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A Three-Component Reaction by Photoinduced Electron Transfer Mechanism with *N*-Protected Pyrroles as Neutral Carbon Nucleophiles

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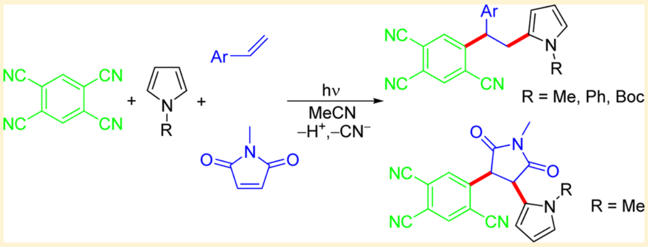
Supporting Information

ABSTRACT: A new photoinduced three-component reaction between a cyanoarene, an alkene and an *N*-protected pyrrole has been developed. This reaction extended the scope of the photo-NOCAS reaction by introducing pyrrole as a neutral carbon-centered nucleophile. The cyanoarenes used include tetracyanobenzene (TCB), 2,3,5,6-tetrafluoro-1,4-dicyanobenzene (TFDCB) and 1,4-dicyanobenzene (DCB). *N*-Methyl, *N*-phenyl and *N*-Boc pyrroles are suitable nucleophiles in the reaction. Taking advantage of the strong electron acceptor ability of the singlet excited TCB, a wide range of alkenes, including the highly electron deficient 4-fluoro-, 4-chloro-, 2,3,4,5,6-pentafluorostyrenes and *N*-methylmaleimide take part in this reaction, leading to the simultaneous 1,2-diarylation of the alkene and the regioselective 2-alkylation of the pyrrole ring via sequential formation of two new C−C bonds between the three reactants.



■ INTRODUCTION

Multicomponent reactions (MCRs) are important in organic synthesis because they allow rapid and direct access of molecular complexity in one-pot procedures from simple starting materials.[1] A vast array of thermal MCRs have been developed in recent years. In sharp contrast, only a limited number of photoinduced MCRs have been reported,[2−4] of which a large part belongs to the photo-NOCAS (nucleophile-olefin combination, aromatic substitution) reaction.[2] In this type of reactions, olefin cation radical generated via photoinduced electron transfer (PET) with a singlet excited state cyanoarene is trapped by a nucleophile (nucleophile-olefin combination), and the formed olefin-nucleophile addition radical then combines with the cyanoarene anion radical followed by extrusion of a cyanide anion (aromatic substitution) to give the product. Despite the obvious mechanistic and synthetic importance, the photo-NOCAS reaction has so far suffered from its limited reaction scope, a fact that deters its application in organic synthesis.[2] 1,4-Dicyanobenzene (DCB) is the main cyanoarene used, for which only aliphatic olefins are thought to be suitable substrates because the nucleophile-olefin radicals derived from aromatic olefins are so electrophilic as to accept an electron from the cyanoarene anion radical to regenerate the neutral cyanoarene, thus obviating the three-component reaction.[5] As for the nucleophile, alcohols,[6] amines[7] and fluoride[8] are commonly used, while cyanide anion[9] was the only carbon-centered nucleophile tested. Recently, photo-NOCAS reactions using the conjugate base of malononitrile and other active methylene compounds have been reported.[10] At the same time, we reported the application of the enol form of a series of 1,3-dicarbonyl compounds as neutral nucleophile in the photoinduced tetracyanobenzene (TCB)-olefin-nucleophile reactions.[11] These results significantly expanded the range of nucleophiles in the photo-NOCAS reaction in particular, and in PET reactions in general, and increased their synthetic merit by enabling them for C−C bond formation between the reactants. We also showed that,[11] with TCB as the electron acceptor, aromatic olefins such as styrene derivatives are suitable olefin substrates because in this case, the nucleophile-olefin radical as a *β*-alkylated benzyl radical (reduction potential ∼ −1.60 V, SCE[12]) is not electrophilic enough to accept an electron from the TCB anion radical (oxidation potential −0.66 V, SCE[13]) efficiently, and as a result, radical pair combination of the olefin-nucleophile radical with the TCB anion radical followed by

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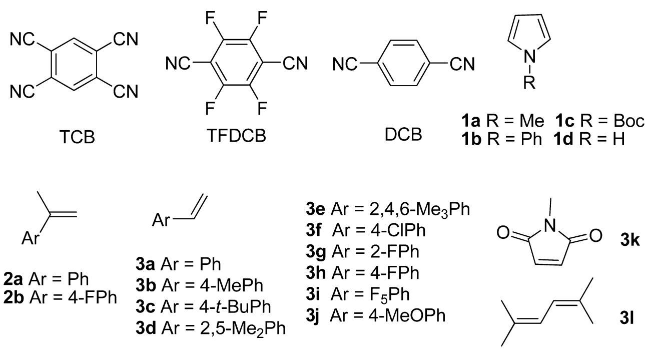
elimination of cyanide anion to give the three-component product predominates. Similarly, in the absence of added nucleophile, dimeric olefin radical formed by trapping of the olefin radical cation by a neutral olefin followed by deprotonation is not electrophilic enough to undergo efficient electron transfer from the TCB anion radical, and in this case, radical pair combination of the dimeric olefin radical with TCB anion radical followed by elimination of cyanide anion to give the olefin dimerization, aromatic substitution (ODAS) product takes place preferentially,[14] with the SET from the TCB anion radical to the dimeric olefin radical followed by protonation to lead to olefin dimerization as a side reaction.[15] With the aim of developing new photo-MCR and explore the application of new type of nucleophiles in PET reactions, we wish to examine the use of further carbon-centered nucleophiles in these reactions.

The pyrrole ring is widely found in a number of natural products[16] and in a variety of optoelectric functional materials.[17] Pyrrole derivatives are also important starting materials in organic synthesis.[18] Therefore, regioselective alkylation of the pyrrole ring has long been an interesting topic in organic synthesis. However, as a highly π-excessive compound, pyrrole is notoriously unstable under the actions of Brönsted and Lewis acids, and upon light and heat exposure in the presence of air. As a result, pyrrole cannot withstand the conventional harsh Friedel−Crafts alkylation reaction conditions, and the search for methods to achieve regioselective alkylation of the pyrrole ring under mild reaction conditions has been drawing much recent research efforts.[19] We repot here the use of several *N*-protected pyrroles as neutral carbon nucleophiles in the photoinduced cyanoarene-olefin-nucleophile three-component reactions, which leads to a concomitant formation of two new C−C bonds between the three reactants, resulting in regioselective 2-alkylation of the pyrrole ring and the 1,2-diarylation of the olefins under mild, metal-free conditions.

■ RESULTS AND DISCUSSION

The cyanoarenes, olefins and pyrroles applied in the reactions are shown in Chart 1.

Chart 1



Photoinduced reactions of TCB, α-methylstyrene **2a** and *N*-methylpyrrole **1a** in different solvents were first examined (entries 1−8 in Table 1). The results show that acetonitrile or dichloromethane is the best choice in which the reaction goes comparatively smoothly and cleanly, while the reaction is sluggish in chloroform and acetone probably due to the poor solubility of TCB, and could not proceed at all in the nonpolar hexane. Therefore, acetonitrile was chosen as the solvent. The initial concentration of TCB has a significant effect on the conversion and product yield in the reaction (entries 8 vs 11 and entries 12 vs 13). Lower initial TCB concentration led to higher conversion and gave higher yield of products. Addition of biphenyl (BP) as a cosensitizer[20] resulted in significant increase in the TCB conversions, but has no significantly beneficial effect to the product yield, except at lower conversion (entries 12, 14 and 15). From a practical standpoint, an initial TCB concentration of 0.025 mol/L was chosen for all the following reactions.

The photoreaction of TCB (0.025 mol/L) and α-methylstyrene (0.1 mol/L) in the presence of *N*-methylpyrrole **1a** (0.2 mol/L) in acetonitrile gave the three-component product **4a** in 46% isolated yield together with minor amount of two diastereomeric products **5a** (3%) and **6a** (3%) derived from the olefin dimerization, aromatic substitution (ODAS) reaction[14] (Chart 2).[21] The structures of these products are based on spectral (IR, ^{1}H and ^{13}C NMR and MS) and analytical data and are unambiguously established by X-ray crystallographic analysis of **4a** and **6a** (see Supporting Information). Is is also noted that in this and the following reactions of TCB with alkenes **2** and **3**, and in the photoreactions of TFDCB with **3b**, **3c** and **3d** (vide infra), small and various amounts of the alkene dimers[14,15] were also formed. They constitute the low-polarity fraction in the chromatographic separation and were eluted out as mixtures of isomers by pure petroleum ether. Because of the difficulty in separating them, the isomers were not quantified.

We have further found that, a wide range of alkenes such as 4-fluoro-α-methylstyrenes **2b**, styrenes **3a**−**3h** and the cyclic alkene maleimide **3k** also take part in this reaction. In all cases, the TCB-olefin-pyrrole three-component product **4b**, **7a**−**7h** and **7k**, respectively, is the main or sole product, and the ODAS products **5b** and **8a**−**8d** is only formed in some cases as minor products (Chart 2). The steric structures of **7k** and **8a** are also established by X-ray crystallographic analyses (see Supporting Information).

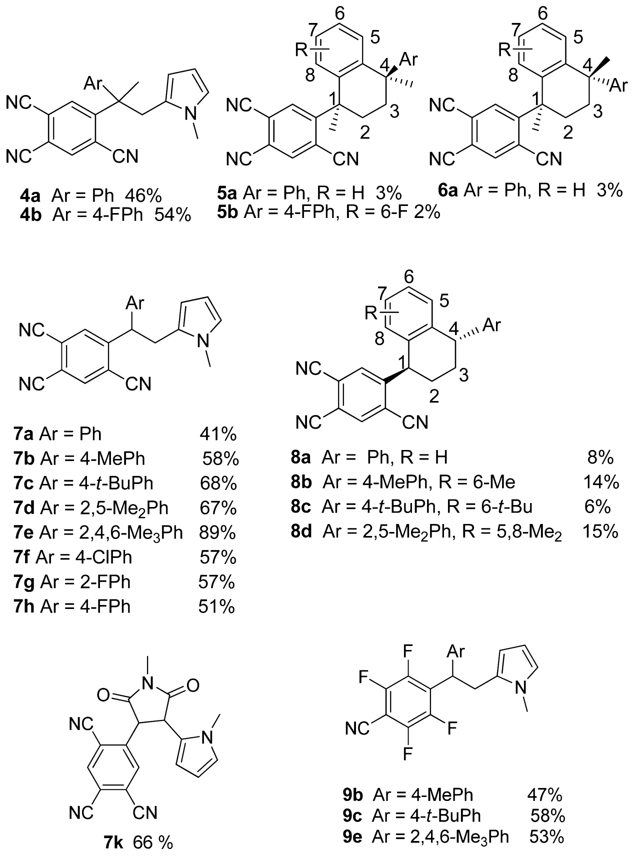
Single electron transfer (SET) processes of singlet excited TCB[13] with *N*-methylpyrrole (**1a**) and with the alkenes are both possible thermodynamically (vide infra), however, a control experiment showed that irradiation of TCB with **1a** resulted in no net chemical reactions between them and both reagents were essentially not consumed, indicating that back electron transfer in the formed ion radical pair prevails. At the same time, it is known that photolysis of TCB with styrene derivatives leads to ODAS reactions between the two.[14] Possible mechanism for the three-component reaction is therefore proposed in Scheme 1 with the reaction of styrene as an example. SET between singlet excited TCB and the ground state olefin results in the formation of the ion radical pair **A**, where the olefin cation radical is trapped by pyrrole and by the neutral olefin as nucleophiles competitively. The pyrrole trapping takes place regioselectively at its more nucleophilic C-2 atom,[19,22] leading to an anti-Markovnikov addition of the pyrrole to the styrene cation radical to give the cation radical **B**, which combines with the TCB anion radical followed by deprotonation and extrusion of a cyanide anion to give product **7a**.[23] The olefin cation radical can also be trapped to a minor extent by the neutral olefin as a weak nucleophile[24] to give the dimer cation radical **C**. Intramolecular cyclization in **C** leading to **D** followed by combination with the TCB anion radical and elimination of hydrogen cyanide affords products **8a**.

Table 1. Standardization of Reaction Conditions

entry	TCB concentration mol/L	molar ratio of reactants (TCB:**2a**:**1a**)	reaction time/h	solvent	conversion[a] /%	yield (**4a**)[a] /%
1	0.025	1:4:8	15	benzene	25	8
2	0.025	1:4:8	15	*n*-hexane	0	0
3	0.025	1:4:8	15	dichloromethane	68	48
4	0.025	1:4:8	15	acetone	32	14
5	0.025	1:4:8	15	chloroform	17	3
6	0.025	1:3:4	15	acetonitrile	48	39
7	0.025	1:3:6	15	acetonitrile	52	50
8	0.025	**1:4:8**	**15**	**acetonitrile**	**60**	**58**
9	0.025	1:2:6	15	acetonitrile	53	48
10	0.025	1:4:10	15	acetonitrile	65	45
11	0.01	1:4:8	8	acetonitrile	88	69[b]
12	0.025	1:4:8[c]	15	acetonitrile	52	58[d]
13	0.015	1:4:8[c]	8	acetonitrile	86	66[d]
14	0.025	1:4:8[e]	12	acetonitrile	84	56[d]
15	0.025	1:4:8[e]	8	acetonitrile	61	75[d]

[a] Determined by HPLC (external standard method). [b] Isolated yield. [c] The photoinduced reaction was carried out using TCB with **3b** and **1a**. [d] Isolated yield for compound **7b**. [e] The photoinduced reaction was carried out using TCB (0.025 M) with BP (0.05 M), **3b** (0.1 M) and **1a** (0.2 M).

Chart 2



It is noteworthy that taking advantage of the exceedingly strong electron acceptor ability of the singlet excited TCB,[13] even the highly electron deficient olefins as 4-chloro- and 4-fluoro- styrenes (**3f** and **3h**)[25] and *N*-methylmaleimide (**3k**)[26] take part in the reaction to give the three-component product in moderate yield. Also, in these cases, because of the low nucleophilicity of the neutral olefin, the ODAS byproduct is not formed in appreciable amount.

Photoinduced reactions of 2,3,5,6-tetrafluoro-1,4-dicyanobenzene (TFDCB) with **3b**, **3c** and **3e** in the presence of **1a** similarly gave **9b**, **9c** and **9e**, respectively as products (Chart 2).

N-phenylpyrrole **1b** performs well in this kind of photoreactions to give the corresponding three-component products **10b**, **10c**, **10d**, **10j** and **11b** in high yield, together with small amount of the ODAS products **8b**–**8d** and **5b**, respectively (Chart 3). Nevertheless, we curiously found that, reaction of the unsubstituted styrene **3a** itself with TCB and **1b** under same conditions afforded the ODAS product **8a** as main product without significant amount of three-component product. An inspection of the favorable conformations for the olefin-pyrrole cation radical **B** or radical **E** (Scheme 1) revealed possible reason for this seemingly strange results. Therefore, a DFT-B3LYP-6-31+G(d,p) calculation[27] of the low energy conformations for **B** (R = Ph) and **E** (R = Ph) was carried out and the results show that for **E**, the minimum energy conformation is stabilized by partial π–π stacking interaction between the two phenyls from styrene and the pyrrole, while for **B**, there is also a low energy conformation with similar π–π stacking between the two phenyls (Figure 1). However, radical pair combination of **B** (or **E**) in this conformation with the TCB anion radical is impeded by steric hindrance between the C–H bond at the β-carbon atom and the tetracyanobenzene ring (**H** in Figure 1). As a result, **B** may revert to the styrene cation radical and pyrrole in the reversible addition process between the two, or reverts to neutral styrene and *N*-phenyl pyrrole after accepting an electron from TCB anion radical to form **G** (Scheme 1), and radical pair combination of **B** with TCB anion radical leading to the three-component product competes unfavorably with that between **D** (or **F**) with TCB anion radical giving the ODAS product. The preferential reversion of **B** to styrene cation radical and pyrrole or to the starting alkene and pyrrole after accepting an electron may also explain why two-component products derived from side reaction of **B** were not observed. Meanwhile, for the ring substituted styrenes **3b**–**3d** and **3j**, steric hindrance of the ring substituent hampers π–π stacking interaction between the phenyls, and **B** and **E** may engage in combination with TCB anion radical in sterically more favorable conformations.

N-*t*-Butyloxycarbonylpyrroles (*N*-Boc-pyrroles) are important building blocks in the synthesis of pyrrole- and pyrrolidine-

Scheme 1. Possible Mechanism of the Photoreactions between TCB, Pyrrole and Styrene

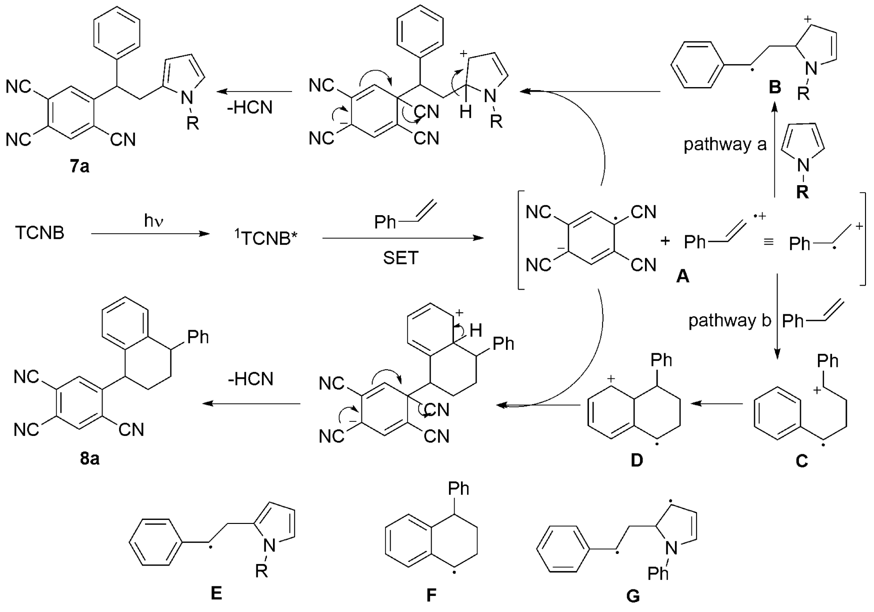
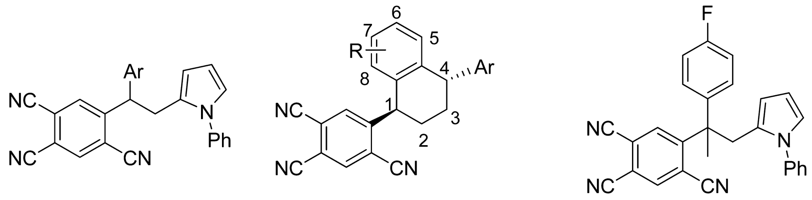


Chart 3



10b Ar = 4-MePh 78%
10c Ar = 4-*t*-BuPh 85%
10d Ar = 2,5-Me_2Ph 80%
10j Ar = 4-MeOPh 65%

8b Ar = 4-MePh, R = 6-Me 3%
8c Ar = 4-*t*-BuPh, R = 6-*t*-Bu 5%
8d Ar = 2,5-Me_2Ph, R = 5,8-Me_2 3%

11b 65% **5b** 2%

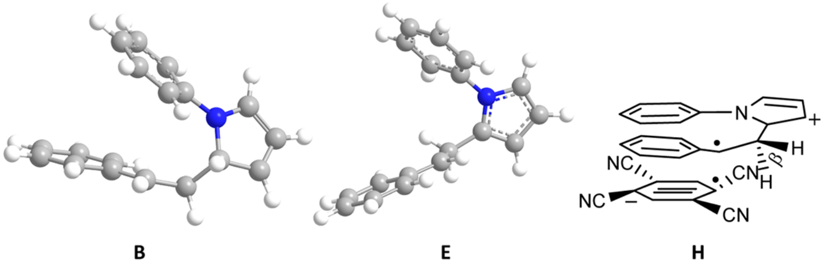
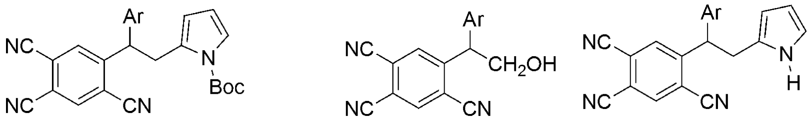


Figure 1. Low energy conformation of **B**, **E** and steric hindrance for combination of **B**, **E** with TCB anion radical (**H**).

Chart 4



12a Ar = Ph 64%
12c Ar = 4-t-BuPh 42%
12h Ar = 4-FPh 79%
12i Ar = F_5Ph 33%

8a 2%
8c 9%

13 Ar = F_5Ph 54%

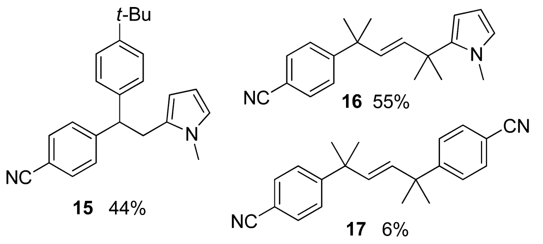
14 Ar = 4-t-BuPh, 62%
8c 2%

containing compounds, by virtue of the ease of installation and removing of the Boc-protecting group and their stability under many types of reaction conditions.[28,29] Therefore, photo-induced reactions of TCB with alkene and *N*-Boc pyrrole **1c** were investigated. These reactions proceeded smoothly to give products **12** along with minor amount of **8** in some cases (Chart 4). Again, for the more electron deficient alkenes **3h** and **3i**, the ODAS products were not formed because of the low nucleophilicity of the neutral alkene. It is interesting to note that even 2,3,4,5,6-pentafluorostyrene **3i** takes part in the reaction. To lend more insight into the reaction mechanism, a control experiment was carried out where irradiation of TCB (0.025 mol/L) and pentafluorostyrene (0.1 mol/L) in acetonitrile/water (97:3, V/V) afforded the water-trapping product **13** in 54% yield. This indicates that PET process between the singlet excited TCB and pentafluorostyrene indeed takes place.

The application of the unprotected pyrrole **1d** in the reaction with TCB and the alkenes under similar conditions is also tested. Reactions are usually sluggish to lead to low conversion upon lengthy irradiation and give complicated products. The only exception is for **3c**, where product **14** can be isolated in 62% yield along with the ODAS product **8c** (2%) (Chart 4).

To further extend the reaction scope in regard to the electron acceptors, photoreactions of 1,4-dicyanobenzene (DCB) with the aromatic alkene **3c** and the aliphatic alkene **3l** in the presence of **1a** were conducted, respectively (Chart 5). The reaction with **3c** gave the normal product **15**, while for **3l**, the three-component product **16** was formed together with a two-component (DCB:alkene = 2:1) product **17** (For crystallographic structure, see Supporting Information), which was probably formed by trapping of the formal distonic alkene cation radical **I** at its two termini by two DCB anion radicals, respectively (Scheme 2).

Chart 5



■ CONCLUSION

In summary, a new photoinduced three-component reaction of a cyanoarene with an alkene in the presence of an *N*-protected pyrrole as a neutral carbon nucleophile has been developed. A wide range of alkenes, including some with high oxidation potential can take part in the reaction. This reaction leads to the regioselective 2-alkylation of the pyrrole and the 1,2-diarylation of the alkene concomitantly via sequential formation of two new C−C bonds between the three reactants. The use of pyrrole as a neutral carbon-centered nucleophile extended the reaction scope in the photo-NOCAS reaction and may find further applications in other PET reactions.

■ EXPERIMENTAL SECTION

General Methods. All reagents were used without further purification. All solvents were dried according to standard procedures. Melting points are uncorrected. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 400, 376, and 100 MHz, using $CDCl_3$ as solvent. IR spectra were taken with a FT-IR spectrometer. Mass spectra were obtained using ESI techniques. For X-ray crystallographic analysis, the X-ray diffraction intensities and the unit cell parameters were determined on a CCD diffractometer employing graphite-monochromated (Mo Kα) radiation (λ = 0.71073 Å).

General Procedures for the Preparative Photolysis of TCB with Alkene and Pyrrole Derivative. The light source was a medium-pressure mercury lamp (500 W) in a glass, cooling water jacket to cut off light of wavelengths shorter than 300 nm. The solution of TCB, an alkene and a pyrrole derivative in MeCN was purged with argon for 15 min and then irradiated under continuous argon purging. The reaction course was monitored by TLC. After the reaction, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate as eluents (gradient elution). The product yields are based on consumed cyanoarene.

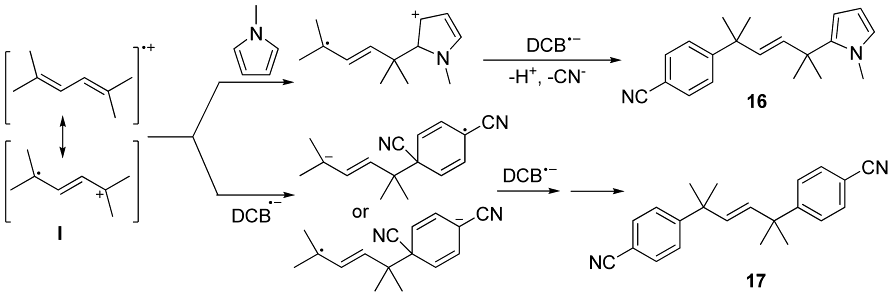
Photolysis of TCB with α-Methylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), α-methylstyrene (1.418 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 58% conversion of TCB. The solvent was removed and the residue was separated as mentioned above to give **4a** (280 mg, 46%) and **5a** (20 mg, 3%) and **6a** (20 mg, 3%).

*5-(1-(1-Methyl-1H-pyrrol-2-yl)-2-phenylpropan-2-yl)benzene-1,2,4-tricarbonitrile (**4a**).* Yellow solid from chloroform/petroleum ether: mp 177 °C; IR (KBr) ν 2927, 2236, 1577, 1490, 1416, 802, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.80 (s, 3H), 3.17 (s, 3H), 3.48 (d, 1H, J = 14.4 Hz), 3.68 (d, 1H, J = 14.4 Hz), 5.25 (dd, 1H, J = 3.4, 1.8 Hz), 5.95 (t, 1H, J = 3.2 Hz), 6.45 (dd, 1H, J = 2.4, 2.0 Hz), 7.02−7.04 (m, 2H), 7.32−7.34 (m, 3H), 7.96 (s, 1H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.6, 33.6, 36.0, 49.1, 107.1, 109.6, 113.5, 114.4, 114.6, 114.7, 118.5, 118.6, 122.4, 126.0, 127.5, 127.6, 128.8, 133.3, 138.9, 144.9, 158.6; ESI-MS m/z [M + H]$^+$ Calcd for $C_{23}H_{18}N_4$ 351.16, found 351.15. EA Found: C 78.80, H 5.22, N 15.98. Requires: C 78.83, H 5.18, N 15.99.

X-ray Structure Analysis. $C_{23}H_{18}N_4$ M = 350.41. Triclinic, space group $P\bar{1}$, a = 7.943(2), b = 10.527(3), c = 11.702(4) Å, α = 84.179(4), β = 86.210(4), γ = 79.569(4)°, V = 956.2(5) Å, Z = 2, D_c = 1.217 g cm^{-3}, $F(000)$ = 368.0, absorption coefficient 0.074 mm^{-1}, scan range for data collection 1.75 ≤ θ ≤ 25.50°, 6989 measured reflections, 3506 independent reflections, 1869 reflections with $I > 2\sigma(I)$, R_{int} = 0.0478, 247 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0522, wR_2 (F^2) = 0.1373.

*cis-5-(1,4-Dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)-benzene-1,2,4-tricarbonitrile (**5a**).* White solid from petroleum ether/ethyl acetate: mp 224 °C; IR (KBr) ν 2923, 2236, 1559, 1413, 1137, 775, 641 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.76 (s, 3H), 1.81 (dd, 1H, J = 10.4, 2.8 Hz), 1.94−1.99 (m, 1H), 2.07 (s, 3H), 2.10−2.17 (m, 1H), 2.33−2.39 (m, 1H), 7.01 (d, 1H, J = 7.6 Hz), 7.14−7.19 (m, 4H), 7.25−7.31 (m, 4H), 7.55 (s, 1H), 8.06 (s, 1H); ^{13}C NMR

Scheme 2. Formation of Products 16 and 17



($CDCl_3$, 100 MHz) δ 29.3, 29.7, 35.5, 37.4, 43.3, 45.6, 113.5, 114.2, 114.3, 116.0, 116.3, 118.5, 126.1, 127.0, 127.3, 128.1, 128.2, 128.3, 131.0, 135.7, 139.8, 140.2, 144.6, 150.2, 160.4; ESI-MS m/z [M − H]$^-$ Calcd for $C_{27}H_{21}N_3$ 386.17, found 386.27. EA Found: C 83.66, H 5.51, N 10.83. Requires: C 83.69, H 5.46, N 10.84.

trans-5-(1,4-Dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2,4-tricarbonitrile (***6a***). White solid from petroleum ether/ethyl acetate: mp 256−257 °C; IR (KBr) ν 2923, 2240, 1570, 1416, 1134, 771, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.81−1.84 (m, 2H), 1.87 (s, 3H), 1.98 (s, 3H), 2.24−2.29 (m, 1H), 2.43 (t, 1H, J = 11.2 Hz), 6.63 (d, 1H, J = 7.2 Hz), 7.00 (dd, 1H, J = 4.6, 1.2 Hz), 7.10−7.16 (m, 1H), 7.18−7.24 (m, 4H), 7.28−7.38 (m, 2H), 7.98 (s, 1H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 29.9, 35.9, 37.6, 43.3, 45.4, 113.6, 114.4, 115.0, 117.6, 118.9, 126.0, 127.0, 127.2, 127.4, 127.9, 128.2, 130.9, 133.7, 139.6, 140.8, 144.7, 151.2, 160.8; ESI-MS m/z [M − H]$^-$ Calcd for $C_{27}H_{21}N_3$ 386.17, found 386.22. EA Found: C 83.67, H 5.48, N 10.85. Requires: C 83.69, H 5.46, N 10.84.

X-ray Structure Analysis. $C_{27}H_{21}N_3$ M = 387.47. Monoclinic, space group $P2(1)/c$, a = 9.0828(13), b = 8.2753(12), c = 28.513(4) Å, α = 90, β = 97.494(3), γ = 90°, V = 2124.8(5) Å, Z = 4, D_c = 1.211 g cm^{-3}, $F(000)$ = 816.0, absorption coefficient 0.072 mm^{-1}, scan range for data collection 1.44 ≤ θ ≤ 26.00°, 11769 measured reflections, 4095 independent reflections, 2373 reflections with $I > 2\sigma(I)$, R_{int} = 0.0529, 273 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0537, wR_2 (F^2) = 0.1583.

Photolysis of TCB with 4-Fluoro-α-methylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-fluoro-a-methylstyrene (1.634 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 67% conversion of TCB. The solvent was removed and the residue was separated to give **4b** (400 mg, 54%) and **5b** (17 mg, 2%).

5-(2-(4-Fluorophenyl)-1-(1-methyl-1H-pyrrol-2-yl)propan-2-yl)-benzene-1,2,4-tricarbonitrile (***4b***). Yellow solid from petroleum ether/ethyl acetate: mp 198 °C; IR (KBr) ν 2924, 2236, 1574, 1447 1163, 832, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 3.29 (d, 1H, J = 13.6 Hz), 3.52 (s, 3H), 3.62(d, 1H, J = 13.6 Hz), 5.21 (t, 1H, J = 2.0 Hz), 6.01 (s, 1H), 6.34 (t, 1H, J = 2.4 Hz), 7.03−7.06 (m, 4H), 7.84 (s, 1H), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1, 36.1, 37.7, 48.3, 109.6, 114.3, 114.5, 114.8, 115.4, 115.6, 116.7, 118.3, 121.2, 121.7, 129.2, 129.3, 133.4, 138.8, 158.9; ESI-MS m/z [M + H]$^+$ Calcd for $C_{23}H_{17}FN_4$ 369.15, found 369.15. EA Found: C 74.97, H 4.72, N 15.17. Requires: C 74.98, H 4.65, N 15.21.

cis-5-(6-Fluoro-4-(4-fluorophenyl)-1,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2,4-tricarbonitrile (***5b***). White solid from petroleum ether/ethyl acetate: mp 228 °C; IR (KBr) ν 2927, 2236, 1576, 1442, 1164, 834, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.73 (s, 3H), 1.81−1.85 (m, 1H), 1.96−2.00 (m, 1H), 2.02 (s, 3H), 2.05−2.08 (m, 1H), 2.29−2.35 (m, 1H), 6.84 (dd, 1H, J = 10.4, 2.4 Hz), 6.95−7.00 (m, 4H), 7.15 (dd, 2H, J = 8.8, 5.2 Hz), 7.26 (s, 2H), 7.61 (s, 1H), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 31.1, 35.5, 37.2, 43.1, 45.1, 113.4, 114.2, 114.5, 115.0, 115.1, 115.3, 116.0, 116.2, 117.0, 118.7, 128.6, 128.7, 129.9, 134.9, 139.9, 145.1, 159.9; ESI-MS m/z [M + H]$^+$ Calcd for $C_{27}H_{19}F_2N_3$ 424.16, found 424.21. EA Found: C 76.55, H 4.54, N 9.91. Requires: C 76.58, H 4.52, N 9.92.

Photolysis of TCB with Styrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), styrene (1.250 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 16 h to reach a 65% conversion of TCB. The solvent was removed and the residue was separated to give **7a** (269 mg, 41%) and **8a** (56 mg, 8%).

5-(2-(1-Methyl-1H-pyrrol-2-yl)-1-phenylethyl)benzene-1,2,4-tricarbonitrile (***7a***). Yellow solid from chloroform/petroleum ether: mp 189 °C; IR (KBr) ν 2925, 2238, 1580, 1493, 1419, 718 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.29 (dd, 1H, J = 15.2, 10.4 Hz), 3.44 (dd, 1H, J = 15.2, 5.6 Hz), 3.57 (s, 3H), 4.77 (dd, 1H, J = 10.4, 5.6 Hz), 5.39 (dd, 1H, J = 3.4, 1.8 Hz), 5.92 (t, 1H, J = 3.2 Hz), 6.58 (dd, 1H, J = 2.4, 2.0 Hz), 7.26−7.30 (m, 2H), 7.34−7.42 (m, 3H), 7.78 (s, 1H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.3, 32.1, 48.9, 107.1, 108.5, 113.6, 114.1, 114.2, 114.5, 118.2, 119.2, 122.7, 127.3, 127.7, 127.8 128.2, 129.2, 129.4, 133.2, 136.6, 139.5, 154.0; ESI-MS m/z [M + H]$^+$ Calcd for $C_{22}H_{16}N_4$ 337.15, found 337.15. EA Found: C 78.52, H 4.83, N 16.65. Requires: C 78.55, H 4.79, N 16.66.

trans-5-(4-Phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2,4-tricarbonitrile (***8a***). Yellow solid from petroleum ether/ethyl acetate: mp 218−220 °C; IR (KBr) ν 3434, 2361, 1577, 1424, 1138, 857, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.78−1.85 (m, 1H), 1.92−1.99 (m, 1H), 2.13−2.19 (m, 1H), 2.38−2.44 (m, 1H), 4.30 (t, 1H, J = 6.4 Hz), 4.85 (t, 1H, J = 6.8 Hz), 6.69 (d, 1H, J = 7.6 Hz), 6.99 (d, 1H, J = 7.2 Hz), 7.09−7.25 (m, 5H), 7.32 (t, 2H, J = 7.2 Hz), 7.46 (s, 1H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.9, 30.1, 44.5, 45.2. 113.6, 114.2, 114.5, 114.6, 117.6, 119.3, 126.6, 127.2, 127.9, 128.6, 128.7, 129.3, 131.0, 135.0, 137.2, 140.6, 145.8, 157.6; ESI-MS m/z [M − H]$^-$ Calcd for $C_{25}H_{17}N_3$ 358.13, found 358.25. EA Found: C 83.53, H 4.81, N 11.66. Requires: C 83.54, H 4.77, N 11.69.

X-ray Structure Analysis. $C_{25}H_{17}N_3$ M = 359.42. Orthorhombic, space group $Pna2(1)$, a = 22.249(3), b = 9.2420(14), c = 9.1181(12) Å, α = 90, β = 90, γ = 90°, V = 1874.9(5) Å, Z = 4, D_c = 1.273 g cm^{-3}, $F(000)$ = 752.0, absorption coefficient 0.076 mm^{-1}, scan range for data collection 2.39 ≤ θ ≤ 21.63°, 9824 measured reflections, 3535 independent reflections, 2808 reflections with $I > 2\sigma(I)$, R_{int} = 0.0535, 253 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0471, wR_2 (F^2) = 0.1078.

Photolysis of TCB with 4-Methylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-methylstyrene (1.418 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 52% conversion of TCB. The solvent was removed and the residue was separated to give **7b** (317 mg, 58%) and **8b** (85 mg, 14%).

5-(2-(1-Methyl-1H-pyrrol-2-yl)-1-(p-tolyl)ethyl)benzene-1,2,4-tricarbonitrile (***7b***). Yellow solid from chloroform/petroleum ether: mp 212 °C; IR (KBr) ν 2919, 2236, 1573, 1418, 1295, 907, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.28 (dd, 1H, J = 15.2, 10.0 Hz), 3.41 (dd, 1H, J = 15.2, 5.6 Hz), 3.56 (s, 3H), 4.73 (dd, 1H, J = 10.4, 5.6 Hz), 5.40 (dd, 1H, J = 3.6, 1.6 Hz), 5.89 (t, 1H, J = 3.2 Hz), 6.55 (t, 1H, J = 2.0 Hz), 7.19 (t, 4H, J = 26.4), 7.82 (s, 1H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.0, 29.3, 33.6, 48.6, 107.1, 108.5, 113.6, 114.2, 114.2, 114.3, 118.2, 119.2, 122.4, 127.6, 127.7, 129.9, 130.1, 133.3, 136.5, 136.6, 138.1, 154.3; ESI-MS m/z [M − H]$^-$ Calcd for $C_{23}H_{18}N_4$ 349.15, found 349.28. EA Found: C 78.81, H 5.21, N 15.98. Requires: C 78.83, H 5.18, N 15.99.

trans-5-(6-Methyl-4-(p-tolyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-benzene-1,2,4-tricarbonitrile (***8b***). Yellow solid from petroleum ether/ethyl acetate: mp 182−184 °C; IR (KBr) ν 2926, 2239, 1577, 1425, 1261, 923, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72−1.80 (m, 1H), 1.85−1.92 (m, 1H), 2.05−2.12 (m, 1H), 2.22(s, 3H), 2.31−2.42 (m, 4H), 4.21 (t, 1H, J = 6.2 Hz), 4.79 (t, 1H, J = 6.4 Hz), 6.57 (d, 1H, J = 7.6 Hz), 6.81 (s, 1H), 6.96 (t, 3H, J = 7.8 Hz), 7.13 (d, 2H, J = 7.6 Hz), 7.26 (s, 1H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.0, 29.5, 29.9, 44.0, 44.6, 113.7, 114.2, 114.3, 114.6, 117.5, 119.1, 128.2, 128.4, 128.6, 129.2, 129.4, 131.4, 131.9, 135.0, 136.1, 137.1, 137.7, 140.4, 143.0, 157.9; ESI-MS m/z [M − H]$^-$ Calcd for $C_{27}H_{21}N_3$ 386.17, found 386.40. EA Found: C 83.67, H 5.51, N 10.82. Requires: C 83.69, H 5.46, N 10.84.

Photolysis of TCB with 4-*tert*-Butylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-*tert*-butylstyrene (1.923 g, 12 mmol), and *N*-methylpyrrole (1.947 mg, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 57% conversion of TCB. The solvent was removed and the residue was separated to give **7c** (439 mg, 68%) and **8c** (48 mg, 6%).

5-(1-(4-(tert-Butyl)phenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)-benzene-1,2,4-tricarbonitrile (***7c***). Yellow solid from petroleum ether/ethyl acetate: mp 234 °C; IR (KBr) ν 2962, 2238, 1512, 1416, 1297, 912, 714 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (s, 9H), 3.31 (t, 1H, J = 12.6 Hz), 3.42 (dd, 1H, J = 15.2, 5.2 Hz), 3.55 (s, 3H), 4.74−4.77 (m, 1H), 5.41 (s, 1H), 5.86 (t, 1H, J = 3.2 Hz), 6.52 (t, 1H, J = 2.2 Hz), 7.21−7.26 (m, 2H), 7.40 (d, 2H, J = 8.0 Hz), 7.82 (s, 1H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.3, 32.1, 33.7, 34.6, 48.5, 107.1, 108.4, 113.9, 114.2, 114.5, 114.6, 118.1, 119.2, 122.6, 126.2, 126.4, 127.6, 127.8, 133.4, 136.7, 136.8, 151.2, 154.3; ESI-MS *m*/*z* $[M + H]^+$ Calcd for $C_{26}H_{24}N_4$ 393.21, found 393.25. EA Found: C 79.52, H 6.19, N 14.26. Requires: C 79.56, H 6.16, N 14.27.

*trans-5-(6-(tert-Butyl)-4-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2,4-tricarbonitrile (**8c**).* White solid from petroleum ether/ethyl acetate: mp 230−232 °C; IR (KBr) ν 3431, 2969, 1578, 1420, 1149, 837, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 9H), 1.32 (s, 9H), 1.69−1.77 (m, 1H), 1.88−1.96 (m, 1H), 2.06−2.13 (m, 1H), 2.33−2.41 (m, 1H), 4.27 (t, 1H, *J* = 6.0 Hz), 4.78 (t, 1H, *J* = 6.4 Hz), 6.62 (d, 1H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 1H, *J* = 2.0 Hz), 7.17 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.44 (s, 1H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.3, 29.6, 31.1, 31.4, 34.4, 34.5, 43.8, 44.6, 113.7, 114.2, 114.3, 114.6, 117.6, 119.1, 124.4, 125.2, 125.4, 127.98, 128.03, 128.2, 129.0, 131.9, 135.1, 137.0, 139.9, 142.8, 149.2, 150.8, 158.0; ESI-MS *m*/*z* $[M - H]^-$ Calcd for $C_{33}H_{33}N_3$ 470.26, found 470.50. EA Found: C 84.02, H 7.10, N 8.89. Requires: C 84.04, H 7.05, N 8.91.

Photolysis of TCB with 2,5-Dimethylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 2,5-dimethylstyrene (1.586 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 73% conversion of TCB. The solvent was removed and the residue was separated to give **7d** (534 mg, 67%) and **8d** (137 mg, 15%).

*5-(1-(2,5-Dimethylphenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)-benzene-1,2,4-tricarbonitrile (**7d**).* Yellow solid from petroleum ether/ethyl acetate: mp 193 °C; IR (KBr) ν 2948, 2208, 1577, 1427, 1136, 861, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (s, 3H), 2.42 (s, 3H), 3.16 (dd, 1H, *J* = 14.6, 11.0 Hz), 3.39 (dd, 1H, *J* = 14.8, 4.8 Hz), 3.58 (s, 3H), 4.68 (dd, 1H, *J* = 11.2, 4.4 Hz), 5.20 (dd, 1H, *J* = 3.6, 1.6 Hz), 5.92 (t, 1H, *J* = 3.0 Hz), 6.64 (t, 1H, *J* = 2.0 Hz), 7.10 (s, 2H), 7.20 (s, 1H), 7.64 (s, 1H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.2, 21.3, 32.9, 33.6, 45.4, 107.1, 109.0, 113.70, 113.73, 114.2, 114.4, 118.9, 119.1, 123.0, 126.9, 127.0, 128.9, 131.4, 133.5, 136.0, 136.5, 137.6, 155.3; ESI-MS *m*/*z* $[M + H]^+$ Calcd for $C_{24}H_{20}N_4$ 365.18, found 365.14. EA Found: C 79.06, H 5.55, N 15.39. Requires: C 79.10, H 5.53, N 15.37.

*trans-5-(4-(2,5-Dimethylphenyl)-5,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2,4-tricarbonitrile (**8d**).* Yellow solid from petroleum ether/ethyl acetate: mp 269−270 °C; IR (KBr) ν 2934, 2236, 1576, 1443, 1137, 812, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72−1.83 (m, 2H), 1.91 (s, 3H), 1.93 (s, 3H), 2.15 (s, 3H), 2.42 (s, 3H), 2.44−2.53 (m, 2H), 4.47 (d, 1H, *J* = 5.6 Hz), 4.86 (d, 1H, *J* = 6.0 Hz), 6.18 (s, 1H), 6.91 (d, 1H, *J* = 7.6 Hz), 7.02−7.10 (m, 3H), 7.13 (s, 1H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 19.3, 19.7, 21.2, 23.1, 24.5, 37.4, 41.0, 113.7, 114.3, 114.3, 114.5, 117.5, 118.8, 126.9, 128.6, 129.6, 130.5, 130.7, 132.1, 132.9, 133.3, 134.0, 135.1, 135.8, 137.1, 138.4, 142.8, 157.3; ESI-MS *m*/*z* $[M - H]^-$ Calcd for $C_{29}H_{25}N_3$ 414.20, found 414.24. EA Found: C 83.80, H 6.10, N 10.10. Requires: C 83.82, H 6.06, N 10.11.

Photolysis of TCB with 2,4,6-Trimethylstyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 2,4,6-trimethylstyrene (1.754 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 65% conversion of TCB. The solvent was removed and the residue was separated to give **7e** (631 mg, 89%).

*5-(1-Mesityl-2-(1-methyl-1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**7e**).* Yellow solid from petroleum ether/ethyl acetate: mp 238−239 °C; IR (KBr) ν 2934, 2336, 1578, 1425, 1136, 852, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 6H), 2.26 (s, 3H), 3.21 (dd, 1H, *J* = 15.8, 5.8 Hz), 3.40 (s, 3H), 3.54 (dd, 1H, *J* = 15.8, 9.0 Hz), 4.99 (dd, 1H, *J* = 8.8, 5.6 Hz), 5.58 (dd, 1H, *J* = 3.6, 1.6 Hz), 5.99 (t, 1H, *J* = 3.6 Hz), 6.58 (t, 1H, *J* = 2.2 Hz), 6.84 (s, 2H), 7.91 (s, 1H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.7, 21.5, 29.0, 29.7, 33.4, 44.6, 107.3, 107.9, 113.6, 113.9, 114.1, 114.4, 118.3, 118.6, 122.5, 127.2, 127.9, 128.0, 130.8, 134.1, 134.6, 137.5, 137.9, 154.7; ESI-MS *m*/*z* $[M - H]^-$ Calcd for $C_{25}H_{22}N_4$ 377.18, found 377.42. EA Found: C 79.30, H 5.90, N 14.79. Requires: C 79.34, H 5.86, N 14.80.

Photolysis of TCB with 4-Chlorostyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-chlorostyrene (1.663 g, 12 mmol), and *N*-methylpyrrole (1.947 mg, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 52% conversion of TCB. The solvent was removed and the residue was separated to give **7f** (330 mg, 57%).

*5-(1-(4-Chlorophenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**7f**).* Yellow solid from petroleum ether/ethyl acetate: mp 269−270 °C; IR (KBr) ν 2934, 2236, 1576, 1443, 1137, 812, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.27 (dd, 1H, *J* = 15.2, 10.0 Hz), 3.40 (dd, 1H, *J* = 15.2, 6.0 Hz), 3.57 (s, 3H), 4.74 (dd, 1H, *J* = 10.0, 6.0 Hz), 5.40 (dd, 1H, *J* = 3.6, 1.6 Hz), 5.92 (t, 1H, *J* = 3.6 Hz), 6.58 (t, 1H, *J* = 2.4 Hz), 7.21 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.75 (s, 1H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.0, 33.7, 48.3, 107.2, 108.6, 113.5, 114.1, 114.8, 118.3, 119.5, 122.8, 126.9, 129.2, 129.6, 133.0, 134.3, 136.8, 137.9, 153.4; ESI-MS *m*/*z* $[M - H]^-$ Calcd for $C_{22}H_{15}ClN_4$ 369.09, found 369.33. EA Found: C 71.22, H 4.11, N 15.10. Requires: C 71.25, H 4.08, N 15.11.

Photolysis of TCB with 2-Fluorostyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 2-fluorostyrene (1.466 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 47% conversion of TCB. The solvent was removed and the residue was separated to give **7g** (285 mg, 57%).

*5-(1-(2-Fluorophenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**7g**).* Yellow solid from petroleum ether/ethyl acetate: mp 130 °C; IR (KBr) ν 2923, 2240, 1576, 1443, 1137, 764, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.28 (dd, 1H, *J* = 14.8, 10.4 Hz), 3.46 (dd, 1H, *J* = 14.8, 5.2 Hz), 3.62 (s, 3H), 4.89 (dd, 1H, *J* = 10.4, 5.2 Hz), 5.36 (dd, 1H, *J* = 3.2, 1.6 Hz), 5.91 (dd, 1H, *J* = 3.2, 3.2 Hz), 6.60 (dd, 1H, *J* = 2.4, 2.0 Hz), 7.05−7.10 (m, 1H), 7.26−7.29 (m, 1H), 7.35−7.39 (m, 1H), 7.50 (td, 1H, *J* = 7.6, 1.6 Hz), 7.71 (s, 1H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.0, 33.7, 42.9, 107.1, 108.8, 113.6, 113.8, 114.2, 114.6, 116.2, 116.4, 118.5, 119.1, 123.0, 125.0, 126.6, 128.3, 130.3, 133.3, 136.5, 152.8, 159.4; ESI-MS *m*/*z* $[M + H]^+$ Calcd for $C_{22}H_{15}FN_4$ 355.14, found 355.15. EA Found: C 74.53, H 4.31, N 15.79. Requires: C 74.56, H 4.27, N 15.81.

Photolysis of TCB with 4-Fluorostyrene in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-fluorostyrene (1.466 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 57% conversion of TCB. The solvent was removed and the residue was separated to give **7h** (309 mg, 51%).

*5-(1-(4-Fluorophenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**7h**).* Yellow solid from petroleum ether/ethyl acetate: mp 182 °C; IR (KBr) ν 2964, 2238, 1577, 1442, 1134, 840, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.28 (dd, 1H, *J* = 16.4, 10.0 Hz), 3.40 (dd, 1H, *J* = 15.2, 5.6 Hz), 3.56 (s, 3H), 4.76 (dd, 1H, *J* = 9.2, 6.4 Hz), 5.42 (s, 1H), 5.91 (d, 1H, *J* = 2.0 Hz), 6.56 (s, 1H), 7.08 (t, 2H, *J* = 7.8 Hz), 7.24−7.27 (m, 2H), 7.80 (s, 1H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.2, 32.1, 48.9, 107.1, 108.5, 113.6, 114.2, 114.3, 114.6, 116.3, 116.5, 118.2, 119.4, 122.7, 127.2, 129.5, 133.1, 135.3, 136.8, 153.7, 161.1, 163.5; ESI-MS *m*/*z* $[M + H]^+$ Calcd for $C_{22}H_{15}FN_4$ 355.14, found 355.30. EA Found: C 74.53, H 4.30, N 15.78. Requires: C 74.56, H 4.27, N 15.81.

Photolysis of TCB with *N*-Methylmaleimide in the Presence of *N*-Methylpyrrole. A solution of TCB (530 mg, 3 mmol), *N*-methylmaleimide (1.333 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 81% conversion of TCB. The solvent was removed and the residue was separated to give **7k** (609 mg, 73%).

*trans-5-(1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-2,5-dioxopyrrolidin-3-yl)benzene-1,2,4-tricarbonitrile (**7k**).* Yellow solid from petroleum ether/ethyl acetate: mp 148−150 °C; IR (KBr) ν 3433, 2239, 1564, 1415, 1136, 806, 643 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.16 (s, 3H), 3.67 (s, 3H), 4.19 (d, 1H, *J* = 8.0 Hz), 4.65 (d, 1H, *J* = 7.6 Hz), 6.12−6.14 (m, 1H), 6.16−6.17 (m, 1H), 6.97 (d, 1H, *J* = 2.0 Hz), 7.83 (s, 1H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.9, 34.6, 47.0, 51.9, 107.75, 107.90, 113.1, 113.6, 113.9, 116.7, 117.9, 120.1, 122.8, 125.3, 134.9, 137.7, 145.3, 172.7, 173.0; ESI-MS *m*/*z* $[M - H]^-$ Calcd for $C_{19}H_{13}N_5O_2$ 342.10, found 342.25. EA Found: C 66.44, H 3.83, N 20.43. Requires: C 66.47, H 3.82, N 20.40.

Photolysis of TFDCB with 4-Methylstyrene in the Presence of *N*-Methylpyrrole. A solution of TFDCB (600 mg, 3 mmol), 4-methylstyrene (1.418 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 47% conversion of TFDCB. The solvent was removed and the residue was separated to give **9b** (247 mg, 47%).

*2,3,5,6-Tetrafluoro-4-(2-(1-methyl-1H-pyrrol-2-yl)-1-(p-tolyl)-ethyl)benzonitrile (**9b**).* White solid from petroleum ether/ethyl acetate: mp 164−166 °C; IR (KBr) ν 2934, 2363, 1577, 1425, 1138, 852, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.33 (s, 3H), 3.37 (dd, 1H, J = 15.2, 6.4 Hz), 3.54 (s, 3H), 3.56−3.63 (m, 1H), 4.81 (dd, 1H, J = 10.4, 6.0 Hz), 5.74 (d, 1H, J = 2.0 Hz), 5.94 (t, 1H, J = 3.2 Hz), 6.51 (t, 1H, J = 2.4 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 18.4, 29.7, 33.6, 41.3, 58.5, 106.8. 106.9, 122.0, 127.4, 129.1, 129.7, 136.4, 137.6; ESI-MS m/z [M + H]$^+$ Calcd for $C_{21}H_{16}F_4N_2$ 373.13, found 373.17. EA Found: C 67.75, H 4.35, N 7.50. Requires: C 67.74, H 4.33, N 7.52.

Photolysis of TFDCB with 4-*tert*-Butylstyrene in the Presence of *N*-Methylpyrrole. A solution of TFDCB (600 mg, 3 mmol), 4-*tert*-butylstyrene (1.923 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 53% conversion of Tetrafluoroterephthalonitrile. The solvent was removed and the residue was separated to give **9c** (382 mg, 58%).

*4-(1-(4-(tert-Butyl)phenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)-2,3,5,6-tetrafluorobenzonitrile (**9c**).* White solid from petroleum ether/ethyl acetate: mp 138 °C; IR (KBr) ν 2925, 2336, 1577, 1441, 1137, 855, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.30 (s, 9H), 3.34−3.39 (m, 1H), 3.54 (s, 3H), 3.63 (dd, 1H, J = 15.8, 11.0 Hz), 4.82 (dd, 1H, J = 10.8, 6.0 Hz), 5.75 (d, 1H, J = 2.0 Hz), 5.95 (t, 1H, J = 3.2 Hz), 6.51 (t, 1H, J = 2.4 Hz), 7.28 (d, 2H, J = 8.8 Hz), 7.35 (dd, 2H, J = 8.4, 1.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 29.3, 29.7, 31.2, 31.9, 33.5, 58.5, 106.8, 106.9, 122.0, 125.9, 127.2, 129.2, 129.9, 136.4, 150.9; ESI-MS m/z [M + H]$^+$ Calcd for $C_{24}H_{22}F_4N_2$ 415.18, found 415.17. EA Found: C 69.53, H 5.38, N 6.75. Requires: C 69.55, H 5.35, N 6.76.

Photolysis of TFDCB with 2,4,6-Trimethylstyrene in the Presence of *N*-Methylpyrrole. A solution of TFDCB (600 mg, 3 mmol), 2,4,6-trimethylstyrene (1.755 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 75% conversion of Tetrafluoroterephthalonitrile. The solvent was removed and the residue was to give **9e** (477 mg, 53%).

*2,3,5,6-Tetrafluoro-4-(1-mesityl-2-(1-methyl-1H-pyrrol-2-yl)-ethyl)benzonitrile (**9e**).* White solid from petroleum ether/ethyl acetate: mp 173 °C; IR (KBr) ν 3035, 2246, 1577, 1423, 1137, 853, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.12 (s, 6H), 2.24 (s, 3H), 3.16 (dd, 1H, J = 15.4, 7.8 Hz), 3.22 (s, 3H), 3.65 (dd, 1H, J = 15.4, 8.2 Hz), 5.03 (t, 1H, J = 8.0 Hz), 5.73 (dd, 1H, J = 3.6, 1.6 Hz), 5.99 (t, 1H, J = 3.0 Hz), 6.49 (t, 1H, J = 2.2 Hz), 6.81 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 20.0, 20.7, 28.2, 29.7. 33.2, 40.3, 106.5, 106.9, 107.5, 121.8, 129.0, 129.1, 129.3, 130.1, 130.5, 134.2, 136.6, 137.2; ESI-MS m/z [M − H]$^-$ Calcd for $C_{23}H_{20}F_4N_2$ 399.15, found 399.17. EA Found: C 68.97, H 5.05, N 6.99. Requires: C 68.99, H 5.03, N 7.00.

Photolysis of TCB with 4-Methylstyrene in the Presence of *N*-Phenylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-methylstyrene (1.418 g, 12 mmol), and *N*-phenylpyrrole (1.718 g, 12 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 90% conversion of TCB. The solvent was removed and the residue was separated to give **10b** (869 mg, 78%) and **8b** (31 mg, 3%).

*5-(2-(1-Phenyl-1H-pyrrol-2-yl)-1-(p-tolyl)ethyl)benzene-1,2,4-tricarbonitrile (**10b**).* White solid from petroleum ether/ethyl acetate: mp 208 °C; IR (KBr) ν 3002, 2358, 1577, 1425, 1138, 856, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.30 (s, 3H), 3.32 (dd, 1H, J = 15.2, 10.4 Hz), 3.46 (dd, 1H, J = 15.2, 5.6 Hz), 4.60 (dd, 1H, J = 10.4, 5.6 Hz), 5.88 (dd, 1H, J = 3.6, 1.6 Hz), 6.13 (t, 1H, J = 3.2 Hz), 6.69 (dd, 1H, J = 2.8, 1.6 Hz), 6.97 (d, 2H, J = 8.4 Hz), 7.09 (d, 2H, J = 8.0 Hz), 7.21 (dd, 2H, J =6.8, 1.2 Hz), 7.42−7.50 (m, 3H), 7.55 (s, 1H), 7.88 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 21.0, 29.7, 49.4, 108.6, 109.7, 113.6, 114.16, 114.23, 114.4, 118.0, 119.0, 122.8, 126.1, 127.4, 127.9, 128.3, 128.8, 129.6, 129.9, 130.9, 133.1, 136.7, 136.8, 137.9, 139.6, 154.0; ESI-MS m/z [M + H]$^+$ Calcd for $C_{28}H_{20}N_4$ 413.18, found 413.17. EA Found: C 81.81, H 4.83, N 13.56. Requires: C 81.53, H 4.89, N 13.58.

Photolysis of TCB with 4-*tert*-Butylstyrene in the Presence of *N*-Phenylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-*tert*-butylstyrene (1.923 g, 12 mmol), and *N*-phenylpyrrole (1.718 g, 12 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 83% conversion of TCB. The solvent was removed and the residue was separated to give **10c** (930 mg, 85%) and **8c** (59 mg, 5%).

*5-(1-(4-(tert-Butyl)phenyl)-2-(1-phenyl-1H-pyrrol-2-yl)ethyl)-benzene-1,2,4-tricarbonitrile (**10c**).* White solid from petroleum ether/ethyl acetate: mp 218−219 °C; IR (KBr) ν 2935, 2347, 1578, 1425, 1135, 852, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.28 (s, 9H), 3.35 (dd, 1H, J = 15.2, 10.8 Hz), 3.49 (dd, 1H, J = 15.2, 5.2 Hz), 4.63 (dd, 1H, J = 10.8, 5.2 Hz), 5.90 (dd, 1H, J = 3.6, 1.6 Hz), 6.14 (t, 1H, J = 3.2 Hz), 6.70 (dd, 1H, J = 2.8, 1.6 Hz), 7.02 (d, 2H, J = 8.4 Hz), 7.19−7.21 (m, 2H), 7.30−7.32 (m, 2H), 7.42−7.51 (m, 3H), 7.56 (s, 1H), 7.89 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 29.7, 31.2, 31.9, 49.4, 108.0, 108.6, 109.6, 113.6, 114.2, 114.5, 118.1, 119.0, 122.8, 126.1, 126.2, 127.1, 127.9, 128.4, 128.8, 129.6, 133.2, 136.6, 136.8, 139.6, 140.9, 151.0, 154.0, 162.3; ESI-MS m/z [M − H]$^-$ Calcd for $C_{31}H_{26}N_4$ 453.21, found 453.50. EA Found: C 81.88, H 5.81, N 12.31. Requires: C 81.91, H 5.77, N 12.33.

Photolysis of TCB with 2,5-Dimethylstyrene in the Presence of *N*-Phenylpyrrole. A solution of TCB (530 mg, 3 mmol), 2,5-dimethylstyrene (1.586 g, 12 mmol), and *N*-phenylpyrrole (1.718 g, 12 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 70% conversion of TCB. The solvent was removed and the residue was separated to give **10d** (717 mg, 80%) and **8d** (26 mg, 3%).

*5-(1-(2,5-Dimethylphenyl)-2-(1-phenyl-1H-pyrrol-2-yl)ethyl)-benzene-1,2,4-tricarbonitrile (**10d**).* White solid from petroleum ether/ethyl acetate: mp 176−177 °C; IR (KBr) ν 3036, 2240, 1577, 1443, 1139, 811, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.00 (s, 3H), 2.31 (s, 3H), 3.22 (dd, 1H, J = 15.2, 10.8 Hz), 3.42 (dd, 1H, J = 15.2, 4.8 Hz), 4.61 (dd, 1H, J = 10.8, 4.8 Hz), 5.75 (t, 1H, J = 1.6 Hz), 6.15 (t, 1H, J = 3.2 Hz), 6.74 (t, 1H, J = 1.6 Hz), 6.84 (s, 1H), 7.00 (s, 2H), 7.24 (d, 2H, J = 7.2 Hz), 7.39−7.47 (m, 3H), 7.51 (s, 1H), 7.89 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 18.4, 19.0, 32.6, 46.2, 108.5, 110.1, 113.6, 114.2, 118.7, 118.8, 123.2, 126.2, 126.9, 127.8, 128.1, 128.6, 129.5, 131.2, 133.3, 133.8, 136.3, 136.4, 137.8, 139.6, 153.6; ESI-MS m/z [M − H]$^-$ Calcd for $C_{29}H_{22}N_4$ 425.18, found 425.33. EA Found: C 81.63, H 5.24, N 13.13. Requires: C 81.66, H 5.20, N 13.14.

Photolysis of TCB with 4-Methoxystyrene in the Presence of *N*-Phenylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-Methoxystyrene (1.610 g, 12 mmol), and *N*-phenylpyrrole (1.718 g, 12 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 56% conversion of TCB. The solvent was removed and the residue was separated to give **10j** (468 mg, 65%).

*5-(1-(4-Methoxy)-2-(1-phenyl-1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**10j**).* White solid from petroleum ether/ethyl acetate: mp 216−218 °C; IR (KBr) ν 2925, 2238, 1575, 1423, 1138, 649, 620 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.31 (dd, 1H, J = 15.4, 10.2 Hz), 3.45 (dd, 1H, J = 15.4, 5.8 Hz), 3.77 (s, 3H), 4.58 (dd, 1H, J = 10.4, 5.6 Hz), 5.89 (ddd, 1H, J = 1.6 Hz), 6.13 (t, 1H, J = 2.9 Hz), 6.69 (dd, 1H, J = 2.8, 1.6 Hz), 6.80 (dd, 2H, J = 6.8, 2.0 Hz), 6.99 (dd, 2H, J = 6.2, 2.2 Hz), 7.20 (dd, 2H, J = 7.0, 1.4 Hz), 7.42−7.50 (m, 3H), 7.54 (s, 1H), 7.88 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 32.1, 49.0, 55.3, 108.6, 109.7, 113.6, 114.2, 114.4, 114.6, 118.0, 119.0, 122.8, 126.1, 127.9, 128.4, 128.6, 129.6, 131.7, 133.0, 136.9, 139.6, 154.2, 159.2; ESI-MS m/z [M + H]$^+$ Calcd for $C_{28}H_{20}N_4O$ 429.17, found 429.25. EA Found: C 78.46, H 4.78, N 13.05. Requires: C 78.49, H 4.70, N 13.08.

Photolysis of TCB with 4-Fluoro-α-methylstyrene in the Presence of *N*-Phenylpyrrole. A solution of TCB (530 mg, 3 mmol), 4-fluoro-a-methylstyrene (1.634 g, 12 mmol), and 1-phenylpyrrole (1.718 g, 12 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 78% conversion of TCB. The solvent was removed and the residue was separated to give **11b** (655 mg, 65%) and **5b** (20 mg, 2%).

*5-(2-(4-Fluorophenyl)-1-(1-phenyl-1H-pyrrol-2-yl)propan-2-yl)-benzene-1,2,4-tricarbonitrile (**11b**).* Yellow solid from petroleum ether/ethyl acetate: mp 192−193 °C; IR (KBr) ν 3433, 2233, 1577, 1423, 1139, 836, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.59 (s, 3H), 3.66 (d, 1H, J = 14.4 Hz), 4.02 (d, 1H, J = 14.8 Hz), 5.80 (dd, 1H, J = 3.4, 1.8 Hz), 6.17 (t, 1H, J = 3.2 Hz), 6.20 (dd, 1H, J = 2.8, 1.6 Hz), 6.92–6.96 (m, 6H), 7.33–7.40 (m, 3H), 7.54 (s, 1H), 7.69 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.8, 35.0, 48.0, 108.5, 112.4, 113.5, 114.27, 114.33, 114.49, 115.5, 115.7. 118.2, 123.7, 125.6, 125.8, 127.1, 128.8, 128.9, 129.6, 132.6, 138.6, 139.7, 141.3, 141.4, 157.3, 160.4, 162.8, 171.2; ESI-MS m/z [M + H]$^+$ Calcd for $C_{28}H_{19}FN_4$ 431.17, found 431.17. EA Found: C 78.11, H 4.47, N 13.01. Requires: C 78.12, H 4.45, N 13.02.

Photolysis of TCB with Styrene in the Presence of *N*-Boc-pyrrole. A solution of TCB (530 mg, 3 mmol), styrene (1.250 g, 12 mmol), and *N*-Boc-pyrrole (4.013 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 71% conversion of TCB. The solvent was removed and the residue was separated to give **12a** (576 mg, 64%) and **8a** (15 mg, 2%).

*tert-Butyl 2-(2-phenyl-2-(2,4,5-tricyanophenyl)ethyl)-1H-pyrrole-1-carboxylate (**12a**).* White solid from petroleum ether/ethyl acetate: mp 186 °C; IR (KBr) ν 3435, 2239, 1577, 1415, 1123, 846, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.58 (s, 9H), 3.51 (dd, 1H, J = 14.8, 10.0 Hz), 3.87 (dd, 1H, J = 15.0, 5.4 Hz), 5.01 (dd, 1H, J = 9.6, 5.6 Hz), 5.53 (t, 1H, J = 1.6 Hz), 5.94 (t, 1H, J = 3.2 Hz), 7.21 (dd, 1H, J = 3.2, 1.6 Hz), 7.27–7.39 (m, 5H), 7.82 (s, 1H), 7.89 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.0, 34.2, 48.5, 84.2, 110.0, 113.6, 113.9, 114.2, 114.3, 118.1. 119.1, 122.1, 127.8, 128.0, 129.3, 130.3, 133.6, 136.6, 139.8, 149.3, 154.7; ESI-MS m/z [M − H]$^-$ Calcd for $C_{26}H_{22}N_4O_2$ 421.17, found 421.00. EA Found: C 73.95, H 5.27, N 13.25. Requires: C 73.92, H 5.25, N 13.26.

X-ray Structure Analysis. $C_{26}H_{22}N_4O_2$ M = 422.48. Triclinic, space group $P\bar{1}$, a = 9.5546(12), b =10.2791(13), c = 12.0432(15) Å, α = 98.980(2), β = 98.018(2), γ = 92.406(2) °, V = 1154.4(3) Å, Z = 2, D_c = 1.215 g cm^{-3}, $F(000)$ = 444.0, absorption coefficient 0.079 mm^{-1}, scan range for data collection $2.01 \leq \theta \leq 26.00°$, 10018 measured reflections, 4517 independent reflections, 2744 reflections with $I > 2\sigma(I)$, R_{int} = 0.0426, 293 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0497, wR_2 (F^2) = 0.1327.

Photolysis of TCB with 4-*tert*-Butylstyrene in the Presence of *N*-Boc-pyrrole. A solution of TCB (530 mg, 3 mmol), 4-*tert*-butylstyrene (1.923 g, 12 mmol), and *N*-Boc-pyrrole (4.013 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 48% conversion of TCB. The solvent was removed and the residue was separated to give **12c** (289 mg, 42%) and **8c** (59 mg, 9%).

*tert-Butyl 2-(2-(4-(tert-butyl)phenyl)-2-(2,4,5-tricyanophenyl)-ethyl)-1H-pyrrole-1-carboxylate (**12c**).* White solid from petroleum ether/ethyl acetate: mp 200 °C; IR (KBr) ν 2967, 2066, 1570, 1414, 1126, 806, 643 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.31 (s, 9H), 1.56 (s, 9H), 3.43 (dd, 1H, J = 15.2, 9.2 Hz), 3.72 (dd, 1H, J = 14.8, 6.0 Hz), 4.79 (dd, 1H, J = 9.2, 6.0 Hz), 5.49 (d, 1H, J = 1.6 Hz), 5.89 (t, 1H, J = 3.2 Hz), 7.13–7.16 (m, 3H), 7.26 (s, 1H), 7.32 (d, 2H, J = 8.0 Hz), 7.52 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.0, 31.3, 34.39, 34.43, 47.1, 83.7, 109.8, 113.4, 116.7, 117.0, 121.4, 125.7, 127.5, 131.7, 132.2, 138.2, 146.8, 149.3, 149.9; ESI-MS m/z [M + H]$^+$ Calcd for $C_{30}H_{30}N_4O_2$ 479.24, found 479.41. EA Found: C 75.26, H 6.34, N 11.68. Requires: C 75.29, H 6.32, N 11.71.

Photolysis of TCB with 4-Fluorostyrene in the Presence of *N*-Boc-pyrrole. A solution of TCB (530 mg, 3 mmol), 4-fluorostyrene (1.466 g, 12 mmol), and *N*-Boc-pyrrole (4.013 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 71% conversion of TCB. The solvent was removed and the residue was separated to give **12h** (741 mg, 79%).

*tert-Butyl 2-(2-(4-Fluorophenyl)-2-(2,4,5-tricyanophenyl)ethyl)-1H-pyrrole-1-carboxylate (**12h**).* White solid from petroleum ether/ethyl acetate: mp 214 °C; IR (KBr) ν 3431, 2361, 1578, 1424, 1137, 852, 648 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.58 (s, 9H), 3.49 (dd, 1H, J = 14.4, 9.6 Hz), 3.82 (dd, 1H, J = 14.4, 6.0 Hz), 4.99 (dd, 1H, J = 9.6, 5.6 Hz), 5.53 (dd, 1H, J = 3.2, 2.0 Hz), 5.95 (t, 1H, J = 3.2 Hz), 7.07 (td, 2H, J = 8.8, 2.0 Hz), 7.20 (dd, 1H, J = 3.2, 1.6 Hz), 7.23–7.25 (m, 2H), 7.80 (s, 1H), 7.91 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.0, 34.3, 47.9, 84.3, 110.0, 113.6, 114.0, 114.2, 114.4, 116.1. 116.3, 118.1, 119.3, 122.1, 129.4, 129.5, 130.2, 133.4, 135.6, 136.7, 149.3, 154.3, 161.0, 163.4; ESI-MS m/z [M − H]$^-$ Calcd for $C_{26}H_{21}FN_4O_2$ 439.16, found 438.92. EA Found: C 70.88, H 4.83, N 12.70. Requires: C 70.90, H 4.81, N 12.72.

Photolysis of TCB with 2,3,4,5,6-Pentfluorostyrene in the Presence of *N*-Boc-pyrrole. A solution of TCB (530 mg, 3 mmol), 2,3,4,5,6-pentfluorostyrene (2.329 g, 12 mmol), and *N* -Boc-pyrrole (4.013 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 42% conversion of TCB. The solvent was removed and the residue was separated to give **12i** (213 mg, 33%).

*tert-Butyl 2-(2-(perfluorophenyl)-2-(2,4,5-tricyanophenyl)ethyl)-1H-pyrrole-1-carboxylate (**12i**).* White solid from petroleum ether/ethyl acetate: mp 212 °C; IR (KBr) ν 3002, 2060, 1577, 1424, 1130, 848, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.60 (s, 9H), 3.68–3.80 (m, 2H), 5.34 (t, 1H, J = 7.8 Hz), 5.63 (dd, 1H, J = 3.2, 2.0 Hz), 5.97 (t, 1H, J = 3.4 Hz), 7.21 (dd, 1H, J = 3.6, 1.6 Hz), 7.99 (s, 1H), 8.11 (s, 1H); ^{19}F NMR (CDCl$_3$, 376 MHz) −140.42 (dd, J = 18.8, 3.8 Hz), −152.59 (t, J = 20.7 Hz), −160.28 (td, J = 22.6, 7.5 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27.9, 32.3, 39.0, 84.5, 110.1, 113.3, 113.4, 114.0, 114.5, 115.5, 118.5, 119.6, 122.6, 129.0, 133.6, 136.4, 137.0, 142.2, 144.1, 149.4, 150.3; ESI-MS m/z [M − H]$^-$ Calcd for $C_{26}H_{17}F_5N_4O_2$ 511.12, found 511.00. EA Found: C 60.92, H 3.36, N 10.95. Requires: C 60.94, H 3.34, N 10.93.

Photolysis of TCB with 2,3,4,5,6-Pentfluorostyrene in MeCN–H_2O Solution. A solution of TCB (530 mg, 3 mmol) and 2,3,4,5,6-Pentfluorostyrene (2.329 g, 12 mmol) in MeCN (58.2 mL) and water (1.8 mL) was photolyzed for 12 h to reach a 74% conversion of TCB. The solvent was removed and the residue was separated to give **13** (435 mg, 54%).

*5-(2-Hydroxy-1-(perfluorophenyl)ethyl)benzene-1,2,4-tricarbonitrile (**13**).* White solid from petroleum ether/ethyl acetate: mp 62–64 °C; IR (KBr) ν 2963, 2239, 1577, 1261, 803, 650, 619 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.05 (s, 1H), 4.28–4.33 (m, 1H), 4.36–4.42 (m, 1H), 4.98 (dd, 1H, J = 8.2, 6.2 Hz), 8.08 (s, 1H), 7.88 (s, 1H), 8.14 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 41.8, 62.1, 113.3, 113.8, 114.0, 115.8, 118.6, 119.7, 134.2, 137.2, 148.2; ESI-MS m/z [M + H]$^+$ Calcd for $C_{17}H_6F_5N_3O$ 364.05, found 364.17. EA Found: C 56.20, H 1.68, N 11.56. Requires: C 56.21, H 1.66, N 11.57.

Photolysis of DCB with 4-*tert*-Butylstyrene in the Presence of Pyrrole. A solution of TCB (530 mg, 3 mmol), 4-*tert*-Butylstyrene (1.923 g, 12 mmol), and pyrrole (1.610 g, 24 mmol) in MeCN (60 mL) was photolyzed for 15 h to reach a 46% conversion of TCB. The solvent was removed and the residue was separated to give **14** (311 mg, 62%) and **8c** (13 mg, 2%).

*5-(1-(4-(tert-Butyl)phenyl)-2-(1H-pyrrol-2-yl)ethyl)benzene-1,2,4-tricarbonitrile (**14**).* Yellow solid from petroleum ether/ethyl acetate: mp 269–270 °C; IR (KBr) ν 2934, 2359, 1571, 1416, 1134, 805, 643 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.32 (s, 9H), 3.34 (dd, 1H, J =14.8, 9.2 Hz), 3.50 (dd, 1H, J = 14.8, 6.4 Hz), 4.12 (dd, 1H, J =14.0, 7.2 Hz), 4.79 (dd, 1H, J = 9.2, 6.4 Hz), 5.67 (s, 1H), 6.02 (dd, 1H, J = 6.0, 2.8 Hz), 6.65 (dd, 1H, J = 4.0, 2.4 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.81 (s, 1H), 7.93 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 31.2, 33.5, 34.6, 49.4, 107.7, 108.7, 113.6, 114.2, 114.3, 114.6, 117.8, 119.3, 126.5, 126.9, 127.4, 133.2, 136.2, 136.8, 151.4, 154.4; ESI-MS m/z [M − H]$^-$ Calcd for $C_{25}H_{22}N_4$ 377.18, found 377.08. EA Found: C 79.31, H 5.88, N 14.79. Requires: C 79.34, H 5.86, N 14.80.

Photolysis of DCB with 4-*tert*-Butylstyrene in the Presence of *N*-Methylpyrrole. A solution of DCB (384 mg, 3 mmol), 4-*tert*-butylstyrene (1.923 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 12 h to reach a 69% conversion of Terephthalonitrile. The solvent was removed and the residue was separated to give **15** (312 mg, 44%).

*4-(1-(4-(tert-Butyl)phenyl)-2-(1-methyl-1H-pyrrol-2-yl)ethyl)-benzonitrile (**15**).* Yellow solid from petroleum ether/ethyl acetate: mp 133–135 °C; IR (KBr) ν 2962, 2228, 1561, 1414, 1137, 807, 642 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.29 (s, 9H), 3.26 (d, 2H, J = 7.6 Hz), 3.33 (s, 3H), 4.30 (t, 1H, J = 7.8 Hz), 5.66 (dd, 1H, J = 3.6, 2.0 Hz), 5.96 (dd, 1H, J = 3.2, 2.8 Hz), 6.47 (t, 1H, J = 2.4 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.27–7.32 (m, 4H), 7.53–7.55 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 31.3, 32.3, 33.5, 34.4, 51.0, 106.7, 107.4, 110.1, 119.0, 121.1, 125.6, 127.3, 128.8, 130.3, 132.2, 140.0, 149.8, 150.0; ESI-MS m/z [M + H]$^+$ Calcd for $C_{24}H_{26}N_2$ 343.22, found

343.17. EA Found: C 84.15, H 7.66, N 8.15. Requires: C 84.17, H 7.65, N 8.18.

Photolysis of DCB with 2,5-Dimethylhexa-2,4-diene in the Presence of *N*-Methylpyrrole. A solution of DCB (384 mg, 3 mmol), 2,5-dimethylhexa-2,4-diene (1.322 g, 12 mmol), and *N*-methylpyrrole (1.947 g, 24 mmol) in MeCN (60 mL) was photolyzed for 12 h to reach a 81% conversion of Terephthalonitrile. The solvent was removed and the residue was separated to give **16** (324 mg, 55%), **17** (23 mg, 6%).

*(E)-4-(2,5-Dimethyl-5-(1-methyl-1H-pyrrol-2-yl)hex-3-en-2-yl)-benzonitrile (**16**).* Yellow liquid; IR (KBr) ν 2968, 2227, 1573, 1419, 1136, 839, 650 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.40 (s, 6H), 1.42 (s, 6H), 3.53 (s, 3H), 5.48 (d, 1H, J = 16.0 Hz), 5.64 (d, 1H, J = 16.0 Hz), 5.99 (dd, 1H, J = 3.6, 1.2 Hz), 6.03 (t, 1H, J = 3.2 Hz), 6.52 (t, 1H, J = 2.4 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.57 (d, 2H, J = 8.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.6, 35.9, 37.1, 40.6, 105.5, 105.8, 109.6, 119.1, 123.4, 126.9, 132.0, 135.4, 136.1, 138.8; ESI-MS m/z [M + H]$^+$ Calcd for $C_{20}H_{24}N_2$ 293.2, found 293.17. EA Found: C 82.13, H 8.28, N 9.56. Requires: C 82.15, H 8.27, N 9.58.

*(E)-4,4′-(2,5-Dimethylhex-3-ene-2,5-diyl)dibenzonitrile (**17**).* White solid from petroleum ether/ethyl acetate: mp 110 °C; IR (KBr) ν 2967, 2227, 1578, 1421, 1131, 843, 649 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.42 (s, 12H), 5.62 (s, 2H), 7.41 (d, 4H, J = 8.8 Hz), 7.60 (d, 4H, J = 8.8 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.6, 40.7, 109.7, 118.9, 126.9, 132.0, 136.2, 154.5; ESI-MS m/z [M + H]$^+$ Calcd for $C_{22}H_{22}N_2$ 315.19, found 315.33. EA Found: C 84.00, H 7.09, N 8.90. Requires: C 84.04, H 7.05, N 8.91.

X-ray Structure Analysis. $C_{22}H_{22}N_2$ M = 314.42. Triclinic, space group $P\bar{1}$, a = 10.638(14), b =11.784(14), c = 13.566(15) Å, α = 67.11(3), β = 84.68(3), γ = 63.93(3) °, V = 1401(3) Å, Z = 3, D_c = 1.118 g cm^{-3}, F(000) = 504.0, absorption coefficient 0.066 mm^{-1}, scan range for data collection 3.11 $\leq \theta \leq$ 25.00°, 13520 measured reflections, 4883 independent reflections, 1856 reflections with $I > 2\sigma(I)$, R_{int} = 0.1149, 293 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0620, wR_2 (F^2) = 0.0935.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds. ^{19}F NMR spectra of **12i**. X-ray crystal structure data for **4a**, **6a**, **7k**, **8a**, **12a** and **17** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(21) Throughout these reactions, we have found that a factor that influences the TCB conversion and product yield is the stability of the three-component product **4** as a 2-alkylated pyrrole. Control experiments showed that irradiation of product **4a** either in the presence or absence of TCB resulted in gradual consumption of **4a**, although the decomposition in the absence of TCB is much slower. Presumably, in these cases, PET from **4a** to excited TCB or to excited **4a** and the subsequent reactions caused decomposition of the product. This partial decomposition of product during the course, and especially toward the end of the reaction also rationalizes why lower initial concentration of TCB renders higher product yield because high conversion of TCB can be reached in a short time.

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(23) An alternative reaction sequence can also be envisioned where deprotonation of cation radicals **B** and **D** to the corresponding radicals **E** and **F** (Scheme 1) precedes their combination with the TCB anion radical. Subsequent combination of **E** and **F** with TCB anion radical and extrusion of a cyanide anion afford the products. It is known that the combination of TCB anion radical with alkyl radical is near diffusionally controlled (see a,b). Meanwhile, although common arenium cations such as benzenium ($\mathrm{p}K_\mathrm{a}$ −24.3) and naphthalenium ($\mathrm{p}K_\mathrm{a}$ −20.4) cations deprotonate in aqueous solution with diffusionally controlled rate constant, the deprotonation of carbocations stabilized by conjugation with a β-heteroatom proceeds much slower. As an example, 2*H*-benzofurylium cation ($\mathrm{p}K_\mathrm{a}$ −16.1) deprotonates in aqueous solution in the absence of added base with a rate constant of $6.1 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (see c,d). We therefore tentatively propose that the ion radical pair combination of TCB anion radical with **B** takes place in preference of the deprotonatopn of **B** as shown in Scheme 1. (a) Zhang, X.; Yeh, S. R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211−4220. (b) Protti, S.; Fagnoni, M.; Monti, S.; Rehault, J.; Poizat, O.; Albini, A. *RSC Adv.* **2012**, *2*, 1897−1904. (c) McCormack, A. C.; McDonnell, C. M.; More O'Ferrall, R. A.; O'Donoghue, A. M. C.; Rao, S. N. *J. Am. Chem. Soc.* **2002**, *124*, 8575−8583. (d) Lawlor, D. A.; More O'Ferrall, R. A.; Rao, S. N. *J. Am. Chem. Soc.* **2008**, *130*, 17997−12807.

(24) According to the Mayr's nucleophilicity scale, *N*-methypyrrole (N = 5.85 in dichloromethane) is 4 to 5 orders of magnitude stronger in nucleophilicity than styrene and α-methylstyrene (N = 0.78 and 1.70 in dichloromethane, respectively). Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.

(25) In the styrenes **3a**−**3i**, 4-fluorostyrene **3i** has the highest halfwave oxidation potential, 2.40 V (SCE, MeCN) (see a,b), while singlet excited TCB has a reduction potential of 3.44 V,[13] the free energy for electron transfer between **3i** and ^{1}TCB* is estimated to be exergonic by approximately 1 eV by the Weller equation (see c) as recently reexamined by Farid and his coworkers (see d,e). (a) Yilmaz, H.; Yurtsever, E.; Toppare, L. *J. Electroanal. Chem.* **1989**, *261*, 105−112. (b) Akbulut, U.; Toppare, L.; Türker, L. *Makromol. Chem.* **1983**, *184*, 1661−1667. (c) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271. (d) Farid, S.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Shukla, D.; Guirado, G. *J. Am. Chem. Soc.* **2011**, *133*, 11580−11587. (e) Farid, S.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Shukla, D. *J. Am. Chem. Soc.* **2011**, *133*, 4791−4801.

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