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# Synthesis of substituted naphthalenes from α-substituted ketones and 1,2-bis(halomethyl)benzenes including a rearrangement aromatization of benzo[*c*]oxepine

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ABSTRACT

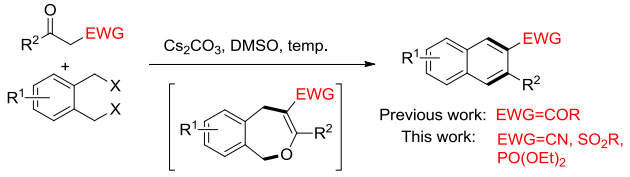
An efficient and practical method for the synthesis of cyano, sulfonyl and phosphoryl substituted naphthalene derivatives via the rearrangement aromatization of benzo[*c*]oxepine has been developed. The system holds the advantages of metal catalysts free, and mild reaction conditions.



## 1. Introduction

Substituted naphthalenes are important building blocks in biologically active molecules,[1] polycyclic aromatic electronic materials[2] and chiral ligands in organic synthesis.[3] The construction of these privileged structural motifs contained two major strategies: (i) the introduction of functional groups onto a naphthalene nucleus and (ii) the assembly of naphthalene ring from benzene precursor. Evidently, the annulation strategy is preferable since high region selectivity (and yields) can be achieved from simple and commercially available reagents.[4] Much recent work has focused on efficient strategies for the construction of various substituted naphthalenes.[5] However, to the best of our knowledge, there have been few reports of annulation strategies for the synthesis of beta-site cyano,[6] sulfonyl[7] and phosphoryl[8] substituted naphthalene derivatives.

In our recent reports,[9] we proposed a novel rearrangement aromatization of benzo[*c*]oxepine and established a simple, efficient method for the preparation of β-substituted naphthalenes from 1,3-dicarbonyl compounds and 1,2-bis(halomethyl) benzene compounds as substrates (Scheme 1). The proposed reaction mechanism suggested that carbonyl was essential for enolation during the conversion to form the important intermediate benzo[*c*]oxepine. However, the other carbonyl group only functioned as an electron-withdrawing group. It was thus supposed that the conversion could be achieved through other electron withdrawing groups, such as nitro, cyano, sulfonyl, phosphoryl to obtain various β-substituted naphthalenes. Herein, the detailed research results from this conversion are presented.




**Scheme 1.** Construction of naphthalenes via rearrangement aromatization of benzo[*c*] oxepine intermediate.

## 2. Results and discussion

To construct various substituted naphthalenes, an initial study using α-cyanoacetophenone and 1,2-bis(bromomethyl)benzene as reactants was performed with $Cs_2CO_3$ in DMSO at 80 °C for 4 h, which gave an 80% yield of the naphthalene-based product. Other bases, such as $K_2CO_3$, KOH, $Na_2CO_3$, *t*-BuOK, $Et_3N$ and DBU were seen to provide lower yields (Table 1, entries 2–7). Interestingly, the conversion was also achieved in low yields using acids, such as

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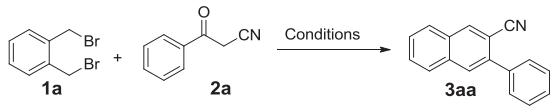
$CH_3COOH$ and Lewis acid $ZnCl_2$ (Table 1, entries 9 and 10). Moreover, the desired product was obtained in DMF and EtOH in moderate yields (Table 1, entries 11 and 12). Other solvents, such as THF, $CH_3CN$, $CHCl_3$ and $H_2O$ were identified as unsuitable for the transformation (Table 1, entries 13–16). The molar ratio and the reaction temperature were then optimized to increase the product yield but with no success (Table 1, entries 16–22). Ultimately, optimal conditions were identified as 1 equiv of 1,2-bis(bromomethyl) benzene (**1a**), 1 equiv of α-cyanoacetophenone (**2a**) and 3 equiv of $Cs_2CO_3$ in DMSO at 80 °C (Table 1, entry 1).

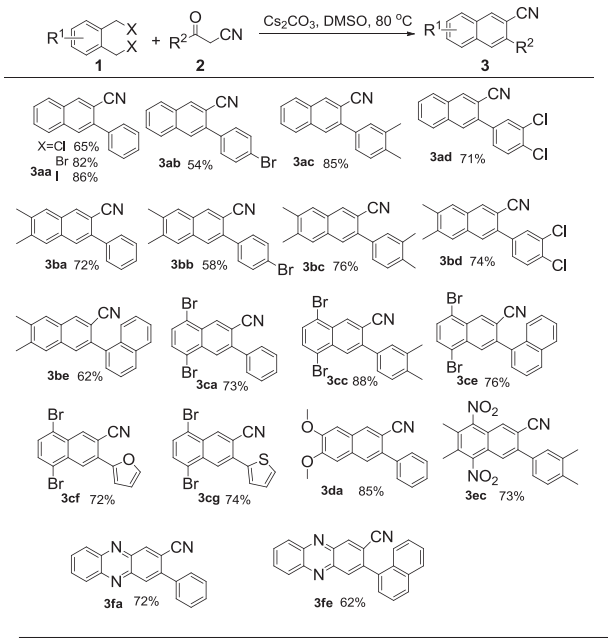
**Table 1**
Optimization of the reaction conditions[a]




| Entry | Solvent | Base (equiv) | Molar ratio | Temp (°C) | Yield[b] (%) |
|---|---|---|---|---|---|
| **1** | **DMSO** | **$Cs_2CO_3$** | **1:1** | **80** | **82** |
| 2 | DMSO | $K_2CO_3$ | 1:1 | 80 | 40 |
| 3 | DMSO | KOH | 1:1 | 80 | 33 |
| 4 | DMSO | $Na_2CO_3$ | 1:1 | 80 | <5 |
| 5 | DMSO | *t*-BuOK | 1:1 | 80 | <5 |
| 6 | DMSO | $Et_3N$ | 1:1 | 80 | <5 |
| 7 | DMSO | DBU | 1:1 | 80 | <5 |
| 8 | DMSO | HCl | 1:1 | 80 | <5 |
| 9 | DMSO | $CH_3COOH$ | 1:1 | 80 | 12 |
| 10 | DMSO | $ZnCl_2$ | 1:1 | 80 | 26 |
| 11 | DMF | $Cs_2CO_3$ | 1:1 | 80 | 72 |
| 12 | EtOH | $Cs_2CO_3$ | 1:1 | 80 | 52 |
| 13 | THF | $Cs_2CO_3$ | 1:1 | 80 | <5 |
| 14 | $CH_3CN$ | $Cs_2CO_3$ | 1:1 | 80 | <5 |
| 15 | $CHCl_3$ | $Cs_2CO_3$ | 1:1 | 80 | <5 |
| 16 | $H_2O$ | $Cs_2CO_3$ | 1:1 | 80 | <5 |
| 17 | DMSO | $Cs_2CO_3$ | 1:0.5 | 80 | 78 |
| 18 | DMSO | $Cs_2CO_3$ | 1:2 | 80 | 82 |
| 19 | DMSO | $Cs_2CO_3$ | 1:1 | 40 | 23 |
| 20 | DMSO | $Cs_2CO_3$ | 1:1 | 120 | 82 |
| 21 | DMSO | $Cs_2CO_3$[c] | 1:1 | 80 | 78 |
| 22 | DMSO | $Cs_2CO_3$[d] | 1:1 | 80 | <5 |

The bold entries signifies the optimum condition.
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), solvent (2 mL). The reaction was performed for 4 h.
[b] Isolated yields.
[c] $Cs_2CO_3$ (2.0 equiv).
[d] $Cs_2CO_3$ (1.0 equiv).

With the optimized conditions in hand, the scope of the reaction was then evaluated using a wide range of α-cyanoacetophenone and 1,2-bis(halomethyl) benzene compounds (Scheme 2). The desired naphthalene products **3** were formed successfully in good to excellent yields in all cases. Different benzyl halides, such as 1,2-bis(chloromethyl)benzene, 1,2-bis(bromomethyl)benzene and 1,2-bis(iodomethyl)benzene obtained the naphthalene-based product **3aa** in 68%, 82% and 86% yields, respectively. Fortunately, the structure of **3aa** was confirmed by X-ray diffraction (Fig. 1). When different substituents were attached to the aromatic rings of the 1,2-bis(halomethyl)benzene and the α-cyanoacetophenone, the reaction gave the corresponding naphthalene-based products in moderate to good yields. In addition, the substrates containing sterically hindered naphthyl ring and heterocycles (furan, thiophene) also delivered the aromatic products in satisfactory yields (Scheme 2, **3be**, **3ce**, **3cf**, **3cg**, 62–76%). Much to our satisfaction, 2,3-bis(bromomethyl)quinoxaline also took place smoothly to furnish substituted phenazines in moderate yield (Scheme 2, **3fa**, **3fe**). Regretfully, 1,2-bis(bromomethyl)-4-nitrobenzene, 2,2′-bis(bromomethyl)-1,1′-biphenyl and 3-(1-methyl-1*H*-indol-3-yl)-3-oxopropanenitrile could not produce the desired products (see Supplementary data).




**Scheme 2.** Scope of α-cyanoacetophenone compounds and 1,2-bis-(halomethyl)benzene compounds.

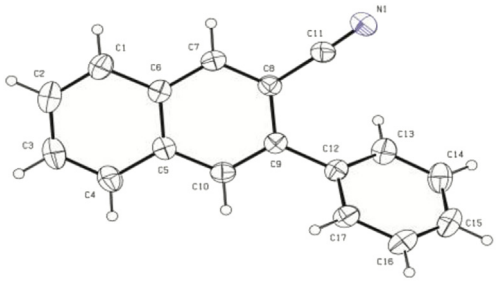
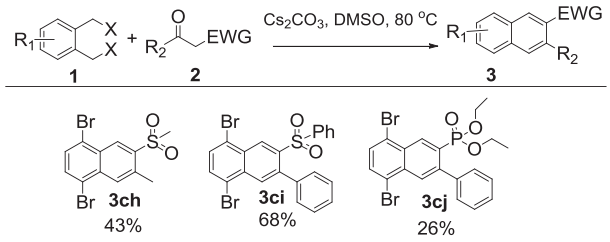


**Fig. 1.** X-ray crystal structure of compound **3aa**.

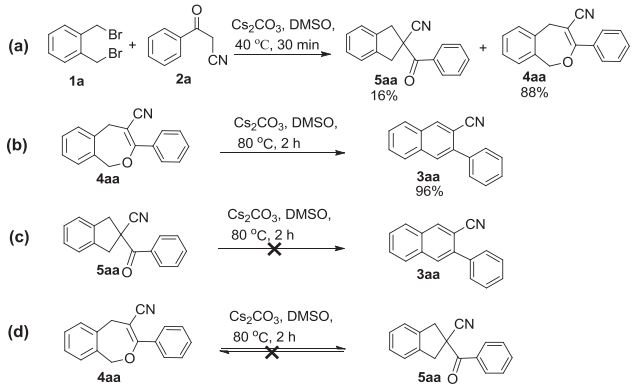
Following our success in the construction of cyano-substituted naphthalenes, the synthesis of other substituted naphthalene compounds were next examined. α-Sulfonyl, phosphoryl, nitro substituted ketones were selected to react with 1,4-dibromo-2,3-bis(bromomethyl)benzene, and 1,2-bis(chloromethyl)-4,5-dimethyl benzene. To our delight, 1,4-dibromo-6-methyl-7-(methylsulfonyl)naphthalene (Scheme 3, **3ch**, 43%), 1,4-dibromo-6-phenyl-7-(phenylsulfonyl)naphthalene (Scheme 3, **3ci**, 68%) and diethyl (5,8-dibromo-3-phenylnaphthalen-2-yl) phosphonate (Scheme 3, **3cj**, 26%) were successfully obtained in low to moderate yields. Fortunately, the structures of **3ci** and **3cj** were confirmed by X-ray diffraction[10].




**Scheme 3.** Scope of α-substituted ketones.

To gain some insight into the mechanism of the reaction, the following experiments were performed (Scheme 4). First, 1,2-

bis(bromomethyl)benzene (**1a**) was reacted with 3-oxo-3-phenylpropanenitrile (**2a**) and $Cs_2CO_3$ in DMSO at 40 °C. The reaction was monitored by TLC and stopped after 30 min to obtained 2-benzoyl-2,3-dihydro-1*H*-indene-2-carbonitrile (**5aa**) and 3-phenyl-1,5-dihydrobenzo[*c*]oxepine-4-carbonitrile (**4aa**) (Scheme 4a). When benzo[*c*]oxepine **4aa** was treated with $Cs_2CO_3$ in DMSO at 80 °C, the aromatic product **3aa** was obtained in good yield after 30 min (96%, Scheme 4b). However, when the by-product indene **5aa** was treated under the same conditions, the aromatic product **3aa** was not observed in the experiment (Scheme 4c). Moreover, there was no indication that the seven-membered ring **4aa** and the five-membered ring **5aa** interconverted under the reaction conditions (Scheme 4d) (Fig. 2).




**Scheme 4.** The controlled experiments to prove the mechanism.

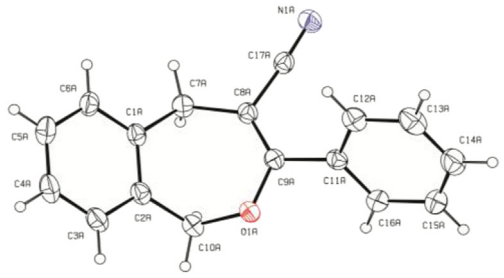
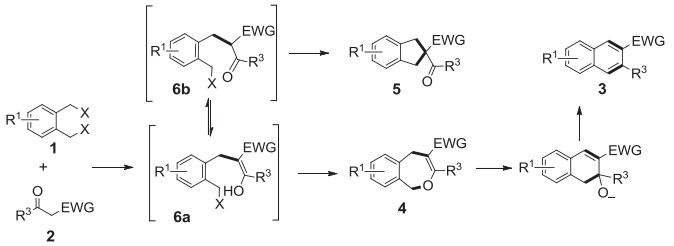


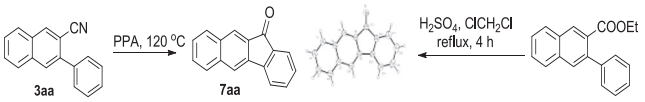

**Fig. 2.** X-ray crystal structure of compound **4aa**.

On the basis of the aforementioned results described above and in the literature,[9,11] a plausible mechanism of this reaction is proposed as illustrated in Scheme 5. First, the C-alkylation of compound **1** provided intermediate **6**, which appeared in two tautomeric forms: **6a** and **6b**. The subsequent O-alkylation of enolic formed **6a** and presented as the seven-membered ring **4**. Meanwhile, the competing C-alkylation yielded the five-membered ring **5** as a by-product. Finally, rearrangement of **4** followed by aromatization in the presence of $Cs_2CO_3$ afforded the desired naphthalene-based product **3**.




**Scheme 5.** The plausible mechanism of the present reaction.

To explore the potential applications of the β-substituted naphthalene derivatives, the privileged structures were exploited in transformations to access various frameworks with high degrees of molecular complexity. Following the literature method,[16] the naphthalene rings we constructed would be converted to benzofluorenones (Scheme 6), which were important basic core of bioactive substances and widespread occurrence in many functional molecules.[17]




**Scheme 6.** Synthesis of 11*H*-benzo[*b*]fluorenone from 3-phenyl-2-naphthonitrile (**3aa**) and ethyl 3-phenyl-2-naphthoate.

## 3. Conclusion

In summary, an efficient method has been proposed for the construction of β-substituted cyano, sulfonyl and phosphoryl naphthalenes from simple and commercially available reagents. The success of this transformation was mainly attributed to the rearrangement of benzo[*c*]oxepine. Further investigations into the detailed mechanism and synthetic applications of this reaction are currently underway in our laboratory.

## 4. Experimental

### 4.1. General

1,4-Dibromo-2,3-bis(bromomethyl)benzene,[12] 1,2-bis(chloromethyl)-4,5-dimethylbenzene,[13] 1,2-bis(bromomethyl)-4,5-dimethoxybenzene[14] and 1,2-bis(iodomethyl)benzene[15] were prepared according to the literature procedures. Other substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrometer as KBr pellets with absorption in $cm^{-1}$. $^1H$ spectra were recorded in $CDCl_3$ or DMSO on 400/600 MHz NMR spectrometers and resonances ($\delta$) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constants (Hertz) and integration. $^{13}C$ spectra were recorded in $CDCl_3$ or DMSO on 100 MHz NMR spectrometers and resonances ($\delta$) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. MS was carried out on a Finnigan Trace MS spectrometer (EI, 70 eV). The X-ray crystal structure determinations of **3aa**, **3ci**, **3cj** and **4aa** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

### 4.2. General procedure for synthesis of 3 (3aa as an example)

A mixture of 1,2-bis(bromomethyl)benzene (1.0 mmol), α-cyanoacetophenone (1.0 mmol) and $Cs_2CO_3$ (3.0 mmol) in DMSO (5 mL) was stirred at 80 °C for 4 h till almost full conversion of the substrates by TLC analysis. The resulting mixture was dropped into 100 mL 1 M HCl (aq) and extracted with EtOAc three times (3×50 mL). The organic extract was dried with $Na_2SO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc=50/1) to afford the product **3aa** as a white solid.

### 4.3. Characterization data

*4.3.1. 3-Phenyl-2-naphthonitrile (**3aa**).* Yield 65% (X=Cl), 82% (X=Br), 86% (X=I); white solid; mp 161.0–162.2 °C; IR (KBr): 3053, 2222, 1587, 1488, 1154, 891, 798, 751, 704, 474 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.32 (s, 1H), 7.90 (s, 1H), 7.88 (t, $J$=7.2 Hz, 2H), 7.63 (t, $J$=7.8 Hz, 3H), 7.58 (t, $J$=7.8 Hz, 1H), 7.50 (t, $J$=7.8 Hz, 2H), 7.45 (t, $J$=7.8 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 138.2, 135.8, 134.7, 131.1, 129.3, 129.1, 128.9, 128.6, 128.4, 128.0, 127.9, 127.45, 118.8, 109.4. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{17}H_{12}N$: 230.0967; found: 230.0964.

*4.3.2. 3-(4-Bromophenyl)-2-naphthonitrile (**3ab**).* Yield 54% (167.8 mg); white solid; mp 204.2–205.2 °C; IR (KBr): 2217, 1489, 1104, 1009, 907, 898, 835, 819, 750, 473 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.37 (s, 1H), 7.94–7.87 (m, 3H), 7.70–7.61 (m, 4H), 7.52 (d, $J$=8.0 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.3, 137.1, 136.0, 134.7, 131.9, 131.3, 130.6, 129.6, 129.0, 128.1, 127.8, 123.0, 119.1, 109.1. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{17}H11BrN$: 308.0070; found: 308.0069.

*4.3.3. 3-(4-Bromophenyl)-2-naphthonitrile3-(3,4-dimethylphenyl)-2-naphthonitrile (**3ac**).* Yield 85% (218.4 mg); white solid; mp 177.8–179.3 °C; IR (KBr): 3052, 2912, 2221, 1725, 1448, 1273, 1151, 894, 827, 751, 477 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.34 (s, 1H), 7.91 (s, 2H), 7.91–7.89 (m, 3H), 7.65 (t, $J$=7.8 Hz, 1H), 7.59 (t, $J$=7.2 Hz, 1H), 7.41 (s, 1H), 7.39 (d, $J$=7.8 Hz, 1H), 7.28 (d, $J$=7.8 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.7, 136.9, 135.7, 130.9, 130.0, 129.8, 129.1, 128.7, 127.9, 127.8, 127.1, 126.3, 118.9, 109.5, 19.7, 19.4. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{19}H_{16}N$: 258.1278; found: 258.1277.

*4.3.4. 3-(3,4-Dichlorophenyl)-2-naphthonitrile (**3ad**).* Yield 71% (210.9 mg); white grey solid; mp 198.3–199.2 °C; IR (KBr): 3060, 2222, 1479, 1454, 1133, 1028, 892, 813, 742, 472 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1H), 7.92 (s, 1H), 7.90 (s, 2H), 7.70 (s, 2H), 7.64 (s, 1H), 7.58 (d, $J$=7.8 Hz, 1H), 7.49 (d, $J$=6.6 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.1, 137.0, 136.1, 134.6, 132.9, 131.5, 130.8, 130.7, 129.8, 129.2, 128.3, 128.2, 128.1, 128.1, 118.4, 109.0. HRMS (ESI): $m/z$ $[M+Na]^+$ calcd for $C_{17}H_9Cl_2NNa$: 320.000576; found: 320.0004.

*4.3.5. 6,7-Dimethyl-3-phenyl-2-naphthonitrile (**3ba**).* Yield 72% (185.1 mg); white solid; mp 138.3–139.9 °C; IR (KBr): 2979, 2218, 1596, 1451, 917, 903, 763, 702, 478 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.16 (s, 1H), 7.76 (s, 1H), 7.61–7.60 (m, 4H), 7.49 (t, $J$=7.2 Hz, 2H), 7.43 (t, $J$=7.2 Hz, 1H), 2.43 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.8, 138.6, 138.5, 137.6, 134.8, 133.6, 130.0, 128.9, 128.5, 128.1, 127.9, 127.4, 127.2, 119.2, 108.2, 20.4, 20.1. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{19}H_{16}N$: 258.1280; found: 258.1277.

*4.3.6. 3-(4-Bromophenyl)-6,7-dimethyl-2-naphthonitrile (**3bb**).* Yield 58% (195.7 mg); white solid; mp 151.1–152.2 °C; IR (KBr): 2970, 2215, 1633, 1485, 1450, 1070, 1006, 915, 828, 813, 481 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (s, 1H), 7.72 (s, 1H), 7.60–7.58 (m, 4H), 7.44 (d, $J$=8.0 Hz, 2H), 2.44 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.1, 137.9, 137.4, 134.9, 133.6, 131.7, 130.5, 130.2, 127.9, 127.5, 127.3, 122.7, 119.0, 107.8, 20.4, 20.2. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{19}H_{15}BrN$: 336.0383; found: 336.0382.

*4.3.7. 3-(3,4-Dimethylphenyl)-6,7-dimethyl-2-naphthonitrile (**3bc**).* Yield 76% (216.6 mg); white solid; mp 176.4–177.7 °C; IR (KBr): 2915, 2218, 1494, 1450, 1377, 1029, 905, 82, 724, 448 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.17 (s, 1H), 7.75 (s, 1H), 7.61 (s, 2H), 7.38 (s, 1H), 7.36 (d, $J$=7.8 Hz, 1H), 7.25 (d, $J$=5.4 Hz, 1H), 2.44 (s, 6H), 2.35 (s, 3H), 2.33 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.7, 139.0, 137.4, 136.8, 136.2, 134.8, 133.8, 130.2, 130.0, 129.9, 127.8, 127.5, 127.3, 126.4, 119.4, 108.5, 20.5, 20.2, 19.9, 19.5. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{21}H_{19}N$: 286.1592; found: 286.1590.

*4.3.8. 3-(3,4-Dichlorophenyl)-6,7-dimethyl-2-naphthonitrile (**3bd**).* Yield 74% (239.4 mg); pale yellow solid; mp 249.1–249.9 °C; IR (KBr): 3061, 2222, 1475, 1377, 1134, 1026, 902, 819, 477 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.23 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 7.67 (s, 1H), 7.66 (s, 1H), 7.58 (d, $J$=7.8 Hz, 1H), 7.49 (d, $J$=7.8 Hz, 1H), 2.48 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.3, 138.6, 138.3, 136.3, 135.1, 133.7, 132.9, 132.8, 130.9, 130.6, 128.4, 128.2, 127.7, 127.5, 118.7, 108.0, 20.4, 20.2. HRMS (ESI): $m/z$ $[M+Na]^+$ calcd for $C_{19}H_{13}Cl_2NNa$: 348.0318; found: 348.0317.

*4.3.9. 6′,7′-Dimethyl-[1,2′-binaphthalene]-3′-carbonitrile (**3be**).* Yield 62% (190.4 mg); pale yellow solid; mp 153.5–154.2 °C; IR (KBr): 2972, 2217, 1588, 1491, 1447, 1376, 1025, 926, 896, 775, 480 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.22 (s, 1H), 7.90 (t, $J$=7.8 Hz, 2H), 7.76 (s, 1H), 7.65 (s, 1H), 7.58 (t, $J$=9.0 Hz, 2H), 7.53 (t, $J$=7.8 Hz, 1H), 7.49 (d, $J$=7.2 Hz, 1H), 7.46 (d, $J$=7.2 Hz, 1H), 7.39–7.36 (m, 1H), 2.43 (s, 3H), 2.42 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.9, 137.8, 137.3, 136.2, 134.1, 133.6, 133.3, 131.9, 130.3, 129.4, 128.8, 128.4, 127.8, 127.5, 127.4, 126.4, 125.9, 125.4, 125.1, 118.6, 110.3, 20.4, 20.2. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{23}H_{18}N$: 308.1434; found: 308.1434.

*4.3.10. 5,8-Dibromo-3-phenyl-2-naphthonitrile (**3ca**).* Yield 73% (281.1 mg); white solid; mp 200.9–201.5 °C; IR (KBr): 2922, 2224, 1444, 1133, 1002, 994, 911, 763, 696, 481 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.77 (s, 1H), 8.35 (s, 1H), 7.79 (d, $J$=7.8 Hz, 1H), 7.73 (d, $J$=7.8 Hz, 1H), 7.68 (d, $J$=7.8 Hz, 2H), 7.56 (t, $J$=7.2 Hz, 2H), 7.52 (t, $J$=7.2 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 142.1, 137.3, 135.8, 134.3, 133.3, 131.5, 131.1, 129.2, 129.1, 128.9, 122.5, 118.0, 112.1. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{17}H_{10}Br_2N$: 358.9171; found: 358.9175.

*4.3.11. 5,8-Dibromo-3-(3,4-dimethylphenyl)-2-naphthonitrile (**3cc**).* Yield 88% (362.5 mg); white solid; mp 231.6–233.2 °C; IR (KBr): 2916, 2226, 1504, 1310, 1176, 990, 924, 888, 873, 817, 429 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.74 (s, 1H), 8.32 (s, 1H), 7.77 (d, $J$=7.2 Hz, 1H), 7.71 (d, $J$=7.8 Hz, 1H), 7.43–7.41 (m, 2H), 7.32 (d, $J$=7.2 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 142.3, 137.8, 137.2, 135.6, 134.9, 134.3, 133.2, 131.2, 131.0, 130.2, 128.9, 126.5, 122.4, 118.1, 112.2, 19.8, 19.6. HRMS (ESI): $m/z$ $[M+Na]^+$ calcd for $C_{19}H_{13}Br_2NNa$: 435.93052; found: 435.93070.

*4.3.12. 5′,8′-Dibromo-[1,2′-binaphthalene]-3′-carbonitrile (**3ce**).* Yield 76% (330.7 mg); pale yellow solid; mp 159.4–162.2 °C; IR (KBr): 2922, 2225, 1578, 1266, 1088, 962, 906, 799, 772 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.83 (d, $J$=2.3 Hz, 1H), 8.41 (t, $J$=9.1 Hz, 1H), 8.01 (d, $J$=7.9 Hz, 1H), 7.97 (d, $J$=8.0 Hz, 1H), 7.81 (t, $J$=7.8 Hz, 1H), 7.78–7.77 (m, 1H), 7.62 (t, $J$=6.0 Hz, 1H), 7.56–7.53 (m, 3H), 7.46 (d, $J$=7.2 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 141.0, 134.9, 134.1, 133.6, 133.4, 131.6, 131.6, 131.4, 130.6, 129.6, 128.6, 127.9, 126.9, 126.3, 125.2, 125.0, 122.6, 122.5, 117.4, 114.2. HRMS (APCI): $m/z$ $[M+Na]^+$ calcd for $C_{21}H_{11}Br_2NNa$: 457.9158; found: 457.9151.

*4.3.13. 5,8-Dibromo-3-(furan-2-yl)-2-naphthonitrile (**3cf**).* Yield 72% (270.7 mg); white grey solid; mp 204.2–206.7 °C; IR (KBr): 3446, 2227, 1662, 1495, 1030, 1002, 905, 736 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.65 (s, 2H), 7.74 (d, $J$=8.0 Hz, 1H), 7.66–7.64 (m, 2H), 7.47 (d, $J$=5.4 Hz, 1H), 6.63–6.62 (m, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 149.0, 144.0, 136.2, 134.2, 133.4, 131.2, 130.3, 129.4, 124.5, 122.5, 122.4, 118.3, 112.5, 111.4, 107.6. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{15}H_8Br_2NO$: 375.8970; found: 375.8967.

*4.3.14. 5,8-Dibromo-3-(thiophen-2-yl)-2-naphthonitrile (**3cg**).* Yield 74% (290.1 mg); pale yellow solid; mp 205.4–207.9 °C; IR (KBr):

3441, 2923, 2227, 1652, 1179, 961, 895, 698 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.71 (s, 1H), 8.43 (s, 1H), 7.79–7.71 (m, 2H), 7.69 (d, $J$=7.8 Hz, 1H), 7.51 (s, 1H), 7.22 (s, 1H). 13C NMR (100 MHz, $CDCl_3$) $\delta$ 138.5, 136.3, 134.2, 133.5, 131.5, 130.8, 128.5, 128.5, 128.3, 128.0, 122.4, 122.3, 118.1, 110.8. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{15}H_8Br_2NS$: 391.8739; found: 391.8739.

*4.3.15. 1,4-Dibromo-6-methyl-7-(methylsulfonyl)naphthalene (**3ch**).* Yield 43% 162.5 mg; white solid; mp 192.3–193.0 °C; IR (KBr): 3465, 2929, 1579, 1457, 1305, 1293, 1169, 1134, 1029, 765, 486 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 9.02 (s, 1H), 8.20 (s, 1H), 7.77 (d, $J$=8.0 Hz, 1H), 7.69 (d, $J$=8.0 Hz, 1H), 3.19 (s, 3H), 2.92 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.2, 134.8, 134.7, 133.1, 131.4, 130.9, 130.6, 123.6, 121.2, 109.7, 43.7, 20.5. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{12}H_{11}$ $Br_2O_2S$: 376.8847; found: 376.8841.

*4.3.16. 1,4-Dibromo-6-phenyl-7-(phenylsulfonyl)naphthalene (**3ci**).* Brown solid (yield 68%); mp 233.1.3–237.6 °C; IR (KBr): 3448, 2982, 1723, 1389, 1236, 1052, 1021, 959, 766, 538 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 9.41 (s, 1H), 8.05 (s, 1H), 7.81–7.77 (m, 2H), 7.42 (t, $J$=7.2 Hz, 1H), 7.36 (t, $J$=7.2 Hz, 1H), 7.26–7.19 (m, 6H), 7.04 (d, $J$=7.8 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.1, 139.9, 137.0, 132.8, 132.1, 131.6, 131.3, 130.5, 130.3, 128.5, 128.0, 127.4, 123.9, 122.0, 114.5. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{22}H_{15}Br_2O_2S$: 500.9154; found: 500.9154.

*4.3.17. Diethyl (5,8-dibromo-3-phenylnaphthalen-2-yl)phosphonate (**3cj**).* Yellow solid (yield 26%); mp 121.7–124.4 °C; IR (KBr): 3446, 2924, 1289, 1149, 735, 640, 562, 549 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.97 (d, $J$=16.2 Hz, 1H), 8.17 (s, 1H), 7.74 (d, $J$=7.8 Hz, 1H), 7.70 (d, $J$=7.2 Hz, 1H), 7.55 (d, $J$=5.4 Hz, 2H), 7.46–7.45 (m, 3H), 4.00–3.98 (m, 2H), 3.94–3.92 (m, 2H), 1.19 (t, $J$=6.6 Hz, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 143.0, 140.4, 135.4, 134.1, 132.5, 130.8, 130.1, 129.7, 127.8, 127.6, 123.3, 122.1, 62.3, 16.1. HRMS (APCI): $m/z$ $[M+H]^+$ calcd for $C_{20}H_{20}Br_2O_3P$: 496.9509; found: 496.9511.

*4.3.18. 6,7-Dimethoxy-3-phenyl-2-naphthonitrile (**3da**).* Yield 85% (246.3 mg); white solid; mp 132.4–133.9 °C; IR (KBr): 3001, 2829, 2224, 1624, 1499, 1478, 1435, 1276, 1240, 1210, 1161, 1141, 1010, 905, 773, 703, 476 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (s, 1H), 7.77 (s, 1H), 7.63 (d, $J$=6.8 Hz, 1H), 7.52–7.48 (m, 2H), 7.45 (d, $J$=6.4 Hz, 1H), 7.15 (s, 2H), 4.04 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 152.0, 150.5, 138.4, 138.2, 133.5, 131.2, 128.8, 128.4, 128.0, 127.2, 127.1, 119.3, 106.9, 106.0, 105.8, 55.9. HRMS (ESI): $m/z$ $[M+Na]^+$ calcd for $C_{19}H_{15}NNaO_2$: 312.0996; found: 312.0995.

*4.3.19. 3-(3,4-Dimethylphenyl)-6,7-dimethyl-5,8-dinitro-2-naphthonitrile (**3ec**).* Yield 73% (273.7 mg); pale yellow solid; mp 222.7–224.0 °C; IR (KBr): 2921, 2227, 1626, 1603, 1529, 1484, 1365, 853, 822 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.13 (s, 1H), 7.70 (s, 1H), 7.34 (d, $J$=5.7 Hz, 2H), 7.34–7.33 (m, 2H), 7.29 (d, $J$=7.8 Hz, 1H), 2.48 (s, 6H), 2.36 (s, 3H), 2.35 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 148.6, 148.2, 143.7, 138.5, 137.5, 133.9, 131.2, 130.2, 129.9, 129.2, 129.0, 126.3, 124.6, 121.3, 117.2, 113.6, 19.8, 19.6, 15.8, 15.6. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{21}H_{18}N_3O_4$: 376.1293; found: 376.1292.

*4.3.20. 3-Phenylphenazine-2-carbonitrile (**3fa**).* Yield 72% (202.7 m g); yellow solid; mp 242.6–244.2 °C; IR (KBr): 2228, 1498, 1442, 1190, 904, 885, 759, 695 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.80 (s, 1H), 8.36 (s, 1H), 8.29–8.25 (m, 2H), 7.93 (, $J$=7.2 Hz, 2H), 7.75 (d, $J$=6.6 Hz, 2H), 7.58 (d, $J$=6.6 Hz, 2H), 7.55 (d, $J$=6.6 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 145.1, 144.4, 143.8, 142.9, 138.3, 137.0, 132.4, 131.6, 130.5, 130.1, 129.7, 129.3, 129.0, 128.9, 117.7, 114.6. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{19}H_{12}N_3$: 282.1027; found: 282.1026.

*4.3.21. 3-(Naphthalen-1-yl)phenazine-2-carbonitrile (**3fe**).* Yield 62% (205.2 mg); yellow solid; mp 230–232.2 °C; IR (KBr): 2921, 2224, 1590, 1498, 1394, 1127, 906, 760, 555 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.85 (s, 1H), 8.42 (s, 1H), 8.32 (t, $J$=7.8 Hz, 1H), 8.28 (t, $J$=7.8 Hz, 1H), 8.04–7.95 (m, 4H), 7.66–7.63 (m, 3H), 7.58–7.54 (m, 1H), 7.49–7.45 (m, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 145.0, 144.5, 143.6, 141.8, 141.2, 137.4, 134.7, 133.6, 132.4, 132.2, 131.7, 131.4, 130.2, 129.8, 128.6, 127.9, 126.9, 126.4, 125.2, 125.0, 117.1, 116.5. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{23}H_{14}N_3$: 332.1183; found: 332.1182.

*4.3.22. 3-Phenyl-1,5-dihydrobenzo[c]oxepine-4-carbonitrile (**4aa**).* Yield 82% (202.9 mg); pale yellow solid; mp 125.3–126.7 °C; IR (KBr): 3030, 2888, 2194, 1607, 1592, 1301, 1268, 1254, 1128, 960, 784, 769, 755 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.58 (d, $J$=8.4 Hz, 1H), 7.40–7.35 (m, 4H), 7.33–7.31 (m, 1H), 7.28 (d, $J$=7.2 Hz, 1H), 5.39 (s, 2H), 3.93 (s, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 168.2, 138.9, 135.0, 134.4, 130.3, 129.5, 128.6, 128.4, 128.2, 127.9, 127.6, 121.7, 83.9, 71.7, 34.2. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{17}H_{14}NO$: 248.10670; found: 248.1070.

*4.3.23. 2-Benzoyl-2,3-dihydro-1H-indene-2-carbonitrile (**5aa**).* Yield 12% (29.7 mg); white grey solid; mp 99.2–101.2 °C; IR (KBr): 2232, 1680, 1448, 1240, 753, 724 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$=7.8 Hz, 1H), 7.66 (t, $J$=7.2 Hz, 1H), 7.56–7.53 (m, 2H), 7.24 (s, 4H), 3.94 (d, $J$=16.2 Hz, 2H), 3.75 (t, $J$=16.2 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 190.8, 137.9, 134.0, 132.8, 129.5, 128.7, 127.5, 124.3, 122.2, 49.7, 42.9. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{17}H_{14}NO$: 248.1070; found: 248.1070.

*4.3.24. 11H-Benzo[b]fluoren-11-one (**7aa**).*[16] Yellow solid; (yield 72%); mp 151.2–152.1 °C (lit.[17a] 152 °C); IR (KBr): 2963, 2926, 1708, 1632, 1602, 1262, 1102, 1021 $cm^{-1}$. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 8.18 (s, 1H), 7.90 (d, $J$=7.8 Hz, 1H), 7.88 (s, 1H), 7.84 (d, $J$=7.8 Hz, 1H), 7.76 (d, $J$=7.8 Hz, 1H), 7.73 (d, $J$=7.2 Hz, 1H), 7.55 (t, $J$=7.8 Hz, 2H). 7.48 (t, $J$=7.2 Hz, 1H), 7.36 (t, $J$=7.2 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 193.1, 144.8, 138.3, 136.8, 136.1, 135.0, 133.5, 130.8, 129.1, 129.0, 128.7. 126.9, 125.6, 124.4, 120.9, 119.0, 109.7. HRMS (ESI): $m/z$ $[M+H]^+$ calcd for $C_{17}H_{11}O$: 231.0804; found: 231.0804.

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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.01.005.

## References and notes

1. (a) Podlesny, E. E.; Kozlowski, M. C. *J. Nat. Prod.* **2012**, *75*, 1125; (b) Foley, P.; Eghbali, N.; Anastas, P. T. *J. Nat. Prod.* **2010**, *73*, 811; (c) Chen, X. M.; Shi, Q. Y.; Lin, G.; Guo, S. X.; Yang, J. S. *J. Nat. Prod.* **2009**, *72*, 1712; (d) Dai, J.; Liu, Y.; Zhou, Y. D.; Nagle, D. G. *J. Nat. Prod.* **2007**, *70*, 1824; (e) Silva, O.; Gomes, E. T. *J. Nat. Prod.* **2003**, *66*, 447; (f) Ward, R. S. *Nat. Prod. Rep.* **1995**, *12*, 183; (g) Wei, J.; Vander Jagt, D. L.; Royer, R. E.; Deck, L. M. *Tetrahedron Lett.* **2010**, *51*, 5757; (h) Wang, Z.; Elokdah, H.; McFarlane, G.; Pan, S.; Antane, M. *Tetrahedron Lett.* **2006**, *47*, 3365; (i) McCulloch, M. W. B.; Barrow, R. A. *Molecules* **2005**, *10*, 1272; (j) Brasholz, M.; Sörgel, S.; Azap, C.; Reissig, H.-U. *Eur. J. Org. Chem.* **2007**, 3801; (k) Krohn, K.; Kounam, S. F.; Cludius-Brandt, S.; Draeger, S.; Schulz, B. *Eur. J. Org. Chem.* **2008**, 3615; (l) Xie, X.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 2661; (m) Gudla, V.; Balamurugan, R. *J. Org. Chem.* **2011**, *76*, 9919; (n) Mulrooney, C. A.; Morgan, B. J.; Li, X. L.; Kozlowski, M. C. *J. Org. Chem.* **2010**, *75*, 16.
2. (a) Watson, M. D.; Fechtenkotter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267; (b) Svoboda, J.; Novotna, V.; Kozmik, V.; Glogarova, M.; Weissflog, W.; Diele, S.; Pelzl, G. *J. Mater. Chem.* **2003**, *13*, 2104; (c) Reddy, R. A.; Baumeister, U.; Keith, C.; Tschierske, C. *J. Mater. Chem.* **2007**, *17*, 62.
3. For a recent review of BINOL-based catalysts, see: Zhou, Q. L. In *Privileged Chiral Ligands and Catalysts*; Wiley: New York, NY, 2011; pp 295–332.

4. (a) Koning, C. B.; Rousseau, A. L.; van OtterloW, A. L. *Tetrahedron* **2003**, *59*, 7; (b) Bradsher, C. K. *Chem. Rev.* **1987**, *87*, 1277; (c) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901.
5. Recent examples: (a) Tan, X.; Liu, B. X.; Li, X. Y.; Li, B.; Xu, S. S.; Song, H. B.; Wang, B. Q. *J. Am. Chem. Soc.* **2012**, *134*, 16163; (b) Chang, M. Y.; Wu, M. H.; Chen, Y. L. *Org. Lett.* **2013**, *15*, 2822; (c) Zhu, S. F.; Xiao, Y. L.; Guo, Z. J.; Jiang, H. F. *Org. Lett.* **2013**, *15*, 898; (d) Jiang, H.; Cheng, Y. Z.; Zhang, Y.; Yu, S. Y. *Org. Lett.* **2013**, *15*, 4884; (e) Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *J. Org. Chem.* **2013**, *78*, 2751; (f) Reddy, R. S.; Prasad, P. K.; Ahuja, B. B.; Sudalai, A. *J. Org. Chem.* **2013**, *78*, 5045; (g) Peng, S. Y.; Wang, L.; Wang, J. *Chem.—Eur. J.* **2013**, *19*, 13322; (h) Lim, J. W.; Kim, K. H.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2012**, *53*, 5449; (i) Umeda, R.; Nishi, S.; Kojima, A.; Kaiba, K.; Nishiyama, Y. *Tetrahedron Lett.* **2013**, *54*, 179; (j) Komeyama, K.; Kashihara, T.; Takaki, K. *Tetrahedron Lett.* **2013**, *54*, 5659; (k) Bu, X. L.; Hong, L. C.; Liu, R. T.; Hong, J. Q.; Zhang, Z. X.; Zhou, X. G. *Tetrahedron* **2012**, *68*, 7960.
6. (a) Zhang, X. Y.; Jia, X. F.; Liu, N.; Guo, X. J.; Song, Y. P.; Fan, X. S. *Tetrahedron* **2013**, *69*, 5374; (b) Gao, P.; Liu, J. J.; Wei, Y. Y. *Org. Lett.* **2013**, *15*, 2872.
7. (a) Back, T. G.; Parvez, M.; Zhai, H. M. *J. Org. Chem.* **2006**, *71*, 5254; (b) Neo, A. G.; López, C.; Romero, V.; Antelo, B.; Delamano, J.; Pérez, A.; Fernández, D.; Almeida, J. F.; Castedo, L.; Tojo, G. *J. Org. Chem.* **2010**, *75*, 6764; (c) Almeida, J. F.; Castedo, L.; Fernández, D.; Neo, A. G.; Romero, V.; Tojo, G. *Org. Lett.* **2003**, *5*, 4939.
8. (a) Murayama, K.; Sawada, Y.; Noguchi, K.; Tanaka, K. *J. Org. Chem.* **2013**, *78*, 6202; (b) Kim, M.; Wiemer, D. F. *Tetrahedron Lett.* **2005**, *46*, 7583.
9. Wang, J. G.; Meng, W.; Xiang, J. C.; Zhu, Y. P.; Xue, W. J.; Wu, A. X. *Org. Lett.* **2012**, *14*, 6060.
10. The details of the crystal data (**3aa**, **3ci**, **3cj** and **4aa**) have been deposited with Cambridge Crystallographic Data Centre as Supplementary Publication, CCDC 971212–971215, 977770.
11. Weinheimer, A. J.; Kantor, S. W.; Hauser, C. R. *J. Org. Chem.* **1953**, *18*, 801.
12. Lai, Y. H.; Yap, A. H. T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1373.
13. Shahak, I.; Bergmann, E. D. *J. Chem. Soc. C* **1966**, 1005.
14. Diederich, F.; Ionas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thilgen, C. *Helv. Chim. Acta* **1993**, *76*, 2445.
15. Takahashi, T.; Li, S.; Huang, W. Y.; Kong, F. Z.; Nakajima, K.; Shen, B. J.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967.
16. Kim, K. H.; Kim, S. H.; Lee, K. Y.; Kim, J. N. *Bull. Korean Chem. Soc.* **2011**, *32*, 1387.
17. (a) Streitweiser, A., Jr.; Brown, S. M. *J. Org. Chem.* **1988**, *53*, 904; (b) Rodríguez, D.; Martínez-Esperón, M. F.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *J. Org. Chem.* **2004**, *69*, 3842; (c) González-Cantalapiedra, E.; de Frutos, Ó.; Atienza, C.; Mateo, C.; Echavarren, A. M. *Eur. J. Org. Chem.* **2006**, *6*, 1430.