SUPPORTING INFORMATION

Nonmetal-catalyzed hydroamination of ynamides with amines

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Table of Contents

Part I Experimental Part

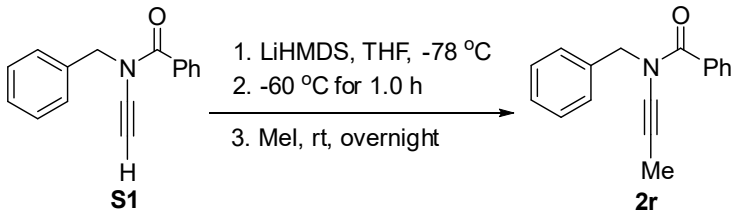
General Information

Unless otherwise indicated, all starting materials were obtained from commercial supplies and used as received. All amines were purchased. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker's Ascend^{TM} 400 NMR spectrometer using $CDCl_3$ as solvent with TMS or residual solvent as standard unless otherwise noted. ^{13}C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra were obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and $KMnO_4$ stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer.

1.1 Synthesis of Ynamides 2.

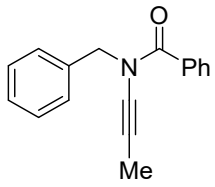
Ynamides **2a**[1], **2b**[2], **2c**[3], **2d**[4], **2e**[5], **2f**[6], **2g**[6], **2h**[7], **2i**[8], **2j**[1], **2k**[1], **2l**[9], **2m**[10], **2n**[11], **2o**[12], **2p**[13], **2q**[14] , **2s**[15] and **2t**[1] were known compounds and synthesized according to corresponding literatures, the data were matched with reported values. Ynamide **2r** was new compounds and synthesized according to literatures[8].

Synthesis of Ynamide 2r.[8]



To an oven-dried flask were charged with ynamide **S1**[16] (470.6 mg, 2.00 mmol) and THF (10.0 mL, ynamide concn = 0.20 *M*). To this solution at -78 °C was added LiHMDS (3.0 mL, 1.0 *M* in THF), and then the mixture was allowed to warm to -60 °C. After the reaction was stirred at -60 °C for 1.0 h, MeI (0.25 mL, 4.00 mmol) was added, the resulting mixture was warmed to rt slowly, stirred overnight (12.0 h) and monitored using TLC analysis, water (10.0 mL) was added to quench the reaction. The quench mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered through a pad of silica gel, concentrated in vacuo, and purified by silica gel flash column

chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford ynamide **2r** (274.2 mg, 1.10 mmol) in 55% yield.

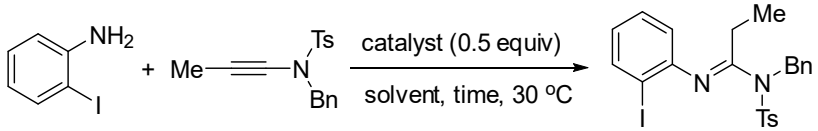


2r

2r: R_f = 0.41 [20:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, CD_3COCD_3) δ 7.81-7.78 (m, 2H), 7.55-7.51 (m, 1H), 7.49-7.42 (m, 4H), 7.41-7.36 (m, 2H), 7.35-7.31 (m, 1H), 4.84 (s, 2H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 170.8, 137.7, 135.1, 131.9, 129.3, 129.2, 129.0, 128.6, 128.5, 76.0, 68.5, 53.1, 2.8; IR (neat) (cm^{-1}) 3028w, 1666s, 1579w, 1392m, 1290s, 1136m; HRMS (ESI): m/z calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226; found 250.1225.

1.2 Condition Optimization of the Hydroamination with Anilines (Table S1).

Table S1. Condition Optimization of the Hydroamination with Anilines



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

entry[a]	catalyst	solvent	time (h)	yield (%)[b]
1	TEA	DCE	21.0	15[c]
2	CSA	DCE	24.0	16[d]
3	TfOH	DCE	0.5	94
4	Tf_2NH	DCE	0.5	93
5	Tf_2O	DCE	0.5	89
6	TfOMe	DCE	0.5	91
7	TMSOTf	DCE	0.5	92
8	TfOH	CH_2Cl_2	0.5	88
9	TfOH	toluene	0.5	83
10	TfOH	THF	2.0	22
11	TfOH	1,4-dioxane	2.0	77
12[e]	TfOH	DCE	0.5	93

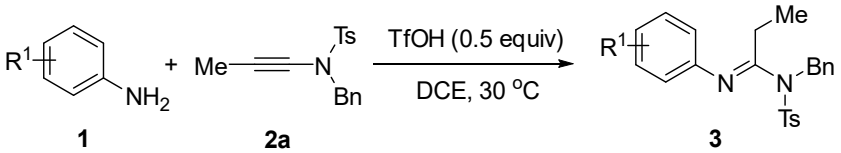
[a]Unless otherwise specified, reactions were carried out using **1a** (0.30 mmol), **2a** (0.25 mmol) with catalyst (0.125 mmol) in solvent (0.625 mL) at 30 °C. [b]Isolated yields. [c]36% of **2a** was recovered. [d]33% of **2a** was recovered [e]**1a** (1.20 mmol) and **2a** (1.00 mmol) were added.

Entry 12: To an oven-dried sealed tube was added aniline **1a** (262.8 mg, 1.20 mmol), ynamide **2a**[1]

(299.4 mg, 1.00 mmol), DCE (2.5 mL, ynamide *concn* = 0.40 *M*), and TfOH (44.3 μL, 0.50 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 0.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3a** (481.5 mg, 0.93 mmol) in 93% yield.

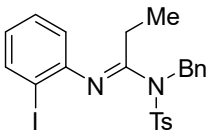
1.3 Hydroamination of Ynamide 2a with Different Anilines (Table 2).

N-arylimines **3a-3ee** were new compounds.



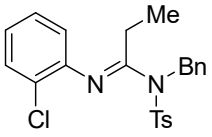
1 **2a** **3**

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 0.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3a** (121.9 mg, 0.24 mmol) in 94% yield.



3a

3a: R_f = 0.45 [10:1 petroleum ether/EtOAc]; white solid; mp = 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 2H, *J* = 8.4 Hz), 7.74 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.43-7.40 (m, 2H), 7.33-7.24 (m, 5H), 7.17-7.13 (m, 1H), 6.72-6.68 (m, 1H), 6.12 (dd, 1H, *J* = 7.9, 1.6 Hz), 4.96 (s, 2H), 2.50-2.44 (m, 5H), 0.92 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 150.1, 144.3, 139.1, 137.1, 136.8, 130.0, 129.0, 128.9, 128.4, 128.0, 127.6, 124.7, 119.7, 90.0, 51.3, 26.1, 21.8, 11.6; IR (neat) (cm^{-1}) 2924w, 1650m, 1458m, 1346s, 1227m, 1162s, 1067w; HRMS (ESI): m/z calcd for $C_{23}H_{23}IN_2O_2S$ $[M+H]^+$: 519.0598; found 519.0597.

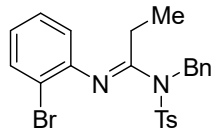


3b

To an oven-dried sealed tube was added aniline **1b** (38.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3b** (102.8 mg, 0.24 mmol) in 96% yield.

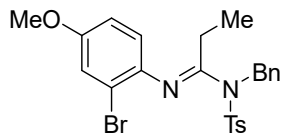
3b: R_f = 0.46 [10:1 petroleum ether/EtOAc]; white solid; mp = 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, J = 8.4 Hz), 7.42-7.40 (m, 2H), 7.34-7.24 (m, 6H), 7.09-7.05 (m, 1H), 6.94-6.90 (m, 1H), 6.19 (dd, 1H, J = 7.8, 1.6 Hz), 4.87 (s, 2H), 2.48 (q, 2H, J = 7.5 Hz), 2.44 (s, 3H), 0.86 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.6, 144.4, 136.8, 136.2, 129.9, 129.8, 129.1, 128.3, 127.8, 127.6, 127.4, 124.3, 123.9, 120.9, 51.3, 26.5, 21.8, 11.3; IR (neat) (cm^{-1}) 2924w, 1654s, 1467m, 1347s, 1226m, 1161s; HRMS (ESI): m/z calcd for $C_{23}H_{23}ClN_2O_2S$ $[M+H]^+$: 427.1242; found 427.1243.



3c

To an oven-dried sealed tube was added aniline **1c** (51.6 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3c** (105.9 mg, 0.22 mmol) in 90% yield.

3c: R_f = 0.48 [10:1 petroleum ether/EtOAc]; white solid; mp = 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.4 Hz), 7.38 (dd, 1H, J = 8.0, 1.3 Hz), 7.33-7.30 (m, 2H), 7.24-7.14 (m, 5H), 7.03-6.99 (m, 1H), 6.77-6.73 (m, 1H), 6.08 (dd, 1H, J = 7.9, 1.6 Hz), 4.81 (s, 2H), 2.40 (q, 2H, J = 7.5 Hz), 2.34 (s, 3H), 0.79 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 147.0, 144.3, 136.9, 136.4, 132.9, 129.9, 129.0, 128.3, 128.1, 127.8, 127.6, 124.5, 120.7, 114.1, 51.3, 26.3, 21.7, 11.4; IR (neat) (cm^{-1}) 2924w, 1654m, 1463w, 1347s, 1227w, 1164s, 1089m; HRMS (ESI): m/z calcd for $C_{23}H_{23}BrN_2O_2S$ $[M+H]^+$: 471.0736; found 471.0737.

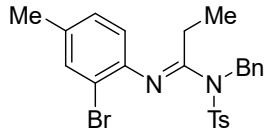


3d

To an oven-dried sealed tube was added aniline **1d** (60.6 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3d** (118.8 mg, 0.24 mmol) in 95% yield.

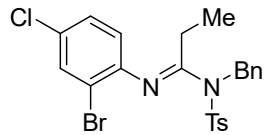
3d: R_f = 0.37 [10:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.42-7.39 (m, 2H), 7.33-7.25 (m, 5H), 7.05 (d, 1H, J = 2.7 Hz), 6.70 (dd, 1H, J = 8.7, 2.8 Hz), 6.10 (d, 1H, J = 8.6 Hz), 4.88 (s, 2H), 3.72 (s, 3H), 2.49 (q, 2H, J = 7.5 Hz), 2.43 (s, 3H), 0.86 (t, 3H J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 156.1, 144.3, 140.4, 137.0, 136.4, 129.9, 129.1, 128.3, 127.8, 127.6, 121.1, 117.8, 114.4, 114.3, 55.8, 51.3, 26.2, 21.7, 11.3; IR (neat) (cm^{-1}) 2937w, 1643m, 1485m, 1350s, 1217w, 1162s, 1090m; HRMS (ESI): m/z calcd for $C_{24}H_{25}BrN_2O_3S$ $[M+H]^+$: 501.0842; found 501.0840.



3e

To an oven-dried sealed tube was added aniline **1e** (55.8 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.2 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 35:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3e** (113.4 mg, 0.23 mmol) in 93% yield.

3e: R_f = 0.35 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.42-7.40 (m, 2H), 7.33-7.24 (m, 6H), 6.93-6.90 (m, 1H), 6.06 (d, 1H, J = 8.0 Hz), 4.88 (s, 2H), 2.48 (q, 2H, J = 7.5 Hz), 2.44 (s, 3H), 2.25 (s, 3H), 0.87 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 144.5, 144.3, 137.0, 136.4, 134.4, 133.2, 129.9, 129.1, 128.8, 128.3, 127.9, 127.6, 120.5, 113.8, 51.3, 26.3, 21.8, 20.5, 11.4; IR (neat) (cm^{-1}) 3033w, 2920w, 1644m, 1455w, 1350s, 1163s, 1090m; HRMS (ESI): m/z calcd for $C_{24}H_{25}BrN_2O_2S$ $[M+H]^+$: 485.0893; found 485.0892.

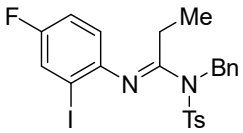


3f

To an oven-dried sealed tube was added aniline **1f** (61.9 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 17.2 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3f** (117.9 mg, 0.23 mmol) in 93% yield.

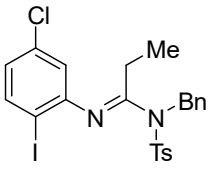
3f: R_f = 0.51 [10:1 petroleum ether/EtOAc]; white solid; mp = 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.47 (d, 1H, J = 2.3 Hz), 7.40-7.37 (m, 2H), 7.34-7.24 (m, 5H), 7.08 (dd, 1H, J = 8.4, 2.3 Hz), 6.07 (d, 1H, J = 8.4 Hz), 4.90 (s, 2H), 2.49-2.43 (m, 5H), 0.88 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.7, 144.4, 136.8, 136.4, 132.4, 129.9, 128.9, 128.8, 128.3, 128.2, 127.8, 127.6, 121.4, 114.5, 51.3, 26.2, 21.7, 11.4; IR (neat) (cm^{-1}) 2933w, 1649w, 1462s, 1351m, 1225s, 1167s, 1090m; HRMS (ESI): m/z calcd for $C_{23}H_{22}BrClN_2O_2S$ $[M+H]^+$: 505.0347; found 505.0345.



3g

To an oven-dried sealed tube was added aniline **1g** (71.1 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3g** (131.2 mg, 0.24 mmol) in 98% yield.

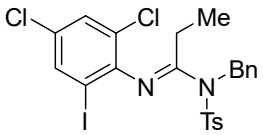
3g: R_f = 0.49 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, 2H, J = 8.1 Hz), 7.45 (dd, 1H, J = 7.9, 2.8 Hz), 7.41-7.39 (m, 2H), 7.32-7.23 (m, 5H), 6.90-6.86 (m, 1H), 6.04 (dd, 1H, J = 8.8, 5.3 Hz), 4.96 (s, 2H), 2.49-2.42 (m, 5H), 0.91 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 158.3 (d, J = 244.8 Hz), 146.5 (d, J = 2.9 Hz), 144.3, 137.0, 136.7, 129.9, 128.8, 128.3, 127.9, 127.6, 125.5 (d, J = 24.3 Hz), 119.8 (d, J = 7.8 Hz), 116.0 (d, J = 21.9 Hz), 89.2 (d, J = 8.4 Hz), 51.2, 25.8, 21.7, 11.5; IR (neat) (cm^{-1}) 3032w, 2937w, 1642s, 1472s, 1350m, 1253m, 1162s, 1089m; HRMS (ESI): m/z calcd for $C_{23}H_{22}FIN_2O_2S$ $[M+H]^+$: 537.0503; found 537.0493.



3h

To an oven-dried sealed tube was added aniline **1h** (76.0 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3h** (134.7 mg, 0.24 mmol) in 97% yield.

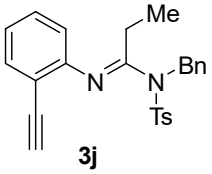
3h: R_f = 0.34 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.63 (d, 1H, J = 8.4 Hz), 7.41-7.39 (m, 2H), 7.34-7.28 (m, 5H), 6.70 (dd, 1H, J = 8.4, 2.4 Hz), 6.09 (d, 1H, J = 2.4 Hz), 4.97 (s, 2H), 2.49-2.43 (m, 5H), 0.94 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 151.2, 144.5, 139.9, 136.9, 136.7, 134.9, 130.0, 128.8, 128.5, 128.0, 127.7, 124.8, 119.7, 87.5, 51.3, 26.1, 21.8, 11.6; IR (neat) (cm^{-1}) 2924w, 1642s, 1547w, 1454m, 1350s, 1227w, 1163s, 1087m; HRMS (ESI): m/z calcd for $C_{23}H_{22}ClIN_2O_2S$ $[M+H]^+$: 553.0208; found 553.0206.



3i

To an oven-dried sealed tube was added aniline **1i** (86.4 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 40:1~30:1 petroleum ether/EtOAc] to afford *N*-arylimine **3i** (140.8 mg, 0.24 mmol) in 96% yield.

3i: R_f = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.62 (d, 1H, J = 2.2 Hz), 7.47-7.44 (m, 2H), 7.31-7.20 (m, 6H), 5.17 (s, 2H), 2.47-2.41 (m, 5H), 1.06 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 146.2, 144.6, 137.4, 137.1, 137.0, 129.9, 129.7, 128.7, 128.4, 128.2, 127.8, 127.5, 123.6, 90.8, 51.2, 26.5, 21.7, 11.3; IR (neat) (cm^{-1}) 2920w, 1624s, 1527w, 1419m, 1354s, 1242m, 1171s; HRMS (ESI): m/z calcd for $C_{23}H_{21}Cl_2IN_2O_2S$ $[M+H]^+$: 586.9818; found 586.9817.

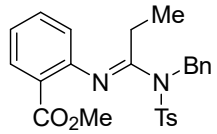


3j

To an oven-dried sealed tube was added aniline **1j** (35.2 mg, 0.30 mmol), ynamide **2a** (74.9 mg,

0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 10.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3j** (96.7 mg, 0.23 mmol) in 93% yield.

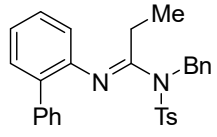
3j: R_f = 0.34 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 2H, J = 8.3 Hz), 7.44-7. 39(m, 3H), 7.33-7.24 (m, 5H), 7.19-7.14 (m, 1H), 6.96-6.92 (m, 1H), 6.21 (d, 1H, J = 8.0 Hz), 4.87 (s, 2H), 2.85 (s, 1H), 2.54 (q, 2H, J = 7.5 Hz), 2.43 (s, 3H), 0.88 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 150.7, 144.2, 137.1, 136.7, 133.4, 129.9, 129.7, 129.1, 128.3, 127.9, 127.6, 123.1, 119.8, 112.3, 81.3, 81.0, 51.2, 26.3, 21.8, 11.5; IR (neat) (cm^{-1}) 3315w, 2940w, 1643s, 1452m, 1349s, 1292m, 1167s, 1090m; HRMS (ESI): m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1631; found 417.1633.



3k

To an oven-dried sealed tube was added aniline **1k** (45.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 12.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3k** (98.0 mg, 0.22 mmol) in 87% yield.

3k: R_f = 0.30 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.86 (dd, 1H, J = 8.0, 1.6 Hz), 7.43-7.40 (m, 2H), 7.35-7.26 (m, 6H), 7.04-7.00 (m, 1H), 6.05 (dd, 1H, J = 8.0, 1.2 Hz), 4.83 (s, 2H), 3.70 (s, 3H), 2.53 (q, 2H, J = 7.5 Hz), 2.44 (s, 3H), 0.89 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.1, 149.2, 144.1, 137.2, 136.8, 133.0, 131.1, 129.8, 129.0, 128.3, 128.0, 127.6, 122.9, 121.0, 120.0, 51.9, 51.2, 26.7, 21.8, 11.5; IR (neat) (cm^{-1}) 2951w, 1655m, 1433w, 1349s, 1294m, 1161s; HRMS (ESI): m/z calcd for $C_{25}H_{26}N_2O_4S$ $[M+H]^+$: 451.1686; found 451.1685.

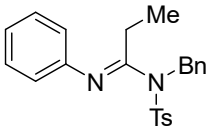


3l

To an oven-dried sealed tube was added aniline **1l** (50.8 mg, 0.30 mmol), ynamide **2a** (74.9 mg,

0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 17.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3l** (99.4 mg, 0.21 mmol) in 85% yield.

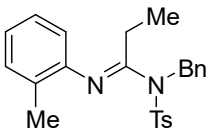
3l: R_f = 0.33 [10:1 petroleum ether/EtOAc]; white solid; mp = 72–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.29-7.15 (m, 14H), 7.09-7.05 (m, 1H), 6.24 (d, 1H, J = 7.7 Hz), 4.76 (s, 2H), 2.42 (s, 3H), 2.33 (q, 2H, J = 7.5 Hz), 0.78 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 146.1, 143.7, 139.9, 137.2, 137.1, 132.2, 130.6, 129.6, 129.3, 128.5, 128.4, 128.2, 128.1, 127.8, 127.5, 126.8, 123.7, 120.0, 50.8, 25.7, 21.8, 11.4; IR (neat) (cm^{-1}) 2920w, 1663s, 1453m, 1341s, 1207m, 1165s, 1087m; HRMS (ESI): m/z calcd for $C_{29}H_{28}N_2O_2S$ $[M+H]^+$: 469.1944; found 469.1943.



3m

To an oven-dried sealed tube was added aniline **1m** (27.9 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 8.3 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3m** (72.4 mg, 0.18 mmol) in 74% yield.

3m: R_f = 0.48 [10:1 petroleum ether/EtOAc]; white solid; mp = 63–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3 Hz), 7.39-7.25 (m, 7H), 7.21 (t, 2H, J =7.8 Hz), 7.02-6.97 (m, 1H), 6.33 (d, 2H, J = 7.5 Hz), 4.75 (s, 2H), 2.52-2.46 (m, 5H), 0.74 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 148.5, 144.3, 136.7, 135.7, 129.9, 129.6, 129.1, 128.3, 127.85, 127.76, 123.4, 119.1, 51.5, 26.0, 21.8, 11.4; IR (neat) (cm^{-1}) 2941w, 1649s, 1456m, 1339s, 1227m, 1159s, 1016m; HRMS (ESI): m/z calcd for $C_{23}H_{24}N_2O_2S$ $[M+H]^+$: 393.1631; found 393.1633.

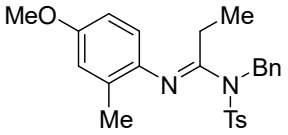


3n

To an oven-dried sealed tube was added aniline **1n** (32.1 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 12.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3n** (75.5 mg, 0.19 mmol) in 74% yield.

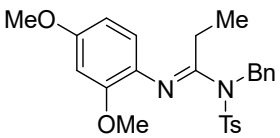
3n: R_f = 0.47 [10:1 petroleum ether/EtOAc]; white solid; mp = 53–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.3 Hz), 7.38-7.23 (m, 7H), 7.06 (d, 1H, J = 7.4 Hz), 7.03-6.99 (m, 1H), 6.92-6.88 (m, 1H), 6.09 (d, 1H, J = 7.6 Hz), 4.89 (s, 2H), 2.46-2.40 (m, 5H), 1.69 (s, 3H), 0.84 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.2, 144.2, 137.0, 136.3, 130.4, 129.8, 128.9, 128.3, 127.7, 127.6, 127.1, 126.4, 123.4, 118.6, 51.2, 25.8, 21.7, 17.7, 11.2; IR (neat) (cm^{-1}) 2933w, 1647m, 1454w, 1348s, 1231m, 1166s; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_2S$ $[M+H]^+$: 407.1788; found 407.1788.



3o

To an oven-dried sealed tube was added aniline **1o** (41.2 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3o** (78.5 mg, 0.18 mmol) in 72% yield.

3o: R_f = 0.33 [10:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.38-7.23 (m, 7H), 6.64 (d, 1H, J = 2.9 Hz), 6.58 (dd, 1H, J = 8.5, 2.8 Hz), 6.03 (d, 1H, J = 8.5 Hz), 4.87 (s, 2H), 3.72 (s, 3H), 2.47-2.41 (m, 5H), 1.68 (s, 3H), 0.82 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 156.0, 144.2, 140.6, 137.1, 136.3, 129.8, 128.9, 128.6, 128.3, 127.7, 127.6, 119.4, 116.0, 111.5, 55.5, 51.3, 25.8, 21.8, 18.1, 11.2; IR (neat) (cm^{-1}) 2939w, 1643m, 1493s, 1348s, 1304w, 1219m, 1150s, 1089m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_3S$ $[M+H]^+$: 437.1893; found 437.1894.

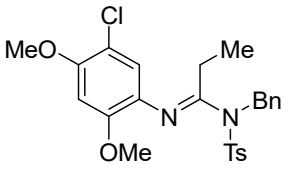


3p

To an oven-dried sealed tube was added aniline **1p** (46.0 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 12.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3p** (70.9 mg, 0.16 mmol) in 63% yield.

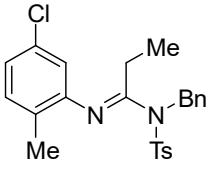
3p: R_f = 0.18 [10:1 petroleum ether/EtOAc]; yellow solid; mp = 74–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.43-7.41 (m, 2H), 7.33-7.25 (m, 5H), 6.44 (d, 1H, J = 2.5 Hz), 6.35 (dd, 1H, J = 8.5, 2.6 Hz), 6.17 (d, 1H, J = 8.4 Hz), 4.72 (s, 2H), 3.75 (s, 3H), 3.70 (s, 3H), 2.47 (q, 2H, J = 7.5 Hz), 2.43 (s, 3H), 0.72 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 157.1, 149.5, 144.0, 136.8, 135.7, 131.0, 129.7, 128.1, 128.0, 127.6, 120.6, 104.2, 99.5, 55.6, 55.4, 51.3, 26.8, 21.7, 10.9, one carbon missing due to overlap, overlapped signal at 129.7 ppm; IR (neat) (cm^{-1}) 2920w, 1647m, 1498m, 1344s, 1259w, 1205s, 1153s; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_4S$ $[M+H]^+$: 453.1843; found 453.1841.



3q

To an oven-dried sealed tube was added aniline **1q** (56.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 20:1~10:1 petroleum ether/EtOAc] to afford *N*-arylimine **3q** (86.1 mg, 0.18 mmol) in 71% yield.

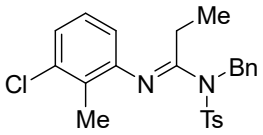
3q: R_f = 0.37 [4:1 petroleum ether/EtOAc]; white solid; mp = 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.41-7.38 (m, 2H), 7.35-7.27 (m, 5H), 6.48 (s, 1H), 6.26 (s, 1H), 4.74 (s, 2H), 3.87 (s, 3H), 3.69 (s, 3H), 2.48-2.43 (m, 5H), 0.76 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 151.8, 148.0, 144.2, 136.7, 135.8, 131.3, 129.8, 129.5, 128.2, 127.9, 127.7, 121.8, 113.8, 98.0, 56.9, 55.9, 51.3, 26.7, 21.8, 11.0; IR (neat) (cm^{-1}) 2924w, 1637m, 1498m, 1348s, 1279w, 1164s, 1032s; HRMS (ESI): m/z calcd for $C_{25}H_{27}ClN_2O_4S$ $[M+H]^+$: 487.1453; found 487.1452.



3r

To an oven-dried sealed tube was added aniline **1r** (42.5 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 12.8 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3r** (99.3 mg, 0.23 mmol) in 90% yield.

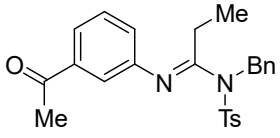
3r: R_f = 0.49 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.37-7.24 (m, 7H), 6.97 (d, 1H, *J* = 8.1 Hz), 6.86 (dd, 1H, *J* = 8.0, 2.2 Hz), 6.07 (d, 1H, *J* = 2.2 Hz), 4.90 (s, 2H), 2.45-2.39 (m, 5H), 1.62 (s, 3H), 0.86 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 148.2, 144.4, 136.9, 136.4, 131.6, 131.5, 129.9, 128.7, 128.5, 127.8, 127.7, 125.9, 123.3, 118.7, 51.2, 25.8, 21.8, 17.2, 11.3; IR (neat) (cm^{-1}) 2920w, 1637m, 1481m, 1348s, 1227w, 1162s, 1089m; HRMS (ESI): m/z calcd for $C_{24}H_{25}ClN_2O_2S$ $[M+H]^+$: 441.1398; found 441.1400.



3s

To an oven-dried sealed tube was added aniline **1s** (42.5 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3s** (98.1 mg, 0.22 mmol) in 89% yield.

3s: R_f = 0.47 [10:1 petroleum ether/EtOAc]; white solid; mp = 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.37-7.24 (m, 7H), 7.00 (dd, 1H, *J* = 8.1, 1.4 Hz), 6.92 (t, 1H, *J* = 7.8 Hz), 5.97 (d, 1H, *J* = 7.6 Hz), 4.91 (s, 2H), 2.45 (s, 3H), 2.41 (q, 2H, *J* = 7.5 Hz), 1.70 (s, 3H), 0.86 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.5, 144.4, 136.9, 136.4, 135.2, 129.9, 128.7, 128.4, 127.7, 126.9, 125.6, 124.1, 117.3, 51.3, 25.8, 21.8, 14.5, 11.3, one carbon missing due to overlap, overlapped signal at 127.7 ppm; IR (neat) (cm^{-1}) 2935w, 1646m, 1455w, 1350s, 1205w, 1162s, 1099m; HRMS (ESI): m/z calcd for $C_{24}H_{25}ClN_2O_2S$ $[M+H]^+$: 441.1398; found 441.1401.

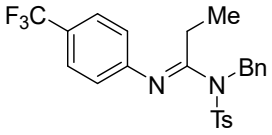


3t

To an oven-dried sealed tube was added aniline **1t** (40.6 mg, 0.30 mmol), ynamide **2a** (74.9 mg,

0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 18:1~10:1 petroleum ether/EtOAc] to afford *N*-arylimine **3t** (74.1 mg, 0.17 mmol) in 68% yield.

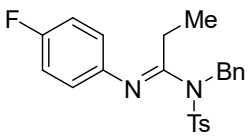
3t: R_f = 0.44 [4:1 petroleum ether/EtOAc]; white solid; mp = 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.60-7.57 (m, 1H), 7.39-7.27 (m, 8H), 6.88 (t, 1H, J = 2.0 Hz), 6.51 (d, 1H, J = 7.7 Hz), 4.80 (s, 2H), 2.52 (s, 3H), 2.49-2.43 (m, 5H), 0.77 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 160.7, 148.8, 144.4, 138.0, 136.6, 135.7, 129.9, 129.4, 129.3, 128.3, 127.8, 124.0, 123.4, 118.8, 51.4, 26.8, 25.8, 21.8, 11.4, one carbon missing due to overlap, overlapped signal at 127.8 ppm; IR (neat) (cm^{-1}) 2924w, 1679s, 1454w, 1344s, 1265m, 1162s, 1090m, 1014m; HRMS (ESI): m/z calcd for $C_{25}H_{26}N_2O_3S$ $[M+H]^+$: 435.1737; found 435.1734.



3u

To an oven-dried sealed tube was added aniline **1u** (48.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3u** (69.8 mg, 0.15 mmol) in 61% yield.

3u: R_f = 0.43 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 8.2 Hz), 7.38-7.28 (m, 7H), 6.38 (d, 2H, J = 8.2 Hz), 4.80 (s, 2H), 2.50-2.45 (m, 5H), 0.79 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 151.5, 144.5, 136.6, 135.8, 129.9, 129.2, 128.4, 127.82, 127.76, 126.4 (q, J = 3.7 Hz), 125.4 (q, J = 32.3 Hz), 124.5 (q, J = 269.7 Hz), 119.4, 51.4, 25.9, 21.8, 11.5; IR (neat) (cm^{-1}) 2943w, 1650m, 1455w, 1332s, 1162s, 1063m; HRMS (ESI): m/z calcd for $C_{24}H_{23}F_3N_2O_2S$ $[M+H]^+$: 461.1505; found 461.1496.

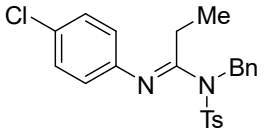


3v

To an oven-dried sealed tube was added aniline **1v** (33.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3v** (69.6 mg, 0.17 mmol) in 68% yield.

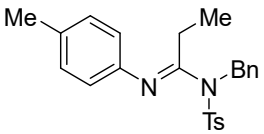
3v: R_f = 0.41 [10:1 petroleum ether/EtOAc]; white solid; mp = 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.37-7.35 (m, 4H), 7.33-7.27 (m, 3H), 6.92-6.88 (m, 2H), 6.29-6.26 (m, 2H), 4.75 (s, 2H), 2.49 (q, 2H, J = 7.5 Hz), 2.45 (s, 3H), 0.74 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 159.3 (d, J = 239.9 Hz), 144.5 (d, J = 2.8 Hz), 144.3, 136.6, 135.6, 129.8, 129.4, 128.3, 127.77, 127.75, 120.4 (d, J = 7.8 Hz), 115.8 (d, J = 22.4), 51.4, 25.8, 21.8, 11.3; IR (neat) (cm^{-1}) 2922w, 1645s, 1598m, 1350s, 1278w, 1202s, 1163s, 1012m; HRMS (ESI): m/z calcd for $C_{23}H_{23}FN_2O_2S$ $[M+H]^+$: 411.1537; found 411.1531.



3w

To an oven-dried sealed tube was added aniline **1w** (38.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford *N*-arylimine **3w** (73.7 mg, 0.17 mmol) in 69% yield.

3w: R_f = 0.49 [10:1 petroleum ether/EtOAc]; white solid; mp = 108–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J =8.3 Hz), 7.37-7.25 (m, 7H), 7.18-7.15 (m, 2H), 6.25 (d, 2H, J = 8.6 Hz), 4.76 (s, 2H), 2.51-2.46 (m, 5H), 0.75 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 147.0, 144.4, 136.6, 135.7, 129.9, 129.3, 129.1, 128.7, 128.3, 127.8, 120.6, 51.4, 25.8, 21.8, 11.4, one carbon missing due to overlap, overlapped signal at 127.8 ppm; IR (neat) (cm^{-1}) 2922w, 1653m, 1482m, 1348s, 1225s, 1156s; HRMS (ESI): m/z calcd for $C_{23}H_{23}ClN_2O_2S$ $[M+H]^+$: 427.1242; found 427.1243.

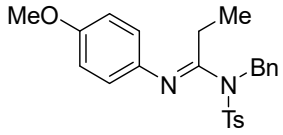


3x

To an oven-dried sealed tube was added aniline **1x** (32.1 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C.

The reaction vessel was capped and stirred at 30 °C for 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3x** (63.7 mg, 0.16 mmol) in 63% yield.

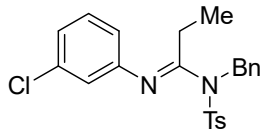
3x: R_f = 0.45 [10:1 petroleum ether/EtOAc]; white solid; mp = 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.38-7.24 (m, 7H), 7.01 (d, 2H, J = 8.0 Hz), 6.26-6.23 (m, 2H), 4.74 (s, 2H), 2.50 (q, 2H, J = 7.5 Hz), 2.44 (s, 3H), 2.26 (s, 3H), 0.72 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 145.9, 144.2, 136.7, 135.6, 132.8, 129.8, 129.64, 129.57, 128.3, 127.8, 127.7, 119.0, 51.4, 25.9, 21.8, 20.9, 11.3; IR (neat) (cm^{-1}) 2924w, 1655m, 1504m, 1345s, 1275s, 1163s, 1090m; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_2S$ $[M+H]^+$: 407.1788; found 407.1789.



3y

To an oven-dried sealed tube was added aniline **1y** (36.9 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.4 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3y** (77.0 mg, 0.18 mmol) in 73% yield.

3y: R_f = 0.32 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, J = 8.3 Hz), 7.38-7.25 (m, 7H), 6.79-6.75 (m, 2H), 6.31-6.28 (m, 2H), 4.73 (s, 2H), 3.75 (s, 3H), 2.51 (q, 2H, J = 7.5 Hz), 2.45 (s, 3H), 0.72 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 156.0, 144.2, 141.8, 136.7, 135.6, 129.8, 129.6, 128.3, 127.9, 127.7, 120.2, 114.4, 55.6, 51.5, 25.9, 21.8, 11.3; IR (neat) (cm^{-1}) 2935w, 1648m, 1503s, 1455w, 1349s, 1240m, 1160s; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_3S$ $[M+H]^+$: 423.1737; found 423.1738.

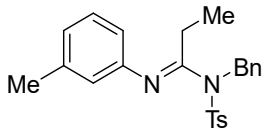


3z

To an oven-dried sealed tube was added aniline **1z** (38.3 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford *N*-arylimine **3z** (79.2 mg, 0.19 mmol) in 74% yield.

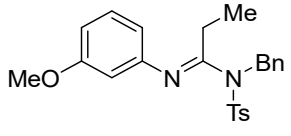
3z: R_f = 0.43 [10:1 petroleum ether/EtOAc]; white solid; mp = 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.4 Hz), 7.37-7.24 (m, 7H), 7.11 (t, 1H, J = 7.9 Hz), 6.97-6.94 (m, 1H), 6.32 (t, 1H, J = 2.0 Hz), 6.19 (d, 1H, J = 7.8 Hz), 4.78 (s, 2H), 2.51-2.45 (m, 5H), 0.78 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 149.6, 144.4, 136.6, 135.8, 134.6, 130.2, 129.9, 129.2, 128.3, 127.8, 127.7, 123.4, 119.4, 117.5, 51.3, 25.9, 21.8, 11.5; IR (neat) (cm^{-1}) 2937w, 1641m, 1587m, 1456w, 1344s, 1218w, 1162s, 1089m; HRMS (ESI): m/z calcd for $C_{23}H_{23}ClN_2O_2S$ $[M+H]^+$: 427.1242; found 427.1242.



3aa

To an oven-dried sealed tube was added aniline **1aa** (32.1 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.4 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3aa** (63.6 mg, 0.16 mmol) in 63% yield.

3aa: R_f = 0.47 [10:1 petroleum ether/EtOAc]; white solid; mp = 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.39-7.26 (m, 7H), 7.09 (t, 1H, J = 7.7 Hz), 6.82-6.79 (m, 1H), 6.17-6.12 (m, 2H), 4.74 (s, 2H), 2.49 (q, 2H, J = 7.5 Hz), 2.45 (s, 3H), 2.26 (s, 3H), 0.74 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 148.5, 144.2, 138.9, 136.7, 135.7, 129.8, 129.5, 128.9, 128.3, 127.8, 127.7, 124.2, 119.7, 116.1, 51.4, 26.0, 21.8, 21.6, 11.4; IR (neat) (cm^{-1}) 2927w, 1648m, 1597m, 1458m, 1344s, 1244w, 1160s; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_2S$ $[M+H]^+$: 407.1788; found 407.1789.

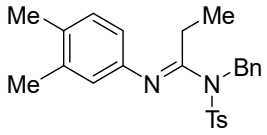


3bb

To an oven-dried sealed tube was added aniline **1bb** (36.9 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3bb** (75.6 mg, 0.18 mmol) in 72% yield.

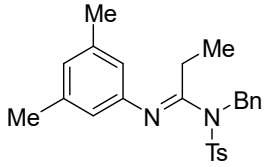
3bb: R_f = 0.29 [10:1 petroleum ether/EtOAc]; yellow solid; mp = 66–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.38-7.25 (m, 7H), 7.11 (t, 1H, J = 8.0 Hz), 6.56-6.53 (m, 1H), 5.95-5.92 (m, 1H), 5.84 (t, 1H, J = 2.2 Hz), 4.74 (s, 2H), 3.71 (s, 3H), 2.50 (q, 2H, J = 7.5 Hz), 2.45 (s, 3H), 0.75 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 160.3, 149.8, 144.3, 136.7, 135.7, 129.9, 129.8, 129.6, 128.3, 127.8, 127.7, 111.6, 108.7, 105.1, 55.3, 51.5, 26.1, 21.8, 11.5; IR (neat) (cm^{-1}) 2918w, 1647m, 1594s, 1468m, 1342s, 1198w, 1152s, 1091m; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_3S$ $[M+H]^+$: 423.1737; found 423.1736.



3cc

To an oven-dried sealed tube was added aniline **1cc** (36.4 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 21.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3cc** (68.7 mg, 0.16 mmol) in 65% yield.

3cc: R_f = 0.51 [10:1 petroleum ether/EtOAc]; yellow solid; mp = 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, J = 8.3 Hz), 7.38-7.23 (m, 7H), 6.96 (d, 1H, J = 7.8 Hz), 6.15 (d, 1H, J= 2.2 Hz), 6.08 (dd, 1H, J = 7.8, 2.2 Hz), 4.73 (s, 2H), 2.50 (q, 2H, J = 7.5 Hz), 2.44 (s, 3H), 2.17 (s, 3H), 2.16 (s, 3H), 0.73 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 146.3, 144.1, 137.3, 136.7, 135.7, 131.4, 130.1, 129.8, 129.6, 128.2, 127.8, 127.7, 120.4, 116.4, 51.4, 25.9, 21.8, 20.0, 19.2, 11.4; IR (neat) (cm^{-1}) 2924w, 1649m, 1456w, 1341s, 1158s, 1089m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_2S$ $[M+H]^+$: 421.1944; found 421.1941.

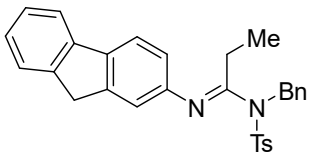


3dd

To an oven-dried sealed tube was added aniline **1dd** (36.4 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 6.0 h. After the reaction was judged to be

complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3dd** (68.5 mg, 0.16 mmol) in 65% yield.

3dd: R_f = 0.49 [10:1 petroleum ether/EtOAc]; white solid; mp = 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.38-7.25 (m, 7H), 6.63 (t, 1H, J = 0.8 Hz), 5.96 (s, 2H), 4.74 (s, 2H), 2.49 (q, 2H, J = 7.5 Hz), 2.45 (s, 3H), 2.215 (s, 3H), 2.214 (s, 3H), 0.75 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.4, 144.1, 138.7, 136.7, 135.8, 129.8, 129.5, 128.3, 127.8, 127.7, 125.1, 116.8, 51.3, 26.0, 21.8, 21.4, 11.4, one carbon missing due to overlap, overlapped signal at 21.4 ppm; IR (neat) (cm^{-1}) 2980w, 1647m, 1452m, 1344s, 1200w, 1162s, 1091m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_2S$ $[M+H]^+$: 421.1944; found 421.1941.



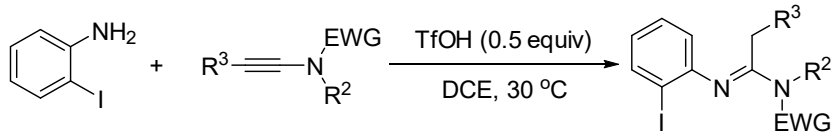
3ee

To an oven-dried sealed tube was added aniline **1ee** (54.4 mg, 0.30 mmol), ynamide **2a** (74.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 12.7 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ee** (84.2 mg, 0.18 mmol) in 70% yield.

3ee: R_f = 0.32 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.1 Hz), 7.68 (d, 1H, J = 7.5 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.49-7.47 (m, 1H), 7.42-7.22 (m, 9H), 6.54 (s, 1H), 6.33 (dd, 1H, J = 8.0, 1.8 Hz), 4.78 (s, 2H), 3.81 (s, 2H), 2.55 (q, 2H, J = 7.5 Hz), 2.46 (s, 3H), 0.77 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 147.5, 144.5, 144.3, 142.9, 141.6, 137.4, 136.7, 135.7, 129.9, 129.5, 128.3, 127.85, 127.76, 126.9, 126.3, 125.1, 120.4, 119.4, 118.0, 115.9, 51.4, 37.1, 26.1, 21.8, 11.4; IR (neat) (cm^{-1}) 2978w, 1736m, 1647m, 1454m, 1349s, 1273w, 1162s, 1089m; HRMS (ESI): m/z calcd for $C_{30}H_{28}N_2O_2S$ $[M+H]^+$: 481.1944; found 481.1945.

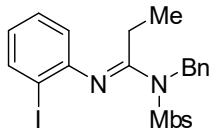
1.4 Hydroamination of Different Ynamides with Aniline 1a (Table 3).

N-arylimines **3oo**[17], **3pp**[18], **3tt**[18] and **3uu**[17] were known compounds, the data were matched with reported values. *N*-arylimines **3ff-3nn**, **3qq-3ss**, **3vv** and **3ww** were new compounds.



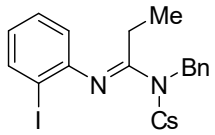
1a **2** **3**

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2b**[2] (78.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ff** (128.4 mg, 0.24 mmol) in 96% yield.



3ff

3ff: R_f = 0.25 [10:1 petroleum ether/EtOAc]; white solid; mp = 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.73 (dd, 1H, J = 8.0, 1.4 Hz), 7.42-7.39 (m, 2H), 7.32-7.23 (m, 3H), 7.16-7.12 (m, 1H), 6.99-6.95 (m, 2H), 6.71-6.66 (m, 1H), 6.14 (dd, 1H, J = 7.8, 1.5 Hz), 4.96 (s, 2H), 3.84 (s, 3H), 2.46 (q, 2H, J = 7.5 Hz), 0.92 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.8, 150.0, 139.0, 137.1, 131.2, 130.1, 129.0, 128.8, 128.3, 127.5, 124.7, 119.7, 114.4, 90.1, 55.8, 51.1, 25.9, 11.5; IR (neat) (cm^{-1}) 2940w, 1641m, 1429w, 1338s, 1255m, 1155s, 1026m; HRMS (ESI): m/z calcd for $C_{23}H_{23}IN_2O_3S$ $[M+H]^+$: 535.0547; found 535.0545.

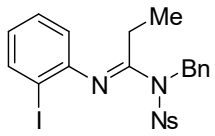


3gg

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2c**[3] (80.0 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford *N*-arylimine **3gg** (128.4 mg, 0.24 mmol) in 95% yield.

3gg: R_f = 0.31 [20:1 petroleum ether/EtOAc]; white solid; mp = 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.74 (dd, 1H, J = 8.0, 1.4 Hz), 7.47-7.44 (m, 2H), 7.40-7.38 (m, 2H), 7.32-7.26 (m, 3H), 7.19-7.15 (m, 1H), 6.74-6.69 (m, 1H), 6.20 (dd, 1H, J = 7.8, 1.6 Hz), 4.97 (s, 2H),

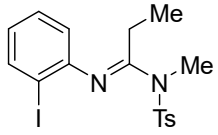
2.42 (q, 2H, J = 7.5 Hz), 0.93 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.8, 139.8, 139.1, 138.2, 136.6, 129.7, 129.4, 129.1, 128.7, 128.5, 127.8, 124.9, 119.6, 89.9, 51.2, 25.8, 11.5; IR (neat) (cm^{-1}) 3059w, 1650m, 1459w, 1344s, 1210m, 1157s, 1087m; HRMS (ESI): m/z calcd for $C_{22}H_{20}ClIN_2O_2S$ $[M+H]^+$: 539.0051; found 539.0049.



3hh

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2d**[4] (82.6 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3hh** (122.4 mg, 0.22 mmol) in 89% yield.

3hh: R_f = 0.32 [10:1 petroleum ether/EtOAc]; white solid; mp = 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.25 (m, 2H), 8.06-8.02 (m, 2H), 7.76 (dd, 1H, J = 8.0, 1.4 Hz), 7.39-7.37 (m, 2H), 7.33-7.29 (m, 3H), 7.25-7.21 (m, 1H), 6.79-6.75 (m, 1H), 6.36 (dd, 1H, J = 7.9, 1.6 Hz), 5.02 (s, 2H), 2.39 (q, 2H, J = 7.5 Hz), 0.99 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 150.2, 149.4, 145.7, 139.2, 136.1, 129.9, 129.2, 128.7, 128.6, 128.2, 125.3, 124.1, 119.6, 89.9, 51.2, 25.4, 11.4; IR (neat) (cm^{-1}) 2935w, 1648s, 1528s, 1457m, 1341s, 1227w, 1171s, 1086m; HRMS (ESI): m/z calcd for $C_{22}H_{20}IN_3O_4S$ $[M+H]^+$: 550.0292; found 550.0289.

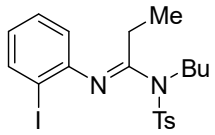


3ii

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2e**[5] (55.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ii** (100.9 mg, 0.23 mmol) in 91% yield.

3ii: R_f = 0.27 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 3H), 7.34 (d, 2H, J = 8.1 Hz), 7.28-7.24 (m, 1H), 6.77-6.73 (m, 1H), 6.59 (dd, 1H, J = 7.9, 1.6 Hz), 3.29 (s, 3H), 2.62 (q, 2H, J = 7.5 Hz), 2.43 (s, 3H), 1.12 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100

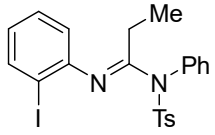
MHz, $CDCl_3$) δ 162.6, 150.0, 144.4, 139.1, 135.5, 130.0, 129.1, 127.6, 124.9, 119.8, 90.9, 36.5, 25.7, 21.7, 12.2; IR (neat) (cm^{-1}) 2935w, 1639m, 1456w, 1351s, 1224m, 1159s; HRMS (ESI): m/z calcd for $C_{17}H_{19}IN_2O_2S$ $[M+H]^+$: 443.0285; found 443.0284.



3jj

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2f**[6] (66.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford *N*-arylimine **3jj** (111.6 mg, 0.23 mmol) in 92% yield.

3jj: R_f = 0.51 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 3H), 7.32-7.30 (m, 2H), 7.29-7.25 (m, 1H), 6.77-6.73 (m, 1H), 6.58 (dd, 1H, *J* = 7.9, 1.5 Hz), 3.82 (t, 2H, *J* = 7.5 Hz), 2.55 (q, 2H, *J* = 7.5 Hz), 2.42 (s, 3H), 1.79-1.72 (m, 2H), 1.43-1.36 (m, 2H), 1.08 (t, 3H, *J* = 7.5 Hz), 0.94 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 150.2, 144.1, 139.2, 137.0, 129.9, 129.1, 127.7, 124.8, 119.8, 90.6, 48.0, 31.7, 21.7, 20.1, 14.0, 11.9, one carbon missing due to overlap, overlapped signal at 20.1 ppm; IR (neat) (cm^{-1}) 2957w, 1638s, 1459m, 1348s, 1228w, 1163s, 1089m; HRMS (ESI): m/z calcd for $C_{20}H_{25}IN_2O_2S$ $[M+H]^+$: 485.0754; found 485.0753.

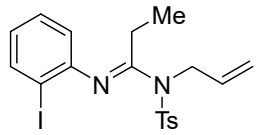


3kk

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2g**[6] (71.3 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3kk** (113.5 mg, 0.23 mmol) in 90% yield.

3kk: R_f = 0.38 [10:1 petroleum ether/EtOAc]; white solid; mp = 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 3H), 7.43 (s, 5H), 7.30-7.26 (m, 1H), 7.19 (d, 2H, *J* = 8.1 Hz), 6.80-6.73 (m, 2H), 2.39 (s, 3H), 1.89 (q, 2H, *J* = 7.5 Hz), 0.96 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ

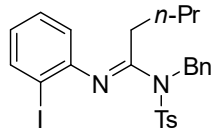
160.0, 150.1, 143.8, 138.9, 137.4, 136.4, 130.7, 130.0, 129.33, 129.29, 129.1, 128.9, 124.8, 119.7, 90.3, 24.6, 21.8, 11.4; IR (neat) (cm^{-1}) 2920w, 1648s, 1458m, 1356s, 1209s, 1166s, 1090m, 1030w; HRMS (ESI): m/z calcd for $C_{22}H_{21}IN_2O_2S$ $[M+H]^+$: 505.0441; found 505.0439.



3ll

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2h**[7] (62.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ll** (107.7 mg, 0.23 mmol) in 92% yield.

3ll: R_f = 0.49 [10:1 petroleum ether/EtOAc]; white solid; mp = 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.77 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.32-7.29 (m, 2H), 7.27-7.23 (m, 1H), 6.76-6.72 (m, 1H), 6.58 (dd, 1H, *J* = 7.8, 1.6 Hz), 6.04-5.94 (m, 1H), 5.36-5.30 (m, 1H), 5.23-5.19 (m, 1H), 4.52 (d, 2H, *J* = 5.7 Hz), 2.48 (q, 2H, *J* = 7.5 Hz), 2.42 (s, 3H), 1.05 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 150.1, 144.2, 139.1, 137.2, 133.8, 129.8, 129.1, 128.0, 124.8, 120.0, 118.4, 90.5, 50.2, 25.5, 21.8, 11.8; IR (neat) (cm^{-1}) 2922w, 1654s, 1429m, 1334s, 1282m, 1165s; HRMS (ESI): m/z calcd for $C_{19}H_{21}IN_2O_2S$ $[M+H]^+$: 469.0441; found 469.0440.

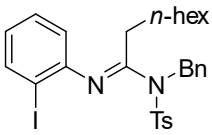


3mm

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2i**[8] (81.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3mm** (130.7 mg, 0.24 mmol) in 96% yield.

3mm: R_f = 0.38 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2H, *J* = 8.3 Hz), 7.72 (dd, 1H, *J* = 8.0, 1.3 Hz), 7.43-7.41 (m, 2H), 7.32-7.23 (m, 5H), 7.16-7.12 (m, 1H), 6.71-6.66 (m, 1H), 6.15 (dd, 1H, *J* = 7.9, 1.6 Hz), 4.95 (s, 2H), 2.45-2.41 (m, 5H), 1.40-1.33 (m, 2H), 1.00-0.90 (m, 2H), 0.66 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 150.0, 144.3,

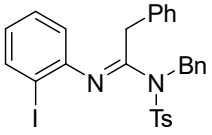
139.0, 137.1, 136.8, 129.9, 129.0, 128.9, 128.3, 128.0, 127.5, 124.7, 119.9, 90.1, 51.2, 32.4, 29.1, 22.4, 21.7, 13.6; IR (neat) (cm^{-1}) 2960w, 1643m, 1457w, 1351s, 1163s, 1089m; HRMS (ESI): m/z calcd for $C_{25}H_{27}IN_2O_2S$ $[M+H]^+$: 547.0911; found 547.0910.



3nn

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2j**[1] (92.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford *N*-arylimine **3nn** (133.1 mg, 0.23 mmol) in 90% yield.

3nn: R_f = 0.38 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 2H, J = 8.3 Hz), 7.73 (dd, 1H, J = 8.0, 1.4 Hz), 7.44-7.41 (m, 2H), 7.32-7.24 (m, 5H), 7.16-7.12 (m, 1H), 6.71-6.67 (m, 1H), 6.16 (dd, 1H, J = 7.9, 1.6 Hz), 4.96 (s, 2H), 2.44-2.40 (m, 5H), 1.40-1.33 (m, 2H), 1.20-1.13 (m, 2H), 1.09-0.98 (m, 4H), 0.94-0.87 (m, 2H), 0.82 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 150.0, 144.2, 139.0, 137.1, 136.8, 129.9, 129.0, 128.9, 128.3, 128.0, 127.6, 124.7, 119.9, 90.1, 51.2, 32.6, 31.6, 29.3, 28.7, 26.9, 22.7, 21.7, 14.2; IR (neat) (cm^{-1}) 2925w, 1641m, 1577w, 1458m, 1350s, 1163s, 1090m; HRMS (ESI): m/z calcd for $C_{28}H_{33}IN_2O_2S$ $[M+H]^+$: 589.1380; found 589.1378.

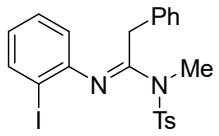


3oo

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2k**[1] (90.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford *N*-arylimine **3oo** (134.1 mg, 0.23 mmol) in 92% yield.

3oo: R_f = 0.42 [10:1 petroleum ether/EtOAc]; white solid; mp = 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, 2H, J = 8.4 Hz), 7.72 (dd, 1H, J = 7.9, 1.3 Hz), 7.27 (d, 2H, J = 7.9 Hz), 7.21-7.08 (m, 9H), 6.88 (dd, 2H, J = 7.4 ,1.7 Hz), 6.68 (td, 1H, J = 7.6, 1.6 Hz), 6.24 (dd, 1H, J = 8.0, 1.7 Hz),

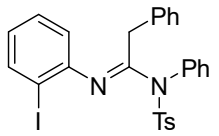
4.83 (s, 2H), 3.79 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.6, 144.3, 139.1, 136.5, 136.4, 134.7, 129.7, 129.0, 128.9, 128.57, 128.56, 128.55, 128.3, 127.5, 126.8, 125.0, 120.2, 90.3, 51.0, 38.2, 21.7; IR (neat) (cm^{-1}) 3028w, 1655m, 1454w, 1350s, 1221m, 1167s; HRMS (ESI): m/z calcd for $C_{28}H_{25}IN_2O_2S$ $[M+H]^+$: 581.0754; found 581.0755. Spectral data are in agreement with literature values[17].



3pp

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2l**[9] (71.3 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3pp** (123.2 mg, 0.24 mmol) in 98% yield.

3pp: R_f = 0.27 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.66 (d, 2H, *J* = 8.4 Hz), 7.27-7.19 (m, 6H), 7.08 (d, 2H, *J* = 6.6 Hz), 6.76-6.72 (m, 1H), 6.61 (dd, 1H, *J* = 7.8, 1.6 Hz), 4.04 (s, 2H), 3.23 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 149.4, 144.3, 139.1, 135.34, 135.28, 129.8, 129.02, 129.00, 128.6, 127.9, 126.8, 125.2, 120.2, 91.5, 37.9, 36.4, 21.7; IR (neat) (cm^{-1}) 2920w, 1660m, 1452w, 1344s, 1255w, 1163s, 1084m; HRMS (ESI): m/z calcd for $C_{22}H_{21}IN_2O_2S$ $[M+H]^+$: 505.0441; found 505.0440. Spectral data are in agreement with literature values[18].

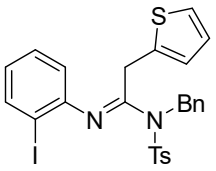


3qq

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2m**[10] (86.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3qq** (128.1 mg, 0.23 mmol) in 90% yield.

3qq: R_f = 0.29 [10:1 petroleum ether/EtOAc]; white solid; mp = 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 3H), 7.38-7.34 (m, 1H), 7.30-7.26 (m, 2H), 7.24-7.18 (m, 6H), 7.08 (d, 2H, *J*

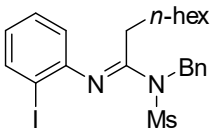
= 7.7 Hz), 6.90-6.87 (m, 2H), 6.81 (dd, 1H, *J* = 7.8, 1.6 Hz), 6.76-6.72 (m, 1H), 3.23 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.9, 143.9, 138.9, 136.9, 136.5, 134.6, 131.1, 130.1, 129.3, 129.1, 129.0, 128.7, 128.6, 126.9, 125.1, 119.9, 90.5, 37.1, 21.8, one carbon missing due to overlap, overlapped signal at 129.0 ppm; IR (neat) (cm^{-1}) 2985w, 1740m, 1671s, 1493m, 1349s, 1267m, 1153s, 1087m; HRMS (ESI): m/z calcd for $C_{27}H_{23}IN_2O_2S$ $[M+H]^+$: 567.0598; found 567.0596.



3rr

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2n**[11] (91.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3rr** (95.0 mg, 0.16 mmol) in 65% yield.

3rr: R_f = 0.24 [20:1 petroleum ether/EtOAc]; white solid; mp = 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 2H, *J* = 8.4 Hz), 7.75 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 7.23-7.10 (m, 7H), 6.86-6.84 (m, 1H), 6.74-6.70 (m, 1H), 6.65 (dd, 1H, *J* = 3.4, 1.2 Hz), 6.19 (dd, 1H, *J* = 7.9, 1.5 Hz), 4.81 (s, 2H), 3.99 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.5, 144.5, 139.1, 136.3, 136.2, 135.7, 129.9, 129.1, 128.5, 128.3, 127.5, 127.4, 126.9, 125.2, 124.8, 120.3, 90.0, 51.3, 33.0, 21.8, one carbon missing due to overlap, overlapped signal at 128.5 ppm; IR (neat) (cm^{-1}) 2910w, 1656m, 1458w, 1349s, 1165s, 1088m; HRMS (ESI): m/z calcd for $C_{26}H_{23}IN_2O_2S_2$ $[M+H]^+$: 587.0318; found 587.0317.

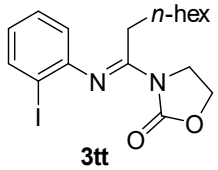


3ss

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2o**[12] (73.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ss** (112.3 mg, 0.22 mmol) in 88% yield.

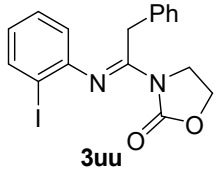
3ss: R_f = 0.35 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, 1H, J = 8.0, 1.4 Hz), 7.50-7.48 (m, 2H), 7.39-7.29 (m, 3H), 7.28-7.24 (m, 1H), 6.80-6.76 (m, 1H), 6.56 (dd, 1H, J = 7.9, 1.6 Hz), 5.00 (s, 2H), 3.23 (s, 3H), 2.33-2.29 (m, 2H), 1.45-1.38 (m, 2H), 1.22-1.15 (m, 2H), 1.11-1.00 (m, 6H), 0.83 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.8, 139.0, 136.6, 129.1, 128.8, 128.6, 128.0, 125.1, 120.1, 90.7, 50.6, 42.7, 31.5, 31.3, 29.3, 28.7, 26.7, 22.7, 14.2; IR (neat) (cm^{-1}) 2927w, 1649s, 1460m, 1348s, 1217w, 1153m; HRMS (ESI): m/z calcd for $C_{22}H_{29}IN_2O_2S$ $[M+H]^+$: 513.1067; found 513.1065.



3tt

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2p**[13] (48.9 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 20:1~10:1 petroleum ether/EtOAc] to afford *N*-arylimine **3tt** (77.2 mg, 0.19 mmol) in 75% yield.

3tt: R_f = 0.24 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, 1H, J = 7.9, 1.3 Hz), 7.32-7.27 (m, 1H), 6.81-6.77 (m, 1H), 6.73 (dd, 1H, J = 7.8, 1.5 Hz), 4.46-4.42 (m, 2H), 4.23-4.19 (m, 2H), 2.71-2.67 (m, 2H), 1.55-1.48 (m, 2H), 1.23-1.12 (m, 8H), 0.83 (t, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 154.1, 149.6, 139.0, 129.0, 124.9, 120.5, 92.3, 62.1, 44.8, 31.6, 29.5, 28.7, 28.3, 27.1, 22.7, 14.2; IR (neat) (cm^{-1}) 2925w, 1768s, 1643m, 1479w, 1387s, 1277w, 1197s, 1093m; HRMS (ESI): m/z calcd for $C_{17}H_{23}IN_2O_2$ $[M+H]^+$: 415.0877; found 415.0877. Spectral data are in agreement with literature values[18].

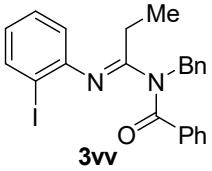


3uu

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2q**[14] (46.8 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 15:1~6:1 petroleum ether/EtOAc] to afford *N*-arylimine **3uu** (82.8 mg, 0.20 mmol) in 82% yield.

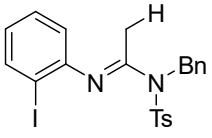
3uu: R_f = 0.36 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, 1H, J = 7.9, 1.4 Hz), 7.23-7.13 (m, 4H), 7.08 (d, 2H, J = 7.1 Hz), 6.76-6.70 (m, 2H), 4.27-4.21 (m, 4H), 4.18-4.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 153.8, 148.7, 138.9, 135.3, 128.9, 128.6, 128.4, 126.6, 125.1, 120.6, 92.8, 61.9, 44.9, 33.5; IR (neat) (cm^{-1}) 2920w, 1762s, 1635m, 1452w, 1386s, 1193s, 1115m; HRMS (ESI): m/z calcd for $C_{17}H_{15}IN_2O_2S$ $[M+H]^+$: 407.0251; found 407.0249. Spectral data are in agreement with literature values[17].



3vv

To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2r** (62.4 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford *N*-arylimine **3vv** (84.9 mg, 0.18 mmol) in 73% yield.

3vv: R_f = 0.23 [20:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 3H), 7.52 (d, 2H, J = 7.1 Hz), 7.49-7.46 (m, 1H), 7.43-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.24 (m, 1H), 7.22-7.18 (m, 1H), 6.75-6.71 (m, 1H), 6.36 (dd, 1H, J = 7.9, 1.6 Hz), 5.30 (s, 2H), 2.06 (q, 2H, J = 7.6 Hz), 0.73 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 163.9, 150.3, 139.1, 138.3, 136.9, 131.6, 129.0, 128.9, 128.8, 128.4, 127.4, 124.9, 119.5, 90.6, 52.1, 26.4, 10.7, one carbon missing due to overlap, overlapped signal at 128.4 ppm; IR (neat) (cm^{-1}) 2931w, 1624s, 1576w, 1358s, 1304m, 1215s, 1144m; HRMS (ESI): m/z calcd for $C_{23}H_{21}IN_2O$ $[M+H]^+$: 469.0771; found 469.0769.



3ww

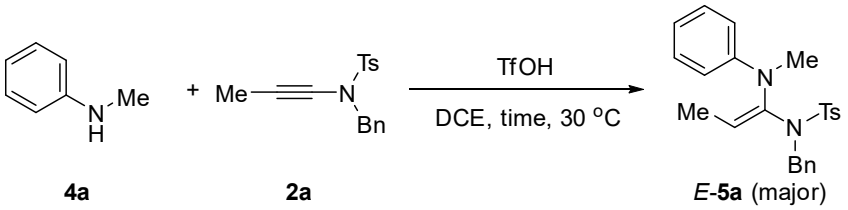
To an oven-dried sealed tube was added aniline **1a** (65.7 mg, 0.30 mmol), ynamide **2s**[15] (71.3 mg, 0.25 mmol), DCE (0.625 mL, ynamide *concn* = 0.40 *M*), and TfOH (11.1 μL, 0.125 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford *N*-arylimine **3ww** (124.3 mg, 0.25 mmol) in 99% yield.

3ww: R_f = 0.37 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.72 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.49-7.46 (m, 2H), 7.34-7.25 (m, 5H), 7.19-7.15 (m, 1H), 6.72-6.68 (m, 1H), 6.30 (dd, 1H, *J* = 7.8, 1.6 Hz), 5.22 (s, 2H), 2.43 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.4, 144.4, 139.1, 137.5, 137.3, 130.0, 129.2, 128.6, 128.5, 127.7, 127.5, 124.8, 120.1, 90.3, 51.0, 21.8, 19.6; IR (neat) (cm^{-1}) 2920w, 1647s, 1460m, 1349s, 1259m, 1163s; HRMS (ESI): m/z calcd for $C_{22}H_{21}IN_2O_2S$ $[M+H]^+$: 505.0441; found 505.0439.

1.5 Condition Optimization of the Hydroamination with Secondary Amines (Table S2).

Table S2. Condition Optimization of the Hydroamination with Secondary Amines



4a **2a** ***E*-5a** (major)

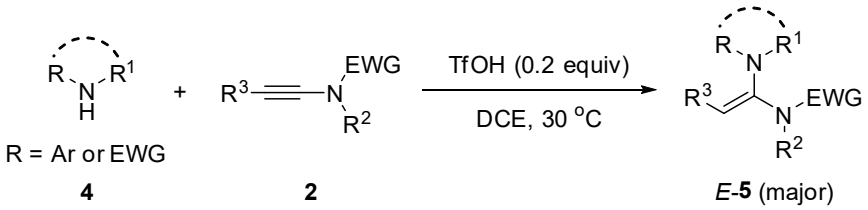
entry[a]	equiv of TfOH	ynamide *concn* (*M*)	time (h)	yield (%)[b]	*E*/*Z*[c]
1	0.5	0.4	0.5	75	11:1
2	1.0	0.4	0.5	44	11:1
3	0.2	0.4	0.5	85	11:1
4	0.2	0.2	1.0	91	11:1

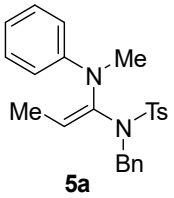
[a]Unless otherwise specified, reactions were carried out using **4a** (0.60 mmol), **2a** (0.50 mmol) with TfOH in DCE at 30 °C. [b]Isolated yields. [c]Determined by ^{1}H NMR spectroscopy of unpurified reaction mixture.

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford a mixture of ethene-1,1-diamines *E*-**5a** and *Z*-**5a**.

1.6 Hydroamination of Ynamides with Secondary Amines (Table 4).

Ethene-1,1-diamines *E*-**5bb**[19], *E*-**5dd**[20] and 3-alkenylindole **(5ll)'**[21] were known compounds, the data were matched with reported values. Ethene-1,1-diamines **5a**-**5o**, **5q**-**5aa**, *Z*-**5bb**, **5cc**, **5ee**-**5kk** and 3-alkenylindoles **(5p)'**, **(5mm)'** were new compounds.

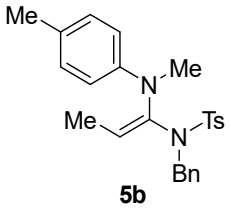




5a

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5a** (169.8 mg, 0.42 mmol) and *Z*-**5a** (15.4 mg, 0.04 mmol) in 91% yield.

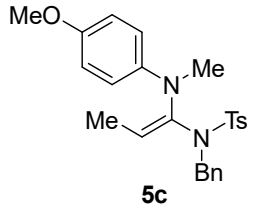
E-**5a**: R_f = 0.37 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.25-7.21 (m, 5H), 7.19-7.16 (m, 2H), 7.10-7.06 (m, 2H), 6.73-6.68 (m, 1H), 6.51 (dd, 2H, *J* = 8.9, 1.2 Hz), 5.19 (q, 1H, *J* = 7.0 Hz), 4.57 (s, 2H), 2.70 (s, 3H), 2.41 (s, 3H), 1.29 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 143.5, 138.0, 137.6, 137.2, 129.5, 128.9, 128.5, 128.4, 127.7, 127.6, 118.4, 115.1, 114.2, 51.7, 35.1, 21.7, 13.4; IR (neat) (cm^{-1}) 2914w, 1658w, 1597s, 1498s, 1454m, 1346s, 1157m; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_2S$ $[M+H]^+$: 407.1788; found 407.1785.



5b

To an oven-dried sealed tube was added secondary amine **4b** (72.7 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5b** (178.1 mg, 0.42 mmol) and *Z*-**5b** (16.2 mg, 0.04 mmol) in 92% yield.

E-**5b**: R_f = 0.41 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.25-7.19 (m, 7H), 6.89 (dd, 2H, *J* = 8.8, 0.8 Hz), 6.46-6.42 (m, 2H), 5.13 (q, 1H, *J* = 7.0 Hz), 4.57 (s, 2H), 2.68 (s, 3H), 2.40 (s, 3H), 2.21 (s, 3H), 1.27 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 143.4, 138.0, 137.8, 137.2, 129.5, 129.4, 128.41, 128.39, 127.7, 127.50, 127.49, 114.4, 114.3, 51.6, 35.1, 21.7, 20.5, 13.3; IR (neat) (cm^{-1}) 2922w, 1657w, 1514s, 1454m, 1344s, 1158s, 1090m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_2S$ $[M+Na]^+$: 443.1764; found 443.1761.

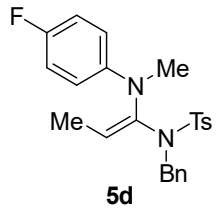


5c

To an oven-dried sealed tube was added secondary amine **4c** (82.3 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 8.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~30:1 petroleum ether/EtOAc] to afford a 5:1 mixture of ethene-1,1-diamines *E*-**5c** (164.0 mg, 0.38 mmol) and *Z*-**5c** (32.8 mg, 0.08 mmol) in 90% yield.

E-**5c** and *Z*-**5c**: R_f = 0.30 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2.0H, *J* = 8.4 Hz, major), 7.59 (d, 0.4H, *J* = 8.4 Hz, minor), 7.26-7.24 (m, 5.0H), 7.21-7.16 (m, 3.4H), 6.85-6.81 (m, 0.4H, minor), 6.73-6.70 (m, 0.4H, minor), 6.68-6.64 (m, 2.0H, major), 6.49-6.45 (m, 2.0H, major), 5.07 (q, 1.0H, *J* = 7.0 Hz, major), 4.86 (q, 0.2H, *J* = 7.0 Hz, minor), 4.57 (s, 2.0H, major), 4.44 (s, 0.4H, minor), 3.75 (s, 0.6H, minor), 3.72 (s, 3.0H, major), 2.66 (s, 3.0H, major), 2.59 (s, 0.6H, minor), 2.41 (s, 3.0H, major), 2.39 (s, 0.6H, minor), 1.54 (d, 0.6H, *J* = 7.1 Hz,

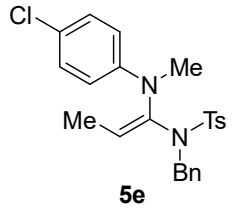
minor), 1.26 (d, 3.0H, J = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5c**, major): δ 152.5, 143.4, 140.7, 138.2, 138.0, 137.2, 129.49, 128.4, 127.7, 127.5, 115.8, 114.3, 113.4, 55.7, 51.8, 35.5, 21.7, 13.3, one carbon missing due to overlap, overlapped signal at 128.4 ppm; (*Z*-**5c**, minor): δ 155.0, 143.3, 142.3, 141.3, 137.8, 136.2, 129.54, 129.4, 128.3, 128.0, 127.8, 122.4, 114.2, 112.0, 55.6, 51.9, 39.0, 21.6, 13.9; IR (neat) (cm^{-1}) 2927w, 1660w, 1509s, 1343m, 1243m, 1157s; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_3S$ $[M+Na]^+$: 459.1713; found 459.1712.



5d

To an oven-dried sealed tube was added secondary amine **4d** (75.1 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~25:1 petroleum ether/EtOAc] to afford a 9:1 mixture of ethene-1,1-diamines *E*-**5d** (180.6 mg, 0.43 mmol) and *Z*-**5d** (20.1 mg, 0.05 mmol) in 95% yield.

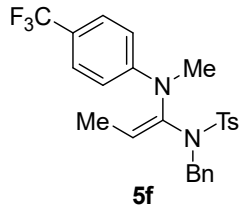
E-**5d** and *Z*-**5d**: R_f = 0.37 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2.2H), 7.27 (d, 0.2H, J = 2.2 Hz, minor), 7.26-7.22 (m, 5.6H), 7.17-7.15 (m, 2.0H, major), 6.83-6.80 (m, 0.2H, minor), 6.79-6.73 (m, 2.2H), 6.43-6.40 (m, 2.0H, major), 5.13 (q, 1.0H, J = 7.0 Hz, major), 4.95 (q, 0.1H, J = 7.1 Hz, minor), 4.57 (s, 2.0H, major), 4.47 (s, 0.2H, minor), 2.65 (s, 3.0H, major), 2.57 (s, 0.3H, minor), 2.41 (s, 3.0H, major), 2.40 (s, 0.3H, minor), 1.59 (d, 0.3H, J = 7.1 Hz, minor), 1.27 (d, 3.0H, J = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5d**, major): δ 156.2 (d, J = 235.3 Hz), 143.6, 142.8 (d, J = 2.0 Hz), 137.9 (d, J = 11.3 Hz), 136.9, 129.6, 128.5, 128.41, 127.7, 127.6, 115.26, 115.23 (d, J = 21.7 Hz), 114.5, 52.00, 35.5, 21.68, 13.3, one carbon missing due to overlap, overlapped signal at 115.34 ppm; (*Z*-**5d**, minor): δ 157.8 (d, J = 238.3 Hz), 144.9 (d, J = 2.4 Hz), 140.9, 137.7, 136.1, 129.4, 128.38, 128.1, 128.0, 127.8, 120.9 (d, J = 7.7 Hz), 115.30 (d, J = 22.1 Hz), 114.1, 51.96, 37.9, 21.66, 14.0, one carbon missing due to overlap, overlapped signal at 115.34 ppm; IR (neat) (cm^{-1}) 2939w, 1658w, 1507s, 1453w, 1343s, 1221m, 1159s, 1056m; HRMS (ESI): m/z calcd for $C_{24}H_{25}FN_2O_2S$ $[M+H]^+$: 425.1694; found 425.1695.



5e

To an oven-dried sealed tube was added secondary amine **4e** (84.6 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~25:1 petroleum ether/EtOAc] to afford a 10:1 mixture of ethene-1,1-diamines *E*-**5e** (190.1 mg, 0.43 mmol) and *Z*-**5e** (19.0 mg, 0.04 mmol) in 95% yield.

E-**5e**: R_f = 0.32 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.25-7.22 (m, 5H), 7.17-7.14 (m, 2H), 7.01-6.97 (m, 2H), 6.41-6.37 (m, 2H), 5.18 (q, 1H, *J* = 7.0 Hz), 4.57 (s, 2H), 2.63 (s, 3H), 2.40 (s, 3H), 1.26 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.7, 137.7, 137.3, 136.8, 129.6, 128.6, 128.5, 128.4, 127.64, 127.58, 123.0, 115.2, 52.0, 35.1, 21.6, 13.3, one carbon missing due to overlap, overlapped signal at 128.5 ppm; IR (neat) (cm^{-1}) 3035w, 1595m, 1493s, 1344s, 1211w, 1157s; HRMS (ESI): m/z calcd for $C_{24}H_{25}ClN_2O_2S$ $[M+H]^+$: 441.1398; found 441.1391.

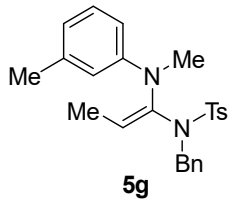


5f

To an oven-dried sealed tube was added secondary amine **4f** (105.1 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 35:1~25:1 petroleum ether/EtOAc] to afford a 13:1 mixture of ethene-1,1-diamines *E*-**5f** (212.7 mg, 0.45 mmol) and *Z*-**5f** (16.4 mg, 0.03 mmol) in 97% yield.

E-**5f**: R_f = 0.32 [10:1 petroleum ether/EtOAc]; white solid; mp = 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, 2H, *J* = 8.3 Hz), 7.28 (d, 2H, *J* = 8.7 Hz), 7.24-7.22 (m, 5H), 7.16-7.14 (m, 2H),

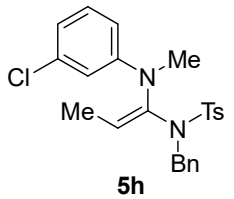
6.48 (d, 2H, J = 8.7 Hz), 5.29 (q, 1H, J = 7.0 Hz), 4.59 (s, 2H), 2.70 (s, 3H), 2.39 (s, 3H), 1.29 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 143.8, 137.6, 136.9, 136.6, 129.6, 128.5, 128.3, 127.7, 127.5, 126.1 (q, J = 3.7 Hz), 125.0 (q, J = 268.7 Hz), 119.7 (q, J = 32.3 Hz), 116.5, 113.2, 52.3, 35.1, 21.6, 13.3; IR (neat) (cm^{-1}) 2941w, 1614m, 1495w, 1322s, 1154s, 1090m; HRMS (ESI): m/z calcd for $C_{25}H_{25}F_3N_2O_2S$ $[M+H]^+$: 475.1662; found 475.1659.



5g

To an oven-dried sealed tube was added secondary amine **4g** (72.7 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford a 12:1 mixture of ethene-1,1-diamines *E*-**5g** (169.5 mg, 0.40 mmol) and *Z*-**5g** (14.1 mg, 0.03 mmol) in 87% yield.

E-**5g**: R_f = 0.41 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.23-7.20 (m, 5H), 7.17-7.15 (m, 2H), 6.97 (t, 1H, J = 7.8 Hz), 6.52 (d, 1H, J = 7.3 Hz), 6.34 (dd, 1H, J = 8.3, 2.6 Hz), 6.25 (t, 1H, J = 2.0 Hz), 5.20 (q, 1H, J = 6.9 Hz), 4.57 (s, 2H), 2.70 (s, 3H), 2.38 (s, 3H), 2.14 (s, 3H), 1.28 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 143.4, 138.4, 137.9, 137.4, 137.1, 129.5, 128.6, 128.32, 128.28, 127.6, 127.4, 119.2, 115.3, 115.0, 111.2, 51.4, 35.0, 21.8, 21.6, 13.3; IR (neat) (cm^{-1}) 2918w, 1601m, 1579w, 1491m, 1349s, 1157s, 1054m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_2S$ $[M+Na]^+$: 443.1764; found 443.1761.

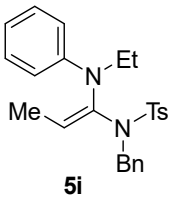


5h

To an oven-dried sealed tube was added secondary amine **4h** (85.0 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent:

35:1~30:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5h** (176.3 mg, 0.40 mmol) and *Z*-**5h** (16.0 mg, 0.04 mmol) in 87% yield.

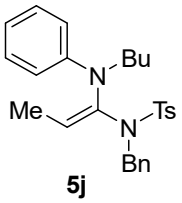
E-**5h**: R_f = 0.43 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.25-7.23 (m, 5H), 7.16-7.14 (m, 2H), 6.96 (t, 1H, J = 8.0 Hz), 6.65 (dd, 1H, J = 7.8, 1.1 Hz), 6.39-6.34 (m, 2H), 5.22 (q, 1H, J = 7.0 Hz), 4.57 (s, 2H), 2.68 (s, 3H), 2.41 (s, 3H), 1.29 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.7, 137.7, 137.0, 136.7, 134.7, 129.8, 129.6, 128.5, 128.4, 127.7, 127.6, 118.2, 116.1, 113.9, 112.1, 52.1, 35.1, 21.7, 13.3; IR (neat) (cm^{-1}) 2925w, 1651w, 1593m, 1484m, 1344s, 1259w, 1163s, 1038m; HRMS (ESI): m/z calcd for $C_{24}H_{25}ClN_2O_2S$ $[M+Na]^+$: 463.1217; found 463.1214.



5i

To an oven-dried sealed tube was added secondary amine **4i** (72.7 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford a 15:1 mixture of ethene-1,1-diamines *E*-**5i** (170.5 mg, 0.41 mmol) and *Z*-**5i** (11.4 mg, 0.03 mmol) in 87% yield.

E-**5i**: R_f = 0.42 [10:1 petroleum ether/EtOAc]; white solid; mp = 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.24-7.19 (m, 7H), 7.06-7.02 (m, 2H), 6.65 (t, 1H, J = 7.2 Hz), 6.51 (dd, 2H, J = 9.0, 1.2 Hz), 5.29 (q, 1H, J = 7.0 Hz), 4.59 (s, 2H), 3.10 (q, 2H, J = 7.0 Hz), 2.38 (s, 3H), 1.24 (d, 3H, J = 7.0 Hz), 0.88 (t, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 143.4, 137.7, 137.2, 135.7, 129.4, 128.9, 128.4, 128.3, 127.7, 127.4, 117.9, 116.4, 113.8, 51.2, 40.6, 21.5, 13.5, 12.0; IR (neat) (cm^{-1}) 2933w, 1595m, 1496m, 1338s, 1209w, 1151s; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_2S$ $[M+Na]^+$: 443.1764; found 443.1763.

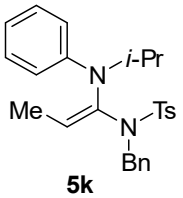


5j

To an oven-dried sealed tube was added secondary amine **4j** (89.5 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at

30 °C. The reaction vessel was capped and stirred at 30 °C for 4.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford a 18:1 mixture of ethene-1,1-diamines *E*-**5j** (186.3 mg, 0.42 mmol) and *Z*-**5j** (10.3 mg, 0.02 mmol) in 88% yield.

E-**5j**: R_f = 0.49 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.24-7.19 (m, 7H), 7.05-7.01 (m, 2H), 6.66-6.62 (m, 1H), 6.48 (dd, 2H, J = 9.0, 1.1 Hz), 5.34 (q, 1H, J = 7.0 Hz), 4.59 (s, 2H), 3.00-2.96 (m, 2H), 2.38 (s, 3H), 1.29-1.22 (m, 5H), 1.13-1.04 (m, 2H), 0.86 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 143.5, 137.7, 137.2, 135.8, 129.4, 128.8, 128.4, 128.3, 127.8, 127.4, 117.8, 116.2, 113.7, 51.1, 46.1, 29.0, 21.5, 20.1, 14.0, 13.6; IR (neat) (cm^{-1}) 2927w, 1658w, 1597m, 1496s, 1342m, 1159s, 1090s; HRMS (ESI): m/z calcd for $C_{27}H_{32}N_2O_2S$ [M+Na]$^+$: 471.2077; found 471.2073.

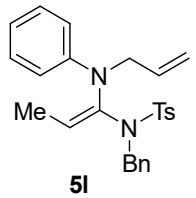


5k

To an oven-dried sealed tube was added secondary amine **4k** (81.1 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 °C. The reaction vessel was capped and stirred at 80 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford a 3:1 mixture of ethene-1,1-diamines *E*-**5k** (145.3 mg, 0.33 mmol) and *Z*-**5k** (48.4 mg, 0.11 mmol) in 89% yield.

E-**5k** and *Z*-**5k**: R_f = 0.37 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2.0H, major), 7.28-7.23 (m, 8.0H), 7.21-7.18 (m, 2.7H), 7.09-7.06 (m, 1.0H, major), 7.04-6.99 (m, 2.3H), 6.71-6.67 (m, 2.7H), 5.09 (q, 1.0H, J = 7.0 Hz, major), 4.94 (q, 0.3H, J = 7.0 Hz, minor), 4.65 (s, 2.0H, major), 4.30 (s, 0.7H, minor)), 3.81-3.74 (m, 1.0H, major), 3.66-3.59 (m, 0.3H, minor)), 2.37 (s, 3.0H, major), 2.32 (s, 1.0H, minor)), 1.53 (d, 1.0H, J = 7.0 Hz, minor)), 1.23 (d, 3.0H, J = 7.1 Hz, major), 1.17 (d, 6.0H, J = 7.0 Hz, major), 0.99 (d, 2.0H, J = 6.5 Hz, minor)); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5k**, major): δ 145.3, 143.3, 138.8, 137.8, 137.5, 129.4, 128.5, 128.4, 128.2, 127.84, 127.3, 119.2, 119.0, 114.0, 50.8, 48.4, 21.53, 20.2, 13.2; (*Z*-**5k**, minor)): δ 143.7, 142.9, 140.8, 137.4, 136.3, 129.27, 129.25, 128.71, 128.66, 128.1, 127.80, 127.7, 125.0, 109.6, 51.5,

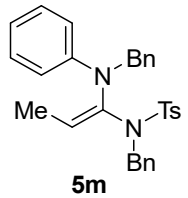
51.2, 21.47, 13.8, one carbon missing due to overlap, overlapped signal at 20.2 ppm; IR (neat) (cm^{-1}) 2978w, 1595m, 1493m, 1312s, 1269w, 1150s; HRMS (ESI): m/z calcd for $C_{26}H_{30}N_2O_2S$ $[M+H]^+$: 435.2101; found 435.2100.



5l

To an oven-dried sealed tube was added secondary amine **4l** (79.9 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^oC. The reaction vessel was capped and stirred at 30 ^oC for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^1H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 50:1~40:1 petroleum ether/EtOAc] to afford a 9:1 mixture of ethene-1,1-diamines *E*-**5l** (161.5 mg, 0.37 mmol) and *Z*-**5l** (17.9 mg, 0.04 mmol) in 83% yield.

E-**5l** and *Z*-**5l**: R_f = 0.42 [10:1 petroleum ether/EtOAc]; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2.2H), 7.25-7.18 (m, 8.0H), 7.08-7.03 (m, 2.0H, major), 6.85 (dd, 0.2H, *J* = 8.9, 1.2 Hz, minor), 6.79-6.75 (m, 0.1H, minor), 6.70-6.66 (m, 1.0H, major), 6.59 (dd, 2.0H, *J* = 8.9, 1.1 Hz, major), 5.70-5.63 (m, 0.1H, minor), 5.62-5.53 (m, 1.0H, major), 5.24 (q, 0.1H, *J* = 7.1 Hz, minor), 5.18 (q, 1.0H, *J* = 7.0 Hz, major), 5.14-5.02 (m, 2.2H), 4.58 (s, 2.0H, major), 4.45 (s, 0.2H, minor), 3.70-3.67 (m, 2.0H, major), 3.57-3.55 (m, 0.2H, minor), 2.38 (s, 3.0H, major), 2.36 (s, 0.3H, minor), 1.62 (d, 0.3H, *J* = 7.1 Hz, minor), 1.27 (d, 3.0H, *J* = 7.1 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5l**, major): δ 145.9, 143.5, 137.6, 137.0, 136.4, 134.4, 129.5, 128.8, 128.6, 128.4, 127.75, 127.5, 118.5, 116.4, 115.9, 114.8, 51.8, 49.4, 21.58, 13.7; (*Z*-**5l**, minor): δ 147.7, 144.2, 138.9, 137.5, 136.3, 134.3, 129.4, 129.3, 128.6, 128.3, 127.79, 127.69, 120.0, 118.3, 117.1, 116.7, 52.0, 50.4, 21.56, 14.1; IR (neat) (cm^{-1}) 3035w, 1653w, 1597m, 1497s, 1362m, 1343s, 1156s, 1090m; HRMS (ESI): m/z calcd for $C_{26}H_{28}N_2O_2S$ $[M+Na]^+$: 455.1764; found 455.1763.

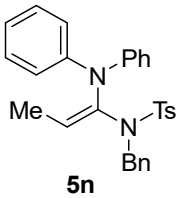


5m

To an oven-dried sealed tube was added secondary amine **4m** (110.0 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^oC. The reaction vessel was capped and stirred at 30 ^oC for 1.0 h. After the reaction was judged to

be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford a 4:1 mixture of ethene-1,1-diamines *E*-**5m** (180.4 mg, 0.37 mmol) and *Z*-**5m** (45.1 mg, 0.09 mmol) in 93% yield.

E-**5m** and *Z*-**5m**: R_f = 0.34 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2.0H, major), 7.57-7.55 (m, 0.5H, minor), 7.22-7.13 (m, 10.0H), 7.08-7.03 (m, 5.0H), 7.02-6.96 (m, 2.5H), 6.84 (dd, 0.5H, *J* = 9.0, 1.3 Hz, minor), 6.74-6.70 (m, 0.2H, minor), 6.68-6.64 (m, 1.0H, major), 6.56 (dd, 2.0H, *J* = 9.0, 1.2 Hz, major), 5.45 (q, 0.2H, *J* = 7.1 Hz, minor), 5.28 (q, 1.0H, *J* = 7.1 Hz, major), 4.58 (s, 2.0H, major), 4.44 (s, 0.5H, minor), 4.27 (s, 2.0H, major), 4.10 (s, 0.5H, minor), 2.30 (s, 0.8H, minor), 2.26 (s, 3.0H, major), 1.62 (d, 0.8H, *J* = 7.1 Hz, minor), 1.36 (d, 3.0H, *J* = 7.1 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5m**, major): δ 146.2, 143.6, 139.5, 137.0, 136.7, 136.4, 129.49, 128.70, 128.65, 128.37, 128.33, 127.73, 127.6, 126.6, 126.4, 118.8, 116.0, 115.1, 51.9, 51.0, 21.6, 14.1; (*Z*-**5m**, minor): δ 148.1, 143.5, 139.0, 138.8, 137.4, 136.1, 129.7, 129.46, 129.38, 128.41, 128.27, 128.0, 127.9, 127.68, 126.7, 119.9, 117.78, 117.75, 52.2, 51.6, 21.7, 14.2; IR (neat) (cm^{-1}) 2920w, 1595m, 1496m, 1336s, 1234w, 1149s, 1089m; HRMS (ESI): m/z calcd for $C_{30}H_{30}N_2O_2S$ $[M+H]^+$: 483.2101; found 483.2102.

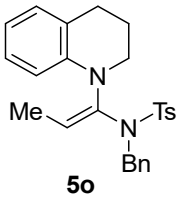


5n

To an oven-dried sealed tube was added secondary amine **4n** (101.6 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~35:1 petroleum ether/EtOAc] to afford a 5:1 mixture of ethene-1,1-diamines *E*-**5n** (185.6 mg, 0.40 mmol) and *Z*-**5n** (37.1 mg, 0.08 mmol) in 95% yield.

E-**5n** and *Z*-**5n**: R_f = 0.40 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2.0H, major), 7.26-7.20 (m, 5.4H), 7.17-7.06 (m, 7.8H), 7.02-6.98 (m, 0.8H, minor), 6.95-6.90 (m, 2.0H, major), 6.83 (dd, 0.8H, *J* = 8.8, 1.4 Hz, minor), 6.74 (dd, 4.0H, *J* = 8.5, 1.2 Hz, major), 5.45 (q, 1.2H, *J* = 7.0 Hz), 4.46 (s, 2.4H), 2.35 (s, 3.0H, major), 2.31 (s, 0.6H, minor), 1.80 (d, 0.6H, *J* = 7.1 Hz, minor), 1.35 (d, 3.0H, *J* = 7.1 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5n**,

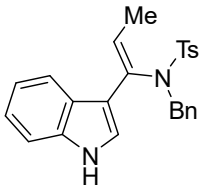
major): δ 144.8, 143.23, 137.1, 137.0, 136.0, 129.4, 129.1, 128.5, 128.2, 127.87, 127.4, 122.7, 122.4, 116.4, 51.5, 21.55, 13.5; (*Z*-**5n**, minor): δ 146.6, 143.16, 139.0, 137.2, 136.5, 129.3, 129.2, 128.9, 128.3, 127.88, 127.82, 123.7, 123.2, 120.7, 52.0, 21.50, 14.4; IR (neat) (cm^{-1}) 2927w, 1660w, 1588m, 1491s, 1342s, 1155s, 1090m; HRMS (ESI): m/z calcd for $C_{29}H_{28}N_2O_2S$ $[M+H]^+$: 469.1944; found 469.1945.



5o

To an oven-dried sealed tube was added secondary amine **4o** (79.9 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford a 4:1 mixture of ethene-1,1-diamines *E*-**5o** (158.1 mg, 0.37 mmol) and *Z*-**5o** (39.5 mg, 0.09 mmol) in 91% yield.

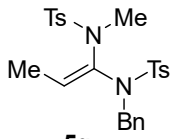
E-**5o** and *Z*-**5o**: R_f = 0.38 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 0.3H, *J* = 8.1 Hz, minor), 7.64 (d, 2.0H, *J* = 8.1 Hz, major), 7.20-7.18 (m, 9.0H), 6.91-6.88 (m, 1.5H), 6.79 (t, 1.0H, *J* = 7.4 Hz, major), 6.64-6.60 (m, 0.3H, minor), 6.55 (t, 1.0H, *J* = 7.3 Hz, major), 6.41 (d, 0.3H, *J* = 7.8 Hz, minor), 6.28 (d, 1.0H, *J* = 8.3 Hz, major), 5.24-5.15 (m, 1.3H), 4.58-4.52 (m, 2.5H), 3.22 (t, 0.5H, *J* = 5.4 Hz, minor), 3.03 (t, 2.0H, *J* = 5.6 Hz, major), 2.71 (t, 0.5H, *J* = 6.4 Hz, minor), 2.62 (t, 2.0H, *J* = 6.4 Hz, major), 2.36 (s, 3.0H, major), 2.11 (s, 0.8H, minor), 1.91-1.85 (m, 0.5H, minor), 1.73-1.67 (m, 2.0H, major), 1.64 (d, 0.8H, *J* = 7.0 Hz, minor), 1.32 (d, 3.0H, *J* = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5o**, major): δ 143.4, 141.9, 138.0, 137.1, 136.8, 129.4, 129.26, 128.4, 128.3, 127.6, 127.4, 126.6, 122.5, 117.6, 115.6, 114.4, 51.3, 46.2, 27.9, 21.7, 21.57, 13.5; (*Z*-**5o**, minor): δ 144.3, 143.5, 139.7, 137.7, 136.3, 129.5, 129.30, 129.2, 128.5, 127.9, 127.8, 126.1, 125.0, 118.9, 118.3, 117.1, 51.6, 46.8, 27.8, 21.10, 21.07, 14.1; IR (neat) (cm^{-1}) 2929w, 1658w, 1600m, 1493s, 1338s, 1302m, 1154s, 1090m; HRMS (ESI): m/z calcd for $C_{26}H_{28}N_2O_2S$ $[M+H]^+$: 433.1944; found 433.1940.



(5p)'

To an oven-dried sealed tube was added secondary amine **4p** (70.5 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *Z*/*E* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 15:1~4:1 petroleum ether/EtOAc] to afford a 2.5:1 mixture of 3-alkenylindoles *Z*-**(5p)'** (122.3 mg, 0.29 mmol) and *E*-**(5p)'** (48.9 mg, 0.12 mmol) in 82% yield.

Z-**(5p)'** and *E*-**(5p)'**: R_f = 0.31 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 0.4H, minor), 8.37 (s, 1.0H, major), 7.81 (d, 2.0H, *J* = 8.2 Hz, major), 7.71 (d, 0.8H, *J* = 8.2 Hz, minor), 7.62 (d, 1.0H, *J* = 7.2 Hz, major), 7.23 (d, 4.0H, *J* = 8.3 Hz, major), 7.18-7.04 (m, 10.0H), 7.01-6.99 (m, 0.4H, minor), 6.63 (d, 1.0H, *J* = 2.6 Hz, major), 6.59 (d, 0.4H, *J* = 2.6 Hz, minor), 6.11 (q, 1.0H, *J* = 6.9 Hz, major), 5.66 (q, 0.4H, *J* = 7.1 Hz, minor), 4.43 (s, 2.8H), 2.37 (s, 3.0H, major), 2.36 (s, 1.2H, minor), 1.48 (d, 1.2H, *J* = 7.1 Hz, minor), 1.37 (d, 3.0H, *J* = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z*-**(5p)'**, major): δ 143.5, 138.25, 136.7, 136.2, 130.9, 129.9, 129.7, 128.2, 127.9, 127.8, 125.9, 124.0, 122.3, 120.2, 120.0, 114.2, 111.6, 111.4, 52.5, 21.70, 14.5; (*E*-**(5p)'**, minor): δ 144.3, 138.30, 137.1, 135.6, 130.3, 129.6, 129.0, 128.4, 128.3, 127.75, 127.72, 127.5, 126.9, 124.8, 122.0, 120.3, 119.9, 52.1, 21.67, 15.1, one carbon missing due to overlap, overlapped signal at 129.0 ppm; IR (neat) (cm^{-1}) 2916w, 1730w, 1529m, 1456m, 1333s, 1154s, 1091m; HRMS (ESI): m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1631; found 417.1621.

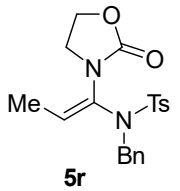


5q

To an oven-dried sealed tube was added secondary amine **4q** (111.2 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 10:1~6:1 petroleum ether/EtOAc] to afford a 1:1 mixture of ethene-1,1-diamines *E*-**5q** (119.5 mg, 0.25 mmol) and *Z*-**5q** (119.5 mg, 0.25 mmol) in 99% yield.

E-**5q** and *Z*-**5q**: R_f = 0.44 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.70-7.65 (m, 6H), 7.48-7.45 (m, 2H), 7.36-7.33 (m, 2H), 7.30-7.21 (m, 14H), 5.19 (q, 1H, *J* = 7.1 Hz), 5.09 (q, 1H, *J* = 7.0 Hz), 4.64(s, 2H), 4.63 (s, 2H), 2.86 (s, 3H), 2.85 (s, 3H),

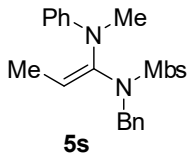
2.40 (s, 6H), 2.38 (s, 6H), 1.28 (dd, 6H, J = 10.0, 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.8, 143.6, 143.5, 137.3, 137.0, 136.6, 136.0, 135.8, 134.3, 133.8, 133.6, 129.8, 129.7, 129.6, 129.51, 129.49, 129.3, 129.0, 128.2, 128.12, 128.11, 127.82, 127.78, 127.6, 127.5, 127.3, 52.5, 51.4, 39.4, 36.7, 21.51, 21.49, 14.0, 13.3, three carbon missing due to overlap, one overlapped signal at 127.82 ppm, two overlapped signal at 21.49 ppm; IR (neat) (cm^{-1}) 3032w, 2924w, 1597m, 1456m, 1342s, 1153s, 1087m; HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_4S_2$ $[M+H]^+$: 485.1563; found 485.1565.



5r

To an oven-dried sealed tube was added secondary amine **4r** (52.2 mg, 0.60 mmol), ynamide **2a** (149.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 20:1~4:1 petroleum ether/EtOAc] to afford a 14:1 mixture of ethene-1,1-diamines *E*-**5r** (137.4 mg, 0.36 mmol) and *Z*-**5r** (9.8 mg, 0.03 mmol) in 76% yield.

E-**5r**: R_f = 0.48 [2:1 petroleum ether/EtOAc]; white solid; mp = 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 2H, J = 8.3 Hz), 7.36-7.29 (m, 7H), 5.68 (q, 1H, J = 7.2 Hz), 4.48 (s, 2H), 4.04 (t, 2H, J = 8.0 Hz), 3.18 (s, 2H), 2.44 (s, 3H), 1.09 (d, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 144.1, 136.8, 135.7, 129.9, 129.8, 129.1, 128.6, 128.4, 127.5, 123.0, 61.6, 53.3, 44.1, 21.6, 12.6; IR (neat) (cm^{-1}) 2924w, 1758s, 1477m, 1398m, 1156s, 1088s; HRMS (ESI): m/z calcd for $C_{20}H_{22}N_2O_4S$ $[M+H]^+$: 387.1373; found 387.1366.

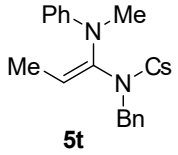


5s

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2b** (157.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent:

20:1~15:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5s** (184.0 mg, 0.44 mmol) and *Z*-**5s** (16.7 mg, 0.04 mmol) in 95% yield.

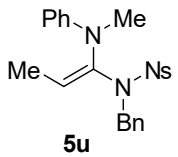
E-**5s**: R_f = 0.36 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2H), 7.24-7.18 (m, 5H), 7.09-7.05 (m, 2H), 6.88-6.84 (m, 2H), 6.71-6.67 (m, 1H), 6.52 (dd, 2H, J = 8.9, 1.2 Hz), 5.21 (q, 1H, J = 7.0 Hz), 4.56 (s, 2H), 3.79 (s, 3H), 2.69 (s, 3H), 1.28 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 146.3, 137.6, 137.1, 132.3, 129.6, 128.8, 128.3, 128.2, 127.4, 118.2, 114.7, 114.0, 113.9, 55.6, 51.6, 34.9, 13.2; IR (neat) (cm^{-1}) 2929w, 1657w, 1596s, 1497s, 1345m, 1259m, 1151s; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_3S$ $[M+H]^+$: 423.1737; found 423.1738.



5t

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2c** (159.9 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5t** (185.8 mg, 0.44 mmol) and *Z*-**5t** (16.9 mg, 0.04 mmol) in 95% yield.

E-**5t**: R_f = 0.30 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.33-7.30 (m, 2H), 7.26-7.19 (m, 5H), 7.11-7.07 (m, 2H), 6.74-6.70 (m, 1H), 6.54 (dd, 2H, J = 8.9, 1.2 Hz), 5.14 (q, 1H, J = 7.0 Hz), 4.60 (s, 2H), 2.72 (s, 3H), 1.29 (d, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 139.4, 138.9, 137.9, 136.8, 129.0, 128.9, 128.8, 128.5, 128.3, 127.7, 118.6, 114.9, 114.1, 52.2, 35.2, 13.2; IR (neat) (cm^{-1}) 2937w, 1598m, 1498m, 1348s, 1212w, 1161s, 1087s; HRMS (ESI): m/z calcd for $C_{23}H_{23}ClN_2O_2S$ $[M+H]^+$: 427.1242; found 427.1241.

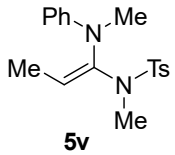


5u

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2d** (165.2 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and

concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford a 11:1 mixture of ethene-1,1-diamines *E*-**5u** (183.1 mg, 0.42 mmol) and *Z*-**5u** (16.6 mg, 0.04 mmol) in 91% yield.

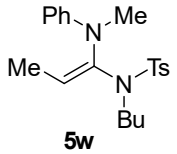
E-**5u**: R_f = 0.29 [10:1 petroleum ether/EtOAc]; yellow solid; mp = 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.09 (m, 2H), 7.74-7.71 (m, 2H), 7.27 (s, 5H), 7.11-7.07 (m, 2H), 6.75-6.71 (m, 1H), 6.54 (dd, 2H, J = 8.9, 1.2 Hz), 5.12 (q, 1H, J = 7.0 Hz), 4.70 (s, 2H), 2.76 (s, 3H), 1.32 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 146.6, 146.0, 138.5, 136.6, 129.1, 128.8, 128.5, 128.4, 128.1, 123.9, 119.1, 115.1, 114.1, 53.2, 35.9, 13.2; IR (neat) (cm^{-1}) 2918w, 1597m, 1521s, 1433w, 1342s, 1226m, 1160s, 1088m; HRMS (ESI): m/z calcd for $C_{23}H_{23}N_3O_4S$ $[M+H]^+$: 438.1482; found 438.1481.



5v

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2e** (112.0 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 25:1~18:1 petroleum ether/EtOAc] to afford a 6:1 mixture of ethene-1,1-diamines *E*-**5v** (136.2 mg, 0.41 mmol) and *Z*-**5v** (22.7 mg, 0.07 mmol) in 96% yield.

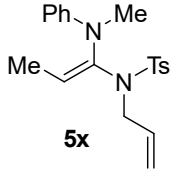
E-**5v** and *Z*-**5v**: R_f = 0.30 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2.3H), 7.23-7.15 (m, 4.7H), 6.95 (d, 0.3H, J = 7.9 Hz, minor), 6.81 (t, 0.2H, J = 7.2 Hz, minor), 6.75 (t, 1.0H, J = 7.3 Hz, major), 6.70 (d, 2.0H, J = 8.0 Hz, major), 5.07-4.99 (m, 1.2H), 3.11 (s, 0.5H, minor), 3.00 (s, 3.0H, major), 2.94 (s, 3.0H, major), 2.64 (s, 0.5H, minor), 2.38 (s, 3.0H, major), 2.34 (s, 0.5H, minor), 1.66 (d, 0.5H, J = 7.1 Hz, minor), 1.40 (d, 3.0H, J = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5v**, major): δ 146.3, 143.3, 140.1, 136.3, 129.4, 128.9, 127.3, 118.2, 113.8, 113.1, 36.8, 36.1, 21.52, 12.9; (*Z*-**5v**, minor): δ 148.1, 143.8, 143.1, 137.0, 129.3, 128.7, 127.2, 119.7, 117.3, 113.3, 37.9, 37.2, 21.48, 12.8; IR (neat) (cm^{-1}) 2900w, 1651m, 1598m, 1498m, 1343s, 1168s, 1011m; HRMS (ESI): m/z calcd for $C_{18}H_{22}N_2O_2S$ $[M+H]^+$: 331.1475; found 331.1476.



5w

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2f** (132.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 45:1~30:1 petroleum ether/EtOAc] to afford a 8:1 mixture of ethene-1,1-diamines *E*-**5w** (163.0 mg, 0.44 mmol) and *Z*-**5w** (20.4 mg, 0.05 mmol) in 98% yield.

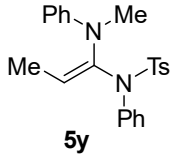
E-**5w** and *Z*-**5w**: R_f = 0.32 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 2.3H, *J* = 8.2 Hz), 7.25 (d, 2.3H, *J* = 8.2 Hz), 7.19 (t, 2.3H, *J* = 7.6 Hz), 7.03 (d, 0.3H, *J* = 8.2 Hz, minor), 6.83 (t, 0.1H, *J* = 7.3 Hz, minor), 6.76 (d, 3.0H, *J* = 7.9 Hz, major), 5.22 (q, 1.1H, *J* = 6.8 Hz), 3.31 (t, 2.3H, *J* = 7.8 Hz), 2.83 (s, 3.0H, major), 2.75 (s, 0.4H, minor), 2.39 (s, 3.0H, major), 2.37 (s, 0.4H, minor), 1.73 (d, 0.4H, *J* = 7.1 Hz, minor), 1.62-1.54 (m, 2.3H), 1.37 (d, 3.0H, *J* = 7.0 Hz, major), 1.24-1.15 (m, 2.3H), 0.88-0.80 (m, 3.4H); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5w**, major): δ 146.6, 143.3, 137.8, 137.2, 129.42, 129.0, 127.57, 118.2, 114.9, 113.9, 48.1, 35.0, 31.2, 21.53, 20.0, 13.7, 13.4; (*Z*-**5w**, minor): δ 148.9, 143.2, 140.4, 137.7, 129.37, 128.8, 127.61, 120.0, 117.7, 116.2, 48.5, 37.1, 30.9, 21.50, 20.1, 14.0, 13.8; IR (neat) (cm^{-1}) 2935w, 1597m, 1498m, 1345s, 1210w, 1159s; HRMS (ESI): m/z calcd for $C_{21}H_{28}N_2O_2S$ $[M+H]^+$: 373.1944; found 373.1944.



5x

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2h** (124.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford a 9:1 mixture of ethene-1,1-diamines *E*-**5x** (151.9 mg, 0.43 mmol) and *Z*-**5x** (16.9 mg, 0.05 mmol) in 95% yield.

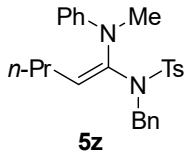
E-**5x** and *Z*-**5x**: R_f = 0.24 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2.2H, J = 8.2 Hz), 7.25-7.23 (m, 2.2H), 7.21-7.16 (m, 2.2H), 7.03 (d, 0.2H, J = 7.9 Hz, minor), 6.84 (t, 0.1H, J = 7.2 Hz, minor), 6.76-6.73 (m, 3.0H, major), 5.87-5.77 (m, 1.1H), 5.19 (q, 1.1H, J = 7.0 Hz), 5.13-5.07 (m, 2.2H), 4.01 (d, 2.2H, J = 6.1 Hz), 2.85 (s, 3.0H, major), 2.72 (s, 0.3H, minor), 2.40 (s, 3.0H, major), 2.38 (s, 0.3H, minor), 1.69 (d, 0.3H, J = 7.0 Hz, minor), 1.35 (d, 3.0H, J = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5x**, major): δ 146.6, 143.44, 137.9, 137.6, 134.0, 129.5, 128.9, 127.6, 118.3, 118.2, 115.1, 114.0, 50.8, 35.2, 21.63, 13.3; (*Z*-**5x**, minor): δ 148.8, 143.36, 141.3, 137.8, 133.6, 129.4, 128.8, 127.7, 120.0, 118.8, 117.9, 115.5, 52.1, 36.9, 21.59, 13.9; IR (neat) (cm^{-1}) 2927w, 1656w, 1596m, 1500m, 1342s, 1157s, 1087m; HRMS (ESI): m/z calcd for $C_{20}H_{24}N_2O_2S$ $[M+H]^+$: 357.1631; found 357.1634.



5y

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2g** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 8.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford a 13:1 mixture of ethene-1,1-diamines *E*-**5y** (171.8 mg, 0.44 mmol) and *Z*-**5y** (13.2 mg, 0.03 mmol) in 94% yield.

E-**5y**: R_f = 0.32 [10:1 petroleum ether/EtOAc]; white solid; mp = 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.24-7.18 (m, 5H), 7.14-7.09 (m, 4H), 6.73-6.68 (m, 1H), 6.64 (dd, 2H, J = 8.9, 1.2 Hz), 5.30 (q, 1H, J = 6.9 Hz), 2.89 (s, 3H), 2.38 (s, 3H), 1.46 (d, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 143.5, 140.1, 138.8, 137.6, 129.9, 129.4, 128.9, 128.7, 128.4, 128.0, 118.4, 114.3, 113.7, 36.8, 21.6, 13.1; IR (neat) (cm^{-1}) 2925w, 1596m, 1496m, 1347s, 1236w, 1162s, 1091s; HRMS (ESI): m/z calcd for $C_{23}H_{24}N_2O_2S$ $[M+Na]^+$: 415.1451; found 415.1450.

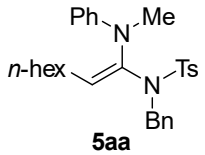


5z

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2i** (163.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and

concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 40:1~30:1 petroleum ether/EtOAc] to afford a 10:1 mixture of ethene-1,1-diamines *E*-**5z** (186.5 mg, 0.43 mmol) and *Z*-**5z** (18.7 mg, 0.04 mmol) in 94% yield.

E-**5z**: R_f = 0.30 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.60 (m, 2H), 7.26-7.18 (m, 7H), 7.10-7.05 (m, 2H), 6.72-6.68 (m, 1H), 6.53 (dd, 2H, J = 8.9, 1.1 Hz), 5.10 (t, 1H, J = 7.2 Hz), 4.58 (s, 2H), 2.71 (s, 3H), 2.40 (s, 3H), 1.61 (q, 2H, J = 7.2 Hz), 1.30-1.21 (m, 2H), 0.78 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 143.4, 137.9, 137.1, 136.8, 129.4, 128.7, 128.30, 128.29, 127.6, 127.4, 120.6, 118.3, 114.0, 51.6, 35.3, 29.7, 22.0, 21.5, 13.8; IR (neat) (cm^{-1}) 2929w, 1598m, 1498s, 1342s, 1209w, 1157s, 1090m; HRMS (ESI): m/z calcd for $C_{26}H_{30}N_2O_2S$ $[M+H]^+$: 435.2101; found 435.2102.

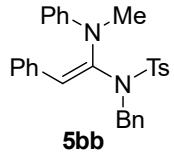


5aa

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2j** (184.8 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 35:1~30:1 petroleum ether/EtOAc] to afford a 9:1 mixture of ethene-1,1-diamines *E*-**5aa** (203.9 mg, 0.43 mmol) and *Z*-**5aa** (22.7 mg, 0.05 mmol) in 95% yield.

E-**5aa** and *Z*-**5aa**: R_f = 0.37 [20:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 0.2H, J = 8.3 Hz, minor), 7.62 (d, 2.0H, J = 8.4 Hz, major), 7.25-7.18 (m, 7.8H), 7.12-7.09 (m, 0.2H, minor), 7.08-7.03 (m, 2.0H, major), 6.82-6.77 (m, 0.3H, minor), 6.71-6.66 (m, 1.0H, major), 6.53 (dd, 2.0H, J = 8.9, 1.2 Hz, major), 5.09 (t, 1.0H, J = 7.2 Hz, major), 4.99 (t, 0.1H, J = 7.2 Hz, minor), 4.58 (s, 2.0H, major), 4.47 (s, 0.2H, minor)), 2.68 (s, 3.0H, major), 2.61 (s, 0.3H, minor), 2.37 (s, 3.0H, major), 2.36 (s, 0.3H, minor), 2.07 (q, 0.2H, J = 6.8 Hz, minor), 1.62 (q, 2.0H, J = 6.9 Hz, major), 1.26-1.19 (m, 4.4H), 1.15-1.11 (m, 4.4H), 0.88-0.82 (m, 3.3H); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5aa**, major): δ 146.5, 143.36, 137.9, 137.1, 136.7, 129.4, 128.7, 128.314, 128.307, 127.6, 127.4, 120.8, 118.3, 114.0, 51.66, 35.3, 31.6, 28.8, 28.70, 27.6, 22.6, 21.6, 14.155; (*Z*-**5aa**, minor): δ 148.7, 143.44, 138.7, 137.7, 136.2, 129.5, 129.3, 128.6, 128.27, 127.9, 127.8, 121.3, 120.1, 118.4, 51.73, 36.8, 31.7, 29.2, 29.0, 28.67, 22.7, 21.5, 14.162; IR (neat) (cm^{-1}) 2925w, 1597m,

1498m, 1342s, 1157s, 1026w; HRMS (ESI): m/z calcd for $C_{29}H_{36}N_2O_2S$ $[M+H]^+$: 477.2570; found 477.2572.

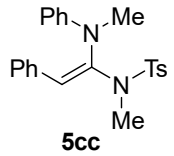


5bb

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2k** (180.8 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 35:1~25:1 petroleum ether/EtOAc] to afford a 9:1 mixture of ethene-1,1-diamines *E*-**5bb** (201.4 mg, 0.43 mmol) and *Z*-**5bb** (22.4 mg, 0.05 mmol) in 96% yield.

E-**5bb**: R_f = 0.33 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, 2H, *J* = 8.4 Hz), 7.25-7.19 (m, 7H), 7.12-6.98 (m, 7H), 6.77-6.73 (m, 1H), 6.63 (dd, 2H, *J* = 8.8, 1.1 Hz), 6.02 (s, 1H), 4.57 (s, 2H), 2.66 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.8, 138.2, 137.4, 136.7, 135.1, 129.6, 128.9, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 126.8, 120.0, 116.5, 116.2, 51.9, 37.4, 21.8; IR (neat) (cm^{-1}) 2943w, 1620m, 1595m, 1343s, 1228w, 1163s; HRMS (ESI): m/z calcd for $C_{29}H_{28}N_2O_2S$ $[M+H]^+$: 469.1944; found 469.1942. Spectral data are in agreement with literature values[19].

Z-**5bb**: R_f = 0.36 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 4H), 7.36 (t, 2H, *J* = 7.6 Hz), 7.25-7.20 (m, 8H), 7.14-7.08 (m, 4H), 6.90-6.86 (m, 1H), 5.78 (s, 1H), 4.50 (s, 2H), 2.34 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 143.4, 142.6, 138.6, 136.2, 135.7, 130.6, 129.3, 128.91, 128.89, 128.41, 128.39, 127.8, 127.7, 126.9, 121.0, 118.7, 114.6, 52.4, 34.5, 21.7; IR (neat) (cm^{-1}) 2918w, 1626m, 1593m, 1342s, 1248w, 1156s; HRMS (ESI): m/z calcd for $C_{29}H_{28}N_2O_2S$ $[M+H]^+$: 469.1944; found 469.1945.

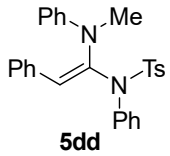


5cc

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2l** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 6.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and

concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 25:1~20:1 petroleum ether/EtOAc] to afford a 5:1 mixture of ethene-1,1-diamines *E*-**5cc** (148.6 mg, 0.38 mmol) and *Z*-**5cc** (29.7 mg, 0.08 mmol) in 91% yield.

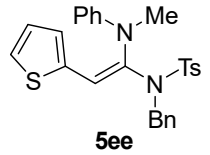
E-**5cc** and *Z*-**5cc**: R_f = 0.28 [10:1 petroleum ether/EtOAc]; white solid; mp = 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2.4H), 7.45-7.40 (m, 0.4H, minor), 7.31 (t, 0.4H, J = 7.6 Hz, minor), 7.20-7.08 (m, 10.0H), 7.02 (dd, 0.4H, J = 8.8, 1.2 Hz, minor), 6.87-6.85 (m, 0.2H, minor), 6.84-6.80 (m, 1.0H, major), 6.75 (dd, 2.0H, J = 8.8, 1.2 Hz, major), 5.79 (s, 0.2H, minor), 5.69 (s, 1.0H, major), 3.10 (s, 3.0H, major), 3.035 (s, 0.6H, minor), 3.027 (s, 3.0H, major), 2.60 (s, 0.6H, minor), 2.39 (s, 3.0H, major), 2.34 (s, 0.6H, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5cc**, major): δ 145.6, 143.6, 141.6, 135.4, 135.0, 129.41, 128.91, 128.5, 127.5, 127.4, 127.0, 119.7, 116.0, 115.2, 38.4, 37.98, 21.7; (*Z*-**5cc**, minor): δ 147.6, 144.0, 143.2, 137.3, 129.45, 129.3, 128.86, 128.7, 127.8, 127.2, 126.8, 120.6, 117.9, 115.0, 37.99, 37.0, 21.6; IR (neat) (cm^{-1}) 2956w, 1595m, 1491m, 1382m, 1344s, 1221w, 1161s; HRMS (ESI): m/z calcd for $C_{23}H_{24}N_2O_2S$ $[M+H]^+$: 393.1631; found 393.1632.



5dd

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2m** (173.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 15:1~10:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine *E*-**5dd** (215.0 mg, 0.47 mmol; *E*/*Z* ≥ 25/1) in 95% yield.

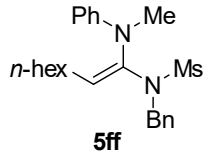
E-**5dd**: R_f = 0.24 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, J = 8.2 Hz), 7.25-7.16 (m, 11H), 7.13-7.08 (m, 1H), 6.99-6.97 (m, 2H), 6.88-6.81 (m, 3H), 6.13 (s, 1H), 2.69 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.9, 140.5, 138.5, 137.3, 135.0, 129.9, 129.5, 128.8, 128.7, 128.5, 128.2, 127.6, 127.0, 120.0, 116.5, 114.9, 38.9, 21.7, one carbon missing due to overlap, overlapped signal at 128.5 ppm; IR (neat) (cm^{-1}) 3028w, 2359m, 1637w, 1596m, 1495m, 1353s, 1163s, 1086s; HRMS (ESI): m/z calcd for $C_{28}H_{26}N_2O_2S$ $[M+H]^+$: 455.1788; found 455.1789. Spectral data are in agreement with literature values[20].



5ee

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2n** (183.8 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 8.7 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine *E*-**5ee** (194.3 mg, 0.41 mmol; *E*/*Z* ≥ 25/1) in 82% yield.

E-**5ee**: R_f = 0.29 [10:1 petroleum ether/EtOAc]; white solid; mp = 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2H, J = 8.4 Hz), 7.23-7.14 (m, 7H), 7.03-6.99 (m, 2H), 6.97-6.95 (m, 1H), 6.83 (dd, 1H, J = 3.7, 1.2 Hz), 6.79 (dd, 1H, J = 5.1, 3.6 Hz), 6.75-6.70 (m, 1H), 6.60-6.56 (m, 3H), 4.54 (s, 2H), 2.73 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.9, 137.1, 136.8, 134.6, 129.6, 128.8, 128.4, 127.9, 127.8, 127.5, 127.2, 126.3, 125.9, 119.6, 114.7, 114.4, 51.2, 36.2, 21.6, one carbon missing due to overlap, overlapped signal at 128.4 ppm; IR (neat) (cm^{-1}) 2929w, 1595m, 1491m, 1335s, 1155s, 1088m; HRMS (ESI): m/z calcd for $C_{27}H_{26}N_2O_2S_2$ $[M+H]^+$: 475.1508; found 475.1506.

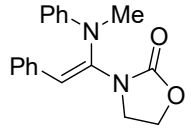


5ff

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2o** (146.8 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 25:1~15:1 petroleum ether/EtOAc] to afford a 4:1 mixture of ethene-1,1-diamines *E*-**5ff** (149.1 mg, 0.37 mmol) and *Z*-**5ff** (37.3 mg, 0.09 mmol) in 93% yield.

E-**5ff** and *Z*-**5ff**: R_f = 0.29 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 1.0H, minor), 7.33-7.27 (m, 5.0H, major), 7.26-7.23 (m, 0.3H, minor), 7.23-7.17 (m, 2.5H), 7.07-7.04 (m, 0.5H, minor), 6.94-6.90 (m, 0.3H, minor), 6.80-6.75 (m, 3.0H, major), 5.16 (t, 1.0H, J = 7.1 Hz, major), 4.97 (t, 0.3H, J = 7.1 Hz, minor), 4.49 (s, 2.0H, major), 4.40 (s, 0.5H,

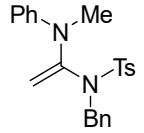
minor), 2.99 (s, 3.0H, major), 2.90 (s, 0.8H, minor), 2.79 (s, 3.0H, major), 2.63 (s, 0.8H, minor), 2.07 (q, 0.5H, J = 7.0 Hz, minor), 1.78 (q, 2.0H, J = 7.1 Hz, major), 1.31-1.13 (m, 10.0H), 0.89-0.81 (m, 3.8H); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5ff**, major): δ 146.6, 137.4, 136.8, 129.1, 128.6, 128.37, 127.8, 121.5, 118.7, 114.2, 51.4, 41.6, 36.6, 31.5, 28.8, 28.7, 27.5, 22.6, 14.11; (*Z*-**5ff**, minor): δ 148.4, 138.6, 136.0, 129.3, 129.0, 128.44, 128.0, 121.6, 120.8, 120.1, 51.3, 40.3, 39.7, 31.8, 29.2, 29.1, 28.4, 22.7, 14.15; IR (neat) (cm^{-1}) 2926w, 1660w, 1598m, 1498m, 1337s, 1147s; HRMS (ESI): m/z calcd for $C_{23}H_{32}N_2O_2S$ $[M+H]^+$: 401.2257; found 401.2257.



5gg

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2q** (93.6 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 80 ^{o}C. The reaction vessel was capped and stirred at 80 ^{o}C for 7.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *E*/*Z* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 10:1~2:1 petroleum ether/EtOAc] to afford a 7:1 mixture of ethene-1,1-diamines *E*-**5gg** (104.7 mg, 0.36 mmol) and *Z*-**5gg** (15.0 mg, 0.05 mmol) in 81% yield.

E-**5gg** and *Z*-**5gg**: R_f = 0.15 [4:1 petroleum ether/EtOAc]; white solid; mp = 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 7.0H), 7.17-7.13 (m, 1.0H, major), 7.07 (d, 0.3H, J = 8.0 Hz, minor), 7.01 (t, 0.1H, J = 7.2 Hz, minor), 6.92-6.87 (m, 3.0H, major), 6.28 (s, 1.0H, major), 5.83 (s, 0.1H, minor), 4.19 (t, 2.0H, J = 7.6 Hz, major), 4.13 (t, 0.3H, J = 7.8 Hz, minor), 3.54 (t, 2.3H, J = 7.7 Hz), 3.29 (s, 0.4H, minor), 3.07 (s, 3.0H, major); ^{13}C NMR (100 MHz, $CDCl_3$) (*E*-**5gg**, major): δ 156.3, 145.1, 135.9, 134.7, 129.6, 128.6, 127.7, 127.1, 119.8, 115.5, 114.5, 61.6, 44.3, 38.2; (*Z*-**5gg**, minor): δ 155.2, 146.3, 137.7, 136.1, 129.4, 128.7, 127.2, 126.2, 122.8, 120.9, 109.8, 62.2, 44.8, 40.8; IR (neat) (cm^{-1}) 2954w, 1764s, 1594m, 1493m, 1400s, 1271m, 1080w; HRMS (ESI): m/z calcd for $C_{18}H_{18}N_2O_2$ $[M+H]^+$: 295.1441; found 295.1441.

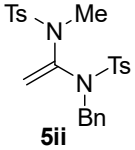


5hh

To an oven-dried sealed tube was added secondary amine **4a** (64.3 mg, 0.60 mmol), ynamide **2s** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine **5hh** (150.2 mg, 0.38 mmol) in 77% yield.

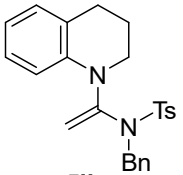
5hh: R_f = 0.42 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, 2H, J = 8.3 Hz), 7.29-7.23 (m, 7H), 7.16-7.12 (m, 2H), 6.92-6.88 (m, 1H), 6.82 (dd, 2H, J = 8.8, 1.3 Hz), 4.55 (s, 2H), 4.41 (d, 1H, J = 1.5 Hz), 4.31 (d, 1H, J = 1.5 Hz), 2.70 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 147.0, 143.7, 137.2, 136.5, 129.5, 128.92, 128.87, 128.4, 128.1, 127.8, 121.9, 120.7, 96.1, 52.3, 37.8, 21.7; IR (neat) (cm^{-1}) 2924w, 1627m, 1596m, 1495s, 1344s, 1157s, 1089m; HRMS (ESI): m/z calcd for $C_{23}H_{24}N_2O_2S$ $[M+H]^+$: 393.1631; found 393.1631.



5ii

To an oven-dried sealed tube was added secondary amine **4q** (111.2 mg, 0.60 mmol), ynamide **2s** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 12:1~8:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine **5ii** (190.5 mg, 0.40 mmol) in 81% yield.

5ii: R_f = 0.42 [4:1 petroleum ether/EtOAc]; white solid; mp = 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.3 Hz), 7.51 (d, 2H, J = 8.3 Hz), 7.37-7.28 (m, 7H), 7.23 (d, 2H, J = 8.1 Hz), 4.81 (d, 1H, J = 2.0 Hz), 4.75 (s, 2H), 4.29 (d, 1H, J = 2.0 Hz), 2.66 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 144.0, 141.6, 136.7, 136.6, 133.3, 129.53, 129.49, 128.9, 128.6, 128.4, 127.8, 107.3, 52.1, 37.7, 21.8, 21.7, one carbon missing due to overlap, overlapped signal at 128.6 ppm; IR (neat) (cm^{-1}) 2925w, 1628w, 1344s, 1233m, 1157s, 1086m; HRMS (ESI): m/z calcd for $C_{24}H_{26}N_2O_4S_2$ $[M+H]^+$: 471.1407; found 471.1406.

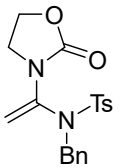


5jj

To an oven-dried sealed tube was added secondary amine **4o** (79.9 mg, 0.60 mmol), ynamide **2s** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine **5jj** (171.9 mg, 0.41 mmol) in 82% yield.

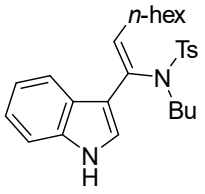
5jj: R_f = 0.38 [10:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.4 Hz), 7.28-7.23 (m, 7H), 6.94 (dd, 1H, J = 7.6, 1.6 Hz), 6.85-6.81 (m, 1H), 6.73-6.69 (m, 1H), 6.65 (dd, 1H, J = 8.3, 1.3 Hz), 4.67 (s, 2H), 4.59 (d, 1H, J = 1.4 Hz), 4.43 (d, 1H, J = 1.4 Hz), 2.96-2.93 (m, 2H), 2.62 (t, 2H, J = 6.6 Hz), 2.40 (s, 3H), 1.57-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 143.6, 142.7, 137.4, 136.8, 129.5, 129.4, 128.7, 128.4, 127.9, 127.6, 126.7, 126.1, 120.4, 120.1, 98.4, 51.8, 46.4, 27.4, 21.6, 21.0; IR (neat) (cm^{-1}) 2935w, 1597m, 1493s, 1346s, 1157s, 1090m; HRMS (ESI): m/z calcd for $C_{25}H_{26}N_2O_2S$ $[M+H]^+$: 419.1788; found 419.1780.



5kk

To an oven-dried sealed tube was added secondary amine **4r** (52.2 mg, 0.60 mmol), ynamide **2s** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~2:1 petroleum ether/EtOAc] to afford ethene-1,1-diamine **5kk** (122.0 mg, 0.33 mmol) in 66% yield.

5kk: R_f = 0.42 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.4 Hz), 7.36-7.32 (m, 7H), 5.41 (d, 1H, J = 2.0 Hz), 4.43 (d, 1H, J = 2.0 Hz), 4.41 (s, 2H), 4.06 (t, 2H, J = 7.8 Hz), 3.45 (t, 2H, J = 7.8 Hz), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.4, 137.2, 134.8, 133.8, 129.7, 129.6, 128.6, 128.5, 128.3, 105.4, 61.7, 55.1, 44.1, 21.7; IR (neat) (cm^{-1}) 2920w, 1763s, 1639m, 1454w, 1345s, 1221m, 1160s, 1048m; HRMS (ESI): m/z calcd for $C_{19}H_{20}N_2O_4S$ $[M+H]^+$: 373.1217; found 373.1215.

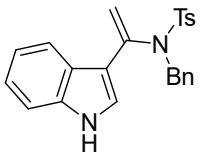


(5ll)'

To an oven-dried sealed tube was added secondary amine **4p** (70.5 mg, 0.60 mmol), ynamide **2t**[1] (167.8 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at

30 °C. The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated in vacuo. After the *Z*/*E* ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 15:1~4:1 petroleum ether/EtOAc] to afford a 2:1 mixture of 3-alkenylindoles *Z*-**(5ll)'** (108.2 mg, 0.24 mmol) and *E*-**(5ll)'** (54.1 mg, 0.12 mmol) in 72% yield.

Z-**(5ll)'** and *E*-**(5ll)'**: R_f = 0.40 [4:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.63 (s, 0.5H, minor), 8.52 (s, 1.0H, major), 7.84 (d, 1.0H, J = 7.4 Hz, major), 7.80 (d, 2.0H, J = 6.7 Hz, major), 7.76 (d, 1.0H, J = 6.6 Hz, minor), 7.52 (d, 0.5H, J = 8.0 Hz, minor), 7.38-7.32 (m, 4.5H), 7.22-7.13 (m, 3.0H), 6.89-6.87 (m, 1.5H), 6.18 (t, 1.0H, J = 7.4 Hz, major), 5.63 (t, 0.5H, J = 7.5 Hz, minor), 3.41-3.31 (m, 3.0H), 2.46 (s, 4.5H), 2.12-2.03 (m, 3.0H), 1.54-1.46 (m, 4.0H), 1.37-1.18 (m, 14.0H), 0.95 (t, 3.0H, J = 6.4 Hz, major), 0.89-0.81 (m, 6.0H); ^{13}C NMR (100 MHz, CD_2Cl_2) (*Z*-**(5ll)'**, major): δ 143.8, 138.32, 137.1, 132.3, 130.6, 129.9, 127.8, 125.8, 124.6, 122.5, 120.5, 120.1, 115.1, 111.9, 49.4, 32.1, 31.4, 29.9, 29.8, 29.52, 23.04, 21.6, 20.4, 14.3, 13.9; (*E*-**(5ll)'**, minor): δ 143.6, 138.28, 136.0, 133.2, 130.0, 129.7, 127.9, 127.3, 125.2, 122.2, 120.3, 120.2, 112.4, 111.7, 48.7, 32.0, 31.0, 29.47, 29.2, 22.96, 20.0, 14.2, 13.8, two carbon missing due to overlap, overlapped signal at 29.8 ppm and 21.6 ppm. Spectral data are in agreement with literature values[21].



(5mm)'

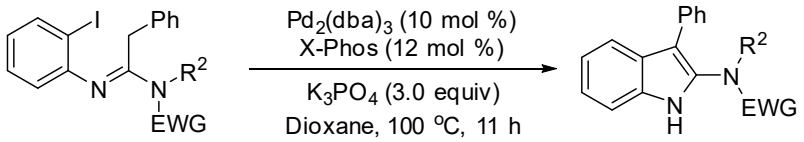
To an oven-dried sealed tube was added secondary amine **4p** (70.5 mg, 0.60 mmol), ynamide **2s** (142.7 mg, 0.50 mmol), DCE (2.5 mL, ynamide *concn* = 0.20 *M*), and TfOH (8.9 μL, 0.10 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 1.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 12:1~4:1 petroleum ether/EtOAc] to afford 3-alkenylindole **(5mm)'** (145.4 mg, 0.36 mmol) in 72% yield.

(5mm)': R_f = 0.26 [4:1 petroleum ether/EtOAc]; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.75 (d, 2H, J = 8.3 Hz), 7.65-7.63 (m, 1H), 7.26-7.22 (m, 3H), 7.20-7.17 (m, 2H), 7.16-7.12 (m, 3H), 7.10-7.06 (m, 2H), 6.94 (d, 1H, J = 2.7 Hz), 5.50 (s, 1H), 4.82 (s, 1H), 4.61 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.0, 136.9, 136.47, 136.45, 129.6, 129.2, 128.3, 128.0, 127.7, 125.8, 125.1, 122.3, 120.5, 119.7, 114.5, 112.0, 111.7, 53.8, 21.6; IR (neat) (cm^{-1}) 2922w,

1620m, 1435m, 1319s, 1209w, 1154s, 1093s, 1036m; HRMS (ESI): m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1475; found 403.1468.

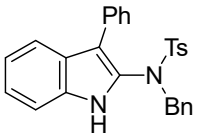
1.7 Application to the Construction of 2-Aminoindoles (Scheme 2).

Synthesis of 2-Aminoindole 6a, 6b and 6c via a Pd(0)-catalyzed ring closing reaction.[18]



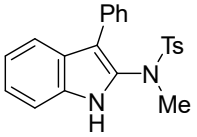
3 **6**

To an oven-dried sealed tube was added *N*-arylimine **3oo** (116.1 mg, 0.20 mmol), XPhos (11.5 mg, 12 mol %), $Pd_2(dba)_3$ (18.4 mg, 10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol) and dioxane (0.8 mL) in sequence. The reaction vessel was capped and stirred at 100 °C in an oil bath for 11.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 15:1~4:1 petroleum ether/EtOAc] to afford 2-aminoindole **6a** (69.1 mg, 0.15 mmol) in 76% yield.



6a

6a: R_f = 0.42 [2:1 petroleum ether/EtOAc]; white solid; mp = 193–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.64-7.61 (m, 2H), 7.48 (d, 1H, J = 8.0 Hz), 7.28 (d, 3H, J = 8.1 Hz), 7.23-7.14 (m, 7H), 7.08-7.03 (m, 3H), 6.63-6.60 (m, 2H), 4.52 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 136.3, 135.7, 133.4, 133.2, 130.1, 129.3, 128.55, 128.48, 128.47, 127.99, 127.97, 127.7, 127.0, 126.6, 123.1, 120.2, 119.6, 112.7, 111.2, 53.7, 21.8. Spectral data are in agreement with literature values[22].

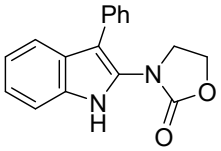


6b

To an oven-dried sealed tube was added imine **3pp** (100.9 mg, 0.20 mmol), XPhos (11.5 mg, 12 mol %), $Pd_2(dba)_3$ (18.4 mg, 10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol) and dioxane (0.8 mL) in sequence. The reaction vessel was capped and stirred at 100 °C in an oil bath for 11.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a

pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 2-aminoindole **6b** (59.9 mg, 0.16 mmol) in 80% yield.

6b: R_f = 0.48 [4:1 petroleum ether/EtOAc]; white solid; mp = 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.56 (d, 2H, J = 7.9 Hz), 7.48 (d, 1H, J = 8.0 Hz), 7.38 (d, 1H, J = 8.1 Hz), 7.26-7.22 (m, 3H), 7.18 (d, 1H, J = 7.1 Hz), 7.15-7.07 (m, 3H), 6.65 (d, 2H, J = 7.1 Hz), 3.04 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 134.2, 133.3, 133.2, 130.5, 130.0, 129.4, 128.3, 127.7, 126.82, 126.80, 123.2, 120.3, 119.5, 111.5, 111.1, 38.5, 21.8. Spectral data are in agreement with literature values[22].

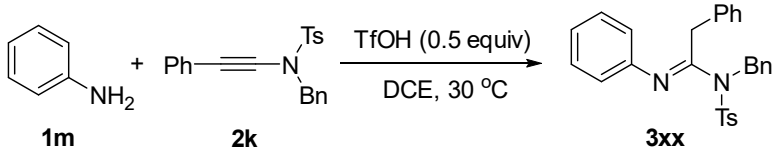


6c

To an oven-dried sealed tube was added imine **3uu** (81.3 mg, 0.20 mmol), XPhos (11.5 mg, 12 mol %), $Pd_2(dba)_3$ (18.4 mg, 10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol) and dioxane (0.8 mL) in sequence. The reaction vessel was capped and stirred at 100 °C in an oil bath for 11.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~4:1 petroleum ether/EtOAc] to afford 2-aminoindole **6c** (43.9 mg, 0.16 mmol) in 79% yield.

6c: R_f = 0.31 [2:1 petroleum ether/EtOAc]; white solid; mp = 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.48-7.40 (m, 5H), 7.37-7.32 (m, 2H), 7.20-7.16 (m, 1H), 7.10-7.06 (m, 1H), 4.36 (t, 2H, J = 7.6 Hz), 3.66 (t, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 133.8, 132.3, 130.8, 129.1, 128.5, 127.6, 127.2, 122.2, 120.4, 118.6, 110.9, 104.8, 63.2, 46.0. Spectral data are in agreement with literature values[18].

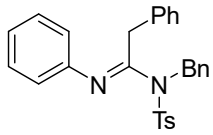
Synthesis of 2-Aminoindole 6a via $CuCl_2$-mediated oxidative cyclization.[22]



1m **2k** **3xx**

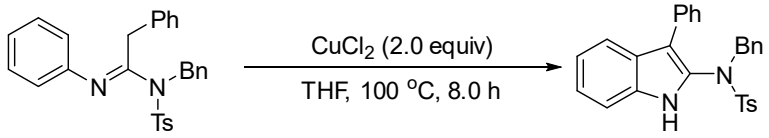
To an oven-dried sealed tube was added aniline **1m** (111.8 mg, 1.20 mmol), ynamide **2k** (361.5 mg, 1.00 mmol), DCE (2.5 mL, ynamide *concn* = 0.40 *M*), and TfOH (44.2 μL, 0.50 mmol) at 30 °C. The reaction vessel was capped and stirred at 30 °C for 9.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel,

concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford imine **3xx** (334.5 mg, 0.74 mmol) in 74% yield.



3xx

3xx: R_f = 0.40 [10:1 petroleum ether/EtOAc]; white solid; mp = 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.3 Hz), 7.34 (d, 2H, J = 8.2 Hz), 7.25-7.19 (m, 3H), 7.16-7.13 (m, 3H), 7.11-7.07 (m, 2H), 7.03-6.99 (m, 3H), 6.79-6.77 (m, 2H), 6.43-6.41 (m, 2H), 4.65 (s, 2H), 3.87 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 148.2, 144.3, 136.0, 135.5, 134.9, 129.7, 129.3, 129.2, 129.0, 128.5, 128.3, 128.2, 127.4, 126.6, 123.7, 119.6, 51.2, 37.9, 21.8. Spectral data are in agreement with literature values[22].



3xx **6a**

To an oven-dried flask were charged with imine **3xx** (181.8 mg, 0.40 mmol), $CuCl_2$ (107.6 mg, 0.80 mmol) and THF (4.0 mL) in sequence. The mixture was vigorously stirred and refluxed for 8.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 15:1~4:1 petroleum ether/EtOAc] to afford 2-aminoindole **6a** (117.3 mg, 0.26 mmol) in 65% yield.

1.8 X-Ray Crystal Structure of 5f.

The relative configuration of the **5f** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of **5f** in petroleum ether/acetone (4:1) at room temperature.

A colorless crystal of approximate dimensions 0.22 x 0.10 x 0.07 mm was selected and collected by an Agilent Xcalibur Eos Gemini diffractometer. The crystal was kept at 293 K during data collection. The structure was solved by direct methods using Olex2 software with the SHELXS structure solution program. The found structural model was further refined by full-matrix least-squares on F2 with SHELXL.

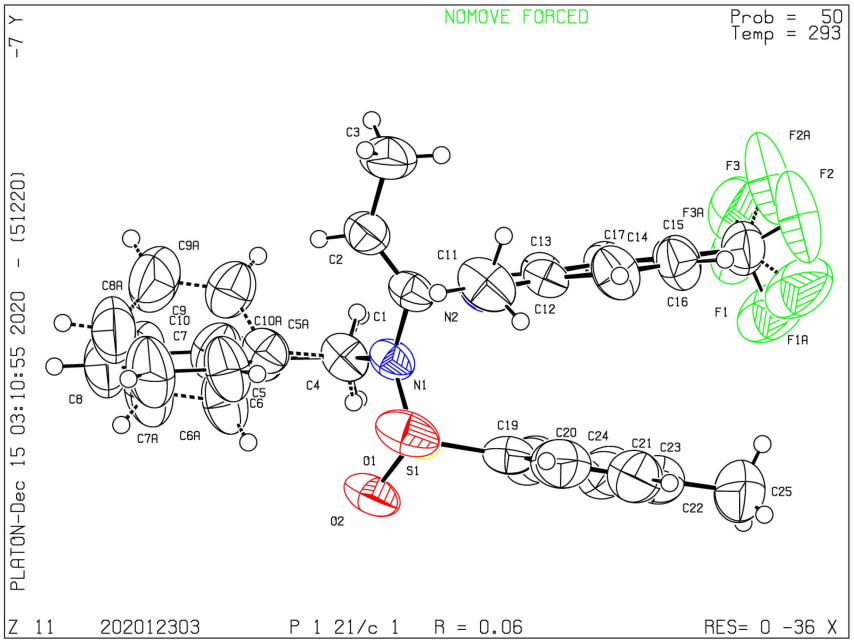


Figure S1. The thermal ellipsoid plot of **5f**.

Table S3 Crystal data and structure refinement for 5f.

Empirical formula	$C_{25}H_{25}F_3N_2O_2S$
Formula weight	474.53
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	24.1413(7)
b/Å	8.2624(2)
c/Å	12.0011(3)
α/°	90
β/°	90.446(3)
γ/°	90
Volume/Å^3	2393.74(11)
Z	4
ρ_{calc}g/cm^3	1.317
μ/mm^{-1}	1.618
F(000)	992.0
Crystal size/mm^3	0.22 × 0.1 × 0.07
Radiation	CuKα (λ = 1.54184)
2$^\Theta$ range for data collection/°	7.324 to 134.142
Index ranges	$-28 \le h \le 28$, $-9 \le k \le 9$, $-14 \le l \le 12$
Reflections collected	9090
Independent reflections	4276 [R_{int} = 0.0250, R_{sigma} = 0.0312]
Data/restraints/parameters	4276/54/306
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1574
Final R indexes [all data]	R_1 = 0.0748, wR_2 = 0.1757
Largest diff. peak/hole / e Å^{-3}	0.29/-0.35

References

(1) Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz and E. L. Vera, Copper sulfate-pentahydrate-1,10-phenanthroline catalyzed amidations of alkynyl bromides. Synthesis of heteroaromatic amine substituted ynamides. *Org. Lett.*, 2004, **6**, 1151.

(2) H. Li, R. P. Hsung, K. A. DeKorver and Y. Wei, Copper-catalyzed ficini [2 + 2] cycloaddition of ynamides. *Org. Lett.*, 2010, **12**, 3780.

(3) Y. Yang, H. Liu, C. Peng, J. Wu, J. Zhang, Y. Qiao, X.-N. Wang and J. Chang, $AlCl_3$-catalyzed annulations of ynamides involving a torquoselective process for the simultaneous control of central and axial chirality. *Org. Lett.*, 2016, **18**, 5022.

(4) H. Liu, Y. Yang, S. Wang, J. Wu, X.-N. Wang and J. Chang, Synthesis of 3-substituted 2-aminochromones via Sn(IV)-promoted annulation of ynamides with 2-methoxyaroyl chlorides. *Org. Lett.*, 2015, **17**, 4472.

(5) X. Y. Mak, A. L. Crombie and R. L. Danheiser, Synthesis of polycyclic benzofused nitrogen heterocycles via a tandem ynamide benzannulation/ring-closing metathesis strategy. Application in a formal total synthesis of (+)-FR900482. *J. Org. Chem.*, 2011, **76**, 1852.

(6) S. J. Mansfield, C. D. Campbell, M. W. Jones and E. A. Anderson, A robust and modular synthesis of ynamides. *Chem.Comm.*, 2015, **51**, 3316.

(7) K. Wang, R. Ran, S. Xiu, and C. Li, Synthesis of 3-aza-bicyclo[3.1.0]hexan-2-one derivatives via gold-catalyzed oxidative cyclopropanation of *N* -allylynamides. *Org. Lett.*, 2013, **15**, 2374.

(8) H. Liu, Y. Yang, J. Wu, X.-N. Wang and J. Chang, Regioselective synthesis of 3,4-disubstituted isocoumarins through the Pd-catalyzed annulation of 2-iodoaromatic acids with ynamides. *Chem. Commun.*, 2016, **52**, 6801.

(9) L. Zhu, Y. Yu, Z. Mao and X. Huang, Gold-catalyzed intermolecular nitrene transfer from 2*H*-azirines to ynamides: A direct approach to polysubstituted pyrroles. *Org. Lett.*, 2014, **17**, 30.

(10) M. D. Santos and P. W. Davies, A gold-catalysed fully intermolecular oxidation and sulfur-ylide formation sequence on ynamides. *Chem. Commun.*, 2014, **50**, 6001.

(11) A. Coste, G. Karthikeyan, F. Couty and G. Evano, Copper-mediated coupling of 1,1-dibromo-1-alkenes with nitrogen nucleophiles: A general method for the synthesis of ynamides. *Angew. Chem. Int. Ed.*, 2009, **48**, 4381.

(12) B. Yao, Z. Liang, T. Niu and Y. Zhang, Iron-catalyzed amidation of alkynyl bromides: A facile route for the preparation of ynamides. *J. Org. Chem.*, 2009, **74**, 4630.

(13) P. Starkov, J. T. Moore, D. C. Duquette, B. M. Stoltz and I. Marek, Enantioselective construction of acyclic quaternary carbon stereocenters: palladium-catalyzed decarboxylative allylic alkylation of fully-substituted amide enolates. *J. Am. Chem. Soc.*, 2017, **139**, 9615.

(14) K. Dooleweerdt, H. Birkedal, T. Ruhland and T. Skrydstrup, Irregularities in the effect of potassium phosphate in ynamide synthesis. *J. Org. Chem.*, 2008, **73**, 9447.

(15) M. R. Tracey, Y. Zhang, M. O. Frederick, J. A. Mulder and R. P. Hsung, Sonogashira cross-couplings of ynamides. syntheses of urethane- and sulfonamide-terminated conjugated phenylacetylenic systems. *Org. Lett.*, 2004, **6**, 2209.

(16) B. Witulski and T. Stengel, *N*-Functionalized 1-alkynylamides: New building blocks for transition metal mediated inter- and intramolecular [2 + 2 + 1] cycloadditions. *Angew. Chem. Int. Ed.*, 1998, **37**, 489.

(17) S. Kramer, K. Dooleweerdt, A. T. Lindhardt, M. Rottländer and T. Skrydstrup, Highly regioselective Au(I)-catalyzed hydroamination of ynamides and propiolic acid derivatives with anilines. *Org. Lett.*, 2009, **11**, 4208.

(18) D. Liu, Q. Nie, R. Zhang and M. Cai, Regiospecific hydroamination of unsymmetrical electron-rich and electron-poor alkynes with anilines catalyzed by gold(I) immobilized in MCM-41. *Adv. Synth. Catal.*, 2018, **360**, 3940.

(19) X.-D. Nie, X.-L. Han, J.-T. Sun, C.-M. Si, B.-G. Wei and G.-Q. Lin, Nickel-catalyzed regioselective hydroamination of ynamides with secondary amines. *J. Org. Chem.*, 2021, **86**, 3433.

(20) L. Li, C. Shu, B. Zhou, Y.-F. Yu, X.-Y. Xiao and L.-W. Ye, Generation of gold carbenes in water: efficient intermolecular trapping of the α-oxo gold carbenoids by indoles and anilines. *Chem. Sci.*, 2014, **5**, 4057.

(21) Y. Zhang, Synthesis of vinylpyrroles, vinylfurans and vinylindoles via a Brønsted acid catalyzed highly regio- and stereoselective cis-hydroarylation of ynamides. *Tetrahedron*, 2006, **62**, 3917.

(22) Y. H. Kim, H. J. Yoo and S. W. Youn, Facile one-pot synthesis of 2-aminoindoles from simple anilines and ynamides. *Chem. Comm.*, 2020, **56**, 13963.

SUPPORTING INFORMATION

Nonmetal-Catalyzed Hydroamination of Ynamides with Amines

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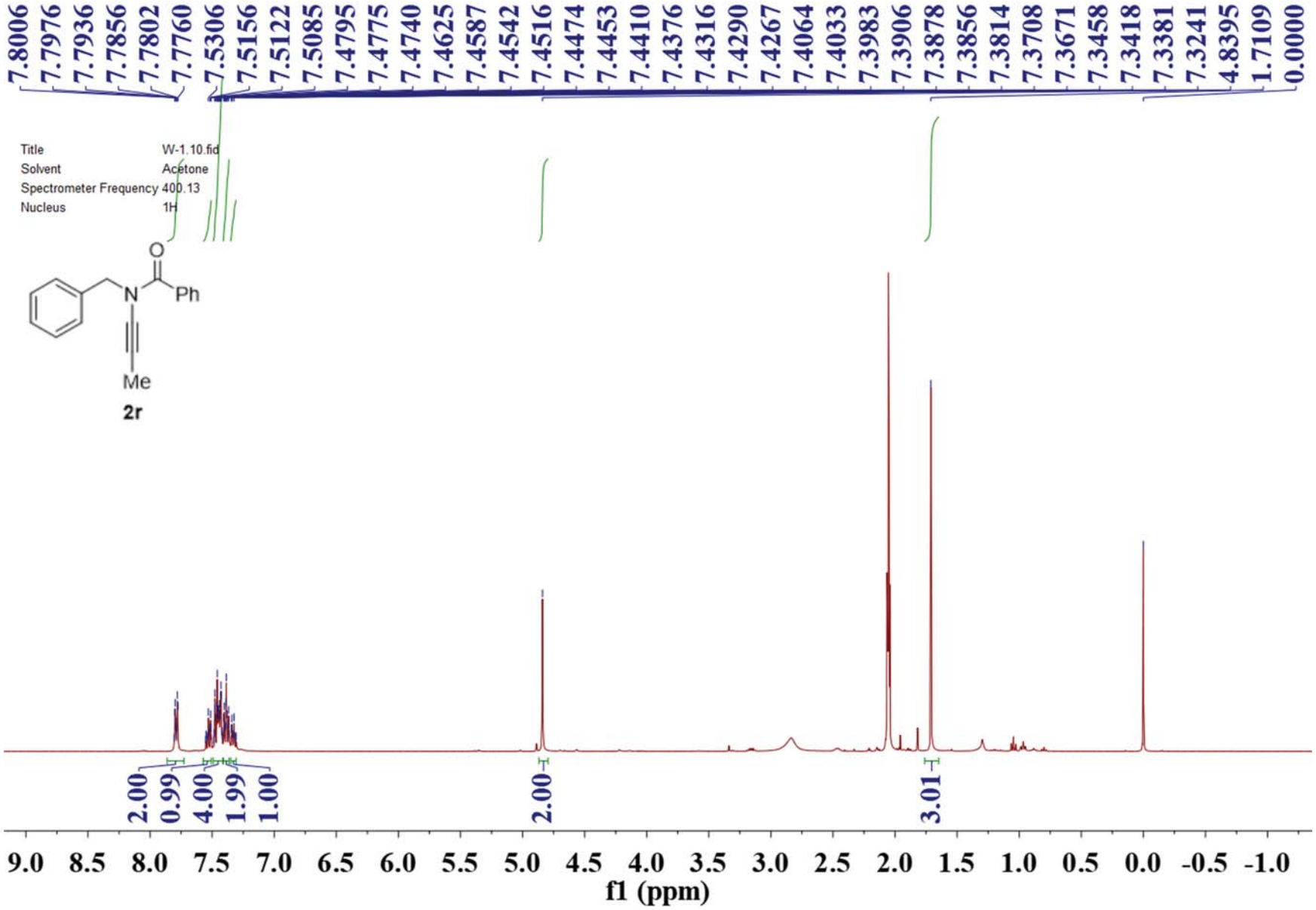
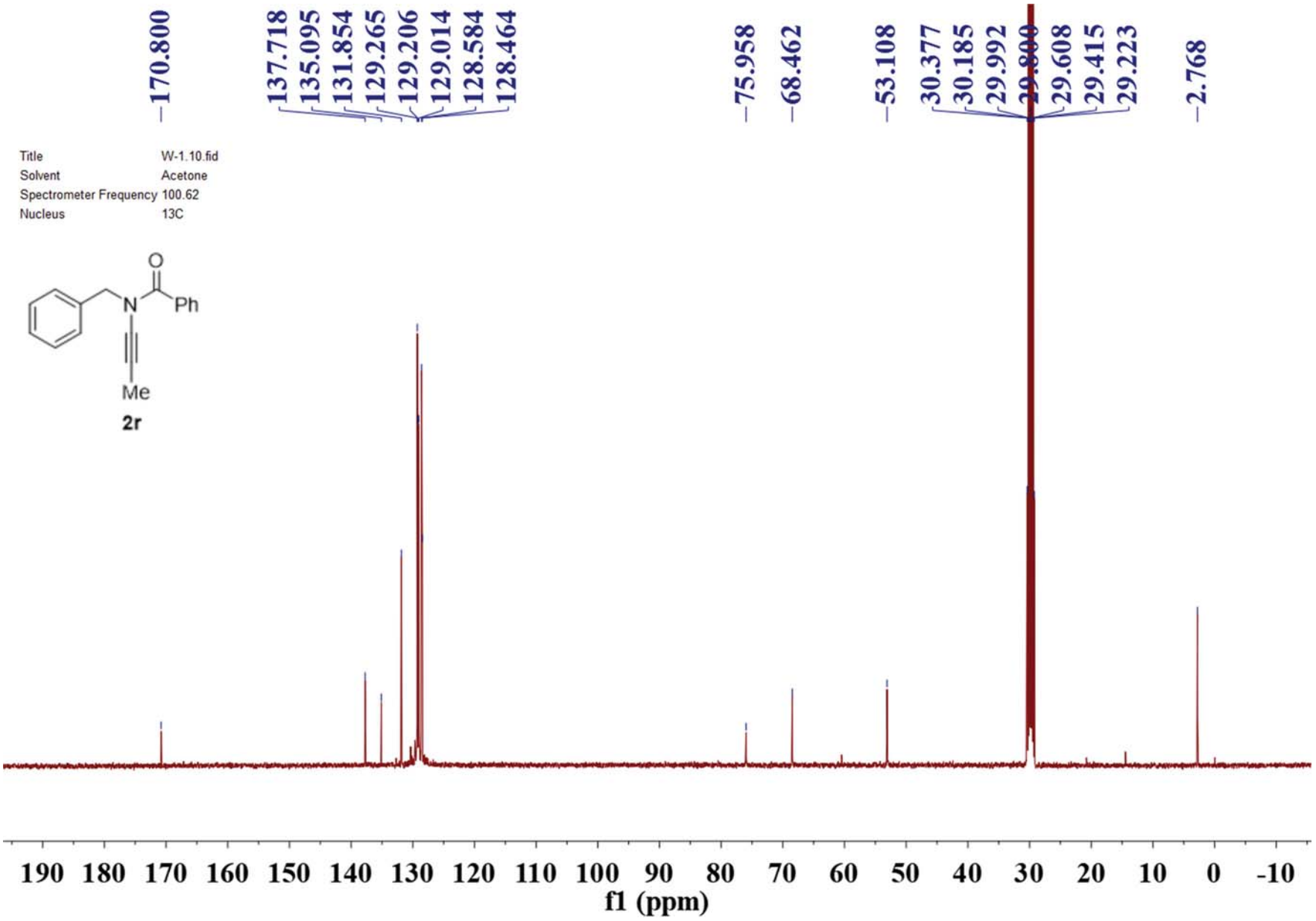
Table of Contents

Part II Copies of ^{1}H NMR and ^{13}C NMR Spectra.

^{1}H NMR and ^{13}C NMR Spectra of Ynamide 2r

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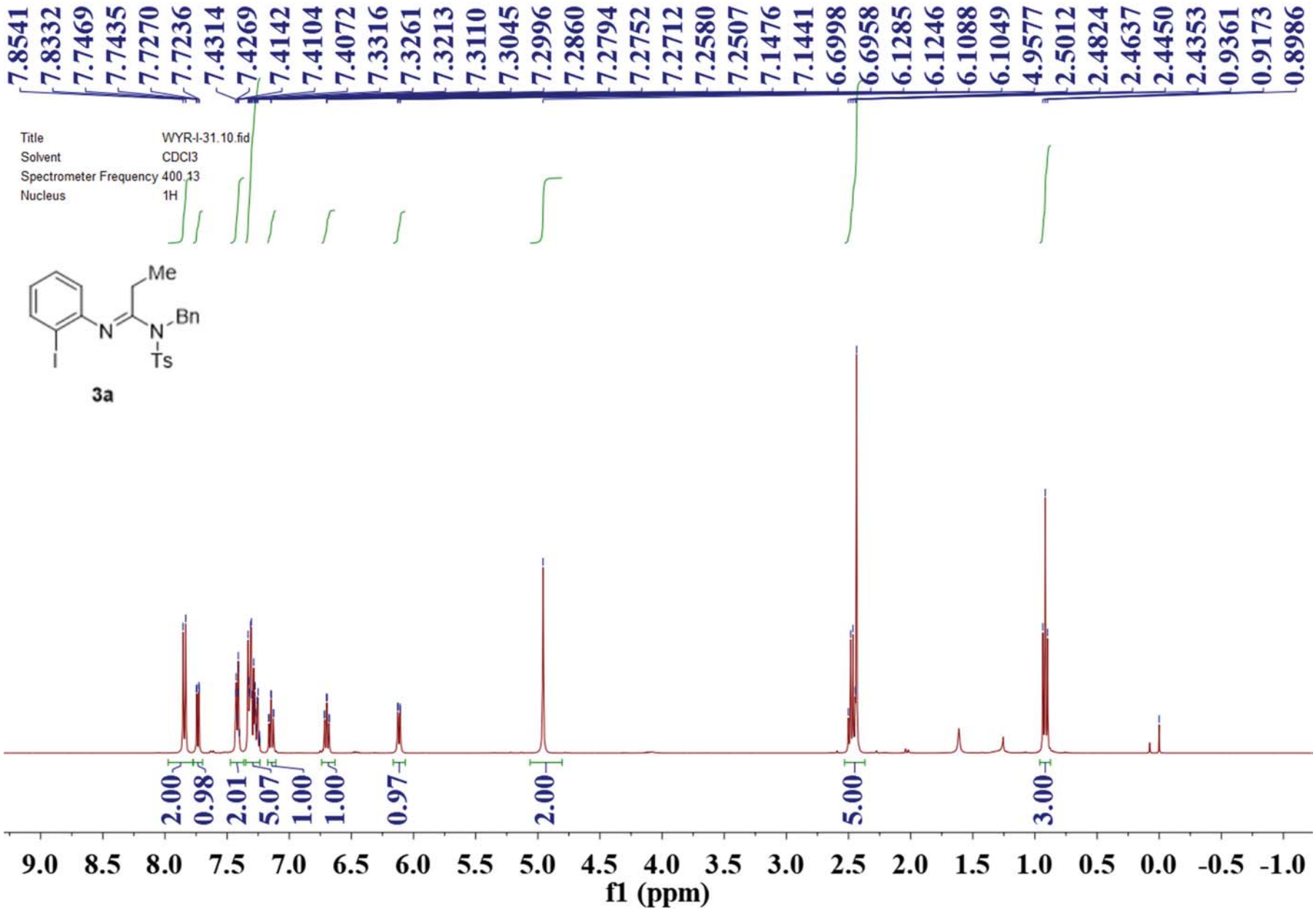
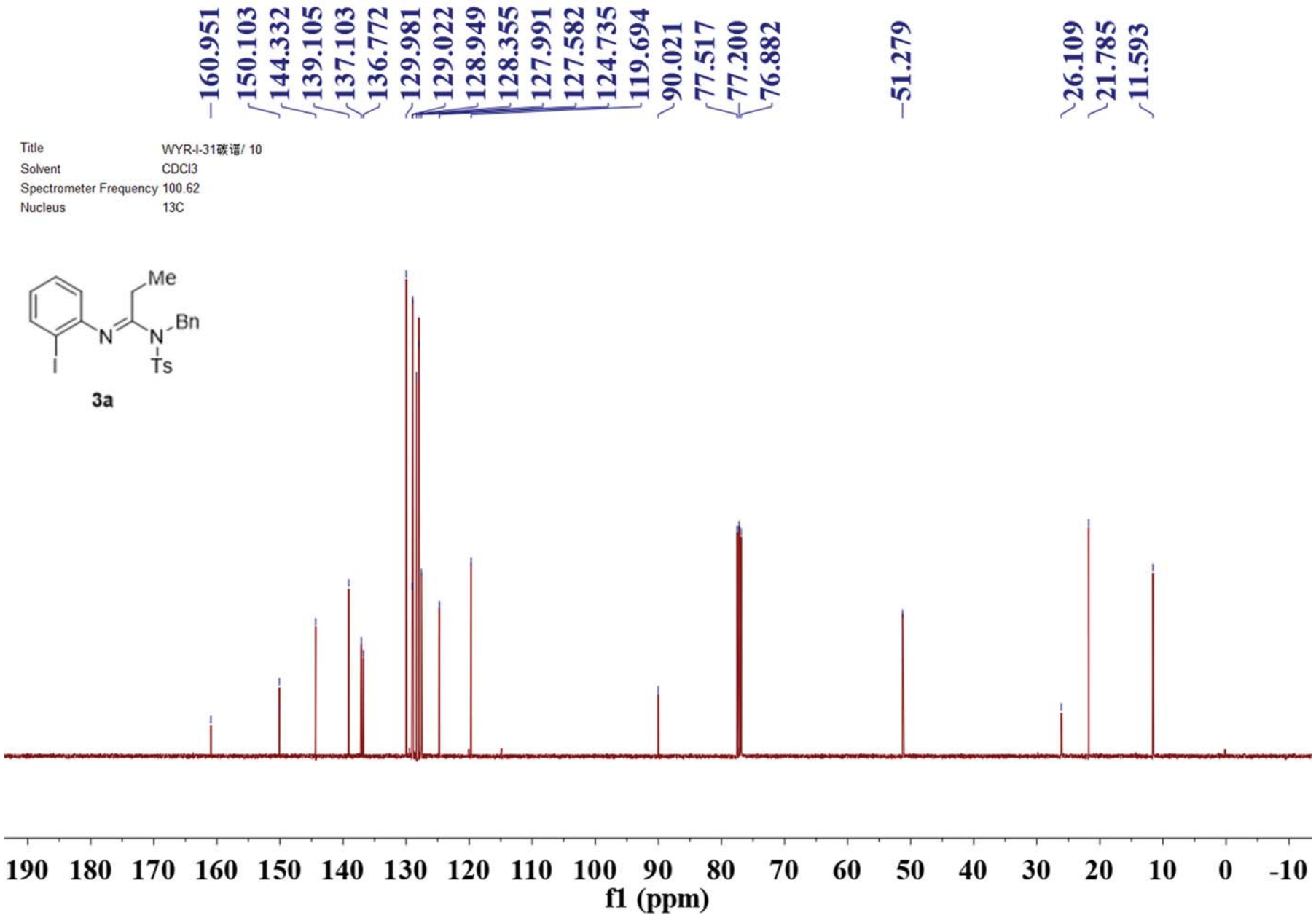
^{1}H NMR and ^{13}C NMR Spectra of *N*-Arylimines 3.

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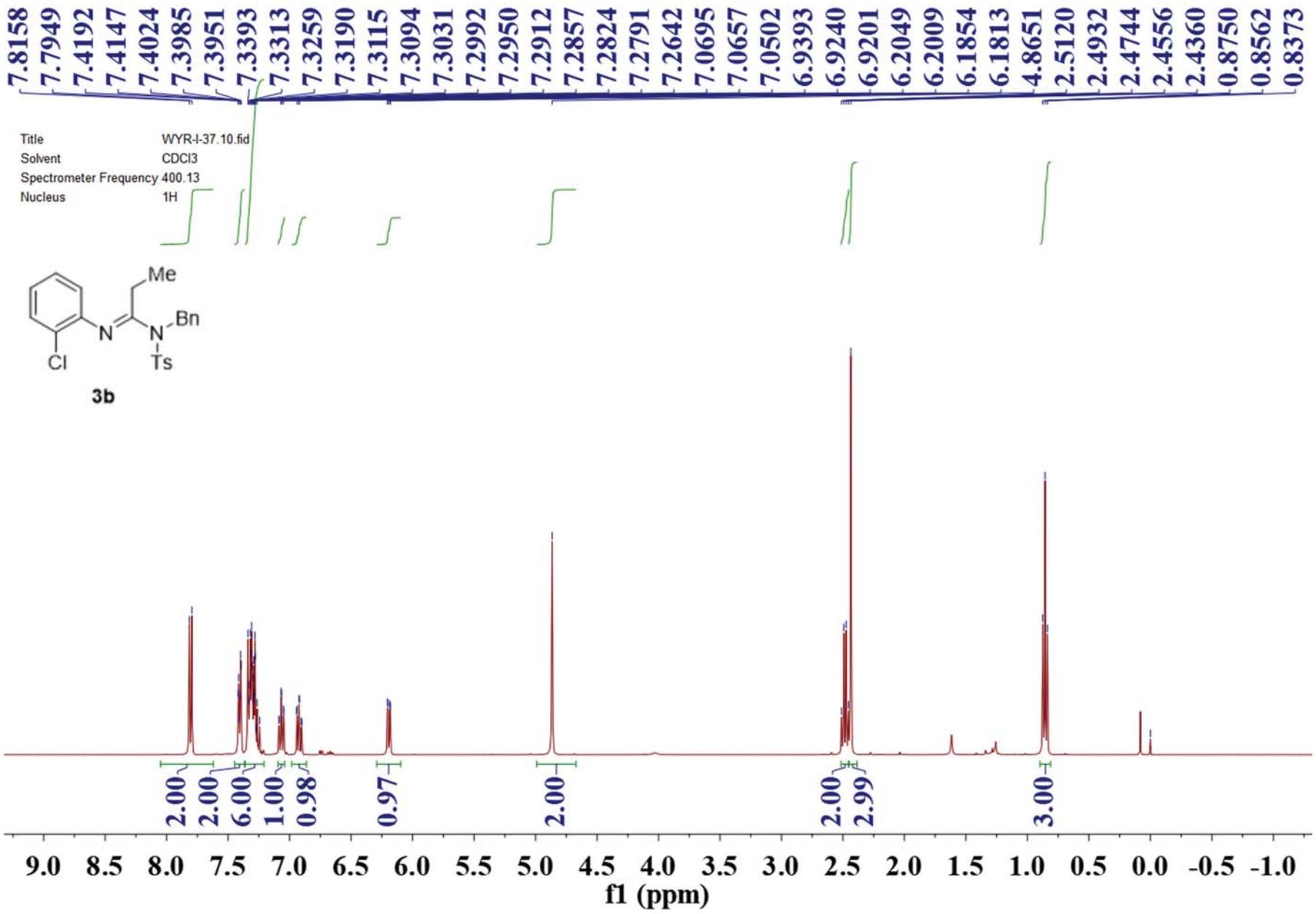
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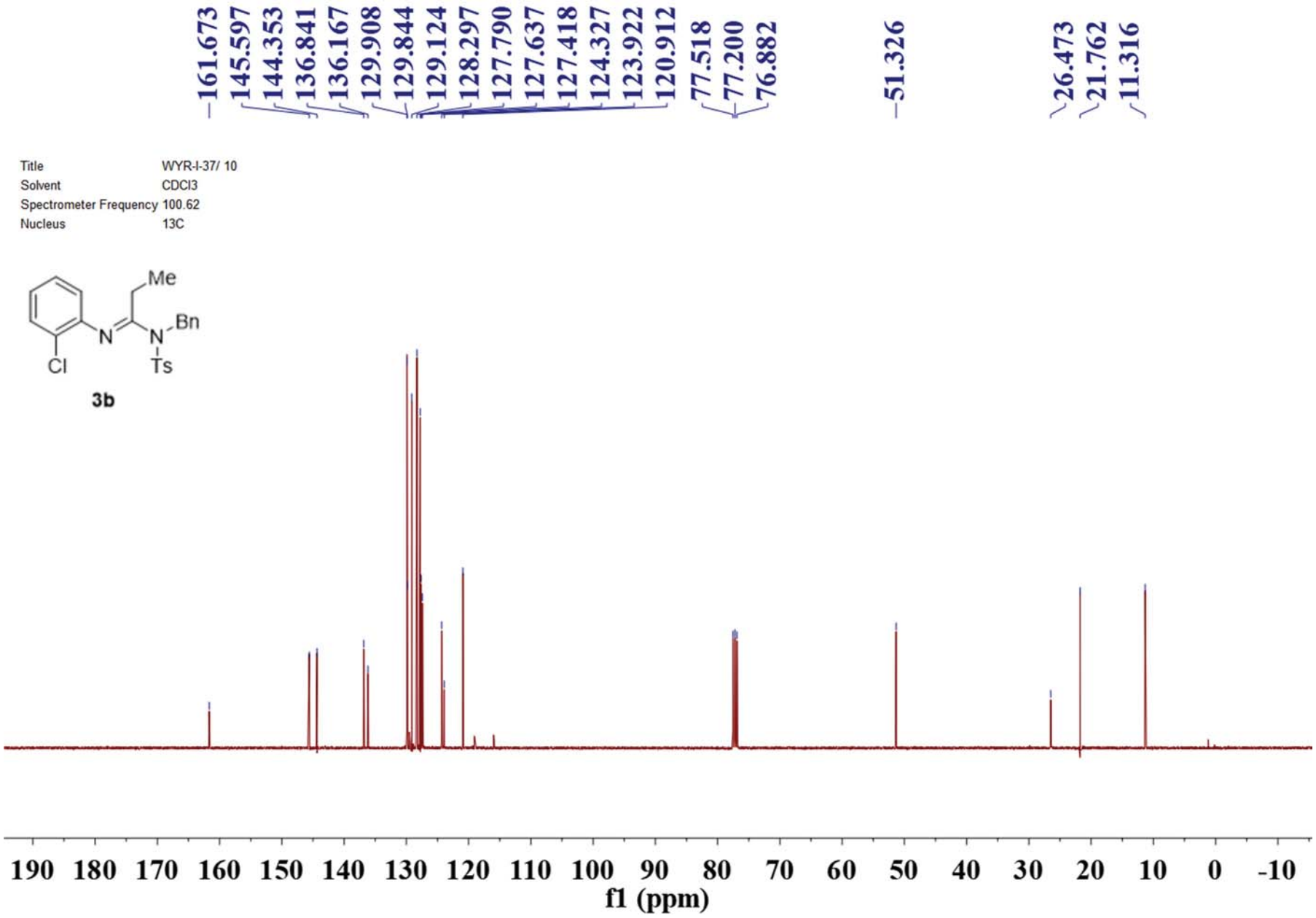
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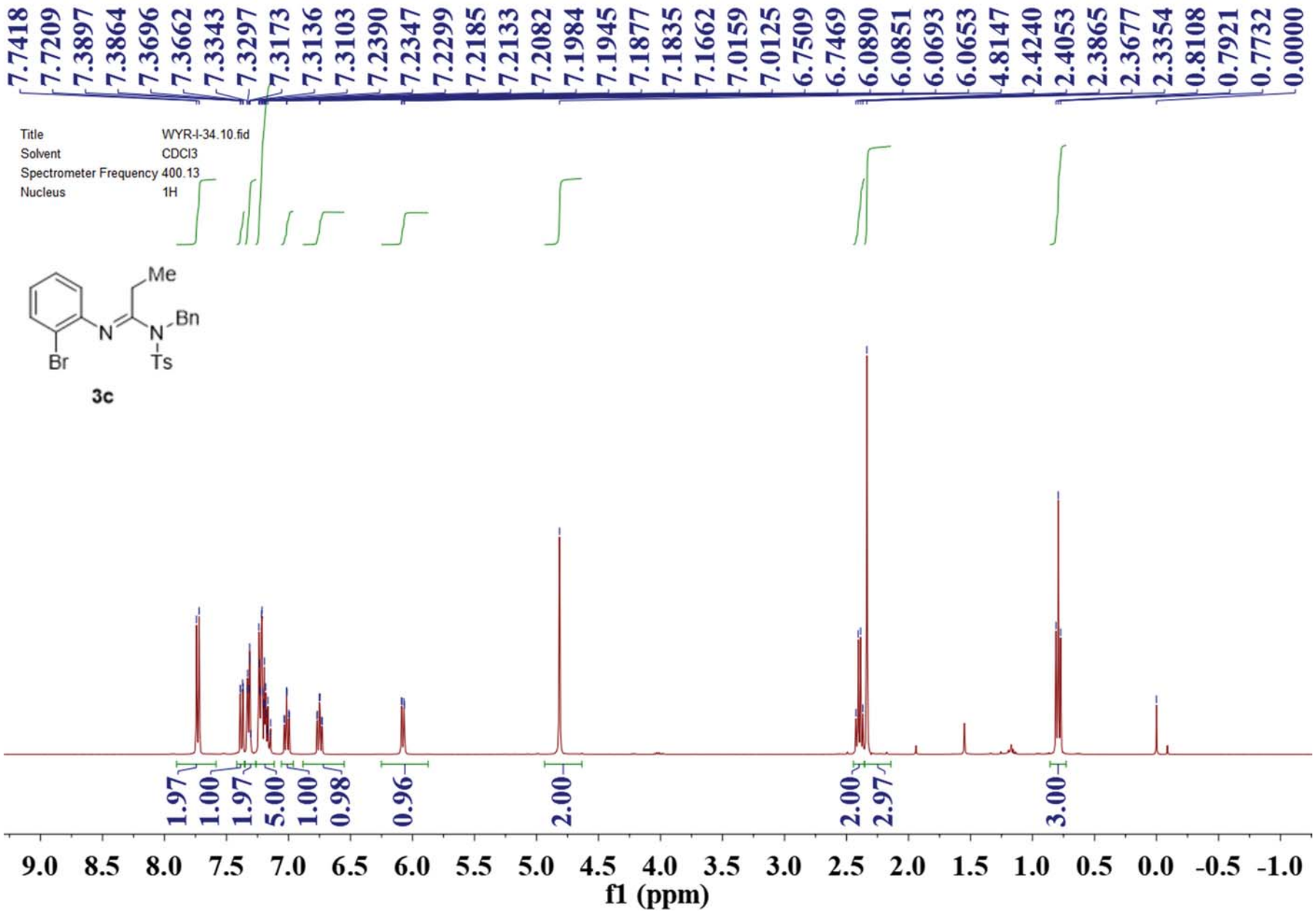
f1 (ppm)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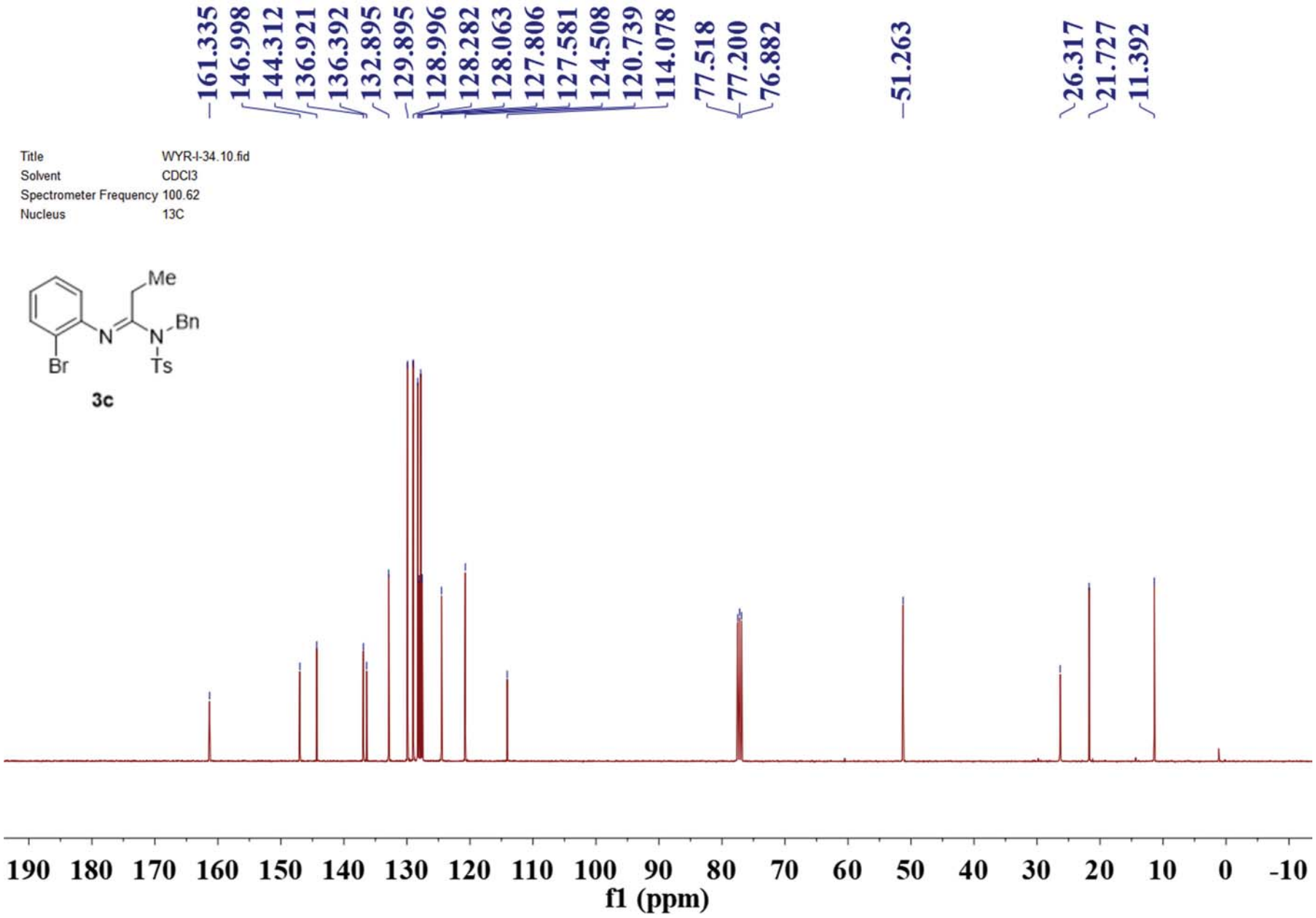
7.7209
7.3897
7.3864
7.3696
7.3662
7.3343
7.3297
7.3173
7.3136
7.3103
7.2390
7.2347
7.2299
7.2185
7.2133
7.2082
7.1984
7.1945
7.1877
7.1835
7.1662
7.0159
7.0125
6.7509
6.7469
6.0890
6.0851
6.0693
6.0653
4.8147
2.4240
2.4053
2.3865
2.3677
2.3354
0.8108
0.7921
0.7732
0.0000
Title WYR-I-34.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Bn
N
Br
Ts
3c
1.97
1.00
1.97
5.00
1.00
0.98
0.96
2.00
2.00
2.97
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 -0.5 -1.0
f1 (ppm)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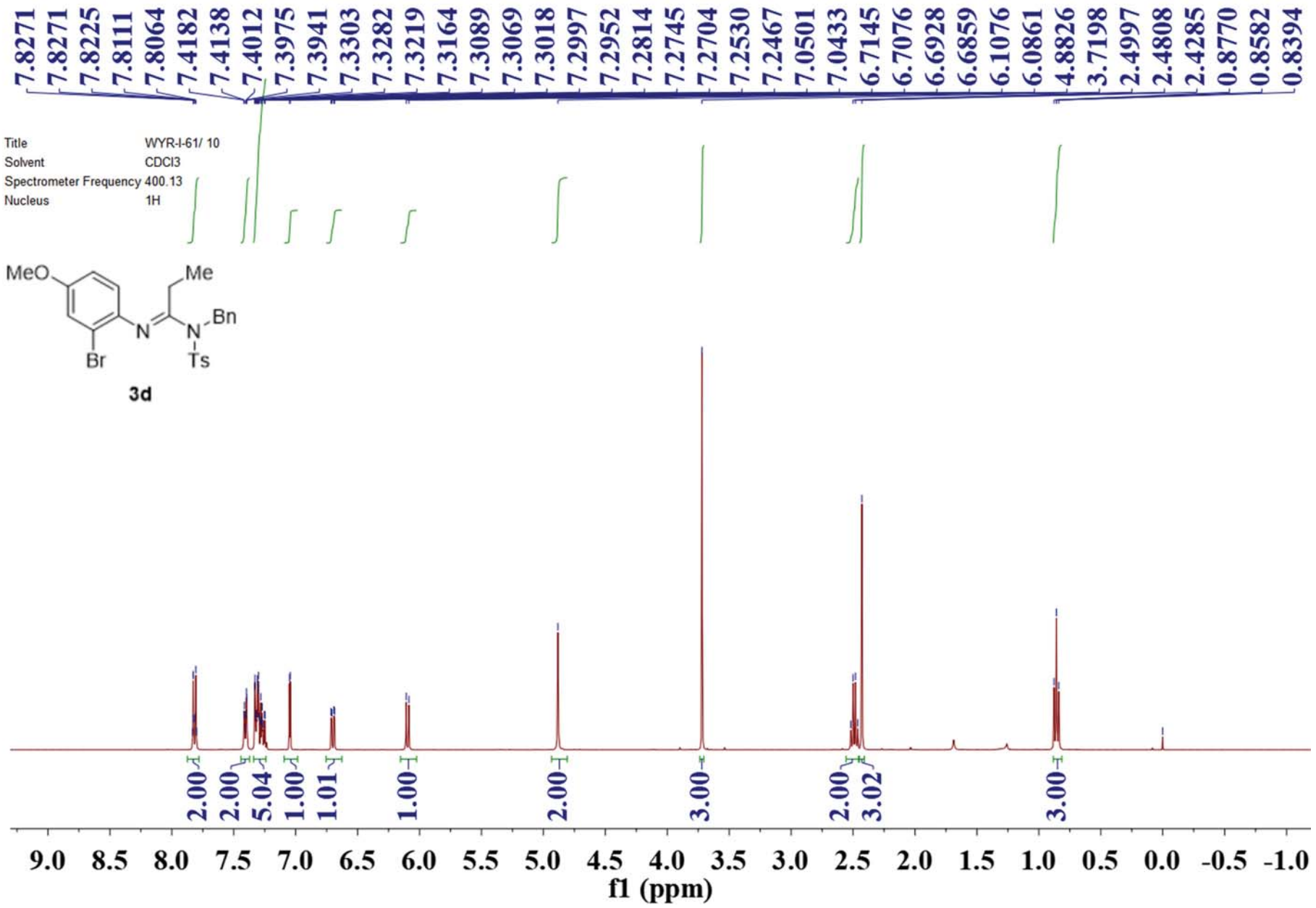
146.998
144.312
136.921
136.392
132.895
129.895
128.996
128.282
128.063
127.806
127.581
124.508
120.739
114.078
77.518
77.200
76.882
51.263
26.317
21.727
11.392
Title WYR-I-34.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Br
Ts
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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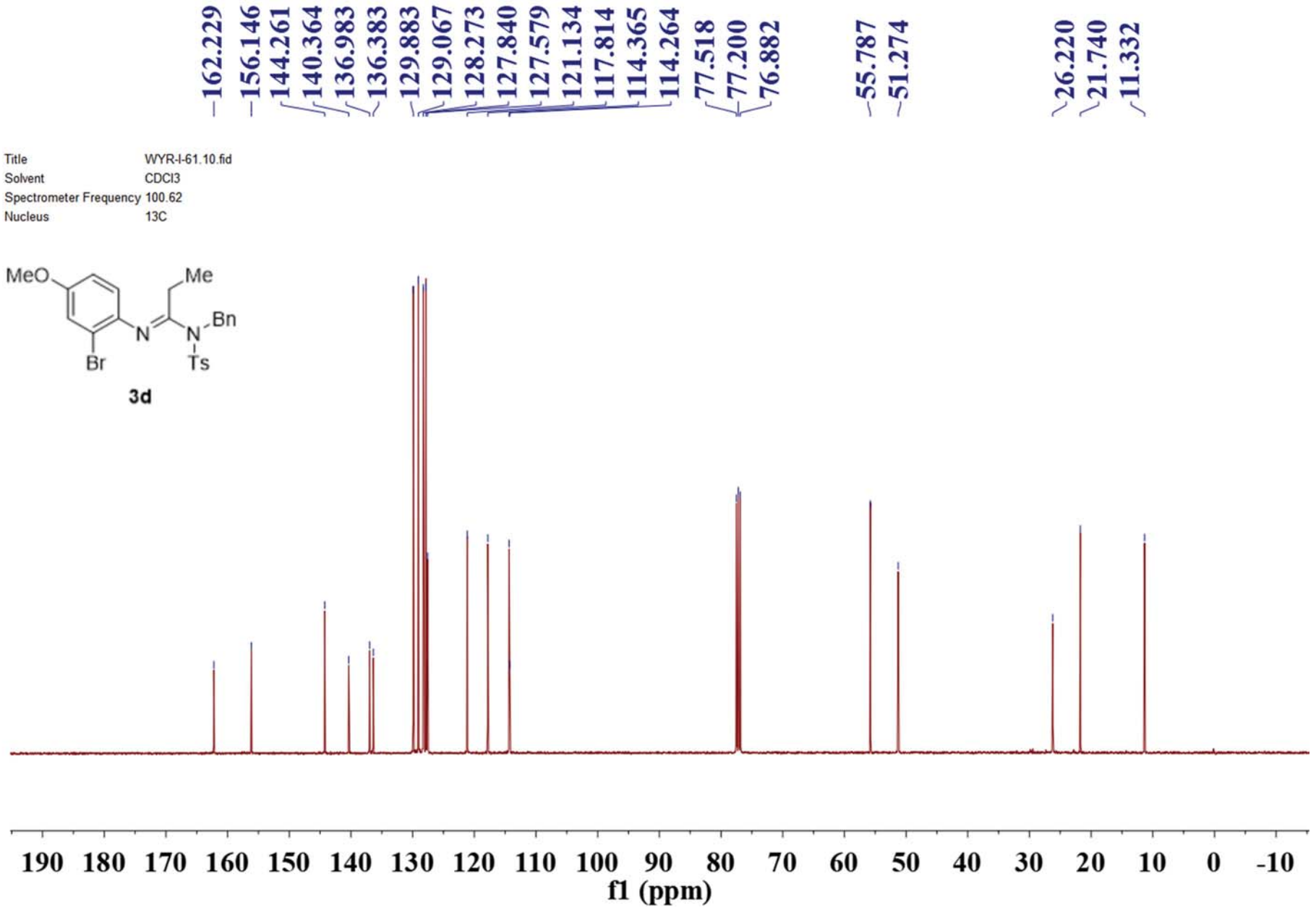
7.8271
7.8225
7.8111
7.8064
7.4182
7.4138
7.4012
7.3975
7.3941
7.3303
7.3282
7.3219
7.3164
7.3089
7.3069
7.3018
7.2997
7.2952
7.2814
7.2745
7.2704
7.2530
7.2467
7.0501
7.0433
6.7145
6.7076
6.6928
6.6859
6.1076
6.0861
4.8826
3.7198
2.4997
2.4808
2.4285
0.8770
0.8582
0.8394
Title WYR-I-61/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Me
Bn
N
N
Br
Ts
3d
2.00
2.00
5.04
1.00
1.01
1.00
2.00
3.00
2.00
3.02
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 -0.5 -1.0
f1 (ppm)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156.146
144.261
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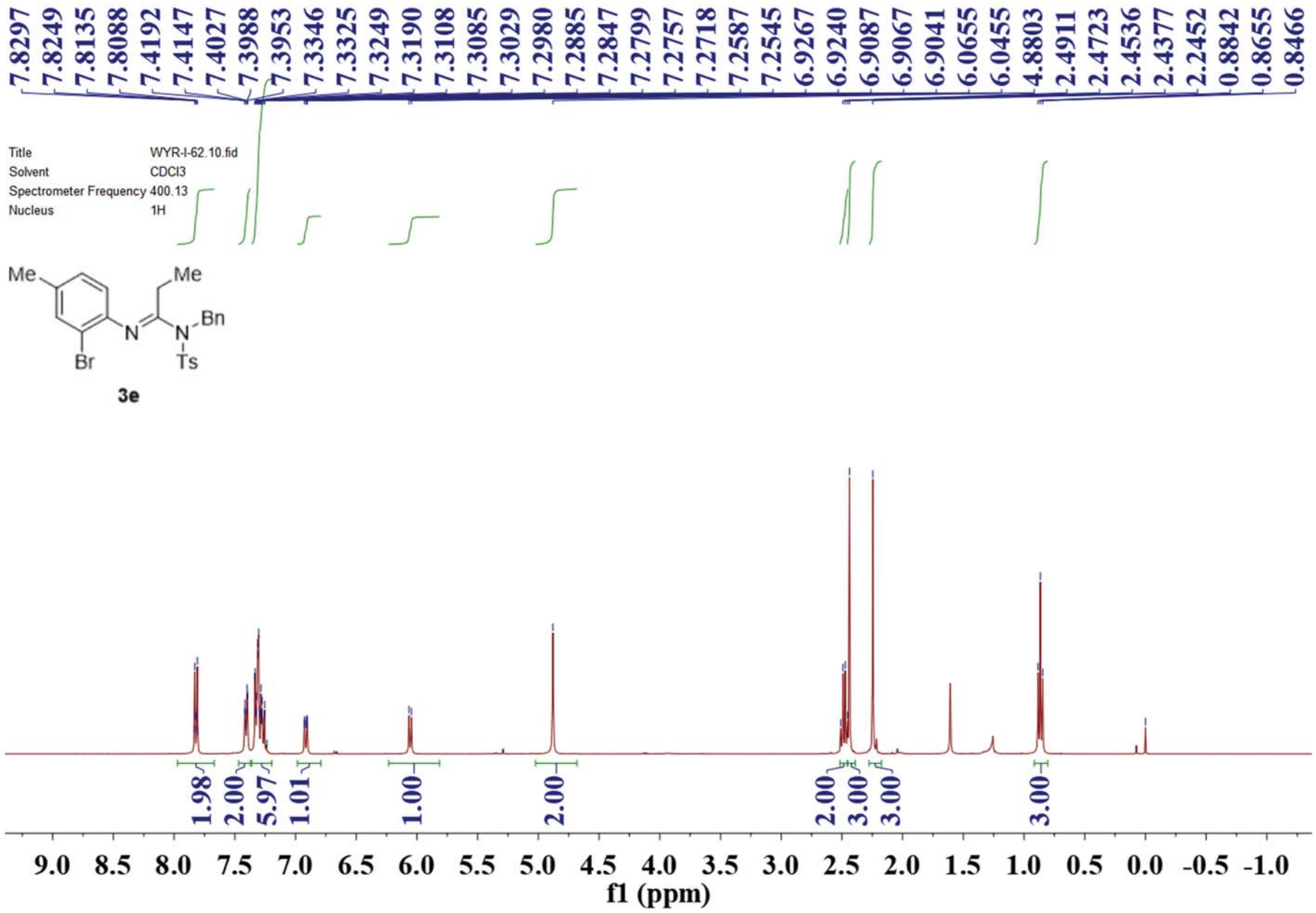
136.983
136.383
129.883
129.067
128.273
127.840
127.579
121.134
117.814
114.365
114.264
77.518
77.200
76.882
55.787
51.274
26.220
21.740
11.332
Title WYR-I-61.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Me
Bn
N
N
Br
Ts
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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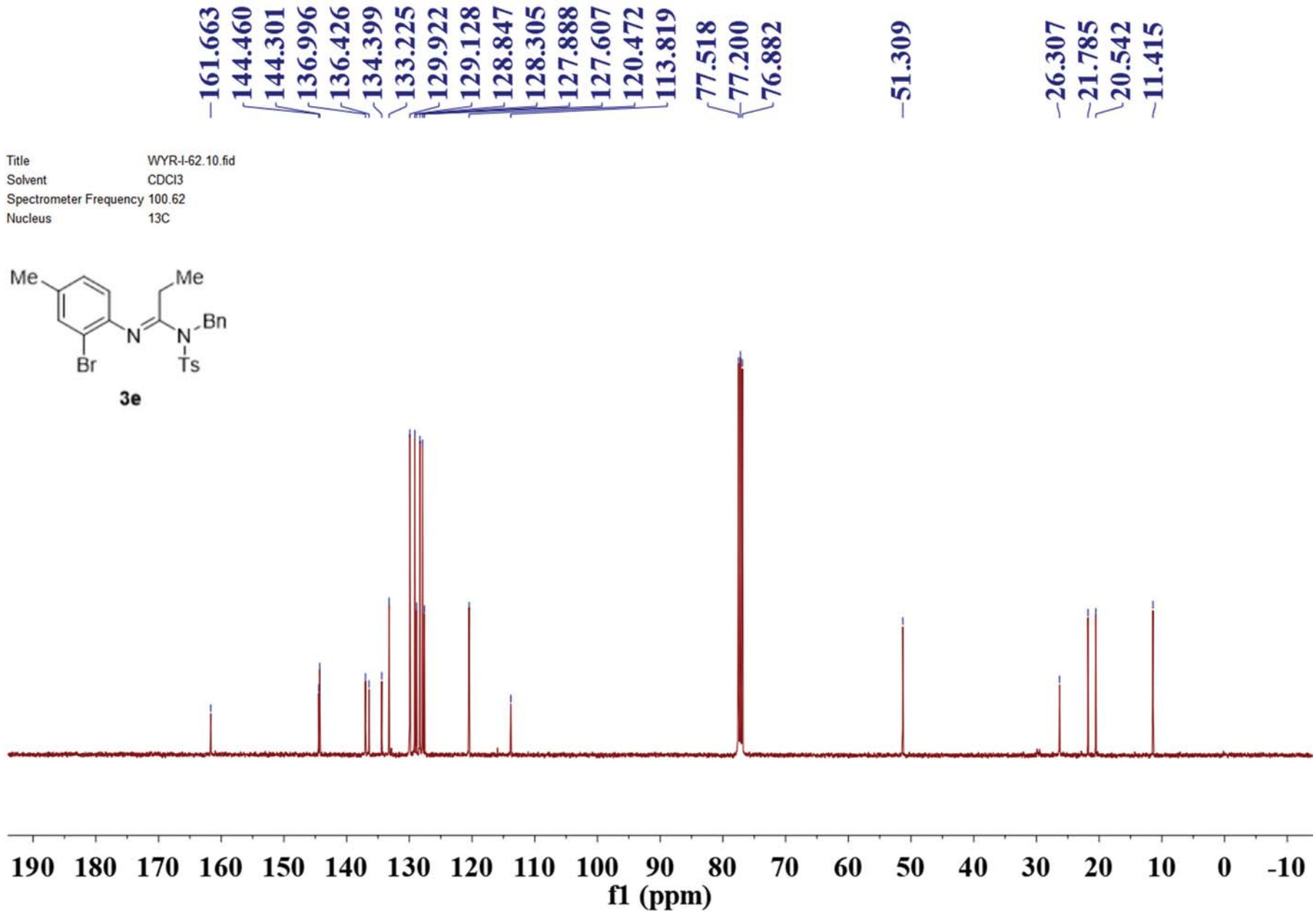
7.8088
7.4192
7.4147
7.4027
7.3988
7.3953
7.3346
7.3325
7.3249
7.3190
7.3108
7.3085
7.3029
7.2980
7.2885
7.2847
7.2799
7.2757
7.2718
7.2587
7.2545
6.9267
6.9240
6.9087
6.9067
6.9041
6.0655
6.0455
4.8803
2.4911
2.4723
2.4536
2.4377
2.2452
0.8842
0.8655
0.8466
Title WYR-I-62.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
N
N
Bn
Br
Ts
3e
1.98
2.00
5.97
1.01
1.00
2.00
2.00
3.00
3.00
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 -0.5 -1.0
f1 (ppm)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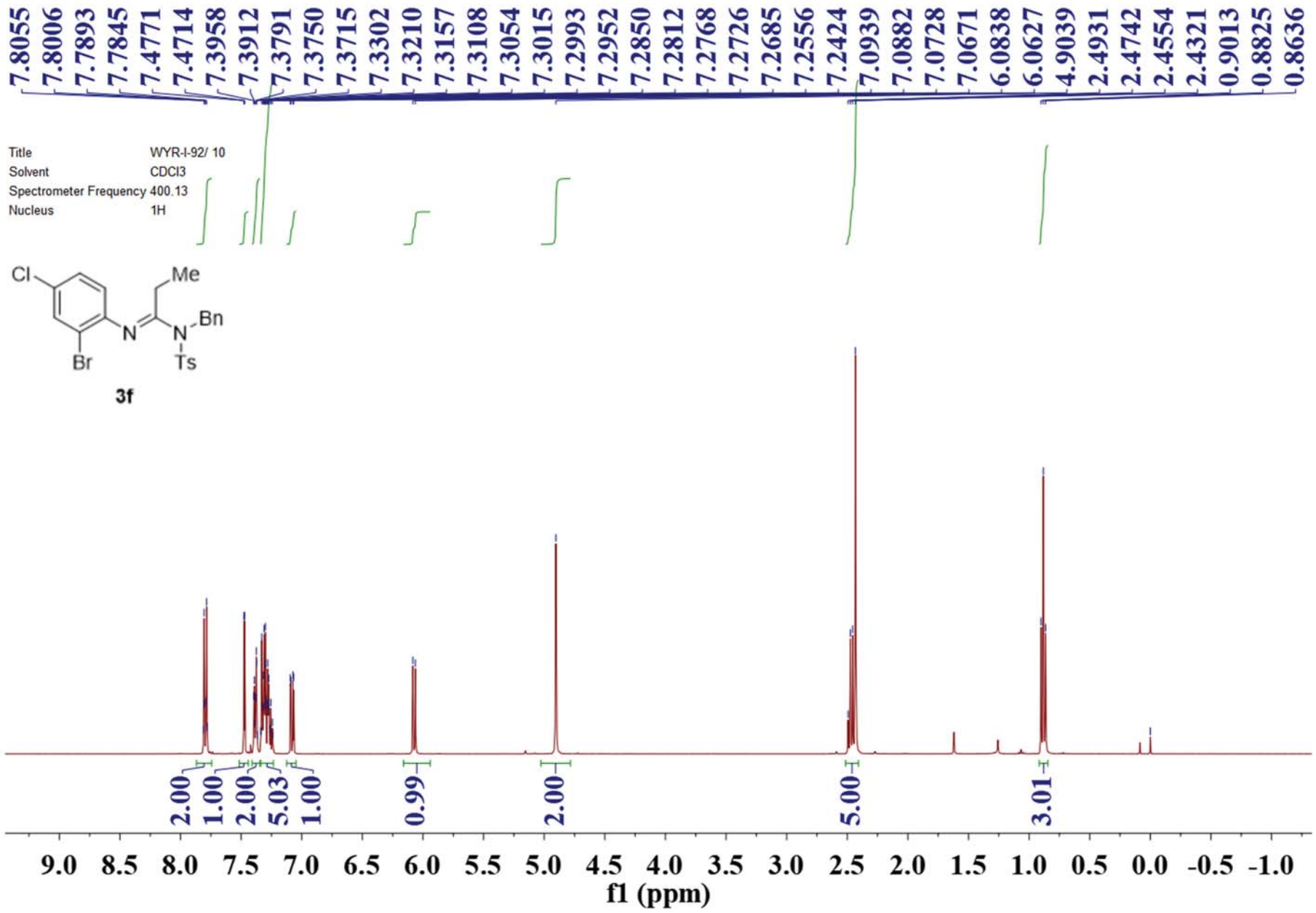
144.460
144.301
136.996
136.426
134.399
133.225
129.922
129.128
128.847
128.305
127.888
127.607
120.472
113.819
77.518
77.200
76.882
51.309
26.307
21.785
20.542
11.415
Title WYR-I-62.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
Bn
N
N
Br
Ts
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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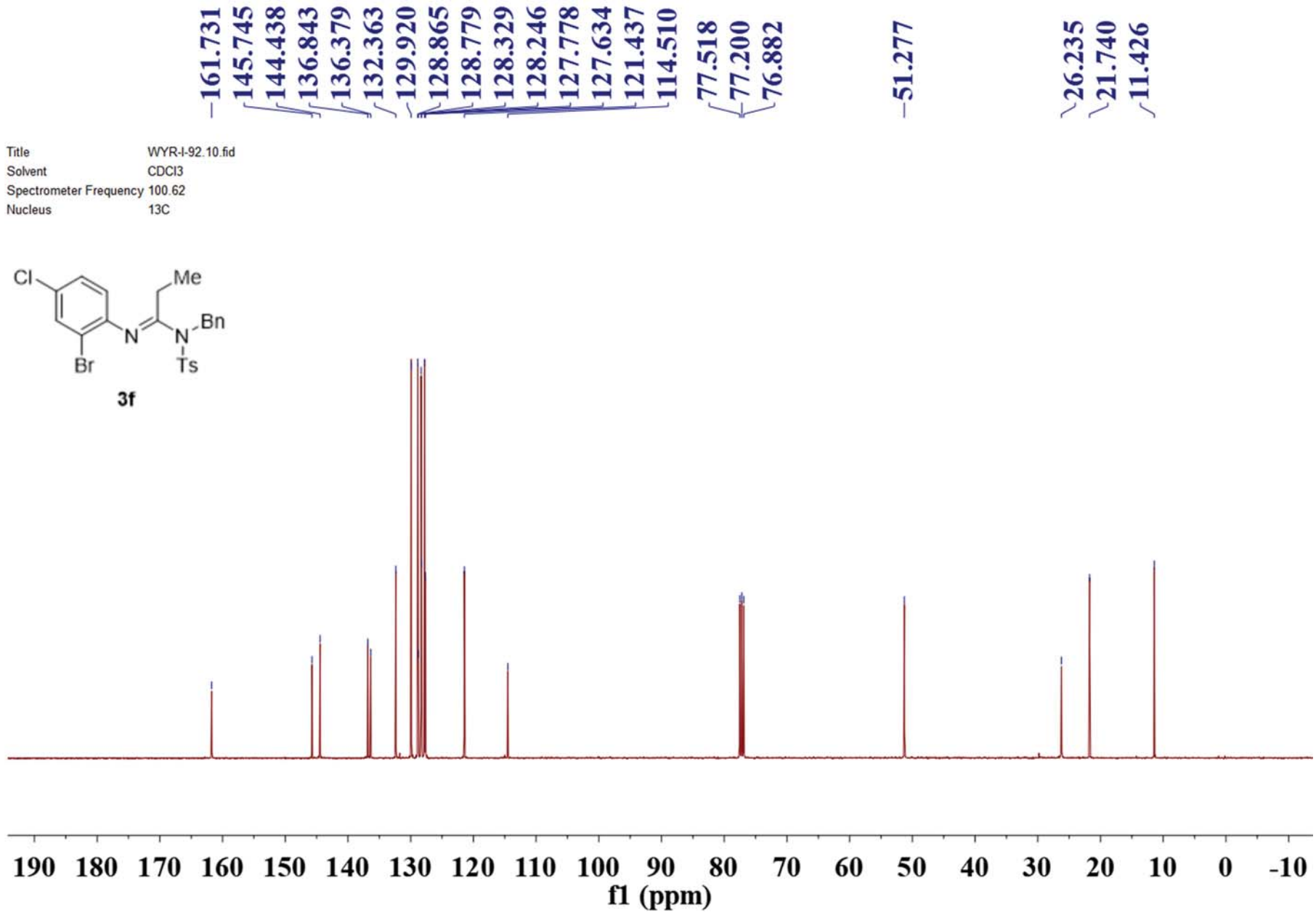
7.7893
7.7845
7.4771
7.4714
7.3958
7.3912
7.3791
7.3750
7.3715
7.3302
7.3210
7.3157
7.3108
7.3054
7.3015
7.2993
7.2952
7.2850
7.2812
7.2768
7.2726
7.2685
7.2556
7.2424
7.0939
7.0882
7.0728
7.0671
6.0838
6.0627
4.9039
2.4931
2.4742
2.4554
2.4321
0.9013
0.8825
0.8636
Title WYR-I-92/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Me
Bn
N
N
Br
Ts
3f
2.00
1.00
2.00
5.03
1.00
0.99
2.00
5.00
3.01
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 -0.5 -1.0
f1 (ppm)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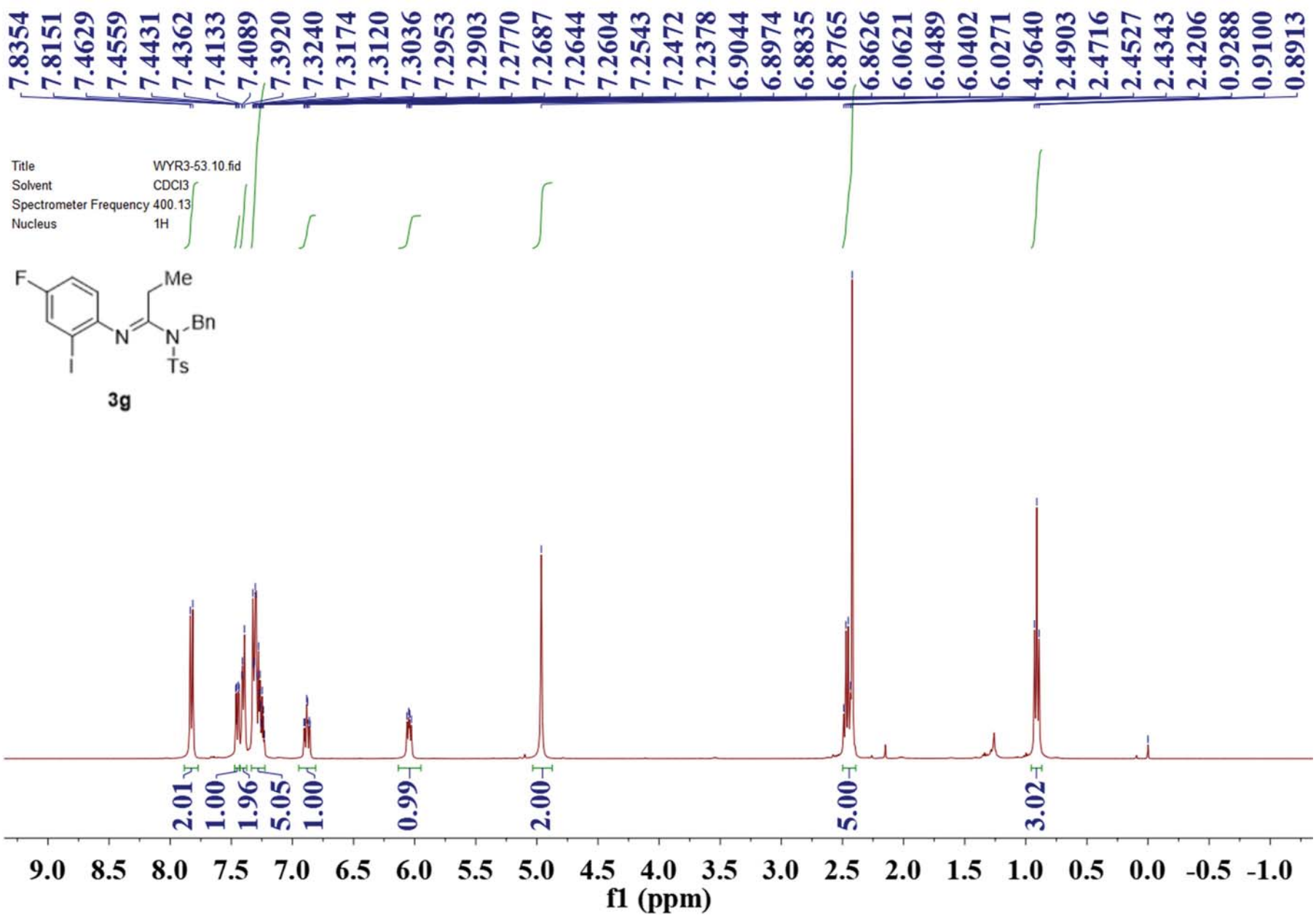
144.438
136.843
136.379
132.363
129.920
128.865
128.779
128.329
128.246
127.778
127.634
121.437
114.510
77.518
77.200
76.882
51.277
26.235
21.740
11.426
Title WYR-I-92.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Me
N
Bn
N
Br
Ts
3f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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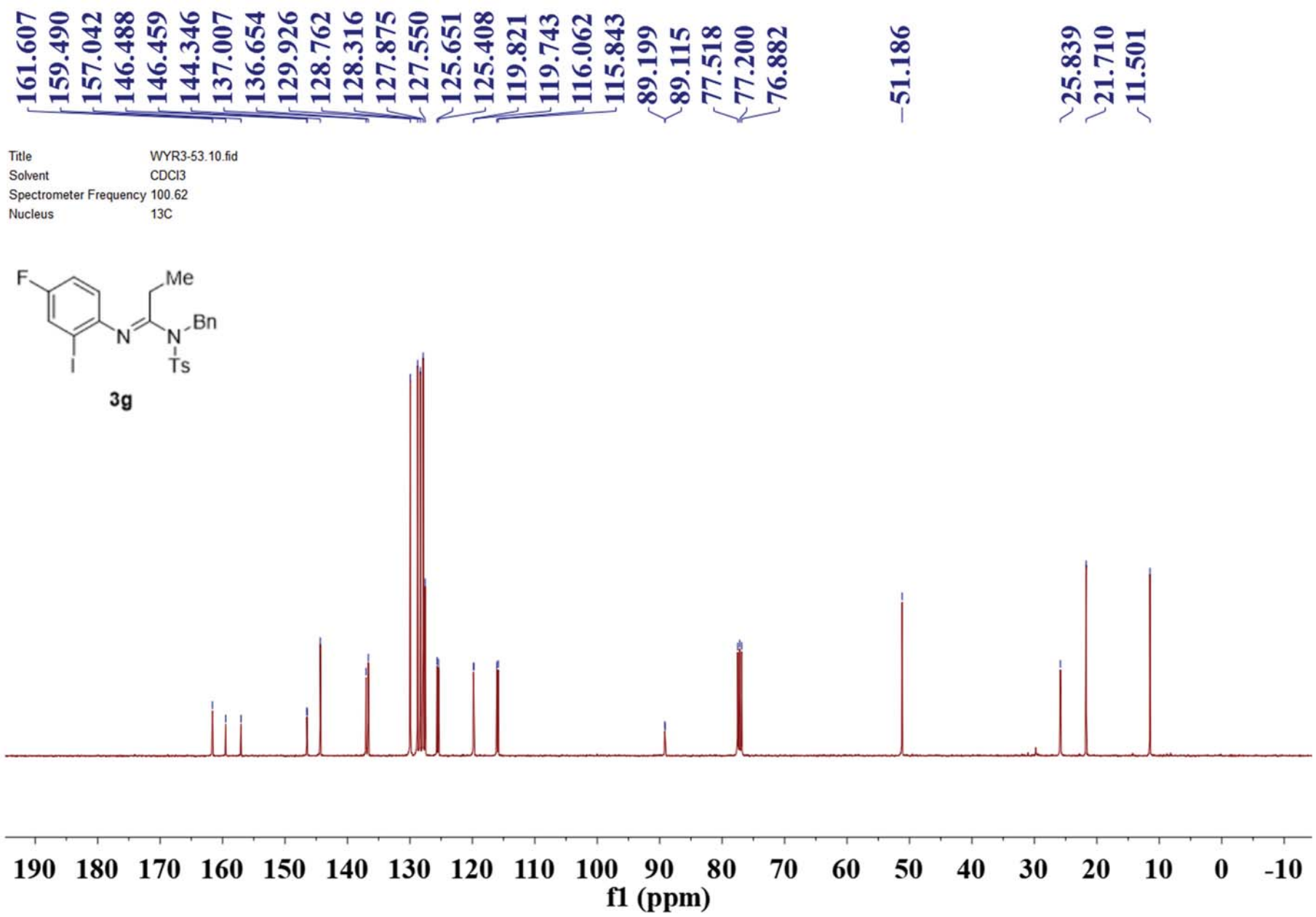
7.8151
7.4629
7.4559
7.4431
7.4362
7.4133
7.4089
7.3920
7.3240
7.3174
7.3120
7.3036
7.2953
7.2903
7.2770
7.2687
7.2644
7.2604
7.2543
7.2472
7.2378
6.9044
6.8974
6.8835
6.8765
6.8626
6.0621
6.0489
6.0402
6.0271
4.9640
2.4903
2.4716
2.4527
2.4343
2.4206
0.9288
0.9100
0.8913
Title WYR3-53.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
Me
Bn
N
N
Ts
I
3g
2.01
1.00
1.96
5.05
1.00
0.99
2.00
5.00
3.02
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 -0.5 -1.0
f1 (ppm)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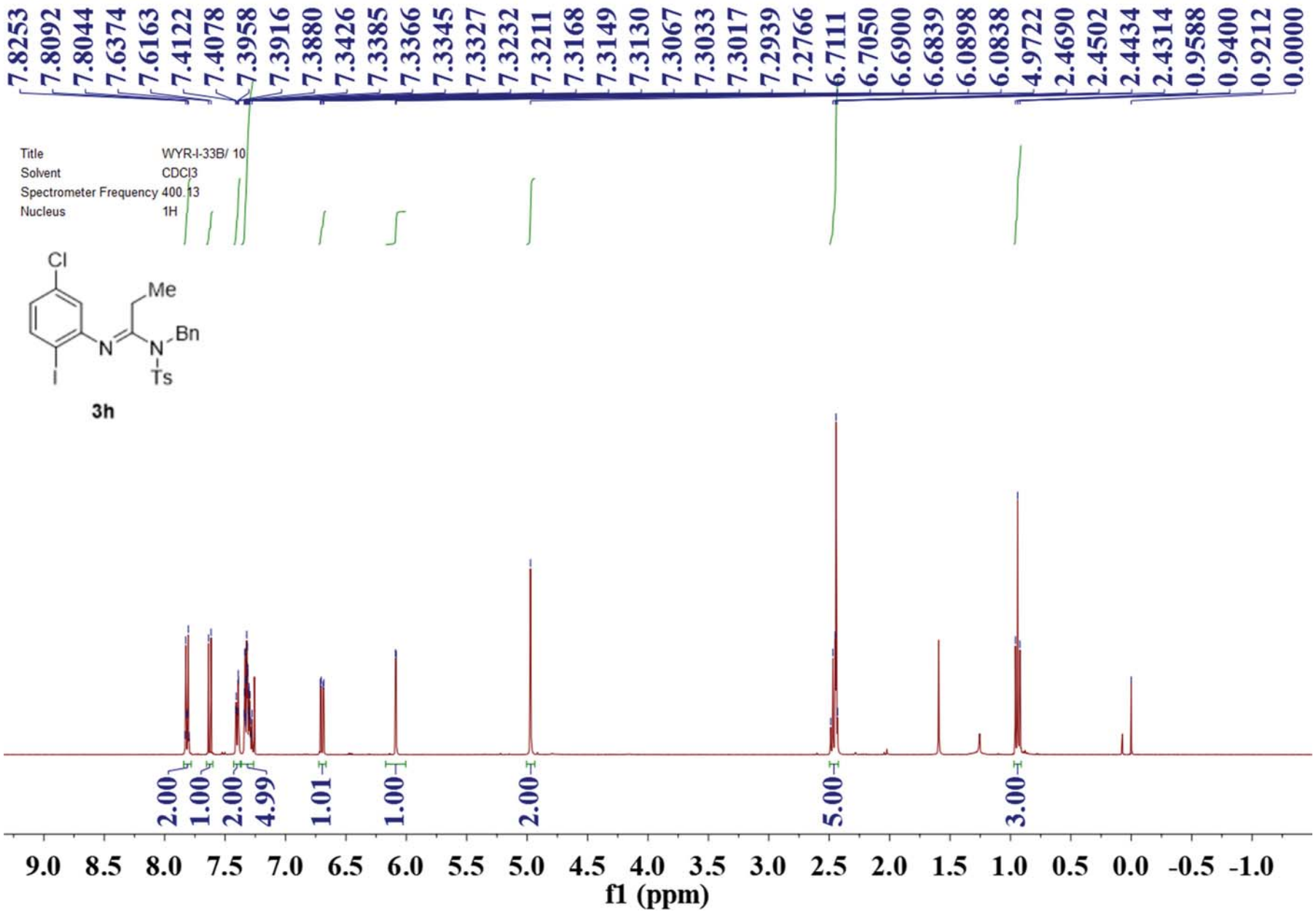
157.042
146.488
146.459
144.346
137.007
136.654
129.926
128.762
128.316
127.875
127.550
125.651
125.408
119.821
119.743
116.062
115.843
89.199
89.115
77.518
77.200
76.882
51.186
25.839
21.710
11.501
Title WYR3-53.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
Me
Bn
N
N
Ts
I
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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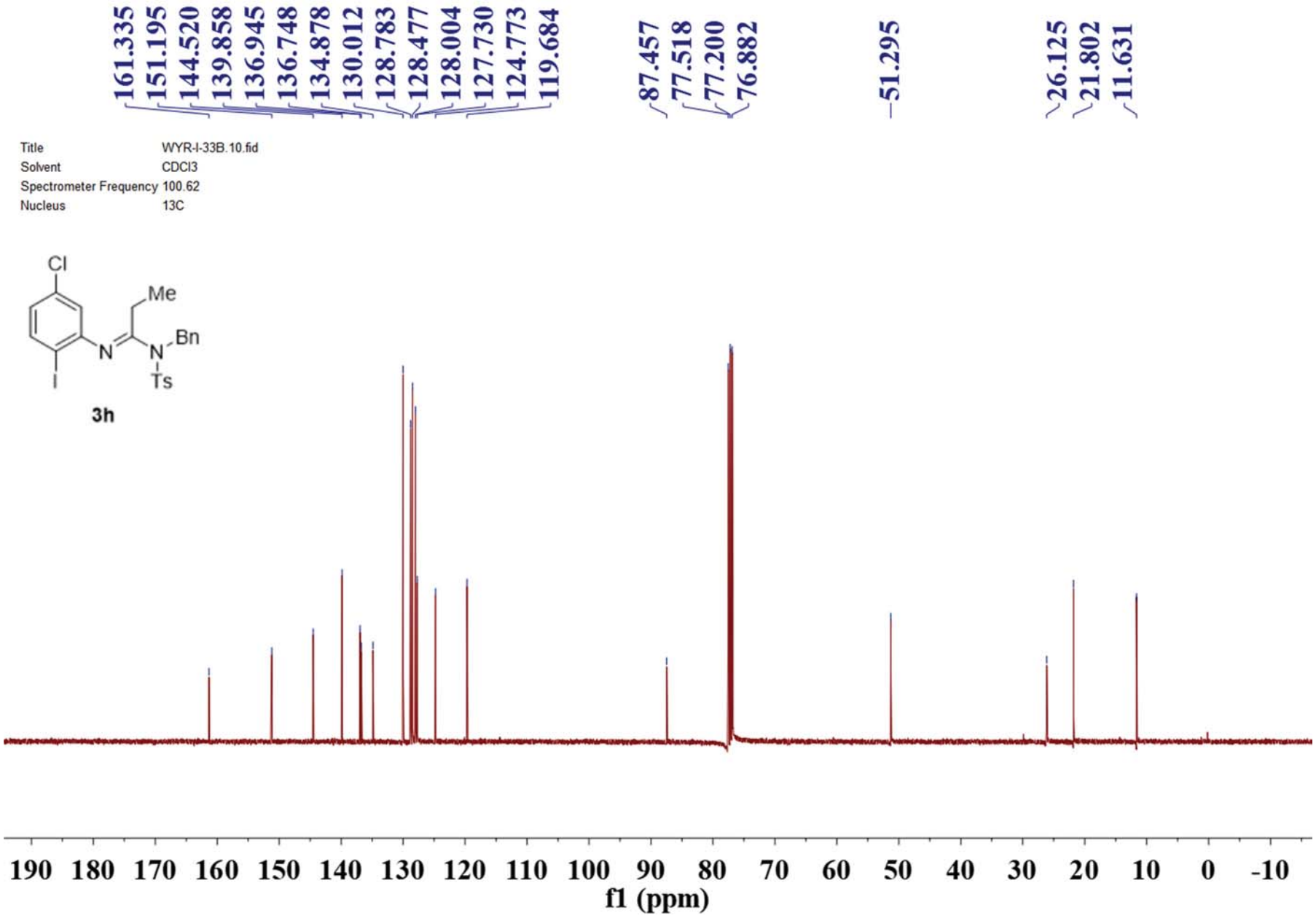
7.8092
7.8044
7.6374
7.6163
7.4122
7.4078
7.3958
7.3916
7.3880
7.3426
7.3385
7.3366
7.3345
7.3327
7.3232
7.3211
7.3168
7.3149
7.3130
7.3067
7.3033
7.3017
7.2939
7.2766
6.7111
6.7050
6.6900
6.6839
6.0898
6.0838
4.9722
2.4690
2.4502
2.4434
2.4314
0.9588
0.9400
0.9212
0.0000
Title WYR-I-33B/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Me
Bn
N
N
Ts
I
3h
2.00
1.00
2.00
4.99
1.01
1.00
2.00
5.00
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 -0.5 -1.0
f1 (ppm)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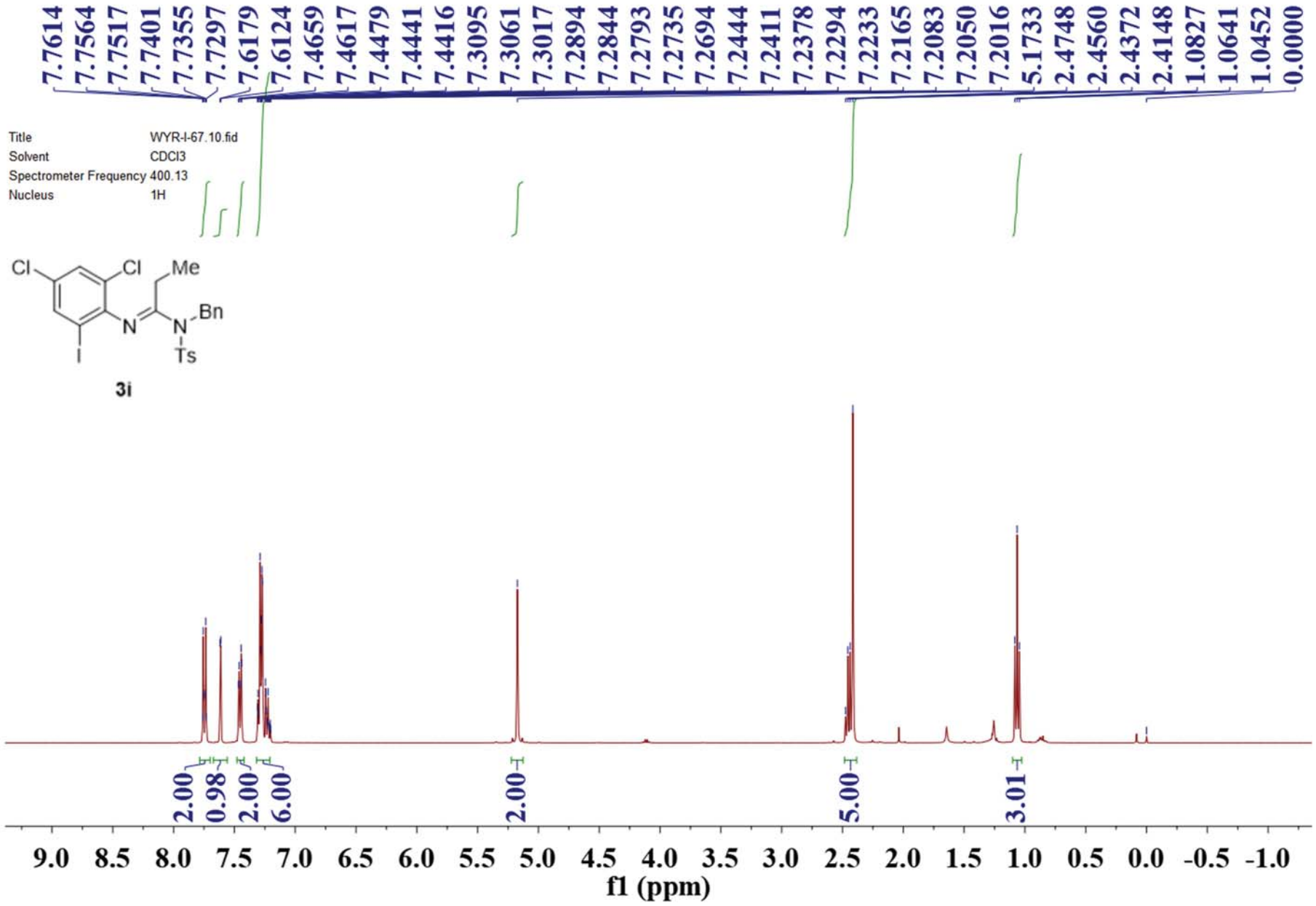
144.520
139.858
136.945
136.748
134.878
130.012
128.783
128.477
128.004
127.730
124.773
119.684
87.457
77.518
77.200
76.882
51.295
26.125
21.802
11.631
Title WYR-I-33B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Me
Bn
N
N
Ts
I
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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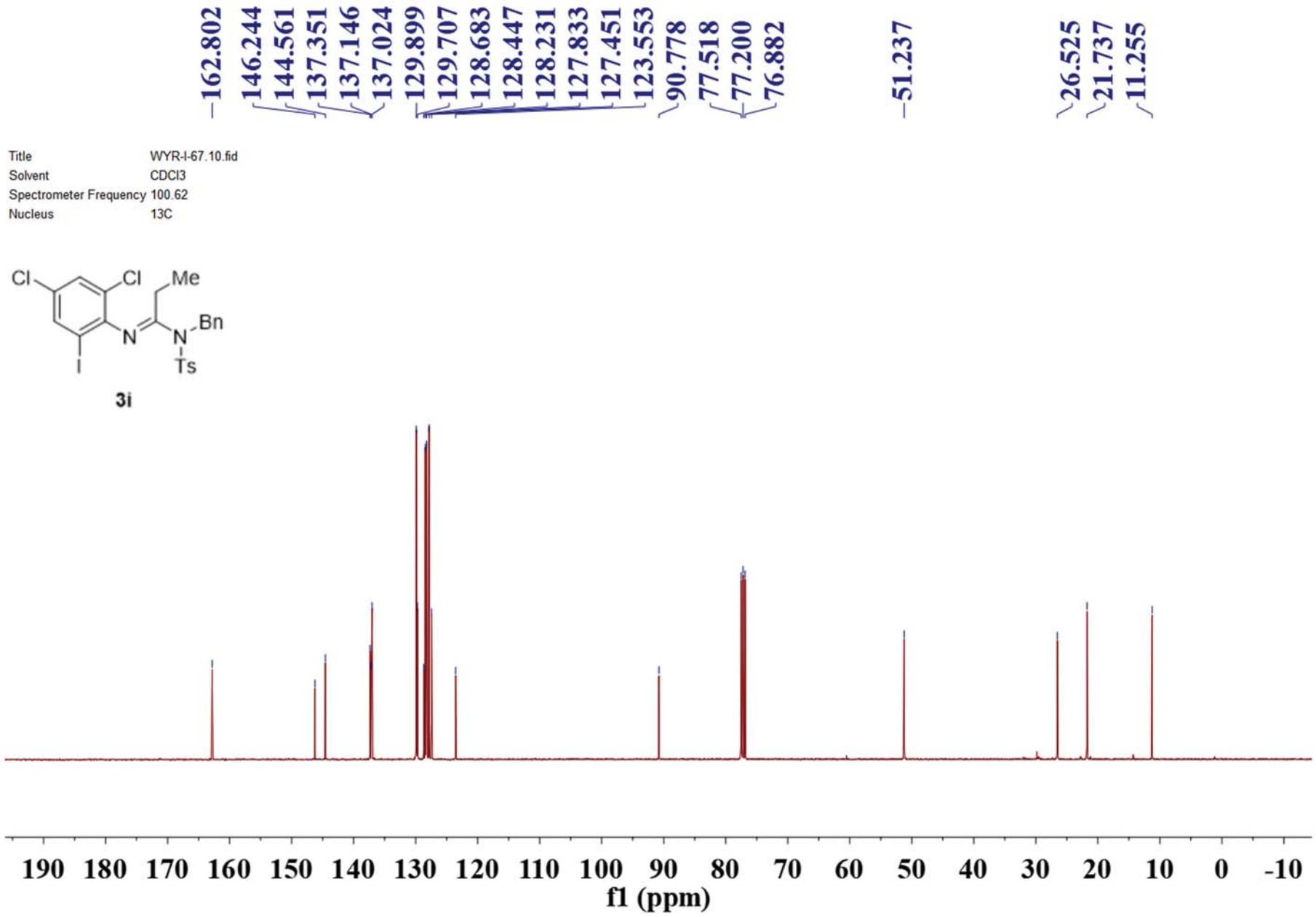
7.7517
7.7401
7.7355
7.7297
7.6179
7.6124
7.4659
7.4617
7.4479
7.4441
7.4416
7.3095
7.3061
7.3017
7.2894
7.2844
7.2793
7.2735
7.2694
7.2444
7.2411
7.2378
7.2294
7.2233
7.2165
7.2083
7.2050
7.2016
5.1733
2.4748
2.4560
2.4372
2.4148
1.0827
1.0641
1.0452
0.0000
Title WYR-I-67.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Cl
Me
Bn
N
N
I
Ts
3i
2.00
0.98
2.00
6.00
2.00
5.00
3.01
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 -0.5 -1.0
f1 (ppm)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144.561
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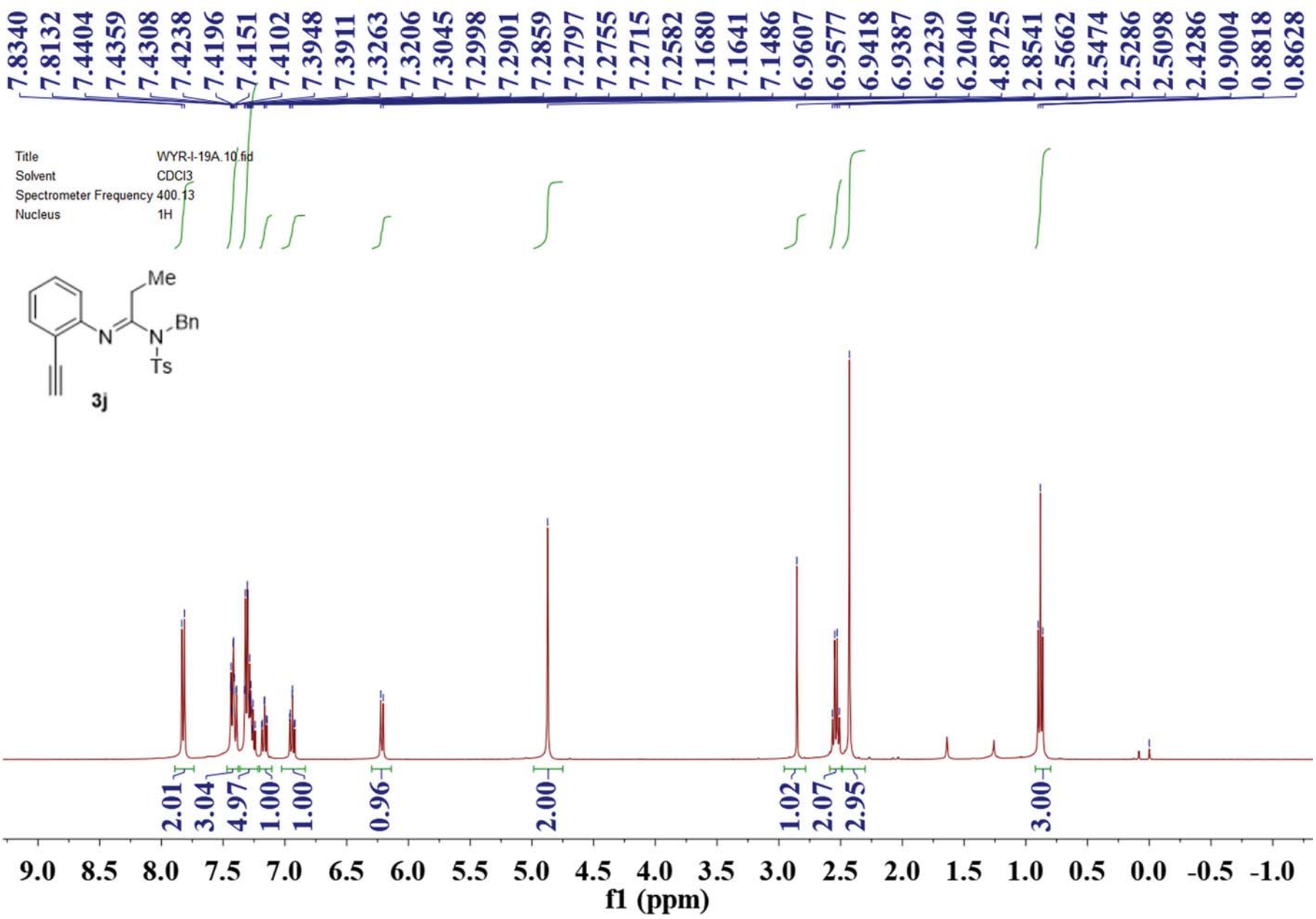
137.146
137.024
129.899
129.707
128.683
128.447
128.231
127.833
127.451
123.553
90.778
77.518
77.200
76.882
51.237
26.525
21.737
11.255
Title WYR-I-67.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Cl
Me
Bn
N
N
I
Ts
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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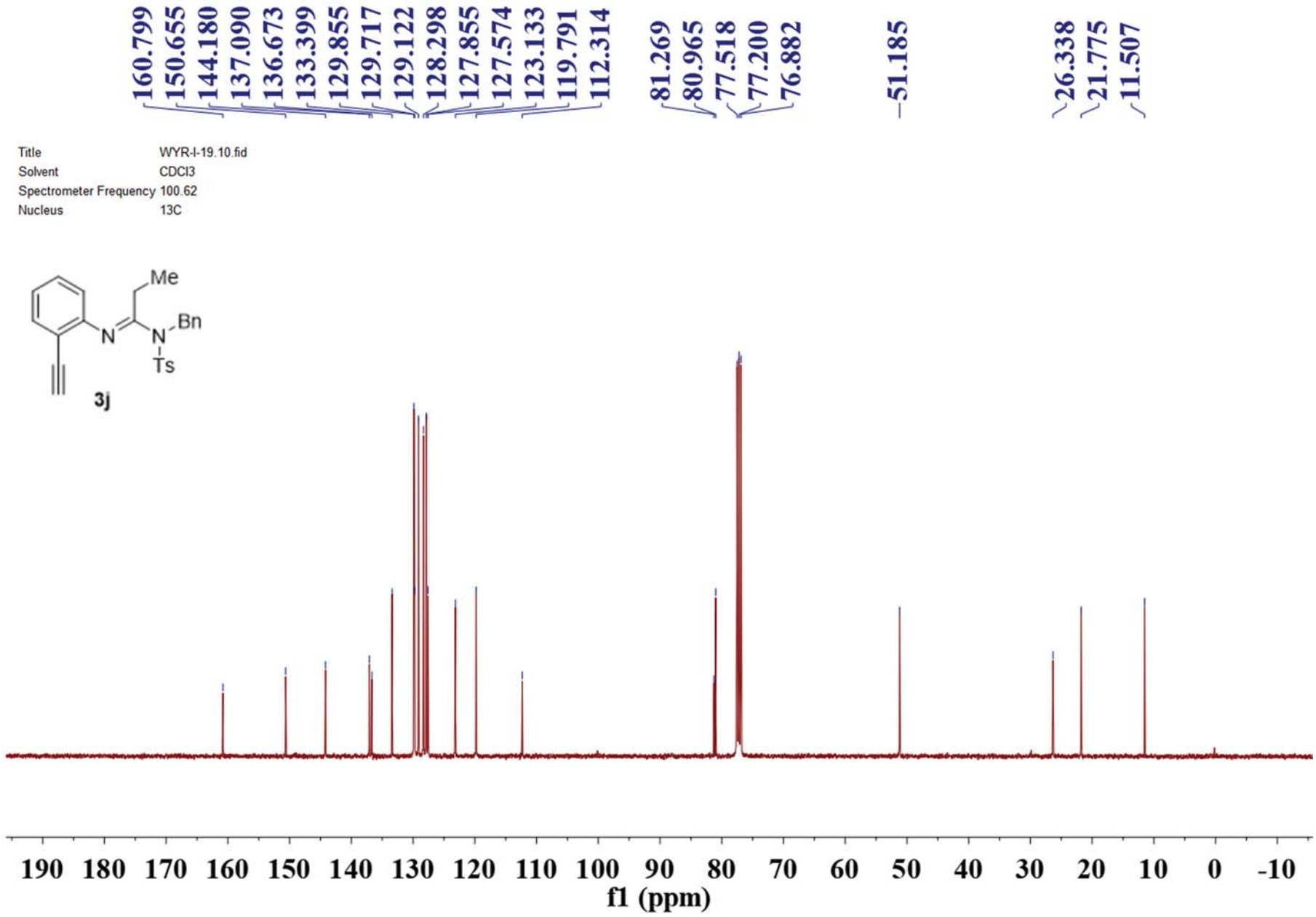
7.4404
7.4359
7.4308
7.4238
7.4196
7.4151
7.4102
7.3948
7.3911
7.3263
7.3206
7.3045
7.2998
7.2901
7.2859
7.2797
7.2755
7.2715
7.2582
7.1680
7.1641
7.1486
6.9607
6.9577
6.9418
6.9387
6.2239
6.2040
4.8725
2.8541
2.5662
2.5474
2.5286
2.5098
2.4286
0.9004
0.8818
0.8628
Title WYR-I-19A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
Ts
3j
2.01
3.04
4.97
1.00
1.00
0.96
2.00
1.02
2.07
2.95
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 -0.5 -1.0
f1 (ppm)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144.180
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136.673
133.399
129.855
129.717
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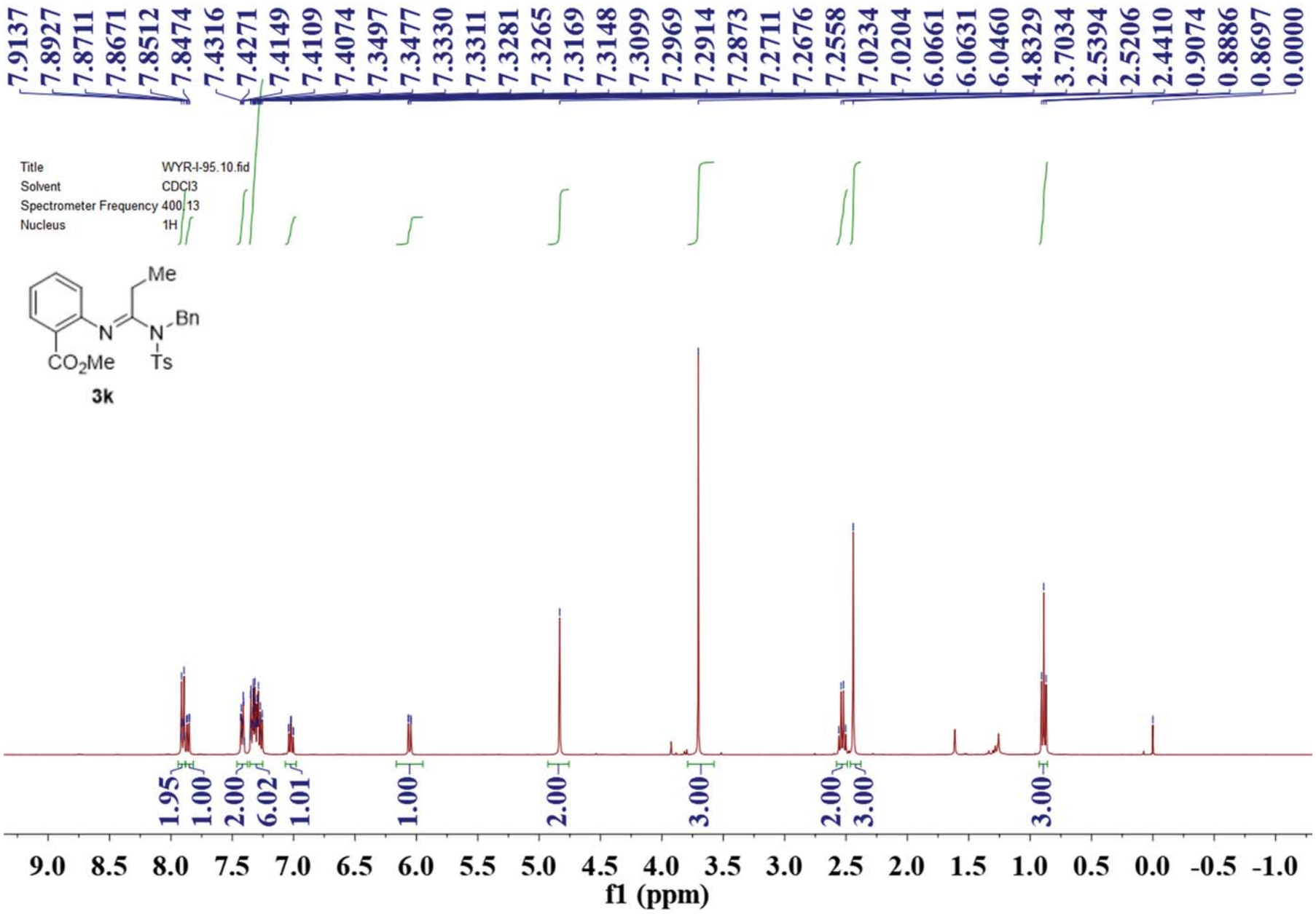
128.298
127.855
127.574
123.133
119.791
112.314
81.269
80.965
77.518
77.200
76.882
51.185
26.338
21.775
11.507
Title WYR-I-19.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Ts
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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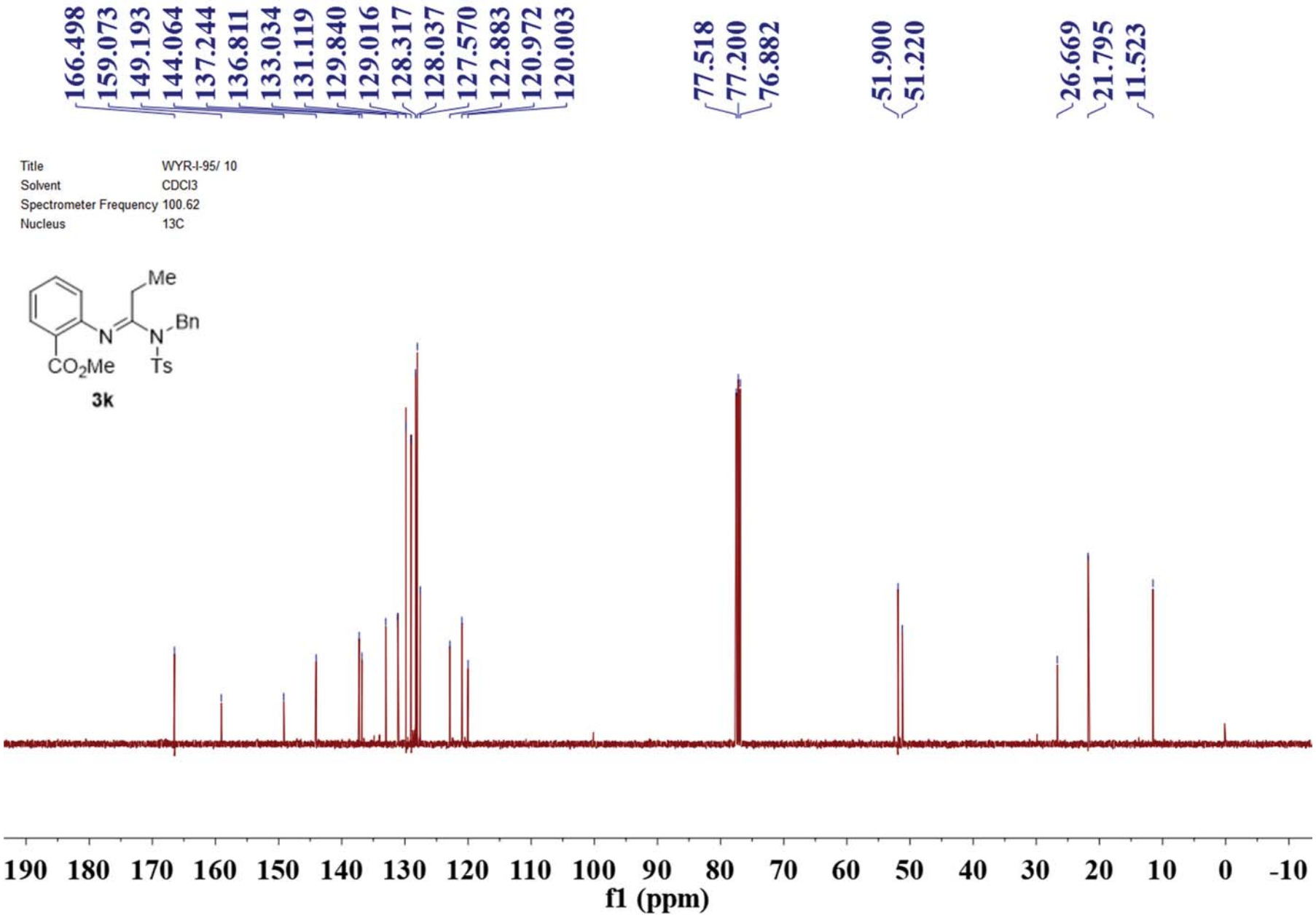
7.8711
7.8671
7.8512
7.8474
7.4316
7.4271
7.4149
7.4109
7.4074
7.3497
7.3477
7.3330
7.3311
7.3281
7.3265
7.3169
7.3148
7.3099
7.2969
7.2914
7.2873
7.2711
7.2676
7.2558
7.0234
7.0204
6.0661
6.0631
6.0460
4.8329
3.7034
2.5394
2.5206
2.4410
0.9074
0.8886
0.8697
0.0000
Title WYR-I-95.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Bn
N
CO2Me
Ts
3k
1.95
1.00
2.00
6.02
1.01
1.00
2.00
3.00
2.00
3.00
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 -0.5 -1.0
f1 (ppm)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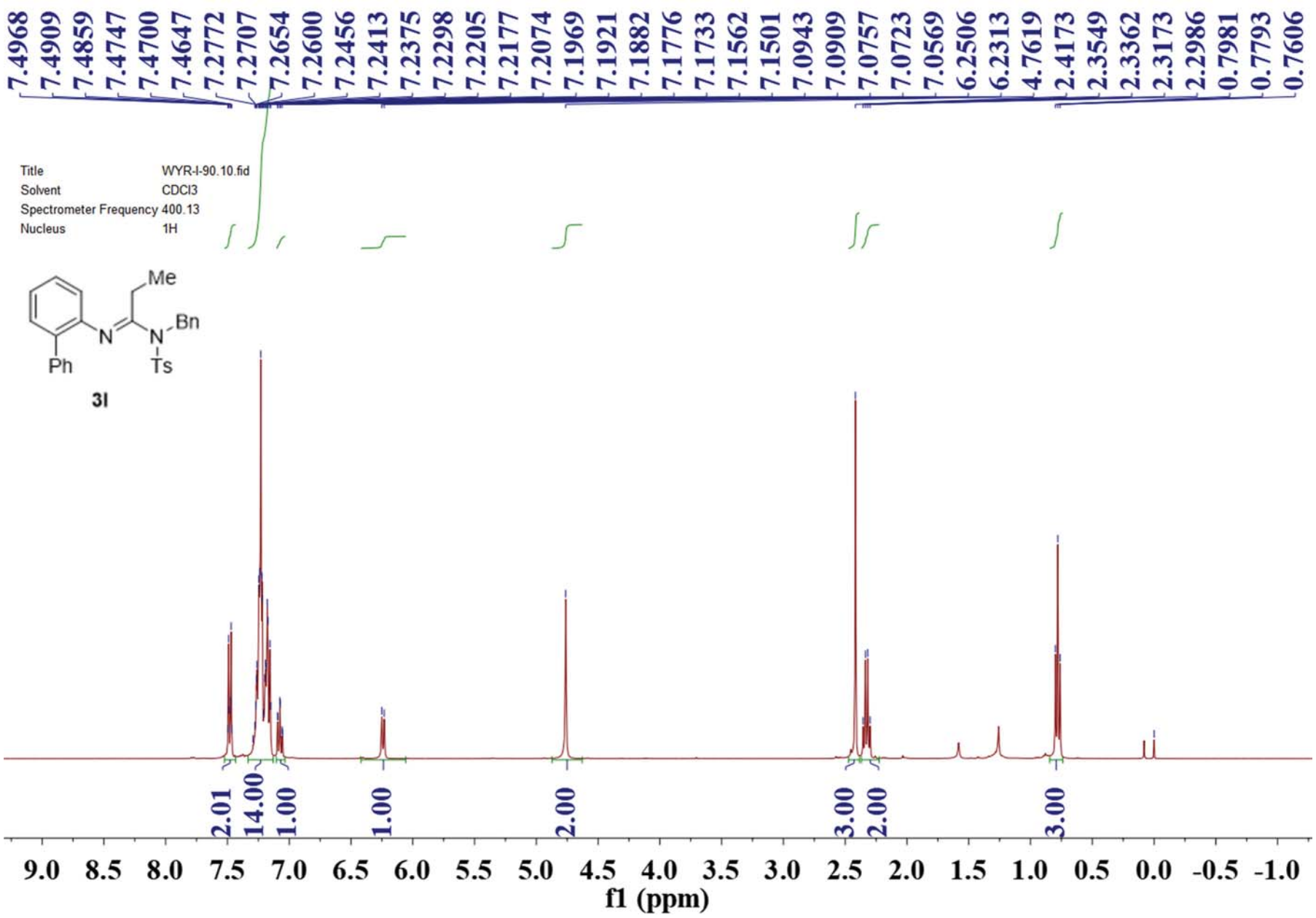
159.073
149.193
144.064
137.244
136.811
133.034
131.119
129.840
129.016
128.317
128.037
127.570
122.883
120.972
120.003
77.518
77.200
76.882
51.900
51.220
26.669
21.795
11.523
Title WYR-I-95/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
CO2Me
Ts
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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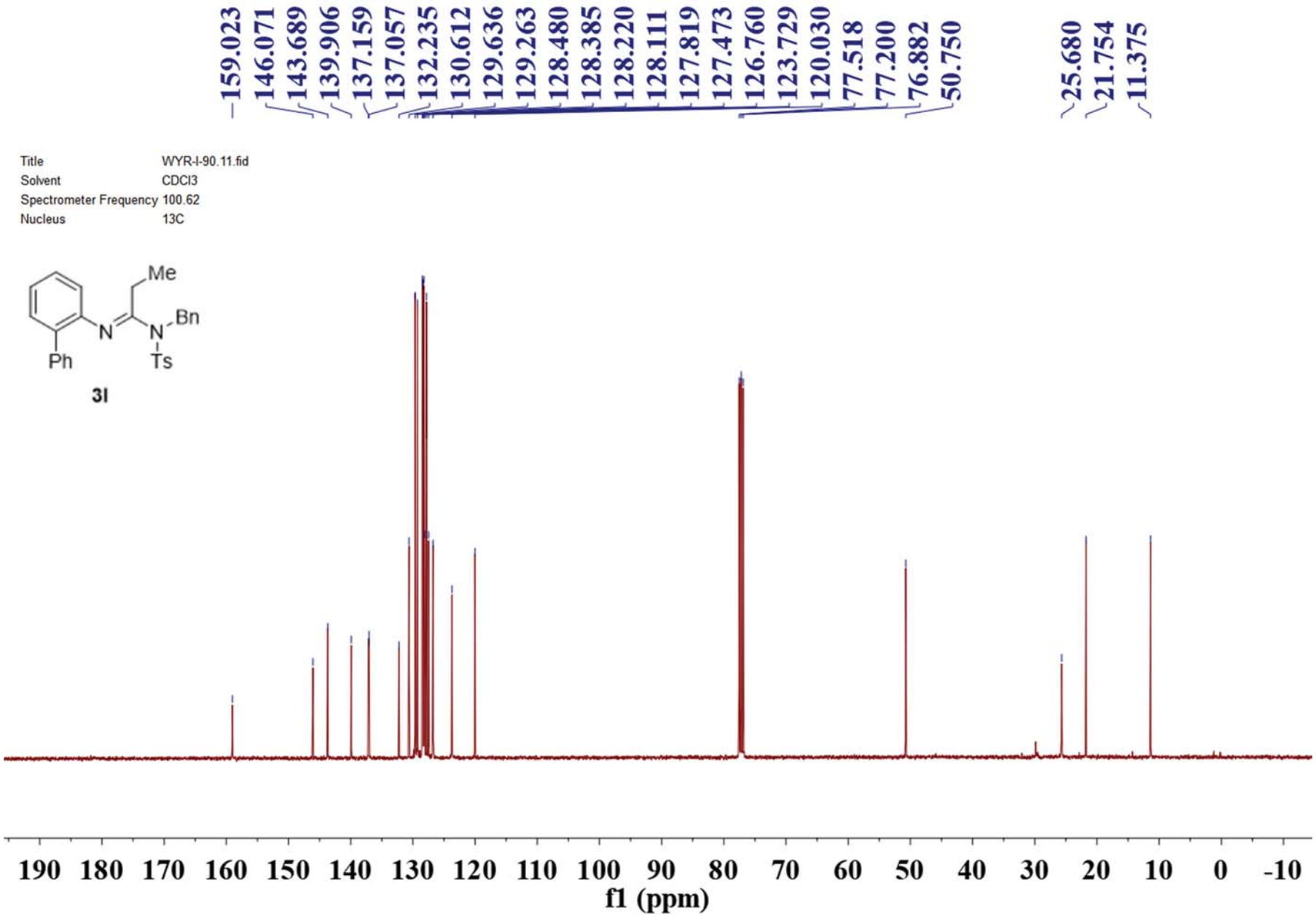
7.4747
7.4700
7.4647
7.2772
7.2707
7.2654
7.2600
7.2456
7.2413
7.2375
7.2298
7.2205
7.2177
7.2074
7.1969
7.1921
7.1882
7.1776
7.1733
7.1562
7.1501
7.0943
7.0909
7.0757
7.0723
7.0569
6.2506
6.2313
4.7619
2.4173
2.3549
2.3362
2.3173
2.2986
0.7981
0.7793
0.7606
Title WYR-I-90.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
N
Bn
Ts
Ph
3l
2.01
14.00
1.00
1.00
2.00
3.00
2.00
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 -0.5 -1.0
f1 (ppm)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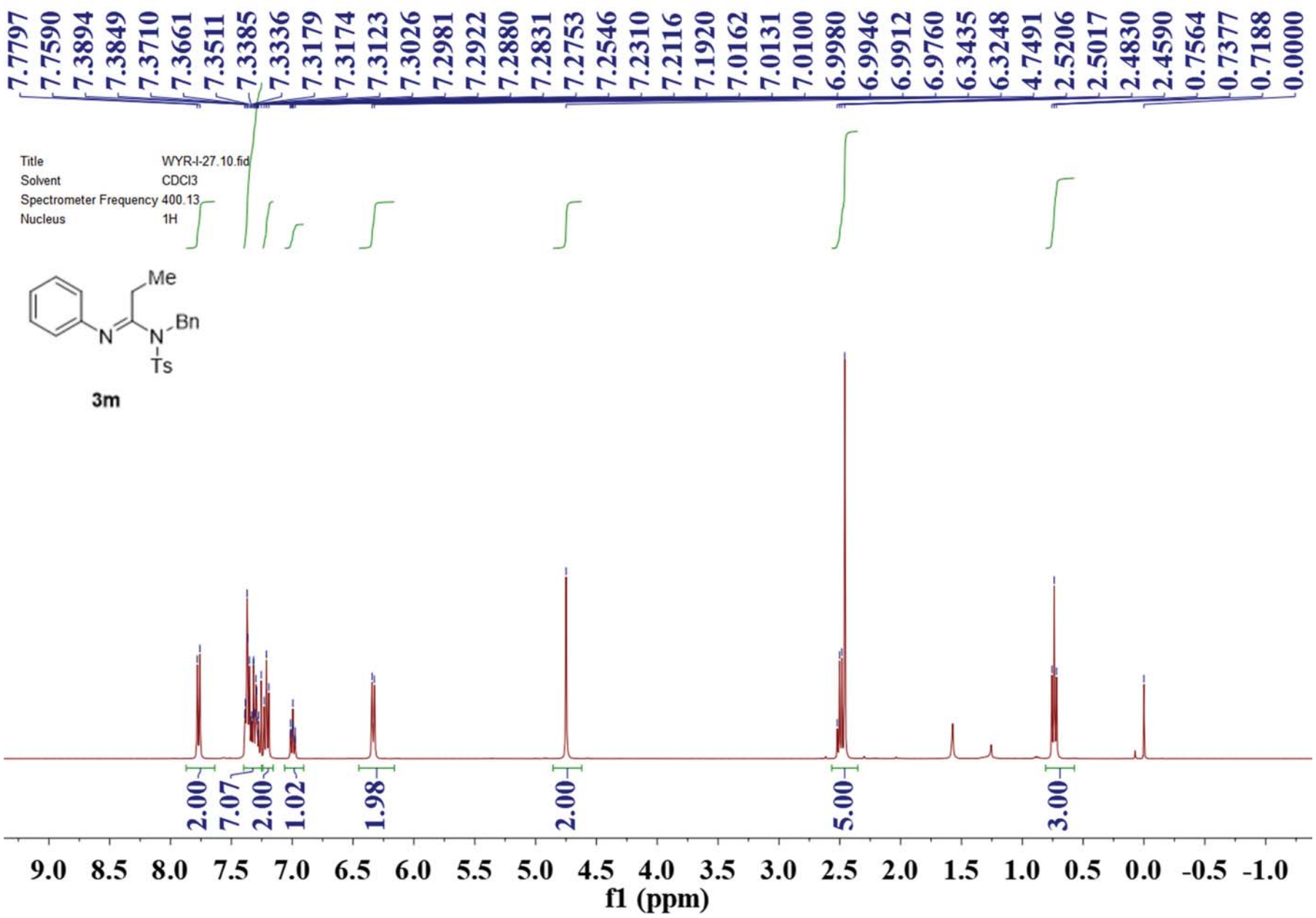
143.689
139.906
137.159
137.057
132.235
130.612
129.636
129.263
128.480
128.385
128.220
128.111
127.819
127.473
126.760
123.729
120.030
77.518
77.200
76.882
50.750
25.680
21.754
11.375
Title WYR-I-90.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Ph
Ts
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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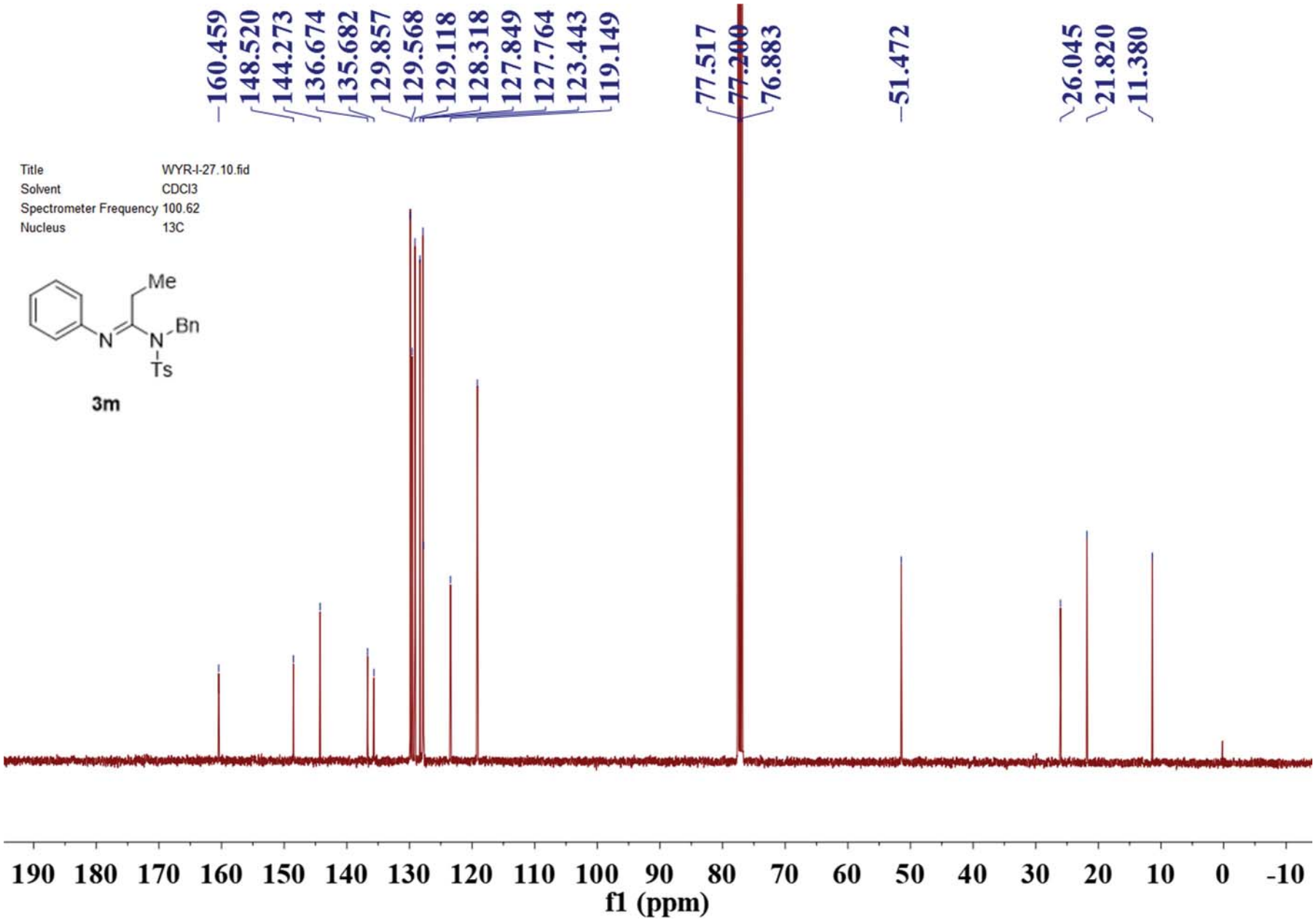
7.3894
7.3849
7.3710
7.3661
7.3511
7.3385
7.3336
7.3179
7.3174
7.3123
7.3026
7.2981
7.2922
7.2880
7.2831
7.2753
7.2546
7.2310
7.2116
7.1920
7.0162
7.0131
7.0100
6.9980
6.9946
6.9912
6.9760
6.3435
6.3248
4.7491
2.5206
2.5017
2.4830
2.4590
0.7564
0.7377
0.7188
0.0000
Title WYR-I-27.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
N
Bn
Ts
3m
2.00
7.07
2.00
1.02
1.98
2.00
5.00
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 -0.5 -1.0
f1 (ppm)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144.273
136.674
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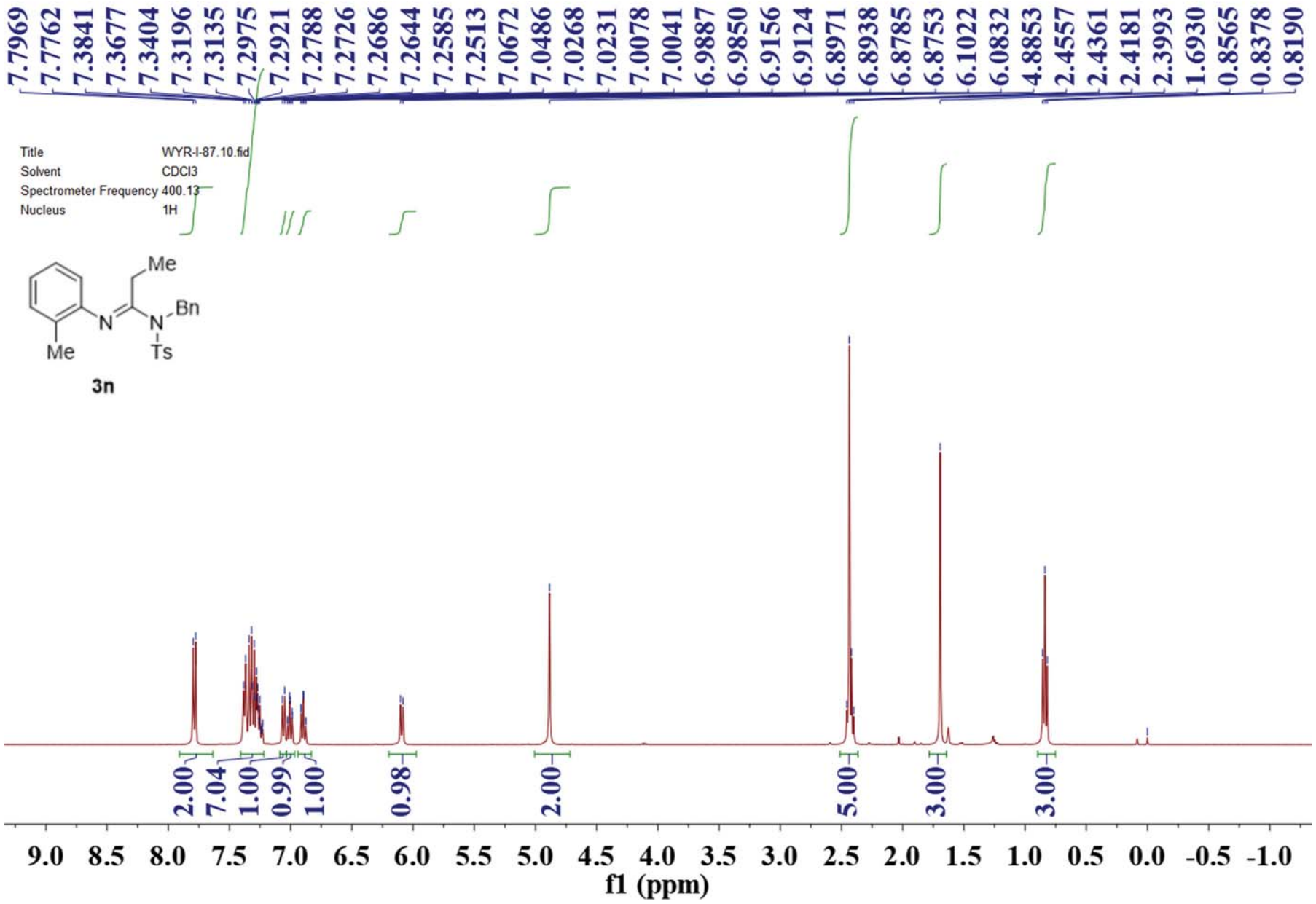
129.857
129.568
129.118
128.318
127.849
127.764
123.443
119.149
77.517
77.200
76.883
51.472
26.045
21.820
11.380
Title WYR-I-27.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Ts
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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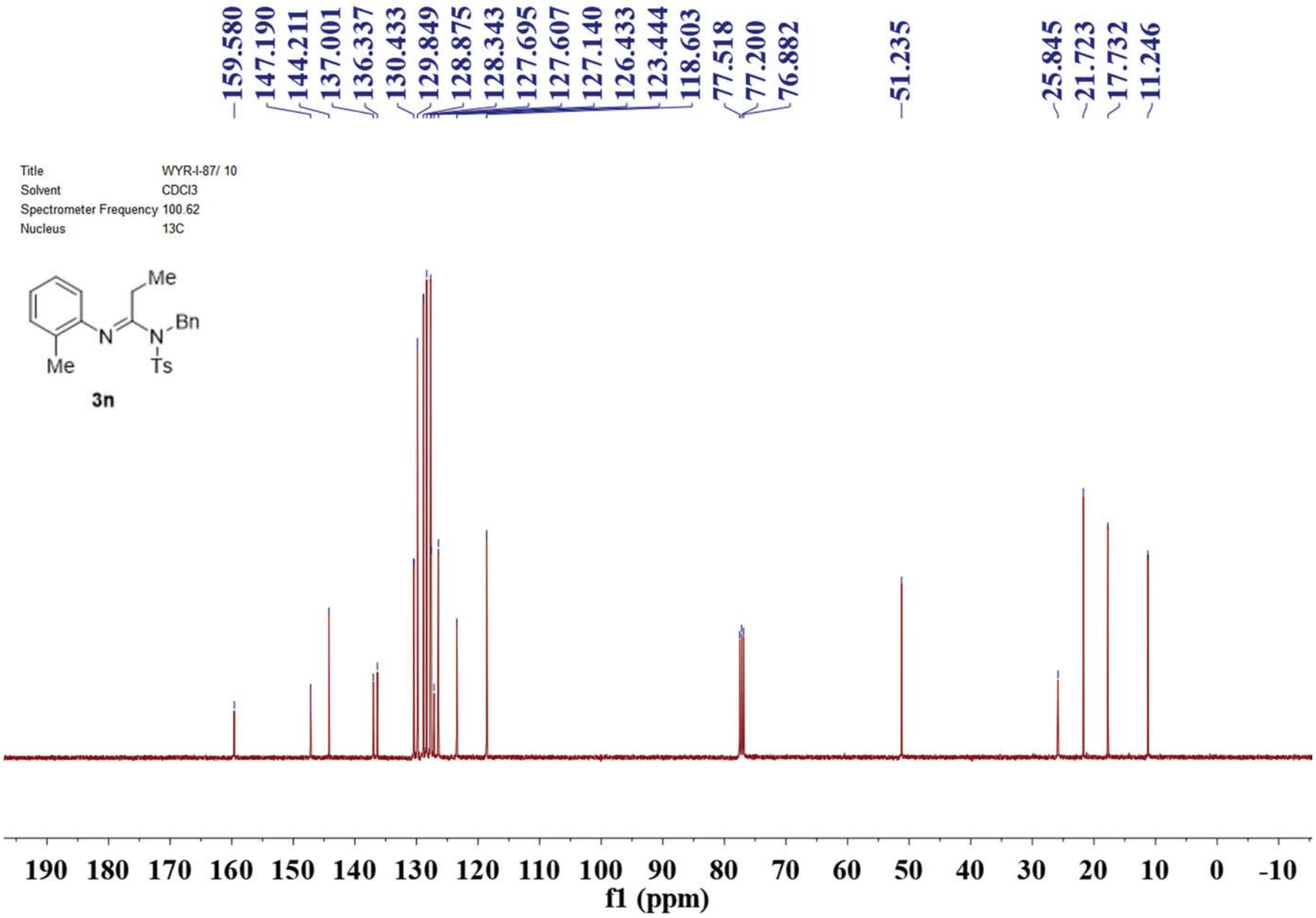
7.7762
7.3841
7.3677
7.3404
7.3196
7.3135
7.2975
7.2921
7.2788
7.2726
7.2686
7.2644
7.2585
7.2513
7.0672
7.0486
7.0268
7.0231
7.0078
7.0041
6.9887
6.9850
6.9156
6.9124
6.8971
6.8938
6.8785
6.8753
6.1022
6.0832
4.8853
2.4557
2.4361
2.4181
2.3993
1.6930
0.8565
0.8378
0.8190
Title WYR-I-87.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
N
Bn
Ts
Me
3n
2.00
7.04
1.00
0.99
1.00
0.98
2.00
5.00
3.00
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 -0.5 -1.0
f1 (ppm)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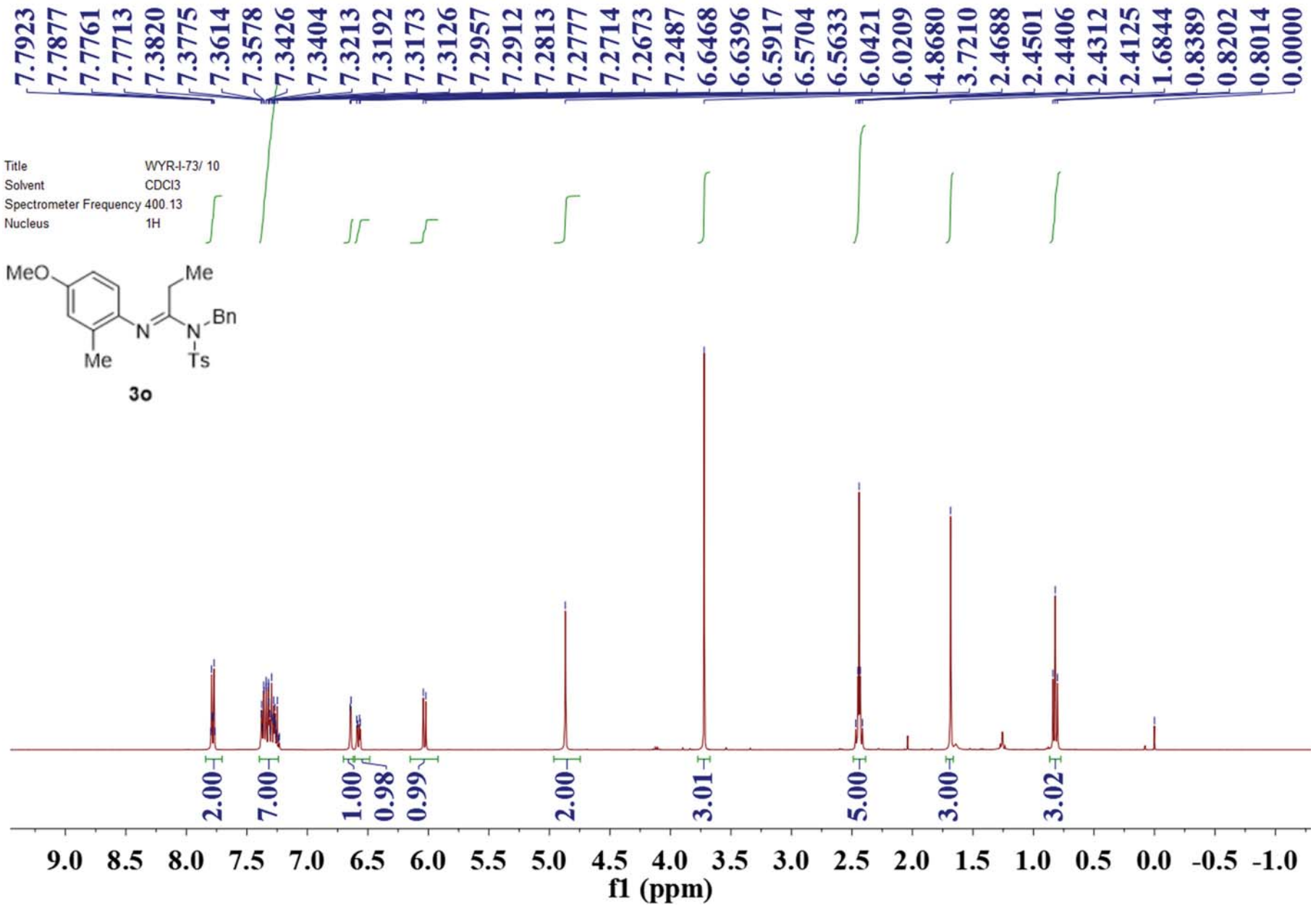
147.190
144.211
137.001
136.337
130.433
129.849
128.875
128.343
127.695
127.607
127.140
126.433
123.444
118.603
77.518
77.200
76.882
51.235
25.845
21.723
17.732
11.246
Title WYR-I-87/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
N
Bn
Ts
Me
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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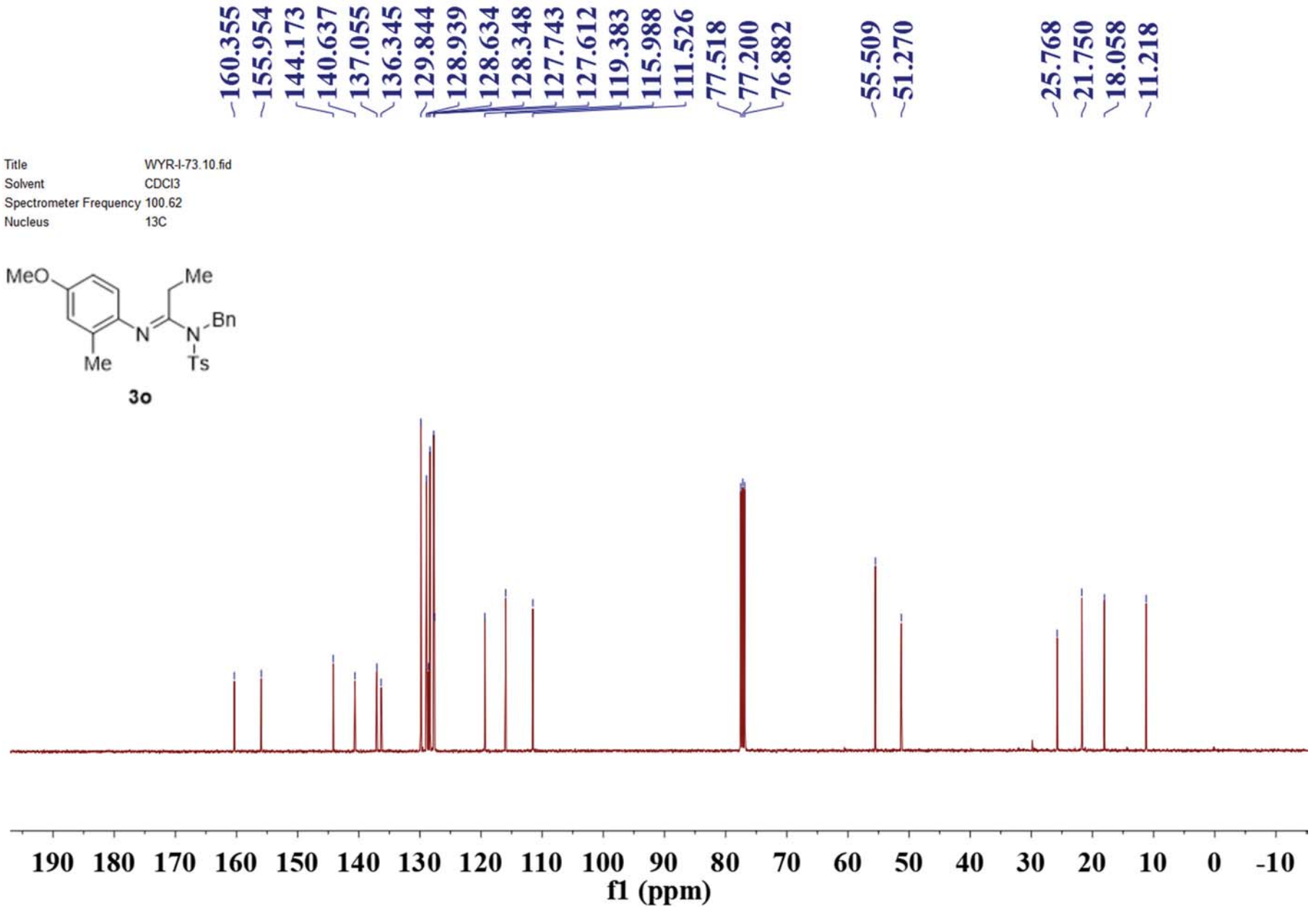
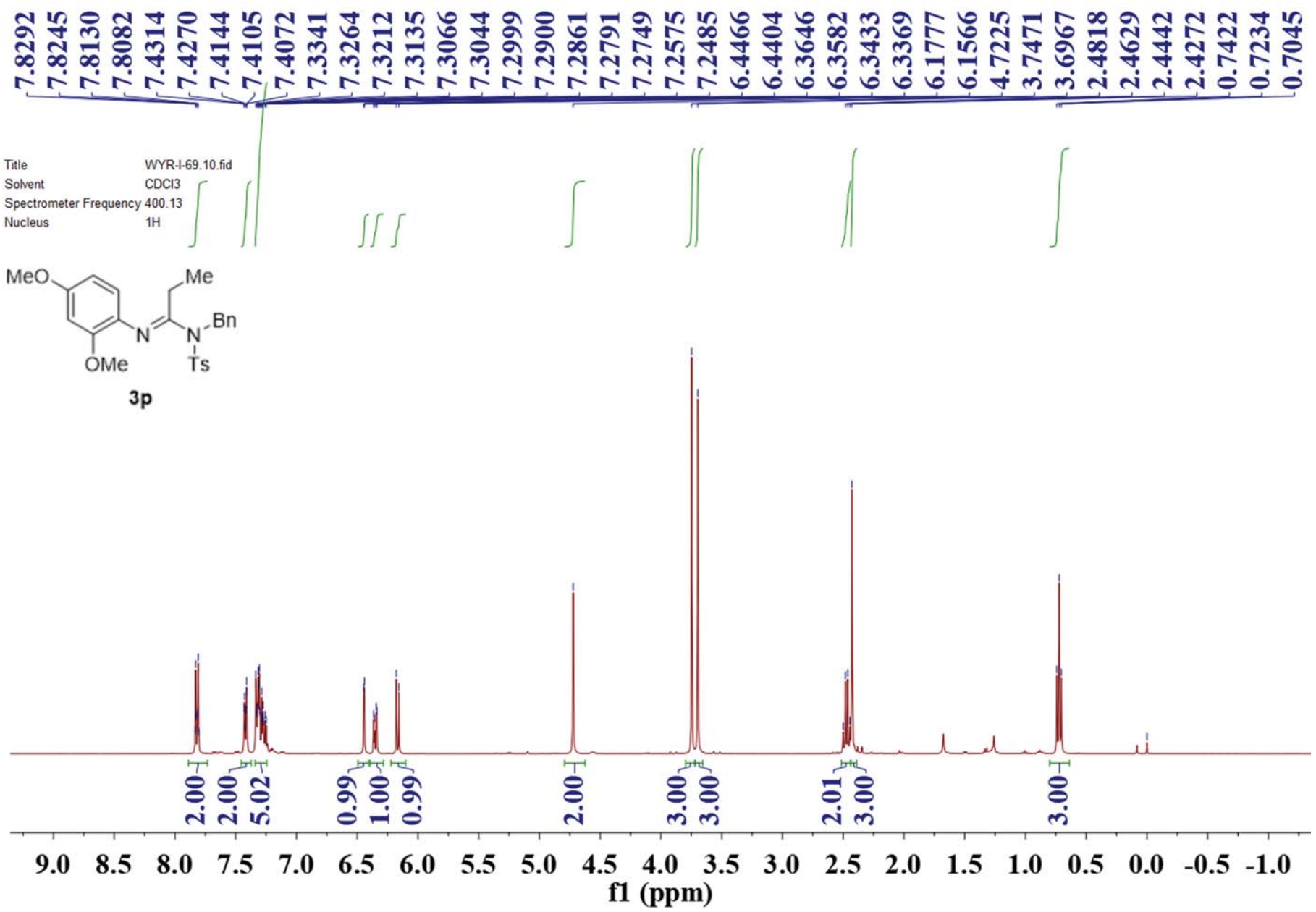
7.7877
7.7761
7.7713
7.3820
7.3775
7.3614
7.3578
7.3426
7.3404
7.3213
7.3192
7.3173
7.3126
7.2957
7.2912
7.2813
7.2777
7.2714
7.2673
7.2487
6.6468
6.6396
6.5917
6.5704
6.5633
6.0421
6.0209
4.8680
3.7210
2.4688
2.4501
2.4406
2.4312
2.4125
1.6844
0.8389
0.8202
0.8014
0.0000
Title WYR-I-73/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Me
N
N
Bn
Ts
Me
3o
2.00
7.00
1.00
0.98
0.99
2.00
3.01
5.00
3.00
3.02
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 -0.5 -1.0
f1 (ppm)


160.355
155.954
144.173
140.637
137.055
136.345
129.844
128.939
128.634
128.348
127.743
127.612
119.383
115.988
111.526
77.518
77.200
76.882
55.509
51.270
25.768
21.750
18.058
11.218
Title WYR-I-73.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Me
N
N
Bn
Me
Ts
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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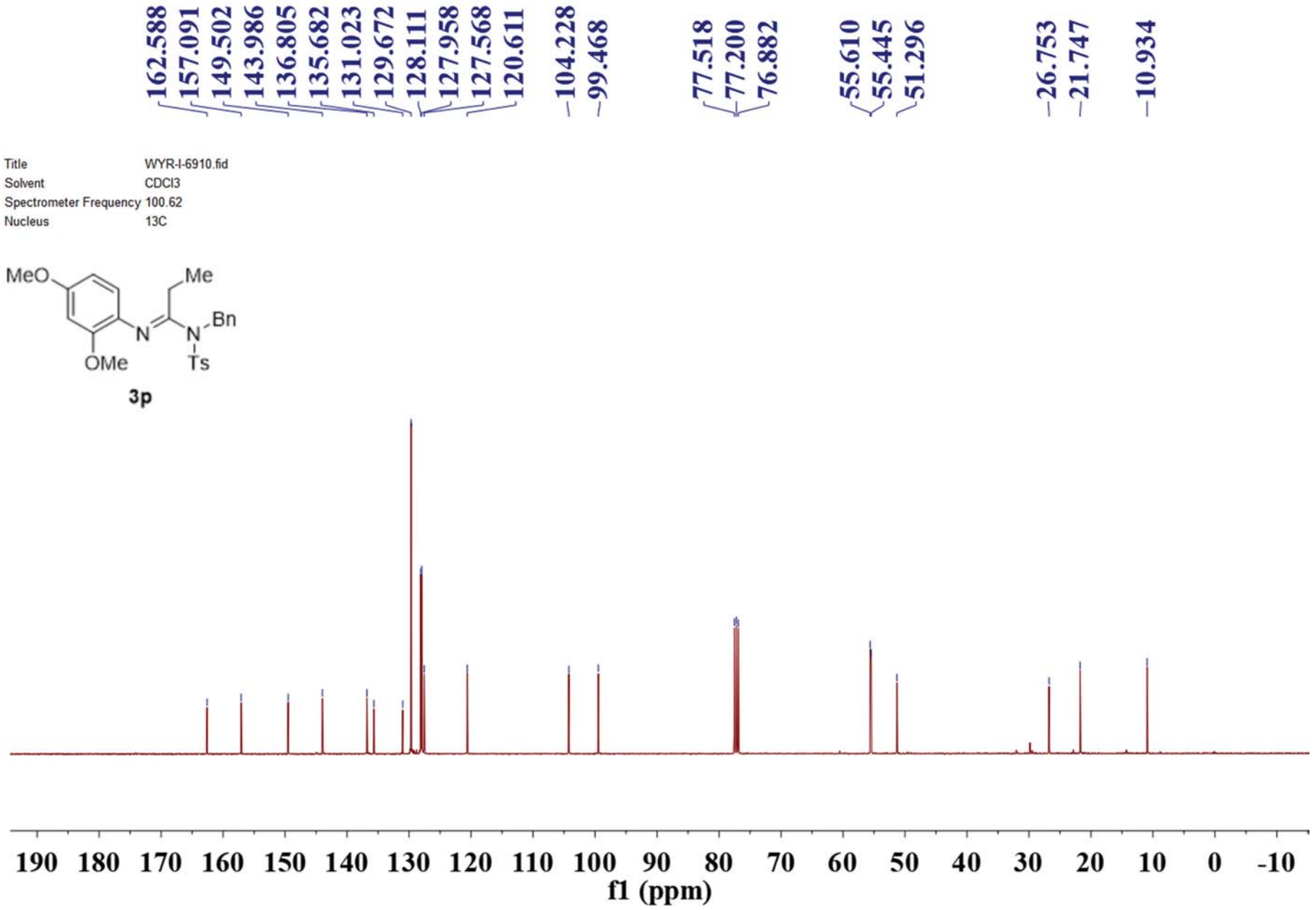
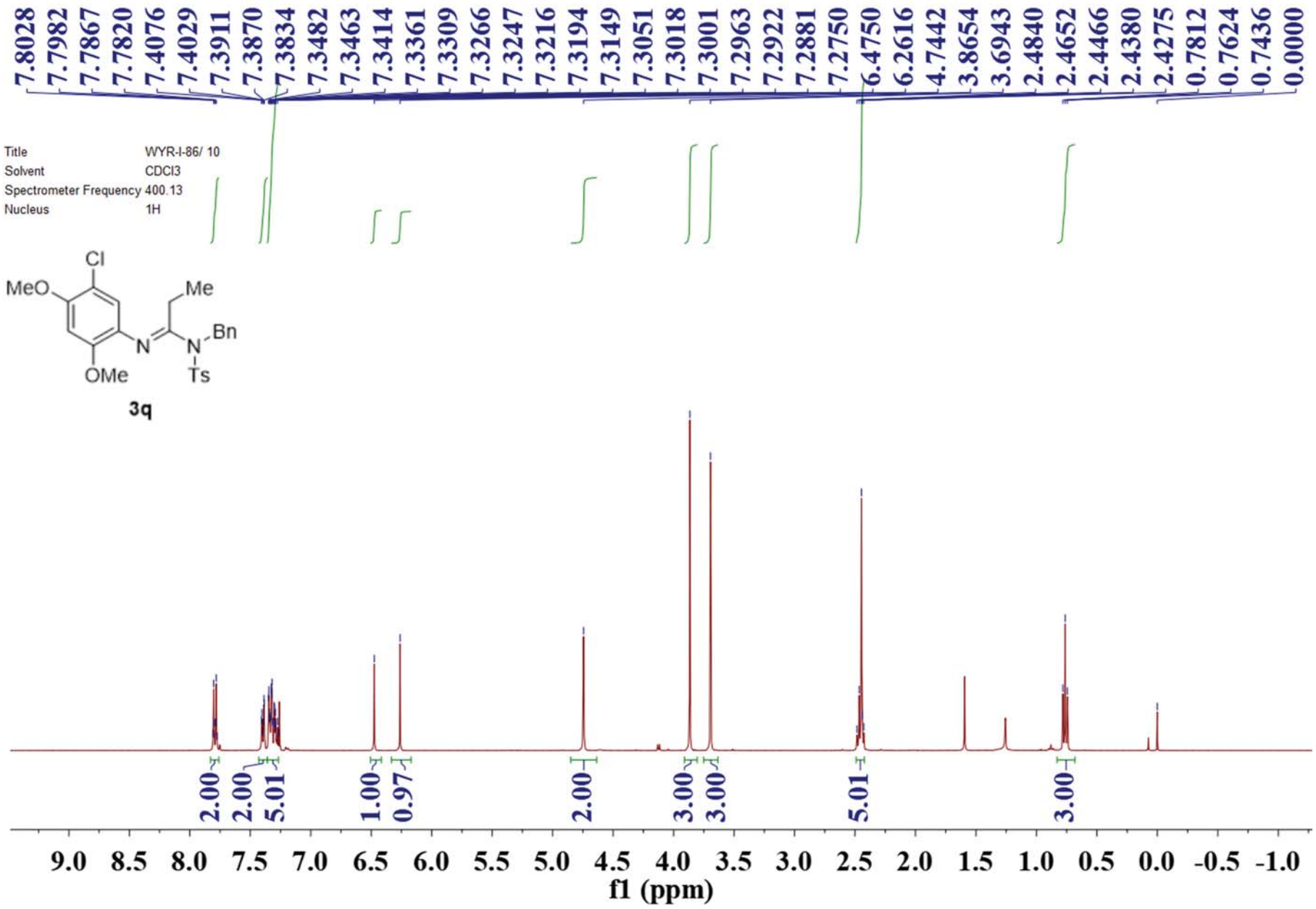
7.8130
7.8082
7.4314
7.4270
7.4144
7.4105
7.4072
7.3341
7.3264
7.3212
7.3135
7.3066
7.3044
7.2999
7.2900
7.2861
7.2791
7.2749
7.2575
7.2485
6.4466
6.4404
6.3646
6.3582
6.3433
6.3369
6.1777
6.1566
4.7225
3.7471
3.6967
2.4818
2.4629
2.4442
2.4272
0.7422
0.7234
0.7045
Title WYR-I-69.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Me
Bn
N
N
OMe
Ts
3p
2.00
2.00
5.02
0.99
1.00
0.99
2.00
3.00
3.00
2.01
3.00
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 -0.5 -1.0
f1 (ppm)


162.588
157.091
149.502
143.986
136.805
135.682
131.023
129.672
128.111
127.958
127.568
120.611
104.228
99.468
77.518
77.200
76.882
55.610
55.445
51.296
26.753
21.747
10.934
Title WYR-I-6910.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Me
Bn
N
N
OMe
Ts
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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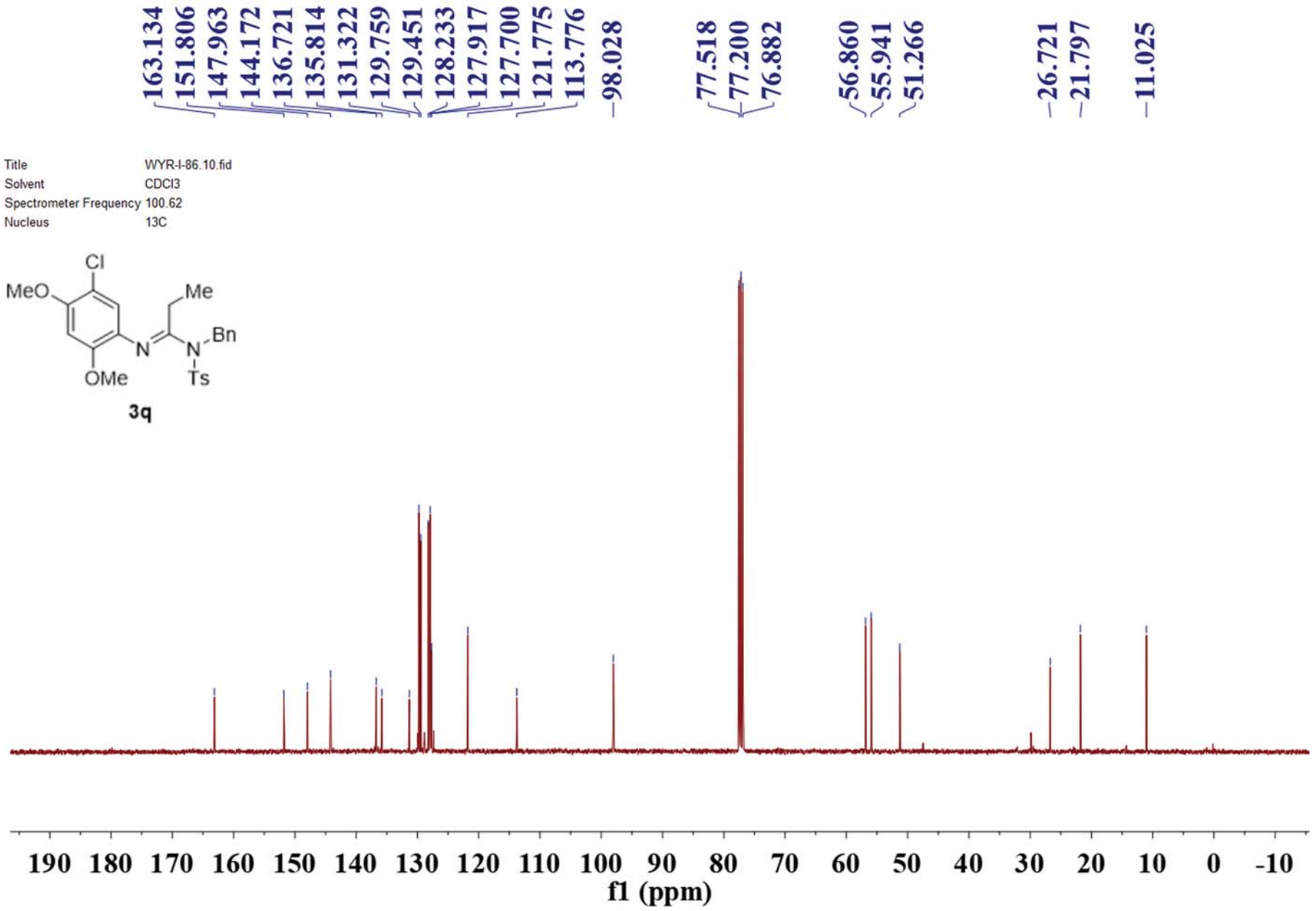
7.7820
7.4076
7.4029
7.3911
7.3870
7.3834
7.3482
7.3463
7.3414
7.3361
7.3309
7.3266
7.3247
7.3216
7.3194
7.3149
7.3051
7.3018
7.3001
7.2963
7.2922
7.2881
7.2750
6.4750
6.2616
4.7442
3.8654
3.6943
2.4840
2.4652
2.4466
2.4380
2.4275
0.7812
0.7624
0.7436
0.0000
Title WYR-I-86/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
MeO
Me
N
N
Bn
OMe
Ts
3q
2.00
2.00
5.01
1.00
0.97
2.00
3.00
3.00
5.01
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 -0.5 -1.0
f1 (ppm)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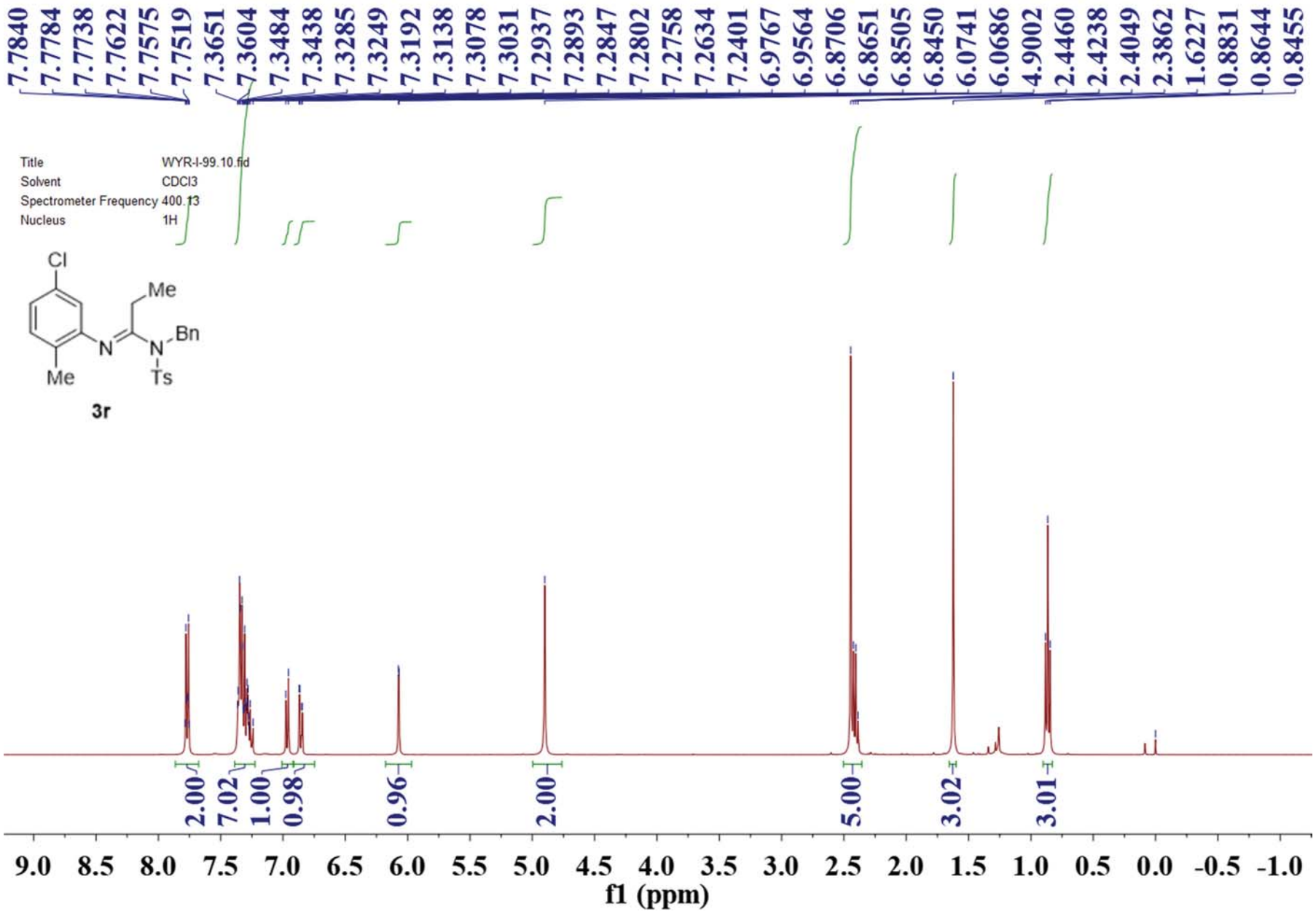
147.963
144.172
136.721
135.814
131.322
129.759
129.451
128.233
127.917
127.700
121.775
113.776
98.028
77.518
77.200
76.882
56.860
55.941
51.266
26.721
21.797
11.025
Title WYR-I-86.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
MeO
Me
N
N
Bn
OMe
Ts
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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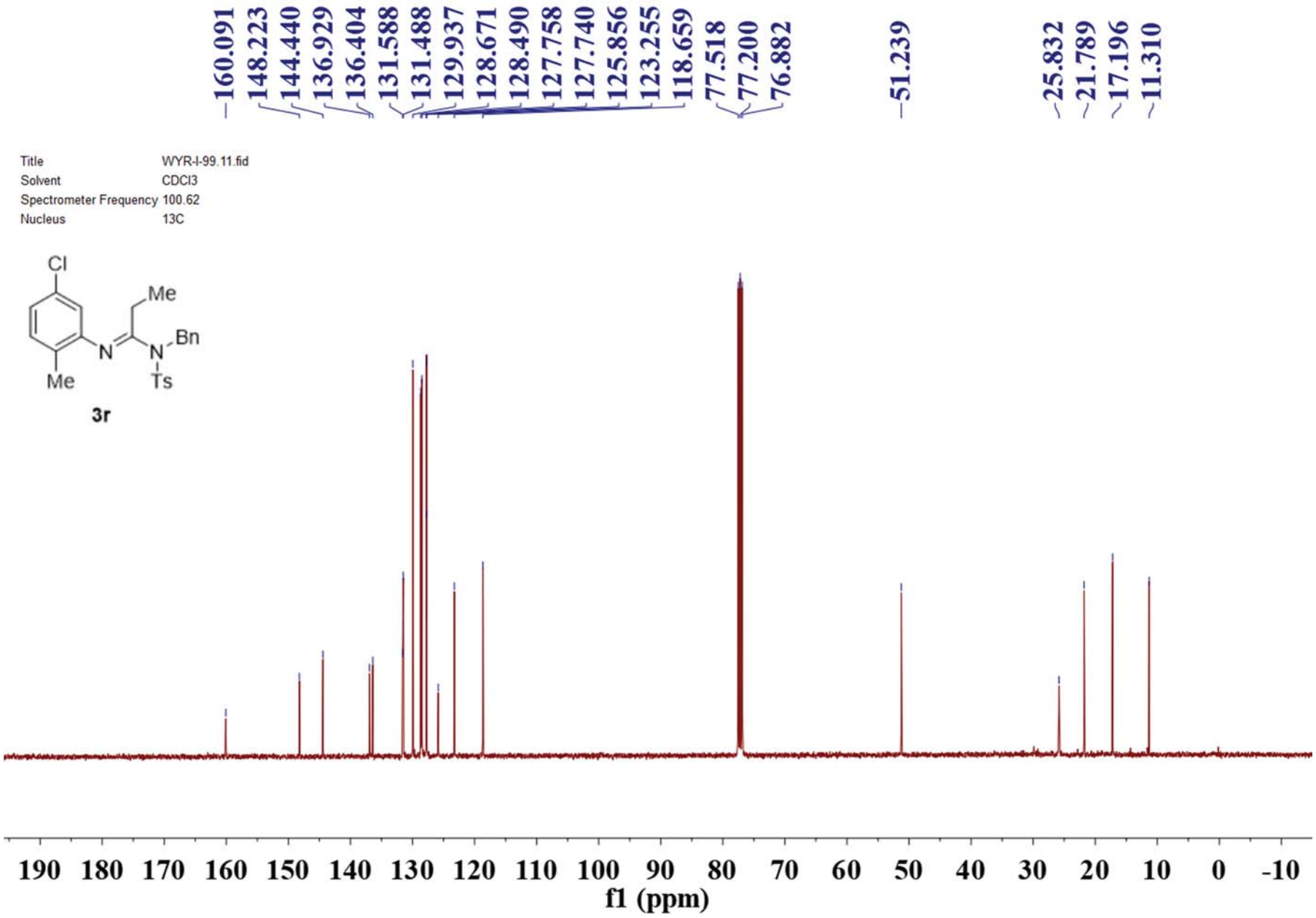
7.7575
7.7519
7.3651
7.3604
7.3484
7.3438
7.3285
7.3249
7.3192
7.3138
7.3078
7.3031
7.2937
7.2893
7.2847
7.2802
7.2758
7.2634
7.2401
6.9767
6.9564
6.8706
6.8651
6.8505
6.8450
6.0741
6.0686
4.9002
2.4460
2.4238
2.4049
2.3862
1.6227
0.8831
0.8644
0.8455
Title WYR-I-99.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Me
Bn
N
N
Me
Ts
3r
2.00
7.02
1.00
0.98
0.96
2.00
5.00
3.02
3.01
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 -0.5 -1.0
f1 (ppm)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144.440
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128.490
127.758
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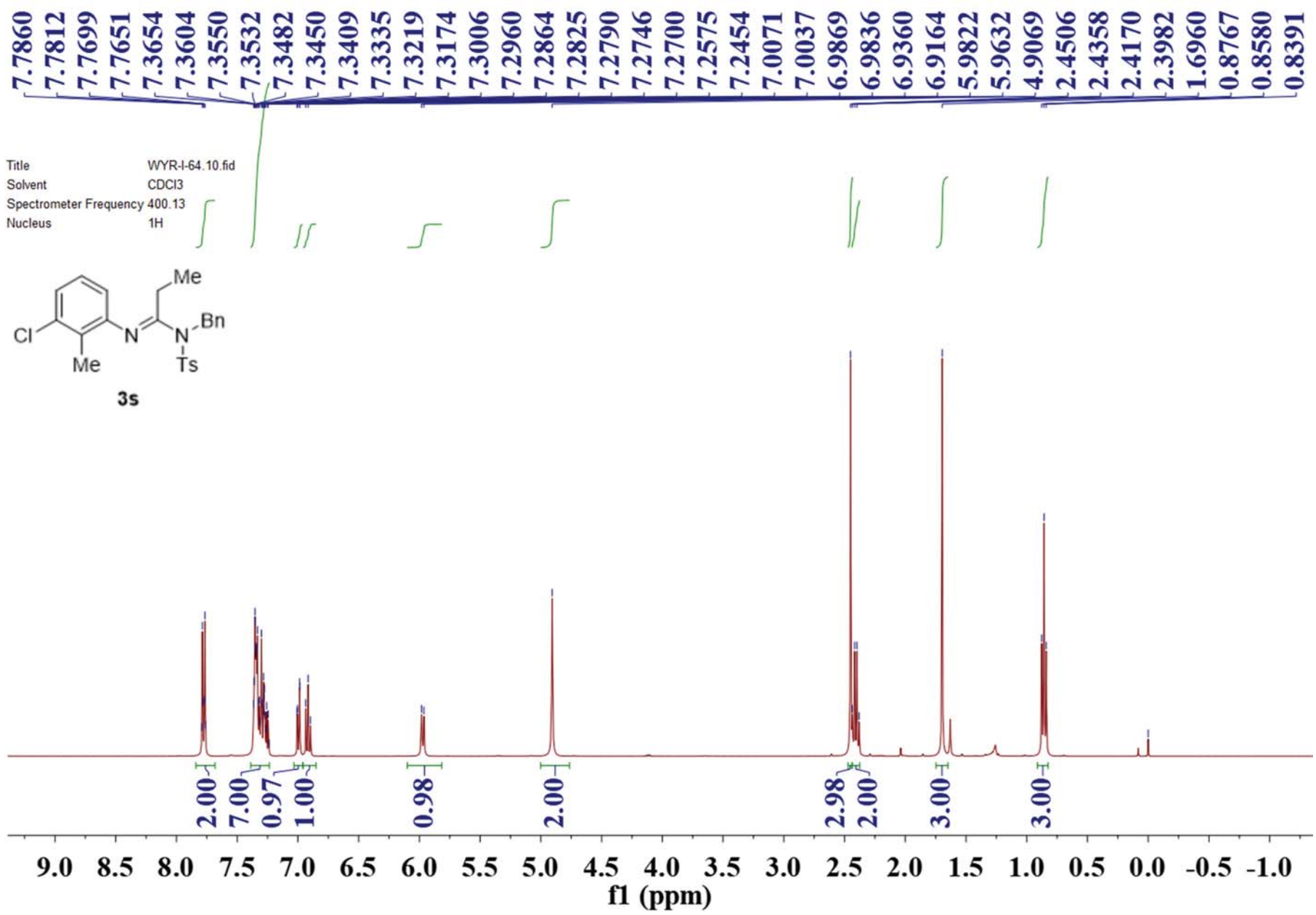
123.255
118.659
77.518
77.200
76.882
51.239
25.832
21.789
17.196
11.310
Title WYR-I-99.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Me
Bn
N
N
Me
Ts
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7699
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7.3654
7.3604
7.3550
7.3532
7.3482
7.3450
7.3409
7.3335
7.3219
7.3174
7.3006
7.2960
7.2864
7.2825
7.2790
7.2746
7.2700
7.2575
7.2454
7.0071
7.0037
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6.9836
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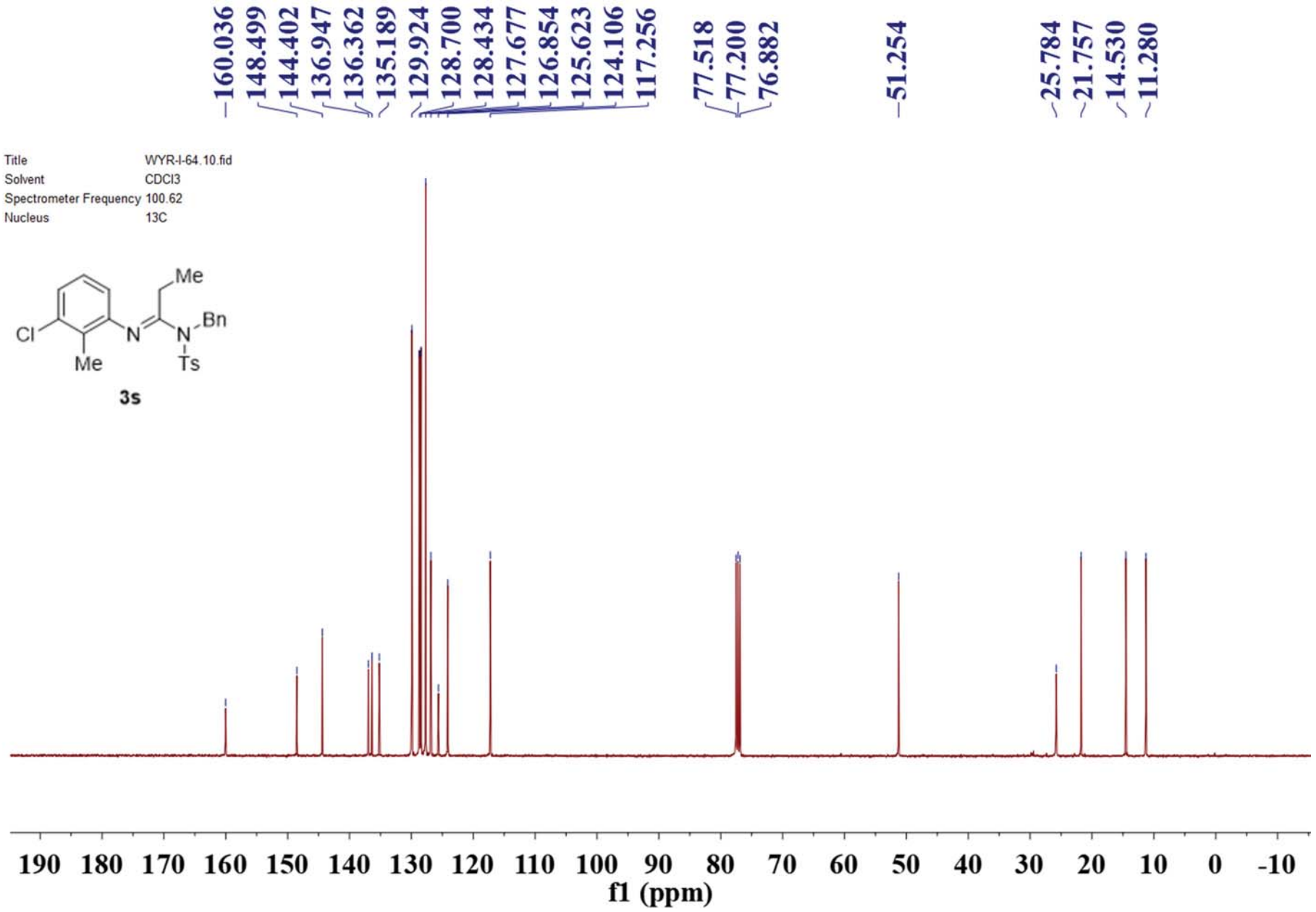
6.9164
5.9822
5.9632
4.9069
2.4506
2.4358
2.4170
2.3982
1.6960
0.8767
0.8580
0.8391
Title WYR-I-64.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Cl
N
N
Bn
Me
Ts
3s
2.00
7.00
0.97
1.00
0.98
2.00
2.98
2.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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135.189
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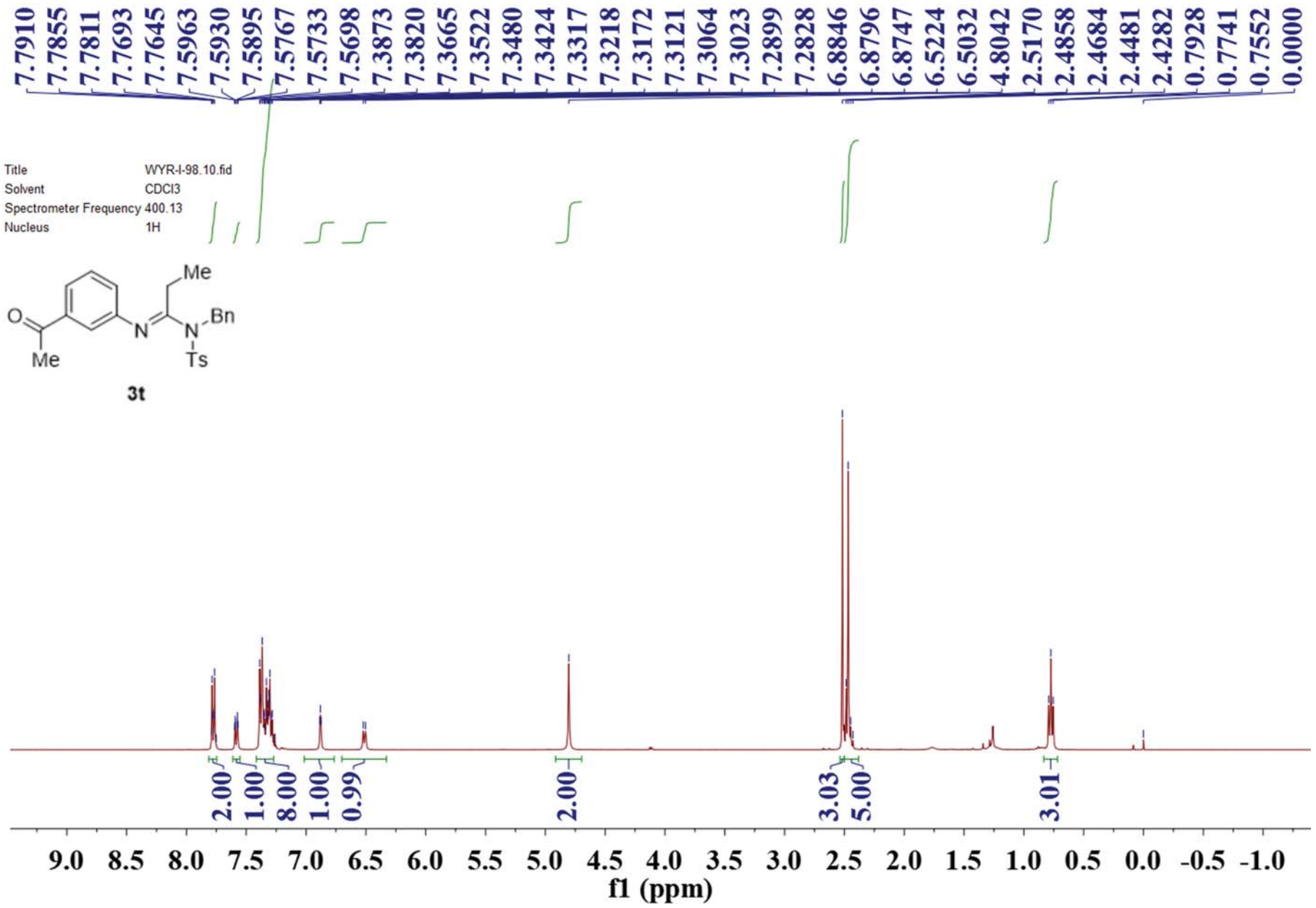
128.700
128.434
127.677
126.854
125.623
124.106
117.256
77.518
77.200
76.882
51.254
25.784
21.757
14.530
11.280
Title WYR-I-64.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Cl
N
N
Bn
Me
Ts
3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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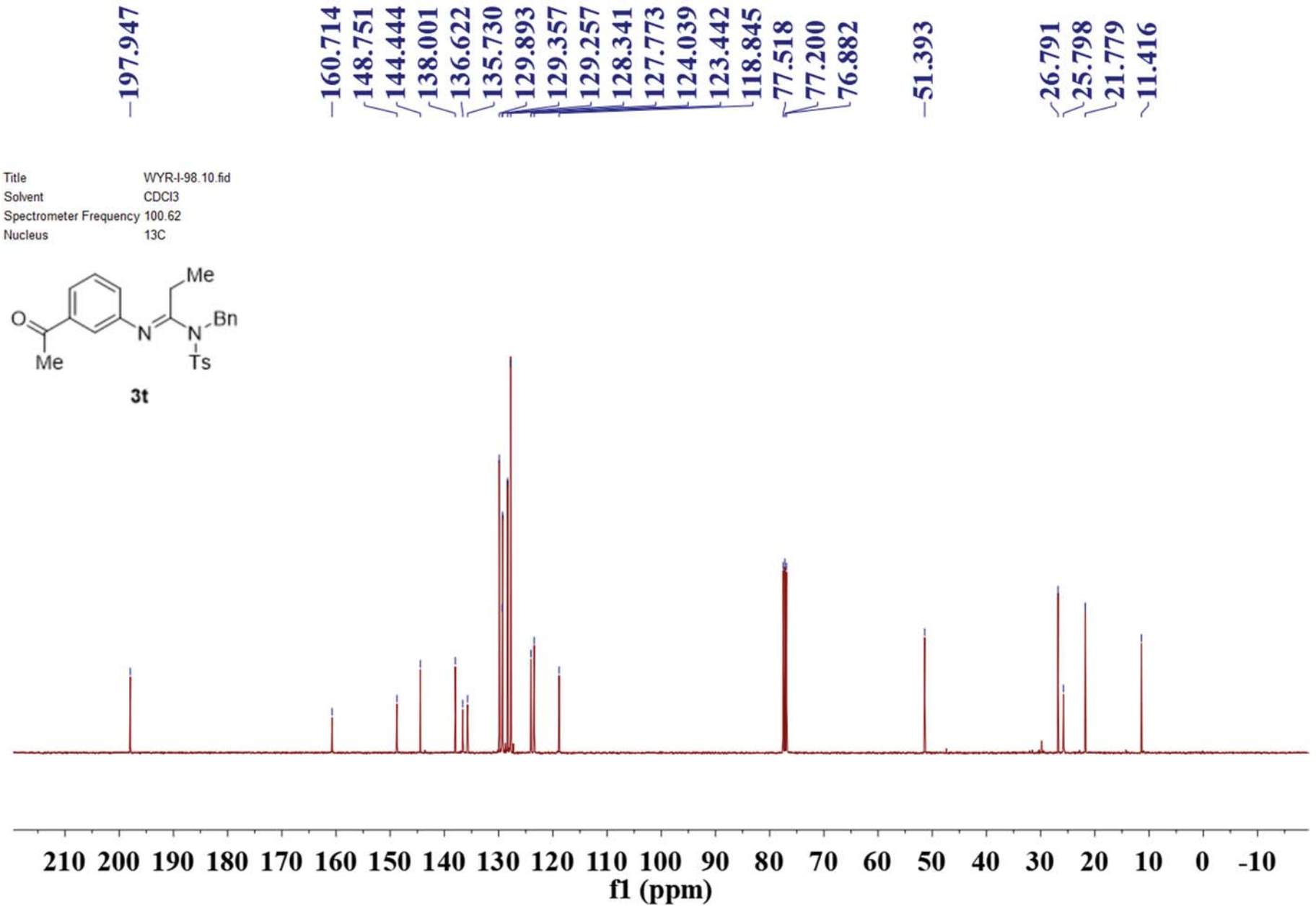
7.5767
7.5733
7.5698
7.3873
7.3820
7.3665
7.3522
7.3480
7.3424
7.3317
7.3218
7.3172
7.3121
7.3064
7.3023
7.2899
7.2828
6.8846
6.8796
6.8747
6.5224
6.5032
4.8042
2.5170
2.4858
2.4684
2.4481
2.4282
0.7928
0.7741
0.7552
0.0000
Title WYR-I-98.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
O
N
N
Bn
Ts
Me
3t
2.00
1.00
8.00
1.00
0.99
2.00
3.03
5.00
3.01
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 -0.5 -1.0
f1 (ppm)


197.947
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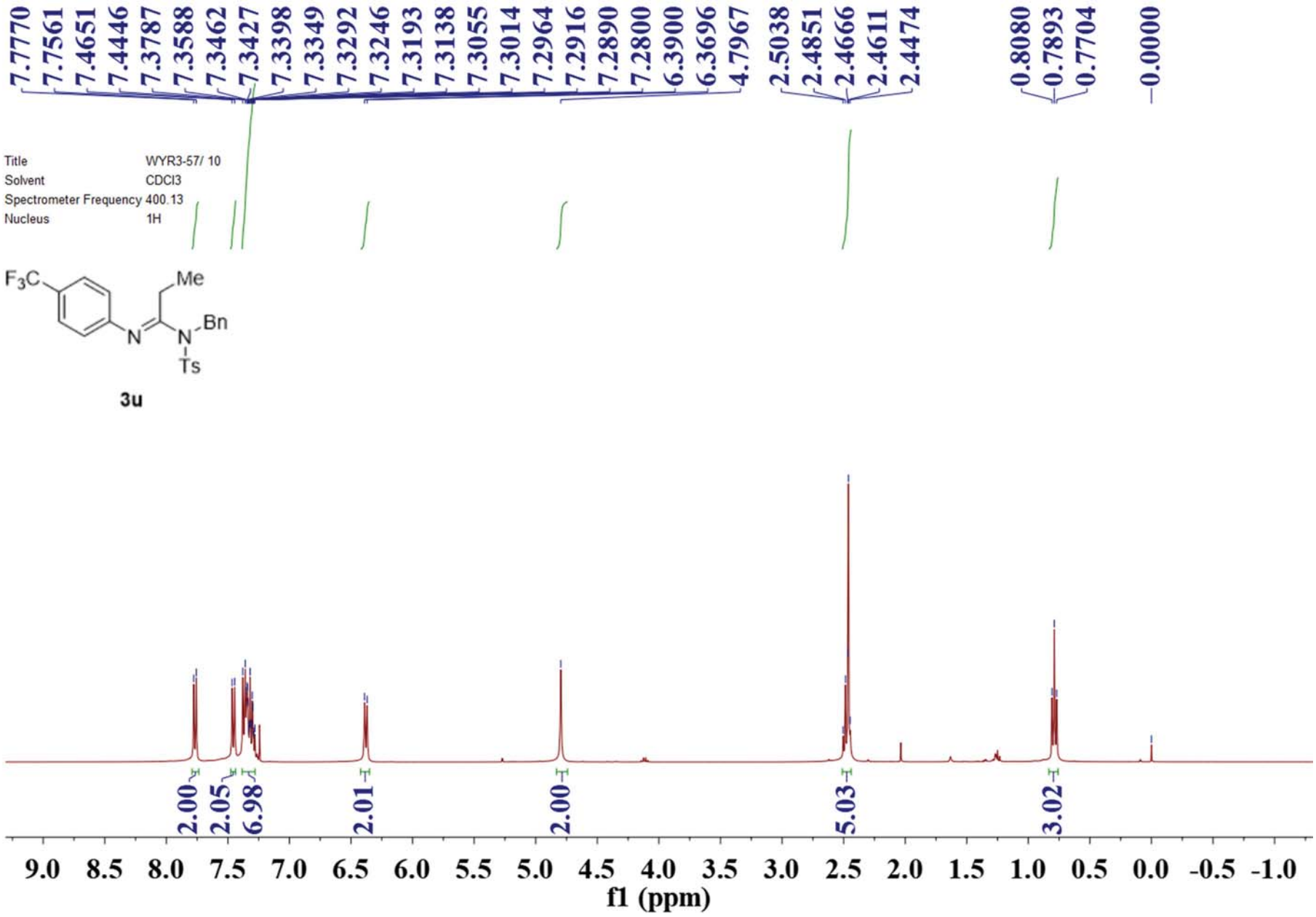
148.751
144.444
138.001
136.622
135.730
129.893
129.357
129.257
128.341
127.773
124.039
123.442
118.845
77.518
77.200
76.882
51.393
26.791
25.798
21.779
11.416
Title WYR-I-98.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
O
N
N
Bn
Me
Ts
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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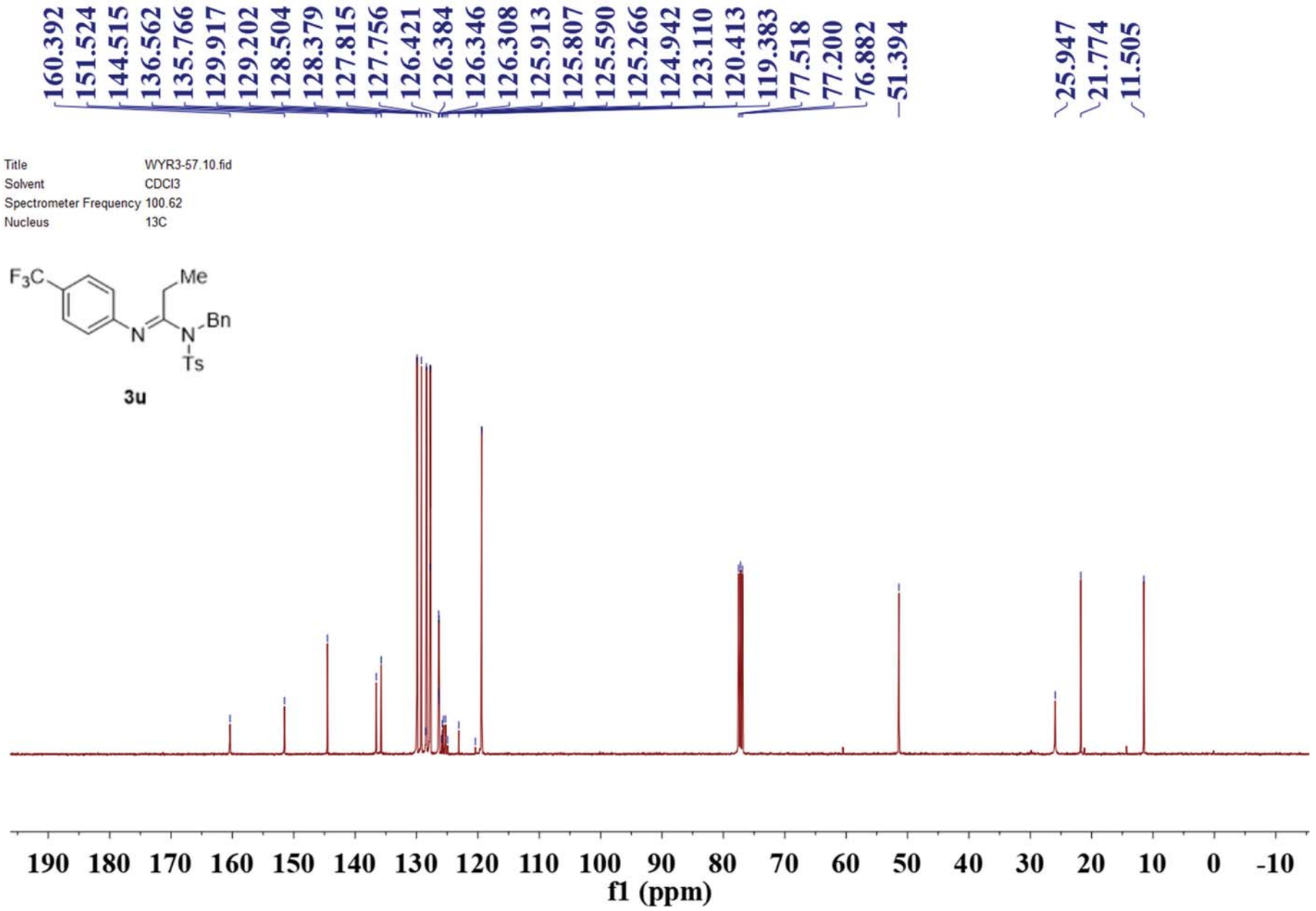
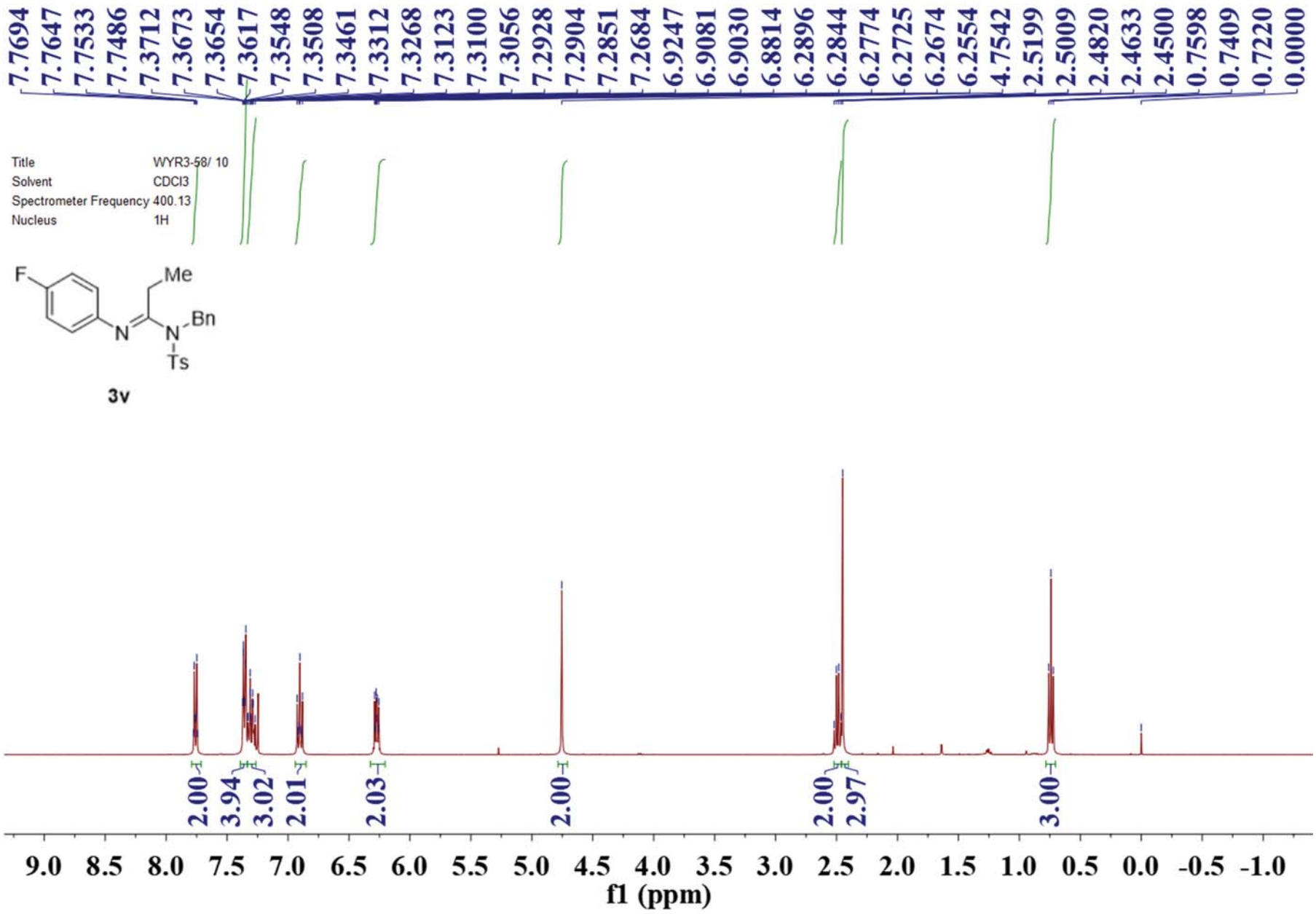
7.7561
7.4651
7.4446
7.3787
7.3588
7.3462
7.3427
7.3398
7.3349
7.3292
7.3246
7.3193
7.3138
7.3055
7.3014
7.2964
7.2916
7.2890
7.2800
6.3900
6.3696
4.7967
2.5038
2.4851
2.4666
2.4611
2.4474
0.8080
0.7893
0.7704
0.0000
Title WYR3-57/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F3C
Me
Bn
N
N
Ts
3u
2.00
2.05
6.98
2.01
2.00
5.03
3.02
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 -0.5 -1.0
f1 (ppm)


160.392
151.524
144.515
136.562
135.766
129.917
129.202
128.504
128.379
127.815
127.756
126.421
126.384
126.346
126.308
125.913
125.807
125.590
125.266
124.942
123.110
120.413
119.383
77.518
77.200
76.882
51.394
25.947
21.774
11.505
Title WYR3-57.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F3C
Me
Bn
N
N
Ts
3u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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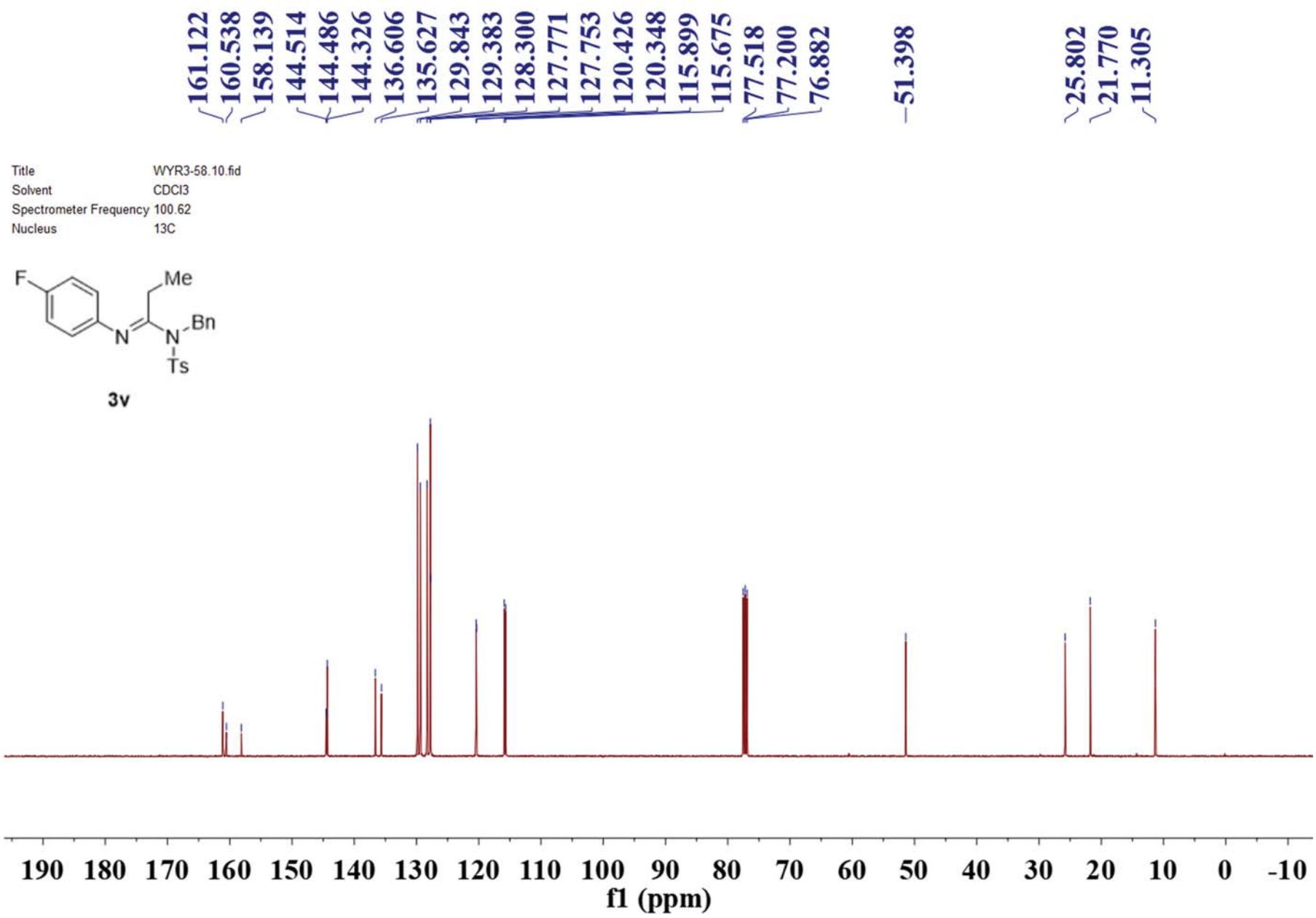
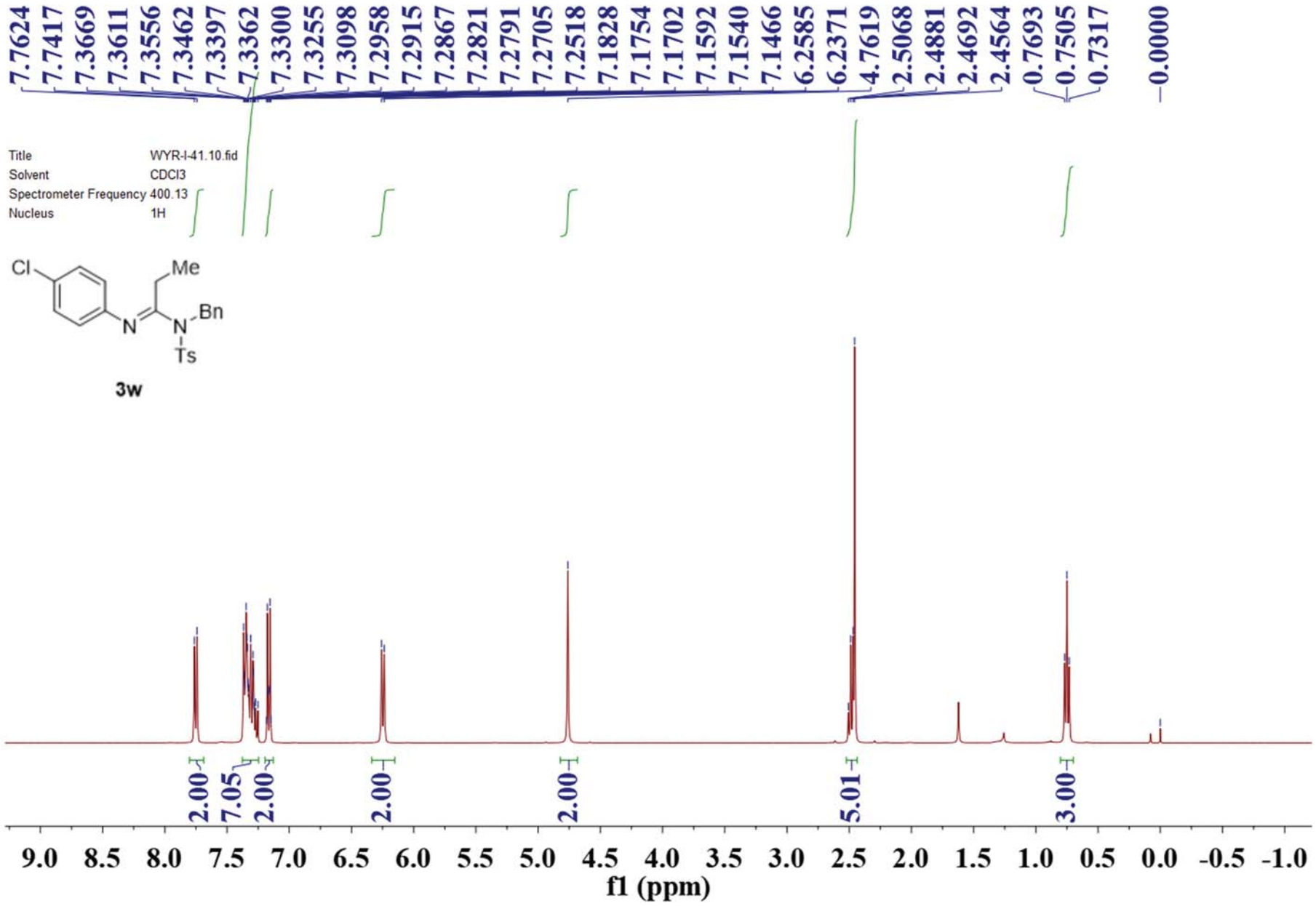
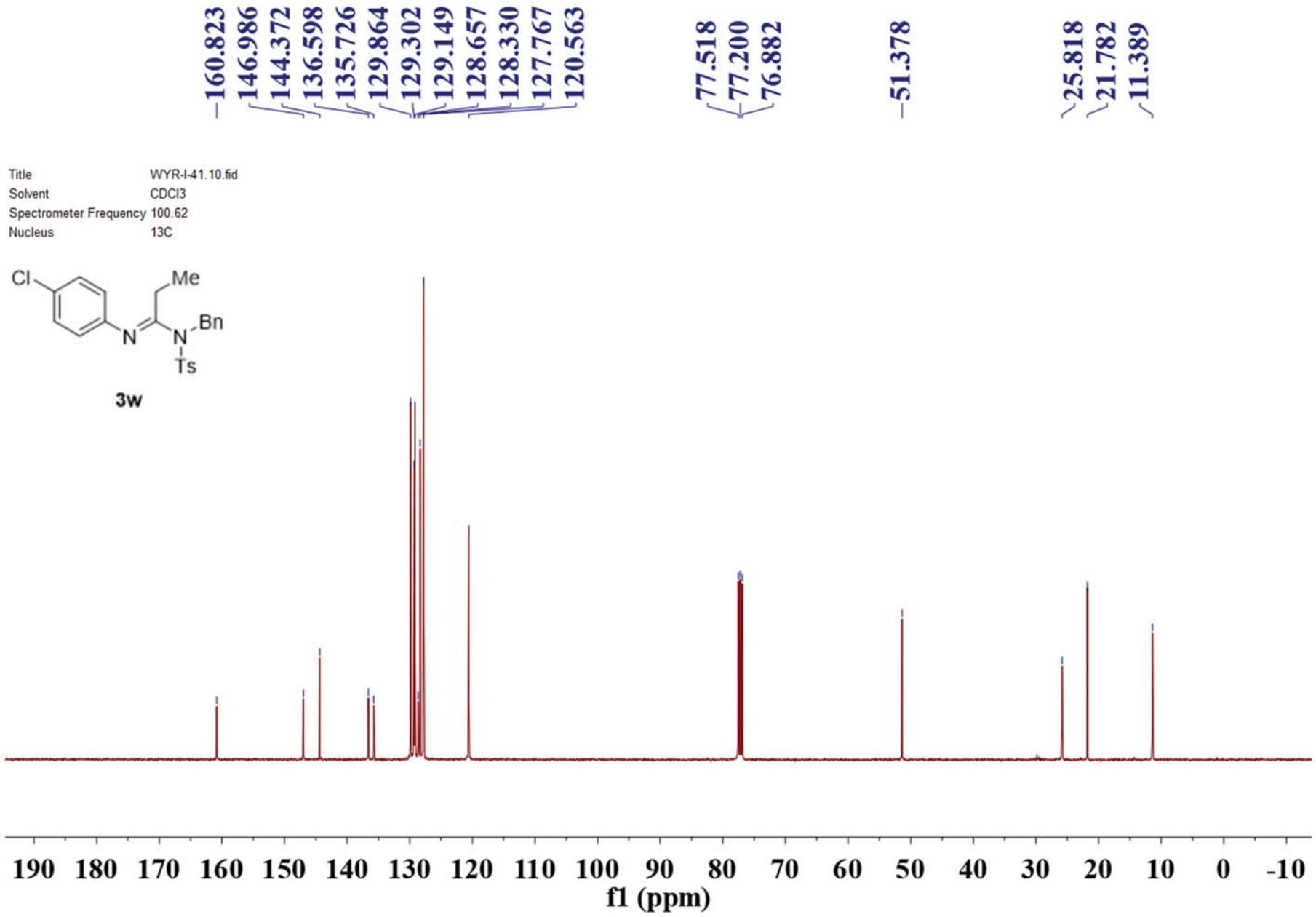
7.7533
7.7486
7.3712
7.3673
7.3654
7.3617
7.3548
7.3508
7.3461
7.3312
7.3268
7.3123
7.3100
7.3056
7.2928
7.2904
7.2851
7.2684
6.9247
6.9081
6.9030
6.8814
6.2896
6.2844
6.2774
6.2725
6.2674
6.2554
4.7542
2.5199
2.5009
2.4820
2.4633
2.4500
0.7598
0.7409
0.7220
0.0000
Title WYR3-58/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
Me
Bn
N
N
Ts
3v
2.00
3.94
3.02
2.01
2.03
2.00
2.00
2.97
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 -0.5 -1.0
f1 (ppm)


161.122
160.538
158.139
144.514
144.486
144.326
136.606
135.627
129.843
129.383
128.300
127.771
127.753
120.426
120.348
115.899
115.675
77.518
77.200
76.882
51.398
25.802
21.770
11.305
Title WYR3-58.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
Me
Bn
N
N
Ts
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.7624
7.7417
7.3669
7.3611
7.3556
7.3462
7.3397
7.3362
7.3300
7.3255
7.3098
7.2958
7.2915
7.2867
7.2821
7.2791
7.2705
7.2518
7.1828
7.1754
7.1702
7.1592
7.1540
7.1466
6.2585
6.2371
4.7619
2.5068
2.4881
2.4692
2.4564
0.7693
0.7505
0.7317
0.0000
Title WYR-I-41.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Me
Bn
N
N
Ts
3w
2.00
7.05
2.00
2.00
2.00
5.01
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 -0.5 -1.0
f1 (ppm)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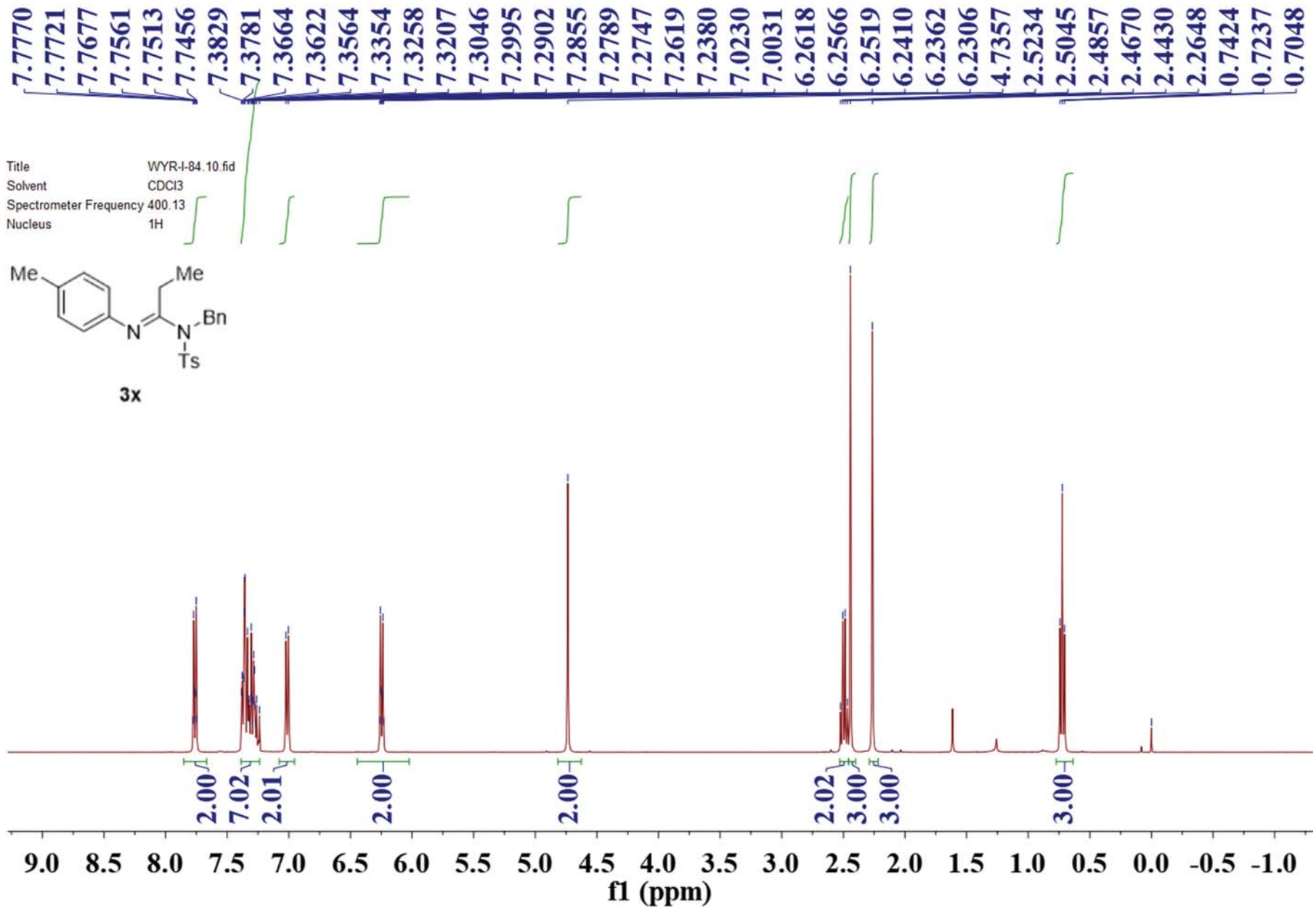
146.986
144.372
136.598
135.726
129.864
129.302
129.149
128.657
128.330
127.767
120.563
77.518
77.200
76.882
51.378
25.818
21.782
11.389
Title WYR-I-41.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Me
Bn
N
N
Ts
3w
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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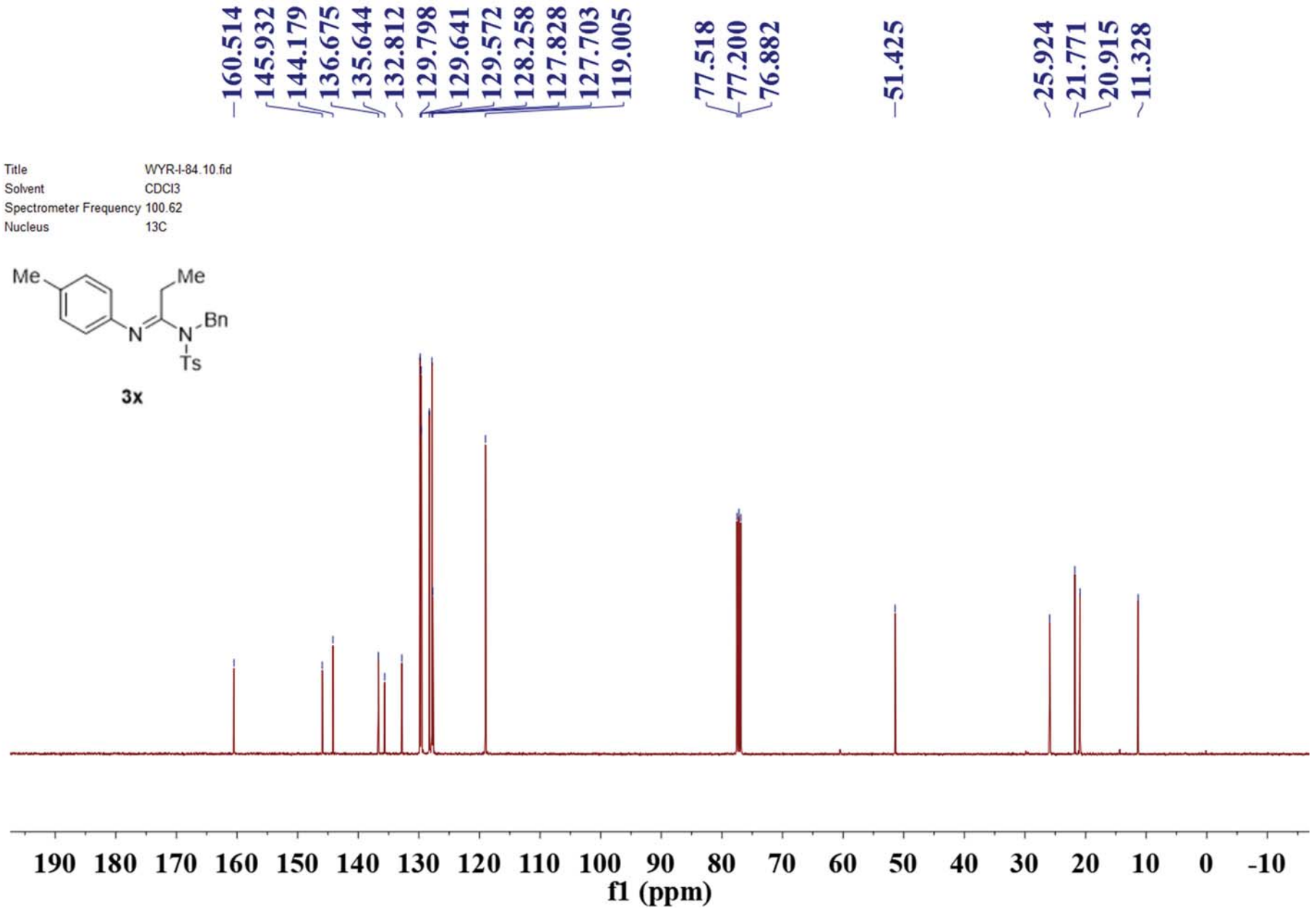
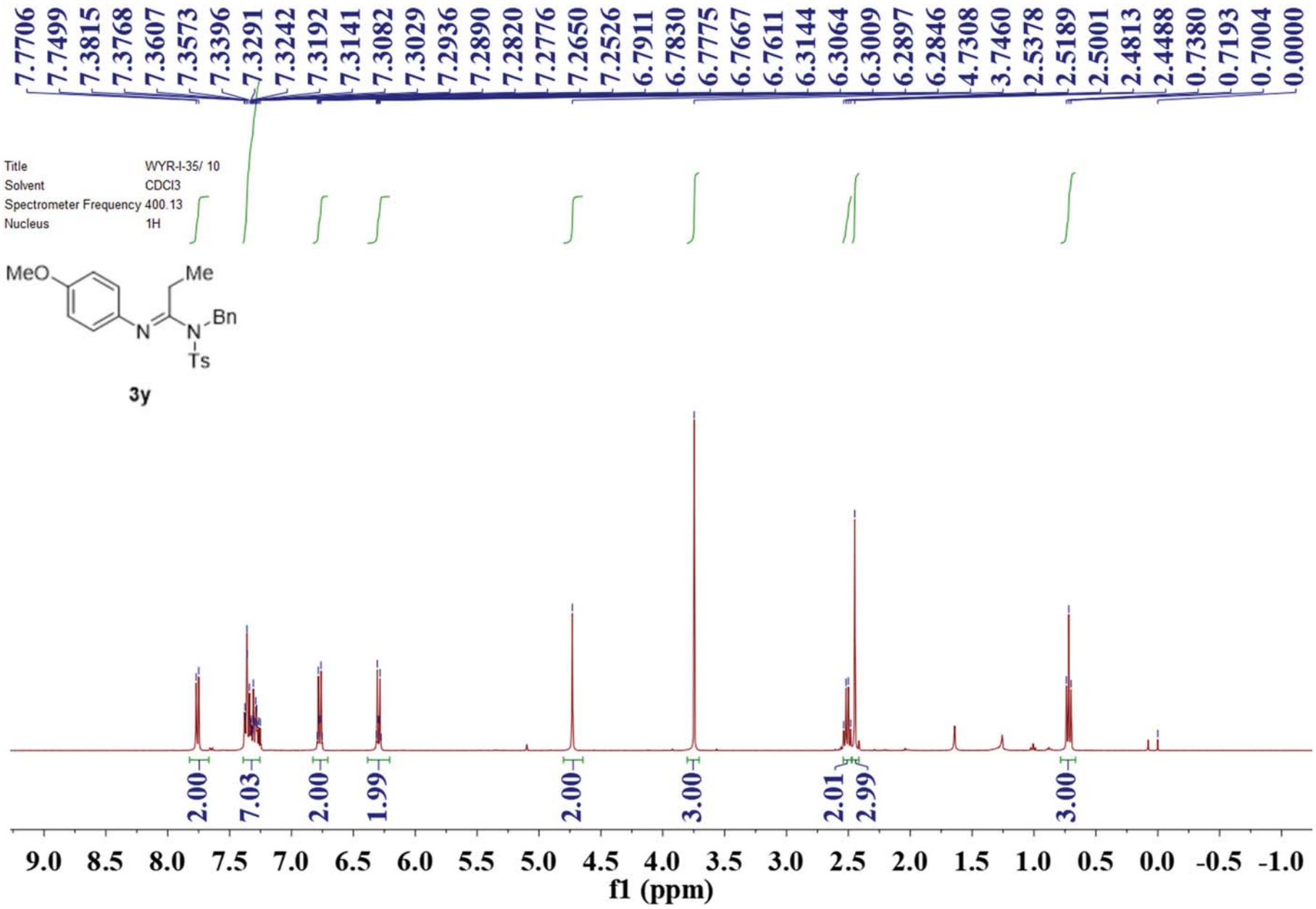
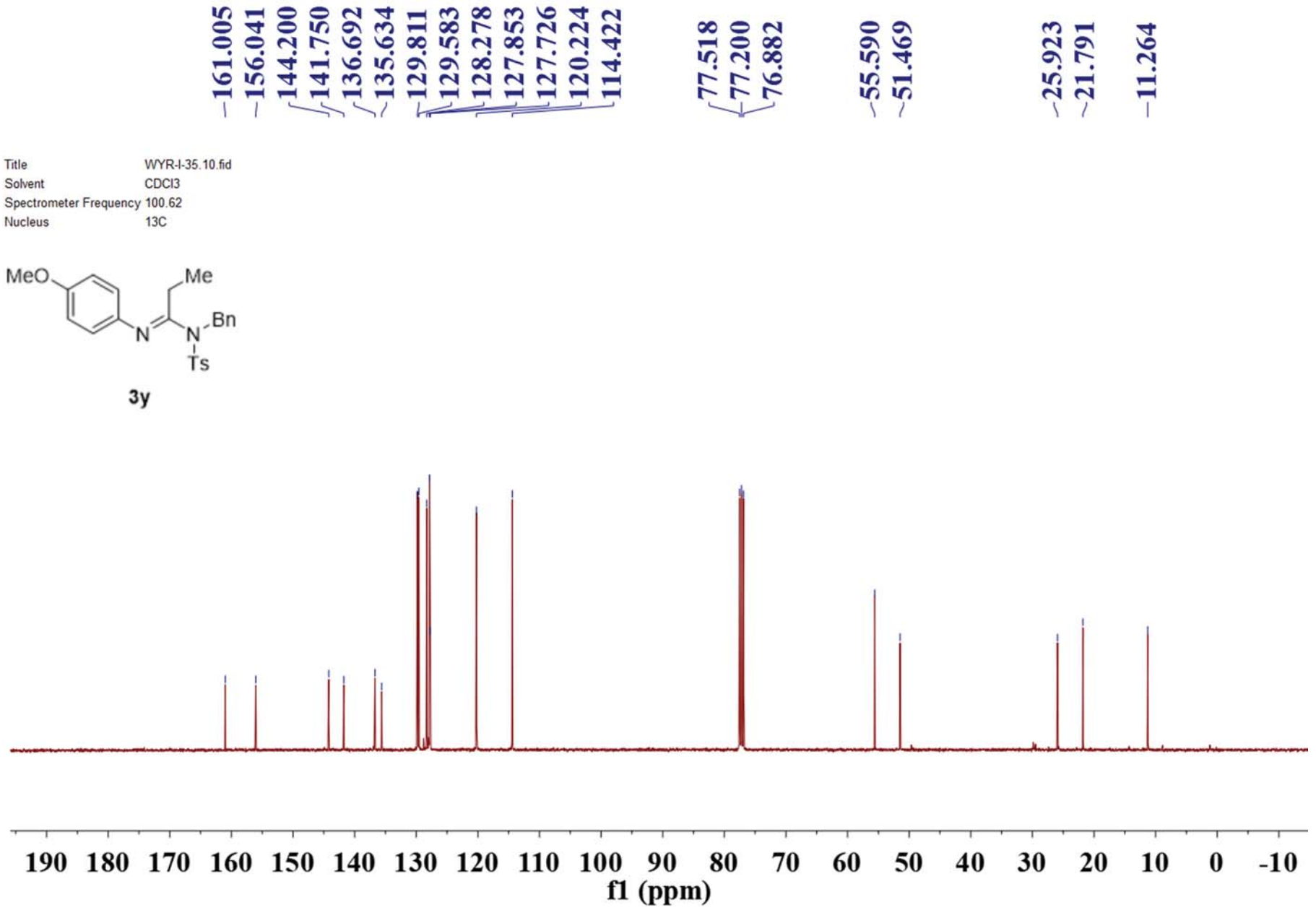
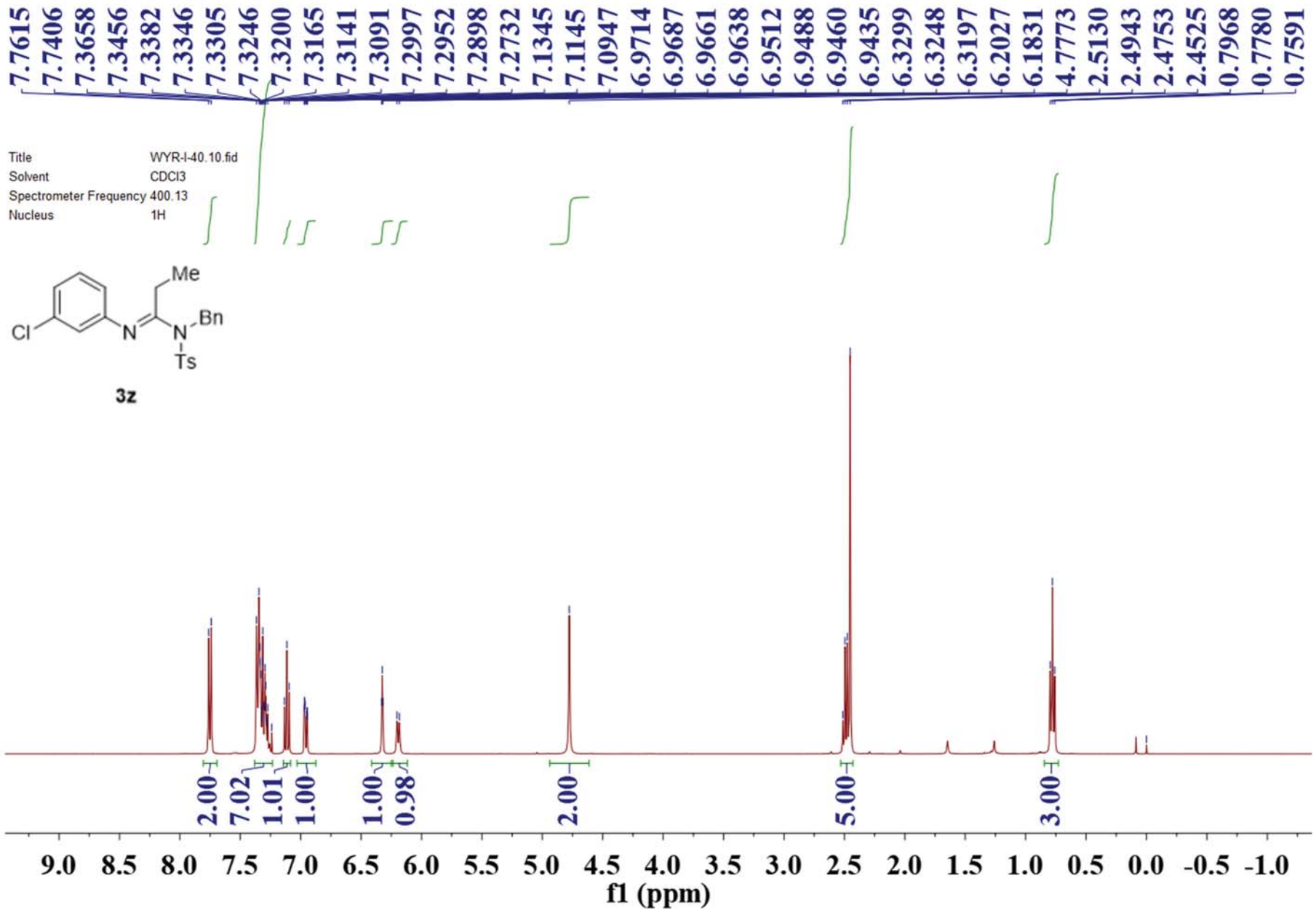
7.7721
7.7677
7.7561
7.7513
7.7456
7.3829
7.3781
7.3664
7.3622
7.3564
7.3354
7.3258
7.3207
7.3046
7.2995
7.2902
7.2855
7.2789
7.2747
7.2619
7.2380
7.0230
7.0031
6.2618
6.2566
6.2519
6.2410
6.2362
6.2306
4.7357
2.5234
2.5045
2.4857
2.4670
2.4430
2.2648
0.7424
0.7237
0.7048
Title WYR-I-84.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
N
N
Bn
Ts
3x
2.00
7.02
2.01
2.00
2.00
2.02
3.00
3.00
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 -0.5 -1.0
f1 (ppm)


160.514
145.932
144.179
136.675
135.644
132.812
129.798
129.641
129.572
128.258
127.828
127.703
119.005
77.518
77.200
76.882
51.425
25.924
21.771
20.915
11.328
Title WYR-I-84.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
N
N
Bn
Ts
3x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.7706
7.7499
7.3815
7.3768
7.3607
7.3573
7.3396
7.3291
7.3242
7.3192
7.3141
7.3082
7.3029
7.2936
7.2890
7.2820
7.2776
7.2650
7.2526
6.7911
6.7830
6.7775
6.7667
6.7611
6.3144
6.3064
6.3009
6.2897
6.2846
4.7308
3.7460
2.5378
2.5189
2.5001
2.4813
2.4488
0.7380
0.7193
0.7004
0.0000
Title WYR-I-35/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Me
Bn
N
N
Ts
3y
2.00
7.03
2.00
1.99
2.00
3.00
2.01
2.99
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 -0.5 -1.0
f1 (ppm)


161.005
156.041
144.200
141.750
136.692
135.634
129.811
129.583
128.278
127.853
127.726
120.224
114.422
77.518
77.200
76.882
55.590
51.469
25.923
21.791
11.264
Title WYR-I-35.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Me
Bn
N
N
Ts
3y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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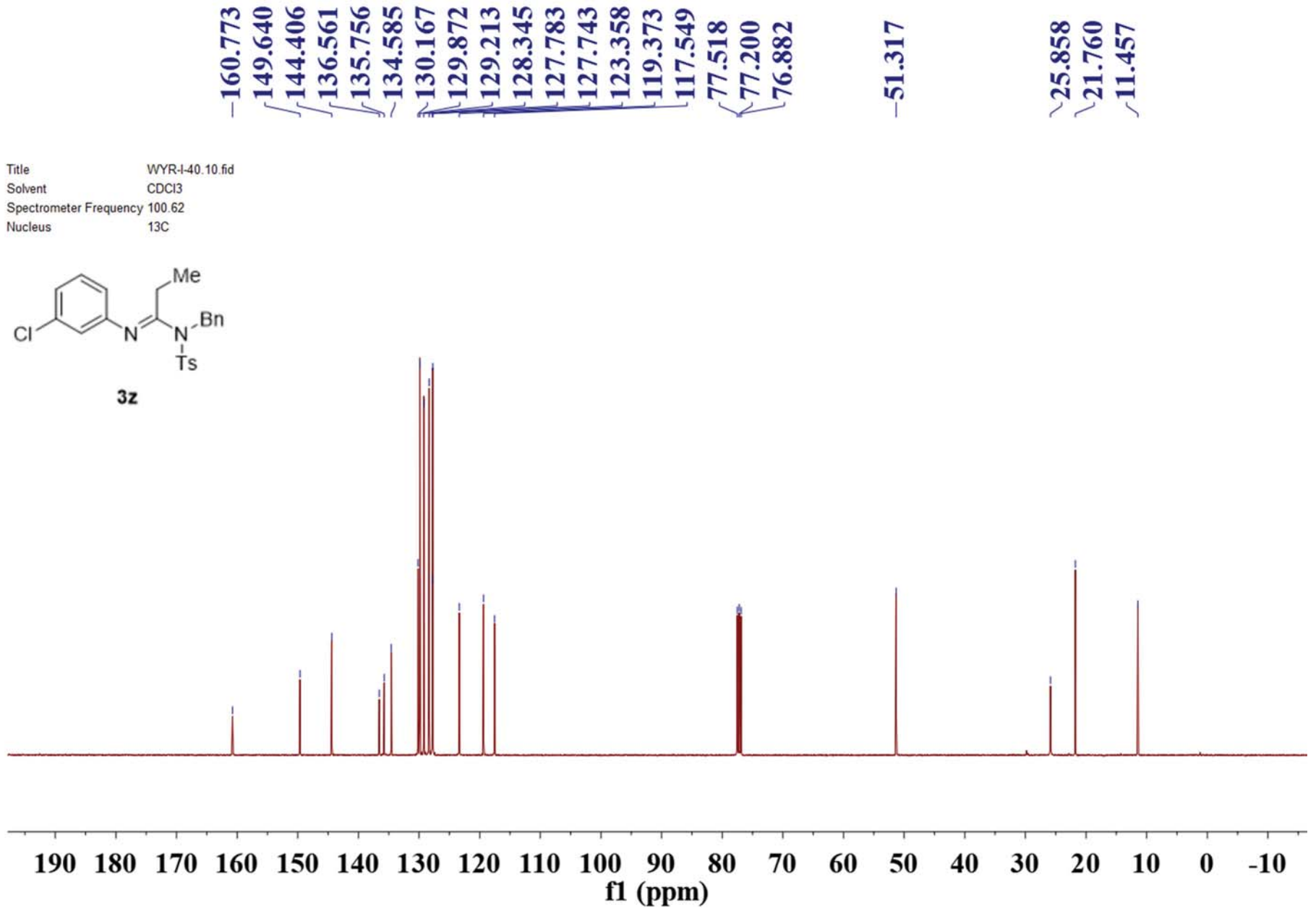
7.7406
7.3658
7.3456
7.3382
7.3346
7.3305
7.3246
7.3200
7.3165
7.3141
7.3091
7.2997
7.2952
7.2898
7.2732
7.1345
7.1145
7.0947
6.9714
6.9687
6.9661
6.9638
6.9512
6.9488
6.9460
6.9435
6.3299
6.3248
6.3197
6.2027
6.1831
4.7773
2.5130
2.4943
2.4753
2.4525
0.7968
0.7780
0.7591
Title WYR-I-40.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
Cl
N
N
Ts
3z
2.00
7.02
1.01
1.00
1.00
0.98
2.00
5.00
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 -0.5 -1.0
f1 (ppm)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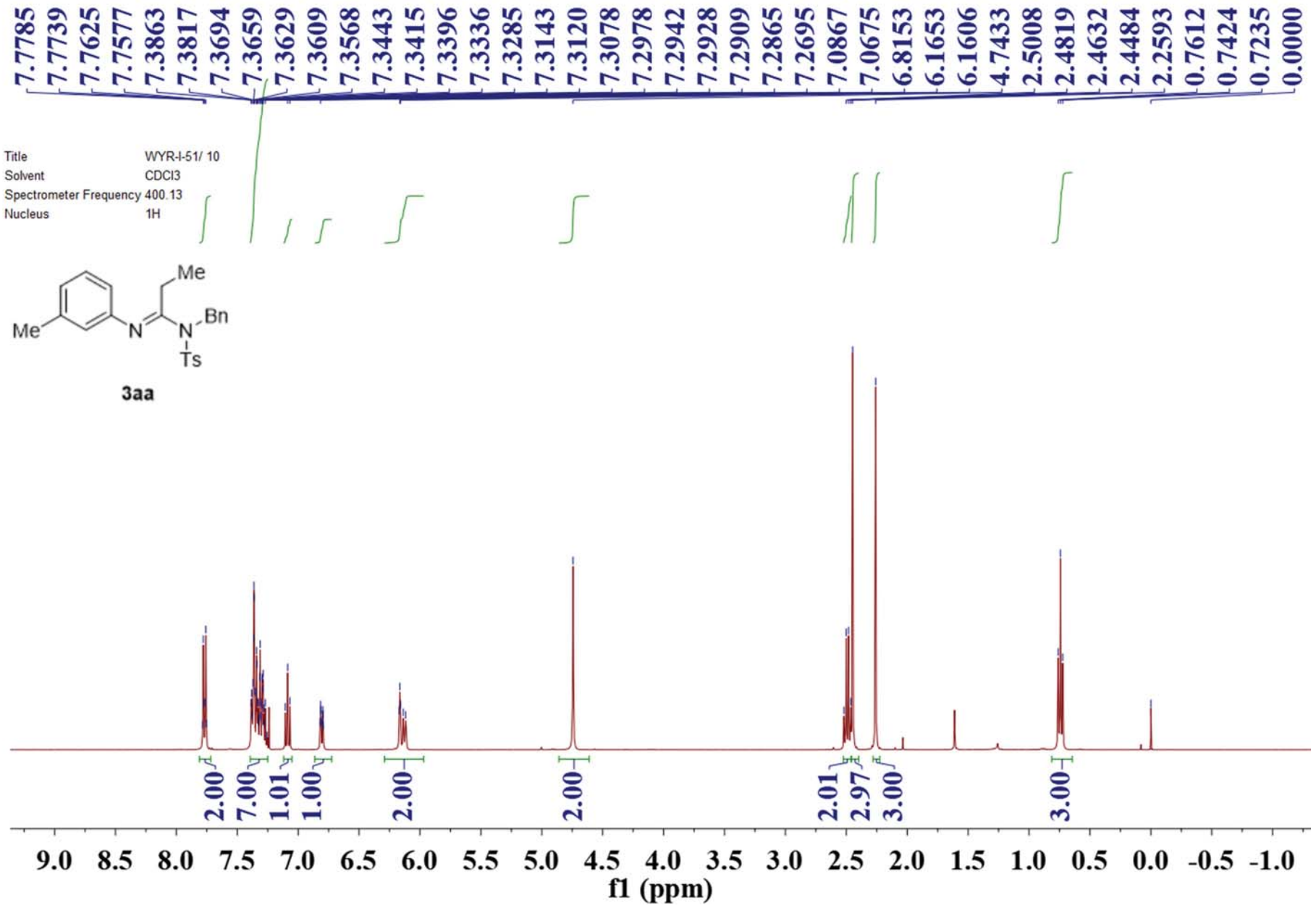
149.640
144.406
136.561
135.756
134.585
130.167
129.872
129.213
128.345
127.783
127.743
123.358
119.373
117.549
77.518
77.200
76.882
51.317
25.858
21.760
11.457
Title WYR-I-40.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Cl
N
N
Bn
Ts
3z
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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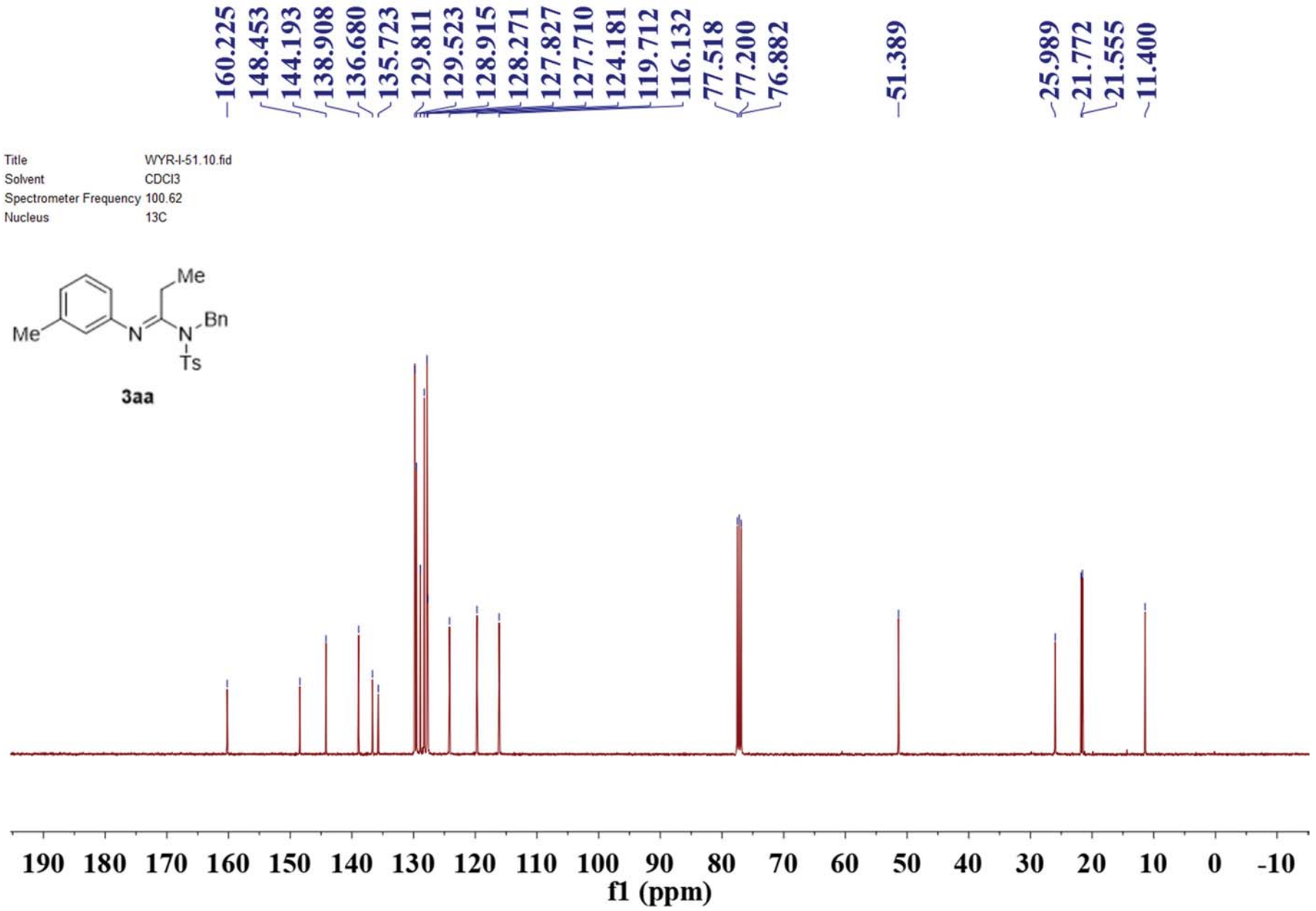
7.7739
7.7625
7.7577
7.3863
7.3817
7.3694
7.3659
7.3629
7.3609
7.3568
7.3443
7.3415
7.3396
7.3336
7.3285
7.3143
7.3120
7.3078
7.2978
7.2942
7.2928
7.2909
7.2865
7.2695
7.0867
7.0675
6.8153
6.1653
6.1606
4.7433
2.5008
2.4819
2.4632
2.4484
2.2593
0.7612
0.7424
0.7235
0.0000
Title WYR-I-51/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
Me
N
N
Ts
3aa
2.00
7.00
1.01
1.00
2.00
2.00
2.01
2.97
3.00
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 -0.5 -1.0
f1 (ppm)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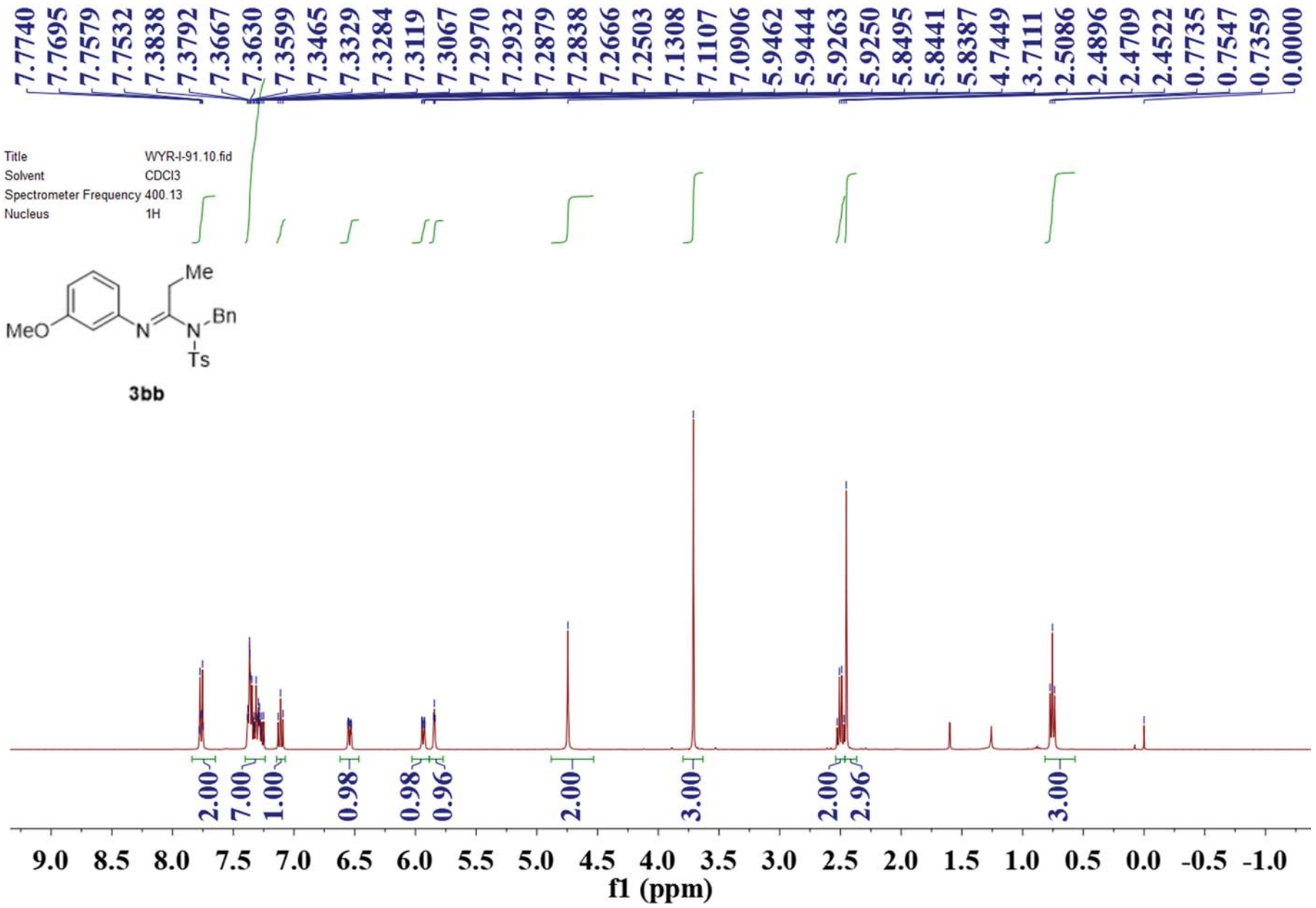
136.680
135.723
129.811
129.523
128.915
128.271
127.827
127.710
124.181
119.712
116.132
77.518
77.200
76.882
51.389
25.989
21.772
21.555
11.400
Title WYR-I-51.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
Me
N
N
Ts
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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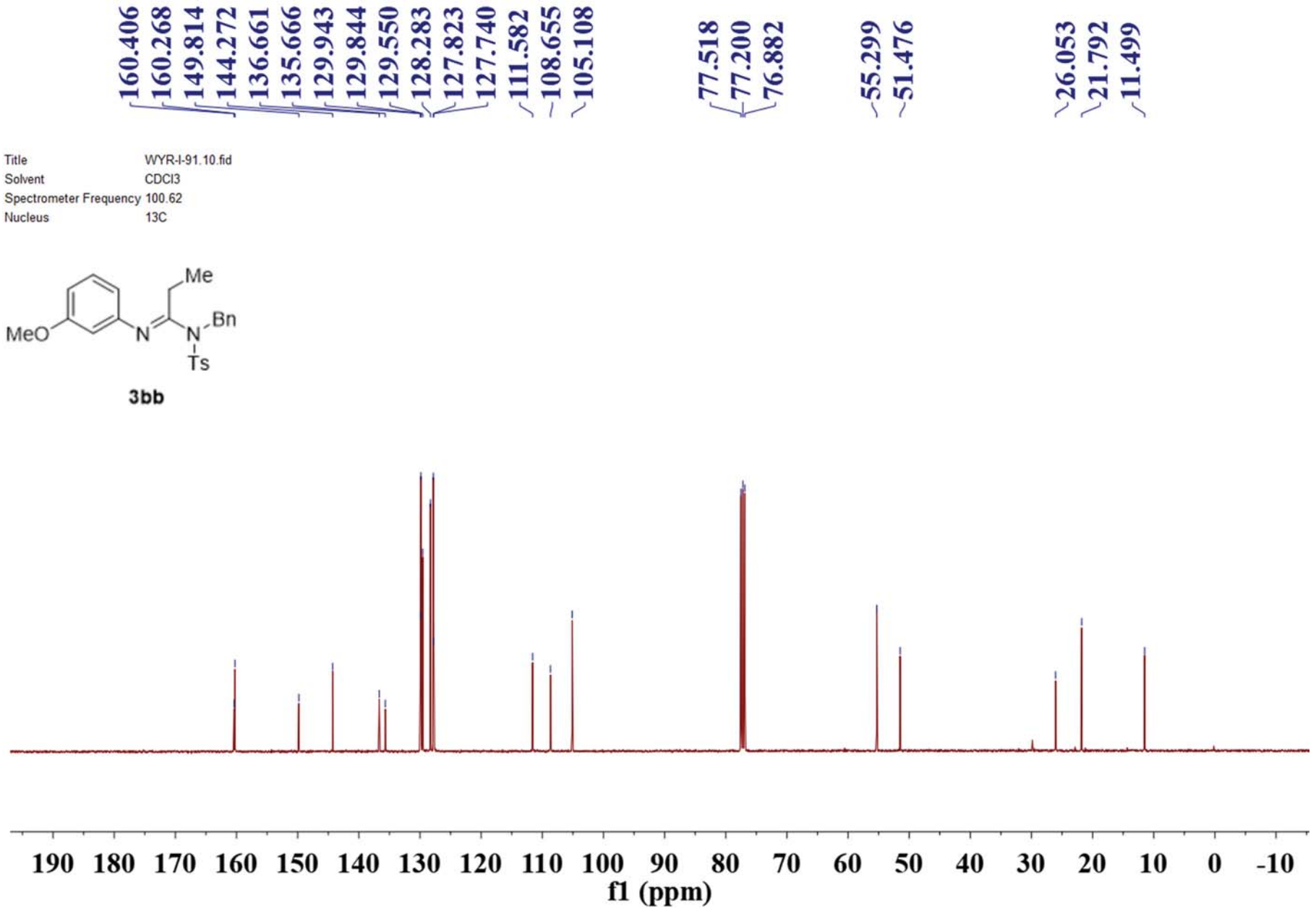
7.7579
7.7532
7.3838
7.3792
7.3667
7.3630
7.3599
7.3465
7.3329
7.3284
7.3119
7.3067
7.2970
7.2932
7.2879
7.2838
7.2666
7.2503
7.1308
7.1107
7.0906
5.9462
5.9444
5.9263
5.9250
5.8495
5.8441
5.8387
4.7449
3.7111
2.5086
2.4896
2.4709
2.4522
0.7735
0.7547
0.7359
0.0000
Title WYR-I-91.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
MeO
N
N
Bn
Ts
3bb
2.00
7.00
1.00
0.98
0.98
0.96
2.00
3.00
2.00
2.96
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 -0.5 -1.0
f1 (ppm)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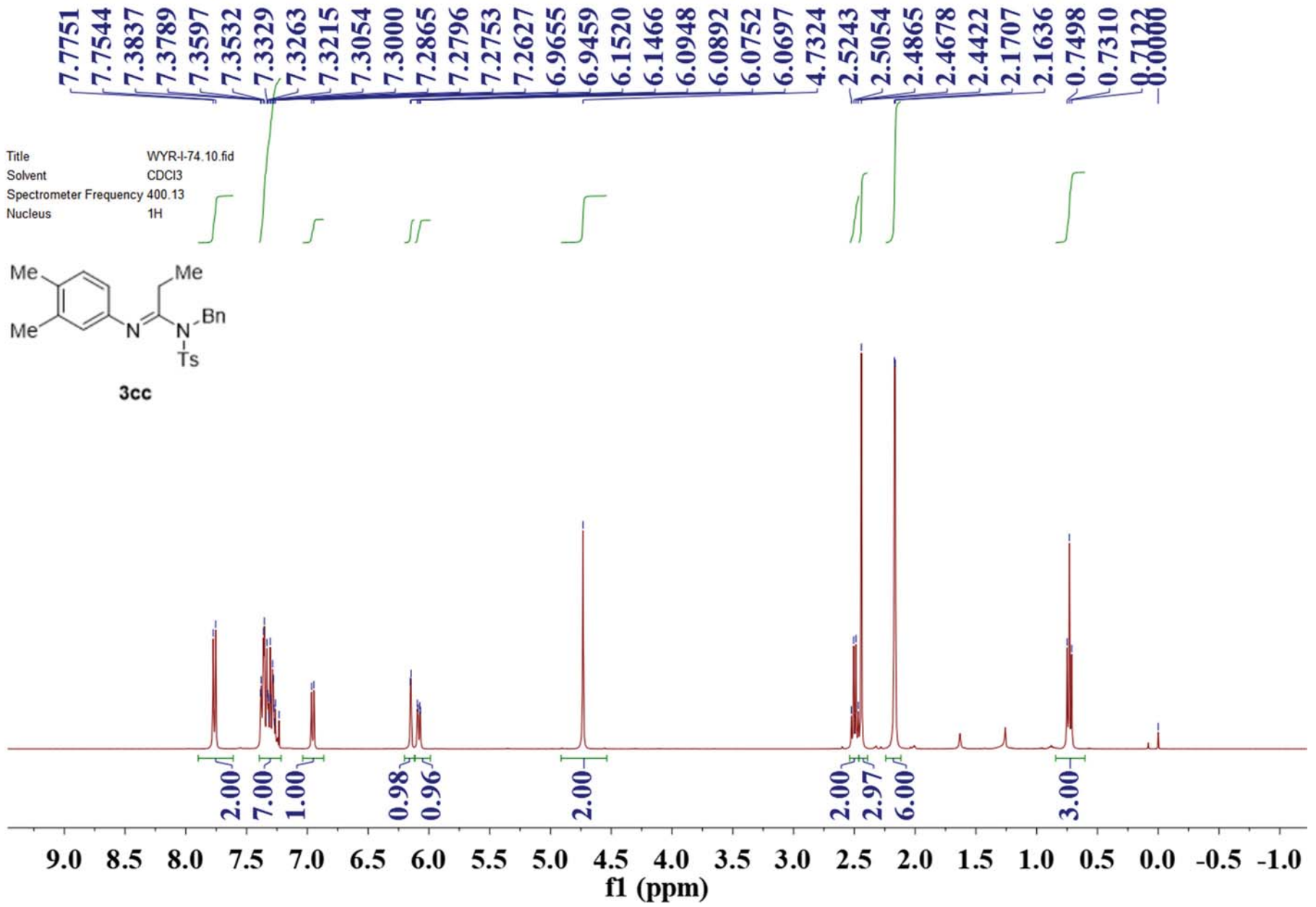
144.272
136.661
135.666
129.943
129.844
129.550
128.283
127.823
127.740
111.582
108.655
105.108
77.518
77.200
76.882
55.299
51.476
26.053
21.792
11.499
Title WYR-I-91.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
N
N
Bn
Me
Ts
3bb
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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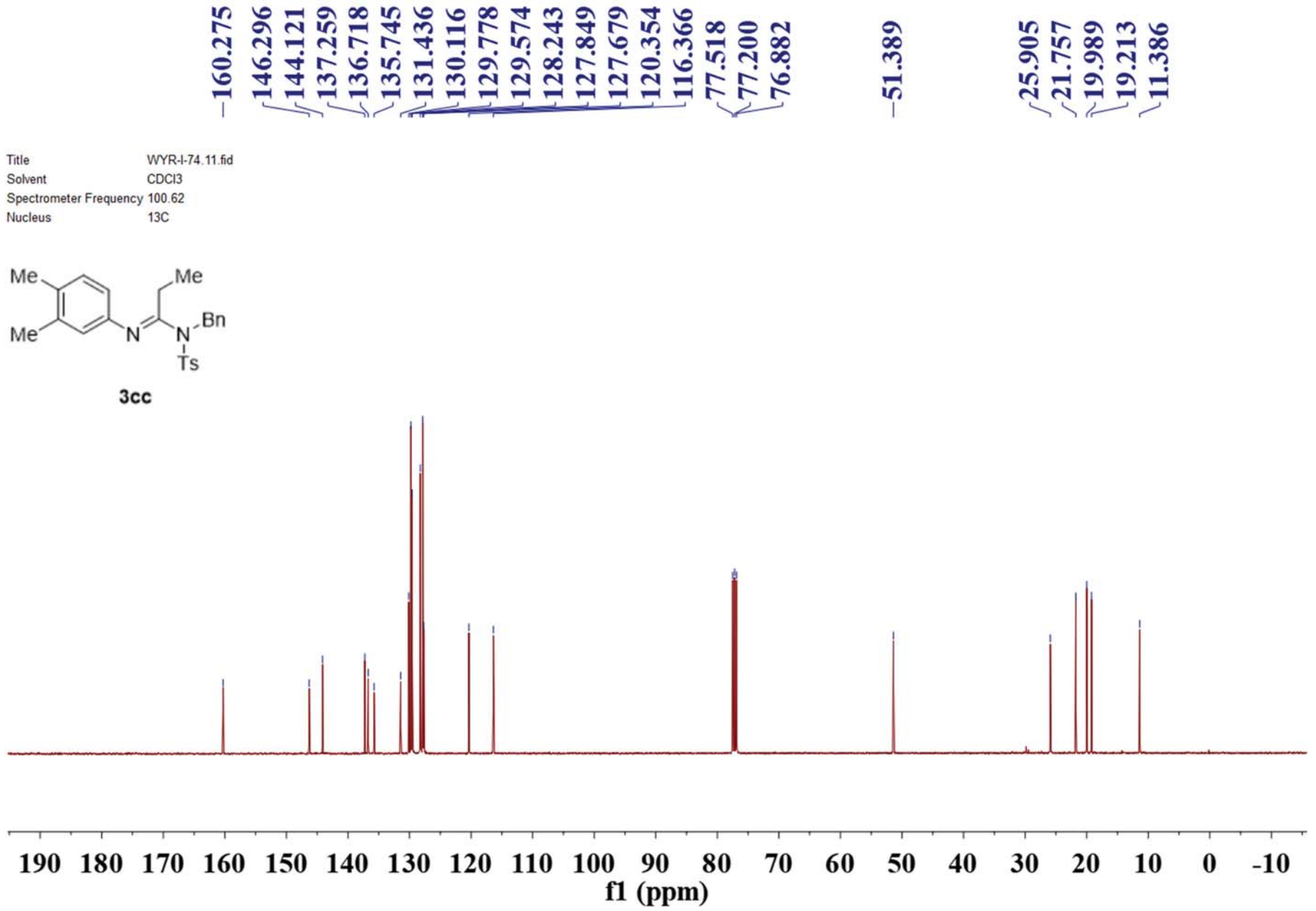
7.7544
7.3837
7.3789
7.3597
7.3532
7.3329
7.3263
7.3215
7.3054
7.3000
7.2865
7.2796
7.2753
7.2627
6.9655
6.9459
6.1520
6.1466
6.0948
6.0892
6.0752
6.0697
4.7324
2.5243
2.5054
2.4865
2.4678
2.4422
2.1707
2.1636
0.7498
0.7310
Title WYR-I-74.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
Me
N
N
Bn
Ts
3cc
2.00
7.00
1.00
0.98
0.96
2.00
2.00
2.97
6.00
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 -0.5 -1.0
f1 (ppm)


160.275
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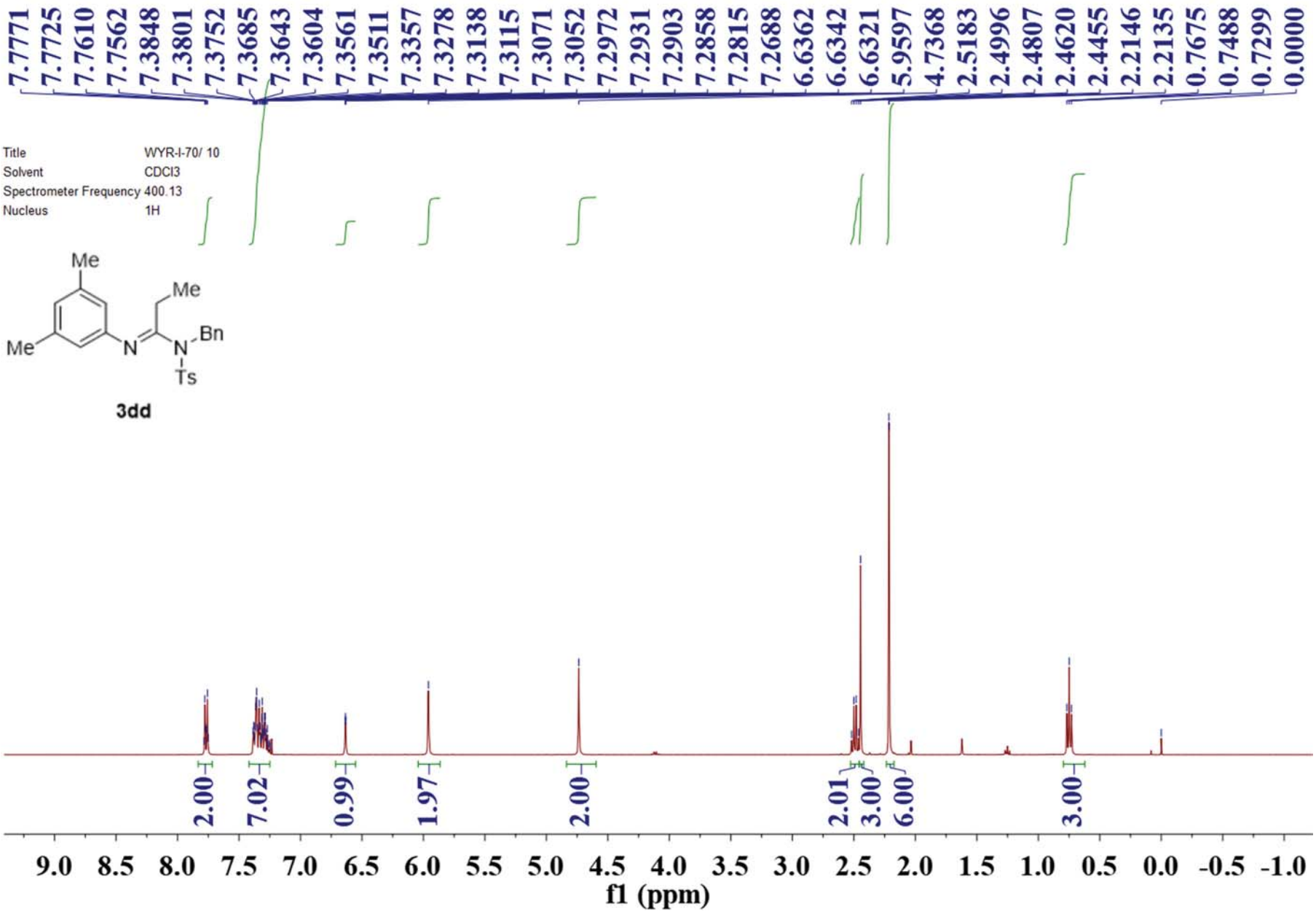
144.121
137.259
136.718
135.745
131.436
130.116
129.778
129.574
128.243
127.849
127.679
120.354
116.366
77.518
77.200
76.882
51.389
25.905
21.757
19.989
19.213
11.386
Title WYR-I-74.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
Me
N
N
Bn
Ts
3cc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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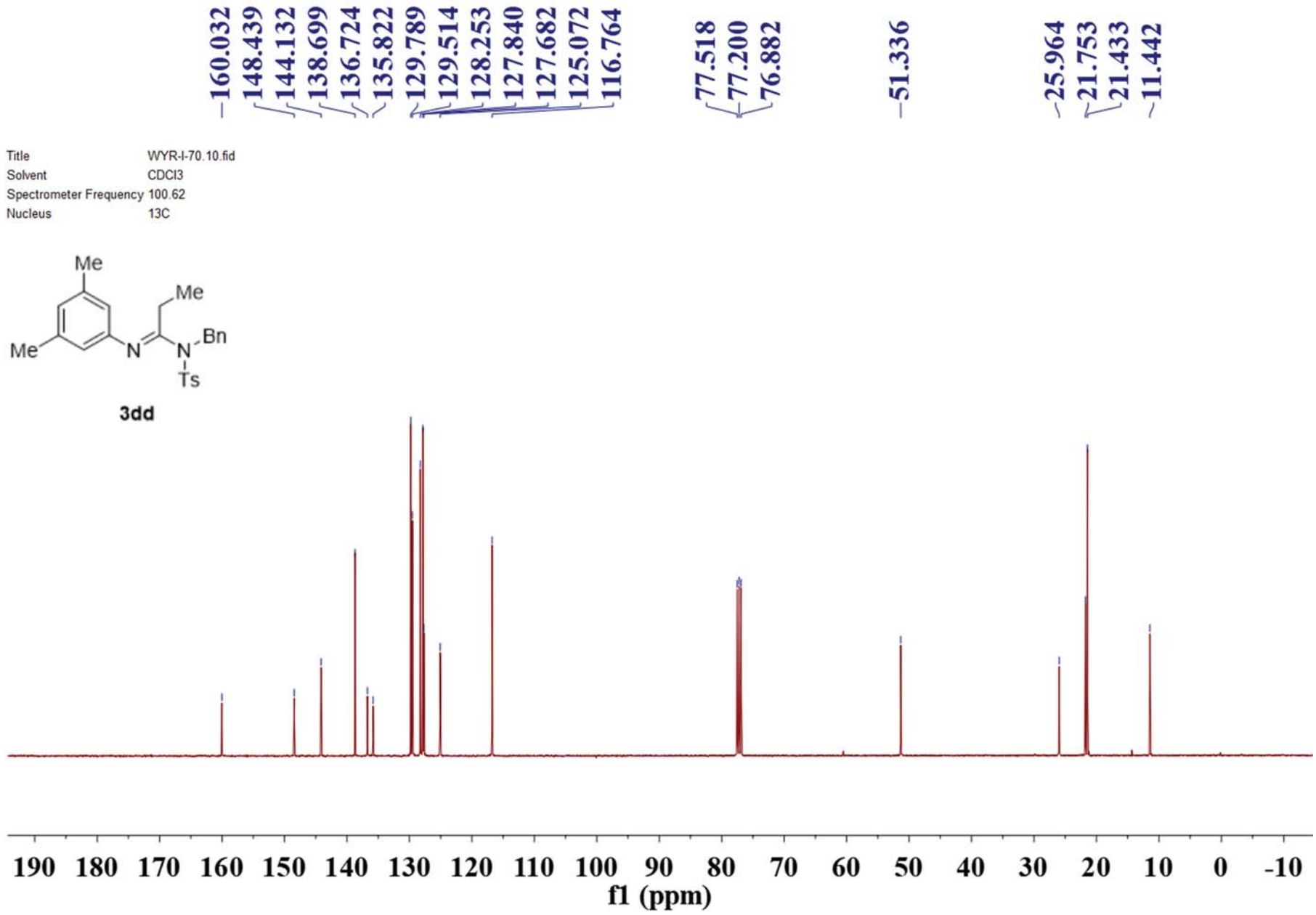
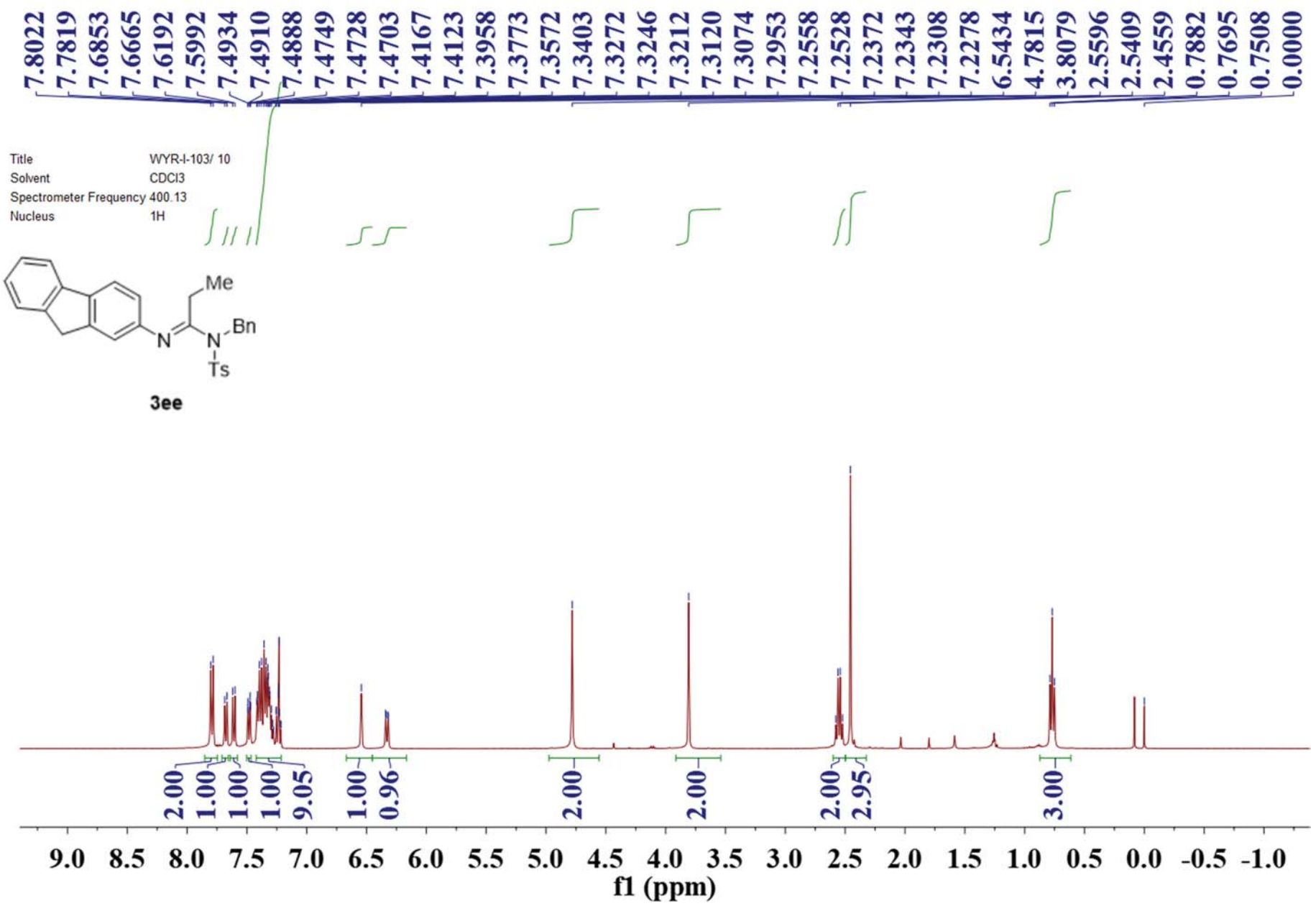
7.7725
7.7610
7.7562
7.3848
7.3801
7.3752
7.3685
7.3643
7.3604
7.3561
7.3511
7.3357
7.3278
7.3138
7.3115
7.3071
7.3052
7.2972
7.2931
7.2903
7.2858
7.2815
7.2688
6.6362
6.6342
6.6321
5.9597
4.7368
2.5183
2.4996
2.4807
2.4620
2.4455
2.2146
2.2135
0.7675
0.7488
0.7299
0.0000
Title WYR-I-70/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
Me
N
N
Bn
Ts
3dd
2.00
7.02
0.99
1.97
2.00
2.01
3.00
6.00
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 -0.5 -1.0
f1 (ppm)


160.032
148.439
144.132
138.699
136.724
135.822
129.789
129.514
128.253
127.840
127.682
125.072
116.764
77.518
77.200
76.882
51.336
25.964
21.753
21.433
11.442
Title WYR-I-70.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
Me
N
N
Bn
Ts
3dd
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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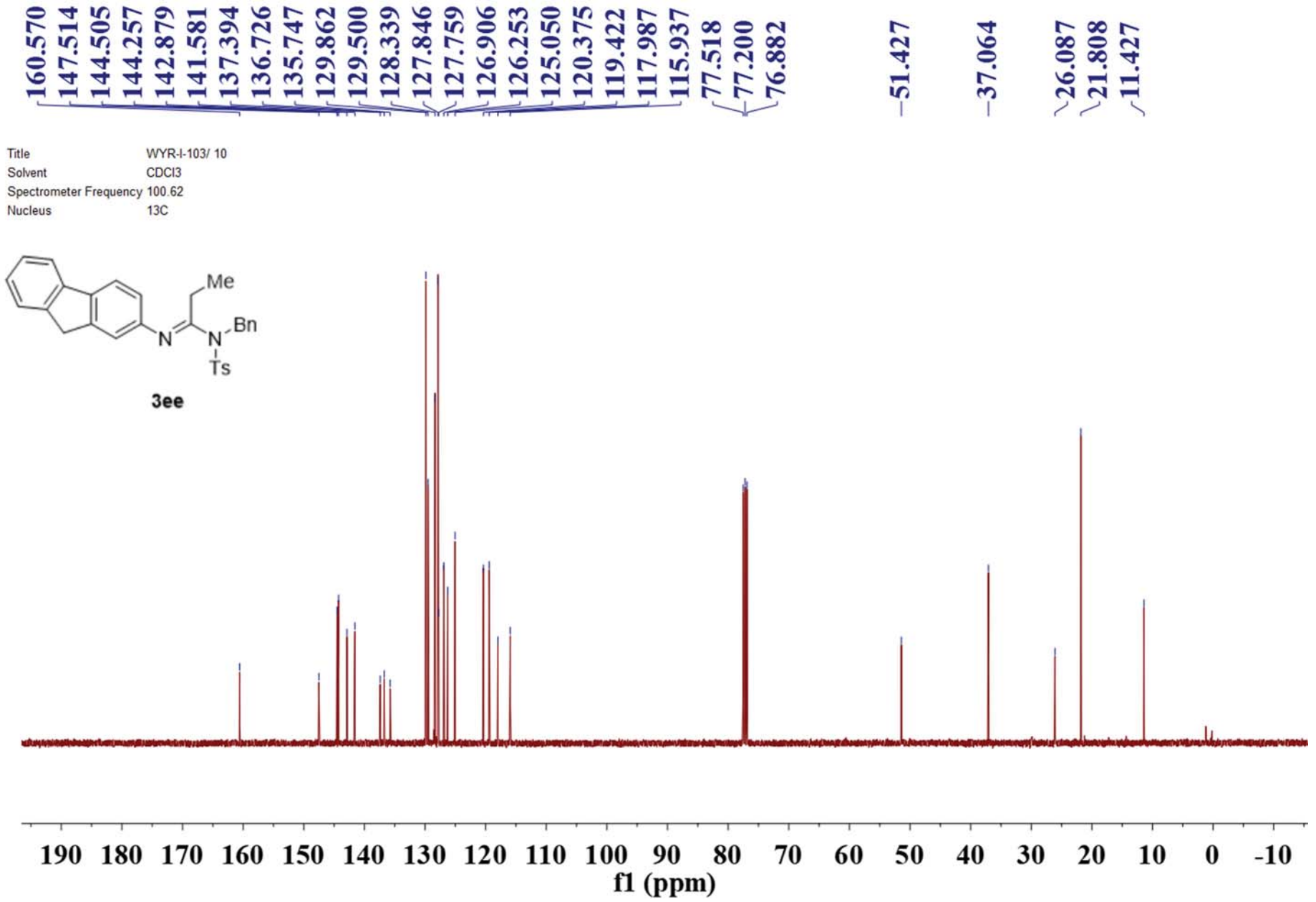
7.6853
7.6665
7.6192
7.5992
7.4934
7.4910
7.4888
7.4749
7.4728
7.4703
7.4167
7.4123
7.3958
7.3773
7.3572
7.3403
7.3272
7.3246
7.3212
7.3120
7.3074
7.2953
7.2558
7.2528
7.2372
7.2343
7.2308
7.2278
6.5434
4.7815
3.8079
2.5596
2.5409
2.4559
0.7882
0.7695
0.7508
0.0000
Title WYR-I-103/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
Ts
3ee
2.00
1.00
1.00
1.00
9.05
1.00
0.96
2.00
2.00
2.00
2.95
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 -0.5 -1.0
f1 (ppm)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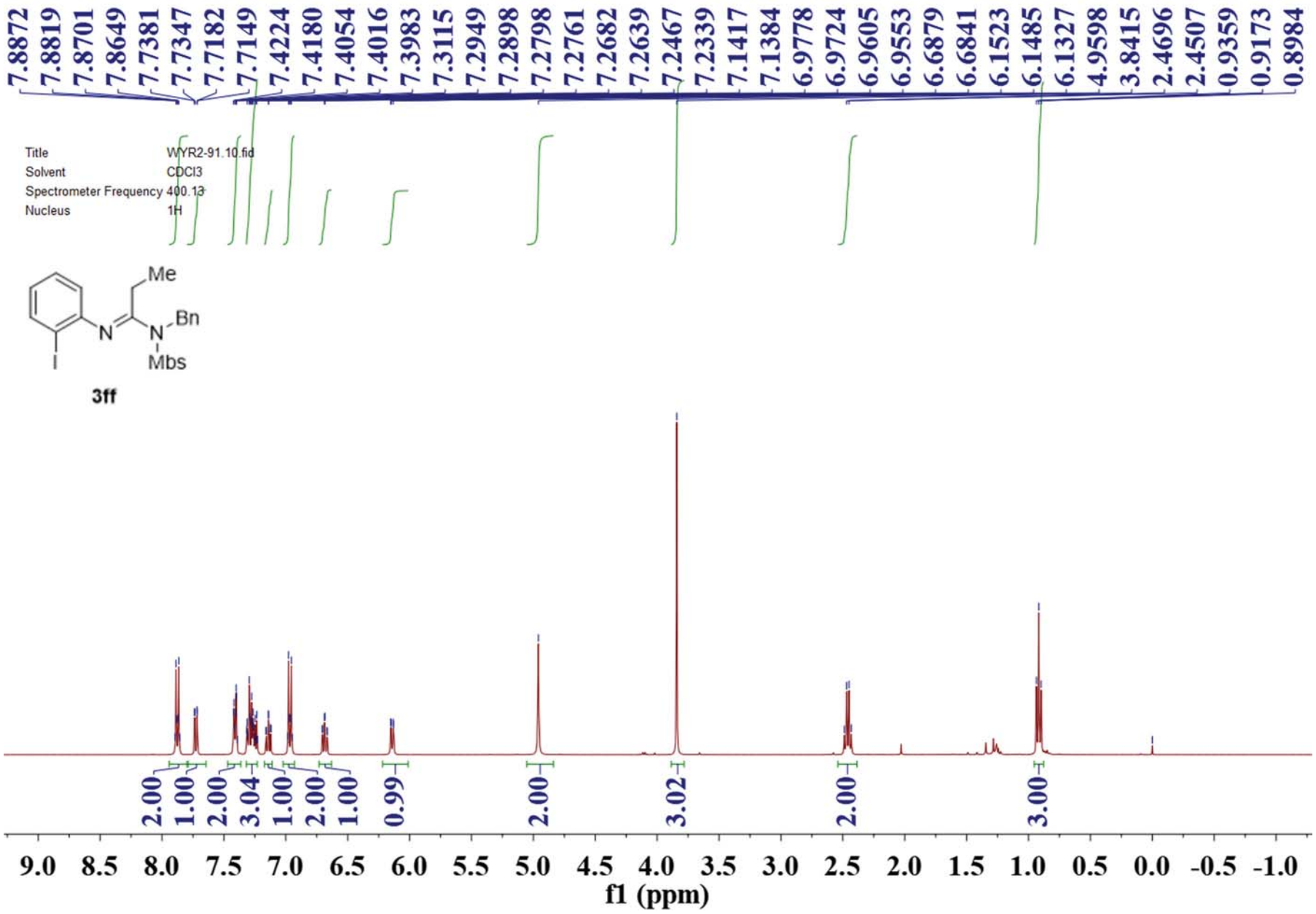
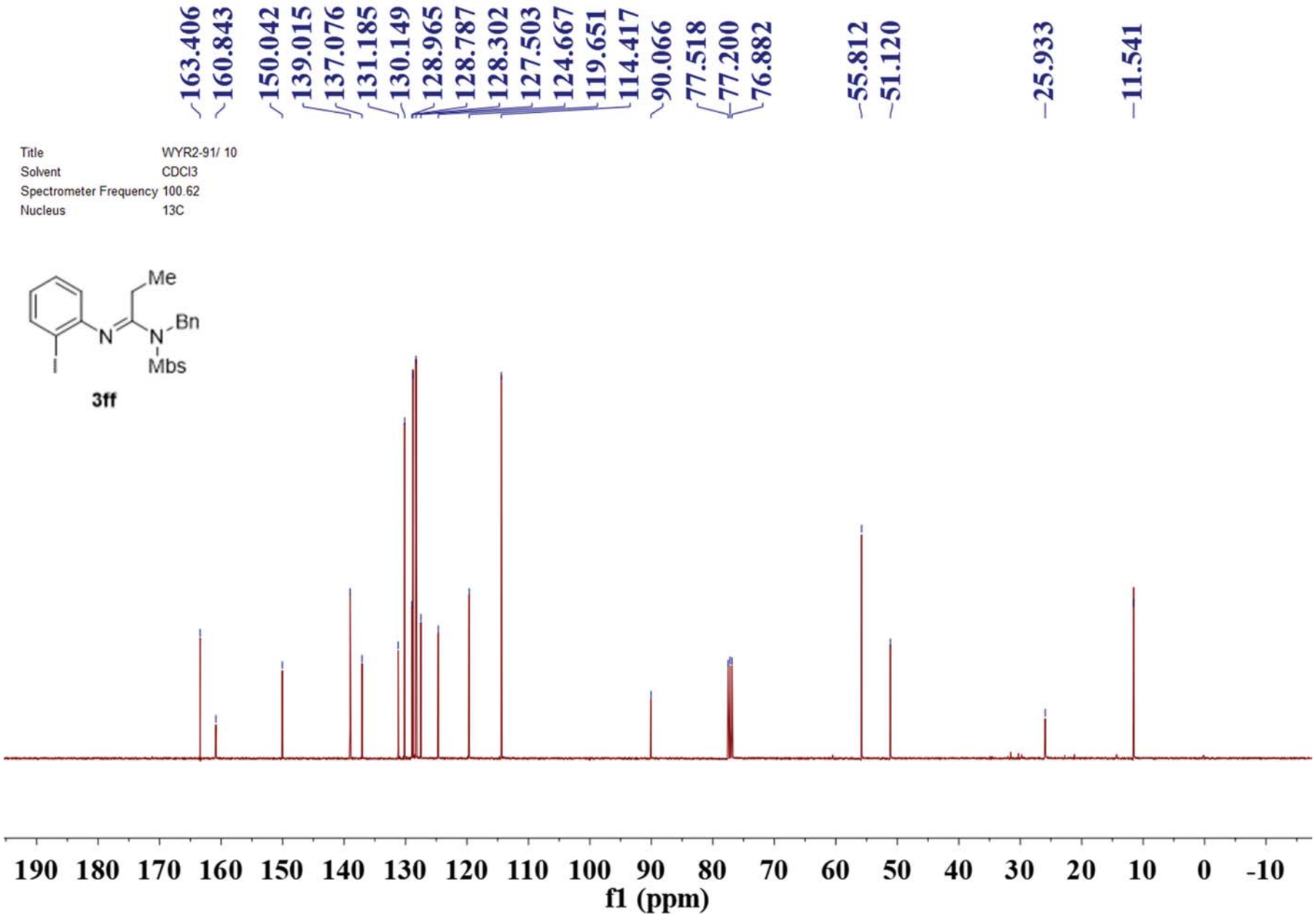
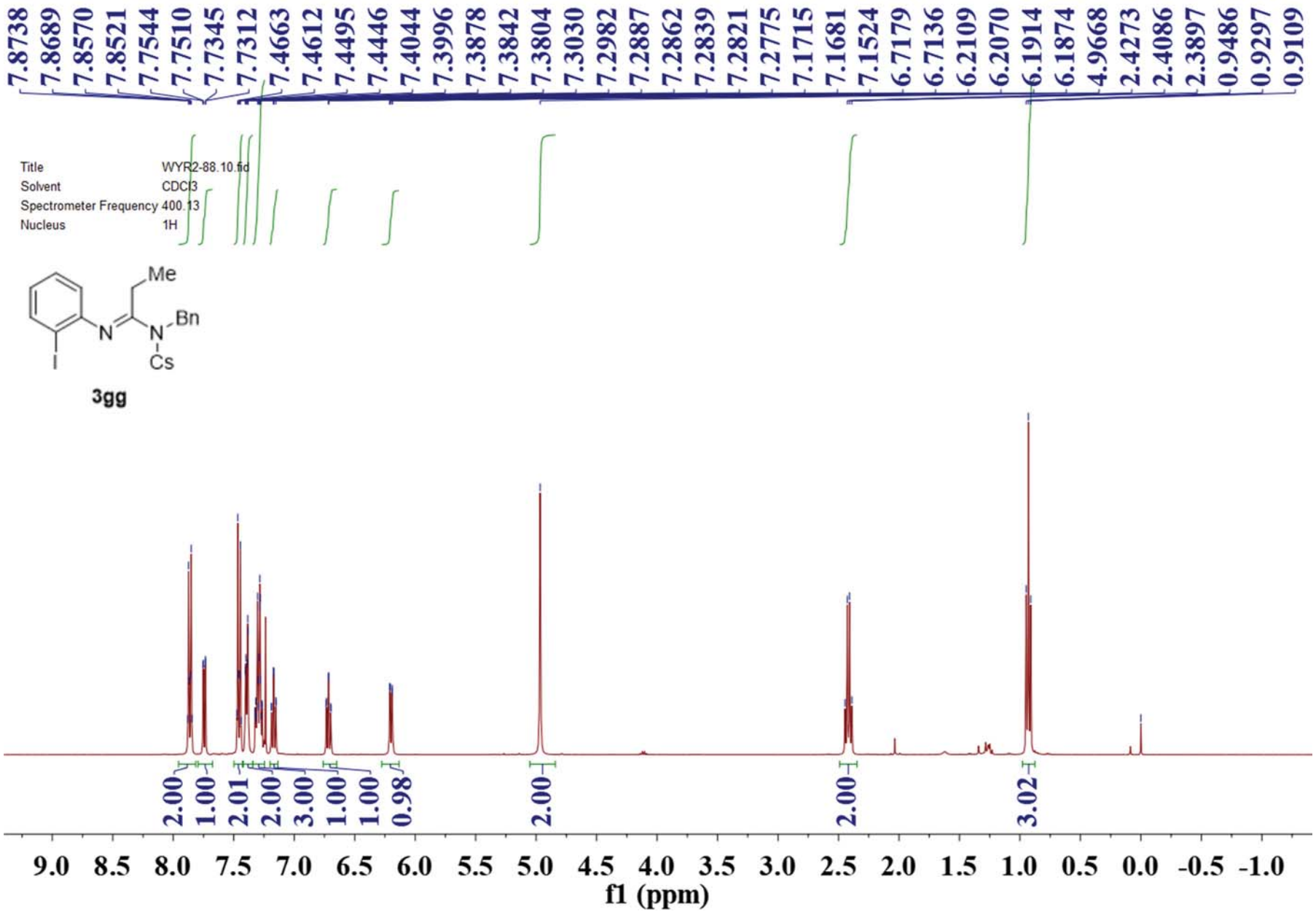
147.514
144.505
144.257
142.879
141.581
137.394
136.726
135.747
129.862
129.500
128.339
127.846
127.759
126.906
126.253
125.050
120.375
119.422
117.987
115.937
77.518
77.200
76.882
51.427
37.064
26.087
21.808
11.427
Title WYR-I-103/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Ts
3ee
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.8872
7.8819
7.8701
7.8649
7.7381
7.7347
7.7182
7.7149
7.4224
7.4180
7.4054
7.4016
7.3983
7.3115
7.2949
7.2898
7.2798
7.2761
7.2682
7.2639
7.2467
7.2339
7.1417
7.1384
6.9778
6.9724
6.9605
6.9553
6.6879
6.6841
6.1523
6.1485
6.1327
4.9598
3.8415
2.4696
2.4507
0.9359
0.9173
0.8984
Title WYR2-91.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
Mbs
I
3ff
2.00
1.00
2.00
3.04
1.00
2.00
1.00
0.99
2.00
3.02
2.00
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 -0.5 -1.0
f1 (ppm)


163.406
160.843
150.042
139.015
137.076
131.185
130.149
128.965
128.787
128.302
127.503
124.667
119.651
114.417
90.066
77.518
77.200
76.882
55.812
51.120
25.933
11.541
Title WYR2-91/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Mbs
I
3ff
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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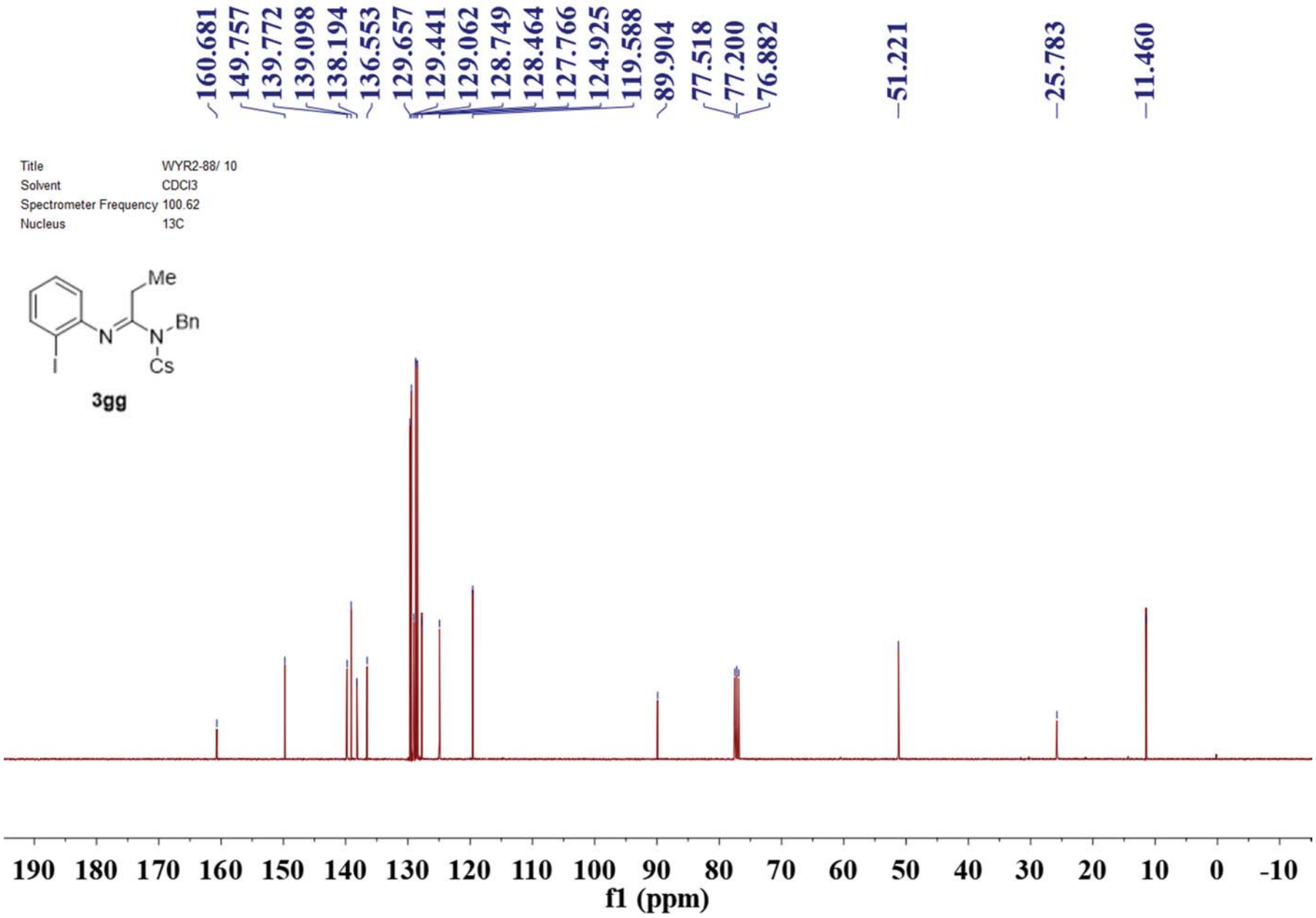
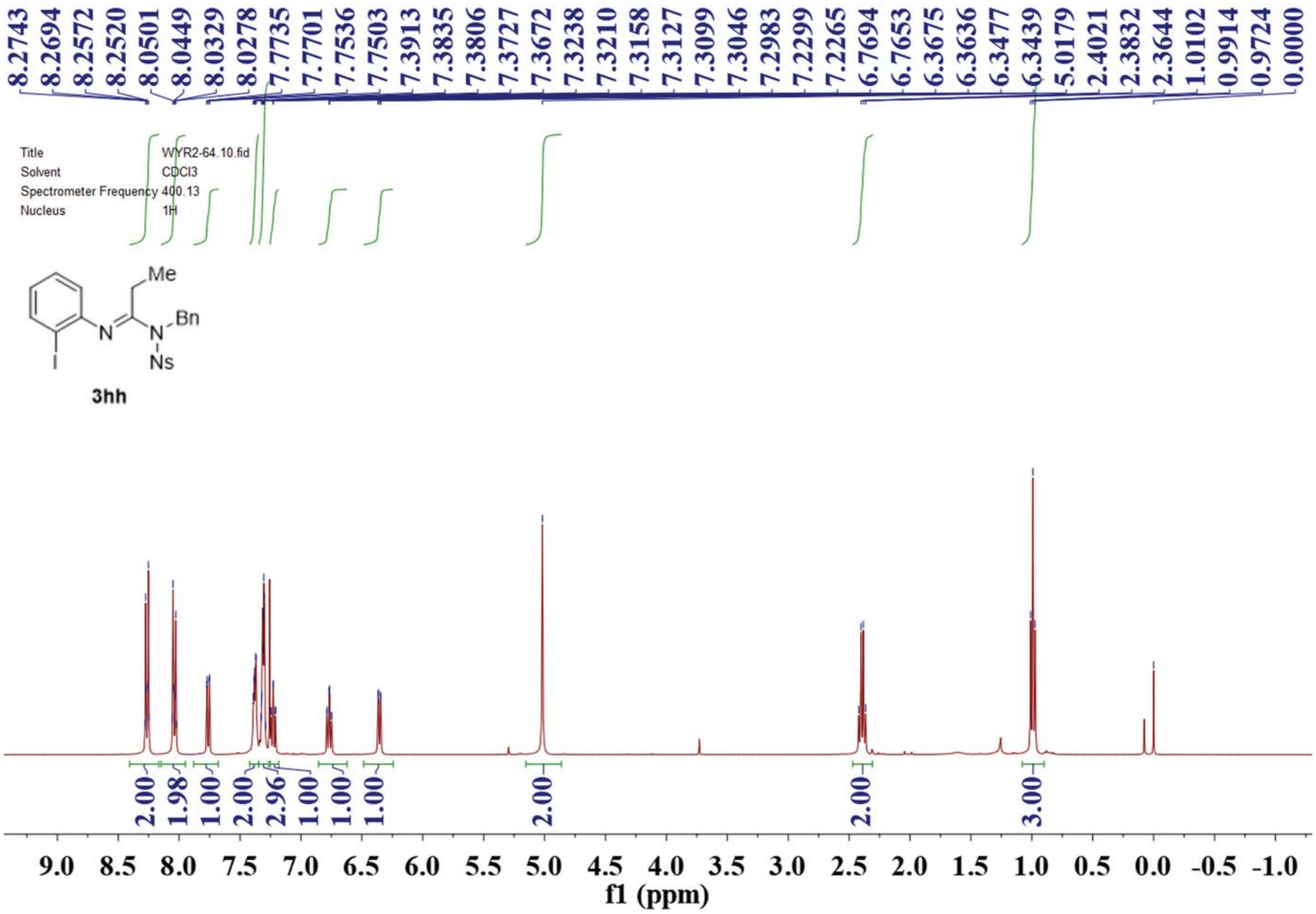
7.8689
7.8570
7.8521
7.7544
7.7510
7.7345
7.7312
7.4663
7.4612
7.4495
7.4446
7.4044
7.3996
7.3878
7.3842
7.3804
7.3030
7.2982
7.2887
7.2862
7.2839
7.2821
7.2775
7.1715
7.1681
7.1524
6.7179
6.7136
6.2109
6.2070
6.1914
6.1874
4.9668
2.4273
2.4086
2.3897
0.9486
0.9297
0.9109
Title WYR2-88.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
Cs
I
3gg
2.00
1.00
2.01
2.00
3.00
1.00
1.00
0.98
2.00
2.00
3.02
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 -0.5 -1.0
f1 (ppm)


160.681
149.757
139.772
139.098
138.194
136.553
129.657
129.441
129.062
128.749
128.464
127.766
124.925
119.588
89.904
77.518
77.200
76.882
51.221
25.783
11.460
Title WYR2-88/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Cs
I
3gg
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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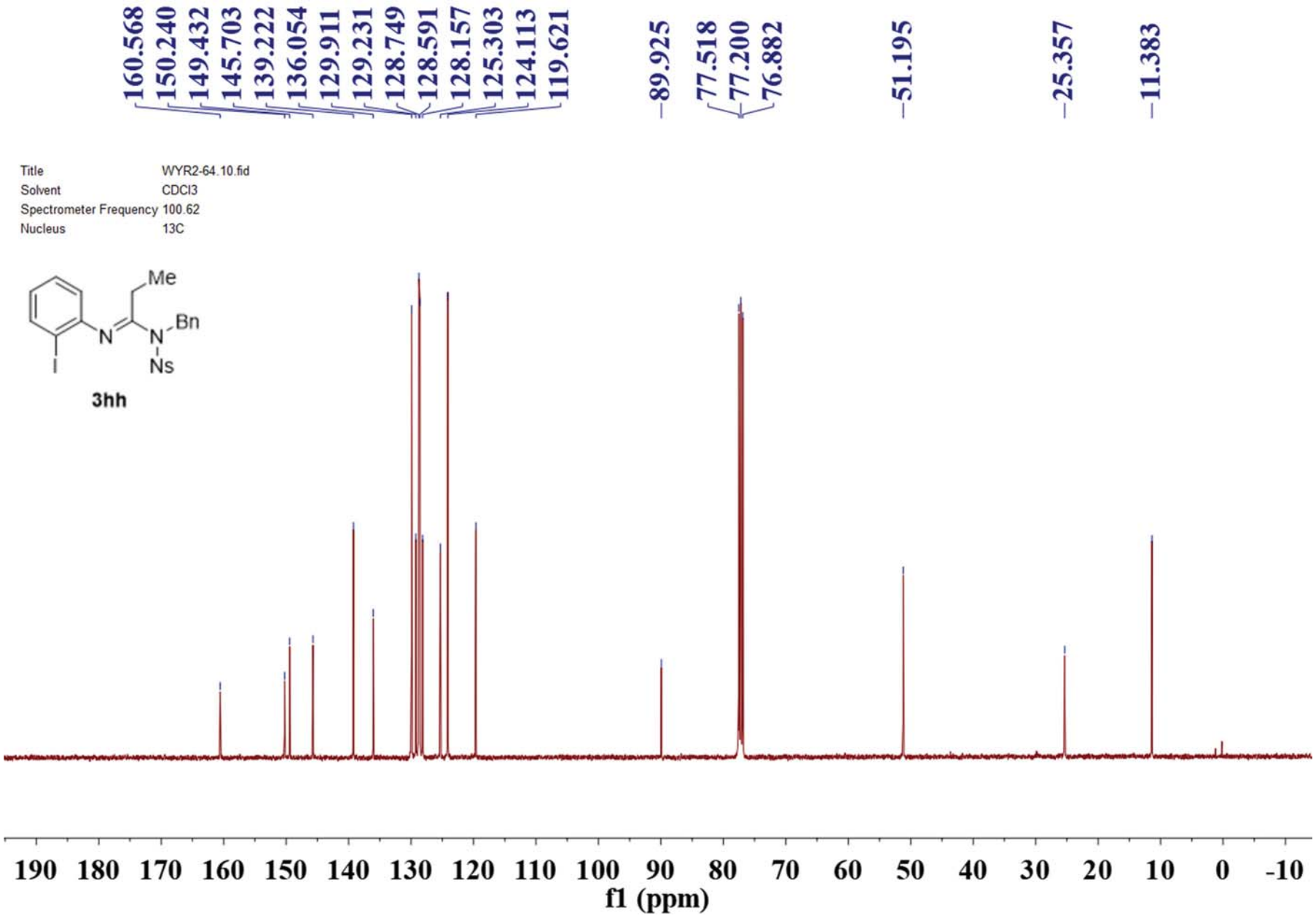
8.2694
8.2572
8.2520
8.0501
8.0449
8.0329
8.0278
7.7735
7.7701
7.7536
7.7503
7.3913
7.3835
7.3806
7.3727
7.3672
7.3238
7.3210
7.3158
7.3127
7.3099
7.3046
7.2983
7.2299
7.2265
6.7694
6.7653
6.3675
6.3636
6.3477
6.3439
5.0179
2.4021
2.3832
2.3644
1.0102
0.9914
0.9724
0.0000
Title WYR2-64.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
Ns
I
3hh
2.00
1.98
1.00
2.00
2.96
1.00
1.00
1.00
2.00
2.00
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 -0.5 -1.0
f1 (ppm)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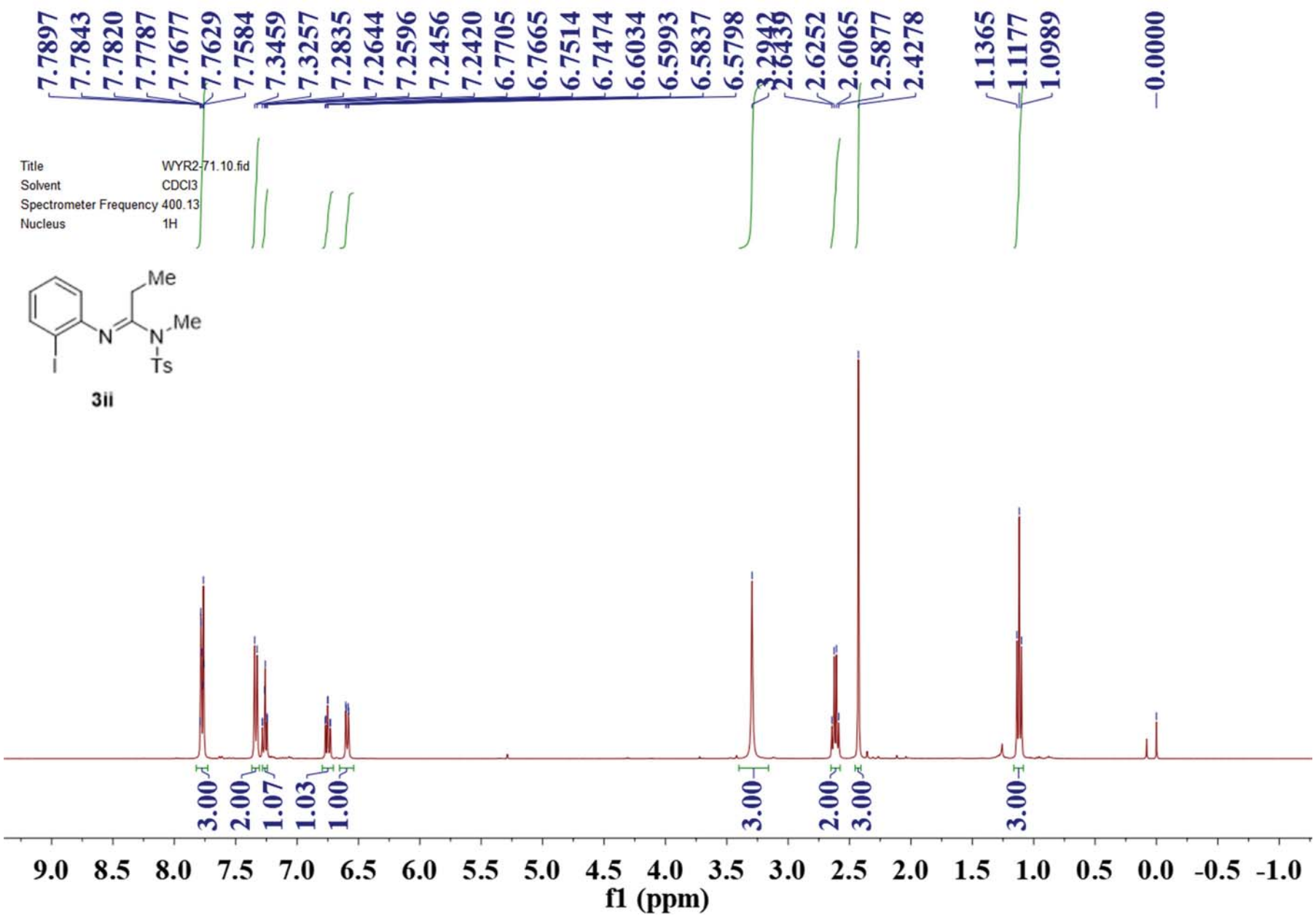
145.703
139.222
136.054
129.911
129.231
128.749
128.591
128.157
125.303
124.113
119.621
89.925
77.518
77.200
76.882
51.195
25.357
11.383
Title WYR2-64.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
Ns
I
3hh
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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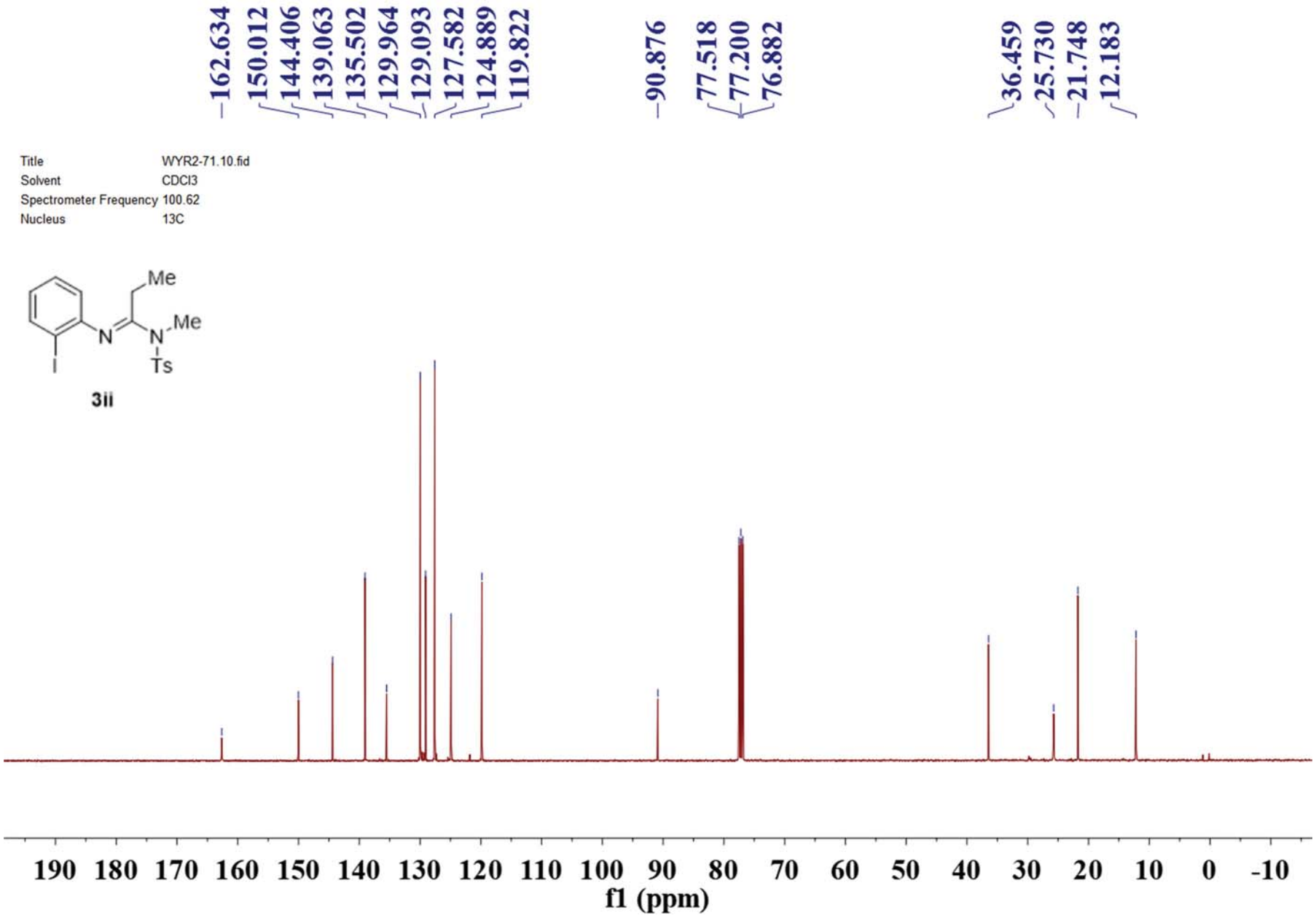
7.7820
7.7787
7.7677
7.7629
7.7584
7.3459
7.3257
7.2835
7.2644
7.2596
7.2456
7.2420
6.7705
6.7665
6.7514
6.7474
6.6034
6.5993
6.5837
6.5798
3.2942
3.2439
2.6252
2.6065
2.5877
2.4278
1.1365
1.1177
1.0989
0.0000
Title WYR2-71.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
N
Me
Ts
I
3ii
3.00
2.00
1.07
1.03
1.00
3.00
2.00
3.00
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 -0.5 -1.0
f1 (ppm)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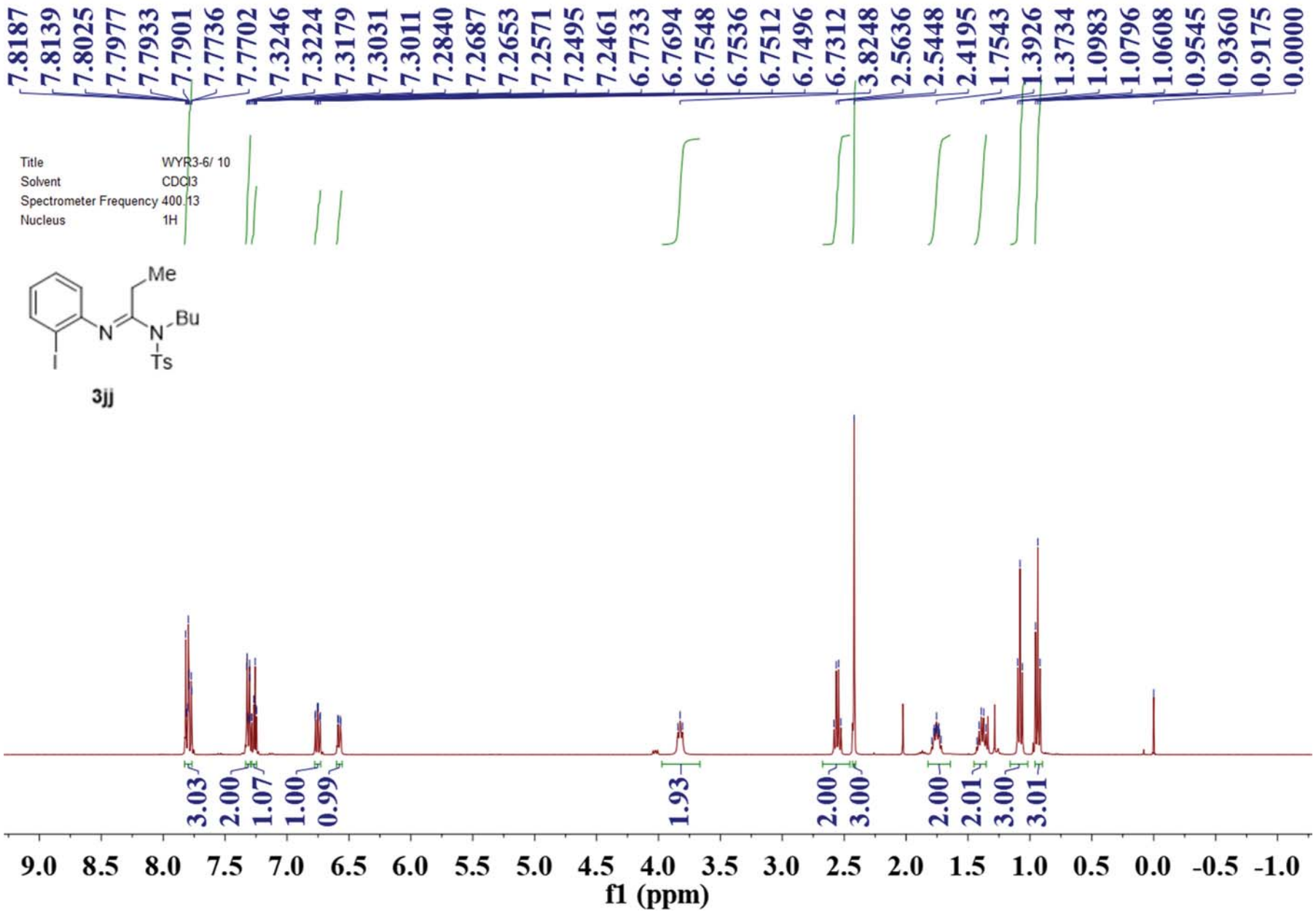
144.406
139.063
135.502
129.964
129.093
127.582
124.889
119.822
90.876
77.518
77.200
76.882
36.459
25.730
21.748
12.183
Title WYR2-71.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
N
Me
Ts
I
3ii
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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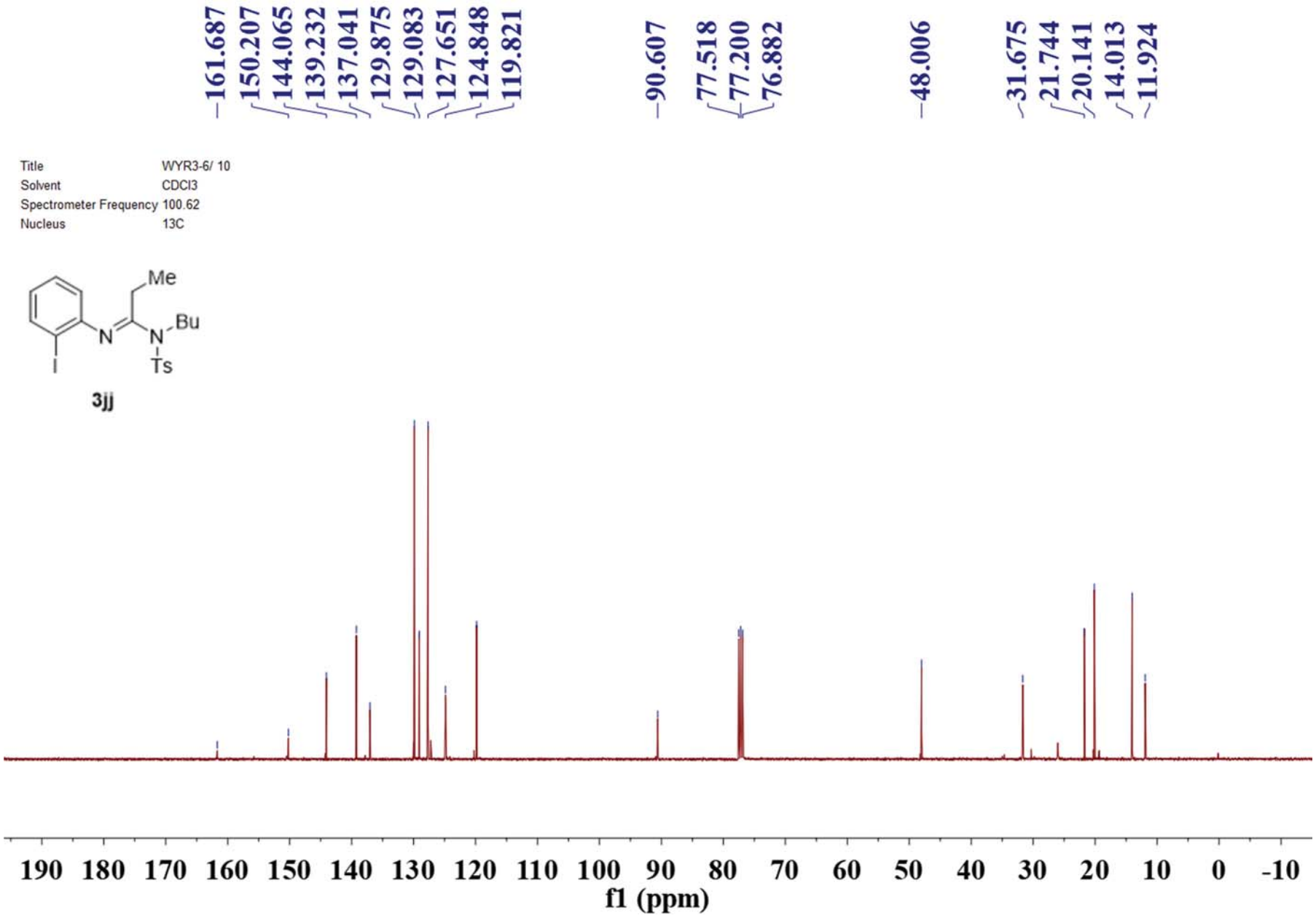
7.8139
7.8025
7.7977
7.7933
7.7901
7.7736
7.7702
7.3246
7.3224
7.3179
7.3031
7.3011
7.2840
7.2687
7.2653
7.2571
7.2495
7.2461
6.7733
6.7694
6.7548
6.7536
6.7512
6.7496
6.7312
3.8248
2.5636
2.5448
2.4195
1.7543
1.3926
1.3734
1.0983
1.0796
1.0608
0.9545
0.9360
0.9175
0.0000
Title WYR3-6/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bu
N
N
Ts
I
3jj
3.03
2.00
1.07
1.00
0.99
1.93
2.00
3.00
2.00
2.01
3.00
3.01
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 -0.5 -1.0
f1 (ppm)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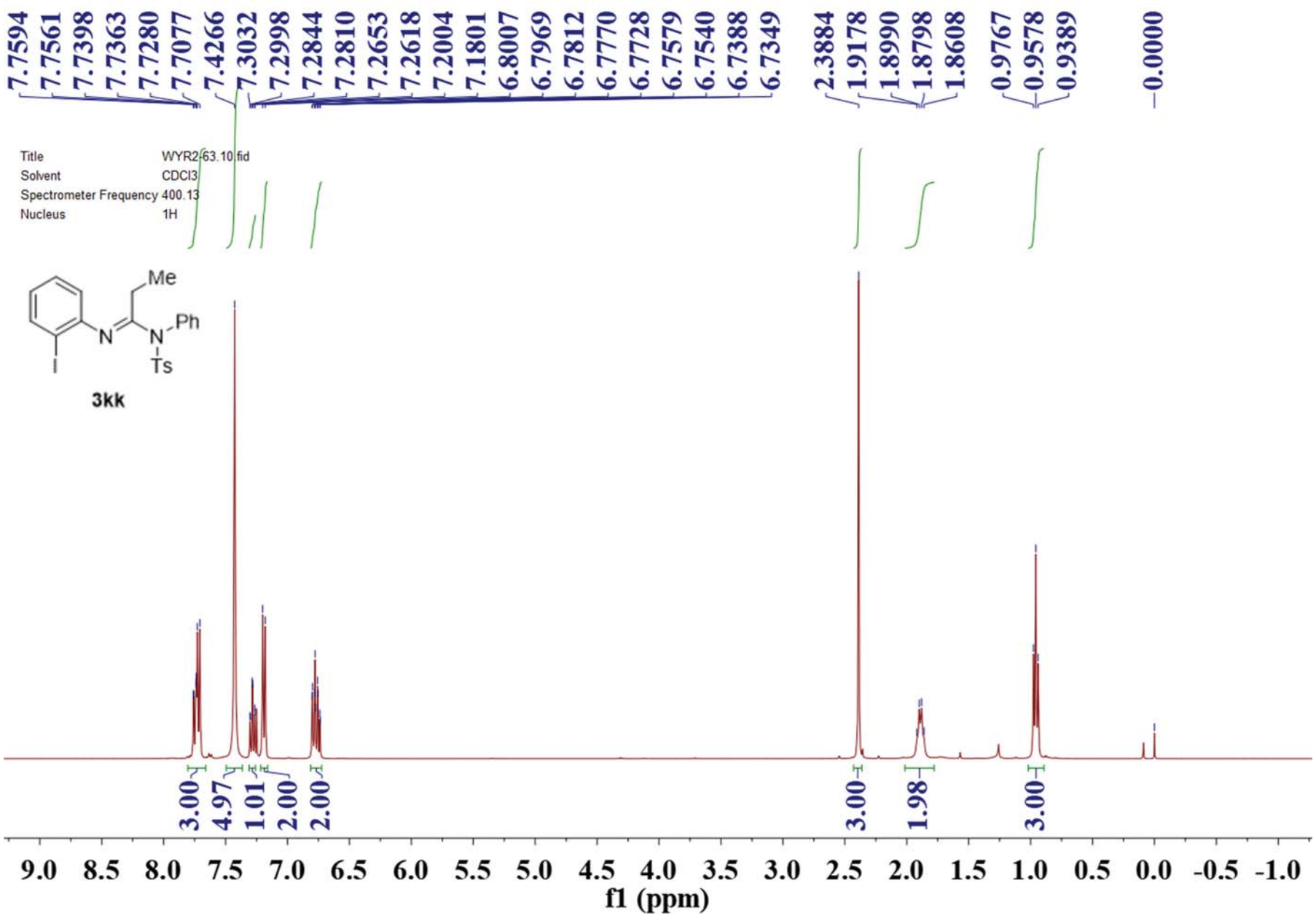
144.065
139.232
137.041
129.875
129.083
127.651
124.848
119.821
90.607
77.518
77.200
76.882
48.006
31.675
21.744
20.141
14.013
11.924
Title WYR3-6/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bu
N
N
Ts
I
3jj
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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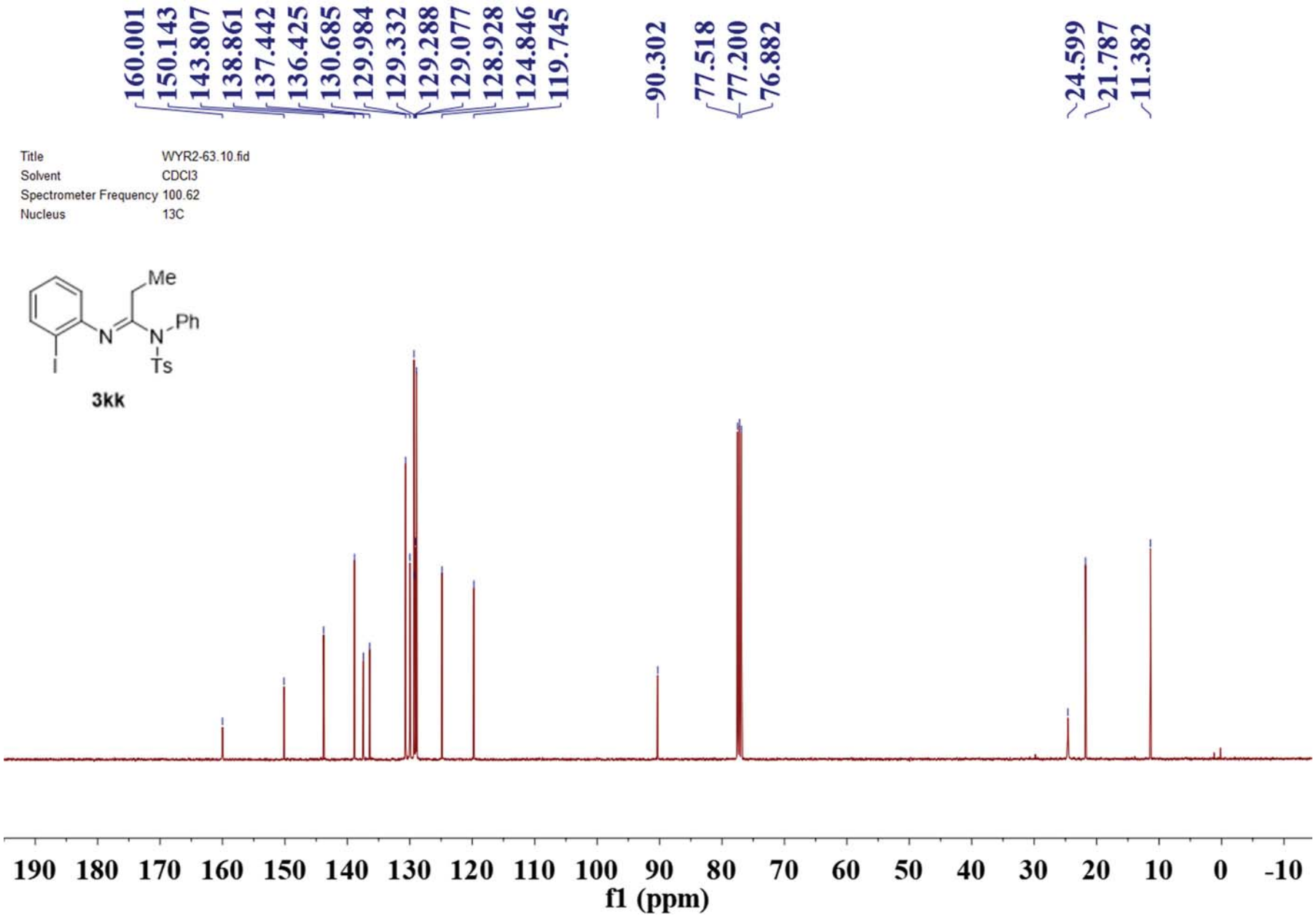
7.7363
7.7280
7.7077
7.4266
7.3032
7.2998
7.2844
7.2810
7.2653
7.2618
7.2004
7.1801
6.8007
6.7969
6.7812
6.7770
6.7728
6.7579
6.7540
6.7388
6.7349
2.3884
1.9178
1.8990
1.8798
1.8608
0.9767
0.9578
0.9389
-0.0000
Title WYR2-63.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ph
N
N
Ts
I
3kk
3.00
4.97
1.01
2.00
2.00
3.00
1.98
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 -0.5 -1.0
f1 (ppm)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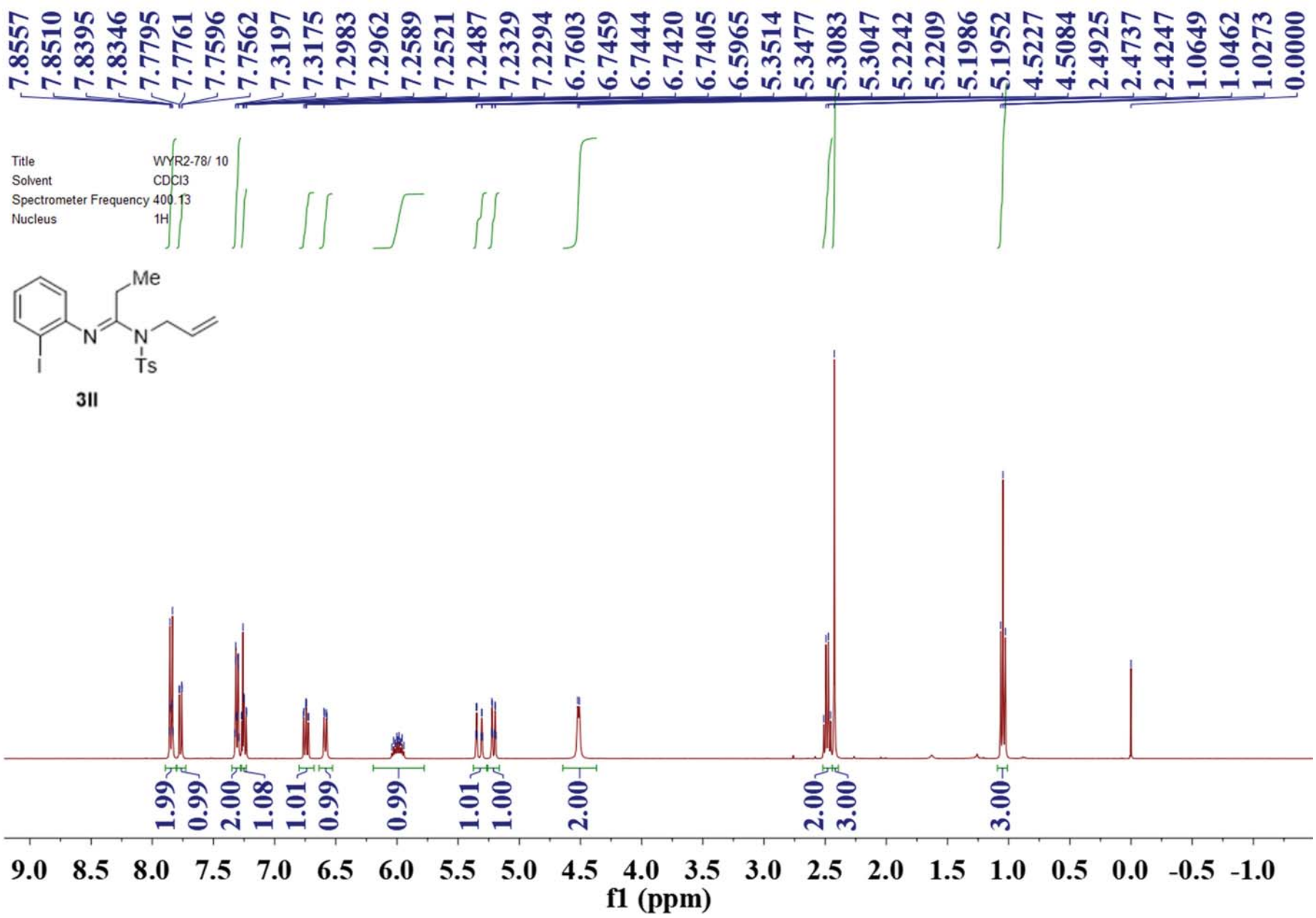
136.425
130.685
129.984
129.332
129.288
129.077
128.928
124.846
119.745
90.302
77.518
77.200
76.882
24.599
21.787
11.382
Title WYR2-63.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Ph
N
N
Ts
I
3kk
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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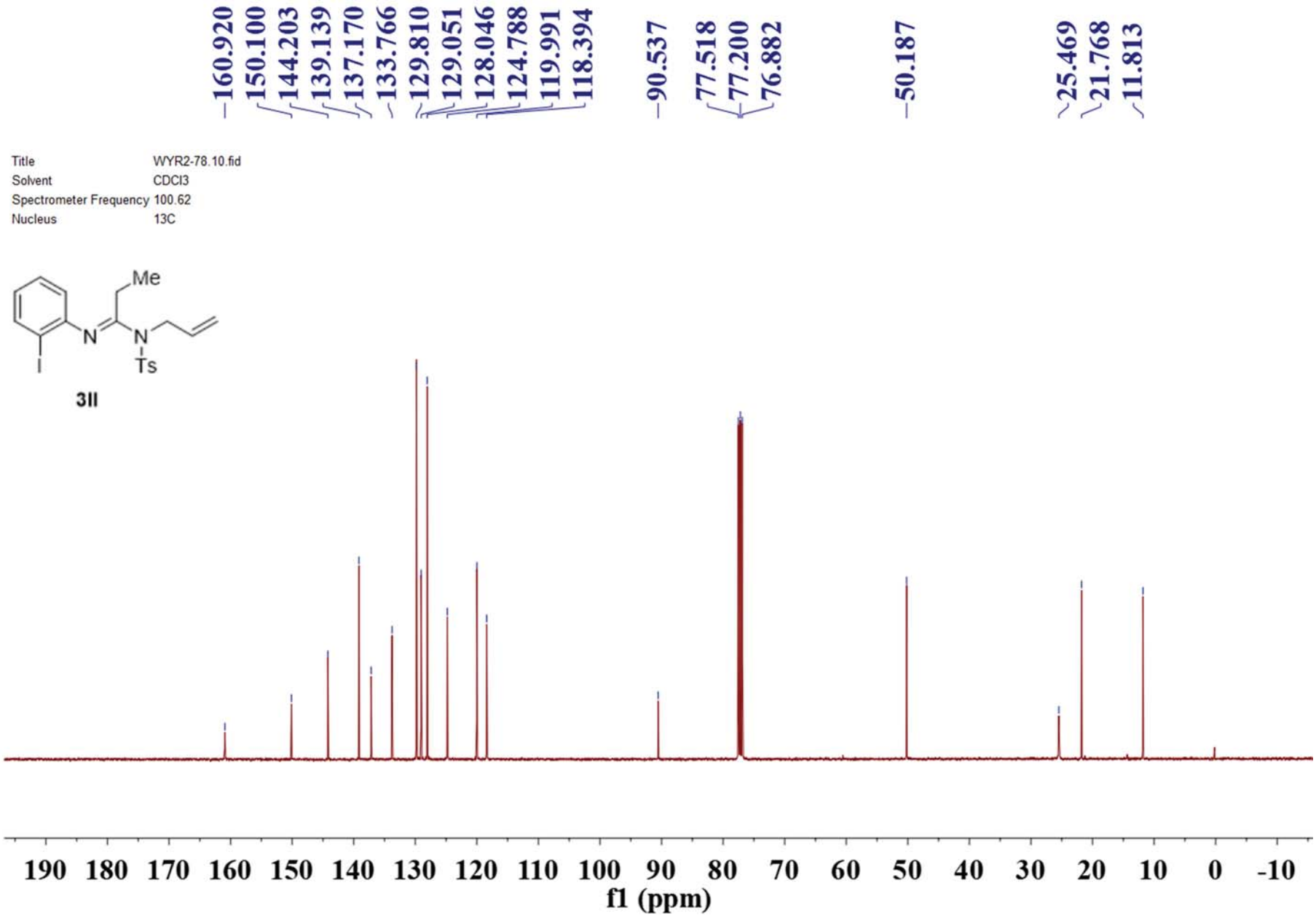
7.7761
7.7596
7.7562
7.3197
7.3175
7.2983
7.2962
7.2589
7.2521
7.2487
7.2329
7.2294
6.7603
6.7459
6.7444
6.7420
6.7405
6.5965
5.3514
5.3477
5.3083
5.3047
5.2242
5.2209
5.1986
5.1952
4.5227
4.5084
2.4925
2.4737
2.4247
1.0649
1.0462
1.0273
0.0000
Title WYR2-78/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
N
Ts
I
3ll
1.99
0.99
2.00
1.08
1.01
0.99
0.99
1.01
1.00
2.00
2.00
3.00
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 -0.5 -1.0
f1 (ppm)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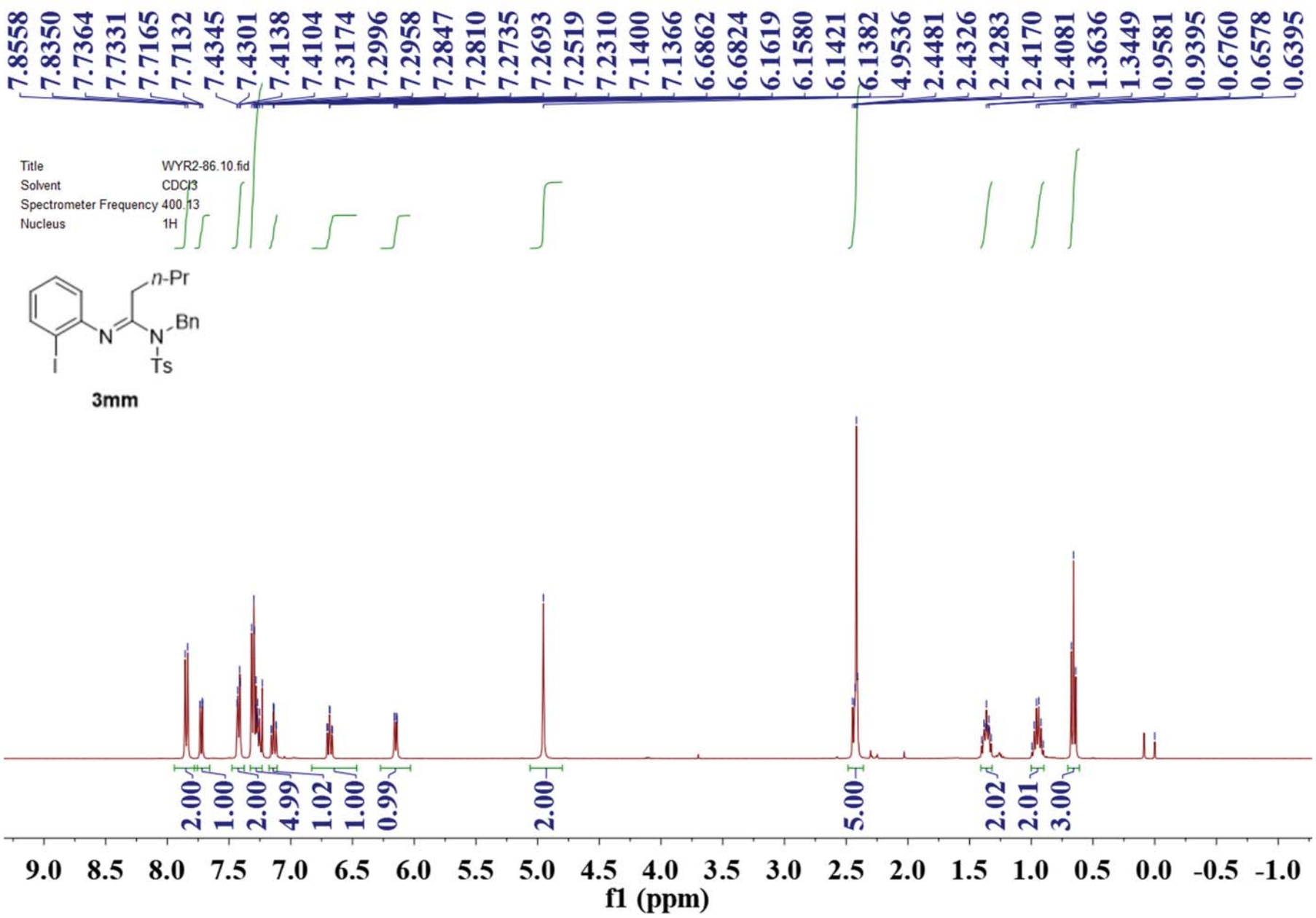
137.170
133.766
129.810
129.051
128.046
124.788
119.991
118.394
90.537
77.518
77.200
76.882
50.187
25.469
21.768
11.813
Title WYR2-78.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
N
Ts
I
3ll
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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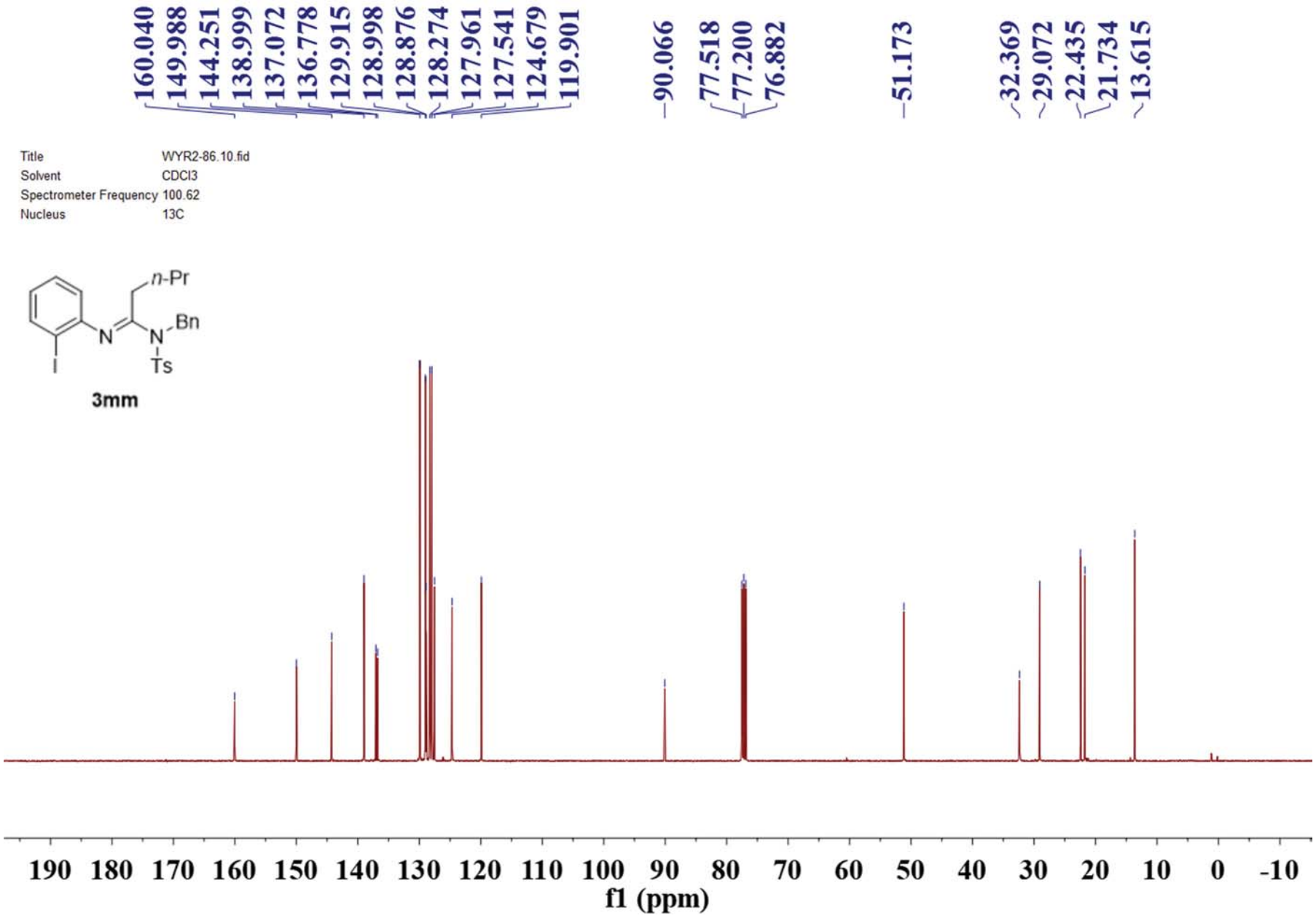
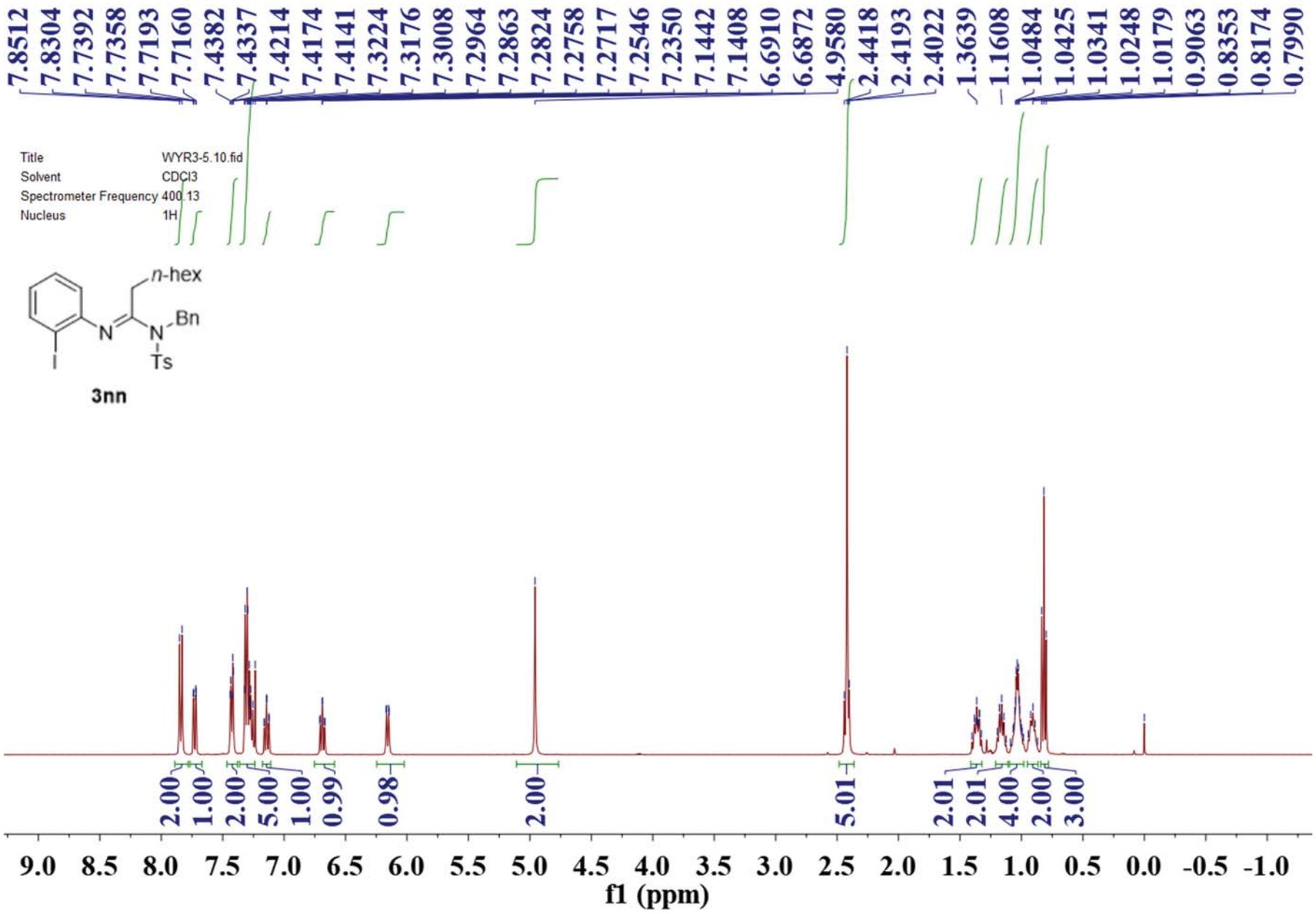
7.7165
7.7132
7.4345
7.4301
7.4138
7.4104
7.3174
7.2996
7.2958
7.2847
7.2810
7.2735
7.2693
7.2519
7.2310
7.1400
7.1366
6.6862
6.6824
6.1619
6.1580
6.1421
6.1382
4.9536
2.4481
2.4326
2.4283
2.4170
2.4081
1.3636
1.3449
0.9581
0.9395
0.6760
0.6578
0.6395
Title WYR2-86.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-Pr
N
N
Bn
Ts
I
3mm
2.00
1.00
2.00
4.99
1.02
1.00
0.99
2.00
5.00
2.02
2.01
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 -0.5 -1.0
f1 (ppm)


160.040
149.988
144.251
138.999
137.072
136.778
129.915
128.998
128.876
128.274
127.961
127.541
124.679
119.901
90.066
77.518
77.200
76.882
51.173
32.369
29.072
22.435
21.734
13.615
Title WYR2-86.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-Pr
N
N
Bn
Ts
I
3mm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7392
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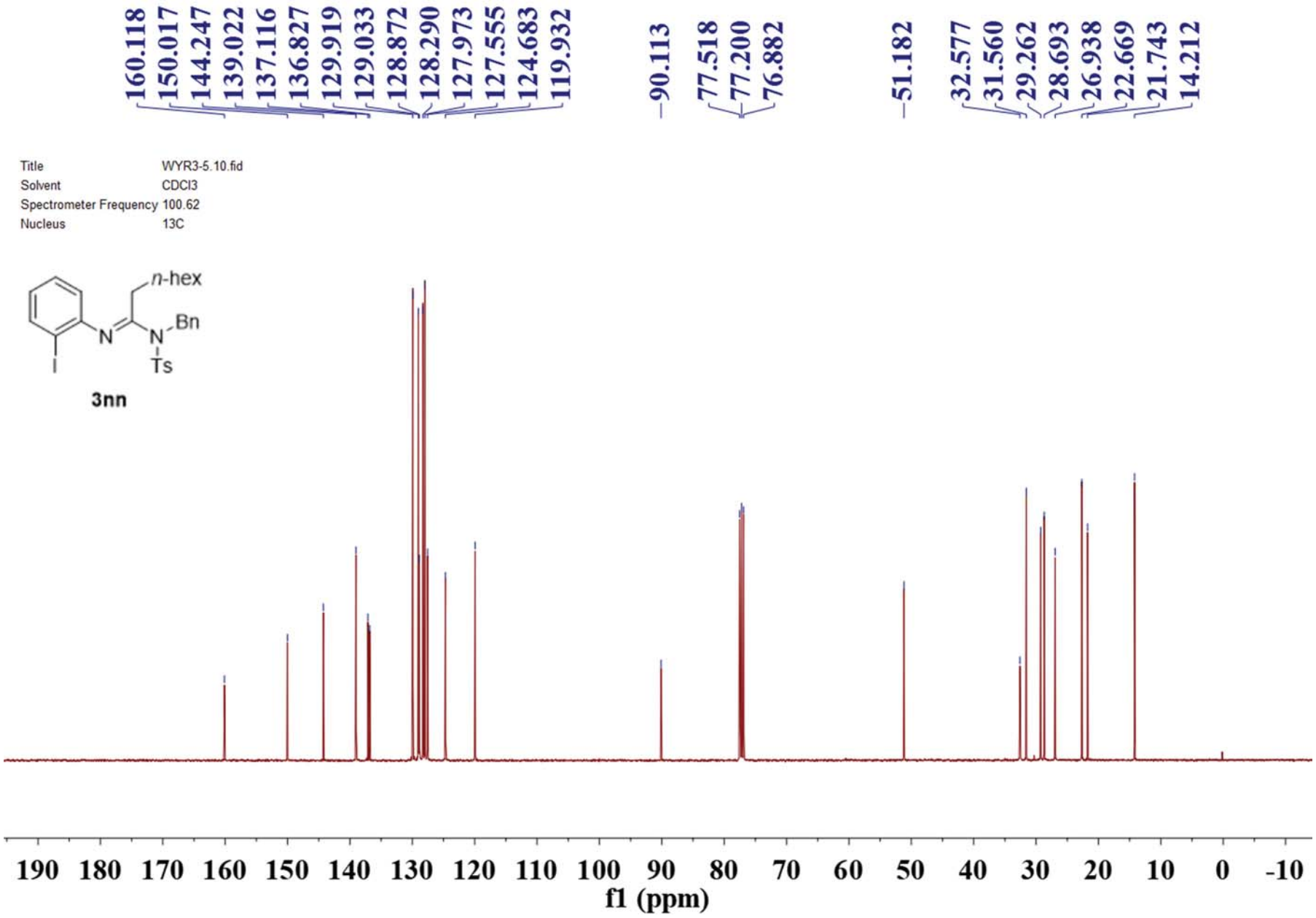
7.7193
7.7160
7.4382
7.4337
7.4214
7.4174
7.4141
7.3224
7.3176
7.3008
7.2964
7.2863
7.2824
7.2758
7.2717
7.2546
7.2350
7.1442
7.1408
6.6910
6.6872
4.9580
2.4418
2.4193
2.4022
1.3639
1.1608
1.0484
1.0425
1.0341
1.0248
1.0179
0.9063
0.8353
0.8174
0.7990
Title WYR3-5.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
Bn
N
N
Ts
I
3nn
2.00
1.00
2.00
5.00
1.00
0.99
0.98
2.00
5.01
2.01
2.01
4.00
2.00
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 -0.5 -1.0
f1 (ppm)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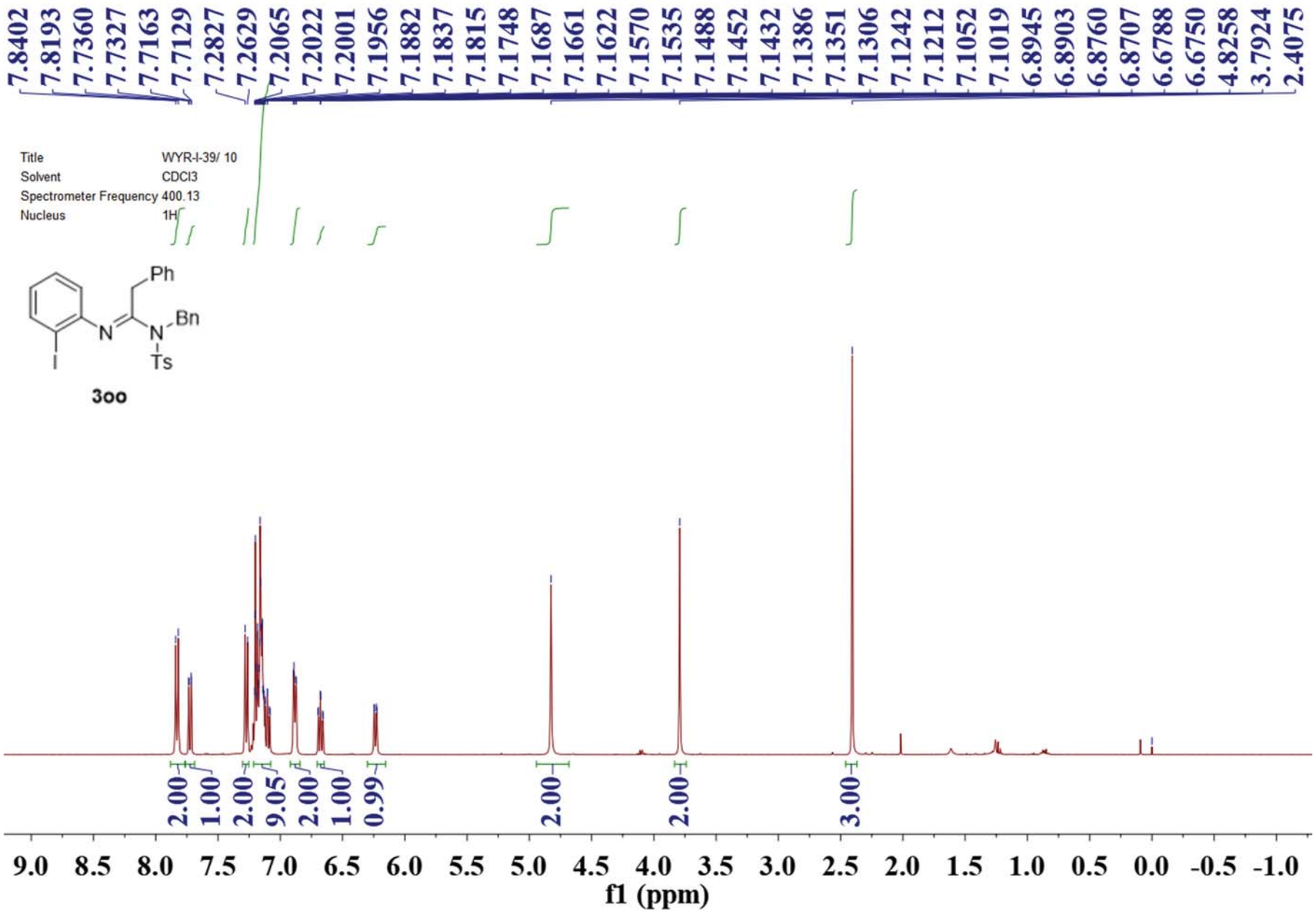
150.017
144.247
139.022
137.116
136.827
129.919
129.033
128.872
128.290
127.973
127.555
124.683
119.932
90.113
77.518
77.200
76.882
51.182
32.577
31.560
29.262
28.693
26.938
22.669
21.743
14.212
Title WYR3-5.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
Bn
N
N
Ts
I
3nn
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7360
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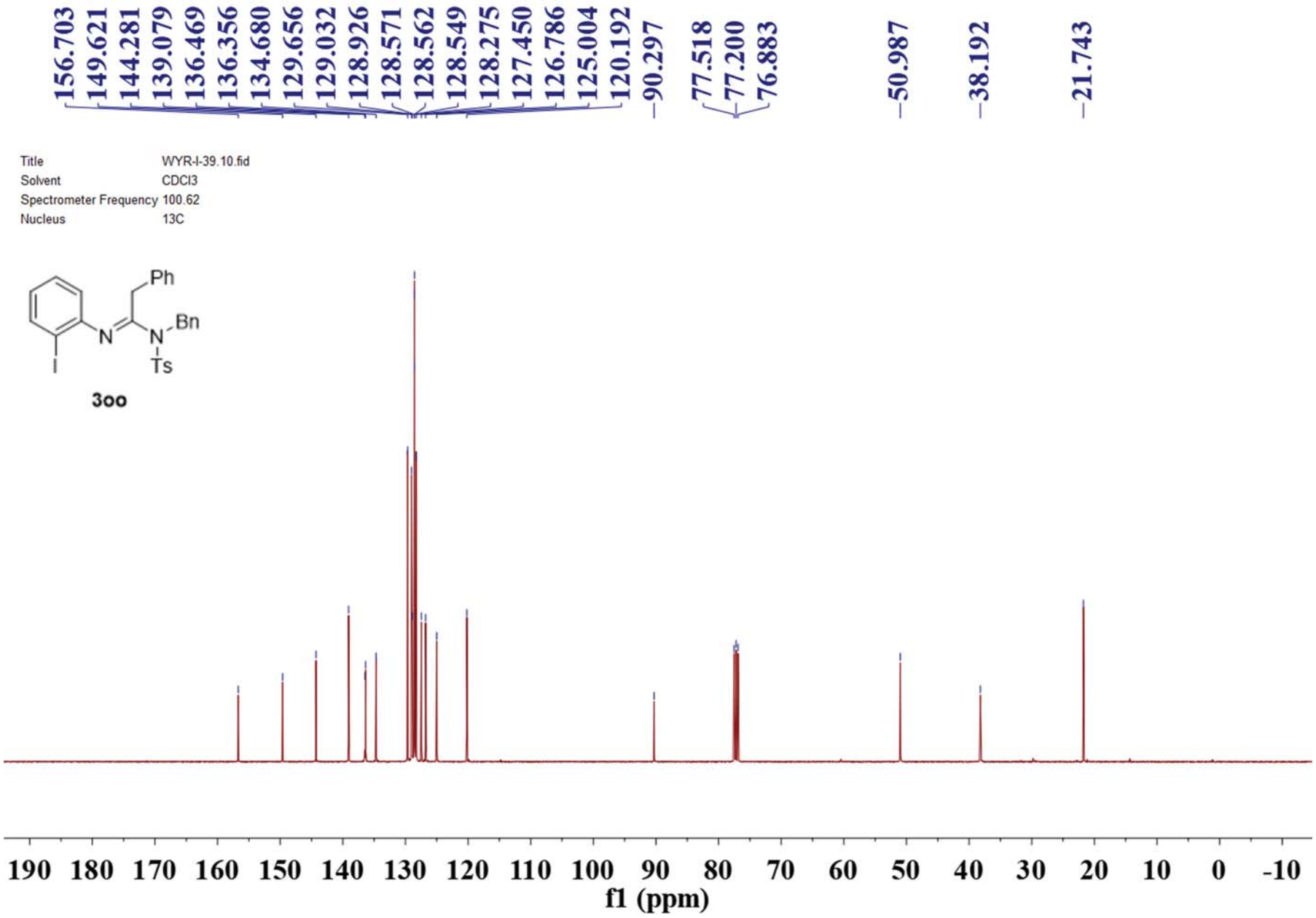
7.7163
7.7129
7.2827
7.2629
7.2065
7.2022
7.2001
7.1956
7.1882
7.1837
7.1815
7.1748
7.1687
7.1661
7.1622
7.1570
7.1535
7.1488
7.1452
7.1432
7.1386
7.1351
7.1306
7.1242
7.1212
7.1052
7.1019
6.8945
6.8903
6.8760
6.8707
6.6788
6.6750
4.8258
3.7924
2.4075
Title WYR-I-39/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
Bn
N
N
Ts
I
3oo
2.00
1.00
2.00
9.05
2.00
1.00
0.99
2.00
2.00
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 -0.5 -1.0
f1 (ppm)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149.621
144.281
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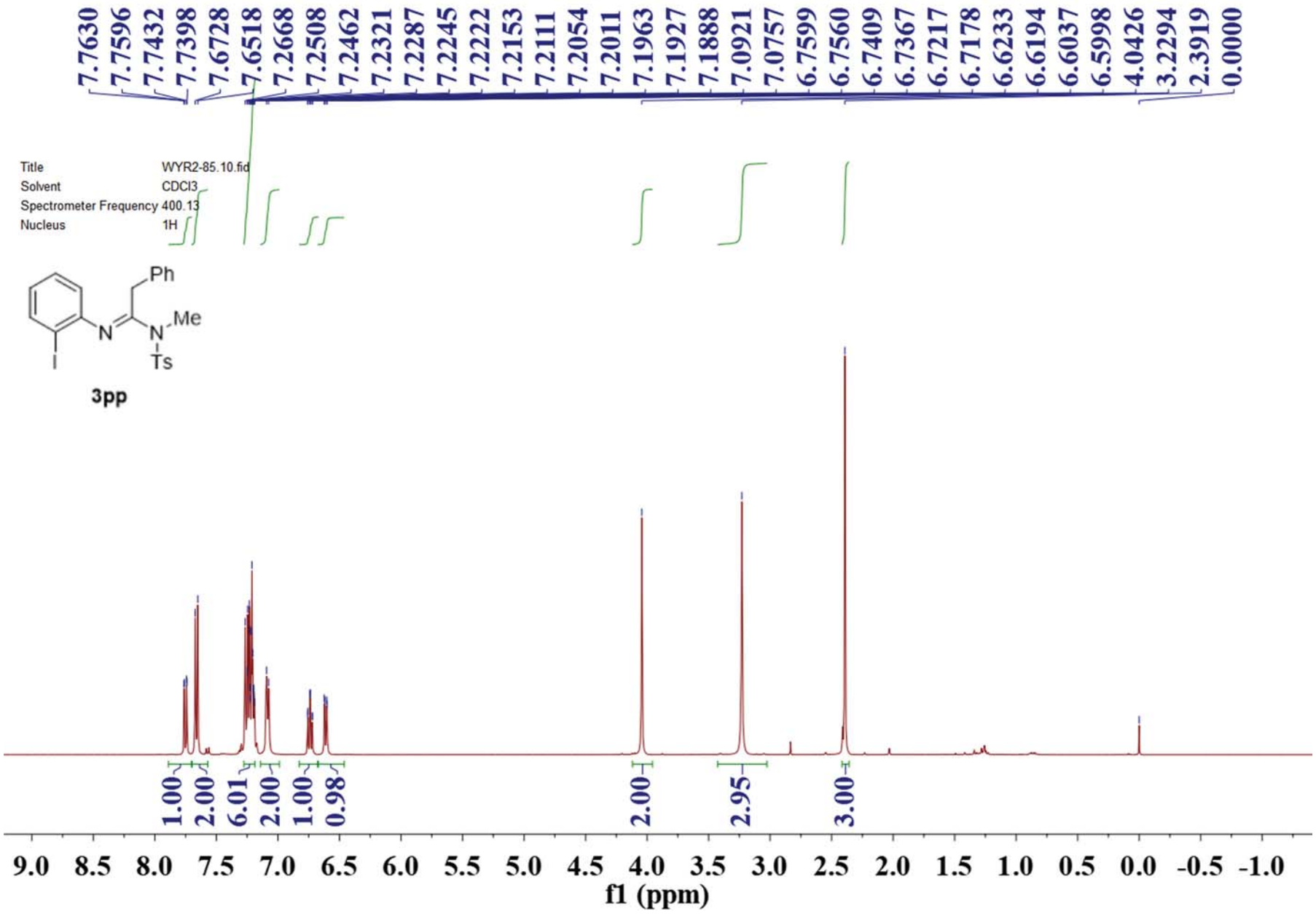
134.680
129.656
129.032
128.926
128.571
128.562
128.549
128.275
127.450
126.786
125.004
120.192
90.297
77.518
77.200
76.883
50.987
38.192
21.743
Title WYR-I-39.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
N
Bn
Ts
I
3oo
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7432
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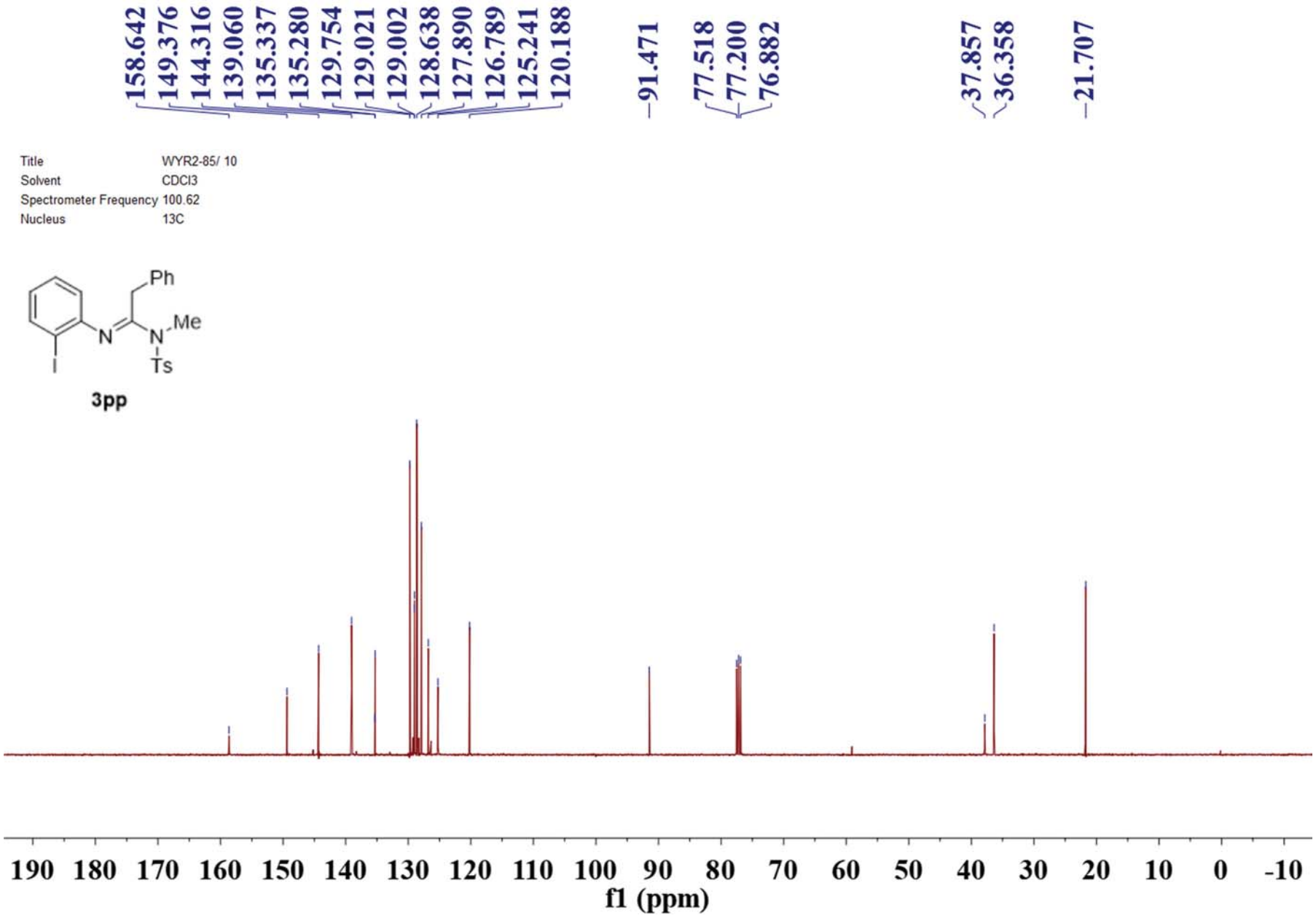
7.6728
7.6518
7.2668
7.2508
7.2462
7.2321
7.2287
7.2245
7.2222
7.2153
7.2111
7.2054
7.2011
7.1963
7.1927
7.1888
7.0921
7.0757
6.7599
6.7560
6.7409
6.7367
6.7217
6.7178
6.6233
6.6194
6.6037
6.5998
4.0426
3.2294
2.3919
0.0000
Title WYR2-85.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
N
Me
Ts
I
3pp
1.00
2.00
6.01
2.00
1.00
0.98
2.00
2.95
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 -0.5 -1.0
f1 (ppm)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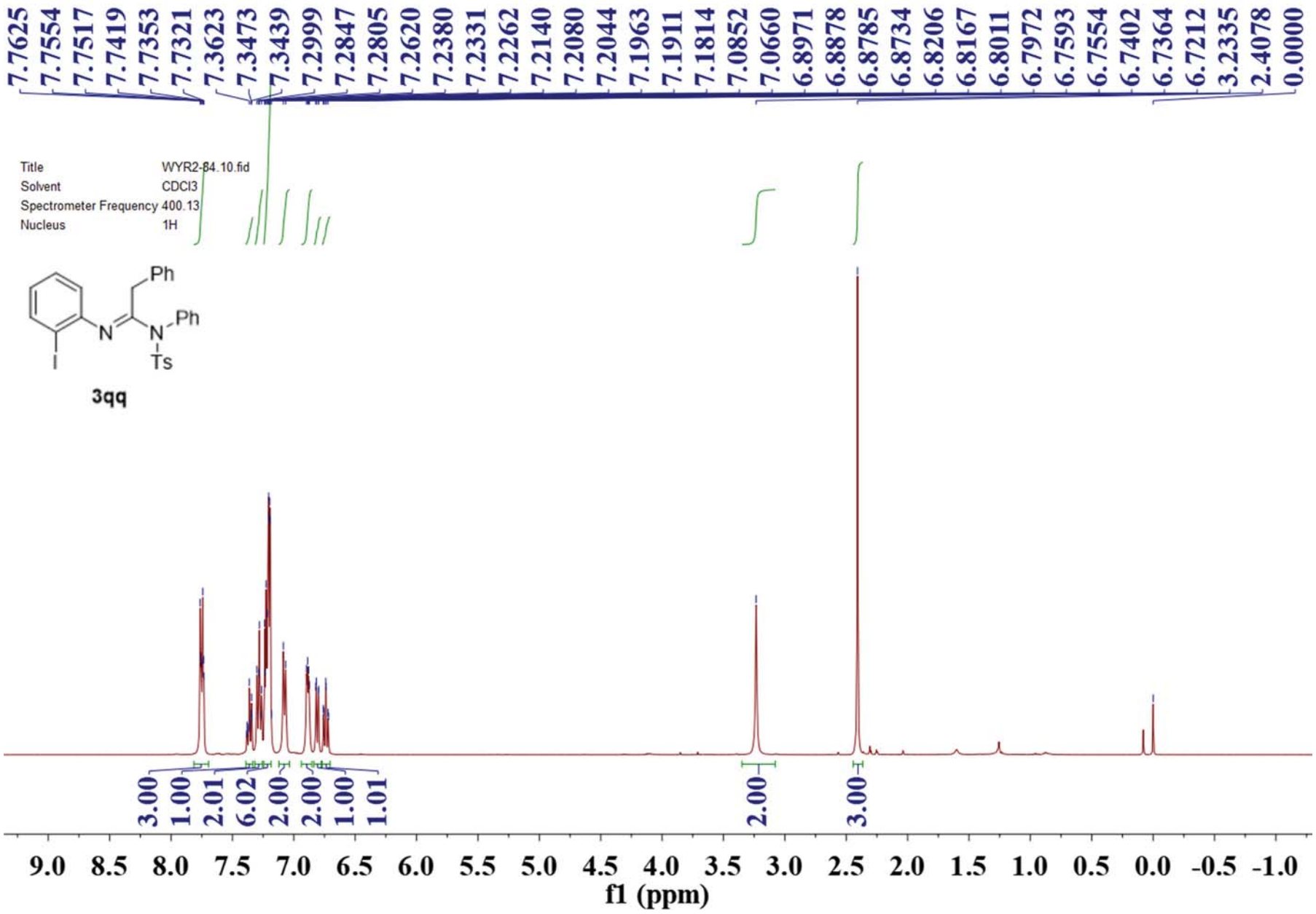
149.376
144.316
139.060
135.337
135.280
129.754
129.021
129.002
128.638
127.890
126.789
125.241
120.188
91.471
77.518
77.200
76.882
37.857
36.358
21.707
Title WYR2-85/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
N
Me
Ts
I
3pp
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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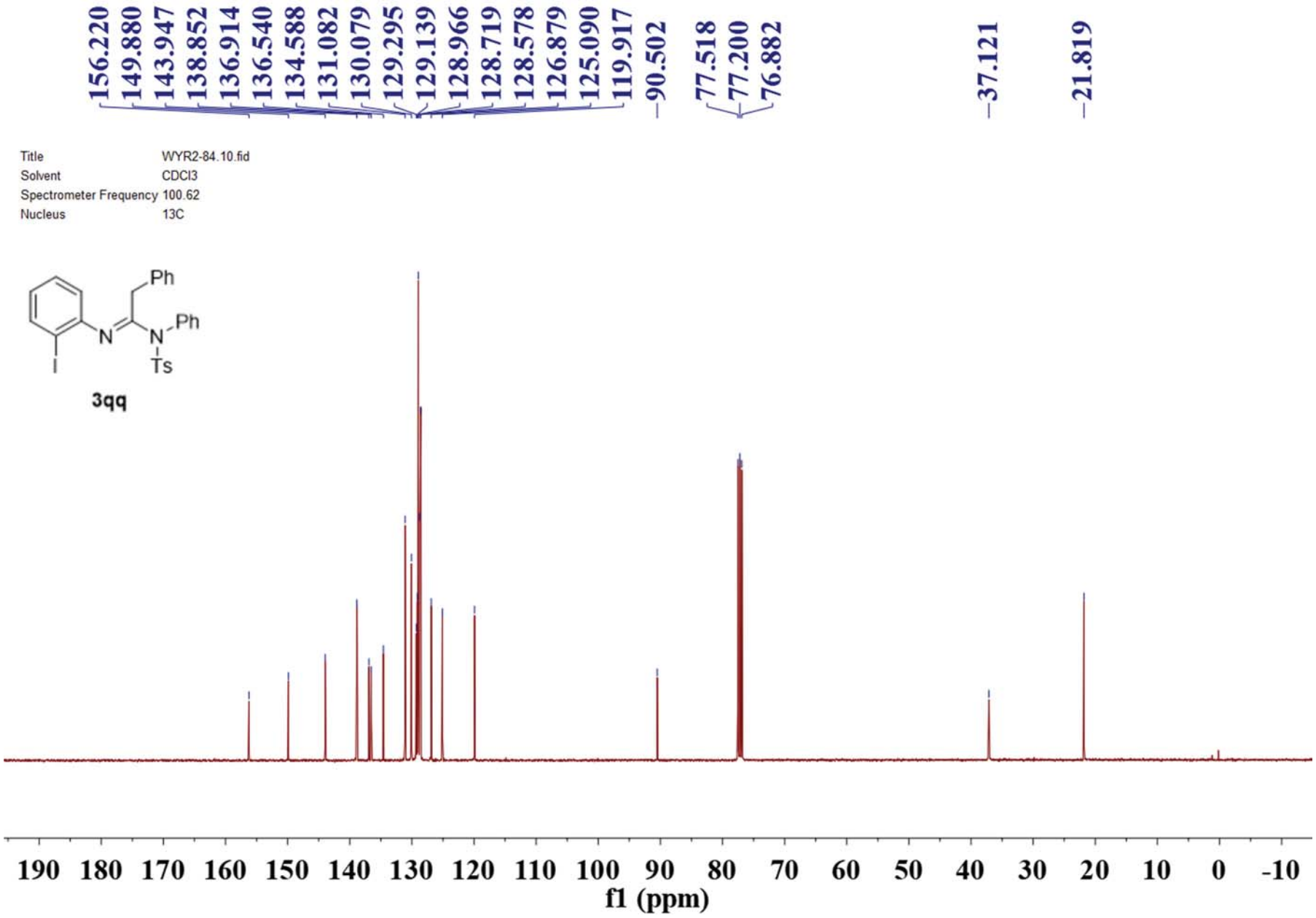
7.7517
7.7419
7.7353
7.7321
7.3623
7.3473
7.3439
7.2999
7.2847
7.2805
7.2620
7.2380
7.2331
7.2262
7.2140
7.2080
7.2044
7.1963
7.1911
7.1814
7.0852
7.0660
6.8971
6.8878
6.8785
6.8734
6.8206
6.8167
6.8011
6.7972
6.7593
6.7554
6.7402
6.7364
6.7212
3.2335
2.4078
0.0000
Title WYR2-84.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
N
Ph
Ts
I
3qq
3.00
1.00
2.01
6.02
2.00
2.00
1.00
1.01
2.00
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 -0.5 -1.0
f1 (ppm)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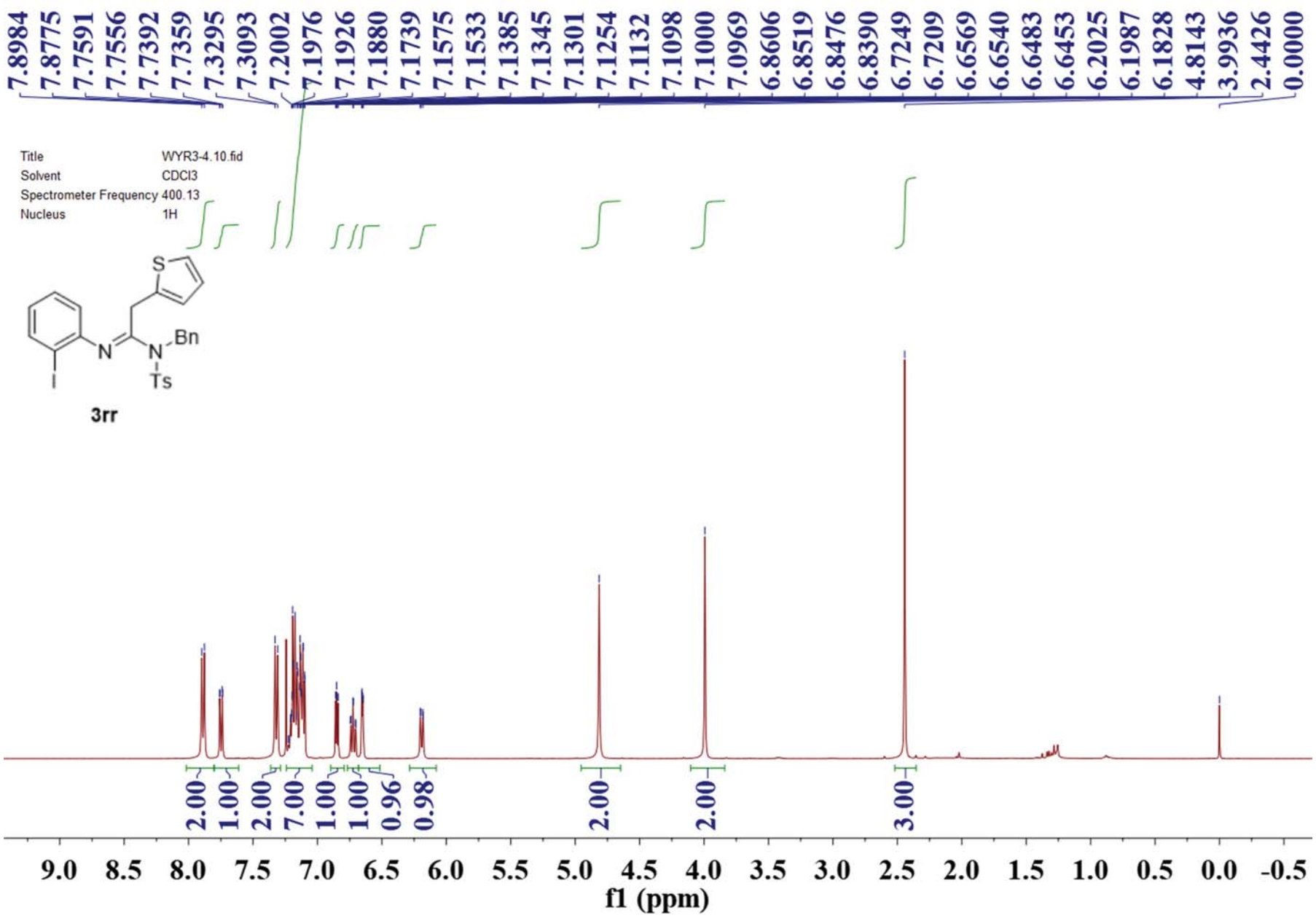
136.540
134.588
131.082
130.079
129.295
129.139
128.966
128.719
128.578
126.879
125.090
119.917
90.502
77.518
77.200
76.882
37.121
21.819
Title WYR2-84.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
N
Ph
Ts
I
3qq
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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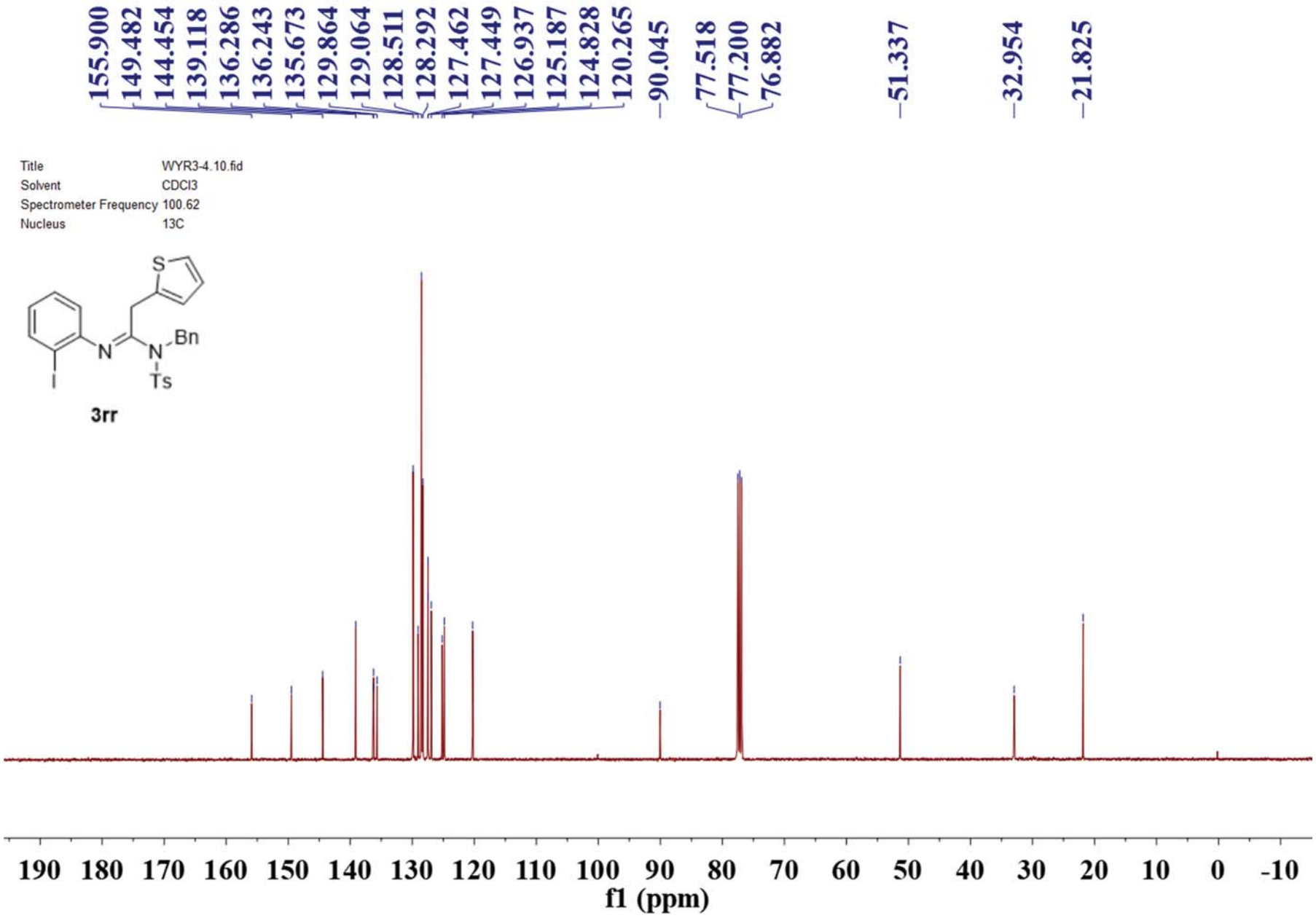
7.7556
7.7392
7.7359
7.3295
7.3093
7.2002
7.1976
7.1926
7.1880
7.1739
7.1575
7.1533
7.1385
7.1345
7.1301
7.1254
7.1132
7.1098
7.1000
7.0969
6.8606
6.8519
6.8476
6.8390
6.7249
6.7209
6.6569
6.6540
6.6483
6.6453
6.2025
6.1987
6.1828
4.8143
3.9936
2.4426
0.0000
Title WYR3-4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
S
N
N
Bn
Ts
I
3rr
2.00
1.00
2.00
7.00
1.00
1.00
0.96
0.98
2.00
2.00
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 -0.5
f1 (ppm)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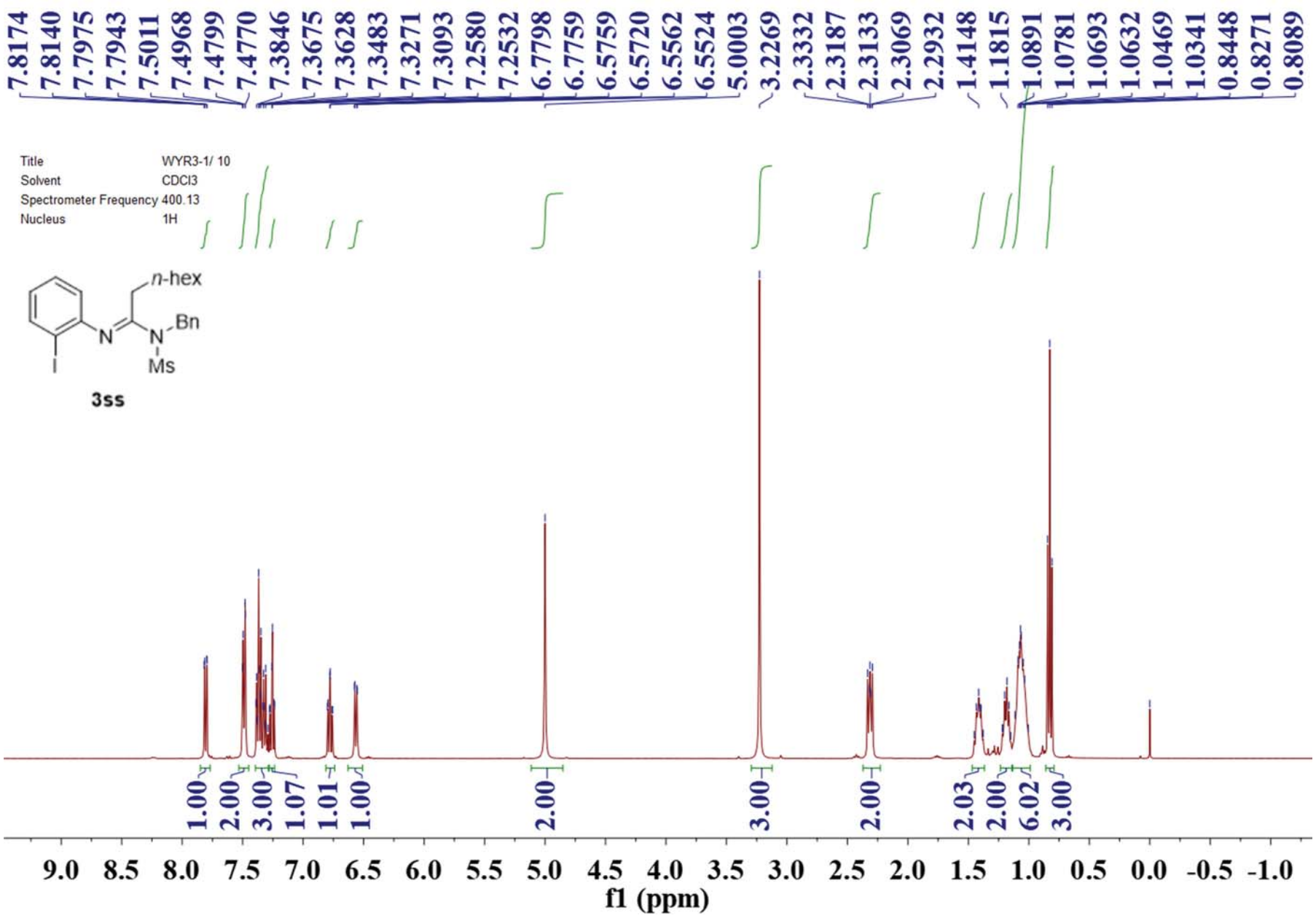
128.511
128.292
127.462
127.449
126.937
125.187
124.828
120.265
90.045
77.518
77.200
76.882
51.337
32.954
21.825
Title WYR3-4.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
S
N
N
Bn
Ts
I
3rr
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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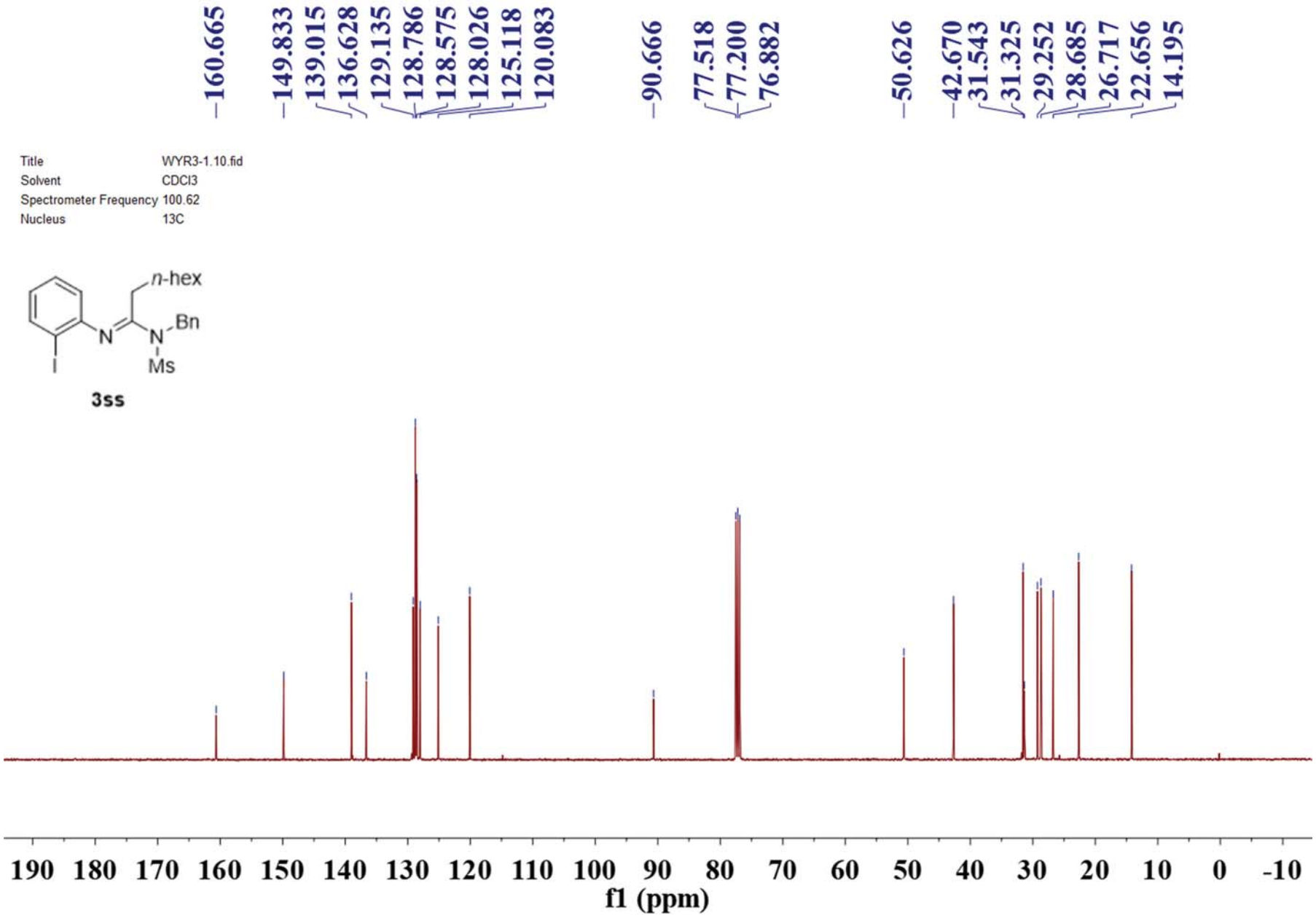
7.4799
7.4770
7.3846
7.3675
7.3628
7.3483
7.3271
7.3093
7.2580
7.2532
6.7798
6.7759
6.5759
6.5720
6.5562
6.5524
5.0003
3.2269
2.3332
2.3187
2.3133
2.3069
2.2932
1.4148
1.1815
1.0891
1.0781
1.0693
1.0632
1.0469
1.0341
0.8448
0.8271
0.8089
Title WYR3-1/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
Bn
N
N
Ms
I
3ss
1.00
2.00
3.00
1.07
1.01
1.00
2.00
3.00
2.00
2.03
2.00
6.02
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 -0.5 -1.0
f1 (ppm)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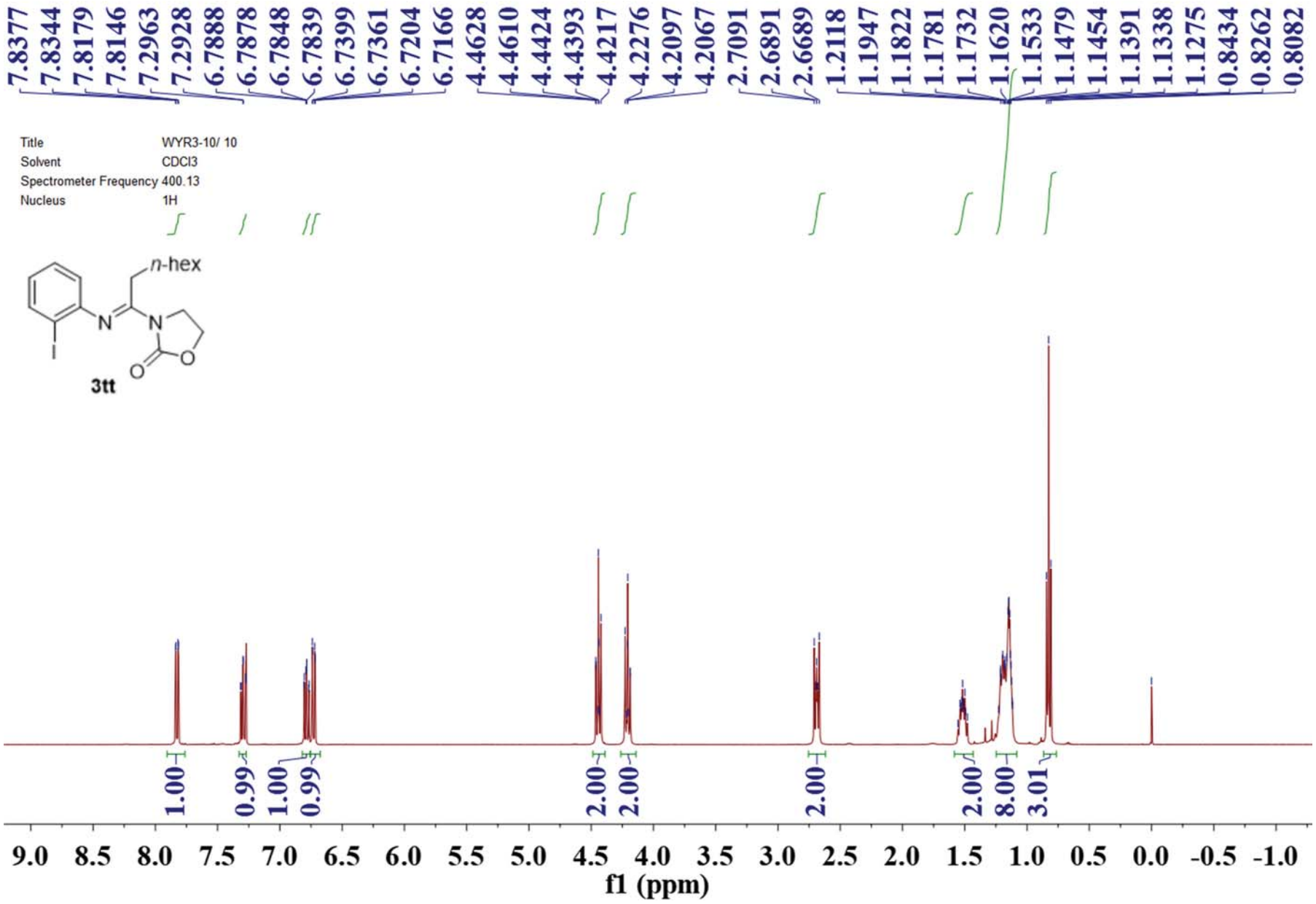
128.786
128.575
128.026
125.118
120.083
90.666
77.518
77.200
76.882
50.626
42.670
31.543
31.325
29.252
28.685
26.717
22.656
14.195
Title WYR3-1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
Bn
N
N
Ms
I
3ss
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.8146
7.2963
7.2928
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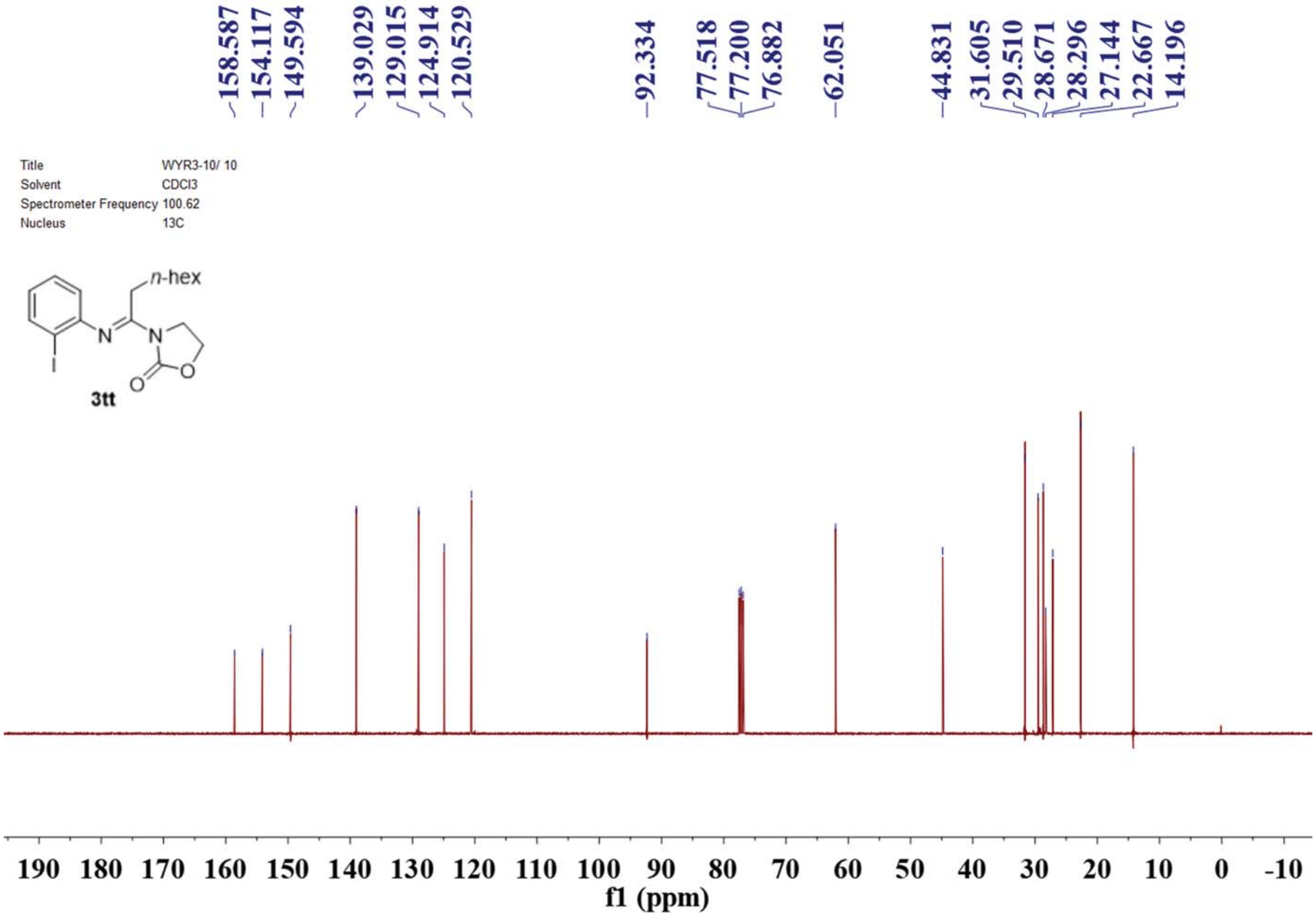
6.7878
6.7848
6.7839
6.7399
6.7361
6.7204
6.7166
4.4628
4.4610
4.4424
4.4393
4.4217
4.2276
4.2097
4.2067
2.7091
2.6891
2.6689
1.2118
1.1947
1.1822
1.1781
1.1732
1.1620
1.1533
1.1479
1.1454
1.1391
1.1338
1.1275
0.8434
0.8262
0.8082
Title WYR3-10/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
N
N
O
O
I
3tt
1.00
0.99
1.00
0.99
2.00
2.00
2.00
2.00
8.00
3.01
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 -0.5 -1.0
f1 (ppm)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139.029
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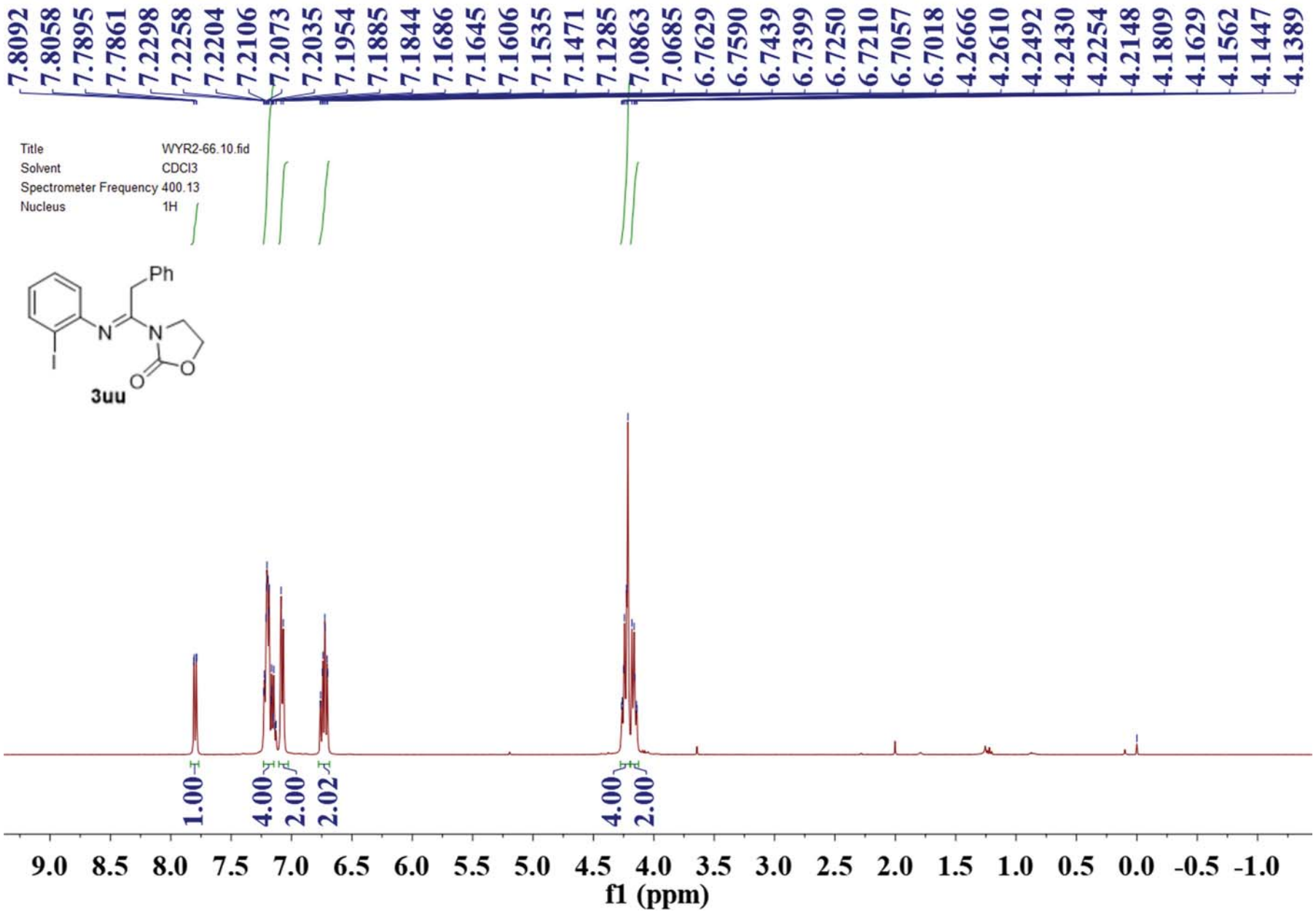
124.914
120.529
92.334
77.518
77.200
76.882
62.051
44.831
31.605
29.510
28.671
28.296
27.144
22.667
14.196
Title WYR3-10/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
N
N
I
O
O
3tt
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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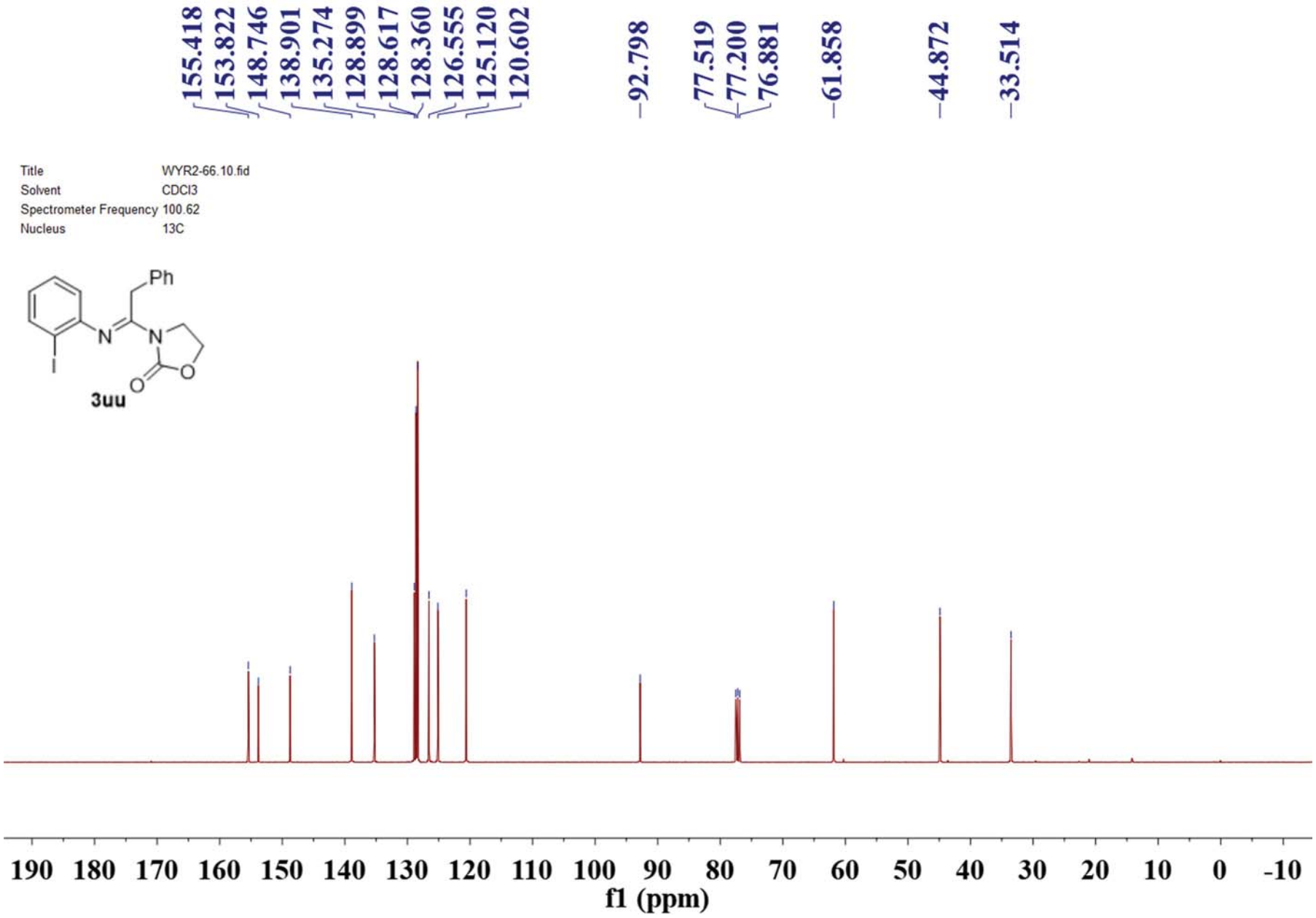
7.2298
7.2258
7.2204
7.2106
7.2073
7.2035
7.1954
7.1885
7.1844
7.1686
7.1645
7.1606
7.1535
7.1471
7.1285
7.0863
7.0685
6.7629
6.7590
6.7439
6.7399
6.7250
6.7210
6.7057
6.7018
4.2666
4.2610
4.2492
4.2430
4.2254
4.2148
4.1809
4.1629
4.1562
4.1447
4.1389
Title WYR2-66.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
N
I
O
O
3uu
1.00
4.00
2.00
2.02
4.00
2.00
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 -0.5 -1.0
f1 (ppm)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128.360
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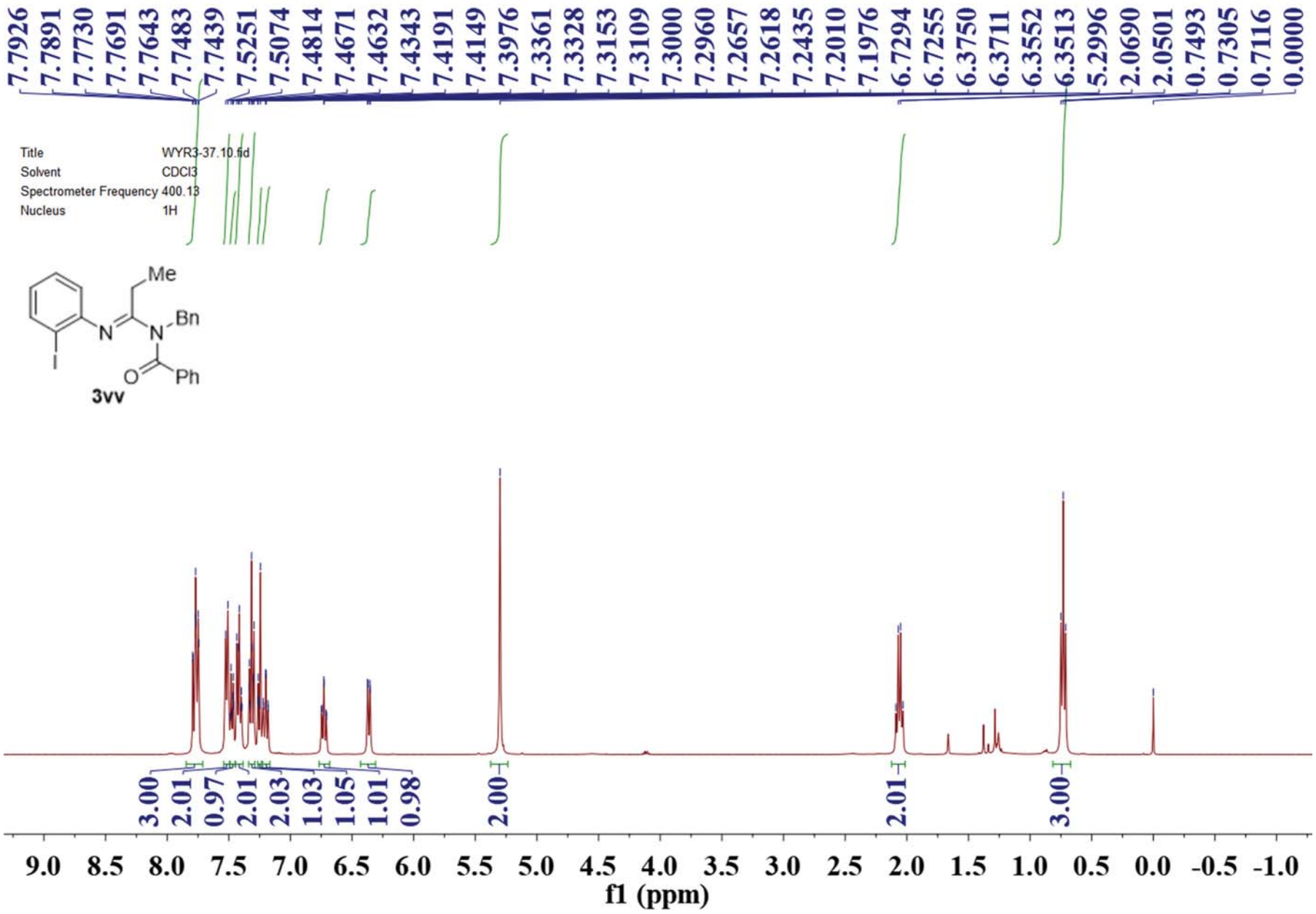
125.120
120.602
92.798
77.519
77.200
76.881
61.858
44.872
33.514
Title WYR2-66.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
N
I
O
O
3uu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7483
7.7439
7.5251
7.5074
7.4814
7.4671
7.4632
7.4343
7.4191
7.4149
7.3976
7.3361
7.3328
7.3153
7.3109
7.3000
7.2960
7.2657
7.2618
7.2435
7.2010
7.1976
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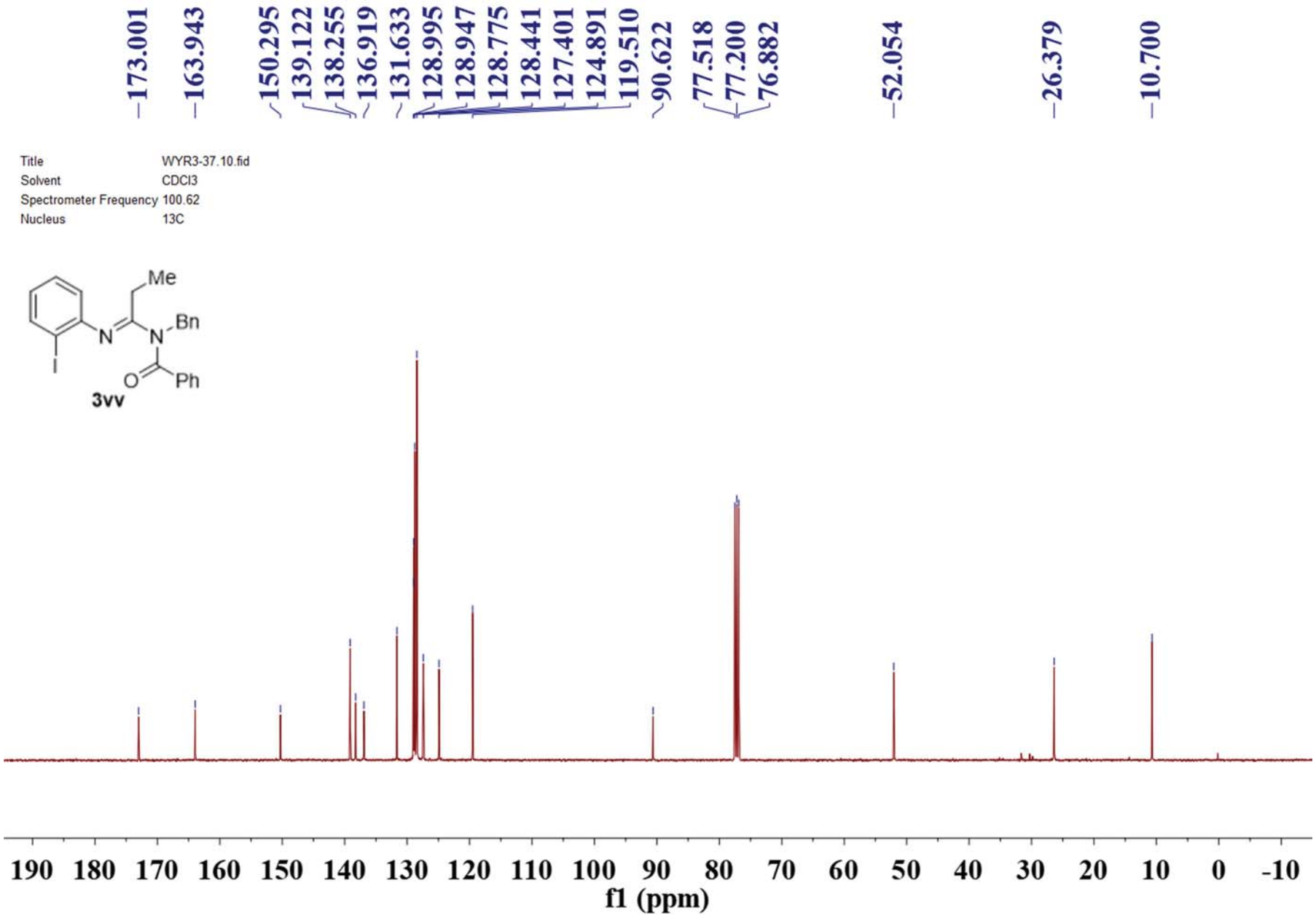
6.7255
6.3750
6.3711
6.3552
6.3513
5.2996
2.0690
2.0501
0.7493
0.7305
0.7116
0.0000
Title WYR3-37.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Bn
N
N
I
O
Ph
3vv
3.00
2.01
0.97
2.01
2.03
1.03
1.05
1.01
0.98
2.00
2.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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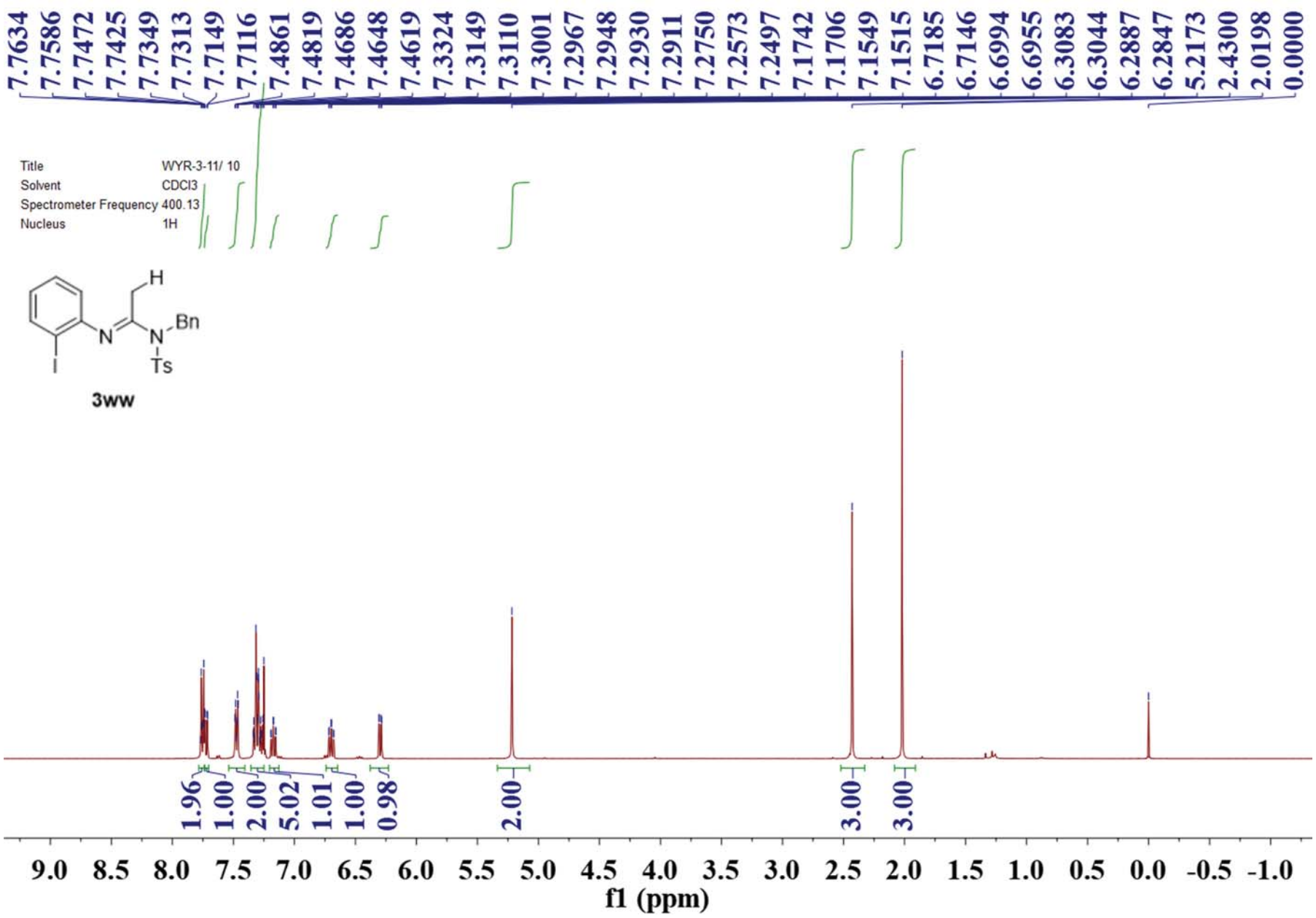
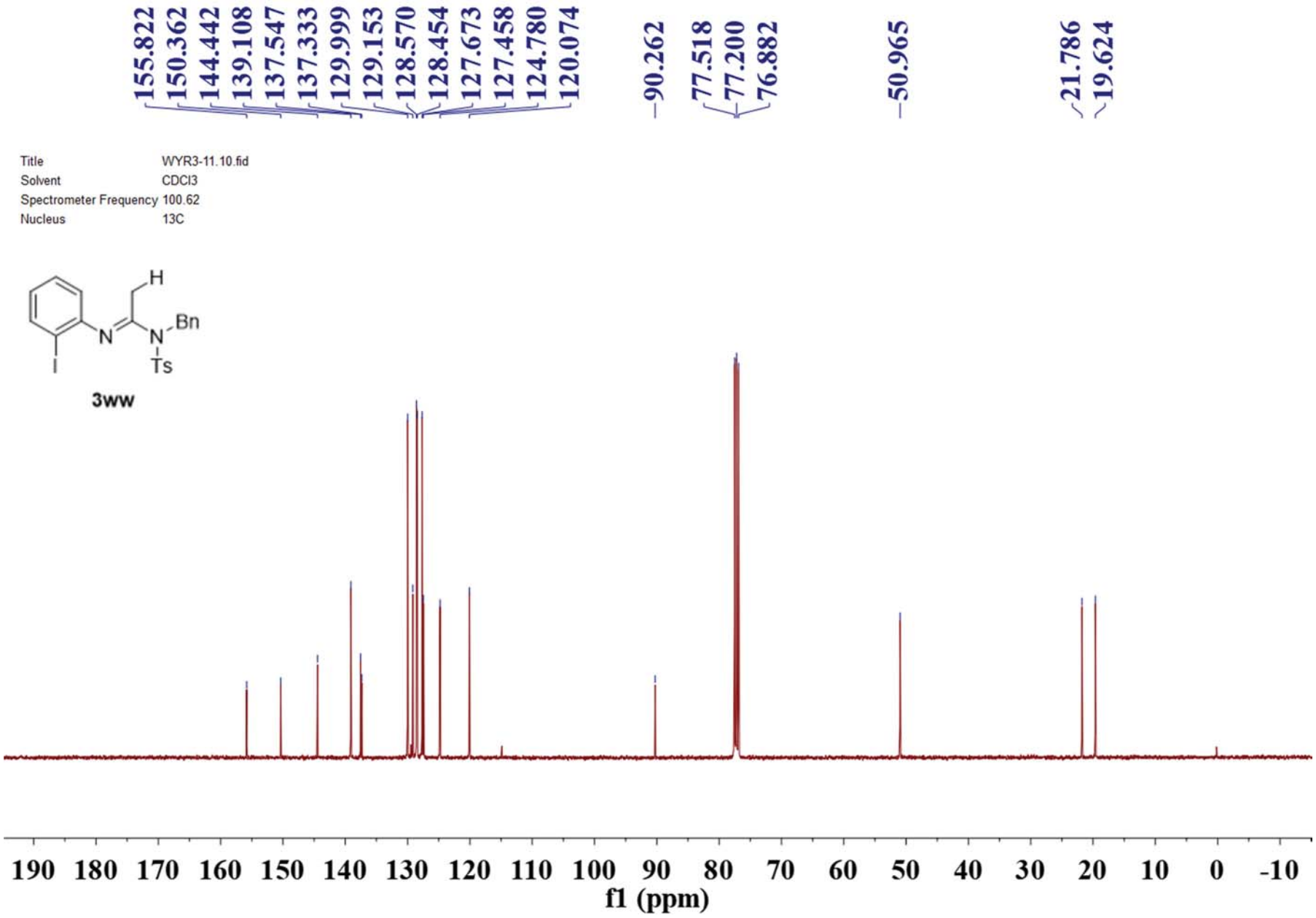
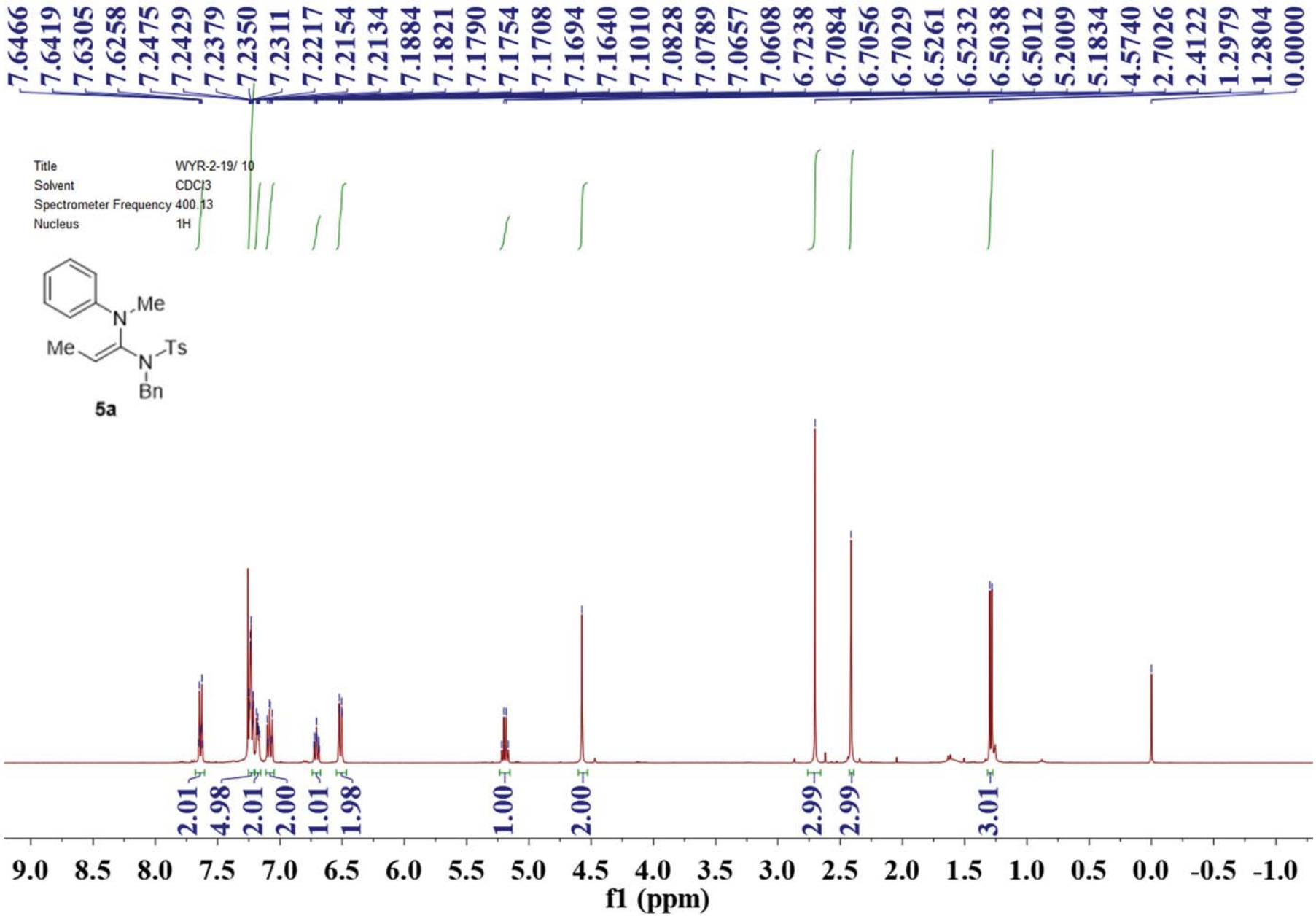
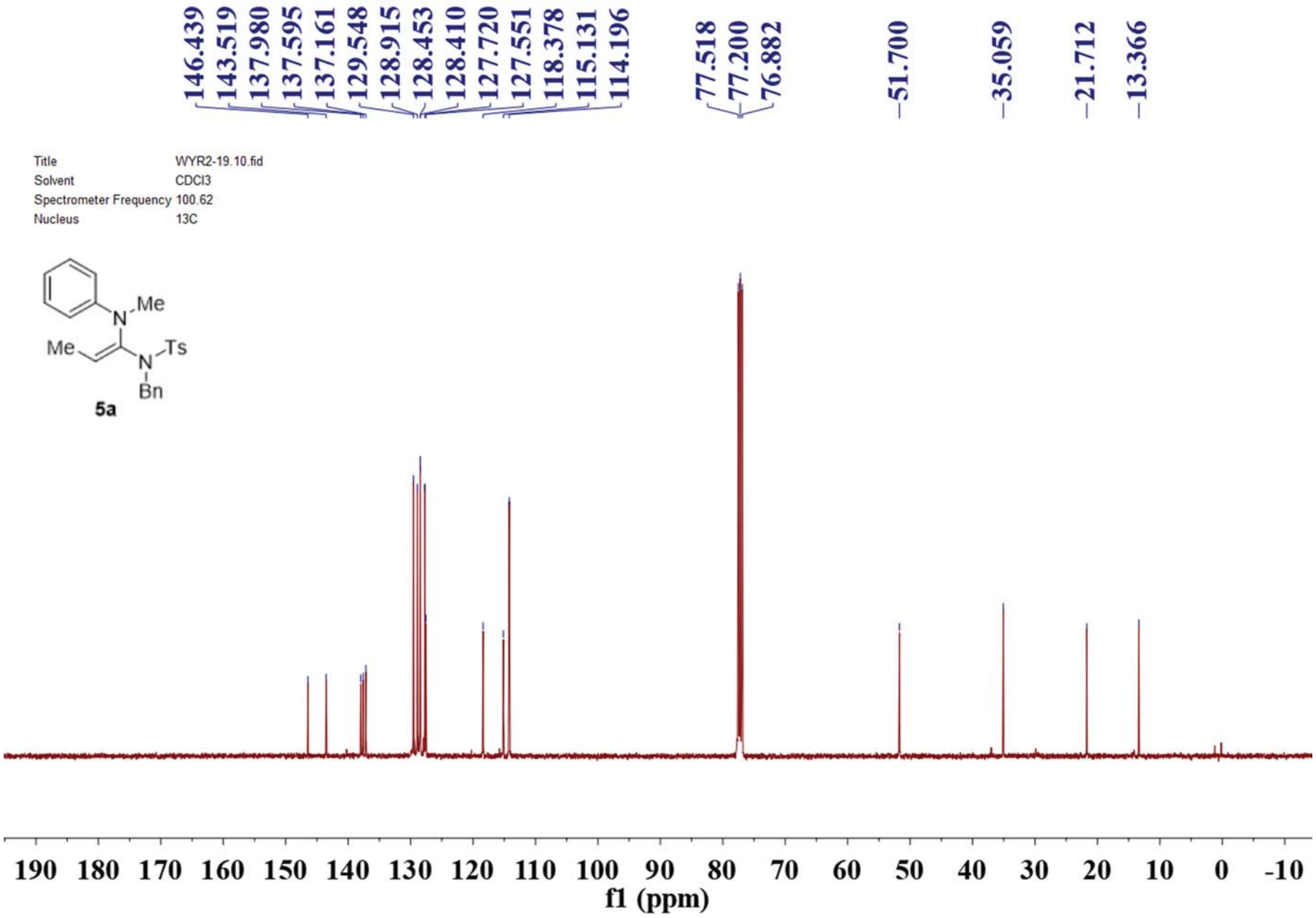
163.943
150.295
139.122
138.255
136.919
131.633
128.995
128.947
128.775
128.441
127.401
124.891
119.510
90.622
77.518
77.200
76.882
52.054
26.379
10.700
Title WYR3-37.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Bn
N
N
I
O
Ph
3vv
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.7634
7.7586
7.7472
7.7425
7.7349
7.7313
7.7149
7.7116
7.4861
7.4819
7.4686
7.4648
7.4619
7.3324
7.3149
7.3110
7.3001
7.2967
7.2948
7.2930
7.2911
7.2750
7.2573
7.2497
7.1742
7.1706
7.1549
7.1515
6.7185
6.7146
6.6994
6.6955
6.3083
6.3044
6.2887
6.2847
5.2173
2.4300
2.0198
0.0000
Title WYR-3-11/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
H
N
N
Bn
Ts
I
3ww
1.96
1.00
2.00
5.02
1.01
1.00
0.98
2.00
3.00
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 -0.5 -1.0
f1 (ppm)


155.822
150.362
144.442
139.108
137.547
137.333
129.999
129.153
128.570
128.454
127.673
127.458
124.780
120.074
90.262
77.518
77.200
76.882
50.965
21.786
19.624
Title WYR3-11.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
H
N
N
Bn
Ts
I
3ww
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR and ^{13}C NMR Spectra of Ethene-1,1-Diamines 5.

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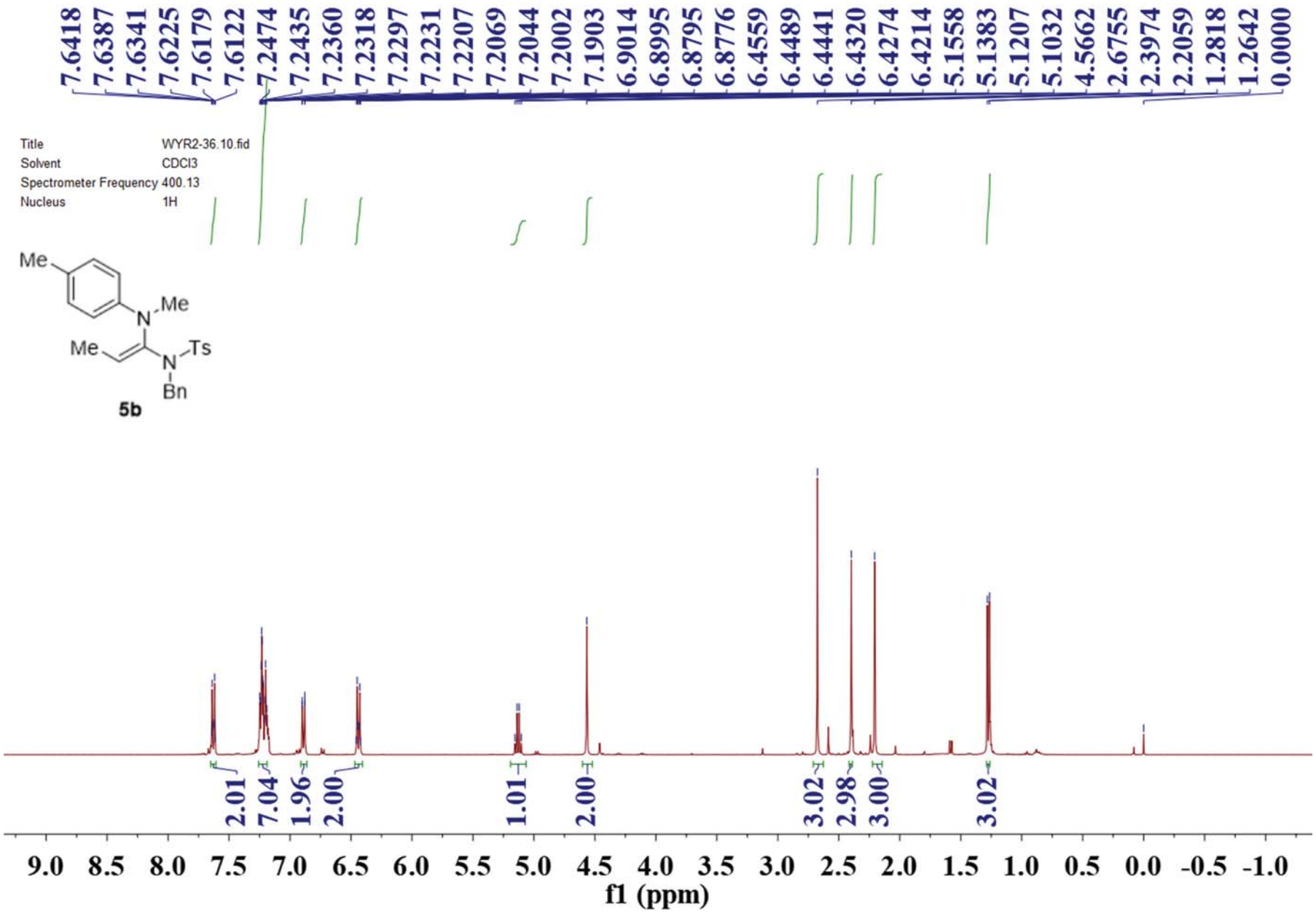
143.519
137.980
137.595
137.161
129.548
128.915
128.453
128.410
127.720
127.551
118.378
115.131
114.196
77.518
77.200
76.882
51.700
35.059
21.712
13.366
Title WYR2-19.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Ts
N
Bn
5a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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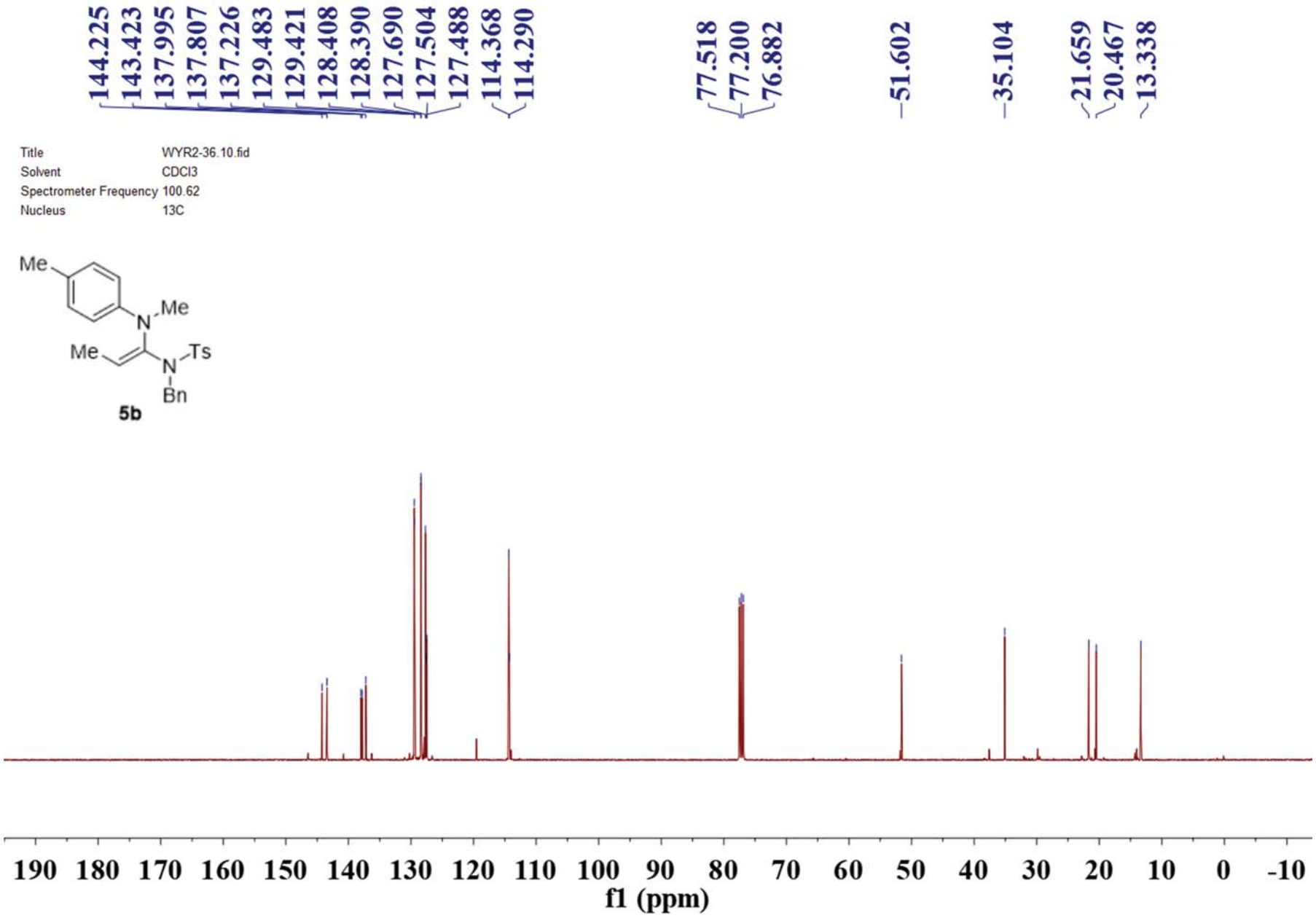
7.6387
7.6341
7.6225
7.6179
7.6122
7.2474
7.2435
7.2360
7.2318
7.2297
7.2231
7.2207
7.2069
7.2044
7.2002
7.1903
6.9014
6.8995
6.8795
6.8776
6.4559
6.4489
6.4441
6.4320
6.4274
6.4214
5.1558
5.1383
5.1207
5.1032
4.5662
2.6755
2.3974
2.2059
1.2818
1.2642
0.0000
Title WYR2-36.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
N
Ts
Bn
5b
2.01
7.04
1.96
2.00
1.01
2.00
3.02
2.98
3.00
3.02
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 -0.5 -1.0
f1 (ppm)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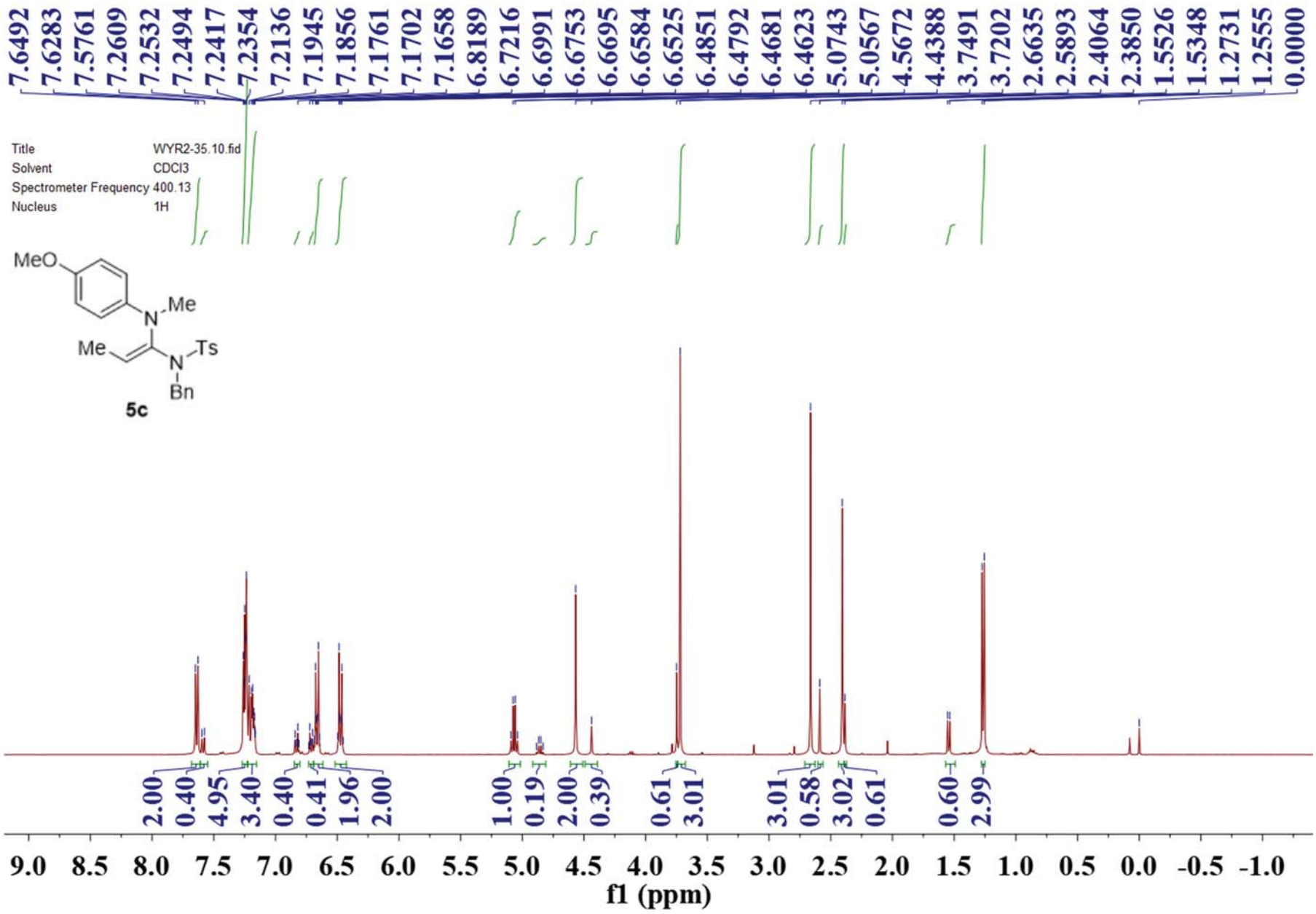
143.423
137.995
137.807
137.226
129.483
129.421
128.408
128.390
127.690
127.504
127.488
114.368
114.290
77.518
77.200
76.882
51.602
35.104
21.659
20.467
13.338
Title WYR2-36.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
N
Ts
Bn
5b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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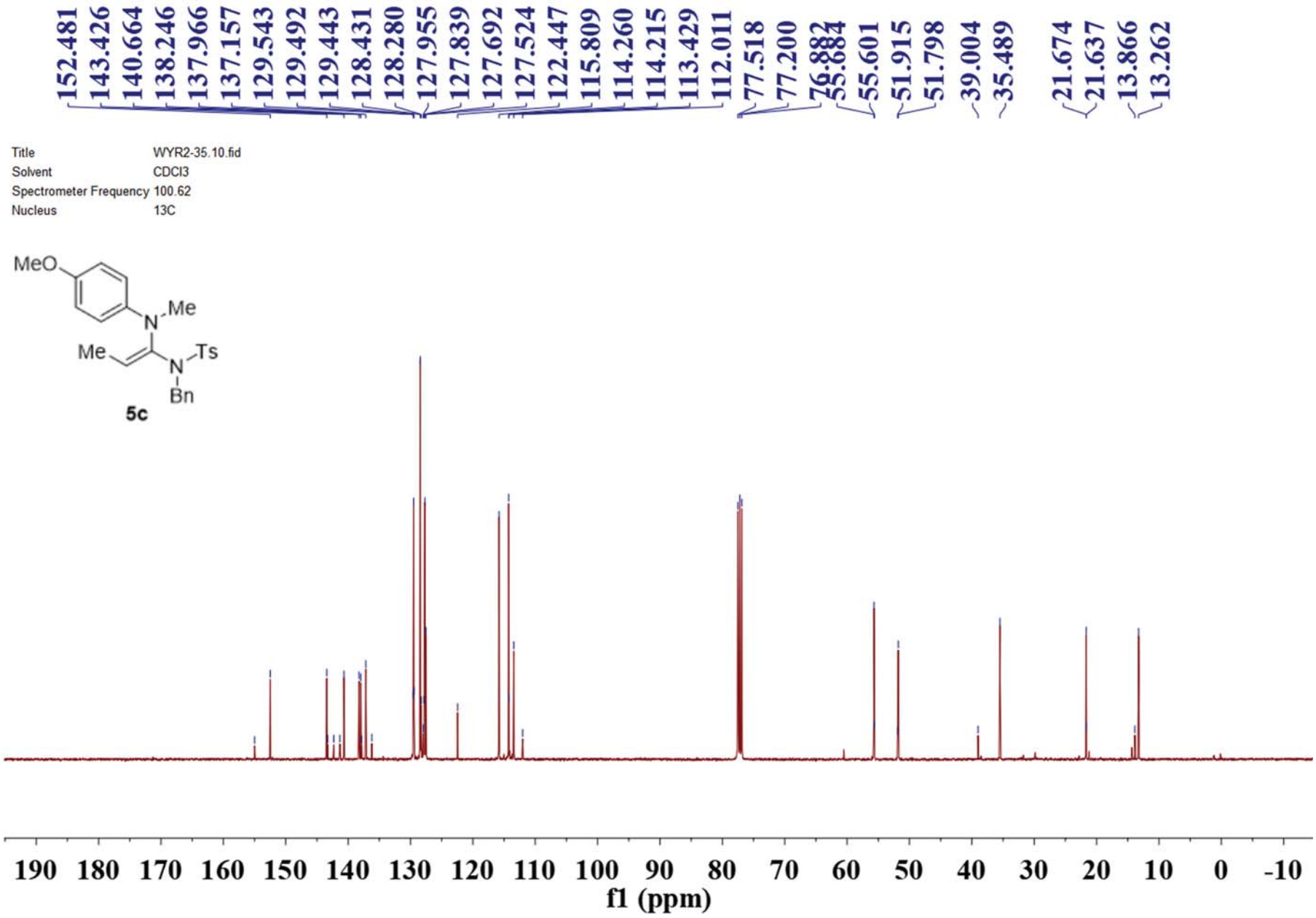
7.6283
7.5761
7.2609
7.2532
7.2494
7.2417
7.2354
7.2136
7.1945
7.1856
7.1761
7.1702
7.1658
6.8189
6.7216
6.6991
6.6753
6.6695
6.6584
6.6525
6.4851
6.4792
6.4681
6.4623
5.0743
5.0567
4.5672
4.4388
3.7491
3.7202
2.6635
2.5893
2.4064
2.3850
1.5526
1.5348
1.2731
1.2555
0.0000
Title WYR2-35.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
N
Me
Me
N
Ts
Bn
5c
2.00
0.40
4.95
3.40
0.40
0.41
1.96
2.00
1.00
0.19
2.00
0.39
0.61
3.01
3.01
0.58
3.02
0.61
0.60
2.99
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 -0.5 -1.0
f1 (ppm)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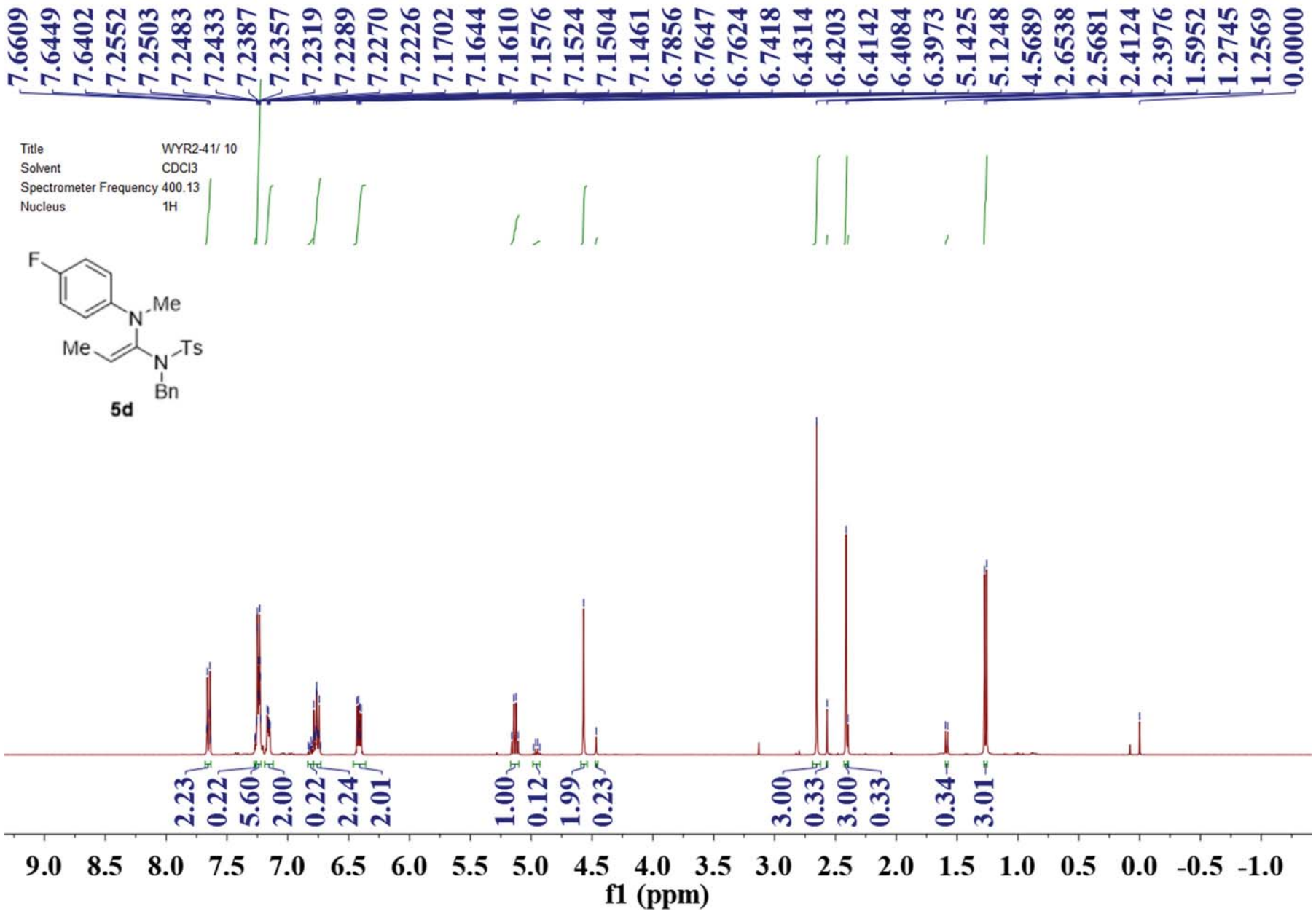
143.426
140.664
138.246
137.966
137.157
129.543
129.492
129.443
128.431
128.280
127.955
127.839
127.692
127.524
122.447
115.809
114.260
114.215
113.429
112.011
77.518
77.200
76.882
76.684
55.601
51.915
51.798
39.004
35.489
21.674
21.637
13.866
13.262
Title WYR2-35.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
N
Me
Me
N
Ts
Bn
5c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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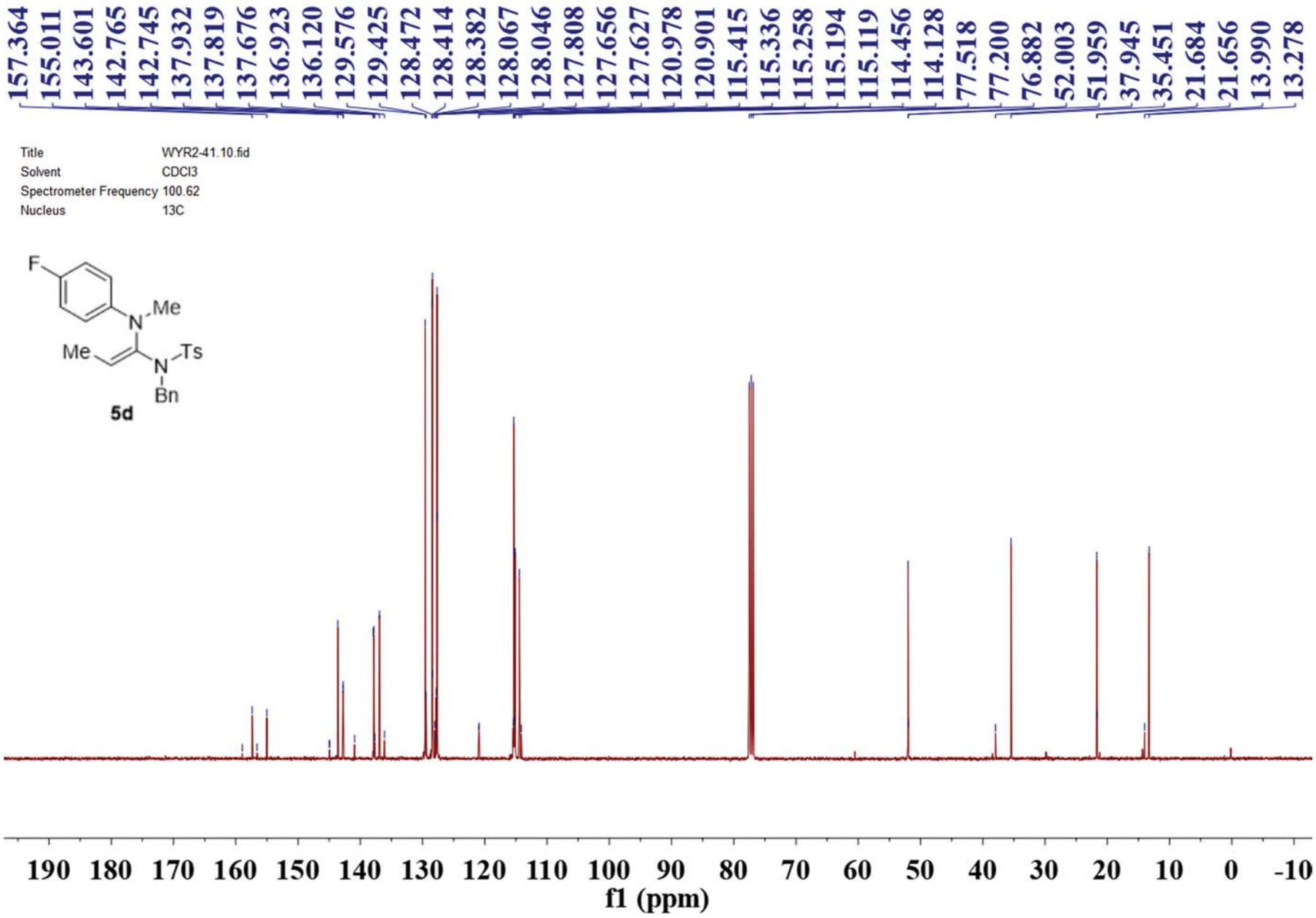
7.2552
7.2503
7.2483
7.2433
7.2387
7.2357
7.2319
7.2289
7.2270
7.2226
7.1702
7.1644
7.1610
7.1576
7.1524
7.1504
7.1461
6.7856
6.7647
6.7624
6.7418
6.4314
6.4203
6.4142
6.4084
6.3973
5.1425
5.1248
4.5689
2.6538
2.5681
2.4124
2.3976
1.5952
1.2745
1.2569
0.0000
Title WYR2-41/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
N
Me
Me
N
Ts
Bn
5d
2.23
0.22
5.60
2.00
0.22
2.24
2.01
1.00
0.12
1.99
0.23
3.00
0.33
3.00
0.33
0.34
3.01
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 -0.5 -1.0
f1 (ppm)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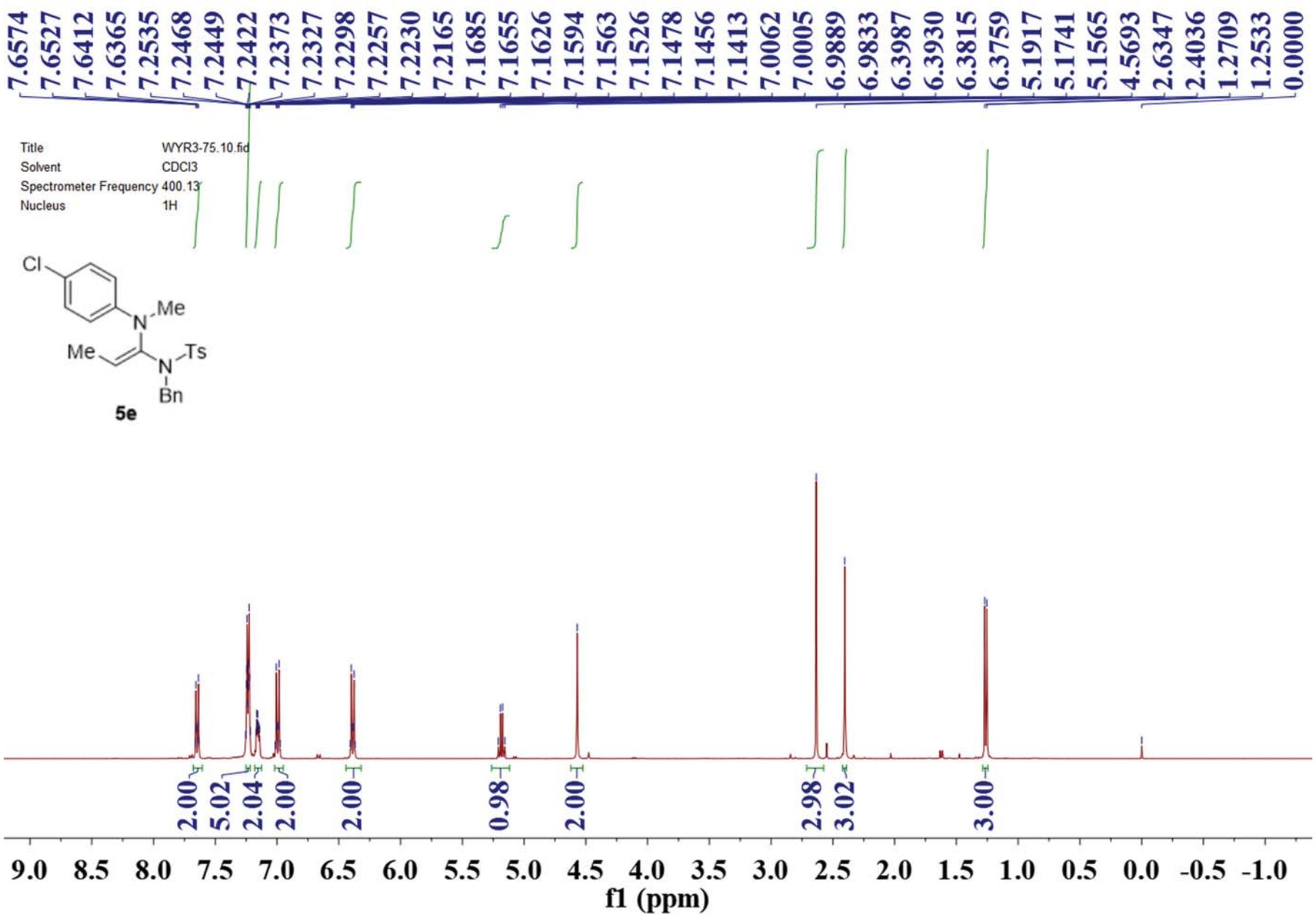
142.745
137.932
137.819
137.676
136.923
136.120
129.576
129.425
128.472
128.414
128.382
128.067
128.046
127.808
127.656
127.627
120.978
120.901
115.415
115.336
115.258
115.194
115.119
114.456
114.128
77.518
77.200
76.882
52.003
51.959
37.945
35.451
21.684
21.656
13.990
13.278
Title WYR2-41.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
N
Me
Me
N
Ts
Bn
5d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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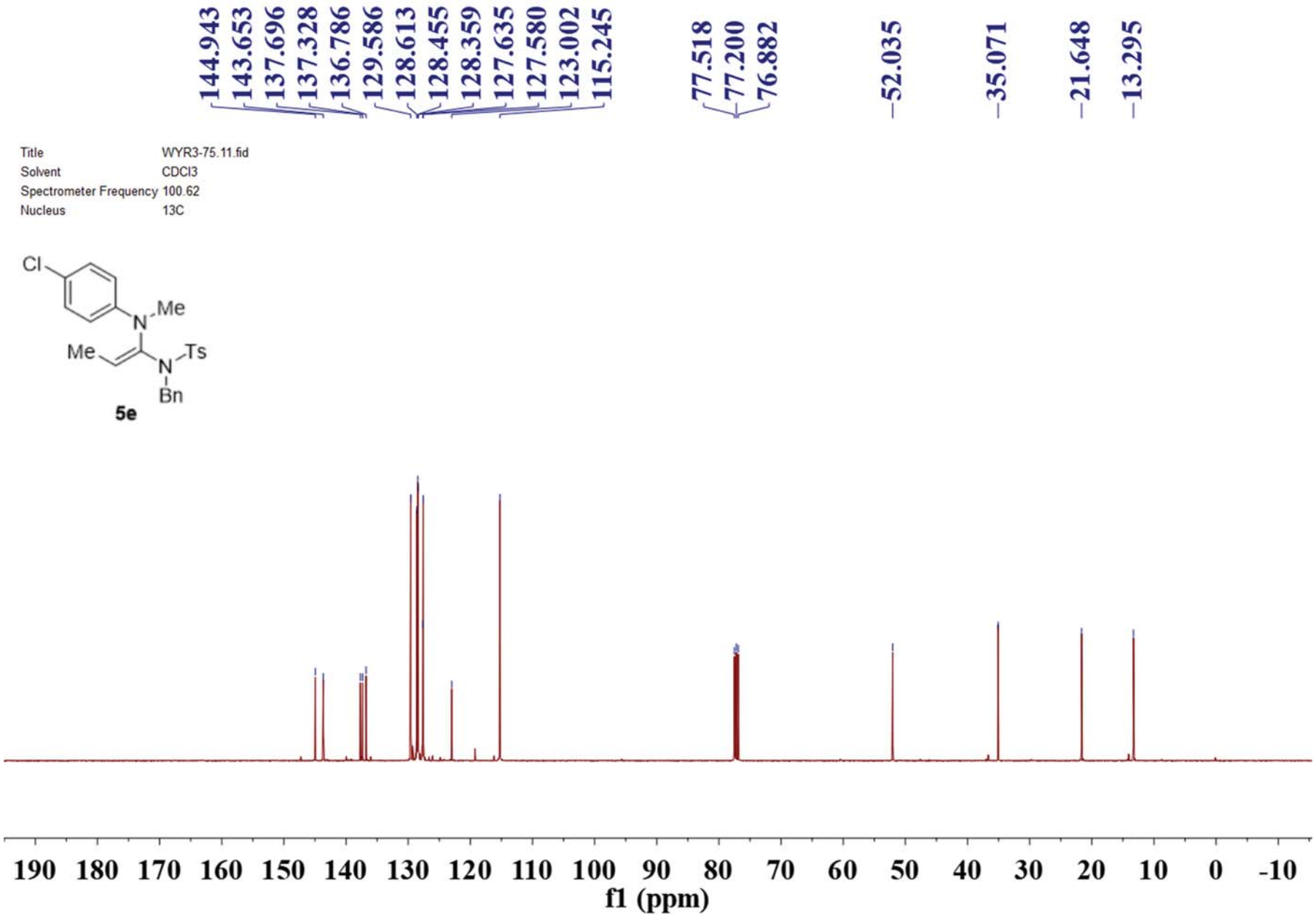
7.6412
7.6365
7.2535
7.2468
7.2449
7.2422
7.2373
7.2327
7.2298
7.2257
7.2230
7.2165
7.1685
7.1655
7.1626
7.1594
7.1563
7.1526
7.1478
7.1456
7.1413
7.0062
7.0005
6.9889
6.9833
6.3987
6.3930
6.3815
6.3759
5.1917
5.1741
5.1565
4.5693
2.6347
2.4036
1.2709
1.2533
0.0000
Title WYR3-75.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
N
Me
Me
N
Ts
N
Bn
5e
2.00
5.02
2.04
2.00
2.00
0.98
2.00
2.98
3.02
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 -0.5 -1.0
f1 (ppm)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137.328
136.786
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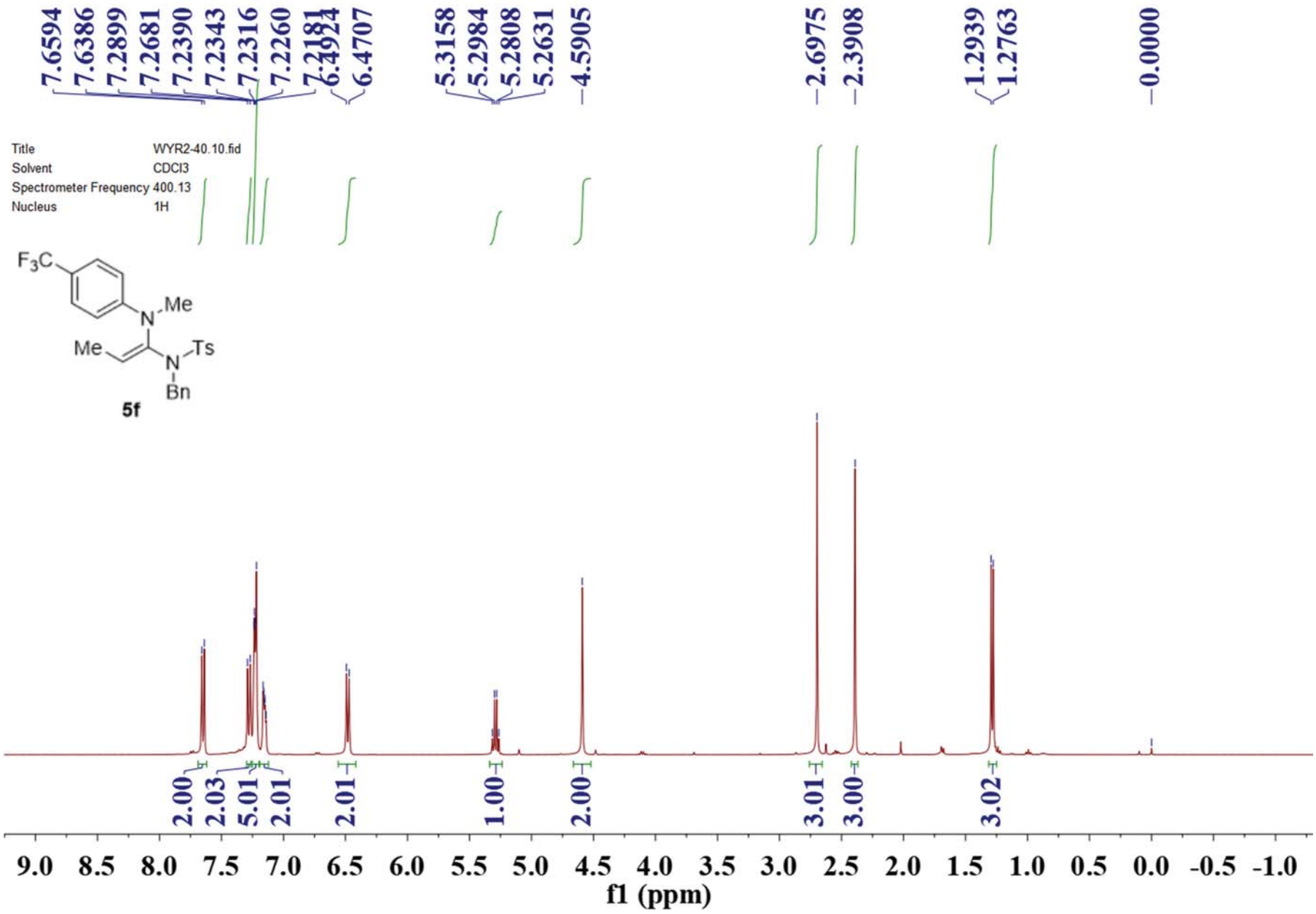
128.613
128.455
128.359
127.635
127.580
123.002
115.245
77.518
77.200
76.882
52.035
35.071
21.648
13.295
Title WYR3-75.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
N
Me
Me
N
Ts
Bn
5e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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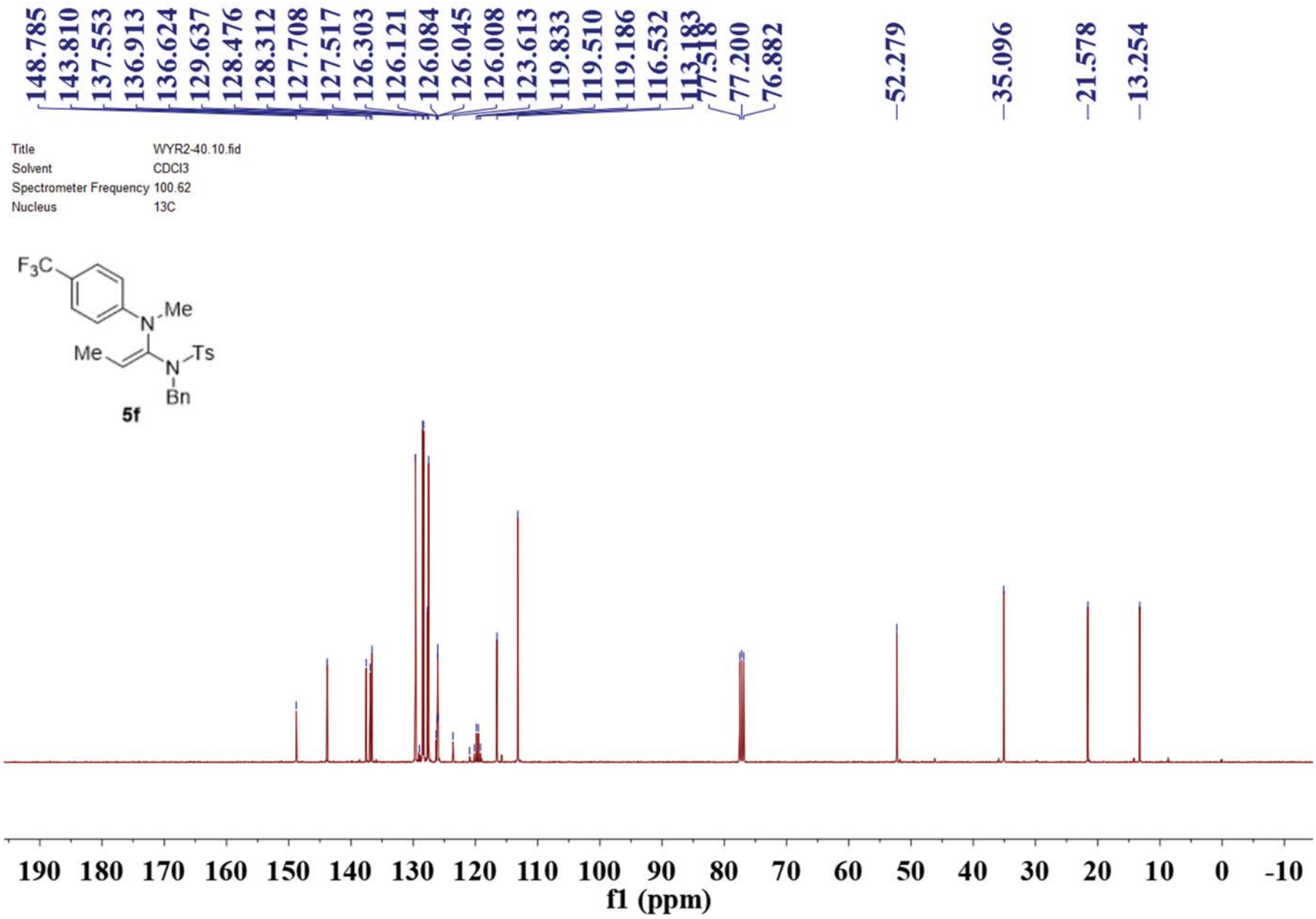
7.2899
7.2681
7.2390
7.2343
7.2316
7.2260
7.2181
6.4924
6.4707
5.3158
5.2984
5.2808
5.2631
4.5905
2.6975
2.3908
1.2939
1.2763
0.0000
Title WYR2-40.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F3C
N
Me
Me
N
Ts
Bn
5f
2.00
2.03
5.01
2.01
2.01
1.00
2.00
3.01
3.00
3.02
9.0 8.5 8.0 7.5 7.0 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 -0.5 -1.0
f1 (ppm)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136.913
136.624
129.637
128.476
128.312
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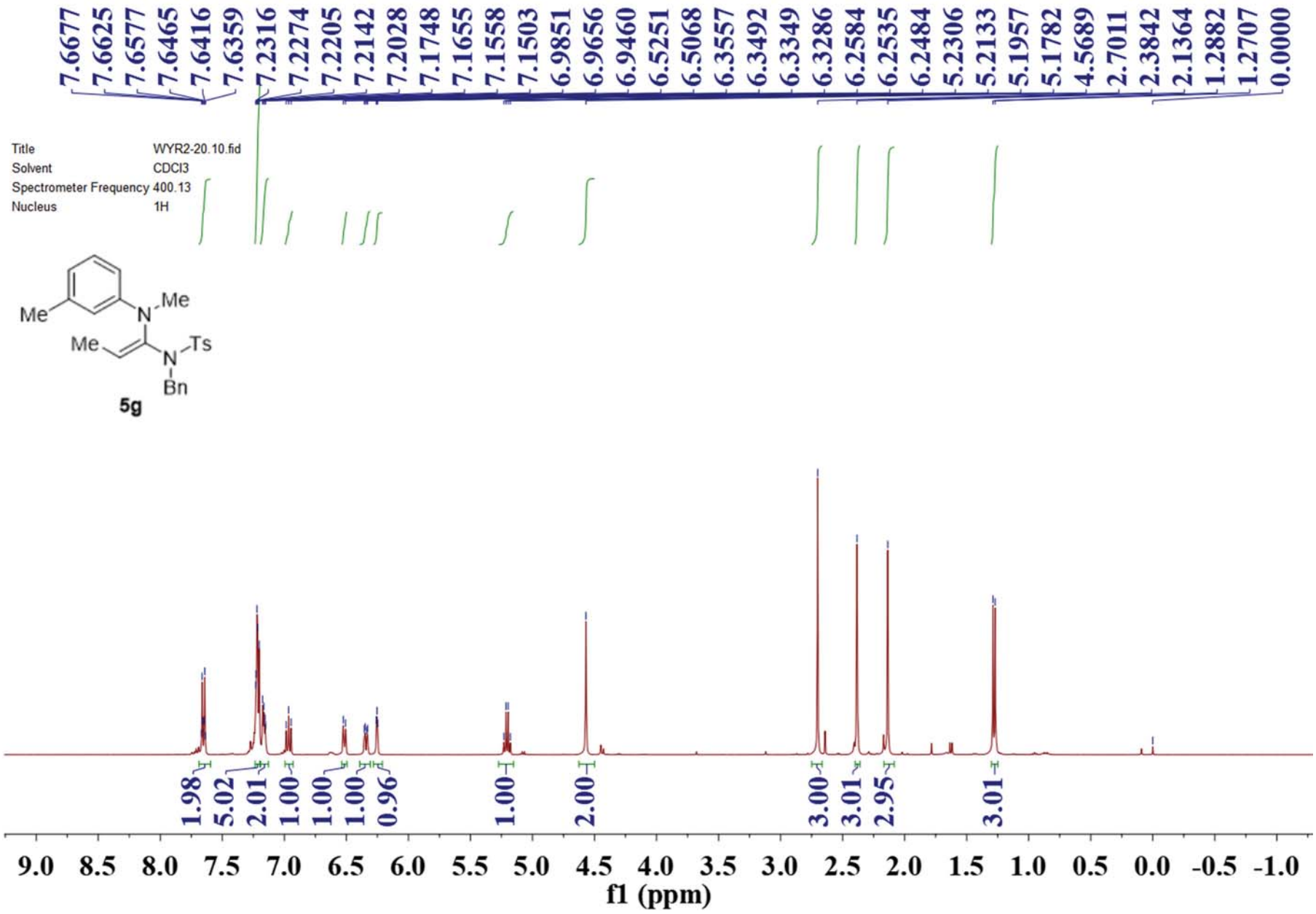
127.517
126.303
126.121
126.084
126.045
126.008
123.613
119.833
119.510
119.186
116.532
113.183
77.518
77.200
76.882
52.279
35.096
21.578
13.254
Title WYR2-40.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F3C
N
Me
Me
N
Ts
Bn
5f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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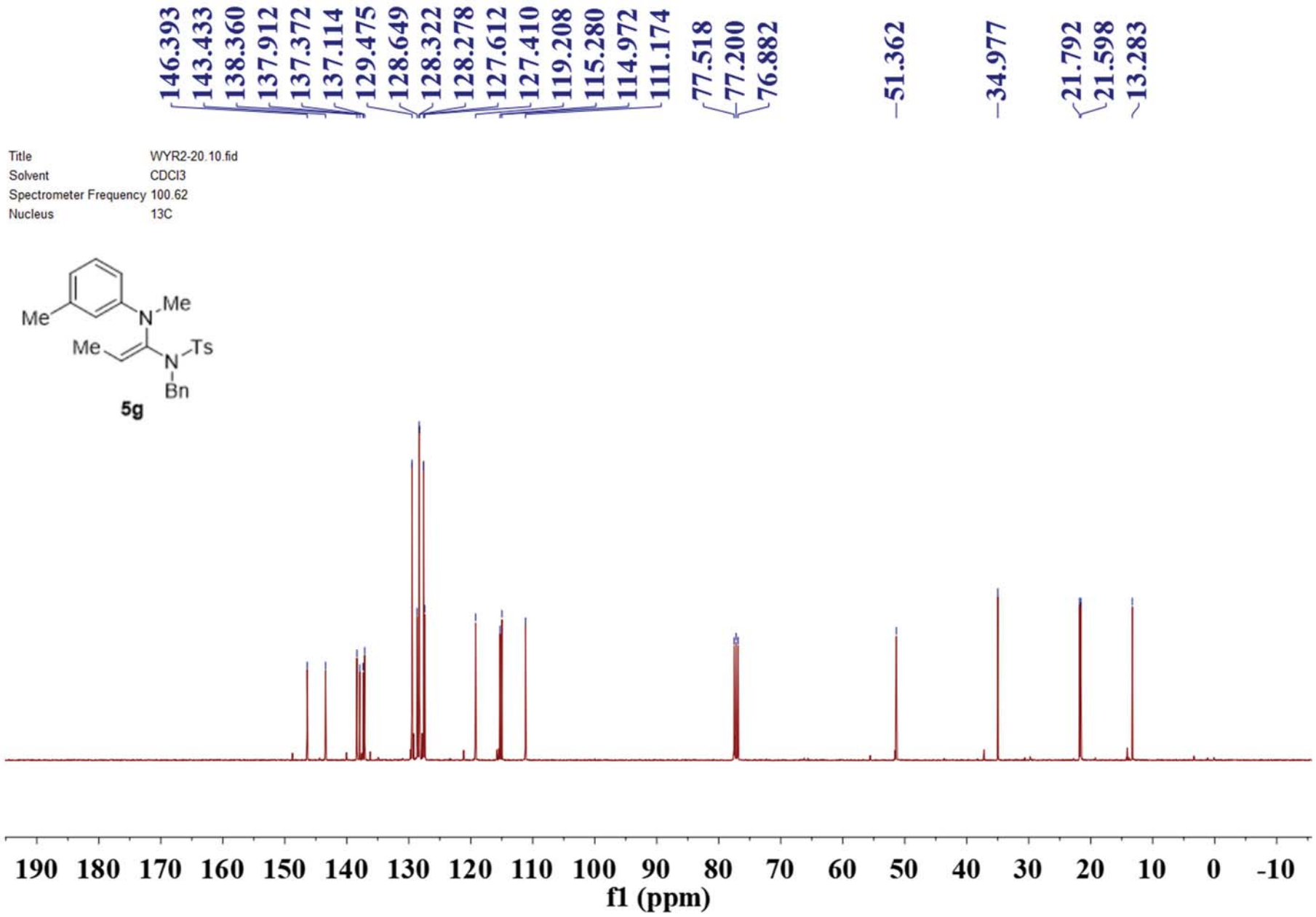
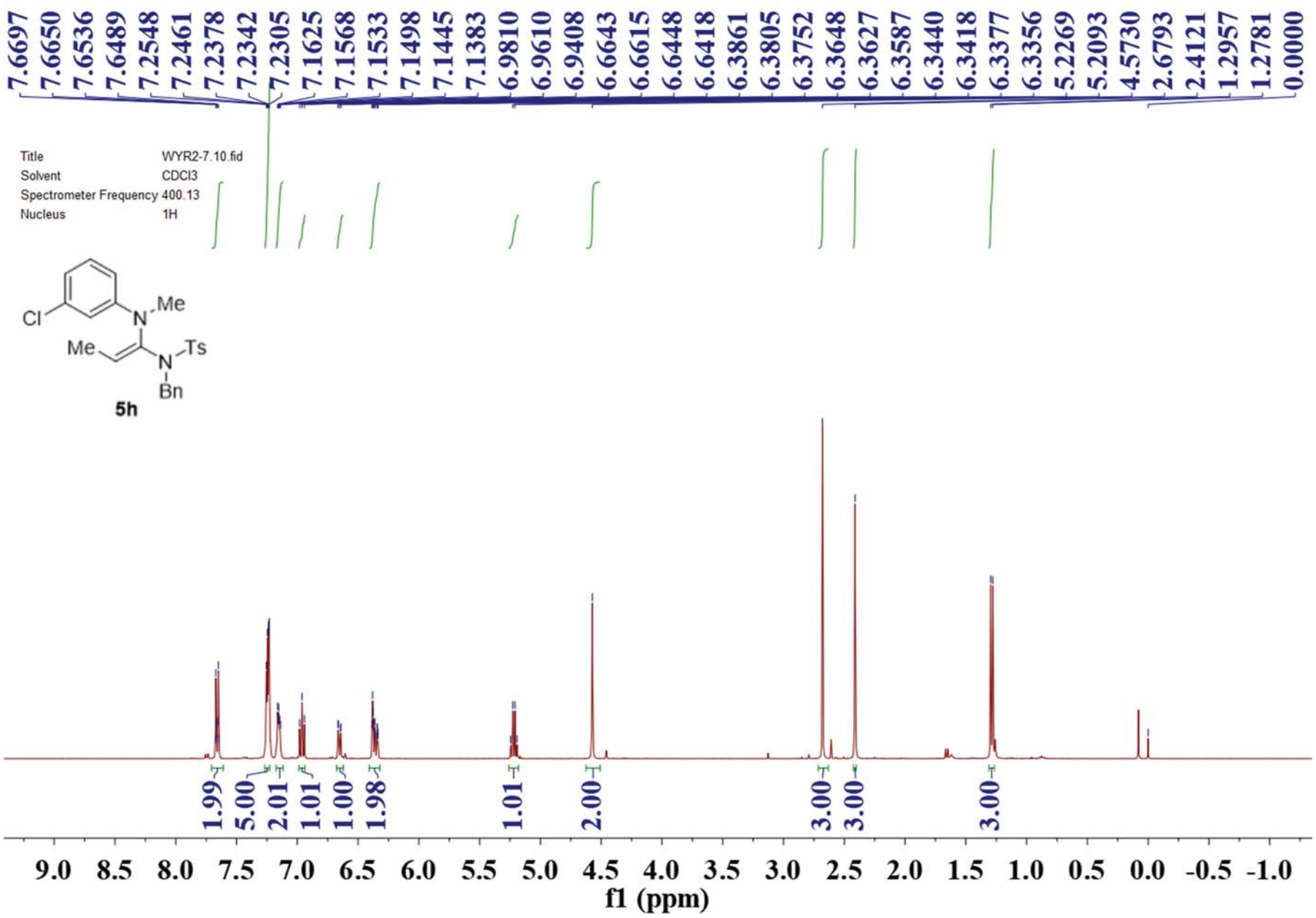
7.2205
7.2142
7.2028
7.1748
7.1655
7.1558
7.1503
6.9851
6.9656
6.9460
6.5251
6.5068
6.3557
6.3492
6.3349
6.3286
6.2584
6.2535
6.2484
5.2306
5.2133
5.1957
5.1782
4.5689
2.7011
2.3842
2.1364
1.2882
1.2707
0.0000
Title WYR2-20.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
Ts
N
Bn
5g
1.98
5.02
2.01
1.00
1.00
1.00
0.96
1.00
2.00
3.00
3.01
2.95
3.01
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 -0.5 -1.0
f1 (ppm)


146.393
143.433
138.360
137.912
137.372
137.114
129.475
128.649
128.322
128.278
127.612
127.410
119.208
115.280
114.972
111.174
77.518
77.200
76.882
51.362
34.977
21.792
21.598
13.283
Title WYR2-20.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
Ts
N
Bn
5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2548
7.2461
7.2378
7.2342
7.2305
7.1625
7.1568
7.1533
7.1498
7.1445
7.1383
6.9810
6.9610
6.9408
6.6643
6.6615
6.6448
6.6418
6.3861
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6.3752
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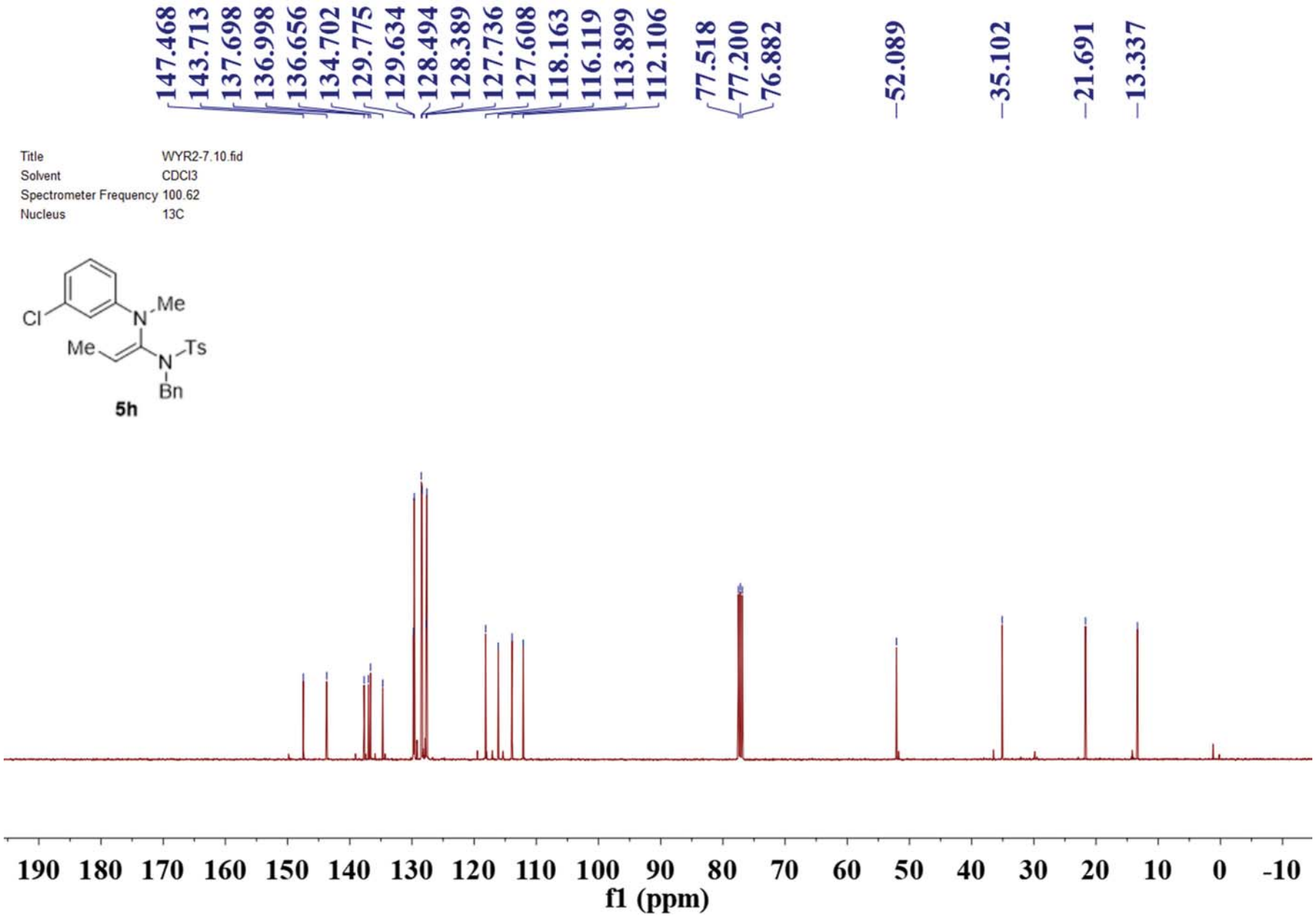
6.3418
6.3377
6.3356
5.2269
5.2093
4.5730
2.6793
2.4121
1.2957
1.2781
0.0000
Title WYR2-7.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
N
Me
Me
N
Ts
Bn
5h
1.99
5.00
2.01
1.01
1.00
1.98
1.01
2.00
3.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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136.998
136.656
134.702
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129.634
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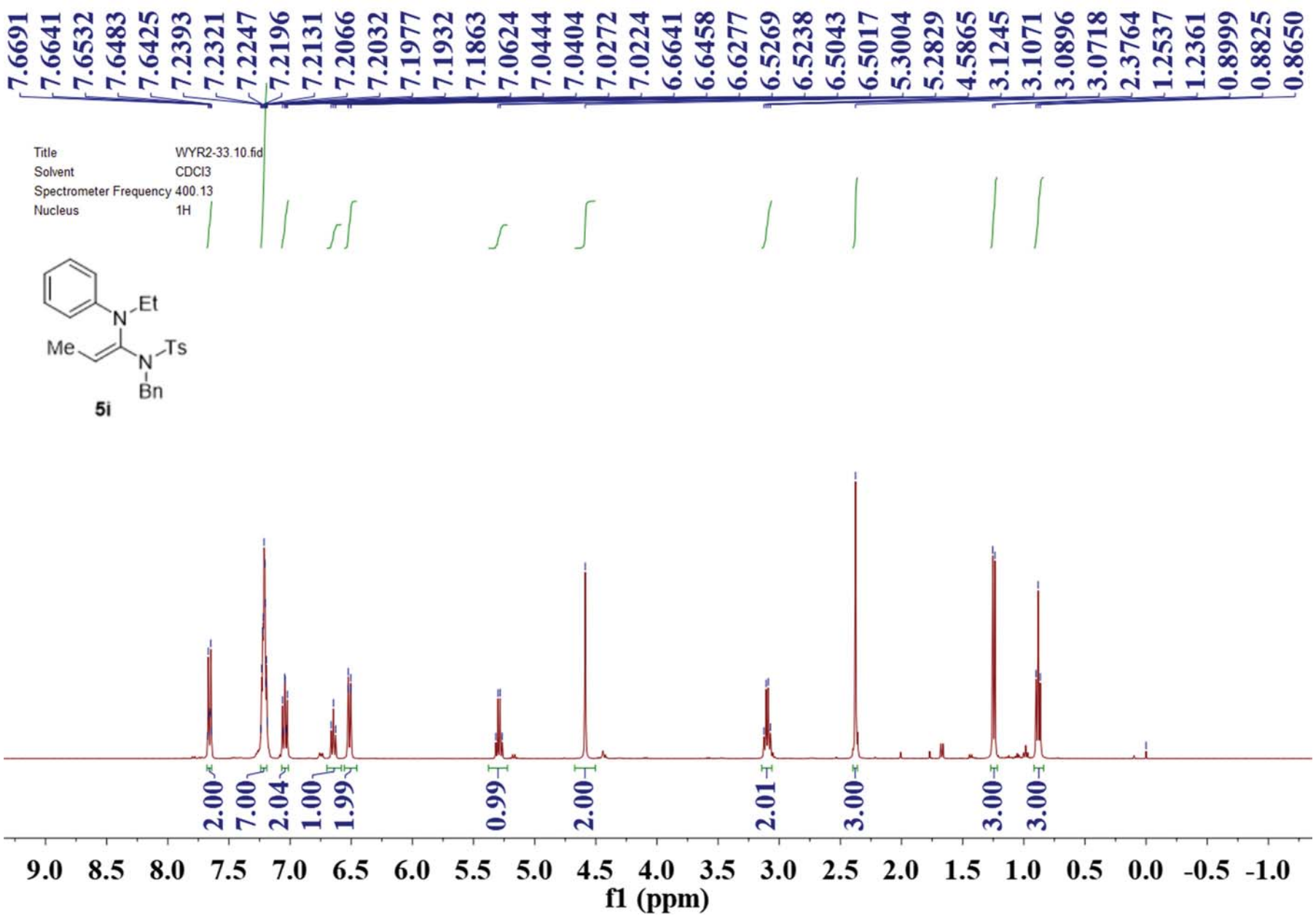
128.389
127.736
127.608
118.163
116.119
113.899
112.106
77.518
77.200
76.882
52.089
35.102
21.691
13.337
Title WYR2-7.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
N
Me
Me
N
Ts
Bn
5h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.6425
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7.2321
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7.2196
7.2131
7.2066
7.2032
7.1977
7.1932
7.1863
7.0624
7.0444
7.0404
7.0272
7.0224
6.6641
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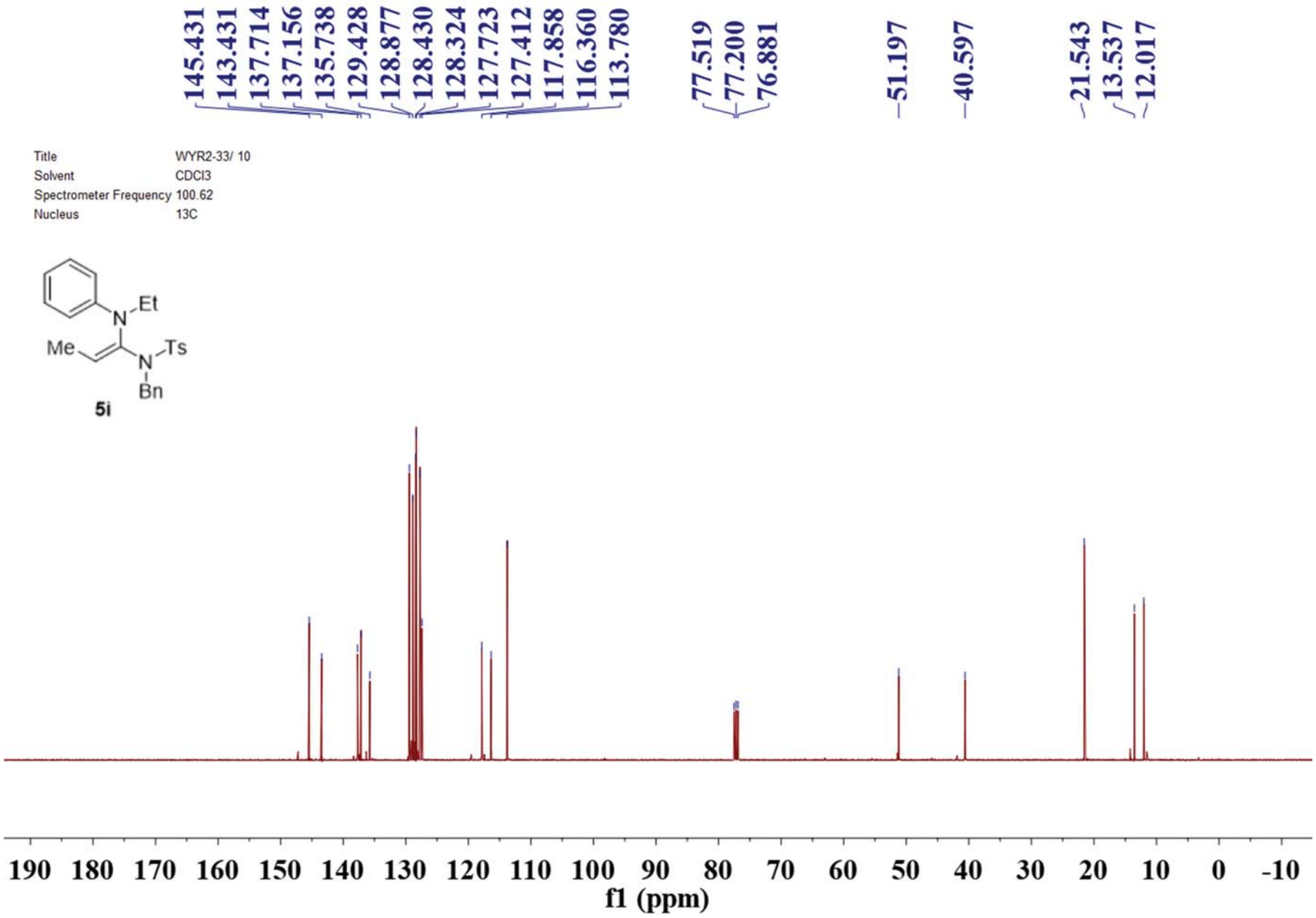
6.5238
6.5043
6.5017
5.3004
5.2829
4.5865
3.1245
3.1071
3.0896
3.0718
2.3764
1.2537
1.2361
0.8999
0.8825
0.8650
Title WYR2-33.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Et
Me
N
Ts
Bn
5i
2.00
7.00
2.04
1.00
1.99
0.99
2.00
2.01
3.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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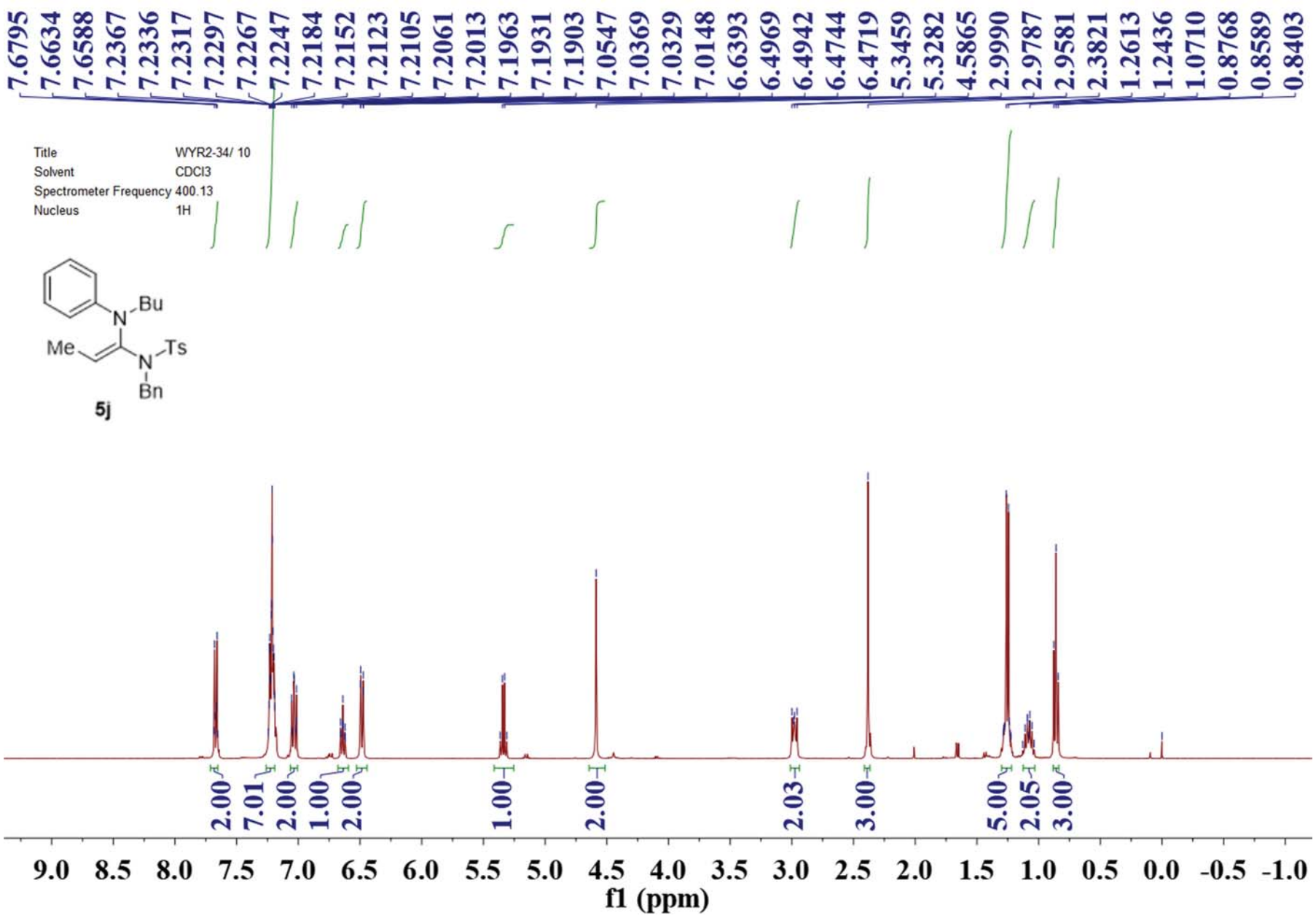
143.431
137.714
137.156
135.738
129.428
128.877
128.430
128.324
127.723
127.412
117.858
116.360
113.780
77.519
77.200
76.881
51.197
40.597
21.543
13.537
12.017
Title WYR2-33/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Et
N
Me
Ts
N
Bn
5i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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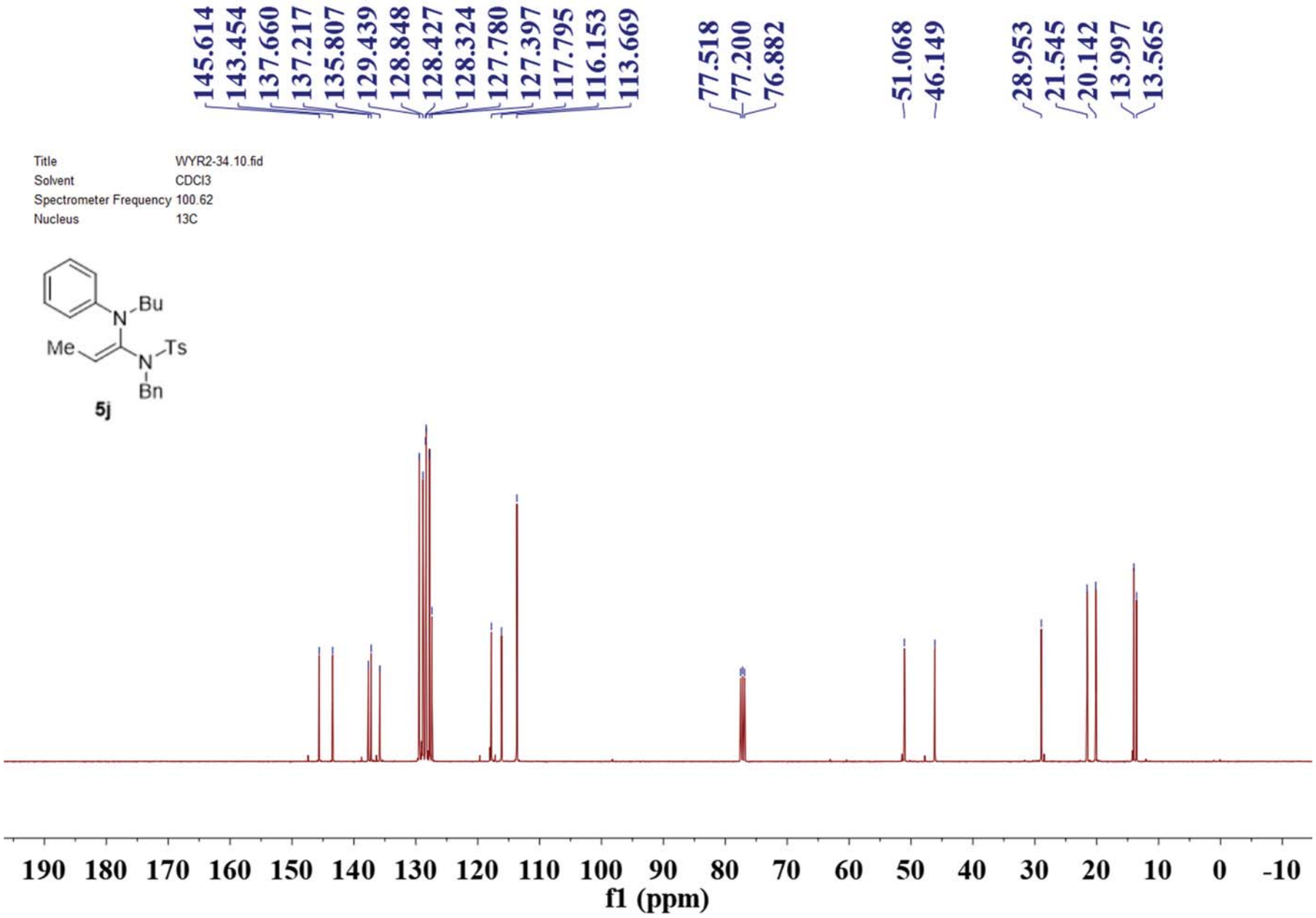
7.6634
7.6588
7.2367
7.2336
7.2317
7.2297
7.2267
7.2247
7.2184
7.2152
7.2123
7.2105
7.2061
7.2013
7.1963
7.1931
7.1903
7.0547
7.0369
7.0329
7.0148
6.6393
6.4969
6.4942
6.4744
6.4719
5.3459
5.3282
4.5865
2.9990
2.9787
2.9581
2.3821
1.2613
1.2436
1.0710
0.8768
0.8589
0.8403
Title WYR2-34/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Bu
N
Me
Ts
N
Bn
5j
2.00
7.01
2.00
1.00
2.00
1.00
2.00
2.03
3.00
5.00
2.05
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 -0.5 -1.0
f1 (ppm)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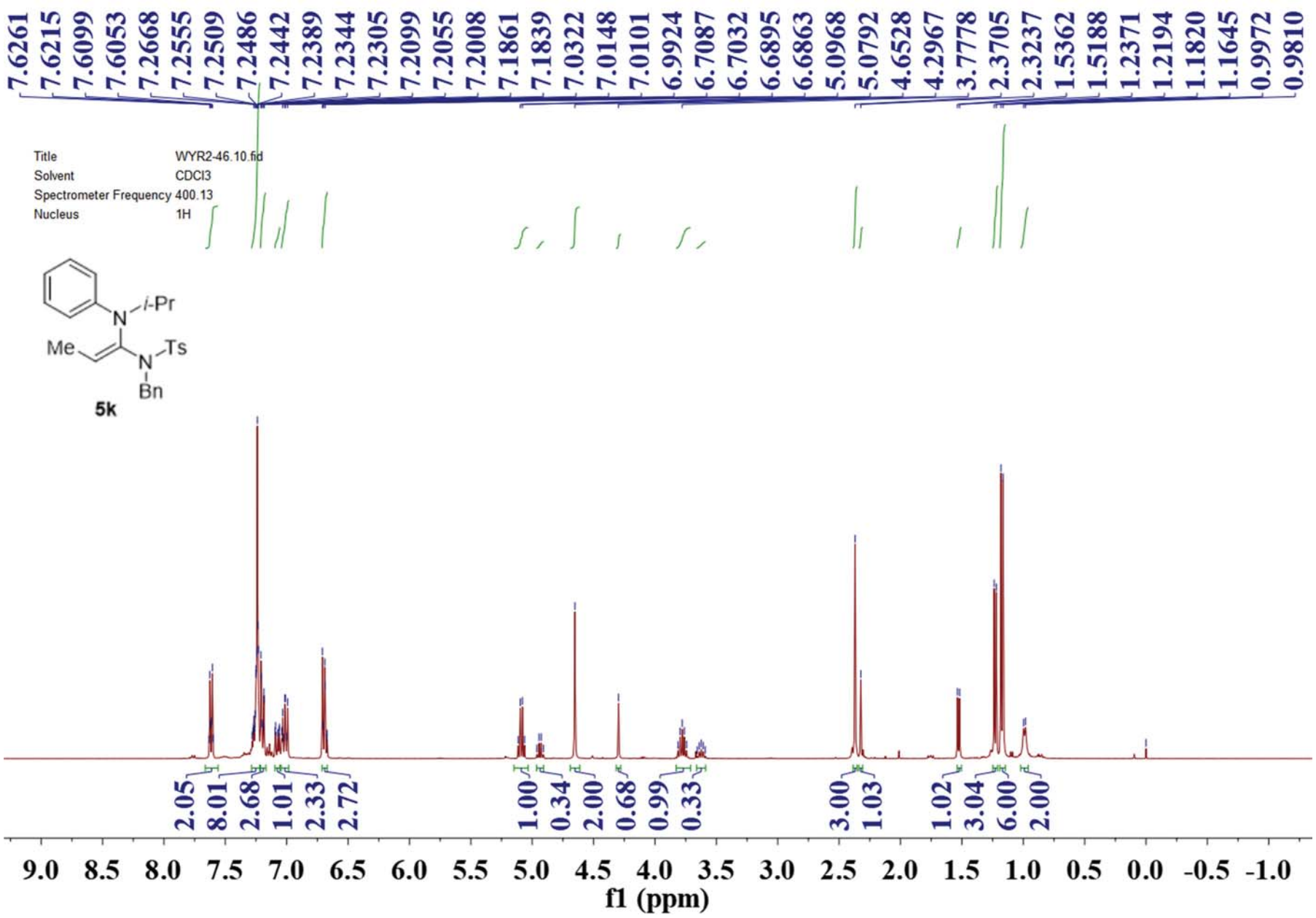
143.454
137.660
137.217
135.807
129.439
128.848
128.427
128.324
127.780
127.397
117.795
116.153
113.669
77.518
77.200
76.882
51.068
46.149
28.953
21.545
20.142
13.997
13.565
Title WYR2-34.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Bu
Me
N
Ts
Bn
5j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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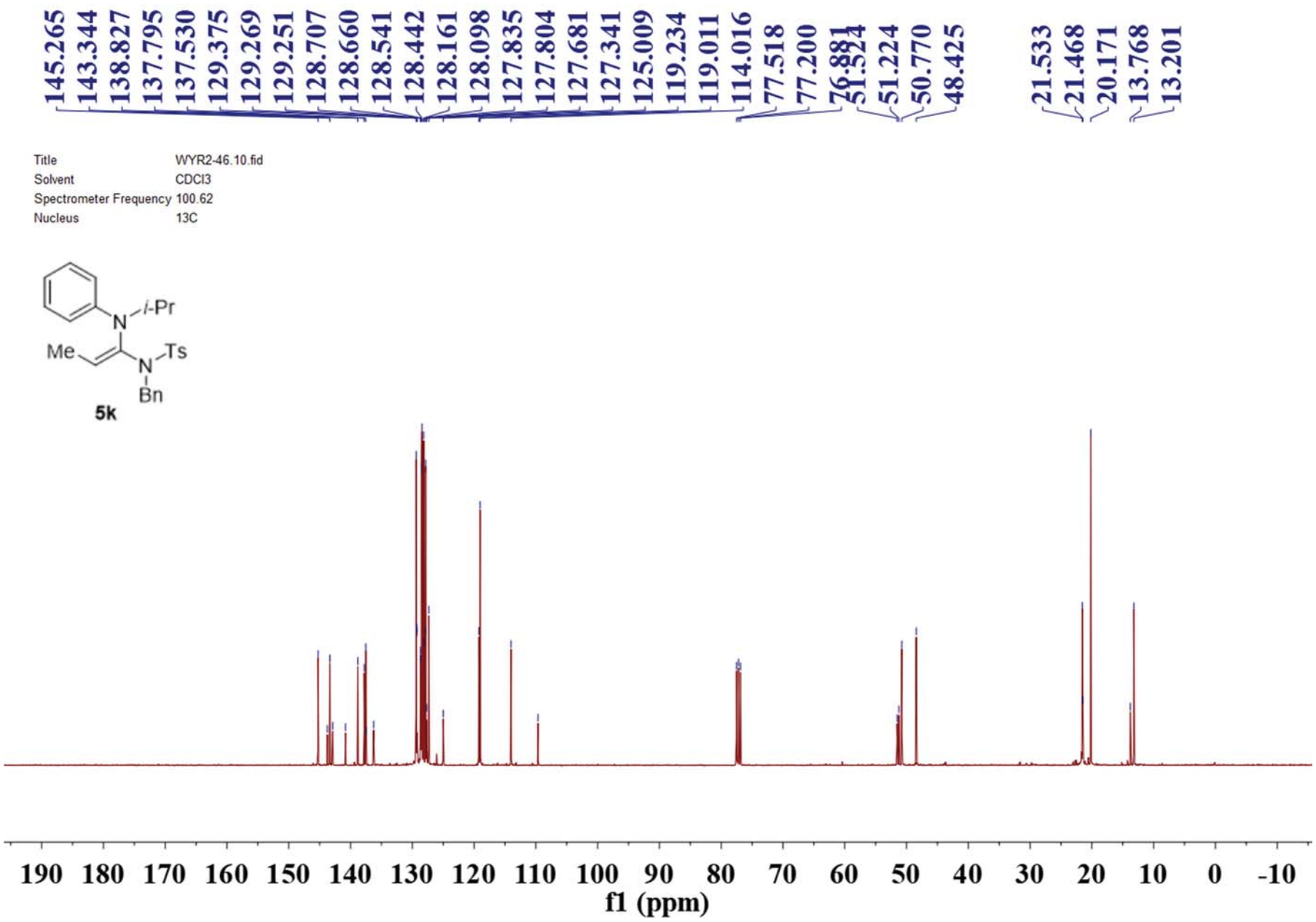
7.6215
7.6099
7.6053
7.2668
7.2555
7.2509
7.2486
7.2442
7.2389
7.2344
7.2305
7.2099
7.2055
7.2008
7.1861
7.1839
7.0322
7.0148
7.0101
6.9924
6.7087
6.7032
6.6895
6.6863
5.0968
5.0792
4.6528
4.2967
3.7778
2.3705
2.3237
1.5362
1.5188
1.2371
1.2194
1.1820
1.1645
0.9972
0.9810
Title WYR2-46.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
i-Pr
Me
N
Ts
Bn
5k
2.05
8.01
2.68
1.01
2.33
2.72
1.00
0.34
2.00
0.68
0.99
0.33
3.00
1.03
1.02
3.04
6.00
2.00
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 -0.5 -1.0
f1 (ppm)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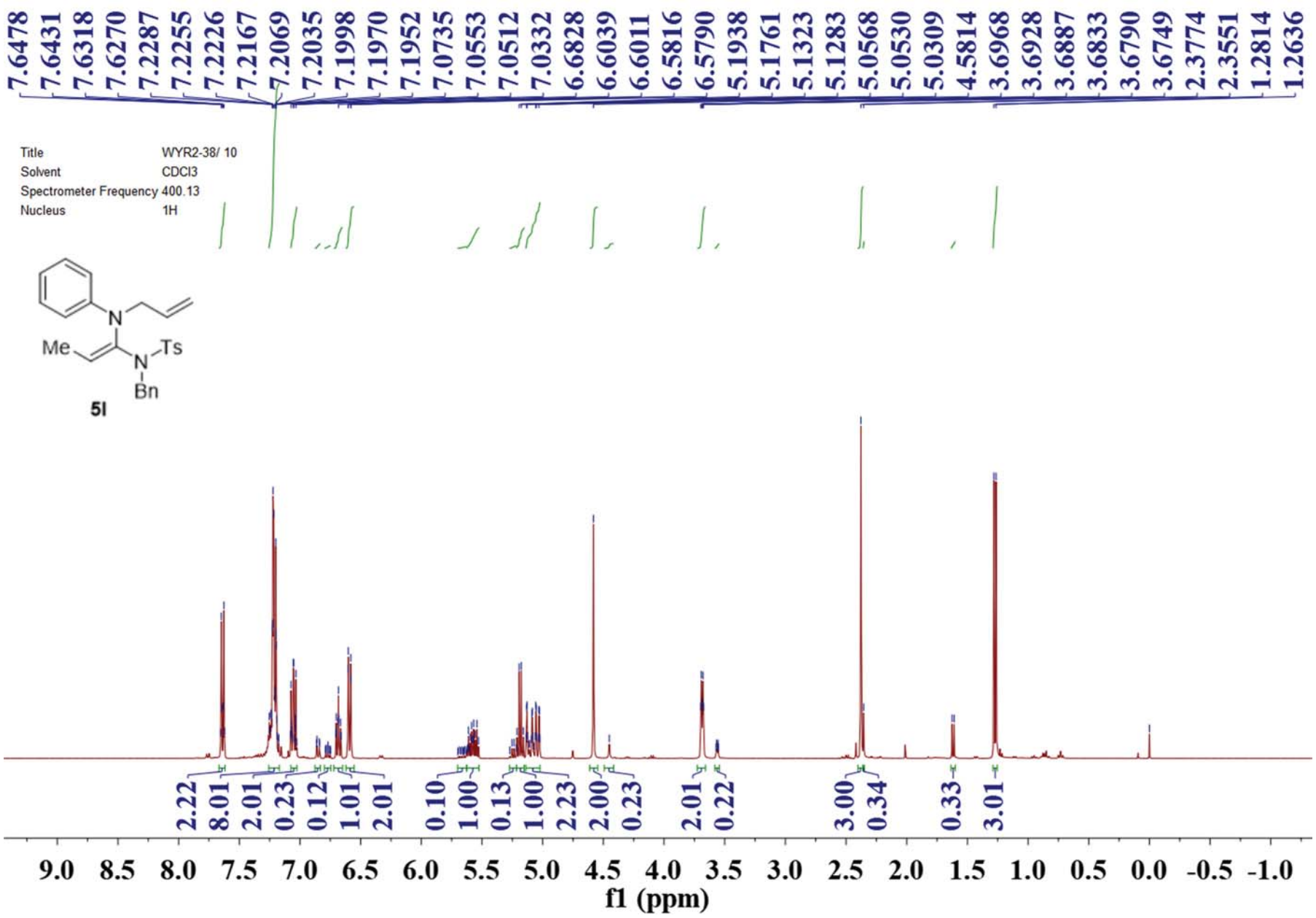
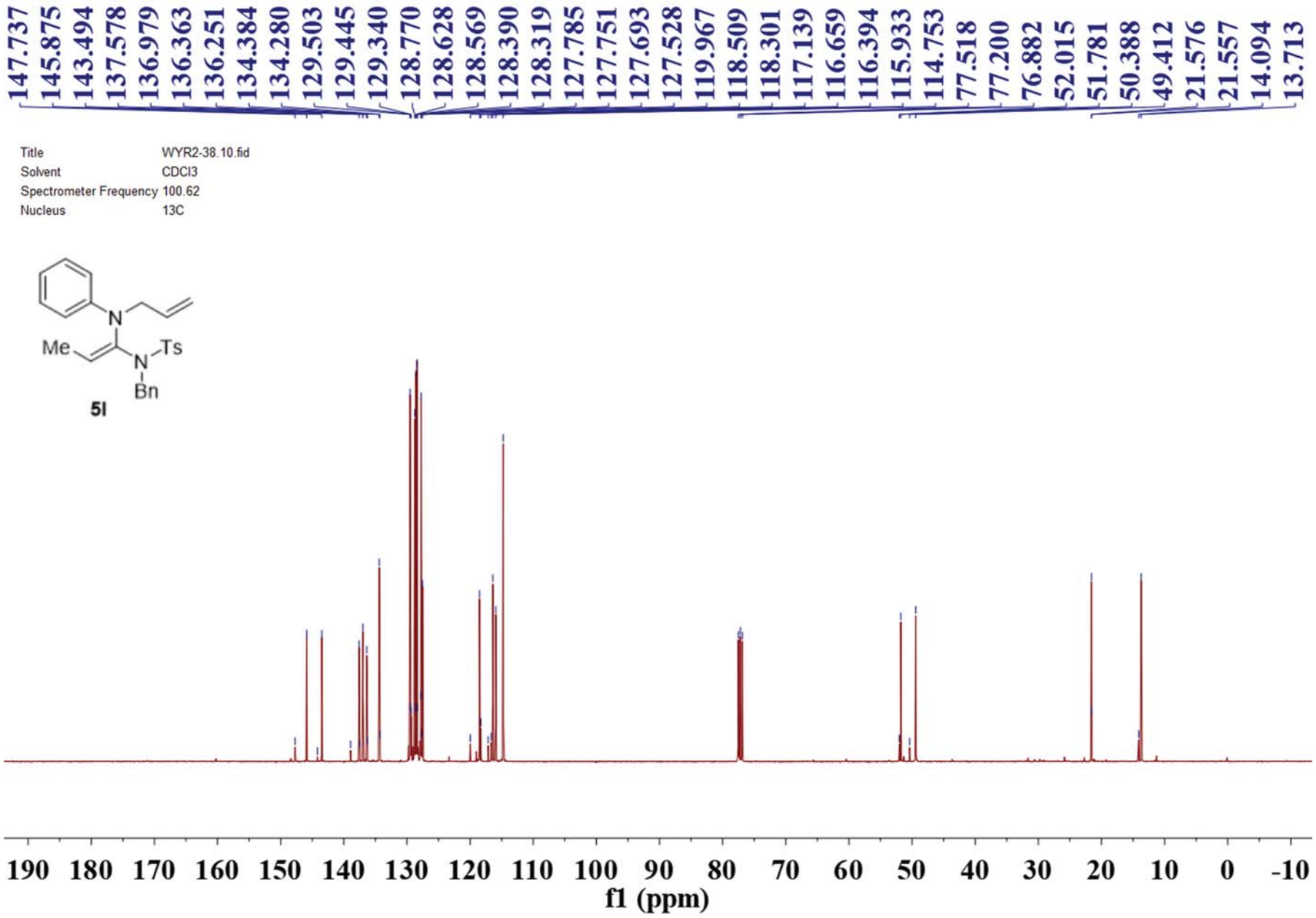
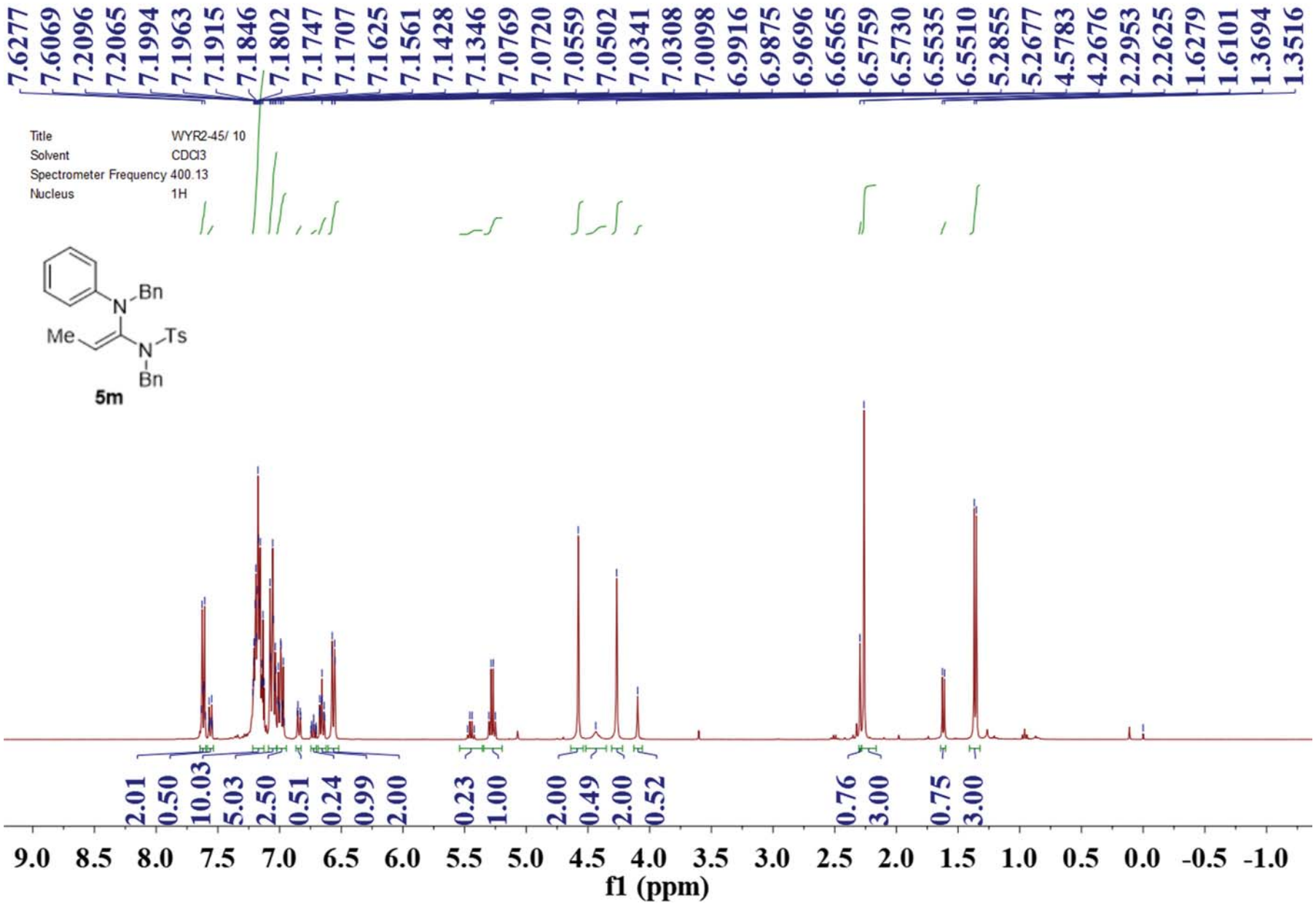
143.344
138.827
137.795
137.530
129.375
129.269
129.251
128.707
128.660
128.541
128.442
128.161
128.098
127.835
127.804
127.681
127.341
125.009
119.234
119.011
114.016
77.518
77.200
76.881
51.524
51.224
50.770
48.425
21.533
21.468
20.171
13.768
13.201
Title WYR2-46.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
i-Pr
Me
N
Ts
Bn
5k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.6478
7.6431
7.6318
7.6270
7.2287
7.2255
7.2226
7.2167
7.2069
7.2035
7.1998
7.1970
7.1952
7.0735
7.0553
7.0512
7.0332
6.6828
6.6039
6.6011
6.5816
6.5790
5.1938
5.1761
5.1323
5.1283
5.0568
5.0530
5.0309
4.5814
3.6968
3.6928
3.6887
3.6833
3.6790
3.6749
2.3774
2.3551
1.2814
1.2636
Title WYR2-38/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
N
Bn
5l
2.22
8.01
2.01
0.23
0.12
1.01
2.01
0.10
1.00
0.13
1.00
2.23
2.00
0.23
2.01
0.22
3.00
0.34
0.33
3.01
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 -0.5 -1.0
f1 (ppm)


147.737
145.875
143.494
137.578
136.979
136.363
136.251
134.384
134.280
129.503
129.445
129.340
128.770
128.628
128.569
128.390
128.319
127.785
127.751
127.693
127.528
119.967
118.509
118.301
117.139
116.659
116.394
115.933
114.753
77.518
77.200
76.882
52.015
51.781
50.388
49.412
21.576
21.557
14.094
13.713
Title WYR2-38.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
N
Ts
Bn
5l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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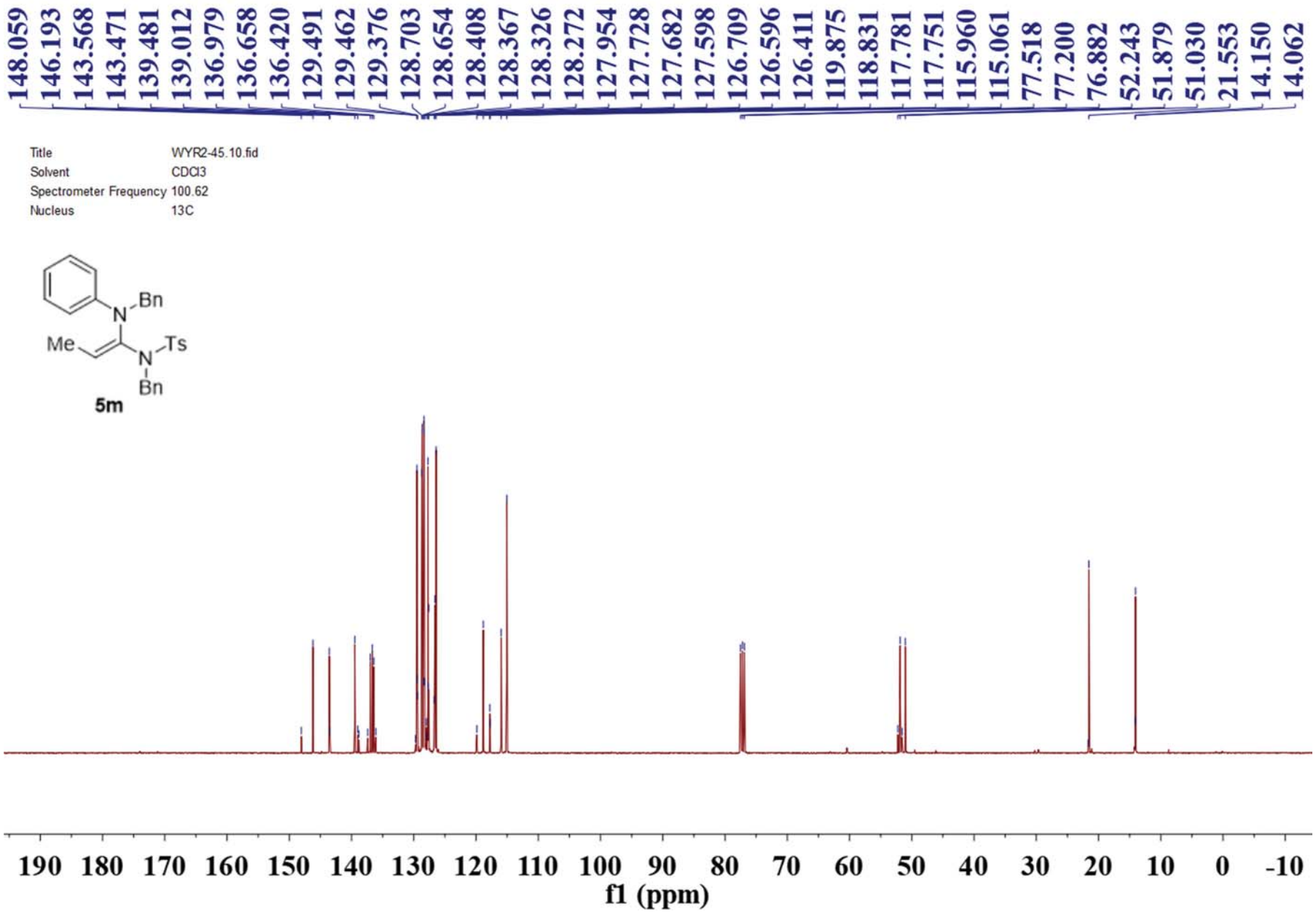
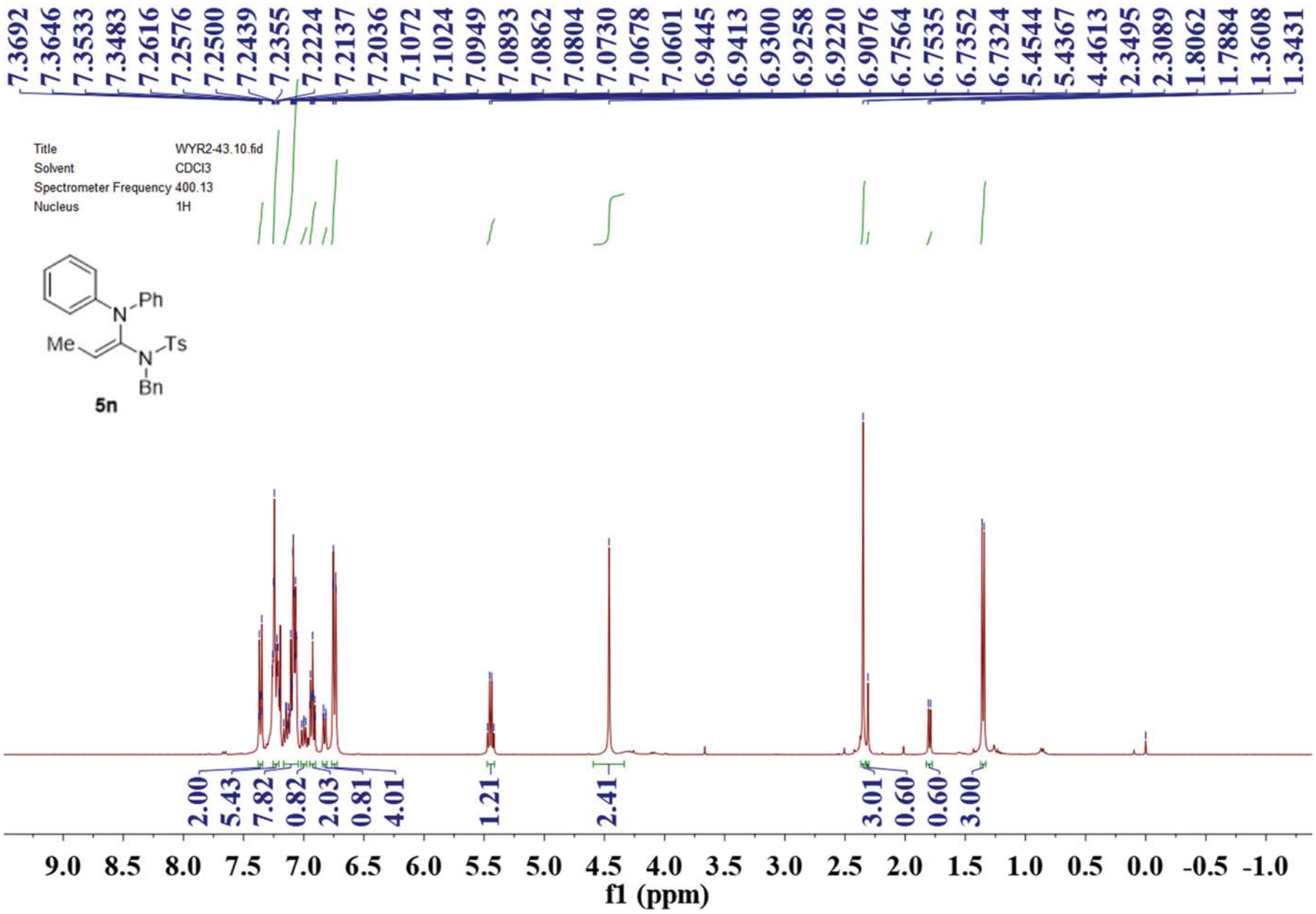
7.6069
7.2096
7.2065
7.1994
7.1963
7.1915
7.1846
7.1802
7.1747
7.1707
7.1625
7.1561
7.1428
7.1346
7.0769
7.0720
7.0559
7.0502
7.0341
7.0308
7.0098
6.9916
6.9875
6.9696
6.6565
6.5759
6.5730
6.5535
6.5510
5.2855
5.2677
4.5783
4.2676
2.2953
2.2625
1.6279
1.6101
1.3694
1.3516
Title WYR2-45/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Bn
N
Me
Ts
N
Bn
5m
2.01
0.50
10.03
5.03
2.50
0.51
0.24
0.99
2.00
0.23
1.00
2.00
0.49
2.00
0.52
0.76
3.00
0.75
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 -0.5 -1.0
f1 (ppm)


148.059
146.193
143.568
143.471
139.481
139.012
136.979
136.658
136.420
129.491
129.462
129.376
128.703
128.654
128.408
128.367
128.326
128.272
127.954
127.728
127.682
127.598
126.709
126.596
126.411
119.875
118.831
117.781
117.751
115.960
115.061
77.518
77.200
76.882
52.243
51.879
51.030
21.553
14.150
14.062
Title WYR2-45.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Bn
Me
N
Ts
Bn
5m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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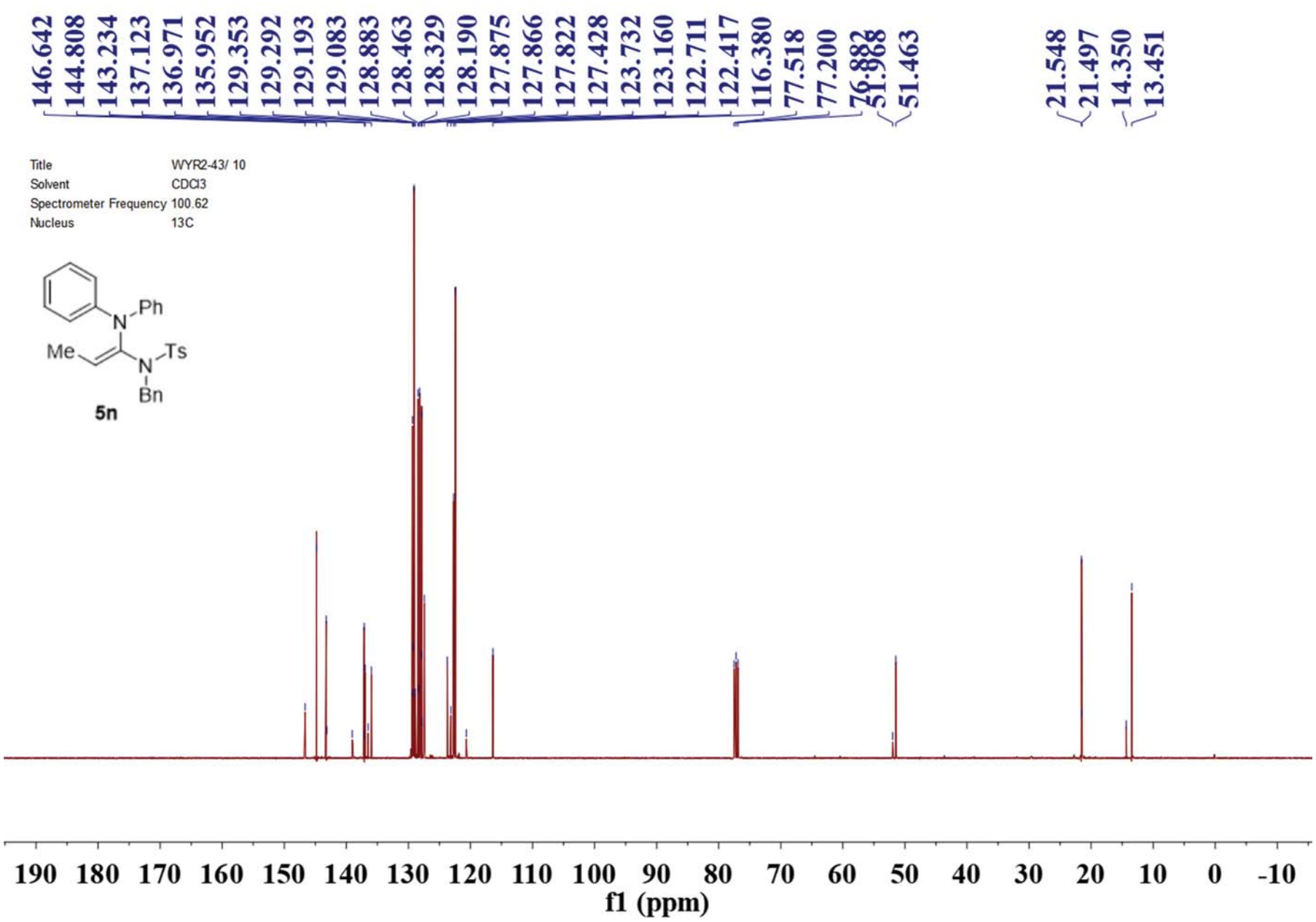
7.3646
7.3533
7.3483
7.2616
7.2576
7.2500
7.2439
7.2355
7.2224
7.2137
7.2036
7.1072
7.1024
7.0949
7.0893
7.0862
7.0804
7.0730
7.0678
7.0601
6.9445
6.9413
6.9300
6.9258
6.9220
6.9076
6.7564
6.7535
6.7352
6.7324
5.4544
5.4367
4.4613
2.3495
2.3089
1.8062
1.7884
1.3608
1.3431
Title WYR2-43.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ts
N
Bn
5n
2.00
5.43
7.82
0.82
2.03
0.81
4.01
1.21
2.41
3.01
0.60
0.60
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 -0.5 -1.0
f1 (ppm)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144.808
143.234
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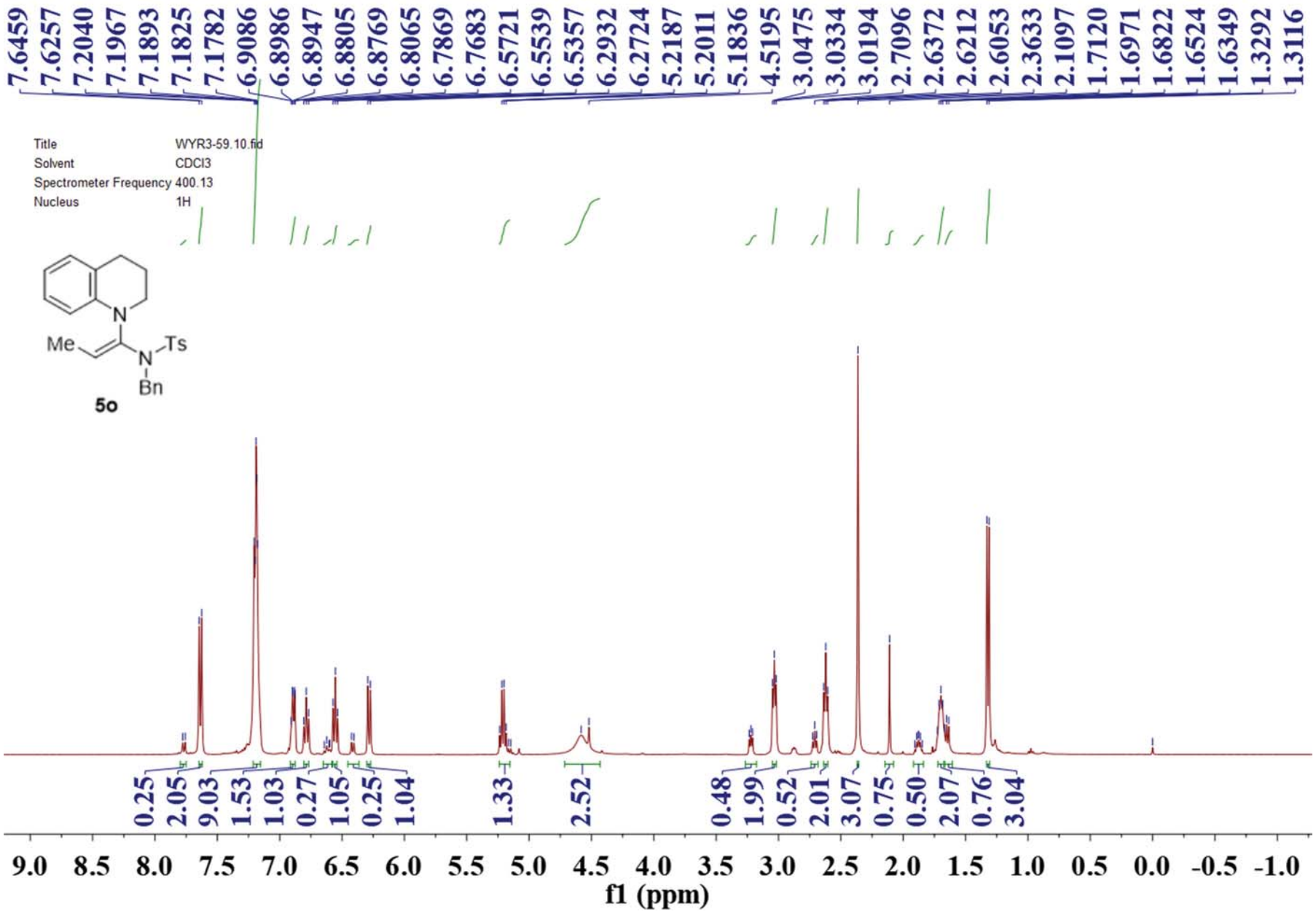
136.971
135.952
129.353
129.292
129.193
129.083
128.883
128.463
128.329
128.190
127.875
127.866
127.822
127.428
123.732
123.160
122.711
122.417
116.380
77.518
77.200
76.882
51.968
51.463
21.548
21.497
14.350
13.451
Title WYR2-43/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
N
Ts
Bn
5n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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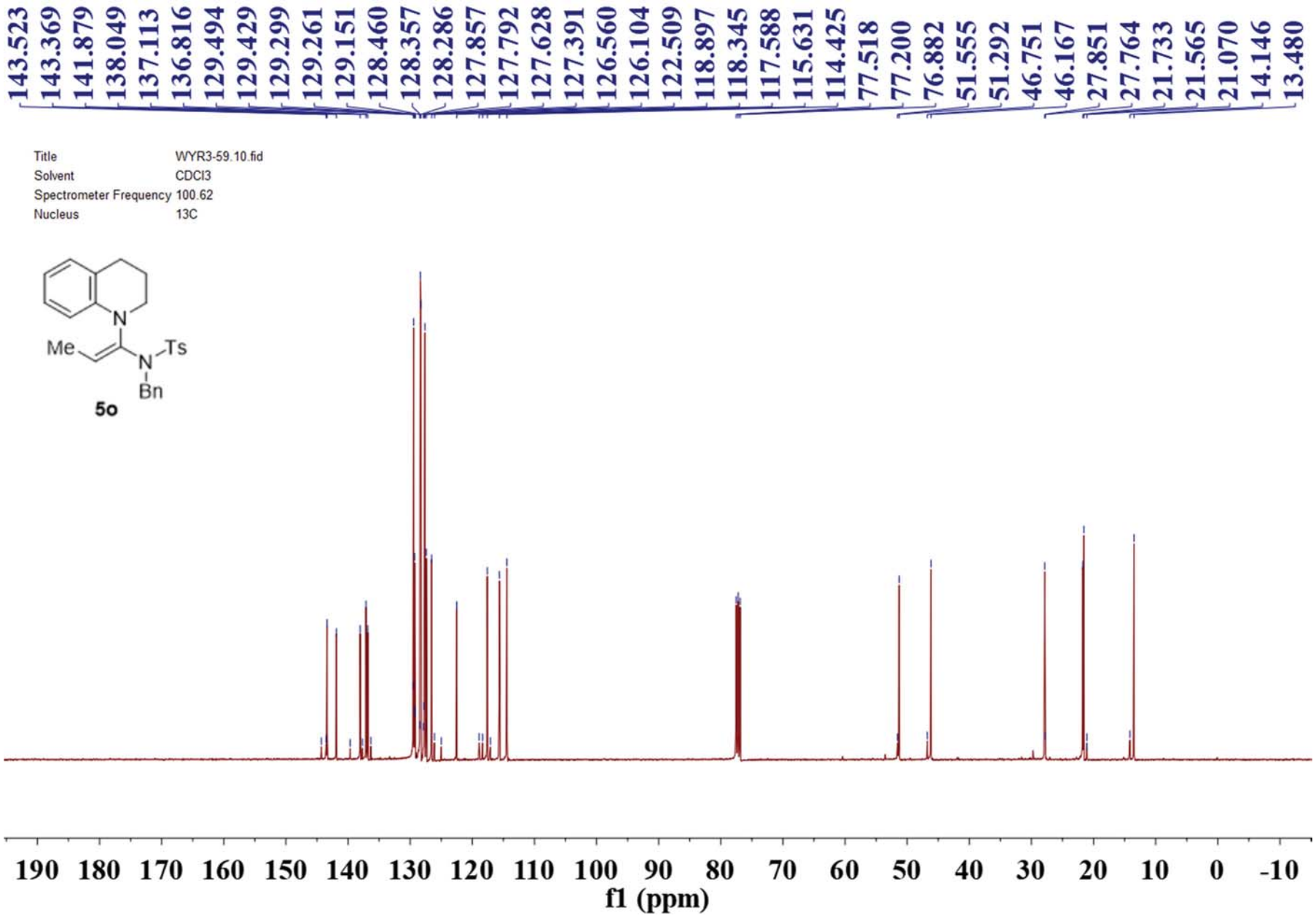
7.6257
7.2040
7.1967
7.1893
7.1825
7.1782
6.9086
6.8986
6.8947
6.8805
6.8769
6.8065
6.7869
6.7683
6.5721
6.5539
6.5357
6.2932
6.2724
5.2187
5.2011
5.1836
4.5195
3.0475
3.0334
3.0194
2.7096
2.6372
2.6212
2.6053
2.3633
2.1097
1.7120
1.6971
1.6822
1.6524
1.6349
1.3292
1.3116
Title WYR3-59.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
N
Bn
5o
0.25
2.05
9.03
1.53
1.03
0.27
1.05
0.25
1.04
1.33
2.52
0.48
1.99
0.52
2.01
3.07
0.75
0.50
2.07
0.76
3.04
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 -0.5 -1.0
f1 (ppm)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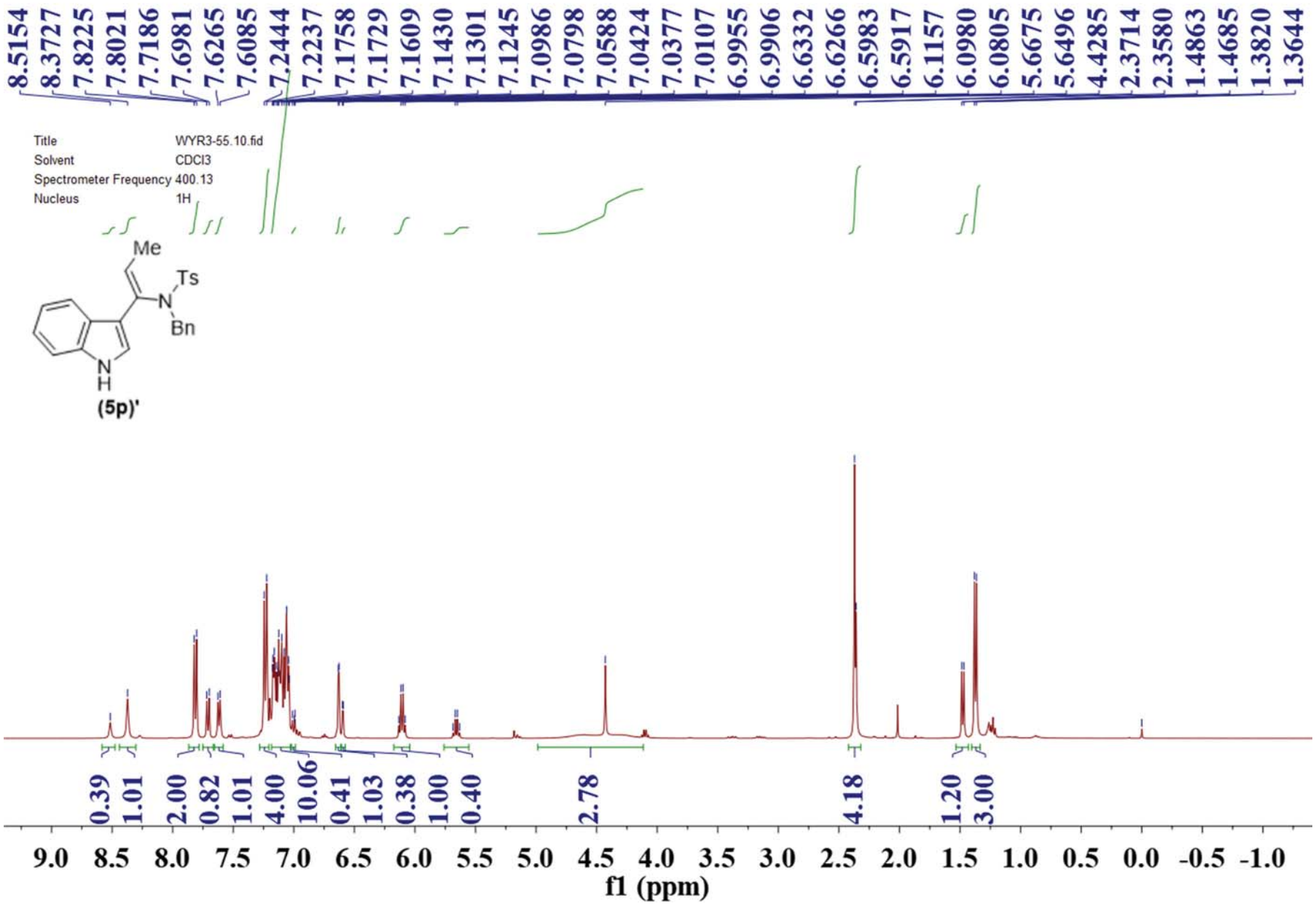
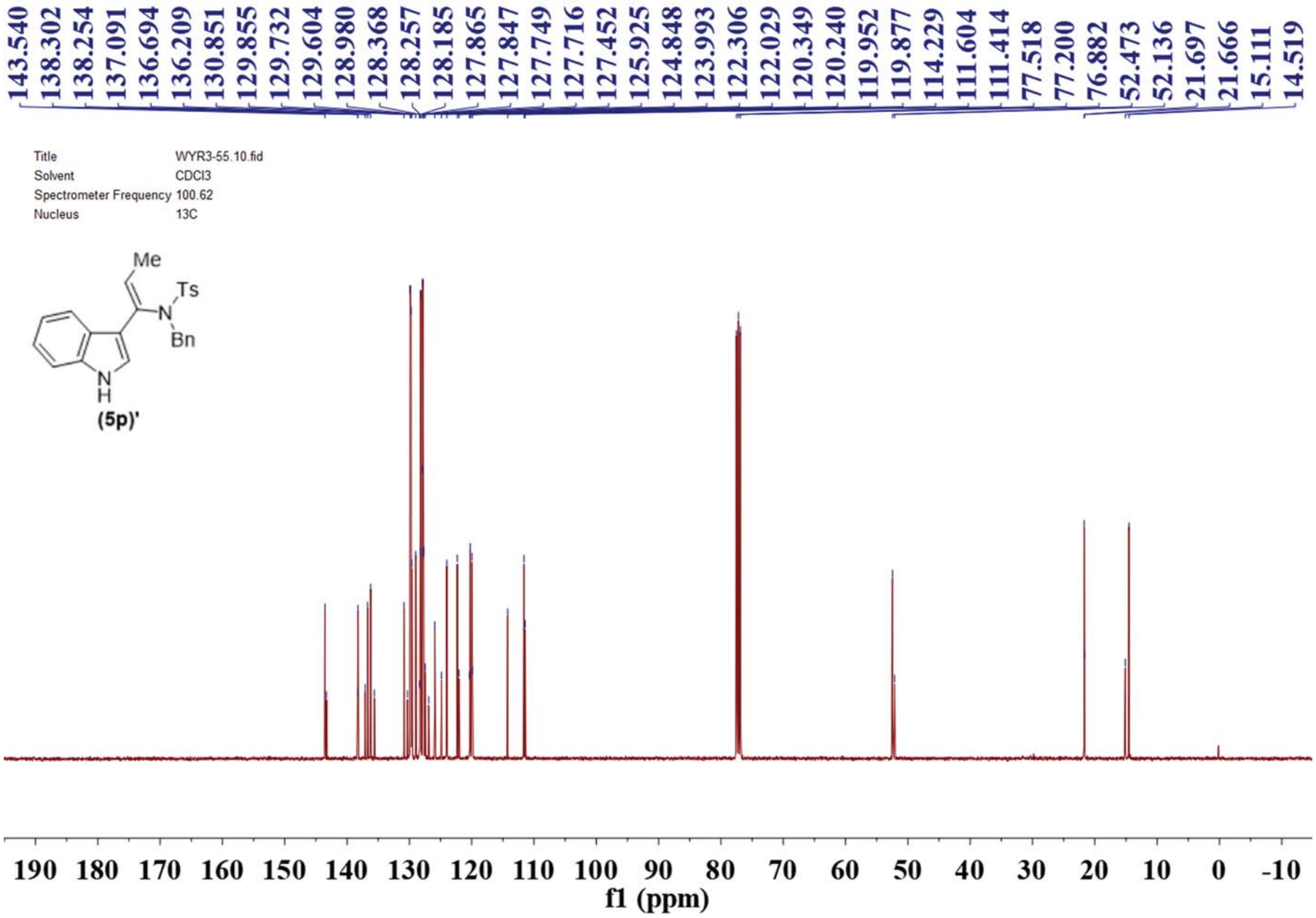
143.369
141.879
138.049
137.113
136.816
129.494
129.429
129.299
129.261
129.151
128.460
128.357
128.286
127.857
127.792
127.628
127.391
126.560
126.104
122.509
118.897
118.345
117.588
115.631
114.425
77.518
77.200
76.882
51.555
51.292
46.751
46.167
27.851
27.764
21.733
21.565
21.070
14.146
13.480
Title WYR3-59.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
N
Ts
Bn
5o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.5154
8.3727
7.8225
7.8021
7.7186
7.6981
7.6265
7.6085
7.2444
7.2237
7.1758
7.1729
7.1609
7.1430
7.1301
7.1245
7.0986
7.0798
7.0588
7.0424
7.0377
7.0107
6.9955
6.9906
6.6332
6.6266
6.5983
6.5917
6.1157
6.0980
6.0805
5.6675
5.6496
4.4285
2.3714
2.3580
1.4863
1.4685
1.3820
1.3644
Title WYR3-55.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ts
N
Bn
N
H
(5p)'
0.39
1.01
2.00
0.82
1.01
4.00
10.06
0.41
1.03
0.38
1.00
0.40
2.78
4.18
1.20
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 -0.5 -1.0
f1 (ppm)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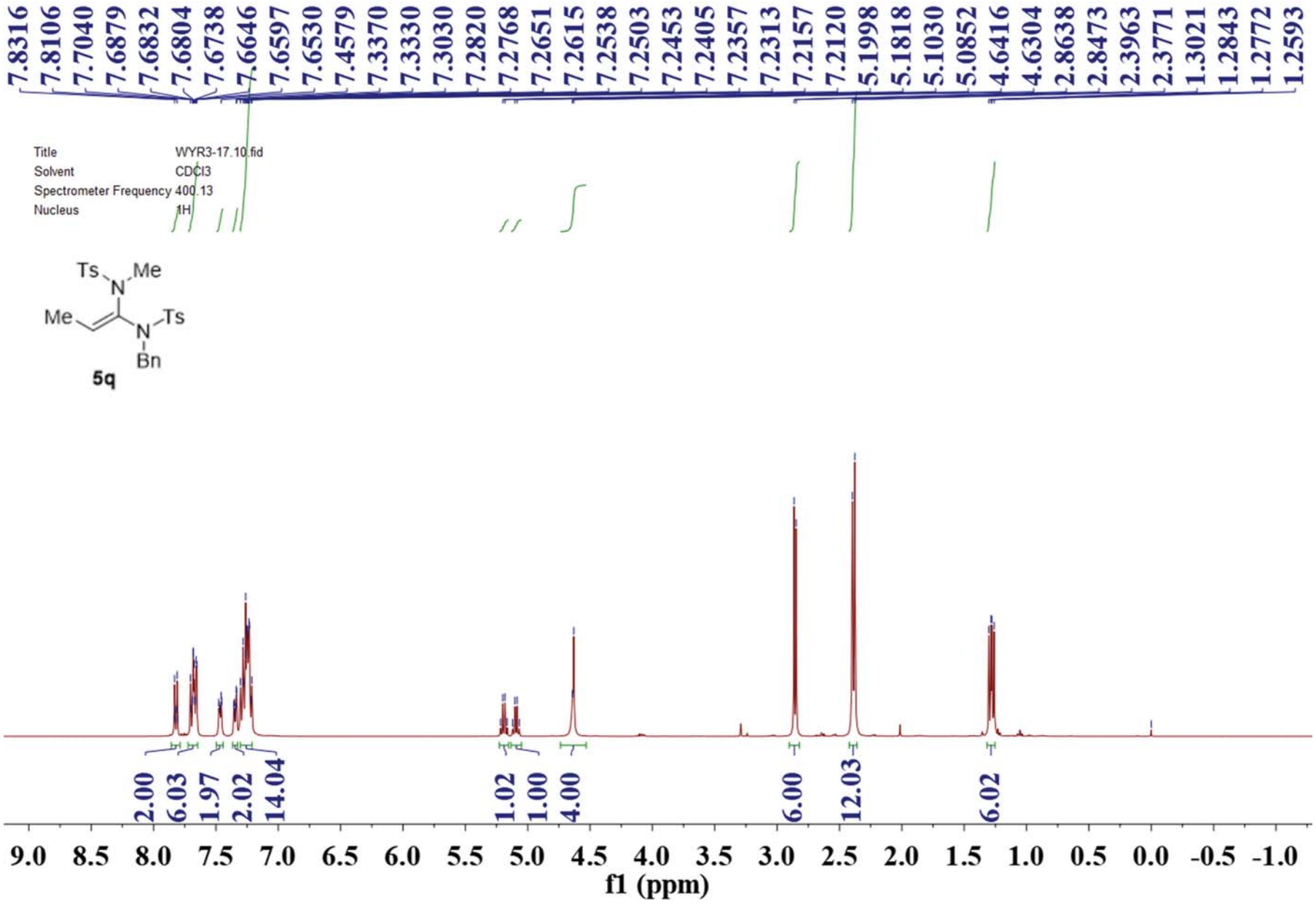
138.254
137.091
136.694
136.209
130.851
129.855
129.732
129.604
128.980
128.368
128.257
128.185
127.865
127.847
127.749
127.716
127.452
125.925
124.848
123.993
122.306
122.029
120.349
120.240
119.952
119.877
114.229
111.604
111.414
77.518
77.200
76.882
52.473
52.136
21.697
21.666
15.111
14.519
Title WYR3-55.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Ts
N
Bn
N
H
(5p)'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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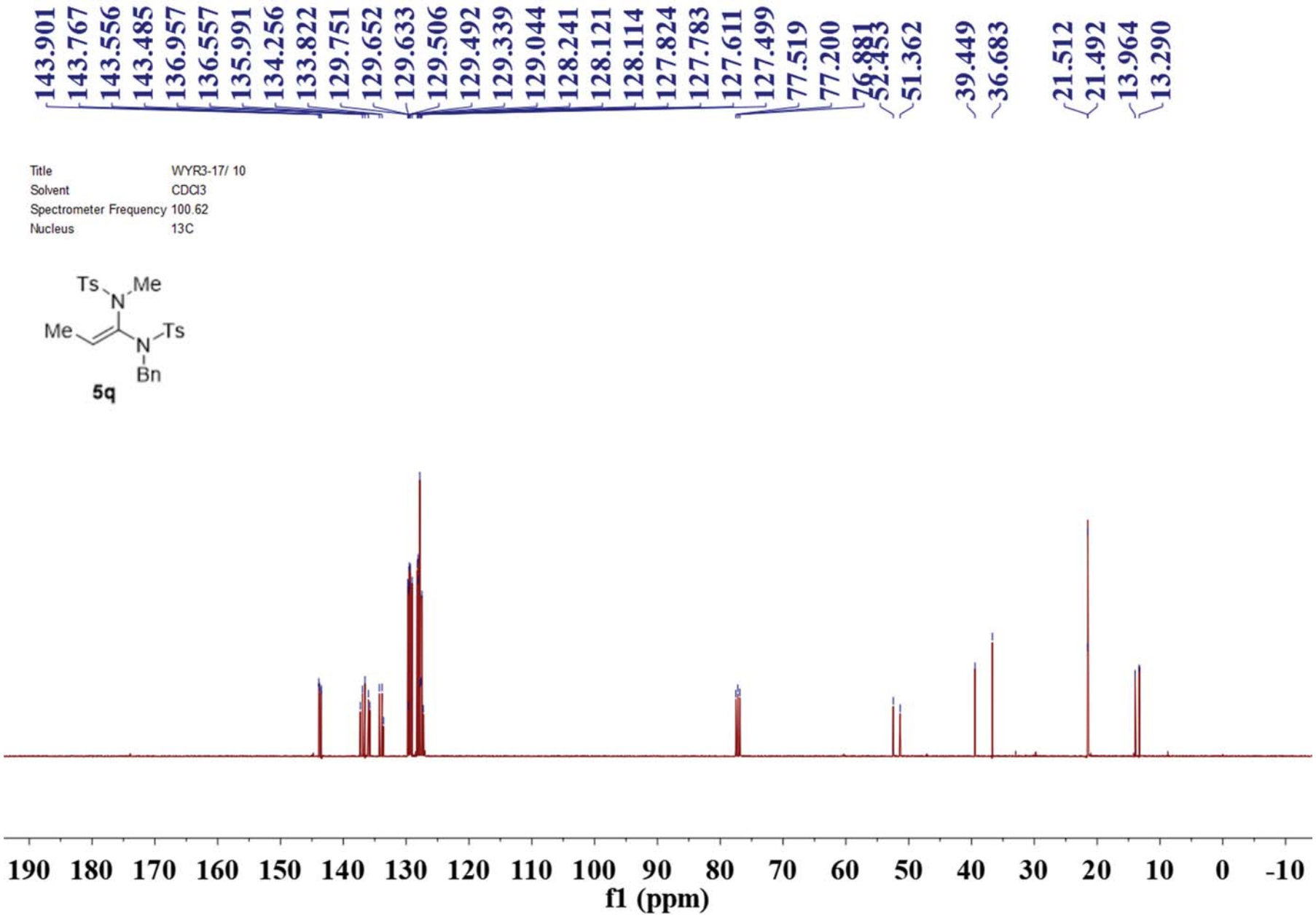
7.7040
7.6879
7.6832
7.6804
7.6738
7.6646
7.6597
7.6530
7.4579
7.3370
7.3330
7.3030
7.2820
7.2768
7.2651
7.2615
7.2538
7.2503
7.2453
7.2405
7.2357
7.2313
7.2157
7.2120
5.1998
5.1818
5.1030
5.0852
4.6416
4.6304
2.8638
2.8473
2.3963
2.3771
1.3021
1.2843
1.2772
1.2593
Title WYR3-17.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
N
Ts
Bn
5q
2.00
6.03
1.97
2.02
14.04
1.02
1.00
4.00
6.00
12.03
6.02
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 -0.5 -1.0
f1 (ppm)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143.556
143.485
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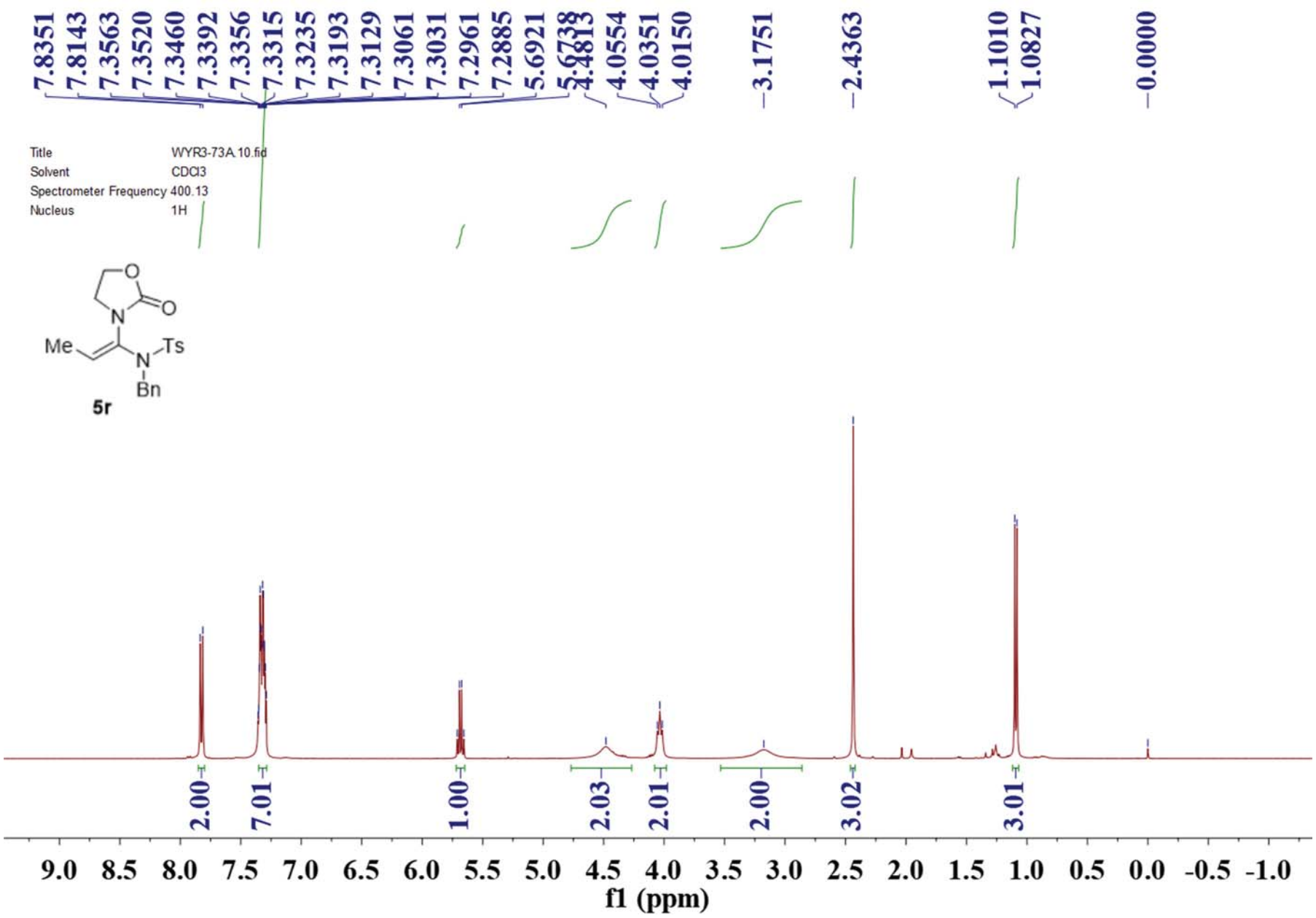
136.557
135.991
134.256
133.822
129.751
129.652
129.633
129.506
129.492
129.339
129.044
128.241
128.121
128.114
127.824
127.783
127.611
127.499
77.519
77.200
76.881
52.453
51.362
39.449
36.683
21.512
21.492
13.964
13.290
Title WYR3-17/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
N
Ts
Bn
5q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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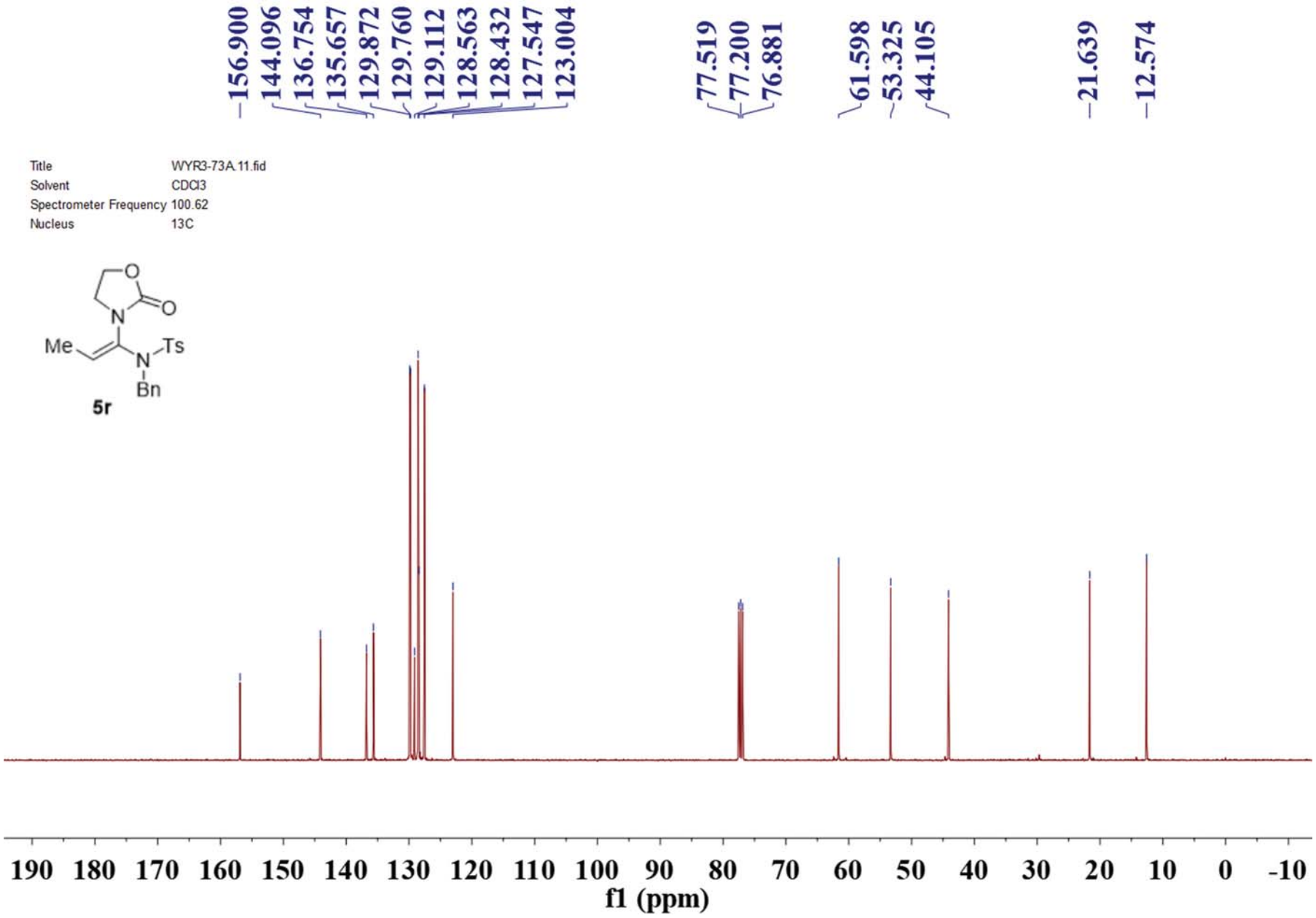
7.8143
7.3563
7.3520
7.3460
7.3392
7.3356
7.3315
7.3235
7.3193
7.3129
7.3061
7.3031
7.2961
7.2885
5.6921
4.0554
4.0351
4.0150
3.1751
2.4363
1.1010
1.0827
0.0000
Title WYR3-73A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ts
Bn
5r
2.00
7.01
1.00
2.03
2.01
2.00
3.02
3.01
9.0 8.5 8.0 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 -0.5 -1.0
f1 (ppm)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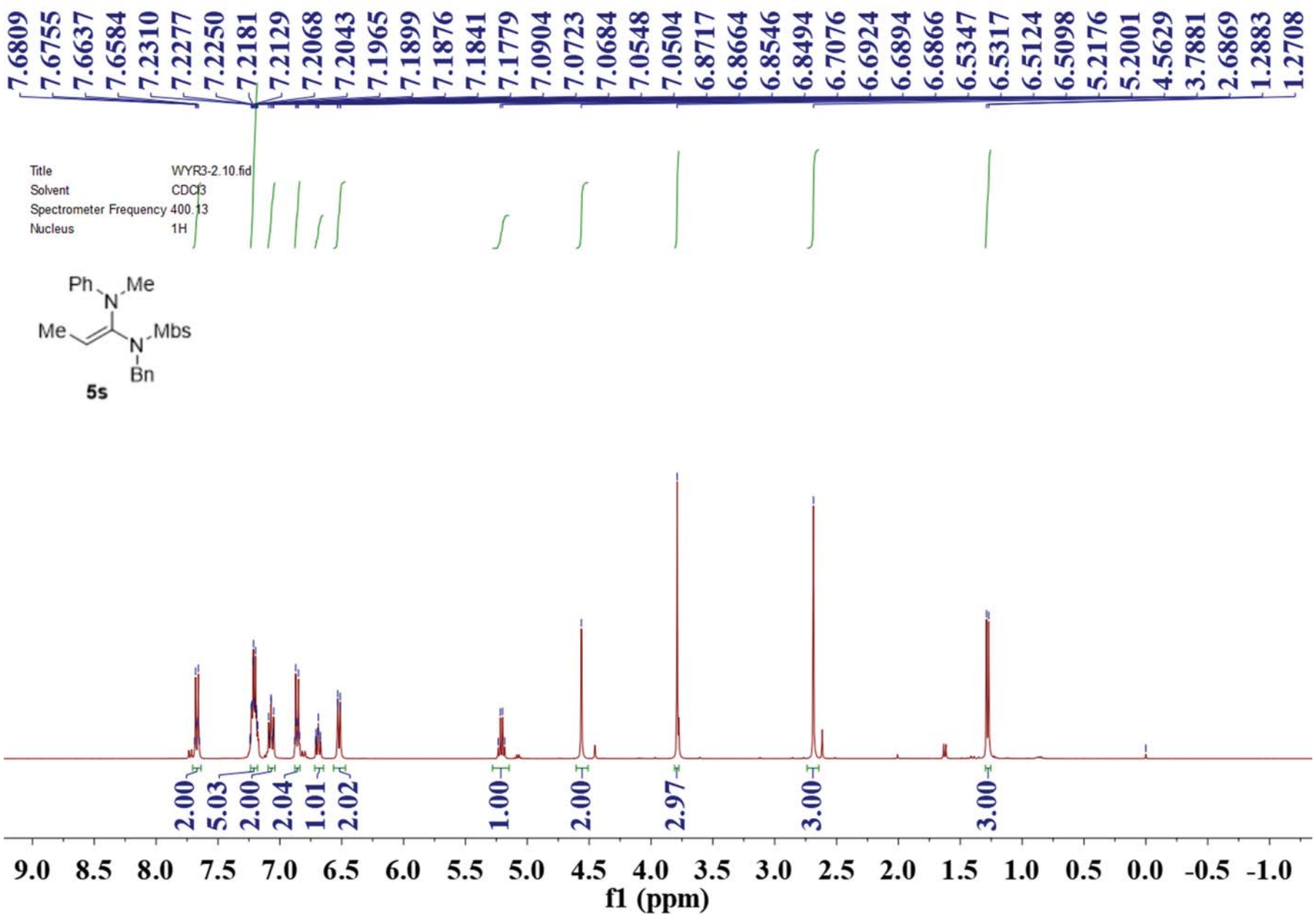
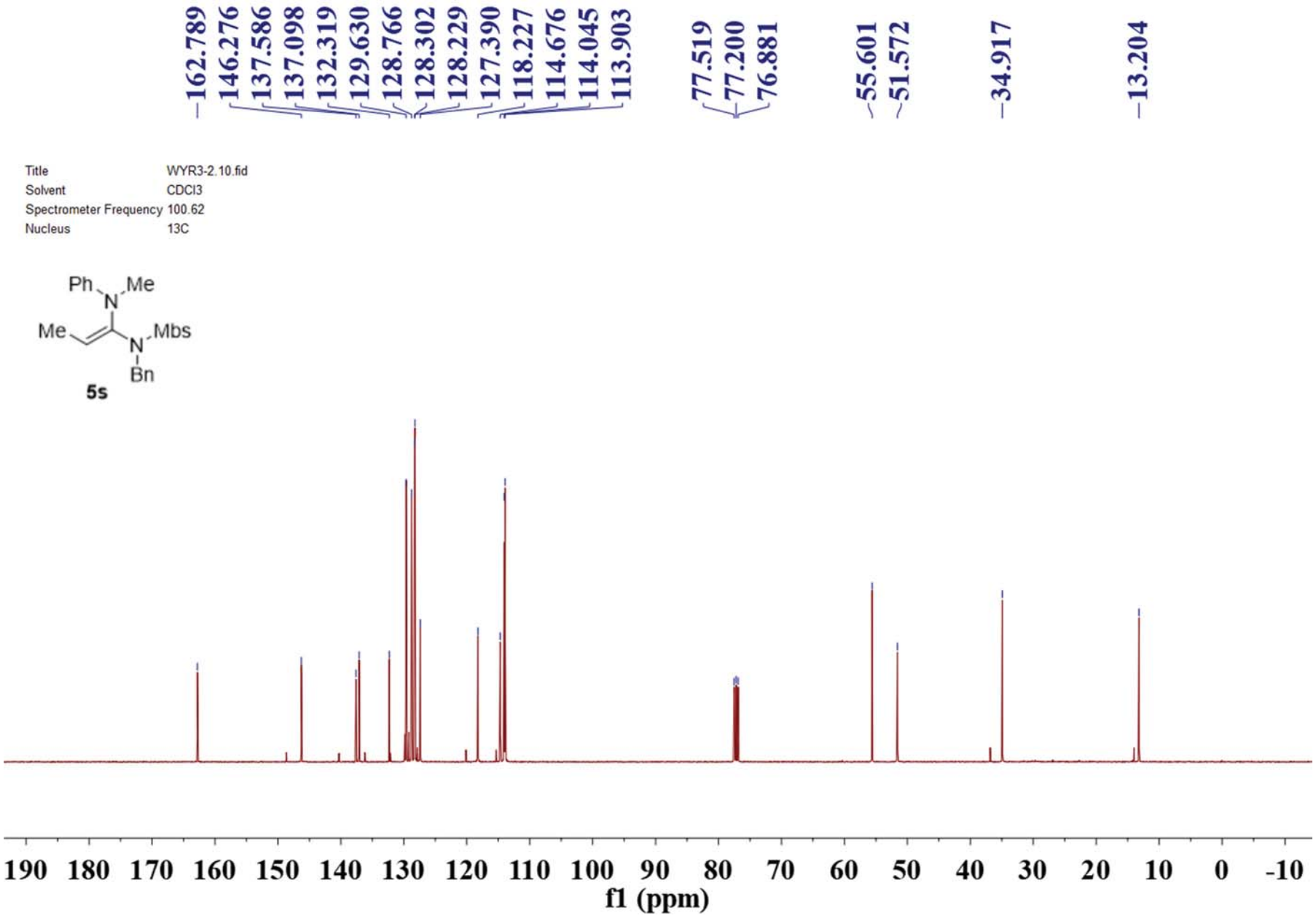
144.096
136.754
135.657
129.872
129.760
129.112
128.563
128.432
127.547
123.004
77.519
77.200
76.881
61.598
53.325
44.105
21.639
12.574
Title WYR3-73A.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Ts
Bn
5r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.6809
7.6755
7.6637
7.6584
7.2310
7.2277
7.2250
7.2181
7.2129
7.2068
7.2043
7.1965
7.1899
7.1876
7.1841
7.1779
7.0904
7.0723
7.0684
7.0548
7.0504
6.8717
6.8664
6.8546
6.8494
6.7076
6.6924
6.6894
6.6866
6.5347
6.5317
6.5124
6.5098
5.2176
5.2001
4.5629
3.7881
2.6869
1.2883
1.2708
Title WYR3-2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Mbs
Bn
5s
2.00
5.03
2.00
2.04
1.01
2.02
1.00
2.00
2.97
3.00
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 -0.5 -1.0
f1 (ppm)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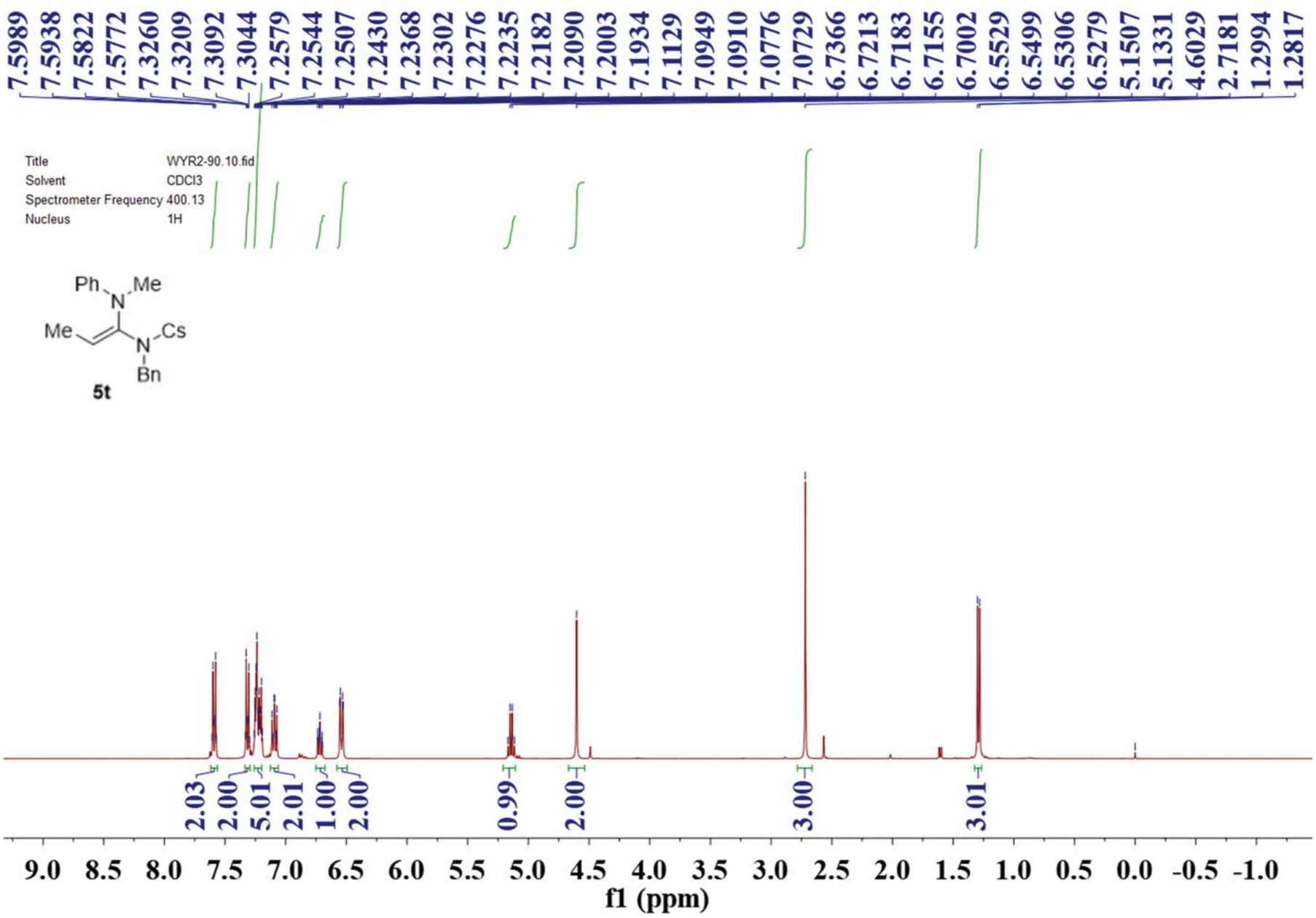
146.276
137.586
137.098
132.319
129.630
128.766
128.302
128.229
127.390
118.227
114.676
114.045
113.903
77.519
77.200
76.881
55.601
51.572
34.917
13.204
Title WYR3-2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Mbs
Bn
5s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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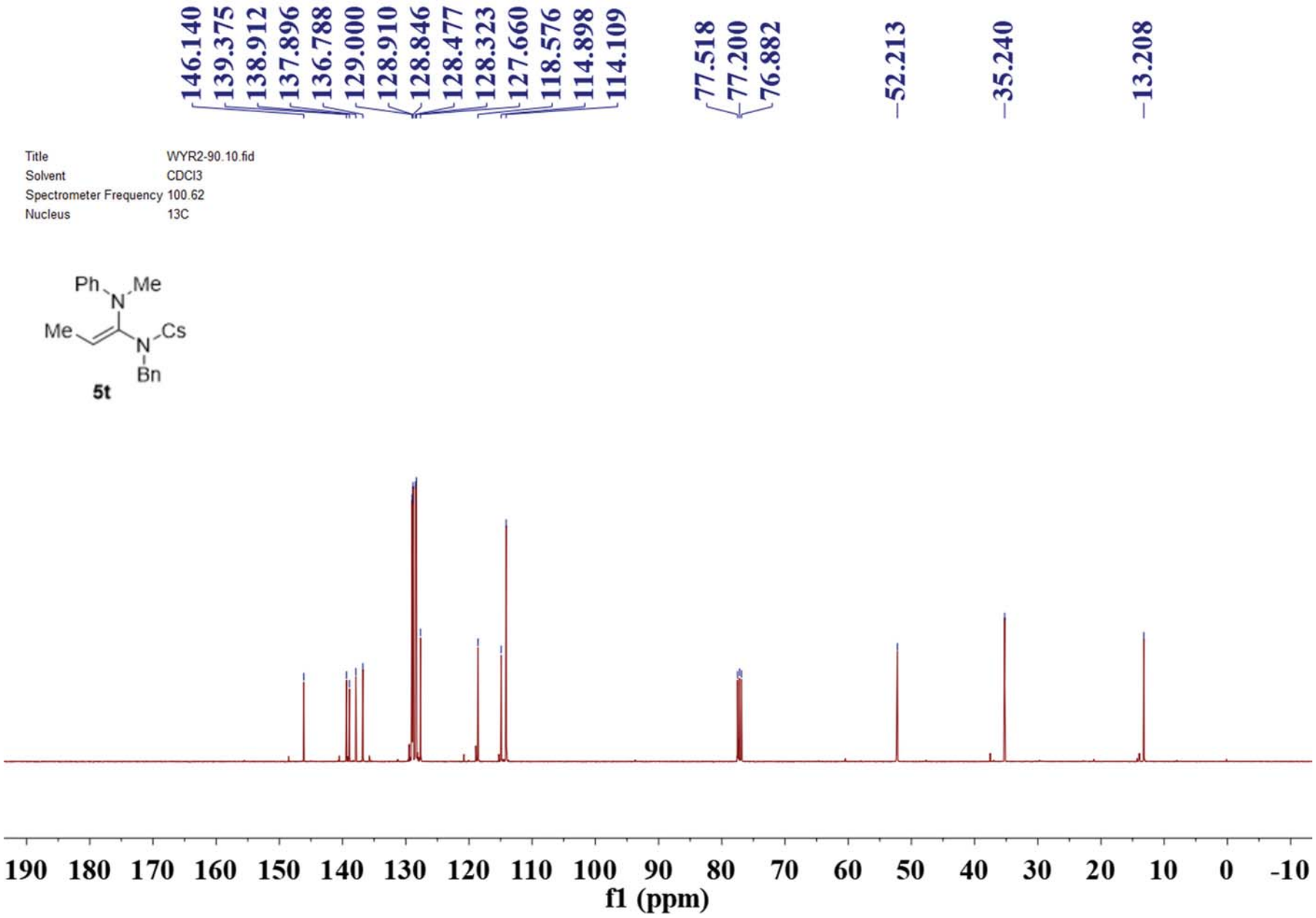
7.5938
7.5822
7.5772
7.3260
7.3209
7.3092
7.3044
7.2579
7.2544
7.2507
7.2430
7.2368
7.2302
7.2276
7.2235
7.2182
7.2090
7.2003
7.1934
7.1129
7.0949
7.0910
7.0776
7.0729
6.7366
6.7213
6.7183
6.7155
6.7002
6.5529
6.5499
6.5306
6.5279
5.1507
5.1331
4.6029
2.7181
1.2994
1.2817
Title WYR2-90.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Cs
Bn
5t
2.03
2.00
5.01
2.01
1.00
2.00
0.99
2.00
3.00
3.01
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 -0.5 -1.0
f1 (ppm)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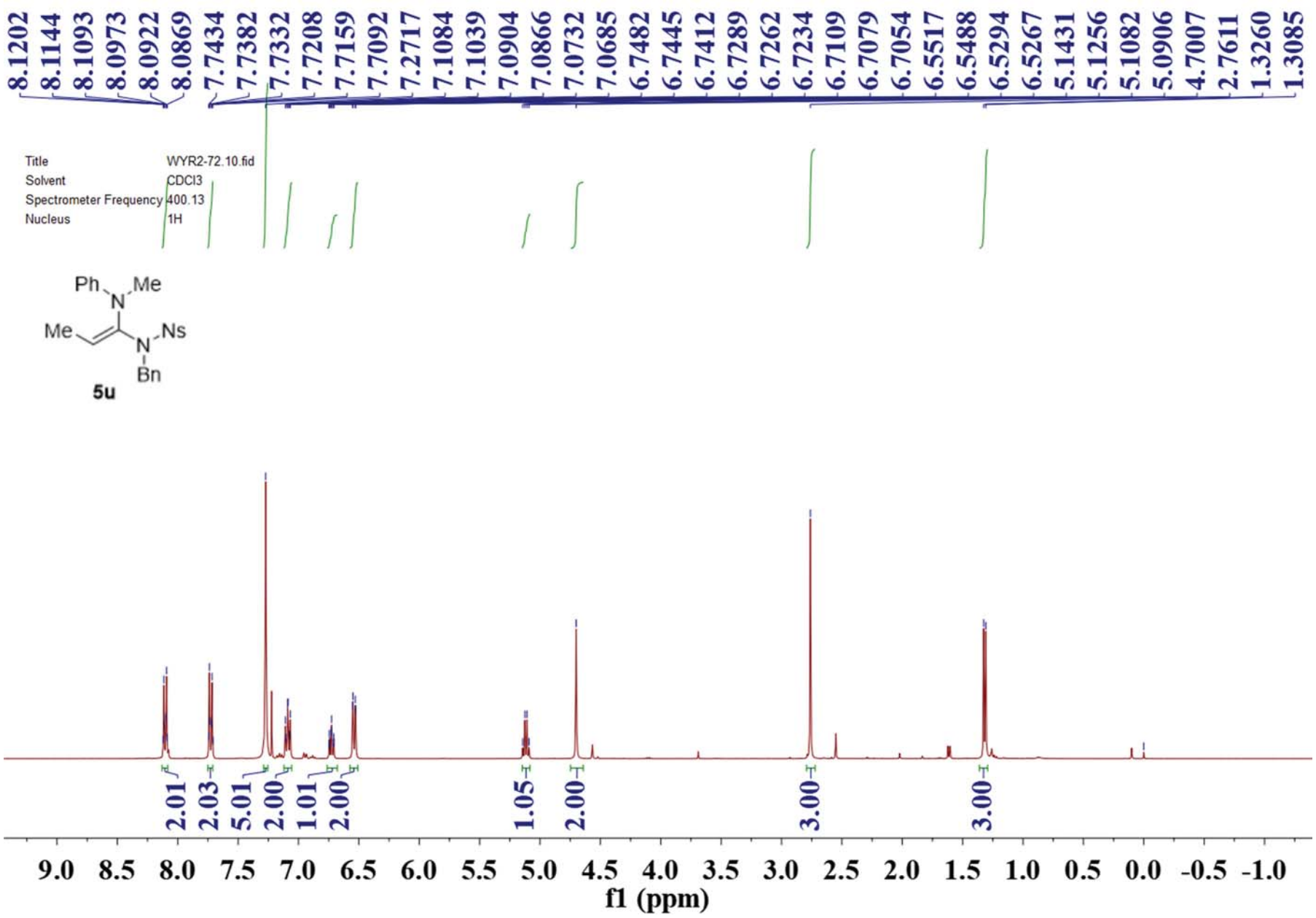
139.375
138.912
137.896
136.788
129.000
128.910
128.846
128.477
128.323
127.660
118.576
114.898
114.109
77.518
77.200
76.882
52.213
35.240
13.208
Title WYR2-90.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Cs
Bn
5t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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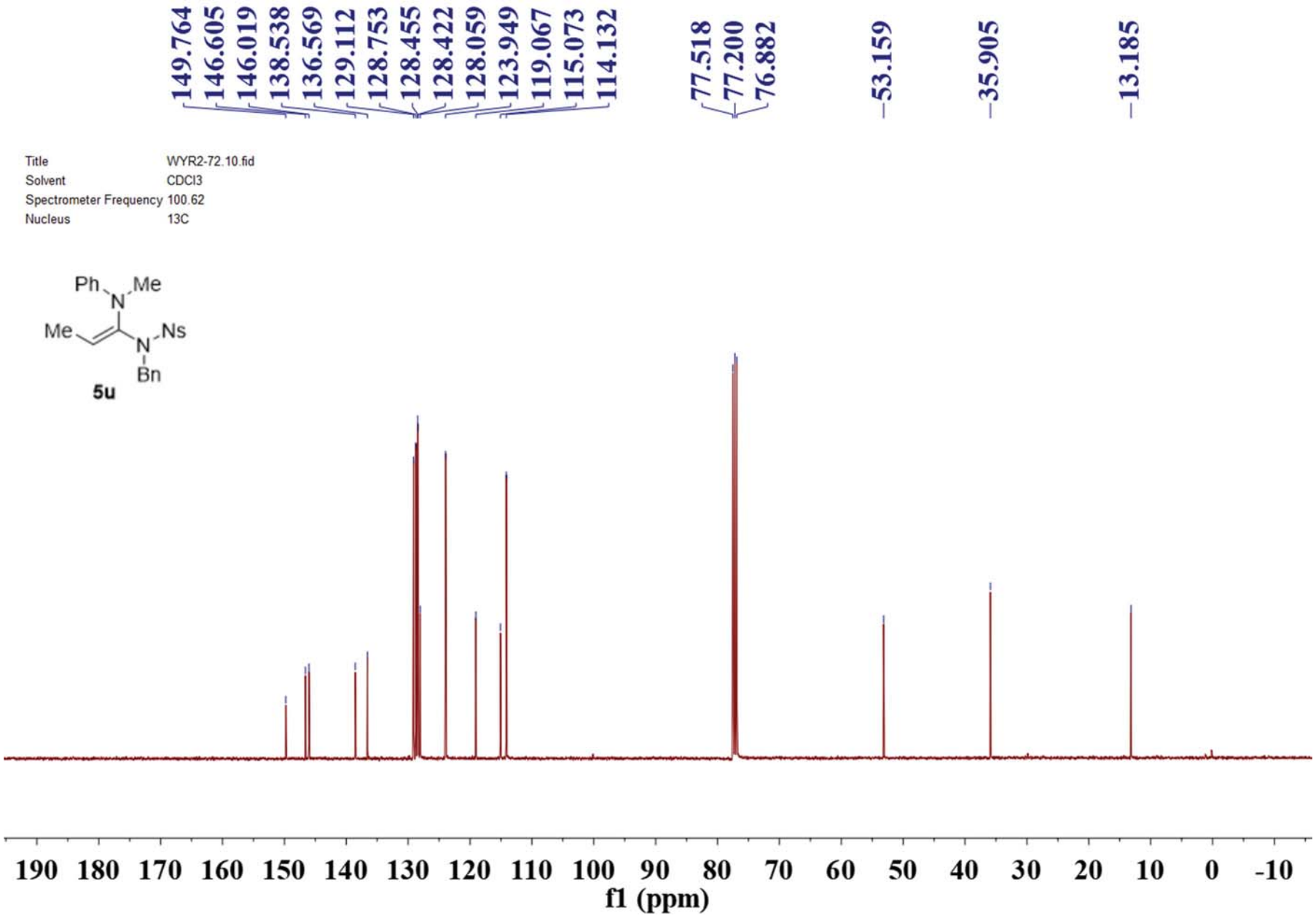
8.1144
8.1093
8.0973
8.0922
8.0869
7.7434
7.7382
7.7332
7.7208
7.7159
7.7092
7.2717
7.1084
7.1039
7.0904
7.0866
7.0732
7.0685
6.7482
6.7445
6.7412
6.7289
6.7262
6.7234
6.7109
6.7079
6.7054
6.5517
6.5488
6.5294
6.5267
5.1431
5.1256
5.1082
5.0906
4.7007
2.7611
1.3260
1.3085
Title WYR2-72.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Ns
Bn
5u
2.01
2.03
5.01
2.00
1.01
2.00
1.05
2.00
3.00
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 -0.5 -1.0
f1 (ppm)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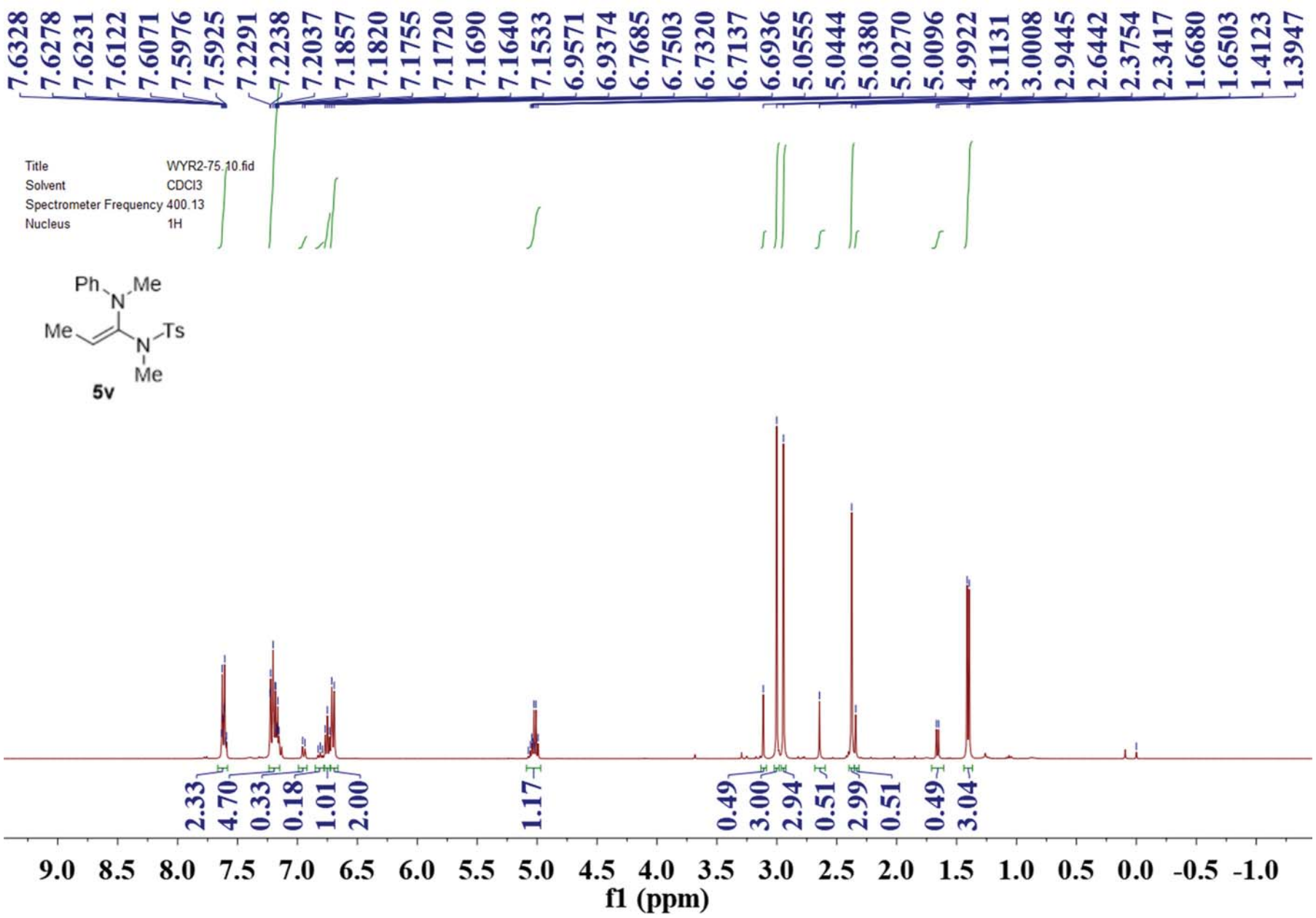
146.605
146.019
138.538
136.569
129.112
128.753
128.455
128.422
128.059
123.949
119.067
115.073
114.132
77.518
77.200
76.882
53.159
35.905
13.185
Title WYR2-72.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Ns
Bn
5u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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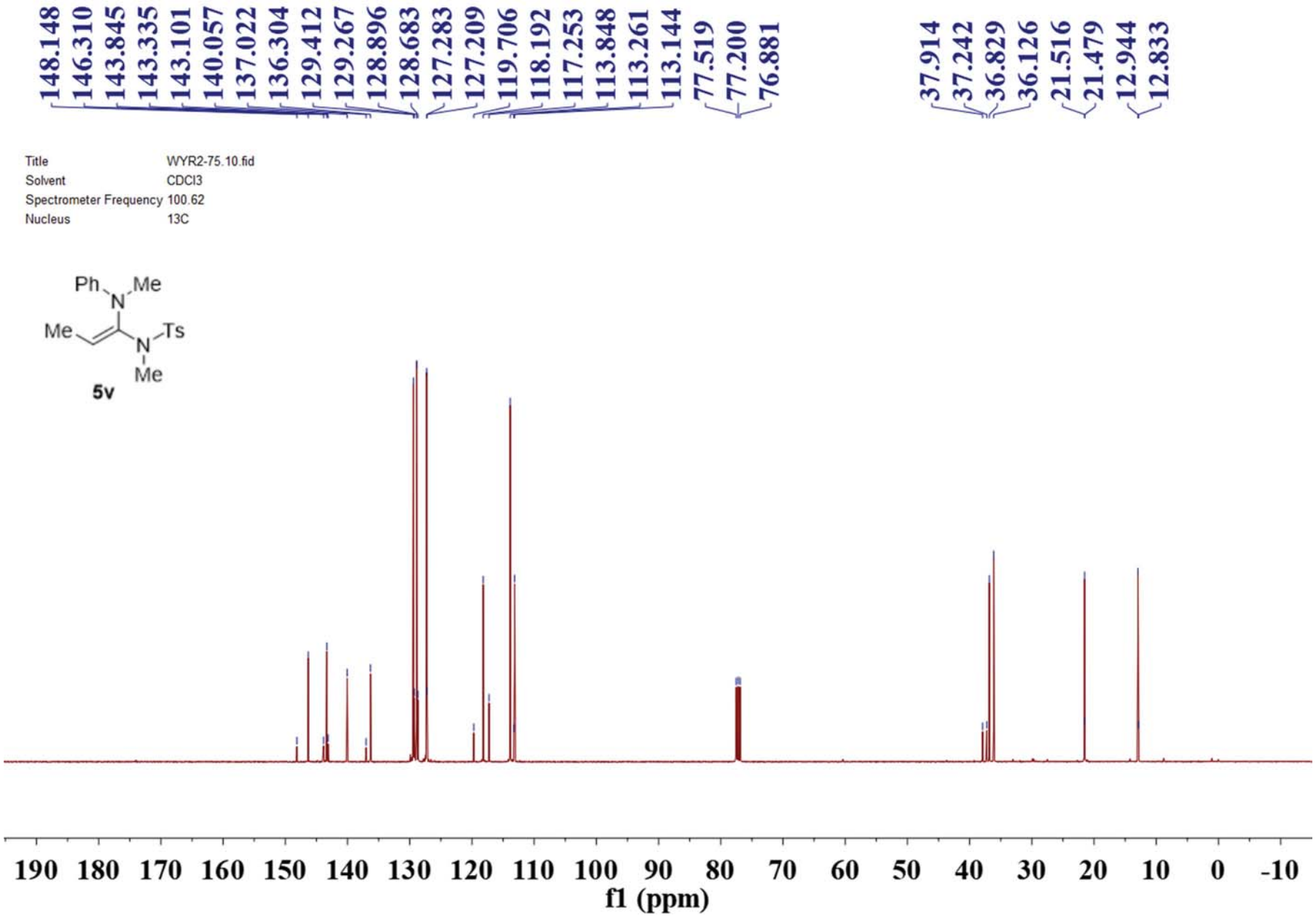
7.6278
7.6231
7.6122
7.6071
7.5976
7.5925
7.2291
7.2238
7.2037
7.1857
7.1820
7.1755
7.1720
7.1690
7.1640
7.1533
6.9571
6.9374
6.7685
6.7503
6.7320
6.7137
6.6936
5.0555
5.0444
5.0380
5.0270
5.0096
4.9922
3.1131
3.0008
2.9445
2.6442
2.3754
2.3417
1.6680
1.6503
1.4123
1.3947
Title WYR2-75.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Ts
Me
5v
2.33
4.70
0.33
0.18
1.01
2.00
1.17
0.49
3.00
2.94
0.51
2.99
0.51
0.49
3.04
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 -0.5 -1.0
f1 (ppm)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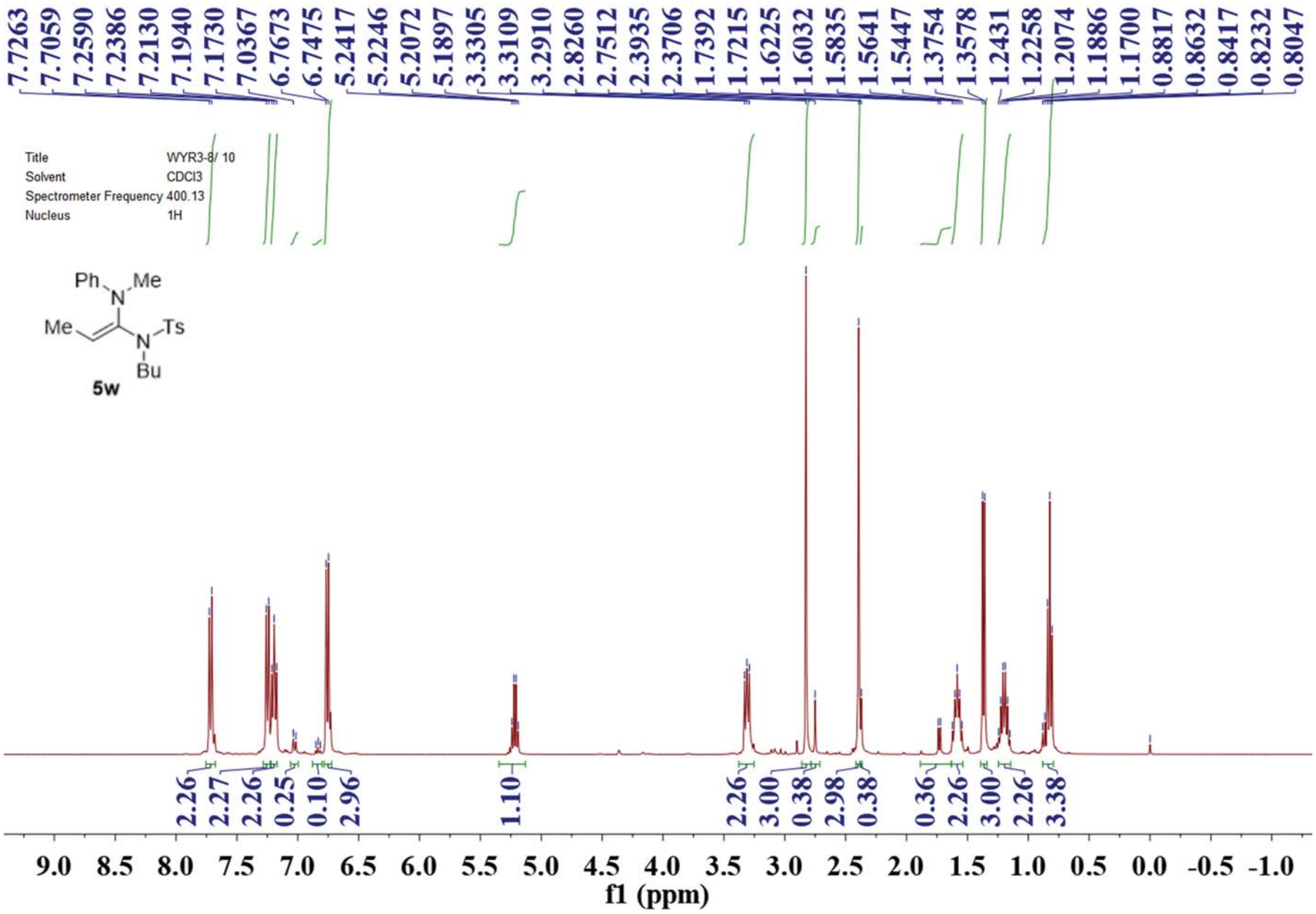
146.310
143.845
143.335
143.101
140.057
137.022
136.304
129.412
129.267
128.896
128.683
127.283
127.209
119.706
118.192
117.253
113.848
113.261
113.144
77.519
77.200
76.881
37.914
37.242
36.829
36.126
21.516
21.479
12.944
12.833
Title WYR2-75.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Ts
Me
5v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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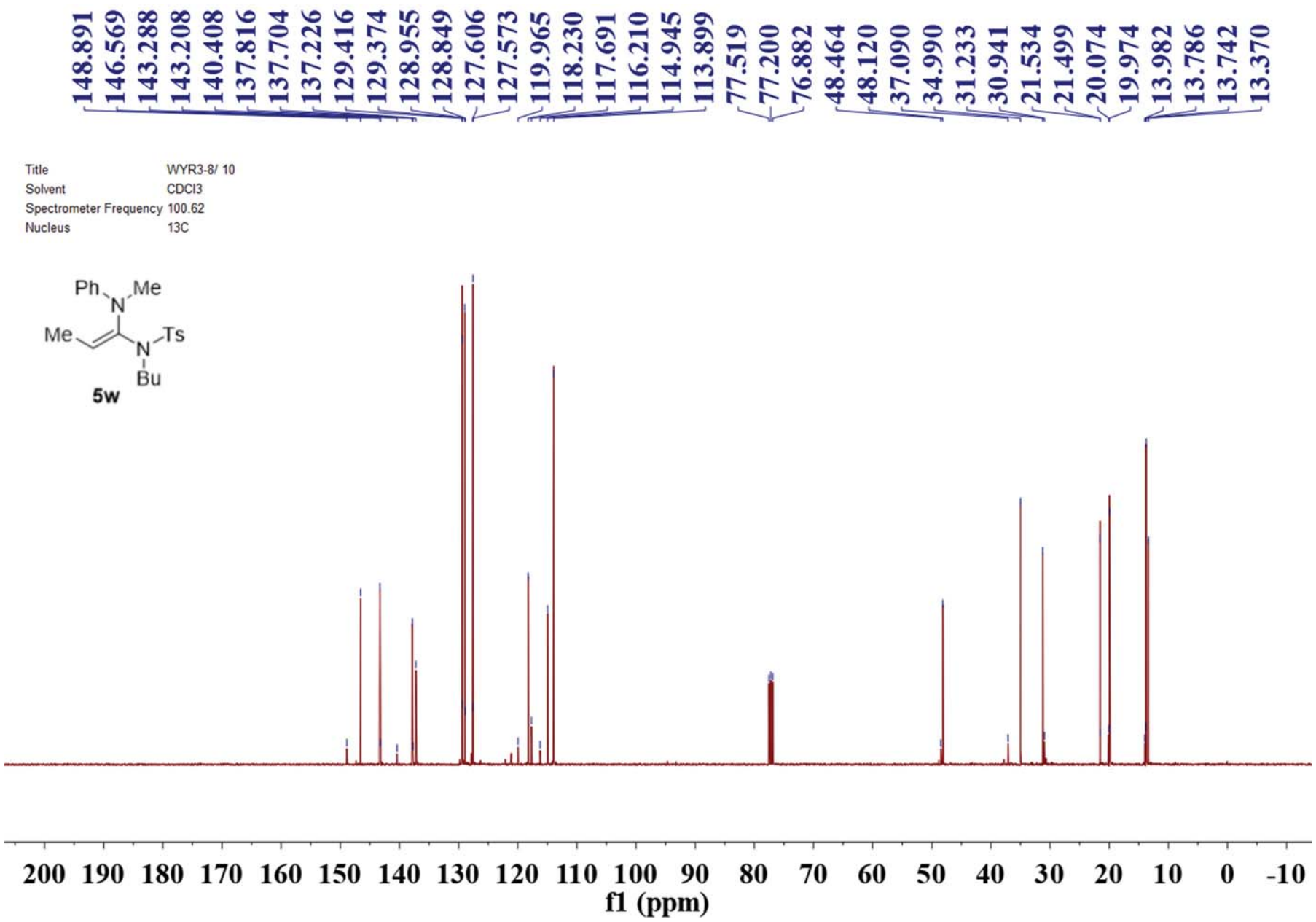
7.7059
7.2590
7.2386
7.2130
7.1940
7.1730
7.0367
6.7673
6.7475
5.2417
5.2246
5.2072
5.1897
3.3305
3.3109
3.2910
2.8260
2.7512
2.3935
2.3706
1.7392
1.7215
1.6225
1.6032
1.5835
1.5641
1.5447
1.3754
1.3578
1.2431
1.2258
1.2074
1.1886
1.1700
0.8817
0.8632
0.8417
0.8232
0.8047
Title WYR3-8/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Ts
Bu
5w
2.26
2.27
2.26
0.25
0.10
2.96
1.10
2.26
3.00
0.38
2.98
0.38
0.36
2.26
3.00
2.26
3.38
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 -0.5 -1.0
f1 (ppm)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143.288
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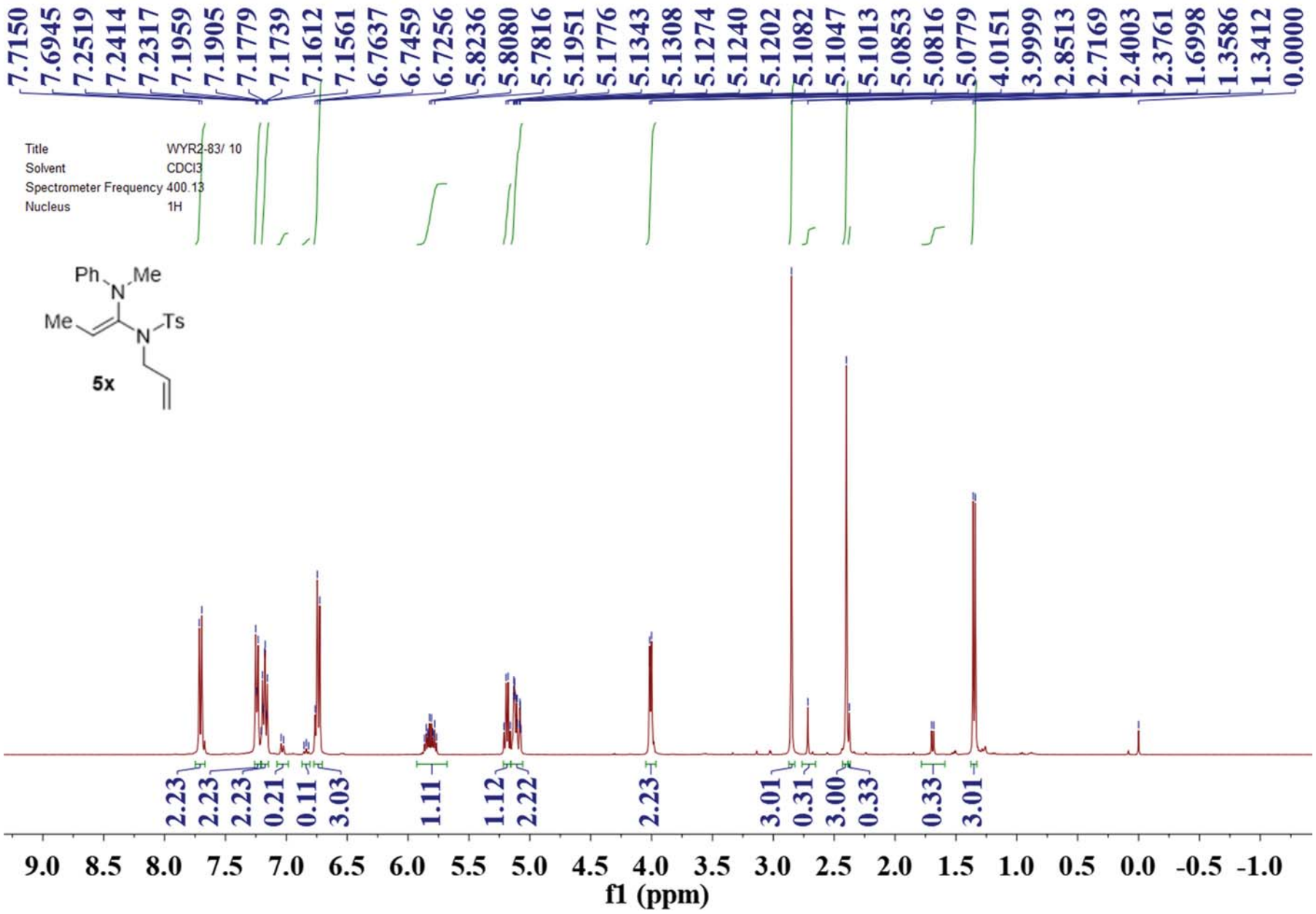
140.408
137.816
137.704
137.226
129.416
129.374
128.955
128.849
127.606
127.573
119.965
118.230
117.691
116.210
114.945
113.899
77.519
77.200
76.882
48.464
48.120
37.090
34.990
31.233
30.941
21.534
21.499
20.074
19.974
13.982
13.786
13.742
13.370
Title WYR3-8/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Ts
Bu
5w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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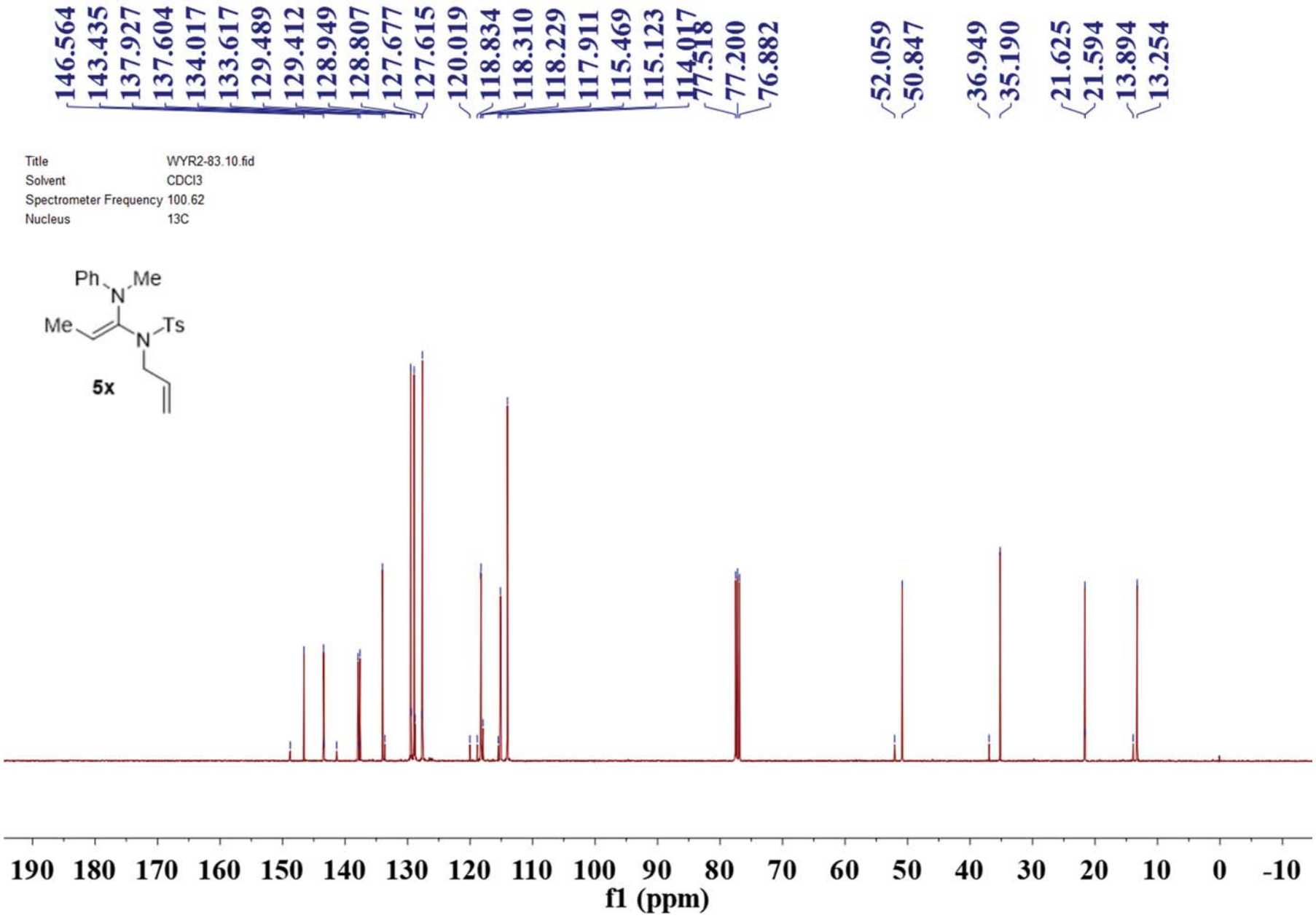
7.6945
7.2519
7.2414
7.2317
7.1959
7.1905
7.1779
7.1739
7.1612
7.1561
6.7637
6.7459
6.7256
5.8236
5.8080
5.7816
5.1951
5.1776
5.1343
5.1308
5.1274
5.1240
5.1202
5.1082
5.1047
5.1013
5.0853
5.0816
5.0779
4.0151
3.9999
2.8513
2.7169
2.4003
2.3761
1.6998
1.3586
1.3412
0.0000
Title WYR2-83/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Ts
5x
2.23
2.23
2.23
0.21
0.11
3.03
1.11
1.12
2.22
2.23
3.01
0.31
3.00
0.33
0.33
3.01
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 -0.5 -1.0
f1 (ppm)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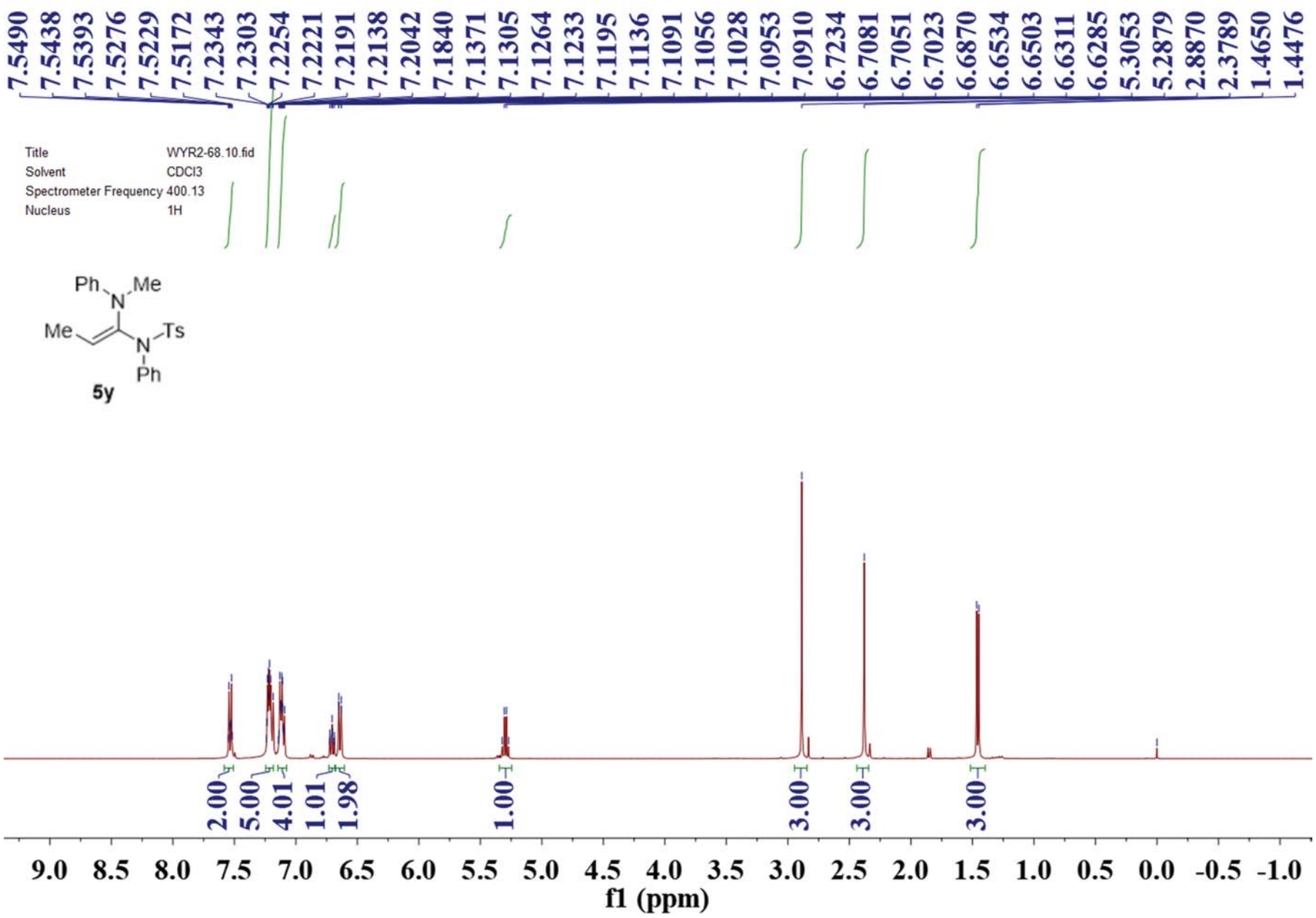
129.412
128.949
128.807
127.677
127.615
120.019
118.834
118.310
118.229
117.911
115.469
115.123
114.017
77.518
77.200
76.882
52.059
50.847
36.949
35.190
21.625
21.594
13.894
13.254
Title WYR2-83.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Ts
5x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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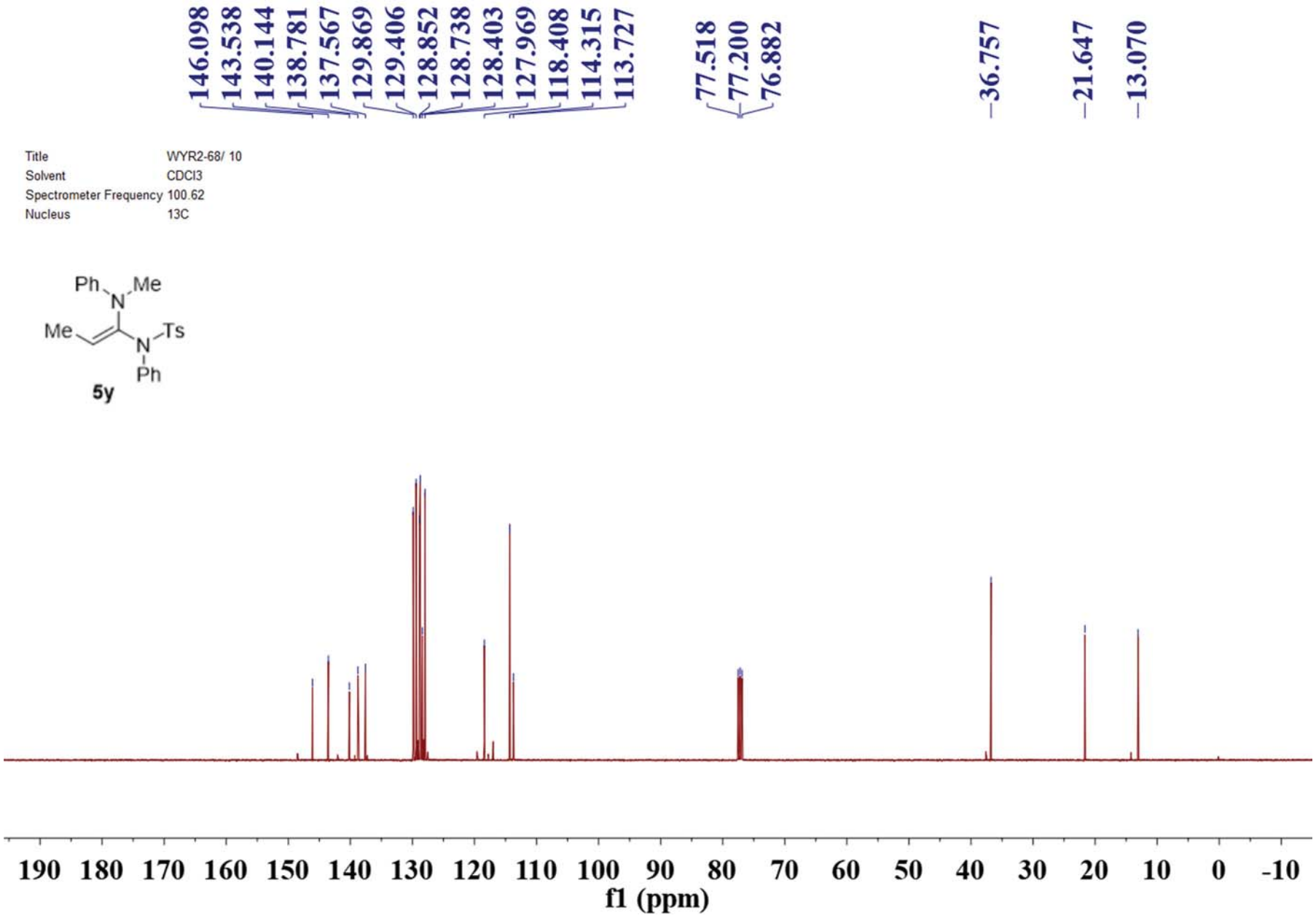
7.5393
7.5276
7.5229
7.5172
7.2343
7.2303
7.2254
7.2221
7.2191
7.2138
7.2042
7.1840
7.1371
7.1305
7.1264
7.1233
7.1195
7.1136
7.1091
7.1056
7.1028
7.0953
7.0910
6.7234
6.7081
6.7051
6.7023
6.6870
6.6534
6.6503
6.6311
6.6285
5.3053
5.2879
2.8870
2.3789
1.4650
1.4476
Title WYR2-68.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Me
N
Ts
Ph
5y
2.00
5.00
4.01
1.01
1.98
1.00
3.00
3.00
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 -0.5 -1.0
f1 (ppm)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140.144
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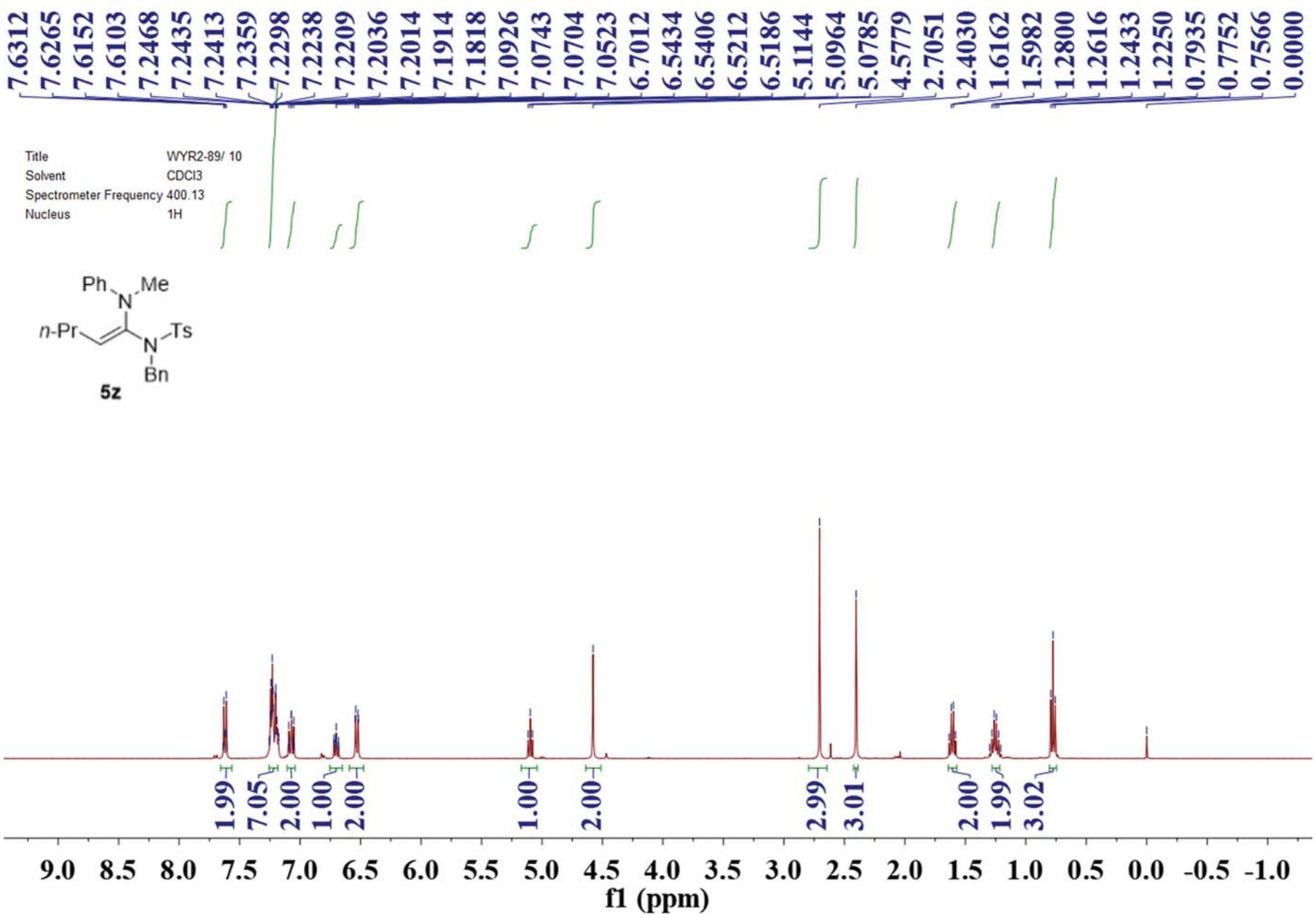
129.869
129.406
128.852
128.738
128.403
127.969
118.408
114.315
113.727
77.518
77.200
76.882
36.757
21.647
13.070
Title WYR2-68/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Me
N
Ts
Ph
5y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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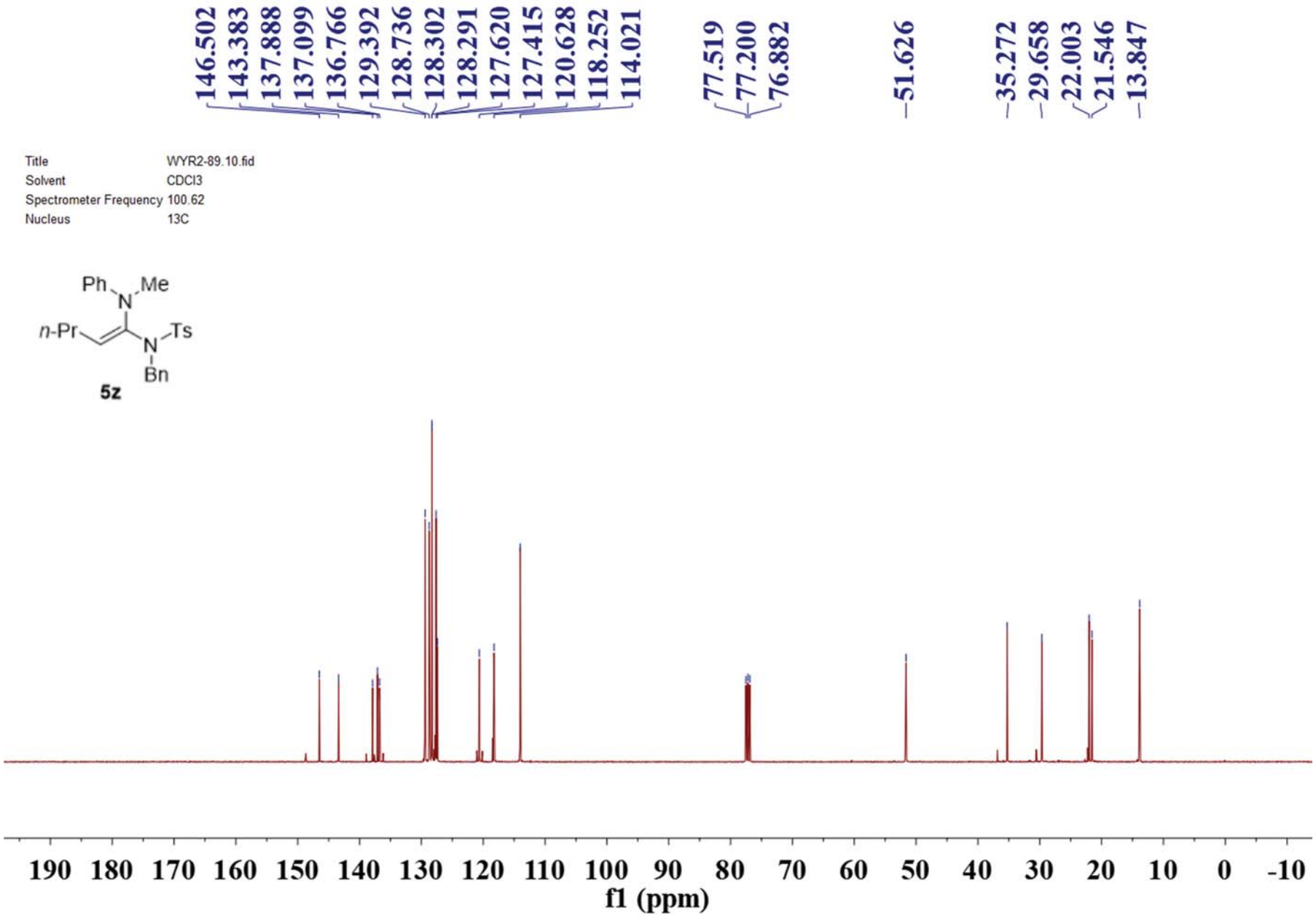
7.6152
7.6103
7.2468
7.2435
7.2413
7.2359
7.2298
7.2238
7.2209
7.2036
7.2014
7.1914
7.1818
7.0926
7.0743
7.0704
7.0523
6.7012
6.5434
6.5406
6.5212
6.5186
5.1144
5.0964
5.0785
4.5779
2.7051
2.4030
1.6162
1.5982
1.2800
1.2616
1.2433
1.2250
0.7935
0.7752
0.7566
0.0000
Title WYR2-89/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
n-Pr
N
Ts
Bn
5z
1.99
7.05
2.00
1.00
2.00
1.00
2.00
2.99
3.01
2.00
1.99
3.02
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 -0.5 -1.0
f1 (ppm)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137.888
137.099
136.766
129.392
128.736
128.302
128.291
127.620
127.415
120.628
118.252
114.021
77.519
77.200
76.882
51.626
35.272
29.658
22.003
21.546
13.847
Title WYR2-89.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
n-Pr
N
Ts
Bn
5z
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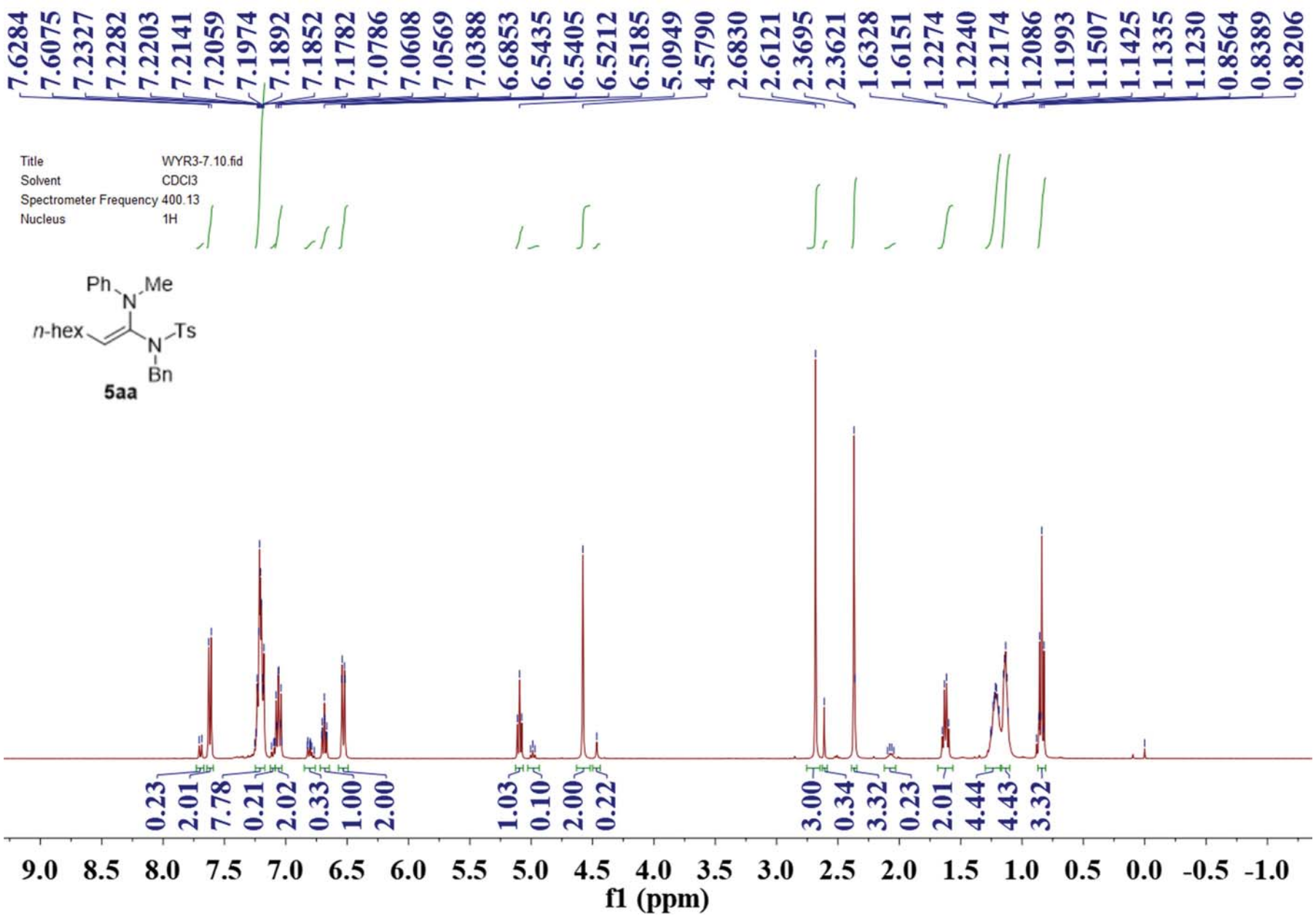
f1 (ppm)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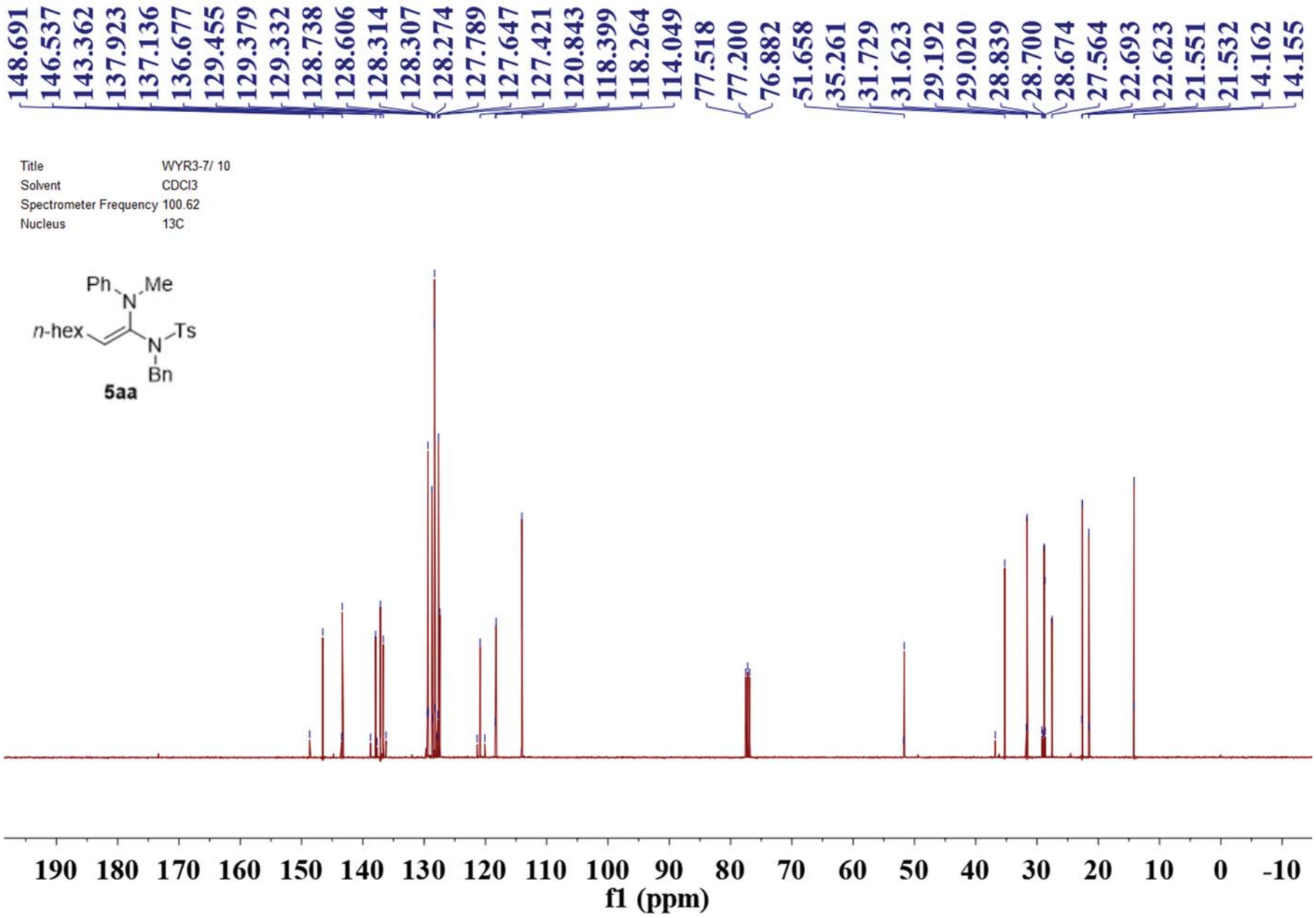
7.2327
7.2282
7.2203
7.2141
7.2059
7.1974
7.1892
7.1852
7.1782
7.0786
7.0608
7.0569
7.0388
6.6853
6.5435
6.5405
6.5212
6.5185
5.0949
4.5790
2.6830
2.6121
2.3695
2.3621
1.6328
1.6151
1.2274
1.2240
1.2174
1.2086
1.1993
1.1507
1.1425
1.1335
1.1230
0.8564
0.8389
0.8206
Title WYR3-7.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
n-hex
N
Ts
Bn
5aa
0.23
2.01
7.78
0.21
2.02
0.33
1.00
2.00
1.03
0.10
2.00
0.22
3.00
0.34
3.32
0.23
2.01
4.44
4.43
3.32
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 -0.5 -1.0
f1 (ppm)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146.537
143.362
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137.136
136.677
129.455
129.379
129.332
128.738
128.606
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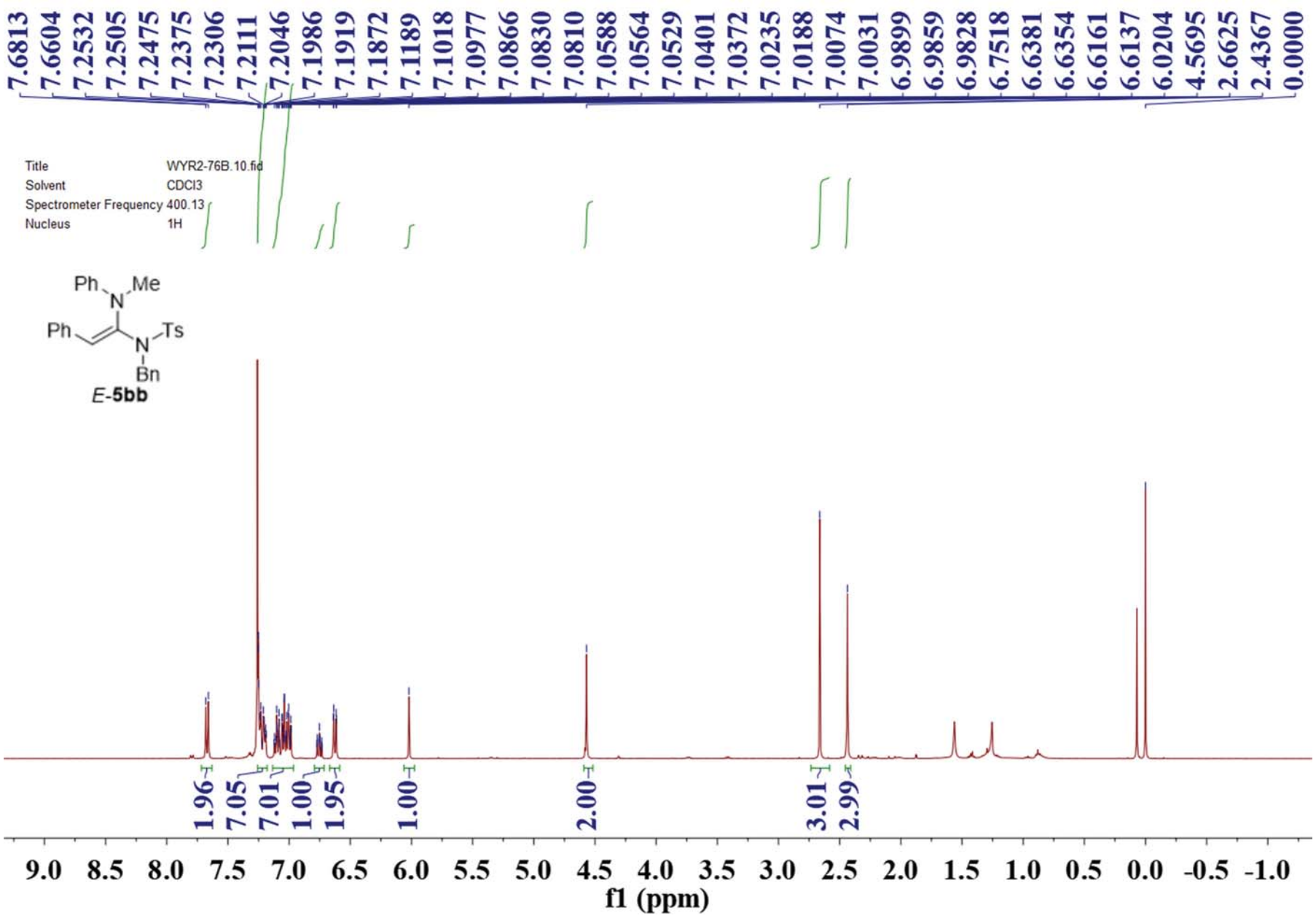
128.307
128.274
127.789
127.647
127.421
120.843
118.399
118.264
114.049
77.518
77.200
76.882
51.658
35.261
31.729
31.623
29.192
29.020
28.839
28.700
28.674
27.564
22.693
22.623
21.551
21.532
14.162
14.155
Title WYR3-7/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
n-hex
N
Ts
Bn
5aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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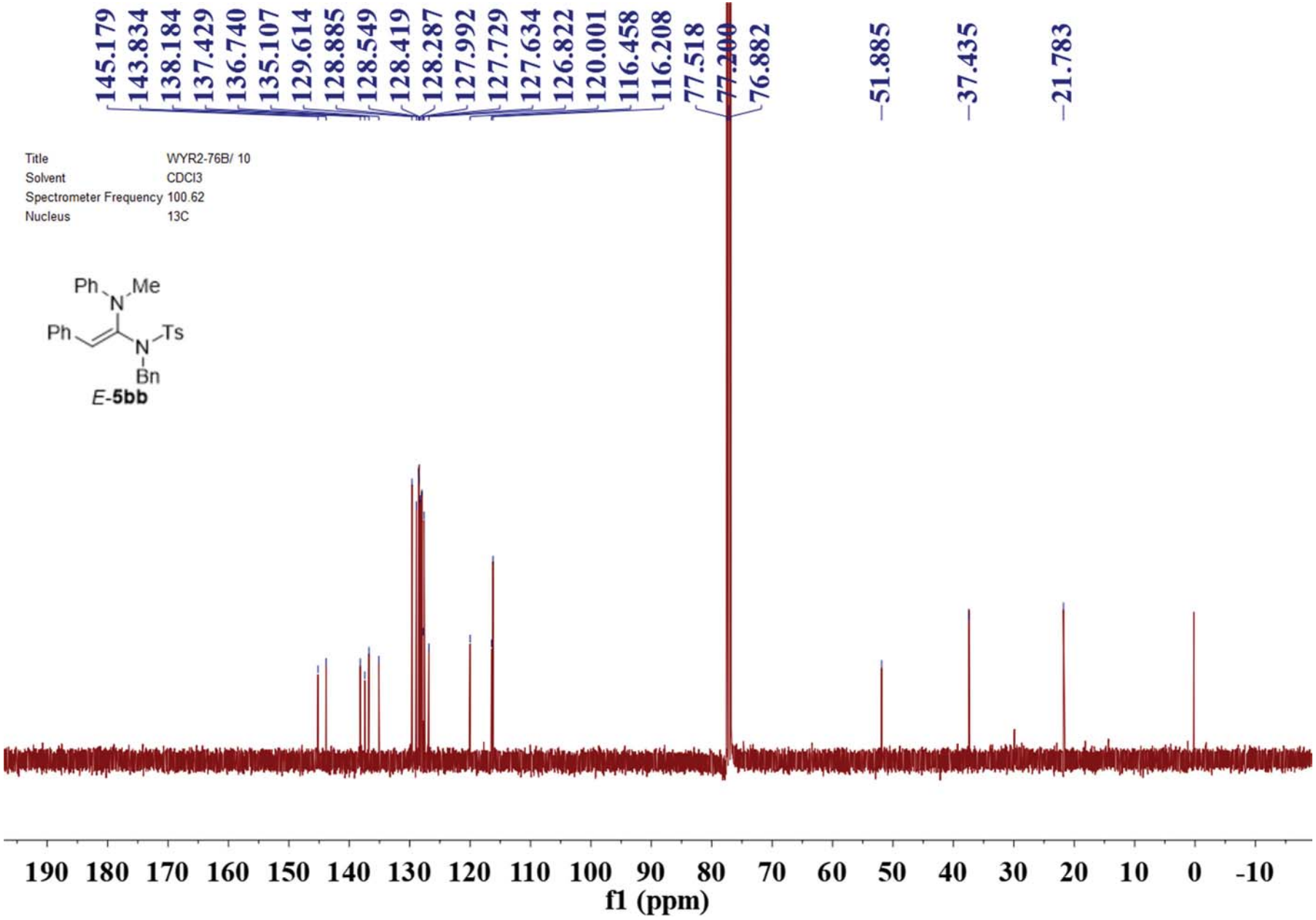
7.2532
7.2505
7.2475
7.2375
7.2306
7.2111
7.2046
7.1986
7.1919
7.1872
7.1189
7.1018
7.0977
7.0866
7.0830
7.0810
7.0588
7.0564
7.0529
7.0401
7.0372
7.0235
7.0188
7.0074
7.0031
6.9899
6.9859
6.9828
6.7518
6.6381
6.6354
6.6161
6.6137
6.0204
4.5695
2.6625
2.4367
0.0000
Title WYR2-76B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ph
N
Ts
Bn
E-5bb
1.96
7.05
7.01
1.00
1.95
1.00
2.00
3.01
2.99
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 -0.5 -1.0
f1 (ppm)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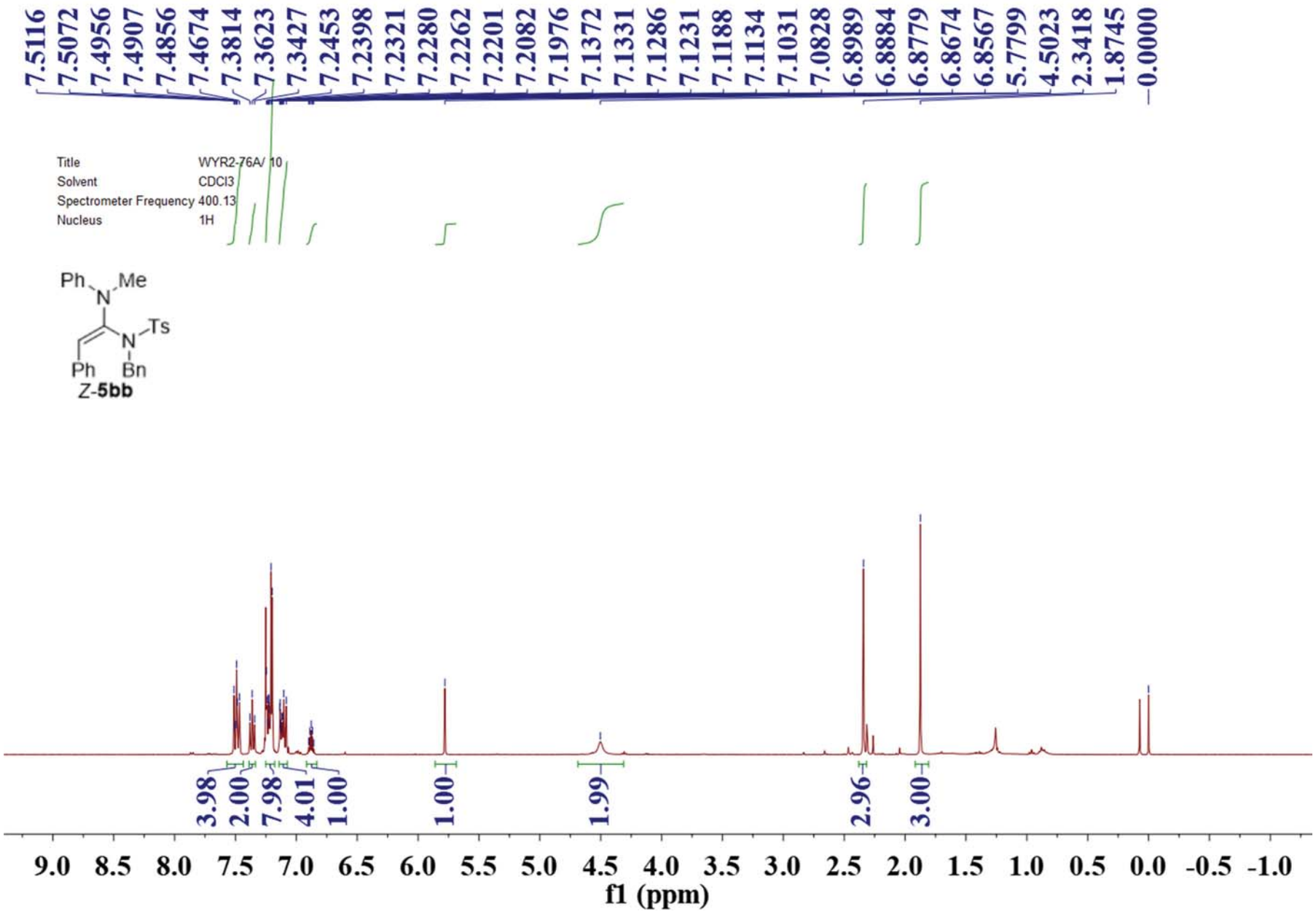
143.834
138.184
137.429
136.740
135.107
129.614
128.885
128.549
128.419
128.287
127.992
127.729
127.634
126.822
120.001
116.458
116.208
77.518
77.200
76.882
51.885
37.435
21.783
Title WYR2-76B/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Ph
N
Ts
Bn
E-5bb
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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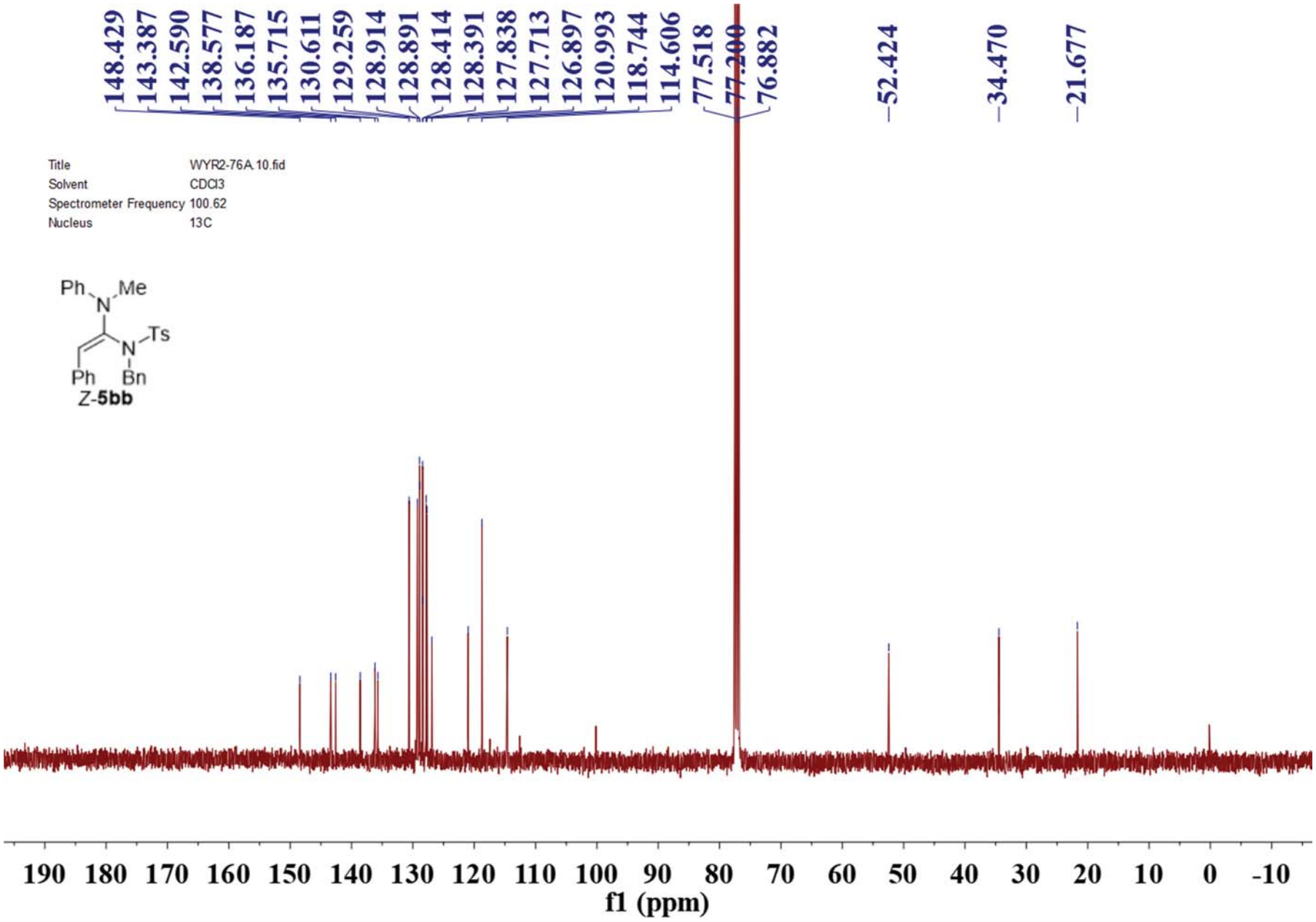
7.4956
7.4907
7.4856
7.4674
7.3814
7.3623
7.3427
7.2453
7.2398
7.2321
7.2280
7.2262
7.2201
7.2082
7.1976
7.1372
7.1331
7.1286
7.1231
7.1188
7.1134
7.1031
7.0828
6.8989
6.8884
6.8779
6.8674
6.8567
5.7799
4.5023
2.3418
1.8745
0.0000
Title WYR2-76A/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ts
N
Ph
Bn
Z-5bb
3.98
2.00
7.98
4.01
1.00
1.00
1.99
2.96
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 -0.5 -1.0
f1 (ppm)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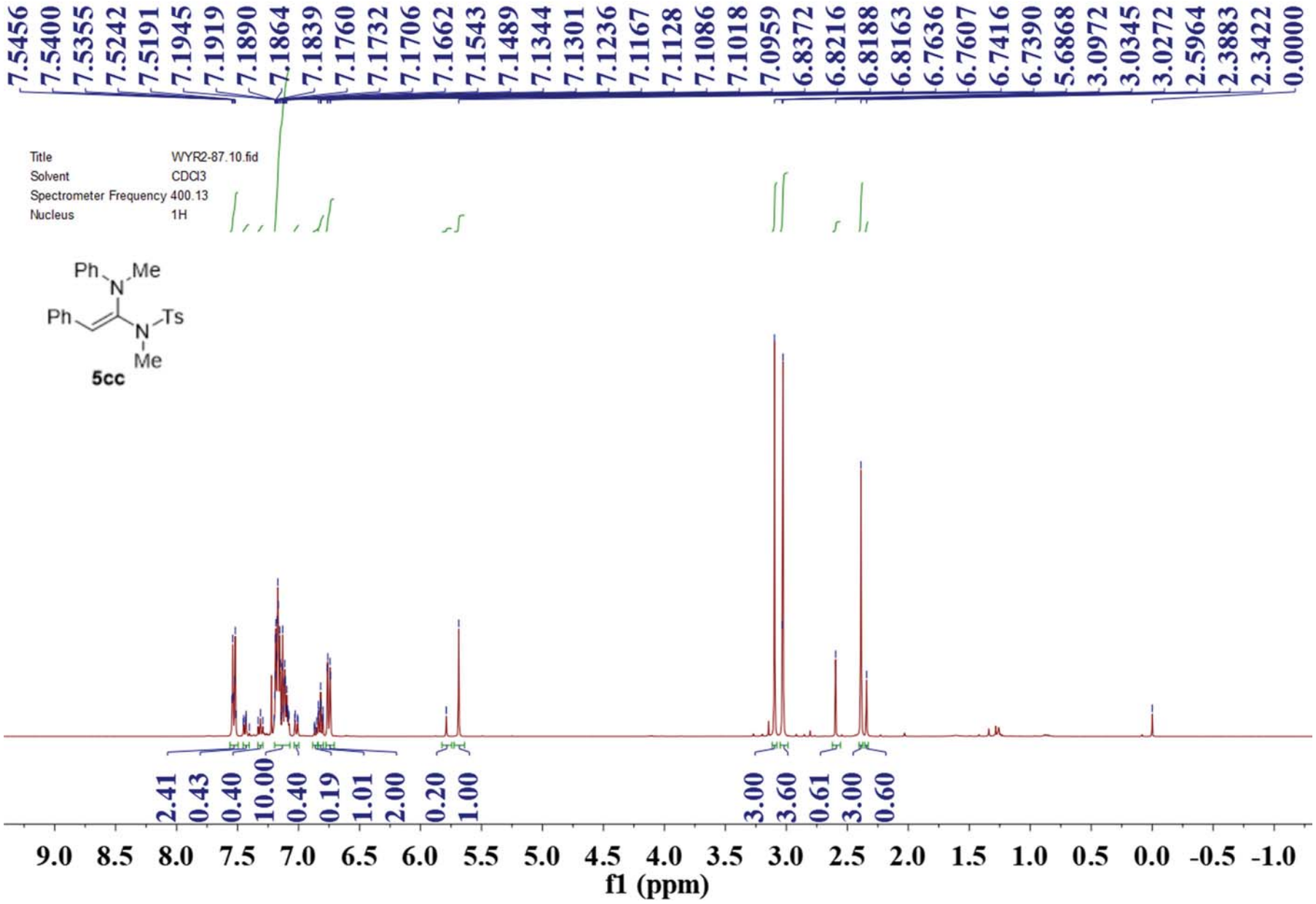
142.590
138.577
136.187
135.715
130.611
129.259
128.914
128.891
128.414
128.391
127.838
127.713
126.897
120.993
118.744
114.606
77.518
77.200
76.882
52.424
34.470
21.677
Title WYR2-76A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph N Me
N Ts
Ph Bn
Z-5bb
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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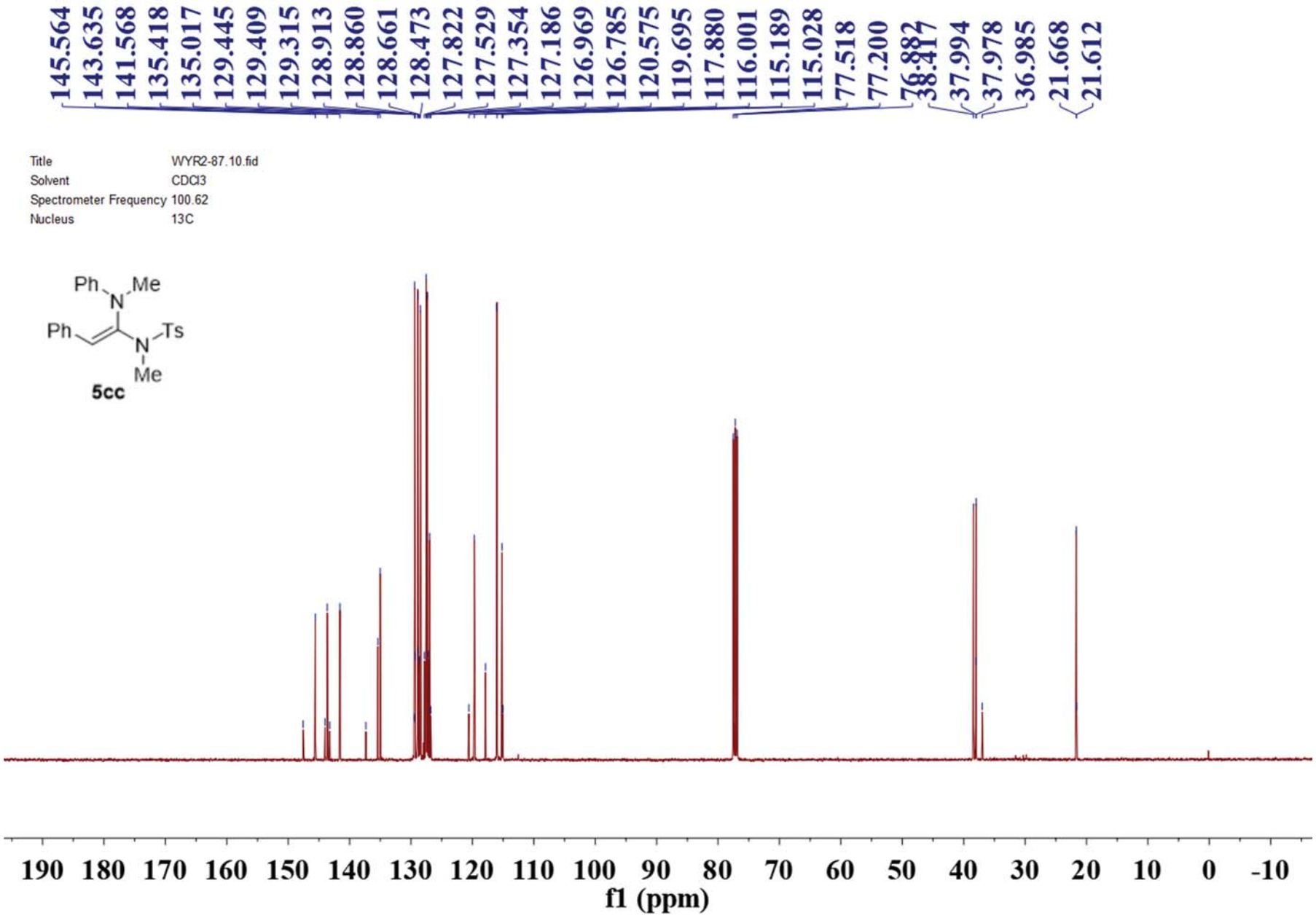
7.5400
7.5355
7.5242
7.5191
7.1945
7.1919
7.1890
7.1864
7.1839
7.1760
7.1732
7.1706
7.1662
7.1543
7.1489
7.1344
7.1301
7.1236
7.1167
7.1128
7.1086
7.1018
7.0959
6.8372
6.8216
6.8188
6.8163
6.7636
6.7607
6.7416
6.7390
5.6868
3.0972
3.0345
3.0272
2.5964
2.3883
2.3422
0.0000
Title WYR2-87.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ph
N
Ts
Me
5cc
2.41
0.43
0.40
10.00
0.40
0.19
1.01
2.00
0.20
1.00
3.00
3.60
0.61
3.00
0.60
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 -0.5 -1.0
f1 (ppm)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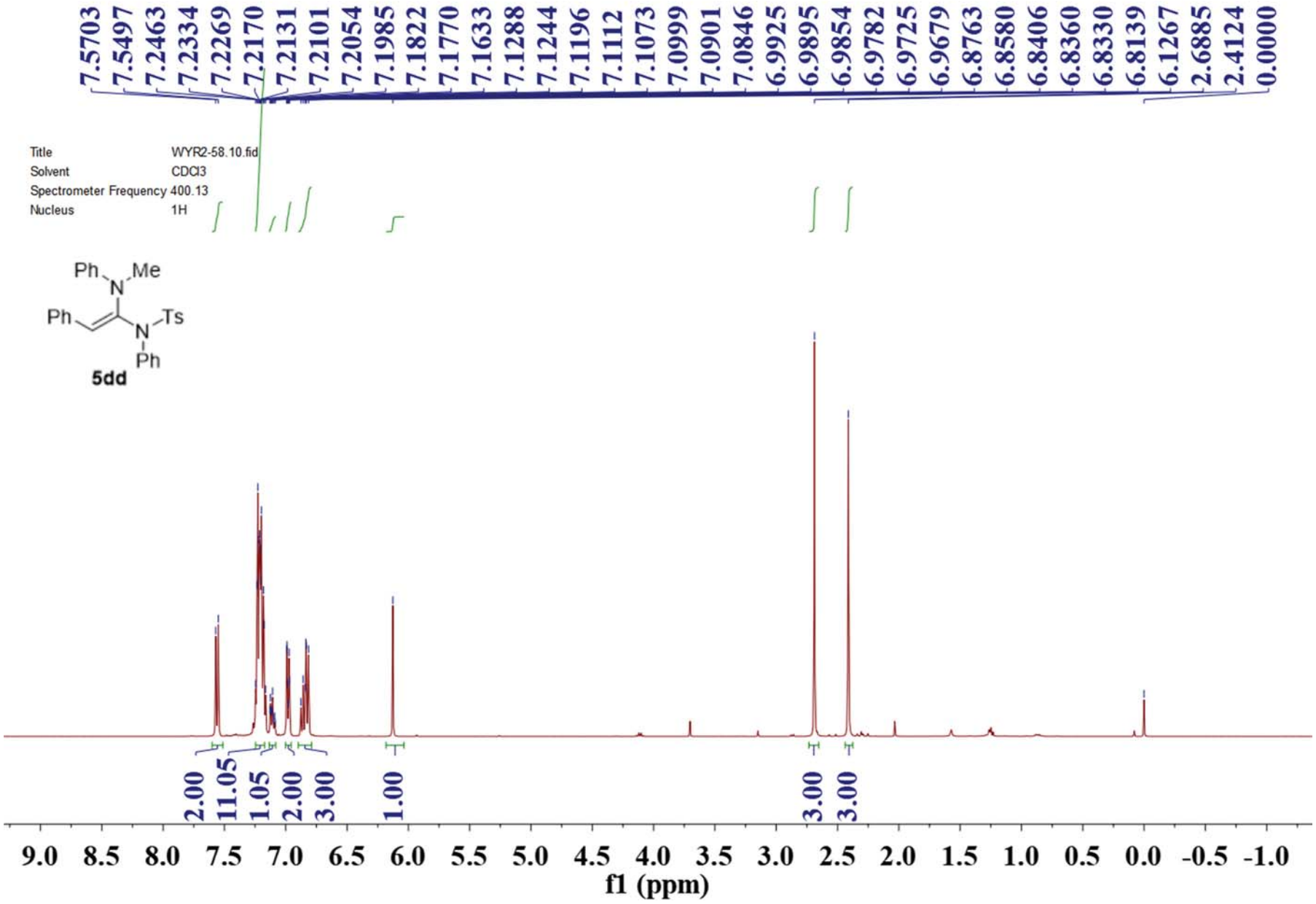
143.635
141.568
135.418
135.017
129.445
129.409
129.315
128.913
128.860
128.661
128.473
127.822
127.529
127.354
127.186
126.969
126.785
120.575
119.695
117.880
116.001
115.189
115.028
77.518
77.200
76.882
38.417
37.994
37.978
36.985
21.668
21.612
Title WYR2-87.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Ph
N
Ts
Me
5cc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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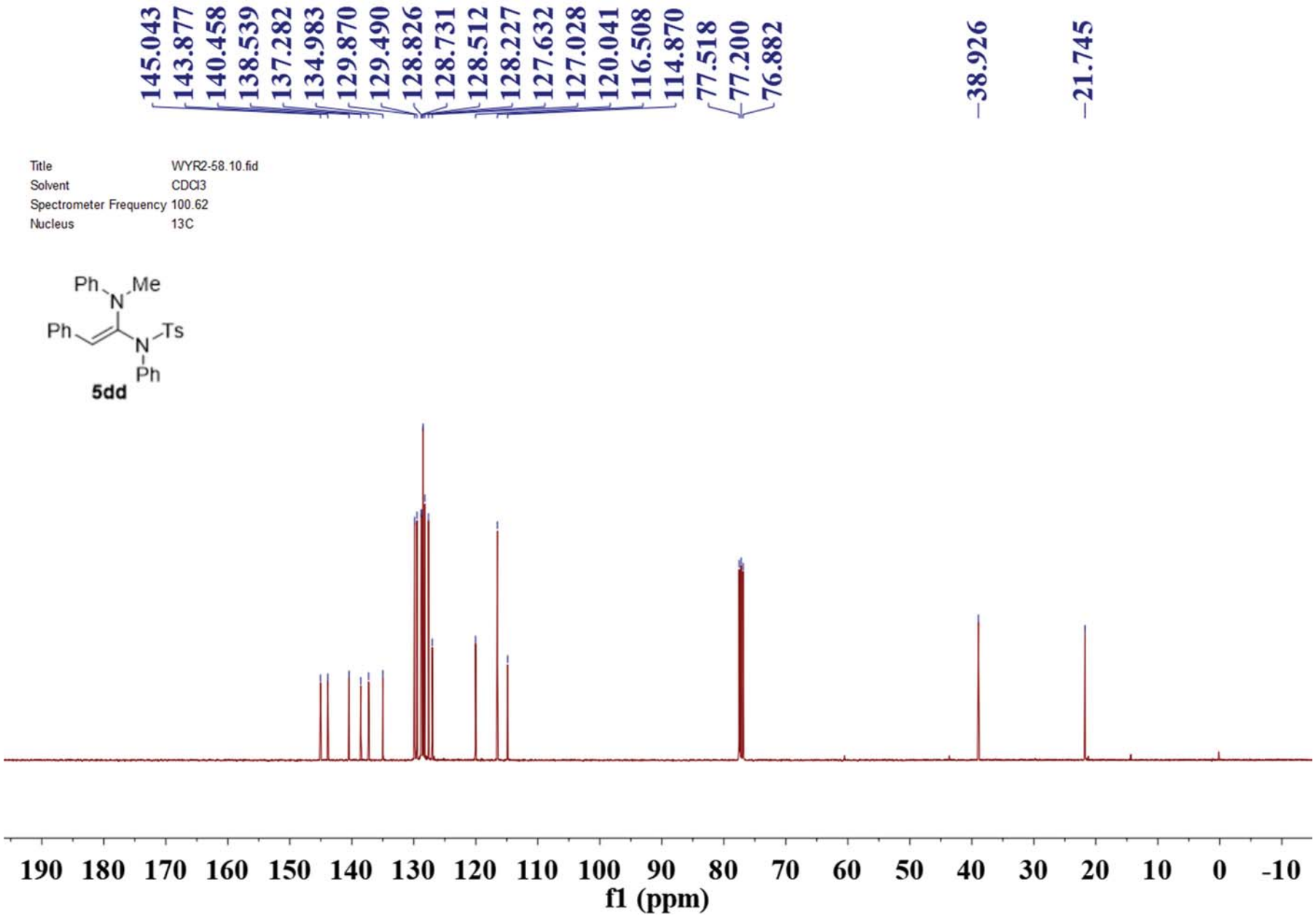
7.2463
7.2334
7.2269
7.2170
7.2131
7.2101
7.2054
7.1985
7.1822
7.1770
7.1633
7.1288
7.1244
7.1196
7.1112
7.1073
7.0999
7.0901
7.0846
6.9925
6.9895
6.9854
6.9782
6.9725
6.9679
6.8763
6.8580
6.8406
6.8360
6.8330
6.8139
6.1267
2.6885
2.4124
0.0000
Title WYR2-58.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ph
N
Ts
Ph
5dd
2.00
11.05
1.05
2.00
3.00
1.00
3.00
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 -0.5 -1.0
f1 (ppm)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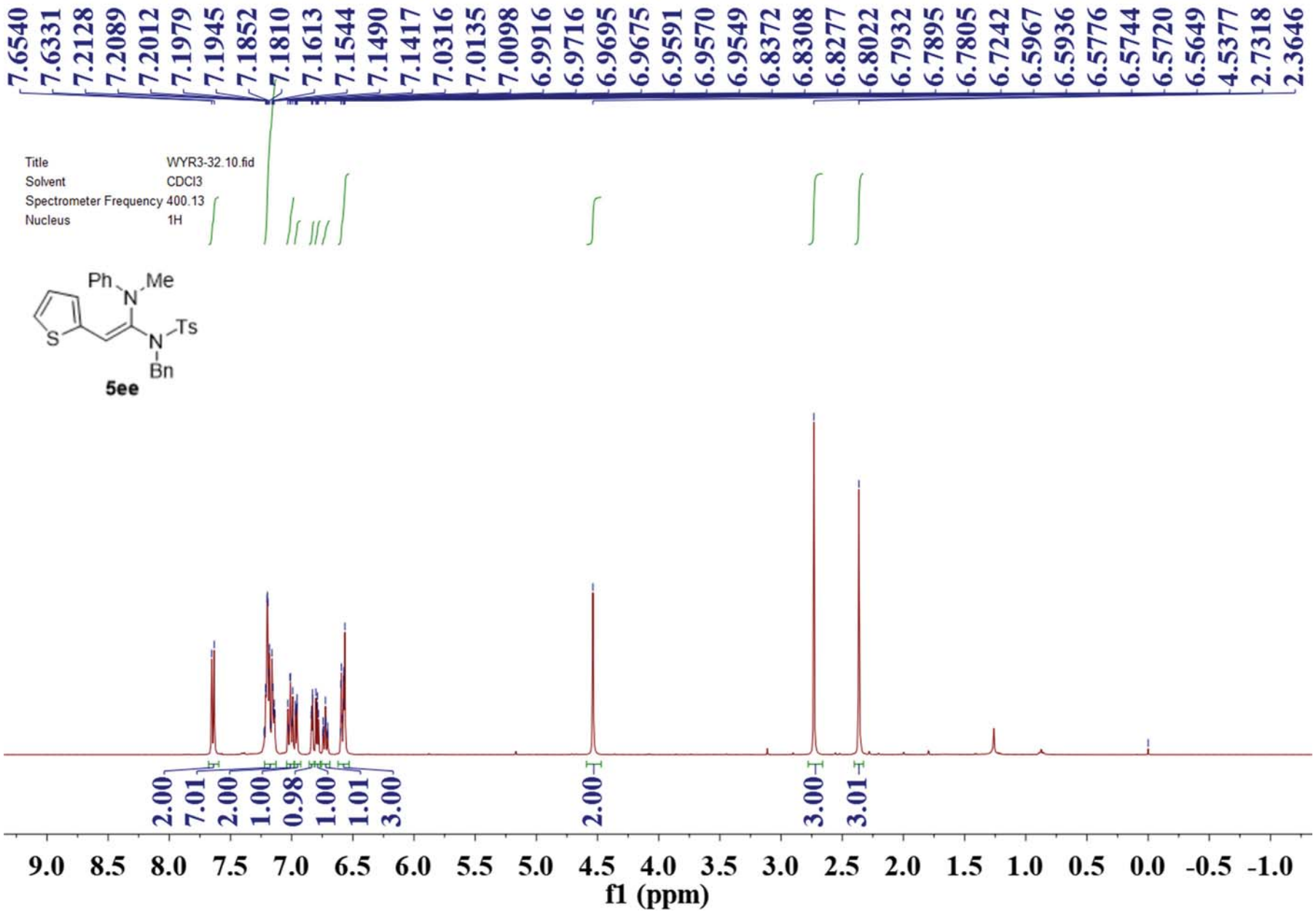
129.490
128.826
128.731
128.512
128.227
127.632
127.028
120.041
116.508
114.870
77.518
77.200
76.882
38.926
21.745
Title WYR2-58.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
Ph
N
Ts
Ph
5dd
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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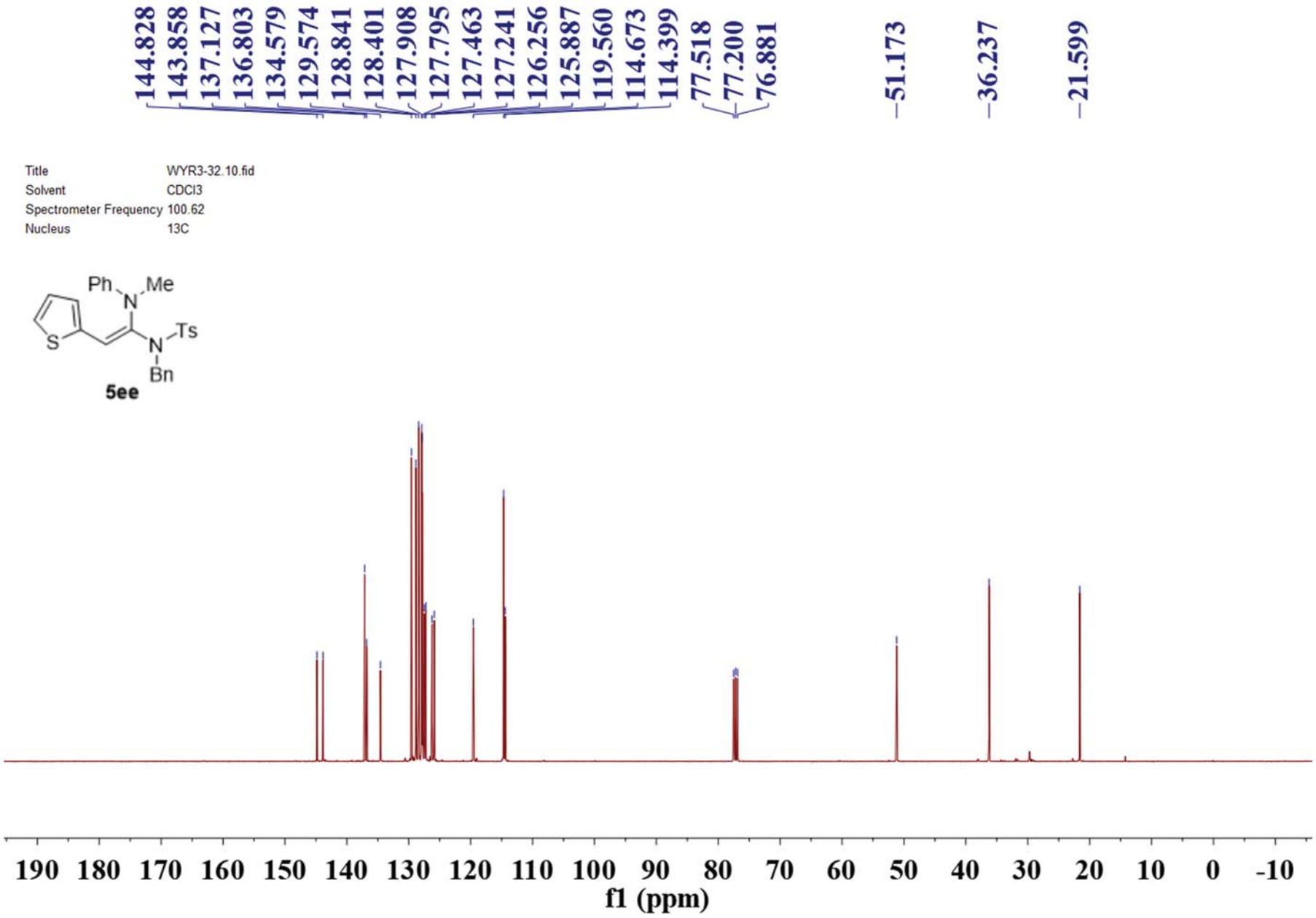
7.2128
7.2089
7.2012
7.1979
7.1945
7.1852
7.1810
7.1613
7.1544
7.1490
7.1417
7.0316
7.0135
7.0098
6.9916
6.9716
6.9695
6.9675
6.9591
6.9570
6.9549
6.8372
6.8308
6.8277
6.8022
6.7932
6.7895
6.7805
6.7242
6.5967
6.5936
6.5776
6.5744
6.5720
6.5649
4.5377
2.7318
2.3646
Title WYR3-32.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
S
N
Ts
Bn
5ee
2.00
7.01
2.00
1.00
0.98
1.00
1.01
3.00
2.00
3.00
3.01
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 -0.5 -1.0
f1 (ppm)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137.127
136.803
134.579
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128.401
127.908
127.795
127.463
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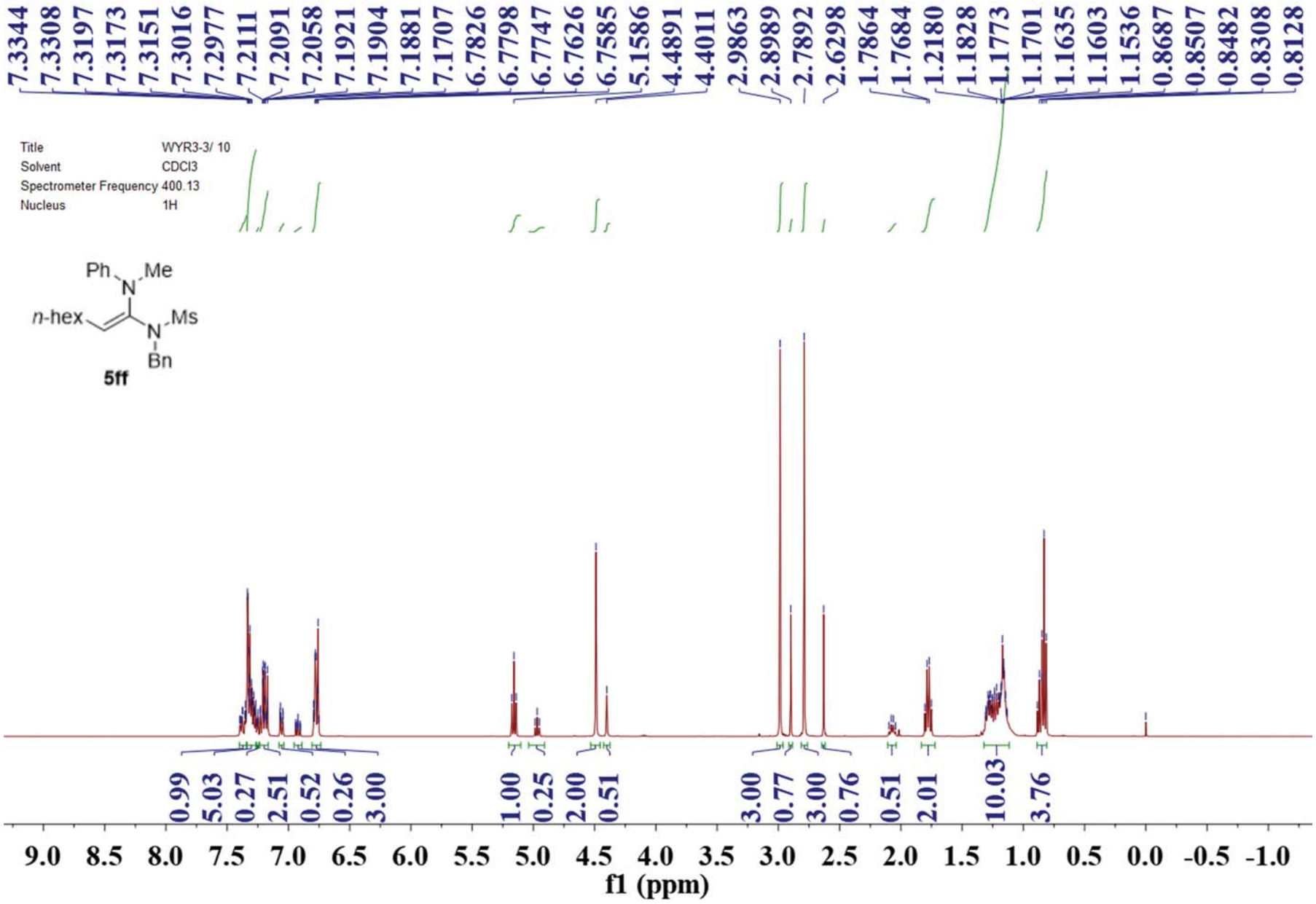
126.256
125.887
119.560
114.673
114.399
77.518
77.200
76.881
51.173
36.237
21.599
Title WYR3-32.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
S
N
Ts
Bn
5ee
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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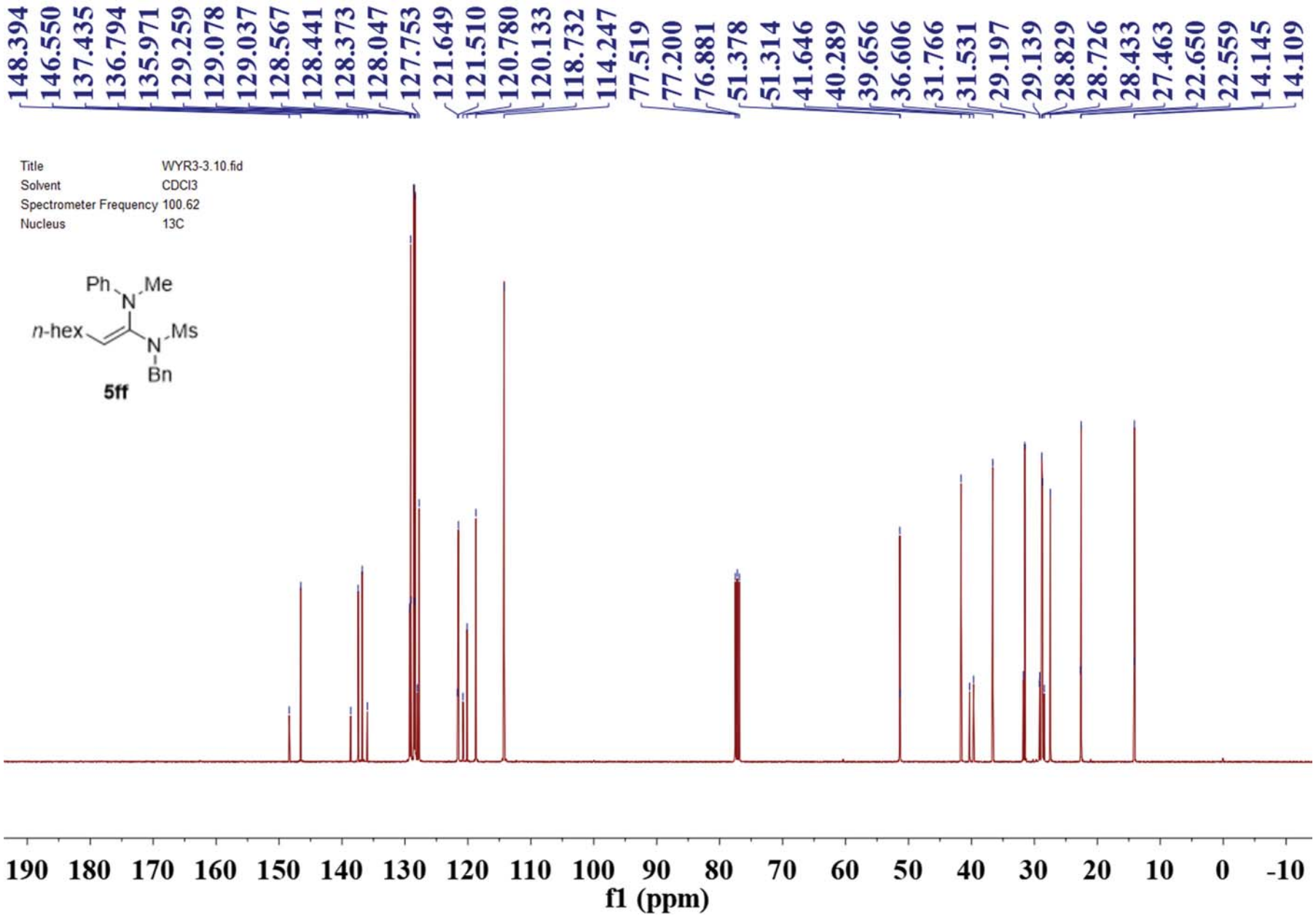
7.3173
7.3151
7.3016
7.2977
7.2111
7.2091
7.2058
7.1921
7.1904
7.1881
7.1707
6.7826
6.7798
6.7747
6.7626
6.7585
5.1586
4.4891
4.4011
2.9863
2.8989
2.7892
2.6298
1.7864
1.7684
1.2180
1.1828
1.1773
1.1701
1.1635
1.1603
1.1536
0.8687
0.8507
0.8482
0.8308
0.8128
Title WYR3-3/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
n-hex
N
Ms
Bn
5ff
0.99
5.03
0.27
2.51
0.52
0.26
3.00
1.00
0.25
2.00
0.51
3.00
0.77
3.00
0.76
0.51
2.01
10.03
3.76
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 -0.5 -1.0
f1 (ppm)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136.794
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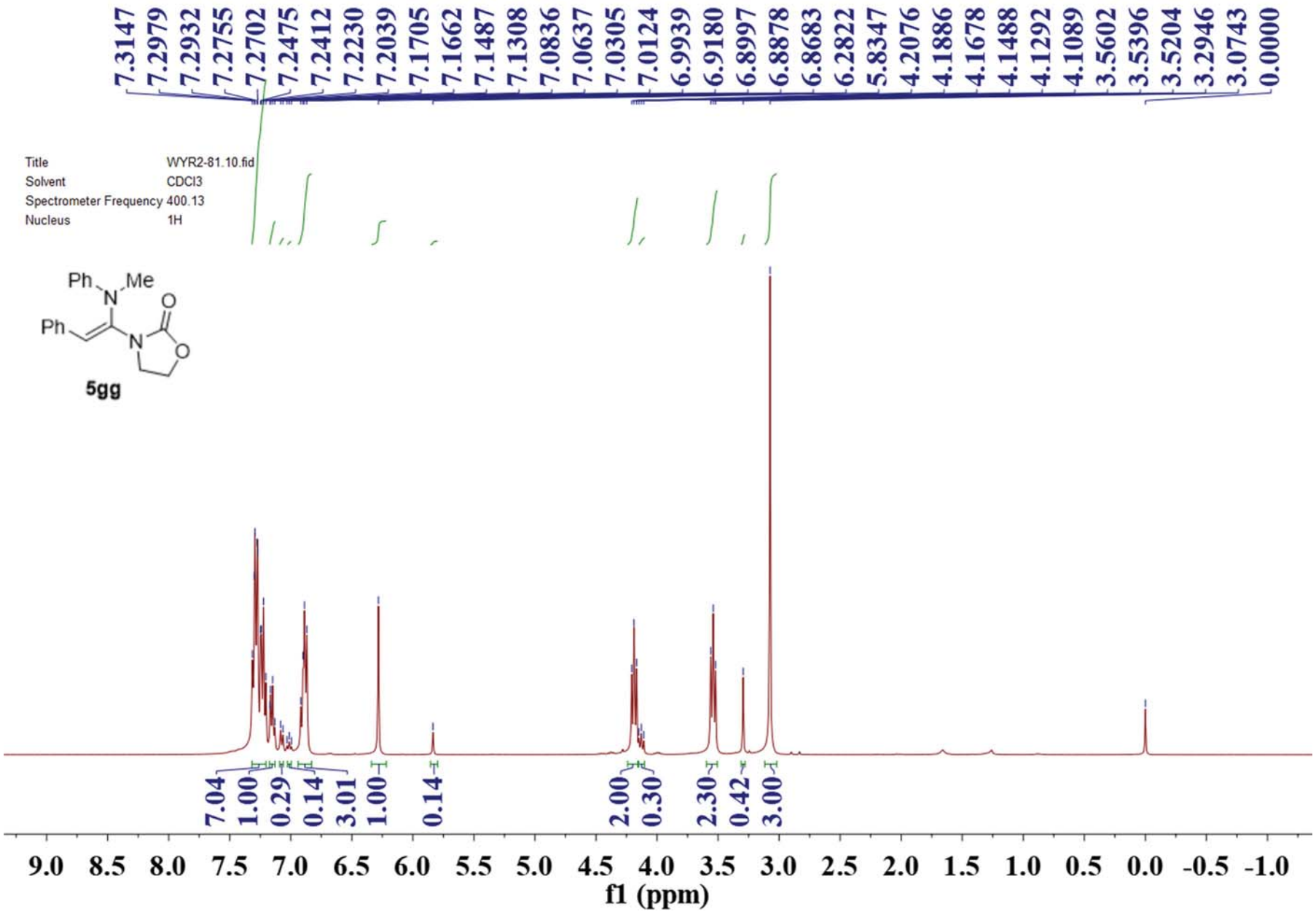
129.259
129.078
129.037
128.567
128.441
128.373
128.047
127.753
121.649
121.510
120.780
120.133
118.732
114.247
77.519
77.200
76.881
51.378
51.314
41.646
40.289
39.656
36.606
31.766
31.531
29.197
29.139
28.829
28.726
28.433
27.463
22.650
22.559
14.145
14.109
Title WYR3-3.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
Me
N
n-hex
N
Ms
Bn
5ff
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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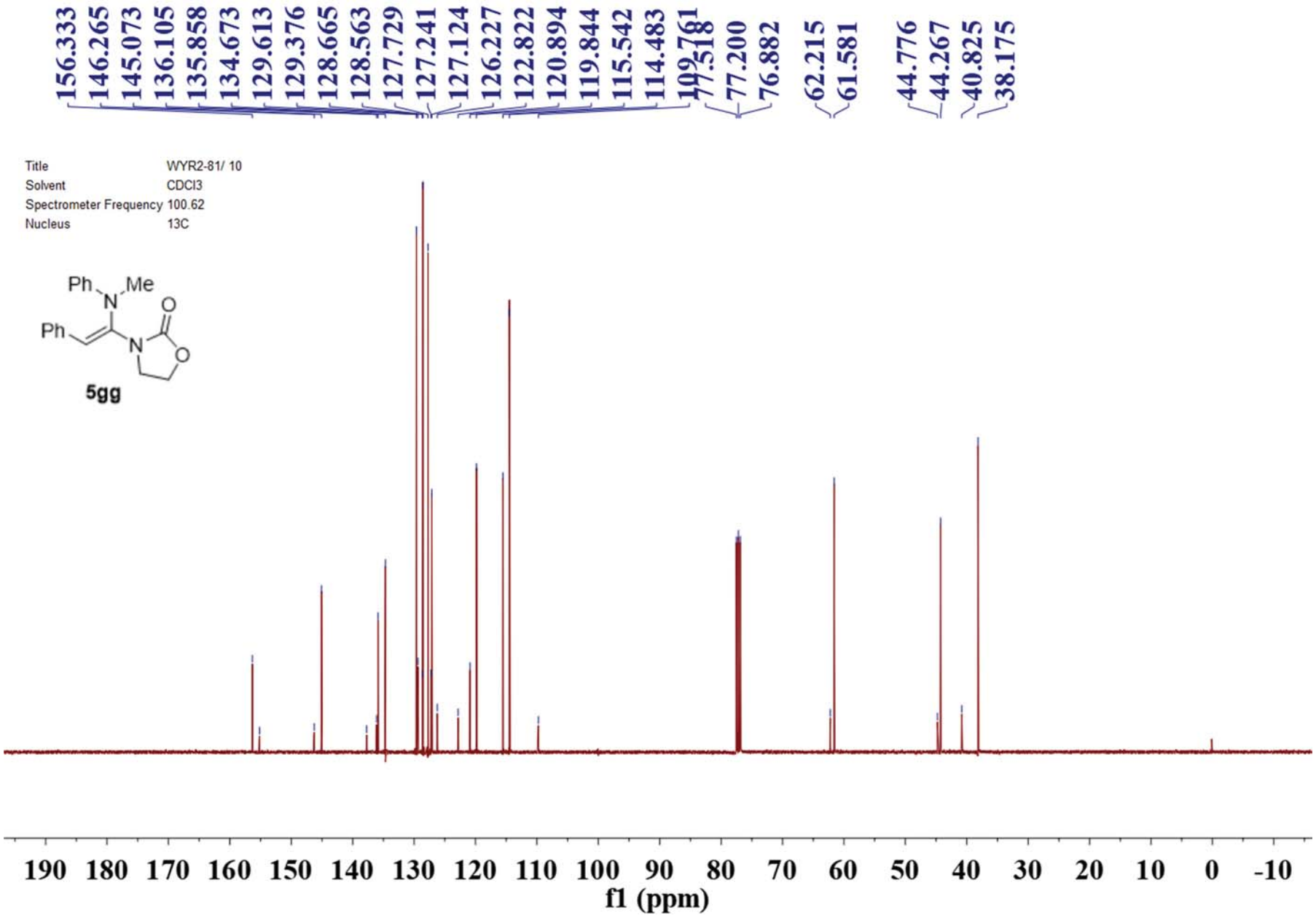
7.2039
7.1705
7.1662
7.1487
7.1308
7.0836
7.0637
7.0305
7.0124
6.9939
6.9180
6.8997
6.8878
6.8683
6.2822
5.8347
4.2076
4.1886
4.1678
4.1488
4.1292
4.1089
3.5602
3.5396
3.5204
3.2946
3.0743
0.0000
Title WYR2-81.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
O
Ph
N
O
5gg
7.04
1.00
0.29
0.14
3.01
1.00
0.14
2.00
0.30
2.30
0.42
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 -0.5 -1.0
f1 (ppm)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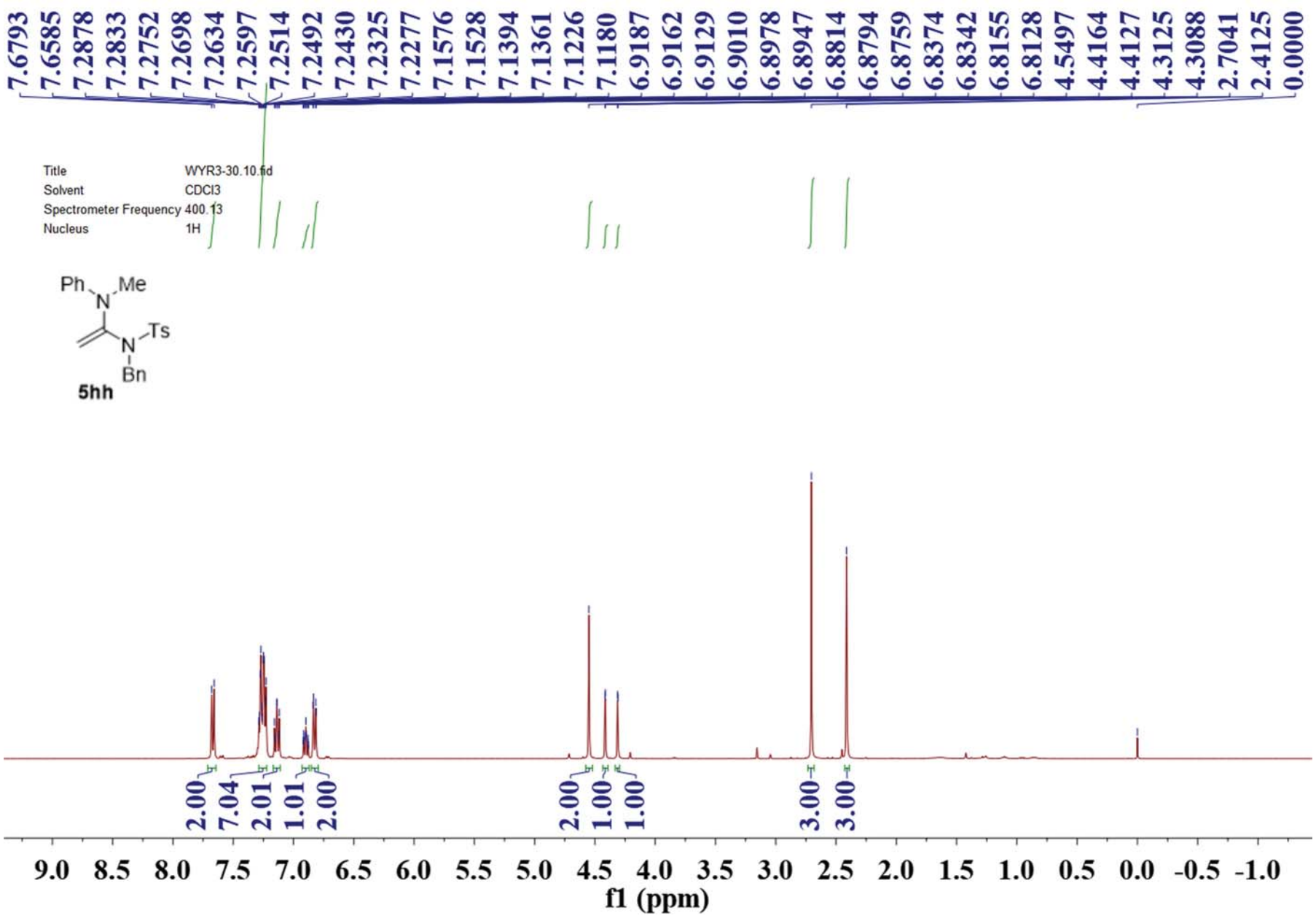
135.858
134.673
129.613
129.376
128.665
128.563
127.729
127.241
127.124
126.227
122.822
120.894
119.844
115.542
114.483
109.761
77.518
77.200
76.882
62.215
61.581
44.776
44.267
40.825
38.175
Title WYR2-81/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
O
Ph
N
O
5gg
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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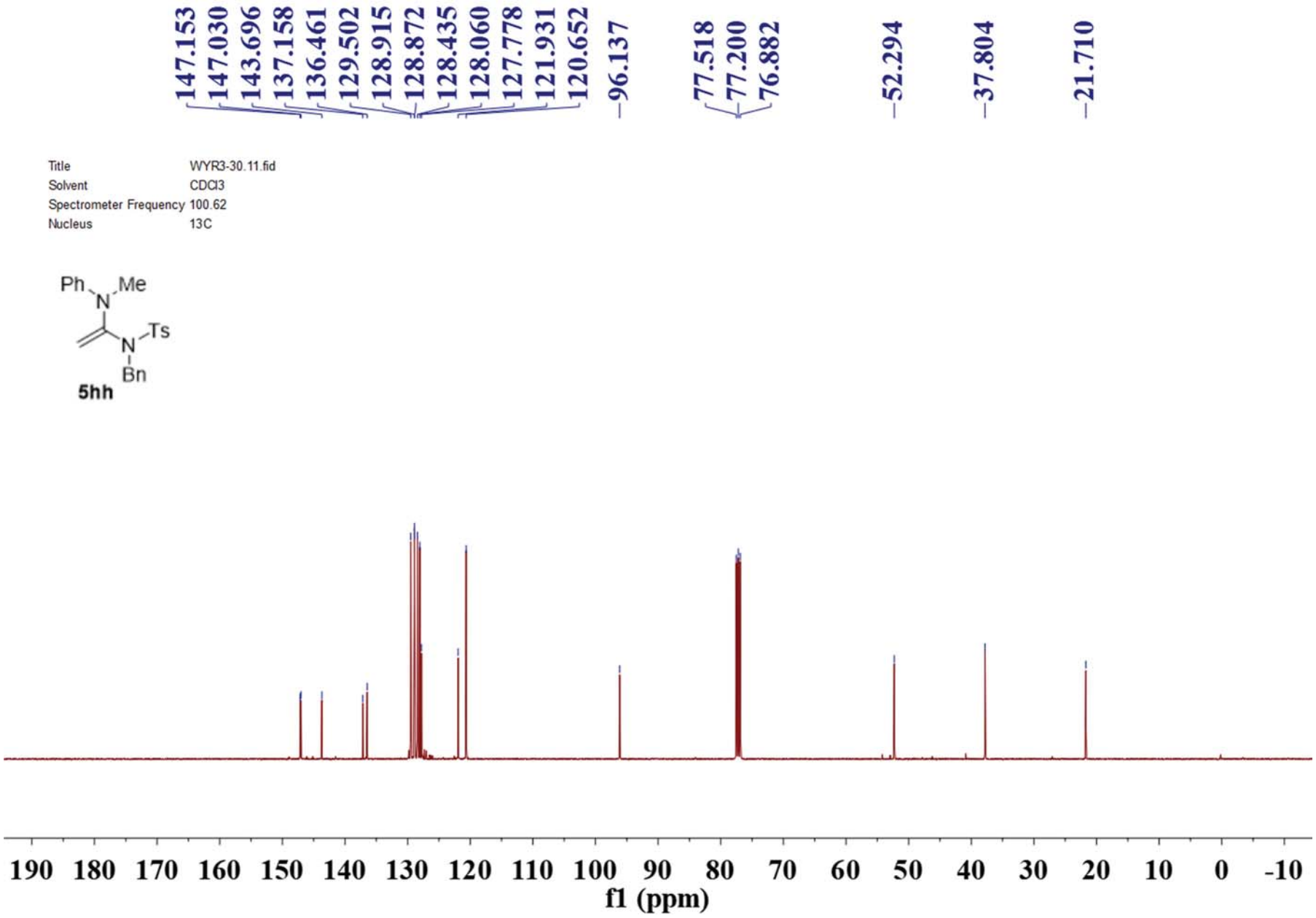
7.2752
7.2698
7.2634
7.2597
7.2514
7.2492
7.2430
7.2325
7.2277
7.1576
7.1528
7.1394
7.1361
7.1226
7.1180
6.9187
6.9162
6.9129
6.9010
6.8978
6.8947
6.8814
6.8794
6.8759
6.8374
6.8342
6.8155
6.8128
4.5497
4.4164
4.4127
4.3125
4.3088
2.7041
2.4125
0.0000
Title WYR3-30.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Me
Ts
N
Bn
5hh
2.00
7.04
2.01
1.01
2.00
2.00
1.00
1.00
3.00
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 -0.5 -1.0
f1 (ppm)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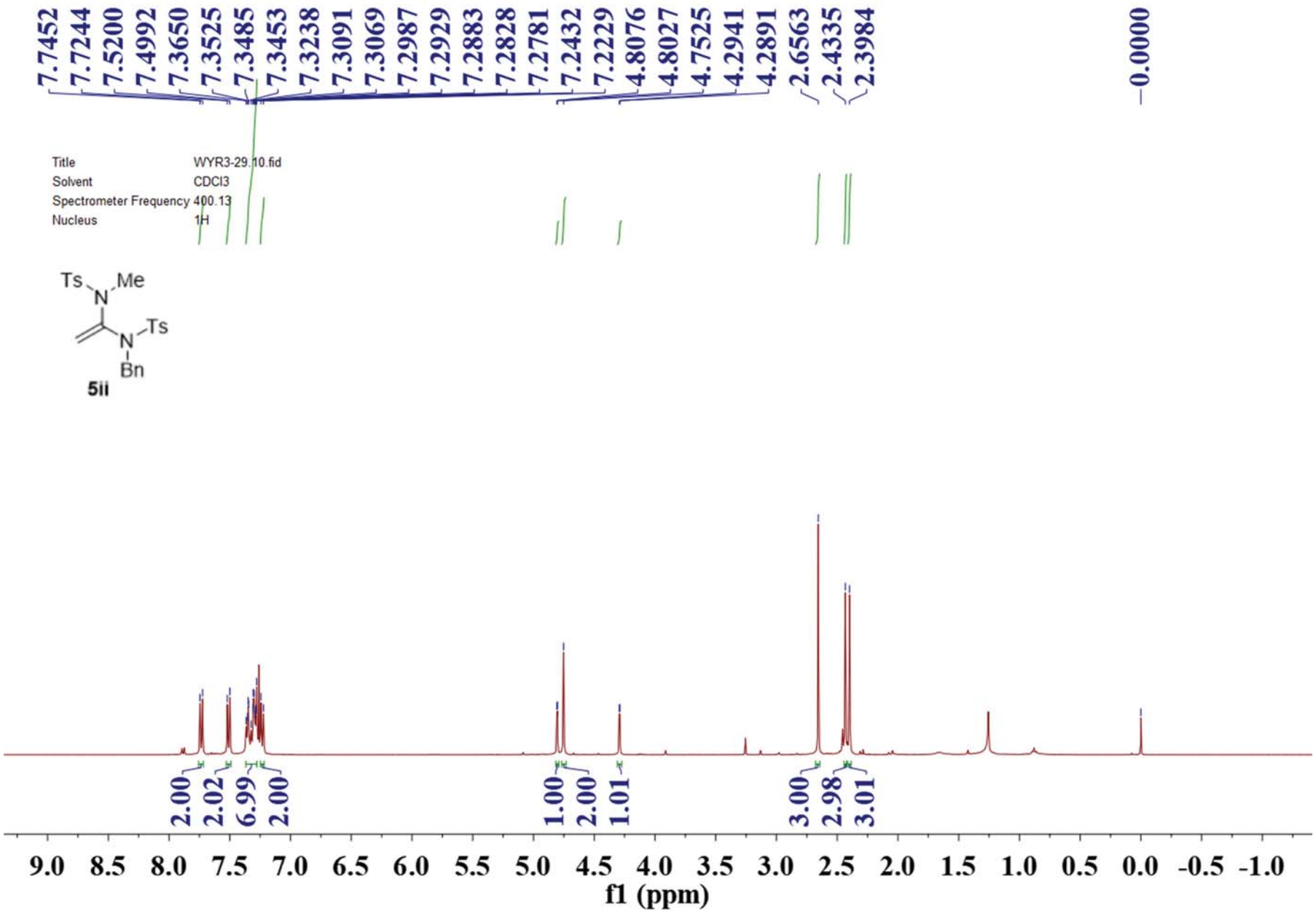
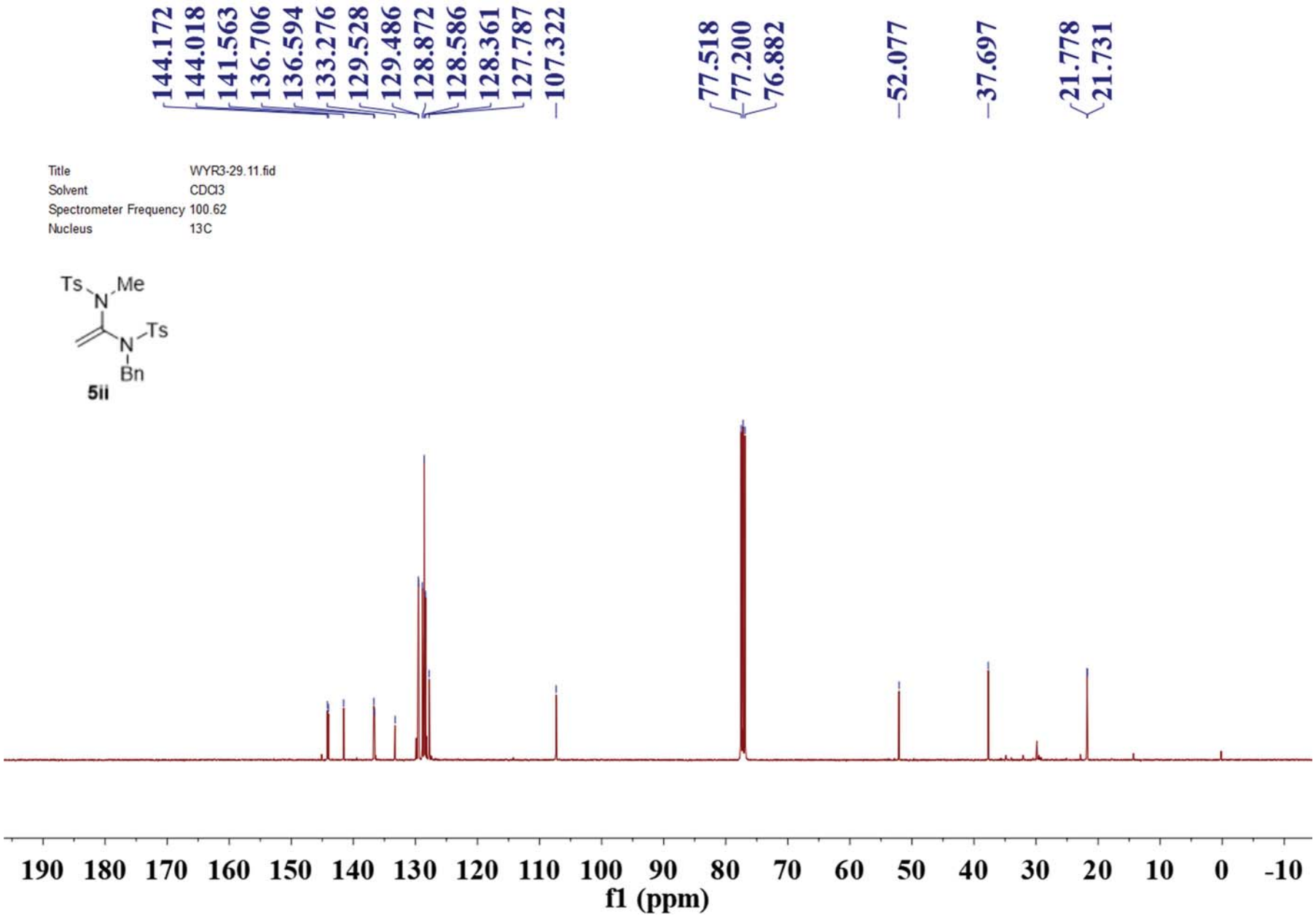
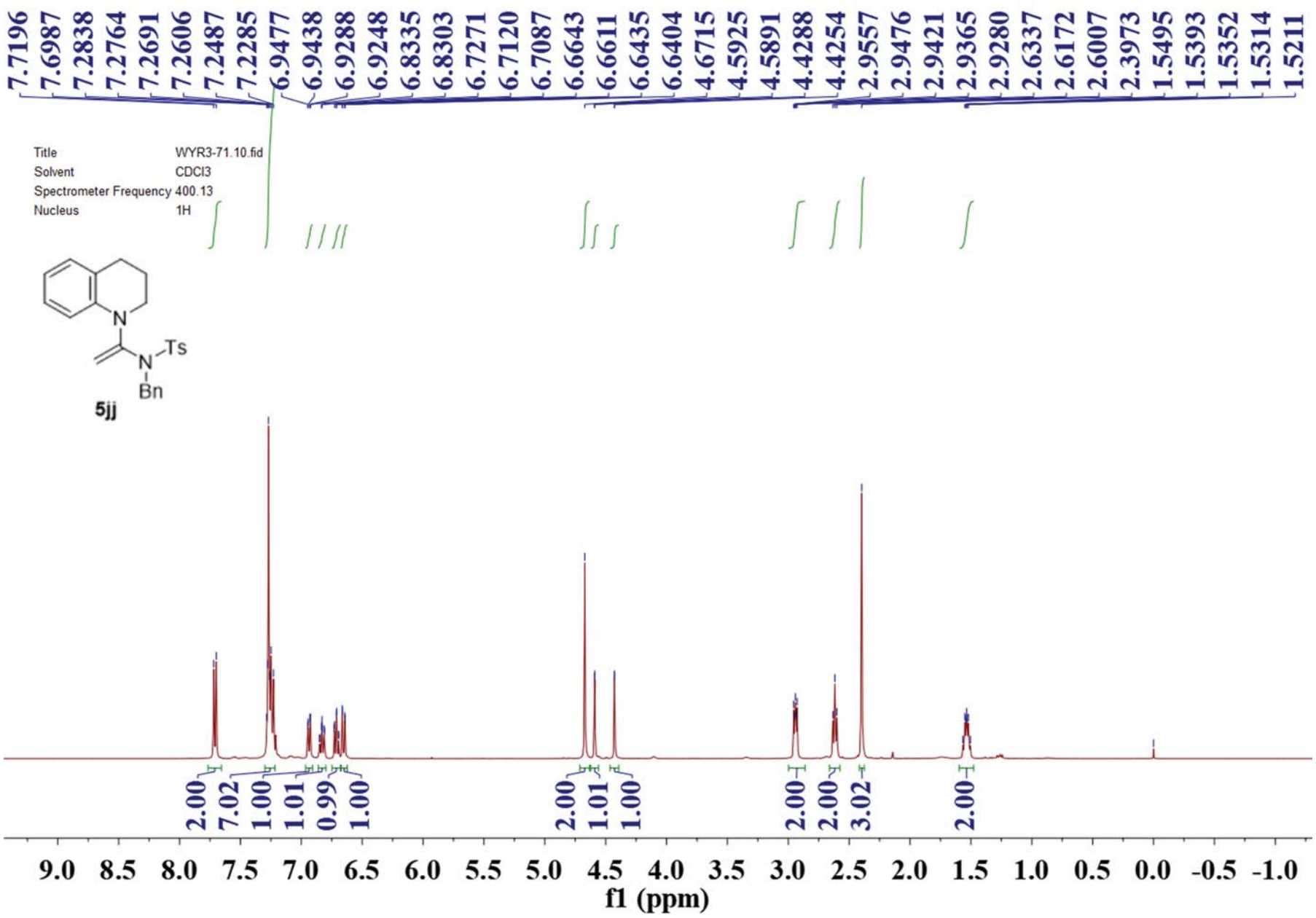
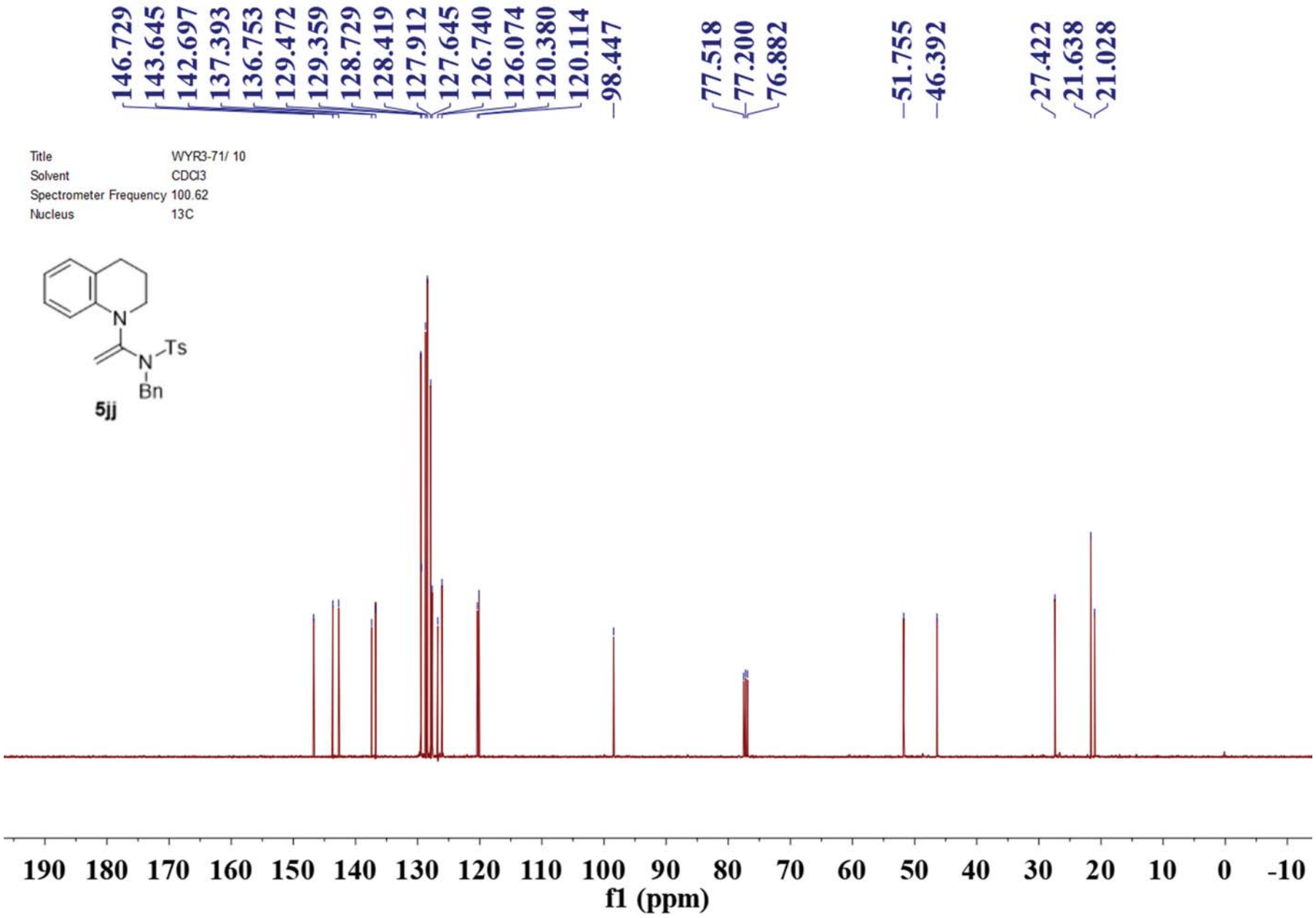
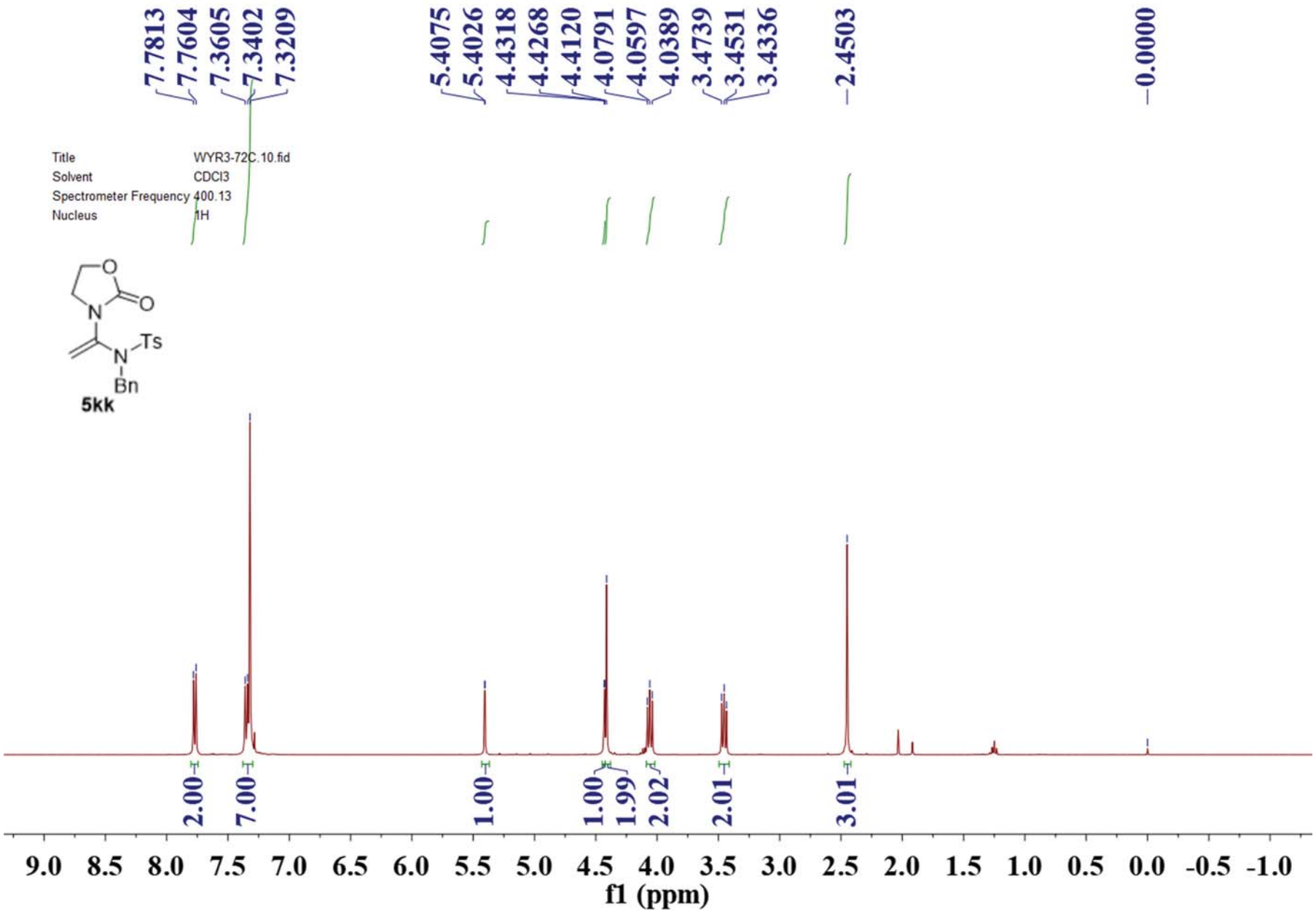
128.872
128.435
128.060
127.778
121.931
120.652
96.137
77.518
77.200
76.882
52.294
37.804
21.710
Title WYR3-30.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Me
N
Ts
Bn
5hh
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

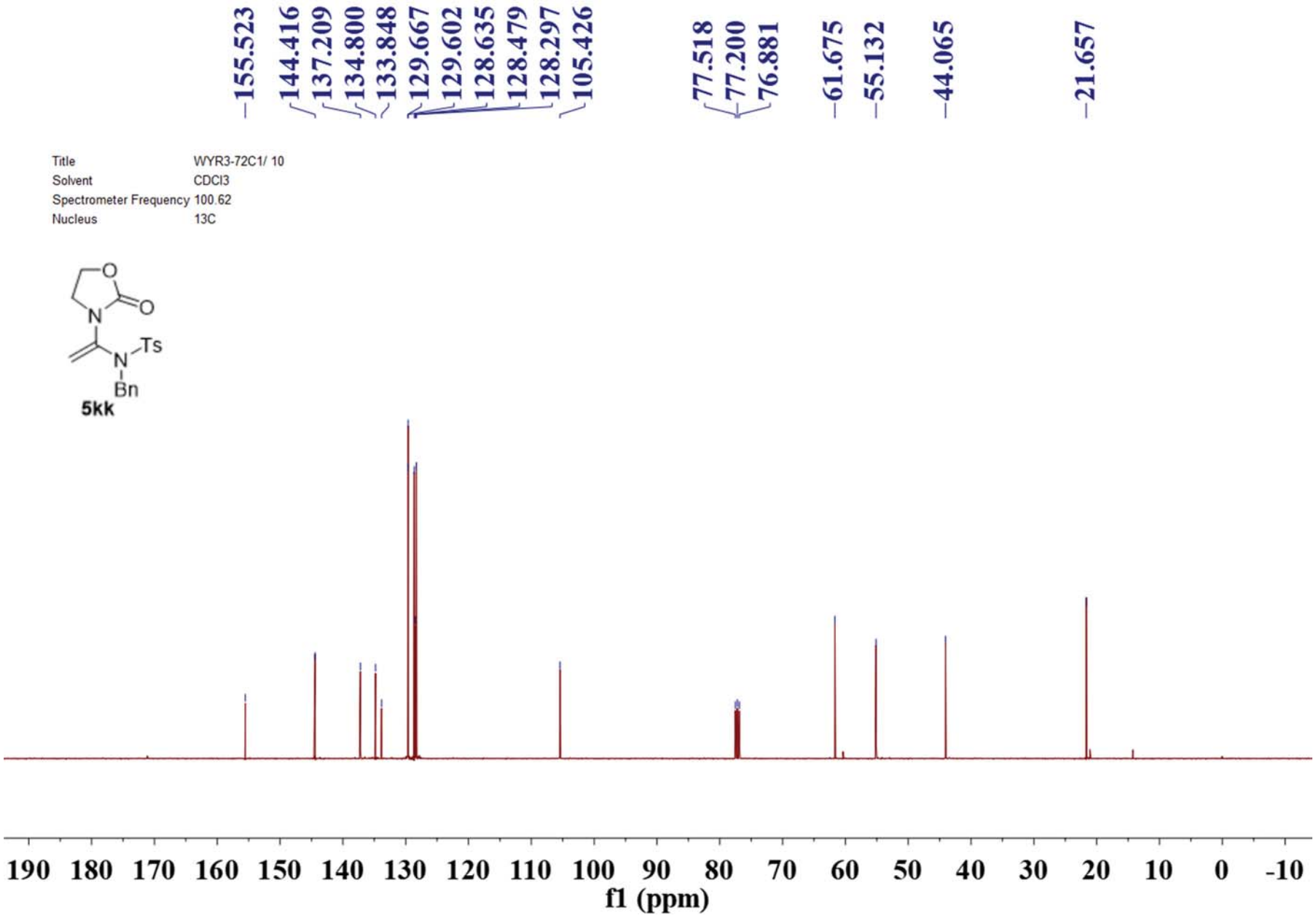

7.7452
7.7244
7.5200
7.4992
7.3650
7.3525
7.3485
7.3453
7.3238
7.3091
7.3069
7.2987
7.2929
7.2883
7.2828
7.2781
7.2432
7.2229
4.8076
4.8027
4.7525
4.2941
4.2891
2.6563
2.4335
2.3984
0.0000
Title WYR3-29.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
N
Ts
Bn
5ii
2.00
2.02
6.99
2.00
1.00
2.00
1.01
3.00
2.98
3.01
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 -0.5 -1.0
f1 (ppm)

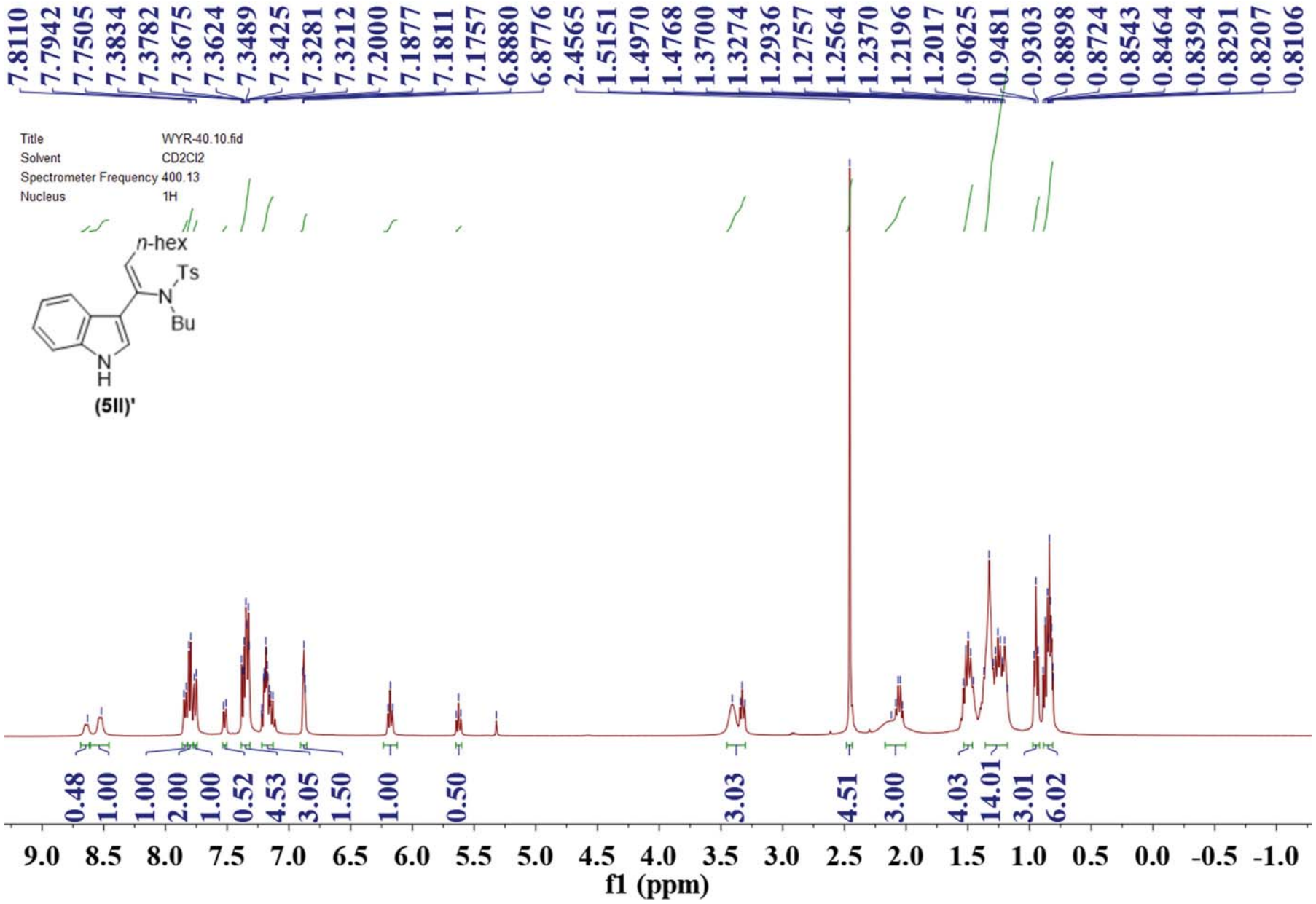

144.172
144.018
141.563
136.706
136.594
133.276
129.528
129.486
128.872
128.586
128.361
127.787
107.322
77.518
77.200
76.882
52.077
37.697
21.778
21.731
Title WYR3-29.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
N
Ts
Bn
5ii
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

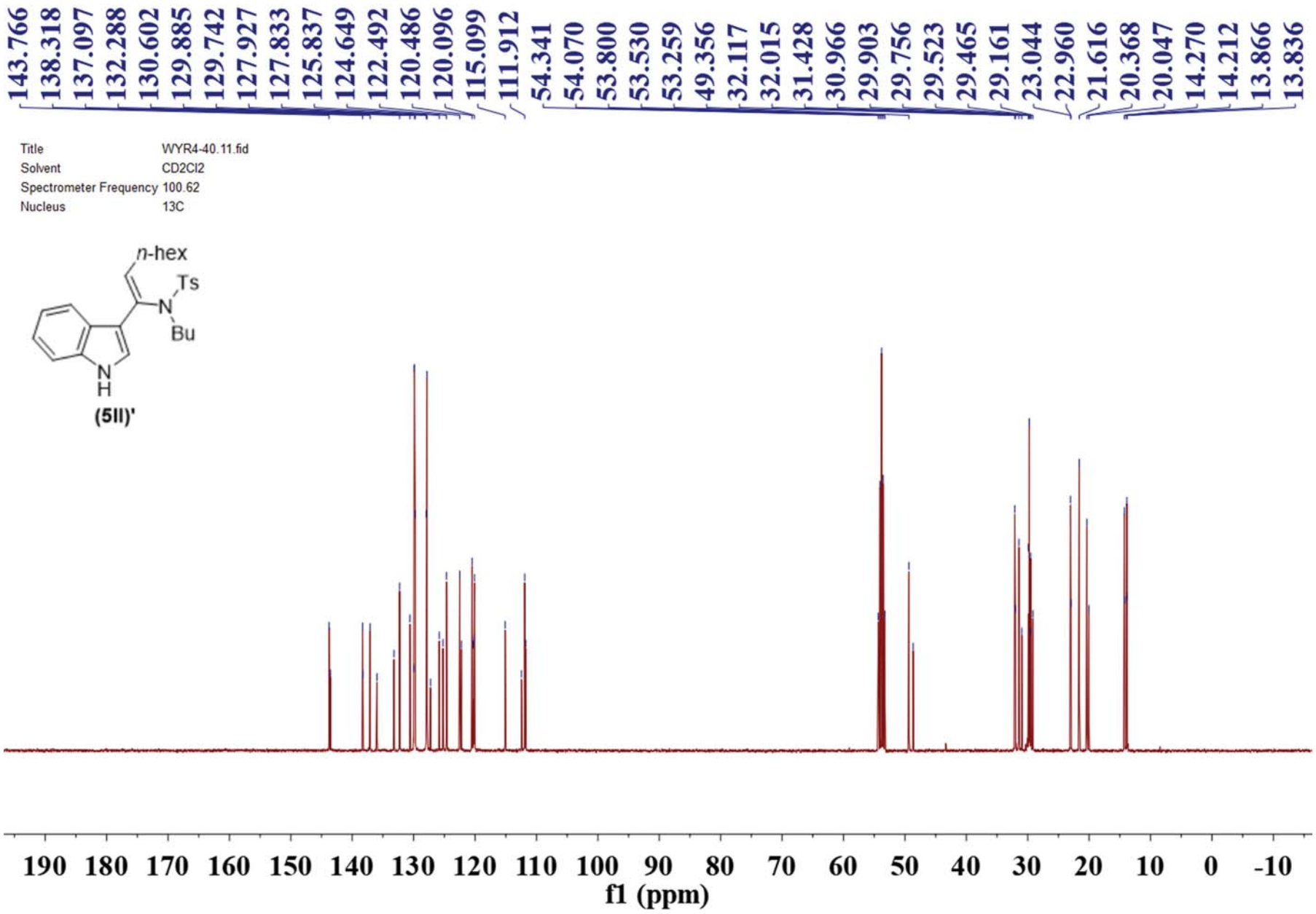

7.7196
7.6987
7.2838
7.2764
7.2691
7.2606
7.2487
7.2285
6.9477
6.9438
6.9288
6.9248
6.8335
6.8303
6.7271
6.7120
6.7087
6.6643
6.6611
6.6435
6.6404
4.6715
4.5925
4.5891
4.4288
4.4254
2.9557
2.9476
2.9421
2.9365
2.9280
2.6337
2.6172
2.6007
2.3973
1.5495
1.5393
1.5352
1.5314
1.5211
Title WYR3-71.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
N
Ts
Bn
5jj
2.00
7.02
1.00
1.01
0.99
1.00
2.00
1.01
1.00
2.00
2.00
3.02
2.00
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 -0.5 -1.0
f1 (ppm)

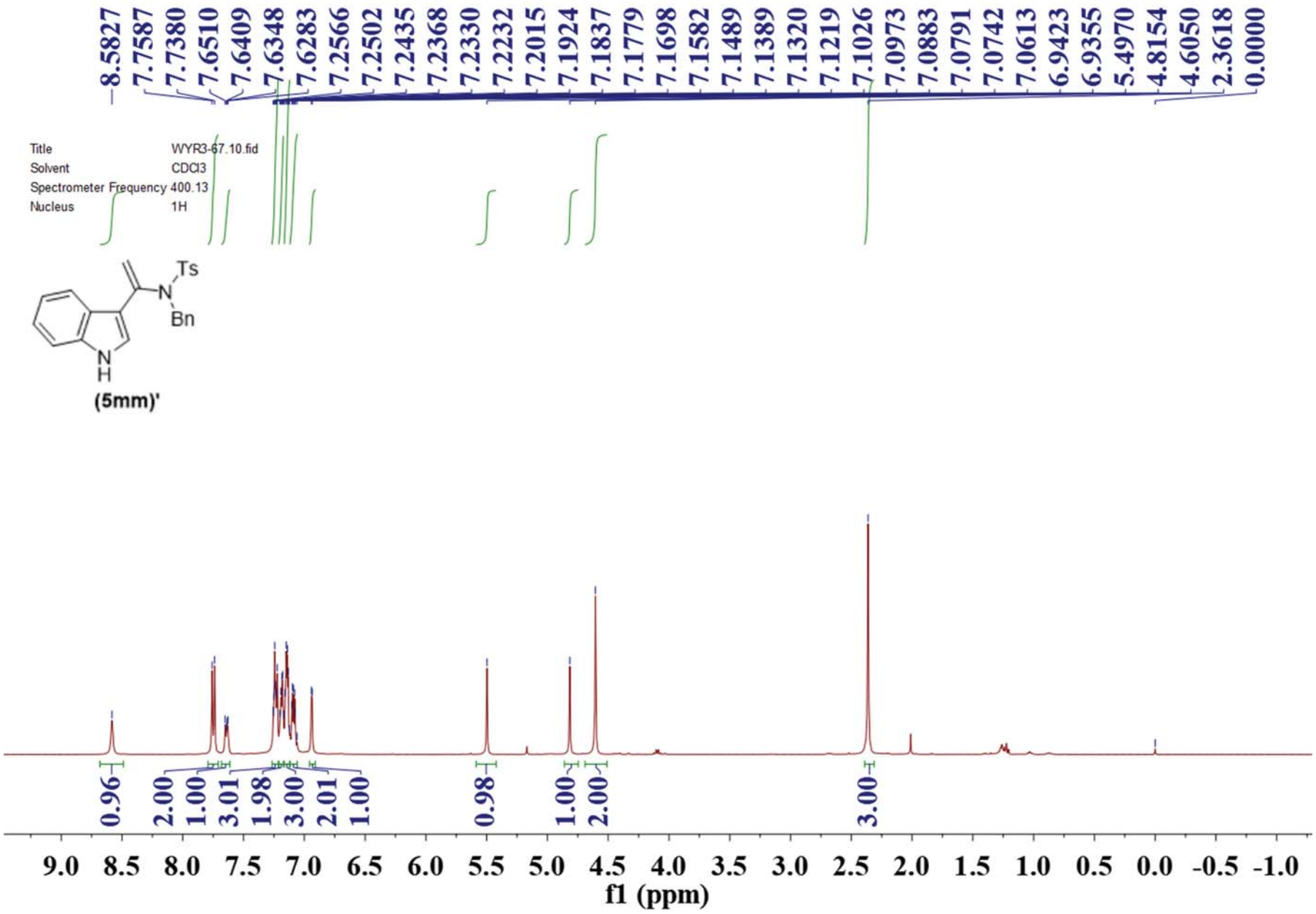

146.729
143.645
142.697
137.393
136.753
129.472
129.359
128.729
128.419
127.912
127.645
126.740
126.074
120.380
120.114
98.447
77.518
77.200
76.882
51.755
46.392
27.422
21.638
21.028
Title WYR3-71/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
N
Ts
Bn
5jj
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

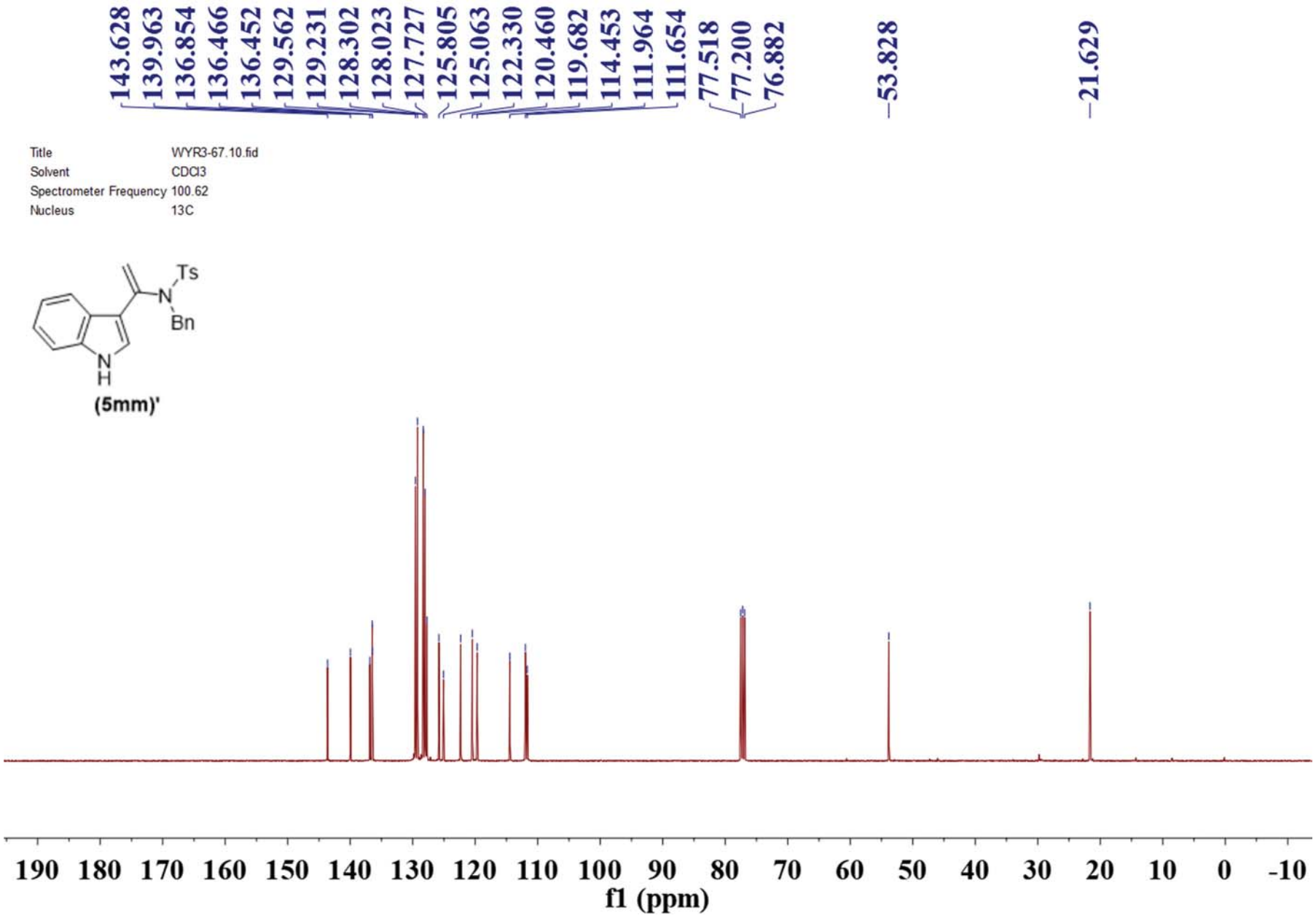

7.7813
7.7604
7.3605
7.3402
7.3209
5.4075
5.4026
4.4318
4.4268
4.4120
4.0791
4.0597
4.0389
3.4739
3.4531
3.4336
2.4503
0.0000
Title WYR3-72C.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
Bn
5kk
2.00
7.00
1.00
1.00
1.99
2.02
2.01
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


155.523
144.416
137.209
134.800
133.848
129.667
129.602
128.635
128.479
128.297
105.426
77.518
77.200
76.881
61.675
55.132
44.065
21.657
Title WYR3-72C1/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
O
N
O
N
Ts
Bn
5kk
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

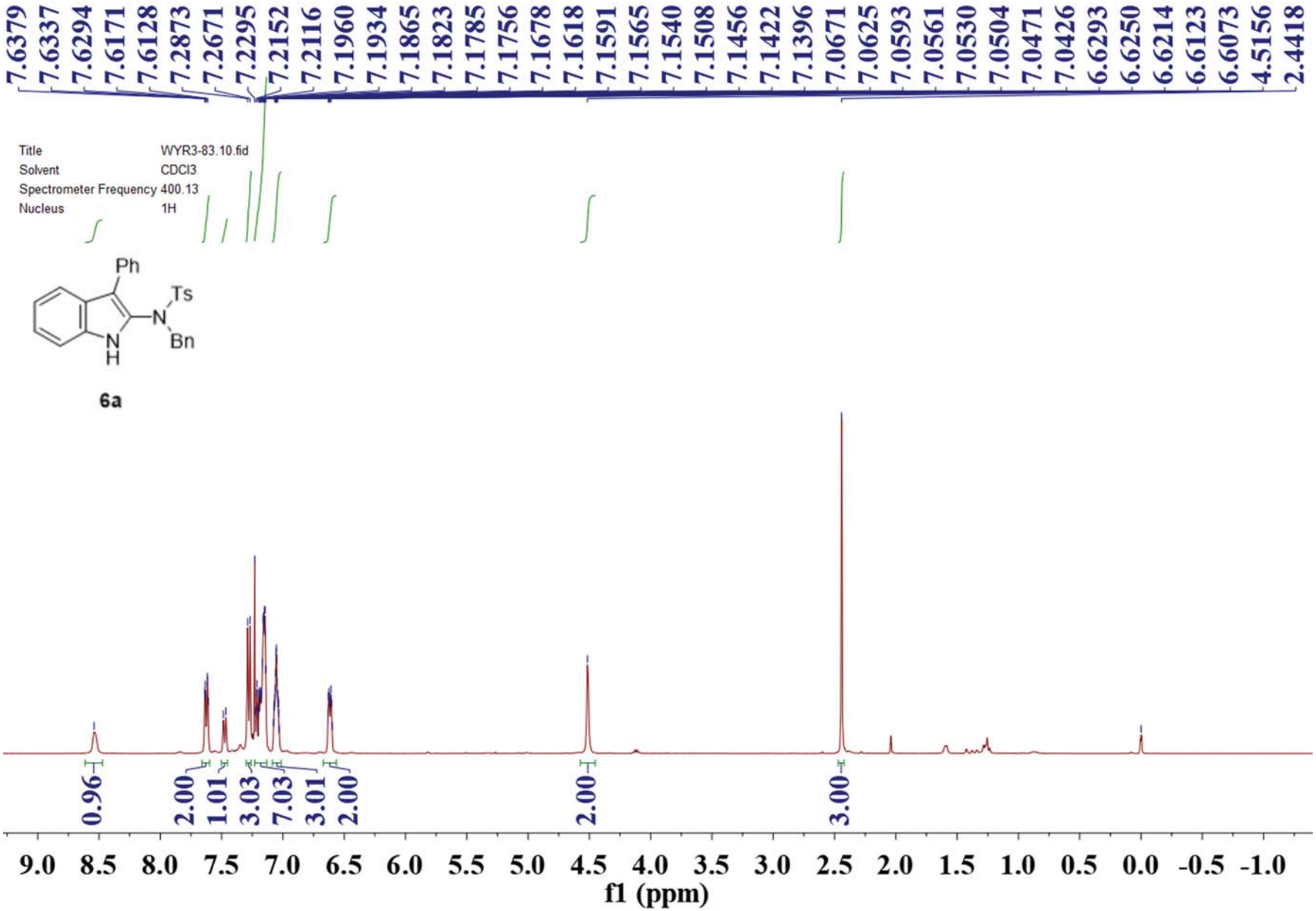

7.8110
7.7942
7.7505
7.3834
7.3782
7.3675
7.3624
7.3489
7.3425
7.3281
7.3212
7.2000
7.1877
7.1811
7.1757
6.8880
6.8776
2.4565
1.5151
1.4970
1.4768
1.3700
1.3274
1.2936
1.2757
1.2564
1.2370
1.2196
1.2017
0.9625
0.9481
0.9303
0.8898
0.8724
0.8543
0.8464
0.8394
0.8291
0.8207
0.8106
Title WYR-40.10.fid
Solvent CD2Cl2
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
Ts
N
Bu
N
H
(5ll)'
0.48
1.00
1.00
2.00
1.00
0.52
4.53
3.05
1.50
1.00
0.50
3.03
4.51
3.00
4.03
14.01
3.01
6.02
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 -0.5 -1.0
f1 (ppm)

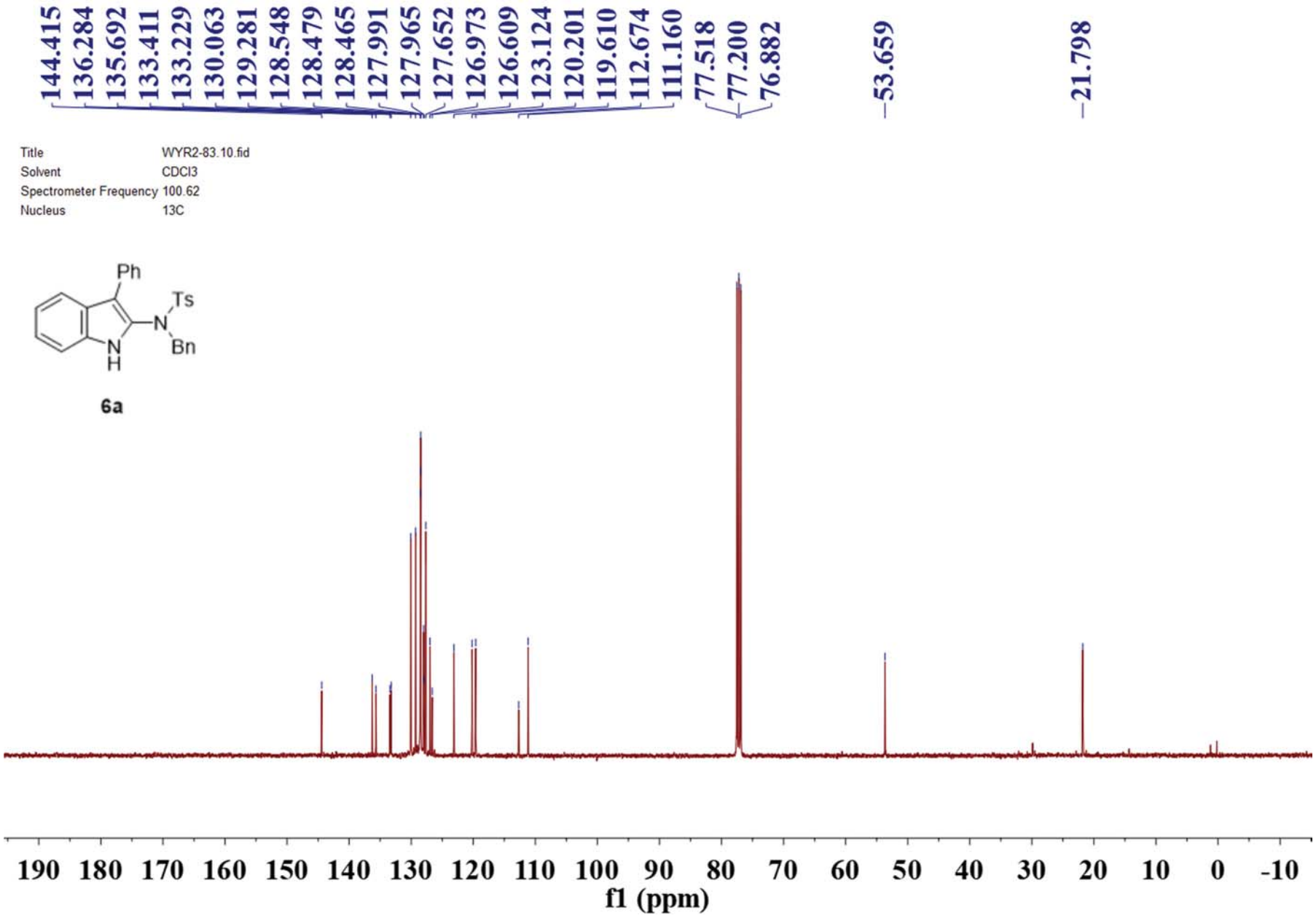

143.766
138.318
137.097
132.288
130.602
129.885
129.742
127.927
127.833
125.837
124.649
122.492
120.486
120.096
115.099
111.912
54.341
54.070
53.800
53.530
53.259
49.356
32.117
32.015
31.428
30.966
29.903
29.756
29.523
29.465
29.161
23.044
22.960
21.616
20.368
20.047
14.270
14.212
13.866
13.836
Title WYR4-40.11.fid
Solvent CD2Cl2
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
Ts
N
Bu
N
H
(5ll)'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

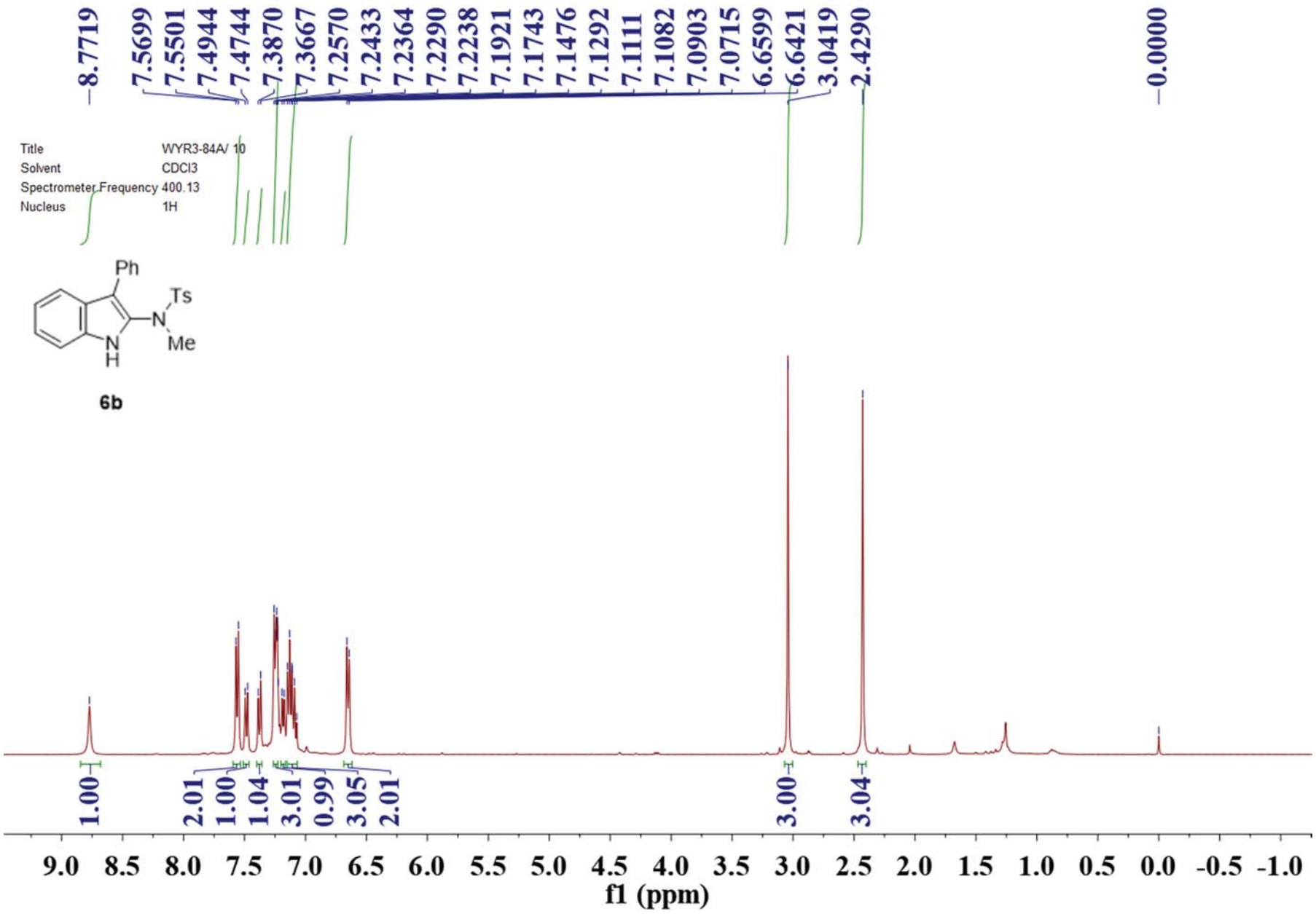

8.5827
7.7587
7.7380
7.6510
7.6409
7.6348
7.6283
7.2566
7.2502
7.2435
7.2368
7.2330
7.2232
7.2015
7.1924
7.1837
7.1779
7.1698
7.1582
7.1489
7.1389
7.1320
7.1219
7.1026
7.0973
7.0883
7.0791
7.0742
7.0613
6.9423
6.9355
5.4970
4.8154
4.6050
2.3618
0.0000
Title WYR3-67.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Bn
N
H
(5mm)'
0.96
2.00
1.00
3.01
1.98
3.00
2.01
1.00
0.98
1.00
2.00
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 -0.5 -1.0
f1 (ppm)

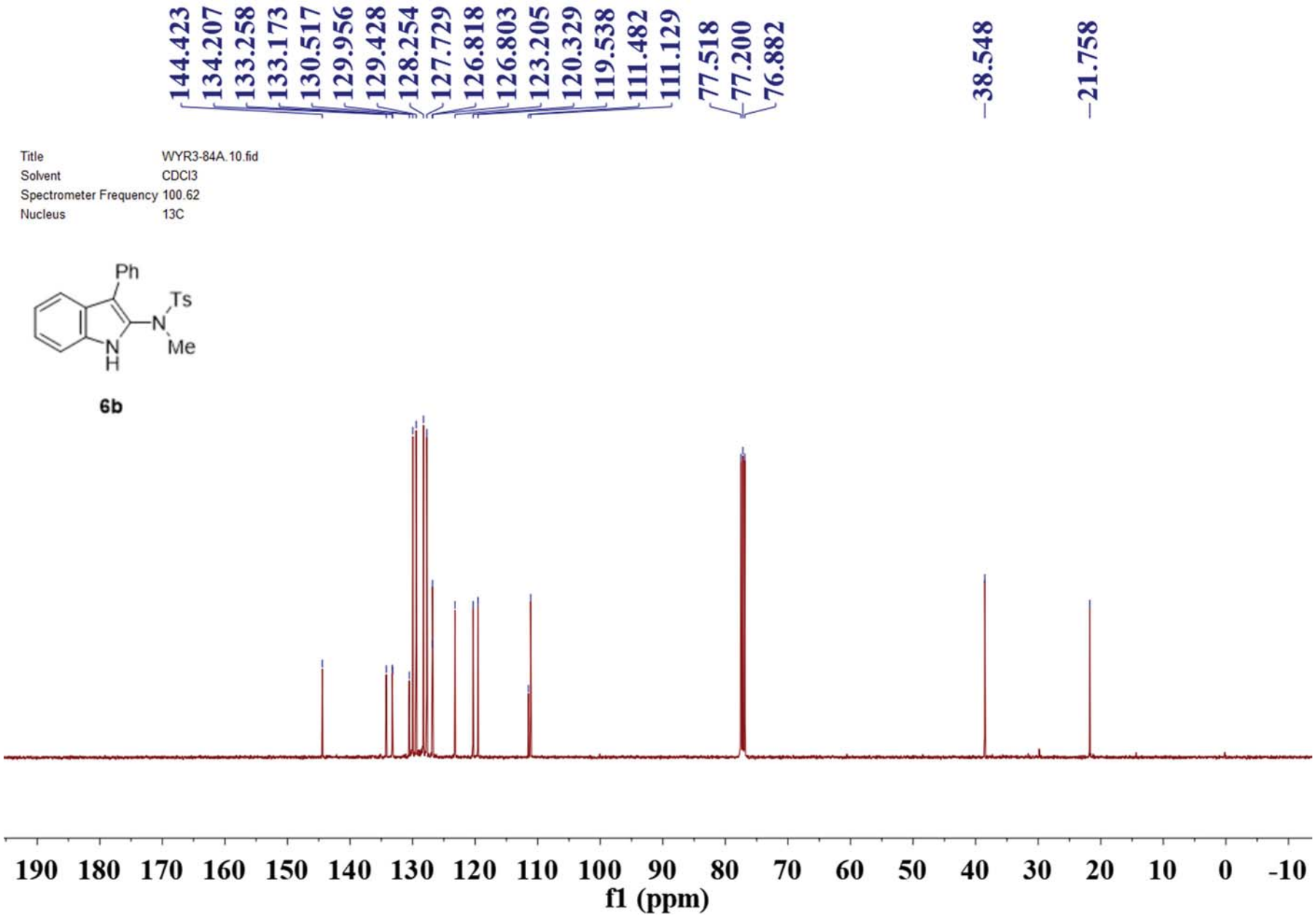

143.628
139.963
136.854
136.466
136.452
129.562
129.231
128.302
128.023
127.727
125.805
125.063
122.330
120.460
119.682
114.453
111.964
111.654
77.518
77.200
76.882
53.828
21.629
Title WYR3-67.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Bn
N
H
(5mm)'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

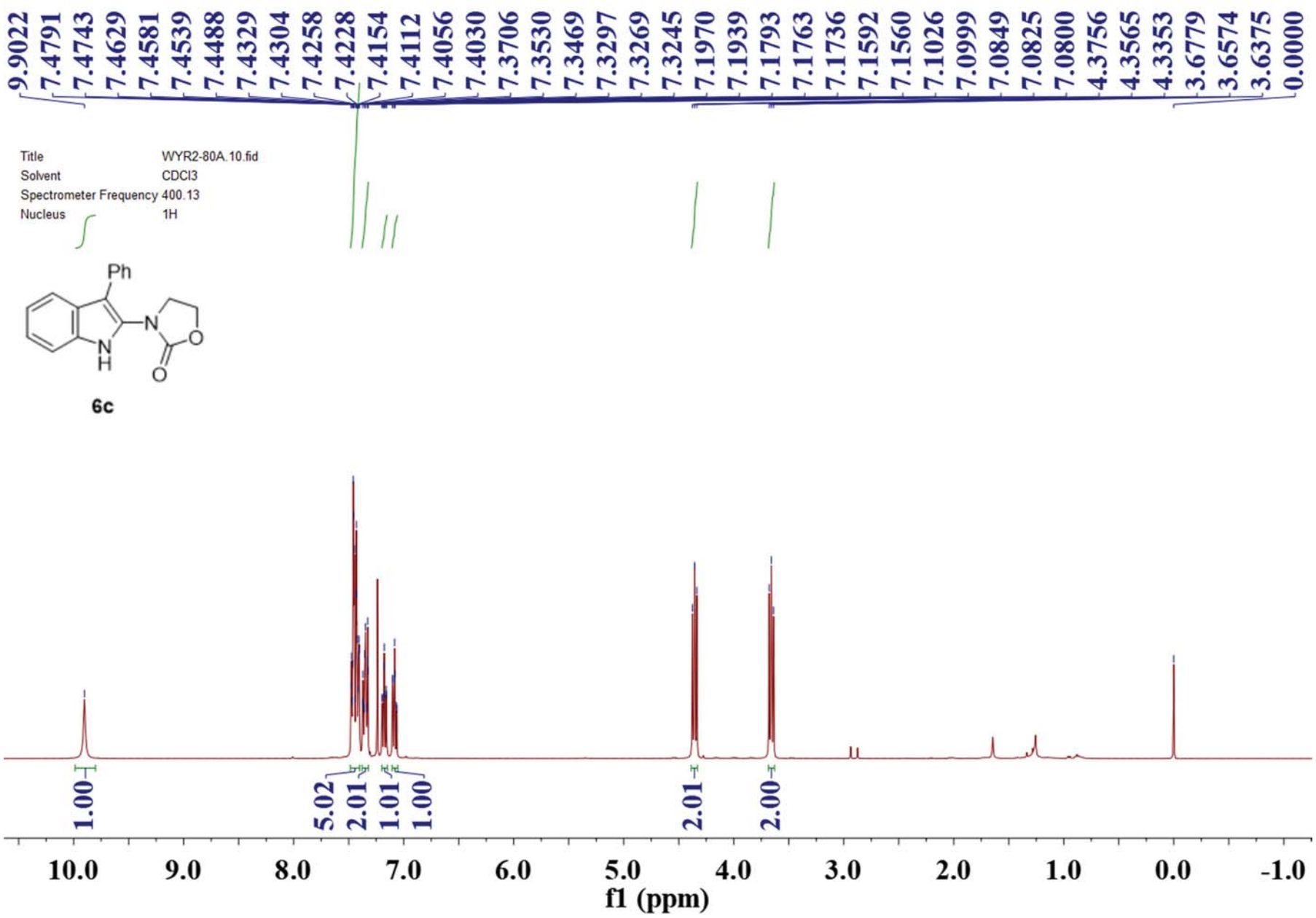
^{1}H NMR and ^{13}C NMR Spectra of 2-Aminoindoles 6.

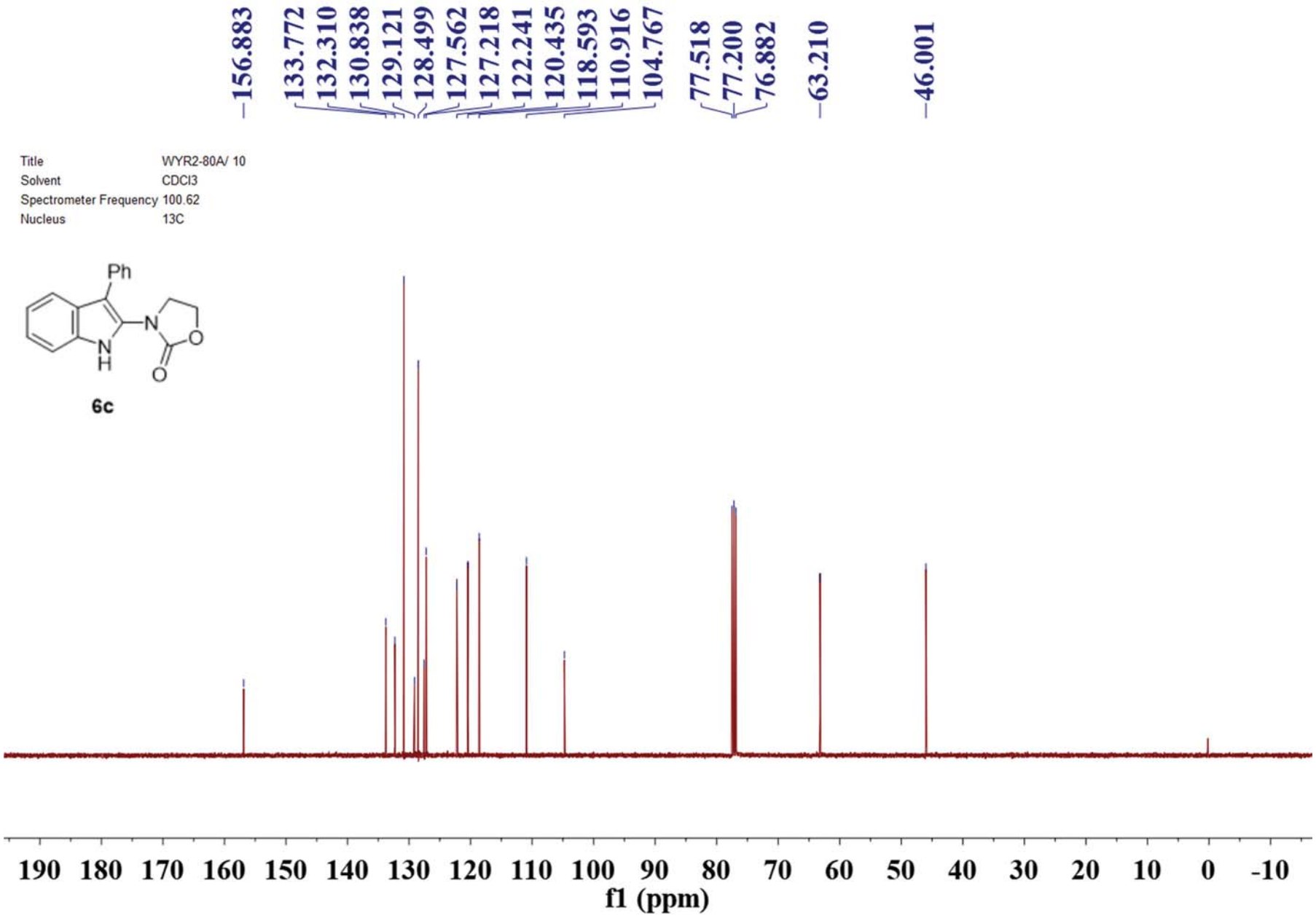


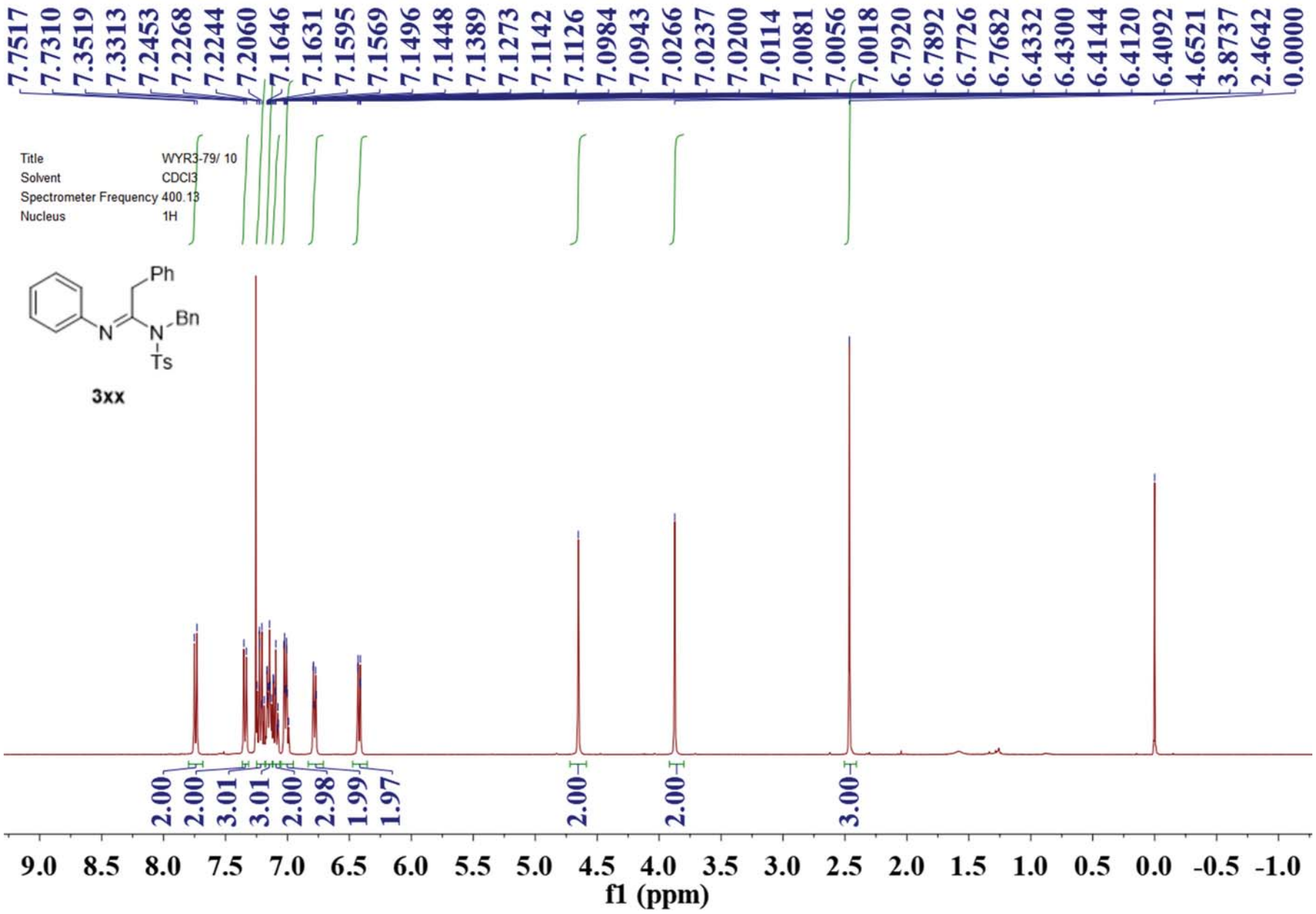

144.415
136.284
135.692
133.411
133.229
130.063
129.281
128.548
128.479
128.465
127.991
127.965
127.652
126.973
126.609
123.124
120.201
119.610
112.674
111.160
77.518
77.200
76.882
53.659
21.798
Title WYR2-83.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
Ts
N
N
H
Bn
6a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

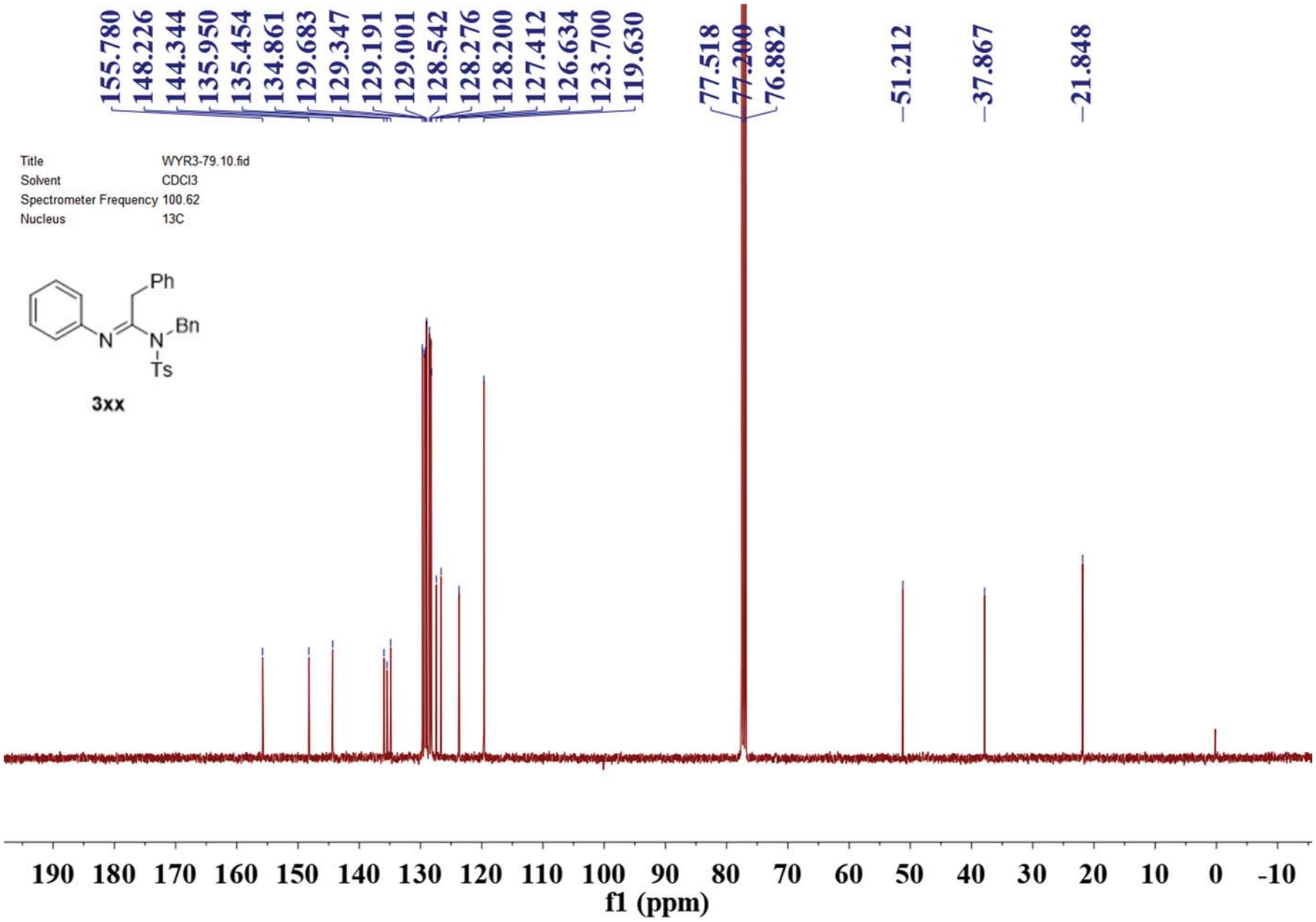

8.7719
7.5699
7.5501
7.4944
7.4744
7.3870
7.3667
7.2570
7.2433
7.2364
7.2290
7.2238
7.1921
7.1743
7.1476
7.1292
7.1111
7.1082
7.0903
7.0715
6.6599
6.6421
3.0419
2.4290
0.0000
Title WYR3-84A/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
Ts
N
N
H
Me
6b
1.00
2.01
1.00
1.04
3.01
0.99
3.05
2.01
3.00
3.04
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 -0.5 -1.0
f1 (ppm)


144.423
134.207
133.258
133.173
130.517
129.956
129.428
128.254
127.729
126.818
126.803
123.205
120.329
119.538
111.482
111.129
77.518
77.200
76.882
38.548
21.758
Title WYR3-84A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
Ts
N
N
H
Me
6b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

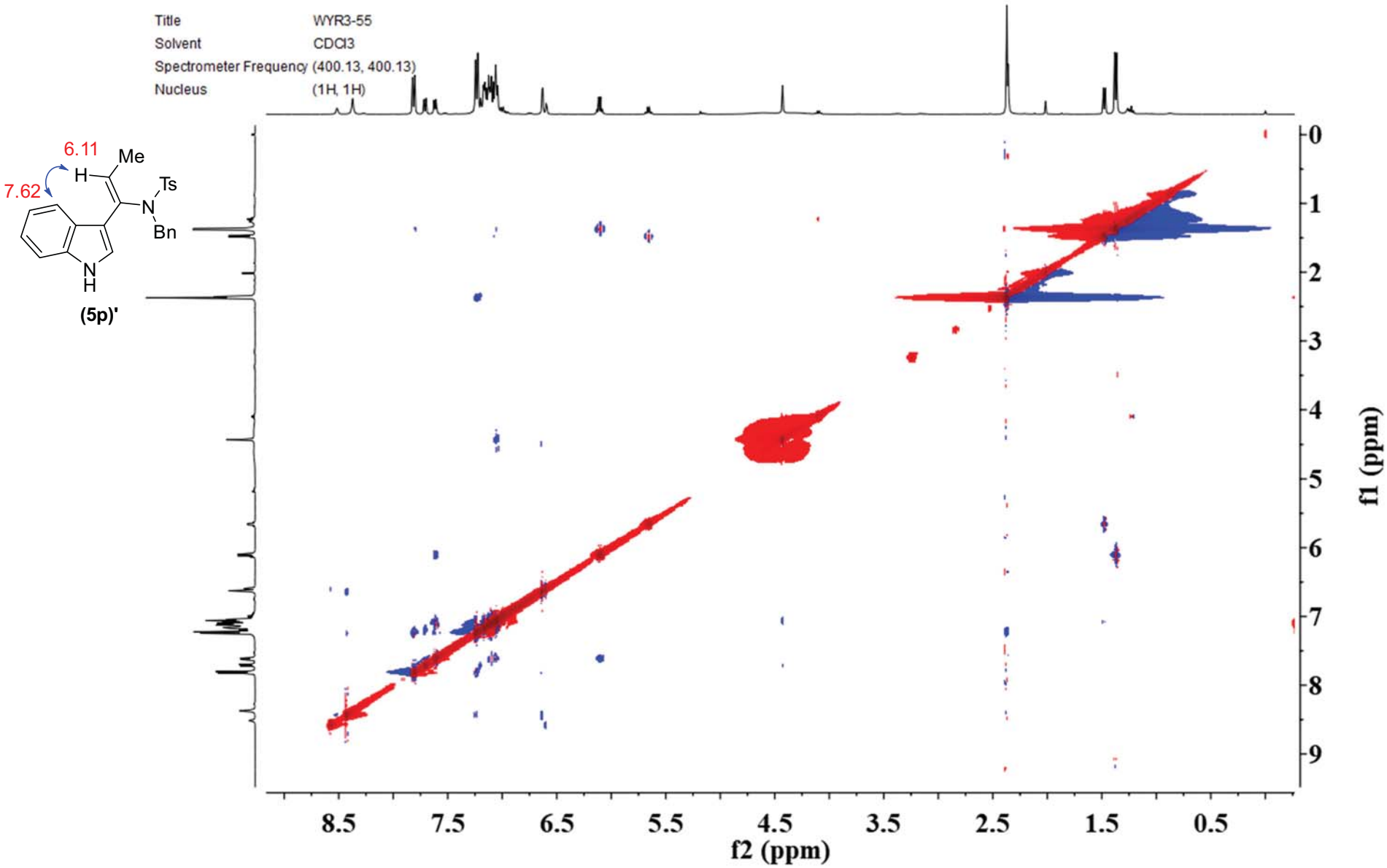

9.9022
7.4791
7.4743
7.4629
7.4581
7.4539
7.4488
7.4329
7.4304
7.4258
7.4228
7.4154
7.4112
7.4056
7.4030
7.3706
7.3530
7.3469
7.3297
7.3269
7.3245
7.1970
7.1939
7.1793
7.1763
7.1736
7.1592
7.1560
7.1026
7.0999
7.0849
7.0825
7.0800
4.3756
4.3565
4.3353
3.6779
3.6574
3.6375
0.0000
Title WYR2-80A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
O
N
H
O
6c
1.00
5.02
2.01
1.01
1.00
2.01
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

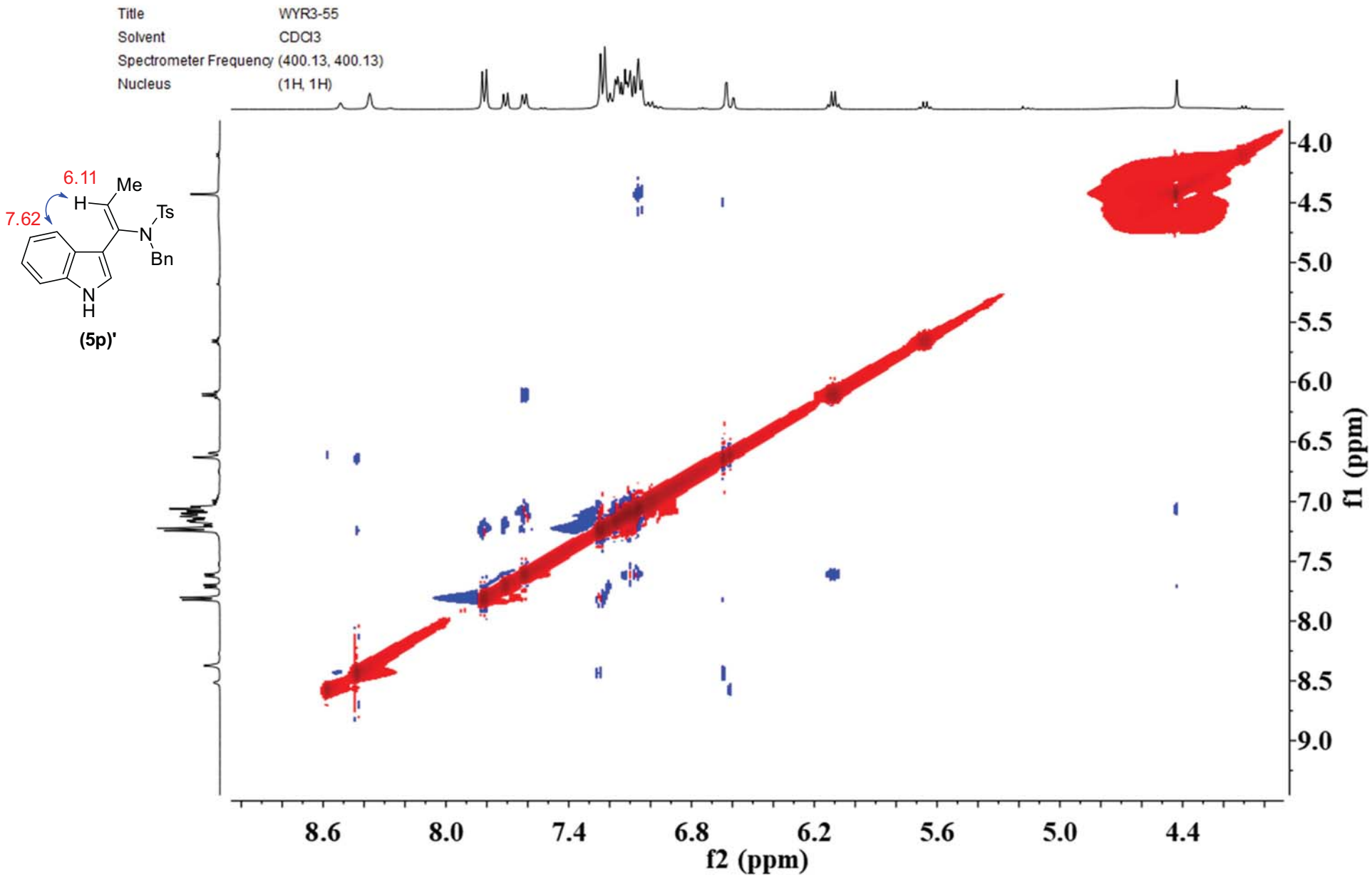

156.883
133.772
132.310
130.838
129.121
128.499
127.562
127.218
122.241
120.435
118.593
110.916
104.767
77.518
77.200
76.882
63.210
46.001
Title WYR2-80A/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
H
O
O
6c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

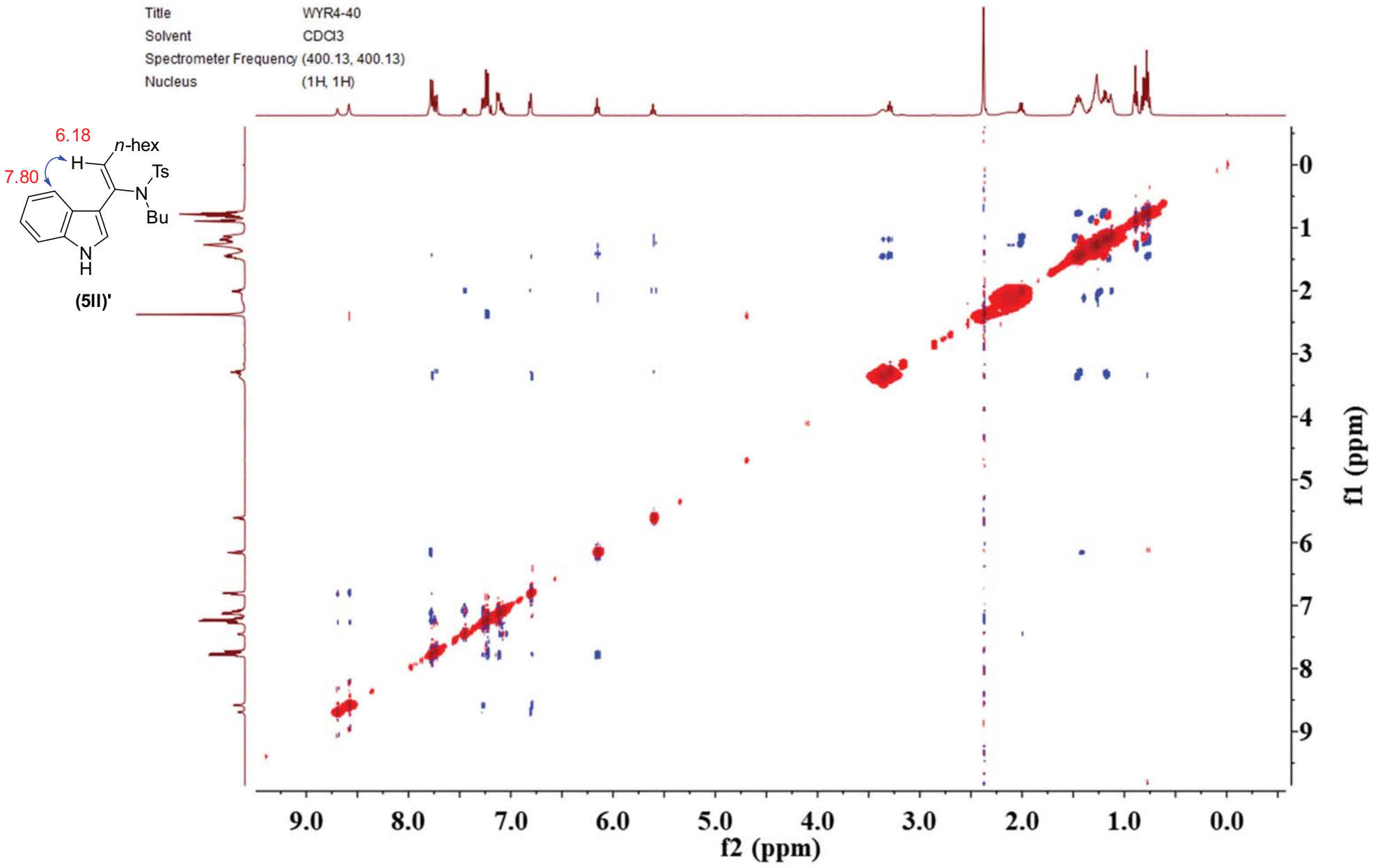

7.7517
7.7310
7.3519
7.3313
7.2453
7.2268
7.2244
7.2060
7.1646
7.1631
7.1595
7.1569
7.1496
7.1448
7.1389
7.1273
7.1142
7.1126
7.0984
7.0943
7.0266
7.0237
7.0200
7.0114
7.0081
7.0056
7.0018
6.7920
6.7892
6.7726
6.7682
6.4332
6.4300
6.4144
6.4120
6.4092
4.6521
3.8737
2.4642
0.0000
Title WYR3-79/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
N
Bn
Ts
3xx
2.00
2.00
3.01
3.01
2.00
2.98
1.99
1.97
2.00
2.00
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 -0.5 -1.0
f1 (ppm)

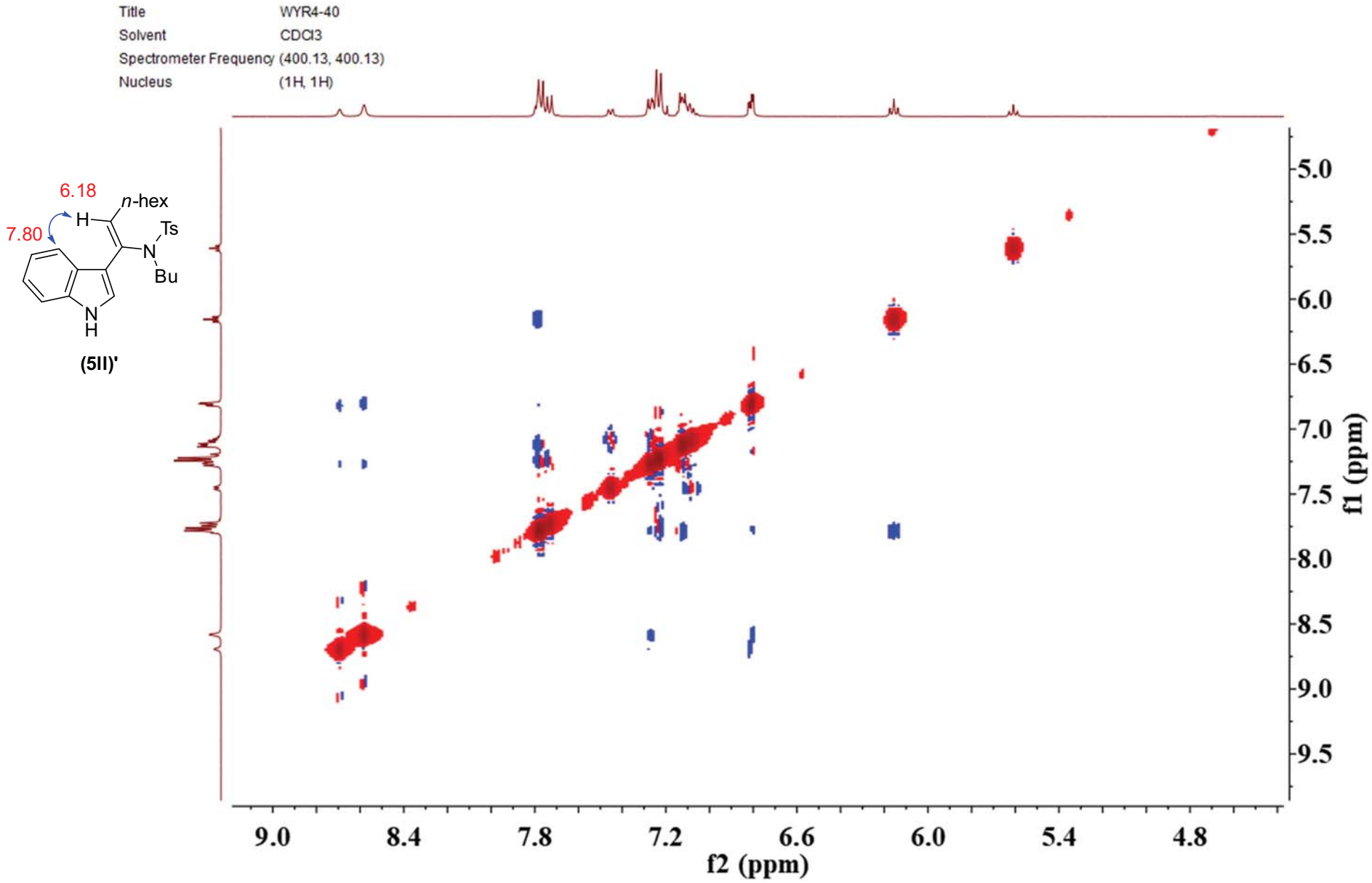

155.780
148.226
144.344
135.950
135.454
134.861
129.683
129.347
129.191
129.001
128.542
128.276
128.200
127.412
126.634
123.700
119.630
77.518
77.200
76.882
51.212
37.867
21.848
Title WYR3-79.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
N
Bn
Ts
3xx
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

NOESY Spectra of 3-Alkenylindoles (5p)' and (5ll)'.




Title WYR3-55
Solvent CDCl3
Spectrometer Frequency (400.13, 400.13)
Nucleus (1H, 1H)
6.11
7.62
H
Me
Ts
N
Bn
N
H
(5p)'
8.6
8.0
7.4
6.8
6.2
5.6
5.0
4.4
f2 (ppm)
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)


Title WYR4-40
Solvent CDCl3
Spectrometer Frequency (400.13, 400.13)
Nucleus (1H, 1H)
6.18
7.80
n-hex
H
Ts
N
Bu
N
H
(5II)'
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)
f1 (ppm)


Title WYR4-40
Solvent CDCl3
Spectrometer Frequency (400.13, 400.13)
Nucleus (1H, 1H)
6.18
7.80
n-hex
H
Ts
N
Bu
N
H
(5ll)'
9.0
8.4
7.8
7.2
6.6
6.0
5.4
4.8
f2 (ppm)
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)