Supporting Information

Palladium-Catalyzed Reactions of Allenes with 2-Iodobenzenesulfonamides: Simple Synthesis of Benzosultams under Green Condition

M. Nagarjuna Reddy and K. C. Kumara Swamy*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, A. P., India
E-mail: kckssc@uohyd.ac.in, kckssc@yahoo.com, kckssc@uohyd.ernet.in

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General experimental details

Chemicals were purified when required according to standard procedures.$^1$ All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded using a 400 MHz spectrometer in CDCl$_3$ (unless stated otherwise) with shifts referenced to SiMe$_4$ ($\delta = 0$) or 85 % H$_3$PO$_4$ ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. LC-MS and HRMS equipment was used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization on a C-18 column.
Synthesis of $O$-/N-substituted allenes (1a-h)

The allenes were prepared by following a known method. Among these, 1a and 1d-h are known, but 1b-c are new.

**Compound 1b**

Yield: 1.62 g [72%; using propargyl 4-bromobenzyl ether (10.0 mmol)].

IR (neat): 2926, 1901, 1721, 1595, 1485, 1403, 1074, 1008, 811 cm$^{-1}$.

$^1$H NMR: $\delta$ 4.58 (s, 2H, $\text{CH}_2$), 5.48 (d, $J \approx 5.6$ Hz, 2H, $=\text{CH}_2$), 6.83 (~t, $J \approx 5.6$ Hz, 1H, $=\text{CH}$), 7.23 (d, $J = 8.0$ Hz, 2H, Ar-$H$), 7.48 (d, $J \approx 8.0$ Hz, 2H, Ar-$H$).

$^{13}$C NMR: $\delta$ 69.8, 91.5, 121.6, 121.8, 129.4, 131.6, 136.6, 201.3.

LC-MS: $m/z$ 225, 227 [M]$^+$.

Anal. Calcd. for C$_{10}$H$_9$BrO: C, 53.36; H, 4.03. Found: C, 53.68; H, 4.06.

**Compound 1c**

Yield: 1.81 g [79%; using propargyl 2-bromobenzyl ether (10.0 mmol)].

IR (neat): 1956, 1567, 1441, 1348, 1222, 1189, 1052, 888 cm$^{-1}$.

$^1$H NMR: $\delta$ 4.71 (s, 2H, $\text{CH}_2$), 5.50 (d, $J = 5.6$ Hz, 2H, $=\text{CH}_2$), 6.88 (t, $J \approx 5.6$ Hz, 1H, $=\text{CH}$), 7.17 (t, $J = 7.6$ Hz, 1H, Ar-$H$), 7.33 (t, $J \approx 7.6$ Hz, 1H, Ar-$H$), 7.48 (d, $J \approx 8.0$ Hz, 1H, Ar-$H$), 7.55 (d, $J = 8.0$ Hz, 1H, Ar-$H$).

$^{13}$C NMR: $\delta$ 69.9, 91.5, 121.5, 122.6, 127.4, 129.1, 132.5, 136.6, 201.0.

LC-MS: $m/z$ 225, 227 [M]$^+$.

Anal. Calcd. for C$_{10}$H$_9$BrO: C, 53.36; H, 4.03. Found: C, 53.46; H, 4.08.

**Preparation of 2-iodo-N-substituted-benzenesulfonamides 2a-f**

2-iodo-N-substituted-benzenesulfonamides 2a-f were prepared by following a known procedure. These compounds were purified by column chromatography (silica gel) using
EtOAc–hexane (15:85) mixture as the eluent. Among these, 2a and 2d are known, but 2b-c and 2e-f are new.

**Compound 2b**

![Chemical Structure of Compound 2b]

Yield: 2.27 g [67%; using N-isopropyl-4-methylbenzenesulfonamide 9b (10.0 mmol)].

Mp: 94-96 °C.

IR (KBr): 3293, 2975, 1595, 1463, 1419, 1342, 1173, 1101, 1030, 838 cm⁻¹.

¹H NMR: δ 1.10 (d, J = 6.8 Hz, 6H, 2 CH₃), 2.38 (s, 3H, ArCH₃), 3.38-3.40 (m, 1H, CH(CH₃)₂), 5.04 (d, J = 6.8 Hz, 1H, NH), 7.27 (dd, J = 8.0 and 2.4 Hz, 1H, Ar-H), 7.89 (s, 1H, Ar-H), 8.06 (d, J = 8.0 Hz, 1H, Ar-H).

¹³C NMR: δ 20.8, 23.5, 46.5, 92.5 (Cl), 129.3, 131.0, 140.0, 142.7, 144.3.

LC-MS: m/z 340 [M+1]⁺.

Anal. Calcd. for C₁₀H₁₄INO₂S: C, 35.41; H, 4.16; N, 4.13. Found: C, 35.52; H, 4.08; N, 4.23.

**Compound 2c**

![Chemical Structure of Compound 2c]

Yield: 2.21 g [57%; using N-benzyl-4-methylbenzenesulfonamide 9c (10.0 mmol)].

Mp: 108-110 °C.

IR (KBr): 3322, 3027, 2918, 1583, 1459, 1407, 1330, 1159, 1030, 817 cm⁻¹.

¹H NMR: δ 2.37 (s, 3H, ArCH₃), 4.04 (d, J = 6.0 Hz, 2H, CH₂), 5.51 (br s, 1H, NH), 7.22-7.29 (m, 6H, Ar-H), 7.86 (s, 1H, Ar-H), 8.03 (d, J = 8.0 Hz, 1H, Ar-H).
**Compound 2e**

![Structure 2e](image)

Yield: 2.54 g [72%; using N-methyl-4-<i>t</i>-butylbenzenesulfonamide 9e (10.0 mmol)].

Mp: 99-101 °C.

IR (KBr): 3353, 2975, 1578, 1468, 1375, 1321, 1178, 1123, 1013, 641 cm⁻¹.

**1H NMR:** δ 1.35 (s, 9H, 3 C₃H₃), 2.59 (d, J = 5.6 Hz, 1H, NHCH₃), 5.10 (br s, 1H, NH), 7.50 (d, J ~ 8.0 Hz, 1H, Ar-H), 8.03 (s, 1H, Ar-H), 8.07 (d, J ~ 8.0 Hz, 1H, Ar-H).

**13C NMR:** δ 29.3, 31.1, 35.0, 92.3 (Cl), 125.7, 131.6, 137.7, 139.6, 157.7.

**LC-MS:** m/z 354 [M+1]+.

Anal. Calcd. for C₁₁H₁₆INO₂S: C, 37.40; H, 4.57; N, 3.97. Found: C, 37.52; H, 4.51; N, 3.89.

**Compound 2f**

![Structure 2f](image)

Yield: 2.28 g [61%; using N-methyl-4-phenylbenzenesulfonamide 9f (10.0 mmol)].

Mp: 127-129 °C.

IR (KBr): 3331, 1578, 1534, 1440, 1375, 1320, 1166, 1112, 1019, 832, 755, 641, 591 cm⁻¹.
**1H NMR:** δ 2.64 (d,  J = 5.2 Hz, 3H, NHCH₃), 5.19 (d,  J = 5.2 Hz, 1H, NH), 7.44-7.51 (m, 3H, Ar-H), 7.58-7.60 (m, 2H, Ar-H), 7.70 (dd,  J = 8.0 and 1.6 Hz, 1H, Ar-H), 8.21 (d,  J = 8.0 Hz, 1H, Ar-H), 8.27 (s, 1H, Ar-H).

**13C NMR:** δ 29.3, 92.7 (C-I), 127.0, 127.4, 129.0, 129.2, 132.0, 137.7, 139.1, 140.7, 146.6.

**LC-MS:** m/z 374 [M+1]^+.

Anal. Calcd. for C₁₃H₁₂INO₂S: C, 41.84; H, 3.24; N, 3.75. Found: C, 41.76; H, 3.28; N, 3.71.

**Synthesis of 2-iodo-N-cinnamyl-N-methyl-benzenesulfonamides 3a-b by Mitsunobu reaction**

To a stirred solution of 2-iodo-N,4-dimethylbenzenesulfonamide 2a (2.0 mmol), cinnamyl alcohol (2.0 mmol) and triphenylphosphine (2.0 mmol) in anhydrous THF (5 mL) was added diisopropyl azodicarboxylate (2.0 mmol) drop-wise via syringe over a period of 15 min under nitrogen atmosphere with continuous stirring at room temperature. The solution was stirred further at room temperature for 12 h. After completion of the reaction (tlc), solvent was removed using a rotary evaporator and the residue was purified by column chromatography on silica gel by using ethyl acetate/hexane (10/90) as eluent to afford the product 3a. Compound 3b was prepared similarly using 2-iodo-N-methyl-4-t-butylbenzenesulfonamide 2e (2.0 mmol).

**Compound 3a**

Yield: 0.614 g (72 %, gummy liquid).

**IR (neat):** 3025, 2921, 1732, 1589, 1452, 1326, 1156, 1107, 1025, 970, 926, 729, 652 cm⁻¹.

**1H NMR:** δ 2.36 (s, 3H, CH₃), 2.85 (s, 3H, CH₃), 4.01 (d,  J = 6.8 Hz, 2H, CH₂), 6.17 (dt,  J = 16.0 and 6.8 Hz, 1H, C=CH), 6.55 (d,  J = 16.0 Hz, 1H, C=CH), 7.27-7.38 (m, 6H, Ar-H), 7.95 (s, 1H, Ar-H), 8.04 (d,  J = 8.0 Hz, 1H, Ar-H).
**13C NMR:** \( \delta 20.7, 34.1, 52.4, 92.6 \) (Cl), 124.0, 126.5, 128.0, 128.6, 129.0, 131.9, 134.3, 136.2, 138.3, 143.5, 144.5.

**LC-MS:** \( m/z \) 428 [M+1]^+.

Anal. Calcd. for C_{17}H_{18}INO_2S: C, 47.79; H, 4.25; N, 3.28. Found: C, 47.85; H, 4.21; N, 3.32.

**Compound 3b**

![Compound 3b](image)

Yield: 0.64 g (68%).

Mp: 107-109 °C.

IR (KBr): 2964, 2866, 1584, 1545, 1452, 1326, 1271, 1118, 1025, 981, 932, 778, 625, 537 cm\(^{-1}\).

**1H NMR:** \( \delta 1.33 \) (s, 9H, C(CH\(_3\))\(_3\)), 2.87 (s, 3H, CH\(_3\)), 4.02 (d, \( J = 6.8 \) Hz, 2H, CH\(_2\)), 6.17 (dt, \( J = 16.0 \) and 6.8 Hz, 1H, C=CH), 6.55 (d, \( J = 16.0 \) Hz, 1H, C=CH), 7.27-7.37 (m, 5H, Ar-H), 7.47-7.49 (m, 1H, Ar-H), 8.06-8.08 (m, 2H, Ar-H).

**13C NMR:** \( \delta 31.0, 34.2, 34.9, 52.5, 92.8 \) (Cl), 124.1, 125.4, 126.6, 128.0, 128.8, 131.8, 134.3, 136.3, 138.4, 140.4, 157.5.

**LC-MS:** \( m/z \) 469 [M+1]^+.

References:


Figure S1. $^1$H NMR spectrum of compound 1b

Figure S2. $^{13}$C NMR spectrum of compound 1b
**Figure S3.** $^1$H NMR spectrum of compound 1c

**Figure S4.** $^{13}$C NMR spectrum of compound 1c
Figure S5. $^1$H NMR spectrum of compound 2b

Figure S6. $^{13}$C NMR spectrum of compound 2b
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Figure S30. $^{13}$C NMR spectrum of compound 9
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Figure S52. $^{13}$C NMR spectrum of compound 20
**Figure S53.** $^1$H NMR spectrum of compound 21

**Figure S54.** $^{13}$C NMR spectrum of compound 21
**Figure S55.** $^1$H NMR spectrum of compound 22

**Figure S56.** $^{13}$C NMR spectrum of compound 22
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Figure S58. $^{13}$C NMR spectrum of compound 23
Figure S59. $^1$H NMR spectrum of compound 24

Figure S60. $^{13}$C NMR spectrum of compound 24
Figure S61. $^1$H NMR spectrum of compound 25

Figure S62. $^{13}$C NMR spectrum of compound 25
Figure S63. $^1$H NMR spectrum of compound 26

Figure S64. $^{13}$C NMR spectrum of compound 26