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Regioselective synthesis of 1-arylnaphthalenes from *N*-tosylaziridine derivatives

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Abstract—Regioselective synthesis of 1-arylnaphthalene derivatives was carried out from *N*-tosylaziridines, which was made from the reaction of *N*-tosylimines and cinnamyl bromides by using the sulfur ylide chemistry.

Regioselective synthesis of naphthalene derivatives has been and continues to be of great interest in organic synthesis.[1–3] A new synthetic procedure is still highly desired due to the abundance of the skeleton in many biologically important natural products. Recently, we have reported the synthesis of naphthalenes from the reaction of the Baylis–Hillman acetates derived from *o*-halobenzaldehydes and primary nitroalkanes via the successive S_N2'–S_NAr-elimination strategy.[2a] Later we extended the concept to a more general one by using the Mn(III)-assisted radical cyclization protocol.[2b]

The ring-opening reaction of *N*-tosylaziridines with a variety of nucleophiles has been used in organic synthesis. The Friedel–Crafts type ring-opening reaction of *N*-tosylaziridines with arene compounds was also studied deeply.[4] In these respects, we pursued the synthesis of 1-arylnaphthalene derivatives via the intramolecular ring-opening reaction of *N*-tosylaziridines derived from Baylis–Hillman adducts as depicted in Figure 1.

We thought that the synthesis of requisite aziridine derivatives **4** could be carried out by using the well-known ylide chemistry[5] from the reaction of *N*-tosylimine **3** and cinnamyl bromide **2**, which could be synthesized from the Baylis–Hillman adduct **1**.[6] We also expected that we could prepare the target 1-arylnaphthalene **5** by the intramolecular Friedel–Crafts type ring-opening reaction of **4** and the following elimination of *p*-toluenesulfonamide moiety.

As an initial try, we prepared **4a** from the reaction of cinnamyl bromide **2a** and *N*-tosylimine **3a** in the presence of Me_2S and K_2CO_3 in CH_3CN at room temperature according to the previous paper (Scheme 1).[5] The corresponding sulfur ylide reacted with **3a** successfully to give the desired *N*-tosylaziridine **4a** in 62% yield as a mixture of two diastereomers (trans/cis = 7:5). The two isomers were difficult to separate in pure states. However, the stereochemistry will not affect the next reaction (vide infra), thus we used the mixture for the next reaction. The other aziridine derivatives **4b**–**f** were prepared similarly in 60–70% yields (Fig. 2).[5–7]

With these compounds **4** in our hand we examined the next aziridine-opening and Friedel–Crafts reaction

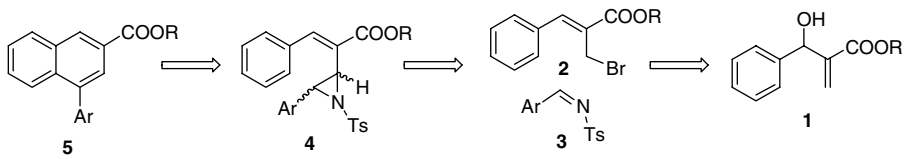

Figure 1.

Keywords: 1-Arylnaphthalenes; Baylis–Hillman adducts; *N*-Tosylaziridines; Sulfur ylide.
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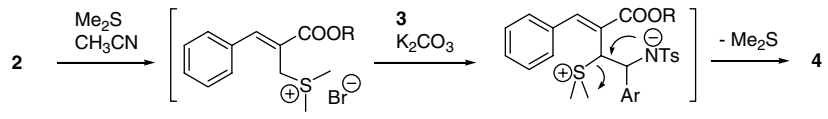


Scheme 1.

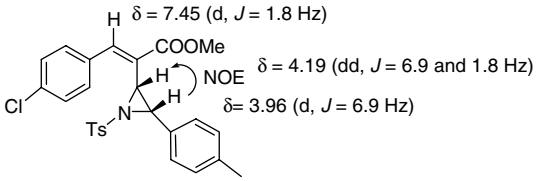
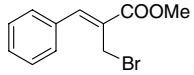
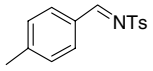
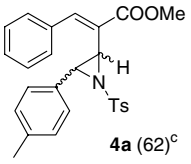
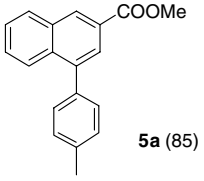
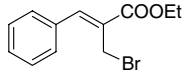
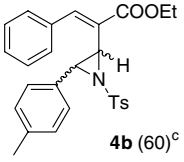
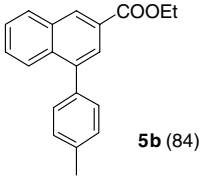
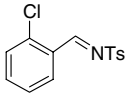
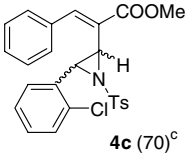
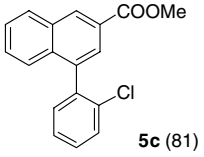
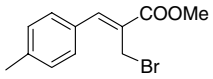
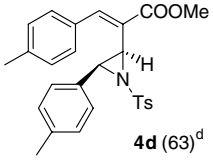
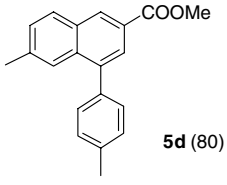
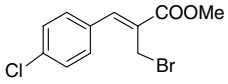
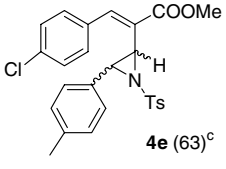
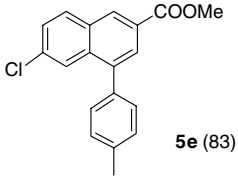
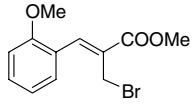
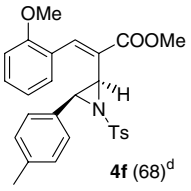
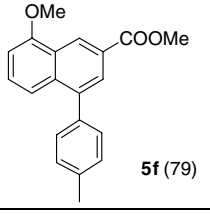


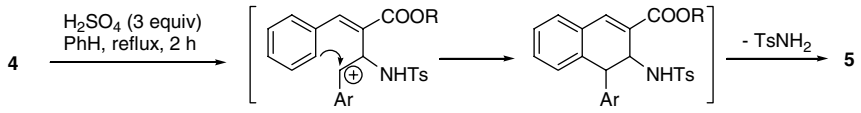
Figure 2. NOE of *cis*-**4e**.

under a variety of acidic conditions. To our delight we could obtain the final compound **5a** directly in 85% yield when we subjected **4a** under benzene/H_2SO_4 (3 equiv)/ refluxing conditions within 2 h. By using the same conditions we prepared **5b**–**f** successfully in 79–84% yields (Table 1). As shown in Scheme 2, the reaction might occur via the aziridine ring-opening and Friedel–Crafts

Table 1. Synthesis of *N*-tosyl aziridines and 1-arylnaphthalenes

Entry	Substrate **2**	Substrate **3**	Aziridine **4** (%)[a]	Naphthalene **5** (%)[b]
1	 **2a**	 **3a**	 **4a** (62)[c]	 **5a** (85)
2	 **2b**	**3a**	 **4b** (60)[c]	 **5b** (84)
3	**2a**	 **3b**	 **4c** (70)[c]	 **5c** (81)
4	 **2c**	**3a**	 **4d** (63)[d]	 **5d** (80)
5	 **2d**	**3a**	 **4e** (63)[c]	 **5e** (83)
6	 **2e**	**3a**	 **4f** (68)[d]	 **5f** (79)

[a] CH_3CN, Me_2S (1.5 equiv), K_2CO_3 (1.0 equiv), rt, 5 h.
[b] Benzene, H_2SO_4 (3 equiv), reflux, 2 h.
[c] Mixtures of cis/trans.[6]
[d] Pure cis-isomer.[6]



Scheme 2.

type reaction and the concomitant elimination of *p*-toluenesulfonamide to furnish the naphthalene compound.[8]

In summary, we developed an efficient synthetic method of 1-arylnaphthalenes starting from the Baylis–Hillman adducts.

Acknowledgements

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6. Typical procedure for the synthesis of aziridine **4a** and 1-arylnaphthalene **5a**: The cinnamyl bromide derivative **2a** was prepared by the reaction of the Baylis–Hillman adduct **1** and aq HBr (rt, 5 h) in 92% yield. Synthesis of **2b–e** was also carried out similarly with HBr at room temperature (5–16 h, 85–95%). To a stirred mixture of cinnamyl bromide **2a** (254 mg, 1.0 mmol) and *N*-tosylimine **3a** (273 mg, 1.0 mmol) in CH_3CN (3 mL) was added Me_2S (93 mg, 1.5 mmol) and K_2CO_3 (138 mg, 1.0 mmol) at room temperature and stirred for 5 h. After usual workup and column chromatographic purification process (hexanes/ether, 4:1) we obtained **4a**, 278 mg (62%) as a mixture of two diastereoisomers (trans/cis = 7:5 based on ^{1}H NMR). A mixture of aziridine **4a** (224 mg, 0.5 mmol) and H_2SO_4 (147 mg, 1.5 mmol) in benzene (5 mL) was heated to reflux for 2 h. After usual workup and column chromatographic purification process (hexanes/ether, 20:1) we obtained **5a**, 117 mg (85%). The other aziridines **4b–f** and naphthalenes **5b–f** were synthesized analogously and the spectroscopic data of prepared compounds are as follows.
Compound **4a**: 62% (trans/cis = 7:5); clear oil; IR (KBr) 1705, 1331, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, trans-isomer) δ 2.30 (s, 3H), 2.34 (s, 3H), 3.72 (dd, $J = 5.0$ and 1.0 Hz, 1H), 3.84 (s, 3H), 4.34 (d, $J = 5.0$ Hz, 1H), 7.05–7.34 (m, 9H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.95 (s. 1H); ^{1}H NMR ($CDCl_3$, 500 MHz, cis-isomer) δ 2.17 (s, 3H), 2.40 (s, 3H), 3.49 (s, 3H), 3.97 (d, $J = 7.0$ Hz, 1H), 4.23 (dd, $J = 7.0$ and 2.0 Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 6.71 (d, $J = 8.0$ Hz, 2H), 7.05–7.34 (m, 7H), 7.48 (d, $J = 2.0$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, cis+trans mixture) δ 21.03, 21.17, 21.54, 21.61, 44.66, 46.54, 48.39, 49.52, 51.76, 52.31, 123.72, 124.49, 126.86, 127.07, 127.84, 127.91, 127.98, 128.12, 128.41, 128.56, 128.41, 129.06, 129.38, 129.49, 129.52, 130.19, 131.62, 133.88, 133.98, 135.48, 136.56, 137.00, 138.13, 143.69, 144.07, 144.33, 145.55, 167.29, 167.49.
Compound **4b**: 60% (trans/cis = 2:1); clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz, trans-isomer) δ 1.39 (t, $J = 7.2$ Hz, 3H), 2.29 (s, 3H), 2.33 (s, 3H), 3.69 (dd, $J = 4.8$ and 1.2 Hz, 1H), 4.25–4.41 (m, 2H), 4.42 (d, $J = 4.8$ Hz, 1H), 7.06–7.44 (m, 11H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.94 (s, 1H); ^{1}H NMR ($CDCl_3$, 300 MHz, cis-isomer) δ 1.26 (t, $J = 7.2$ Hz, 3H), 2.17 (s, 3H), 2.37 (s, 3H), 3.93 (d, $J = 6.6$ Hz, 1H), 3.98–4.41 (m, 3H), 6.52 (d, $J = 8.1$ Hz, 2H), 6.73 (d, $J = 8.1$ Hz, 2H), 7.06–7.44 (m, 7H), 7.50 (d, $J = 1.5$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 2H).

Compound **4c**: 70% (trans/cis = 3:1); clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz, trans-isomer) δ 2.32 (s, 3H), 3.66 (dd, J = 4.8 and 1.2 Hz, 1H), 3.89 (s, 3H), 5.08 (d, J = 4.8 Hz, 1H), 6.92–7.42 (m, 11H), 7.83 (d, J = 8.1 Hz, 2H), 8.00 (s, 1H); ^{1}H NMR ($CDCl_3$, 300 MHz, cis-isomer) δ 2.38 (s, 3H), 3.56 (s, 3H), 4.35 (dd, J = 6.6 and 1.5 Hz, 1H), 4.44 (d, J = 6.6 Hz, 1H), 6.92–7.42 (m, 11H), 7.54 (d, J = 1.5 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H).

Compound **4d**: 63% (cis only); clear oil; IR (KBr) 1716, 1331, 1265, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, cis-isomer) δ 2.16 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 3.46 (s, 3H), 3.99 (d, J = 6.6 Hz, 1H), 4.22 (dd, J = 6.6 and 1.8 Hz, 1H), 6.55 (d, J = 8.1 Hz, 2H), 6.71 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H).

Compound **4e**: 63% (trans/cis = 1:5); clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz, trans-isomer) δ 2.31 (s, 3H), 2.36 (s, 3H), 3.62 (dd, J = 5.1 and 1.2 Hz, 1H), 3.85 (s, 3H), 4.43 (d, J = 5.1 Hz, 1H), 7.00–7.43 (m, 10H), 7.78 (d, J = 8.4 Hz, 2H), 7.88 (s, 1H); ^{1}H NMR ($CDCl_3$, 300 MHz, cis-isomer) δ 2.20 (s, 3H), 2.40 (s, 3H), 3.52 (s, 3H), 3.96 (d, J = 6.9 Hz, 1H), 4.19 (dd, J = 6.9 and 1.8 Hz, 1H), 6.55 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.1 Hz, 2H), 7.00–7.32 (m, 6H), 7.45 (d, J = 1.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, cis-isomer) δ 21.03, 21.60, 44.29, 46.61, 51.87, 124.30, 126.36, 127.05, 127.99, 128.02, 128.13, 129.54, 130.68, 132.39, 134.83, 135.28, 137.28, 142.32, 144.43, 167.12.

Compound **4f**: 68% (cis-only); clear oil; IR (KBr) 1716, 1331, 1250, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, cis-isomer) δ 2.18 (s, 3H), 2.36 (s, 3H), 3.47 (s, 3H), 3.51 (s, 3H), 3.86 (d, J = 6.9 Hz, 1H), 4.18 (dd, J = 6.9 and 1.8 Hz, 1H), 6.50–7.26 (m, 10H), 7.68 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H).

Compound **5a**: 85%; yellow solid, mp 95–96 °C; IR (KBr) 1720, 1246 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 3.97 (s, 3H), 7.29 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.50–7.54 (m, 2H), 7.92–7.99 (m, 2H), 8.00 (d, J = 1.8 Hz, 1H), 8.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.21, 52.20, 126.03, 126.11, 126.43, 126.87, 128.23, 129.04, 129.71, 129.85, 130.33, 133.02, 133.88, 136.99, 137.27, 140.67, 167.23; ESIMS m/z 277.1 (M^++H).

Compound **5b**: 84%; yellow solid, mp 96–97 °C; IR (KBr) 1716, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (t, J = 6.9 Hz, 3H), 2.45 (s, 3H), 4.43 (q, J = 6.9 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.47–7.55 (m, 2H), 7.91–8.00 (m, 2H), 8.01 (d, J = 1.8 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.36, 21.19, 61.07, 126.03, 126.08, 126.37, 127.22, 128.14, 129.03, 129.68, 129.85, 130.24, 133.02, 133.84, 137.06, 137.24, 140.58, 166.73; ESIMS m/z 291.1 (M^++H).

Compound **5c**: 81%; yellow solid, mp 139–140 °C; IR (KBr) 1720, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.97 (s, 3H), 7.34–7.43 (m, 3H), 7.50–7.58 (m, 4H), 7.98–8.03 (m, 2H), 8.67 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.25, 125.91, 126.37, 126.63, 128.71, 126.80, 128.51, 129.26, 129.58, 129.73, 131.22, 131.97, 132.62, 133.80, 133.97, 137.85, 138.50, 167.04; ESIMS m/z 297.1 (M^++H).

Compound **5d**: 80%; yellow solid, mp 89–90 °C; IR (KBr) 1720, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 2.46 (s, 3H), 3.96 (s, 3H), 7.29–7.40 (m, 5H), 7.69 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 1.8 Hz, 1H), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.23, 22.11, 52.13, 125.02, 125.98, 126.23, 128.70, 129.04, 129.56, 129.83, 130.14, 131.24, 134.06, 137.15, 137.19, 138.48, 139.90, 167.35; ESIMS m/z 291.1 (M^++H).

Compound **5e**: 83%; yellow solid, mp 94–95 °C; IR (KBr) 1724, 1246 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.47 (s, 3H), 3.97 (s, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.48 (dd, J = 8.7 and 2.1 Hz, 1H), 7.91 (s, 1H), 7.93 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 2.1 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.24, 52.31, 125.10, 127.09, 127.18, 127.49, 129.27, 129.72, 129.99, 131.19, 131.28, 134.52, 134.56, 136.28, 137.65, 140.03, 166.90; ESIMS m/z 311.1 (M^++H).

Compound **5f**: 79%; yellow solid, mp 123–124 °C; IR (KBr) 1720, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 3.97 (s, 3H), 4.03 (s, 3H), 6.85 (dd, J = 7.2 and 1.2 Hz, 1H), 7.27–7.50 (m, 6H), 8.01 (d, J = 1.2 Hz, 1H), 9.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.20, 52.12, 55.64, 104.26, 118.25, 124.49, 125.27, 126.02, 126.74, 128.41, 128.95, 129.85, 134.96, 137.13, 137.35, 140.21, 156.58, 167.39; ESIMS m/z 307.1 (M^++H).

7. As reported the cis/trans ratios of the diastereoisomers were much different depending upon the structure of the substrates.[5] We obtained cis-isomers exclusively for the cases of **4d** and **4f**. However, cis/trans mixtures were obtained for **4a**–**c** and **4e** in a variable ratios.[6] In Figure 2 we show the NOE data of pure *cis*-**4e** as an example.
8. During the evaluation process of this paper, one of the reviewers suggested the synthesis of naphthalenes from the reaction of *N*-aryl(or *N*-alkyl)aziridine of Baylis–Hillman adducts instead of **4a**–**f**. However, the preparation of *N*-phenylaziridine derivative from the reaction of **2a** and benzaldehyde *N*-phenylimine failed as reported in Ref. 5a.