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Aza-Morita–Baylis–Hillman reaction with ion-supported Ph_3P

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ABSTRACT

Various *N*-tosyl arylimines reacted with methyl vinyl ketone and ethyl vinyl ketone in the presence of ion-supported Ph_3P **A** and **B** to give adducts, *N*-(2′-methylene-3′-oxo-1′-arylbutyl)-4-methylbenzenesulfonamides and *N*-(2′-methylene-3′-oxo-1′-arylpentyl)-4-methylbenzenesulfonamides, respectively, in good yields with high purity by simple diethyl ether extraction of the reaction mixture. Moreover, ion-supported Ph_3P **A** and **B** could be repeatedly used for the same reaction to provide the corresponding adducts while maintaining good yields with high purity.

1. Introduction

The aza-Morita–Baylis–Hillman (aza-MBH) reaction with *N*-tosyl arylimines with vinyl ketones is a very attractive and important tool for C–C bond formation as it provides enriched β-amino carbonyl compounds bearing an α-*exo*-methylene group and yields potent and useful building blocks for organic synthesis. Therefore, the active study for the aza-MBH reaction of *N*-tosyl arylimines with vinyl ketones using tertiary amines, phosphines, and chiral amines and phosphines as the catalyst has been well carried out.[1] Generally, the reaction must be performed under mild reaction conditions, i.e., room temperature, in the presence of 10–20 mol % catalyst to give products in good yields. However, the reaction mixture must undergo troublesome purification by column chromatography to remove the catalyst. Recently, polymer-supported diphenylphosphine and DMAP,[2a,b] and calix[4]arene-supported diphenylphosphine[2c] for the aza-MBH reaction were reported to generate products in good yields, although purification of the filtrates by short column chromatography was still required.[1g,2] In view of process chemistry and environmentally benign organic synthesis, simple experimental procedure and simple isolation of the desired product are very important. Therefore, we have set our sights on elucidating the synthetic use of ion-supported reagents, such as ion-supported PhI,[3] ion-supported Ph_3P,[4] and ion-supported methyl sulfoxide.[5] We expected that the use of an ion-supported reagent would enable the easy separation of the desired product from the reaction mixture by simple ether extraction or filtration, and the reuse of the recovered ion-supported reagent should be possible. Previously, we examined the synthetic use of 4-(diphenylphosphino)benzyltrimethyl-ammonium bromide **A** and *N*-methyl-*N*-[4-(diphenyl-phosphino)benzyl]pyrrolidinium bromide **B**, and found that these ion-supported Ph_3P **A** and **B** were stable under argon gas for long time and could be used for the halogenation of alcohols, the esterification of carboxylic acids,[4a] and the Wittig reaction[4b] as an equivalent required reagent. We also found that the quantitatively recovered ion-supported Ph_3PO was regenerated to ion-supported Ph_3P **A** and **B**, which could be reused for the same reactions. Here, we would like to report the aza-MBH reaction of *N*-tosyl arylimines with vinyl ketones using ion-supported Ph_3P **A** and **B** as the catalyst.

2. Results and discussion

First, the optimization of the aza-MBH reaction of *N*-tosyl 4-chlorophenylimine with methyl vinyl ketone in the presence of 0.5 equiv of ion-supported Ph_3P **A** or **B** was carried out at room temperature, and the results are shown in Tables 1 and 2. CH_2Cl_2 showed the best reactivity among the solvents used, including THF, $ClCH_2CH_2Cl$, $CHCl_3$, CH_3CN, and EtOH (entries 1–6, Tables 1 and 2). Ion-supported Ph_3P (0.5 equiv) was required to give the adduct in good yield with high purity by simple filtration of the reaction mixture, and a long reaction time (over 50 h) was required when the amount of ion-supported Ph_3P **A** or **B** was reduced to 0.2 equiv Then, ionic liquids, such as [bmim]PF_6, [bmpy]NTf_2, [bmim]BF_4, and [emim]OTs, containing ion-supported Ph_3P due to reuse of reaction media containing ion-supported Ph_3P **A** or **B**, were used under the same conditions. However, the yield of adduct by extraction with ether and removal of the solvent from the extract was low (entries 7–10, Tables 1 and 2). On the basis of these results, the aza-MBH reaction of *N*-tosyl 4-chlorophenylimine with methyl vinyl ketone in the presence of both ion-supported Ph_3P **A** or **B**, and MS 4 Å (~0.1 g) was carried out to provide the adduct in high yields with high purity (entry 11 in Tables 1 and 2). We believe MS4 Å remove a trace amount of moisture from IS-Ph_3P **A** and **B**. On the other

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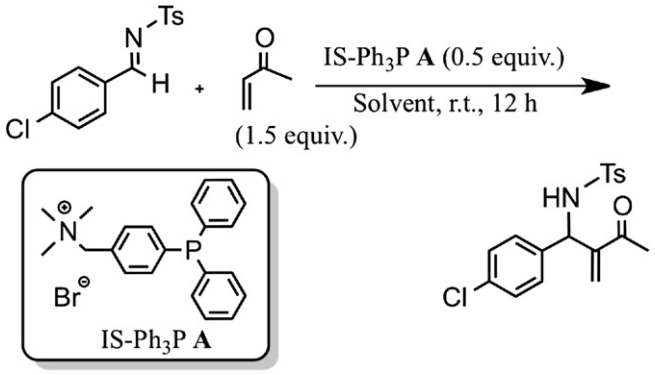
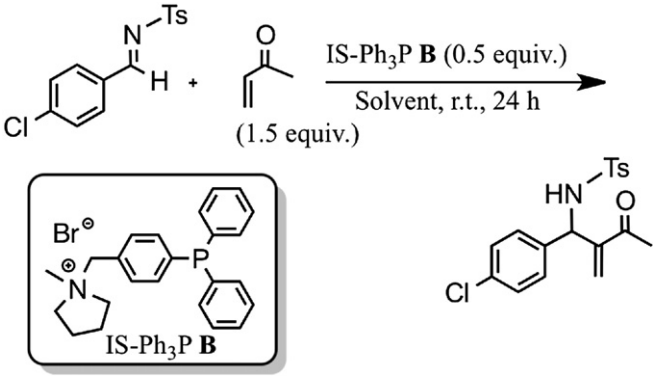
Table 1
Optimization of aza-MBH reaction using ion-supported Ph_3P **A**



Entry	Solvent	Yield (%)	Purity (%)
1	THF	64 (34)[a]	52
2	CH_2C1_2	85 (trace)[a]	99
3	$C1CH_2CH_2C1$	77 (14)[a]	75
4	$CHC1_3$	82 (7)[a]	80
5	MeCN	70 (16)[a]	67
6	EtOH	52 (20)[a] (16)[b]	36
7	[bmim]PF_6	30 (58)[a]	26
8	[bmpy]NTf_2	42 (38)[a]	30
9	[bmim]BF_4	9 (13)[a] (68)[b]	—
10	[emim]OTs	56 (36)[a]	51
11[c]	CH_2C1_2	quant.	>99
12[c,d]	CH_2C1_2	99	60

[a] Yield of aldehyde.
[b] Yield of starting material.
[c] MS 4 Å was added.
[d] Ph_3P was used instead of IS-Ph_3P.

Table 2
Optimization of aza-MBH reaction using ion-supported Ph_3P **B**



Entry	Solvent	Yield (%)	Purity (%)
1	THF	10 (trace)[a] (85)[b]	5
2	CH_2C1_2	85 (trace)[a]	99
3	$C1CH_2CH_2C1$	71 (5)[a] (trace)[b]	70
4	$CHC1_3$	73 (trace)[a]	70
5	MeCN	65 (16)[a] (trace)[b]	60
6	EtOH	60 (14)[a] (25)[b]	45
7	[bmim]PF_6	20 (53)[a] (6)[b]	—
8	[bmpy]NTf_2	72 (27)[a]	48
9	[bmim]BF_4	0 (90)[b]	—
10	[emim]OTs	26 (20)[a] (49)[b]	—
11[c]	CH_2C1_2	95	>99

[a] Yield of aldehyde.
[b] Yield of starting material.
[c] MS 4 Å was added.

hand, when Ph_3P, instead of ion-supported Ph_3P **A**, was used under the same conditions, the adduct was obtained in high yield, although its purity was 60% due to the presence of Ph_3P in the filtrate after the same filtration of the reaction mixture, and the residue could not be reused at all (entry 12, Table 1).

Based on these results, the aza-MBH reaction of *N*-tosyl arylimines, such as *N*-tosyl 4-chlorophenylimine, 4-bromophenylimine, 4-fluorophenylimine, 4-nitrophenylimine, phenylimine, 4-methylphenylimine, 4-methoxyphenylimine, 1-naphthylimine, and 2-thienylimine, with methyl vinyl ketone in the presence of ion-supported Ph_3P **A** or **B** was carried out to give the corresponding adducts in good yields with high purity by simple filtration of the reaction mixture and removal of the solvent from the filtrate, as shown in Tables 3 and 4 (entries 1–9). There are not much difference in the reactivity and yield between ion-supported Ph_3P **A** and **B**.

Unfortunately, the yield of the corresponding adduct in the reaction of *N*-tosyl 3-pyridylimine with methyl vinyl ketone in the presence of ion-supported Ph_3P **A** and **B** was not high, although the purity of the adduct was good (entry 10 in Tables 3 and 4). Then, the same treatment of *N*-tosyl arylimines, such as *N*-tosyl 4-chlorophenylimine, 4-bromophenylimine, 4-fluorophenylimine, 4-nitrophenylimine, phenylimine, 4-methylphenylimine, 4-methoxyphenylimine, 1-naphthylimine, and 2-thienylimine, with ethyl vinyl ketone in the presence of ion-supported Ph_3P **A** or **B** was carried out to give the corresponding adducts in good yields with high purity again by simple filtration of the reaction mixture and removal of the solvent from the filtrate, as shown in Tables 5 and 6, except for *N*-tosyl 4-methoxylphenylimine. However, the yield of the adduct in the reaction of ethyl vinyl ketone and *N*-tosyl 4-methoxyphenylimine, which has an electron-donating group on aromatic ring, was improved by increasing the amounts of IS-Ph_3P **A** or **B**, and ethyl vinyl ketone (entries 7 in Tables 5 and 6). Then, the reuse of ion-supported Ph_3P **A** and **B** in the reaction of *N*-tosyl 4-fluorophenylimine with methyl vinyl ketone was carried out and the results are shown in Table 7. After the addition of diethyl ether to the first reaction mixture, the obtained mixture was stirred for 30 min at 0 °C. Then, the mixture was filtered to separate ion-supported Ph_3P **A** or **B** and the filtrate. After removal of the solvent from the filtrate, the adduct was obtained in high yield with 94% and 95% purities, respectively, and ion-supported Ph_3P **A** or **B** was recovered in quantitative yield. Then, the recovered ion-supported Ph_3P **A** or **B** was added to a mixture of *N*-tosyl 4-fluorophenylimine and methyl vinyl ketone in CH_2Cl_2, and the obtained mixture was stirred for 5 h at room temperature again.

After the reaction, diethyl ether was added again to precipitate the ion-supported Ph_3P **A** or **B**, and the obtained mixture was filtered to separate ion-supported Ph_3P **A** or **B** and the filtrate containing the adduct, after stirring for 30 min at 0 °C. By using this procedure, the adduct was obtained in high yields with high purity up to the fourth time, and ion-supported Ph_3P **A** and **B** were recovered in quantitative yields each time, respectively.

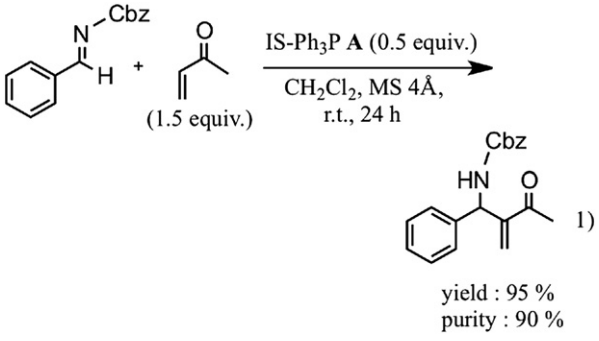
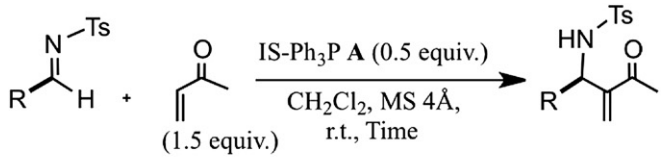


Table 3
Investigation of aza-MBH reaction using ion-supported Ph_3P **A**



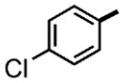
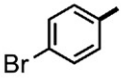
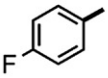
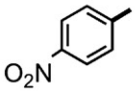
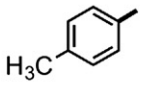
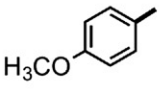
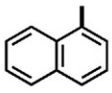
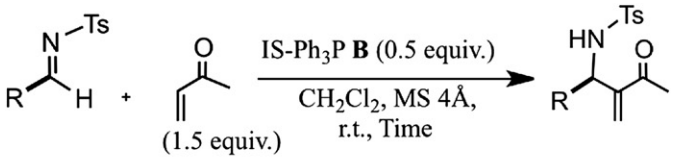
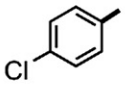
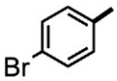
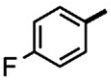
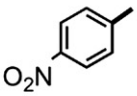
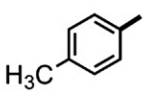
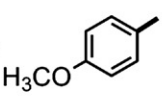
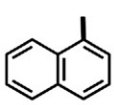
Entry	R	Time (h)	Yield (%)	Purity (%)
1		24	100	92
2		24	95	91
3		5	97	94
4		3	94	90
5		24	96	97
6		24	94	95
7		24	87	90
8		48	74	86
9		50	80	85
10		48	60	80

Table 4
Investigation of aza-MBH reaction using ion-supported Ph_3P **B**



Entry	R	Time (h)	Yield (%)	Purity (%)
1		24	95	99
2		24	94	90
3		5	100	95
4		3	92	93
5		24	97	99
6		24	95	92
7		24	90	90
8		48	66	50
9		50	85	80
10		48	62	78

Additionally, when *O*-benzyl *N*-benzylidinecarbamate was treated with methyl vinyl ketone in the presence of ion-supported Ph_3P **A**, the adduct, *N*-(2′-methylene-3′-oxo-1′-phenylbutyl)-*O*-benzyl-carbamate was obtained in good yield with high purity, as shown in Eq. 1, together with quantitative recovery of ion-supported Ph_3P **A**.

On the other hand, the reactions of *N*-tosyl arylimines with ethyl acrylate, acrolein, or acrylonitrile in the presence of ion-supported Ph_3P **A** or **B** gave the adducts in very low yields.

3. Conclusion

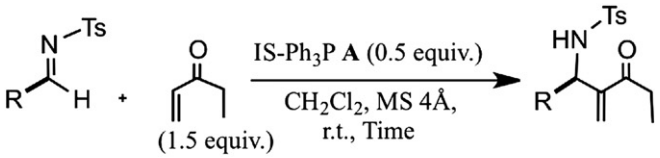
Ion-supported Ph_3P **A** and **B** could be used as a catalyst for the reaction of *N*-tosyl arylimines with vinyl ketones to give the corresponding adducts in good yields with high purity by simple filtration of the reaction mixture, and the recovered ion-supported Ph_3P **A** and **B** could be reused for the same reaction while maintaining good yield and high purity of the adducts. Thus the present ion-supported Ph_3P **A** and **B** are useful recyclable catalysts for aza-MBH reaction.

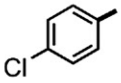
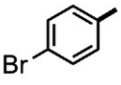
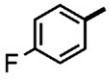
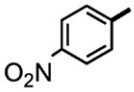
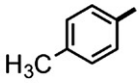
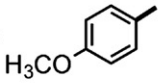
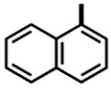
4. Experimental

4.1. General

^1H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in parts per million downfield from TMS in δ units. Mass spectra were recorded on JMS-T100GCV, JMS-

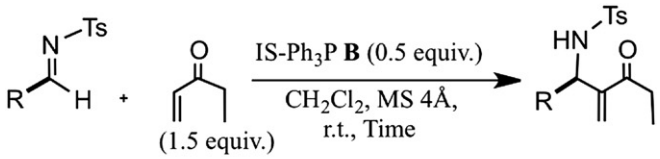
Table 5
Investigation of aza-MBH reaction using ion-supported Ph_3P **A**

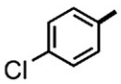
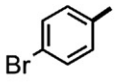
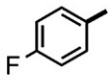
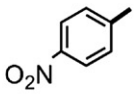
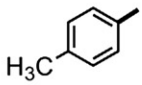
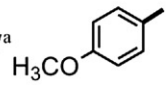
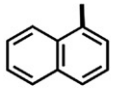


Entry	R	Time (h)	Yield (%)	Purity (%)
1		24	96	99
2		24	100	94
3		12	96	99
4		12	94	95
5		24	95	95
6		24	100	99
7[a]		63	81	72
8		48	73	86
9		50	85	83
10		70	60	90

[a] IS-Ph_3P **A** (2.5 equiv.) and ethyl vinyl ketone (3.0 equiv.) were used. Reaction temperature was 0 °C.

Table 6
Investigation of aza-MBH reaction using ion-supported Ph_3P **B**



Entry	R	Time (h)	Yield (%)	Purity (%)
1		24	97	96
2		24	96	99
3		12	100	99
4		12	92	90
5		24	96	95
6		24	97	95
7[a]		63	83	74
8		48	75	81
9		50	82	80
10		72	61	90

[a] IS-Ph_3P **B** (2.5 equiv.) and ethyl vinyl ketone (3.0 equiv.) were used. Reaction temperature was 0 °C.

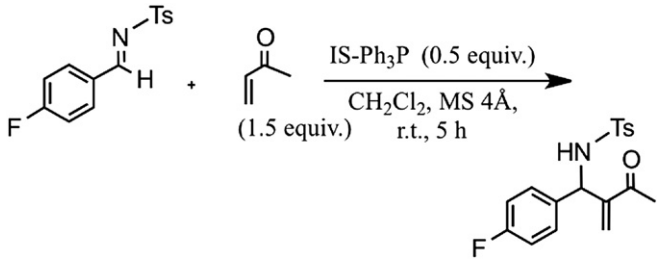
HX110, and Thermo LTQ Orbitrap XL spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography.

4.2. Ion-supported Ph_3P A and B were prepared by the previous method[4]

*4.2.1. 4-(Diphenylphosphino)benzyltrimethylammonium bromide **A**.* Mp 168–170 °C; IR (neat) 1477, 1433, 822, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ=3.39 (s, 9H), 5.02 (s, 2H), 7.27–7.30 (m, 2H), 7.32–7.40 (m, 12H); ^{13}C NMR ($CDCl_3$, TMS) δ=52.66 (p), 68.37 (s), 127.43 (q), 128.65 (d, J_{C-P}=6.7 Hz, t), 129.14 (t), 132.88 (d, J_{C-P}=6.7 Hz, t), 133.88 (d, J_{C-P}=19.6 Hz, t), 133.95 (d, J_{C-P}=18.6 Hz, t), 135.86 (d, J_{C-P}=10.5 Hz, q), 141.50 (d, J_{C-P}=14.3 Hz, q); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ=−4.98; Elemental analysis: calcd for $C_{22}H_{25}BrNP\cdot 1/2CH_3OH$: C, 62.80%; H, 6.32%; N, 3.25%. Found: C, 62.77%; H, 6.09%; N, 3.16%.

*4.2.2. N-Methyl-N-[4-(diphenylphosphino)benzyl]pyrrolidinium bromide **B**.* Mp 207–209 °C; IR (neat) 1433, 742, 696 cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ=2.22 (m, 2H), 2.35 (m, 2H), 3.21 (s, 3H), 3.68 (m, 2H), 4.03 (m, 2H), 5.08 (s, 2H), 7.26–7.40 (m, 12H), 7.62 (d, J=2.8 Hz,

Table 7
Reuse of ion-supported Ph_3P in aza-MBH reaction



Reuse	IS-Ph_3P **A**		IS-Ph_3P B	
	Yield (%)	Purity (%)	Yield (%)	Purity (%)
0	97	94	100	95
1[a]	96	95	98	98
2[a]	96	99	100	98
3[a]	98	98	100	95
4[a]	97	97	95	94

[a] Only *N*-(4-fluorobenzylidene)-4-methylbenzenesulfonamide, methyl vinyl ketone, and MS 4 Å were added.

2H); ^{13}C NMR ($CDCl_3$, TMS) δ=21.21 (s), 47.81 (p), 63.12 (s), 65.58 (s) 128.54 (q), 128.79 (d, J_{C-P}=7.7 Hz, t), 129.27 (t), 132.70 (d, J_{C-P}=6.7 Hz, t), 133.91 (d, J_{C-P}=20.1 Hz, t), 134.03 (d, J_{C-P}=18.2 Hz, t), 136.08 (d, J_{C-P}=10.5 Hz, q), 141.23 (d, J_{C-P}=14.4 Hz, q); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ=−5.00; Elemental analysis: calcd for $C_{24}H_{27}BrNP\cdot 1/2H_2O$: C, 64.15%; H, 6.28%; N, 3.12%. Found: C, 64.09%; H, 6.11%; N, 2.96%.

4.3. Typical procedure for the aza-MBH with ion-supported Ph_3P A or B

Methyl vinyl ketone (122.0 μL, 1.5 mmol) was added to a solution of *N*-(4′-fluorobenzylidene)-4-methylbenzenesulfonamide (277.0 mg, 1.0 mmol), catalyst **B** (220.0 mg, 0.5 mmol) and MS 4 Å (~100 mg) in CH_2Cl_2 (4 mL). The obtained mixture was stirred for 5 h at room temperature under an argon atmosphere. After the reaction, diethyl ether (10 mL) was added and the obtained mixture was stirred for 30 min at 0 °C. After that, the mixture was filtered and washed with diethyl ether. Removal of the solvent from the filtrates gave *N*-[1′-(4″-fluorophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide quantitatively with 95% purity, which was estimated by ^{1}H NMR. Pure *N*-[1′-(4″-chlorophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide was obtained in 100% yield by very short flash column chromatography on silica gel (AcOEt/hexane=1:2).Ion-supported Ph_3P, **B** was recovered by the above filtration in 100% yield.

*4.3.1. Typical reuse of ion-supported Ph_3P **B**.* The ion-supported Ph_3P **B** was dried by a vacuum pump for 2 h at 80 °C. Methyl vinyl ketone (122.0 μL, 1.5 mmol) was added to a flask containing catalyst **B** (220.0 mg, 0.5 mmol), *N*-(4′-fluorobenzylidene)-4-methylbenzenesulfon-amide (277.0 mg, 1.0 mmol), and MS 4 Å (~100 mg) in CH_2Cl_2 (4 mL). The obtained mixture was stirred for 5 h at room temperature under an argon atmosphere. After the reaction, diethyl ether (10 mL) was added and the obtained mixture was stirred for 30 min at 0 °C. After that, the mixture was filtered and washed with diethyl ether. Removal of the solvent from the filtrates gave *N*-[1′-(4″-fluorophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide in 98% purity, which was estimated by ^{1}H NMR. Pure *N*-[1′-(4″-fluorophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide was obtained in 98% yield by very short flash column chromatography on silica gel (AcOEt/hexane=1:2). The ion-supported Ph_3P, **B** was recovered by the above filtration in 100% yield.

4.3.2. N-[1′-(4″-Chlorophenyl)-2′-methylene-3′-oxobutyl] 4-methylbenzenesulfonamide. Mp 109–112 °C (lit.[1g] mp 112–113 °C); IR (Nüjol): 3264 (N–H), 1674 (C=O), 1596, 1492, 1416, 1327, 1281, 1163, 1092, 1055, 1014, 961, 815, 720, 676 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.41 (s, 3H), 5.24 (d, *J*=8.9 Hz, 1H), 5.85 (d, *J*=8.9 Hz, 1H), 6.06 (s, 1H), 6.09 (s, 1H), 7.04 (d, *J*=8.3 Hz, 2H), 7.16 (d, *J*=8.6 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 7.63 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.41 (p), 26.14 (p), 57.94 (s), 127.10 (t), 127.84 (t), 128.41 (t), 128.43 (t), 129.43 (t), 133.26 (q), 137.23 (q), 137.42 (q), 143.42 (q), 146.07 (q), 198.63 (q); HRMS (ESI) calcd for $C_{18}H_{18}O_3NClNaS$ $[M+Na]^+$: 386.0582. Found: 386.0588.

4.3.3. N-[1′-(4″-Bromophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide. Mp 100–102 °C (lit.[1g] mp 115–116 °C); IR (Nüjol): 3244 (N–H), 1669 (C=O), 1488, 1319, 1121, 1073, 1010, 947, 807, 671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.42 (s, 3H), 5.21 (d, *J*=8.9 Hz, 1H), 5.77 (d, *J*=8.9 Hz, 1H), 6.06 (s, 1H), 6.09 (s, 1H), 6.99 (d, *J*=8.3 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 7.32 (d, *J*=8.3 Hz, 2H), 7.63 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.52 (p), 26.28 (p), 58.60 (s), 121.60 (q), 127.21 (t), 128.12 (t), 128.66 (t), 129.53 (t), 131.53 (t), 137.36 (q), 137.92 (q), 143.53 (q), 145.97 (q), 198.80 (q); HRMS (ESI) calcd for $C_{18}H_{18}O_3NBrNaS$ $[M+Na]^+$: 430.0080. Found: 430.0083.

4.3.4. N-[1′-(4″-Fluorophenyl)-2′-methylene-3′-oxobutyl] 4-methylbenzenesulfonamide. Mp 113–118 °C (lit.[1g] mp 104–106 °C); IR (Nüjol): 3252 (N–H), 1669 (C=O), 1598, 1507, 1334, 1220, 1157, 1072, 953, 835, 719, 662 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.16 (s, 3H), 2.41 (s, 3H), 5.25 (d, *J*=8.9 Hz, 1H), 5.73 (d, *J*=8.9 Hz, 1H), 6.07 (s, 1H), 6.10 (s, 1H), 6.88 (dd, *J*=8.7, 8.6 Hz, 2H), 7.08 (dd, *J*=8.4, 5.3 Hz, 2H), 7.24 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.50 (p), 26.32 (p), 58.39 (s), 115.33 (d, J_{C-F}=21.6 Hz, t), 126.84 (t), 127.80 (t), 127.87 (d, J_{C-F}=2.7 Hz, t), 129.52 (t), 134.64 (q), 137.38 (q), 143.47 (q), 146.24 (q), 162.05 (d, J_{C-F}=247.1 Hz, q), 198.84 (q); HRMS (ESI) calcd for $C_{18}H_{18}O_3NFNaS$ $[M+Na]^+$: 370.0875. Found: 370.0884.

4.3.5. N-[1′-(4″-Nitrophenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide. Mp 121–125 °C (lit.[1g] mp 120–122 °C); IR (Nüjol): 3239 (N–H), 1656 (C=O), 1597, 1515, 1376, 1342, 1239, 1158, 1092, 1069, 812, 740, 706, 669 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.16 (s, 3H), 2.42 (s, 3H), 5.31 (d, *J*=8.9 Hz, 1H), 5.83 (d, *J*=8.9 Hz, 1H), 6.08 (s, 1H), 6.14 (s, 1H), 7.25 (d, *J*=8.3 Hz, 2H), 7.35 (d, *J*=8.9 Hz, 2H), 7.65 (d, *J*=8.3 Hz, 2H), 7.08 (d, *J*=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.51 (p), 26.18 (p), 58.00 (t), 123.63 (t), 127.18 (t), 127.23 (t), 129.62 (t), 129.68 (s), 137.33 (q), 143.78 (q), 145.40 (q), 146.16 (q), 147.19 (q), 198.76 (q); HRMS (ESI) calcd for $C_{18}H_{17}N_2O_5S$ $[M-H]^-$: 373.0864. Found: 373.0863.

4.3.6. N-[2′-Methylene-3′-oxo-1′-phenylbutyl]-4-methyl-benzenesulfonamide. Mp 110–114 °C (lit.[1g] mp 113–114 °C); IR (Nüjol): 3257 (N–H), 1664 (C=O), 1597, 1496, 1323, 1304, 1165, 741, 675 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.41 (s, 3H), 5.27 (d, *J*=8.9 Hz, 1H), 5.70 (d, *J*=8.9 Hz, 1H), 6.09 (s, 1H), 6.10 (s, 1H), 7.07–7.11 (m, 2H), 7.16–7.21 (m, 3H), 7.23 (d, *J*=8.0 Hz, 2H), 7.65 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.50 (p), 26.31 (p), 58.87 (s), 126.36 (t), 127.26 (t), 127.59 (t), 128.26 (t), 128.49 (t), 129.48 (t), 137.43 (q), 138.82 (q), 143.33 (q), 146.38 (q), 198.82 (q); HRMS (ESI) calcd for $C_{18}H_{19}O_3NNaS$ $[M+Na]^+$: 352.0968. Found: 352.0978.

4.3.7. N-[1′-(4″-Methylphenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide. Mp 116–119 °C (lit.[1g] mp 118–119 °C); IR (Nüjol): 3281 (N–H), 1682 (C=O), 1595, 1508, 1316, 1264, 1154,

1093, 1073, 957, 936, 826, 813, 661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.26 (s, 3H), 2.41 (s, 3H), 5.24 (d, J=8.6 Hz, 1H), 5.66 (d, J=8.6 Hz, 1H), 6.09 (s, 2H), 6.96 (d, J=8.0 Hz, 2H), 7.00 (d, J=8.0 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H), 7.65 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=20.94 (p), 21.48 (p), 26.31 (p), 58.49 (s), 126.29 (t), 127.26 (t), 127.96 (t), 129.16 (t), 129.44 (t), 135.88 (q), 137.33 (q), 137.40 (q), 143.27 (q), 146.54 (q), 198.80 (q); HRMS (ESI) calcd for $C_{19}H_{21}O_3NNaS$ $[M+Na]^+$: 366.1130. Found: 366.1134.

4.3.8. N-[1′-(4″-Methoxyphenyl)-2′-methylene-3′-oxobutyl]-4-methylbenzenesulfonamide. Mp 132–133 °C (lit.[1g] mp 136–137 °C); IR (Nüjol): 3282 (N–H), 1670 (C=O), 1609, 1512, 1325, 1256, 1233, 1178, 1161, 1094, 1030, 962, 834, 814, 723, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.16 (s, 3H), 2.42 (s, 3H), 3.74 (s, 3H), 5.22 (d, J=8.3 Hz, 1H), 5.56 (d, J=8.3 Hz, 1H), 6.10 (s, 1H), 6.10 (s, 1H), 6.72 (d, J=8.9 Hz, 2H), 6.99 (d, J=8.3 Hz, 2H), 7.24 (d, J=8.0 Hz, 2H), 7.65 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.51 (p), 26.38 (p), 55.20 (p), 58.30 (s), 113.86 (t), 127.29 (t), 127.67 (t), 127.83 (t), 129.49 (t), 130.93 (q), 137.40 (q), 143.31 (q), 146.62 (q), 158.97 (q), 198.88 (q); HRMS (ESI) calcd for $C_{19}H_{21}O_4NNaS$ $[M+Na]^+$: 382.1075. Found: 382.1084.

4.3.9. N-[2′-Methylene-1′-(naphthalen-1″-yl)-3′-oxobutyl]-4-methylbenzenesulfonamide. Mp 118–120 °C (lit.[6] mp 119–120 °C); IR (Nüjol): 3274 (N–H), 1678 (C=O), 1596, 1508, 1320, 1286, 1154, 1093, 1063, 949, 779, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.22 (s, 3H), 2.42 (s, 3H), 5.17 (d, J=7.2 Hz, 1H), 6.20 (d, J=7.2 Hz, 1H), 6.22 (s, 1H), 6.27 (s, 1H), 7.20 (d, J=8.0 Hz, 2H), 7.25–7.36 (m, 3H), 7.44 (t, J=7.9 Hz, 1H), 7.72 (d, J=8.6 Hz, 2H), 7.64 (d, J=8.3 Hz, 2H), 7.79 (dd, J=1.3, 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.64 (p), 26.48 (p), 53.46 (s), 123.01 (t), 125.00 (t), 125.09 (t), 125.94 (t), 126.65 (t), 127.60 (t), 128.00 (t), 128.82 (t), 129.05 (t), 129.65 (t), 130.45 (q), 134.01 (q), 134.64 (q), 136.99 (q), 143.61 (q), 147.50 (q), 198.58 (q); HRMS (ESI) calcd for $C_{22}H_{21}O_3NNaS$ $[M+Na]^+$: 402.1129. Found: 402.1134.

4.3.10. N-[2′-Methylene-3′-oxo-1-(thiophen-2″-yl)butyl]-4-methylbenzenesulfonamide. Mp 107–108 °C (lit.[2c] mp 106–107 °C); IR (Nüjol): 3215 (N–H), 1671 (C=O), 1596, 1507, 1319, 1229, 1159, 1093, 1071, 983, 925, 815, 721, 671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.19 (s, 3H), 2.42 (s, 3H), 5.45 (d, J=9.2 Hz, 1H), 5.87 (d, J=9.2 Hz, 1H), 6.08 (s, 1H), 6.09 (s, 1H), 6.69 (dd, J=1.1, 3.3 Hz, 1H), 6.83 (dd, J=3.3, 5.1 Hz, 1H), 7.12 (dd, J=1.2, 5.1 Hz, 1H), 7.26 (d, J=7.7 Hz, 2H), 7.68 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.53 (p), 26.32 (p), 55.72 (s), 124.94 (t), 125.31 (t), 126.94 (t), 127.31 (t), 128.47 (t), 129.53 (t), 137.36 (q), 143.05 (q), 143.46 (q), 145.88 (q), 198.84 (q); HRMS (ESI) calcd for $C_{16}H_{17}O_3NNaS_2$ $[M+Na]^+$: 358.0533. Found: 358.0542.

4.3.11. N-[2′-Methylene-3′-oxo-1-(pyridin-3″-yl)butyl]-4-methylbenzenesulfonamide. Mp 105–109 °C; IR (Nüjol): 1676 (C=O), 1593, 1428, 1323, 1303, 1266, 1182, 1155, 1093, 1071, 1049, 1030, 984, 954, 850, 817, 710, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.39 (s, 3H), 5.27 (br, 1H), 5.94 (br, 1H), 6.09 (s, 1H), 6.12 (s, 1H), 7.13 (dd, J=8.2, 4.8 Hz, 1H), 7.22 (d, J=8.2 Hz, 2H), 7.52 (dt, J=8.2, 1.7 Hz, 1H), 7.63 (d, J=8.2 Hz, 2H), 8.29 (d, J=1.7 Hz, 1H), 8.40 (dd, J=4.8, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.60 (p), 26.31 (p), 57.45 (t), 123.38 (t), 127.29 (t), 129.28 (s), 129.72 (t), 134.24 (t), 134.73 (q), 137.49 (q), 143.72 (q), 145.66 (q), 148.06 (t), 148.89 (t), 198.88 (q); HRMS (ESI) calcd for $C_{17}H_{19}O_3N_2S$ $[M+H]^+$: 331.111. Found: 331.1099.

4.3.12. N-[1′-(4″-Chlorophenyl)-2′-methylene-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 111–113 °C (lit.[7] mp 112–113 °C); IR (Nüjol): 3278 (N–H), 1675 (C=O), 1597, 1159, 1072, 1013, 952, 813, 721, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.95 (t, 3H, J=7.3 Hz), 2.41 (s, 3H), 2.43–2.60 (m, 2H), 5.23 (d, J=9.2 Hz, 1H), 5.69 (d, J=9.2 Hz, 1H), 6.01 (s, 1H), 6.08 (s, 1H), 7.05 (d, J=8.2 Hz, 2H), 7.17 (d, J=8.2 Hz, 2H), 7.23 (d, J=8.0 Hz, 2H), 7.63 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.83 (p), 21.59 (p), 31.44 (s), 59.14 (t), 127.32 (t), 127.40 (s), 127.81 (t), 128.69 (t), 129.58 (t), 133.46 (q), 137.35 (q), 137.50 (q), 143.48 (q), 145.51 (q), 201.56 (q); HRMS (ESI) calcd for $C_{19}H_{20}O_3NClNaS$ $[M+Na]^+$: 400.0745. Found: 4000.0739.

4.3.13. N-[1′-(4″-Bromophenyl)-2′-methylene-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 122–125 °C (lit.[7] mp 122–124 °C); IR (Nüjol): 3254 (N–H), 1673 (C=O), 1597, 1335, 1159, 1074, 1010, 951, 812, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.93 (t, 3H, J=7.2 Hz), 2.41 (s, 3H), 2.46–2.60 (m, 2H), 5.20 (d, J=8.9 Hz, 1H), 5.81 (d, J=8.9 Hz, 1H), 6.01 (s, 1H), 6.08 (s, 1H), 6.99 (d, J=8.8 Hz, 2H), 7.22 (d, J=8.2 Hz, 2H), 7.31 (d, J=8.5 Hz, 2H), 7.62 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.84 (p), 21.60 (p), 31.45 (s), 59.14 (t), 121.68 (t), 127.32 (t), 127.42 (s), 128.20 (t), 129.60 (t), 131.65 (q), 137.59 (q), 138.14 (q), 143.60 (q), 145.57 (q), 201.63 (q); HRMS (ESI) calcd for $C_{19}H_{20}O_3NBrNaS$ $[M+Na]^+$: 444.0239. Found: 430.0233.

4.3.14. N-[1′-(4″-Fluorophenyl)-2′-methylene-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 113–115 °C (lit.[7] mp 111–112 °C); IR (Nüjol): 3294 (N–H), 1670 (C=O), 1597, 1508, 1408, 1344, 1307, 1212, 1161, 1094, 1072, 954, 921, 866, 814, 673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=0.94 (t, J=7.2 Hz, 3H), 2.41 (s, 3H), 2.42–2.60 (m, 2H), 5.24 (d, J=8.9 Hz, 1H), 5.69 (d, J=8.9 Hz, 1H), 6.01 (s, 1H), 6.08 (s, 1H), 6.88 (dd, J=8.8, 8.6 Hz, 2H), 7.08 (dd, J=8.8, 4.6 Hz, 2H), 7.23 (d, J=7.7 Hz, 2H), 7.64 (d, J=7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.76 (p), 21.47 (p), 31.39 (s), 58.88 (t), 115.43 (d, J_{C-F}=22.0 Hz, t), 127.14 (t), 127.34 (t), 128.19 (d, J_{C-F}=7.7 Hz, t), 129.58 (t), 134.71 (d, J_{C-F}=3.7 Hz, t), 137.54 (q), 143.42 (q), 145.76 (q), 161.94 (d, J_{C-F}=247.1 Hz, q), 201.59 (q); HRMS (ESI) calcd for $C_{19}H_{20}O_3NFNaS$ $[M+Na]^+$: 384.1040. Found: 384.1026.

4.3.15. N-[2′-Methylene-1′-(4″-nitrophenyl)-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 147–150 °C (lit.[7] mp 147–149 °C); IR (Nüjol): 3283 (N–H), 1671 (C=O), 1597, 1516, 1206, 1162, 1075, 813, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.93 (t, J=7.3 Hz, 3H), 2.41 (s, 3H), 2.42–2.59 (m, 2H), 5.33 (d, J=9.4 Hz, 1H), 5.96 (d, J=9.4 Hz, 1H), 6.04 (s, 1H), 6.13 (s, 1H), 7.24 (d, J=8.2 Hz, 2H), 7.35 (d, J=8.9 Hz, 2H), 7.64 (d, J=8.2 Hz, 2H), 8.02 (d, J=8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.77 (p), 21.59 (p), 31.35 (s), 59.36 (t), 123.71 (t), 126.46 (t),127.27 (t), 127.28 (t), 128.42 (s), 129.69 (t),137.54 (q), 143.87 (q), 144.98 (q), 146.39 (q), 201.53 (q); HRMS (ESI) calcd for $C_{19}H_{20}N_2O_5NaS$ $[M+Na]^+$: 411.0985. Found: 411.0982.

4.3.16. N-[2′-Methylene-3′-oxo-1′-phenylpentyl]-4-methylbenzenesulfonamide. Mp 87–90 °C (lit.[7] mp 84–86 °C); IR (Nüjol): 3281 (N–H), 1677 (C=O), 1599, 1495, 1453, 1378, 1334, 1161, 1092, 1066, 1029, 949, 815, 698, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.93 (t, J=7.3 Hz, 3H), 2.40 (s, 3H), 2.43–2.59 (m, 2H), 5.27 (d, J=8.7 Hz, 1H), 5.68 (d, J=8.7 Hz, 1H), 6.04 (s, 1H), 6.09 (s, 1H), 7.08–7.11 (m, 2H), 7.16–7.26 (m, 3H), 7.23 (d, J=8.0 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.87 (p), 21.59 (p), 31.45 (s), 59.42 (t), 126.43 (t), 126.97 (s), 127.38 (s), 127.66 (t), 128.60 (t), 129.55 (t), 137.67 (q), 139.03 (q), 143.40 (q), 146.00 (q), 201.64 (q); HRMS (APPI) calcd for $C_{19}H_{20}O_3NS$ $[M-H]^-$: 342.1169. Found: 342.1173.

4.3.17. N-[2′-Methylene-1′-(4″-methylphenyl)-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 116–119 °C; IR (Nüjol): 3289 (N–H), 1676 (C=O), 1598, 1513, 1160, 1075, 1022, 953, 814, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=0.93 (t, 3H, J=7.3 Hz), 2.41 (s, 3H), 2.43–2.64 (m, 2H), 5.23 (d, J=8.5 Hz, 1H), 5.56 (d, J=8.5 Hz, 1H), 6.05 (s, 1H), 6.09 (s, 1H), 6.97 (d, J=8.2 Hz, 2H), 7.01 (d, J=8.2 Hz, 2H), 7.23 (d, J=8.5 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ=7.76 (p), 20.96 (p), 21.48 (p), 31.36 (s), 59.03 (t), 126.25 (t), 126.64 (s), 127.30 (t), 129.20 (t), 129.43 (t), 136.00 (q), 137.34 (q), 137.55 (q), 143.26 (q), 146.05 (q), 201.52 (q); HRMS (ESI) calcd for $C_{20}H_{23}O_3NNaS$ $[M+Na]^+$: 380.1291. Found: 380.1283.

4.3.18. N-[1′-(4″-Methoxyphenyl)-2′-methylene-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 137–139 °C; IR (Nüjol): 3281 (N–H), 1672 (C=O), 1600, 1512, 1329, 1163, 1093, 1030, 956, 814, 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=0.94 (t, J=8.4 Hz), 2.41 (s, 3H), 2.43–2.63 (m, 2H), 3.74 (s, 3H), 5.22 (d, J=8.5 Hz, 1H), 5.52 (d, J=8.5 Hz, 1H), 6.04 (s, 1H), 6.08 (s, 1H), 6.73 (d, J=9.1 Hz, 2H), 7.00 (d, J=8.7 Hz, 2H), 7.25 (d, J=8.3 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=7.8 (p), 21.59 (p), 31.49 (s), 55.31 (p), 58.75 (t), 113.97 (t), 127.39 (t), 127.75 (t), 127.98 (t), 129.56 (t), 131.15 (q), 137.61 (q), 143.37 (q), 146.24 (q), 159.06 (q), 201.69 (q); HRMS (ESI) calcd for $C_{20}H_{23}O_4NNaS$ $[M+Na]^+$: 396.1240. Found: 396.1228.

4.3.19. N-[2′-Methylene-1′-(naphthalen-1″-yl)-3′-oxopentyl]-4-methylbenzenesulfonamide. Mp 119–120 °C; IR (Nüjol): 3269 (N–H), 1666 (C=O), 1597, 1336, 1157, 1092, 1070, 1024, 933, 804, 780, 721, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.94 (t, J=7.3 Hz, 3H), 2.42 (s, 3H), 2.47–2.71 (m, 2H), 5.14 (d, J=7.1 Hz, 1H), 6.17 (s, 1H), 6.21 (d, J=7.1 Hz, 1H), 6.25 (s, 1H), 7.20 (d, J=8.5 Hz, 2H), 7.25–7.35 (m, 3H), 7.44 (t, J=8.0 Hz, 1H), 7.64 (d, J=8.2 Hz, 2H), 7.72 (dd, J=3.6, 4.8 Hz, 1H), 7.64 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.92 (p), 21.59 (p), 31.54 (s), 53.71 (t), 122.99 (t), 124.96 (t), 125.07 (t), 125.92 (t), 126.47 (s), 126.64 (t), 127.57 (t), 128.80 (t), 129.00 (t), 129.61 (t), 130.45 (q), 134.01 (q), 134.70 (q), 137.08 (q), 143.63 (q),147.08 (q), 201.31 (q); HRMS (ESI) calcd for $C_{23}H_{23}O_3NNaS$ $[M+Na]^+$: 416.1291. Found: 416.1285.

4.3.20. N-[2′-Methylene-3′-oxo-1′-(thiophen-2″-yl)-pentyl]-4-methylbenzenesulfonamide. Mp 107–108 °C; IR (Nüjol): 3280 (N–H), 1676 (C=O), 1434, 1411, 1377, 1334, 1306, 1161, 1093, 1070, 815, 756, 706, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=0.98 (t, J=7.3 Hz, 3H), 2.41 (s, 3H), 2.42–2.63 (m, 2H), 5.45 (d, J=9.4 Hz, 1H), 5.89 (d, J=9.4 Hz, 1H), 6.03 (s, 1H), 6.08 (s, 1H), 6.70 (dd, J=1.2, 3.4 Hz, 1H), 6.82 (dd, J=3.4, 5.1 Hz, 1H), 7.11 (dd, J=1.2, 5.2 Hz, 1H), 7.25 (d, J=7.7 Hz, 2H), 7.68 (d, J=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.80 (p), 21.60 (p), 31.48 (s), 56.26 (t), 124.99 (t), 125.35 (t), 127.05 (t), 127.23 (s), 127.42 (t), 129.53 (t), 137.89 (q), 143.10 (q), 143.46 (q), 145.40 (q), 201.52 (q); HRMS (ESI) calcd for $C_{17}H_{19}O_3NNaS_2$ $[M+Na]^+$: 372.0699. Found: 372.0688.

4.3.21. N-[2′-Methylene-3′-oxo-1′-(pyridin-3″-yl)pentyl[-4-methylbenzenesulfonamide. Mp 106–110 °C; IR (Nüjol): 1688 (C=O), 1594, 1327, 1180, 1153, 1091, 1067, 1028, 946, 855, 807, 719 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=0.94 (t, J=7.3 Hz, 3H), 2.41 (s, 3H), 2.43–2.62 (m 2H), 5.28 (d, J=9.2 Hz, 1H), 5.90 (d, J=9.2 Hz, 1H), 6.06 (s, 1H), 6.12 (s, 1H), 7.16 (dd, J=8.0, 4.8 Hz, 1H), 7.24 (d, J=8.0 Hz, 2H), 7.55 (dt, J=8.0, 2.1 Hz, 1H), 7.65 (d, J=8.0 Hz, 2H), 8.31 (d, J=2.1 Hz, 1H), 8.43 (dd, J=4.8, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=7.80 (p), 21.59 (p), 31.39 (s), 57.96 (t), 123.39 (t), 127.20 (t), 127.23 (s), 127.29 (t), 128.03 (t), 129.68 (q), 132.01 (q), 134.14 (q), 137.55 (q), 145.04 (t), 148.90 (t), 223.97 (q); HRMS (ESI) calcd for $C_{18}H_{21}O_3N_2S$ $[M+H]^+$: 345.1267. Found: 345.1259.

4.3.22. N-(2-Methylene-3-oxo-1-phenylbutyl)-O-benzyl-carbamate. Mp 81–82 °C; IR (Nüjol): 3322 (N–H), 1684 (C=O), 1283, 1158, 1117, 1043, 965, 916, 866, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.29 (s, 3H), 5.11 (s, 2H), 5.71 (d, J=8.6 Hz, 1H), 5.82 (br s, J=8.6 Hz, 1H), 6.13 (s, 1H), 6.21 (s, 1H), 7.19–7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=26.67 (p), 56.90 (t), 67.04 (s), 126.48 (t), 127.38 (s), 127.57 (t), 128.24 (t), 128.62 (t), 128.66 (t), 136.44 (q), 139.91 (q), 147.59 (q), 155.69 (q), 199.01 (q); HRMS (ESI) calcd for $C_{19}H_{20}O_3N$ $[M+H]^+$: 310.1438. Found: 310.1434.

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