Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Triton-B-Catalyzed, Efficient, One-Pot Synthesis of Dithiocarbazates Through Alcoholic Tosylates

Devdutt Chaturvedi [a], Nisha Mishra [b], Amit K. Chaturvedi [b] & Virendra Mishra [b]

[a] Bio-organic Chemistry Division, Indian Institute of Integrative Medicine, Jammu-Tawi, India

[b] Synthetic Research Laboratory, Department of Chemistry, B. S. A. College, Mathura, India

Published online: 04 Mar 2009.

To cite this article: Devdutt Chaturvedi , Nisha Mishra , Amit K. Chaturvedi & Virendra Mishra (2009) Triton-B-Catalyzed, Efficient, One-Pot Synthesis of Dithiocarbazates Through Alcoholic Tosylates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:7, 1273-1281

To link to this article: http://dx.doi.org/10.1080/00397910802519141

Synthetic Communications®, 39: 1273–1281, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802519141

Taylor & Francis
Taylor & Francis Group

Triton-B-Catalyzed, Efficient, One-Pot Synthesis of Dithiocarbazates Through Alcoholic Tosylates

Devdutt Chaturvedi,[1] Nisha Mishra,[2] Amit K. Chaturvedi,[2] and Virendra Mishra[2]

[1]Bio-organic Chemistry Division, Indian Institute of Integrative Medicine, Jammu-Tawi, India

[2]Synthetic Research Laboratory, Department of Chemistry, B. S. A. College, Mathura, India

Abstract: A quick, efficient, one-pot synthesis of dithiocarbazates was accomplished in high yields by the reaction of various tosylates of primary, secondary, and tertiary alcohols with a variety of substituted hydrazines using the benzyltrimethylammonium hydroxide (Triton-B)/CS_2 system. The reaction conditions are mild with simpler workup procedures than the reported methods.

Keywords: Alcoholic tosylates, benzyltrimethylammonium hydroxide, carbon disulfide, dithiocarbazates, substituted hydrazines

INTRODUCTION

Organic dithiocarbazates have received much attention because of their numerous remarkable medicinal, industrial, and synthetic applications.[1,2] They have extensively been used as pharmaceuticals,[3] as agrochemicals,[4] as intermediates in organic synthesis,[5] for protection of amino groups in peptide synthesis,[6] as linkers in solid-phase organic synthesis,[7] and as donor ligands in complexation reactions with transition metals.[8] To satisfy the demand, their synthesis has changed from the use of costly and toxic chemicals such as thiophosgene[9] and its derivatives,[10] directly

Received July 8, 2008.

Address correspondence to Devdutt Chaturvedi, Bio-organic Chemistry Division, Indian Institute of Integrative Medicine, Canal Road, Jammu-Tawi 180001, J & K, India. E-mail: ddchaturvedi002@yahoo.co.in

or indirectly, to abundantly available, cheap, and safe reagents such as like CS_2. However, their formation using CS_2 employed harsh reaction conditions, such as use of strong bases, high reaction temperatures, and long reaction times.[11] Thus, we were prompted to improve procedures. Our group[12] has been engaged during the past several years with the development of new methodologies for the preparation of carbamates, dithiocarbamates, and related compounds using cheap, abundantly available, and safe reagents such as CO_2 and CS_2. Recently,[13] we found that benzyltrimethyl ammonium hydroxide (Triton-B) is the best catalyst for the synthesis of carbamates, dithiocarbamates, and dithiocarbonates (xanthates). We report here an efficient, one-pot synthesis of dithiocarbazates from a variety of primary, secondary, and tertiary alcoholic tosylates and substituted hydrazines using the Triton-B/CS_2 system.

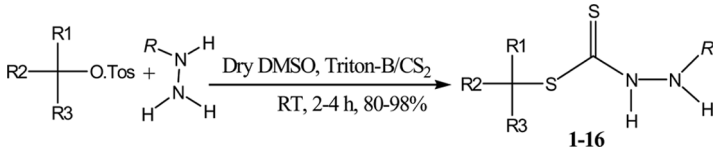
RESULTS AND DISCUSSION

A mixture of substituted hydrazine and CS_2 was taken in dry dimethyl sulfoxide (DMSO), and Triton-B was added to it. The reaction was stirred for 30 min at room temperature, and then the corresponding alcoholic tosylate was added. The reaction was continued until completion as checked by thin-layer chromatography (TLC; see Table 1). We proposed

Table 1. Conversion of alcoholic tosylates into dithiocarbazates of formula **1–16**

Entry	R^1	R^2	R^3	R	Time (h)
1	*n*-C_3H_7	H	H	4-MeO-Ph	2
2	$PhCH_2CH_2$	H	H	Ph	2
3	$PhCH_2$	H	H	Ph	2.5
4	Ph	H	H	Bn	3
5	C_2H_5	Me	H	Bn	3
6	Ph-4-MeO	H	H	Ph-3-NO_2	3
7	C_3H_7	H	H	Ph-4-NO_2	3
8	C_3H_7	H	H	Ph-2,4-NO_2	4
9	C_3H_7	H	H	Naphthyl	3
10	C_4H_9	C_4H_9	H	Ph	3
11	C_4H_9	C_4H_9	C_4H_9	Ph	3
12	C_5H_{11}	H	H	*n*-C_4H_9	2.5
13	C_7H_{15}	H	H	Ph	2.5
14	C_9H_{19}	H	H	*n*-C_4H_9	2
15	C_3H_7	C_3H_7	H	Ph	3
16	Ph	CH_3	H	Ph	3.5

Note. All the products were characterized by IR, NMR, and mass spectroscopic data.



Scheme 1.

that the S^- of the dithiocarbazate ion produced will attack the electrophilic carbon of the respective alcoholic tosylates to afford dithiocarbazates in high yields (80–98%) at room temperature in 2–4 h, as mentioned in Table 1. The reaction proved to be successful, and the desired products were isolated. Their structures were confirmed by various spectroscopic and analytical techniques. The alcoholic tosylates of primary, secondary, and tertiary alcohols were prepared following the standard procedure.[14] The whole reaction conditions are shown in Scheme 1.

We tried several solvents such as like *n*-heptane, *n*-hexane, acetonitrile, benzene, toluene, methanol, dichloromethane, chloroform, DMSO, dimethylformamide, and hexamethylphosphoric triamide, of which dry DMSO proved to be most suitable at room temperature.

In conclusion, we developed a convenient and efficient protocol for the one-pot, three-component coupling of various amines with a variety of primary, secondary, and tertiary alcoholic tosylates via the CS_2 bridge using Triton-B. This method generates the corresponding dithiocarbazates in good to excellent yields. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and experimental convenience. This synthetic protocol is believed to offer a more general method for the formation of carbon–sulfur bonds, which are essential to numerous organic syntheses.

EXPERIMENTAL

General

Chemicals were procured from Merck, Aldrich, and Fluka chemical companies. Reactions were carried out under an atmosphere of argon. IR spectra (4000–200 cm^{-1} were recorded on a Bomem MB-104 Fourier transform infrared (FTIR) spectrophotometer using the neat technique, where as NMR spectra were scanned on an AC-300 F NMR (300-MHz) instrument using $CDCl_3$ and some other deutrated solvents, with tetra methylsilane (TMS) as internal standard. Elemental analyses were conducted by means of a Carlo-Erba EA 1110-CNNO-S analyzer and agreed favorably with calculated values.

Typical Experimental Procedure

Carbon disulfide ($8\,cm^3$) were slowly added and Triton-B ($2\,cm^3$) to a stirred solution (under Ar) of 3 mmol substituted hydrazine in $5\,cm^3$ anhyd. DMSO at room temperature. Then the mixture was stirred for 0.5 h, at which point 3 mmol of the required alcoholic tosylate were added over a period of 5 min. The stirring was further continued until the completion of reaction (Table 1). The reaction mixture was poured into $20\,cm^3$ distilled water, and the organic layer was extracted with $3\times10\,cm^3$ EtOAc. The organic layer was washed with $20\,cm^3$ 0.1 *N* HCl, $25\,cm^3$ saturated solution of $NaHCO_3$, and $30\,cm^3$ brine; dried (Na_2SO_4), and concentrated to get the desired compound.

Data

N′-(4-Methoxyphenyl)hydrazinecarbodithioc Acid Butyl Ester
(**1**, $C_{12}H_{18}N_2OS_2$)

Yield: 94%; yellow oil; IR (neat) $\ddot{\upsilon} = 675$, $1210\,cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 0.85$ (t, 3H, $J = 7.3$ Hz), 1.33 (m, 2H), 1.85 (m, 2H), 2.0 (s, NH), 2.95 (t, 2H, $J = 6.3$ Hz), 3.73 (s, 3H), 4.05 (m, NH), 6.75–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 13.5$, 21.8, 32.4, 33.9, 43.7, 55.6, 112.5, 114.9, 134.5, 152.4, 222.5 (C = S) ppm; MS (EI): $m/z = 270$.

N′-Phenyl Hydrazine Carbodithioc Acid 3-Phenyl Propyl Ester
(**2**, $C_{16}H_{18}N_2S_2$)

Yield: 96%; yellow oil; IR (neat) $\ddot{\upsilon} = 676$, $1205\,cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 2.05$ (s, H, NH), 2.30 (m, 2H, Ph · CH_2 · CH_2 · CH_2-S), 2.56 (t, 2H, $J = 7.2$ Hz, Ph · CH_2), 2.87 (t, 2H, Ph · CH_2 · CH_2 · CH_2 · S), 4.03 (m, H, Ph · *NH*), 6.66–7.12 (m, 10H, Ar-H); ^{13}C NMR ($CDCl_3$), $\delta = 32.2$, 33.6, 34.4, 112.5, 119.2, 125.8, 128.6, 129.5, 138.6, 221.6 (C = S) ppm; MS: $m/z = 302$.

N′-Phenyl-hydrazine Carbodithioc Acid Phenethyl Ester
(**3**, $C_{15}H_{16}N_2S_2$)

Yield: 87%; yellow oil; IR (neat) $\ddot{\upsilon} = 673$, $1203\,cm^{-1}$; ^1H NMR ($CDCl_3$) $\delta = 2.10$ (s, H, NH), 3.20 (2H, t, $J = 6.5$, Hz, Ph · CH_2CH_2S), 3.24 (m, 2H, $J = 7.2$ Hz, PhCH_2), 4.52 (m, H, Ph*NH*), 6.69–7.15 (m, 10H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 34.5$, 37.3, 47.2, 49.9, 118.6, 192.7, 223.3 (C = S) ppm; MS: $m/z = 288$.

N′-Butyl Hydrazine Carbodithioc Acid Benzyl Ester (**4**, $C_{12}H_{18}N_2S_2$)

Yield: 92%; yellow oil; IR (neat) $\ddot{v} = 676$, 1207 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.05$ (t, 3H, CH_3), 1.33 (m, 2H, CH_2CH_3), 1.56 (m, 2H, $CH_2 \cdot CH_2CH_3$), 2.05 (br, NH), 2.65 (m, 2H, $NHCH_2$), 4.13 (s, 2H, $PhCH_2$), 7.06–7.15 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 13.7$, 20.2, 31.5, 38.5, 50.9, 126.8, 127.6, 128.5, 141.8, 223.5 ppm; MS: $m/z = 254$.

N′-Butyl-hydrazine Carbodithioc Acid Sec-butyl Ester (**5**, $C_9H_{20}N_2S_2$)

Yield: 90%; IR (neat) $\ddot{v} = 682$, 1214 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.99$ (t, 3H, CH_3), 1.05 (t, 3H, CH_3), 1.35 (m, 2H, $CH_2 \cdot CH_3$), 1.41 (d, 3H, $CHCH_3$), 1.55 (m, 2H, $CH_3CH_2CH_2$), 1.96 (m, 2H, $CHCH_2$), 2.0 (br, H, NH), 2.65 (m, 2H, $NHCH_2$), 2.70 (m, H, *CH*-S); ^{13}C NMR ($CDCl_3$) $\delta = 10.2$, 13.7, 20.2, 21.5, 31.2, 32.3, 40.1, 49.9, 223.4 ppm; MS: $m/z = 220$.

N′-(3-Nitrophenyl)-hydrazine Carbodithioc Acid 4-Methoxy Benzyl Ester (**6**, $C_{15}H_{15}N_3O_3S_2$)

Yield: 86%; yellow oil; IR (neat) $\ddot{v} = 678$, 1211 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.05$ (br, H, *NHPh* · *OMe*), 3.73 (s, 3H, OCH_3), 4.06 (br, H, $NHPh \cdot NO_2$), 6.65–7.66 (m, 8H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 38.3$, 56.7, 107.5, 114.6, 118.4, 128.5, 129.9, 133.6, 143.6, 148.7, 160.6, 223.2 ppm; MS: $m/z = 349$.

N′-(4-Nitrophenyl)-hydrazine Carbodithioc Acid Butyl Ester (**7**, $C_{11}H_{15}N_3O_2S_2$)

Yield: 86%; yellow oil; IR (neat) $\ddot{v} = 666$, 1203 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.96$ (t, 3H, CH_3), 1.33 (m, 2H, CH_2CH_3), 1.96 (m, 2H, $SCH_2 \cdot CH_2$), 2.05 (br, H, N*H*), 2.87 (t, 2H, SCH_2), 4.04 (br, N, $NHArNO_2$), 6.92–8.15 (m, 4H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 13.7$, 21.6, 32.2, 33.7, 113.5, 124.6, 138.8, 143.3, 223.5 ppm; MS: $m/z = 285$.

N′-(2,4-Dinitro-phenyl)hydrazinecarbodithioc Acid Butyl Ester (**8**, $C_{11}H_{14}N_4O_4S_2$)

Yield: 80%; yellow oil; IR (neat) $\ddot{v} = 670$, 1212 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.94$ (t, 3H, CH_3), 1.32 (m, 2H, CH_2CH_3), 1.95 (m, 2H, $SCH_2 \cdot CH_2$),

2.02 (br, H, N*H*), 2.83 (t, 2H, S*CH*$_2$), 4.04 (br, N, *NH*ArNO$_2$), 7.19–9.50 (m, 3H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 13.8$, 21.9, 32.3, 33.8, 113.6, 119.2, 130.2, 132.8, 139.7, 143.3, 222.5 ppm; MS: $m/z = 330$.

N′-Naphthalen-2-yl Hydrazine Carbodithioc Acid Butyl Ester (**9**, $C_{15}H_{18}N_2S_2$)

Yield: 83%, yellow oil; IR (neat) $\ddot{\nu} = 677$, 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.95$ (t, 3H, CH_3), 1.33 (m, 2H, *CH*$_2$CH$_3$), 1.97 (m, 2H, SCH$_2$ · *CH*$_2$), 2.05 (br, H, N*H*), 2.84 (t, 2H, S*CH*$_2$), 4.05 (br, N, *NH*ArNO$_2$), 6.76–7.55 (m, 7H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 13.9$, 22.1, 32.5, 33.9, 107.4, 117.2, 121.3, 124.5, 126.6, 127.2, 133.5, 142.6, 224.1 ppm; MS: $m/z = 290$.

N′-Phenyl-hydrazine Carbodithioc Acid 1-Butyl Pentyl Ester (**10**, $C_{16}H_{26}N_2S_2$)

Yield: 89%; yellow oil; IR (neat) $\ddot{\nu} = 677$, 1212 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.96$ (t, 6H, CH_3), 1.29 (m, 4H, *CH*$_2$CH$_2$CH), 1.33 (m, 4H, *CH*$_2$CH$_3$), 1.92 (m, 4H, CH*CH*$_2$), 2.05 (br, H, N*H*), 2.52 (t, H, S*CH*), 4.05 (br, H, *NH*Ar), 6.66–7.18 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 14.2$, 23.1, 28.5, 36.2, 41.4, 112.2, 119.3, 129.0, 142.4, 223.3 ppm; MS: $m/z = 310$.

N′-Phenyl-hydrazine Carbodithioc Acid 1,1-Dibutyl Pentyl Ester (**11**, $C_{20}H_{34}N_2S_2$)

Yield: 87%; yellow oil; IR (neat) $\ddot{\nu} = 669$, 1210 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.96$ (t, 6H, CH_3), 1.29 (m, 4H, *CH*$_2$CH$_2$C), 1.33 (m, 4H, *CH*$_2$CH$_3$), 1.88 (m, 4H, CH*CH*$_2$), 2.04 (br, H, N*H*), 4.0 (br, H, *NH*-Ar), 6.67–7.19 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 14.1$, 23.4, 26.7, 39.6, 41.1, 112.5, 119.3, 129.6, 142.2, 223.5 ppm; MS: $m/z = 366$.

N′-Butyl-hydrazine Carbodithioc Acid Hexyl Ester (**12**, $C_{11}H_{24}N_2S_2$)

Yield: 96%; yellow oil; IR (neat) $\ddot{\nu} = 674$, 1208 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.96$ (t, 6H, CH_3), 1.29 (m, 4H, *CH*$_2$*CH*$_2$CH$_2$CH$_3$), 1.33 (t, 2H, *CH*$_2$CH$_3$), 1.55 (m, 2H, NHCH$_2$*CH*$_2$), 1.96 (m, 2H, SCH$_2$*CH*$_2$), 2.0 (br, 2H, NH), 2.65 (t, 2H, NH*CH*$_2$), 2.87 (t, 2H, S*CH*$_2$); ^{13}C NMR ($CDCl_3$) $\delta = 13.7$, 14.1, 20.2, 23.1, 28.6, 31.5, 32.6, 49.9, 223.1 ppm; MS: $m/z = 248$.

N′-Phenyl-hydrazine Carbodithioc Acid n-Octyl Ester (**13**, $C_{15}H_{24}N_2S_2$)

Yield: 97%; yellow oil; IR (neat) $\ddot{v} = 679$, 1211 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.96$ (t, 3H, CH_3), 1.29 (m, 8H, CH_2), 1.33 (m, 2H, CH_2CH_3), 1.96 (m, 2H, SCH_2CH_2), 2.0 (br, H, NH), 2.88 (t, 2H, SCH_2), 4.0 (br, H, Ph · *NH*), 6.65–7.20 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 14.5$, 23.10, 28.9, 30.5, 31.5, 32.5, 112.2, 129.6, 118.9, 142.2, 223.6 ppm; MS: $m/z = 296$.

N′-Butyl Hydrazine Carbodithioc Acid Decyl Ester (**14**, $C_{15}H_{32}N_2S_2$)

Yield: 98%; yellow oil; IR (neat) $\ddot{v} = 673$, 1220 cm^{-1}; ^1H NMR ($CDCl_3$), $\delta = 0.97$ (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.29 (m, 12H, CH_2), 1.34 (m, 4H, CH_2CH_3), 1.55 (m, 2H, $CH_2CH_2CH_3$), 1.96 (m, 2H, SCH_2CH_2), 2.0 (br, 2H, NH · NH), 2.65 (m, 2H, $NHCH_2$), 2.87 (t, 2H, SCH_2); ^{13}C NMR ($CDCl_3$) · $\delta = 13.7$, 14.5, 20.3, 23.1, 28.9, 30.6, 30.9, 31.5, 32.5, 222.1 ppm; MS: $m/z = 304$.

N′-Phenyl Hydrazine Carbodithioc Acid 1-Propyl Butyl Ester (**15**, $C_{14}H_{22}N_2S_2$)

Yield: 86%; yellow oil; IR (neat) $\ddot{v} = 675$, 1210 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.97$ (s, 3H, CH_3), 1.33 (m, 4H, CH_2CH_3), 1.92 (m, 4H, $CHCH_2$), 2.0 (br, H, NH), 2.52 (m, H, C*H*-S), 4.1 (br, H, NH-Ar), 6.66–7.22 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$) $\delta = 14.5$, 20.1, 38.4, 40.8, 112.5, 118.3, 129.6, 143.3, 222.1 ppm; MS: $m/z = 282$.

N′-Phenyl Hydrazine Carbodithioc Acid 1-Phenyl Ethyl Ester (**16**, $C_{15}H_{16}N_2S_2$)

Yield: 83%; yellow oil; IR (neat) $\ddot{v} = 678$, 1210 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.69$ (d, 3H, CH_3), 2.2 (br, H, NH), 3.98 (m, H, *CH*-S), 4.2 (br, H, NH-Ar), 6.66–7.22 (m, 10H, Ar-H), ^{13}C NMR ($CDCl_3$) $\delta = 23.4$, 41.1, 112.5, 118.9, 126.5, 128.5, 129.7, 141.3, 142.5, 222.1 ppm; MS: $m/z = 288$.

ACKNOWLEDGMENTS

Authors thank the Sophisticated Analytical Instrument Facility (SIAF) division of Central Drug Research Institute (CDRI) for providing spectroscopic and analytical data.

REFERENCES

1. Ragnarsson, U. Synthetic methodologies for alkyl substituted hydrazines. *Chem. Soc. Rev.* **2001**, *30*, 205–213.
2. Schmidt, E. U. *Hydrazine and Its Derivatives: Preparation, Properties, Applications,* 2nd ed.; Wiley-Interscience: New York, 2001; pp. 1–86.
3. (a) Bharti, N.; Maurya, M. R.; Naqvi, F.; Azam, A. Synthesis and anti-amoebic activity of new cyclo-octadiene ruthenium (II) complexes with 2-acetylpyridine and benzimidazole derivatives. *Bio-Org. Med. Chem. Lett.* **2000**, *10*, 2243–2245; (b) Bharti, N.; Mannar, M. R.; Fehmida, N.; Bhattacharya, A.; Bhattacharya, S.; Azam, A. Palladium (II) complexes of NS donor ligend derived from S-methyl dithiocarbazate, S-benzyl dithiocarbazate, thiosemicarbazide as anti-amoebic agents. *Eur. J. Med. Chem.* **2000**, *35*, 481–486.
4. Sengupta, S.; Pandey, O. P.; Rao, G. P. Sugarcane pathology: Fungal disease. **1999**, *1*, 279–302.
5. (a) Connolly, T. J.; Crittal, A. J.; Ebrahim, A. S.; Ji, G. Development and scale up of a route to cyclohecylhydrazine dimethanesulfonate. *Org. Process. Res. Dev.* **2000**, *4*, 526–529; (b) Gordan, M. S.; Krause, J. G.; Linneman-Mohr, M. A.; Parchue, R. R. Hydrazides and hydrazones from carbazates. *Synthesis* **1980**, *3*, 244–246; (c) Hauser, M. J. The preparation and cyclization of some chloroethyl carbazates: Some clarifications. *J. Org. Chem.* **1966**, *31*, 968–970.
6. Wuts, P. G. M.; Greene, T. W. Greene's protective groups in organic synthesis (John Wiley & Sons, New York, 2006), pp. 706–887.
7. (a) Huang, J. Y.; Choi, H. S.; Lee, D. H.; Yoo, S. E.; Gong, Y. D. Solid phase synthesis of 5-amino-1-(substituted thiocarbomyl) pyrazole and 1, 2, 4-triazole derivatives via dithiocarbazate linker. *J. Comb. Chem.* **2005**, *7*, 136–141; (b) Hwang, J. Y.; Choi, H. S.; Lee, D. H.; Gong, Y. D. Solid phase synthesis of 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives via selective reagent based cyclization of acyldithiocarbazate resins. *J. Comb. Chem.* **2005**, *7*, 816–819.
8. (a) Bolzati, C.; Benini, E.; Cavazza-Ceccato, M.; Cozzala, E.; Malago, E.; Agostini, S.; Tisato, F.; Rofosco, F.; Bandoli, G. From symmetrical to assymetrical nitrido, phosphino-thiol complexes: A new class of neutral mixed ligends ^{99m}TC compounds as potential brain imaging agents. *Bioconjugate Chem.* **2006**, *17*, 419–428; (b) Ali, M. A.; Mirza, A. H.; Butcher, R. J.; Krause, K. A. The preparation, characterization and biological activity of palladium (II) and platinum (II) complexes of tridentate NNS ligends derived from S-methyl and S-benzyldithiocarbazates and x-ray crystal structure of the [Pd(mpasme)cl] complexes. *Transition Met. Chem. (N.Y.)* **2006**, *31*, 79–87.
9. Dyker, H.; Scherkenbeck, J.; Gondol, D.; Goehrt, A.; Harder, A. Azadepsipetides: Synthesis and evaluation of a novel class of peptidomimetics. *J. Org. Chem.* **2001**, *66*, 3760–3766.
10. Nara, S.; Sakamoto, T.; Miyazawa, E.; Kikugawa, Y. A convenient synthesis of 1-alkyl 1-phenylhydrazines from 1-aminopthalimide. *Synth. Commun.* **2003**, *33*, 87–98.
11. Fox, D. L.; Ruxer, J. T.; Oliver, R. M.; Alford, K. L.; Salvatore, R. N. Mild and efficient synthesis of carbazates and dithiocarbazates via a three component coupling using Cs_2CO_3 and TBAI. *Tetrahedron Lett.* **2004**, *45*, 401–405.

12. For reviews, see (a) Chaturvedi, D.; Ray, S. Versatile use of carbon dioxide in the synthesis of organic carbamates. *Curr. Org. Chem.* **2007**, *11*, 987–998; (b) Chaturvedi, D.; Misra, N.; Mishra, V. Various approaches for the synthesis of organic carbamates. *Curr. Org. Synth.* **2007**, *3*, 308–320; For our research work, see (c) Chaturvedi, D.; Kumar, A.; Ray, S. An efficient, one-pot synthesis of carbamate esters through alcoholic tosylates. *Synth. Commun.* **2002**, *32*, 2651–2655; (d) Chaturvedi, D.; Kumar, A.; Ray, S. A high-yielding, one-pot novel synthesis of carbamate esters from corresponding alcohols using Mitsunobu's reagent. *Tetrahedron Lett.* **2003**, *44*, 7637–7639; (e) Chaturvedi, D.; Ray, S. An efficient, one-pot, basic resin catalyzed, novel synthesis of carbamate esters through alcoholic tosylayes. *Lett. Org. Chem.* **2005**, *2*, 742–744; (f) Chaturvedi, D.; Ray, S. An efficient, basic resin mediated, one-pot synthesis of dithiocarbamate esters through alcoholic tosylates. *J. Sulfur Chem.* **2005**, *26*, 365–371; (g) Chaturvedi, D.; Ray, S. An efficient, basic resin mediated, one-pot synthesis of O-alkyl S-methyl dithiocarbonates from the corresponding alcohols. *J. Sulfur Chem.* **2006**, *27*, 265–271; (h) Chaturvedi, D.; Ray, S. An efficient, one-pot synthesis of dithiocarbamates from the corresponding alcohols using Mitsunobu's reagent. *Tetrahedron Lett.* **2006**, *47*, 1307–1309; (i) Chaturvedi, D.; Mishra, N.; Mishra, V. An efficient and novel synthesis of carbamate esters from the coupling of amines, halides, and carbon dioxide in the presence of basic resin. *Chin. Chem. Lett.* **2006**, *17*, 1309–1312; (j) Chaturvedi, D.; Ray, S. A high-yielding, one-pot synthesis of O,S-dialkyl dithiocarbonates from alcohols using Mitsunobu's reagent. *Tetrahedron Lett.* **2007**, *48*, 149–151; (k) Chaturvedi, D.; Mishra, N.; Mishra, V. An efficient, basic resin mediated, one-pot synthesis of dithiocarbamates by Michael addition of dithiocarbamate to activated olefins. *J. Sulfur Chem.* **2007**, *28*, 39–44; (l) Chaturvedi, D.; Mishra, N.; Mishra, V. A high-yielding, one-pot synthesis of dialkylcarbonates from alcohols using Mitsunobu's reagent. *Tetrahedron Lett.* **2007**, *48*, 5043–5045; (m) Chaturvedi, D.; Mishra, N.; Mishra, V. An efficient, one-pot synthesis of S-alkyl thiocarbamates from the corresponding thiols using Mitsunobu's reagent. *Synthesis* **2008**, 355–357.

13. (a) Chaturvedi, D.; Ray, S. A high-yielding, one-pot, Triton-B-catalyzed expeditious synthesis of carbamate esters through four-component coupling methodology. *Monatsh. Chem.* **2006**, *137*, 201–206; (b) Chaturvedi, D.; Ray, S. Triton-B-catalyzed, efficient, one-pot synthesis of dithiocarbamate esters. *Monatsh. Chem.* **2006**, *137*, 311–317; (c) Chaturvedi, D.; Ray, S. Triton-B-catalyzed, efficient, one-pot synthesis of carbamate esters from alcoholic tosylates. *Monatsh. Chem.* **2006**, *137*, 459–463; (d) Chaturvedi, D.; Ray, S. A high yielding, one-pot synthesis of dithiocarbamates using alcoholic tosylates. *Monatsh. Chem.* **2006**, *137*, 465–459; (e) Chaturvedi, D.; Ray, S. An efficient, one-pot, Triton-B-catalyzed synthesis of O-alkyl S-methyl dithiocarbonates. *Monatsh. Chem.* **2006**, *137*, 1219–1223.

14. Kabalka, G. W.; Varma, M.; Varma, R. S.; Srivastava, P. C.; Knapp, F. F. Tosylation of alcohols. *J. Org. Chem.* **1986**, *51*, 2386–2388.