Synthesis of Three Ring Type Compounds with Fluorine and NCS Groups as Candidates for VA mode Liquid Crystal Display

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Abstract

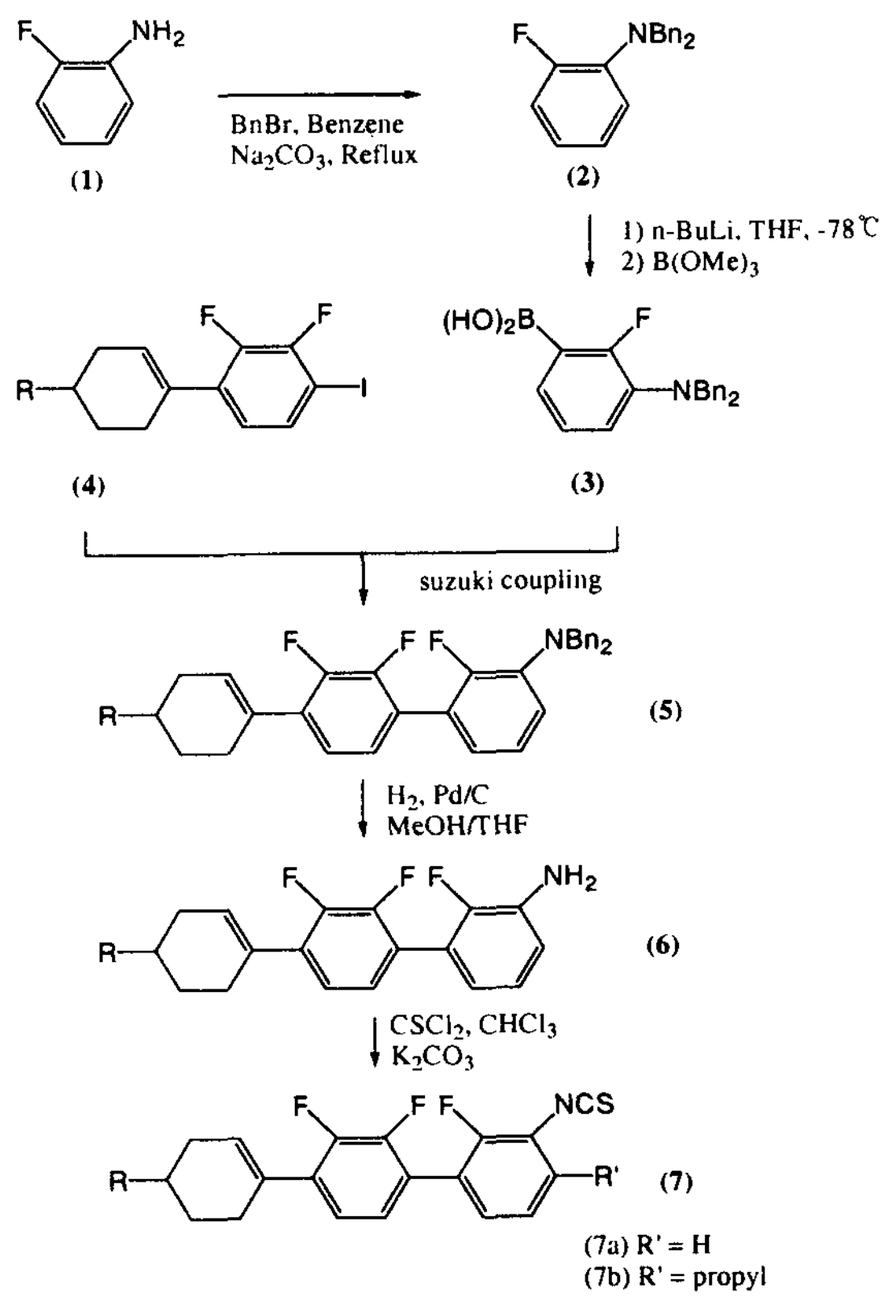
Three ring type liquid crystalline compounds having 4-alklycyclohexyl group, 1,2-difluorobenzene and phenylisothiocyanate moieties as main skeleton were designed to have negative dielectricity. However, the compounds with 2,3,2'-trifluoro-3'-isothiocyanated biphenylcyclohexane core did not exhibit the nematic liquid crystalline phase because of two conformers by interaction of isothiocyanate and adjacent fluorine atoms. Also, 4-alkyl-2,2',3'-trifluoro-3-isothiocyanated biphenylcyclohexane core was designed expecting to have uniform conformers of isothiocyanate group. In the course of developing polyimides for VA mode LCD, we synthesized alkyl-3,5-diaminobenzene efficiently with various length of alkyl chains from commercially available di-t-butyl malonate and 3,5-dinitrobenzoyl chloride as starting material.

1. Introduction

In the course of developing new liquid crystal compounds for high speed LCD, we decided to synthesize the compounds with negative dielectric constant. Although, the switching speed of LCDs is a relatively complicated function of driving voltages, optical anisotropy, elastic constants, dielectric anisotropies and rotational viscosity,[1,2] we focused on the negative dielectric anisotropy and low rotational viscosity. In order to increase anisotropy, 2,3-difluorophenyl moieties was introduced as core unit and -NCS group together with adjacent fluorine atom was introduced to increase optical retardation and stability. Also, terminal propyl group was introduced to increase nematic range and to maintain uniform conformer of -NCS group. Relatively, 1-alkyl-3,5-diaminobenzene derivatives were synthesized as starting materials of polyimides for vertical alignment of liquid crystal molecules.[3] In this paper, we focused on the synthetic procedure for the preparation of the designed compounds.

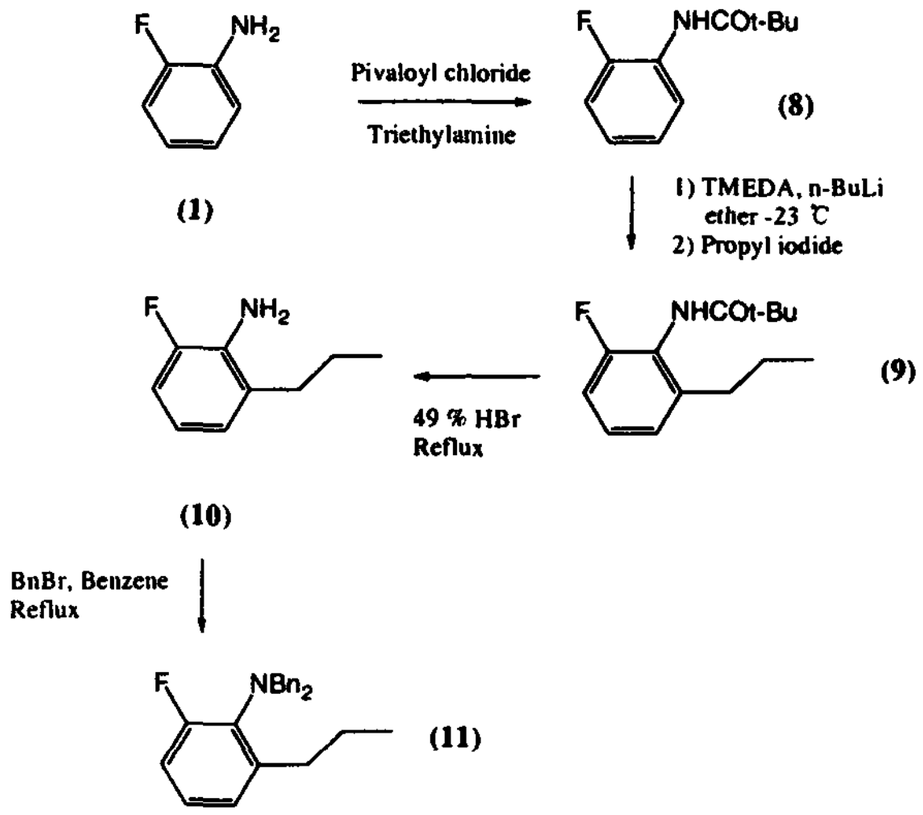
2. Experiment

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are obtained using Bruker Avanced 400 spectrometer and are reported in ppm from TMS on the δ scale. The main skeleton such as 2,3,2'-trifluoro-3'-isothiocyanated biphenylcyclohexane were synthesized by Suzuki coupling[4] from arylboronic acid (**3**) and aryl halide (**4**). The synthetic procedure for the preparation of 2,3,2'-trifluro-3'-isothiocyanato-4-(4-pentyl-cyclohexyl)biphenyl from commercially available 2-fluoroaniline, 1,2-difluoro-benzene and 4-pentyl-cyclohexanone is described in **Scheme 1.**



Scheme 1. Preparation of 2,3,2'-trifluro-3'-isothiocyanato-4-(4-pentylcyclohexyl)-biphenyl

For preparation of compounds (**7b**) with alkyl group on the phenyl ring, dibenzyl-(2-fluoro-6-propyl)amine (**11**) was introduced from the *ortho*-direct lithiation[5] of pivaloylamide (**8**). The synthetic procedure for the preparation of dibenzyl-(2-fluoro-6-propyl)amine (**11**) is described as follows.(**Scheme 2**) Preparation of 2,3,2'-trifluro-3'-isothiocyanato-4-(4-pentyl-cyclohexyl)-4-propylbiphenyl (**7b**) was similar to procedures for the compound (**7a**). Also, synthetic procedures of 1-alkyl-3,5-diaminobenzenes as key starting materials for polyimides were described bellow.(**Scheme 3**)

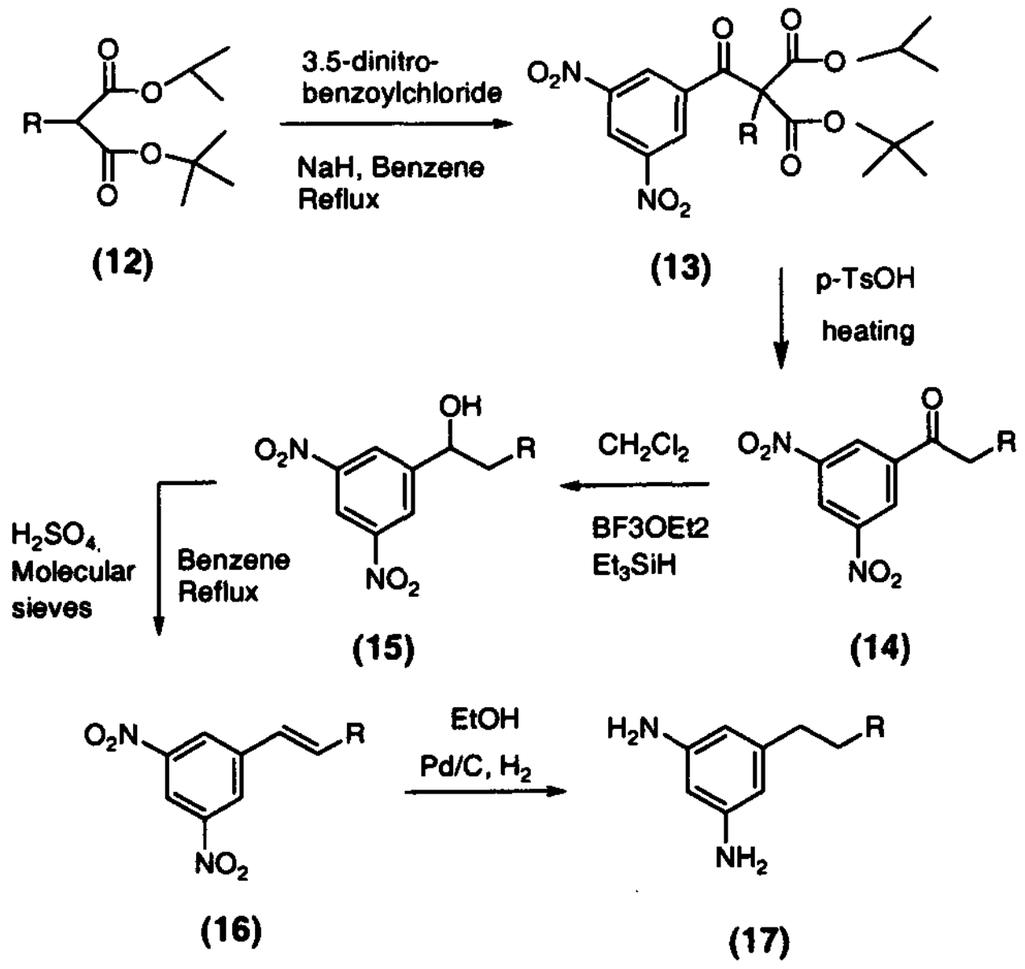


Scheme 2. The synthesis of dibenzyl-2-fluoro-6-propylaniline

Experimental procedures for the new key compounds are as follows:

Dibenzyl[2,2',3'-trifluoro-4'-(4-pentyl-cyclohex-1-enyl)biphenyl-3-yl]amine (5).
A solution of compound (**4**) (1.5 g, 5.04 mmol) in ethanol (10 mL) was added to a stirred mixture of compound 3 (2.08 g, 5 mmol) and $(PPh_3)_4Pd(0)$ (0.03 g, 0.15 mmol) in tolune (5 mL) and aqueous Na_2CO_3 (2 M, 2 mL) at room temperature under argon. The mixture was heated to reflux for 23 h. The reaction mixture was extracted with ethyl acetate, the organic layer was dried over anhydrous magnesium sulfate, evaporated and chromatographed on silica gel to give (**5**) (2.2 g, 88 %).

2,2',3'-Trifluoro-4'-(4-pentylcyclohex-1-enyl)-biphenyl-3-ylamine (6). The reaction mixture of



$R = C_nH_{2n+1}$ n = 10, 12, 14, 16

Scheme 3. Synthesis of 1-alkyl-3,5-diamino-benzene

compound (**5**) (8.8 g, 15.8 mmol) and palladium on activated carbon (0.1 g) in methanol / THF (20 mL / 10 mL) was maintained for 6 h under H_2 stream of 60 psi. The Pd/C was filtered off and the residue was evaporated *in vacuo* to give (**6**) (5.3 g, 89 %). The pure white solid *trans*-(**6**) (2 g, 5.32 mmol) was obtained by the recrystallization.

2,3,2'-Trifluoro-3'-isothiocyanato-4-(4-pentyl-cyclohexyl)biphenyl (7a). To a solution of *trans*-(**6**) (0.6 g, 1.6 mmol) in chloroform (10 mL) cooled at 0 ℃ were added a solution of K_2CO_3 (0.33 g, 2.4 mmol) in water (4 mL) and tetrabutylammonium bromide (0.05 mg). The mixture was treated dropwise with thiophosgene (0.15 mL, 1.92 mmol). The reaction mixture was allowed to stir at room temperature for 4 h. The mixture was extracted with methylene chloride, the organic layer was dried over anhydrous magnesium sulfate, evaporated and chromatographed on silica gel to give (**7a**) (0.55 g, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ0.89(3H, t), 1.10(2H, m), 1.28(9H, m), 1.53(3H, m), 1.90(4H, m), 2.88(1H, td), 7.04(2H, m), 7.20(4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ14.34, 22.94, 26.84, 27.58, 27.76, 30.34, 31.54, 32.41, 32.94, 33.51, 37.48, 118.78, 121.84, 122.21, 123.08, 124.58, 125.32, 126.27, 130.01, 137.52, 146.86, 149.35, 157.32.

***N*-(2-fluoro-6-propylphenyl)-2,2-dimethyl-propionamide (9).** A solution of compound **(8)** (9.73 g, 50 mmol) and TMEDA (5.7 mL, 37.8 mmol) in diethyl ether (100 mL) was cooled at –23 ℃, was treated dropwise with 2.5 M *n*-BuLi (50 mL, 125 mmol) and was allowed to stir for 65 min. To the reaction mixture, propyl iodide (9 mL, 96.4 mmol) in diethyl ether (9 mL) was added and allowed to stir at room temperature for 1 h. The reaction mixture was extracted with ethyl acetate, the organic layer was dried over anhydrous magnesium sulfate, evaporated and chromatographed on silica gel to give **(9)** (7.4 g, 62 %).

Dibenzyl-(2-fluoro-6-propylphenyl)-amine (11). A solution of compound **(9)** (3.3 g, 14 mmol) in 48 % HBr (11 mL) was heated to reflux for 4 h and was allowed to stir at room temperature for 12 h. The reaction mixture was treated with 10 M NaOH solution (10 mL) and extracted with hexane, the organic layer was dried over anhydrous magnesium sulfate, evaporated and chromatographed on silica gel to give **(10)** (1.6 g, 80 %). To a solution of compound **(10)** in benzene (20 mL) was added a solution of Na_2CO_3 (4.4 g, 44 mmol) in water (15 mL), catalytic amount of tetrabutylammonium hydroxide and benzyl bromide (3.1 mL, 25 mmol). The reaction mixture was heated to reflux for 48 h, was reduced fractional distillation to give **(11)** (2.3 g, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ0.90 (3H, t), 1.38 (2H, m), 2.58(2H, t), 4.15 (4H, s), 6.82 (2H, m), 6.96 (1H, m), 7.20 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ14.48, 24.02, 33.68, 58.12, 113. 75, 124.76, 126.55, 127.15, 128.24, 129.34, 136.18, 139.36, 144.67, 163.06.

2,2',3'-Trifluoro-3'-isothiocyanato-4-(4-pentyl-cyclohexyl)-4'-propylbiphenyl. (7 b) Preparation of compound **(7b)** was similar to procedures of the compound **(7a)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78(3H, t), 0.89(3H, t), 1.00(2H, m), 1.18(9H, m), 1.25(2H, m), 1.55(2H, m), 1.78(4H, d), 2.58(2H, t), 2.75(1H, td), 6.53(1H, t), 6.75(1H, m), 6,91(2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ13.91, 14.28, 22.92, 23.47, 26.84, 32.42, 32.95, 33.55, 34.31, 37.45, 37.52, 37.61, 119.35, 120.02, 121.34, 122.06, 124.95, 125.29, 128.99, 137.06, 140.72, 141.63, 149.84, 150.01, 155.82.

3,5-dinitro-1-tetradecyloylbenzene (14) To a mixture of alkylmalonate **12** (1.73 g, 5.0 mmol) and sodium hydride (0.39 g, 7.5 mmol), which was refluxed for 2 hr in the mixture of benzene (20 mL) and THF (10 mL), was added 3,5-dinitrobenzoyl chloride (1.15 g, 5.0 mmol) at once. The mixture was refluxed for 1 min, cooled to rt, filtered over Celite and washed with hexane. The organic layer was dried over anhydrous magnesium sulfate, evaporated *in vacuo* to give almost pure compound 13. To the mixture of **13** (0.65 g, 1.12 mmol) and catalytic amount of *p*-toluenesulfonic acid was added 3 drops of trifluoroacetic acid, stirred in reduced pressure for 1hr. Decarboxylation was carried out simply by further heating with a heat gun under reduced pressure and chromatographed on silica gel to give exclusively the product **14**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.3 (dd, 1H) 9.2 (q, 2H), 2.9 (t, 2H), 1.9 (m, 2H), 1.2~1.4 (m, 20H), 0.8~0.9 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.01, 149.08, 139.87, 127.90, 122.26, 39.26, 32.12, 29.88, 29.85, 29.80, 29.66, 29.60, 29.56, 29.29, 23.92, 22.89, 14.33.

1,3-diamino-5-tetradecylbenzene (17). To the solution **14** (0.38 g, 1.0 mmol) in dichloromethane (5 mL) was added triethylsilane (1 mL, 6.3 mmol) and boron trifluoride etherate (2 mL, 15.8 mmol), stirred at room temperature for 3hr and then extracted with ether. The organic layer was dried over anhydrous magnesium sulfate, evaporated *in vacuo* and chromatographed on silica gel to give the product **15** (0.32 g, 84 %). And the solution of **15** (0.76 g, 2.0 mmol) with catalytic amount of sulfuric acid and molecular sieves in benzene was refluxed for 4 hr and then filtered over Celite, extracted with ether, washed with 5% sodium bicarbonate and water. The organic layer was dried over anhydrous magnesium sulfate, evaporated *in vacuo* and chromatographed on silica gel to give the product **16** (0.60 g, 86 %). The solution of **16** (0.36 g, 1.0 mmol) in ethanol was reduced with catalytic amount of Pd/C(10%) under H_2 stream of 40 psi.. The Pd/C was filtered off and the solvent was evaporated to give pure **17**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.0 (s, 2H), 5.9 (s, 1H), 3.5 (s, 4H), 2.4 (m, 2H), 1.5 (m, 2H), 1.3 (m, 22H), 0.9 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.51, 145.60, 106.51, 99.80, 36.21, 32.11, 31.41, 29.88, 29.84, 29.80, 29.75, 29.64, 29.54, 22.87, 14.30.

3. Result and Discussion

The key reactions in the synthetic procedure are *ortho*-directed lithiation[6] of *N,N*-dibenzyl-(2-fluorophenyl)amine and 1,2-difluorobenzene. It has been reported that organolithium reagent was formed to *ortho*-position of substituents with lone pair electron in aromatic ring. It is important to keep the temperature low during the *o*-directed lithiation with *n*-BuLi and TMEDA. Also, introduction of alkyl group in phenyl ring was prepared *via o*-directed lithiation of pivaloylamide from 2-fluoroaniline. Formation of the main skeleton was carried out using well-known Suzuki coupling reaction. Synthesized liquid crystal compounds with 2,3,2'-trifluoro-3'-isothiocyanato-4-(4-pentylcyclohexyl)biphenyl did

not exhibit the nematic liquid crystalline phase, probably because two possible conformers from interaction[7] of -NCS and adjacent fluorine atoms reduce vertical dipole moment at molecular long axis. If other substituents exist next to the –NCS in terminal group, interaction with -NCS and adjacent fluorine atom will diminish to stand vertically at molecular long axis. Accordingly, we synthesized 2,2',3'-trifluoro-3'-isothiocyanato-4-(4-pentyl-cyclohexyl)-4'-propylbiphenyl, however, unexpectedly, these don't showed nematic phase. We are now investigating the physical properties of the synthesized compounds and possibilities as mixed LC materials with other LC materials. Also, we have developed a facile and efficient synthetic method of 1-alkyl-3,5-diaminobenzenes with various length of alkyl chains as key starting materials for polyimides. To introduce various length of alkyl chain, di-*t*-butyl malonate and n-alkylbromides were used.[8] The use of di-*t*-butyl *n*-alkylmalonate, which is one of the key points in our synthetic method, offered efficient removal of the carbobutoxy moieties of the ketones **13** with the aid of catalytic amount of *p*-toluenesulfonic acid to give almost quantitatively 1-acylated 3,5-dinitrobenzenes **14** in one pot reaction. Although general reagents for reduction nitrophenone compounds reported in literatures are borohydrides such as $NaBH_4$ and KBH_4,[9] sodium borohydride reduction of 1-acylated 3,5-dinitrobenzenes **14** resulted in poor yield of benzyl alcohol **15**. We found that triethylsilane with boron trifluoride etherate was very efficient to prepare benzylic alcohol cleanly without spoilage of dinitro group in dinitrobenzenes.[10] We are now studying the utilization of 1-alkyl-3,5-diaminobenzenes to polyimides using dianhydrides such as *cis*-1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) and 1,2,4,5-benzenetetracarboxylic dianhydrides (PMDA) for VA mode LCD.

4. Acknowledgement

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[8] **Di-*t*-butyl alkylmalonate 12**:To solution di-*t*-butyl malonate (4.36 g, 20 mmol) in anhydrous THF (20 mL) was added sodium hydride (60% in mineral oil, 0.60 g, 25 mmol) at –5 °C and heated occasionally with a heat gun to complete the deprotonation. To this mixture was added bromododecane (5.50 g, 22 mmol) at 0 °C, refluxed for 2 hr, cooled to rt, quenched with saturated ammonium chloride and extracted with hexane. The organic layer was dried over anhydrous magnesium sulfate, evaporated and chromatographed on silica gel to give product **12** (5.83g, 83.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.1 (t, 1H), 1.7 (m, 2H), 1.5 (m, 18H), 1.3 (m, 20H), 0.8-1.0 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.21, 81.26, 54.20, 32.11, 29.85, 29.82, 29.80, 29.72, 29.54, 29.46, 28.78, 28.12, 27.39, 22.86, 14.28.

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