



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

SYNTHESIS AND PHASE BEHAVIOR OF LIQUID CRYSTALLINE DIPHENYLACETYLENE DERIVATIVES POSSESSING HIGH CLEARING TEMPERATURES

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Version of record first published: 15 Jul 2010

To cite this article: Douglas D. Young, Eric Scharrer & Mark V. Yoa (2004): SYNTHESIS AND PHASE BEHAVIOR OF LIQUID CRYSTALLINE DIPHENYLACETYLENE DERIVATIVES POSSESSING HIGH CLEARING TEMPERATURES, *Molecular Crystals and Liquid Crystals*, 408:1, 21-31

To link to this article: <http://dx.doi.org/10.1080/15421400490425784>

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SYNTHESIS AND PHASE BEHAVIOR OF LIQUID CRYSTALLINE DIPHENYLACETYLENE DERIVATIVES POSSESSING HIGH CLEARING TEMPERATURES

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A series of diphenylacetylene derivatives were synthesized to serve as ligands for metal alkyne complexes. The target compounds, alkyl 4'-(4-phenylethynylbenzoyloxy)-biphenyl-4-carboxylates, were prepared using a three-step synthetic procedure. Both the diphenylacetylene derivatives as well as their immediate precursors, alkyl 4'-(4-iodobenzoyloxy)-biphenyl-4-carboxylates, exhibit liquid crystalline behavior. The diphenylacetylene derivatives possess large liquid crystalline phase ranges and high clearing temperatures. Synthetic details and the phase behavior of these compounds are discussed.

Keywords: crystalline polymorphism; diphenylacetylene; high melting and clearing temperatures; smectic A and nematic phases

INTRODUCTION

The incorporation of diphenylacetylene or a related moiety into liquid crystalline compounds allows for a number of favorable characteristics. For example, such compounds have been investigated for their enhanced optical anisotropy [1], nonlinear optical properties [2], and ferroelectric [3] or antiferroelectric behavior [4]. The diphenylacetylene moiety also

We wish to thank the Donors of the American Chemical Society Petroleum Research Fund and the National Science Foundation (CCLI-A&I program) for partial support of this research. Additional support, in the form of startup funds and summer student stipends, was provided by the University of Puget Sound and Franklin & Marshall College.

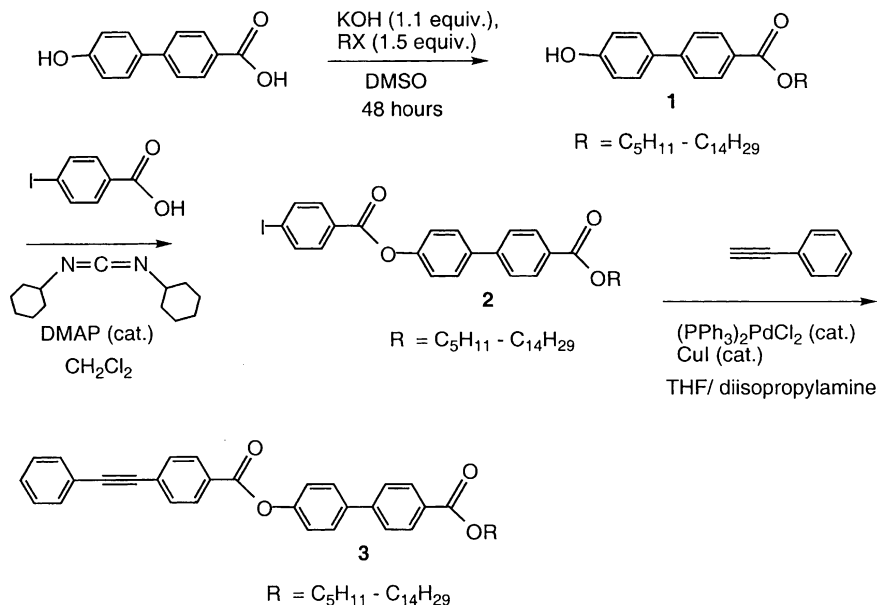
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provides several sites for metal coordination. It is this feature of these molecules that interests us because we wish to prepare new metal-containing liquid crystals. There has been a great deal of interest in metallomesogens over the past fifteen years due to their potential to exhibit unique physical properties [5]. Most of the metallomesogens reported possess a metal center that adopts a square planar or linear geometry. There are far fewer examples of metallomesogens in which the geometry about the metal is octahedral. The incorporation of an octahedral metal center significantly broadens the molecule. In many [6a–6e], but not all [6f], cases this lowers the phase transition temperatures of the complex relative to the organic precursor; liquid crystallinity is sometimes destroyed entirely. Nevertheless, we are greatly interested in preparing metallomesogens possessing an octahedral metal center because it may allow for the possibility of obtaining liquid crystallinity at or near room temperature. In particular, we wish to study the phase behavior of $\text{Co}_2(\text{CO})_6$ complexes of diphenylacetylene derivatives because alkyne complexes of this cobalt fragment are relatively stable [7]. However, the $\text{Co}_2(\text{CO})_6$ moiety will introduce a large molecular kink, which may inhibit mesomorphism. Bruce and Deschenaux have carried out research on some complexes in which the octahedral metal center creates a large disruption to packing [6a–6e]. In these cases, they demonstrated that if one starts with a sufficiently anisotropic organic derivative (that possesses a high clearing point), the resulting octahedral metal complex will also maintain liquid crystallinity. Our initial goal, therefore, was to prepare a homologous series of mesomorphic diphenylacetylene derivatives that possessed high clearing temperatures, and we report here the synthesis and phase behavior of these compounds.

RESULTS AND DISCUSSION

Synthesis

The synthesis of a homologous series of the target compounds was achieved using a three-step procedure (Scheme 1). Compound **1**, alkyl 4'-hydroxybiphenyl-4-carboxylate, was prepared by selective alkylation of 4'-hydroxybiphenyl-4-carboxylic acid in the presence of 1 equivalent of potassium hydroxide and 1.5 equivalents of the appropriate alkyl halide. Average yields for this step were 56% after purification. An alternate procedure to prepare these derivatives (via Fischer esterification) has been previously reported [8]. While the reported yields were comparable to ours, our method represents an improvement because it does not require a vacuum distillation as part of the purification procedure. Upon treatment of compound **1** with 4-iodobenzoic acid, dicyclohexyl carbodiimide (DCC)



SCHEME 1 Synthesis of diphenylacetylene derivatives.

and catalytic dimethylaminopyridine (DMAP), alkyl 4'-(4-iodobenzoyloxy)-biphenyl-4-carboxylate, **2**, was obtained with an average yield of 52%. This was then reacted with phenylacetylene in the presence of catalytic $(\text{PPh}_3)_2\text{PdCl}_2$ and CuI to yield the diphenylacetylene target compound (alkyl 4'-(4-phenylethynylbenzoyloxy)-biphenyl-4-carboxylate), **3**, in an average yield of 54%.

Phase Behavior

Both the diphenylacetylene compounds, **3**, as well as the intermediate iodo derivatives, **2**, exhibit liquid crystallinity. The identities of the liquid crystalline phases were established by examining their optical textures using polarizing microscopy. As can be seen in Table I, at least two crystalline phases are observed for all of the iodo derivatives, **2**. However, the even chain derivatives, as well as the derivative in which $\text{R} = \text{C}_{13}\text{H}_{27}$, possess a third crystalline phase; in these cases, the first crystal-to-crystal transition occurs at relatively low temperatures ($\leq 90^\circ\text{C}$) and generally has a low transition enthalpy. Upon further heating, all of these derivatives exhibit one liquid crystal phase, a smectic A phase, before clearing to the isotropic liquid. The range of the Smectic A phase varies from 45°C when $\text{R} = \text{C}_5\text{H}_{11}$,

TABLE I Phase Transition Temperatures and Enthalpies for alkyl 4'-(4-iodobenzoyloxy)-biphenyl-4-carboxylate Derivatives, 2

Compound	Transition Temperature to Indicated Phase [#]					
	Crystal 2 phase (Cr ₂)		Crystal 3 phase (Cr ₃)		Smectic A (SnA)	
	T [°C]	(enthalpy [kJ/mol])	T [°C]	(enthalpy [kJ/mol])	T [°C]	(enthalpy [kJ/mol])
2a, R = C ₅ H ₁₁	—		60.1 (3.19)		141.6 (26.46)	186.9 (5.58)
2b, R = C ₆ H ₁₃	90.3		96.7 (8.78) [†]		142.1 (29.17)	187.9 (5.94)
2c, R = C ₇ H ₁₅	—		80.1 (9.03)		140.4 (31.44)	185.9 (6.63)
2d, R = C ₈ H ₁₇	70.4 (4.55)		88.0 (4.94)		140.3 (32.88)	183.6 (6.60)
2e, R = C ₉ H ₁₉	—		79.9 (11.29)		139.3 (34.48)	182.0 (6.89)
2f, R = C ₁₀ H ₂₁	68.4 (0.81)		94.3 (12.45)		139.0 (36.32)	180.1 (7.06)
2g, R = C ₁₁ H ₂₃	—		92.1 (14.31)		137.7 (38.30)	177.3 (7.32)
2h, R = C ₁₂ H ₂₅	47.4 (1.38)		100.4 (11.77)		137.8 (40.39)	175.6 (7.30)
2i, R = C ₁₃ H ₂₇	89.9		97.9 (15.17) [†]		136.1 (37.65)	171.8 (7.29)
2j, R = C ₁₄ H ₂₉	65.3 (2.58)		103.7 (10.64)		137.6 (44.92)	172.1 (7.44)

[#]All temperatures and enthalpies are based on the second DSC heating run with the exception of those for 2d (first heating run).

[†]Combined enthalpies.

2a, to 36°C when $R = C_{14}H_{29}$, **2j**. The observation of an exclusively orthogonal smectic phase is expected because these derivatives possess only one alkyl chain [9].

The phase behavior of the iodo derivatives, **2**, can be compared to that of the 4''-iodophenyl-4'-alkoxy-biphenyl-4-carboxylate derivatives, **4**, prepared by Bruce et al [10] (Figure 1). Bruce's compounds possess a reversed ester linkage relative to our derivatives, and they exhibit significantly higher clearing points and larger mesophase ranges. These differences can be ascribed to the higher dipole moment in Bruce's compound; Spartan calculations show that compound **4** has a dipole moment of 4.68 debye, while compound **2c** possesses a dipole moment of 1.41 debye.

Phase transition temperatures and enthalpies for the diphenylacetylene derivatives, **3**, are presented in Table II. The mesophase range for these compounds varies from 84°C to 134°C. Two crystalline phases are observed along with a smectic A phase, and in some cases a nematic phase. As is typically observed in homologous series of liquid crystals, the range of the nematic phase and the clearing temperature increase as the length of the alkyl chain is shortened [11]. For example, the derivative in which $R = C_5H_{11}$, **3a**, clears to an isotropic liquid at 278°C, and the nematic phase shows a range of 44°C. The derivative in which $R = C_{12}H_{25}$, **3h**, clears to the isotropic state at 224°C, and the nematic phase range is only 1°C. The derivatives in which $R = C_{13}H_{27}$, **3i**, and $C_{14}H_{29}$, **3j**, do not exhibit a nematic phase and show clearing points of 222°C and 218°C, respectively. These trends are illustrated in Figure 2.

The homologues with higher clearing temperatures decompose slightly upon entering the isotropic state. Interestingly, this affects the texture of the smectic phase upon cooling. If the derivatives are heated to the isotropic liquid and then cooled, the focal conic texture appears broken and ill defined. However, if the compounds are heated only to the nematic phase and then cooled, the focal conic texture is much better defined and is clearly representative of the smectic A phase.

Given the high clearing points and large liquid crystal phase ranges of the diphenylacetylene derivatives, it is possible that the $Co_2(CO)_6$

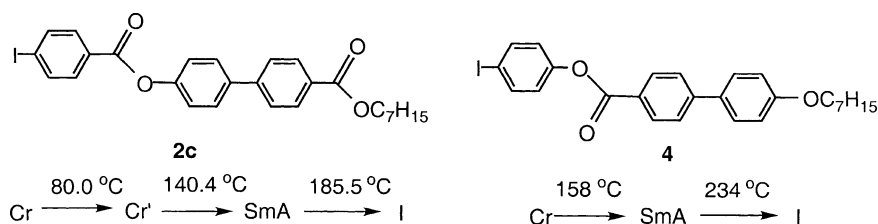


FIGURE 1 Comparison of phase behavior for derivatives with a reversed linkage.

TABLE II Phase Transition Temperatures and Enthalpies For Diphenylacetylene Derivatives, alkyl 4'-(4-phenylethynylbenzoyloxy)-biphenyl-4-carboxylate 5, 3

Compound	Transition Temperature to Indicated Phase [#]					
	Crystal 2 (Cr ₂)		Smectic A (SmA)		Nematic (N)	
	T [°C]	(enthalpy [kJ/mol])	T [°C]	(enthalpy [kJ/mol])	T [°C]	(enthalpy [kJ/mol])
3a, R = C ₆ H ₁₁	133.0	(3.91)	143.6	(27.10)	234.2	(1.70)
3b, R = C ₆ H ₁₃	84.4	(7.98)	145.7	(21.63)	233.8	(1.87)
3c, R = C ₇ H ₁₅	103.4	(10.64)	141.9	(24.81)	232.2	(2.08)
3d, R = C ₈ H ₁₇	94.4	(16.12)	141.1	(22.86)	231.7	(2.41)
3e, R = C ₉ H ₁₉	95.6	(13.72)	138.7	(24.90)	229.5	(2.22)
3f, R = C ₁₀ H ₂₁	100.2	(20.93)	138.5	(24.65)	227.9	(1.75)
3g, R = C ₁₁ H ₂₃	101.4	(22.19)	137.3	(25.03)	225.8	(1.97)
3h, R = C ₁₂ H ₂₅	109.4	(27.95)	137.2	(23.90)	223.0 [†]	224.2 [†] (4.62) [†]
3i, R = C ₁₃ H ₂₇	108.1	(26.15)	136.2	(22.73)	—	222.3 (4.58)
3j, R = C ₁₄ H ₂₉	110.0	(32.18)	134.5	(23.61)	—	218.0 (5.34)

[#]All temperatures and enthalpies are based on the second DSC heating run.

[†]Combined enthalpies.

[‡]Microscopy temperatures.

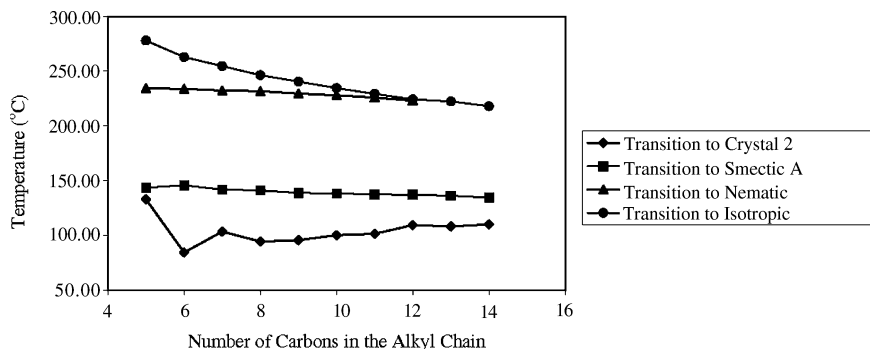


FIGURE 2 Phase transition temperatures of diphenylacetylene derivatives, 3.

complexes of these ligands may exhibit liquid crystallinity. We are currently in the process of preparing such complexes and examining their phase behavior.

EXPERIMENTAL

General

NMR spectra were obtained using a Varian Gemini 300 MHz FT NMR spectrometer and analyzed using a Sun Microsystems Workstation. Thermal analysis was conducted with a TA Instruments DSC 2920 and a Nikon Labophot-2-Pol microscope equipped with a Mettler Toledo Hot Stage FP82HT and FP 90 Central Processor. Unless otherwise noted, transition temperatures were determined by DSC using a heating rate of 10°C/min. Spartan '02 Version 1.0 was used to calculate dipole moments. Davisil Silica Gel, 100–200 mesh, 150 Å and Aluminum Oxide-Activated (Brockman I) Neutral, 150 mesh were used for column chromatography. Unless otherwise noted, reactions were carried out under standard atmosphere and at room temperature. Elemental analysis was conducted by Quantitative Technologies Inc. in Whitehouse, New Jersey. Dry THF was obtained from Aldrich. Dichloromethane was dried by stirring over 4 Å molecular sieves for 24 h. 4'-hydroxy-biphenyl-4-carboxylic acid was purchased from TCI (Portland, Oregon). All other chemicals were purchased from Aldrich.

Synthesis of pentyl-4'-hydroxybiphenyl-4-carboxylate, (1a)

(The synthesis (via a different method) and characterization of these derivatives has been reported elsewhere) [8].

A 500 mL round-bottom flask was charged with 4'-hydroxybiphenyl-4-carboxylic acid (2.02 g, 9.43 mmol), DMSO (30 mL) and pulverized KOH (0.58 g, 10.37 mmol). After stirring this mixture for 20 min, bromopentane (2.20 g, 14.5 mmol) was added. The reaction was stirred for 48 h and then quenched by the addition of 30 mL of water. Ether (40 mL) was added to the reaction mixture, and the organic layer was washed three times with water. The aqueous layer was back-extracted once with ether, and the organic layers were combined, dried over MgSO_4 , filtered, and solvent was removed by rotary evaporation. The solid product was dissolved in hexane and loaded onto a short column of activated alumina. Hexane (100 mL) was rinsed through the column to remove residual alkyl halide. The eluent was switched to ether, and this solution was collected and concentrated by rotary evaporation. The crude product was recrystallized from 3:2 $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to yield a white powder, 1.62 g (5.70 mmol, 60.5% yield). ^1H NMR (300 MHz CDCl_3) δ 0.95 ppm (t, 3H, $-\text{CH}_3$, $J = 7$ Hz), 1.42 (m, 4H, $-\text{C}_2\text{H}_4$), 1.78 (p, 2H, $-\text{OCH}_2\text{CH}_2$, $J = 6.9$ Hz), 4.34 (t, 2H, $-\text{OCH}_2$, $J = 6.6$ Hz), 5.16 (s, 1H, $-\text{OH}$), 6.94 (d, 2H, aromatic, $J = 8.8$ Hz), 7.54 (d, 2H, aromatic, $J = 8.8$ Hz), 7.62 (d, 2H, aromatic, $J = 8.5$ Hz), 8.08 (d, 2H, aromatic, $J = 8.5$ Hz). ^{13}C NMR (75.5 MHz CDCl_3) δ 13.99 ppm, 22.36, 28.20, 28.43, 65.27 (aliphatic); 115.87, 126.44, 128.45, 128.57, 130.07, 132.47, 145.21, 156.09 (aromatic); 167.00 ($\text{C}=\text{O}$).

All other derivatives were prepared in a similar manner. Yields are shown in Table III.

Synthesis of pentyl 4'-(4-iodobenzoyloxy)-biphenyl-4-carboxylate, (2a)

A 250 mL flask equipped with condenser was charged with compound 1a (1.00 g, 3.53 mmol), 4-iodobenzoic acid (0.88 g, 3.53 mmol), 4-(dimethylamino)-pyridine (DMAP) (0.05 g, 0.36 mmol) and 150 mL dry CH_2Cl_2 .

TABLE III Yields for Compound 1

Compound	Percent yield
1a, R = C_5H_{11}	60.5
1b, R = C_6H_{13}	70.5
1c, R = C_7H_{15}	95.3
1d, R = C_8H_{17}	53.9
1e, R = C_9H_{19}	37.4
1f, R = $\text{C}_{10}\text{H}_{21}$	32.6
1g, R = $\text{C}_{11}\text{H}_{23}$	43.5
1h, R = $\text{C}_{12}\text{H}_{25}$	55.7
1i, R = $\text{C}_{13}\text{H}_{27}$	57.8
1j, R = $\text{C}_{14}\text{H}_{29}$	55.8

Dicyclohexylcarbodiimide (DCC) (0.733 g, 5.55 mmol) was added to the reaction mixture, and this was stirred for 24 h. The solution was then refluxed for an additional 4 h. After cooling to room temperature, the solution was gravity filtered to remove dicyclohexylurea, and the solvent was removed by rotary evaporation. The solid was then redissolved in CH_2Cl_2 and washed through a short plug of alumina. Solvent was removed by rotary evaporation to yield a white powder. This was recrystallized with 3:2 $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to give 1.42 g of a white solid (2.75 mmol, 78% yield). ^1H NMR (300 MHz, CDCl_3) δ 0.95 ppm (t, 3H, $-\text{CH}_3$, $J = 7.1$ Hz), 1.42 (m, 4H, $-\text{C}_2\text{H}_4$), 1.80 (p, 2H, $-\text{OCH}_2\text{CH}_2$, $J = 7.1$ Hz), 4.35 (t, 2H, $-\text{OCH}_2$, $J = 6.9$ Hz), 7.31 (d, 2H, aromatic, $J = 8.5$ Hz), 7.66 (d, 2H, aromatic, $J = 8.3$ Hz), 7.68 (d, 2H, aromatic, $J = 8.7$ Hz), 7.89, 7.94 (ABq, 4H, aromatic, $J = 8.9$ Hz), 8.12 (d, 2H, aromatic, $J = 8.5$ Hz). ^{13}C NMR (75.5 MHz, CDCl_3) δ 14.03 ppm, 22.40, 28.23, 28.46, 65.23 (aliphatic); 101.80, 122.13, 127.02, 128.46, 128.86, 129.44, 130.12, 131.57, 138.04 (2 overlapping peaks), 144.55, 150.78 (aromatic); 164.75 ($\text{C}=\text{O}$), 166.54 ($\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{O}_4$: C 58.38; H 4.51. Found: C 58.31; H 4.59.

All other derivatives were prepared in an analogous manner. Yields and results of elemental analysis are provided in Table IV.

Synthesis of pentyl 4'-(4-phenylethynylbenzoyloxy)-biphenyl-4-carboxylate, (3a)

A three-neck round-bottom flask equipped with a condenser and a gas inlet adapter was charged with compound 2a (1.00 g, 1.89 mmol), phenylacetylene (0.19 g, 1.89 mmol), and $(\text{PPh}_3)_2\text{PdCl}_2$ (0.03 g, 0.05 mmol) under a nitrogen atmosphere. Dry THF (40 mL), and diisopropyl amine (1.32 mL, 9.45 mmol) were added via syringe. The solution was stirred and degassed by a nitrogen purge for approximately 15 min. CuI (0.05 g, 0.25 mmol) was

TABLE IV Elemental Analysis and Yields for Compound 2

Compound	C% calc. (found)	H% calc. (found)	Percent yield
2a, R = C_5H_{11}	58.38 (58.31)	4.51 (4.59)	77.9
2b, R = C_6H_{13}	59.10 (58.88)	4.77 (4.57)	60.7
2c, R = C_7H_{15}	59.79 (59.68)	5.02 (4.89)	60.5
2d, R = C_8H_{17}	60.44 (60.49)	5.25 (5.19)	57.5
2e, R = C_9H_{19}	61.06 (60.87)	5.48 (5.45)	73.0
2f, R = $\text{C}_{10}\text{H}_{21}$	61.74 (61.70)	5.70 (5.57)	64.7
2g, R = $\text{C}_{11}\text{H}_{23}$	62.61 (62.25)	5.89 (5.86)	44.2
2h, R = $\text{C}_{12}\text{H}_{25}$	62.74 (62.66)	6.10 (6.07)	45.8
2i, R = $\text{C}_{13}\text{H}_{27}$	63.26 (62.85)	6.27 (6.26)	17.5
2j, R = $\text{C}_{14}\text{H}_{29}$	63.75 (63.78)	6.45 (6.48)	10.7

TABLE V Elemental Analysis and Yields for Compound 3

Compound	C% calc. (found)	H% calc. (found)	Percent yield
3a, R = C ₅ H ₁₁	81.12 (81.11)	5.78 (5.78)	47.6
3b, R = C ₆ H ₁₃	81.25 (80.85)	6.02 (6.01)	35.4
3c, R = C ₇ H ₁₅	81.37 (81.18)	6.24 (6.20)	54.6
3d, R = C ₈ H ₁₇	81.48 (81.26)	6.46 (6.44)	55.5
3e, R = C ₉ H ₁₉	81.59 (81.41)	6.66 (6.60)	65.2
3f, R = C ₁₀ H ₂₁	81.69 (81.55)	6.85 (6.81)	85.9
3g, R = C ₁₁ H ₂₃	81.78 (81.52)	7.04 (7.01)	42.6
3h, R = C ₁₂ H ₂₅	81.88 (81.60)	7.21 (7.15)	45.0
3i, R = C ₁₃ H ₂₇	81.96 (81.56)	7.38 (7.47)	49.5
3j, R = C ₁₄ H ₂₉	82.05 (81.76)	7.54 (7.51)	61.5

then added to the reaction mixture, which caused the solution to immediately darken. The solution was allowed to stir for 48 h under nitrogen. The reaction mixture was rinsed through an activated alumina column with 150 mL THF, and the filtrate was collected and solvent removed by rotary evaporation. The product was extracted three times with CH₂Cl₂. The combined organic layers were washed with dilute HCl, dried over MgSO₄, and solvent was removed in vacuo. The solid product was recrystallized from 1:1 CH₂Cl₂/EtOH. This material was further purified by flash chromatography (eluent: 3:2 CH₂Cl₂/Hexane, R_f = 0.45). A final recrystallization with 1:1 CH₂Cl₂/EtOH was necessary to obtain reproducible phase behavior (0.44 g (0.90 mmol, 47.6% yield). ¹H NMR (300 MHz, CDCl₃) δ 0.87 ppm (t, 3H, -CH₃, J = 7.1 Hz), 1.35 (m, 4H, -C₂H₄), 1.72 (p, 2H, -OCH₂CH₂, J = 7.1 Hz), 4.27 (t, 2H, -OCH₂, J = 6.6 Hz), 7.28 (m, 5H, aromatic), 7.50 (m, 2H, aromatic), 7.61 (m, 6H, aromatic), 8.04 (d, 2H, aromatic, J = 8.2 Hz), 8.13 (d, 2H, aromatic, J = 8.2 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ 14.03 ppm, 22.41, 28.25, 28.50, 65.17 (aliphatic); 88.50 (alkyne), 92.97 (alkyne); 122.09, 122.54, 126.92, 128.34, 128.39, 128.59, 128.83 (2 overlapping peaks), 129.38, 130.06 (2 overlapping peaks), 131.63, 131.71, 137.85, 144.52, 150.86 (aromatic); 164.48 (C=O), 166.38 (C=O). Anal. Calcd. for C₃₃H₂₈O₄: C 81.12; H 5.78. Found: C 81.11; H 5.78.

All other derivatives were prepared in a similar manner. Yields and results of elemental analysis are provided in Table V.

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