Synthesis and Spectroscopic Studies of Various Arylene Ethynylene Fluorophores

Guang Shao, Akihiro Orita,* Hisataka Taniguchi, Kanako Ishimaru, Junzo Otera*

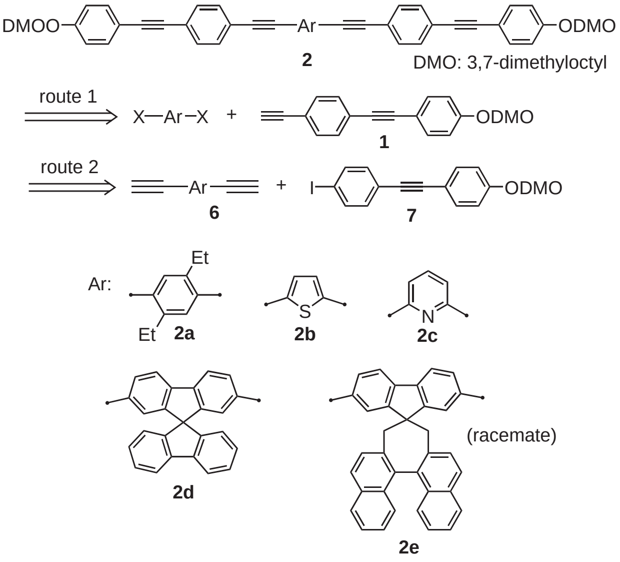
Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-005, Japan
Fax +81(86)2564292; E-mail: orita@high.ous.ac.jp; E-mail: otera@high.ous.ac.jp

Received 26 October 2006

Abstract: A series of arylene cores substituted by phenylene ethynylenes were synthesized by Sonogashira coupling of diethynyl aromatic compounds with an iododiphenylethyne which had been prepared conveniently by making use of a one-shot double-elimination reaction. Photoluminescence properties of the arylene ethynylenes thus prepared were recorded both in solution and in the solid state.

Key words: alkynes, sulfones, sldehydes, eliminations, spectroscopy

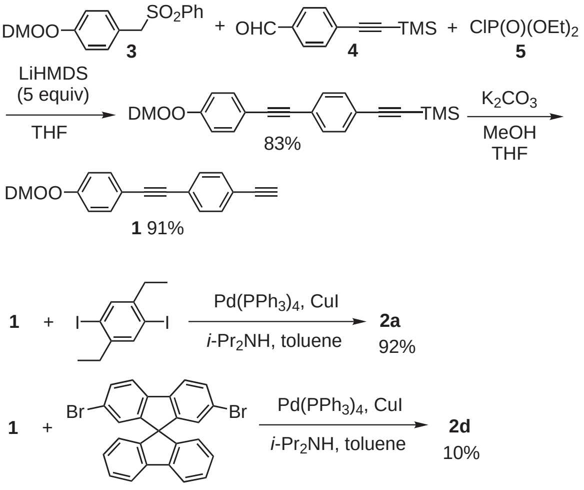
Phenylene ethynylenes have attracted great attention because they have characteristic features emerging from the rigid array and labile π-electron systems,[1] leading to construction of frameworks of nanocars[2] and helical foldamers.[3] We have been interested in such unique features of the phenylene ethynylenes and already succeeded to prepare various structurally intriguing motifs such as magazine-rack molecules,[4] double helical cyclic acetylenes[5] and acetylenic double helicates.[6] Recently, we have presented that the deposited films of 1,2-bis[4-(phenylethynyl)phenyl]ethynes demonstrate photoluminescence peaked at λ = 440–450 nm with high quantum yields (Φ_{PL} = 39–80%).[7] Thus, we were intrigued by synthesizing various arylene cores substituted by a highly soluble and readily accessible phenylene ethynylene fluorophore **1** to modulate spectroscopic properties.[8] We report herein attachment of this fluorophore **1** to heteroaromatic and sterically bulky arylene cores to provide highly fluorescent materials **2** (Scheme 1).



Scheme 1

First, for preparation of **2**, a coupling between arylene dihalide and **1** was attempted (route 1 in Scheme 1). The phenylene ethynylene fluorophore **1** was successfully obtained by a one-shot double-elimination process:[9] a mixture of 4-DMO-O-benzyl sulfone **3** (DMO = 3,7-dimethyloctyl), 4-(trimethylsilylethynyl)benzaldehyde (**4**) and diethylchlorophosphate (**5**) in THF was treated with LiHMDS followed by desilylation with K_2CO_3/MeOH.[10] When Sonogashira coupling of 1,4-diethyl-2,5-diiodobenzene with **1** was carried out, the desired product **2a** was obtained in 92% yield. However, when the same coupling reaction with a sterically bulky fluorene derivative was attempted, the coupling proceeded sluggishly because of poor reactivity of the dibromide to afford only a 10% yield of **2d** after 17 hours (Scheme 2).

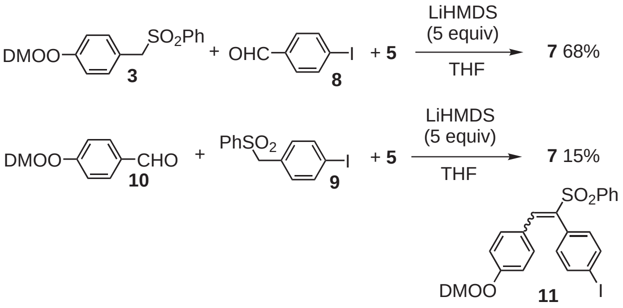
In order to avoid the poor reactivity of arylene dibromide, an alternative coupling between **6** and **7** was our next choice (route 2 in Scheme 1). Previously, we disclosed that double elimination protocol offers a simple route to afford halogen-substituted phenylene ethynylenes.[9] Thus, a one-shot double elimination process was invoked for



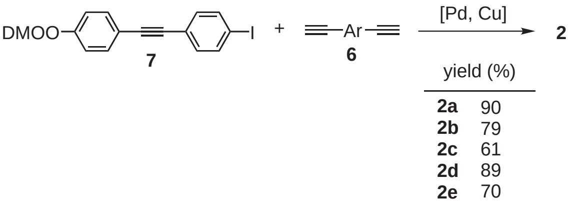
Scheme 2

SYNLETT 2007, No. 2, pp 0231–0234
Advanced online publication: 24.01.2007
DOI: 10.1055/s-2007-968015; Art ID: U12706ST

preparation of **7** (Scheme 3).[10] Reaction of sulfone **3** with iodoaldehyde **8** gave rise to **7** in satisfactory yield. In sharp contrast, an alternative combination using iodosulfone **9** and DMOO-aldehyde **10** resulted in a poor yield of **7**, and a large amount of vinylsulfone intermediate **11** was observed upon monitoring TLC of the crude products after 16 hours. Then, an aryl iodide **7** was subjected to Sonogashira coupling with 1,4-diethyl-2,5-diethynylbenzene (**6a**) to afford the desired product **2a** in 90% yield (Scheme 4).[11] This coupling route was applicable to the synthesis of other derivatives, **2b**–**e**: **2b** (79%), **2c** (61%), **2d** (89%) and **2e** (70%). All derivatives exhibited great solubility in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. The profiles and summary of UV/Vis absorption spectra of **2a**–**e** in $CHCl_3$ were shown in Figure 1 and Table 1. All compounds exhibit large ε_{max} (>10^5), and the λ_{max} varies depending on the arylene cores of **2**. Although diethylbenzene derivative **2a** has λ_{max} at 360 nm, thiophene derivative **2b** and pyridine derivative **2c** demonstrate λ_{max} at 380 and 340 nm, respectively. Sterically bulky derivatives **2d** and **2e** show red-shifted λ_{max} values at 372 and 370 nm, respectively.



Scheme 3



Scheme 4

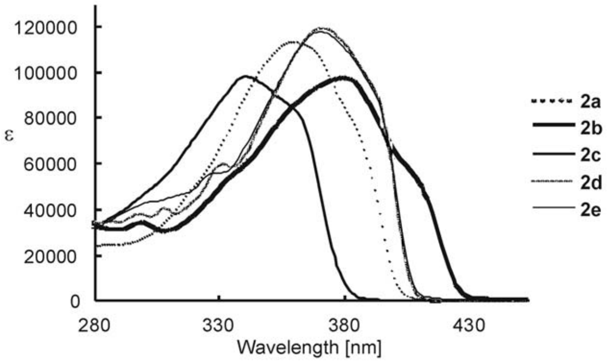


Figure 1 UV/Vis absorption spectra of **2a**–**e** in $CHCl_3$

Table 1 Summary of UV/Vis Absorption of **2a**–**e**

Compd	λ_{max} (nm)[a]	ε_{max} (L cm/mol)[a]
2a	360	$1.1 \cdot 10^5$
2b	380	$9.8 \cdot 10^4$
2c	340	$9.9 \cdot 10^4$
2d	372	$1.2 \cdot 10^5$
2e	370	$1.2 \cdot 10^5$

[a] In $CHCl_3$.

Figure 2 shows photoluminescence spectra of **2** excited at λ_{max} of UV/Vis absorption in CH_2Cl_2 ($9.4 \cdot 10^{-7}$ M), and Table 2 summarizes λ_{max} of **2** in solution and of powder. Absolute quantum yields were measured using an integrating sphere. All derivatives exhibited high quantum yields (Φ_{PL} = 0.54–0.96) in solution. Although **2a**,**b**,**d**,**e** demonstrate vibronic absorption bands, **2c** did a broad spectra. In the PL spectra, the effect of arylene core on λ_{max} is somewhat smaller than in UV/Vis spectra. Although thiophene derivative **2b** demonstrates λ_{max} at 426 nm, other derivatives **2a**,**c**–**e** exhibit the similar λ_{max} of emission (402–407 nm). Notably, these compounds **2** exhibited considerably high quantum efficiencies even in the solid, but λ_{max} of powdery **2** varies from 430 nm to 452 nm. The differences of λ_{max} between solution and solid are dependent on the core of **2**. Thiophene derivative **2b** shows the largest difference (64 nm), and pyridine derivative does the smallest (27 nm).

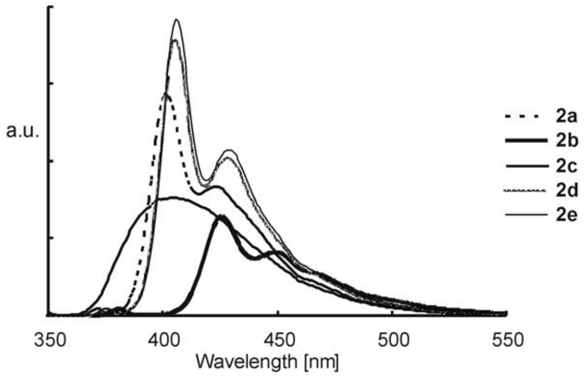


Figure 2 Photoluminescence spectra of **2a**–**e** in CH_2Cl_2

In conclusion, we have succeeded to prepare various arylene ethynylene fluorophores. For access to these compounds, the one-shot process for preparation of an iododiphenylethyne followed by Sonogashira coupling is a facile and practical synthetic route. In measurements of PL of **2**, each compound showed different λ_{max} of emission in the powdery state as is ascribable to intermolecular interaction while the solution λ_{max} values were alike, regardless of the arylene core. The emission of the dropcast film was observed for **2a**–**e** as well, and each λ_{max} was located between those of the corresponding solution and powder. The high quantum efficiencies are promising for

Table 2 Summary of λ_{max} (nm) of emission of **2a**–**e**

Compd	Solution[a] (Φ_{PL})[b]	Powder[c] (Φ_{PL})[b]	$\Delta\lambda$ (nm)[d]
2a	402 (0.92)	440 (0.21)	38
2b	426 (0.54)	490 (0.10)	64
2c	403 (0.95)	430 (0.26)	27
2d	406 (0.69)	452 (0.35)	46
2e	407 (0.96)	446 (0.58)	39

[a] Fluorescence in $CHCl_2$ ($9.4\cdot10^{-7}$ M).
[b] Absolute quantum yields (Hamamatsu photonics C9920-02).
[c] After evaporation from CH_2Cl_2.
[d] λ_{max}(powder) – λ_{max}(solution).

applications of these phenylene ethynylenes to organic electronics devices. Studies along this line are in progress in our laboratory.

Acknowledgment

This work has been supported financially by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

References and Notes

(1) (a) *Acetylene Chemistry: Chemistry, Biology, and Material Science*; Diederich, F.; Stang, P. J.; Tykwinski, R. R., Eds.; VCH: Weinheim, **2005**. (b) *Modern Acetylene Chemistry*; Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, **1995**. For reviews of phenylene ethynylenes, see: (c) James, D. K.; Tour, J. M. In *Topics in Current Chemistry*, Vol. 257; Springer: Berlin, **2005**, 33–62. (d) Stone, M. T.; Heemstra, J. M.; Moore, J. S. *Acc. Chem. Res.* **2006**, *39*, 11. (e) Ray, C. R.; Moore, J. S. *Adv. Polym. Sci.* **2005**, *177*, 91.

(2) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, *5*, 2330.

(3) (a) Wackerly, J. W.; Moore, J. S. *Macromolecules* **2006**, *39*, 7269. (b) Elliott, E. L.; Ray, C. R.; Kraft, S.; Atkins, J. R.; Moore, J. S. *J. Org. Chem.* **2006**, *71*, 5282.
(c) Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 6576; and references therein.

(4) Orita, A.; Jiang, L.; Tsuruta, M.; Otera, J. *Chem. Lett.* **2002**, 136.

(5) Orita, A.; An, D.-L.; Nakano, T.; Yaruva, J.; Ma, N.; Otera, J. *Chem. Eur. J.* **2002**, *8*, 2005.

(6) Orita, A.; Nakano, T.; An, D.-L.; Tanikawa, K.; Wakamatsu, K.; Otera, J. *J. Am. Chem. Soc.* **2004**, *126*, 10389.

(7) Oyamada, T.; Shao, G.; Uchiuzou, H.; Nakanotani, H.; Orita, A.; Otera, J.; Yahiro, M.; Adachi, C. *Jpn. J. Appl. Phys.* **2006**, *45*, 1331.

(8) A part of optical property of 4-(4-methoxyphenylethynyl)phenylethyne has been reported. See: Shao, G.; Orita, A.; Nishijima, K.; Ishimaru, K.; Takezaki, M.; Wakamatsu, K.; Otera, J. *Chem. Lett.* **2006**, *35*, 1284.

(9) Orita, A.; Taniguchi, H.; Otera, J. *Chem. Asian J.* **2006**, *1*, 430.

(10) **Double Elimination Method for 1 and 7: 1-(3,7-Dimethyloctyloxy)-4-(4-ethynylphenylethynyl)benzene (1).**
To a THF solution (15 mL) of 4-(3,7-dimethyloctyloxy)phenylmethyl phenyl sulfone (**3**, 466 mg, 1.2 mmol), 4-(trimethylsilylethynyl)benzaldehyde (**4**, 202 mg, 1.0 mmol) and diethylchlorophosphate (0.17 mL, 1.2 mmol) was added a THF solution of LiHMDS (1.0 M, 5.0 mL, 5.0 mmol) at 0 °C, and the mixture was stirred at r.t. for 16 h under argon. After usual work-up, the organic layer was evaporated and the residue was subjected to a column chromatography on silica gel (10% EtOAc–hexane) to give 1-(3,7-dimethyloctyloxy)-4-[4-(trimethylsilylethynyl)phenylethynyl]benzene in a pure form (358 mg, 83%). To a solution of 1-(3,7-dimethyloctyloxy)-4-[4-(trimethylsilylethynyl)phenylethynyl]benzene (2.15 g, 5.0 mmol) in THF (25 mL) and MeOH (25 mL) was added 6.91 g of K_2CO_3. The reaction mixture was stirred for 1.5 at r.t. After H_2O had been added, the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered. The solvents were evaporated, and the residue was subjected to column chromatography on silica gel (20% CH_2Cl_2–hexane) to afford **1** in a pure form (1.63 g, 91%).
Compound **1**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.5 Hz, 6 H), 0.94 (d, J = 6.3 Hz, 3 H), 1.14–1.32 (m, 6 H), 1.48–1.64 (m, 3 H), 1.78–1.84 (m, 1 H), 3.16 (s, 1 H), 3.98–4.03 (m, 2 H), 6.87 (d, J = 8.9 Hz, 2 H), 7.43–7.46 (m, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 22.5, 22.6, 24.6, 27.9, 29.8, 36.0, 37.2, 39.2, 66.3, 78.6, 83.3, 87.5, 91.6, 114.5, 114.6, 121.3, 124.1, 131.2, 132.0, 133.0, 159.4.
According to the same procedure, compound **7** was prepared from **3** and 4-iodobenzaldehyde.
Compound **7**: 68%. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 0.88 (d, J = 6.7 Hz, 6 H), 0.95 (d, J = 6.7 Hz, 3 H), 1.15–1.34 (m, 6 H), 1.52–1.68 (m, 3 H), 1.80–1.85 (m, 1 H), 3.99–4.03 (m, 2 H), 6.88 (d, J = 7.9 Hz, 2 H), 7.24 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.6 Hz, 2 H), 7.68 (d, J = 8.6 Hz, 2 H). ^{13}C NMR (125 HMz $CDC1_3$): δ = 19.6, 22.6, 22.7, 24.6, 28.0, 29.8, 36.1, 37.3, 39.2, 66.4, 87.1, 91.0, 93.6, 114.6, 114.6, 123.2, 132.9, 133.0, 137.4, 159.4.

(11) **Typical Procedure for Sonogashira Coupling.**
A 50 mL flask was charged with **7** (318 mg, 0.69 mmol), 1,4-diethyl-2,5-diethynylbenzene (55 mg, 0.30 mmol), $Pd(PPh_3)_4$ (34 mg, 0.03 mmol), CuI (5.0 mg, 0.03 mmol), *i*-Pr_2NH (1.0 mL) and toluene (20 mL), and the mixture was heated at 65 °C for 12 h. After filtration, the filtrate was poured into aq NH_4Cl and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered. After evaporation, the residue was subjected to column chromatography to afford **2a** as white powder in a pure form (228 mg, 90%).
Compound **2a**: mp 151–153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.7 Hz, 12 H), 0.94 (d, J = 6.4 Hz, 6 H), 1.15–1.20 (m, 6 H), 1.25–1.37 (m, 12 H), 1.50–1.67 (m, 6 H), 1.82–1.85 (m, 2 H), 2.85 (q, J = 7.5 Hz, 4 H), 3.99–4.05 (m, 4 H), 6.88 (d, J = 8.8 Hz, 4 H), 7.39 (s, 2 H), 7.45–7.49 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.7, 19.6, 22.6, 22.7, 24.6, 27.1, 27.9, 29.8, 36.0, 37.2, 39.2, 66.4, 88.0, 89.8, 91.5, 94.1, 114.5, 114.7, 122.4, 122.7, 123.5, 131.3, 131.4, 131.5, 133.0, 143.4, 159.3. Anal. Calcd for $C_{62}H_{70}O_2$: C, 87.90; H, 8.33. Found: C, 88.12; H, 8.60.
Compound **2b**: mp 178–181 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.4 Hz, 12 H), 0.94 (d, J = 6.7 Hz, 6 H), 1.15–1.34 (m, 12 H), 1.50–1.69 (m, 6 H), 1.80–1.86 (m, 2 H), 3.97–4.04 (m, 4 H), 6.87 (d, J = 8.8 Hz, 4 H), 7.17 (s, 2 H), 7.45–7.48 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 22.6, 22.7, 24.6, 27.9, 29.8, 36.0, 37.2, 39.2, 66.4,

83.9, 87.7, 91.8, 94.0, 114.5, 114.7, 121.8, 123.9, 124.6, 131.3, 131.4, 132.0, 133.0, 159.4. ESI-MS: *m/z* calcd for $C_{56}H_{60}O_2S$ [M + H^+]: 797.4; found: 797.3.

Compound **2c**: mp 235–238 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.7 Hz, 12 H), 0.94 (d, *J* = 6.7 Hz, 6 H), 1.15–1.37 (m, 12 H), 1.49–1.67 (m, 6 H), 1.80–1.86 (m, 2 H), 3.97–4.05 (m, 4 H), 6.87 (d, *J* = 8.8 Hz, 4 H), 7.45–7.50 (m, 10 H), 7.56 (d, *J* = 8.2 Hz, 4 H), 7.69 (t, *J* = 7.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 22.5, 22.6, 24.6, 27.9, 29.8, 36.0, 37.2, 39.2, 66.3, 87.6, 89.4, 89.7, 91.9, 114.5, 114.6, 121.3, 124.4, 126.3, 131.3, 132.0, 133.1, 136.4, 143.6, 159.4. ESI-MS: *m/z* calcd for $C_{57}H_{61}NO_2$ [M + H^+]: 792.3; found: 792.5.

Compound **2d**: mp 208–212 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 12 H), 0.93 (d, *J* = 6.7 Hz, 6 H), 1.14–1.33 (m, 12 H), 1.50–1.65 (m, 6 H), 1.80–1.84 (m, 2 H), 3.97–4.01 (m, 4 H), 6.77 (d, *J* = 7.6 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 4 H), 6.91 (s, 2 H), 7.15 (t, *J* = 7.4 Hz, 2 H), 7.35–7.43 (m, 14 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.82 (d, *J* = 7.9 Hz, 2 H), 7.87 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 22.5, 22.6, 24.6, 27.9, 29.8, 36.0, 37.2, 39.2, 65.5, 66.3, 87.7, 89.9, 91.3, 91.5, 114.5, 114.7, 120.1, 120.2, 122.4, 122.6, 123.4, 124.1, 127.2, 128.0, 128.1, 131.2, 131.3, 131.5, 133.0, 141.2, 141.7, 147.6, 149.2, 159.3. Anal. Calcd for $C_{77}H_{72}O_2$: C, 89.84; H, 7.05. Found: C, 89.79; H, 7.27.

Compound **2e**: mp 263–266 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.4 Hz, 12 H), 0.95 (d, *J* = 6.4 Hz, 6 H), 1.15–1.37 (m, 12 H), 1.49–1.67 (m, 6 H), 1.80–1.87 (m, 2 H), 2.49 (d, *J* = 13.4 Hz, 2 H), 3.32 (d, *J* = 13.4 Hz, 2 H), 3.97–4.05 (m, 4 H), 6.88 (d, *J* = 8.8 Hz, 4 H), 6.99 (s, 2 H), 7.31 (t, *J* = 7.1 Hz, 2 H), 7.43–7.56 (m, 20 H), 7.73 (d, *J* = 7.9 Hz, 2 H), 8.07 (d, *J* = 8.2 Hz, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 22.6, 22.7, 24.6, 28.0, 29.8, 36.1, 37.3, 39.2, 42.4, 61.0, 66.4, 87.8, 89.7, 91.5, 91.8, 114.6, 114.8, 120.1, 121.9, 122.7, 123.4, 125.3, 125.8, 127.4, 127.6, 128.0, 128.4, 128.9, 131.3, 131.4, 131.5, 131.9, 133.1, 133.2, 134.5, 135.6, 138.8, 151.4, 159.4. ESI-MS: *m/z* calcd for $C_{87}H_{80}O_2$ [M + H^+]: 1157.5; found: 1157.6.