Supporting Information for

Silver-Catalyzed Cascade Reaction of Tosylmethyl Isocyanide (TosMIC) with Propargylic Alcohols to (*E*)-Vinyl Sulfones: Dual Roles of TosMIC

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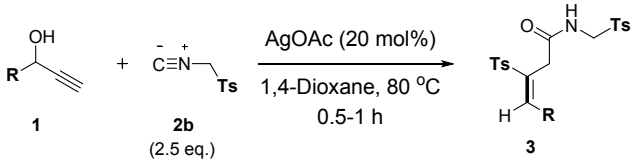
Contents

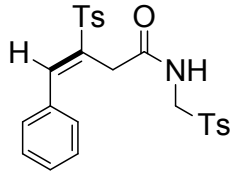
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method**.**

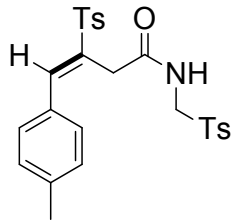
II. Synthesis and analytical data of compounds 3a-3p



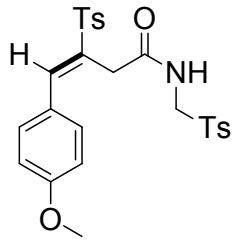
Typical synthetic procedure (with **3a** as an example): To a mixture of 1-phenylprop-2-yn-1-ol (**1a**) (66mg, 0.5 mmol) and AgOAc (16.7mg, 0.1 mmol) in 1,4-dioxane (0.5 mL), 1-isocyanomethanesulfonyl-4-methyl-benzene (**2b**) (244mg, 1.25 mmol) which was dissolved in 2.0 mL 1,4-dioxane and added in 10 minutes at 80 ºC. The reaction mixture was then stirred for 0.5 h-1 h until substrate **1a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane. The organic layer was washed with brine, dried over MgSO4 and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 3: 1) gave **3a** in 88% yield as a white solid.



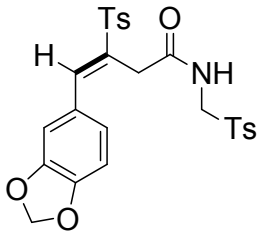
(*E*)-4-phenyl-3-tosyl-*N*-(tosylmethyl)but-3-enamide (3a). White solid, m.p. 157-158 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.43 (s, 3H), 3.24 (s, 2H), 4.70 (d, J = 6.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.37-7.45 (m, 5H); 7.74 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.94 (s, 1H), 8.02 (t, J = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.1, 60.3, 128.3, 128. 8, 129.0, 129.9, 130.2, 130.4, 130.8, 132.0, 133.1,133.7, 134.8, 142.5, 145.16, 145.21, 167.7; HRMS (ESI) m/z calculated for $C_{25}H_{26}NO_5S_2$ $[M+H]^+$: 484.1141, found: 484.1145.



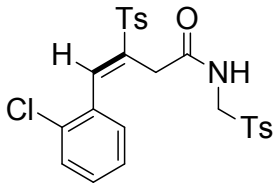
(*E*)-4-(p-tolyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3b**). White solid, m.p. 161-162 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.38 (s, 3H), 2.44 (s, 3H), 3.21 (s, 2H), 4.68 (d, *J* = 6.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 4H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.91 (s, 1H), 8.00 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.7, 35.2, 60.3, 128.2, 128.8, 129.3, 129.7, 129.9, 130.1, 130.6, 131.7, 133.7; 134.9, 141.5, 142.5, 145.08, 145.10, 167.8; **HRMS** (ESI) m/z calculated for $C_{26}H_{28}NO_5S_2$ $[M+H]^+$: 498.1403, found: 498.1408.



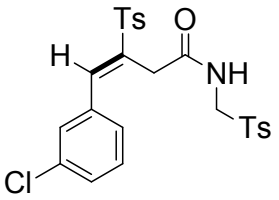
(*E*)-4-(4-methoxyphenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3c**). White solid, m.p. 165-166 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.42 (s, 3H), 3.20 (s, 2H), 3.83 (s, 3H), 4.67 (d, *J* = 6.5 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.87 (s, 1H), 8.06 (t, *J* = 7.0Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.2, 55.4, 60.3, 114.4, 124.7, 128.1, 128.8, 129.75, 129.81, 130.1, 132.6, 133.7, 135.1, 142.0, 144.95, 145.04, 161.7, 168.0; **HRMS** (ESI) m/z calculated for $C_{26}H_{28}NO_6S_2$ $[M+H]^+$: 514.1353, found: 514.1352.



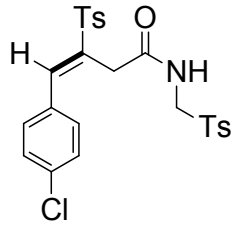
(*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3d**). White solid, m.p. 133-134 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.43 (s, 3H), 3.20 (s, 2H), 4.67 (d, *J* = 6.5 Hz, 2H), 6.01 (s, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.73-7.76 (m, 4H), 7.82 (s, 1H), 8.00 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.0, 60.3, 101.8, 108.7, 109.8, 126.2, 126.7, 128.1, 128.8, 129.8, 130.1, 130.6, 133.7, 135.0, 142.1, 145.0, 145.1, 148.2, 149.9, 167.8; **HRMS** (ESI) m/z calculated for $C_{26}H_{26}NO_7S_2$ $[M+H]^+$: 528.1145, found: 528.1148.



(*E*)-4-(2-chlorophenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (3e). White solid, m.p. 180-181 °C; **^{1}H NMR** (500 MHz, CDCl3) δ 2.29 (s, 3H), 2.45 (s, 3H), 3.10 (s, 2H), 4.69 (d, *J* = 6.5 Hz, 2H), 7.25-7.30 (m, 5H), 7.33-7.38 (m,3H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.87 (t, *J* = 6.5 Hz, 1H), 8.17 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.6, 21.7, 34.9, 60.4, 127.1, 128.4, 128.9, 129.6, 130.2, 130.5, 131.3, 133.8, 134.5, 134.8, 136.3, 140.1, 145.3, 145.3, 167.7; **HRMS** (ESI) m/z calculated for $C_{25}H_{25}ClNO_5S_2$ $[M+H]^+$: 518.0867, found: 518.0870.

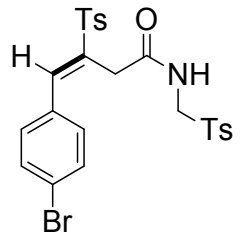


(*E*)-4-(3-chlorophenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3f**). White solid, m.p. 159-160 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.45 (s, 3H), 3.20 (s, 2H), 4.70 (d, *J* = 6.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.31-7.35 (m, 2H), 7.36-7.41 (m, 3H), 7.42 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.84 (s, 1H), 7.99 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 34.9, 60.3, 128.0, 128.3, 128.8, 129.8, 130.0, 130.05, 130.13, 130.2, 130.5, 133.7, 133.8, 134.6, 134.8, 135.1, 140.8, 145.2,145.4, 167.4; **HRMS** (ESI) m/z calculated for $C_{25}H_{25}ClNO_5S_2$ $[M+H]^+$: 518.0950, found: 518.0954.

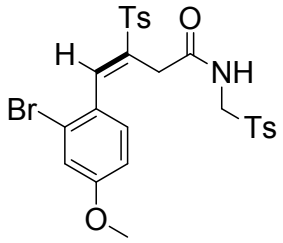


(*E*)-4-(4-chlorophenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3g**). White solid, m.p. 189-190 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.44 (s, 3H), 3.20 (s, 2H), 4.68 (d, *J* = 6.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.34-7.40 (m, 6H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H), 7.99 (t, *J* = 6.0 Hz,1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.7, 35.1, 60.3, 128.3, 128.8, 129.2, 129.9, 130.2, 130.5, 133.8, 131.7, 133.76,

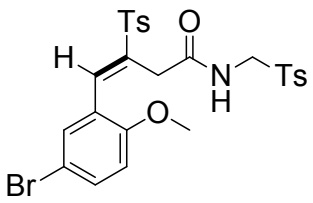
133.79, 134.6, 137.0, 141.0, 145.2, 145.4, 167.6; **HRMS** (ESI) m/z calculated for $C_{25}H_{25}ClNO_5S_2$ $[M+H]^+$: 518.0977, found: 518.0980.



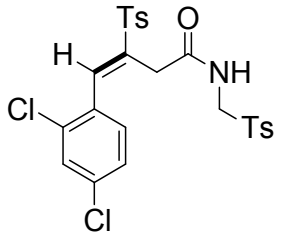
(*E*)-4-(4-bromophenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (3h). White solid, m.p. 185-186 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.42 (s, 3H), 3.21 (s, 2H), 4.67 (d, *J* = 6.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0Hz, 2H), 7.84 (s, 1H), 7.99 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.0, 60.3, 125.3, 128.3, 128.8, 129.9, 130.2, 131.0, 131.7, 132.2, 133.7; 134.1, 134.6, 141.0, 145.2, 145.3, 167.5; **HRMS** (ESI) m/z calculated for $C_{25}H_{24}BrNaNO_5S_2$ $[M+Na]^+$: 586.0148, found: 586.0145.



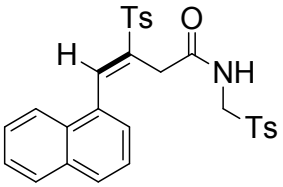
(*E*)-4-(2-bromo-4-methoxyphenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3i**). White solid, m.p.174-175 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.43 (s, 3H), 3.13 (s, 2H), 3.71 (s, 3H), 4.70 (d, *J* = 6.5 Hz, 2H), 6.80-6.82 (m, 1H), 6.94 (s, 1H), 7.26 (d, *J* = 8.0, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 8.04 (t, *J* = 6.5 Hz, 1H), 8.10 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.0, 56.0, 60.5, 114.7, 114.9, 118.9, 128.4, 128.8, 130.0, 130.1, 132.8, 133.3; 133.8, 134.8, 136.1, 142.6, 145.27, 145.32, 159.0, 167.8; **HRMS** (ESI) m/z calculated for $C_{26}H_{26}BrNO_6S_2$ $[M+H]^+$: 594.0463. found: 594.0461.



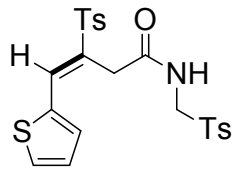
(*E*)-4-(5-bromo-2-methoxyphenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3j**). White solid, m.p. 169-170 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.43 (s, 3H), 3.10 (s, 2H), 3.88 (s, 3H), 4.66 (d, *J* = 6.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 2.5 Hz, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 6.5 Hz, 1H), 8.14 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 21.7, 34.9, 56.0, 60.3, 112.3, 112.9, 123.0, 128.3, 128.9, 129.9, 130.1, 132.4, 133.5, 134.4, 135.0, 137.4, 145.1, 145.2, 156.9, 167.3; **HRMS** (ESI) m/z calculated for $C_{26}H_{27}BrNO_5S_2$ $[M+H]^+$: 592.0463, found: 592.0465.



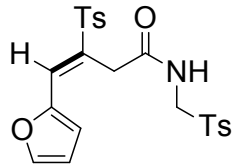
(*E*)-4-(2,4-dichlorophenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3k**). White solid, 195-196 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.45 (s, 3H), 3.10 (s, 2H), 4.70 (d, *J* = 6.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.27-7.32 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.79-7.81 (m, 4H), 7.89 (t, *J* = 6.5 Hz, 1H), 8.08 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.6, 21.7, 35.0, 60.3, 127.6, 128.4, 128.9, 129.0, 129.6, 130.0, 130.3, 131.4, 133.8, 134.6, 135.3, 136.9, 138.9, 145.4, 145.5, 167.6; **HRMS** (ESI) m/z calculated for $C_{25}H_{24}Cl_2NO_5S_2$ $[M+H]^+$: 552.0467, found: 552.0470.



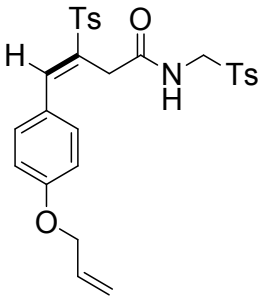
(*E*)-4-(naphthalen-1-yl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3l**). White solid, m.p. 196-197 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.90 (s, 3H), 2.45 (s, 3H), 3.30 (s, 2H), 4.73 (d, *J* = 6.5 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.50-7.57 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.81-7.85 (m, 5H), 7.93 (s, 1H), 8.09 (s, 1H), 8.11 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2, 21.7, 35.4, 60.3, 126.7, 126.9, 127.5, 128.0, 128.3, 128.6, 129.1, 129.4, 129.8, 130.2, 131.4, 132.9, 133.1, 133.7, 133.9, 134.8, 142.5, 145.1, 145.3, 167.9; **HRMS** (ESI) m/z calculated for $C_{29}H_{28}NO_5S_2$ $[M+H]^+$: 534.1389, found: 534.1387.



(*E*)-4-(thiophen-2-yl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3m**). White solid, m.p. 177-178 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.44 (s, 3H), 3.29 (s, 2H), 4.64 (d, *J* = 6.5 Hz, 2H), 7.13-7.17 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.56 (d, *J* = 5.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.75-7.80 (m, 3H), 8.03 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.6, 35.3, 60.3, 128.2, 128.6, 128.8, 129.4, 129.7, 130.2, 131.7, 133.7, 133.8, 133.9, 134.8, 135.2, 145.0, 145.2, 166.9; **HRMS** (ESI) m/z calculated for $C_{23}H_{23}NNaO_5S_3$ $[M+Na]^+$: 512.0631, found: 512.0635.

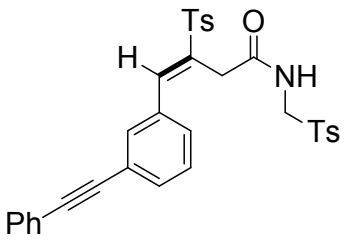


(*E*)-4-(furan-2-yl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3n**). White solid, m.p. 141-142 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.43 (s, 3H), 3.36 (s, 2H), 4.61 (d, *J* = 7.0 Hz, 2H), 6.50 -6.52 (m, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 6.5 Hz, 1H), 7.56 (s, 1H), 7.67-7.69 (m, 3H), 7.74 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.6, 21.7, 35.2, 60.3, 112.8, 118.7, 128.0, 128.2, 128.7, 129.1, 129.8, 130.1, 133.8, 134.9, 145.0, 145.1, 146.3, 148.4, 167.3; **HRMS** (ESI) m/z calculated for $C_{23}H_{24}NO_6S_2$ $[M+H]^+$: 474.1040, found: 474.1044**.**



(*E*)-4-(4-(allyloxy)phenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3o**). White solid, m.p. 165-166 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.14 (s, 3H), 2.36 (s, 3H), 3.13 (s, 2H), 4.90 (d, *J* = 5.0 Hz, 2H), 4.61 (d, *J* = 7.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.92-6.00 (m, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.80

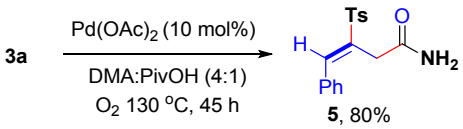
(s, 1H), 8.00 (t, J = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 35.2, 60.3, 68.8, 115.1, 118.2, 124.8, 128.1, 128.8, 129.8, 129. 9, 130.1, 132.4, 132.6, 133.7, 135.1, 142.0, 144.9,145.1, 160.7, 168.0; **HRMS** (ESI) m/z calculated for $C_{28}H_{30}NO_6S_2$ $[M+H]^+$: 540.1515, found: 540.1520.



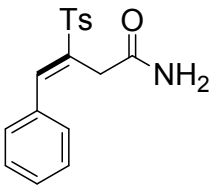
(*E*)-4-(3-(phenylethynyl)phenyl)-3-tosyl-*N*-(tosylmethyl)but-3-enamide (3p). White solid, m.p. 149-150 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.44 (s, 3H), 3.24 (s, 2H), 4.70 (d, J = 6.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.36-7.42 (m, 7H), 7.53-7.57 (m, 4H), 7.74 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.89 (s, 1H), 7.96 (t, J = 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5, 21.6, 35.0, 60.4, 88.1, 90.7, 122.7, 124.2, 128.3, 128.4, 128.6, 128.8, 129.1, 129.2, 129.9, 130.2, 131.7, 132.4, 133.3, 133.6, 133.8,134.6, 134.8, 141.6, 145.2, 145.3, 167.5; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}NO_5S_2$ $[M+H]^+$: 584.1567, found: 584.1567.

III. Synthesis and analytical data of compounds 5 and 7

Synthesis of 5 from 3a

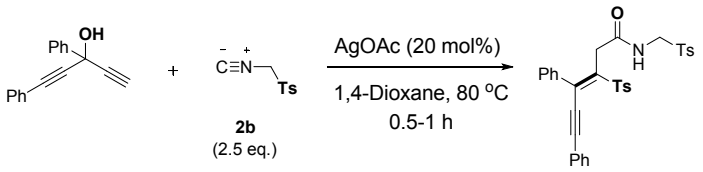


To a mixture of (*E*)-4-phenyl-3-tosyl-*N*-(tosylmethyl)but-3-enamide (**3a**) (242 mg, 0.5 mmol) in 2.5 mL of N,N-dimethylformamide: pivalic acid (4:1) at 130 °C with oxygen balloon, $Pd(OAc)_2$ (11.3 mg, 0.05 mmol) was added . The reaction mixture was then stirred for 45 h until substrate **3a** had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 1: 1) gave **5** in 80% yield as a white solid.



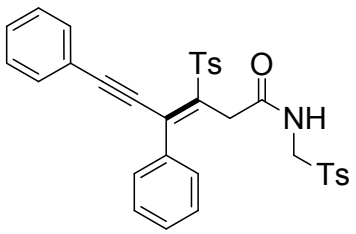
(*E*)-4-phenyl-3-tosylbut-3-enamide (**5**). White solid, m.p. 193-194 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.33 (s, 2H), 5.45 (s, 1H), 6.90 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.42-7.47 (m, 3H), 7.59-7.63 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.99 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.7, 35.3, 128.3, 129.1, 130.1, 130.3, 130.7, 132.3, 134.0, 135.0, 142.0, 145.1, 170.3; **HRMS** (ESI) m/z calculated for $C_{17}H_{18}NO_3S$ $[M+H]^+$: 518.0950, found: 518.0954.

Synthetic procedure for 7



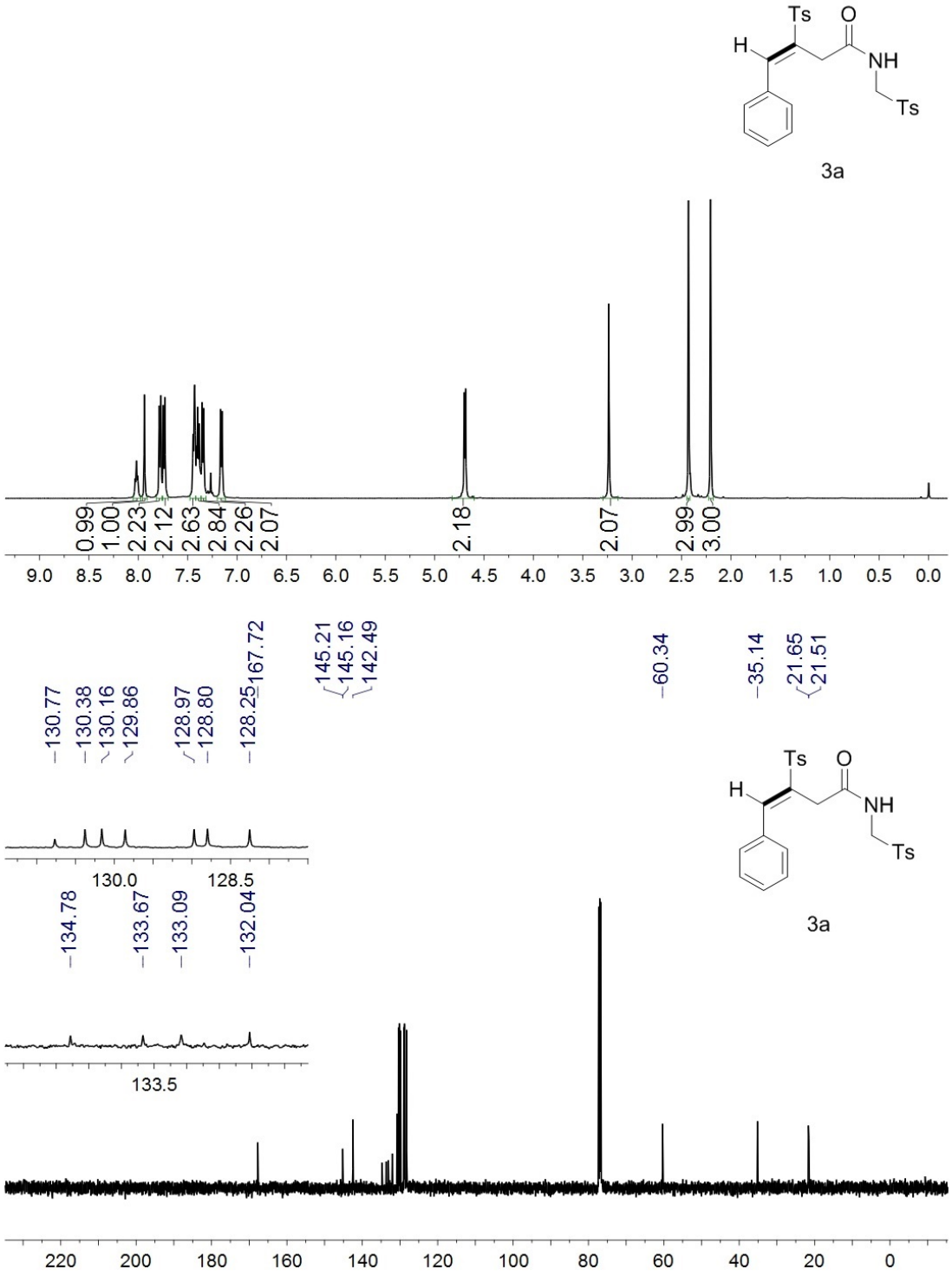
6 **7**

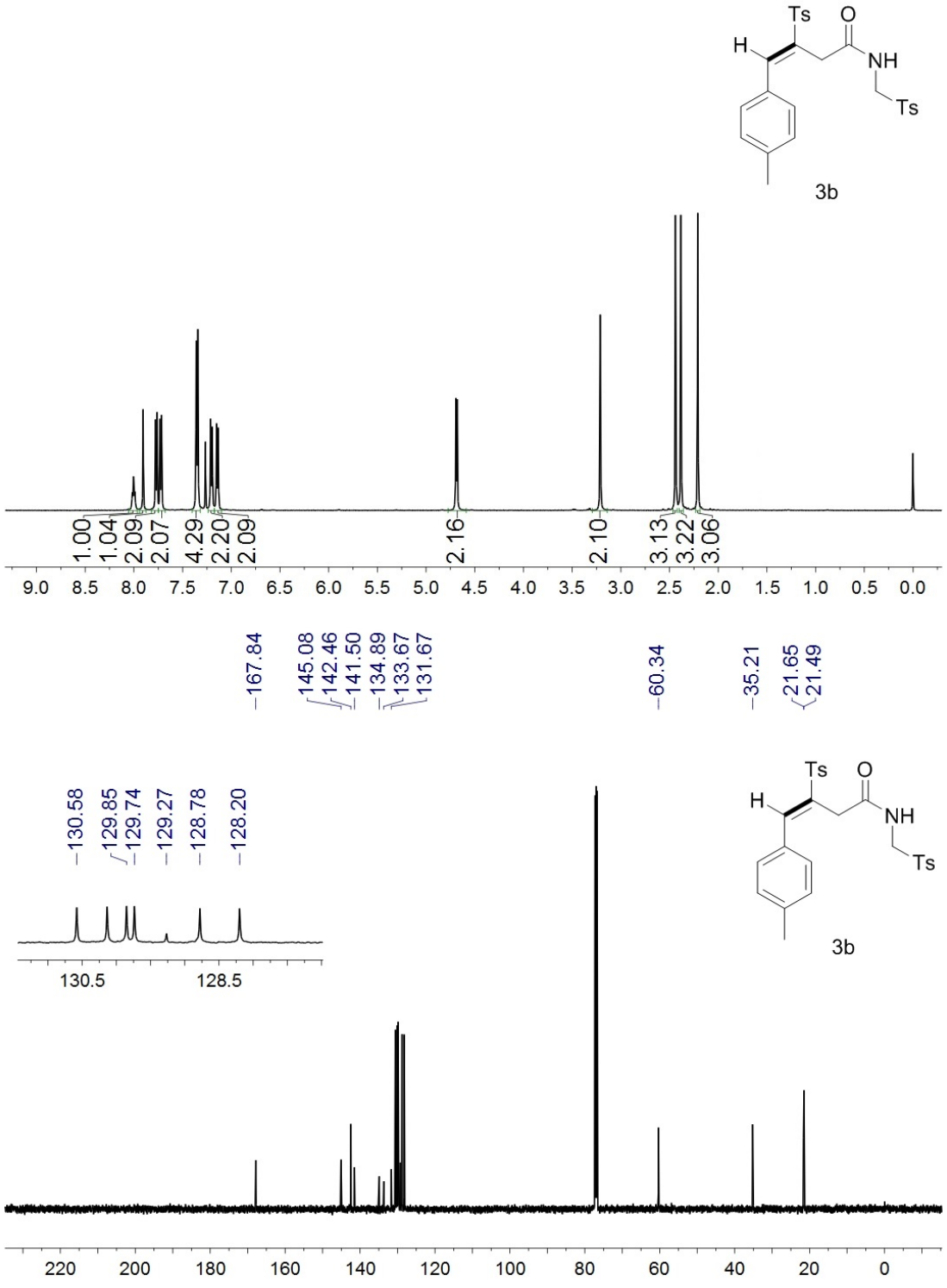
To a mixture of 1,3-diphenylpenta-1,4-diyn-3-ol (**6**) (116 mg, 0.5 mmol) and AgOAc (16.7 mg, 0.1 mmol) in 1,4-dioxane (0.5 mL), 1-isocyanomethanesulfonyl-4-methyl -benzene (**2b**) (244 mg, 1.25 mmol) which was dissolved in 2.0 mL 1,4-dioxane and added in 10 minutes at 80 °C. The reaction mixture was then stirred for 0.5 h-1 h until substrate 1a had been consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 3: 1) gave **7** in 37% yield as a white solid.



(*Z*)-4,6-diphenyl-3-tosyl-*N*-(tosylmethyl)hex-3-en-5-ynamide (7). White solid, m.p. 215-216 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.38 (s, 3H), 3.48 (s, 2H), 4.75 (d, *J* = 6.5 Hz, 2H), 7.00 (t, *J* = 6.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.33-7.42 (m, 10H), 7.84–7.88 (m, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.65, 21.70, 31.0, 37.9, 60.5, 86.9, 106.3, 121.9, 128.2, 128.41, 128.43, 128.5, 129.0, 129.2, 129.4, 129.7, 130.1, 131.7, 136.9, 137.0, 137.1, 141.0, 144.3, 145.2, 168.6; **HRMS** (ESI) m/z calculated for $C_{33}H_{29}NO_5S_2$ $[M+H]^+$: 518.0950, found: 518.0954.

IV. NMR spectra copies

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3.22
3.06
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141.50
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131.67
60.34
35.21
21.65
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128.20
130.5
128.5
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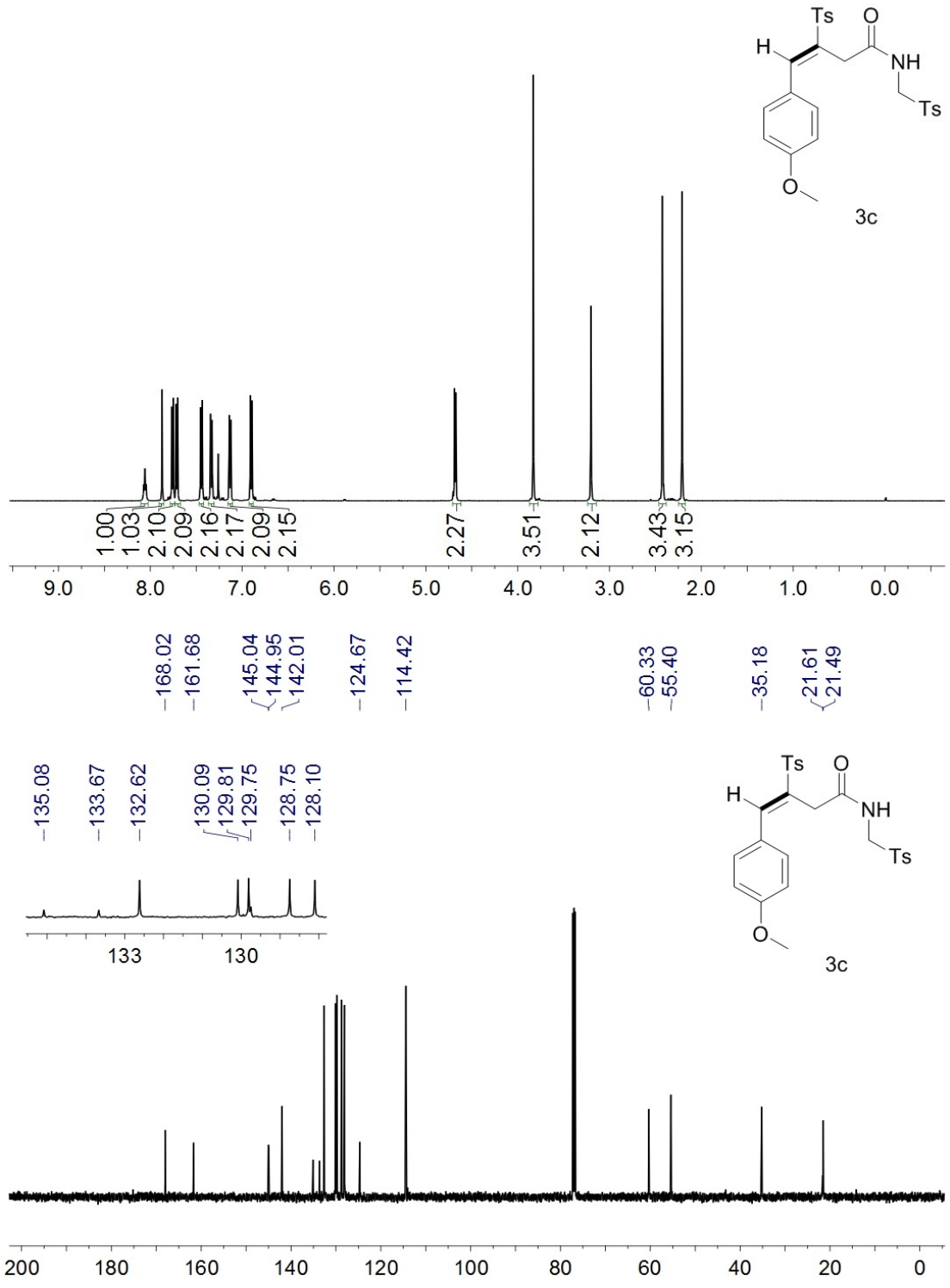
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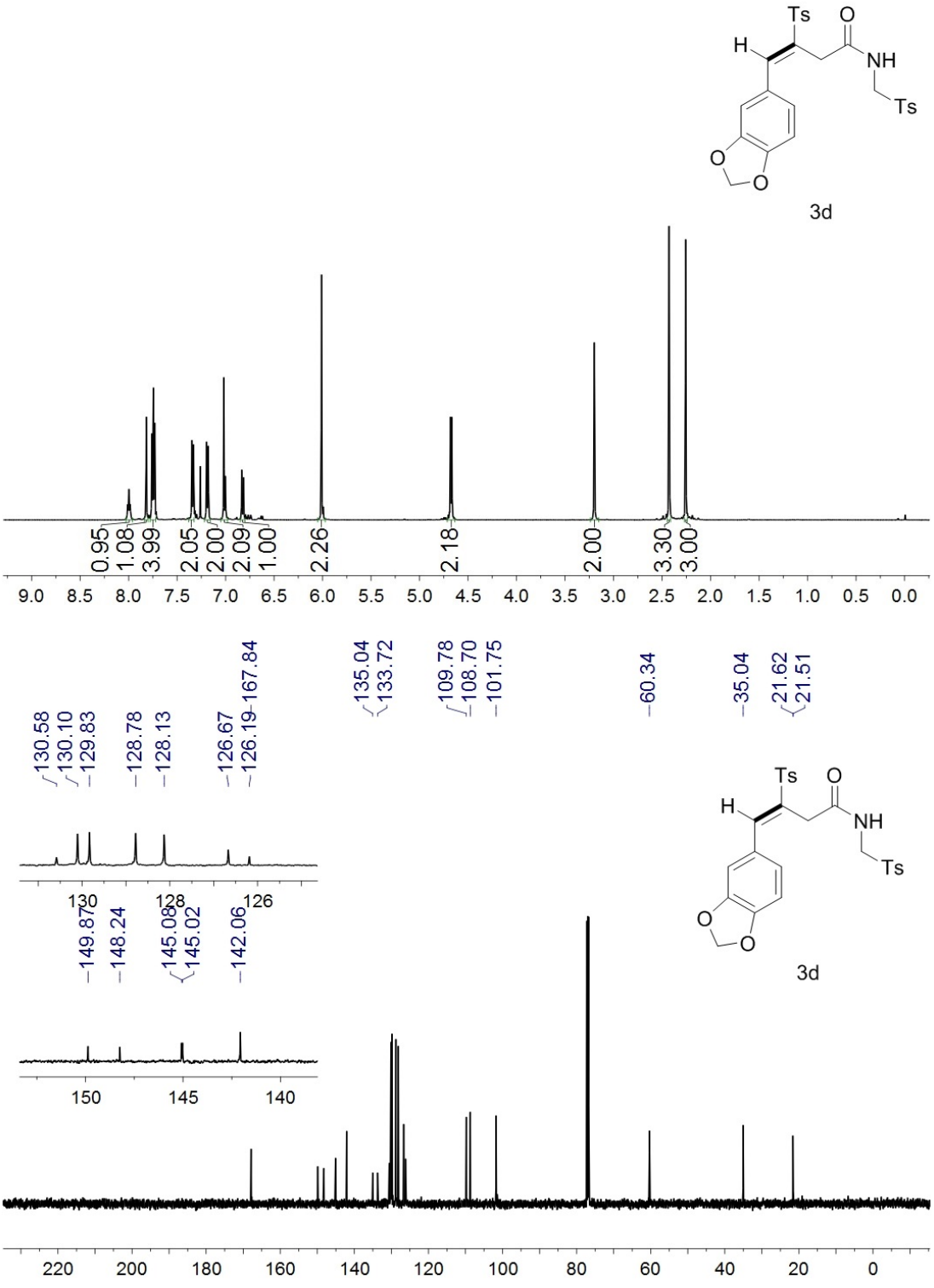
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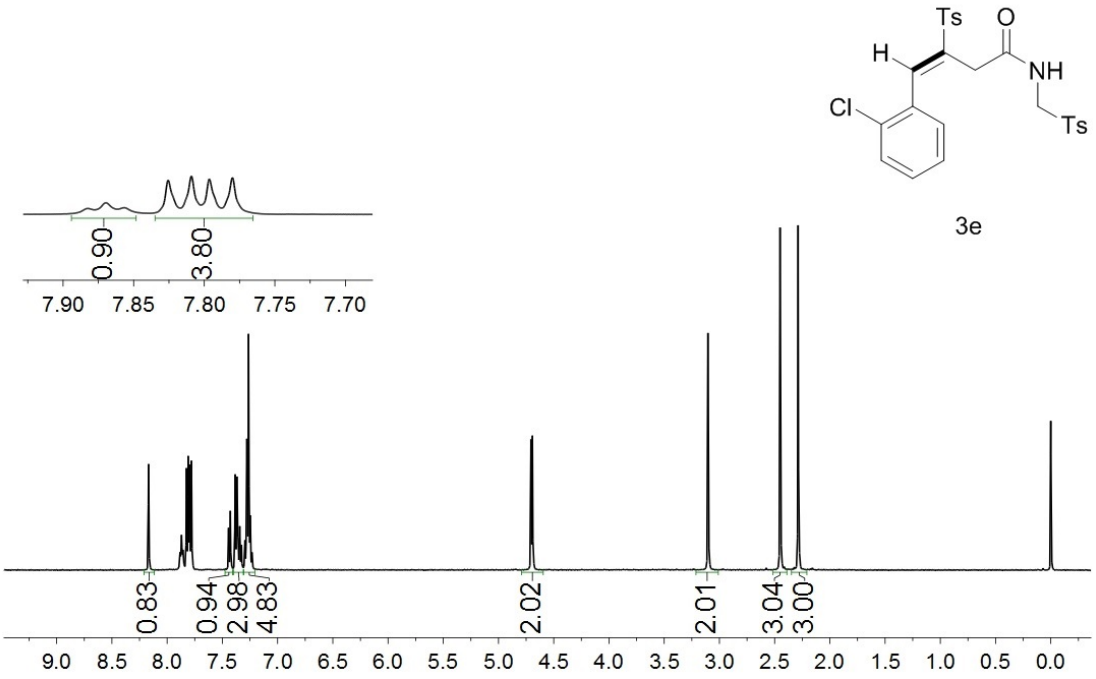
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2.98
4.83
2.02
2.01
3.04
3.00
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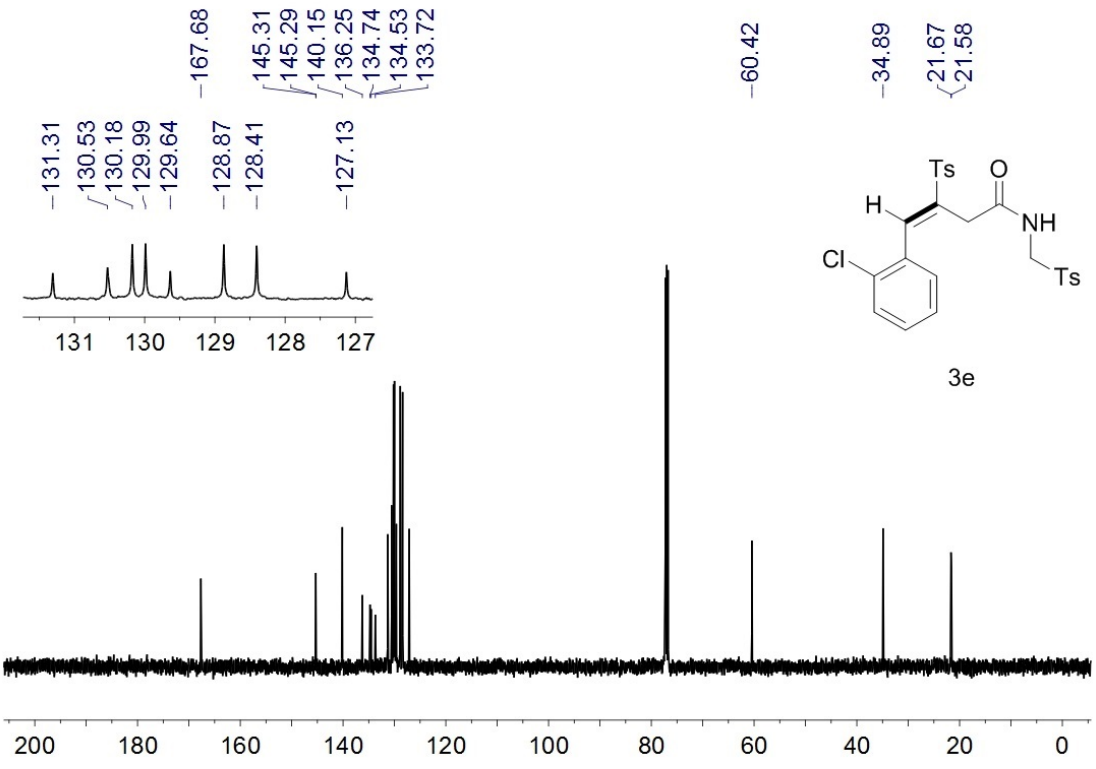
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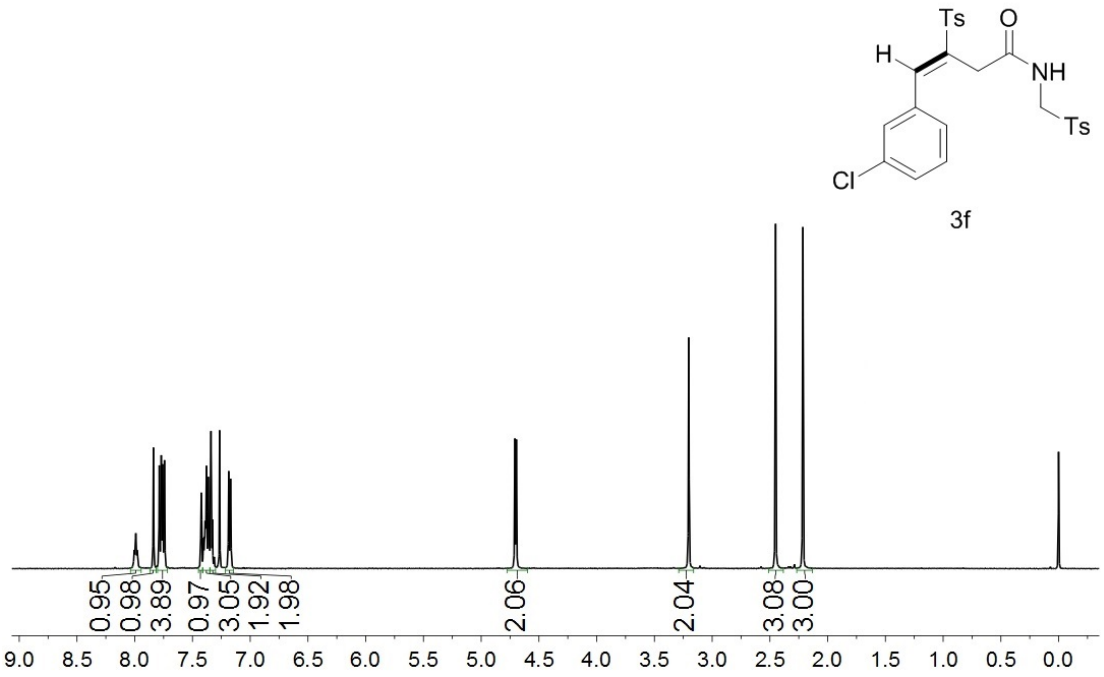
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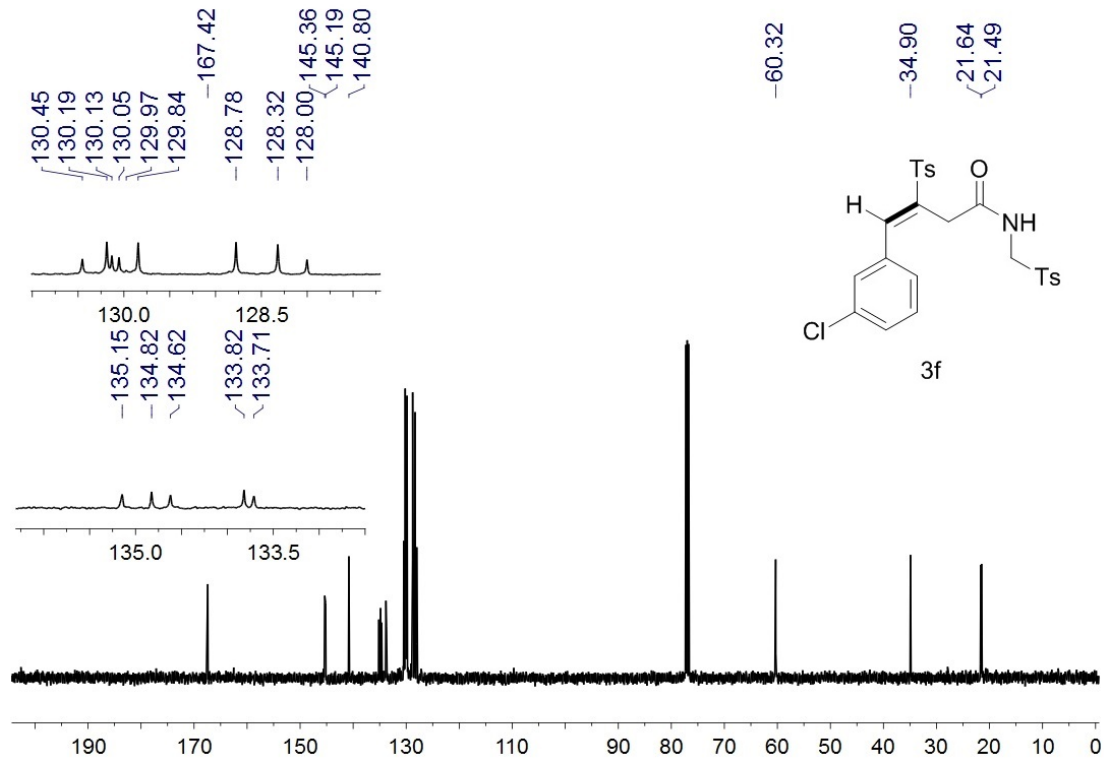
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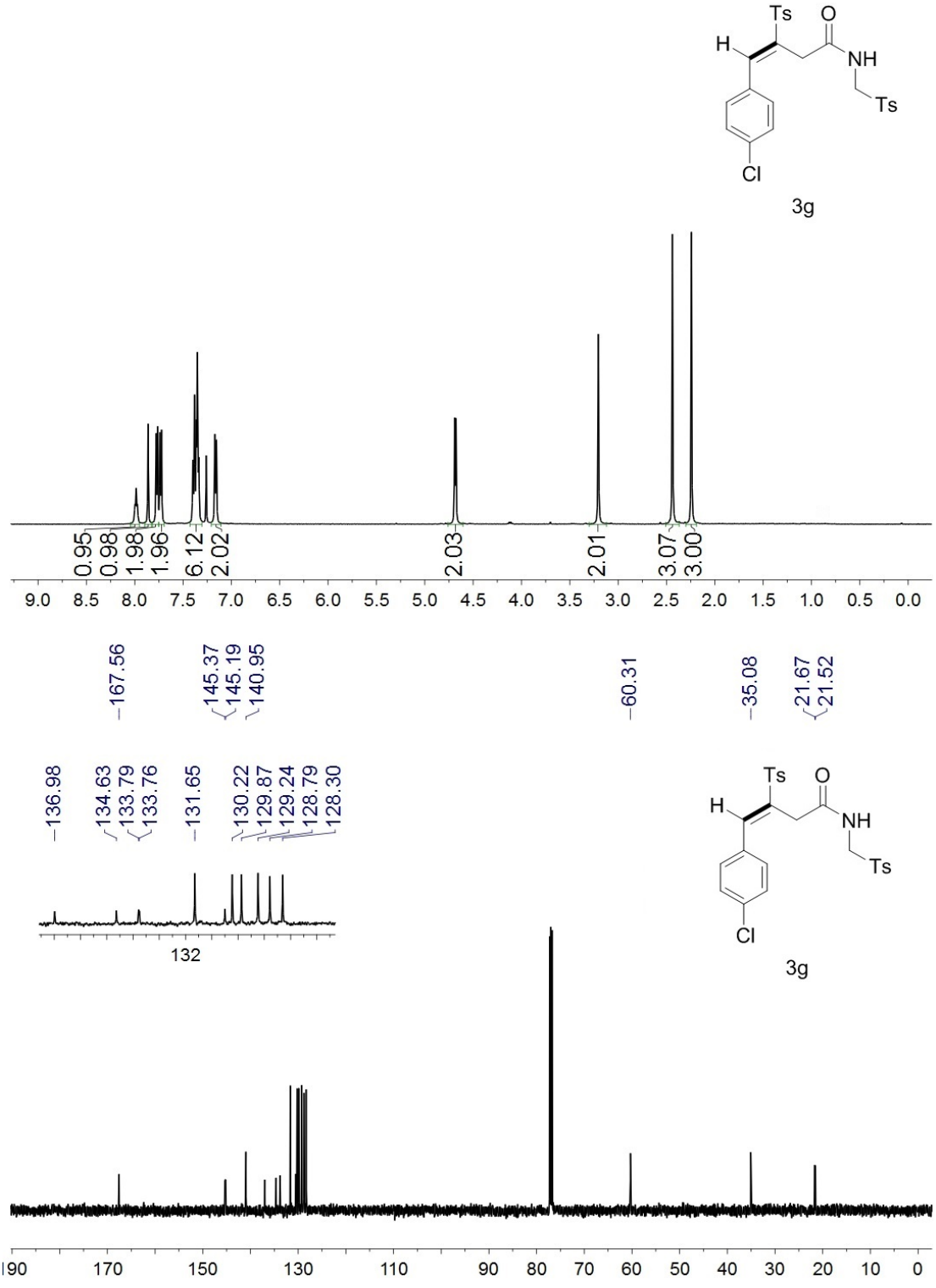
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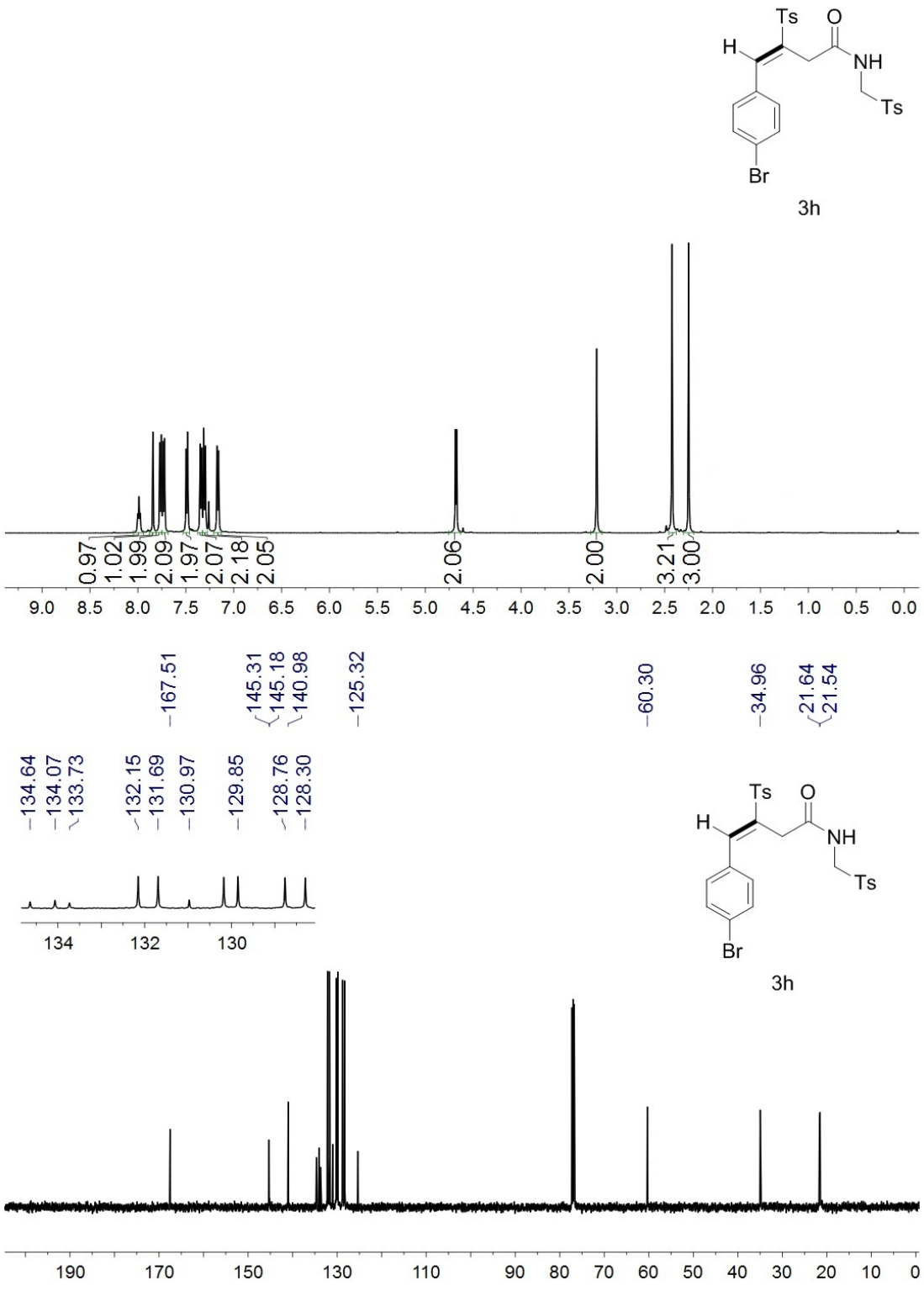
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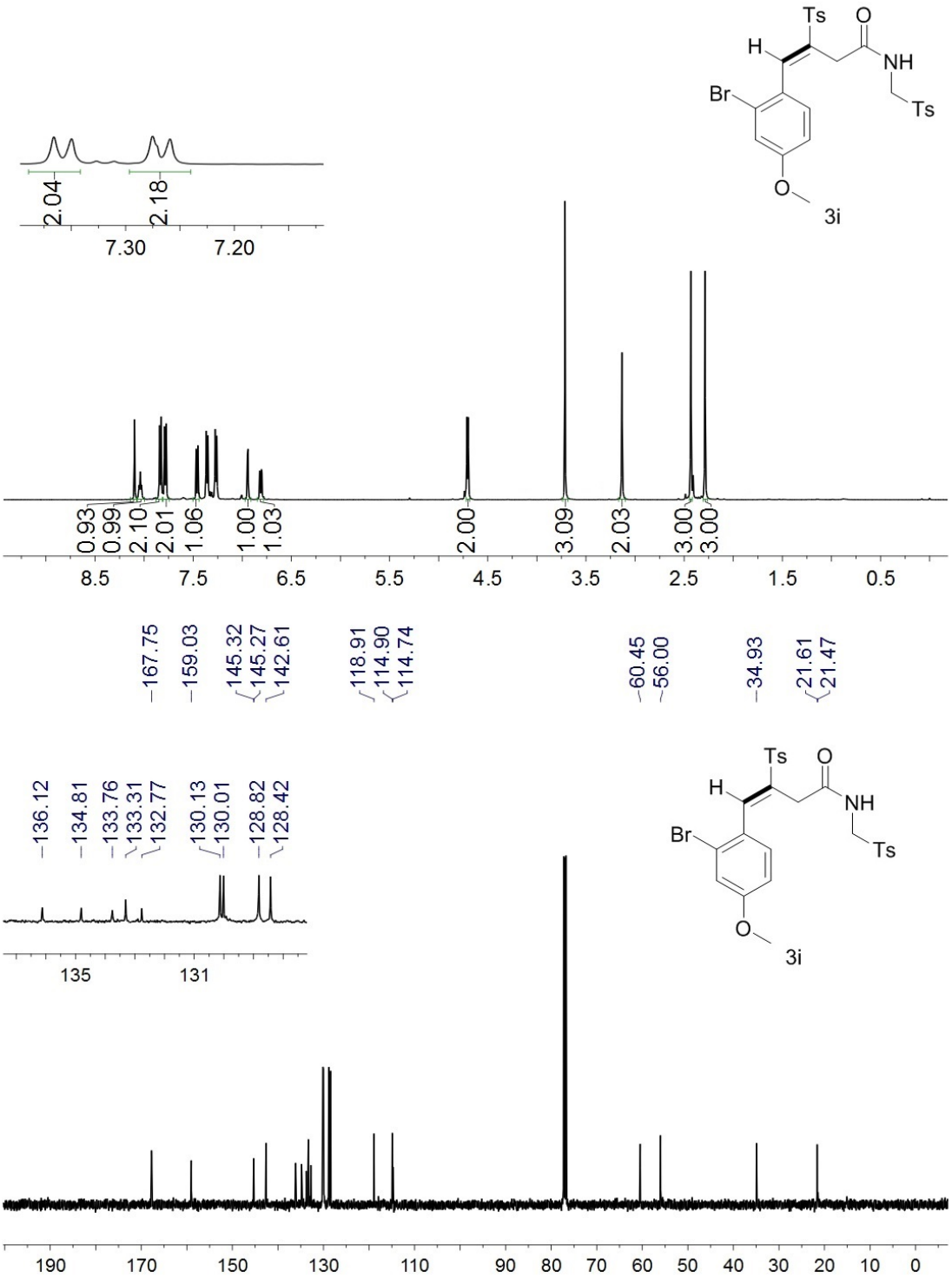
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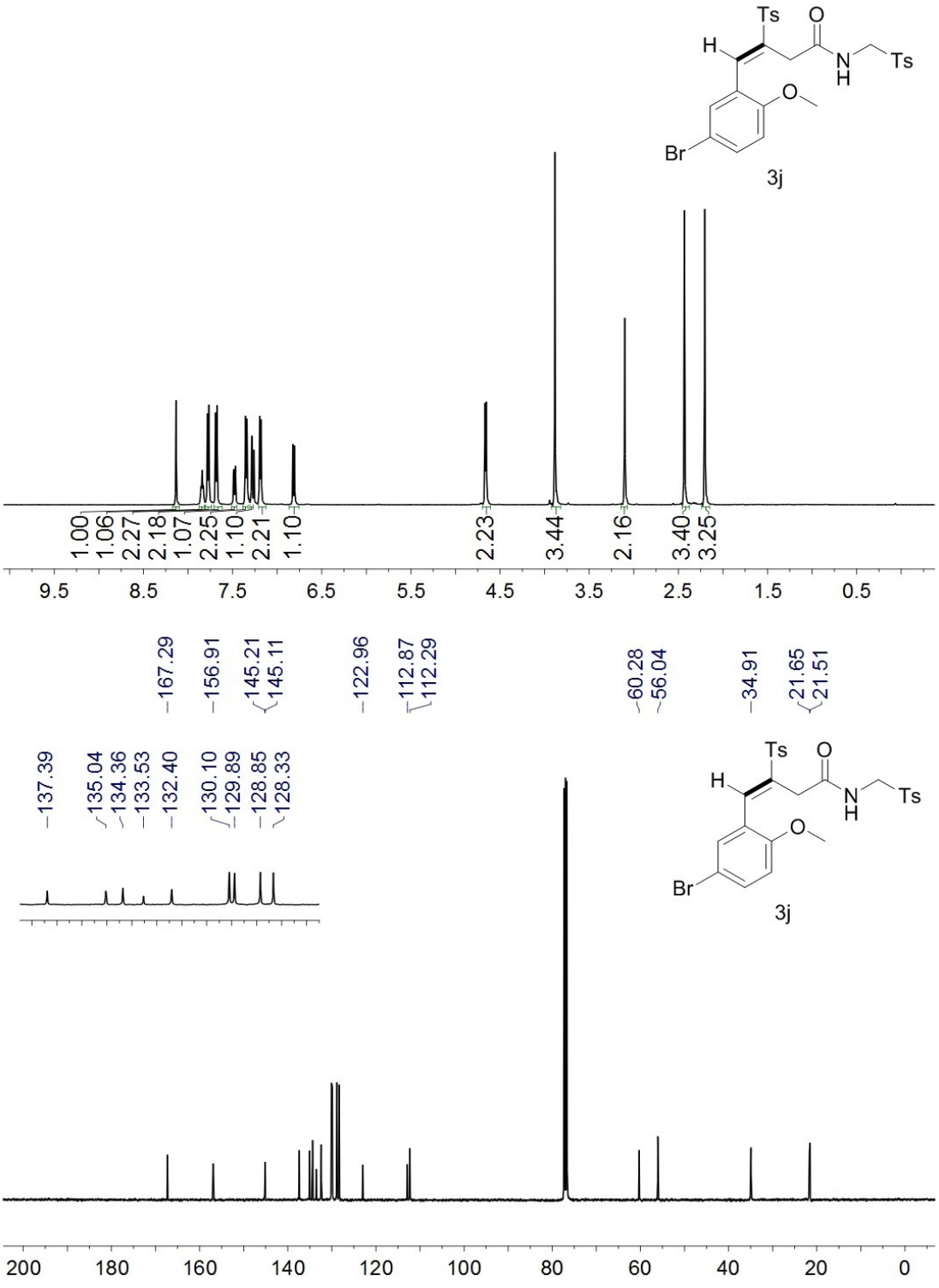
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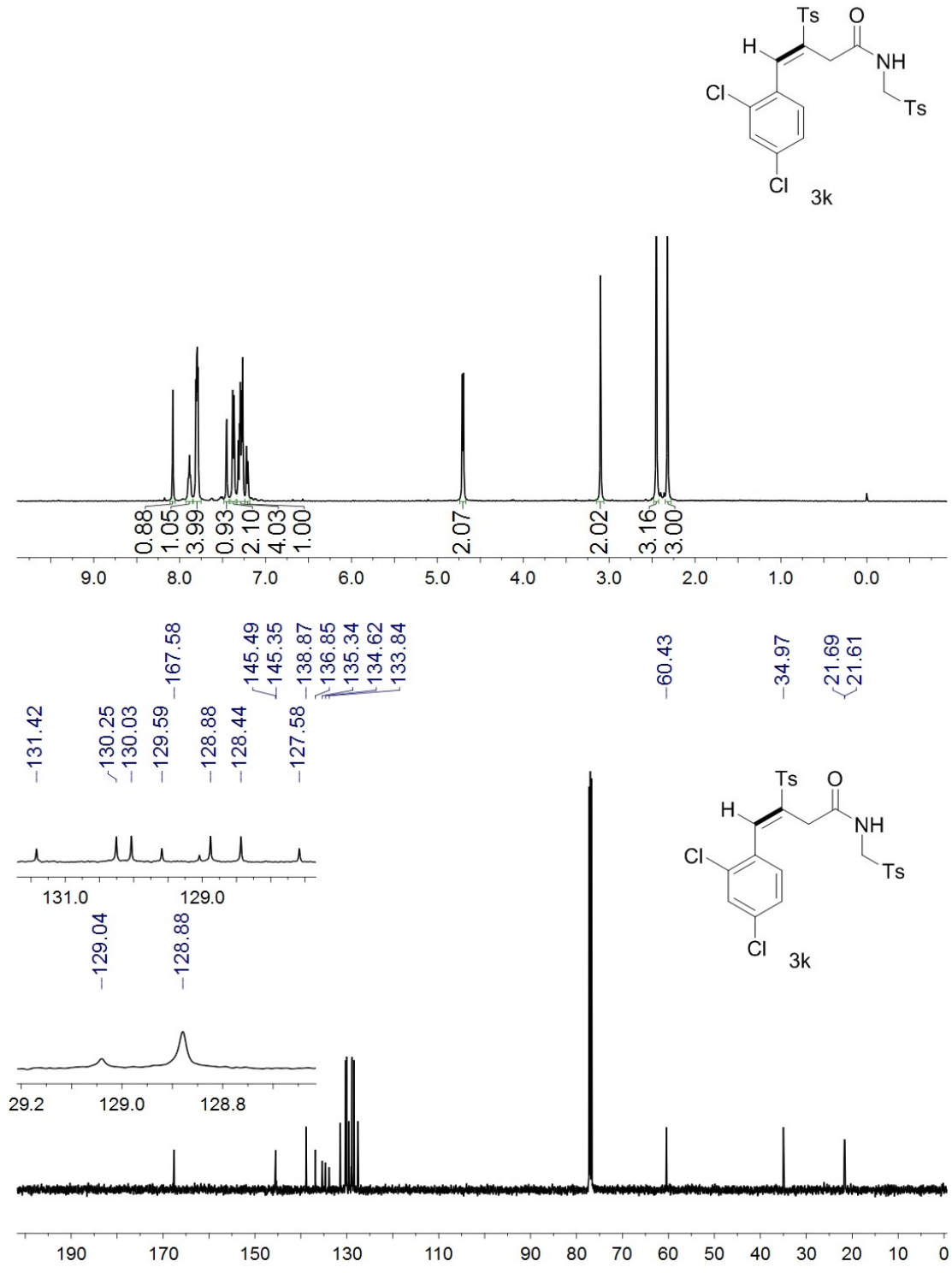
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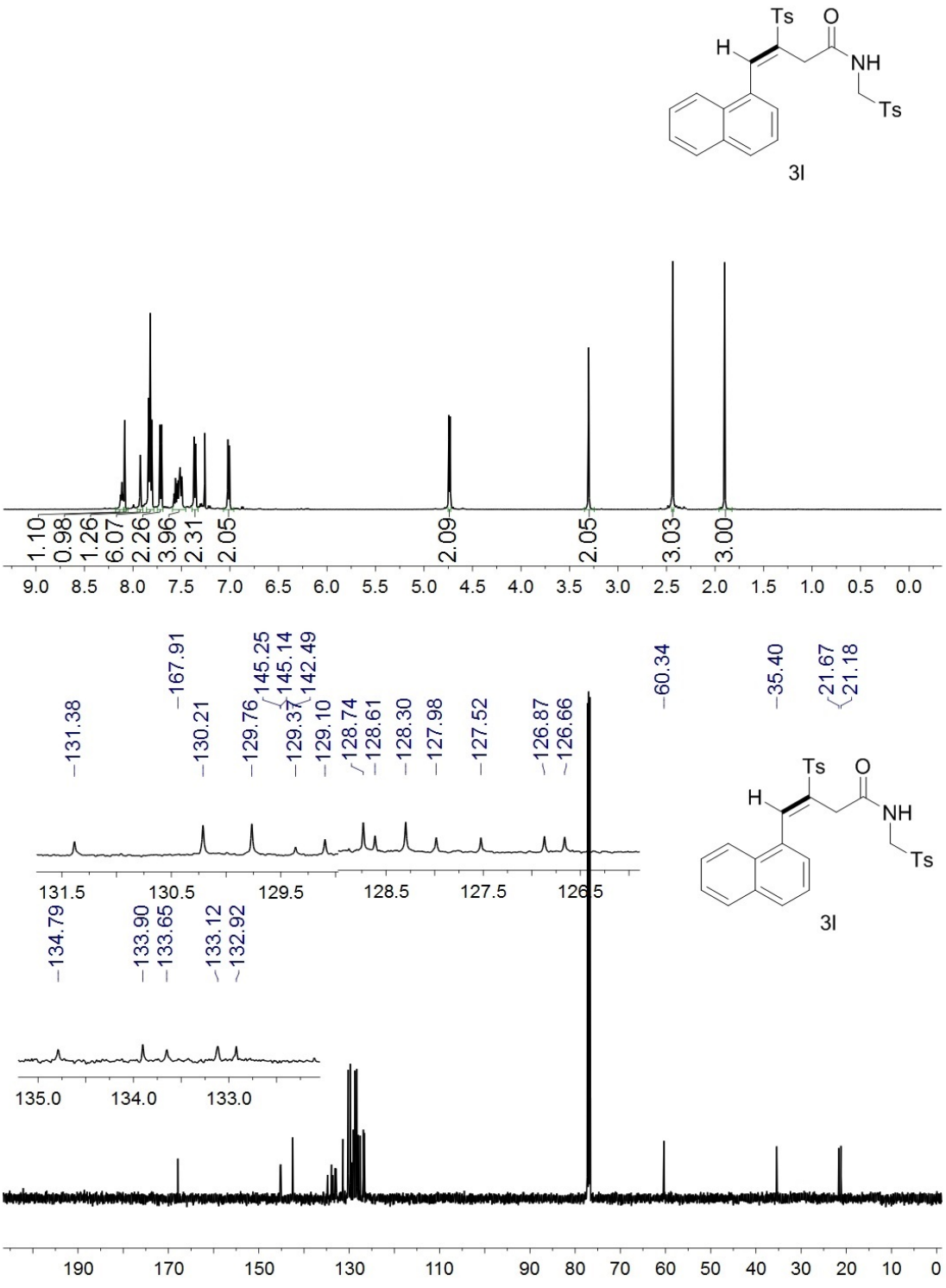
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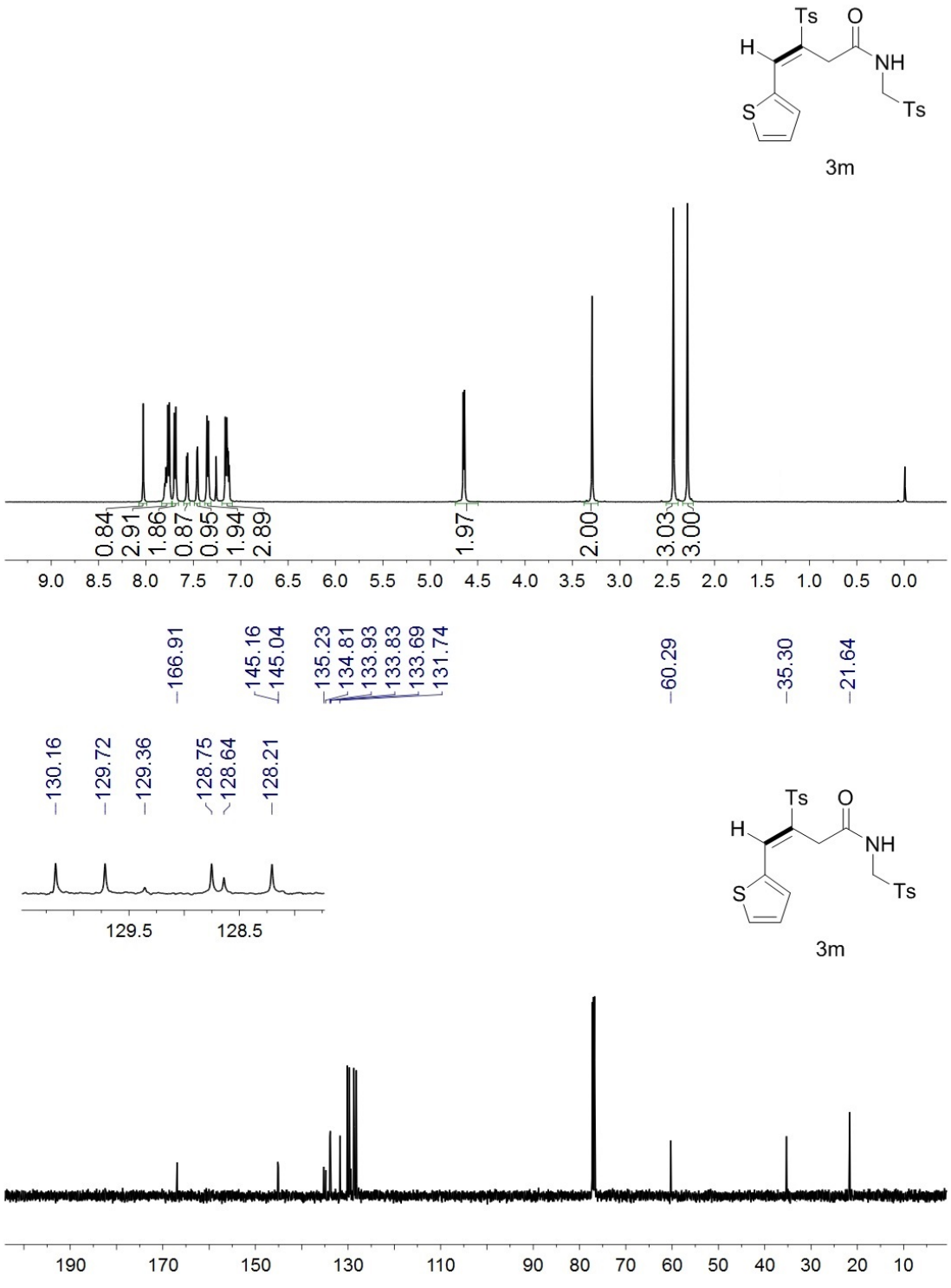
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H
NH
S
Ts
3m
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1.86
0.87
0.95
1.94
2.89
1.97
2.00
3.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
166.91
145.16
145.04
135.23
134.81
133.93
133.83
133.69
131.74
60.29
35.30
21.64
130.16
129.72
129.36
128.75
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128.21
129.5
128.5
Ts
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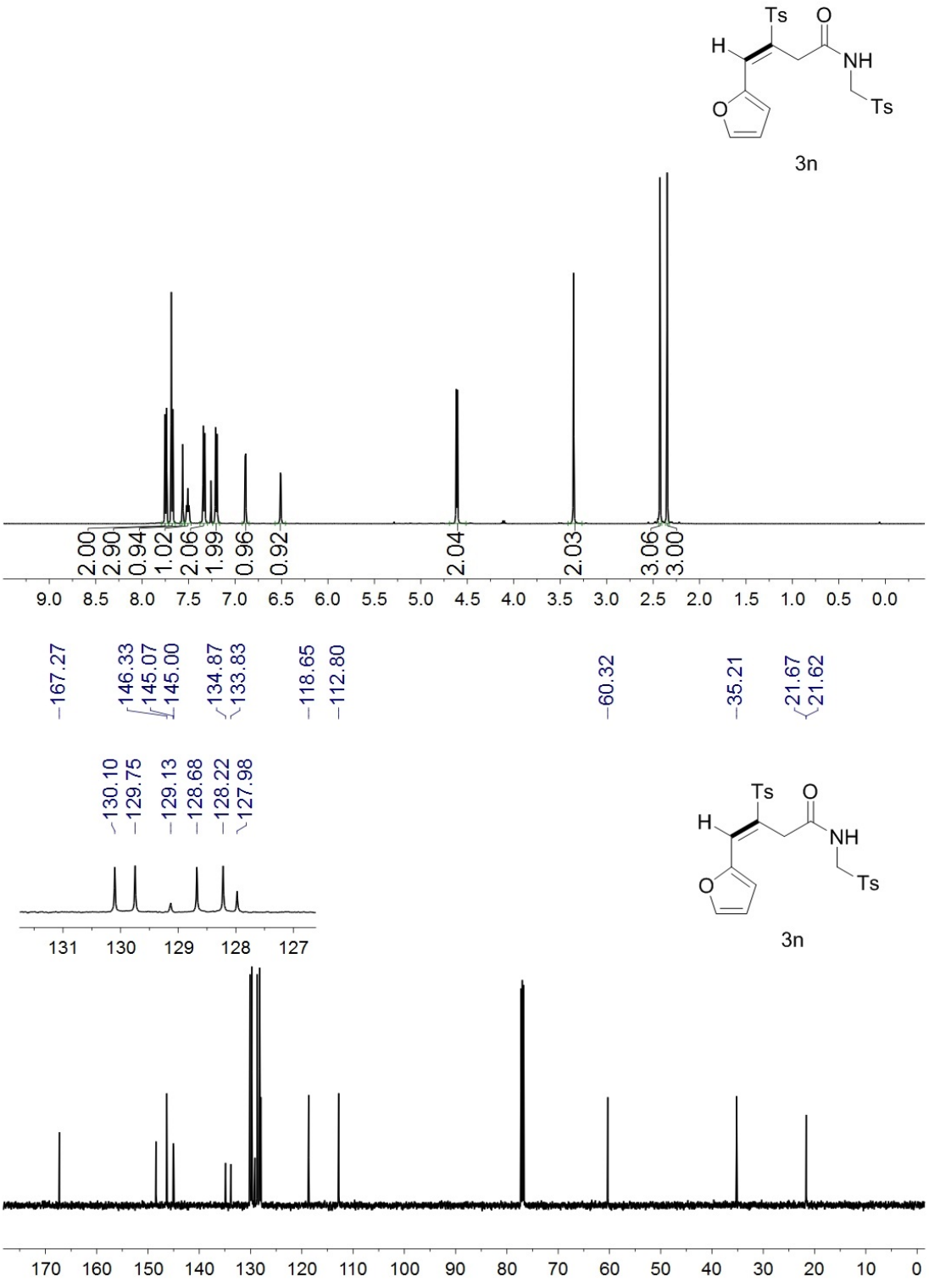
H
NH
S
Ts
3m
190 170 150 130 110 90 80 70 60 50 40 30 20 10


Ts
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NH
O
Ts
3n
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2.04
2.03
3.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
167.27
146.33
145.07
145.00
134.87
133.83
118.65
112.80
60.32
35.21
21.67
21.62
130.10
129.75
129.13
128.68
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131 130 129 128 127
Ts
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H
NH
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Ts
3n
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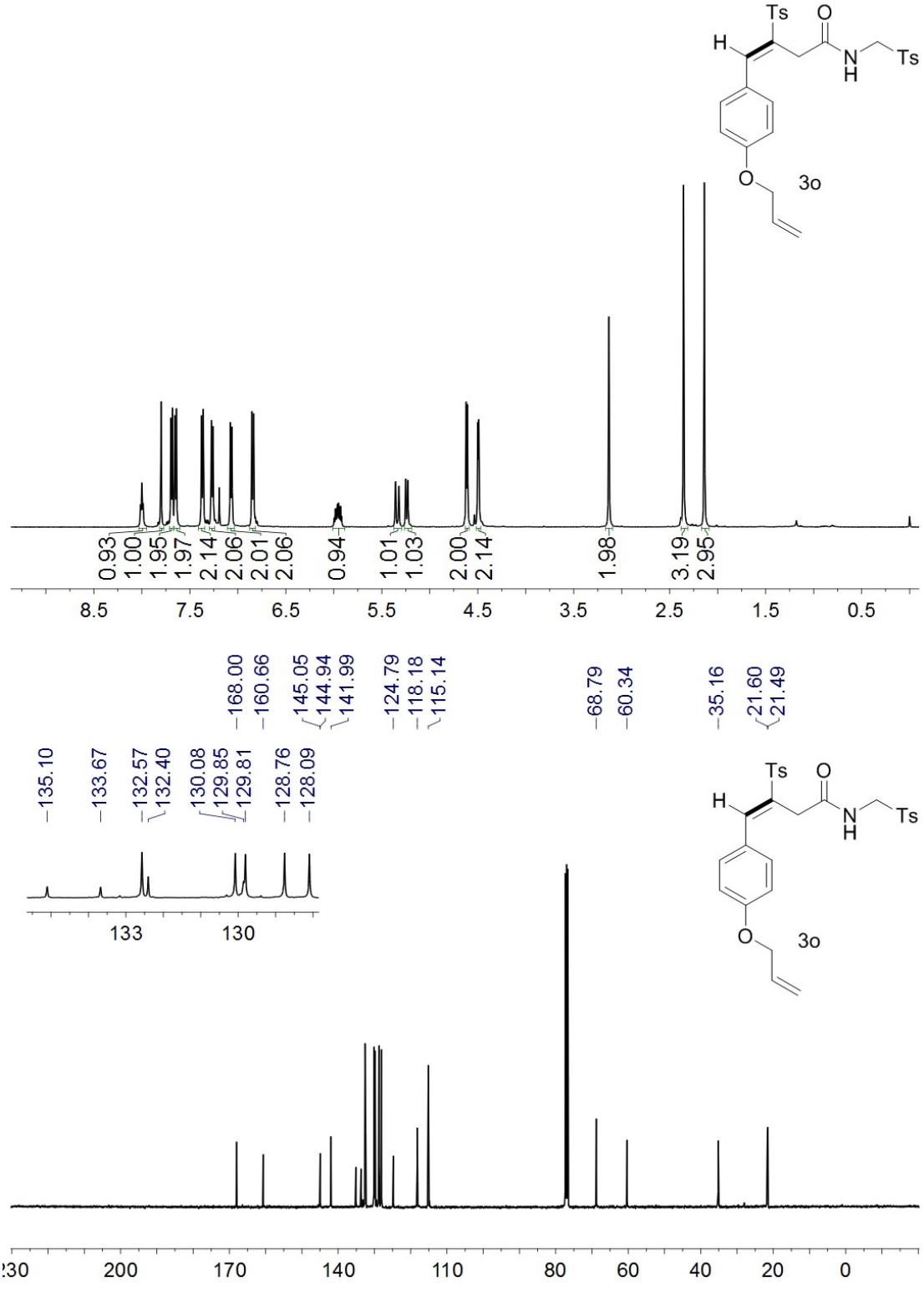
Ts
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H
N
H
Ts
O
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0.94
1.01
1.03
2.00
2.14
1.98
3.19
2.95
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
168.00
160.66
145.05
144.94
141.99
124.79
118.18
115.14
68.79
60.34
35.16
21.60
21.49
135.10
133.67
132.57
132.40
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128.09
133
130
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200
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140
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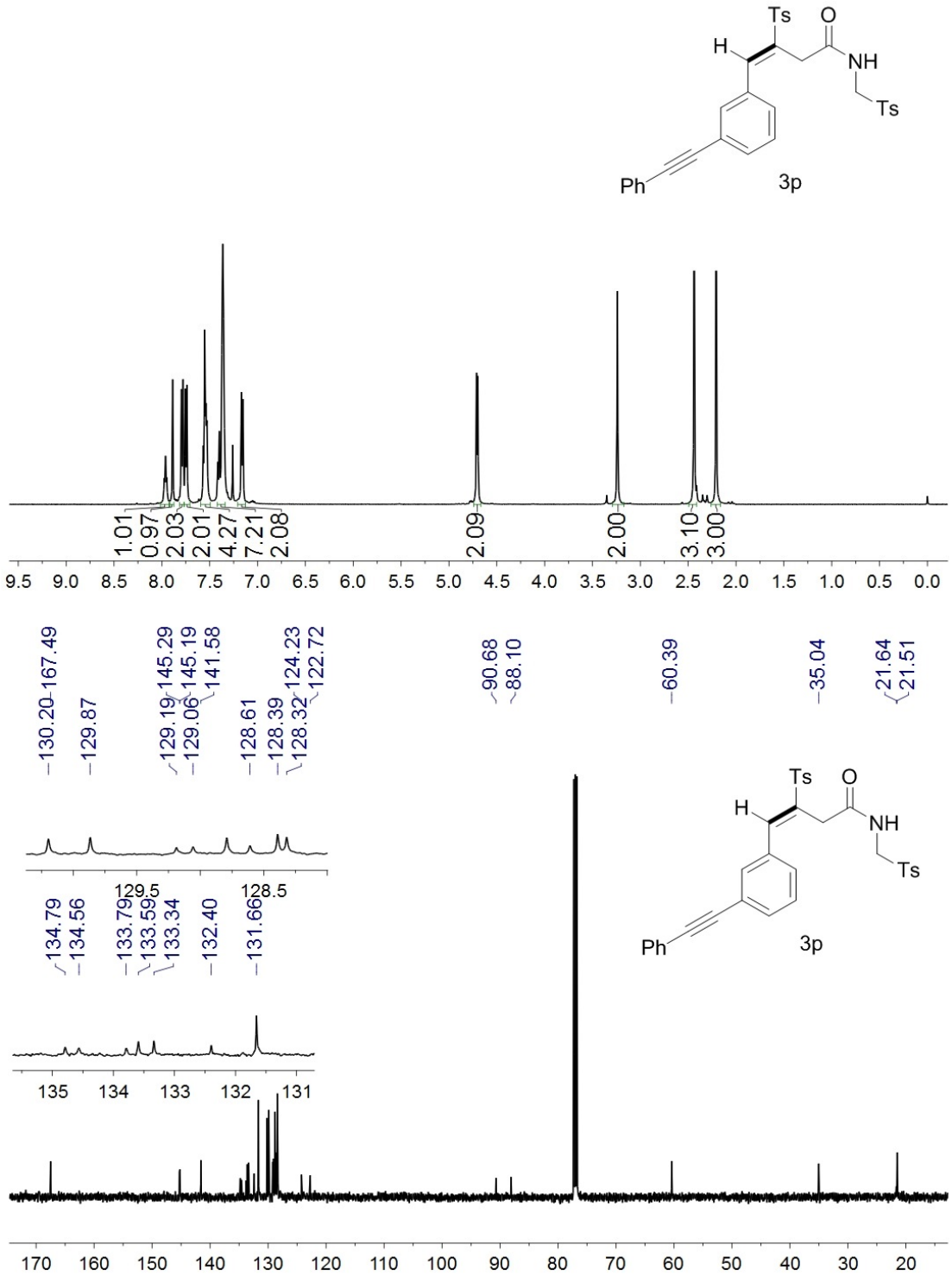
20
0


Ts
O
H
NH
Ts
Ph
3p
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0.97
2.03
2.01
4.27
7.21
2.08
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2.00
3.10
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
130.20
167.49
129.87
129.19
145.29
129.06
145.19
141.58
128.61
128.39
128.32
124.23
122.72
90.68
88.10
60.39
35.04
21.64
21.51
129.5
128.5
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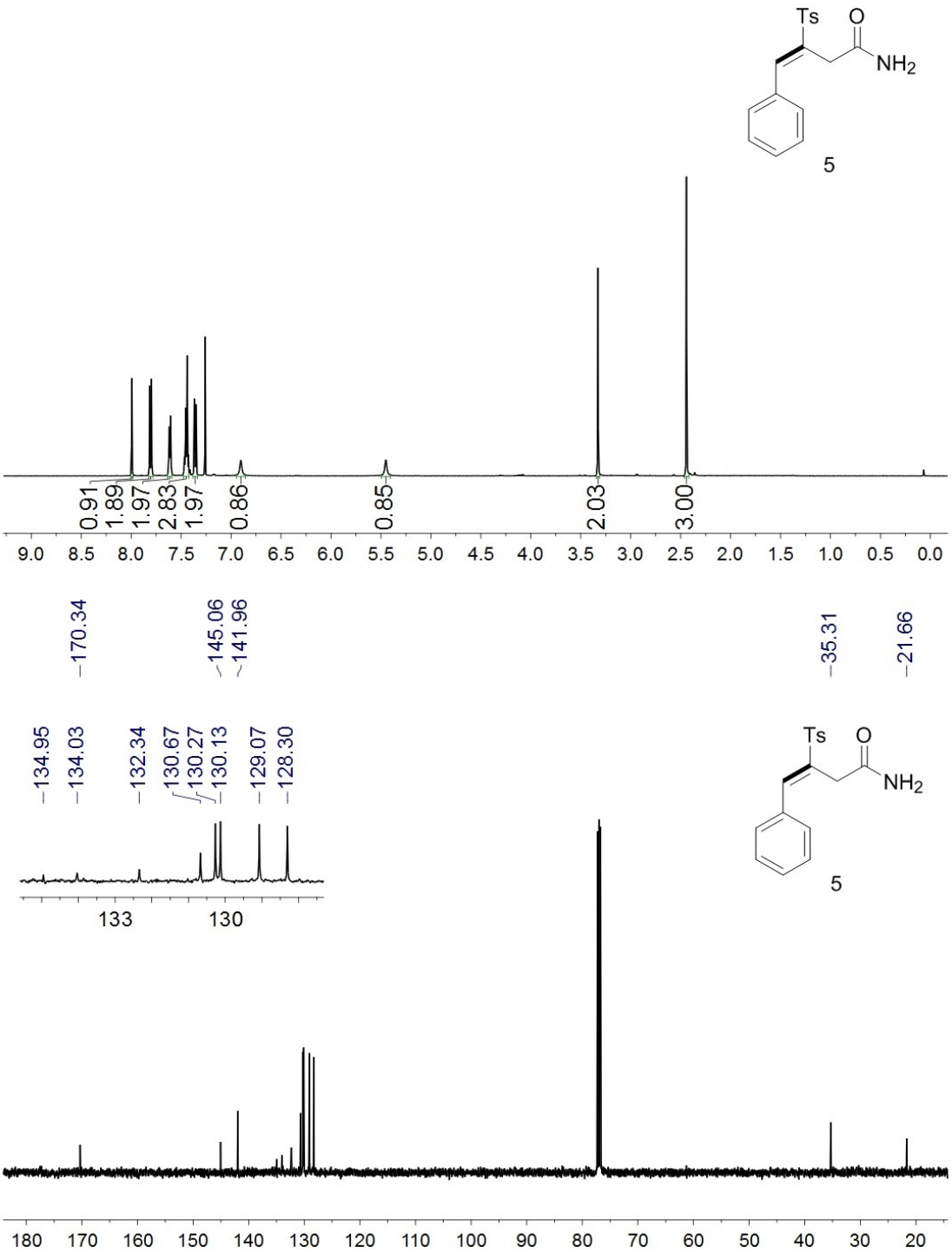
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20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NH2
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1.89
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2.83
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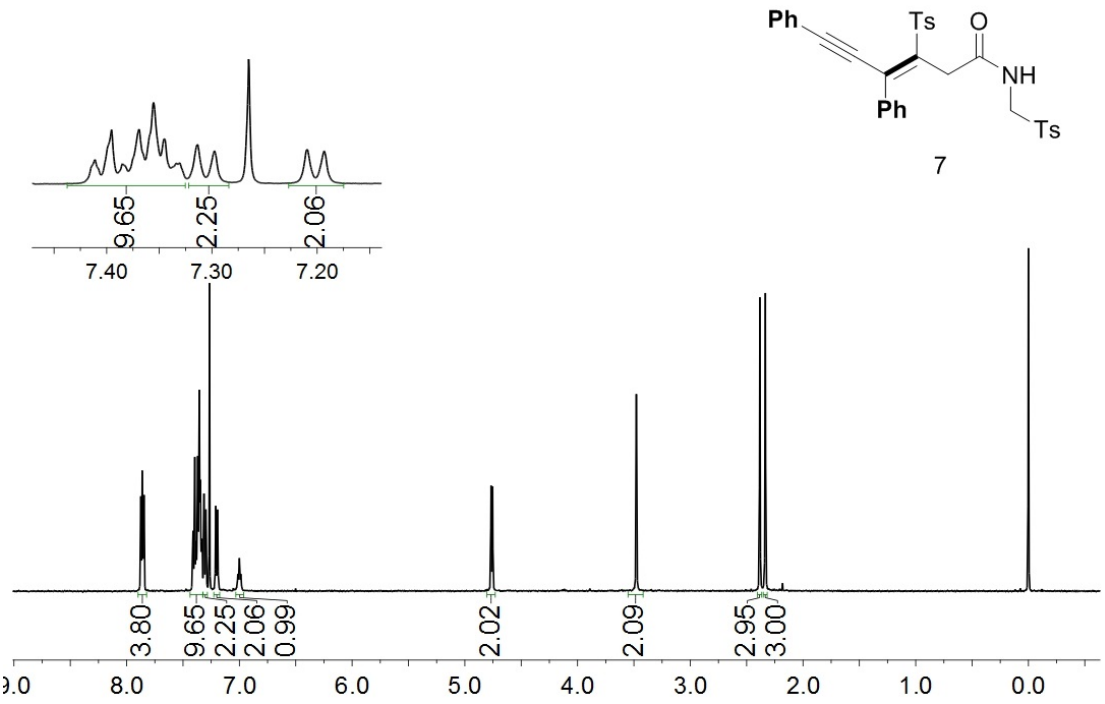
0.86
0.85
2.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
170.34
145.06
141.96
35.31
21.66
134.95
134.03
132.34
130.67
130.27
130.13
129.07
128.30
133
130
Ts
O
NH2
5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20


Ph
Ts
O
NH
Ph
Ts
7
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2.25
2.06
7.40
7.30
7.20
3.80
9.65
2.25
2.06
0.99
2.02
2.09
2.95
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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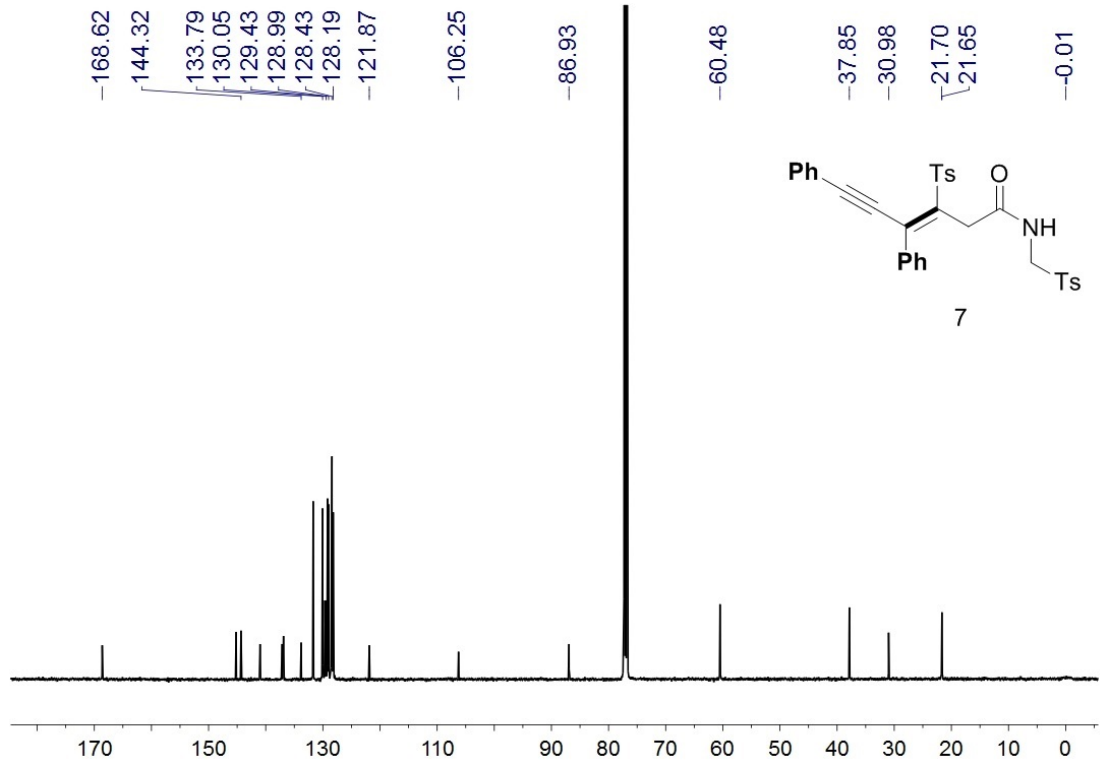
0.0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133.79
130.05
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128.19
121.87
106.25
86.93
60.48
37.85
30.98
21.70
21.65
0.01
Ph
Ts
O
NH
Ph
Ts
7
170
150
130
110
90
80
70
60
50
40
30
20
10
0

2D-NOSEY of **3a**: