



# DALHOUSIE UNIVERSITY

Retrieved from DalSpace, the institutional repository of  
Dalhousie University

<https://dalspace.library.dal.ca/handle/10222/76388>

Version: Pre-print

**Publisher's version:** Hilborn, James W., Moya-Barrios, Reinaldo, Thompson, Alison. (2019).

The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes. ACS Publication (pre-publication).

# The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

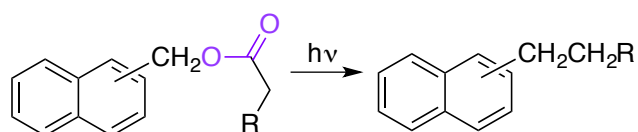
James W. Hilborn,<sup>†\*</sup> Reinaldo Moya-Barrios<sup>§</sup> and Alison Thompson<sup>§\*</sup>

<sup>†</sup>2 Wilwood Dr., R.R.#2, Falmouth, Nova Scotia, B0P 1L0, Canada

<sup>§</sup>Department of Chemistry, Dalhousie University, P.O. Box 15000,

Halifax, Nova Scotia, B3H 4R2, Canada

## Table of Contents graphic



## light-activated decarboxylation of esters

### Abstract

The synthesis of naphthylarylethanes via the photodecarboxylation of naphthylmethyl arylacetate esters is reported where the aryl group is able to stabilize a charge transfer reaction. The reaction proceeds via intramolecular charge transfer from the donor to acceptor thereby enhancing a pathway to produce, within the solvent cage, the desired diarylethane products. These in-cage naphthylarylethanes are produced in good yields, in a single photochemical step, with the use of cyclohexane as solvent providing optimal yields.

### Introduction

Diarylethanes are important for the preparation of pharmaceutically active species, such as the combretastatin analogues, which exhibit anti-neoplastic properties,<sup>1-4</sup> as well as synthetic intermediates for the preparation of polycyclicaromatic hydrocarbons.<sup>5</sup> Access to diarylethanes typically relies upon one of three strategies that involve either: Wittig<sup>6</sup> or Mizoroki-Heck<sup>7</sup> chemistry following by reduction; carbon-hydrogen activation of toluyl substrates;<sup>8</sup> or the

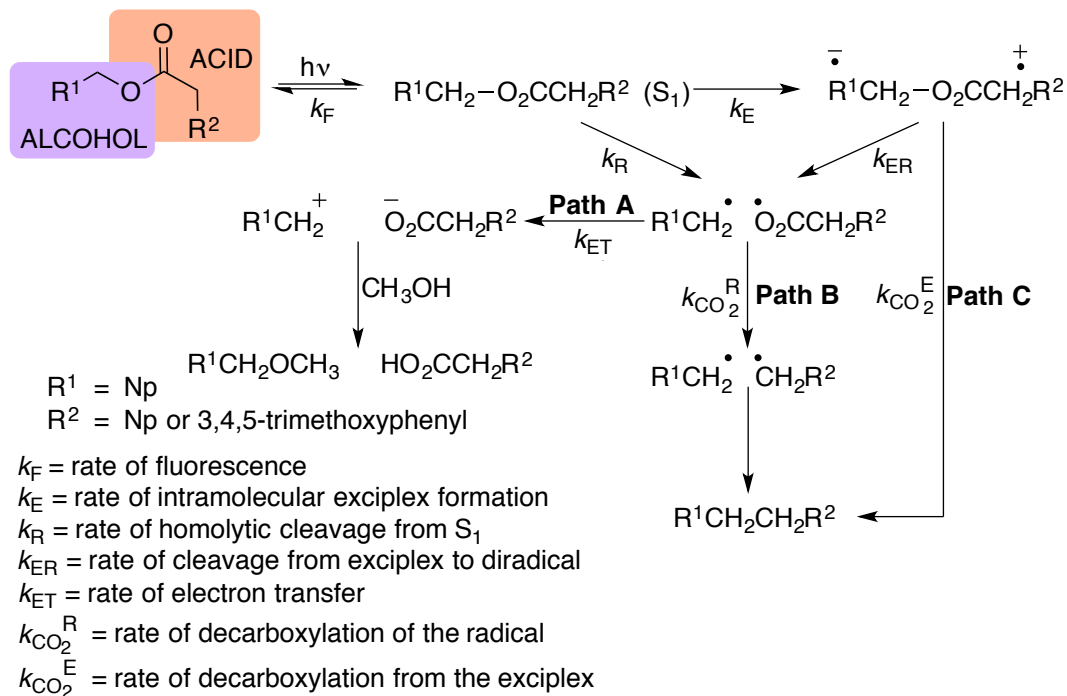
## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

production and subsequent coupling of benzylic radicals produced from benzyl halides and the use of chemical initiators.<sup>9-13</sup> Although the latter route is attractive, these radicals must successfully scavenge other benzyl radicals in order to form the desired diarylethane. Reactions are therefore fraught with challenges, and result in low yields due to the inevitability of other radical-derived reactions, undesired scavenging and the formation of unwanted by-products and polymeric materials. These intermolecular reactions have thus been limited to substrates that serve to provide, via geminate radical pair combination reactions, diarylethane products lacking substituents that would undesirably react with radicals. Furthermore, the conditions typically used for these reactions involve the use of toxic or expensive catalysts, as well as the use of high temperature. For instance, recent examples utilize nickel (II) chloride as the catalyst with samarium and a THF/HMPA mixed solvent system at reflux temperature.<sup>14</sup>

Preparation of diarylethanes could be envisioned within a solvent cage by the extrusion of carbon dioxide (i.e. photodecarboxylation) of suitably substituted esters. In this case the respective moieties of the ester could be tuned so as to produce species that combine, in-cage, to produce diarylethanes. Thus, in order for this reaction to be without complication it would be advantageous for it to proceed through the singlet excited state ( $S_1$ ). Naphthylmethyl esters are known<sup>15-18</sup> to exclusively cleave via the singlet excited state, providing a unique platform for the proposed synthesis of naphthylarylethanes as shown in ~~Figure 1~~Figure 1.

# The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

Figure 1. Radical pathway to diarylethanes via decarboxylation of esters



Reports show that unsymmetrical diarylethanes have been produced, albeit within complex product mixtures, via the photodecarboxylation of naphthylmethyl acetate and benzylic esters under mild conditions in dioxane or methanol at room temperature.<sup>16,17,19</sup> The viability of the mechanistic pathways involving naphthylmethyl ester substrates was elucidated in methanol. Once excited, the ester ( $S_1$ ) undergoes homolytic cleavage (denoted via the rate constant  $k_R$ ), whereupon two processes then compete: Path A where electron transfer ( $k_{ET}$ ) provides cations and anions, which subsequently form ionic-derived products; and Path B where decarboxylation ( $k_{CO_2}^R$ ) of the acyloxy radical ( $R^2\text{-CH}_2\text{CO}_2^\bullet$ ) produces the benzylic-type radical that combines with  $R^1\text{-CH}_2^\bullet$  to provide diarylethanes within the solvent cage. An alternative route, Path C, involves charge transfer ( $k_E$ ) from the initial excited singlet state to produce an intramolecular

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

exciplex, and also provides diarylethanes but this time via  $k_{CO_2^E}$ , i.e. decarboxylation from the intramolecular exciplex.

In order for this process to have synthetic utility for the preparation of naphthylarylethanes, Paths B (geminate combination only) and C would need to become the dominant processes thereby reducing the potential for Path A to be competitive. This could potentially be achieved via use of a non-polar solvent, such as to minimize Path A, and by tuning the ester substrates in order to stabilize intramolecular charge transfer (exciplex formation, Path C) and thereby support formation of the desired diarylethane product. For example, selecting naphthylmethyl phenylacetate esters would present the acyloxy group of the ester as a good donor that would stabilize a radical cation to promote Path C. Indeed, when a single methoxy group is added to the phenylacyloxy group of the naphthylmethyl ester the charge transfer pathway ( $k_E$ ) leads to the production of radical derived products ( $k_{CO_2^E}$ ).<sup>20</sup> In methanol, this single substituent preferentially directed the dominant mechanism to proceed via the charge transfer (exciplex) to form the diarylethane but was insufficient to effect sole formation of the exciplex. Given this, we suspect that the addition of a more effective electron donor on the acyloxy group of the ester, and an electron acceptor on the naphthalene (alkyl) group, would enhance the  $k_{CO_2^E}$  pathway (Path C, and thus  $k_{CO_2^E} \gg k_{ER}$ ). Examples of intramolecular electron transfer (exciplex formation) have been reported in a corresponding systems.<sup>21-24</sup> For instance in the 1-naphthylmethyl benzoate system,<sup>22</sup> electron transfer occurs between the naphthalene ring and the benzene ring, paralleling the original naphthylmethyl phenylacetate work.

Promoting Paths B and C, and thereby a practical preparation of diarylethanes from suitably substituted esters, exploits the advantages of this synthetic strategy over reported methods, i.e. room temperature, requires no catalyst and the reaction work-up is straightforward.

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

The photochemistry promises to be relatively uncomplicated since it occurs exclusively via the singlet excited state. The products are rapidly formed, and almost exclusively within the solvent cage<sup>17,20</sup> so the substrate esters can include substituents (i.e. nitriles) that normally would react with radicals diffusing through the solvent. For these ester substrates, this methodology eliminates the need for complex synthetic steps and provides good yields of the desired naphthylarylethanes.

### Results and Discussion

Herein we report our success promoting naphthylarylethane formation by using either a naphthyl group or a 3,4,5-trimethoxyphenyl group in the acyloxy moiety of the naphthylmethyl ester ( $R^2$  in Figure 1). The nature of the naphthyl or substituted-naphthyl alkyl moiety of the ester ( $R^1$  in Figure 1) tunes the electron acceptor character of  $R^2CH_2$  and thereby promotes Path C, as well as enables investigation of the tolerance of the methodology to these functional groups.

The desired esters (**1a-1i**) were synthesized through the coupling of respective alcohols and (activated) acids (see GP1 and GP2 in the Experimental Section). This series was selected so as to determine whether judicious use of substituent effects within the acyloxy and alkyl groups of the ester could serve to promote naphthylarylethane formation via direct photolysis.

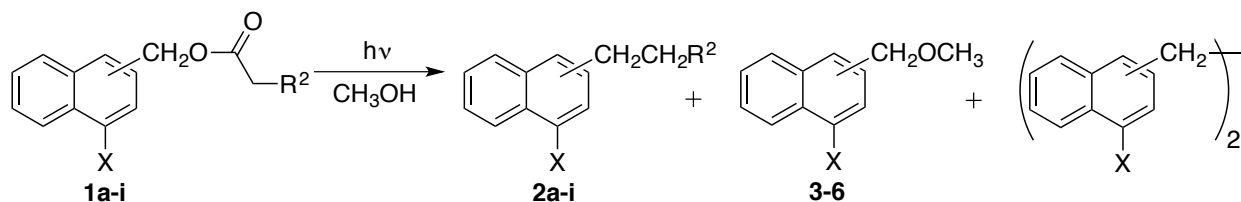
Photolysis of methanolic solutions of esters **1a-1i** was achieved using a 200 W Hanovia medium pressure Quartz Hg lamp in a Pyrex immersion well, as described in the Experimental Section.

Reactions were monitored using GC and taken to completion for the preparative scale runs.

Analytical runs were monitored by GC, using previously isolated, purified and characterized materials to enable quantitative analysis (see GP3, GP4 and GP5 in the Experimental Section).

# The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

**Table 1.** Photolysis of esters **1a-1i** in methanol



Starting Material				Products <sup>a</sup>			
Ester	Np - Position	X Substitution	R <sup>2</sup>	Out of Cage Naphthyl Dimer (%)	In-Cage Reaction Product (2a-2i) (%)	Methylether (3-6) (%)	Total (%)
<b>a</b>	1	H	1-Np	NA	51	30	81
<b>b</b>	1	H	2-Np	2	46	31	79
<b>c</b>	2	H	1-Np	2	45	22	69
<b>d</b>	2	H	2-Np	NA	62	33	95
<b>e</b>	1	H	3,4,5-trimethoxy Ph	3	64	19	86
<b>f</b>	2	H	3,4,5-trimethoxy Ph	ND <sup>b</sup>	86 <sup>b</sup>	10 <sup>b</sup>	96 <sup>b</sup>
<b>g</b>	1	4-Me	1-Np	ND	47	15	62
<b>h</b>	1	4-CN	1-Np	ND	54	2	56
<b>i</b>	1	4-CN	3,4,5-trimethoxy Ph	ND	23	3	26

<sup>a</sup> Yield determined by calibrated GC-FID. <sup>b</sup> Yield determined by calibrated GC-MS in an attempt to enable

identification of any other products of photolysis

ND – Not detected; NA – Not Applicable; Np - Naphthyl

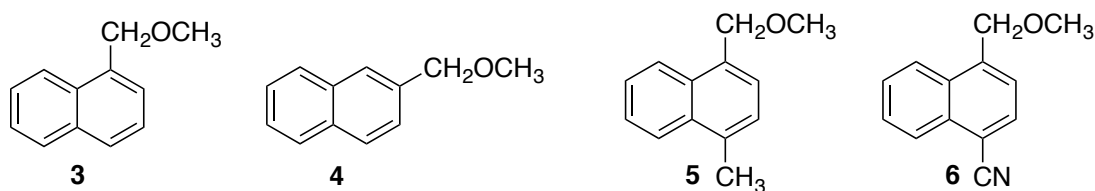
For the naphthylmethyl esters (**1a-1i**) in methanol ([Table 1](#)), the major product in each case was the desired diarylethane (**2a-2i**) formed by in-cage reaction by the stabilization of the charge transfer intermediate pathway (Path C) and/or Path B. However, the methylethers (**3-6**, [Figure 2](#)) were also obtained in significant amounts courtesy of the respective ionic-derived minor pathway being operative (Path [AA](#), [Figure 1](#)). For the mechanism given in [Figure](#)

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

1, the effects on product formation of inter- ( $k_{ET}$ ) and intramolecular ( $k_E$ ) charge / electron transfer, i.e. Path A vs. Paths B and C, respectively, are understood.<sup>20</sup>

Nevertheless, overall conversions were reasonably high (see [Table 1](#) ~~Table 1~~), the exception being ester **1i**. It should be noted that, although considered, the corresponding methylnaphthalene photoproducts were not observed in these reactions, as consistent with previous studies involving 1-naphthylmethyl acetate esters.<sup>15,17,20</sup>

**Figure 2.** Undesired methylether photoproducts



For esters (**1a-1h**), the yields from the photolysis in methanol ([Table 1](#) ~~Table 1~~) ranged from 45-86% yield for the naphthylarylethane products (**2a-2h**), while the methylether (**3-6**) was obtained in 2-33% yield. These results demonstrate that the undesired methylethers are produced in significant amounts (via Path A) even when the acyloxy group of the ester ( $R^2CH_2$  in Figure 1, where  $R^2$  is a naphthyl or 3,4,5-trimethoxyphenyl group) has been tuned to enhance the electron-donor ability in an effort to form greater amounts of the desired in-cage radical products. Evidently, since Path A is still operative, the substitution effects on the acyloxy donor of the ester are insufficient to direct the reaction to the single desired product. Evaluating the yields when using the same naphthyl-substituted alkyl group ( $R^1CH_2$  in [Figure 1](#) ~~Figure 1~~) [1-position on the naphthalene ring (**1a**, **1b** and **1e**)] with a different acyloxy donor ( $R^2CH_2$ ), the yield of the naphthylarylethane increases going from the naphthalene ring to the 3,4,5-trimethoxy group, which provides supporting evidence that this group is a better electron donor and therefore better stabilizes the radical cation and perhaps directs more of the reaction to proceed by Path C.



## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

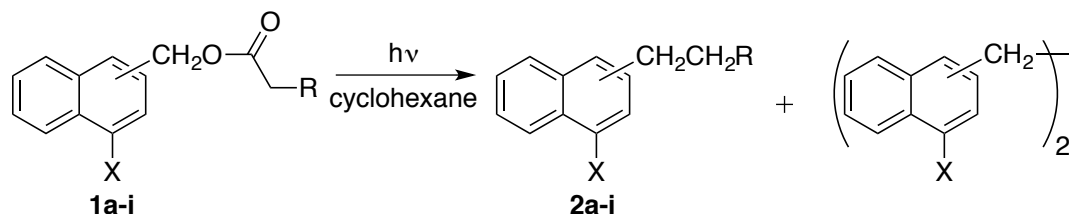
This same behaviour is seen for the 2-substituted naphthylmethyl esters (**1c**, **1d** and **1f**) which also provide increased yields of the naphthylarylethane products (**2c**, **2d** and **2f**), since the 3,4,5-trimethoxyphenylacetyloxy group is a better electron donor than the naphthyl group and thereby presumably stabilizes the radical cation enroute, via Path C. We can therefore propose that the acyloxy donor group of the ester ( $R^2CH_2$  in ~~Figure 1~~[Figure 1](#)) has a dominating influence in the production of the naphthylarylethane coupling product (**2a-2i**) than the position of the substituent on the naphthalene of the alkyl acceptor ( $R^1CH_2$ ) group of the ester. This is supported by the fact that photolysis of ester **1g**, bearing an electron donating methyl group on the naphthalene ring, results in similar yield to those obtained for esters **1a** and **1c**. For esters **1h** and **1i**, the incorporation of a nitrile group on the naphthalene ring (alkyl group of the ester) with the same donor group (acyloxy group of the ester) provides the most extreme case for charge transfer (Path C). However, the overall yields for the naphthonitrile substrates (**1h** and **1i**) are lower for the photoreactions in methanol (Table 1) supporting the notion that, although Path C ( $k_E$ ) is dominant, another pathway is also present. In previous work the photochemistry of naphthonitrile in the presence of similar methoxy-substituted phenylacetic acid derivatives provides a mixture of different products thereby supporting this conclusion.<sup>25</sup>

From the results obtained in methanol (see Table 1), it is clear that the substituent (electronic) effects were not sufficient to influence the process to form only a single product (diarylethane) and thereby direct the process exclusively through Pathways B and C ( $k_E$ ). In an effort to promote the radical production, the use of cyclohexane as solvent was investigated. The non-polar, and non-nucleophilic nature of cyclohexane was expected to shut down the ionic-derived photosolvolysis reaction (Path A) and instead support formation of the radical-derived products. Cognizant that success would result in a practical route to radical-derived

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

diarylethanes, solutions of esters **1a-1i** in cyclohexane were photolysed using the same conditions as used for reactions involving methanol ([Table 2](#)). Gratifyingly, the desired diarylethanes were essentially the only products observed.

**Table 2.** Photolysis of esters **1a-1i** in cyclohexane



Starting Material				Products		
Ester <b>1</b>	Np - Position	X Substitution	R	Out of Cage Naphthyl Dimer (%)	In-Cage Reaction Product ( <b>2a-2i</b> ) (%)	Methylether ( <b>3-6</b> ) (%)
<b>a</b>	1	H	1-Np	NA	72	-
<b>b</b>	1	H	2-Np	ND	55	-
<b>c</b>	2	H	1-Np	1	60	-
<b>d</b>	2	H	2-Np	NA	74	-
<b>e</b>	1	H	3,4,5-trimethoxy Ph	6	81	-
<b>f</b>	2	H	3,4,5-trimethoxy Ph	1	65	-
<b>g</b>	1	4-Me	1-Np	ND	79	-
<b>h</b>	1	4-CN	1-Np	ND	71	-
<b>i</b>	1	4-CN	3,4,5-trimethoxy Ph	ND	50	-

Yield determined by calibrated GC-FID.

ND – Not detected; NA – Not Applicable; Np - Naphthyl

The out of cage reaction products (naphthyl dimer) were observed at trace levels. The reaction provides a single synthetic step to the desired naphthylarylethanes (**2a-2i**, in-cage products) from the corresponding esters. The use of cyclohexane as solvent renders Path A

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

unavailable, and therefore photolysis presents only Paths B and C and thus formation of only the in-cage product. In cyclohexane, no appreciable differences were noticed in the individual product yields by changing the substitution pattern of the donor ( $R^2CH_2$ ) at the 1- and 2-positions on the naphthalene ester (**1a-1d**), as seen in [Table 2](#). Varying the substituents on the naphthalene ring on the acceptor (alkyl moiety of the ester), while maintaining the 1-naphthalene group on the acyloxy donor (**1a**, **1c**, **1g** and **1h**), provides the naphthylarylethane (in-cage) product (**2a**, **2c**, **2g** and **2h**) in similar yields, no matter what the substitution pattern.

### Conclusions

Naphthylmethyl esters (**1a-1i**) were photolyzed in methanol and cyclohexane resulting in appropriately substituted naphthylarylethanes (**2a-2i**) as the major product in each case. In methanol, the ester photolysis does not produce the diarylethanes exclusively as the charge transfer (exciplex) pathway (via Path C) does not dominate. The photolysis of these same esters in cyclohexane renders the photosolvolytic pathway (Path A) unavailable and thereby provides a synthetically useful method for the preparation the naphthylarylethanes in good yield. In short, solvent effects have a greater impact on the product distribution than do changes to substituent patterns around these substrates.

### Experimental Section

All reactions were carried out under an inert atmosphere of nitrogen or argon with magnetic stirring. Reagents and solvents were used as received from commercial sources except: 4-methyl-1-naphthalenemethanol,<sup>15</sup> 4-cyano-1-naphthalenemethanol was prepared from the corresponding benzyl bromide<sup>26</sup> followed by hydrolysis using aq.  $CaCO_3$ ,<sup>27</sup> 1-naphthylacetyl chloride<sup>28</sup> and 2-naphthylacetyl chloride<sup>28</sup> were prepared according to literature procedures. Preparative reactions were followed using TLC analysis involving pre-coated (silica gel 60 F254,

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

0.25 mm) plates with plastic backing, and UV light as visualizing agent. Column chromatography was carried out using silica gel (63-200  $\mu\text{m}$  particle size, 70-230 mesh). Melting points were measured using a Fisher-Johns Melting Point apparatus and are uncorrected. IR spectra, provided in  $\text{cm}^{-1}$ , were recorded using an FTIR instrument after either preparing a KBr pellet or dissolving the sample in  $\text{CH}_2\text{Cl}_2$  and allowing the solvent to evaporate to provide a film on NaCl plates. Only the significant absorption bands ( $\text{cm}^{-1}$ ) are reported. UV spectra are provided in nm and were obtained in acetonitrile using a UV-VIS spectrophotometer, and molar absorption coefficients ( $\epsilon$ ) are defined in  $\text{L mol}^{-1}\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained in deuterated chloroform ( $\text{CDCl}_3$ ) and were recorded using a 500 MHz spectrometer.  $^1\text{H}$  chemical shifts are reported in ppm relative to tetramethylsilane using the  $\text{CDCl}_3$  residual solvent signal at  $\delta = 7.26$  as an internal standard.  $^{13}\text{C}$  NMR spectra were recorded using the proton-decoupled UDEFT pulse sequence, and chemical shifts are reported in ppm referenced to the  $\text{CDCl}_3$  signal at  $\delta = 77.2$ . Multiplicity is presented as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. Coupling constant(s),  $J$ , are reported in hertz (Hz), alongside integration. HRMS data were obtained using a microOTOF mass spectrometer operating in positive ion ESI mode. Reaction samples were analyzed using a GC-FID instrument equipped with a DB-5 megabore column (30 m x 0.53 mm with a 1.5  $\mu\text{m}$  film thickness), an FID detector and an AOC-20i autosampler: initial temperature 140°C for 4 minutes then a 25°C / min ramp to 300°C and hold for 10 minutes; injector and detector temperatures set at 320°C with an injection volume of 3.0  $\mu\text{L}$ . For the GC/MS analysis a HP 6890 GC with a HP 5973 mass selective detector was used equipped with a HP-5 5% Phenyl Methyl Siloxane column (30 m x 0.25 mm x 0.5  $\mu\text{m}$  film thickness): initial temperature 140°C for 4 minutes then a 25°C / min ramp to 300°C

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

and hold for 10 minutes; injector and detector temperatures set at 230°C with an injection volume of 1.0  $\mu$ L.

### Synthesis of Substituted 1- and 2-Naphthylmethyl Substituted Acetate Esters (1a-1i)

#### General Procedure 1 (GP1) for the preparation of esters (1a-1d, 1g)

With modification of a reported procedure,<sup>15</sup> to a well-stirred solution of the naphthalenemethanol (20 mmol, 1 equiv; i.e. 3.16 g in the case of 1-naphthalenemethanol to enable preparation of **1a**) in toluene (50 mL) was added pyridine (1 mL). To this solution was slowly added a solution of the required acid chloride (22 mmol, 1.1 equiv; i.e. 4.50 g in the case of 1-naphthylacetyl chloride to enable preparation of **1a**) in toluene (30 mL) over 30 minutes. Stirring was continued for an additional 16 h at room temperature. The reaction was quenched by adding water and the two layers separated. The toluene layer was washed with 10% aq. HCl (2 x 50 mL), 5% aq. NaOH (50 mL) and water (50 mL). The organic layer was then dried ( $\text{MgSO}_4$ ), filtered, and the solvent removed *in vacuo* to yield the crude ester. The crude material was purified via column chromatography over silica gel using 3% EtOAc:hexane as eluent. The resultant ester was crystallized from hexane.

#### General Procedure 2 (GP2) for the preparation of esters (1e-1f, 1h-1i)

The acid (5.3 mmol, 1 equiv; i.e. 1.20 g in the case of 3,4,5-trimethoxyphenylacetic acid to enable preparation of **1e**) was dissolved in dry THF (20 mL) and the solution cooled to 0°C. 1,1'-Carbonyldiimidazole (1.04 g 6.4 mmol, 1.2 equiv) was then added as a solid. The solution was allowed to warm to room temperature and then stirred at this temperature for 1 h. To this solution was added a solution of the alcohol (6.9 mmol, 1.3 equiv; i.e. 1.01 g in the case of 1-

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

naphthalenemethanol to enable preparation of **1e**) dissolved in dry THF (10 mL) and stirring was continued for 72 h. The solvent was removed *in vacuo* and the residue dissolved in EtOAc (50 mL). The solution was washed with aq. 5% HCl (20 mL), aq. 2% NaHCO<sub>3</sub> (20 mL) and water (20 mL). The organic layer was then dried (MgSO<sub>4</sub>), filtered and the solvent removed *in vacuo*. The residue was purified via column chromatography using 30% EtOAc:hexane as eluent. The resultant ester was crystallized from warm CH<sub>2</sub>Cl<sub>2</sub>:hexane.

**1-Naphthylmethyl 1-naphthylacetate (1a):**<sup>29</sup> According to GP1, the title compound was prepared from 1-naphthylacetyl chloride and 1-naphthalenemethanol; white solid; yield 73%; mp 103-104°C; UV:  $\lambda_{\max}$  261 ( $\epsilon$  7.25 x 10<sup>3</sup>), 271 (1.13 x 10<sup>4</sup>), 281 (1.36 x 10<sup>4</sup>), 292 (9.65 x 10<sup>3</sup>) nm; IR (KBr): 3038, 2959, 1728 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 7.95 (d,  $J$  = 8.1 Hz, 1H), 7.87-7.77 (m, 5H), 7.51-7.38 (m, 8H), 5.58 (s, 2H), 4.11 (s, 2H) ppm; 125 MHz <sup>13</sup>C {<sup>1</sup>H} NMR  $\delta$ : 171.5, 133.9, 133.7, 132.1, 131.6, 131.3, 130.5, 129.3, 128.7, 128.6, 128.1, 128.1, 127.5, 126.5, 126.3, 125.9, 125.8, 125.5, 125.2, 123.8, 123.6, 65.2, 39.3 ppm. [CAS 72977-58-3]. No literature data available.

**1-Naphthylmethyl 2-naphthylacetate (1b):**<sup>30</sup> According to GP1, the title compound was prepared from 2-naphthylacetyl chloride and 1-naphthalenemethanol; white solid: yield 53%; mp 77-78°C; UV:  $\lambda_{\max}$  261 ( $\epsilon$  7.27 x 10<sup>3</sup>), 271 (1.04 x 10<sup>4</sup>), 280 (1.10 x 10<sup>4</sup>), 289 (7.99 x 10<sup>3</sup>) nm; IR (KBr): 3044, 2962, 1727 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 7.91 (d,  $J$  = 8.4 Hz, 1H), 7.87-7.70 (m, 6H), 7.51-7.38 (m, 7H), 5.59 (s, 2H), 3.82 (s, 2H) ppm; 125 MHz <sup>13</sup>C {<sup>1</sup>H} NMR  $\delta$ : 171.4, 133.7, 133.5, 132.5, 131.6, 131.4, 131.3, 129.3, 128.7, 128.2, 128.0, 127.7, 127.6, 127.5, 127.4, 126.5, 126.1, 125.9, 125.8, 125.2, 123.6, 65.1, 41.6 ppm. [CAS 86328-64-5]. Only mass spectral<sup>30</sup> literature data available.

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

**2-Naphthylmethyl 1-naphthylacetate (1c):**<sup>31</sup> According to GP1, the title compound was prepared from 1-naphthylacetyl chloride and 2-naphthalenemethanol; white solid: yield 83%; mp 75-76°C although lit.<sup>31</sup> 57-59°C; UV:  $\lambda_{\max}$  261 ( $\epsilon$  7.25 x 10<sup>3</sup>), 272 (1.02 x 10<sup>4</sup>), 280 (1.05 x 10<sup>4</sup>), 292 (6.11 x 10<sup>3</sup>) nm; IR (KBr): 3045, 2958, 1725 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 8.00-7.99 (m, 1H), 7.87-7.85 (m, 1H), 7.81-7.75 (m, 3H), 7.72-7.68 (m, 1H), 7.63 (s, 1H), 7.48-7.45 (m, 4H), 7.43-7.41 (m, 2H), 7.32 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.5 Hz, 1H), 5.28 (s, 2H), 4.14 (s, 2H) ppm in accord with lit.;<sup>31</sup> 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 171.4, 133.9, 133.2, 133.1, 133.0, 132.1, 130.5, 128.7, 128.2, 128.1, 128.1, 127.9, 127.6, 127.0, 126.4, 126.2, 126.2, 125.8, 125.6, 125.5, 123.8, 66.7, 39.2 ppm. [CAS 129633-45-0].

**2-Naphthylmethyl 2-naphthylacetate (1d):**<sup>17</sup> According to GP1, the title compound was prepared from 2-naphthylacetyl chloride and 2-naphthalenemethanol; white solid: yield 87%; mp 138-140°C; UV:  $\lambda_{\max}$  257 ( $\epsilon$  6.82 x 10<sup>3</sup>), 268 (9.18 x 10<sup>3</sup>), 275 (9.66 x 10<sup>3</sup>), 286 (6.43 x 10<sup>3</sup>) nm; IR (KBr): 3051, 2950, 1732 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 7.82-7.70 (m, 8H), 7.48-7.38 (m, 6H), 5.30 (s, 2H), 3.85 (s, 2H) ppm in accord with lit.<sup>17</sup>; 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 171.4, 133.5, 133.3, 133.2, 133.1, 132.5, 131.4, 128.3, 128.3, 128.0, 128.0, 127.7, 127.7, 127.6, 127.4, 127.2, 126.3, 126.2, 126.2, 125.8, 125.7, 66.8, 41.6 ppm. [CAS 53342-33-9].

**1-Naphthylmethyl 3,4,5-trimethoxyphenylacetate (1e):** According to GP2, the title compound was prepared from 3,4,5-trimethoxyphenylacetic acid and 1-naphthalenemethanol; white solid: yield 50%; mp 73-74°C; UV:  $\lambda_{\max}$  262 ( $\epsilon$  4.75 x 10<sup>3</sup>), 270 (6.96 x 10<sup>3</sup>), 279 (7.82 x 10<sup>3</sup>), 290 (5.07 x 10<sup>3</sup>) nm; IR (film): 2997, 2960, 2939, 2837, 1735 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 7.93-7.91 (m, 1H), 7.87-7.84 (m, 2H), 7.52-7.50 (m, 3H), 7.46 (t,  $J$  = 7.7 Hz, 1H), 6.44 (s, 2H), 5.59 (s, 2H), 3.82 (s, 3H), 3.71 (s, 6H), 3.59 (s, 2H) ppm; 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 171.5, 153.3, 137.2, 133.8, 131.7, 133.3, 129.5, 129.4, 128.7, 127.7, 126.6, 126.0, 125.3, 123.6, 106.3, 65.2,

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

60.8, 56.0, 41.8 ppm; HRMS (ESI/TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{22}H_{22}O_5Na$  389.1359; Found 389.1358. [CAS 1003966-04-8]

**2-Naphthylmethyl 3,4,5-trimethoxyphenylacetate (1f):** According to GP2, the title compound was prepared from 3,4,5-trimethoxyphenylacetic acid and 2-naphthalenemethanol; white solid: yield 70%; mp 75-76°C; UV:  $\lambda_{max}$  266 ( $\epsilon$  5.16 x 10<sup>3</sup>), 274 (5.49 x 10<sup>3</sup>), 286 (3.32 x 10<sup>3</sup>) nm; IR (film): 2962, 2943, 2831, 1732 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 7.83-7.77 (m, 4H), 7.50-7.47 (m, 2H), 7.41 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.5 Hz, 1H), 6.50 (s, 2H), 5.31 (s, 2H), 3.83 (s, 3H), 3.78 (s, 6H), 3.62 (s, 2H) ppm; 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 171.3, 153.2, 137.2, 133.2, 133.1, 133.1, 129.4, 128.3, 127.9, 127.7, 127.3, 126.3, 126.3, 125.7, 106.3, 66.7, 60.8, 56.0, 41.6 ppm; HRMS (ESI/TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{22}H_{22}O_5Na$  389.1359; Found 389.1367.

**4-Methyl-1-naphthylmethyl 1-naphthylacetate (1g):** According to GP1, the title compound was prepared from 1-naphthylacetyl chloride and 4-methyl-1-naphthalenemethanol; white solid: yield 34%; mp 73-74°C; UV:  $\lambda_{max}$  276 ( $\epsilon$  1.30 x 10<sup>4</sup>), 281 (1.42 x 10<sup>4</sup>), 285 (1.39 x 10<sup>4</sup>) nm; IR (film): 3069, 3045, 2964, 2947, 1733 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 8.02 (d,  $J$  = 8.3 Hz, 1H), 7.95 (d,  $J$  = 8.6 Hz, 1H), 7.85 (d,  $J$  = 8.3 Hz, 2H), 7.77 (t,  $J$  = 4.6 Hz, 1H), 7.53 (t,  $J$  = 8.0 Hz, 1H), 7.47-7.38 (m, 5H), 7.35 (d,  $J$  = 7.1 Hz, 1H), 7.24 (s, 1H), 5.54 (s, 2H), 4.08 (s, 2H), 2.68 (s, 3H) ppm; 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 171.5, 135.8, 133.9, 132.9, 132.1, 131.7, 130.5, 129.5, 128.7, 128.1, 128.1, 127.5, 126.4, 126.2, 126.0, 125.8, 125.8, 125.5, 124.8, 124.2, 123.9, 65.4, 39.3, 19.6 ppm; HRMS (ESI/TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{24}H_{20}O_2Na$  363.1356; Found 363.1362.

**4-Cyano-1-naphthylmethyl 1-naphthyl acetate (1h):** According to GP2, the title compound was prepared from 1-naphthaleneacetic acid and 4-cyano-1-naphthalenemethanol; pale yellow solid: yield 58%; mp 127-128°C; UV:  $\lambda_{max}$  282 ( $\epsilon$  1.13 x 10<sup>4</sup>), 292 (1.21 x 10<sup>4</sup>), 300 (1.10 x 10<sup>4</sup>) nm; IR (film): 3061, 2227, 1744 cm<sup>-1</sup>. 500 MHz <sup>1</sup>H NMR  $\delta$ : 8.24 (d,  $J$  = 8.3 Hz, 1H), 7.91-7.74



## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

(m, 5H), 7.67 (t,  $J = 7.3$  Hz, 1H), 7.53-7.35 (m, 6H), 5.58 (s, 2H), 4.14 (s, 2H) ppm; 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 171.1, 137.2, 133.8, 132.4, 132.0, 132.0, 130.8, 130.1, 128.8, 128.4, 128.3, 128.2, 128.0, 126.4, 125.9, 125.9, 125.5, 125.3, 124.0, 123.6, 117.6, 111.0, 64.0, 39.3 ppm; HRMS (ESI/TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{24}\text{H}_{17}\text{NO}_2\text{Na}$  374.1152; Found 374.1161.

**4-Cyano-1-naphthylmethyl 3,4,5-trimethoxyphenyl acetate (1i)**: According to GP2, the title compound was prepared from 3,4,5-trimethoxyphenylacetic acid and 4-cyano-1-naphthalenemethanol; pale yellow solid: yield 63%; mp 120-121°C; UV:  $\lambda_{\text{max}}$  287 ( $\epsilon$   $7.60 \times 10^3$ ), 289 ( $9.21 \times 10^3$ ), 308 ( $7.51 \times 10^3$ ) nm; IR (film): 3088, 3071, 3007, 2970, 2946, 2838, 2230, 1740  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR  $\delta$ : 8.29 (d,  $J = 8.3$  Hz, 1H), 7.98 (d,  $J = 8.6$  Hz, 1H), 7.88 (d,  $J = 7.3$  Hz, 1H), 7.73 (t,  $J = 8.0$  Hz, 1H), 7.63 (t,  $J = 7.7$  Hz, 1H), 7.56 (d,  $J = 7.4$  Hz, 1H), 6.45 (s, 2H), 5.62 (s, 2H), 3.83 (s, 3H), 3.75 (s, 6H), 3.62 (s, 2H) ppm; 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 171.1, 153.3, 137.4, 137.3, 132.5, 132.1, 131.0, 129.0, 128.6, 128.2, 126.1, 125.7, 124.2, 117.5, 111.2, 106.4, 64.2, 60.9, 56.1, 41.6 ppm; HRMS (ESI/TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}_5\text{Na}$  414.1312; Found 414.1326.

### Irradiations

#### Analytical Photolysis

Irradiations for analytical work were carried out using a medium pressure Hanovia 200 W Quartz Hg lamp in a Pyrex 400 mL water-jacketed immersion well. The ester, **1a-1i**, (~ 300 mg) was dissolved in the solvent (methanol or cyclohexane) and irradiated at room temperature. The progress of the reaction was monitored via GC-FID analysis.

#### Analytical Standards

#### Preparative Photolysis

#### General Procedure 3 (GP3) for the Isolation of the Major Photoproduct (2a-2i)

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

In order to obtain the major photoproduct products (in-cage coupling) for full characterization and use as standards for the subsequent photolysis-based analytical work, these compounds were prepared from preparatory photolysis of each of the corresponding esters. Thus, a solution of the ester ( $\approx 300$  mg) in cyclohexane was placed in a Pyrex 400 mL water-jacketed immersion well. In some cases, the solvent was warmed in order to dissolve the ester. The solution was bubbled with argon before and during the irradiation. The temperature for the irradiations was maintained at room temperature. The light source was a 200 W medium pressure Hanovia Quartz Hg lamp. The irradiations were continued for 48 h. After this period of time the photolysis solutions were filtered through a filter paper to remove any insoluble products (dimeric/polymeric material) and the solvent evaporated to dryness. The above procedure was performed twice in order to obtain sufficient material to be used as a standard. The resultant oil was purified via column chromatography using 2% EtOAc:hexane as the eluent. The first eluting fractions were always the in-cage reaction product.

**1-(1-Naphthyl)-2-(1-naphthyl)ethane (2a):**<sup>11,32</sup> Prepared according to GP3 using ester **1a**; light beige solid; mp = 164-165°C, lit.<sup>33</sup> 162-163°C; 500 MHz <sup>1</sup>H NMR  $\delta$ : 8.13 (d,  $J$  = 8.3 Hz, 2H), 7.89-7.87 (m, 2H), 7.75 (d,  $J$  = 8.2 Hz, 2H), 7.55-7.48 (m, 4H), 7.40 (t,  $J$  = 7.6 Hz, 2H), 7.35 (d,  $J$  = 6.3 Hz, 2H), 3.52 (s, 4H) ppm; 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$ : 138.1, 134.0, 131.9, 128.9, 126.8, 125.9, 125.9, 125.6, 125.5, 123.7, 34.1 ppm. [CAS 15374-45-5] Only melting point data available in the literature.

**1-(1-Naphthyl)-2-(2-naphthyl)ethane (2b/c):** Prepared according to GP3 using either ester **1b** or **1c**; light beige solid; mp = 84-85°C; 500 MHz <sup>1</sup>H NMR  $\delta$ : 8.15 (d,  $J$  = 8.6 Hz, 1H), 7.88 (d,  $J$  = 8.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.71 (d,  $J$  = 8.0 Hz, 1H), 7.67 (s, 1H), 7.56-7.36 (m, 6H), 7.31 (d,  $J$  = 6.8 Hz, 1H), 3.47 (t,  $J$  = 8.3 Hz, 2H), 3.22 (t,  $J$  = 8.2 Hz, 2H) ppm; 125 MHz <sup>13</sup>C{<sup>1</sup>H}

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

NMR  $\delta$ : 139.6, 137.8, 134.0, 133.8, 132.2, 131.9, 128.9, 128.0, 127.7, 127.5, 127.4, 126.9, 126.5, 126.1, 126.0, 125.6, 125.6, 125.5, 125.4, 123.7, 37.3, 35.1 ppm; HRMS (ESI/TOF)  $m/z$ :  $[M + H]^+$  Calculated for  $C_{22}H_{19}$  282.1487; Found 282.1462. [CAS 83313-24-0] No literature data available.

**1-(2-Naphthyl)-2-(2-naphthyl)ethane (2d):**<sup>34</sup> Prepared according to GP3 using ester **1d**; white solid; mp = 185-186°C, lit.<sup>35</sup> 182-184°C; 500 MHz  $^1H$  NMR  $\delta$ : 7.81-7.75 (m, 6H), 7.65 (s, 2H), 7.46-7.40 (m, 4H), 7.36 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 3.18 (s, 4H) ppm in accord with lit.;<sup>34</sup> 125 MHz  $^{13}C\{1H\}$  NMR  $\delta$ : 139.3, 133.7, 132.1, 127.9, 127.6, 127.5, 127.4, 126.5, 125.9, 125.2, 38.0 ppm. [CAS 21969-45-9]

**1-(1-Naphthyl)-2-(3,4,5-trimethoxyphenyl)ethane (2e):** Prepared according to GP3 using ester **1e**; off white solid; mp = 98-99°C; 500 MHz  $^1H$  NMR  $\delta$ : 8.05 (d,  $J = 8.3$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.72 (d,  $J = 8.3$  Hz, 1H), 7.51-7.47 (m, 2H), 7.38 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 6.8$  Hz, 1H), 6.37 (s, 2H), 3.83 (s, 3H), 3.79 (s, 6H), 3.37 (t,  $J = 6.8$  Hz, 2H), 2.99 (t,  $J = 8.0$  Hz, 2H) ppm; 125 MHz  $^{13}C\{1H\}$  NMR  $\delta$ : 153.2, 137.7, 136.5, 134.0, 131.9, 128.9, 126.8, 126.2, 125.9, 125.6, 125.5, 123.7, 105.6, 60.9, 56.2, 37.5, 35.0 ppm (one  $^{13}C$  signal missing); HRMS (ESI/TOF)  $m/z$ :  $[M + H]^+$  Calculated for  $C_{21}H_{23}O_3$  323.1642; Found 323.1643.

**1-(2-Naphthyl)-2-(3,4,5-trimethoxyphenyl)ethane (2f):** According to GP3 using ester **1f**; white solid; mp = 86-87°C; 500 MHz  $^1H$  NMR  $\delta$ : 7.81-7.75 (m, 3H), 7.60 (s, 1H), 7.46-7.40 (m, 2H), 7.33 (d,  $J = 8.3$  Hz, 1H), 6.38 (s, 2H), 3.83 (s, 3H), 3.78 (s, 6H), 3.08 (t,  $J = 7.5$  Hz, 2H), 2.95 (t,  $J = 7.9$  Hz, 2H) ppm; 125 MHz  $^{13}C\{1H\}$  NMR  $\delta$ : 153.1, 139.2, 137.5, 136.4, 133.7, 132.1, 127.9, 127.6, 127.5, 127.4, 126.6, 126.0, 125.3, 105.6, 60.9, 56.1, 38.3, 38.2 ppm; HRMS (ESI/TOF)  $m/z$ :  $[M + H]^+$  Calculated for  $C_{21}H_{23}O_3$  323.1642; Found 323.1655. [CAS 162408-75-5]

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

**1-(4-Methyl-1-naphthyl)-2-(1-naphthyl)ethane (2g):** Prepared according to GP3 using ester **1g**; white solid; mp = 114-115°C; 500 MHz  $^1\text{H}$  NMR  $\delta$ : 8.15-8.10 (m, 2H), 8.04 (dd,  $J_1 = 6.4$  Hz,  $J_2 = 3.2$  Hz, 1H), 7.87 (d,  $J = 7.1$  Hz, 1H), 7.73 (d,  $J = 7.7$  Hz, 1H), 7.54-7.45 (m, 4H), 7.41-7.33 (m, 2H), 7.23 (s, 2H), 3.48 (s, 4H), 2.67 (s, 3H) ppm; 125 MHz  $^{13}\text{C}$  {1H} NMR  $\delta$ : 138.3, 136.3, 134.0, 133.1, 132.8, 132.0, 131.9, 128.9, 126.8, 126.4, 126.0, 126.0, 125.7, 125.7, 125.6, 125.6, 125.4, 125.0, 124.3, 123.8, 34.3, 34.1, 19.5 ppm; HRMS (ESI/TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calculated for  $\text{C}_{23}\text{H}_{21}$  297.1638; Found 297.1634.

**1-(4-Cyano-1-naphthyl)-2-(1-naphthyl)ethane (2h):** Prepared according to GP3 using ester **1h**; white solid; mp = 146-147°C; 500 MHz  $^1\text{H}$  NMR  $\delta$ : 8.30 (d,  $J = 8.0$  Hz, 1H), 8.16 (d,  $J = 8.3$  Hz, 1H), 8.04 (d,  $J = 8.0$  Hz, 1H), 7.89 (d,  $J = 7.0$  Hz, 1H), 7.80 (d,  $J = 7.1$  Hz, 1H), 7.75 (d,  $J = 8.3$  Hz, 1H), 7.70 (t,  $J = 7.4$  Hz, 1H), 7.64 (t,  $J = 7.7$  Hz, 1H), 7.55-7.47 (m, 2H), 7.36 (t,  $J = 7.7$  Hz, 1H), 7.31 (d,  $J = 7.3$  Hz, 1H), 7.23 (t,  $J = 7.1$  Hz, 1H), 3.60-3.56 (m, 2H), 3.51-3.48 (m, 2H) ppm; 125 MHz  $^{13}\text{C}$  {1H} NMR  $\delta$ : 144.5, 137.0, 134.0, 132.8, 132.4, 131.7, 131.6, 129.0, 128.2, 127.6, 127.2, 126.2, 126.1, 126.1, 125.7, 125.6, 125.3, 124.4, 123.3, 118.2, 108.8, 34.3, 33.7 ppm; HRMS (ESI/TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calculated for  $\text{C}_{23}\text{H}_{18}\text{N}$  308.1434; Found 308.1432.

**1-(4-Cyano-1-naphthyl)-2-(3,4,5-trimethoxyphenyl)ethane (2i):** Prepared according to GP3 using ester **1i**; white solid; mp = 120-121°C; 500 MHz  $^1\text{H}$  NMR  $\delta$ : 8.29 (d,  $J = 7.7$  Hz, 1H), 8.13 (d,  $J = 7.7$  Hz, 1H), 7.82 (d,  $J = 7.6$  Hz, 1H), 7.73-7.62 (m, 2H), 7.32 (d,  $J = 7.3$  Hz, 1H), 6.34 (s, 2H), 3.83 (s, 3H), 3.80 (s, 6H), 3.43 (t,  $J = 7.9$  Hz, 2H), 3.00 (t,  $J = 7.9$  Hz, 2H) ppm; 125 MHz  $^{13}\text{C}$  {1H} NMR  $\delta$ : 153.2, 144.2, 136.6, 132.7, 132.3, 132.3, 131.6, 128.2, 127.5, 126.1, 125.4, 124.4, 118.1, 108.8, 105.5, 60.9, 56.1, 37.1, 35.2 ppm; HRMS (ESI/TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calculated for  $\text{C}_{22}\text{H}_{22}\text{NO}_3$  348.1594; Found 348.1609.

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

### General Procedure 4 (GP4) for the Synthesis of Naphthylmethyl Methylethers (3-4)

The 1- and 2-naphthylmethyl methyl ethers were prepared through benzylic bromination of the corresponding methylnaphthalenes. Thus, a solution of the appropriate methylnaphthalene (14 mmol; i.e. 2.00 g in the case of 1-methylnaphthalene to enable preparation of **3**), NBS (3.1 g, 17 mmol) and a catalytic amount of benzoyl peroxide were added to carbon tetrachloride (35 mL). The solution was heated to reflux temperature, and stirring continued at this temperature for 4 h. The reaction mixture was then cooled to room temperature, and filtered. The filtrate was diluted with CHCl<sub>3</sub> (50 mL) and washed with a 5% aq. NaHCO<sub>3</sub> (25 mL) and water (25 mL). The organic layer was dried (MgSO<sub>4</sub>), filtered and the solvent removed *in vacuo*. The resultant oil was dissolved in methanol (50 mL). To the solution was added sodium methoxide (0.65 g, 12 mmol) as a solid and the mixture was then warmed until the solution was homogeneous. The solution was stirred for 20 h at room temperature and then the methanol was removed *in vacuo*. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with 1% aq. HCl (25 mL) and water (25 mL). The organic layer was dried (MgSO<sub>4</sub>), filtered and the solvent removed *in vacuo*. The crude material was purified via column chromatography using 5% EtOAc:hexane as eluent. The resulting oil was further purified by bulb-to-bulb distillation to obtain a colourless oil.

**1-Naphthylmethyl methylether (3):**<sup>15</sup> Prepared according to GP4 using 1-methylnaphthalene; yield 0.65 g (27%); liquid, bp 105-108°C (5 Torr), lit.<sup>15</sup> 108-110°C (5 Torr); 500 MHz <sup>1</sup>H NMR δ: 8.11 (d, *J* = 7.9 Hz, 1H), 7.86-7.78 (m, 2H), 7.55-7.39 (m, 4H), 4.89 (s, 2H), 3.44 (s, 3H) ppm on accord with lit.;<sup>15</sup> 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR δ: 133.9, 133.7, 131.8, 128.7, 128.6, 126.5, 126.3, 125.8, 125.2, 124.0, 73.3, 58.3 ppm. [CAS 5903-23-1]

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

**2-Naphthylmethyl methylether (4):** Prepared according to GP4 using 2-methylnaphthalene; yield 1.0 g (41%); liquid; bp 133-136°C (5 Torr); 500 MHz <sup>1</sup>H NMR δ: 7.84-7.78 (m, 4H), 7.47-7.44 (m, 3H), 4.62 (s, 2H), 3.42 (s, 3H) ppm in accord with lit.<sup>36</sup> [CAS 42101-92-8]

### General Procedure 5 (GP5) for Preparation of Ethers for the Synthesis of Substituted Naphthylmethyl Methylethers (5-6)

The 4-methyl- and 4-cyano-1-naphthylmethyl methylethers (**5** and **6**) were prepared by dissolving the corresponding alcohols (3.1 mmol; i.e. 0.53 g in the case of 4-methyl-1-naphthalenemethanol to enable preparation of **5**) in dry THF (10 mL). To the solution was added sodium hydride (80 mg, 3.3 mmol) as a solid, previously washed with pentane and dried. Effervescence was observed immediately. After stirring for 5 minutes, methyl iodide (200 μL, 3.2 mmol) was added. The reaction mixture was stirred at room temperature for 48 h. The solvent was removed *in vacuo* and the residue then dissolved in EtOAc (50 mL). The solution was washed with 3% aq. HCl (25 mL), 5% aq. NaHCO<sub>3</sub> (25 mL) and water (25 mL). The organic layer was then dried (MgSO<sub>4</sub>), filtered and the solvent removed *in vacuo* to provide the crude oil.

**4-Methyl-1-methoxymethylnaphthalene (5):**<sup>15</sup> Prepared according to GP5 using 4-methyl-1-naphthalenemethanol. The crude oil was purified via column chromatography over silica using 10% EtOAc:hexane as the eluent. The residual oil was further purified via bulb-to-bulb distillation to obtain a colourless oil. Yield 0.28 g (48%); liquid, bp 147-150°C (5 Torr), lit.<sup>15</sup> 89-93°C (0.2 Torr); 500 MHz <sup>1</sup>H NMR δ: 8.16-8.09 (m, 1H), 8.04-7.98 (m, 1H), 7.56-7.49 (m, 2H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 4.87 (s, 2H), 3.42 (s, 3H), 2.68 (s, 3H) ppm in accord with lit.;<sup>15</sup> 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR δ: 134.9, 133.1, 131.9, 131.9, 126.5, 125.9, 125.9, 125.7, 124.7, 124.6, 73.4, 58.0, 19.7 ppm. [CAS 71235-76-2]

# The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

**4-Methoxymethyl-1-naphthonitrile (6):**<sup>37</sup> Prepared according to GP5 using 4-cyano-1-naphthalenemethanol. The crude oil was purified via column chromatography over silica using 1% MeOH:CH<sub>2</sub>Cl<sub>2</sub> as eluent. The residual oil was further purified via crystallization from CH<sub>2</sub>Cl<sub>2</sub>:hexane to provide a white solid. Yield 0.2 g (35%); mp = 70-71°C, lit.<sup>37</sup> 70.5-71.0°C; 500 MHz <sup>1</sup>H NMR δ: 8.28 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.73-7.65 (m, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 4.94 (s, 2H), 3.51 (s, 3H) ppm in accord with lit.;<sup>37</sup> 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR δ: 140.0, 132.5, 132.2, 130.9, 128.3, 127.8, 125.9, 124.5, 124.3, 117.9, 110.3, 72.3, 58.7 ppm. [112929-94-9]

## Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: XXX. NMR spectra of the products (PDF)

## Author Information

### Corresponding Authors

jimwhilborn@gmail.com; alison.thompson@dal.ca

## Notes

The authors declare no competing financial interest.

## ORCID

Alison Thompson: 0000-0003-4231-3446

## Acknowledgements

JWH would like to thank J., M. & J., Dr. James Pincock, Teng Fei Qin, Pankaj Subedi, Dr. Scott Banfield, Scott MacLellan, Kelly Swyers, and Margo Frost. The authors also thank Mr. Xiao Feng (mass spectrometry) and Dr. Mike Lumsden (NMR) for assistance acquiring data at

## **The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes**

Dalhousie University. Dr. Norman Schepp is thanked for access to laboratory infrastructure. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).



# The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

## References

- (1) Medarde, M.; Ramos, A.; Caballero, E.; Clairac, R. P.-L. d.; López, J. L.; Grávalos, D. G.; Feliciano, A. S. Synthesis and Antineoplastic Activity of Combretastatin Analogues: Heterocombretastatins. *Eur. J. Med. Chem.* **1998**, *33*, 71.
- (2) Maya, A. B. S.; Rey, B. d.; Pelaez Lamamie de Clairac, R.; Caballero, E.; Barasoain, I.; Andreu, J. M.; Medarde, M. Design, Synthesis and Cytotoxic Activities of Naphthyl Analogues of Combretastatin A-4. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2549.
- (3) Maya, A. B. S.; Pérez-Melero, C.; Mateo, C.; Alonso, D.; Fernández, J. L.; Gajate, C.; Mollinedo, F.; Peláez, R.; Caballero, E.; Medarde, M. Further Naphthylcombretastatins. An Investigation on the Role of the Naphthalene Moiety. *J. Med. Chem.* **2005**, *48*, 556.
- (4) del Rey, B.; Ramos, A. C.; Caballero, E.; Inchausti, A.; Yaluff, G.; Medarde, M.; Rojas de Arlas, A.; San Feliciano, A. Leishmanicidal Activity of Combretastatin Analogues and Heteroanalogues. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2711.
- (5) Okamoto, H.; Yamaji, M.; Gohda, S.; Kubozono, Y.; Komura, N.; Sato, K.; Sugino, H.; Satake, K. Facile Synthesis of Picene from 1,2-Di(1-naphthyl)ethane by 9-Fluorenone-sensitized Photolysis. *Org. Lett.* **2011**, *13*, 2758.
- (6) Mamidyala, S. K.; Ramu, S.; Huang, J. X.; Robertson, A. A. B.; Cooper, M. A. Efficient Synthesis of Anacardic Acid Analogues and their Antibacterial Activities. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 1667.
- (7) Mino, T.; Shirai, Y.; Sasai, Y.; Sakamoto, M.; Fujita, T. Phosphine-free Palladium Catalyzed Mizoroki–Heck Reaction using Hydrazone as a Ligand. *J. Org. Chem.* **2006**, *71*, 6834.
- (8) Sahoo, S. K. An Unprecedented Oxidative Intermolecular Homo Coupling Reaction Between Two sp<sup>3</sup>C–sp<sup>3</sup>C Centers Under Metal-free Condition. *Tetrahedron Lett.* **2016**, *57*, 3476.
- (9) Deng, M.; Su, B.; Zhang, H.; Liu, Y.; Wang, Q. Total Synthesis of Phenanthroindolizidine Alkaloids via Asymmetric Deprotonation of N-Boc-pyrrolidine. *RSC Adv.* **2014**, *4*, 14979.
- (10) Gozhina, O. V.; Thomassen, I. K.; Lejon, T. Ultrasound-promoted Dimerization of Benzylic Halides. *Synth. Commun.* **2013**, *43*, 1867.
- (11) Iyoda, M.; Sakaitan, M.; Otsuka, H.; Oda, M. Reductive Coupling of Benzyl Halides using Nickel(0)-complex Generated in situ in the Presence of Tetraethylammonium Iodide, a Simple and Convenient Synthesis of Bibenzyls. *Chem. Lett.* **1985**, *14*, 127.
- (12) Kumar, P.; Guntreddi, T.; Singh, R.; Singh, K. N. A Practical Protocol for the Synthesis of Bibenzyls via C(sp<sup>3</sup>)–H Activation of Methyl Arenes under Metal-free Conditions. *Org. Chem. Front.* **2017**, *4*, 147.
- (13) Liu, J.; Li, B. Facile Synthesis of Bibenzyl by Reductive Homocoupling of Benzyl Halides in Aqueous Media. *Synth. Commun.* **2007**, *37*, 3273.
- (14) Liu, Y.; Xiao, S.; Qi, Y.; Du, F. Reductive Homocoupling of Organohalides using Nickel(II) Chloride and Samarium Metal. *Chem. Asian J.* **2017**, *12*, 673.
- (15) DeCosta, D. P.; Pincock, J. A. Photochemistry of Substituted 1-Naphthylmethyl Esters of Phenylacetic and 3-Phenylpropanoic Acid: Radical Pairs, Ion Pairs, and Marcus Electron Transfer. *J. Am. Chem. Soc.* **1993**, *115*, 2180.

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

- (16) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. Photodecarboxylation. A Labeling Study. Mechanistic Studies in Photochemistry. 15. *J. Am. Chem. Soc.* **1977**, *99*, 1896.
- (17) Givens, R. S.; Matuszewski, B.; Neywick, C. V. Mechanistic and Synthetic Studies in Organic Photochemistry. XII. Photodecarboxylation of Esters. Photolysis of Alpha- and Beta-naphthalenemethyl Derivatives. *J. Am. Chem. Soc.* **1974**, *96*, 5547.
- (18) Pincock, J. A. Photochemistry of Arylmethyl Esters in Nucleophilic Solvents: Radical Pair and Ion Pair Intermediates. *Acc. Chem. Res.* **1997**, *30*, 43.
- (19) Pincock, J. A.; Wedge, P. J. The Photochemistry of Conformationally Rigid Benzylic Esters: 2,2-Dimethyl-1-indanyl Acetates and Pivalates. *J. Org. Chem.* **1995**, *60*, 4067.
- (20) Hilborn, J. W.; Pincock, J. A. Photolysis of the 1-Naphthylmethyl Ester of Substituted Phenylacetic Acids: Intramolecular Charge Transfer and Rates of Decarboxylation of Arylacyloxy Radicals. *Can. J. Chem.* **1992**, *70*, 992.
- (21) Coyle, J. D.; Kingston, D. H. Electron Transfer in the Photochemistry of Substituted Benzoate and Naphthoate Esters. *J. Chem. Soc. Perkin Trans. 2* **1976**, 1475.
- (22) DeCosta, D. P.; Pincock, J. A. Intramolecular Electron Transfer in the Photochemistry of Substituted 1-Naphthylmethyl Esters of Benzoic Acids. *Can. J. Chem.* **1992**, *70*, 1879.
- (23) Slocum, G. H.; Schuster, G. B. Photochemistry of Naphthylmethyl Halides. Direct and Sensitized Paths to Homolytic and Heterolytic Carbon-halogen Bond Cleavage. *J. Org. Chem.* **1984**, *49*, 2177.
- (24) Michiko, I.; Kazuko, T.; Noboru, K.; Hiizu, I. Photoreactivity of 1-Pyrenylmethyl Esters. Dependence on the Structure of the Carboxylic Acid Moieties and the Nature of the Excited States. *Chem. Lett.* **1987**, *16*, 1729.
- (25) Libman, J. Light Induced Charge Transfer Processes. Photochemical Behavior of 1-Cyanonaphthalene in the Presence of Phenylacetic Acid Derivatives. *J. Am. Chem. Soc.* **1975**, *97*, 4139.
- (26) Dewar, M. J. S.; Grisdale, P. J. Substituent Effects. II.1a The Preparation of a Series of Substituted 1-Naphthoic Acids. *J. Am. Chem. Soc.* **1962**, *84*, 3541.
- (27) Smith, J. G.; Dibble, P. W.; Sandborn, R. E. The Preparation and Reactions of Naphtho[1,2-c]furan and Naphtho[2,3-c]furan. *J. Org. Chem.* **1986**, *51*, 3762.
- (28) Das, G.; Bharadwaj, P. K.; Basu Roy, M.; Ghosh, S. Photophysical Studies of Cryptand Based Fluorophore Systems in Different Environments. *Chem. Phys.* **2002**, *277*, 145.
- (29) Beecroft, R. A.; Davidson, R. S.; Goodwin, D.; Pratt, J. E. Quenching of singlet and triplet excited aromatic hydrocarbons by sulphides :- the amine and sulphide enhanced photo-induced degradation of chloro- and cyanoaromatic hydrocarbons. *Tetrahedron* **1984**, *40*, 4487.
- (30) Corina, D. L.; Isaac, K. Gas Chromatographic and Mass Spectrometric Properties of Naphthalenemethyl Esters and Cyclohexanemethyl Esters of Organic Acids. *J. Chromatogr. A* **1983**, *260*, 51.
- (31) Holdcroft, S.; Yuen, K. H.; Guillet, J. E. Studies of the Photolysis of Aromatic Esters in Solution and in Polymer Films. *J. Polym. Sci. A Polym. Chem.* **1990**, *28*, 1495.
- (32) Carpino, L. A. Synthesis and Alkaline Degradation of the Arenesulfonyl Derivatives of  $\alpha$ -Menaphthyl- and 1,1-Di- $\alpha$ -menaphthylhydrazine. *J. Org. Chem.* **1965**, *30*, 321.
- (33) Schorigin, P. Weitere Versuche über die Umsetzungen von Äthern mit metallischem Natrium. *Ber. dtsh. Chem. Ges. A/B* **1926**, *59*, 2510.

## The Photodecarboxylation of Substituted Naphthylmethyl Arylacetate Esters: Synthesis of Naphthylarylethanes

(34) Inaba, S.; Matsumoto, H.; Rieke, R. D. Highly Reactive Metallic Nickel: Reductive Homocoupling Reagent for Benzylic Mono- and Polyhalides. *J. Org. Chem.* **1984**, *49*, 2093.

(35) Friedmann, W. Einwirkung von Schwefel auf  $\beta$ -Methyl-naphthalin unter Druck. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1352.

(36) Álvarez-Bercedo, P.; Martín, R. Ni-Catalyzed Reduction of Inert C–O Bonds: A New Strategy for Using Aryl Ethers as Easily Removable Directing Groups. *J. Am. Chem. Soc.* **2010**, *132*, 17352.

(37) Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehbey, C. Substituent Effects on Homolytic versus Heterolytic Photocleavage of (1-Naphthylmethyl)trimethylammonium Chlorides. *Can. J. Chem.* **1987**, *65*, 1599.