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Azidosulfonylation of alkenes, dienes, and enynes

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ABSTRACT

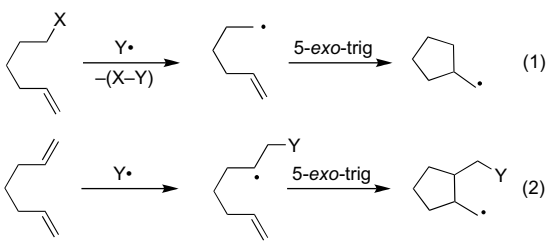
The radical mediated azidosulfonylation of various alkenes and alkynes that are able to undergo a rapid radical rearrangement is reported. For instance, treatment of 1,6-dienes or 1-en-6-ynes with benzenesulfonyl azide affords cyclic azidosulfones. High yields are observed when tertiary alkyl radicals are azidated in the last step of the cascade process. The azidosulfonylation of β-pinene involving ring opening of the bicyclic skeleton is also reported.

1. Introduction

Radical reactions represent a unique tool for the ring-closing and ring-opening reactions.[1] Most radical chain reactions are based on the generation of the starting radicals from alkyl halides and chalcogenides. A general representation of a 5-*exo*-*trig* cyclization process is depicted in Scheme 1 (Eq. 1). In this example, the radical Y• abstracts an atom X to generate the radical that undergoes the cyclization process. For this approach, stannyl radicals (Y•=R_3Sn•) are frequently used due to their unique ability to abstract halogen and chalcogen atoms. An alternative procedure consists of adding a radical to alkenes and alkynes to generate the starting radical as shown in Scheme 1 (Eq. 2). Interestingly, this second approach is not limited to the use of stannyl radicals and excellent results are also obtained with thiyl and sulfonyl radicals (Y=RS• and $RSO_2^•$) that are known to add efficiently and rapidly to alkenes.

The free-radical cyclization reaction of 1,6-dienes with thiyl radicals is well documented and involves in most cases thiols as reagents[2] (for a typical example, see Scheme 2, Eq. 3).[3] Sulfonyl radicals have been used for similar cyclization reactions and, interestingly, they offer the possibility to terminate the chain process by a variety of C–X (X=halogen or SeR) and C–C bonds when sulfonyl halides, selenides (Scheme 2, Eq. 4),[4] and cyanides are used.[5] So far, no examples involving the formation of a C–N bond in the terminal step has been developed.

Recently, we reported the use of sulfonyl azides as very efficient radical traps for secondary and tertiary alkyl radicals.[6,7] For instance, sulfonyl azides have been used as a key reagent for the carbazidation of olefins (Scheme 3, Eq. 5).[8] In this process, the benzenesulfonyl radical resulting from the azidation step is used to generate an electrophilic carbon centered radical that efficiently adds to olefins. This takes place via reaction of the sulfonyl radical with hexabutylditin affording a tin radical that rapidly abstracts the iodine atom. The azidosulfonylation of the olefin (Scheme 3, Eq. 6) is a potential side reaction of the carboazidation. However, this process was never observed, presumably due to the fact that the addition of the sulfonyl radical is a reversible process[9] and the azidation step is slow. We report here that benzenesulfonyl azide is a suitable reagent to conduct an azidosulfonylation reaction coupled with a fast cyclization or ring-opening process.



Scheme 1.

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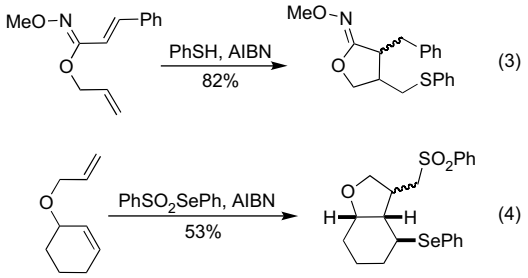
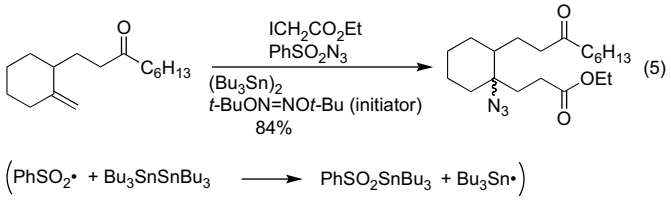
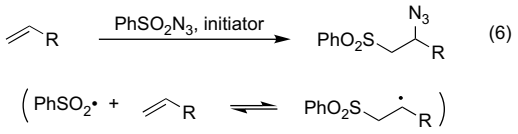


Scheme 2.

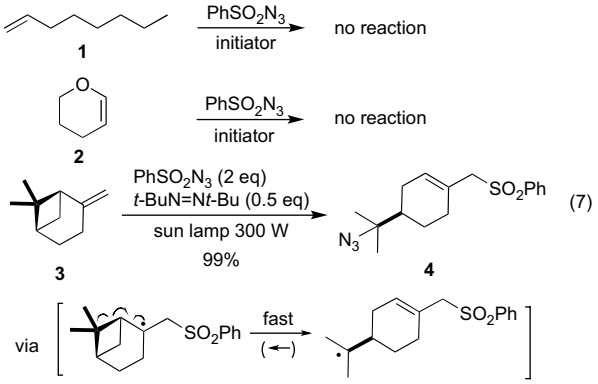




Scheme 3.

2. Azidosulfonylation of alkenes

In a preliminary study, several simple alkenes such as 1-octene **1** and 3,4-dihydro-2*H*-pyran **2** were treated with benzenesulfonyl azide in the presence of different radical initiators. However, as expected from our previous observations during the carboazidation process, no trace of products resulting from the azidosulfonylation was detected. Our hypothesis (vide supra) is that this absence of reaction is resulting from the reversibility of the addition of the sulfonyl radical and the slowness of the azidation step. Indeed, the rate of fragmentation of a 2-tosylated secondary alkyl radical has been measured to be $k_{fragm}=1.5\times10^6\ s^{-1}$ at 20 °C.[9] The rate of azidation of a secondary alkyl radical has not been determined but is expected to be $k_{azidation}\leq10^4\ M^{-1}\ s^{-1}$ at 20 °C.[10] This incited us to examine a system where the radical adduct is undergoing a fast radical rearrangement competing with the β-fragmentation of the sulfonyl radical. Therefore, β-pinene **3** was examined next since the ring opening of the intermediate cyclobutylmethyl radical is known to occur readily.[11] Different initiation methods were tested. An electron rich carbon centered radical, such as a tertiary alkyl radical, is needed to initiate efficiently the chain reaction via reaction with the electrophilic benzenesulfonyl azide. Best results were obtained when the reaction was initiated with di-*tert*-butyldiazene upon irradiation with a 300 W sun lamp. Di-*tert*-butyldiazene was also chosen for its ease of use and availability.[12] Under these conditions, the reaction is completed within a few hours. The product **4** resulting from ring opening of the cyclobutane moiety was obtained in 99% yield (Scheme 4, Eq. 7) demonstrating that when the reversibility of the initial addition of the benzenesulfonyl radical is suppressed by a fast and irreversible (or slowly reversible) process,[13] the azidosulfonylation can take place efficiently.

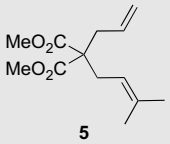
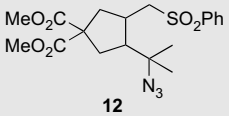
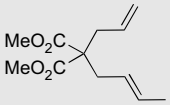
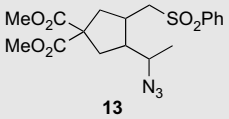
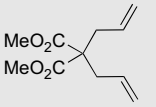
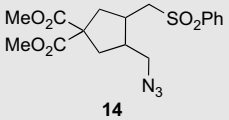
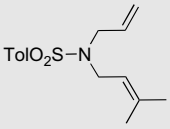
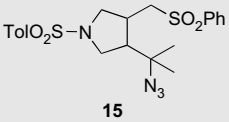
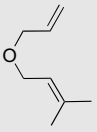
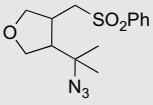
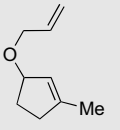
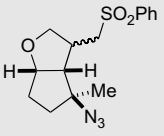
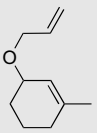
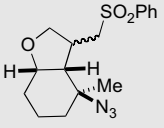


Scheme 4.

3. Azidosulfonylation of 1,6-dienes

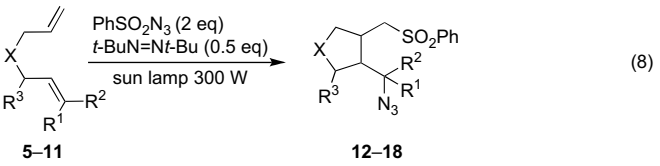
The azidosulfonylation was then applied to a series of 1,6-dienes **5**–**11** (Eq. 8). With these substrates, a fast 5-*exo*-*trig* cyclization

Table 1
Cyclization of 1,6-dienes via azidosulfonylation

Entry	Substrate	Product	Yield % (dr)
1	 **5**	 **12**	76 (2.7:1)[a]
2	 **6**	 **13**	41 (3:3:1:1)
3	 **7**	 **14**	—
4	 **8**	 **15**	89 (1:1)
5	 **9**	 **16**	67 (1:1)
6	 **10**	 **17**	89 (1.2:1)
7	 **11**	 **18**	82 (2:1)

[a] It is assumed that the major product is the cis isomer.[14]

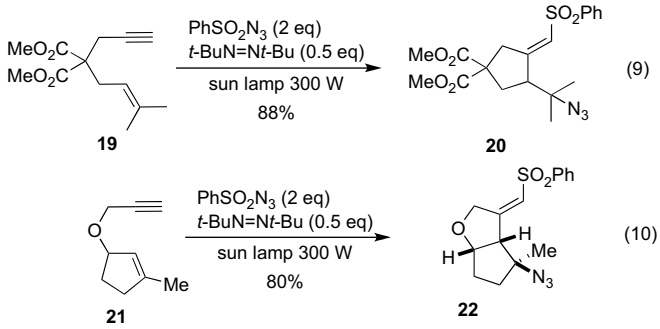
($k_{cyclization} \geq 10^6\ s^{-1}$ at 20 °C) is expected to lead to cyclic derivatives. The results are summarized in Table 1. Excellent yields (67–89%) are obtained with reactions leading to tertiary azides (Table 1, entries 1, 4–7). Secondary azides (entry 2) are formed in moderate yields (41%) and finally, the formation of primary azides was not observed (entry 3). These results are a consequence of the electrophilic nature of the radical trap that strongly favors reactions with the more nucleophilic secondary and tertiary alkyl radicals.[7]



(8)

4. Azidosulfonylation of 1-en-6-ynes

The cyclization of the 1-ene-6-ynes **19** and **21** was examined next (Scheme 5, Eqs. 9 and 10). These substrates afford in excellent yields (80–89%) the tertiary azides **20** and **22**, respectively.



Scheme 5.

5. Conclusions

We developed an azidosulfonylation reaction that works efficiently with alkenes that undergo a rapid and irreversible (or slowly reversible) rearrangement upon radical addition. Ring opening of a cyclobutylmethyl radical as well as 5-*exo*-*trig* cyclizations of alkyl and vinyl radicals were shown to meet these criteria. Application of the method for the synthesis of alkaloids is currently under investigation.

6. Experimental section

6.1. General

All reactions were performed under a nitrogen atmosphere in oven-dried flasks (120 °C) unless otherwise stated. Dry solvents for reactions were filtered through a column of dry alumina under a positive pressure of argon. Solvents for flash chromatography were of technical grade and used without purification. Other chemicals were obtained from commercial sources and used without further purifications. The reaction were monitored by TLC (analytical plates, *Merck silica gel 60 F_{254}*) and visualized under UV light and/or stained with a solution of $KMnO_4$ or phosphomolybdic acid followed by heating. Flash chromatography (FC) was performed using *Baker* silica gel (0.065–0.200 mm). Melting points (mp) are not corrected. ^1H and ^{13}C NMR spectra were recorded on *Bruker Avance-300* (^1H: 300 MHz, ^{13}C: 75.5 MHz) or *Bruker DRX-400* (^1H: 400 MHz, ^{13}C: 100 MHz) spectrometer. The ^1H spectra were referred to an internal standard (TMS, 0 ppm) or to the residual ^1H of $CDCl_3$ (7.27 ppm). The ^{13}C spectra were referred to residual signal of $CDCl_3$ (77.16 ppm). IR spectra were recorded on *Jasco FT-IR 460 plus*. Mass spectroscopy (MS) and high resolution mass spectroscopy (HRMS) analysis were performed on *Waters Micromass Autospec Q* or *Qstar Pulsar*.

6.2. Starting materials

The starting diallyl malonates **5**, **6**, and **7** were obtained by alkylation of diethyl allylmalonate with the corresponding allylic bromide.[15] The starting allyl and propargyl ethers **9**, **10**, **11**, and **21** were synthesized by the reaction of the corresponding allylic alcohols with allyl or propargyl bromide in THF in the presence of sodium hydride.[16] Compounds **8**[17] and **19**[18] were prepared according to the literature.

6.3. General procedure for azidosulfonylation

Benzenesulfonyl azide (366 mg, 2.0 mmol) and di-*tert*-butyldiazene (94 μL, 0.5 mmol) were added to a solution of the diene or enyne (1.0 mmol) in dry benzene (2 mL). The mixture was irradiated with a 300 W sun lamp for 2–4 h until the starting material was consumed (TLC monitoring). The solvent was evaporated and the crude mixture was purified by column chromatography on silica gel (cyclohexane/EtOAc).

6.4. (−)-((4-(2-Azidopropan-2-yl)cyclohex-1-enyl)-methylsulfonyl)benzene (4)

According to general procedure, (−)-β-pinene (157 ml, 1.0 mmol) afforded **4** (316 mg, 99%). White solid. Mp=83–84 °C. $[\alpha]_D^{23}$ −55.6° (*c* 1.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J*=8.3, 2H), 7.70–7.62 (m, 1H), 7.56 (t, *J*=7.8, 2H), 5.44 (s, 1H), 3.70 (s, 2H), 2.18 (d, *J*=5.5, 2H), 2.11–1.97 (m, 1H), 1.91–1.74 (m, 2H), 1.54–1.45 (m, 1H), 1.25 (s, 3H), 1.24 (s, 3H), 1.23–1.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.79, 132.07, 129.12, 128.59, 126.26, 64.36, 63.84, 42.85, 29.70, 27.32, 24.08, 23.72, 23.48. IR (diamond ATR): 2096 (N_3), 1305, 1250, 1141, 1083 cm^{-1}. MS (ESI^+): 342.1 (100, $[M+Na]^+$). HRMS calcd for $C_{16}H_{21}N_3O_2NaS$ 342.1252; found 342.1239.

6.5. Diethyl 3-(2-azidopropan-2-yl)-4-(phenylsulfonylmethyl)-cyclopentane-1,1-dicarboxylate (12)

According to general procedure, compound **5** (268 mg, 1.0 mmol) afforded **12** (343 mg, 76%) as a 2.1:1 mixture of diastereomers, which was not separated. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97–7.91 (m, 3H), 7.72–7.64 (m, 1H), 7.63–7.56 (m, 3H), 4.27–4.11 (m, 6H), 3.74 (d, *J*=14.4, 1H), 3.55 (dd, *J*=1.8, 14.3, 1H), 3.18 (ddd, *J*=11.1, 14.4, 25.7, 1H), 2.78–2.72 (m, 1H), 2.71–2.64 (m, 1H), 2.52 (dd, *J*=8.9, 13.8, 4H), 2.11–1.89 (m, 3H), 1.79 (dt, *J*=8.1, 10.8, 1H), 1.56 (t, *J*=11.2, 1H), 1.37 (s, 3H), 1.29 (s, 3H), 1.28–1.21 (m, 10H), 1.10 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.72, 172.51, 140.20, 133.89, 133.79, 129.48, 129.46, 128.26, 128.16, 63.05, 62.02, 61.92, 61.84, 61.79, 61.62, 60.99, 59.36, 57.60, 54.87, 53.28, 53.02, 39.46, 38.82, 35.62, 35.08, 34.34, 33.81, 26.99, 26.06, 26.03, 22.33, 14.16, 14.13. IR (diamond ATR): 2978, 2100 (N_3), 1722, 1256, 1144, 1085 cm^{-1}. MS (ESI^+): 409.17 (30, $[M-N_3]^+$), 424.18 (100), 452.18 (20, $[M+H]^+$), 474.17 (61, $[M+Na]^+$). HRMS calcd for $C_{21}H_{29}N_3O_6NaS$ 474.1674; found 474.1684.

6.6. Diethyl 3-(1-azidoethyl)-4-(phenylsulfonylmethyl)-cyclopentane-1,1-dicarboxylate (13)

According to general procedure, compound **6** (254 mg, 1.0 mmol) afforded **13** (180 mg, 41%) as a 3:3:1:1 mixture of four

diastereomers, which was not separated. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88–7.81 (m, 4H), 7.64–7.56 (m, 2H), 7.55–7.47 (m, 4H), 4.18–4.03 (m, 9H), 3.64–3.52 (m, 1H), 3.20–2.94 (m, 5H), 2.68–1.78 (m, 13H), 1.22–1.13 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.36, 172.03, 171.91, 171.84, 171.72, 171.69, 171.35, 171.26, 139.53, 139.51, 139.41, 139.25, 133.87, 133.85, 133.72, 133.70, 129.41, 129.36, 129.31, 129.26, 127.99, 127.96, 127.92, 61.94, 61.73, 61.67, 61.65, 61.58, 61.56, 61.37, 60.85, 60.28, 59.29, 58.68, 58.61, 58.47, 57.48, 56.89, 56.74, 55.64, 54.75, 49.46, 49.10, 48.66, 46.12, 39.50, 39.42, 39.10, 38.24, 37.68, 37.31, 36.47, 36.40, 36.10, 35.44, 35.36, 35.13, 34.38, 34.06, 18.20, 17.99, 17.82, 17.72, 17.59, 15.22, 13.97, 13.95, 13.77, 12.16. IR (diamond ATR): 2103 (N_3), 1724, 1249, 1146, 1085 cm^{-1}. MS (ESI$^+$): 410.12 (100), 438.15 (57, $[M+H]^+$), 460.13 (31, $[M+Na]^+$). HRMS calcd for $C_{20}H_{27}N_3O_6NaS$ 460.1518; found 460.1531.

6.7. 3-(2-Azidopropan-2-yl)-4-(phenylsulfonylmethyl)-1-tosylpyrrolidine (15)

According to general procedure, compound **8** (280 mg, 1.0 mmol) afforded **15** (412 mg, 89) as a 1:1 mixture of diastereomers, which was not separated. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.84 (m, 2H), 7.84–7.77 (m, 2H), 7.77–7.63 (m, 6H), 7.58 (td, J=2.6, 7.4, 4H), 7.35 (d, J=8.1, 4H), 3.71 (d, J=10.9, 1H), 3.59 (d, J=14.5, 1H), 3.47–2.98 (m, 9H), 2.82 (dd, J=7.2, 10.1, 1H), 2.77–2.62 (m, 1H), 2.47 (d, J=10.2, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.31 (dd, J=11.1, 14.5, 1H), 2.07 (ddd, J=4.6, 6.5, 8.7, 1H), 1.92 (dd, J=6.9, 15.1, 1H), 1.28 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.14, 143.89, 139.43, 139.06, 134.16, 134.07, 133.85, 131.83, 130.01, 129.86, 129.54, 128.02, 128.01, 127.93, 127.48, 62.41, 60.33, 59.92, 53.47, 53.22, 53.12, 52.52, 50.98, 48.50, 46.32, 34.40, 34.25, 26.90, 25.44, 25.15, 22.71, 21.64. IR (diamond ATR): 2971, 2102 (N_3), 1144 cm^{-1}. MS (ESI$^+$): 463.0 (81, $[M+H]^+$), 480.2 (65), 485.1 (100, $[M+Na]^+$). HRMS calcd for $C_{21}H_{26}N_4O_4NaS_2$ 485.1293; found 485.1288.

6.8. 3-(2-Azidopropan-2-yl)-4-(phenylsulfonylmethyl)-tetrahydrofuran (16)

According to general procedure, compound **9** (126 mg, 1.0 mmol) afforded **16** (208 mg, 67%) as a 1:1 mixture of diastereomers, which was not separated. Brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.89 (m, 4H), 7.74–7.64 (m, 2H), 7.64–7.54 (m, 4H), 4.05–3.51 (m, 9H), 3.37 (dd, J=2.9, 14.0, 1H), 3.23–3.09 (m, 2H), 2.87–2.67 (m, 1H), 2.64–2.43 (m, 1H), 2.41–2.26 (m, 1H), 1.93 (dt, J=6.2, 8.1, 1H), 1.34 (s, 3H), 1.31 (s, 3H), 1.23 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.86, 139.32, 134.11, 133.97, 129.58, 129.56, 128.11, 128.06, 73.56, 73.11, 68.85, 66.93, 62.58, 60.81, 60.28, 54.77, 54.39, 52.23, 36.03, 35.61, 26.91, 26.33, 25.29, 23.16. IR (diamond ATR): 2973, 2870, 2099 (N_3), 1304, 1143, 1085 cm^{-1}. MS (ESI$^+$): 327.2 (69), 332.0 (100, $[M+Na]^+$). HRMS calcd for $C_{14}H_{19}N_3O_3NaS$ 332.1044; found 332.1036.

6.9. 4-Azido-4-methyl-3-(phenylsulfonylmethyl)hexahydro-2*H*-cyclopenta[*b*]furan (17)

According to general procedure, compound **10** (138 mg, 1.0 mmol) afforded **17** (286 mg, 89%) as a 1.2:1 mixture of diastereomers, which was not separated. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.89 (m, 5H), 7.75–7.54 (m, 7H), 4.53–4.41 (m, 2H), 4.29–4.12 (m, 1H), 4.04 (t, J=8.6, 1H), 3.70–3.57 (m, 2H), 3.38–3.25 (m, 2H), 3.14 (dd, J=10.5, 14.1, 1H), 3.04–2.90 (m, 1H), 1.44 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.20, 139.05, 134.22, 134.19, 129.81, 129.66, 128.14, 128.06, 84.24, 84.17, 73.17, 72.71, 72.28, 69.24, 59.02, 58.19, 56.09, 55.31, 40.56, 37.50, 36.06, 35.39, 30.77, 30.18, 21.72, 19.60. IR (diamond ATR): 2943, 2360, 2094 (N_3), 1447, 1306, 1148, 1085 cm^{-1}. MS (ESI$^+$): 344.11 (100, $[M+Na]^+$). HRMS calcd for $C_{15}H_{19}N_3O_3NaS$ 344.1044; found 344.1057.

6.10. 4-Azido-4-methyl-3-(phenylsulfonylmethyl)-octahydrobenzofuran (18)

According to general procedure, compound **11** (152 mg, 1.0 mmol) afforded **18** (275 mg, 82%) as a 2:1 mixture diastereomers, which was not separated. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.81 (m, 3H), 7.65–7.58 (m, 1.5H), 7.57–7.48 (m, 3H), 4.11–3.85 (m, 3H), 3.63 (ddt, J=4.0, 7.7, 13.0, 2.5H), 3.32–3.21 (m, 1.5H), 3.10 (dd, J=10.2, 14.0, 0.5H), 2.98–2.74 (m, 1H), 2.68–2.43 (m, 0.5H), 1.94 (dd, J=4.9, 6.2, 1H), 1.88–1.77 (m, 0.5H), 1.74–1.36 (m, 9H), 1.29 (s, 3H), 1.20 (s, 1.5H), 0.88–0.73 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.16, 139.07, 134.11, 134.05, 129.53, 128.05, 127.99, 77.26, 76.39, 71.66, 70.90, 63.58, 62.74, 61.70, 56.67, 52.20, 49.01, 36.86, 36.81, 34.26, 33.13, 27.78, 25.60, 23.99, 22.49, 18.21. IR (diamond ATR): 2938, 2097(N_3), 1447, 1306, 1251, 1143, 1085 cm^{-1}. HRMS calcd for $C_{16}H_{21}N_3O_3NaS$ 358.1201; found 358.1208.

6.11. (*E*)-Dimethyl 3-(2-azidopropan-2-yl)-4-(phenylsulfonylmethylene)cyclopentane-1,1-dicarboxylate (20)

According to general procedure, compound **19** (238 mg, 1.0 mmol) afforded **20** (371 mg, 88%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.80 (m, 2H), 7.68–7.59 (m, 1H), 7.58–7.48 (m, 2H), 6.70 (dt, J=1.7, 3.3, 1H), 4.02 (ddd, J=12.0, 13.7, 25.7, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.00–2.88 (m, 1H), 2.80 (dd, J=8.3, 10.5, 1H), 2.53 (ddd, J=2.1, 8.3, 13.3, 1H), 1.90 (dt, J=23.1, 46.1, 1H), 1.32 (s, 3H), 1.17 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.08, 170.77, 157.53, 141.90, 133.46, 129.37, 127.36, 127.25, 63.39, 58.47, 53.27, 53.20, 52.73, 39.72, 34.82, 25.63, 21.23. IR (diamond ATR): 2954, 2101(N_3), 1733, 1446, 1435, 1250, 1145 cm^{-1}. MS (ESI$^+$): 444.13(23, $[M+Na]^+$), 422.14 (100, $[M+H]^+$), 394.13 (88). HRMS calcd for $C_{19}H_{24}N_3O_6S$ 422.1385; found 422.1377.

6.12. (*Z*)-4-Azido-4-methyl-3-(phenylsulfonylmethylene)-hexahydro-2*H*-cyclopenta[*b*]furan (22)

According to general procedure, compound **21** (136 mg, 1.0 mmol) afforded **22** (255 mg, 80%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 2H), 7.52–7.42 (m, 3H), 6.22 (td, J=1.5, 2.5, 1H), 4.95–4.88 (m, 1H), 4.68 (dd, J=2.5, 17.4, 1H), 4.50–4.46 (m, 1H), 2.95 (d, J=5.7, 1H), 2.00–1.76 (m, 4H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.44, 143.11, 133.87, 129.58, 127.35, 123.92, 84.65, 71.65, 71.06, 60.19, 38.42, 30.46, 22.00. IR (diamond ATR): 2950, 2095 (N_3), 1448, 1316, 1151 cm^{-1}. MS (ESI$^+$): 320.1 (80, $[M+H]^+$), 342.1(100, $[M+Na]^+$). HRMS calcd for $C_{15}H_{17}N_3O_3NaS$ 342.0888; found 342.0883.

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Supplementary data

^{1}H and ^{13}C NMR spectra of all azidosulfones. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.096.

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