Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

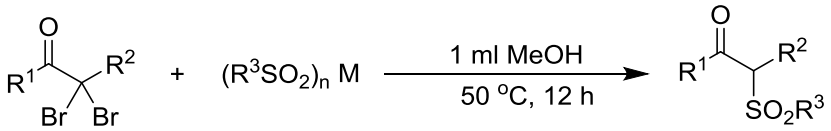

*Supporting Information*

# A One-pot Protocol for the Synthesis of $\beta$-Ketosulfones from $\alpha,\alpha$-Dibromoketones

## 1. General information

Commercially available materials were used as received, unless otherwise noted. $^{1}H$ NMR and $^{13}C$ NMR spectras were measured on a 500 MHz spectrometer ($^{1}H$: 500 MHz, $^{13}C$: 125 MHz), using $d^{6}$-DMSO or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in $\delta$ relative to TMS, the coupling constants $J$ are given in Hz. Melting points were measured on X4 melting point apparatus and uncorrected. α,α-Dibromoketones **1** are synthesized according to procedure in literature.[1]

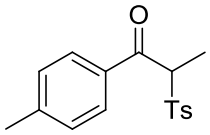
## 2. General Procedure for the Synthesis of $\beta$-ketosulfones 3.



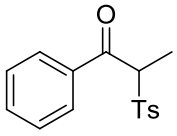

**1** **2** **3**

To a 10 mL-Schlenk tube with a magnetic stirring bar was charged with sulfinate **2** (0.6 mmol), *α,α*-dibromoketone **1** (0.2 mmol), and MeOH (2 mL) under nitrogen atmosphere. The reaction was stirred at 50 ℃ for 12 h. The reaction mixture was then cooled to room temperature and evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the target products (**3**).

## 3. Data for compounds

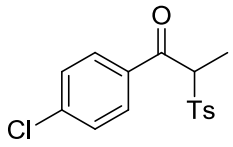



**1-*p*-tolyl-2-tosylpropan-1-one 3aa**:[2] white solid (isolated yield: 93%); m.p. 104–105 $^{o}C$; $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 7.88 (d, $J$ = 7.8 Hz, 2 H), 7.65 (d, $J$ = 7.8 Hz, 2 H), 7.37 – 7.21 (m, 4 H), 5.13 (q, $J$ = 6.6 Hz, 1 H), 2.48 – 2.33 (m, 6 H), 1.54 (d, $J$ = 6.7 Hz, 3 H); $^{13}C$ NMR (125 MHz; $CDCl_3$) δ 192.1, 145.3, 145.2, 133.9, 133.1, 129.8, 129.5, 129.4, 129.4, 64.9, 21.7, 21.7, 13.2.

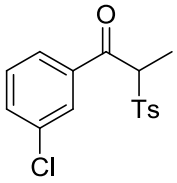



**1-phenyl-2-tosylpropan-1-one (3ba)**:[3] white solid (isolated yield: 98% from reaction

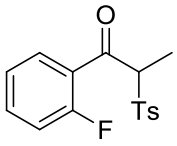
of **1b** and **2a**, 92% from reaction of **1b** and **2g**); m.p. 93–95 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.15 (q, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz; $CDCl_3$) δ 192.6, 145.3, 136.3, 134.0, 133.1, 129.8, 129.5, 129.2, 128.7, 65.1, 21.7, 13.2.



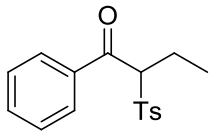

**1-(4-chlorophenyl)-2-tosylpropan-1-one (3ca)**:[2] white solid (isolated yield: 96%); m.p. 126–127 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.10 (q, *J* = 6.9 Hz, 1 H), 2.43 (s, 3 H), 1.54 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz; $CDCl_3$) δ 191.4, 145.5, 140.7, 134.7, 132.9, 130.6, 129.8, 129.6, 129.1, 65.2, 21.7, 13.1.



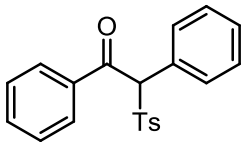

**1-(3-chlorophenyl)-2-tosylpropan-1-one (3da)**:[2] white solid (isolated yield: 96%); m.p. 105 – 106 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.42 (t, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.08 (q, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 1.55 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.5, 145.6, 137.8, 135.1, 133.8, 133.0, 130.0, 129.8, 129.6, 129.0, 127.3, 65.3, 21.7, 13.0; HRMS (ESI): calcd for $C_{16}H_{16}ClO_3S^+$ ($[M + H]^+$) 323.0503, found 323.0511.



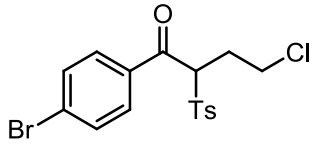

**1-(2-fluorophenyl)-2-tosylpropan-1-one (3ea)**:[2] white solid (isolated yield: 96%); m.p. 83–84 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 –7.72 (m, 1 H), 7.67 (d, *J* = 8.3 Hz, 2 H), 7.58 – 7.50 (m, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.25 – 7.18 (m, 1 H), 7.10 (dd, *J* = 11.5, 8.4 Hz, 1 H), 5.17 (qd, *J* = 6.9, 3.0 Hz, 1 H), 2.42 (s, 3 H), 1.57 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz; $CDCl_3$) δ 191.1 (d, *J* = 3.8 Hz), 161.5 (d, *J* = 252.5 Hz), 145.2, 135.4 (d, *J* = 8.8 Hz), 133.8, 131.1 (d, *J* = 1.3 Hz), 129.6, 129.5, 125.7 (d, *J* = 11.3Hz), 124.7 (d, *J* = 2.5 Hz), 116.7 (d, *J* = 23.8 Hz), 69.2 (d, *J* = 8.8 Hz), 21.6, 12.4.



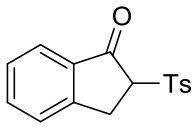

**1-phenyl-2-tosylbutan-1-one (3fa)**:[3] white solid (isolated yield: 90%); m.p. 73–74 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 5.01 (dd, *J* = 10.8, 3.6 Hz, 1 H), 2.41 (s, 3 H), 2.21–2.11 (m, 1 H), 2.10–1.99 (m, 1 H), 0.87 (t, *J* = 7.4 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.8, 145.3, 137.5, 133.9, 133.6, 129.8, 129.5, 129.0, 128.7, 71.5, 22.0, 21.6, 11.5.




**1,2-diphenyl-2-tosylethanone (3ga)**:[2] white solid (isolated yield: 94%); m.p. 145–146 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2 H), 7.51 (d, *J* = 8.3 Hz, 3 H), 7.43–7.31 (m, 5 H), 7.31–7.25 (m, 2 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 6.14 (s, 1 H), 2.39 (s, 3 H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 190.82, 145.0, 136.1, 134.0, 133.9, 130.5, 130.3, 129.6, 129.1, 128.9, 128.8, 128.8, 128.7, 76.1, 21.7.

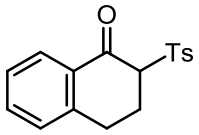



**1-(4-bromophenyl)-4-chloro-2-tosylbutan-1-one (3ha)**:[2] white solid (isolated yield: 82%); m.p. 145–146 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2 H), 7.60 (t, *J* = 8.5 Hz, 4 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 5.35 (dd, *J* = 8.1, 5.8 Hz, 1 H), 3.71–3.64 (m, 1 H), 3.37–3.29 (m, 1 H), 2.57–2.50 (m, 2 H), 2.43 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.9, 145.9, 135.5, 133.2, 132.1, 130.6, 129.8, 129.8, 129.6, 67.4, 41.6, 30.5, 21.7; HRMS (ESI): calcd for $C_{17}H_{17}BrClO_3S^+$ ($[M + H]^+$) 414.9765, found 414.9765.

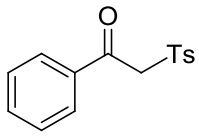



**2-tosyl-2,3-dihydro-1*H*-inden-1-one (3ia)**:[4] white solid (isolated yield: 94%); m.p. 131–132 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2 H), 7.71 (d, *J* = 7.7 Hz, 1 H), 7.64–7.59 (m, 1 H), 7.49 (d, *J* = 7.7 Hz, 1 H), 7.40–7.33 (m, 3 H), 4.26 (dd, *J* = 8.4, 3.4 Hz, 1 H), 3.80 (dd, *J* = 18.2, 3.3 Hz, 1 H), 3.53 (dd, *J* = 18.2, 8.4 Hz, 1 H), 2.44 (s, 3

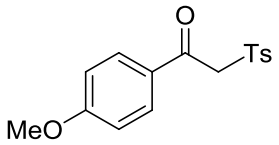
H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.6, 151.9, 145.3, 135.9, 135.8, 134.6, 129.7, 129.3, 128.2, 126.4, 124.8, 68.8, 28.2, 21.7.



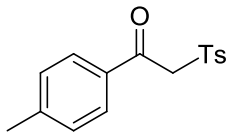

**2-tosyl-3,4-dihydronaphthalen-1(2H)-one (3ja)**:[5] white solid (isolated yield: 71%); m.p. 138–140 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.79 (d, *J* = 8.3 Hz, 2 H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 4.09 (t, *J* = 5.7 Hz, 1 H), 3.56 – 3.44 (m, 1 H), 3.02 – 2.93(m, 1 H), 2.90 – 2.79 (m, 1 H), 2.68 – 2.58 (m, 1 H), 2.45 (s, 3 H); $^{13}$C NMR (125 MHz, DMSO) δ 188.6, 144.5, 143.8, 136.2, 134.4, 131.6, 129.6, 129.1, 128.5, 126.9, 126.9, 68.3, 25.9, 23.3, 21.2.




**1-phenyl-2-tosylethanone (3ka, Table 2)**:[6] white solid (isolated yield: 94%); m.p. 98–99 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 2 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.72 (s, 2 H), 2.43 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 188.2, 145.4, 135.9, 135.8, 134.3, 129.8, 129.3, 128.8, 128.6, 63.6, 21.7.

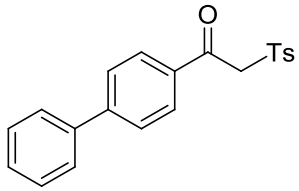



**1-(4-methoxyphenyl)-2-tosylethanone (3la)**:[3] white solid (isolated yield: 94%); m.p. 122–123 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.94 (d, *J* = 8.9 Hz, 2 H), 4.66 (s, 2 H), 3.87 (s, 3 H), 2.43 (s, 3 H); $^{13}$C NMR (125 MHz, DMSO) δ 187.0, 163.9, 144.4, 136.8, 131.6, 129.6, 128.8, 128.0, 113.9, 62.3, 55.7, 21.0.

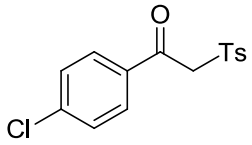



**1-*p*-tolyl-2-tosylethanone (3ma)**:[6] white solid (isolated yield: 94%); m.p. 110–112 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 4.69 (s, 2 H), 2.44 (s, 3 H), 2.42 (s, 3 H);

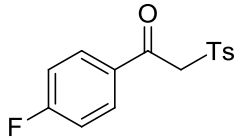
$^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.7, 145.5, 145.3, 135.9, 133.4, 129.8, 129.5, 129.5, 128.6, 63.6, 21.8, 21.7.



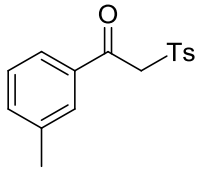

**1-(biphenyl-4-yl)-2-tosylethanone (3na)**:[7] white solid (isolated yield: 92%); m.p. 117–118 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.4 Hz, 2 H), 7.41 (t, *J* = 7.3 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 4.74 (s, 2 H), 2.42 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.7, 147.0, 145.4, 139.4, 135.8, 134.5, 130.0, 129.9, 129.1, 128.6, 128.6, 127.4, 127.3, 63.7, 21.7.



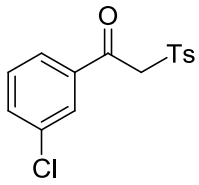

**1-(4-chlorophenyl)-2-tosylethanone (3oa)**:[6] white solid (isolated yield: 83%); m.p. 133–134 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.68 (s, 2 H), 2.45 (s, 3 H); $^{13}$C NMR (125 MHz, d$^6$-DMSO) δ 188.1, 144.6, 139.2, 136.5, 134.5, 130.9, 129.6, 128.8, 128.0, 62.5, 21.0.



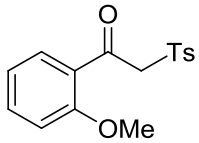

**1-(4-fluorophenyl)-2-tosylethanone (3pa)**:[3] white solid (isolated yield: 87%); m.p. 132–133 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04–7.96 (m, 2 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 8.6 Hz, 2 H), 4.69 (s, 2 H), 2.45 (s, 3 H); $^{13}$C NMR (125 MHz, d$^6$-DMSO) δ 187.6, 165.5 (d, *J* = 251.3 Hz), 144.6, 136.6, 132.6 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 8.8 Hz), 129.6, 128.0, 115.8 (d, *J* = 21.3 Hz), 62.4, 21.0.



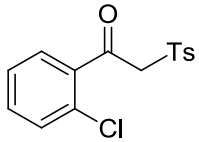

**1-*m*-tolyl-2-tosylethanone (3qa)**:[3] white solid (isolated yield: 88%); m.p. 93–94 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81–7.66 (m, 4 H), 7.45–7.28 (m, 4 H), 4.70 (s, 2H), 2.43 (s, 3 H), 2.39 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 188.3, 145.3, 138.7, 135.9, 135.8, 135.1, 129.8, 129.7, 128.7, 128.6, 126.6, 63.6, 21.7, 21.3.



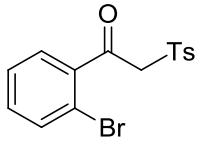

**1-(3-chlorophenyl)-2-tosylethanone (3ra)**:[3] white solid (isolated yield: 86%); m.p. 120–121 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.60 – 7.55 (m, 1 H), 7.43 (t, *J* = 8.1 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.69 (s, 2 H), 2.44 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.1, 145.6, 137.3, 135.6, 135.2, 134.2, 130.2, 129.9, 129.1, 128.6, 127.6, 63.7, 21.7.



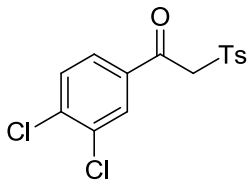

**1-(2-methoxyphenyl)-2-tosylethanone (3sa)**:[3] white solid (isolated yield: 97%); m.p. 84–85 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2 H), 7.65 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.51 – 7.45 (m, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 6.98 (t, *J* = 7.1 Hz, 1 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 4.92 (s, 2 H), 3.86 (s, 3 H), 2.41 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 189.2, 159.0, 144.8, 136.7, 135.2, 131.2, 129.5, 128.5, 126.3, 120.9, 111.7, 67.5, 55.7, 21.6.



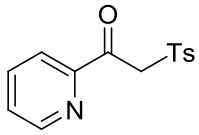

**1-(2-chlorophenyl)-2-tosylethanone (3ta)**:[8] faint yellow solid (isolated yield: 89%); m.p. 95–96 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2 H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.46–7.40 (m, 1 H), 7.39–7.28 (m, 4 H), 4.81 (s, 2 H), 2.44 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 190.3, 145.4, 137.3, 136.0, 133.1, 131.6, 130.7, 130.6, 129.9, 128.6, 127.2, 66.4, 21.7.



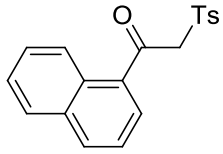

**1-(2-bromophenyl)-2-tosylethanone (3ua)**:[9] white solid (isolated yield: 87%); m.p. 104–105 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2 H), 7.57 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.51 (dd, *J* = 7.6, 1.8 Hz, 1 H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.36–7.31 (m, 3 H), 4.80 (s, 2 H), 2.44 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 191.0, 145.4, 139.5, 135.9,133.9, 132.9, 130.4, 129.9, 128.6, 127.7, 119.4, 66.1, 21.7.



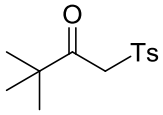

**1-(3,4-dichlorophenyl)-2-tosylethanone (3va)**: white solid (isolated yield: 77%); m.p. 168–170 $^{o}$C; $^{1}$H NMR (500 MHz, DMSO) δ 8.13 (d, *J* = 1.8 Hz, 1 H), 7.88 (dd, *J* = 8.4, 1.9 Hz, 1 H), 7.82–7.72 (m, 3 H), 7.42 (d, *J* = 8.1 Hz, 2 H), 5.32 (s, 2 H), 2.40 (s, 3 H). $^{13}$C NMR (125 MHz, d$^{6}$-DMSO) δ 187.4, 144.8, 137.0, 136.3, 135.8, 131.8, 131.0, 131.0, 129.6, 128.7, 128.1, 62.6, 21.0; HRMS (ESI): calcd for $C_{15}H_{12}Cl_2NaO_3S^+$ ([M + Na]$^+$) 364.9776, found 364.9803.



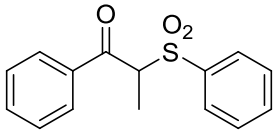

**1-(pyridin-2-yl)-2-tosylethanone (3wa)**:[6] brown solid (isolated yield: 86%); m.p. 86–87 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.7 Hz, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H), 7.85–7.77 (m, 3 H), 7.50–7.45 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 5.14 (s, 2 H), 2.42 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 189.8, 151.9, 149.1, 144.9, 137.1, 136.7, 129.6, 128.6, 127.9, 122.5, 61.1, 21.6.



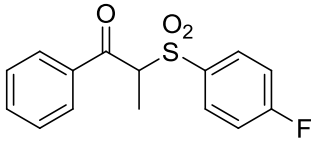

**1-(naphthalen-1-yl)-2-tosylethanone (3xa)**:[6] faint yellow solid (isolated yield: 94%); m.p. 103–104 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.6 Hz, 1 H), 8.03–7.96 (m, 2 H), 7.85 (d, *J* = 7.9 Hz, 1 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 7.60–7.44 (m, 3 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 4.83 (s, 2 H), 2.39 (s, 3 H); $^{13}$C NMR (125 MHz, d$^{6}$-DMSO) δ 191.7, 144.5, 136.6, 133.9, 133.4, 133.3, 130.9, 129.6, 129.5, 128.6, 128.3, 127.9, 126.6, 124.9, 124.5, 65.3, 21.0.



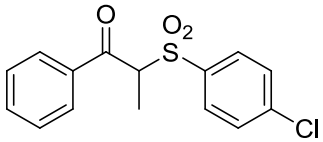

**3,3-dimethyl-1-tosylbutan-2-one (3ya):**[10] white solid (isolated yield: 88%); m.p. 110–111 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 4.31 (s, 2 H), 2.45 (s, 3 H), 1.12 (s, 9 H); $^{13}$C NMR (125 MHz, d$^{6}$-DMSO) δ 204.0, 144.1, 137.3, 129.4, 128.0, 60.3, 44.6, 25.0, 21.0.



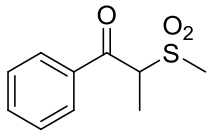
**1-phenyl-2-(phenylsulfonyl)propan-1-one (3bb, Entry 1, Table 3):**[11] white solid (isolated yield: 85%); m.p. 75–76 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2 H), 7.79 (d, J = 7.2 Hz, 2 H), 7.68–7.57 (m, 2 H), 7.55–7.43 (m, 4 H), 5.18 (q, *J* = 6.9 Hz, 1 H), 1.57 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.5, 136.2, 136.1, 134.2, 134.1, 129.8, 129.1, 128.9, 128.8, 65.0, 13.2.



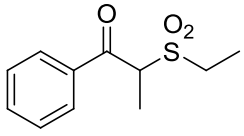

**2-(4-fluorophenylsulfonyl)-1-phenylpropan-1-one (3bc).** white solid (isolated yield: 77%); m.p. 103–104 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2 H), 7.80 (dd, *J* = 8.9, 5.1 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 2 H), 7.19 (t, *J* = 8.5 Hz, 2 H), 5.18 (q, *J* = 6.9 Hz, 1 H), 1.57 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.6, 166.1 (d, *J* = 256.3 Hz), 13.6.1, 134.2, 132.8 (d, *J* = 10.0 Hz), 132.0 (d, *J* = 2.5 Hz), 129.2, 128.9, 116.3 (d, *J* = 22.5 Hz), 65.0, 13.3; HRMS (ESI): calcd for $C_{15}H_{14}FO_3S^+$ ($[M + H]^+$) 293.0642, found 293.0644.




**2-(4-chlorophenylsulfonyl)-1-phenylpropan-1-one (3bd)**:[12] white solid (isolated yield: 87%); m.p. 117–118 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2 H), 7.72 (d, *J* = 8.6 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.53 – 7.45 (m, 4 H), 5.18 (q, *J* = 6.9 Hz, 1 H), 1.57 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 192.5, 141.2, 136.0, 134.4, 134.3, 131.3, 129.2, 129.2, 128.9, 65.1, 13.3.

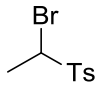



**2-(methylsulfonyl)-1-phenylpropan-1-one (3be)**.[13] white solid (isolated yield: 92%); m.p. 55–56 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.4, 1.1 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 4.97 (q, *J* = 7.1 Hz, 1 H), 2.98 (d, *J* = 0.6 Hz, 3 H), 1.74 (d, *J* = 7.1 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.0, 135.7, 134.5, 129.2, 129.0, 64.0, 37.0, 13.9.




**2-(ethylsulfonyl)-1-phenylpropan-1-one (3bf).**[14] colorless liquid (isolated yield: 90%); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.3, 1.1 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz,

1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 5.02 (q, *J* = 7.1 Hz, 1 H), 3.22–3.09 (m, 2 H), 1.74 (d, *J* = 7.1 Hz, 3 H), 1.38 (t, *J* = 7.5 Hz, 3 H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.8, 135.8, 134.4, 129.2, 129.0, 63.63, 43.7, 13.4, 5.1.




**1-(1-bromoethylsulfonyl)-4-methylbenzene 5:**[15] white solid (isolated yield: 82%); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 4.85 (q, *J* = 6.9 Hz, 1 H), 2.48 (s, 3 H), 1.96 (d, *J* = 6.9 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 145.8, 131.6, 130.1, 129.8, 59.2, 21.7, 19.5.

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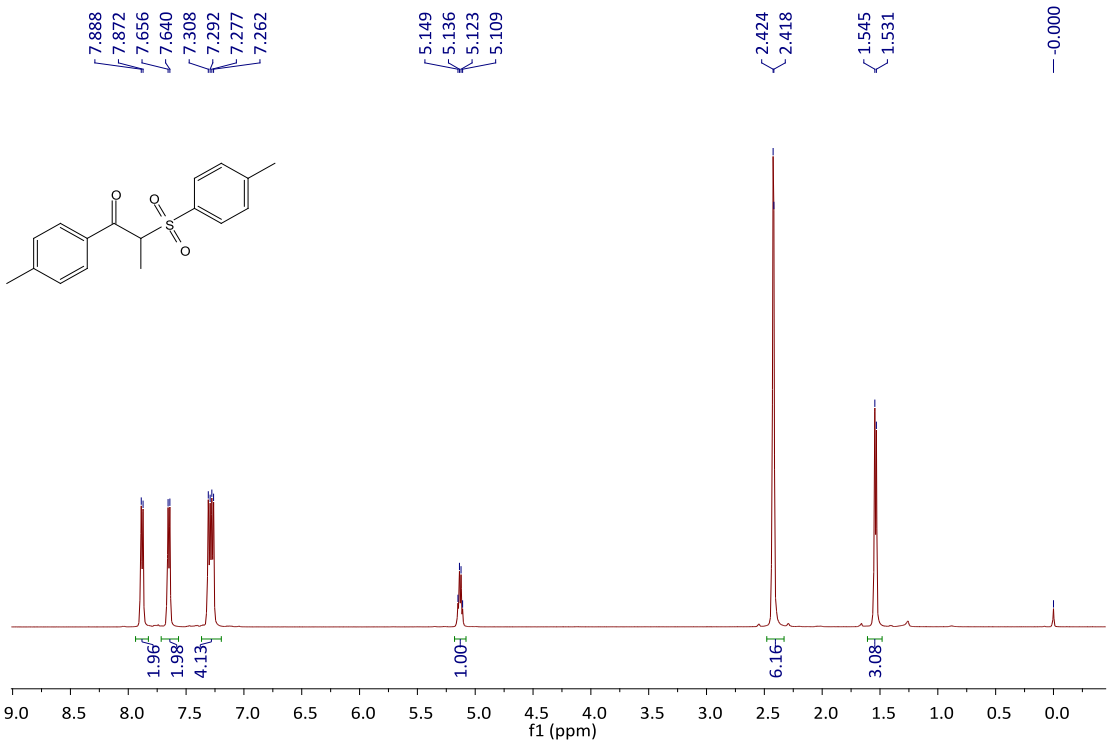
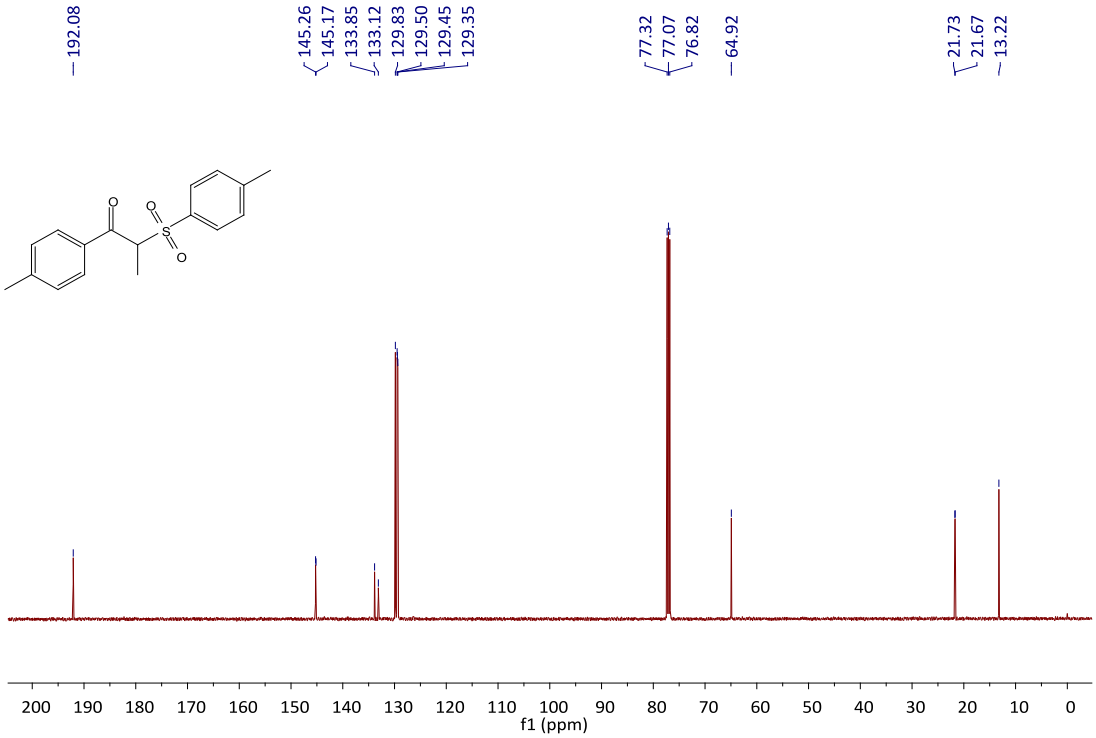
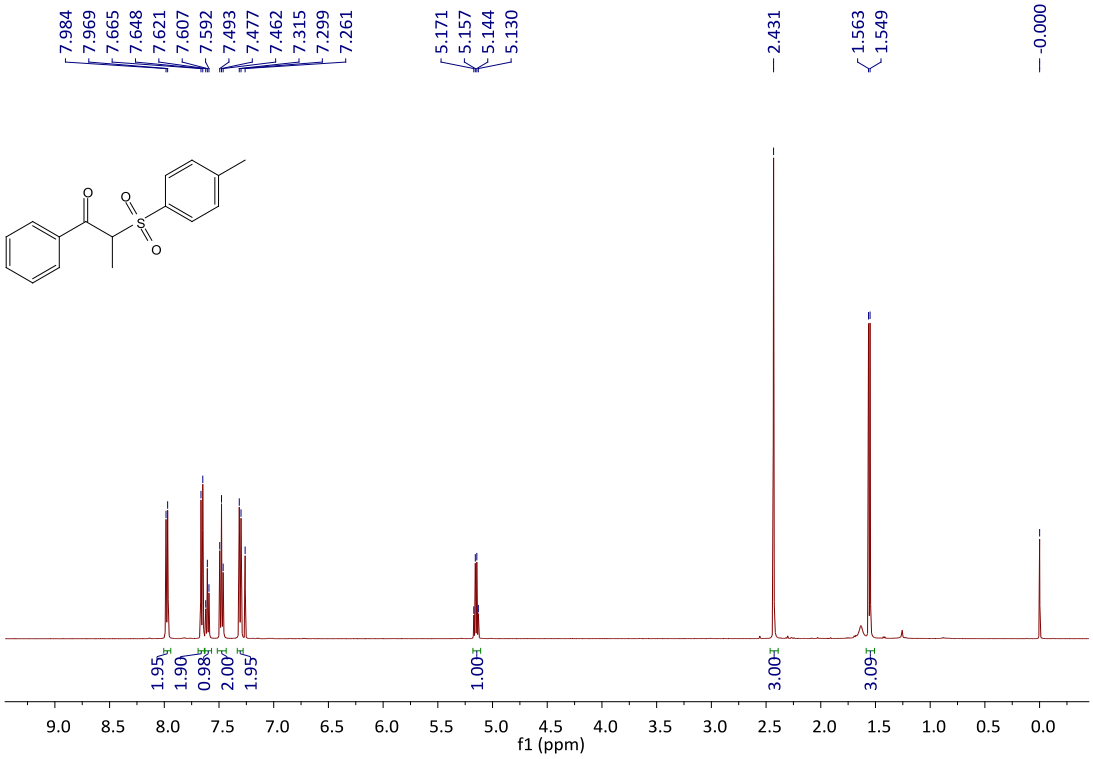
## 4. Copy of NMR spectra



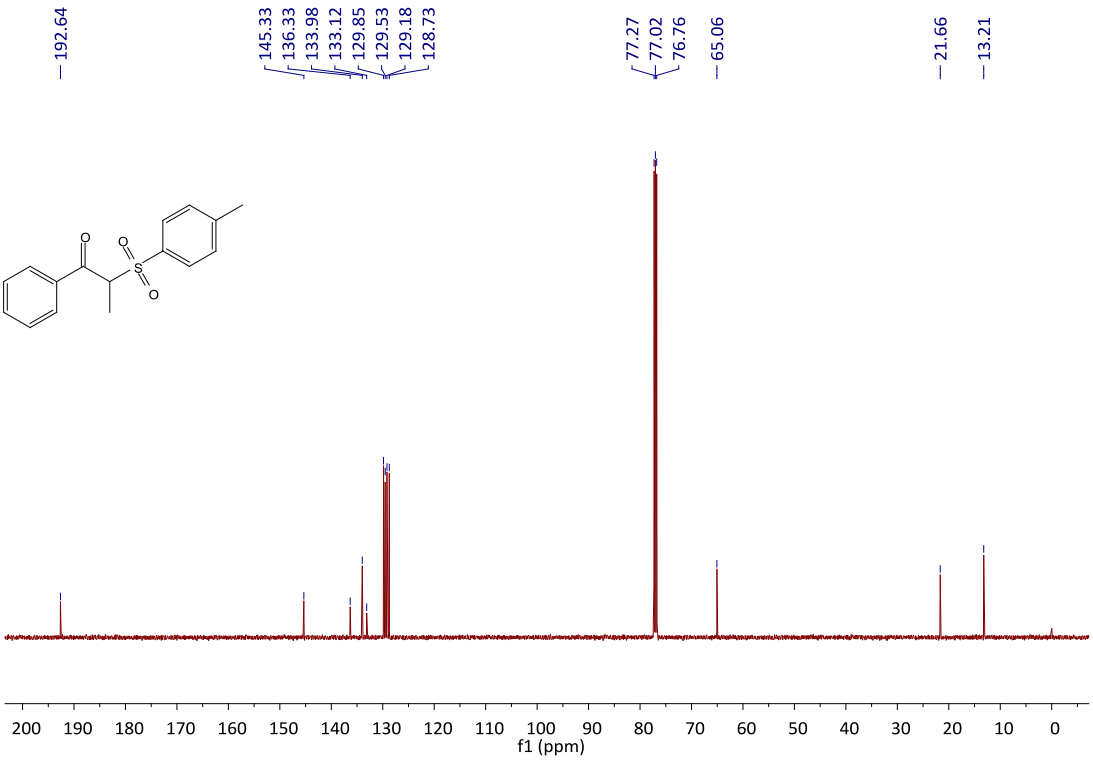

$^{1}$H NMR (500 Hz, $CDCl_3$): **3aa**



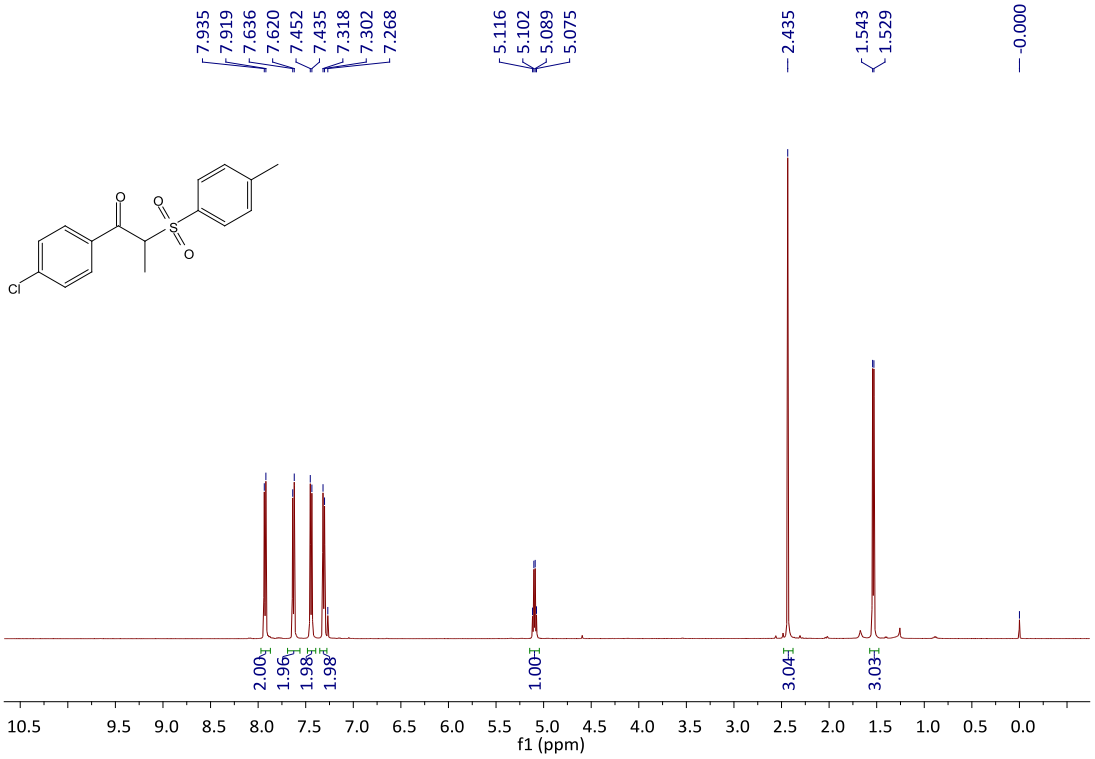

$^{13}$C NMR (125 Hz, $CDCl_3$): **3aa**



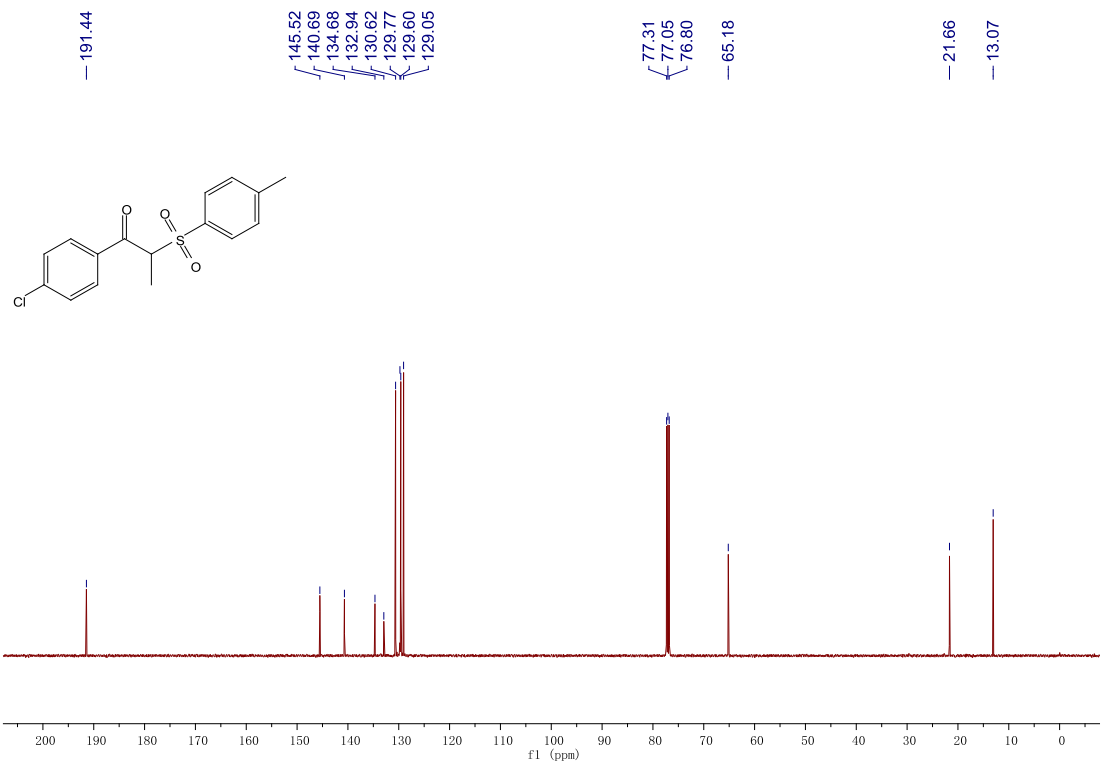

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ba** (Table 2)



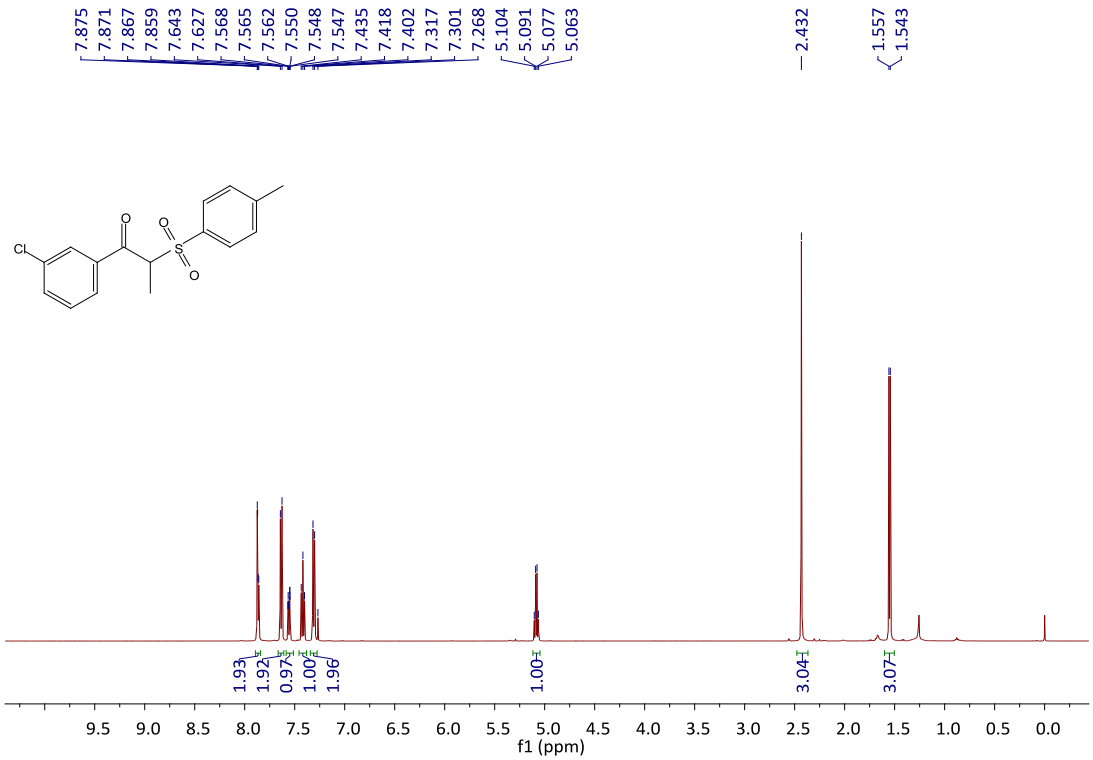

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ba** (Table 2)



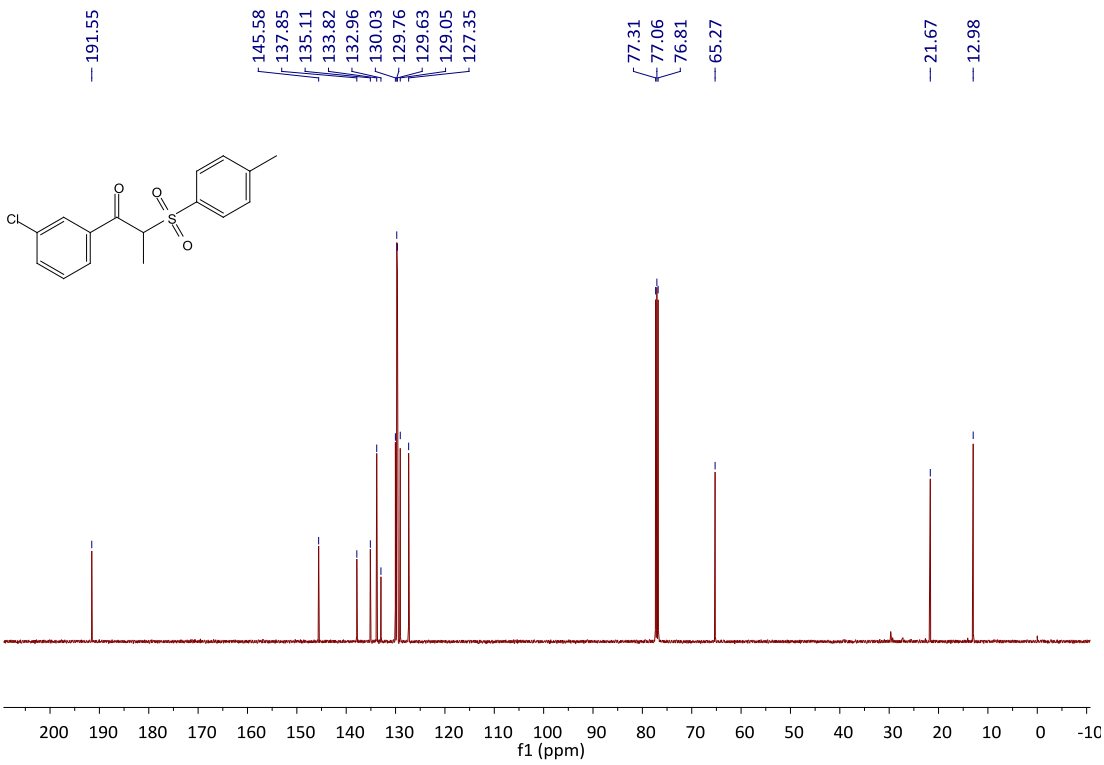

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ca**



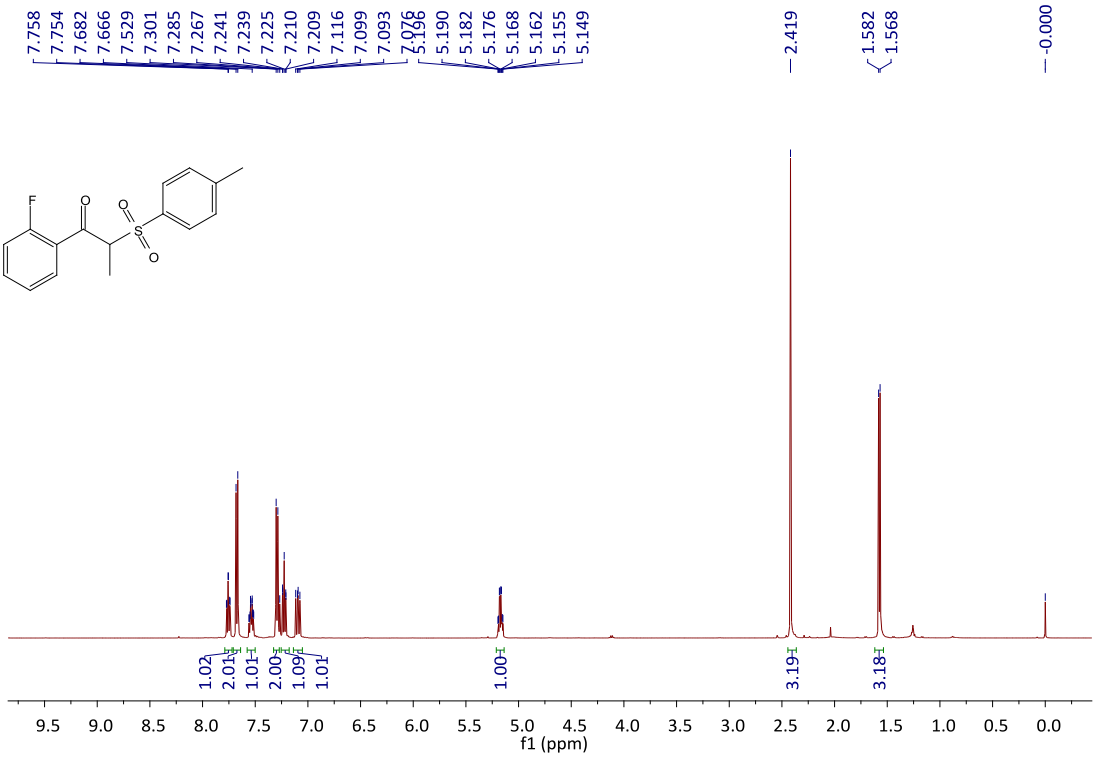

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ca**



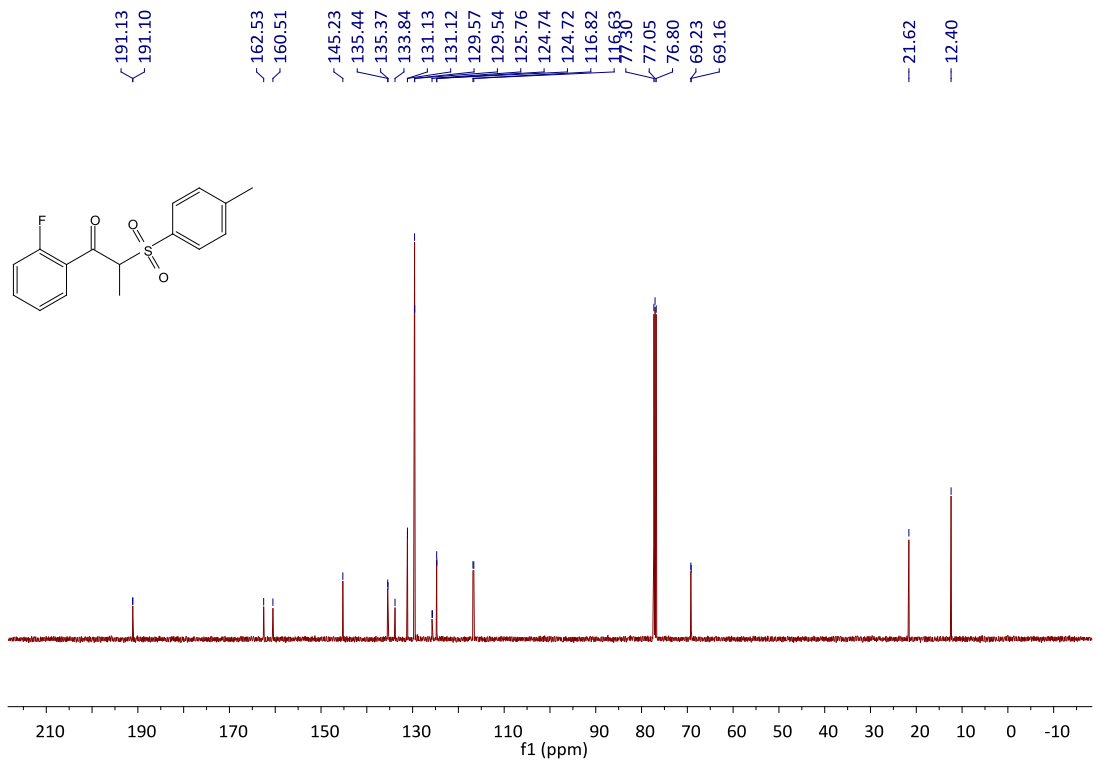

$^{1}$H NMR (500 Hz, $CDCl_3$): **3da**



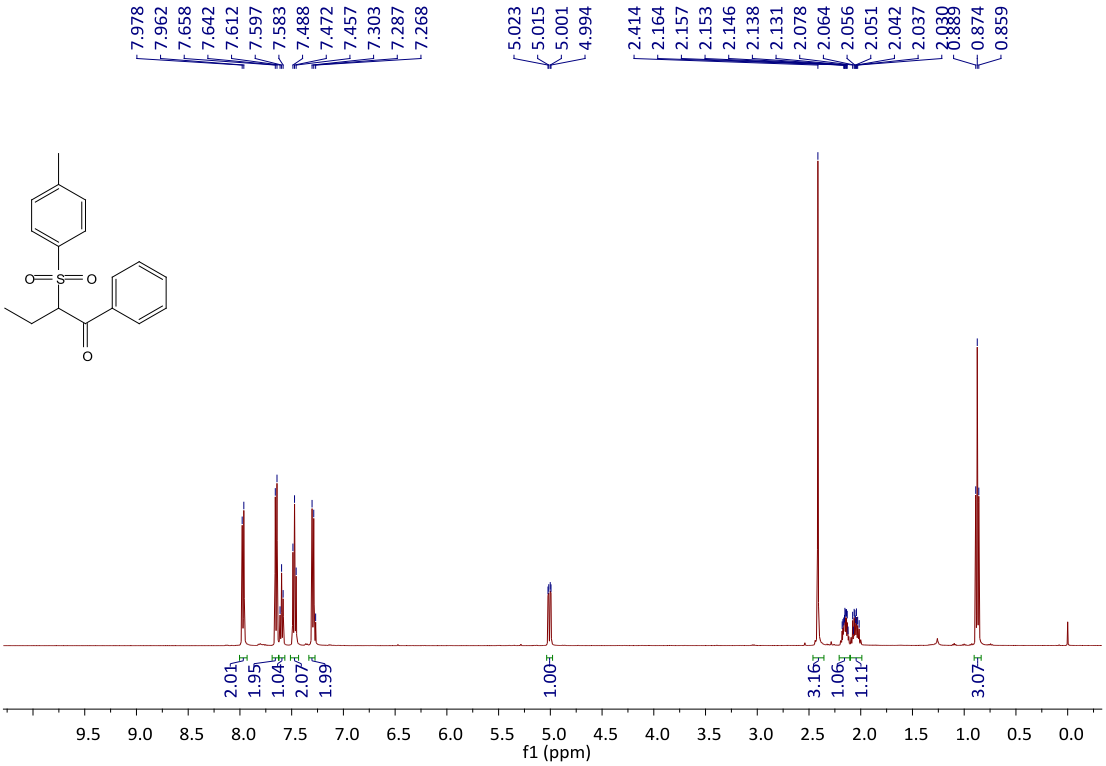

$^{13}$C NMR (125 Hz, $CDCl_3$): **3da**



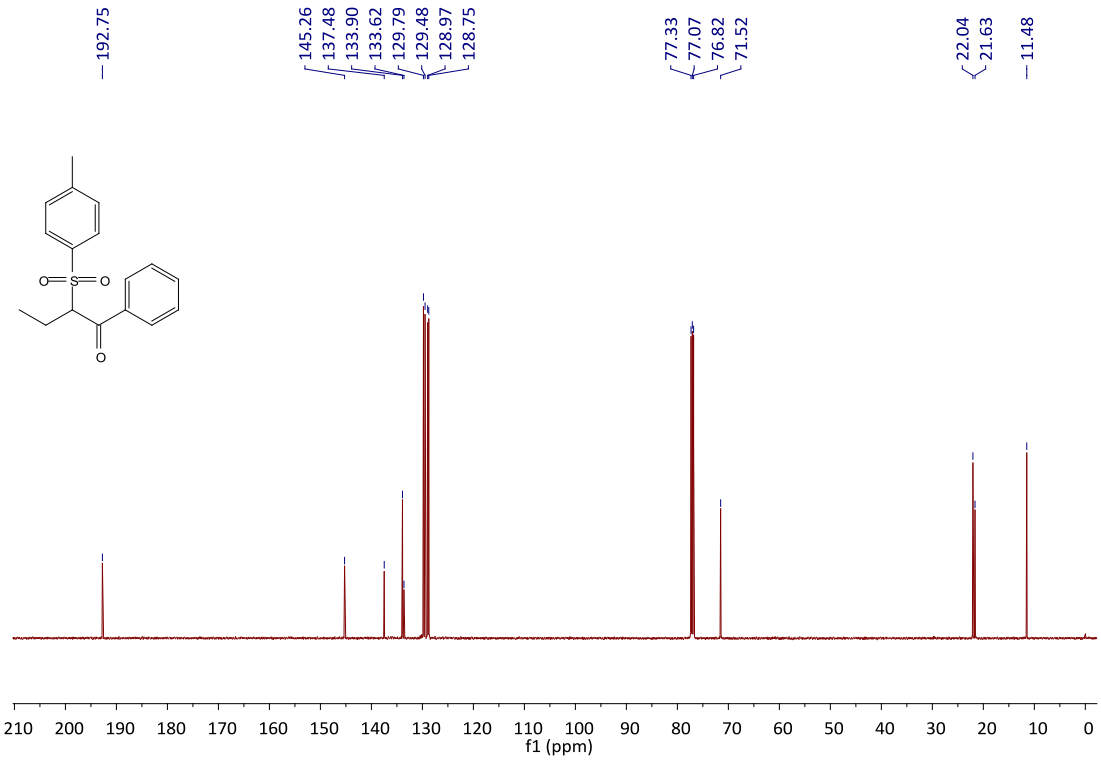

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ea**



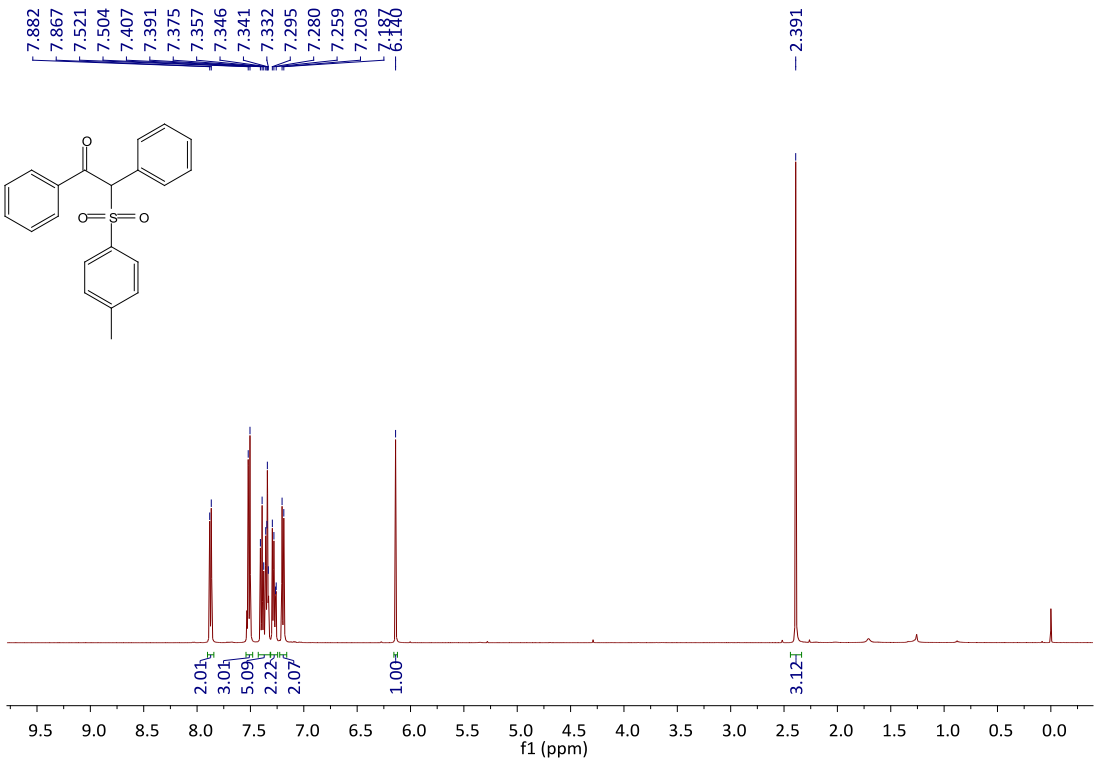

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ea**



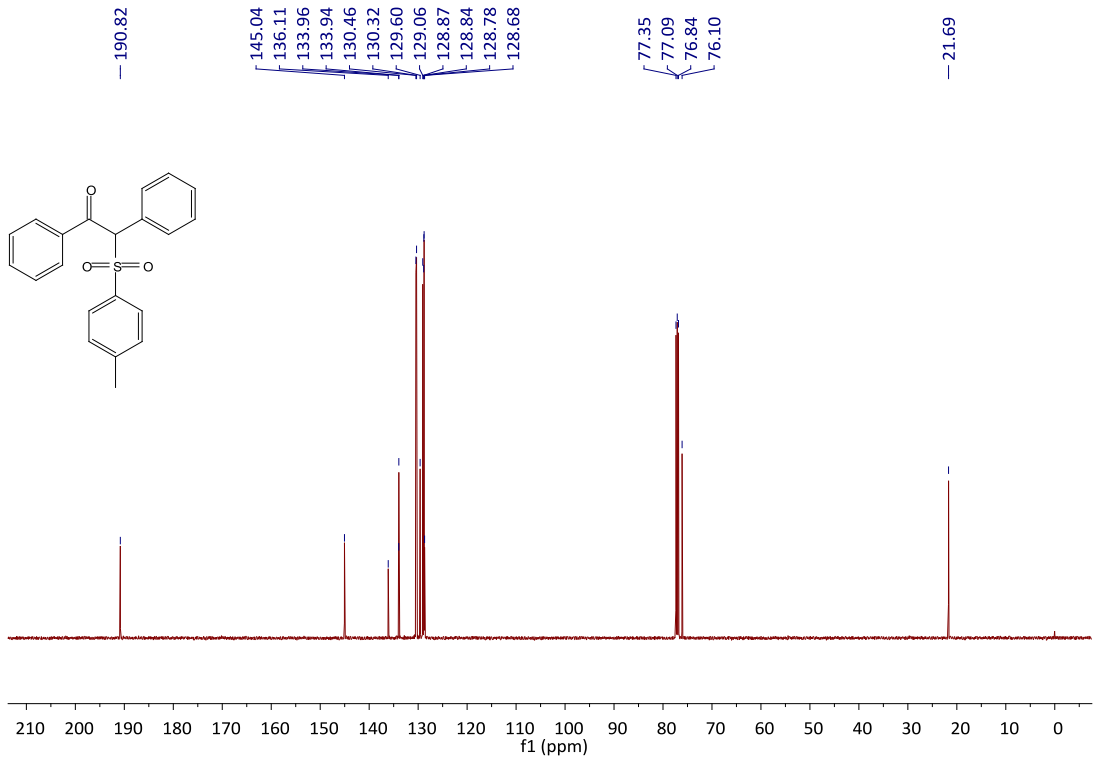

$^{1}$H NMR (500 Hz, $CDCl_3$): **3fa**




$^{13}$C NMR (125 Hz, $CDCl_3$): **3fa**




$^{1}$H NMR (500 Hz, $CDCl_3$): **3ga**

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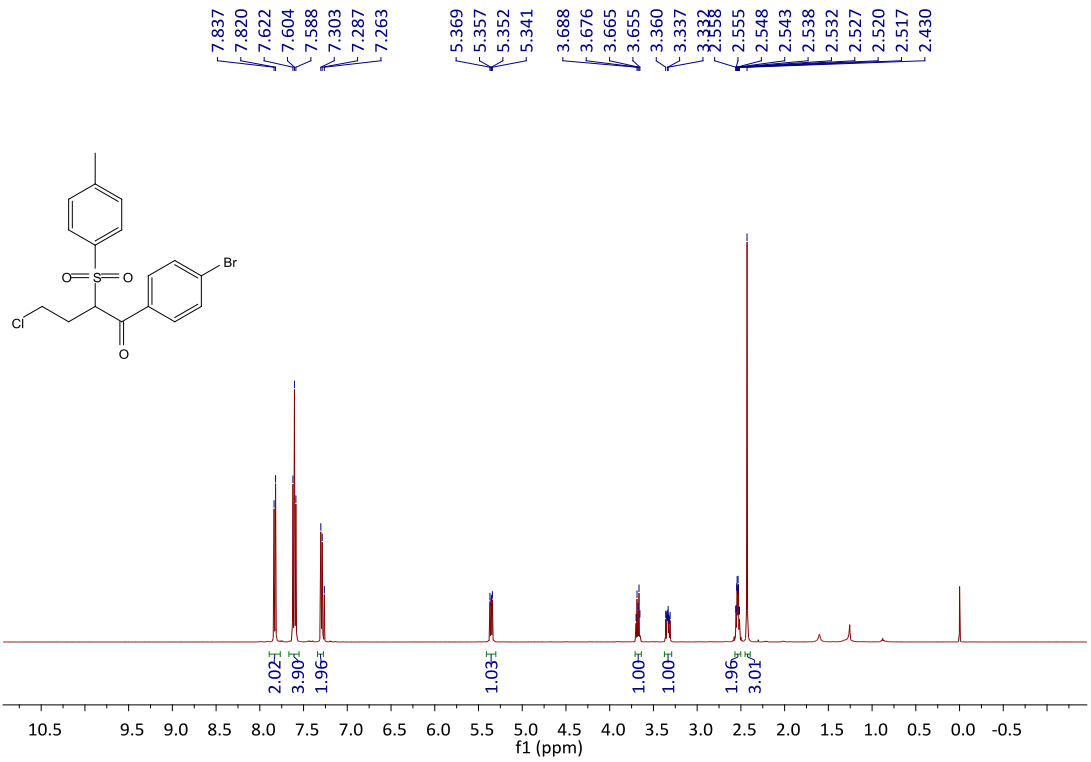


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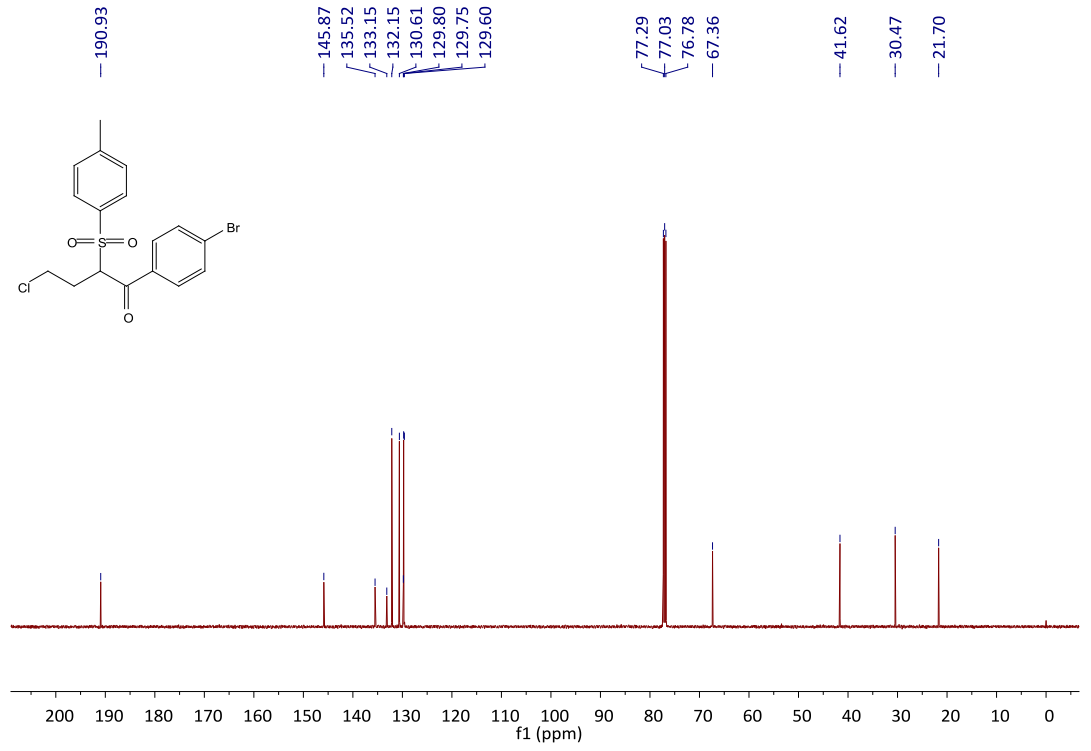
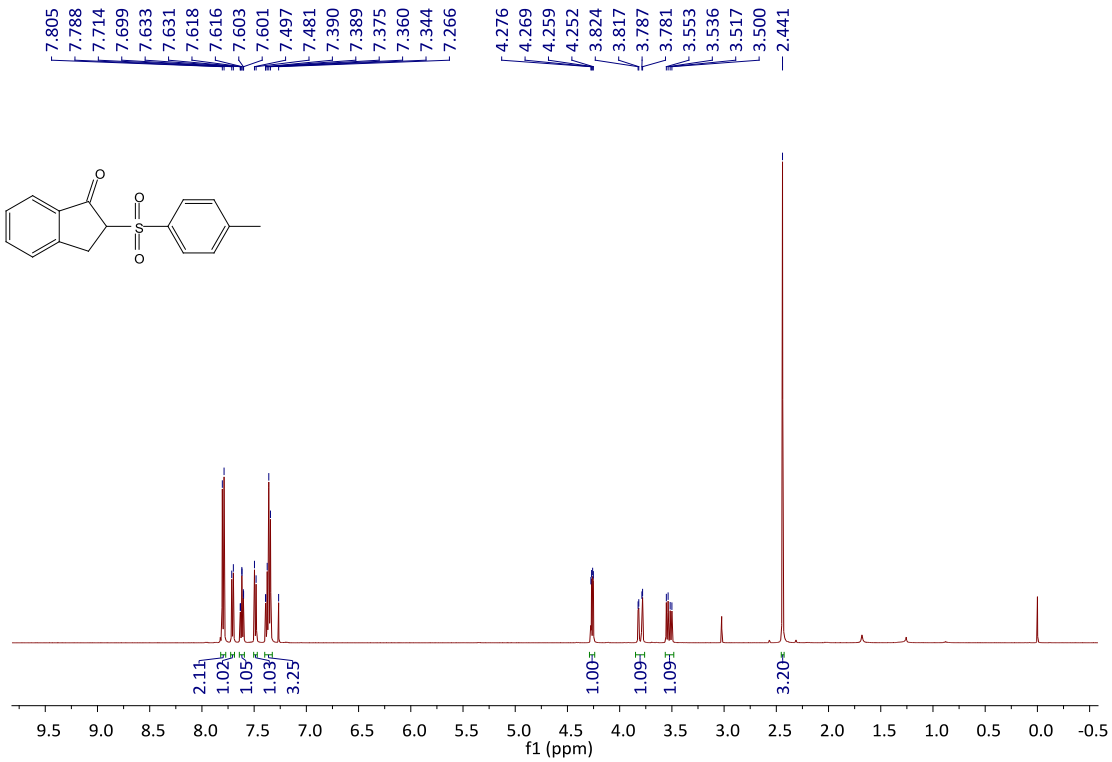
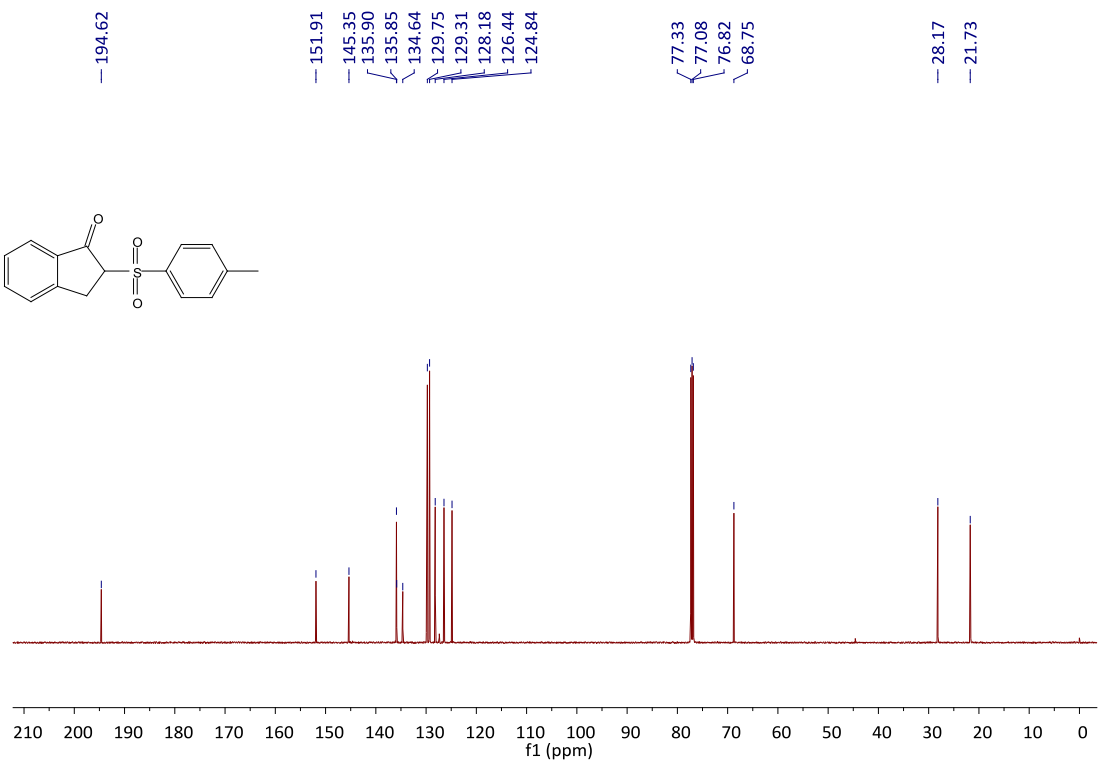


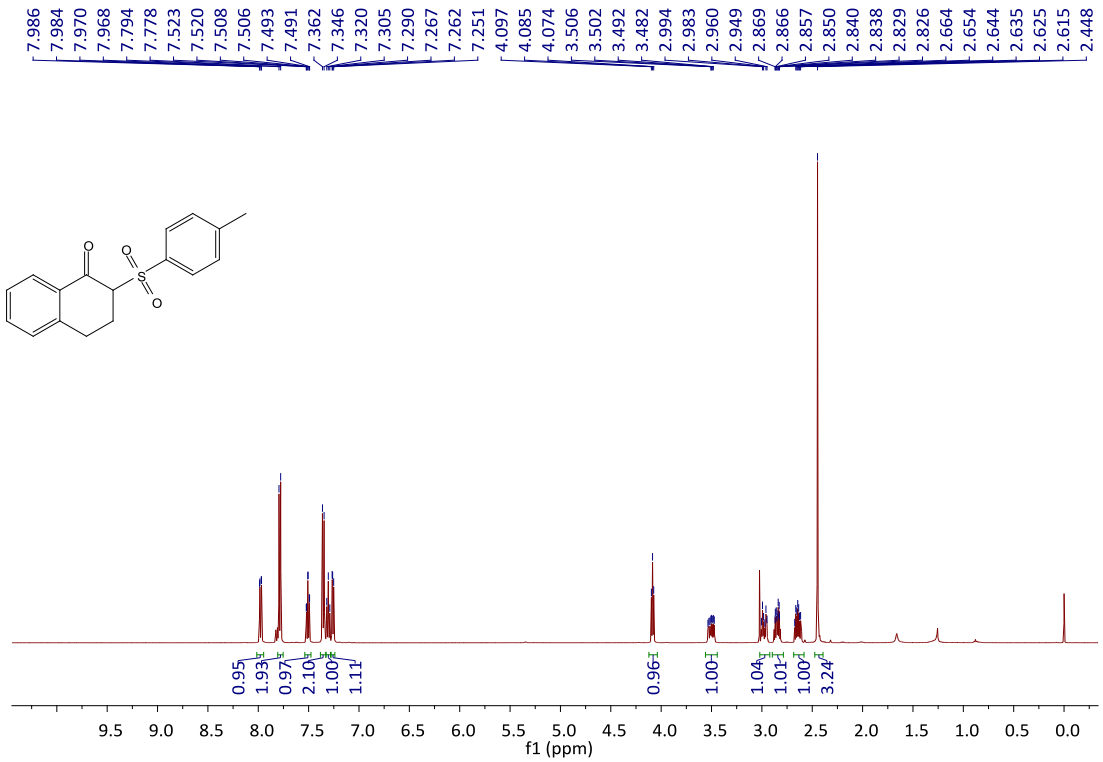

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ha**



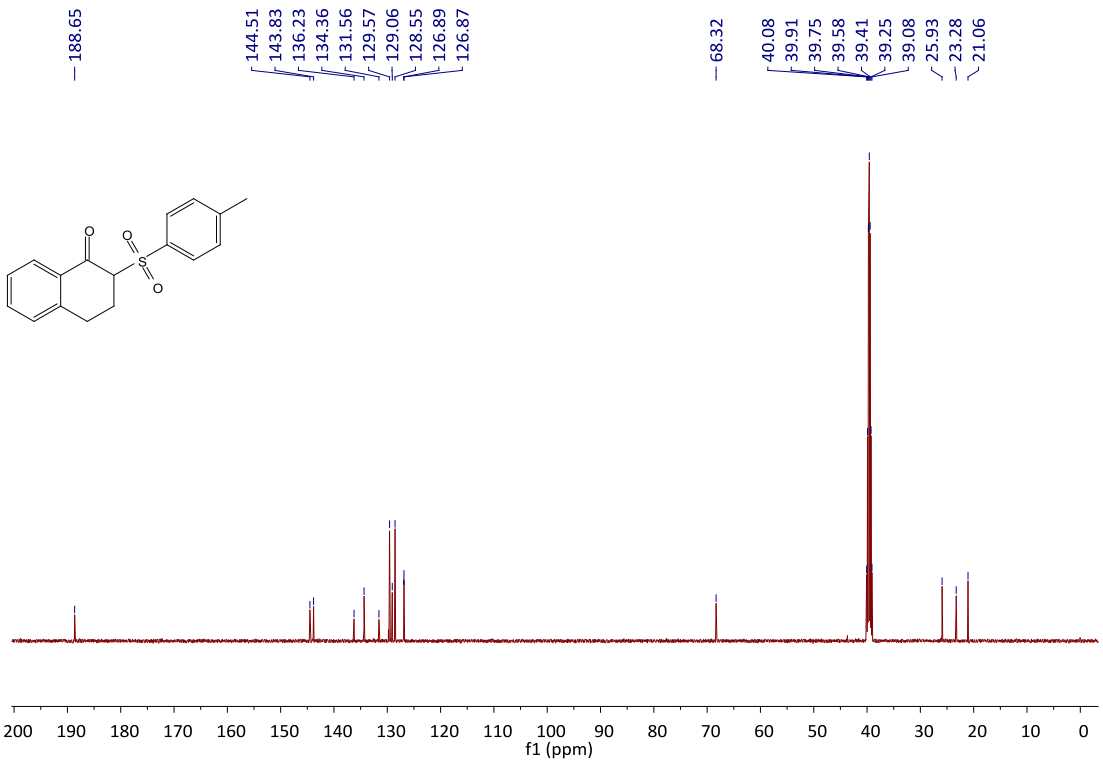

$^{1}$H NMR (125 Hz, $CDCl_3$): **3ia**



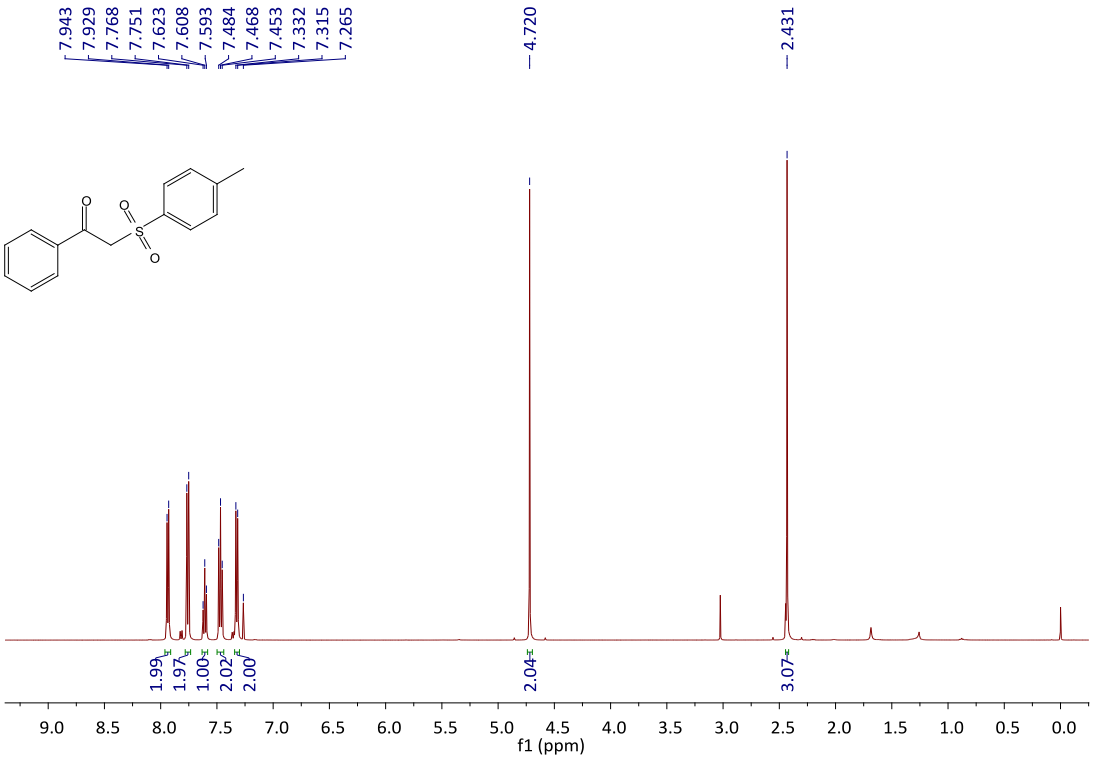

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ia**



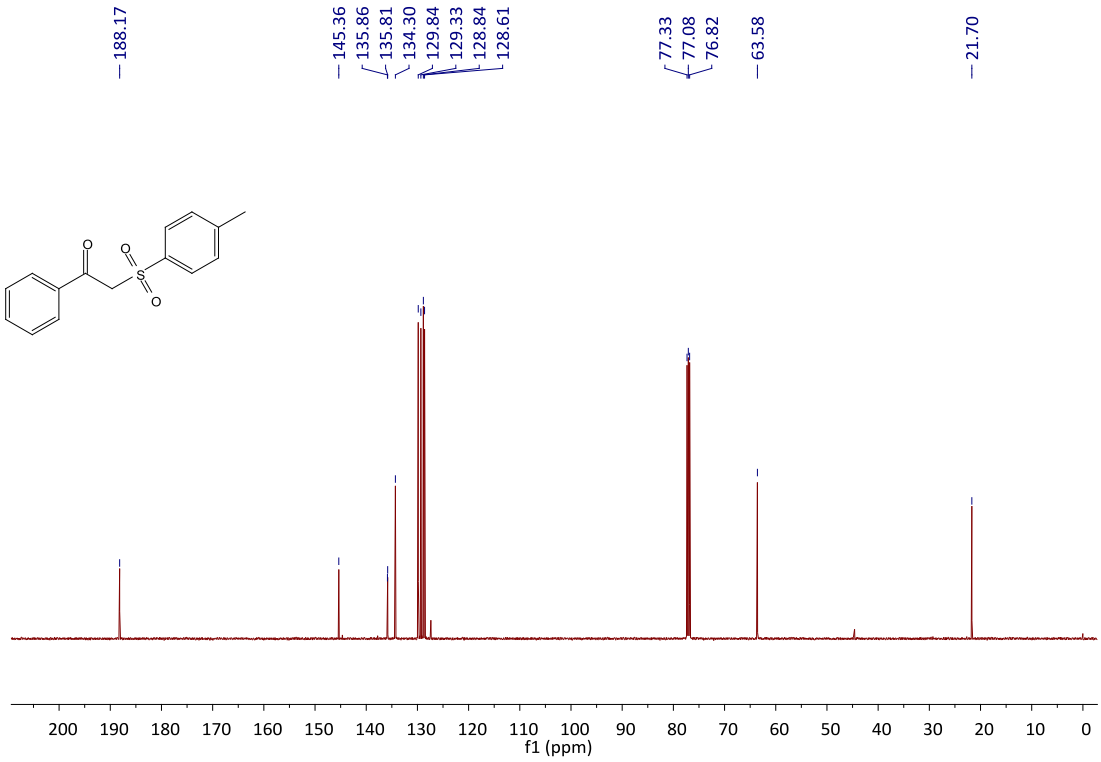

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ja**



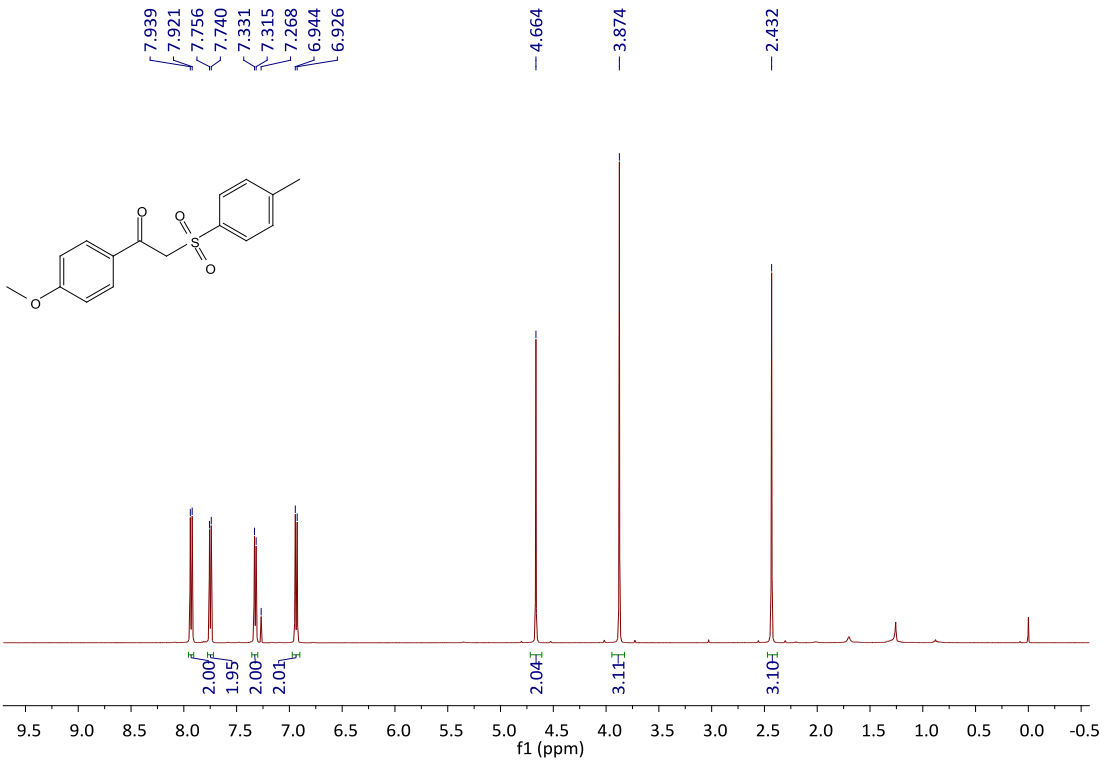

$^{13}$C NMR (125 Hz, DMSO): **3ja**



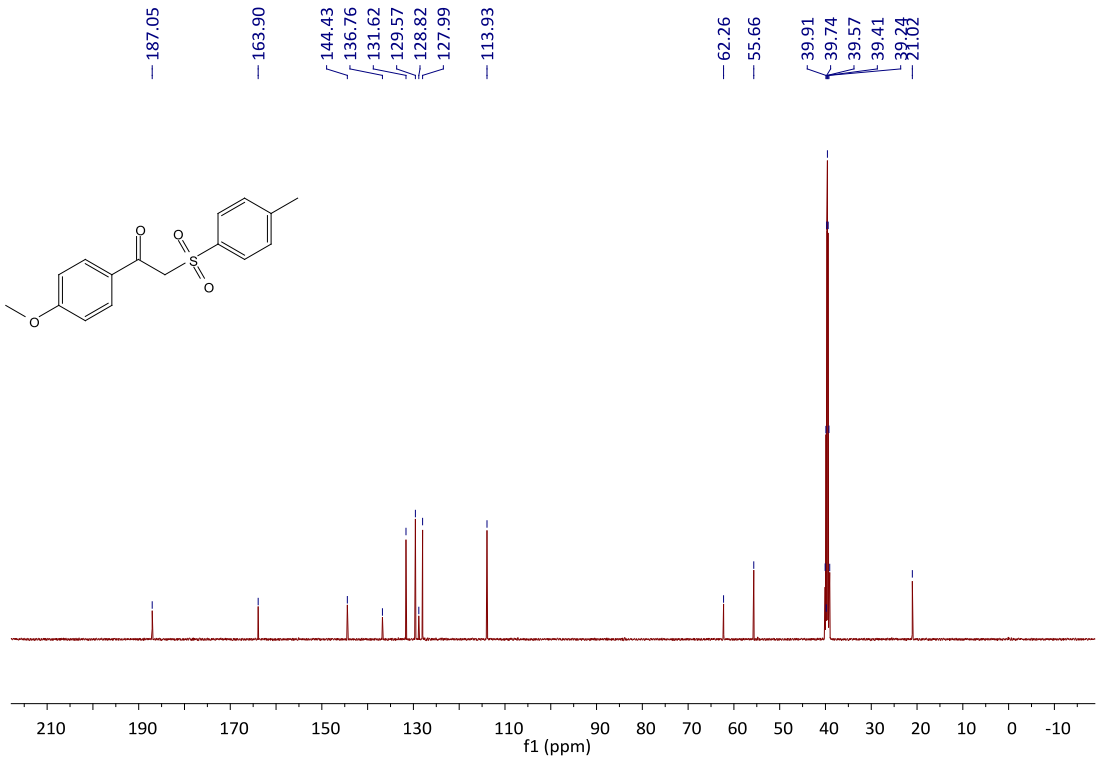

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ka** (Table 2)



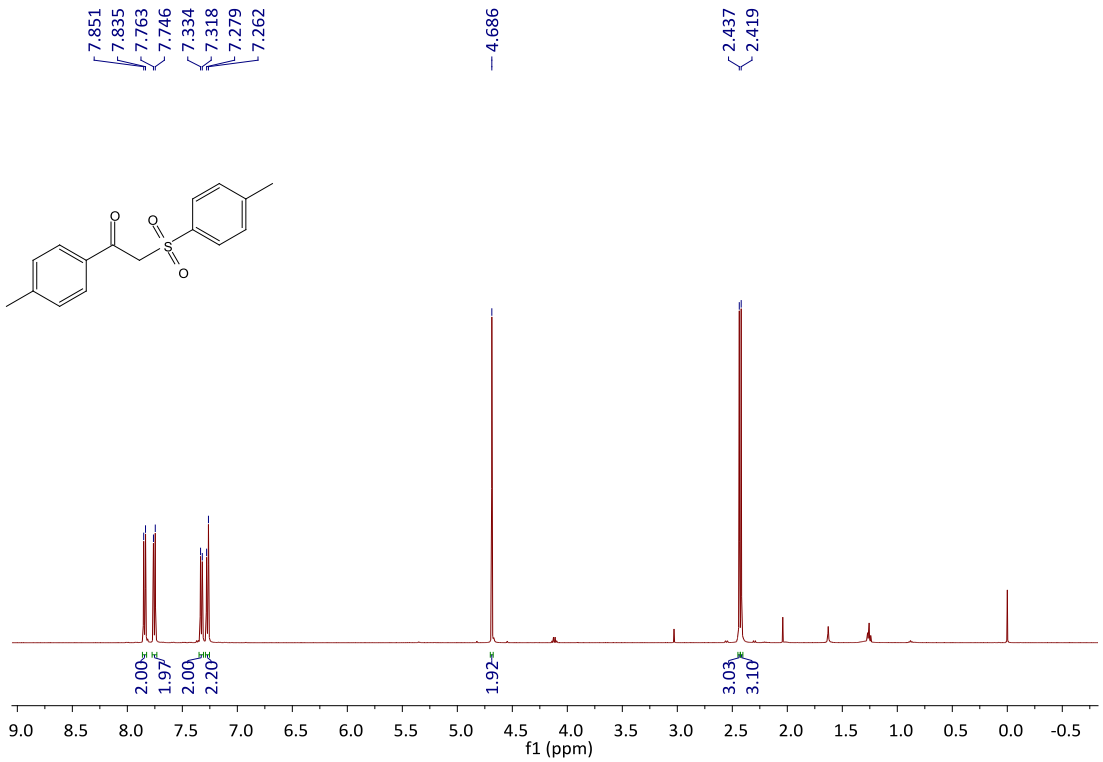

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ka** (Table 2)



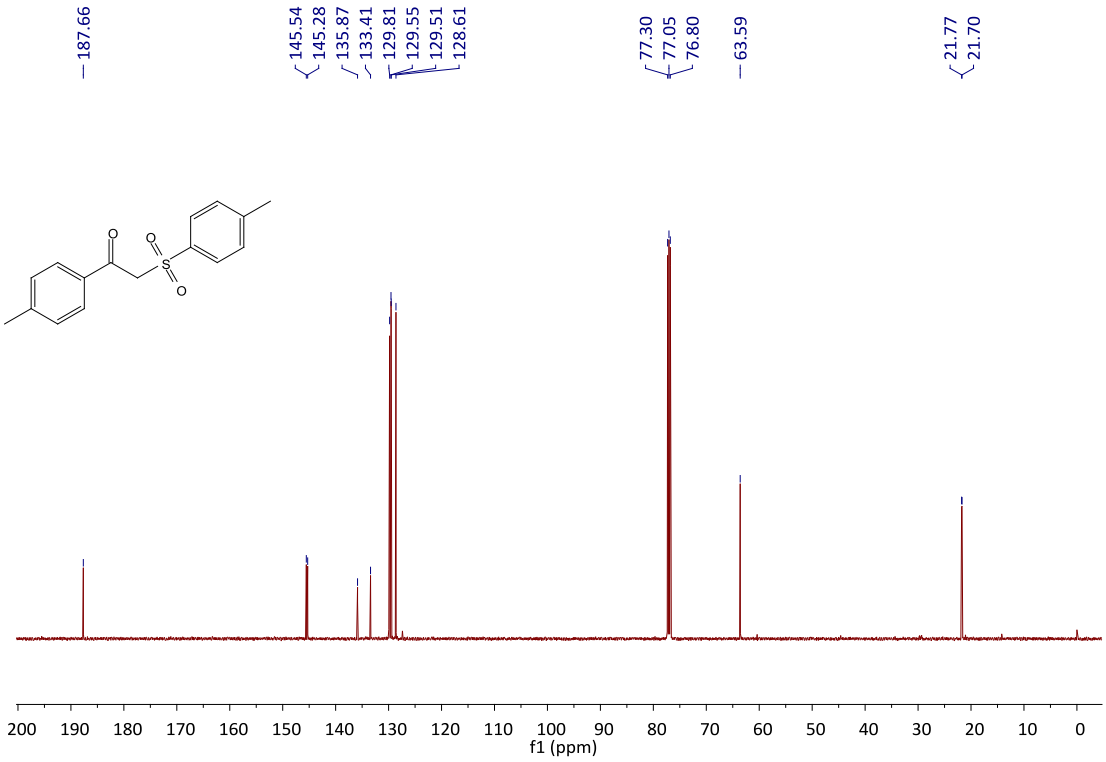

$^{1}$H NMR (500 Hz, $CDCl_3$): **3la**



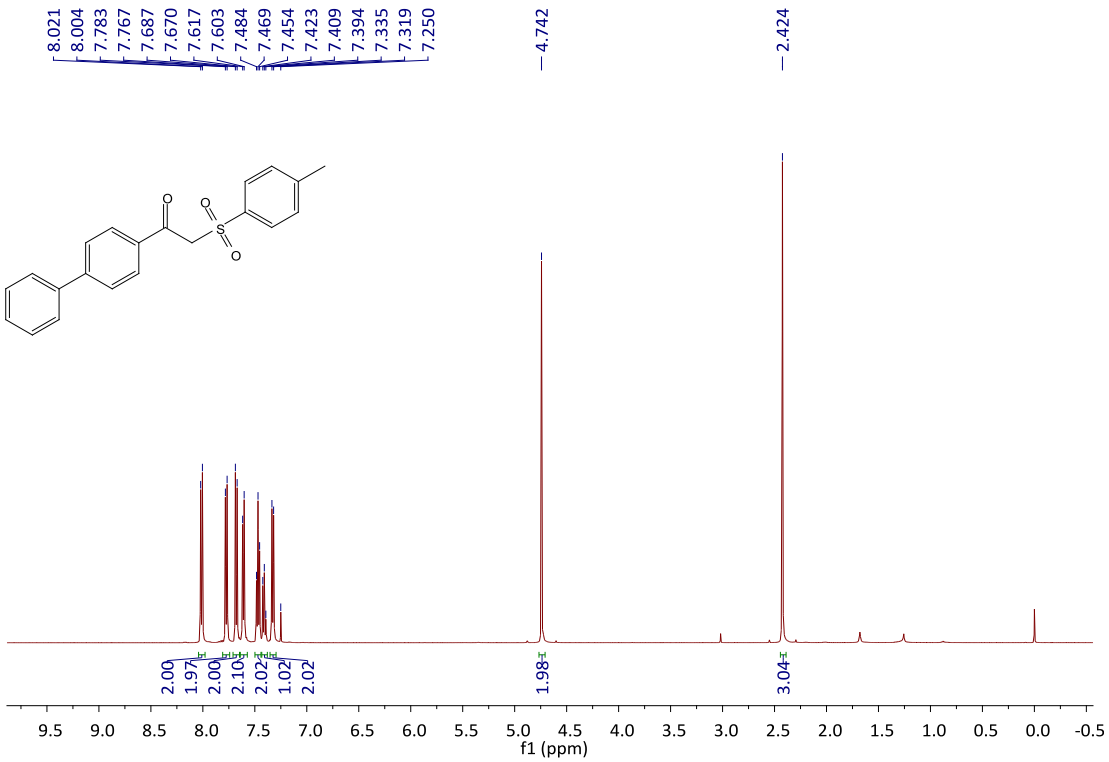

$^{13}$C NMR (125 Hz, DMSO): **3la**



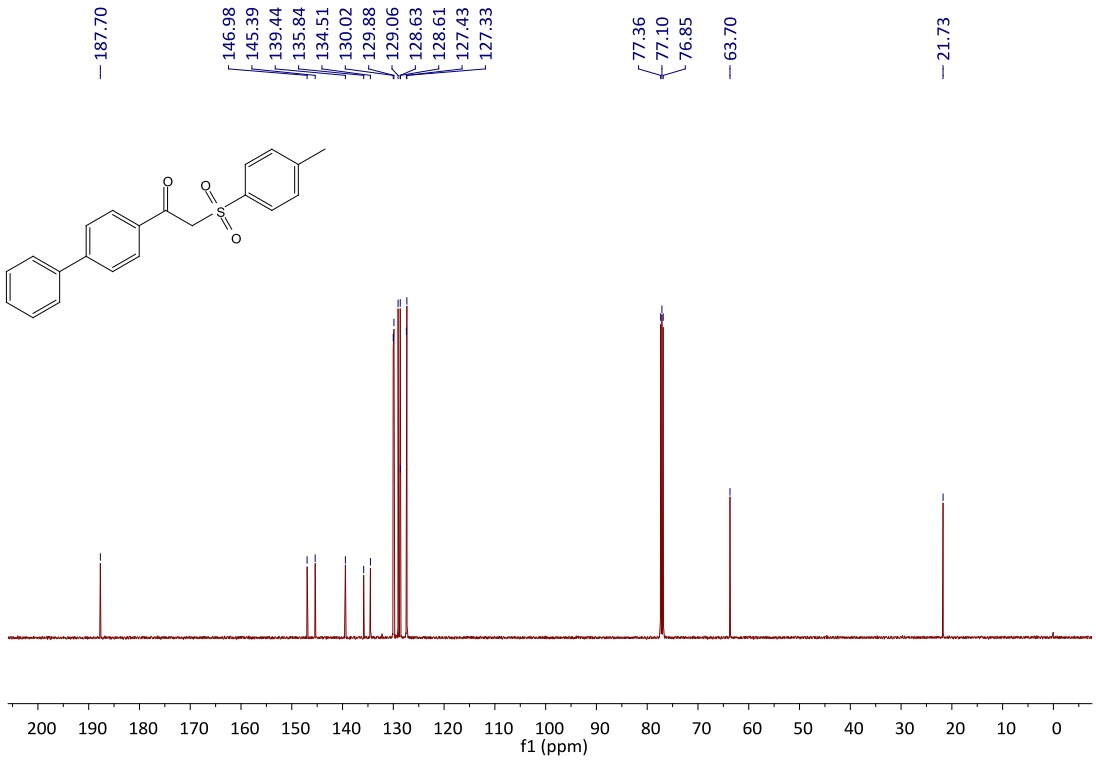

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ma**



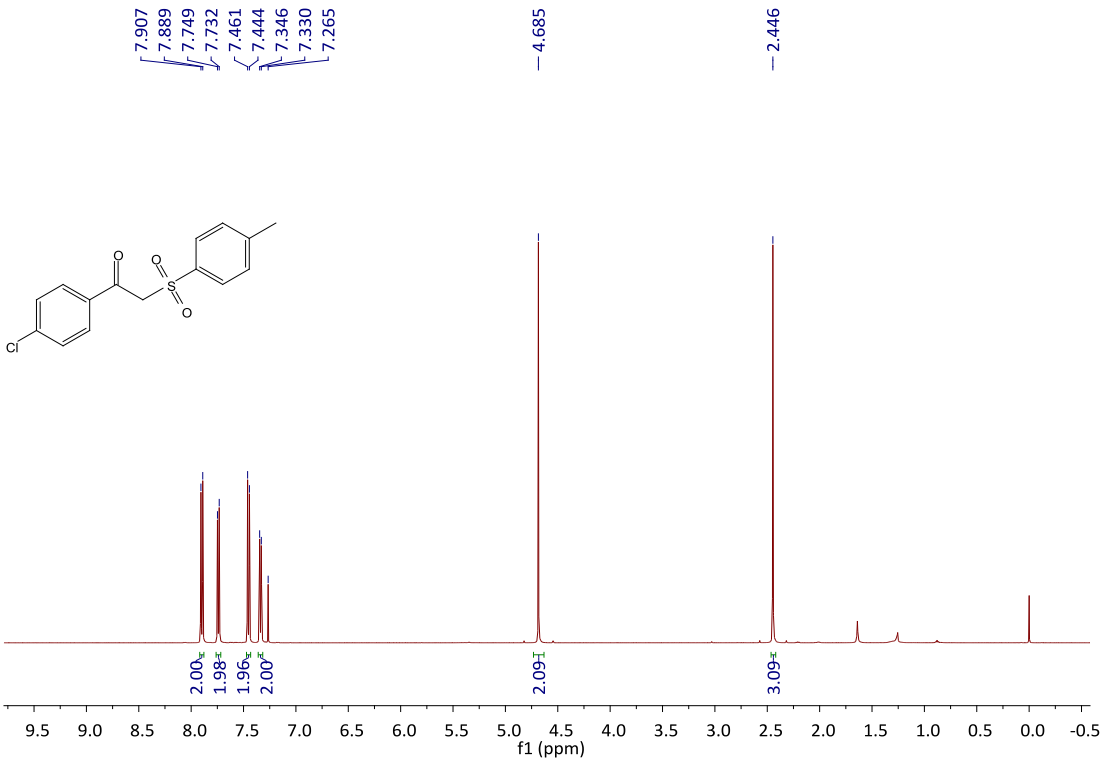

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ma**



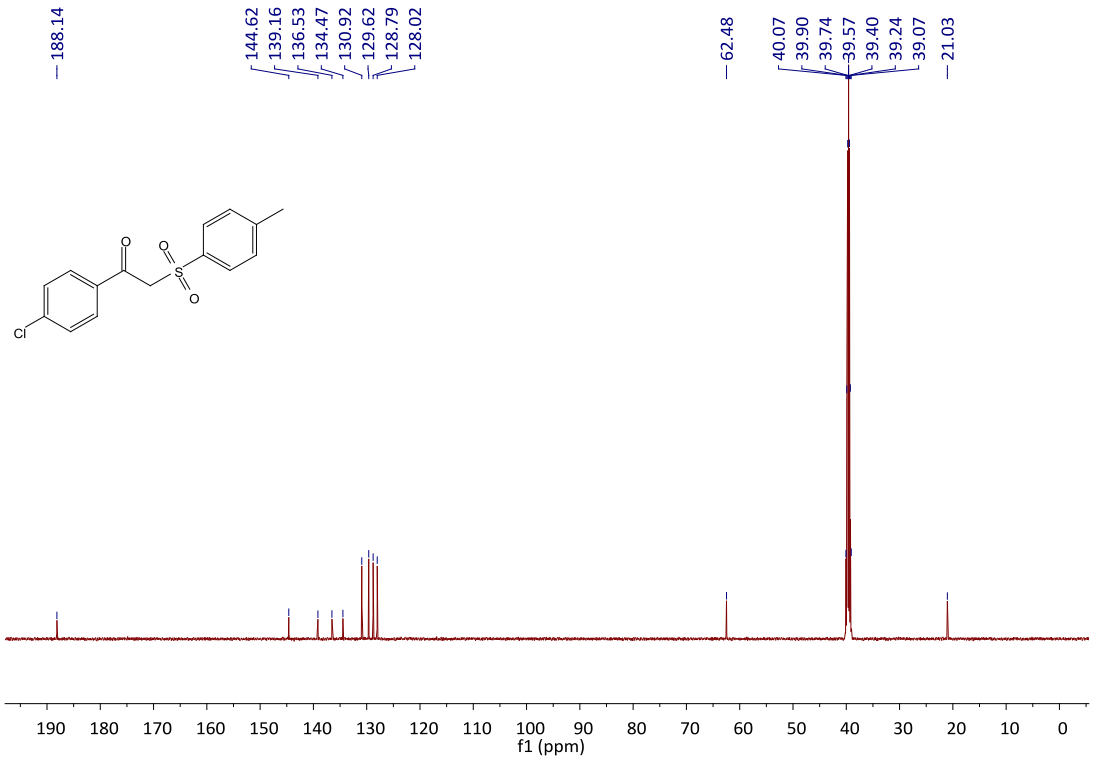

$^{1}$H NMR (500 Hz, $CDCl_3$): **3na**



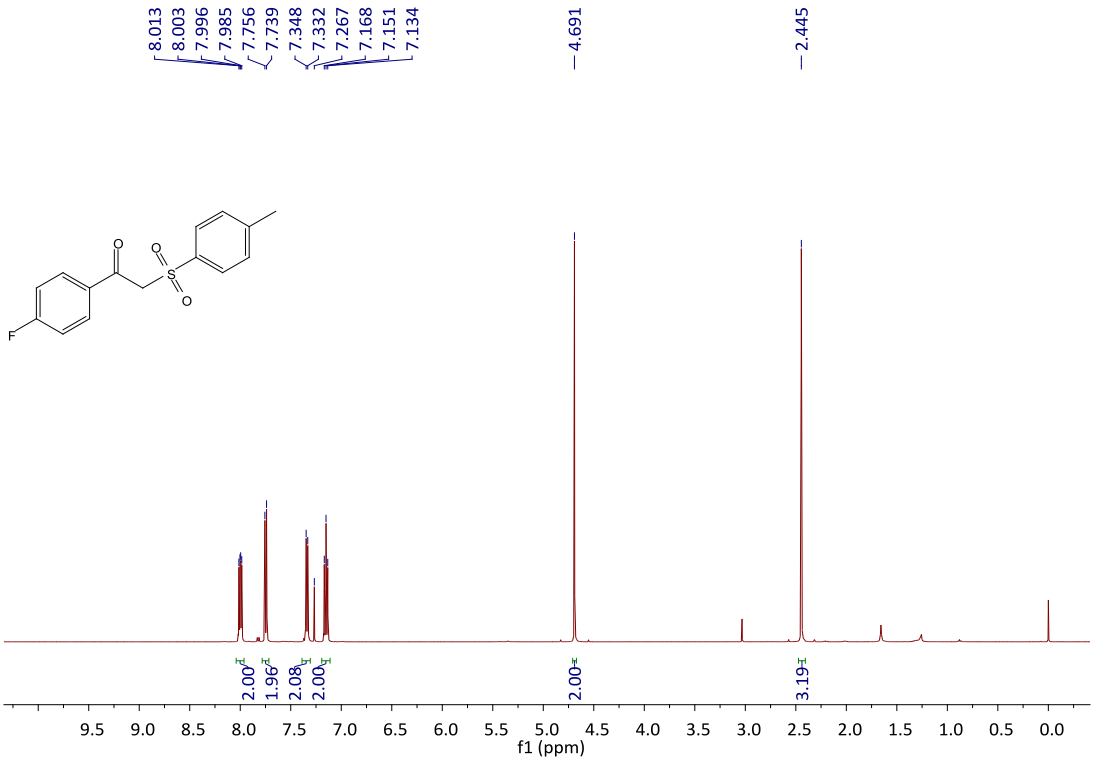

$^{13}$C NMR (125 Hz, $CDCl_3$): **3na**



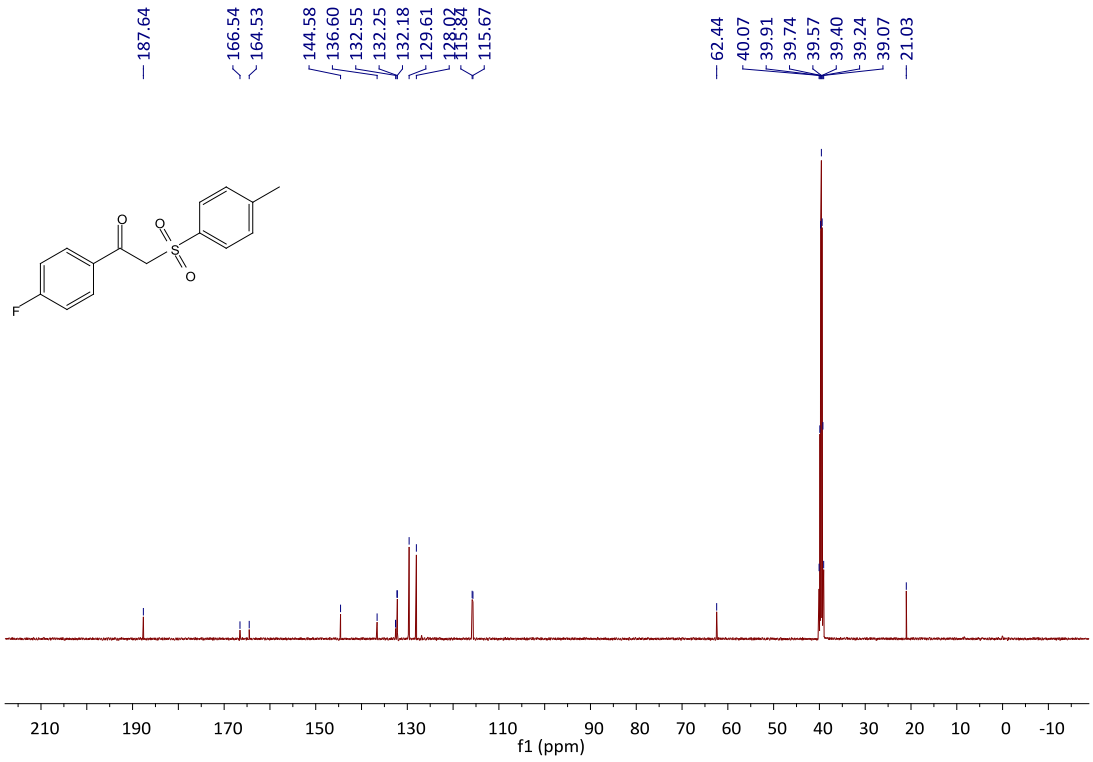

$^{1}$H NMR (500 Hz, $CDCl_3$): **3oa**



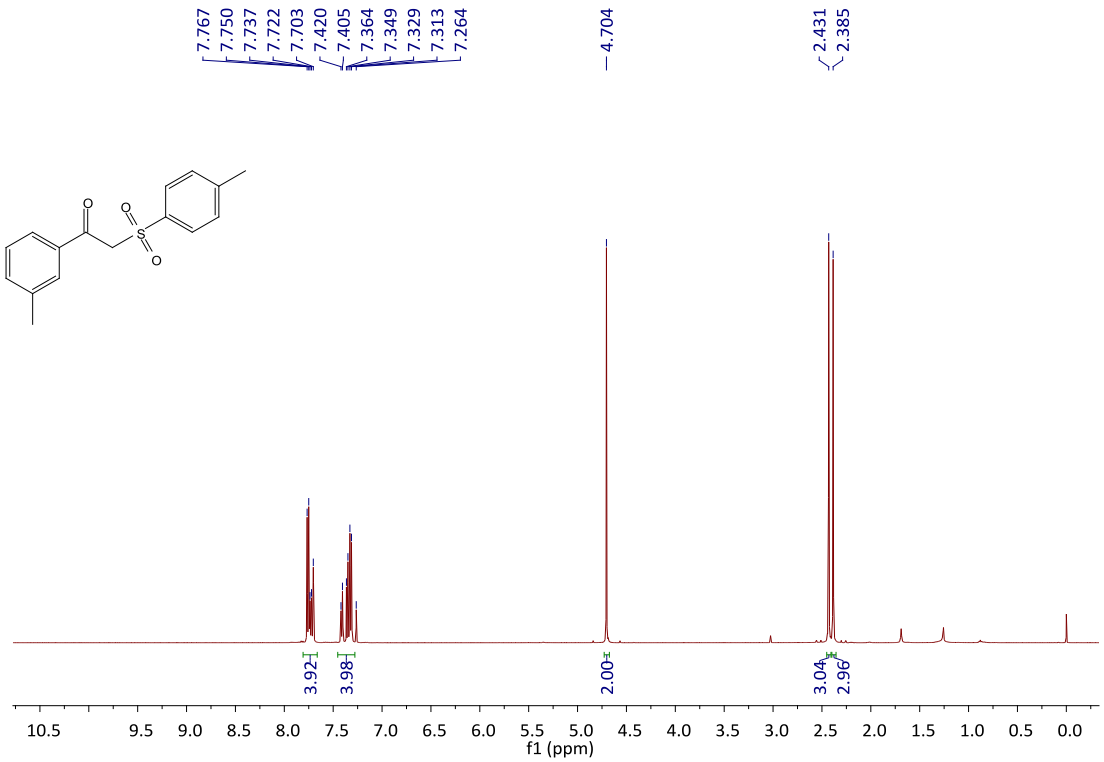

$^{13}$C NMR (125 Hz, DMSO): **3oa**



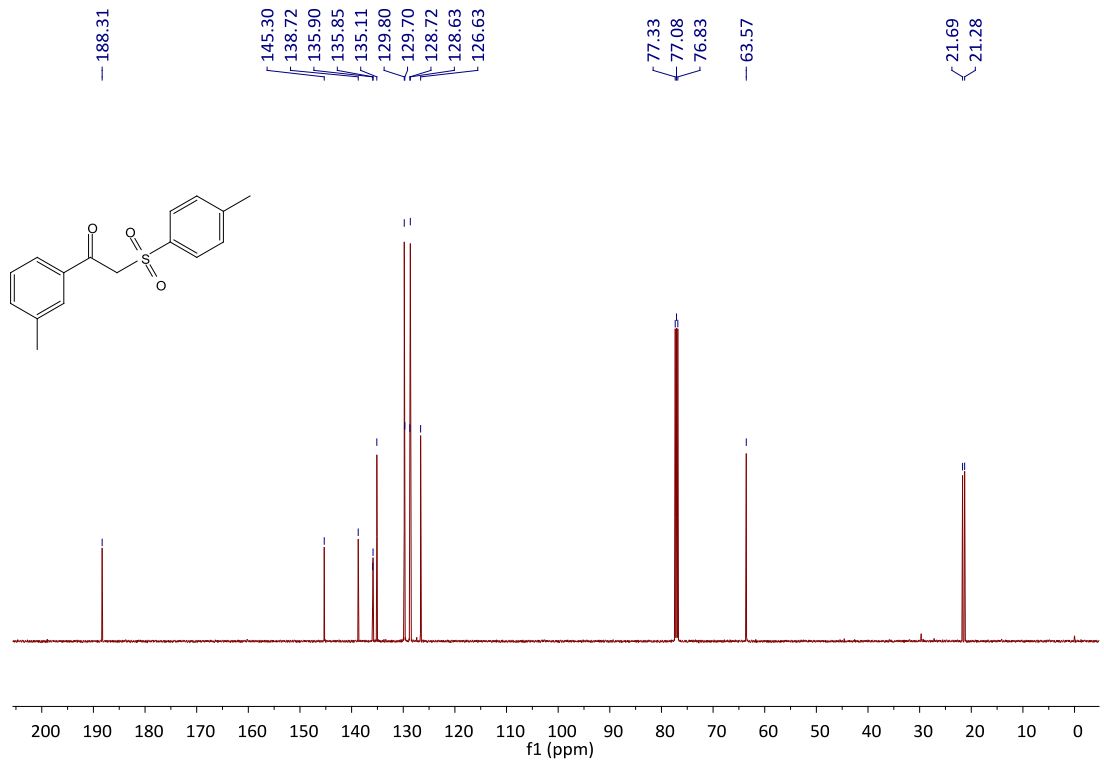

$^{1}$H NMR (500 Hz, $CDCl_3$): **3pa**



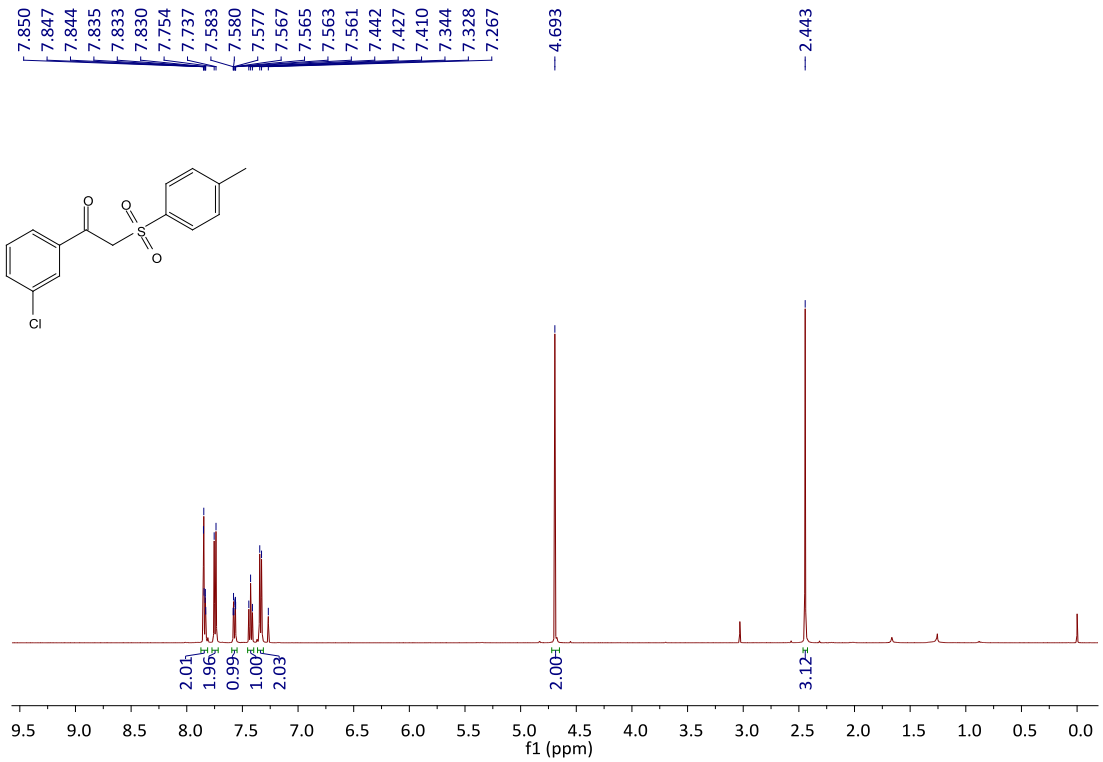

$^{13}$C NMR (500 Hz, DMSO): **3pa**



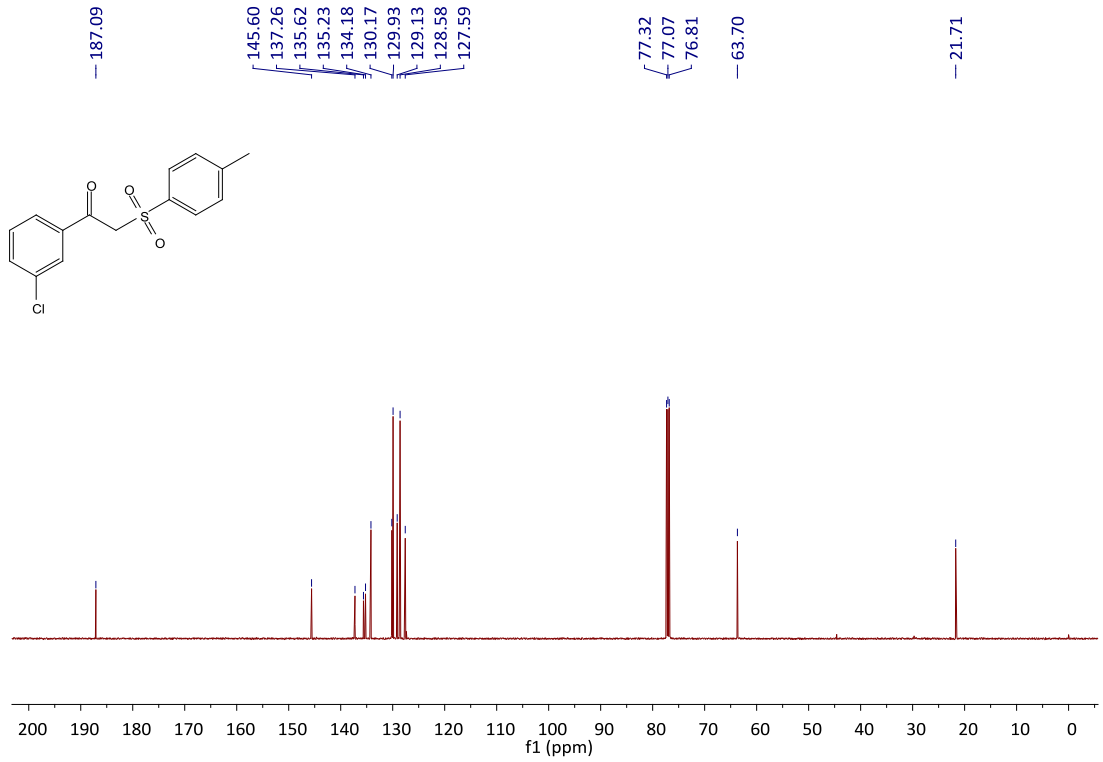

$^{1}$H NMR (500 Hz, $CDCl_3$): **3qa**



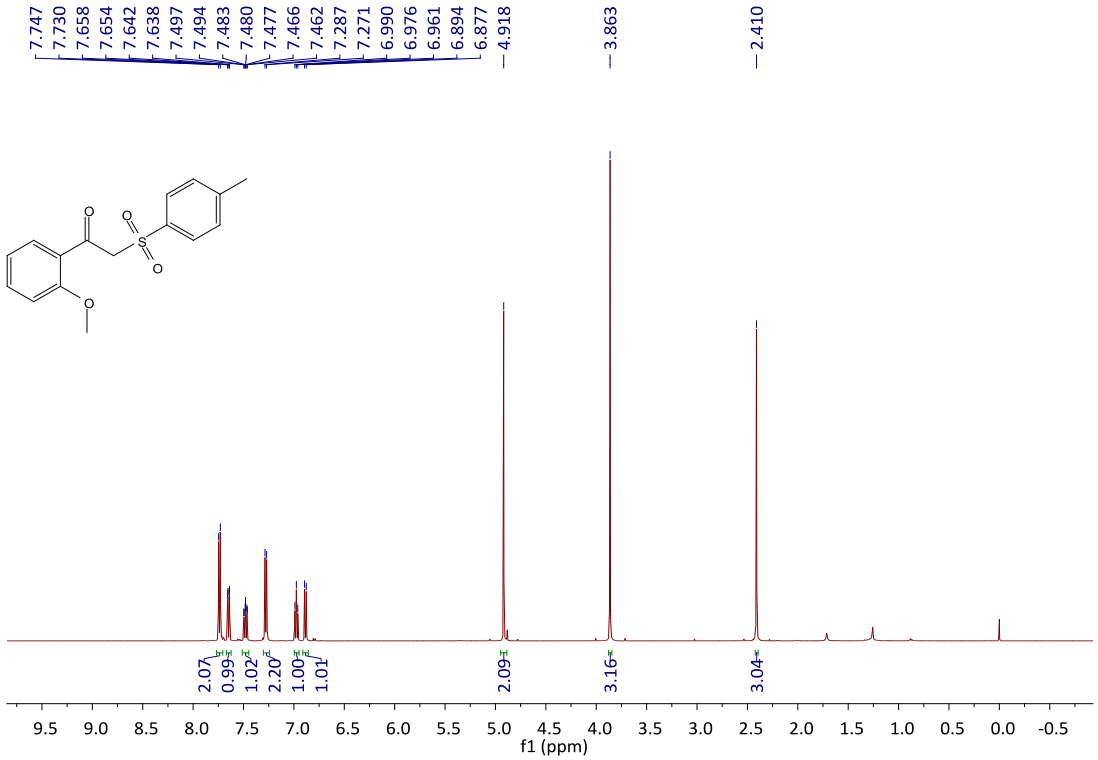

$^{13}$C NMR (125 Hz, $CDCl_3$): **3qa**



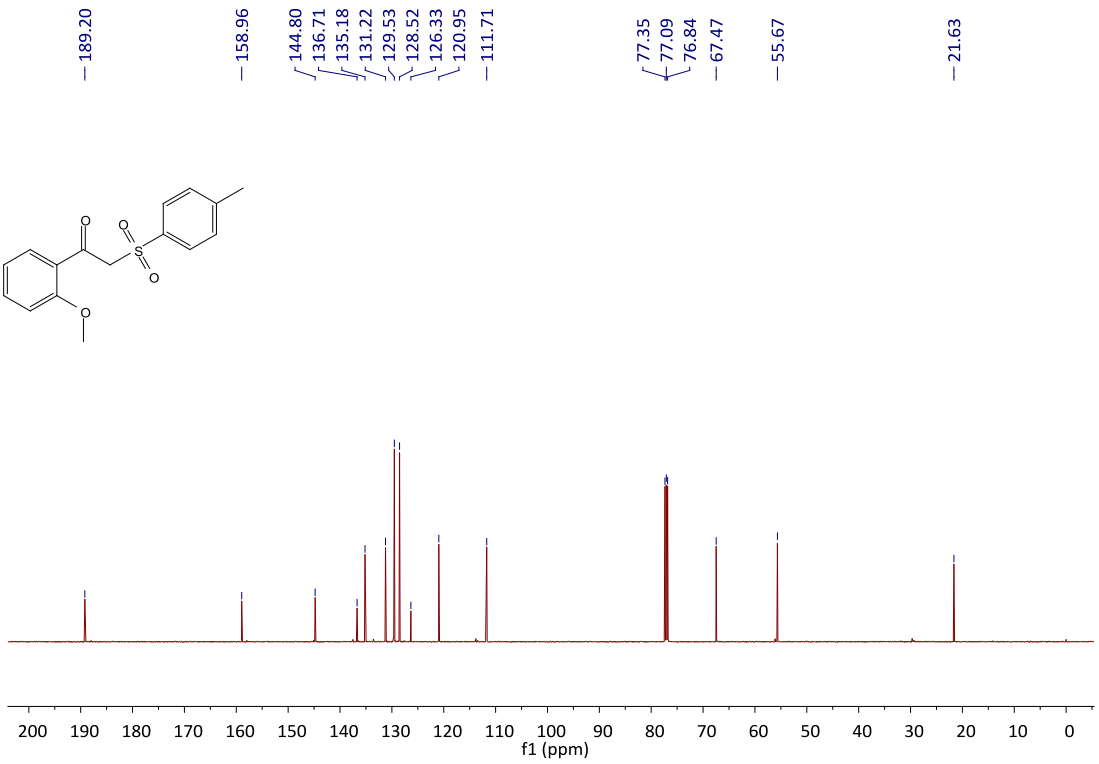

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ra**



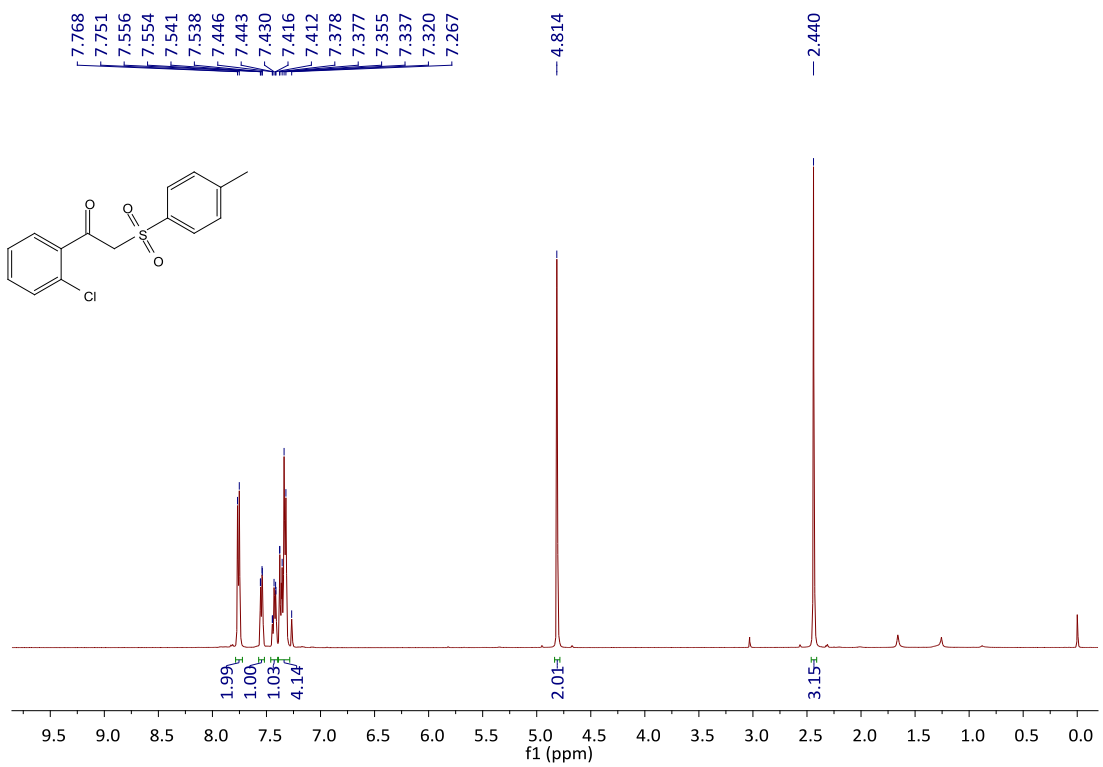

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ra**



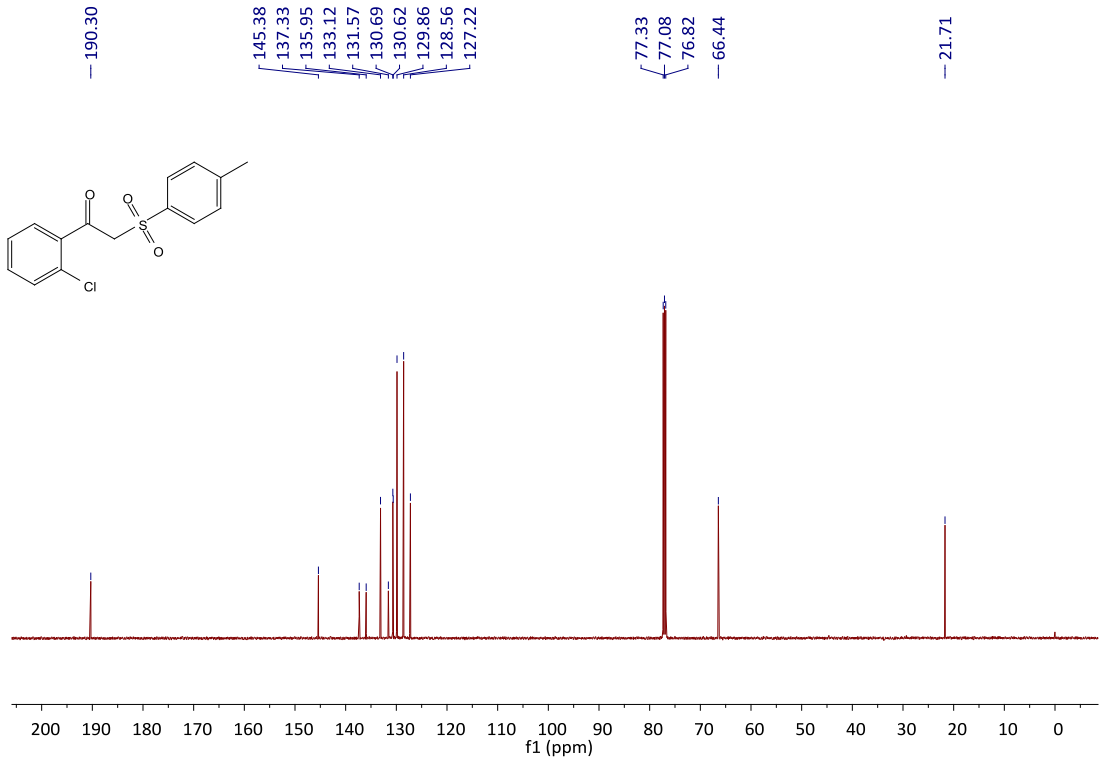

$^{1}$H NMR (500 Hz, $CDCl_3$): **3sa**



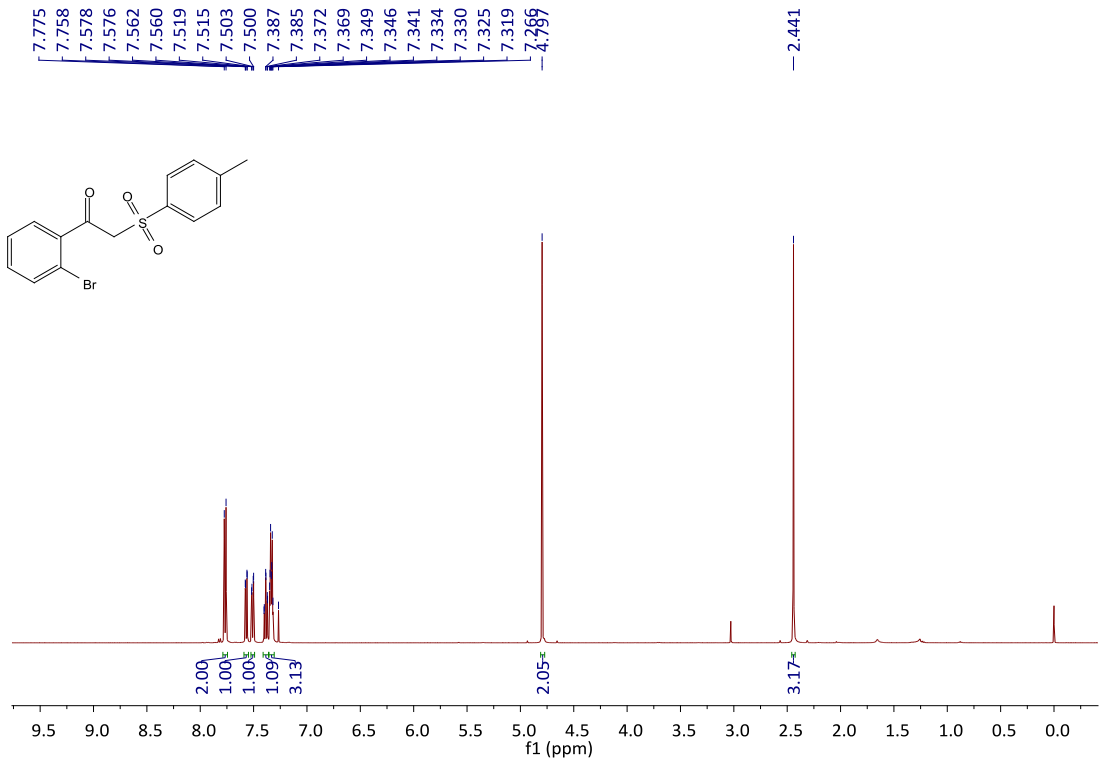

$^{13}$C NMR (125 Hz, $CDCl_3$): **3sa**



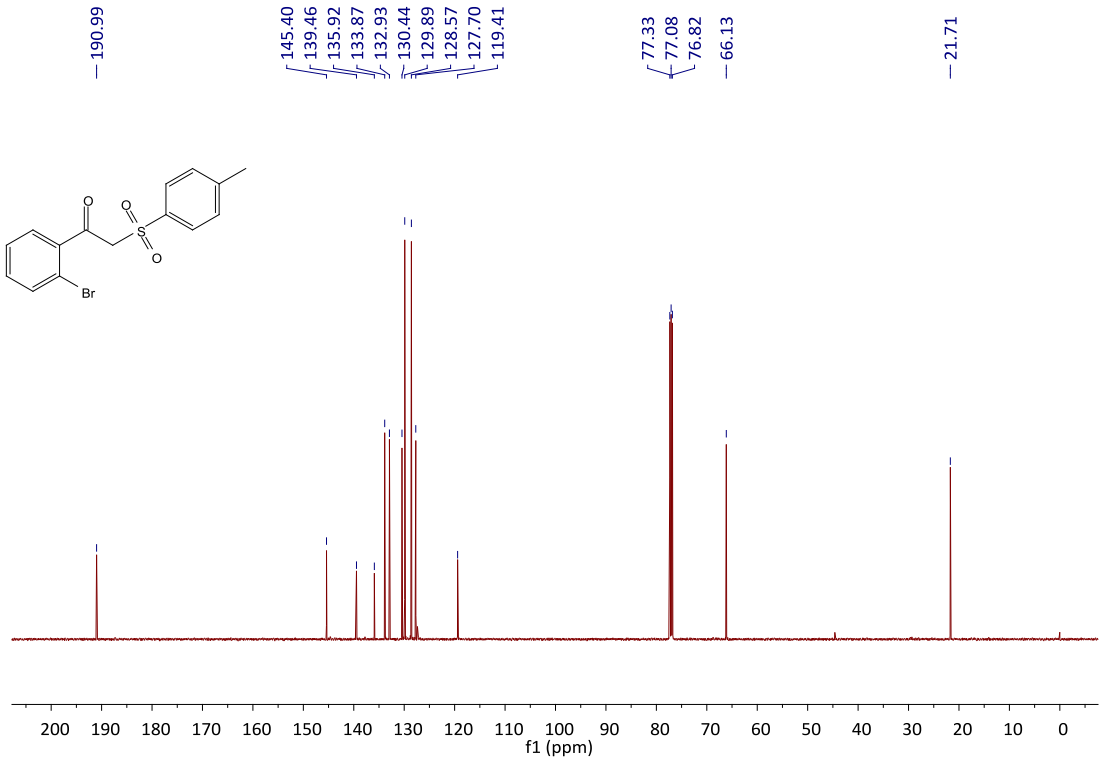

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ta**



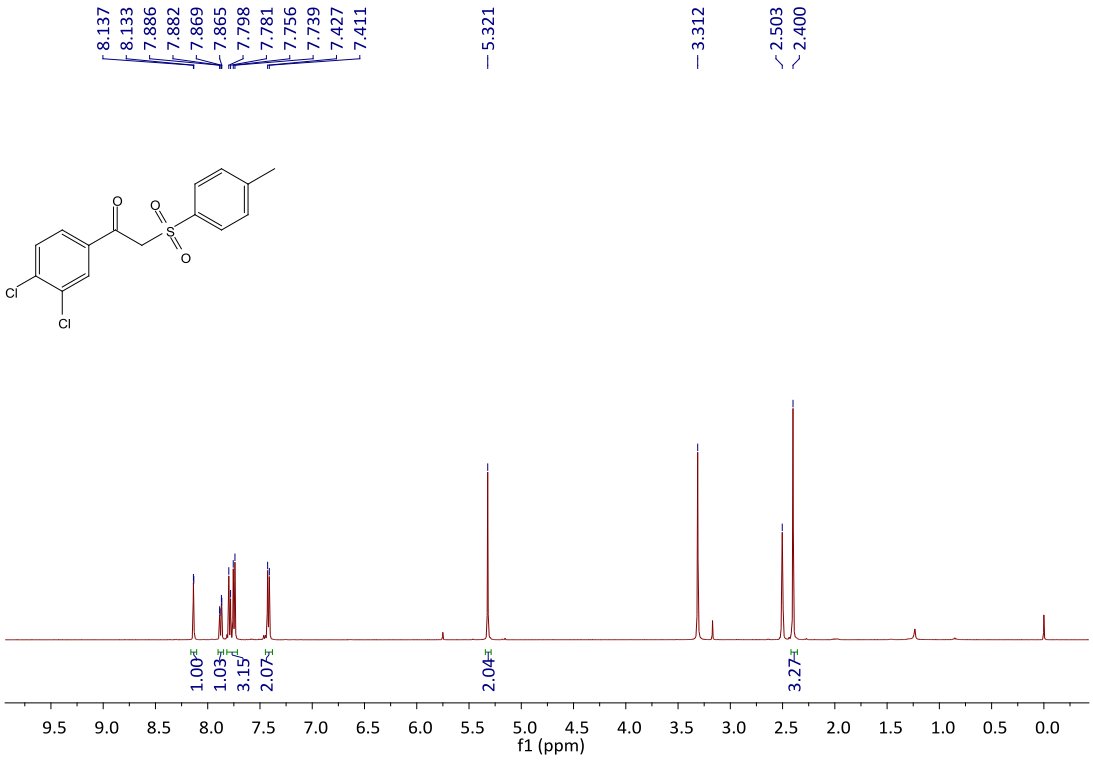

$^{13}$C NMR (500 Hz, CDCl3): **3ta**



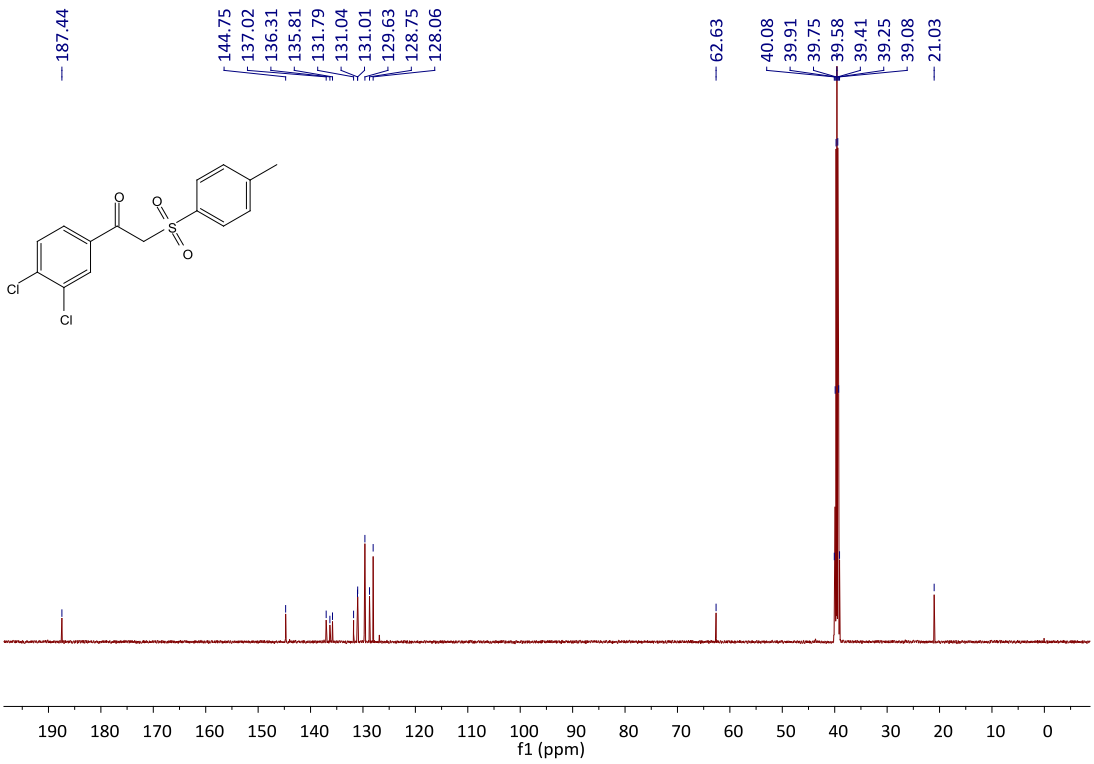

$^{1}$H NMR (500 Hz, $CDCl_3$): **3ua**



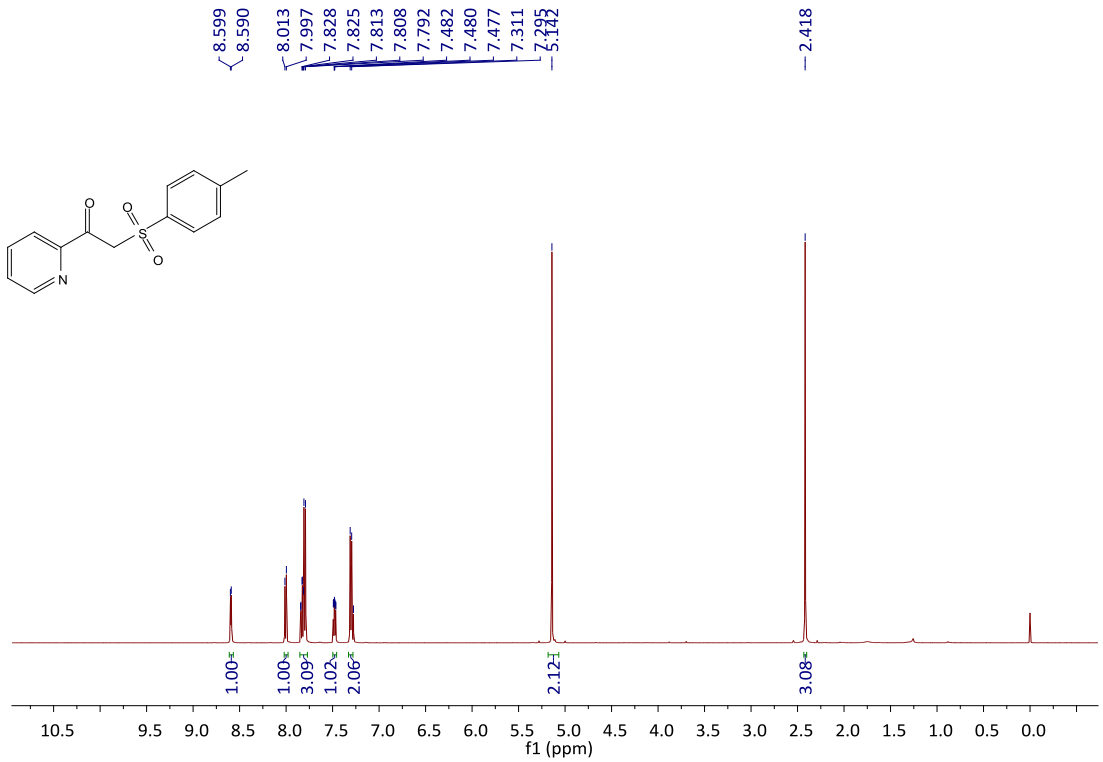

$^{13}$C NMR (125 Hz, $CDCl_3$): **3ua**



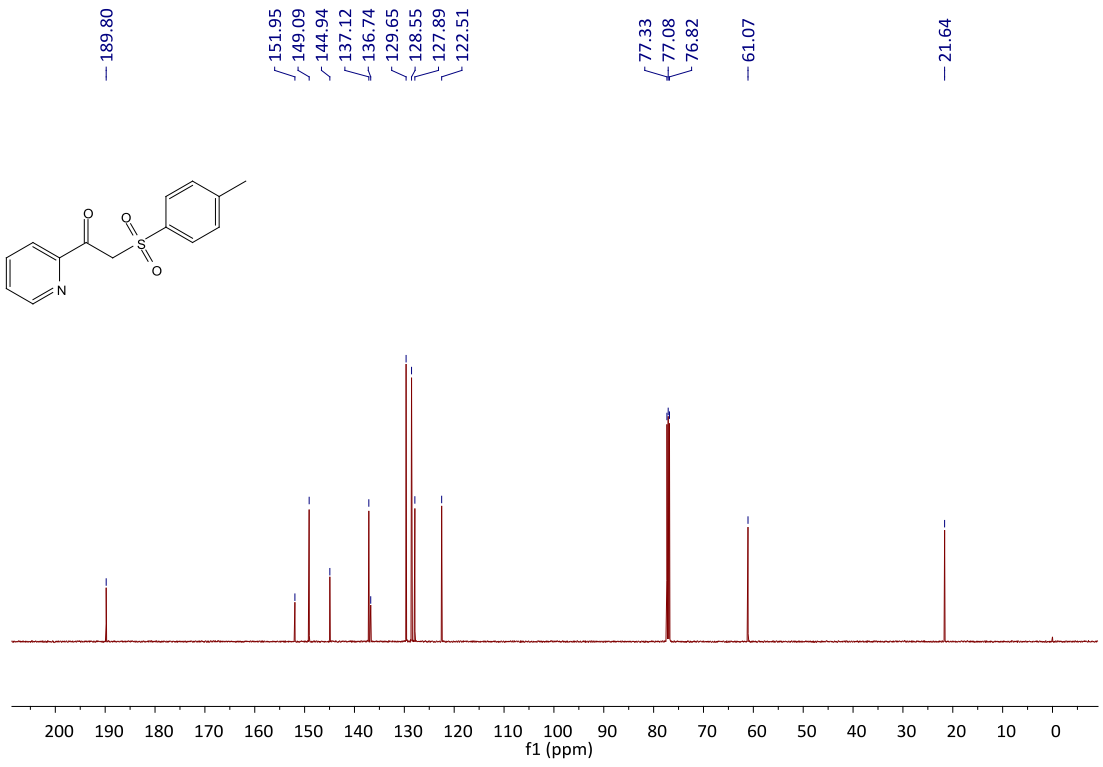

$^{1}$H NMR (500 Hz, DMSO): **3va**



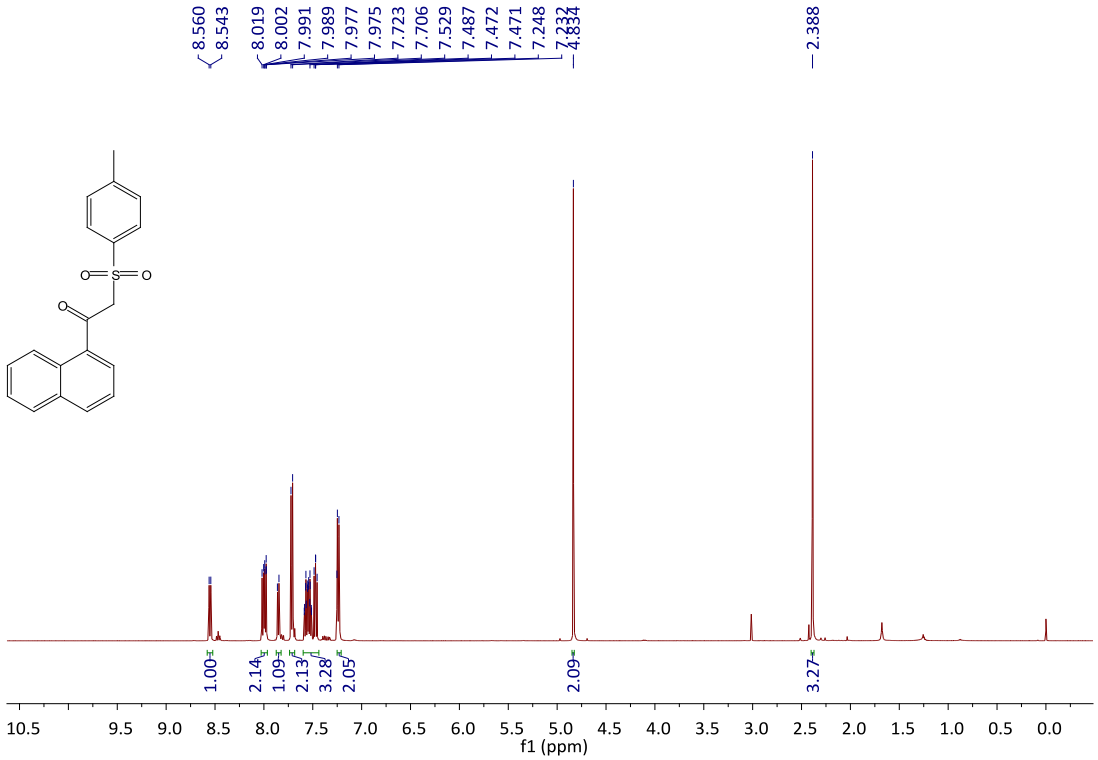

$^{13}$C NMR (125 Hz, DMSO): **3va**



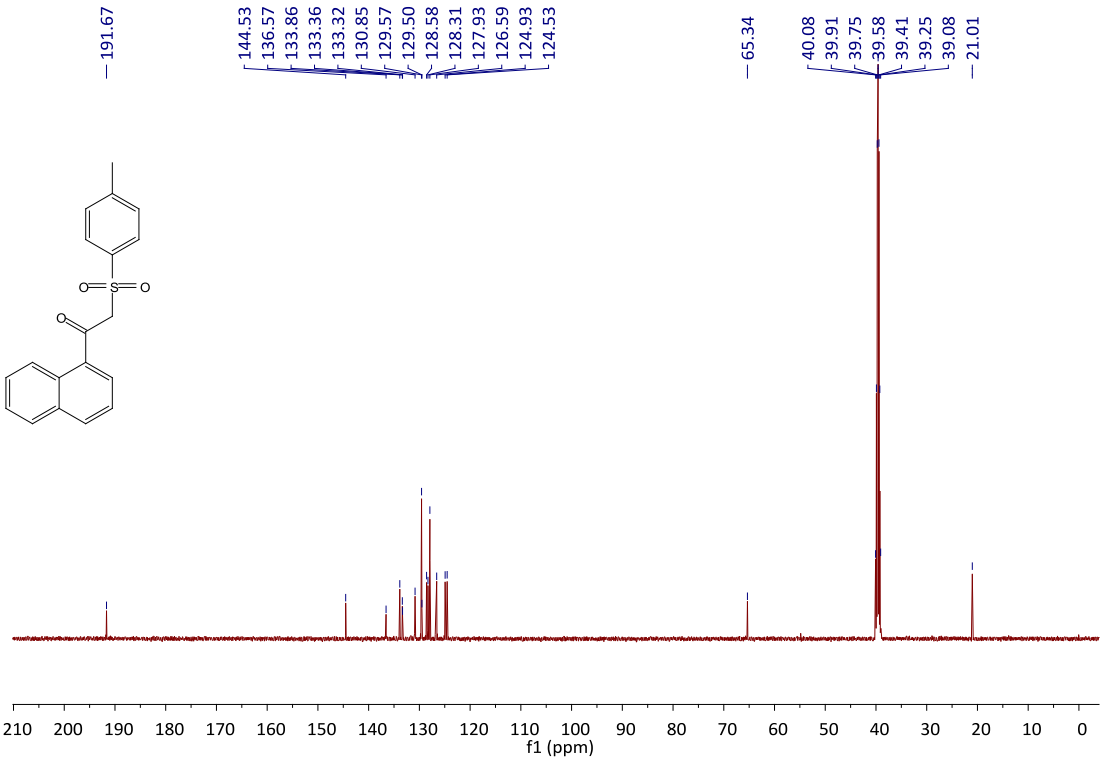

$^{1}$H NMR (500 Hz, $CDCl_3$): **3wa**



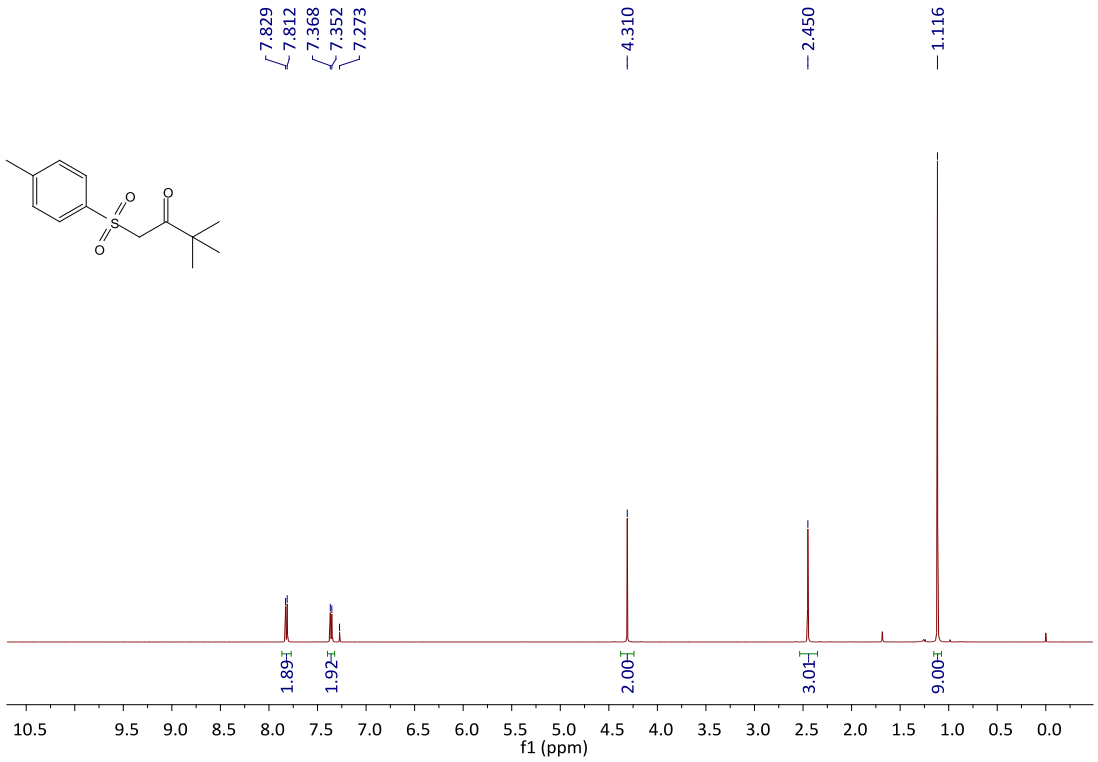

$^{13}$C NMR (125 Hz, $CDCl_3$): **3wa**



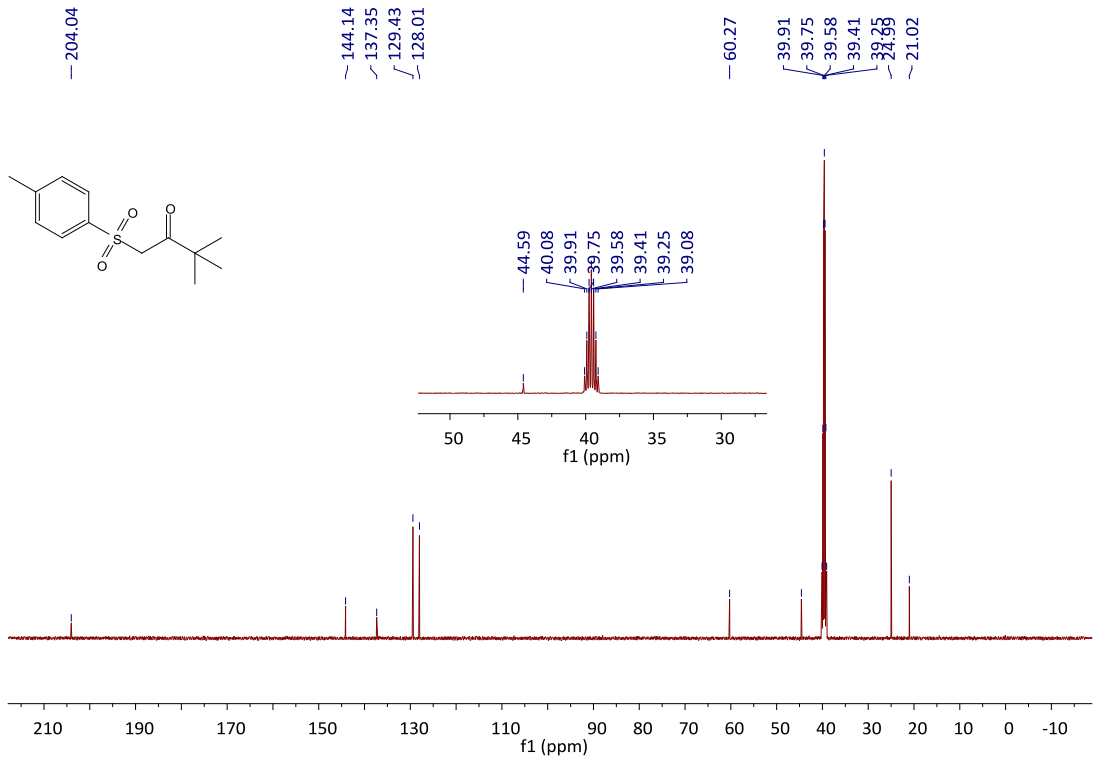

$^{1}$H (500 Hz, $CDCl_3$)NMR: **3xa**



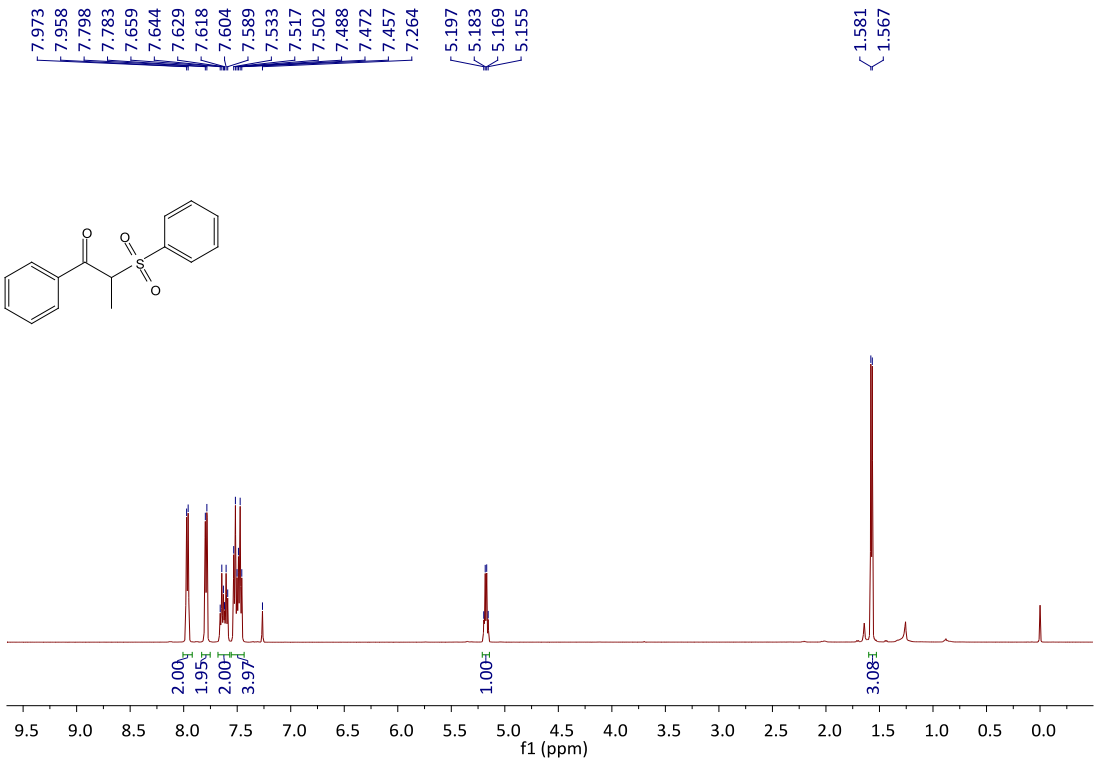

$^{13}$C NMR(125 Hz, DMSO): **3xa**



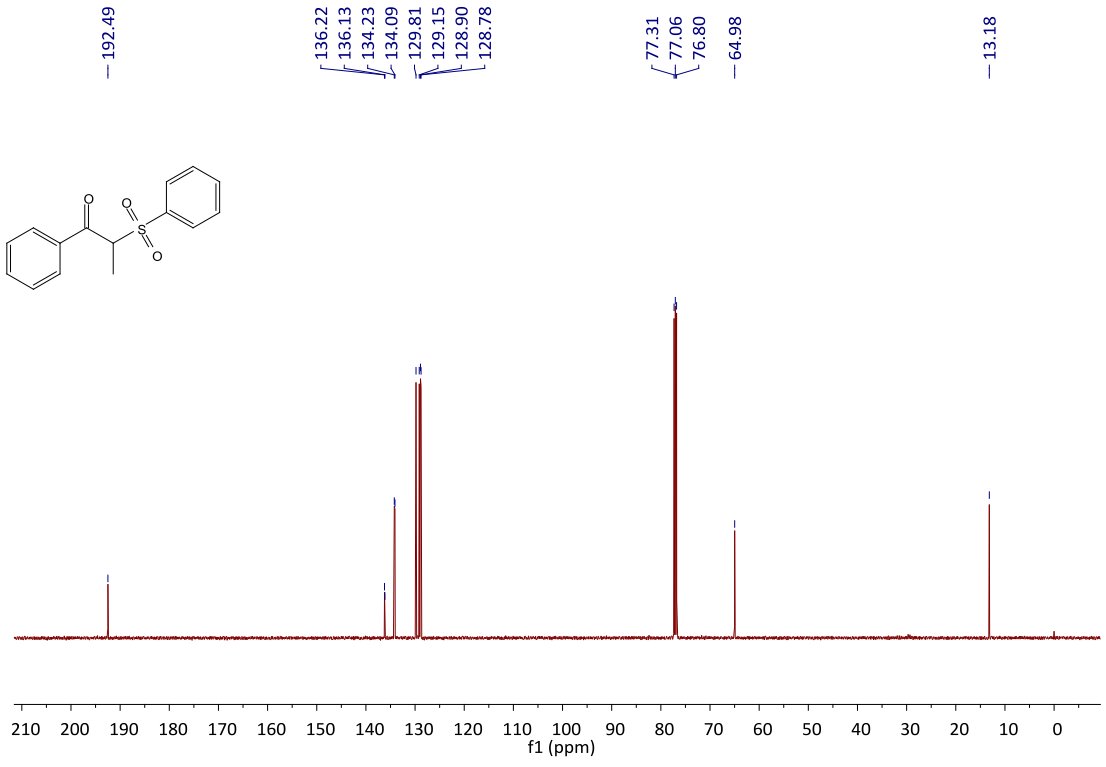

$^{1}$H NMR(500 Hz, $CDCl_3$): **3ya**



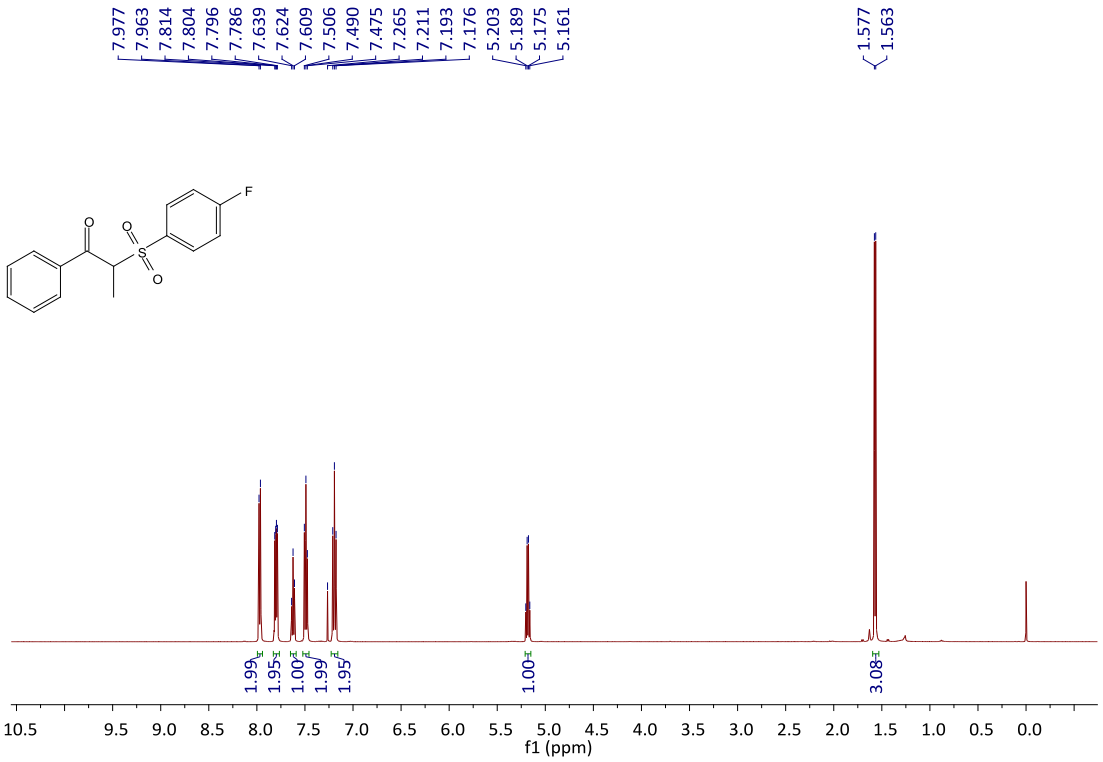

$^{13}$C NMR(125 Hz, DMSO): **3ya**



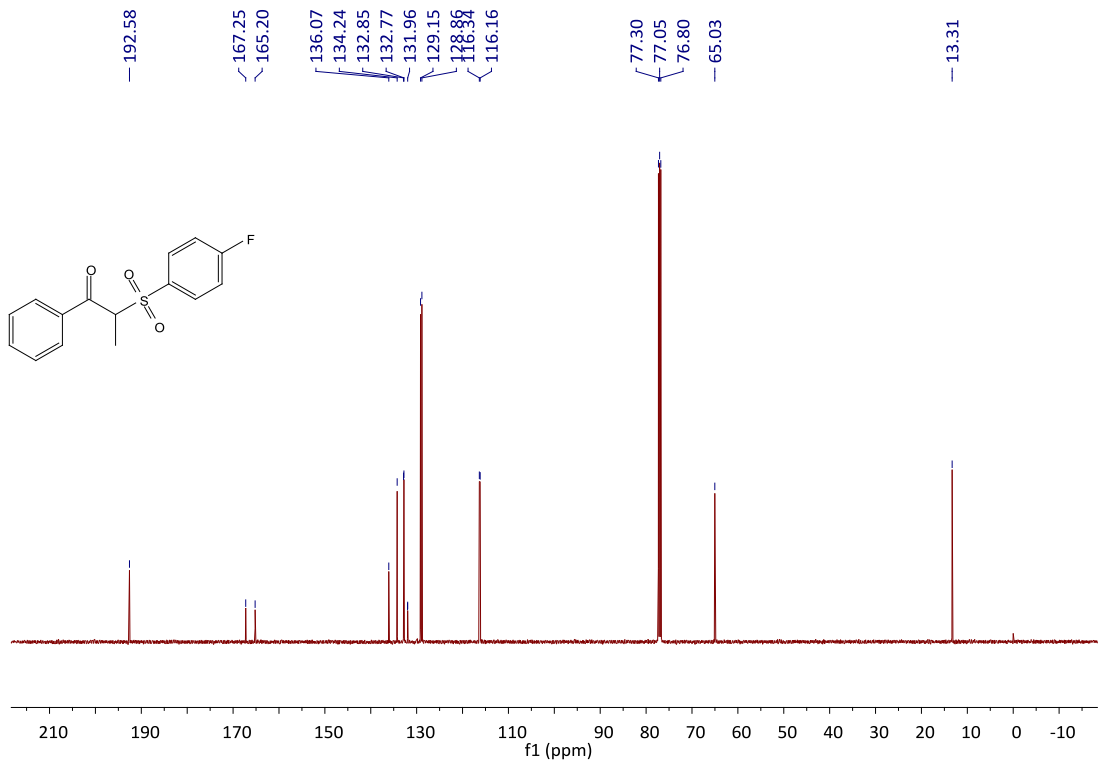

$^{1}$H NMR(500 Hz, $CDCl_3$): **3bb** (Entry 1, Table 3)



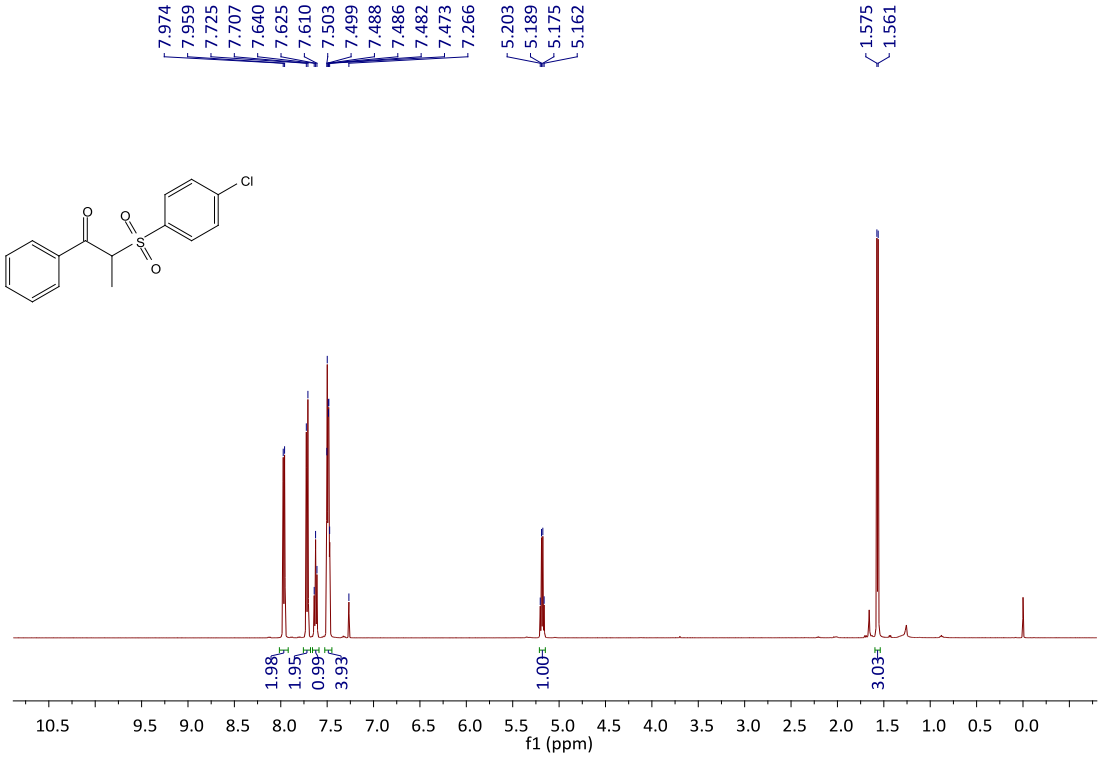

$^{13}$C NMR(125 Hz, $CDCl_3$): **3bb** (Entry 1, Table 3)



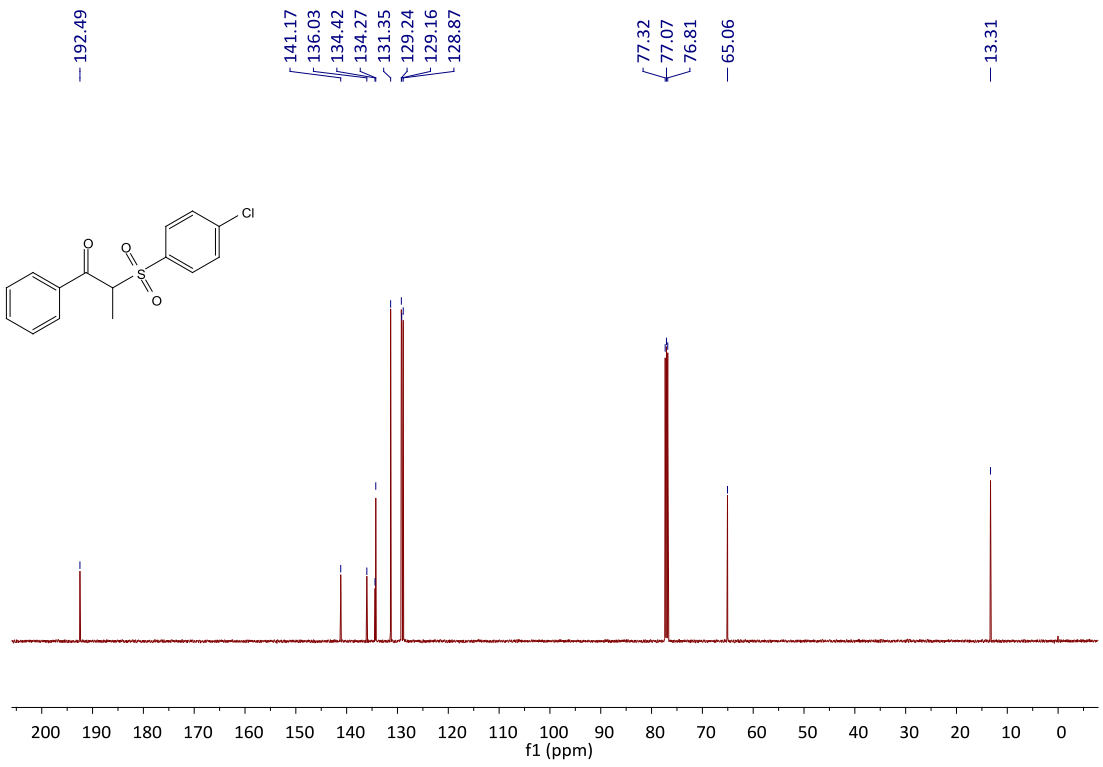

$^{1}$H NMR(500 Hz, $CDCl_3$): **3bc**



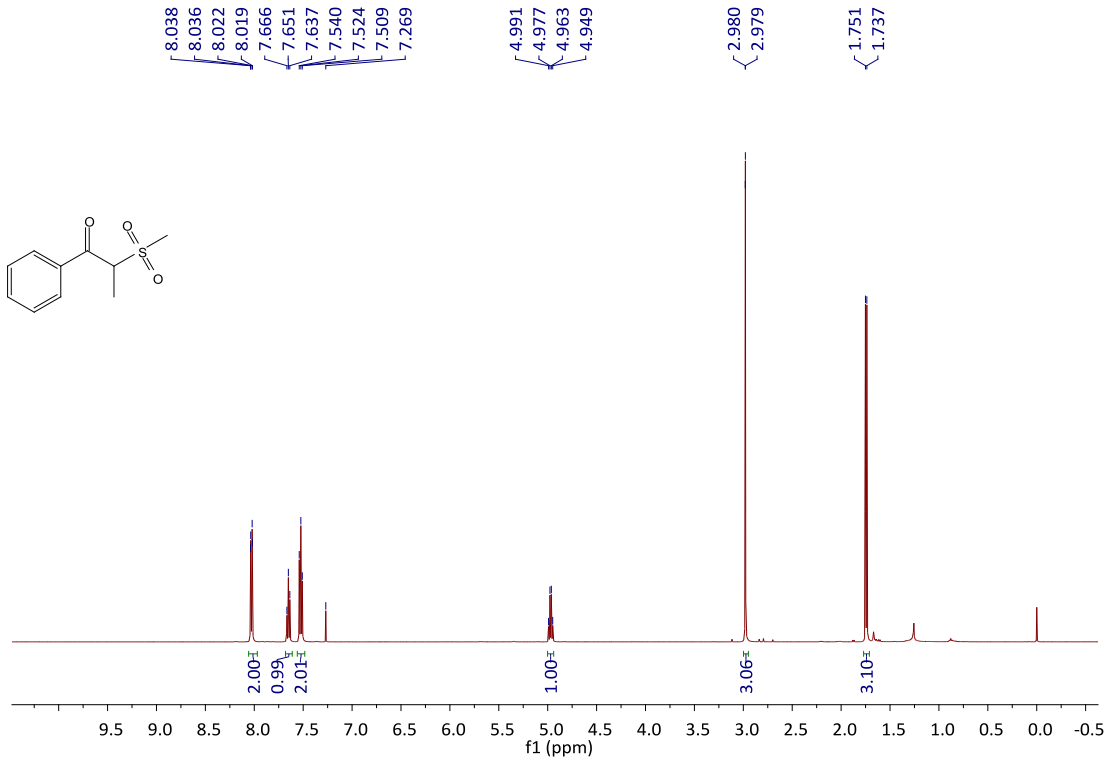

$^{13}$C NMR(125 Hz, $CDCl_3$): **3bc**



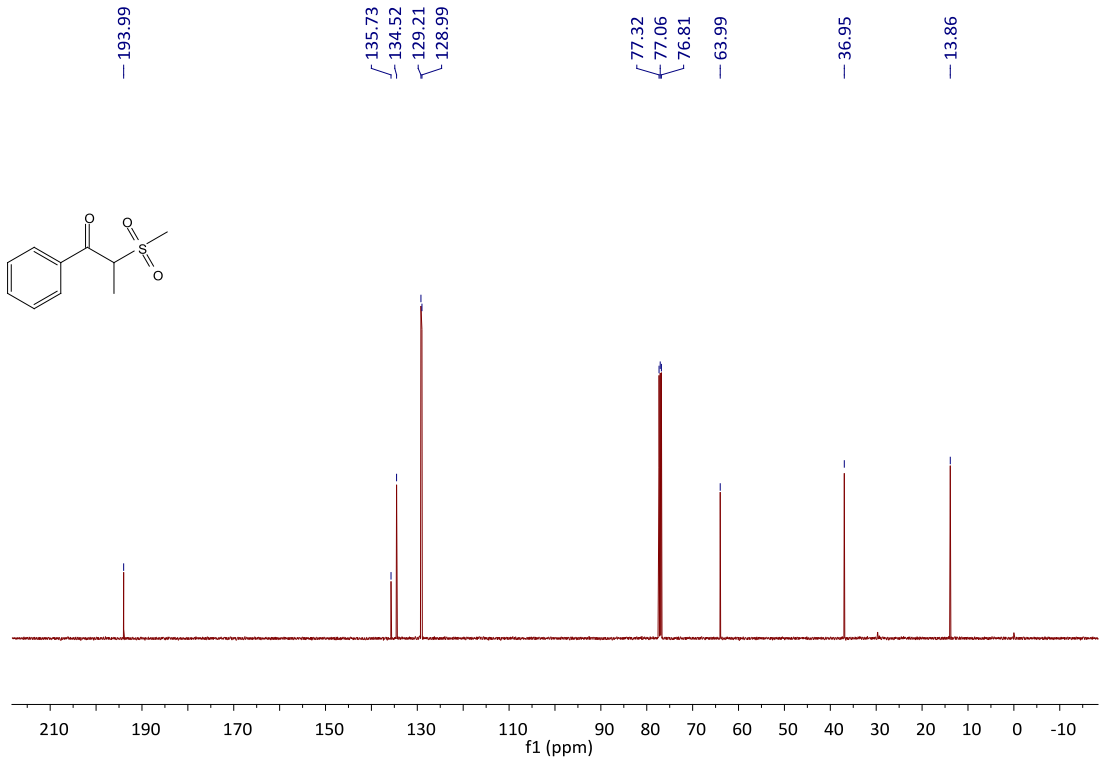

$^{1}$H NMR(500 Hz, $CDCl_3$): **3bd**



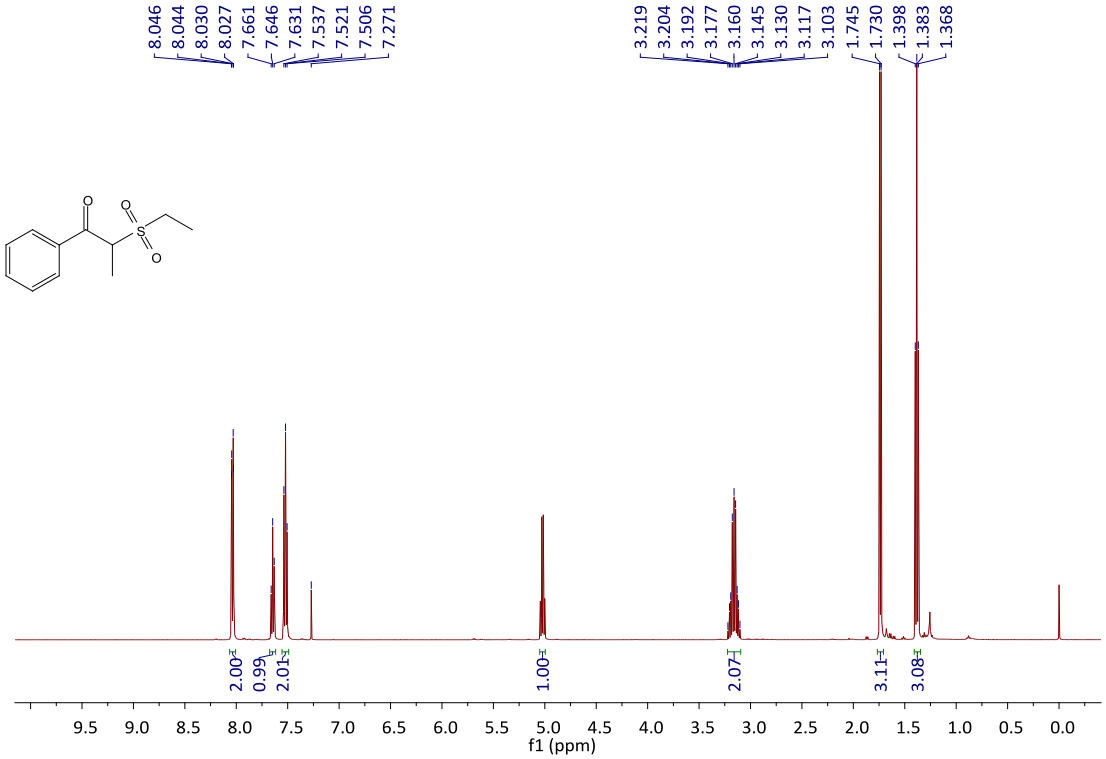

$^{13}$C NMR(125 Hz, $CDCl_3$): **3bd**



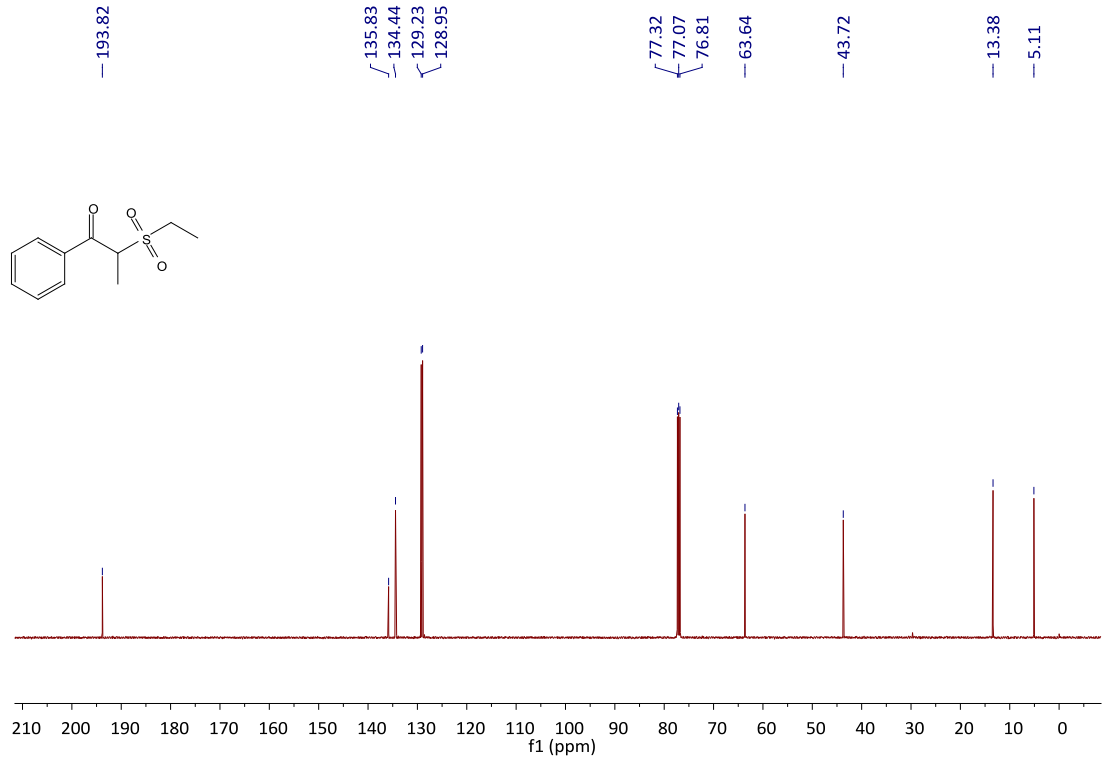

$^{1}$H NMR(500 Hz, $CDCl_3$): **3be**



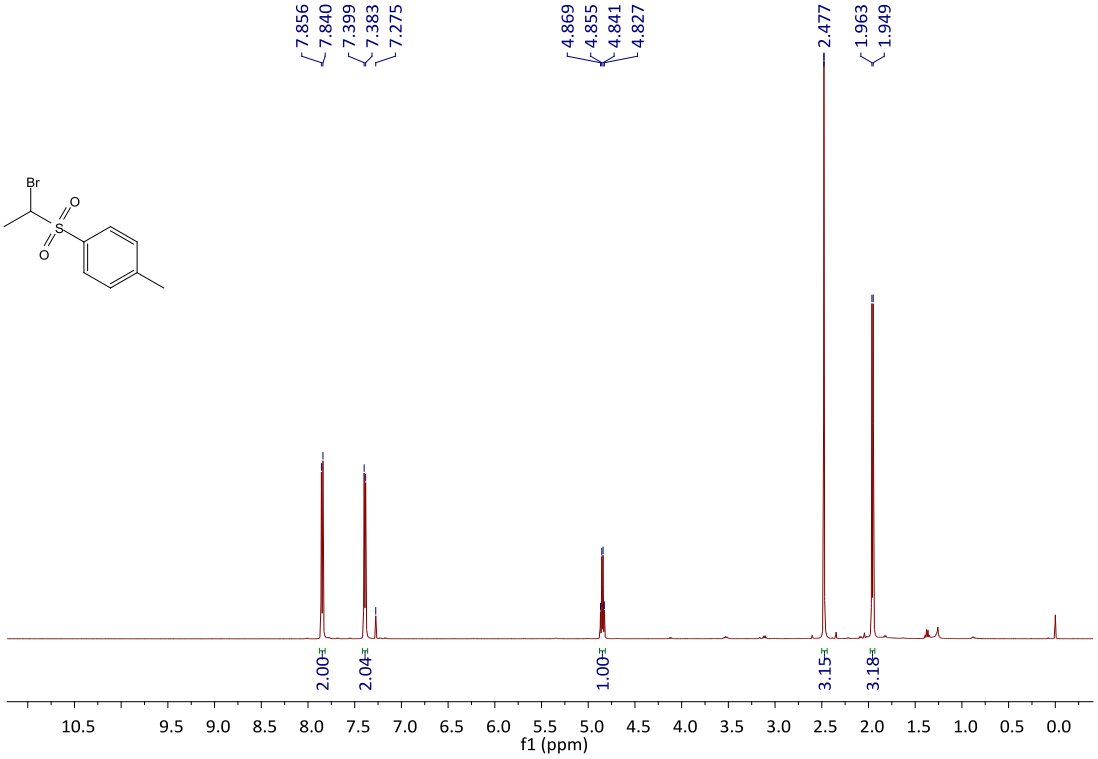

$^{13}$C NMR(125 Hz, $CDCl_3$): **3be**



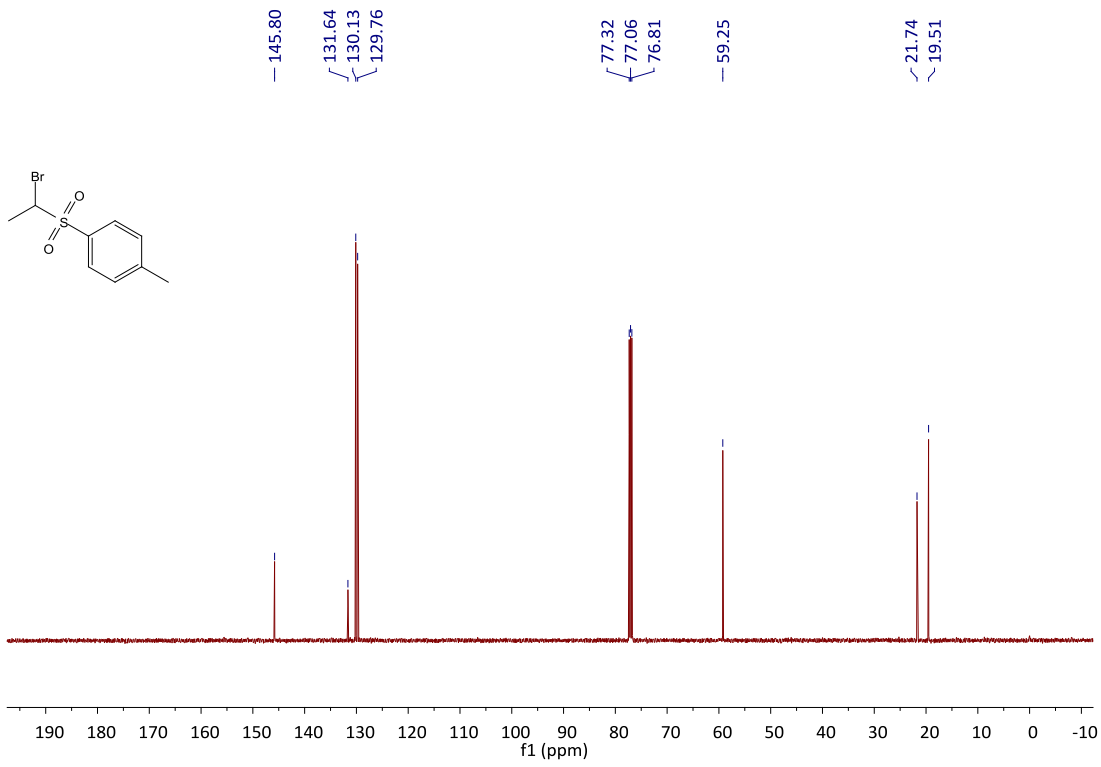

$^{1}$H NMR(500 Hz, $CDCl_3$): **3bf**



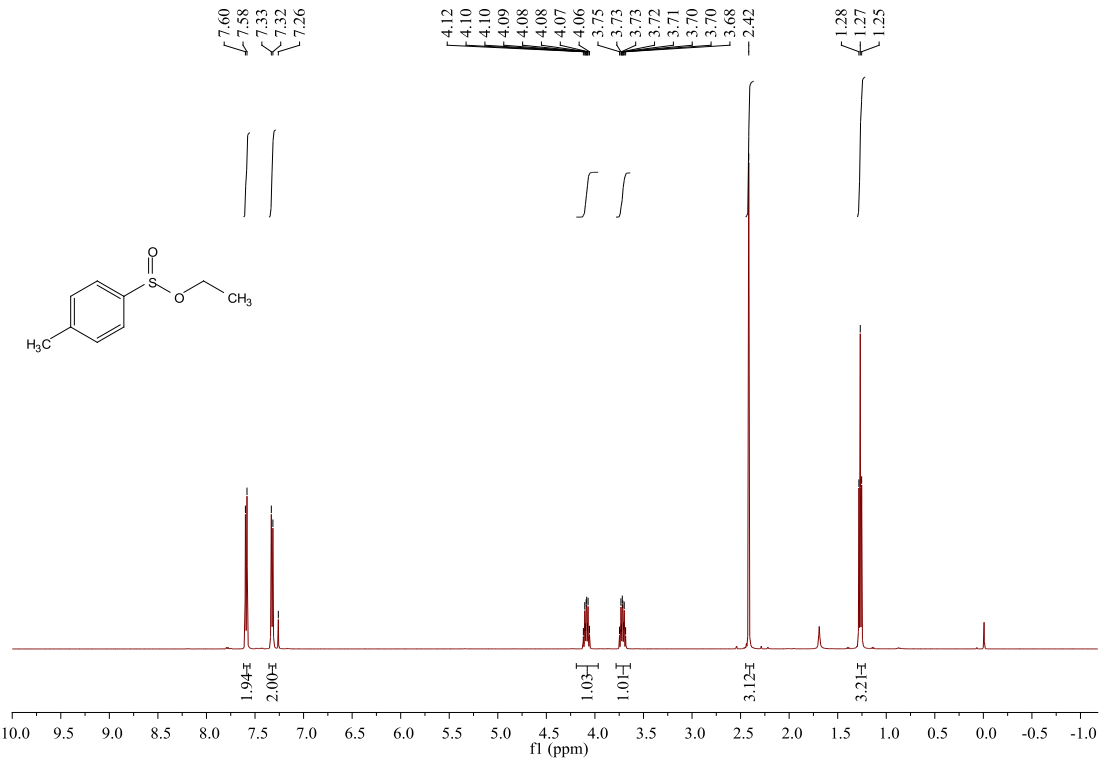
$^{13}$C NMR(125 Hz, $CDCl_3$): **3bf**



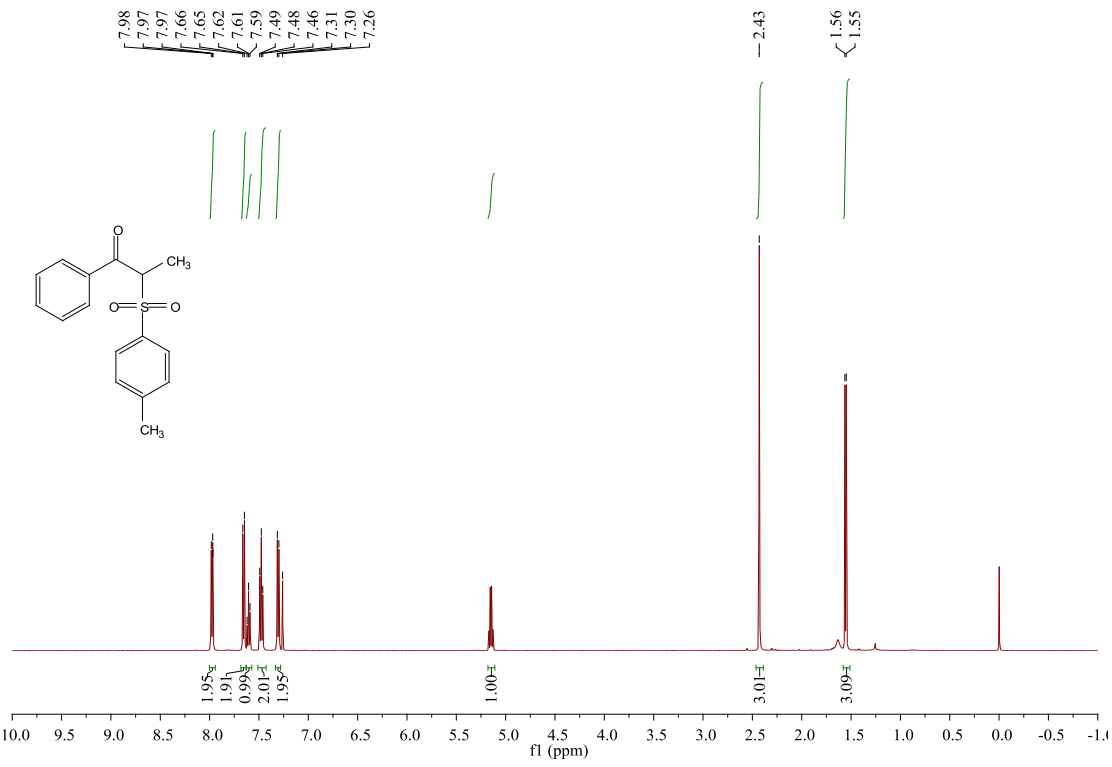

$^{1}$H NMR(500 Hz, $CDCl_3$): **5**



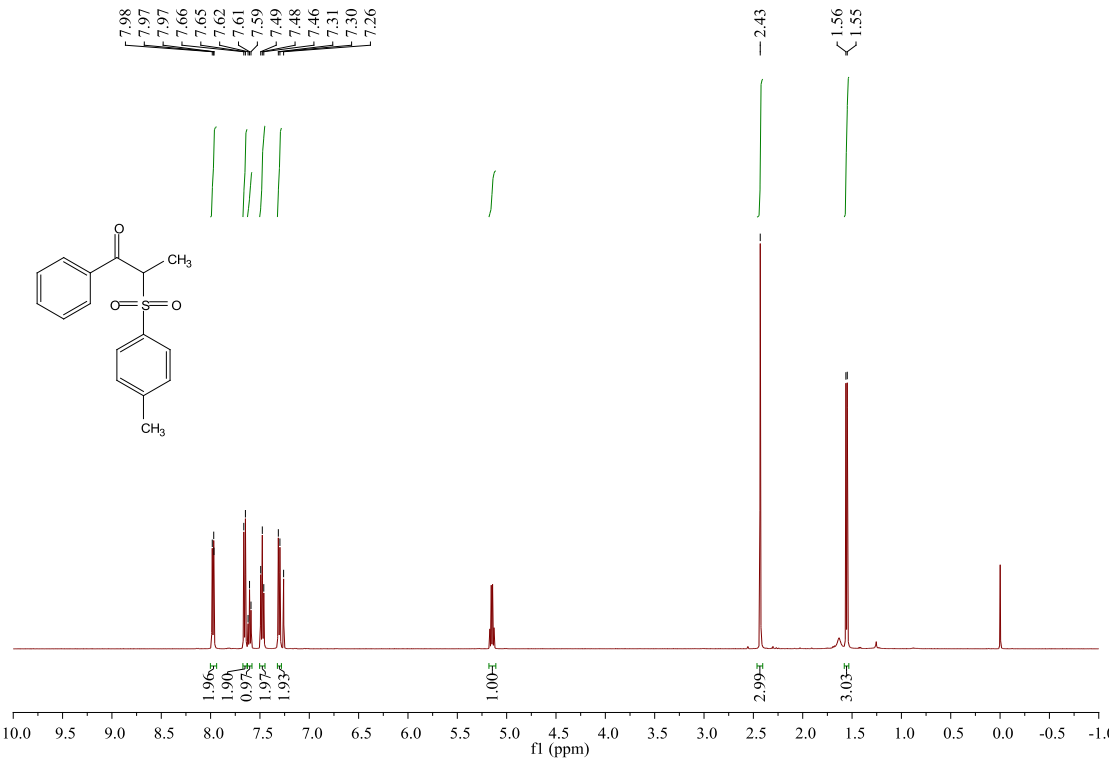

$^{13}$C NMR(125 Hz, $CDCl_3$): **5**



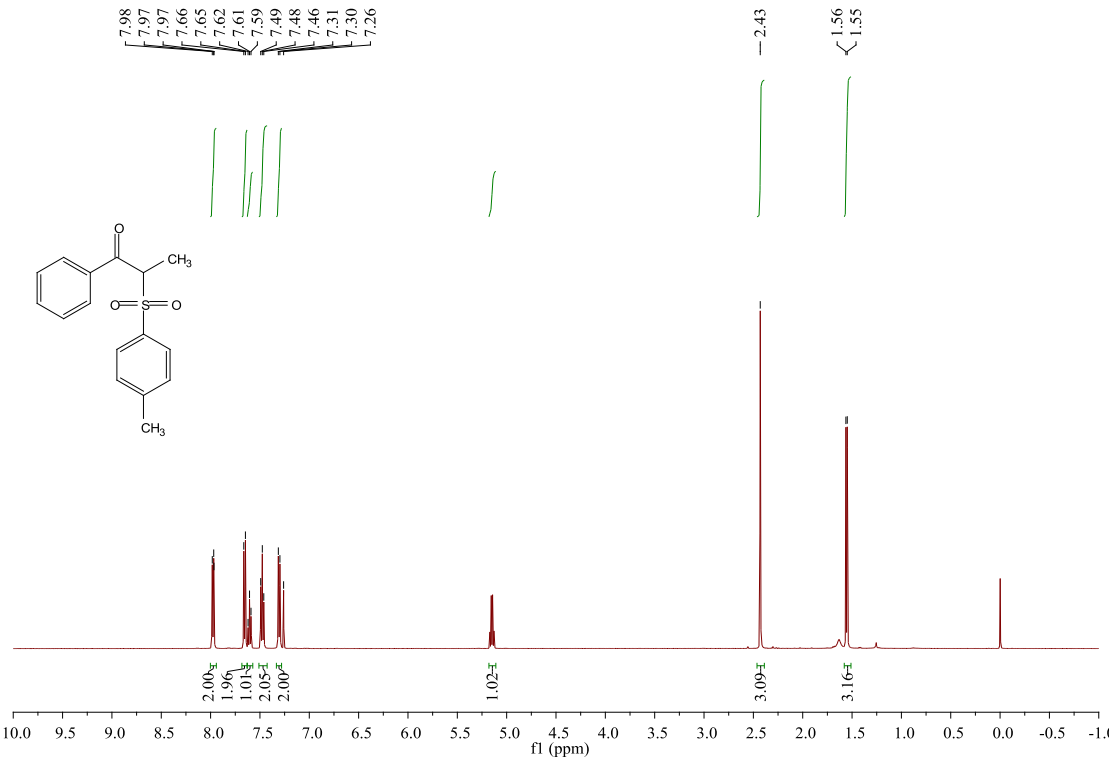

$^1$H NMR(500 Hz, $CDCl_3$): **6**



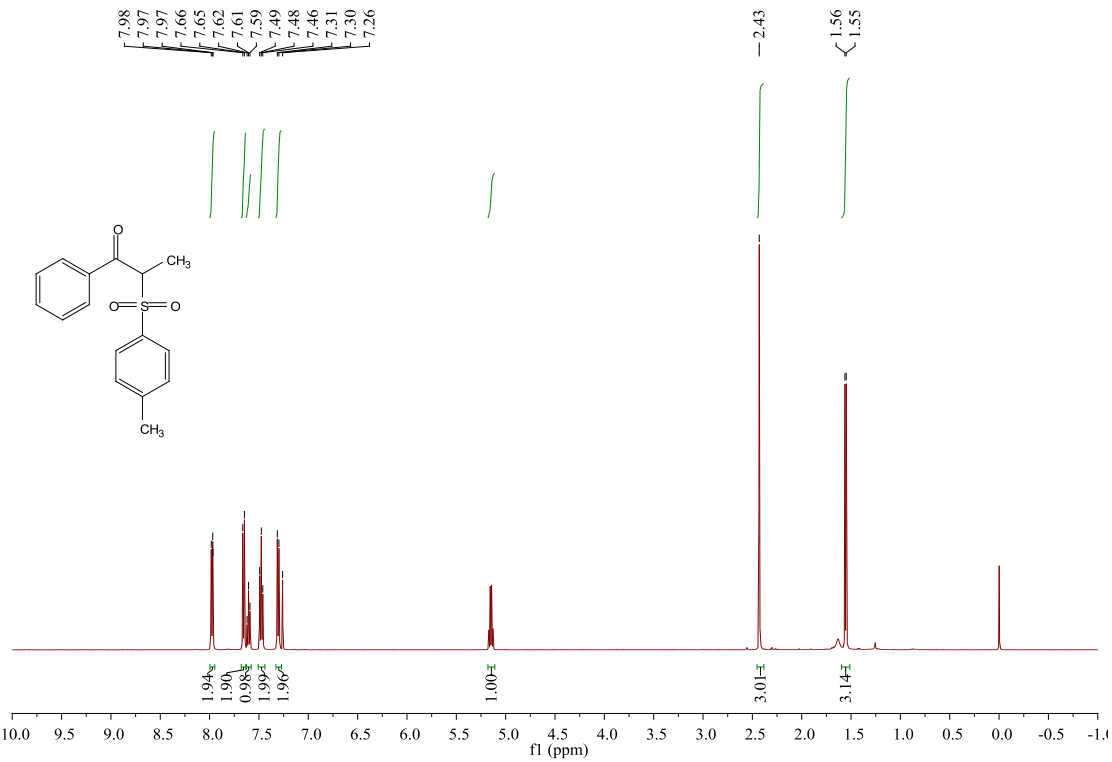

$^1$H NMR (500 Hz, $CDCl_3$): **3ba** (Table 3)



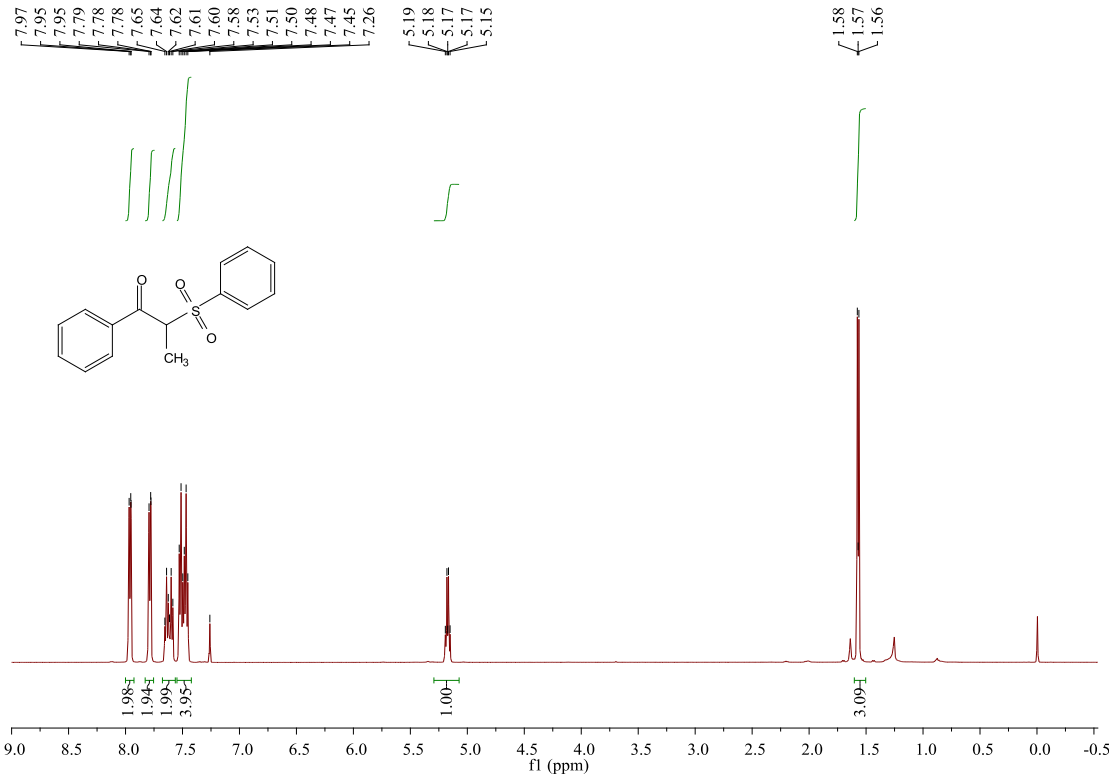

$^1$H NMR (500 Hz, $CDCl_3$): **3ba** (Scheme 3a)



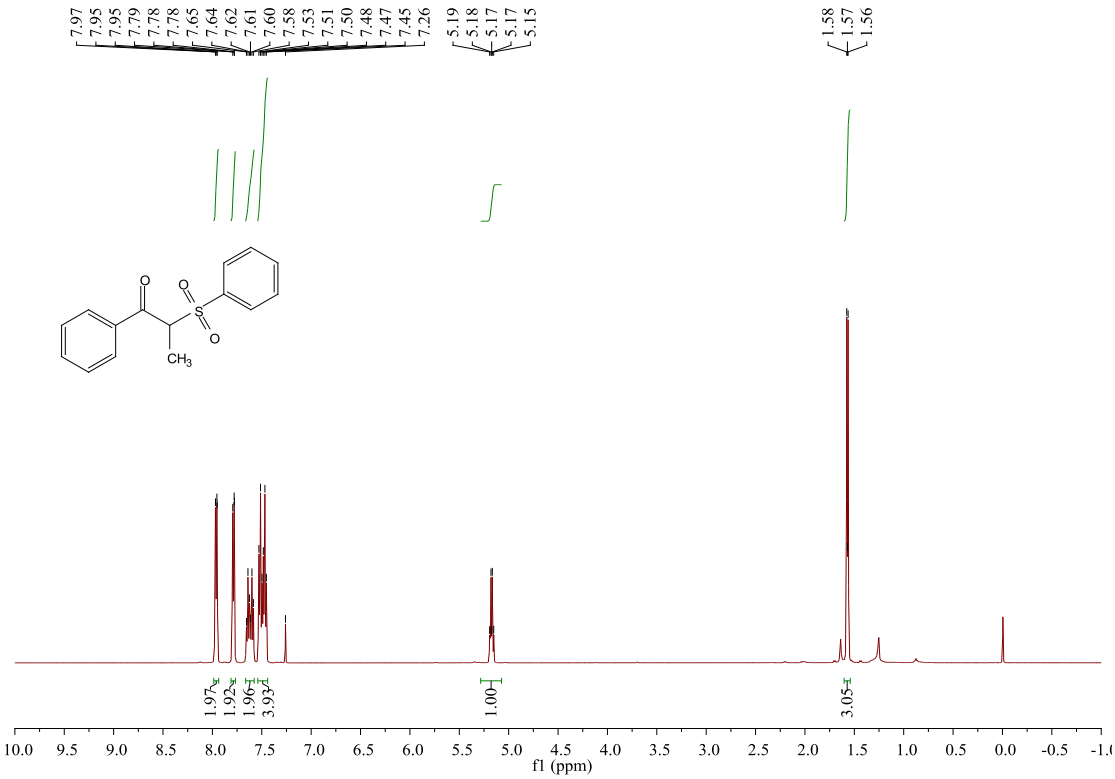

$^1$H NMR (500 Hz, $CDCl_3$): **3ba** (Scheme 3b)



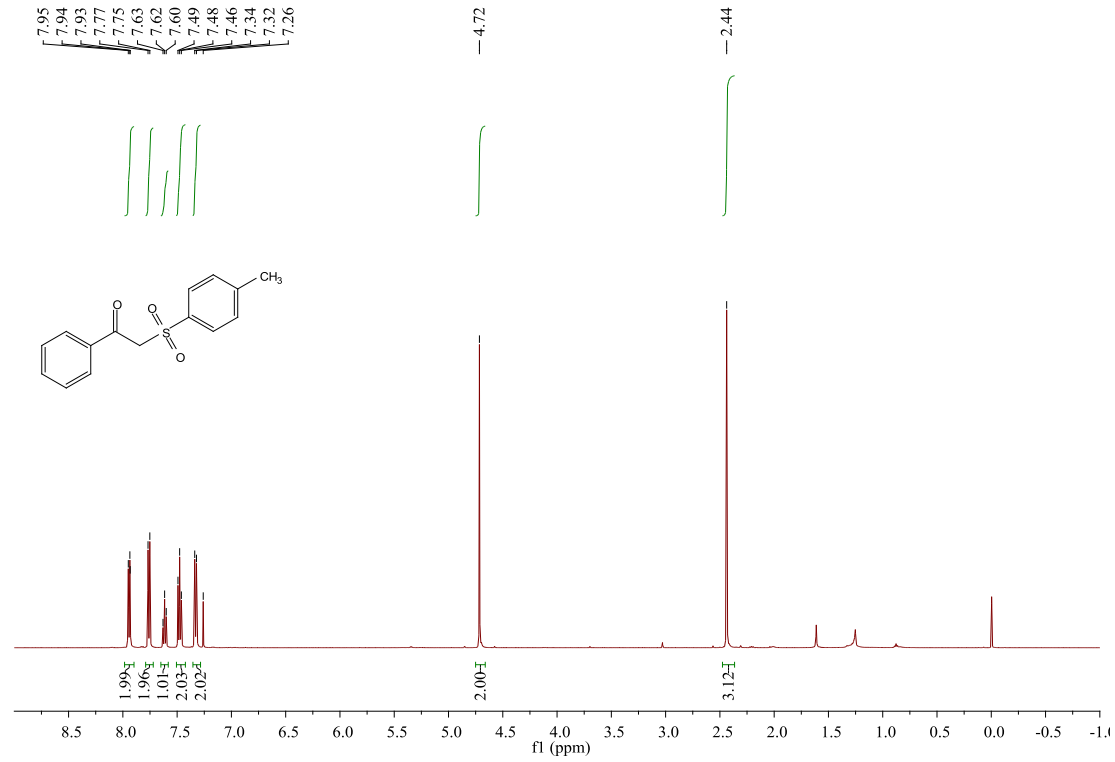

$^1$H NMR (500 Hz, $CDCl_3$): **3ba** (Scheme 3c)



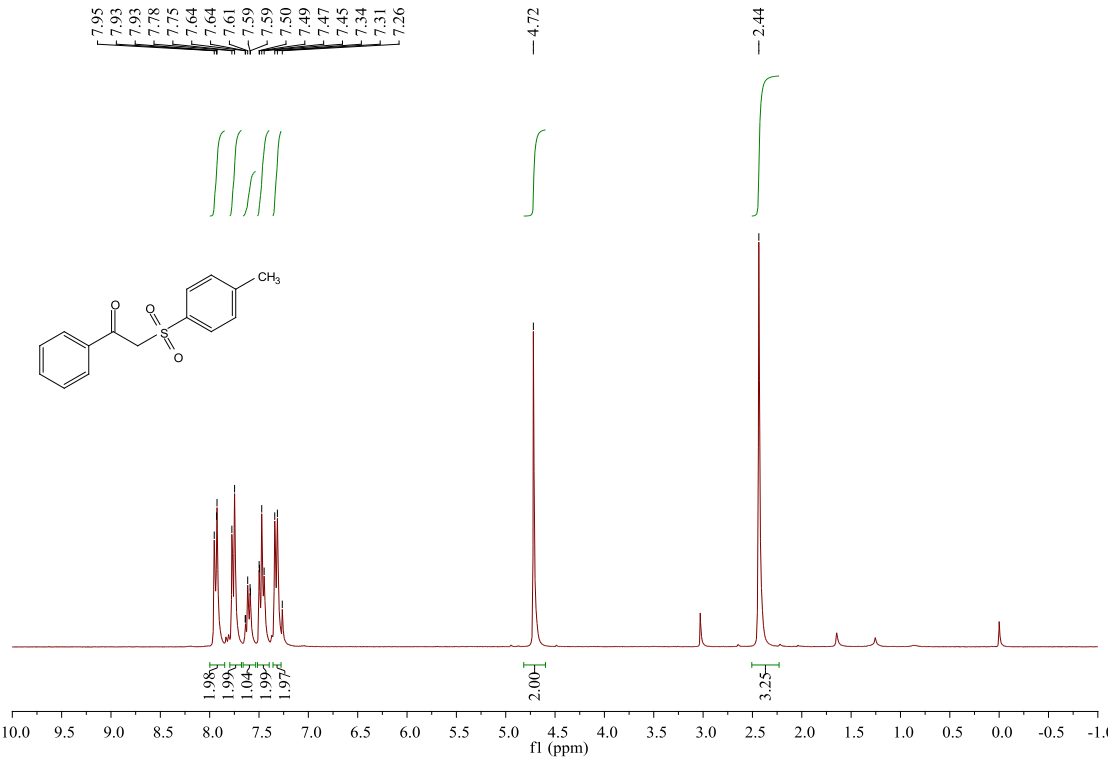

$^1$H NMR (500 Hz, $CDCl_3$): **3bb** (Entry 7, Table 3)




$^1$H NMR (500 Hz, $CDCl_3$): **3bb** (Entry 7, Table 3)




$^1$H NMR (500 Hz, $CDCl_3$): **3ka** (eq.1)




$^{1}$H NMR (500 Hz, $CDCl_3$): **3ka** (Scheme 3b)