

## Supporting Information

# Copper-catalyzed aminobromination/elimination process: an efficient access to $\alpha,\beta$ -unsaturated vicinal haloamino ketones and esters

Hao Sun,<sup>a</sup> Guangqian Zhang,<sup>a</sup> Sanjun Zhi,<sup>a</sup> Jianlin Han,<sup>\*a</sup> Guigen Li<sup>b</sup> and Yi Pan<sup>\*a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering; State of Key Laboratory of Coordination, Nanjing University, Nanjing, 210093, China. Fax: 86-25-83592846; Tel: 86-25-83593153; E-mail: hanjl@nju.edu.cn, yipan@nju.edu.cn

<sup>b</sup> Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409-1061, USA.

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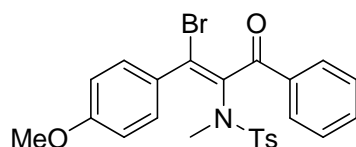
**1. General Information.** Solvents were dried and distilled prior to use. Melting points were uncorrected. IR spectra were collected on Bruker Vector 22 in KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR (TMS used as internal standard) spectra were collected in  $\text{CDCl}_3$  with a Bruker ARX 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 elemental analysis instrument. Mass spectrum was done by Finnigan TSQ7000 Electrospray Mass Spectrometer. Thin layer chromatography was carried out on Silica Gel 60 F-254 TLC plates. 20 cm  $\times$  20 cm Gel 60 F-254 TLC plates were used for Isolation.

**2. Typical procedure for the tandem reaction.** Into a dry vial was added olefin **1** (1 mmol),  $\text{CuCl}_2$  (6.6 mg, 0.05 equiv), 4 Å MS (500 mg, pre-dried in an oven at 200 °C overnight in vacuo), and freshly distilled  $\text{CH}_2\text{Cl}_2$  (3.0 mL) under a nitrogen atmosphere. A solution of  $\text{TsNMeBr}$  (473 mg, 1.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (3.0 mL) was added dropwise to the mixture. The mixture was stirred at 35 °C for 36 h in the capped vial. The reaction was quenched with saturated aqueous  $\text{Na}_2\text{SO}_3$  solution (2 mL). The organic phases were separated and the aqueous phase was extracted with  $\text{EtOAc}$  (3  $\times$  10 mL). The combined organic layers were washed with brine, dried with anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated and purified by TLC plate ( $\text{EtOAc}$ /petroleum ether, 1:4 v/v) to give the product **2**.

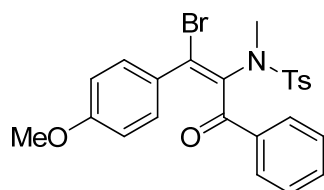
**3. Procedure for the tandem reaction with  $\text{TsNHMe}$ /NBS.** To a solution of **1a** (238mg, 1 mmol),  $\text{TsNHMe}$  (1.5 mmol, 278 mg),  $\text{CuCl}_2$  (6.6 mg, 0.05 equiv) and 4 Å MS (500 mg) in  $\text{CH}_2\text{Cl}_2$  (3 mL), NBS (2 mmol, 354 mg) dissolving in  $\text{CH}_2\text{Cl}_2$  (3 mL) was added dropwise to the above mixture. The resulting mixture was stirred at 35 °C for 36 h in the capped vial. The reaction was quenched with saturated aqueous  $\text{Na}_2\text{SO}_3$  solution (3 mL). The organic phases were separated and the aqueous phase was extracted with  $\text{EtOAc}$  (3  $\times$  10 mL). The combined organic layers were washed with brine, dried with anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated and purified by TLC plate ( $\text{EtOAc}$ /petroleum ether, 1:4 v/v) to give the product **2a**.

**4. The procedure for intermediate 5:** Into a dry vial was added **1g** (252 mg, 1 mmol), CuCl<sub>2</sub> (6.6 mg, 0.05 equiv), 4 Å MS (500 mg, pre-dried in an oven at 200 °C overnight in vacuo), freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) and stirred under a nitrogen atmosphere. A solution of TsNMeBr (473 mg, 1.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was added dropwise to the mixture. After the mixture was stirred at 35 °C for 1 h, it was directly transferred into column (EtOAc/petroleum ether, 1:9 v/v) to give the product **5**.

### 5. Spectral data for 2, 3, 4 and 5

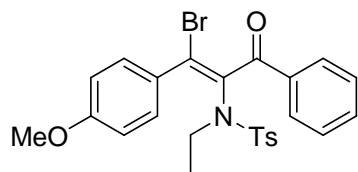


(*E*)-3-Bromo-3-(4-methoxyphenyl)-1-phenyl-2-(*N*-methyltosylamino)prop-2-en-1-one (**2aa**): white solid, mp 165-166 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.14 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.64-7.60 (m, 3H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.79 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 193.3, 160.9, 143.8, 136.3, 134.9, 133.5, 130.9, 130.2, 129.4, 129.1, 129.0, 128.6, 127.8, 113.8, 55.4, 38.1, 21.6. IR (KBr): *v* = 3004, 2976, 2935, 1651, 1600, 1505, 1344, 1257, 1181, 954, 814, 752, 681, 552 cm<sup>-1</sup>. ESIMS calcd. for C<sub>24</sub>H<sub>22</sub>BrNNaO<sub>4</sub>S (M+Na<sup>+</sup>): 522.04; found: 522.17. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>BrNO<sub>4</sub>S: C, 57.60; H, 4.43; N, 2.80; found: C, 57.67; H, 4.41; N, 2.68.

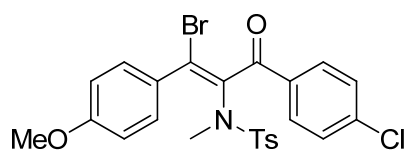


(*Z*)-3-Bromo-3-(4-methoxyphenyl)-1-phenyl-2-(*N*-methyltosylamino)prop-2-en-1-one (**2ab**): white solid, mp 142-144 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.70 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.64 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.32-7.28 (m, 1H), 7.24-7.14 (m, 6H), 6.55 (d, *J* = 6.94 Hz, 2H), 3.66 (s, 3H), 3.35 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>)  $\delta$ : 187.5, 161.0, 143.6, 136.6, 135.9, 134.6, 132.7, 131.6, 129.9, 129.6, 129.4, 127.9, 127.8, 113.6, 55.3, 37.6, 21.6. IR (KBr):  $\nu$  = 3065, 2933, 1653, 1600, 1500, 1334, 1252, 1171, 1066, 950, 731, 672, 551 cm<sup>-1</sup>; ESIMS calcd. for C<sub>24</sub>H<sub>22</sub>BrNNaO<sub>4</sub>S (M+Na<sup>+</sup>): 522.04; found: 522.17. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>BrNO<sub>4</sub>S: C, 57.60; H, 4.43; N, 2.80; found: C, 57.50; H, 4.37; N, 2.92.

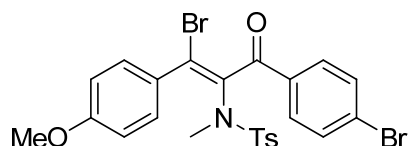


(*E*)-3-Bromo-3-(4-methoxyphenyl)-1-phenyl-2-(*N*-ethyltosylamino)prop-2-en-1-one (**2b**) white solid, mp 149-151 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.21 (d,  $J$  = 6.9 Hz, 2H), 7.70 (d,  $J$  = 9.0 Hz, 2H), 7.61 (t,  $J$  = 7.2 Hz, 1H), 7.54-7.46 (m, 4H), 7.16 (d,  $J$  = 8.4 Hz, 2H), 6.95 (d,  $J$  = 9.0 Hz, 2H), 3.87 (s, 3H), 3.02 (q,  $J$  = 7.2 Hz, 2H), 2.37 (s, 3H), 0.88 (t,  $J$  = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 193.5, 161.1, 143.8, 136.7, 135.6, 133.3, 131.2, 130.4, 130.3, 129.6, 129.4, 129.2, 128.5, 127.9, 113.8, 55.4, 44.2, 21.6, 13.1. IR (KBr):  $\nu$  = 2978, 2933, 1664, 1599, 1502, 1335, 1254, 1174, 1024, 811, 742, 678, 552 cm<sup>-1</sup>. ESIMS calcd. for C<sub>25</sub>H<sub>24</sub>BrNNaO<sub>4</sub>S (M+Na<sup>+</sup>): 536.05; found: 536.08. Anal. Calcd for C<sub>25</sub>H<sub>24</sub>BrNO<sub>4</sub>S: C, 58.37; H, 4.70; N, 2.72; found: C, 58.35; H, 4.63; N, 2.71.

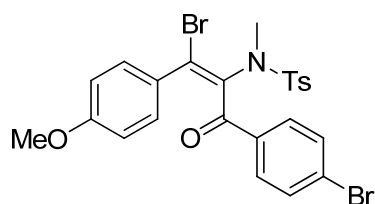


(*E*)-3-Bromo-1-(4-chlorophenyl)-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2c**) white solid, mp 205-206 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (dd,  $J$  = 6.7, 2.0 Hz, 2H), 7.61 (dd,  $J$  = 6.8, 2.2 Hz, 2H), 7.49 (dd,  $J$  = 6.6, 1.8 Hz, 2H), 7.41 (d,  $J$  = 8.4 Hz, 2H), 7.18 (d,  $J$  = 8.4 Hz, 2H), 6.94 (dd,  $J$  = 6.6, 2.1 Hz, 2H), 3.87 (s, 3H), 2.76 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 192.2, 161.1, 144.0, 140.0, 134.8, 134.8, 133.4, 131.6, 130.9, 129.5, 129.1, 129.0, 128.8, 127.8, 113.9,

55.4, 38.0, 21.6. IR (KBr):  $\nu = 3101, 2930, 1654, 1600, 1505, 1344, 1255, 1163, 1088, 901, 813, 657, 552 \text{ cm}^{-1}$ . ESIMS calcd. for  $\text{C}_{24}\text{H}_{21}\text{BrClINaO}_4\text{S}$  ( $\text{M}+\text{Na}^+$ ): 556.00; found: 556.08. Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{BrClINO}_4\text{S}$ : C, 53.89; H, 3.96; N, 2.62; found: C, 53.78; H, 3.97; N, 2.54.

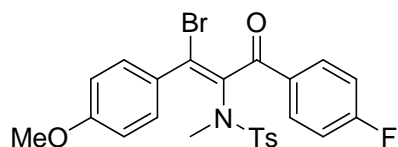


(*E*)-3-Bromo-1-(4-bromophenyl)-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2da**) white solid, mp 208-210 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (dd,  $J = 6.8, 1.7 \text{ Hz}$ , 2H), 7.66 (dd,  $J = 6.9, 1.8 \text{ Hz}$ , 2H), 7.61 (dd,  $J = 6.6, 2.1 \text{ Hz}$ , 2H), 7.42 (d,  $J = 8.4 \text{ Hz}$ , 2H), 7.18 (d,  $J = 8.4 \text{ Hz}$ , 2H), 6.94 (dd,  $J = 6.7, 2.0 \text{ Hz}$ , 2H), 3.87 (s, 3H), 2.76 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 192.4, 161.1, 144.0, 135.3, 134.7, 133.3, 132.0, 131.7, 130.9, 129.5, 129.1, 128.8, 128.7, 127.7, 113.9, 55.5, 38.0, 21.6. IR (KBr):  $\nu = 3098, 2931, 1655, 1601, 1504, 1343, 1254, 1175, 1071, 951, 814, 757, 552 \text{ cm}^{-1}$ . ESIMS calcd. for  $\text{C}_{24}\text{H}_{21}\text{Br}_2\text{NNaO}_4\text{S}$  ( $\text{M}+\text{Na}^+$ ): 599.95; found: 599.92. Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{Br}_2\text{NO}_4\text{S}$ : C, 49.76; H, 3.65; N, 2.42; found: C, 49.79; H, 3.67; N, 2.41.

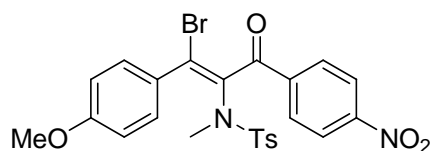


(*Z*)-3-Bromo-1-(4-bromophenyl)-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2db**) white solid, mp 179-181 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.64-7.55 (m, 4H), 7.32 (dd,  $J = 6.5, 1.6 \text{ Hz}$ , 2H), 7.24 (d,  $J = 8.4 \text{ Hz}$ , 2H), 7.14 (dd,  $J = 6.9, 2.1 \text{ Hz}$ , 2H), 6.59 (dd,  $J = 6.6, 2.1 \text{ Hz}$ , 2H), 3.70 (s, 3H), 3.34 (s, 3H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.0, 161.3, 143.8, 136.6, 135.8, 135.8, 135.4, 131.6, 131.3, 131.1, 129.6, 129.5, 129.5, 127.8, 113.8, 55.4, 37.7, 21.6. IR (KBr):  $\nu = 2932, 1658, 1596, 1503, 1340, 1251, 1158, 1072, 954, 813, 756, 695, 548 \text{ cm}^{-1}$ . ESIMS calcd. for  $\text{C}_{24}\text{H}_{21}\text{Br}_2\text{NNaO}_4\text{S}$  ( $\text{M}+\text{Na}^+$ ): 599.95; found: 599.92. Anal. Calcd

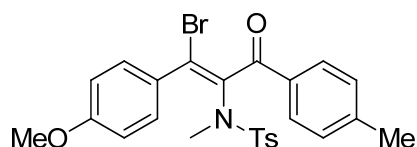
for C<sub>24</sub>H<sub>21</sub>Br<sub>2</sub>NO<sub>4</sub>S: C, 49.76; H, 3.65; N, 2.42; found: C, 49.46; H, 3.64; N, 2.78.



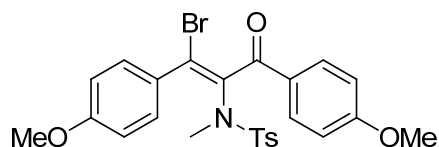
(*E*)-3-Bromo-1-(4-Fluorophenyl)-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2e**) white solid, mp 162-163 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.20-8.15 (m, 2H), 7.62 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.22-7.15 (m, 4H), 6.94 (dd, *J* = 6.6, 2.1 Hz, 2H), 3.87 (s, 3H), 2.78 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 191.8, 167.8, 164.4, 161.0, 144.0, 134.9, 133.5, 133.0, 132.9, 132.8, 132.7, 130.9, 129.5, 129.0, 128.8, 127.7, 116.0, 115.7, 113.9, 55.4, 38.1, 21.6. IR (KBr): *v* = 3006, 2973, 2933, 1654, 1598, 1503, 1346, 1256, 1154, 954, 836, 747, 660, 554 cm<sup>-1</sup>. ESIMS calcd. for C<sub>24</sub>H<sub>21</sub>BrFNO<sub>4</sub>S (M+Na<sup>+</sup>): 540.03; found: 540.08. Anal. Calcd for C<sub>24</sub>H<sub>21</sub>BrFNO<sub>4</sub>S: C, 55.61; H, 4.08; N, 2.70; found: C, 55.64; H, 4.04; N, 2.64.



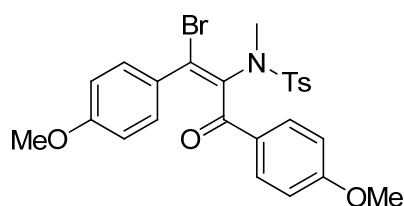
(*E*)-3-Bromo-3-(4-methoxyphenyl)-1-(4-nitrophenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2f**) white solid, mp 164-165 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.38-8.28 (m, 4H), 7.58 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.93 (dd, *J* = 7.2, 2.1 Hz, 2H), 3.87 (s, 3H), 2.71 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 192.1, 161.3, 150.2, 144.3, 141.5, 134.3, 133.1, 130.9, 130.8, 129.6, 129.3, 128.3, 127.8, 123.8, 114.0, 55.4, 37.7, 21.6. IR (KBr): *v* = 3112, 2934, 1660, 1600, 1528, 1344, 1257, 1156, 954, 813, 705, 553 cm<sup>-1</sup>. ESIMS calcd. for C<sub>24</sub>H<sub>21</sub>BrN<sub>2</sub>NaO<sub>6</sub>S (M+Na<sup>+</sup>): 567.02; found: 567.08. Anal. Calcd for C<sub>24</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>6</sub>S: C, 52.85; H, 3.88; N, 5.14; found: C, 52.73; H, 3.78; N, 5.12.



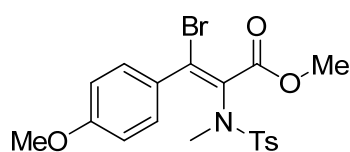
(*E*)-3-Bromo-3-(4-methoxyphenyl)-1-(4-methylphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2g**) white solid, mp 161-162 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.05 (d, *J* = 8.1 Hz, 2H), 7.63 (dd, *J* = 6.9, 2.4 Hz, 2H), 7.39 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.94 (dd, *J* = 6.5, 2.2 Hz, 2H), 3.87 (s, 3H), 2.79 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 192.7, 160.8, 144.6, 143.7, 134.8, 133.7, 130.8, 130.3, 129.4, 129.3, 129.0, 128.7, 127.7, 113.8, 55.4, 38.1, 21.9, 21.5. IR (KBr): *v* = 3000, 2971, 2932, 1649, 1601, 1505, 1343, 1255, 1180, 951, 833, 747, 660, 552 cm<sup>-1</sup>. ESIMS calcd. for C<sub>25</sub>H<sub>24</sub>BrNNaO<sub>4</sub>S (M+Na<sup>+</sup>): 536.05; found: 536.08. Anal. Calcd for C<sub>25</sub>H<sub>24</sub>BrNO<sub>4</sub>S: C, 58.37; H, 4.70; N, 2.72; found: C, 58.37; H, 4.69; N, 2.61.



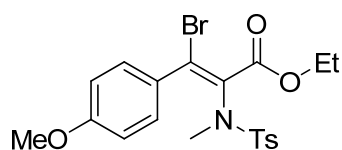
(*E*)-3-Bromo-3-(4-methoxyphenyl)-1-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2ha**) white solid, mp 132-133 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.13 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.65 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.02-6.93 (m, 4H), 3.92 (s, 3H), 3.87 (s, 3H), 2.81 (s, 3H), 2.36 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 191.6, 164.1, 160.8, 143.7, 135.0, 133.8, 132.8, 130.9, 129.4, 129.2, 129.1, 128.7, 127.7, 114.0, 113.9, 55.6, 55.4, 38.2, 21.6. IR (KBr): *v* = 2936, 2842, 1646, 1599, 1507, 1345, 1294, 1250, 1167, 1027, 819, 662, 552 cm<sup>-1</sup>. ESIMS calcd. for C<sub>25</sub>H<sub>24</sub>BrNNaO<sub>5</sub>S (M+Na<sup>+</sup>): 552.05; found: 552.08. Anal. Calcd for C<sub>25</sub>H<sub>24</sub>BrNO<sub>5</sub>S: C, 56.61; H, 4.56; N, 2.64; found: C, 56.72; H, 4.52; N, 2.61.



(*Z*)-3-Bromo-3-(4-methoxyphenyl)-1-(4-methoxyphenyl)-2-(*N*-methyltosylamino)prop-2-en-1-one (**2hb**) white solid, mp 175-176 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.72 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.57 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.21-7.17 (m, 4H), 6.68 (dd, *J* = 6.9, 2.1 Hz, 2H), 6.58 (dd, *J* = 6.6, 2.1 Hz, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.34 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 191.2, 163.4, 160.8, 143.5, 135.9, 135.7, 132.3, 131.4, 129.9, 129.3, 129.3, 127.8, 113.6, 113.3, 55.4, 55.3, 37.7, 21.6. IR (KBr): *v* = 2929, 1644, 1600, 1505, 1331, 1297, 1256, 1170, 1025, 812, 751, 545 cm<sup>-1</sup>; ESIMS calcd. for C<sub>25</sub>H<sub>24</sub>BrNNaO<sub>5</sub>S (M+Na<sup>+</sup>): 552.05; found: 552.17. Anal. Calcd for C<sub>25</sub>H<sub>24</sub>BrNO<sub>5</sub>S: C, 56.61; H, 4.56; N, 2.64; found: C, 56.41; H, 4.72; N, 2.78.



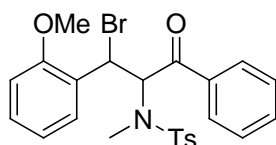
(*E*)-3-Bromo-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)-methlyacrylate (**2i**) white solid, mp 115-116 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.37-7.32 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.85-6.80 (m, 2H), 3.83 (s, 3H), 3.66 (s, 3H), 2.74 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 165.0, 160.6, 143.8, 135.1, 132.2, 130.3, 129.8, 129.5, 129.4, 127.7, 113.6, 55.3, 52.1, 37.4, 21.5. IR (KBr): *v* = 2930, 1735, 1603, 1504, 1343, 1281, 1147, 1028, 909, 666, 548 cm<sup>-1</sup>. ESIMS calcd. for C<sub>19</sub>H<sub>20</sub>BrNNaO<sub>5</sub>S (M+Na<sup>+</sup>): 476.01; found: 476.08. Anal. Calcd for C<sub>19</sub>H<sub>20</sub>BrNO<sub>5</sub>S: C, 50.23; H, 4.44; N, 3.08; found: C, 50.03; H, 4.49; N, 3.19.



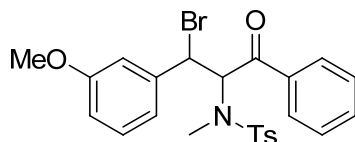
(*E*)-3-Bromo-3-(4-methoxyphenyl)-2-(*N*-methyltosylamino)-ethlyacrylate (**2j**)



white solid, mp 78-79 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60 (d,  $J = 8.1$  Hz, 2H), 7.36 (d,  $J = 9.0$  Hz, 2H), 7.27 (d,  $J = 7.8$  Hz, 2H), 6.83 (d,  $J = 8.7$  Hz, 2H), 4.13 (q,  $J = 7.2$  Hz, 2H), 3.82 (s, 3H), 2.75 (s, 3H), 2.43 (s, 3H), 1.23 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.5, 160.5, 143.7, 135.3, 131.9, 130.3, 130.1, 129.6, 129.4, 127.8, 113.6, 61.6, 55.3, 37.4, 21.5, 13.7. IR (KBr):  $\nu = 2935, 1729, 1605, 1508, 1350, 1255, 1153, 1037, 922, 667, 559$   $\text{cm}^{-1}$ . ESIMS calcd. for  $\text{C}_{20}\text{H}_{22}\text{BrNNaO}_5\text{S}$  ( $\text{M}+\text{Na}^+$ ): 490.03; found: 490.33. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{BrNO}_5\text{S}$ : C, 51.29; H, 4.73; N, 2.99; found: C, 51.32; H, 4.81; N, 3.24.

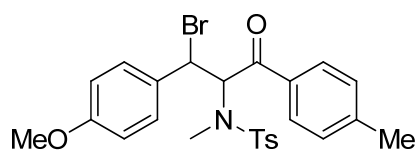


3-Bromo-3-(2-methoxyphenyl)-1-phenyl-2-(*N*-methyltosylamino)propan-1-one  
(**3**) white solid, mp 156-158 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (d,  $J = 7.2$  Hz, 2H), 7.75-7.65 (m, 2H), 7.58-7.53 (m, 1H), 7.42-7.36 (m, 2H), 7.12-7.07 (m, 1H), 6.99-6.88 (m, 5H), 6.65 (d,  $J = 11.1$  Hz, 1H), 6.00 (d,  $J = 11.1$  Hz, 1H), 3.90 (s, 3H), 2.54 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.6, 157.0, 143.1, 136.2, 135.2, 133.9, 130.5, 130.4, 129.2, 129.1, 128.8, 127.2, 125.1, 121.1, 111.2, 58.5, 55.6, 43.0, 29.3, 21.3. IR (KBr):  $\nu = 3066, 3022, 2980, 2944, 2840, 1670, 1593, 1491, 1316, 1252, 1155, 925, 759, 549$   $\text{cm}^{-1}$ . ESIMS calcd. for  $\text{C}_{24}\text{H}_{24}\text{BrNNaO}_4\text{S}$  ( $\text{M}+\text{Na}^+$ ): 524.05; found: 524.33. Anal. Calcd for  $\text{C}_{24}\text{H}_{24}\text{BrNO}_4\text{S}$ : C, 57.37; H, 4.81; N, 2.79; found: C, 57.34; H, 4.82; N, 2.79.



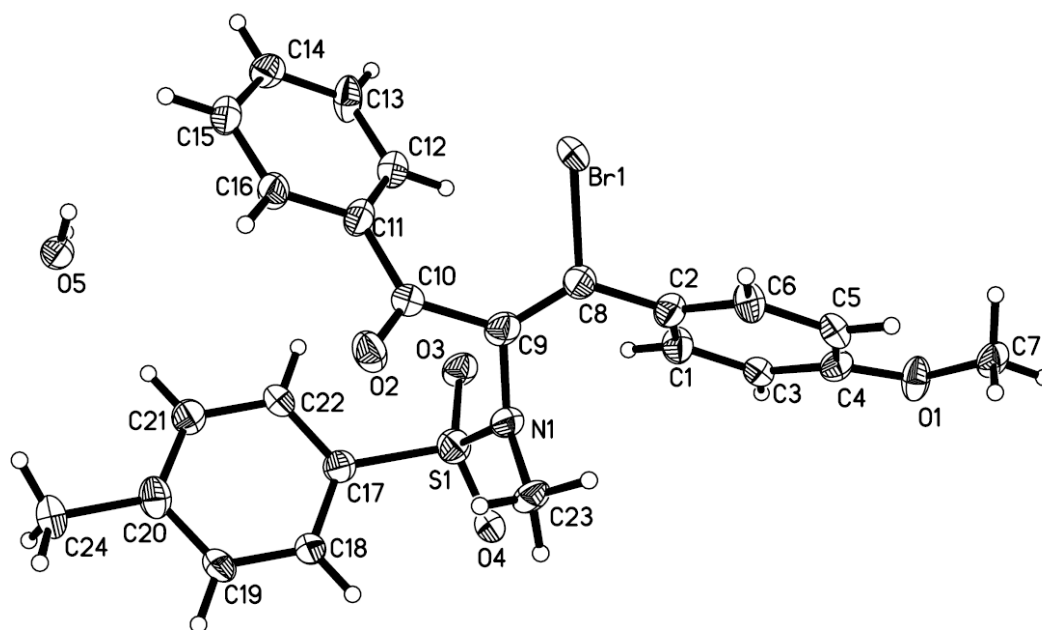
3-Bromo-3-(3-methoxyphenyl)-1-phenyl-2-(*N*-methyltosylamino)propan-1-one  
(**4**) white solid, mp 134-135 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.20 (d,  $J = 7.5$  Hz, 2H), 7.68 (t,  $J = 7.2$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 2H), 7.33 (t,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 6.3$  Hz, 2H), 6.99-6.88 (m, 5H), 6.54 (d,  $J = 11.2$  Hz, 1H), 5.44 (d,  $J = 11.2$  Hz,

1H), 3.88 (s, 3H), 2.53 (s, 3H), 2.27 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 194.2, 159.9, 143.3, 138.6, 135.9, 135.1, 134.1, 129.9, 129.3, 129.2, 128.8, 127.2, 121.0, 115.5, 113.8, 59.3, 55.4, 48.7, 29.2, 21.3. IR (KBr):  $\nu = 3010, 2937, 2837, 1675, 1590, 1453, 1326, 1251, 1159, 920, 760, 679, 551 \text{ cm}^{-1}$ . ESIMS calcd. for C<sub>24</sub>H<sub>24</sub>BrNNaO<sub>4</sub>S (M+Na<sup>+</sup>): 524.05; found: 524.17. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>BrNO<sub>4</sub>S: C, 57.37; H, 4.81; N, 2.79; found: C, 57.34; H, 4.87; N, 2.84.

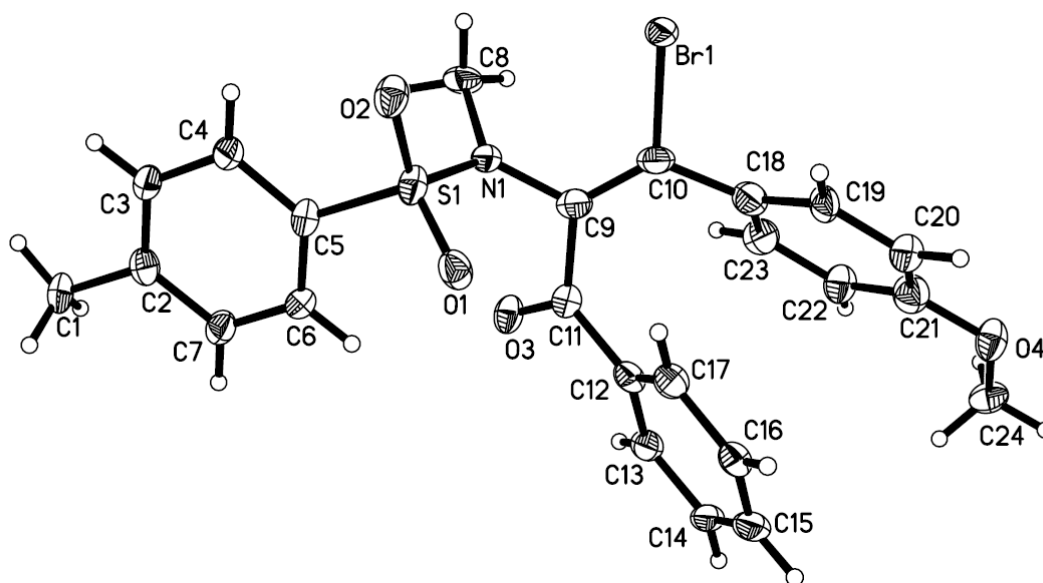


3-Bromo-1-(4-methylphenyl)-3-(3-methoxyphenyl)-2-(*N*-methyltosylamino)propan-1-one (**5**) white solid, mp 148-149 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.10 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.01-6.89 (m, 6H), 6.48 (d, *J* = 11.0 Hz, 1H), 5.45 (d, *J* = 11.0 Hz, 1H), 3.86 (s, 3H), 2.54 (s, 3H), 2.48 (s, 3H), 2.28 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 193.9, 160.2, 145.1, 143.2, 135.2, 133.4, 130.0, 129.5, 129.4, 129.2, 129.1, 127.2, 114.3, 59.1, 55.2, 49.3, 29.2, 21.8, 21.3. IR (KBr):  $\nu = 3004, 2935, 2835, 1674, 1606, 1513, 1337, 1271, 1160, 1031, 927, 788, 671, 549 \text{ cm}^{-1}$ . ESIMS calcd. for C<sub>26</sub>H<sub>29</sub>NNaO<sub>5</sub>S (M-Br+MeO+Na<sup>+</sup>): 490.17; found: 490.33. Anal. Calcd for C<sub>25</sub>H<sub>26</sub>BrNO<sub>4</sub>S: C, 58.14; H, 5.07; N, 2.71; found: C, 58.24; H, 5.05; N, 2.78.

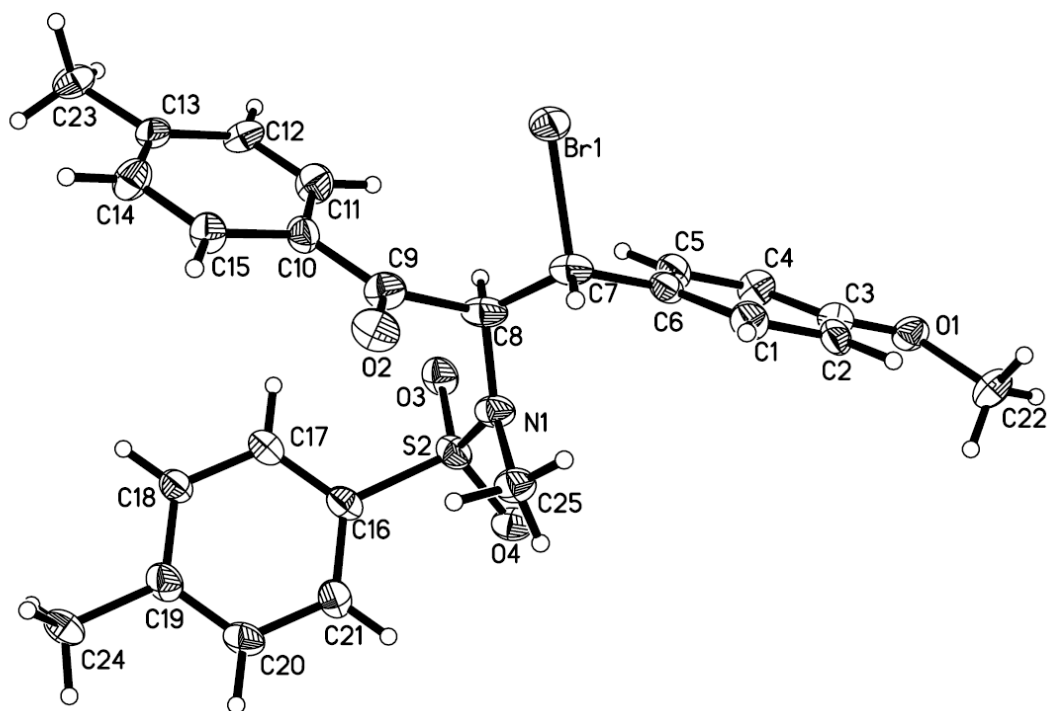
## 6. ORTEP diagram showing Compound 2aa, 2ab and 5



Compound 2aa (CCDC number: 724865)



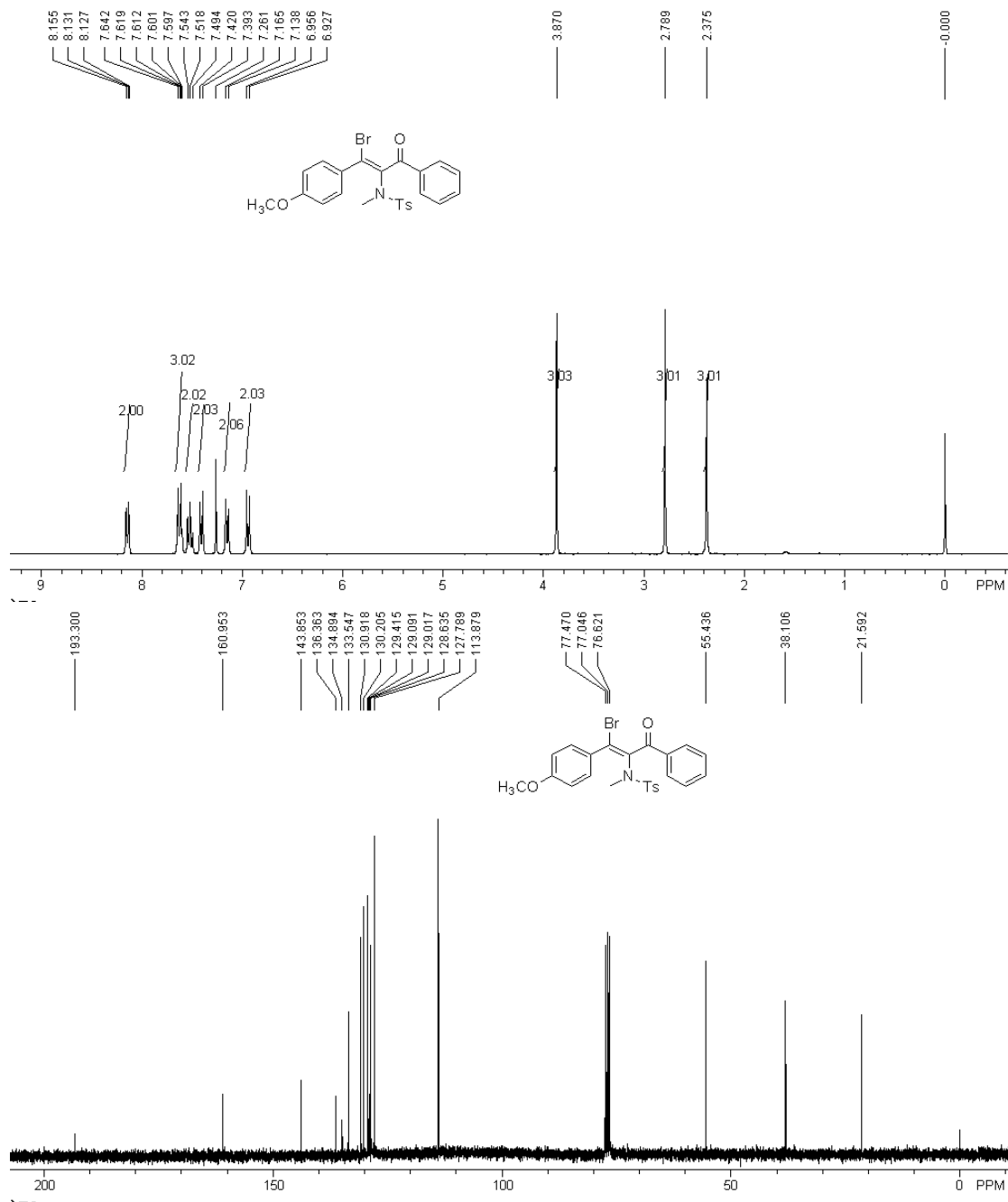
Compound 2ab (CCDC number: 772859)



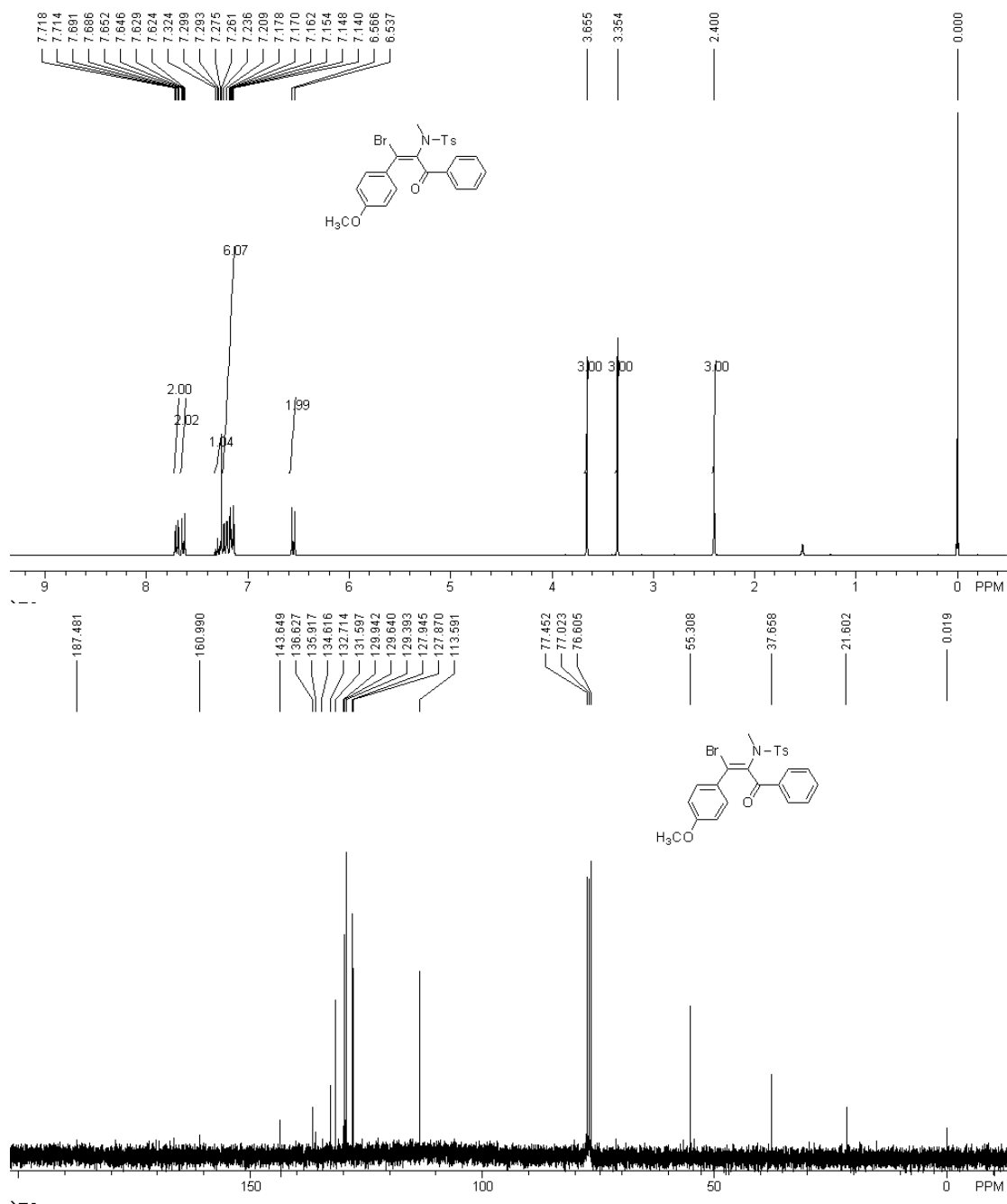
**Compound 5 (CCDC number: 772637)**

## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR for product 2, 3, 4 and 5

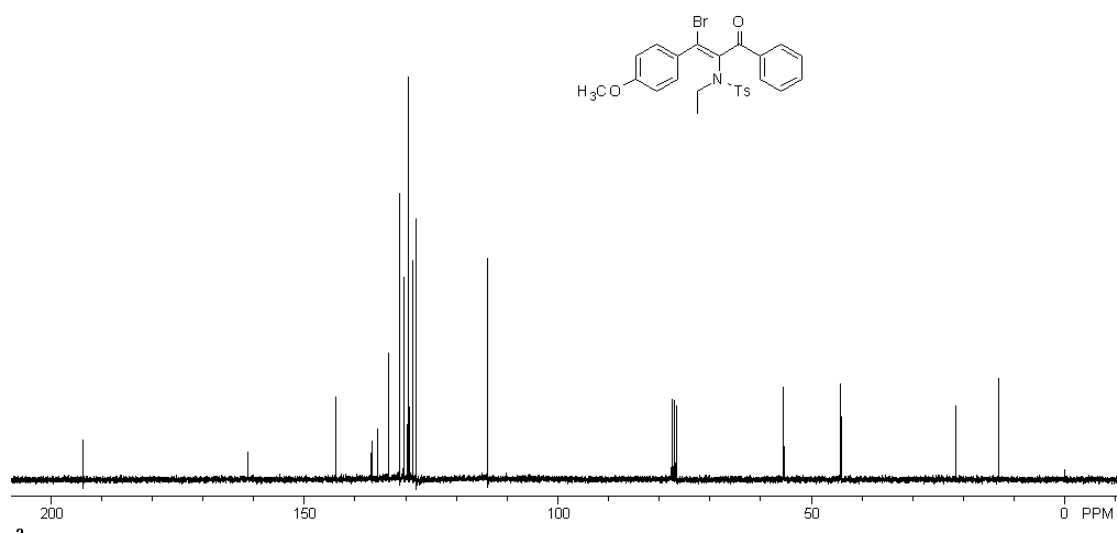
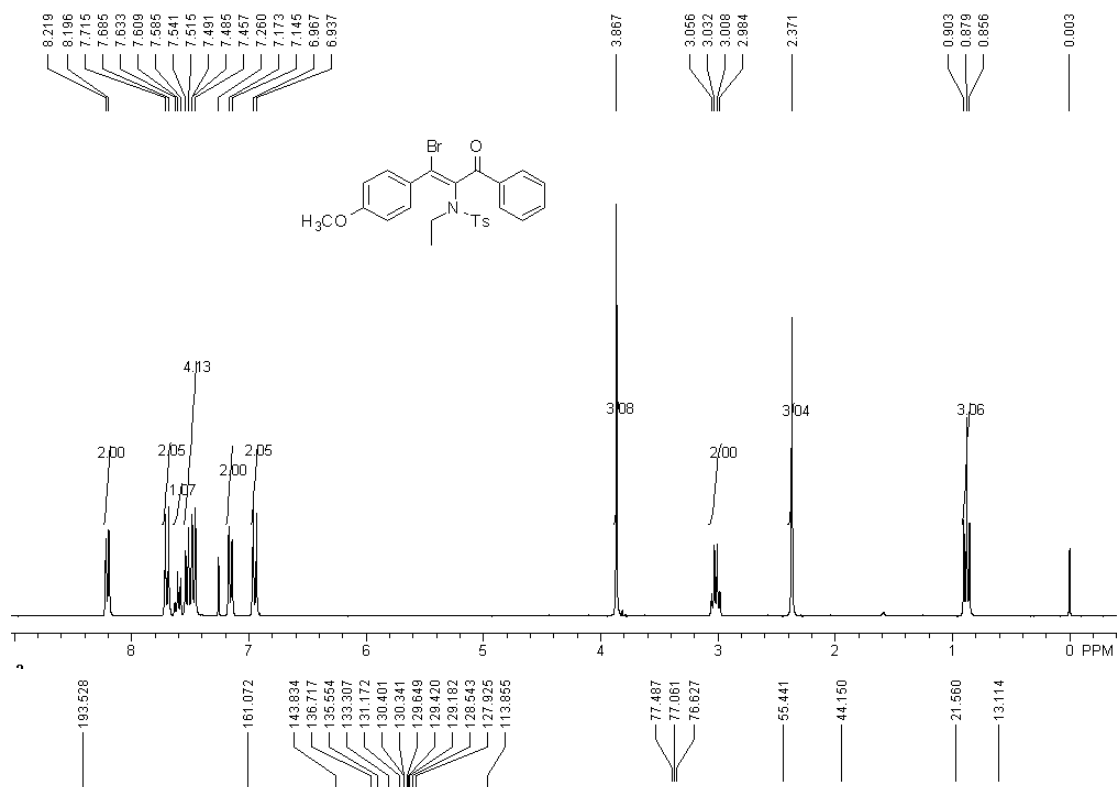
### 2aa



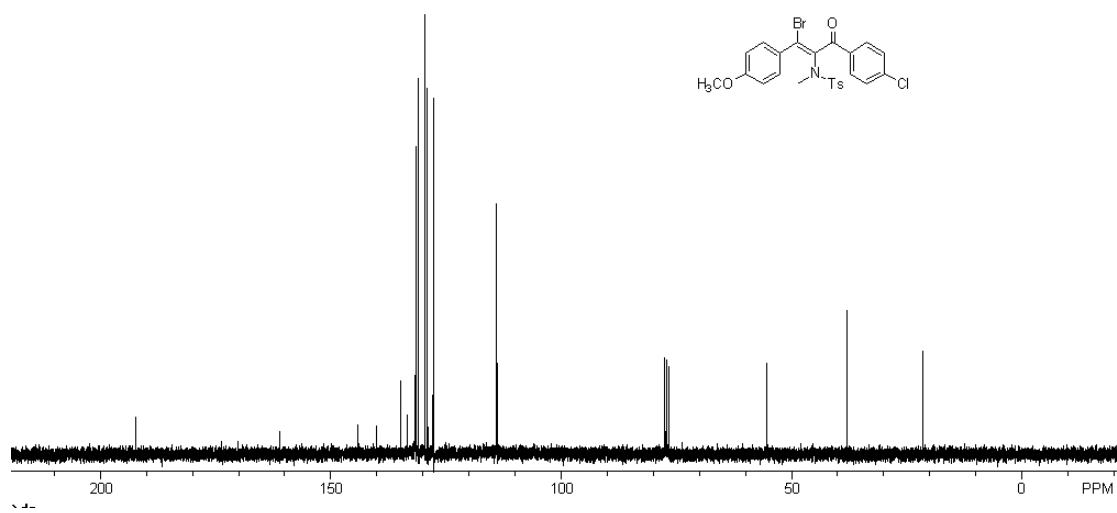
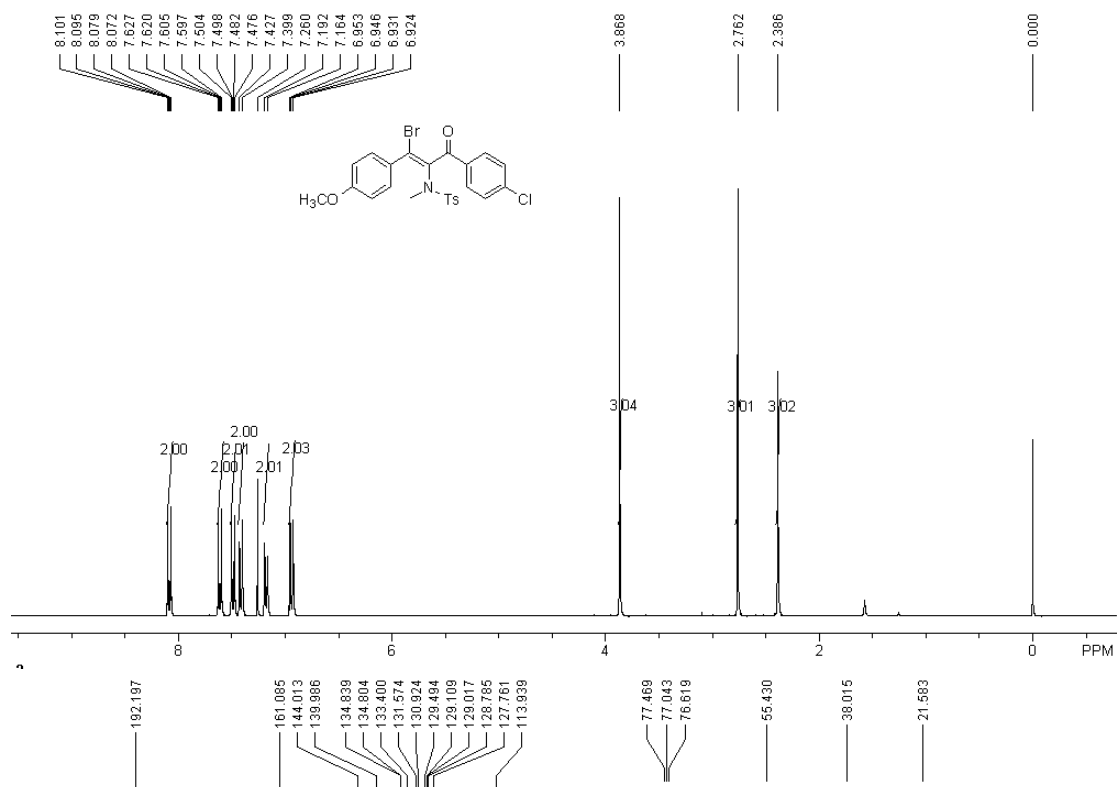
## 2ab



2b

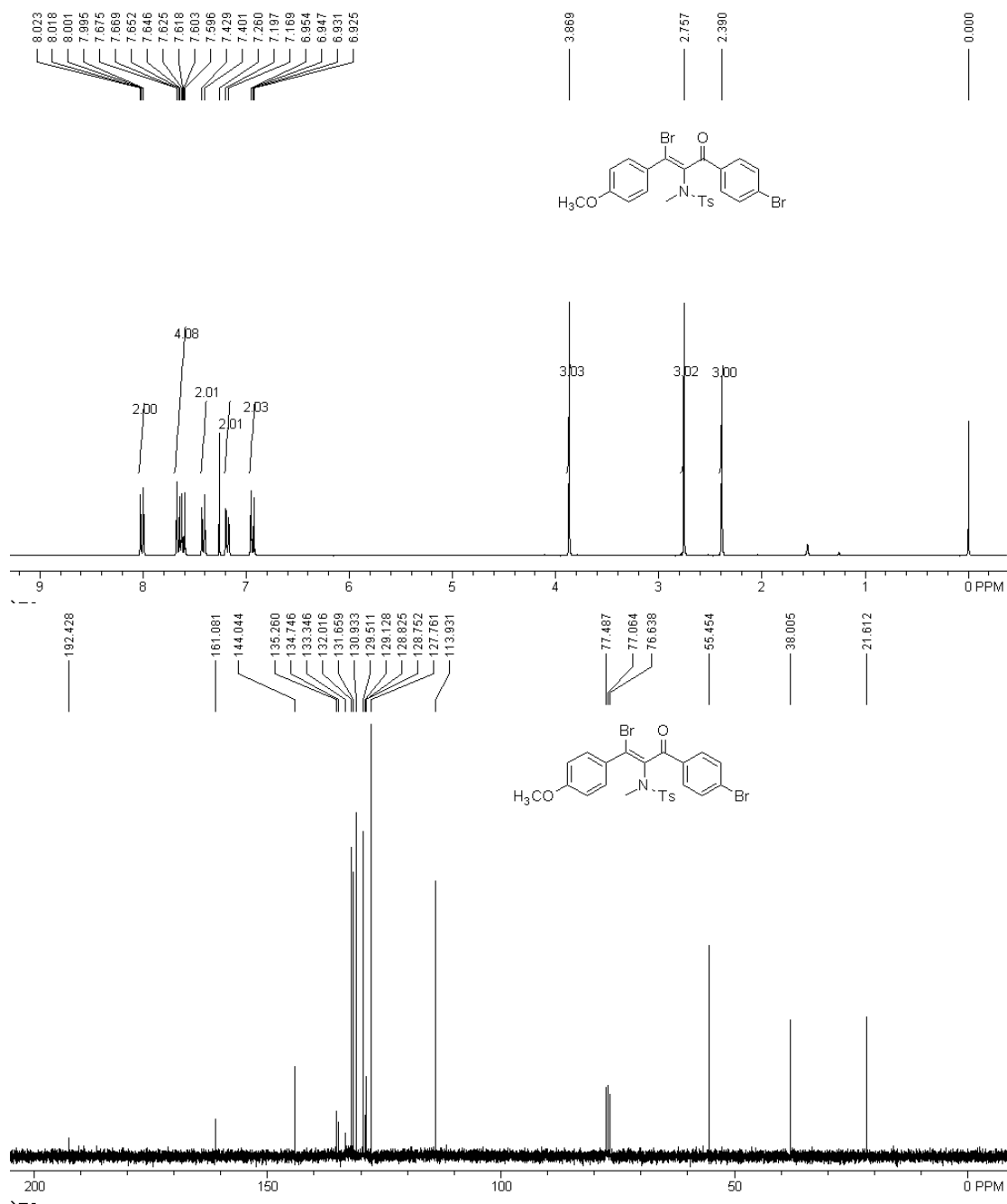


2c

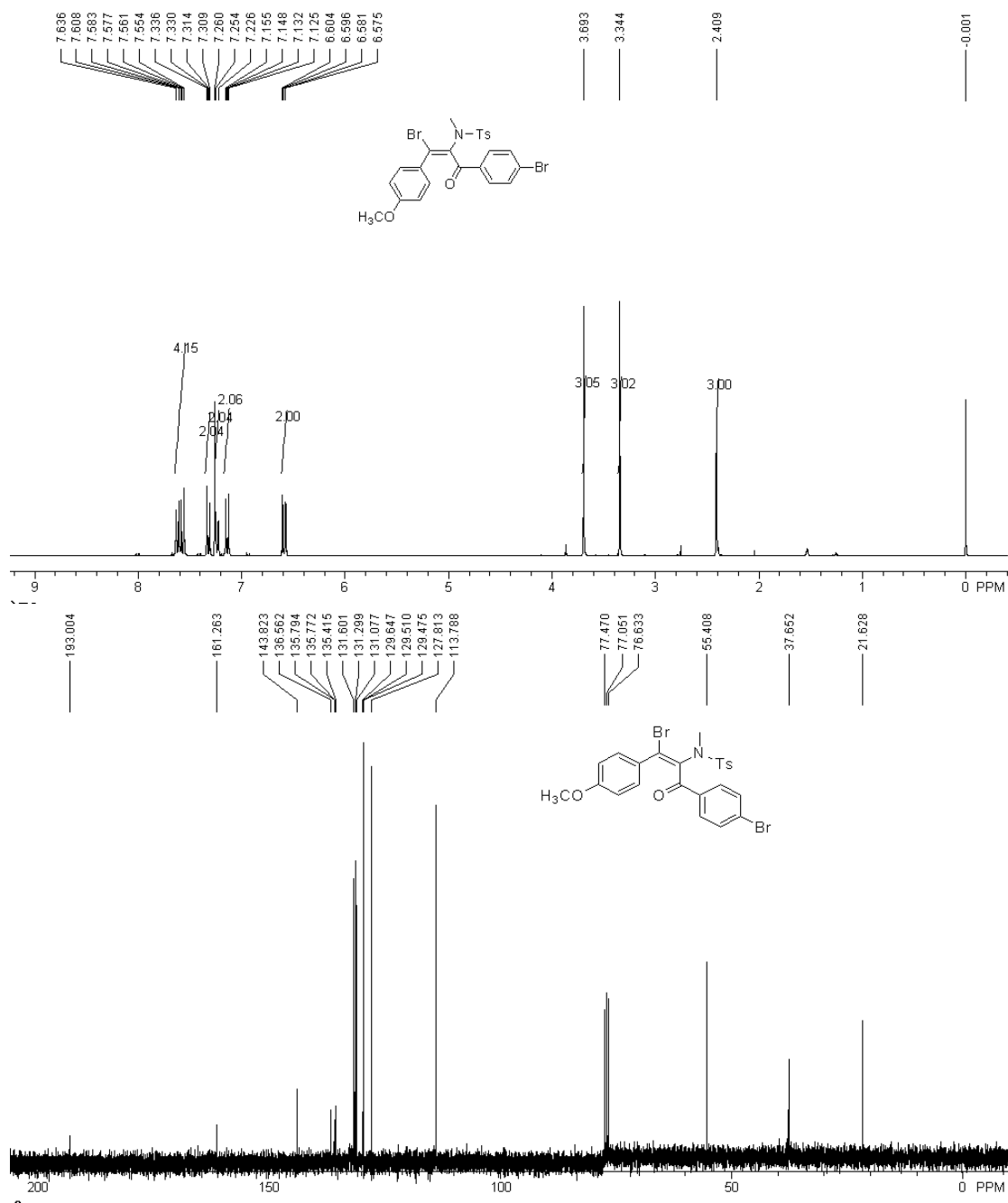




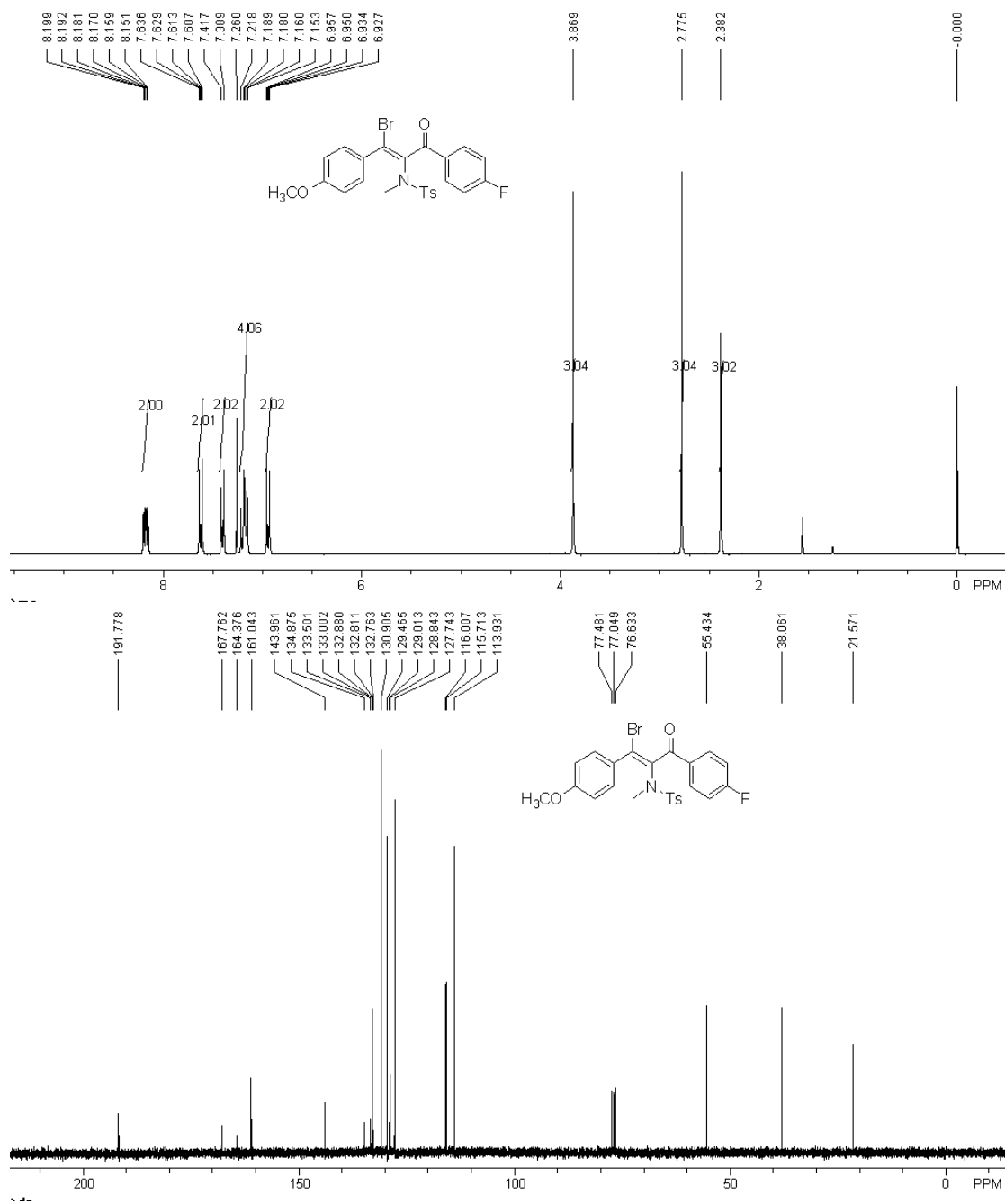
## 2da



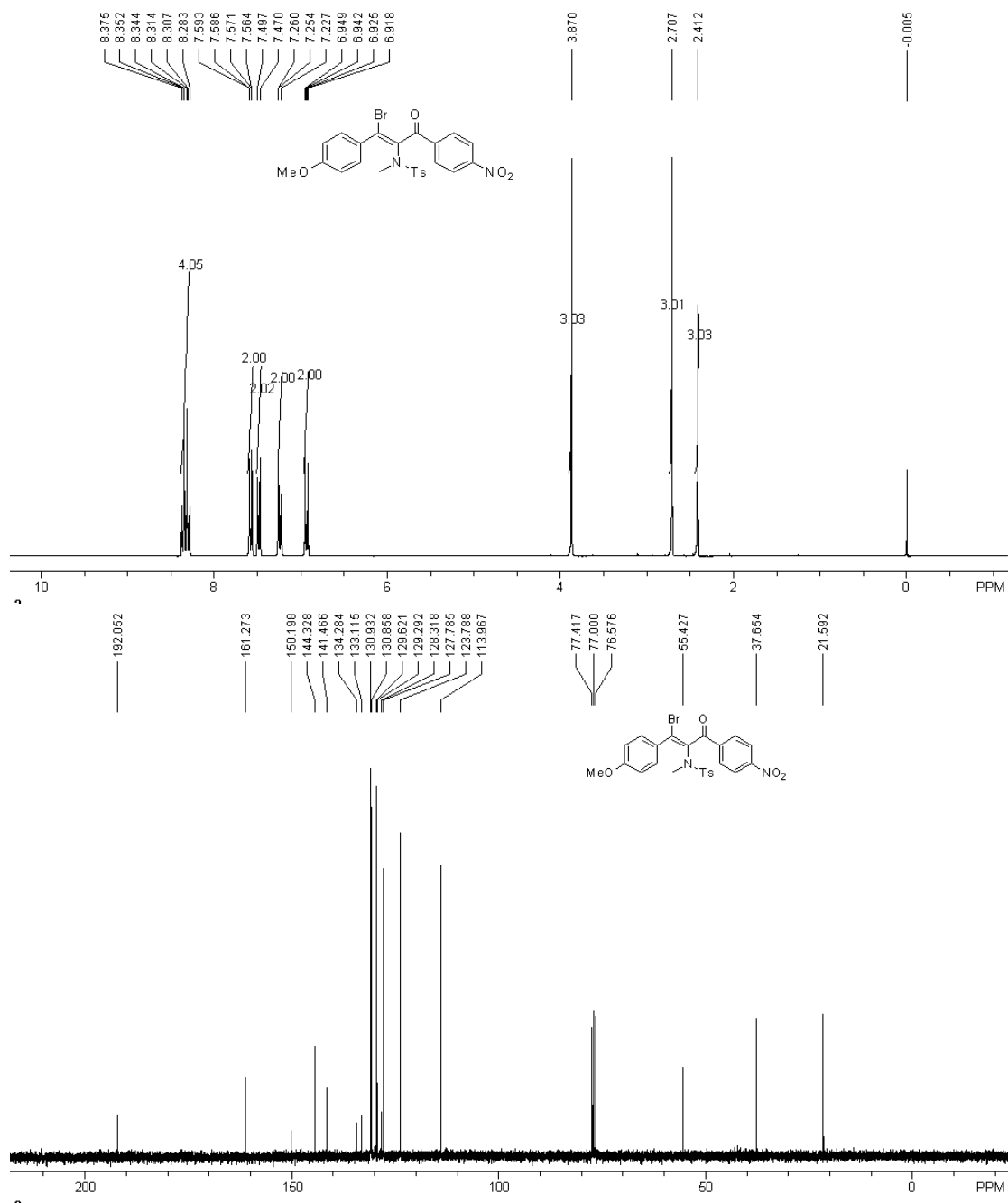
## 2db



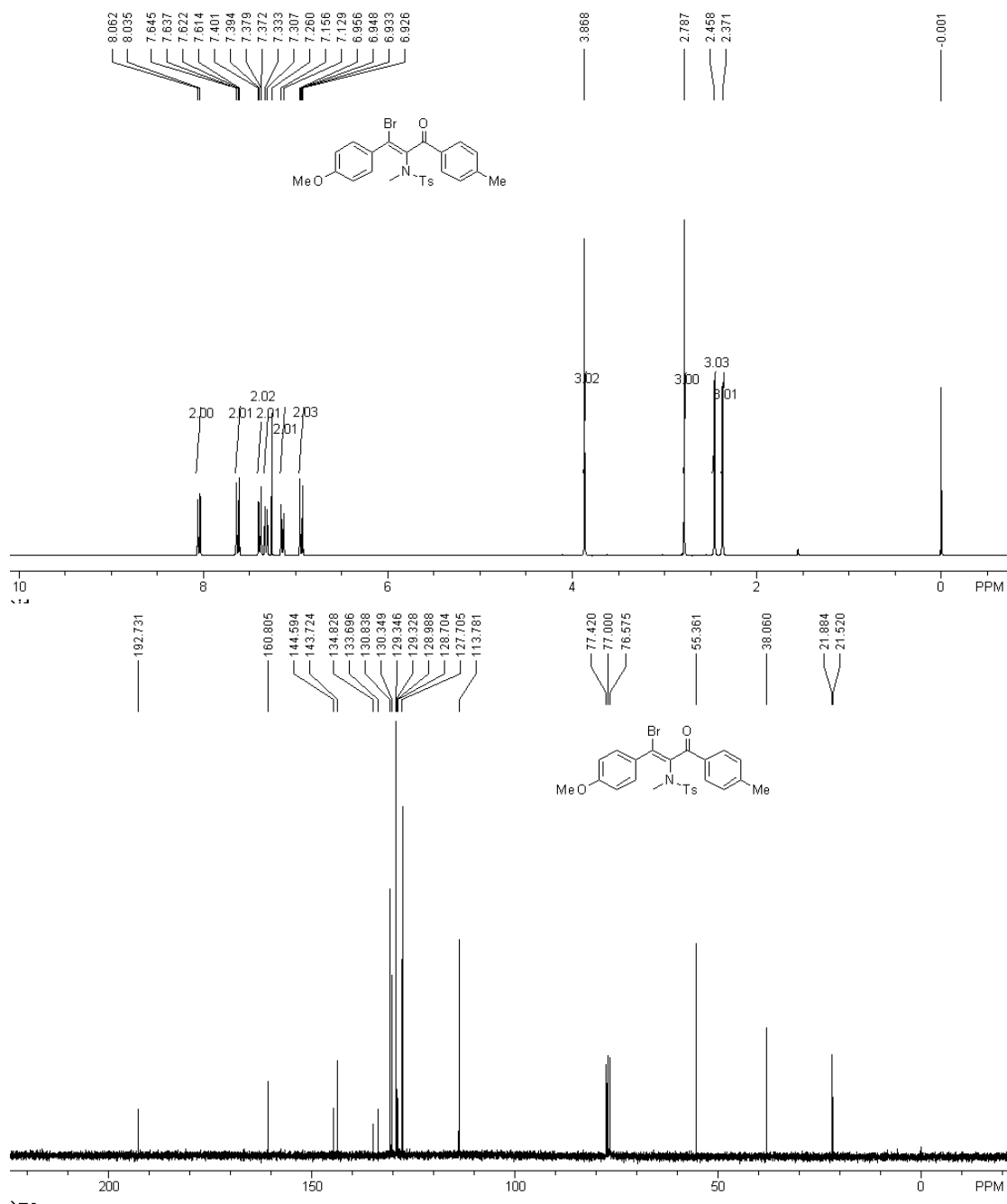
2e



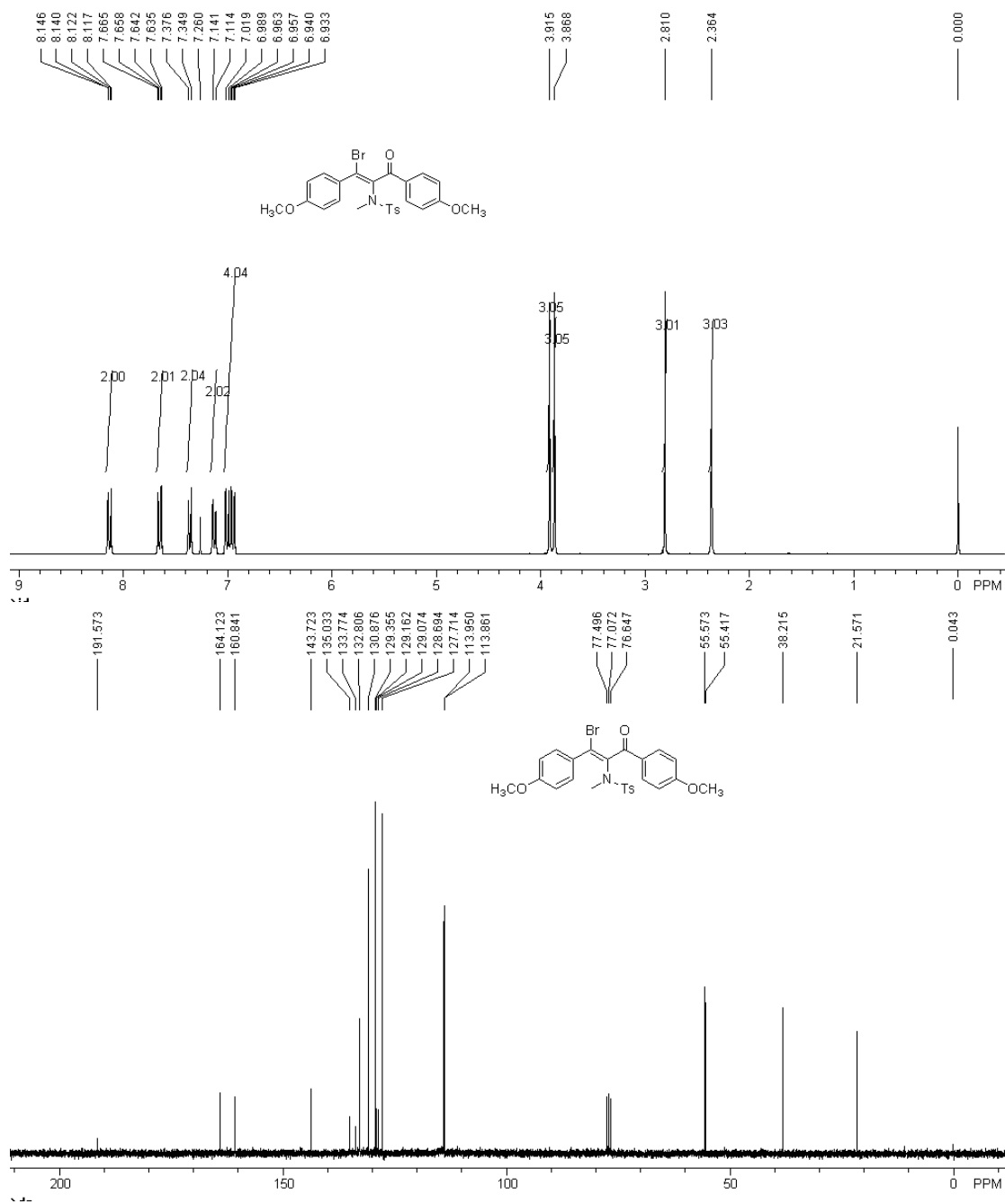
2f



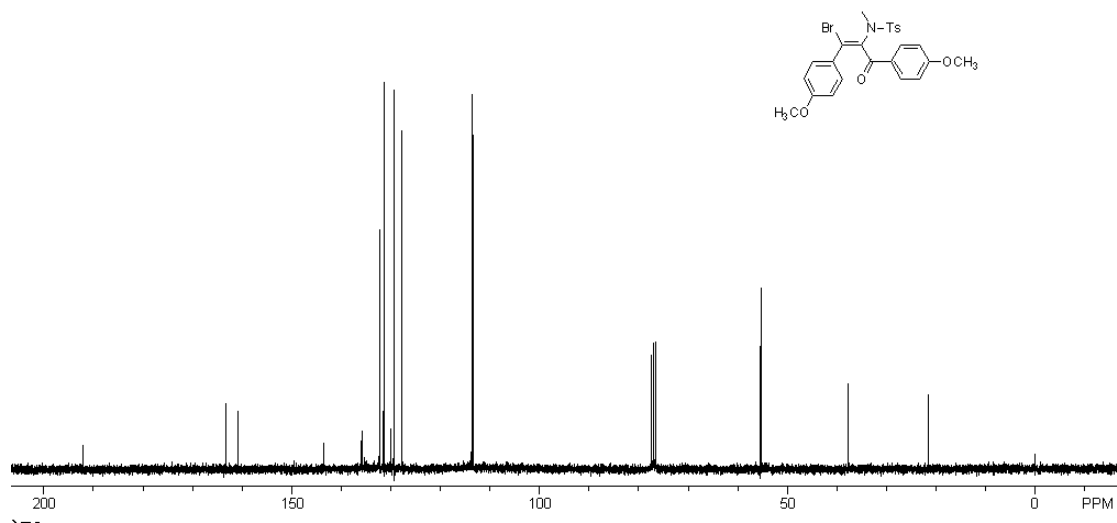
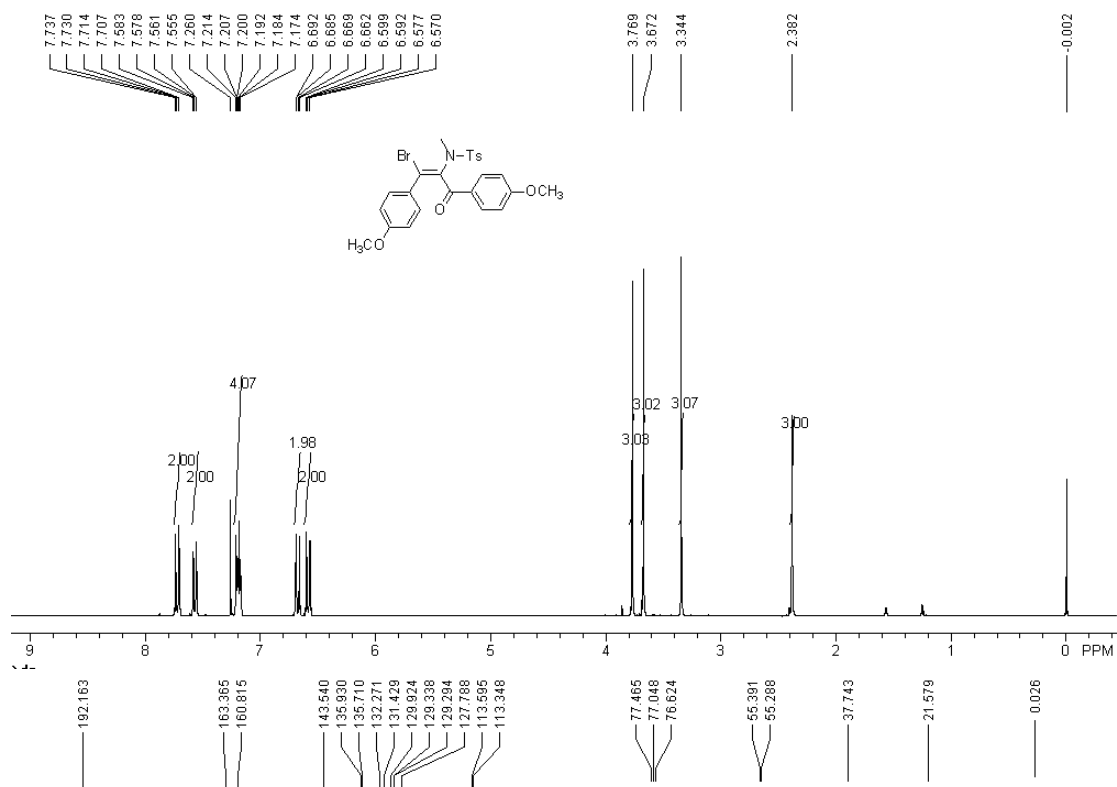
2g



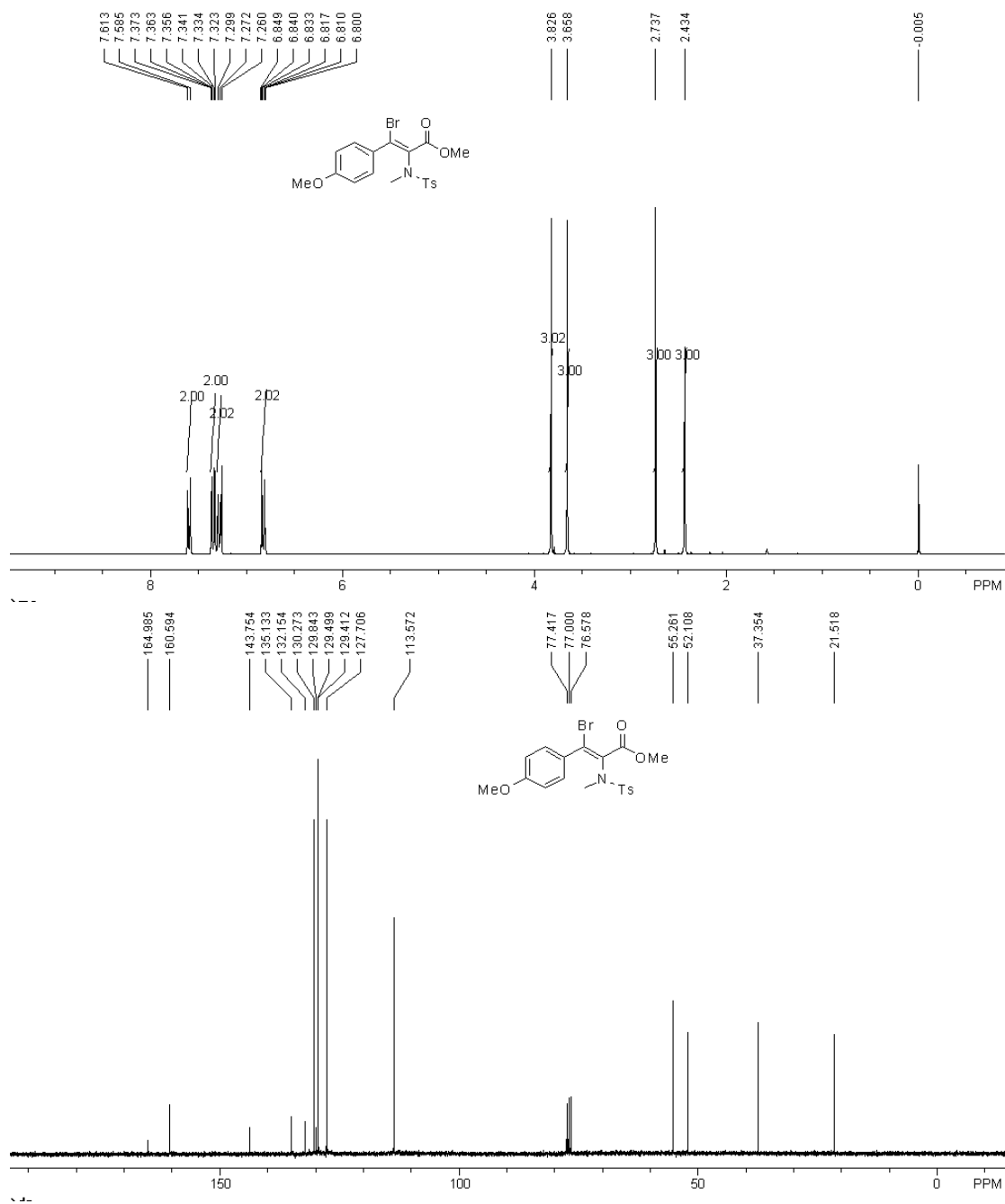
## 2ha



## 2hb

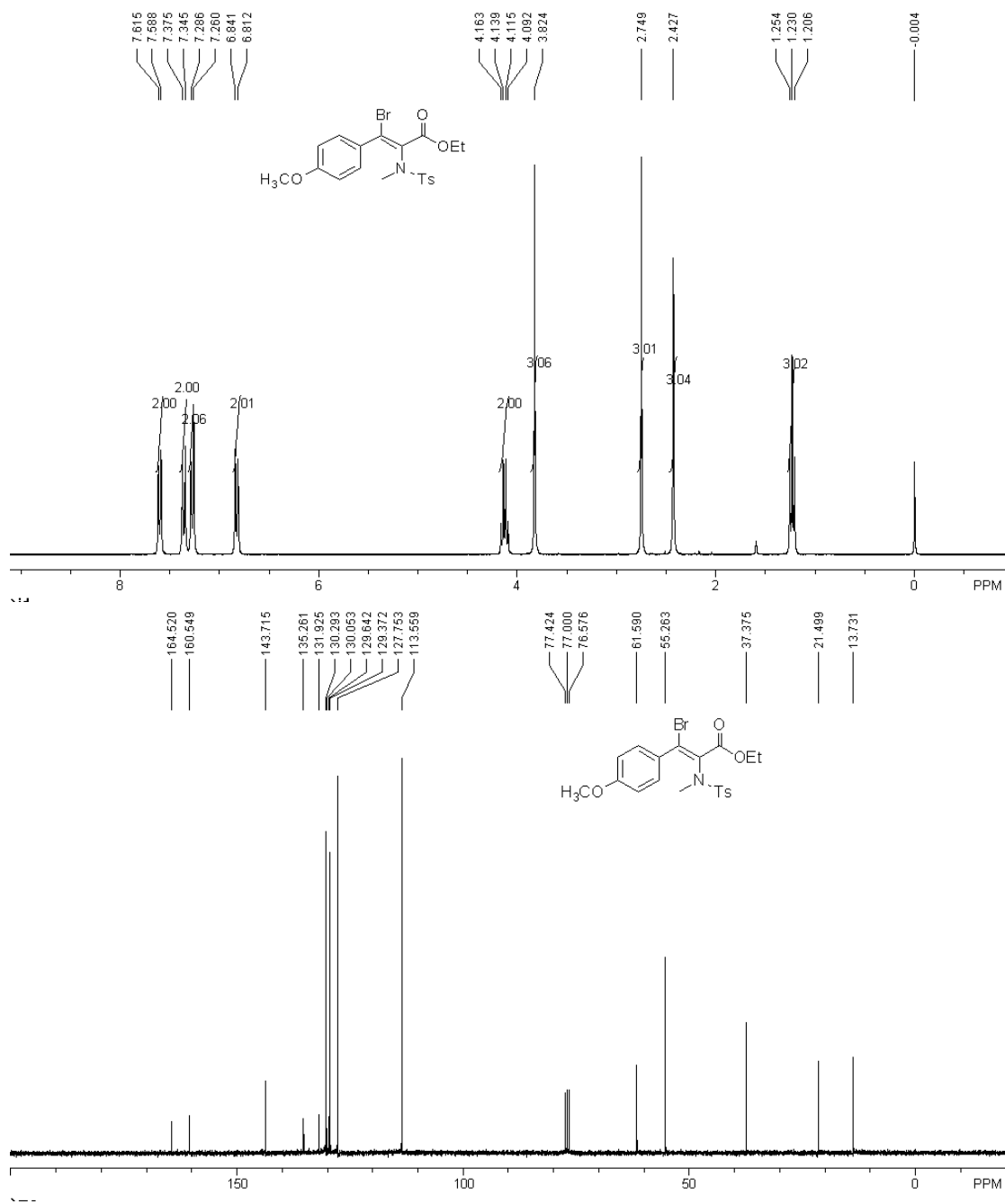


2i

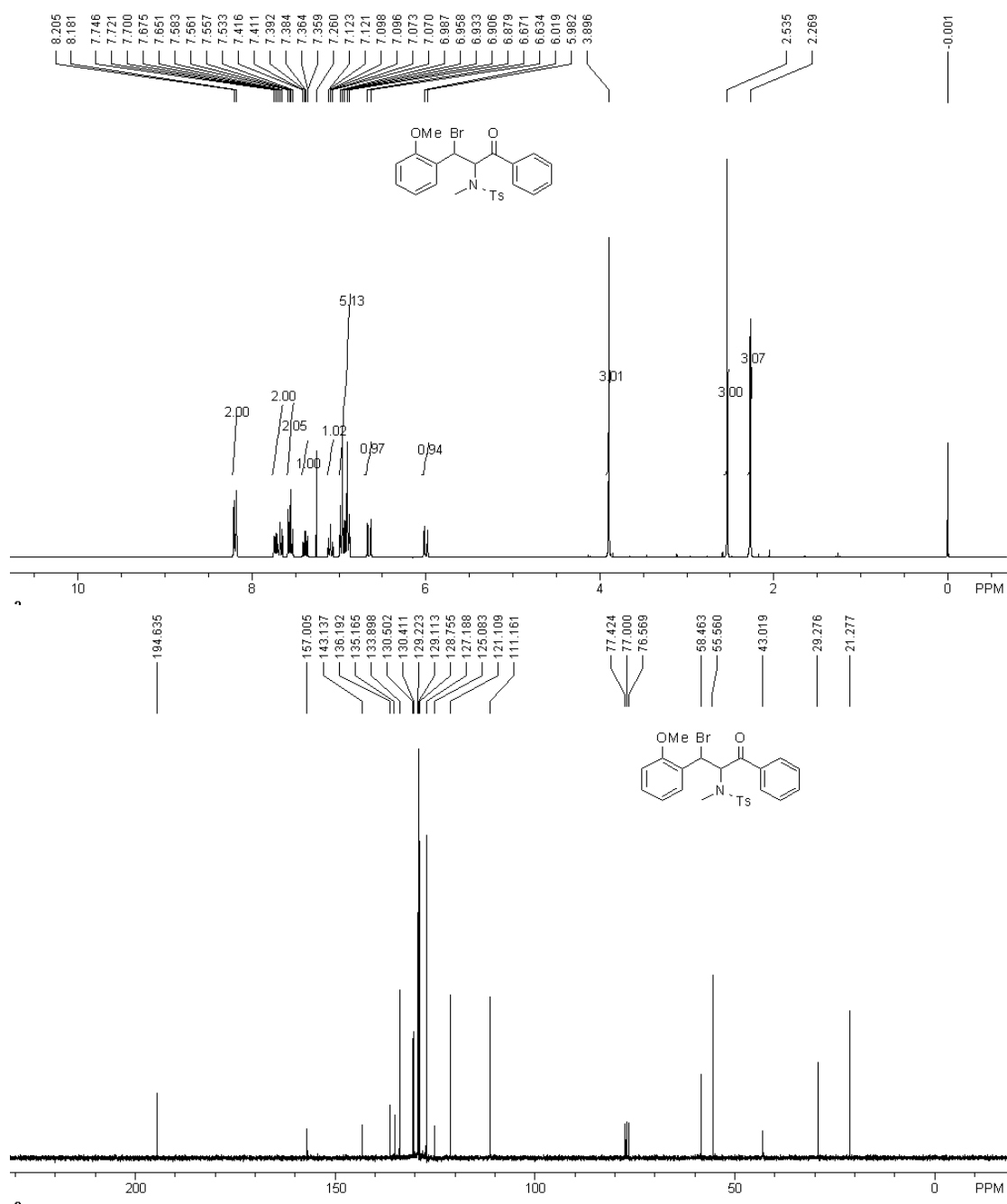




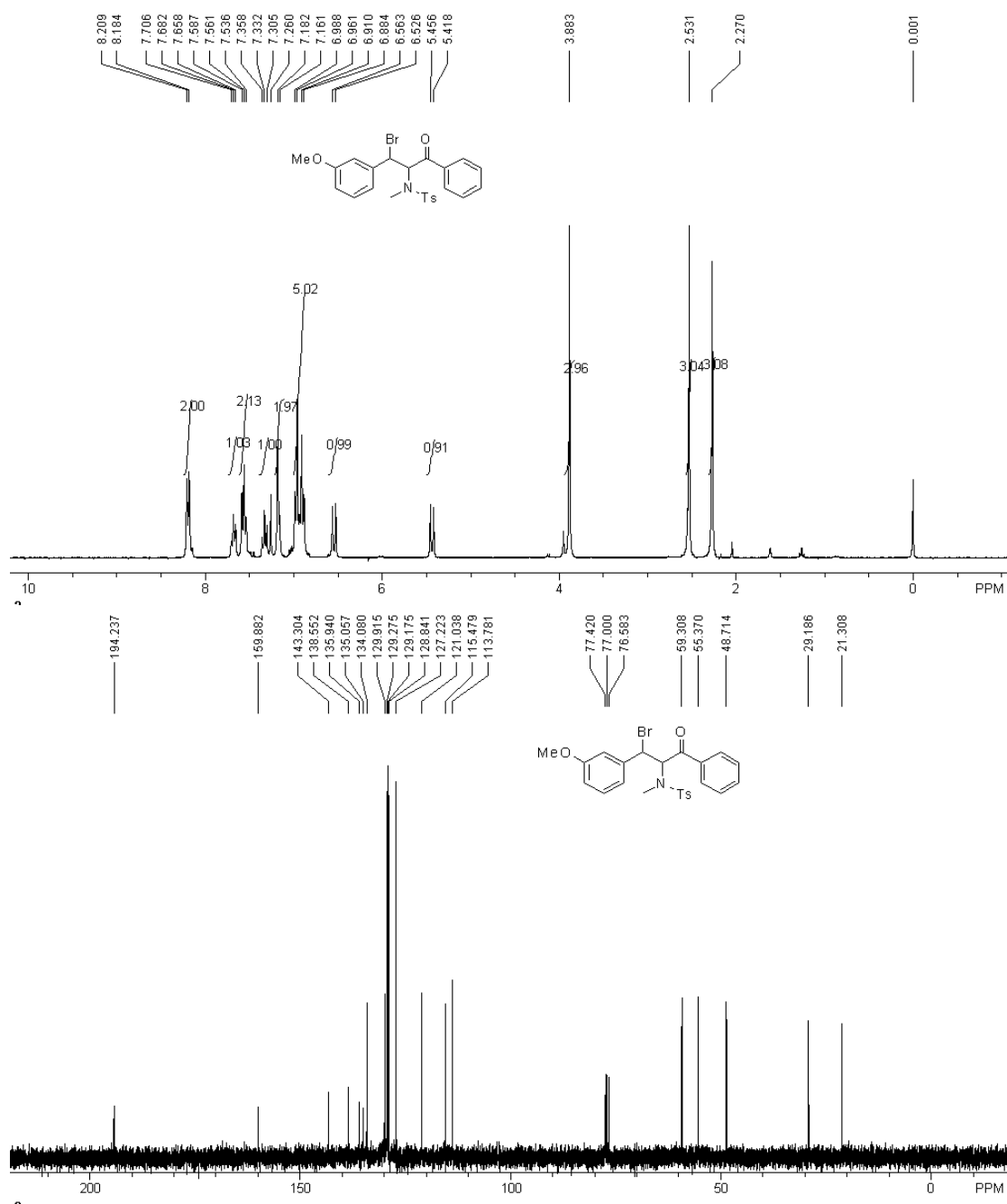
2j



3



4



5

