Synthesis Y. Wang et al. Paper

A Novel Three-Step Tandem Reaction for Efficient Syntheses of Bulky Anthracenyl Esters from 2-Benzylbenzoic Acids

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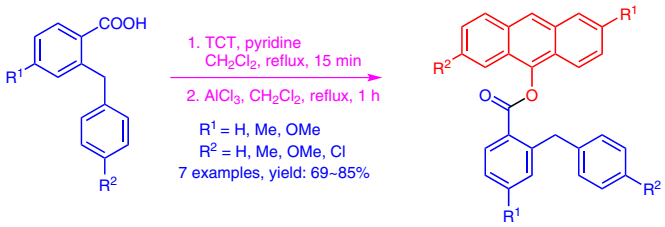

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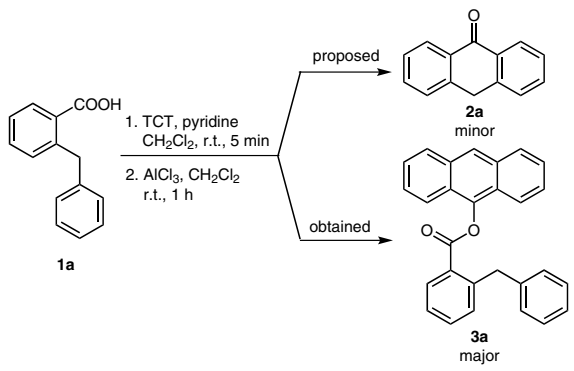
Abstract Bulky anthracenyl esters could be efficiently synthesized from 2-benzylbenzoic acids via a novel three-step tandem reaction containing intramolecular Friedel–Crafts acylation, enolization, and esterification. A mechanism for the tandem reaction is proposed.

Key words tandem reaction, Friedel–Crafts acylation, enolization, esterification, anthracenyl esters

The preparation of complex organic molecules via multistep organic reactions is usually a tedious and laborious work owing to the necessity of protection/deprotection of functional groups and purification of intermediate products.[1] In comparison with the traditional approach, tandem reaction can overcome these drawbacks and is an efficient modern organic synthetic methodology.[2] Therefore, it is of great practical significance to develop novel tandem reactions.[3] Anthracene derivatives are widely applied in organic light-emitting diodes (OLEDs) as emitting and charge-transporting materials.[4] Besides, they are important structural units of anticancer agents such as azonafides.[5] So far, a large number of synthetic methods have been developed for the syntheses of functional compounds containing anthracene skeleton, most of which are modified directly from anthracene via multiple reactions.[6] Herein, we report a novel tandem reaction, which can be applied to prepare anthracenyl esters in one pot from 2-benzylbenzoic acids.

This novel tandem reaction was discovered in our lab during the preparation of anthrone (**2a**) from 2-benzylbenzoic acid (**1a**) in the presence of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine, TCT), pyridine, and aluminum chloride using Kangani's method,[7] which had been reported to be efficient for the Friedel–Crafts acylation[8] of various carboxylic acids to form ketones. Instead of **2a**, a novel anthracenyl ester **3a** was obtained as the main product (Scheme 1), whose structure was confirmed by X-ray photoelectron spectroscopy (XPS) as shown in Figure 1.



Scheme 1 The reaction of compound **1a** with cyanuric chloride, pyridine, and $AlCl_3$

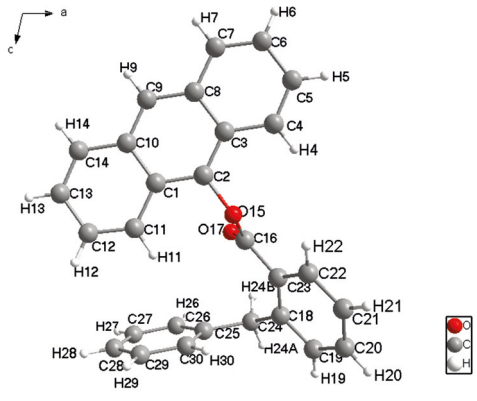


Figure 1 Ball-and-stick representation of **3a** viewed down the b-axis

Table 1 Optimization of the Reaction Conditions for the Tandem Reaction

Entry	Pyridine (equiv)	$AlCl_3$ (equiv)	TCT (equiv)	Temp (°C)	Solvent	Yield (%)[a]		
						3a	**2a**[b]	**1a**[b]
1	1	1	1.6	r.t.	CH_2Cl_2	38	<5	53
2	1.2	1	1.6	r.t.	CH_2Cl_2	46	6	43
3	1.5	1	1.6	r.t.	CH_2Cl_2	25	<5	65
4	1.2	1.2	1.6	r.t.	CH_2Cl_2	55	8	32
5	1.2	2	1.6	r.t.	CH_2Cl_2	76	<5	15
6	1.2	2.5	1.6	r.t.	CH_2Cl_2	40	<5	39
7	1.2	2	2	r.t.	CH_2Cl_2	35	10	49
8	**1.2**	**2**	**1.6**	**reflux (40)**	**CH_2Cl_2**	**81**	**<5**	**<5**
9	1.2	2	1.6	reflux (61)	$CHCl_3$	50	<5	36
10	1.2	2	1.6	reflux (81)	MeCN	21	<5	64
11	1.2	2	1.6	reflux (84)	$ClCH_2CH_2Cl$	<5	<5	83

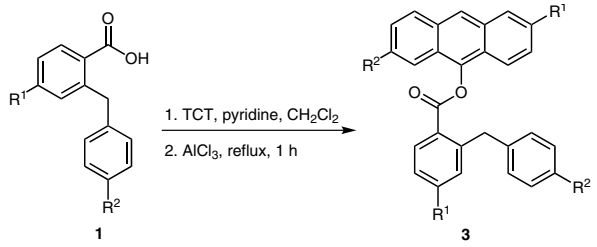
[a] Isolated yields.
[b] Recovered yields of starting materials **1a** and **2a**.

The initial reaction gave us only 38% yield of **3a** (Table 1, entry 1). To improve the yield of **3a**, the experimental conditions of the reaction were optimized. Investigation on the loadings of TCT, pyridine, and $AlCl_3$ at room temperature in CH_2Cl_2 showed that the best ratio of pyridine/$AlCl_3$/TCT was 1.2:2:1.6 giving 76% yield of **3a** (entries 2–7). Running the reaction in refluxing CH_2Cl_2 (40 °C) increased the yield to 81% (entry 8). By replacing CH_2Cl_2 with other solvents having higher boiling points and running the corresponding reactions at their reflux temperatures, the product yields dropped dramatically due to the instability of 2-benzylbenzoyl chloride at high temperatures (entries 9–11, see also the Supporting Information). The substrate scope of the reaction system was explored following the optimized conditions shown in entry 8 of Table 1. Products **3b**, **3c**, **3d**, **3e**, **3f**, and **3g** were obtained in a yield of 70, 69, 85, 80, 81, and 84% from **1b**, **1c**, **1d**, **1e**, **1f**, and **1g**, respectively (Table 2, entries 2–7), which proved the applicability of the tandem reaction in the syntheses of bulky anthracenyl esters from various 2-benzylbenzoic acids.

On the basis of our experimental results, we propose that the formation of **3a** involved a Friedel–Crafts acylation, enolization, and esterification via three steps in one pot (Scheme 2). 2-Benzylbenzoyl chloride was quickly generated from **1a** in the presence of TCT and pyridine, and then reacted with $AlCl_3$ to form **2a** via the intramolecular Friedel–Crafts acylation. Afterwards, enolization of **2a** gave anthracen-9-ol, which further reacted with 2-benzylbenzoyl chloride to afford the final product **3a**. We hypothesized that the Friedel–Crafts acylation was the rate-determining step in the tandem reaction. To verify the hypothesis, a competitive experiment was carried out by adding 1-naphthol in the reaction system. In the presence of 1-naphthol, the esterification product of 1-naphthol was the main product instead of **3a**, indicating that the esterification reaction was a faster reaction than the Friedel–Crafts acylation (see Supporting Information).

In summary, we have developed a three-step tandem reaction involving intramolecular Friedel–Crafts acylation, enolization, and esterification. Bulky anthracenyl esters could be simply approached by this efficient reaction from 2-benzylbenzoic acids. In addition, a reasonable mechanism is proposed. To the best of our knowledge, this is a novel three-step tandem reaction and can be used for efficient syntheses of anthracene derivatives.

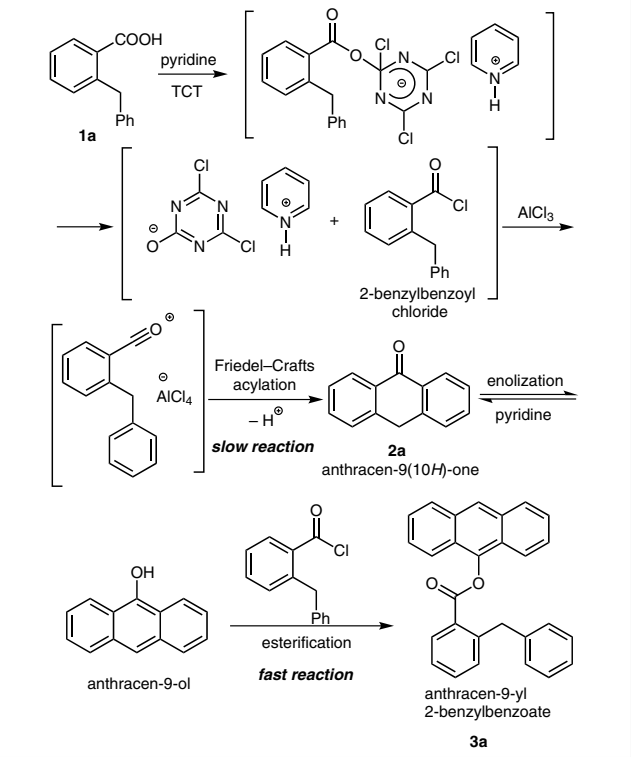
Table 2 Scope of the Tandem Reaction



1 3

Entry	Product	R^1	R^2	Yield (%)[a]
1	**3a**	H	H	81
2	**3b**	H	Me	70
3	**3c**	H	Cl	69
4	**3d**	H	OMe	85
5	**3e**	Me	H	80
6	**3f**	Me	OMe	81
7	**3g**	OMe	H	84

[a] Isolated yields.



Scheme 2 Proposed mechanism of the tandem reaction

All commercial reagents were used as received without further purification unless otherwise stated. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solution using a 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) using $CDCl_3$ (δ_H = 7.26, δ_C = 77.16) as internal standards. Standard abbreviations were used to indicate multiplicities of the signals. High-resolution mass spectra (HRMS) were obtained by the ESI ionization sources using TOF MS technique. Melting point was obtained on a micro melting point apparatus. Substrates **1a** and **1g** are available from commercial sources. Substrates **1b**,[9] **1c**,[10] **1d**,[10] **1e**,[11] and **1f**[11] were prepared according to literature procedures (for details, see Supporting Information).

Bulky Anthracenyl Esters via Three-Step Tandem Reaction; General Procedure

To a solution of **1** (1 mmol) in anhyd CH_2Cl_2 (5 mL) at r.t. was added TCT (295 mg, 1.6 mmol), followed by the dropwise addition of pyridine (95 mg, 1.2 mmol) within 5 min. After stirring the reaction mixture at reflux temperature (40 °C) for 15 min, $AlCl_3$ (267 mg, 2 mmol) was added portionwise. The resulting reaction mixture was further stirred at the reflux temperature for 1 h. Then, the mixture was cooled to 0 °C and quenched with aq 1 M HCl (5 mL). The aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, and dried (anhyd Na_2SO_4). The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography (PE/EtOAc = 200:1) to afford the desired product **3**.

3a

Yellow solid; yield: 157 mg (81%); mp 133.1–133.9 °C.

IR (KBr): 1739.25, 1240.68, 1127.22, 1072.92, 731.83 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (dd, *J* = 7.8, 1.3 Hz, 1 H), 8.43 (d, *J* = 11.6 Hz, 1 H), 8.05 (d, *J* = 8.5 Hz, 2 H), 7.84–7.77 (m, 2 H), 7.67 (m, 1 H), 7.58–7.38 (m, 6 H), 7.32–7.23 (m, 3 H), 7.22–7.16 (m, 2 H), 4.59 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.72, 144.16, 142.16, 140.84, 133.28, 132.38, 131.90, 131.85, 129.07, 128.47, 128.38, 128.26, 126.84, 126.29, 126.07, 125.55, 124.76, 124.12, 121.47, 39.78.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{20}O_2Na$: 411.1356; found: 411.1356.

X-ray Crystal Structure Analysis

Product **3a** was recrystallized from EtOH to give yellow nubby crystals stable in air. A single crystal suitable for X-ray analysis was selected by hand. For details of X-ray crystal data, see the Supporting Information.

3b

Yellow solid; yield: 146 mg (70%); mp 105.0–106.1 °C.

IR (KBr): 1730.85, 1236.42, 1187.81, 1101.16, 1070.56, 729.56 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (dd, *J* = 7.8, 1.2 Hz, 1 H), 8.37 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.7 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.70–7.62 (m, 2 H), 7.56–7.51 (m, 1 H), 7.49–7.42 (m, 2 H), 7.43–7.37 (m, 1 H), 7.34 (dd, *J* = 8.7, 1.3 Hz, 1 H), 7.13–7.06 (m, 4 H), 4.56 (s, 2 H), 2.50 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.80, 144.53, 141.40, 137.77, 136.11, 135.43, 133.23, 132.24, 131.87, 131.37, 130.67, 129.15, 128.93, 128.50, 128.39, 128.27, 128.18, 126.71, 126.10, 125.11, 124.58, 124.39, 124.24, 121.42, 119.53, 39.30, 22.36, 21.07.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{24}O_2Na$: 439.1669; found: 439.1664.

3c

Yellow solid; yield: 158 mg (69%); mp 130.2–131.4 °C.

IR (KBr): 1740.00, 1240.35, 1082.23, 1066.55, 1014.15, 750.19 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.8 Hz, 1 H), 8.39 (s, 1 H), 8.02 (dd, *J* = 16.6, 8.7 Hz, 2 H), 7.85 (s, 1 H), 7.69 (dd, *J* = 17.8, 8.4 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.54–7.49 (m, 1 H), 7.49–7.38 (m, 3 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 4.52 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.38, 143.86, 141.29, 139.19, 133.66, 132.46, 132.12, 131.99, 131.92, 130.24, 129.88, 128.57, 128.47, 127.67, 127.22, 126.97, 125.95, 125.02, 124.65, 124.40, 121.30, 119.93, 39.30.

HRMS (ESI) *m*/*z* [M + Na]$^+$calcd for $C_{28}H_{18}Cl_2O_2Na$: 479.0576; found: 479.0576.

3d

Yellow solid; yield: 190 mg (85%); mp 125.8–126.7 °C.

IR (KBr): 3462.34, 1745.03, 1631.77, 1508.98, 1469.06, 1227.96, 1181.68, 1066.59, 1025.76 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 7.2 Hz, 1 H), 8.34 (s, 1 H), 8.02 (d, *J* = 7.5 Hz, 1 H), 7.95 (d, *J* = 9.2 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 7.0 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.50–7.37 (m, 3 H), 7.19 (dd, *J* = 9.2, 2.3 Hz, 1 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 7.06 (d, *J* = 1.9 Hz, 1 H), 6.80 (d, *J* = 8.6 Hz, 2 H), 4.52 (s, 2 H), 3.80 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.65, 157.97, 157.92, 144.74, 140.60, 133.20, 132.87, 132.21, 131.64, 130.42, 130.26, 130.03, 128.61, 128.46, 128.20, 126.72, 126.41, 125.12, 124.70, 124.64, 124.58, 120.98, 120.80, 113.81, 97.09, 55.21, 55.15, 38.81.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{25}O_4$: 449.1747; found: 449.1747.

3e

Yellow solid; yield: 166.5 mg (80%); mp 150.8–151.9 °C.

IR (KBr): 3053.22, 3027.03, 2920.46, 1746.22, 1247.19, 1229.32, 1132.62, 1070.69, 1012.34, 724.75 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 7.8 Hz, 1 H), 8.29 (s, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.79 (s, 2 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.46 (t, *J* = 7.3 Hz, 1 H), 7.36 (dd, *J* = 19.7, 8.1 Hz, 2 H), 7.27 (m, 5 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 4.56 (s, 2 H), 2.56 (s, 3 H), 2.50 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.68, 144.18, 144.03, 142.25, 140.99, 135.14, 133.12, 132.28, 132.08, 132.05, 129.09, 129.00, 128.39, 128.31, 127.17, 126.51, 125.97, 125.75, 125.40, 125.35, 123.67, 123.56, 122.81, 121.54, 121.39, 39.72, 21.92, 21.74.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{24}O_2Na$: 439.1669; found: 439.1669.

3f

Yellow solid; yield: 193 mg (81%); mp 148.1–149.5 °C.

IR (KBr): 1746.15, 1247.07, 1229.31, 1132.44, 1070.59 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 7.9 Hz, 1 H), 8.22 (s, 1 H), 7.91 (d, *J* = 9.2 Hz, 1 H), 7.76 (s, 1 H), 7.64 (d, *J* = 8.7 Hz, 1 H), 7.33 (d, *J* = 7.9 Hz, 1 H), 7.26 (t, *J* = 9.2 Hz, 2 H), 7.15 (dd, *J* = 16.2, 5.4 Hz, 3 H), 7.04 (s, 1 H), 6.80 (d, *J* = 8.5 Hz, 2 H), 4.49 (s, 2 H), 3.79 (d, *J* = 5.2 Hz, 6 H), 2.54 (s, 3 H), 2.49 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.60, 157.83, 157.58, 144.82, 143.98, 140.74, 134.12, 133.06, 132.98, 131.88, 130.79, 130.11, 129.98, 129.18, 128.77, 127.46, 126.65, 125.25, 124.57, 123.57, 123.23, 120.92, 120.60, 113.23, 97.18, 55.18, 55.11, 38.77, 21.80, 21.73.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{32}H_{28}O_4Na$: 499.1880; found: 499.1880.

3g

Yellow solid; yield: 188 mg (84%); mp 165.2–166.6 °C.

IR (KBr): 1736.73, 1635.45, 1602.16, 1236.50, 1218.48, 1127.61, 1080.72 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.7 Hz, 1 H), 8.24 (s, 1 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 7.81 (d, *J* = 8.6 Hz, 1 H), 7.69 (d, *J* = 9.4 Hz, 1 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.42–7.34 (m, 1 H), 7.34–7.16 (m, 6 H), 7.11 (d, *J* = 9.3 Hz, 1 H), 7.01 (d, *J* = 8.6 Hz, 1 H), 6.94 (s, 1 H), 4.57 (s, 2 H), 3.98 (s, 3 H), 3.93 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.16, 163.35, 157.26, 147.01, 142.63, 140.60, 134.36, 133.13, 132.61, 129.03, 128.44, 127.78, 126.08, 125.67, 125.19, 123.41, 122.93, 122.44, 121.67, 121.32, 120.80, 120.16, 118.00, 111.56, 103.75, 55.50, 55.32, 40.14.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{25}O_4$: 449.1747; found: 449.1747.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588384.

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