Heteroatom Chemistry
Volume 12, Number 3, 2001

Conversion of Bis(o-nitrophenyl)disulfides to Heterocycles Containing Sulfur and Nitrogen by the Action of Samarium Diiodide

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Received 13 September 2000; revised 29 December 2000

ABSTRACT: *Treatment of bis(o-nitrophenyl)disulfides* **1** *with* SmI_2 *led to simultaneous reduction of nitro groups and reductive cleavage of S–S bonds as well as the formation of the active intermediates* **2**. *The intermediates* **2** *reacted smoothly with aldehydes or ketones, acid chlorides or anhydrides, α-bromoketones, and α,β-unsaturated ketones at room temperature to afford the desired benzothiazolines* **3**, *benzothiazoles* **4**, *2H-1,4-benzothiazines* **5**, *and 2,3-dihydro-1,5-benzothiazepines* **6**, *respectively, in moderate to high yields under mild and neutral conditions*. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:156–160, 2001

INTRODUCTION

Heterocycles containing sulfur and nitrogen, such as benzothiazolines and 1,5-benzothiazepines, are biologically and industrially important compounds [1]. The main method for preparing these compounds makes use of *o*-aminothiophenols as starting materials; however, it usually involves harsh conditions such as using acid or base catalysts, moderate to high temperature, and a long reaction time [2].

The Kagan [3] reagent, samarium diiodide (SmI_2), has evolved into an exceedingly reliable, mild, neutral, selective, and versatile single-electron-reducing agent for promoting reductive reactions difficult to accomplish by other existing methodologies. Its broad application in organic synthesis during the last decade has been reviewed [4]. The reduction of nitro compounds [5] and reductive cleavage of S–S, Se–Se and Te–Te bonds by SmI_2 [6] has been investigated extensively. However, to our knowledge, the simultaneous reduction of more than one group by SmI_2 has not been reported. Here we wish to report our preliminary studies on the simultaneous reduction of nitro groups and S–S bonds in bis(o-nitrophenyl)disulfides by SmI_2 and its use in the synthesis of some heterocycles containing sulfur and nitrogen.

RESULTS AND DISCUSSION

When 0.5 equivalents of a bis(*o*-nitrophenyl)disulfide **1** was added dropwise to 7.0 equivalents of SmI_2 at room temperature under a nitrogen atmosphere, the deep blue color of the solution gradually changed to an orange-yellow color. This observation suggested that nitro groups were reduced and S–S bonds were reductively cleaved by SmI_2. The inter-

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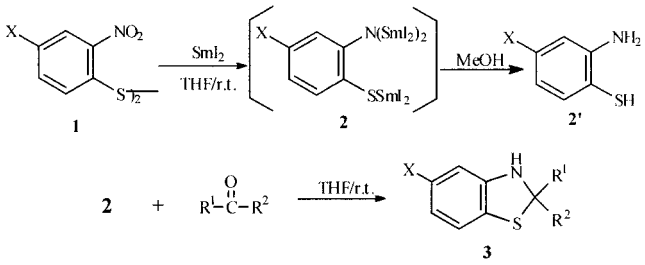
Contract Grant Sponsor: National Natural Science Foundation of China
Contract Grant Number: 29872010.
Contract Grant Sponsor: NSF of Zhejiang province of China.

mediates **2**, formed at the same time, had high activity and reacted smoothly with aldehydes or ketones to give the desired benzothiazolines **3** in good yields (Scheme 1). When MeOH (0.2 mL) was added to the solution of the intermediates **2**, the orange-yellow color of the mixture turned into light yellow immediately, and *o*-aminothiophenols **2′** were formed. Table 1 shows that *o*-aminothiophenols **2′** were less reactive toward aldehydes than the intermediates **2** (entry 2). Table 1 summarizes the results of the reaction of the intermediates **2** with aldehydes or ketones. Aldehydes or aliphatic ketones gave satisfactory yields of benzothiazolines **3**. Aromatic ketones, however, gave similar products but with poor yields or did not react at all (entries 5 and 7) probably due to steric hidrance.

When acid chlorides or anhydrides were added to a solution of intermediates **2** at room temperature, benzothiazoles **4** were obtained (Scheme 2). The results are summarized in Table 2. It seems that the yield when using acid andydrides is higher than when using acid chlorides.

α-Bromoketones underwent displacement by the active intermediates **2** successfully to give the corresponding 2*H*-1,4-benzothiazines **5** (Scheme 3). Results are summarized in Table 3 and indicate that yields were affected by substituents on the aromatic rings of *α*-bromoketones (i.e., entries 13–16). The presence of electron-withdrawing groups on the aromatic ring resulted in higher yields than when electron-donating groups were present. Moreover, aromatic *α*-bromoketones (entry 13) are more reactive toward intermediates **2** than aliphatic *α*-bromoketones (entry 17).

Ring-closure reactions between *α,β*-unsaturated ketones and intermediates **2** took place readily to afford 2,3-dihydro-1,5-benzothiazepines **6** (Scheme 4). The results are summarized in Table 4. It was found

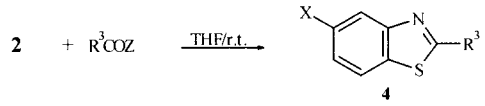


SCHEME 1

TABLE 1 Synthesis of Benzothiazolines **3** Promoted by SmI_2

Entry	*X*	R^1	R^2	*T (h)*	*Product*	*Yield (%)*[a]
1	H	*n*-Pr	H	2	**3a**	80
2[b]	H	*n*-Pr	H	4	**3a**	25
3	H	*p*-$NO_2C_6H_5$	H	2	**3b**	75
4	H	Me	*n*-Bu	2	**3c**	74
5	Cl	Me	Ph	4	**3d**	52
6	Cl	-$(CH_2)_5$-		3	**3e**	78
7	Cl	Ph	Ph	24	**3f**	0[c]

[a]Yields of crude product based on bis(*o*-nitrophenyl)disulfides.
[b]MeOH was added to the solution of the intermediate **2**, followed by reaction with aldehyde.
[c]The reaction was studied at 0°C, 25°C, and THF-refluxing temperature.

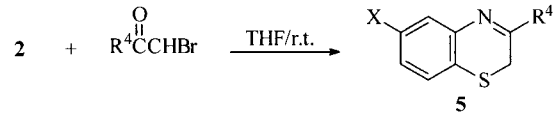


SCHEME 2

TABLE 2 Synthesis of Benzothiazoles **4** Promoted by SmI_2

Entry	*X*	R^3	*Z*	*T (h)*	*Products*	*Yield (%)*[a]
8	H	*n*-Pr	Cl	2	**4a**	65
9	H	*n*-Pr	*n*-$PrCO_2$	2	**4a**	83
10	Cl	Et	Cl	2	**4b**	68
11	Cl	Et	$EtCO_2$	2	**4b**	86
12	Cl	Ph	Cl	2	**4c**	72

[a]Yields of crude product based on bis(*o*-nitrophenyl)disulfides.

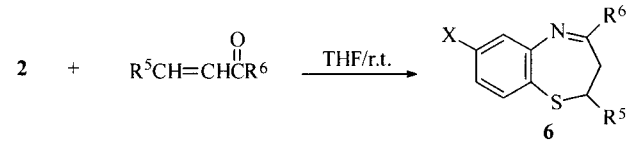


SCHEME 3

TABLE 3 Synthesis of 2H-1,4-Benzothiazines **5** Promoted by SmI_2

Entry	*X*	R^4	*T (h)*	*Products*	*Yield (%)*[a]
13	H	C_6H_5	2	**5a**	62
14	H	*p*-MeC_6H_4	2	**5b**	68
15	H	*p*-BrC_6H_4	4	**5c**	79
16	H	*m*-$NO_2C_6H_4$	8	**5d**	86
17	Cl	CH_3	24	**5e**	40
18	Cl	2-benzofuryl	4	**5f**	65
19	Cl	*p*-$MeOC_6H_4$	4	**5g**	64
20	Cl	*p*-ClC_6H_5	4	**5h**	71

[a]Yields of crude product based on bis(*o*-nitrophenyl)disulfides.



SCHEME 4

TABLE 4 Synthesis of 2,3-Dihydro-1,5-Benzothiazepines **6** Promoted by SmI_2

Entry	X	R^5	R^6	T (h)	Products	Yield (%)[a]
21	H	C_6H_5	Ph	4	**6a**	86
22	Cl	C_6H_5	Ph	4	**6b**	83
23	Cl	*p*-ClC_6H_4	Ph	3	**6c**	78
24	Cl	*p*-$CH_3C_6H_4$	Ph	4	**6d**	80
25	Cl	*p*-$CH_3OC_6H_4$	Ph	4	**6e**	77
26	Cl	3,4-$(OCH_2O)C_6H_3$	Ph	4	**6f**	85
27	Cl	C_6H_5	PhCH=CH	8	**6g**	52
28	H	C_6H_5	CH_3	10	**6h**	43

[a]Yields of crude product based on bis(*o*-nitrophenyl)disulfides.

that chalcones are more reactive toward the new anionic species **2** than any other *α,β*-unsaturated ketones (entries 27 and 28).

In conclusion, the intermediates **2** derived from bis(*o*-nitrophenyl)disulfides by SmI_2 treatment were found to be more reactive than *o*-aminothiophenols. The present study provides a new, simple, and versatile synthetic method for preparing some heterocycles containing sulfur and nitrogen using bis(*o*-nitrophenyl)disulfides as synthons.

EXPERIMENTAL

Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. Infrared spectra were recorded on an Shimadzu IR-408 spectrometer using KBr pellets or a thin film with maximum absorption indicated in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AC-80 spectrometer using $CDCl_3$ solutions, *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Microanalyses were carried out on a Carlo Erba EA 1110 instrument.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. All organic compounds, such as aldehydes, ketones, and acid chlorides or anhydrides were commercially available and were used without further purification. *α*-Bromoketones and *α,β*-unsaturated ketones were prepared by known procedures. All reactions were performed in a Schlenk-type glass apparatus under a nitrogen atmosphere.

Formation of the Intermediates **2** *Promoted by* SmI_2

Samarium powder (1.05 g, 7 mmol, 99.9%) was placed in a well-dried three-necked round-bottom flask containing a magnetic stir bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (30 mL) was added through a rubber septum by a syringe. Iodine (1.75 g, 7 mmol) was added to the flask, and the mixture was stirred at room temperature until the solution became deep blue and homogeneous (1–2 hours). The solution of SmI_2 was now ready for subsequent use. To the solution of SmI_2 was added bis(*o*-nitrophenyl)disulfide **1** (0.154 g, 0.5 mmol) in THF (3 mL) by syringe at room temperature under a nitrogen atmosphere. The deep-blue solution gradually became brown within 0.5 hours, which showed that the nitro groups were reduced and the S–S bond were reductively cleaved by SmI_2; the intermediates **2** had been generated.

Reactions of the Intermediates **2** *with Aldehydes or Ketones*

An aldehyde (1.1 mmol) or a ketones (1.1 mmol) in THF (1 mL) was added by syringe. After having been stirred for a given time (Table 1) (the reaction was monitored by thin-layer chromatography), the reaction was quenched with dilute hydrochloride acid (0.1 mol/L, 3 mL), and the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were washed with saturated aqueous $Na_2S_2O_3$ (15 mL) and saturated aqueous NaCl (15 mL), and then dried over anhydrous $MgSO_4$. After evaporating the solvent under reduced pressure, the crude product was purified by preparative thin-layer chromatography on silica gel using ethyl acetate/cyclohexane (1:5) as eluant.

Reactions of the Intermediates **2** *with Acid Chlorides or Anhydrides, α-Bromoketones, and α,β-Unsaturated Ketones*

The preparation of the intermediates **2** is the same as described previously. An acid chloride (or anhydride, *α*-bromoketone, *α,β*-unsaturated ketone, 1.1 mmol) in THF (1 mL) was then added by syringe, and the mixture was stirred at room temperature for a given time (Tables 2–4). The crude product was isolated as before and purified by preparative thin-

layer chromatography on silica gel using ethyl acetate/cyclohexane (1:7) as eluant.

DATA OF PRODUCTS

3a, 2-*n*-Propylbenzothiazoline: oil [7], ν_{max}(cm^{-1}) 3350 (NH); δ_H 7.15–6.20 (4H, m), 4.92 (1H, m), 3.07 (1H, br s), 1.78–1.22 (4H, m), 0.85 (3H, t, J = 6 Hz).

3b, 2-(4′-Nitrophenyl)benzothiazoline: yellow crystals, m.p. 116–118°C (lit. [8a] 117–118°C); ν_{max}(cm^{-1}) 3375 (NH), 1520, 1350 (NO_2); δ_H 8.21–7.48 (4H, m), 7.09–6.47 (4H, m), 6.29 (1H, s), 4.10 (1H, br s).

3c, 2-*n*-Butyl-2-methylbenzothiazoline: oil, ν_{max}(cm^{-1}) 3340 (NH); δ_H 6.90–6.30 (4H, m), 3.65 (1H, br s), 1.92–1.13 (9H, m), 0.85 (3H, t, J = 6 Hz); *m/z* 207 (M^+, 1.5), 136 (25), 101 (50), 43 (100); Anal. calcd. for $C_{12}H_{17}NS$: C, 69.52; H, 8.26; N, 6.76%; found: C, 69.67; H, 8.13; N, 6.64.

3d, 5-Chloro-2-methyl-2-phenylbenzothiazoline: light-yellow crystals, m.p. 68–70°C (lit. [8b] 71°C); ν_{max}(cm^{-1}) 3345 (NH); δ_H 7.85–6.48 (8H, m), 5.65 (1H, br s), 4.75 (1H, m), 2.63 (3H, s).

3e, 5-Chloro-2,2-pentamethylenebenzothiazoline: yellow crystals, m.p. 43–45°C (lit. [8b] 47°C); ν_{max}(cm^{-1}) 3352 (NH); δ_H 6.76–6.24 (3H, m), 3.89 (1H, br s), 2.02–1.20 (10H, m).

4a, 2-Propylbenzothiazole: light-yellow oil [9]; ν_{max}(cm^{-1}) 1620–1580 (C=N), 760 (C–S); δ_H 7.80–7.30 (4H, m, ArH), 2.73 (2H, t, J = 6 Hz), 2.10–1.35 (2H, m), 0.95 (3H, t, J = 6.5 Hz);.

4b, 5-Chloro-2-ethylbenzothiazole: pale-yellow crystals, m.p. 54–56°C (lit. [10] 56–57°C); ν_{max}(cm^{-1}) 1618–1577 (C=N), 763 (C–S); δ_H 7.75–7.31 (3H, m, ArH), 2.80 (2H, q, J = 6.5 Hz), 1.18 (3H, t, J = 6.5 Hz).

4c, 5-Chloro-2-phenylbenzothiazole: light-yellow crystals, m.p. 136–138°C (lit. [10] 139°C); ν_{max}(cm^{-1}) 1625–1583 (C=N), 1500, 1450 (Ar), 762 (C–S); δ_H 7.83–7.06 (8H, m).

5a, 3-Phenyl-2H-1,4-benzothiazine: light-yellow crystals, m.p. 46–48°C (lit. [11a] 47–48°C); ν_{max}(cm^{-1}) 2930, 1475 (CH_2), 1650 (C=N), 765 (C–S); δ_H 7.42–6.87 (9H, m), 3.63 (2H, s).

5b, 3-(4′-Methylphenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 52–54°C (lit. [11b] 53–55°C); ν_{max}(cm^{-1}) 2980, 2930 (CH_2), 1475, 1380 (CH_3), 1660 (C=N), 760 (C–S); δ_H 8.00–6.60 (8H, m), 3.48 (2H, s), 2.32 (3H, s).

5c, 3-(4′-Bromophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 60–62°C (lit. [11b] 59–61°C); ν_{max}(cm^{-1}) 2940, 1475 (CH_2), 1685 (C=N), 760 (C–S); δ_H 8.04–6.72 (8H, m), 3.74 (2H, s).

5d, 3-(3′-Nitrophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 86–88°C; ν_{max}(cm^{-1}) 2930, 1475 (CH_2), 1675 (C=N), 1560, 1350 (NO_2), 760 (C–S); δ_H 8.21–6.85 (8H, m), 3.63 (2H, s); *m/z* (%): 270 (M^+, 15), 256 (100), 210 (34), 134 (57); Anal. calcd. for $C_{14}H_{10}N_2O_2S$: C, 62.21; H, 3.73; N, 10.36; found: C, 62.08; H, 3.89; N, 10.14.

5e, 6-Chloro-3-Methyl-2H-1,4-benzothiazine: oil, ν_{max}(cm^{-1}) 2980, 2930, 1475, 1380 (CH_3, CH_2), 1650 (C=N), 760 (C–S), 742 (C–Cl); δ_H 7.58–6.92 (3H, m), 2.75 (2H, s), 2.13 (3H, s); *m/z* (%): 199 (M + 2, 3.2), 197 (M^+, 8.7), 184 (32.7), 182 (100); Anal. calcd. for C_9H_8ClNS: C, 54.68; H, 4.08; N, 7.09; found: C, 54.77; H, 3.89; N, 6.83.

5f, 6-Chloro-3-(2′-benzofuryl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 125–127°C; ν_{max}(cm^{-1}) 2940, 1465 (CH_2), 1645 (C=N), 1250 (C–O–C), 763 (C–S), 740 (C–Cl); δ_H 7.63–6.83 (8H, m), 3.53 (2H, s); *m/z* (%): 301 (M + 2, 1.2), 299 (M^+, 3.5), 286 (32.4), 284 (100). Anal. calcd. for $C_{16}H_{10}ClNOS$: C, 64.11; H, 3.36; N, 4.67; found: C, 64.27; H, 3.29; N, 4.49.

5g, 6-Chloro-3-(4′-methoxyphenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 117–119°C; ν_{max}(cm^{-1}) 2980, 2925, 1475, 1380 (CH_3, CH_2), 1650 (C=N), 1250 (C–O–C), 760 (C–S), 740 (C–Cl); δ_H 7.85–6.70 (7H, m), 3.86 (3H, s), 3.68 (2H, s); *m/z* (%): 291 (M + 2, 4.8), 289 (M^+, 14.9), 276 (31.7), 274 (100); Anal. calcd. for $C_{15}H_{12}ClNOS$: C, 62.17; H, 4.17; N, 4.83; found: C, 62.02; H, 4.22; N, 4.99.

5h, 6-Chloro-3-(4′-chlorophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 119–121°C; ν_{max}(cm^{-1}) 2935, 1470 (CH_2), 1660 (C=N), 760 (C–S), 742 (C–Cl); δ_H 8.01–7.05 (7H, m), 3.82 (2H, s); *m/z* 294 (M^+, 12.7), 279 (100). Anal. Calcd. for $C_{14}H_9Cl_2NS$: C, 57.16; H, 3.08; N, 4.76; found: C, 56.97; H, 3.14; N, 4.56.

6a, 2,3-Dihydro-2,4-diphenyl-1,5-benzothiazepine: pale-yellow crystals, m.p. 112–114°C (lit. [12] 114–115°C); ν_{max}(cm^{-1}) 1610–1590 (C=N), 758 (C–S); δ_H 8.06–6.76 (14H, m), 4.90–4.45 (1H, m), 3.10–2.45 (2H, m).

6b, 7-Chloro-2,3-dihydro-2,4-diphenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 132–134°C; ν_{max}(cm^{-1}) 1610–1580 (C=N), 755 (C–S); δ_H 8.07–6.57 (13H, m), 4.87–4.57 (1H, m), 3.47–2.77 (2H, m); *m/z* 349 (M^+, 2.0), 248 (36), 246 (100), 105 (67), 77 (36); Anal. calcd. for $C_{21}H_{16}ClNS$: C, 72.09; H, 4.61; N, 4.00%; found: C, 72.20; H, 4.53; N, 3.78.

6c, 7-Chloro-2-(4′-chlorophenyl)-2,3-dihydro-4-phenyl-1,5-benzothiazepine: yellow crystals, m.p. 145–147°C; ν_{max}(cm^{-1}) 1610–1580 (C=N), 760 (C–S); δ_H 8.00–6.40 (12H, m), 5.90–5.67 (1H, m), 2.62–2.34 (2H, m); *m/z* 383 (M^+, 1.6), 279 (38), 248 (36), 246 (100); Anal. calcd. for $C_{21}H_{15}Cl_2NS$: C, 65.63; H, 3.93; N, 3.64%; found: C, 65.39; H, 4.04; N, 3.78.

6d, 7-Chloro-2,3-dihydro-2-(4′-methylphenyl)-4-

phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 165–167°C; ν_{max}(cm^{-1}) 1610–1578 (C=N), 760 (C–S); δ_H 8.04–6.92 (8H, m, ArH), 4.90–4.62 (1H, m), 3.14–2.74 (2H, m), 2.24 (3H, s); *m/z* 363 (M^+, 1.9), 259 (19), 245 (14), 221 (39), 207 (100), 105 (35), 77 (37); Anal. calcd. for $C_{22}H_{18}ClNS$: C, 72.61; H, 4.99; N, 3.85%; found: C, 72.47; H, 5.10; N, 3.62.

6e, 7-Chloro-2,3-dihydro-2-(4′-methoxylphenyl)-4-phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 148–150°C; ν_{max}(cm^{-1}) 1613–1585 (C=N), 1250 (=C–OMe), 755 (C–S); δ_H 8.02–6.40 (12H, m), 4.25–4.05 (1H, m), 3.51 (3H, s), 3.25–2.85 (2H, m); *m/z* 379 (M^+, 1.2), 248 (19), 246 (49), 134 (100); Anal. calcd. for $C_{22}H_{18}ClNOS$: C, 69.56; H, 4.78; N, 3.69%; found: C, 69.44; H, 4.52; N, 3.51.

6f, 7-Chloro-2,3-dihydro-2-(3′,4′-dioxomethylenephenyl)-4-phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 178–180°C; ν_{max}(cm^{-1}) 2780, 925, 720 (OCH_2O), 1615–1580 (C=N), 760 (C–S); δ_H 8.00–6.42 (11H, m), 5.77 (2H, s), 4.96–4.62 (1H, m), 3.36–2.80 (2H, m); *m/z* 393 (M^+, 4.2), 289 (23.3), 246 (24.8), 149 (100); Anal. calcd. for $C_{22}H_{16}ClNO_2S$: C, 67.09; H, 4.09; N, 3.56%; found: C, 67.20; H, 3.92; N, 3.43.

6g, 7-Chloro-2,3-dihydro-2-phenyl-4-styryl-1,5-benzothiazepine: light-yellow crystals, m.p. 102–104°C; ν_{max}(cm^{-1}) 1650, 965 (C=C), 1615–1582 (C=N), 760 (C–S); δ_H 8.10–6.70 (13H, m), 6.23–5.76 (2H, m), 4.53–4.23 (1H, m), 3.10–2.53 (2H, m); *m/z* 375 (M^+, 1.2), 272 (16), 270 (33), 247 (38.6), 245 (100); Anal. calcd. for $C_{23}H_{18}ClNS$: C, 73.49; H, 4.83; N, 3.73%; found: C, 73.33; H, 4.76; N, 3.57.

6h, 2,3-Dihydro-4-methyl-2-phenyl-1,5-benzothiazepine: yellow crystals, m.p. 123–124°C (lit. [13], 121–123°C); ν_{max}(cm^{-1}) 2980, 1380 (CH_3), 1610–1590 (C=N), 758 (C–S); δ_H 7.82–6.74 (9H, m), 4.70–4.35 (1H, m), 3.10–2.75 (2H, m), 2.03 (3H, s).

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