Organic & Biomolecular Chemistry

Supporting Information

Copper-catalyzed asymmetric allylation of chiral *N-tert*-butanesulfinyl imines: Dual stereocontrol with nearly perfect diastereoselectivity

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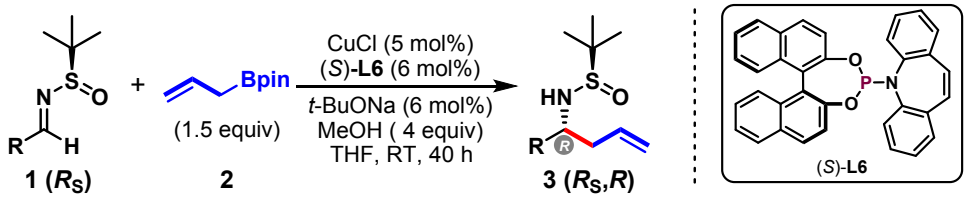
1. General Information

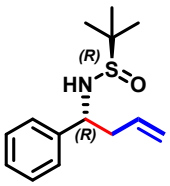
All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz.IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A.

2. General Procedure For The Allylation Of Aldimnes



A dried Schlenk flask was charged with CuCl (0.01mmol, 5 mol%), NaO*t*Bu (0.012 mmol, 6 mol%), (*S*)-**L6** (0.012mmol, 6 mol%), and freshly distilled dry THF (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then allylboronic acid pinacol ester (**2**, 0.4 mmol, 2.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of aldimine **1** (0.2mmol) in freshly distilled THF (1 mL) and MeOH (32 μL, 4.0 equiv) was then added to the Schlenk flask. The mixture was allowed to stir for 40 h at room temperature under argon atmosphere. The resulting mixture was cooled to 0 °C, quenched with ethylenediamine (2 mL) and saturated aqueous NaCl (2 mL), then extracted with ethyl acetate (4 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **3**.

(*R*)-2-Methyl-*N*-((*R*)-1-phenylbut-3-en-1-yl)propane-2-sulfinamide (3a)[1]

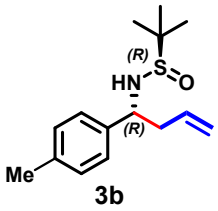


3a

White solid. 97% yield; $[\alpha]_D^{23.5}$ −32.8 (*c* 0.55, $CHCl_3$) for dr > 99:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 1.15 (s, 9H), 2.44−2.51 (m, 1H), 2.62−2.68 (m, 1H), 3.44 (s, 1H), 4.35−4.40 (m, 1H), 4.93−4.98 (m, 2H), 5.50−5.57 (m, 1H), 7.18−7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 22.61, 41.16, 55.93, 58.42, 118.15, 127.21, 127.81, 128.60, 133.74, 141.82.

(1) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

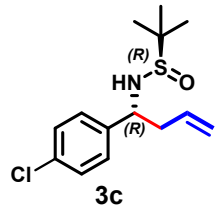
(*R*)-2-Methyl-*N*-((*R*)-1-(*p*-tolyl)but-3-en-1-yl)propane-2-sulfinamide (3b)[2]



3b

White solid. 99% yield; $[\alpha]_D^{24}$ −76.7 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21 (s, 9H), 2.33 (s, 3H), 2.50–2.57 (m, 1H), 2.68–2.76 (m,1H), 3.45 (s, 1H), 4.38–4.43 (m, 1H), 4.99–5.06 (m, 2H), 5.56–5.65 (m, 1H), 7.14 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.20, 22.73, 41.17, 55.96, 58.29, 118.13, 127.23, 129.38, 134.02, 137.61, 138.92.

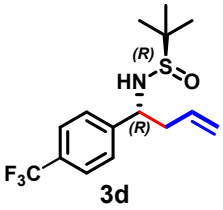
(*R*)-*N*-((*R*)-1-(4-Chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3c)[2]



3c

White solid. 93% yield; $[\alpha]_D^{24}$ −29.9 (*c* 2.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 2.48–2.56 (m, 1H), 2.68–2.75 (m, 1H), 3.48 (s, 1H), 4.41–4.45 (m, 1H), 5.01–5.06 (m, 2H), 5.55–5.65 (m, 1H), 7.25–7.28 (m, 2H), 7.30–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.68, 41.20, 56.15, 57.98, 118.70, 128.70, 128.88, 133.40, 133.65, 140.41.

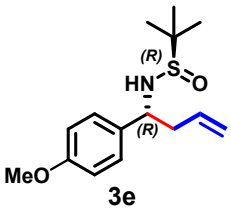
(*R*)-2-Methyl-*N*-((*R*)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)propane-2-sulfinamide (3d)[2]



3d

White solid. 99% yield; $[\alpha]_D^{24}$ −19.0 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 2.49–2.57 (m, 1H), 2.68–2.76 (m, 1H), 3.49 (d, 1H, *J* = 4.00 Hz), 4.46 (dd, 1H, *J* = 11.2, 6.4 Hz), 5.02–5.07 (m, 2H), 5.56–5.66 (m, 1H), 7.19 (d, 2H, *J* = 8.0 Hz) , 7.36 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.69, 41.31, 56.20, 58.07, 118.74, 119.27, 121.11, 121.82, 128.76,133.38, 140.64, 148.80.

(*R*)-*N*-((*R*)-1-(4-Methoxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide(3e)[2]

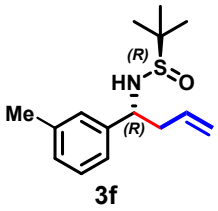


3e

White solid. 98% yield; $[\alpha]_D^{24}$ −29.2 (*c* 2.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 2.48–2.56 (m, 1H), 2.69–2.77 (m, 1H), 3.42 (d, 1H, *J* = 3.2 Hz), 3.80 (s, 3H) 4.37–4.43 (m, 1H), 5.00–5.06 (m, 2H), 5.56–5.67 (m, 1H), 6.87 (d, 2H, *J* = 8.4 Hz) , 7.24 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.70, 41.17, 55.31, 55.92, 57.98, 113.99, 118.13, 128.48, 133.94, 134.02, 159.17.

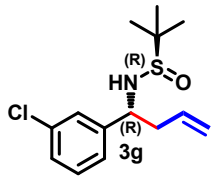
(2) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

(*R*)-2-Methyl-*N*-((*R*)-1-(*m*-tolyl)but-3-en-1-yl)propane-2-sulfinamide (3f)



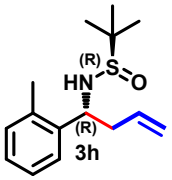
White solid. 99% yield; $[\alpha]_D^{24}$ –51.7 (*c* 2.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 2.35 (s, 1H), 2.50–2.58 (m, 1H), 2.70–2.74 (m, 1H), 3.47 (d, 1H, *J* = 3.2 Hz), 4.37–4.43 (m, 1H), 5.00–5.07(m, 2H), 5.58–5.65 (m, 1H), 7.08–7.13 (m, 1H), 7.21–7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.54, 22.72, 41.26, 56.00, 58.06, 118.09, 124.30, 128.06, 128.60, 128.67, 138.34, 141.91; IR (KBr) *v* (cm^{-1}) 3214, 3074, 2978, 2955, 2923, 2866, 1640, 1608, 1489, 1363, 1058, 913, 786, 705; ESI-MS (m/z): 266.2 $(M+H)^{\oplus}$, 288.1 $(M+Na)^{\oplus}$; HRMS (FTMS-ESI) for $[C_{15}H_{24}NOS]^{\oplus}$: calcd. 266.1579, found 266.1572.

(*R*)-*N*-((*R*)-1-(3-Chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3g)[3]



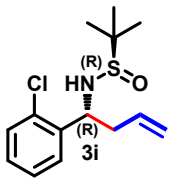
White solid. 92% yield; $[\alpha]_D^{25}$ –28.1 (*c* 3.5, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 2.49–2.55 (m, 1H), 2.67–2.75 (m, 1H), 3.55 (d, 1H, *J* = 4.0 Hz), 4.42 (dd, 1H, *J* = 12.0, 6.0 Hz), 5.02–5.07 (m, 2H), 5.55–5.64 (m, 1H), 7.20–7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.61, 41.16, 56.12, 58.09, 118.66, 125.57, 127.27, 128.01, 129.92, 133.26, 134.45, 143.99.

(*R*)-2-Methyl-*N*-((*R*)-1-(o-tolyl)but-3-en-1-yl)propane-2-sulfinamide (3h)[3]



White solid. 90% yield; $[\alpha]_D^{24}$ –76.5 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21 (s, 9H), 2.38 (s, 3H), 2.56–2.59 (m, 1H), 2.69–2.71 (m, 1H), 3.44(d, 1H, *J* = 2.0 Hz), 4.69–4.74 (m, 1H), 5.00–5.08 (m, 2H), 5.58–5.64 (m, 1H), 7.14–7.20 (m, 3H), 7.35 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.56, 22.73, 40.66, 53.74, 55.97, 118.33, 126.40, 126.41, 127.63, 130.76, 133.91, 135.77, 139.89.

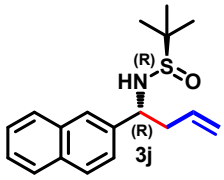
(*R*)-*N*-((*R*)-1-(2-Bromophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3i)[3]



White solid. 91% yield; $[\alpha]_D^{25}$–5.0 (*c* 1.05, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21 (s,9H), 2.60–2.69 (m, 2H), 3.78 (d, 1H, *J* = 5.6 Hz), 4.92 (dd, 1H, *J* =12.4, 6.4 Hz), 5.06–5.11 (m, 2H), 5.63–5.73 (m, 1H), 7.25–7.23 (m, 1H), 7.26–7.30 (m, 1H), 7.35 (dd, 1H, *J* = 8.0, 1.2Hz), 7.42 (dd, 1H, *J* = 7.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.67, 40.43, 56.48, 57.32, 118.87, 123.32,127.69, 128.78, 129.14, 133.24, 133.48, 140.87.

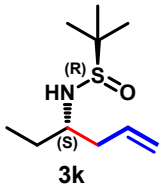
(3) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

(*R*)-2-Methyl-*N*-((*R*)-1-(naphthalen-2-yl)but-3-en-1-yl)propane-2-sulfinamide (3j)[4]



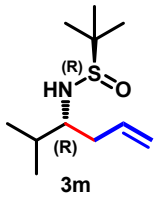
White solid. 94% yield; $[\alpha]_D^{25}$– 59.8 (*c* 0.5, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.24 (s, 9H), 2.61–2.70 (m, 1H), 2.80–2.88 (m, 1H), 3.60 (s,1H), 4.59–4.64 (m, 1H), 5.00–5.08 (m, 2H), 5.59–5.70(m, 1H), 7.44–7.50 (m, 3H), 7.77 (s, 1H), 7.79–7.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.72, 41.08, 56.10, 58.87, 118.36, 125.12, 126.15, 126.32, 126.36, 127.73, 128.08, 128.60, 133.09, 133.30, 133.81, 139.20.

(*R*)-*N*-((*S*)-Hex-5-en-3-yl)-2-methylpropane-2-sulfinamide (3k)[4]



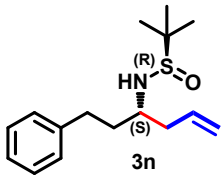
Yellow oil. 99% yield; $[\alpha]_D^{25}$ –73.4 (*c* 1.0, $CHCl_3$); for dr>99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.96 (t, 3H, *J* = 7.6 Hz), 1.20 (s, 9H), 1.57–1.65 (m, 2H), 2.24–2.30 (m, 2H), 3.06 (d, 1H, J = 5.6 Hz), 3.21–3.26 (m, 1H), 5.05–5.10 (m, 2H), 5.73–5.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 10.18, 22.74, 28.55, 39.35, 55.90, 57.38, 117.79, 134.54.

(*R*)-2-Methyl-*N*-((*R*)-2-methylhex-5-en-3-yl)propane-2-sulfinamide (3m)[4]



Yellow oil. 90% yield; $[\alpha]_D^{25}$ –41.4 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.96 (dd, 6H, *J* = 11.6, 6.8 Hz), 1.21(s, 9H), 1.90–1.98 (m, 1H), 2.19–2.30 (m,2H), 3.11–3.16 (m, 2H), 5.04–5.10 (m, 2H), 5.73–5.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.14, 18.32, 31.84, 36.85, 56.02, 61.40, 117.19, 135.28.

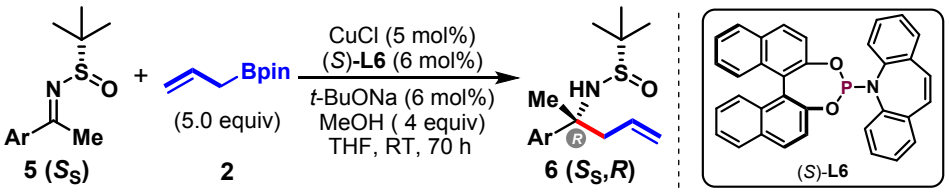
(*R*)-2-Methyl-*N*-((*S*)-1-phenylhex-5-en-3-yl)propane-2-sulfinamide (3n)[4]



White solid. 91% yield; $[\alpha]_D^{25}$ –85.5 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.19 (s, 9H), 1.88–1.94 (m, 2H), 2.33 (t, 2H, *J* = 6.4 Hz), 2.70–2.76 (m, 2H), 3.11 (d, 1H, *J* = 6.0 Hz), 3.35 (dd, 1H, *J* = 12.0, 6.0 Hz), 5.08–5.12 (m, 2H), 5.70–5.81 (m, 1H),7.15–7.22 (m, 3H), 7.24–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.74, 32.00, 37.20, 40.15, 55.58, 55.94, 118.11, 126.04, 128.54, 128.57, 134.30, 141.53.

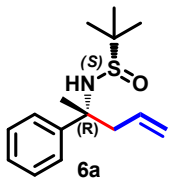
(4) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

3. General Procedure For The Allylation Of Ketimines



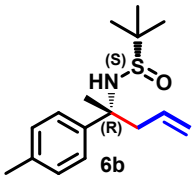
A dried Schlenk flask was charged with CuCl (0.01mmol, 5 mol%), NaO*t*Bu (0.012 mmol, 6 mol%), (*S*)-**L6** (0.012mmol, 6 mol%), and freshly distilled dry THF (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then allylboronic acid pinacol ester (**2**, 0.4 mmol, 2.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of ketimine **5** (0.2 mmol) in freshly distilled THF (1 mL) and MeOH (32 μL, 4.0 equiv) was then transferred to the Schlenk flask. The mixture was allowed to stir for 40 h at room temperature under argon atmosphere. The resulting mixture was cooled to 0 °C, quenched with ethylenediamine (2 mL) and saturated aqueous NaCl (2 mL), then extracted with ethyl acetate (4 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **6**.

(*S*)-2-Methyl-*N*-((*R*)-2-phenylpent-4-en-2-yl)propane-2-sulfinamide (6a)[5]



White solid. 91% yield; $[\alpha]_D^{25}$ +68.7 (c 1.0, $CHCl_3$); for dr > 99:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.23 (s, 9H), 1.77(s, 3H), 2.69 (d, 2H, J = 7.6 Hz), 3.75 (s, 1H), 5.12–5.20 (m, 2H), 5.53–5.61 (m, 1H), 7.23–7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.92, 27.90, 49.17, 56.32, 60.01,120.54, 126.43, 127.12, 128.33, 133.21, 145.42

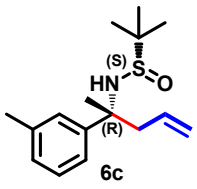
(*S*)-2-Methyl-*N*-((*R*)-2-(p-tolyl)pent-4-en-2-yl)propane-2-sulfinamide (6b)[6]



White solid. 93% yield; $[\alpha]_D^{25}$ +86.8 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 1.75(s, 3H), 2.34(s, 3H), 2.66 (d, 2H, *J* = 7.6 Hz), 3.72 (s, 1H), 5.11–5.19 (m, 2H), 5.53–5.62 (m, 1H), 7.15 (d, 2H, *J* = 8.0 Hz), 7.32 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.05, 22.92, 27.93, 49.21, 56.27, 59.80, 120.35, 126.37, 129.03, 133.37, 136.74, 142.45.

(5) J. A. Sirvent, F. Foubelo and M. Yus, *Chem. Commun.*, 2012, **48**, 2543.
(6) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

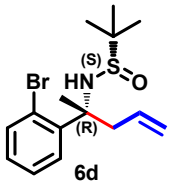
(*S*)-2-Methyl-*N*-((*R*)-2-(m-tolyl)pent-4-en-2-yl)propane-2-sulfinamide (6c)[7]



6c

White solid. 93% yield; $[\alpha]_D^{25}$ +52.1 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.23 (s, 9H), 1.76(s, 3H), 2.36 (s, 3H), 2.67 (d, 2H, *J* = 7.2 Hz), 3.73 (s, 1H), 5.12–5.20 (m, 2H), 5.54–5.62 (m, 1H), 7.06–7.08 (m, 1H), 7.22–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.79, 22.94, 27.89, 49.26, 56.32, 59.95, 120.42, 123.53, 127.24, 127.84, 128.21, 133.38, 137.82, 145.59.

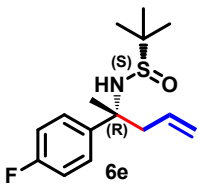
(*S*)-*N*-((*R*)-2-(2-Bromophenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6d)[8]



6d

Yellow solid. 91% yield; $[\alpha]_D^{25}$ +37.3 (*c* 0.2, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.23 (s, 9H), 1.90 (s, 3H), 3.10–3.23 (m, 2H), 4.57 (s, 1H), 5.05 (d, 1H, *J* = 6.4 Hz), 5.09–5.18 (m, 1H), 5.41–5.51 (m, 1H), 7.09–7.14 (m, 1H), 7.27–7.31 (m, 1H), 7.49 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.61 (dd, *J* = 8.0, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.97, 26.23, 45.30, 56.31, 61.04, 119.57, 121.71, 127.51, 128.95, 129.01, 133.44, 135.94.

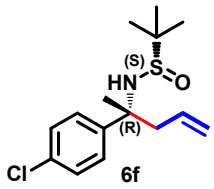
(*S*)-*N*-((*R*)-2-(4-Fluorophenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6e)[7]



6e

White solid. 92% yield; $[\alpha]_D^{24}$ +62.5 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 1.76 (s, 3H), 2.64 (d, 2H, *J* = 7.6 Hz), 3.72 (s, 1H), 5.13–5.19 (m, 2H), 5.50–5.60 (m, 1H), 7.00–7.04 (m, 2H), 7.38–7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.90, 27.93, 49.34, 56.34, 59.71, 115.08 (d, 1C, *J* = 20.5 Hz), 120.70, 128.27, 128.36, 132.93, 141.06, 161.84 (d, 1C, *J* = 222.5 Hz).

(*S*)-*N*-((*R*)-2-(4-Chlorophenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6f)[7]

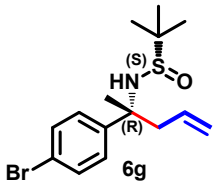


6f

White solid. 92% yield; $[\alpha]_D^{25}$ +59.7 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (s, 9H), 1.76 (s, 3H), 2.63 (d, 2H, *J* = 7.2 Hz), 3.74 (s, 1H), 5.13–5.19 (m, 2H), 5.51–5.56 (m, 1H), 7.31 (d, 2H, *J* = 8.8 Hz), 7.37 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.90, 27.77, 49.19, 56.41, 59.77, 120.84, 128.07, 128.45, 132.77,133.02, 143.95.

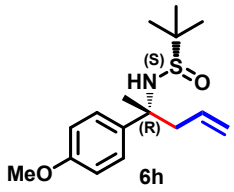
(7) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.
(8) J. A. Sirvent, F. Foubelo and M. Yus, *Eur. J. Org. Chem.*, 2013, 2461.

(*S*)-*N*-((*R*)-2-(4-Bromophenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6g)[9]



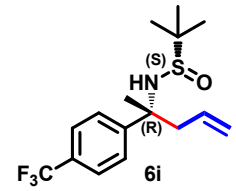
Yellow solid. 91% yield; $[\alpha]_D^{24}$ +48.6 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21 (s, 9H), 1.75 (s, 3H), 2.62 (d, 2H, *J* = 7.2 Hz), 3.72 (s, 1H), 5.13–5.19 (m, 2H), 5.50–5.56 (m, 1H), 7.30 (d, 2H, *J* = 8.8 Hz), 7.46 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.91, 27.75, 49.17, 56.42, 59.81, 120.90, 121.21, 128.43, 131.43, 132.75, 144.53.

(*S*)-*N*-((*R*)-2-(4-Methoxyphenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6h)[9]



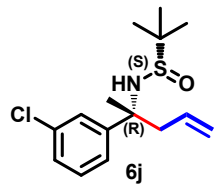
White solid. 93% yield; $[\alpha]_D^{25}$ +67.9 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.21 (s, 9H), 1.74(s, 3H), 2.64 (d, 2H, *J* = 7.6 Hz), 3.69 (s, 1H), 3.81 (s, 3H), 5.11–5.18 (m, 2H), 5.50–5.62 (m, 1H), 6.87 (d, 2H, *J* = 8.4 Hz), 7.35 (d, 2H, *J* = 8.4 Hz) ;^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.91, 27.90, 49.34, 55.29, 56.23, 59.63, 113.54, 120.26, 127.76, 133.39, 137.33, 158.54.

(*S*)-2-Methyl-*N*-((*R*)-2-(4-(trifluoromethyl)phenyl)pent-4-en-2-yl)propane-2-sulfinamide (6i)[9]



White solid. 90% yield; $[\alpha]_D^{25}$ +41.0 (*c* 1.0, $CHCl_3$); dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.24 (s, 9H), 1.80 (s, 3H), 2.67 (d, 2H, *J* = 7.6 Hz), 3.82 (s, 1H), 5.15–5.21 (m, 2H), 5.50–5.57 (m, 1H), 7.56 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.90, 27.80, 29.77, 49.09, 56.53, 59.99, 121.23, 122.80, 125.25, 125.29, 125.33, 125.36, 126.93, 129.19, 129.51, 132.47, 149.55.

(*S*)-*N*-((*R*)-2-(3-Chlorophenyl)pent-4-en-2-yl)-2-methylpropane-2-sulfinamide (6j)[9]

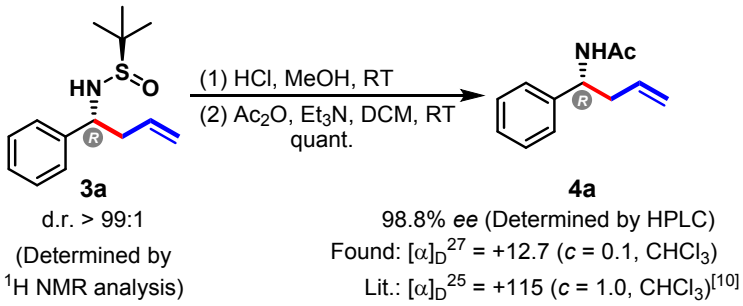


White solid. 91% yield; $[\alpha]_D^{24}$ +35.5 (*c* 1.0, $CHCl_3$); for dr > 99:1; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.24 (s, 9H), 1.77 (s, 3H), 2.64 (d, 2H, *J* = 7.2 Hz), 3.75 (s, 1H), 5.15–5.21 (m, 2H), 5.50–5.60 (m, 1H), 7.22–7.25 (m, 1H), 7.26–7.34 (m, 2H), 7.40–7.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.90, 27.74, 49.18, 56.48, 59.84, 121.05, 124.67, 127.00, 127.27, 129.61, 132.67, 134.28, 147.72.

(9) X.-W. Sun, M.-H. Xu and G.-Q. Lin, *Org. Lett.*, 2006, **8**, 4979.

4. DETERMINATION OF THE DR/EE VALUES

The dr value of the allylation aldimine product was determined by ^{1}H NMR analysis of the crude products. In the case of product **3a**, the dr value was further confirmed by the HPLC analysis of its acetyl derivative **4a**, which ensured the accuracy of ^{1}H NMR analysis.[10]



3a
d.r. > 99:1
(Determined by ^{1}H NMR analysis)

4a
98.8% *ee* (Determined by HPLC)
Found: $[\alpha]_D^{27}$ = +12.7 (*c* = 0.1, $CHCl_3$)
Lit.: $[\alpha]_D^{25}$ = +115 (*c* = 1.0, $CHCl_3$)[10]

HPLC: Daicel Chiralpak OD-H column, detected at 214 nm, eluent: *n*-hexane / *iso*- propanol = 90:10.

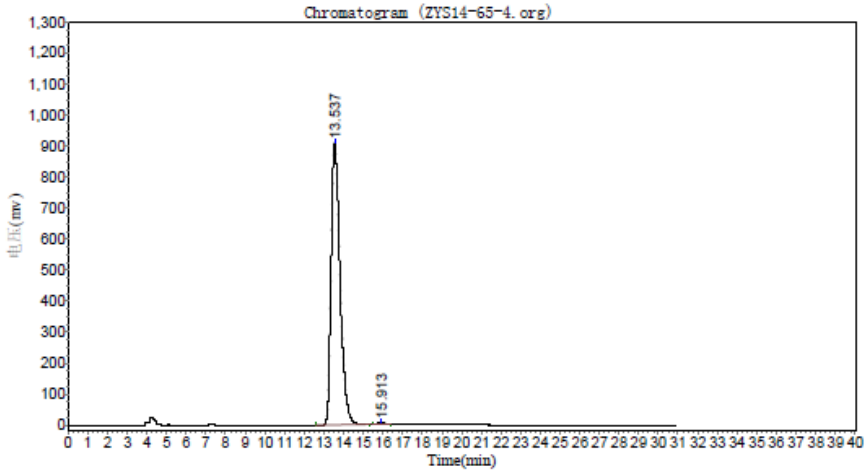
(a) Determined by ^{1}H NMR analysis

d.r.[(*R*s,*R*) :(*R*s,*S*)] = >99:1

[10] (a) A. Hietanen, T. Saloranta, S. Rosenberg, E. Laitinen, R. Leino and L. T. Kanerva, *Eur. J. Org. Chem.*, 2010, 909; (b) T. Kohara, Y. Hashimoto and K. Saigo, *Tetrahedron*, 1999, **55**, 6453.

(b) Confirmed by the HPLC analysis of its acetyl derivative.

Sample Description:
OD-H;n-hexane/iPrOH=90/10 , 0.7ml/min, 214 nm



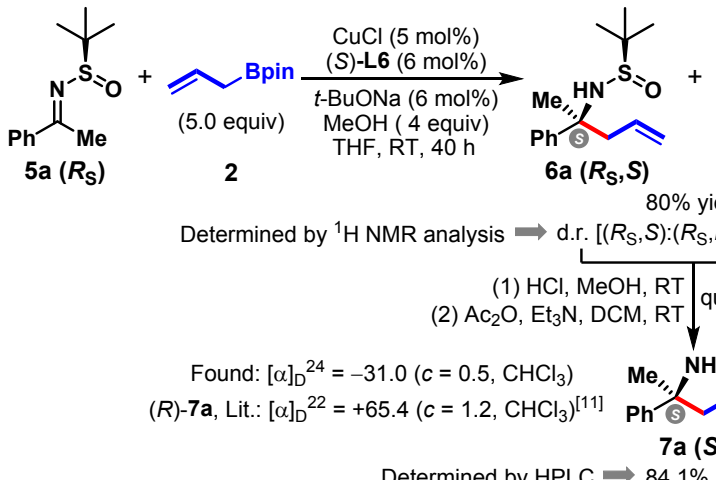
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.537	909873.500	29067844.000	99.4094
2		15.913	5903.666	172680.406	0.5906
Total			915777.166	29240524.406	100.0000

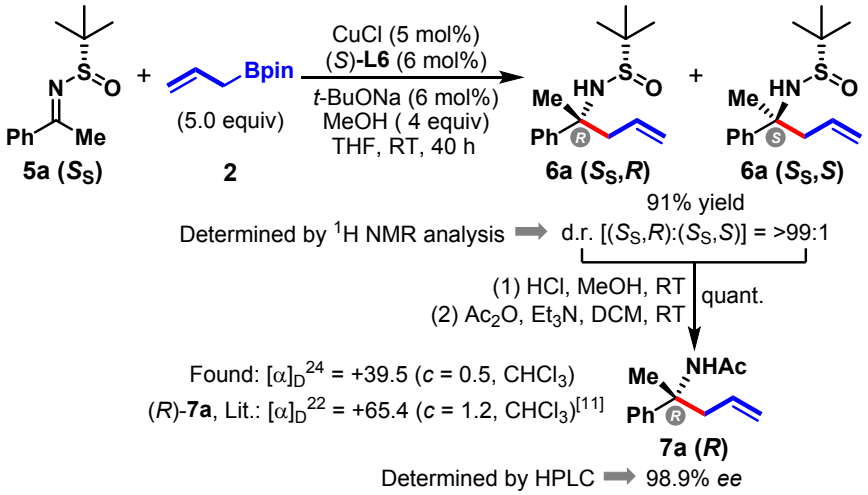
Integeration Parameters

Peak Width	Slope	Drift	Min Area	Time Param	Locking Time	End Time	Sample Wt.
5	70.000	0.000	900000.000	0.000	6.000	30.853	100.0000

The dr value of the allylation ketimine product was determined by ^{1}H NMR analysis of the crude products. In the case of product **6a**, the dr value was further confirmed by the HPLC analysis of its acetyl derivative **7a**, which ensured the accuracy of ^{1}H NMR analysis.[11]

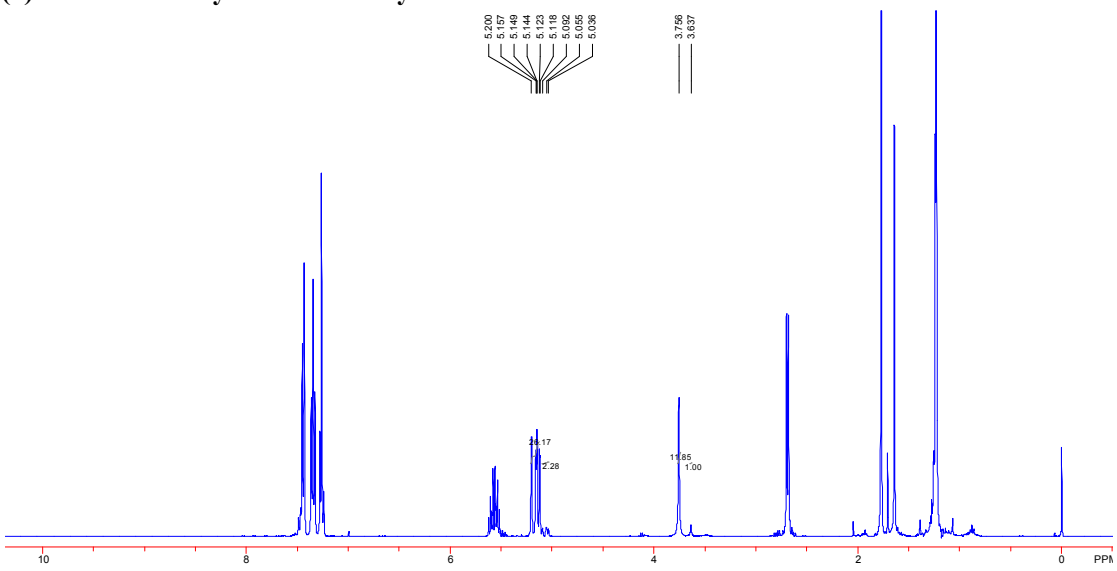


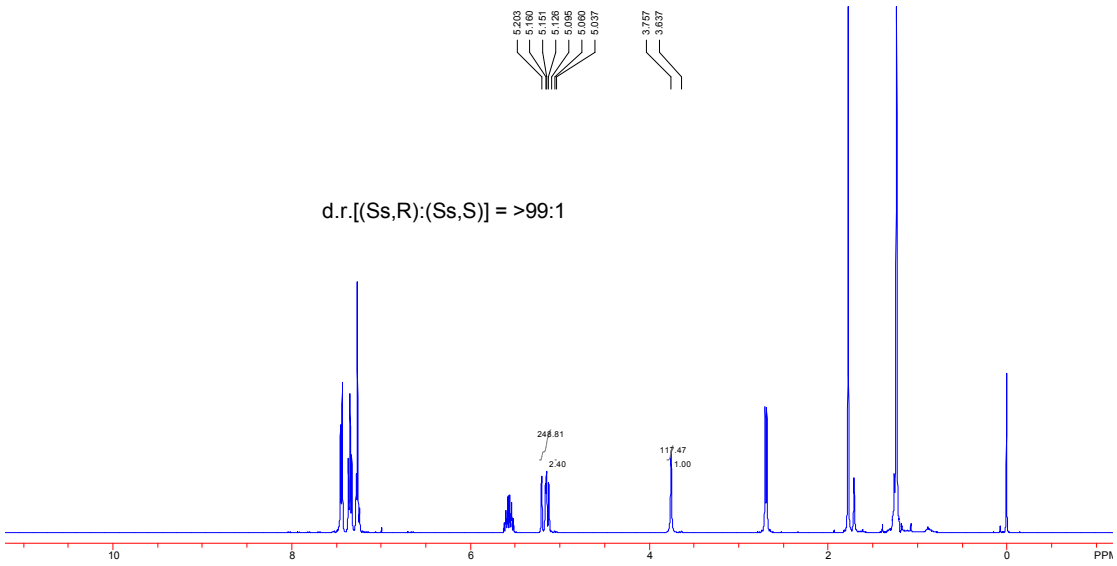
[11] D. H. Hua, S. W. Miao, J. S. Chen and S. Iguchi, *J. Org. Chem.*, 1991, **56**, 4.



HPLC: Daicel Chiralpak OD-H column, detected at 214 nm, eluent: *n*-hexane / *iso*- propanol 90:10.

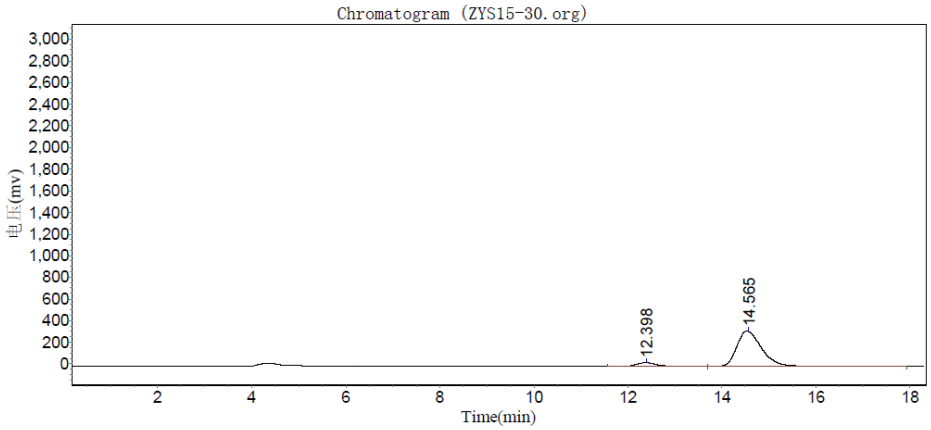
(a) Determined by ^{1}H NMR analysis





(b) Confirmed by the HPLC analysis of its acetyl derivative.

Sample Description:
OD-H;n-hexane/iPrOH=90/10 ,0.7ml/min,214



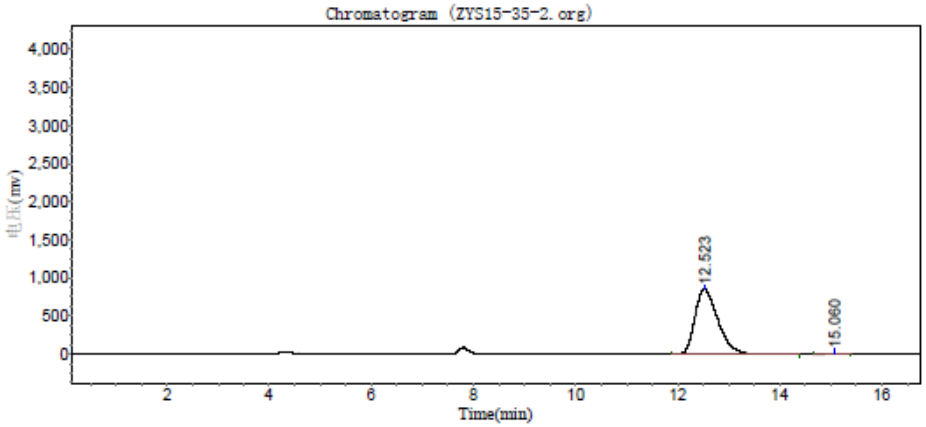
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.398	36397.176	1051122.750	7.9512
2		14.565	326494.281	12168519.000	92.0488
Total			362891.457	13219641.750	100.0000

Integeration Parameters

Peak Width	Slope	Drift	Min Area	Time Param	Locking Time	End Time	Sample Wt.
5	70.000	0.000	100000.000	0.000	6.000	17.998	100.0000

Sample Description:
OD-H;n-hexane/iPrOH=90/10 ,0.7ml/min,214



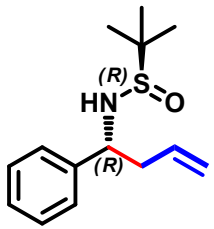
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.523	845849.938	26413248.000	99.4639
2		15.060	5289.934	142364.203	0.5361
Total			851139.872	26555612.203	100.0000

Integeration Parameters

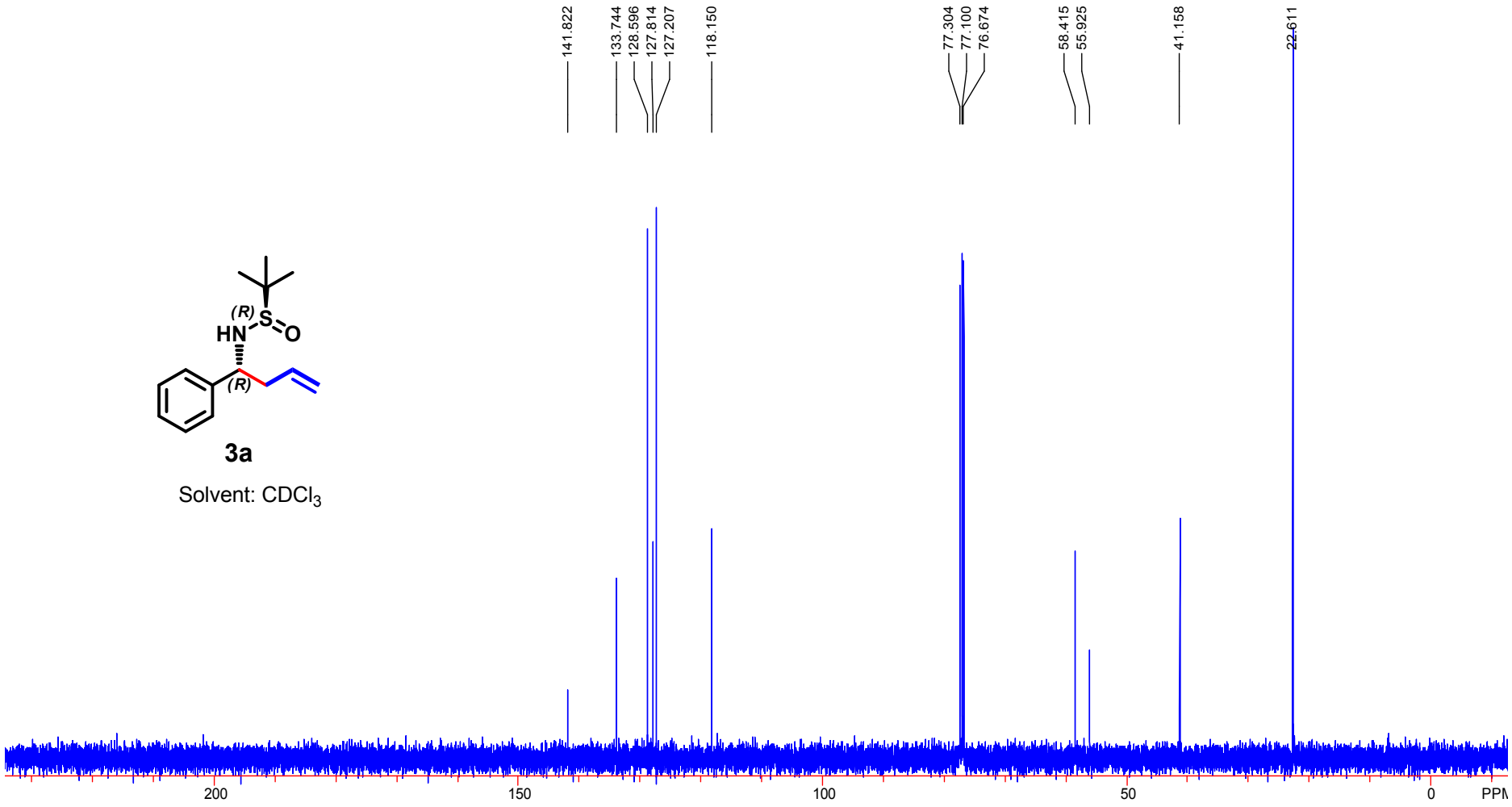
Peak Width	Slope	Drift	Min Area	Time Param	Locking Time	End Time	Sample Wt.
5	70.000	0.000	100000.000	0.000	6.000	16.665	100.0000

5. COPIES OF NMR SPECTRA



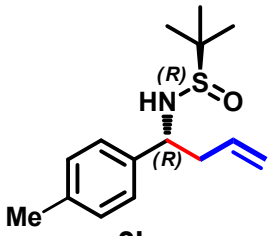
3a

Solvent: $CDCl_3$



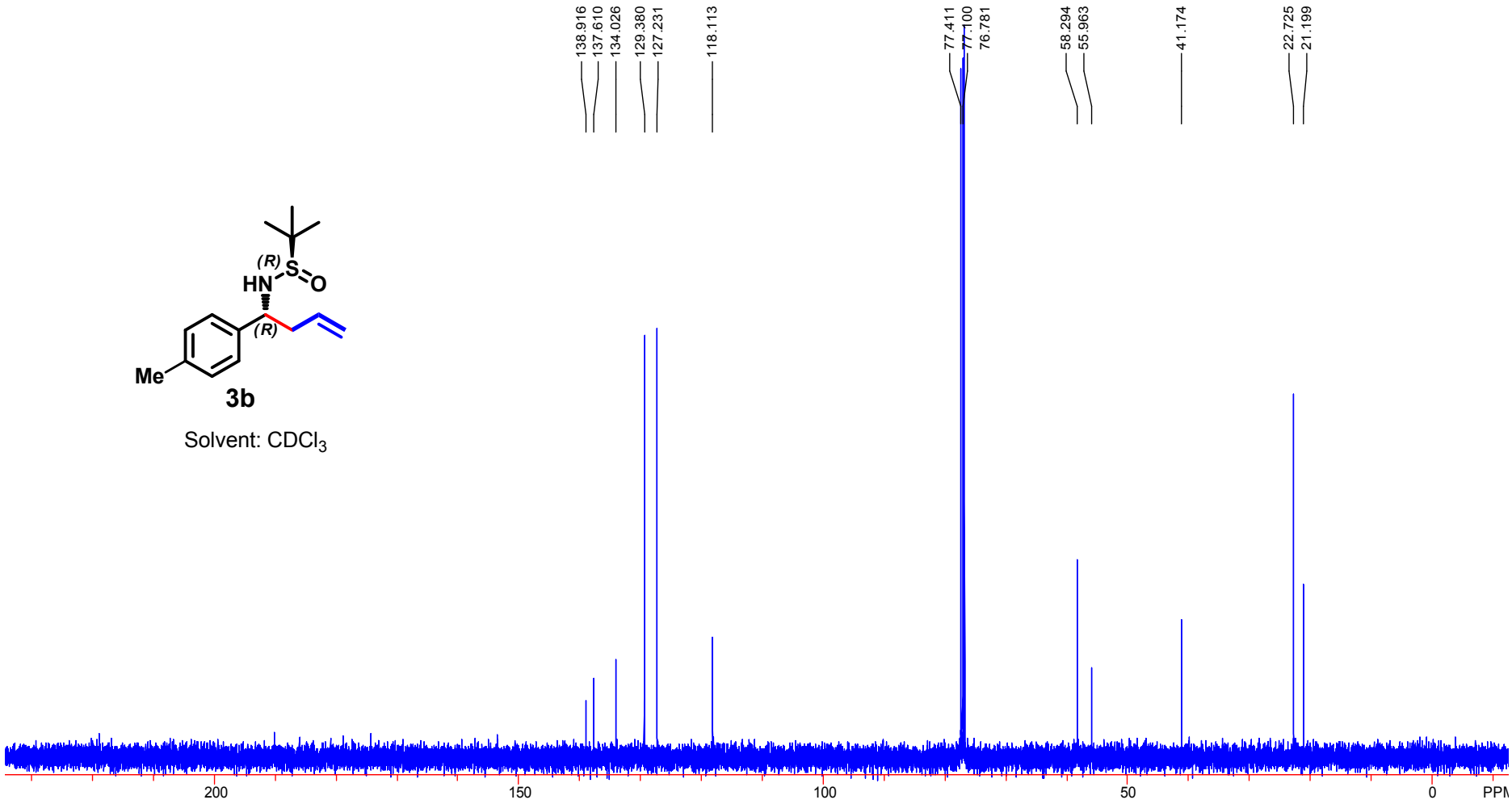
3a

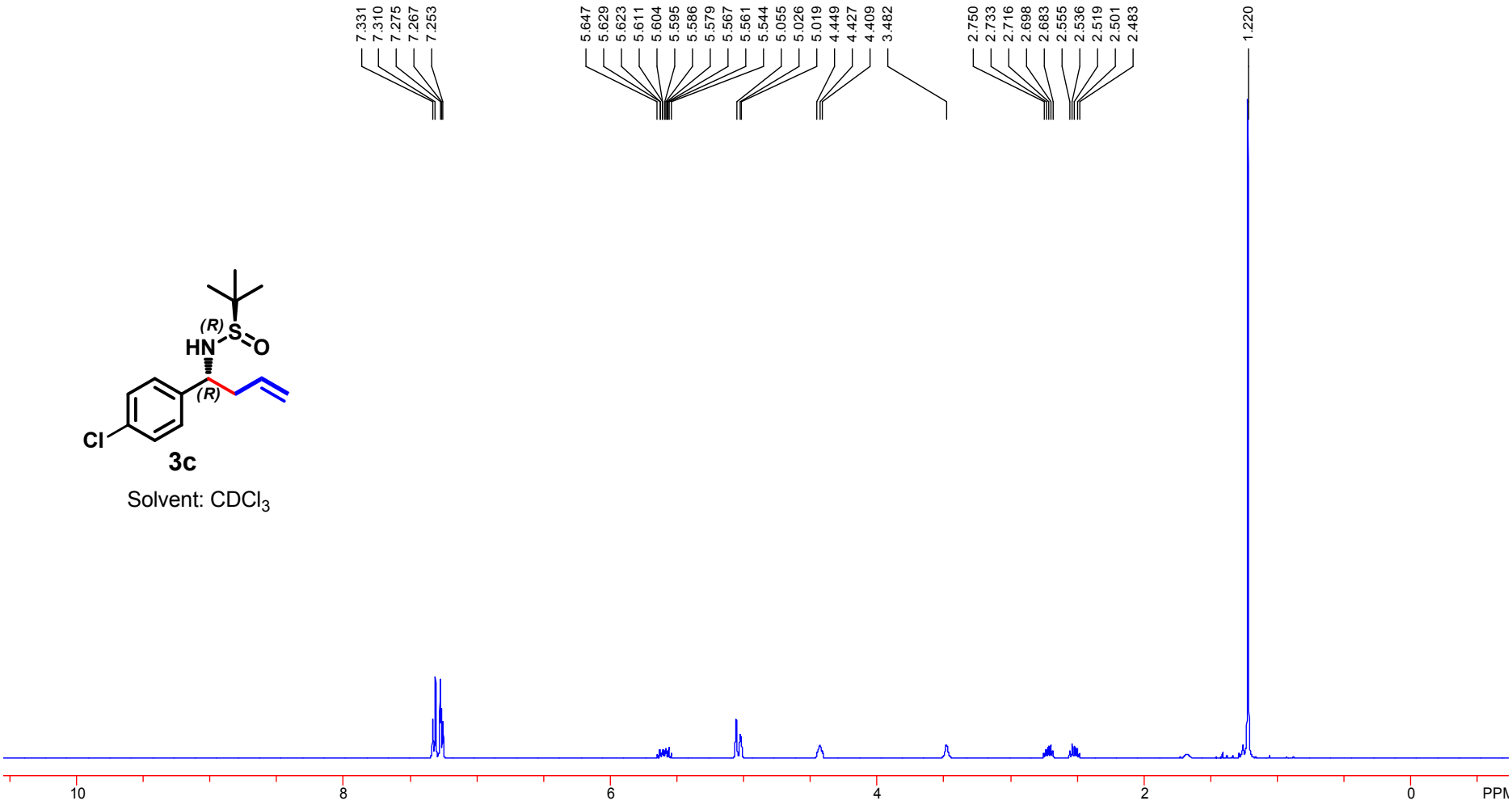
Solvent: $CDCl_3$

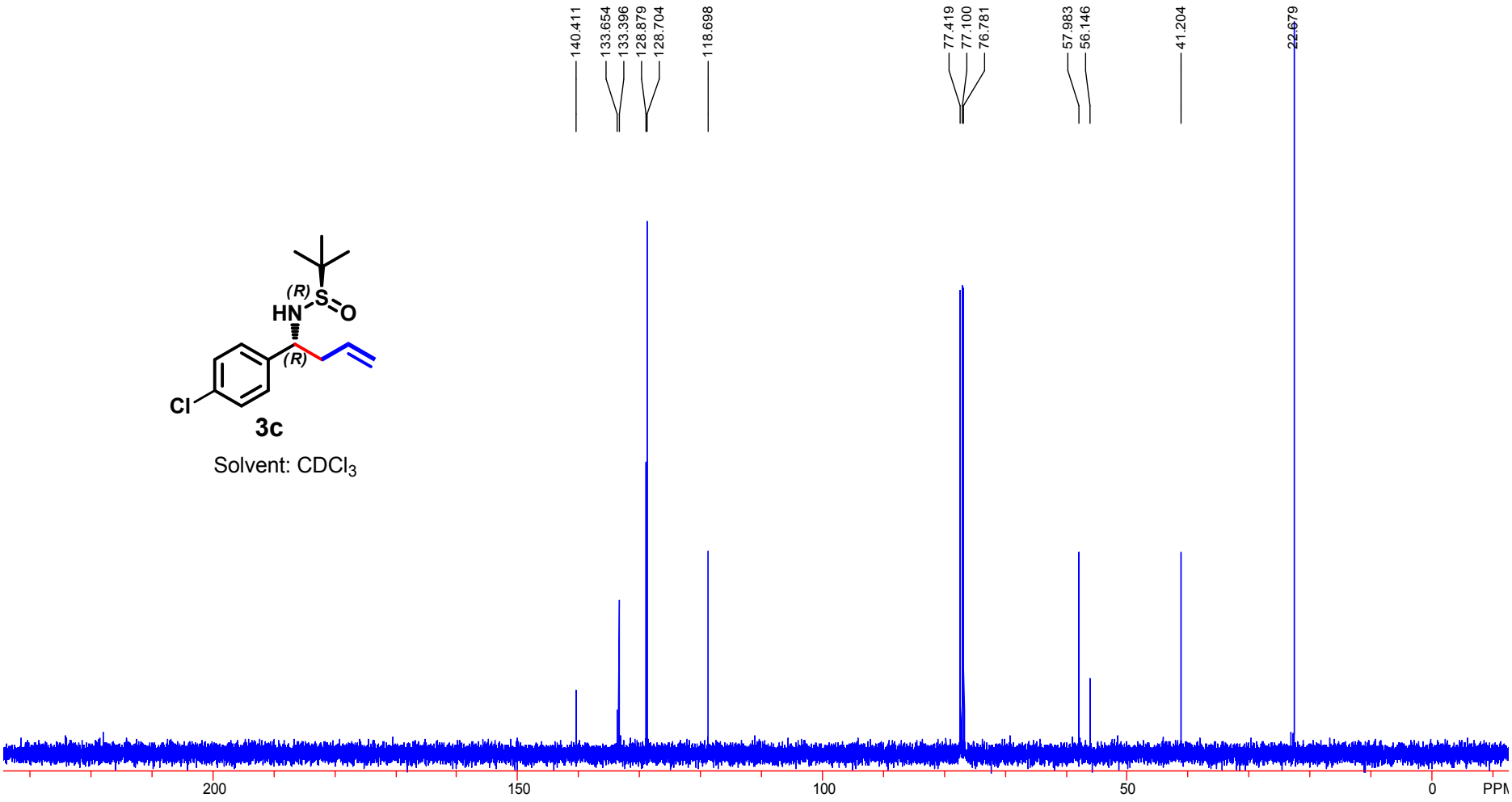


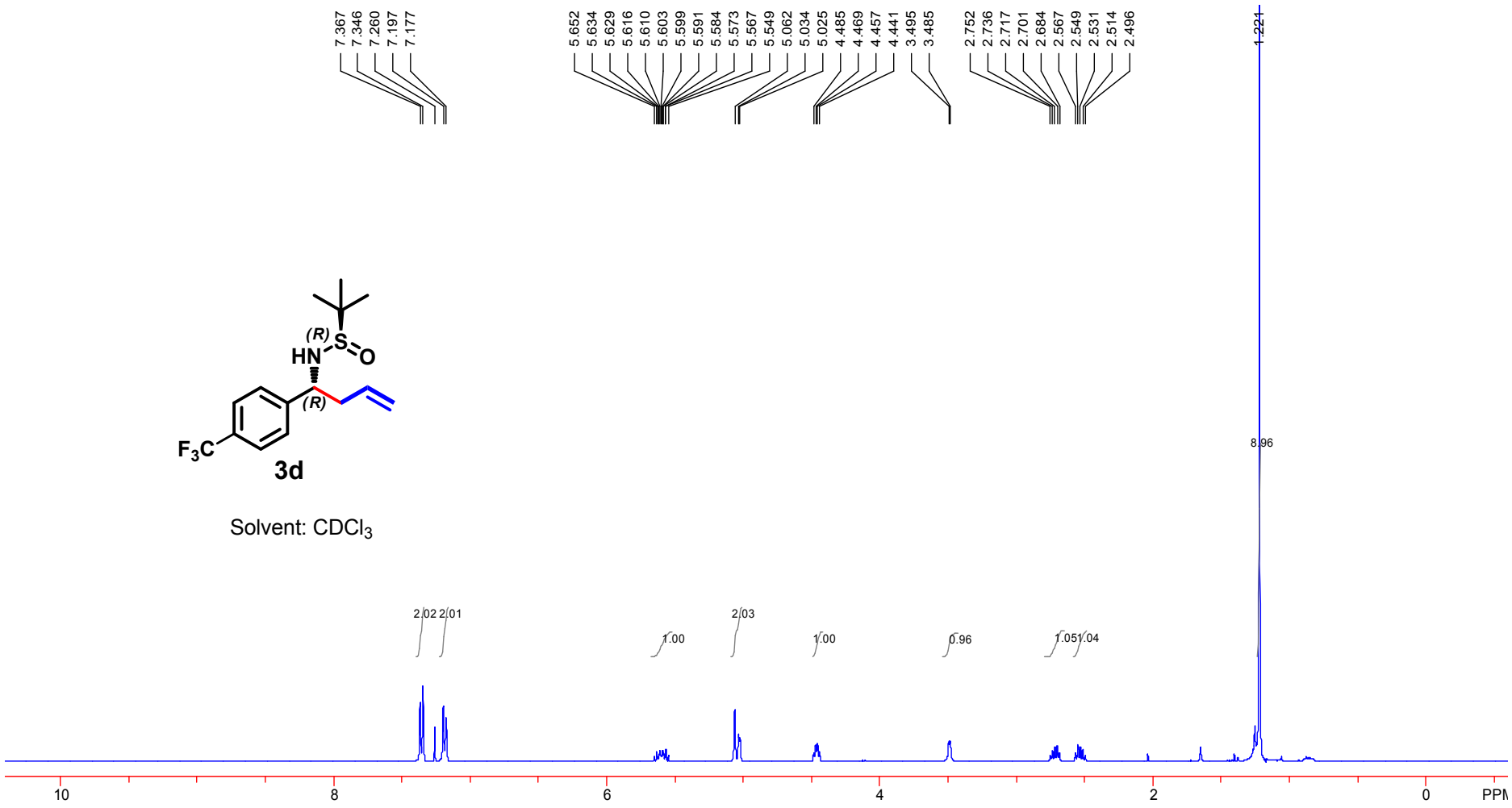
3b

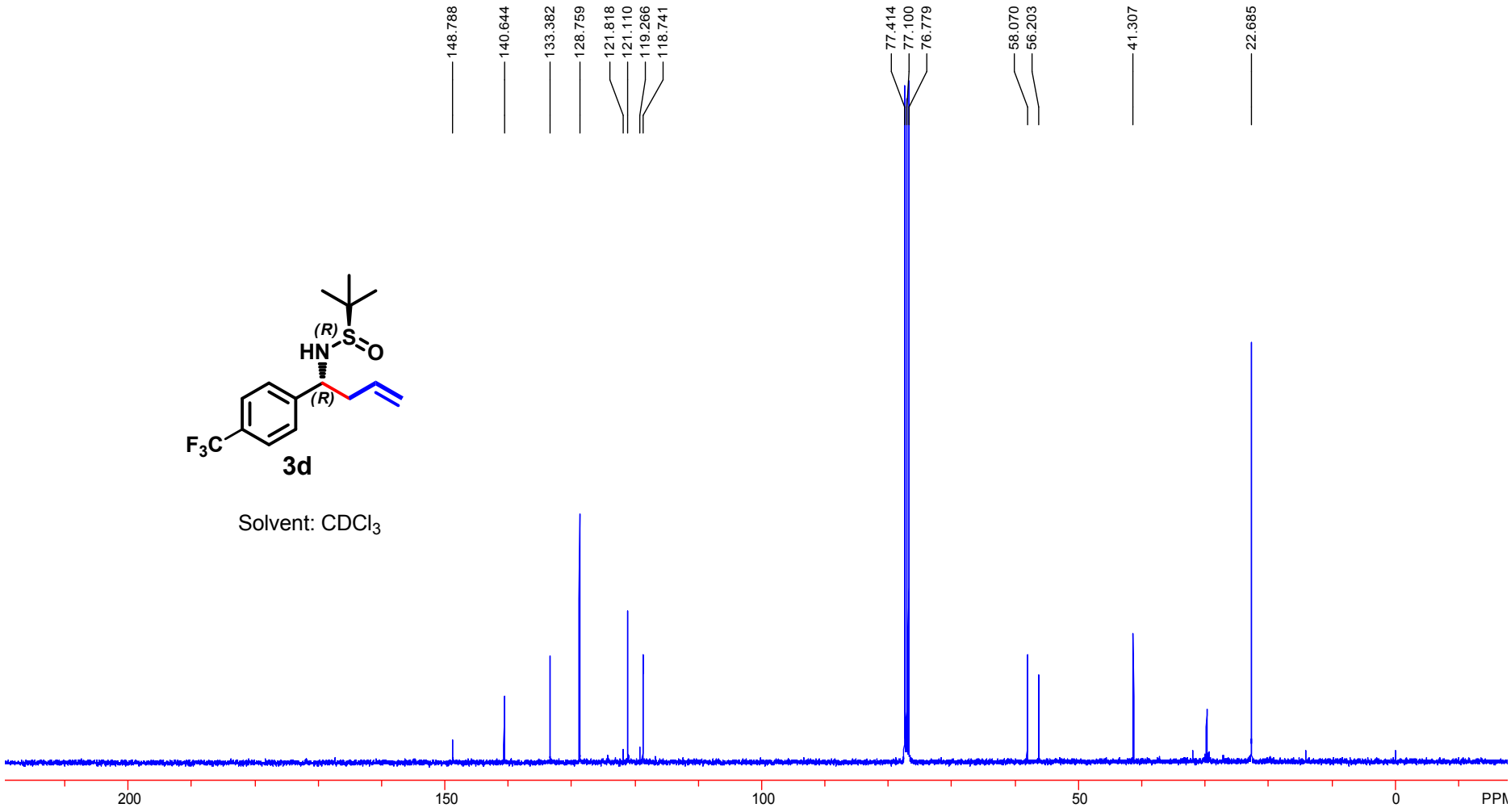
Solvent: $CDCl_3$

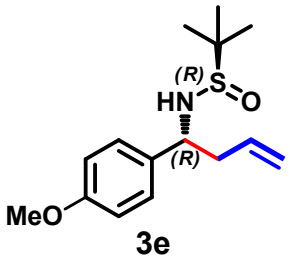

138.916
137.610
134.026
129.380
127.231
118.113
77.411
77.100
76.781
58.294
55.963
41.174
22.725
21.199
(R)
HN
S
O
(R)
Me
3b
Solvent: CDCl3
200
150
100
50
0
PPM


7.331
7.310
7.275
7.267
7.253
5.647
5.629
5.623
5.611
5.604
5.595
5.586
5.579
5.567
5.561
5.544
5.055
5.026
5.019
4.449
4.427
4.409
3.482
2.750
2.733
2.716
2.698
2.683
2.555
2.536
2.519
2.501
2.483
1.220
(R)
HN
S
O
(R)
Cl
3c
Solvent: CDCl3
10
8
6
4
2
0
PPM


140.411
133.654
133.396
128.879
128.704
118.698
77.419
77.100
76.781
57.983
56.146
41.204
22.679
(R)
HN
S
O
(R)
Cl
3c
Solvent: CDCl3
200
150
100
50
0
PPM

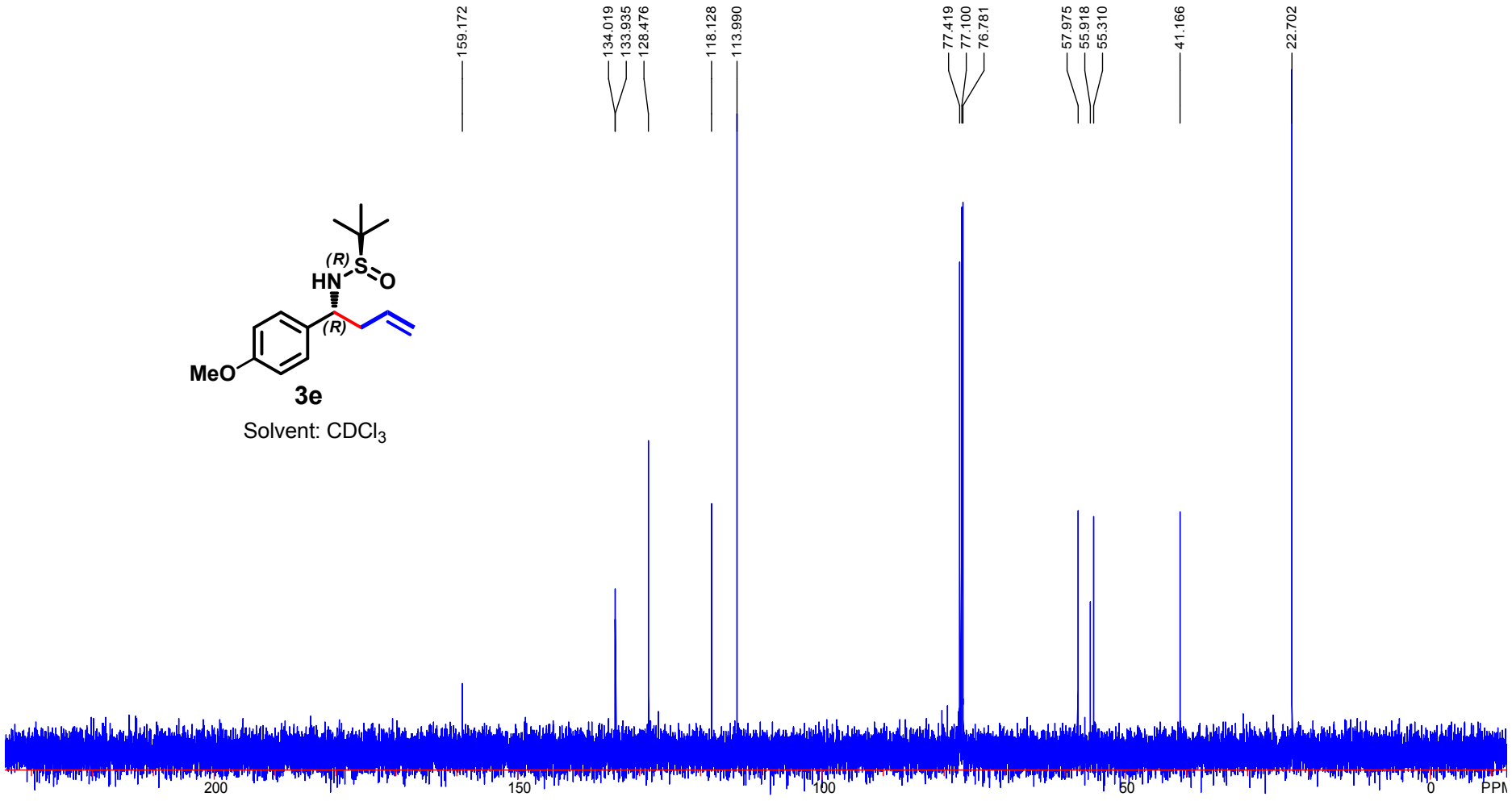

7.367
7.346
7.260
7.197
7.177
5.652
5.634
5.629
5.616
5.610
5.603
5.599
5.591
5.584
5.573
5.567
5.549
5.062
5.034
5.025
4.485
4.469
4.457
4.441
3.495
3.485
2.752
2.736
2.717
2.701
2.684
2.567
2.549
2.531
2.514
2.496
1.221
(R)
HN
S
O
(R)
F3C
3d
Solvent: CDCl3
2.02
2.01
1.00
2.03
1.00
0.96
1.05
1.04
8.96
10
8
6
4
2
0
PPM

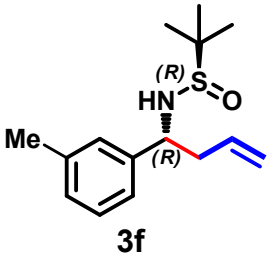

148.788
140.644
133.382
128.759
121.818
121.110
119.266
118.741
77.414
77.100
76.779
58.070
56.203
41.307
22.685
(R)
HN
S
O
(R)
F3C
3d
Solvent: CDCl3
200
150
100
50
0
PPM



3e

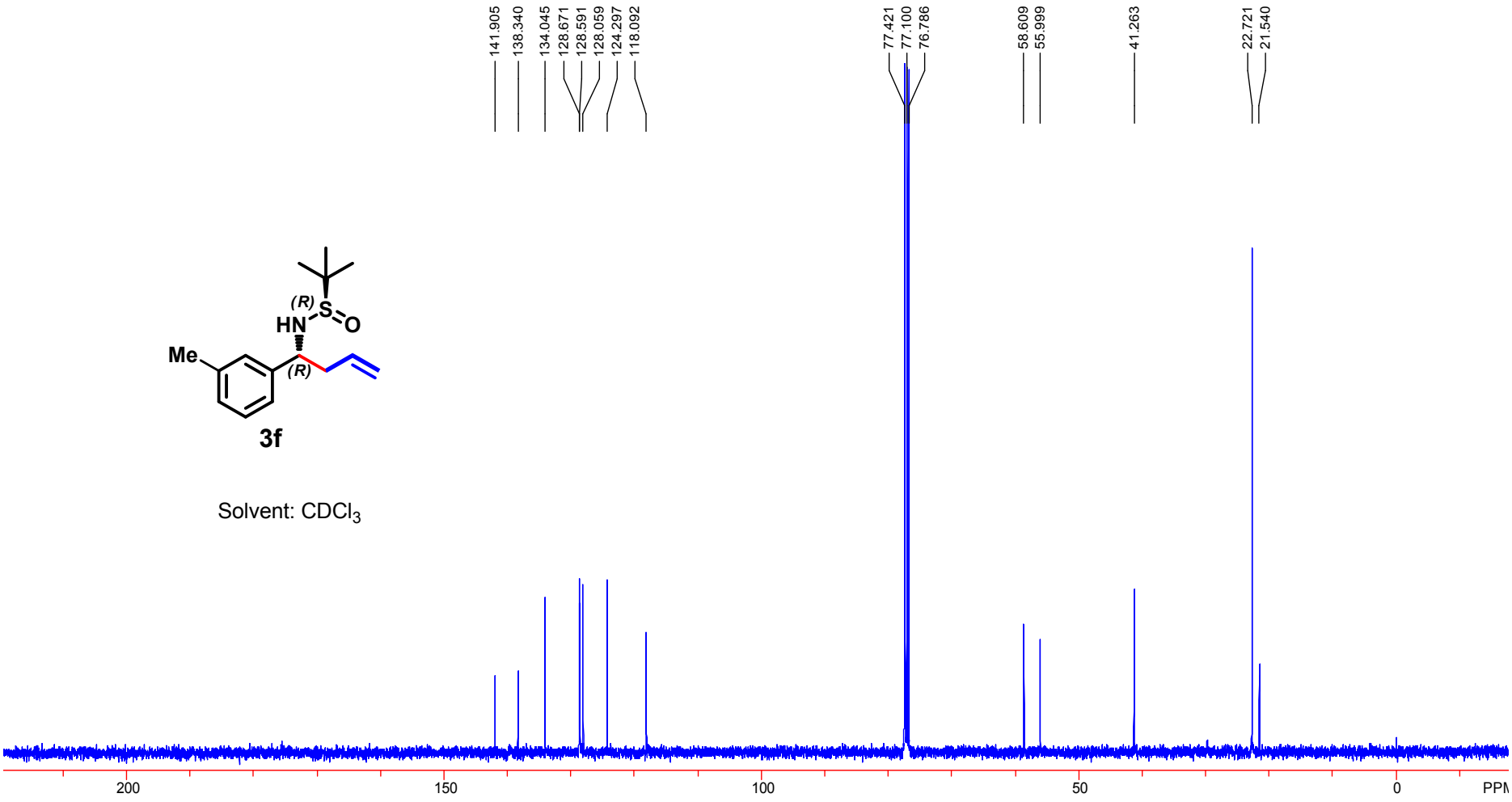
Solvent: $CDCl_3$


159.172
134.019
133.935
128.476
118.128
113.990
77.419
77.100
76.781
57.975
55.918
55.310
41.166
22.702
(R)
S
O
HN
(R)
MeO
3e
Solvent: CDCl3
200
150
100
50
0
PPM



3f

Solvent: $CDCl_3$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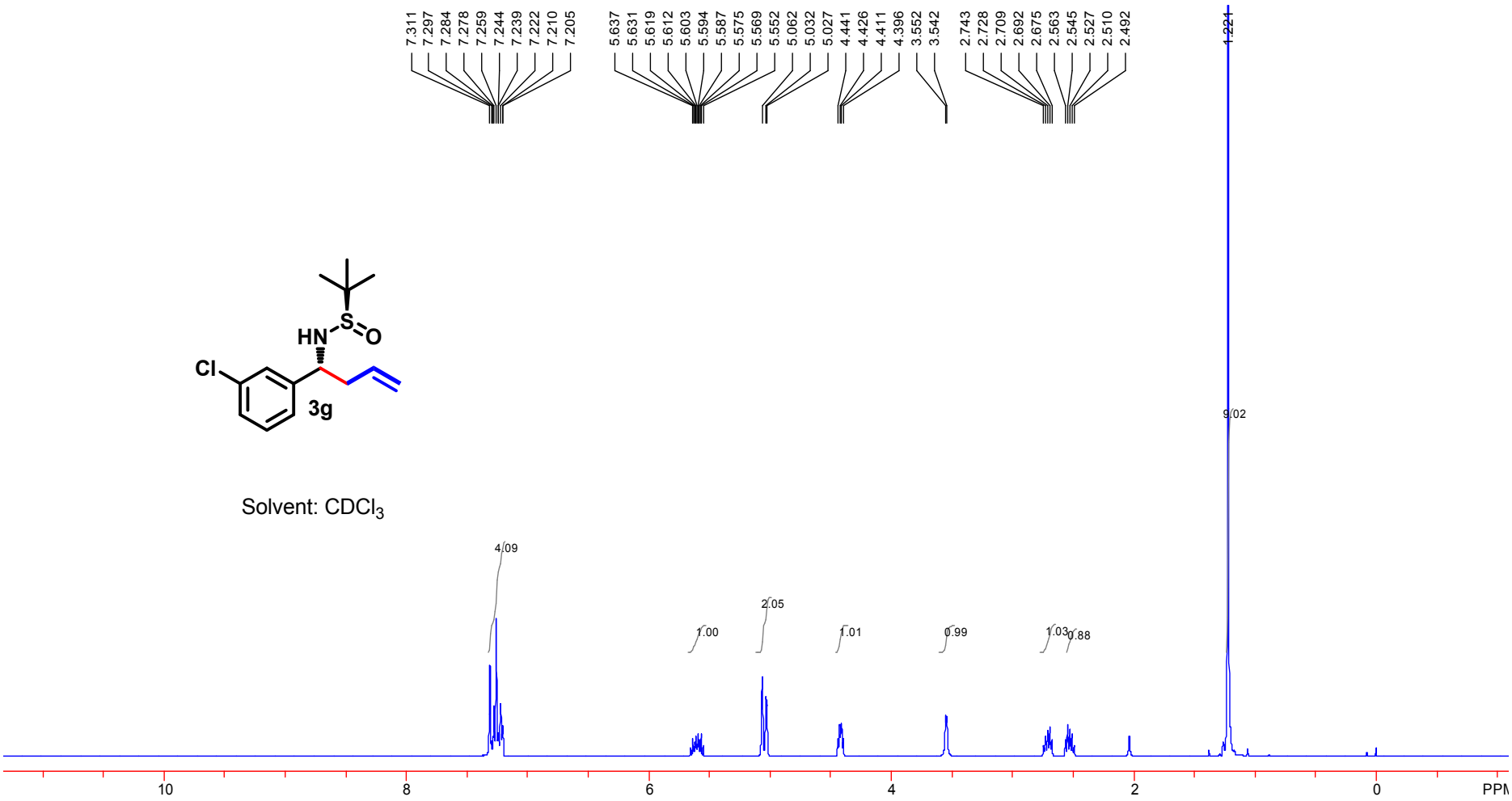
138.340
134.045
128.671
128.591
128.059
124.297
118.092
77.421
77.100
76.786
58.609
55.999
41.263
22.721
21.540
(R)
HN
S
O
Me
(R)
3f
Solvent: CDCl3
200
150
100
50
0
PPM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7.297
7.284
7.278
7.259
7.244
7.239
7.222
7.210
7.205
5.637
5.631
5.619
5.612
5.603
5.594
5.587
5.575
5.569
5.552
5.062
5.032
5.027
4.441
4.426
4.411
4.396
3.552
3.542
2.743
2.728
2.709
2.692
2.675
2.563
2.545
2.527
2.510
2.492
1.221
9.02
HN
S
O
Cl
3g
Solvent: CDCl3
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1.01
0.99
1.03
0.88
10
8
6
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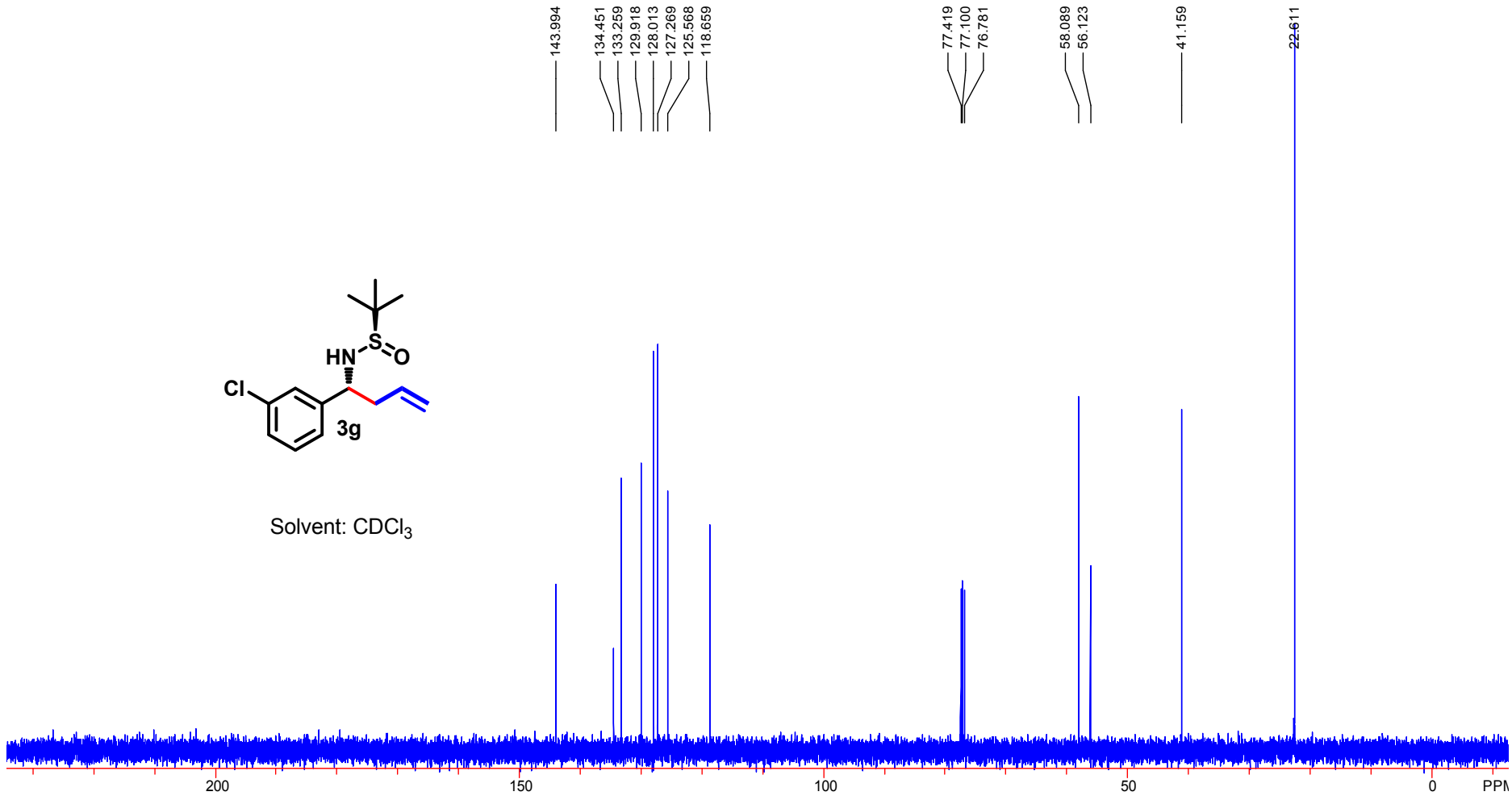
0
PPM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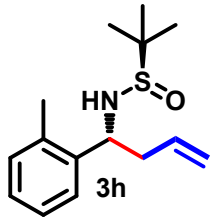
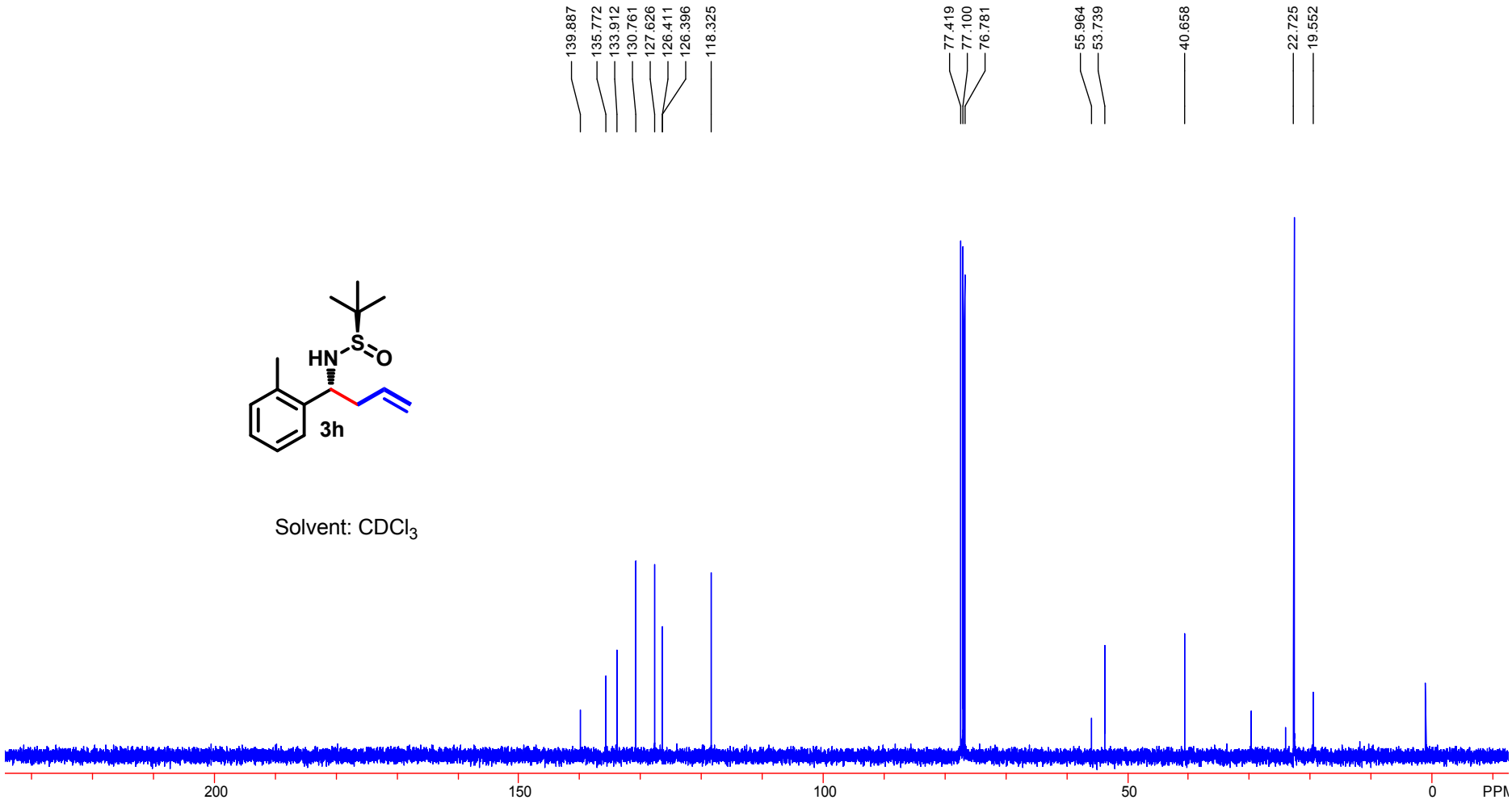
133.259
129.918
128.013
127.269
125.568
118.659
77.419
77.100
76.781
58.089
56.123
41.159
22.611
HN
S
O
Cl
3g
Solvent: CDCl3
200
150
100
50
0
PPM



Solvent: $CDCl_3$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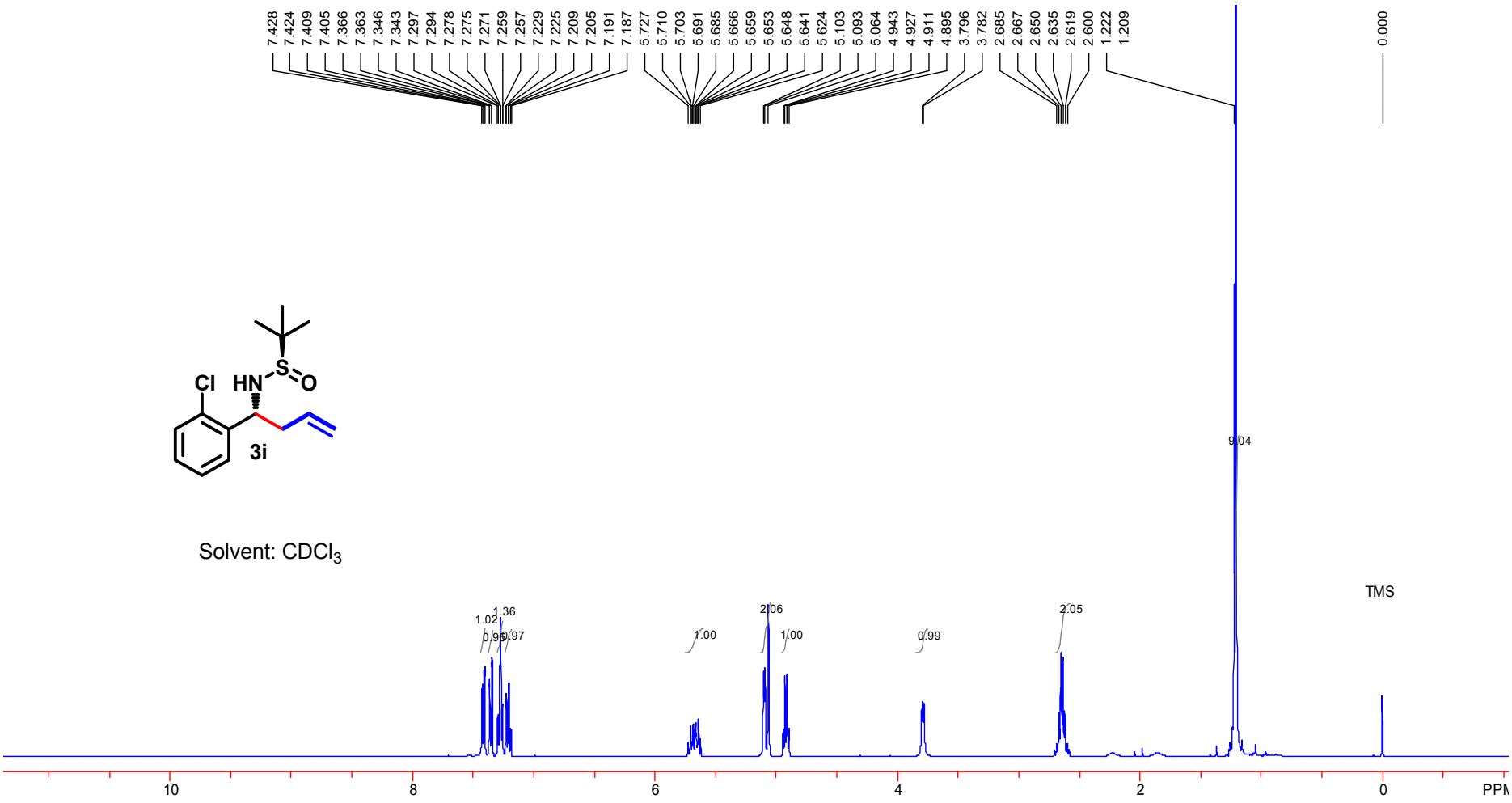
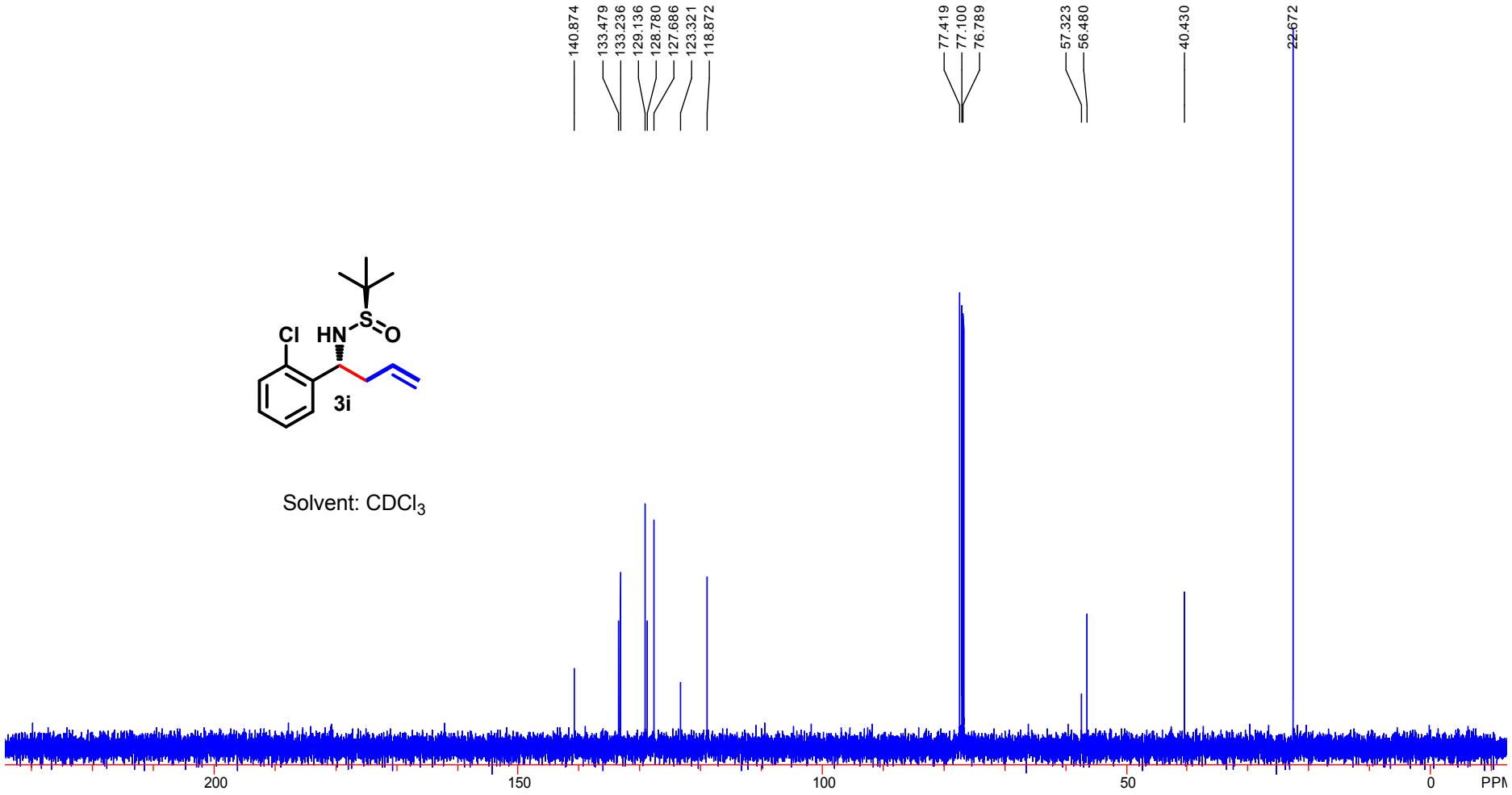
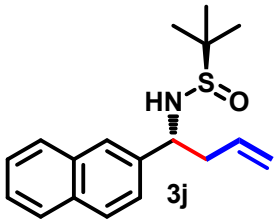
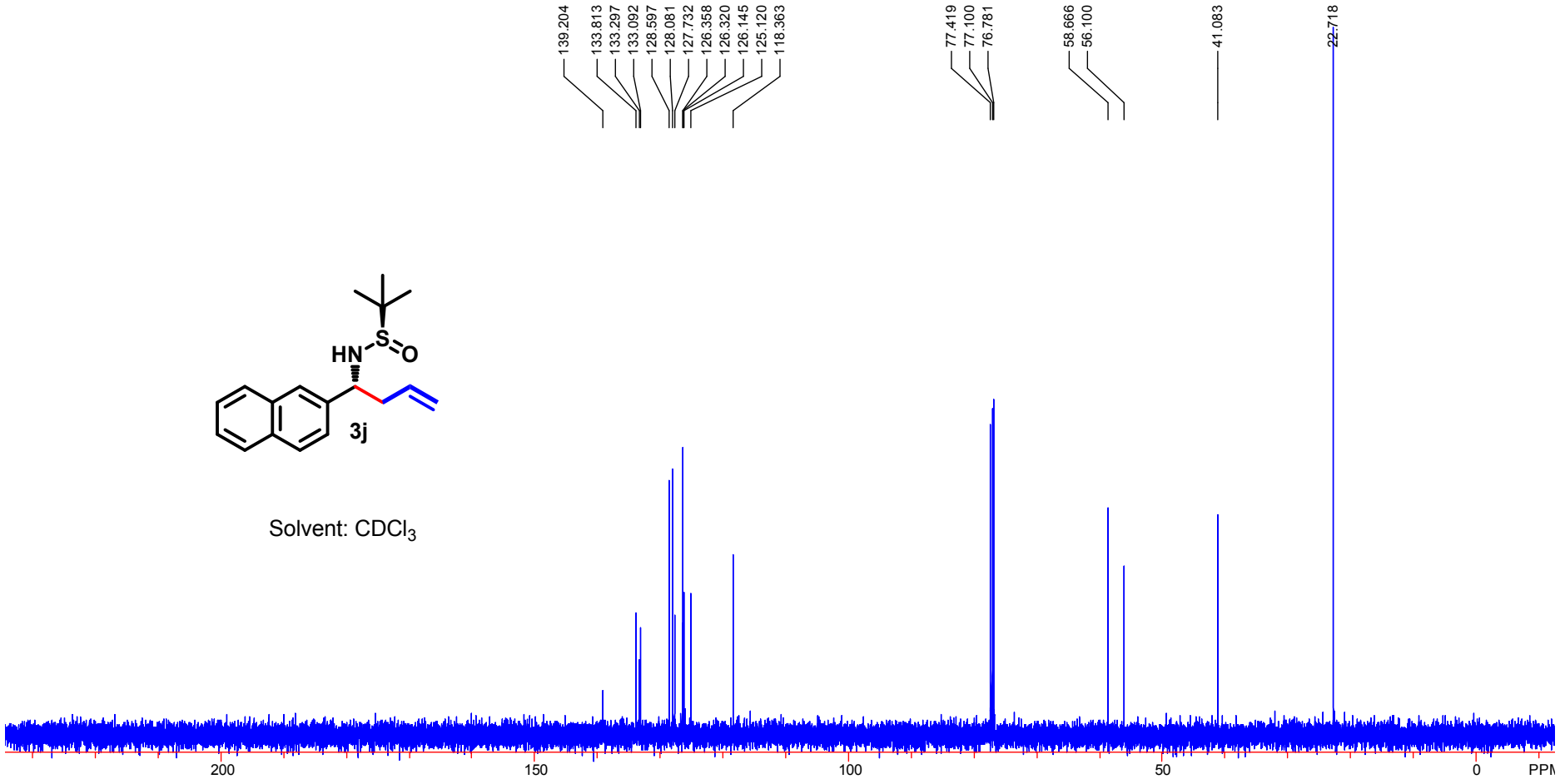
135.772
133.912
130.761
127.626
126.411
126.396
118.325
77.419
77.100
76.781
55.964
53.739
40.658
22.725
19.552
HN
S
O
3h
Solvent: CDCl3
200
150
100
50
0
PPM


7.428
7.424
7.409
7.405
7.366
7.363
7.346
7.343
7.297
7.294
7.278
7.275
7.271
7.259
7.257
7.229
7.225
7.209
7.205
7.191
7.187
5.727
5.710
5.703
5.691
5.685
5.666
5.659
5.653
5.648
5.641
5.624
5.103
5.093
5.064
4.943
4.927
4.911
4.895
3.796
3.782
2.685
2.667
2.650
2.635
2.619
2.600
1.222
1.209
0.000
Cl
HN
S
O
3i
Solvent: CDCl3
1.02
1.36
0.99
0.97
1.00
2.06
1.00
0.99
2.05
9.04
TMS
10
8
6
4
2
0
PPM


140.874
133.479
133.236
129.136
128.780
127.686
123.321
118.872
77.419
77.100
76.789
57.323
56.480
40.430
22.672
Cl
HN
S
O
3i
Solvent: CDCl3
200
150
100
50
0
PPM



Solvent: $CDCl_3$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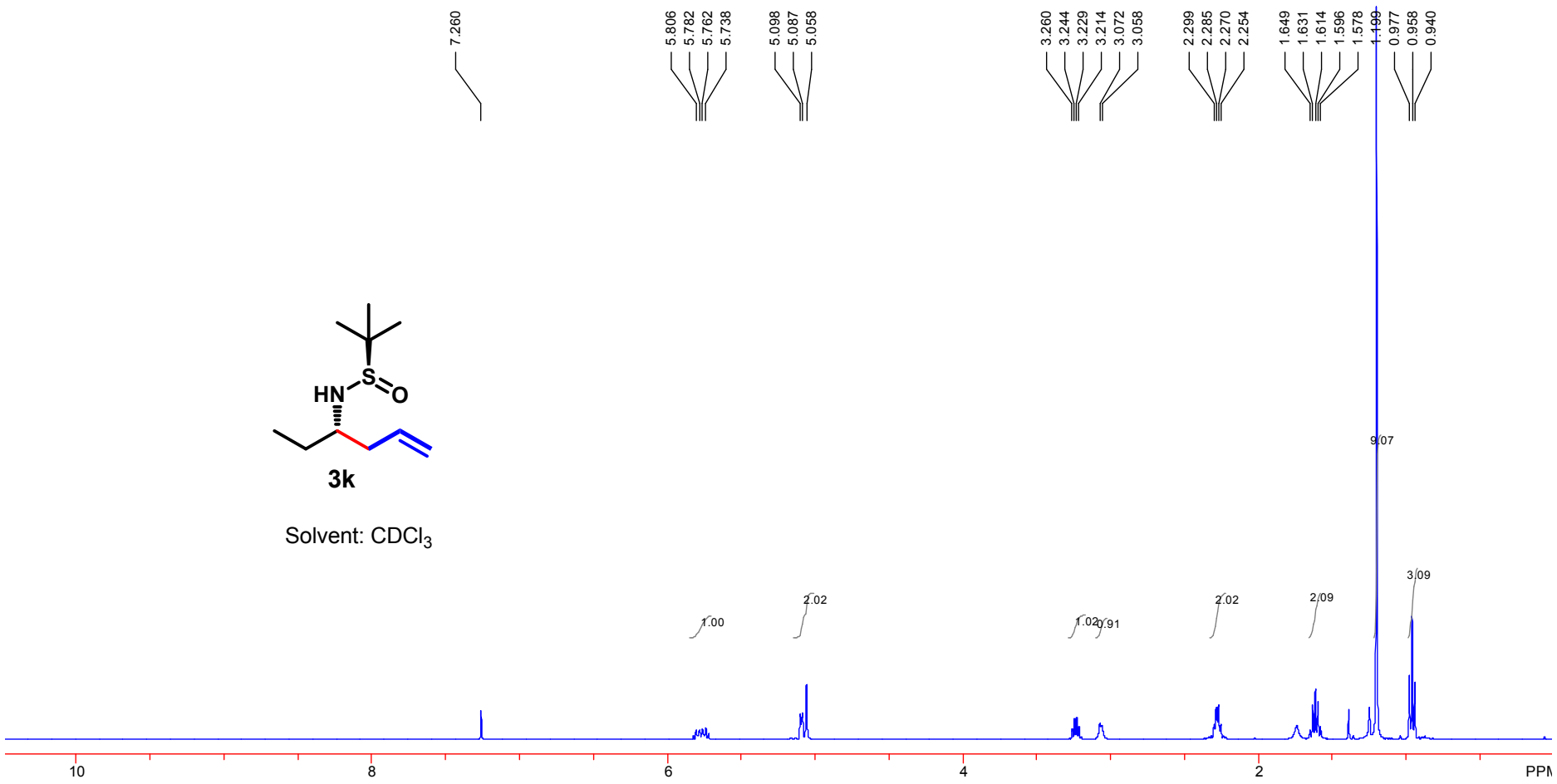
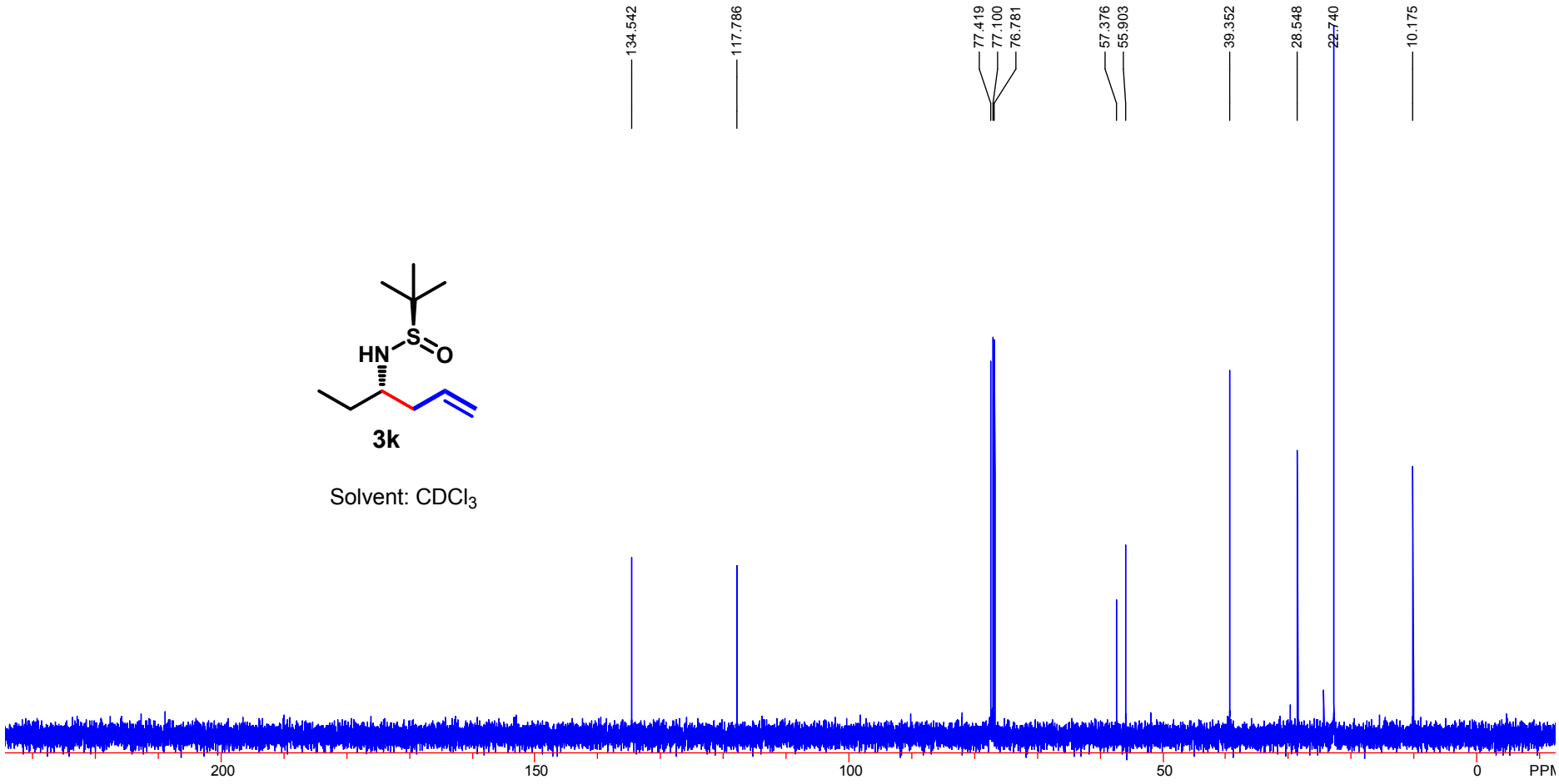
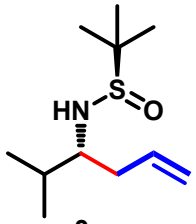
133.813
133.297
133.092
128.597
128.081
127.732
126.358
126.320
126.145
125.120
118.363
77.419
77.100
76.781
58.666
56.100
41.083
22.718
HN
S
O
3j
Solvent: CDCl3
200
150
100
50
0
PPM

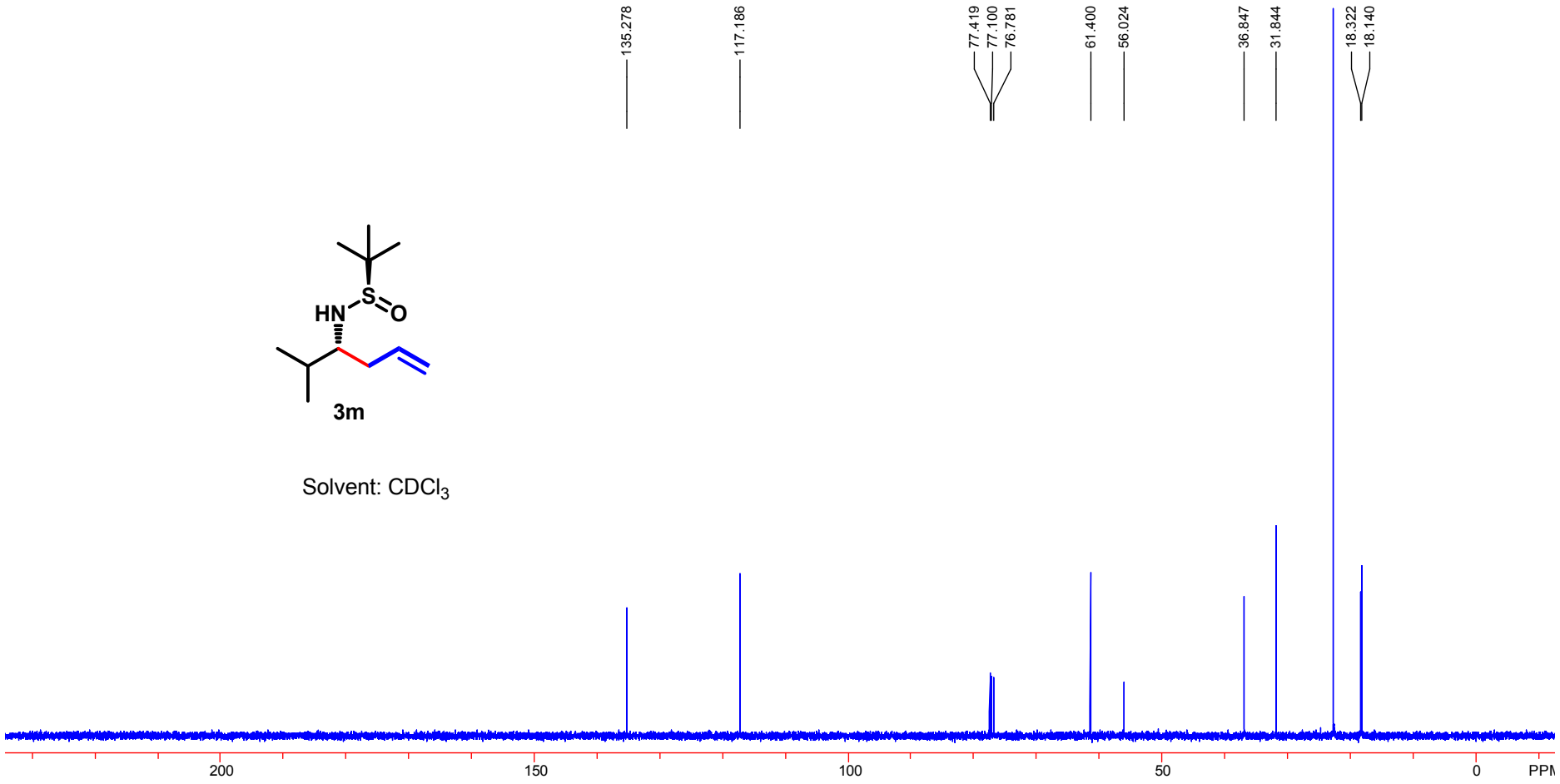

7.260
5.806
5.782
5.762
5.738
5.098
5.087
5.058
3.260
3.244
3.229
3.214
3.072
3.058
2.299
2.285
2.270
2.254
1.649
1.631
1.614
1.596
1.578
1.199
0.977
0.958
0.940
HN
S
O
3k
Solvent: CDCl3
1.00
2.02
1.02
0.91
2.02
2.09
9.07
3.09
10
8
6
4
2
PPM


134.542
117.786
77.419
77.100
76.781
57.376
55.903
39.352
28.548
22.740
10.175
HN
S
O
3k
Solvent: CDCl3
200
150
100
50
0
PPM



3m

Solvent: $CDCl_3$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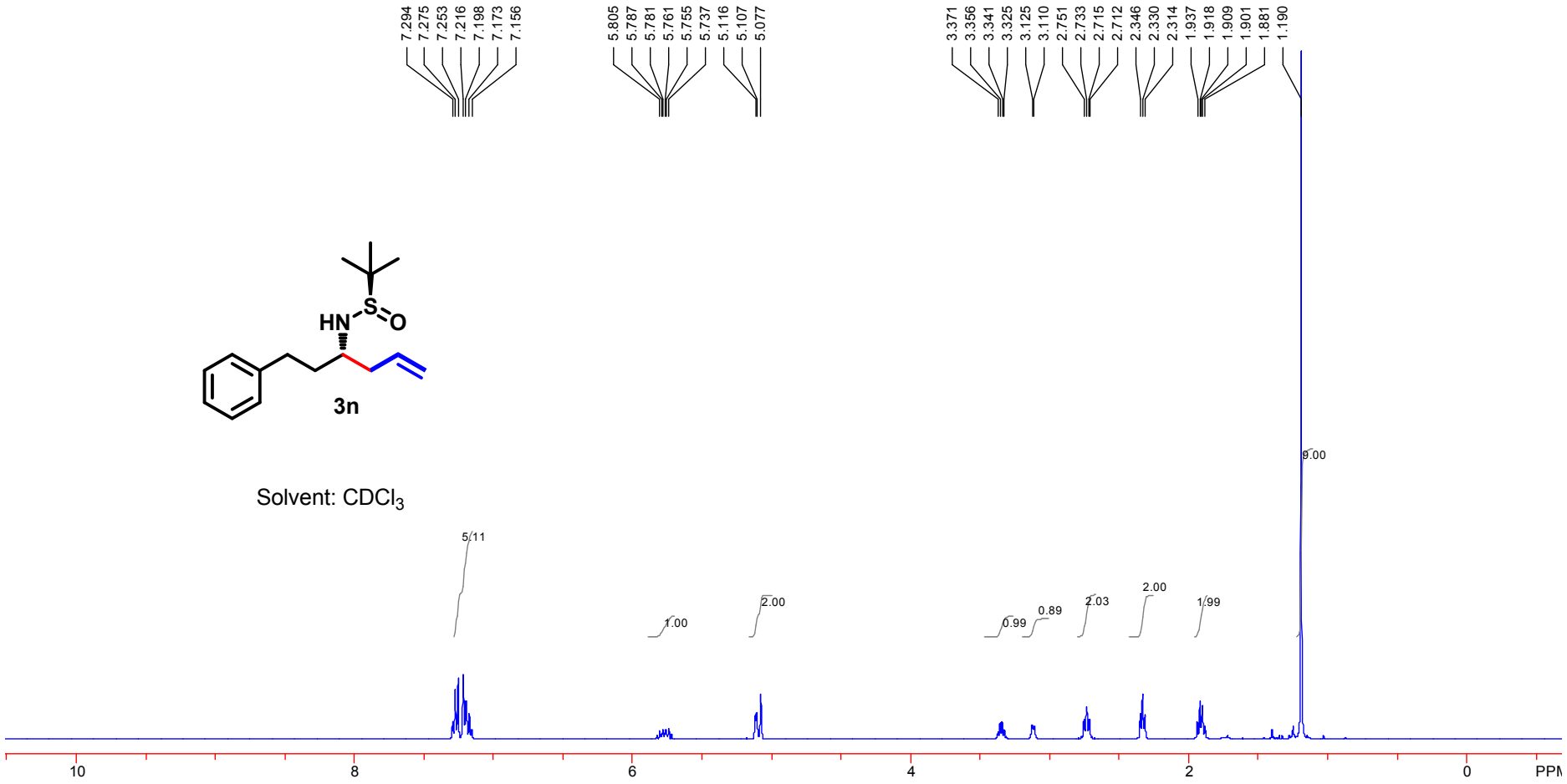
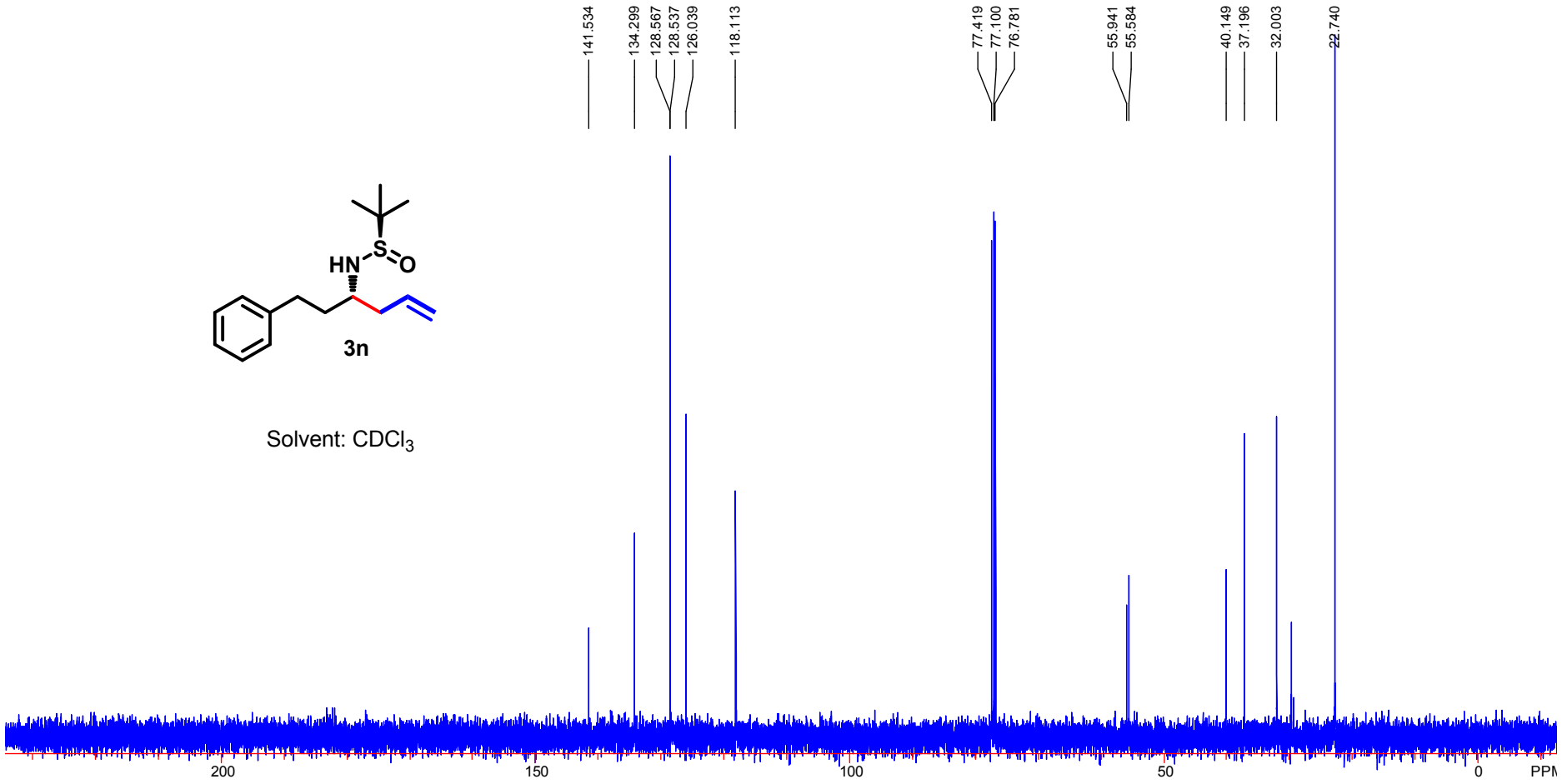
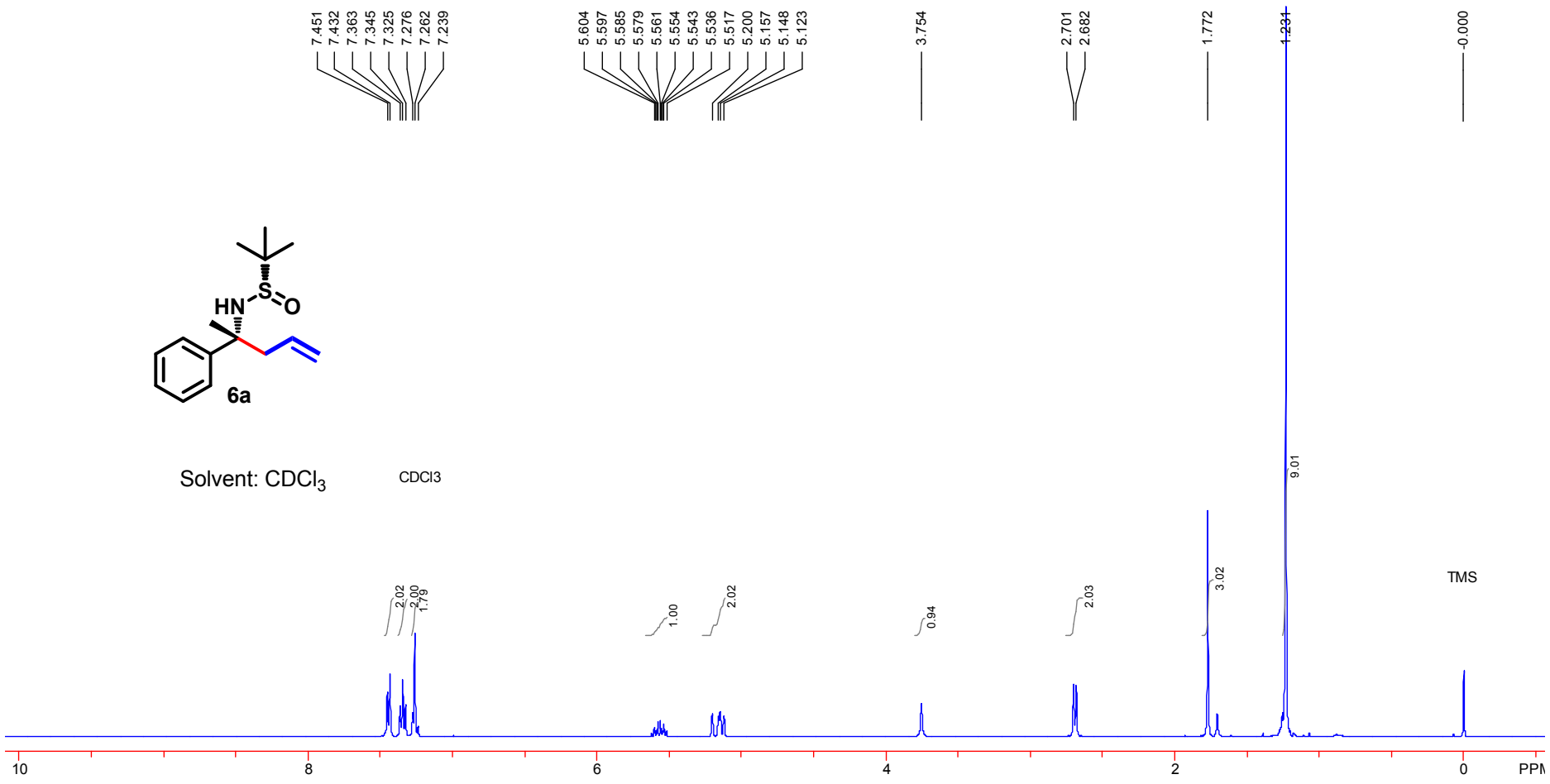
117.186
77.419
77.100
76.781
61.400
56.024
36.847
31.844
18.322
18.140
HN
S
O
3m
Solvent: CDCl3
200
150
100
50
0
PPM


7.294
7.275
7.253
7.216
7.198
7.173
7.156
5.805
5.787
5.781
5.761
5.755
5.737
5.116
5.107
5.077
3.371
3.356
3.341
3.325
3.125
3.110
2.751
2.733
2.715
2.712
2.346
2.330
2.314
1.937
1.918
1.909
1.901
1.881
1.190
HN
S
O
3n
Solvent: CDCl3
5.11
1.00
2.00
0.99
0.89
2.03
2.00
1.99
9.00
10
8
6
4
2
0
PPM


141.534
134.299
128.567
128.537
126.039
118.113
77.419
77.100
76.781
55.941
55.584
40.149
37.196
32.003
22.740
HN
S
O
3n
Solvent: CDCl3
200
150
100
50
0
PPM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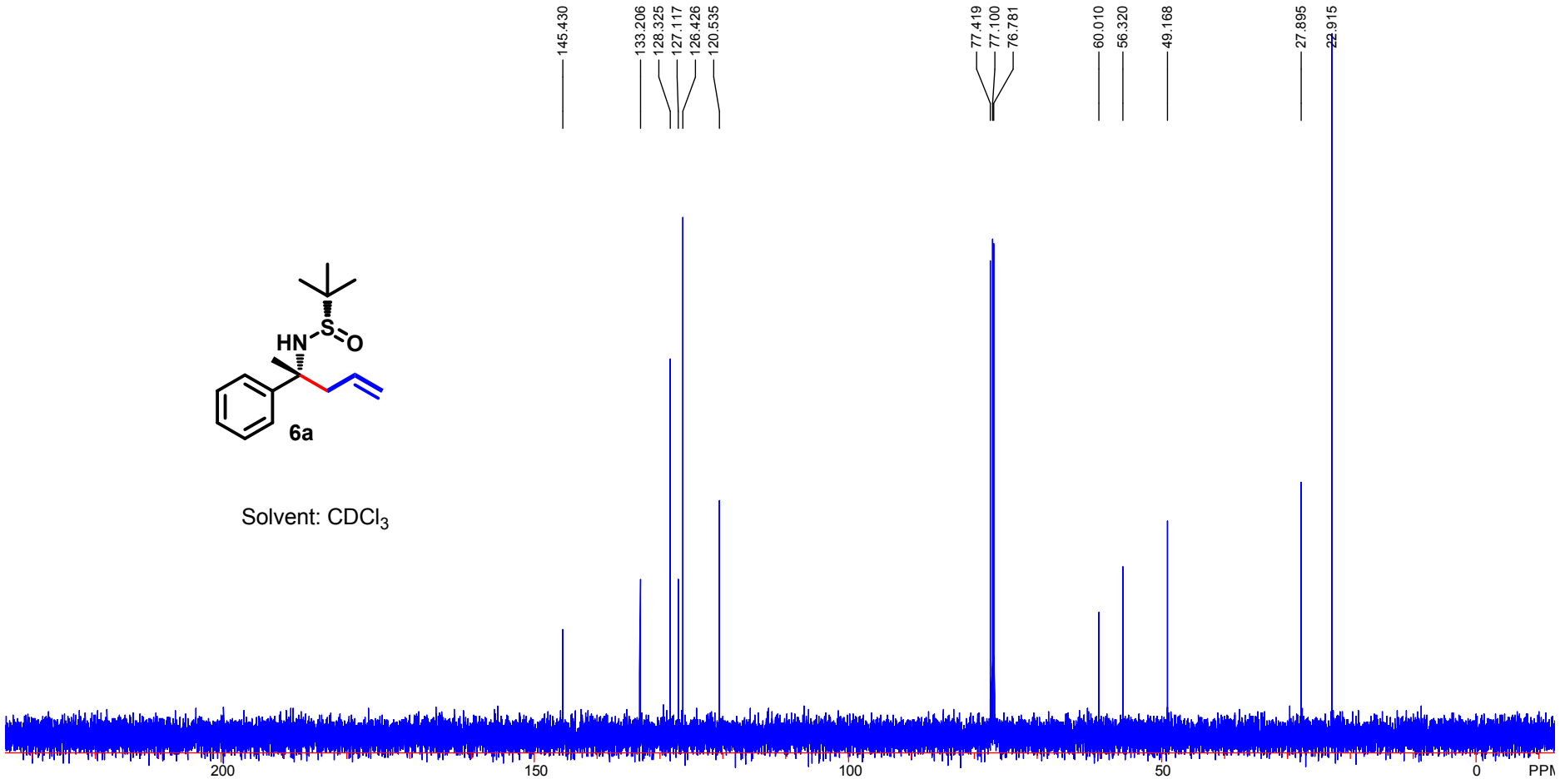
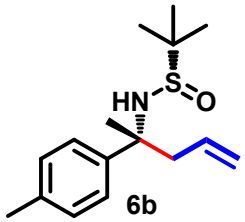
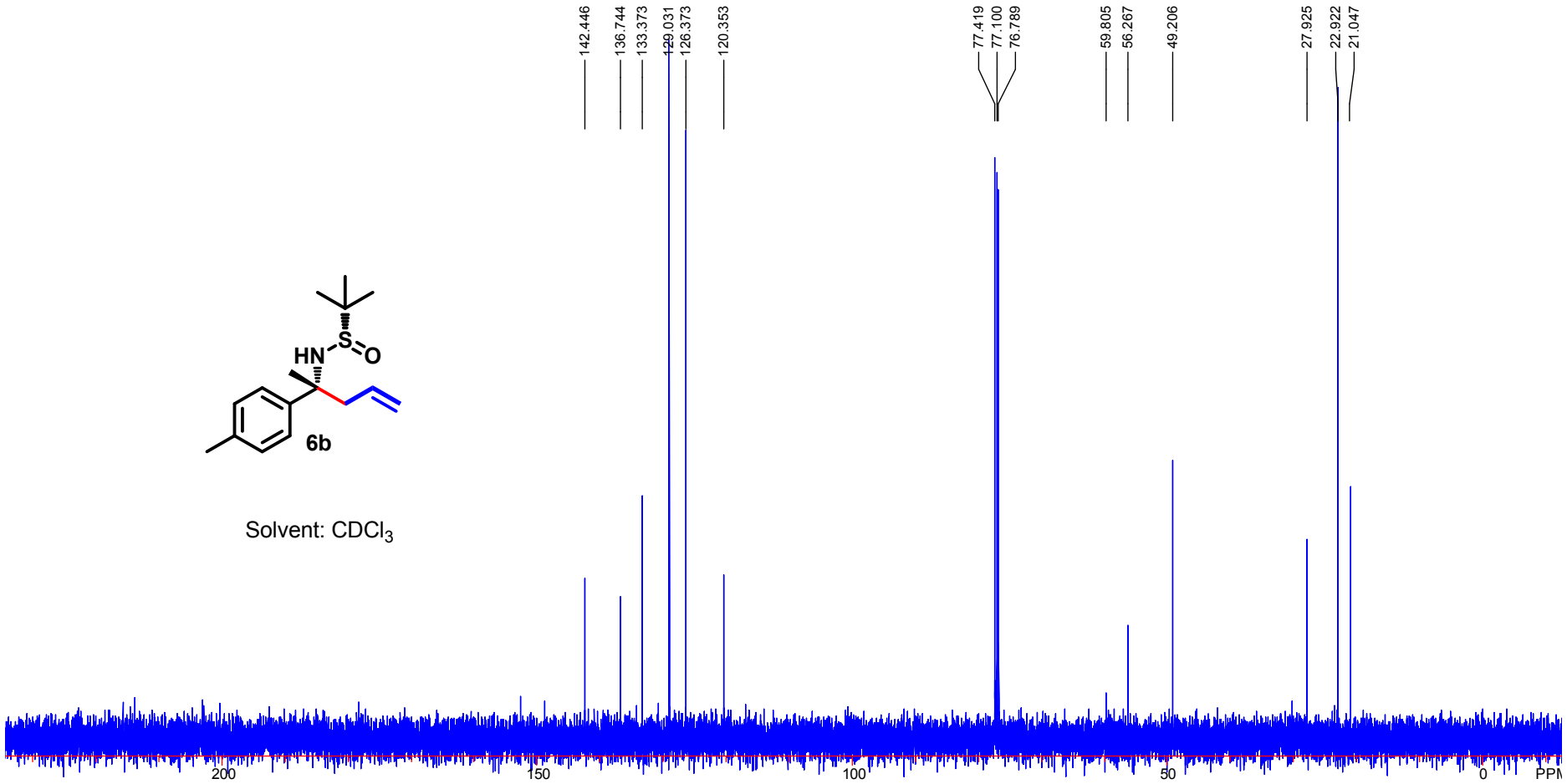
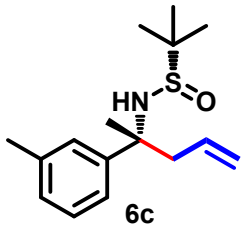
7.432
7.363
7.345
7.325
7.276
7.262
7.239
5.604
5.597
5.585
5.579
5.561
5.554
5.543
5.536
5.517
5.200
5.157
5.148
5.123
3.754
2.701
2.682
1.772
1.231
-0.000
HN
S
O
6a
Solvent: CDCl3
CDCl3
2.02
2.00
1.79
1.00
2.02
0.94
2.03
3.02
9.01
TMS
10
8
6
4
2
0
PPM


145.430
133.206
128.325
127.117
126.426
120.535
77.419
77.100
76.781
60.010
56.320
49.168
27.895
22.915
HN
S
O
6a
Solvent: CDCl3
200
150
100
50
0
PPM



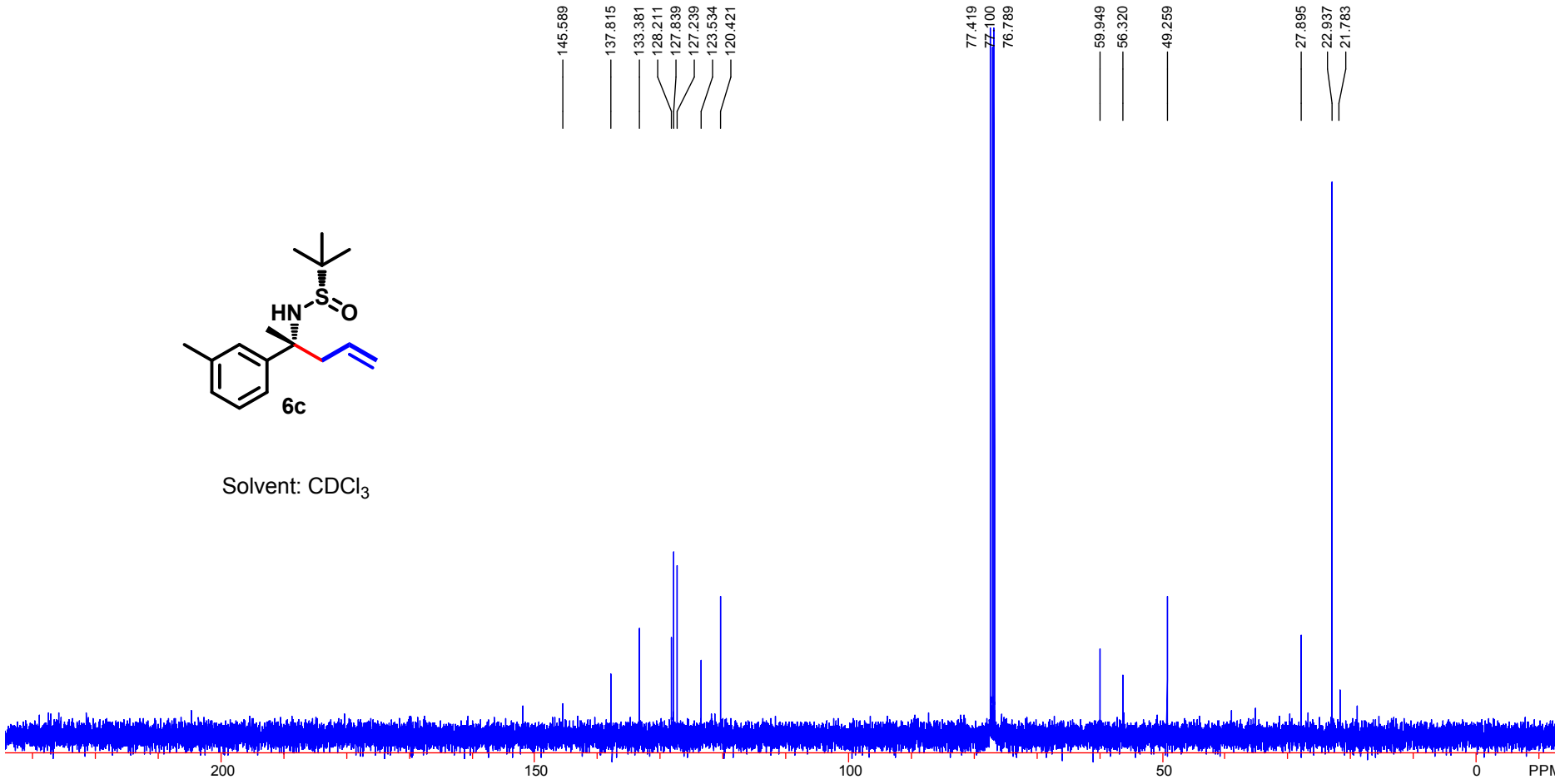
Solvent: $CDCl_3$

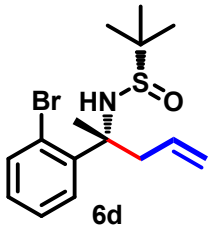

142.446
136.744
133.373
129.031
126.373
120.353
77.419
77.100
76.789
59.805
56.267
49.206
27.925
22.922
21.047
HN
S
O
6b
Solvent: CDCl3
200
150
100
50
0
PPM



6c

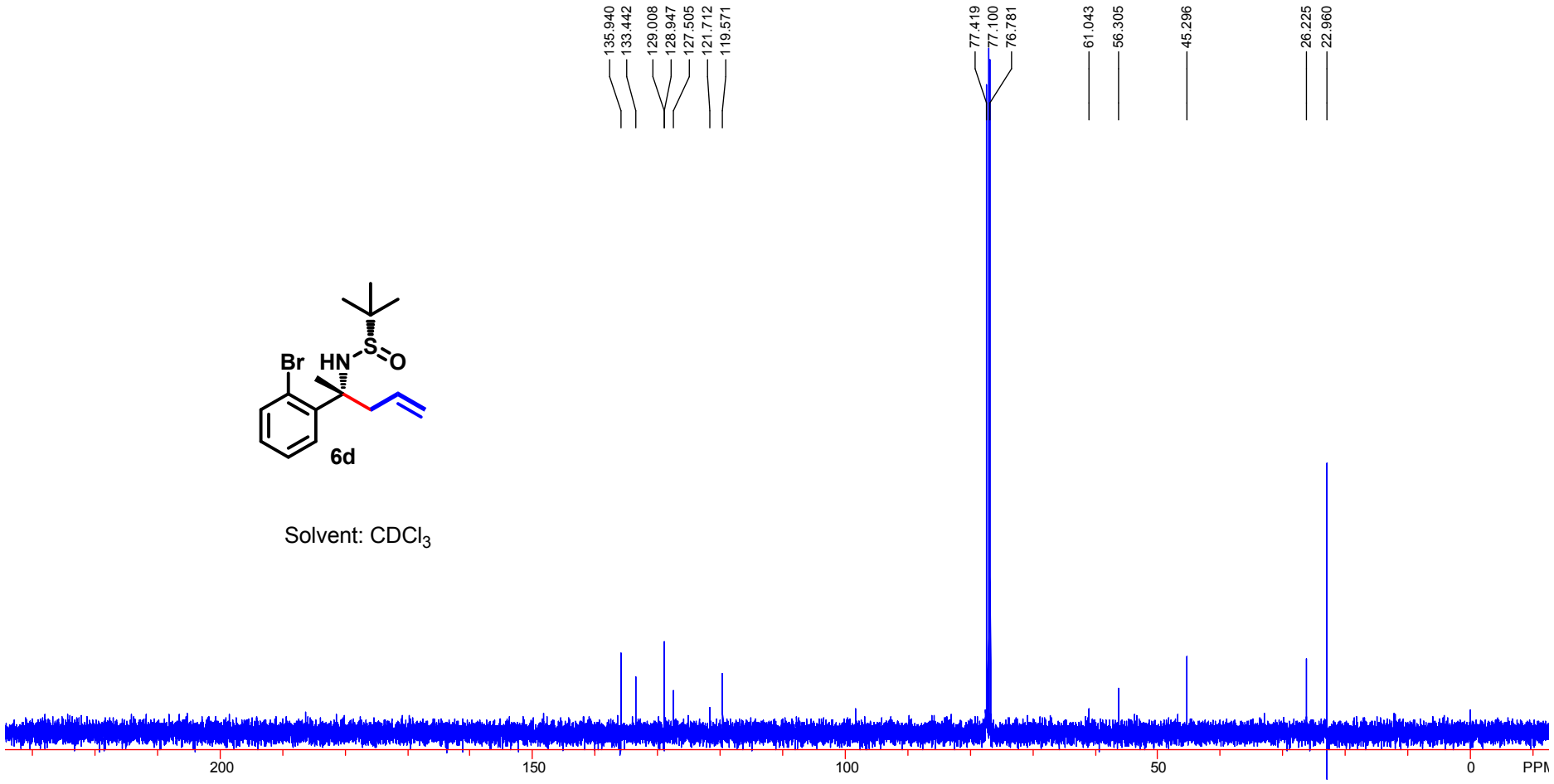
Solvent: $CDCl_3$


145.589
137.815
133.381
128.211
127.839
127.239
123.534
120.421
77.419
77.100
76.789
59.949
56.320
49.259
27.895
22.937
21.783
HN
S
O
6c
Solvent: CDCl3
200
150
100
50
0
PPM



6d

Solvent: $CDCl_3$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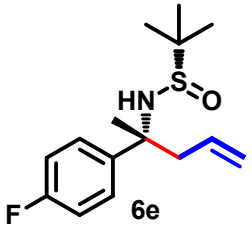
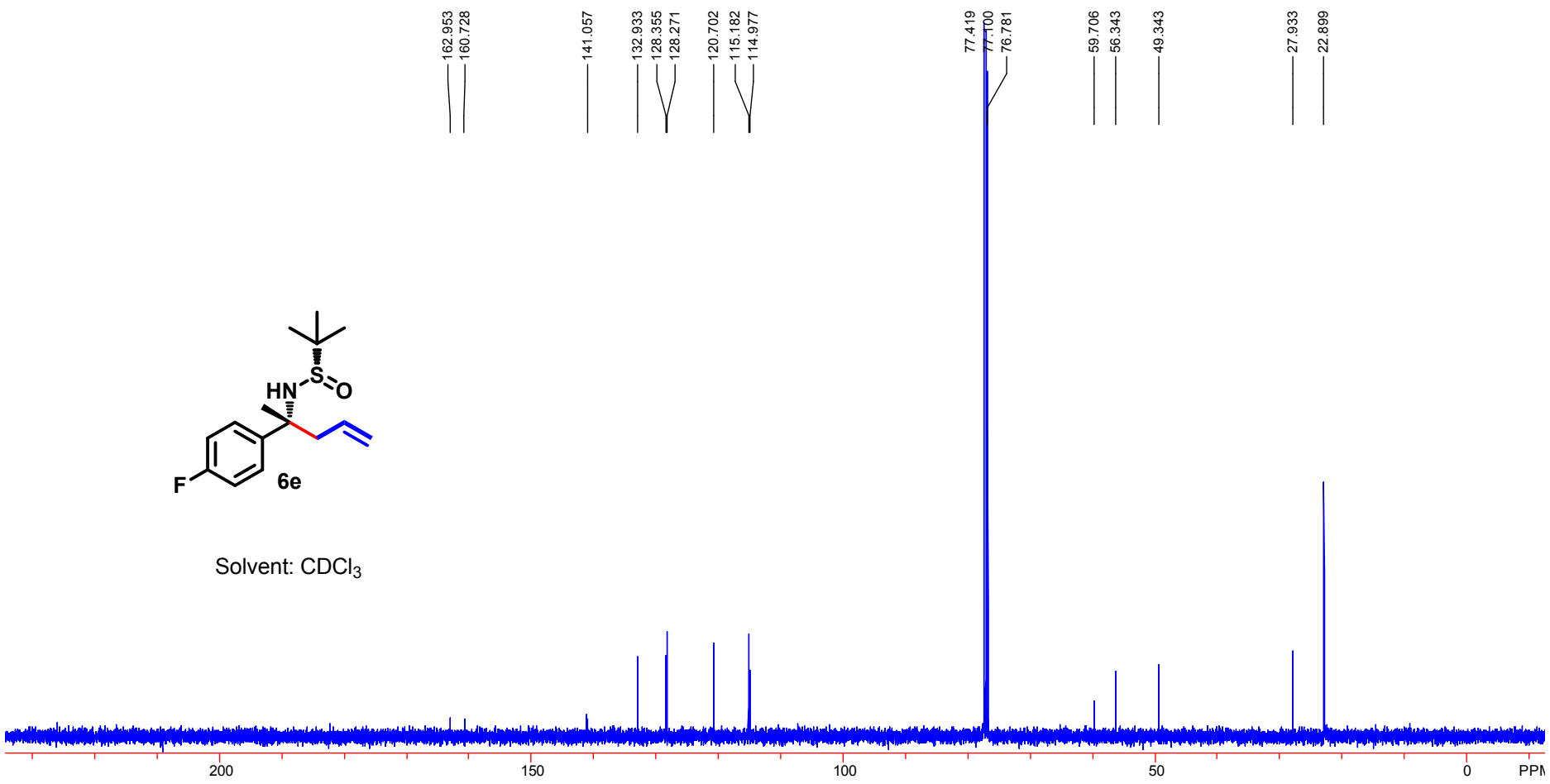
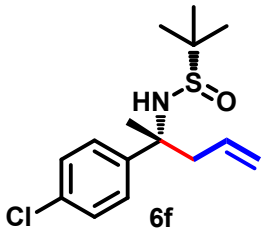
133.442
129.008
128.947
127.505
121.712
119.571
77.419
77.100
76.781
61.043
56.305
45.296
26.225
22.960
Br
HN
S
O
6d
Solvent: CDCl3
200
150
100
50
0
PPM



6e

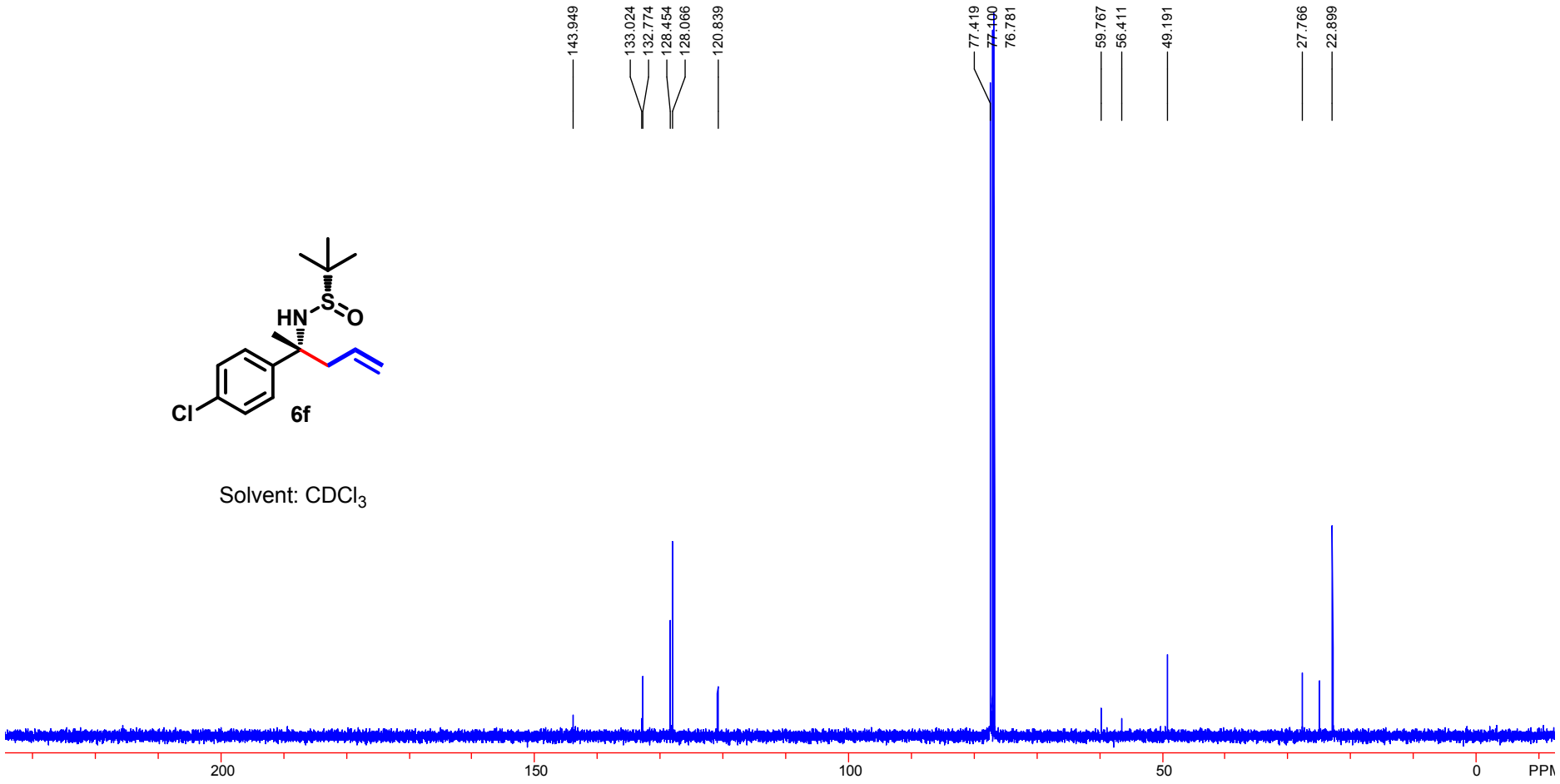
Solvent: $CDCl_3$


162.953
160.728
141.057
132.933
128.355
128.271
120.702
115.182
114.977
77.419
77.100
76.781
59.706
56.343
49.343
27.933
22.899
HN
S
O
F
6e
Solvent: CDCl3
200
150
100
50
0
PPM



6f

Solvent: $CDCl_3$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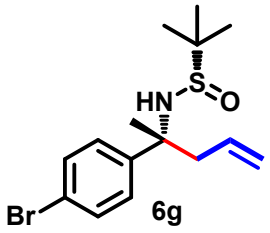
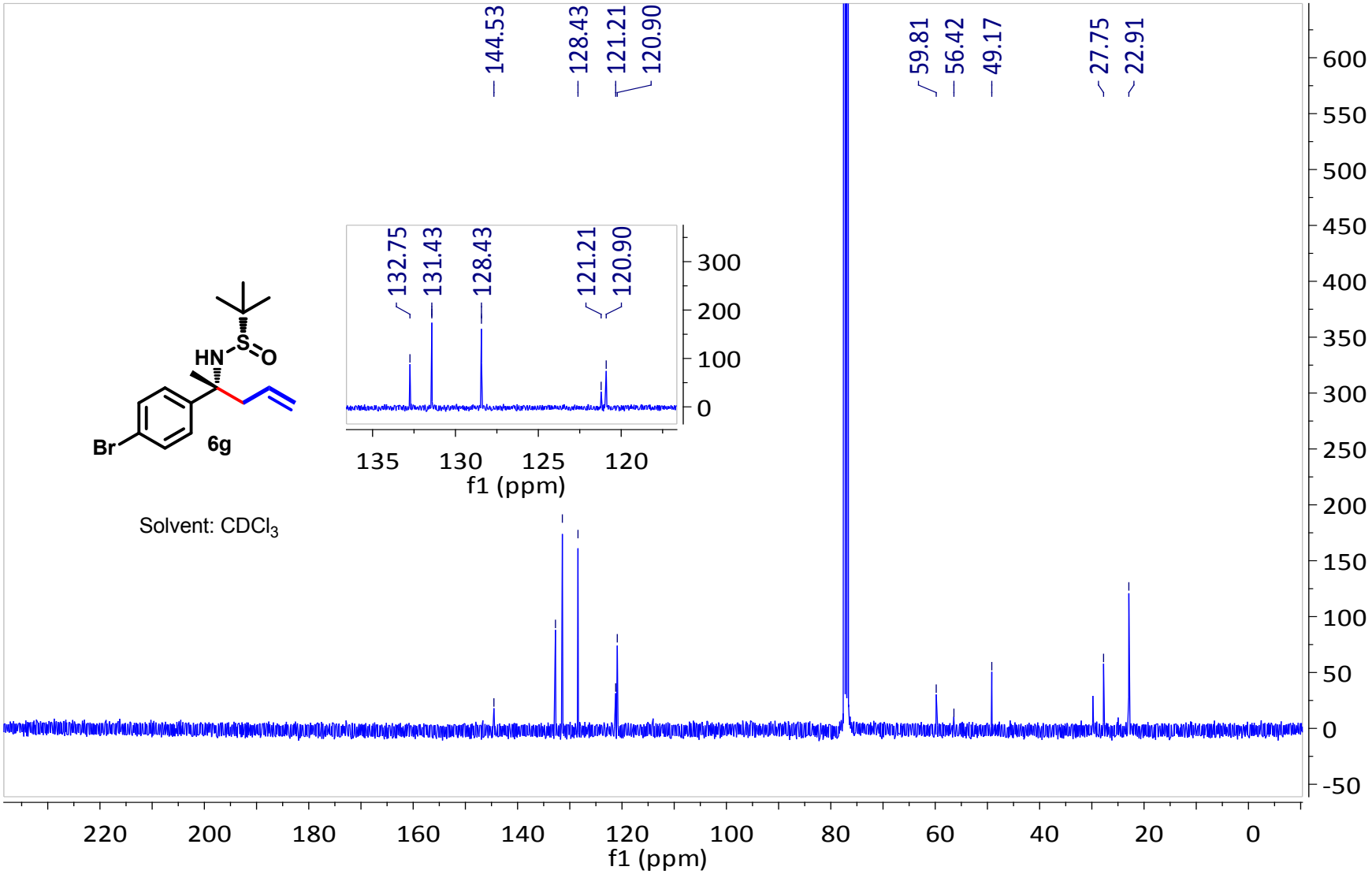
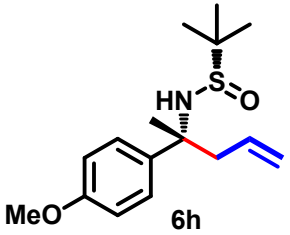
132.774
128.454
128.066
120.839
77.419
77.100
76.781
59.767
56.411
49.191
27.766
22.899
HN
S
O
Cl
6f
Solvent: CDCl3
200
150
100
50
0
PPM



Solvent: $CDCl_3$

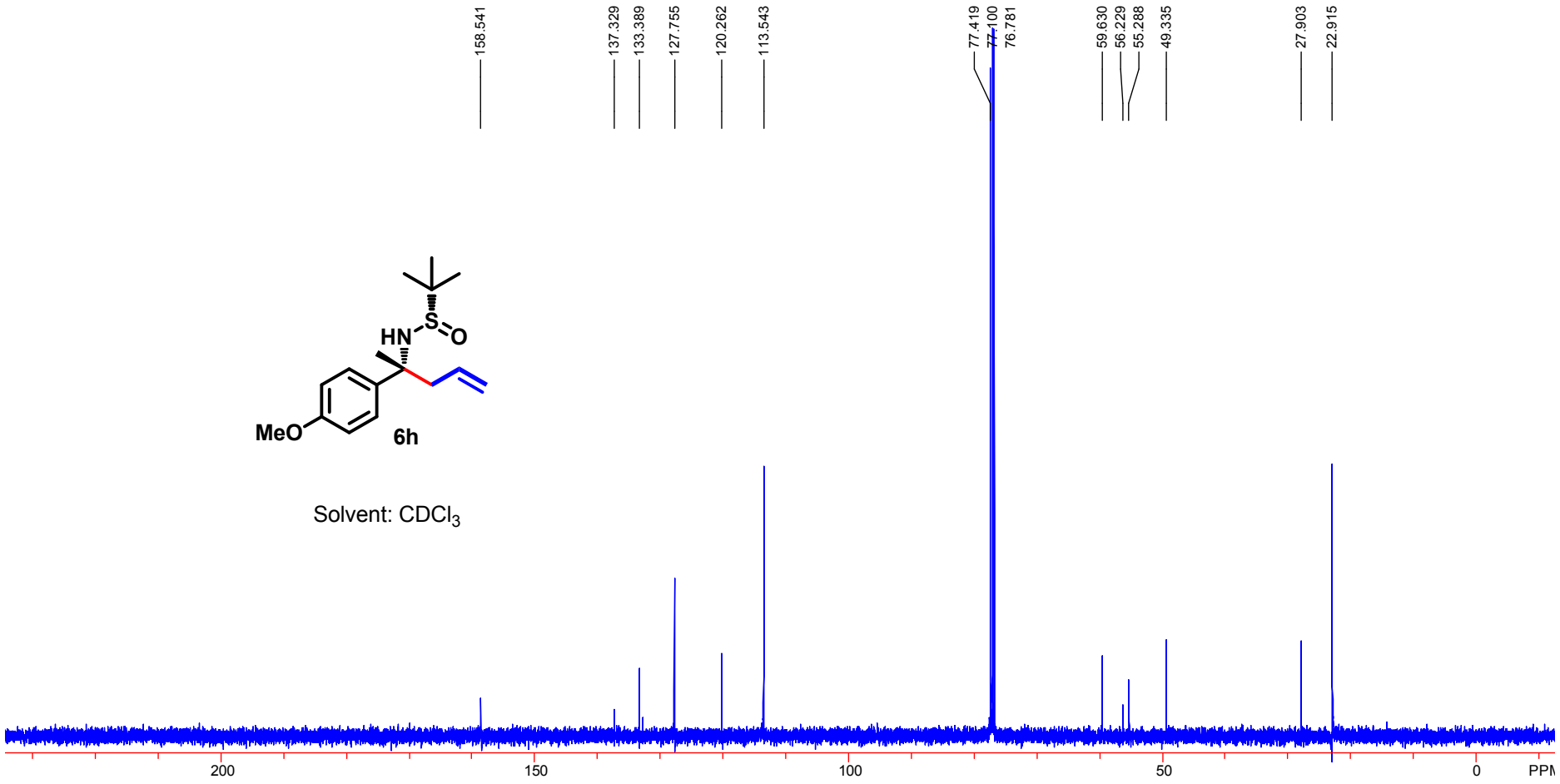

144.53
128.43
121.21
120.90
59.81
56.42
49.17
27.75
22.91
132.75
131.43
128.43
121.21
120.90
HN
S
O
Br
6g
Solvent: CDCl3
f1 (ppm)
f1 (ppm)

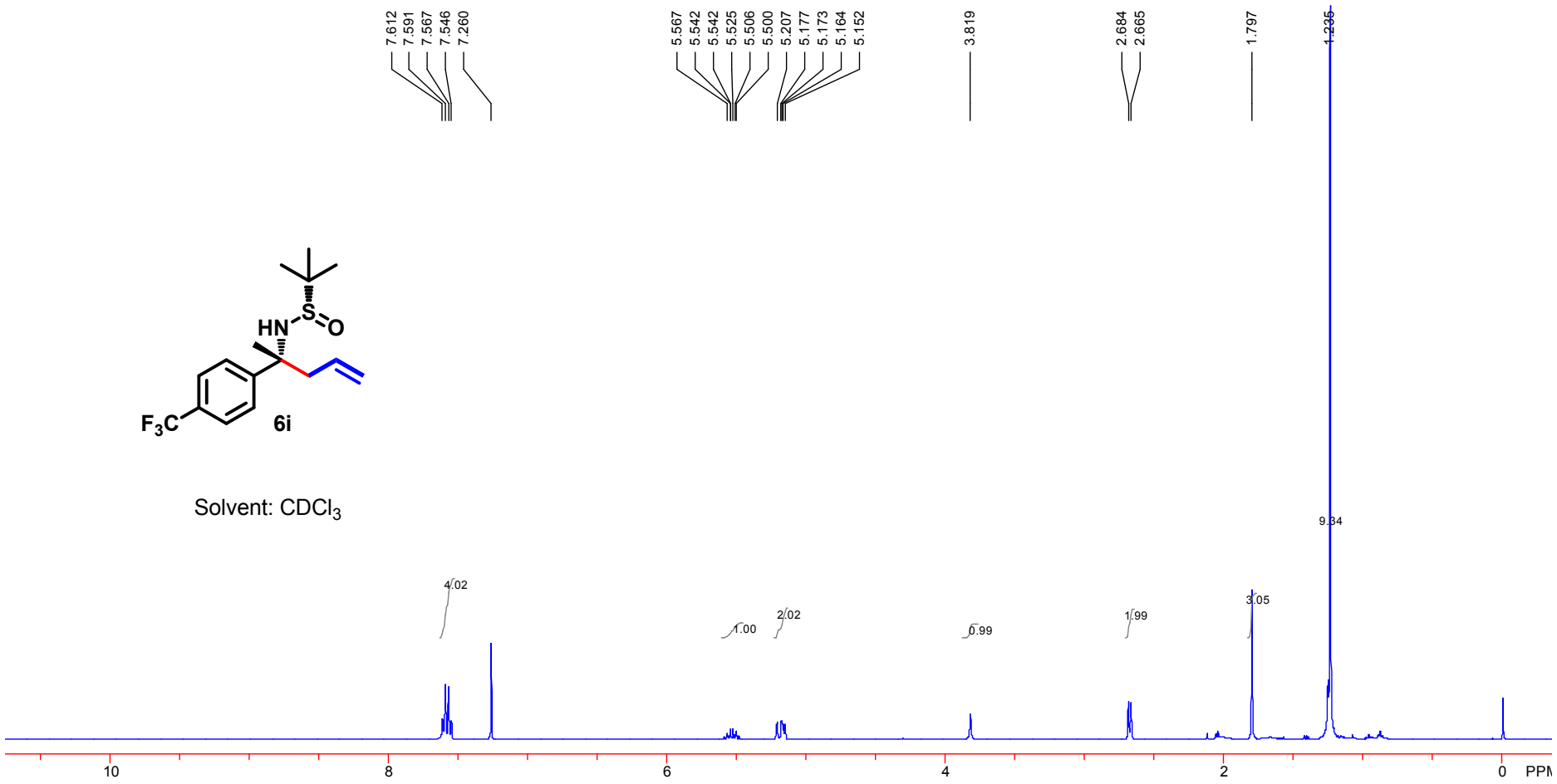
–

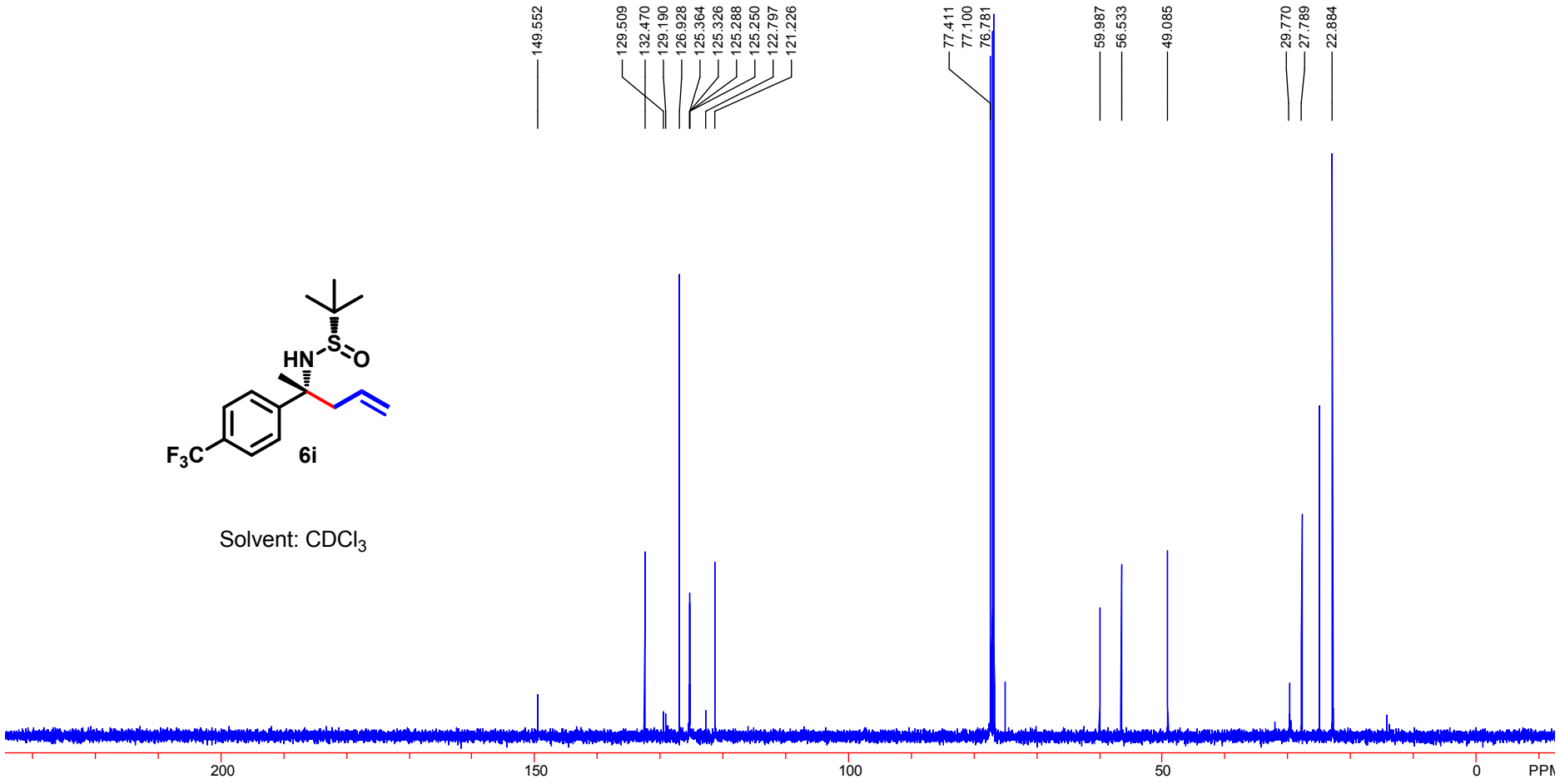


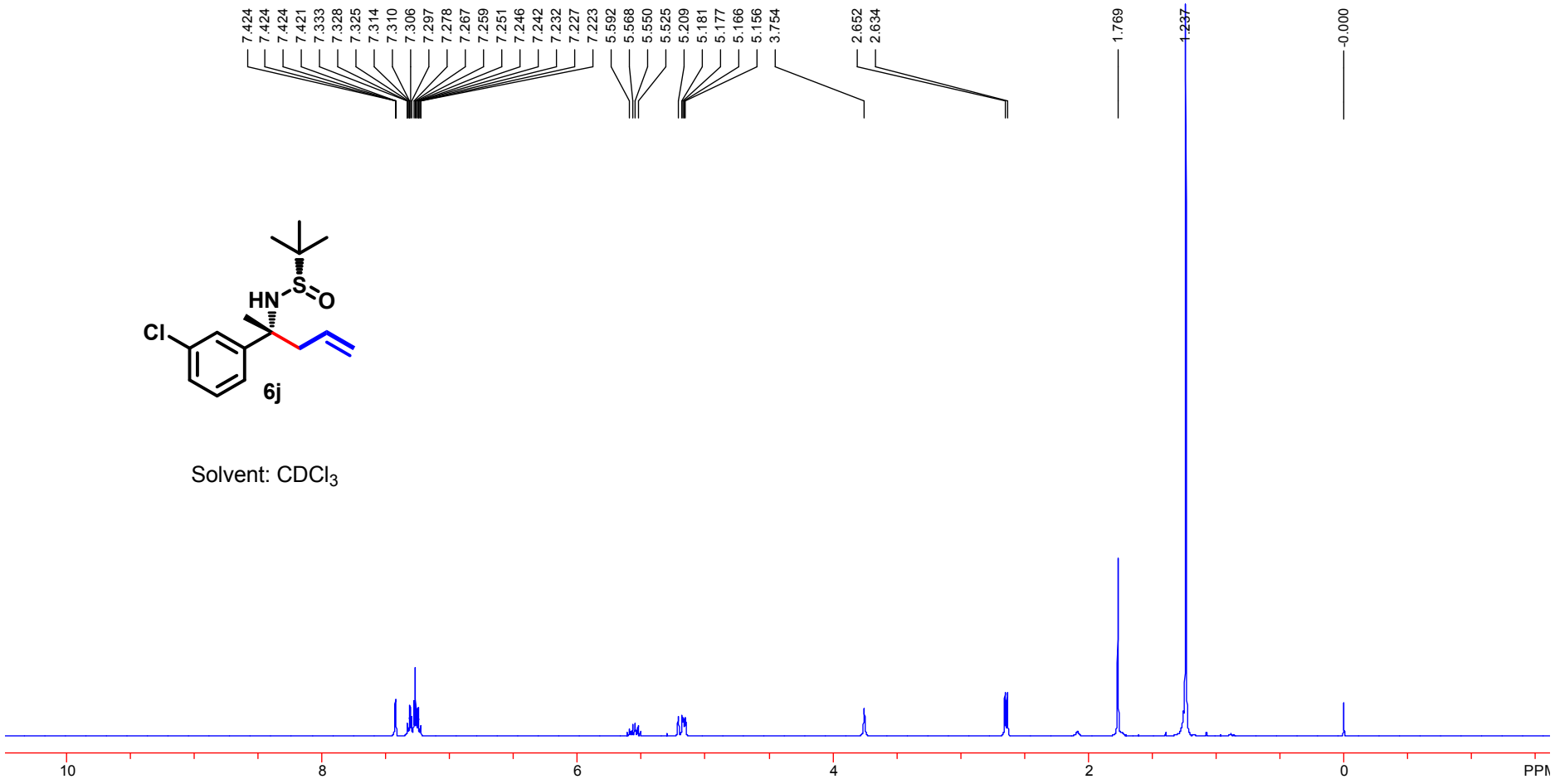
6h

Solvent: $CDCl_3$


158.541
137.329
133.389
127.755
120.262
113.543
77.419
77.100
76.781
59.630
56.229
55.288
49.335
27.903
22.915
HN
S
O
MeO
6h
Solvent: CDCl3
200
150
100
50
0
PPM


7.612
7.591
7.567
7.546
7.260
5.567
5.542
5.542
5.525
5.506
5.500
5.207
5.177
5.173
5.164
5.152
3.819
2.684
2.665
1.797
1.235
HN
S
O
F3C
6i
Solvent: CDCl3
4.02
1.00
2.02
0.99
1.99
3.05
9.84
10
8
6
4
2
0
PPM


149.552
129.509
132.470
129.190
126.928
125.364
125.326
125.288
125.250
122.797
121.226
77.411
77.100
76.781
59.987
56.533
49.085
29.770
27.789
22.884
HN
S
O
F3C
6i
Solvent: CDCl3
200
150
100
50
0
PPM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5.209
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5.177
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5.156
3.754
2.652
2.634
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Cl
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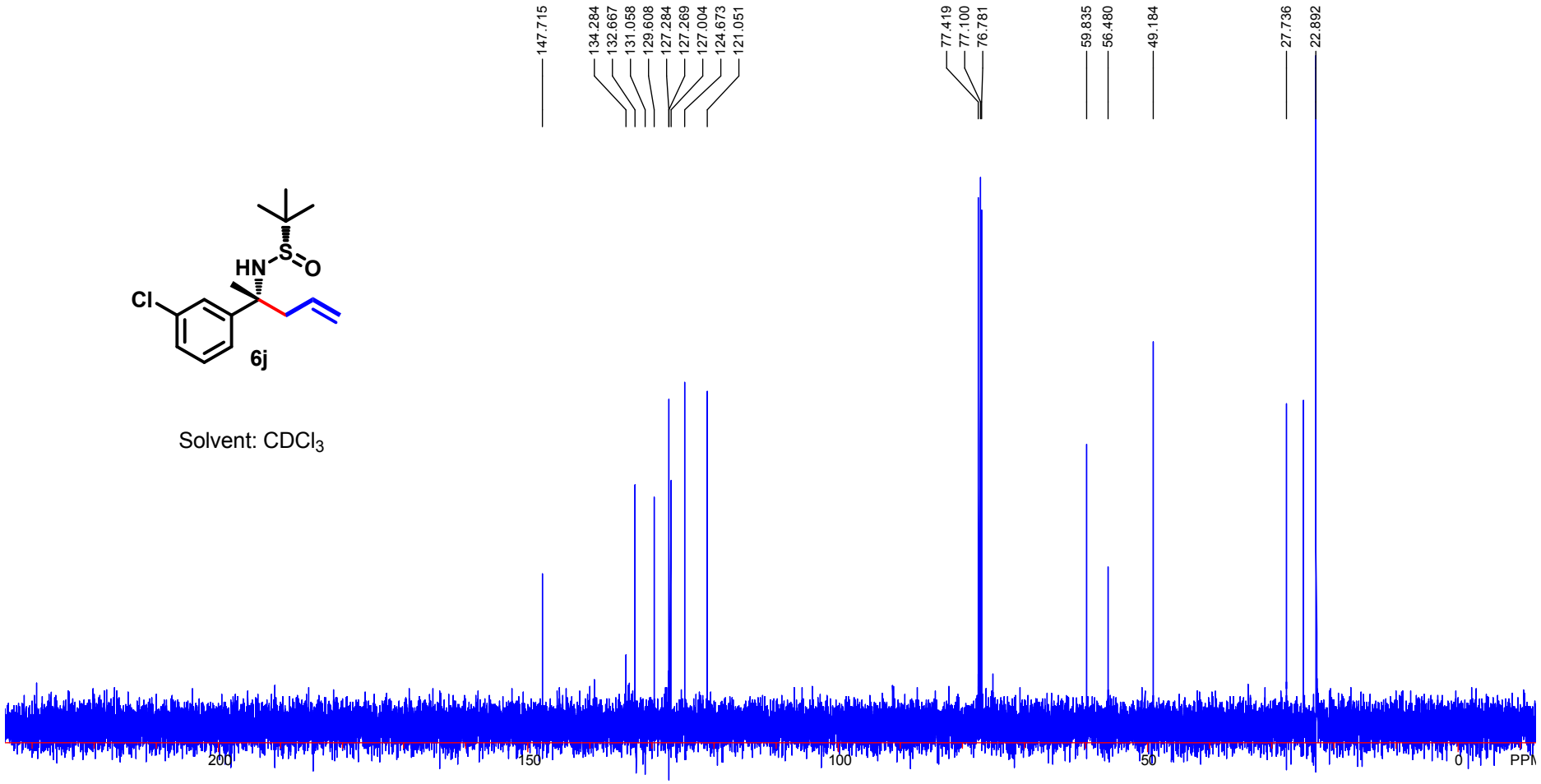
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Cl
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Solvent: CDCl3
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150
100
50
0
PPM