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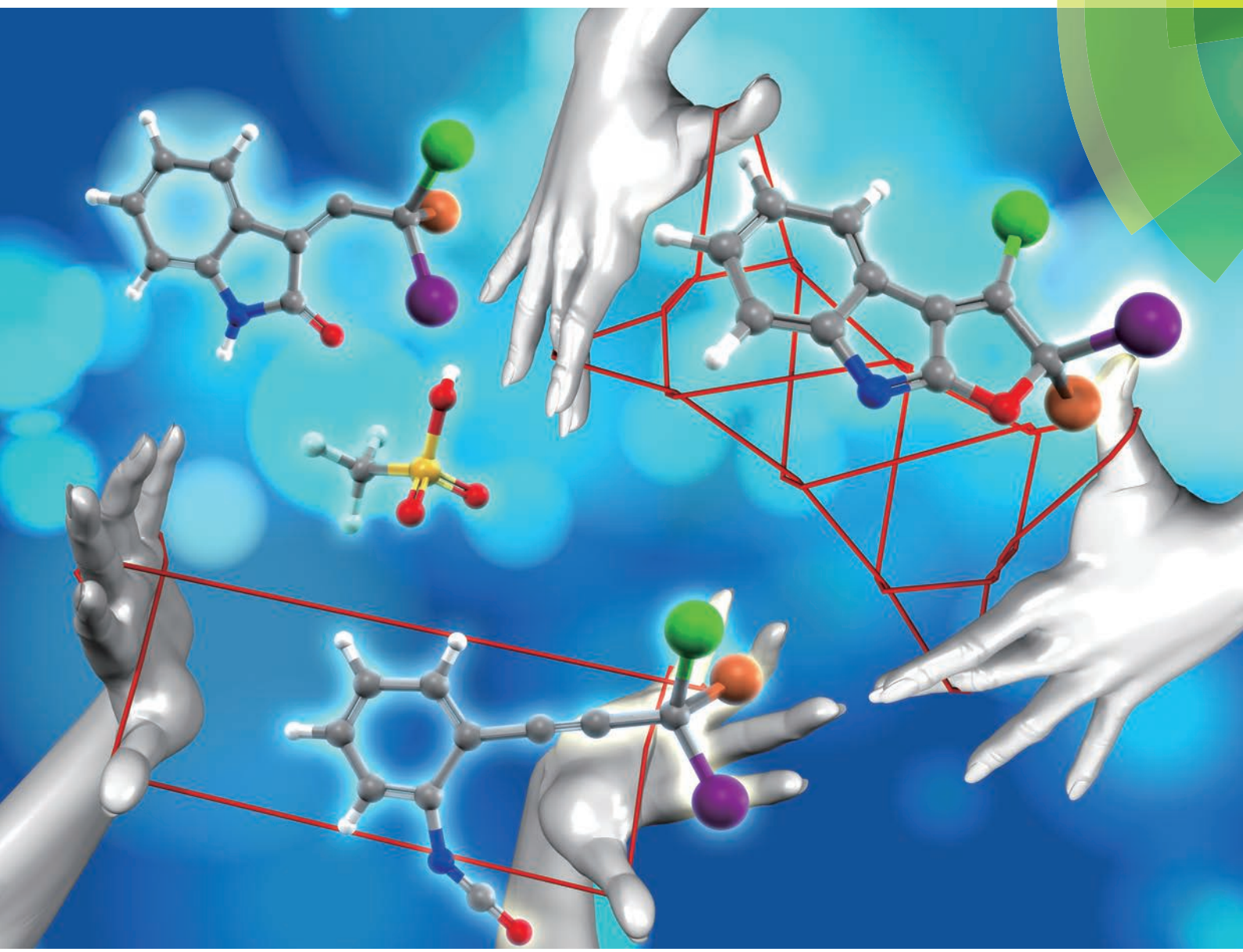

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PAPER

Takao Saito, Takashi Otani *et al.*

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Triflic acid-promoted cycloisomerization of 2-alkynylphenyl isothiocyanates and isocyanates: a novel synthetic method for a variety of indole derivatives†

Takao Saito,*[a] Yoshihiko Sonoki,[a] Takashi Otani*[a] and Noriki Kutsumura[a,b]

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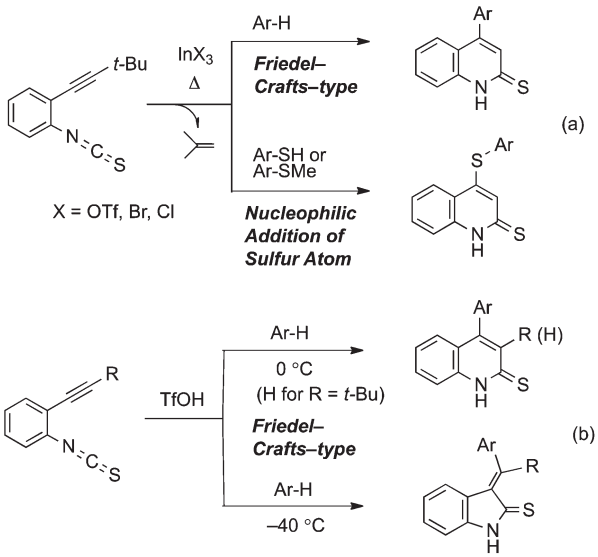
A new approach towards the synthesis of indole derivatives *via* triflic acid-promoted cycloisomerization with rearrangement of 2-(alkyn-1-yl)phenyl isothiocyanates and 2-(alkyn-1-yl)phenyl isocyanates has been achieved. By this methodology, structurally diverse types of indole derivatives such as thieno- and furo-indoles, spiro-indolethiones, spiro-oxindoles, and 3-alkylidene-oxindoles were synthesized.

1. Introduction

The indole ring system is probably the most important and common heterocyclic core found in nature and in many biologically active compounds and pharmaceuticals,[1] and various synthetic methods for producing structurally diverse indole derivatives have been developed.[2–4] By contrast, functionalized heterocumulenes such as carbodiimides, isocyanates, isothiocyanates, and ketenimines are useful synthetic building blocks for nitrogen-containing heterocycles, because they often take part in a variety of synthetic transformations with high reactivity, especially in ring-forming reactions, by incorporating both the heterocumulene moiety and other available functional group(s) in the molecule.[5] In this context, we recently reported In(III)-promoted cycloaddition of 2-(alkyn-1-yl)phenyl isothiocyanates with arenes at 150 °C giving 4-aryl- or 4-arylthioquinoline-2-thiones, which were involved in the tandem regioselective Friedel–Crafts-type alkenylation–6π-electrocyclization mode process (Scheme 1-(a)).[6] Triflic acid (TfOH) was also found to efficiently accelerate the same reaction even at a lower temperature of 0 °C to produce 4-arylquinoline-2-thiones.[7] Alternatively, 3-(arylmethylene)indole-2-thiones were predominantly formed at −40 °C *via* a tandem 5-*dig*-mode cyclization and Friedel–Crafts-type alkenylation (Scheme 1-(b)).[7,8] With these results in mind, we wondered what would happen when the reaction was performed in the absence of an arene (a Friedel–Crafts-type nucleophile) in the reaction system. A not completely unexpected, but nevertheless somewhat surprising, result was obtained when 2-(3,3-dimethylbutyn-1-yl)phenyl isothiocyanate (**1a**) was treated with TfOH at −40 to 0 °C; predominantly 2,2,3-trimethyl-2*H*-thieno-[2,3-*b*]indole (**5**)[9] was formed (Scheme 2). This observation suggests that a methyl group in the *t*-Bu group must migrate in the process of the thieno-indole formation from alkynylphenyl isothiocyanate **1a**. Thus far, to our knowledge, no precedent involving such a tandem cycloisomerization/rearrangement sequence reaction of alkyne-heterocumulene species has been reported.[8c,10] Since we became interested in revealing this highly unique reaction and the potential for a new entry to the

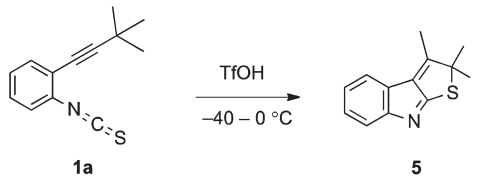


Scheme 1 In(III)- and triflic acid-promoted Friedel–Crafts-type reaction of alkynyl isothiocyanates to produce quinolinethiones and indolethiones.

[a]*Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. E-mail: tsaito@rs.kagu.tus.ac.jp, totani@rs.tus.ac.jp*

[b]*International Institute for Integrative Sleep Medicine (WPI-IIIS), University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan*

†Electronic supplementary information (ESI) available: Experimental details. CCDC 995430 and 995431. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob00825a



Scheme 2 Triflic acid-promoted cycloisomerization of **1a** to produce thieno-indole **5**.

synthesis of indole derivatives, we started to investigate this reaction in more depth to examine its scope and limitations. Here, we report the triflic acid-promoted cycloisomerization reaction of 2-(alkyn-1-yl)phenyl isothiocyanates and isocyanates as a novel synthetic method for structurally diverse types of indole derivatives (thieno- and furo-fused indoles, spiro-indolethiones, spiro-oxindoles, and 3-alkylidene-oxindoles). Characteristic and unique features of this tandem reaction are that it involves the triflic acid-promoted indole-forming process and the Wagner–Meerwein-type rearrangement[11] of the hydrogen or the substituent to the α-sp^2 carbocation ([1,2]-shift) arising from the substituted ethynyl group.

2. Results and discussion

2.1. Preparation of starting materials

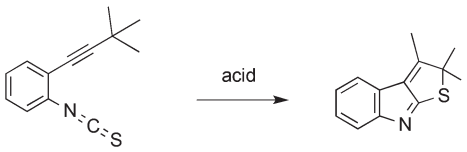
First, the key substrates, 2-(alkyn-1-yl)phenyl isothiocyanates **1** and isocyanates **4**, were prepared from 2-alkynylanilines **2** as outlined in Scheme 3.[6,12,13] 2-Alkynylanilines **2**, which were readily synthesized from commercially available 2-iodoaniline and alkynes *via* a Sonogashira coupling, were converted to the corresponding iminophosphoranes **3**, followed by the aza-Wittig reaction of **3** with carbon disulfide to give 2-(alkyn-1-yl)-phenyl isothiocyanates **1a–1k**. Isothiocyanate **1l** was conveniently prepared from the reaction of **2l** with di(1*H*-imidazol-1-yl)methanethione.[13] 2-(Alkyn-1-yl)phenyl isocyanates **4** were prepared by the reaction of anilines **2** with triphosgene (see ESI†).

2.2. Triflic acid-promoted reaction of 2-(alkyn-1-yl)phenyl isothiocyanates (1)

Initially, we screened Brønsted acids with optimization of their stoichiometry and reaction conditions using isothiocyanate **1a** (R = *t*-Bu) as a model substrate. Representative results shown in Table 1 suggest that triflic acid is the most effective of the acids used (entry 3 *vs.* entries 11–15); three equivalents of triflic acid are necessary and sufficient to obtain a good yield (78%) of the expected product **5**[9] when the reaction is conducted for only 10 min in dichloromethane at 0 °C (entry 3 *vs.* entries 1, 2 and 4); and the reactions in the other solvents except 1,2-dichloroethane or at rt or −40 °C (entry 3 *vs.* entries 5–10) bring less efficiency. The solvent effect is consistent with the consideration that polar solvents with more coordination ability tend to reduce the practical acidity of triflic acid to activate the substrate transforming to the cyclized product **5**.

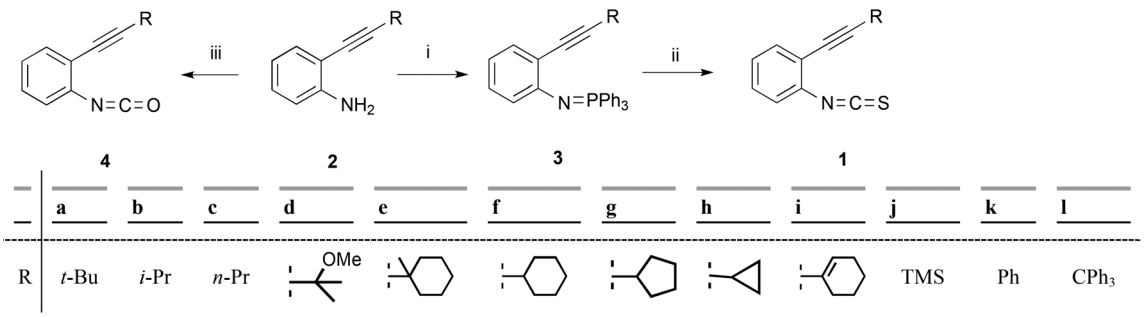
A possible reaction pathway is illustrated in Scheme 4. Protonation at the nitrogen and subsequent nucleophilic attack

Table 1 Screening of Brønsted acids and optimization of stoichiometry and reaction conditions[a]

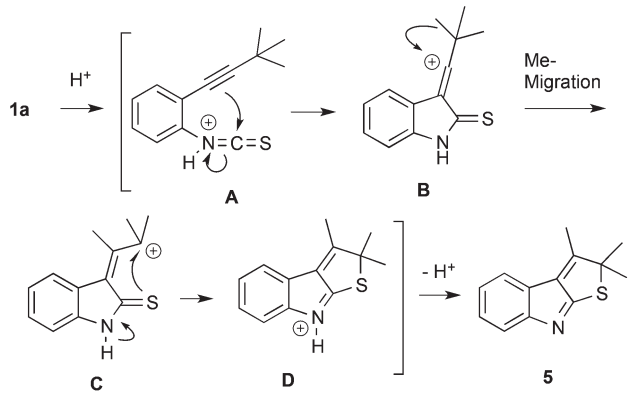


Entry	Acid (equiv.)	Solvent	Temp./°C	Time	Yield[b,c]/%
1	TfOH (1.0)	CH_2Cl_2	0	24 h	48 (27)
2	TfOH (2.0)	CH_2Cl_2	0	10 min	69 (6)
3	TfOH (3.0)	CH_2Cl_2	0	10 min	78
4	TfOH (4.0)	CH_2Cl_2	0	10 min	78
5	TfOH (3.0)	CH_2Cl_2	rt	10 min	69
6	TfOH (3.0)	CH_2Cl_2	−40	10 min	54 (17)
7	TfOH (3.0)	Dioxane	0	10 min	NR (*ca.* 100)
8	TfOH (3.0)	THF	0	10 min	NR (90)
9	TfOH (3.0)	$ClCH_2CH_2Cl$	0	10 min	70
10	TfOH (3.0)	$MeNO_2$	0	10 h	54
11	H_2SO_4 (3.0)	CH_2Cl_2	0	10 min	NR (*ca.* 100)
12	HCl (3.0)	CH_2Cl_2	0	10 min	NR (*ca.* 100)
13	TsOH–H_2O (3.0)	CH_2Cl_2	0	10 min	NR (96)
14	TFA (3.0)	CH_2Cl_2	0	10 min	NR (91)
15	Tf_2NH (3.0)	CH_2Cl_2	0	10 min	7 (80)

[a] Each reaction was performed such that a solution of **1a** was added dropwise to a solution of triflic acid or the other acids because when triflic acid was added to a solution of **1a**, **1a** partially deteriorated and/or dimerized leading to a decreased yield of **5**. [b] Isolated yield. [c] NR: no reaction; no trace of **5** was detected by TLC. In parentheses, yield of the recovered starting material **1a**.



Scheme 3 Preparation of 2-(alkyn-1-yl)phenyl isothiocyanates **1** and isocyanates **4**. *Reagents and conditions*: (i) PPh_3 (1.2 equiv.), C_2Cl_6 (1.2 equiv.), Et_3N (2.4 equiv.), CH_2Cl_2, rt, 4 h; (ii) CS_2, rt, 12 h; (iii) triphosgene (0.37–1.1 equiv.), Et_3N (2.0 equiv.), toluene, 0 °C → rt.

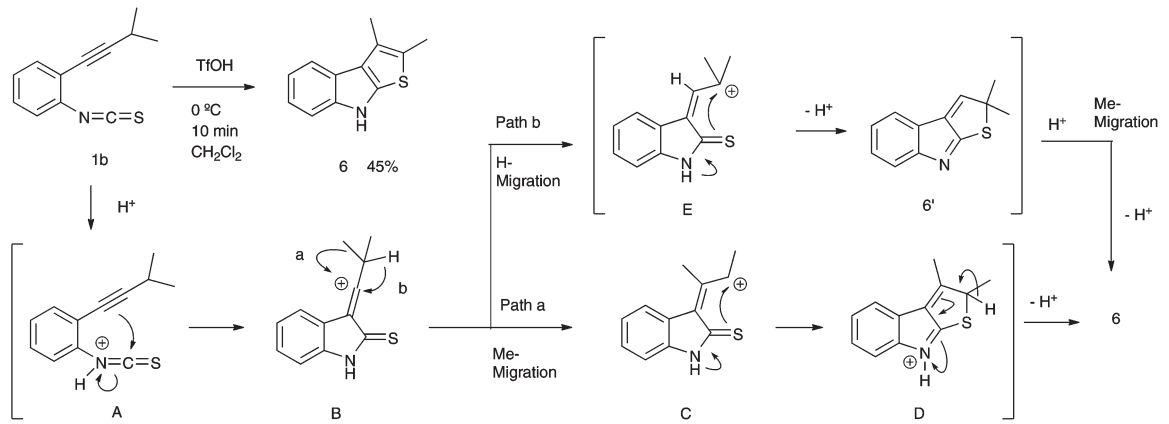


Scheme 4 A possible reaction pathway *via* rearrangement leading to thieno-indole **5**.

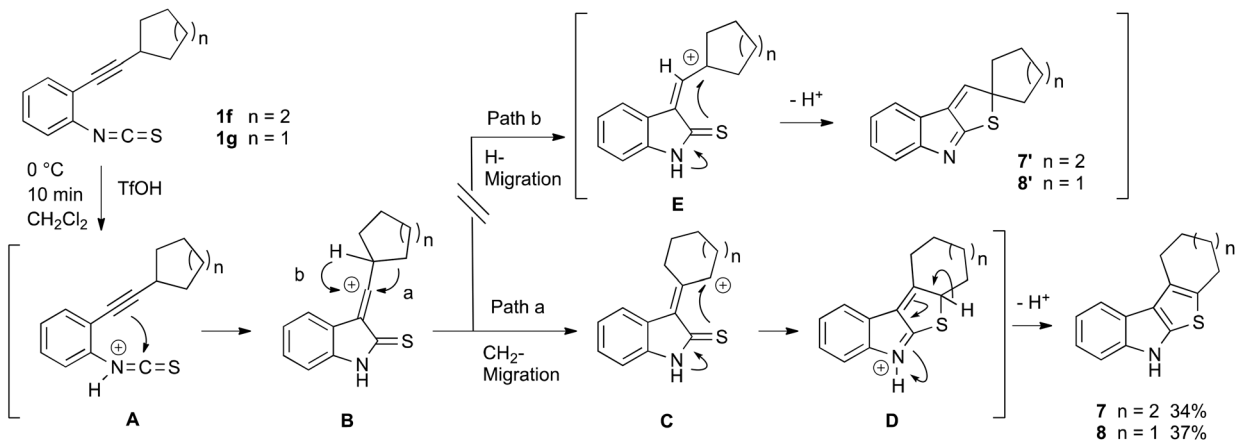
by the inner acetylenic π-bond in a 5-*endo-dig* mode[7,8] give cation **B**. Anionotropic rearrangement of the methyl group in **B** affords the allylic cation intermediate **C**, followed by the nucleophilic cyclization and deprotonation from **D** to produce 2,2,3-trimethyl-2*H*-thieno[2,3-*b*]indole (**5**) as the final product.

We next conducted the reaction of **1b–1l** with a variety of substituents R on the ethyne carbon to determine the scope and limitations of this type of reaction. The reaction of **1b** containing a noncyclic secondary substituent of R = *i*-Pr under optimal reaction conditions produced 2,3-dimethyl-8*H*-thieno-[2,3-*b*]indole (**6**) in 45% yield (Scheme 5). Similar to the reaction pathway illustrated in Scheme 4, protonation of **1b**, 5-*endo-dig*-mode cyclization of **A** and rearrangement of the methyl group at the key intermediate **B** (Path a) occurred to afford **C**. The nucleophilic cyclization of **C** and deprotonation from **D** gave the thieno[2,3-*b*]indole **6**. Alternatively, the formation of 2,2-dimethyl-2*H*-thieno[2,3-*b*]indole (**6′**) from the cation **B** *via* hydrogen migration (Path b) occurred, and the post-migration of the methyl group in **6′** gave **6**.[14a]

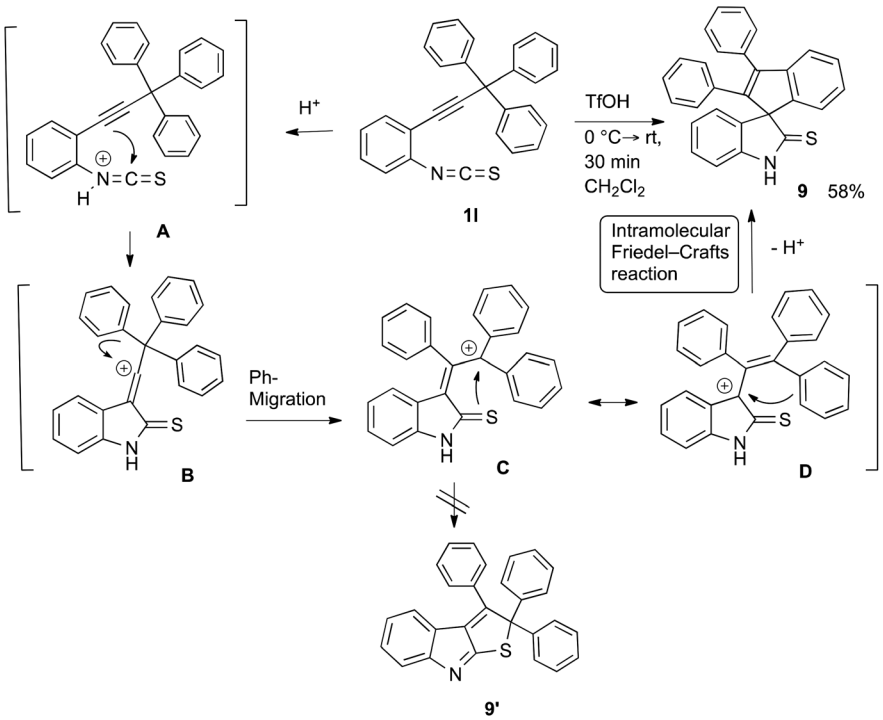
The reactions of isothiocyanates **1c–1e** and **1h–1k** with various substituents in R failed; intractable product mixtures were formed. However, isothiocyanates **1f** and **1g** having a cyclic secondary substituent [R = *c*-Hex (*n* = 2) and *c*-Pent (*n* = 1)] produced the ring-expanded cycloalkane-fused 8*H*-thieno[2,3-*b*]indoles **7** and **8** in 34% and 37% yields, respectively (Scheme 6). At the cation **B**, the methylene group of the cycloalkane (Path a) should rearrange (**B** → **C**) leading to



Scheme 5 Possible reaction pathways *via* rearrangement leading to thieno-indoles **6**/**6′**.



Scheme 6 Possible reaction pathways *via* rearrangement leading to thieno-indoles **7** and **8**/**7′** and **8′**.



Scheme 7 Possible reaction pathways *via* rearrangement leading to indoles **9**/**9′**.

compounds **7** and **8** *via* the cyclization (**C** → **D**) with deprotonation. Possible spiro-thieno[2,3-*b*]indole products **7′** and **8′** *via* a hydrogen migration (Path b) were not detected.

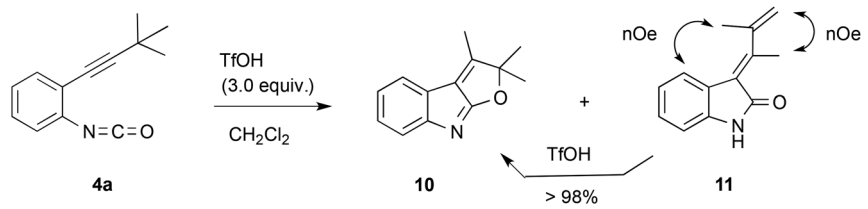
In the present cycloisomerization of the *o*-alkynylphenyl isothiocyanate **1**, a tertiary or a secondary substituent R on the acetylenic terminal seems to be necessary for the rearrangement in which its branching alkyl substituent migrates successfully onto the alkylidene sp^2-carbocation in **B** to form the target thieno[2,3-*b*]indole derivative (Schemes 4–6). Therefore, we next conducted the reaction of isothiocyanate **1l** having a trityl substituent with high migrating ability (Scheme 7). However, the expected thieno[2,3-*b*]indole **9′** was not formed. Instead, the spiro-indolethione **9** was obtained in good yield (58%). In the second cyclization step after the migration of the phenyl group (**B** → **C**/**D**), the intramolecular Friedel–Crafts-type reaction[15] of **D** must take place at the *ortho* position of the proximal benzene ring (**D** → **9**) in preference to the thiophene ring-forming cyclization (**C** → **9′**). The structure of **9** was established unambiguously by X-ray crystallographic analysis (Fig. 1).[16]

Fig. 1 Molecular structure for compound **9** as an ORTEP plot. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability levels.

2.3. Triflic acid-promoted reaction of 2-(alkyn-1-yl)phenyl isocyanates (4)

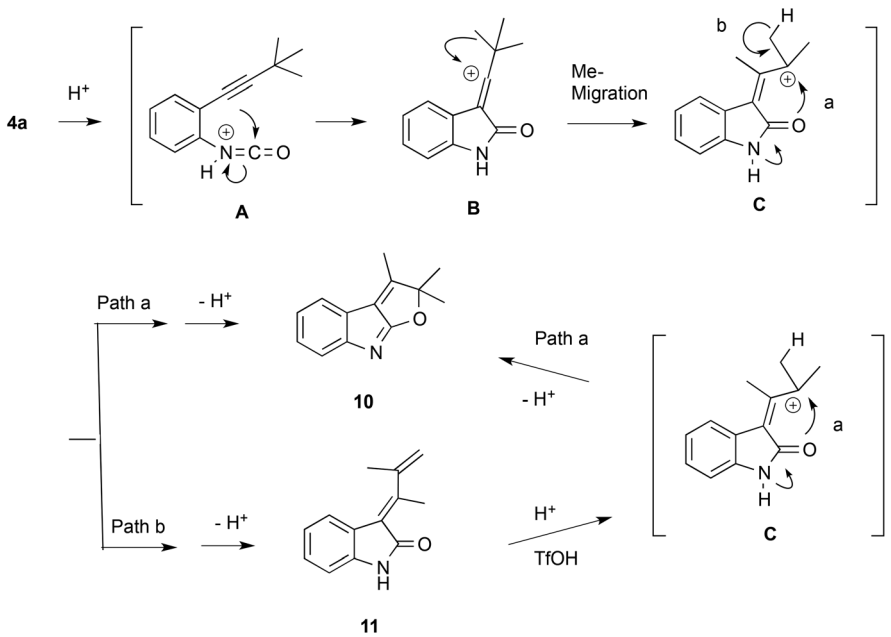
When isocyanate **4a** (R = *t*-Bu) was similarly treated with triflic acid (3.0 equiv.) at 0 °C for 10 min in dichloromethane, 2,2,3-trimethylfuro[2,3-*b*]indole (**10**) was obtained in 85% yield together with 3-(prop-3-en-2-ylidene)oxindole (**11**) in 9% yield (Scheme 8). The same reaction in one pot from **4a** for 25 h afforded furo[2,3-*b*]indole **10** in 99% yield. When the isolated oxindole **11** was treated with triflic acid (3.0 equiv.) under the conditions of 0 °C → rt for 25 h in dichloromethane, the furo-[2,3-*b*]indole **10** was obtained quantitatively. The *E* geometry of **11** was determined by nOe using ^{1}H NMR spectroscopy.

A possible reaction pathway is illustrated in Scheme 9. Protonation of **4a** and 5-*endo*-*dig*-mode cyclization of **A**, and subsequent methyl group migration at **B** give the allylic cation intermediate **C**. The following nucleophilic cyclization by O-attack with deprotonation *via* Path a produces 2,2,3-trimethyl-2*H*-furo[2,3-*b*]indole (**10**) as the major product. This process is very similar to the reaction of the corresponding isothiocyanate **1a** leading to the exclusive formation of 2,2,3-trimethyl-2*H*-thieno[2,3-*b*]indole (**5**) (see Scheme 4). An alternative, Path b, with deprotonation from the methyl group of the intermediate **C** occurs at a lower temperature of 0 °C to give oxindole **11** as the minor product. The fact that transform-



Entry	Conditions	Yield (%) 10	11
1	0 °C, 10 min	85	9
2	0 °C → rt, 25 h	99	0

Scheme 8 Triflic acid-promoted cycloisomerization of **4a** to produce indoles **10** and **11**.



Scheme 9 Possible reaction pathways *via* rearrangement leading to indoles **10** and **11**.

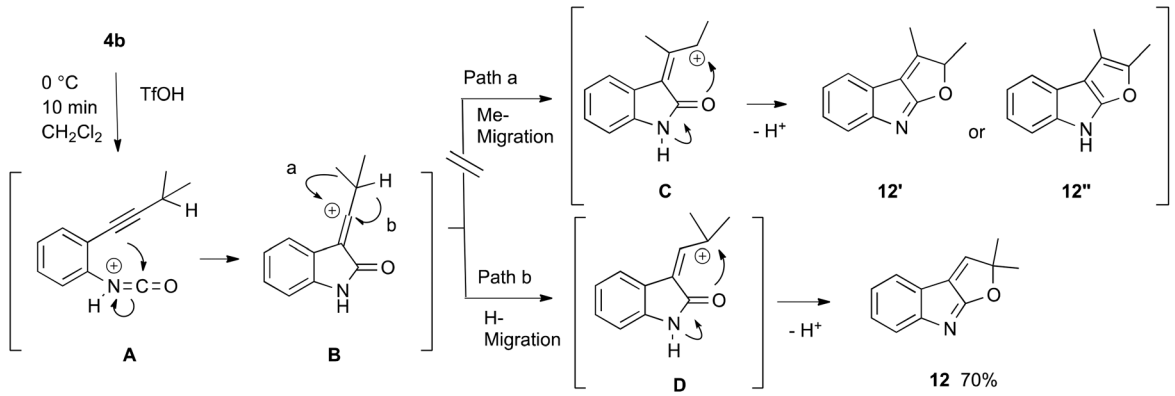
ation of **11** to **10** proceeds exclusively at a higher temperature (rt) in the presence of triflic acid suggests that this reaction is thermodynamically controlled *via* the intermediate **C**.

The reaction of isocyanate **4b** (R = *i*-Pr) under the optimal reaction conditions [TfOH (3.0 equiv.) at 0 °C for 10 min in CH_2Cl_2] afforded the furo[2,3-*b*]indole **12** in 70% yield (Scheme 10). This compound **12** can be formed by H-migration from the cation **B** *via* Path b, and cyclization of **D**. Neither the Me-migrated product **12′** nor **12″** was obtained. The selectivity of the migrating group (H) of **4b** is in contrast to that (Me) of the corresponding isothiocyanate **1b** (R = *i*-Pr) (Scheme 5).[14b]

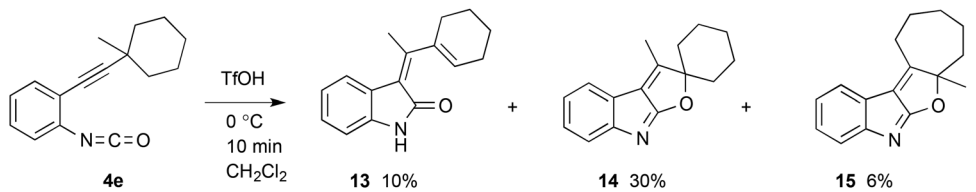
From the reaction of isocyanate **4e** (R = 1-methyl-1-cyclohexyl) under the optimal reaction conditions, three indole derivatives **13**, **14**, and **15** were obtained in 10%, 30%, and 6% yields, respectively (Scheme 11). As shown in Scheme 12, the protonated cationic intermediate **A** cyclizes to give the intermediate **B**, from which the methyl group migration (Path a) and following deprotonation *via* Path c produces 3-methylene-oxindole **13**, while the O-attack cyclization at **C** *via* Path d produces spiro-furo[2,3-*b*]indole **14**.

Alternatively, rearrangement of the methylene group at **B** *via* Path b formed the ring-expanded oxindole intermediate **D**, which gave furo-indole **15** *via* Path f. Probable compound **16** was not obtained, but the formation of **15** from **16** is possible.

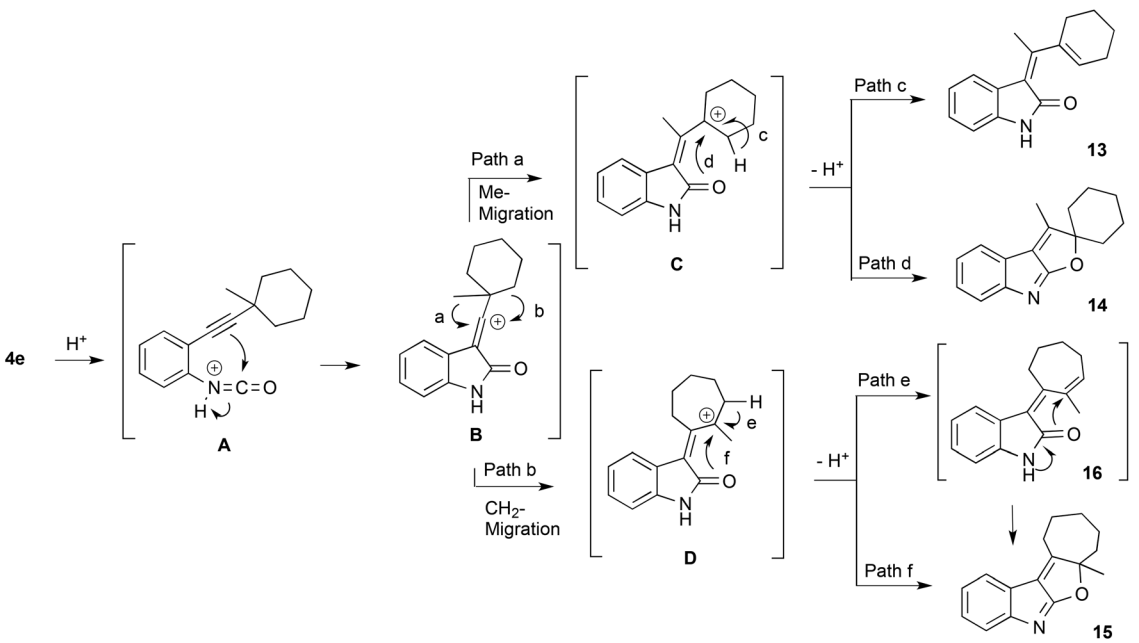
When the reaction of *o*-(cyclohexylethynyl)phenyl isocyanate (**4f**) was conducted under optimal conditions, (1-cyclohexenylmethylene)oxindole **17** (*Z*) and allenyloxindole **18**, which were probably formed *via* Path b with H-migration and deprotonation, were obtained in 26% and 20% yields, respectively (Scheme 13, entry 1). Neither the ring-expanded compound **19** nor **20** was formed. The reaction of **4f** at a lower temperature of −40 °C or −78 °C for 10 min gave the allenic oxindole **18** as a sole product (entries 2 and 3). When the reaction was conducted at −78 °C for 10 min, followed by standing at room temperature for a day, 3-methylene-oxindoles **17** (*E*) and **17** (*Z*) were obtained in 27% and 67% yields, respectively, in place of



Scheme 10 Possible reaction pathways *via* rearrangement leading to indoles **12**/**12′** or **12″**.



Scheme 11 Triflic acid-promoted cycloisomerization of **4e** to produce indoles **13**, **14** and **15**.

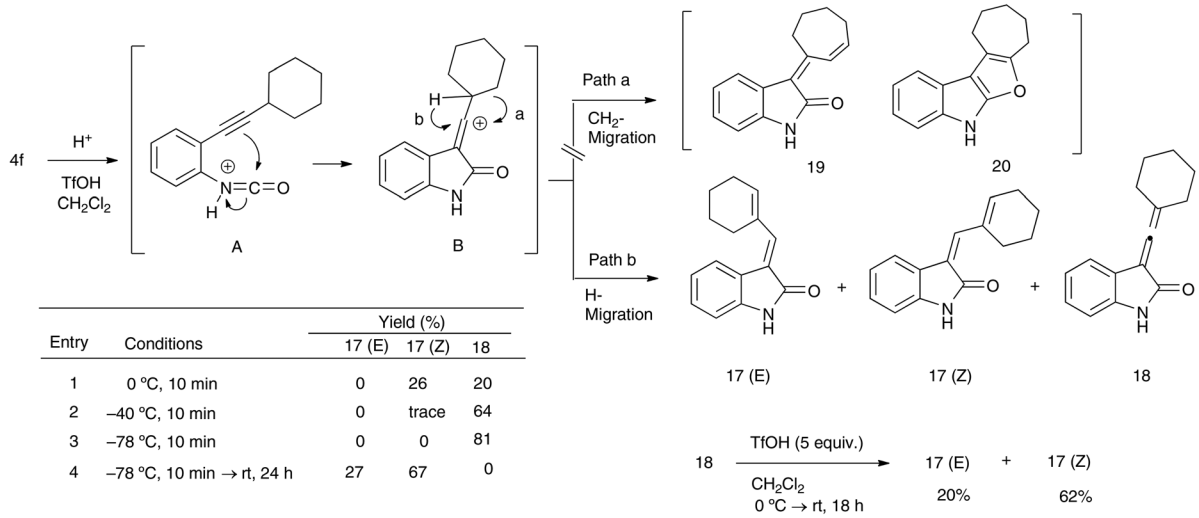


Scheme 12 Possible reaction pathways *via* rearrangement leading to indoles **13**, **14**, and **15**.

18 (entry 4). The isolated allene **18** was isomerized by treating it with TfOH to give **17** (*E*) and **17** (*Z*) in 20% and 62% yields, respectively.

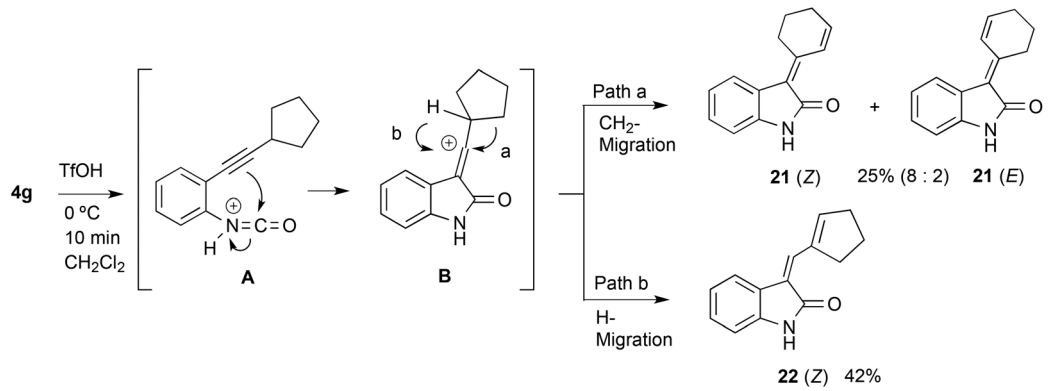
In contrast to the above reaction (Scheme 13), the ring-expanded product **21** (25%, $Z:E$ = 8 : 2) and the H-migrated product **22** (*Z*) (42%) were both obtained in the reaction of **4g** under optimal reaction conditions (Scheme 14). The structure of **22** (*Z*) was established unambiguously by X-ray crystallographic analysis (Fig. 2).[17] The reaction at a lower temperature of −40 °C or −78 °C for 10 min did not give the allenic oxindole of the cyclopentylidene analogue corresponding to **18**.

In the reaction of *o*-(cyclopropylethynyl)phenyl isocyanate (**4h**), only the geometrically pure *cis*-oxindole **23** was isolated as an identified product in 12% yield (Scheme 15). The cyclization (**A** → **B**) and cyclopropane ring-expansion by the methylene rearrangement formed the cation **C**.[10a–c] Subsequent



Entry	Conditions	Yield (%) 17 (E)	17 (Z)	18
1	0 °C, 10 min	0	26	20
2	–40 °C, 10 min	0	trace	64
3	–78 °C, 10 min	0	0	81
4	–78 °C, 10 min → rt, 24 h	27	67	0

Scheme 13 Possible reaction pathways *via* rearrangement leading to indoles **17** and **18**/**19** and **20**.



Scheme 14 Possible reaction pathways *via* rearrangement leading to indoles **21** and **22**.

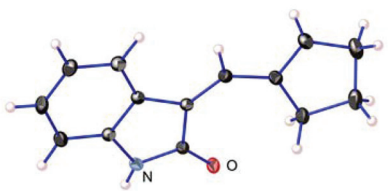
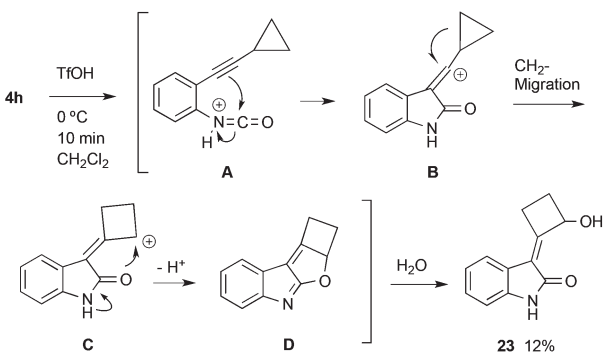


Fig. 2 Molecular structure for compound **22** as an ORTEP plot. Thermal ellipsoids are shown at 30% probability levels.



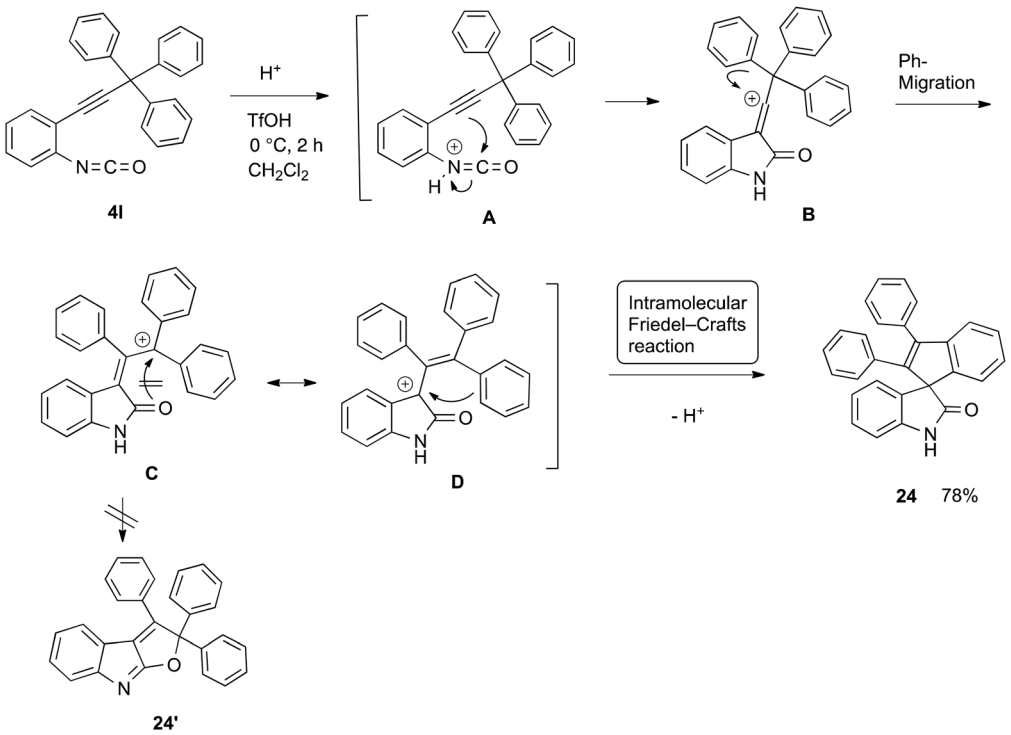
Scheme 15 A possible reaction pathway *via* rearrangement leading to indole **23**.

cyclization of **C** and hydrolysis of the formed cyclobuta-furo-fused oxindole **D** gave **23**. This pathway is consistent with the observation that *cis*-compound **23** was formed during purification/isolation by silica gel chromatography.

In the reaction of trityl-substituted isocyanate **4l** the spiro-oxindole **24** was obtained in 78% yield, no formation of triphenylfuro[2,3-*b*]indole **24′** was observed (Scheme 16). The pathway is very similar to the reaction of the corresponding isothiocyanate **1l** (Scheme 7).

3. Conclusions

In conclusion, we have developed a new and unique, metal-free approach to the synthesis of structurally diverse types of indole derivatives such as thieno- and furo-indoles, spiro-indo-



Scheme 16 Possible reaction pathways *via* rearrangement leading to indoles **24**/**24'**.

lethiones, spiro-oxindoles, and 3-alkylidene-oxindoles. The methodology involves triflic acid-promoted cycloisomerization with anionotropic rearrangement of a substituent or hydrogen in R of 2-(alkyn-1-yl)phenyl isothiocyanates and isocyanates, although, as anticipated, the substituents R are limited to those having rich migrating ability.

4. Experimental

4.1. Typical procedure for reaction of 2-(alkyn-1-yl)phenyl isothiocyanates 1

In an oven-dried flask equipped with a septum and a magnetic stirring bar, trifluoromethanesulfonic acid (123.7 μL, 1.41 mmol) was dissolved in dry dichloromethane (3 mL) and the solution was cooled to 0 °C under an argon atmosphere. Then, a solution of isothiocyanate **1a** (101.2 mg, 0.470 mmol) in dichloromethane (3 mL) was slowly added through a syringe and the mixture was stirred at 0 °C for 10 min. The reaction was quenched with saturated aq. $NaHCO_3$ solution and the reaction mixture was extracted with dichloromethane (3 mL × 3) and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel with hexane–ethyl acetate (4 : 1) as an eluant to give thienoindole **5** (79 mg, 78%).

4.1.1. 2,2,3-Trimethyl-2*H*-thieno[2,3-*b*]indole (5). Pale yellow oil; IR (neat): 3401.8, 2969.8, 1666.2 cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.59 (s, 6H), 2.19 (s, 3H), 7.04 (dd, J = 7.1, 7.3 Hz, 1H), 7.26 (dd, J = 7.1, 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 11.99 (CH_3), 26.5 ($2CH_3$), 72.2 (C), 117.8 (CH), 121.6 (CH), 122.1 (CH), 125.6 (C), 128.3 (CH), 137.9 (C), 158.3 (C), 162.7 (C), 180.0 (C); HRMS–ESI (m/z): $[M + H]^+$ calcd for $C_{13}H_{14}NS$: 216.0841, found: 216.0834.

4.1.2. 2,3-Dimethyl-8*H*-thieno[2,3-*b*]indole (6). Colorless solid; mp 159.7–161.2 °C; IR (KBr): 1635.3, 2908 cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$): δ 1.72 (s, 3H), 2.22 (s, 3H), 6.43 (d, J = 7.9 Hz, 1H), 6.84 (dd, J = 7.3, 7.9 Hz, 1H), 7.06 (dd, J = 7.3, 7.6, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.40–7.46 (br. s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 22.5 (CH_3), 23.3 (CH_3), 110.2 (CH), 114.0 (C), 115.9 (CH), 117.1 (C), 120.2 (CH), 121.6 (CH), 128.3 (C), 129.4 (C), 135.6 (C), 140.4 (C); Anal. calcd for $C_{12}H_{11}NS$: C 71.60, H 5.51, N 6.96, found: C 71.38, H 5.89, N 7.31.

4.2. Typical procedure for reaction of 2-(alkyn-1-yl)phenyl isocyanates 4

In an oven-dried flask equipped with a septum and a magnetic stirring bar, trifluoromethanesulfonic acid (134.3 μL, 1.53 mmol) was dissolved in dry dichloromethane (3 mL) and the solution was cooled to 0 °C under an argon atmosphere. A solution of isocyanate **4a** (102 mg, 0.513 mmol) in dichloromethane (3 mL) was slowly added through a syringe and the mixture was stirred at 0 °C for 10 min. The reaction was continued at room temperature for 25 h and quenched with saturated aq. $NaHCO_3$ solution. The reaction mixture was extracted with dichloromethane (3 mL × 3) and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel with hexane–ethyl acetate (4 : 1) as an eluant to give furoindole **10** (101 mg, 99%) as pale yellow needles (crystallized from CH_2Cl_2–hexane).

When the reaction at 0 °C was quenched after 10 min, furoindole **10** (86.7 mg, 85%) and oxindole **11** (9.2 mg, 9%) were obtained.

4.2.1. 2,2,3-Trimethyl-2*H*-furo[2,3-*b*]indole (10). Pale yellow needles; mp 262–264 °C; IR (KBr): 3448, 2854, 1666, 1435, 748 cm^{-1}; ^1H NMR (300.4 MHz, $CDCl_3$): δ 1.54 (s, 6H), 2.22 (s, 3H), 7.02 (dd, J = 7.4, 7.5 Hz, 1H), 7.27 (dd, J = 7.5, 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.0 (CH_3), 23.8 ($2CH_3$), 103.1 (C), 118.5 (CH), 121.7 (CH), 122.4 (CH), 122.7 (C), 127.5 (C), 129.1 (CH), 155.0 (C), 162.4 (C), 181.4 (C); HRMS–ESI (m/z): $[M + H]^+$ calcd for $C_{13}H_{14}NO$: 200.1070, found: 200.1062.

4.2.2. (*E*)-3-(3-Methylbut-3-en-2-ylidene)-1,3-dihydroindol-2-one (11). Yellow solid; mp 115.9–117.0 °C; IR (KBr): 3185.8, 3085.6, 2923.6, 1689.3, 1612.2 cm^{-1}; ^1H NMR (600.1 MHz, $CDCl_3$): δ 2.04 (dd, J = 1.4, 1.4 Hz, 3H), 2.59 (s, 3H), 4.67 (dq, J = 1.0, 1.4 Hz, 1H), 5.15 (dq, J = 1.0, 1.4 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.92 (dd, J = 7.7, 7.8 Hz, 1H), 7.16 (dd, J = 7.7, 7.8 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 8.15–8.23 (br. s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 20.45 (CH_3), 20.48 (CH_3), 109.2 (CH), 113.0 (CH_2), 121.1 (C), 121.5 (CH), 123.1 (C), 123.5 (CH), 128.0 (CH), 139.4 (C), 146.7 (C), 157.8 (C), 168.0 (C); HRMS–ESI (m/z): $[M + Na]^+$ calcd for $C_{13}H_{13}NNaO$: 222.0889, found: 222.0886.

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