

## Supporting information for:

# Polystyrene-Supported Phosphine Catalyzed Aza-Baylis-Hillman Reactions and the Relationship Between Resin Loading Level and Catalyst Efficiency

Lin-Jing Zhao,<sup>#</sup> Helen Song He,<sup>‡</sup> Min Shi,<sup>#,†,\*</sup> and Patrick H. Toy<sup>‡,\*</sup>

<sup>#</sup>School of Chemistry & Pharmaceutics, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, People's Republic of China, <sup>†</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China, and <sup>‡</sup>Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

mshi@pub.sioc.ac.cn and phtoy@hku.hk

### Contents:

Experimental procedures.....	S2-S3
Characterization data for <b>4a-h</b> .....	S4-S9

**General Procedures.** Commercially available reagents were used as received. Tetrahydrofuran was distilled under an inert atmosphere over sodium and benzophenone. All reactions were monitored by TLC analysis using GF<sub>254</sub> silica gel coated plates. Column chromatography was carried out using silica gel (300-400 mesh) at increased pressure. Resin swelling was measured using fritted syringes after equilibration in the solvents for 2 h as described previously (see: Toy, P.

H.; Reger, T. S.; Garibay, P.; Garno, J. C.; Malikayil, J. A.; Liu, G.-Y.; Janda, K. *J. Comb. Chem.* **2001**, *3*, 117-124.)

**General Procedure for Preparing Catalysts 1a-c (JandaJel-PPh<sub>3</sub>).** A solution of acacia gum (6.0 g) and NaCl (3.8 g) in warm deionized water (45 °C, 150 mL) was placed in a 150 mL flanged reaction vessel equipped with a mechanical stirrer and deoxygenated by purging with N<sub>2</sub> for 2 h. A solution of approximately 10 g in total of 4-styryldiphenylphosphine (**A**),<sup>1</sup> styrene, 1,4-bis(4-vinylphenoxy)butane (2 mol % compared to the other monomers), and AIBN (0.2 g, 1.3 mmol) in chlorobenzene (10 mL) was injected into the rapidly stirred aqueous solution. The resulting suspension was heated at 85 °C for 20 h. At this time the crude polymer was collected and washed with hot water (3 × 100 mL) and then placed in a Soxhlet extractor and washed with THF for 24 h. The beads were then washed sequentially with methanol (250 mL), diethyl ether (250 mL), and hexanes (250 mL), and then dried in vacuo for 24 h to afford **1a-c** (See table below). Elemental analysis was used to determine the phosphorous content and thus the loading level of PPh<sub>3</sub>/g for **1a-c**. IR analysis of the polymers did not show any significant oxidation of the phosphine groups to phosphine oxide moieties based on the absence of the strong stretching signals at 1120 and 1190 cm<sup>-1</sup>.

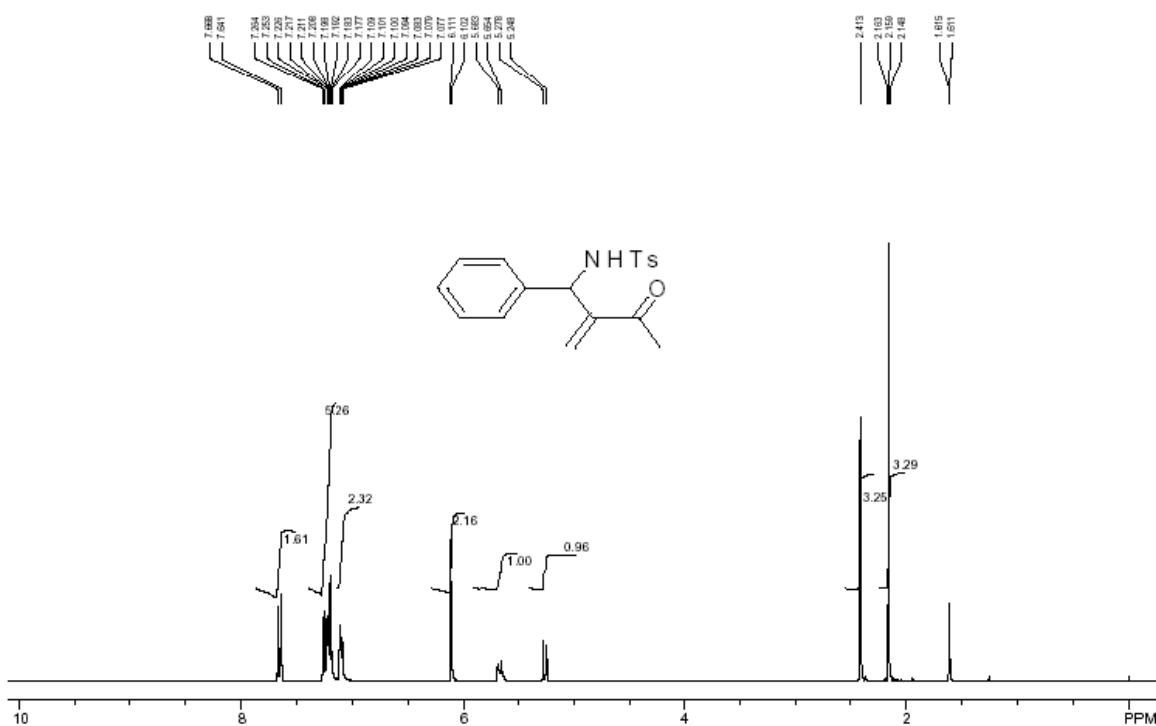
	<b>A</b> (mmol)	Styrene (mmol)	P content (%)		Loading (mmol/g)		Yield (%)
			Theoretical	Observed	Theoretical	Observed	
<b>1a</b>	5	82	1.55	1.57	0.5	0.5	75
<b>1b</b>	16	52	4.96	4.80	1.6	1.5	84
<b>1c</b>	35	0	10.85	9.85	3.5	3.2	96

(1) **A** was prepared by the literature method: Choi, M. K. W.; He, H. S.; Toy, P. H. *J. Org. Chem.*

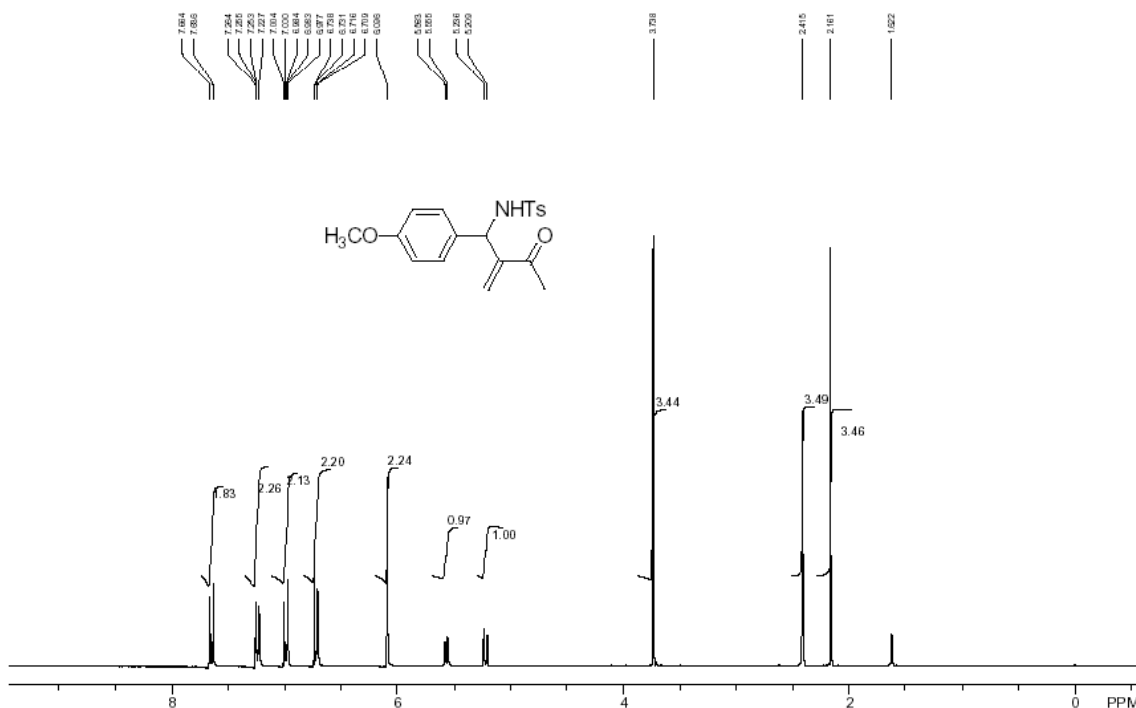
**2003**, *68*, 9831.

**General Procedure for the polymer-supported phosphine catalyzed aza-Baylis-Hillman reactions of *N*-sulfonated imines **2** with **3**:** Catalyst **1** (0.05 mmol) was added to anhydrous THF (1.0 mL) under an argon atmosphere and the suspension was stirred for 1 h at rt (swelling time). At this time, the *N*-sulfonated imine **2** (0.5 mmol) and **3** (63  $\mu$ L, 0.75 mmol) were added to the suspension. The reaction mixture was stirred at rt for the indicated time or until TLC analysis indicated the disappearance of **2**. The reaction mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub> (7.0 mL) and the catalyst was filtered off and recovered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (EtOAc)/petroleum ether, 1/4) to afford the desired product **4**. Characterization data for **4a-h** agrees with previously reported data: Shi, M.; Chen, L.-H. *Chem. Commun.* **2003**, 1310.

**4-Methyl-*N*-[2-methylene-1-phenyl-3-oxobutyl]benzenesulfonamide 4a.** A colorless solid; mp. 113-114 °C. IR (CHCl<sub>3</sub>):  $\nu$  3266, 3025, 1667 (C=O), 1597, 1491, 1449, 1366, 1323, 1304, 1161, 750, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.42 (3H, s, Me), 5.26 (1H, d,  $J$  = 8.6 Hz), 5.61 (1H, d,  $J$  = 8.6 Hz), 6.10 (1H, s), 6.11 (1H, s), 7.11-7.17 (2H, m, Ar), 7.20-7.27 (5H, m, Ar), 7.66 (2H, d,  $J$  = 8.1 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  21.74, 26.51, 58.64, 126.78, 127.48, 127.75, 128.44, 128.67, 129.72, 137.72, 139.18, 143.56, 146.81, 199.05. MS (EI):  $m/e$  260 (M<sup>+</sup>-69, 14.09), 174 (M<sup>+</sup>-155, 100), 155 (MePhSO<sub>2</sub><sup>+</sup>, 29.60). Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S requires C, 65.63; H, 5.81; N, 4.25%. Found: C, 65.64; H, 5.74; N, 4.14%.

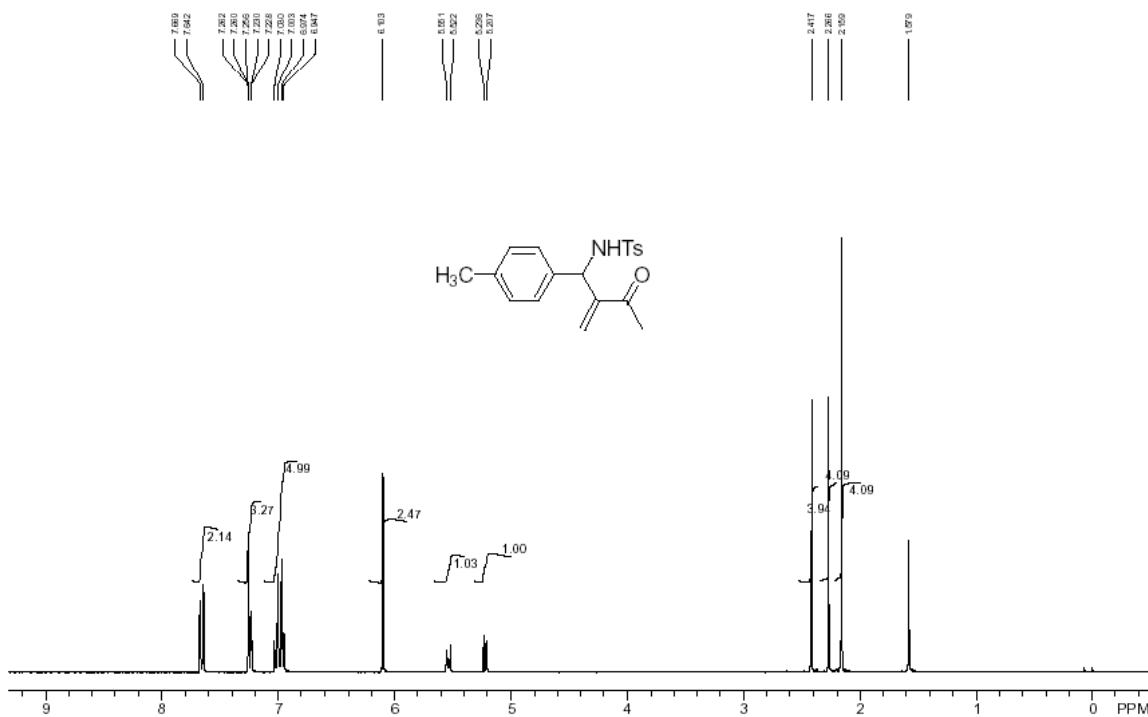


**4-Methyl-N-[2-methylene-1-(4-methoxyphenyl)-3-oxobutyl]benzenesulfonamide 4b.** A colorless solid; mp. 136-137 °C. IR (CHCl<sub>3</sub>):  $\nu$  3284, 3020, 2955, 2837, 1675 (C=O), 1608, 1507, 1440, 1366, 1331, 1251, 1216, 1178, 1160, 1093, 1034, 951, 924, 815, 757, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.17 (3H, s, Me), 2.41 (3H, s, Me), 3.74 (3H, s, Me), 5.21 (1H, d,  $J$  = 8.3 Hz, NH), 5.57 (1H, d,  $J$  = 8.3 Hz, CH), 6.10 (2H, s), 6.73 (2H, d,  $J$  = 6.8 Hz, Ar), 6.99 (2H, d,  $J$  = 6.8 Hz, Ar), 7.25 (2H, d,  $J$  = 9.3 Hz, Ar), 7.65 (2H, d,  $J$  = 9.3 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz)  $\delta$  21.47, 26.33, 55.16, 58.08, 113.78, 127.23, 127.66, 127.80, 129.44, 130.88, 137.30, 143.27, 146.58, 158.89, 198.84. MS (EI):  $m/e$  359 (M<sup>+</sup>, 0.30), 290 (M<sup>+</sup>-69, 9.61), 204 (M<sup>+</sup>-155, 100), 91 (PhMe<sup>+</sup>, 45.58). Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>NO<sub>4</sub>S requires C, 63.49; H, 5.89; N, 3.90%. Found: C, 63.24; H, 5.81; N, 3.73%.

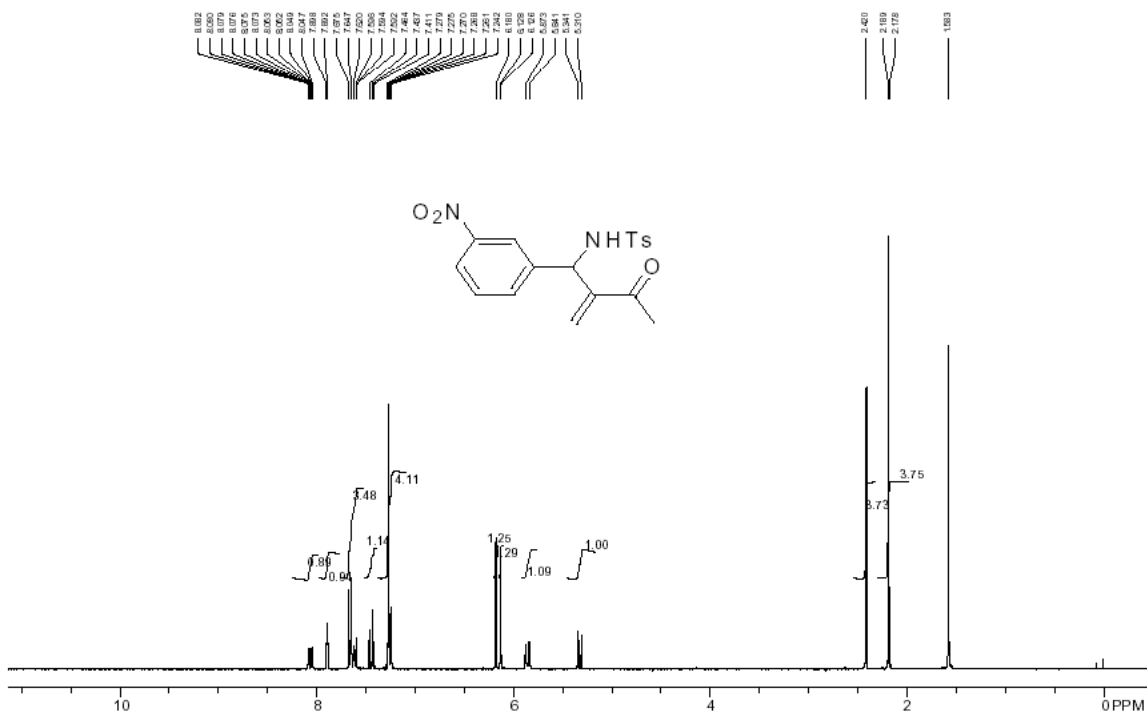


**4-Methyl-*N*-[2-methylene-1-(4-methylphenyl)-3-oxobutyl]benzenesulfonamide 4c.** A

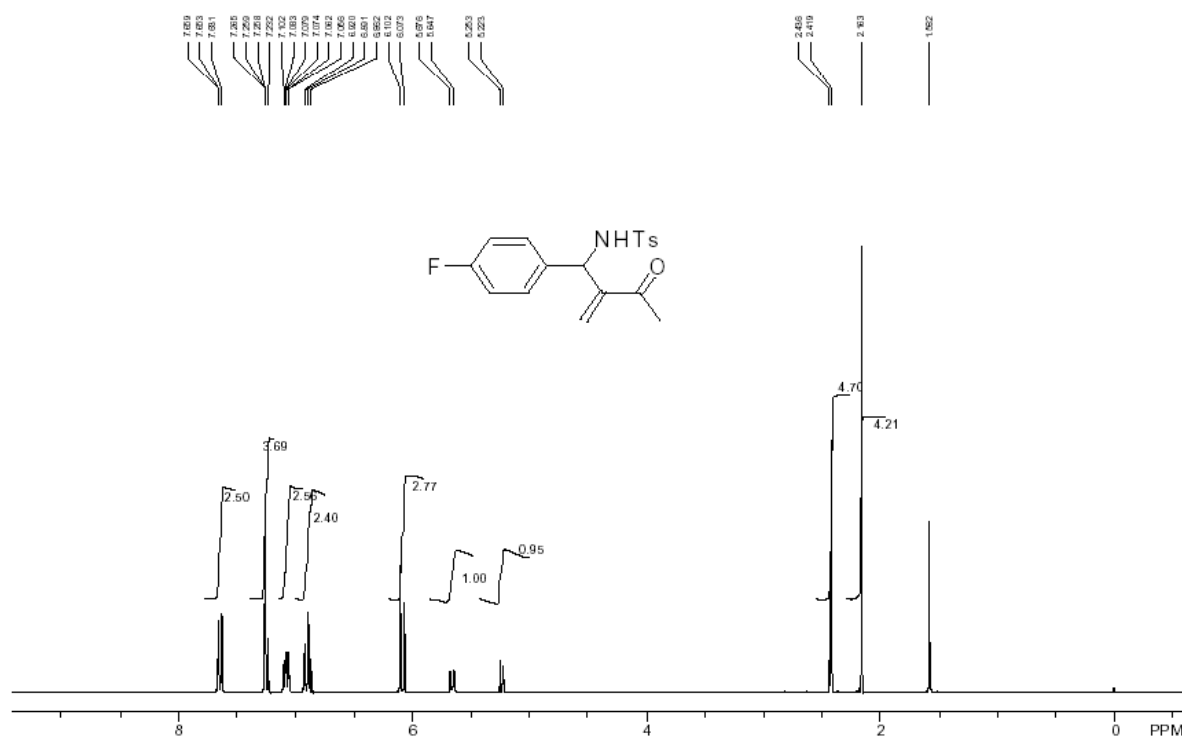
colorless solid; mp. 118-119 °C. IR (KBr):  $\nu$  3219, 3023, 2924, 2884, 1918, 1664 (C=O), 1598, 1512, 1456, 1369, 1323, 1271, 1158, 1095, 1069, 963, 932, 824, 812, 663  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.27 (3H, s, Me), 2.42 (3H, s, Me), 5.23 (1H, d,  $J = 8.4$  Hz), 5.56 (1H, d,  $J = 8.4$  Hz), 6.10 (2H, s), 6.95 (2H, d,  $J = 8.2$  Hz, Ar), 7.00 (2H, d,  $J = 8.2$  Hz, Ar), 7.24 (2H, d,  $J = 8.2$  Hz, Ar), 7.65 (2H, d,  $J = 8.2$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.55, 22.07, 26.88, 58.81, 127.01, 127.84, 128.48, 129.73, 130.04, 136.58, 137.83, 138.09, 143.84, 147.31, 199.39. MS (EI):  $m/e$  274 ( $\text{M}^+ - 69$ , 4.44), 188 ( $\text{M}^+ - 155$ , 100), 91 ( $\text{PhMe}^+$ , 50.98). Anal. Calcd. for  $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$  requires C, 66.47; H, 6.12; N, 4.08%. Found: C, 66.74; H, 6.47; N, 3.89%.



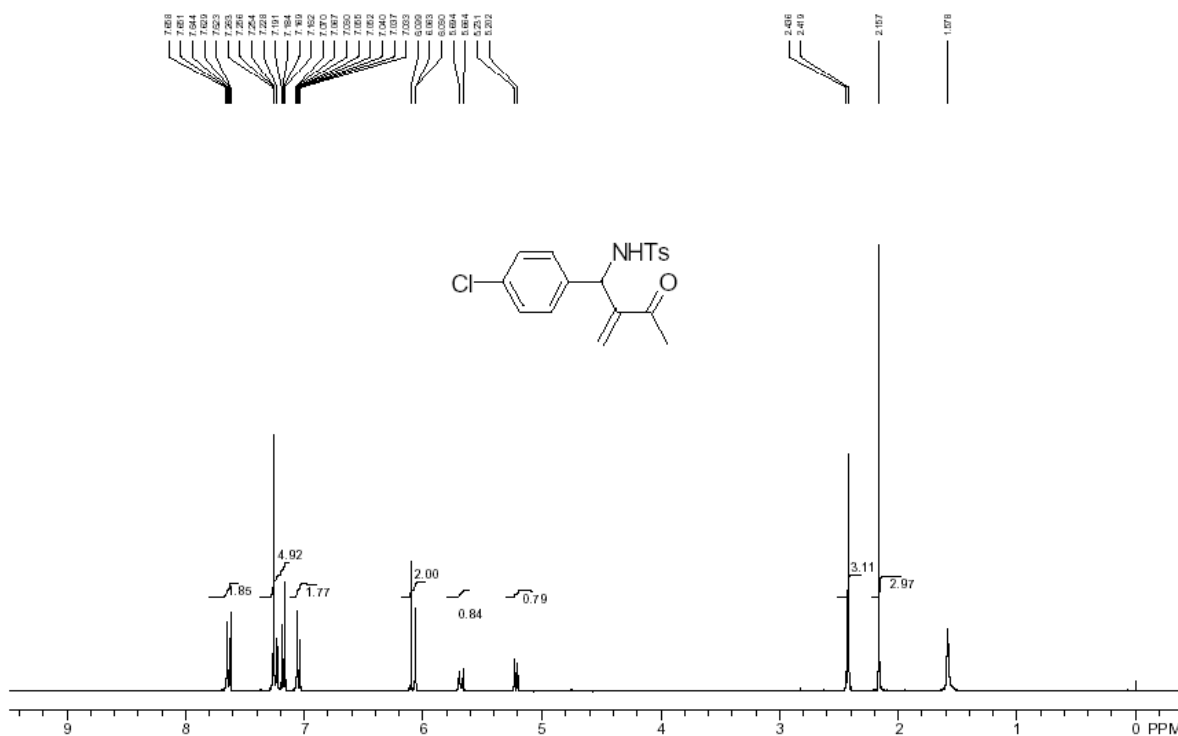
**4-Methyl-*N*-[2-methylene-1-(3-nitrophenyl)-3-oxobutyl]benzenesulfonamide 4e.** A colorless solid; mp: 122-124 °C. IR (KCl):  $\nu$  3317 (N-H), 1671 (C=O), 1595, 1538, 1432, 1349, 1323, 1160, 1087, 1066, 981, 956, 919, 812, 689  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.18 (3H, s, Me), 2.41 (3H, s, Me), 5.32 (1H, d,  $J = 9.4$  Hz), 5.85 (1H, d,  $J = 9.4$  Hz), 6.12 (1H, s), 6.18 (1H, s), 7.25 (2H, d,  $J = 8.6$  Hz), 7.44 (1H, dd,  $J_1 = 8.2$  Hz,  $J_2 = 7.8$  Hz), 7.61 (1H, d,  $J = 7.8$  Hz), 7.65 (2H, d,  $J = 8.6$  Hz), 7.89 (1H, s), 8.05 (1H, d,  $J = 8.2$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.65, 26.33, 58.10, 121.76, 122.61, 127.34, 129.63, 129.79, 129.85, 133.01, 137.41, 141.49, 144.00, 145.81, 148.24, 198.88. MS (EI):  $m/e$  91 ( $\text{M}^+ - 283$ , 52.79), 65 ( $\text{M}^+ - 283 - 26$ , 37.97), 43 ( $\text{M}^+ - 331$ , 100). Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$  requires C, 57.74; H, 4.84; N, 7.48%. Found: C, 57.74; H, 5.07; N, 7.34%.



***N*-[1-(4-Fluorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 4f.** A colorless solid; Mp: 104-106 °C. IR (KCl):  $\nu$  3255 (N-H), 1663 (C=O), 1600, 1510, 1437, 1367, 1325, 1228, 1159, 1094, 1065, 960, 812, 666, 550  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.15 (3H, s, Me), 2.41 (3H, s, Me), 5.24 (1H, d,  $J = 8.7$  Hz, NH), 5.75 (1H, d,  $J = 8.7$  Hz, CH), 6.07 (1H, s, =CH), 6.09 (1H, s, =CH), 6.84-6.90 (2H, dd,  $J_1 = 9.0$  Hz,  $J_2 = 8.6$  Hz, Ar), 7.04-7.09 (2H, dd,  $J_1 = 8.6$  Hz,  $J_2 = 5.2$  Hz, Ar), 7.23 (2H, d,  $J = 8.1$  Hz, Ar), 7.63 (2H,  $J = 8.1$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.09, 25.88, 57.74, 114.88 (d,  $J = 21.8$  Hz), 126.83, 127.78, 127.87 (d,  $J = 2.7$  Hz), 129.11, 134.35, 137.01, 143.07, 146.03, 161.64 (d,  $J = 244$  Hz), 198.38. MS (EI):  $m/e$  192 ( $\text{M}^+ - 155$ , 8.79), 155 ( $\text{M}^+ - 192$ , 7.08), 95 ( $\text{M}^+ - 155 - 97$ , 11.72), 91 ( $\text{M}^+ - 192 - 64$ , 70.98), 65 ( $\text{M}^+ - 155 - 64 - 26$ , 45.32), 43 ( $\text{M}^+ - 304$ , 100). Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{FNO}_3\text{S}$  requires C, 62.24; H, 5.22; N, 4.03%. Found: C, 61.98; H, 5.29; N, 4.04%.



**4-Methyl-N-[2-methylene-1-(4-chlorophenyl)-3-oxobutyl]benzenesulfonamide 4g.** A colorless solid; mp.112-113 °C. IR (CHCl<sub>3</sub>):  $\nu$  3282, 3022, 1674 (C=O), 1596, 1489, 1419, 1366, 1332, 1216, 1161, 1092, 1068, 1015, 955, 814, 756, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.11 (3H, s, Me), 2.38 (3H, s, Me), 5.24 (1H, d,  $J$  = 9.1 Hz, NH), 5.69 (1H, d,  $J$  = 9.1 Hz, CH), 6.03 (1H, s), 6.06 (1H, s), 7.01 (2H, d,  $J$  = 8.6 Hz, Ar), 7.12 (2H, d,  $J$  = 8.6 Hz, Ar), 7.19 (2H, d,  $J$  = 8.1 Hz, Ar), 7.59 (2H, d,  $J$  = 8.1 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz)  $\delta$  21.42, 26.18, 58.14, 127.14, 127.85, 128.38, 128.48, 129.46, 133.34, 137.33, 137.44, 143.44, 146.17, 198.66. MS (EI):  $m/e$  294 (M<sup>+</sup>-69, 2.36), 208 (M<sup>+</sup>-155, 100), 91 (PhMe<sup>+</sup>, 39.81). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>ClNO<sub>3</sub>S requires C, 59.42; H, 4.99; N, 3.85%. Found: C, 59.43; H, 4.94; N, 3.78%.



**4-Methyl-*N*-[2-methylene-1-(4-bromophenyl)-3-oxobutyl]benzenesulfonamide 4h.** A colorless solid; mp. 115-116 °C. IR (CHCl<sub>3</sub>):  $\nu$  3295 (N-H), 1669 (C=O), 1696, 1485, 1441, 1324, 1162, 1069, 1010, 960, 814, 664 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.42 (3H, s, Me), 5.20 (1H, d,  $J$  = 8.9 Hz), 5.71 (1H, d,  $J$  = 8.9 Hz), 6.06 (1H, s), 6.10 (1H, s), 6.99 (2H, d,  $J$  = 6.7 Hz, Ar), 7.24 (2H, d,  $J$  = 8.4 Hz, Ar), 7.32 (2H, d,  $J$  = 6.7 Hz, Ar), 7.63 (2H, d,  $J$  = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  20.99, 25.73, 57.84, 121.05, 126.68, 127.70, 127.99, 129.01, 130.99, 136.87, 137.48, 143.01, 145.63, 198.21. MS (EI):  $m/e$  252 (M<sup>+</sup>-155, 92.12), 254 (M<sup>+</sup>-153, 85.18), 130 (M<sup>+</sup>-277, 100), 91 (PhMe<sup>+</sup>, 73.41). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>BrNO<sub>3</sub>S requires C, 52.94; H, 4.41; N, 3.43%. Found: C, 52.96; H, 4.46; N, 3.42%.

