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$PhI(OAc)_2$-mediated additions of 2,4-dinitrophenylsulfenamide with methylenecyclopropanes (MCPs) and a methylenecyclobutane (MCB)

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Abstract—We report herein stereoselective additions of a nitrene derived from $PhI(OAc)_2$ and 2,4-dinitrophenylsulfenamide with methylenecyclopropanes (MCPs) and a methylenecyclobutane (MCB) to give the corresponding ring enlargement products, (cyclobutylidene)amide or (cyclopentylidene)amide derivatives, in moderate to excellent yields. The reaction mechanism has been discussed on the basis of control experiments and previous investigation.

1. Introduction

Thermal and photochemical skeleton rearrangements of highly strained small rings with multiple bonds and functional groups have attracted much attention from both synthetic and mechanistic viewpoints. At the core of these developments resides the multifaceted reactivity of methylidenecyclopropanes, for which a wide variety of transformations have been discovered.[1,2] Recently, Yu and co-workers reported *N*-aminophthalimide and diacetoxyiodobenzene [$PhI(OAc)_2$] as the nitrene equivalent mediated metal-free ring expansions of alkylidenecyclopropanes and an alkylidenecyclobutane to give a series of aryl-substituted cyclobutylidene and cyclopentylidene hydrazine derivatives under mild conditions in moderate to good yields.[3] However, in some cases, the corresponding cyclobutylidene hydrazine derivatives were obtained as separable *Z*- and *E*-isomers. In this paper, we wish to report another example of stereoselective additions of a nitrene derived from $PhI(OAc)_2$ and 2,4-dinitrophenylsulfenamide with methylenecyclopropanes (MCPs) to exclusively give the corresponding ring enlargement products as *E*-configuration in moderate to excellent yields.[4] The reaction mechanism has also been discussed on the basis of control experiments and previous investigation.

Keywords: $PhI(OAc)_2$; 2,4-Dinitrophenylsulfenamide; Nitrene; Methylenecyclopropanes (MCPs); Methylenecyclobutane; Stereoselective addition.
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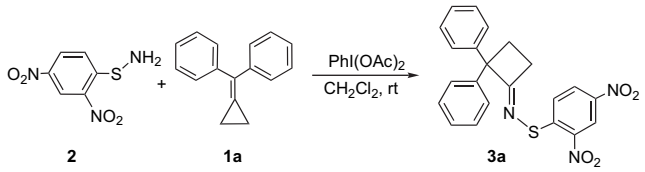
2. Results and discussion

Initial examination was carried out by the reaction of diphenylmethylenecyclopropane **1a** (37 mg, 0.18 mmol) with 2,4-dinitrophenylsulfenamide **2** (38.5 mg, 0.18 mmol, 1.0 equiv) mediated by $PhI(OAc)_2$ (58 mg, 0.18 mmol, 1.0 equiv) in dichloromethane (3.0 mL).[5] The reaction proceeded smoothly to exclusively give the corresponding ring enlargement product **3a** in 91% yield as *E*-configuration at room temperature (20 °C) after 24 h (Table 1, entry 1). Then, the employed amounts of **2** and $PhI(OAc)_2$ were carefully examined in dichloromethane, and it was found that **3a** was obtained in 98% yield in the presence of 1.2 equiv of **2** and 1.2 equiv of $PhI(OAc)_2$ under otherwise identical conditions within 4 h (Table 1, entries 2–4). In the presence of 0.5 equiv of $PhI(OAc)_2$, the reaction became sluggish to give **3a** in 53% yield after 48 h, indicating that stoichiometric amount of $PhI(OAc)_2$ is required (Table 1, entry 5). The examination of various solvents revealed that 1,2-dichloroethane and dichloromethane are optimal for the reaction (Table 1, entries 5–11). The *E*-configuration of **3a** was unambiguously determined by X-ray diffraction (Fig. 1).[6]

With these optimized reaction conditions in hand, we next turned our interest to the reaction generality. A variety of methylenecyclopropanes **1** were examined under these optimal conditions. As for disubstituted MCPs **1b–j** (R^1=aromatic and R^2=aromatic or alkyl group), all of the reactions proceeded smoothly to afford the corresponding ring enlargement products **3** in good to excellent yields as single isomers (Table 2, entries 1–9).

Table 1. $PhI(OAc)_2$-mediated additions of 2,4-dinitrophenylsulfenamide **2** with diphenylmethylenecyclopropane **1a**



2 **1a** **3a**

Entry	Solvent	**2** (equiv)	$PhI(OAc)_2$ (equiv)	Time (h)	Yield[a] (%) **3a**
1	CH_2Cl_2	1.0	1.0	24	91
2	CH_2Cl_2	1.0	1.2	24	90
3	CH_2Cl_2	1.2	1.0	4	91
4	CH_2Cl_2	1.2	1.2	4	98
5[b]	CH_2Cl_2	1.2	0.5	48	53
6	PhMe	1.2	1.2	24	84
7[c]	MeCN	1.2	1.2	24	78
8	Et_2O	1.2	1.2	24	85
9[d]	THF	1.2	1.2	24	53
10[e]	Hexane	1.2	1.2	24	54
11	$ClCH_2CH_2Cl$	1.2	1.2	24	98

[a] Isolated yields.
[b] Recovered **1a**: 30%.
[c] Recovered **1a**: 21%.
[d] Recovered **1a**: 32%.
[e] Recovered **1a**: 40%.

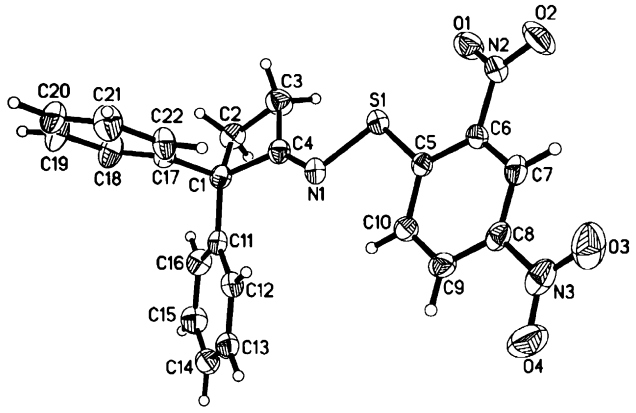
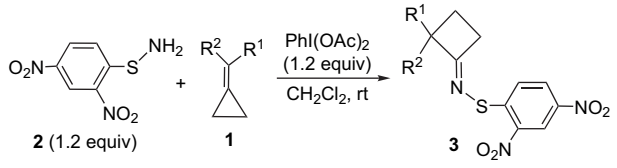


Figure 1. ORTEP drawing of **3a**.

Table 2. $PhI(OAc)_2$-mediated additions of 2,4-dinitrophenylsulfenamide **2** with various methylenecyclopropanes (MCPs) **1** under the optimized conditions

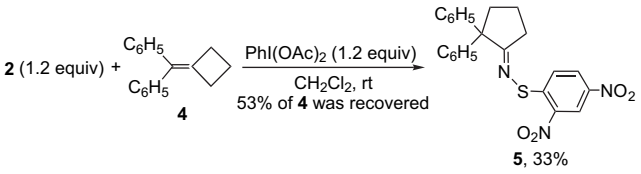


2 (1.2 equiv) **1** **3**

Entry	R^1/R^2	Time (h)	Yield[a] (%)
1	*p*-MeC_6H_4/*p*-MeC_6H_4, **1b**	3	**3b**, 99
2	*m*,*p*-$Me_2C_6H_3$/C_6H_5, **1c**	3	**3c**, 91
3	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$, **1d**	2	**3d**, 96
4	*p*-$MeOC_6H_4$/C_6H_5, **1e**	2	**3e**, 99
5	*p*-FC_6H_4/*p*-FC_6H_4, **1f**	3	**3f**, 84
6	*p*-ClC_6H_4/*p*-ClC_6H_4, **1g**	3	**3g**, 66
7	*p*-ClC_6H_4/C_6H_5, **1h**	3	**3h**, 69
8	C_6H_5/CH_3, **1i**	4	**3i**, 67
9	*p*-$EtOC_6H_4/CH_3$, **1j**	3	**3j**, 52

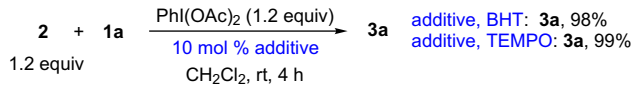
[a] Isolated yield.

As for methylenecyclobutane **4**, the corresponding ring enlargement product **5** was obtained in 33% yield along with 53% recovery of the starting material **4** under identical conditions, suggesting that a highly strained three-membered ring is essential to give the corresponding ring enlargement product in good yield (Scheme 1).



Scheme 1. $PhI(OAc)_2$-mediated addition of 2,4-dinitrophenylsulfenamide **2** with diphenylmethylenecyclobutane **4**.

To further understand this interesting ring enlargement reaction, two control experiments using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) as the radical inhibitors were performed under the standard conditions (Scheme 2). We confirmed that this addition reaction under these optimized conditions was unaffected by the addition of these radical inhibitors, rendering unlikely the intervention of a radical or a biradical pathway.

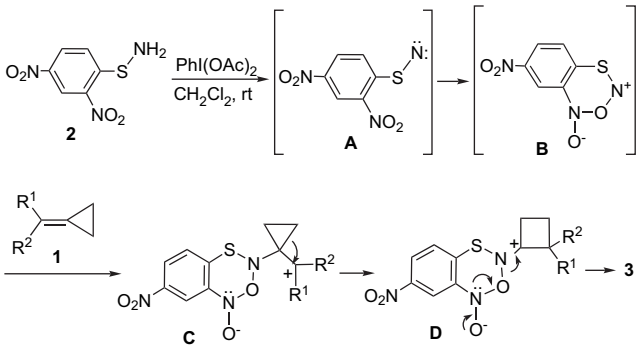


Scheme 2. $PhI(OAc)_2$-mediated additions of 2,4-dinitrophenylsulfenamide **2** with diphenylmethylenecyclopropane **1a** in the presence of BHT and TEMPO.

It has been reported that oxidation of 2,4-dinitrophenylsulfenamide **2** with lead tetraacetate in the presence of (*Z*)-1-phenylpropene gives a ca. 3:1 mixture of *cis*- and *trans*-aziridines, indicating that both singlet nitrene and triplet nitrene should be involved in a free nitrene addition reaction.[5] Since a sulfur atom stabilized triplet nitrene is a biradical species,[7] it can be trapped by a radical inhibitor. We believe that a free nitrene species derived from $PhI(OAc)_2$ and 2,4-dinitrophenylsulfenamide is not directly involved in the addition reaction to MCPs **1**. In addition, it should be emphasized here that an *ortho*-position nitro-group in sulfenamide is required for the addition of a nitrene to alkenes because no reaction occurred while using 4-nitrophenylsulfenamide to replace 2,4-dinitrophenylsulfenamide **2** under identical conditions.

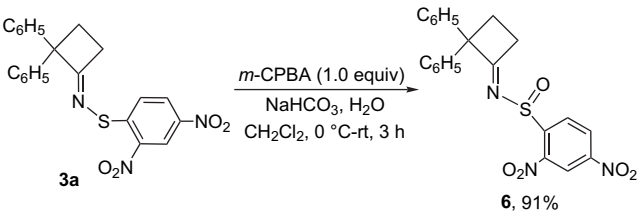
On the basis of above control experiments, a plausible mechanism has been outlined in Scheme 3. The generated nitrene species **A** bearing a nitro-group in the *ortho*-position affords a zwitterionic intermediate **B** as a neighboring group participation,[5] which adds to MCP **1** to give the corresponding intermediate **C**. The rearrangement of intermediate **C** gives ring expanded cyclobutyl cation **D**,[8] which affords the final product **3** (Scheme 3).[9] The steric repulsion between 2,4-dinitrophenylsulfenyl group and R^1 and R^2 groups leads to the formation of **3** in *E*-configuration exclusively.

The obtained 2,4-dinitrobenzenesulfinic acid (2,2-diphenylcyclobutylidene)amide **3a** can be transformed to the corresponding sulfoxide **6** in 91% yield with *m*-CPBA in



Scheme 3. Plausible reaction mechanism.

dichloromethane in the presence of $NaHCO_3$ after 3 h (Scheme 4). The structure of **6** was also unambiguously determined by X-ray diffraction (Fig. 2).[10]



Scheme 4. Further transformation of **3a** with *m*-CPBA.

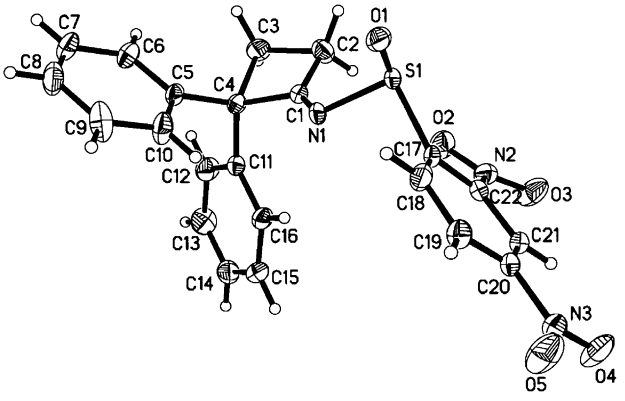


Figure 2. ORTEP drawing of **6**.

In conclusion, we have found an interesting and stereoselective addition of a nitrene derived from $PhI(OAc)_2$ and 2,4-dinitrophenylsulfenamide with methylenecyclopropanes (MCPs) or a methylenecyclobutane (MCB) to give the corresponding ring enlargement products in moderate to excellent yields. A variety of (cyclobutylidene)amide derivatives were obtained under mild conditions and the reaction mechanism has been discussed on the basis of control experiments and previous investigation. Efforts are underway to elucidate the mechanistic details and the scope and limitations of this reaction in the laboratory.

3. Experimental section

3.1. General remarks

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass and HRMS spectra were recorded by EI methods. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

3.2. General procedure for the addition reaction

Methylenecyclopropanes **1** (37 mg, 0.18 mmol), 2,4-dinitrophenylsulfenamide **2** (47 mg, 0.22 mmol), $PhI(OAc)_2$ (98% purity, 71 mg, 0.22 mmol), and CH_2Cl_2 (3.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and then the residue was purified by flash column chromatography on silica gel (300–400 mesh) with EtOAc–petroleum ether (EtOAc=5–10%) as eluent to afford the pure product.

3.3. General procedure for the oxidation reaction of 3a

The compound **3a** (146 mg, 0.35 mmol), $NaHCO_3$ (132 mg, 1.57 mmol) in 6.0 mL of water, and 15 mL of CH_2Cl_2 were added into a 50 mL flask, then cooled to 0 °C by an ice-water bath. Then *m*-CPBA (85% purity, 78 mg, 0.36 mmol) in 15 mL of CH_2Cl_2 was added into the stirring mixture dropwise during 30 min, and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by the addition of saturated aqueous Na_2SO_3 solution (10 mL), and the reaction mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed by brine (2×20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and then the residue was purified by flash column chromatography on silica gel (300–400 mesh) with EtOAc–petroleum ether (EtOAc=25%) as eluent to afford the pure product.

3.3.1. Product 3a. A yellow solid, mp: 194–196 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.97 (t, 2H, J=8.1 Hz, CH_2), 3.18 (t, 2H, J=8.1 Hz, CH_2), 7.21–7.48 (m, 10H, Ar), 8.46 (dd, 1H, J=9.0, 2.1 Hz, Ar), 8.66 (d, 1H, J=9.0 Hz, Ar), 9.15 (d, 1H, J=2.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.1, 34.0, 67.6, 121.2, 126.6, 126.9, 127.0, 127.4, 128.6, 141.3, 143.6, 144.3, 148.2, 180.9. IR (CH_2Cl_2) ν 3105, 2991, 1650, 1589, 1512, 1447, 1395, 1304, 1115, 1086, 1053, 907, 846, 746, 735, 704, 604, 532 cm^{-1}. MS (%) *m*/*z* 220 (100, M^+−2,4-dinitrophenylsulfenyl), 165 (41), 179 (37), 180 (29), 178 (26), 219 (25), 84 (22), 221 (18). Anal. Calcd for $C_{22}H_{17}N_3O_4S$: C, 63.00%; H, 4.09%; N, 10.02%. Found: C, 63.25%; H, 4.38%; N, 10.10%.

3.3.2. Product 3b. A yellow solid, mp: 198–200 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.32 (s, 6H, CH_3), 2.90 (t, 2H, J=8.1 Hz, CH_2), 3.16 (t, 2H, J=8.1 Hz, CH_2), 7.14 (d, 4H, J=8.1 Hz, Ar), 7.33 (d, 4H, J=8.1 Hz, Ar), 8.46 (dd, 1H, J=9.0, 2.1 Hz, Ar), 8.66 (d, 1H, J=9.0 Hz, Ar), 9.16 (d, 1H, J=2.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.0, 29.1, 34.0, 67.1, 121.2, 126.5, 127.1, 127.4, 129.3, 136.6, 140.9, 141.3, 144.3, 148.4, 181.4. IR (CH_2Cl_2) ν 3096, 2919, 1652, 1595, 1446, 1339, 1305, 1135, 1052, 917, 832, 735, 540 cm^{-1}. MS (%) *m*/*z* 248 (100, M^+−2,4-dinitrophenylsulfenyl), 247 (39), 232 (36),

208 (23), 178 (22), 193 (21), 249 (21), 192 (12). Anal. Calcd for $C_{24}H_{21}N_3O_4S$: C, 64.41%; H, 4.73%; N, 9.39%. Found: C, 64.74%; H, 4.74%; N, 9.45%.

3.3.3. Product 3c. A yellow solid, mp: 162–164 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.22 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.93 (t, 2H, J=7.8 Hz, CH_2), 3.15 (t, 2H, J=7.8 Hz, CH_2), 7.08–7.48 (m, 8H, Ar), 8.42 (dd, 1H, J=9.3, 2.4 Hz, Ar), 8.66 (d, 1H, J=9.3 Hz, Ar), 9.13 (d, 1H, J=2.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.3, 20.0, 29.1, 34.0, 67.3, 121.1, 124.0, 126.5, 126.8, 127.0, 127.3, 127.8, 128.5, 129.7, 135.3, 136.8, 141.1, 141.2, 143.9, 144.2, 148.3, 181.3. IR (CH_2Cl_2) ν 3105, 2962, 2923, 2854, 1652, 1595, 1519, 1447, 1339, 1304, 1135, 1089, 1052, 917, 832, 746, 735, 699, 613 cm^{-1}. MS (%) m/z 248 (100, M^+−2,4-dinitrophenylsulfenyl), 247 (80), 232 (46), 178 (28), 246 (26), 249 (21), 193 (20), 208 (20). Anal. Calcd for $C_{24}H_{21}N_3O_4S$: C, 64.41%; H, 4.73%; N, 9.39%. Found: C, 64.59%; H, 4.94%; N, 9.46%.

3.3.4. Product 3d. A yellow solid, mp: 216–218 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.88 (t, 2H, J=8.1 Hz, CH_2), 3.17 (t, 2H, J=8.1 Hz, CH_2), 3.79 (s, 6H, 2OCH_3), 6.87 (dd, 4H, J=6.6, 2.1 Hz, Ar), 7.33 (dd, 4H, J=6.6, 2.1 Hz, Ar), 8.46 (dd, 1H, J=9.3, 2.7 Hz, Ar), 8.63 (d, 1H, J=9.3 Hz, Ar), 9.17 (d, 1H, J=2.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.4, 34.0, 55.3, 66.5, 113.9, 121.2, 127.1, 127.4, 127.8, 136.0, 141.3, 144.3, 148.4, 158.4, 181.7. IR (CH_2Cl_2) ν 2956, 2925, 2854, 1646, 1595, 1509, 1462, 1340, 1303, 1248, 1177, 1088, 1027, 832, 735 cm^{-1}. MS (%) m/z 280 (100, M^+−2,4-dinitrophenylsulfenyl), 279 (58), 248 (29), 281 (22), 225 (21), 240 (19), 165 (13), 152 (9). Anal. Calcd for $C_{24}H_{21}N_3O_6S$: C, 60.12%; H, 4.41%; N, 8.76%. Found: C, 60.05%; H, 4.50%; N, 8.64%.

3.3.5. Product 3e. A yellow solid, mp: 170–172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.92 (t, 2H, J=8.1 Hz, CH_2), 3.17 (t, 2H, J=8.1 Hz, CH_2), 3.78 (s, 3H, OCH_3), 6.87 (d, 2H, J=9.0 Hz, Ar), 7.23–7.37 (m, 5H, Ar), 7.45 (d, 2H, J=9.0 Hz, Ar), 8.45 (dd, 1H, J=9.0, 2.1 Hz, Ar), 8.64 (d, 1H, J=9.0 Hz, Ar), 9.15 (d, 1H, J=2.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.2, 34.0, 55.2, 67.0, 113.9, 121.2, 126.6, 126.8, 127.1, 127.4, 127.8, 128.6, 135.7, 141.3, 143.9, 144.3, 148.3, 158.4, 181.3. IR (CH_2Cl_2) ν 3105, 3002, 2961, 2836, 1653, 1594, 1510, 1446, 1393, 1340, 1304, 1249, 1180, 1135, 1089, 1052, 1024, 917, 832, 735, 700, 612, 573, 545 cm^{-1}. MS (%) m/z 250 (100, M^+−2,4-dinitrophenylsulfenyl), 249 (72), 210 (32), 248 (32), 165 (27), 251 (19), 152 (19), 178 (18). Anal. Calcd for $C_{23}H_{19}N_3O_5S$: C, 61.46%; H, 4.26%; N, 9.35%. Found: C, 61.64%; H, 4.46%; N, 9.38%.

3.3.6. Product 3f. A yellow solid, mp: 204–206 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.92 (t, 2H, J=8.4 Hz, CH_2), 3.20 (t, 2H, J=8.4 Hz, CH_2), 7.01–7.07 (m, 4H, Ar), 7.36–7.41 (m, 4H, Ar), 8.49 (dd, 1H, J=9.3, 2.4 Hz, Ar), 8.59 (d, 1H, J=9.3 Hz, Ar), 9.17 (d, 1H, J=2.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.4, 34.1, 66.4, 115.6 (d, J_{C-F}=21.2 Hz), 121.3, 126.9, 127.5, 128.3 (d, J_{C-F}=8.0 Hz), 139.2, 141.4, 144.5, 147.9, 161.7 (d, J_{C-F}=240.0 Hz), 163.3, 180.3. IR (CH_2Cl_2) ν 3106, 1654, 1595, 1506, 1340, 1305, 1232, 1160, 1136, 1089, 1052, 917, 832, 735, 547 cm^{-1}. MS (%) m/z 256 (100, M^+−2,4-dinitrophenylsulfenyl), 201 (85), 216 (80), 255 (35), 215 (33), 203 (27), 214 (26), 257 (21). Anal. Calcd for $C_{22}H_{15}F_2N_3O_4S$: C, 58.02%; H, 3.32%; N, 9.23%. Found: C, 58.33%; H, 3.59%; N, 9.09%.

3.3.7. Product 3g. A yellow solid, mp: 224–226 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.91 (t, 2H, J=8.4 Hz, CH_2), 3.20 (t, 2H, J=8.4 Hz, CH_2), 7.30–7.37 (m, 8H, Ar), 8.50 (dd, 1H, J=9.0, 2.4 Hz, Ar), 8.58 (d, 1H, J=9.0 Hz, Ar), 9.18 (d, 1H, J=2.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.2, 34.1, 66.5, 121.3, 126.8, 127.5, 128.0, 128.9, 133.1, 141.4, 141.6, 144.5, 147.7, 179.6. IR (CH_2Cl_2) ν 3098, 1655, 1594, 1518, 1490, 1401, 1339, 1305, 1092, 1052, 1011, 832, 735, 535 cm^{-1}. MS (%) m/z 288 (100, M^+−2,4-dinitrophenylsulfenyl), 252 (77), 290 (69), 178 (58), 289 (53), 44 (49), 248 (48), 287 (42). Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_4S$: C, 54.11%; H, 3.10%; N, 8.60%. Found: C, 54.01%; H, 3.33%; N, 8.59%.

3.3.8. Product 3h. A yellow solid, mp: 188–190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.95 (t, 2H, J=8.4 Hz, CH_2), 3.19 (t, 2H, J=8.4 Hz, CH_2), 7.26–7.45 (m, 9H, Ar), 8.48 (dd, 1H, J=9.0, 2.4 Hz, Ar), 8.62 (d, 1H, J=9.0 Hz, Ar), 9.17 (d, 1H, J=2.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.1, 34.1, 67.1, 121.2, 126.6, 127.0, 127.2, 127.5, 128.1, 128.7, 128.8, 132.9, 141.4, 142.1, 143.1, 144.4, 148.0, 180.3. IR (CH_2Cl_2) ν 3105, 2959, 2925, 2853, 1653, 1594, 1519, 1490, 1447, 1399, 1339, 1304, 1236, 1196, 1135, 1092, 1052, 1012, 918, 832, 747, 735, 718, 699, 535 cm^{-1}. MS (%) m/z 254 (100, M^+−2,4-dinitrophenylsulfenyl), 253 (88), 218 (86), 178 (56), 255 (48), 191 (47), 165 (43), 140 (38). Anal. Calcd for $C_{22}H_{16}ClN_3O_4S$: C, 58.21%; H, 3.55%; N, 9.26%. Found: C, 58.15%; H, 3.75%; N, 9.22%.

3.3.9. Product 3i. A yellow solid, mp: 160–162 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.67 (s, 3H, CH_3), 2.31 (m, 1H, CH), 2.65 (m, 1H, CH), 3.15 (m, 2H, CH_2), 7.26–7.50 (m, 5H, Ar), 8.49 (dd, 1H, J=9.6, 2.7 Hz, Ar), 8.70 (d, 1H, J=9.6 Hz, Ar), 9.18 (d, 1H, J=2.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 28.5, 29.0, 33.5, 59.9, 121.2, 125.7, 126.7, 127.0, 127.3, 128.6, 141.2, 144.1, 144.2, 148.4, 183.5. IR (CH_2Cl_2) ν 3092, 2923, 2854, 1657, 1586, 1514, 1446, 1335, 1303, 1134, 1089, 1053, 914, 839, 767, 746, 733, 702 cm^{-1}. MS (%) m/z 158 (100, M^+−2,4-dinitrophenylsulfenyl), 117 (55), 115 (40), 157 (34), 91 (28), 103 (24), 77 (21), 156 (19). Anal. Calcd for $C_{17}H_{15}N_3O_4S$: C, 57.13%; H, 4.23%; N, 11.76%. Found: C, 57.13%; H, 4.44%; N, 11.82%.

3.3.10. Product 3j. A yellow solid, mp: 176–178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.35 (t, 3H, J=7.2 Hz, CH_3), 1.56 (s, 3H, CH_3), 2.14–2.24 (m, 1H, CH), 2.47–2.56 (m, 1H, CH), 2.94–3.17 (m, 2H, CH_2), 3.96 (q, 2H, J=7.2 Hz, OCH_2), 6.83 (d, 2H, J=8.4 Hz, Ar), 7.30 (d, 2H, J=8.4 Hz, Ar), 8.41 (d, 1H, J=9.0 Hz, Ar), 8.62 (d, 1H, J=9.0 Hz, Ar), 9.11 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.8, 28.4, 29.1, 33.5, 59.3, 63.5, 114.4, 121.2, 126.8, 127.0, 127.3, 136.0, 141.2, 144.2, 148.6, 157.7, 183.9. IR (CH_2Cl_2) ν 3096, 2962, 1649, 1586, 1515, 1477, 1335, 1303, 1250, 1231, 1177, 1089, 1045, 915, 839, 800, 733, 677 cm^{-1}. MS (%) m/z 202 (100, M^+−2,4-dinitrophenylsulfenyl), 174 (34), 134 (24), 43 (22), 57 (19), 55

(18), 69 (17), 203 (17). Anal. Calcd for $C_{19}H_{19}N_3O_5S$: C, 56.85%; H, 4.77%; N, 10.47%. Found: C, 56.98%; H, 4.87%; N, 10.68%.

3.3.11. Product 5. A yellow solid, mp: 178–180 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.90–2.00 (m, 2H, CH_2), 2.67–2.78 (m, 4H, $2CH_2$), 7.22–7.36 (m, 10H, Ar), 8.22 (dd, 1H, J=9.0, 2.1 Hz, Ar), 8.28 (d, 1H, J=9.0 Hz, Ar), 9.10 (d, 1H, J=2.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.9, 34.1, 39.3, 63.7, 121.0, 126.7, 126.8, 127.1, 127.5, 128.0, 128.2, 128.3, 128.4, 141.4, 143.7, 144.3, 148.6, 184.6. IR (CH_2Cl_2) ν 3085, 2918, 1736, 1623, 1594, 1446, 1340, 1305, 1134, 1088, 1051, 832, 735, 700 cm^{-1}. MS (%) m/z 234 (80, M^+−2,4-dinitrophenylsulfenyl), 193 (100), 115 (99), 178 (48), 165 (41), 91 (39), 233 (38), 167 (29). Anal. Calcd for $C_{23}H_{19}N_3O_4S$: C, 63.73%; H, 4.42%; N, 9.69%. Found: C, 63.35%; H, 4.64%; N, 9.67%.

3.3.12. Product 6. A yellow solid, mp: 120–122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.92–2.99 (m, 2H, CH_2), 3.53–3.60 (m, 2H, CH_2), 7.10–7.26 (m, 10H, Ar), 8.53 (d, 1H, J=8.7 Hz, Ar), 8.67 (dd, 1H, J=8.7, 2.1 Hz, Ar), 9.01 (d, 1H, J=2.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.8, 35.1, 67.9, 120.4, 126.4, 126.9, 127.0, 128.1, 128.49, 128.53, 128.7, 142.4, 142.6, 145.8, 149.2, 149.4, 193.1. IR (CH_2Cl_2) ν 3060, 2959, 2924, 2851, 1780, 1649, 1597, 1538, 1492, 1447, 1345, 1193, 1157, 1080, 1023, 833, 745, 702, 573, 527 cm^{-1}. MS (%) m/z 219 (100, M^+−2,4-dinitrophenylsulfenyl), 218 (64), 192 (41), 165 (32), 191 (29), 178 (27), 141 (25), 220 (19). Anal. Calcd for $C_{22}H_{17}N_3O_5S$: C, 60.68%; H, 3.93%; N, 9.65%. Found: C, 60.60%; H, 4.14%; N, 9.78%.

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Supplementary data

The spectroscopic charts (^{1}H, ^{13}C spectroscopic data) of the compounds shown in Tables 1 and 2 and Schemes 1–4 and the X-ray crystal structures of compounds **3a** and **6** are included in the Supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.062.

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