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Brief Report

Preparation of Dibenzofurotropones via Pd-Catalyzed Cyclization

Yu-Wei Lin and Shiuh-Tzung Liu *

Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan; r10223114@ntu.edu.tw
* Correspondence: stliu@ntu.edu.tw; Tel.: +886-23366-1661

Abstract: A synthetic approach to dibenzofurotropone derivatives **1** has been developed through the palladium-catalyzed cyclization of (2-bromoaryl)(3-arylfuran-2-yl)methanones **2** via the activation of arylic C–H bonds. Compounds **2** were easily prepared from the palladium-promoted acyl migration and cyclization of (*Z*)-pent-2-en-4-yn-1-yl acetates **3** in the presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), followed by oxidative decarbonylation and oxidation with O_2. Ten new tropone compounds are reported and these compounds show absorption in the UV-vis region and emission in the visible region.

Keywords: tropones; palladium; cyclization

1. Introduction

Tropones, a class of non-benzenoid aromatic compounds, have been found in numerous natural products, showing distinct biological activities [1–5]. Aryl-annulated tropone derivatives such as benzotropones [6–17] and furotropones [18–23] are also attractive molecules because their extended conjugations might exhibit intriguing chemical and photophysical properties (Figure 1A). Considering their application potential, the development of synthesizing tropones annulated with three aromatic rings (Figure 1B) has attracted substantial interest in material chemistry [11–17].

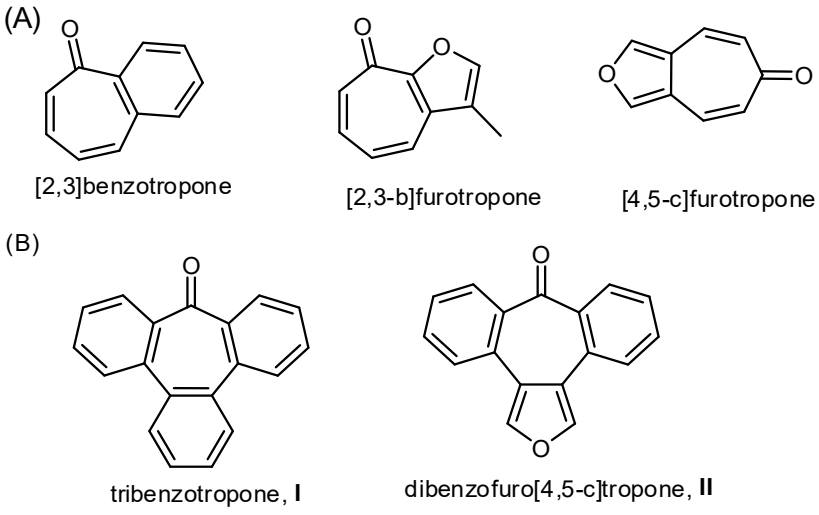

Figure 1. Structures of (**A**) mono-aryl-annulated tropones [6–17,21–23] and (**B**) triaryl-annulated tropones.

Various strategies have been developed for the synthesis of tribenzotropone derivatives **I** involving Diels−Alder reactions of dibenzotropones [15–17], Friedel−Crafts reactions of terphenyl carboxylic acids [17], cyclotrimerization of diynes [10], diazotization followed by 1,3-rearrangement of 9-*o*-aminophenyl-9-fluorenol [11], and Pd-catalyzed decarboxylative cyclization of 2-iodobiphenyls and 2-(2-bromophenyl)-2-oxoacetic acid [15].

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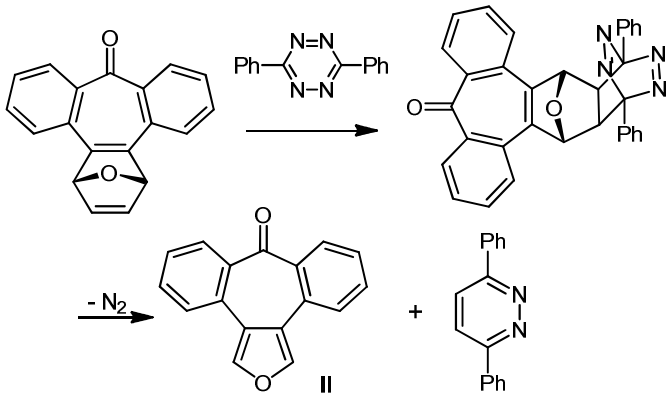
Citation: Lin, Y.-W.; Liu, S.-T. Preparation of Dibenzofurotropones via Pd-Catalyzed Cyclization. *Reactions* **2024**, *5*, 111–119. https://doi.org/10.3390/reactions5010005

Academic Editors: Wenping Ma and Dmitry Yu. Murzin

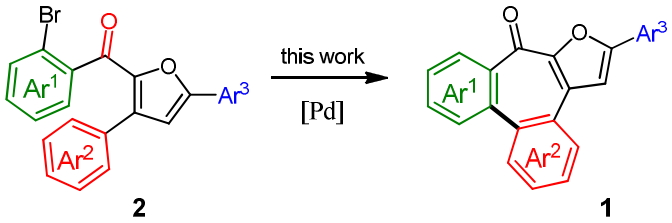
Received: 8 December 2023
Revised: 9 January 2024
Accepted: 19 January 2024
Published: 22 January 2024

Compared to tribenzotropones, methods to access hetero-aryl-annulated benzotropones derivatives are less often reported. For example, compound **II** was obtained from the Diels–Alder reaction of 1*H*-1,4-epoxytribenzo[7]annulen-9(4*H*)-one with 3,6-diphenyl-1,2,4,5-tetrazine followed by the elimination of N_2 and retro-Diels–Alder reaction (Scheme 1) [20]. Besides **II**, other isomeric dibenzofurotropones, such as dibenzo[2,3-b]furotropones, are not known.



Scheme 1. Synthesis of furotropone **II** via Diels–Alder reactions.

The palladium-catalyzed direct C–H arylation of arenes with aryl halides ought to be one of the most powerful tools for C-C bond formation, typically for the construction of a carbocycles [24–29]. In this work, we would like to report an approach for the preparation of dibenzo[2,3-b]furotropones **1** via the palladium-catalyzed oxidative addition of C-Br in **2** followed by C-H activation/cyclization leading to the desired tropones **1** (Scheme 2).



Scheme 2. Pd-catalyzed cyclization leading to tropones.

2. Materials and Methods

2.1. Materials and Instrumentation

All chemicals were purchased commercially and used without further purification. Flash chromatography was performed using silica gel 230–400 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MH_Z spectrometer in $CDCl_3$ referenced to TMS. Melting points were determined using a Fargo MP-1D instrument. UV-VIS and fluorescence spectra were determined on JASCO V-670 EX and HITACHI F450 spectrophotometers, respectively. Unless otherwise noted, all the reactions were performed under a nitrogen atmosphere without any other precautions. Compounds **2** were prepared according to our reported procedure [30].

2.2. General Procedure for Preparation of **2**

A mixture of **3** (2.5 mmol) and $Pd(OAc)_2$ (0.125 mmol) was dissolved in ethyl acetate (10 mL) with stirring. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1.6 mL, 12.5 mmol) was then added and the resulting mixture was heated in an oil bath at 65 °C for 1.5 h under a nitrogen atmosphere. After the reaction, ethyl acetate (10 mL) was added to dilute the solution and was washed with brine (10 mL × 2). The organic layer was collected, dried with anhydrous $MgSO_4$ and concentrated. The residue was filtrated through silica gel with an elution of ethyl acetate/hexane to give the desired crude product **4** upon concentration,

which was subjected to the next step without further purification. A mixture of **4** and DBU (5 eq.) in acetonitrile (2 mL) was heated in an oil bath at 65 °C under an oxygen atmospheric environment for overnight. Ethyl acetate (15 mL) was added and washed with brine (10 mL × 2). The organic extract was dried with anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on silica gel with an elution of ethyl acetate/hexane to yield the desired product **2** upon concentration.

2.3. General Procedure for Preparation of Tropones **1**

A mixture of **2** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), $PCy_3{\cdot}HBF_4$ (0.04 mmol) and Cs_2CO_3 (0.24 mmol) was placed in a 10 mL reaction tube. The reaction tube was evacuated and flashed with N_2. DMSO (2 mL) was added and the tube was immersed to a pre-heated oil bath at 140 °C. After stirring for 20 h, the reaction mixture was cooled to room temperature and brine (20 mL) was added. This mixture was extracted with ether (30 mL × 3). The extracts were dried and concentrated, and the residue was chromatographed on silica gel with an elution of ethyl acetate/hexane (5/95) giving a colored band, which was collected and concentrated to give the desired product **1**.

2.4. Spectroscopic Characterization

(2-Bromophenyl)(3-(4-chlorophenyl)-5-(*p*-tolyl)furan-2-yl)methanone (**2aa**). Pale yellow solid (383 mg, 38%); m.p.: 92–93 °C; Eluent: ethyl acetate:hexane = 3:97; ^{1}H NMR (400 Mz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 3H), 7.48 (dd, *J* = 7.9, 1.1 Hz 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.33–7.28 (m, 4H), 7.24 (d, *J* = 8.0Hz, 2H), 6.90 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 157.6, 145.1, 140.6, 140.0, 137.8, 134.5, 132.9, 131.2, 130.4, 130.1, 129.6, 129.5, 128.2, 127.0, 126.1, 125.1, 120.2, 109.3, 21.4. IR (KBr) $\upsilon_{C=O}$ 1648 cm^{-1}. HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ Calcd. for $C_{24}H_{17}BrClO_2$: 451.0095. Found: 451.0090.

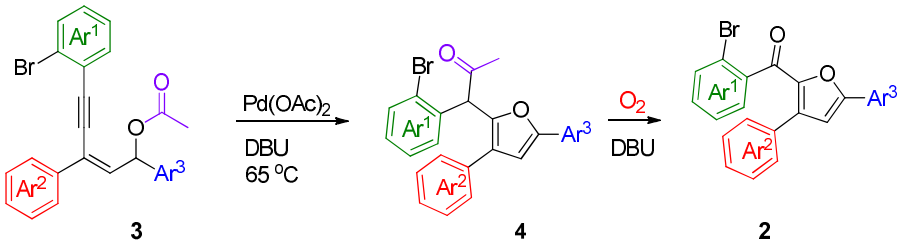
2-Chloro-6-(p-tolyl)-8H-dibenzo[3,4:5,6]cyclohepta[1,2-b]furan-8-one (**1aa**). Pale yellow solid (65.9 mg, 89%); m.p.: 194–195 °C; Eluent: ethyl acetate:hexane = 5:95; ^{1}H NMR (400 MHz, ($CDCl_3$): δ 8.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.81 (t, *J* = 8.1 Hz, 3H), 7.72 (td, *J* = 7.3, 1.1 Hz, 1H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.53 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.20 (s, 1H), 2.41 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 158.1, 149.3, 139.9, 138.4, 138.0, 136.1, 133.9, 132.0, 131.8, 131.6, 131.4, 129.6, 129.5, 129.2, 128.8, 128.6, 126.8, 126.1, 125.3, 104.0, 21.4. IR (KBr) $\upsilon_{C=O}$ 1628 cm^{-1}. HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ Calcd. for $C_{24}H_{16}ClO_2$: 371.0833. Found: 371.0823.

All spectral data of other compounds can be found in the Supplementary Materials.

3. Results and Discussion

3.1. Preparation and Optimization of Reaction Conditions

Bromo-substituted 2-benzoyl-3-arylfuran derivatives **2** were prepared according to our previously reported method (Scheme 3) [30]. The Pd-promoted cyclization of (Z)-pent-2-en-4-yn-1-yl acetates **3** provided **4**, which subsequently underwent decarbonylation followed by oxidation in the air to deliver the desired compounds **1**. This multi-step reaction could be subsequently manipulated without the isolation of **4**. Compounds **2**, used for this study, are summarized in Figure 2. Compounds **2ab**–**2ag** are those with the *ortho*-bromo substituent at the Ar^1 ring, whereas **2ba**–**2ga** are those with the *ortho*-bromo substituent at the Ar^2 ring.



Scheme 3. Bezyoyl furan derivatives **2** from acetate of enynol.

2ab-2ag **2ba-2ga**

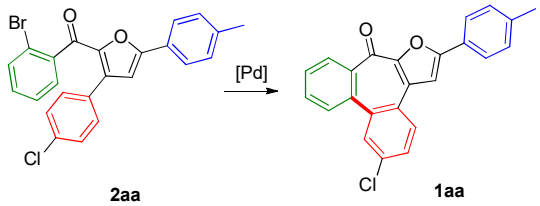
2aa, Ar^2 = 4-ClOC$_6$H$_4$; Ar^3 = 4-MeC$_6$H$_4$
2ab, Ar^2 = 4-MeOC$_6$H$_4$; Ar^3 = 4-MeC$_6$H$_4$
2ac, Ar^2 = 4-MeC$_6$H$_4$; Ar^3 = 4-MeC$_6$H$_4$
2ad, Ar^2 = C$_6$H$_5$; Ar^3 = 4-MeC$_6$H$_4$
2ae, Ar^2 = 2-thienyl ; Ar^3 = 4-MeC$_6$H$_4$
2af, Ar^2 = 4-MeC$_6$H$_4$; Ar^3 = 2-thienyl
2ag, Ar^2 = 4-BrC$_6$H$_4$; Ar^3 = 4-MeC$_6$H$_4$

2ba, Ar^1 = C$_6$H$_5$, Ar^3 = 4-MeC$_6$H$_4$
2ca, Ar^1 = 2-BrC$_6$H$_4$, Ar^3 = 4-MeC$_6$H$_4$
2da, Ar^1 = C$_6$H$_5$, Ar^3 = 4-ClC$_6$H$_4$
2ea, Ar^1 = C$_6$H$_5$, Ar^3 = 4-MeOC$_6$H$_4$
2ga, Ar^1 = 3-FC$_6$H$_4$, Ar^3 = 4-MeC$_6$H$_4$

Figure 2. Structures of bromo-substituted 2-benzoyl-3-arylfurans studied in this work.

To test the possibility of cyclization leading to tropone, **2aa** was selected as a model substrate for screening and the results of the search for the optimization conditions are summarized in Table 1. By using a combination of $Pd(OAc)_2$ and $PCy_3{\cdot}HBF_4$ as the catalyst, running the reaction in DMF for 20 h provided the desired product **1aa** at 68% (Table 1, entry 1). By changing to using DMSO as the solvent, **1aa** was obtained quantitatively, showing that DMSO is the best medium for this coupling (Table 1, entry 2). When using DBU as the base, the reaction did not provide the desired product (Table 1, entry 4). Shortening the reaction period to 10 h, the yield of **1aa** dropped down to 58%. Next, we screened various phosphine ligands for further improvements (Table 1, entries 6–9). It appears that the bulky ligands do assist this cyclization. The reaction was inhibited by the presence of oxygen (Table 1, entry 11). The optimal conditions for this reaction are established as running the reaction of **2aa** in the presence $Pd(OAc)_2/PCy_3{\cdot}HBF_4$ in DMSO (Table 1, entry 2).

Table 1. Optimization of reaction conditions [1].



2aa **1aa**

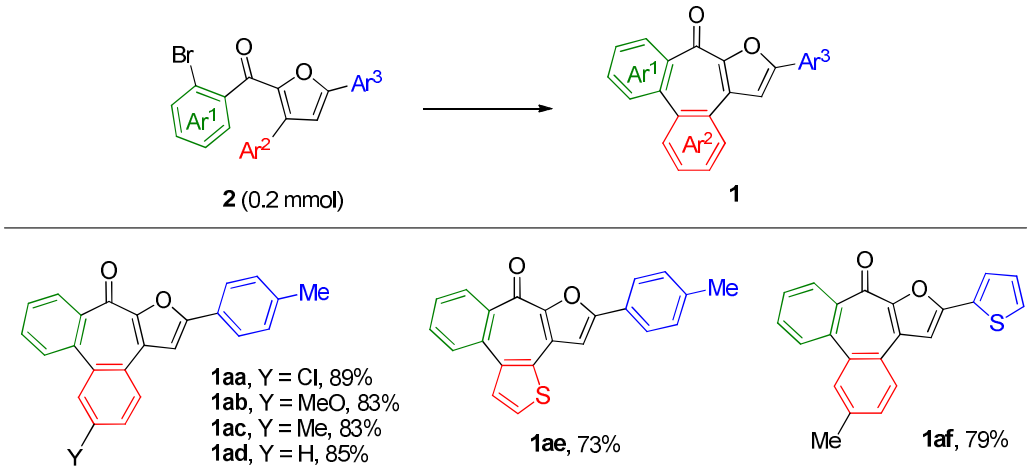
Entry	Complex/Ligand	Base (eq.)	Solvent	Temp./Time	Yield [2]
1	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	DMF	140 °C/20 h	68%
2	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	98%
3	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (3)	DMF	140 °C/20 h	95%
4	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	DBU (1.2)	DMSO	140 °C/20 h	-
5	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	DMSO	140 °C/10 h	58%
6	$Pd(OAc)_2/PPh_3$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	42%
7	$Pd(OAc)_2/P(o\text{-}tol)_3$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	21%
8	$Pd(OAc)_2/PCy_3$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	78%
9	$Pd(OAc)_2$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	-
10	$Pd(PPh3)_4$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	74%
11 [3]	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	DMSO	140 °C/20 h	-
12	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	DMSO	120 °C/20 h	-
13	$Pd(OAc)_2/PCy_3{\cdot}HBF_4$	Cs_2CO_3 (1.2)	toluene	110 °C/20 h	-

[1] Reaction conditions: A mixture of **2aa** (0.2 mmol), [Pd] (10 mol%), ligand (20 mol%) and base in solvent (2 mL) was heated in an oil bath under N_2. [2] NMR yields. [3] Under air atmosphere.

The structure of **1aa** was determined by spectroscopic methods. The infrared carbonyl stretching wavenumber of **1aa** appears at 1628 cm^{-1}, which is red-shifted by ca. 20 cm^{-1} in comparison to **2aa.** This stretching frequency is similar to those of furotropones [10–17]. Meanwhile, the ^{13}C NMR shift of carbonyl function in **1aa** emerges at 178.6 ppm, which resembles those of tropones. HRMS-ESI shows m/z at 371.0823, which is consistent with $[M + H]^+$, implying the formation of a seven-member ring by the elimination of HBr in this reaction.

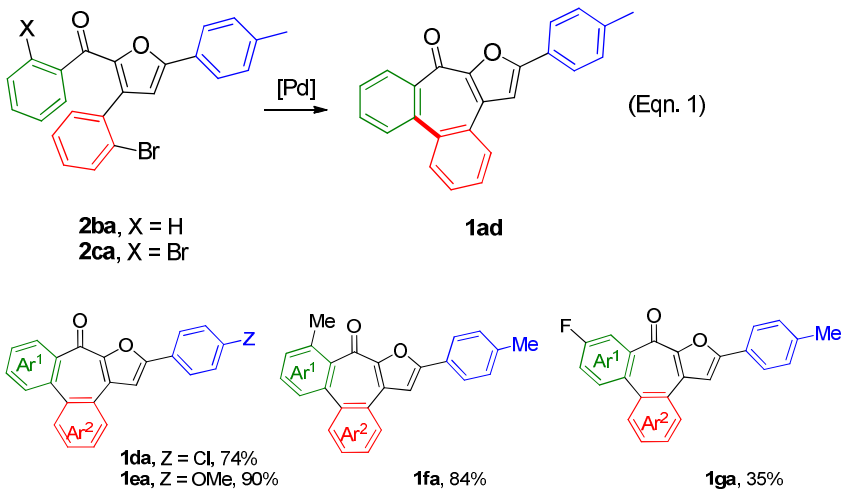
3.2. Reaction Scope

With the optimized reaction conditions in hand, a series of substrates with bromide modified on the Ar^1 ring **2aa**–**2ag** were investigated. As shown in Scheme 4, **2aa**–**2ad**, with various substituted groups at the *para* position in the Ar^2 ring, could provide the corresponding products **1aa**–**1ad** in excellent isolated yields (83–89% yield). We noticed that **2ae** underwent the cyclization smoothly to **1ae**, giving a 73% yield, showing that the thiophenyl ring is able to proceed with such a reaction via Pd-catalyzed C-H activation. As expected, compound **2af,** a reactant with a thiophenyl substituent at C(5) of the furan ring, gave the desired product **1af** at a high yield. It is worth mentioning that compound **2ag**, with the *para* bromo substituent in the Ar^2 ring, provided **1ad** at 7% and a mixture of unidentified products under the optimized reaction conditions. Apparently, de-bromination took place to yield **1ad,** but the oxidative addition of C-Br bonds in the Ar^2 ring also caused complications in the reaction.



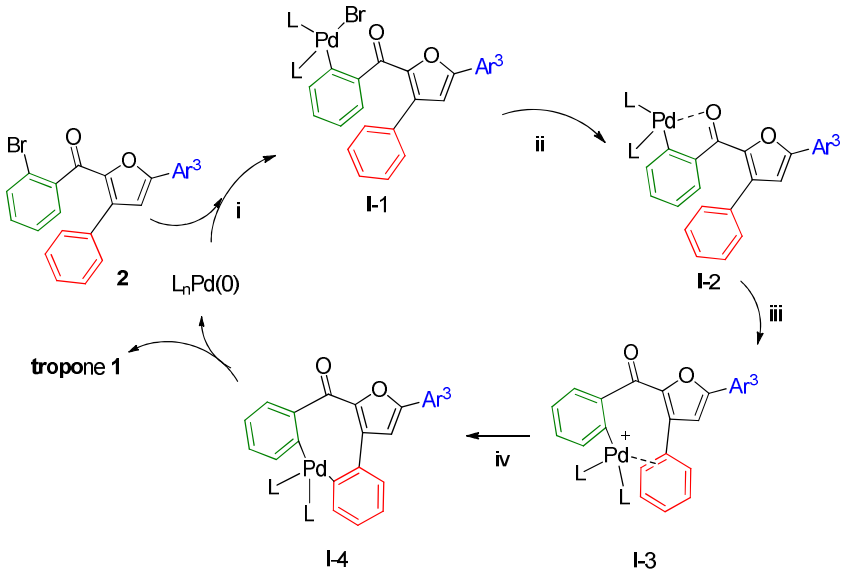
Scheme 4. Pd-catalyzed cyclization with bromide at Ar^1 ring. Conditions: **2** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), $PCy_3{\cdot}HBF_4$ (0.04 mmol), Cs_2CO_3 (0.24 mmol) in DMSO (2 mL) at 140 °C for 20 h.

This palladium-catalyzed arylation leading to the tropone ring is also be applied to those with the *ortho* bromo-substituent in the Ar^2 ring (**2ba**–**2ga**). Similar to the transformation of **2ad** into **1ad**, **the** cyclization of **2ba** gave the same product **1ad** at a 95% yield [Equation (1)]. However, substrate **2ca**, which has *o*-bromo groups in both the Ar^1 and Ar^2 rings, did render the expected product **1ad**, showing the poor efficiency of the coupling of di-bromide moieties. Other substituents in both the Ar^1 and Ar^3 ring are also applicable for this cyclization, leading to the corresponding tropones (Scheme 5) and illustrating a possible introduction of various substituents in this methodology.



Scheme 5. Product of Pd-catalyzed cyclization with bromide at Ar^2 ring.

A possible mechanistic pathway leading the tropone ring is shown in Scheme 6 [24–29]. Initially, the oxidative addition of C-Br bond toward the metal center (Scheme 6, step i) gives intermediate **I-1**, which then undergoes the dissociation of bromide from the metal center to yield **I-2** or **I-3** (Scheme 6, step ii or iii)**.** The arylic C-H bond is activated by the palladium center to render intermediate **I-4** (Scheme 6, step iv). Reductive elimination takes place from the metal center to produce the tropone and regenerates the palladium catalyst, completing the catalytic cycle.



Scheme 6. Possible pathway leading to the formation of the tropone ring.

3.3. Photo-Physical Property of Tropones **1**

The absorption and emission spectra of the newly prepared dibenzo[3,4:5,6]cyclohepta[1,2-*b*]furan-8-ones were examined. The spectroscopic data of all the compounds in ethanol (10 μM) are summarized in Table 2. All the compounds have an absorption maximum around 360 nm, giving these compounds a light yellow color. This series of compounds also give emissions in the range of 425~486 nm, showing a slightly substituent effect on the photo-physical property.

Table 2. Spectral data of Dibenzofurotropones **1aa–1ga** [1].

Compd.	λ_{abs} (nm) [2]	λ_{max} (nm)	λ_{emi} (nm)	Δλstoke [3]
1aa	273 (20,002), 363 (11,677)	363	462	99
1ab	279 (26,170), 360 (17,098)	360	464	104
1ac	275 (19,714), 361 (11,859)	361	447	86
1ad	275 (29,226), 362 (15,367)	362	448	86
1ae	313 (26,321), 361 (14,403)	361	425	64
1af	274 (12,257), 371 (9087)	371	477	106
1da	278 (23,794), 358 (15,537)	358	439	81
1ea	273 (24,253), 374 (16,325)	374	486	112
1fa	282 (29,814), 359 (16,748)	359	464	105
1ga	282 (21,399), 368 (16,729)	368	473	105

[1] in EtOH (10 μM); [2] ε($M^{-1}cm^{-1}$) given in parentheses; [3] $\Delta\lambda_{stokes} = \lambda_{emi} - \lambda_{max}$, in nm.

Furthermore, we surveyed the absorption and emission spectra of **1ad** under various solvent systems. The absorption maximum of $n \rightarrow \pi^*$ transition in toluene comes at 355 nm, while, in a polar solvent of ethanol, absorption is displayed at 362 nm, suggesting a bathochromic shift of about 7 nm. In addition, the fluorescence emission spectra of **1ad** were recorded in different solvents and the results showed that fluorescence emission is also solvent-dependent (Table 3). It appeared that there was a maximum Stokes shift of 86 nm in the ethanol solution. These observations are quite similar to those of furo[2,3-d]tropones, as reported by Ramasastry's group [19].

Table 3. Spectral data of Dibenzofurotropones of **1ad** in various solvents [1].

Solvent	λ_{abs} (nm) [2]	λ_{max} (nm)	λ_{emi} (nm)	$\Delta\lambda_{stoke}$ [3]
Toluene	292 (14,833), 355 (14,988)	355	426	71
THF	296 (15,599), 351 (13,012)	351	393	42
EtOAc	276 (30,563), 351 (19,608)	351	396	45
EtOH	275 (29,226), 362 (15,367)	362	448	86
CH3CN	276 (28,451), 353 (17,793)	353	433	80

[1] 10 μM in various solvents; [2] ε($M^{-1}cm^{-1}$) given in parentheses; [3] $\Delta\lambda_{stokes} = \lambda_{emi} - \lambda_{max}$, in nm.

4. Conclusions

In summary, we have developed a procedure for the preparation of a series of substituted dibenzo[3,4:5,6]cyclohepta[1,2-*b*]furan-8-ones via the palladium-catalyzed cyclization of (2-bromoaryl)(3-arylfuran-2-yl)methanones through the activation of arylic C–H bonds. In particular, compound **1ae** is the first molecule with three different aromatic rings annulated with tropone (benzothiophenfurotropone). These newly prepared tropones show absorptions around 360 nm and emissions around 440~486 nm. Detailed photophysical studies of the applications of these compounds are currently under investigation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/reactions5010005/s1, Table S1 Physical and spectral data of **2aa–2ga**; Table S2 Physical and spectral data of **1aa–1ga**; Figure S11H NMR spectrum of compound **2aa**; Figure S2 ^{1}H NMR spectrum of compound **2ab**; Figure S3 ^{1}H NMR spectrum of compound **2ac**; Figure S4 ^{1}H NMR spectrum of compound **2ad**; Figure S5 ^{1}H NMR spectrum of compound **2ae**; Figure S6 ^{1}H NMR spectrum of compound **2af**; Figure S7 ^{1}H NMR spectrum of compound **2ag**; Figure S8 ^{1}H NMR spectrum of compound **2ba**; Figure S9 ^{1}H NMR spectrum of compound **2ca**; Figure S10 ^{1}H NMR spectrum of compound **2da**; Figure S11 ^{1}H NMR spectrum of compound **2ea**; Figure S12 ^{1}H NMR spectrum of compound **2fa**; Figure S13 ^{1}H NMR spectrum of compound **2ga**; Figure S14 ^{1}H NMR spectrum of compound **1aa**; Figure S15 ^{1}H NMR spectrum of compound **1ab**; Figure S16 ^{1}H NMR spectrum of compound **1ac**; Figure S17 ^{1}H NMR spectrum of compound **1ad**; Figure S18 ^{1}H NMR spectrum of compound **1ae**; Figure S19 ^{1}H NMR spectrum of compound **1af**; Figure S20 ^{1}H NMR spectrum of compound **1da**; Figure S21 ^{1}H NMR spectrum of compound **1ea**; Figure S22 ^{1}H NMR spectrum of compound **1fa**; Figure S23 ^{1}H NMR spectrum of compound **1ga**.

Author Contributions: Conceptualization, S.-T.L.; methodology, investigation, and data collection, Y.-W.L.; writing—original draft preparation, S.-T.L.; data checking and editing, Y.-W.L. and S.-T.L.; supervision, S.-T.L. funding acquisition, S.-T.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Technology, Taiwan (MOST111-2113-M-002-007).

Data Availability Statement: The data reported in this article can be obtained from the authors upon reasonable request.

Acknowledgments: We acknowledge the mass spectrometry technical research services of the NTU Consortia of Key Technologies for mass measurement.

Conflicts of Interest: The authors declare no conflicts of interest.

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