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Ultrasound-promoted solvent-free aza-Michael addition of *p*-toluenesulfonamide to fumaric esters by potassium carbonate: Synthesis of *p*-toluenesulfonamide derivatives

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ABSTRACT

An efficient, mild, inexpensive and eco-friendly protocol for the synthesis of *p*-toluenesulfonamide derivatives by aza-Michael addition reaction of *p*-toluenesulfonamide to fumaric esters using potassium carbonate under ultrasound irradiation was developed. This method is simple, convenient and the desired compounds are produced in good to excellent yield. The bulkiness of alkoxy group (–OR) of fumaric esters did not affect significantly on the yields and reaction times. This reaction worked well on linear and non-linear alkyl fumarates. The reaction, surprisingly, was not successful on methyl fumarate. In this case methyl fumarate has been hydrolyzed to fumaric acid under reaction conditions.

1. Introduction

Sulfonamides exhibit a wide spectrum of biological activities [1–4]. They are used as antibacterial, anticonvulsant, anticancer, anti-inflammatory, and antiviral agents [5–7]. These compounds are also used as herbicides [8] and plaguicides [9]. It has been reported that the some of sulfonamide derivatives are antihypertensive agent bosentan [9], HIV protease inhibitors [10], and the phosphodiesterase-5 inhibitor sildenafi [11]. Sulfonamides have been also applied in the prevention of diabetes mellitus, oedema, hypertension and gout [12]. It has been well established that sulfonamides have antiproliferative [13] and antimalarial [14] properties. Besides clinical uses, sulfonamides have been employed, to construct molecular recognition molecules [15], and for organocatalysts for Michael and aldol reactions [16]. These compounds and their derivatives are prepared by various synthetic methods [17–22]. Among these methods the most classically method involves the nucleophilic attack of ammonia, primary amines, and secondary amines to sulfonyl chlorides, but the most untraditionally method, which is scarce in literature [23], involves the use of aza-Michael addition of sulfonamides to α,β-unsaturated compounds. For these reasons and for mentioned advantages of sulfonamide derivatives, recently, we reported a very efficient method for synthesis of sulfonamide derivatives by addition reaction of sulfonamides to acrylates in the presence of potassium carbonate and tetrabutylamonium bromide (TBAB) under microwave irradiation [24]. Herein, we report another method for preparing of a new series of these compounds by the aza-Michael addition of *p*-toluenesulfonamide to fumaric esters by using potassium carbonate, a cheap and green base under ultrasound irradiation conditions. Although potassium carbonate accompanied with ionic liquid 1-butyl-3-methylimidazolium bromide has been used previously for Michael addition of sulfonamides to acrylates, not to fumarates [25], but in presence work we employed this base in Michael addition of sulfonamides on fumarates in the absence of ionic liquid media under ultrasound irradiation, which surprisingly no other references available in the literature reported to date (Scheme 1).

2. Experimental

2.1. General

All alkyl fumarates were synthesized in our laboratory according to the literature procedure [26] and their structures were confirmed by IR and ^{1}H NMR spectroscopy. The progress of the reactions was followed by TLC using silica gel SILIG/UV 254 plates. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker 300 MHz instrument. FT-IR spectra were recorded on a Perkin-Elmer RX-1 instrument. Mass spectra were recorded on a

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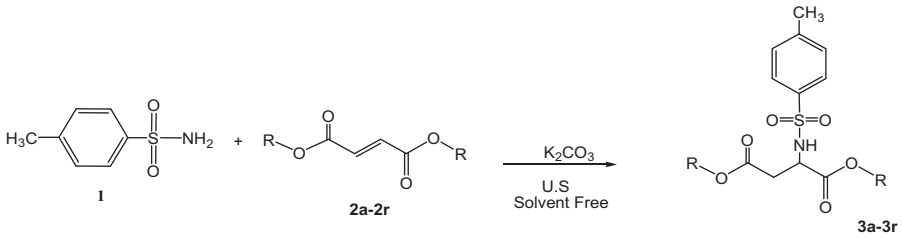


Scheme. 1. Synthetic pathway of sulfonamides 3a-3r.

Shimadzu GC–MS-QP 1000PX. Elemental analysis for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. The melting points were determined in open capillaries with a Stuart Melting Point Apparatus and are uncorrected.

Sonication was performed in a Parsonic 2600s ultrasonic bath, with a frequency of 28 kHz and a power 500 W was used for ultrasonic irradiation.

2.1.1. General procedure under conventional conditions (method A)

To a well ground mixture of *p*-toluenesulfonamide (3 mmol) and K_2CO_3 (3 mmol) was added fumaric esters (3 mmol) and mixed thoroughly with a glass rod. The resulting mixture was kept in an oil bath at 53 °C for appropriate time (Table 2). The progress of reaction was monitored by TLC. After completion of reaction the mixture was suspended in chloroform (45 mL), filtered and the filtrate was washed with water (3 × 20 ml) and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude material was purified on short silica-gel column with ethyl acetate/*n*-hexane (1:9) as the eluent.

2.1.2. General procedure under sonochemical conditions (method B)

To a well ground mixture of *p*-toluenesulfonamide (1.5 mmol) and K_2CO_3 (1.5 mmol) was added fumaric esters (1.5 mmol) and mixed thoroughly with a glass rod. The mixture was irradiated in the water bath of an ultrasonic cleaner at 53 °C. In order to control the temperature of the water bath, addition or removal water technique was used. After completion of reaction the mixture was suspended in chloroform (30 mL), filtered and the filtrate was washed with water (3 × 15 ml) and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude material was purified on short silica-gel column with ethyl acetate/*n*-hexane (1:9) as the eluent.

*2.1.2.1. Diethyl 2-(tosylamino)succinate **(3b)**.* White Solid, mp 73–75 °C. FT IR (KBr) 3282, 2984, 1733, 1599, 1344, 1280, 1193, 1167, 1091, 956, 815, 555 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 1.13 (t, J = 7.8 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 2.42 (s, 3H), 2.83 (dd, J = 17.1 Hz, J = 4.8 Hz, 1H), 2.96 (dd, J = 17.1 Hz, J = 4.2 Hz, 1H), 4.10–4.30 (m, 5H), 5.64 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 13.82, 14.06, 21.51, 37.99, 52.20, 61.15, 62.17, 127.24, 129.65, 133.62, 136.85, 169.91, 170.15. MS (EI, 70 eV) *m*/*z* (%): 344 (M^+ + 1, 2.49), 270 (100.00), 224 (15.22), 188 (9.72), 155 (43.89), 91 (54.07), 70 (5.63), 65 (10.93). Analysis calculated for $C_{15}H_{21}NO_6S$: C, 52.46; H, 6.16; N, 4.08. Found C, 52.55; H, 6.24; N, 4.13.

*2.1.2.2. Dipropyl 2-(tosylamino)succinate **(3c)**.* White Solid, mp 79–81 °C. FT-IR (KBr) 3283, 2968, 1733, 1598, 1343, 1279, 1189, 1169, 1092, 812, 561 cm^{-1}. ^1H NMR ($CDCl_3$), δ 0.84 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.50–1.65 (m, 4H), 2.42 (s, 3H), 2.84 (dd, J = 16.8 Hz, J = 5.1 Hz, 1H), 2.97 (dd, J = 16.8 Hz, J = 4.2 Hz, 1H), 3.94 (t, J = 7.5 Hz, 2H), 4.01 (t, J = 7.2 Hz, 2H), 4.15 (ddd, J = 8.1 Hz, J = 5.1 Hz, J = 4.2 Hz, 1H), 5.63 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 10.13, 10.28, 21.50, 21.64, 21.82, 37.96, 52.19, 66.75, 67.73, 127.23, 129.65, 136.86, 143.65, 169.98, 170.23. MS (EI, 70 eV) *m*/*z* (%): 372 (M^+ + 1, 1.81) 284 (100.00), 242 (13.51), 224 (11.38), 216 (13.02), 155 (46.88), 91 (58.65), 65 (11.25), 43 (24.11), 41 (11.37). Analysis calculated for $C_{17}H_{25}NO_6S$: C, 54.97; H, 6.78; N, 3.77. Found C, 54.88; H, 6.69; N, 3.71.

*2.1.2.3. Dibutyl 2-(tosylamino)succinate **(3d)**.* White Solid, mp 81–82 °C. FT-IR (KBr) 3278, 2962, 1733, 1599, 1345, 1281, 1187, 1168, 820, 562 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.88 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.20–1.57 (m, 8H), 2.42 (s, 3H), 2.83 (dd, J = 17.0 Hz, J = 5.1 Hz, 1H), 2.97 (dd, J = 17.0 Hz, J = 4.5 Hz, 1H), 3.99–4.17 (m, 5H), 5.64 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 13.57, 13.64, 18.87, 19.03, 21.52, 30.25, 30.47, 37.97, 52.18, 65.05, 66.02, 127.23, 129.66, 136.84, 143.64, 169.98, 170.26. MS (EI, 70 eV) *m*/*z* (%): 400 (M^+ + 1, 1.14), 298 (100.00), 284 (3.32), 242 (16.77), 224 (9.39), 155 (37.77), 91 (43.60), 70 (11.26), 41 (2.43). Analysis calculated for $C_{19}H_{29}NO_6S$: C, 57.12; H, 7.32; N, 3.51. Found C, 57.18; H, 7.25; N, 3.60.

*2.1.2.4. Dipentyl 2-(tosylamino)succinate **(3e)**.* White Solid, mp 51–53 °C. FT-IR (KBr) 3286, 2957, 1739, 1600, 1346, 1188, 1167, 1119, 1049, 815, 568 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.89 (t, J = 6.9 Hz, 3H), 0.93 (t, J = 6.6 Hz, 3H), 1.16–1.33 (m, 8H), 1.50 (quintet, J = 6.9 Hz, 2H), 1.61 (quintet, J = 6.9 Hz, 2H), 2.43 (s, 3H), 2.84 (dd, J = 17.4 Hz, J = 4.8 Hz, 1H), 2.96 (dd, J = 17.4 Hz, J = 4.5 Hz, 1H) , 3.99 (t, J = 6.9 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 4.13 (ddd , J = 8.1 Hz, J = 4.8 Hz, J = 4.5 Hz, 1H), 5.62 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 13.85, 13.90, 21.51, 22.17, 22.25, 27.76, 27.93, 28.14, 37.98, 52.19, 65.34, 66.31, 127.23, 129.65, 136.88, 143.62, 169.96, 170.24. MS (EI, 70 eV) *m*/*z* (%): 428 (M^+ + 1, 2.1), 382 (5.53), 312 (100.00), 272 (14.70), 242 (19.94), 224 (8.04), 155 (35.21), 91 (43.80), 70 (2.22), 43 (4.16), 41 (4.96). Analysis calculated for $C_{21}H_{33}NO_6S$: C, 58.99; H, 7.78; N, 3.28. Found C, 58.92; H, 7.78; N, 3.38.

*2.1.2.5. Dihexyl 2-(tosylamino)succinate **(3f)**.* White Solid, mp 49–52 °C. FT-IR (KBr) 3289, 2954, 1745, 1600, 1457, 1342, 1187, 1123, 1092, 815 , 567 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.87–0.91 (m, 6H), 1.24–1.31 (m, 12H), 1.47–1.60 (m, 4H), 2.43 (s, 3H), 2.84 (dd, J = 16.8 Hz, J = 4.8 Hz, 1H), 2.97 (dd, J = 16.8 Hz, J = 4.5 Hz, 1H), 3.99 (t, J = 6.9 Hz, 2H), 4.05 (t, J = 7.2 Hz, 2H), 4.14 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 4.5 Hz, 1H), 5.62 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 HZ, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 13.95, 21.52, 22.45, 22.49, 25.31, 25.48, 28.20, 28.42, 31.29, 31.37, 37.98, 52.18, 65.37, 66.33, 127.24, 129.66, 136.86, 143.62, 169.97, 170.25. MS (EI, 70 eV) *m*/*z* (%): 456 (M^+ + 1) (2.36), 326 (100.00), 300 (12.99), 242 (17.94), 224 (5.40), 155 (25.54), 91 (28.31), 70 (7.62), 43

(15.66), 41 (5.93). Analysis calculated for $C_{23}H_{37}NO_6S$: C, 60.63; H, 8.19; N, 3.07. Found C, 60.55; H, 8.13; N, 3.14.

2.1.2.6. Dioctyl 2-(tosylamino)succinate ***(3g)***. White Solid, mp 49–50 °C. FT-IR (KBr) 3291, 2924, 1747, 1342, 1292, 1093, 815, 679, 542 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.89 (t, J = 7.0 Hz, 6H), 1.26–1.60 (m, 24H), 2.43 (s, 3H), 2.84 (dd, J = 16.8 Hz, J = 4.8 Hz, 1H), 2.97 (dd, J = 16.8 Hz, J = 4.2 Hz, 1H), 4.01 (t, J = 6.6 Hz, 2H) 4.05 (t, J = 6.9 Hz, 2H), 4.15 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 4.2 Hz, 1H), 5.62 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 14.05, 21.52, 22.61, 25.65, 25.82, 28.25, 28.46, 29.10, 29.17, 31.75, 37.98, 52.19, 65.37, 66.33, 127.23, 129.65, 136.89, 143.60, 169.96, 170.24. Ms. m/z (%): 512 (M^+ + 1) (1.16), 400 (1.73), 354 (100.00), 242 (16.99), 224 (4.39), 155 (20.24), 91 (21.94), 70 (4.39), 57 (8.67), 43 (11.4). Analysis calculated for $C_{27}H_{45}NO_6S$: C, 63.37; H, 8.86; N, 2.74. Found C, 63.42; H, 8.91; N, 2.78.

2.1.2.7. Didecyl 2-(tosylamino)succinate ***(3h)***. White Solid, mp 42–43 °C. FT-IR (KBr) 3291, 2925, 1747, 1468, 1341, 1292, 1165, 1123, 1093, 815, 678, 542 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.89 (t, J = 6.9 Hz, 6H), 1.28–1.60 (m, 32H), 2.43 (s, 3H), 2.83 (dd, J = 16.8 Hz, J = 4.8 Hz, 1H), 2.97 (dd, J = 16.8 Hz, J = 4.5 Hz, 1H), 3.96 (t, J = 6.9 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 4.12 (ddd, J = 8.4 Hz, J = 4.8 Hz, J = 4.5 Hz, 1H), 5.63 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 13.84, 21.51, 22.66, 25.66, 25.82, 28.26, 28.47, 29.15, 29.22, 29.28, 29.47, 29.50, 29.51, 31.87, 37.98, 52.19, 65.37, 66.33, 127.23, 129.66, 136.89, 143.60, 169.96, 170.24. Ms. m/z (%): 568 (M^+ + 1) (3.27), 428 (2.68), 412 (18.92), 342 (100.00), 242 (14.12), 155 (18.83), 91 (20.66), 70 (8.67), 57 (10.60), 43 (14.81). Analysis calculated for $C_{31}H_{53}NO_6S$: C, 65.57; H, 9.41; N, 2.47. Found C, 65.49; H, 9.37; N, 2.54.

2.1.2.8. Didodecyl 2-(tosylamino)succinate ***(3i)***. White Solid, mp 57–59 °C. FT-IR (KBr) 3292, 2956, 2851, 1749, 1600, 1468, 1340, 1292, 1165, 1123, 1093, 816, 679, 544 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.89 (t, J = 6.9 Hz, 6H), 1.18–1.39 (m, 40H), 2.43 (s, 3H), 2.86 (dd, J = 16.9 Hz, J = 4.8 Hz), 2.94 (dd, J = 16.9 Hz, J = 4.5 Hz), 3.96–4.13 (m, 5H), 5.63 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 14.07, 21.51, 22.66, 25.66, 25.73, 28.26, 28.47, 29.15, 29.23, 29.32, 29.42, 29.47, 29.50, 29.57, 29.61, 29.63, 31.90, 37.98, 52.19, 65.38, 66,33, 127.23, 129.64, 136.90, 143.59, 169.96, 170.23. Analysis calculated for $C_{35}H_{61}NO_6S$: C, 67.38; H, 9.85; N, 2.24. Found C, 67.34; H, 9.78; N, 2.29.

2.1.2.9. Diisobutyl 2-(tosylamino)succinate ***(3j)***. White Solid, mp 67–71 °C. FT-IR (KBr) 3291, 2962, 1740, 1598, 1473, 1344, 1284, 1122, 1091, 1048, 819, 672, 565 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.82 (d, J = 6.6 Hz, 6H), 0.89 (d, J = 6.9 Hz, 6H), 1.74–1.92 (m, 2H), 2.40 (s, 3H), 2.84 (dd, J = 16.9 HZ, J = 4.8 Hz, 1H), 2.97 (dd, J = 16.9 Hz, J = 4.5 Hz, 1H), 3.77 (d, J = 6 Hz, 2H), 3.83 (d, J = 6.9 Hz, 2H), 4.15 (ddd, J = 8.1 Hz, J = 4.8 Hz, J = 4.5 Hz, 1H), 5.69 (d, J = 8.1 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS ,75 MHz), δ ppm 18.81, 18.98, 21.48, 27.47, 27.56, 37.89, 52.16, 71.22, 72.14, 127.21, 129.66, 136.84, 143.63, 169.94, 170.27. Ms. m/z (%): 400 (M^+ + 1, 1.52), 298 (100.00), 270 (2.83), 242 (40.45), 224 (7.46), 173 (4.61), 155 (40.31), 132 (4.15), 91 (51.90), 70 (13.82), 57 (21.50), 41 (15.92). Analysis calculated for $C_{19}H_{29}NO_6S$: C, 57.12; H, 7.32; N, 3.51. Found C, 57.18; H, 7.41; N, 3.48.

2.1.2.10. Diisopentyl 2-(tosylamino)succinate ***(3k)***. White Solid, mp 68–72 °C. FT-IR (KBr) 3289, 2958, 1739, 1600, 1465, 1346, 1285, 1168, 1118, 1092, 816, 675, 567 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.84 (d, J = 6 Hz, 6H), 0.89 (d, J = 6.6 Hz, 6H), 1.36 (q, J = = 7.2 Hz, 2H), 1.48 (q, J = 6.9 Hz, 2H), 1.51–1.66 (m, 2H), 2.40 (s, 3H), 2.80 (dd, J = 16.9 Hz, J = 5.1 Hz, 1H), 2.93 (dd, J = 16.9 Hz, J = 4.5 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 4.13 (ddd, J = 8.1 Hz, J = 5.1 Hz, J = 4.5 Hz, 1H), 5.68 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS ,75 MHz), δ ppm 21.48, 22.25, 22.30, 24.82, 24.96, 36.87, 37.11, 37.96, 52.20, 63.84, 64.80, 127.21, 129.63, 136.92, 143.57, 169.95, 170.21. Ms. m/z (%): 428 (M^+ + 1) (1.06), 312 (100.00), 272 (12.26), 242 (17.43), 224 (5.99), 155 (29.48), 91 (37.27), 71 (10.59), 43 (26.68). Analysis calculated for $C_{21}H_{33}NO_6S$: C, 58.99; H, 7.78; N, 3.28. Found C, 58.91; H, 7.69; N, 3.31.

2.1.2.11. Bis(2-methylbutyl) 2-(tosylamino)succinate ***(3l)***. White Solid, mp 57–61 °C. FT-IR (KBr) 3288, 2965, 1600, 1343, 1194, 1169, 819, 674, 566 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 M Hz), δ ppm 0.76–0.90 (m, 12H), 1.05–1.42 (m, 4H), 1.53–1.68 (m, 2H), 2.39 (s, 3H), 2.82 (dd, J = 17.1 Hz, J = 5.1 Hz, 1H), 2.95 (dd, J = 17.1 Hz, J = 4.5 Hz, 1H), 3.74–3.96 (m, 4H), 4.14 (ddd, J = 8.1 Hz, J = 5.1 Hz, J = 4.5 Hz, 1H), 5.69 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 11.01, 11.10, 16.10, 16.27, 21.46, 25.72, 25.89, 33.84, 33.95, 37.89, 52.17, 69.76, 70.69, 127.19, 129.64, 136.90, 143.58, 169.98, 170.25. Ms. m/z (%): 428 (M^+ + 1. 2.41) 312 (100.00), 272 (16.47), 242 (52.72), 155 (41.59), 91 (48.93), 70 (23.28), 43 (57.43). Analysis calculated for $C_{21}H_{33}NO_6S$: C, 58.99; H, 7.78; N, 3.28. Found C, 58.84; H, 7.83; N, 3.19.

2.1.2.12. Bis(2-ethylhexyl) 2-(tosylamino)succinate ***(3m)***. Viscous colorless oil. FT-IR (Neat) 3284, 2960, 1740, 1599, 1462, 1346, 1165, 1093, 814, 664, 562 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 M Hz), δ ppm 0.81 (t, J = 7.5 Hz, 6 Hz), 0.87 (t, J = 6.9 Hz, 6H), 1.16–1.37 (m, 16H), 1.40–1.55 (m, 2H), 2.40 (s, 3H), 2.83 (dd, J = 17.1 Hz, J = 4.9 Hz, 1H), 2.95 (dd, J = 17.1 Hz, J = 4.2 Hz, 1H), 3.88–3.98 (m, 4H), 4.13 (ddd, J = 8.2 Hz, J = 4.9 Hz, J = 4.2 Hz, 1H), 5.67 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 10.79, 10.87, 13.96, 13.97, 21.47, 22.86, 22.90, 23.49, 23.64, 28.76, 28.85, 30.07, 30.10, 37.91, 38.52, 38.61, 52.15, 67.61, 68.47, 127.19, 129.64, 136.91, 143.56, 170.01, 170.29. Ms. m/z (%): 512 (M^+ + 1, 3.67), 354 (100.00), 288 (4.26), 242 (65.33), 155 (32.04), 91 (37.24), 70 (21.18), 57 (42.68), 43 (25.17), 41 (16.43). Analysis calculated for $C_{27}H_{45}NO_6S$: C, 63.37; H, 8.86; N, 2.74. Found C, 63.41; H, 8.92; N, 2.65.

2.1.2.13. Diisopropyl 2-(tosylamino)succinate ***(3n)***. White Solid, mp 89–90 °C. FT-IR (KBr) 3287, 2984, 1743, 1600, 1333, 1043, 815, 664, 563 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz) , δ ppm 1.22 (d, J = 6.3 Hz, 6H), 1.25 (d, J = 7.5 Hz, 6H), 2.42 (s, 3H), 2.77 (dd, J = 16.8 Hz, J = 5.1 Hz, 1H), 2.91 (dd, J = 16.8 Hz, J = 4.5 Hz, 1H), 4.10 (ddd, J = 8.1 Hz, J = 5.1 Hz, J = 4.5 Hz , 1H), 4.89 (septed, J = 6.3 Hz, 1H), 4.99 (septed, J = 7.5 Hz, 1H), 5.62 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 21.31, 21.43, 21.6, 21.69, 38.26, 52.31, 68.80, 70.05, 127.24, 129.62, 136.94, 143.58, 169.40, 169.60. Ms. m/z (%): 372 (M^+ + 1, 1.45) 284 (99.68), 242 (92.53), 216 (16.06), 155 (70.40), 91 (100.00), 70 (34.87), 65 (22.79), 43 (65.27), 41 (20.96). Analysis calculated for $C_{17}H_{25}NO_6S$: C, 54.97; H, 6.78; N, 3.77. Found C, 54.88; H, 6.84; N, 3.65.

2.1.2.14. Di-sec-butyl 2-(tosylamino)succinate ***(3o)***. White Solid, mp 66–67 °C. FT-IR (KBr) 3290, 2977, 1743, 1600, 1344, 1197, 1168, 817, 677, 554 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz), δ ppm 0.78–0.86 (m, 6H), 1.04–1.21 (m, 6H), 1.42–1.63 (m, 4H), 2.42 (s, 3H), 2.80 (dd, J = 16.8 Hz, J = 4.5 Hz, 1H), 2.94 (dd, J = 16.8 Hz,

Table 1
The addition of *p*-toluenesulfonamide to diethyl fumarate under various solvents.[a]

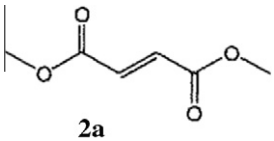
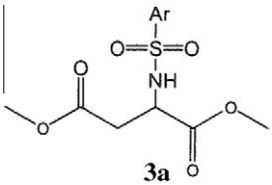
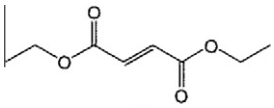
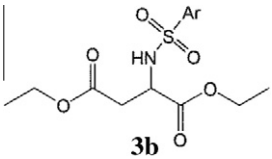
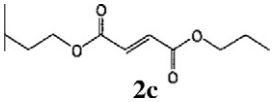
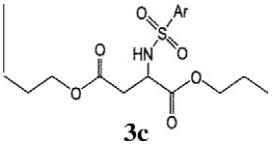
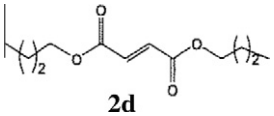
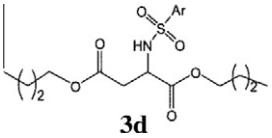
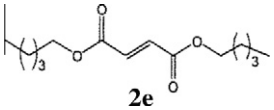
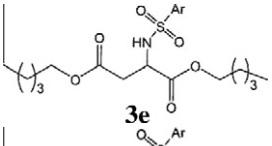
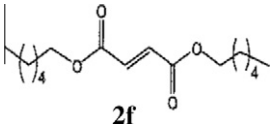
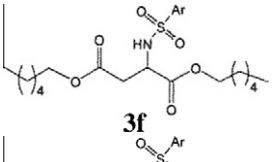
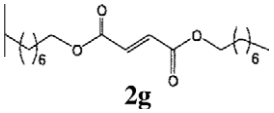
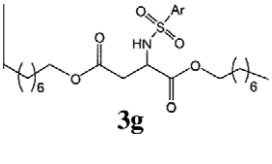
Entry	Solvent	Time (min)		Yield (%)[b]	
		U.S	Δ	U.S	Δ
1	DMF	30	100	38	17
2	DMSO	30	100	57	30
3	CH_2Cl_2	30	120	32	–
4	THF	30	100	25	–
5	CH_3CN	30	100	27	–
6	CH_3COCH_3	30	120	40	–
7	CH_3COOEt	30	120	36	–
8	MeOH	30	100	30	–
9	EtOH	30	120	21	–
10	Dioxane	30	120	43	15
11	Toluene	30	100	–	–
12	H_2O	30	100	–	–
13	None	30	120	65	34

[a] All reactions were run with **1** (1 mmol), **2b** (1 mmol) and K_2CO_3 (1 mmol) in 5 mL solvent at 38 °C.
[b] Isolated yields.

J = 4.2 Hz, 1H), 4.12 (ddd, *J* = 7.8 Hz, *J* = 4.5 Hz, *J* = 4.2 Hz, 1H), 4.71–4.86 (m, 2H), 5.63 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H).[13]C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 9.60, 18.93, 19.05, 19.26, 19.30, 21.48, 28.40, 28.65, 38.19, 52.27, 52.31, 73.38, 74.60, 74.71, 127.25, 129.64, 136.93, 143.59, 169.52, 169.78. Ms. *m*/*z* (%): 400 (M^+ + 1, 2.30) (1.07), 298 (79.47), 284 (1.72), 270 (14.93), 242 (100.00), 224 (7.46), 173 (7.19), 155 (52.74), 149 (27.51), 91 (60.48), 70 (28.31), 57 (22.57), 43 (12.04), 41 (22.40). Analysis calculated for $C_{19}H_{29}NO_6S$: C, 57.12; H, 7.32; N, 3.51. Found C, 57.22; H, 7.28; N, 3.46.

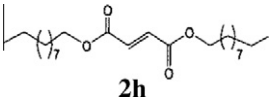
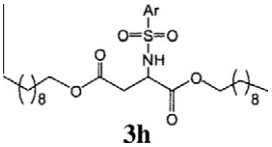
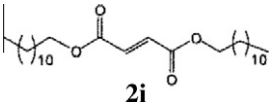
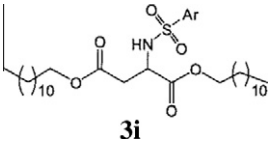
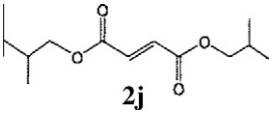
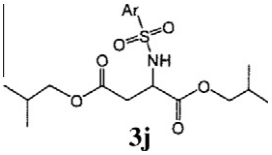
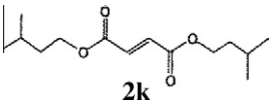
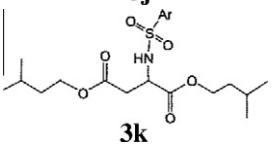
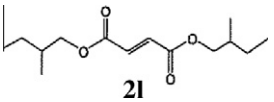
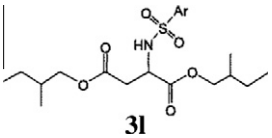
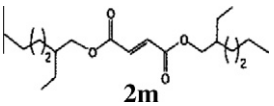
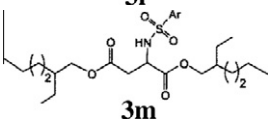
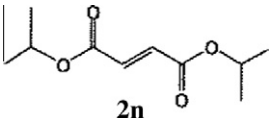
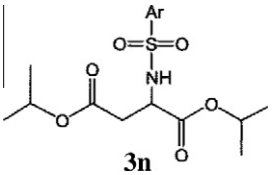
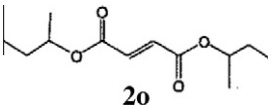
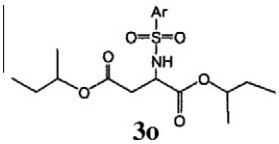
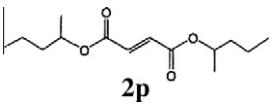
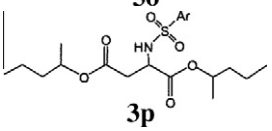
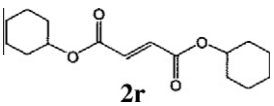
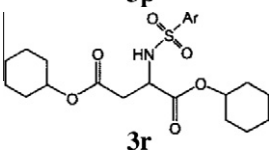
2.1.2.15. Dipentan-2-yl 2-(tosylamino)succinate ***(3p)***. Viscous colorless oil. FT-IR (Neat) 3283, 2961, 1734, 1599, 1457, 1343, 1165, 1093, 815, 664, 563 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 M Hz), δ ppm 0.79–0.92 (m, 6H), 1.17–1.59 (m, 14), 2.40 (s, 3H), 2.72–2.81 (m, 1H), 2.90 (dd, *J* = 17.1 Hz, *J* = 4.2 Hz, 1H), 4.09 (ddd, *J* = 8.1 Hz, *J* = 4.5 Hz, *J* = 4.2 Hz, 1H), 4.79 (sextet, *J* = 6.3 Hz, 1H), 4.88 (sextet, *J* = 6 Hz, 1H), 5.66 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz), δ ppm 18.37, 18.40, 18.55, 19.43, 19.53, 19.76, 19.80, 19.84, 21.47, 37.62, 37.66, 37.88, 38.13, 38.15, 38.19, 52.25, 52.30, 71.91, 71.97, 73.13, 73.26, 127.23, 129.61, 136.94, 143.53, 169.48, 169.52, 169.75, 169.78. Ms. *m*/*z* (%): 428 (M^+ + 1, 3.21) (4.56), 358 (4.64), 312 (84.14), 272 (13.34), 242 (100.00), 224

Table 2
Solvent-free Michael addition of *p*-toluenesulfonamide to fumaric esters in the presence of K_2CO_3 in a molar ratio of 1:1:1, respectively, under conventional thermal heating and ultrasound irradiation at 53 °C.[a]

Entry	Ester	Product	Time		Yield (%)[c]	
			U.S	Δ	U.S	Δ
1	 **2a**	 **3a**	10[b]	20	–	–
2	 **2b**	 **3b**	40[b]	3	90	85
3	 **2c**	 **3c**	1	14	89	86
4	 **2d**	 **3d**	1	14	87	87
5	 **2e**	 **3e**	1	15	85	85
6	 **2f**	 **3f**	1	20	81	80
7	 **2g**	 **3g**	1	22	70	49

(*continued on next page*)

Table 2 (*continued*)

Entry	Ester	Product	Time		Yield (%)[c]	
			U.S	Δ	U.S	Δ
8	 **2h**	 **3h**	1.5	22	67	14
9	 **2i**	 **3i**	2	22	60	60
10	 **2j**	 **3j**	1.5	20	80	82
11	 **2k**	 **3k**	1	19	87	85
12	 **2l**	 **3l**	1.5	20	86	84
13	 **2m**	 **3m**	2	25	80	78
14	 **2n**	 **3n**	1	19	85	85
15	 **2o**	 **3o**	1	24	83	80
16	 **2p**	 **3p**	1.5	42	78	75
17	 **2r**	 **3r**	1.5	29	74	74

[a] Ar: 4-CH_3Ph.
[b] Time (min).
[c] Isolated yields.

(5.86), 155 (37.34), 133 (10.09), 119 (10.92), 91 (35.21), 70 (21.01), 43 (18.65). Analysis calculated for $C_{21}H_{33}NO_6S$: C, 58.99; H, 7.78; N, 3.28. Found C, 58.83; H, 7.65; N, 3.36.

2.1.2.16. Dicyclohexyl 2-(tosylamino)succinate ***(3r)***. White Solid, mp 99–102 °C. FT-IR (KBr) 3268, 2938, 1748, 1704, 1599, 1345, 1220, 1127, 814, 666, 559 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 M Hz), δ ppm 1.24–1.78 (m, 20H), 2.39 (s, 3H), 2.77 (dd, J = 16.8 Hz, J = 5.1 Hz, 1H), 2.90 (dd, J = 16.8 Hz, J = 4.5 Hz, 1H), 4.10 (ddd, J = 8.1 Hz, J = 5.1 Hz, J = 4.5 Hz, 1H), 4.63–4.74 (m, 2H), 5.65 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H). ^{13}C NMR (CDCl3, TMS ,75 MHz), δ ppm 21.46, 23.36, 23.38, 23.65,

25.14, 25.24, 30.98, 31.09, 31.46, 38.31, 52.36, 73.72, 74.71, 127.22, 129.62, 136.98, 143.54, 169.32, 169.50. Ms. *m*/*z* (%): 452 (M^+ + 1, 4.08), 324 (86.39), 296 (12.34), 242 (100.00), 155 (27.69), 91 (21.61), 70 (12.08), 55 (13.96), 41 (8.1). Analysis calculated for $C_{23}H_{33}NO_6S$: C, 61.17; H, 7.37; N, 3.10. Found C, 61.22; H, 7.25; N, 3.21.

3. Results and discussion

Initially, we investigated the reaction under conventional thermal heating condition. In order to find the optimal reaction conditions, the model reaction of diethyl fumarate **2b** with *p*-toluenesulfonamide was conducted in the presence of K_2CO_3 in a molar ratio of 1:1:1, respectively, at 38 °C in divers solvents which the results were listed in Table 1.

Among all the solvents tested, only in a few of them the reaction was successful (Table 1, entries 1, 2, 10, Δ). The solvent DMSO as well as none solvent media afforded better yield than some other solvents tested under conventional thermal heating conditions (Table 1, entries 2, 13, Δ). However, the results did not satisfy our interest of the reaction due to undesirable yields and long reaction times.

In two last decades, ultrasonic irradiation technique has received considerable attention [27,28]. In comparison with traditional heating methods, this technique has advantages such as formation of purer products in high yields, shorter reaction times, and easier manipulation and developed new reactions [29–31]. We have, therefore, decided to apply this technique to the above mentioned model reaction. The effectiveness of ultrasound to promote this conversion was tested in various solvents, at 38 °C (Table 1, entries 1–12, U.S). Surprisingly, this conversion was successful in almost of solvents tested (Table 1, entries 1–12, U.S) and the best result were obtained in DMSO (Table 1, entry 2, U.S). Encouraged by these results, we tried the reaction under solvent-free condition at 38 °C. To our surprise, the result was satisfactory and even better than in DMSO media (Table 1, entry 13, U.S). The new findings promoted us to repeat this reaction with different fumarates to explore the scope of reaction under solvent-free condition (Table 2).

It is seen from results of Table 2 that in comparison with conventional methods, the protocol using ultrasound irradiation in all cases showed a significant decrease of reaction times (Table 2, entries 2 and 16). It has been observed that the bulkiness of alkoxy group (–OR) of fumaric esters did not affect significantly on the yields and reaction times under both conventional thermal heating and ultrasound irradiation conditions (Table 2). Michael addition of *p*-toluenesulfonamide to methyl fumarate was not successful (Table 2, entry 1). The reaction gave fumaric acid and *p*-toluenesulfonamide **1** without the formation of any Michael adduct. We believe that methyl fumarate is more susceptible to hydrolysis under the reaction conditions, due to its smaller alkoxy groups (–OMe). Interestingly, in all these reactions only monosubstituted products were obtained and no disubstituted products were observed at all (Table 2). We repeated all of the reactions, even in the presence of excess fumaric esters, and observed monosubstituted Michael adducts as the exclusive products of the reactions. This can be related to the steric influence of the first substitute on nitrogen atom of *p*-toluenesulfonamide that makes it poorer nucleophile.

The influence of different organic and inorganic bases on this reaction was also investigated under model reaction conditions (Table 3). It appeared that the reasonable yield was given only under the catalysis by K_2CO_3 (Table 3, entry 5).

Table 3
Michael addition of *p*-toluenesulfonamide (1 mmol) to diethyl fumarate (1 mmol) in the presence of different bases (1 mmol) under ultrasound irradiation conditions at 53 °C.

Entry	Base	Time (min)	Yield (%)[a]
1	NEt_3	90	30
2	DABCO[b]	100	12
3	Li_2CO_3	60	–
4	Na_2CO_3	90	20
5	K_2CO_3	40	90
6	Ca_2CO_3	100	–
7	NaOH[c]	90	30
8	KOH[c]	60	50
9	PPh_3	90	–
10	CaO	90	–
11	MgO	90	–
12	ZnO	90	–

[a] Isolated yield.
[b] DABCO:1,4-diazabicyclo[2.2.2] octane.
[c] In these cases fumaric acid was obtained as by product.

4. Conclusion

In summary, we have developed a new methodology using ultrasound irradiation for the synthesis of *p*-toluenesulfonamide derivatives by aza-Michael addition reaction of *p*-toluenesulfonamide to fumaric esters under solvent-free condition. This technique is very simple, efficient, and environmentally friendly. It was demonstrated that, among the organic and inorganic bases, potassium carbonate, as a cheap and green base, effectively catalysis this reaction.

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