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A NEW METHOD FOR THE PREPARATION OF NITROGEN-CONTAINING HETEROCYCLES USING DIPHENYLSULFONIUM TRIFLATES

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Abstract – Various nitrogen heterocycles were produced by the reactions of ω-bromoalkyldiphenylsulfonium or diphenylvinylsulfonium triflates with nitrogen nucleophiles. Further, the reactions of diphenylstyrylsulfonium triflates with *N*-metalated phthalimide and imidazoles afforded α-phthalimidostyrenes and α-(imidazol-1-yl)styrenes in good yields, respectively.

INTRODUCTION

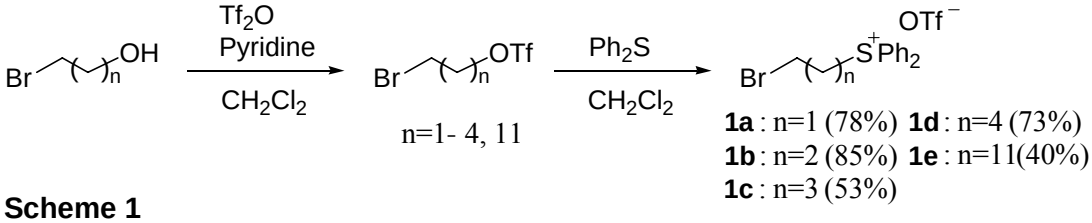
Nitrogen-containing heterocycles are often found in a wide variety of biologically active natural and synthetic compounds,[1] and are used as versatile synthetic intermediates to prepare various nitrogen-containing organic compounds. For example, activated aziridines react with nucleophiles to give ring-opening products with high regio- and stereoselectivities.[2] Further, they are also employed as useful chiral auxiliaries and ligands for the asymmetric synthesis.[3] Therefore, many preparative methods for nitrogen heterocycles have been developed.[4]

Heterocyclization reactions using sulfonium salts, which date back to work by Corey *et al*.,[5] usually proceed *via* sulfonium ylides generated from the sulfonium salts.[6] However, there are few examples of direct applications of the sulfonium salts for the synthesis of nitrogen heterocycles.

Recent work in our laboratory has revealed that a diphenylsulfonio group, unlike a dimethylsulfonio one, worked quite effectively as both an activating group for nucleophilic additions and a leaving group in the syntheses of 2-arylaziridines,[7a,d] allylamines,[7b,d] and α-imidostyrenes.[7c,d] In this paper, we would like to

describe a new synthetic approach to nitrogen-containing heterocycles by utilizing diphenylsulfonium triflates.

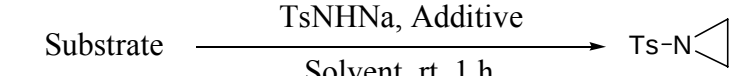
RESULTS AND DISCUSSION



Scheme 1

In the first place, the synthesis of *N*-tosylazacycloalkanes by the reaction of *ω*-bromoalkyldiphenylsulfonium salts with the sodium salt of *p*-toluenesulfonamide (TsNHNa) was examined. *ω*-Bromoalkyldiphenylsulfonium triflates (**1a**−**e**) (n = 1−4, 11) were synthesized in 40−85% yields from the corresponding *ω*-bromoalkanols *via* *ω*-bromoalkyl triflates (Scheme 1).

Table 1. Synthesis of *N*-tosylaziridine.

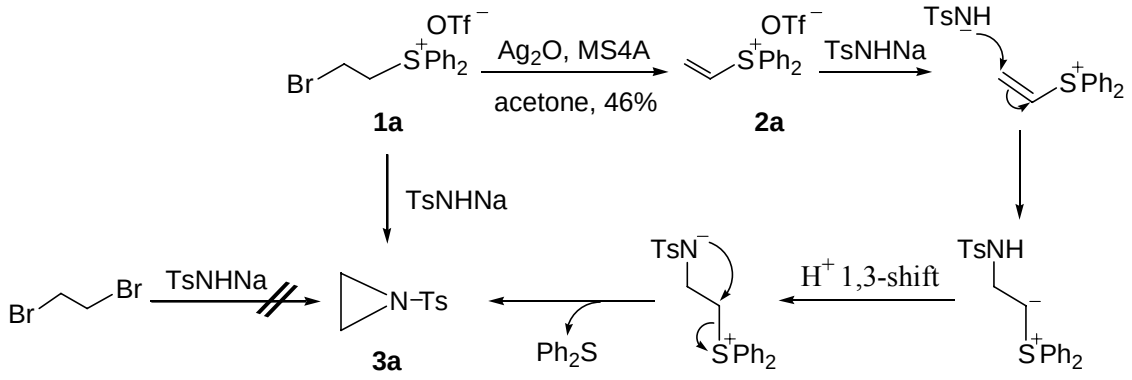


3a

Entry	Substrate	TsNHNa[a] / equiv	Solvent	Additive (equiv)	Yield[b] / %
1[c]		1.2	DMF	none	27
2		2.0	DMF	none	75
3	Br S+Ph2 OTf− **1a**	2.0	DMF	KI (1)	87
4		2.0	DMF	KI (0.1)	87
5		2.0	THF	KI (0.1)	76
6		2.0	DMSO	KI (1)	79
7	Br Br	2.0	DMF	KI (0.1)	0
8		2.0	DMF	*t*-BuOK (1)	0
9	S+Ph2 OTf− **2a**	1.2	THF	none	93

[a]Sodium hydride was employed to prepare TsNHNa. [b]Isolated yield. [c]Reaction time was 3 h. *N*,*N*-Bis(2-bromoethyl)-*p*-toluenesulfonamide was also obtained in 27% yield.

2-Bromoethyldiphenylsulfonium triflate (**1a**)[8] reacted with TsNHNa to afford *N*-tosylaziridine (**3a**) (Table 1). When 1.2 equiv. of TsNHNa was used, **3a** was obtained in 27% yield along with *N*,*N*-bis(2-bromoethyl)-*p*-toluenesulfonamide (27%) (Entry 1). Slow charge of **1a** in this reaction had no effect on the reaction outcome, whereas treatment of **1a** with 2 equiv. of TsNHNa resulted in reducing greatly the by-product formation and increasing the yield of **3a** up to 75% (Entry 2). Moreover, the aziridination in the presence of a catalytic amount of KI afforded **3a** in 87% yield (Entry 4), and DMF gave the best result among the solvents examined (Entries 4−6). By contrast, 1,2-dibromoethane (Entries 7, 8) or 1,2-diiodoethane disappeared immediately under the reaction conditions but did not give **3a** even in the presence of a strong base such as *t*-BuOK. On the other hand, diphenylvinylsulfonium triflate (**2a**),[8] prepared by the elimination of HBr from **1a** using silver(I) oxide, reacted with 1.2 equiv. of TsNHNa to produce **3a** in high yield (Entry 9). These results indicated that this aziridination proceeded *via* the vinylsulfonium intermediate (**2a**) rather than *N*-(2-bromoethyl)-*p*-toluenesulfonamide (Scheme 2).

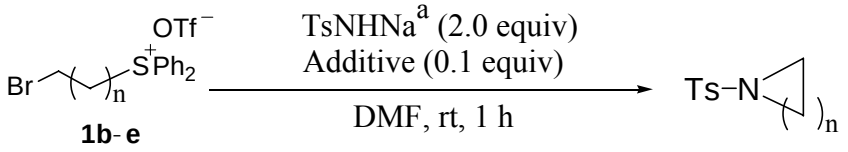


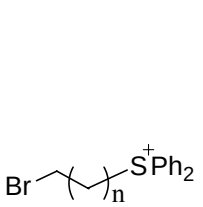
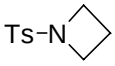
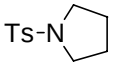
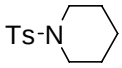
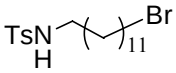
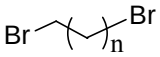
Scheme 2

The results of the reactions between *ω*-bromoalkyldiphenylsulfonium triflates (**1b**−**e**) or dibromoalkanes and TsNHNa are summarized in Table 2. The sulfonium salts (**1c**,**d**) produced *N*-tosylpyrrolidine (**5**) (Entry 2) and *N*-tosylpiperidine (**6**) (Entry 3) rather efficiently compared with 1,4-dibromobutane (Entry 6) and 1,5-dibromopentane (Entry 7), respectively. Unexpectedly, *N*-tosylazetidine (**4**) was obtained from **1b** in low yield (Entry 1), and incomplete consumption of **1b** was observed even after heating the reaction mixture at 100 °C or adding $AgClO_4$ or a base such as *t*-BuOK. The reaction of **1e** with TsNHNa did not give the desired 13-membered azacycloalkane but gave **7** (Entry 4) even when a base such as *t*-BuOK was used. In all cases shown in Table 2, the addition of a catalytic amount of KI had little or no effect on the formation of azacycloalkanes unlike the aziridination.

Next, the reactions of *ω*-bromoalkyldiphenylsulfonium triflates (**1**) or diphenylvinylsulfonium triflates (**2**) with various nitrogen nucleophiles were examined (Table 3). *N*-Tosylaziridines (**3b**,**c**) were obtained by the reaction of diphenylvinylsulfonium triflates (**2b**,**c**) with TsNHNa (Entries 1, 2). The sulfonium salt

Table 2. Synthesis of *N*-tosylazacycloalkanes.



Entry	Substrate		n	Additive	Product		Yield[b] / %
1[c]		**1b**	2	KI		**4**	10
2		**1c**	3	none		**5**	84
3		**1d**	4	none		**6**	79
4		**1e**	11	none		**7**	41
5			2	none	**4**		47
6			3	none	**5**		70
7			4	none	**6**		68
8			11	none	**7**		32

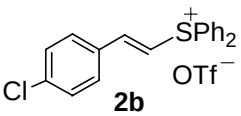
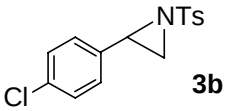
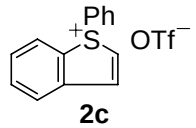
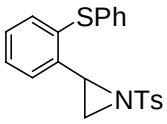
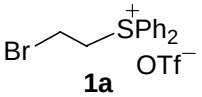
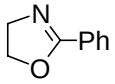
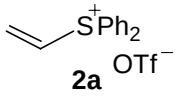
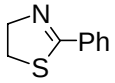
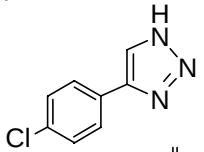
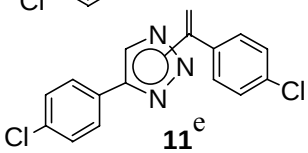
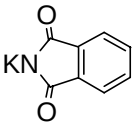
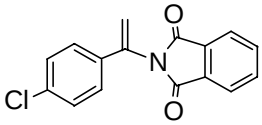
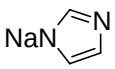
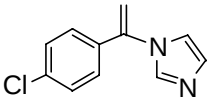
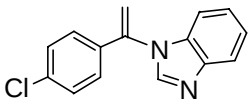
[a]Sodium hydride was employed to prepare TsNHNa. [b]Isolated yield. [c]Reaction was carried out at 100 °C for 3 h.

(**1a**) reacted with the sodium salts of benzamide and thiobenzamide to afford 2-phenyl-2-oxazoline (**8**) and 2-phenyl-2-thiazoline (**9**), respectively (Entries 3, 5). 1,2-Dihaloethane did not give these heterocycles under the same conditions,[9] whereas diphenylvinylsulfonium triflate (**2a**) gave **8** and **9** (Entries 4, 6), indicating that **2a** was a possible intermediate of these heterocyclizations just as the aziridination (**1a** to **3a**). Further, 4-(4-chlorophenyl)-1*H*-1,2,3-triazole (**10**) was produced by the reaction of **2b** with sodium azide (Entry 7). The formation of the by-product (**11**) in this reaction led our attention turn to study on the selective introduction of amino functions into the α-position of styrenes by the reaction of diphenylstyrylsulfonium salts with aprotic nitrogen nucleophiles ($RR'N^-$) that can not lead to formation of 2-arylaziridines.[7a,d] As we expected, α-phthalimidostyrene (**12**) and α-(imidazol-1-yl)styrenes (**13**, **14**) were obtained in high yields by the reaction of **2b** with *N*-metalated phthalimide or imidazoles (Entries 8−10).

In conclusion, it was noted that ω-bromoalkyldiphenylsulfonium triflates (**1**) and diphenylvinylsulfonium triflates (**2**) reacted with nitrogen nucleophiles to give 3- to 6-membered azacycloalkanes and several unsaturated nitrogen heterocycles. When 2-bromoethyldiphenylsulfonium triflate (**1a**) was used, aziridine, oxazoline, and thiazoline rings were formed probably *via* diphenylvinylsulfonium triflate (**2a**). Further,

the selective introduction of phthalimido and imidazol-1-yl groups into the α-position of styrenes was successfully carried out by the reactions of diphenylstyrylsulfonium triflates with *N*-metalated phthalimide and imidazoles, respectively.

Table 3. Reactions of sulfonium salts with various nitrogen nucleophiles.

Entry	Sulfonium salt	Nucleophile[a] (equiv)	Conditions	Product	Yield[b] / %
1	 **2b**	TsNHNa (1.2)	/ THF, rt, 19 h	 **3b**	91
2	 **2c**	TsNHNa (1.2)	/ THF, rt, 24 h	 **3c**	40
3	 **1a**	PhCONHNa[c] (2)	KI (0.1) / DMSO rt, 2 h	 **8**	26 (38[d])
4	 **2a**	PhCONHNa[c] (1.2)	/ DMSO, rt, 2 h		24 (45[d])
5	**1a**	PhCSNHNa (2)	KI (0.1) / DMF 50 °C, 0.5 h	 **9**	65
6	**2a**	PhCSNHNa (1.2)	/ DMF 50 °C, 0.5 h		43
7	**2b**	NaN_3 (2)	/ DMSO 120 °C, 0.5 h	 **10**	47
				 **11**[e]	25
8	**2b**	 (1.1)	/ DMSO rt, 12 h	 **12**	90
9	**2b**	 (1.3)	/ DMSO rt, 0.5 h	 **13**	80
10	**2b**	 (1.5)	/ DMSO rt, 1 h	 **14**	92

[a]Sodium hydride was employed to prepare the sodium salt unless otherwise noted. [b]Isolated yield. [c]Sodium hydroxide was used to prepare PhCONHNa. [d]Determined by ^{1}H NMR spectral analysis using Ph_3CH as an internal standard. [e]Substituted nitrogen position was not determined.

EXPERIMENTAL

Melting points were measured on a micro melting point apparatus (Yanaco MP-S3) and were not corrected. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer (KBr or neat) or a Thermo Electron Nicolet Avatar 370 spectrometer (ATR). ^{1}H NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz) spectrometer. Chemical shifts (δ_H) in $CDCl_3$ are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts (δ_C) in $CDCl_3$ are reported in ppm relative to TMS using the solvent resonance ($CDCl_3$: δ_C 77.0 ppm) as an internal standard. In the case of DMSO-d_6, the solvent peak was set to 2.49 ppm (^{1}H) and 39.50 ppm (^{13}C), respectively. MS spectra (LC−MS) were recorded on a Thermo Electron Navigator mass spectrometer with an Agilent Technologies HP-1100 Series. HRMS spectra were recorded on a JEOL LCmate, a JEOL JMS-T100LC, or an Applied Biosystems Mariner (ESI-TOF) mass spectrometer. Analytical TLC was performed on Merck TLC plates coated with silica gel (60 F_{254}, 0.25 mm). Silica gel column chromatography was performed on Merck Silica gel 60 (0.063−0.200 mm). Preparative TLC was carried out on glass plates coated with silica gel (Wakogel B-5F). All solvents were distilled from appropriate drying agents, and commercially available reagents were used without purification. Unless otherwise noted, reactions were carried out in oven-dried glassware with magnetic stirring under the argon atmosphere.

General procedure for the preparation of *ω*-bromoalkyldiphenylsulfonium triflates (1a−e).[8]

To a stirred solution of pyridine (1.7 mL, 21 mmol) in CH_2Cl_2 (20 mL) was added dropwise triflic anhydride (3.4 mL, 21 mmol) followed by *ω*-bromoalkanol (20 mmol) at –20 °C. After being stirred for 0.5 h, the reaction mixture was warmed to rt and stirred overnight. The reaction mixture was then filtered and the residue was washed with CH_2Cl_2−petroleum ether (1:1). The filtrate was run through a short column with 100 mL of CH_2Cl_2−petroleum ether (1:1). The eluate was then concentrated and the residue was dried in vacuo to give the corresponding *ω*-bromoalkyl triflate as a syrup (68−93%). The mixture of thus obtained *ω*-bromoalkyl triflate (8 mmol) and diphenyl sulfide (1.49 g, 8 mmol) in CH_2Cl_2 (10 mL) was refluxed for 2 days. The reaction mixture was then cooled to rt and concentrated in vacuo. Ether was added to the residue to precipitate the corresponding *ω*-bromoalkyldiphenylsulfonium triflate (**1a−e**) as crystals (40−85% based on *ω*-bromoalkanol).

2-Bromoethyldiphenylsulfonium trifluoromethanesulfonate (1a).[8]

Yield: 78% (2 steps). Off-white crystals, mp 88.5–89.5 °C (ether) (lit.,[8] mp 86.5–88.0 °C). IR (ATR, cm^{-1}) 3066, 2988, 2927, 1479, 1447, 1408, 1253, 1223, 1174, 1145, 1074, 1029, 1000, 928, 847, 753, 745. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.22–7.97 (m, 4H), 7.85–7.58 (m, 6H), 4.87 (t, J = 5.8 Hz, 2H), 3.68 (t, J

= 5.8 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 135.12, 131.72, 130.96, 122.71, 48.22, 23.88. HRMS (APCI$^+$) Calcd for $C_{14}H_{14}BrS^+$: 292.9994. Found: *m*/*z* 293.0001, (APCI$^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: *m*/*z* 148.9518.

3-Bromopropyldiphenylsulfonium trifluoromethanesulfonate (**1b**).

Yield: 85% (2 steps). Colorless crystals, mp 102–103 °C (ether). IR (ATR, cm^{-1}) 3073, 2946, 1583, 1481, 1447, 1343, 1243, 1224, 1152, 1077, 1026, 998, 934, 825, 741. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.13–7.94 (m, 4H), 7.85–7.63 (m, 6H), 4.40 (t, *J* = 7.6 Hz, 2H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.47–2.21 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 134.80, 131.59, 130.51, 123.73, 43.59, 30.00, 27.66. HRMS (APCI$^+$) Calcd for $C_{15}H_{16}BrS^+$: 307.0151. Found: *m*/*z* 307.0162, (APCI$^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: *m*/*z* 148.9519.

4-Bromobutyldiphenylsulfonium trifluoromethanesulfonate (**1c**).

Yield: 53% (2 steps). Slightly yellow crystals, mp 67–68 °C (ether). IR (ATR, cm^{-1}) 3066, 3011, 2949, 1484, 1445, 1256, 1220, 1162, 1074, 1025, 999, 922, 882, 812, 759, 741. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.07–7.95 (m, 4H), 7.79–7.62 (m, 6H), 4.31 (t, *J* = 7.7 Hz, 2H), 3.44 (t, *J* = 6.1 Hz, 2H), 2.21–2.06 (m, 2H), 2.03–1.86 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 134.67, 131.51, 130.56, 124.00, 43.93, 32.51, 30.36, 23.34. HRMS (APCI$^+$) Calcd for $C_{16}H_{18}BrS^+$: 321.0307. Found: *m*/*z* 321.0320, (APCI$^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: *m*/*z* 148.9520.

5-Bromopentyldiphenylsulfonium trifluoromethanesulfonate (**1d**).

Yield: 73% (2 steps). Colorless crystals, mp 63–65 °C (ether). IR (ATR, cm^{-1}) 3067, 3001, 2949, 1482, 1448, 1269, 1252, 1223, 1158, 1075, 1025, 999, 929, 898, 759, 743. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.09–7.91 (m, 4H), 7.80–7.62 (m, 6H), 4.28 (t, *J* = 7.0 Hz, 2H), 3.36 (t, *J* = 6.3 Hz, 2H), 1.95–1.64 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 134.68, 131.54, 130.55, 124.05, 44.94, 33.16, 31.53, 26.40, 23.85. HRMS (APCI$^+$) Calcd for $C_{17}H_{20}BrS^+$: 335.0464. Found: *m*/*z* 335.0470, (APCI$^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: *m*/*z* 148.9518.

12-Bromododecyldiphenylsulfonium trifluoromethanesulfonate (**1e**).

Yield: 40% (2 steps). Colorless crystals, mp 63–63.5 °C (ether). IR (ATR, cm^{-1}) 3064, 3002, 2925, 2854, 1481, 1466, 1448, 1274, 1249, 1224, 1159, 1074, 1026, 998, 926, 758, 743. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.10–7.96 (m, 4H), 7.78–7.61 (m, 6H), 4.22 (t, *J* = 7.5 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.92–1.66 (m, 4H), 1.61–1.47 (m, 2H), 1.47–1.10 (m, 14H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 134.54, 131.47, 130.57, 124.26, 45.13, 34.19, 32.82, 29.40, 29.36, 29.33, 29.11, 28.93, 28.72, 28.15, 28.01, 24.75. HRMS (APCI$^+$) Calcd for $C_{24}H_{34}BrS^+$: 433.1559. Found: *m*/*z* 433.1556, (APCI$^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: *m*/*z* 148.9517.

Preparation of diphenylvinylsulfonium trifluoromethanesulfonate (2a–c).

Diphenylvinylsulfonium trifluoromethanesulfonate (**2a**).[8]

To a stirred solution of **1a** (2.15 g, 4.85 mmol) in acetone (12 mL) was added activated molecular sieves 4A (2.43 g) followed by Ag_2O (843 mg, 3.64 mmol) at rt. The reaction mixture was stirred at rt in the dark for 18 h and then filtered through a Celite pad. The filtrate was concentrated and dried in vacuo to give an orange syrup (2.01 g). To this syrup was added acetone (10 mL) followed by activated molecular sieves 4A (2.25 g) and Ag_2O (525 mg, 2.27 mmol) at rt. The reaction mixture was stirred at rt in the dark for 41 h and then filtered through a Celite pad. The filtrate was concentrated and run through a short column [(1) CH_2Cl_2 followed by acetone, (2) $CHCl_3$]. The eluate was concentrated and dried in vacuo to give **2a** (808 mg, 46%) as a colorless syrup. IR (ATR, cm^{-1}) 3564, 3057, 1580, 1478, 1447, 1388, 1251, 1223, 1149, 1072, 1027, 997, 749. ^1H NMR (270 MHz, $CDCl_3$) δ_H 7.92–7.83 (m, 4H), 7.78–7.62 (m, 6H), 7.51 (dd, J = 15.9, 8.9 Hz, 1H), 6.69 (dd, J = 8.9, 1.9 Hz, 1H), 6.51 (dd, J = 15.9, 1.9 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 137.88, 134.53, 131.51, 130.37, 124.94, 123.08. HRMS ($APCI^+$) Calcd for $C_{14}H_{13}S^+$: 213.0732. Found: m/z 213.0735, ($APCI^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: m/z 148.9520.

[(*E*)-2-(4-Chlorophenyl)vinyl]diphenylsulfonium trifluoromethanesulfonate (**2b**).[7d]

To a stirred solution of diphenyl sulfoxide (2.43 g, 12.0 mmol) in CH_2Cl_2 (40 mL) was added dropwise triflic anhydride (2.0 mL, 12.2 mmol) followed by a solution of 4-chlorostyrene (1.66 g, 12.0 mmol) in CH_2Cl_2 (12 mL) at –78 °C. After being stirred at –78 °C for 10 min, the reaction mixture was gradually warmed up to 0 °C for 50 min and concentrated in vacuo. Ether (10 mL) was added to the residue to give **2b** as colorless crystals (4.61 g, 81%). mp 106–107 °C (ether). IR (KBr, cm^{-1}) 3050, 1595, 1490, 1480, 1445, 1270, 1250, 1220, 1150, 1090, 1035, 1000, 990, 810, 750, 740, 680, 640. ^1H NMR (270 MHz, $CDCl_3$) δ_H 8.00–7.87 (m, 6H), 7.78 (d, J = 8.5 Hz, 2H), 7.68–7.58 (m, 6H), 7.31 (d, J = 8.5 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 151.75, 138.61, 134.16, 131.38, 130.81, 130.47, 129.85, 129.42, 127.02, 110.41. HRMS ($APCI^+$) Calcd for $C_{20}H_{16}ClS^+$: 323.0656. Found: m/z 323.0657, ($APCI^-$) Calcd for $CO_3F_3S^-$: 148.9526. Found: m/z 148.9524. Anal. Calcd for $C_{21}H_{16}O_3ClF_3S_2$: C, 53.33; H, 3.41; Cl, 7.50; F, 12.05; S, 13.56. Found: C, 53.60; H, 3.42; Cl, 7.43; F, 12.21; S, 13.32.

1-Phenyl-1-benzothiophenium trifluoromethanesulfonate (**2c**).[10]

A mixture of 1-benzothiophene (142.5 mg, 1.06 mmol), diphenyliodonium triflate (559 mg, 1.30 mmol), and copper(II) acetate (2.4 mg, 0.013 mmol) was stirred at 140 ^oC for 0.5 h. The reaction mixture was cooled to rt and ether (1 mL) was added. After filtration, **2c** was obtained as gray crystals (298.5 mg, 78%). mp 153–154 °C (ether) (lit.,[10] mp 152–153 °C). IR (KBr, cm^{-1}) 1260, 1220, 1150, 1030, 770, 750, 635. ^1H NMR (270 MHz, DMSO-d_6) δ_H 8.28–8.21 (m, 2H), 8.07 (d, J = 7.6 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.81–7.57 (m, 7H), ^{13}C NMR (68 MHz, DMSO-d_6) δ_C 142.38, 140.83, 135.55, 133.96. 133.20, 131.02, 130.56, 129.86, 127.40, 127.18, 126.43, 124.86.

1-Tosylaziridine (**3a**).[11]

Table 1, Entry 4: To a stirred suspension of NaH (55% dispersion in mineral oil, 6.5 mg, 0.15 mmol) in

DMF (0.4 mL) was added *p*-toluenesulfonamide (25.6 mg, 0.15 mmol) at rt. After 0.5 h, KI (1.3 mg, 0.008 mmol) and **1a** (33.2 mg, 0.075 mmol) were added, and the reaction mixture was stirred at rt for 1 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **3a** (12.8 mg, 87%) as a slightly yellow syrup along with diphenyl sulfide (12.9 mg, 92%) and *N*,*N*-bis(2-bromoethyl)-*p*-toluenesulfonamide (0.6 mg, 2%). Preservation of **3a** in the refrigerator for two months led to crystallization. **3a**: R_f = 0.23 [hexane−EtOAc (4:1)]. Colorless crystals, mp 49–50 °C (lit.,[11b] mp 51 °C). IR (KBr, cm^{-1}) 1590, 1450, 1320, 1300, 1290, 1230, 1155, 1100, 1080, 905, 820, 715, 690, 645, 560, 535. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H.7.83 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H), 2.37 (s, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.52, 134.64, 129.61, 127.86, 27.48, 21.71. HRMS (ESI-TOF) Calcd for $C_9H_{12}NO_2S^+$, $[M+H]^+$: 198.0583. Found: *m*/*z* 198.0584.

***N*,*N*-Bis(2-bromoethyl)-*p*-toluenesulfonamide**.

R_f = 0.42 [hexane−EtOAc (4:1)]. Colorless crystals, mp 69–70 °C (hexane). IR (ATR, cm^{-1}) 2969, 1596, 1493, 1452, 1373, 1334, 1292, 1232, 1208, 1184, 1157, 1108, 1089, 1062, 1027, 998, 934, 861, 823, 801, 732. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.72 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 3.51 (s, 8H), 2.45 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.05, 135.48, 129.91, 127.09, 51.53, 29.60, 21.66. HRMS (APCI) Calcd for $C_{11}H_{16}NO_2Br_2S^+$, $[M+H]^+$: 383.9263. Found: *m*/*z* 383.9262.

2-(4-Chlorophenyl)-1-tosylaziridine (**3b**).[12]

To a stirred suspension of NaH (55% dispersion in mineral oil, 44.3 mg, 1.02 mmol) in THF (4.0 mL) was added *p*-toluenesulfonamide (174 mg, 1.02 mmol) at rt. After 0.5 h, **2b** (400mg, 0.85 mmol) was added, and the reaction mixture was stirred at rt for 19 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with EtOAc (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography [hexane−EtOAc (8:1 to 4:1)] to give **3b** (237 mg, 91%) as a colorless amorphous solid. IR (KBr, cm^{-1}) 1490, 1320, 1305, 1160, 1090, 910, 820, 735, 700, 575, 555. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H.7.85 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 3.73 (dd, J = 7.0, 4.3 Hz, 1H), 2.98 (d, J = 7.0 Hz, 1H), 2.44 (s, 3H), 2.34 (d, J = 4.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.67, 134.68, 134.08, 133.52, 129.69, 128.66, 127.82, 127.79, 40.31, 36.10, 21.74. HRMS (APCI) Calcd for $C_{15}H_{15}NO_2ClS^+$, $[M+H]^+$: 308.0507. Found: *m*/*z* 308.0512.

1-Tosyl-2-(2-phenylthiophenyl)aziridine (**3c**).

Synthesized from **2c** according to the procedure described for **3b**. Reaction time: 24 h. Yield: 40%. Slightly yellow syrup. IR (neat, cm^{-1}) 3459, 3060, 2995, 2923, 1924, 1807, 1735, 1596, 1582, 1494, 1476, 1440, 1374, 1328, 1306, 1293, 1226, 1186, 1163, 1093, 1060, 1037, 1024, 981, 912, 848, 815, 748, 713, 692, 670, 660. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.80 (d, J = 8.4 Hz, 2H), 7.38–7.10 (m, 11H), 4.09 (dd, J =

7.3, 4.6 Hz, 1H), 2.80 (d, J = 7.3 Hz, 1H), 2.42 (s, 3H), 2.10 (d, J = 4.6 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 144.49, 136.86, 135.65, 134.28, 133.55, 133.50, 129.60, 129.49, 129.09, 128.60, 128.40, 127.94, 126.60, 115.17, 39.62, 36.19, 21.72. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_2S_2^+$, $[M+H]^+$: 382.0930. Found: m/z 382.0929.

1-Tosylazetidine (**4**).[13]

Table 2, Entry 1: To a stirred suspension of NaH (55% dispersion in mineral oil, 6.5 mg, 0.15 mmol) in DMF (0.4 mL) was added *p*-toluenesulfonamide (25.7 mg, 0.15 mmol) at rt. After 0.5 h, KI (1.2 mg, 0.007 mmol) and **1b** (34.3 mg, 0.075 mmol) were added, and the reaction mixture was stirred at 100 °C for 3 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **4** (1.6 mg, 10%) as colorless crystals. mp 121–122 °C (EtOAc−hexane) (lit.,[13b] mp 119–121 °C). IR (ATR, cm^{-1}) 2996, 2915, 2872, 1593, 1489, 1445, 1337, 1300, 1157, 1129, 1088, 1058, 1017, 952, 869, 818, 802, 749. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.73 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.76 (t, J = 7.6 Hz, 4H), 2.47 (s, 3H), 2.06 (quin, J = 7.6 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 143.78, 131.38, 129.58, 128.27, 50.87, 21.65, 15.35. MS (APCI) $[M]^+$: m/z 211. HRMS (APCI) Calcd for $C_{10}H_{14}NO_2S^+$, $[M+H]^+$: 212.0740. Found: m/z 212.0747.

1-Tosylpyrrolidine (**5**).[14]

Table 2, Entry 2: To a stirred suspension of NaH (55% dispersion in mineral oil, 6.5 mg, 0.15 mmol) in DMF (0.4 mL) was added *p*-toluenesulfonamide (25.6 mg, 0.15 mmol) at rt. After 0.5 h, **1c** (35.3 mg, 0.075 mmol) was added, and the reaction mixture was stirred at rt for 1 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **5** (14.2 mg, 84%) as colorless crystals. mp 122–123 °C (hexane) (lit.,[14] mp 123–125 °C). IR (ATR, cm^{-1}) 3054, 2976, 2867, 1596, 1492, 1457, 1383, 1331, 1302, 1200, 1156, 1091, 1059, 1018, 1002, 911, 846, 814, 748. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.71 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 3.32–3.16 (m, 4H), 2.43 (s, 3H), 1.83–1.67 (m, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 143.13, 133.64, 129.45, 127.39, 47.90, 25.21, 21.55. HRMS (APCI) Calcd for $C_{11}H_{16}NO_2S^+$, $[M+H]^+$: 226.0896. Found: m/z 226.0898.

1-Tosylpiperidine (**6**).[15]

Synthesized from **1d** according to the procedure described for **5**. Colorless crystals, mp 98–99 °C (hexane) (lit.,[15] mp 96–98 °C). IR (ATR, cm^{-1}) 2946, 2924, 2859, 2828, 1596, 1493, 1452, 1383, 1355, 1336, 1274, 1213, 1162, 1091, 1069, 1050, 1026, 929, 858, 837, 812. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.64 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.96 (t, J = 5.5 Hz, 4H), 2.44 (s, 3H), 1.69–1.55 (m,

4H), 1.47–1.34 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 143.14, 133.01, 129.40, 127.58, 46.95, 25.20, 23.56, 21.60. HRMS (APCI) Calcd for $C_{12}H_{18}NO_2S^+$, $[M+H]^+$: 240.1053. Found: *m*/*z* 240.1054.

***N*-Tosyl-12-bromododecylamine (7).**

Synthesized from **1e** according to the procedure described for **5**. Colorless crystals, mp 65–66 °C (hexane). IR (ATR, cm^{-1}) 3267, 2917, 2850, 1597, 1493, 1472, 1427, 1321, 1289, 1262, 1237, 1211, 1185, 1156, 1092, 1068, 1040, 1018, 978, 900, 813. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.74 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.36 (br t, J = 6.0 Hz, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.93 (q, J = 6.8 Hz, 2H), 2.43 (s, 3H), 1.85 (quin, J = 7.1 Hz, 2H), 1.51–1.11 (m, 18H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 143.18, 136.90, 129.56, 127.00, 43.28, 34.13, 32.88, 29.64, 29.52, 29.50, 29.46, 29.11, 28.81, 28.23, 26.57, 21.60. HRMS (APCI) Calcd for $C_{19}H_{33}NO_2BrS^+$, $[M+H]^+$: 418.1410. Found: *m*/*z* 418.1409.

2-Phenyl-2-oxazoline (8).[16]

Table 3, Entry 3: To a stirred suspension of NaOH (4.0 mg, 0.10 mmol) in DMSO (0.25 mL) was added benzamide (12.1 mg, 0.10 mmol) at rt. After 0.5 h, KI (0.8 mg, 0.005 mmol) and **1a** (22.2 mg, 0.05 mmol) were added, and the reaction mixture was stirred at rt for 2 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **8** (1.9 mg, 26%) as a slightly yellow syrup. IR (neat, cm^{-1}) 3412, 3063, 2973, 2935, 2905, 2878, 2322, 1965, 1912, 1722, 1650, 1604, 1580, 1496, 1480, 1450, 1412, 1360, 1331, 1261, 1196, 1177, 1079, 1064, 1026, 975, 944, 897, 779, 695, 674. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.04–7.89 (m, 2H), 7.56–7.34 (m, 3H), 4.42 (t, J = 9.5 Hz, 2H), 4.05 (t, J = 9.5 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 164.41, 131.09, 128.15, 127.98, 127.58, 67.53, 54.88. MS (APCI) $[M+H]^+$: *m*/*z* 148.

2-Phenyl-2-thiazoline (9).[17]

Table 3, Entry 5: To a stirred suspension of NaH (55% dispersion in mineral oil, 6.5 mg, 0.15 mmol) in DMF (0.4 mL) was added thiobenzamide (20.6 mg, 0.15 mmol) at rt. After 0.5 h, KI (1.3 mg, 0.008 mmol) and **1a** (33.2 mg, 0.075 mmol) were added, and the reaction mixture was stirred at 50 ^{o}C for 0.5 h. The reaction was quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **9** (8.0 mg, 65%) as a light yellow syrup. IR (neat, cm^{-1}) 3401, 3061, 3028, 2941, 2850, 1959, 1894, 1811, 1608, 1578, 1491, 1447, 1317, 1239, 1177, 1158, 1076, 1027, 999, 946, 928, 846, 766, 691, 675, 658, 605. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.90–7.80 (m, 2H), 7.52–7.37 (m, 3H), 4.47 (t, J = 8.4 Hz, 2H), 3.43 (t, J = 8.4 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 168.45, 132.96, 131.04, 128.35, 128.23, 65.05, 33.65. MS (APCI) $[M]^+$: *m*/*z* 163.

4-(4-Chlorophenyl)-1*H*-1,2,3-triazole (10).[18]

Table 3, Entry 7: The mixture of **2b** (23.6 mg, 0.05 mmol) and sodium azide (6.6 mg, 0.10 mmol) in DMSO (0.25 mL) was stirred at 120 °C for 0.5 h. The reaction mixture was cooled to rt and quenched with a 0.1 M NaOH solution (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (4:1)] to give **10** (4.2 mg, 47%) as colorless crystals along with **11** (3.9 mg, 25%) as colorless crystals. **10**: R_f = 0.10 [hexane−EtOAc (4:1)]. Colorless crystals, mp 160–161 °C (hexane) (lit.,[18] mp 161–161.5 °C). IR (ATR, cm^{-1}) 3123, 2839, 2209, 1523, 1458, 1416, 1334, 1224, 1131, 1098, 1072, 1013, 999, 969, 947, 873, 833, 739. ^{1}H NMR (270 MHz, DMSO-d_6) δ_H 8.38 (s, 1H), 7.88 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H). ^{13}C NMR (68 MHz, DMSO-d_6) δ_C 132.35, 129.17, 128.79, 127.06. MS (APCI) $[M]^+$: m/z 179. HRMS (APCI) Calcd for $C_8H_7N_3Cl^+$, $[M+H]^+$: 180.0323. Found: m/z 180.0326.

11: The substituted nitrogen position was not determined. R_f = 0.62 [hexane−EtOAc (4:1)]. Colorless crystals, mp 119–121 °C (MeOH). IR (ATR, cm^{-1}) 3132, 1901, 1784, 1630, 1594, 1536, 1490, 1476, 1426, 1405, 1388, 1338, 1293, 1270, 1249, 1217, 1181, 1111, 1090, 1014, 976, 885, 852, 824, 732. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.98 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.49–7.33 (m, 6H), 5.97 (s, 1H), 5.38 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 147.68, 144.85, 135.28, 134.72, 132.95, 132.36, 129.57, 129.07, 128.47, 128.14, 127.34, 107.61. HRMS (APCI) Calcd for $C_{16}H_{12}N_3Cl_2^+$, $[M+H]^+$: 316.0403. Found: m/z 316.0402.

2-[1-(4-Chlorophenyl)vinyl]isoindoline-1,3-dione (12).[7d]

A mixture of **2b** (23.6 mg, 0.05 mmol) and potassium phthalimide (10.2 mg, 0.055 mmol) in DMSO (0.25 mL) was stirred at rt for 12 h. The reaction was quenched with cold water (10 mL), and the organic material was extracted with ether (10 mL x 2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC [hexane−EtOAc (5:1)] to give **12** (12.8 mg, 90%) as slightly yellow crystals. An analytical sample was prepared by crystallizing **12** from MeOH. Colorless crystals, mp 132–133 °C. IR (KBr, cm^{-1}) 1780, 1720, 1630, 1370, 1360, 1120, 1110, 1070, 890, 840, 730, 720. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.00–7.86 (m, 2H), 7.86–7.72 (m, 2H), 7.31 (s, 4H), 5.98 (s, 1H), 5.46 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 166.80, 136.07, 134.70, 134.40, 133.90, 131.60, 128.75, 126.66, 123.80, 116.44. HRMS (APCI) Calcd for $C_{16}H_{11}NO_2Cl^+$, $[M+H]^+$: 284.0473. Found: m/z 284.0470.

1-[1-(4-Chlorophenyl)vinyl]-1*H*-imidazole (13).[19]

Synthesized from **2b** and sodium *1H*-imidazole according to the procedure described for **12**.

Yield: 80%. Orange syrup. IR (ATR, cm^{-1}) 3112, 1635, 1593, 1487, 1397, 1372, 1315, 1245, 1186, 1093, 1065, 1004, 901, 833, 736. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.64 (s, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.14 (s, 1H), 7.00 (s, 1H), 5.33 (s, 1H), 5.32 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C

142.03, 136.92, 135.63, 133.95, 129.76, 128.88, 128.37, 119.07, 106.86. HRMS (APCI) Calcd for $C_{11}H_{10}N_2Cl^+$, $[M+H]^+$: 205.0527. Found: *m*/*z* 205.0531.

1-[1-(4-Chlorophenyl)vinyl]-1*H*-benzimidazole (**14**).

Synthesized from **2b** and sodium *1H*-benzimidazole according to the procedure described for **12**.

Yield: 92%. Slightly yellow crystals, mp 88–89 °C (hexane). IR (ATR, cm^{-1}) 3059, 1716, 1622, 1603, 1487, 1449, 1401, 1371, 1303, 1285, 1255, 1207, 1185, 1149, 1112, 1083, 1011, 942, 881, 848, 828, 814, 770, 750, 733. ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.03 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.40–7.16 (m, 6H), 7.03 (d, J = 8.1 Hz, 1H), 5.68 (d, J = 1.0 Hz, 1H), 5.49 (d, J = 1.0 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ_C 143.76, 142.72, 141.04, 135.68, 133.56, 133.44, 129.01, 127.88, 123.44, 122.69, 120.45, 111.51, 109.85. HRMS (APCI) Calcd for $C_{15}H_{12}N_2Cl^+$, $[M+H]^+$: 255.0684. Found: *m*/*z* 255.0684.

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