Figure 8.^{1}H NMR (400 MHz, $CDCl_3$) of diethyl 1,12-dodecanedioate **5**.

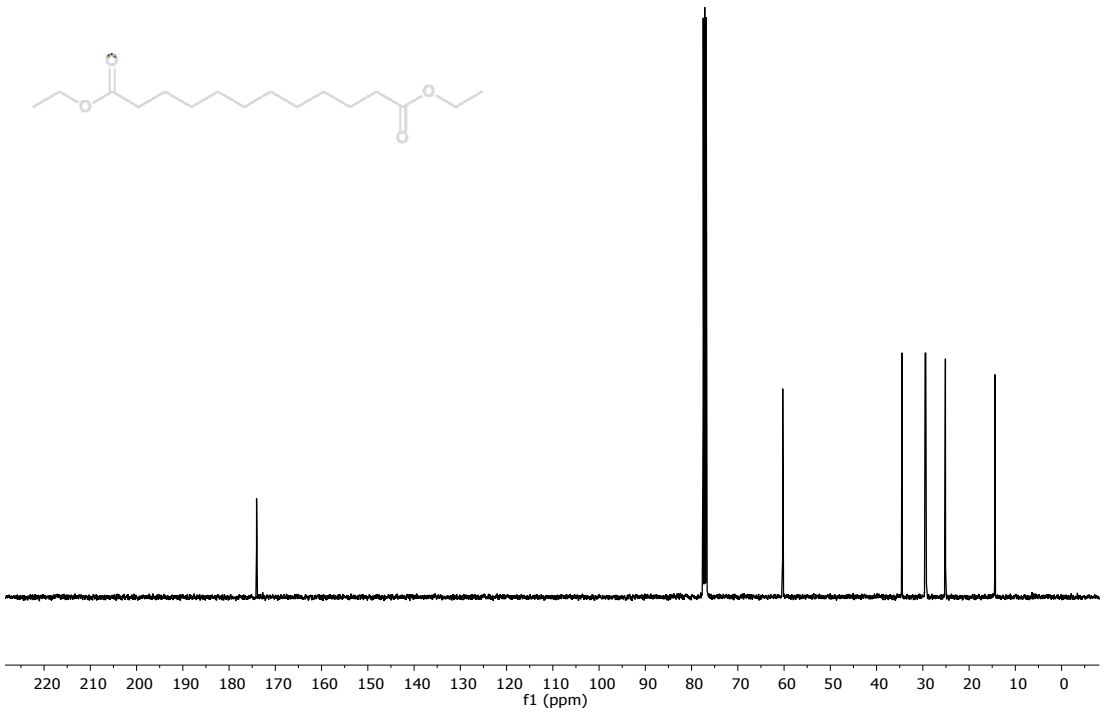


Figure 9. ^{13}C NMR (101 MHz, $CDCl_3$) of diethyl 1,12-dodecanedioate **5**.

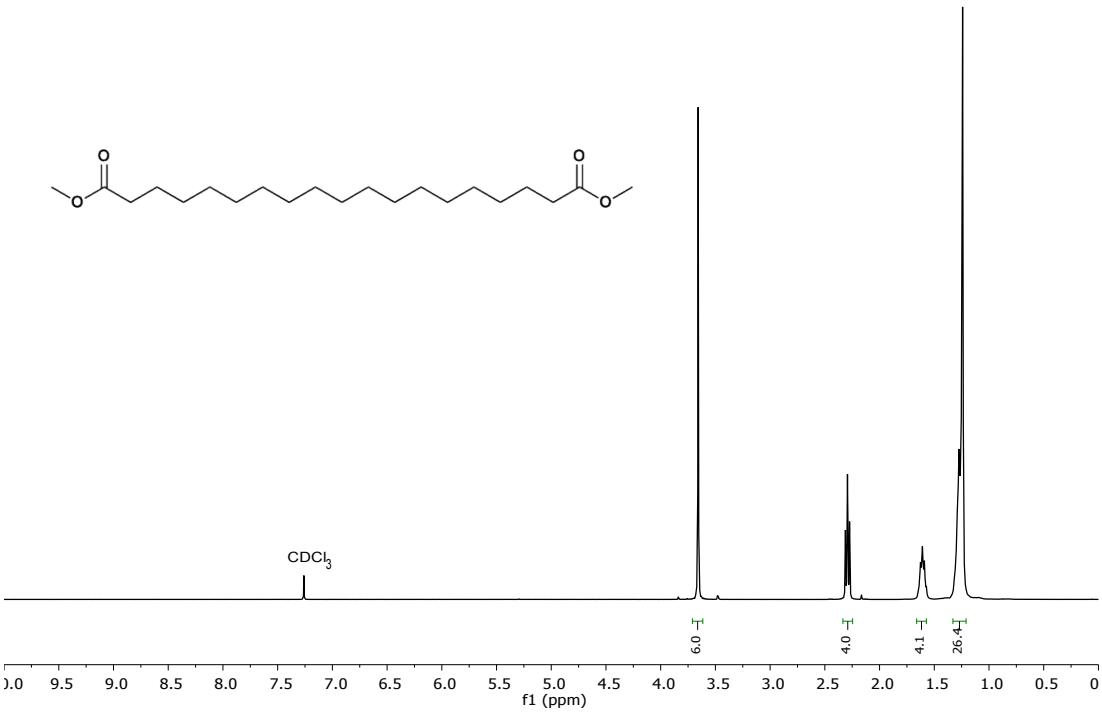


Figure 10. ^{1}H NMR (400 MHz, $CDCl_3$) of dimethyl 1,19-nonadecanedioate **7**.

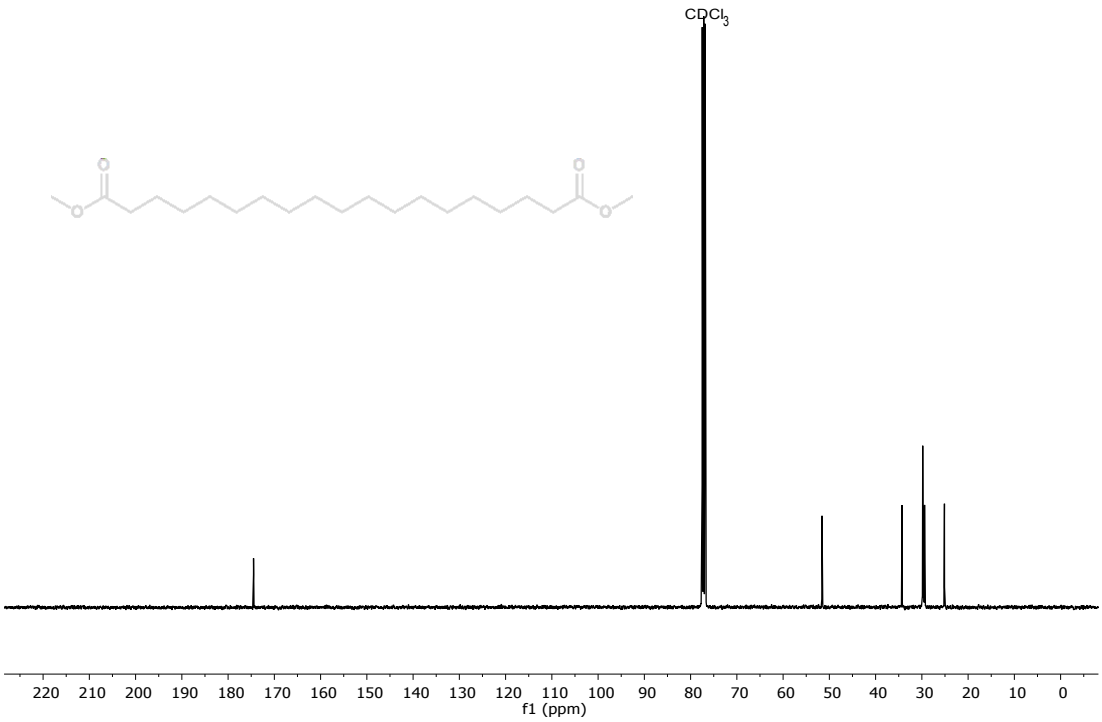


Figure 11. ^{13}C NMR (101 MHz, $CDCl_3$) of dimethyl 1,19-nonadecanedioate **7**.

3.3. Diols

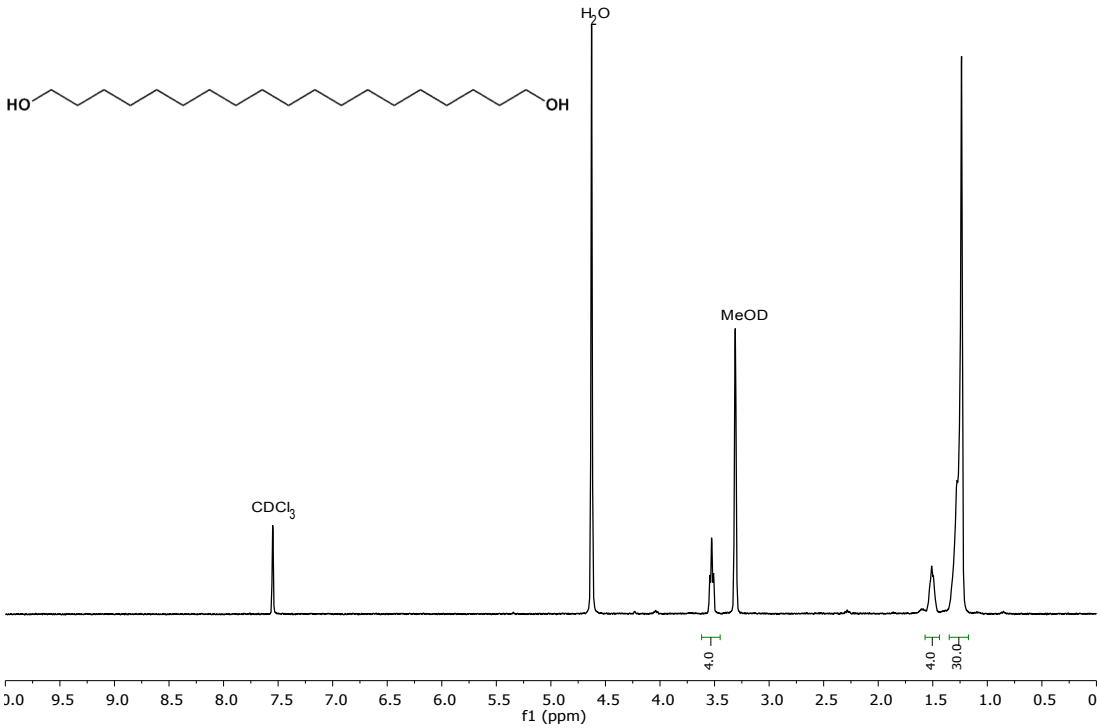


Figure 12. ^{1}H NMR (400 MHz, $CDCl_3$/ d^4-MeOD) of 1,19-nonadecanediol. Spectrum referenced to MeOD.

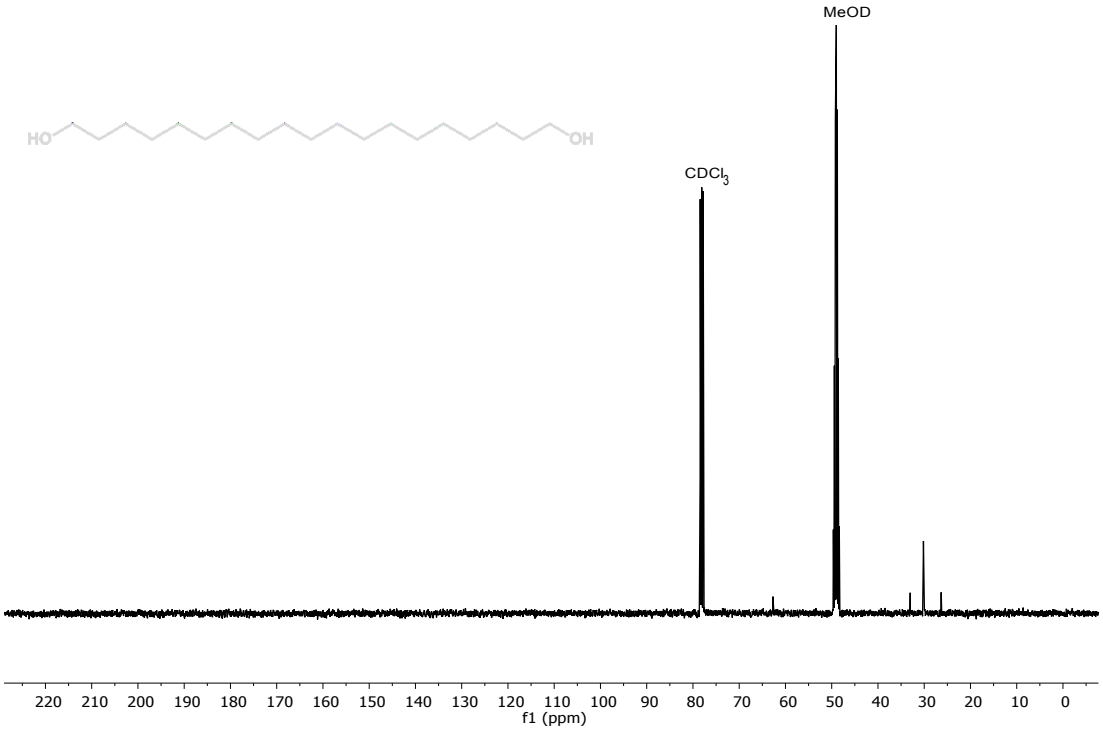


Figure 13. ^{13}C NMR (101 MHz, $CDCl_3$/ d^4-MeOD) of 1,19-nonadecanediol. Spectrum referenced to MeOD.

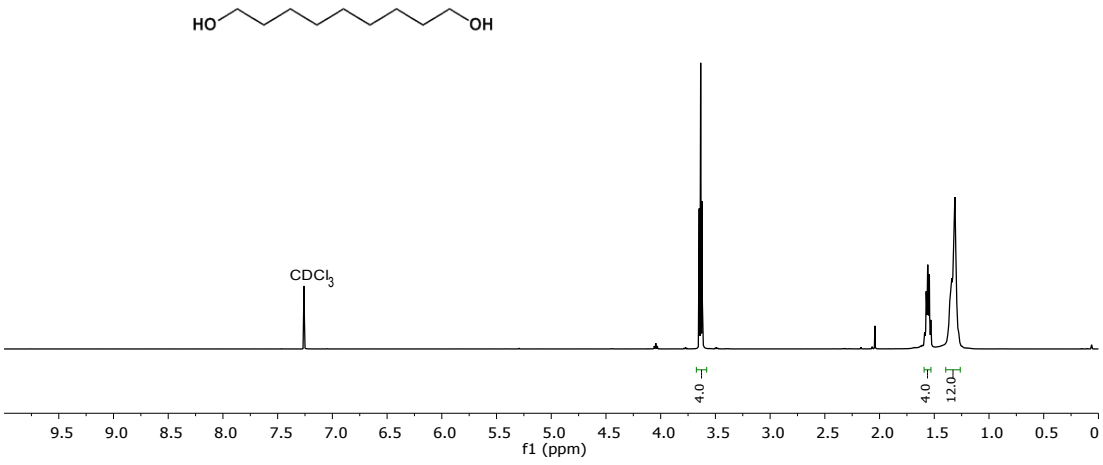


Figure 14. ^1H NMR (400 MHz, $CDCl_3$) of 1,9-nonanediol.

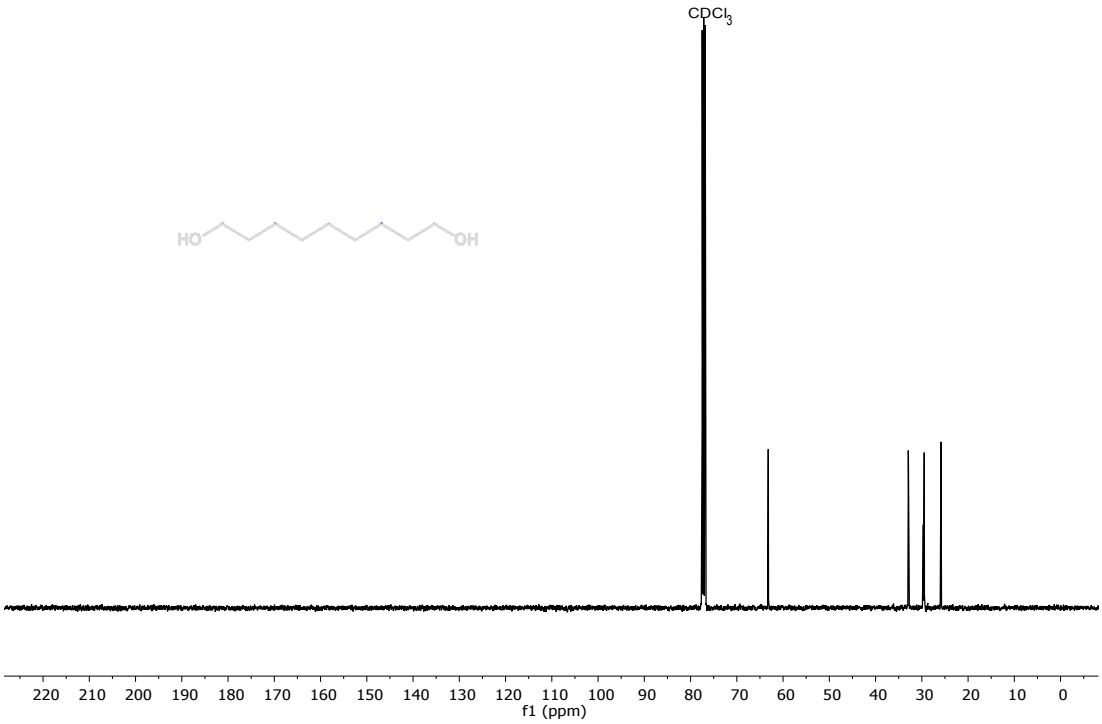


Figure 15. ^{13}C NMR (101 MHz, $CDCl_3$) of 1,9-nonanediol.

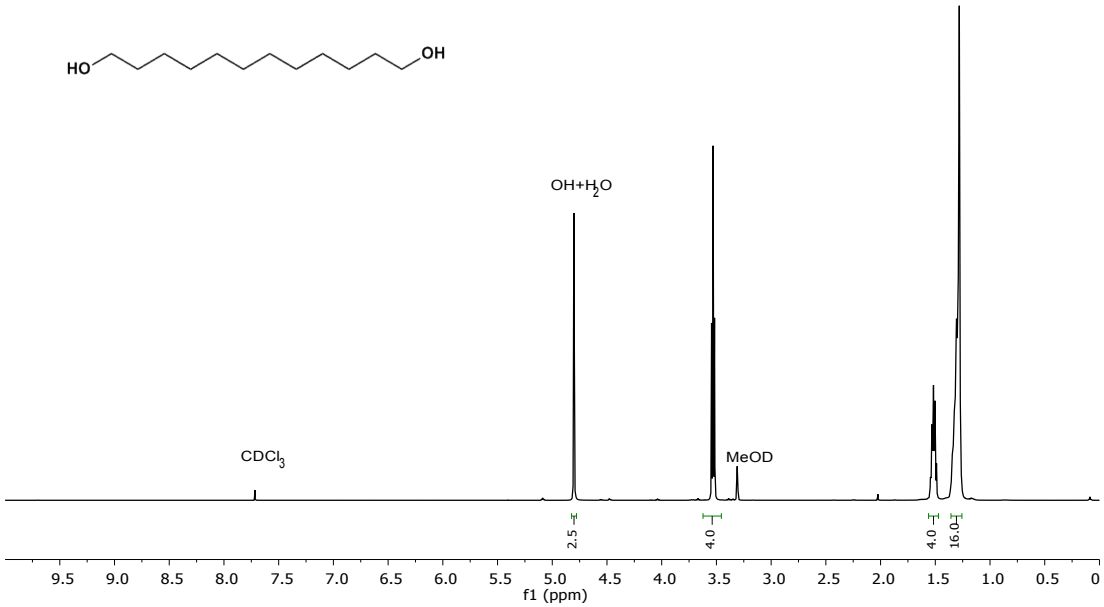


Figure 16. ^{1}H NMR (500 MHz, $CDCl_3$/ d^4-MeOD) of 1,12-dodecanediol. Spectrum referenced to MeOD.

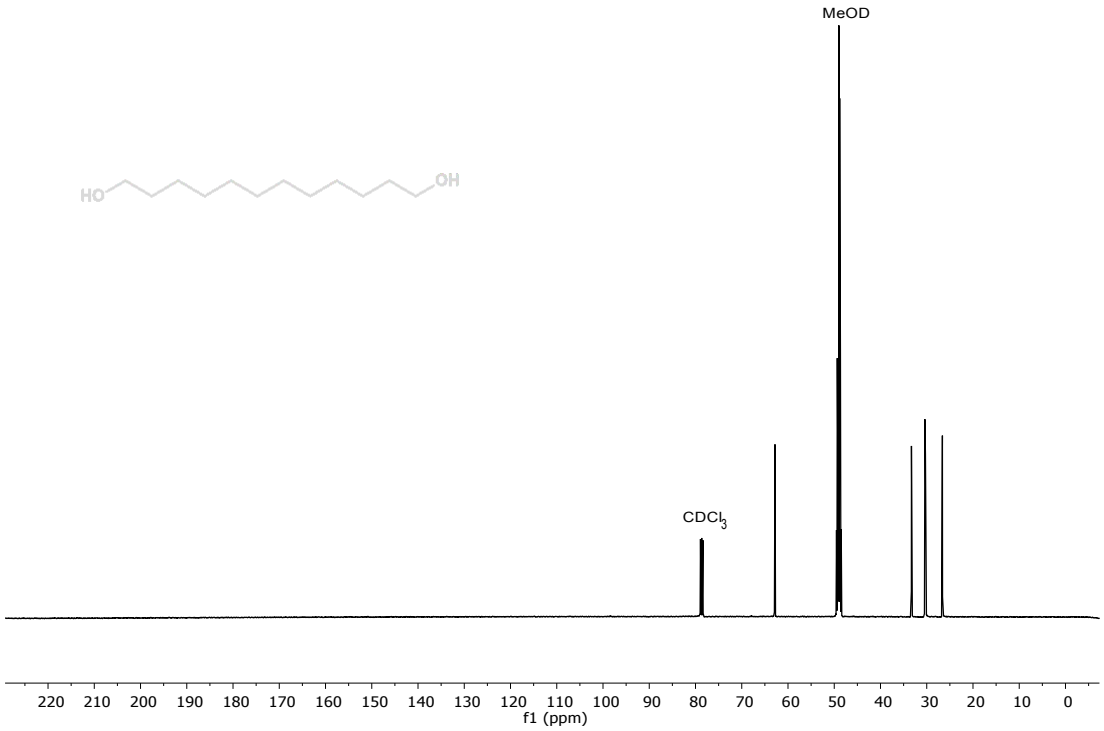


Figure 17. ^{13}C NMR (126 MHz, $CDCl_3$/ d^4-MeOD) of 1,12-dodecanediol. Spectrum referenced to MeOD.

3.4. Diamides

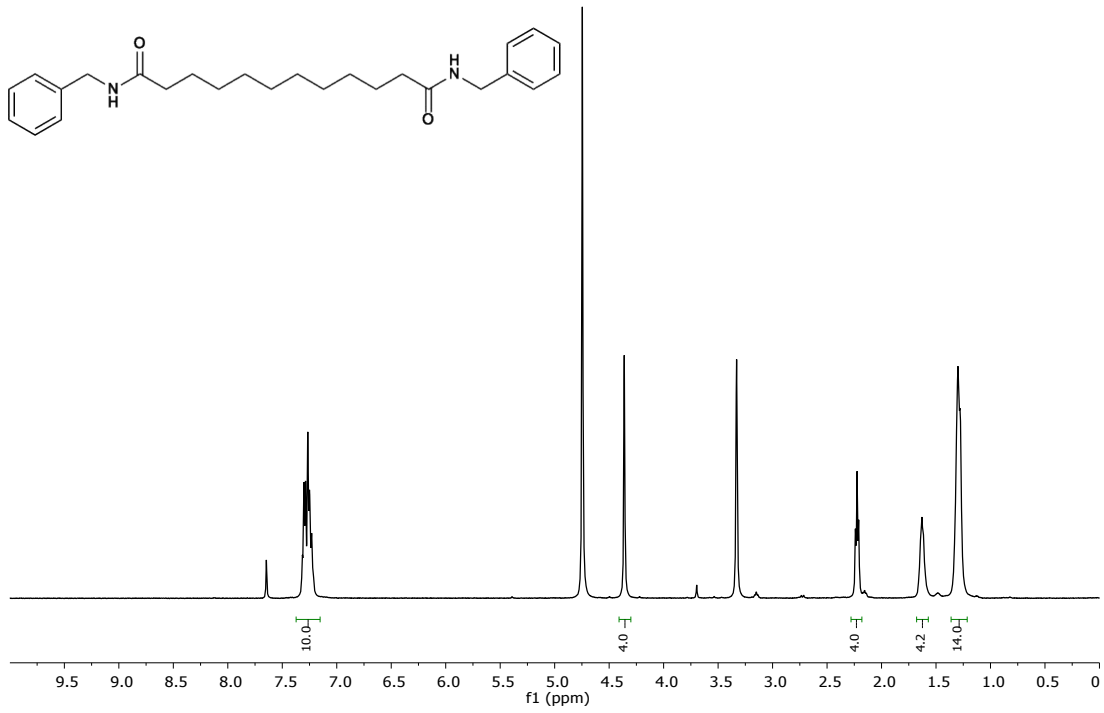


Figure 18. ^1H NMR (500 MHz, $CDCl_3$/ d^4-MeOD) of N_1,N_{12}-dibenzyldodecanediamide. Spectrum referenced to MeOD.

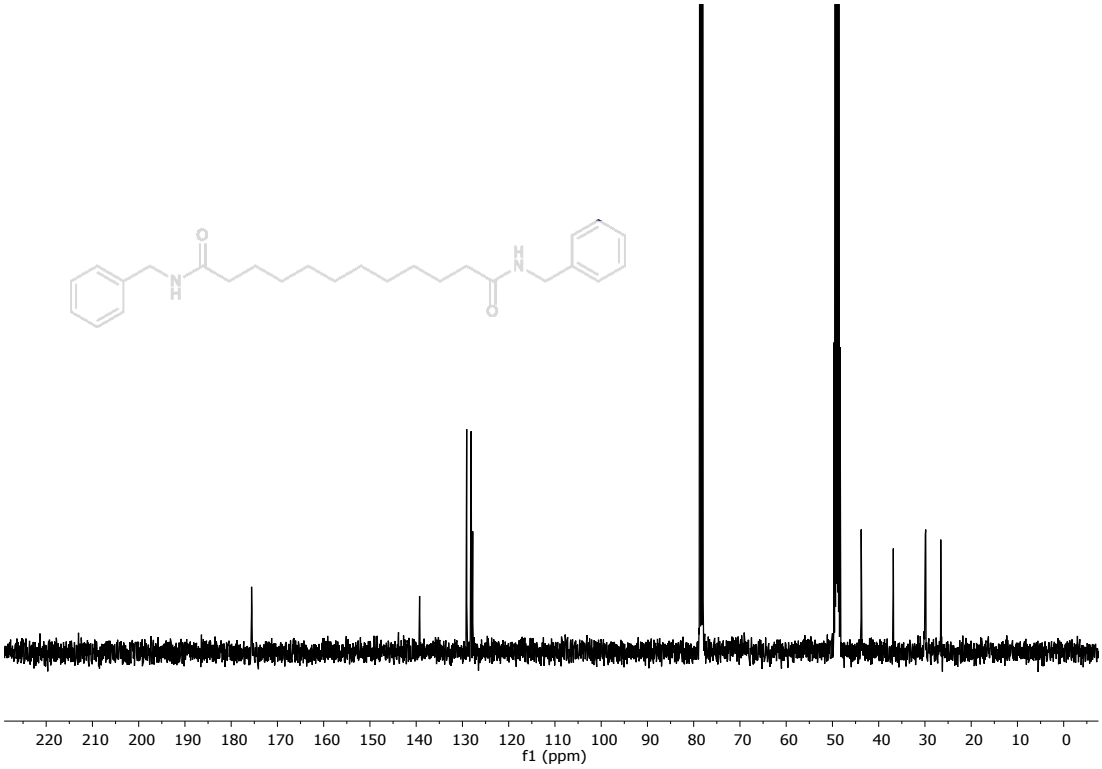


Figure 19. ^{13}C NMR (101 MHz, $CDCl_3$/ d^4-MeOD) of N_1,N_{12}-dibenzyldodecanediamide. Spectrum referenced to MeOD.

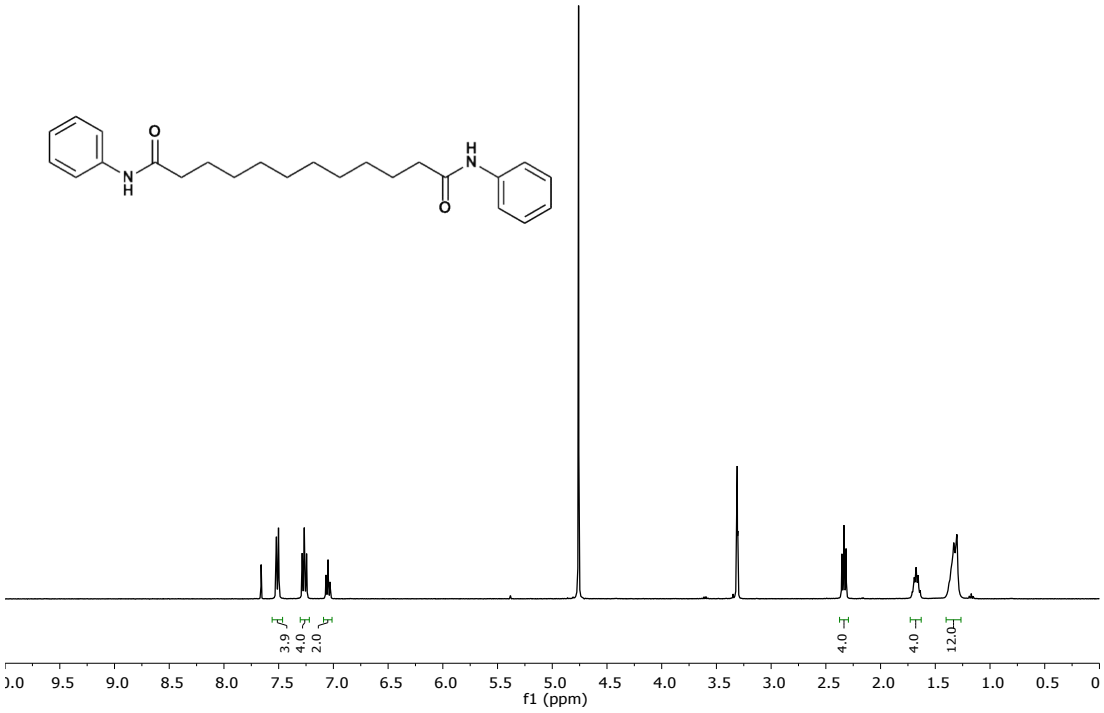


Figure 20. ^1H NMR (400 MHz, $CDCl_3$/ d^4-MeOD) of N_1,N_{12}-diphenyldodecanediamide. Spectrum referenced to MeOD.

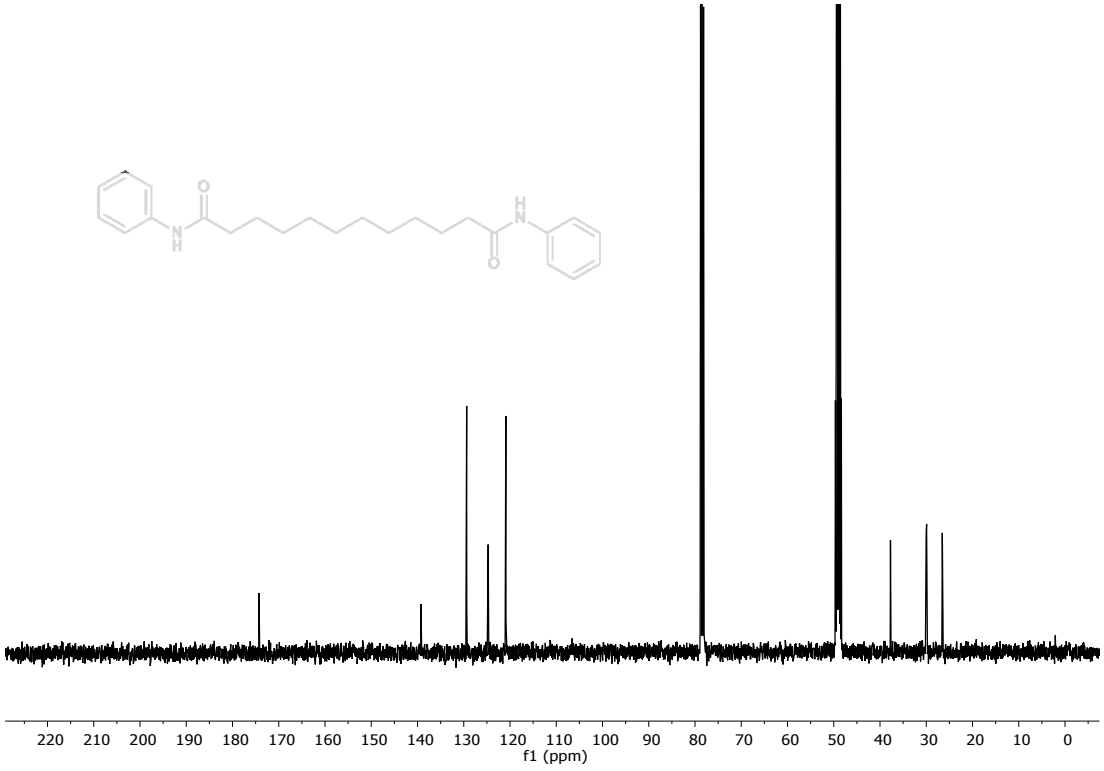


Figure 21. ^{13}C NMR (101 MHz, $CDCl_3$/ d^4-MeOD) of N_1,N_{12}-diphenyldodecanediamide. Spectrum referenced to MeOD.

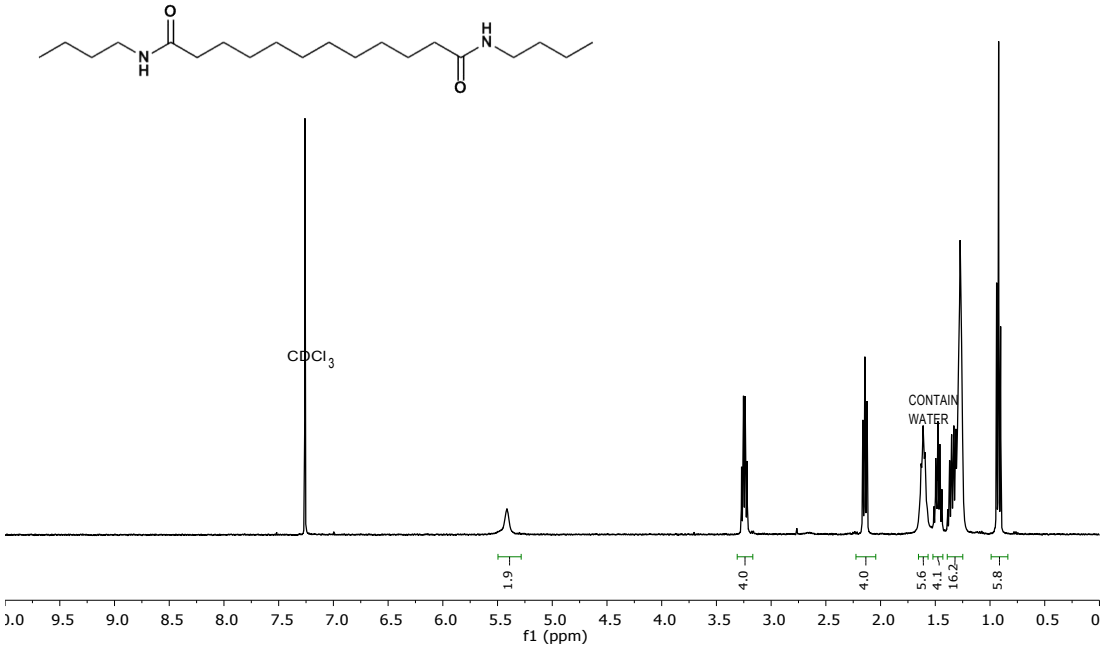


Figure 22. ^1H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-dibutyldodecanediamide.

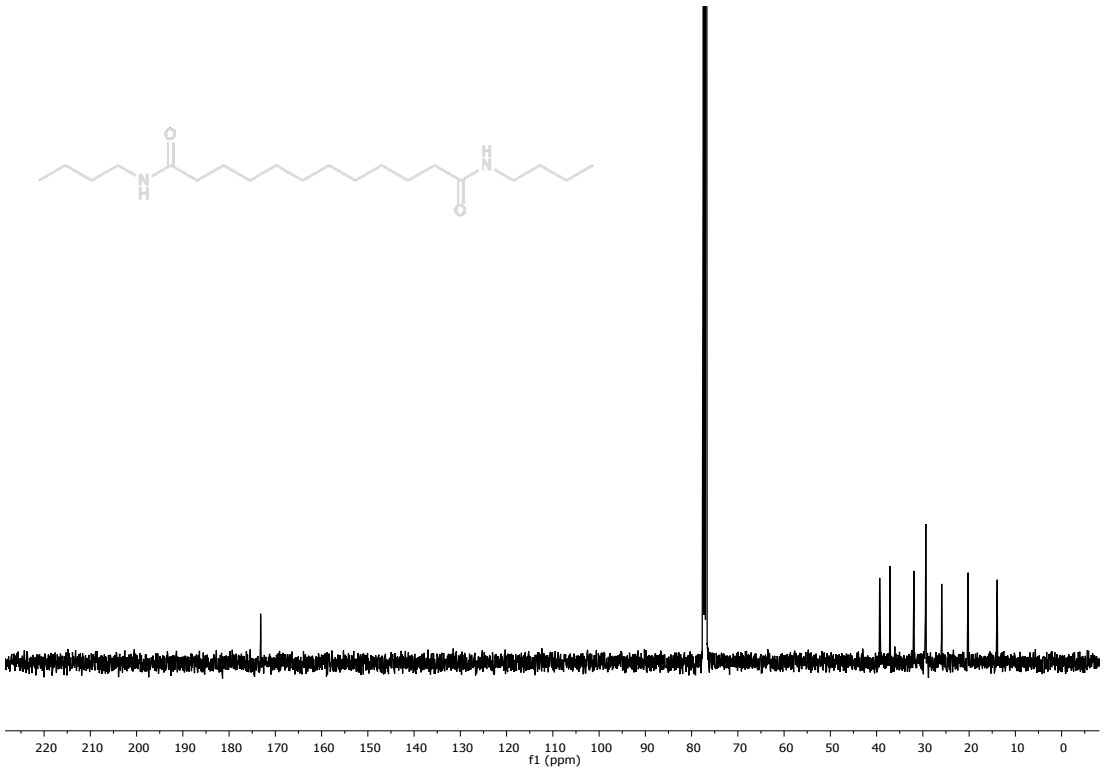


Figure 23. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-dibutyldodecanediamide.

3.5. Diamines

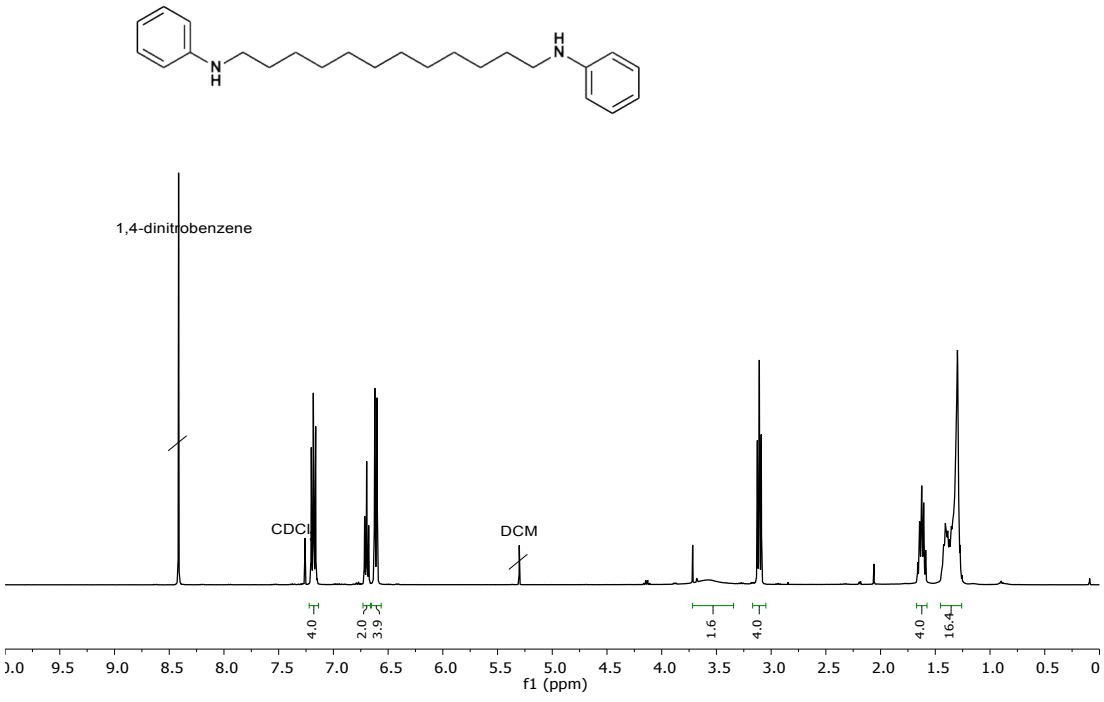


Figure 24. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-diphenyldodecane-1,12-diamine **1**.

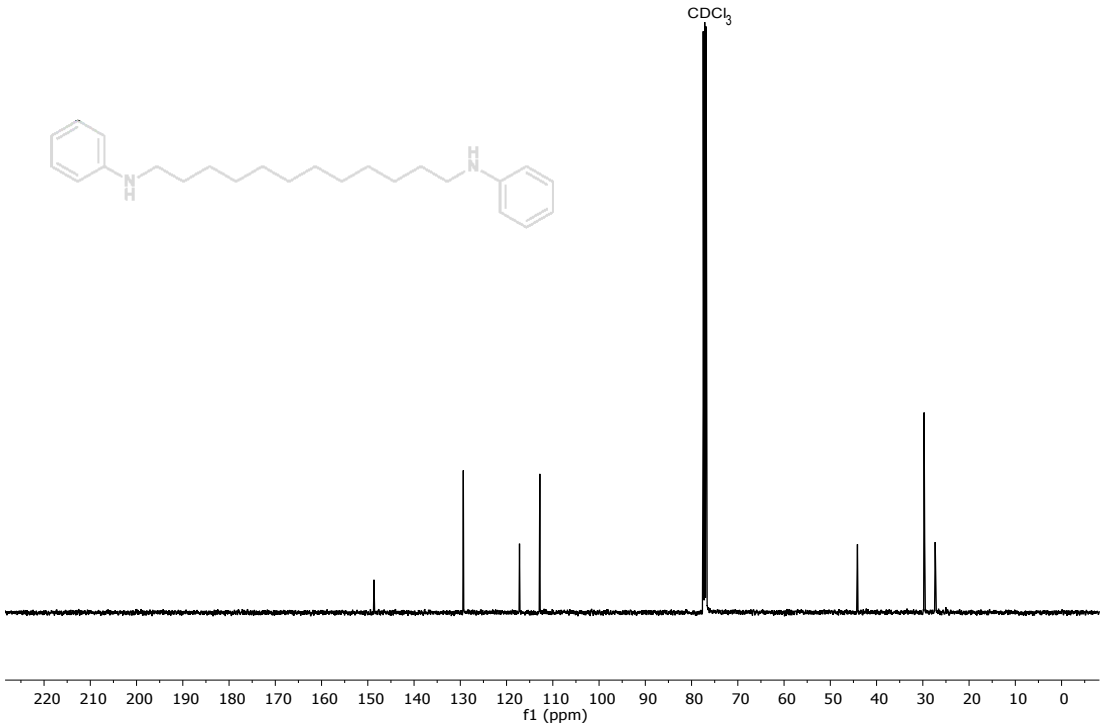


Figure 25. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-diphenyldodecane-1,12-diamine **1**.

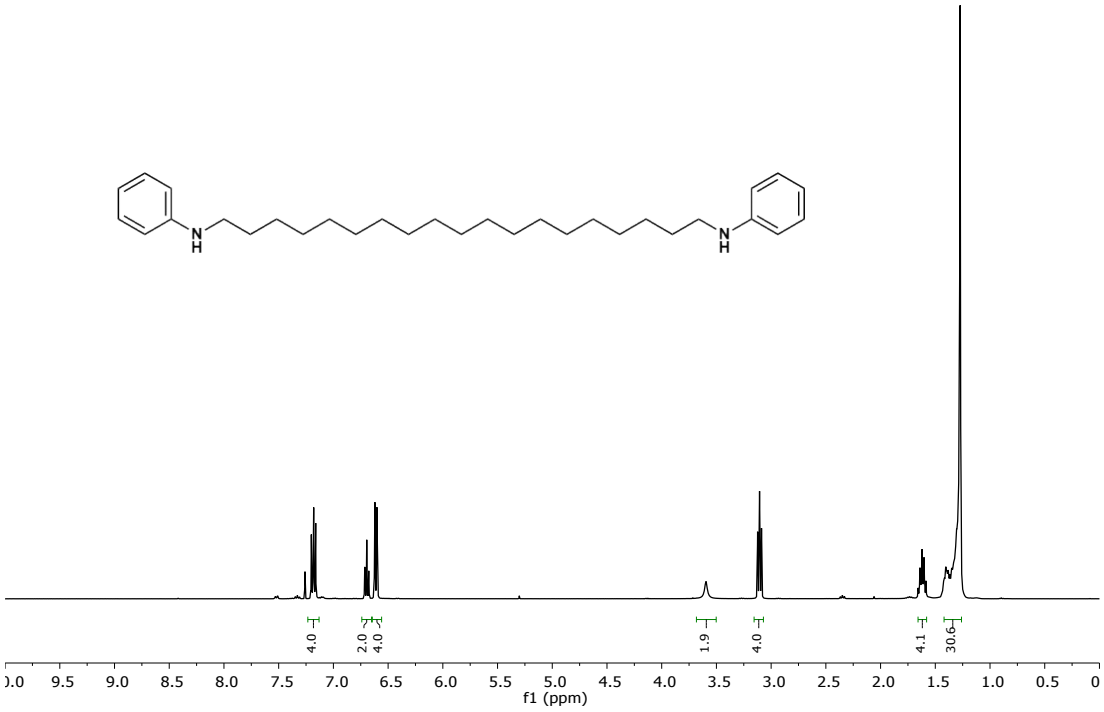


Figure 26. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_{19}-diphenylnonadecane-1,19-diamine **8**.

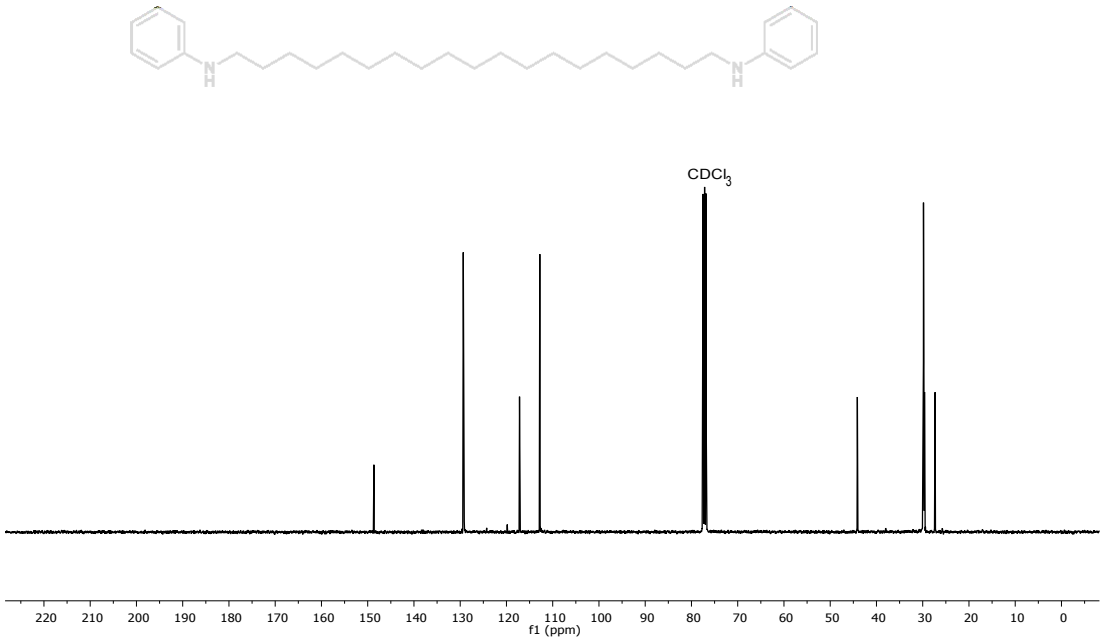


Figure 27. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{19}-diphenylnonadecane-1,19-diamine **8**.

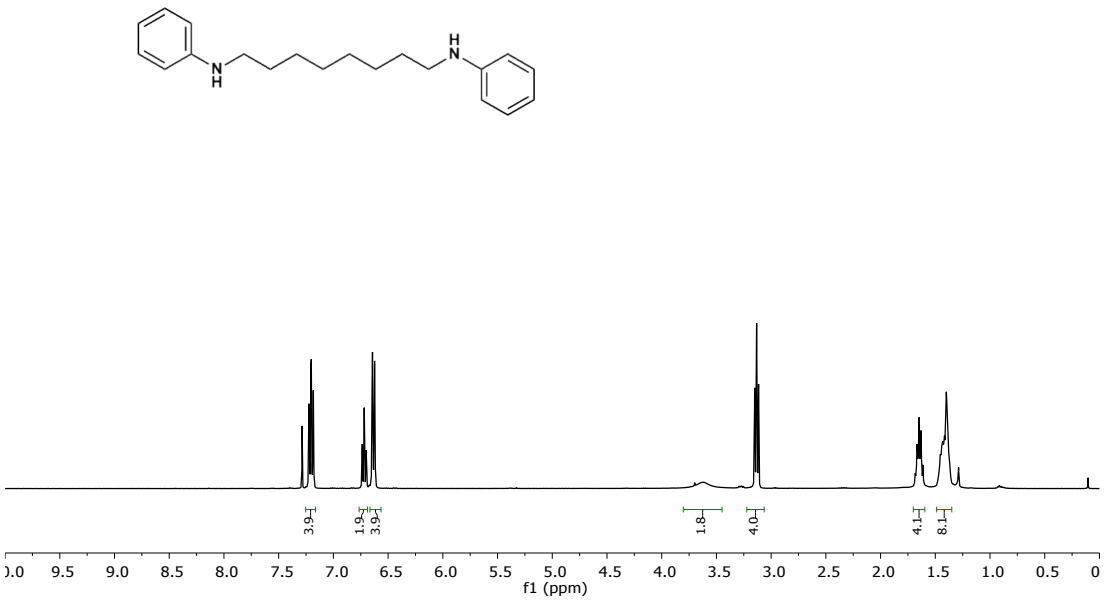


Figure 28. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_8-diphenyloctane-1,8-diamine.

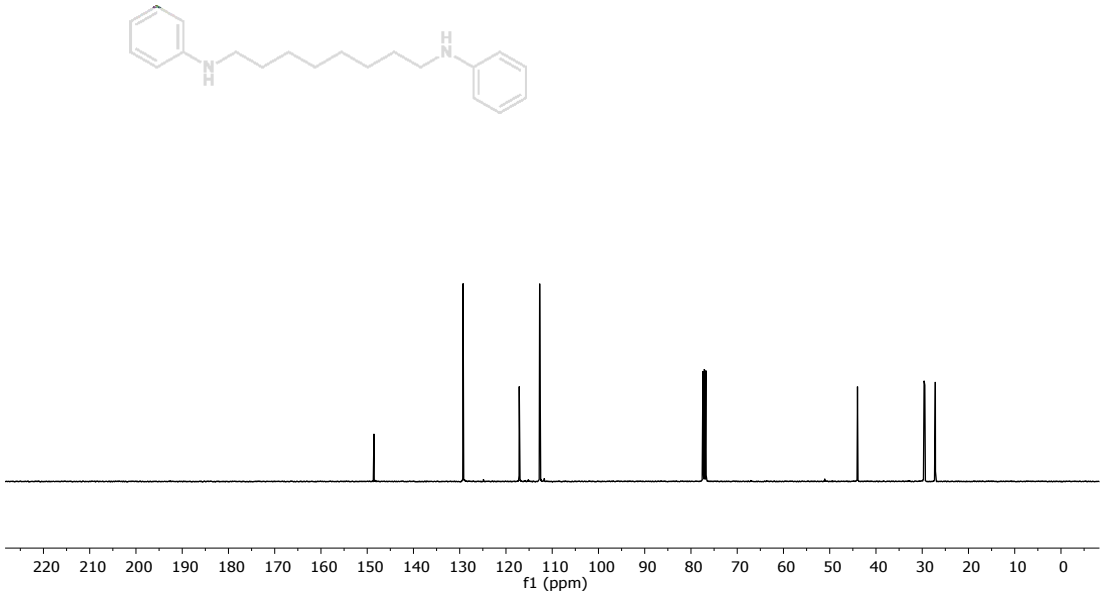


Figure 29. ^{13}C NMR (101 MHz, $CDCl_3$) of *N_1,N_8*-diphenyloctane-1,8-diamine.

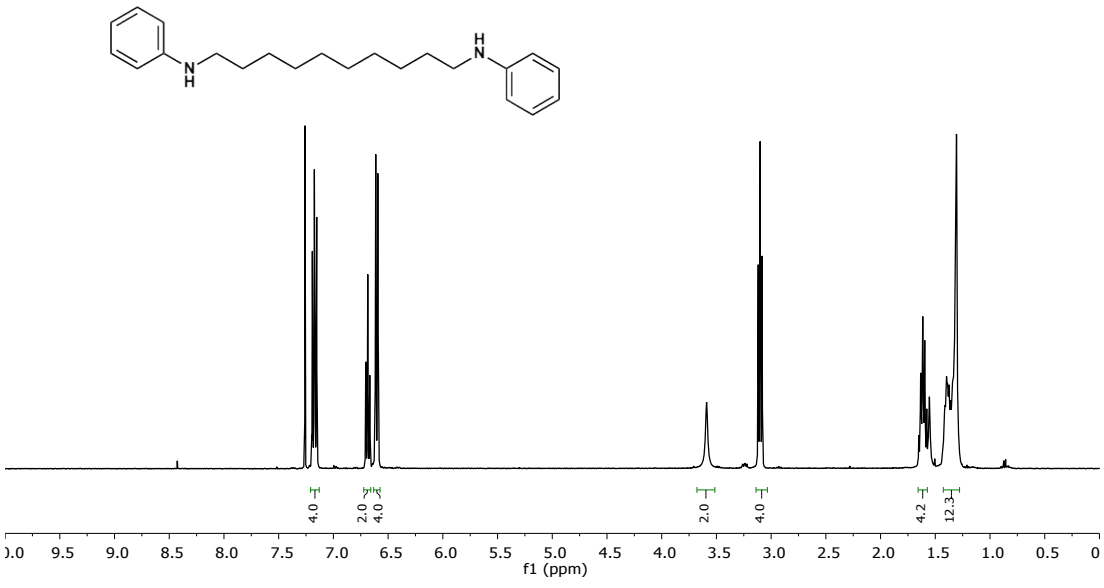


Figure 30. ^{1}H NMR (400 MHz, $CDCl_3$) of *N_1,N_{10}*-diphenyldecane-1,10-diamine.

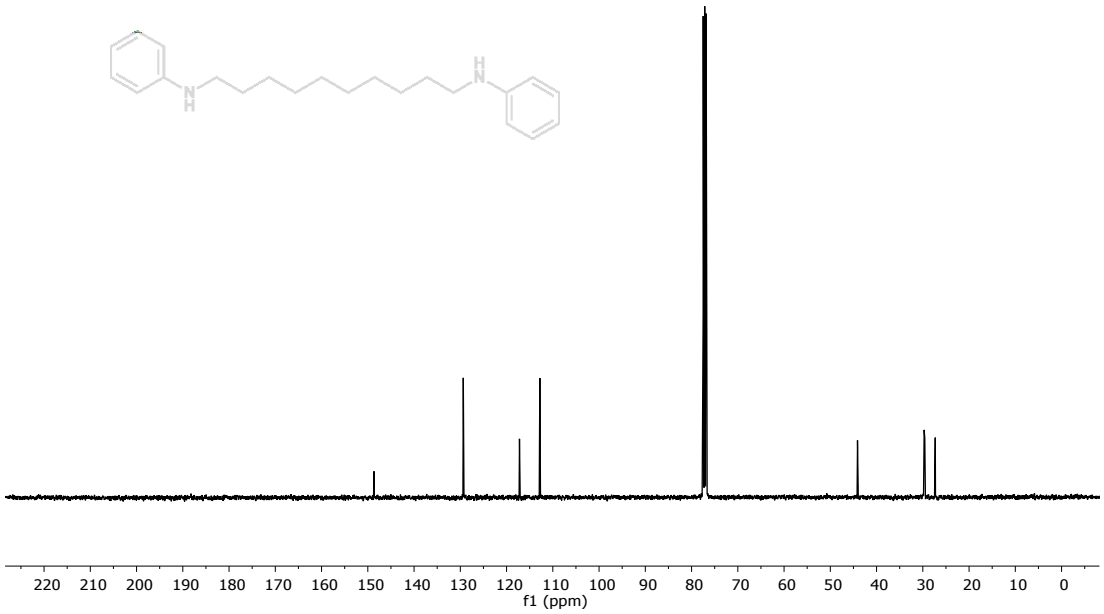


Figure 31. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{10}-diphenyldecane-1,10-diamine.

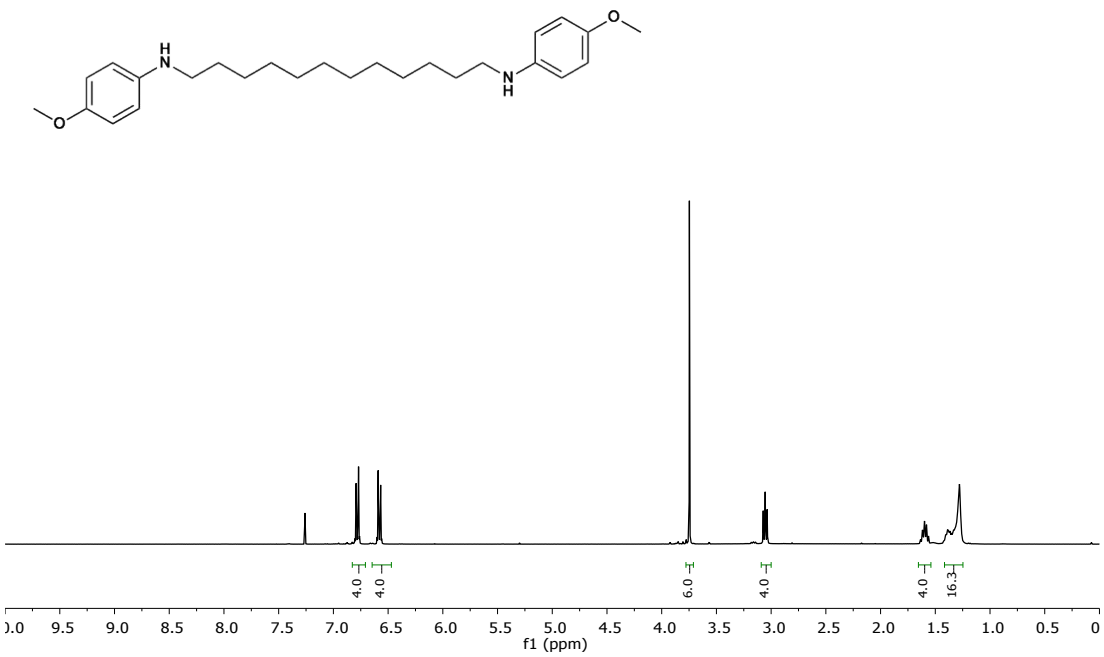


Figure 32. ^1H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-bis(4-methoxyphenyl)dodecane-1,12-diamine.

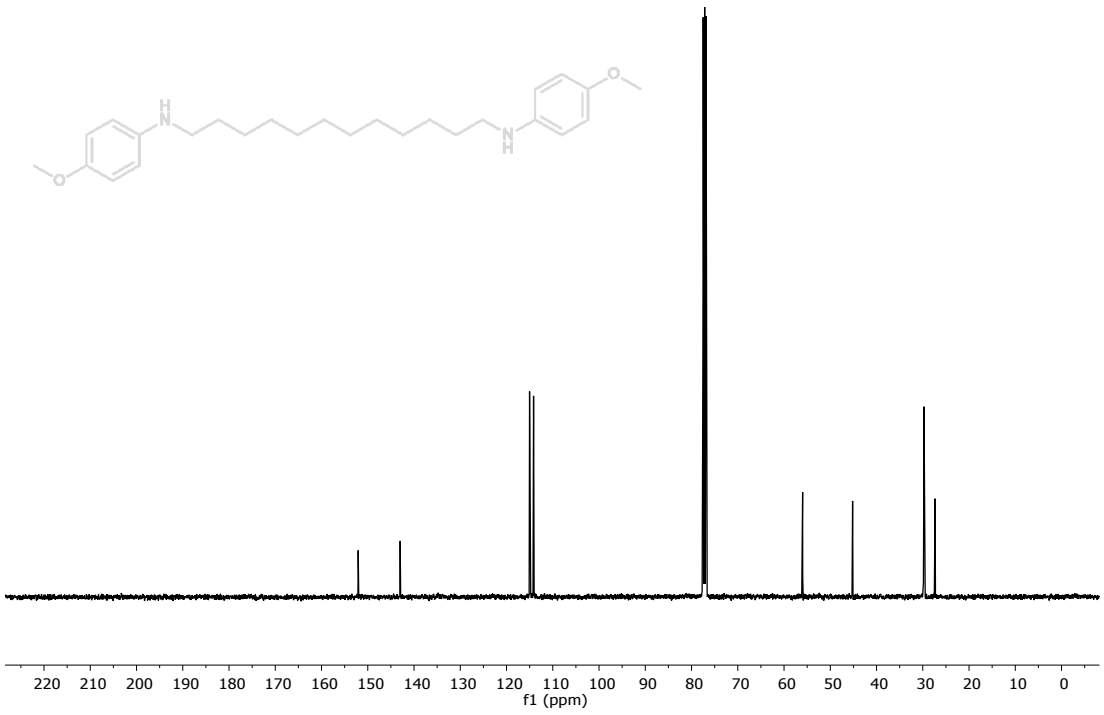


Figure 33. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-bis(4-methoxyphenyl)dodecane-1,12-diamine.

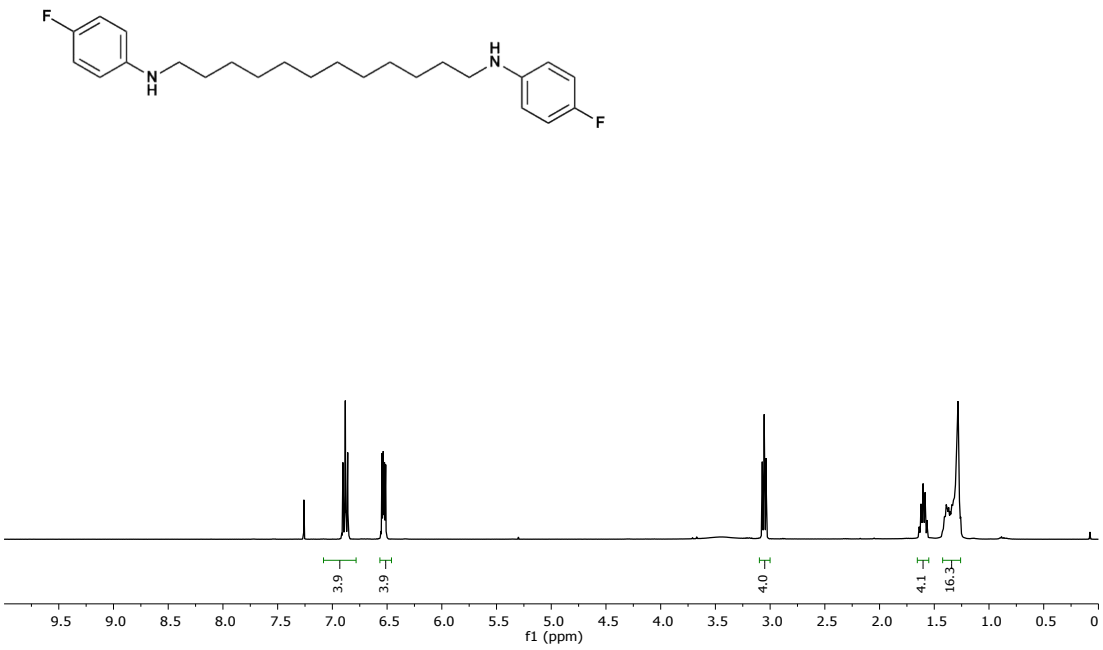


Figure 34. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-bis(4-fluorophenyl)dodecane-1,12-diamine.

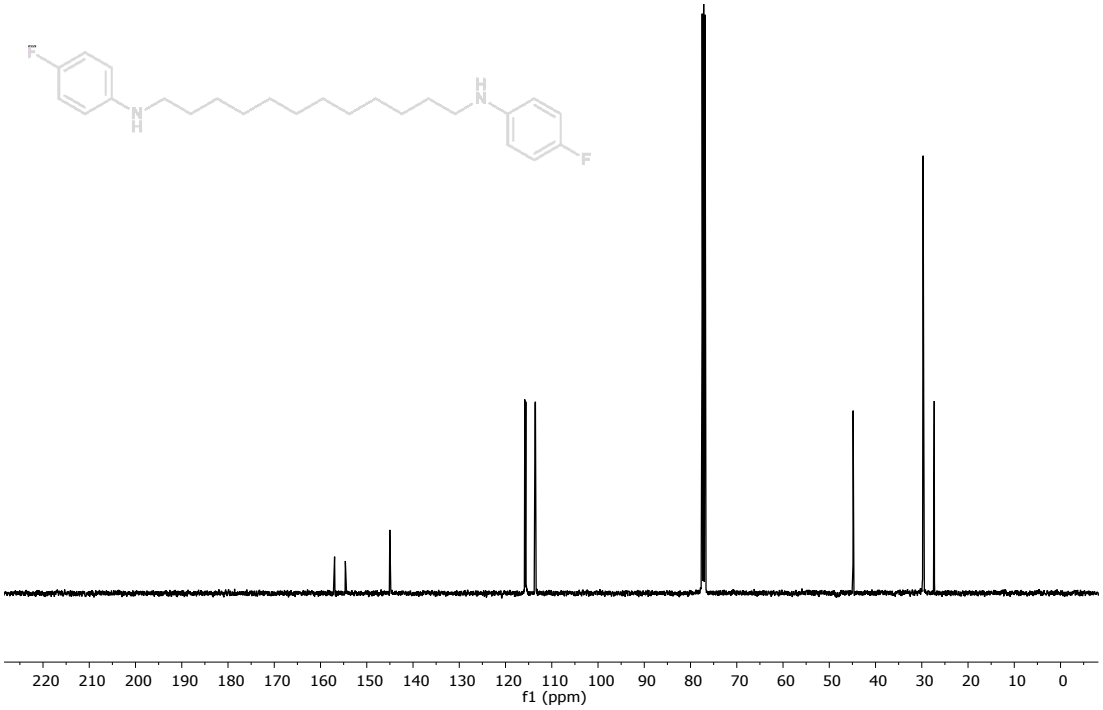


Figure 35. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-bis(4-fluorophenyl)dodecane-1,12-diamine.

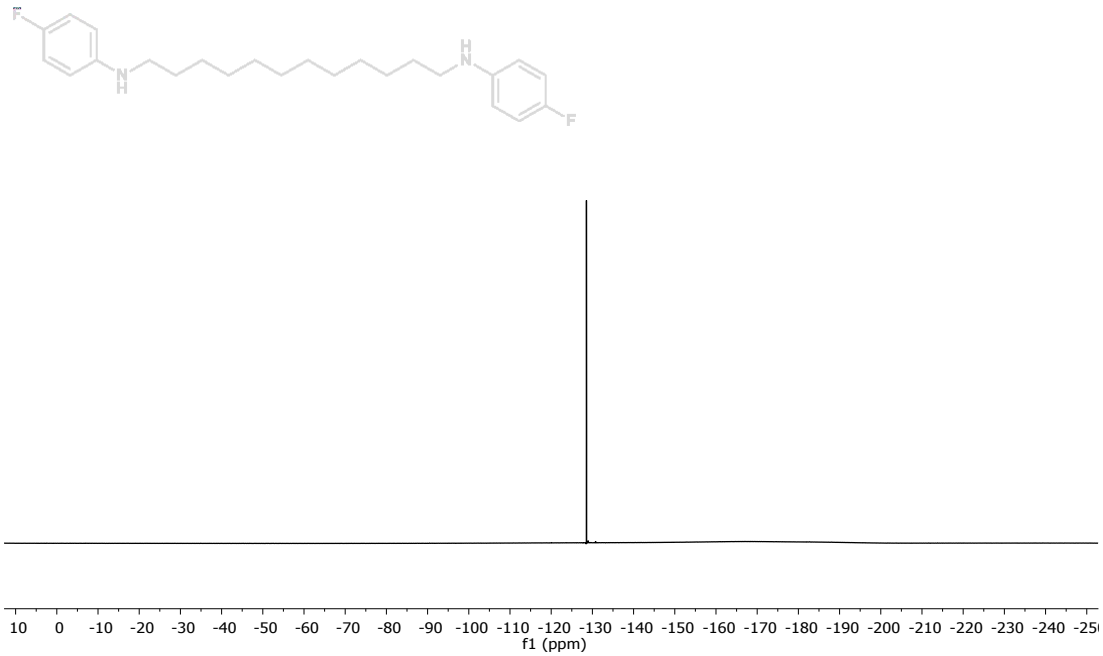


Figure 36. ^{19}F NMR (376 MHz, $CDCl_3$) of N_1,N_{12}-bis(4-fluorophenyl)dodecane-1,12-diamine.

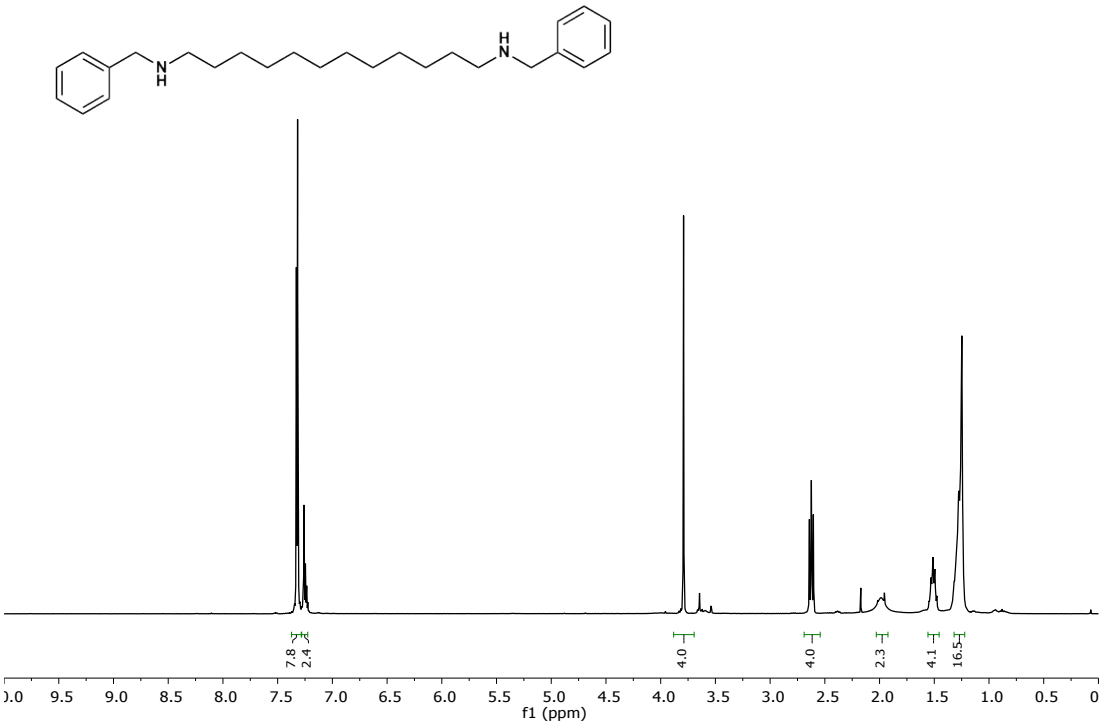


Figure 37. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-dibenzyldodecane-1,12-diamine **11**.

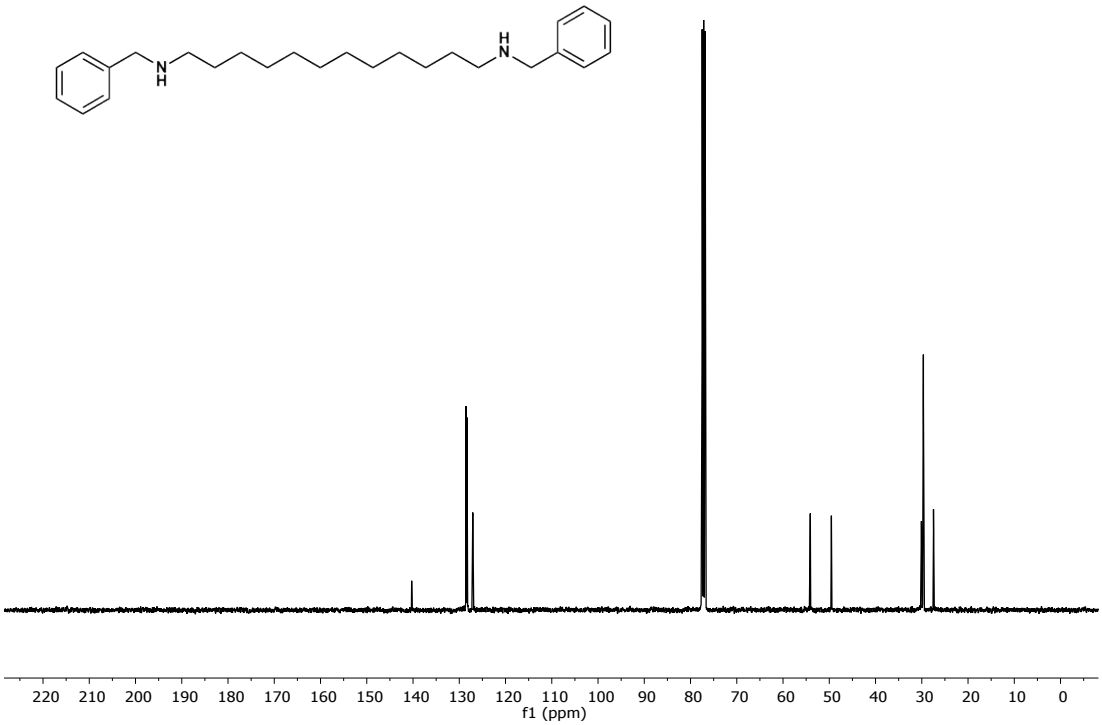


Figure 38. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-dibenzyldodecane-1,12-diamine **11**.

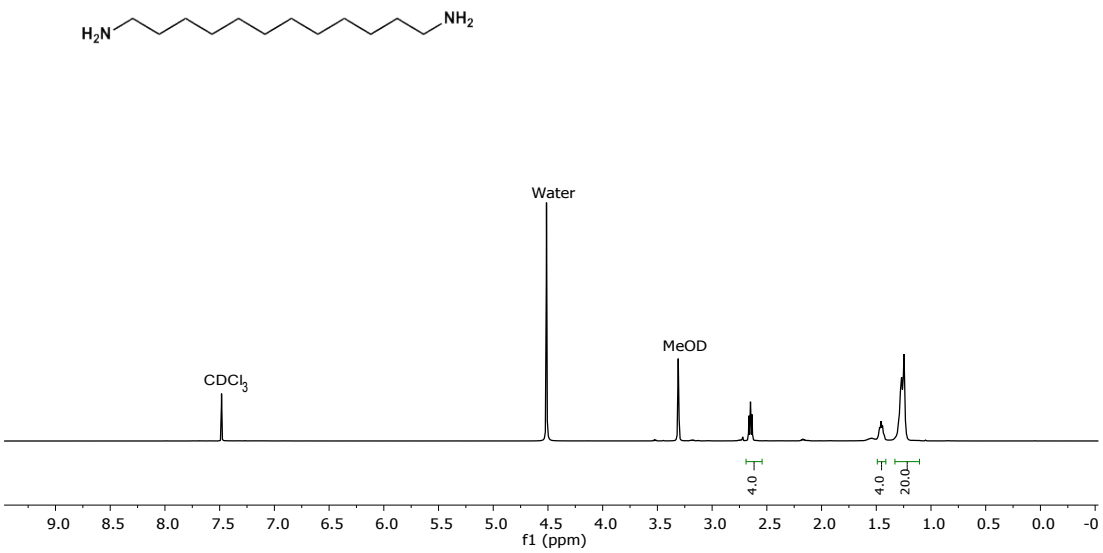


Figure 39. ^{1}H NMR (500 MHz, $CDCl_3$/ d^4-MeOD) of 1,12-diaminododecane **13**. Spectrum referenced to MeOD.

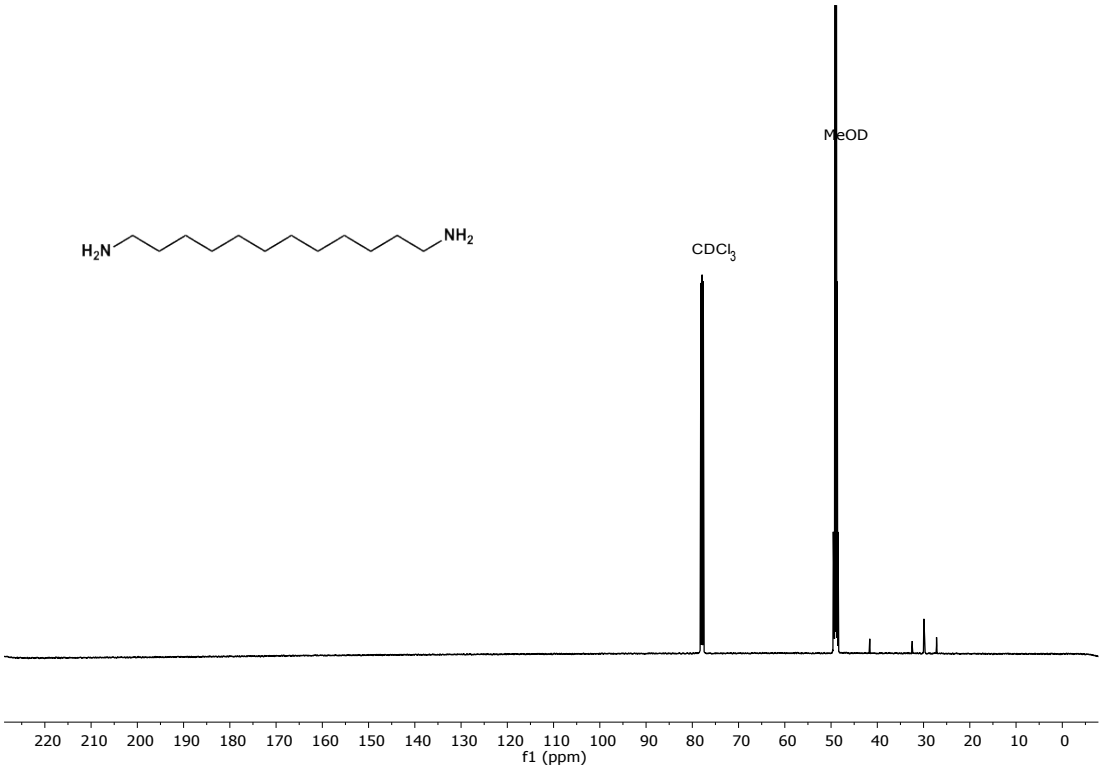


Figure 40. ^{13}C NMR (126 MHz, $CDCl_3$/ d^4-MeOD) of 1,12-diaminododecane **13**. Spectrum referenced to MeOD.

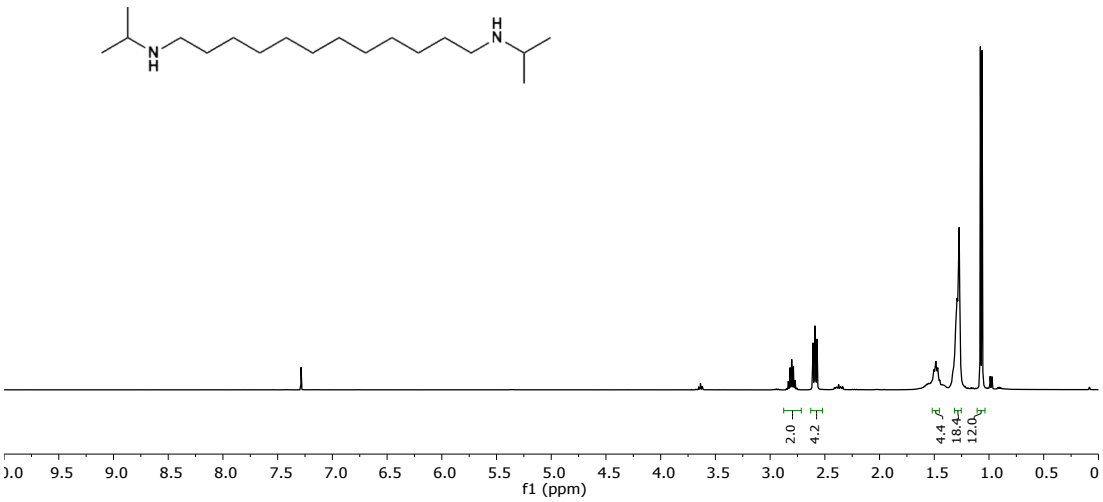


Figure 41. ^{1}H NMR (400 MHz, $CDCl_3$) of N_1,N_{12}-diisopropyldodecane-1,12-diamine **12**.

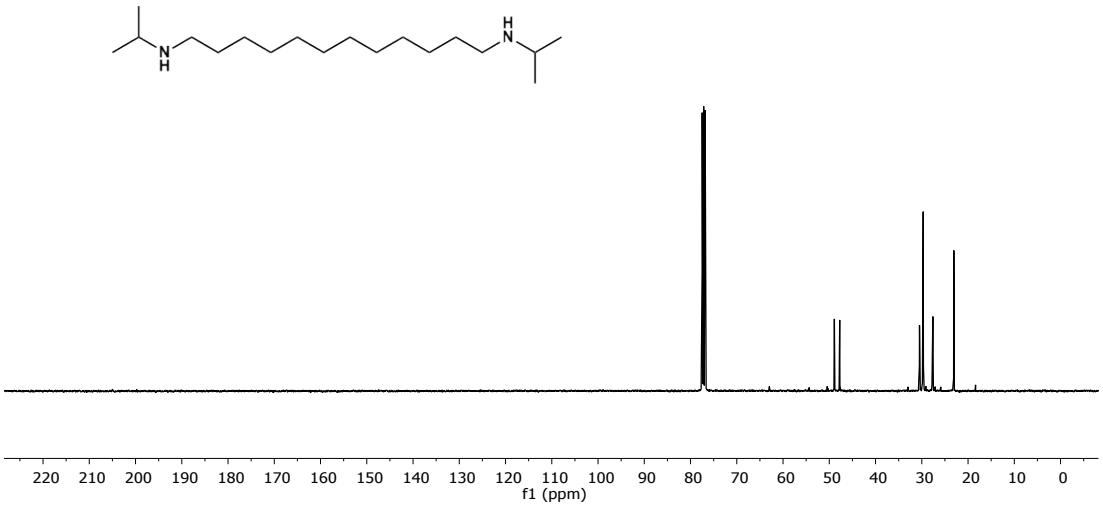


Figure 42. ^{13}C NMR (101 MHz, $CDCl_3$) of N_1,N_{12}-diisopropyldodecane-1,12-diamine **12**.

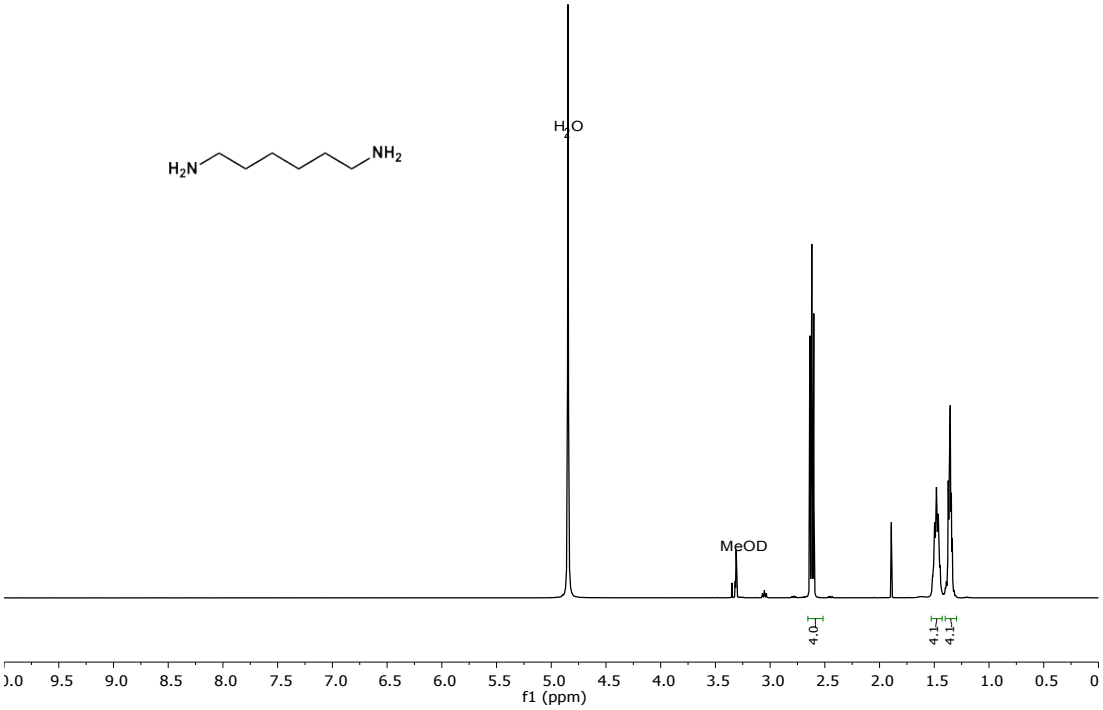


Figure 43. ^{1}H NMR (400 MHz, d^{4}-MeOD) of 1,6-diaminohexane **14**.

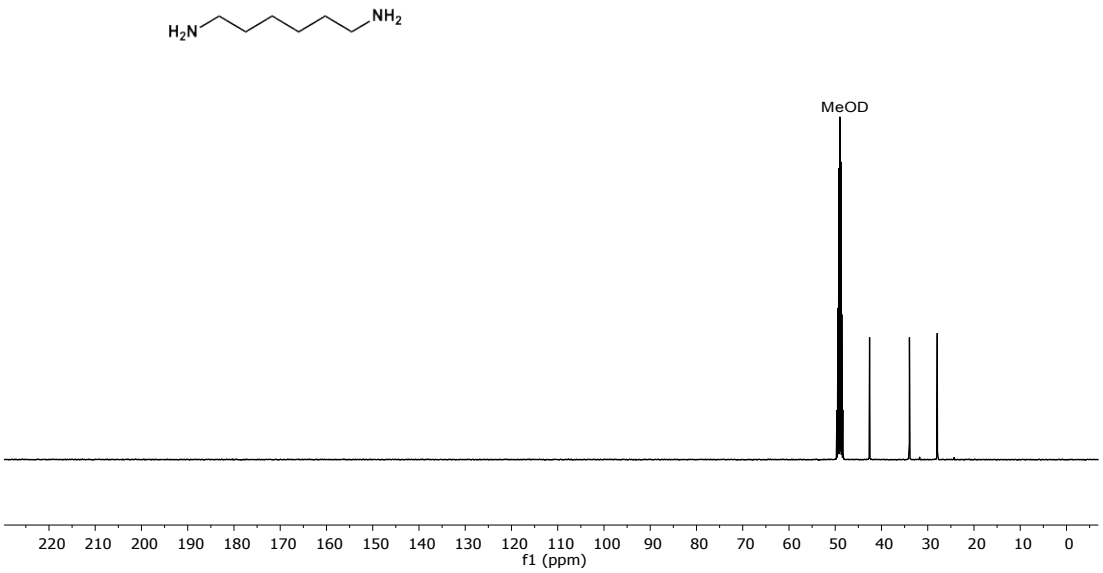


Figure 44. ^{13}C NMR (101 MHz, d^{4}-MeOD) of 1,6-diaminohexane **14**.

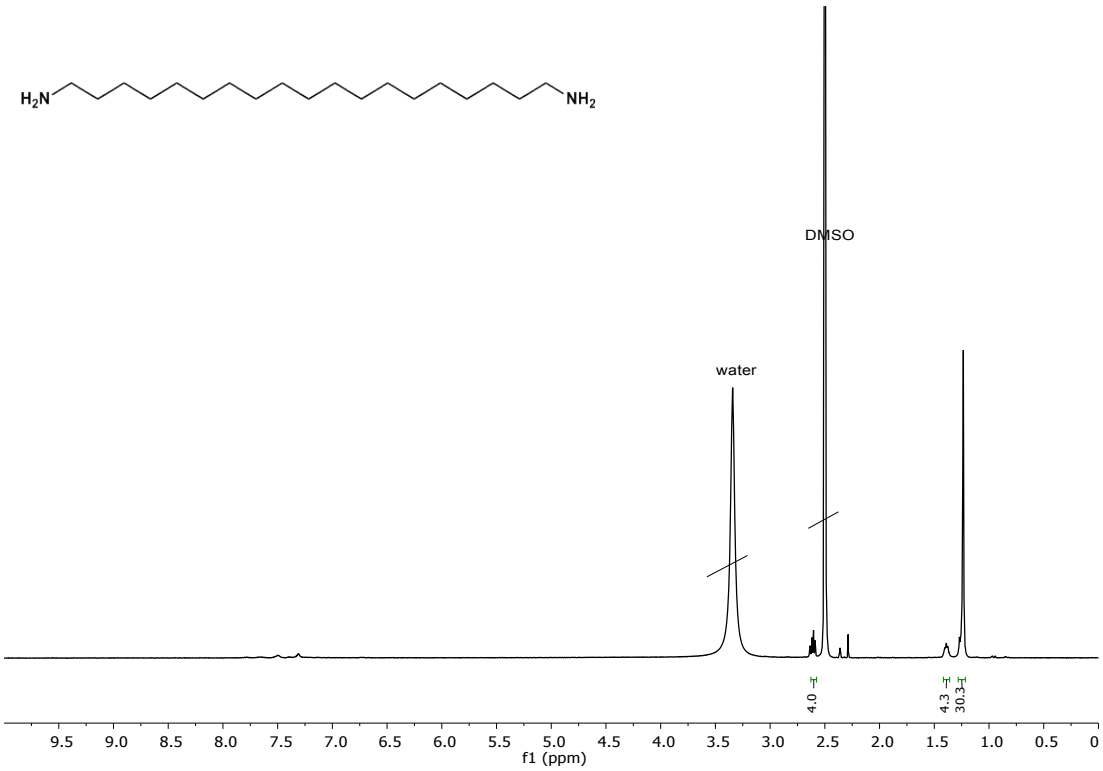


Figure 45. ^{1}H NMR (500 MHz, d^{6}-DMSO) of 1,19-diaminononadecane **15**.

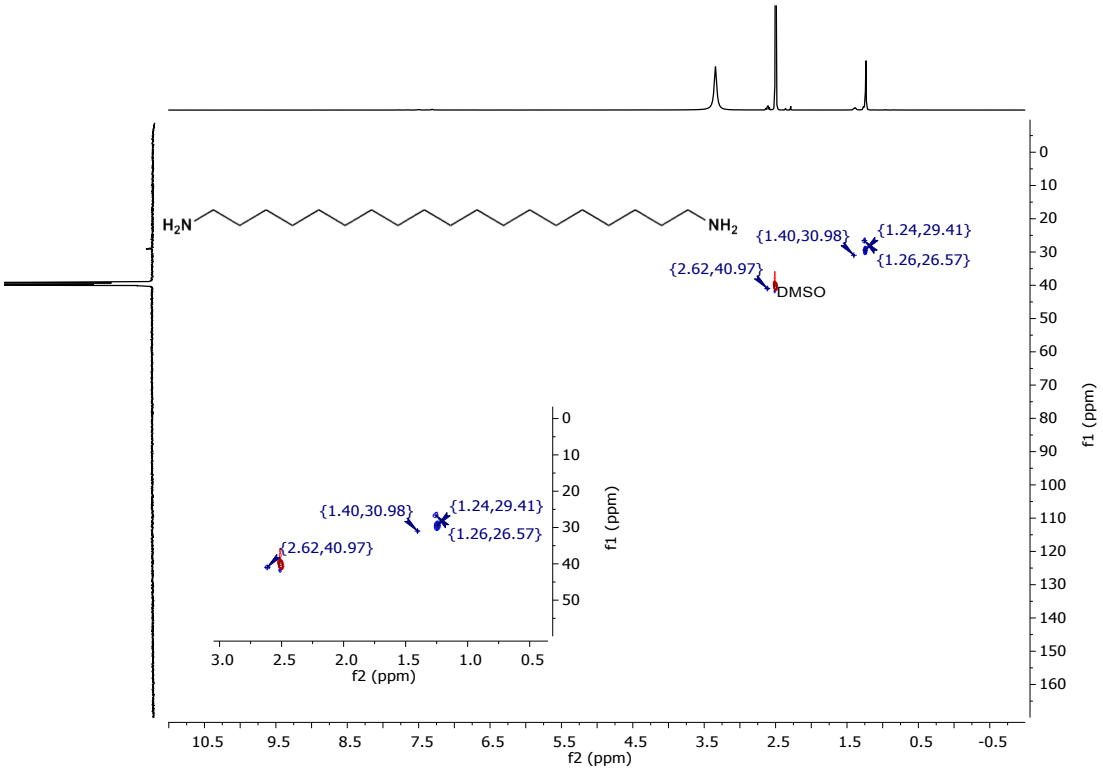


Figure 46. HSQC NMR (d^{6}-DMSO) of 1,19-diaminononadecane **15**.

4. Analysis of reaction mixtures:

4.1. Representative NMR spectra of reaction mixtures

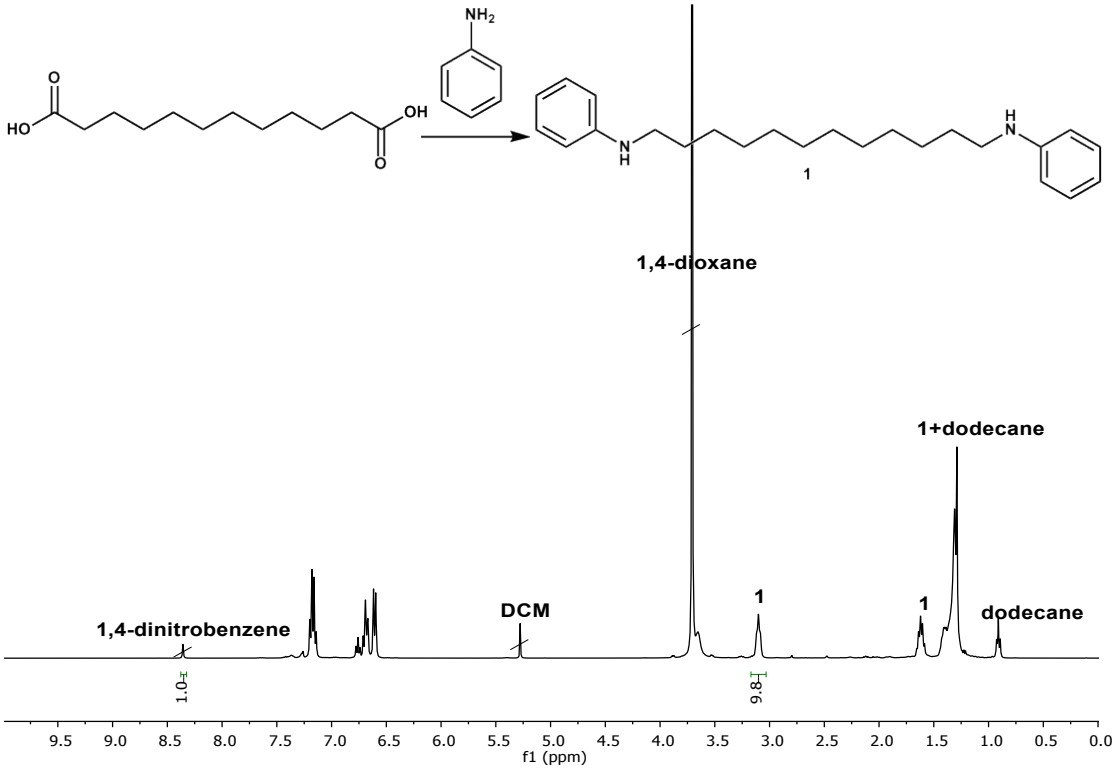


Figure 47. ^{1}H NMR of reaction mixture using 1,12-dodecanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene (0.25 mmol) was used as the internal standard for quantitative NMR analysis.

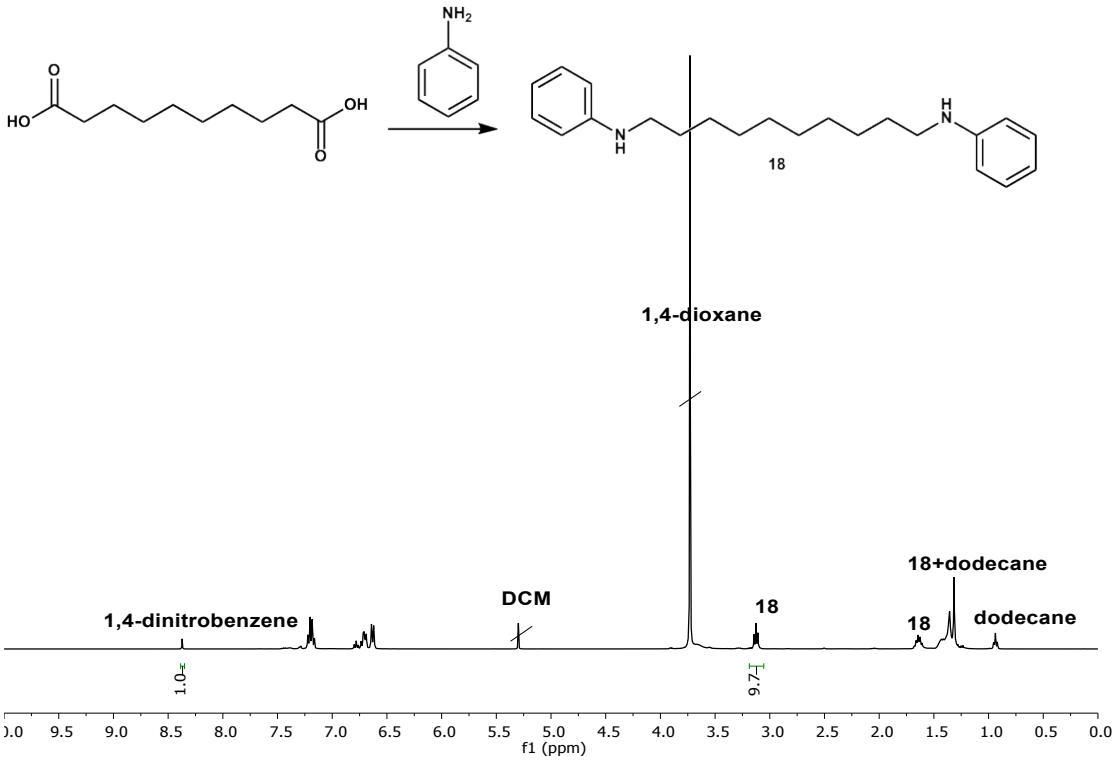


Figure 48. ^{1}H NMR of reaction mixture using 1,10-decanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene (0.25 mmol) was used as the internal standard for quantitative NMR analysis.

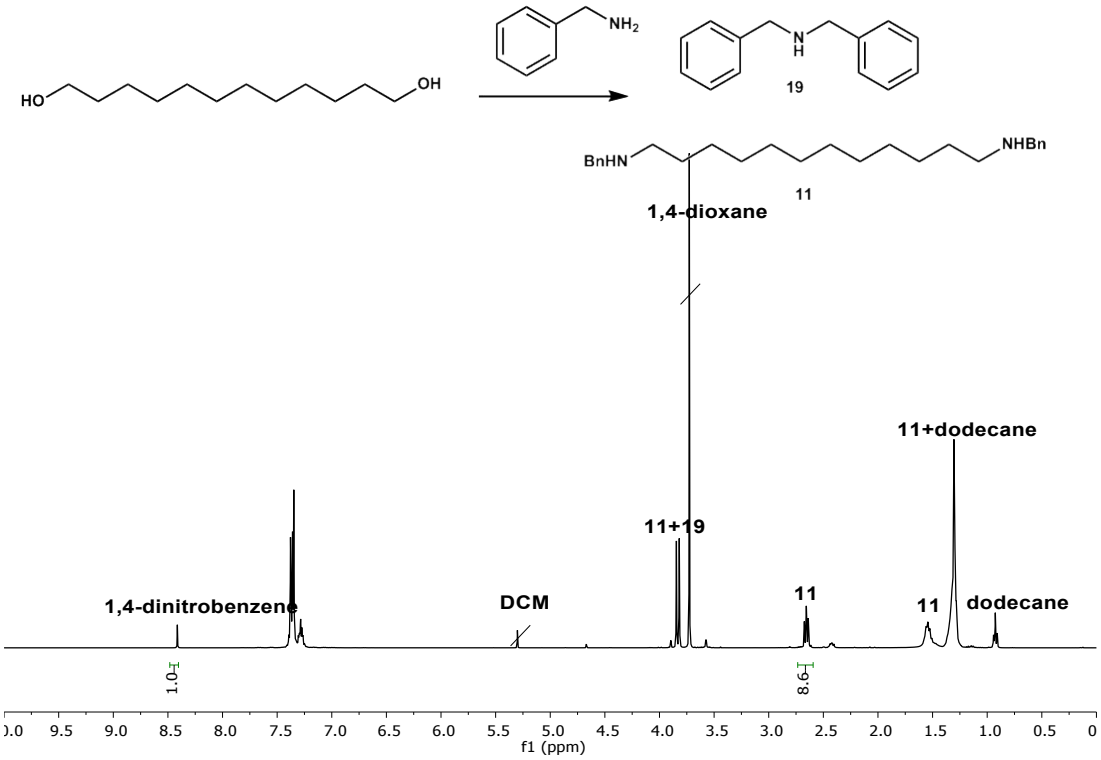


Figure 49. ^{1}H NMR of reaction mixture using 1,10-decanediol and benzylamine. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene (0.25 mmol) was used as the internal standard for quantitative NMR analysis.

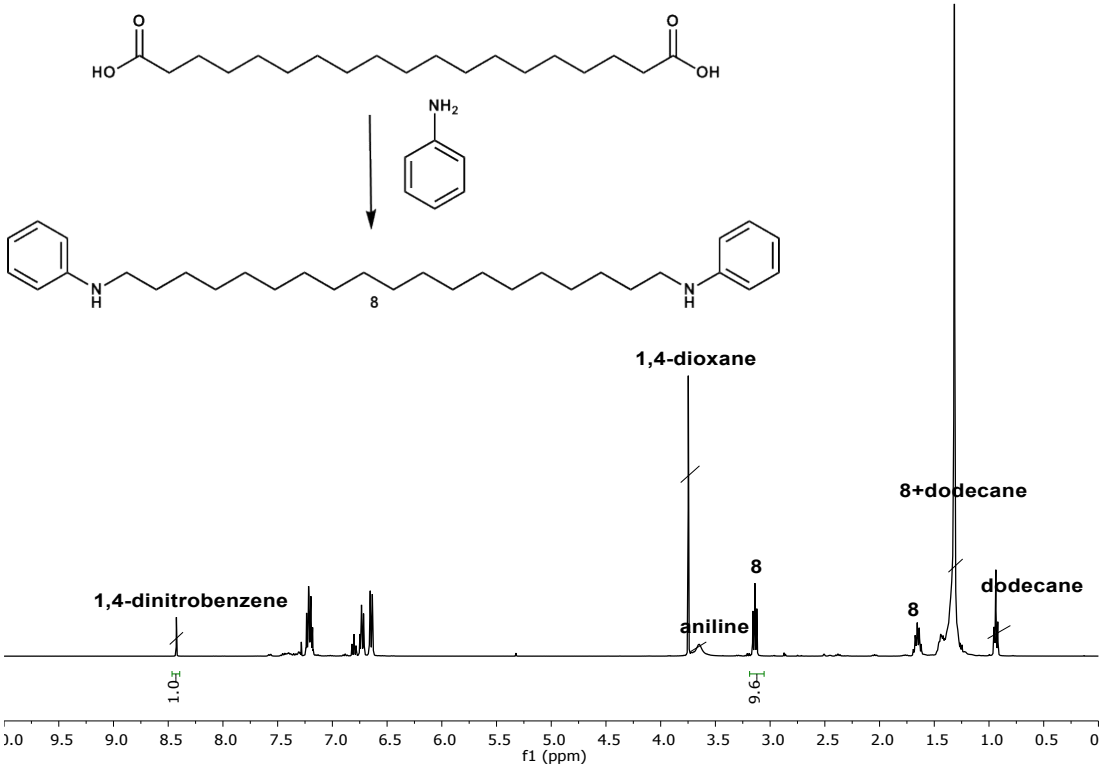
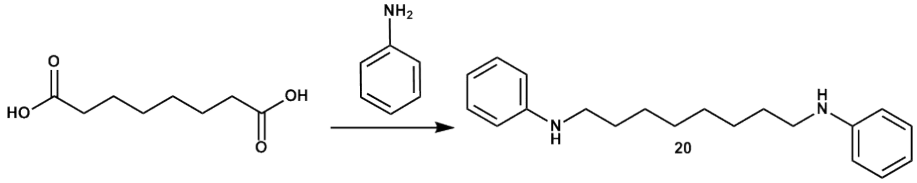


Figure 50. ^{1}H NMR of reaction mixture using 1,19-nonadecanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis.1,4-Dinitrobenzene (0.25 mmol) was used as the internal standard for quantitative NMR analysis.



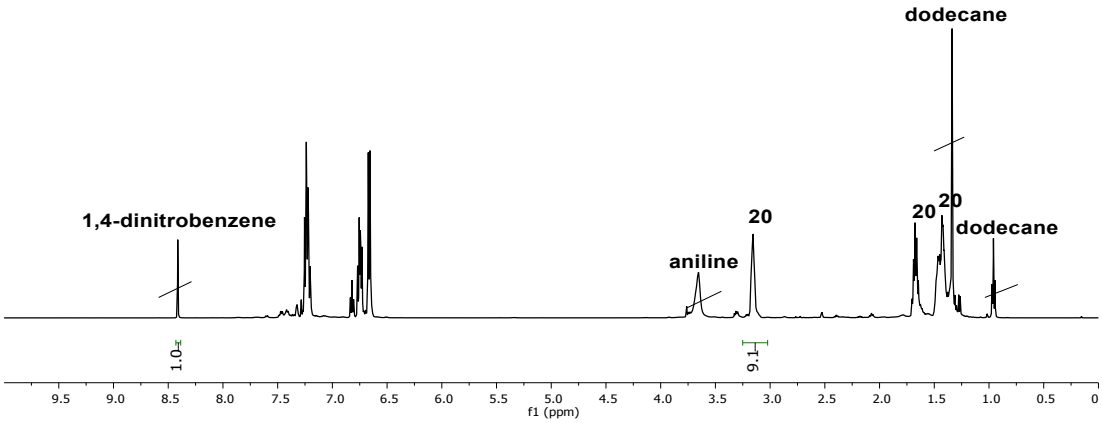


Figure 51. ^{1}H NMR of reaction mixture using 1,8-octanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene (0.25 mmol) was used as the internal standard for quantitative NMR analysis.

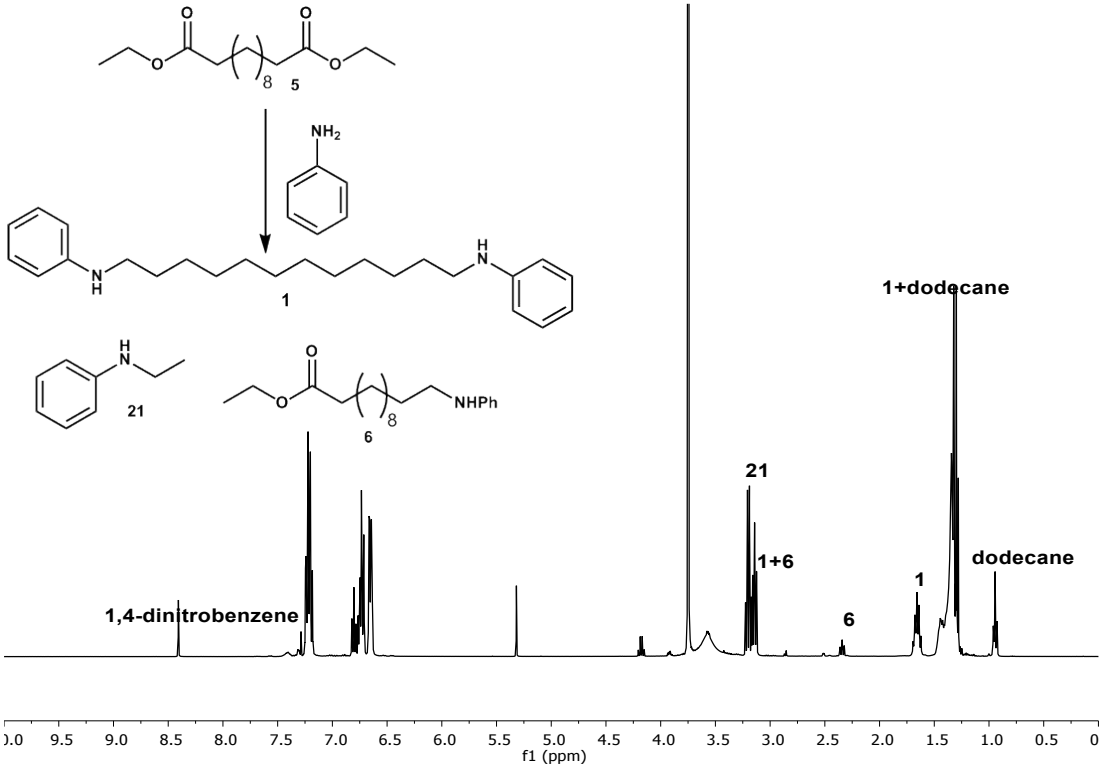


Figure 52. ^{1}H NMR of reaction mixture using diethyl 1,12-dodecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

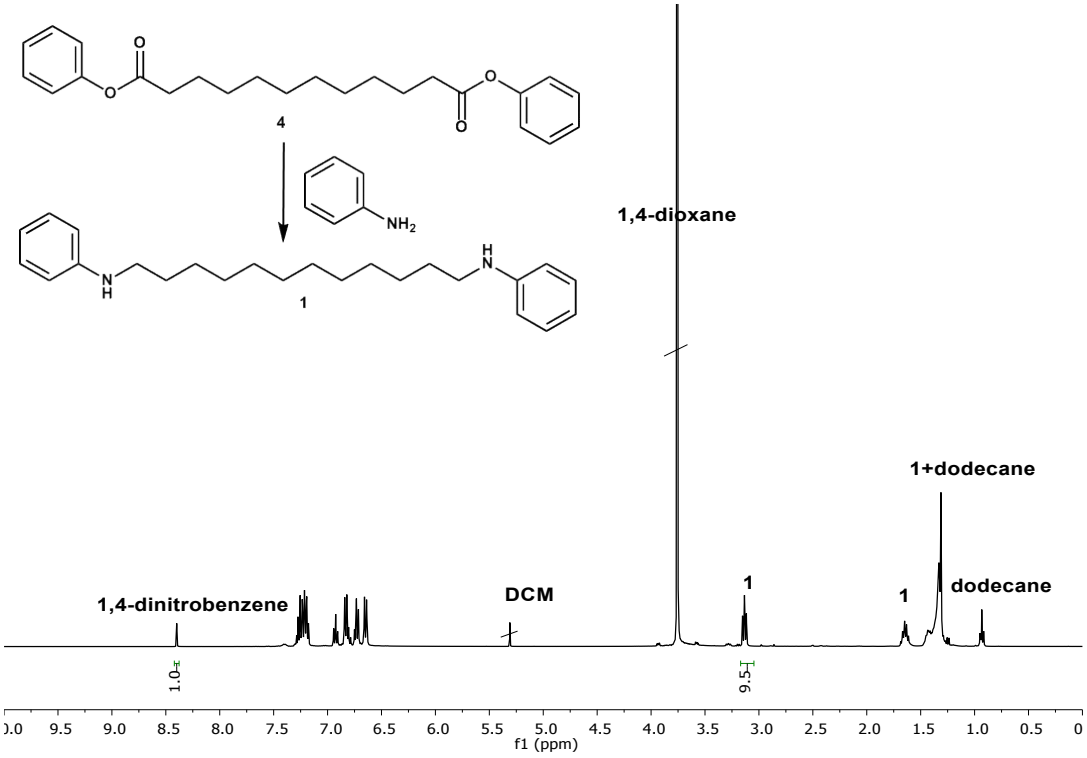


Figure 53. ^{1}H NMR of reaction mixture using diphenyl 1,12-dodecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

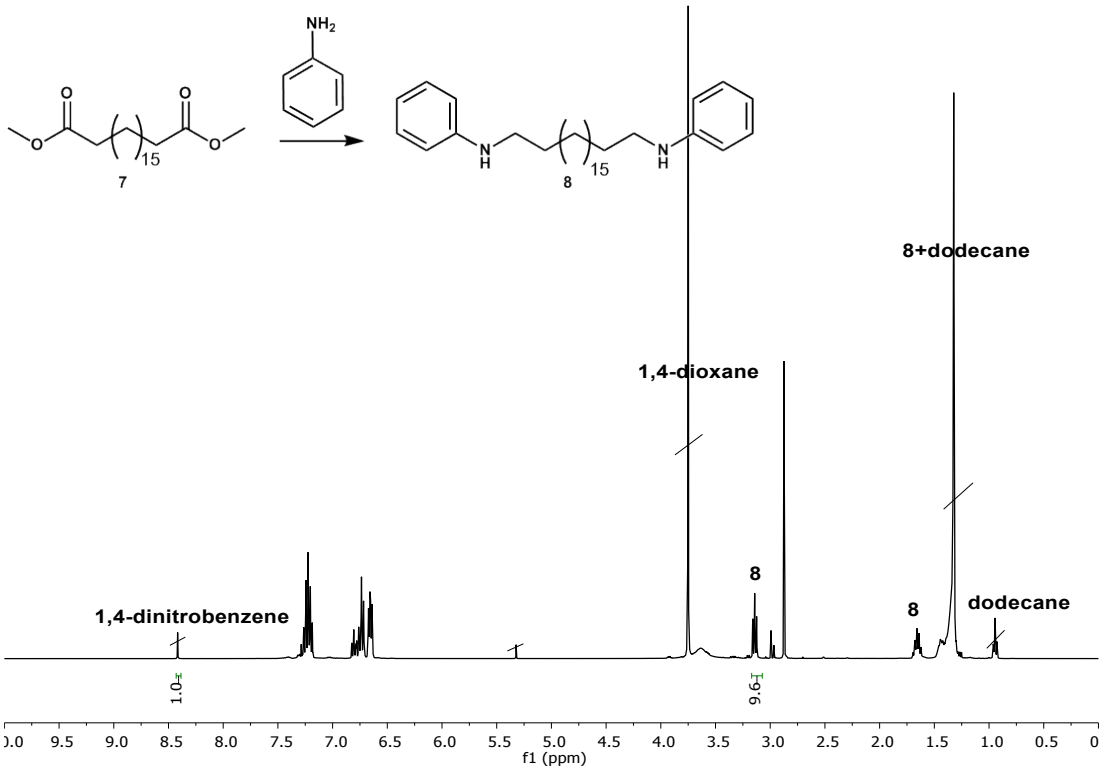


Figure 54. ^{1}H NMR of reaction mixture using 1,19-dimethylnonadecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

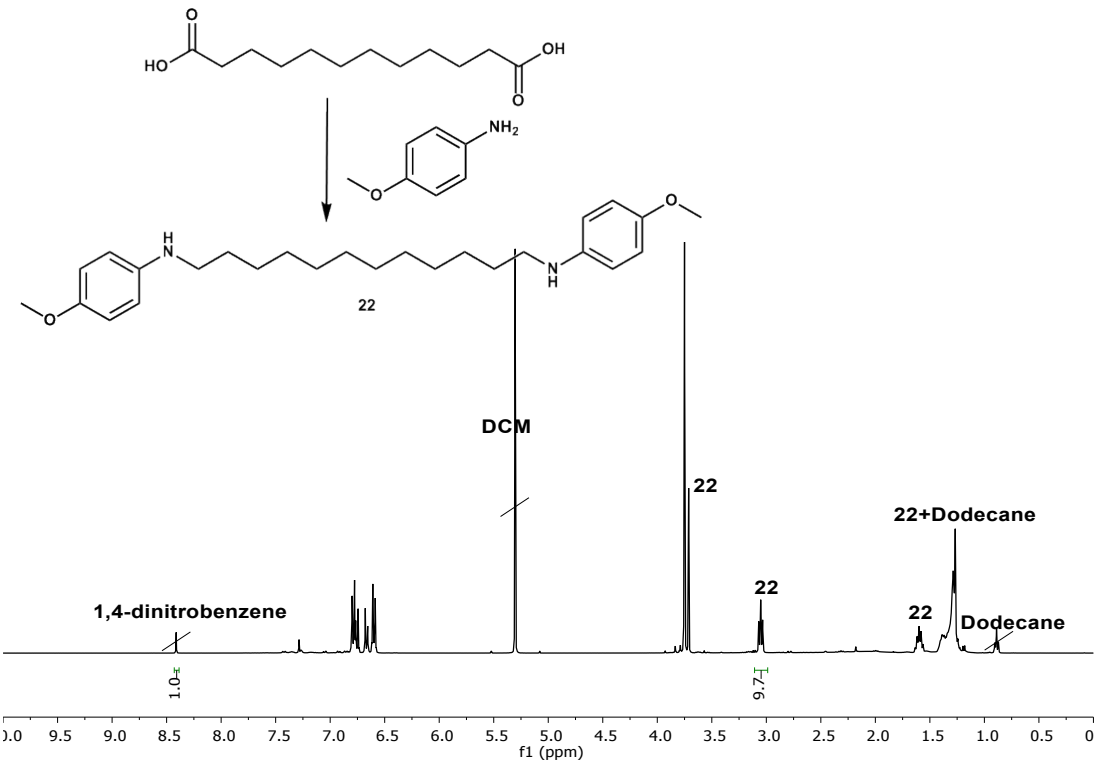


Figure 55. ^{1}H NMR of reaction mixture using 1,10-decanedioic acid and *para*-methoxy aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

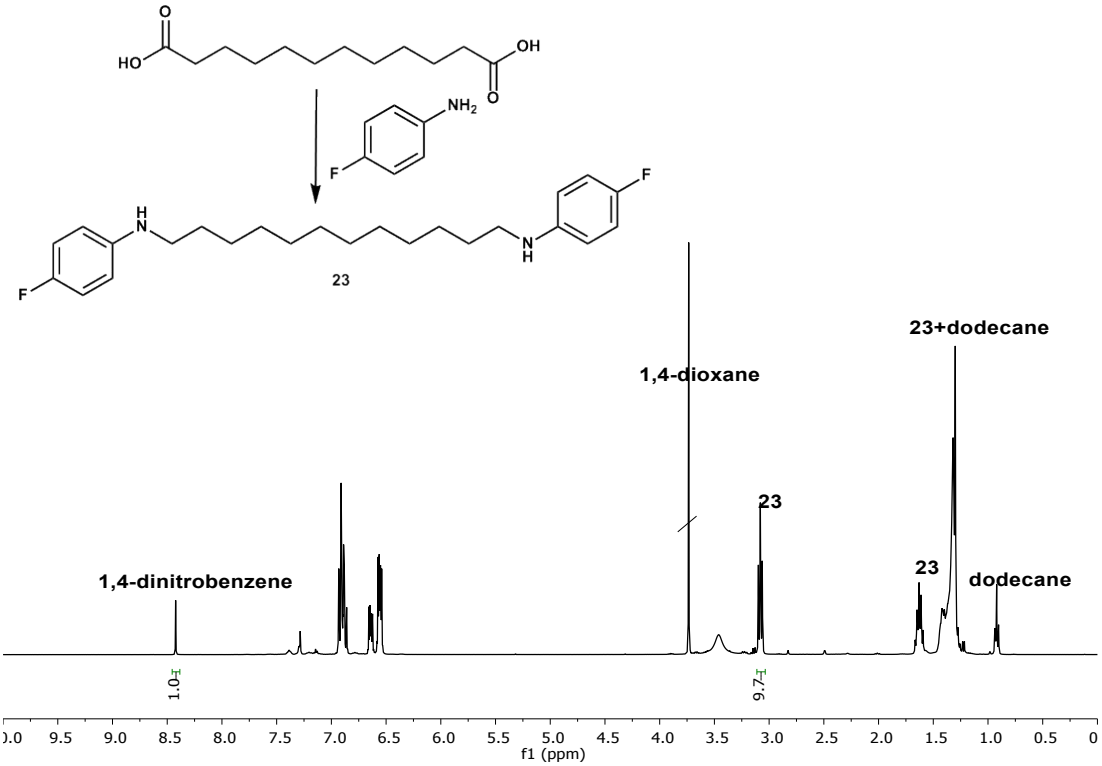


Figure 56. ^{1}H NMR of reaction mixture using 1,10-decanedioic acid and *para*-fluoro aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

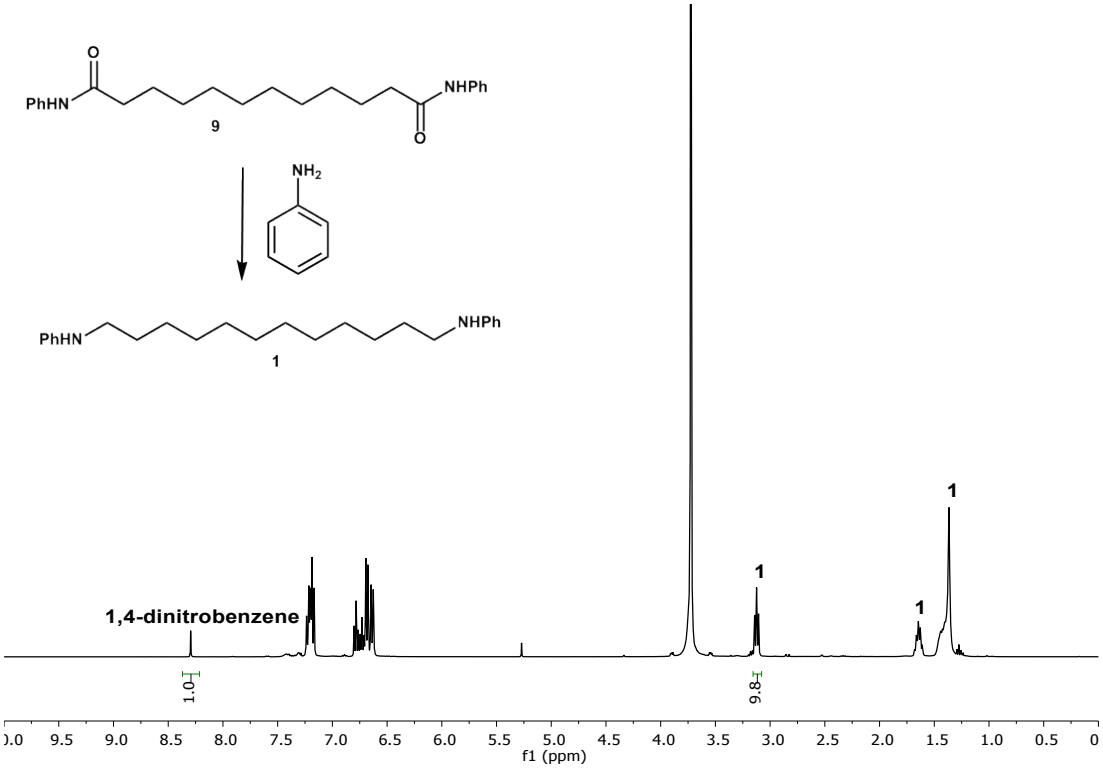


Figure 57. ^{1}H NMR of reaction mixture using N_1,N_{12}-diphenyldodecane-1,12-diamide and aniline. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

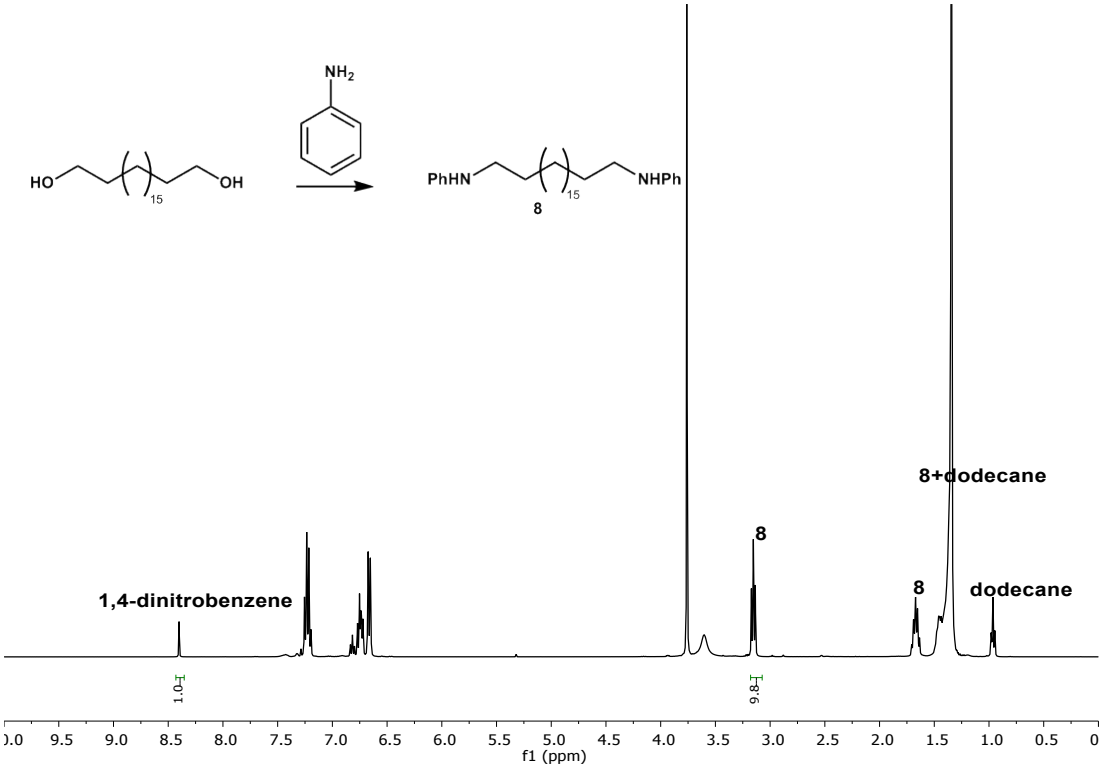


Figure 58. ^{1}H NMR of reaction mixture using 1,19-nonadecanediol and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

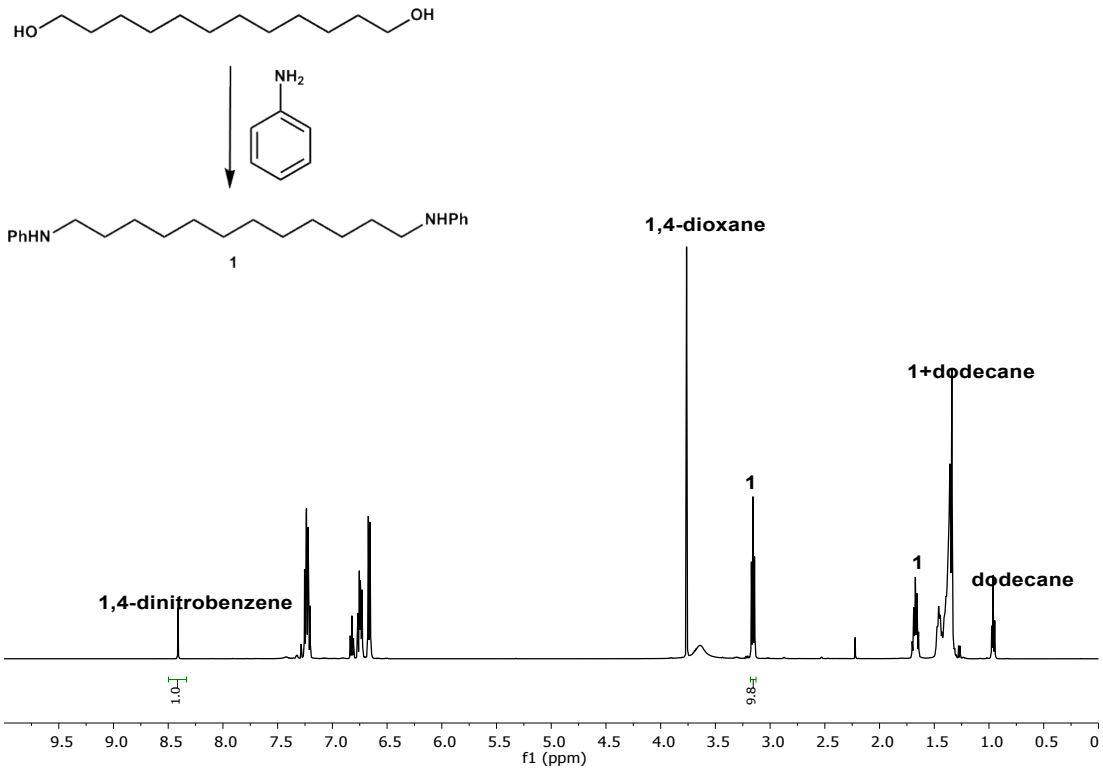


Figure 59. ^{1}H NMR of reaction mixture using 1,12-dodecanediol and aniline. Dodecane was used as the internal standard for quantitative GC analysis. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

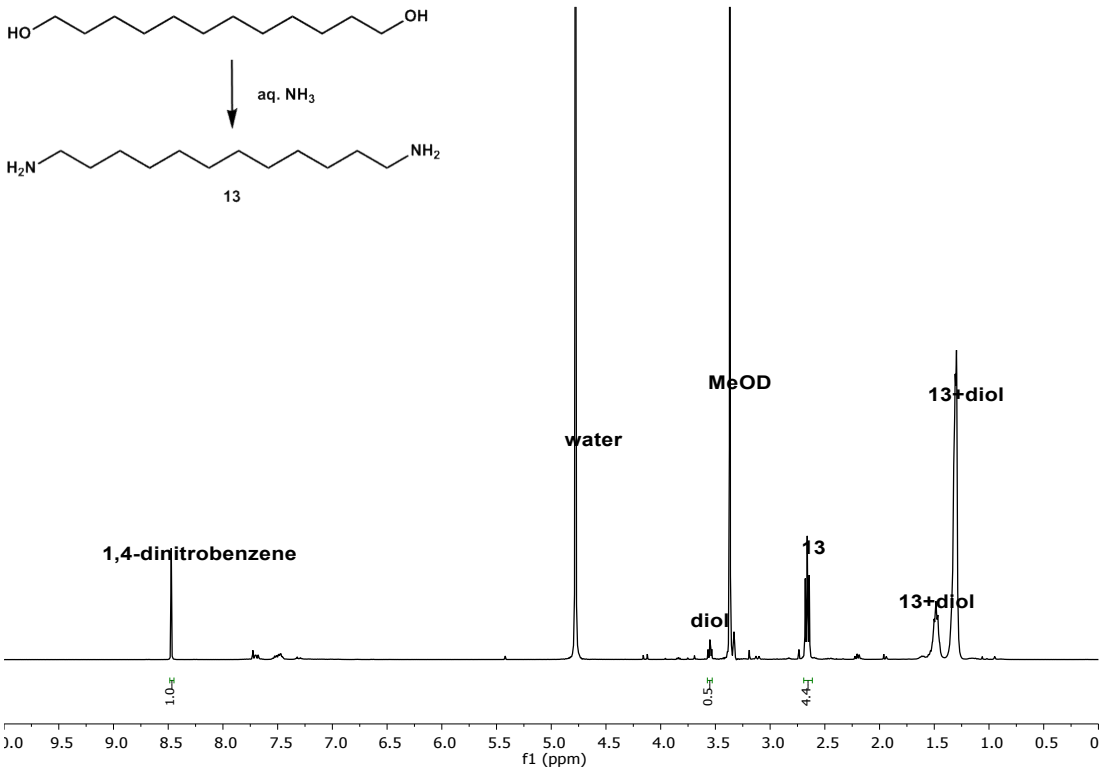


Figure 60. ^{1}H NMR of reaction mixture using 1,12-dodecanediol and aqueous ammonia. 1,4-Dinitrobenzene was used as the internal standard for quantitative NMR analysis.

4.2. Representative GC spectra (GCMS) of reaction mixtures

Injection mode	Split
Split ratio	100
Carrier gas	He
Flow control	Flow rate
Flow rate	1.5 mL min^{-1}
Oven temperature programme	50-300 °C at 15 °C min^{-1}, then hold 20 min
Column type	THERMO TR-5 5% Phenyl Methylpolysiloxane
Column dimensions	30 m × 0.25 mm × 0. 25 µm

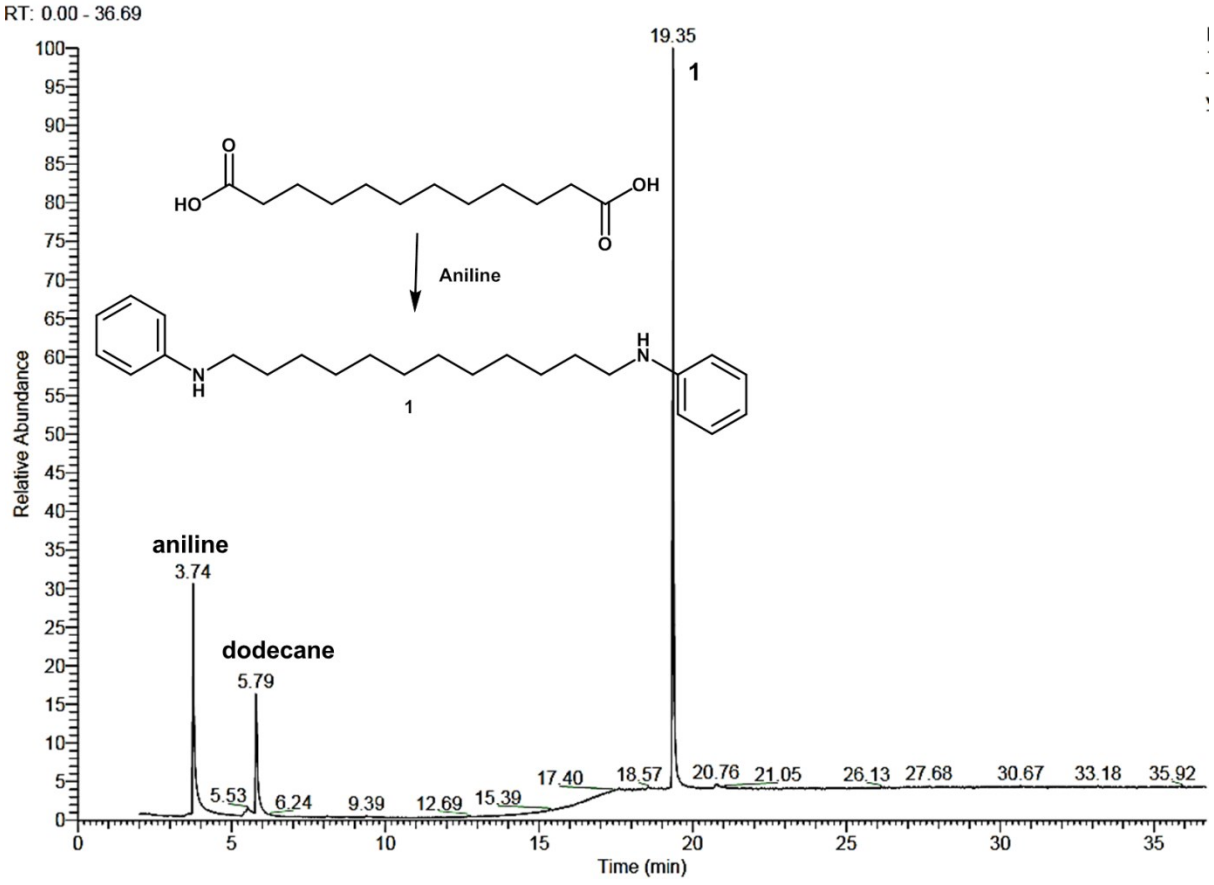


Figure 61. GC spectrum of reaction mixture using 1,12-dodecanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis.

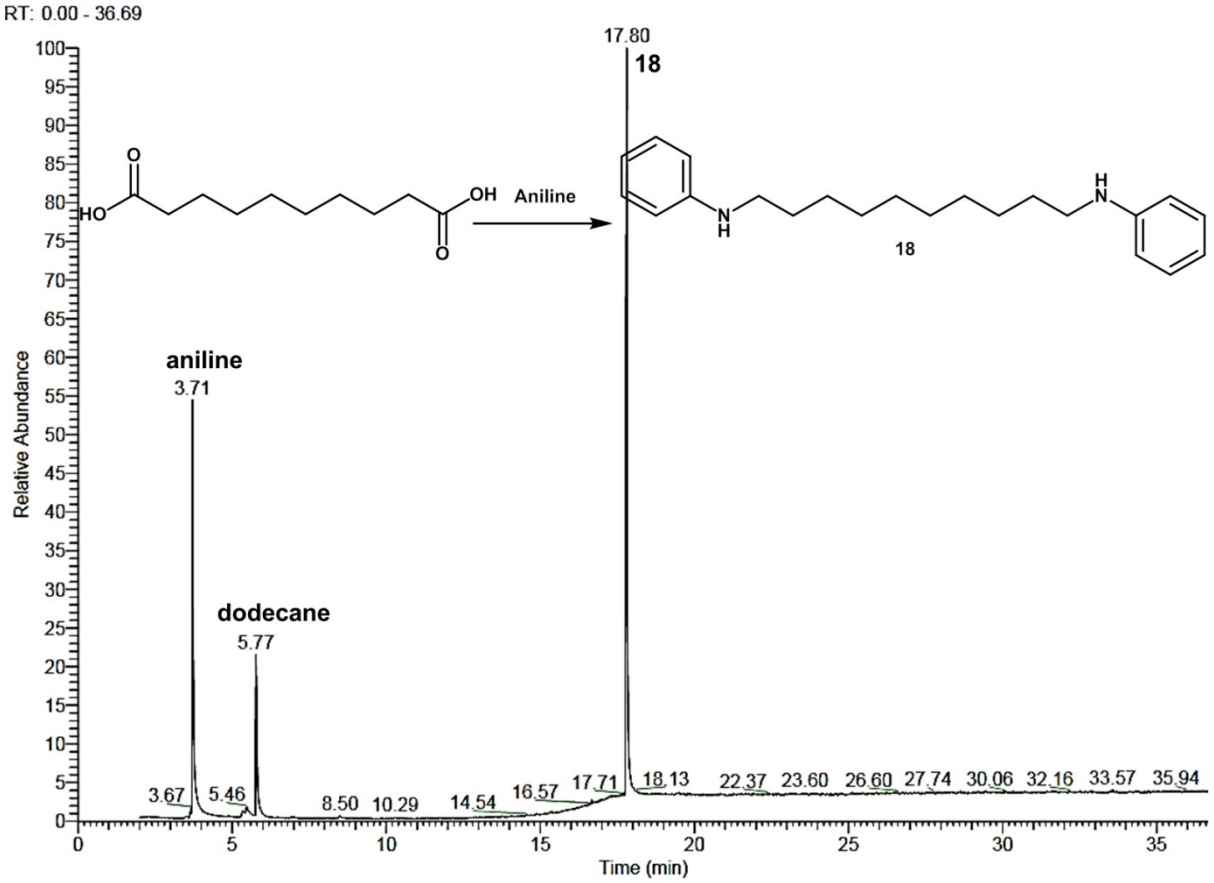


Figure 62. GC spectrum of reaction mixture using 1,10-decanedioic acid and aniline. Dodecane was used as the internal standard for quantitative GC analysis.

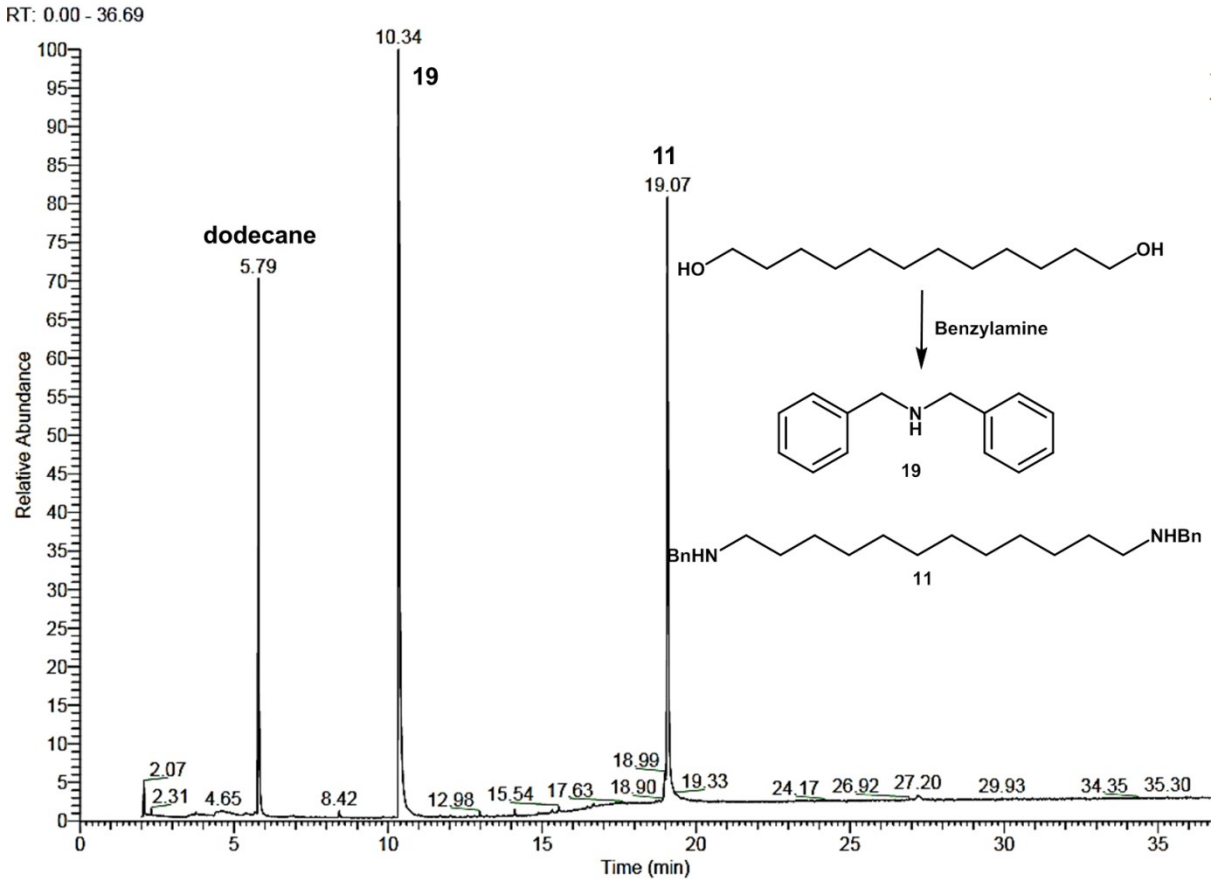


Figure 63. GC spectrum of reaction mixture using 1,12-dodecanediol and benzylamine. Dodecane was used as the internal standard for quantitative GC analysis.

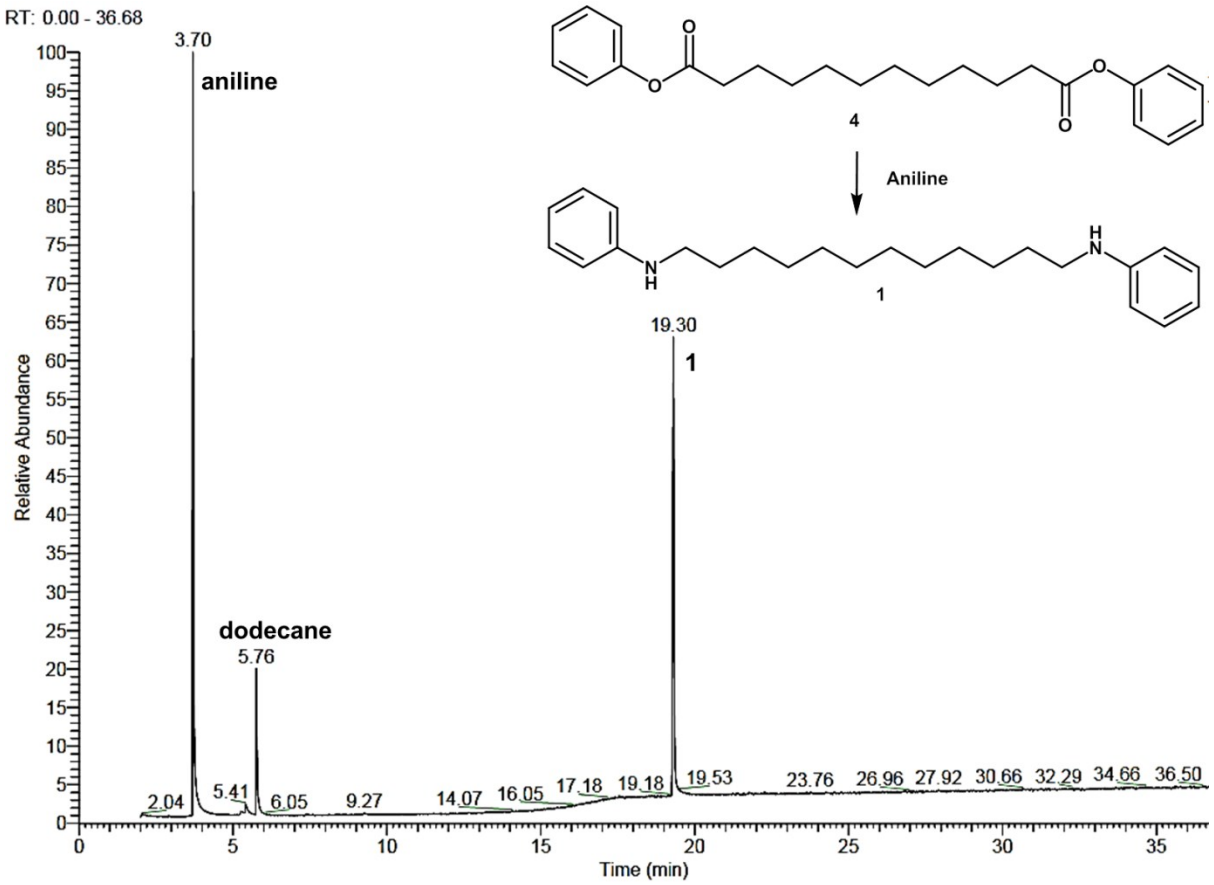


Figure 64. GC spectrum of reaction mixture using diphenyl 1,12-dodecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis.

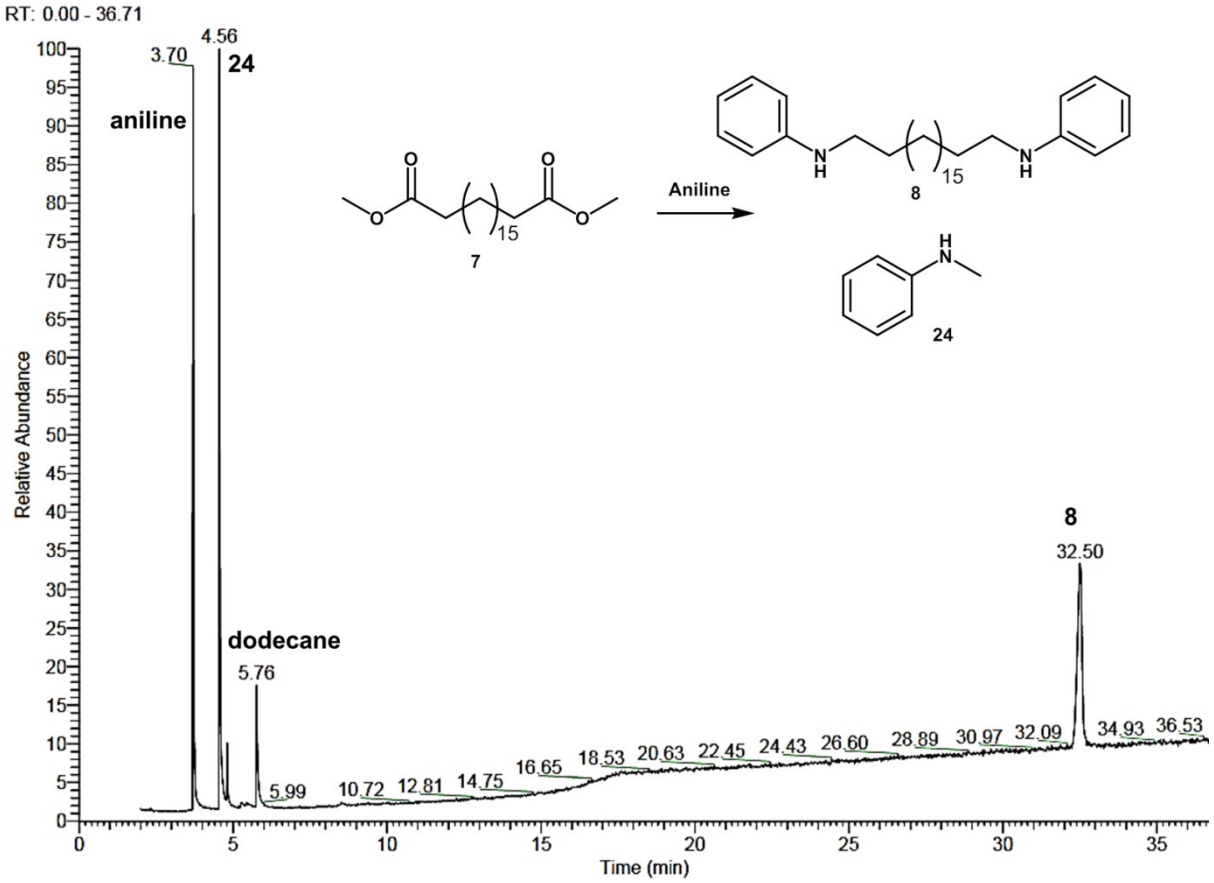


Figure 65. GC spectrum of reaction mixture using dimethyl 1,19-nonadecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis.

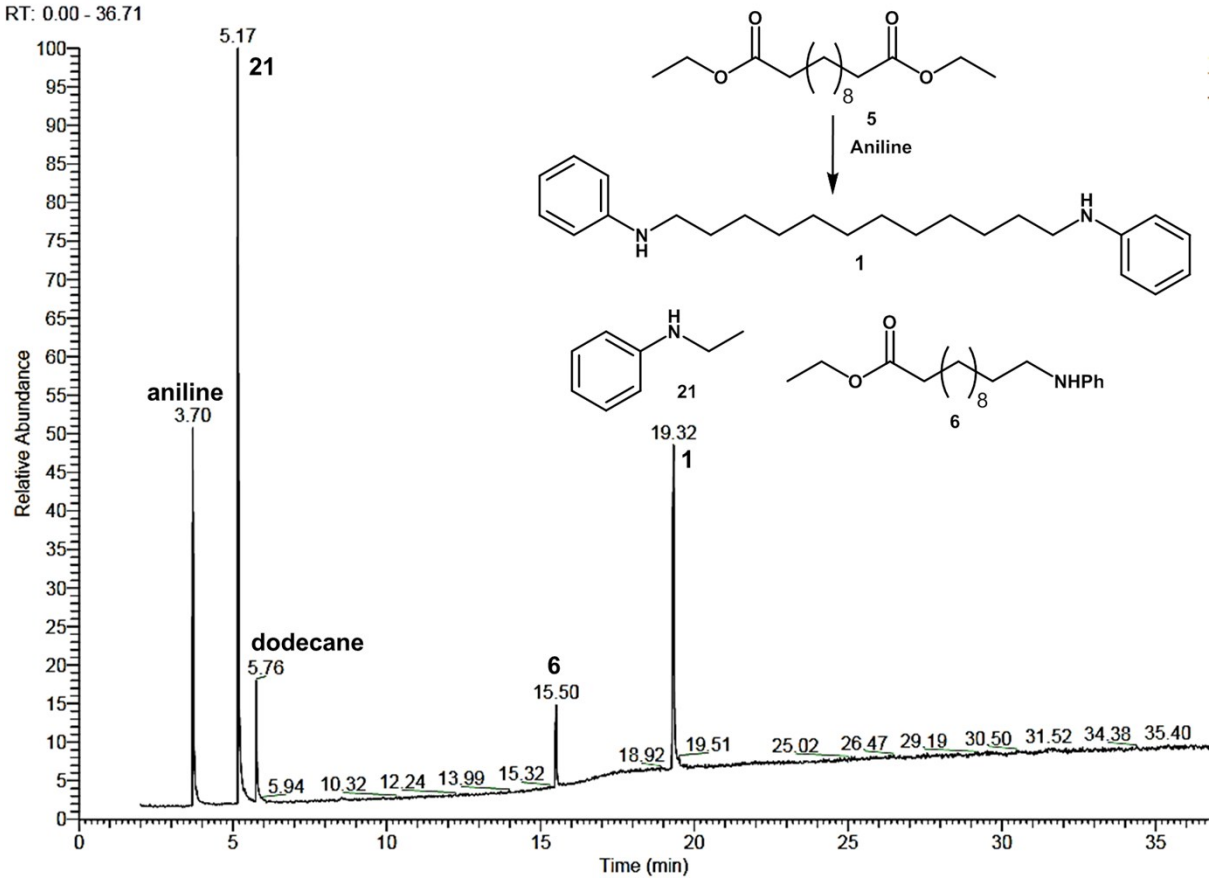
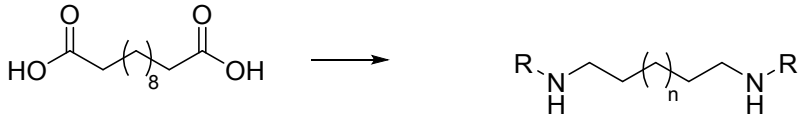
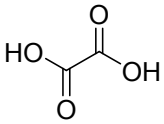
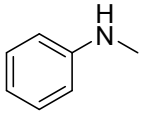
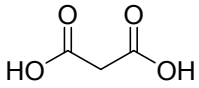
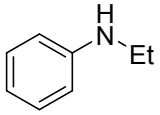
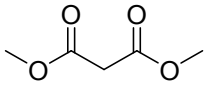
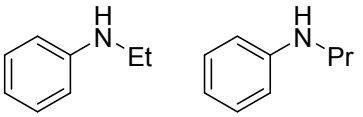


Figure 66. GC spectrum of reaction mixture using diethyl 1,12-dodecanedioate and aniline. Dodecane was used as the internal standard for quantitative GC analysis.

5. Reaction with different substrates and amines.

Table S1. Reaction with different substrates and amines.[a]

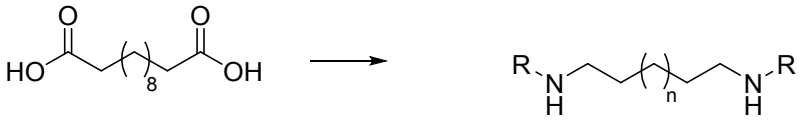


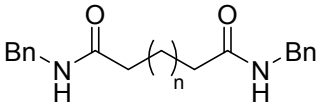
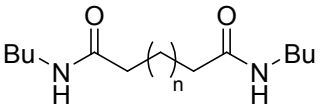
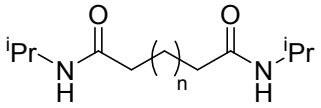
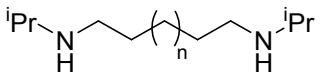
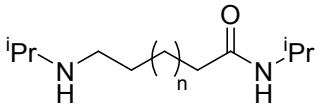
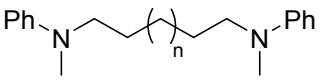
Entry	Substrate	Amine	Conv. (%)	Product
1		aniline	100	 23%
2		aniline	100	 70%
3[b]		aniline	100	 36 % 63%

[a] $[Ru(acac)_3]$ (2 mol%), triphos (4 mol %), MSA (2 mol %), dioxane (15 mL), substrate (2.5 mmol), aniline (3 equiv.), H_2 (10 bar), 220 °C, 42 h; [b]aniline (5 equiv.)

Reaction of oxalic acid and malonic acid were carried out with aniline, *N*-methyl aniline and *N*-ethyl aniline were observed, as both decompose at high temperature to give carbon dioxide and formic acid and acetic acid respectively, which were subsequently converted to *N*-methyl aniline and *N*-ethyl aniline in 23 % and 70 % yield. Reaction of dimethyl malonate gave a mixture of *N*-ethyl aniline and *N*-propyl aniline (Table S1, Entry 1-3). *N*-ethyl aniline might come from decomposition of the ester and *N*-propyl aniline may be obtained by hydrogenation of one end to alcohol, dehydration, and hydrogenation to the methyl propionate before being introduced to the aniline.

Table S2. Reaction with different substrates and amines.



Entry	Amine	Conv.	Product
1	Allylamine	100	n.d.
2	benzylamine	100	 42 %
3	Butylamine	100	 58 %
			 28 %
4	Isopropylamine	100	 18 %
			 47 %
5	Benzylamide	n.d	n.d.
7	4-nitrobenzylamine	100	polymer
8	Diphenylamine	100	n.d
9	Dibenzylamine	100	n.d
10	*N*-methyl aniline	100	 Yield not determined
11	diisopropylamine	100	n.d.

[a] $[Ru(acac)_3]$ (2 mol%), triphos (4 mol %), MSA (2 mol %), 1,4-dioxane (15 mL), substrate (2.5 mmol), amines (3 equiv.), H_2 (10 bar), 220 °C, 42 h;
n.d. Means a complex mixture of products obtained.

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