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Regioselective Photoalkylation of 2-Cyano-6-methoxynaphthalene by Methoxy-substituted 1,2-Diarylcyclopropanes

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Abstract

Photoreactions of 2-cyano-6-methoxynaphthalene with methoxy-substituted 1,2-diarylcyclopropanes in benzene give 2-cyano-1-(1,3-diarylpropyl)-6-methoxynaphthalenes. The excellent regioselectivity seen in these processes can be explained by initial formation of singlet exciplexes, in which the dipoles of each component are oriented in opposite directions.

Keywords

Photoreaction; 2-Cyano-6-methoxynaphthalene; 1,2-Diarylcyclopropanes; Exciplex

1. Introduction

Photocycloaddition between aromatic substances and alkenes is a useful reaction for the construction of polycyclic compounds [1-16]. (2 + 2) Photocycloaddition of naphthalene derivatives with alkenes gives cyclobutane-fused compounds, which can be chemically converted to various alkylated naphthalene derivatives [17-23]. Cyclopropanes, whose bonding and antibonding σ-orbitals are banana-shaped, are expected to behave chemically like unsaturated compounds. However, only a few reports have appeared describing photoreactions between aromatic compounds and cyclopropanes [24-30]. Included in this group are processes involving (i) (2 + 3) photocycloaddition and photoalkylation of 9-cyanophenanthrene with 1,2-diarylcyclopropanes [24], (ii) (4 + 3) photocycloaddition of 9,10-dicyanoanthracene with 1,2-diarylcyclopropanes [25,26], 1-amino-2-phenylcyclopropanes [27], and methylenecyclopropanes [28], and (iii) photoalkylation of 2,3-dicyanonaphthalene with 1,2-diarylcyclopropanes [29].

Among these processes, the photoalkylation reactions of aromatic compounds by cyclopropanes, probed in our preliminary communication [29], is expected to serve as a direct method for the facile one-pot synthesis of alkylated naphthalene derivatives. In the course of recent studies aimed at investigating photoreactions of 2-cyano-6-methoxynaphthalene [31-34] with 1,2-diarylcyclopropanes, we observed that alkylation takes place at the 1-position of the naphthalene derivative in a highly regioselective manner. Below, the findings of this study are described.

2. Experimental

2-1. General

Benzene was distilled from CaH_2 and then from Na. Dichloromethane was distilled

from $CaCl_2$ and then CaH_2.   Acetonitrile was distilled from P_2O_5 and then from Na.   2-Bromo-6-methoxynaphthalene, acetophenone, and methoxy-substituted benzaldehydes were purchased and used without purification.

A 300W high-pressure mercury lamp (Eikosha, PIH-300, emission lines: 254 nm, 365 nm, and others) was used as a light source of the photoreactions.   Melting points were determined on a Yanagimoto Micro Melting Point apparatus, Yanaco MP-500 and are uncorrected.   ^{1}H and ^{13}C NMR spectra were recorded on a Varian MERCURY-300 (300 MHz and 75 MHz, respectively) spectrometer using Me_4Si as an internal standard.   IR spectra were determined on a Jasco FT/IR-230 spectrometer.   UV-vis spectra were recorded on Jasco V-530 spectrophotometer.   Fluorescence spectra were taken on Jasco FP-6300 spectrophotometer.   Fluorescence lifetimes were measured by HORIBA NAES-550 nano-second fluorometer equipped with SSU-111A photomultiplier, SCU-121A optical chamber, SGM-121A monochromator, and LPS-111 lamp power supply.   Mass spectra (EI) were taken on a SHIMADZU GCMS-QP5050 operating in the electron impact mode (70 eV) equipped with GC-17A and DB-5MS column (J&W Scientific Inc., Serial: 8696181).   HPLC separations were performed on a recycling preparative HPLC equipped with Jasco PU-2086 Plus, RI-2031 Plus differential refractometer, Megapak GEL 201C columns (GPC) using $CHCl_3$ as an eluent.   Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60N (spherical, neutral, 0.063-0.210 mm).

2.2 Preparation of 2-cyano-6-methoxynaphthalene (1)

A mixture of 2-bromo-6-methoxynaphthalene (2.00 g), copper(I) cyanide (1.80 g), and *N*-methyl-2-pyrrolidone (35 mL) was stirred and refluxed at 202 °C for 40 min.   After

cooling the mixture to room temperature, CHCl₃ (100 mL) and H₂O (100 mL) were added. The organic layer was separated, dried, and evaporated. *N*-methyl-2-pyrrolidone was removed by distillation under reduced pressure. The residue was purified by column chromatography on silica gel (eluent; hexane : toluene = 1 : 2) to give 2-cyano-6-methoxynaphthalene (**1**, 0.81 g, 59% yield). Data for **1**: colorless powder; mp 107 °C; ^{1}H NMR (300 MHz, CDCl₃) δ 3.95 (s, 3 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 7.25 (dd, *J* = 8.9, 2.5 Hz, 1 H), 7.57 (dd, *J* = 8.3, 1.6 Hz, 1 H), 7.79 (d, *J* = 8.6 Hz, 2 H), 8.14 (d, *J* = 0.9 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, CDCl₃) δ 55.9, 106.1, 106.9, 119.7, 120.8, 127.2, 127.8, 127.9, 130.1, 133.8, 136.5, 160.0 ppm ; IR (KBr) 1266, 1622, 2221 (CN) cm^{-1}; MS (EI) *m/z* (relative intensity, %) = 140 (92), 183 (100, M$^+$).

*2.3 Preparation of trans-1-phenyl-2-(3,4,5-trimethoxyphenyl)cyclopropane (trans-**2c**)*

To a methanol (380 mL) solution of acetophenone (26.80 g) and 3,4,5-trimethoxybenzaldehyde (41.06 g) was added NaOH (0.55 g). The mixture was stirred at room temperature for 24 h. The collected precipitate by suction filtration is pure *trans*-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (39.07 g, 63% yield). To a part of the compound (38.08 g) were added hydrazine monohydrate (29.6 mL) and ethanol (375 mL). The solution was refluxed for 1.5 h. Ethanol and hydrazine were removed by distillation. KOH (1.40 g) was added. The mixture was heated to 170 °C and was stirred until evolution of N₂ gas ceased. After cooling to room temperature, benzene (300 mL) and H₂O (300 mL) were added. The organic layer was separated, dried, and evaporated. The crude mixture (29.86 g) contained *trans*- and *cis*-1-phenyl-2-(3,4,5-trimethoxyphenyl)cyclopropane (*trans*-**2c** and *cis*-**2c**, 84 : 16). Recrystallization from EtOH gave pure *trans*-**2c** (9.17 g, 25% yield).

Data for *trans*-**2c**: pale yellow solid; mp 76 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.43 (t, J = 7.4 Hz, 2 H), 2.13 (t, J = 7.3 Hz, 2 H), 3.82 (s, 3 H), 3.86 (s, 6 H), 6.37 (s, 2 H), 7.12-7.22 (m, 3 H), 7.24-7.34 (m, 2 H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.4, 28.2, 28.8, 56.3, 61.1, 102.9, 125.7, 125.8, 128.4, 136.2, 138.2, 142.3, 153.1 ppm; MS (EI) *m/z* (relative intensity, %) = 253 (70, M$^+$–MeO), 284 (100, M$^+$).

*2.4 Preparation of trans-1-phenyl-2-(2,4,6-trimethoxyphenyl)cyclopropane (trans-**2e**)*

To a methanol (80 mL) solution of acetophenone (5.03 g) and 2,4,6-trimethoxybenzaldehyde (8.18 g) was added NaOH (0.23 g). The mixture was stirred at 52 °C for 72 h. After cooling to room temperature, the solution was evaporated. Column chromatography on silica gel (eluent; AcOEt : toluene = 1 : 2) gave *trans*-1-phenyl-3-(2,4,6-trimethoxyphenyl)prop-2-en-1-one (8.97 g, 72% yield). To a part of the compound (4.03 g) were added hydrazine monohydrate (3.05 mL) and ethanol (43 mL). The solution was refluxed for 1.5 h. Ethanol and hydrazine were removed by distillation. KOH (0.28 g) was added. The mixture was heated to 170 °C and was stirred until evolution of N$_2$ gas ceased. After cooling to room temperature, benzene (150 mL) and H$_2$O (150 mL) were added. The organic layer was separated, dried, and evaporated. Column chromatography on silica gel (eluent; toluene) gave *trans*-1-phenyl-2-(2,4,6-trimethoxyphenyl)cyclopropane (*trans*-**2e**, 0.82 g, 21% yield). Data for *trans*-**2e**: yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.28-1.38 (m, 1 H), 1.42-1.50 (m, 1 H), 1.85-1.93 (m, 1 H), 2.22-2.30 (m, 1 H), 3.80 (s, 6 H), 3.80 (s, 3 H), 6.12 (s, 2 H), 7.11-7.22 (m, 3 H), 7.24-7.31 (m, 2 H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 16.7, 19.4, 24.8, 55.7, 56.1, 91.1, 110.5, 125.3, 126.2, 128.3, 144.3, 159.4, 160.2 ppm; MS (EI) *m/z* (relative intensity, %) = 253 (81, M$^+$–MeO), 284 (100, M$^+$).

2-5. General procedure for the photoreaction

A benzene (7 mL) solution containing 2-cyano-6-methoxynaphthalene (**1**, 38.4 mg, 0.03 mol/L) and *trans*-1-phenyl-2-(3,4,5-trimethoxyphenyl)cyclopropane (*trans*-**2c**, 59.8 mg, 0.03 mol/L) was placed in a Pyrex vessel and was degassed by Ar bubbling. The solution was photoirradiated by a 300 W high pressure mercury lamp at room temperature. The temperature of the solution was kept around room temperature by circulated cooling water during irradiation. Column chromatography on silica gel (eluent; AcOEt : hexane = 1 : 3) followed by HPLC (GPC) gave 1-(1-phenyl-3-(3,4,5-trimethoxyphenyl)propyl)-2-cyano-6-methoxynaphthalene (**3c**, 49.0 mg, 50% yield). Data for **3c**: colorless oil, ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.28-2.96 (m, 4 H), 3.75 (s, 6 H), 3.79 (s, 3 H), 3.90 (s, 3 H), 5.17 (dd, J = 9.2, 5.9 Hz, 1 H), 6.24 (s, 2 H), 7.04 (d, J = 9.3 Hz, 1 H), 7.12 (d, J = 2.6 Hz, 1 H), 7.16-7.32 (m, 5 H), 7.58 (d, J = 8.6 Hz, 1 H), 7.69 (d, J = 8.6 Hz, 1 H), 7.87 (d, J = 9.3 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 35.0, 35.2, 55.8, 56.2, 56.4, 61.1, 77.6, 105.4, 107.3, 119.8, 120.0, 126.6, 127.1, 127.4, 127.6, 127.8, 128.2, 128.6, 136.2, 137.2, 137.9, 142.5, 146.8, 153.0, 159.1 ppm; IR (neat) 1125, 2217 (CN), 2937 cm^{-1}; MS (EI) *m/z* (relative intensity, %) = 151 (15, C$_{10}$H$_5$CN$^+$), 182 (100, C$_{10}$H$_5$(OCH$_3$)CN$^+$), 467 (8, M$^+$).

3. Results and Discussion

Irradiation of a benzene solution containing equimolar amounts of 2-cyano-6-methoxynaphthalene (**1**) and *trans*-1-phenyl-2-(3,4,5-trimethoxyphenyl)cyclopropane (*trans*-**2c**) in a Pyrex vessel with a 300 W high pressure mercury lamp for 120 h gives rise to formation of the photoalkylation product **3c** in 50% isolated yield (Scheme 1, entry 4 in Table

1).   Cyclopropane substrates that contain a lower number of aromatic methoxy-substituents or a cyano group undergo photoalkylation sluggishly (entries 1, 2, and 5).   Unlike the 3,4,5-trimethoxyphenyl substituted-cyclopropane (*trans*-**2c**), the 2,4,6-trimethoxyphenyl substituted analog (*trans*-**2e**) reacts with **1** in an inefficient manner (entry 6).   Photoreactions of **1** with symmetrically substituted cyclopropanes (*trans*-**2f-h**) in benzene proceed to give the corresponding alkylation products **3f-h** in good yields (entries 7-9).   While other solvents, such as Et$_2$O, THF, and CH$_2$Cl$_2$, can be used for the photoreactions, the observed dependence of yield on solvent and the fact that alkylation reactions do not take place in acetonitrile (entry 13) indicates that nonpolar solvents lead to higher reaction efficiencies (entries 3, 10-13).   In all reactions, the recovered cyclopropanes **2** are mixtures of *cis* and *trans* isomers.

(insert Scheme 1 here)

(insert Table 1 here)

It is noteworthy that among the six possible sites on the naphthalene ring of **1**, monoalkylation takes place exclusively at the 1-position.   Proof that photoalkylation of **1** occurs at this site comes from the analysis of spectroscopic data for product **3c**.   The ^{1}H NMR spectrum of this substance contains two pairs of doublets at 7.58 and 7.69 ppm ($J = 8.6$ Hz), and 7.04 and 7.87 ppm ($J = 9.3$ Hz) and a pseudo-singlet at 7.12 ppm.   These resonances are ascribable to hydrogens at the respective C3-C4, C7-C8, and C5 positions of **3c** [35-39].   The assignment of the C-1 alkylated structures to the products of these processes is consistent with the X-ray crystallographic data obtained for a product previously reported to form in an analogous reaction of 2,3-dicyanonaphthalene [29].   The positions of phenyl and 3,4,5-trimethoxyphenyl groups in **3c** was determined by using fluorescence data (*vide infra*).

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The UV absorption spectra of benzene solutions of **1**, **3c**, **3g**, and **3h** (Figure 1) display absorption maxima at 335 nm (**1**) and 337 nm (**3c**, **3g**, and **3h**). The findings indicate that intramolecular charge transfer in the ground states of **3** is negligible. On the other hand, typical intramolecular exciplex emission bands are observed in the fluorescence spectra of **3** (Figure 2) at maxima of 447 nm (**3c**), 426 nm (**3g**), and 440 nm (**3h**), with a monomer emission band of naphthalene at maximum of 361 nm in the case of **3c**. Since compounds containing electron-rich and electron-poor aromatic moieties connected by a three carbon tether typically show intramolecular exciplex emission [40,41], the assignment of structures of **3** in which the methoxy-substituted phenyl groups are located at the terminal position of the propyl-tether is reasonable.

(insert Figure 1 here)

(insert Figure 2 here)

Photoreaction of **1** with *trans*-**2c** does not occur when excess amounts of triplet photosensitizers, such as benzophenone and Michler's ketone, are employed (entries 14 and 15). Furthermore, the fluorescence of **1** in benzene is efficiently quenched by addition of *trans*-**2c** (Figure 3). Moreover, emission from an intermolecular exciplex between **1** and *trans*-**2c**, with an isoemissive point at 401 nm, steadily increases upon addition of *trans*-**2c**. From a Stern-Volmer plot of the fluorescence quenching data, the rate constant (k_q) for quenching of the singlet excited state of **1** by *trans*-**2c** is calculated to be 5.1 x 10^9 $M^{-1}s^{-1}$ ($k_q\tau$ = 45 M^{-1}, τ(**1**) = 8.9 ns). *Trans*-**2a** also quenches the fluorescence of **1** but in this case, the quenching rate constant is lower ($k_q\tau$ = 6.2 M^{-1}, k_q = 6.7 x 10^8 $M^{-1}s^{-1}$) and no intermolecular exciplex emission is observed.

(insert Figure 3 here)

Based on the observations summarized above, we propose that alkylation reaction takes place by mechanism shown in Scheme 2 (exemplified by the photoreaction of **1** with *trans-***2c**). The proposed pathway followed in the photoreaction carried out in a benzene solution proceeds via the intermediacy of a singlet exciplex. The structure of the exciplex is governed by the maximization π-π overlap of the aromatic rings and the minimized energy alignment of the dipoles of each component. An exciplex, in which the dipoles of both molecules are aligned in opposite directions, should be favored [42]. Since the exciplex is likely to possess charge transfer character, nucleophilic attack of the C1 carbon of the naphthalene ring on cyclopropyl group results in C–C bond formation and cyclopropane ring opening to give a 1,5-biradical. Ensuing intramolecular hydrogen transfer forms **3c**. From the facts that number of methoxy substitution in **2** accelerates the reaction and the presence of cyano group in **2** retards the reaction, formation of exciplex with appropriate donor-acceptor interaction might be required for the photoalkylation. A possible reason for why **3c** is not formed and *cis-trans* photoisomerization of **2c** takes place when reactions are conducted in acetonitrile is that single electron transfer from **2c** to **1** takes place efficiently in this more polar medium. Back electron transfer in the ion radicals formed in this manner then occurs to give a mixture containing **1**, *trans-***2c**, and *cis-***2c** [26,43-47].

(insert Scheme 2 here)

4. Conclusion

In conclusion, regioselective photoalkylation of naphthalene derivative **1** by cyclopropanes *trans-***2** takes place in good yields. The excellent regioselectivity observed in these processes is attributable to favorable dipole-dipole alignment in singlet exciplexes that

serve as intermediates in the reaction pathway.

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Captions

Figure 1.   UV absorption spectra of **1**, **3c**, **3g**, and **3h** (1.0×10^{-4} M in benzene).

Figure 2.   Fluorescence spectra of **3c**, **3g**, and **3h** (1.0×10^{-4} M in benzene, $\lambda_{ex} = 337$ nm).

Figure 3.   Fluorescence quenching of **1** by *trans*-**2c**. $\lambda_{ex} = 335$ nm, [**1**] = 1.0×10^{-4} M in benzene, [*trans*-**2c**] = $0–2.5 \times 10^{-2}$ M.

Scheme 1.   Photoalkylation of **1** by *trans*-**2a-h**

Scheme 2.   Reaction mechanism for the regioselective photoalkylation of **1** by *trans*-**2c**.

Table 1.   Photoalkylation of 2-cyano-6-methoxynaphthalene (**1**) by *trans*-1,2-diarylcyclopropanes (*trans*-**2**)

Scheme 1. Photoalkylation of **1** by *trans*-**2a-h**
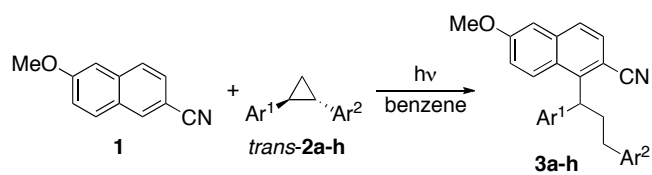
a: Ar^1 = Ar^2 = Ph

b: Ar^1 = Ph, Ar^2 = 4-MeOC$_6$H$_4$

c: Ar^1 = Ph, Ar^2 = 3,4,5-(MeO)$_3$C$_6$H$_2$

d: Ar^1 = 4-NCC$_6$H$_4$, Ar^2 = 3,4,5-(MeO)$_3$C$_6$H$_2$

e: Ar^1 = Ph, Ar^2 = 2,4,6-(MeO)$_3$C$_6$H$_2$

f: Ar^1 = Ar^2 = 4-MeOC$_6$H$_4$

g: Ar^1 = Ar^2 = 3,4-(MeO)$_2$C$_6$H$_3$

h: Ar^1 = Ar^2 = 3,4,5-(MeO)$_3$C$_6$H$_2$

Table 1. Photoalkylation of 2-cyano-6-methoxynaphthalene (**1**) by *trans*-1,2-diarylcyclopropanes (*trans*-**2**)

Entry	Compound **2**	Ar^1	Ar^2	Solvent[b]	Dielectric constant of solvent	Additive	Irradiation time / h	Yield[c] / %
1	*trans*-**2a**	Ph	Ph	benzene	2.27	none	60	< 1
2	*trans*-**2b**	Ph	4-MeOC$_6$H$_4$	benzene	2.27	none	60	7
3	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	none	60	31
4	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	none	120	50[d]
5	*trans*-**2d**	4-NCC$_6$H$_4$	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	none	60	0
6	*trans*-**2e**	Ph	2,4,6-(MeO)$_3$C$_6$H$_2$	benzene	2.27	none	60	10
7	*trans*-**2f**	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	benzene	2.27	none	60	21
8	*trans*-**2g**	3,4-(MeO)$_2$C$_6$H$_3$	3,4-(MeO)$_2$C$_6$H$_3$	benzene	2.27	none	60	53
9	*trans*-**2h**	3,4,5-(MeO)$_3$C$_6$H$_2$	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	none	60	54
10	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	Et$_2$O	4.22	none	60	21
11	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	THF	7.39	none	60	16
12	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	CH$_2$Cl$_2$	8.9	none	60	3
13	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	CH$_3$CN	37.5	none	60	0
14	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	benzophenone[e]	60	0
15	*trans*-**2c**	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$	benzene	2.27	Michler's ketone[e]	60	0

[a] [**1**] = [*trans*-**2**] = 0.03 mol/L. Irradiated to solution in a Pyrex vessel by a 300 W high pressure mercury lamp.

[b] 7 mL.

[c] Yields were determined by ^{1}H NMR.

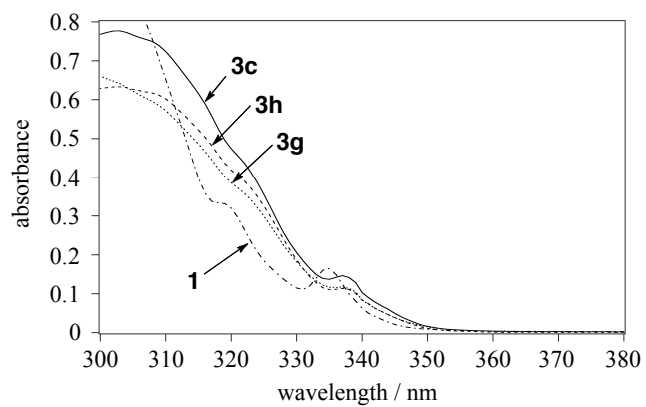[d] Isolated yield.

[e] 5 equiv based on **1**.

Figure 1. UV absorption spectra of **1**, **3c**, **3g**, and **3h** (1.0 x 10^{-4} M in benzene).
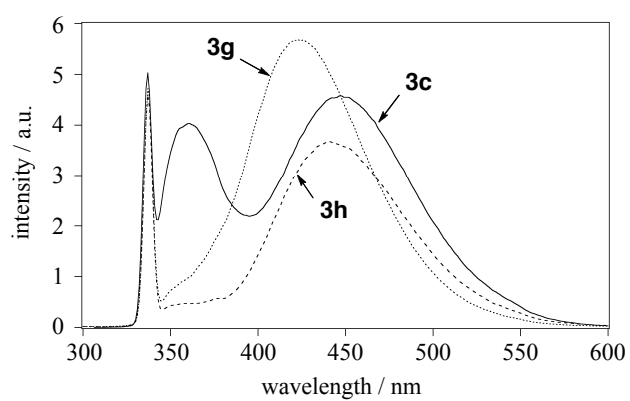
Figure 2. Fluorescence spectra of **3c**, **3g**, and **3h** (1.0 x 10^{-4} M in benzene, λ_{ex} = 337 nm).
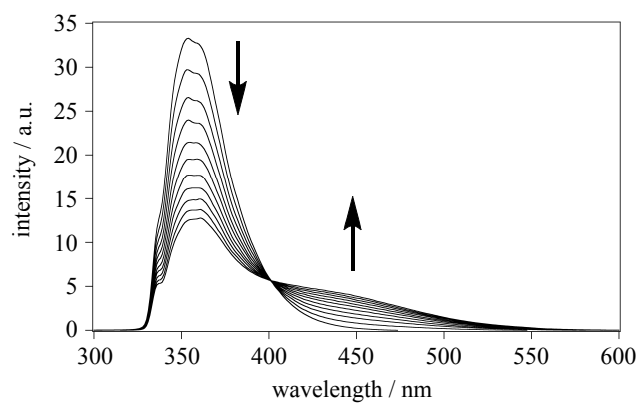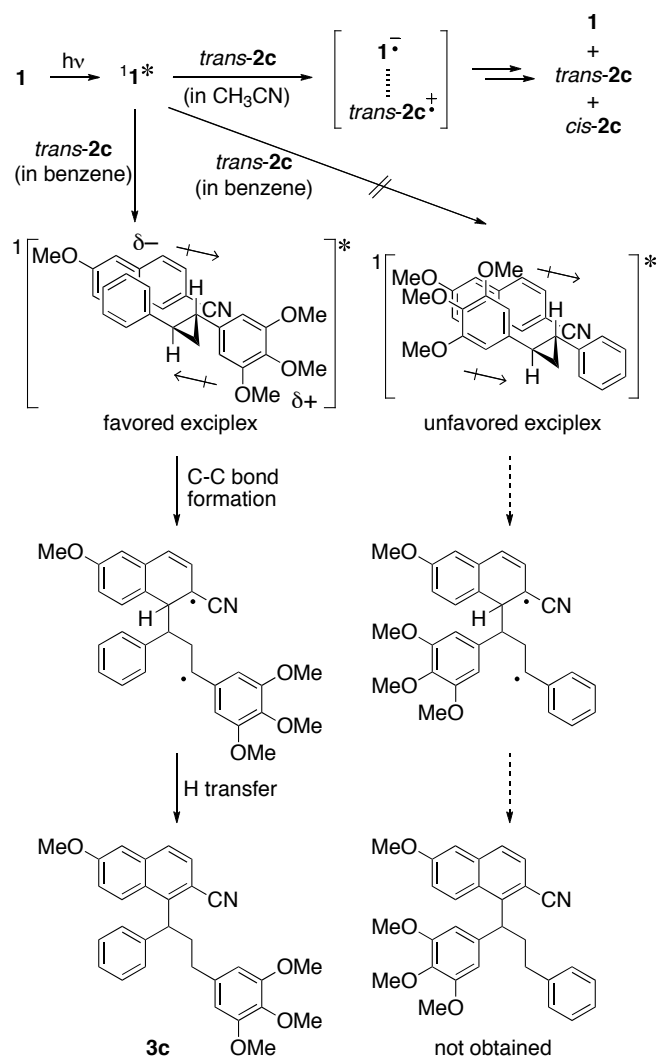
Figure 3. Fluorescence quenching of **1** by *trans*-**2c**. λ_{ex} = 335 nm, [**1**] = 1.0 x 10^{-4} M in benzene, [*trans*-**2c**] = 0–2.5 x 10^{-2} M.

Scheme 2. Reaction mechanism for the regioselective photoalkylation of **1** by *trans*-**2c**.