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Synthesis of diarylenynes by olefination of 1-arylpropyne with arylaldehyde and their optical properties

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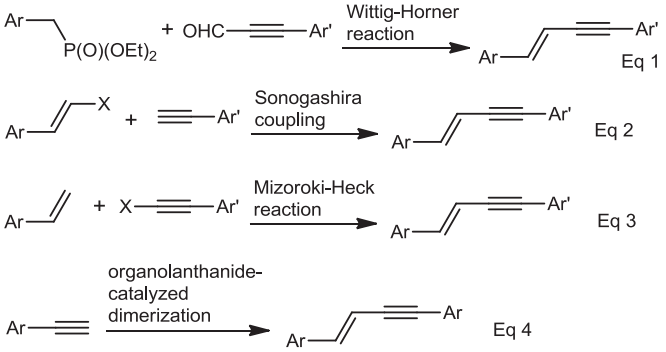
ABSTRACT

A new synthetic protocol of 1-arylpropyne was developed by taking advantage of 1-(diphenylphosphoryl)propyne as propyne equivalent in Sonogashira coupling: consecutive subjection of phosphorylpropyne to *t*-BuOK and to aryl halides in the presence of Pd and Cu catalysts afforded the corresponding 1-arylpropynes. The following olefination of the 1-arylpropyne with aldehyde provided the corresponding diarylenyne. When the enynes thus obtained were irradiated with UV light, they showed strong emission in organic solvents and in the solid states. In solution, Ph_2N-substituted enynes exhibited remarkable solvatofluorochromism, and Lippert–Mataga plot analysis demonstrated that they undergo the larger polarization in the excited states than in the ground states.

1. Introduction

Great attention is paid to highly expanded π-systems because they can be used as organic materials such as light-emitting diodes (LEDs),[1] field-effect transistors (FETs)[2] and dye-sensitized solar cells (DSSCs).[3] Although various π-expanded materials were developed, only few enyne motifs were explored as organic materials in spite of the high potentials as sensing fluorophore[4] and as emitter of white light-emitting devices (WOLEDs).[5] For syntheses of the enyne motifs, several synthetic routes were reported; Wittig–Horner olefination of propynal (Eq. 1 in Scheme 1),[4] Sonogashira coupling of vinyl halide with terminal ethyne (Eq. 2),[6] Mizoroki–Heck reaction of propynyl halide with olefin (Eq. 3)[7] and organolanthanide-catalyzed dimerization of arylethyne (Eq. 4).[5] On the other hand, we developed a new protocol of one-pot olefination between arylaldehyde and arylpropyne and achieved syntheses of a series of fluorescent arylenyne derivatives (Eq. 6 in Scheme 2).[8] For instance, when naphthylpropyne **1** was treated successively with BuLi, benzaldehyde, $ClP(O)(OEt)_2$, and *t*-BuOK, naphthyl, phenyl-substituted enyne **2** was provided. This olefination was composed of a number of transformations such as deprotonation of **1**, addition of the propargyl anion to aldehyde, transformation of the resulting alkoxide to phosphate and *t*-BuOK-promoted elimination of phosphoric acid, and all the transformations could be carried out in one-pot manner. Arylpropyne **1**, a starting compound in this olefination, was easily obtained from ethylsulfone and arylaldehyde by one-pot synthesis (Eq. 5).

For the synthesis of 1-arylpropyne such as **1**, Sonogashira coupling of the corresponding aryl halide with propyne would be straightforward. However, this reaction suffers from inconvenience,



Scheme 1. Synthetic routes of enyne motif.

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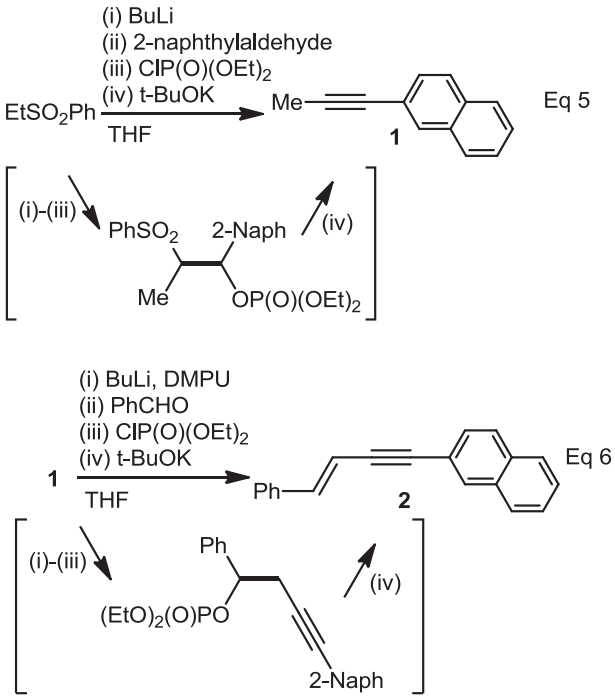
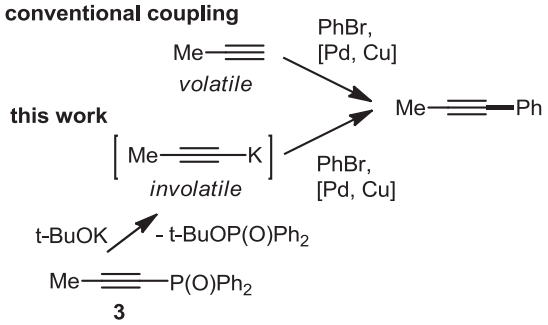


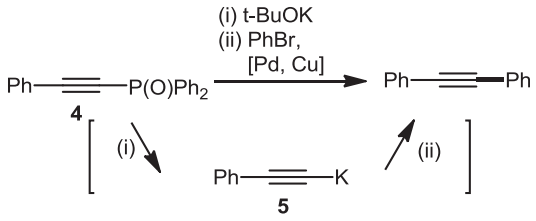
Scheme 2. Our synthetic process for enyne **2**.

because gaseous propyne (boiling point: −23 °C) must be manipulated for the coupling.[9] In order to avoid this drawback of propynylation in Sonogashira coupling, we planned to take advantage of 1-(diphenylphosphoryl)propyne (**3**) as propyne equivalent (Scheme 3). We envisioned that 1-phosphorylpropyne **3** would be transformed to involatile potassium propynide by treatment with *t*-BuOK, and the propynide could be used in the following Sonogashira coupling with aryl halides. We already reported that phosphoryl(phenyl)ethyne **4** could be used as phenylethyne equivalent in Sonogashira coupling. In this reaction, potassium phenylethynide **5** which was in situ prepared by treatment of **4** with *t*-BuOK was incorporated to the desired coupling product successfully (Scheme 4).[10]



Scheme 3. One-pot propynylation using **3**.

We envisioned that when 1-(phosphoryl)propyne **3** was subjected to the one-pot dephosphorylation–Sonogashira coupling technology, the desired propynylation could be achieved without any tedious operation because involatile potassium propynide would be in situ formed and supplied to the following Sonogashira coupling. We disclose herein the usability of 1-(phosphoryl)propyne **3** which could serve as propyne equivalent in the one-pot dephosphorylation–Sonogashira coupling protocol as well as one-pot transformation of the resulting 1-arylpropynes to 1,4-

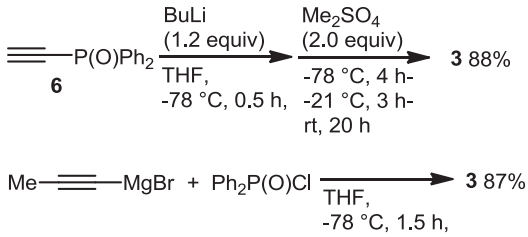


Scheme 4. One-pot dephosphorylation–Sonogashira coupling.

diarylbut-1-en-3-ynes. We also report optical properties of the enynes such as UV–vis absorption and fluorescence in solution and in the solid state together with electrochemical data as well.

2. Results and discussion

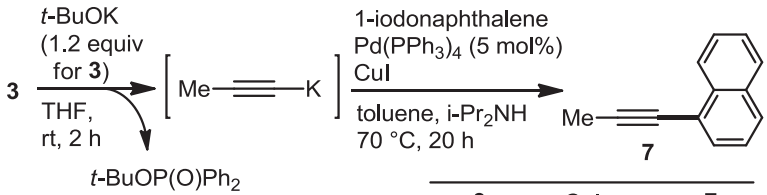
1-(Phosphoryl)propyne **3** was synthesized by successive treatment of phosphorylethyne **6** with BuLi and Me_2SO_4 in 88% yield (Scheme 5). In this methylation route, BuLi served well as a base while lithium diisopropylamide (LDA) or MeMgBr did not. The $Ph_2P(O)$-substituted ethynide anion required strong methylating reagent such as Me_2SO_4 because of its poor nucleophilicity ascribable to the strong electron-withdrawing effect of $Ph_2P(O)$ group.[10c] When MeI (10 equiv) was used as a mild methylating reagent, a chemical yield of **3** decreased to 42%. Alternatively, **3** was synthesized by treatment of 1-propynylmagnesium bromide with $Ph_2P(O)Cl$.[11]



Scheme 5. Syntheses of phosphorylpropyne **3**.

When *t*-BuOK (1.2 equiv of **3**) was added to a THF solution of **3**, the expected dephosphorylation proceeded smoothly, and TLC analysis showed complete consumption of **3** in 2 h (Scheme 6). By consecutive addition of Pd and Cu catalysts and 1-iodonaphthalene in toluene/*i*-Pr_2NH to this reaction mixture, the following Sonogashira coupling occured leading to the formation of **7**. When 5.0 or 3.0 equiv of **3** was subjected to this reaction in the presence of 1.1 equiv of CuI, **7** was obtained in 82% and 64% yields, respectively. In contrast, when 2.5 equiv of **3** and 0.05 equiv of CuI were used, the coupling proceeded somewhat sluggishly, and **7** was obtained in 50% yield. Because of the cost for preparation of **3** and inconvenience of separation of **7** from *t*-$BuOP(O)Ph_2$ which was produced in the dephosphorylation, we employed 3.0 equiv of **3** in further reactions. In this one-pot reaction, the addition of 1.1 equiv of CuI enabled the subsequent Sonogashira coupling to proceed smoothly, and the acceleration effect would be ascribable to the formation of an equimolar amount of copper propynide and/or the concomitant formation of KI.

This one-pot propynylation protocol served well for other aryl halides, and the corresponding propynylarenes were synthesized in moderate yields (Scheme 7). When bromoiodobenzenes were used, the propynylation proceeded selectively at iodine moieties, and bromine remained intact (Entries 1–3). Diiodobenzenes underwent double propynylation by using 6.0 equiv of **3** and 7.2 equiv of *t*-BuOK to lead 1,3- and 1,4-di(1-propynyl)benzenes in 65% and



3	CuI	7
5.0 equiv	1.1 equiv	82%
3.0 equiv	1.1 equiv	64%
2.5 equiv	0.05 equiv	50%

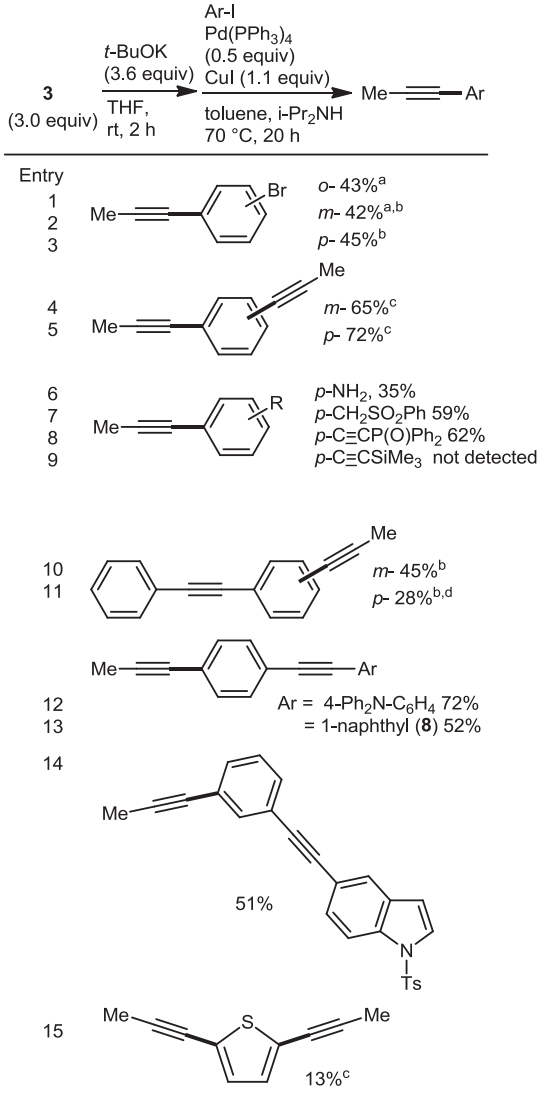
Scheme 6. One-pot synthesis of **7** from **3**.

72% yields, respectively (Entries 4 and 5). Iodobenzenes having functional groups such as H_2N–, $PhSO_2CH_2$– and $Ph_2P(O)$–C≡C– were transformed successfully to the corresponding (1-propynyl) benzenes in moderate yields (Entries 6–8). Although the one-pot propynylation worked well in the reaction of $Ph_2P(O)$-protected ethynylphenyl iodode (Entry 8), Me_3Si-protected ethynyl iodide decomposed in the same reaction conditions, and no formation of the desired Me_3Si-protected ethynylphenylpropyne was observed (Entry 9). The propynylation could be applied to aryl iodides having expanded π-systems (Entries 10 and 11), and Ph_2N– and 1-naphthyl-substituted arylpropynes were also synthesized in good yields (Entries 12 and 13). Indol and thiophene derivatives could be subjected to the propynylation as well (Entries 14 and 15). In the double propynylation of thienylene diiodide, the reaction proceeded rather sluggishly, and the formation of a number of unidentified byproducts was observed (Entries 15).

Next, the arylpropynes **7** and **8** thus obtained were transformed to enynes **9**–**12** by the one-pot olefination depicted in Eq. 6 of Scheme 2. When 1-(1-naphthyl)propyne (**7**) was treated successively with BuLi, amino-aldehyde **13**, $ClP(O)(OEt)_2$, and *t*-BuOK, the expected olefination occurred in one-pot manner, and the desired enyne **9** was provided in 51% yield (*E*-isomer) (Scheme 8). When propyne **7** and aldehyde **14** were subjected to the one-pot olefination protocol, enediyne **10** was provided in 69% yield. From the combination of **8** and **13**, an amino-substituted enediyne **11** which was one of regioisomer of **10** was synthesized in 13% yield. In the synthesis of **11**, the final elimination step proceeded rather sluggishly to give a number of unidentified byproducts. From the same one-pot reaction between **7** and **15**, dinaphthyl-substituted enediyne **12** was afforded in a moderated yield.

Because a series of enynes **9**–**12** were synthesized, their UV–vis absorption and fluorescence spectra in CH_2Cl_2 and in the solid states were recorded, and all the data were summarized in Table 1. In Figs. 1–3 were shown the profiles of UV–vis absorption and photoluminescence (PL) spectra of **9**–**12**.

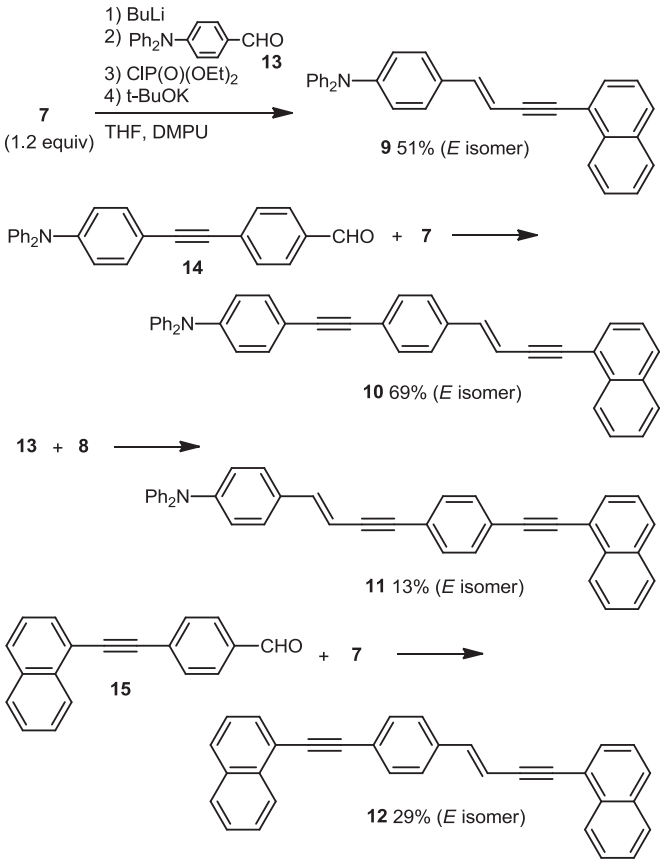
The Ph_2N-substituted enyne derivatives **9**–**11** had strong absorption bands exhibiting λ_{max} in a range of 380–400 nm, while enynes **12** did at the shorter wavelength 370 nm (Table 1, Fig. 1). Enyne derivative **9** indicated rather smaller molar extinction coefficient ε than yne–enyne derivatives **10**–**11**: 31,000 versus >50,000 $Lmol^{-1}cm^{-1}$. Also in photoluminescence spectra in CH_2Cl_2, Ph_2N-substituted enyne derivatives **9**–**11** indicated emission at longer wavelengths than di(naphthyl)enyne **16**; emission maxima E_{max} 470–520 nm for **9**–**11**, 411 nm for **12** (Table 1, Fig. 2). Enyne **9** exhibited a little smaller fluorescence quantum yield than others because of the shorter π-system; Φ_F=0.62 for **9** and >0.74 for **10**–**12**. In emission of the solid states, di(naphthyl)enyne **12** showed emission at 463 nm, and amino-substituted enynes **9**–**11** did at 500–511 nm (Table 1, Fig. 3).



[a] NMR yield. [b] 2.5 equiv of **3**. [c] 6 equiv of **3**. [d] From bromide.

Scheme 7. One-pot synthesis of 1-arylpropynes.

When fluorescence spectra of **9** were recorded in various solvents, large solvatochromism was observed; upon changing the solvents from toluene to acetonitrile, 71 nm of bathochromic shift was demonstrated (Table 2). Fig. 4 shows the emission profiles of **9** in a series of solvents.



Scheme 8. Synthesis of enynes **9**–**12** by olefination of arylpropynes with arylaldehydes.

Table 1
Summary of UV–vis absorption and PL spectra[a]

	λ_{max} [nm][a]/ε [$10^3\times$L/mol cm] (CH_2Cl_2)[b]	E_{max} [nm][c] (CH_2Cl_2)[d]/Φ_F[e]	E_{max} [nm][c] (powder)/Φ_F[e]
9	390/31.3	472/0.62	501/0.28
10	385/50.1	516/0.83	511/0.21
11	397/52.4	506/0.74	500/0.23
12	370/48.4	411/0.98	463/0.27

[a] The longest wavelength of absorption bands.
[b] 1.0×10^{-4} mol/L.
[c] The wavelength of the strongest emission band.
[d] 1.0×10^{-6} mol/L.
[e] Absolute fluorescence quantum yield.

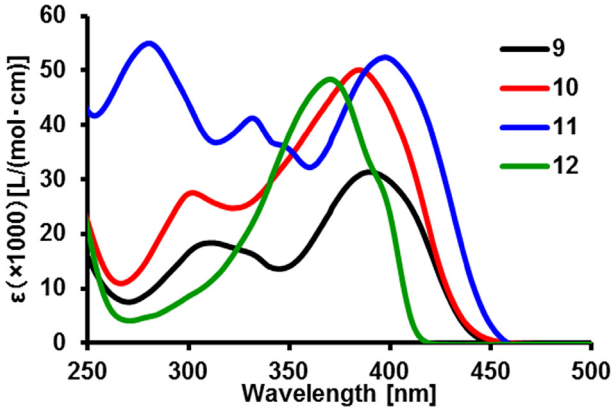


Fig. 1. UV–vis absorption spectra of **9**–**12** in CH_2Cl_2 (1.0×10^{-4} M).

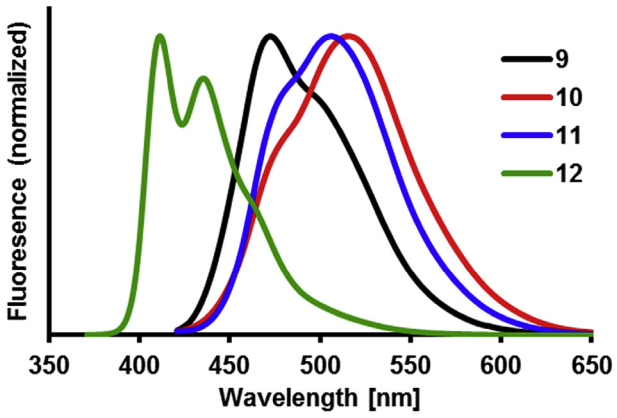


Fig. 2. Photoluminescence spectra of **9**–**12** in CH_2Cl_2 (1.0×10^{-6} M).

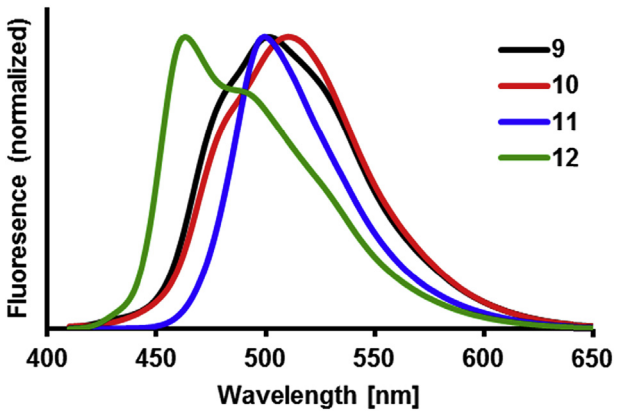


Fig. 3. Photoluminescence spectra of **9**–**12** in the solid states.

Table 2
Summary of emission maxima E_{max} of **9** in a series of solvents.[a]

Solv[b]	Tol	$CHCl_3$	DCM	DMF	ACN
E_{max} [nm]	442	465	473	512	513
Stokes shift [cm^{-1}]	3282	4401	4765	6375	6413

[a] 1.0×10^{-6} mol/L.
[b] Tol: toluene, DCM: dichloromethane, DMF: *N*,*N*-dimethylformamide, ACN: acetonitrile.

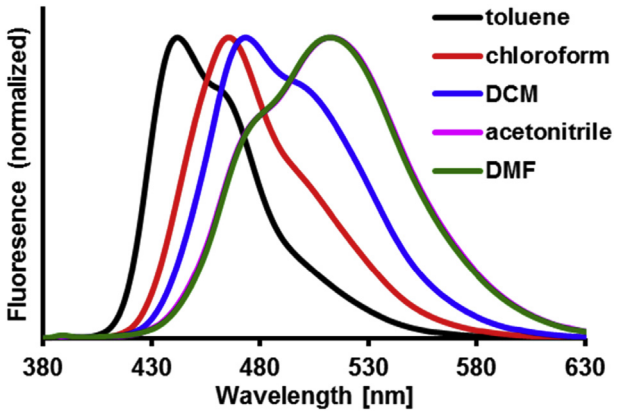


Fig. 4. Photoluminescence spectra of **9** in a series of solvents (1.0×10^{-6} M).

The large solvatofluorochromism observed in **9** suggests the increase of the dipole moment in the excited state S_1 (μ_e) compared to that in the ground state S_0 (μ_g). In order to rationalize the solvent effects, we invoked Lippert–Mataga plot.[12] Lippert–Mataga plot provides quantitative relationship between the solvent orientation polarizability Δf and Stokes shift $\Delta\nu$ as shown in Eq. 7.

$$\Delta\nu = \frac{2\left(\mu_e - \mu_g\right)^2}{4\pi\varepsilon_0 hca^3}\Delta f + \text{Constant} = \rho\Delta f + \text{C} \quad (7)$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (8)$$

$\Delta\nu$: Stokes shift
μ_e: dipole moment in the excited state
μ_g: dipole moment in the ground state
ε_0: vacuum permittivity (8.8542×10^{-12} $C^2N^{-1}m^{-2}$)
h: the Planck constant (6.6262×10^{-34} Js)
c: the light velocity (2.9979×10^{-8} ms^{-1})
a: the Onsager radius of the solute
ε: solvent dielectric constant
n: refractive index

The solvent orientation polarizability Δf is calculated by using Eq. 8. When $\Delta\nu$ was plotted against Δf, $2(\mu_e-\mu_g)^2/4\pi\varepsilon_0 hca^3$ was provided as the slope ρ of linear fit in Eq. 7. As presented in Fig. 5, **9** exhibited large slope value ρ 11,100 cm^{-1} representing that the amino-substituted enyne **9** underwent intramolecular charge-transfer (ICT) in photo-excitation to provide highly polarized excited state.[13] The Onsager cavity radius a was estimated from the optimized distance between the farthest atoms in the direction of charge separation within **9**. Because the DFT calculations (B3LYP/6-31G(d)) indicated that the optimized molecule lengths of **9** would be 19.1 Å, the Onsager cavity radius a of **9** was provided as 7.6 by multiplying a reduction factor 0.4.[14] According to Eq. 7, the change of dipole moment upon excitation ($\mu_e-\mu_g$) in **9** was estimated to be 22.0 D. The change of dipole moments observed in **9** (22.0 D) was comparable to that of amino-substituted diyne analog **16** ($\Delta\mu$=24.4 D) presenting the similar polarizabilities of **9** and **16** (Scheme 9).[15]

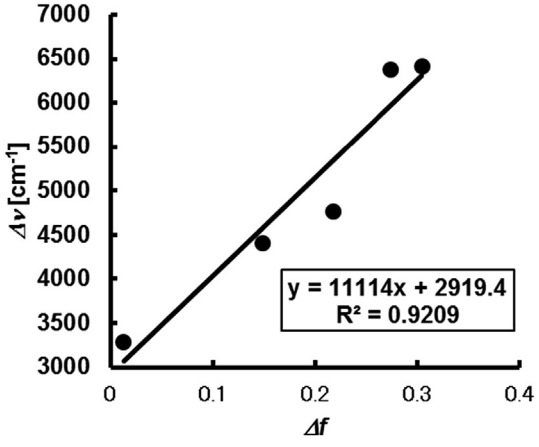
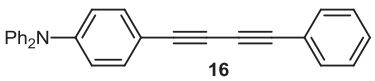


Fig. 5. Lippert–Mataga plot for **9**.



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Scheme 9. Structure of amino-substituted phenyleneethynylene **16**.

In Fig. 6 were demonstrated HOMO and LUMO of **9** which were calculated by DFT method (B3LYP/6-31G(d)). The HOMO expands mainly at triphenylamine moiety, and a lone pair of nitrogen enables the HOMO to expand efficiently among three benzene rings. In contrast to this, the LUMO is located mainly at naphthyl- and phenylene-substituted butenyne moiety. TDDFT calculation revealed that the first excitation in **9** would be ascribable to HOMO-LUMO transition (f=1.38). These results also unambiguously support the fact that **9** would undergo ICT in the photo-excitation leading to largely charge-separated excited state.[16]

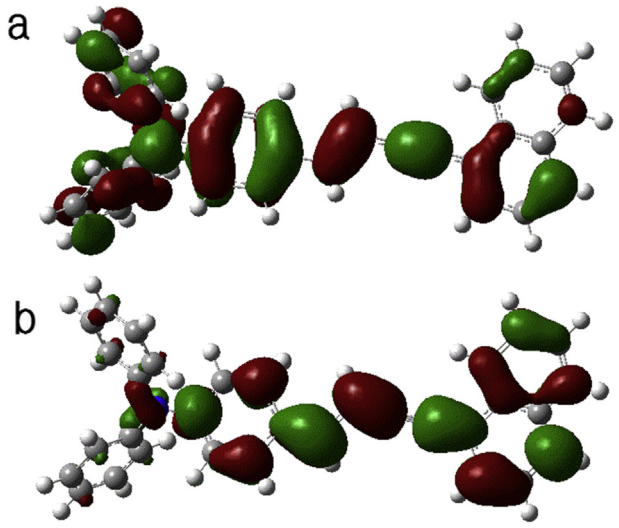

Fig. 6. Frontier orbitals of **9** calculated at the B3LYP/6-31G(d) level (a, HOMO; b, LUMO).

Cyclic voltammetry was recorded for **9**–**12** in CH_2Cl_2, and the results were summarized in Table 3 together with their HOMO and LUMO levels calculated at the B3LYP/6-31G(d) level. The amino-substituted enyne derivatives **9**–**11** underwent smooth oxidation because of the efficient participation of amino group in HOMO, and exhibited their first oxidation potentials in a range between 0.28 and 0.37 V. In comparison with these amino-substituted enynes, **12** showed remarkably positive oxidation potentials (>0.89 V), and the deeper HOMO levels were consistent with the DFT calculation results; ca. −4.9 V for **9**–**11**, −5.2 V for **12**. Reduction potential of **12** (>−2.33 V) was more positive than those of the amino derivatives **9**–**11** (−2.38 V to −2.49 V) diagnostic of the shallower LUMO levels of **9**–**11** which were attributable to the electron-donating effect of amino group.

Table 3
Summary of cyclic voltammogram[a] and calculated HOMO and LUMO levels[b]

	Oxidation potentials [V][c]	HOMO level [V]	Reduction potentials [V][c]	LUMO level [V]
9	0.37	−4.82	−2.49	−1.71
10	0.28, 0.43, 1.06[c]	−4.87	−2.46[c]	−1.98
11	0.36, 0.53, 1.11	−4.84	−2.38[c]	−1.92
12	0.89[c], 1.23[c]	−5.15	−2.33[c]	−2.10

[a] The reduction and oxidation potentials (vs Fc/Fc^+) were measured under the following conditions: in CH_2Cl_2 (1.0×10^{-4} M, 100 mV/s scan rate, 0.1 M Bu_4NPF_6), a glassy carbon as the working electrode, a Pt counter electrode, and an Ag/Ag^+ reference electrode (0.01M $AgNO_3$ and 0.1 M tetrabutylammonium perchlorate in acetonitrile) in 0.1 M $LiClO_4$/acetonitrile.
[b] Calculated at the B3LYP/6-31G(d) level.
[c] Irreversible oxidation or reduction potentials.

3. Conclusion

In conclusion, we developed a new methodology to synthesize 1-arylpropyne by Sonogashira coupling between the corresponding

aryl halide and potassium propynide which was in situ prepared by treatment of 1-(phosphoryl)propyne **3** with *t*-BuOK. The one-pot dephosphorylation/Sonogashira coupling protocol served well for syntheses of a series of (1-propynyl)arenes having functional groups such as amino, sulfonyl and phosphorylethynyl groups. This protocol exhibited a high haloselectivity between bromine and iodine, and Sonogashira coupling proceeded preferentially with aryl iodide. 1-Arylpropynes thus obtained were transformed to 1,4-diarylbutenynes by successive treatment with BuLi, arylaldehydes, $ClP(O)(OEt)_2$ and *t*-BuOK. A series of 1,4-diarylbutenynes emitted strong fluorescence both in solution and in the solid states when they were irradiated with UV light. Ph_2N-substituted enynes exhibited remarkably strong emission in solution, and, in polar solvents, large solvatofluorochromism was observed. Lippert–Mataga plot analysis demonstrated that in the photo-excitation, Ph_2N-substituted diarylbutenyne underwent an intramolecular charge transfer (ICT) with a large change of dipole moments.

4. Experimental

4.1. Materials and methods

Chemicals were purchased from Aldrich and TCI and used without further purification. NMR spectra were recorded in parts per million (ppm) in $CDCl_3$ and CD_2Cl_2 on JEOL ECP 400 NMR and LAMBDA 300 and 500 instruments using TMS as an internal standard. Mass spectra were recorded on JEOL JMS-700 mass spectrometer and Bruker MALDI-TOF/TOF MS autoflex speed.

4.2. Synthesis of 3[11]

Route 1. To a THF solution (60.0 mL) of ethynyldiphenylphosphine oxide (**6**) (4.53 g, 20.0 mmol) was added a hexane solution of butyllithium (1.6 M, 15.0 mL, equivalent to 24.0 mmol of BuLi), and the mixture was stirred at −78 °C for 30 min. To the mixture was added dimethyl sulfate (3.80 mL, 40.0 mmol), and the mixture was stirred at −78 °C for 3 h, at −21 °C for 3 h and at rt for 12 h. After workup with CH_2Cl_2/satd NH_4Claq, the combined organic layer was washed with satd NaClaq and dried over $MgSO_4$. After evaporation, the crude product was subjected to column chromatography on silica gel (AcOEt/hexane 80: 20) to provide 1-propynyldiphenylphosphine oxide (**3**) in a pure form (4.24 g, 17.7 mmol, 88% yield).

3: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (d, *J*=3.6 Hz, 3H), 7.43–7.56 (m, 6H), 7.79–7.87 (m, 4H).

Route 2.[11] To a THF solution (6.0 mL) of chlorodiphenylphosphine oxide (0.473 g, 2.00 mmol) was added a THF solution of 1-propynylmagnesium bromide (0.5 M, 4.0 mL, equivalent to 2.0 mmol), and the mixture was stirred at −78 °C for 1.5 h. After workup with CH_2Cl_2/satd NH_4Claq, the combined organic layer was washed with satd NaClaq and dried over $MgSO_4$. After evaporation, the crude product was subjected to column chromatography on silica gel (AcOEt/hexane 80: 20) to provide 1-propynyldiphenylphosphine oxide (**3**) in a pure form (0.418 g, 1.74 mmol, 87% yield).

4.3. One-pot synthesis of 7 from 3 (representative for Schemes 6 and 7)

To a THF solution (4.0 mL) of phosphorylpropyne **3** (0.361 g, 1.50 mmol) was added *t*-BuOK (0.201 g, 1.79 mmol), and the mixture was stirred at rt for 2 h. To the solution were added 1-iodonaphthalene (0.09 mL, 0.5 mmol), $Pd(PPh_3)_4$ (30.5 mg, 0.025 mmol), CuI (0.105 g, 0.55 mmol), toluene (8.0 mL) and *i*-Pr_2NH (1.0 mL, 13.7 mmol), and the mixture was stirred at 70 °C for 20 h. After workup with CH_2Cl_2/satd NH_4Claq, the combined organic layer was washed with satd NaClaq and dried over $MgSO_4$. After evaporation, the crude product was subjected to column chromatography on silica gel (CH_2Cl_2/hexane 10: 90) to provide 1-(1-propynyl)naphthalene (**7**) in a pure form (50.1 mg, 0.301 mmol, 60% yield).

7: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 7.37 (t, *J*=7.7 Hz, 1H), 7.47–7.58 (m, 3H), 7.78 (d, *J*=8.4 Hz, 1H), 7.83 (d, *J*=7.5 Hz, 1H), 8.35 (d, *J*=8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 4.64, 77.73, 90.78, 121.74, 125.21, 126.20, 126.28, 126.44, 127.90, 128.16, 129.96, 133.17, 133.51; HRMS (EI): 166.0786 (M^+); calcd for $C_{13}H_{10}$: 166.0783.

4.3.1. 1-Bromo-3-(1-propynyl)benzene (Entry 1 in Scheme 7).[8] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 7.15 (dt, *J*=1.8, 7.8 Hz, 1H), 7.22 (dt, *J*=1.8, 7.8 Hz, 1H), 7.42 (dd, *J*=1.5, 7.8 Hz, 1H), 7.55 (dd, *J*=1.5, 7.8 Hz, 1H).

4.3.2. 1-Bromo-3-(1-propynyl)benzene (Entry 2 in Scheme 7).[9d] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.03 (s, 3H), 7.13 (t, *J*=7.8 Hz, 1H), 7.29 (d, *J*=7.8 Hz, 1H), 7.39 (d, *J*=7.8 Hz, 1H), 7.52 (s, 1H).

4.3.3. 1-Bromo-4-(1-propynyl)benzene (Entry 3 in Scheme 7).[8] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H), 7.24 (d, *J*=8.4 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 2H).

4.3.4. 1,3-Di-(1-propynyl)benzene (Entry 4 in Scheme 7).[9c] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 6H), 7.18 (t, *J*=7.6 Hz, 1H), 7.28 (d, *J*=7.6 Hz, 2H), 7.41 (s, 1H).

4.3.5. 1,4-Di-(1-propynyl)benzene (Entry 5 in Scheme 7).[17] White powder; mp 160 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (s, 6H), 7.29 (s, 4H).

4.3.6. 4-(1-Propynyl)aniline (Entry 6 in Scheme 7).[18] Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (br, 2H), 2.10 (s, 3H), 7.52 (d, *J*=8.6 Hz, 2H), 7.84 (d, *J*=8.6 Hz, 2H).

4.3.7. 1-(1-propynyl)-4-phenylsulfonylmethylbenzene (Entry 7 in Scheme 7). White powder; mp 159–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 3H), 4.28 (s, 2H), 7.37 (d, *J*=8.1 Hz, 2H), 7.27 (d, *J*=8.1 Hz, 2H), 7.45 (t, *J*=8.1 Hz, 2H), 7.58–7.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.33, 62.68, 79.08, 87.32, 124.62, 127.32, 128.63, 128.92, 130.61, 133.77, 137.66; HRMS (MALDI): 129.0972 (M^+); calcd for $C_{16}H_{14}O_2S$ (−$PhSO_2$): 129.0704.

4.3.8. 4-(1-Propynyl)phenylethynyl(diphenyl)phosphine oxide (Entry 8 in Scheme 7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H), 7.37 (d, *J*=8.0 Hz, 2H), 7.47–7.57 (m, 8H), 7.87 (d, *J*=8.0 Hz, 2H), 7.91 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.45 79.14, 83.24, 84.91, 89.74, 105.02 (d, *J*=118.0 Hz), 118.73 (d, *J*=19.2 Hz), 126.69, 128.66 (d, *J*=53.2 Hz), 130.97 (d, *J*=45.6 Hz), 131.58, 132.29 (d, *J*=30.4 Hz), 133.58; HRMS (MALDI): 340.1020 (M^+); calcd for $C_{23}H_{17}OP$: 340.1017.

4.3.9. 3-(1-Propynyl)phenylethynlbenzene (Entry 10 in Scheme 7).[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H), 7.26 (t, *J*=7.8 Hz, 1H), 7.34–7.37 (m, 4H), 7.43 (d, *J*=7.6 Hz, 1H), 7.51–7.54 (m, 2H), 7.56 (s, 1H).

4.3.10. 3-(1-Propynyl)phenylethynlbenzene (Entry 11 in Scheme 7).[8] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.07 (s, 3H), 7.34–7.37 (m, 5H), 7.43 (s, 1H), 7.47 (d, *J*=5.4 Hz, 1H), 7.51–7.54 (m, 2H).

4.3.11. 4-(4-(1-Propynyl)phenylethynyl)phenyl(diphenyl)amine (Entry 12 in Scheme 7). Yellow powder; mp 163–164 °C; ^{1}H NMR

(300 MHz, $CDCl_3$) δ 2.07 (s, 3H), 7.00 (d, *J*=8.9 Hz, 2H), 7.06 (t, *J*=7.3 Hz, 2H), 7.11 (d, *J*=8.5 Hz, 4H), 7.26–7.29 (m, 4H), 7.35 (t, *J*=8.1 Hz, 4H), 7.41 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 4.44, 79.58, 87.70, 88.39, 91.09, 115.83, 122.20, 122.70, 123.51, 123.56, 124.99, 129.38, 131.24, 131.39, 132.50, 147.14, 147.98; HRMS (MALDI): 383.1640 (M^+); calcd for $C_{29}H_{21}N$: 383.1644.

4.3.12. 4-(1-Propynyl)phenylethynylnaphthalene (Entry 13 in Scheme 7). White powder; mp 97 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 7.41 (d, *J*=8.4 Hz, 2H), 7.45 (t, *J*=7.8 Hz, 1H), 7.51–7.61 (m, 4H), 7.75 (d, *J*=7.2 Hz, 1H), 7.85 (t, *J*=8.4 Hz, 2H), 8.41 (d, *J*=8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.44, 79.56, 88.00, 88.91, 94.06, 120.75, 122.45, 124.08, 125.26, 126.15, 126.44, 126.80, 128.31, 128.87, 130.40, 131.46, 131.51, 133.20; HRMS (MALDI): 266.1109 (M^+); calcd for $C_{21}H_{14}$: 266.1096.

4.3.13. 1-Tosyl-5-(3-(1-propynyl)phenylethynyl)indole (Entry 14 in Scheme 7). White powder; mp 119 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.35 (s, 3H), 6.64 (dd, *J*=0.9, 3.8 Hz, 1H), 7.23 (d, *J*=8.6 Hz, 2H), 7.26 (t, *J*=3.8 Hz, 1H), 7.33 (td, *J*=1.4, 8.0 Hz, 1H), 7.41 (td, *J*=1.5, 7.6 Hz, 1H), 7.46 (dd, *J*=1.5, 8.6 Hz, 1H), 7.54 (s, 1H), 7.58 (d, *J*=3.8 Hz, 1H), 7.70 (d, *J*=0.9 Hz, 1H),7.76 (d, *J*=8.6 Hz, 2H), 7.96 (d, *J*=8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.28, 21.49, 78.94, 86.54, 87.89, 89.80, 108.81, 113.53, 118.02, 123.42, 124.30, 124.80, 126.72, 127.23, 128.00, 128.27, 129.90, 130.50, 130.71, 131.12, 134.30, 134.39, 134.99, 145.14; HRMS (MALDI): 409.1137 (M^+); calcd for $C_{26}H_{19}NO_2S$: 409.1139.

4.3.14. 2,5-Di-(1-propynyl)thiophene (Entry 15 in Scheme 7).[19] Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 2.06 (s, 6H), 6.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.64, 72.72, 90.41, 124.19, 130.58.

4.4. Synthesis of 9 by olefination of 8 with 13 (representative for Scheme 8)

To a THF solution (2.0 mL) of 1-(1-propynyl)naphthalene (**8**) (0.083 g, 0.499 mmol) were added DMPU (2.0 mL, 16.5 mmol) and a hexane solution of butyl lithium (1.6 M, 0.375 mL, equivalent to 0.600 mmol of BuLi), and the mixture was stirred at −78 °C for 30 min. To the mixture was added a THF solution (2.0 mL) of 4-formylpheny(diphenyl)amine (**13**) (0.164 g 0.600 mmol), and the mixture was stirred at −78 °C for 30 min. To the mixture was added diethyl chlorophosphate (0.087 mL, 0.605 mmol), and the mixture was stirred at rt for 2 h. To the mixture was added *t*-BuOK (0.337 g, 3.00 mmol), and the mixture was stirred at rt for 12 h. After workup with CH_2Cl_2/satd NH_4Claq, the combined organic layer was washed with satd NaClaq and dried over MgSO4. After evaporation, the crude product was subjected to column chromatography on silica gel (CH_2Cl_2/hexane 20: 80) and recrystallization (ethanol) to provide 4-(1-naphtylethynylethenyl) phenyl(diphenyl)amine (**9**) in a pure form (0.106 g, 0.256 mmol, 51% yield).

9: yellow powder; mp 171 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 6.40 (d, *J*=15.9 Hz, 1H), 7.02–7.08 (m, 5H), 7.13 (d, *J*=7.6 Hz, 4H), 7.28 (t, *J*=7.9 Hz, 4H), 7.33 (d, *J*=8.6 Hz, 2H), 7.43 (t, *J*=7.8 Hz, 1H), 7.52 (t, *J*=7.5 Hz, 1H), 7.58 (t, *J*=7.3 Hz, 1H), 7.69 (d, *J*=7.4 Hz, 1H), 7.81 (d, *J*=8.3 Hz, 1H), 7.85 (d, *J*=8.3 Hz, 1H), 8.40 (d, *J*=7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 89.45, 94.43, 105.87, 121.27, 122.73, 123.39, 124.84, 125.28, 126.23, 126.35, 126.63, 127.23, 128.23, 128.42, 129.33, 130.08, 130.10, 133.12, 133.16, 140.87, 147.24, 148.32; HRMS (MALDI): 421.1822 (M^+); calcd for $C_{32}H_{23}N$: 421.1830.

10: yellow powder; mp 81 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 6.56 (d, *J*=16.2 Hz, 1H), 7.01 (d, *J*=8.9 Hz, 2H), 7.07 (tt, *J*=1.8, 7.3 Hz, 2H), 7.11–7.16 (m, 5H), 7.28 (t, *J*=8.0 Hz, 4H), 7.38 (td, *J*=2.3, 8.9 Hz, 2H), 7.43–7.46 (m, 3H), 7.50 (d, *J*=8.3 Hz, 2H), 7.53 (dt, *J*=1.3, 7.5 Hz, 1H), 7.60 (dt, *J*=1.2, 7.5 Hz, 1H), 7.71 (dd, *J*=1.2, 7.2 Hz, 1H), 7.83 (d, *J*=8.3 Hz, 1H), 7.86 (d, *J*=8.0 Hz, 1H), 8.38 (d, *J*=8.9 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 88.66, 90.72, 91.33, 93.86, 108.86, 115.86, 121.01, 122.22, 123.60, 123.83, 125.03, 125.31, 126.21, 126.26, 126.46, 126.80, 128.32, 128.79, 129.41, 130.39, 131.81, 132.56, 133.18, 133.20, 135.83, 140.63, 147.15, 148.04; HRMS (MALDI): 521.2141 (M^+); calcd for $C_{40}H_{27}N$: 521.2144.

11: yellow powder; mp 160 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 6.26 (d, *J*=16.2 Hz, 1H), 6.99–7.02 (m, 3H), 7.06 (t, *J*=7.3 Hz, 2H), 7.12 (d, *J*=7.7 Hz, 4H), 7.26–7.30 (m, 6H), 7.45–7.49 (m, 3H), 7.54 (t, *J*=7.3 Hz, 1H), 7.59–7.62 (m, 3H), 7.76 (d, *J*=7.0 Hz, 1H), 7.86 (t, *J*=8.9 Hz, 2H), 8.42 (d, *J*=8.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 89.64, 91.28, 92.00, 94.43, 105.72, 120.91, 122.87, 123.18, 123.90, 124.04, 125.31, 125.71, 126.37, 126.91, 127.30, 127.64, 128.72, 129.37, 129.73, 130.20, 130.87, 131.77, 131.93, 133.49, 141.73, 147.61, 148.93; HRMS (EI): 521.2149 (M^+); calcd for $C_{40}H_{27}N$: 521.2144.

12: yellow powder; mp 192 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 6.60 (d, *J*=16.2 Hz, 1H), 7.17 (d, *J*=16.2 Hz, 1H), 7.45 (d, *J*=8.6 Hz, 1H), 7.48 (d, *J*=8.9 Hz, 1H), 7.51 (d, *J*=8.2 Hz, 2H), 7.53–7.56 (m, 2H), 7.59–7.62 (m, 2H), 7.65 (d, *J*=8.2 Hz, 2H), 7.72 (d, *J*=7.1 Hz, 1H), 7.78 (d, *J*=7.3 Hz, 1H), 7.83–7.89 (m, 4H), 8.39 (d, *J*=8.3 Hz, 1H), 8.44 (d, *J*=8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 89.10, 90.89, 93.80, 94.28, 109.20, 120.78, 120.98, 123.54, 125.31, 125.33, 126.19, 126.20, 126.36, 126.48, 126.49, 126.81, 126.85, 128.33, 128.36, 128.79, 128.85, 128.92, 130.44, 130.47, 136.63, 132.06, 133.19, 133.23, 136.33, 140.54; HRMS (MALDI): 404.1567 (M^+); calcd for $C_{32}H_{20}$: 404.1565.

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