SUPPORTING INFORMATION

Metal-free [2 + 2] and [4 + 2] cycloadditions of *N*-aryl-substituted ynamides to construct functionalized aminocyclobutenes and 4-aminoquinolines

Lixia Ding,[a] Zhifei Zhu,[a] Xinyue Zhou,[a] Gongming Zhu,[b] Jian-Hua Wang,[c,d] Shu-Tong Zhu,[c] Bing Hu,[d] Xiao-Na Wang,*[a] and Junbiao Chang*[a]

[a]*Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province, Key Laboratory of Advanced Drug Preparation Technologies, Ministry of Education, School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou 450001, P. R. China. E-mail: wangxn@zzu.edu.cn, changjunbiao@zzu.edu.cn*
[b]*Pingyuan Laboratory, NMPA (National Medical Products Administration) Key Laboratory for Research and Evaluation of Innovative Drug, Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China*
[c]*Guangzhou Institutes of Biomedicine and Health, Chinese Academy of Sciences, Guangzhou, 510530, China*
[d]*College of Life Sciences, Henan Normal University, Xinxiang, 453007, China*

Table of Contents

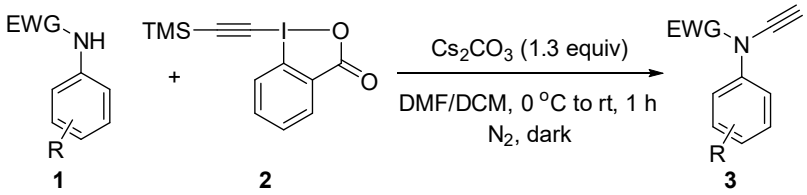
Part I Experimental Part

General Information

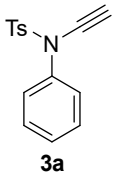
Unless otherwise indicated, all starting materials were obtained from commercial supplies and used as received. All reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker's Ascend^{TM} 400 NMR spectrometer using $CDCl_3$, CD_3OD, or $(CD_3)_2SO$ 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, methanol signal at 49.0 ppm or dimethyl sulfoxide signal at 39.5 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 Terminal *N*-Aryl Ynamides 3.

Ynamides **3a**[2], **3b**[3], **3d**[2], **3e**[2], **3f**[2], **3g**[3], **3h**[2], **3i**[3], **3j**[4], **3l**[3], **3m**[5] **3n**[2], **3p**[5], **3r**[2], **3s**[4] and **3t**[2] were known compounds, the data were matched with reported literature values. Ynamides **3c**, **3k**, **3o** and **3q** were new compounds.



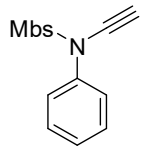
Scheme S1. Synthesis of terminal *N*-aryl ynamides **3**



3a

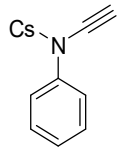
To a round bottom flask was added the corresponding sulfonamide **1a** (123.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2**[1] (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution 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 ynamide **3a** (135.2 mg, 0.50 mmol) in 99% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.3 Hz), 7.34-7.31 (m, 3H), 7.30-7.24 (m, 4H), 2.84 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.4, 133.0, 129.7, 129.3, 128.6, 128.4, 126.4, 76.7, 59.1, 21.9. Spectral data are in agreement with literature values.[2]



3b

To a round bottom flask was added the corresponding sulfonamide **1b** (130.6 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^{o}C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 8:1~4:1 petroleum ether/EtOAc] to afford ynamide **3b** (137.1 mg, 0.48 mmol) in 95% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 2H, J = 9.0 Hz), 7.35-7.31 (m, 3H), 7.28-7.25 (m, 2H), 6.94 (d, 2H, J = 9.0 Hz), 3.88 (s, 3H), 2.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 138.5, 130.7, 129.3, 128.6, 127.6, 126.5, 114.2, 76.9, 59.1, 55.9. Spectral data are in agreement with literature values.[3]

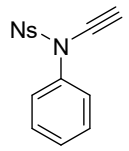


3c

To a round bottom flask was added the corresponding sulfonamide **1c** (133.9 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^{o}C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3c** (124.3 mg, 0.43 mmol) in 85% yield.

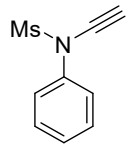
3c: R_f = 0.55 [5:1 petroleum ether/EtOAc]; white solid; mp = 109–110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 2H, J = 8.8 Hz), 7.48 (d, 2H, J = 8.8 Hz), 7.37-7.33 (m, 3H), 7.26-7.24 (m, 2H), 2.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.1, 134.3, 129.8, 129.5, 128.9, 126.4, 76.2, 59.4, one carbon missing due to overlap, overlapped signal at 129.5 ppm; IR (neat) (cm^{-1}) 3307m, 2129w, 1488m, 1371s, 1175s, 1087s, 1012m; HRMS (ESI): m/z calcd for $C_{14}H_{11}ClNO_2S$ $[M + H]^+$

292.0194, found 292.0197.



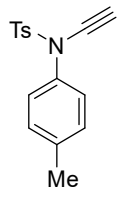
3d

To a round bottom flask was added the corresponding sulfonamide **1d** (139.1 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3d** (124.8 mg, 0.41 mmol) in 83% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, 2H, J = 8.8 Hz), 7.88 (d, 2H, J = 8.8 Hz), 7.39-7.35 (m, 3H), 7.25-7.23 (m, 2H), 2.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 137.7, 133.5, 129.7, 129.3, 126.3, 124.3, 75.6, 59.9, one carbon missing due to overlap, overlapped signal at 129.7 ppm. Spectral data are in agreement with literature values.[2]



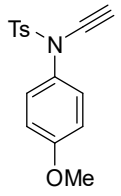
3e

To a round bottom flask was added the corresponding sulfonamide **1e** (85.6 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~6:1 petroleum ether/EtOAc] to afford ynamide **3e** (96.6 mg, 0.50 mmol) in 99% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 2H, J = 8.0 Hz), 7.44 (t, 2H, J = 7.1 Hz), 7.39-7.35 (m, 1H), 3.12 (s, 3H), 2.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 129.7, 128.8, 125.8, 75.9, 59.9, 36.9. Spectral data are in agreement with literature values.[2]



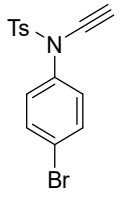
3f

To a round bottom flask was added the corresponding sulfonamide **1f** (130.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3f** (128.8 mg, 0.45 mmol) in 90% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.14-7.09 (m, 4H), 2.81 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.8, 135.8, 133.1, 129.9, 129.7, 128.4, 126.4, 76.9, 58.7, 21.9, 21.3. Spectral data are in agreement with literature values.[2]



3g

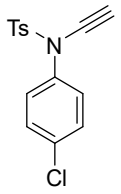
To a round bottom flask was added the corresponding sulfonamide **1g** (138.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 8:1~4:1 petroleum ether/EtOAc] to afford ynamide **3g** (148.7 mg, 0.49 mmol) in 99% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.12 (d, 2H, J = 9.0 Hz), 6.82 (d, 2H, J = 9.0 Hz), 3.80 (s, 3H), 2.80 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 145.2, 133.0, 131.0, 129.7, 128.5, 128.1, 114.4, 77.1, 58.4, 55.7, 21.9. Spectral data are in agreement with literature values.[3]



3h

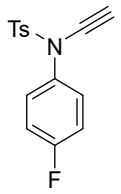
To a round bottom flask was added the corresponding sulfonamide **1h** (163.1 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash

silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3h** (139.0 mg, 0.40 mmol) in 79% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.3 Hz), 7.45 (d, 2H, J = 8.6 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.14 (d, 2H, J = 8.6 Hz), 2.85 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 137.5, 132.7, 132.5, 129.8, 128.4, 127.9, 122.5, 76.2, 59.6, 21.9. Spectral data are in agreement with literature values.[2]



3i

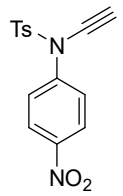
To a round bottom flask was added the corresponding sulfonamide **1i** (140.9 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^{o}C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3i** (121.9 mg, 0.40 mmol) in 80% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.3 Hz), 7.30 (d, 4H, J = 8.9), 7.20 (d, 2H, J = 8.8 Hz), 2.85 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.0, 134.4, 132.7, 129.8, 129.5, 128.4, 127.6, 76.2, 59.6, 21.9. Spectral data are in agreement with literature values.[3]



3j

To a round bottom flask was added the corresponding sulfonamide **1j** (132.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^{o}C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3j** (126.8 mg, 0.44 mmol) in 88% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.24-7.19 (m, 2H), 7.04-6.99 (m, 2H), 2.84 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (C-F, $^{1}J_{C\text{-}F}$ = 247.4 Hz), 145.5, 134.3 (C-F, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 132.7, 129.8, 128.5 (C-F, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 128.4, 116.3 (C-F, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 76.6, 59.2,

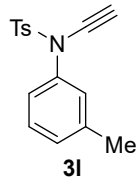
21.9. Spectral data are in agreement with literature values.[4]



3k

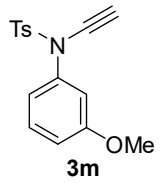
To a round bottom flask was added the corresponding sulfonamide **1k** (146.2 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 8:1~3:1 petroleum ether/EtOAc] to afford ynamide **3k** (108.0 mg, 0.34 mmol) in 68% yield.

3k: R_f = 0.4 [5:1 petroleum ether/EtOAc]; white solid; mp = 120–121 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 2H, J = 9.1 Hz), 7.61 (d, 2H, J =8.4 Hz), 7.55 (d, 2H, J = 9.2 Hz), 7.31 (d, 2H, J = 8.2 Hz), 3.02 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 146.1, 143.9, 132.7, 130.1, 128.3, 125.5, 124.7, 74.9, 61.7, 21.9; IR (neat) (cm^{-1}) 3272m, 2124w, 1591m, 1518s, 1340s, 1166s, 682s; HRMS (ESI): m/z calcd for $C_{15}H_{13}N_2O_4S$ $[M + H]^+$ 317.0591, found 317.0594.



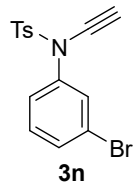
3l

To a round bottom flask was added the corresponding sulfonamide **1l** (130.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3l** (132.7 mg, 0.47 mmol) in 93% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.20 (t, 1H, J = 7.8 Hz), 7.14-7.08 (m, 2H), 7.01 (d, 1H, J = 7.8 Hz), 2.82 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.4, 138.3, 133.2, 129.7, 129.4, 129.0, 128.5, 127.2, 123.4, 76.8, 58.9, 21.9, 21.4. Spectral data are in agreement with literature values.[3]



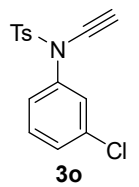
3m

To a round bottom flask was added the corresponding sulfonamide **1m** (138.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3m** (136.8 mg, 0.45 mmol) in 91% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.21 (t, 1H, J = 8.4 Hz), 6.87-6.81 (m, 3H), 3.76 (s, 3H), 2.84 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 145.3, 139.4, 133.1, 129.9, 129.7, 128.4, 118.4, 114.5, 112.0, 76.9, 59.3, 55.6, 21.9. Spectral data are in agreement with literature values.[5]



3n

To a round bottom flask was added the corresponding sulfonamide **1n** (163.1 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 ^oC and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3n** (126.2 mg, 0.36 mmol) in 72% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 2H, J = 8.4 Hz), 7.46-7.43 (m, 1H), 7.42 (t, 1H, J = 2.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.25-7.24 (m, 1H), 7.23-7.19 (m, 1H), 2.89 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.6, 132.8, 131.6, 130.5, 129.9, 129.1, 128.4, 124.9, 122.5, 76.0, 60.0, 21.9. Spectral data are in agreement with literature values.[2]

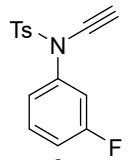


3o

To a round bottom flask was added the corresponding sulfonamide **1o** (140.9 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature.

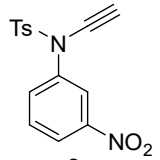
The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3o** (109.9 mg, 0.36 mmol) in 72% yield.

3o: R_f = 0.5 [5:1 petroleum ether/EtOAc]; white solid; mp = 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.4 Hz), 7.32-7.27 (m, 5H), 7.22-7.19 (m, 1H), 2.88 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.5, 134.8, 132.8, 130.2, 129.9, 128.7, 128.4, 126.3, 124.4, 76.0, 60.0, 21.9; IR (neat) (cm^{-1}) 3290w, 2131w, 1587m, 1371s, 1166s, 1085m, 670s; HRMS (ESI): m/z calcd for $C_{15}H_{13}ClNO_2S$ $[M + H]^+$ 306.0350, found 306.0346.



3p

To a round bottom flask was added the corresponding sulfonamide **1p** (132.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3p** (116.8 mg, 0.40 mmol) in 81% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.3 Hz), 7.30 (d, 3H, J = 8.3 Hz), 7.12-7.10 (m, 1H), 7.05-7.00 (m, 2H), 2.89 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (C-F, $^1J_{C\text{-}F}$ = 246.7 Hz), 145.6, 139.8 (C-F, $^3J_{C\text{-}F}$ = 9.8 Hz), 132.8, 130.3 (C-F, $^3J_{C\text{-}F}$ = 8.9 Hz), 129.9, 128.4, 121.7 (C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 115.5 (C-F, $^2J_{C\text{-}F}$ = 20.8 Hz), 113.5 (C-F, $^2J_{C\text{-}F}$ = 24.4 Hz), 76.0, 60.0, 21.9. Spectral data are in agreement with literature values.[5]

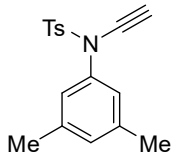


3q

To a round bottom flask was added the corresponding sulfonamide **1q** (146.2 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by

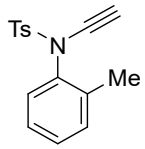
TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3q** (96.8 mg, 0.31 mmol) in 61% yield.

3q: R_f = 0.35 [5:1 petroleum ether/EtOAc]; white solid; mp = 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (ddd, 1H, J = 8.2 Hz, 2.2 Hz, 1.0 Hz), 8.11 (t, 1H, J = 2.2 Hz), 7.76 (ddd, 1H, J = 8.1, 2.2, 1.0 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.56 (t, 1H, J = 8.2 Hz), 7.32 (d, 2H, J = 8.0 Hz), 2.96 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.1, 139.8, 132.5, 132.0, 130.2, 130.1, 128.4, 123.0, 120.6, 75.3, 61.0, 22.0; IR (neat) (cm^{-1}) 3296w, 2129w, 1527s, 1348s, 1165s, 1077m, 666s; HRMS (ESI): m/z calcd for $C_{15}H_{13}N_2O_4S$ $[M + H]^+$ 317.0591, found 317.0593.



3r

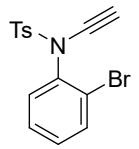
To a round bottom flask was added the corresponding sulfonamide **1r** (137.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3r** (128.9 mg, 0.43 mmol) in 86% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.1 Hz), 6.95 (s, 1H), 6.85 (s, 2H), 2.81 (s, 1H), 2.45 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.1, 138.2, 133.3, 130.4, 129.6, 128.5, 124.2, 77.0, 58.8, 21.9, 21.3. Spectral data are in agreement with literature values.[2]



3s

To a round bottom flask was added the corresponding sulfonamide **1s** (130.7 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3s** (123.6 mg, 0.43 mmol) in 87% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71

(d, 2H, J = 8.4 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.28-7.24 (m, 2H), 7.14-7.10 (m, 1H), 6.88 (d, 1H, J = 7.8 Hz), 2.78 (s, 1H), 2.48 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.0, 137.0, 134.4, 131.8, 129.9, 129.7, 128.5, 128.1, 126.9, 76.9, 58.0, 21.9, 18.1. Spectral data are in agreement with literature values.[4]



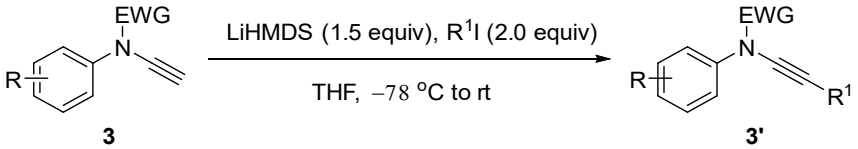
3t

To a round bottom flask was added the corresponding sulfonamide **1t** (163.1 mg, 0.50 mmol), $CsCO_3$ (211.8 mg, 0.65 mmol) and dry DMF (1.0 mL), then stirred for 0.5 h at room temperature. The DCM (2.5 mL) solution of **2** (258.0 mg, 0.75 mmol) was added to the reaction at 0 °C and stirred for another 0.5 h at room temperature in the dark. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3t** (114.2 mg, 0.33 mmol) in 65% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3 Hz), 7.65-7.62 (m, 1H), 7.37-7.34 (m, 2H), 7.32-7.30 (m, 1H), 7.28-7.23 (m, 2H), 2.86 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 136.9, 134.5, 134.4, 131.0, 130.6, 129.9, 128.7, 128.5, 123.9, 75.6, 59.3, 22.0. Spectral data are in agreement with literature values.[2]

1.2 Synthesis of Internal *N*-Aryl Ynamides 3'.

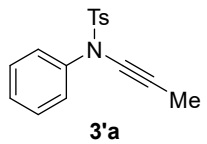
Ynamides **3'a**[6,7], **3'b**[6,8], **3'c**[9], **3'd**[10] and **3'i**[6,7] were known compounds and synthesized according to corresponding literatures, the data were matched with reported literature values. Ynamides **3'e-3'h** and **3'j-3'q** were new compounds and synthesized according to literatures.[6,9]

Synthesis of Ynamides 3'a, 3'b, 3'e-3'o and 3'q.[6-8]



3 **3'**

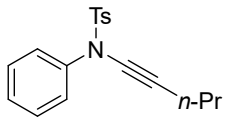
Scheme S2. Synthesis of internal *N*-aryl ynamides **3'**



3'a

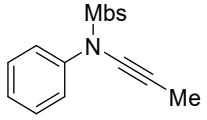
To a solution of **3a** (543.0 mg, 2.00 mmol) in dry THF (10.0 mL) was added LiHMDS (3.0 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (568.0 μL, 4.00 mmol) was added at –60 °C and the

temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 30:1~25:1 petroleum ether/EtOAc] to afford ynamide **3'a** (556.0 mg, 1.95 mmol) in 97% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H, J = 8.3 Hz), 7.32-7.22 (m, 7H), 2.43 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.4, 133.2, 129.6, 129.1, 128.3, 128.1, 126.4, 72.9, 65.9, 21.9, 3.5. Spectral data are in agreement with literature values.[7]



3'b

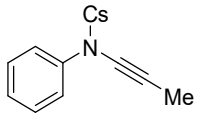
To a solution of **3a** (406.9 mg, 1.5 mmol) in dry THF (10.0 mL) was added LiHMDS (2.3 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then 1-iodopropane (291.0 μL, 3.00 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [eluent: 30:1 petroleum ether/EtOAc] to afford ynamide **3'b** (146.3 mg, 0.47 mmol) in 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H, J = 8.3 Hz), 7.33-7.24 (m, 7H), 2.43 (s, 3H), 2.27 (t, 2H, J = 7.0 Hz), 1.58-1.49 (m, 2H), 0.96 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.5, 133.1, 129.5, 129.1, 128.4, 128.0, 126.2, 74.1, 70.4, 22.5, 21.8, 20.6, 13.6. Spectral data are in agreement with literature values.[8]



3'e

To a solution of **3b** (534.0 mg, 1.86 mmol) in dry THF (10.0 mL) was added LiHMDS (2.8 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (231.0 μL, 3.7 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash

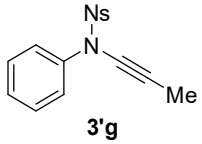
silica gel column chromatography [gradient eluent: 10:1~5:1 petroleum ether/EtOAc] to afford ynamide **3'e** (537.3 mg, 1.78 mmol) in 96% yield.**3'e**: R_f = 0.21 [10:1 petroleum ether/EtOAc]; white solid; mp = 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 9.0 Hz), 7.33-7.24 (m, 5H), 6.93 (d, 2H, J = 9.0 Hz), 3.87 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 139.4, 130.5, 129.1, 128.1, 127.7, 126.4, 114.1, 73.0, 65.8, 55.8, 3.5; IR (neat) (cm^{-1}) 1594s, 1524s, 1313w, 1183s, 1158s, 1092m; HRMS (ESI): m/z calcd for $C_{16}H_{16}NO_3S$ $[M + H]^+$ 302.0845, found 302.0850.



3'f

To a solution of **3c** (752.0 mg, 2.58 mmol) in dry THF (10.0 mL) was added LiHMDS (3.87 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (321.0 μL, 5.16 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [eluent: 20:1:1 petroleum ether/EtOAc/DCM] to afford ynamide **3'f** (782.0 mg, 2.56 mmol) in 99% yield.

3'f: R_f = 0.5 [10:1 petroleum ether/EtOAc]; white solid; mp = 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.7 Hz), 7.46 (d, 2H, J = 8.7 Hz), 7.36-7.30 (m, 3H), 7.25-7.23 (m, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 139.1, 134.4, 129.7, 129.30, 129.27, 128.4, 126.4, 72.5, 66.3, 3.5; IR (neat) (cm^{-1}) 1583w, 1488m, 1365s, 1279m, 1181s, 1089m; HRMS (ESI): m/z calcd for $C_{15}H_{12}ClNNaO_2S$ $[M + Na]^+$ 328.0169, found 328.0172.

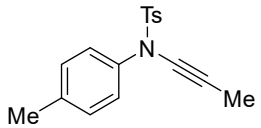


3'g

To a solution of **3d** (763.0 mg, 2.53 mmol) in dry THF (10.0 mL) was added LiHMDS (3.80 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (314.0 μL, 5.05 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford

ynamide **3'g** (600.0 mg, 1.90 mmol) in 75% yield.

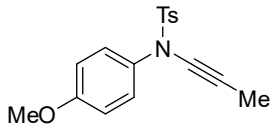
3'g: R_f = 0.34 [10:1 petroleum ether/EtOAc]; white solid; mp = 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, 2H, J = 8.9 Hz), 7.85 (d, 2H, J = 8.9 Hz), 7.38-7.33 (m, 3H), 7.25-7.21 (m, 2H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 141.3, 138.6, 129.52, 129.45, 128.8, 126.2, 124.2, 72.0, 66.8, 3.5; IR (neat) (cm^{-1}) 2263w, 1525s, 1374s, 1307m, 1183s, 1088w; HRMS (ESI): m/z calcd for $C_{15}H_{12}N_2NaO_4S$ $[M + Na]^+$ 339.0410, found 339.0411.



3'h

To a solution of **3f** (956.0 mg, 3.35 mmol) in dry THF (20.0 mL) was added LiHMDS (5.02 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (417.3 μL, 6.70 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'h** (802.4 mg, 2.68 mmol) in 80% yield.

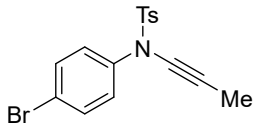
3'h: R_f = 0.39 [10:1 petroleum ether/EtOAc]; white solid; mp = 63–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, J = 8.3 Hz), 7.27 (d, 2H, J = 7.2 Hz), 7.12-7.08 (m, 4H), 2.43 (s, 3H), 2.33 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 138.3, 136.8, 133.3, 129.7, 129.5, 128.3, 126.3, 73.1, 65.4, 21.8, 21.2, 3.5; IR (neat) (cm^{-1}) 1595w, 1507m, 1367s, 1291w, 1172s, 1088m; HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_2S$ $[M + H]^+$ 300.1053, found 300.1053.



3'i

To a solution of **3g** (972.5 mg, 3.23 mmol) in dry THF (20.0 mL) was added LiHMDS (4.85 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (402.3 μL, 6.46 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash

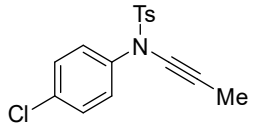
silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'i** (883.1 mg, 2.80 mmol) in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, J = 8.2 Hz), 7.28 (d, 2H, J = 9.3 Hz), 7.11 (d, 2H, J = 9.0 Hz), 6.81 (d, 2H, J = 8.9 Hz), 3.79 (s, 3H), 2.44 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 144.7, 133.2, 132.1, 129.5, 128.4, 128.1, 114.3, 73.3, 65.2, 55.6, 21.9, 3.5. Spectral data are in agreement with literature values.[7]



3'j

To a solution of **3h** (632.1 mg, 1.80 mmol) in dry THF (10.0 mL) was added LiHMDS (2.70 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (224.2 μL, 3.60 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'j** (557.3 mg, 1.53 mmol) in 85% yield.

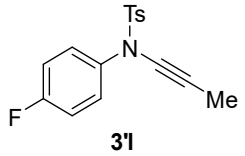
3'j: R_f = 0.41 [10:1 petroleum ether/EtOAc]; white solid; mp = 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H, J = 8.3 Hz), 7.42 (d, 2H, J = 8.8 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.8 Hz), 2.44 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 138.6, 132.9, 132.2, 129.7, 128.3, 127.8, 121.9, 72.4, 66.5, 21.9, 3.5; IR (neat) (cm^{-1}) 2259w, 1594m, 1484s, 1371s, 1164s, 1014m; HRMS (ESI): m/z calcd for $C_{16}H_{14}BrNNaO_2S$ $[M + Na]^+$ 385.9821, found 385.9822.



3'k

To a solution of **3i** (867.0 mg, 2.84 mmol) in dry THF (15.0 mL) was added LiHMDS (4.26 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (353.8 μL, 5.68 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'k** (817.0 mg, 2.55 mmol) in 90% yield.

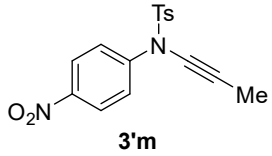
3'k: R_f = 0.41 [10:1 petroleum ether/EtOAc]; white solid; mp = 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 7.9 Hz), 7.29-7.18 (m, 6H), 2.44 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 138.0, 133.9, 132.9, 129.7, 129.3, 128.3, 127.5, 72.5, 66.5, 21.9, 3.5; IR (neat) (cm^{-1}) 2922w, 22259w, 1594m, 1488m, 1371m, 1089s; HRMS (ESI): m/z calcd for $C_{16}H_{14}ClNNaO_2S$ [M + Na]$^+$ 342.0326, found 342.0328.



3'l

To a solution of **3j** (808.3 mg, 2.79 mmol) in dry THF (15.0 mL) was added LiHMDS (4.19 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (347.5 μL, 5.58 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'l** (688.3 mg, 2.27 mmol) in 81% yield.

3'l: R_f = 0.38 [10:1 petroleum ether/EtOAc]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 7.9 Hz), 7.28 (d, 2H, J = 8.3 Hz), 7.22-7.19 (m, 2H), 6.99 (t, 2H, J = 8.4 Hz), 2.45 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (C-F, $^1J_{C\text{-}F}$ = 246.7 Hz), 145.0, 135.4 (C-F, $^4J_{C\text{-}F}$ = 3.1 Hz), 132.8, 129.6, 128.36 (C-F, $^3J_{C\text{-}F}$ = 8.7 Hz), 128.34, 116.0 (C-F, $^2J_{C\text{-}F}$ = 22.8 Hz), 72.8, 66.0, 21.9, 3.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1; IR (neat) (cm^{-1}) 2259w, 1595m, 1501s, 1369s, 1225m, 1166s; HRMS (ESI): m/z calcd for $C_{16}H_{14}FNNaO_2S$ [M + Na]$^+$ 326.0621, found 326.0621.

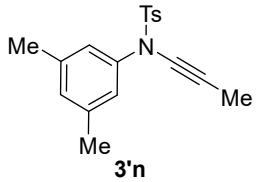


3'm

To a solution of **3k** (854.1 mg, 2.70 mmol) in dry THF (10.0 mL) was added LiHMDS (4.05 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (336.3 μL, 5.40 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash

silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford **3'm** (650.8 mg, 1.97 mmol) in 73% yield.

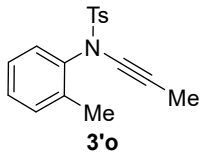
3'm : R_f = 0.25 [10:1 petroleum ether/EtOAc]; white solid; mp = 108–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, 2H, J = 9.2 Hz), 7.59 (d, 2H, J = 8.3 Hz), 7.54 (d, 2H, J = 9.2 Hz), 7.30 (d, 2H, J = 8.0 Hz), 2.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 145.7, 145.0, 132.9, 129.9, 128.1, 125.1, 124.6, 71.3, 68.9, 21.9, 3.6; IR (neat) (cm^{-1}) 2256w, 1591m, 1523s, 1488m, 1178s, 1085w; HRMS (ESI): m/z calcd for $C_{16}H_{14}N_2NaO_4S$ $[M+Na]^+$ 353.0566, found 353.0567.



3'n

To a solution of **3r** (449.1 mg, 1.50 mmol) in dry THF (10.0 mL) was added LiHMDS (2.25 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (186.8 μL, 3.00 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'n** (395.0 mg, 1.26 mmol) in 84% yield.

3'n: R_f = 0.44 [10:1 petroleum ether/EtOAc]; white solid; mp = 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.1 Hz), 6.91 (s, 1H), 6.84 (s, 2H), 2.44 (s, 3H), 2.26 (s, 6H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.1, 138.9, 133.5, 130.0, 129.5, 128.4, 124.1, 73.1, 65.5, 21.9, 21.3, 3.6; IR (neat) (cm^{-1}) 2918w, 2257w, 1953m, 1364s, 1166s, 1089m; HRMS (ESI): m/z calcd for $C_{18}H_{19}NNaO_2S$ $[M + Na]^+$ 336.1029, found 336.1029.

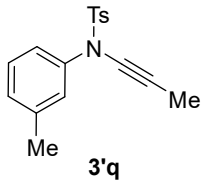


3'o

To a solution of **3s** (856.3 mg, 3.00 mmol) in dry THF (15.0 mL) was added LiHMDS (4.50 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (373.7 μL, 6.00 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with

anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'o** (727.5 mg, 2.43 mmol) in 81% yield.

3'o: R_f = 0.44 [10:1 petroleum ether/EtOAc]; white solid; mp = 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 8.3 Hz), 7.33 (d, 2H, J = 8.2 Hz), 7.24 (d, 2H, J = 4.2 Hz), 7.12-7.08 (m, 1H), 6.85 (d, 1H, J = 7.8 Hz), 2.47 (s, 3H), 2.31 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 138.0, 134.6, 131.6, 129.7, 129.3, 128.5, 128.1, 126.7, 73.2, 64.6, 21.9, 18.2, 3.5, one carbon missing due to overlap, overlapped signal at 128.5 ppm; IR (neat) (cm^{-1}) 2921w, 2256w, 1595w, 1361s, 1168s, 1110m; HRMS (ESI): m/z calcd for $C_{17}H_{17}NNaO_2S$ [M + Na]$^+$ 322.0872, found 322.0873.

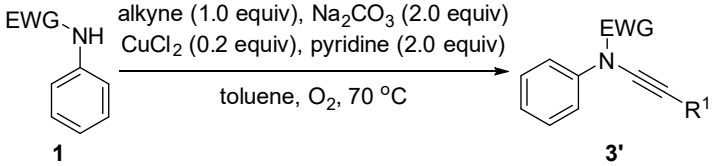


3'q

To a solution of **3l** (673.2 mg, 2.36 mmol) in dry THF (10.0 mL) was added LiHMDS (3.54 mL of a 1.0 *M* solution in THF) at –78 °C. The reaction mixture was gradually taken to –60 °C and kept at this temperature for 1.0 h, then iodomethane (294.0 μL, 4.72 mmol) was added at –60 °C and the temperature was slowly raised to room temperature and stirred 12.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was added water, separated the layers and extracted the aqueous layer with ethyl acetate (3 × 10.0 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified by flash silica gel column chromatography [gradient eluent: 5:1~2:1 petroleum ether/DCM] to afford ynamide **3'q** (599.7 mg, 2.00 mmol) in 85% yield.

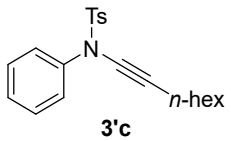
3'q: R_f = 0.47 [10:1 petroleum ether/EtOAc]; white solid; mp = 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H, J = 8.3 Hz), 7.28 (d, 2H, J = 7.6 Hz), 7.18 (t, 1H, J = 7.7 Hz), 7.09 (d, 2H, J = 8.7 Hz), 7.00 (d, 1H, J = 8.1 Hz), 2.44 (s, 3H), 2.31 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.3, 139.2, 133.4, 129.5, 129.0, 128.9, 128.4, 127.1, 123.3, 73.0, 65.7, 21.9, 21.5, 3.6; IR (neat) (cm^{-1}) 2131m, 1067m, 1594m, 1486m, 1296w, 1087s; HRMS (ESI): m/z calcd for $C_{17}H_{17}NNaO_2S$ [M + Na]$^+$ 322.0872, found 322.0873.

Synthesis of Ynamides 3'c, 3'd and 3'p.[9,10]



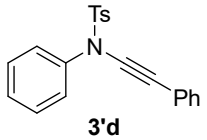
1 **3'**

Scheme S3. Synthesis of internal *N*-aryl ynamides **3'**



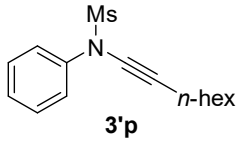
3'c

To a round bottom flask was added the corresponding sulfonamide **1a** (3.7 g, 15.00 mmol), $CuCl_2$ (80.7 mg, 0.60 mmol) and Na_2CO_3 (635.9 mg, 6.00 mmol) and purged with oxygen for three times. Then pyridine (482.8 μL, 6.00 mmol), and toluene (20.0 mL) were added to the reaction flask, and the mixture was heated to 70 ^oC under oxygen atmosphere. 1-octyne (424.0 μL, 3.00 mmol) was added to the reaction flask over 4.0 h using a syringe pump. The reaction mixture was allowed to stir for 8.0 h at 70 ^oC and was then cooled to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatography [gradient eluent: 15:1~10:1 petroleum ether/EtOAc] to afford ynamide **3'c** (913.0 mg, 2.57 mmol) in 86% yield as light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H, J = 8.3 Hz), 7.33-7.23 (m, 7H), 2.43 (s, 3H), 2.29 (t, 2H, J = 7.0 Hz), 1.53-1.46 (m, 2H), 1.39-1.23 (m, 6H), 0.89 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.5, 133.1, 129.5, 129.1, 128.4, 128.0, 126.3, 74.0, 70.6, 31.5, 29.0, 28.7, 22.8, 21.9, 18.6, 14.2. Spectral data are in agreement with literature values.[9]



3'd

To a round bottom flask was added the corresponding sulfonamide **1a** (2.5 g, 10.00 mmol), $CuCl_2$ (53.8 mg, 0.40 mmol) and Na_2CO_3 (424.0 mg, 4.00 mmol) and purged with oxygen for three times. Then pyridine (322.0 μL, 4.00 mmol), and toluene (15.0 mL) were added to the reaction flask, and the mixture was heated to 70 ^oC under oxygen atmosphere. Phenylacetylene (220.0 μL, 2.00 mmol) was added to the reaction flask over 4.0 h using a syringe pump. The reaction mixture was allowed to stir for 8.0 h at 70 ^oC and was then cooled to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatography [gradient eluent: 30:1~20:1 petroleum ether/EtOAc] to afford ynamide **3'd** (326.2 mg, 0.94 mmol) in 47% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 2H, J = 6.8 Hz), 7.40-7.28 (m, 12H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.1, 133.0, 131.6, 129.7, 129.3, 128.4, 128.1, 126.4, 122.8, 83.1, 70.6, 21.9, two carbons missing due to overlap, overlapped signals at 128.4 and 126.4 ppm. Spectral data are in agreement with literature values.[10]



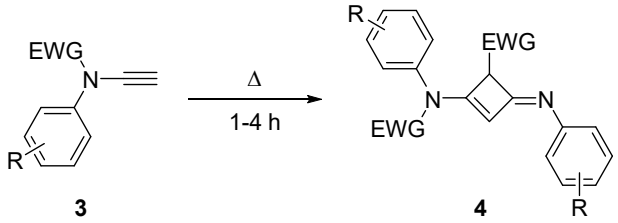
3'p

To a round bottom flask was added the corresponding sulfonamide **1e** (2.5 g, 15.0 mmol), $CuCl_2$

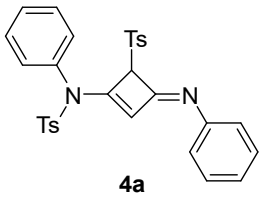
(80.7 mg, 0.6 mmol) and Na_2CO_3 (635.9 mg, 6.0 mmol) and purged with oxygen for three times. Then pyridine (482.8 μL, 6.0 mmol), and toluene (20.0 mL) were added to the reaction flask, and the mixture was heated to 70 °C under oxygen atmosphere. 1-octyne (424.0 μL, 3.0 mmol) was added to the reaction flask over 4.0 h using a syringe pump. The reaction mixture was allowed to stir for 8.0 h at 70 °C and was then cooled to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatography [gradient eluent: 20:1~15:1 petroleum ether/EtOAc] to afford ynamide **3'p** (829.8 mg, 2.97 mmol) in 99% yield.

3'p: R_f = 0.38 [10:1 petroleum ether/EtOAc]; white solid; mp = 40–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H, J = 8.0 Hz), 7.41 (t, 2H, J = 7.3 Hz), 7.35-7.31 (m, 1H), 3.06 (s, 3H), 2.34 (t, 2H, J = 7.1 Hz,), 1.59-1.52 (m, 2H), 1.44-1.37 (m, 2H), 1.34-1.24 (m, 4H), 0.89 (t, 3H, J = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 129.4, 128.1, 125.5, 73.3, 71.3, 36.2, 31.4, 28.9, 28.7, 22.7, 18.7, 14.2; IR (neat) (cm^{-1}) 2256m, 1594w, 1491m, 1351s, 1272w, 1157s; HRMS (ESI): m/z calcd for $C_{15}H_{22}NO_2S$ $[M + H]^+$ 280.1366, found 280.1363.

1.3 Synthesis of Aminocyclobutenes 4.



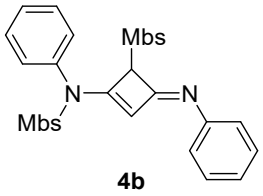
Scheme S4. Synthesis of aminocyclobutenes **4**



To a 50.0 mL conical flask was added ynamide **3a** (81.4 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 °C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 3.5:1 petroleum ether/EtOAc] to afford aminocyclobutene **4a** (70.8 mg, 0.13 mmol) in 87% yield.

4a: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 86–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.3 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.46-7.38 (m, 3H), 7.33-7.24 (m, 6H), 7.18-7.08 (m, 3H), 6.76-6.73 (m, 2H), 5.94 (s, 1H), 4.91 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 152.0, 148.9, 146.0, 145.5, 135.7, 133.1, 132.9, 130.2, 130.1, 130.02, 129.97, 129.5, 129.4, 129.1, 128.4, 124.8, 121.7, 118.6, 76.0, 21.94, 21.89; IR (neat) (cm^{-1}) 1769w, 1695w,

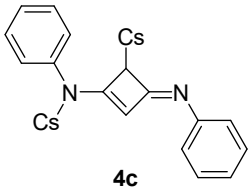
1552s, 1486m, 1320m, 1173s, 694s; HRMS (ESI): m/z calcd for $C_{30}H_{27}N_2O_4S_2$ $[M + H]^+$ 543.1407, found 543.1411.



4b

To a 50.0 mL conical flask was added ynamide **3b** (86.2 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 °C and kept at this temperature for 3.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 3:1~2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4b** (70.7 mg, 0.12 mmol) in 82% yield.

4b: R_f = 0.12 [2:1 petroleum ether/EtOAc]; white solid; mp = 94–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 2H, J = 8.9 Hz), 7.52 (d, 2H, J = 9.0 Hz), 7.46-7.38 (m, 3H), 7.28 (t, 2H, J = 7.7 Hz), 7.17-7.09 (m, 3H), 6.98 (d, 2H, J = 8.9 Hz), 6.89 (d, 2H, J = 9.0 Hz), 6.78 (d, 2H, J = 7.3 Hz), 5.93 (s, 1H), 4.91 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 153.3, 152.2, 148.9, 135.7, 132.2, 130.6, 130.11, 130.07, 129.3, 129.1, 127.3, 124.8, 121.8, 118.2, 114.5, 114.0, 76.1, 55.9, 55.8, one carbon missing due to overlap, overlapped signal at 129.1 ppm; IR (neat) (cm^{-1}) 1697w, 1592m, 1551s, 1260s, 1136s, 1083s, 832s; HRMS (ESI): m/z calcd for $C_{30}H_{27}N_2O_6S_2$ $[M + H]^+$ 575.1305, found 575.1303.

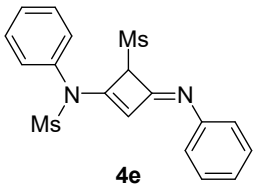


4c

To a 50.0 mL conical flask was added ynamide **3c** (87.5 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 110 °C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 4:1 petroleum ether/EtOAc] to afford aminocyclobutene **4c** (64.8 mg, 0.11 mmol) in 74% yield.

4c: R_f = 0.50 [2:1 petroleum ether/EtOAc]; white solid; mp = 105–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2H, J = 8.7 Hz), 7.60 (d, 2H, J = 8.8 Hz), 7.50 (d, 3H, J = 8.8 Hz), 7.48-7.43 (m, 3H), 7.30 (t, 3H, J = 7.5 Hz), 7.17-7.11 (m, 3H), 6.75 (d, 2H, J = 7.3 Hz), 5.94 (s, 1H), 5.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 151.7, 148.6, 141.7, 141.4, 135.3, 135.0, 134.5, 131.3, 130.5, 130.0, 129.9, 129.78, 129.76, 129.3, 125.2, 121.6, 119.2, 76.1, one carbon missing due to overlap,

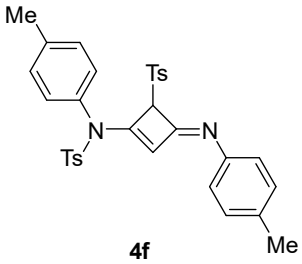
overlapped signal at 129.3 ppm; IR (neat) (cm^{-1}) 2920w, 1645w, 1560s, 1260m, 1083s, 1013s, 756s; HRMS (ESI): m/z calcd for $C_{28}H_{21}Cl_2N_2O_4S_2$ $[M + H]^+$ 583.0314, found 583.0317.



4e

To a 50.0 mL conical flask was added ynamide **3e** (58.6 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 80 °C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 3:1 petroleum ether/EtOAc] to afford aminocyclobutene **4e** (41.6 mg, 0.11 mmol) in 71% yield.

4e: R_f = 0.24 [2:1 petroleum ether/EtOAc]; white solid; mp = 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 5H), 7.30-7.26 (m, 2H), 7.10 (t, 1H, J = 7.4 Hz), 6.96 (d, 2H, J = 7.4 Hz), 5.53 (s, 1H), 5.41 (s, 1H), 3.35 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 152.1, 148.5, 136.1, 130.5, 130.3, 129.5, 129.2, 125.1, 121.7, 117.5, 74.9, 42.9, 40.0; IR (neat) (cm^{-1}) 1699m, 1591w, 1564s, 1483m, 1299s, 1124m, 760s; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O_4S_2$ $[M + H]^+$ 391.0781, found 391.0780.

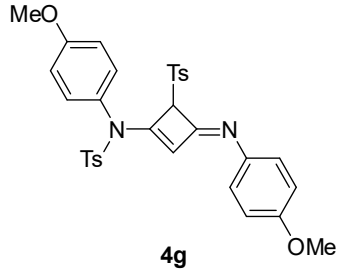


4f

To a 50.0 mL conical flask was added ynamide **3f** (85.6 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 °C and kept at this temperature for 3.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 4:1 petroleum ether/EtOAc] to afford aminocyclobutene **4f** (69.3 mg, 0.12 mmol) in 81% yield.

4f: R_f = 0.37 [2:1 petroleum ether/EtOAc]; white solid; mp = 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.3 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.25 (d, 2H, J = 8.0 Hz), 7.19 (d, 2H, J = 8.3 Hz), 7.08 (d, 2H, J = 8.0 Hz), 7.02 (d, 2H, J = 8.1 Hz), 6.64 (d, 2H, J = 8.2 Hz), 5.93 (s, 1H), 4.87 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.9, 146.4, 145.9, 145.4, 140.4, 134.5, 133.1, 133.0, 132.7, 130.1, 130.0, 129.9, 129.8, 129.7, 129.4, 128.4, 121.7, 118.6, 76.0, 21.94, 21.88, 21.5, 21.1; IR (neat) (cm^{-1})

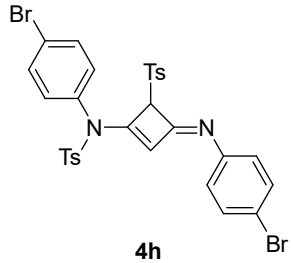
1695w, 1554s, 1450w, 1320m, 1172s, 1137s, 667s; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ [M + H]$^+$ 571.1720, found 571.1716.



4g

To a 50.0 mL conical flask was added ynamide **3g** (90.4 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 110 ^{o}C and kept at this temperature for 3.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4g** (68.7 mg, 0.11 mmol) in 76% yield.

4g: R_f = 0.13 [2:1 petroleum ether/EtOAc]; white solid; mp = 95–97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.2 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.2 Hz), 7.26 (d, 2H, J = 9.6 Hz), 7.05 (s, 2H), 6.87 (d, 2H, J = 9.0 Hz), 6.82 (d, 2H, J = 8.9 Hz), 6.71 (d, 2H, J = 8.9 Hz), 5.96 (s, 1H), 4.86 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.1, 151.99, 151.95, 145.9, 145.4, 142.1, 133.1, 132.8, 131.4, 130.0, 129.9, 129.4, 128.4, 127.9, 123.0, 118.5, 114.4, 114.3, 76.0, 55.63, 55.58, 21.93, 21.87; IR (neat) (cm^{-1}) 1768w, 1555s, 1501s, 1242s, 1170s, 1082m, 668s; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_6S_2$ [M + H]$^+$ 603.1618, found 603.1614.

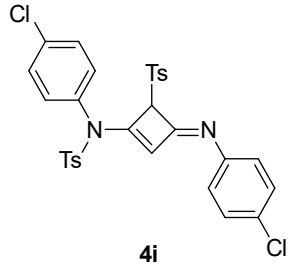


4h

To a 50.0 mL conical flask was added ynamide **3h** (105.1 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 105 ^{o}C and kept at this temperature for 1.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 3.5:1~2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4h** (89.3 mg, 0.13 mmol) in 85% yield.

4h: R_f = 0.50 [2:1 petroleum ether/EtOAc]; white solid; mp = 99–102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.3 Hz), 7.54-7.49 (m, 4H), 7.39 (d, 2H, J = 8.6 Hz), 7.33-7.28 (m, 4H), 7.02 (d, 2H, J = 8.1 Hz), 6.61 (d, 2H, J = 8.6 Hz), 5.92 (s, 1H), 4.87 (s, 1H), 2.46 (s, 3H), 2.44 (s,

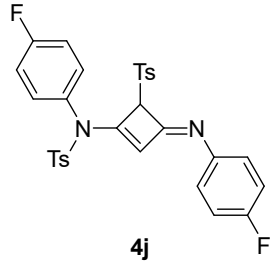
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 151.9, 147.9, 146.4, 145.7, 134.6, 132.9, 132.8, 132.7, 132.2, 131.6, 130.2, 129.9, 129.6, 128.4, 124.7, 123.4, 118.4, 118.1, 75.8, 21.99, 21.95; IR (neat) (cm^{-1}) 1695w, 1551s, 1399w, 1373m, 1284m, 1174s, 662s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Br_2N_2O_4S_2$ $[M + H]^+$ 698.9617, found 698.9615.



4i

To a 50.0 mL conical flask was added ynamide **3i** (91.7 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 ^{o}C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 4:1 petroleum ether/EtOAc] to afford aminocyclobutene **4i** (77.0 mg, 0.13 mmol) in 84% yield.

4i: R_f = 0.46 [2:1 petroleum ether/EtOAc]; white solid; mp = 104–105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.3 Hz), 7.50 (d, 2H, J = 8.3 Hz), 7.37-7.27 (m, 6H), 7.24 (d, 2H, J = 8.6 Hz), 7.12-7.06 (m, 2H), 6.67 (d, 2H, J = 8.6 Hz), 5.93 (s, 1H), 4.88 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 151.9, 147.4, 146.4, 145.7, 136.5, 134.1, 132.9, 132.8, 131.3, 130.3, 130.2, 129.9, 129.7, 129.6, 129.2, 128.4, 123.0, 118.4, 75.8, 22.0, 21.9; IR (neat) (cm^{-1}) 1690w, 1554s, 1374m, 1138s, 1083s, 1016m, 666s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Cl_2N_2O_4S_2$ $[M + H]^+$ 611.0627, found 611.0630.

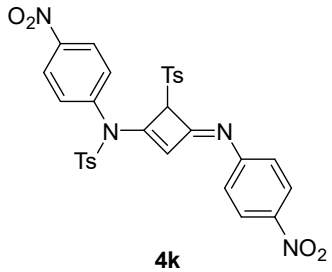


4j

To a 50.0 mL conical flask was added ynamide **3j** (86.8 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 80 ^{o}C and kept at this temperature for 1.5 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 3.5:1 petroleum ether/EtOAc] to afford aminocyclobutene **4j** (75.5 mg, 0.13 mmol) in 87% yield.

4j: R_f = 0.37 [2:1 petroleum ether/EtOAc]; white solid; mp = 90–91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.2 Hz), 7.51 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.28 (d, 2H, J = 8.2 Hz),

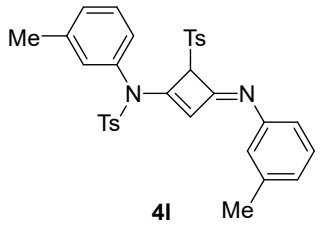
7.15-7.06 (m, 4H), 6.97 (t, 2H, J = 8.6 Hz), 6.73-6.68 (m, 2H), 5.95 (s, 1H), 4.86 (s, 1H), 2.46 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (C-F, $^1J_{C\text{-}F}$ = 250.1 Hz), 160.3 (C-F, $^1J_{C\text{-}F}$ = 242.2 Hz), 153.0, 151.9, 146.3, 145.6, 144.9 (C-F, $^4J_{C\text{-}F}$ = 2.9 Hz), 132.9, 132.8, 132.1 (C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 131.5 (C-F, $^4J_{C\text{-}F}$ = 3.2 Hz), 130.1, 129.9, 129.5, 128.3, 123.0 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 118.2, 116.5 (C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 115.8 (C-F, $^2J_{C\text{-}F}$ = 22.3 Hz), 75.9, 21.91, 21.87; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.2, -118.3; IR (neat) (cm^{-1}) 1695w, 1558s, 1498s, 1219m, 1082m, 1017w, 668s; HRMS (ESI): m/z calcd for $C_{30}H_{25}F_2N_2O_4S_2$ $[M + H]^+$ 579.1218, found 579.1221.



4k

To a 50.0 mL conical flask was added ynamide **3k** (94.9 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 120 °C and kept at this temperature for 1.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 2.5:1 petroleum ether/EtOAc] to afford aminocyclobutene **4k** (49.1 mg, 0.08 mmol) in 52% yield.

4k: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 174–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, 2H, J = 8.6 Hz), 8.17 (d, 2H, J = 8.5 Hz), 7.73 (d, 2H, J = 8.0 Hz), 7.52 (d, 2H, J = 8.0 Hz), 7.39-7.31 (m, 6H), 6.82 (d, 2H, J = 8.8 Hz), 5.99 (s, 1H), 4.93 (s, 1H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 154.6, 152.1, 148.4, 147.1, 146.2, 144.9, 141.0, 132.9, 132.6, 131.0, 130.5, 129.8, 128.3, 125.2, 124.8, 121.9, 118.2, 75.6, 22.0, two carbons missing due to overlap, overlapped signals at 129.8 and 22.0 ppm; IR (neat) (cm^{-1}) 1700w, 1555s, 1339s, 1170m, 1081m, 1016w, 662s; HRMS (ESI): m/z calcd for $C_{30}H_{25}N_4O_8S_2$ $[M + H]^+$ 633.1108, found 633.1110.

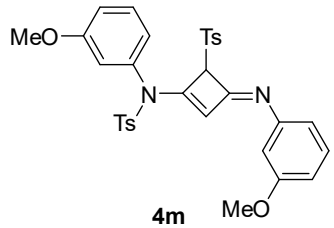


4l

To a 50.0 mL conical flask was added ynamide **3l** (85.6 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 90 °C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 3:1 petroleum ether/EtOAc] to afford

aminocyclobutene **4l** (77.9 mg, 0.14 mmol) in 91% yield.

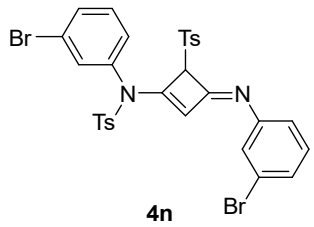
4l: R_f = 0.40 [2:1 petroleum ether/EtOAc]; white solid; mp = 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.3 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 7.9 Hz), 7.27-7.24 (m, 4H), 7.16 (t, 1H, J = 7.9 Hz), 6.98-6.89 (m, 3H), 6.54-6.51 (m, 2H), 5.90 (s, 1H), 4.90 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 151.9, 148.9, 145.9, 145.4, 139.5, 138.9, 135.5, 133.2, 133.0, 130.9, 130.7, 130.1, 129.9, 129.4, 129.0, 128.9, 128.5, 127.0, 125.6, 122.4, 118.7, 118.6, 76.1, 21.93, 21.88, 21.6, 21.5; IR (neat) (cm^{-1}) 1769w, 1595w, 1551s, 1370m, 1172s, 1136s, 670s; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ $[M + H]^+$ 571.1720, found 571.1718.



4m

To a 50.0 mL conical flask was added ynamide **3m** (90.4 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 75 °C and kept at this temperature for 4.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 2.5:1~2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4m** (81.4 mg, 0.14 mmol) in 90% yield.

4m: R_f = 0.19 [2:1 petroleum ether/EtOAc]; white solid; mp = 76–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.3 Hz), 7.53 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.29-7.25 (m, 3H), 7.17 (t, 1H, J = 8.4 Hz), 6.99 (dd, 1H, J = 8.0, 2.1 Hz), 6.74 (s, 1H), 6.68-6.65 (m, 2H), 6.31-6.29 (m, 2H), 5.92 (s, 1H), 4.94 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 160.1, 153.3, 152.0, 150.3, 146.0, 145.4, 136.5, 133.2, 133.1, 130.0, 129.9, 129.81, 129.76, 129.5, 128.5, 122.0, 118.7, 116.0, 113.8, 110.5, 107.6, 76.1, 55.7, 55.4, 21.92, 21.88, one carbon missing due to overlap, overlapped signal at 129.9 ppm; IR (neat) (cm^{-1}) 1700w, 1551s, 1449w, 1370m, 1135s, 1040m, 673s; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_6S_2$ $[M + H]^+$ 603.1618, found 603.1622.

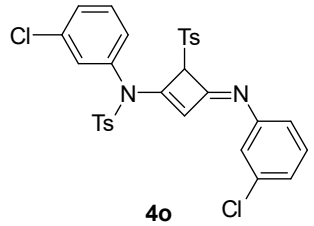


4n

To a 50.0 mL conical flask was added ynamide **3n** (105.1 mg, 0.30 mmol) evenly at the bottom

and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 90 °C and kept at this temperature for 1.5 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 4:1~3:1 petroleum ether/EtOAc] to afford aminocyclobutene **4n** (95.6 mg, 0.14 mmol) in 91% yield.

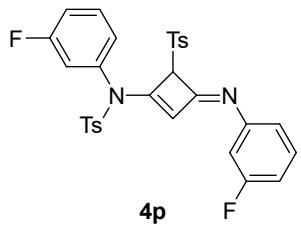
4n: R_f = 0.42 [2:1 petroleum ether/EtOAc]; white solid; mp = 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.3 Hz), 7.60 (d, 1H, J = 8.1 Hz), 7.52 (d, 2H, J = 7.8 Hz), 7.35-7.29 (m, 5H), 7.23 (d, 2H, J = 8.1 Hz), 7.14 (t, 2H, J = 7.8 Hz), 6.72 (t, 1H, J = 1.8 Hz), 6.70 (d, 1H, J = 7.8 Hz), 5.89 (s, 1H), 4.91 (s, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 151.9, 150.3, 146.5, 145.8, 136.7, 133.4, 132.9, 132.8, 132.7, 130.6, 130.5, 130.2, 129.9, 129.6, 128.9, 128.4, 127.7, 124.4, 122.6, 122.5, 120.4, 118.3, 75.8, 22.0, 21.9; IR (neat) (cm^{-1}) 1696w, 1547s, 1373m, 1288s, 1175s, 1019w, 664s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Br_2N_2O_4S_2$ $[M + H]^+$ 698.9617, found 698.9614.



4o

To a 50.0 mL conical flask was added ynamide **3o** (91.7 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 90 °C and kept at this temperature for 3.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 3.5:1 petroleum ether/EtOAc] to afford aminocyclobutene **4o** (83.4 mg, 0.14 mmol) in 91% yield.

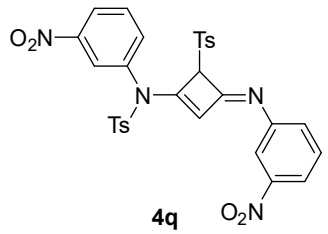
4o: R_f = 0.35 [2:1 petroleum ether/EtOAc]; white solid; mp = 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.3 Hz), 7.52 (d, 2H, J = 8.2 Hz), 7.45 (d, 1H, J = 8.1 Hz), 7.37-7.29 (m, 5H), 7.20 (t, 1H, J = 8.0 Hz), 7.13-7.07 (m, 3H), 6.64 (d, 1H, J = 7.8 Hz), 6.60 (t, 1H, J = 2.0 Hz), 5.91 (s, 1H), 4.91 (s, 1H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 151.9, 150.1, 146.5, 145.8, 136.6, 134.9, 134.6, 132.9, 132.8, 130.5, 130.3, 130.17, 130.16, 130.13, 129.9, 129.6, 128.4, 124.8, 121.6, 120.0, 118.4, 75.9, 21.95, 21.92, one carbon missing due to overlap, overlapped signal at 130.16 ppm; IR (neat) (cm^{-1}) 1696w, 1550s, 1288m, 1175m, 1081m, 1021w, 667s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Cl_2N_2O_4S_2$ $[M + H]^+$ 611.0627, found 611.0628.



4p

To a 50.0 mL conical flask was added ynamide **3p** (86.8 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 85 ^{o}C and kept at this temperature for 1.5 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 4:1~3:1 petroleum ether/EtOAc] to afford aminocyclobutene **4p** (76.4 mg, 0.13 mmol) in 88% yield.

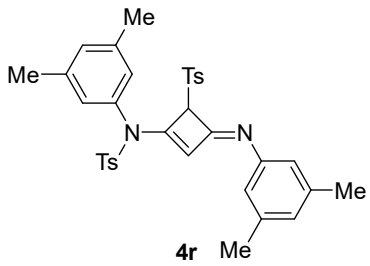
4p: R_f = 0.37 [2:1 petroleum ether/EtOAc]; white solid; mp = 81–82 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H, J = 8.0 Hz), 7.53 (d, 2H, J = 8.0 Hz), 7.41-7.29 (m, 5H), 7.24-7.11 (m, 2H), 6.97-6.92 (m, 2H), 6.82 (td, 1H, J = 8.4, 2.6 Hz), 6.54 (d, 1H, J = 8.0 Hz), 6.41 (dt, 1H, J = 10.0, 2.1 Hz), 5.94 (s, 1H), 4.92 (s, 1H), 2.47 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (C-F, $^{1}J_{C\text{-}F}$ = 244.8 Hz), 162.5 (C-F, $^{1}J_{C\text{-}F}$ = 248.2 Hz), 153.7, 151.9, 150.6 (C-F, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 146.4, 145.8, 136.8 (C-F, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 133.0, 132.9, 130.4 (C-F, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 130.3 (C-F, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 130.1, 129.9, 129.6, 128.3, 125.7 (C-F, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 118.5, 117.6 (C-F, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 117.5 (C-F, $^{2}J_{C\text{-}F}$ = 20.8 Hz), 117.4 (C-F, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 111.6 (C-F, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 108.9 (C-F, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 75.9, 21.9, one carbon missing due to overlap, overlapped signal at 21.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9, -112.4; IR (neat) (cm^{-1}) 1702w, 1552s, 1480m, 1373m, 1173s, 1024w, 670s; HRMS (ESI): m/z calcd for $C_{30}H_{25}F_2N_2O_4S_2$ $[M + H]^+$ 579.1218, found 579.1216.



4q

To a 50.0 mL conical flask was added ynamide **3q** (94.9 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 120 ^{o}C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [gradient eluent: 3:1~2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4q** (67.4 mg, 0.11 mmol) in 71% yield.

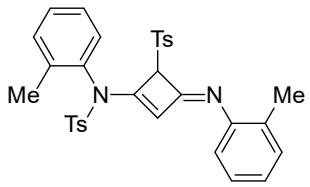
4q: R_f = 0.17 [2:1 petroleum ether/EtOAc]; white solid; mp = 211–213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 7.98 (d, 1H, J = 8.1 Hz), 7.90 (s, 1H), 7.74 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 5.6 Hz), 7.53 (d, 2H, J = 8.2 Hz), 7.47 (t, 1H, J = 8.0 Hz), 7.40-7.33 (m, 5H), 7.13 (d, 1H, J = 8.6 Hz), 5.97 (s, 1H), 4.92 (s, 1H), 2.49 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 152.0, 150.0, 148.9, 148.4, 147.2, 146.4, 136.8, 136.6, 132.52, 132.48, 130.5, 130.5, 130.1, 129.9, 129.8, 128.3, 128.0, 125.2, 124.8, 119.7, 118.0, 116.1, 75.7, 22.01, 21.99; IR (neat) (cm^{-1}) 1706w, 1563s, 1522s, 1347s, 1174m, 1079m, 672s; HRMS (ESI): m/z calcd for $C_{30}H_{25}N_4O_8S_2$ $[M + H]^+$ 633.1108, found 633.1111.



4r

To a 50.0 mL conical flask was added ynamide **3r** (89.8 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 °C and kept at this temperature for 1.5 h. After the reaction was judged to be complete by TLC, purified by flash silica gel column chromatography [eluent: 4:1 petroleum ether/EtOAc] to afford aminocyclobutene **4r** (78.1 mg, 0.13 mmol) in 87% yield.

4r: R_f = 0.50 [2:1 petroleum ether/EtOAc]; white solid; mp = 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.2 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.26 (d, 2H, J = 8.2 Hz), 7.06 (s, 1H), 6.78-6.72 (m, 3H), 6.30 (s, 2H), 5.88 (s, 1H), 4.89 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.29 (s, 6H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 151.9, 148.9, 145.8, 145.2, 139.1, 138.7, 135.3, 133.3, 133.0, 131.8, 130.1, 129.8, 129.4, 128.6, 127.6, 126.4, 119.4, 118.8, 76.1, 21.92, 21.88, 21.5, 21.4; IR (neat) (cm^{-1}) 2920w, 1594w, 1553s, 1318m, 1147s, 1082m, 683s; HRMS (ESI): m/z calcd for $C_{34}H_{35}N_2O_4S_2$ $[M + H]^+$ 599.2033, found 599.2031.

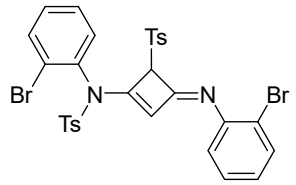


4s (major and minor)

To a 50.0 mL conical flask was added ynamide **3s** (85.6 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 100 °C and kept at this temperature for 2.0 h. After the reaction was judged to be complete by TLC, the atropisomers ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [eluent: 60:20:1 DCM/petroleum ether/EtOAc] to afford an inseparable 1.7:1.0 mixture of aminocyclobutene **4s** (major) (50.7 mg, 0.09 mmol) and **4s** (minor) (29.8 mg, 0.05 mmol) in 94% yield.

4s (major and minor): R_f = 0.31 [3:1 petroleum ether/EtOAc]; white solid; mp = 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 3.4H, J = 8.2 Hz, major), 7.75 (d, 2.0H, J = 8.2 Hz, minor), 7.69 (d, 3.4H, J = 8.3 Hz, major), 7.54 (d, 2.0H, J = 8.2 Hz, minor), 7.43-7.38 (m, 2.0H, minor), 7.35-7.18 (m, 15.9H), 7.15-6.95 (m, 10.8H), 6.52-6.47 (m, 2.7H), 6.39 (d, 1.0H, J = 7.6 Hz, minor), 5.96 (s, 1.0H, minor), 5.64 (s, 1.7H, major), 5.16 (s, 1.7H, major), 4.88 (s, 1.0H, minor), 2.63 (s, 3.0H, minor),

2.43-2.42 (m, 13.2H), 2.39 (s, 3.0H, minor), 2.14 (s, 5.1H, major), 2.10 (s, 3.0H, minor), 1.91 (s, 5.1H, major); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 152.6, 151.9, 151.8, 151.6, 147.8, 147.7, 146.0, 145.8, 145.1, 141.3, 138.1, 135.29, 135.26, 134.4, 134.03, 134.98, 132.9, 132.4, 131.6, 131.5, 131.1, 130.9, 130.6, 130.5, 130.43, 130.36, 129.9, 129.8, 129.7, 129.41, 129.40, 129.1, 128.8, 128.7, 126.9, 126.22, 126.19, 126.16, 124.53, 124.48, 119.9, 119.7, 118.4, 117.9, 76.6, 76.2, 21.9, 21.84, 21.82, 21.79, 19.4, 18.20, 18.14, 17.4; two carbons missing due to overlap; IR (neat) (cm^{-1}) 1697w, 1550s, 1369m, 1320m, 1173m, 1085m; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ $[M + H]^+$ 571.1720, found 571.1723.

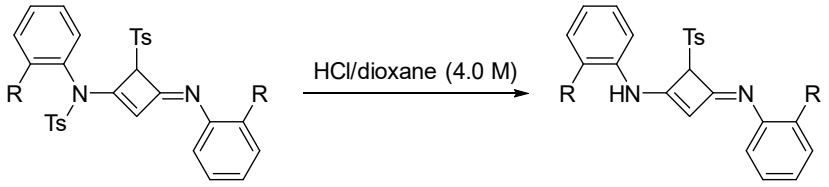


4t (major and minor)

To a 50.0 mL conical flask was added ynamide **3t** (105.1 mg, 0.30 mmol) evenly at the bottom and connected to a balloon filled with nitrogen. Then the reaction system was gradually taken to 90 ^{o}C and kept at this temperature for 1.0 h. After the reaction was judged to be complete by TLC, the atropisomers ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [eluent: 80:20:3 petroleum ether/DCM/Et_3N] to afford an inseparable 8.0:1.0 mixture of aminocyclobutene **4t** (major) (59.9 mg, 0.09 mmol) and **4t** (minor) (7.5 mg, 0.01 mmol) in 64% yield.

4t (major and minor): R_f = 0.22 [3:1 petroleum ether/EtOAc]; white solid; mp = 54–55 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.2 Hz, minor), 7.82 (d, 16H, J = 8.2 Hz, major), 7.72 (dd, 8H, J = 8.0, 1.4 Hz, major), 7.63-7.54 (m, 36H), 7.51-7.47 (m, 8H, major), 7.40-7.35 (m, 13H), 7.33-7.29 (m, 32H), 7.23-7.19 (m, 8H, major), 7.15 (d, 3H, J = 8.0 Hz, minor), 6.98-6.92 (m, 9H), 6.68-6.62 (m, 9H), 6.20 (s, 1H, minor), 5.99 (s, 8H, major), 5.18 (s, 1H, minor), 4.87 (s, 8H, major), 2.47 (s, 27H), 2.43 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) (major) δ 154.5, 151.5, 147.8, 146.4, 145.5, 134.7, 134.2, 133.9, 133.7, 133.6, 133.3, 132.0, 130.28, 130.0, 129.6, 128.5, 128.4, 127.93, 125.8, 124.1, 122.0, 118.2, 116.9, 76.8, 22.01, 21.96; (minor) δ 154.7, 151.8, 147.0, 146.0, 145.4, 130.9, 130.32, 130.1, 129.7, 129.5, 129.1, 128.9, 128.6, 128.3, 127.86, 123.9, 121.8, nine carbons missing due to overlap; IR (neat) (cm^{-1}) 1701m, 1585m, 1556s, 1466m, 1435w, 1376m, 1295s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Br_2N_2O_4S_2$ $[M + H]^+$ 698.9617, found 698.9602.

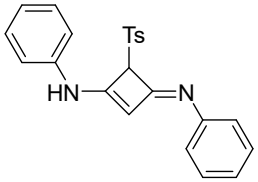
1.4 Chemical Transformation of Cycloadducts 4.



4a: R = H
4s: R = Me
4t: R = Br

4a': 82%
4s': 75%
4t': 85%

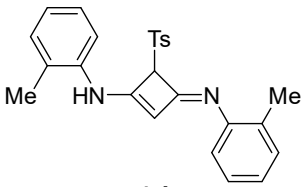
Scheme S5. Chemical transformation of cycloadducts **4**



4a'

To an oven-dried sealed tube was added aminocyclobutene **4a** (108.5 mg, 0.20 mmol) and hydrogen chloride (2.5 mL, 4.0 mol/L in 1,4-dioxane). The reaction vessel was capped and stirred at 30 °C for 12.0 h. After the reaction was judged to be complete by TLC, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 4:1~2:1 petroleum ether/EtOAc] to afford aminocyclobutene **4a'** (63.7 mg, 0.16 mmol) in 82% yield.

4a': R_f = 0.25 [3:1 petroleum ether/EtOAc]; white solid; mp = 166–169 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.81 (d, 2H, J = 8.3 Hz), 7.52-7.48 (m, 4H), 7.45 (d, 2H, J = 8.2 Hz), 7.38 (t, 2H, J = 7.4 Hz), 7.28 (d, 4H, J = 7.8 Hz), 6.07 (s, 1H), 5.84 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) 161.2, 148.8, 137.9, 131.4, 131.2, 130.6, 129.1, 122.2, 106.0, 73.4, 21.7, two carbons missing due to overlap; IR (KBr) (cm^{-1}) 1620.8m, 1561.9s, 1521.3s, 1495.4s, 1251.8, 1083w; HRMS (ESI): m/z calcd for $C_{23}H_{21}N_2O_2S$ $[M + H]^+$ 389.1318, found 389.1304.

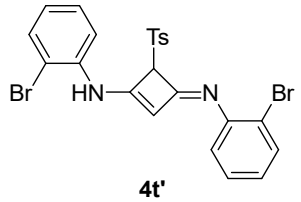


4s'

To an oven-dried sealed tube was added aminocyclobutene **4s** (114.1 mg, 0.20 mmol) and hydrogen chloride (5.0 mL, 4.0 mol/L in 1,4-dioxane). The reaction vessel was capped and stirred at 50 °C for 23.0 h. After the reaction was judged to be complete by TLC, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 4:1~3:1 petroleum ether/EtOAc] to afford aminocyclobutene **4s'** (62.4 mg, 0.15 mmol) in 75% yield.

4s': R_f = 0.30 [3:1 petroleum ether/EtOAc]; white solid; mp = 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, J = 7.0 Hz), 7.32 (d, 2H, J = 7.2 Hz), 7.19 (d, 2H, J = 7.0 Hz), 7.11-7.08 (m, 2H), 7.02-6.98 (m, 2H), 6.77 (s, 2H), 5.40 (s, 1H), 5.12 (s, 1H), 2.43 (s, 3H), 2.32 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 151.9, 145.7, 133.1, 131.0, 129.74, 129.67, 126.7, 124.3, 118.9, 106.3, 74.7, 21.9, 17.9, three carbons missing due to overlap; IR (KBr) (cm^{-1}) 1699w, 1599m, 1560s, 1488m, 1458w, 1153m, 1084m; HRMS (ESI): m/z calcd for $C_{25}H_{25}N_2O_2S$ $[M + H]^+$: 417.1631, found 417.1631.



4t'

To an oven-dried sealed tube was added aminocyclobutene **4t** (105.1 mg, 0.15 mmol) and hydrogen chloride (2.0 mL, 4.0 mol/L in 1,4-dioxane). The reaction vessel was capped and stirred at 30 °C for 11.0 h. After the reaction was judged to be complete by TLC, concentrated in vacuo, and purified by flash silica gel column chromatography [gradient eluent: 60:30:2~60:20:2 DCM/petroleum ether/EtOAc] to afford aminocyclobutene **4t'** (69.8 mg, 0.13 mmol) in 85% yield.

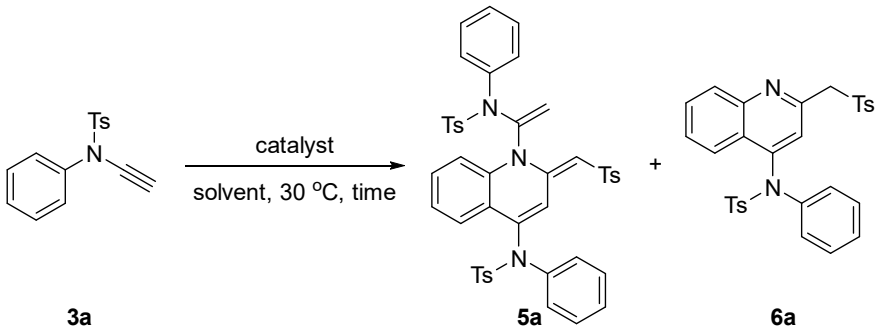
4t': R_f = 0.20 [3:1 petroleum ether/EtOAc]; white solid; mp = 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, 2H, J = 8.0 Hz), 7.60 (d, 2H, J = 7.1 Hz), 7.34 (d, 2H, J = 7.9 Hz), 7.22 (s, 2H), 6.99-6.95 (m, 2H), 6.75 (s, 2H), 5.51 (s, 1H), 5.17 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.8, 133.4, 132.9, 130.0, 129.8, 128.3, 125.5, 117.9, 107.1, 74.7, 22.0, four carbons missing due to overlap; IR (KBr) (cm^{-1}) 2922w, 1593s, 1523s, 1463m, 1439w, 1142m, 1082m; HRMS (ESI): m/z calcd for $C_{23}H_{19}Br_2N_2O_2S$ $[M + H]^+$ 544.9529, found 544.9526.

1.5 Optimization of the [4 + 2] Self-Cycloaddition (Table S1).

Entry 5: To an oven-dried sealed tube was added ynamide **3a** (108.5 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TfOH (17.8 μL, 0.20 mmol) was added 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford a separable mixture of 4-aminoquinoline **5a** (42.3 mg, 0.05 mmol) and **6a** (36.9 mg, 0.07 mmol) in 39% and 34% yield, respectively.

Entry 24: To an oven-dried sealed tube was added ynamide **3a** (271.3 mg, 1.00 mmol), DCM (2.5 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (108.9 μL, 0.60 mmol) and TfOH (17.8 μL, 0.20 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5a** (247.1 mg, 0.30 mmol) in 91% yield.

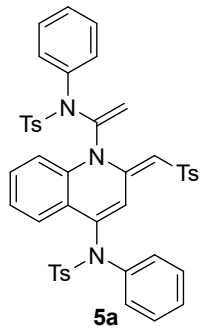
Table S1. Optimization of the [4 + 2] Self-Cycloaddition.



3a **5a** **6a**

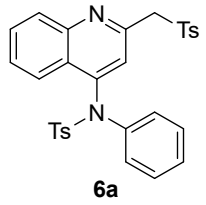
entry[a]	catalyst (equiv)	solvent	time (h)	yield (%)[b]	
				5a	**6a**
1	BF_3•Et_2O (0.5)	DCM	8.5	41	18
2	$FeCl_3$ (0.5)	DCM	6.0	13	6
3	$AlCl_3$ (0.5)	DCM	7.5	70	4
4	$ZnCl_2$ (0.5)	DCM	10.0	0	18
5	TfOH (0.5)	DCM	0.5	39	34
6	Tf_2NH (0.5)	DCM	7.0	69	8
7	TBSOTf (0.5)	DCM	9.0	59	0
8	TMSOTf (0.5)	DCM	2.0	72	0
9	TMSOTf (0.5)	DCE	1.0	63	0
10	TMSOTf (0.5)	toluene	3.3	60	0
11	TMSOTf (0.5)	THF	1.0	0	0
12	TMSOTf (0.5)	EtOAc	3.0	32	0
13	TMSOTf (0.6)	DCM	2.0	74	0
14	TMSOTf (1.0)	DCM	0.2	74	0
15	TfOH (0.3)	DCM	3.0	62	9
16	TfOH (0.2)	DCM	6.0	74	0
17[c]	TfOH (0.2)	DCM	3.0	65	0
18	TMSOTf (0.4)/TfOH (0.2)	DCM	0.5	86	0
19	TMSOTf (0.5)/TfOH (0.2)	DCM	0.5	84	0
20	TMSOTf (0.6)/TfOH (0.2)	DCM	0.5	91	0
21	TMSOTf (0.8)/TfOH (0.2)	DCM	0.5	75	5
22	TMSOTf (0.6)/TfOH (0.15)	DCM	0.5	86	0
23	TMSOTf (0.6)/TfOH (0.4)	DCM	0.5	72	17
24[c]	TMSOTf (0.6)/TfOH (0.2)	DCM	0.5	91	0

[a]Unless otherwise noted, reactions were carried out using **3a** (0.40 mmol) with catalyst in solvent (1.0 mL) at 30 °C. [b]Isolated yields. [c]Reaction carried out at 50 °C. [d]**3a** (1.00 mmol) was added.



5a

5a: R_f = 0.3 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 1H, J = 7.5 Hz), 7.61 (d, 2H, J = 8.3 Hz), 7.53-7.46 (m, 5H), 7.30-7.18 (m, 11H), 7.10-7.02 (m, 4H), 6.82 (s, 2H), 6.71 (s, 2H), 5.86 (d, 1H, J = 2.4 Hz), 5.68 (s, 1H), 5.07 (d, 1H, J = 2.4 Hz), 2.44 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.1, 144.4, 142.7, 142.1, 141.8, 140.2, 139.4, 136.2, 135.4, 135.3, 135.1, 131.1, 130.4, 130.1, 129.9, 129.6, 129.5, 129.3, 128.8, 128.5, 128.1, 127.8, 127.2, 126.3, 125.1, 123.3, 120.7, 118.4, 115.9, 107.8, 97.2, 21.83, 21.80, 21.7; IR (neat) (cm^{-1}) 1732w, 1629m, 1526m, 1356m, 1164s, 1082s, 694s; HRMS (ESI): m/z calcd for $C_{45}H_{40}N_3O_6S_3$ $[M + H]^+$ 814.2074, found 814.2078.



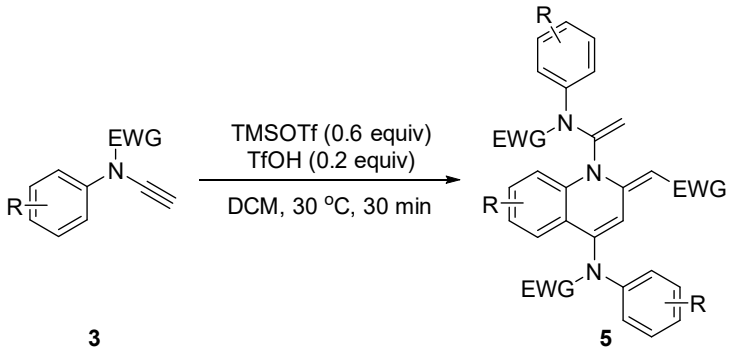
6a

6a: R_f = 0.24 [2:1 petroleum ether/EtOAc]; white solid; mp = 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, 1H, J = 8.4, 1.0 Hz), 7.80 (dd, 1H, J = 8.4, 0.6 Hz), 7.68 (d, 2H, J = 8.3 Hz), 7.65-7.63 (m, 1H), 7.59 (s, 1H), 7.58-7.55 (m, 1H), 7.49 (d, 2H, J = 8.3 Hz), 7.42-7.39 (m, 2H), 7.36-7.23 (m, 5H), 7.15 (d, 2H, J = 8.1 Hz), 4.68 (s, 2H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.8, 146.9, 145.0, 144.6, 140.3, 136.5, 135.0, 130.5, 130.1, 129.8, 129.55, 129.52, 128.6, 128.3, 127.9, 127.6, 126.6, 123.9, 122.4, 65.3, 21.9, 21.7, one carbon missing due to overlap, overlapped signal at 128.3 ppm; IR (neat) (cm^{-1}) 1591m, 1452w, 1360s, 1318s, 1168s, 1152s, 1131m, 1087s; HRMS (ESI): m/z calcd for $C_{32}H_{30}N_2NaO_6S_2$ $[M + Na]^+$ 543.1407, found 543.1411.

1.6 [4 + 2] Self-Cycloaddition of Terminal *N*-Aryl Ynamides.

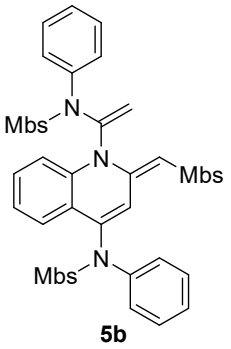
To an oven-dried sealed tube was added ynamide **3a** (108.5 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously at 30 °C. The reaction vessel was capped and stirred at 30 °C for 0.5 h. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel,

concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5a** (98.5 mg, 0.12 mmol) in 91% yield.



3 **5**

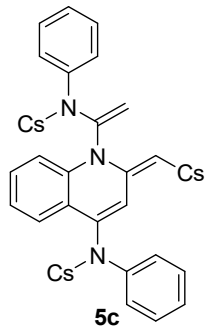
Scheme S6. [4 + 2] Self-cycloaddition of terminal *N*-aryl ynamides



5b

To an oven-dried sealed tube was added ynamide **3b** (114.9 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5b** (112.9 mg, 0.13 mmol) in 98% yield.

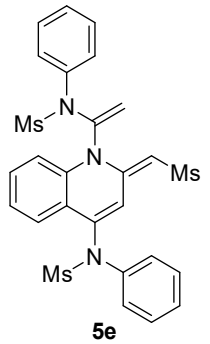
5b: R_f = 0.44 [1:2 petroleum ether/EtOAc]; yellow solid; mp = 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.64 (m, 3H), 7.60-7.54 (m, 4H), 7.49 (s, 1H), 7.29-7.21 (m, 5H), 7.11-7.08 (m, 2H), 7.04-7.00 (m, 2H), 6.92-6.86 (m, 8H), 6.75 (s, 2H), 5.86 (d, 1H, J = 2.4 Hz), 5.69 (s, 1H), 5.07 (d, 1H, J = 2.4 Hz), 3.87 (s, 3H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.5, 162.6, 147.2, 141.7, 140.2, 139.4, 136.8, 135.29, 135.26, 131.0, 130.8, 130.5, 130.4, 130.3, 129.5, 129.4, 129.3, 128.8, 128.4, 127.7, 127.1, 125.0, 123.2, 120.6, 118.3, 115.8, 114.6, 114.4, 114.1, 107.6, 97.6, 55.90, 55.88, 55.8; IR (neat) (cm^{-1}) 1629m, 1593m, 1390w, 1259s, 1157s, 1083s, 1022m, 694s; HRMS (ESI): m/z calcd for $C_{45}H_{40}N_3O_9S_3$ $[M + H]^+$ 862.1921, found 862.1923.



5c

To an oven-dried sealed tube was added ynamide **3c** (116.7 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5c** (102.7 mg, 0.12 mmol) in 88% yield.

5c: R_f = 0.25 [4:1 petroleum ether/EtOAc]; yellow solid; mp = 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 7.4 Hz), 7.63-7.56 (m, 6H), 7.49-7.45 (m, 3H), 7.41-7.39 (m, 4H), 7.32-7.26 (m, 5H), 7.13-7.04 (m, 4H), 6.93 (s, 2H), 6.75 (d, 2H, J = 7.8 Hz), 5.83 (d, 1H, J = 2.6 Hz), 5.70 (s, 1H), 5.15 (d, 1H, J = 2.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.3, 142.1, 140.7, 140.1, 138.9, 138.6, 137.3, 136.5, 135.1, 134.9, 131.4, 130.4, 129.89, 129.86, 129.82, 129.6, 129.5, 129.3, 129.2, 128.4, 127.7, 127.3, 125.1, 123.6, 120.4, 117.8, 115.9, 109.2, 96.3, two carbons missing due to overlap, overlapped signals at 129.6 and 129.3 ppm; IR (neat) (cm^{-1}) 1629m, 1524m, 1314w, 1167s, 1082s, 1011m, 750s; HRMS (ESI): m/z calcd for $C_{42}H_{31}Cl_3N_3O_6S_3$ $[M + H]^+$ 874.0435, found 874.0437.

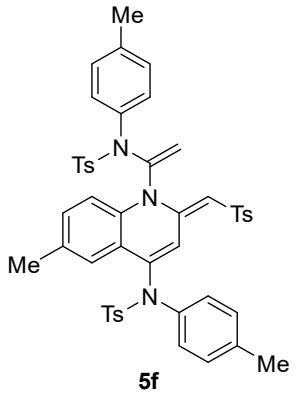


5e

To an oven-dried sealed tube was added ynamide **3e** (78.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient

eluent: 1:1~1:2 petroleum ether/EtOAc] to afford 4-aminoquinoline **5e** (65.3 mg, 0.11 mmol) in 84% yield.

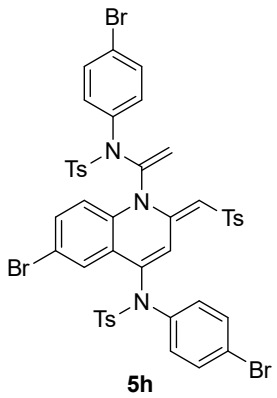
5e: R_f = 0.2 [1:2 petroleum ether/EtOAc]; yellow solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.57 (dd, 1H, J = 7.9, 1.1 Hz), 7.44-7.36 (m, 5H), 7.34-7.24 (m, 3H), 7.18 (t, 2H, J = 7.7 Hz), 7.11 (d, 2H, J = 7.7 Hz), 7.02 (t, 1H, J = 7.3 Hz), 5.90 (d, 1H, J = 2.4 Hz), 5.68 (s, 1H), 5.33 (d, 1H, J = 2.4 Hz), 3.149 (s, 3H), 3.147 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.4, 140.1, 139.2, 135.0, 134.5, 131.4, 130.2, 130.1, 129.8, 129.6, 127.8, 125.6, 125.0, 123.5, 119.9, 117.6, 115.8, 111.6, 96.0, 45.9, 40.0, 39.9; IR (neat) (cm^{-1}) 1634m, 1591w, 1530m, 1347s, 1156s, 1113s, 962s; HRMS (ESI): m/z calcd for $C_{27}H_{28}N_3O_6S_3$ $[M + H]^+$ 586.1135, found 586.1139.



5f

To an oven-dried sealed tube was added ynamide **3f** (114.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5f** (107.3 mg, 0.13 mmol) in 94% yield.

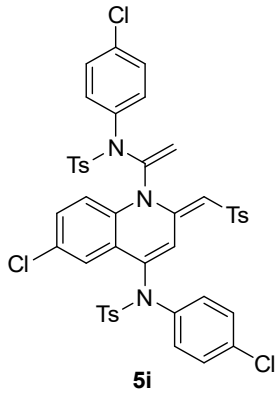
5f: R_f = 0.23 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.2 Hz), 7.51-7.49 (m, 3H), 7.41 (d, 2H, J = 8.2 Hz), 7.31-7.25 (m, 6H), 7.21-7.16 (m, 3H), 7.07 (dd, 1H, J = 8.6, 2.0 Hz), 7.02-6.95 (m, 4H), 6.57 (s, 3H), 5.79 (d, 1H, J = 2.4 Hz), 5.59 (s, 1H), 5.02 (d, 1H, J = 1.4 Hz), 2.44 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.9, 144.1, 142.4, 142.2, 142.0, 138.1, 137.8, 136.7, 136.3, 135.6, 132.9, 132.4, 132.2, 130.0, 129.8, 129.45, 129.42, 128.4, 128.0, 127.4, 126.3, 124.9, 120.6, 118.0, 116.0, 107.1, 95.8, 21.79, 21.76, 21.7, 21.3, 21.2, 21.0, four carbons missing due to overlap, overlapped signals at 130.0, 129.8, 129.45 and 126.3 ppm; IR (neat) (cm^{-1}) 1629m, 1525m, 1429w, 1355m, 1163s, 1082s, 654s; HRMS (ESI): m/z calcd for $C_{48}H_{46}N_3O_6S_3$ $[M + H]^+$ 856.2543, found 856.2548.



5h

To an oven-dried sealed tube was added ynamide **3h** (140.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously at 30 ^{o}C. The reaction vessel was capped and stirred at 30 ^{o}C for 0.5 h. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5h** (114.4 mg, 0.11 mmol) in 82% yield.

5h: R_f = 0.38 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 102–103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.57 (d, 2H, J = 8.2 Hz), 7.52 (s, 2H), 7.44-7.30 (m, 11H), 7.24 (d, 2H, J = 8.1 Hz), 7.16 (d, 1H, J = 8.8 Hz), 6.96 (s, 3H), 6.50 (s, 2H), 5.86 (s, 1H), 5.67 (s, 1H), 5.12 (s, 1H), 2.473 (s, 3H), 2.467 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.6, 144.9, 143.3, 141.4, 140.2, 138.9, 138.1, 135.6, 135.1, 134.6, 134.3, 134.1, 132.8, 132.2, 131.8, 130.4, 130.2, 129.9, 128.5, 128.4, 128.1, 127.4, 126.3, 123.9, 122.1, 119.5, 117.8, 116.8, 98.7, 21.89, 21.86, 21.80, two carbons missing due to overlap, overlapped signals at 130.2 and 129.9 ppm; IR (neat) (cm^{-1}) 2924w, 1630m, 1527m, 1358m, 1165s, 1081s, 660s; HRMS (ESI): m/z calcd for $C_{45}H_{37}Br_3N_3O_6S_3$ $[M + H]^+$ 1047.9389, found 1047.9398.

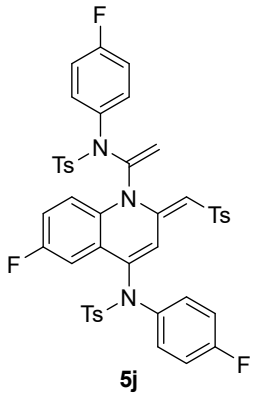


5i

To an oven-dried sealed tube was added ynamide **3i** (122.3 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol)

were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5i** (96.6 mg, 0.11 mmol) in 79% yield.

5i: R_f = 0.37 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.56 (m, 3H), 7.51 (s, 2H), 7.43-7.38 (m, 3H), 7.34-7.30 (m, 5H), 7.25-7.22 (m, 5H), 7.04 (s, 2H), 6.89-6.46 (m, 4H), 5.86 (d, 1H, J = 2.7 Hz), 5.67 (s, 1H), 5.12 (d, 1H, J = 2.7 Hz), 2.47 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.6, 144.9, 143.3, 141.4, 140.4, 138.4, 137.5, 135.6, 135.5, 135.0, 134.6, 134.0, 133.5, 131.5, 131.4, 130.3, 130.1, 129.8, 129.7, 129.3, 129.2, 128.4, 128.3, 128.0, 126.2, 124.4, 119.5, 117.5, 98.5, 21.9, 21.8, 21.7, two carbons missing due to overlap, overlapped signals at 129.8 and 129.7 ppm; IR (neat) (cm^{-1}) 1629m, 1528m, 1357m, 1243w, 1165s, 1082s, 661s; HRMS (ESI): m/z calcd for $C_{45}H_{37}Cl_3N_3O_6S_3$ $[M + H]^+$ 916.0905, found 916.0907.

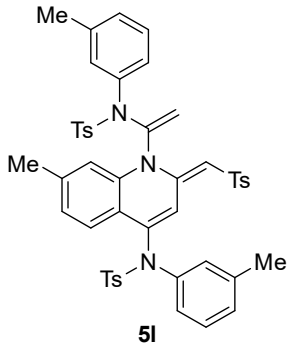


5j

To an oven-dried sealed tube was added ynamide **3j** (115.7 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5j** (97.5 mg, 0.11 mmol) in 84% yield.

5j: R_f = 0.19 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.4 Hz), 7.51-7.48 (m, 3H), 7.44 (d, 2H, J = 8.2 Hz), 7.40 (dd, 1H, J = 8.7, 2.8 Hz), 7.32-7.27 (m, 5H), 7.22 (d, 2H, J = 8.0 Hz), 7.10-6.92 (m, 5H), 6.62-6.46 (m, 4H), 5.88 (d, 1H, J = 2.6 Hz), 5.65 (s, 1H), 5.11 (d, 1H, J = 2.6 Hz), 2.46 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100

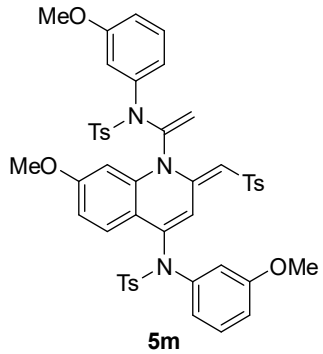
MHz, $CDCl_3$) δ 162.7 (C-F, $^1J_{C\text{-}F}$ = 247.6 Hz), 162.0 (C-F, $^1J_{C\text{-}F}$ = 248.2 Hz), 158.7 (C-F, $^1J_{C\text{-}F}$ = 243.0 Hz), 146.9, 145.4, 144.8, 143.2, 141.7, 141.0 (C-F, $^4J_{C\text{-}F}$ = 2.5 Hz), 136.3 (C-F, $^4J_{C\text{-}F}$ = 1.9 Hz), 135.5, 134.9 (C-F, $^3J_{C\text{-}F}$ = 12.0 Hz), 134.8 (C-F, $^4J_{C\text{-}F}$ = 2.8 Hz), 132.2 (C-F, $^3J_{C\text{-}F}$ = 9.2 Hz), 130.9 (C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.2, 130.1, 129.7, 129.6 (C-F, $^3J_{C\text{-}F}$ = 8.7 Hz), 128.4, 128.0, 126.2, 119.3, 118.8 (C-F, $^2J_{C\text{-}F}$ = 23.5 Hz), 117.8 (C-F, $^3J_{C\text{-}F}$ = 7.7 Hz), 116.4 (C-F, $^2J_{C\text{-}F}$ = 22.6 Hz), 115.9 (C-F, $^2J_{C\text{-}F}$ = 22.4 Hz), 111.0 (C-F, $^2J_{C\text{-}F}$ = 24.6 Hz), 97.7, 21.83, 21.81, 21.7, three carbons missing due to overlap, overlapped signals at 130.1, 129.7 and 126.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.8, -112.0, -117.9; IR (neat) (cm^{-1}) 1634m, 1573m, 1501s, 1265w, 1164s, 1082s, 813s; HRMS (ESI): m/z calcd for $C_{45}H_{37}F_3N_3O_6S_3$ $[M + H]^+$ 868.1791, found 868.1790.



5l

To an oven-dried sealed tube was added ynamide **3l** (114.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5l** (101.4 mg, 0.12 mmol) in 89% yield.

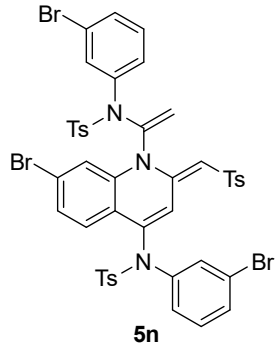
5l: R_f = 0.38 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 3H), 7.51-7.45 (m, 4H), 7.34-7.24 (m, 6H), 7.17-7.14 (m, 3H), 7.06-7.04 (m, 3H), 6.88 (d, 2H, *J* = 8.1 Hz), 6.76 (s, 1H), 6.63-6.52 (m, 2H), 5.80 (d, 1H, *J* = 2.5 Hz), 5.65 (s, 1H), 5.04 (d, 1H, *J* = 2.4 Hz), 2.43 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 144.9, 144.2, 142.5, 142.3, 142.1, 141.8, 140.2, 139.4, 139.3, 139.0, 136.3, 135.6, 135.5, 135.0, 131.2, 130.2, 130.1, 130.0, 129.8, 129.5, 128.9, 128.7, 128.5, 128.3, 128.1, 127.2, 126.2, 124.9, 124.4, 124.3, 118.6, 117.2, 116.3, 107.6, 96.3, 22.0, 21.8, 21.7, 21.5, 20.9, one carbon missing due to overlap, overlapped signal at 21.8 ppm; IR (neat) (cm^{-1}) 1732w, 1626m, 1528m, 1355m, 1183s, 1082s, 696s; HRMS (ESI): m/z calcd for $C_{48}H_{46}N_3O_6S_3$ $[M + H]^+$ 856.2543, found 856.2544.



5m

To an oven-dried sealed tube was added ynamide **3m** (120.5 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5m** (104.3 mg, 0.12 mmol) in 87% yield.

5m: R_f = 0.17 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.62 (m, 4H), 7.54 (d, 2H, J = 7.9 Hz), 7.40 (d, 2H, J = 8.1 Hz), 7.30-7.24 (m, 5H), 7.14-7.05 (m, 5H), 6.81 (t, 1H, J = 2.4 Hz), 6.77 (dd, 1H, J = 8.3, 2.6 Hz), 6.67 (dd, 1H, J = 8.8, 2.4 Hz), 6.54 (s, 1H), 6.35-6.20 (m, 2H), 5.80 (d, 1H, J = 2.6 Hz), 5.62 (s, 1H), 5.13 (d, 1H, J = 2.4 Hz), 3.87 (s, 3H), 3.72 (s, 3H), 3.30 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.1, 159.6, 148.3, 145.0, 144.2, 142.5, 142.0, 141.9, 141.7, 140.6, 136.2, 135.9, 135.6, 135.4, 130.0, 129.9, 129.8, 129.5, 129.2, 128.3, 128.0, 127.7, 126.6, 126.0, 122.4, 118.9, 117.1, 115.5, 114.6, 113.1, 113.0, 111.0, 108.4, 100.8, 95.9, 56.0, 55.5, 55.1, 21.7, 21.6, one carbon missing due to overlap, overlapped signal at 21.7 ppm; IR (neat) (cm^{-1}) 1734w, 1599m, 1528m, 1252m, 1163s, 1081s, 657s; HRMS (ESI): m/z calcd for $C_{48}H_{46}N_3O_9S_3$ $[M + H]^+$ 904.2391, found 904.2393.

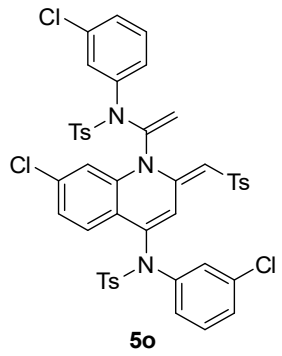


5n

To an oven-dried sealed tube was added ynamide **3n** (140.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol)

were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5n** (96.4 mg, 0.09 mmol) in 69% yield.

5n: R_f = 0.38 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.54 (m, 7H), 7.46-7.23 (m, 12H), 7.16-7.07 (m, 3H), 6.81-6.62 (m, 2H), 5.83 (d, 1H, J = 2.6 Hz), 5.78 (s, 1H), 5.14 (d, 1H, J = 2.6 Hz), 2.44 (s, 6H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 145.6, 145.0, 143.3, 141.5, 141.0, 140.8, 140.5, 136.4, 135.6, 134.7, 134.6, 133.7, 133.0, 131.1, 130.7, 130.4, 130.2, 129.9, 129.7, 129.1, 128.5, 128.1, 126.6, 126.35, 126.25, 125.7, 125.4, 122.8, 122.1, 119.4, 119.0, 118.4, 109.3, 99.8, 21.91, 21.89, 21.82, one carbon missing due to overlap, overlapped signal at 130.2 ppm; IR (neat) (cm^{-1}) 2924w, 1628m, 1527m, 1359m, 1164s, 1082s, 682s; HRMS (ESI): m/z calcd for $C_{45}H_{37}Br_3N_3O_6S_3$ $[M + H]^+$ 1047.9389, found 1047.9401.

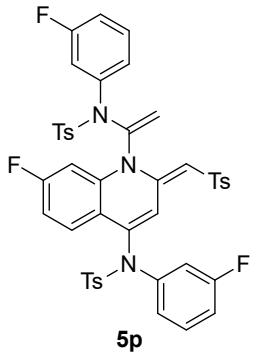


5o

To an oven-dried sealed tube was added ynamide **3o** (122.3 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5o** (85.7 mg, 0.09 mmol) in 70% yield.

5o: R_f = 0.38 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.51 (m, 9H), 7.34 (d, 2H, J = 8.0 Hz), 7.29-7.17 (m, 6H), 7.13 (s, 2H), 7.06 (d, 1H, J = 7.8 Hz), 6.99 (dd, 1H, J = 8.5, 1.8 Hz), 6.89-6.69 (m, 2H), 6.58 (d, 1H, J = 7.9 Hz), 5.86 (d, 1H, J = 2.6 Hz), 5.78 (s, 1H), 5.14 (d, 1H, J = 2.7 Hz), 2.43 (s, 6H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 145.6, 145.0, 143.3, 141.5, 141.0, 140.6, 140.4, 137.4, 136.2, 135.6, 134.9, 134.7, 134.6, 134.4, 130.8, 130.5, 130.4, 130.2, 130.0, 129.9, 129.8, 128.6, 128.5, 128.1, 126.6, 126.3,

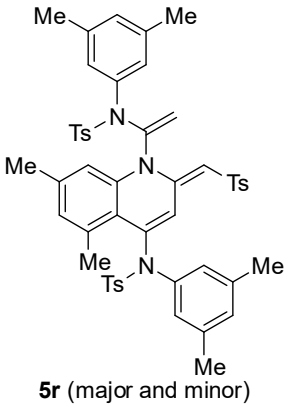
126.2, 124.9, 123.7, 119.1, 118.9, 115.5, 109.2, 99.7, 21.89, 21.88, 21.8, one carbon missing due to overlap, overlapped signal at 129.8 ppm; IR (neat) (cm^{-1}) 2923w, 1626m, 1528m, 1359m, 1165s, 1082s, 687s; HRMS (ESI): m/z calcd for $C_{45}H_{37}Cl_3N_3O_6S_3$ $[M + H]^+$ 916.0905, found 916.0902.



5p

To an oven-dried sealed tube was added ynamide **3p** (115.7 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **5p** (92.3 mg, 0.11 mmol) in 80% yield.

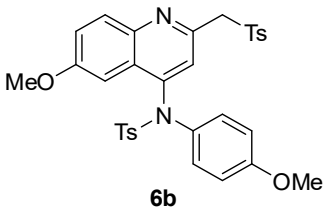
5p: R_f = 0.38 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-6.54 (m, 5H), 7.51-7.46 (m, 3H), 7.35-7.30 (m, 5H), 7.22 (d, 2H, J = 8.0 Hz), 7.00-6.89 (m, 4H), 6.77-6.70 (m, 3H), 6.58-6.37 (m, 2H), 5.88 (d, 1H, J = 2.7 Hz), 5.77 (s, 1H), 5.13 (d, 1H, J = 2.7 Hz), 2.45 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (C-F, $^1J_{C\text{-}F}$ = 250.1 Hz), 162.7 (C-F, $^1J_{C\text{-}F}$ = 246.6 Hz), 162.0 (C-F, $^1J_{C\text{-}F}$ = 245.9 Hz), 146.7, 145.7, 144.9, 143.4, 141.8 (C-F, $^3J_{C\text{-}F}$ = 11.2 Hz), 141.4, 140.7 (C-F, $^4J_{C\text{-}F}$ = 3.2 Hz), 140.6 (C-F, $^4J_{C\text{-}F}$ = 4.3 Hz), 136.4 (C-F, $^3J_{C\text{-}F}$ = 9.6 Hz), 135.7, 134.7 (C-F, $^3J_{C\text{-}F}$ = 6.1 Hz), 130.6 (C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 130.3, 130.2, 129.9 (C-F, $^3J_{C\text{-}F}$ = 7.7 Hz), 129.8, 128.5, 128.0, 127.2 (C-F, $^3J_{C\text{-}F}$ = 10.1 Hz), 126.3, 126.2 (C-F, $^4J_{C\text{-}F}$ = 2.9 Hz), 121.8, 117.85, 117.80 (C-F, $^2J_{C\text{-}F}$ = 21.1 Hz), 117.1 (C-F, $^2J_{C\text{-}F}$ = 21.0 Hz), 114.6 (C-F, $^2J_{C\text{-}F}$ = 21.0 Hz), 113.3 (C-F, $^2J_{C\text{-}F}$ = 21.9 Hz), 111.1 (C-F, $^2J_{C\text{-}F}$ = 22.9 Hz), 108.7, 103.1, 102.8, 99.5, 21.9, 21.8, 21.7, one carbon missing due to overlap, overlapped signal at 117.1 (C-F, $^2J_{C\text{-}F}$ = 21.0 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5, -110.1, -111.1; IR (neat) (cm^{-1}) 2922w, 1768w, 1593m, 1531m, 1359m, 1185s, 1082s, 686s; HRMS (ESI): m/z calcd for $C_{45}H_{36}F_3N_3NaO_6S_3$ $[M + Na]^+$ 890.1611, found 890.1609.



5r (major and minor)

To an oven-dried sealed tube was added ynamide **3r** (119.8 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the isomer ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford an inseparable 2.0:1.0 mixture of 4-aminoquinoline **5r** (major) (64.2 mg, 0.07 mmol) and **5r** (minor) (32.1 mg, 0.04 mmol) in 80% yield.

5r (major and minor): R_f = 0.30 [2:1 petroleum ether/EtOAc]; yellow solid; mp = 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, 4H, J = 8.2 Hz), 7.56-7.37 (m, 12H), 7.31-7.23 (m, 16H), 7.20-7.08 (m, 7H), 7.02-6.95 (m, 8H), 6.88-6.71 (m, 14H), 6.41 (s, 2H), 5.81 (d, 2H, J = 1.9 Hz), 5.66 (s, 2H), 5.63 (s, 1H), 5.57 (s, 1H), 5.053 (s, 2H), 5.048 (s, 1H), 2.81 (s, 3H), 2.69 (s, 6H), 2.46 (s, 7H), 2.40 (s, 6H), 2.38 (s, 3H), 2.34 (s, 12H), 2.28 (s, 6H), 2.25 (s, 3H), 2.21-2.15 (m, 29H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 147.7, 147.4, 144.8, 144.6, 144.2, 144.1, 142.5, 142.4, 142.3, 142.2, 142.1, 142.0, 141.7, 141.4, 140.9, 140.69, 140.65, 139.6, 139.0, 138.7, 138.4, 136.9, 136.4, 136.2, 136.1, 135.9, 135.74, 135.66, 135.3, 134.7, 131.5, 131.1, 129.98, 129.92, 129.7, 129.5, 129.32, 129.26, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 126.6, 126.0, 125.9, 125.8, 121.5, 120.4, 120.2, 119.1, 118.4, 117.8, 115.6, 115.3, 108.1, 107.0, 95.4, 94.1, 23.7, 23.1, 21.8, 21.70, 21.65, 21.61, 21.54, 21.47, 21.2, 20.8, eight carbons missing due to overlap; IR (neat) (cm^{-1}) 2922w, 1606s, 1453m, 1355m, 1166s, 1085m; HRMS (ESI): m/z calcd for $C_{51}H_{51}N_3O_6S_3$ $[M + H]^+$ 898.3013, found 898.3006.

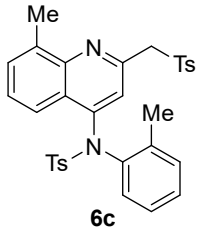


6b

To an oven-dried sealed tube was added ynamide **3g** (120.5 mg, 0.40 mmol), DCM (1.0 mL,

ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **6b** (52.2 mg, 0.09 mmol) in 43% yield.

6b: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 3H), 7.54 (d, 1H, J = 2.8 Hz), 7.53 (s, 1H), 7.47 (d, 2H, J = 8.3 Hz), 7.37-7.32 (m, 4H), 7.28-7.25 (m, 1H), 7.14 (d, 2H, J = 7.8 Hz), 6.82 (d, 2H, J = 9.1 Hz), 4.62 (s, 2H), 3.92 (s, 3H), 3.77 (s, 3H), 2.49 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 159.1, 146.9, 146.0, 145.9, 144.9, 144.5, 136.5, 135.0, 132.7, 131.0, 130.1, 129.8, 129.6, 128.7, 128.4, 127.7, 123.4, 122.1, 114.7, 101.3, 65.2, 55.8, 55.6, 21.9, 21.8; IR (neat) (cm^{-1}) 2927w, 1620m, 1595m, 1504s, 1230s, 1181s, 1067s, 1028m; HRMS (ESI): m/z calcd for $C_{32}H_{30}N_2NaO_6S_2$ [M + Na]$^+$ 625.1437, found 625.1437.

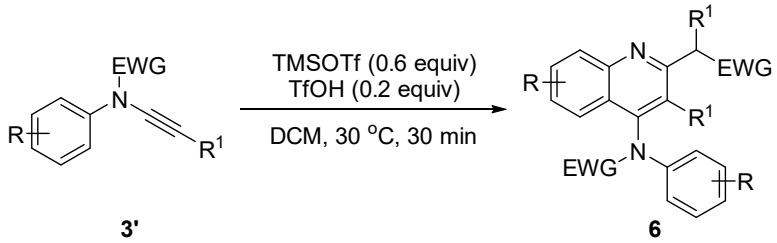


6c

To an oven-dried sealed tube was added ynamide **3s** (114.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford 4-aminoquinoline **6c** (75.9 mg, 0.13 mmol) in 66% yield.

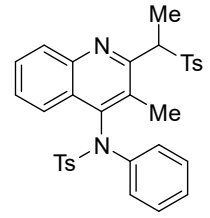
6c: R_f = 0.28 [5:1 petroleum ether/EtOAc]; white solid; mp = 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.45 (m, 1H), 7.62 (d, 2H, J = 8.3 Hz), 7.54 (s, 1H), 7.48-7.46 (m, 2H), 7.42 (d, 2H, J = 8.3 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.22-7.18 (m, 2H), 7.15-7.11 (m, 4H), 4.62 (s, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 148.1, 147.2, 144.7, 144.6, 139.5, 139.3, 137.5, 136.2, 135.1, 132.3, 130.3, 130.2, 130.0, 129.5, 129.1, 128.7, 127.0, 126.7, 126.6, 123.2, 122.1, 65.3, 21.8, 21.7, 20.2, 17.9, one carbon missing due to overlap, overlapped signal at 128.7 ppm; IR (neat) (cm^{-1}) 2918w, 1591m, 1500m, 1348s, 1154s, 1067s, 664s; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ [M + H]$^+$ 571.1720, found 571.1723.

1.7 [4 + 2] Self-Cycloaddition of Internal *N*-Aryl Ynamides.



3' 6

Scheme S7. [4 + 2] Self-cycloaddition of internal *N*-aryl ynamides



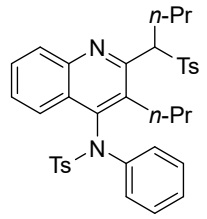
6d (major and minor)

To an oven-dried sealed tube was added ynamide **3'a** (114.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 6:1~4:1 petroleum ether/EtOAc] to afford a separable 1.3:1.0 mixture of 4-aminoquinoline **6d** (major) (59.8 mg, 0.11 mmol) and **6d** (minor) (46.0 mg, 0.08 mmol) in 93% yield.

6d (major): R_f = 0.14 [5:1 petroleum ether/EtOAc]; white solid; mp = 227–229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 1H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz), 7.64 (d, 1H, J = 8.4 Hz), 7.60-7.56 (m, 1H), 7.43 (d, 2H, J = 8.3 Hz), 7.37-7.33 (m, 1H), 7.26-7.24 (m, 6H), 7.14-7.08 (m, 3H), 5.04 (q, 1H, J = 6.8 Hz), 2.57 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H), 1.87 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.6, 144.8, 144.6, 143.5, 140.8, 137.5, 133.83, 133.76, 129.9, 129.84, 129.78, 129.5, 129.3, 129.1, 128.3, 127.8, 126.8, 125.5, 124.3, 122.2, 63.8, 21.74, 21.70, 16.3, 15.1; IR (neat) (cm^{-1}) 2925w, 1596m, 1490m, 1159s, 1088s, 1036m; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ $[M + H]^+$ 571.1720, found 571.1723.

6d (minor): R_f = 0.23 [5:1 petroleum ether/EtOAc]; white solid; mp = 226–228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 1H, J = 8.3 Hz), 7.81 (d, 2H, J = 8.3 Hz), 7.74 (d, 1H, J = 8.2 Hz), 7.65-7.61 (m, 1H), 7.57-7.53 (m, 1H), 7.41-7.36 (m, 4H), 7.23-7.17 (m, 6H), 7.10-7.06 (m, 1H), 4.92 (q, 1H, J

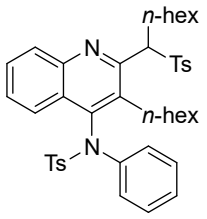
= 6.9 Hz), 2.46 (s, 3H), 2.41 (s, 3H), 2.22 (s, 3H), 1.80 (d, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 147.3, 144.9, 144.7, 143.9, 141.4, 137.7, 132.9, 132.2, 130.21, 130.17, 129.5, 129.4, 129.32, 129.26, 128.4, 128.3, 128.1, 125.4, 125.2, 122.2, 64.0, 21.8, 16.0, 15.2, one carbon missing due to overlap, overlapped signal at 21.8 ppm; IR (neat) (cm^{-1}) 2923w, 1594m, 1490m, 1355s, 1163s, 1085m; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_4S_2$ $[M + H]^+$ 571.1720, found 571.1726.



6e (minor and major)

To an oven-dried sealed tube was added ynamide **3'b** (125.4 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 15:1~8:1 petroleum ether/EtOAc] to afford an inseparable 1.0:1.7 mixture of 4-aminoquinoline **6e** (minor) (42.7 mg, 0.07 mmol) and **6e** (major) (72.7 mg, 0.12 mmol) in 92% yield.

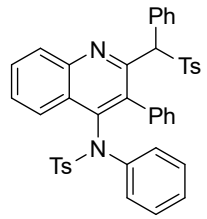
6e (minor and major): R_f = 0.30, 0.39 [5:1 petroleum ether/EtOAc]; white solid; mp = 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.29 (m, 1.7H, major), 7.85 (d, 3.4H, J = 8.3 Hz, major), 7.81 (d, 1.0H, J = 8.4 Hz, minor), 7.72-7.59 (m, 10.0H), 7.44-7.39 (m, 9.0H), 7.33 (d, 3.4H, J = 8.2 Hz, major), 7.27 (s, 1.7H, major), 7.23-7.06 (m, 15.7H), 4.81 (dd, 1.0H, J = 10.8, 3.5 Hz, minor), 4.70 (dd, 1.7H, J = 10.9, 3.5 Hz, major), 2.87-2.68 (m, 3.4H, major), 2.49-2.38 (m, 21.2H), 2.34-2.24 (m, 3.4H, major), 2.01-1.87 (m, 1.0H, minor), 1.43-1.35 (m, 2.0H, minor), 1.24-1.04 (m, 6.8H, major), 0.99 (t, 3.0H, J = 7.1 Hz, minor), 0.91(t, 3.0H, J = 7.2 Hz, minor), 0.84 (t, 5.1H, J = 7.2 Hz, major), 0.51 (t, 5.1H, J = 7.2 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 155.0, 154.1, 147.7, 147.1, 144.7, 144.63, 144.59, 144.5, 143.7, 143.6, 142.6, 141.1, 138.0, 137.9, 136.9, 136.8, 134.3, 133.0, 130.22, 130.18, 129.71, 129.69, 129.5, 129.3, 129.18, 129.15, 129.1, 129.0, 128.34, 128.29, 128.0, 127.7, 127.4, 125.9, 125.7, 125.6, 124.9, 122.7, 122.6, 69.2, 68.9, 32.5, 31.4, 30.9, 30.7, 29.8, 23.0, 22.6, 21.8, 21.7, 20.8, 20.7, 15.0, 14.5, 14.34, 14.27, four carbons missing due to overlap; IR (neat) (cm^{-1}) 3441, 2961m, 1597m, 1489m, 1313w, 1166s, 1084m; HRMS (ESI): m/z calcd for $C_{36}H_{39}N_2O_4S_2$ $[M + H]^+$ 627.2346, found 627.2345.



6f (minor and major)

To an oven-dried sealed tube was added ynamide **3'c** (142.2 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 15:1~12:1 petroleum ether/EtOAc] to afford an inseparable 1.0:1.8 mixture of 4-aminoquinoline **6f** (minor) (45.2 mg, 0.06 mmol) and **6f** (major) (81.5 mg, 0.12 mmol) in 89% yield.

6f (minor and major): R_f = 0.25, 0.34 [5:1 petroleum ether/EtOAc]; white solid; mp = 46–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.28 (m, 1.8H, major), 7.87-7.83 (m, 4.6H), 7.73-7.59 (m, 10.2H), 7.43-7.38 (m, 8.4H), 7.32 (d, 3.6H, J = 8.2 Hz, major), 7.25-7.23 (m, 2.8H), 7.19 (d, 7.2H, J = 4.2 Hz, major), 7.16 (d, 4.0H, J = 8.2 Hz, minor), 7.14-7.06 (m, 5.0H), 4.79 (dd, 1.0H, J = 10.8, 3.5 Hz, minor), 4.68 (dd, 1.8H, J = 10.8, 3.4 Hz, major), 2.88-2.67 (m, 4.0H), 2.53-2.27 (m, 27.6H), 1.95-1.83 (m, 1.0H, minor), 1.43-1.08 (m, 22.6H), 1.04-0.73 (m, 34.4H); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 154.9, 154.1, 147.6, 147.0, 144.7, 144.6, 144.53, 144.46, 143.55, 143.53, 142.5, 141.1, 138.0, 137.8, 137.0, 136.9, 134.4, 133.0, 130.2, 130.1, 130.0, 129.7, 129.6, 129.4, 129.3, 129.2, 129.13, 129.10, 129.0, 128.4, 128.2, 128.0, 127.7, 127.4, 125.8, 125.6, 125.4, 124.9, 122.6, 122.5, 69.2, 69.0, 31.53, 31.51, 31.4, 31.3, 30.3, 30.2, 29.7, 29.45, 29.39, 29.3, 29.15, 29.07, 28.83, 28.75, 27.3, 27.2, 22.7, 22.6, 22.5, 22.4, 21.71, 21.67, 14.2, 14.09, 14.07, 14.0, four carbons missing due to overlap; IR (neat) (cm^{-1}) 2955m, 2926s, 1596m, 1362s, 1302w, 1084m; HRMS (ESI): m/z calcd for $C_{42}H_{51}N_2O_4S_2$ $[M + H]^+$ 711.3285, found 711.3287.



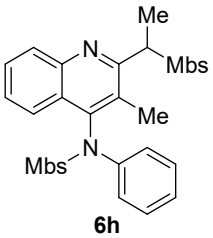
6g (minor and major)

To an oven-dried sealed tube was added ynamide **3'd** (139.0 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol)

were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 8:1~6:1 petroleum ether/EtOAc] to afford a separable 1.0:1.05 mixture of 4-aminoquinoline **6g** (minor) (44.2 mg, 0.06 mmol) and **6g** (major) (46.4 mg, 0.07 mmol) in 65% yield.

6g (minor): R_f = 0.25 [6:1:1 petroleum ether/EtOAc/DCM]; white solid; mp = 263–264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, 1H, J = 8.4 Hz), 7.83 (d, 1H, J = 8.4 Hz), 7.80-7.76 (m, 1H), 7.52-7.47 (m, 2H), 7.44-7.39 (m, 3H), 7.30 (d, 3H, J = 8.0 Hz), 7.23 (d, 2H, J = 7.6 Hz), 7.20-7.15 (m, 4H), 7.13-7.06 (m, 7H), 6.84 (d, 3H, J = 7.9 Hz), 5.52 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.0, 144.4, 144.3, 143.9, 141.0, 137.9, 136.7, 135.3, 134.8, 131.8, 131.3, 131.2, 130.5, 130.4, 130.1, 129.6, 129.5, 129.0, 128.82, 128.75, 128.6, 128.4, 128.3, 128.1, 127.1, 125.51, 125.45, 123.2, 74.0, 21.9, 21.7; IR (neat) (cm^{-1}) 2923w, 1597w, 1486m, 1365m, 1309m, 1163s, 1131m, 1083m; HRMS (ESI): m/z calcd for $C_{42}H_{35}N_2O_4S_2$ $[M + H]^+$ 695.2033, found 695.2030.

6g (major): R_f = 0.12 [6:1:1 petroleum ether/EtOAc/DCM]; white solid; mp = 245–246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, 1H, J = 8.1 Hz), 7.84-7.78 (m, 2H), 7.55-7.49 (m, 3H), 7.47-7.41 (m, 4H), 7.38-7.34 (m, 4H), 7.21-7.16 (m, 6H), 7.08-7.02 (m, 1H), 6.99-6.89 (m, 3H), 6.61 (d, 2H, J = 8.1 Hz), 6.11 (d, 1H, J = 7.6 Hz), 5.50 (s, 1H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 148.8, 144.8, 144.6, 144.2, 140.4, 137.3, 137.1, 135.3, 134.4, 131.9, 131.4, 131.3, 130.4, 130.1, 129.7, 129.5, 129.02, 128.99, 128.95, 128.7, 128.3, 128.2, 128.1, 127.6, 127.3, 126.4, 125.5, 123.2, 73.7, 21.9, 21.8; IR (neat) (cm^{-1}) 2923w, 1596m, 1486m, 1366s, 1312m, 1163s, 1088m; HRMS (ESI): m/z calcd for $C_{42}H_{35}N_2O_4S_2$ $[M + H]^+$ 695.2033, found 695.2032.

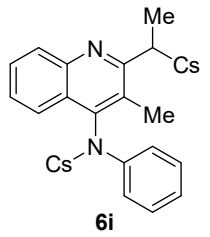


6h

To an oven-dried sealed tube was added ynamide **3'e** (120.5 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H

NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford an inseparable 1.0:1.0 mixture of 4-aminoquinoline **6h** (114.3 mg, 0.19 mmol) in 95% yield.

6h: R_f = 0.14, 0.20 [2:1 petroleum ether/EtOAc]; white solid; mp = 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 1H, J = 8.2 Hz), 7.87-7.74 (m, 6H), 7.66-7.52 (m, 4H), 7.47-7.41 (m, 4H), 7.38-7.34 (m, 1H), 7.25-7.24 (m, 4H), 7.20-7.17 (m, 4H), 7.11-7.04 (m, 2H), 7.02 (d, 2H, J = 8.9 Hz), 6.92 (d, 2H, J = 8.9 Hz), 6.86-6.80 (m, 4H), 5.05 (q, 1H, J = 6.8 Hz), 4.93 (q, 1H, J = 6.8 Hz), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 (s, 6H), 2.62 (s, 3H), 2.23 (s, 3H), 1.87 (d, 3H, J = 6.8 Hz), 1.81 (d, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 163.93, 163.88, 163.63, 163.61, 155.23, 155.16, 147.6, 147.3, 143.8, 143.5, 141.2, 140.8, 133.9, 132.19, 132.16, 132.06, 131.91, 131.89, 130.5, 129.9, 129.55, 129.49, 129.3, 129.2, 129.1, 128.2, 128.1, 127.8, 127.3, 126.8, 125.4, 125.2, 125.0, 124.2, 122.0, 121.9, 114.6, 114.3, 113.9, 113.8, 64.0, 63.9, 55.9, 55.8, 55.7, 16.4, 15.9, 15.2, 15.1; three carbons missing due to overlap; IR (neat) (cm^{-1}) 1595s, 1496s, 1359m, 1317w, 1090m, 1026w; HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_6S_2$ $[M + H]^+$ 603.1618, found 603.1616.

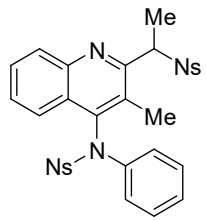


6i

To an oven-dried sealed tube was added ynamide **3'f** (122.3 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 7:1~5:1 petroleum ether/EtOAc] to afford an inseparable 1.0:1.0 mixture of 4-aminoquinoline **6i** (112.7 mg, 0.18 mmol) in 92% yield.

6i: R_f = 0.32 [5:1 petroleum ether/EtOAc]; white solid; mp = 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 1H, J = 8.3 Hz), 7.86 (d, 2H, J = 8.7 Hz), 7.82-7.80 (m, 1H), 7.75-7.72 (m, 3H), 7.67-7.53 (m, 6H), 7.46-7.42 (m, 6H), 7.41-7.28 (m, 9H), 7.23-7.19 (m, 4H), 7.18-7.08 (m, 2H), 5.08 (q, 1H, J = 6.8 Hz), 4.97 (q, 1H, J = 6.8 Hz), 2.64 (s, 3H), 2.29 (s, 3H), 1.87 (d, 3H, J = 6.9 Hz), 1.80 (d, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 154.74, 154.71, 147.5, 147.2, 143.6, 143.4, 140.8, 140.63, 140.58, 140.4, 140.21, 140.20, 138.8, 134.8, 134.1, 133.7, 132.1, 131.6, 131.5, 129.84, 129.80, 129.73, 129.66, 129.61, 129.55, 129.52, 129.42, 129.41, 128.9, 128.8, 128.4, 128.1,

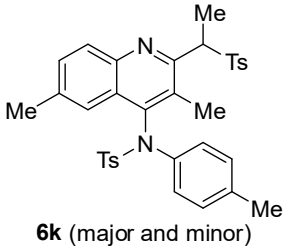
128.0, 126.6, 126.2, 125.8, 124.8, 124.0, 122.5, 122.3, 64.07, 63.96, 16.5, 16.1, 15.3, 15.2, two carbons missing due to overlap; IR (neat) (cm^{-1}) 1584m, 1490m, 1363s, 1314m, 1165s, 1089s; HRMS (ESI): m/z calcd for $C_{30}H_{25}Cl_2N_2O_4S_2$ $[M + H]^+$ 611.0627, found 611.0629.



6j (minor and major)

To an oven-dried sealed tube was added ynamide **3'g** (126.5 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 5:1~2:1 petroleum ether/EtOAc] to afford an inseparable 1.0:1.2 mixture of 4-aminoquinoline **6j** (minor) (38.6 mg, 0.06 mmol) and **6j** (major) (46.3 mg, 0.07 mmol) in 68% yield. Due to the poor solubility of 4-aminoquinoline **6j**, the ratio of the mixture has an error after purification.

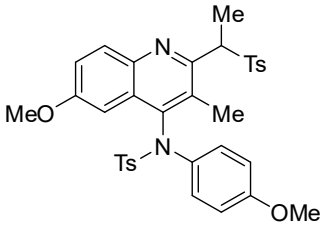
6j (minor and major): R_f = 0.11 [5:1 petroleum ether/EtOAc]; white solid; mp =253–255 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.48-8.39 (m, 7.6H), 8.29 (d, 2.0H, J = 8.4 Hz, minor), 8.07 (d, 4.0H, J = 7.9 Hz, major), 7.91-7.69 (m, 11.2H), 7.64-7.57 (m, 2.4H), 7.40-7.32 (m, 4.4H), 7.27-7.21 (m, 5.8H), 5.51 (q, 1.0H, J = 6.6 Hz, minor), 5.44 (q, 1.2H, J = 6.6 Hz, major), 2.39 (s, 3.6H, major), 2.36 (s, 3.0H, minor), 1.82 (d, 3.0H, J = 6.4 Hz, minor), 1.76 (d, 3.6H, J = 6.4 Hz, major); ^{13}C NMR (100 MHz, DMSO) (major and minor) δ 154.7, 154.5, 150.7, 150.55, 150.49, 150.47, 146.7, 146.6, 144.3, 144.2, 142.6, 142.3, 142.23, 142.15, 142.0, 139.9, 139.7, 133.4, 133.1, 131.0, 130.97, 129.9, 129.83, 129.77, 129.5, 129.4, 129.3, 129.2, 128.7, 128.6, 126.5, 126.34, 126.32, 126.2, 125.12, 125.08, 124.21, 124.16, 123.7, 123.6, 122.6, 122.5, 63.2, 62.9, 15.9, 15.6, 14.9, 14.8; IR (neat) (cm^{-1}) 1606w, 1534s, 1490m, 1351s, 1305m, 1136m; HRMS (ESI): m/z calcd for $C_{30}H_{25}N_4O_8S_2$ $[M + H]^+$ 633.1108, found 633.1109.



6k (major and minor)

To an oven-dried sealed tube was added ynamide **3'h** (119.8 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 7:1~5:1 petroleum ether/EtOAc] to afford an inseparable 1.3:1.0 mixture of 4-aminoquinoline **6k** (major) (65.5 mg, 0.11 mmol) and **6k** (minor) (50.4 mg, 0.08 mmol) in 97% yield.

6k (major and minor): R_f = 0.16, 0.23 [5:1 petroleum ether/EtOAc]; white solid; mp = 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.73 (m, 4.6H), 7.67-7.64 (m, 3.6H), 7.45-7.33 (m, 9.2H), 7.27 (d, 2.6H, J = 5.1 Hz, major), 7.24-7.17 (m, 4.9H), 7.13-7.06 (m, 7.6H), 7.00 (d, 2.0H, J = 8.5 Hz, minor), 4.99 (q, 1.3H, J = 6.8 Hz, major), 4.89 (q, 1.0H, J = 6.9 Hz, minor), 2.52 (s, 3.9H, major), 2.44 (s, 6.0H, minor), 2.42 (s, 3.9H, major), 2.39 (s, 3.0H, minor), 2.34 (s, 3.9H, major), 2.28 (s, 7.8H, major), 2.233 (s, 3.0H, minor), 2.226 (s, 3.0H, minor), 1.87 (d, 3.9H, J = 6.8 Hz, major), 1.79 (d, 3.0H, J = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 153.9, 153.7, 146.3, 146.0, 144.7, 144.6, 144.38, 144.35, 143.5, 143.2, 138.6, 138.1, 138.0, 137.73, 137.67, 135.5, 135.4, 133.8, 133.5, 133.1, 132.1, 131.4, 131.2, 130.1, 130.0, 129.89, 129.88, 129.76, 129.64, 129.59, 129.27, 129.25, 129.17 128.3, 128.22, 128.19, 128.0, 126.8, 123.7, 123.2, 122.8, 122.7, 63.9, 63.7, 22.1, 21.9, 21.73, 21.70, 21.68, 21.66, 20.9, 20.8, 16.1, 15.8, 15.0, 14.9; IR (neat) (cm^{-1}) 2924w, 1597w, 1508m, 1357m, 1164s, 1147m, 1088m; HRMS (ESI): m/z calcd for $C_{34}H_{35}N_2O_4S_2$ $[M + H]^+$ 599.2033, found 599.2040.

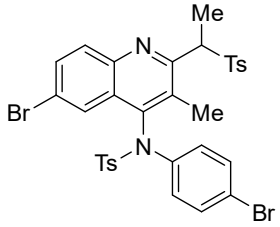


6l (major and minor)

To an oven-dried sealed tube was added ynamide **3'i** (126.2 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 15:1~12:1 petroleum ether/EtOAc] to afford an inseparable 1.3:1.0 mixture of

4-aminoquinoline **6l (**major) (69.2 mg, 0.11 mmol) and **6l** (minor) (53.2 mg, 0.08 mmol) in 97% yield.

6l (major and minor): R_f = 0.1 [5:1 petroleum ether/EtOAc]; white solid; mp = 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.64 (m, 6.9H), 7.41-7.39 (m, 5.9H), 7.33 (d, 2.0H, J = 8.2 Hz, minor), 7.29-7.25 (m, 5.2H), 7.26-7.17 (m, 6.0H), 7.10 (d, 2.6H, J = 8.2 Hz, major), 6.99 (d, 1.3H, J = 2.7 Hz, major), 6.80 (d, 2.6H, J = 9.2 Hz, major), 6.73 (d, 2.0H, J = 9.2 Hz, minor), 5.00(q, 1.3H, J = 6.8 Hz, major), 4.90 (q, 1.0H, J = 6.9 Hz, minor), 3.77 (s, 3.0H, minor), 3.72 (s, 3.9H, major), 3.69 (s, 3.0H, minor), 3.55 (s, 3.9H, major), 2.63 (s, 3.9H, major), 2.43 (s, 3.0H, minor), 2.41 (s, 3.9H, major), 2.38 (s, 3.0H, minor), 2.35 (s, 3.9H, major), 2.33 (s, 3.0H, minor), 1.85 (d, 3.9H, J = 6.8 Hz, major), 1.79 (d, 3.0H, J = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 159.0, 158.8, 157.71, 157.68, 151.9, 151.7, 144.64, 144.59, 144.4, 144.3, 143.8, 143.7, 143.4, 143.1, 138.0, 137.9, 133.8, 133.6, 133.5, 133.3, 132.3, 131.4, 131.1, 129.91, 129.85, 129.76, 129.2, 129.1, 129.0, 128.12, 128.10, 127.9, 125.5, 125.3, 122.0, 121.9, 114.6, 114.5, 102.5, 101.9, 63.8, 63.7, 55.45, 55.42, 55.1, 21.67, 21.65, 21.59, 16.6, 16.1, 14.95, 14.89, four carbons missing due to overlap; IR (neat) (cm^{-1}) 1621m, 1507s, 1493s, 1232m, 1146s, 1088m; HRMS (ESI): m/z calcd for $C_{34}H_{35}N_2O_6S_2$ $[M + H]^+$ 631.1931, found 631.1929.

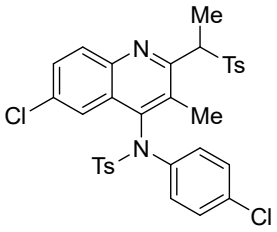


6m (major and minor)

To an oven-dried sealed tube was added ynamide **3'j** (145.7 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 6:1~4:1 petroleum ether/EtOAc] to afford an inseparable 1.2:1.0 mixture of 4-aminoquinoline **6m** (major) (73.2 mg, 0.10 mmol) and **6m** (minor) (61.0 mg, 0.08 mmol) in 92% yield.

6m (major and minor): R_f = 0.22, 0.27 [5:1 petroleum ether/EtOAc]; white solid; mp = 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 1.0H, J = 1.8 Hz, minor), 7.78-7.74 (m, 3.2H), 7.70-7.63 (m, 5.6H), 7.47 (d, 1.2H, J = 1.9 Hz, major), 7.41-7.30 (m, 13.2H), 7.21-7.13 (m, 6.8H), 7.08 (d, 2.0H, J

= 9.0 Hz, minor), 5.01 (q, 1.2H, *J* = 6.8 Hz, major), 4.92 (q, 1.0H, *J* = 6.8 Hz, minor), 2.56 (s, 3.6H, major), 2.44 (s, 6.6H), 2.40 (s, 3.0H, minor), 2.38 (s, 3.6H, major), 2.26 (s, 3.0H, minor), 1.86 (d, 3.6H, *J* = 6.8 Hz, major), 1.79 (d, 3.0H, *J* = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 155.7, 155.5, 146.0, 145.8, 145.2, 145.1, 144.90, 144.88, 142.3, 142.1, 139.8, 139.4, 136.52, 136.47, 135.1, 133.69, 133.66, 133.0, 132.8, 132.7, 132.6, 132.4, 131.7, 131.3, 130.2, 130.0, 129.8, 129.6, 129.32, 129.29, 128.6, 128.1, 128.0, 127.6, 126.6, 126.2, 123.6, 123.4, 122.6, 122.4, 119.0, 118.6, 63.9, 63.7, 21.71, 21.68, 16.1, 15.9, 15.0, 14.8, two carbons missing due to overlap; IR (neat) (cm^{-1}) 1596w, 1488s, 1361m, 1232w, 1167s, 1086m; HRMS (ESI): m/z calcd for $C_{32}H_{28}Br_2N_2NaO_4S_2$ $[M + Na]^+$ 748.9749, found 748.9747.

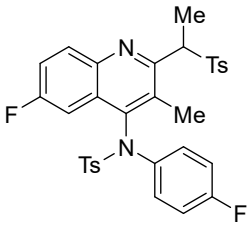


6n (major and minor)

To an oven-dried sealed tube was added ynamide **3'k** (127.9 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 6:1~5:1 petroleum ether/EtOAc] to afford an inseparable 1.2:1.0 mixture of 4-aminoquinoline **6n** (major) (63.3 mg, 0.10 mmol) and **6n** (minor) (52.7 mg, 0.08 mmol) in 91% yield.

6n (major and minor): R_f = 0.22, 0.27 [5:1 petroleum ether/EtOAc]; white solid; mp = 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2.2H), 7.75 (d, 2.0H, *J* = 8.3 Hz, minor), 7.71 (d, 1.0H, *J* = 8.9 Hz, minor), 7.66 (d, 2.4H, *J* = 8.3 Hz, major), 7.54 (td, 2.4H, *J* = 9.3, 2.2 Hz, major), 7.41-7.35 (m, 7.8H), 7.30 (d, 2.4H, *J* = 8.2 Hz, major), 7.25 (d, 4.0H, *J* = 0.8 Hz, minor), 7.21-7.13 (m, 8.8H), 5.02 (q, 1.2H, *J* = 6.8 Hz, major), 4.92 (q, 1.0H, *J* = 6.8 Hz, minor), 2.56 (s, 3.6H, major), 2.45 (s, 3.0H, minor), 2.44 (s, 3.6H, major), 2.40 (s, 3.0H, minor), 2.38 (s, 3.6H, major), 2.25 (s, 3.0H, minor), 1.86 (d, 3.6H, *J* = 6.8 Hz, major), 1.79 (d, 3.0H, *J* = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 155.6, 155.3, 145.9, 145.6, 145.3, 145.1, 145.0, 142.6, 142.4, 139.4, 138.9, 136.7, 136.6, 135.0, 134.4, 134.1, 133.7, 133.62, 133.60, 132.9, 131.7, 131.3, 130.9, 130.3, 130.2, 130.0, 129.9, 129.71, 129.68, 129.5, 129.4, 129.3, 128.4, 128.2, 128.0, 127.3, 123.49, 123.46, 123.3, 122.9, 63.9, 63.7, 21.73, 21.72, 16.2, 15.9, 15.0, 14.9, four carbons missing due to overlap; IR

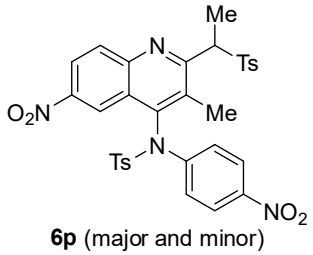
(neat) (cm^{-1}) 3447w, 1596m, 1490s, 1360m, 1292m, 1167s, 1087m; HRMS (ESI): m/z calcd for $C_{32}H_{29}Cl_2N_2O_4S_2$ $[M + H]^+$ 639.0940, found 639.0940.



6o (major and minor)

To an oven-dried sealed tube was added ynamide **3'l** (121.3 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 6:1~4:1 petroleum ether/EtOAc] to afford an inseparable 1.3:1.0 mixture of 4-aminoquinoline **6o** (major) (55.1 mg, 0.09 mmol) and **6o** (minor) (42.3 mg, 0.07 mmol) in 80% yield.

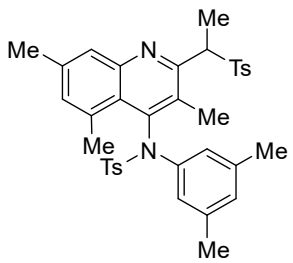
6o (major and minor): R_f = 0.16, 0.22 [5:1 petroleum ether/EtOAc]; white solid; mp = 80–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1.3H, major), 7.78-7.74 (m, 3.0H, minor), 7.68-7.65 (m, 3.3H), 7.42-7.36 (m, 8.5H), 7.32-7.28 (m, 5.6H), 7.24-7.19 (m, 5.6H), 7.15 (d, 2.6H, J = 8.1 Hz, major), 7.01-6.96 (m, 2.6H, major), 6.94-6.90 (m, 2.0H, minor), 5.01 (q, 1.3H, J = 6.8 Hz, major), 4.91 (q, 1.0H, J = 6.8 Hz, minor), 2.60 (s, 3.9H, major), 2.46 (s, 3.0H, minor), 2.45 (s, 3.9H, major), 2.41 (s, 3.0H, minor), 2.38 (s, 3.9H, major), 2.27 (s, 3.0H, minor), 1.85 (d, 3.9H, J = 6.8 Hz, major), 1.79 (d, 3.0H, J = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 161.8 (C-F, $^1J_{C\text{-}F}$ = 248.5 Hz), 161.6 (C-F, $^1J_{C\text{-}F}$ = 248.6 Hz), 160.5 (C-F, $^1J_{C\text{-}F}$ = 245.7 Hz), 160.3 (C-F, $^1J_{C\text{-}F}$ = 245.4 Hz), 154.5 (C-F, $^4J_{C\text{-}F}$ = 2.9 Hz), 154.3 (C-F, $^4J_{C\text{-}F}$ = 2.9 Hz), 145.1, 144.97, 144.94, 144.92, 144.8, 144.5, 143.5 (C-F, $^4J_{C\text{-}F}$ = 5.6.0 Hz), 143.3 (C-F, $^4J_{C\text{-}F}$ = 5.6.0 Hz), 137.15, 137.08, 136.9 (C-F, $^4J_{C\text{-}F}$ = 3.1 Hz), 136.4 (C-F, $^4J_{C\text{-}F}$ = 3.0 Hz), 134.6, 133.7, 133.2, 132.9, 132.7 (C-F, $^3J_{C\text{-}F}$ = 9.4 Hz), 132.3 (C-F, $^3J_{C\text{-}F}$ = 9.2 Hz), 130.2, 130.0, 129.8, 129.35, 129.32, 129.1 (C-F, $^3J_{C\text{-}F}$ = 9.8 Hz), 128.2, 128.1, 127.9 (C-F, $^3J_{C\text{-}F}$ = 9.8 Hz), 125.1 (C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 124.9 (C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 119.6 (C-F, $^2J_{C\text{-}F}$ = 25.8 Hz), 119.5 (C-F, $^2J_{C\text{-}F}$ = 25.6 Hz), 116.5 (C-F, $^2J_{C\text{-}F}$ = 22.5 Hz), 116.3 (C-F, $^2J_{C\text{-}F}$ = 22.5 Hz), 108.5 (C-F, $^2J_{C\text{-}F}$ = 24.0 Hz), 107.8 (C-F, $^2J_{C\text{-}F}$ = 24.1 Hz), 63.8, 63.7, 21.76, 21.74, 16.5, 16.1, 15.0, four carbons missing due to overlap; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9, -110.1, -115.2, -115.6; IR (neat) (cm^{-1}) 1597m, 1505s, 1493s, 1358m, 1163s, 1088m; HRMS (ESI): m/z calcd for $C_{32}H_{29}F_2N_2O_4S_2$ $[M + H]^+$ 607.1531, found 607.1531.



6p (major and minor)

To an oven-dried sealed tube was added ynamide **3'm** (132.1 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 7:1~1:1 petroleum ether/EtOAc] to afford afford an inseparable 1.5:1.0 mixture of 4-aminoquinoline **6p** (major) (17.3 mg, 0.03 mmol) and **6p** (minor) (11.5 mg, 0.02 mmol) in 22% yield.

6p (major and minor): R_f = 0.41 [5:1 petroleum ether/EtOAc]; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, 1.0H, J = 2.4 Hz, minor), 8.43-8.37 (m, 2.5H), 8.19-8.08 (m, 8.0H), 7.96 (d, 1.0H, J = 9.2 Hz, minor), 7.84 (d, 2.0H, J = 8.4 Hz, minor), 7.75 (d, 3.0H, J = 8.4 Hz, major), 7.52 (d, 3.0H, J = 8.2 Hz, major), 7.43 (d, 4.0H, J = 7.9 Hz, minor), 7.37-7.33 (m, 6.0H, major), 7.28 (d, 3.0H, J = 8.6 Hz, major), 7.26-7.23 (m, 4.0H, minor), 5.10 (q, 1.5H, J = 6.8 Hz, major), 4.99 (q, 1.0H, J = 6.8 Hz, minor), 2.72 (s, 4.5H, major), 2.47-2.45 (m, 15.0H), 2.28 (s, 3.0H, minor), 1.88 (d, 4.5H, J = 6.8 Hz, major), 1.85 (d, 3.0H, J = 6.9 Hz, minor); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 159.8, 159.7, 149.3, 149.0, 147.0, 146.62, 146.60, 146.4, 146.2, 145.7, 145.52, 145.47, 144.2, 143.98, 143.95, 143.7, 137.1, 135.4, 135.3, 135.1, 133.6, 132.6, 132.3, 131.9, 130.8, 130.6, 130.1, 129.9, 129.7, 129.6, 128.6, 128.4, 126.8, 125.7, 125.54, 125.48, 123.2, 123.1, 121.2, 120.5, 120.0, 119.8, 64.4, 64.2, 21.92, 21.91, 21.89, 16.6, 16.2, 15.19, 15.17, one carbon missing due to overlap; IR (neat) (cm^{-1}) 2924w, 1593m, 1519m, 1343s, 1169m, 1084m; HRMS (ESI): m/z calcd for $C_{32}H_{28}N_4NaO_8S_2$ $[M+Na]^+$ 683.1241, found 683.1242.

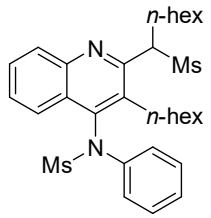


6q (major and minor)

To an oven-dried sealed tube was added ynamide **3'n** (125.4 mg, 0.40 mmol), DCM (1.0 mL,

ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 7:1~5:1 petroleum ether/EtOAc] to afford an inseparable 1.3:1.0 mixture of 4-aminoquinoline **6q** (major) (70.5 mg, 0.11 mmol) and **6q** (minor) (54.2 mg, 0.09 mmol) in 99% yield.

6q (major and minor): R_f = 0.36, 0.42 [5:1 petroleum ether/EtOAc]; white solid; mp = 264–266 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2.6H, J = 8.3 Hz, major), 7.65 (d, 2.0H, J = 8.3 Hz, minor), 7.46-7.40 (m, 8.2H), 7.29-7.25 (m, 7.6H), 7.22-7.19 (m, 2.6H, major), 6.92 (s, 2.0H, minor), 6.76 (s, 2.6H, major), 6.72 (s, 1.0H, minor), 6.67 (s, 1.3H, major), 4.84-4.78 (m, 2.3H), 2.91 (s, 3.9H, major), 2.73 (s, 3.0H, minor), 2.48-2.42 (m, 20.7H), 2.26 (s, 6.0H, minor), 2.21 (s, 7.8H, major), 1.80-1.71(m, 13.8H); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor) δ 154.1, 153.8, 149.3, 148.8, 144.8, 144.72, 144.71, 144.68, 142.8, 142.3, 141.9, 141.6, 139.4, 139.2, 138.95, 138.86, 137.2, 137.1, 134.5, 134.3, 134.1, 133.6, 132.5, 132.0, 131.0, 130.6, 130.4, 130.1, 129.9, 129.3, 129.2, 128.8, 128.1, 127.8, 127.4, 127.2, 126.4, 125.4, 125.2, 116.5, 116.3, 63.8, 63.6, 23.2, 23.1, 22.0, 21.9, 21.83, 21.81, 21.4, 16.2, 16.1, 15.6, 15.4, four carbons missing due to overlap; IR (neat) (cm^{-1}) 2921w, 1595m, 1458w, 1175s, 1162m, 1084m; HRMS (ESI): m/z calcd for $C_{36}H_{39}N_2O_4S_2$ $[M + H]^+$ 627.2346, found 627.2346.



6s (major and minor)

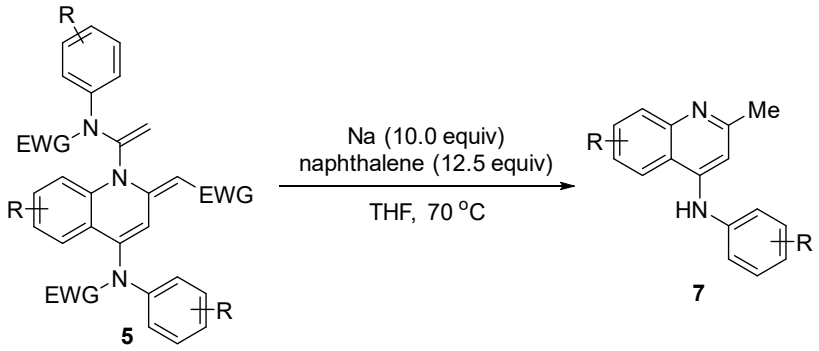
To an oven-dried sealed tube was added ynamide **3'p** (111.8 mg, 0.40 mmol), DCM (1.0 mL, ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously at 30 °C. The reaction vessel was capped and stirred at 30 °C for 0.5 h. After the reaction was judged to be complete by TLC, filtered the solution through a pad of silica gel and concentrated in vacuo. After the atropisometric ratio of the crude product was confirmed by ^{1}H NMR spectroscopy, the mixture was purified by neutral aluminum oxide column chromatography [gradient eluent: 8:1~5:1 petroleum ether/EtOAc] to afford a separable 1.2:1.0 mixture of 4-aminoquinoline **6s** (major) (40.1 mg, 0.07 mmol) and **6s** (minor) (33.8 mg, 0.06 mmol) in 66% yield.

6s (major): R_f = 0.30 [5:1 petroleum ether/EtOAc]; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 1H, J = 8.3 Hz), 7.94 (d, 1H, J = 8.2 Hz), 7.69 (t, 1H, J = 8.1 Hz), 7.57 (t, 1H, J = 8.1 Hz), 7.30 (d, 4H, J = 4.2 Hz), 7.14-7.08 (m, 1H), 4.62 (dd, 1H, J = 10.9, 3.2 Hz), 3.39 (s, 3H), 3.18-3.11 (m, 1H), 3.03 (s, 3H), 2.86-2.78 (m, 1H), 2.75-2.66 (m, 1H), 2.49-2.41 (m, 1H), 1.88-1.78 (m, 1H), 1.42-1.25 (m, 15H), 0.90-0.82 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.8, 142.4, 140.6, 138.3, 130.0, 129.8, 129.6, 128.7, 127.5, 124.8, 123.8, 119.6, 68.5, 40.1, 36.7, 31.6, 31.5, 30.9, 30.4, 29.5, 29.4, 29.3, 27.6, 22.7, 22.6, 14.2, 14.1; IR (neat) (cm^{-1}) 2923s, 1490m, 1360m, 1303s, 1157s, 1114m; HRMS (ESI): m/z calcd for $C_{30}H_{43}N_2O_4S_2$ $[M + H]^+$ 559.2659, found 559.2665.

6s (minor): R_f = 0.17 [5:1 petroleum ether/EtOAc]; white solid; mp = 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.74 (t, 1H, J = 7.2 Hz), 7.63 (t, 1H, J = 7.3 Hz), 7.31-7.27 (m, 2H), 7.22 (d, 2H, J = 7.8 Hz), 7.14 (t, 1H, J = 7.2 Hz), 4.55 (dd, 1H, J = 11.0, 3.1 Hz), 3.35 (s, 3H), 3.10-2.96 (m, 2H), 2.93 (s, 3H), 2.76-2.67 (m, 1H), 2.47-2.39 (m, 1H), 1.34-1.04 (m, 16H), 0.84-0.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 147.6, 142.7, 141.9, 137.5, 129.8, 129.7, 128.6, 128.1, 125.0, 124.7, 120.8, 68.2, 41.0, 36.6, 31.6, 31.5, 30.3, 30.1, 29.5, 29.4, 29.0, 27.6, 22.6, 22.6, 14.2, two carbons missing due to overlap; IR (neat) (cm^{-1}) 2923s, 1659w, 1495m, 1357m, 1301s, 1160s, 1133m; HRMS (ESI): m/z calcd for $C_{30}H_{43}N_2O_4S_2$ $[M + H]^+$ 559.2659, found 559.2667.

1.8 Chemical Transformation of Cycloadducts 5 and 6.[11]

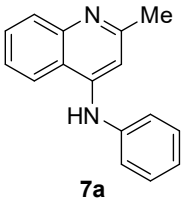
Chemical Transformation of Cycloadducts 5.



Scheme S8. Chemical transformation of cycloadducts **5**

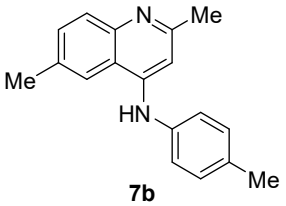
To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **5a** (81.4 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 8:1~6:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7a** (20.6 mg, 0.09 mmol) in 88% yield.

The experiment procedure is the same as above, when the substrate is changed to **5b** (86.2 mg, 0.10 mmol), 4-aminoquinoline **7a** (21.3 mg, 0.09 mmol) was obtained in 91% yield; when the substrate is changed to **5c** (87.5 mg, 0.10 mmol), 4-aminoquinoline **7a** (20.9 mg, 0.09 mmol) was afford in 89% yield; when the substrate is changed to **5e** (58.6 mg, 0.10 mmol), 4-aminoquinoline **7a** (22.3 mg, 0.10 mmol) was afford in 95% yield; when the substrate is changed to **5h** (105.1 mg, 0.10 mmol), 4-aminoquinoline **7a** (20.8 mg, 0.09 mmol) was afford in 89% yield; when the substrate is changed to **5i** (91.7 mg, 0.10 mmol), 4-aminoquinoline **7a** (21.4 mg, 0.09 mmol) was afford in 91% yield; when the substrate is changed to **5j** (86.8 mg, 0.10 mmol), 4-aminoquinoline **7a** (21.3 mg, 0.09 mmol) was afford in 91% yield; when the substrate is changed to **5n** (105.1 mg, 0.10 mmol), 4-aminoquinoline **7a** (21.5 mg, 0.09 mmol) was afford in 92% yield; when the substrate is changed to **5o** (91.7 mg, 0.10 mmol), 4-aminoquinoline **7a** (20.8 mg, 0.09 mmol) was afford in 89% yield; when the substrate is changed to **5p** (86.8 mg, 0.10 mmol), 4-aminoquinoline **7a** (20.2 mg, 0.09 mmol) was afford in 86% yield.



7a

7a: R_f = 0.38 [1:1 petroleum ether/EtOAc]; white solid; mp = 126–128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.91 (m, 2H), 7.62 (t, 1H, J = 7.2 Hz), 7.41 (t, 3H, J = 8.1 Hz), 7.31-7.28 (m, 2H), 7.18 (t, 1H, J = 7.4 Hz), 6.99 (s, 1H), 6.87 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 148.6, 147.9, 140.1, 129.8, 129.7, 129.0, 124.7, 124.6, 122.8, 119.9, 118.4, 102.5, 25.6; IR (neat) (cm^{-1}) 1602m, 1581m, 1492s, 1403m, 1299w, 1248w; HRMS (ESI): m/z calcd for $C_{16}H_{15}N_2$ $[M + H]^+$ 235.1230, found 235.1229.

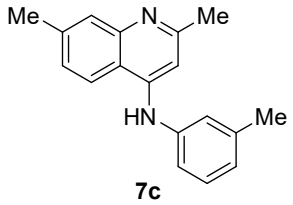


7b

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **5f** (85.6 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 5:1~3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired

product 4-aminoquinoline **7b** (23.9 mg, 0.09 mmol) in 91% yield.

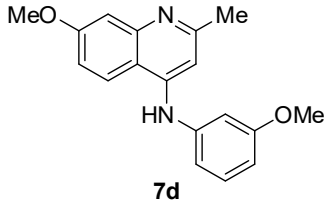
7b: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 127–128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 1H, J = 8.5 Hz), 7.64 (s, 1H), 7.47 (dd, 1H, J = 8.6, 1.8 Hz), 7.24-7.18 (m, 4H), 6.77 (s, 1H), 6.57 (s, 1H), 2.53 (s, 3H), 2.52 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 147.6, 147.3, 137.5, 134.5, 134.3, 131.6, 130.4, 129.1, 123.4, 118.7, 118.1, 102.1, 25.6, 21.9, 21.1; IR (neat) (cm^{-1}) 2919w, 1586s, 1534m, 1512s, 1401m, 1271m; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2$ $[M + H]^+$ 263.1543, found 263.1547.



7c

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **5l** (85.6 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7c** (23.5 mg, 0.09 mmol) in 90% yield.

7c: R_f = 0.25 [2:1 petroleum ether/EtOAc]; white solid; mp = 78–79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.32-7.24 (m, 2H), 7.13-7.10 (m, 2H), 7.00 (d, 1H, J = 7.5 Hz), 6.79 (s, 1H), 6.77 (s, 1H), 2.54 (s, 3H), 2.50 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 148.7, 147.9, 140.1, 139.9, 139.8, 129.6, 128.2, 126.8, 125.4, 123.4, 119.8, 119.5, 116.2, 102.0, 25.5, 21.8, 21.7; IR (neat) (cm^{-1}) 2919w, 1584s, 1538m, 1452m, 1395m, 1283w; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2$ $[M + H]^+$ 263.1543, found 263.1549.

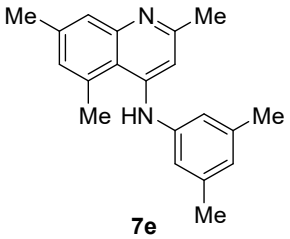


7d

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **5m** (90.3 mg, 0.10 mmol) in THF (1.0 mL) to this reaction

mixture, then heated to 70 °C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7d** (27.3 mg, 0.09 mmol) in 93% yield.

7d: R_f = 0.13 [2:1 petroleum ether/EtOAc]; white solid; mp = 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 1H, J = 9.1 Hz), 7.33-7.29 (m, 2H), 7.07 (dd, 1H, J = 9.2, 2.5 Hz), 6.89-6.83 (m, 3H), 6.72 (dd, 1H, J = 8.3, 1.7 Hz), 6.65 (s, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.8, 159.9, 150.7, 147.6, 141.5, 130.5, 121.1, 117.2, 114.7, 113.0, 109.7, 108.3, 107.6, 102.0, 55.6, 55.5, 25.6; IR (neat) (cm^{-1}) 2923w, 1582s, 1463s, 1328m, 1218m, 1035m; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O_2$ $[M + H]^+$ 295.1441, found 295.1449.

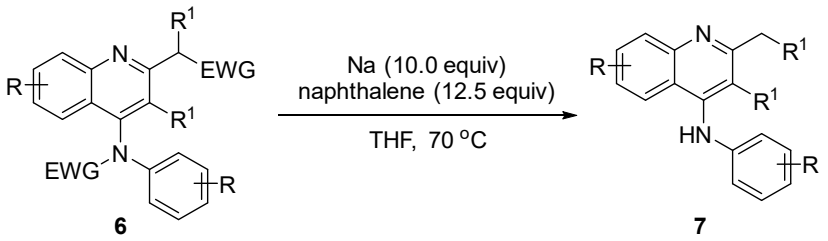


7e

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **5r** (89.8 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7e** (23.6 mg, 0.08 mmol) in 81% yield.

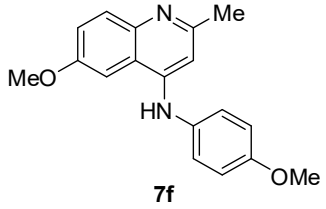
7e: R_f = 0.41 [1:1 petroleum ether/EtOAc]; white solid; mp = 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.98 (s, 1H), 6.86 (s, 2H), 6.81 (s, 1H), 6.79 (s, 1H), 6.72 (s, 1H), 2.94 (s, 3H), 2.50 (s, 3H), 2.43 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.2, 150.4, 140.4, 139.7, 138.7, 132.2, 130.4, 127.3, 126.1, 120.3, 117.0, 104.3, 25.2, 24.9, 21.5, 21.4; IR (neat) (cm^{-1}) 1602m, 1561w, 1492s, 1403m, 1300w, 1248w; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2$ $[M + H]^+$ 291.1856, found 291.1857.

Chemical Transformation of Cycloadducts 6.



Scheme S9. Chemical transformation of cycloadducts **6**

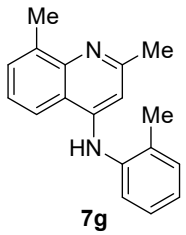
To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6a** (54.3 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 5.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 8:1~6:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7a** (21.6 mg, 0.09 mmol) in 92% yield.



7f

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6b** (60.3 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 2.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 3:1~1:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7f** (27.2 mg, 0.09 mmol) in 92% yield.

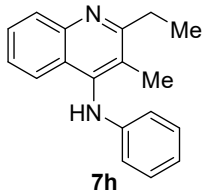
7f: R_f = 0.21 [1:1 petroleum ether/EtOAc]; white solid; mp = 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, 1H, J = 9.2 Hz), 7.31-7.28 (m, 1H), 7.25-7.22 (m, 2H), 7.17 (d, 1H, J = 2.2 Hz), 6.98 (d, 2H, J = 8.8 Hz), 6.77-6.56 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.8, 148.6, 132.8, 130.3, 126.0, 121.2, 118.4, 115.1, 102.1, 99.1, 55.8, 55.7, 25.1, two carbons missing due to overlap, overlapped signals at 126.0 and 115.1 ppm; IR (neat) (cm^{-1}) 2924w, 1589m, 1530m, 1511s, 1464w, 1414w, 1243m; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O_2$ [M + H]$^+$ 295.1441, found 295.1439.



7g

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6c** (57.1 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7g** (25.0 mg, 0.10 mmol) in 95% yield.

7g: R_f = 0.45 [5:1 petroleum ether/EtOAc]; white solid; mp = 137–138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 1H, J = 8.3 Hz), 7.51 (d, 1H, J = 6.9 Hz), 7.35-7.24 (m, 4H), 7.21-7.17 (m, 1H), 6.39 (s, 1H), 6.33 (s, 1H), 2.79 (s, 3H), 2.54 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 148.2, 147.9, 138.4, 137.3, 133.4, 131.5, 129.7, 127.3, 125.9, 125.4, 124.1, 117.9, 117.3, 102.3, 26.1, 18.9, 18.0; IR (neat) (cm^{-1}) 2920w, 1586m, 1526s, 1492m, 1385m, 1256m; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2$ $[M + H]^+$ 263.1543, found 263.1549.



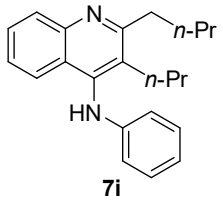
7h

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6d** (57.2 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 6:1~5:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7h** (25.2 mg, 0.10 mmol) in 96% yield.

The experiment procedure is the same as above, when the substrate is changed to **6h** (60.3 mg, 0.10 mmol), 4-aminoquinoline **7h** (23.9 mg, 0.09 mmol) was afford in 91% yield; when the substrate is changed to **6i** (61.2 mg, 0.10 mmol), 4-aminoquinoline **7h** (23.9 mg, 0.09 mmol) was afford in 91%

yield; when the substrate is changed to **6j** (63.3 mg, 0.10 mmol), 4-aminoquinoline **7h** (24.1 mg, 0.09 mmol) was afford in 92% yield; when the substrate is changed to **6m** (72.9 mg, 0.10 mmol), 4-aminoquinoline **7h** (22.9 mg, 0.09 mmol) was afford in 87% yield.

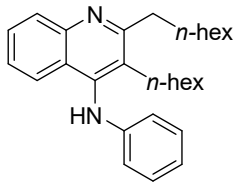
7h: R_f = 0.36 [5:1 petroleum ether/EtOAc]; white solid; mp = 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 1H, J = 8.4 Hz), 7.82 (dd, 1H, J = 8.4, 0.6 Hz), 7.62-7.58 (m, 1H), 7.38- 7.34(m, 1H), 7.20 (t, 2H, J = 7.9 Hz), 6.86 (t, 1H, J = 7.4 Hz), 6.65 (d, 2H, J = 7.7 Hz), 5.92 (s, 1H), 3.05 (q, 2H, J = 7.5 Hz), 2.31 (s, 3H), 1.38 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 147.4, 145.1, 143.1, 129.5, 129.2, 128.7, 125.6, 124.0, 123.2, 122.9, 120.2, 115.8, 30.6, 14.3, 13.3; IR (neat) (cm^{-1}) 1597m, 1491s, 1370w, 1299m, 1254m, 1046w; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2$ [M + H]$^+$: 263.1543; found 263.1542.



7i

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6e** (62.7 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 15:1~10:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7i** (26.9 mg, 0.09 mmol) in 85% yield.

7i: R_f = 0.61 [5:1 petroleum ether/EtOAc]; white solid; mp = 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 8.4 Hz), 7.77-7.74 (m, 1H), 7.59-7.55 (m, 1H), 7.32-7.27 (m, 1H), 7.19-7.14 (m, 2H), 6.87-6.83 (m, 1H), 6.65-6.62 (m, 2H), 5.81 (s, 1H), 3.03-2.99 (m, 2H), 2.77-2.73 (m, 2H), 1.84-1.77 (m, 2H), 1.61-1.46 (m, 4H), 0.99 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 147.7, 145.9, 143.4, 129.4, 129.1, 128.7, 128.1, 125.3, 124.1, 123.9, 120.2, 115.9, 36.6, 32.4, 30.1, 23.7, 23.3, 14.7, 14.2; IR (neat) (cm^{-1}) 2957s, 1602s, 1511s, 1402m, 1321w, 1258m; HRMS (ESI): m/z calcd for $C_{22}H_{27}N_2$ [M + H]$^+$ 319.2169, found 319.2170.

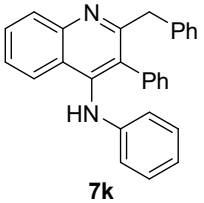


7j

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6f** (71.1 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 10:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7j** (33.6 mg, 0.08 mmol) in 83% yield.

The experiment procedure is the same as above, when the substrate is changed to **6s** (55.9 mg, 0.10 mmol), to afford 4-aminoquinoline **7j** (36.8 mg, 0.09 mmol) in 91% yield.

7j: R_f = 0.72 [2:1 petroleum ether/EtOAc]; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 8.4 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.59-7.55 (m, 1H), 7.32-7.28 (m, 1H), 7.18-7.14 (m, 2H), 6.85 (t, 1H, J = 7.4 Hz), 6.63 (d, 2H, J = 7.7 Hz), 5.80 (s, 1H), 3.00 (t, 2H, J = 8.0 Hz), 2.76 (t, 2H, J = 8.2 Hz), 1.85-1.77 (m, 2H), 1.55-1.44 (m, 4H), 1.43-1.25(m, 12H), 0.90-0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 147.6, 145.9, 143.4, 129.4, 129.1, 128.7, 128.4, 125.3, 124.1, 124.0, 120.2, 115.9, 36.9, 32.0, 31.7, 30.3, 30.1, 29.8, 29.4, 28.0, 22.8, 22.7, 14.3, 14.2, one carbon missing due to overlap, overlapped signal at 30.3 ppm; IR (neat) (cm^{-1}) 1602m, 1561w, 1492s, 1403m, 1378m, 1300w; HRMS (ESI): m/z calcd for $C_{28}H_{39}N_2$ $[M + H]^+$ 403.3108, found 403.3111.

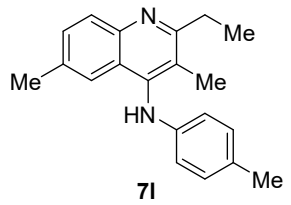


7k

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6g** (69.4 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 4:1~3:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7k** (36.7 mg, 0.10 mmol) in 95% yield.

7k: R_f = 0.52 [5:1 petroleum ether/EtOAc]; white solid; mp = 41–42 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 1H, J = 8.4 Hz), 7.68-7.63 (m, 2H), 7.39-7.27 (m, 4H), 7.16-7.08 (m, 5H), 7.02-7.00 (m, 2H), 6.93-6.89 (m, 3H), 6.67 (d, 2H, J = 7.9 Hz), 5.61 (s, 1H), 4.14 (s, 2H); ^{13}C NMR (100 MHz,

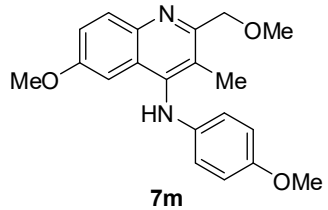
$CDCl_3$) δ 159.9, 148.5, 145.12, 145.06, 139.4, 135.5, 130.3, 129.7, 129.4, 129.2, 129.0, 128.3, 128.1, 126.8, 126.0, 125.4, 125.1, 122.0, 121.5, 118.8, 43.8, one carbon missing due to overlap, overlapped signal at 129.2 ppm; IR (neat) (cm^{-1}) 2291w, 1580m, 1488s, 1402m, 1369w, 1246w; HRMS (ESI): m/z calcd for $C_{28}H_{23}N_2$ $[M + H]^+$ 387.1856, found 387.1859.



7l

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6k** (59.9 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^oC and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 10:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7l** (26.7 mg, 0.09 mmol) in 92% yield.

7l: R_f = 0.38 [5:1 petroleum ether/EtOAc]; oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, J = 8.5 Hz), 7.57 (s, 1H), 7.42 (dd, 1H, J = 8.6, 1.9 Hz), 7.00 (d, 2H, J = 8.1 Hz), 6.57 (d, 2H, J = 8.4 Hz), 5.90 (s, 1H), 3.01 (q, 2H, J = 7.6 Hz), 2.41 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 1.36 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 145.8, 143.1, 142.7, 135.3, 130.9, 129.9, 129.5, 128.8, 123.9, 122.8, 121.5, 115.9, 30.3, 21.9, 20.7, 14.4, 13.3; IR (neat) (cm^{-1}) 1614m, 1502s, 1494m, 1385m, 1296w, 1254w; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2$ $[M + H]^+$ 291.1856, found 291.1859.

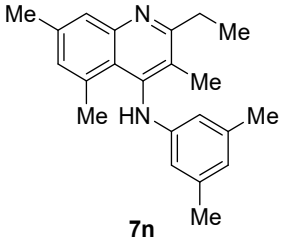


7m

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6l** (63.1 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^oC and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 10:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product

4-aminoquinoline **7m** (29.3 mg, 0.09 mmol) in 91% yield.

7m: R_f = 0.18 [5:1 petroleum ether/EtOAc]; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 1H, J = 9.1 Hz), 7.23 (dd, 1H, J = 9.1, 2.8 Hz), 7.02 (d, 1H, J = 2.8 Hz), 6.78 (d, 2H, J = 9.0 Hz), 6.66 (d, 2H, J = 9.0 Hz), 5.85 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.99 (q, 2H, J = 7.5 Hz), 2.27 (s, 3H), 1.35 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 156.9, 154.2, 143.6, 143.1, 138.5, 130.4, 123.9, 121.5, 120.8, 118.4, 114.7, 101.7, 55.8, 55.5, 30.2, 14.1, 13.4; IR (neat) (cm^{-1}) 1622m, 1509s, 1463w, 1229s, 1179w, 1034m; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2O_2$ $[M + H]^+$ 323.1754, found 323.1762.

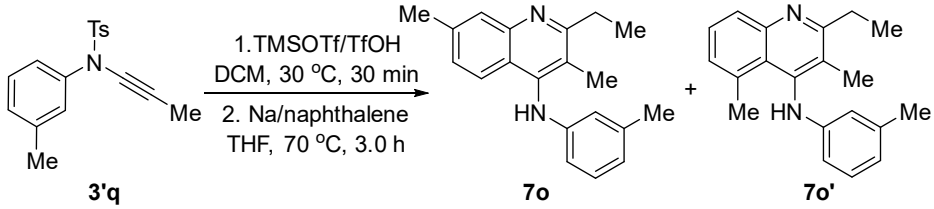


7n

To an oven-dried sealed tube was added sodium metal (23.0 mg, 1.00 mmol), naphthalene (160.1 mg, 1.25 mmol), and THF (1.5 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of **6q** (62.7 mg, 0.10 mmol) in THF (1.0 mL) to this reaction mixture, then heated to 70 ^{o}C and stirred for 7.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [gradient eluent: 4:1~2:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7n** (30.1 mg, 0.09 mmol) in 94% yield.

7n: R_f = 0.5 [5:1 petroleum ether/EtOAc]; white solid; mp = 158–159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.00 (s, 1H), 6.45 (s, 1H), 6.10 (s, 2H), 5.63 (s, 1H), 2.99 (q, 2H, J = 7.6 Hz), 2.68 (s, 3H), 2.44 (s, 3H), 2.23 (s, 3H), 2.18 (s, 6H), 1.36 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 149.4, 145.5, 143.9, 139.3, 138.0, 133.2, 131.6, 127.3, 125.8, 123.1, 121.3, 112.3, 30.4, 24.2, 21.6, 21.4, 14.1, 13.1; IR (neat) (cm^{-1}) 1604s, 1585m, 1451w, 1333w, 1180m, 1105w; HRMS (ESI): m/z calcd for $C_{22}H_{27}N_2$ $[M + H]^+$ 319.2169, found 319.2172.

One-Pot Synthesis of 4-Aminoquinolines 7o and 7o'.

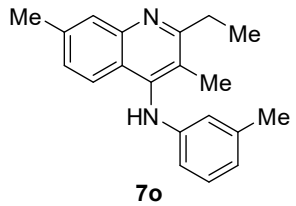


3'q **7o** **7o'**

Scheme S10. One-pot synthesis of 4-aminoquinolines **7o** and **7o'**

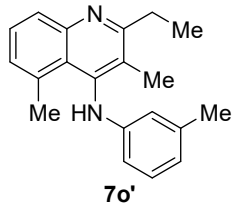
To an oven-dried sealed tube was added ynamide **3'q** (119.8 mg, 0.40 mmol), DCM (1.0 mL,

ynamide *concn* = 0.40 *M*). Then TMSOTf (43.5 μL, 0.24 mmol) and TfOH (7.1 μL, 0.08 mmol) were added simultaneously 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, filtered the solution through a pad of silica gel, concentrated in vacuo, and the crude product was directly for the next step. To an oven-dried sealed tube was added sodium metal (46.0 mg, 2.00 mmol), naphthalene (320.4 mg, 2.5 mmol) and THF (3.0 mL) at room temperature and stirred for 1.0 h. After the intense green color was observed, added a solution of the crude product in THF (2.0 mL) to this reaction mixture, then heated to 70 °C and stirred for 3.0 h. After completed the reaction, the mixture was quenched by addition of a small amount of water and filtered over a celite pad. Then the solvent was concentrated under the reduced pressure and the residue was purified by flash silica gel column chromatrography [eluent: 8:1 petroleum ether/EtOAc/3% Et_3N] to afford the desired product 4-aminoquinoline **7o** (32.8 mg, 0.11 mmol) and **7o'** (21.5 mg, 0.07 mmol) in 56% and 37% yield, respectively.



7o

7o: R_f = 0.50 [5:1 petroleum ether/EtOAc]; white solid; mp = 41–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.70 (d, 1H, J = 8.5 Hz), 7.19 (dd, 1H, J = 8.5, 1.4 Hz), 7.07 (t, 1H, J = 7.8 Hz), 6.68 (d, 1H, J = 7.5 Hz), 6.49 (s, 1H), 6.43 (d, 1H, J = 8.0 Hz), 5.84 (s, 1H), 3.03 (q, 2H, J = 7.6 Hz), 2.50 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H), 1.37 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 147.6, 145.1, 143.2, 139.4, 138.8, 129.3, 128.3, 127.7, 122.7, 122.2, 121.9, 121.1, 116.6, 112.9, 30.5, 21.8, 21.7, 14.2, 13.3; IR (neat) (cm^{-1}) 3362w, 2922s, 2851m, 1633m, 1470m, 1301w, 1188w; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2$ $[M + H]^+$ 291.1856, found 291.1856.



7o'

7o': R_f = 0.52 [5:1 petroleum ether/EtOAc]; white solid; mp = 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 1H, J = 8.2 Hz), 7.49-7.45 (m, 1H), 7.18 (d, 1H, J = 7.0 Hz), 7.07 (t, 1H, J = 7.8 Hz), 6.42 (d, 1H, J = 7.5 Hz), 6.35 (s, 1H), 6.29 (dd, 1H, J = 8.0, 2.4 Hz), 5.79 (s, 1H), 3.03 (q, 2H, J = 7.5 Hz), 2.75 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H), 1.38 (t, 3H, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 149.1, 145.4, 143.9, 139.6, 133.5, 129.5, 129.4, 128.3, 128.2, 126.6, 125.2, 120.4, 115.3, 111.7, 30.4, 24.4, 21.8, 14.3, 13.1; IR (neat) (cm^{-1}) 2922s, 1659m, 1633m, 1470m, 1425w, 1191w; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2$ $[M + H]^+$: 291.1856; found 291.1854.

1.9 X-Ray Crystal Structures of 4a, 5a and 6a.

The relative configuration of the **4a** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of **4a** in petroleum ether/acetone at room temperature. A colorless crystal of approximate dimensions 0.16 x 0.1 x 0.07 mm was selected and collected by an Agilent Xcalibur Eos Gemini diffractometer. The crystal was kept at 273 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.

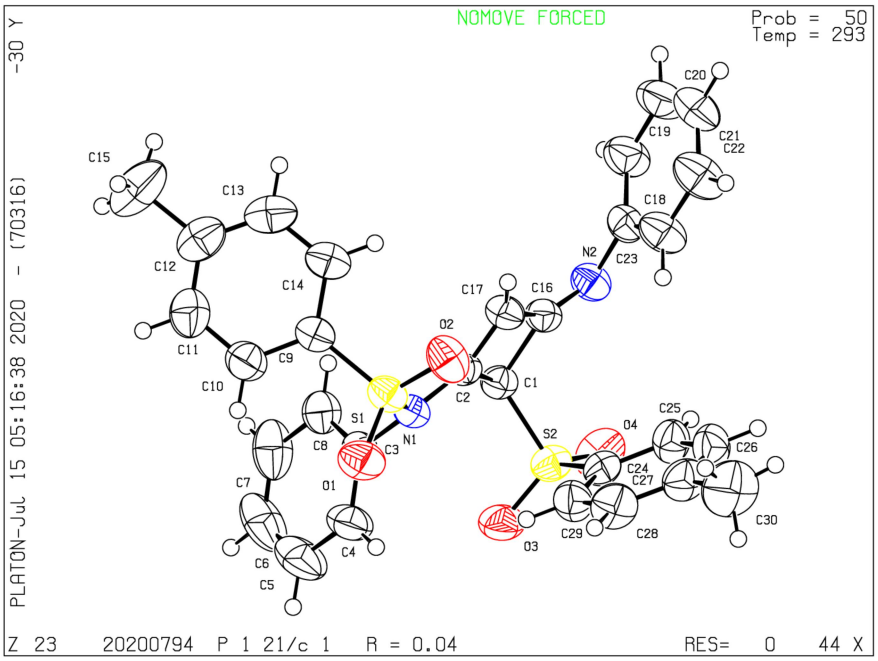


Figure S1. The thermal ellipsoid plot of **4a**.

The relative configuration of the **5a** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of **5a** in petroleum ether/DCM at room temperature. A colorless crystal of approximate dimensions 0.15 x 0.1 x 0.05 mm was selected and collected by an Agilent Xcalibur Eos Gemini diffractometer. The crystal was kept at 273 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.

The relative configuration of the **6a** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of **6a** in petroleum ether/EtOAc at room temperature. A colorless crystal of approximate dimensions 0.15 x 0.12 x 0.08 mm was selected and collected by an Agilent Xcalibur Eos Gemini diffractometer. The crystal was kept at 273 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.

Table S2. Crystal Data and Structure Refinement for 4a.

Empirical formula	$C_{30}H_{26}N_2O_4S_2$
Formula weight	542.65
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.8339(3)
b/Å	12.30923(16)
c/Å	16.3416(3)
α/°	90
β/°	113.684(2)
γ/°	90
Volume/Å^3	2732.55(10)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	2.081
F(000)	1136.0
Crystal size/mm^3	0.16 × 0.1 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.302 to 134.126
Index ranges	$-17 \le h \le 16$, $-9 \le k \le 14$, $-19 \le l \le 17$
Reflections collected	10154
Independent reflections	4869 [R_{int} = 0.0238, R_{sigma} = 0.0334]
Data/restraints/parameters	4869/0/345
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1191
Final R indexes [all data]	R_1 = 0.0552, wR_2 = 0.1295
Largest diff. peak/hole / e Å^{-3}	0.27/-0.29

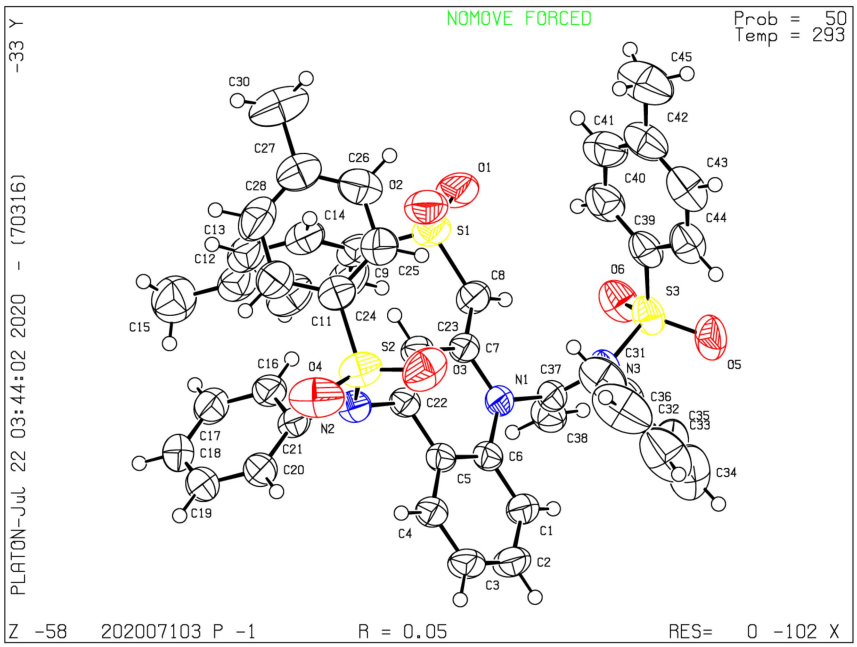


Figure S2. The thermal ellipsoid plot of **5a**.

Table S3. Crystal Data and Structure Refinement for 5a.

Empirical formula	$C_{45}H_{39}N_3O_6S_3$
Formula weight	813.97
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.7191(7)
b/Å	13.8788(10)
c/Å	14.3563(9)
α/°	82.141(5)
β/°	76.913(5)
γ/°	69.117(6)
Volume/Å^3	2120.9(3)
Z	2
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	2.011
F(000)	852.0
Crystal size/mm^3	0.15 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.83 to 134.194
Index ranges	-8 ≤ h ≤ 14, -16 ≤ k ≤ 16, -16 ≤ l ≤ 17
Reflections collected	15356
Independent reflections	7565 [R_{int} = 0.0339, R_{sigma} = 0.0548]
Data/restraints/parameters	7565/0/517
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1135
Final R indexes [all data]	R_1 = 0.0808, wR_2 = 0.1324
Largest diff. peak/hole / e Å^{-3}	0.20/-0.31

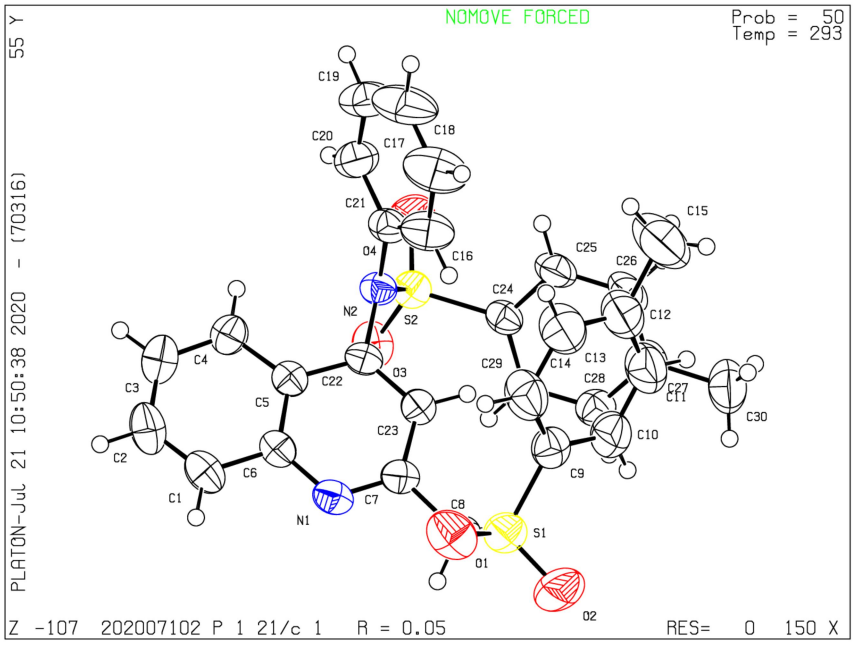


Figure S3. The thermal ellipsoid plot of **6a**.

Table S4. Crystal Data and Structure Refinement for 6a.

Empirical formula	$C_{30}H_{26}N_2O_4S_2$
Formula weight	542.65
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.4850(4)
b/Å	19.8890(6)
c/Å	10.2754(3)
α/°	90
β/°	98.645(3)
γ/°	90
Volume/Å^3	2724.59(15)
Z	4
ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	2.087
F(000)	1136.0
Crystal size/mm^3	0.15 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.63 to 134.158
Index ranges	$-9 \le h \le 16$, $-23 \le k \le 23$, $-12 \le l \le 12$
Reflections collected	10589
Independent reflections	4851 [R_{int} = 0.0294, R_{sigma} = 0.0377]
Data/restraints/parameters	4851/0/345
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1221
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.1357
Largest diff. peak/hole / e Å^{-3}	0.25/-0.32

1.10 Protocols for Biological Tests

Anti-SARS-CoV-2 Test

Preliminary screening of antiviral activity of compounds: We tested the newly synthesized aminocyclobutenes and 4-aminoquinolines for their bioactivity as anti-SARS-CoV-2 agents. GFP signal of recombinant SARS-CoV-2 GFP/ΔN virus-like-particles[12] with transcription and replication-competent (SARS-CoV-2 GFP/ΔN trVLP) was observed by fluorescence microscopy to detect the replication of virus. Briefly, human colorectal adenocarcinoma cells (Caco2-N) were seeded into 24-well culture plates (5 x 10^4 cells/well) and cultured at 37 °C for 24 h. One hour prior to infection, cells were treated with diluted compounds with a final concentration of 5.0 μM. Next, 20 μM of SARS-CoV-2 GFP/△N trVLP (multiplicity of infection, MOI = 0.6) solution was added into each well and continued incubated for 48 h. After post-infection, the levels of GFP in

SARS-CoV-2 GFP/△N trVLP-exposed cells were observed using fluorescence microscopy, and the result showed that compounds **4a**, **4f**, **4g**, **4j**, **4l**, **4m**, **4o**, **4r**, **7l**, **7m**, and **7p** exhibited antiviral activity at 5.0 μM.

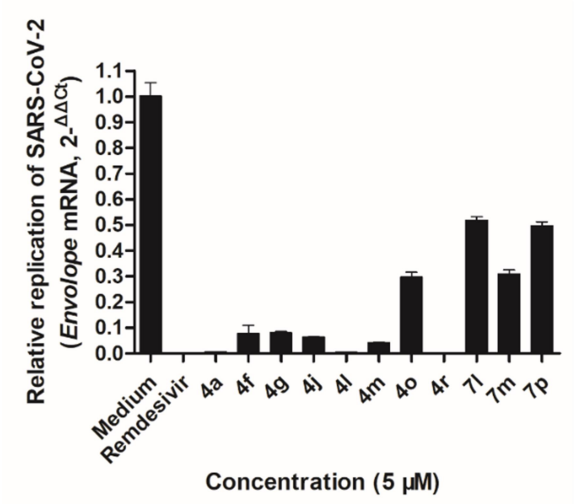


Figure S4. The relative replication ability of SARS-CoV-2.

Confirmation of antiviral activity of compounds: Through preliminary screening, the antiviral activity of compounds **4a**, **4f**, **4g**, **4j**, **4l**, **4m**, **4o**, **4r**, **7l**, **7m**, and **7p** next to be confirmed. Remdesivir was used as the positive control drug, and the expression of *envelope* gene of SARS-CoV-2 was detected by quantitative real-time polymerase chain reaction (qRT-PCR) to confirm antiviral activity of these compounds at the concentration of 5.0 μM. Briefly, Caco2-N cells were seeded into 24-well culture plates (6.0 x 10^4 cells/well) and added 300 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^{o}C for 24 h. One hour prior to infection, the medium was removed from each well, 200 μL of compounds solution with a concentration of 5.0 μM were added into each well. After incubation, 30 μL of SARS-CoV-2 GFP/△N trVLP was added into each well and the final concentration of all compounds was 5.0 μM. After post-infection for 24 h, changed the medium and washed away the free virus to incubate for another 48 h. Then, cells were harvested and digested, and the extracted total RNA was reverse transcribed into cDNA. Finally, the expression of *envelope* gene of SARS-CoV-2 was detected via qRT-PCR, and glyceraldehyde-3-phosphate dehydrogenase (GAPDH) was used as the reference gene to calculate the relative replication ability of the virus. The result showed that compounds **4a**, **4f**, **4g**, **4j**, **4l**, **4m**, **4o**, and **4r** exhibited obvious antiviral activity at 5.0 μM (Figure S4).

Cytotoxicity of compounds against human Caco-2-N cells: After confirming the antiviral activity of compounds **4a**, **4f**, **4g**, **4j**, **4l**, **4m**, **4o**, and **4r**, remdesivir was used as the positive control drug, and the cytotoxicity of these compounds was determined by MTT assay after culture of Caco-2-N cells and serially diluted compounds. Briefly, Caco2-N cells were seeded into 96-well

culture plates (8.0 x 10^3 cells/well) and added 100 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^oC for 24 h. Then, 100 μL of compounds solution (0.2 μM, 1.0 μM, 5.0 μM, 25.0 μM) were added into each well and incubated for 48 h, at the same time, set control group without compounds. After 48 h, 100 μL of cell culture supernatants were removed from each well, 20 μL of MTT solution (5 mg/mL in PBS) was added into each well and incubated at 37 ^oC for 4 h. After incubation, 100 μL of the supernatants were discarded and 100 μL of DMSO was added into each well to solubilize the formazan crystals by shaking. The absorbance values were read at 595 nm wavelength with ELISA microplate reader. CC_{50} values (50% cytotoxic concentration) were calculated using GraphPad Prism software 8.0 (Table S5), and the result showed that compounds **4a**, **4m**, **4o**, and **4r** exhibited low cytotoxicity.

Table S5. Cytotoxicity and Anti-SARS-CoV-2 Activity of Representative Compounds 4.[a]

Compd	[b]CC_{50} (μM)	[c]EC_{50} (μM)
4a	417.18 ± 22.12	0.05 ± 0.01
4f	4.21 ± 0.63	n.d.
4g	4.62 ± 0.15	n.d.
4j	12.77 ± 0.69	n.d.
4l	12.26 ± 0.83	0.10 ± 0.00
4m	> 450	0.14 ± 0.03
4o	> 25	n.d.
4r	19.21 ± 4.73	0.14 ± 0.00
Remdesivir	> 125	0.03 ± 0.01

[a]Each value represents the average results from three independent experiments. [b]CC_{50}: 50% cytotoxic concentration. [c]EC_{50}: 50% effective concentration. n.d.: EC_{50} not determined.

The antiviral activity of compounds 4a, 4l, 4m, and 4r: Based on these result, compounds **4a**, **4m**, and **4r** all exhibited good antiviral activity (at 5.0 μM) and low cytotoxicity, compound **4l** exhibited good antiviral activity (at 5.0 μM) and slightly higher cytotoxicity, therefore, further antiviral assay of these compounds was tested. Remdesivir was used as the positive control drug, and the expression of *envelope* gene of SARS-CoV-2 was detected by qRT-PCR at different concentrations of these compounds. Briefly, Caco2-N cells were seeded into 24-well culture plates (6.0 x 10^4 cells/well) and added 300 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^oC for 24 h. One hour prior to infection, the medium was removed from each well, 200 μL of compounds solution were added into each well. After incubation, 30 μL of SARS-CoV-2 GFP/△N trVLP was added into each well and incubated for 24 h, and the final concentrations of all compounds were 0.0 μM, 0.04 μM, 0.2 μM, 1.0 μM, and 5.0 μM. After 24 h, changed the medium and washed away the free virus to incubate for another 48 h. Then, cells were harvested and digested, and the extracted total RNA was reverse transcribed into cDNA. Finally, the expression of *envelope* gene of SARS-CoV-2 was detected by qRT-PCR, and GAPDH was used as the reference gene to calculate

the relative replication ability of the virus. EC_{50} values (50% effective concentration) were calculated using GraphPad Prism software 8.0 (Table S5), and the result showed that compound **4a** exhibited the best antiviral activity, second only to redesivir.

Anti-DENV-2 Test

Preliminary screening of antiviral activity: We then tested aminocyclobutenes and 4-aminoquinolines for their bioactivity as anti-DENV-2 agents. 100 μL of ribavirin was used as the positive control drug, and the expression of 3'-UTR gene of DENV-2 was detected by qRT-PCR. The antiviral activity of these compounds was preliminarily screened at the concentration of 50.0 μM. The primer sequences of 3'-UTR gene are exhibited in Table S6. Briefly, african green monkey kidney cells (vero) were seeded into 24-well culture plates (2.0 x 10^5 cells/well) and added 600 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^oC for 24 h. After incubation, the medium was removed from each well, 100 μL of DMEM/10%FBS/1%Pen/Strep and 100 μL of DENV-2 (16681) virus stock solution were added into each well and incubated for 4 h. After post-infection for 4 h, washed away the free virus, and 600 μL of diluted compounds solution were added into each well with a final concentration of 50.0 μM and continued incubated for 48 h. After incubation, the cells were harvested and digested, and the extracted total RNA was reverse transcribed into cDNA. Finally, the expression of 3'-UTR gene of DENV-2 was detected by qRT-PCR, and GAPDH was used as the reference gene to calculate the relative replication ability of the virus (Figure S5), and the result showed that compounds **4a**, **4f**, **4h**, **4i**, **4j**, and **4p** exhibited antiviral activity at 50.0 μM.

Table S6. The Primer Sequences of 3'-UTR Gene.

primer	primer sequences（5'—3'）
DENV- F	GCATATTGACGCTGGGAGAGA
DENV- R	GGCGTTCTGTGCCTGGAAT

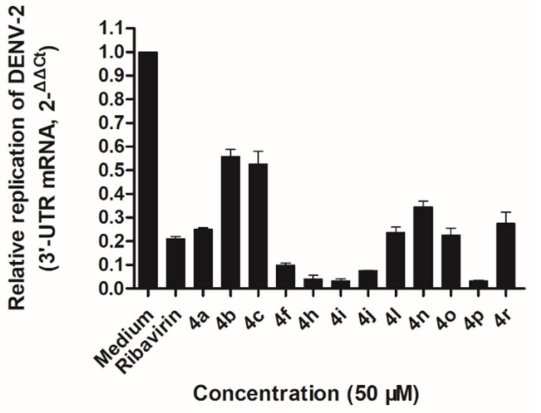


Figure S5. The relative replication ability of DENV-2.

Cytotoxicity of compounds against vero cells: After preliminary screening the antiviral activity,

the cytotoxicity of compounds **4a**, **4f**, **4h**, **4i**, **4j**, and **4p** was determined by MTT assay after culture of vero cells and serially diluted compounds. Briefly, vero cells were seeded into 96-well culture plates (2.5 x 10^4 cells/well) and added 200 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^oC for 24 h. After incubation, culture medium was removed from each well, fresh medium and serially diluted compounds with different concentrations were added into each well and incubated for 48 h, at the same time, set control group without compounds. After 48 h, 100 μL of culture medium were removed from each well, 10 μL of MTT solution (5 mg/mL in PBS) was added into each well and incubated at 37 ^oC for 4 h. After incubation, 100 μL of the supernatants were discarded and 100 μL of DMSO was added into each well to solubilize the formazan crystals by shaking. The absorbance values were read at 595 nm wavelength with ELISA microplate reader. CC_{50} values were calculated using GraphPad Prism software 8.0 (Table S7), and the result showed that except for **4f**, compounds **4a**, **4h**, **4i**, **4j**, and **4p** all exhibited low cytotoxicity.

Table S7. Cytotoxicity and Anti-DENV-2 Activity of Representative Compounds 4.[a]

Compd	CC_{50} (μM)	EC_{50} (μM)
4a	651.95 ± 6.20	3.93 ± 0.06
4f	11.05 ± 0.83	6.82 ± 1.07
4h	167.02 ± 10.62	4.22 ± 0.04
4i	207.92 ± 17.61	5.51 ± 0.56
4j	658.88 ± 4.61	5.32 ± 0.04
4p	556.99 ± 17.21	4.87 ± 0.45
Ribavirin	560.15 ± 43.43	4.24 ± 0.87

[a]Each value represents the average results from three independent experiments.

The antiviral activity of compounds 4a, 4f, 4h, 4i, 4j, and 4p: Based on these results, except for **4f** (obvious antiviral activity but slightly higher cytotoxicity), compounds **4a**, **4h**, **4i**, **4j**, and **4p** all showed obvious antiviral activity (at 50.0 μM) and low cytotoxicity, therefore, further antiviral assay of these compounds was tested. Ribavirin was used as the positive control drug, and the expression of 3'-UTR gene of DENV-2 was detected by qRT-PCR at different concentrations of these compounds. Briefly, vero cells were seeded into 24-well culture plates (2.0 x 10^5 cells/well) and added 600 μL of DMEM/10%FBS/1%Pen/Strep, incubated at 37 ^oC for 24 h. After incubation, the medium was removed from each well, 100 μL of DMEM/10%FBS/1%Pen/Strep and 100 μL of DENV-2 (16681) virus stock solution were added into each well and incubated for 4 h. After washing and removal of the free virus, 600 μL of diluted compounds solution were added into each well and incubated for 48 h, the final concentrations of all compounds were 0.0 μM, 2.0 μM, 10.0 μM, 50.0 μM. After incubation, the cells were harvested and digested, and the extracted total RNA was reverse transcribed into cDNA. Finally, the expression of 3'-UTR gene of DENV-2 was detected

by qRT-PCR, and GAPDH was used as the reference gene to calculate the relative replication ability of the virus. EC_{50} values were calculated using GraphPad Prism software 8.0 (Table S7), and the result showed that compound **4a** exhibited the best antiviral activity.

Antitumor Test

Preliminary screening of antitumor activity: We also tested aminocyclobutenes and 4-aminoquinolines for their bioactivity as antitumor agents. First, the cytotoxic effects of these compounds were evaluated against hepatocellular carcinoma cells HepG2, lung cancer cells A549 and breast cancer cells MCF-7 based on cell cytotoxicity assays, using a commercially available proliferation assay kit (CCK-8). Briefly, the cancer cells in logarithmic growth phase were seeded into 96-well culture plates (5 x 10^4 cells/well) and cultured 4-8 h at 37 ^oC and 5% CO_2 atmosphere in culture medium. Then treated with 10 μL of vehicle (control group without compounds) or compounds of different concentrations for 48 h. After incubation, the medium was removed from each well, 100 μL of WST-8 solution (10%) was added into each well and incubated for another 1-4 h. The absorbance values were read at 450 nm wavelength with ELISA microplate reader. IC_{50} values (compound concentrations required to inhibit tumor cell viability by 50%) were calculated using GraphPad Prism software 8.0. As shown in Table S8, compounds **4b**, **4g**, **7b**, **7d**, **7e**, **7l**, **7m**, and **7o'** all exhibited obvious inhibitory effect on these cancer cells.

Based on this result, vincristine was used as the positive control drug and the cytotoxic effects of compounds **4b**, **4g**, **7b**, **7d**, **7e**, **7l**, **7m**, and **7o'** were evaluated against a panel of human cancer cells, including hepatocellular carcinoma cells HepG2, lung cancer cells A549, breast cancer cells MCF-7, bladder cancer cells 5637, glioblastoma cells A172, malignant melanoma cells A375, cervical carcinoma cell lines C33A and Hela, colon cancer cells lines HCT116 and SW480, pancreatic cancer cells CFPAC-1, and normal human renal epithelial cells 293T based on cell cytotoxicity assays, using CCK-8 assay. Briefly, the cancer cells in logarithmic growth phase were seeded into 96-well culture plates (5 x 10^4 cells/well) and cultured 4-8 h at 37 ^oC and 5% CO_2 atmosphere in culture medium. Then treated with 10 μL of vehicle (control group without compounds) or compounds of different concentrations for 48 h. After incubation, the medium was removed from each well, 100 μL of WST-8 solution (10%) was added into each well and incubated for another 1-4 h. The absorbance values were read at 450 nm wavelength with ELISA microplate reader. IC_{50} values were calculated using GraphPad Prism software 8.0. As shown in (Table S9), the tested compounds all exhibited notable inhibitory effect on this panel of cancer cells proliferation. Particularly, compound **7d** showed the most significant inhibitory effect on A172 cells.

Table S8. The Antitumor Activities of Compounds against HepG2, A549, and MCF-7.[a]

Compd	[b]IC_{50} (μM)		
	Hep G2	A549	MCF-7
4a	>50	>50	>50
4b	6.0	12.0	7.0
4c	>50	>50	>50
4f	8.5	15.0	6.0
4g	6.5	5.0	2.5
4h	>50	>50	>50
4i	>50	>50	>50
4j	>50	>50	>50
4k	>50	>50	>50
4l	>50	>50	>50
4m	>50	>50	>50
4n	>50	>50	>50
4o	>50	>50	>50
4p	>50	>50	>50
4q	>50	>50	>50
4r	50.0	>50	20.5
5a	>50	>50	>50
5e	50.0	>50	>50
5f	>50	>50	>50
5h	>50	>50	>50
5i	>50	>50	>50
5j	>50	>50	>50
5m	>50	>50	>50
5n	>50	>50	>50
5o	>50	>50	>50
5p	>50	>50	>50
6d (major)	>50	>50	>50
6d (minor)	>50	>50	12.0
6s (major)	>50	>50	>50
6s (minor)	>50	>50	>50
7a	12.0	40.0	10.0
7b	2.5	6.5	3.0
7c	8.5	18.5	5.0
7d	1.2	1.0	0.7
7e	4.0	8.5	3.5
7g	8.5	12.0	4.5
7h	>50	>50	>50
7i	22.0	48.0	12.5
7j	>50	>50	>50
7k	>50	>50	>50
7l	8.5	20.0	3.1
7m	5.0	9.0	6.0
7n	>50	>50	>50
7o	20.0	40.0	8.5
7o'	5.5	17.5	5.0

[a]Each value represents the average results from three independent experiments. [b]IC_{50}: 50% inhibiting concentration.

Table S9. The Antitumor Activities of Representative Compounds 4 and 7 against Human Cell Lines.[a]

Compd	IC_{50} (μM)											
	5637	A172	A375	C33A	HCT 116	Hela	CFPAC-1	SW480	Hep G2	A549	MCF-7	293T
4b	5.96	>50	>50	>50	>50	>50	21.30	>50	6.02	12.05	7.10	>12.50
4g	1.72	>50	>50	>50	>50	2.80	>50	2.24	3.43	3.34	3.62	2.07
7b	2.28	14.95	33.04	46.92	28.81	46.81	>50	14.13	2.50	9.40	3.12	>12.50
7d	3.16	0.86	1.72	3.05	4.06	9.51	6.14	20.05	3.22	3.02	3.11	2.15
7e	1.30	5.02	14.80	11.73	10.95	12.83	7.49	>50	12.95	8.53	3.51	>12.50
7l	1.83	11.47	32.89	32.66	16.26	25.62	23.66	29.05	8.50	20.12	3.11	>12.50
7m	1.59	12.70	22.26	26.43	9.27	22.53	20.78	>50	5.51	9.11	6.01	>12.50
7o'	2.36	12.80	11.17	16.92	23.63	3.06	21.43	12.85	5.50	17.50	5.10	11.30
Vincristine	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10	<3.10

[a]Each value represents the average results from three independent experiments.

References

1 D. Fernández González, J. P. Brand and J. Waser, Ethynyl-1,2-benziodoxol-3(1*H*)-one (EBX): an exceptional reagent for the ethynylation of keto, cyano, and nitro esters, *Chem. Eur. J.*, 2010, **16**, 9457-9461.

2 M. Yudasaka, D. Shimbo, T. Maruyama, N. Tada and A. Itoh, Synthesis, characterization, and reactivity of an ethynyl benziodoxolone (EBX)–acetonitrile complex, *Org. Lett.*, 2019, **21**, 1098-1102.

3 L.-Q. Yang, K.-B. Wang and C.-Y. Li, Synthesis of oxindoles through the gold-catalyzed oxidation of *N*-arylynamides, *Eur. J. Org. Chem.*, 2013, 2775-2779.

4 Y. Tu, X. Zeng, H. Wang and J. Zhao, A robust one-step approach to ynamides, *Org. Lett.*, 2018, **20**, 280-283.

5 M. Tayu, R. Watanabe, S. Isogi and N. Saito, A catalytic construction of indoles via formation of ruthenium vinylidene species from *N*-arylynamides, *Adv. Synth. Catal.*, 2021, **363**, 1147-1151.

6 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**, 6801-6804.

7 S. J. Mansfield, C. D. Campbell, M. W. Jones and E. A. Anderson, A robust and modular synthesis of ynamides, *Chem. Commun.*, 2015, **51**, 3316-3319.

8 S. J. Mansfield, R. C. Smith, J. R. J. Yong, O. L. Garry and E. A. Anderson, A general copper-catalyzed synthesis of ynamides from 1,2-dichloroenamides, *Org. Lett.*, 2019, **21**, 2918-2922.

9 R. N. Straker, M. K. Majhail and M. C. Willis, Exploiting rhodium-catalysed ynamide hydroacylation as a platform for divergent heterocycle synthesis. *Chem. Sci.*, 2017, **8**, 7963-7968.

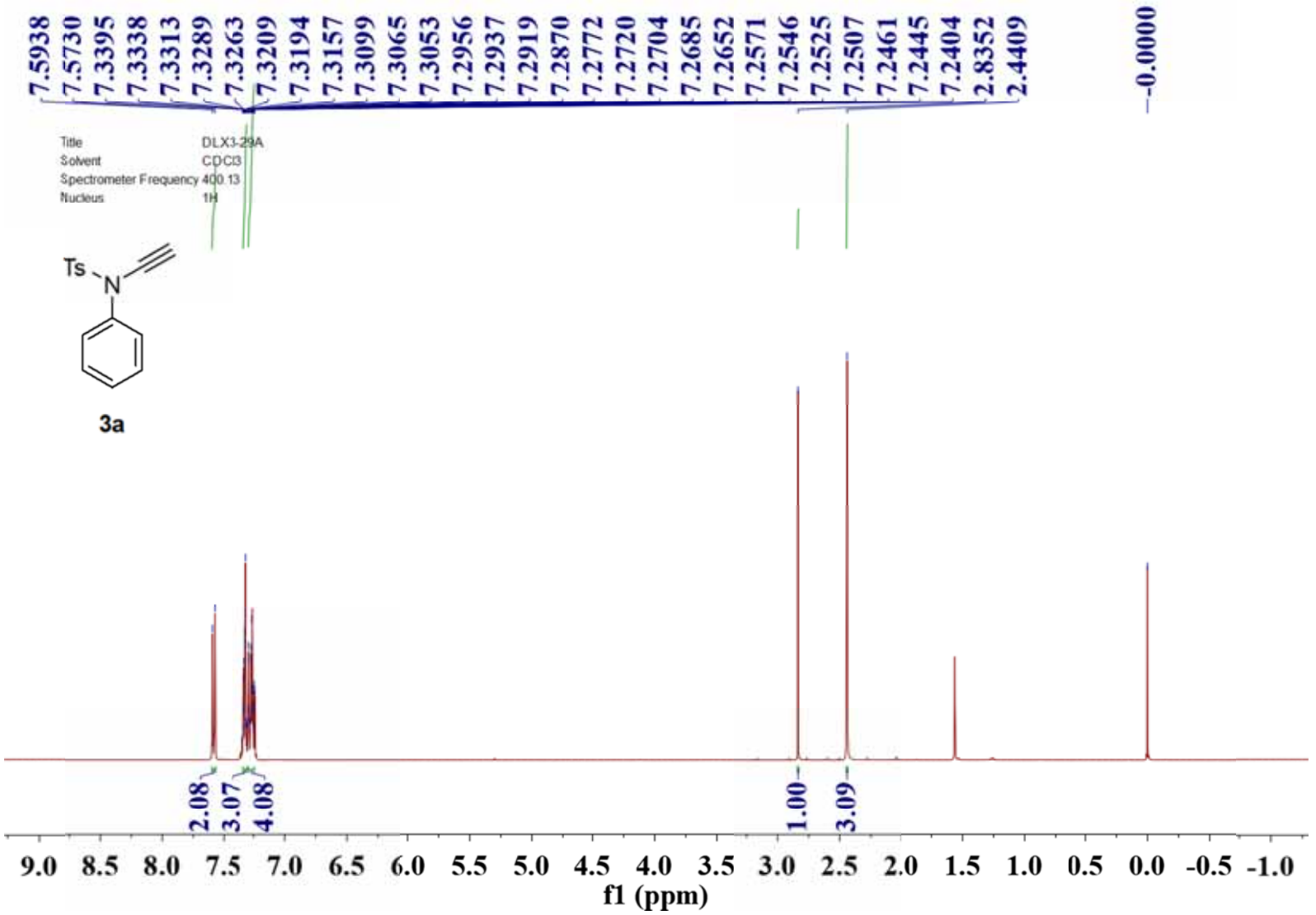
10 P. W. Davies, A. Cremonesi and N. Martin, Site-specific introduction of gold-carbenoids by intermolecular oxidation of ynamides or ynol ethers, *Chem. Commun.*, 2011, **47**, 379-381.

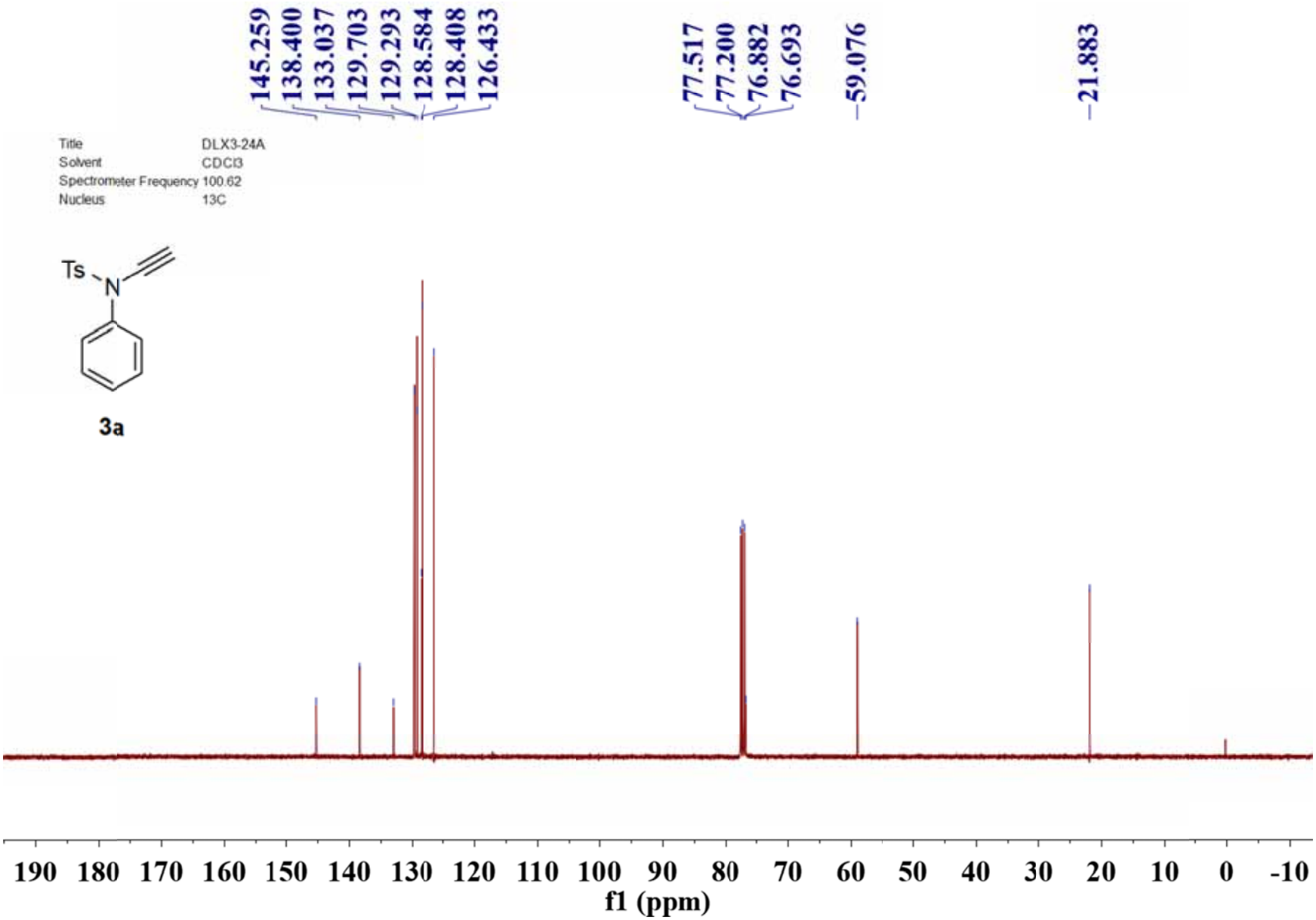
11 J. Zhang, M. Guo, Y. Chen, S. Zhang, X.-N. Wang and J. Chang, Synthesis of amino-substituted α- and δ-carbolines via metal-free [2 + 2 + 2] cycloaddition of functionalized alkyne-nitriles with ynamides, *Org. Lett.*, 2019, **21**, 1331-1336.

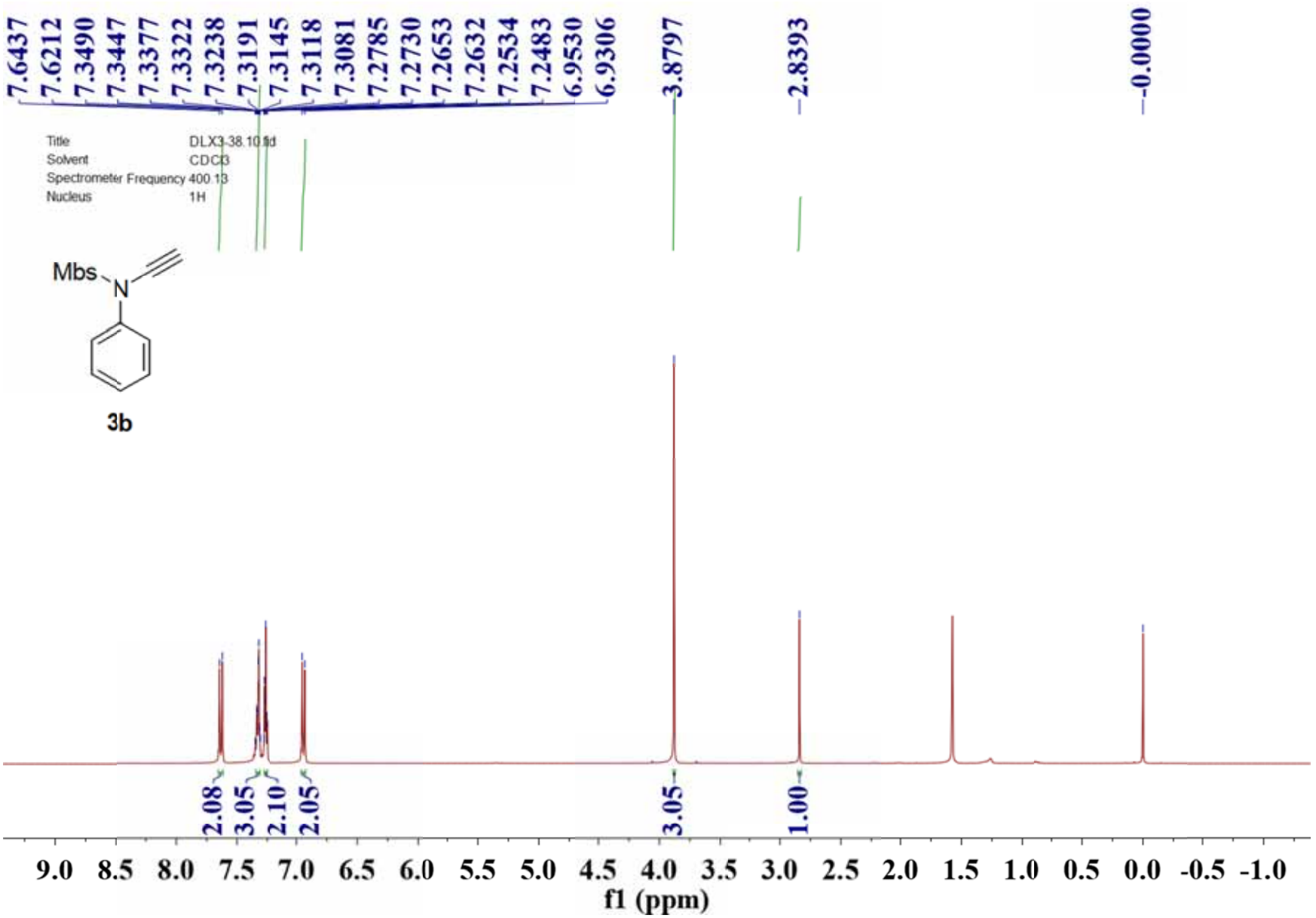
12 X. Ju, Y. Zhu, Y. Wang, J. Li, J. Zhang, M. Gong, W. Ren, S. Li, J. Zhong, L. Zhang, Q. C. Zhang, R. Zhang and Q. Ding, A novel cell culture system modeling the SARS-CoV-2 life cycle. *PLoS Pathog.*, 2021, **17**, e1009439.

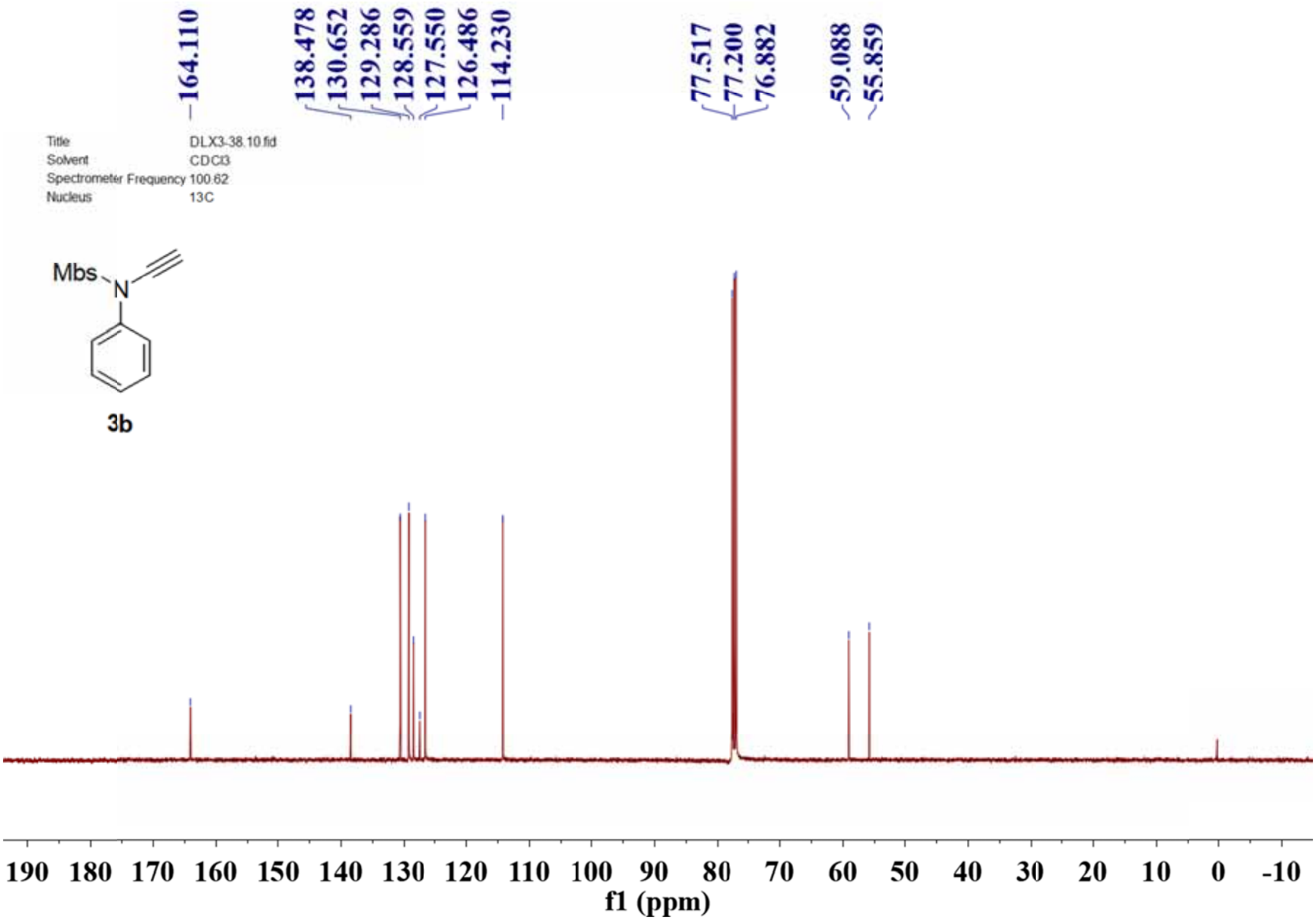
Part II Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra.

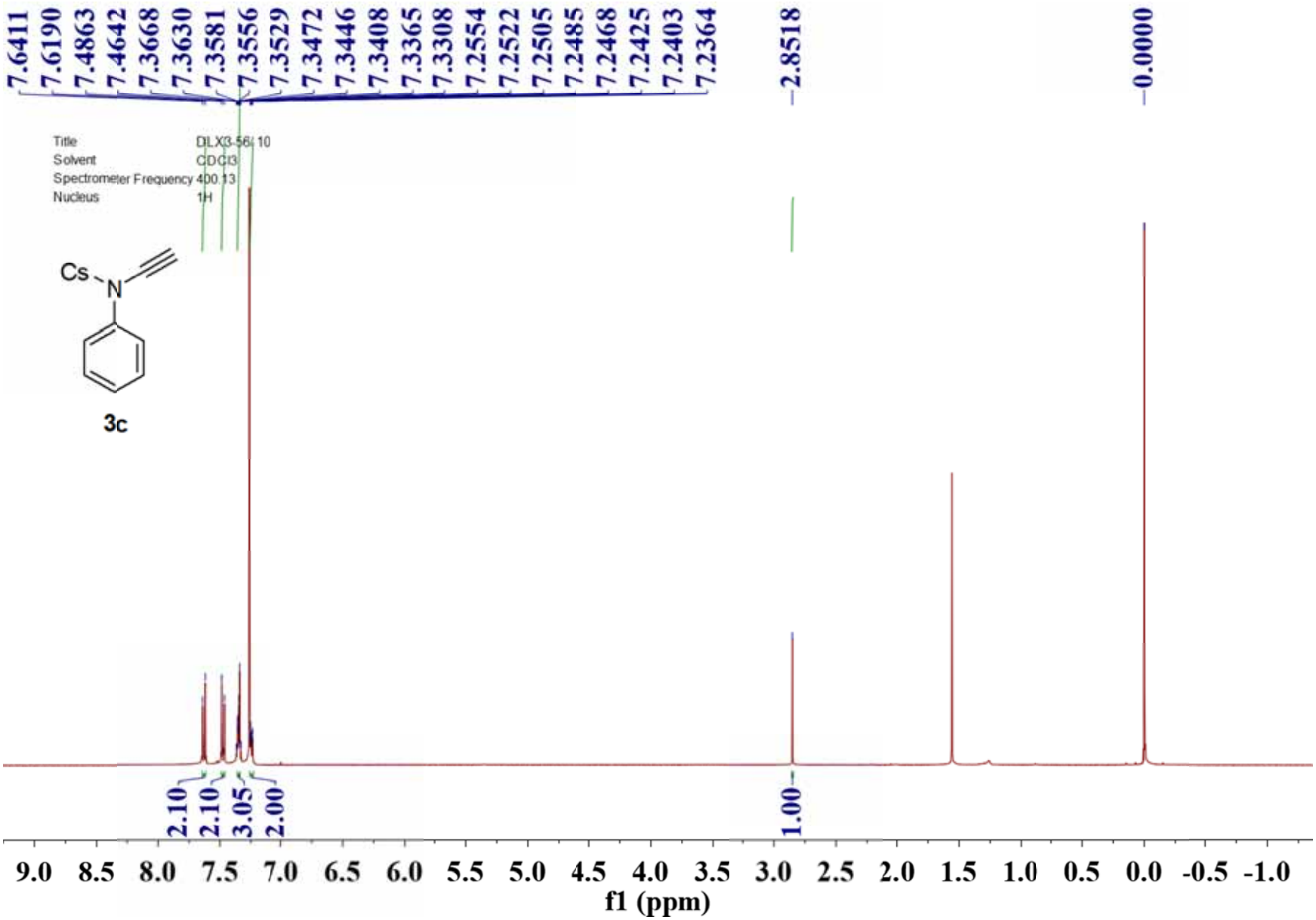
^{1}H NMR and ^{13}C NMR Spectra of Terminal *N*-Aryl Ynamides 3.

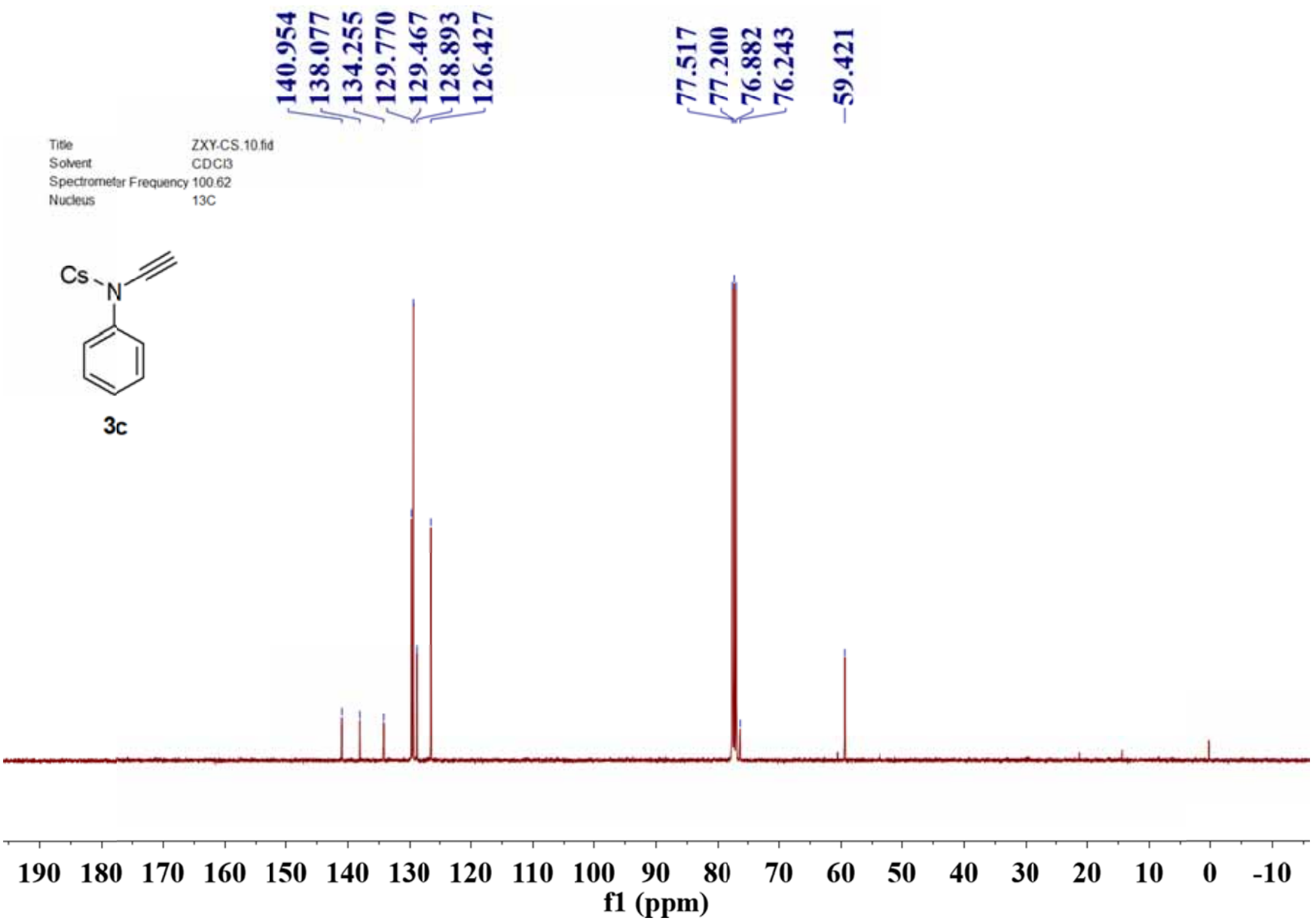


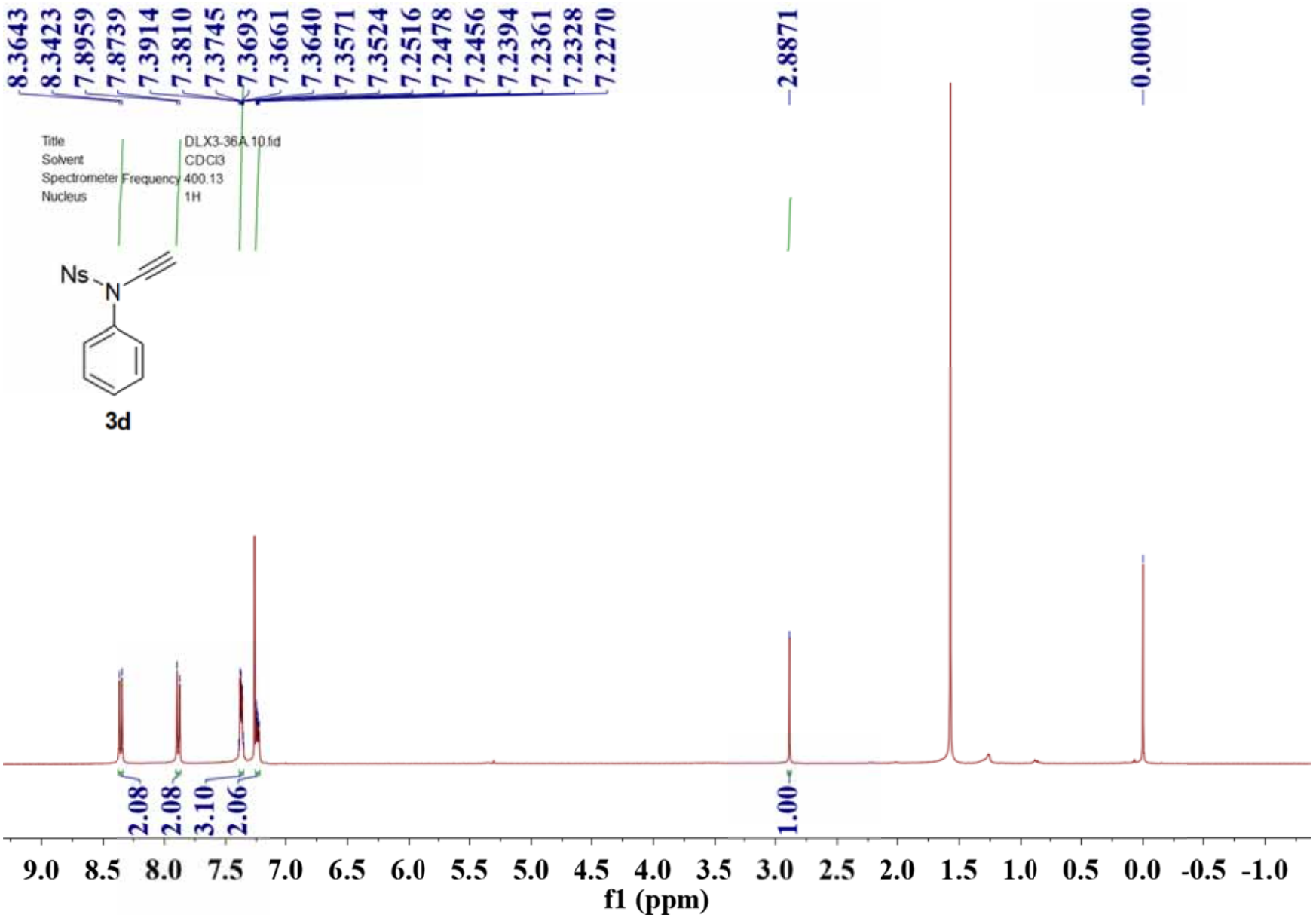

145.259
138.400
133.037
129.703
129.293
128.584
128.408
126.433
77.517
77.200
76.882
76.693
59.076
21.883
Title DLX3-24A
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

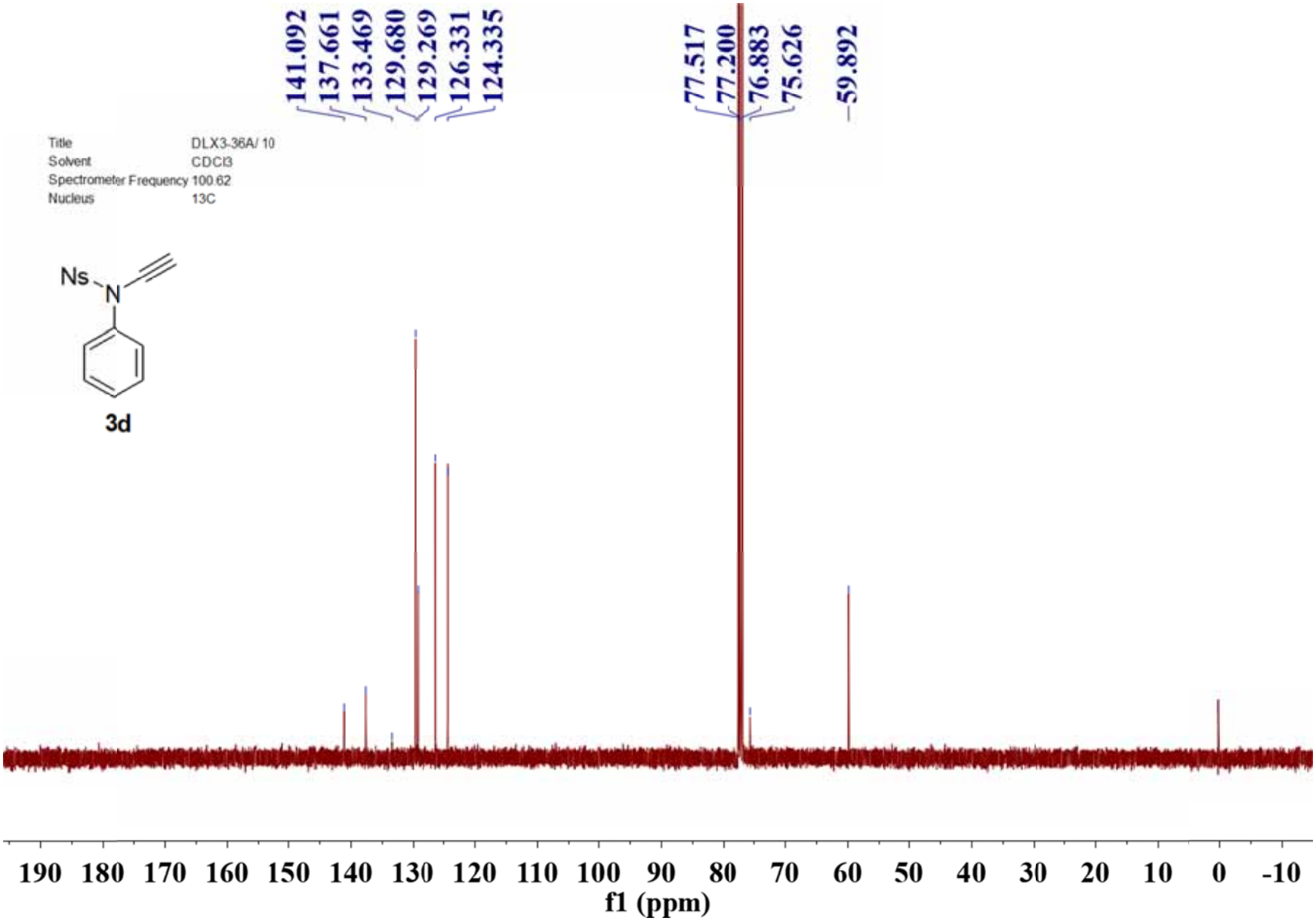

7.6437
7.6212
7.3490
7.3447
7.3377
7.3322
7.3238
7.3191
7.3145
7.3118
7.3081
7.2785
7.2730
7.2653
7.2632
7.2534
7.2483
6.9530
6.9306
3.8797
2.8393
0.0000
Title
Solvent
Spectrometer Frequency 400.13
Nucleus 1H
Mbs
N
3b
2.08
3.05
2.10
2.05
3.05
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

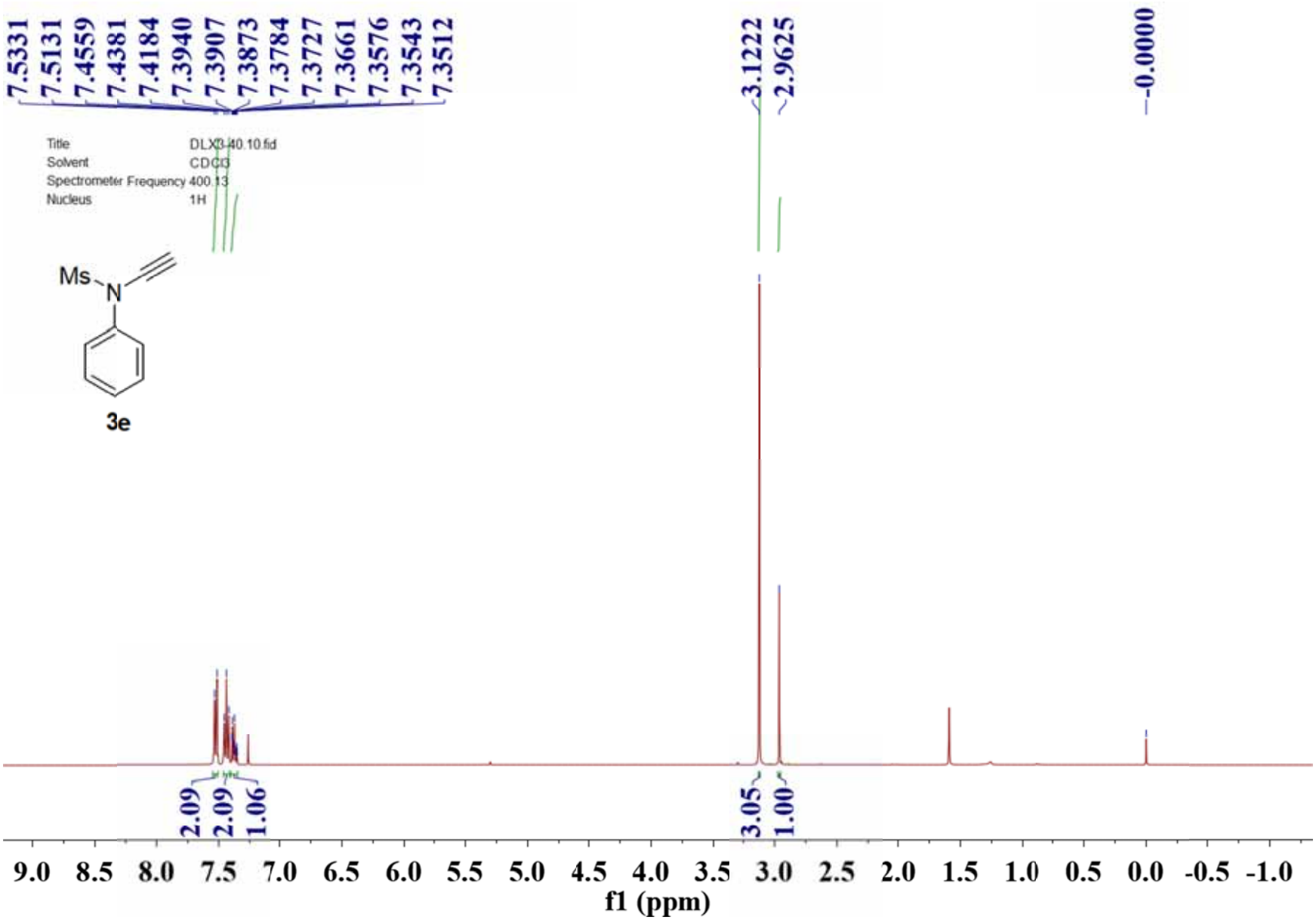

164.110
138.478
130.652
129.286
128.559
127.550
126.486
114.230
77.517
77.200
76.882
59.088
55.859
Title DLX3-38.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Mbs
N
3b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

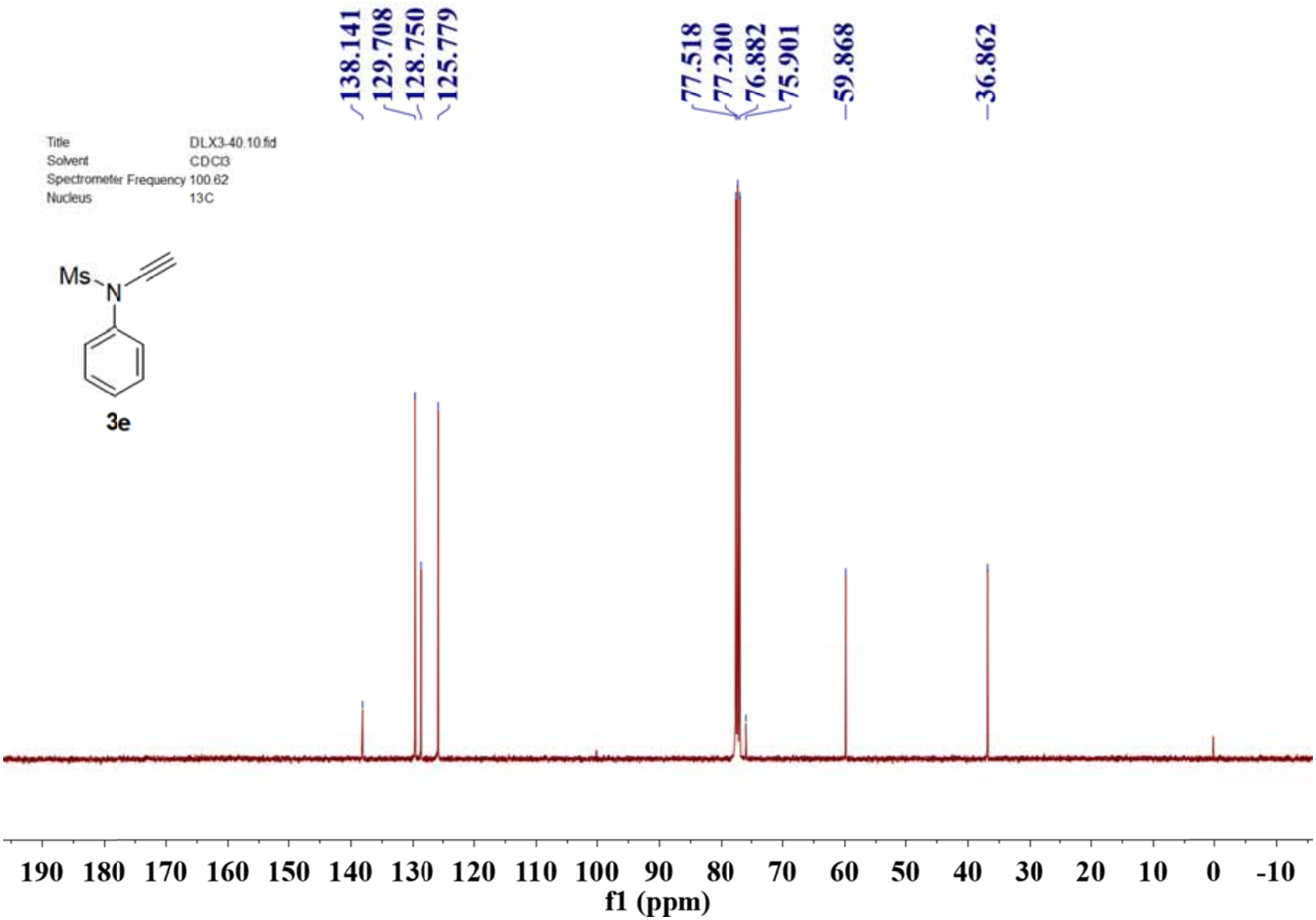

7.6411
7.6190
7.4863
7.4642
7.3668
7.3630
7.3581
7.3556
7.3529
7.3472
7.3446
7.3408
7.3365
7.3308
7.2554
7.2522
7.2505
7.2485
7.2468
7.2425
7.2403
7.2364
2.8518
0.0000
Title DILX3-56-10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cs
N
3c
2.10
2.10
3.05
2.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

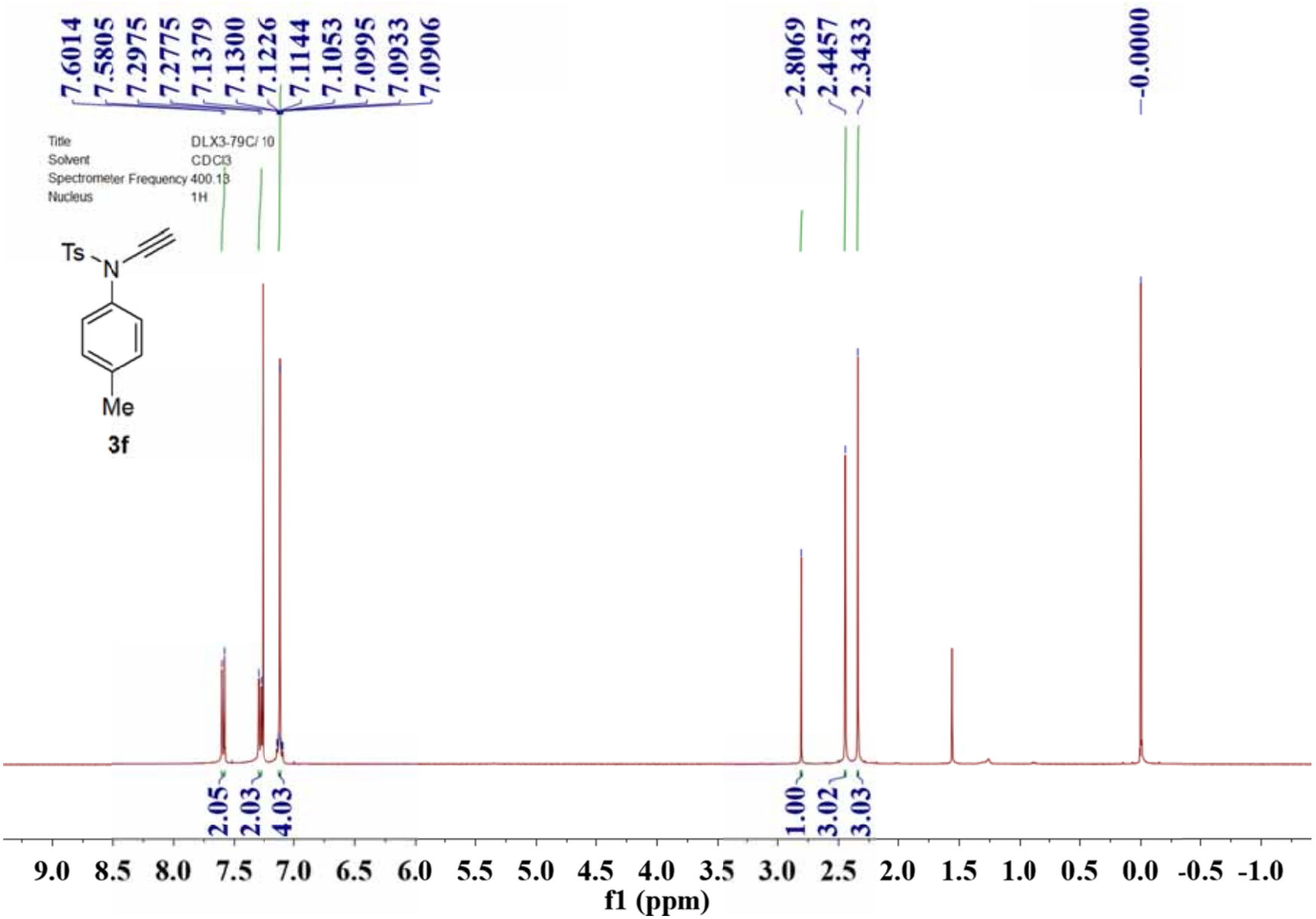

140.954
138.077
134.255
129.770
129.467
128.893
126.427
77.517
77.200
76.882
76.243
59.421
Title ZXY-CS.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cs
N
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

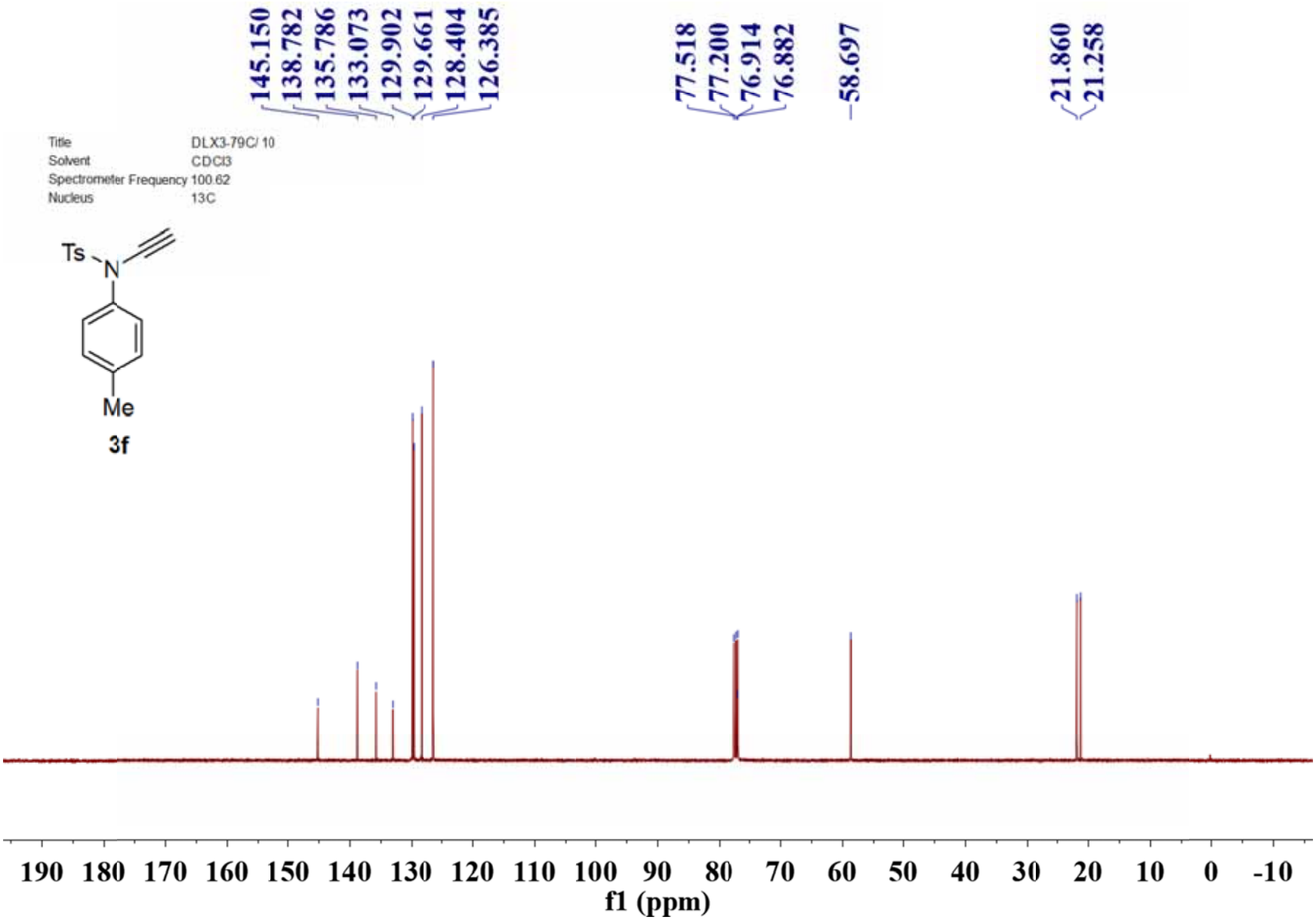

8.3643
8.3423
7.8959
7.8739
7.3914
7.3810
7.3745
7.3693
7.3661
7.3640
7.3571
7.3524
7.2516
7.2478
7.2456
7.2394
7.2361
7.2328
7.2270
2.8871
0.0000
Title DLX3-36A 10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ns
N
3d
2.08
2.08
3.10
2.06
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

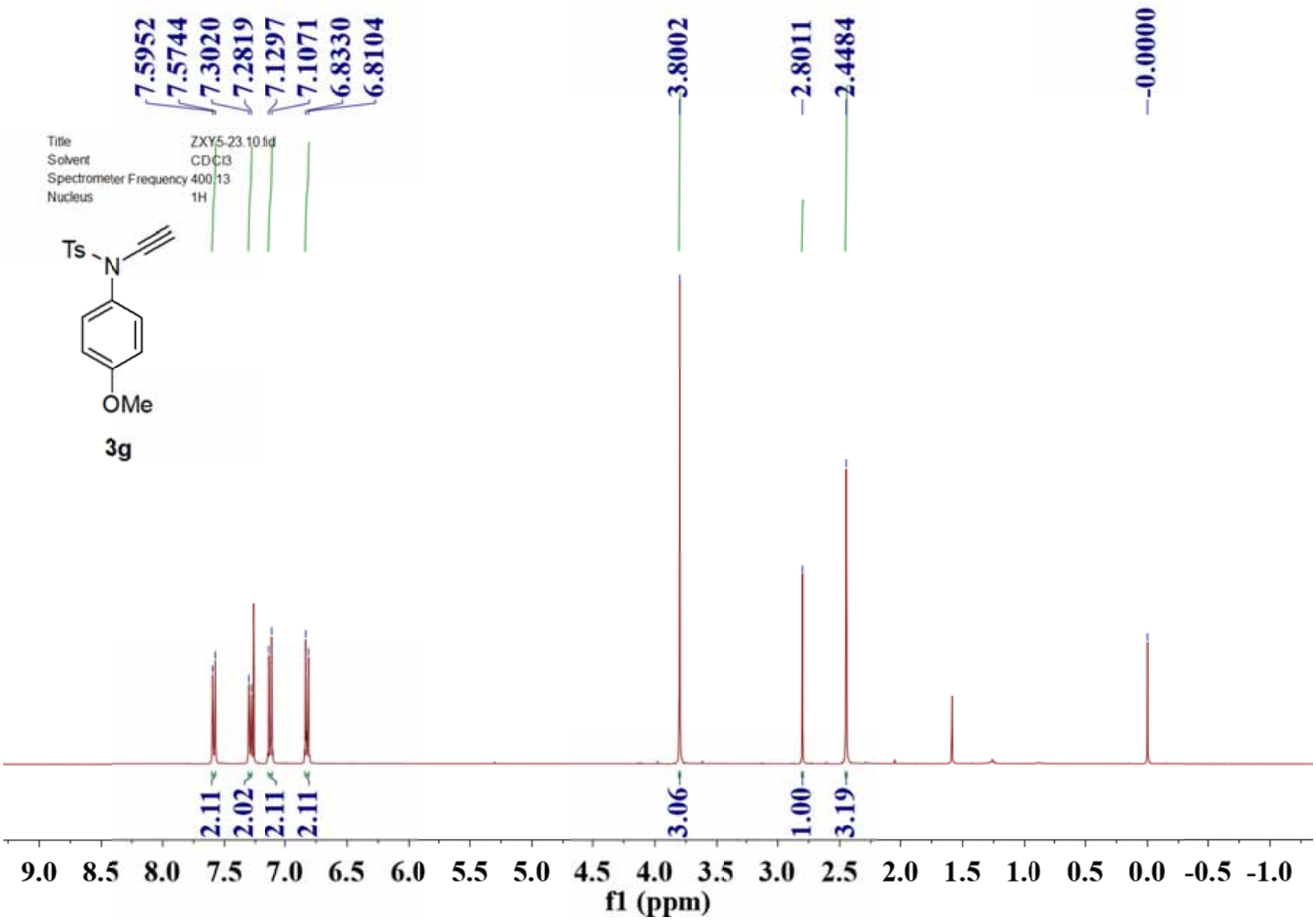

141.092
137.661
133.469
129.680
129.269
126.331
124.335
77.517
77.200
76.883
75.626
59.892
Title DLX3-36A/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ns
N
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

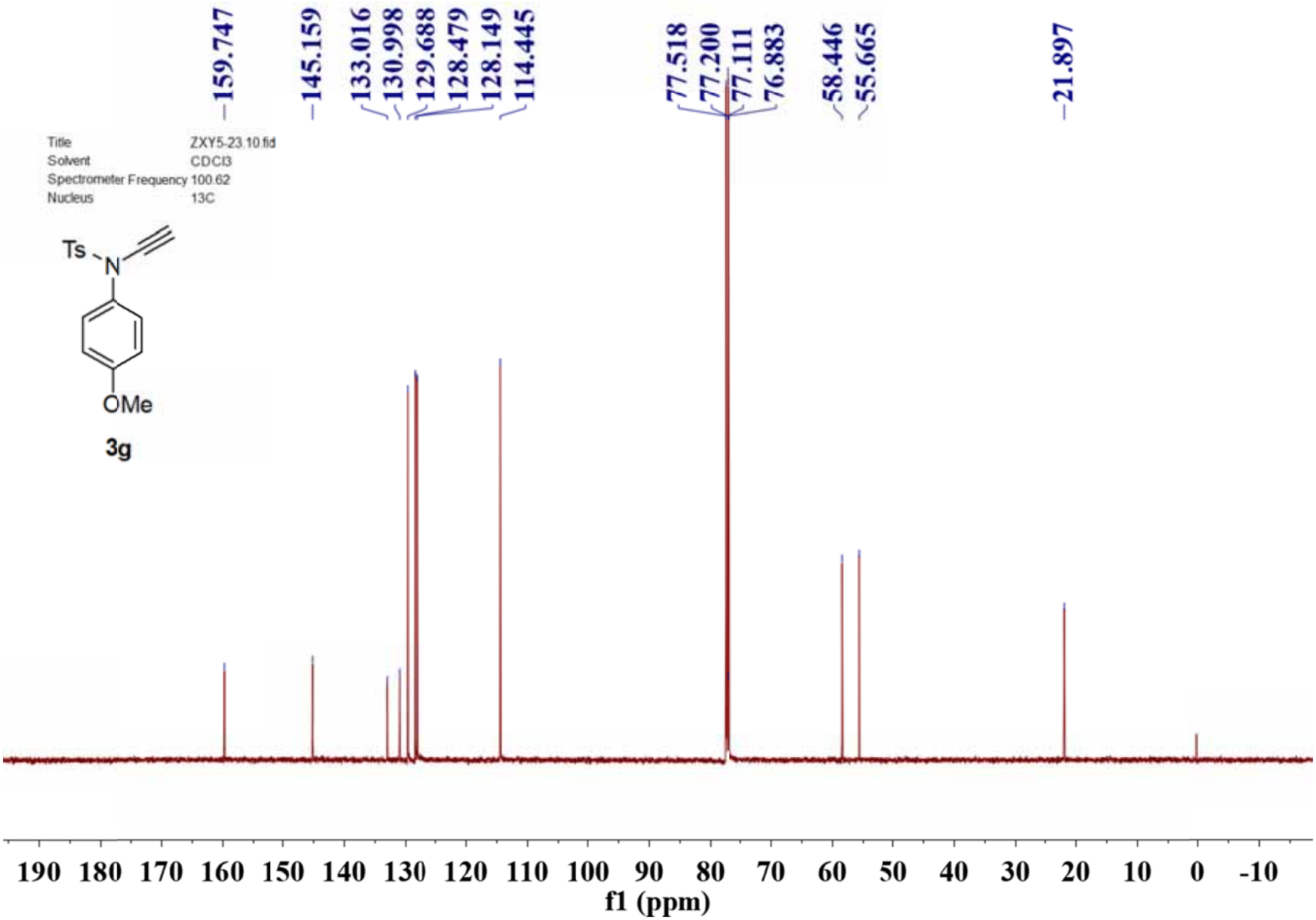

7.5331
7.5131
7.4559
7.4381
7.4184
7.3940
7.3907
7.3873
7.3784
7.3727
7.3661
7.3576
7.3543
7.3512
3.1222
2.9625
-0.0000
Title DLXB-40.10.fid
Solvent CDCG
Spectrometer Frequency 400.13
Nucleus 1H
Ms
N
3e
2.09
2.09
1.06
3.05
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

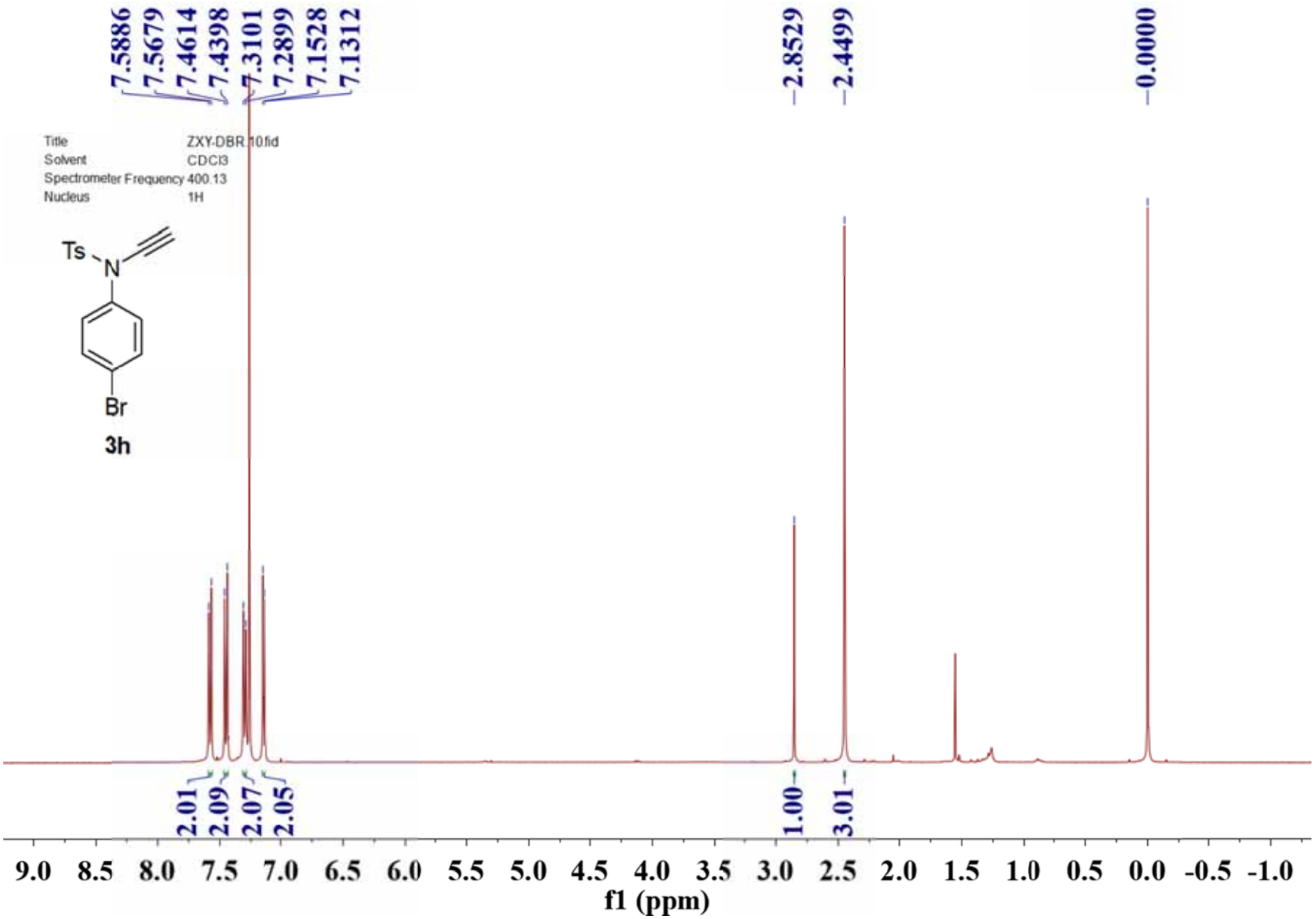

138.141
129.708
128.750
125.779
77.518
77.200
76.882
75.901
59.868
36.862
Title DLX3-40.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ms
N
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

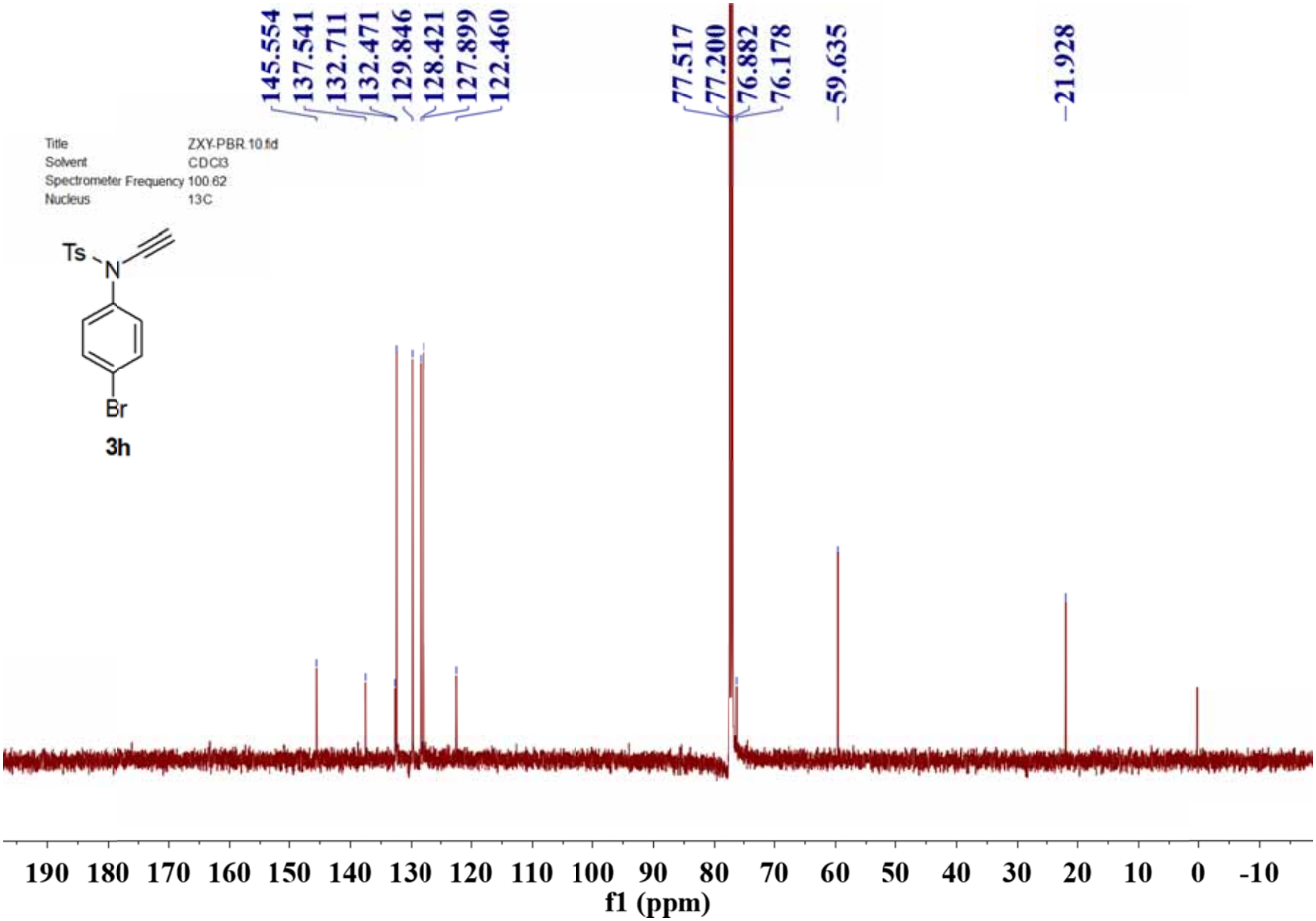

7.6014
7.5805
7.2975
7.2775
7.1379
7.1300
7.1226
7.1144
7.1053
7.0995
7.0933
7.0906
2.8069
2.4457
2.3433
-0.0000
Title DLX3-79C/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
3f
2.05
2.03
4.03
1.00
3.02
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

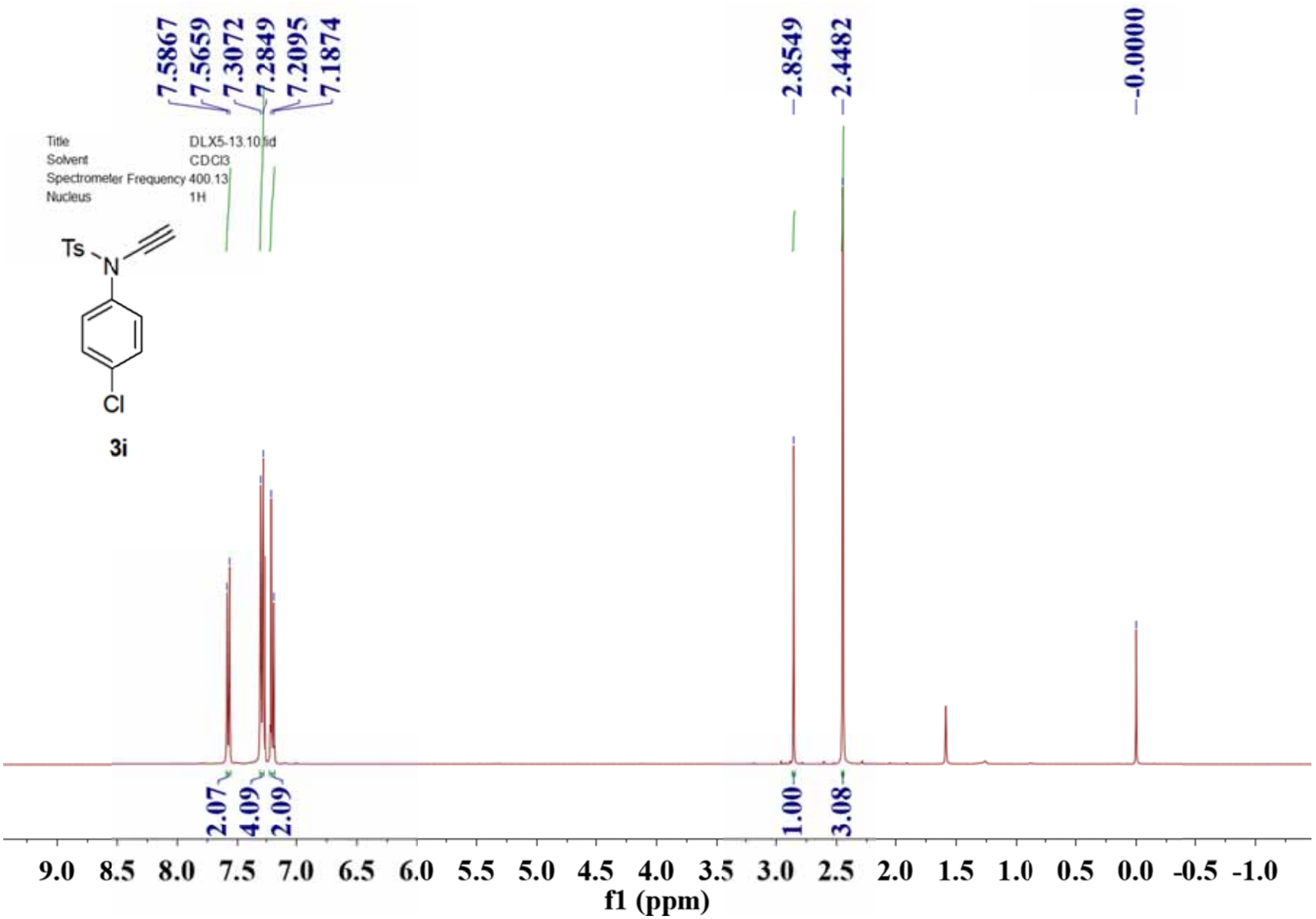

145.150
138.782
135.786
133.073
129.902
129.661
128.404
126.385
77.518
77.200
76.914
76.882
58.697
21.860
21.258
Title DLX3-79C/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
3f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

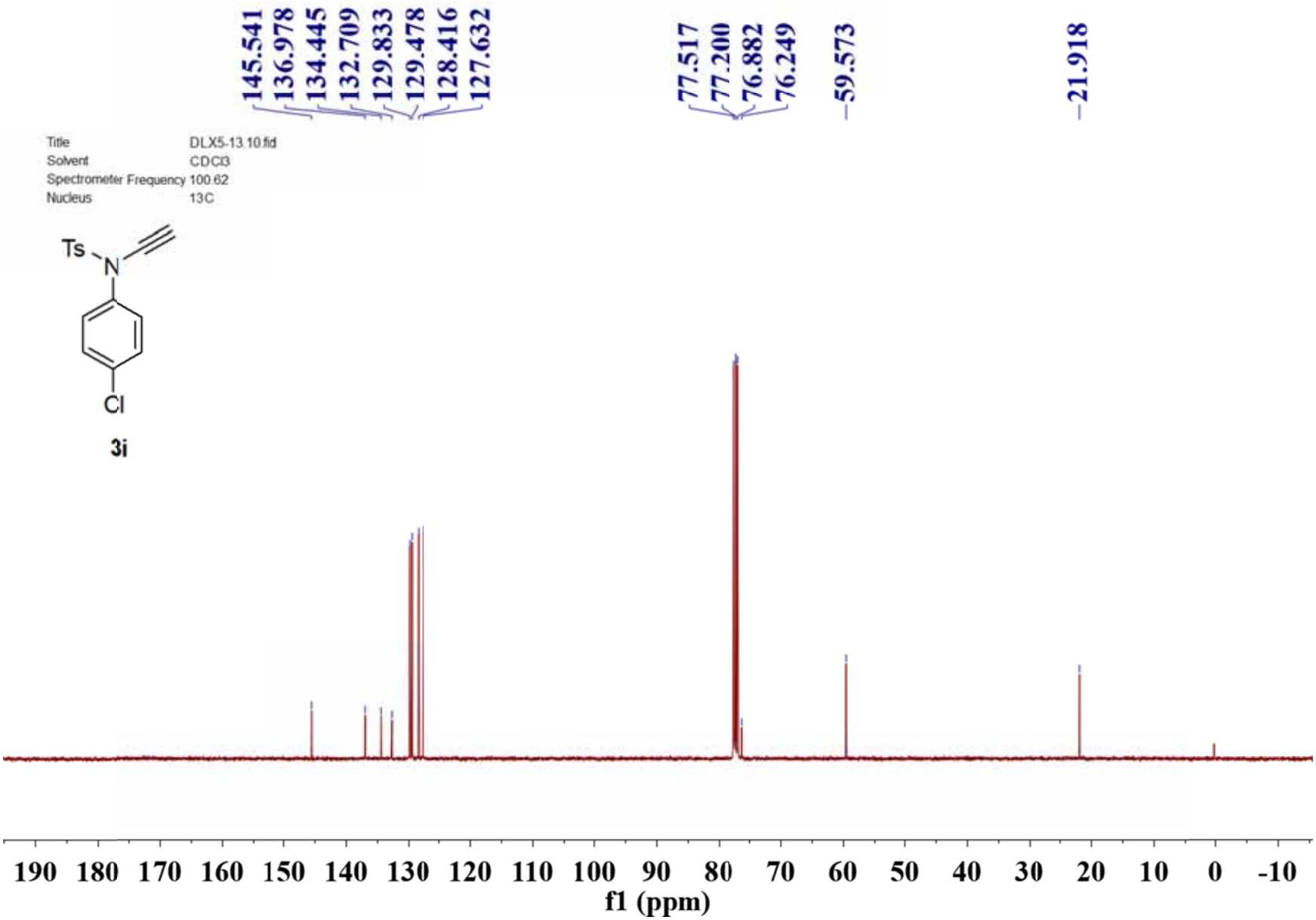

7.5952
7.5744
7.3020
7.2819
7.1297
7.1071
6.8330
6.8104
3.8002
2.8011
2.4484
-0.0000
Title ZXY5-23.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
OMe
3g
2.11
2.02
2.11
2.11
3.06
1.00
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

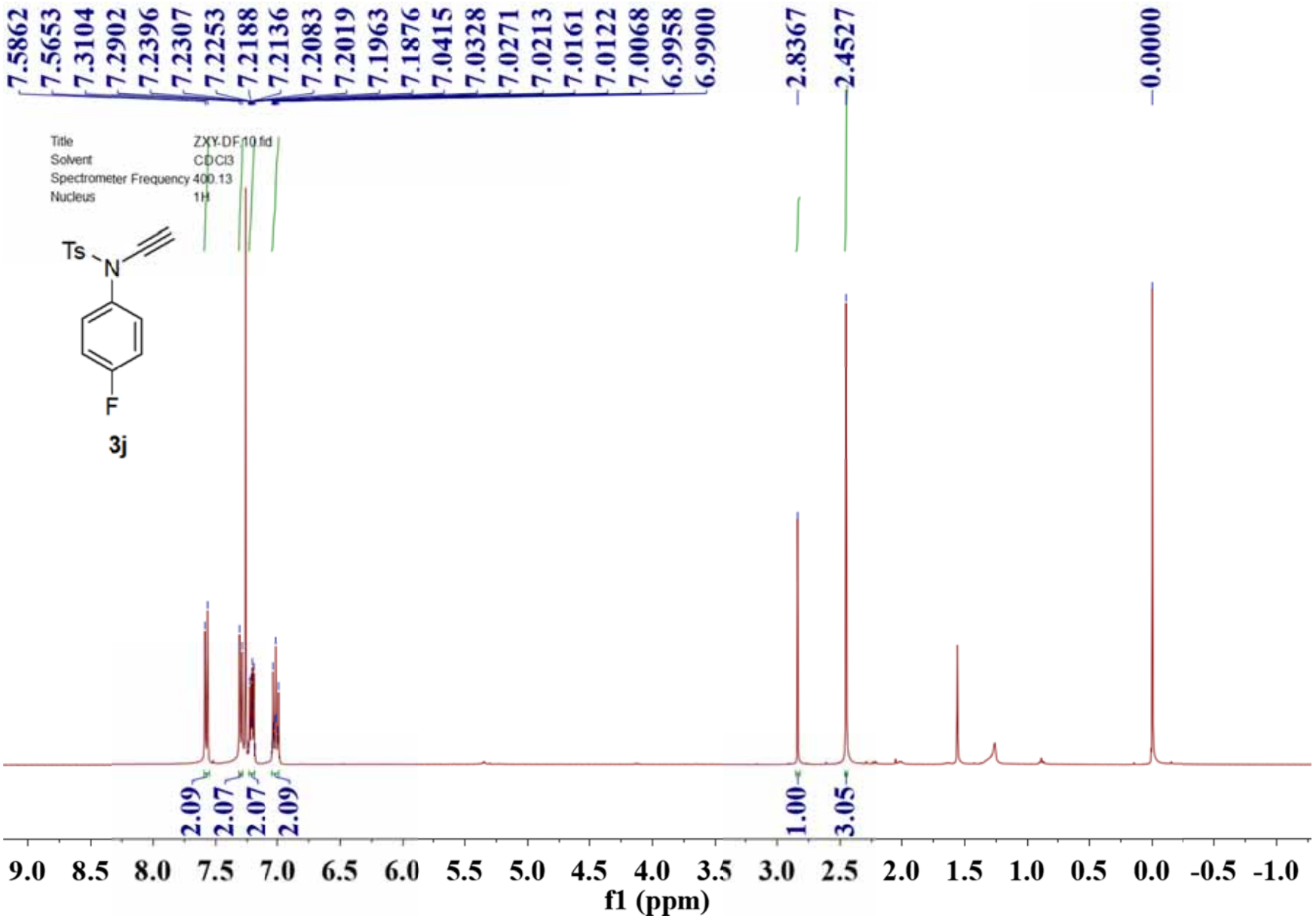

159.747
145.159
133.016
130.998
129.688
128.479
128.149
114.445
77.518
77.200
77.111
76.883
58.446
55.665
21.897
Title ZXY5-23.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
OMe
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

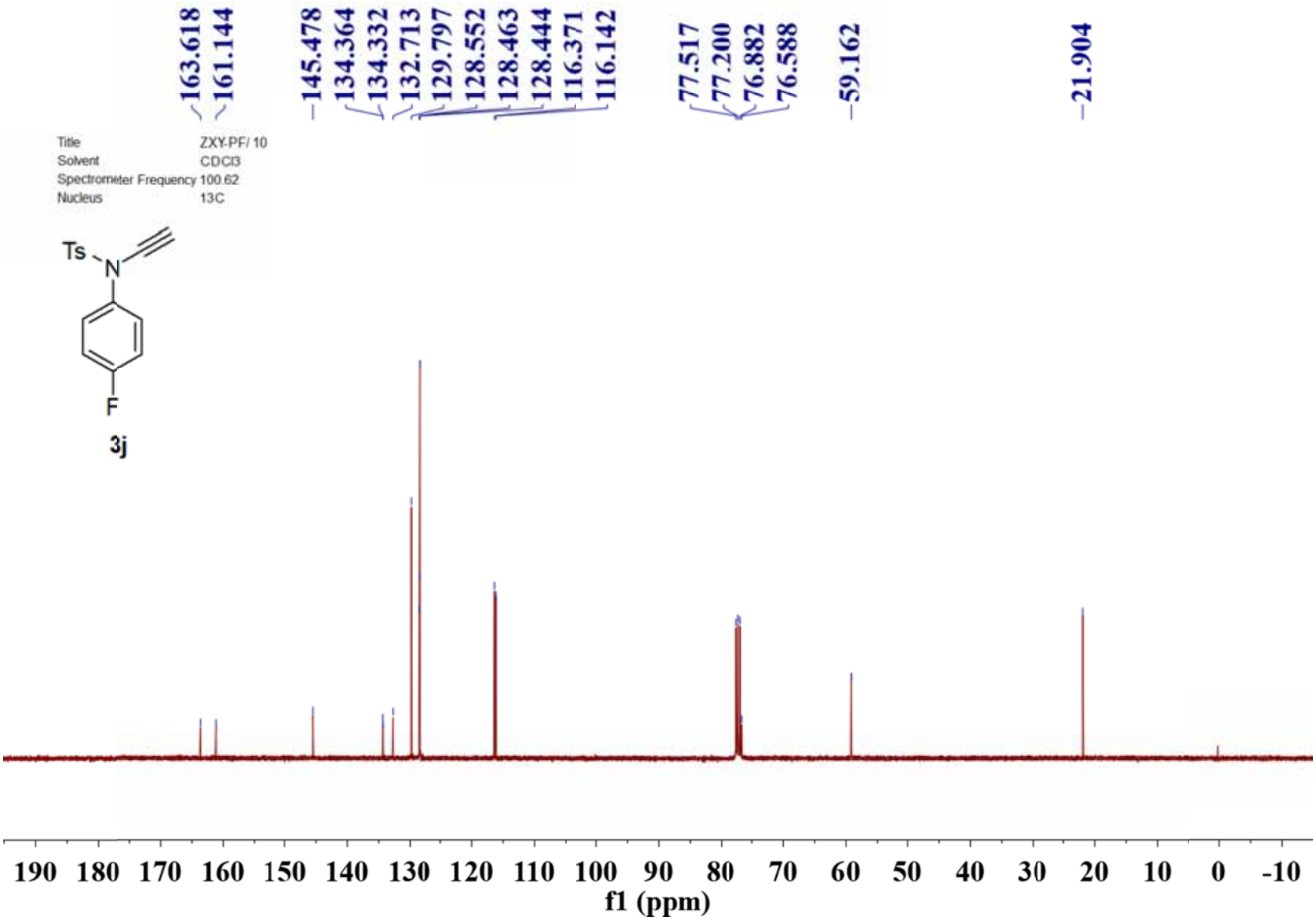

7.5886
7.5679
7.4614
7.4398
7.3101
7.2899
7.1528
7.1312
2.8529
2.4499
0.0000
Title ZXY-DBR-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Br
3h
2.01
2.09
2.07
2.05
1.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

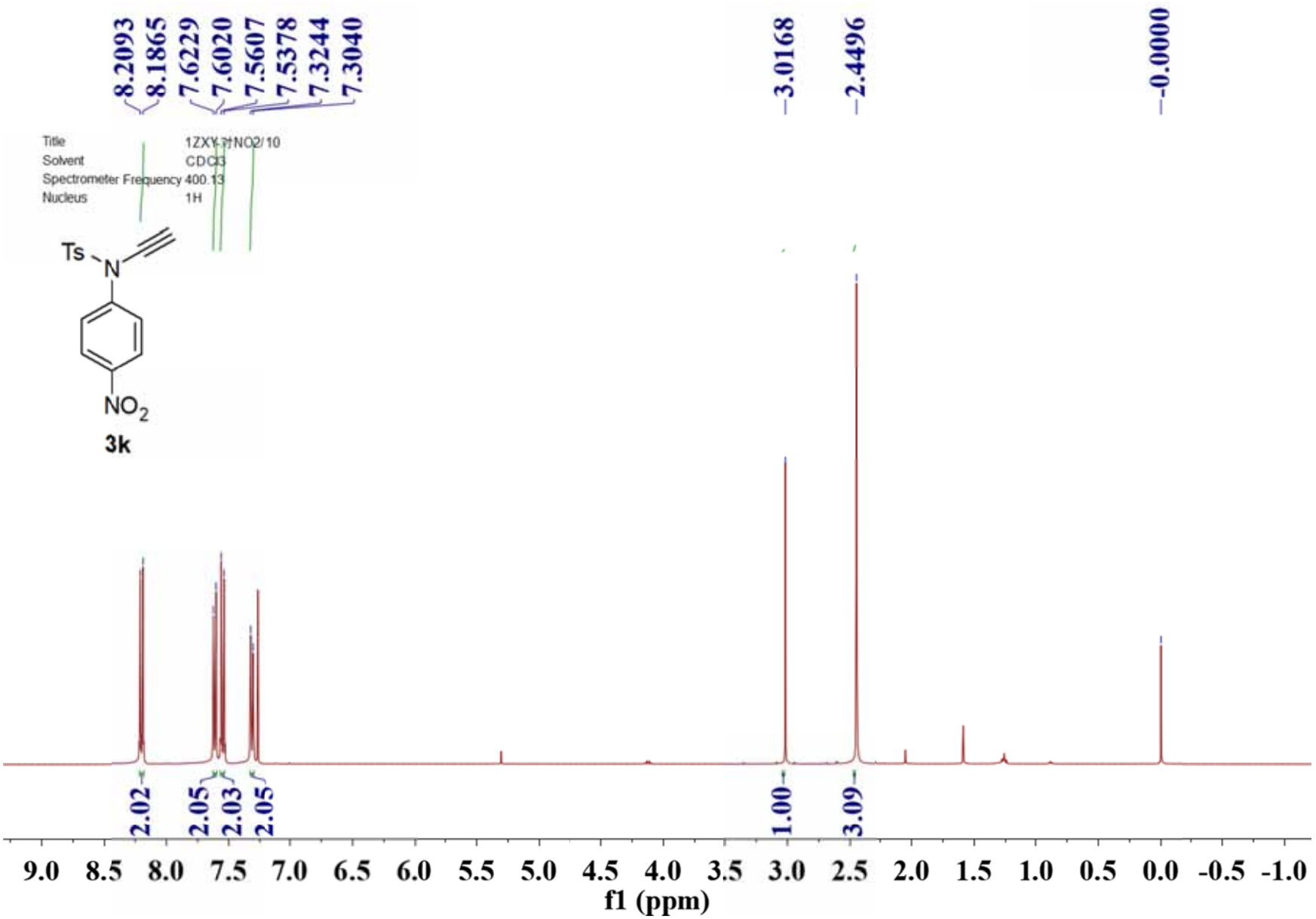

145.554
137.541
132.711
132.471
129.846
128.421
127.899
122.460
77.517
77.200
76.882
76.178
59.635
21.928
Title ZXY-PBR-10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Br
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

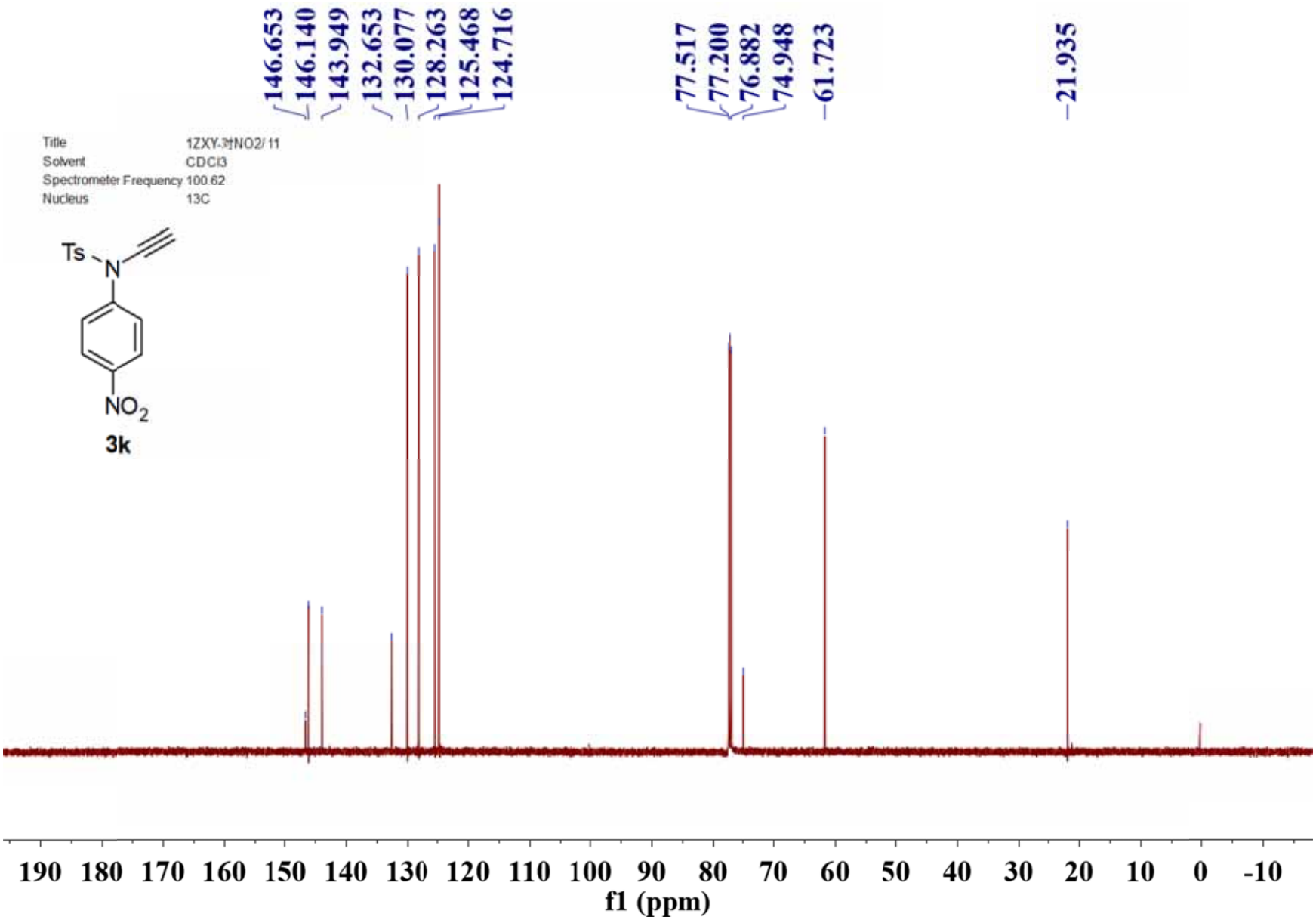

7.5867
7.5659
7.3072
7.2849
7.2095
7.1874
2.8549
2.4482
0.0000
Title DLX5-13.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Cl
3i
2.07
4.09
2.09
1.00
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

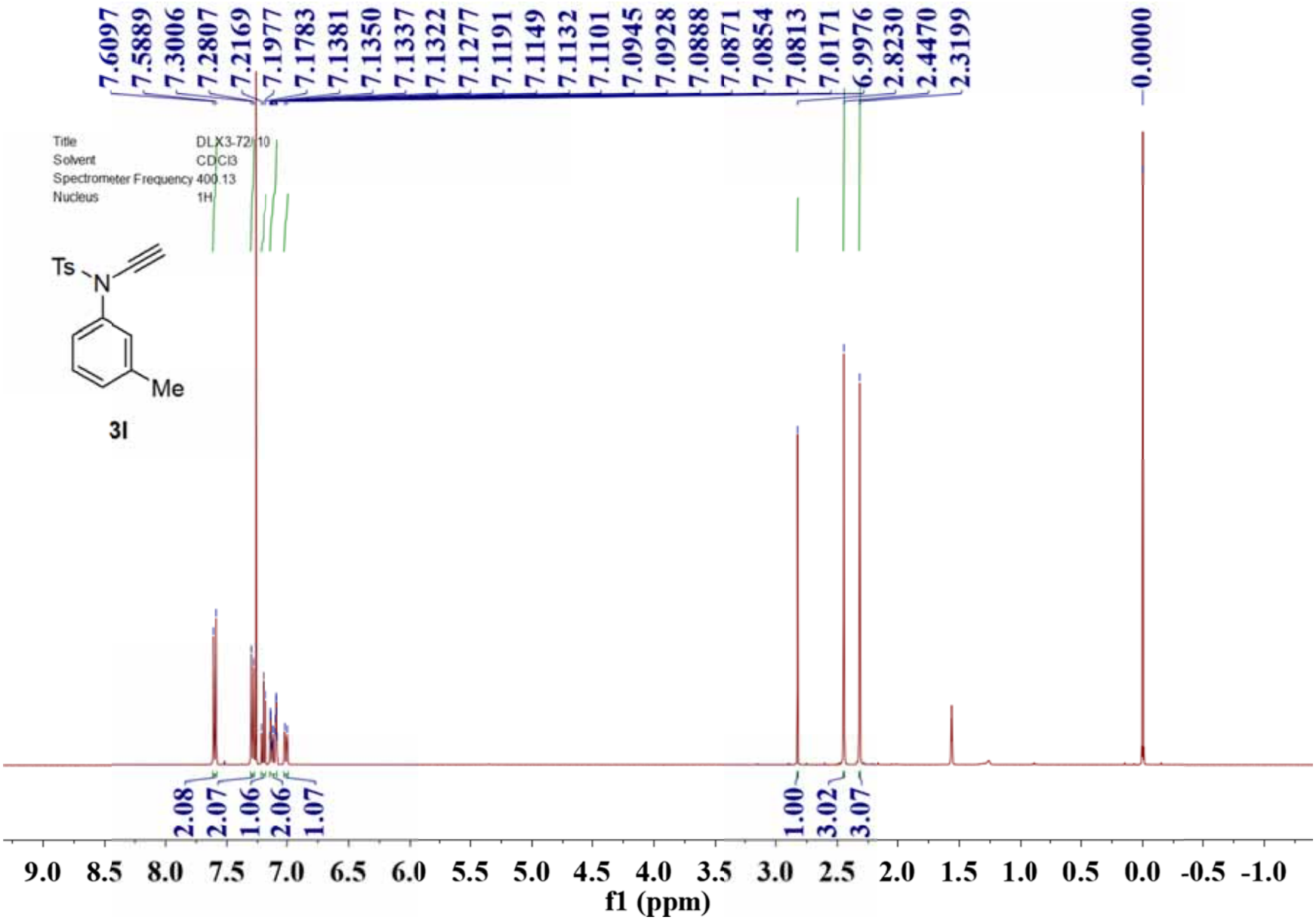

145.541
136.978
134.445
132.709
129.833
129.478
128.416
127.632
77.517
77.200
76.882
76.249
59.573
21.918
Title DLX5-13.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Cl
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

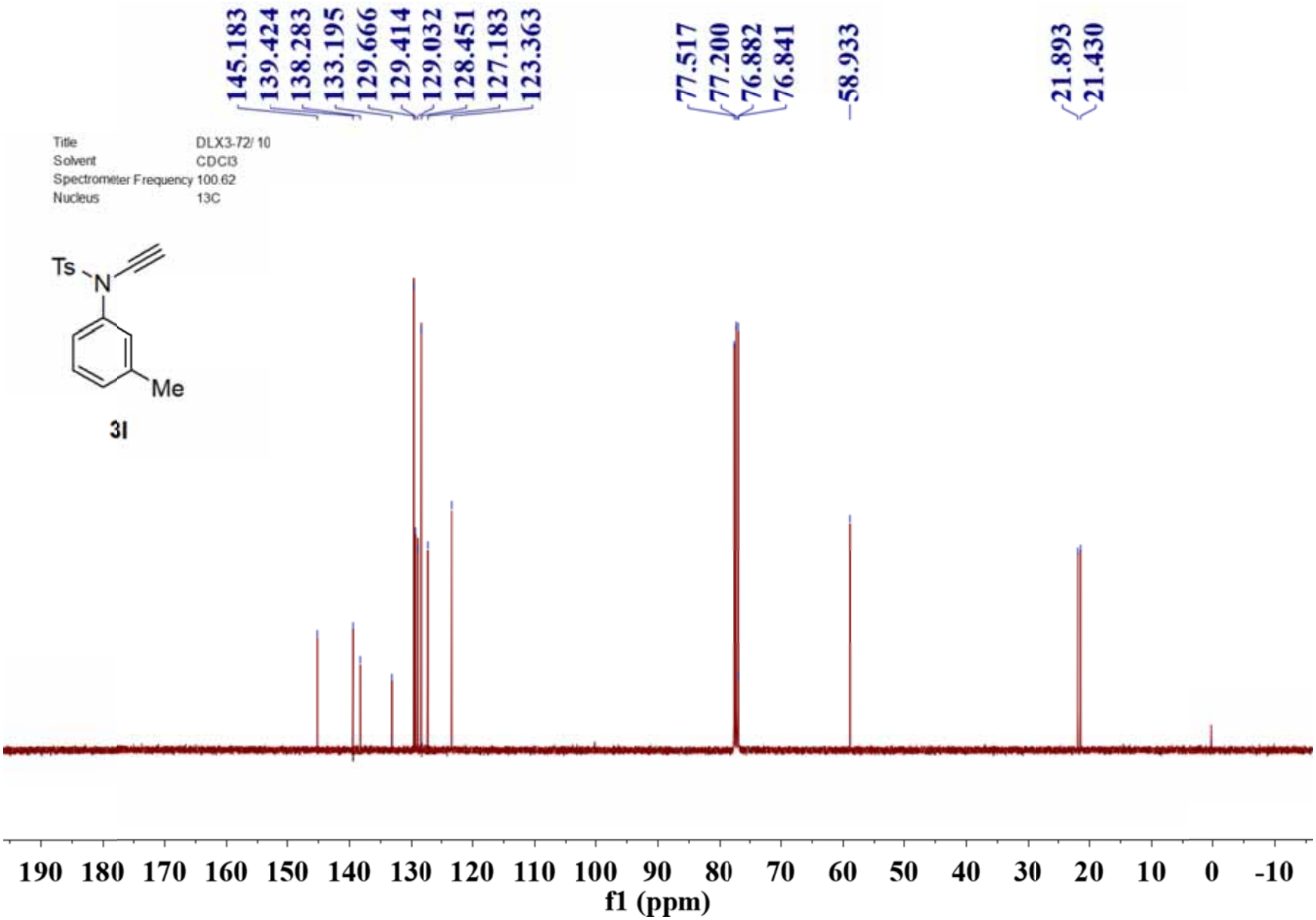

7.5862
7.5653
7.3104
7.2902
7.2396
7.2307
7.2253
7.2188
7.2136
7.2083
7.2019
7.1963
7.1876
7.0415
7.0328
7.0271
7.0213
7.0161
7.0122
7.0068
6.9958
6.9900
2.8367
2.4527
0.0000
Title ZXY-DF-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
F
3j
2.09
2.07
2.07
2.09
1.00
3.05
9.0 8.5 8.0 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)

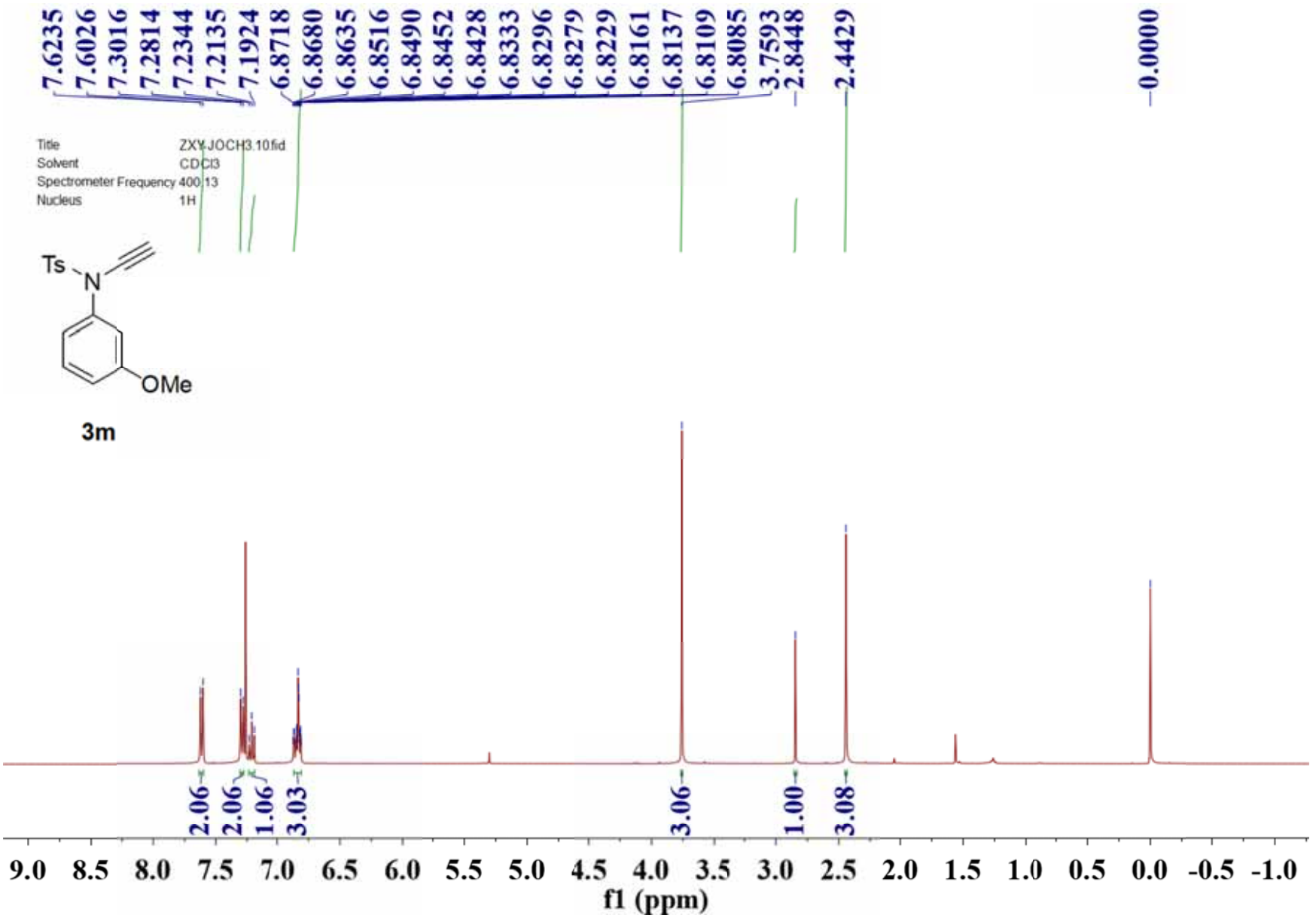

163.618
161.144
145.478
134.364
134.332
132.713
129.797
128.552
128.463
128.444
116.371
116.142
77.517
77.200
76.882
76.588
59.162
21.904
Title ZXY-PF/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
F
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

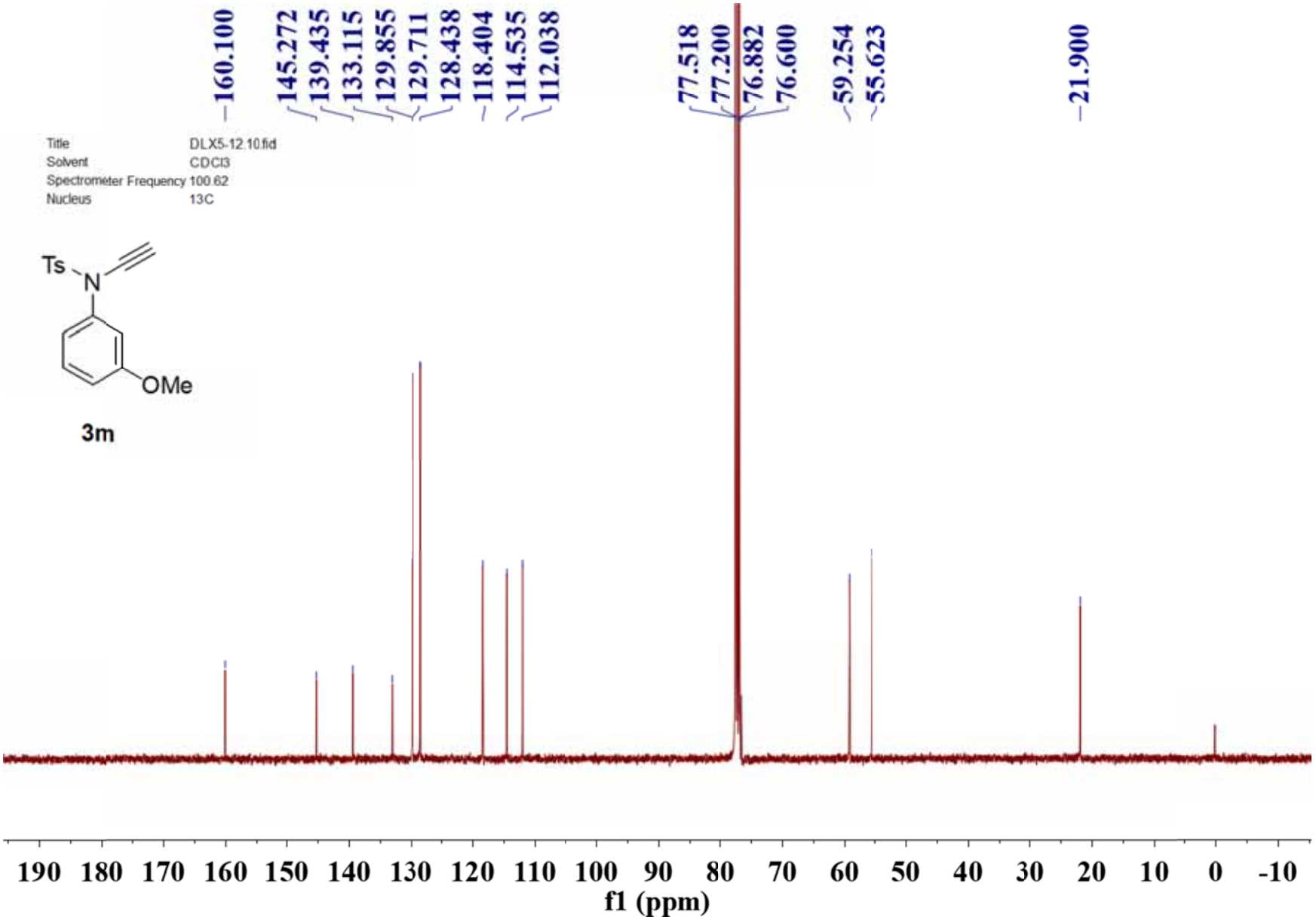

8.2093
8.1865
7.6229
7.6020
7.5607
7.5378
7.3244
7.3040
3.0168
2.4496
0.0000
Title 1ZXY-ynNO2/10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
NO2
3k
2.02
2.05
2.03
2.05
1.00
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

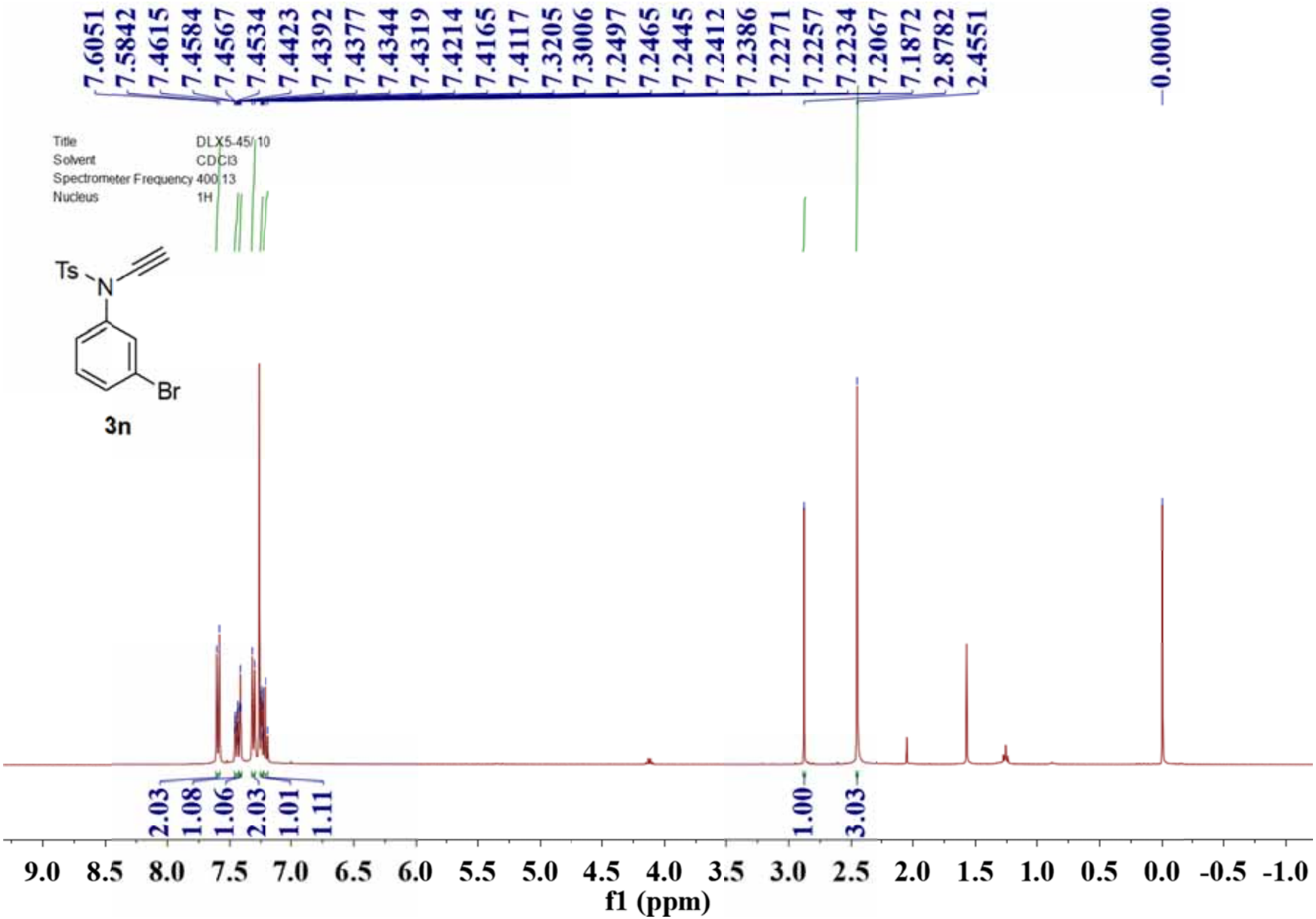

146.653
146.140
143.949
132.653
130.077
128.263
125.468
124.716
77.517
77.200
76.882
74.948
61.723
21.935
Title 1ZXY-对NO2/11
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
NO2
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

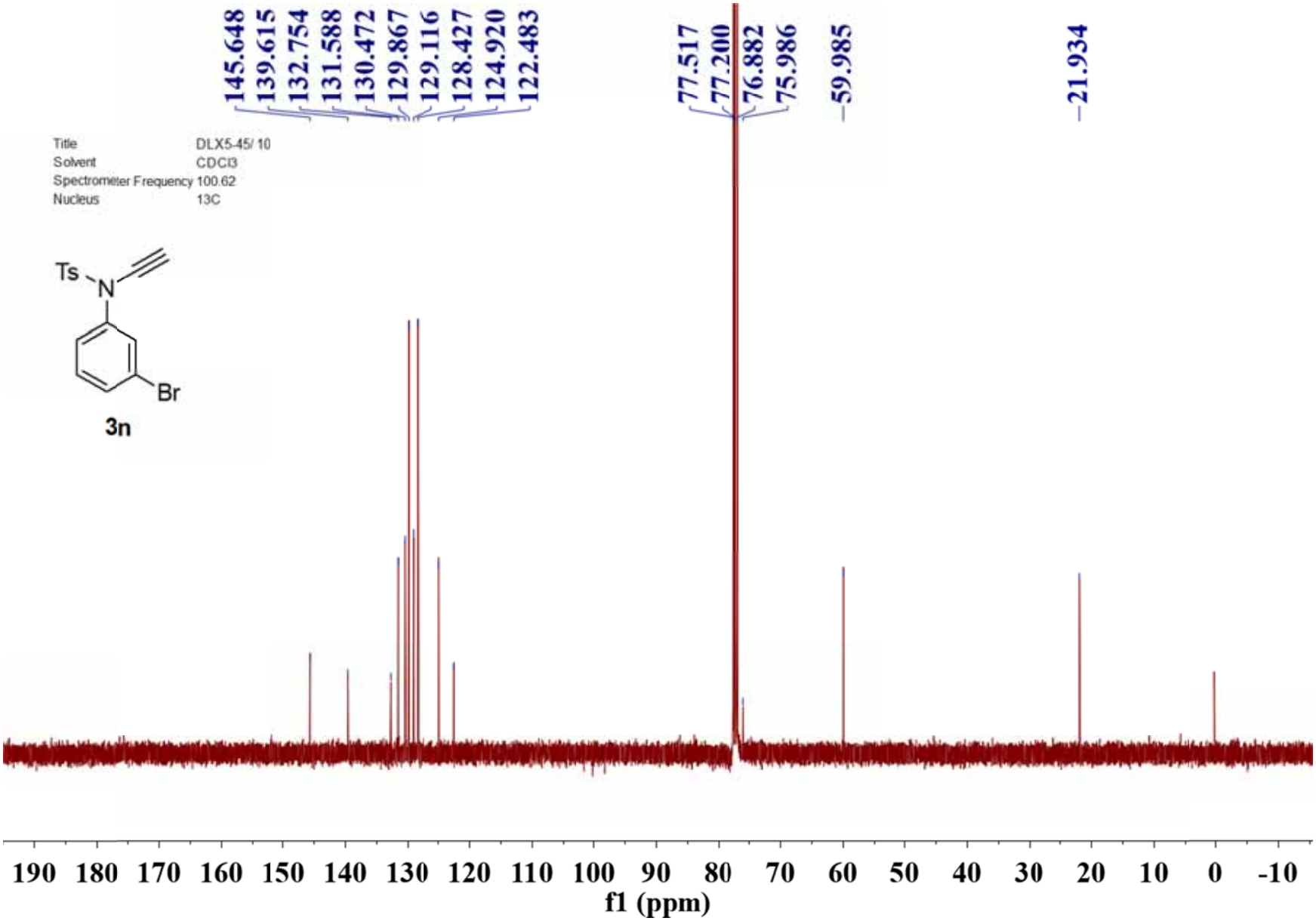

7.6097
7.5889
7.3006
7.2807
7.2169
7.1977
7.1783
7.1381
7.1350
7.1337
7.1322
7.1277
7.1191
7.1149
7.1132
7.1101
7.0945
7.0928
7.0888
7.0871
7.0854
7.0813
7.0171
6.9976
2.8230
2.4470
2.3199
0.0000
Title DLX3-72-10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
3l
2.08
2.07
1.06
2.06
1.07
1.00
3.02
3.07
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)

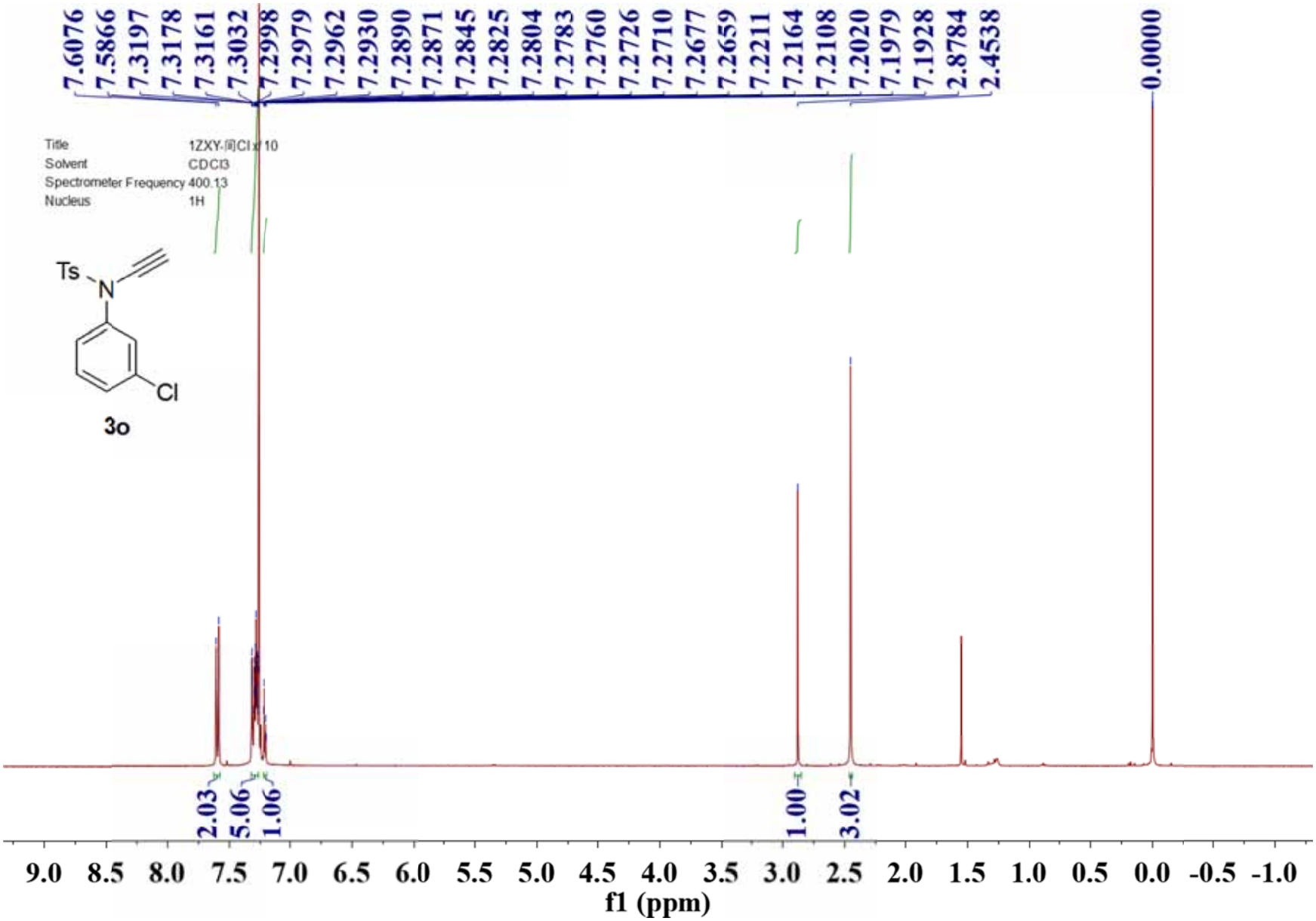

145.183
139.424
138.283
133.195
129.666
129.414
129.032
128.451
127.183
123.363
77.517
77.200
76.882
76.841
58.933
21.893
21.430
Title DLX3-72/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

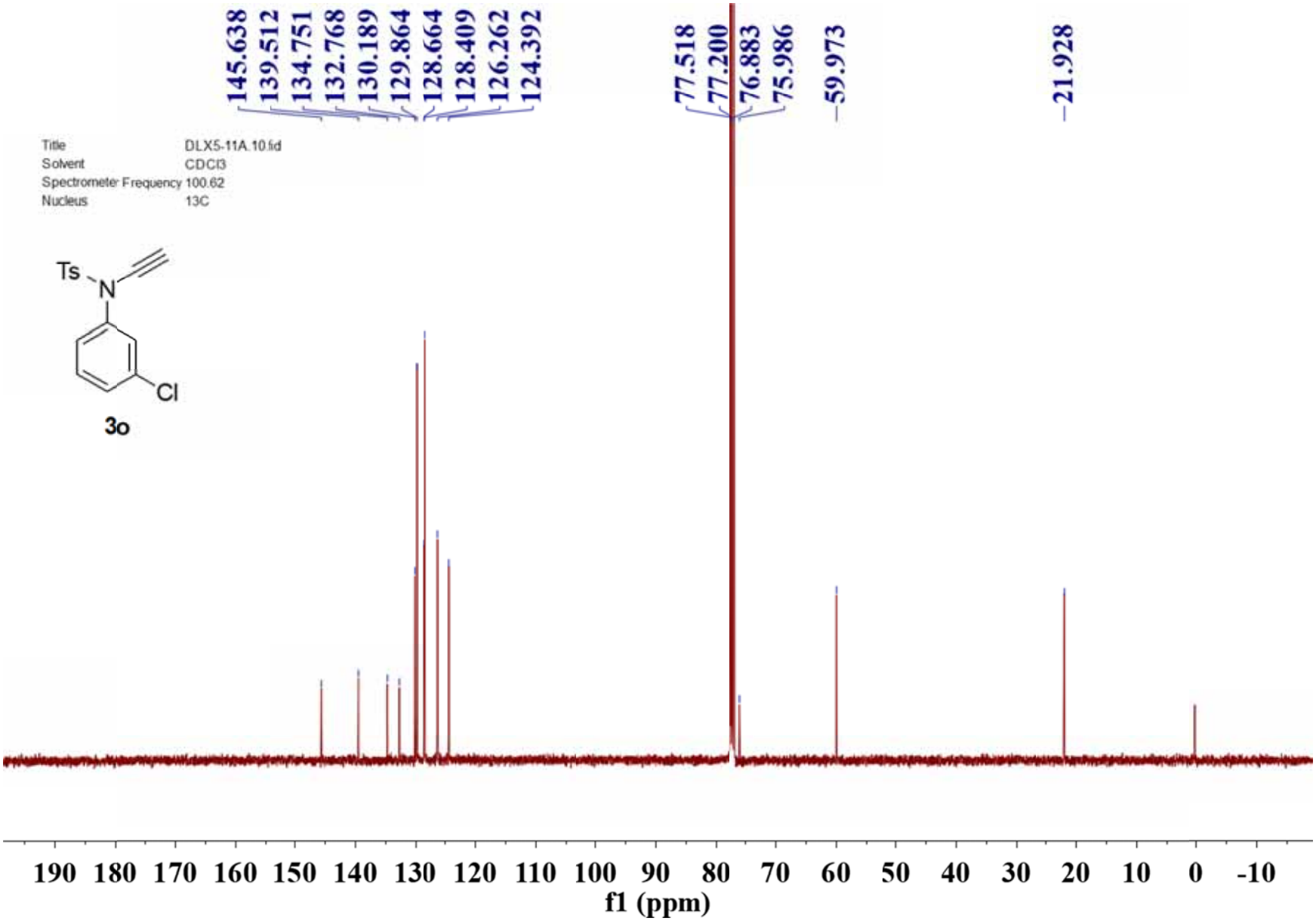

7.6235
7.6026
7.3016
7.2814
7.2344
7.2135
7.1924
6.8718
6.8680
6.8635
6.8516
6.8490
6.8452
6.8428
6.8333
6.8296
6.8279
6.8229
6.8161
6.8137
6.8109
6.8085
3.7593
2.8448
2.4429
0.0000
Title ZXY-JOCH3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
OMe
3m
2.06
2.06
1.06
3.03
3.06
1.00
3.08
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)

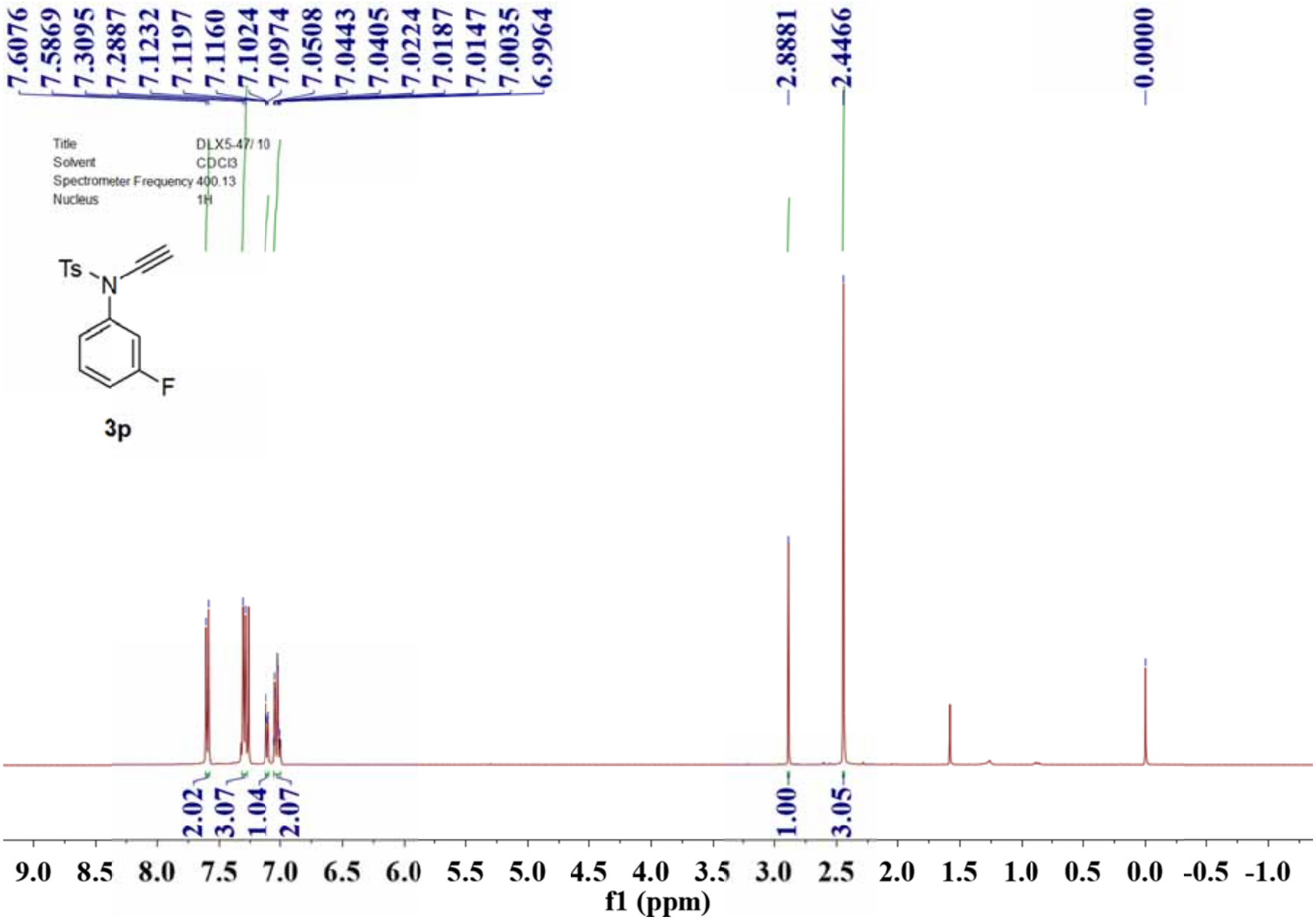

160.100
145.272
139.435
133.115
129.855
129.711
128.438
118.404
114.535
112.038
77.518
77.200
76.882
76.600
59.254
55.623
21.900
Title DLX5-12.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
OMe
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

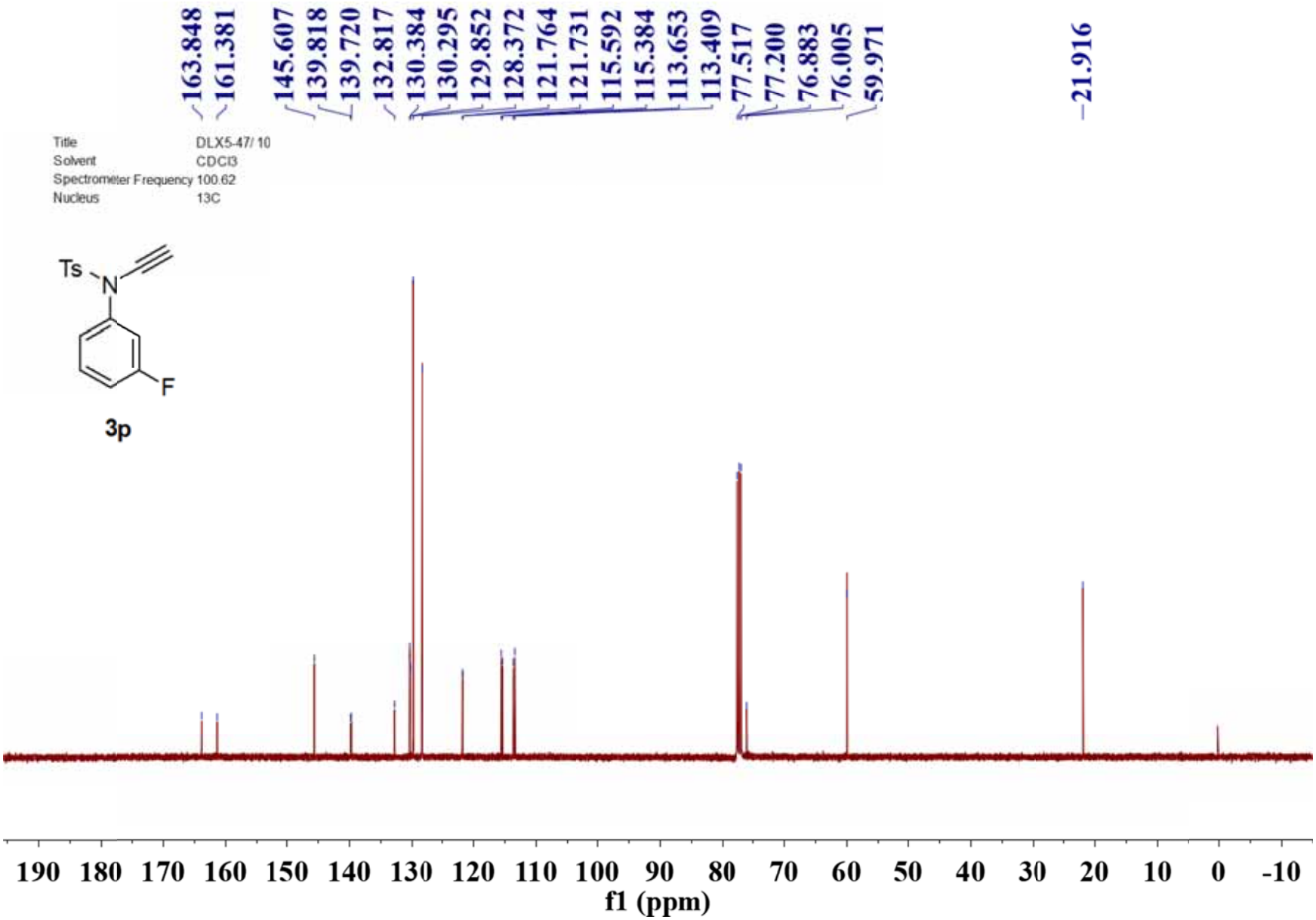

7.6051
7.5842
7.4615
7.4584
7.4567
7.4534
7.4423
7.4392
7.4377
7.4344
7.4319
7.4214
7.4165
7.4117
7.3205
7.3006
7.2497
7.2465
7.2445
7.2412
7.2386
7.2271
7.2257
7.2234
7.2067
7.1872
2.8782
2.4551
0.0000
Title DLX5-45/10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Br
3n
2.03
1.08
1.06
2.03
1.01
1.11
1.00
3.03
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)

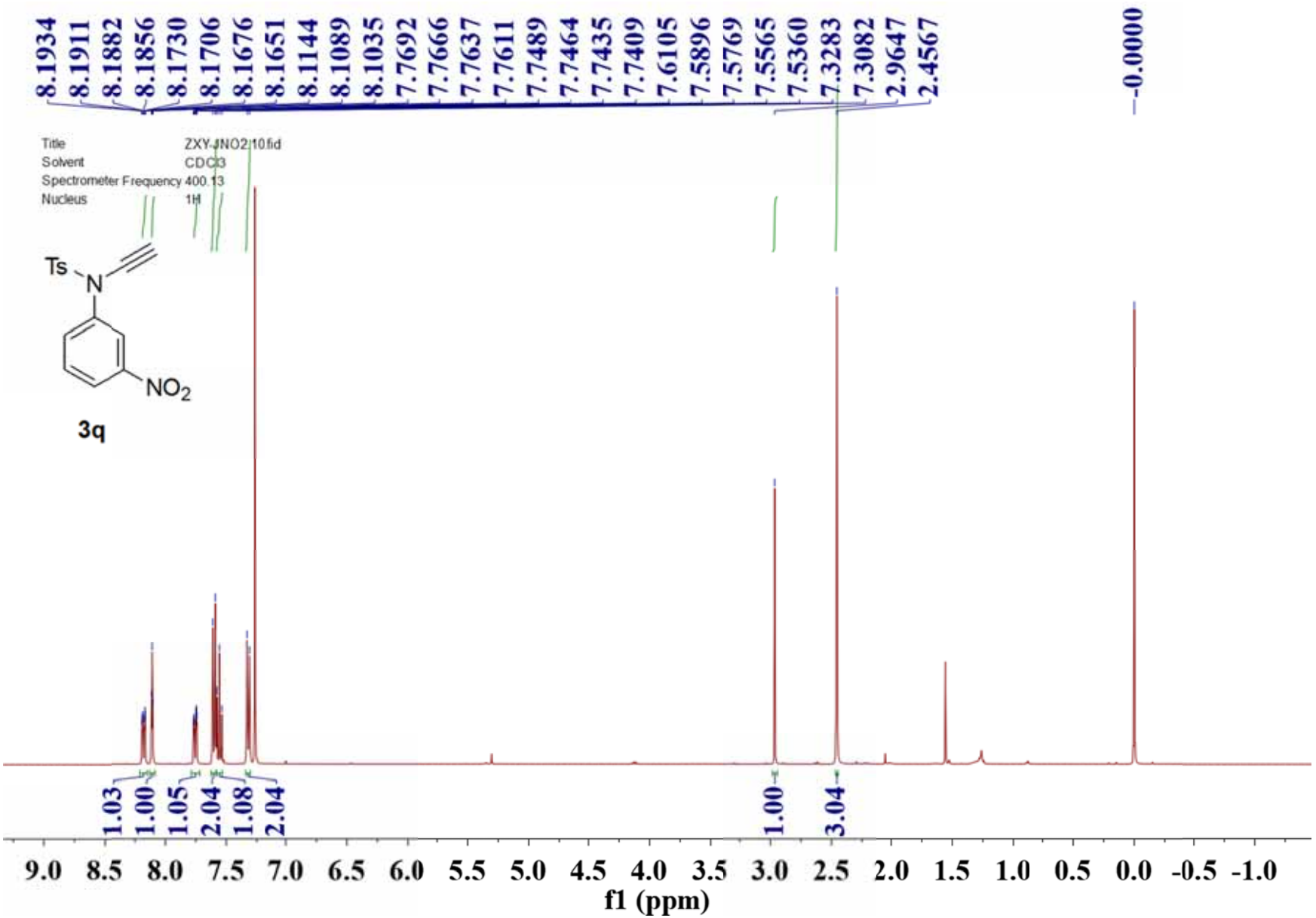

145.648
139.615
132.754
131.588
130.472
129.867
129.116
128.427
124.920
122.483
77.517
77.200
76.882
75.986
59.985
21.934
Title DLX5-45/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Br
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

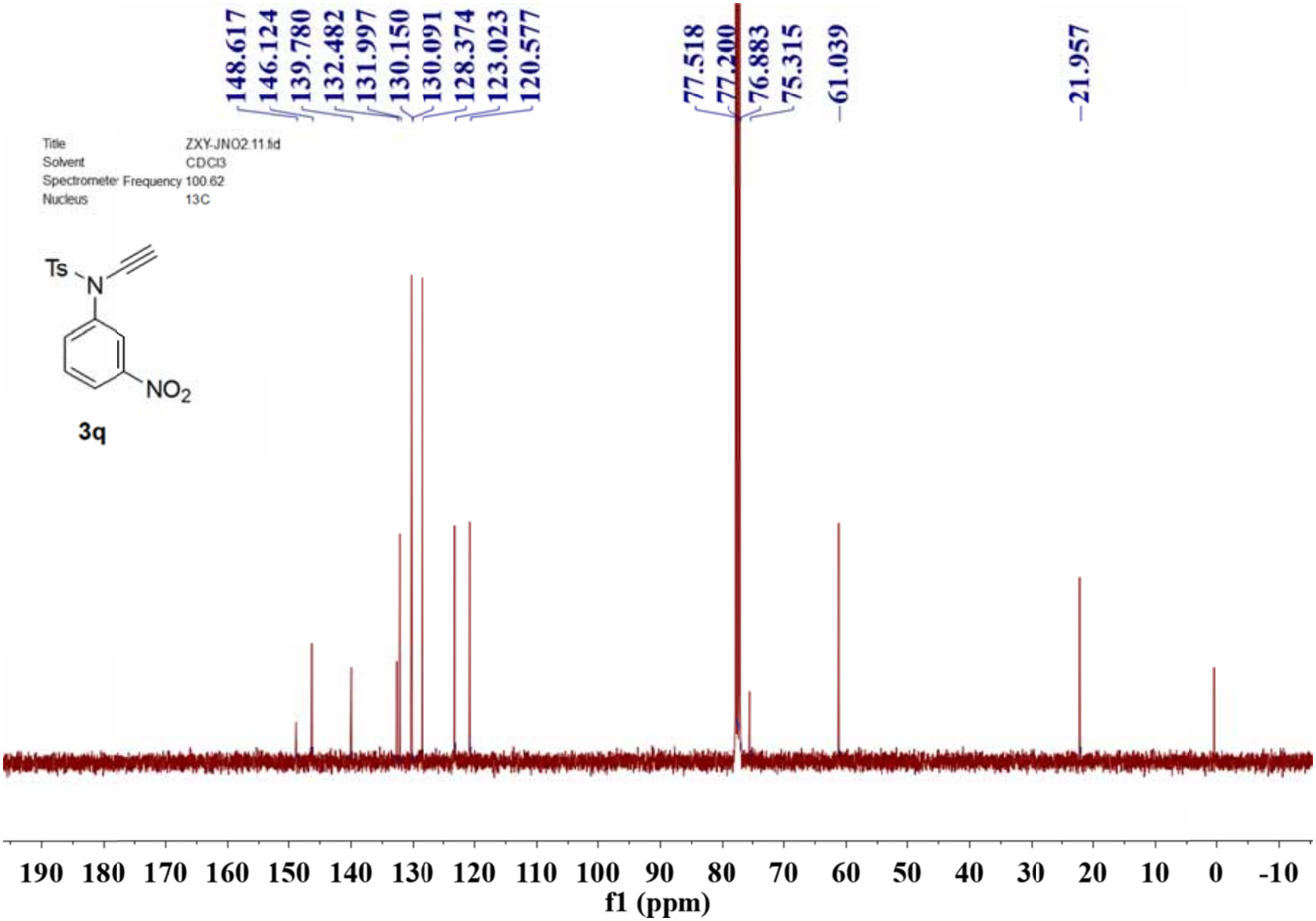

7.6076
7.5866
7.3197
7.3178
7.3161
7.3032
7.2998
7.2979
7.2962
7.2930
7.2890
7.2871
7.2845
7.2825
7.2804
7.2783
7.2760
7.2726
7.2710
7.2677
7.2659
7.2211
7.2164
7.2108
7.2020
7.1979
7.1928
2.8784
2.4538
0.0000
Title
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Cl
3o
2.03
5.06
1.06
1.00
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)

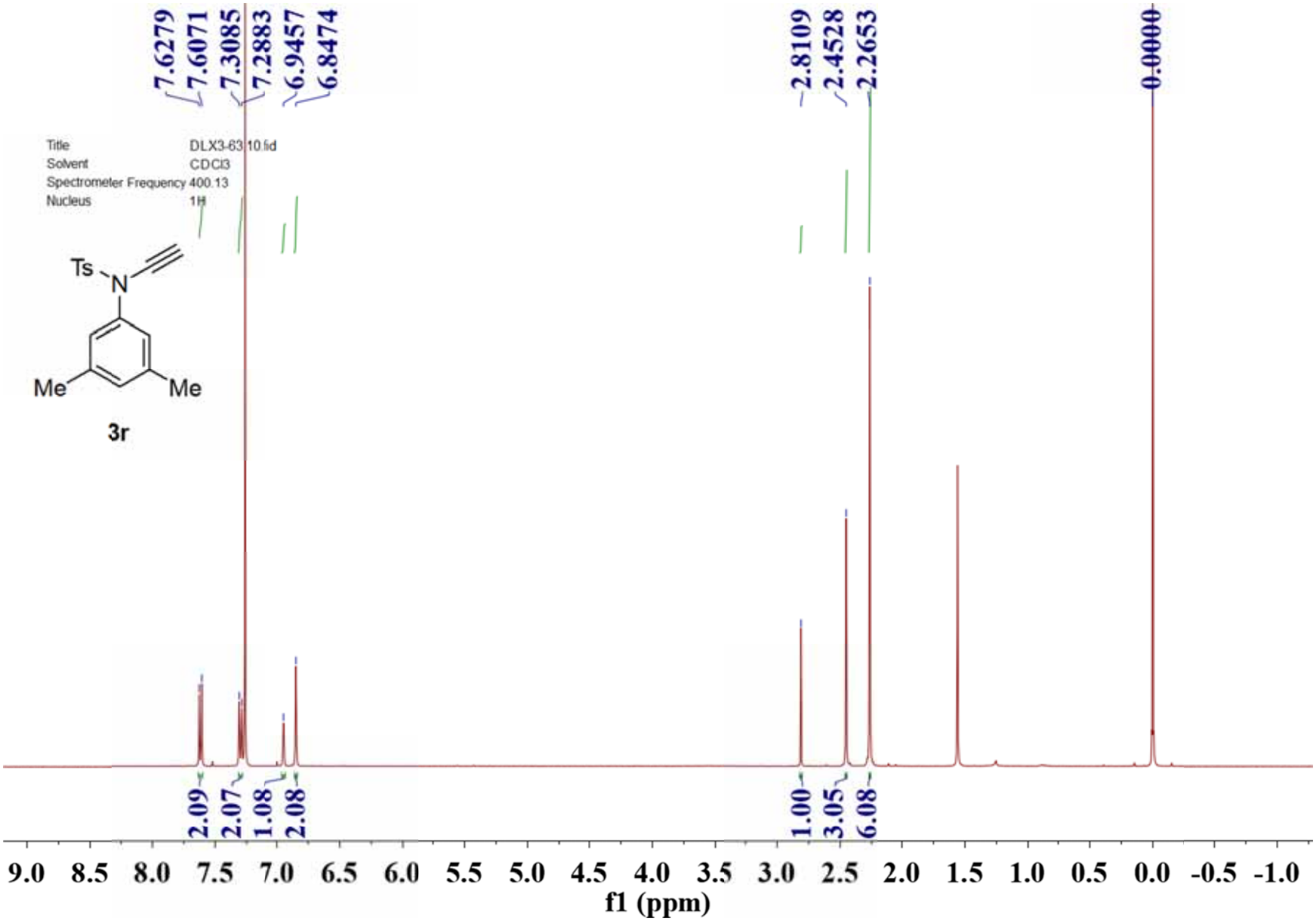

145.638
139.512
134.751
132.768
130.189
129.864
128.664
128.409
126.262
124.392
77.518
77.200
76.883
75.986
59.973
21.928
Title DLX5-11A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Cl
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

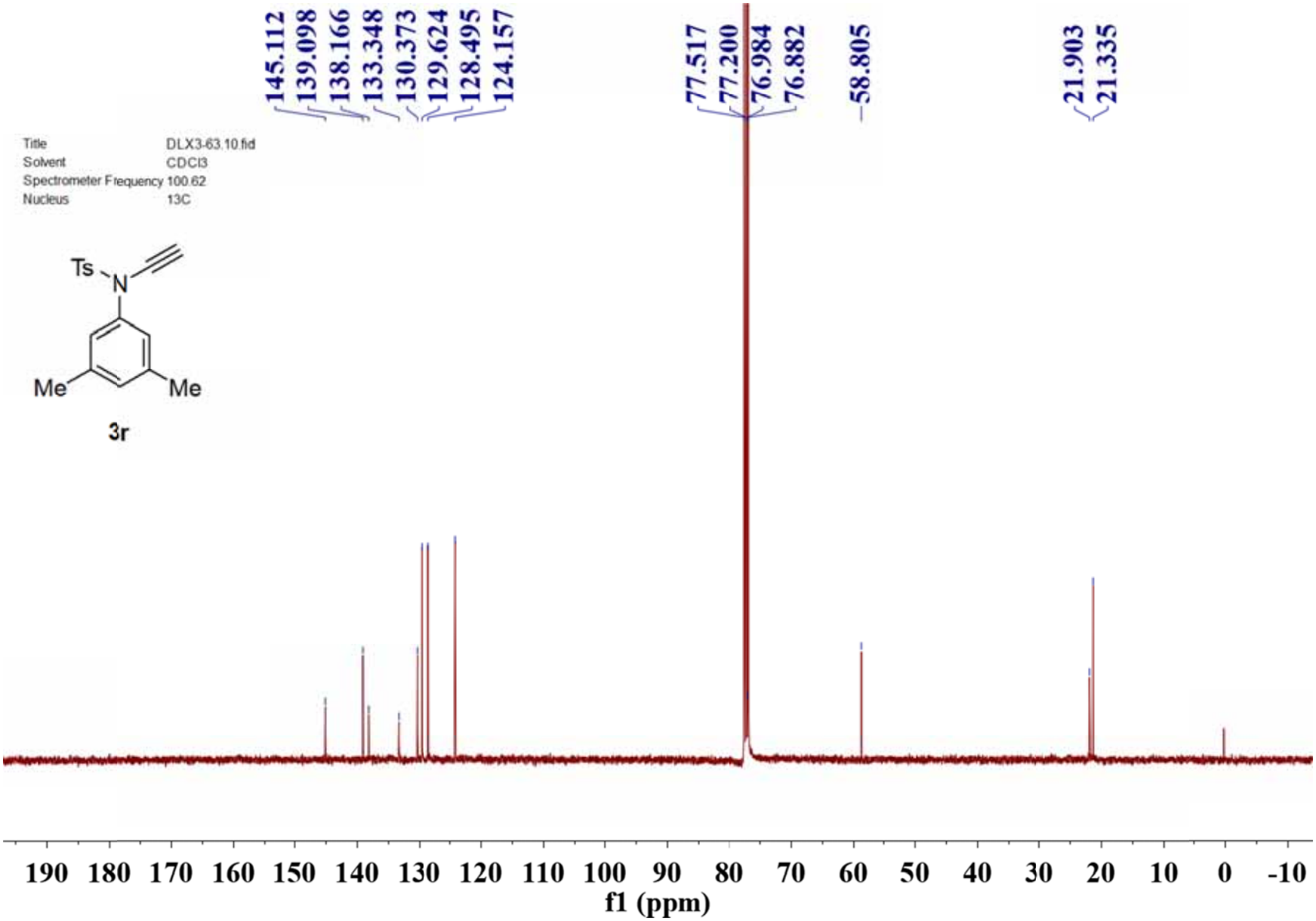

7.6076
7.5869
7.3095
7.2887
7.1232
7.1197
7.1160
7.1024
7.0974
7.0508
7.0443
7.0405
7.0224
7.0187
7.0147
7.0035
6.9964
2.8881
2.4466
0.0000
Title DLX5-47/10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
F
3p
2.02
3.07
1.04
2.07
1.00
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

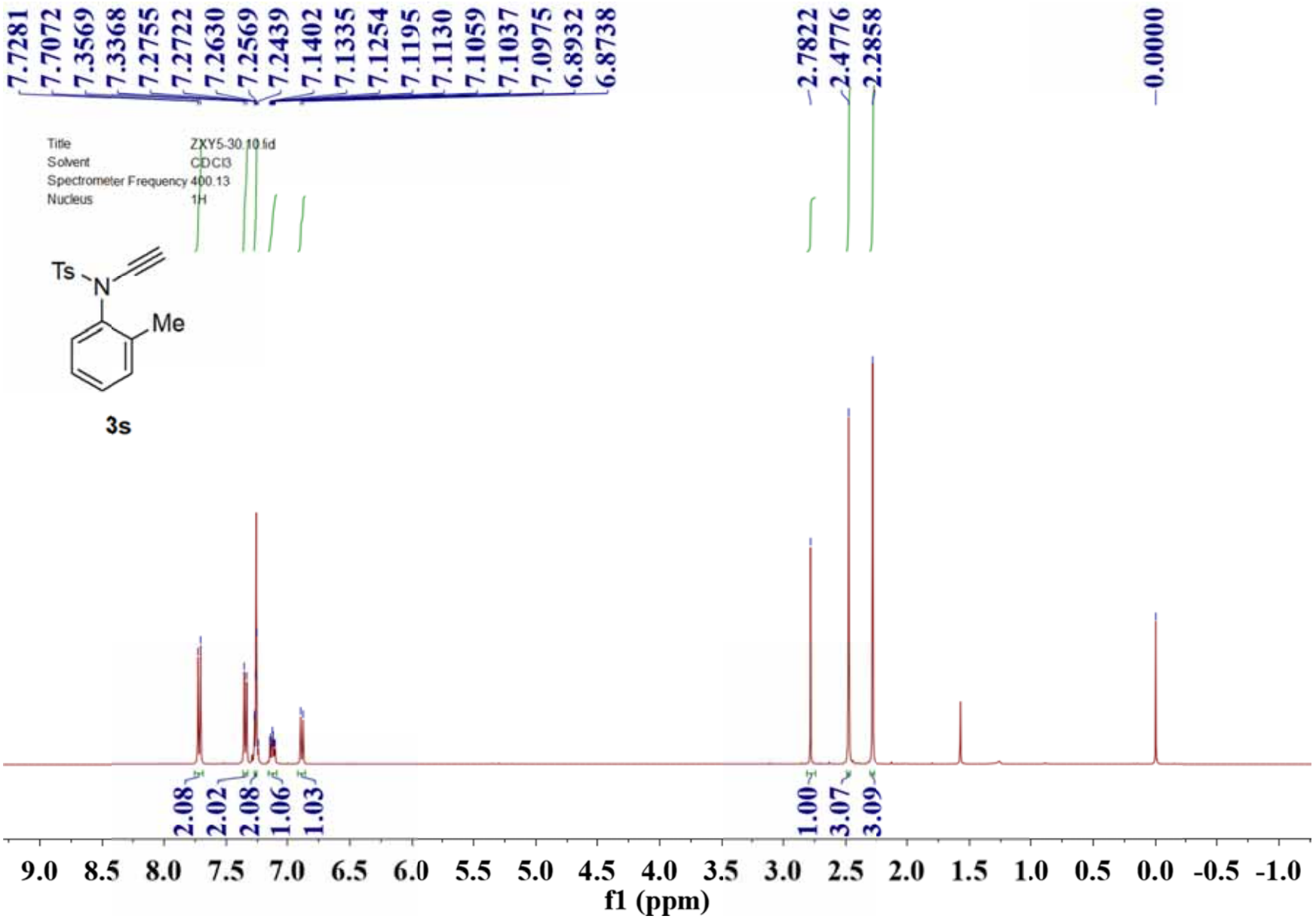

163.848
161.381
145.607
139.818
139.720
132.817
130.384
130.295
129.852
128.372
121.764
121.731
115.592
115.384
113.653
113.409
77.517
77.200
76.883
76.005
59.971
21.916
Title DLX5-47/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
F
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

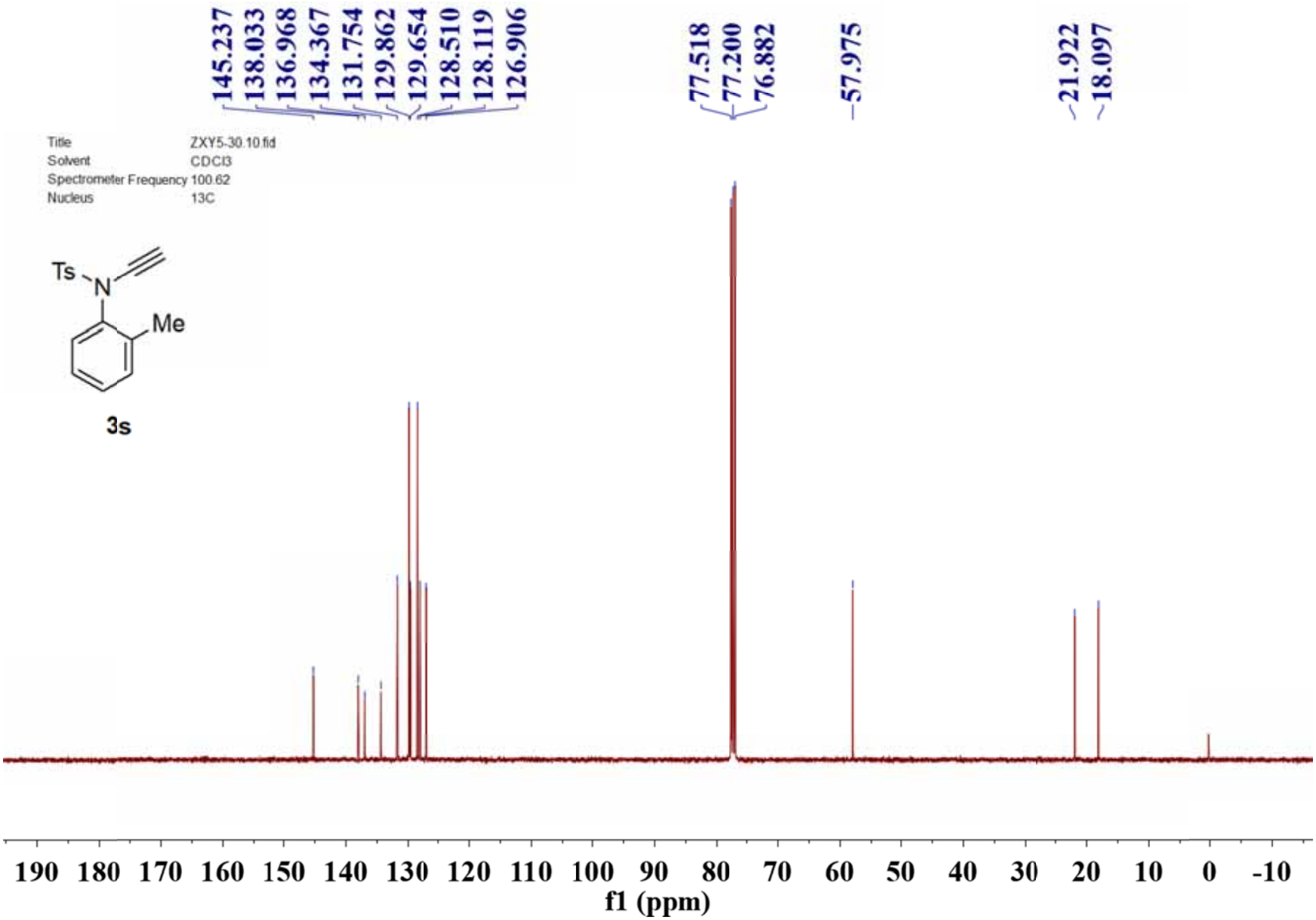

8.1934
8.1911
8.1882
8.1856
8.1730
8.1706
8.1676
8.1651
8.1144
8.1089
8.1035
7.7692
7.7666
7.7637
7.7611
7.7489
7.7464
7.7435
7.7409
7.6105
7.5896
7.5769
7.5565
7.5360
7.3283
7.3082
2.9647
2.4567
-0.0000
Title ZXY-JNO2-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
NO2
3q
1.03
1.00
1.05
2.04
1.08
2.04
1.00
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)

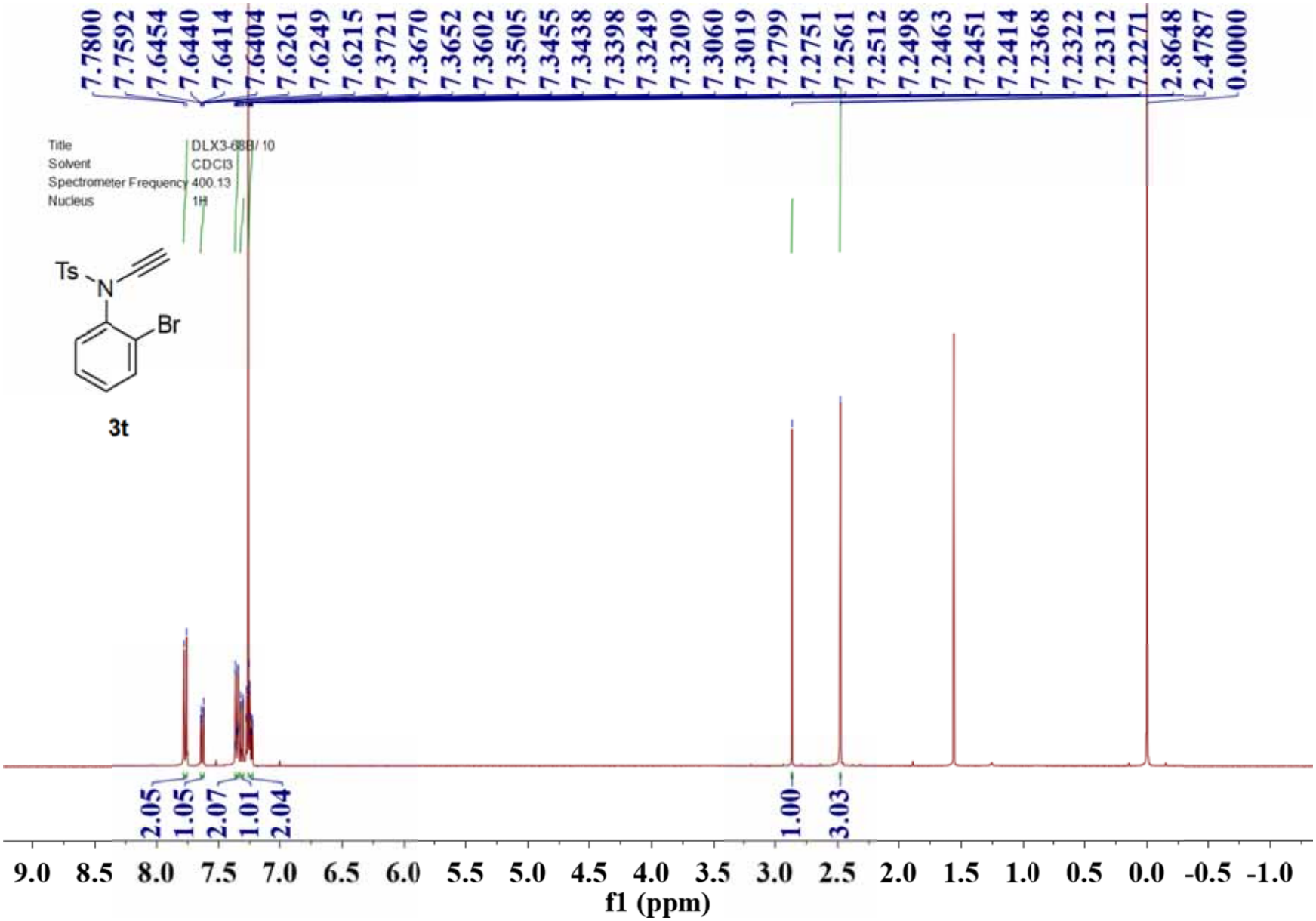

148.617
146.124
139.780
132.482
131.997
130.150
130.091
128.374
123.023
120.577
77.518
77.200
76.883
75.315
61.039
21.957
Title ZXY-JNO2.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
NO2
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

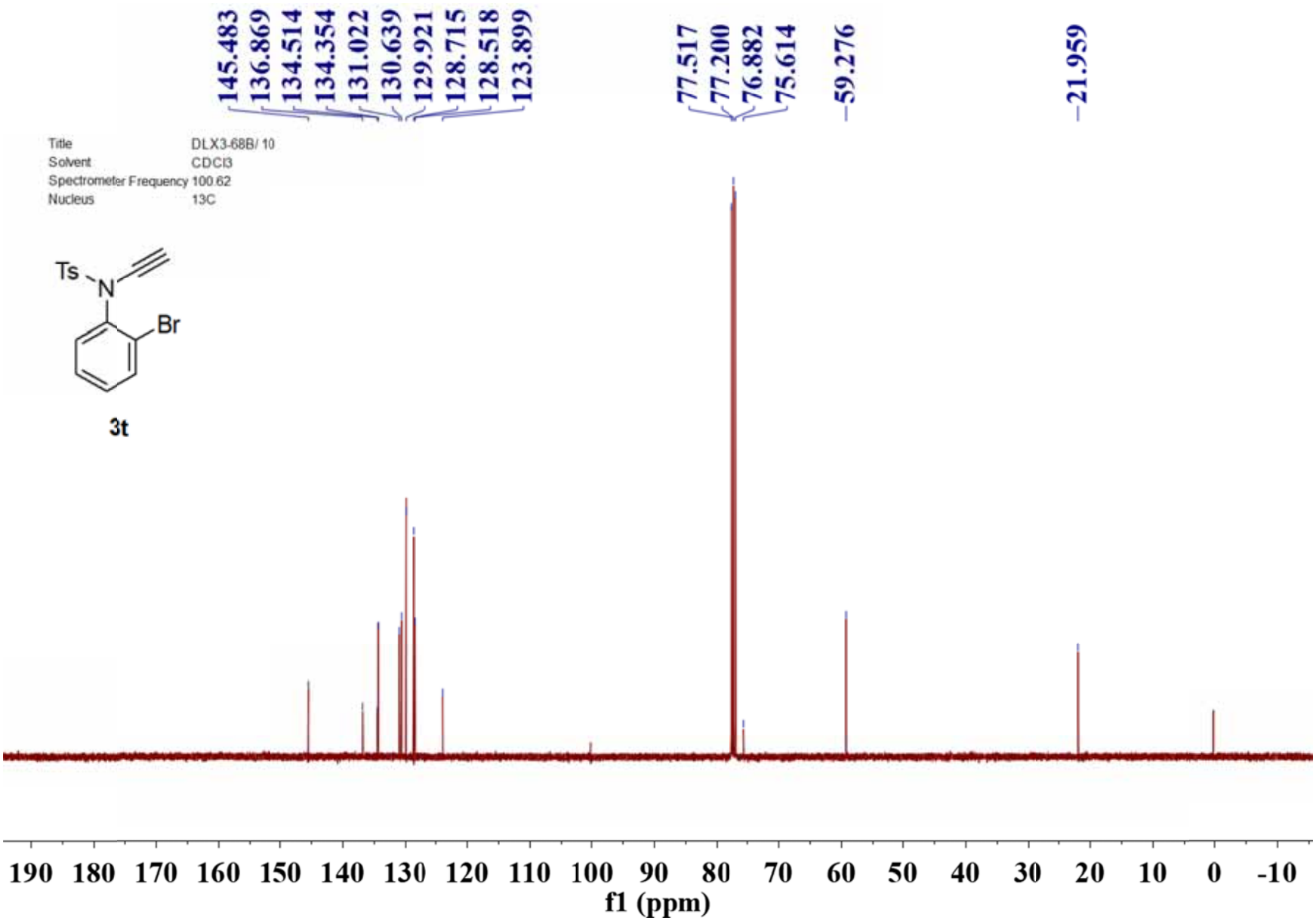

7.6279
7.6071
7.3085
7.2883
6.9457
6.8474
2.8109
2.4528
2.2653
0.0000
Title DLX3-63 10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
3r
2.09
2.07
1.08
2.08
1.00
3.05
6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


145.112
139.098
138.166
133.348
130.373
129.624
128.495
124.157
77.517
77.200
76.984
76.882
58.805
21.903
21.335
Title DLX3-63.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

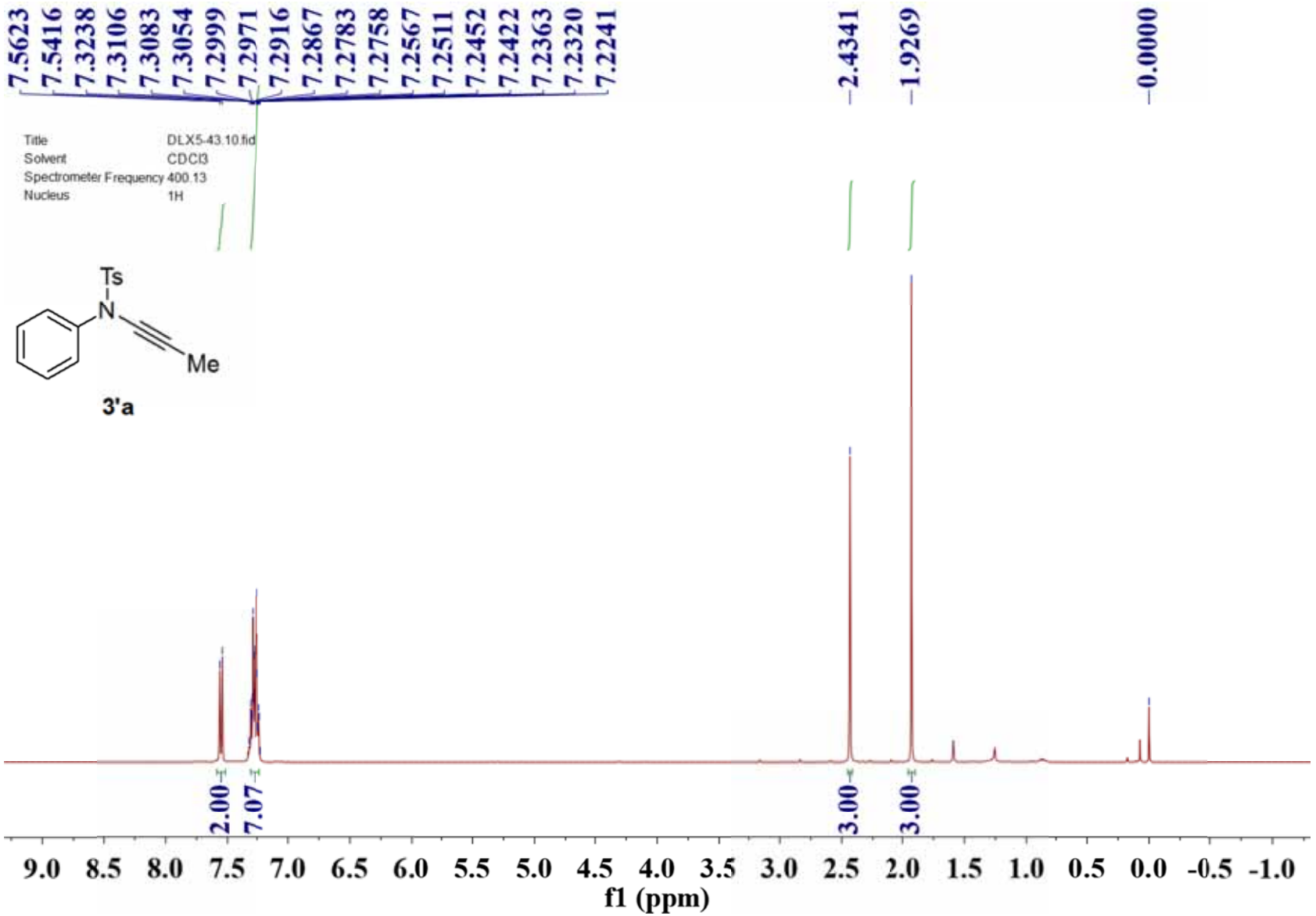

7.7281
7.7072
7.3569
7.3368
7.2755
7.2722
7.2630
7.2569
7.2439
7.1402
7.1335
7.1254
7.1195
7.1130
7.1059
7.1037
7.0975
6.8932
6.8738
2.7822
2.4776
2.2858
0.0000
Title ZXY5-30.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
3s
2.08
2.02
2.08
1.06
1.03
1.00
3.07
3.09
9.0 8.5 8.0 7.5 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)

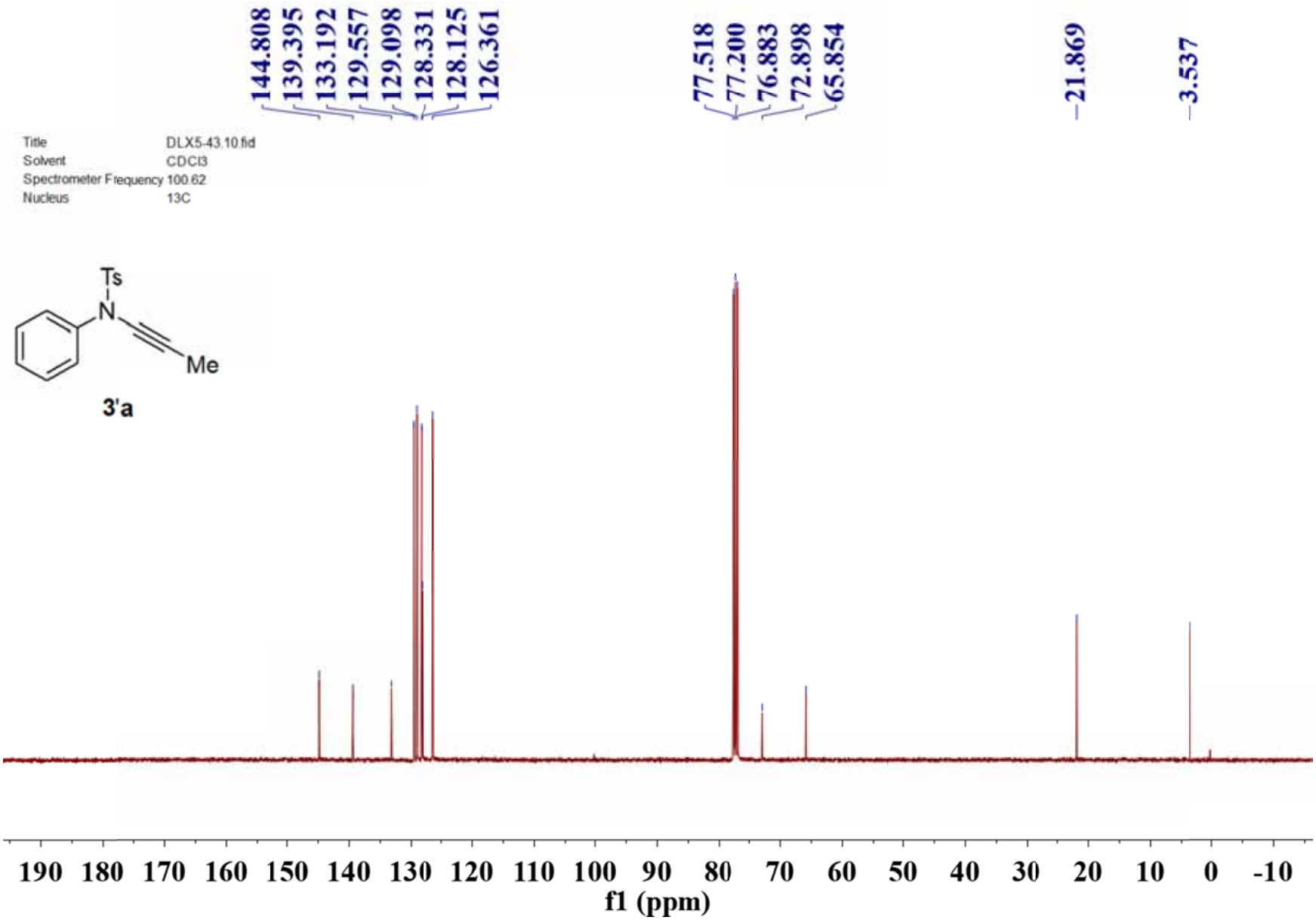

145.237
138.033
136.968
134.367
131.754
129.862
129.654
128.510
128.119
126.906
77.518
77.200
76.882
57.975
21.922
18.097
Title ZXY5-30.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

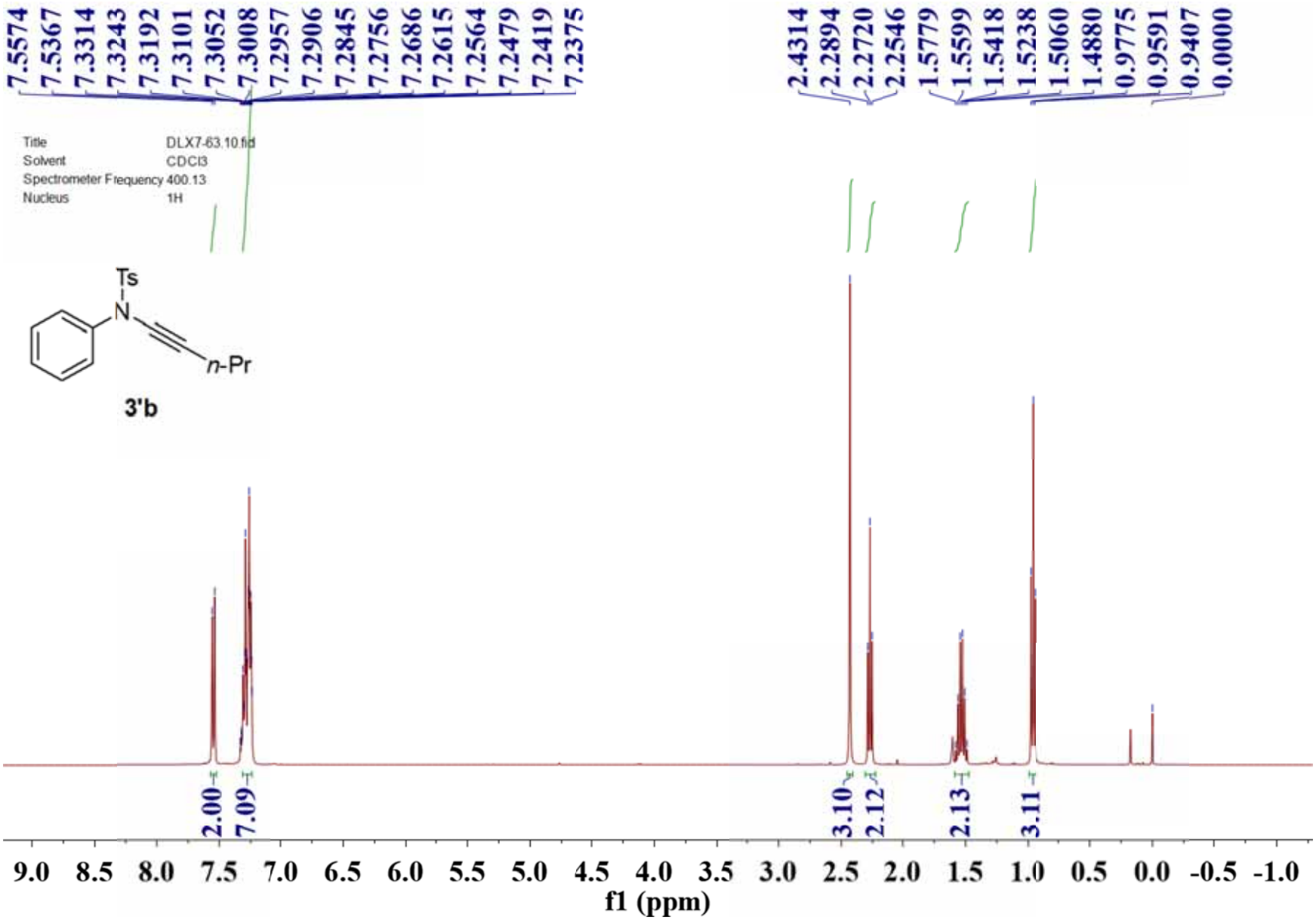

7.7800
7.7592
7.6454
7.6440
7.6414
7.6404
7.6261
7.6249
7.6215
7.3721
7.3670
7.3652
7.3602
7.3505
7.3455
7.3438
7.3398
7.3249
7.3209
7.3060
7.3019
7.2799
7.2751
7.2561
7.2512
7.2498
7.2463
7.2451
7.2414
7.2368
7.2322
7.2312
7.2271
2.8648
2.4787
0.0000
Title DLX3-68B/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Br
3t
2.05
1.05
2.07
1.01
2.04
1.00
3.03
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)

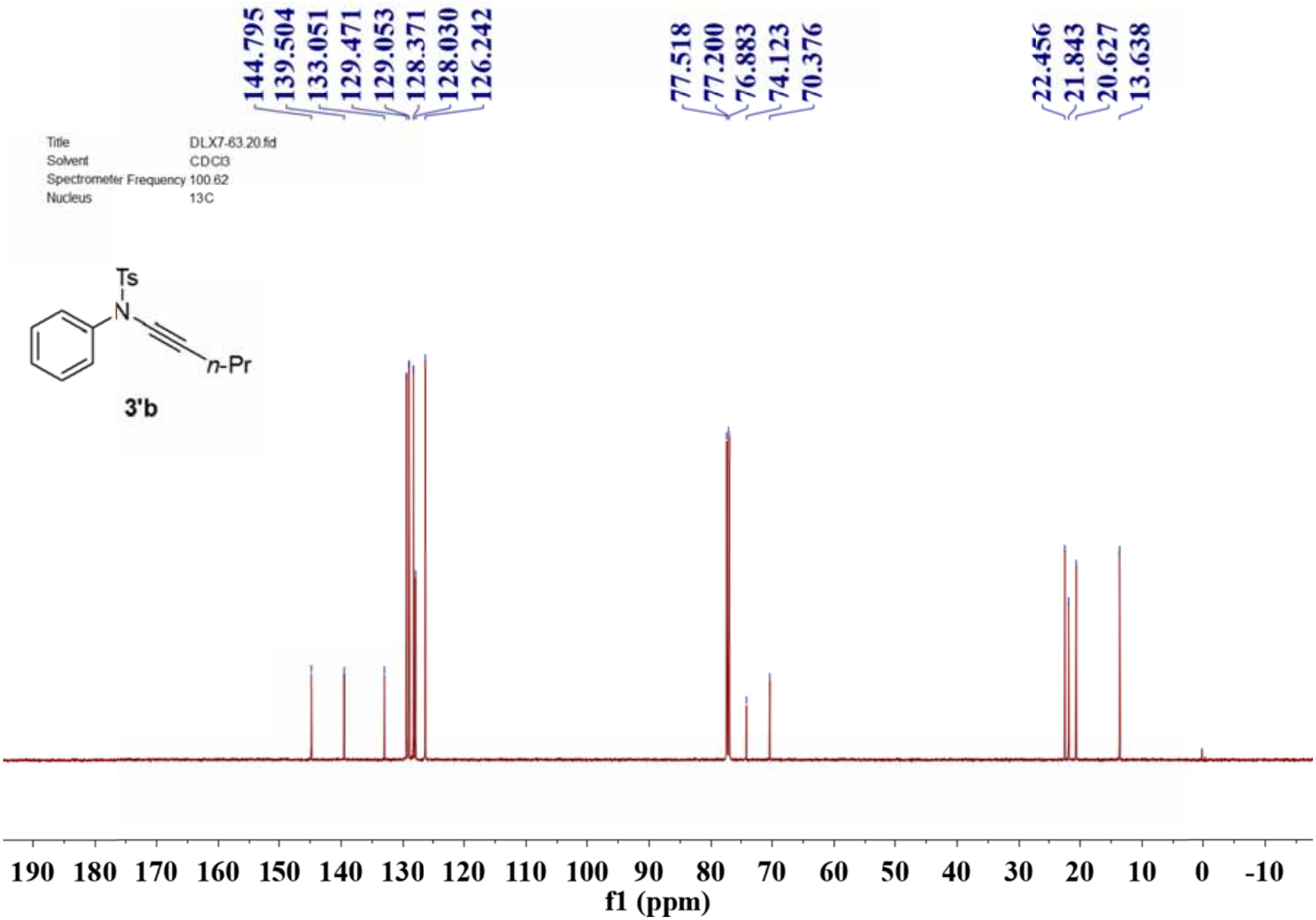

145.483
136.869
134.514
134.354
131.022
130.639
129.921
128.715
128.518
123.899
77.517
77.200
76.882
75.614
59.276
21.959
Title DLX3-68B/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Br
3t
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

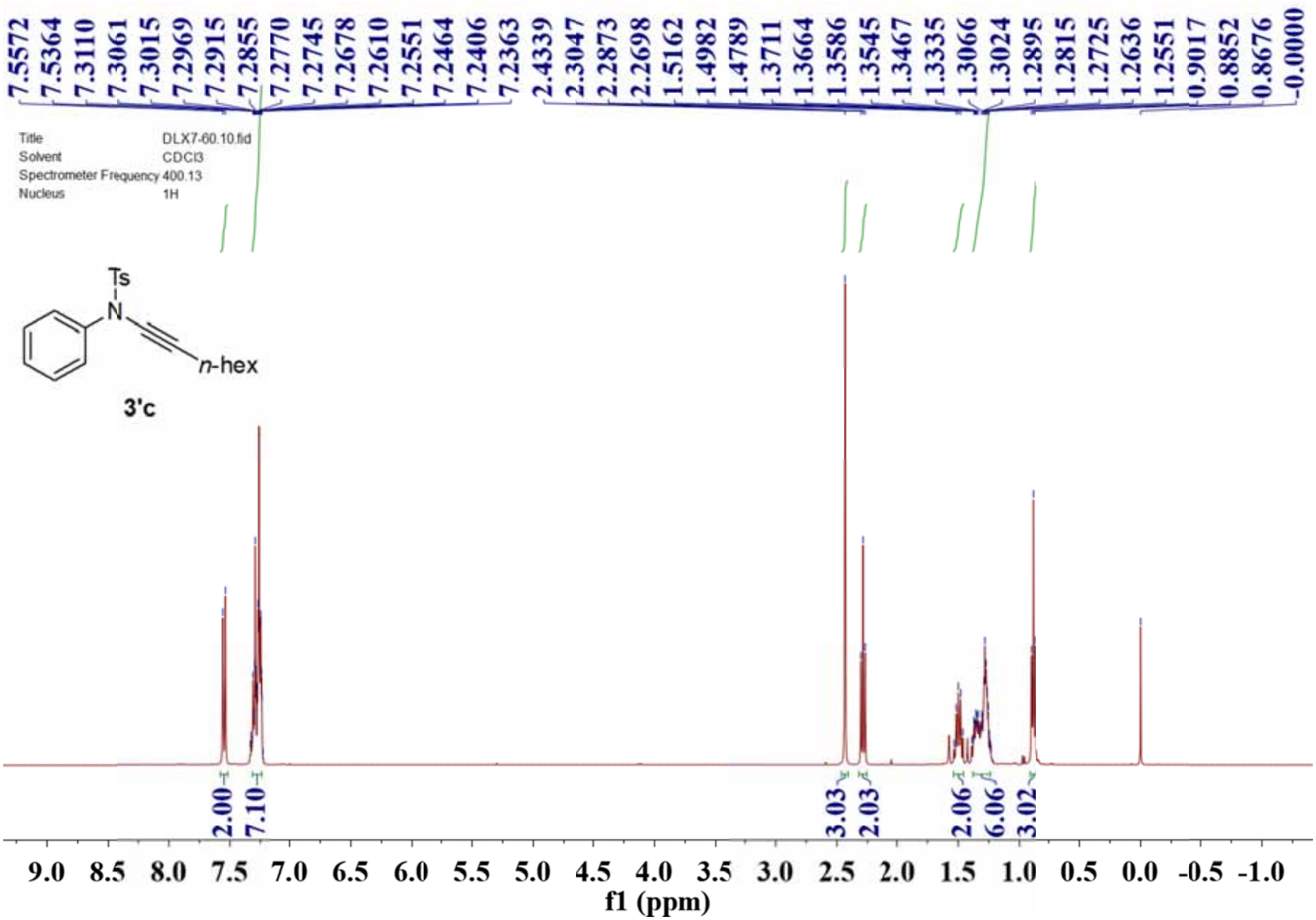
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Internal *N*-Aryl Ynamides 3'.

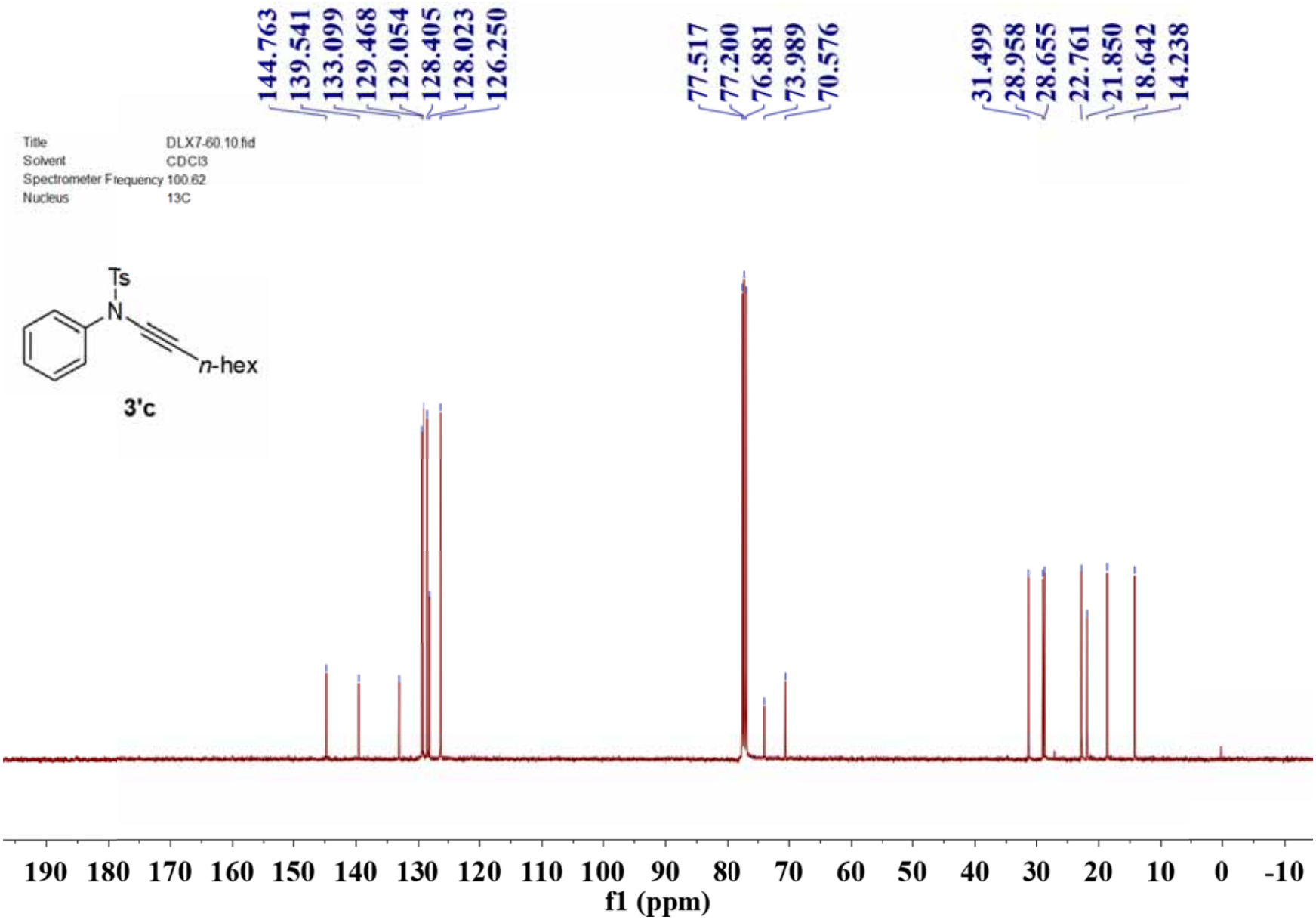


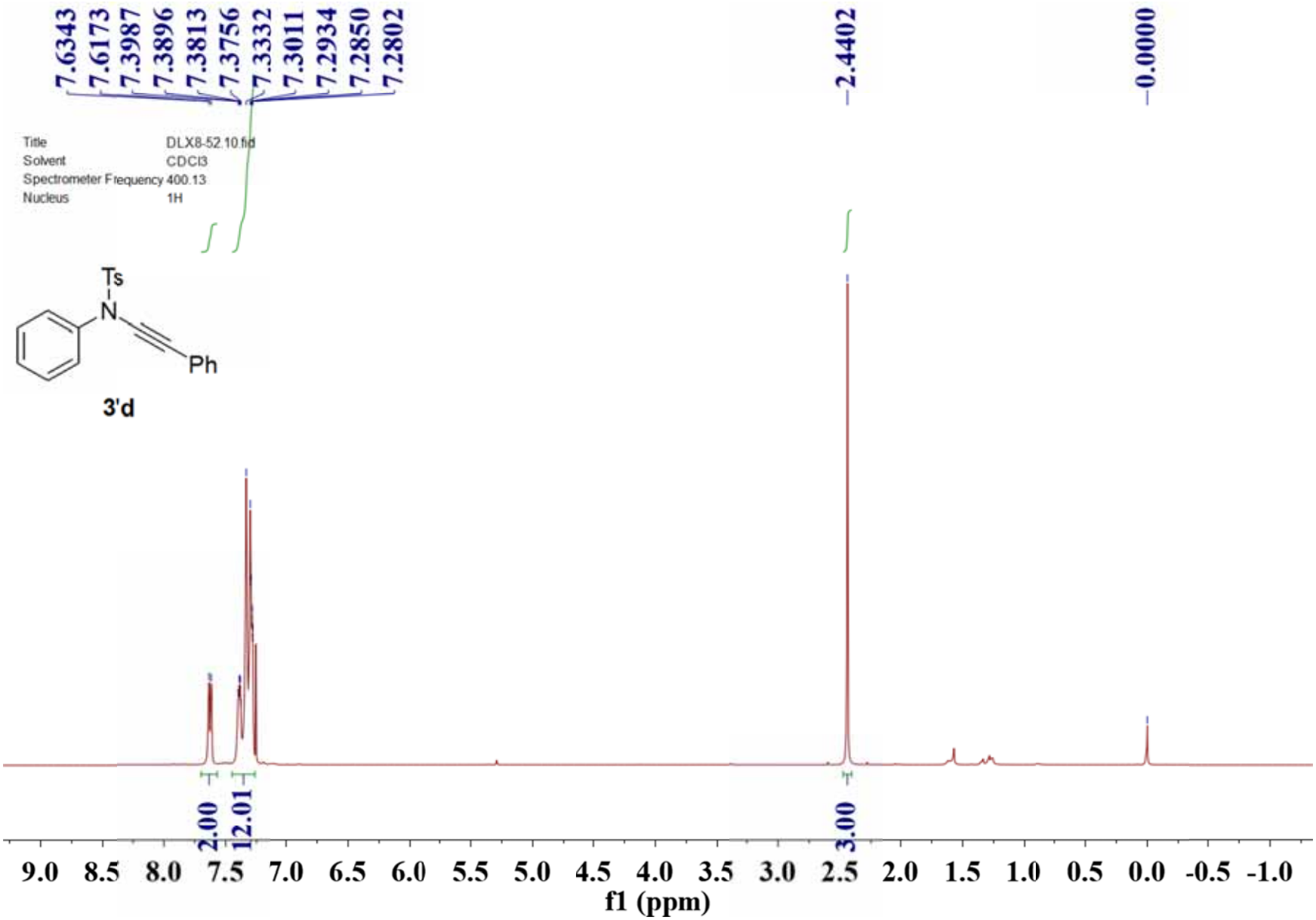

144.808
139.395
133.192
129.557
129.098
128.331
128.125
126.361
77.518
77.200
76.883
72.898
65.854
21.869
3.537
Title DLX5-43.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
3'a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

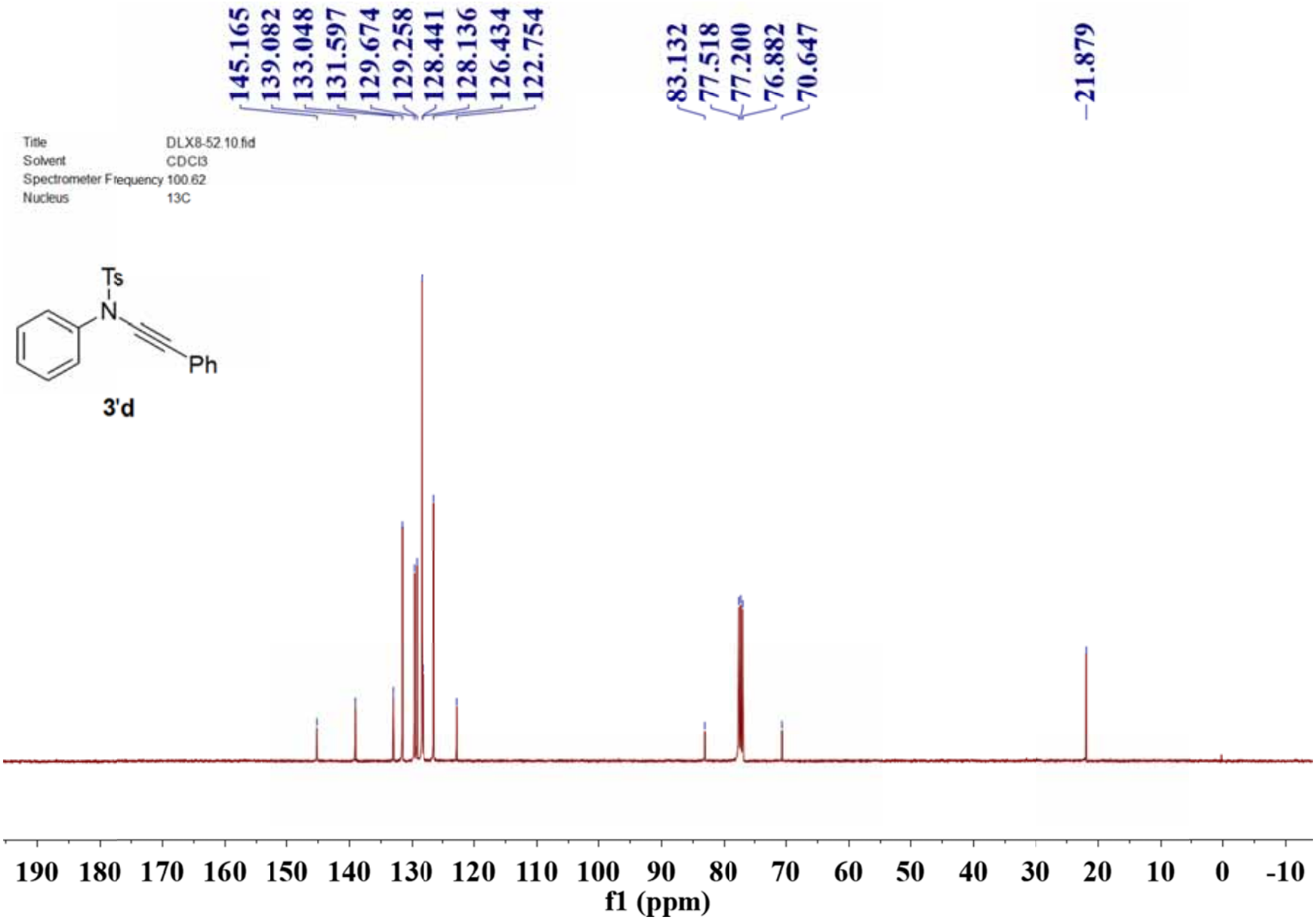

7.5574
7.5367
7.3314
7.3243
7.3192
7.3101
7.3052
7.3008
7.2957
7.2906
7.2845
7.2756
7.2686
7.2615
7.2564
7.2479
7.2419
7.2375
2.4314
2.2894
2.2720
2.2546
1.5779
1.5599
1.5418
1.5238
1.5060
1.4880
0.9775
0.9591
0.9407
0.0000
Title DLX7-63.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
n-Pr
3'b
2.00
7.09
3.10
2.12
2.13
3.11
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)

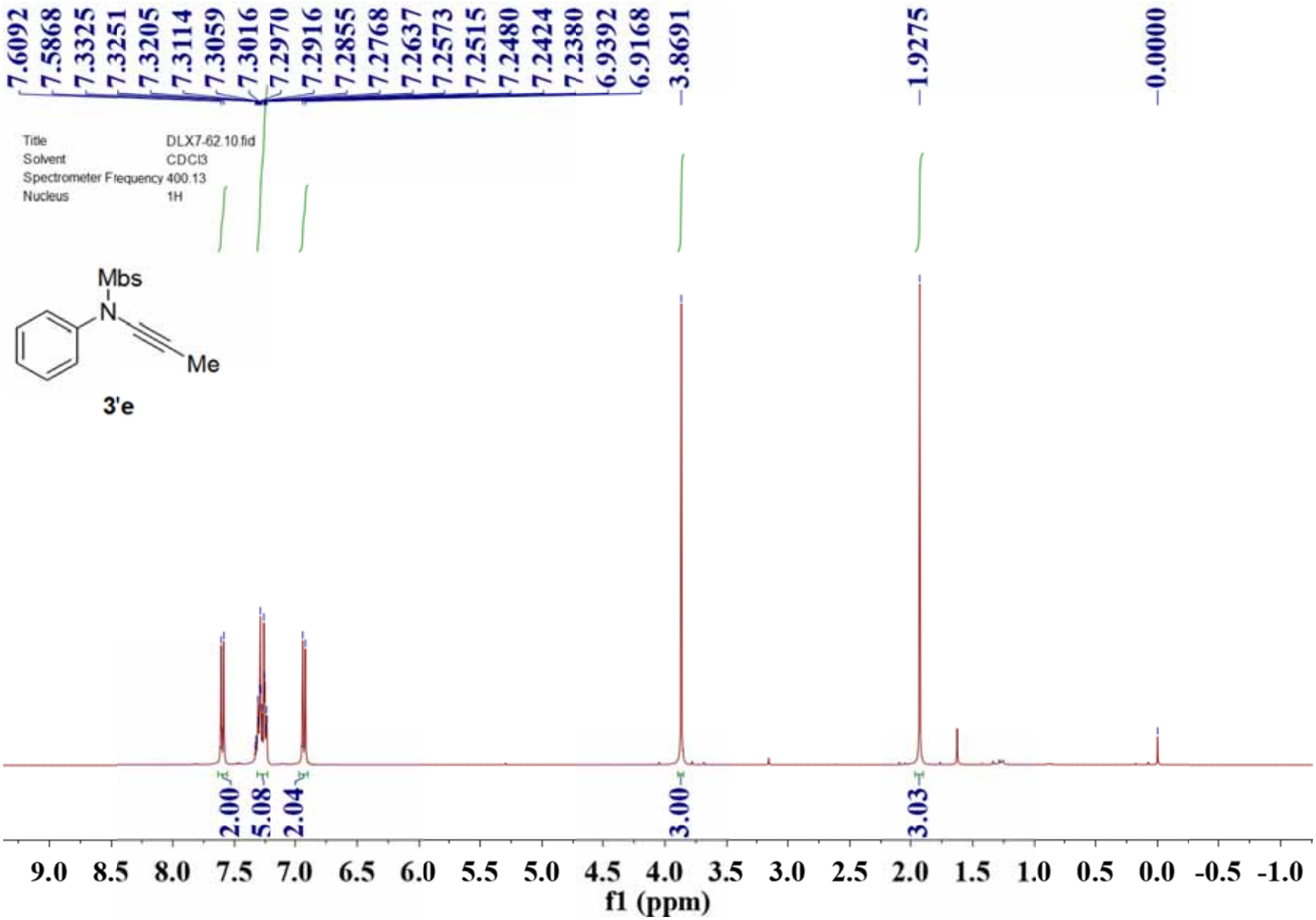

144.795
139.504
133.051
129.471
129.053
128.371
128.030
126.242
77.518
77.200
76.883
74.123
70.376
22.456
21.843
20.627
13.638
Title DLX7-63.20.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
n-Pr
3'b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

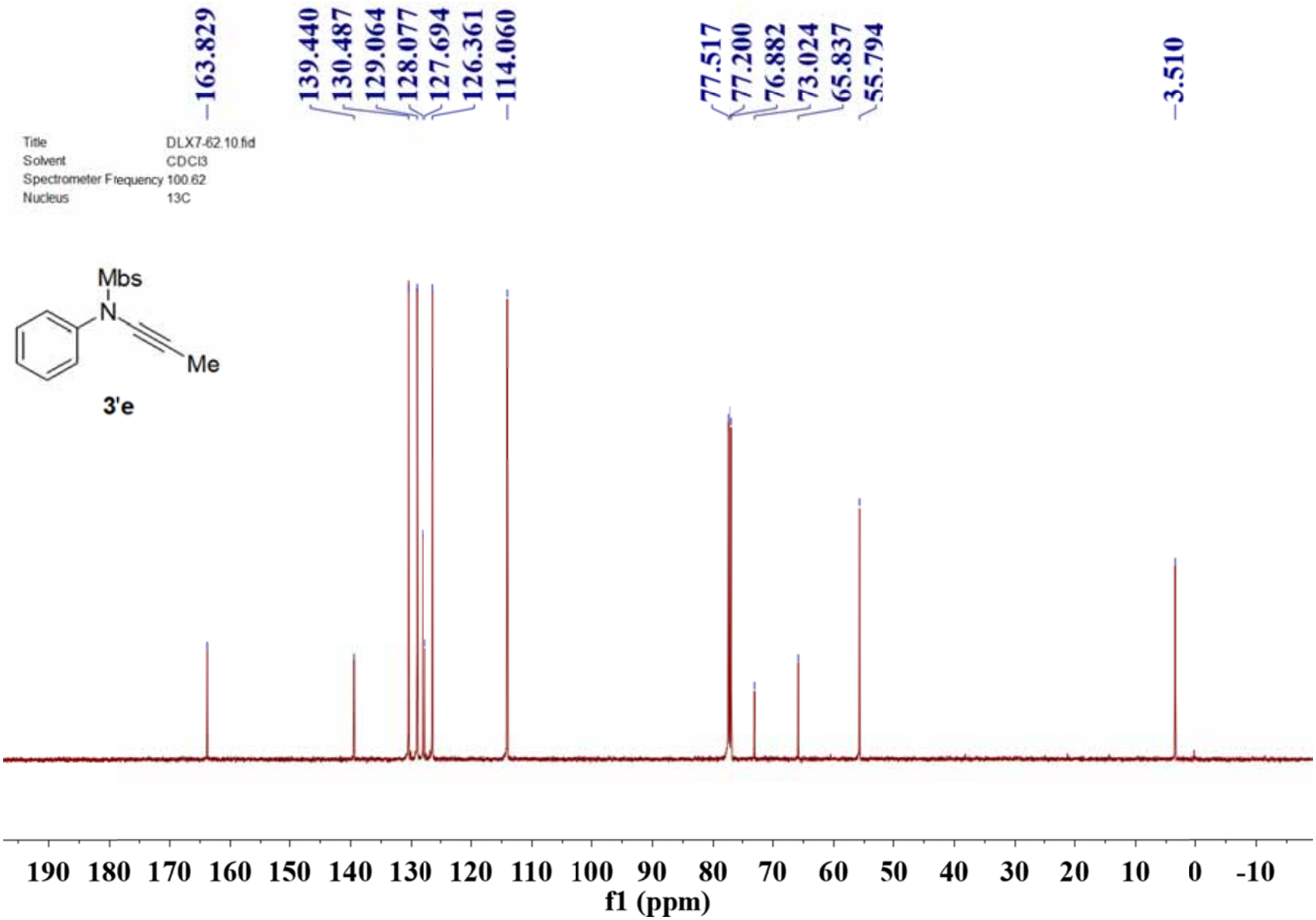

7.5572
7.5364
7.3110
7.3061
7.3015
7.2969
7.2915
7.2855
7.2770
7.2745
7.2678
7.2610
7.2551
7.2464
7.2406
7.2363
2.4339
2.3047
2.2873
2.2698
1.5162
1.4982
1.4789
1.3711
1.3664
1.3586
1.3545
1.3467
1.3335
1.3066
1.3024
1.2895
1.2815
1.2725
1.2636
1.2551
0.9017
0.8852
0.8676
-0.0000
Title DLX7-60.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
n-hex
3'c
2.00
7.10
3.03
2.03
2.06
6.06
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)

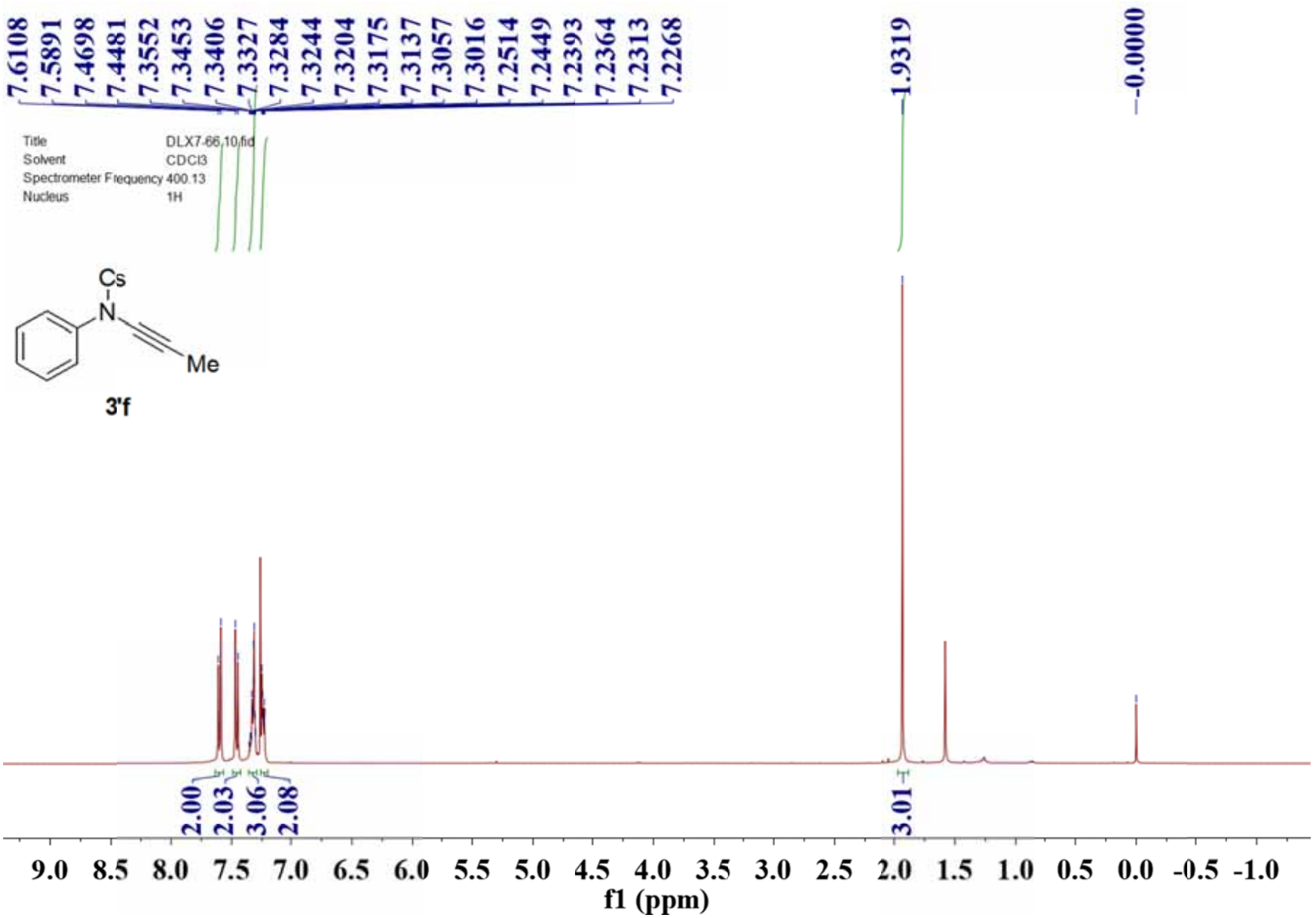

144.763
139.541
133.099
129.468
129.054
128.405
128.023
126.250
77.517
77.200
76.881
73.989
70.576
31.499
28.958
28.655
22.761
21.850
18.642
14.238
Title DLX7-60.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
n-hex
3'c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

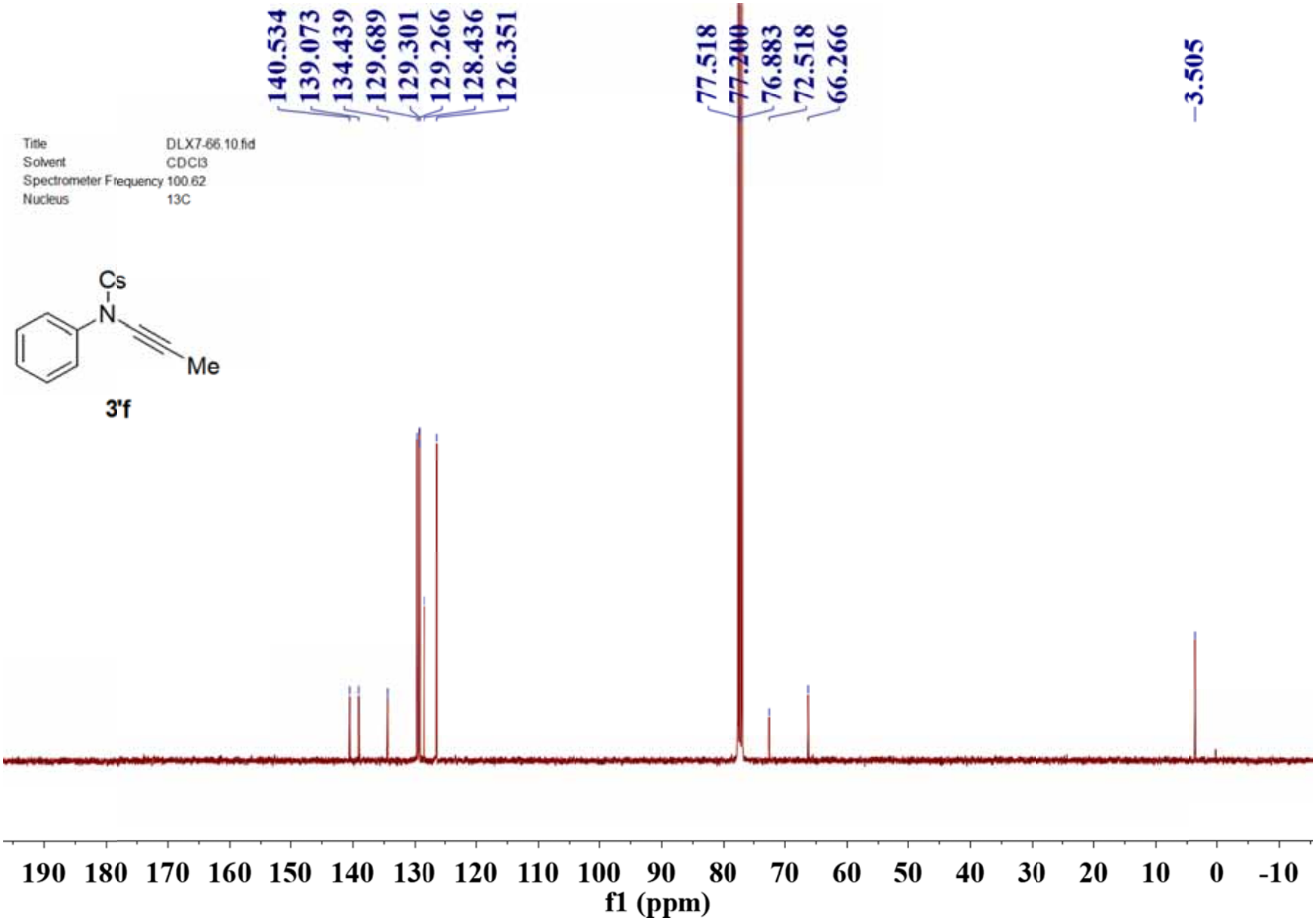

7.6343
7.6173
7.3987
7.3896
7.3813
7.3756
7.3332
7.3011
7.2934
7.2850
7.2802
2.4402
0.0000
Title DLX8-52.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Ph
3'd
2.00
12.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

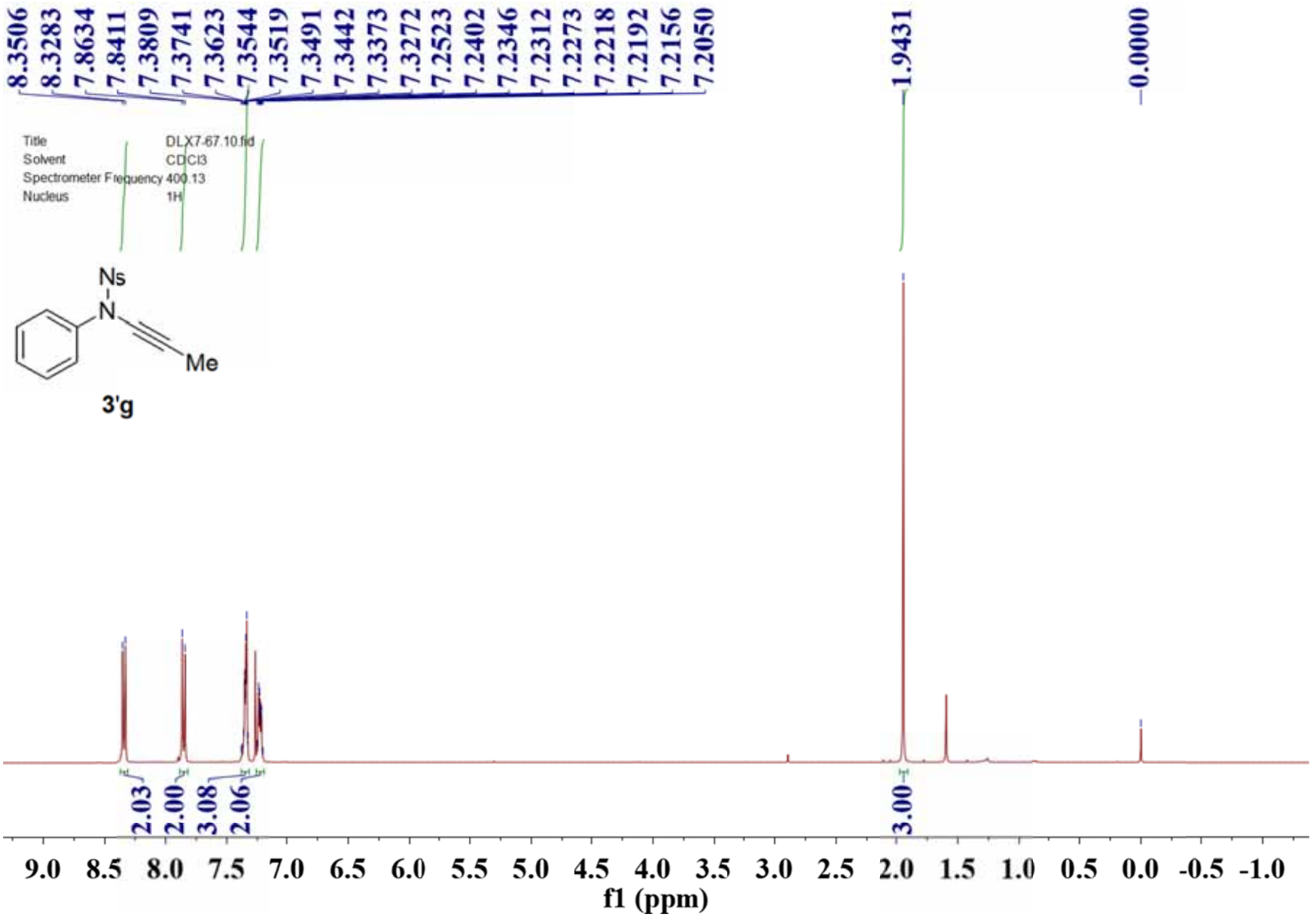

145.165
139.082
133.048
131.597
129.674
129.258
128.441
128.136
126.434
122.754
83.132
77.518
77.200
76.882
70.647
21.879
Title DLX8-52.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Ph
3'd
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

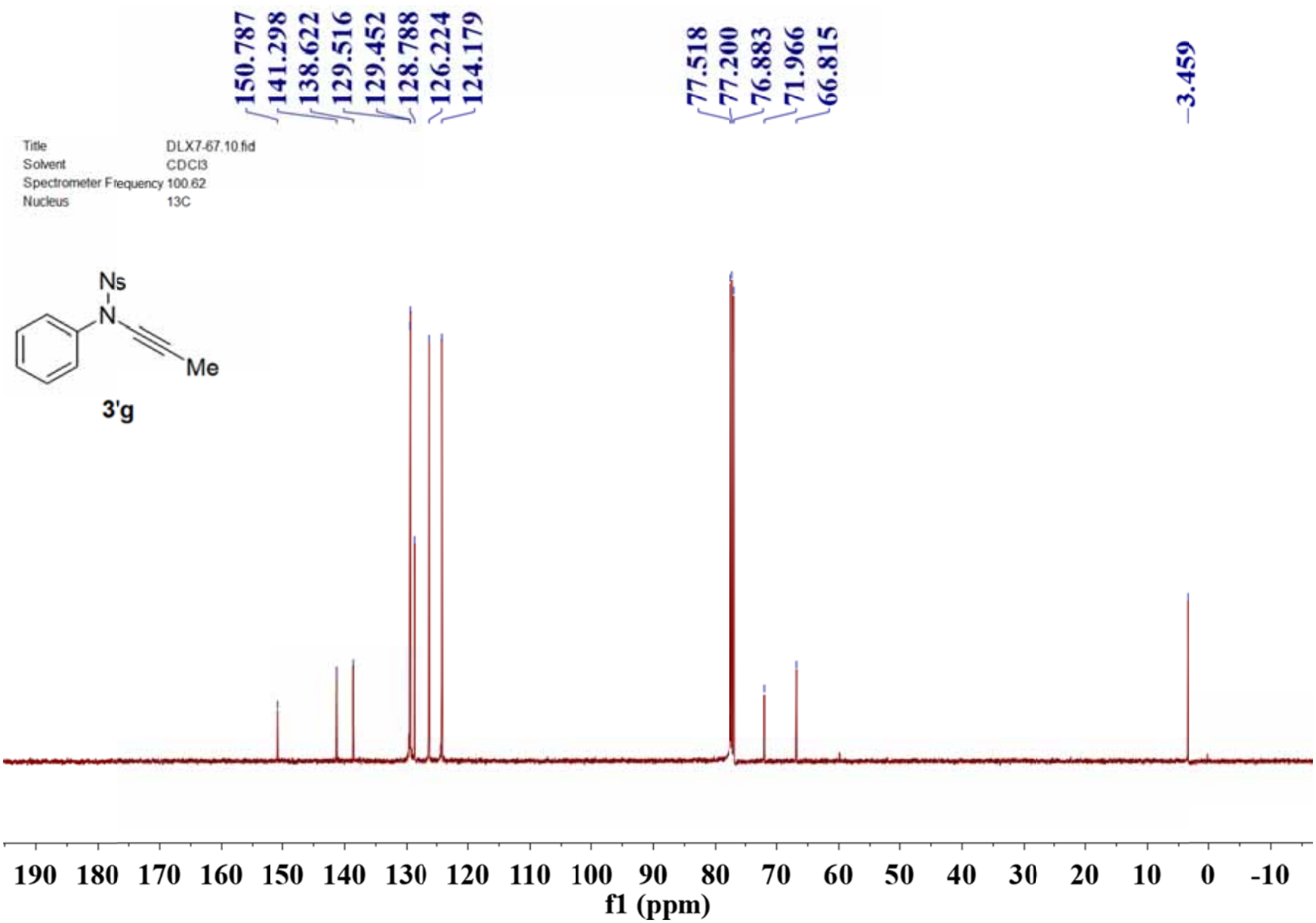

7.6092
7.5868
7.3325
7.3251
7.3205
7.3114
7.3059
7.3016
7.2970
7.2916
7.2855
7.2768
7.2637
7.2573
7.2515
7.2480
7.2424
7.2380
6.9392
6.9168
3.8691
1.9275
0.0000
Title DLX7-62.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Mbs
N
Me
3'e
2.00
5.08
2.04
3.00
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

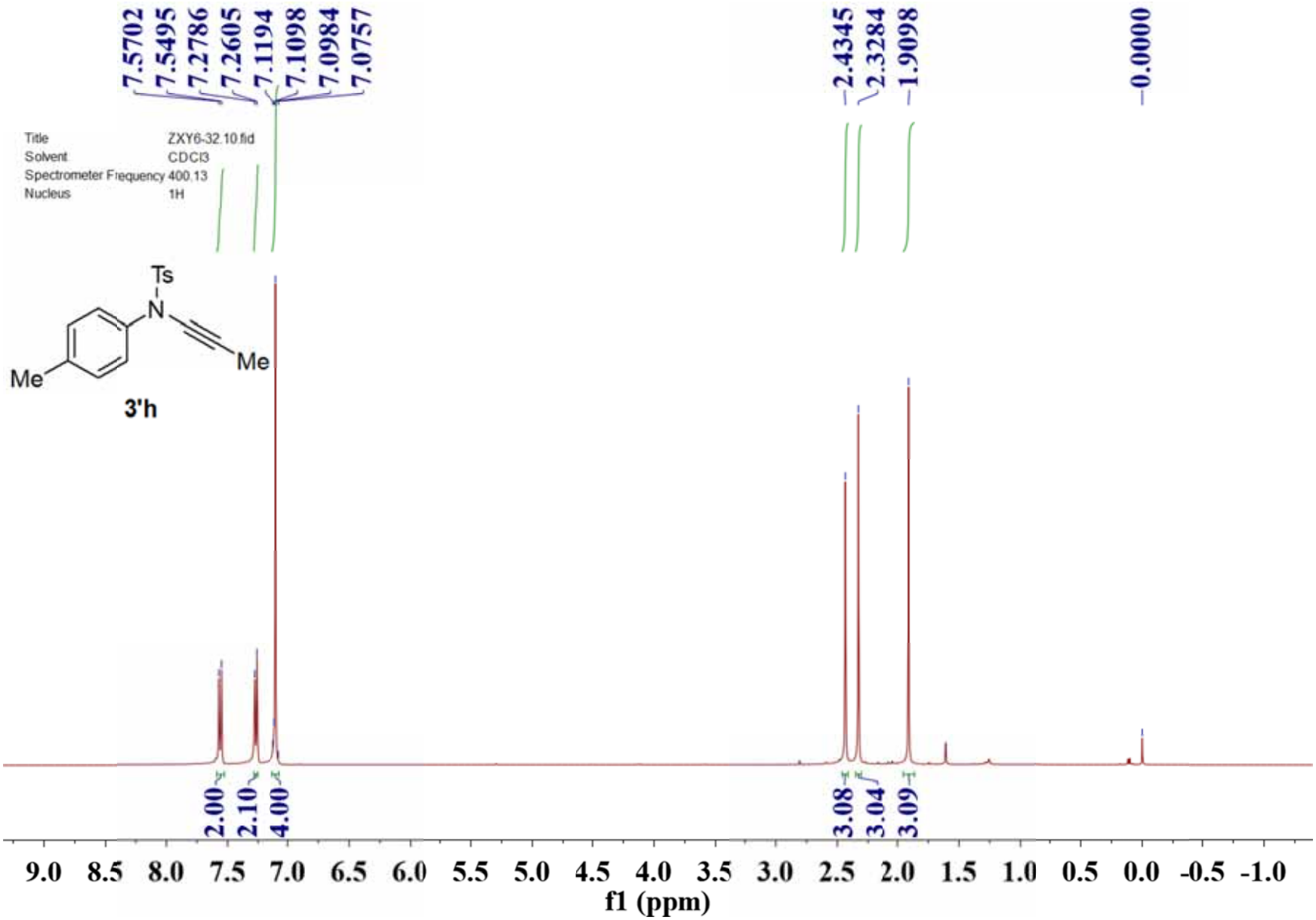

163.829
139.440
130.487
129.064
128.077
127.694
126.361
114.060
77.517
77.200
76.882
73.024
65.837
55.794
3.510
Title DLX7-62.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Mbs
N
Me
3'e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

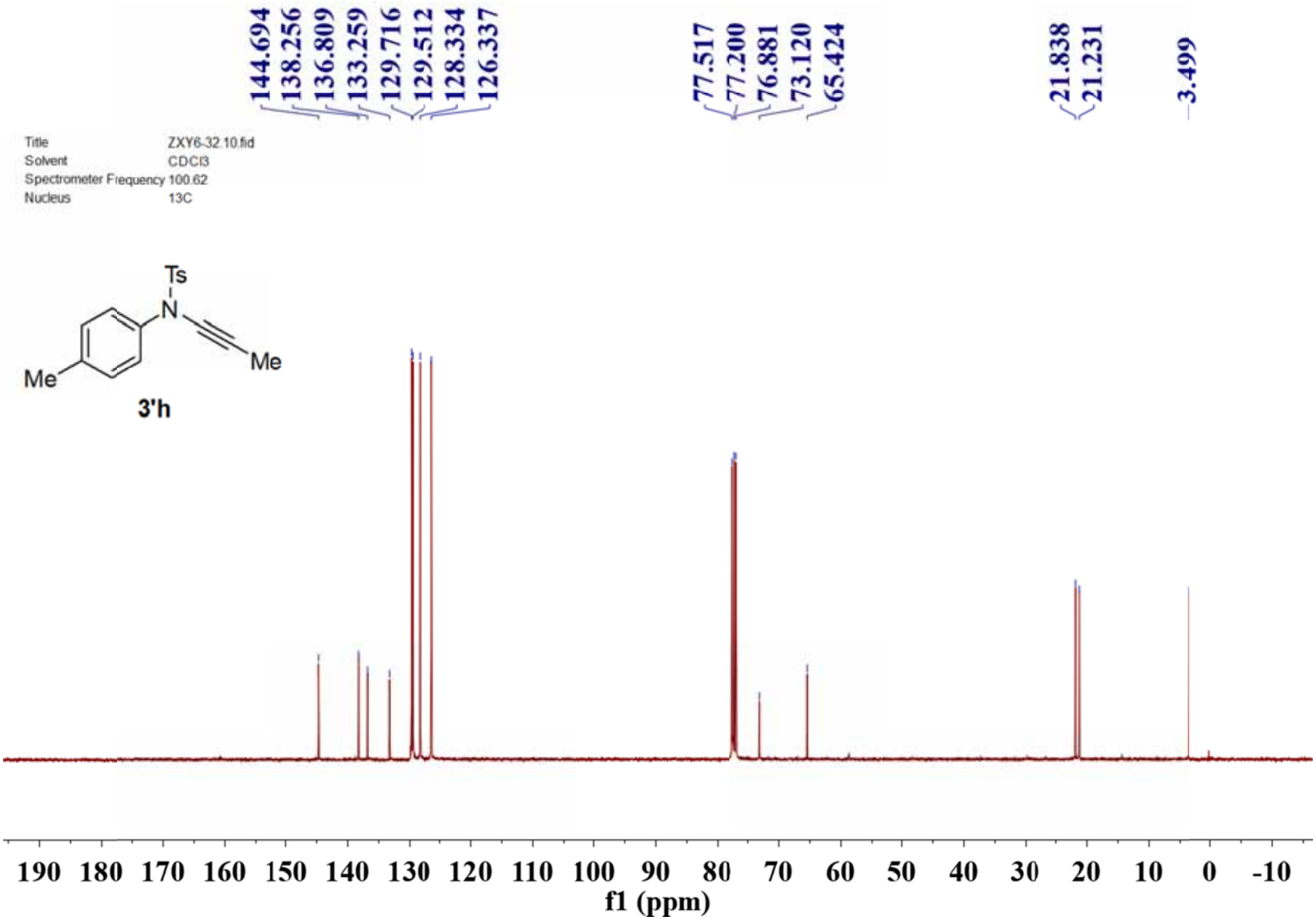

7.6108
7.5891
7.4698
7.4481
7.3552
7.3453
7.3406
7.3327
7.3284
7.3244
7.3204
7.3175
7.3137
7.3057
7.3016
7.2514
7.2449
7.2393
7.2364
7.2313
7.2268
1.9319
-0.0000
Title DLX7-66,10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cs
N
Me
3'f
2.00
2.03
3.06
2.08
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

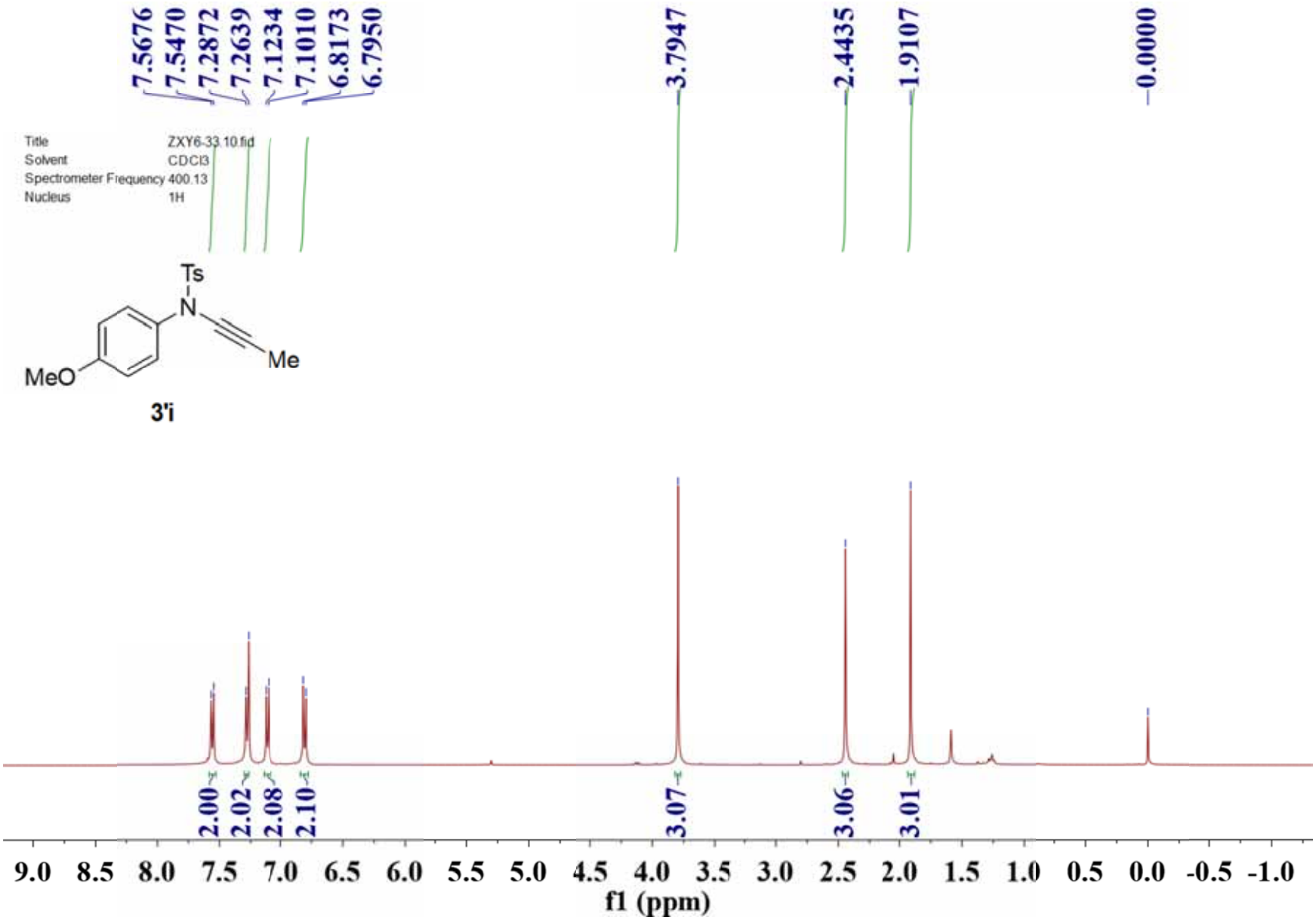

140.534
139.073
134.439
129.689
129.301
129.266
128.436
126.351
77.518
77.200
76.883
72.518
66.266
-3.505
Title DLX7-66.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cs
N
Me
3'f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

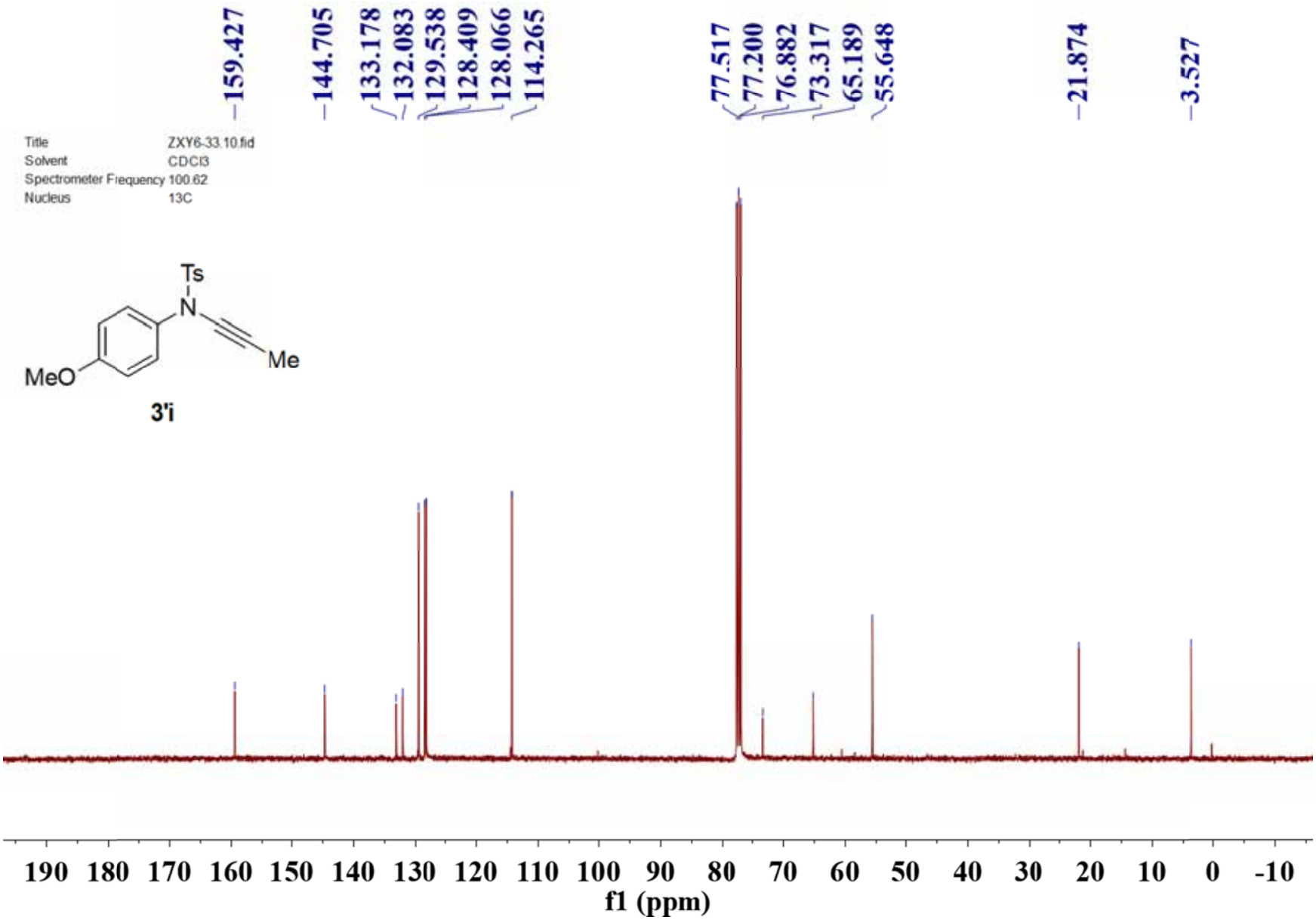

8.3506
8.3283
7.8634
7.8411
7.3809
7.3741
7.3623
7.3544
7.3519
7.3491
7.3442
7.3373
7.3272
7.2523
7.2402
7.2346
7.2312
7.2273
7.2218
7.2192
7.2156
7.2050
1.9431
0.0000
Title DLX7-67.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ns
N
Me
3'g
2.03
2.00
3.08
2.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

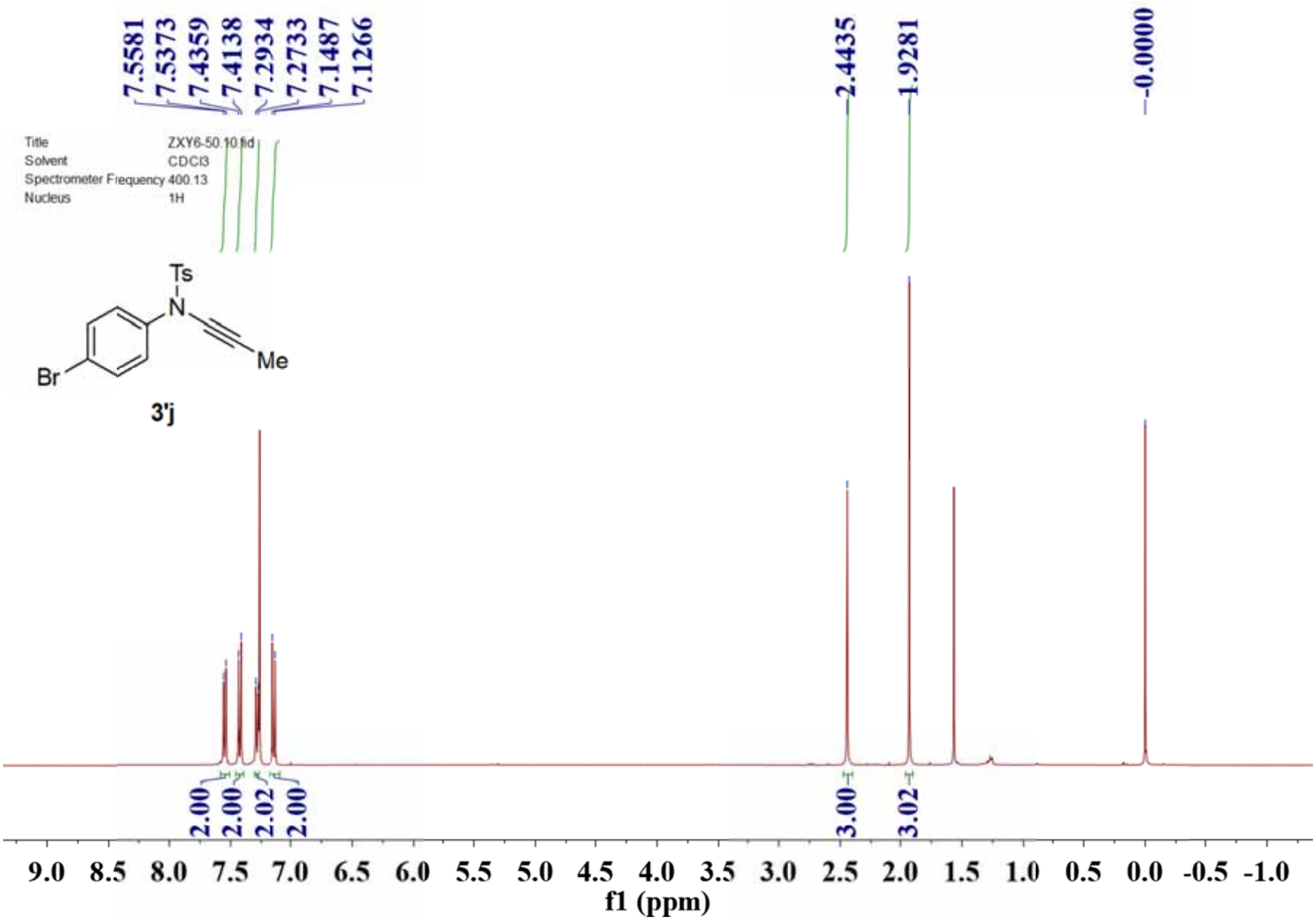

150.787
141.298
138.622
129.516
129.452
128.788
126.224
124.179
77.518
77.200
76.883
71.966
66.815
3.459
Title DLX7-67.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ns
N
Me
3'g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

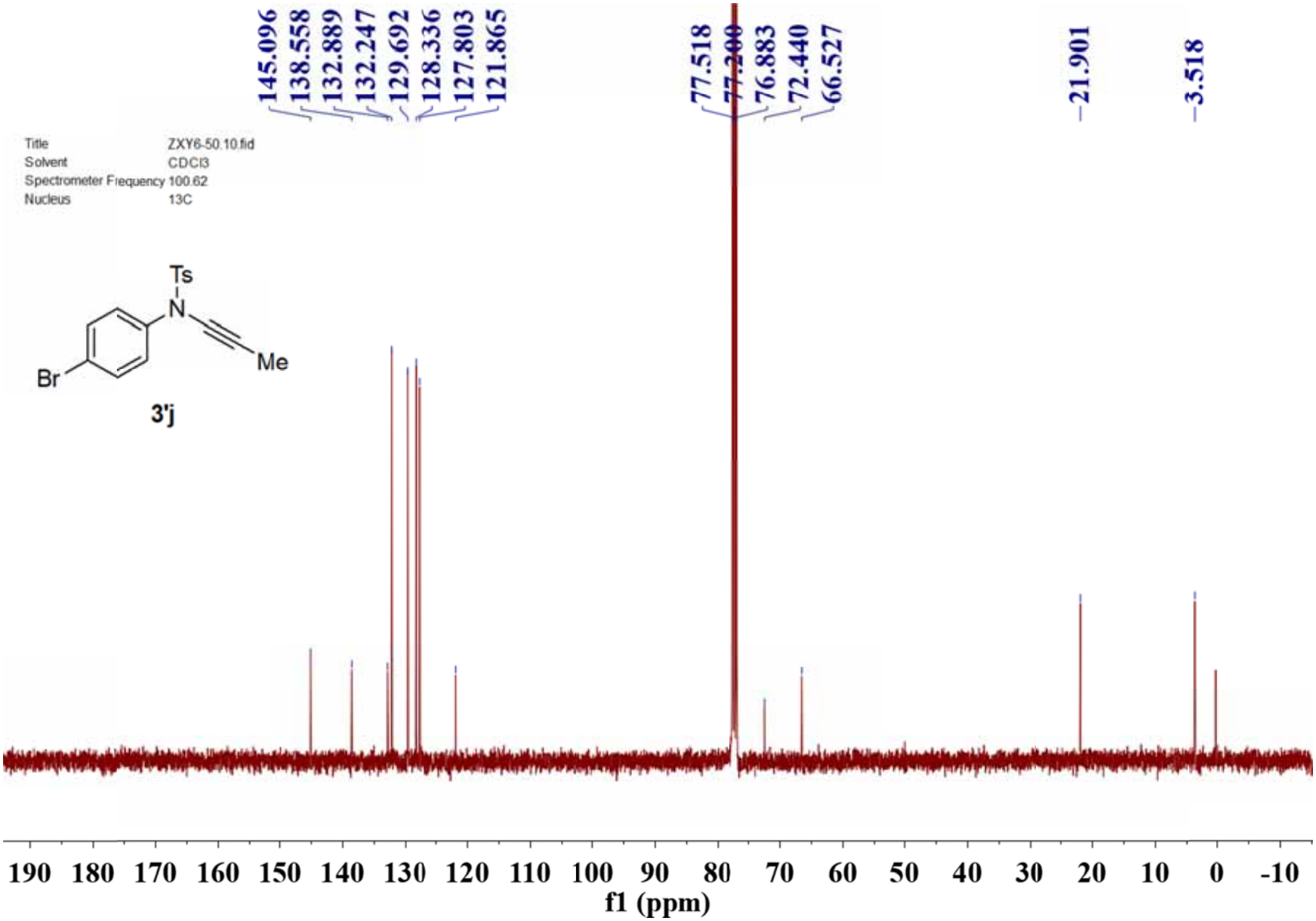

7.5702
7.5495
7.2786
7.2605
7.1194
7.1098
7.0984
7.0757
2.4345
2.3284
1.9098
0.0000
Title ZXY6-32.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
3'h
2.00
2.10
4.00
3.08
3.04
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

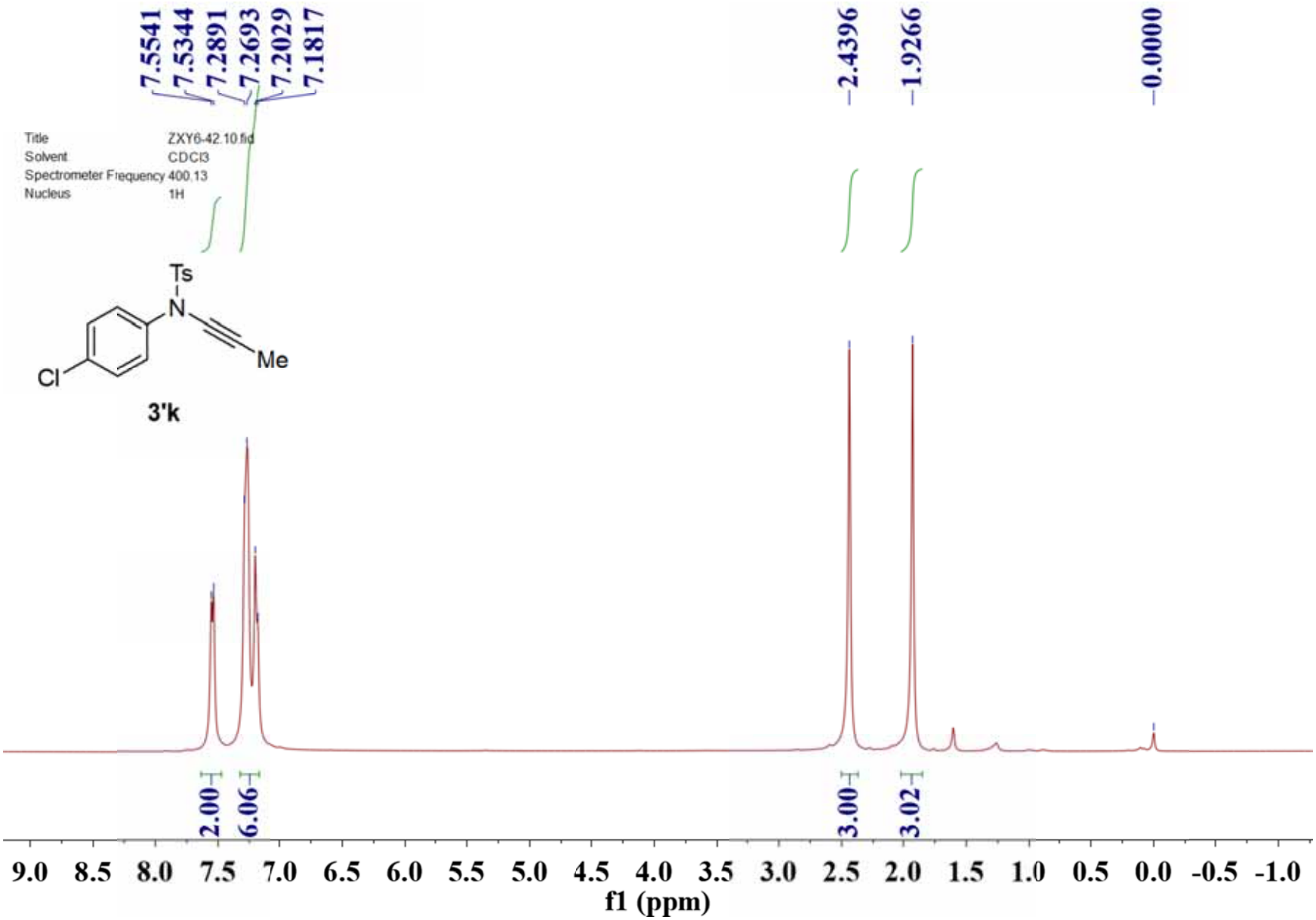

144.694
138.256
136.809
133.259
129.716
129.512
128.334
126.337
77.517
77.200
76.881
73.120
65.424
21.838
21.231
3.499
Title ZXY6-32.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
3'h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

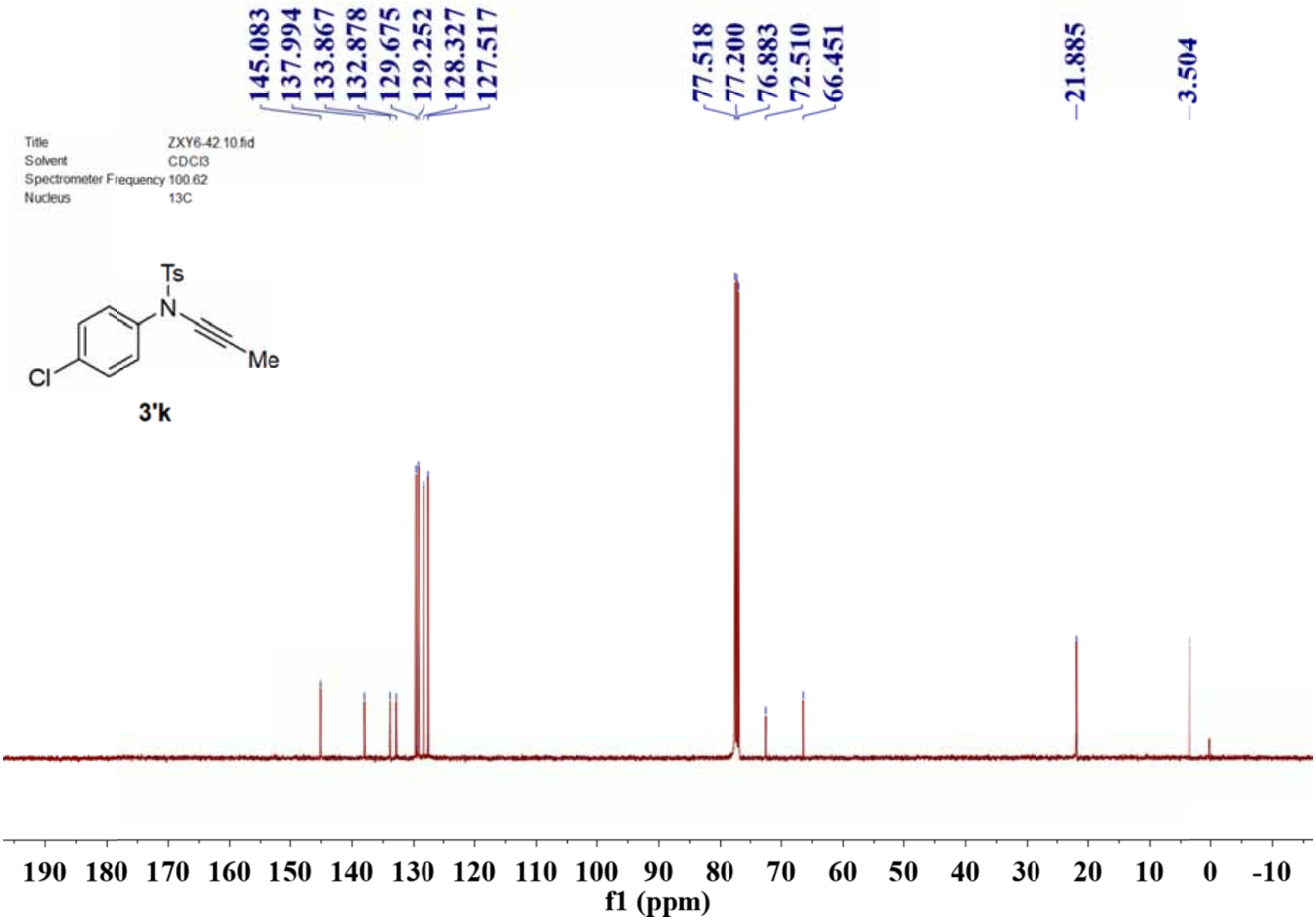

7.5676
7.5470
7.2872
7.2639
7.1234
7.1010
6.8173
6.7950
3.7947
2.4435
1.9107
0.0000
Title ZXY6-33.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
MeO
3'i
2.00
2.02
2.08
2.10
3.07
3.06
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

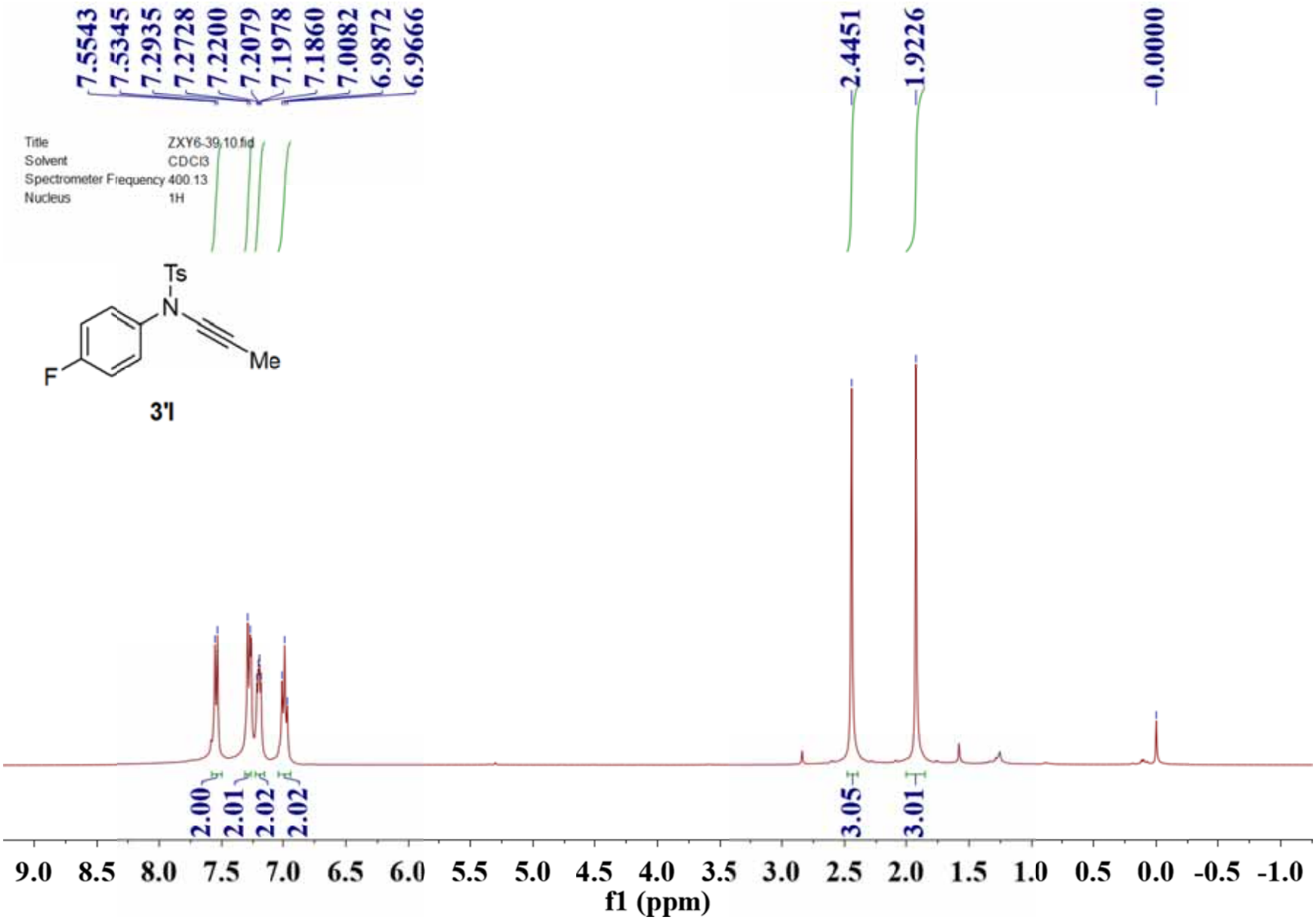

159.427
144.705
133.178
132.083
129.538
128.409
128.066
114.265
77.517
77.200
76.882
73.317
65.189
55.648
21.874
3.527
Title ZXY6-33.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
MeO
3'i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

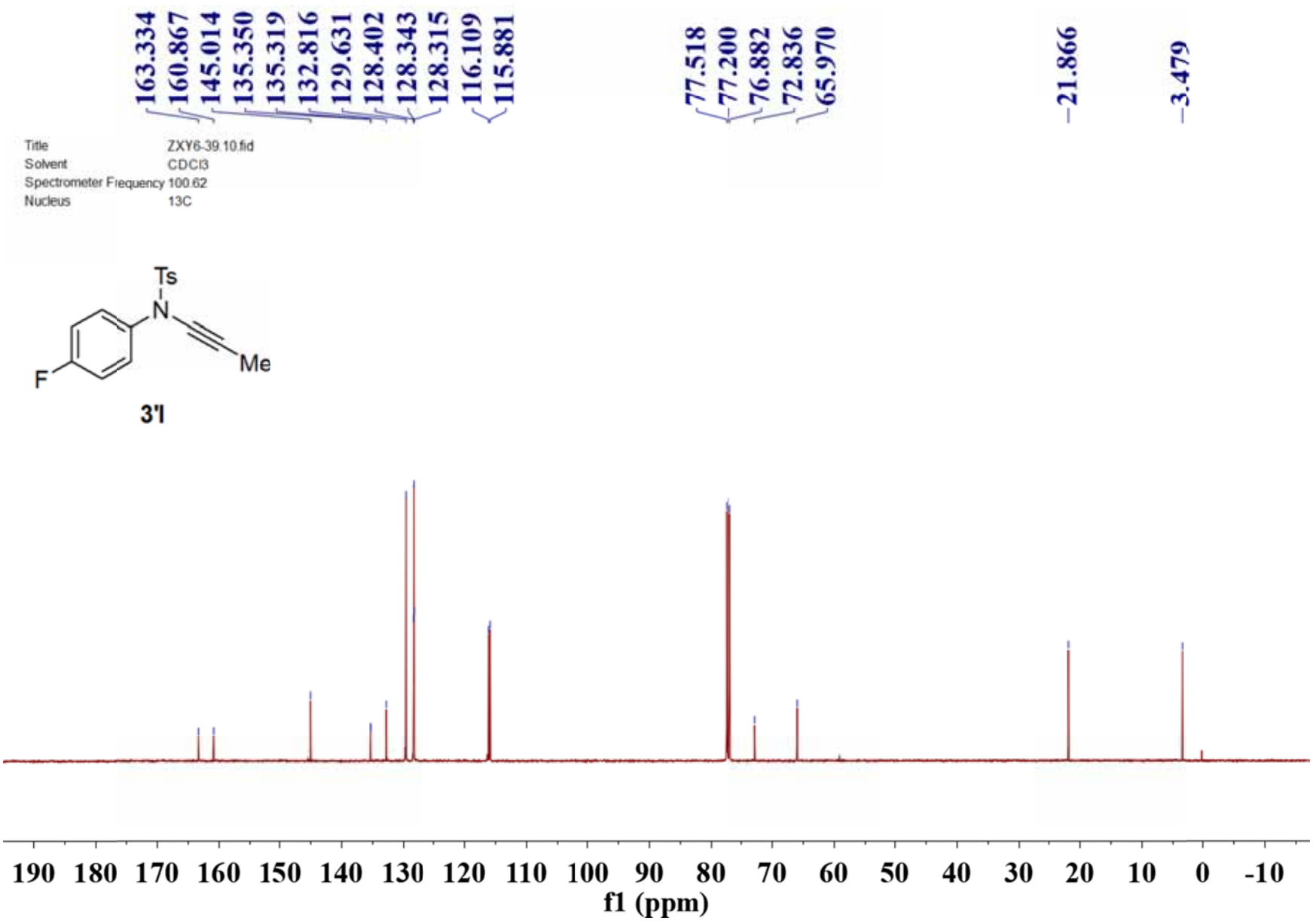

7.5581
7.5373
7.4359
7.4138
7.2934
7.2733
7.1487
7.1266
2.4435
1.9281
-0.0000
Title ZXY6-50.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Br
3'j
2.00
2.00
2.02
2.00
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

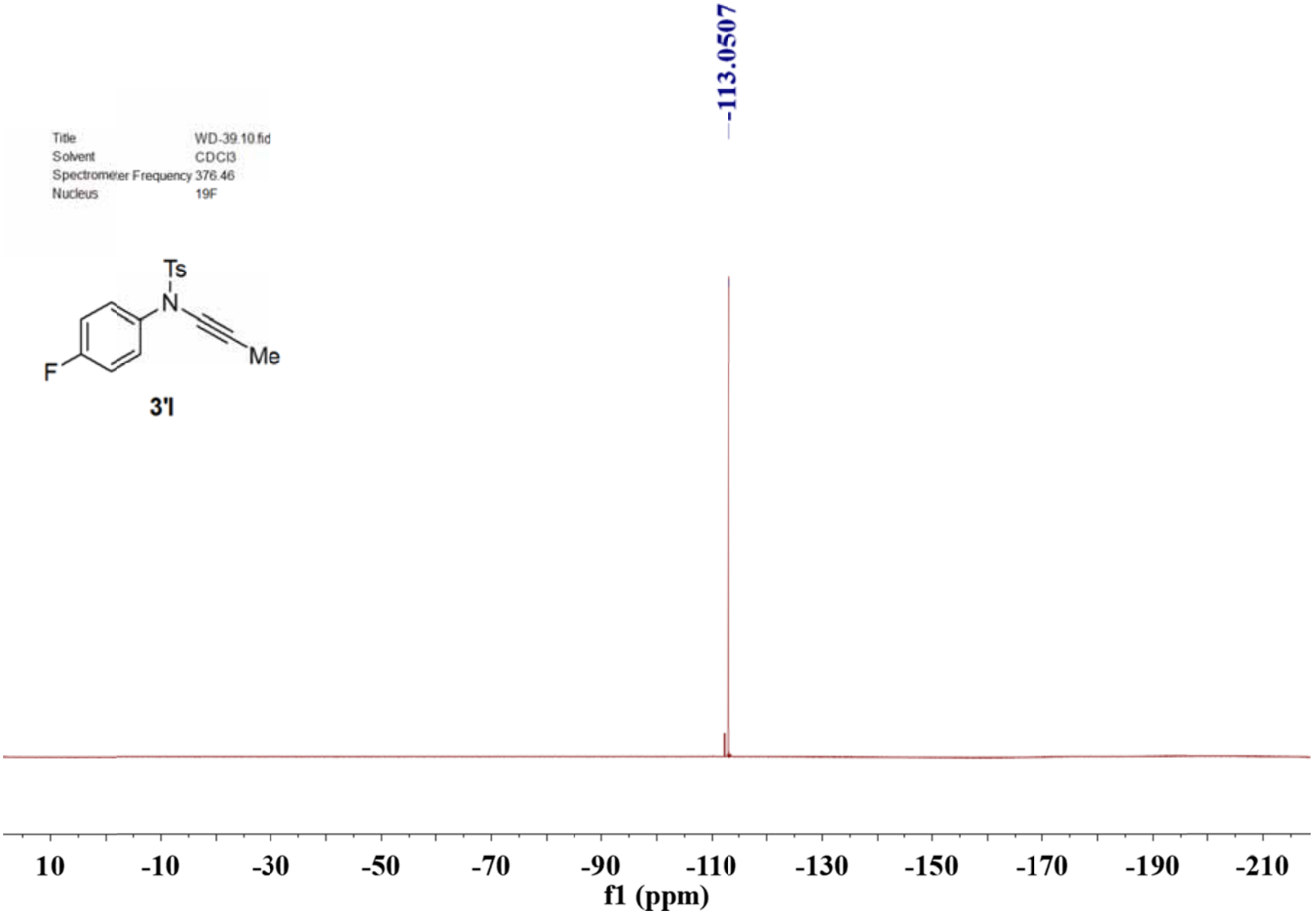

145.096
138.558
132.889
132.247
129.692
128.336
127.803
121.865
77.518
77.200
76.883
72.440
66.527
21.901
3.518
Title ZXY6-50.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Br
3'j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

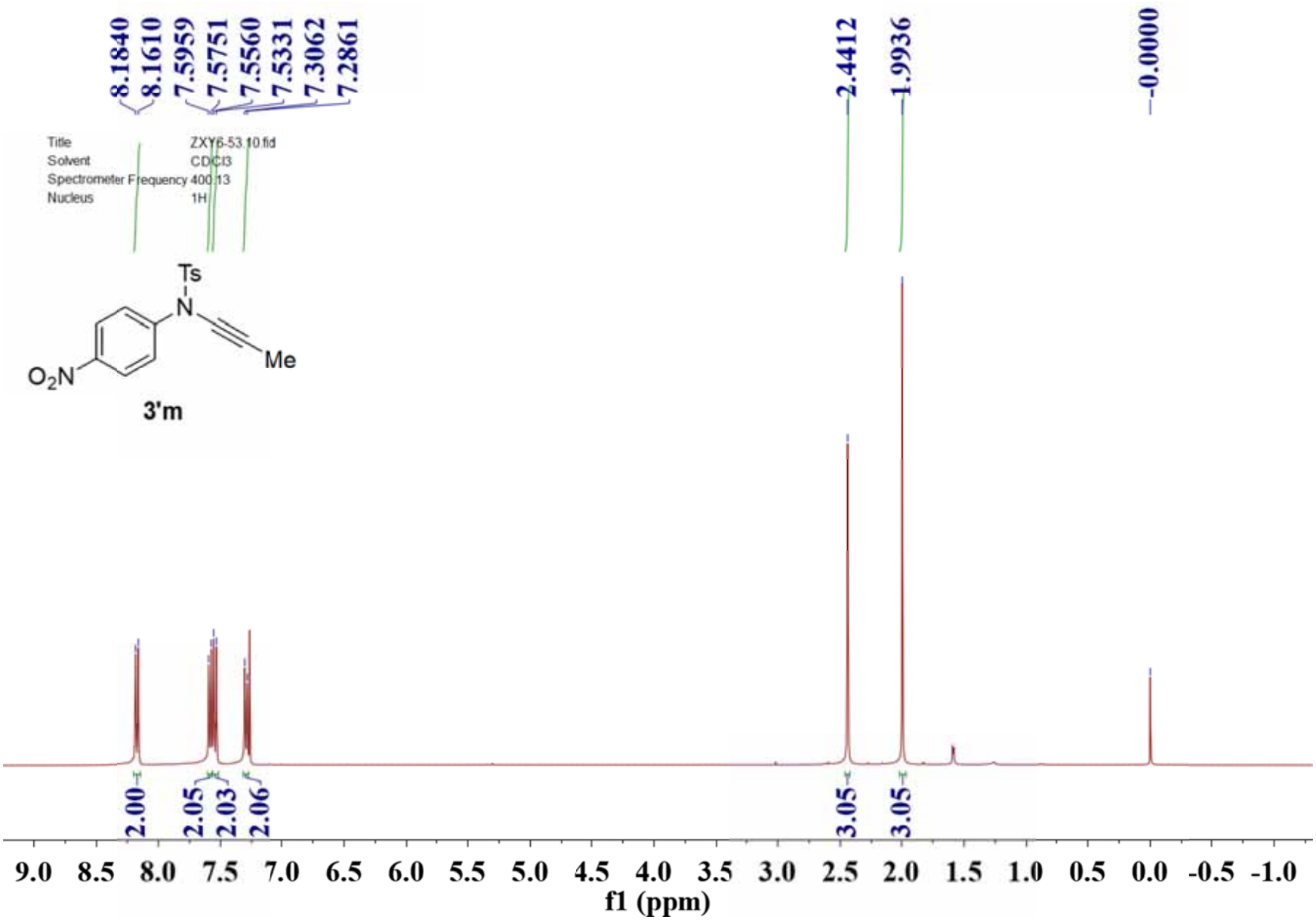

7.5541
7.5344
7.2891
7.2693
7.2029
7.1817
2.4396
1.9266
0.0000
Title ZXY6-42.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Cl
3'k
2.00
6.06
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

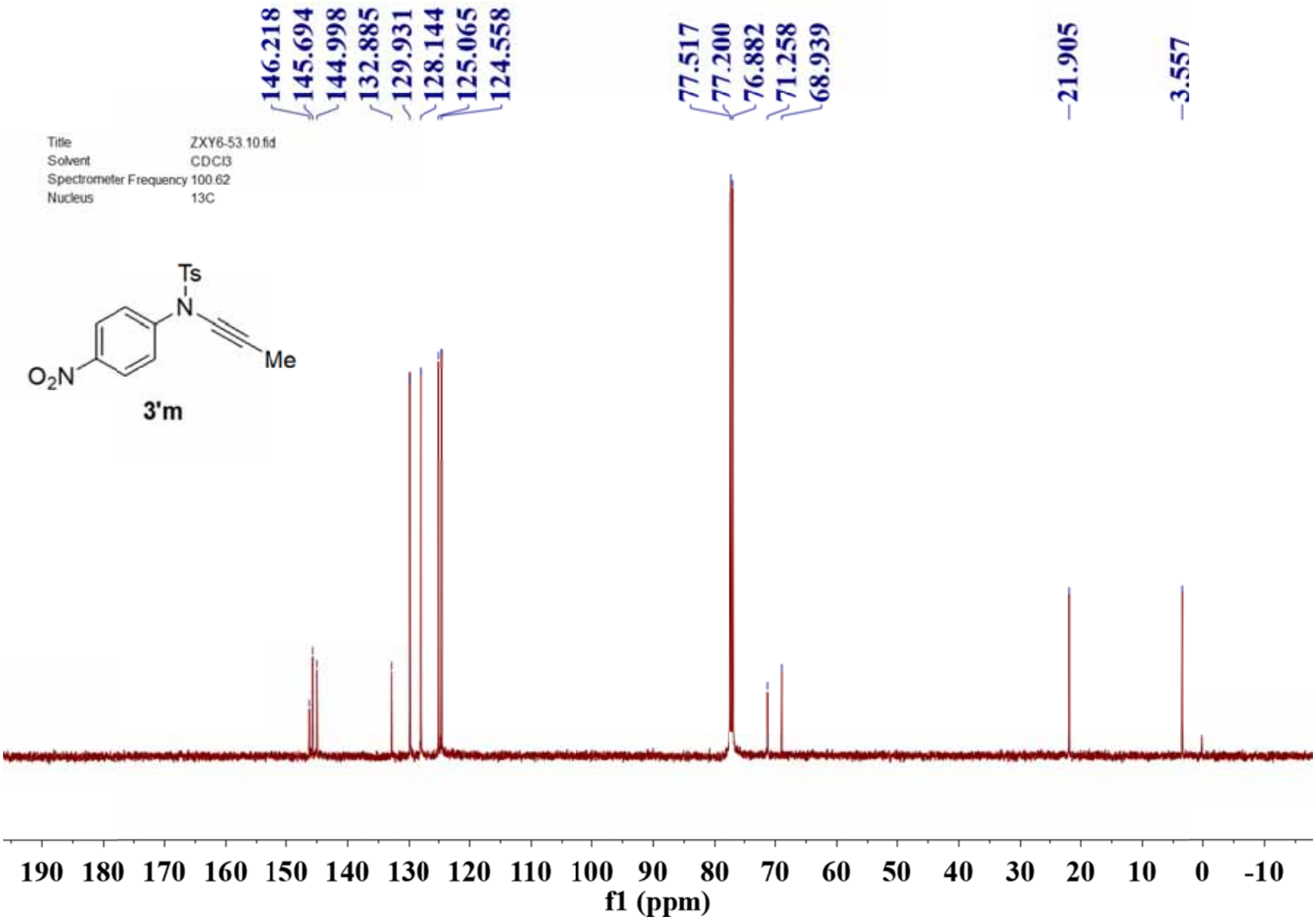

145.083
137.994
133.867
132.878
129.675
129.252
128.327
127.517
77.518
77.200
76.883
72.510
66.451
21.885
3.504
Title ZXY6-42.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Cl
Me
3'k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

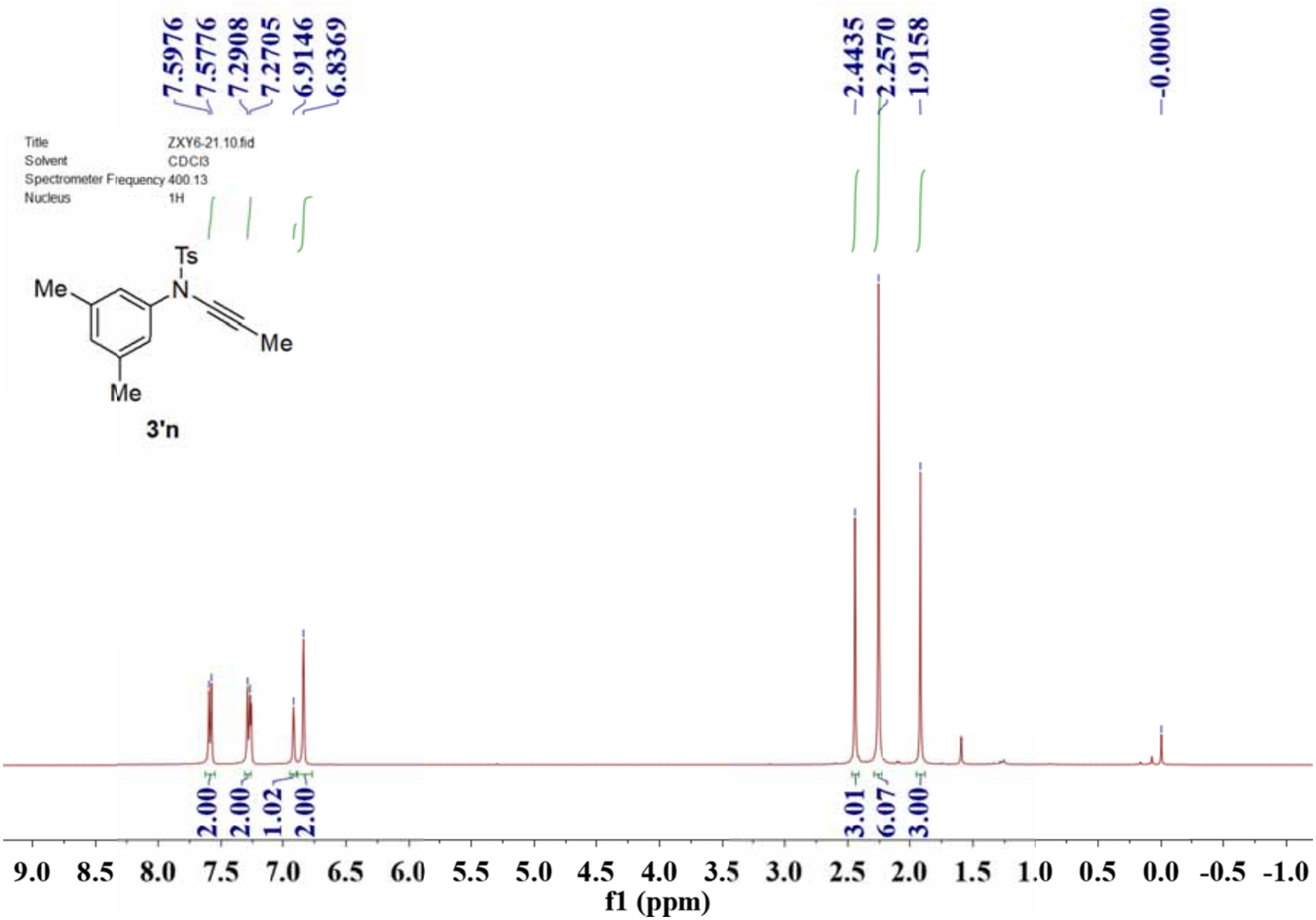

7.5543
7.5345
7.2935
7.2728
7.2200
7.2079
7.1978
7.1860
7.0082
6.9872
6.9666
2.4451
1.9226
0.0000
Title ZXY6-39-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
F
3'l
2.00
2.01
2.02
2.02
3.05
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

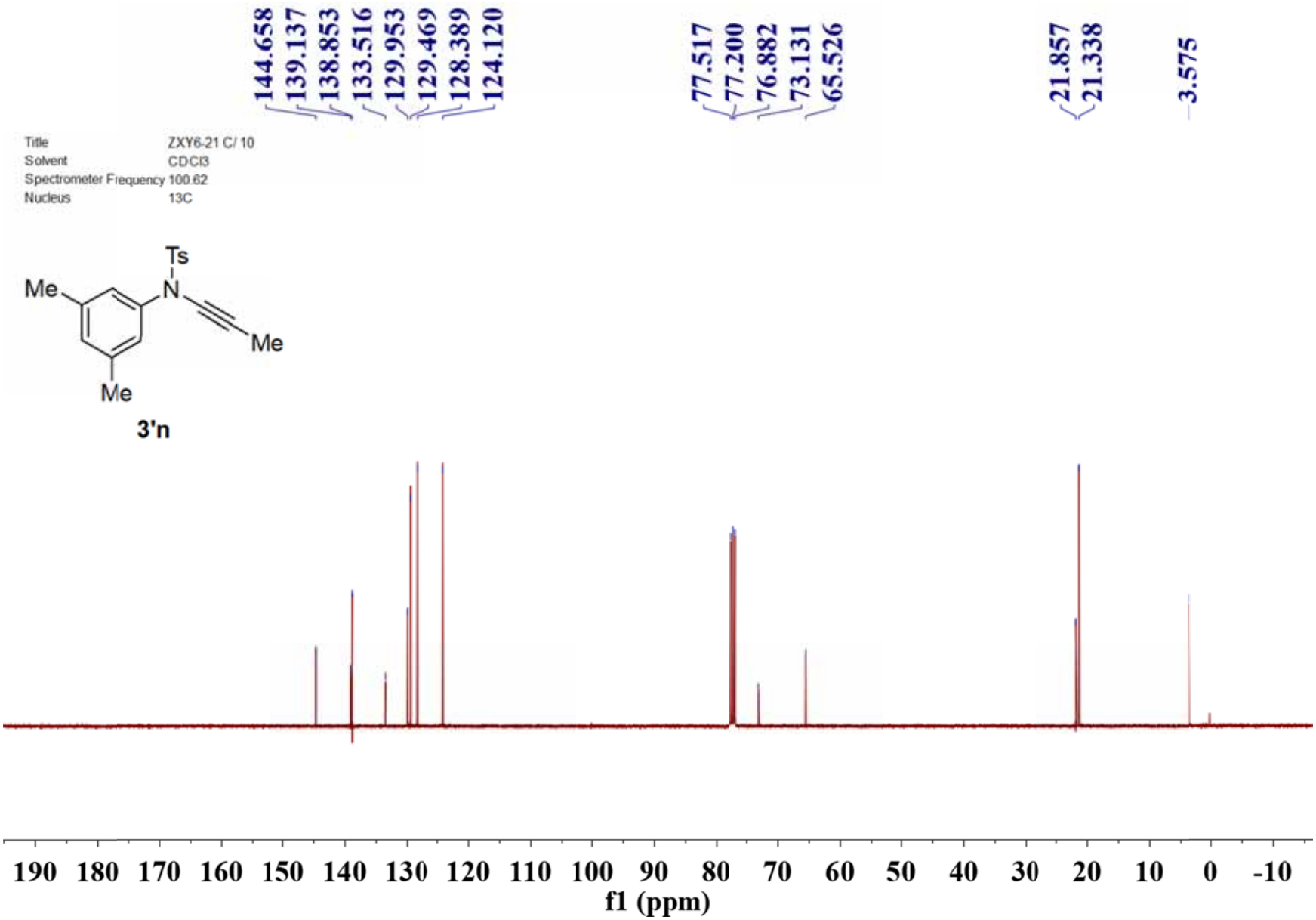

163.334
160.867
145.014
135.350
135.319
132.816
129.631
128.402
128.343
128.315
116.109
115.881
77.518
77.200
76.882
72.836
65.970
21.866
3.479
Title ZXY6-39.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
F
Me
3'l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

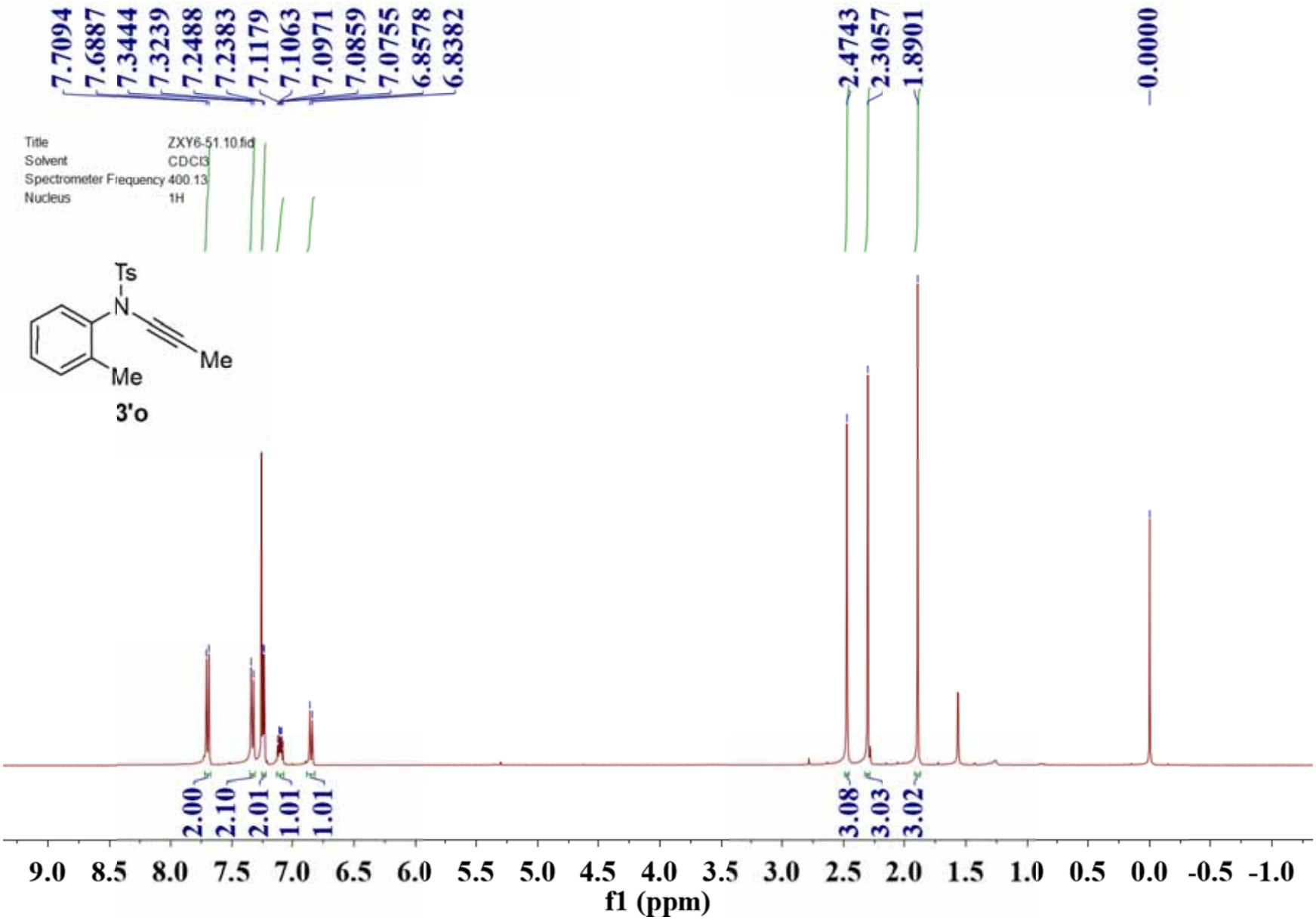

-113.0507
Title WD-39.10.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
Ts
N
Me
F
3'l
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

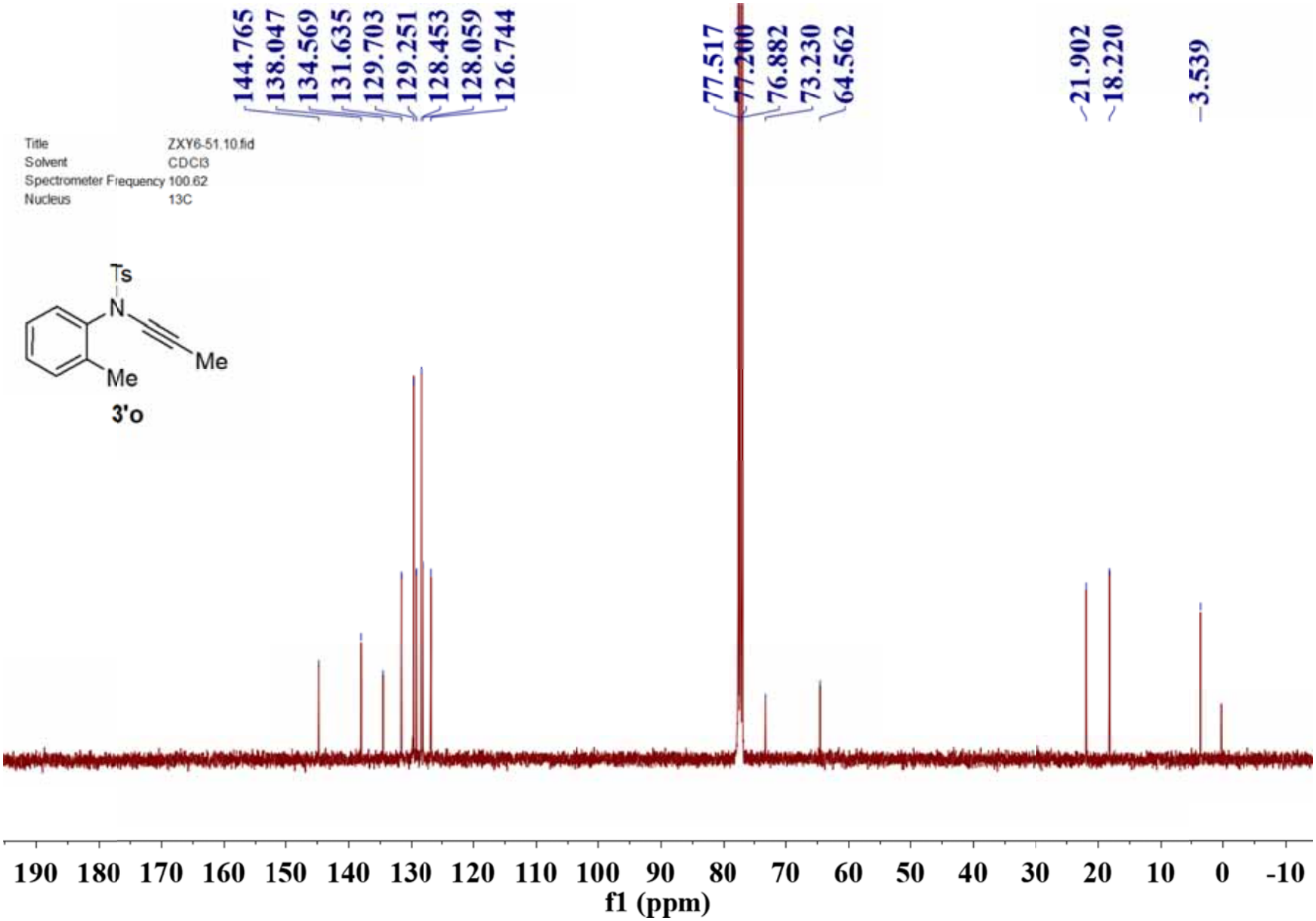

8.1840
8.1610
7.5959
7.5751
7.5560
7.5331
7.3062
7.2861
2.4412
1.9936
-0.0000
Title ZXY6-53.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
O2N
3'm
2.00
2.05
2.03
2.06
3.05
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

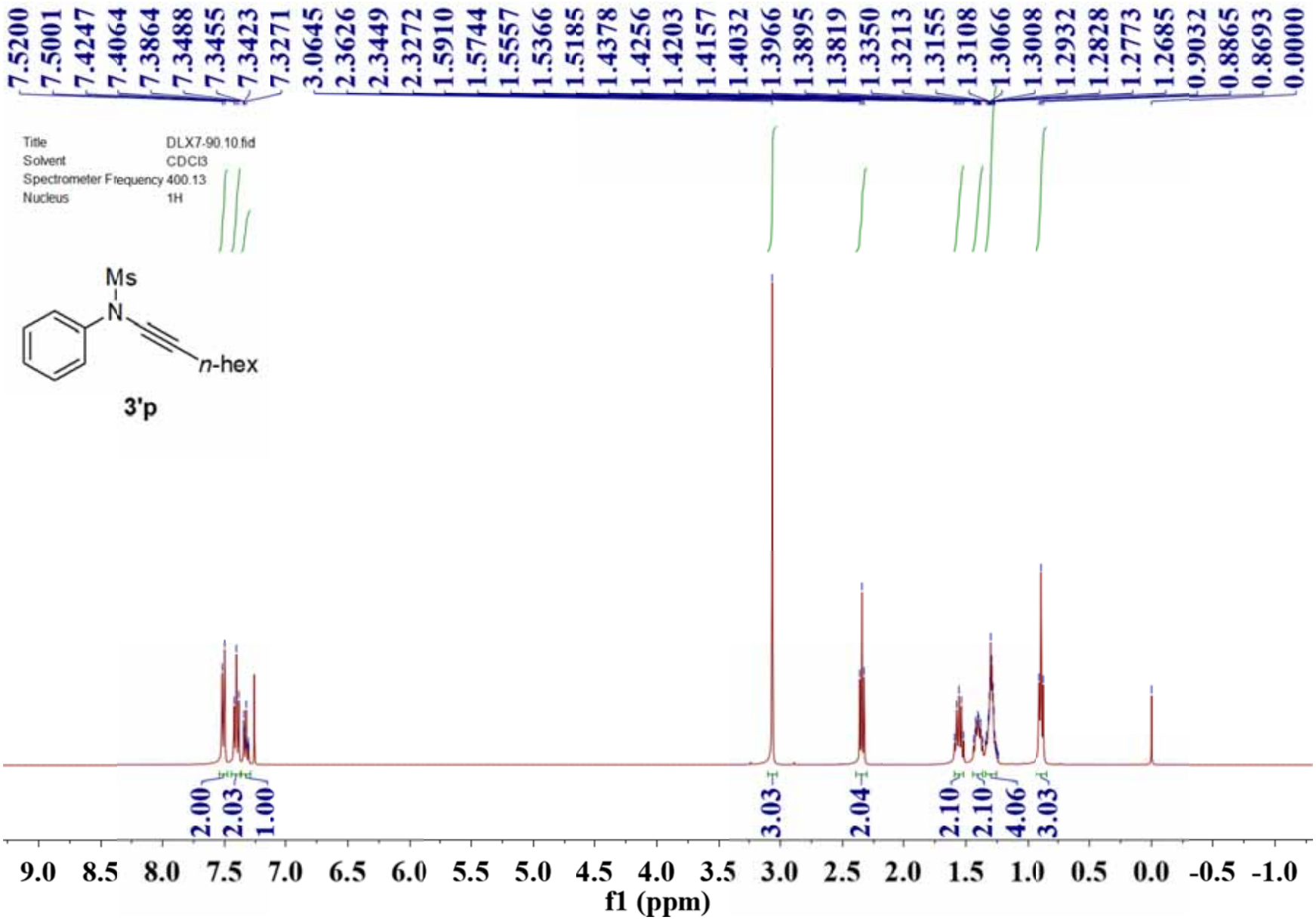

146.218
145.694
144.998
132.885
129.931
128.144
125.065
124.558
77.517
77.200
76.882
71.258
68.939
21.905
3.557
Title ZXY6-53.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
O2N
3'm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

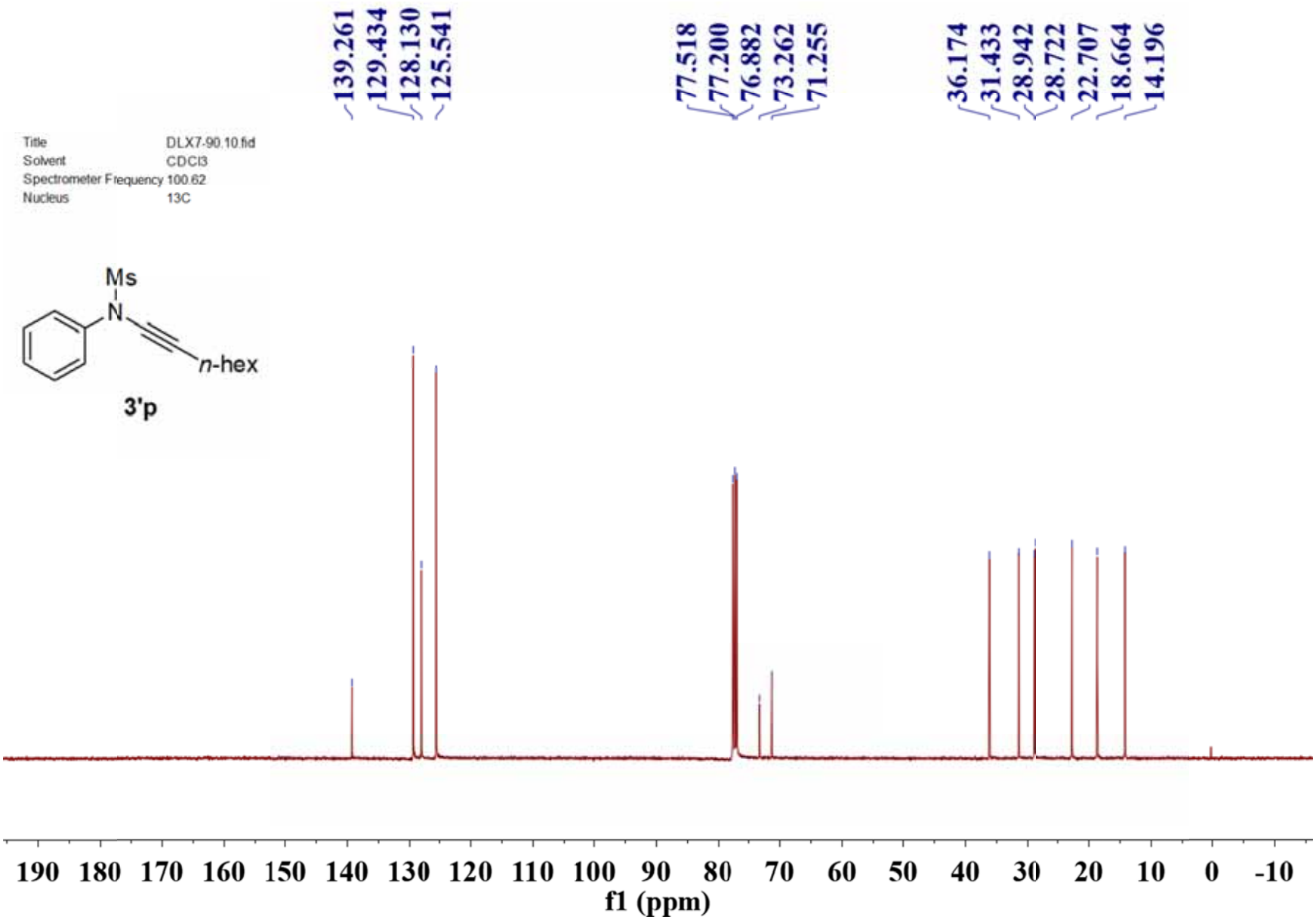

7.5976
7.5776
7.2908
7.2705
6.9146
6.8369
2.4435
2.2570
1.9158
-0.0000
Title ZXY6-21.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
Me
3'n
2.00
2.00
1.02
2.00
3.01
6.07
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

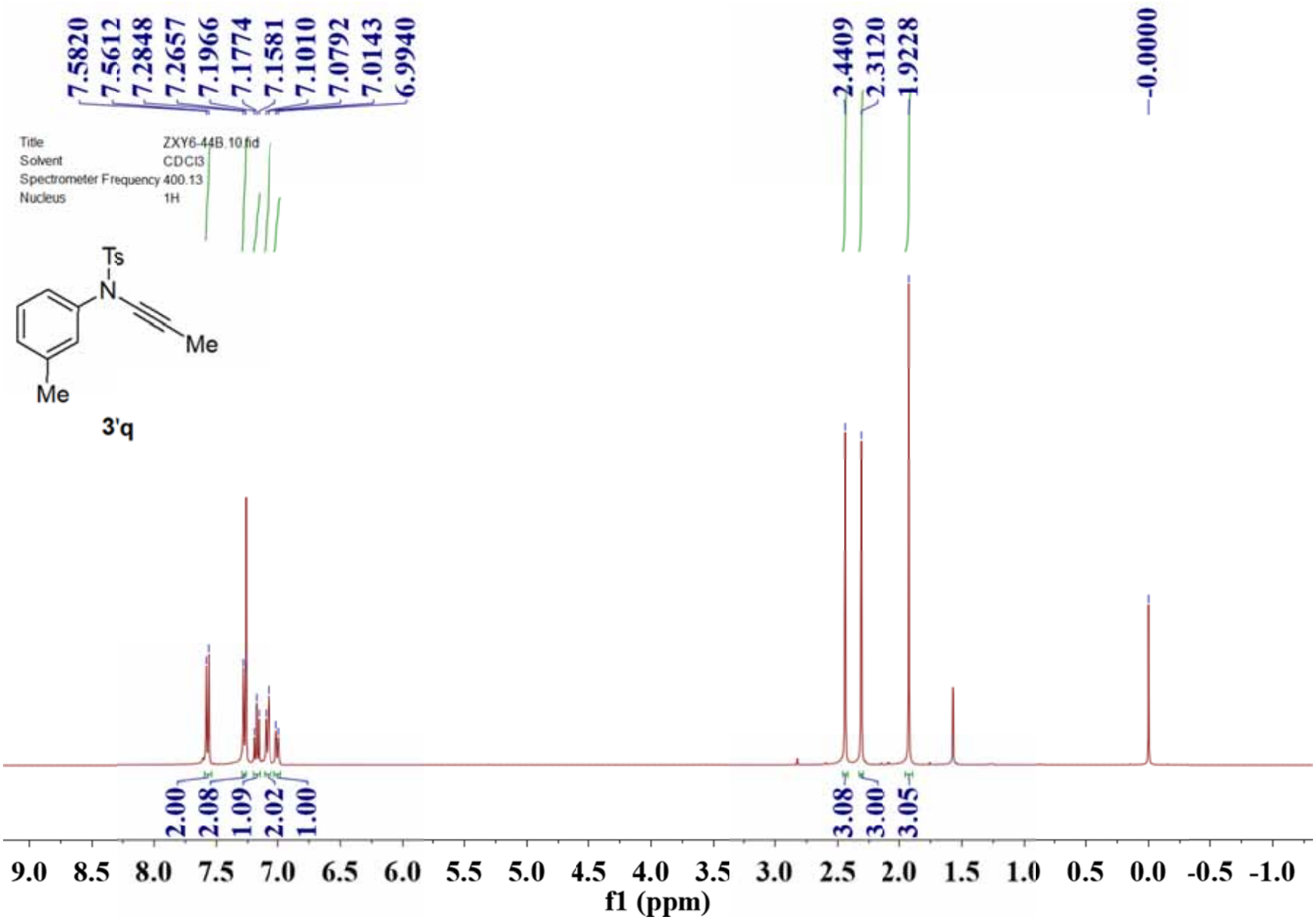

144.658
139.137
138.853
133.516
129.953
129.469
128.389
124.120
77.517
77.200
76.882
73.131
65.526
21.857
21.338
3.575
Title ZXY6-21 C/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
Me
3'n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

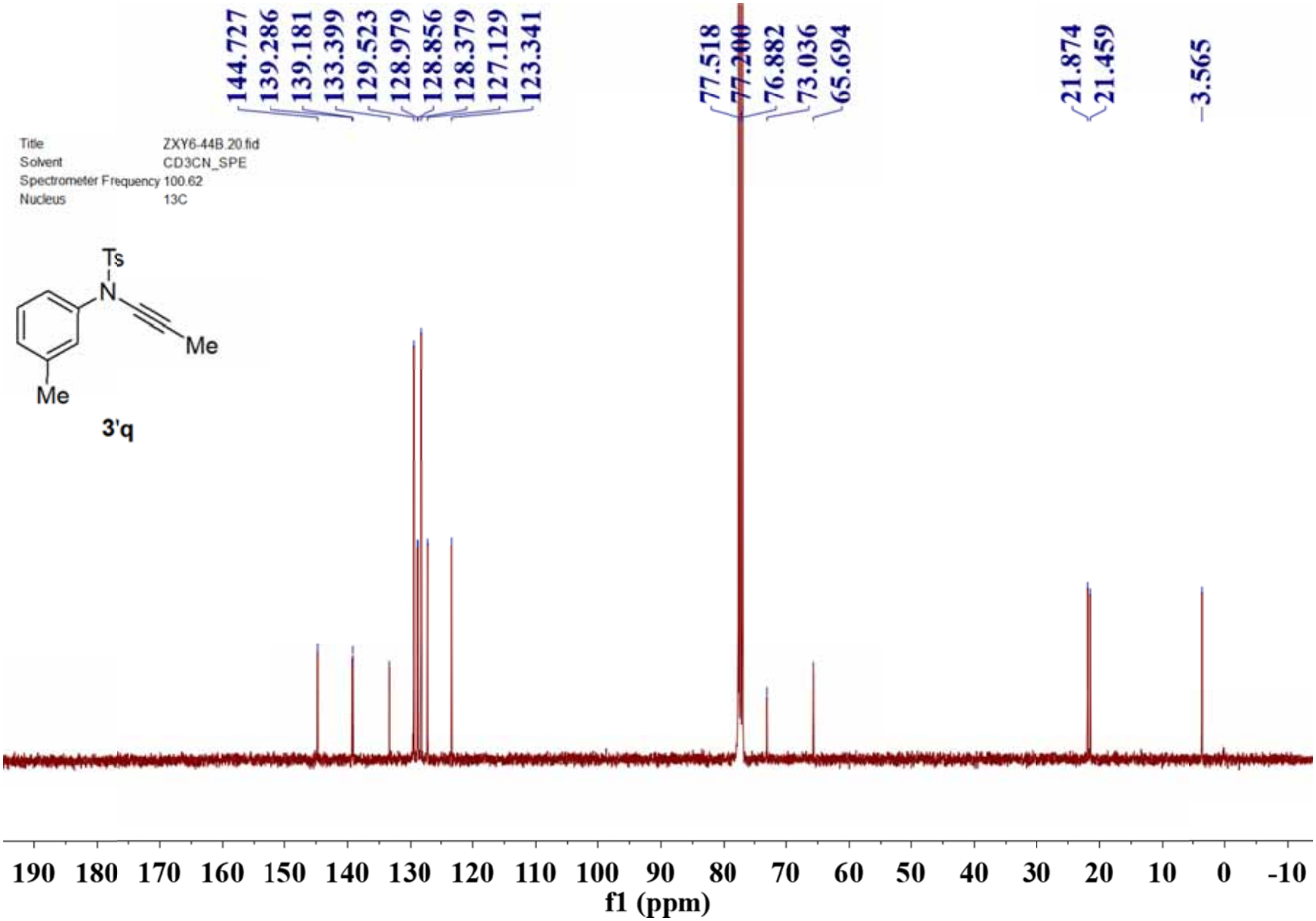

7.7094
7.6887
7.3444
7.3239
7.2488
7.2383
7.1179
7.1063
7.0971
7.0859
7.0755
6.8578
6.8382
2.4743
2.3057
1.8901
0.0000
Title ZXY6-51.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
3'o
2.00
2.10
2.01
1.01
1.01
3.08
3.03
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


144.765
138.047
134.569
131.635
129.703
129.251
128.453
128.059
126.744
77.517
77.200
76.882
73.230
64.562
21.902
18.220
3.539
Title ZXY6-51.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
3'o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

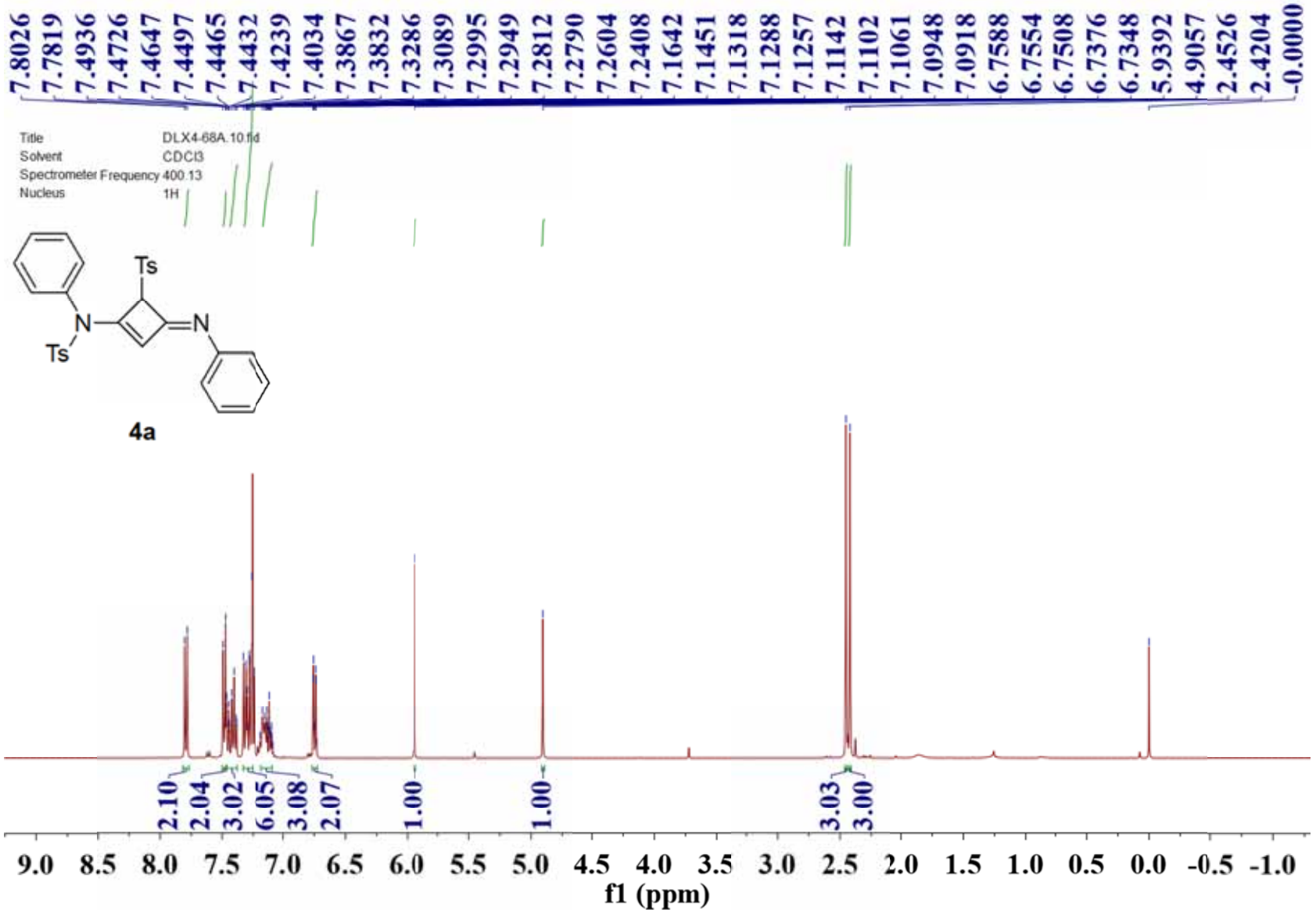

7.5200
7.5001
7.4247
7.4064
7.3864
7.3488
7.3455
7.3423
7.3271
3.0645
2.3626
2.3449
2.3272
1.5910
1.5744
1.5557
1.5366
1.5185
1.4378
1.4256
1.4203
1.4157
1.4032
1.3966
1.3895
1.3819
1.3350
1.3213
1.3155
1.3108
1.3066
1.3008
1.2932
1.2828
1.2773
1.2685
0.9032
0.8865
0.8693
0.0000
Title DLX7-90.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ms
N
n-hex
3'p
2.00
2.03
1.00
3.03
2.04
2.10
2.10
4.06
3.03
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)

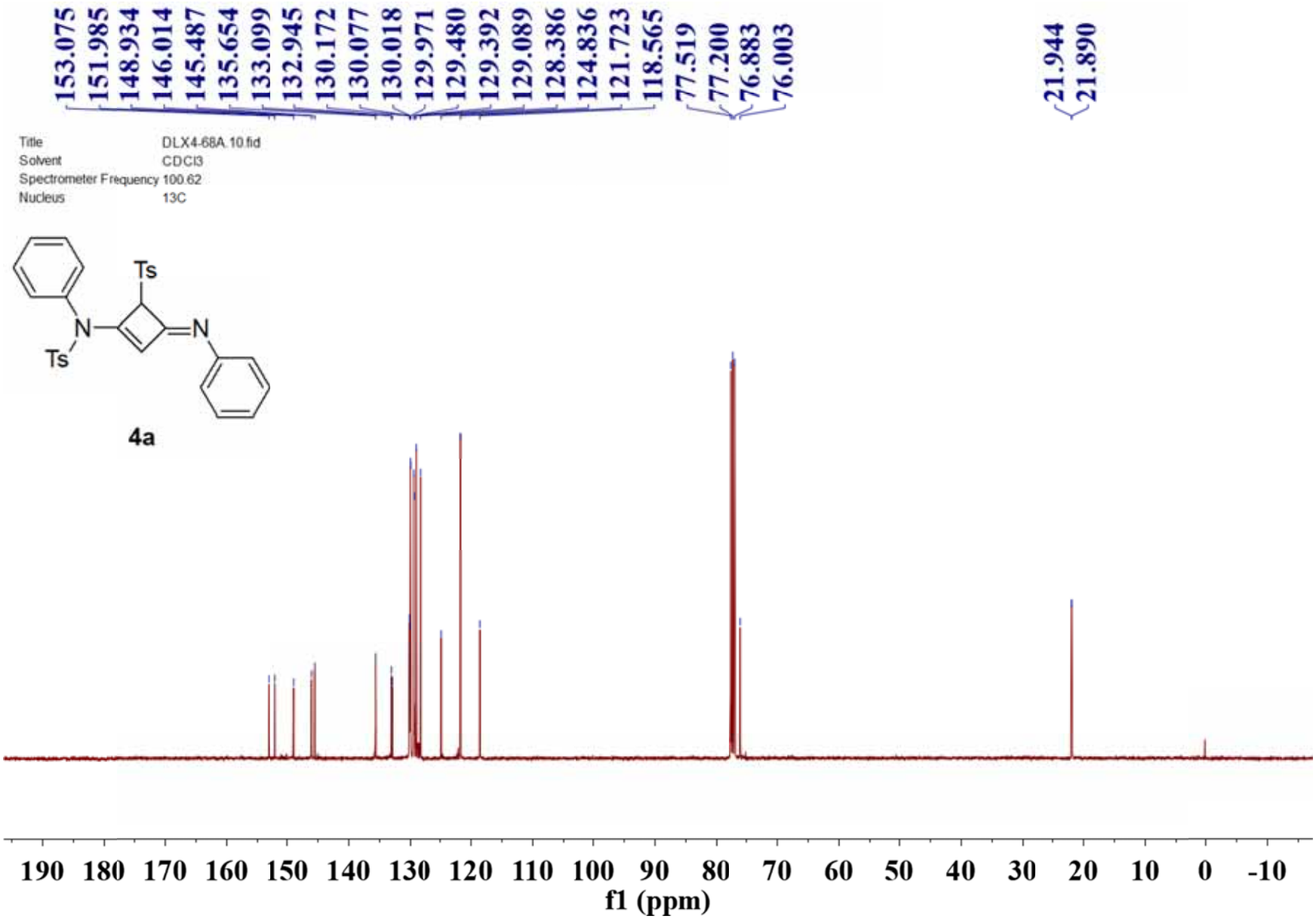

139.261
129.434
128.130
125.541
77.518
77.200
76.882
73.262
71.255
36.174
31.433
28.942
28.722
22.707
18.664
14.196
Title DLX7-90.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ms
N
n-hex
3'p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

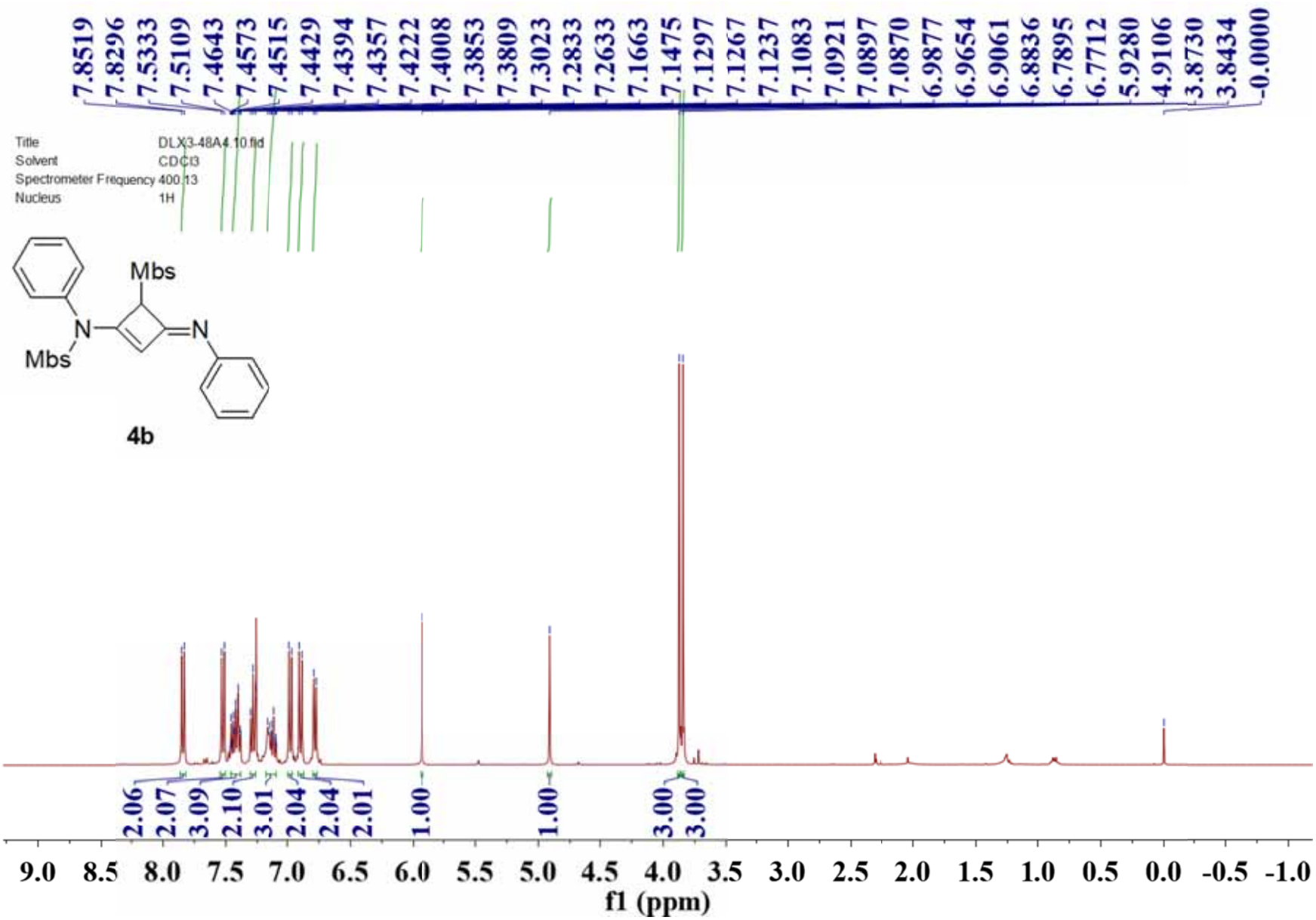

7.5820
7.5612
7.2848
7.2657
7.1966
7.1774
7.1581
7.1010
7.0792
7.0143
6.9940
2.4409
2.3120
1.9228
-0.0000
Title ZXY6-44B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
N
Me
Me
3'q
2.00
2.08
1.09
2.02
1.00
3.08
3.00
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

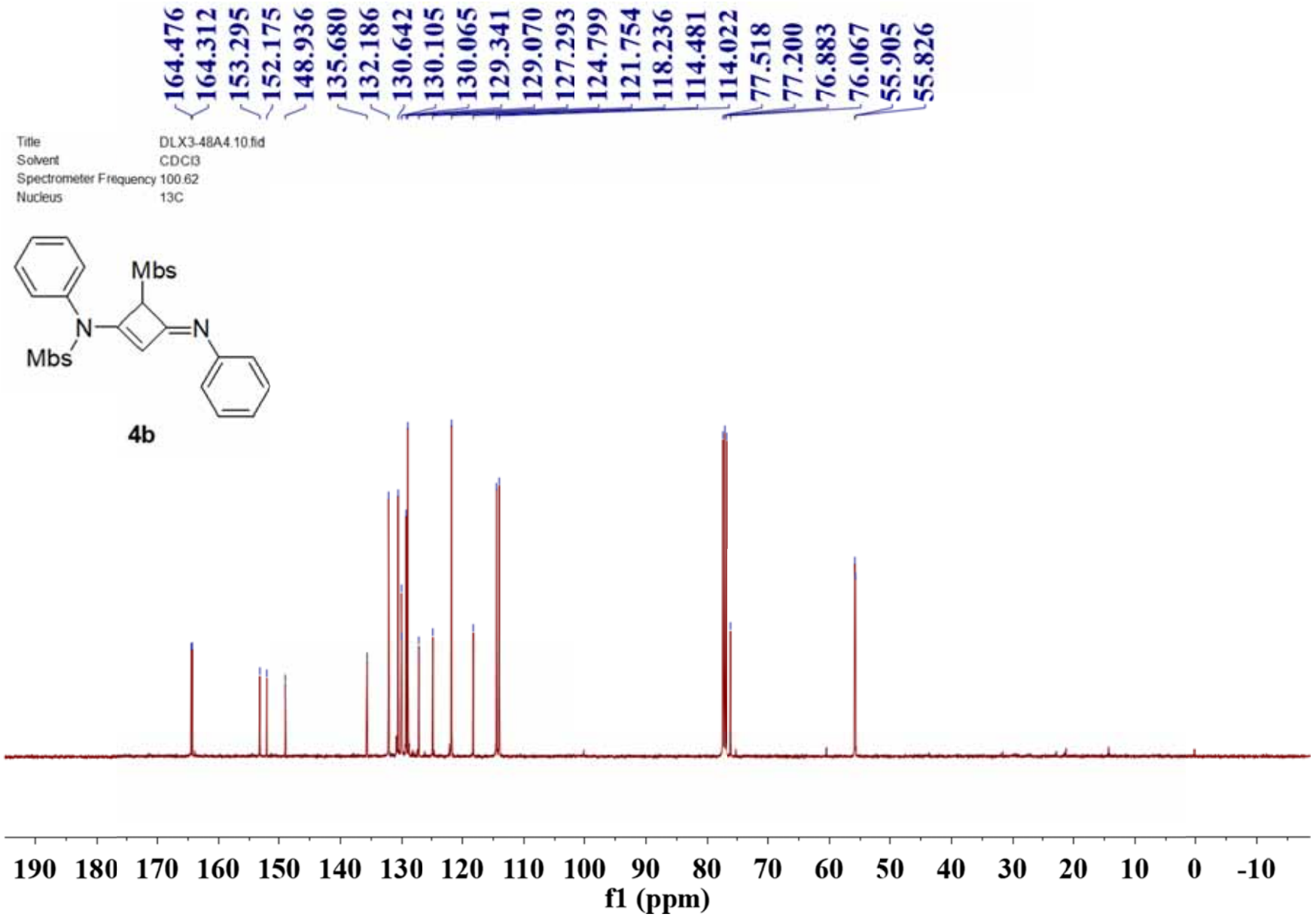

144.727
139.286
139.181
133.399
129.523
128.979
128.856
128.379
127.129
123.341
77.518
77.200
76.882
73.036
65.694
21.874
21.459
-3.565
Title ZXY6-44B.20.fid
Solvent CD3CN_SPE
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Me
Me
3'q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

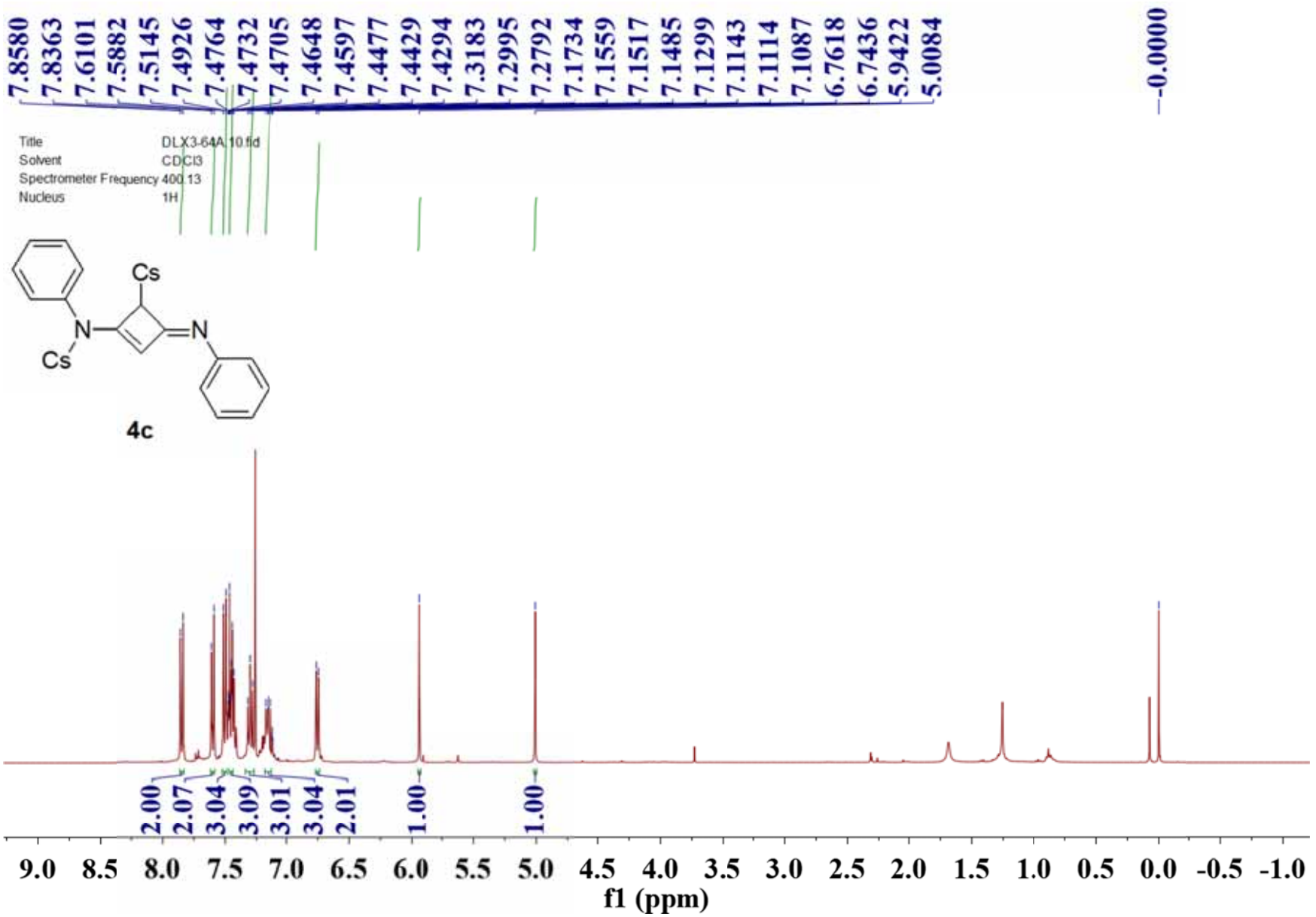
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Aminocyclobutenes 4.

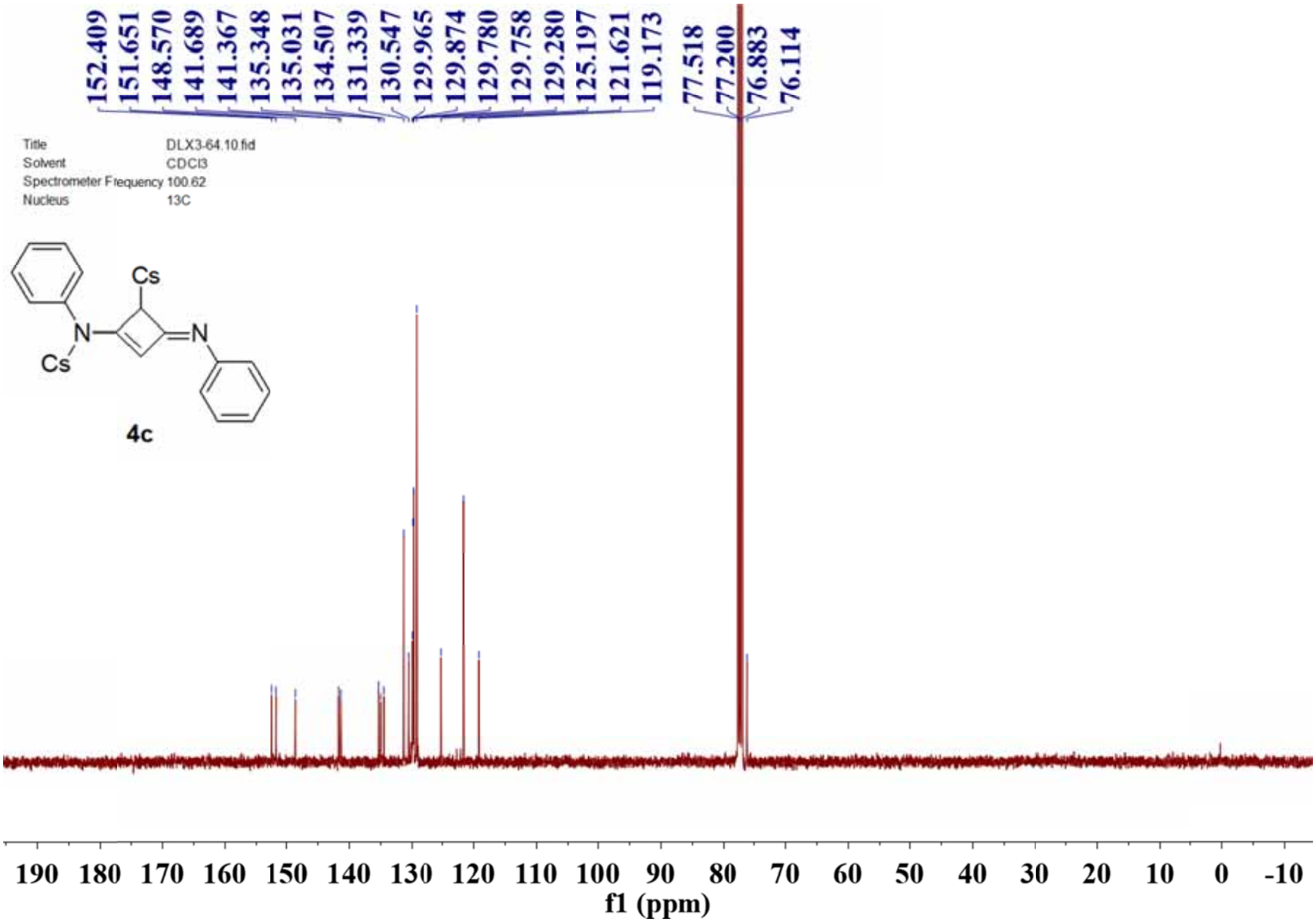


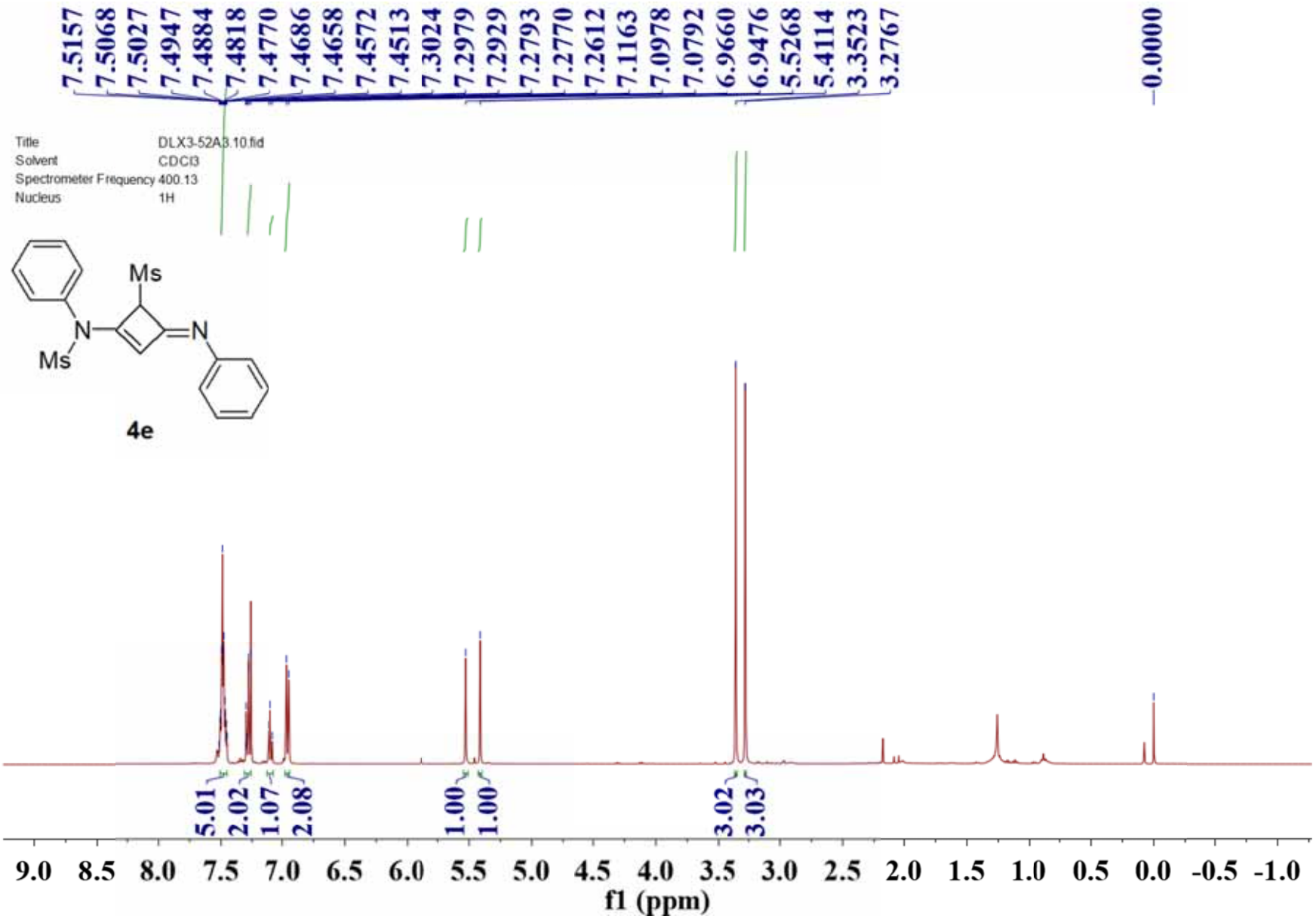

153.075
151.985
148.934
146.014
145.487
135.654
133.099
132.945
130.172
130.077
130.018
129.971
129.480
129.392
129.089
128.386
124.836
121.723
118.565
77.519
77.200
76.883
76.003
21.944
21.890
Title DLX4-68A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
Ts
N
4a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

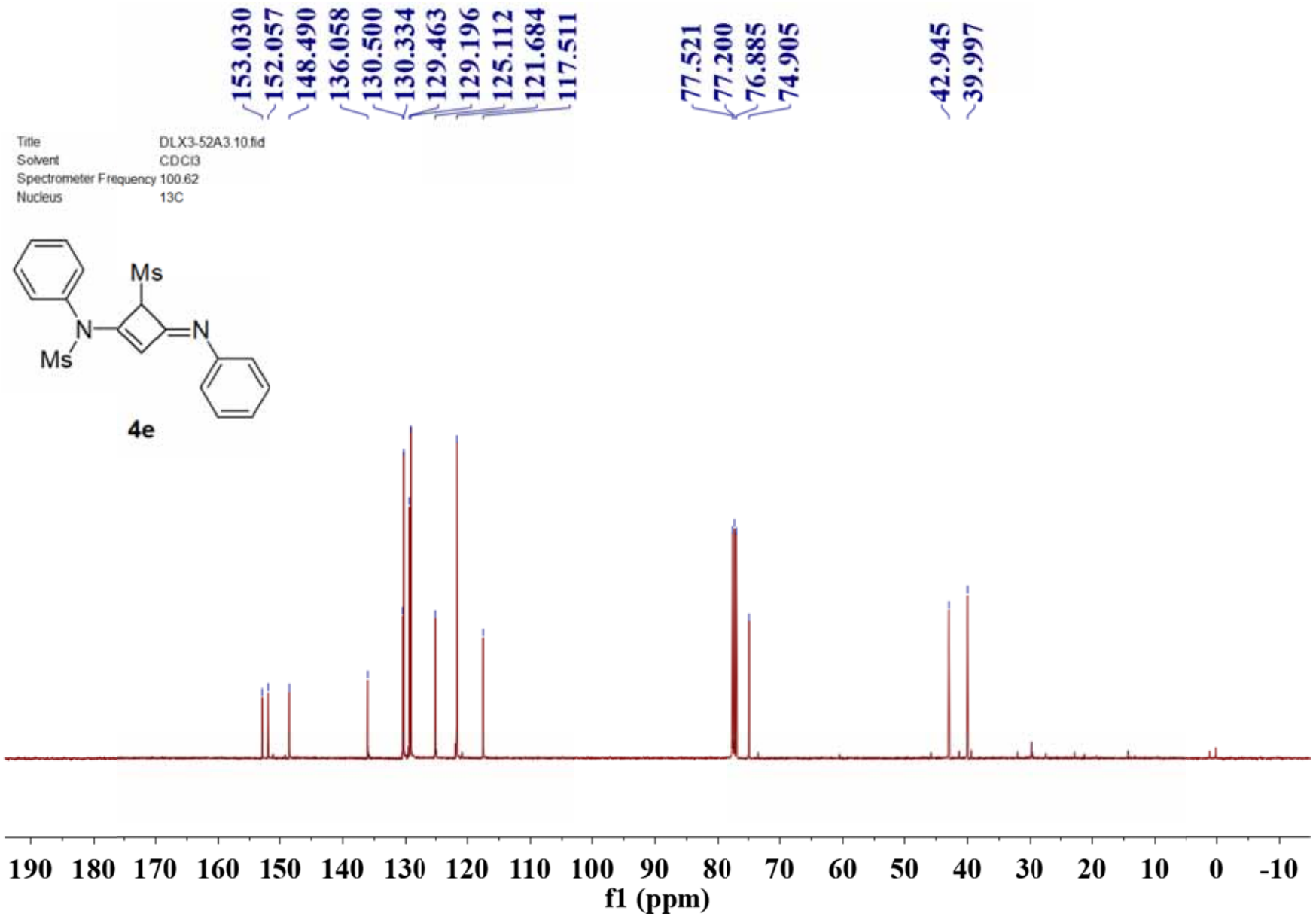

7.8519
7.8296
7.5333
7.5109
7.4643
7.4573
7.4515
7.4429
7.4394
7.4357
7.4222
7.4008
7.3853
7.3809
7.3023
7.2833
7.2633
7.1663
7.1475
7.1297
7.1267
7.1237
7.1083
7.0921
7.0897
7.0870
6.9877
6.9654
6.9061
6.8836
6.7895
6.7712
5.9280
4.9106
3.8730
3.8434
-0.0000
Title DLX3-48A4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Mbs
N
N
Mbs
4b
2.06
2.07
3.09
2.10
3.01
2.04
2.04
2.01
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)

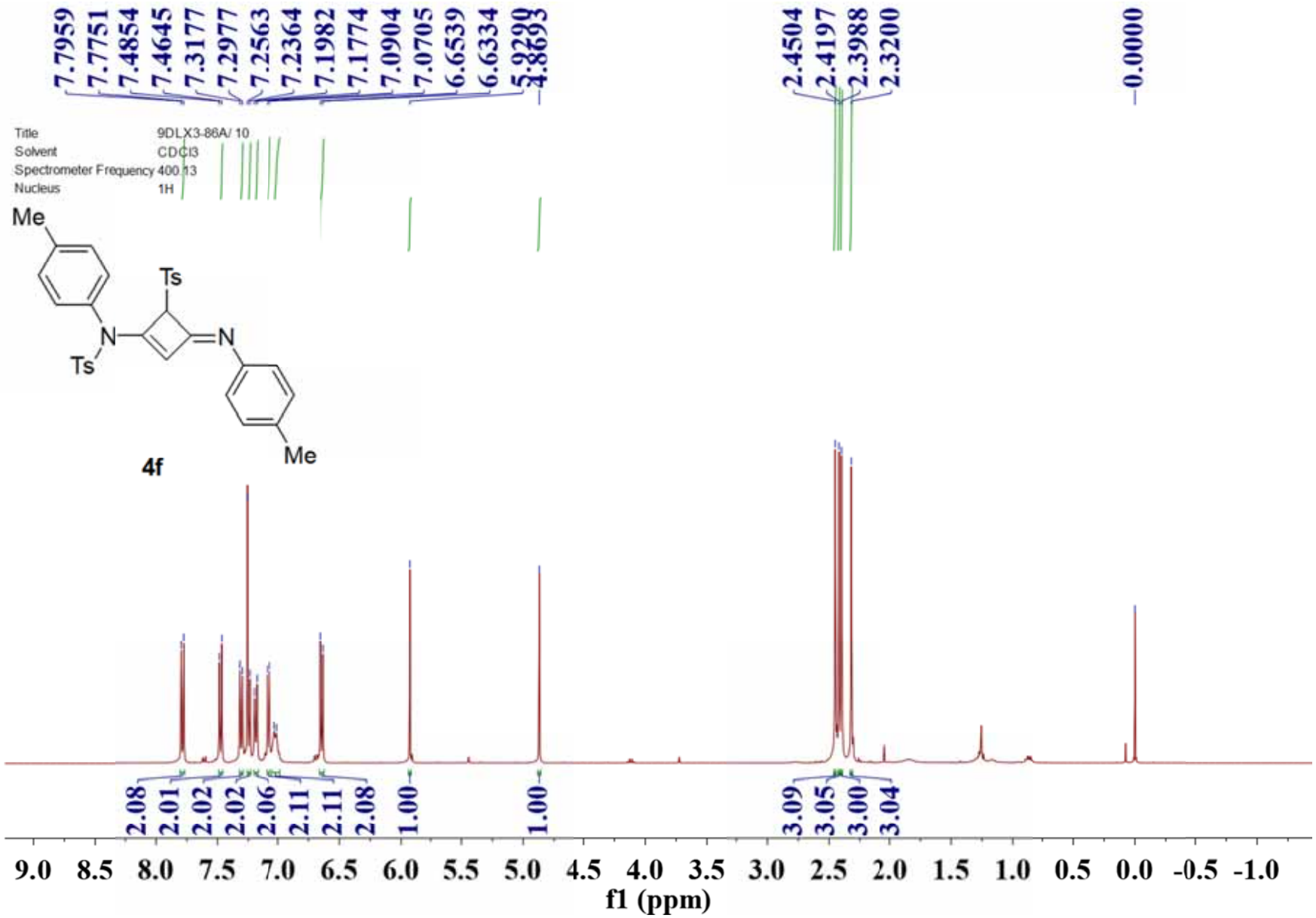

164.476
164.312
153.295
152.175
148.936
135.680
132.186
130.642
130.105
130.065
129.341
129.070
127.293
124.799
121.754
118.236
114.481
114.022
77.518
77.200
76.883
76.067
55.905
55.826
Title DLX3-48A4.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Mbs
N
N
Mbs
4b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

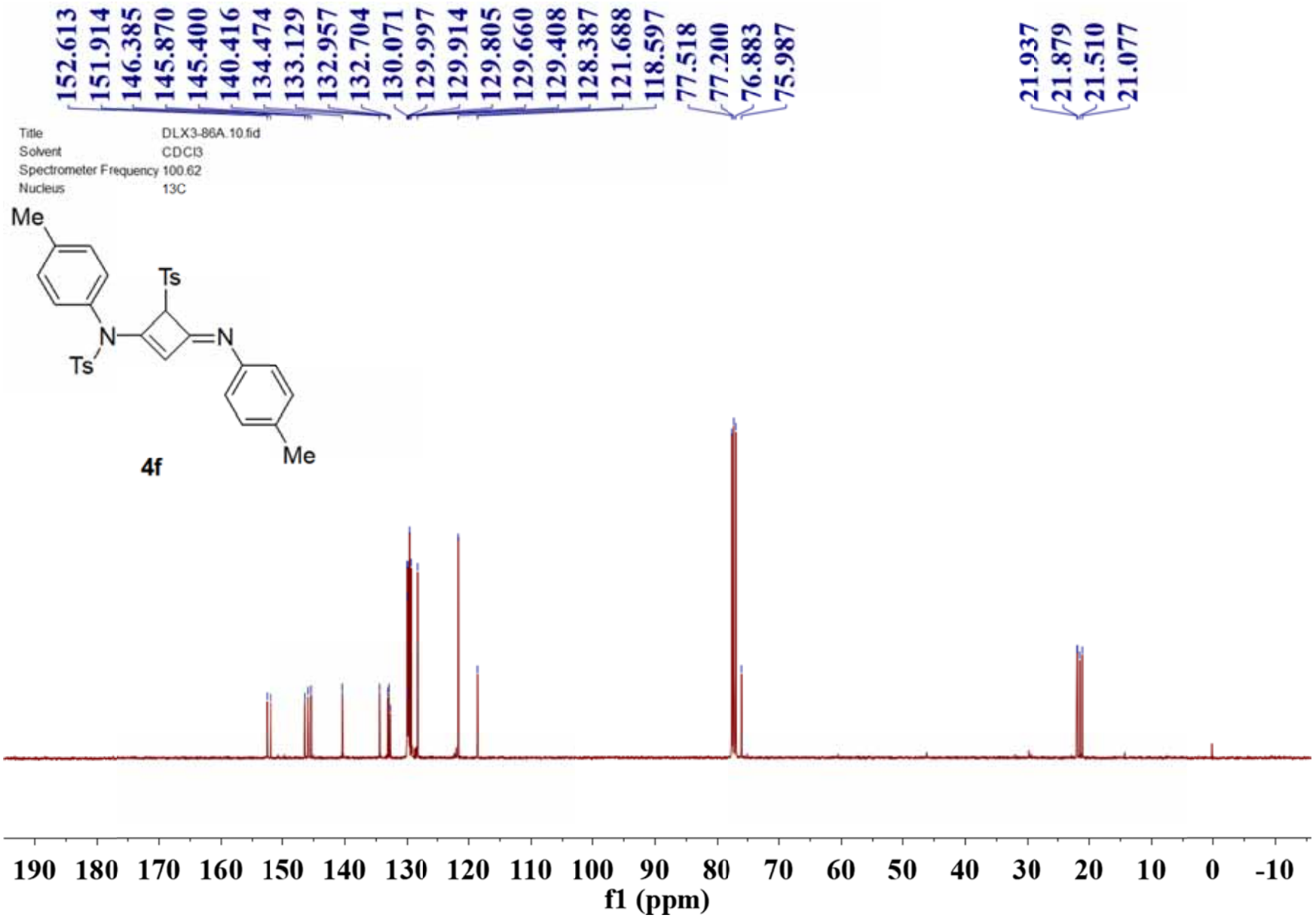

7.8580
7.8363
7.6101
7.5882
7.5145
7.4926
7.4764
7.4732
7.4705
7.4648
7.4597
7.4477
7.4429
7.4294
7.3183
7.2995
7.2792
7.1734
7.1559
7.1517
7.1485
7.1299
7.1143
7.1114
7.1087
6.7618
6.7436
5.9422
5.0084
-0.0000
Title DLX3-64A-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cs
N
Cs
N
4c
2.00
2.07
3.04
3.09
3.01
3.04
2.01
1.00
1.00
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)

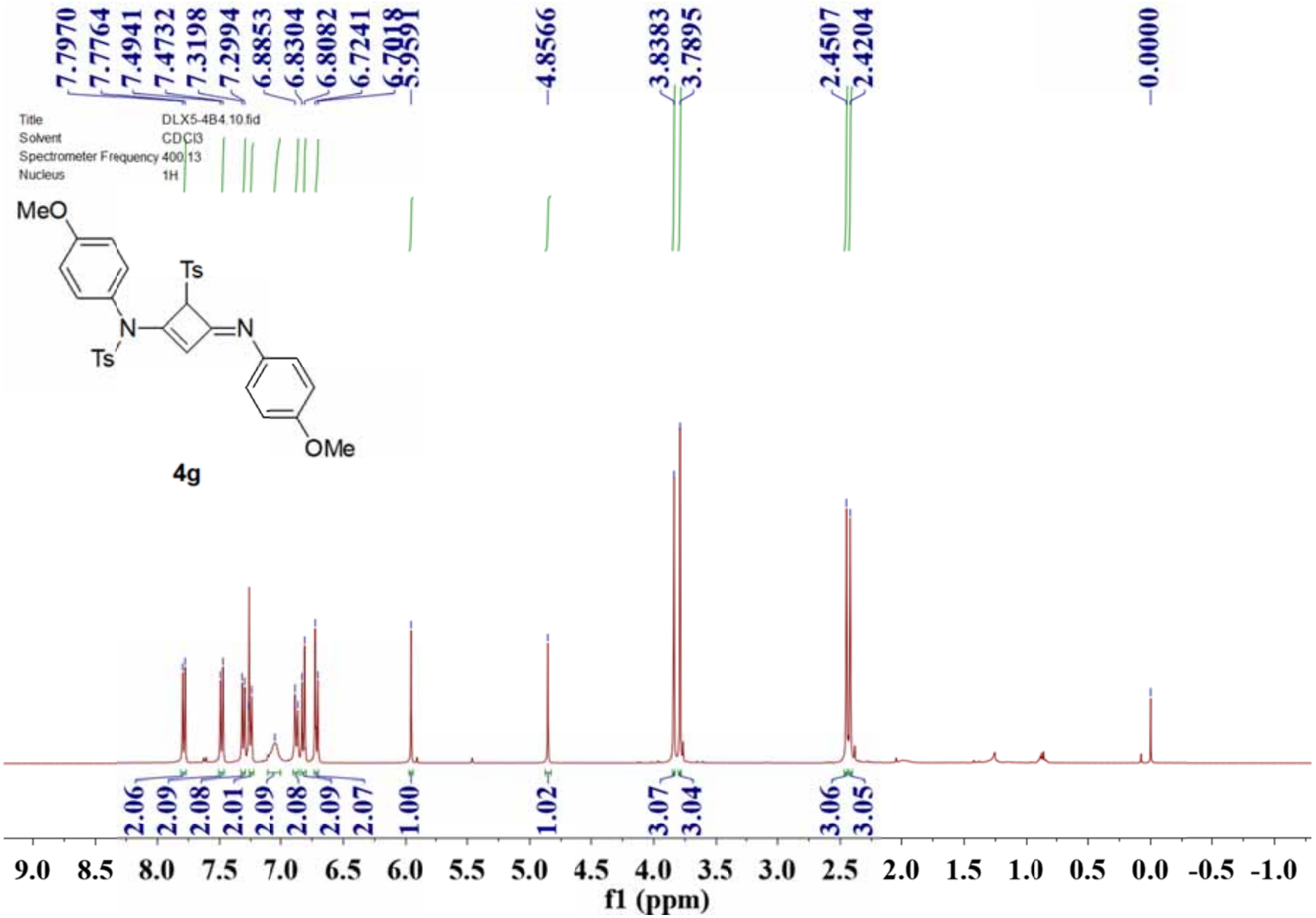

152.409
151.651
148.570
141.689
141.367
135.348
135.031
134.507
131.339
130.547
129.965
129.874
129.780
129.758
129.280
125.197
121.621
119.173
77.518
77.200
76.883
76.114
Title DLX3-64.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cs
N
Cs
N
4c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

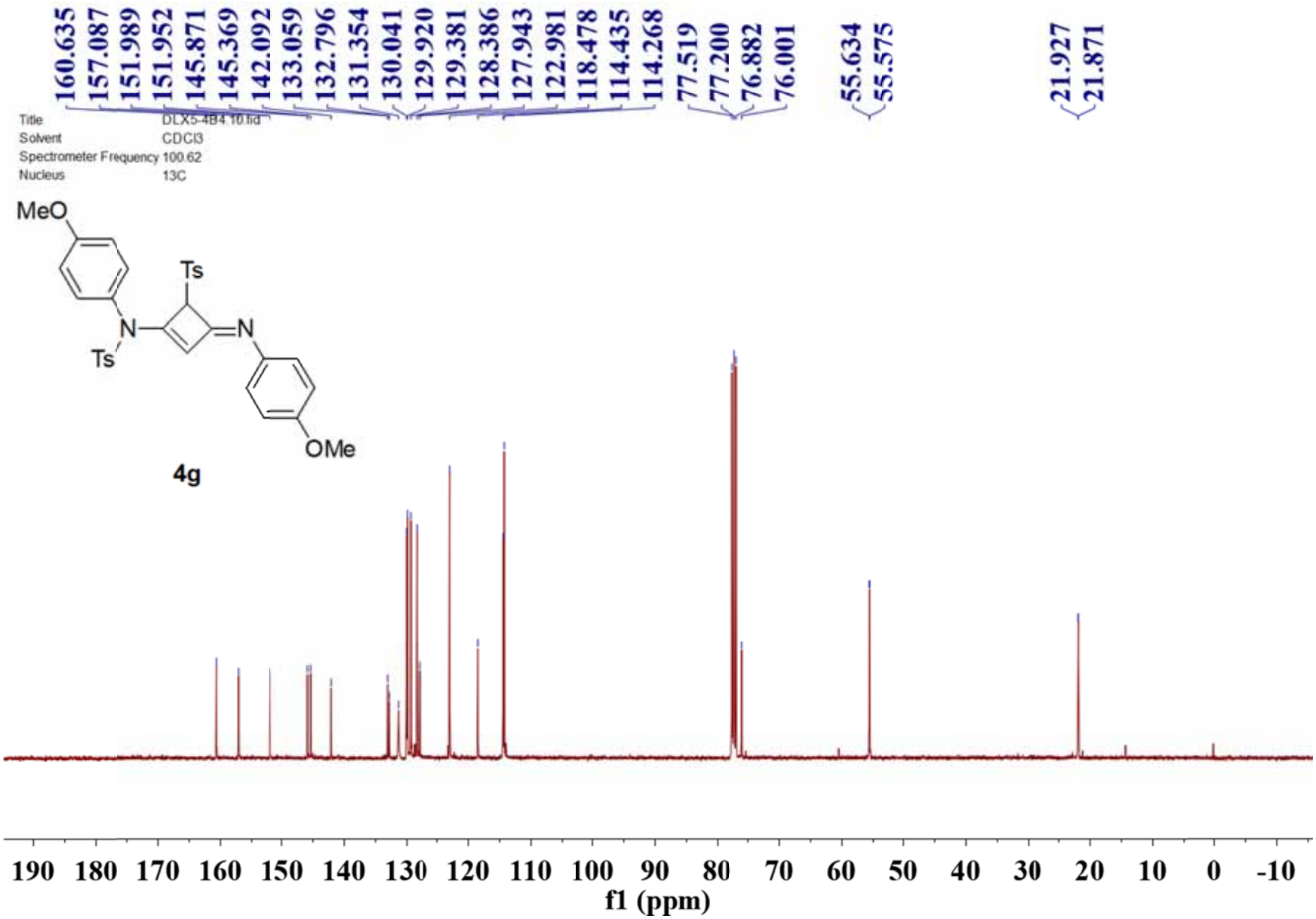

7.5157
7.5068
7.5027
7.4947
7.4884
7.4818
7.4770
7.4686
7.4658
7.4572
7.4513
7.3024
7.2979
7.2929
7.2793
7.2770
7.2612
7.1163
7.0978
7.0792
6.9660
6.9476
5.5268
5.4114
3.3523
3.2767
0.0000
Title DLX3-52A3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ms
N
Ms
N
4e
5.01
2.02
1.07
2.08
1.00
1.00
3.02
3.03
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)

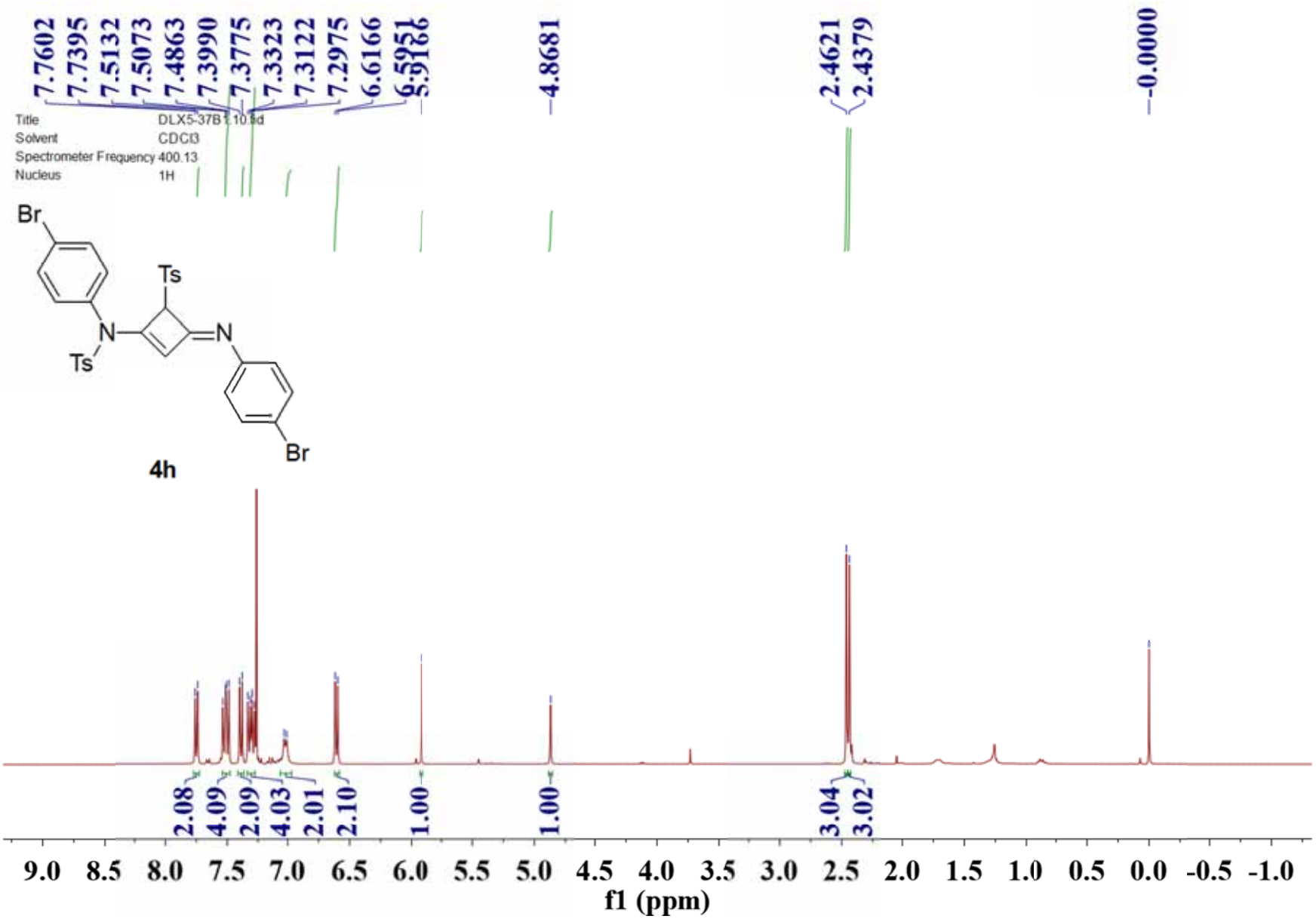

153.030
152.057
148.490
136.058
130.500
130.334
129.463
129.196
125.112
121.684
117.511
77.521
77.200
76.885
74.905
42.945
39.997
Title DLX3-52A3.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ms
N
Ms
N
4e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

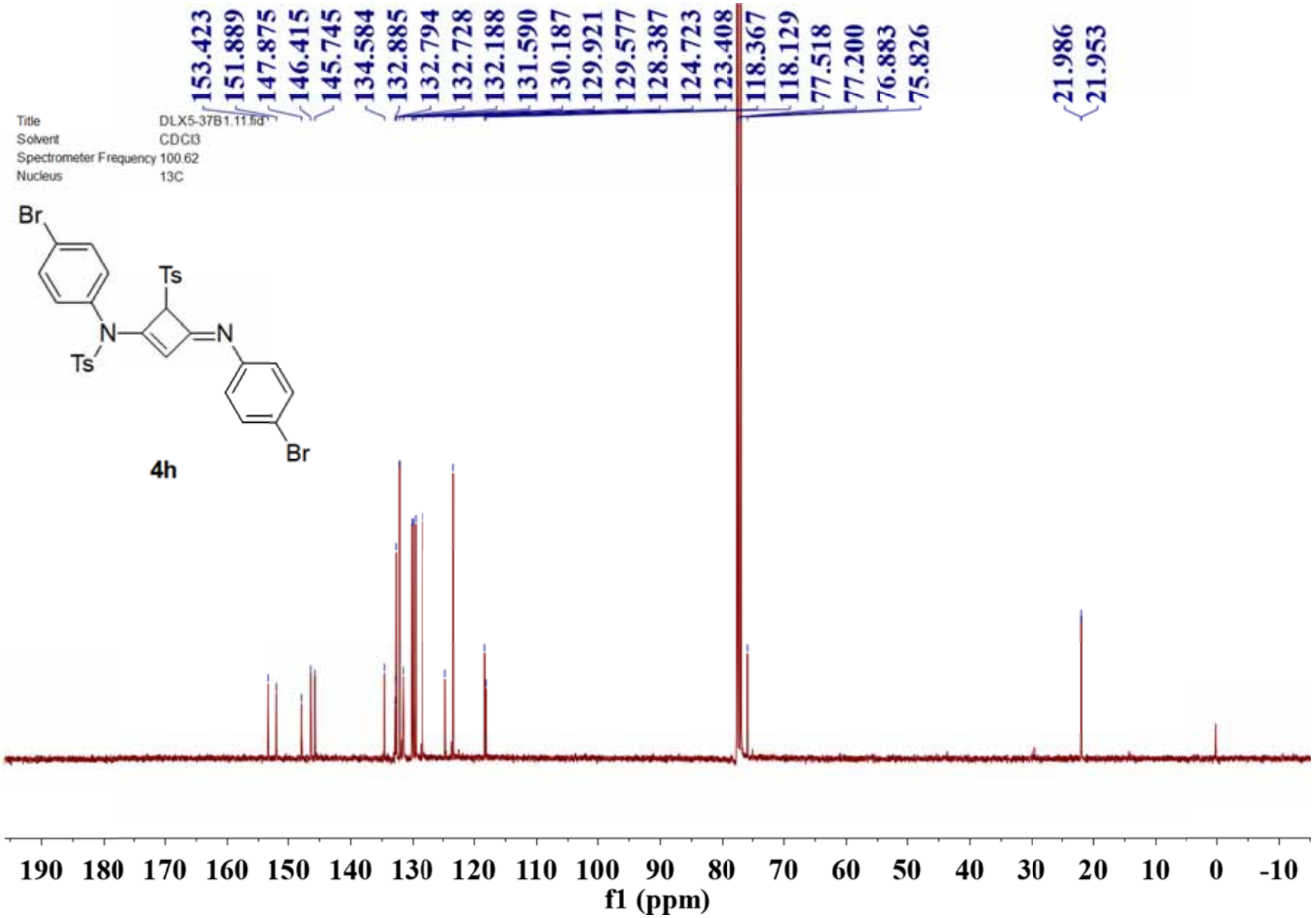

7.7959
7.7751
7.4854
7.4645
7.3177
7.2977
7.2563
7.2364
7.1982
7.1774
7.0904
7.0705
6.6539
6.6334
5.9290
4.8693
2.4504
2.4197
2.3988
2.3200
0.0000
Title 9DLX3-86A/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ts
N
Ts
N
Me
4f
2.08
2.01
2.02
2.02
2.06
2.11
2.11
2.08
1.00
1.00
3.09
3.05
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)

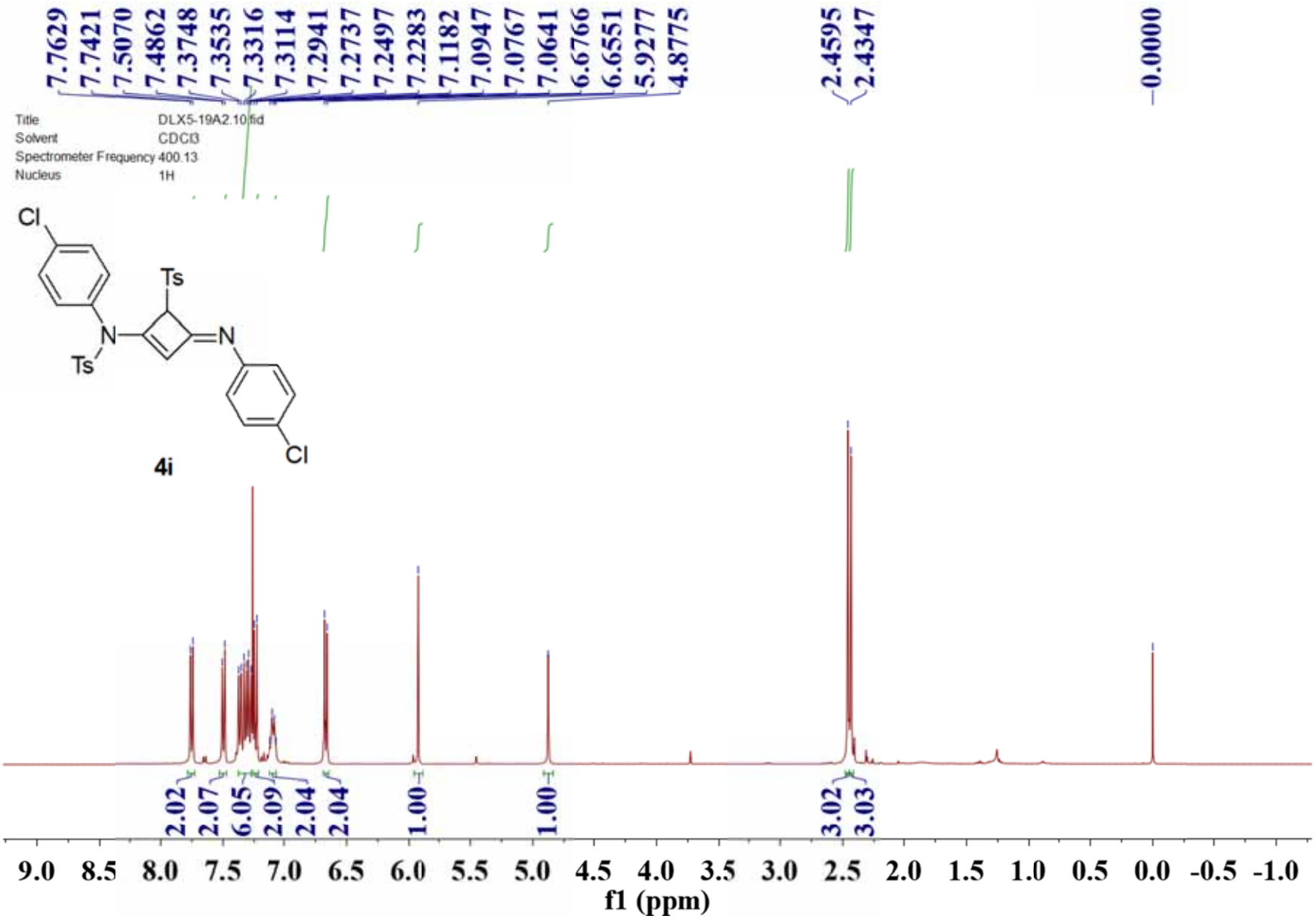

152.613
151.914
146.385
145.870
145.400
140.416
134.474
133.129
132.957
132.704
130.071
129.997
129.914
129.805
129.660
129.408
128.387
121.688
118.597
77.518
77.200
76.883
75.987
21.937
21.879
21.510
21.077
Title DLX3-86A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Ts
N
Ts
N
Me
4f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

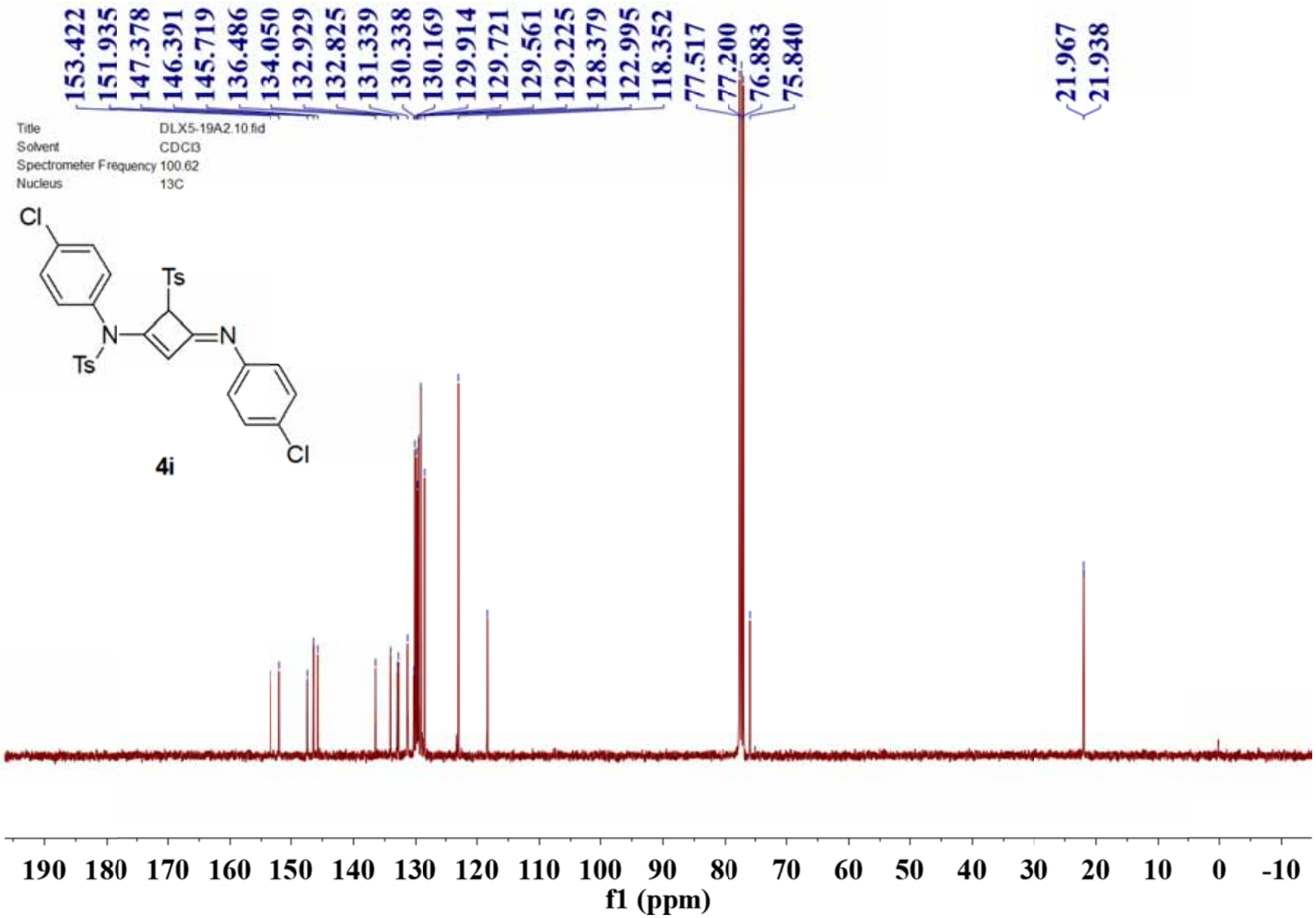

7.7970
7.7764
7.4941
7.4732
7.3198
7.2994
6.8853
6.8304
6.8082
6.7241
6.7018
5.9591
4.8566
3.8383
3.7895
2.4507
2.4204
0.0000
Title DLX5-4B4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Ts
N
Ts
N
OMe
4g
2.06
2.09
2.08
2.01
2.09
2.08
2.09
2.07
1.00
1.02
3.07
3.04
3.06
3.05
9.0 8.5 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)

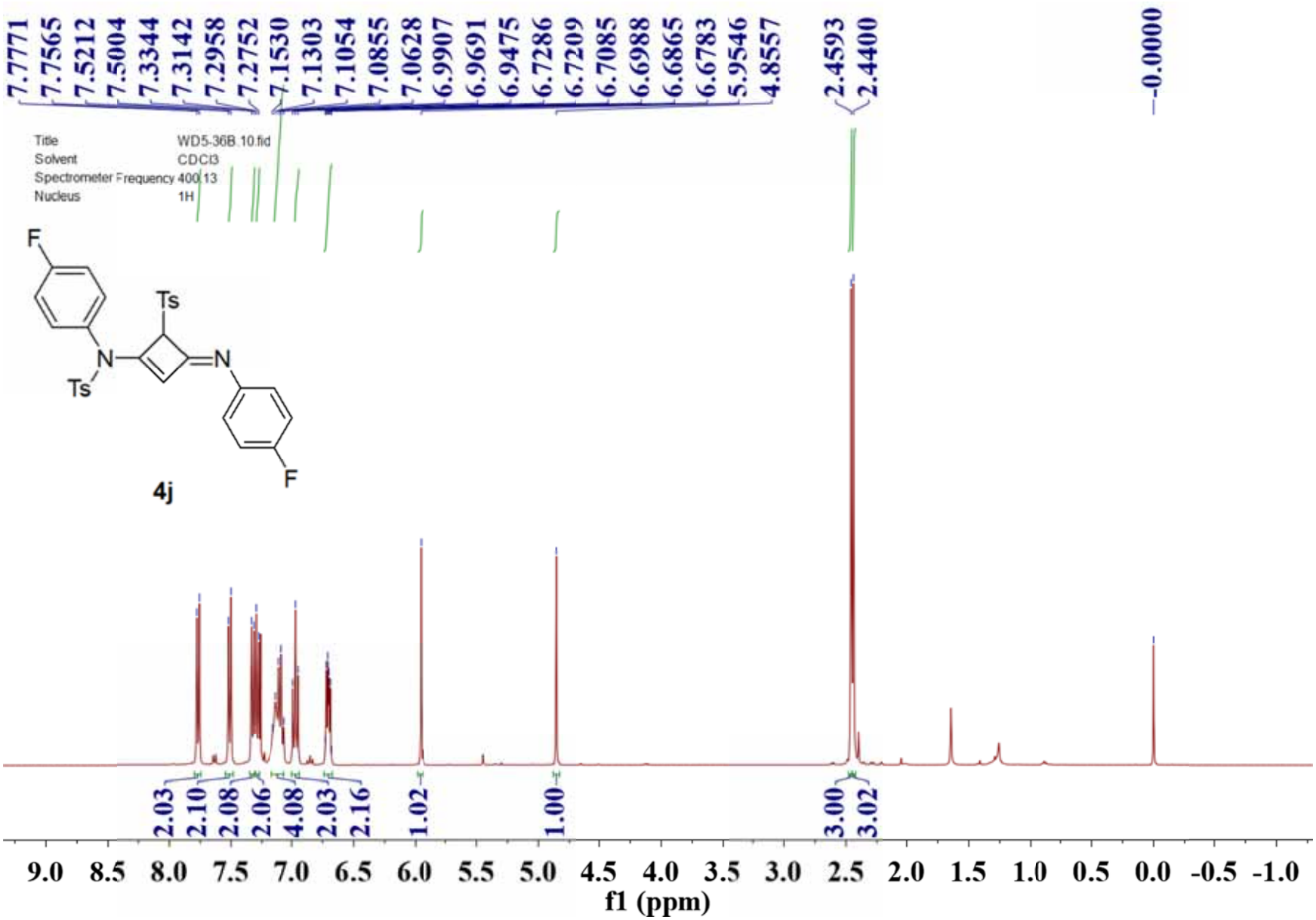

160.635
157.087
151.989
151.952
145.871
145.369
142.092
133.059
132.796
131.354
130.041
129.920
129.381
128.386
127.943
122.981
118.478
114.435
114.268
77.519
77.200
76.882
76.001
55.634
55.575
21.927
21.871
Title DLX5-4B4.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Ts
N
Ts
N
OMe
4g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

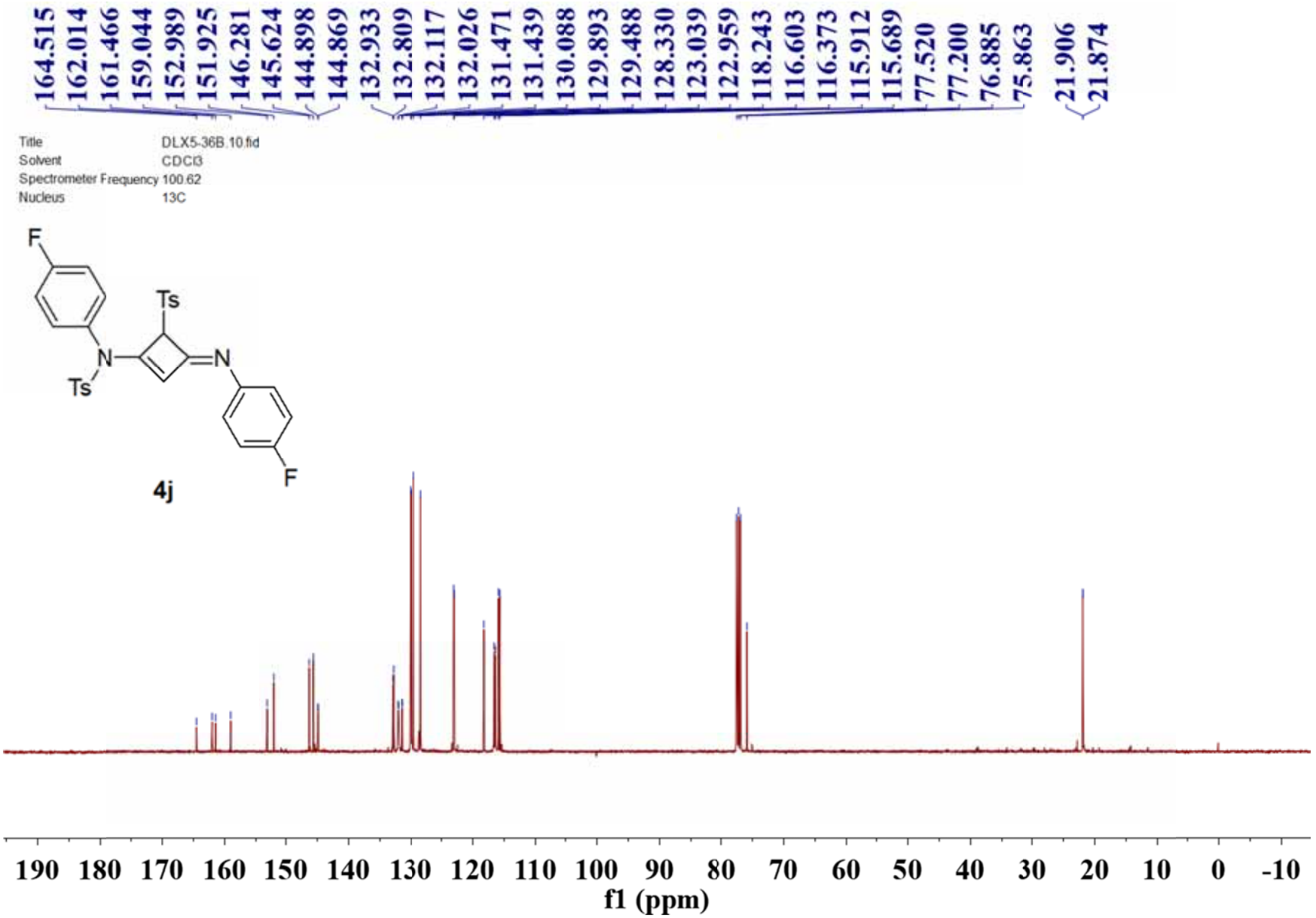

7.7602
7.7395
7.5132
7.5073
7.4863
7.3990
7.3775
7.3323
7.3122
7.2975
6.6166
6.5951
5.9166
4.8681
2.4621
2.4379
-0.0000
Title DLX5-37B1 10.1d
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Br
Ts
N
Ts
N
Br
4h
2.08
4.09
2.09
4.03
2.01
2.10
1.00
1.00
3.04
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 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)

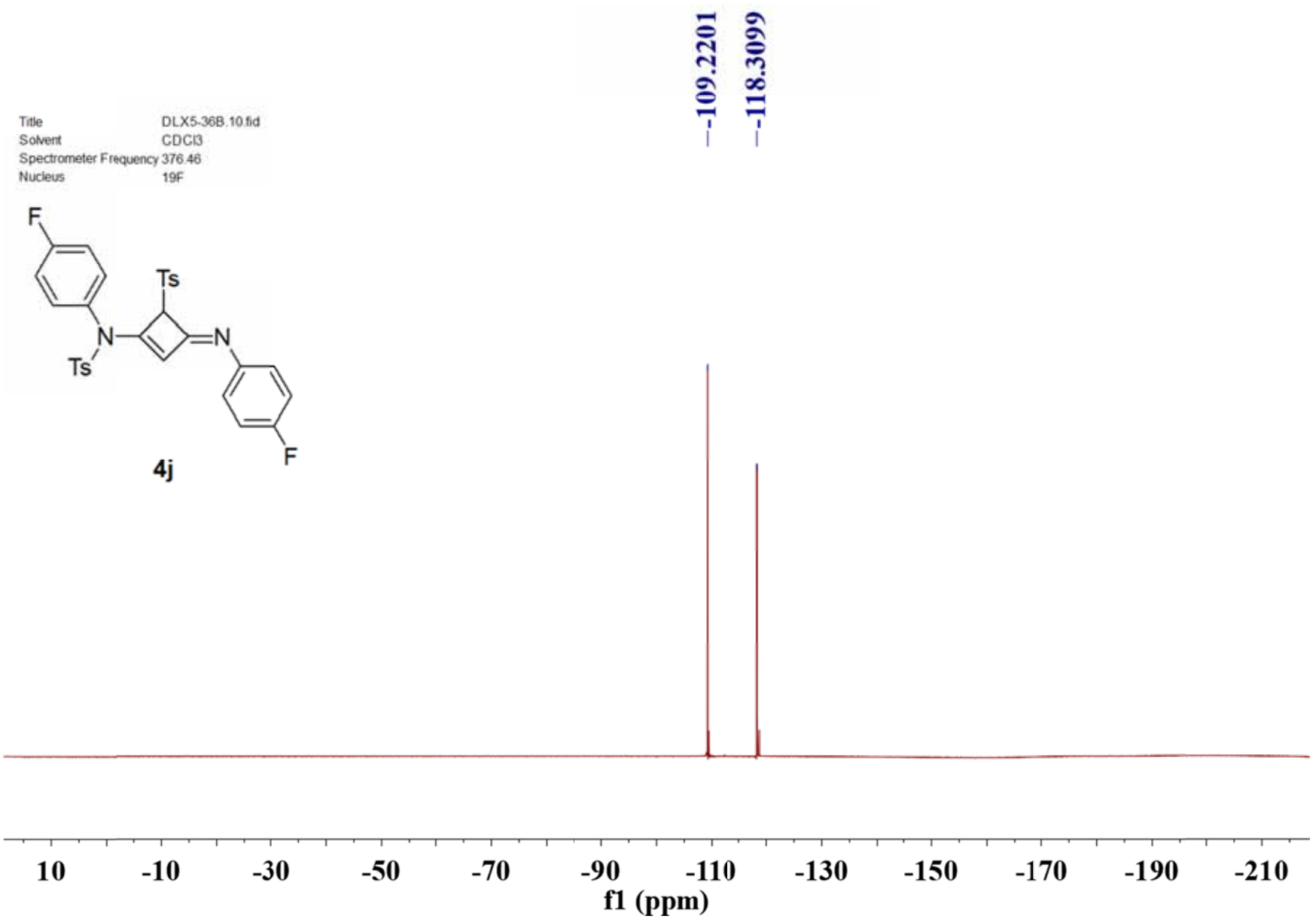

153.423
151.889
147.875
146.415
145.745
134.584
132.885
132.794
132.728
132.188
131.590
130.187
129.921
129.577
128.387
124.723
123.408
118.367
118.129
77.518
77.200
76.883
75.826
21.986
21.953
Title DLX5-37B1.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Br
Ts
N
Ts
N
Br
4h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

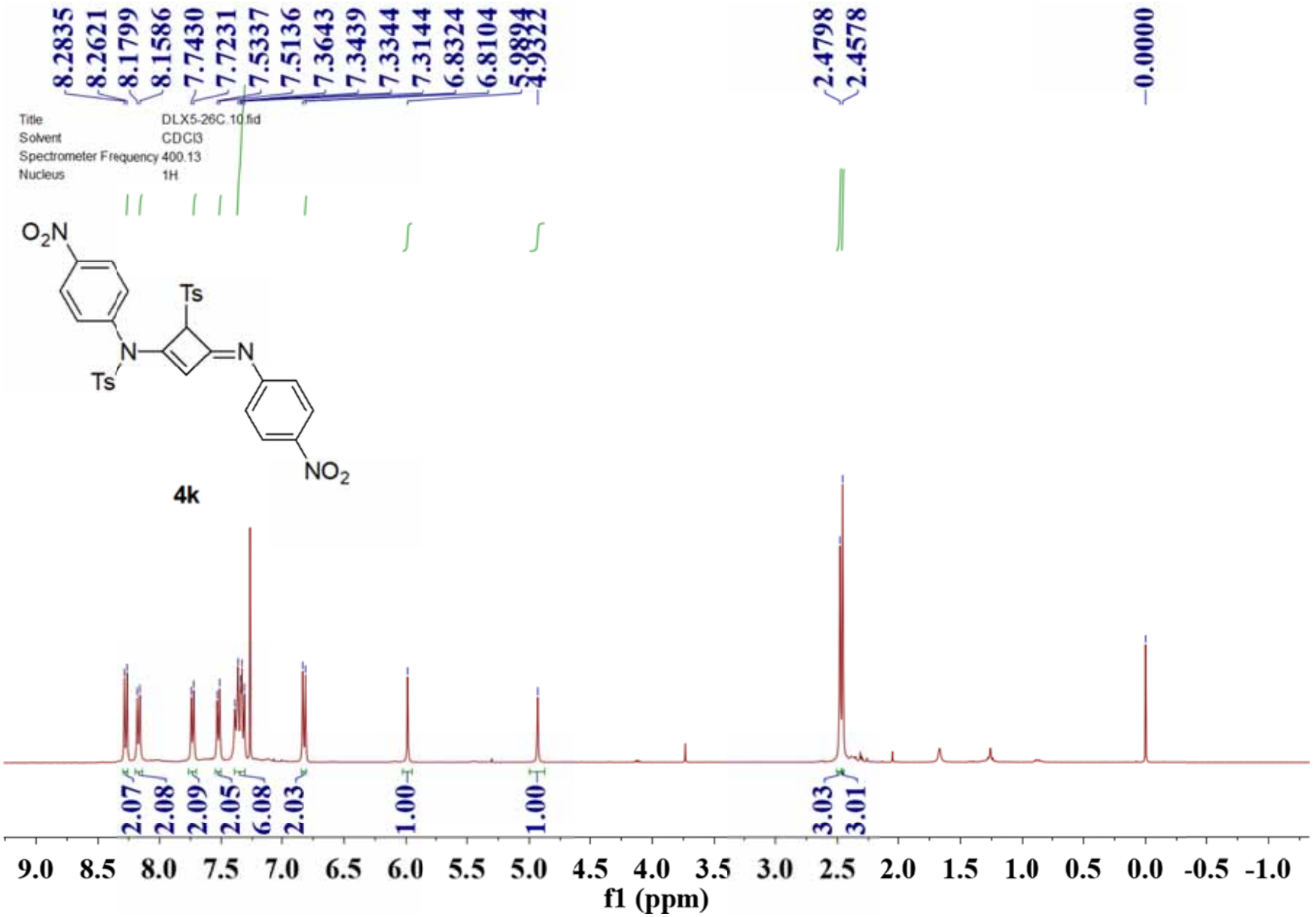

7.7629
7.7421
7.5070
7.4862
7.3748
7.3535
7.3316
7.3114
7.2941
7.2737
7.2497
7.2283
7.1182
7.0947
7.0767
7.0641
6.6766
6.6551
5.9277
4.8775
2.4595
2.4347
0.0000
Title DLX5-19A2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Ts
N
Ts
N
Cl
4i
2.02
2.07
6.05
2.09
2.04
2.04
1.00
1.00
3.02
3.03
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)

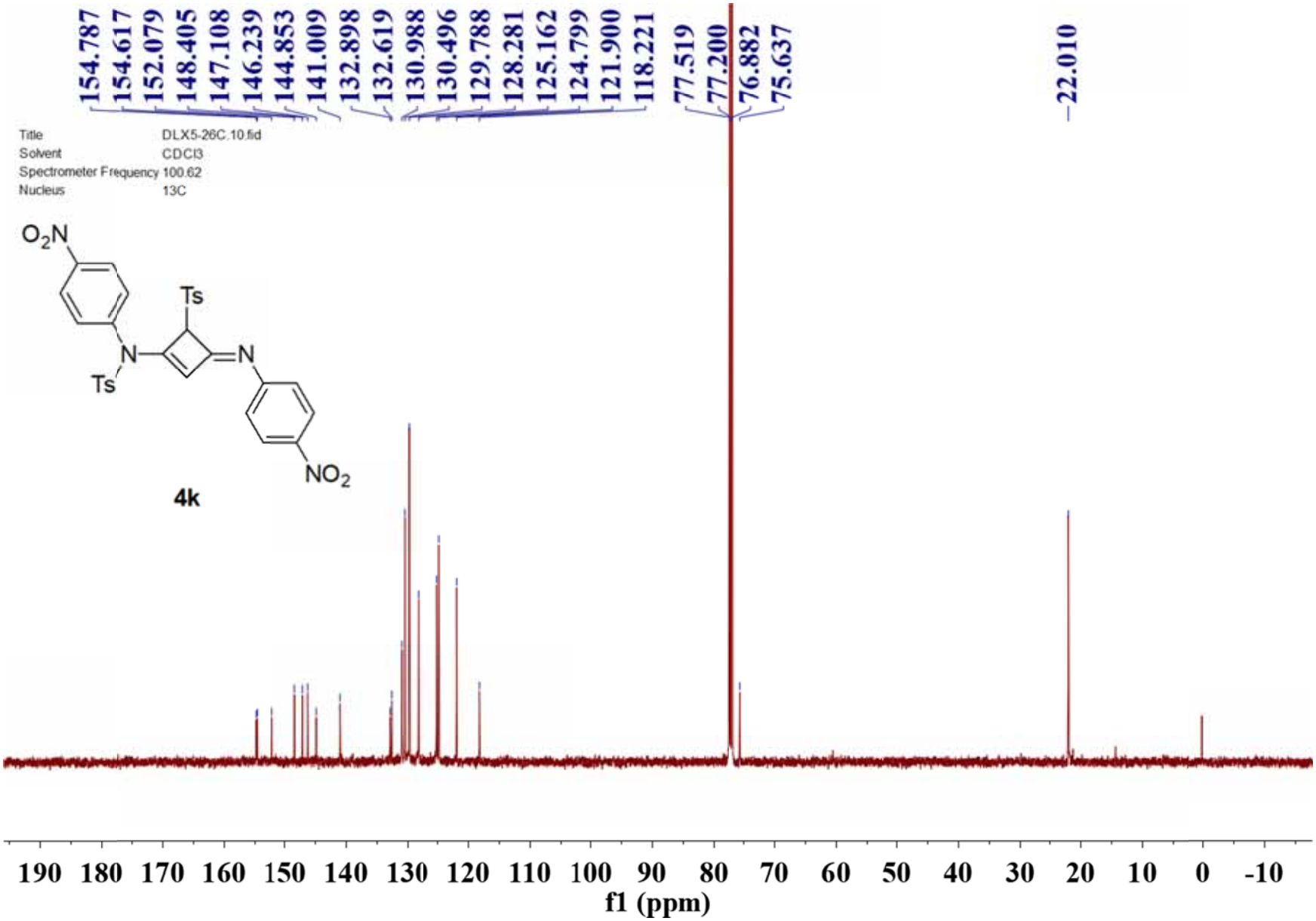

153.422
151.935
147.378
146.391
145.719
136.486
134.050
132.929
132.825
131.339
130.338
130.169
129.914
129.721
129.561
129.225
128.379
122.995
118.352
77.517
77.200
76.883
75.840
21.967
21.938
Title DLX5-19A2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Ts
N
Ts
N
Cl
4i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

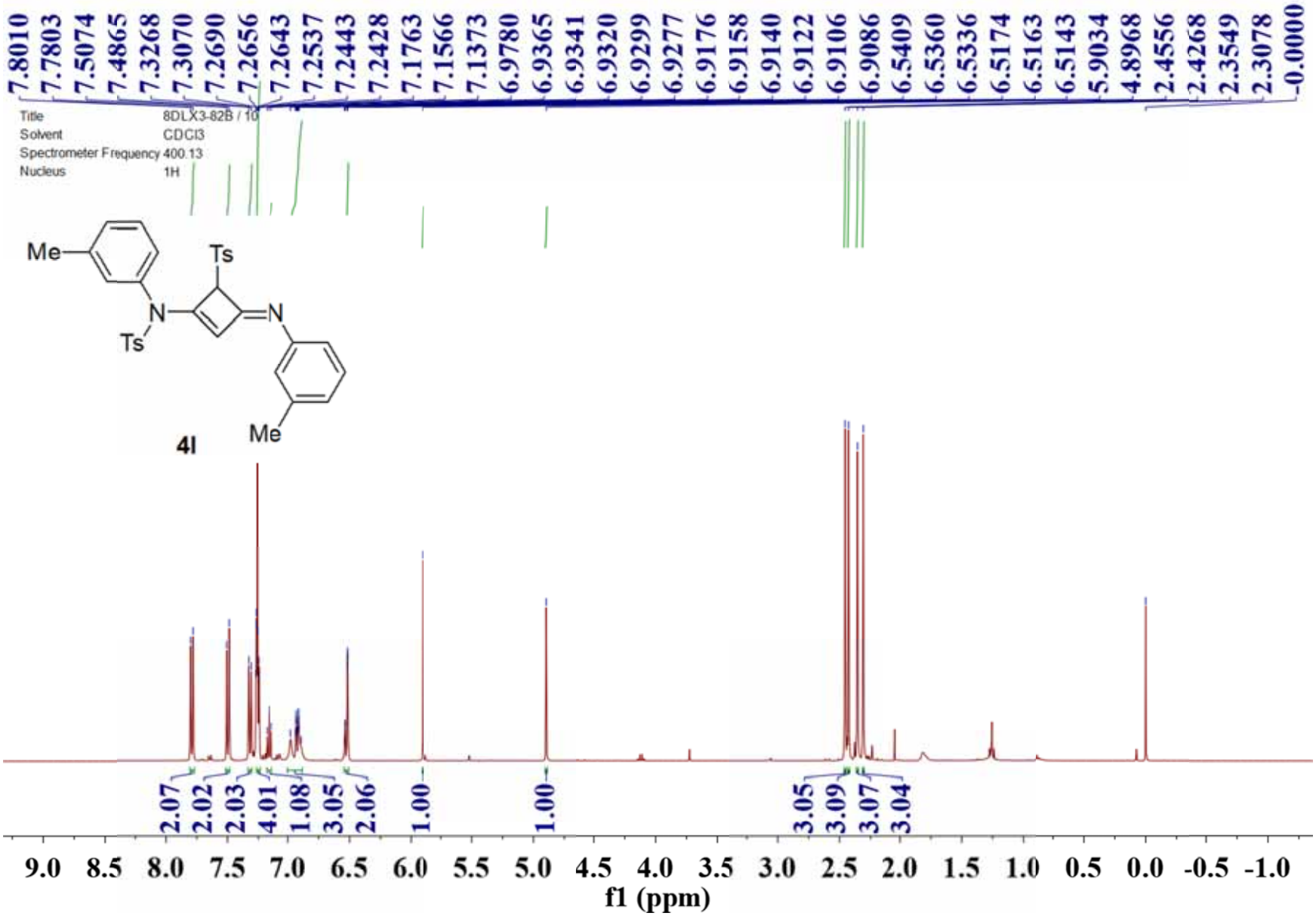

7.7771
7.7565
7.5212
7.5004
7.3344
7.3142
7.2958
7.2752
7.1530
7.1303
7.1054
7.0855
7.0628
6.9907
6.9691
6.9475
6.7286
6.7209
6.7085
6.6988
6.6865
6.6783
5.9546
4.8557
2.4593
2.4400
-0.0000
Title WD5-36B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
Ts
N
Ts
N
F
4j
2.03
2.10
2.08
2.06
4.08
2.03
2.16
1.02
1.00
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)

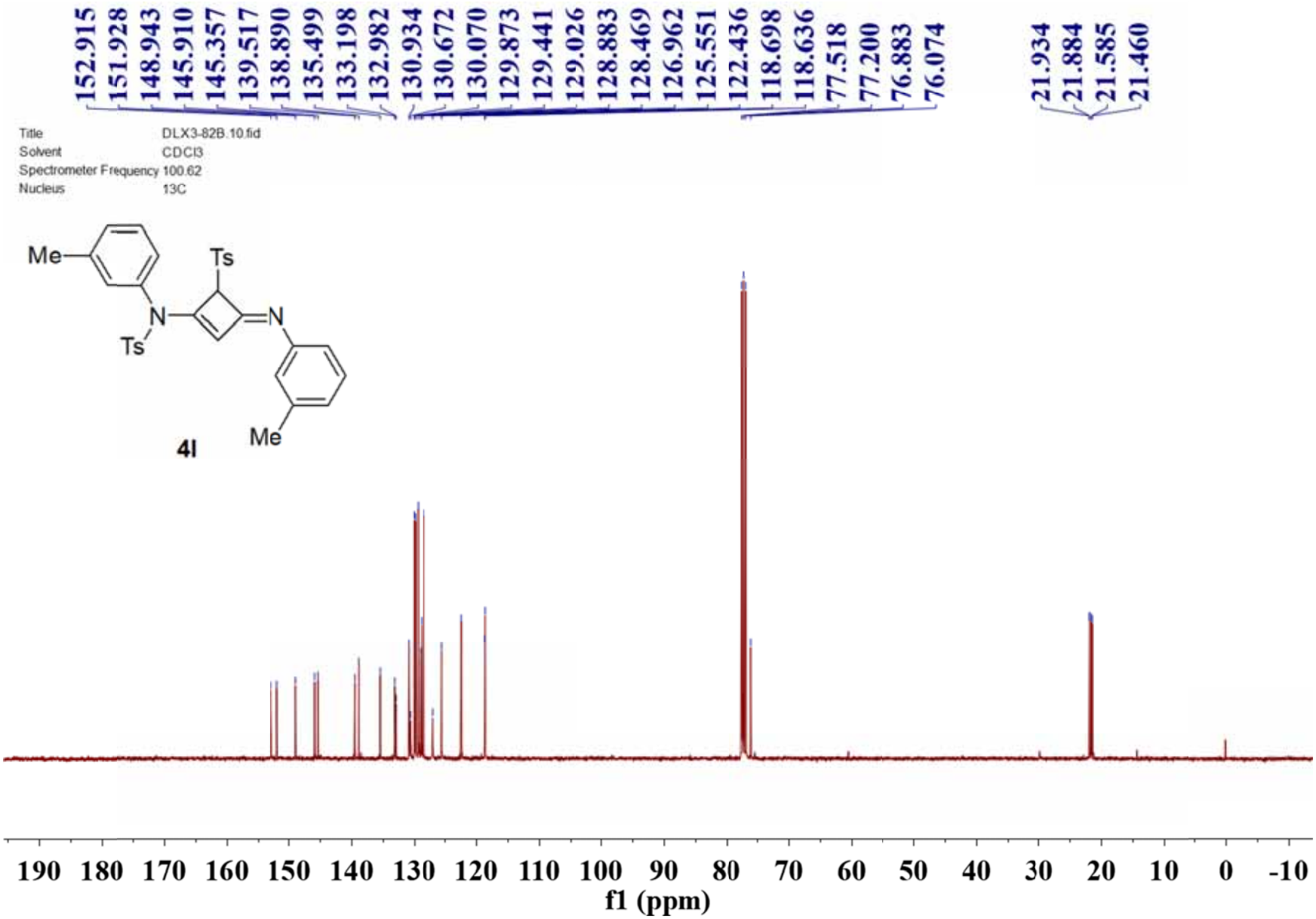

164.515
162.014
161.466
159.044
152.989
151.925
146.281
145.624
144.898
144.869
132.933
132.809
132.117
132.026
131.471
131.439
130.088
129.893
129.488
128.330
123.039
122.959
118.243
116.603
116.373
115.912
115.689
77.520
77.200
76.885
75.863
21.906
21.874
Title DLX5-36B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
Ts
N
Ts
N
F
4j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

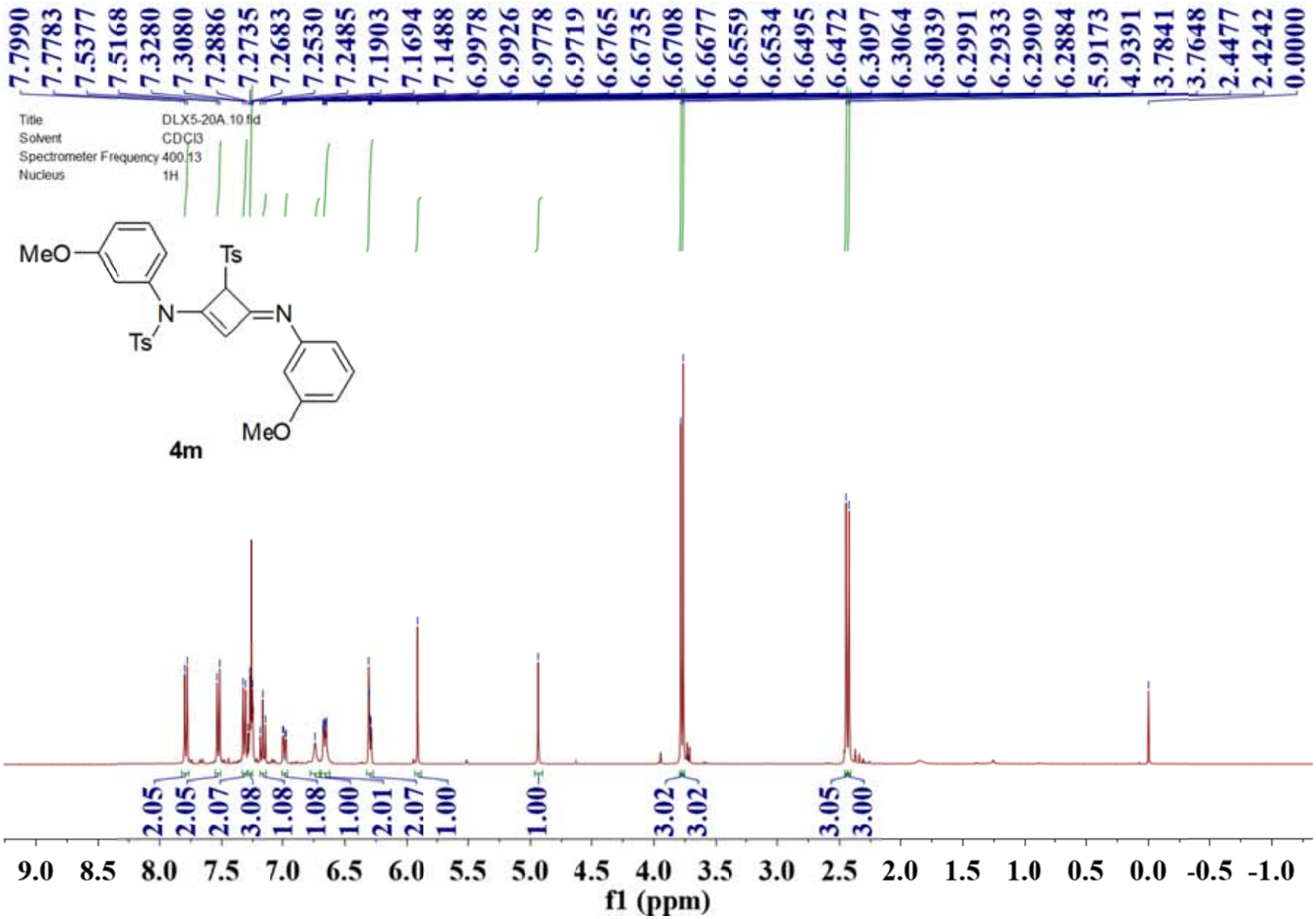

Title DLX5-36B.10.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
F
Ts
N
Ts
N
F
4j
-109.2201
-118.3099
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

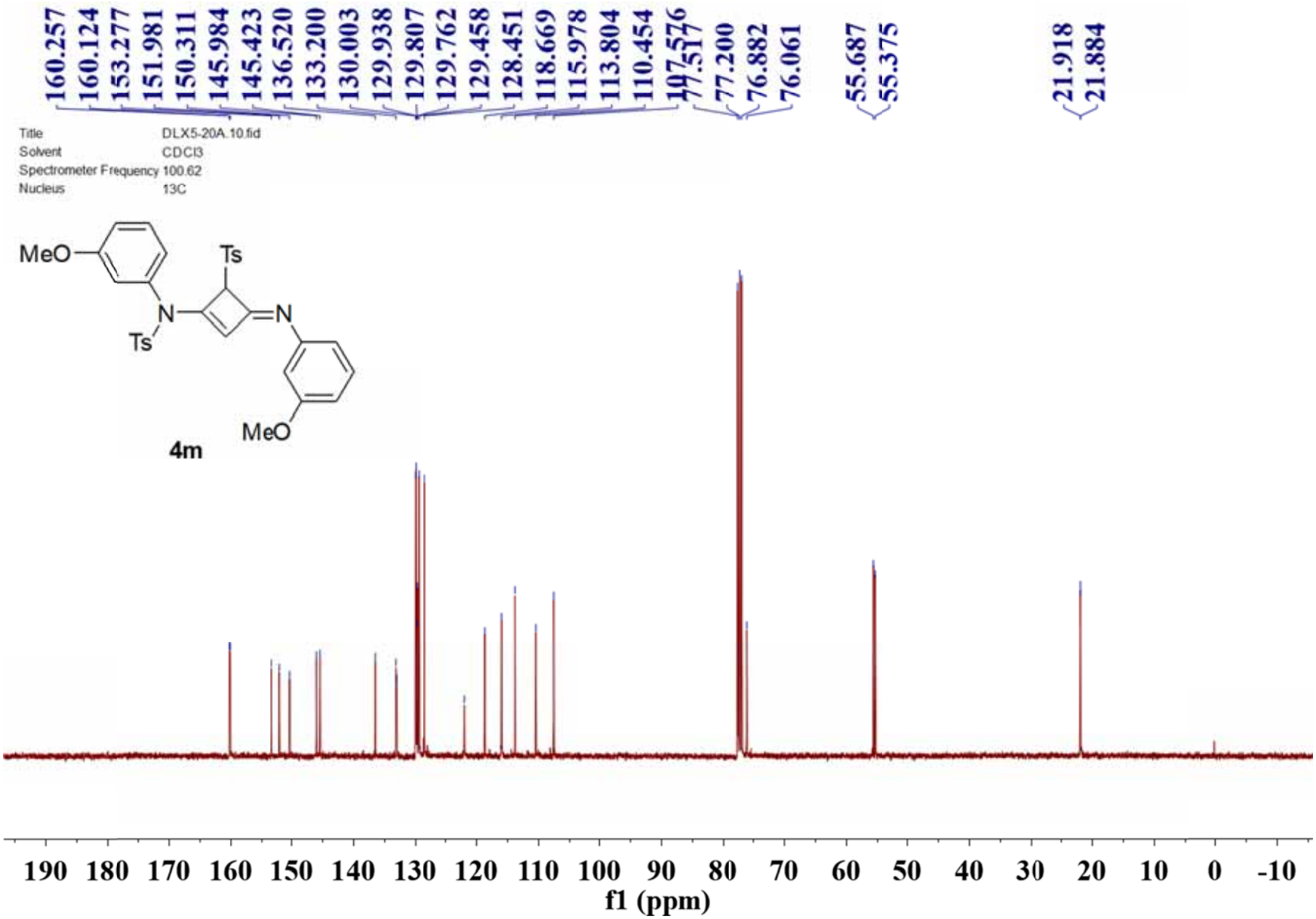

8.2835
8.2621
8.1799
8.1586
7.7430
7.7231
7.5337
7.5136
7.3643
7.3439
7.3344
7.3144
6.8324
6.8104
5.9824
4.9322
2.4798
2.4578
0.0000
Title DLX5-26C.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
O2N
Ts
N
Ts
N
NO2
4k
2.07
2.08
2.09
2.05
6.08
2.03
1.00
1.00
3.03
3.01
9.0 8.5 8.0 7.5 7.0 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)

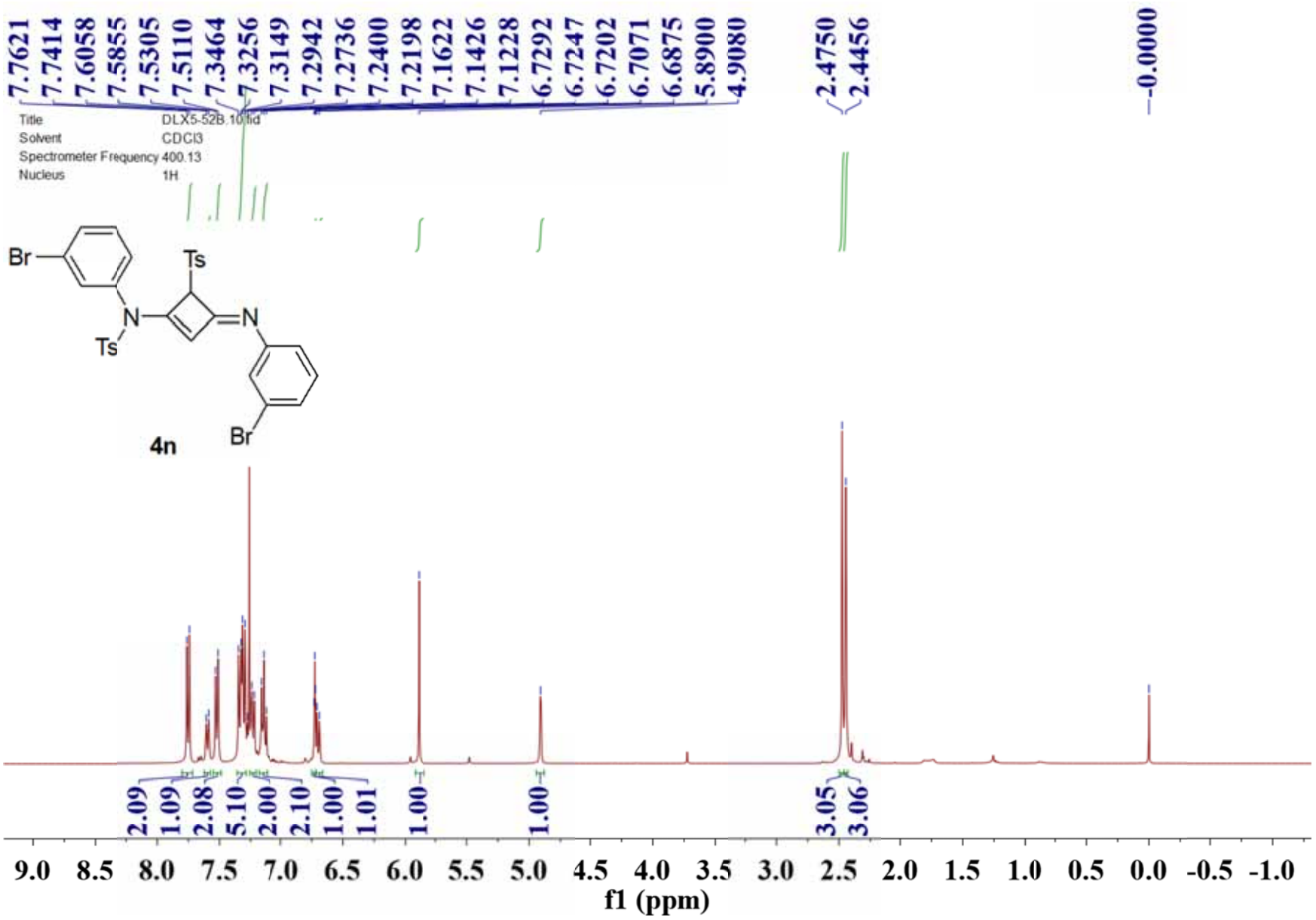

154.787
154.617
152.079
148.405
147.108
146.239
144.853
141.009
132.898
132.619
130.988
130.496
129.788
128.281
125.162
124.799
121.900
118.221
77.519
77.200
76.882
75.637
22.010
Title DLX5-26C.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
O2N
Ts
N
Ts
N
NO2
4k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

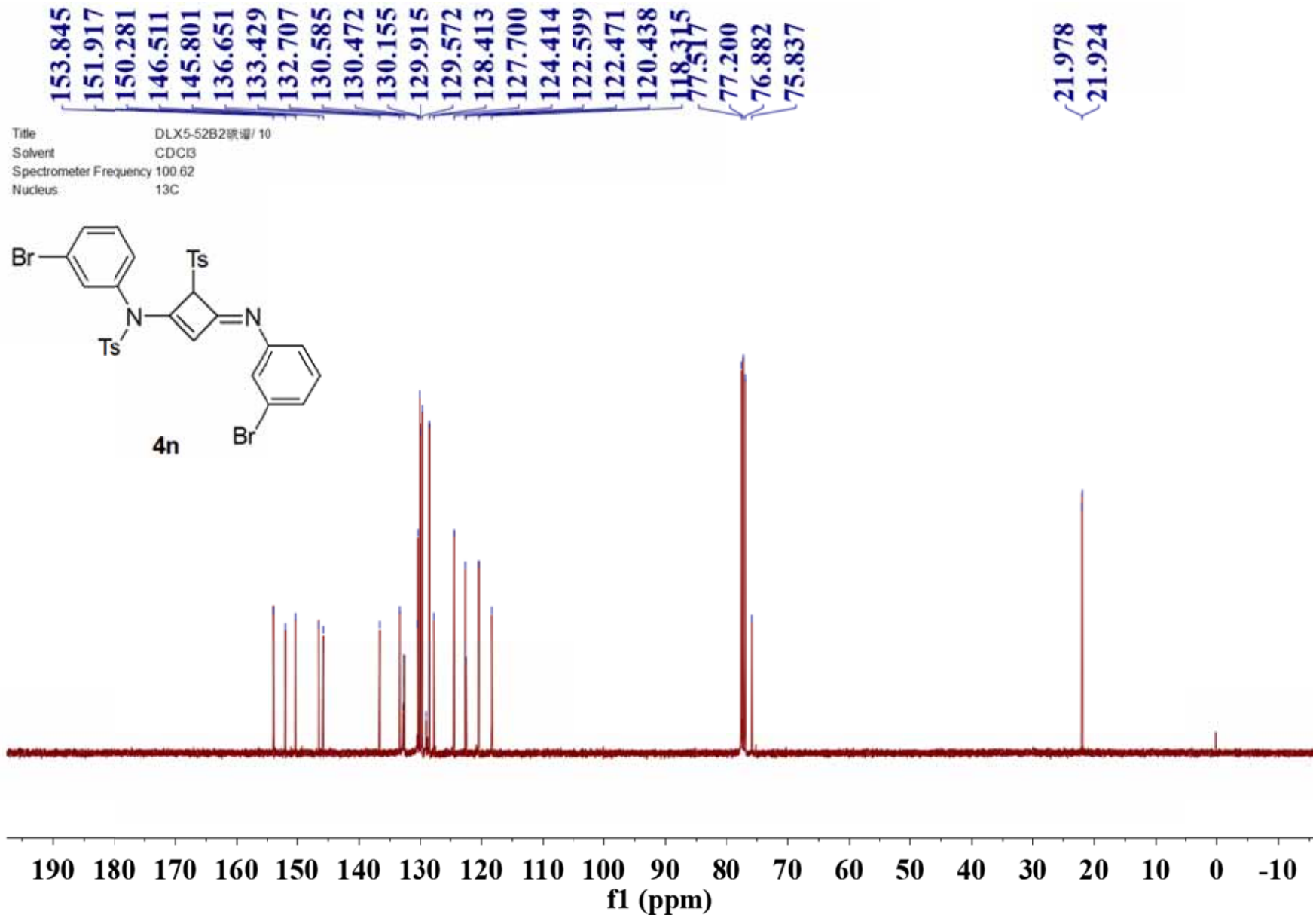

7.8010
7.7803
7.5074
7.4865
7.3268
7.3070
7.2690
7.2656
7.2643
7.2537
7.2443
7.2428
7.1763
7.1566
7.1373
6.9780
6.9365
6.9341
6.9320
6.9299
6.9277
6.9176
6.9158
6.9140
6.9122
6.9106
6.9086
6.5409
6.5360
6.5336
6.5174
6.5163
6.5143
5.9034
4.8968
2.4556
2.4268
2.3549
2.3078
-0.0000
Title 8DLX3-82B / 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ts
N
Ts
N
Me
4l
2.07
2.02
2.03
4.01
1.08
3.05
2.06
1.00
1.00
3.05
3.09
3.07
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)

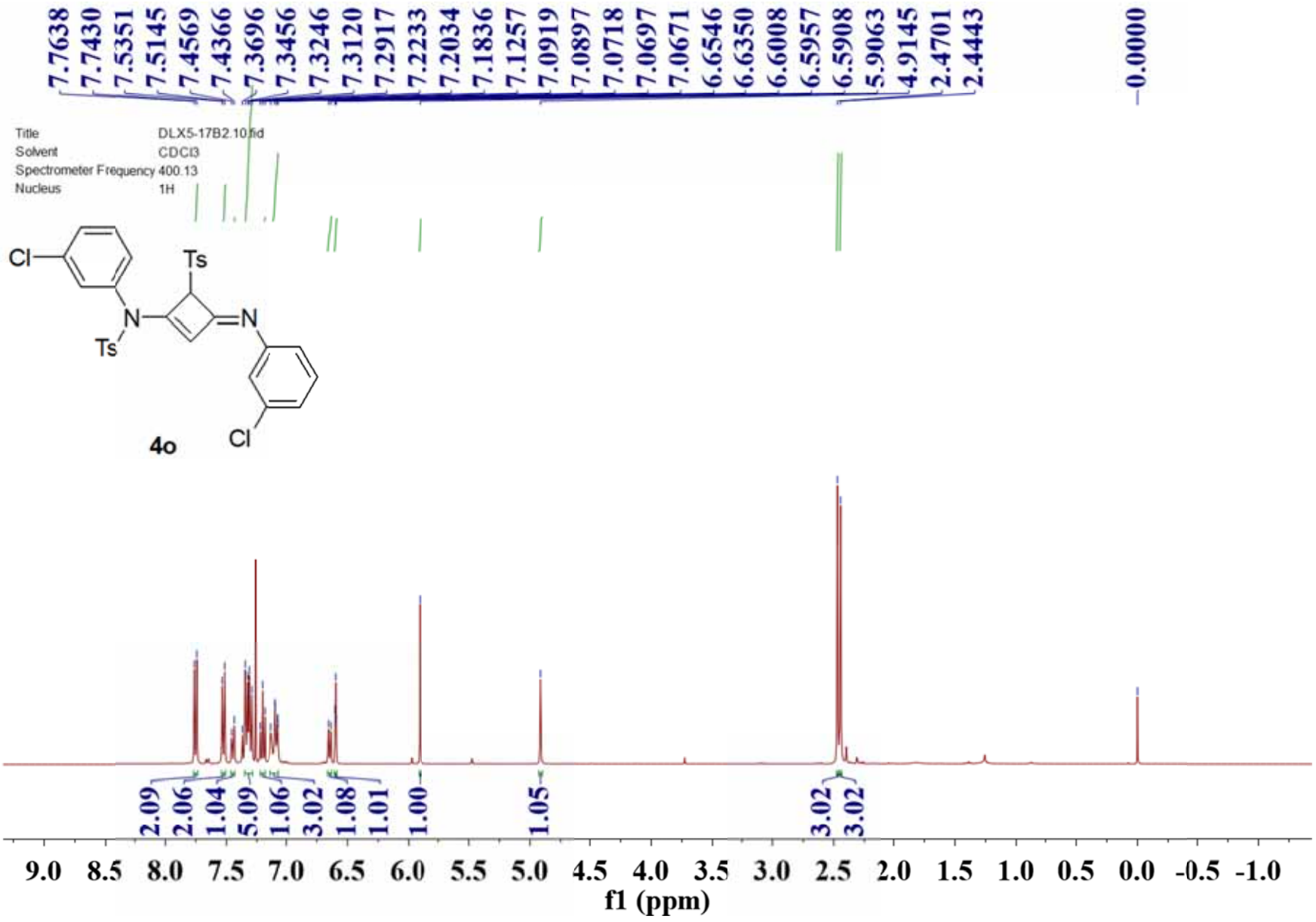

152.915
151.928
148.943
145.910
145.357
139.517
138.890
135.499
133.198
132.982
130.934
130.672
130.070
129.873
129.441
129.026
128.883
128.469
126.962
125.551
122.436
118.698
118.636
77.518
77.200
76.883
76.074
21.934
21.884
21.585
21.460
Title DLX3-82B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Ts
N
Ts
N
Me
4l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

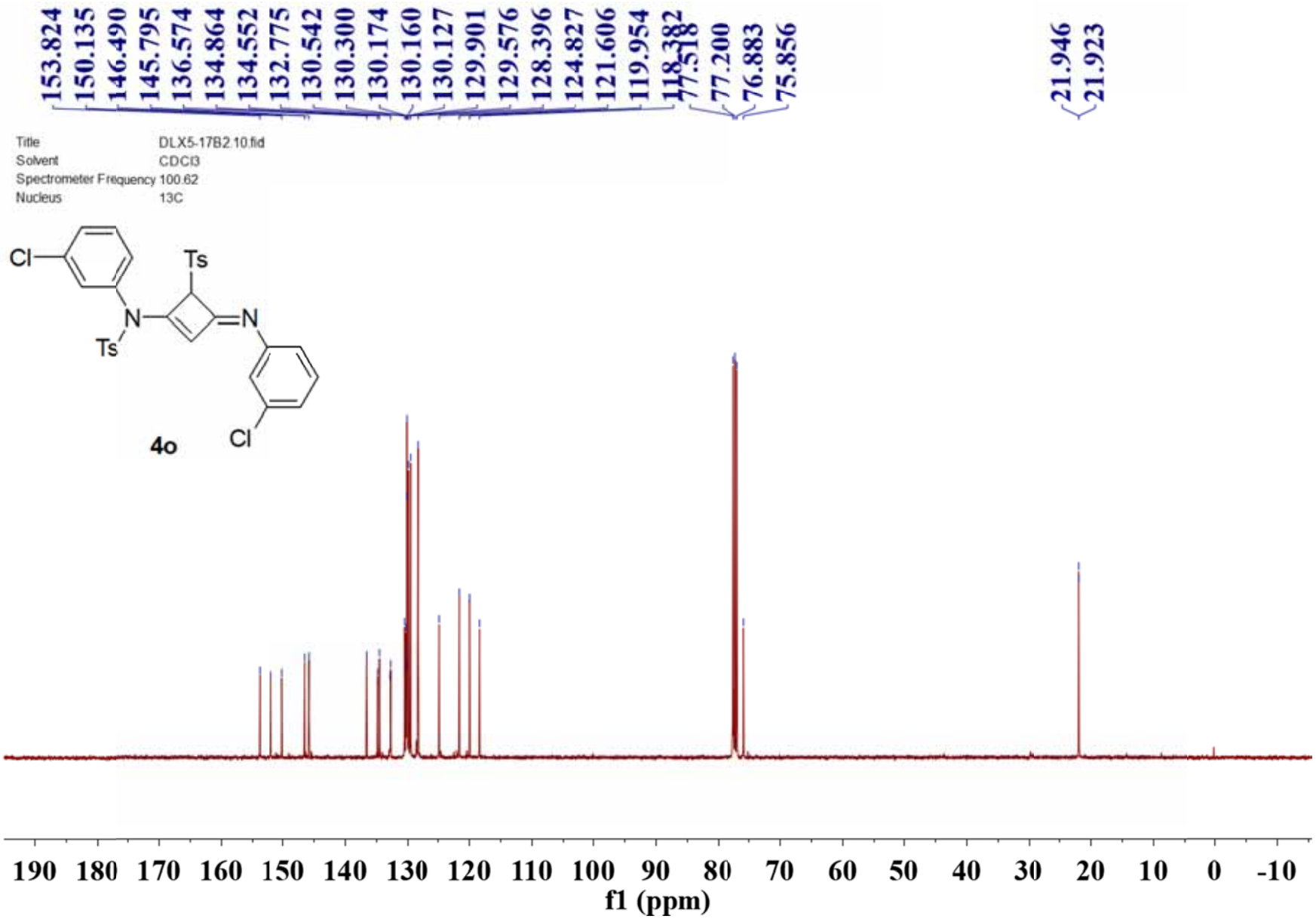

7.7990
7.7783
7.5377
7.5168
7.3280
7.3080
7.2886
7.2735
7.2683
7.2530
7.2485
7.1903
7.1694
7.1488
6.9978
6.9926
6.9778
6.9719
6.6765
6.6735
6.6708
6.6677
6.6559
6.6534
6.6495
6.6472
6.3097
6.3064
6.3039
6.2991
6.2933
6.2909
6.2884
5.9173
4.9391
3.7841
3.7648
2.4477
2.4242
0.0000
Title DLX5-20A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Ts
N
Ts
N
MeO
4m
2.05
2.05
2.07
3.08
1.08
1.08
1.00
2.01
2.07
1.00
1.00
3.02
3.02
3.05
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)

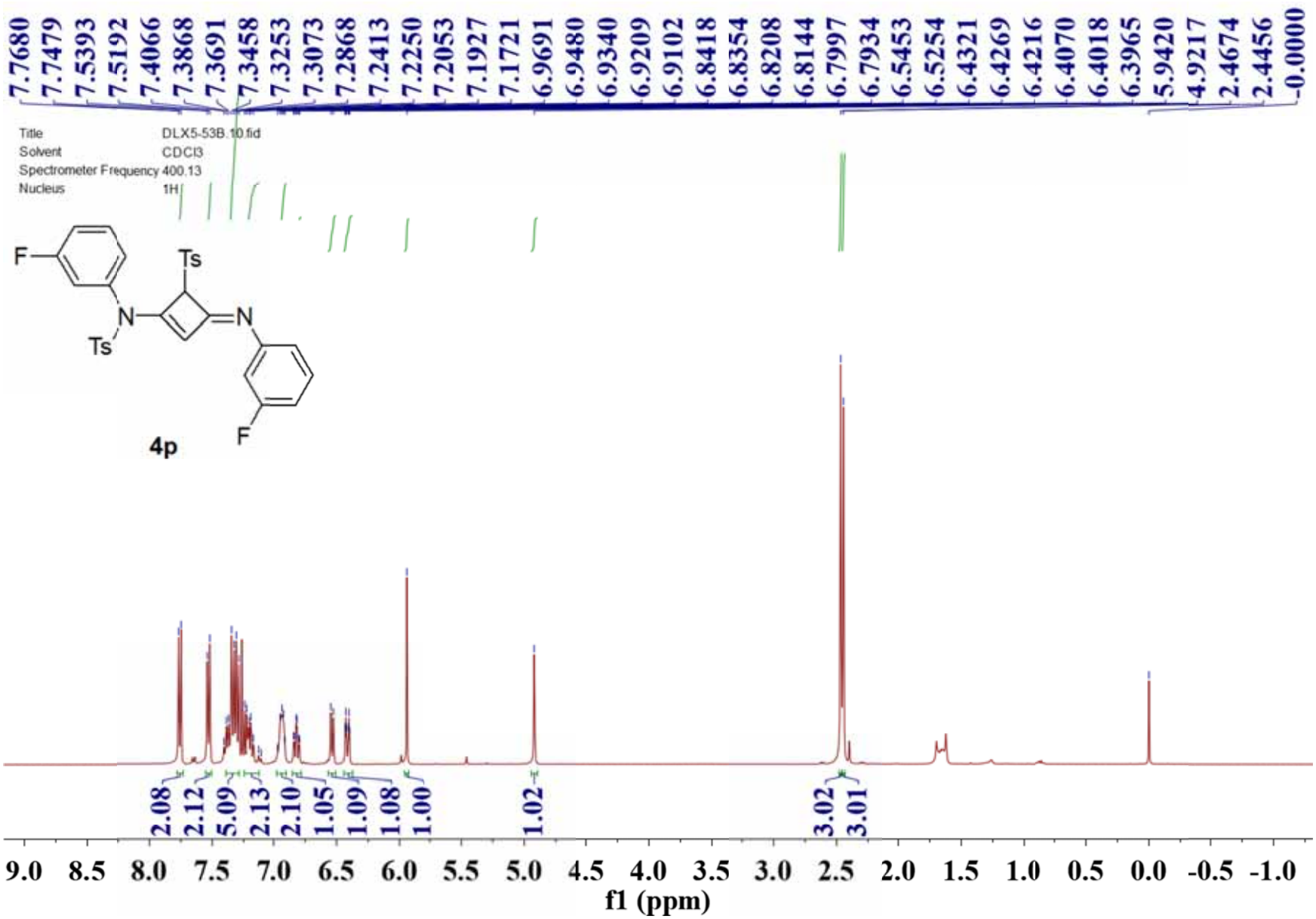

160.257
160.124
153.277
151.981
150.311
145.984
145.423
136.520
133.200
130.003
129.938
129.807
129.762
129.458
128.451
118.669
115.978
113.804
110.454
107.576
77.517
77.200
76.882
76.061
55.687
55.375
21.918
21.884
Title DLX5-20A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Ts
N
Ts
N
MeO
4m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

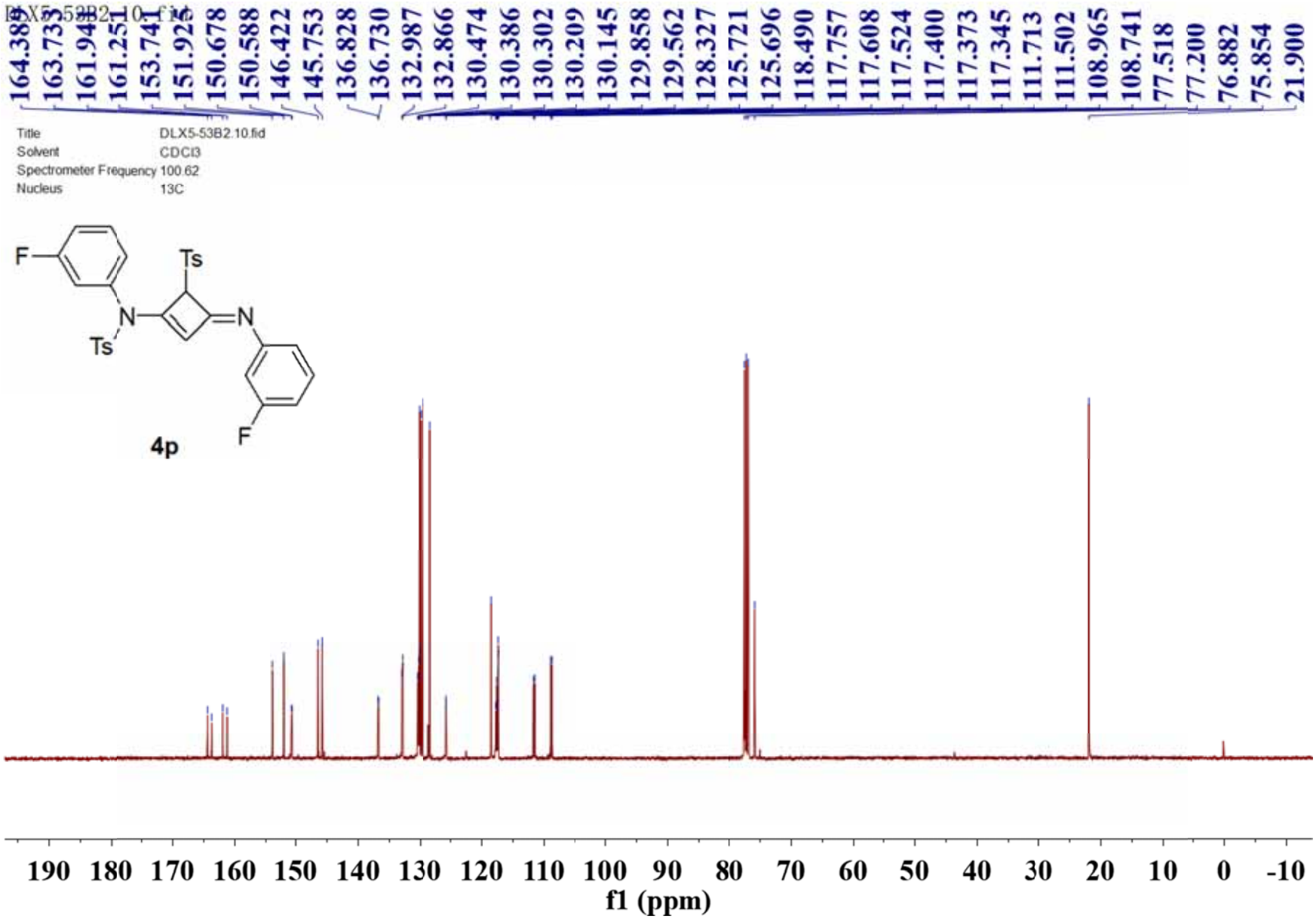

7.7621
7.7414
7.6058
7.5855
7.5305
7.5110
7.3464
7.3256
7.3149
7.2942
7.2736
7.2400
7.2198
7.1622
7.1426
7.1228
6.7292
6.7247
6.7202
6.7071
6.6875
5.8900
4.9080
2.4750
2.4456
-0.0000
Title DLX5-52B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Br
Ts
N
Ts
N
Br
4n
2.09
1.09
2.08
5.10
2.00
2.10
1.00
1.01
1.00
1.00
3.05
3.06
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)

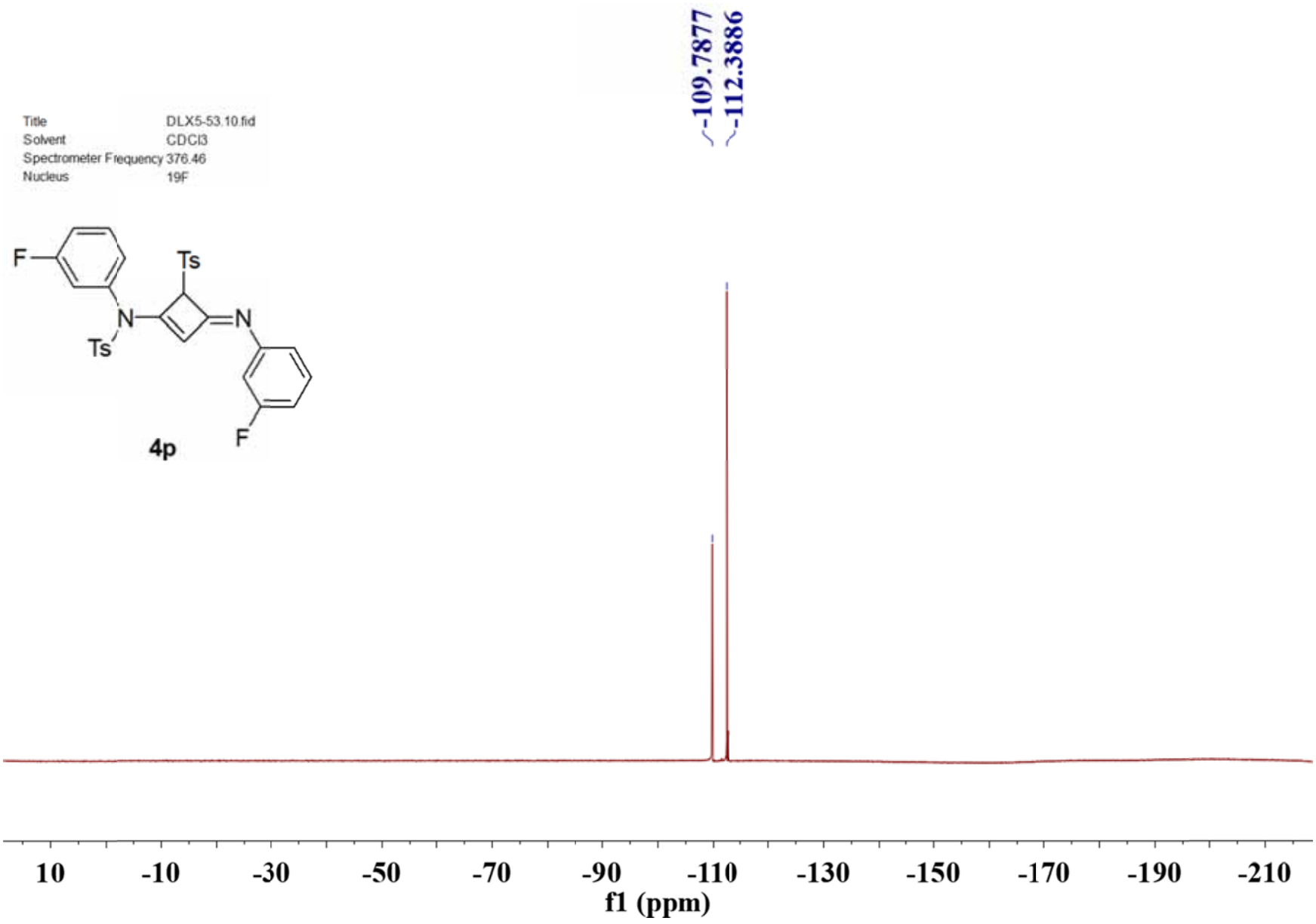

153.845
151.917
150.281
146.511
145.801
136.651
133.429
132.707
130.585
130.472
130.155
129.915
129.572
128.413
127.700
124.414
122.599
122.471
120.438
118.315
77.517
77.200
76.882
75.837
21.978
21.924
Title DLX5-52B2碳谱/ 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Br
Ts
N
Ts
N
Br
4n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

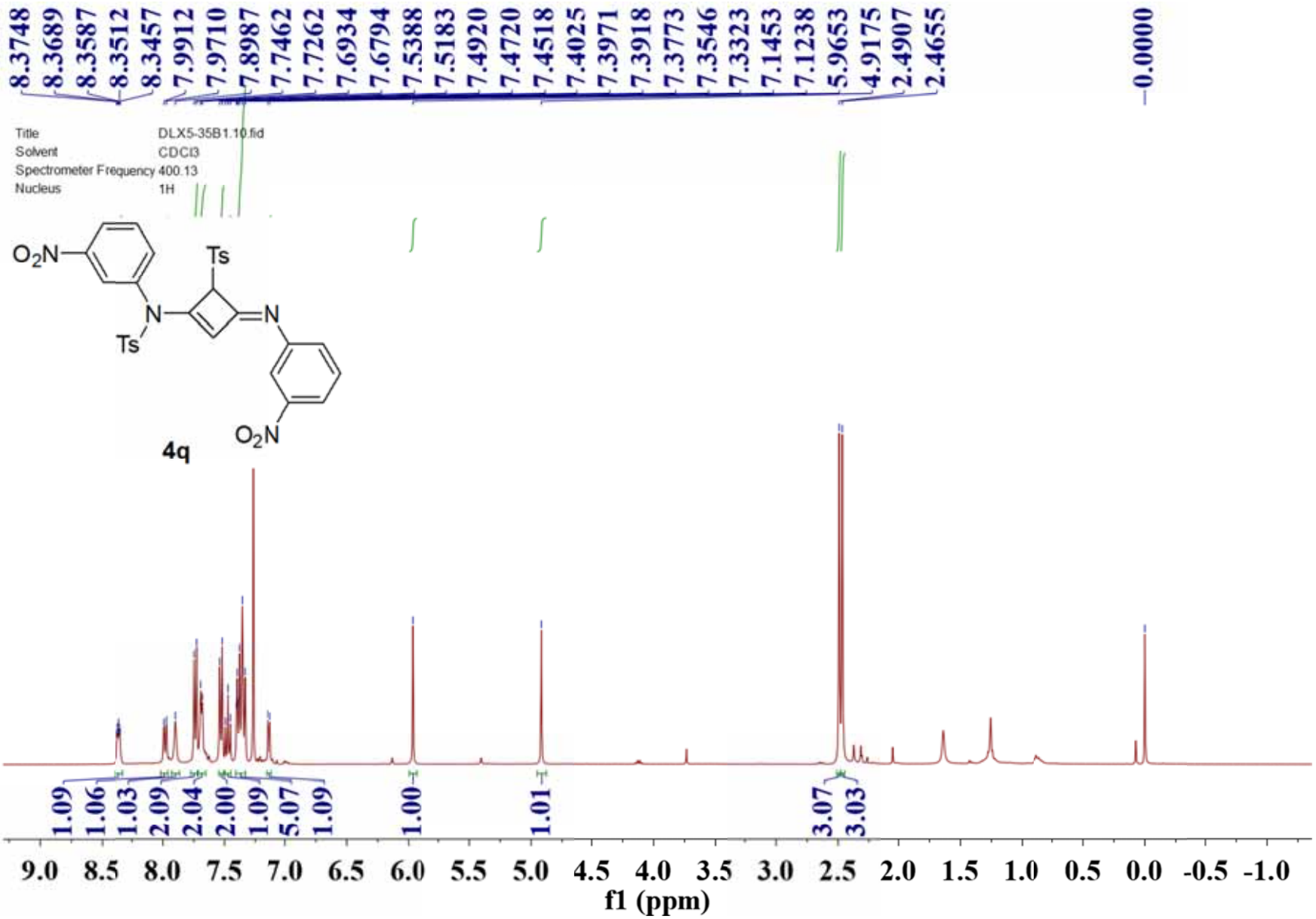

7.7638
7.7430
7.5351
7.5145
7.4569
7.4366
7.3696
7.3456
7.3246
7.3120
7.2917
7.2233
7.2034
7.1836
7.1257
7.0919
7.0897
7.0718
7.0697
7.0671
6.6546
6.6350
6.6008
6.5957
6.5908
5.9063
4.9145
2.4701
2.4443
0.0000
Title
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Ts
N
Ts
N
Cl
4o
2.09
2.06
1.04
5.09
1.06
3.02
1.08
1.01
1.00
1.05
3.02
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)

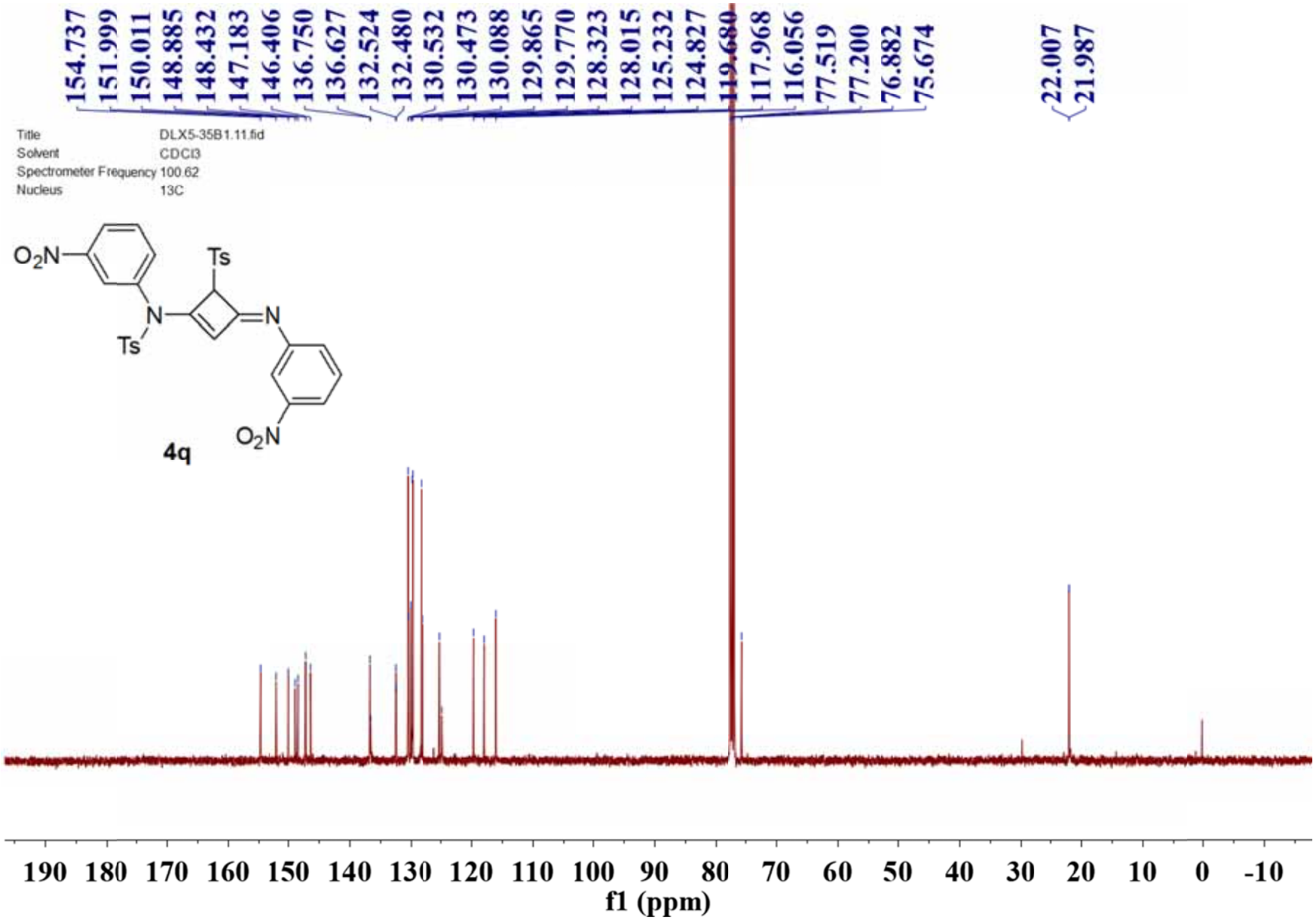

153.824
150.135
146.490
145.795
136.574
134.864
134.552
132.775
130.542
130.300
130.174
130.160
130.127
129.901
129.576
128.396
124.827
121.606
119.954
118.382
77.518
77.200
76.883
75.856
21.946
21.923
Title DLX5-17B2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Ts
N
Ts
N
Cl
4o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

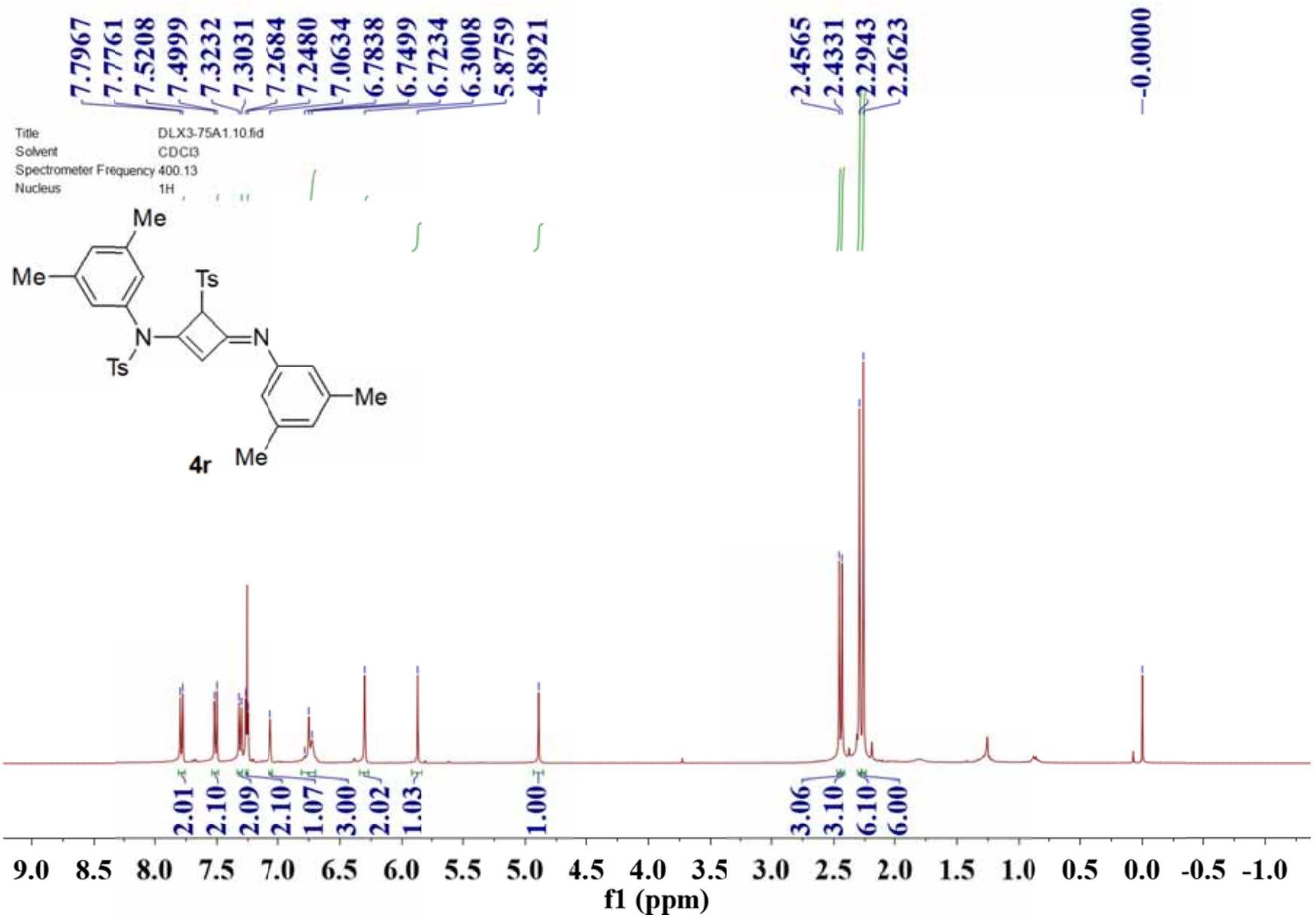

7.7680
7.7479
7.5393
7.5192
7.4066
7.3868
7.3691
7.3458
7.3253
7.3073
7.2868
7.2413
7.2250
7.2053
7.1927
7.1721
6.9691
6.9480
6.9340
6.9209
6.9102
6.8418
6.8354
6.8208
6.8144
6.7997
6.7934
6.5453
6.5254
6.4321
6.4269
6.4216
6.4070
6.4018
6.3965
5.9420
4.9217
2.4674
2.4456
-0.0000
Title DLX5-53B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
Ts
N
Ts
N
F
4p
2.08
2.12
5.09
2.13
2.10
1.05
1.09
1.08
1.00
1.02
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)

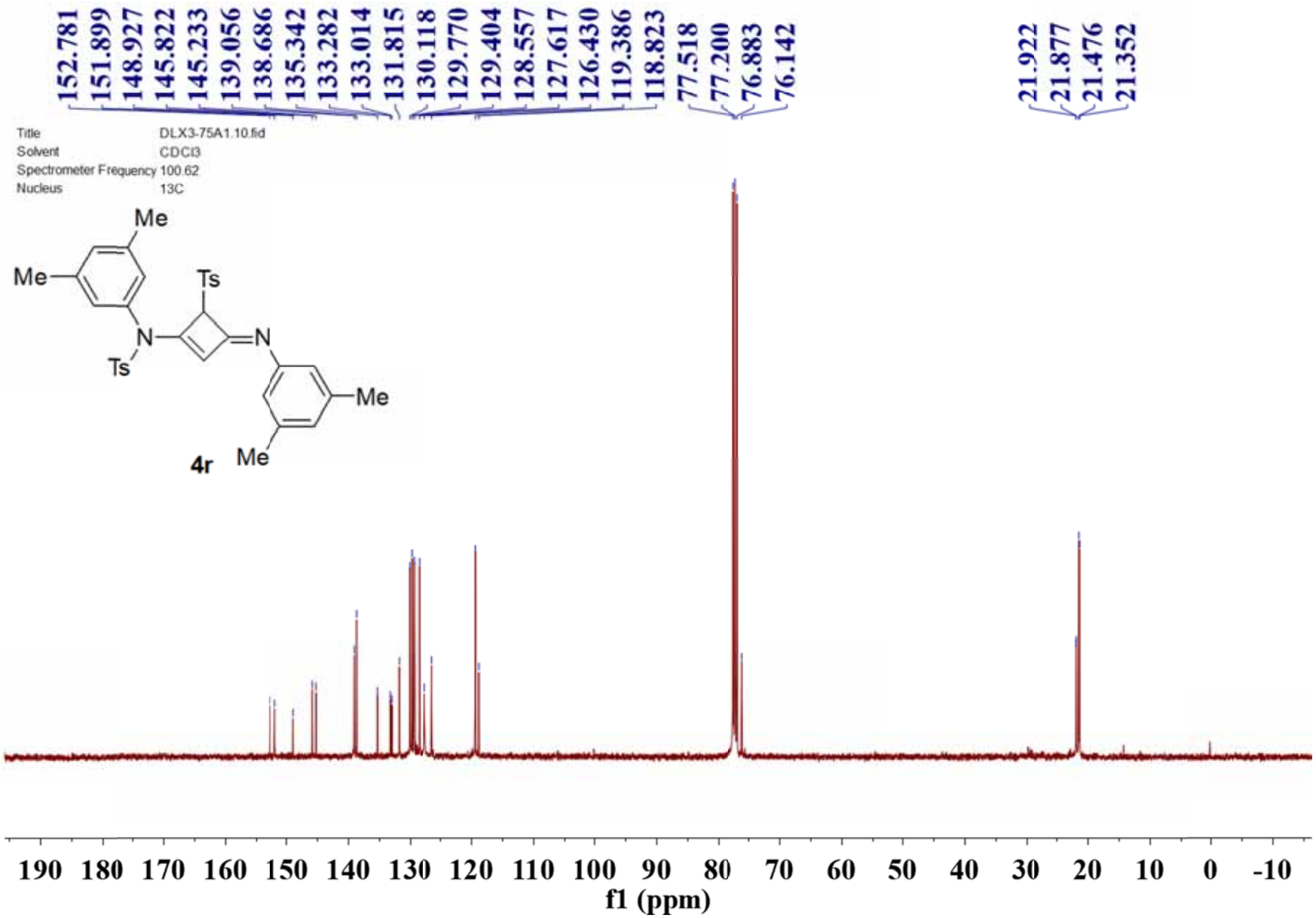

164.388
163.733
161.944
161.251
153.741
151.925
150.678
150.588
146.422
145.753
136.828
136.730
132.987
132.866
130.474
130.386
130.302
130.209
130.145
129.858
129.562
128.327
125.721
125.696
118.490
117.757
117.608
117.524
117.400
117.373
117.345
111.713
111.502
108.965
108.741
77.518
77.200
76.882
75.854
21.900
Title DLX5-53B2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
Ts
N
Ts
N
F
4p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

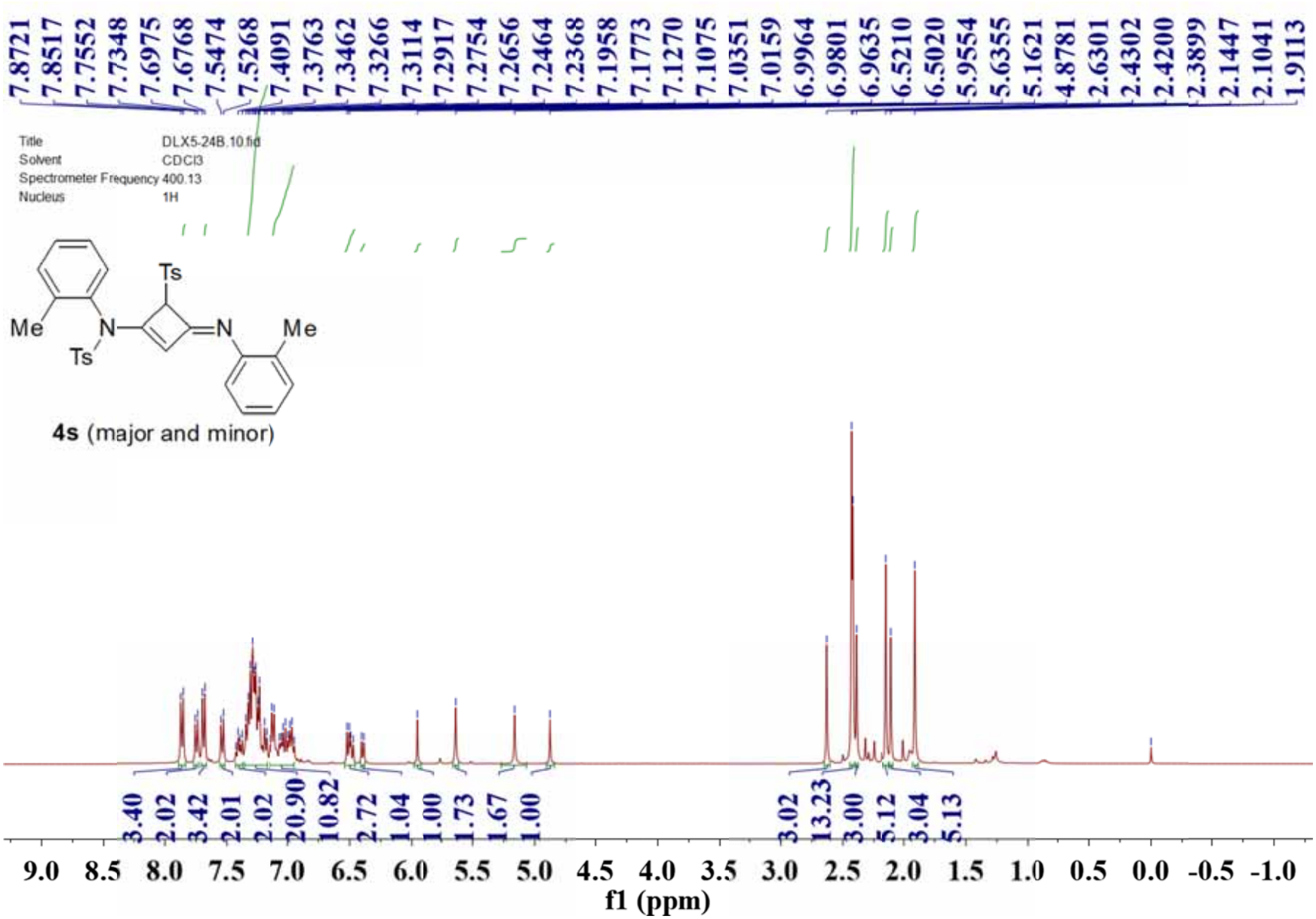

-109.7877
-112.3886
Title DLX5-53.10.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
F
Ts
N
Ts
N
F
4p
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

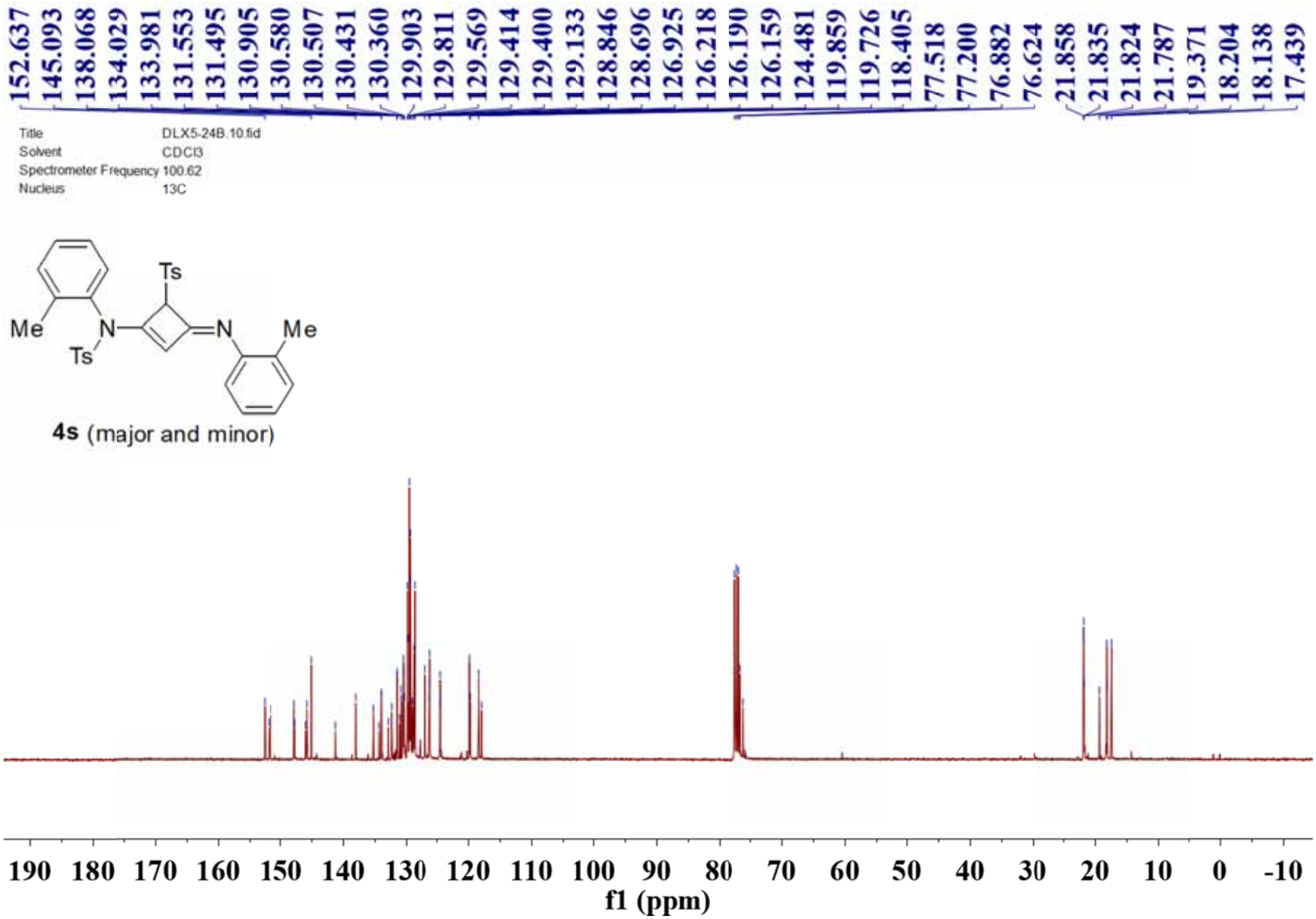

8.3748
8.3689
8.3587
8.3512
8.3457
7.9912
7.9710
7.8987
7.7462
7.7262
7.6934
7.6794
7.5388
7.5183
7.4920
7.4720
7.4518
7.4025
7.3971
7.3918
7.3773
7.3546
7.3323
7.1453
7.1238
5.9653
4.9175
2.4907
2.4655
0.0000
Title DLX5-35B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
O2N
Ts
N
N
Ts
O2N
4q
1.09
1.06
1.03
2.09
2.04
2.00
1.09
5.07
1.09
1.00
1.01
3.07
3.03
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)

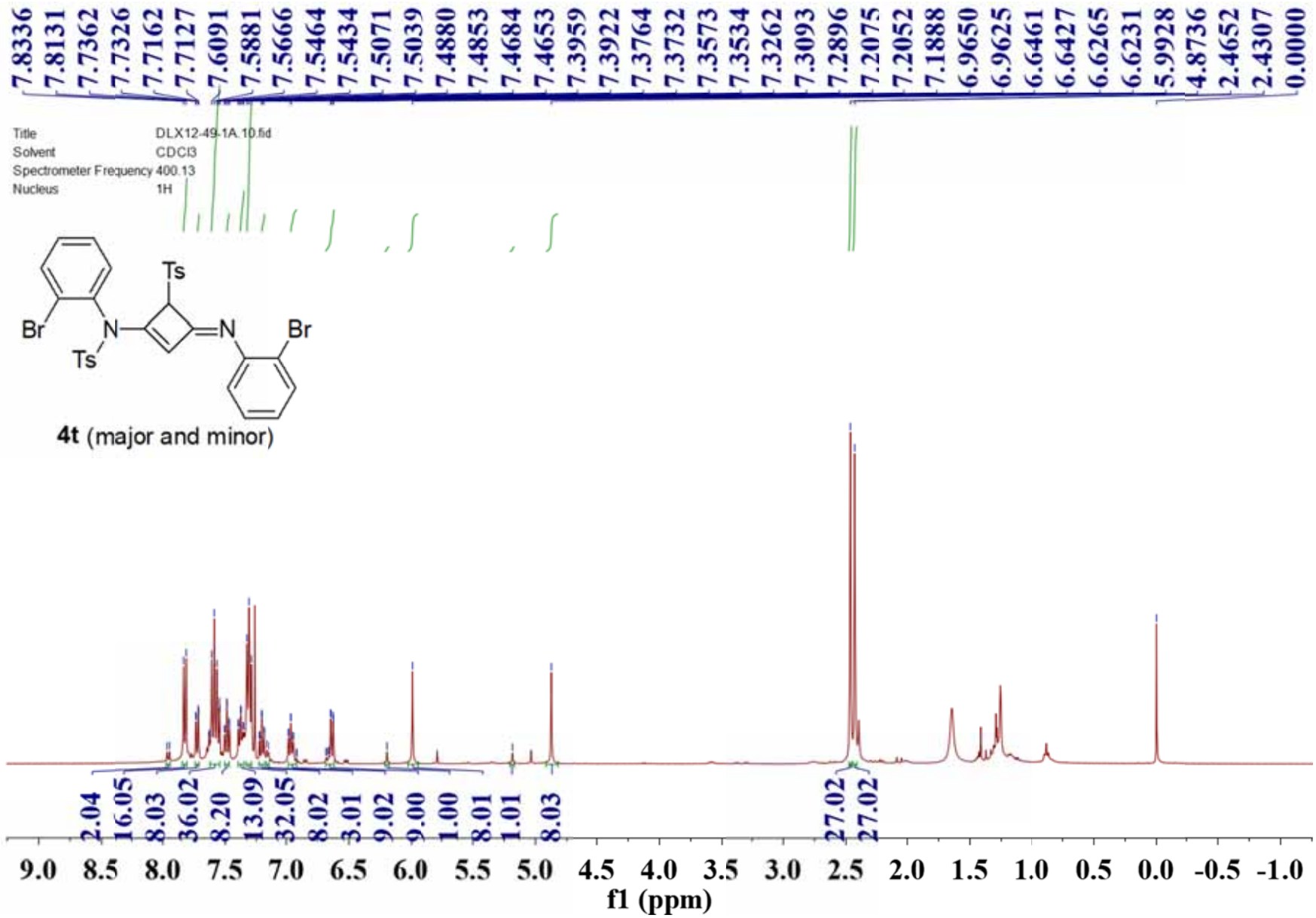

154.737
151.999
150.011
148.885
148.432
147.183
146.406
136.750
136.627
132.524
132.480
130.532
130.473
130.088
129.865
129.770
128.323
128.015
125.232
124.827
119.680
117.968
116.056
77.519
77.200
76.882
75.674
22.007
21.987
Title DLX5-35B1.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
O2N
Ts
N
Ts
N
O2N
4q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

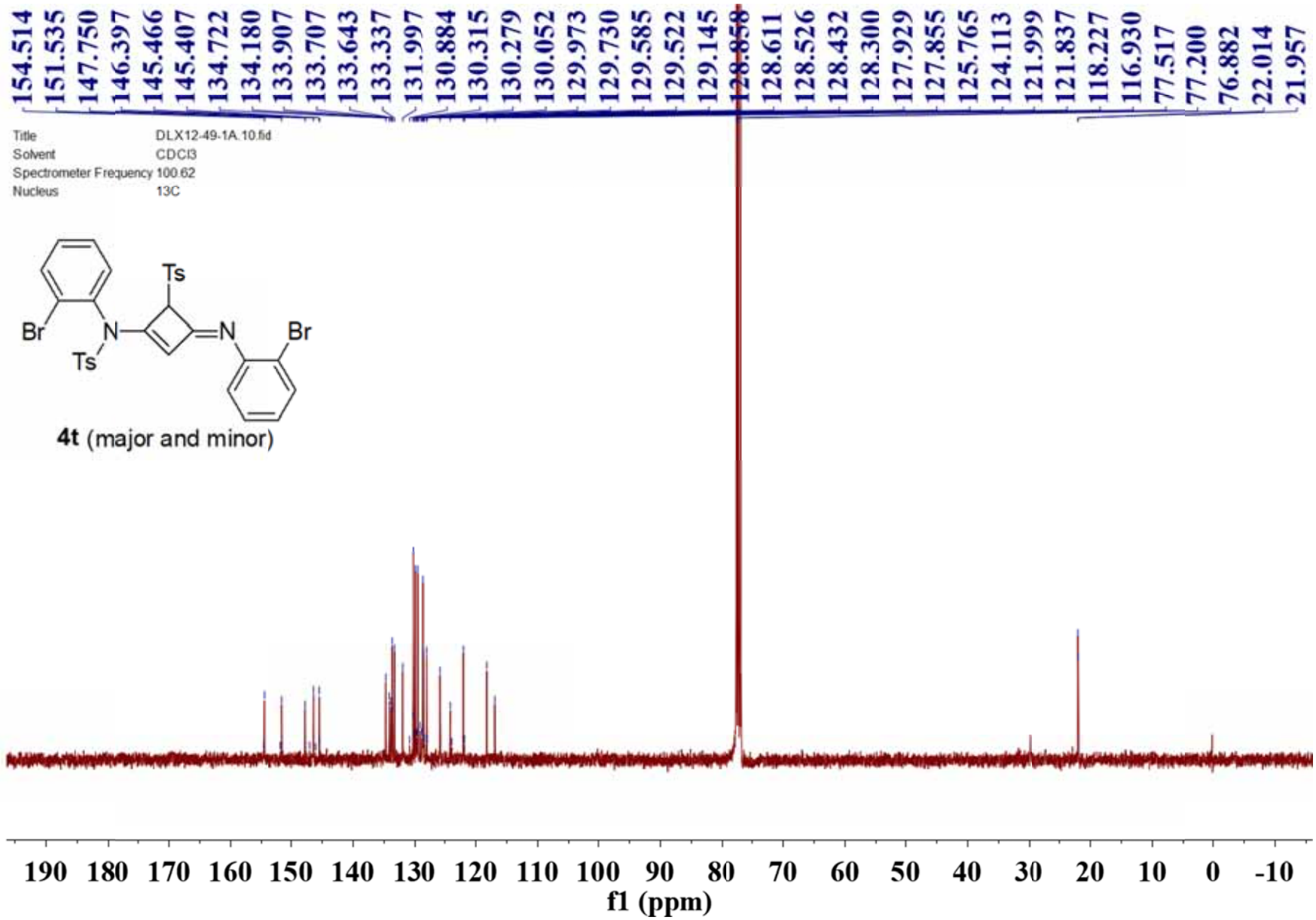

7.7967
7.7761
7.5208
7.4999
7.3232
7.3031
7.2684
7.2480
7.0634
6.7838
6.7499
6.7234
6.3008
5.8759
4.8921
2.4565
2.4331
2.2943
2.2623
0.0000
Title DLX3-75A1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
Ts
N
Ts
N
Me
Me
4r
2.01
2.10
2.09
2.10
1.07
3.00
2.02
1.03
1.00
3.06
3.10
6.10
6.00
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)


152.781
151.899
148.927
145.822
145.233
139.056
138.686
135.342
133.282
133.014
131.815
130.118
129.770
129.404
128.557
127.617
126.430
119.386
118.823
77.518
77.200
76.883
76.142
21.922
21.877
21.476
21.352
Title DLX3-75A1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
Ts
N
Ts
N
Me
Me
4r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

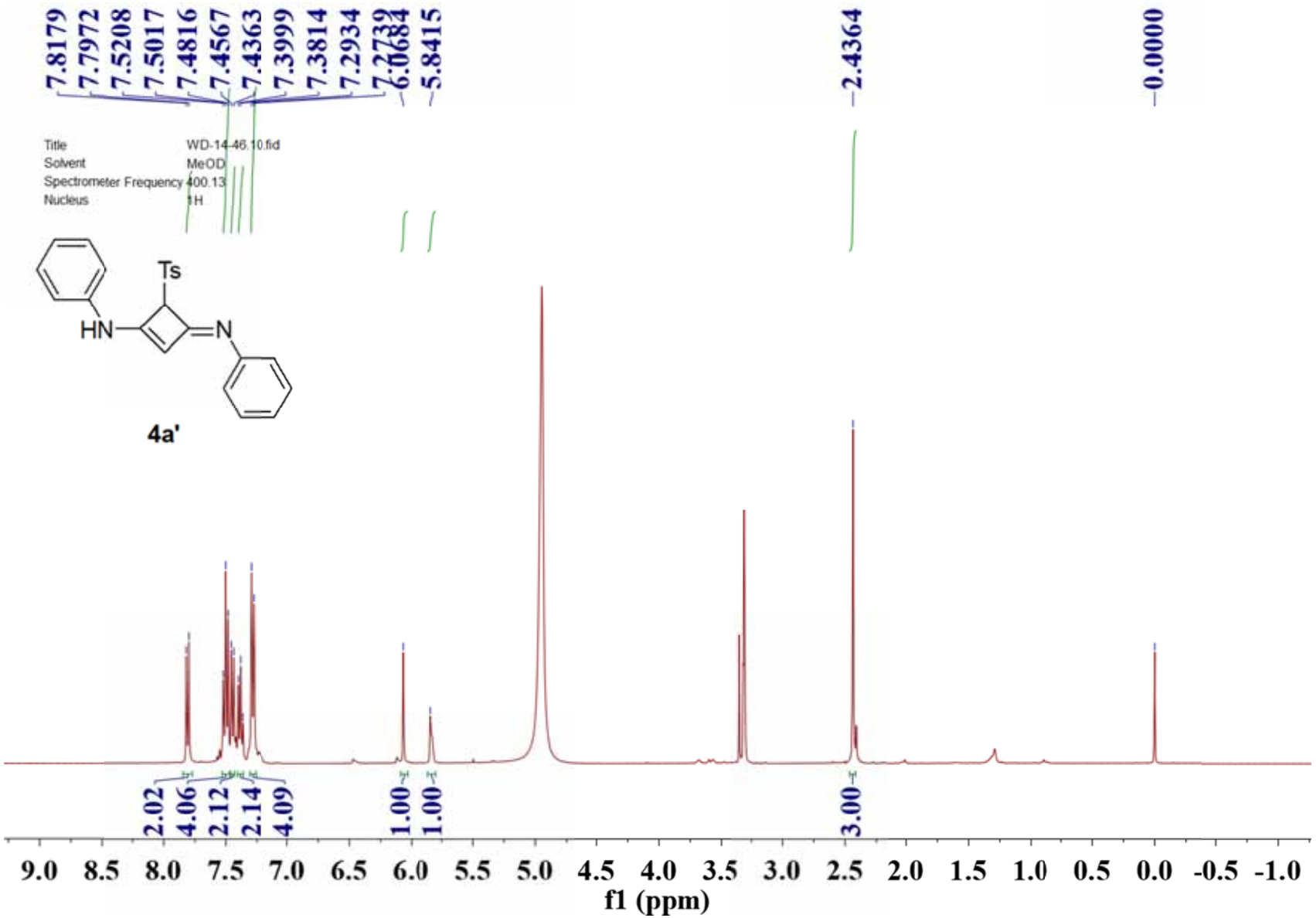

7.8721
7.8517
7.7552
7.7348
7.6975
7.6768
7.5474
7.5268
7.4091
7.3763
7.3462
7.3266
7.3114
7.2917
7.2754
7.2656
7.2464
7.2368
7.1958
7.1773
7.1270
7.1075
7.0351
7.0159
6.9964
6.9801
6.9635
6.5210
6.5020
5.9554
5.6355
5.1621
4.8781
2.6301
2.4302
2.4200
2.3899
2.1447
2.1041
1.9113
Title DLX5-24B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Ts
N
Me
4s (major and minor)
3.40
2.02
3.42
2.01
2.02
20.90
10.82
2.72
1.04
1.00
1.73
1.67
1.00
3.02
13.23
3.00
5.12
3.04
5.13
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)

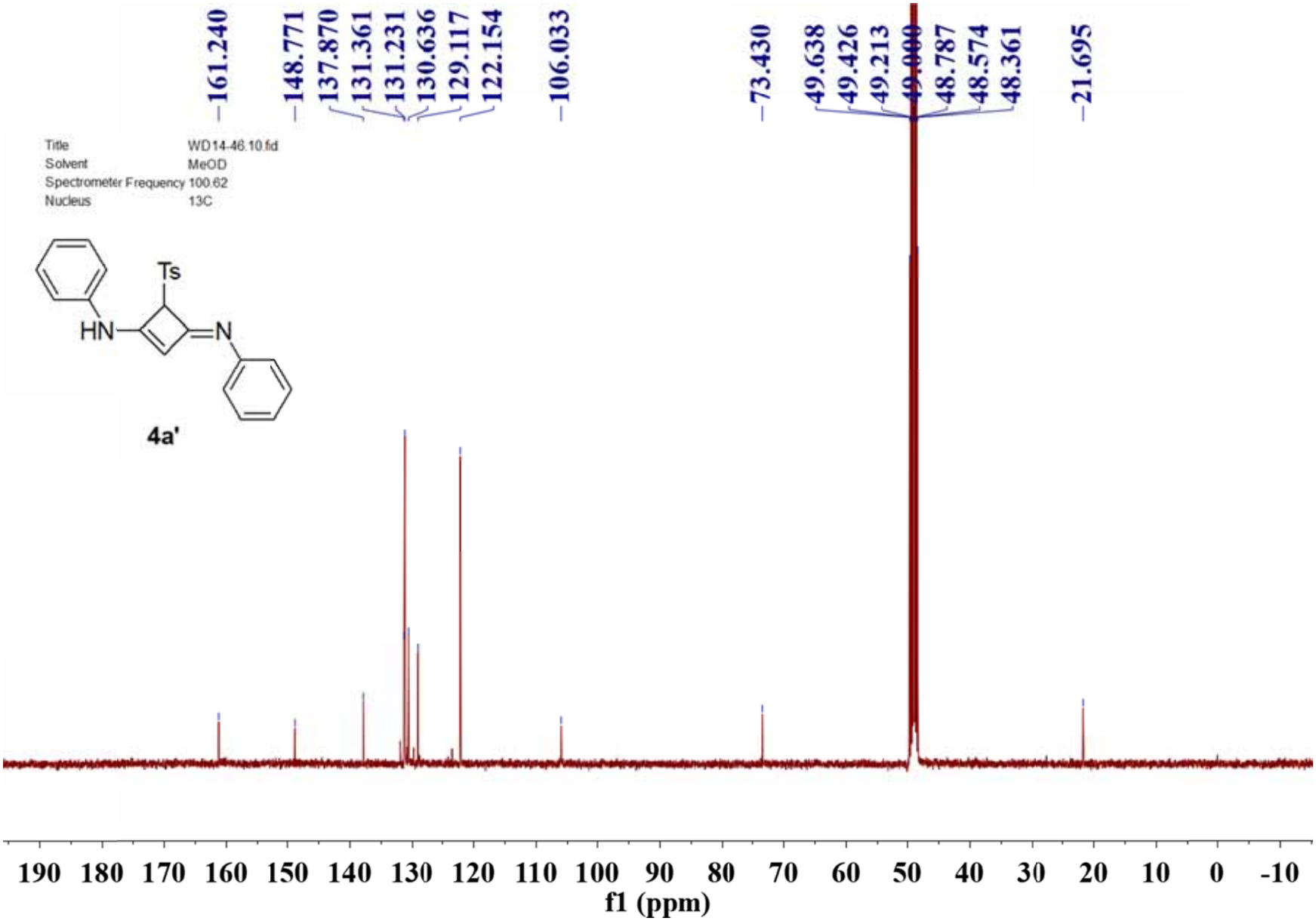

152.637
145.093
138.068
134.029
133.981
131.553
131.495
130.905
130.580
130.507
130.431
130.360
129.903
129.811
129.569
129.414
129.400
129.133
128.846
128.696
126.925
126.218
126.190
126.159
124.481
119.859
119.726
118.405
77.518
77.200
76.882
76.624
21.858
21.835
21.824
21.787
19.371
18.204
18.138
17.439
Title DLX5-24B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Ts
N
Me
4s (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

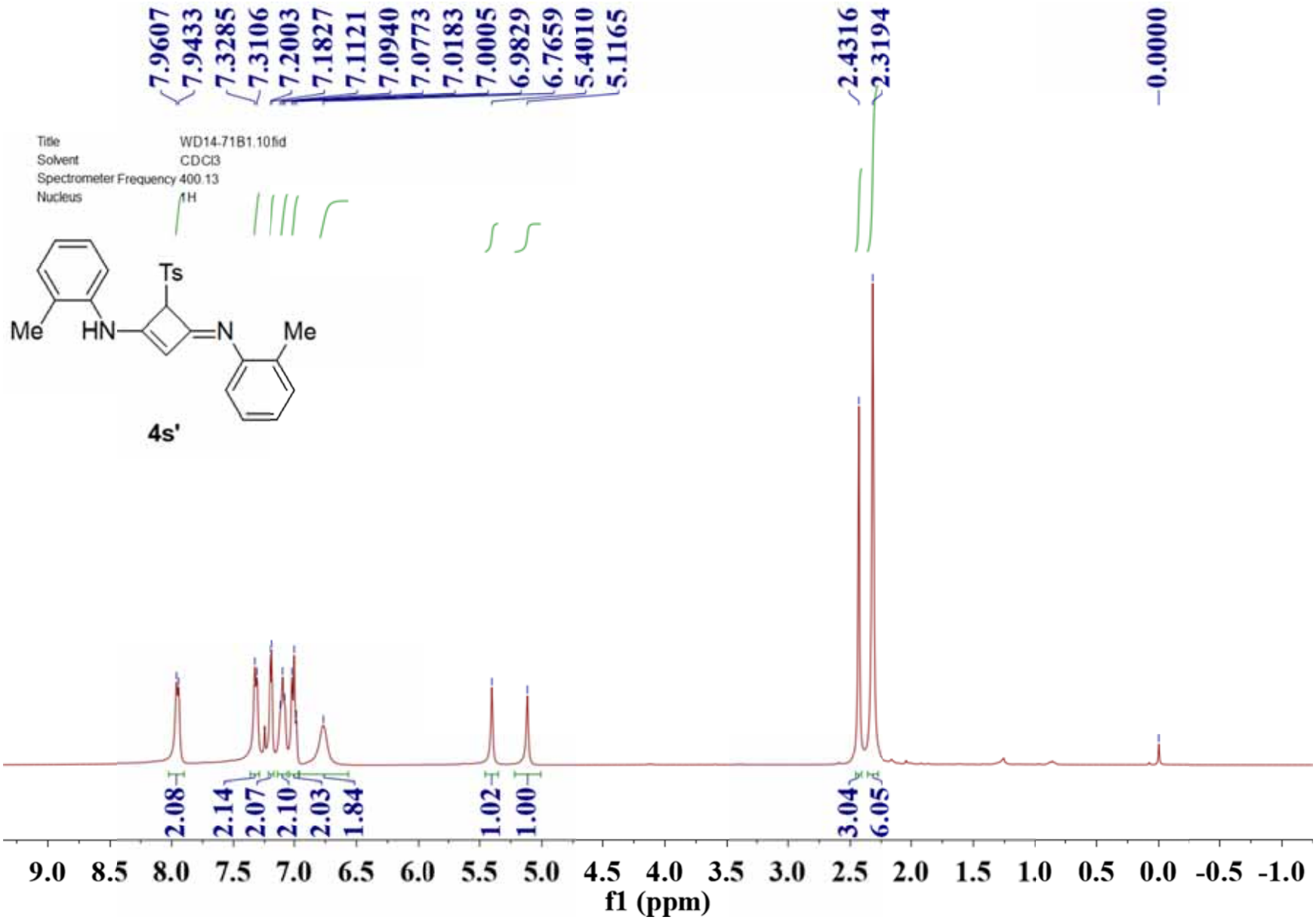

7.8336
7.8131
7.7362
7.7326
7.7162
7.7127
7.6091
7.5881
7.5666
7.5464
7.5434
7.5071
7.5039
7.4880
7.4853
7.4684
7.4653
7.3959
7.3922
7.3764
7.3732
7.3573
7.3534
7.3262
7.3093
7.2896
7.2075
7.2052
7.1888
6.9650
6.9625
6.6461
6.6427
6.6265
6.6231
5.9928
4.8736
2.4652
2.4307
0.0000
Title DLX12-49-1A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
Br
N
N
Br
Ts
4t (major and minor)
2.04
16.05
8.03
36.02
8.20
13.09
32.05
8.02
3.01
9.02
9.00
1.00
8.01
1.01
8.03
27.02
27.02
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)

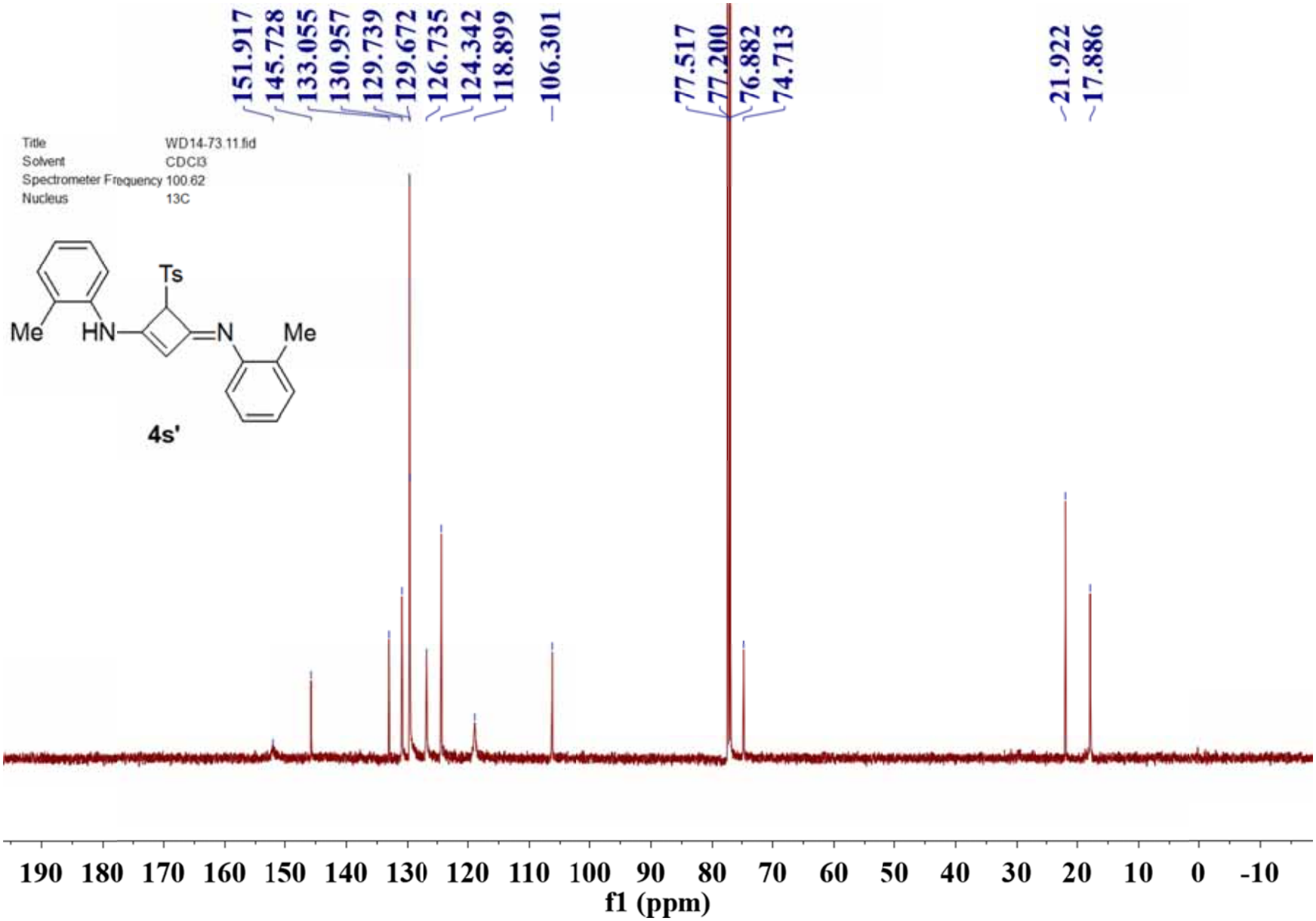

154.514
151.535
147.750
146.397
145.466
145.407
134.722
134.180
133.907
133.707
133.643
133.337
131.997
130.884
130.315
130.279
130.052
129.973
129.730
129.585
129.522
129.145
128.858
128.611
128.526
128.432
128.300
127.929
127.855
125.765
124.113
121.999
121.837
118.227
116.930
77.517
77.200
76.882
22.014
21.957
Title DLX12-49-1A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
Br
N
N
Br
Ts
4t (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

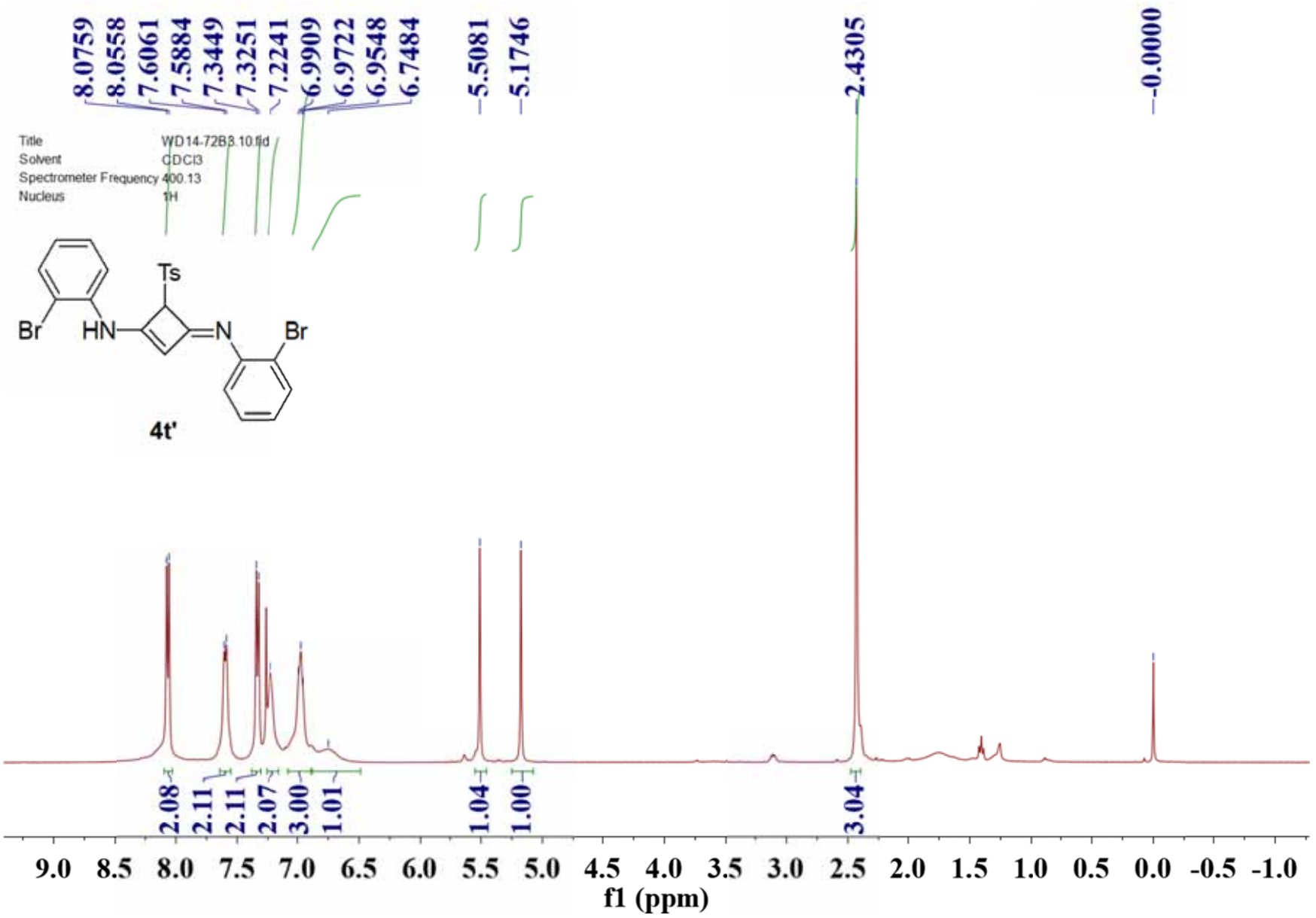
^{1}H NMR and ^{13}C NMR Spectra of Aminocyclobutenes 4a', 4s' and 4t'.

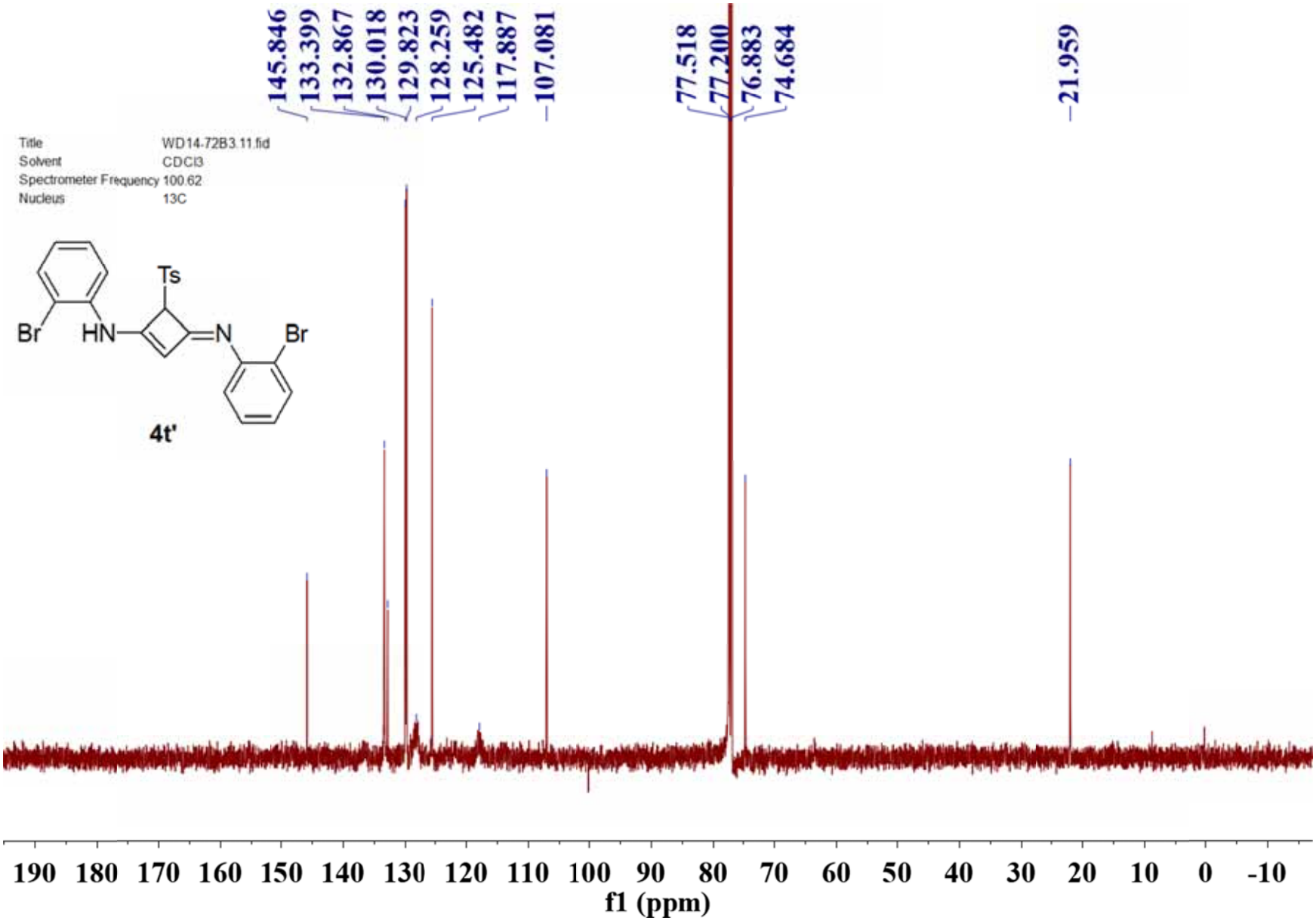



161.240
148.771
137.870
131.361
131.231
130.636
129.117
122.154
106.033
73.430
49.638
49.426
49.213
49.000
48.787
48.574
48.361
21.695
Title WD14-46.10.fid
Solvent MeOD
Spectrometer Frequency 100.62
Nucleus 13C
Ts
HN
N
4a'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

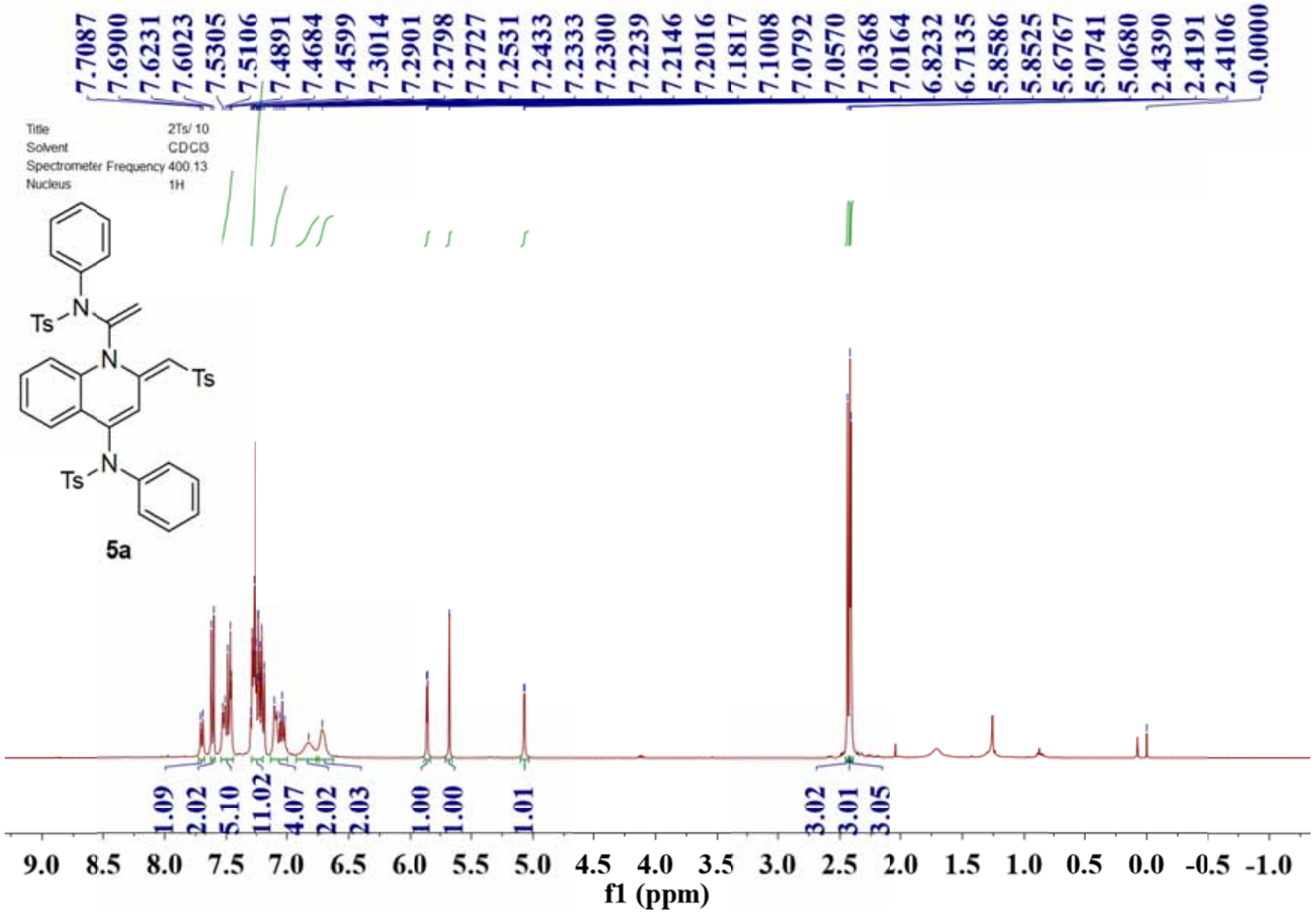

7.9607
7.9433
7.3285
7.3106
7.2003
7.1827
7.1121
7.0940
7.0773
7.0183
7.0005
6.9829
6.7659
5.4010
5.1165
2.4316
2.3194
0.0000
Title WD14-71B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
Me
HN
N
Me
4s'
2.08
2.14
2.07
2.10
2.03
1.84
1.02
1.00
3.04
6.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 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)

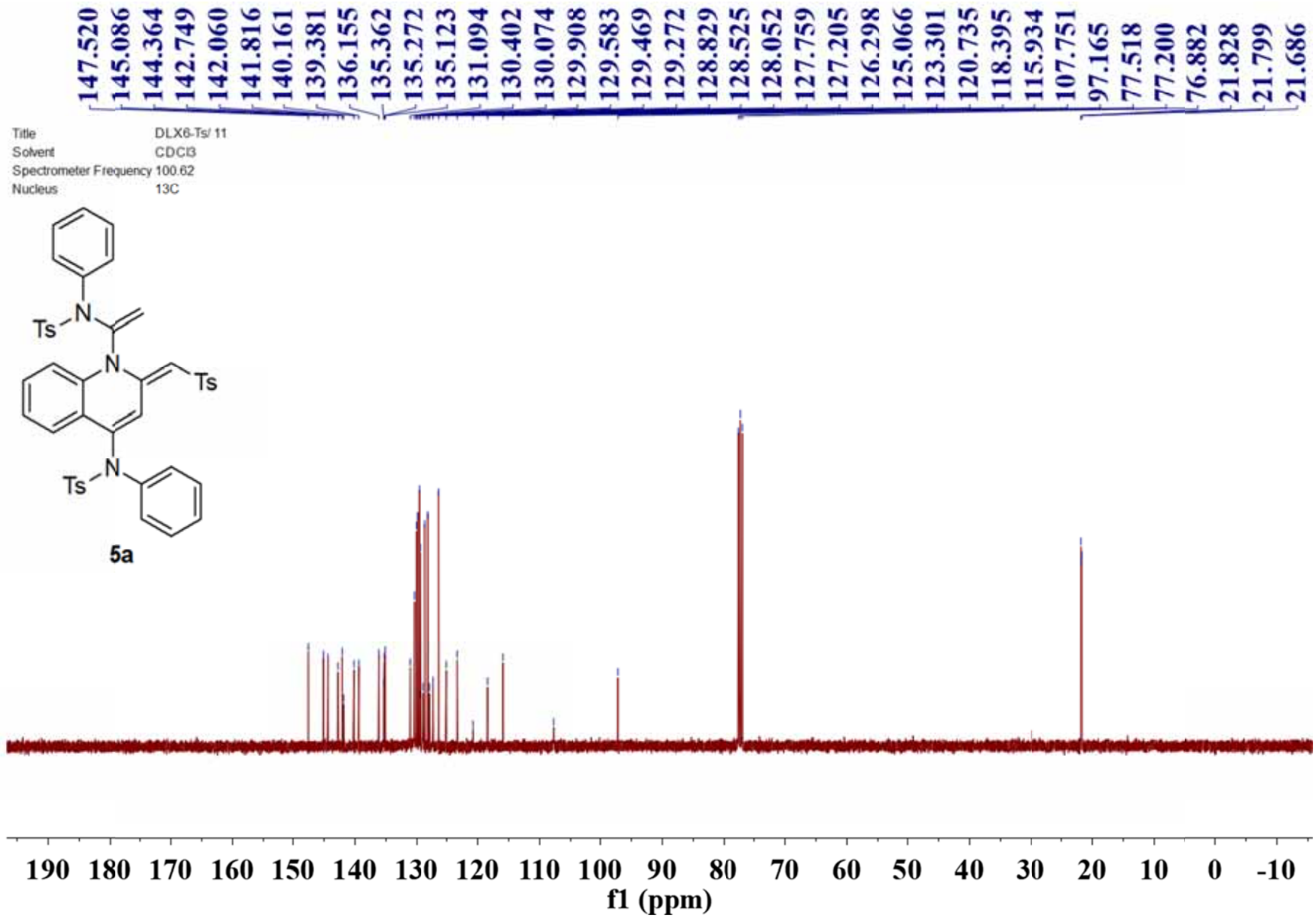

151.917
145.728
133.055
130.957
129.739
129.672
126.735
124.342
118.899
106.301
77.517
77.200
76.882
74.713
21.922
17.886
Title WD14-73.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
Me
HN
N
Me
4s'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

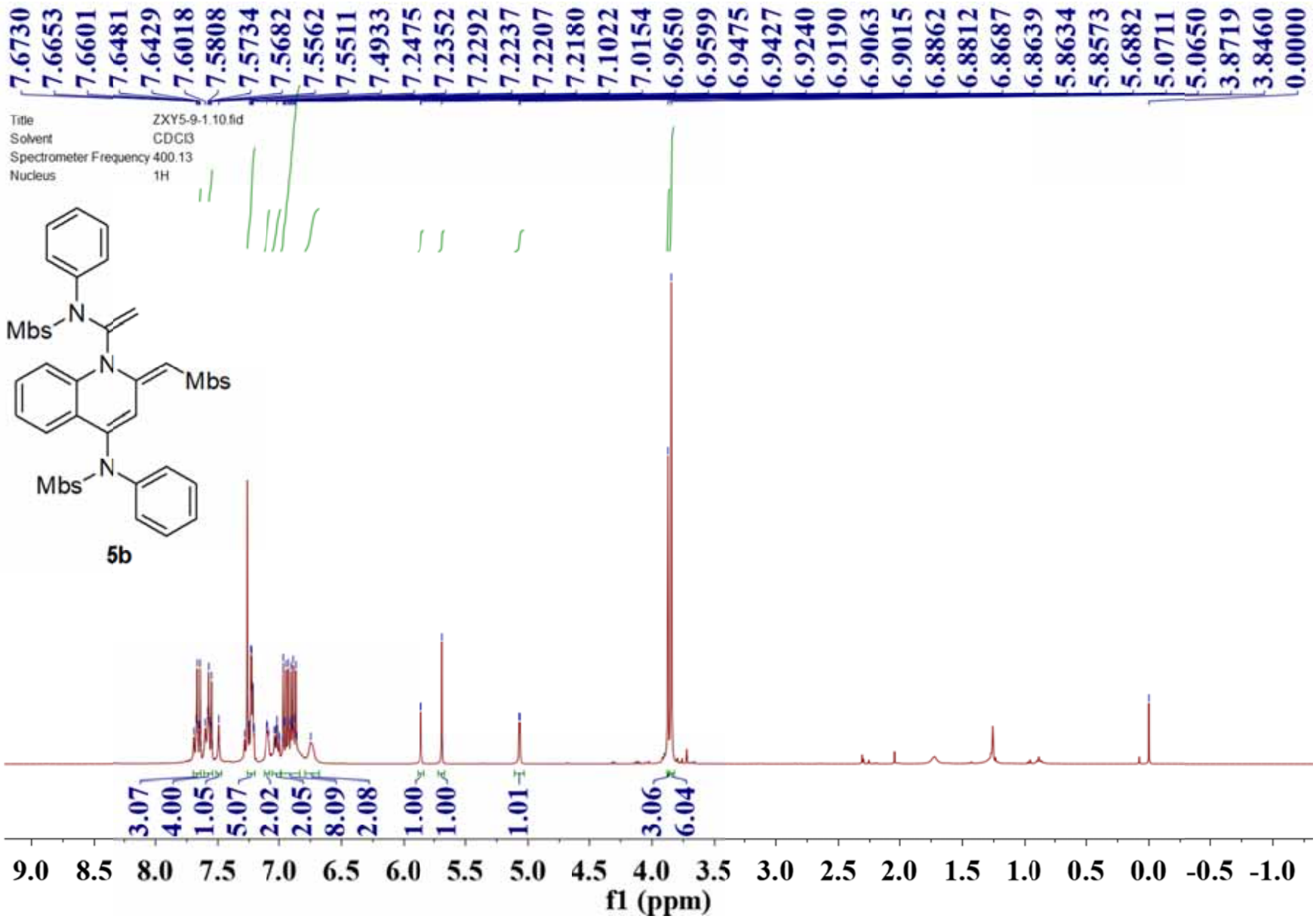

8.0759
8.0558
7.6061
7.5884
7.3449
7.3251
7.2241
6.9909
6.9722
6.9548
6.7484
5.5081
5.1746
2.4305
0.0000
Title WD14-72B3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ts
Br
HN
N
Br
4t'
2.08
2.11
2.11
2.07
3.00
1.01
1.04
1.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

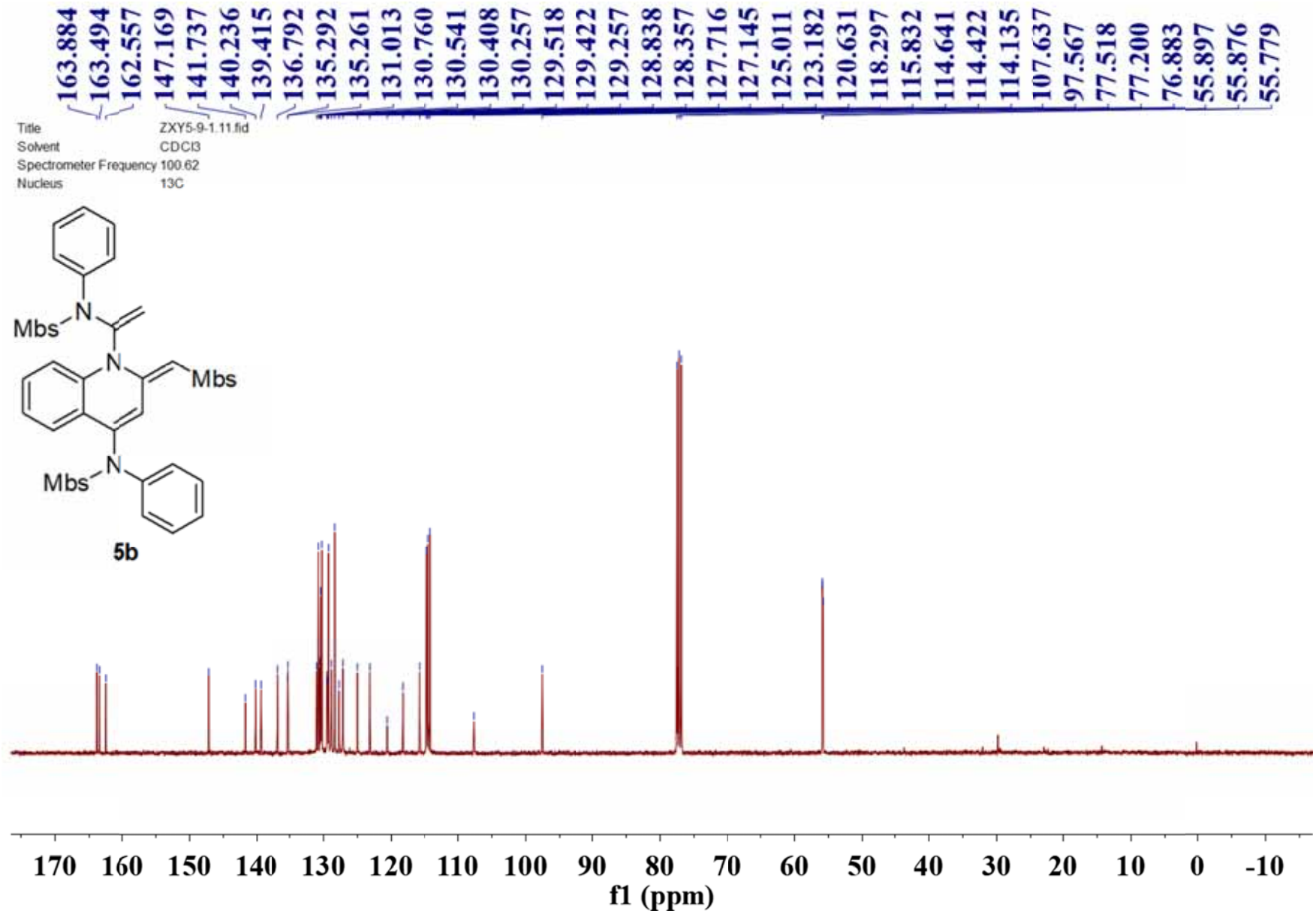

145.846
133.399
132.867
130.018
129.823
128.259
125.482
117.887
107.081
77.518
77.200
76.883
74.684
21.959
Title WD14-72B3.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
Br
HN
N
Br
4t'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

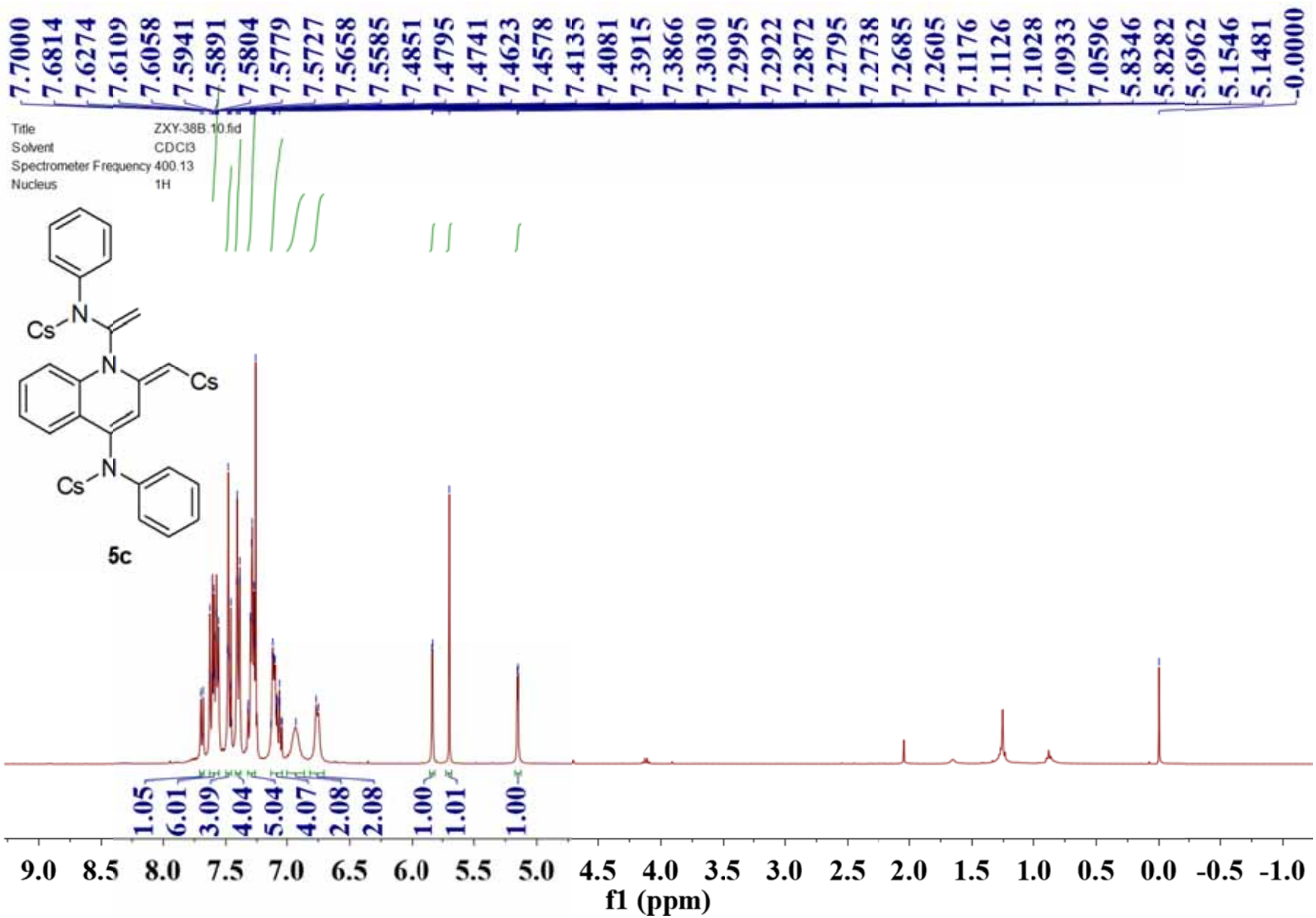
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of 4-Aminoquinolines 5.

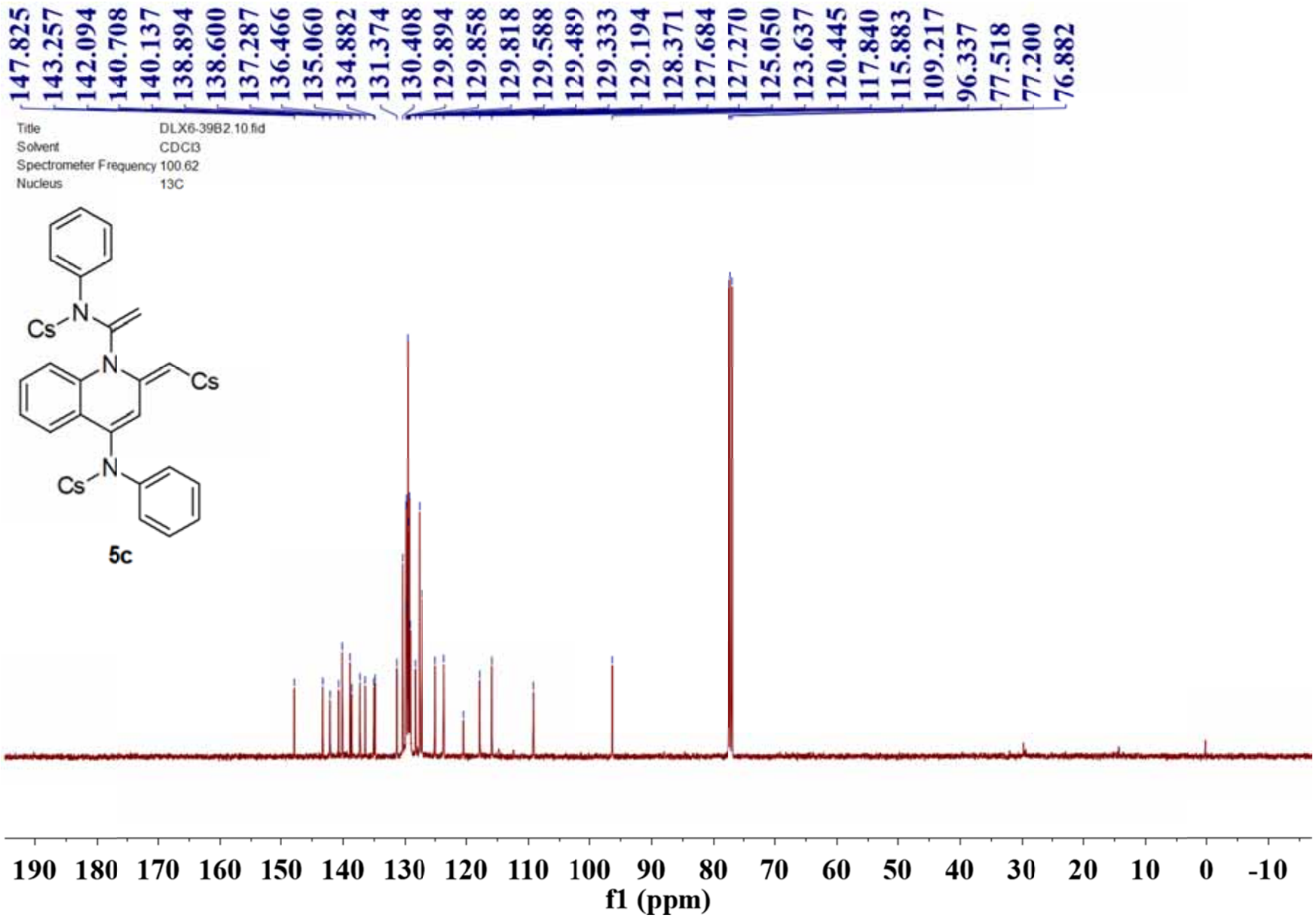


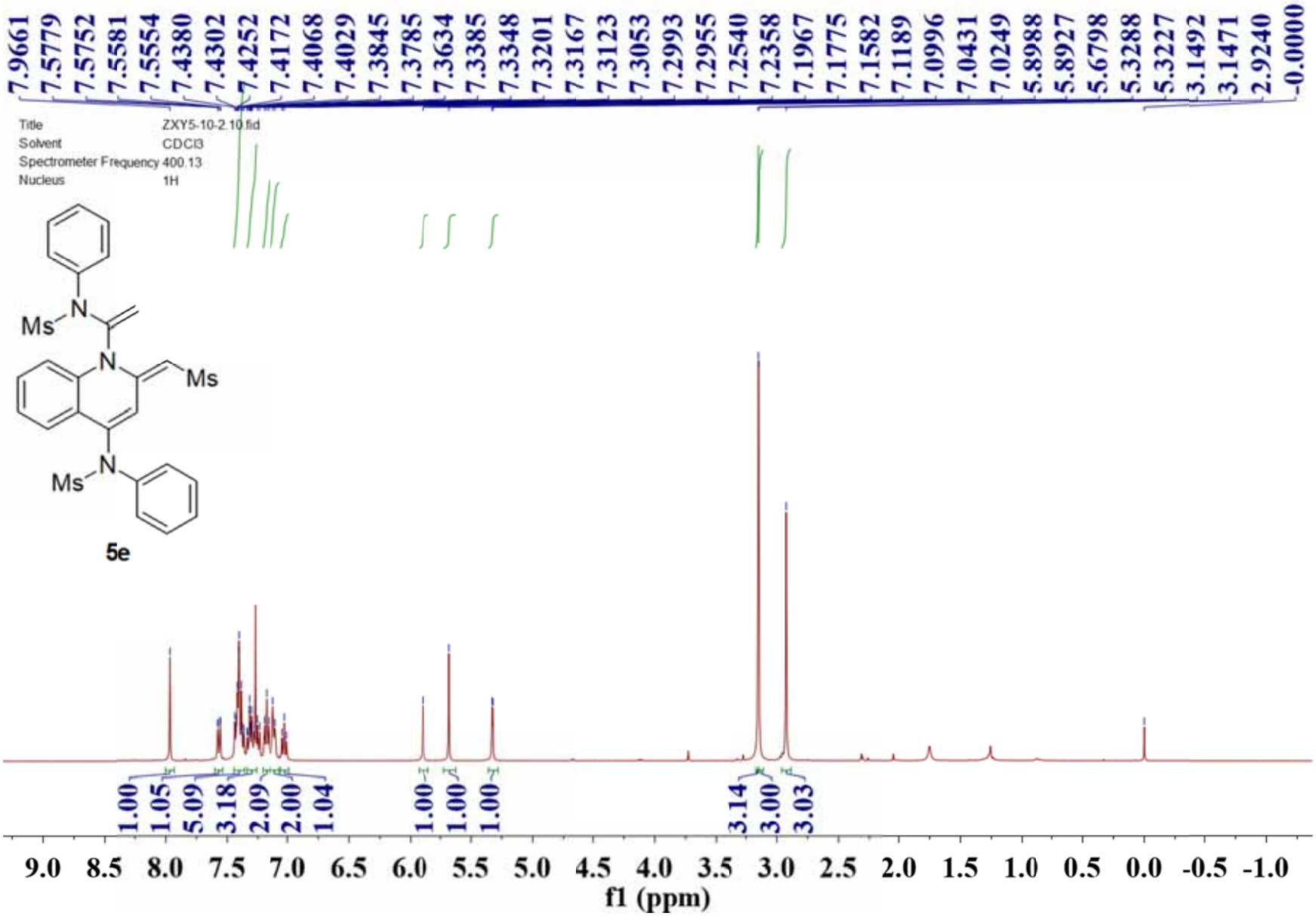

147.520
145.086
144.364
142.749
142.060
141.816
140.161
139.381
136.155
135.362
135.272
135.123
131.094
130.402
130.074
129.908
129.583
129.469
129.272
128.829
128.525
128.052
127.759
127.205
126.298
125.066
123.301
120.735
118.395
115.934
107.751
97.165
77.518
77.200
76.882
21.828
21.799
21.686
Title DLX6-Ts/ 11
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ts
N
N
Ts
N
Ts
5a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

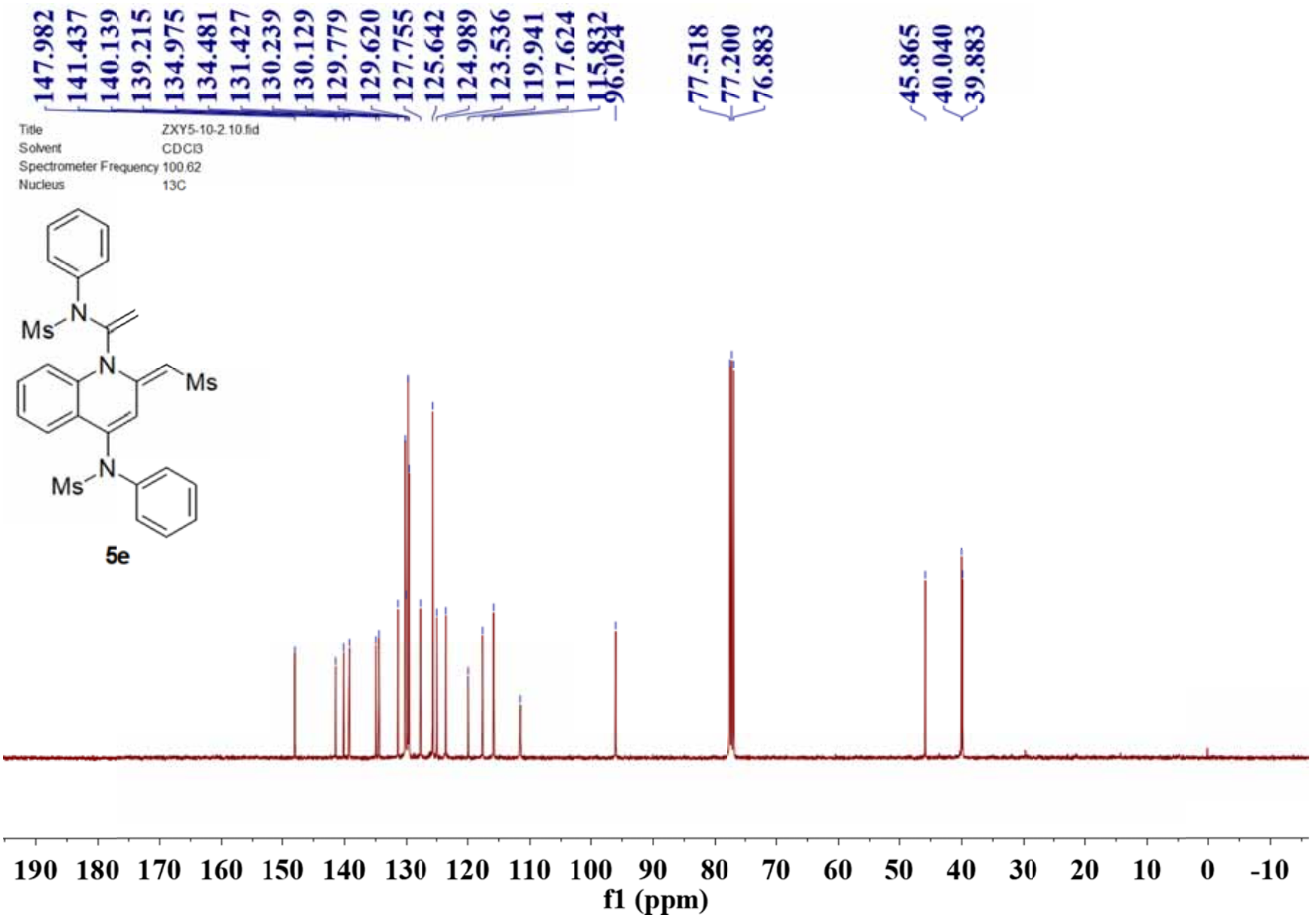

7.6730
7.6653
7.6601
7.6481
7.6429
7.6018
7.5808
7.5734
7.5682
7.5562
7.5511
7.4933
7.2475
7.2352
7.2292
7.2237
7.2207
7.2180
7.1022
7.0154
6.9650
6.9599
6.9475
6.9427
6.9240
6.9190
6.9063
6.9015
6.8862
6.8812
6.8687
6.8639
5.8634
5.8573
5.6882
5.0711
5.0650
3.8719
3.8460
0.0000
Title ZXY5-9-1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Mbs
N
N
Mbs
Mbs
N
5b
3.07
4.00
1.05
5.07
2.02
2.05
8.09
2.08
1.00
1.00
1.01
3.06
6.04
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)

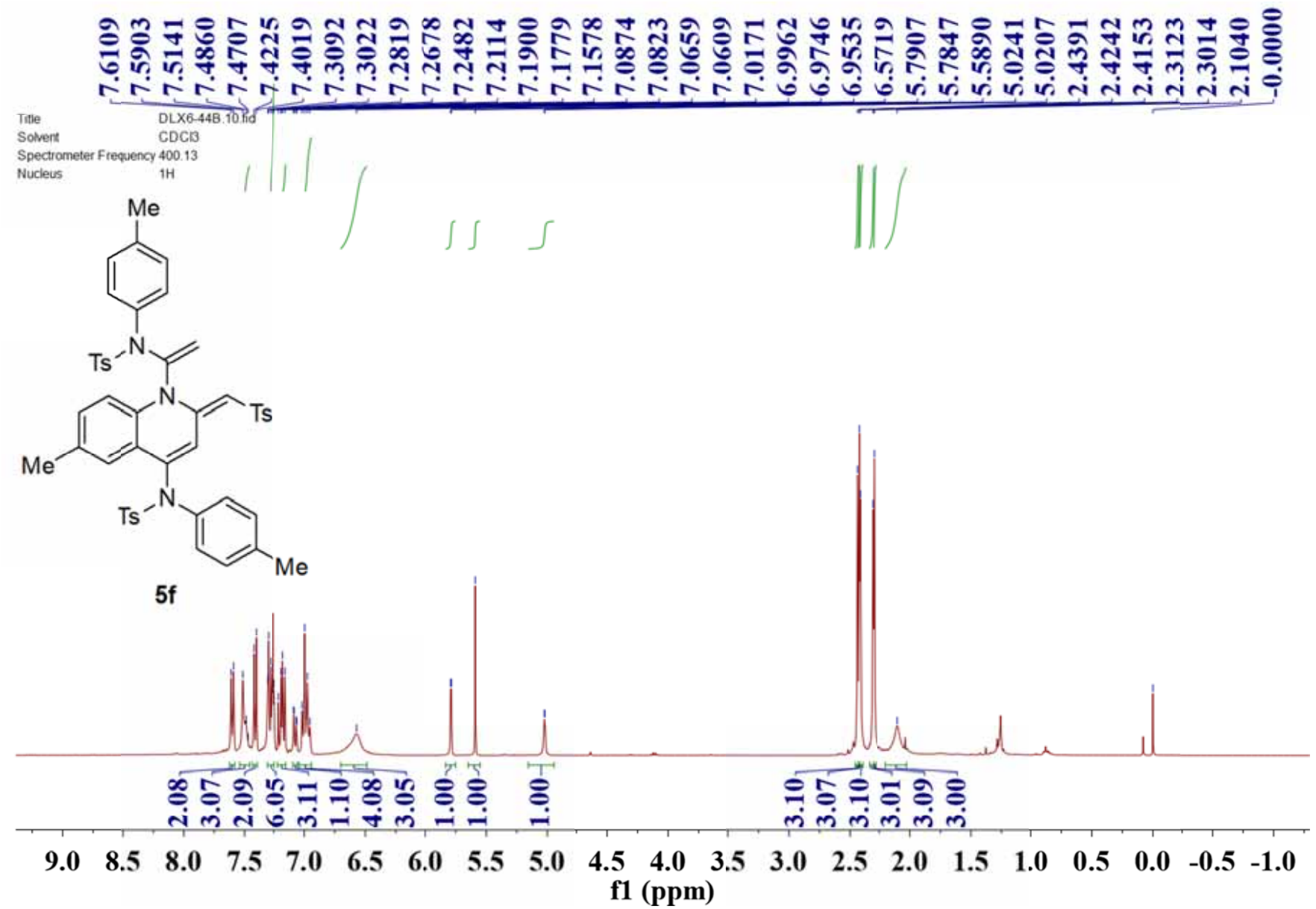

163.884
163.494
162.557
147.169
141.737
140.236
139.415
136.792
135.292
135.261
131.013
130.760
130.541
130.408
130.257
129.518
129.422
129.257
128.838
128.357
127.716
127.145
125.011
123.182
120.631
118.297
115.832
114.641
114.422
114.135
107.637
97.567
77.518
77.200
76.883
55.897
55.876
55.779
Title ZXY5-9-1.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Mbs
N
N
Mbs
Mbs
N
5b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

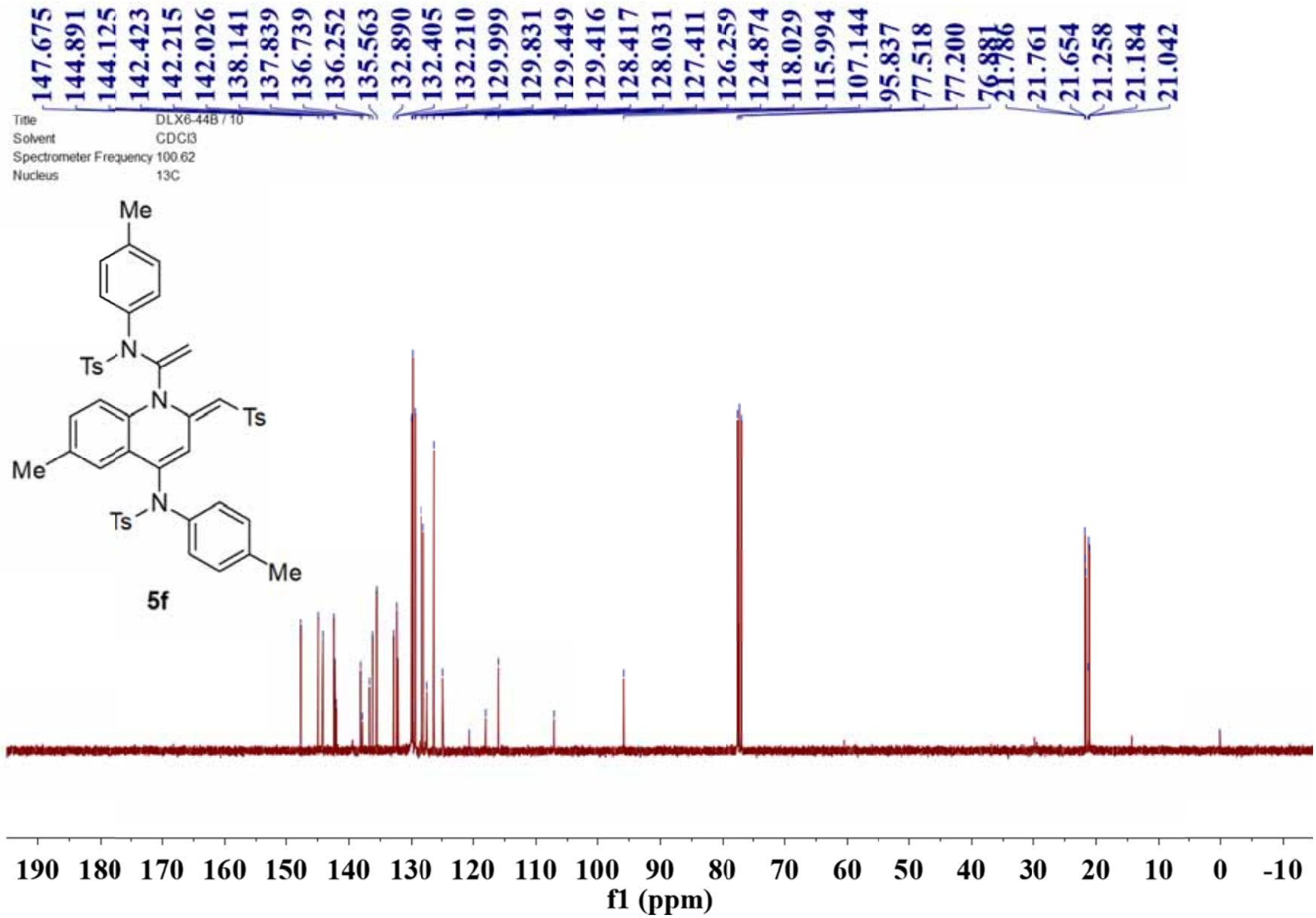

7.7000
7.6814
7.6274
7.6109
7.6058
7.5941
7.5891
7.5804
7.5779
7.5727
7.5658
7.5585
7.4851
7.4795
7.4741
7.4623
7.4578
7.4135
7.4081
7.3915
7.3866
7.3030
7.2995
7.2922
7.2872
7.2795
7.2738
7.2685
7.2605
7.1176
7.1126
7.1028
7.0933
7.0596
5.8346
5.8282
5.6962
5.1546
5.1481
-0.0000
Title ZXY-38B-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cs
N
N
Cs
Cs
N
5c
1.05
6.01
3.09
4.04
5.04
4.07
2.08
2.08
1.00
1.01
1.00
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)

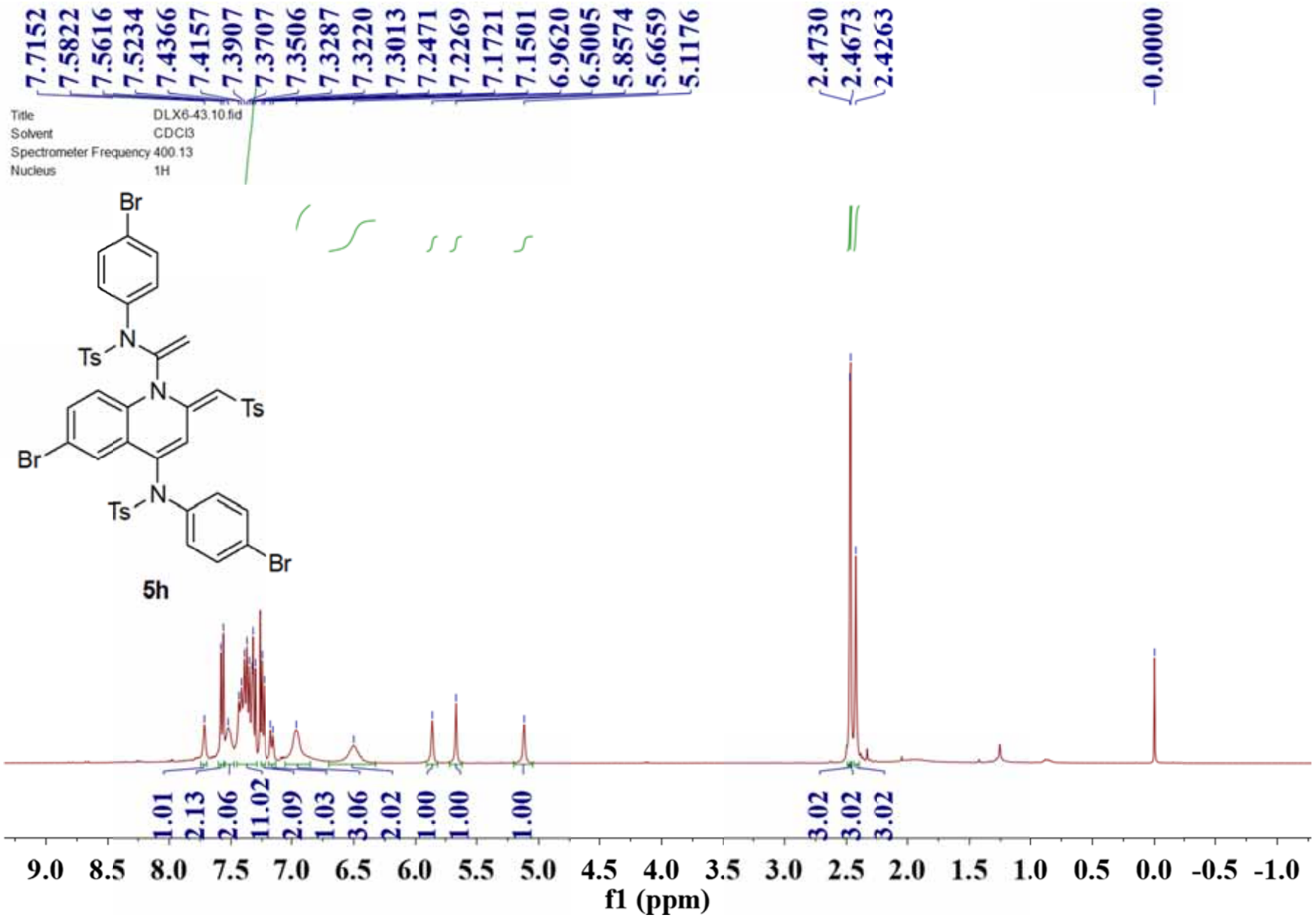

147.825
143.257
142.094
140.708
140.137
138.894
138.600
137.287
136.466
135.060
134.882
131.374
130.408
129.894
129.858
129.818
129.588
129.489
129.333
129.194
128.371
127.684
127.270
125.050
123.637
120.445
117.840
115.883
109.217
96.337
77.518
77.200
76.882
Title DLX6-39B2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cs
N
N
Cs
Cs
N
5c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

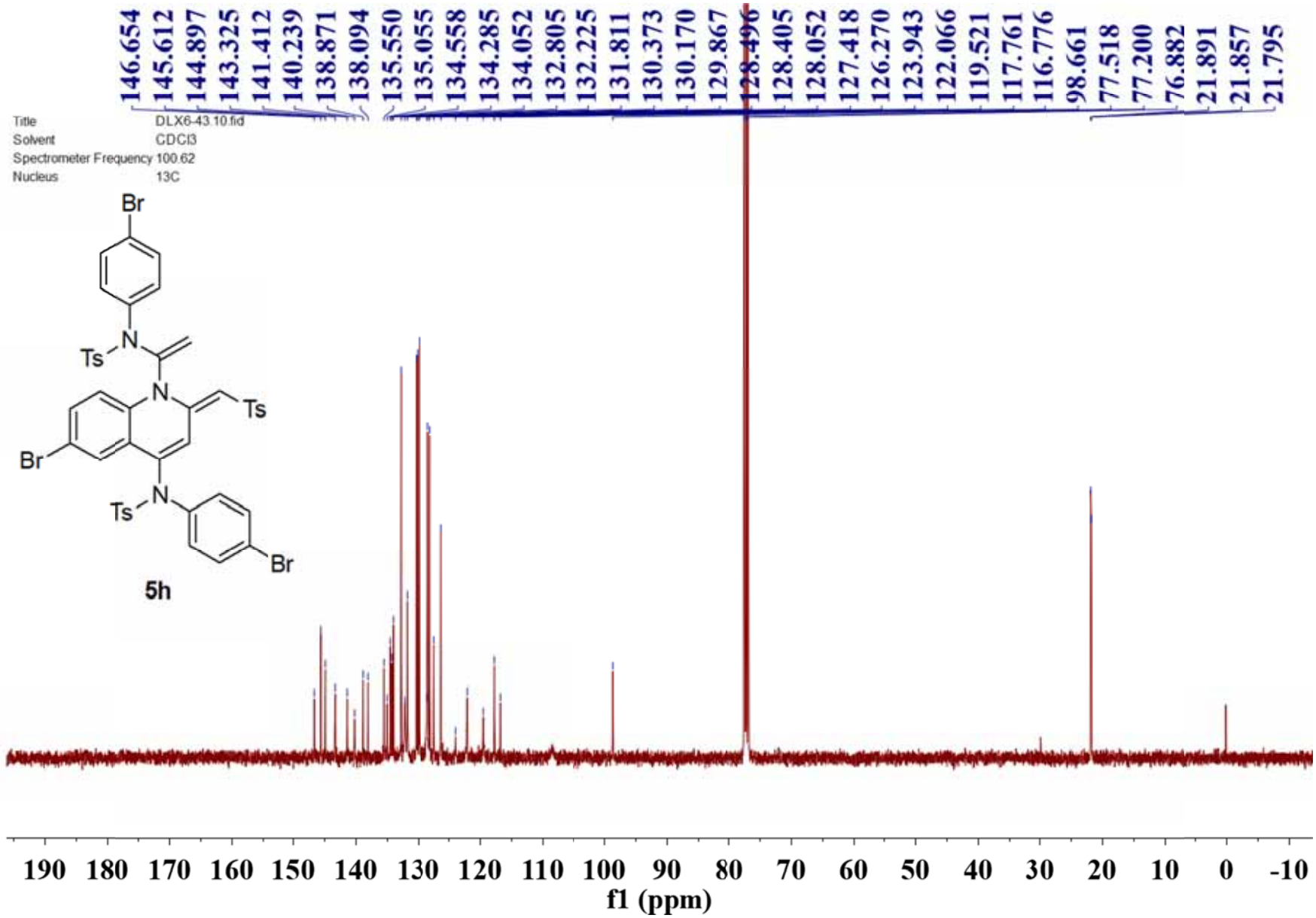

7.9661
7.5779
7.5752
7.5581
7.5554
7.4380
7.4302
7.4252
7.4172
7.4068
7.4029
7.3845
7.3785
7.3634
7.3385
7.3348
7.3201
7.3167
7.3123
7.3053
7.2993
7.2955
7.2540
7.2358
7.1967
7.1775
7.1582
7.1189
7.0996
7.0431
7.0249
5.8988
5.8927
5.6798
5.3288
5.3227
3.1492
3.1471
2.9240
-0.0000
Title ZXY5-10-2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ms
N
N
Ms
Ms
N
5e
1.00
1.05
5.09
3.18
2.09
2.00
1.04
1.00
1.00
1.00
3.14
3.00
3.03
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)

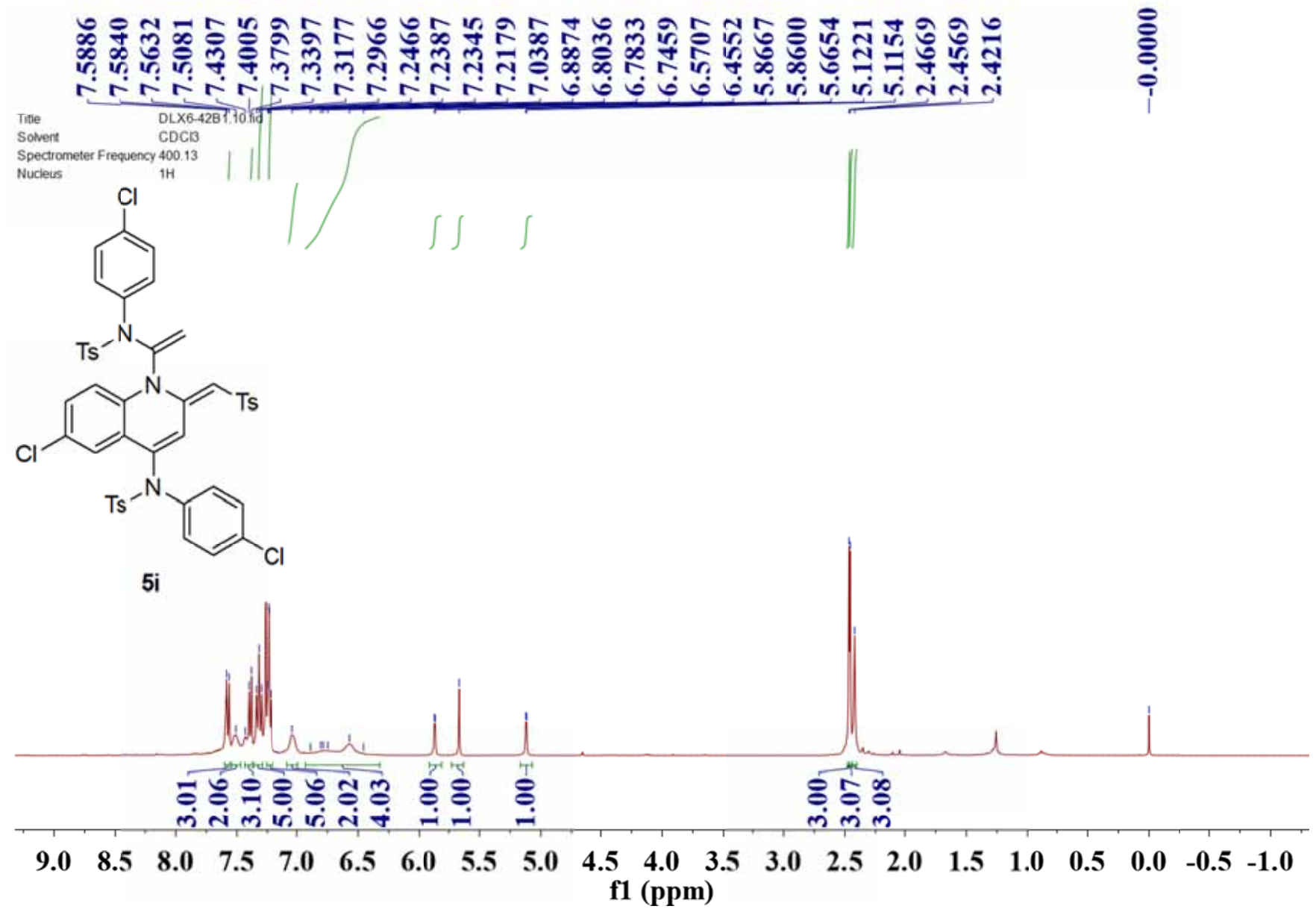

147.982
141.437
140.139
139.215
134.975
134.481
131.427
130.239
130.129
129.779
129.620
127.755
125.642
124.989
123.536
119.941
117.624
115.832
96.024
77.518
77.200
76.883
45.865
40.040
39.883
Title ZXY5-10-2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ms
N
N
Ms
N
Ms
5e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

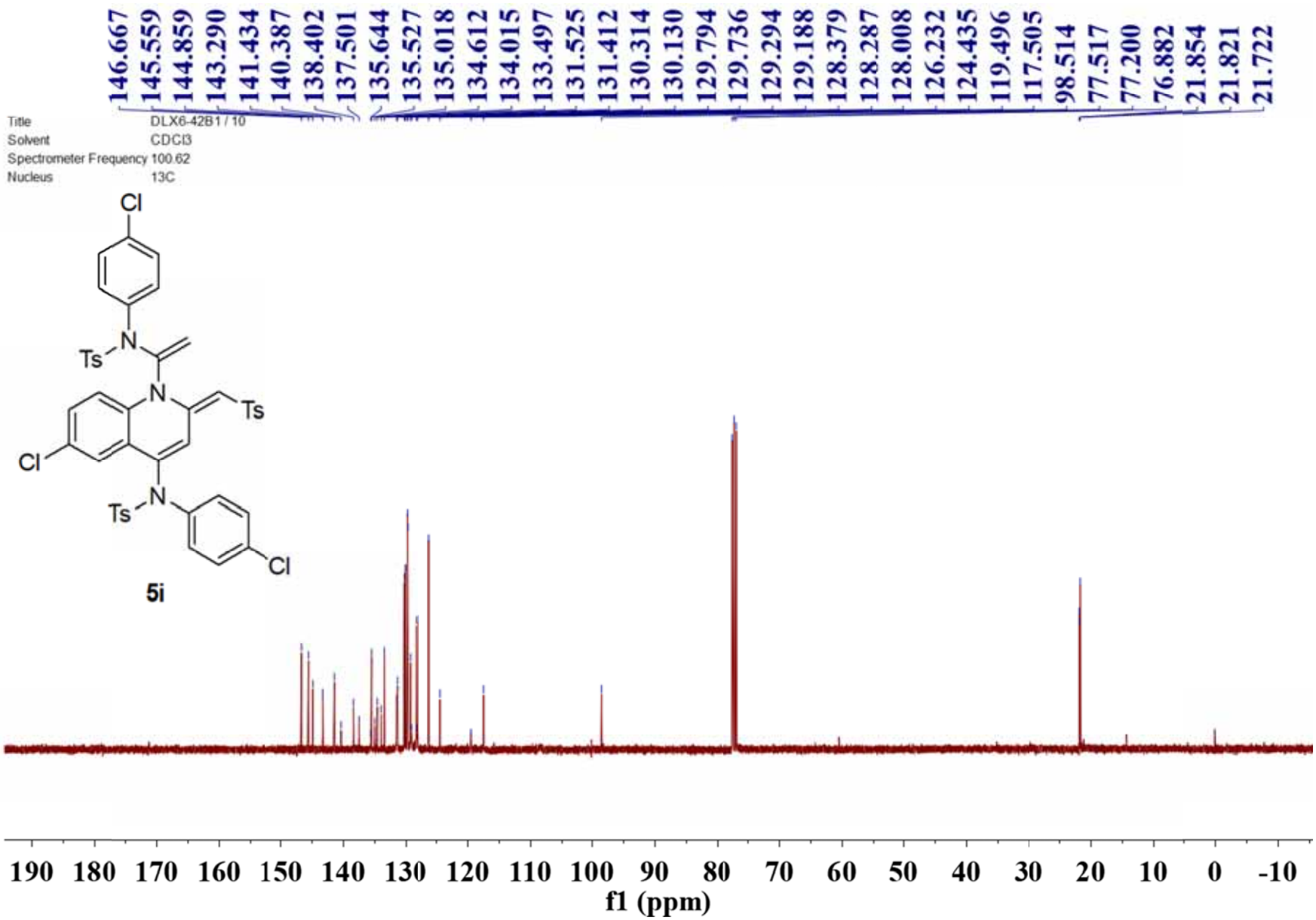

7.6109
7.5903
7.5141
7.4860
7.4707
7.4225
7.4019
7.3092
7.3022
7.2819
7.2678
7.2482
7.2114
7.1900
7.1779
7.1578
7.0874
7.0823
7.0659
7.0609
7.0171
6.9962
6.9746
6.9535
6.5719
5.7907
5.7847
5.5890
5.0241
5.0207
2.4391
2.4242
2.4153
2.3123
2.3014
2.1040
-0.0000
Title DLX6-44B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Ts
N
Ts
N
Me
Ts
N
Me
5f
2.08
3.07
2.09
6.05
3.11
1.10
4.08
3.05
1.00
1.00
1.00
3.10
3.07
3.10
3.01
3.09
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)

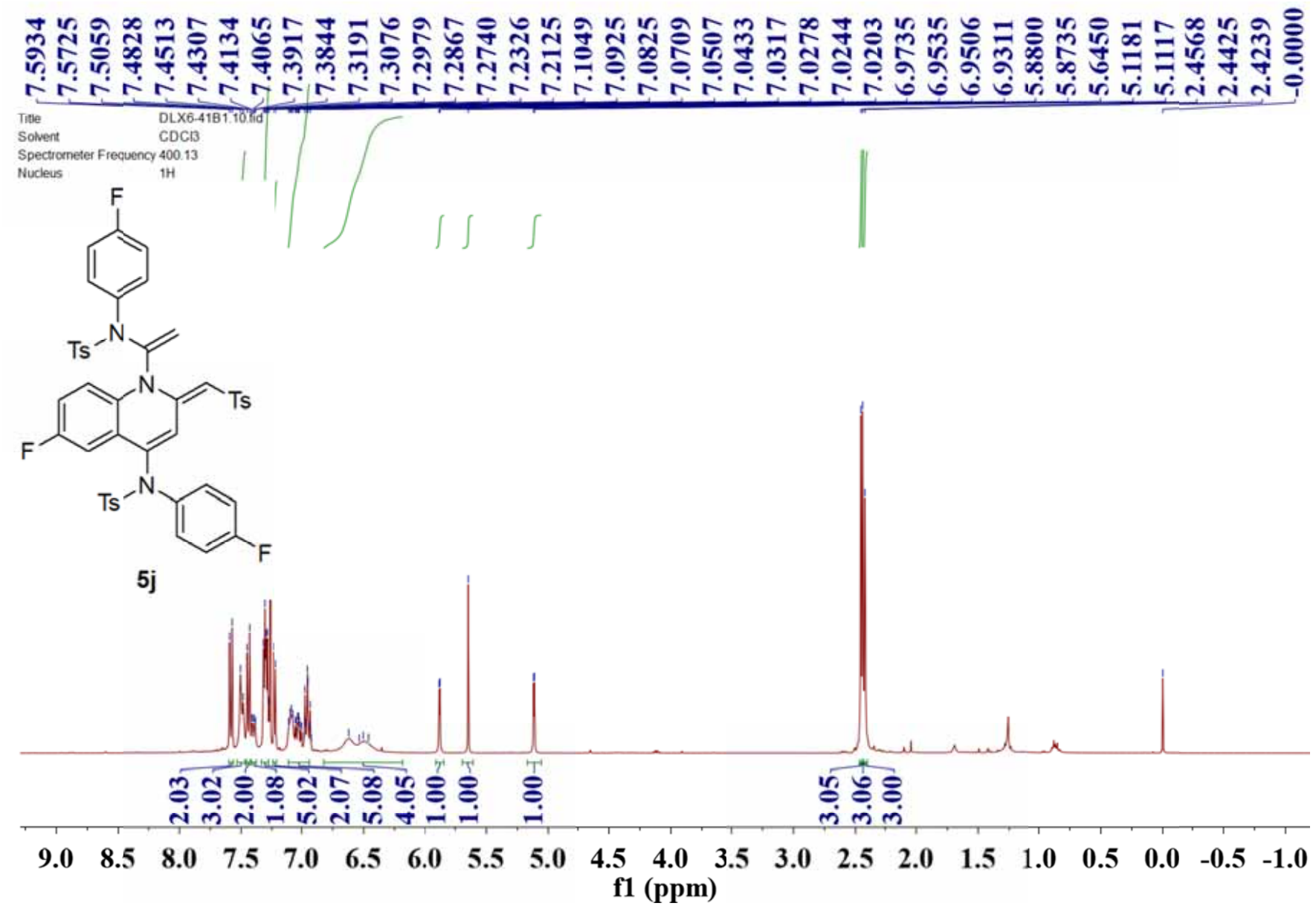

147.675
144.891
144.125
142.423
142.215
142.026
138.141
137.839
136.739
136.252
135.563
132.890
132.405
132.210
129.999
129.831
129.449
129.416
128.417
128.031
127.411
126.259
124.874
118.029
115.994
107.144
95.837
77.518
77.200
76.881
21.786
21.761
21.654
21.258
21.184
21.042
Title DLX6-44B / 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
N
Ts
Me
N
Ts
Me
5f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

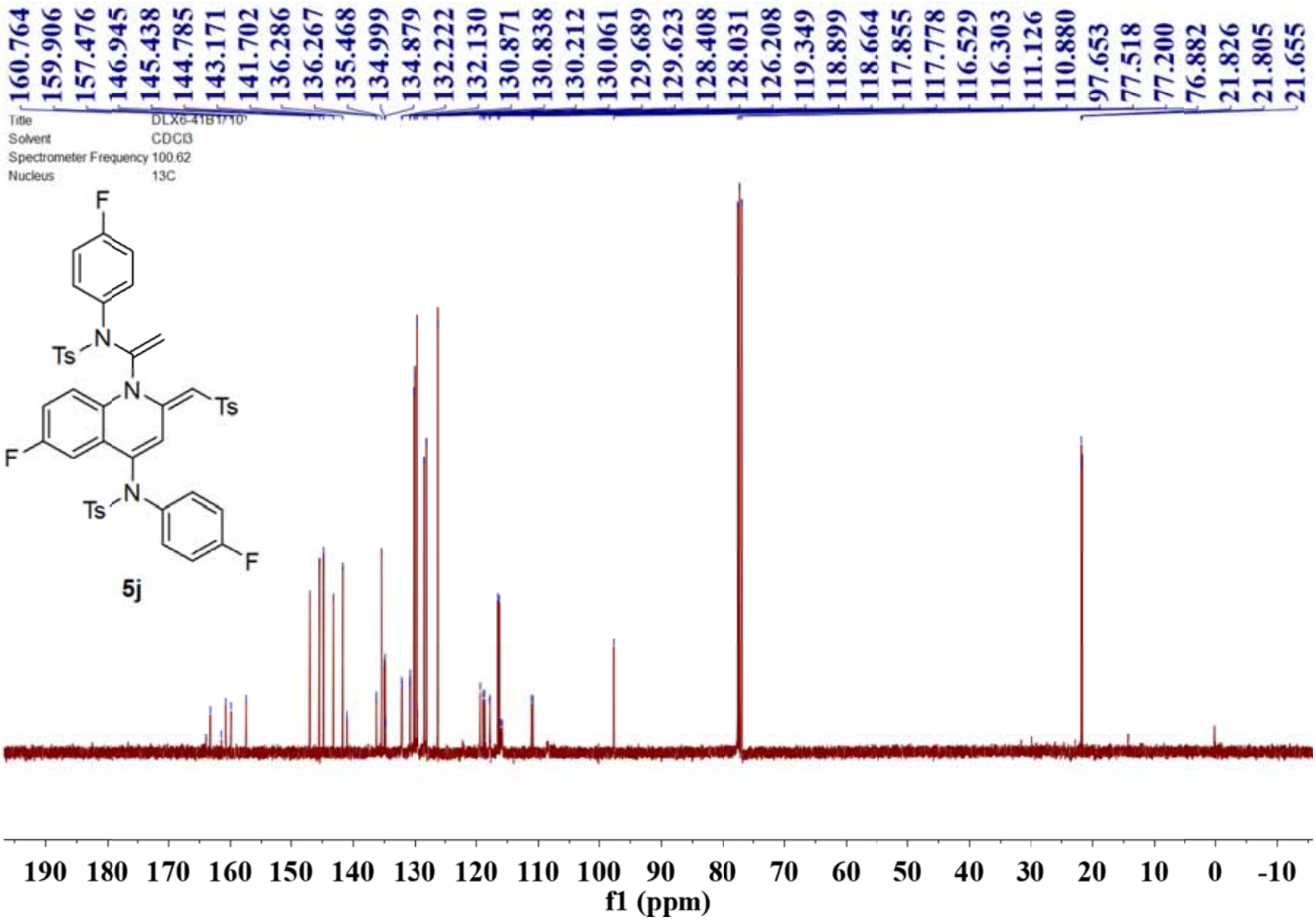

7.7152
7.5822
7.5616
7.5234
7.4366
7.4157
7.3907
7.3707
7.3506
7.3287
7.3220
7.3013
7.2471
7.2269
7.1721
7.1501
6.9620
6.5005
5.8574
5.6659
5.1176
2.4730
2.4673
2.4263
0.0000
Title DLX6-43.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Br
Ts
N
Ts
N
Ts
Br
Ts
N
Br
5h
1.01
2.13
2.06
11.02
2.09
1.03
3.06
2.02
1.00
1.00
1.00
3.02
3.02
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)

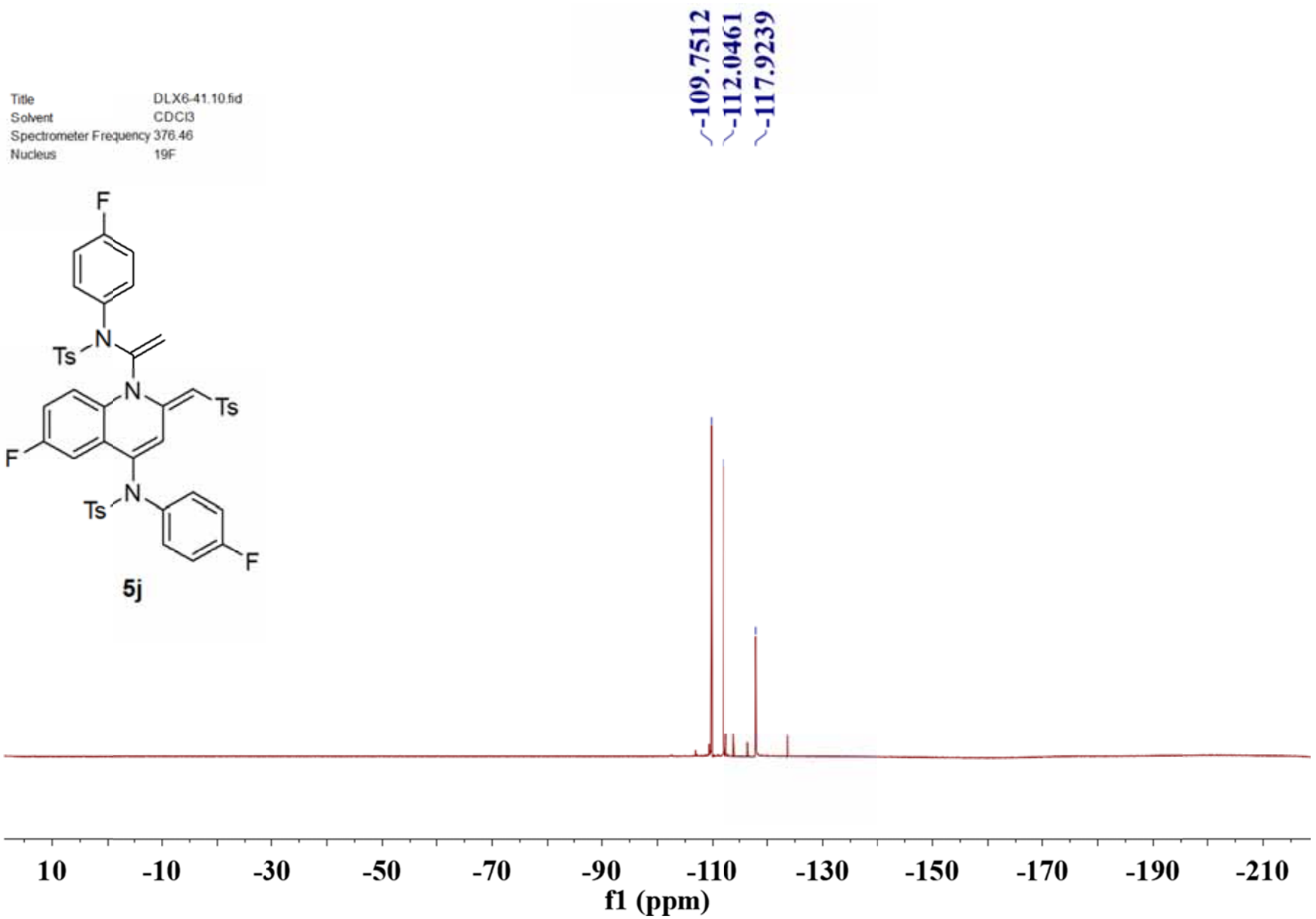

146.654
145.612
144.897
143.325
141.412
140.239
138.871
138.094
135.550
135.055
134.558
134.285
134.052
132.805
132.225
131.811
130.373
130.170
129.867
128.496
128.405
128.052
127.418
126.270
123.943
122.066
119.521
117.761
116.776
98.661
77.518
77.200
76.882
21.891
21.857
21.795
Title DLX6-43.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Br
N
Ts
N
Ts
Br
N
Ts
Br
5h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

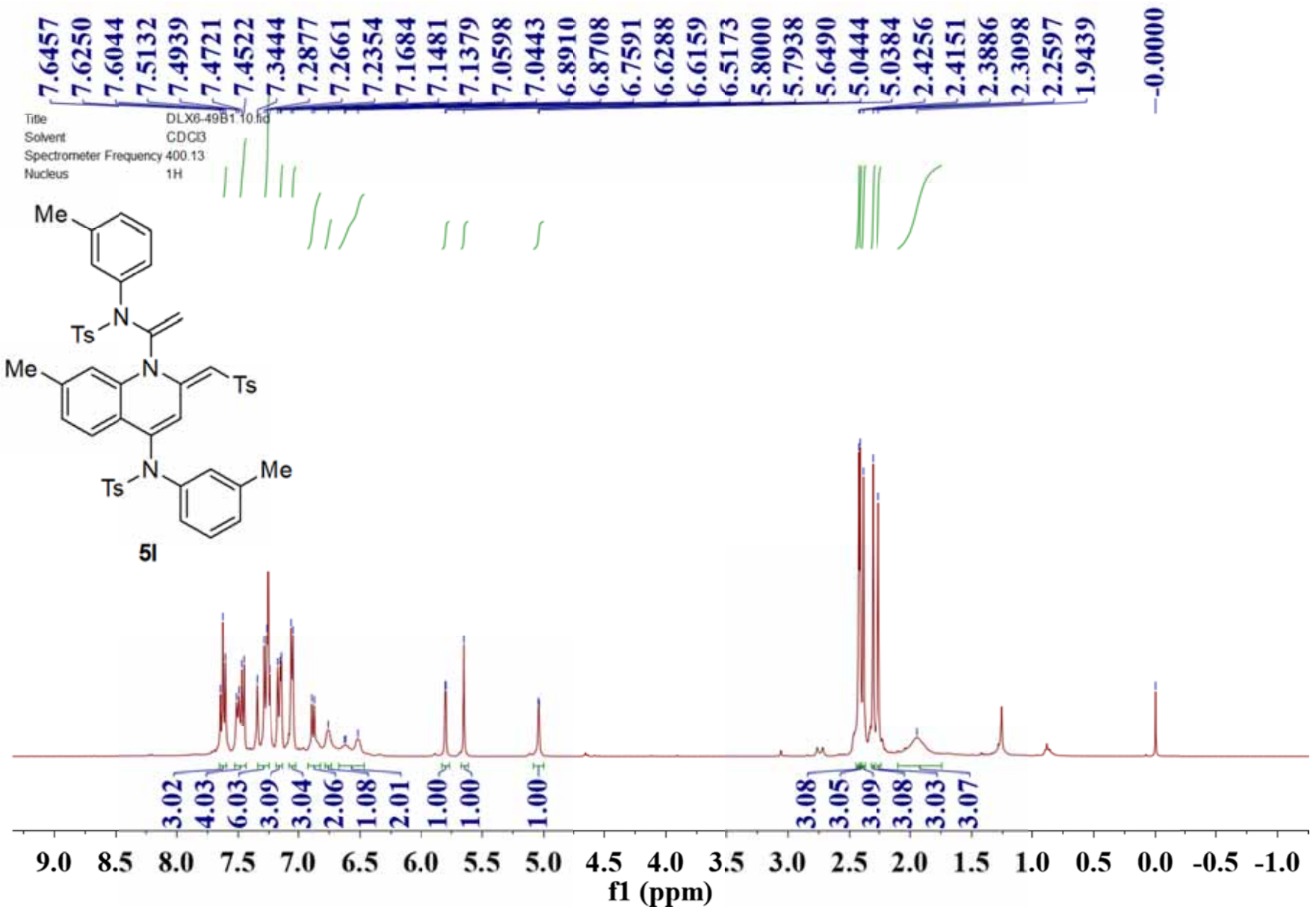

7.5886
7.5840
7.5632
7.5081
7.4307
7.4005
7.3799
7.3397
7.3177
7.2966
7.2466
7.2387
7.2345
7.2179
7.0387
6.8874
6.8036
6.7833
6.7459
6.5707
6.4552
5.8667
5.8600
5.6654
5.1221
5.1154
2.4669
2.4569
2.4216
-0.0000
Title DLX6-42B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
N
Ts
N
Ts
Cl
N
Ts
Cl
5i
3.01
2.06
3.10
5.00
5.06
2.02
4.03
1.00
1.00
1.00
3.00
3.07
3.08
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)

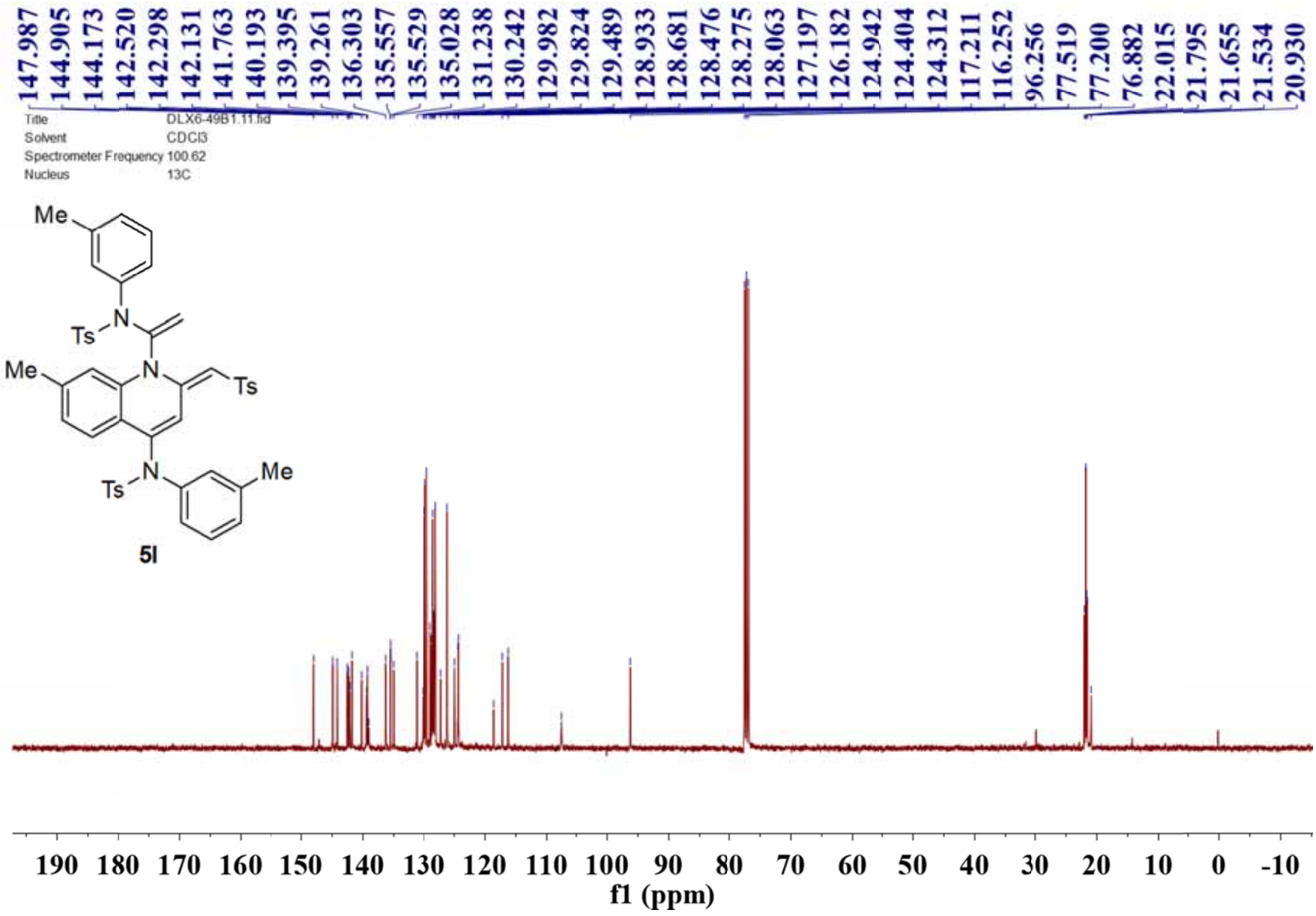

146.667
145.559
144.859
143.290
141.434
140.387
138.402
137.501
135.644
135.527
135.018
134.612
134.015
133.497
131.525
131.412
130.314
130.130
129.794
129.736
129.294
129.188
128.379
128.287
128.008
126.232
124.435
119.496
117.505
98.514
77.517
77.200
76.882
21.854
21.821
21.722
Title DLX6-42B1 / 10
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
N
Ts
N
Ts
Cl
N
Ts
Cl
5i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

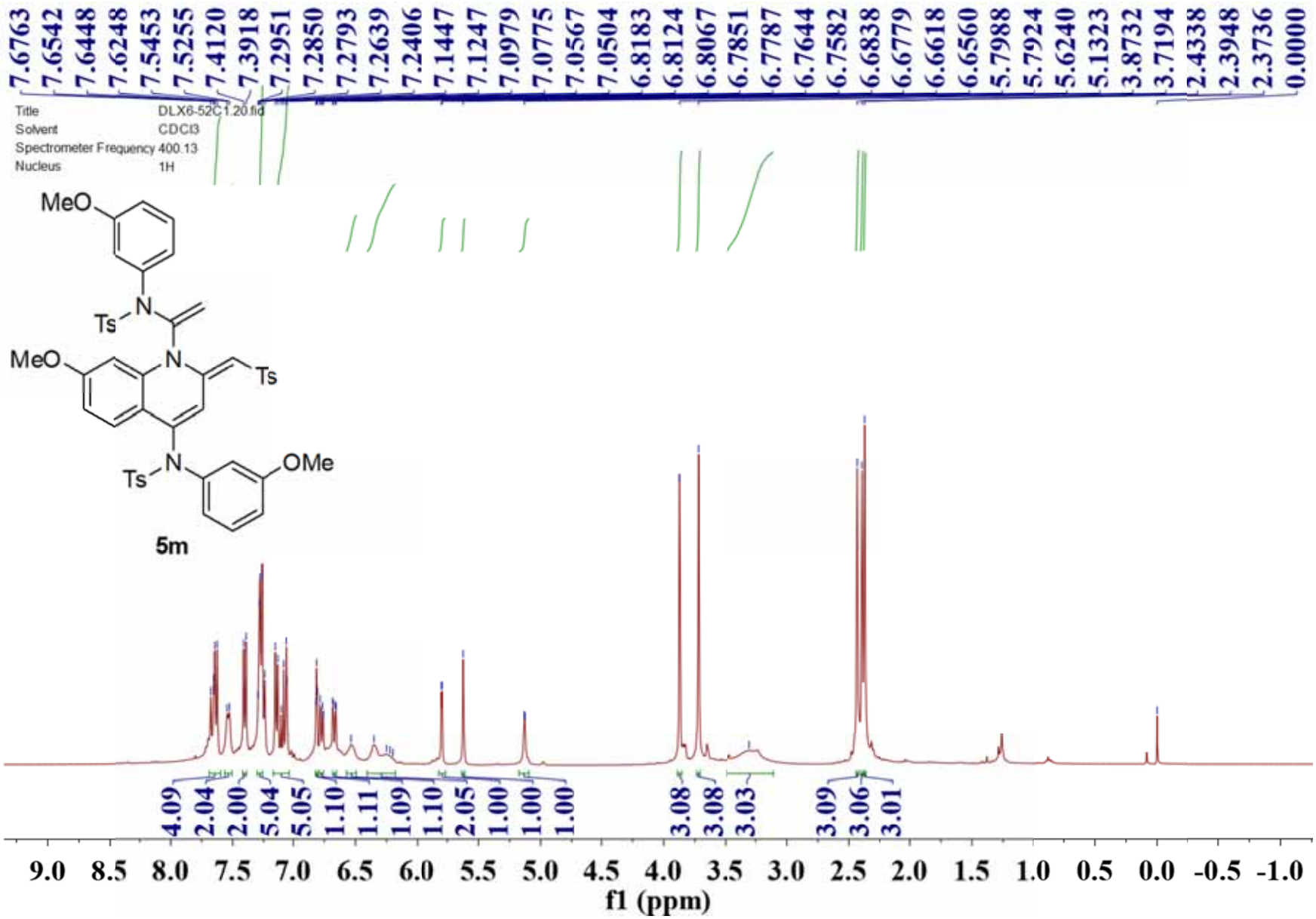

7.5934
7.5725
7.5059
7.4828
7.4513
7.4307
7.4134
7.4065
7.3917
7.3844
7.3191
7.3076
7.2979
7.2867
7.2740
7.2326
7.2125
7.1049
7.0925
7.0825
7.0709
7.0507
7.0433
7.0317
7.0278
7.0244
7.0203
6.9735
6.9535
6.9506
6.9311
5.8800
5.8735
5.6450
5.1181
5.1117
2.4568
2.4425
2.4239
-0.0000
Title DLX6-41B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
Ts
N
Ts
N
Ts
F
Ts
N
F
5j
2.03
3.02
2.00
1.08
5.02
2.07
5.08
4.05
1.00
1.00
1.00
3.05
3.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

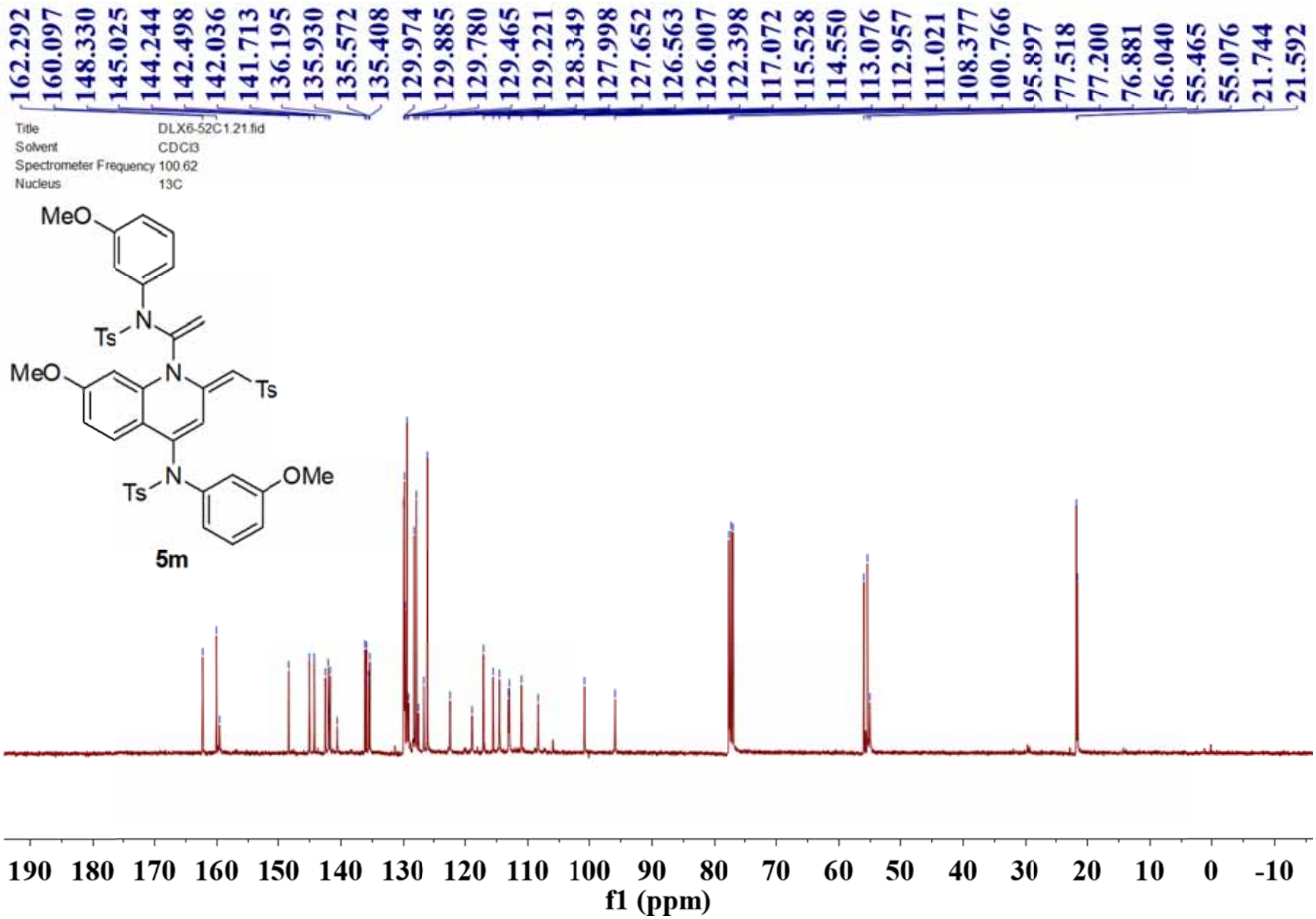

160.764
159.906
157.476
146.945
145.438
144.785
143.171
141.702
136.286
136.267
135.468
134.999
134.879
132.222
132.130
130.871
130.838
130.212
130.061
129.689
129.623
128.408
128.031
126.208
119.349
118.899
118.664
117.855
117.778
116.529
116.303
111.126
110.880
97.653
77.518
77.200
76.882
21.826
21.805
21.655
Title DLX6-41B1710
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
Ts
N
Ts
N
Ts
F
Ts
N
F
5j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

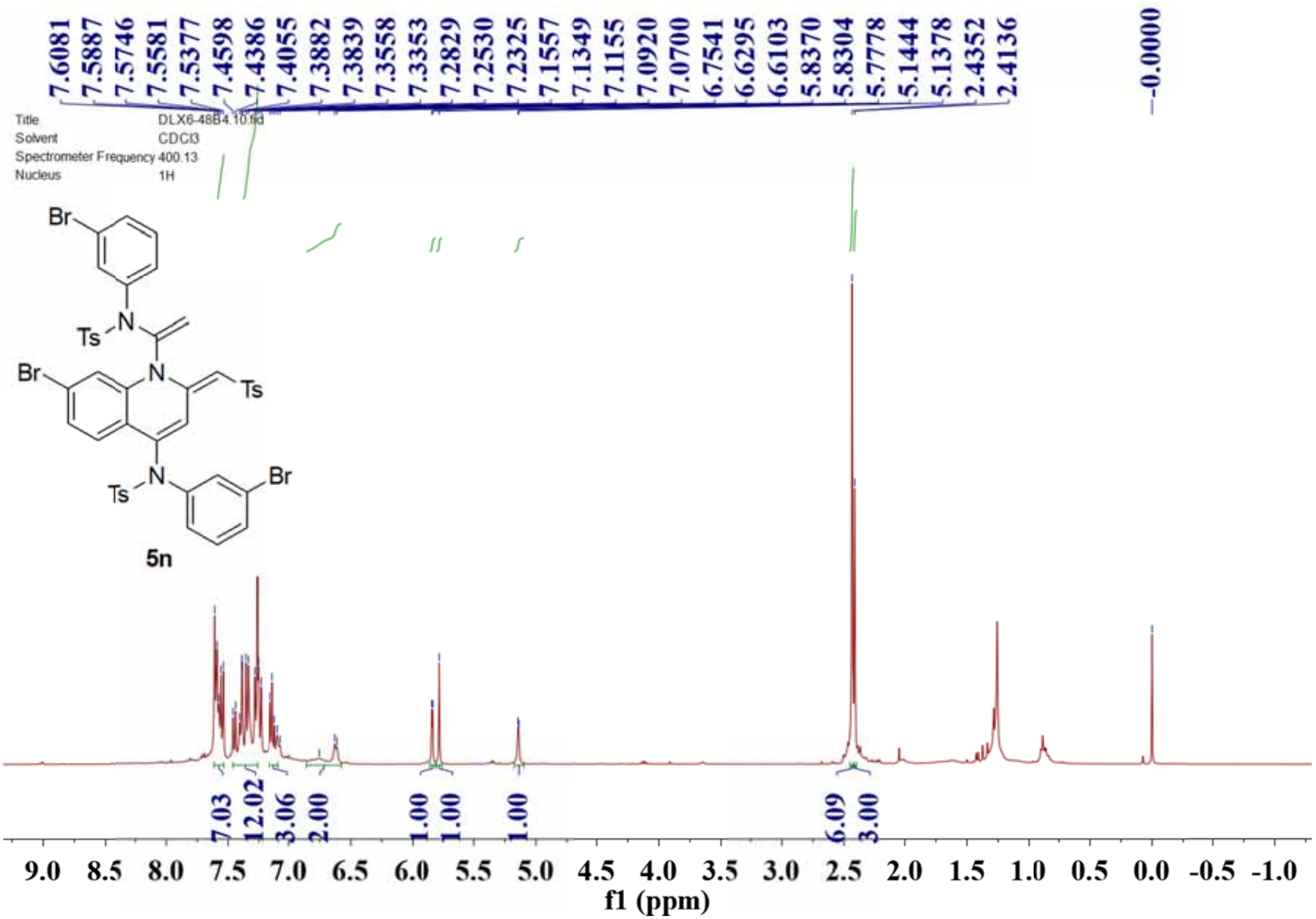

Title DLX6-41.10.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
-109.7512
-112.0461
-117.9239
F
Ts
N
N
Ts
F
N
Ts
F
5j
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

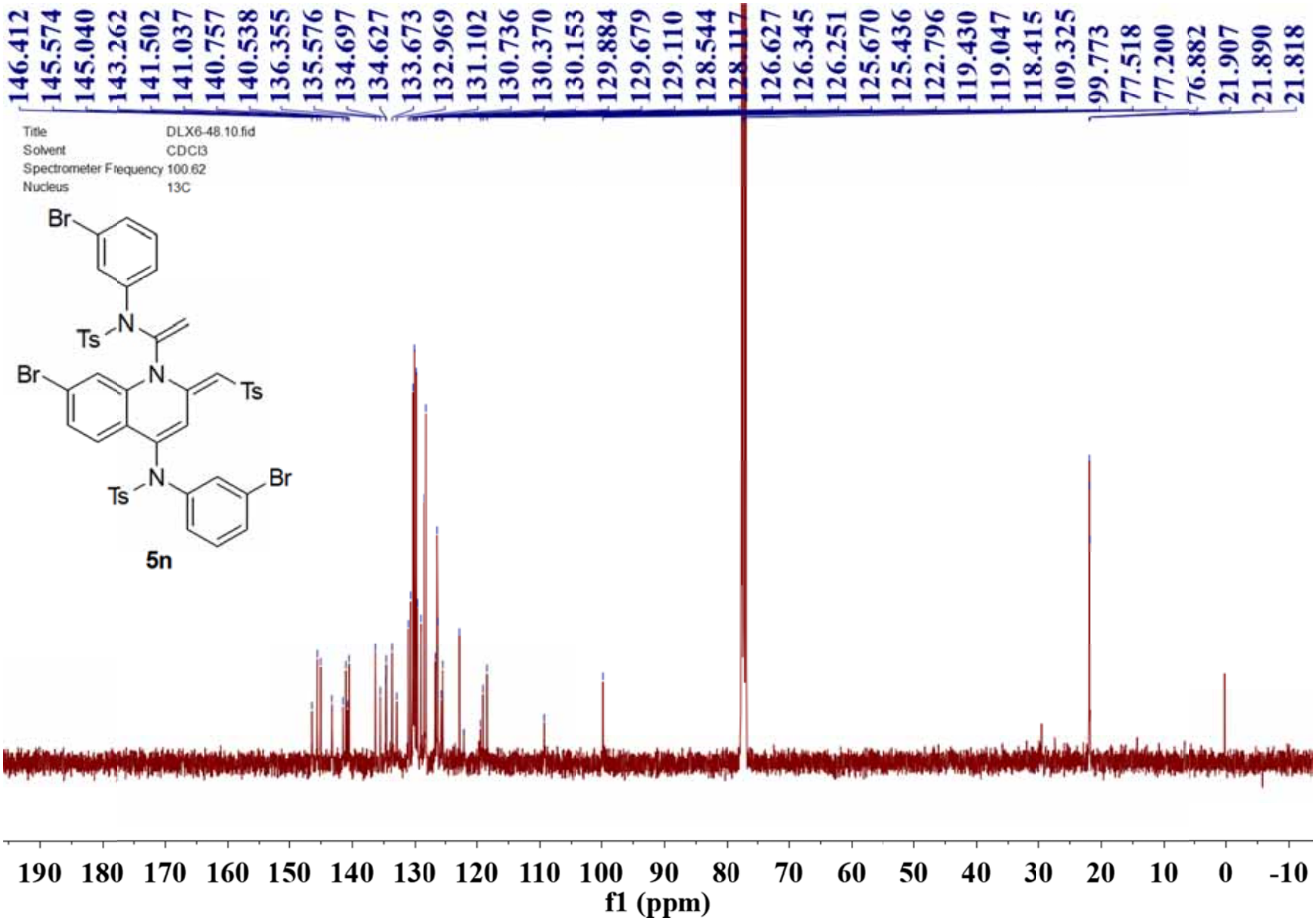

7.6457
7.6250
7.6044
7.5132
7.4939
7.4721
7.4522
7.3444
7.2877
7.2661
7.2354
7.1684
7.1481
7.1379
7.0598
7.0443
6.8910
6.8708
6.7591
6.6288
6.6159
6.5173
5.8000
5.7938
5.6490
5.0444
5.0384
2.4256
2.4151
2.3886
2.3098
2.2597
1.9439
-0.0000
Title DLX6-49B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
N
Me
Ts
N
Ts
Me
5l
3.02
4.03
6.03
3.09
3.04
2.06
1.08
2.01
1.00
1.00
1.00
3.08
3.05
3.09
3.08
3.03
3.07
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)

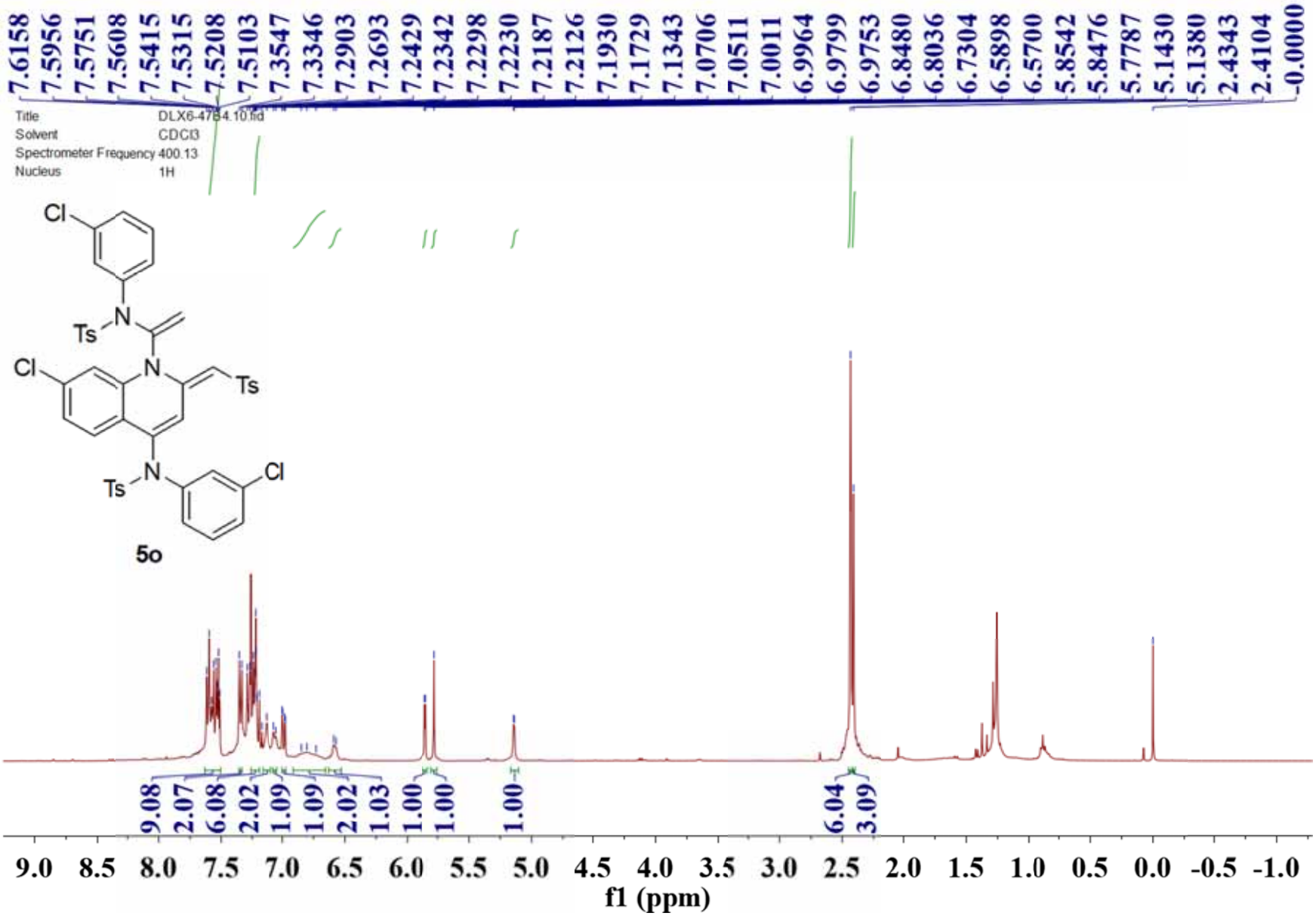

147.987
144.905
144.173
142.520
142.298
142.131
141.763
140.193
139.395
139.261
136.303
135.557
135.529
135.028
131.238
130.242
129.982
129.824
129.489
128.933
128.681
128.476
128.275
128.063
127.197
126.182
124.942
124.404
124.312
117.211
116.252
96.256
77.519
77.200
76.882
22.015
21.795
21.655
21.534
20.930
Title DLX6-49B1.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Me
N
Ts
Ts
N
Me
5l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

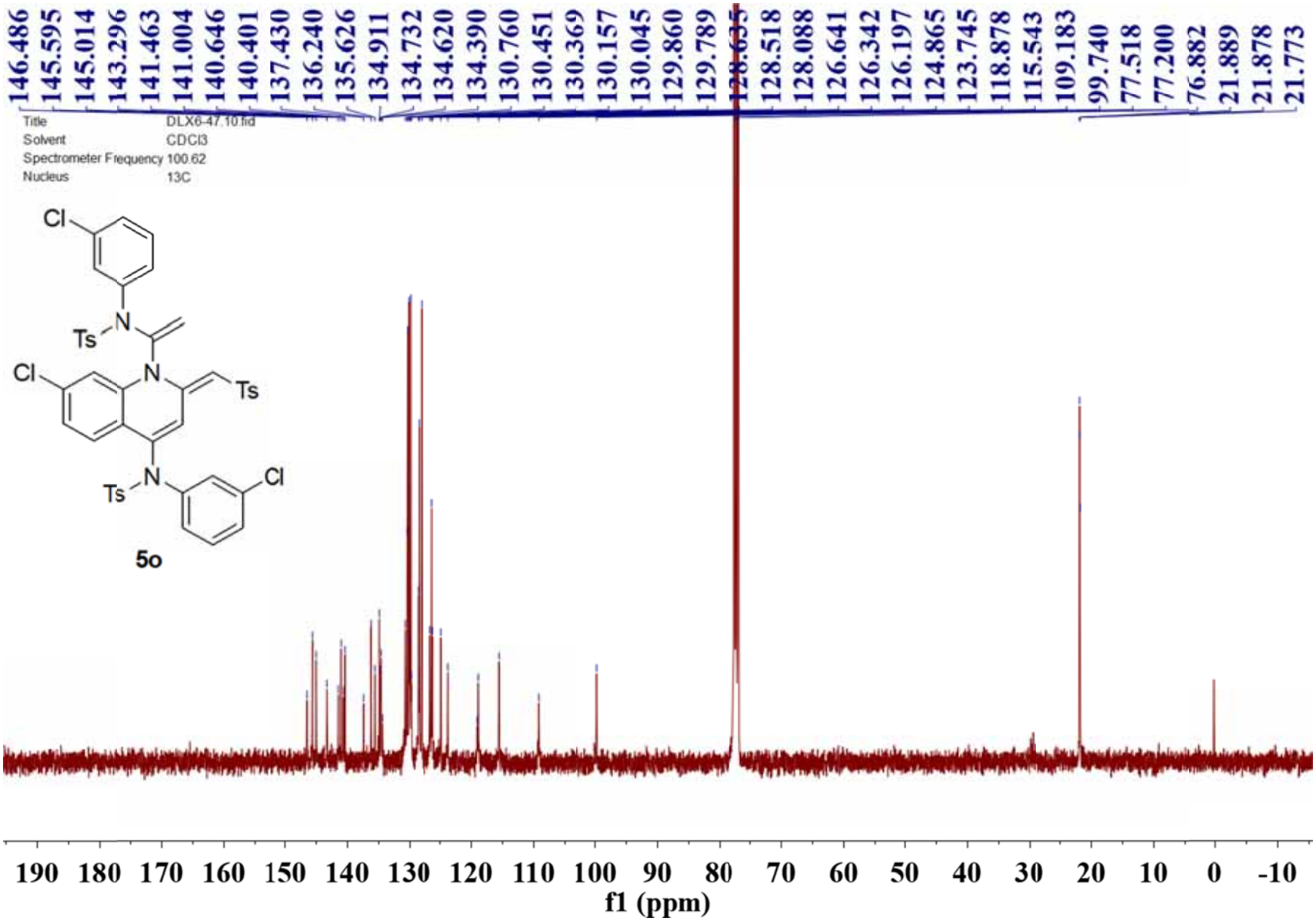

7.6763
7.6542
7.6448
7.6248
7.5453
7.5255
7.4120
7.3918
7.2951
7.2850
7.2793
7.2639
7.2406
7.1447
7.1247
7.0979
7.0775
7.0567
7.0504
6.8183
6.8124
6.8067
6.7851
6.7787
6.7644
6.7582
6.6838
6.6779
6.6618
6.6560
5.7988
5.7924
5.6240
5.1323
3.8732
3.7194
2.4338
2.3948
2.3736
0.0000
Title DLX6-52C1.20.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
Ts
N
MeO
N
Ts
Ts
N
OMe
5m
4.09
2.04
2.00
5.04
5.05
1.10
1.11
1.09
1.10
2.05
1.00
1.00
1.00
3.08
3.08
3.03
3.09
3.06
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)

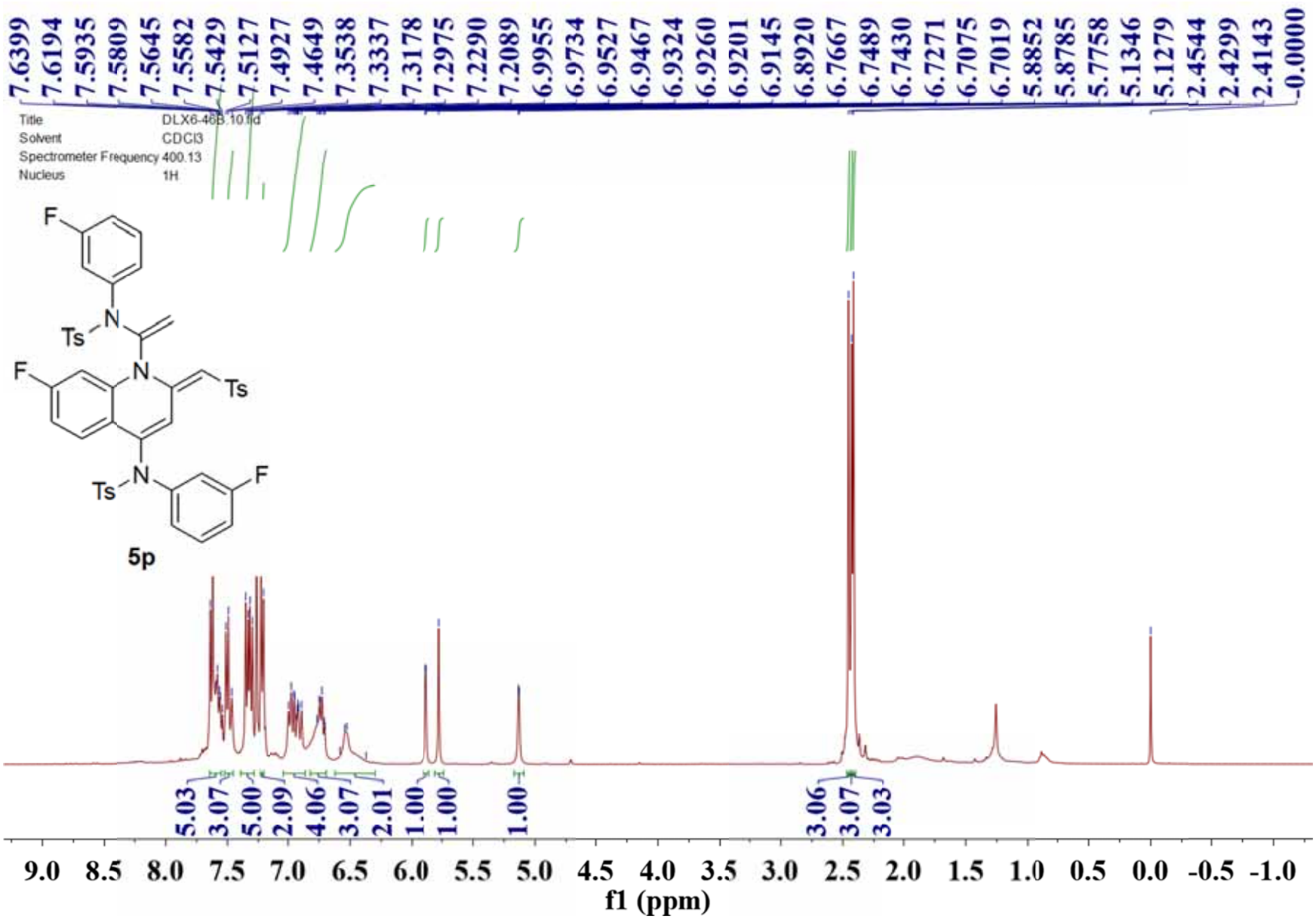

162.292
160.097
148.330
145.025
144.244
142.498
142.036
141.713
136.195
135.930
135.572
135.408
129.974
129.885
129.780
129.465
129.221
128.349
127.998
127.652
126.563
126.007
122.398
117.072
115.528
114.550
113.076
112.957
111.021
108.377
100.766
95.897
77.518
77.200
76.881
56.040
55.465
55.076
21.744
21.592
Title DLX6-52C1.21.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
Ts
N
MeO
N
Ts
Ts
N
OMe
5m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

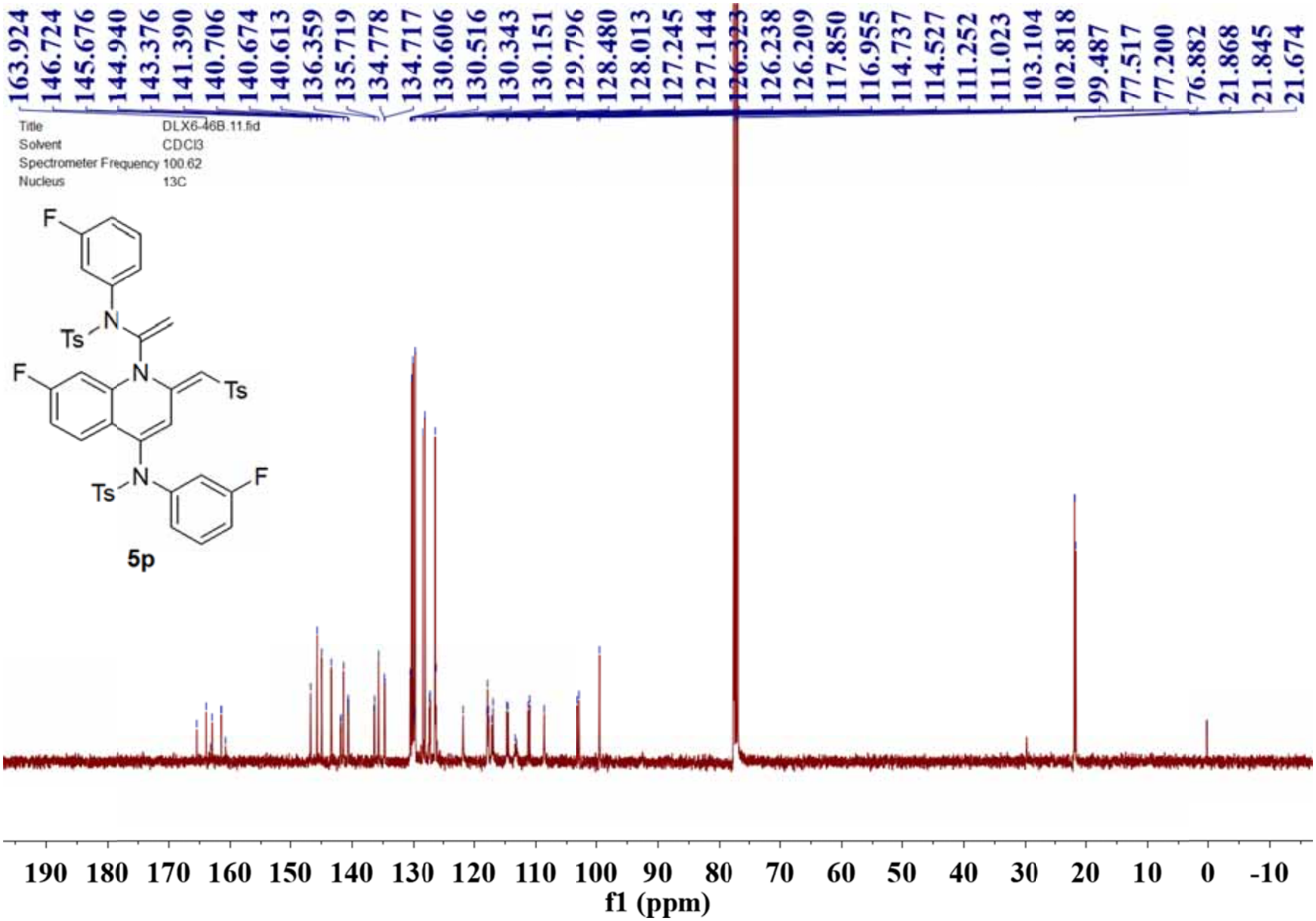

7.6081
7.5887
7.5746
7.5581
7.5377
7.4598
7.4386
7.4055
7.3882
7.3839
7.3558
7.3353
7.2829
7.2530
7.2325
7.1557
7.1349
7.1155
7.0920
7.0700
6.7541
6.6295
6.6103
5.8370
5.8304
5.7778
5.1444
5.1378
2.4352
2.4136
-0.0000
Title DLX6-48B4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Br
Ts
N
Br
Ts
N
Ts
N
Br
5n
7.03
12.02
3.06
2.00
1.00
1.00
1.00
6.09
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)

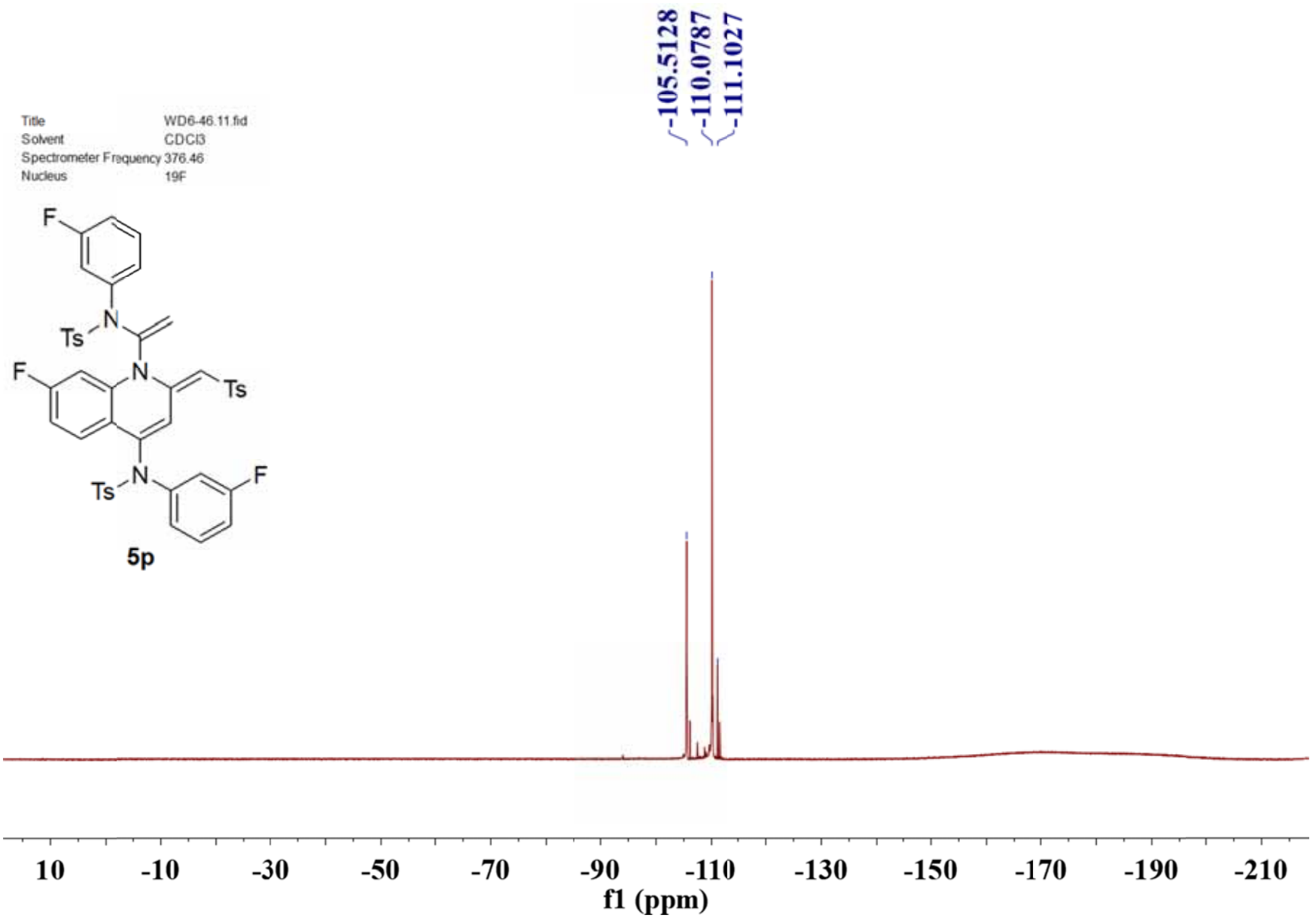

146.412
145.574
145.040
143.262
141.502
141.037
140.757
140.538
136.355
135.576
134.697
134.627
133.673
132.969
131.102
130.736
130.370
130.153
129.884
129.679
129.110
128.544
128.117
126.627
126.345
126.251
125.670
125.436
122.796
119.430
119.047
118.415
109.325
99.773
77.518
77.200
76.882
21.907
21.890
21.818
Title DLX6-48.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Br
Ts
N
Br
Ts
N
Ts
Br
Ts
N
5n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

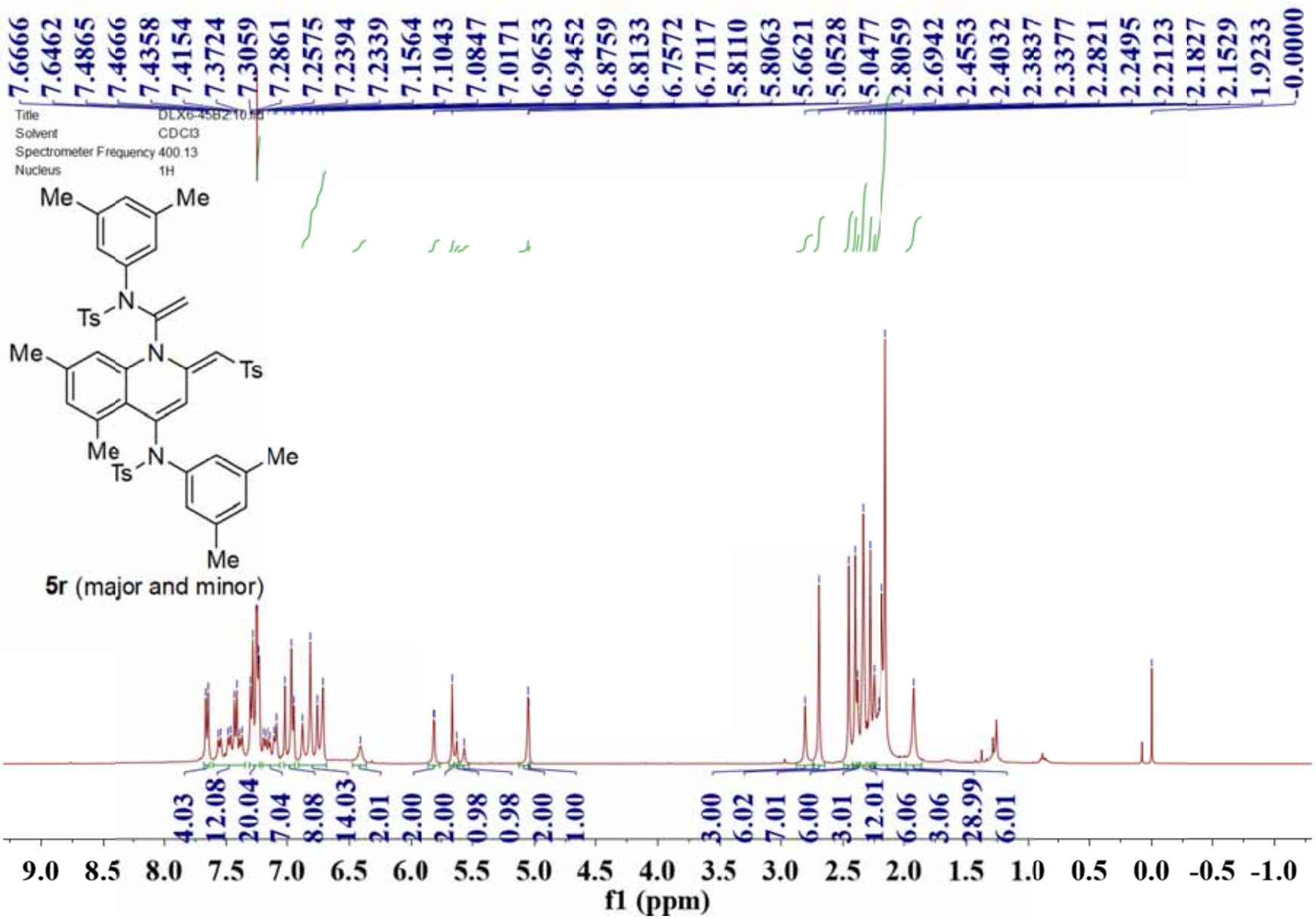

7.6158
7.5956
7.5751
7.5608
7.5415
7.5315
7.5208
7.5103
7.3547
7.3346
7.2903
7.2693
7.2429
7.2342
7.2298
7.2230
7.2187
7.2126
7.1930
7.1729
7.1343
7.0706
7.0511
7.0011
6.9964
6.9799
6.9753
6.8480
6.8036
6.7304
6.5898
6.5700
5.8542
5.8476
5.7787
5.1430
5.1380
2.4343
2.4104
-0.0000
Title DLX6-47B4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Cl
Ts
N
Cl
Ts
Ts
N
Cl
5o
9.08
2.07
6.08
2.02
1.09
1.09
2.02
1.03
1.00
1.00
1.00
6.04
3.09
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)

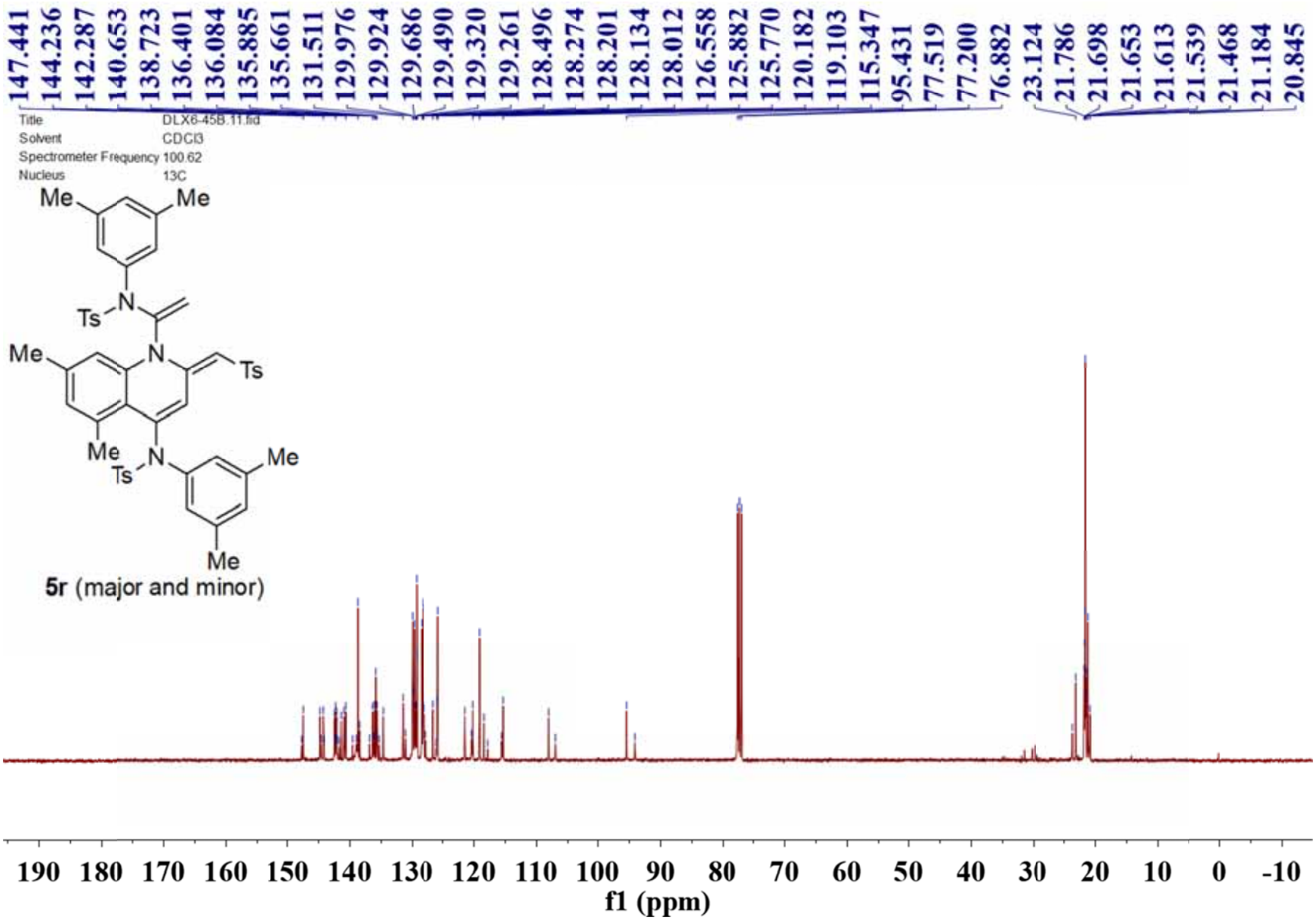

146.486
145.595
145.014
143.296
141.463
141.004
140.646
140.401
137.430
136.240
135.626
134.911
134.732
134.620
134.390
130.760
130.451
130.369
130.157
130.045
129.860
129.789
128.635
128.518
128.088
126.641
126.342
126.197
124.865
123.745
118.878
115.543
109.183
99.740
77.518
77.200
76.882
21.889
21.878
21.773
Title DLX6-47.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Cl
Ts
N
Cl
Ts
N
Ts
N
Cl
5o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.6399
7.6194
7.5935
7.5809
7.5645
7.5582
7.5429
7.5127
7.4927
7.4649
7.3538
7.3337
7.3178
7.2975
7.2290
7.2089
6.9955
6.9734
6.9527
6.9467
6.9324
6.9260
6.9201
6.9145
6.8920
6.7667
6.7489
6.7430
6.7271
6.7075
6.7019
5.8852
5.8785
5.7758
5.1346
5.1279
2.4544
2.4299
2.4143
-0.0000
Title DLX6-46B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
F
N
Ts
F
N
Ts
Ts
N
F
5p
5.03
3.07
5.00
2.09
4.06
3.07
2.01
1.00
1.00
1.00
3.06
3.07
3.03
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)

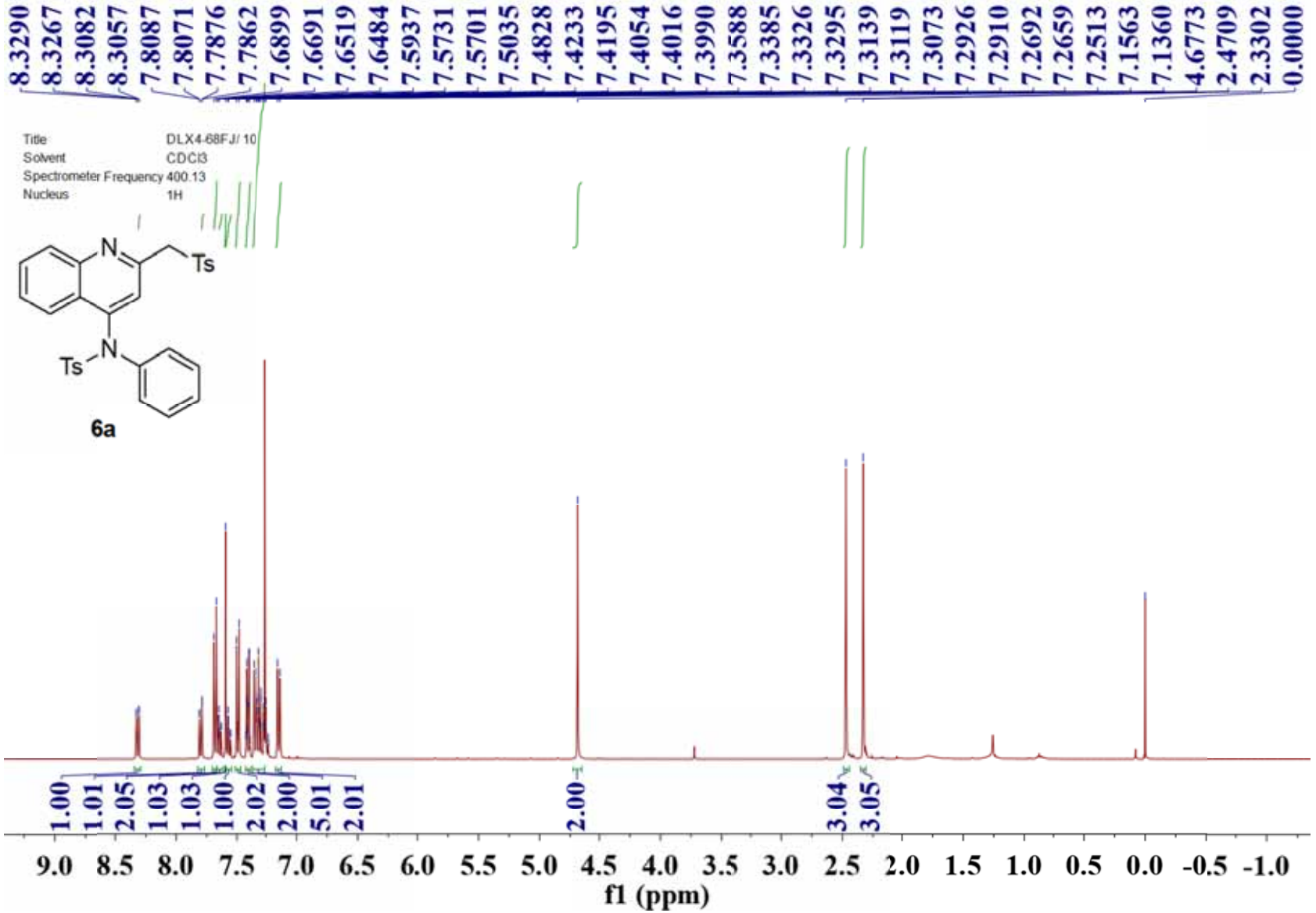

163.924
146.724
145.676
144.940
143.376
141.390
140.706
140.674
140.613
136.359
135.719
134.778
134.717
130.606
130.516
130.343
130.151
129.796
128.480
128.013
127.245
127.144
126.323
126.238
126.209
117.850
116.955
114.737
114.527
111.252
111.023
103.104
102.818
99.487
77.517
77.200
76.882
21.868
21.845
21.674
Title DLX6-46B.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
F
N
Ts
N
F
Ts
N
Ts
F
5p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

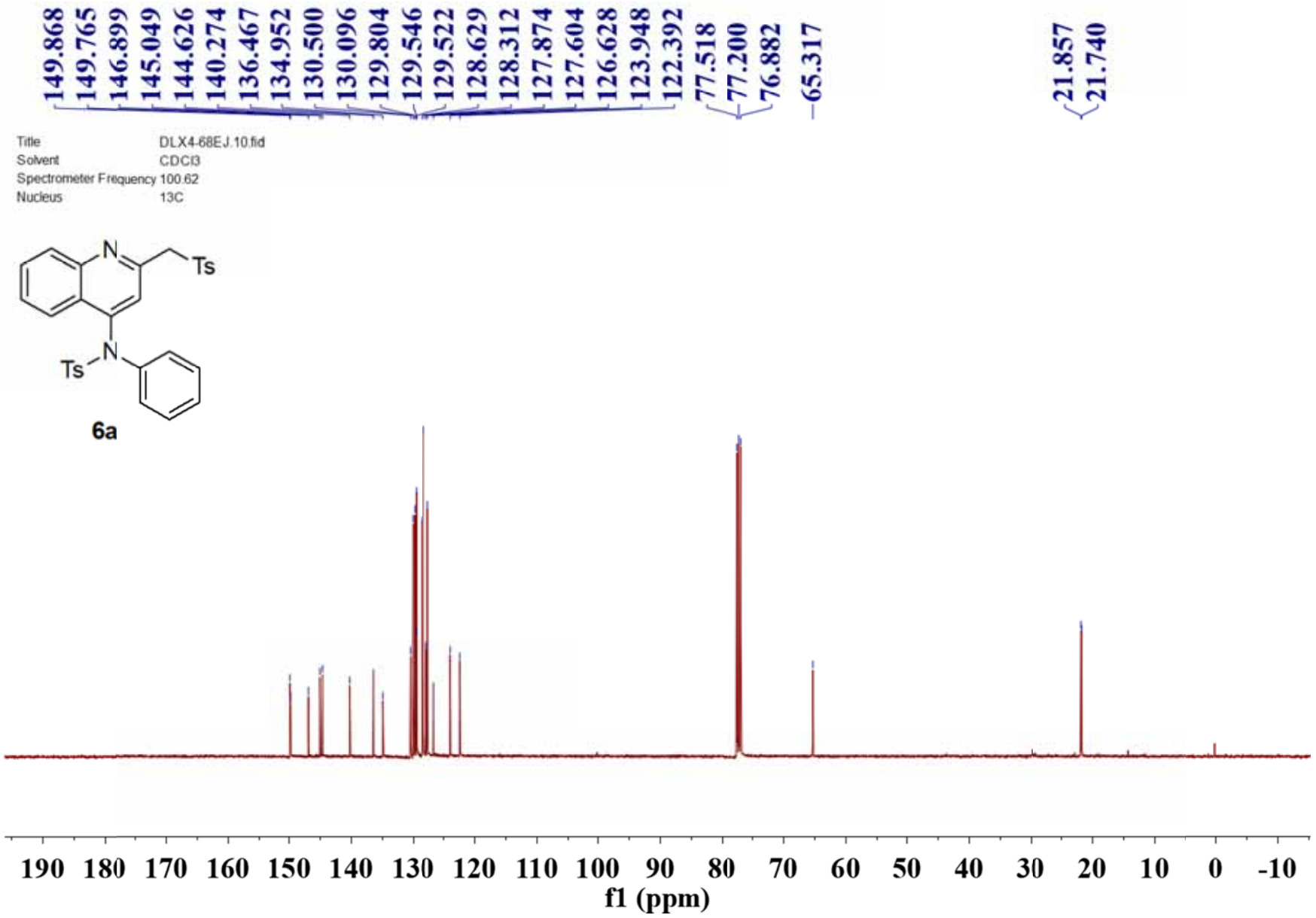

-105.5128
-110.0787
-111.1027
Title WD6-46.11.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
F
N
Ts
F
N
Ts
N
Ts
F
5p
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

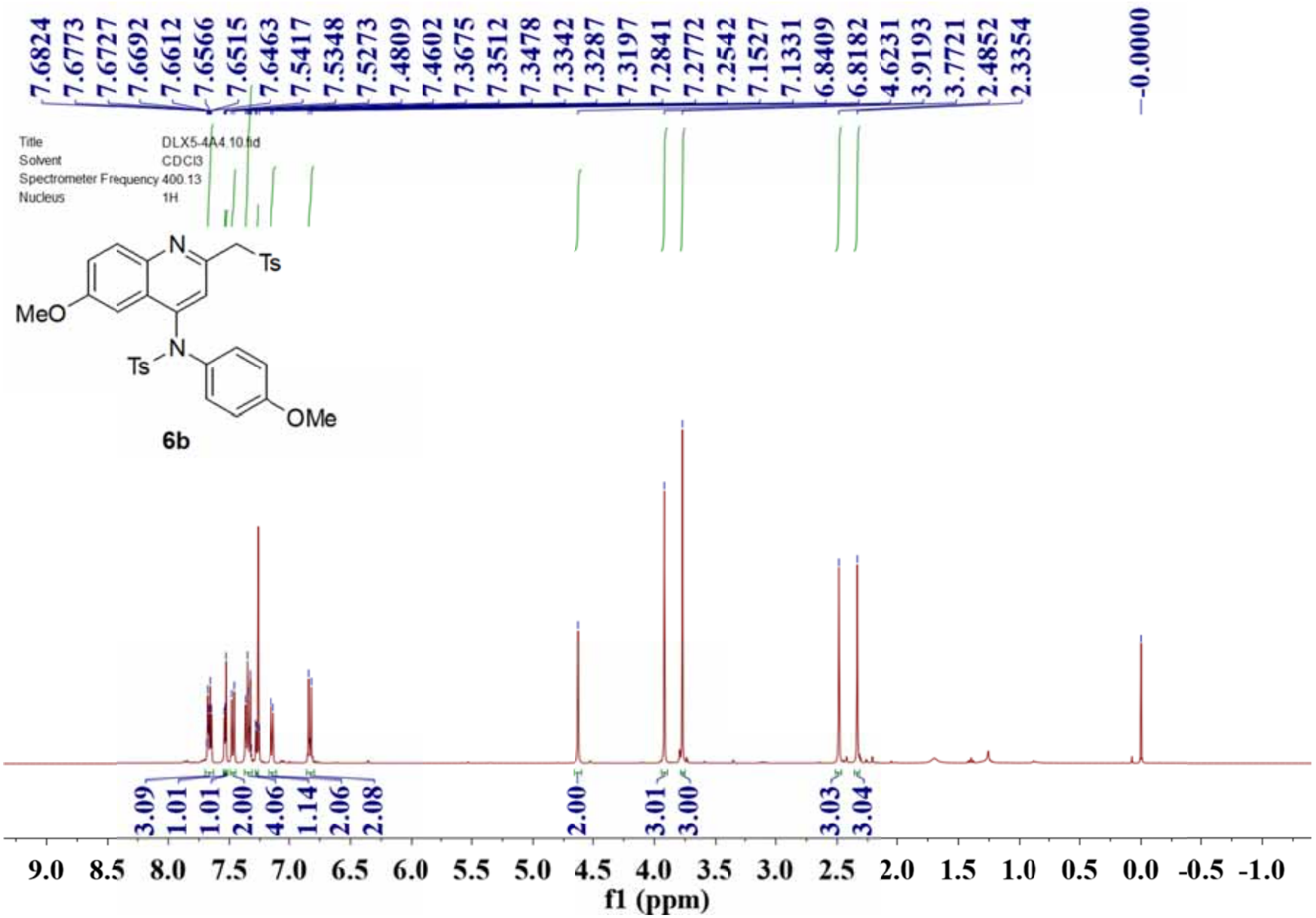

7.6666
7.6462
7.4865
7.4666
7.4358
7.4154
7.3724
7.3059
7.2861
7.2575
7.2394
7.2339
7.1564
7.1043
7.0847
7.0171
6.9653
6.9452
6.8759
6.8133
6.7572
6.7117
5.8110
5.8063
5.6621
5.0528
5.0477
2.8059
2.6942
2.4553
2.4032
2.3837
2.3377
2.2821
2.2495
2.2123
2.1827
2.1529
1.9233
-0.0000
Title DLX6-45B2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
Ts
N
Me
N
Ts
Me
Ts
N
Me
Me
5r (major and minor)
4.03
12.08
20.04
7.04
8.08
14.03
2.01
2.00
2.00
0.98
0.98
2.00
1.00
3.00
6.02
7.01
6.00
3.01
12.01
6.06
3.06
28.99
6.01
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)

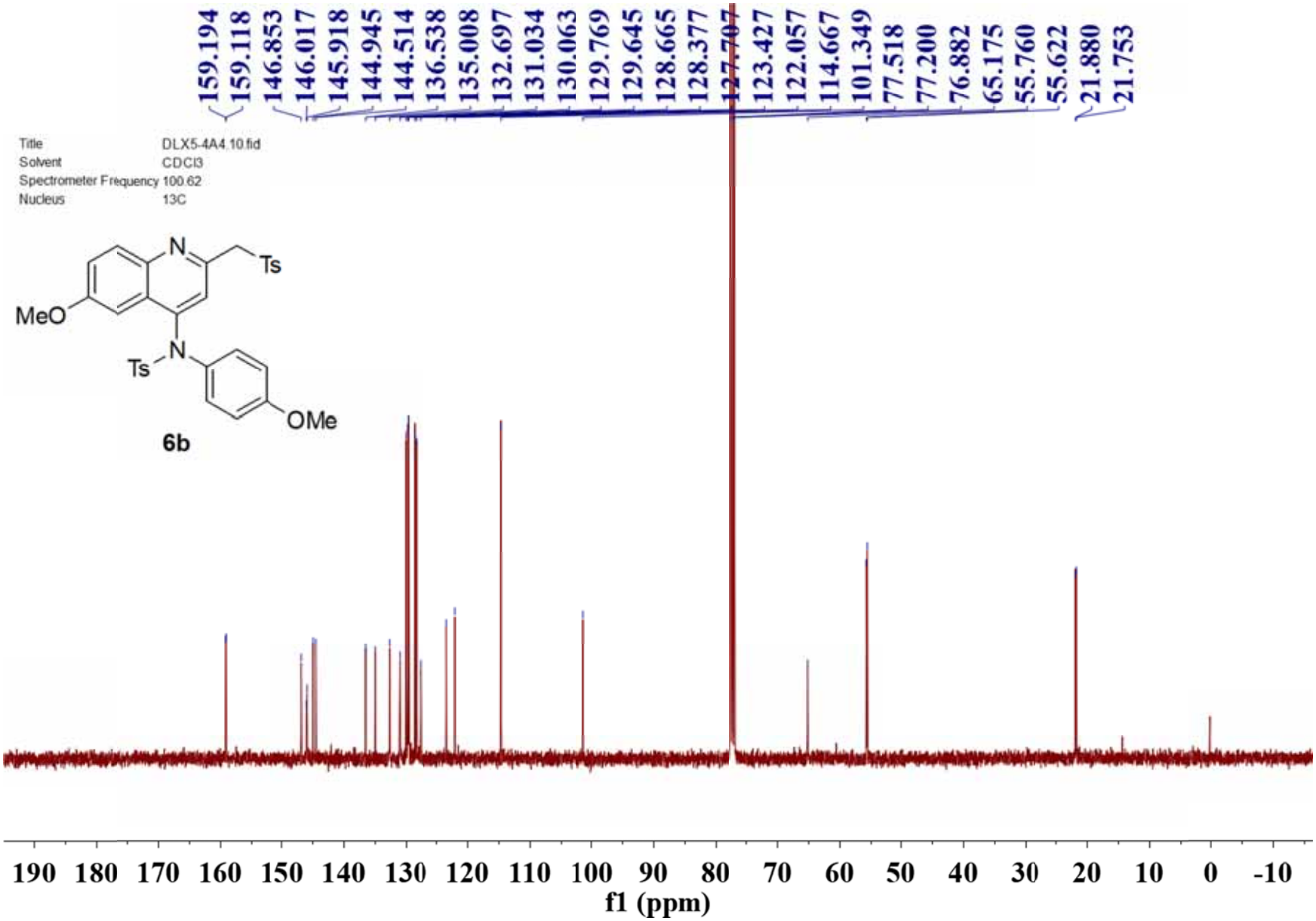

147.441
144.236
142.287
140.653
138.723
136.401
136.084
135.885
135.661
131.511
129.976
129.924
129.686
129.490
129.320
129.261
128.496
128.274
128.201
128.134
128.012
126.558
125.882
125.770
120.182
119.103
115.347
95.431
77.519
77.200
76.882
23.124
21.786
21.698
21.653
21.613
21.539
21.468
21.184
20.845
Title DLX6-45B.11.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
Ts
N
Me
N
Ts
Me
Ts
N
Me
Me
5r (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

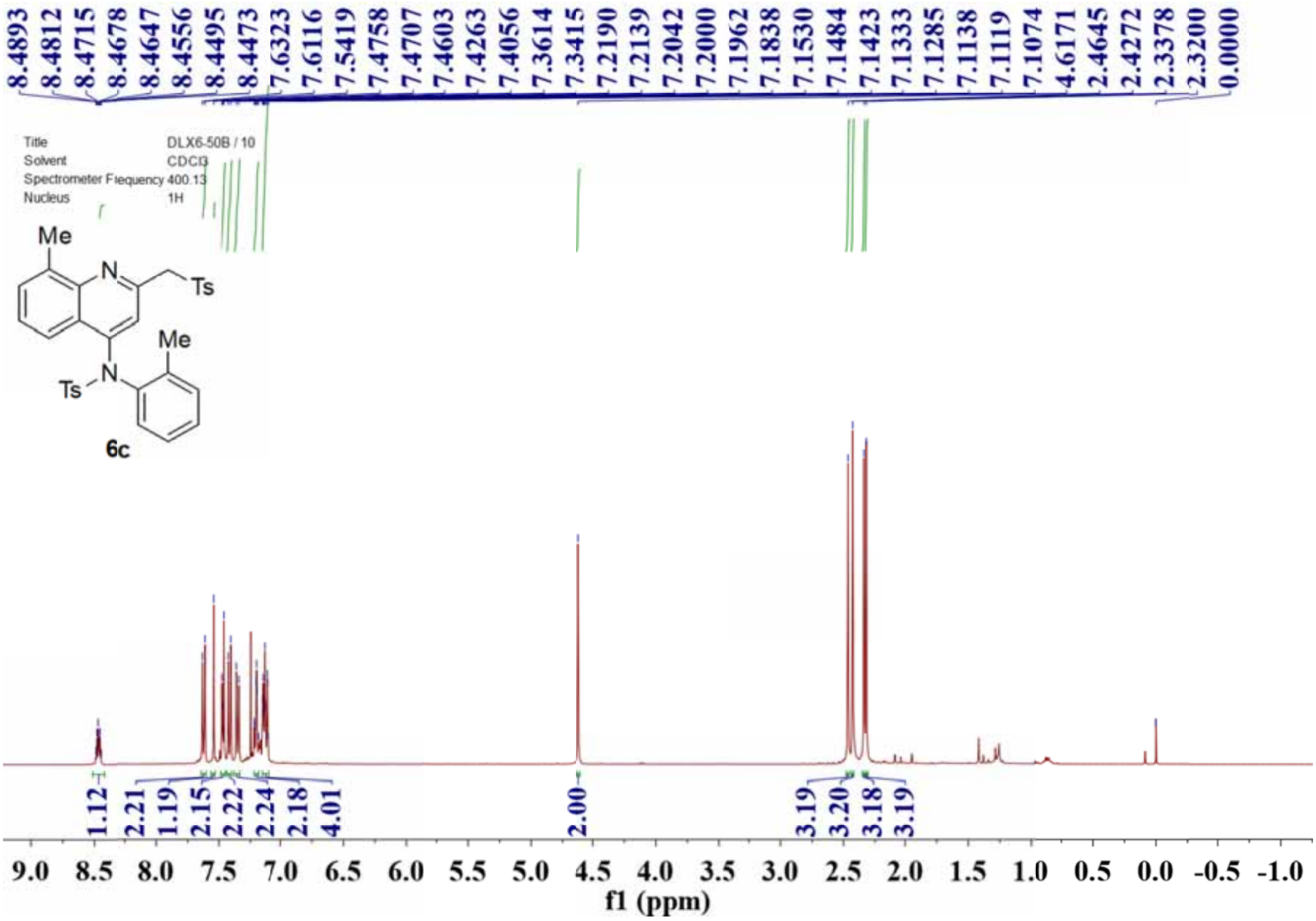
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of 4-Aminoquinolines 6.

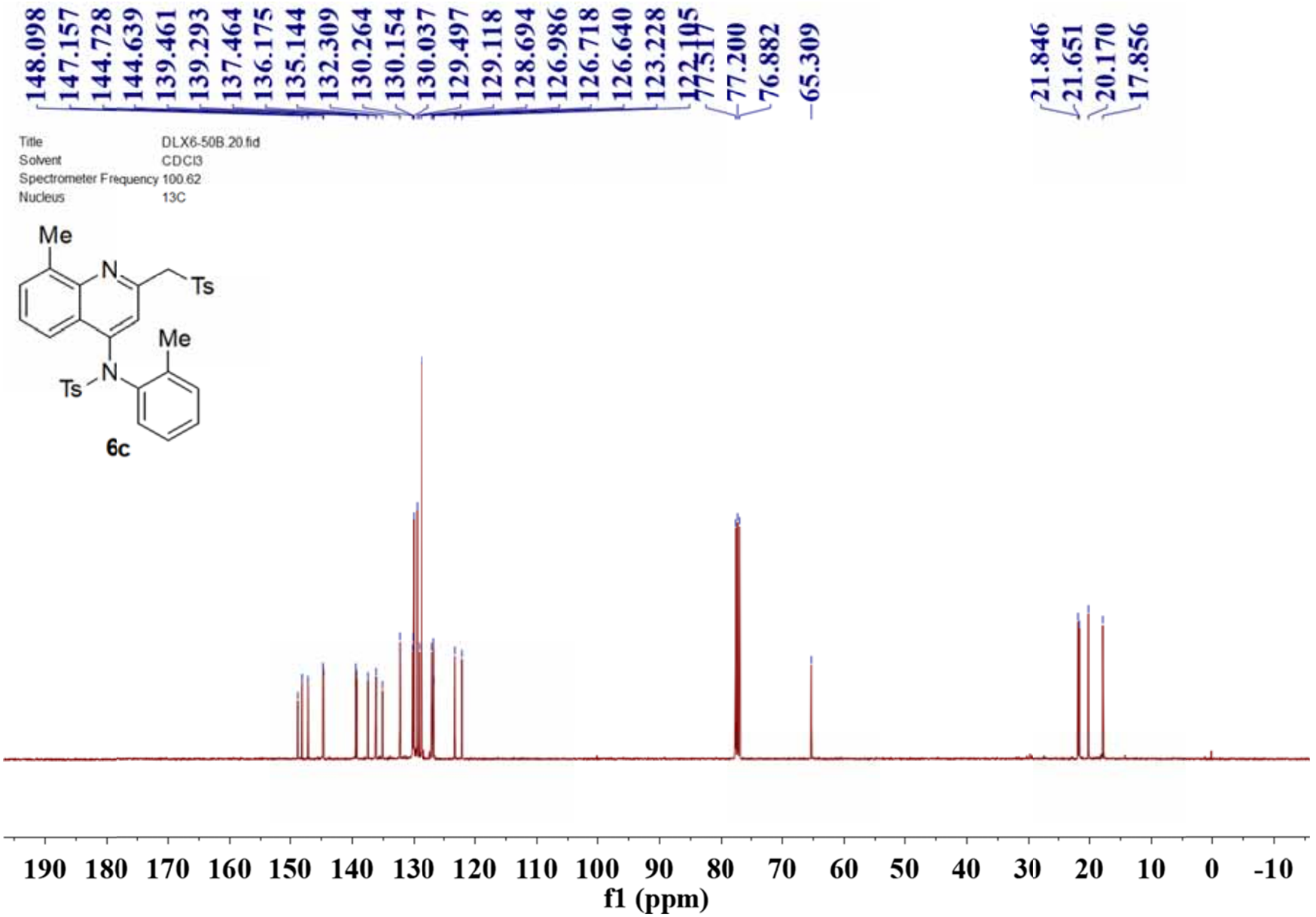


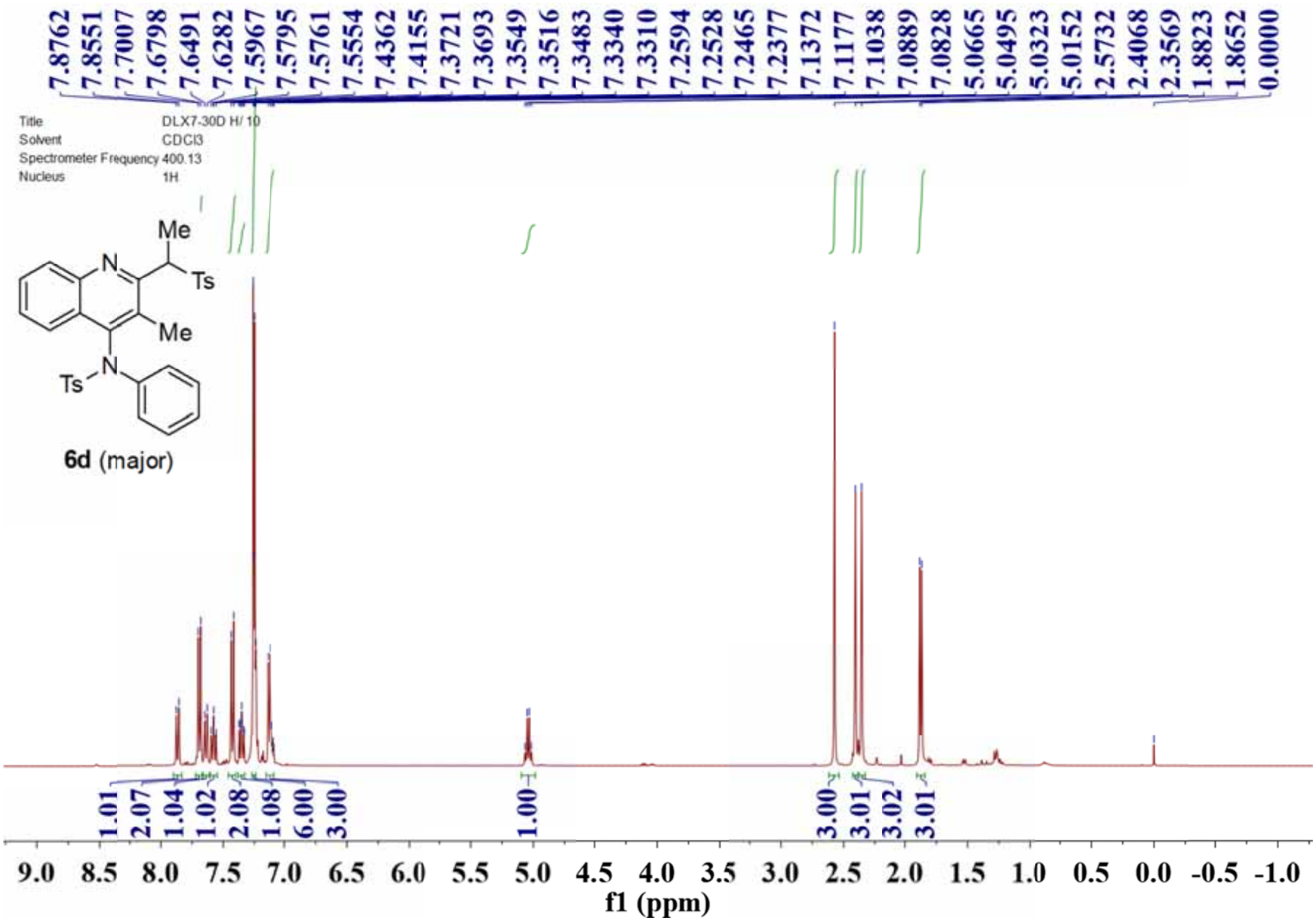

149.868
149.765
146.899
145.049
144.626
140.274
136.467
134.952
130.500
130.096
129.804
129.546
129.522
128.629
128.312
127.874
127.604
126.628
123.948
122.392
77.518
77.200
76.882
65.317
21.857
21.740
Title DLX4-68EJ.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Ts
N
Ts
6a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

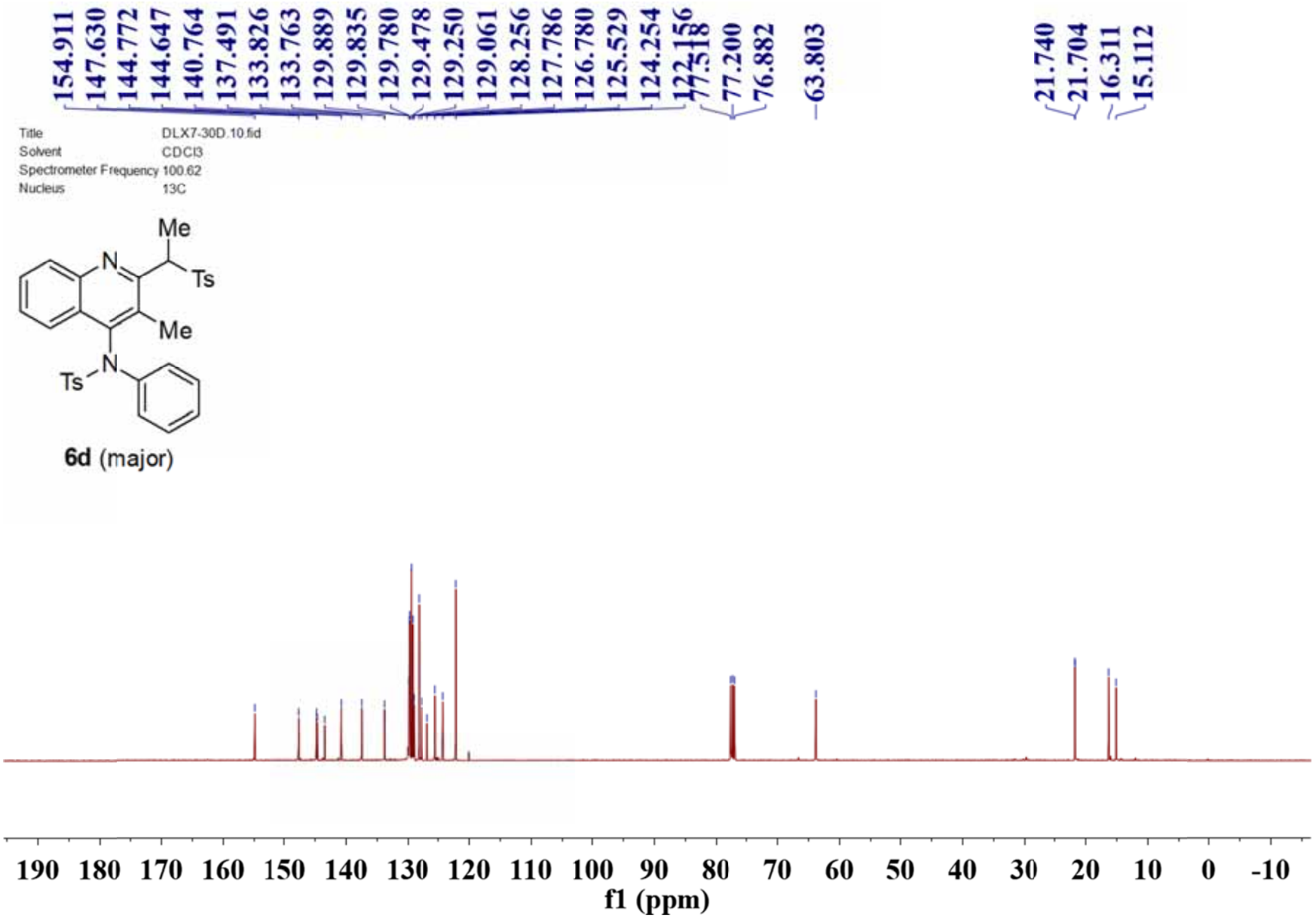

7.6824
7.6773
7.6727
7.6692
7.6612
7.6566
7.6515
7.6463
7.5417
7.5348
7.5273
7.4809
7.4602
7.3675
7.3512
7.3478
7.3342
7.3287
7.3197
7.2841
7.2772
7.2542
7.1527
7.1331
6.8409
6.8182
4.6231
3.9193
3.7721
2.4852
2.3354
-0.0000
Title DLX5-4A4.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Ts
MeO
N
Ts
OMe
6b
3.09
1.01
1.01
2.00
4.06
1.14
2.06
2.08
2.00
3.01
3.00
3.03
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)

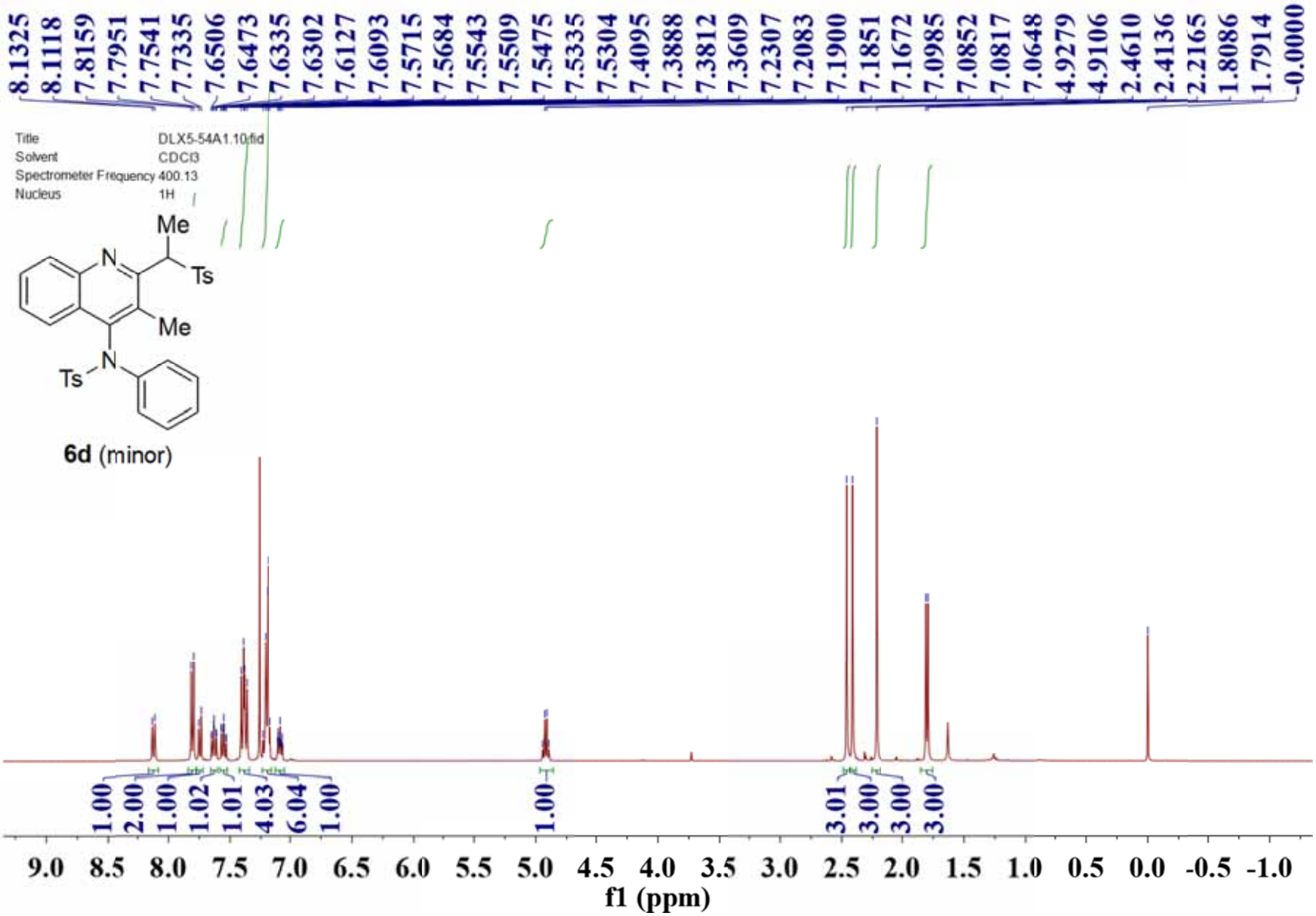

159.194
159.118
146.853
146.017
145.918
144.945
144.514
136.538
135.008
132.697
131.034
130.063
129.769
129.645
128.665
128.377
127.707
123.427
122.057
114.667
101.349
77.518
77.200
76.882
65.175
55.760
55.622
21.880
21.753
Title DLX5-4A4.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Ts
MeO
N
Ts
OMe
6b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

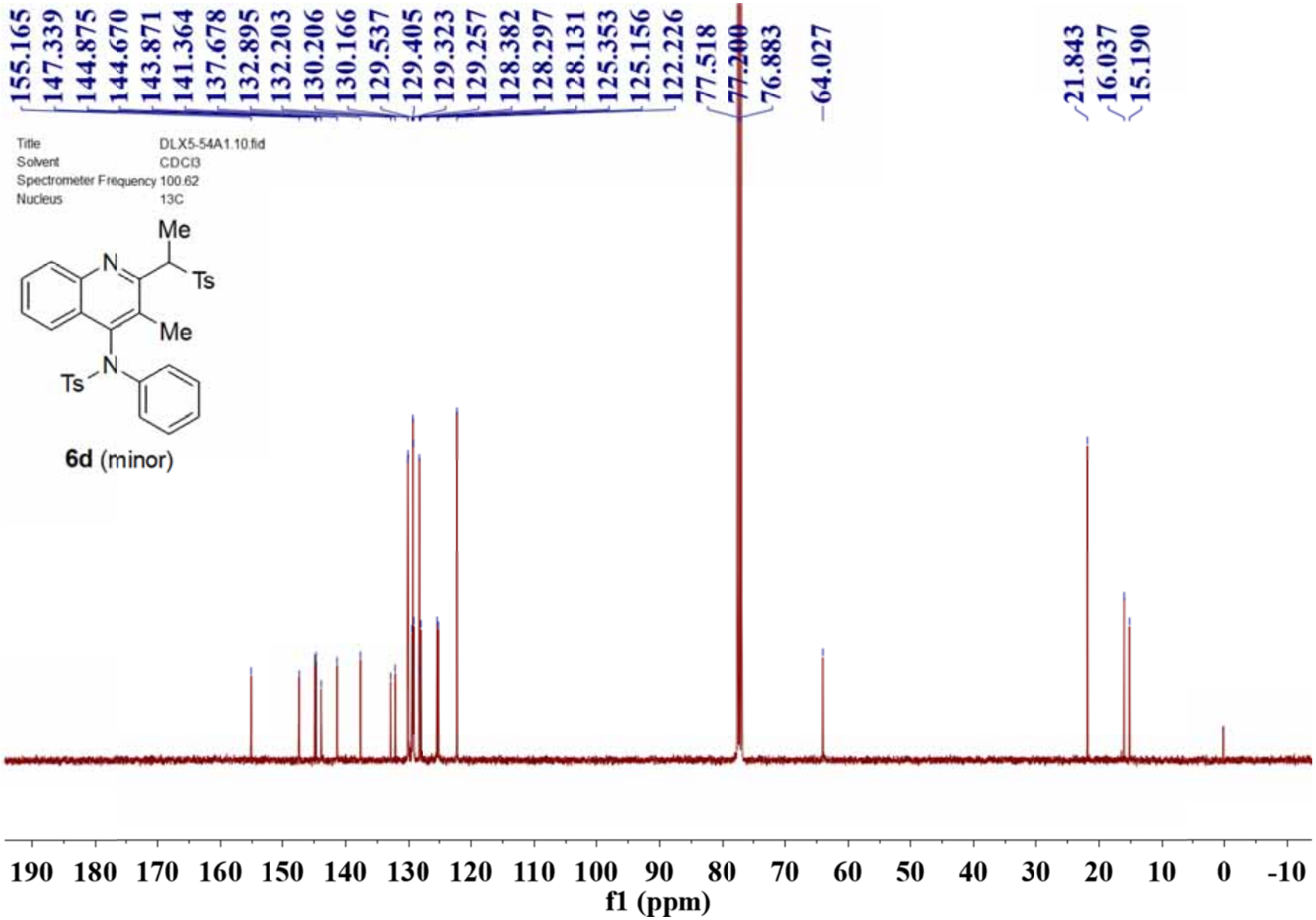

8.4893
8.4812
8.4715
8.4678
8.4647
8.4556
8.4495
8.4473
7.6323
7.6116
7.5419
7.4758
7.4707
7.4603
7.4263
7.4056
7.3614
7.3415
7.2190
7.2139
7.2042
7.2000
7.1962
7.1838
7.1530
7.1484
7.1423
7.1333
7.1285
7.1138
7.1119
7.1074
4.6171
2.4645
2.4272
2.3378
2.3200
0.0000
Title DLX6-50B / 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Me
Ts
N
6c
1.12
2.21
1.19
2.15
2.22
2.24
2.18
4.01
2.00
3.19
3.20
3.18
3.19
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)

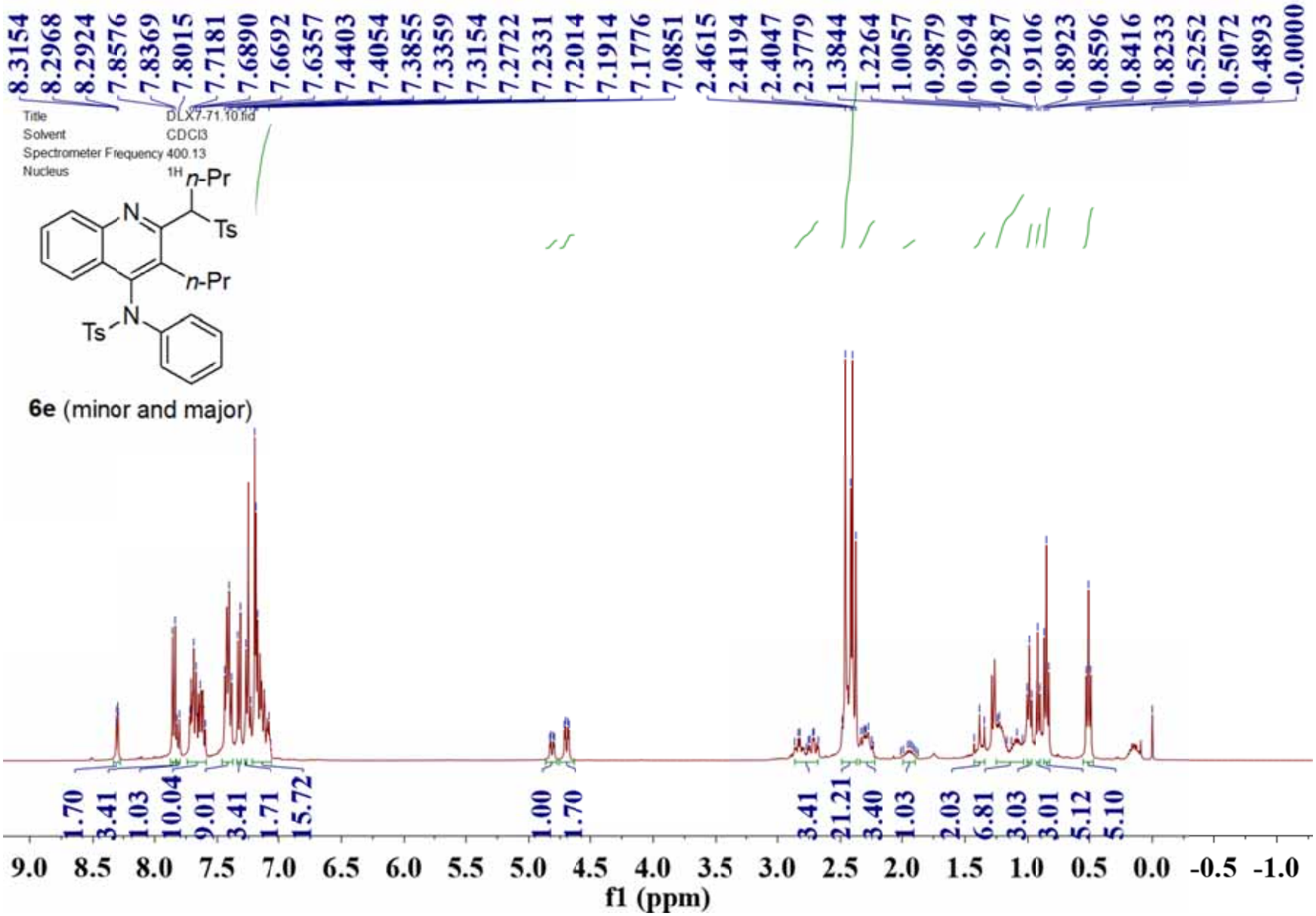

148.098
147.157
144.728
144.639
139.461
139.293
137.464
136.175
135.144
132.309
130.264
130.154
130.037
129.497
129.118
128.694
126.986
126.718
126.640
123.228
122.105
77.517
77.200
76.882
65.309
21.846
21.651
20.170
17.856
Title DLX6-50B.20.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Me
N
Ts
6c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

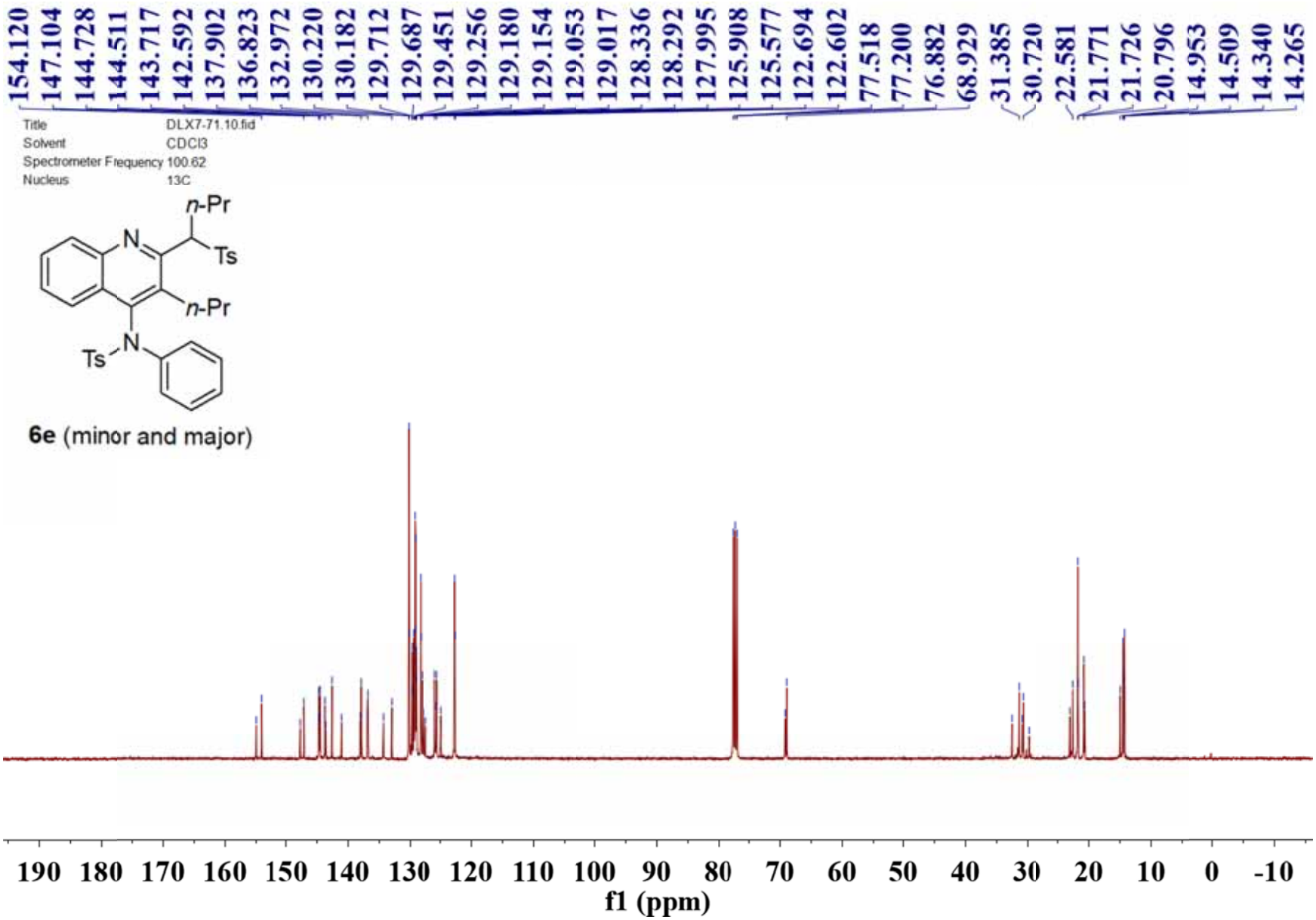

7.8762
7.8551
7.7007
7.6798
7.6491
7.6282
7.5967
7.5795
7.5761
7.5554
7.4362
7.4155
7.3721
7.3693
7.3549
7.3516
7.3483
7.3340
7.3310
7.2594
7.2528
7.2465
7.2377
7.1372
7.1177
7.1038
7.0889
7.0828
5.0665
5.0495
5.0323
5.0152
2.5732
2.4068
2.3569
1.8823
1.8652
0.0000
Title DLX7-30D H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Me
Ts
N
6d (major)
1.01
2.07
1.04
1.02
2.08
1.08
6.00
3.00
1.00
3.00
3.01
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)

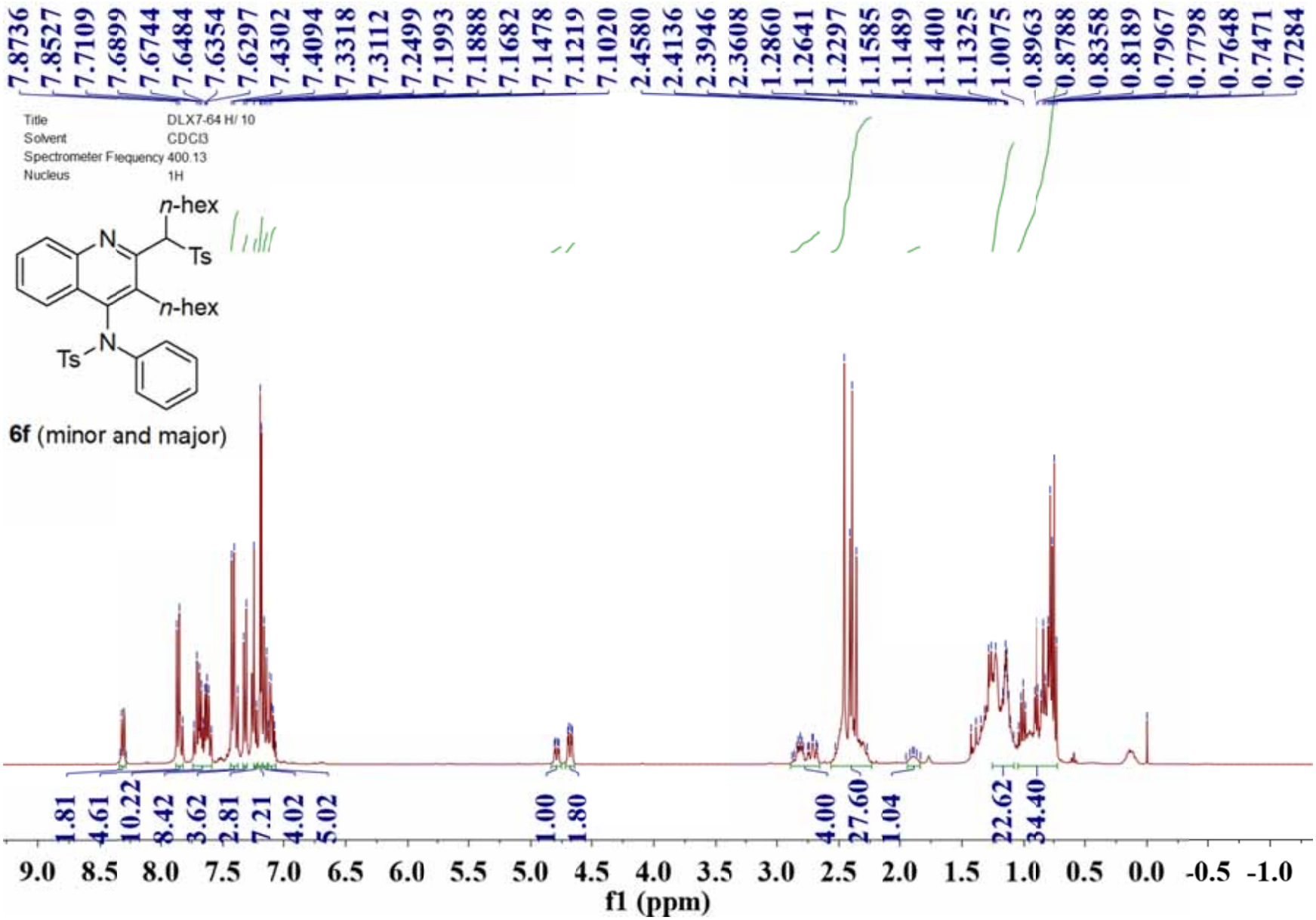

154.911
147.630
144.772
144.647
140.764
137.491
133.826
133.763
129.889
129.835
129.780
129.478
129.250
129.061
128.256
127.786
126.780
125.529
124.254
122.156
77.518
77.200
76.882
63.803
21.740
21.704
16.311
15.112
Title DLX7-30D.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Me
Ts
N
6d (major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

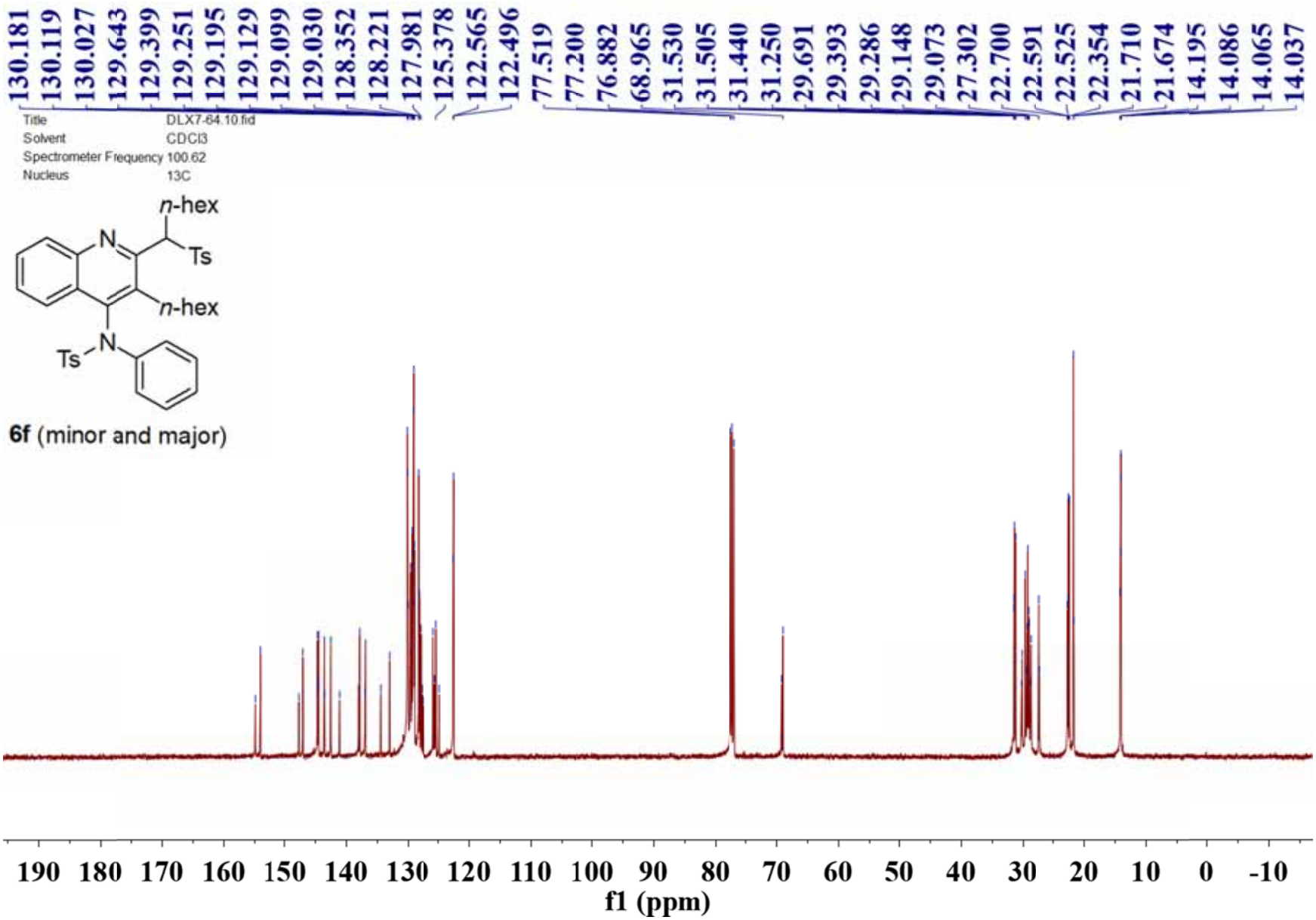

8.1325
8.1118
7.8159
7.7951
7.7541
7.7335
7.6506
7.6473
7.6335
7.6302
7.6127
7.6093
7.5715
7.5684
7.5543
7.5509
7.5475
7.5335
7.5304
7.4095
7.3888
7.3812
7.3609
7.2307
7.2083
7.1900
7.1851
7.1672
7.0985
7.0852
7.0817
7.0648
4.9279
4.9106
2.4610
2.4136
2.2165
1.8086
1.7914
-0.0000
Title DLX5-54A1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Me
Ts
N
6d (minor)
1.00
2.00
1.00
1.02
1.01
4.03
6.04
1.00
1.00
3.01
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)

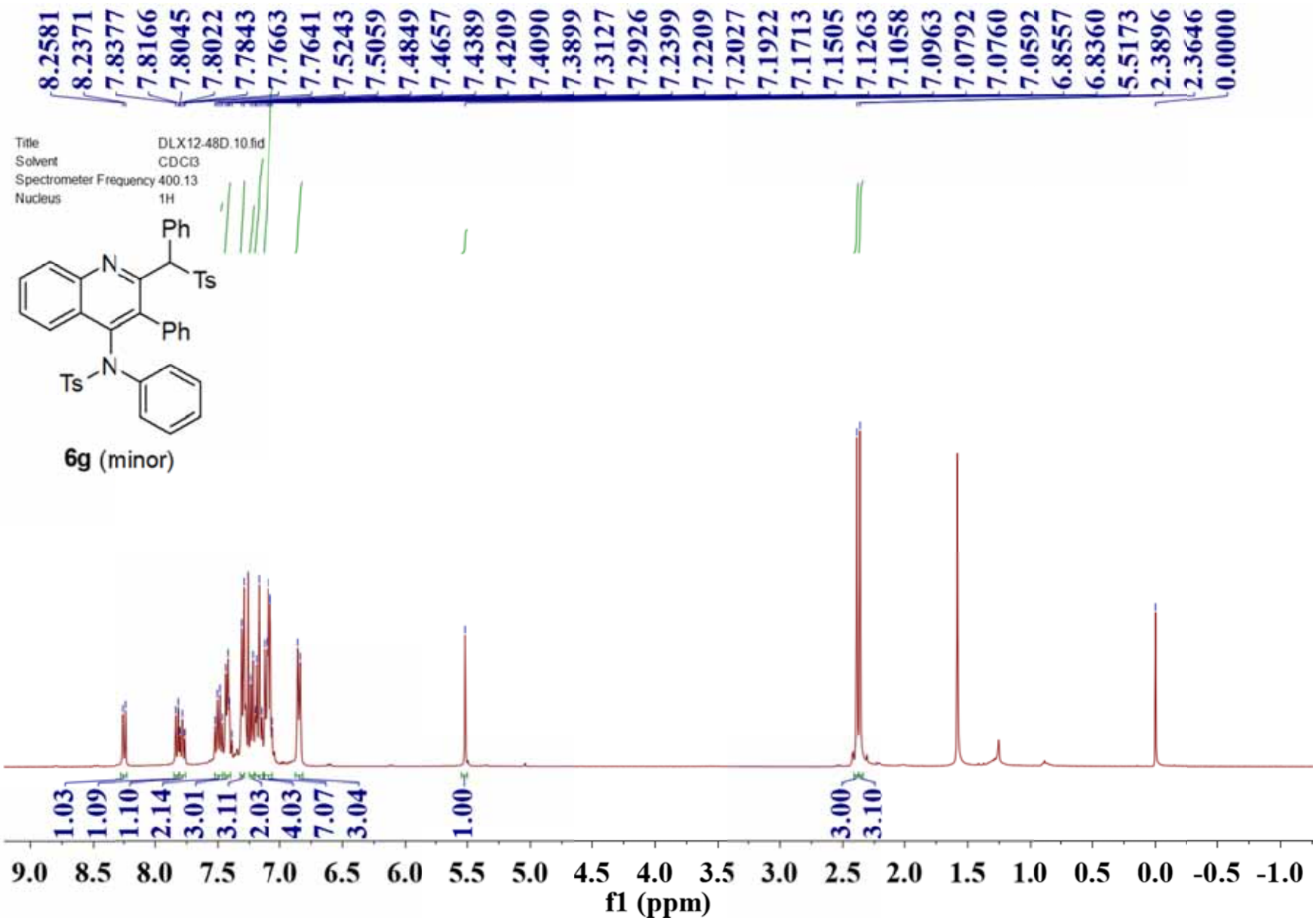

155.165
147.339
144.875
144.670
143.871
141.364
137.678
132.895
132.203
130.206
130.166
129.537
129.405
129.323
129.257
128.382
128.297
128.131
125.353
125.156
122.226
77.518
77.200
76.883
64.027
21.843
16.037
15.190
Title DLX5-54A1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Me
Ts
N
6d (minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

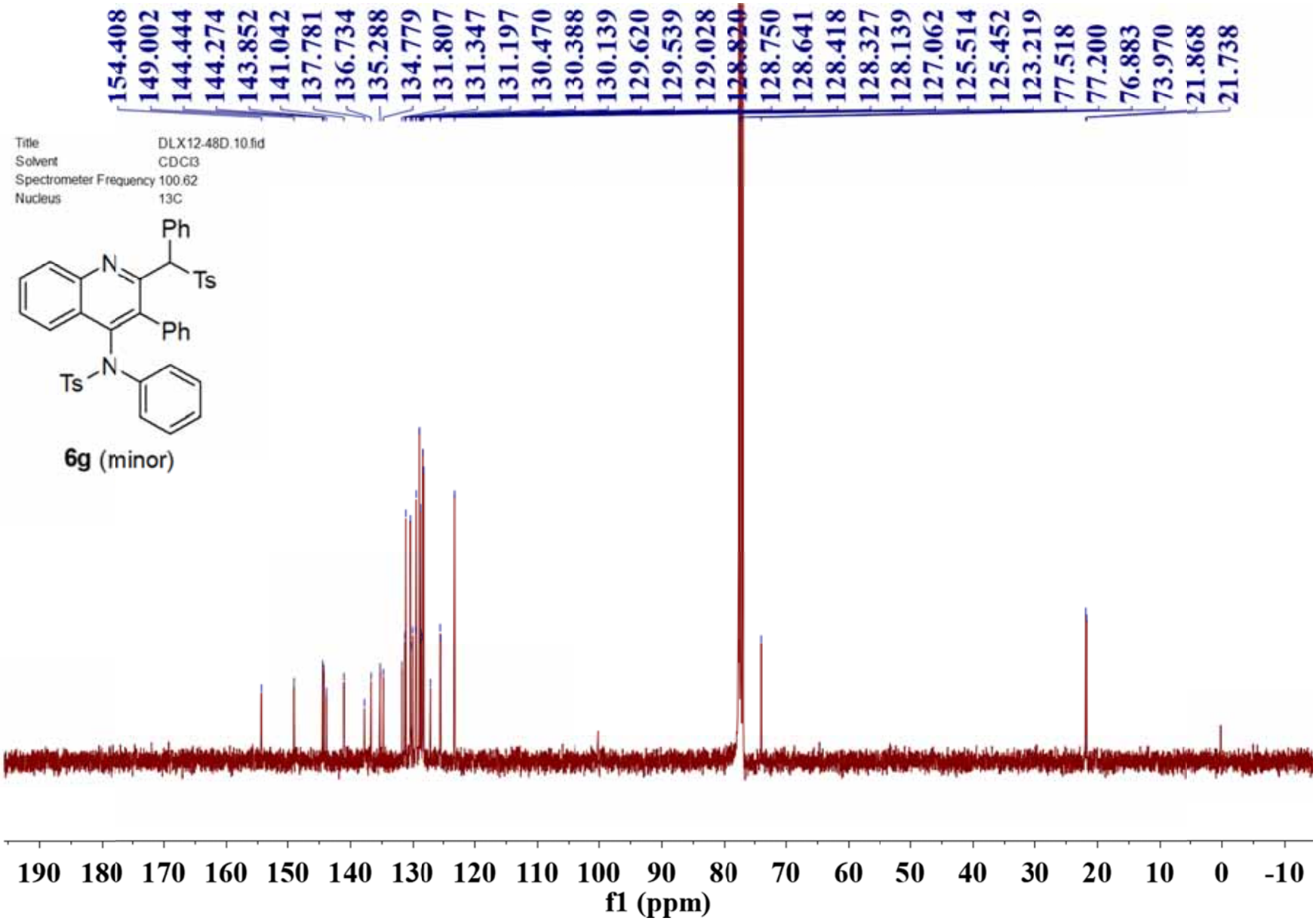

8.3154
8.2968
8.2924
7.8576
7.8369
7.8015
7.7181
7.6890
7.6692
7.6357
7.4403
7.4054
7.3855
7.3359
7.3154
7.2722
7.2331
7.2014
7.1914
7.1776
7.0851
2.4615
2.4194
2.4047
2.3779
1.3844
1.2264
1.0057
0.9879
0.9694
0.9287
0.9106
0.8923
0.8596
0.8416
0.8233
0.5252
0.5072
0.4893
-0.0000
Title DLX7-71.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-Pr
N
Ts
n-Pr
Ts
N
6e (minor and major)
1.70
3.41
1.03
10.04
9.01
3.41
1.71
15.72
1.00
1.70
3.41
21.21
3.40
1.03
2.03
6.81
3.03
3.01
5.12
5.10
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)

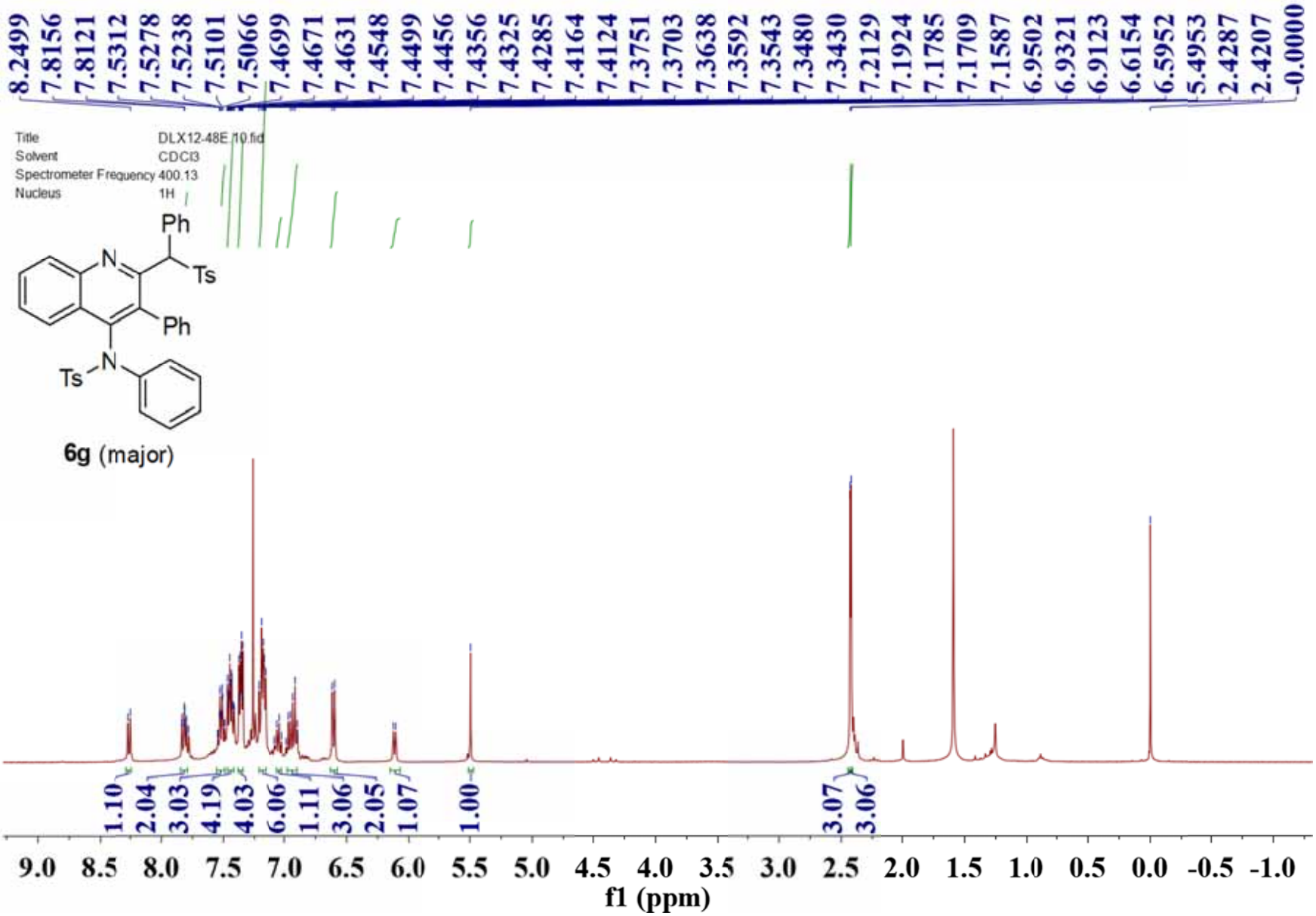

154.120
147.104
144.728
144.511
143.717
142.592
137.902
136.823
132.972
130.220
130.182
129.712
129.687
129.451
129.256
129.180
129.154
129.053
129.017
128.336
128.292
127.995
125.908
125.577
122.694
122.602
77.518
77.200
76.882
68.929
31.385
30.720
22.581
21.771
21.726
20.796
14.953
14.509
14.340
14.265
Title DLX7-71.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-Pr
N
Ts
n-Pr
Ts
N
6e (minor and major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

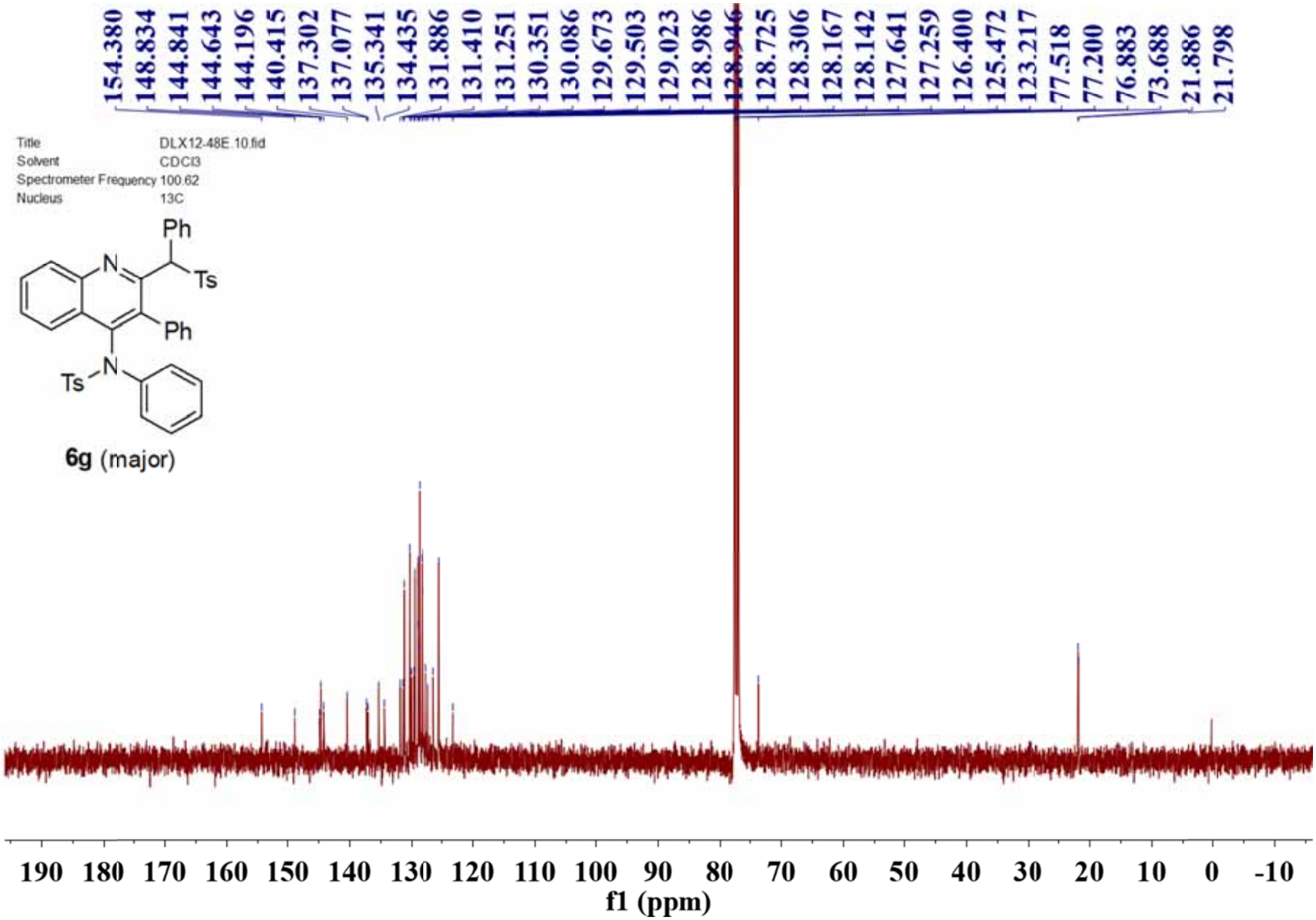

7.8736
7.8527
7.7109
7.6899
7.6744
7.6484
7.6354
7.6297
7.4302
7.4094
7.3318
7.3112
7.2499
7.1993
7.1888
7.1682
7.1478
7.1219
7.1020
2.4580
2.4136
2.3946
2.3608
1.2860
1.2641
1.2297
1.1585
1.1489
1.1400
1.1325
1.0075
0.8963
0.8788
0.8358
0.8189
0.7967
0.7798
0.7648
0.7471
0.7284
Title DLX7-64 H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
N
Ts
n-hex
Ts
N
6f (minor and major)
1.81
4.61
10.22
8.42
3.62
2.81
7.21
4.02
5.02
1.00
1.80
4.00
27.60
1.04
22.62
34.40
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)

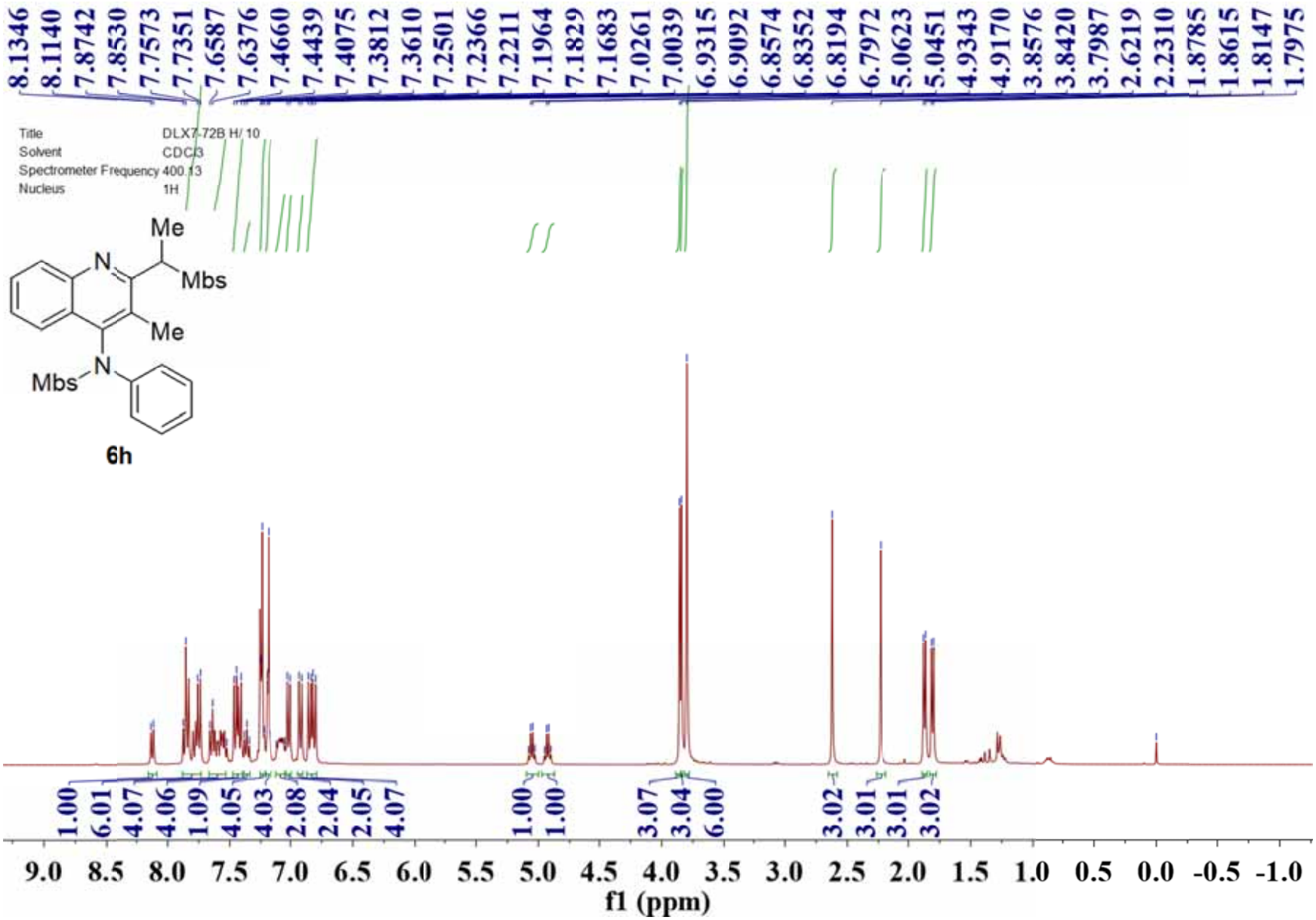

130.181
130.119
130.027
129.643
129.399
129.251
129.195
129.129
129.099
129.030
128.352
128.221
127.981
125.378
122.565
122.496
77.519
77.200
76.882
68.965
31.530
31.505
31.440
31.250
29.691
29.393
29.286
29.148
29.073
27.302
22.700
22.591
22.525
22.354
21.710
21.674
14.195
14.086
14.065
14.037
Title DLX7-64.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
N
Ts
n-hex
Ts
N
6f (minor and major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

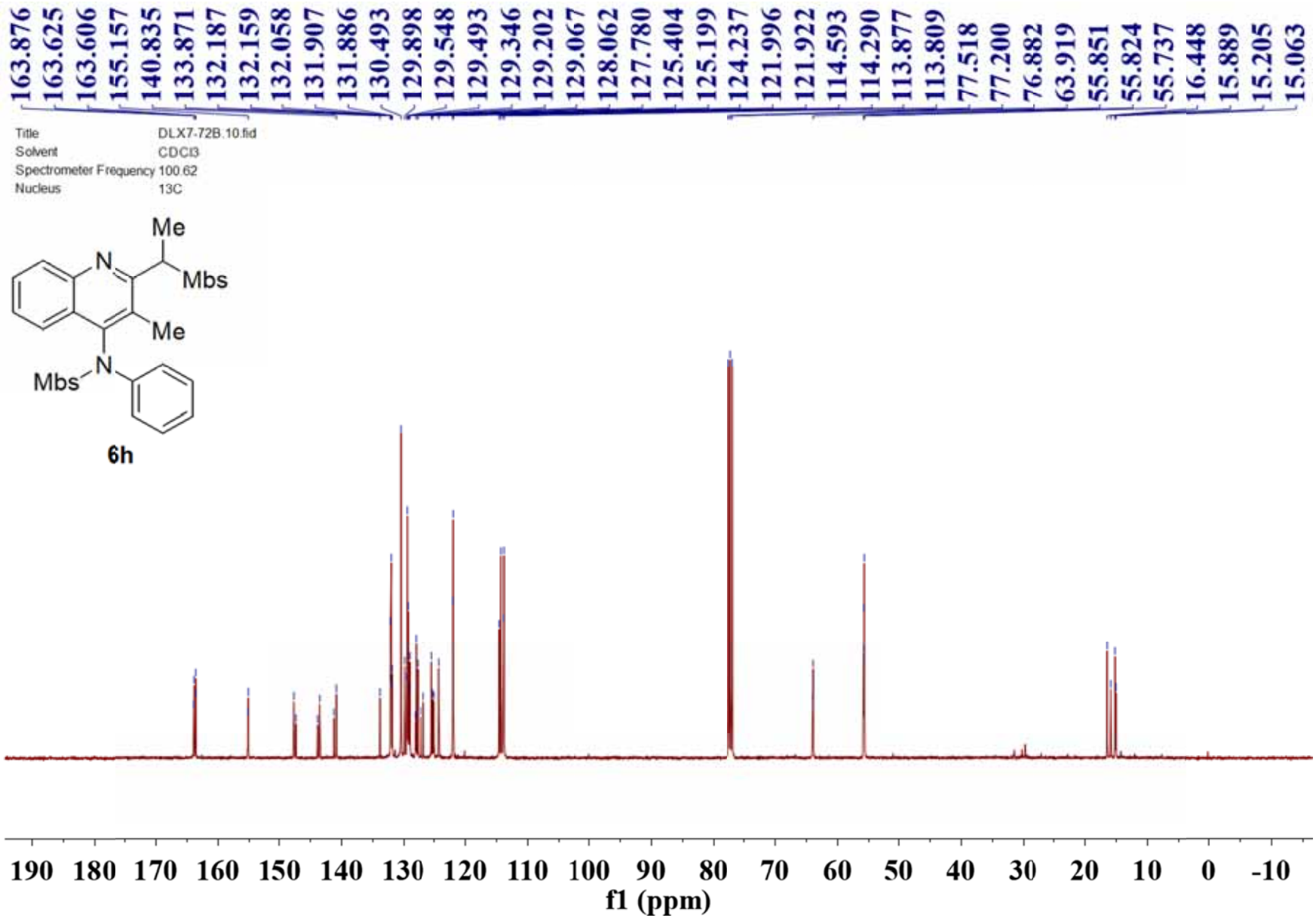

8.2581
8.2371
7.8377
7.8166
7.8045
7.8022
7.7843
7.7663
7.7641
7.5243
7.5059
7.4849
7.4657
7.4389
7.4209
7.4090
7.3899
7.3127
7.2926
7.2399
7.2209
7.2027
7.1922
7.1713
7.1505
7.1263
7.1058
7.0963
7.0792
7.0760
7.0592
6.8557
6.8360
5.5173
2.3896
2.3646
0.0000
Title DLX12-48D.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
Ts
Ph
Ts
N
N
6g (minor)
1.03
1.09
1.10
2.14
3.01
3.11
2.03
4.03
7.07
3.04
1.00
3.00
3.10
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)

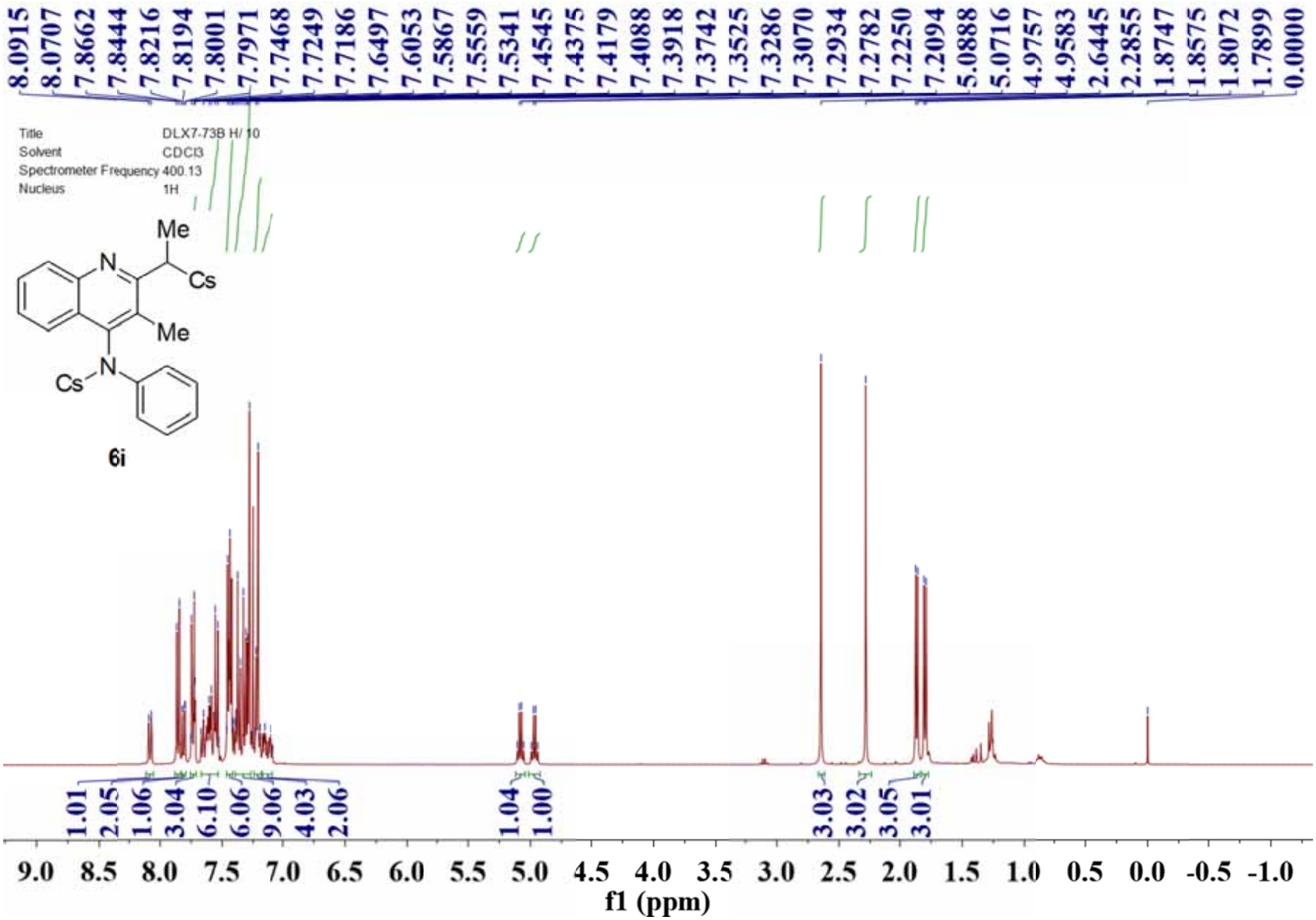

154.408
149.002
144.444
144.274
143.852
141.042
137.781
136.734
135.288
134.779
131.807
131.347
131.197
130.470
130.388
130.139
129.620
129.539
129.028
128.820
128.750
128.641
128.418
128.327
128.139
127.062
125.514
125.452
123.219
77.518
77.200
76.883
73.970
21.868
21.738
Title DLX12-48D.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
Ts
Ph
Ts
N
N
6g (minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

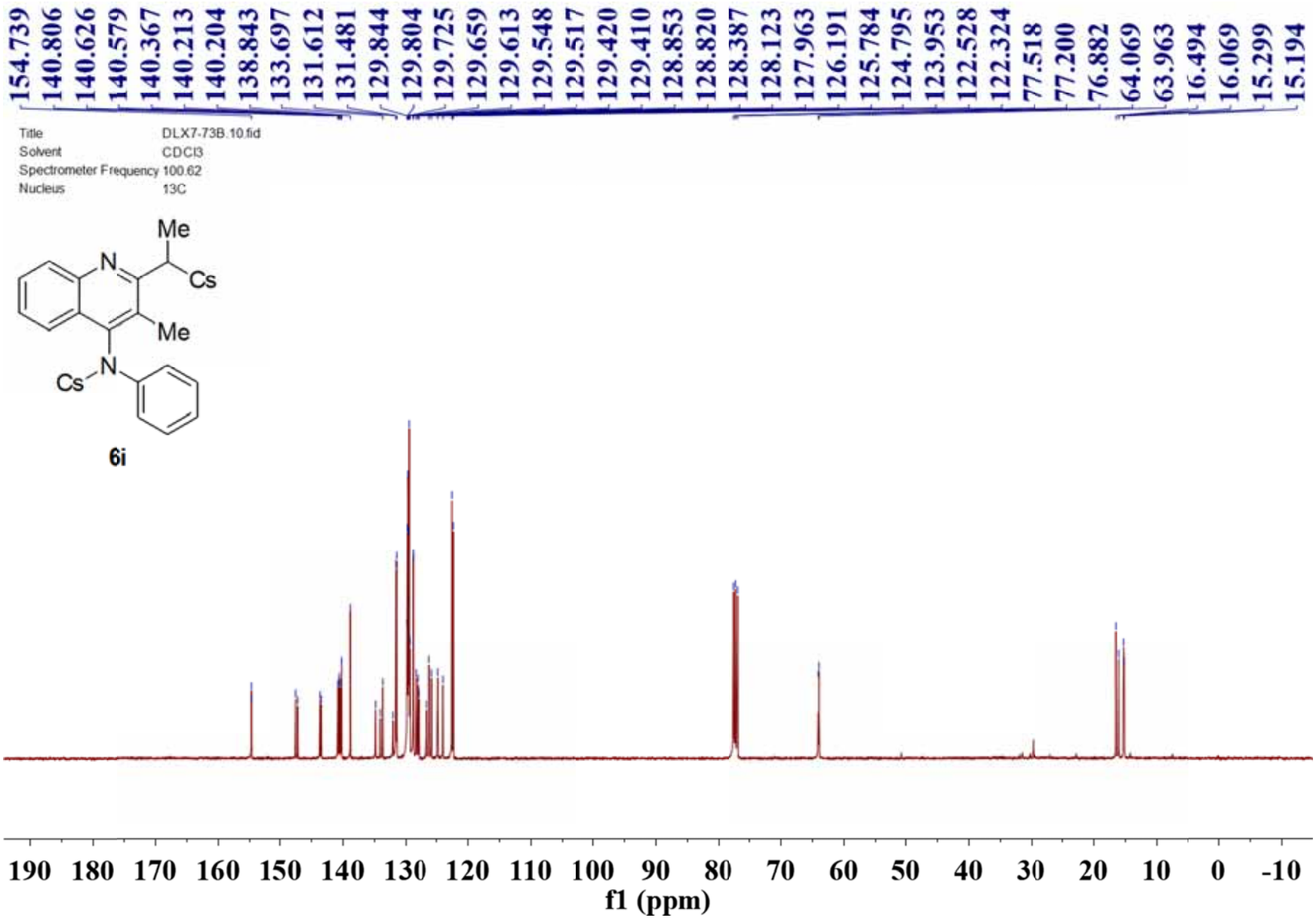

8.2499
7.8156
7.8121
7.5312
7.5278
7.5238
7.5101
7.5066
7.4699
7.4671
7.4631
7.4548
7.4499
7.4456
7.4356
7.4325
7.4285
7.4164
7.4124
7.3751
7.3703
7.3638
7.3592
7.3543
7.3480
7.3430
7.2129
7.1924
7.1785
7.1709
7.1587
6.9502
6.9321
6.9123
6.6154
6.5952
5.4953
2.4287
2.4207
-0.0000
Title DLX12-48E-10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Ph
N
Ts
Ph
Ts
N
6g (major)
1.10
2.04
3.03
4.19
4.03
6.06
1.11
3.06
2.05
1.07
1.00
3.07
3.06
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)

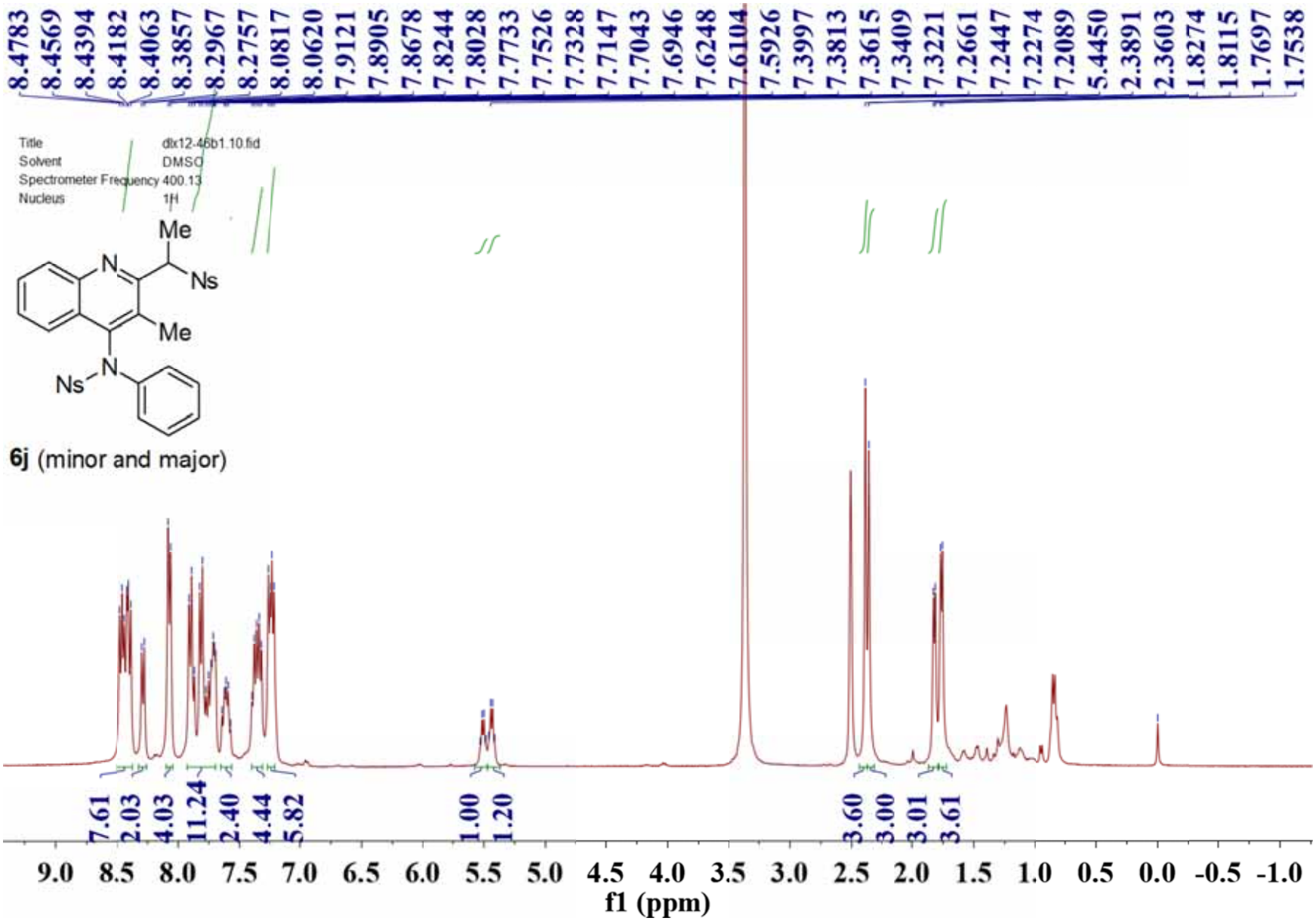

154.380
148.834
144.841
144.643
144.196
140.415
137.302
137.077
135.341
134.435
131.886
131.410
131.251
130.351
130.086
129.673
129.503
129.023
128.986
128.946
128.725
128.306
128.167
128.142
127.641
127.259
126.400
125.472
123.217
77.518
77.200
76.883
73.688
21.886
21.798
Title DLX12-48E.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Ph
N
Ts
Ph
Ts
N
6g (major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

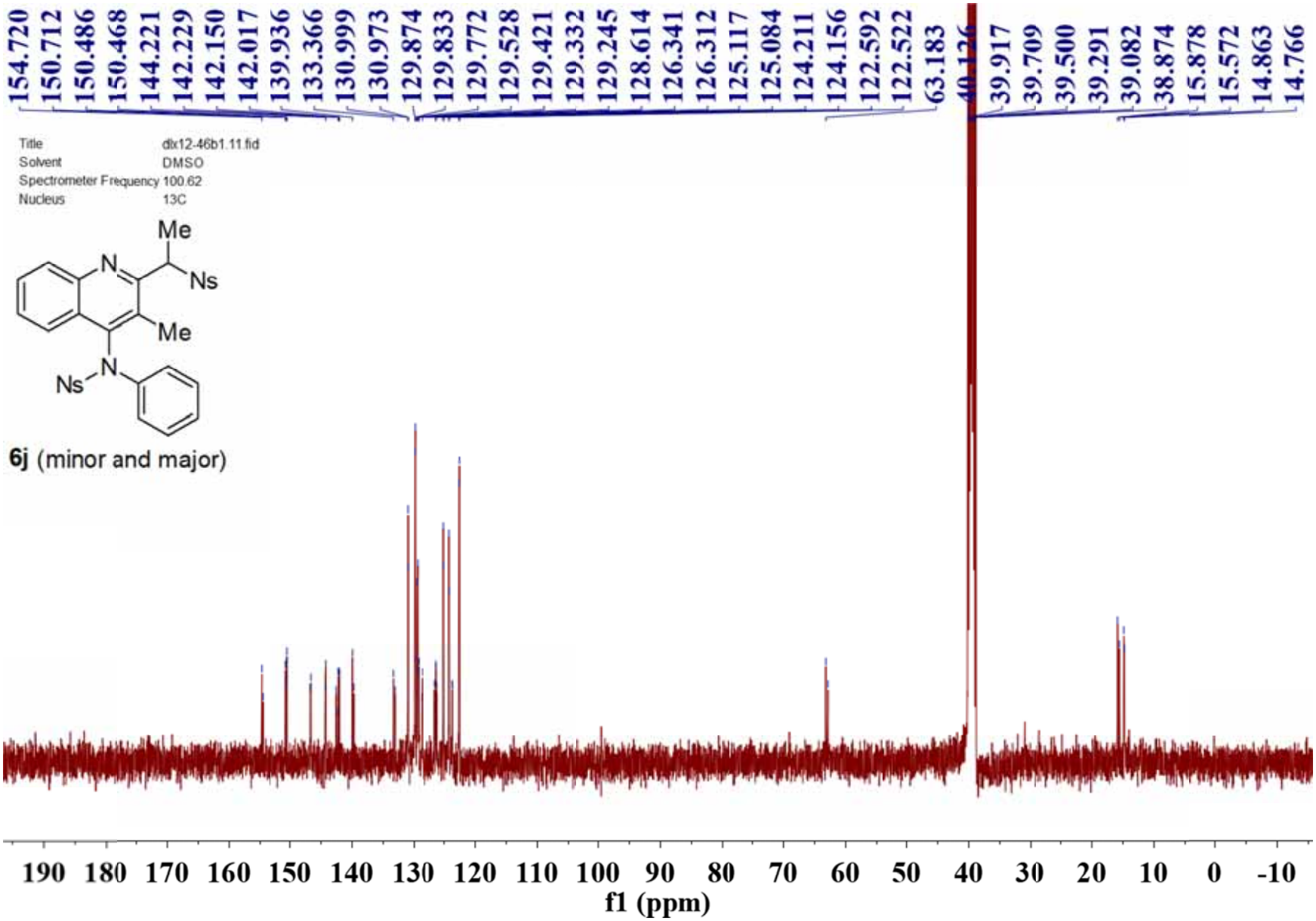

8.1346
8.1140
7.8742
7.8530
7.7573
7.7351
7.6587
7.6376
7.4660
7.4439
7.4075
7.3812
7.3610
7.2501
7.2366
7.2211
7.1964
7.1829
7.1683
7.0261
7.0039
6.9315
6.9092
6.8574
6.8352
6.8194
6.7972
5.0623
5.0451
4.9343
4.9170
3.8576
3.8420
3.7987
2.6219
2.2310
1.8785
1.8615
1.8147
1.7975
Title DLX7-72B H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Mbs
Me
Mbs
N
6h
1.00
6.01
4.07
4.06
1.09
4.05
4.03
2.08
2.04
2.05
4.07
1.00
1.00
3.07
3.04
6.00
3.02
3.01
3.01
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)

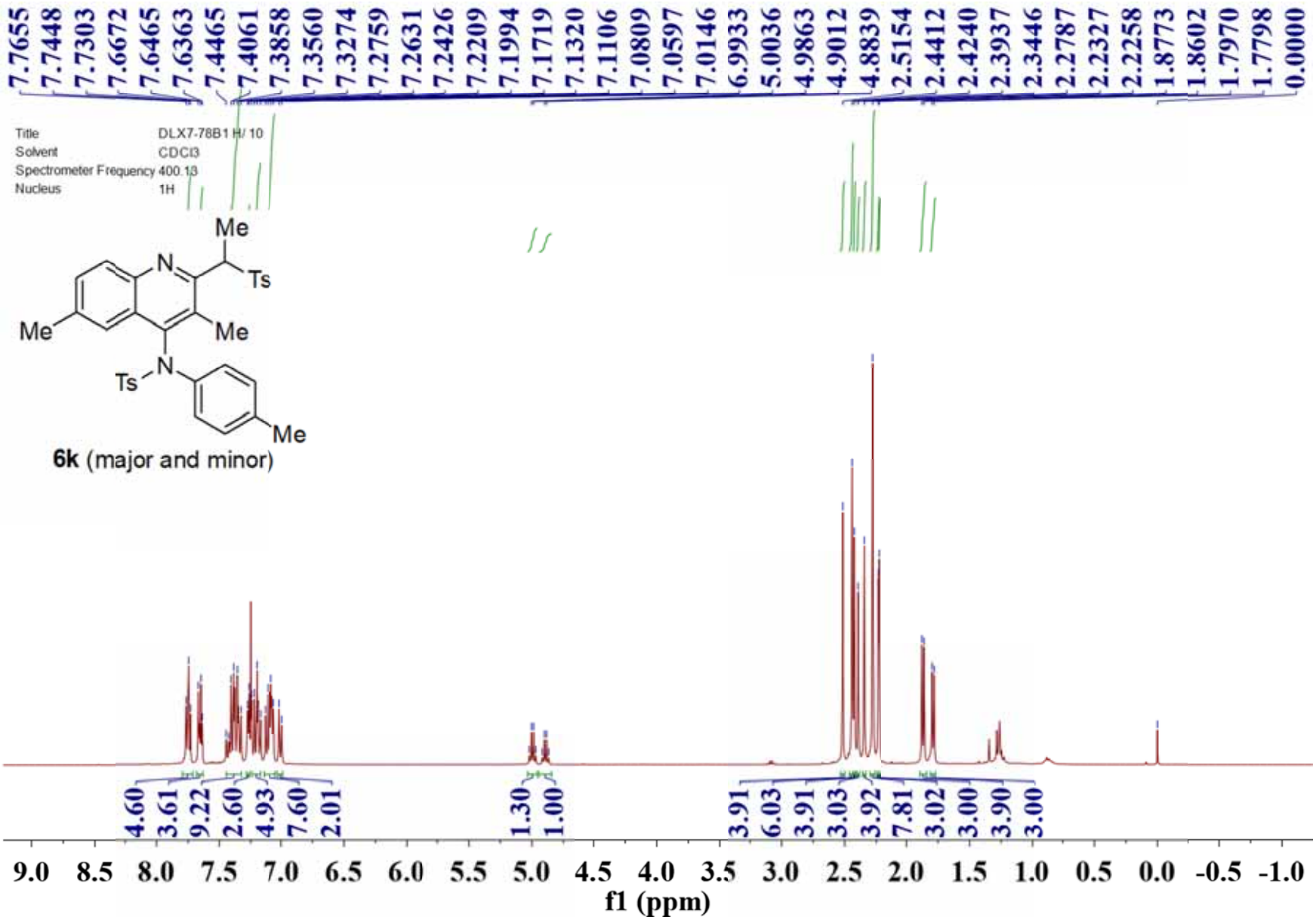

163.876
163.625
163.606
155.157
140.835
133.871
132.187
132.159
132.058
131.907
131.886
130.493
129.898
129.548
129.493
129.346
129.202
129.067
128.062
127.780
125.404
125.199
124.237
121.996
121.922
114.593
114.290
113.877
113.809
77.518
77.200
76.882
63.919
55.851
55.824
55.737
16.448
15.889
15.205
15.063
Title DLX7-72B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Mbs
Me
Mbs
N
6h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

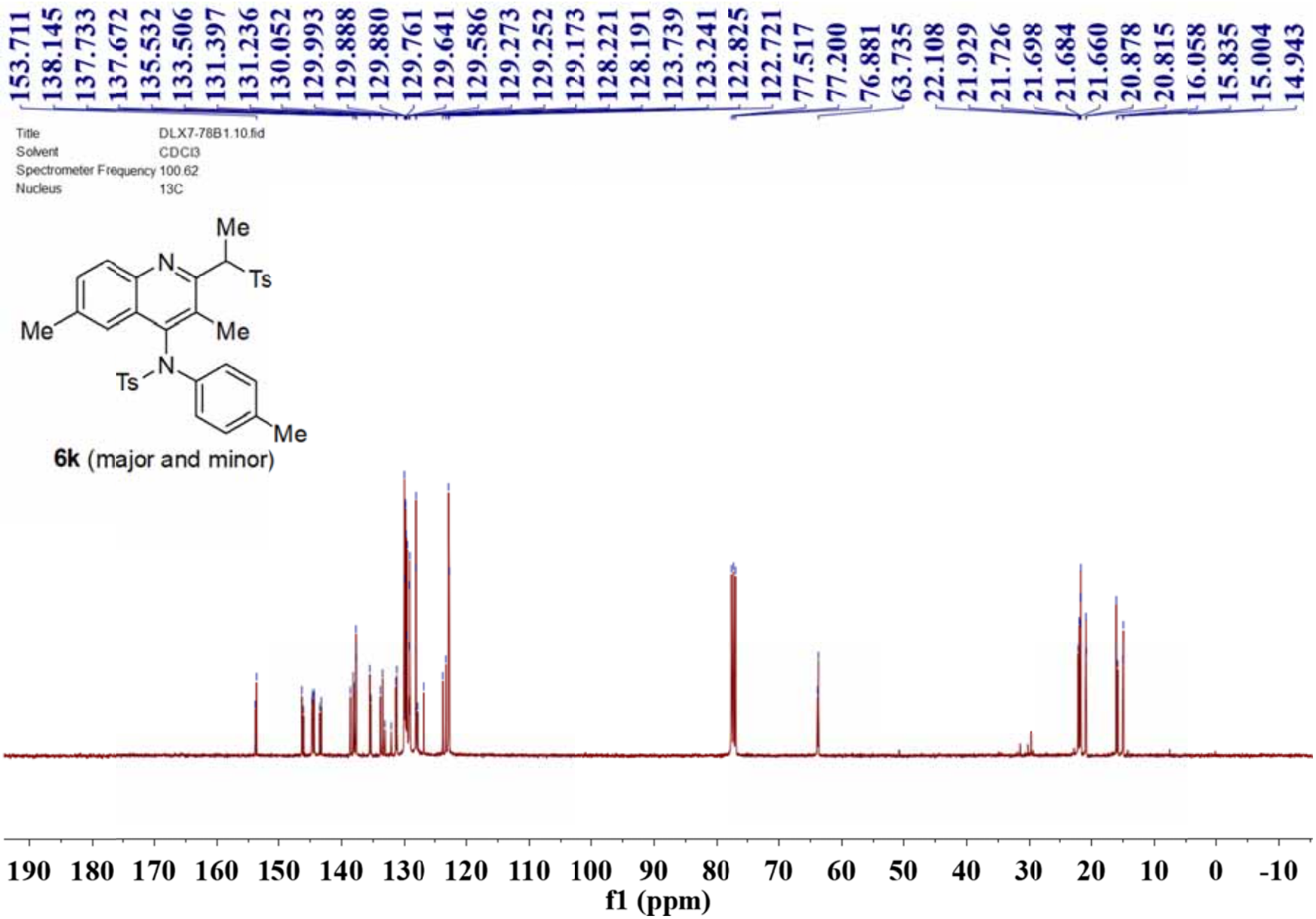

8.0915 8.0707 7.8662 7.8444 7.8216 7.8194 7.8001 7.7971 7.7468 7.7249 7.7186 7.6497 7.6053 7.5867 7.5559 7.5341 7.4545 7.4375 7.4179 7.4088 7.3918 7.3742 7.3525 7.3286 7.3070 7.2934 7.2782 7.2250 7.2094 5.0888 5.0716 4.9757 4.9583 2.6445 2.2855 1.8747 1.8575 1.8072 1.7899 0.0000
Title DLX7-73B H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Cs
Me
Cs
N
6i
1.01 2.05 1.06 3.04 6.10 6.06 9.06 4.03 2.06 1.04 1.00 3.03 3.02 3.05 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)

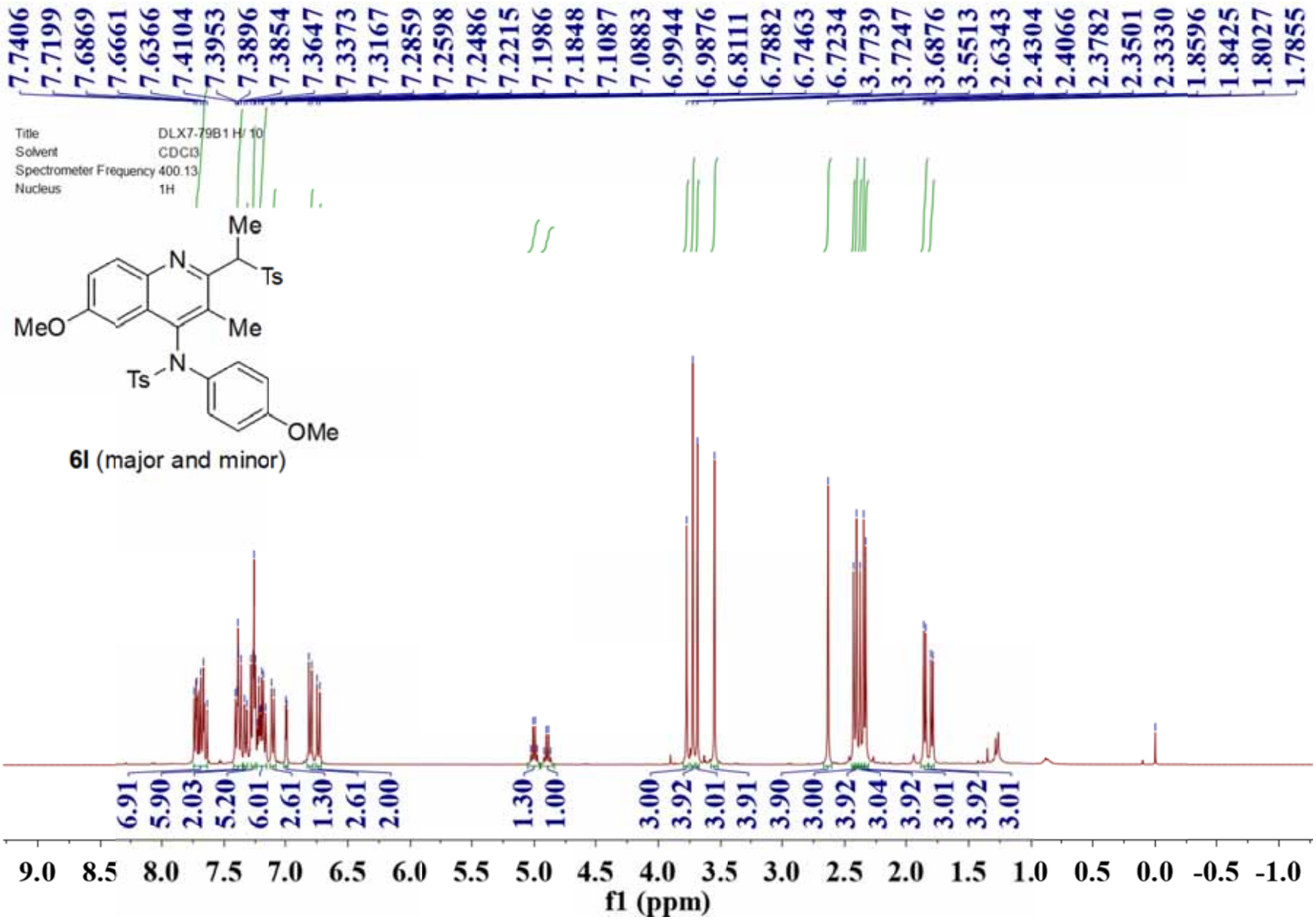

154.739
140.806
140.626
140.579
140.367
140.213
140.204
138.843
133.697
131.612
131.481
129.844
129.804
129.725
129.659
129.613
129.548
129.517
129.420
129.410
128.853
128.820
128.387
128.123
127.963
126.191
125.784
124.795
123.953
122.528
122.324
77.518
77.200
76.882
64.069
63.963
16.494
16.069
15.299
15.194
Title DLX7-73B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Cs
Me
Cs
N
6i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.4783
8.4569
8.4394
8.4182
8.4063
8.3857
8.2967
8.2757
8.0817
8.0620
7.9121
7.8905
7.8678
7.8244
7.8028
7.7733
7.7526
7.7328
7.7147
7.7043
7.6946
7.6248
7.6104
7.5926
7.3997
7.3813
7.3615
7.3409
7.3221
7.2661
7.2447
7.2274
7.2089
5.4450
2.3891
2.3603
1.8274
1.8115
1.7697
1.7538
Title dlx12-46b1.10.fid
Solvent DMSO
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ns
Me
Ns
N
6j (minor and major)
7.61
2.03
4.03
11.24
2.40
4.44
5.82
1.00
1.20
3.60
3.00
3.01
3.61
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)

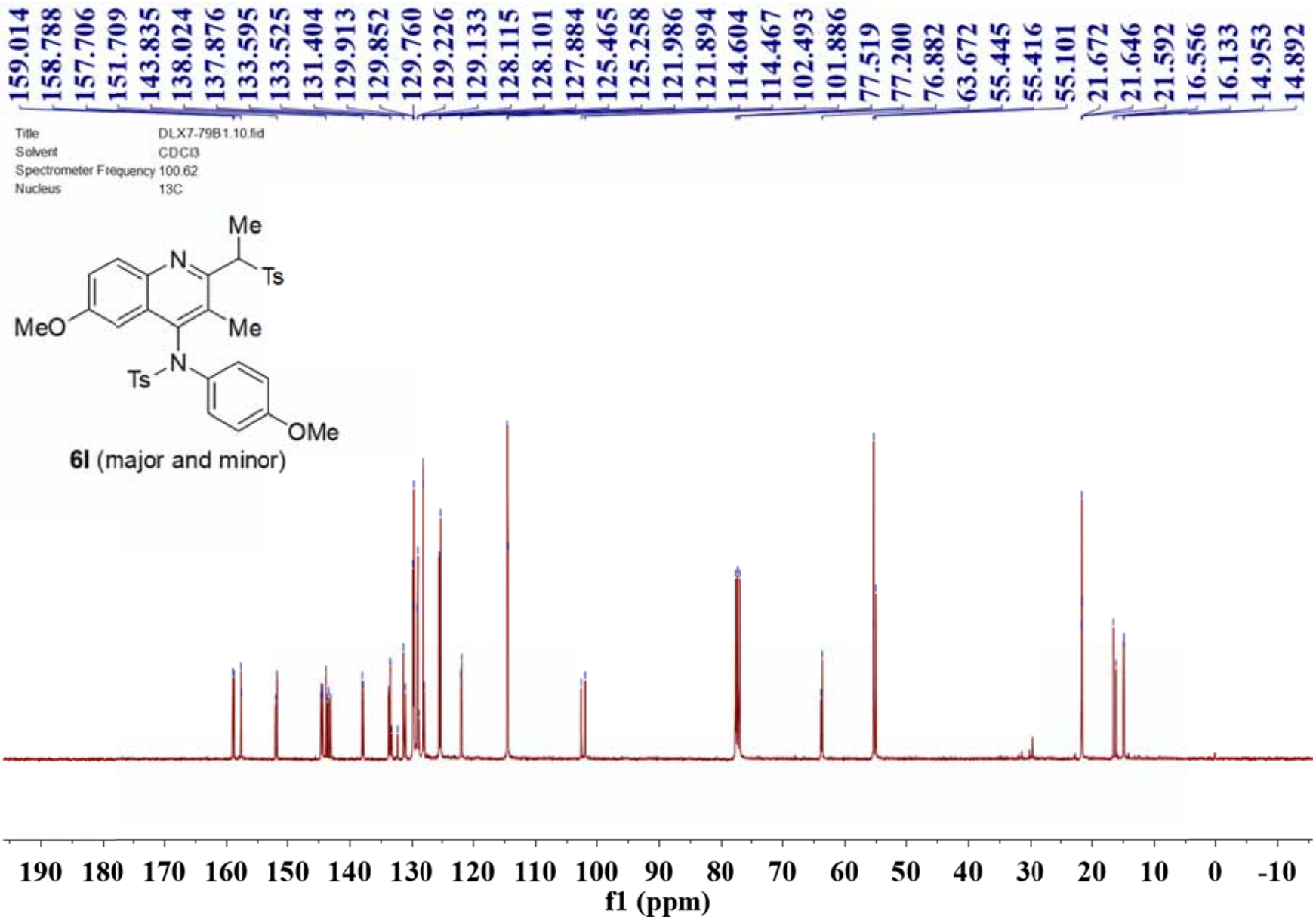

154.720
150.712
150.486
150.468
144.221
142.229
142.150
142.017
139.936
133.366
130.999
130.973
129.874
129.833
129.772
129.528
129.421
129.332
129.245
128.614
126.341
126.312
125.117
125.084
124.211
124.156
122.592
122.522
63.183
40.126
39.917
39.709
39.500
39.291
39.082
38.874
15.878
15.572
14.863
14.766
Title dlx12-46b1.11.fid
Solvent DMSO
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ns
Me
Ns
N
6j (minor and major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

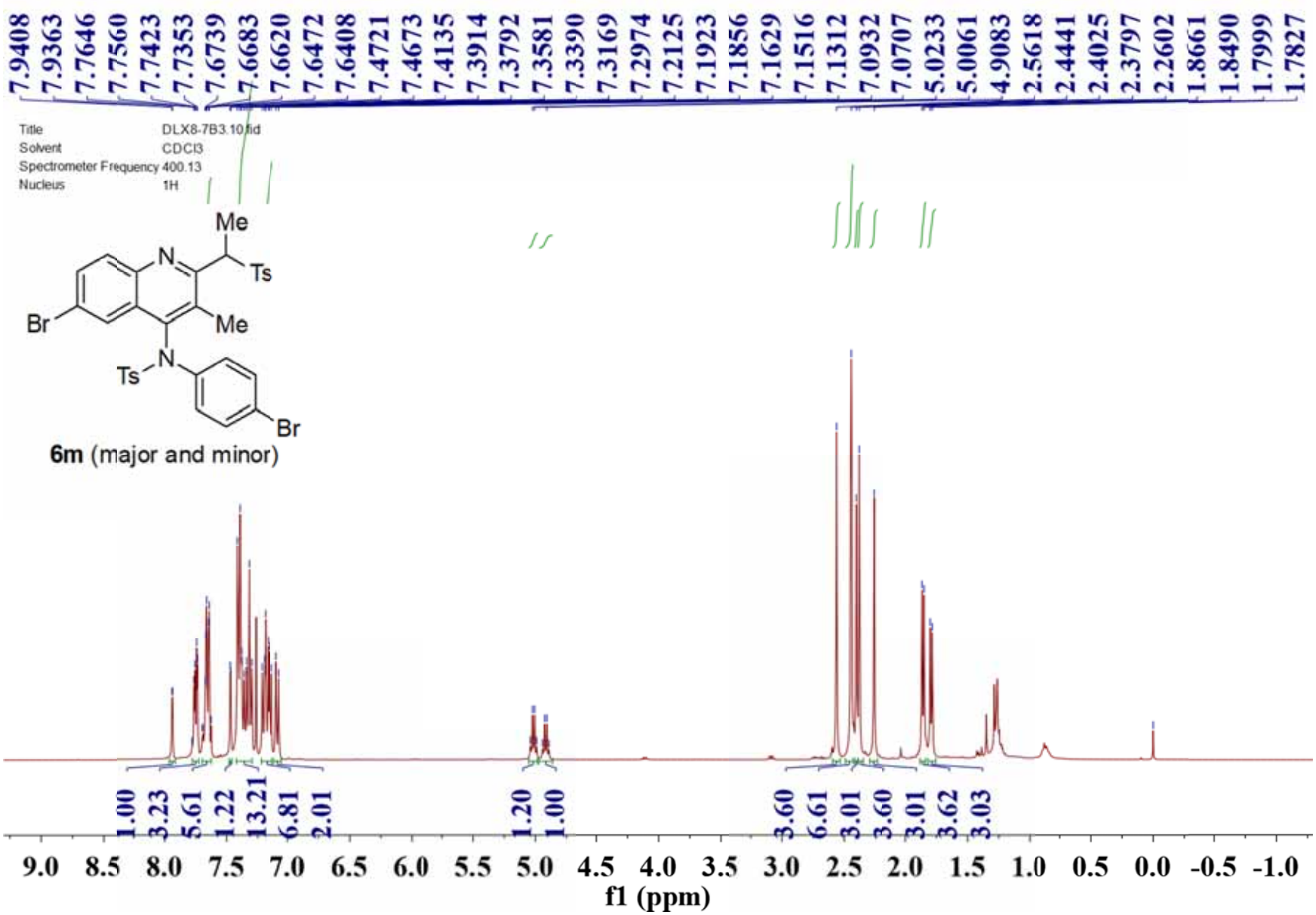

7.7655
7.7448
7.7303
7.6672
7.6465
7.6363
7.4465
7.4061
7.3858
7.3560
7.3274
7.2759
7.2631
7.2426
7.2209
7.1994
7.1719
7.1320
7.1106
7.0809
7.0597
7.0146
6.9933
5.0036
4.9863
4.9012
4.8839
2.5154
2.4412
2.4240
2.3937
2.3446
2.2787
2.2327
2.2258
1.8773
1.8602
1.7970
1.7798
0.0000
Title DLX7-78B1 H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Me
Me
Ts
N
Me
6k (major and minor)
4.60
3.61
9.22
2.60
4.93
7.60
2.01
1.30
1.00
3.91
6.03
3.91
3.03
3.92
7.81
3.02
3.00
3.90
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)

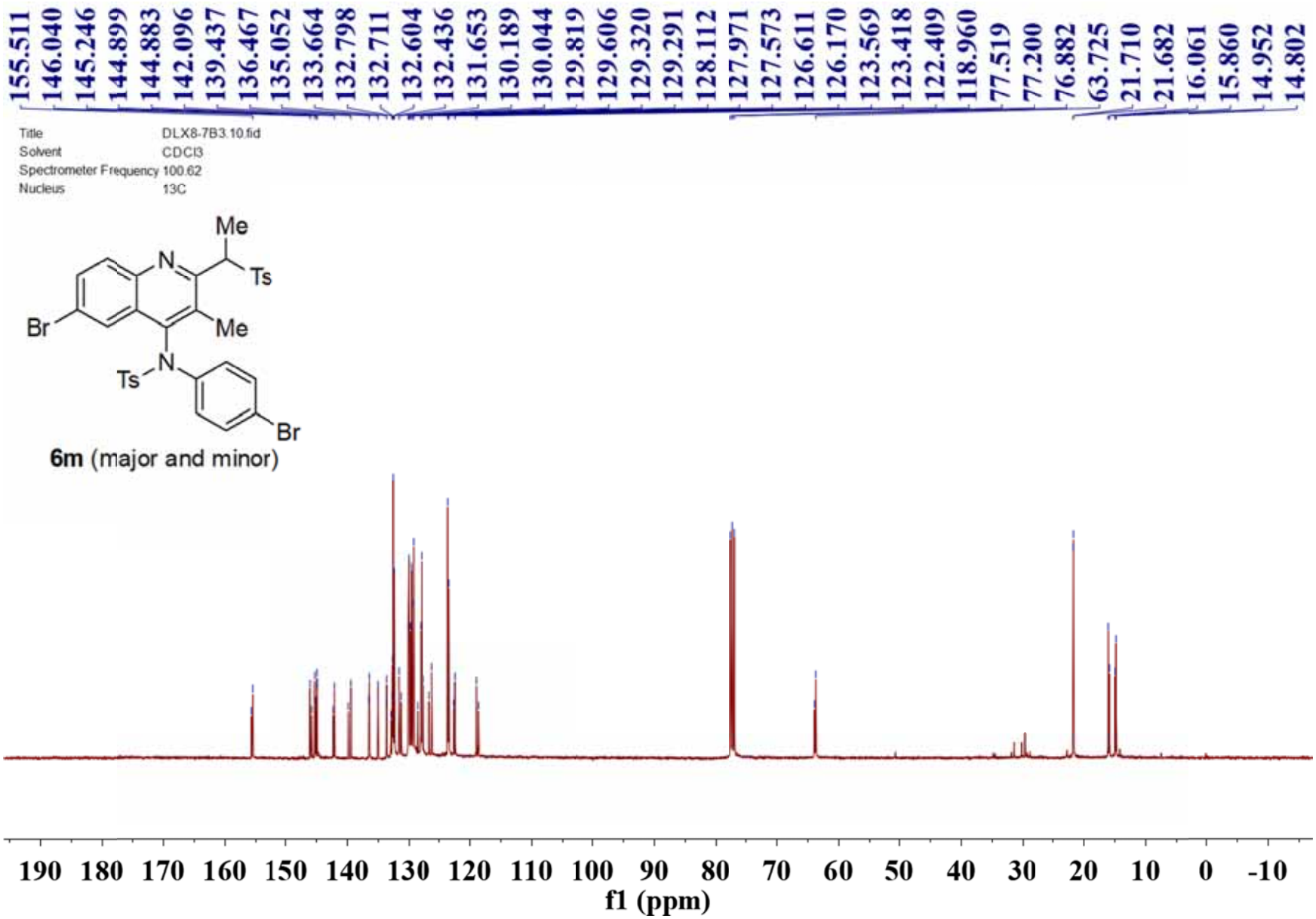

153.711
138.145
137.733
137.672
135.532
133.506
131.397
131.236
130.052
129.993
129.888
129.880
129.761
129.641
129.586
129.273
129.252
129.173
128.221
128.191
123.739
123.241
122.825
122.721
77.517
77.200
76.881
63.735
22.108
21.929
21.726
21.698
21.684
21.660
20.878
20.815
16.058
15.835
15.004
14.943
Title DLX7-78B1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Me
Me
Ts
N
Me
6k (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

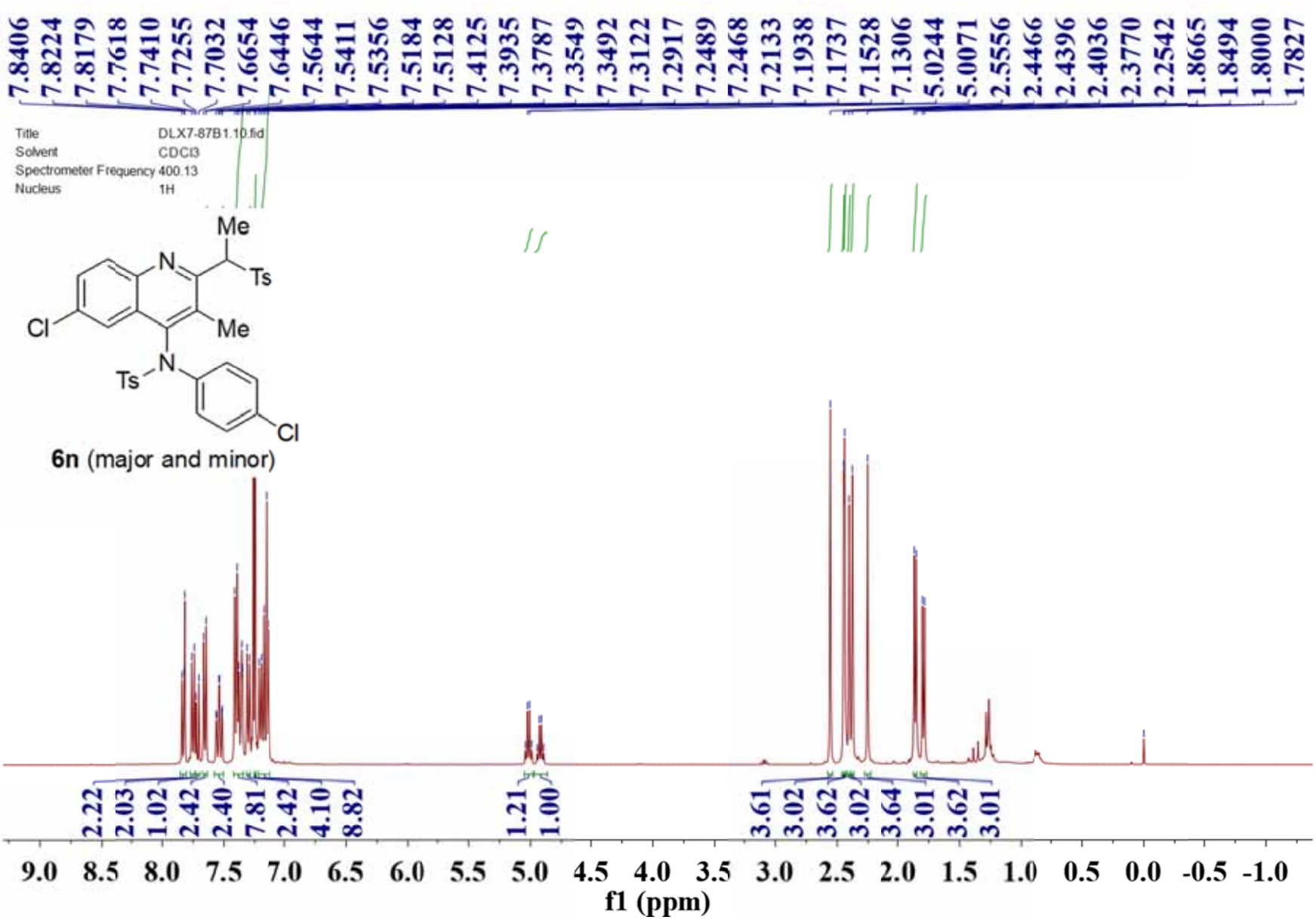


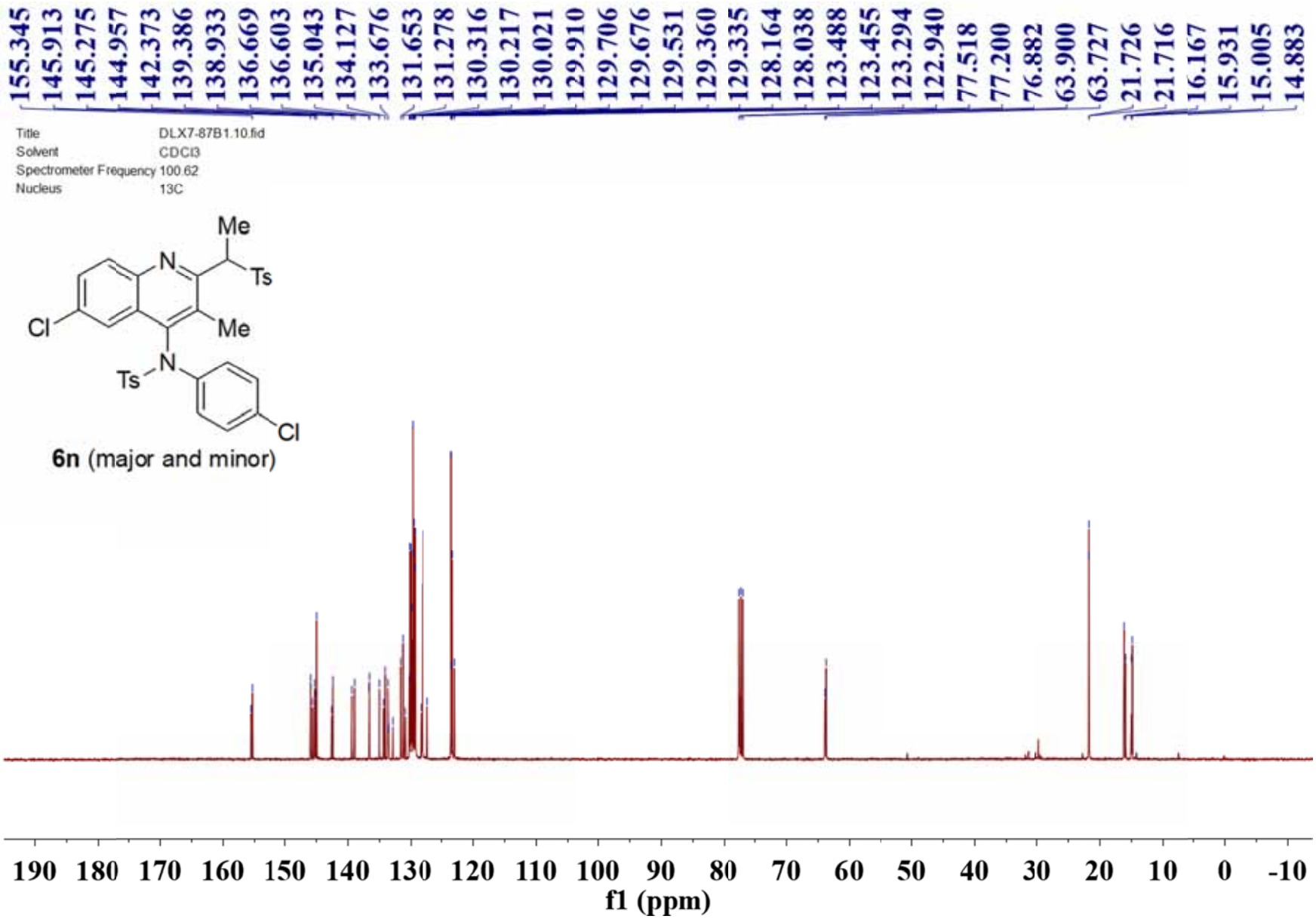
6l (major and minor)

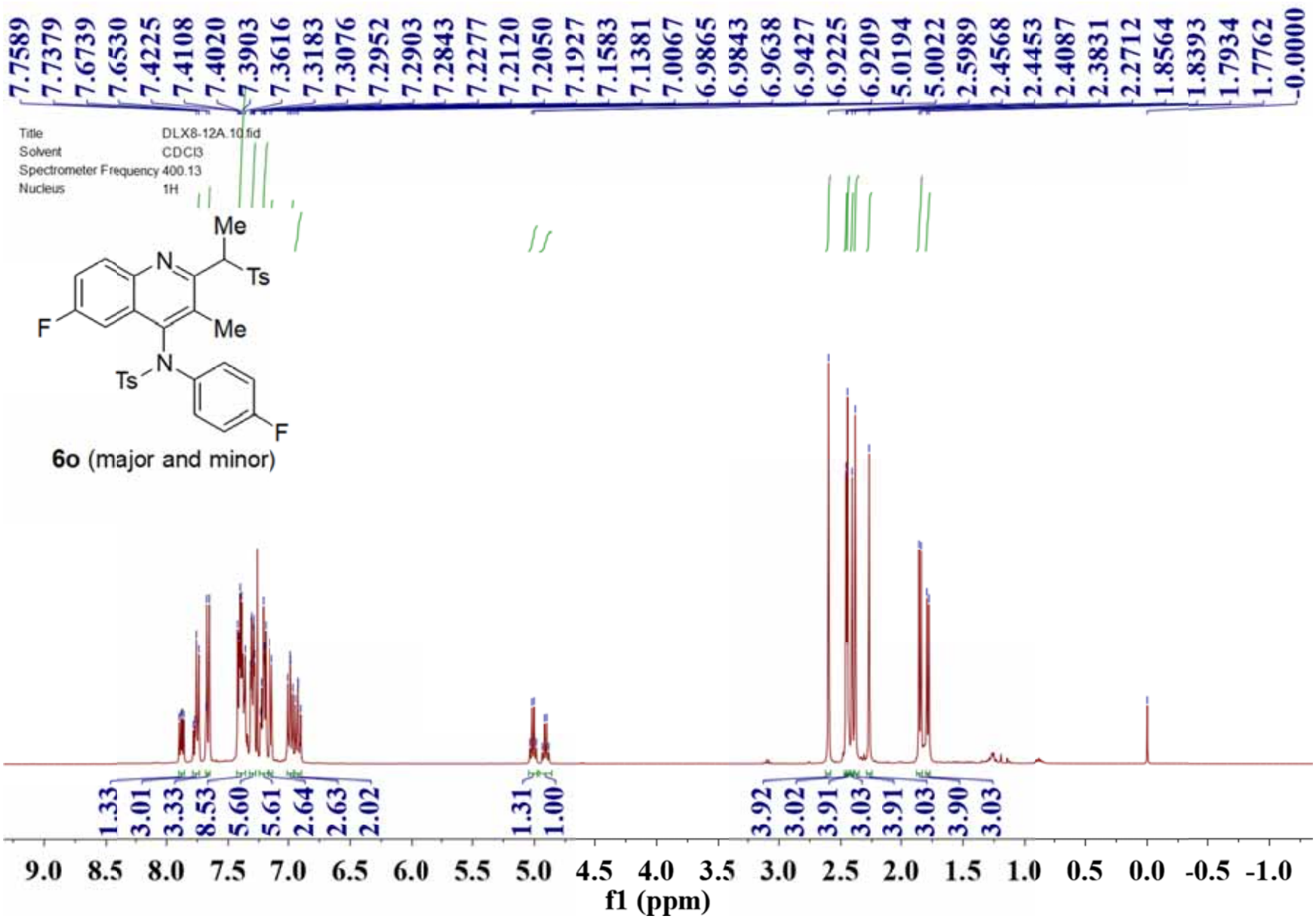

159.014
158.788
157.706
151.709
143.835
138.024
137.876
133.595
133.525
131.404
129.913
129.852
129.760
129.226
129.133
128.115
128.101
127.884
125.465
125.258
121.986
121.894
114.604
114.467
102.493
101.886
77.519
77.200
76.882
63.672
55.445
55.416
55.101
21.672
21.646
21.592
16.556
16.133
14.953
14.892
Title DLX7-79B1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
MeO
Me
Ts
N
OMe
6l (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.9408
7.9363
7.7646
7.7560
7.7423
7.7353
7.6739
7.6683
7.6620
7.6472
7.6408
7.4721
7.4673
7.4135
7.3914
7.3792
7.3581
7.3390
7.3169
7.2974
7.2125
7.1923
7.1856
7.1629
7.1516
7.1312
7.0932
7.0707
5.0233
5.0061
4.9083
2.5618
2.4441
2.4025
2.3797
2.2602
1.8661
1.8490
1.7999
1.7827
Title DLX8-7B3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Br
Me
Ts
N
Br
6m (major and minor)
1.00
3.23
5.61
1.22
13.21
6.81
2.01
1.20
1.00
3.60
6.61
3.01
3.60
3.01
3.62
3.03
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)

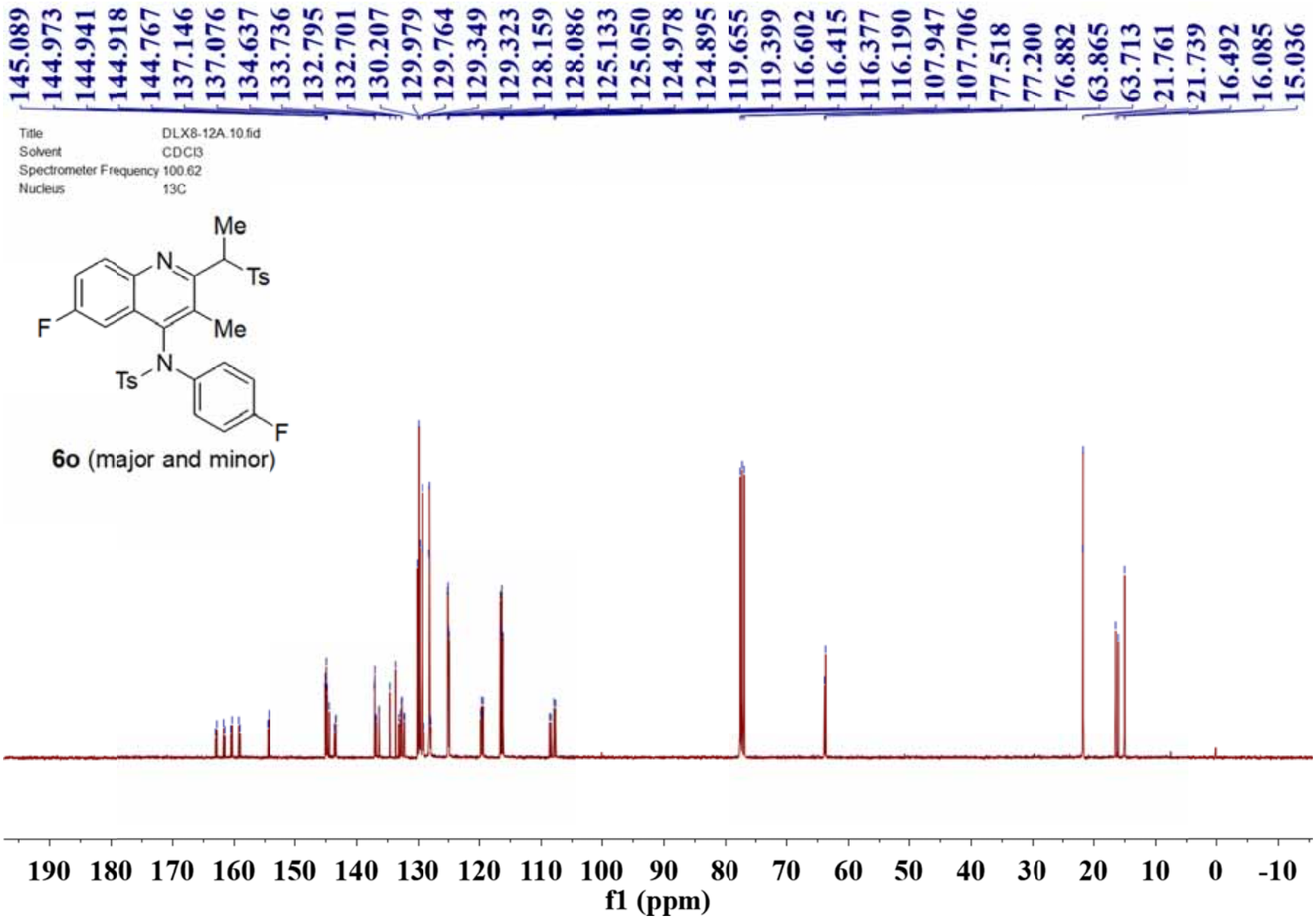

155.511
146.040
145.246
144.899
144.883
142.096
139.437
136.467
135.052
133.664
132.798
132.711
132.604
132.436
131.653
130.189
130.044
129.819
129.606
129.320
129.291
128.112
127.971
127.573
126.611
126.170
123.569
123.418
122.409
118.960
77.519
77.200
76.882
63.725
21.710
21.682
16.061
15.860
14.952
14.802
Title DLX8-7B3.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Br
Me
Ts
N
Br
6m (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

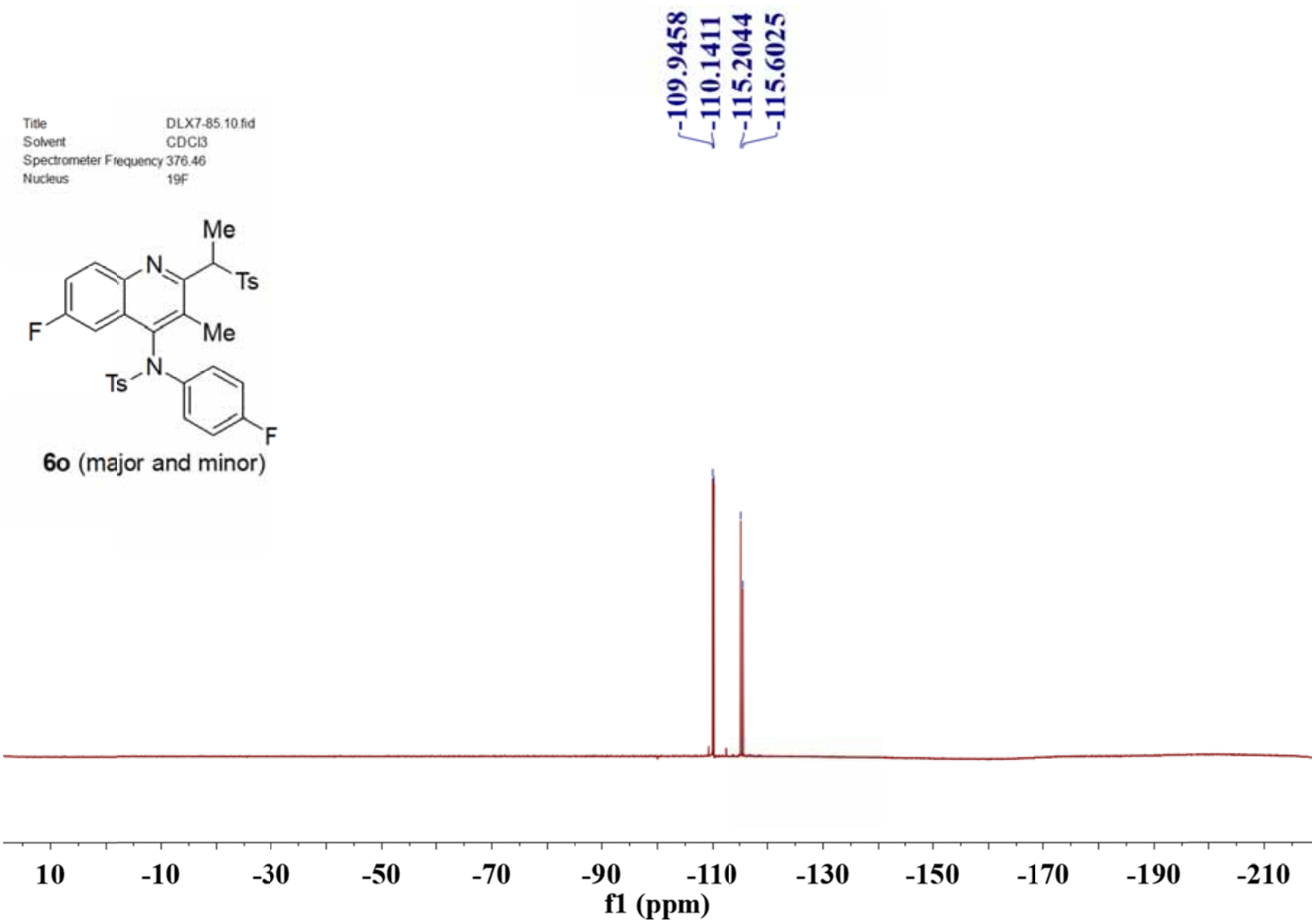

7.8406
7.8224
7.8179
7.7618
7.7410
7.7255
7.7032
7.6654
7.6446
7.5644
7.5411
7.5356
7.5184
7.5128
7.4125
7.3935
7.3787
7.3549
7.3492
7.3122
7.2917
7.2489
7.2468
7.2133
7.1938
7.1737
7.1528
7.1306
5.0244
5.0071
2.5556
2.4466
2.4396
2.4036
2.3770
2.2542
1.8665
1.8494
1.8000
1.7827
Title DLX7-87B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
Cl
Me
Ts
N
Cl
6n (major and minor)
2.22
2.03
1.02
2.42
2.40
7.81
2.42
4.10
8.82
1.21
1.00
3.61
3.02
3.62
3.02
3.64
3.01
3.62
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)

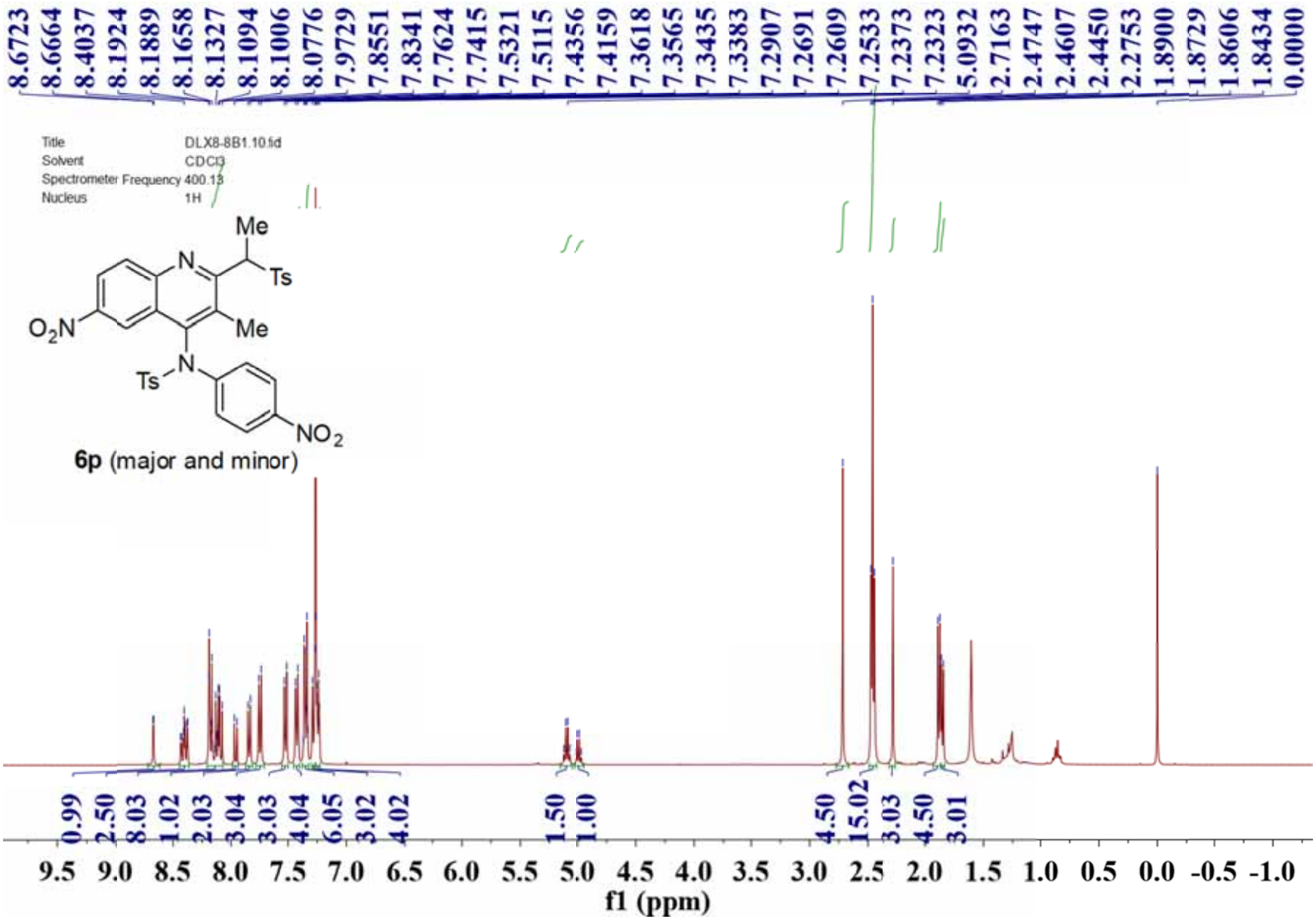

155.345
145.913
145.275
144.957
142.373
139.386
138.933
136.669
136.603
135.043
134.127
133.676
131.653
131.278
130.316
130.217
130.021
129.910
129.706
129.676
129.531
129.360
129.335
128.164
128.038
123.488
123.455
123.294
122.940
77.518
77.200
76.882
63.900
63.727
21.726
21.716
16.167
15.931
15.005
14.883
Title DLX7-87B1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
Cl
Me
Ts
N
Cl
6n (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

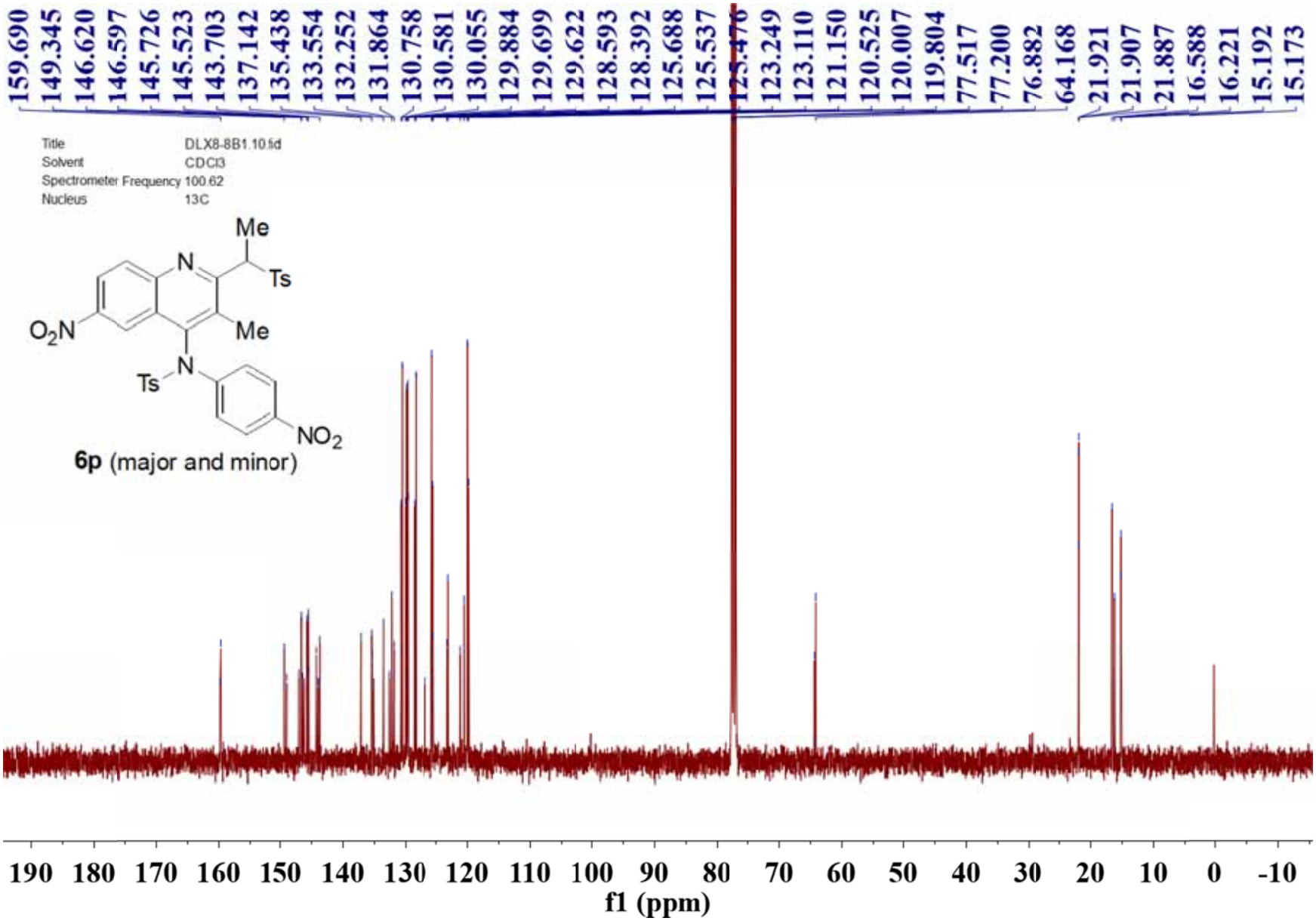


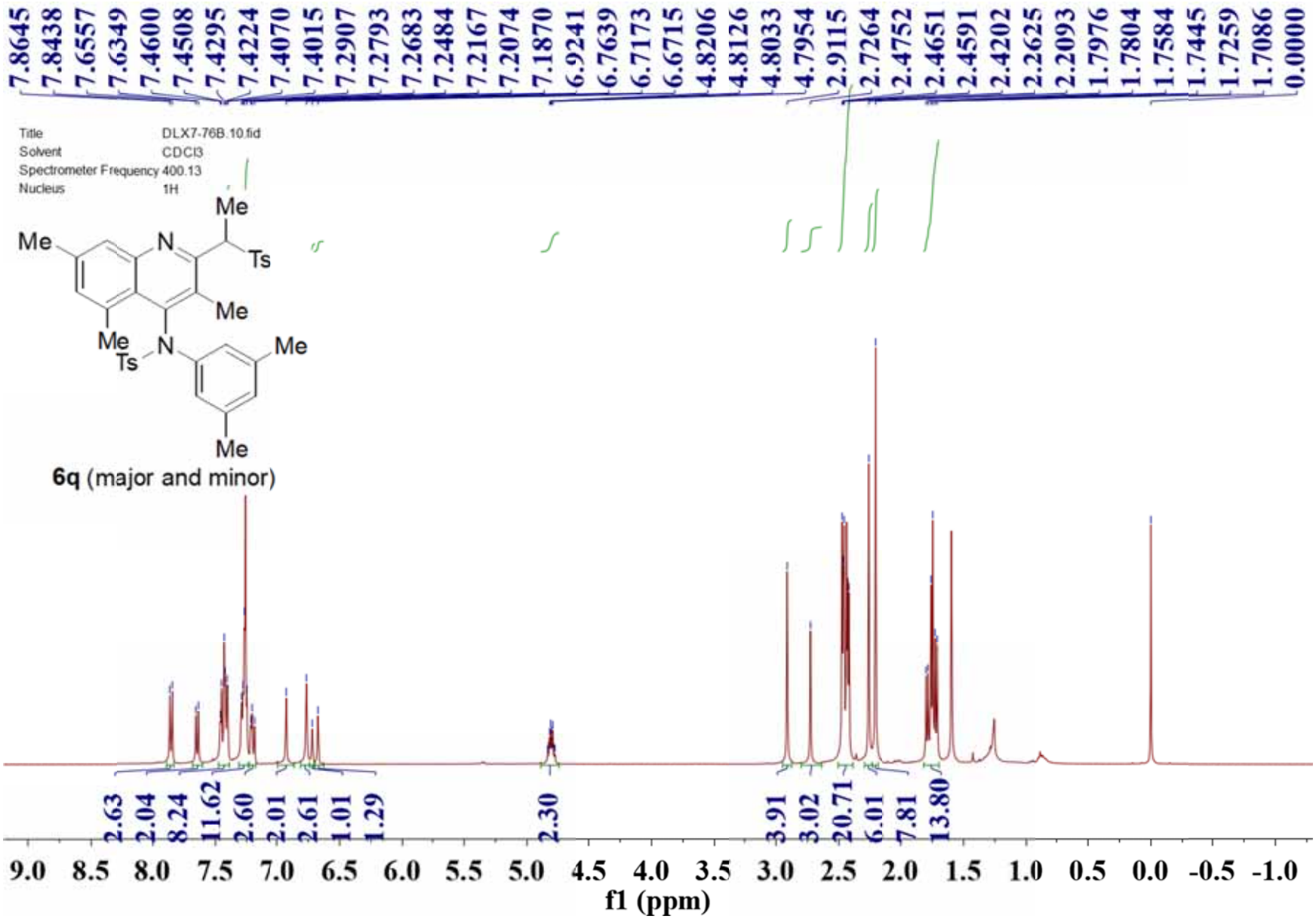
6o (major and minor)

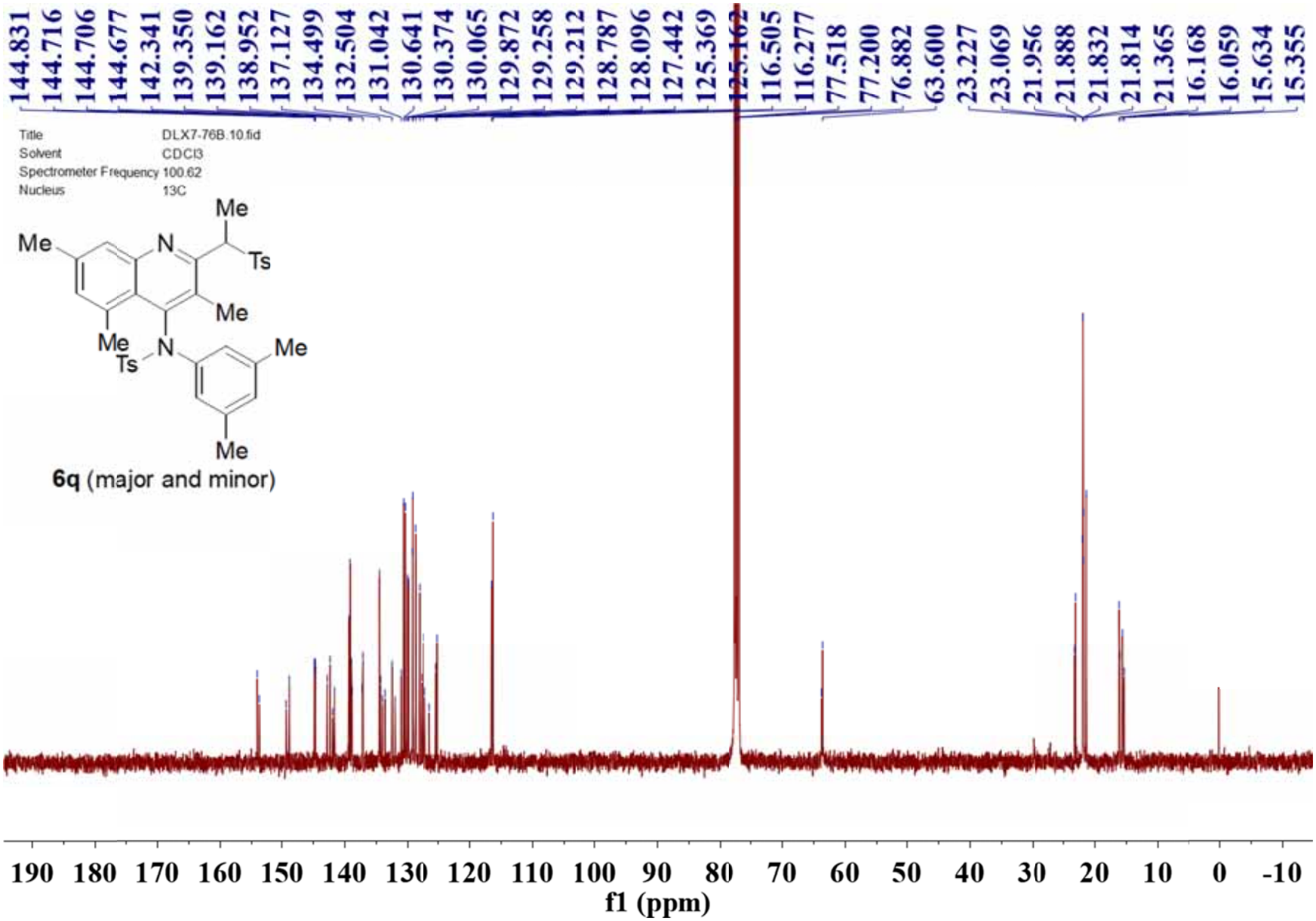

145.089
144.973
144.941
144.918
144.767
137.146
137.076
134.637
133.736
132.795
132.701
130.207
129.979
129.764
129.349
129.323
128.159
128.086
125.133
125.050
124.978
124.895
119.655
119.399
116.602
116.415
116.377
116.190
107.947
107.706
77.518
77.200
76.882
63.865
63.713
21.761
21.739
16.492
16.085
15.036
Title DLX8-12A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
F
Me
Ts
N
F
6o (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

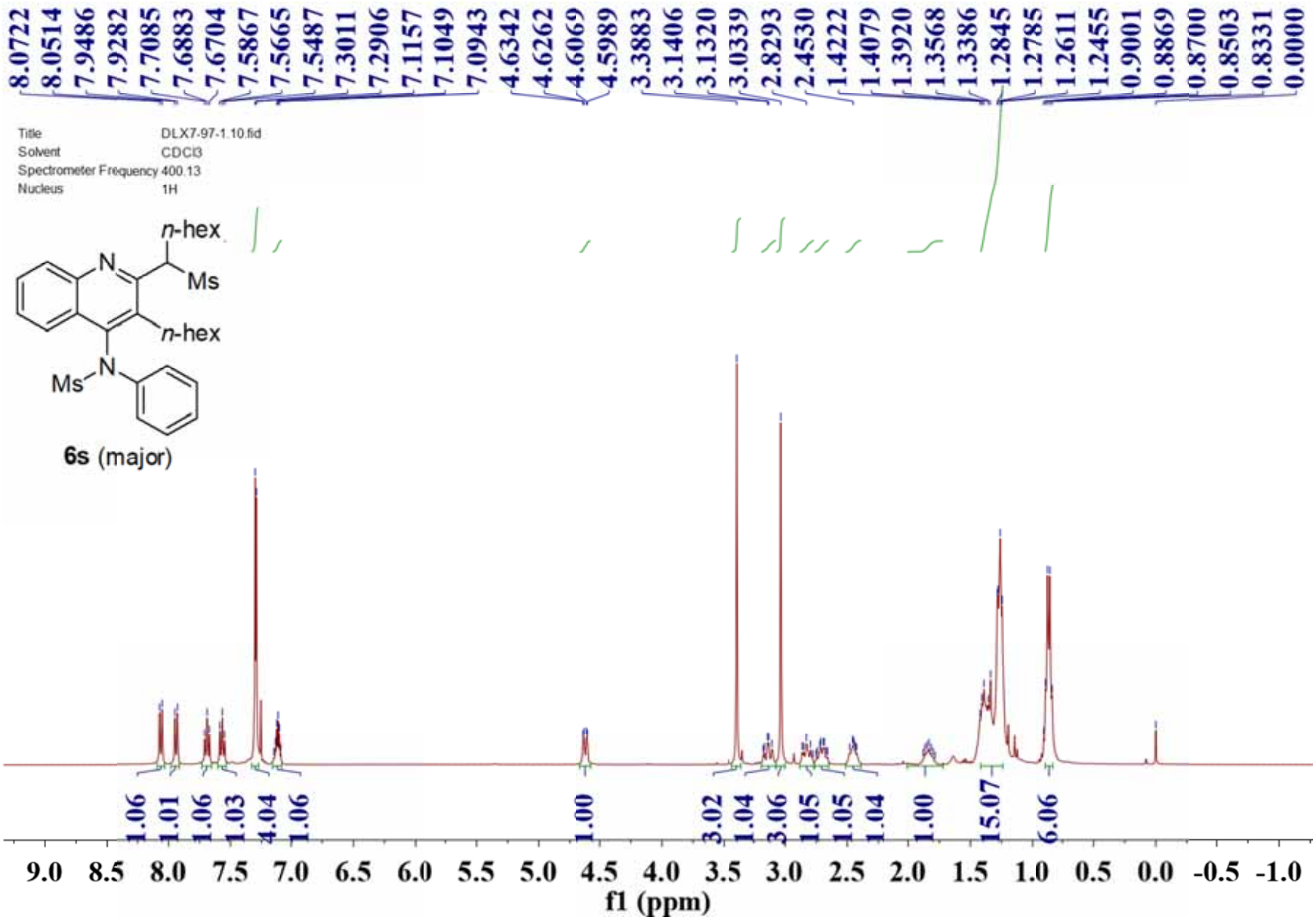

-109.9458
-110.1411
-115.2044
-115.6025
Title DLX7-85.10.fid
Solvent CDCl3
Spectrometer Frequency 376.46
Nucleus 19F
Me
N
Ts
F
Me
Ts
N
F
6o (major and minor)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

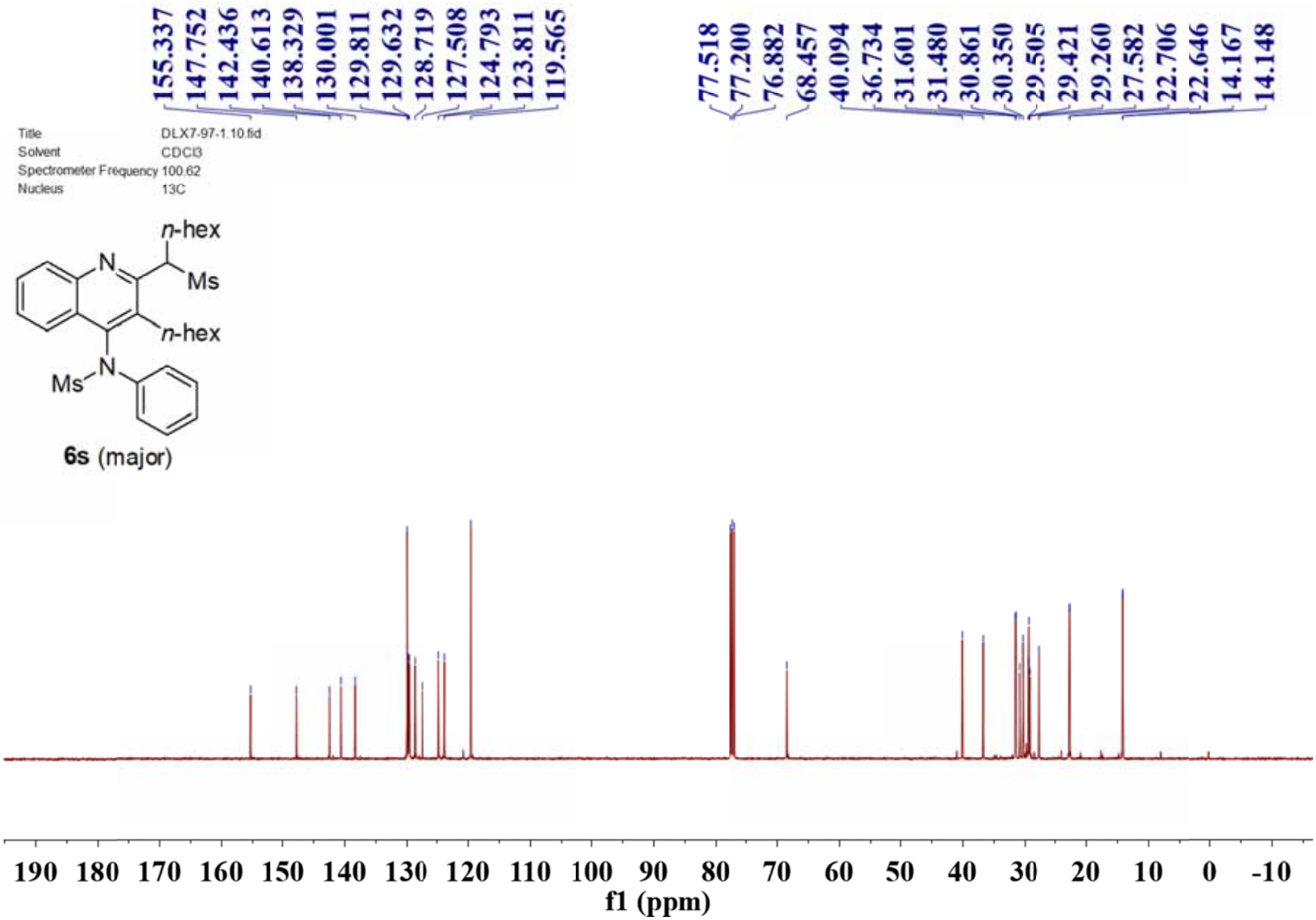

8.6723 8.6664 8.4037 8.1924 8.1889 8.1658 8.1327 8.1094 8.1006 8.0776 7.9729 7.8551 7.8341 7.7624 7.7415 7.5321 7.5115 7.4356 7.4159 7.3618 7.3565 7.3435 7.3383 7.2907 7.2691 7.2609 7.2533 7.2373 7.2323 5.0932 2.7163 2.4747 2.4607 2.4450 2.2753 1.8900 1.8729 1.8606 1.8434 0.0000
Title DLX8-8B1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Ts
O2N
Me
Ts
N
NO2
6p (major and minor)
0.99 2.50 8.03 1.02 2.03 3.04 3.03 4.04 6.05 3.02 4.02 1.50 1.00 4.50 15.02 3.03 4.50 3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

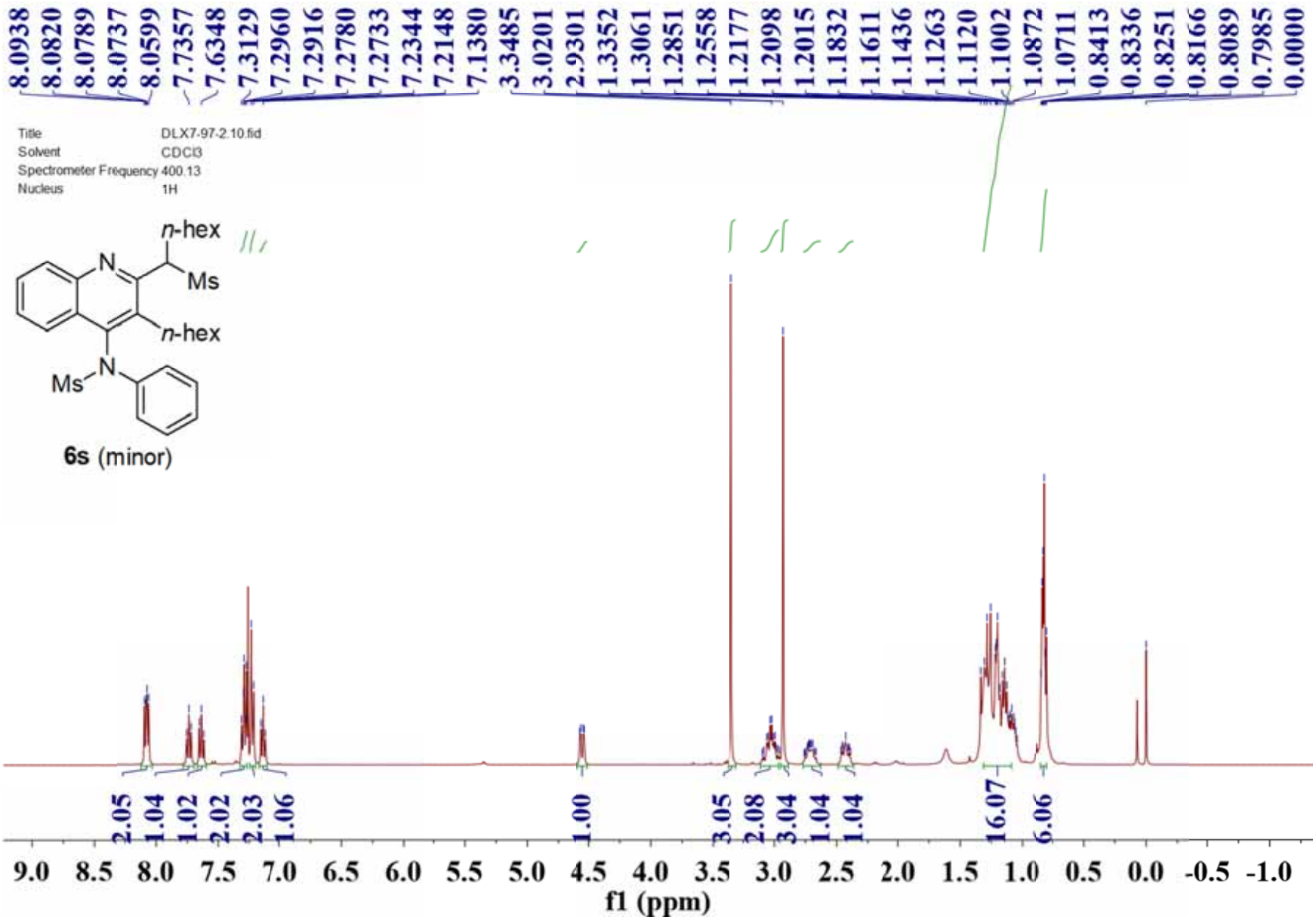

159.690
149.345
146.620
146.597
145.726
145.523
143.703
137.142
135.438
133.554
132.252
131.864
130.758
130.581
130.055
129.884
129.699
129.622
128.593
128.392
125.688
125.537
125.476
123.249
123.110
121.150
120.525
120.007
119.804
77.517
77.200
76.882
64.168
21.921
21.907
21.887
16.588
16.221
15.192
15.173
Title DLX8-8B1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Ts
O2N
Me
Ts
N
NO2
6p (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

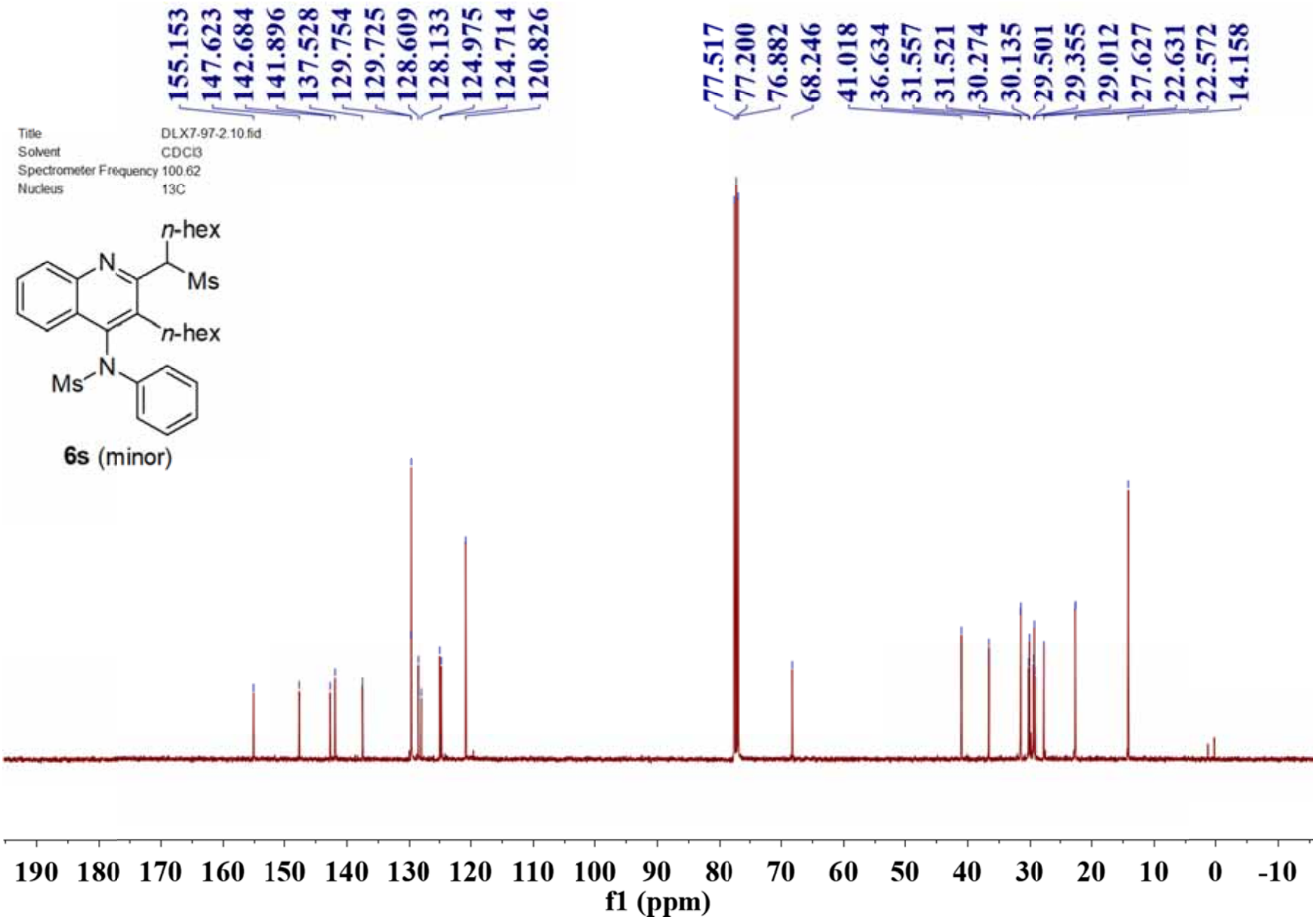

7.8645
7.8438
7.6557
7.6349
7.4600
7.4508
7.4295
7.4224
7.4070
7.4015
7.2907
7.2793
7.2683
7.2484
7.2167
7.2074
7.1870
6.9241
6.7639
6.7173
6.6715
4.8206
4.8126
4.8033
4.7954
2.9115
2.7264
2.4752
2.4651
2.4591
2.4202
2.2625
2.2093
1.7976
1.7804
1.7584
1.7445
1.7259
1.7086
0.0000
Title DLX7-76B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
N
Ts
Me
Me
Ts
N
Me
Me
6q (major and minor)
2.63
2.04
8.24
11.62
2.60
2.01
2.61
1.01
1.29
2.30
3.91
3.02
20.71
6.01
7.81
13.80
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)


144.831
144.716
144.706
144.677
142.341
139.350
139.162
138.952
137.127
134.499
132.504
131.042
130.641
130.374
130.065
129.872
129.258
129.212
128.787
128.096
127.442
125.369
125.162
116.505
116.277
77.518
77.200
76.882
63.600
23.227
23.069
21.956
21.888
21.832
21.814
21.365
16.168
16.059
15.634
15.355
Title DLX7-76B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
Me
N
Ts
Me
Me
Ts
N
Me
Me
6q (major and minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

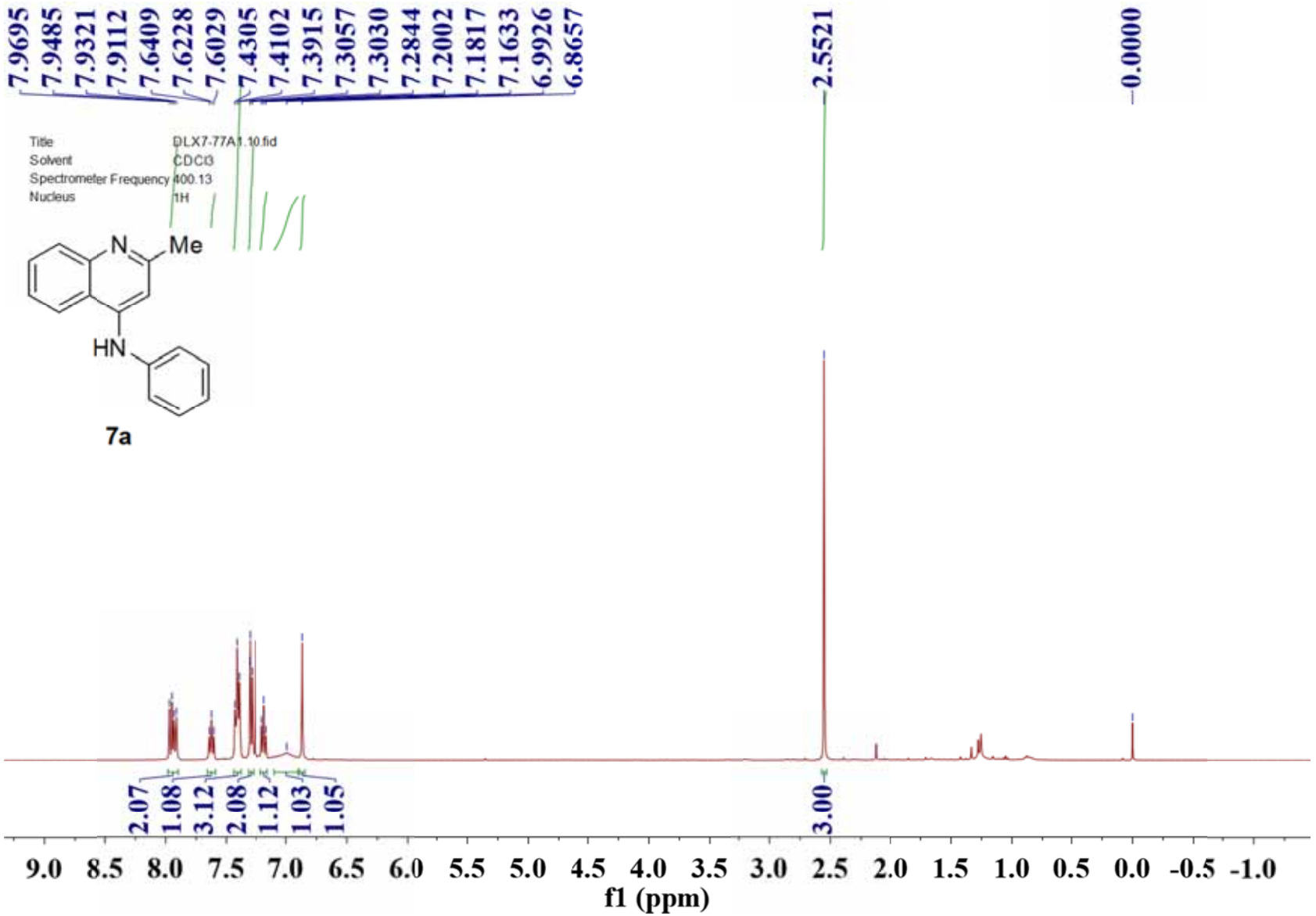

8.0722
8.0514
7.9486
7.9282
7.7085
7.6883
7.6704
7.5867
7.5665
7.5487
7.3011
7.2906
7.1157
7.1049
7.0943
4.6342
4.6262
4.6069
4.5989
3.3883
3.1406
3.1320
3.0339
2.8293
2.4530
1.4222
1.4079
1.3920
1.3568
1.3386
1.2845
1.2785
1.2611
1.2455
0.9001
0.8869
0.8700
0.8503
0.8331
0.0000
Title DLX7-97-1.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
N
Ms
n-hex
Ms
N
6s (major)
1.06
1.01
1.06
1.03
4.04
1.06
1.00
3.02
1.04
3.06
1.05
1.05
1.04
1.00
15.07
6.06
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)

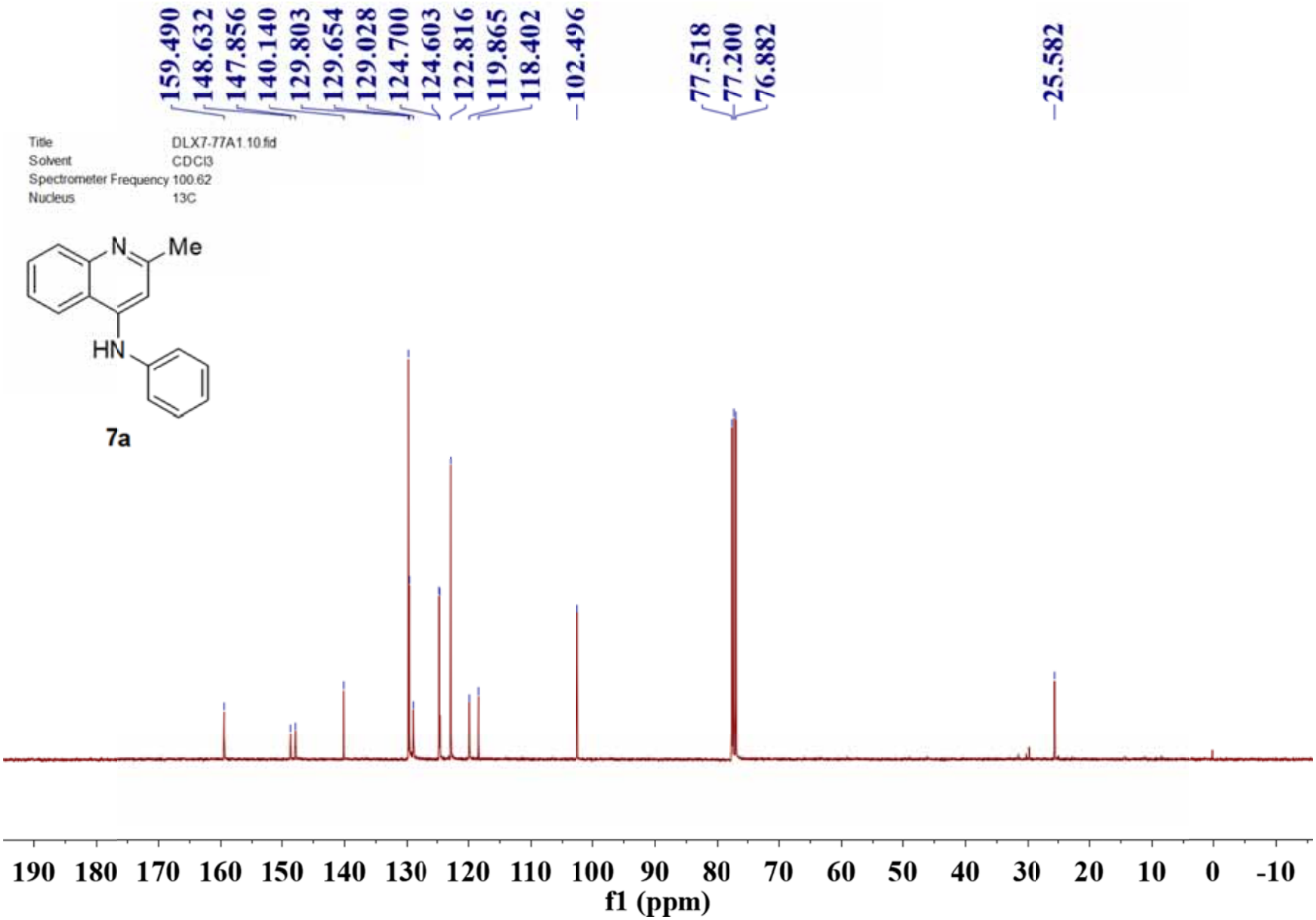

155.337
147.752
142.436
140.613
138.329
130.001
129.811
129.632
128.719
127.508
124.793
123.811
119.565
77.518
77.200
76.882
68.457
40.094
36.734
31.601
31.480
30.861
30.350
29.505
29.421
29.260
27.582
22.706
22.646
14.167
14.148
Title DLX7-97-1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
Ms
n-hex
Ms
N
N
6s (major)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

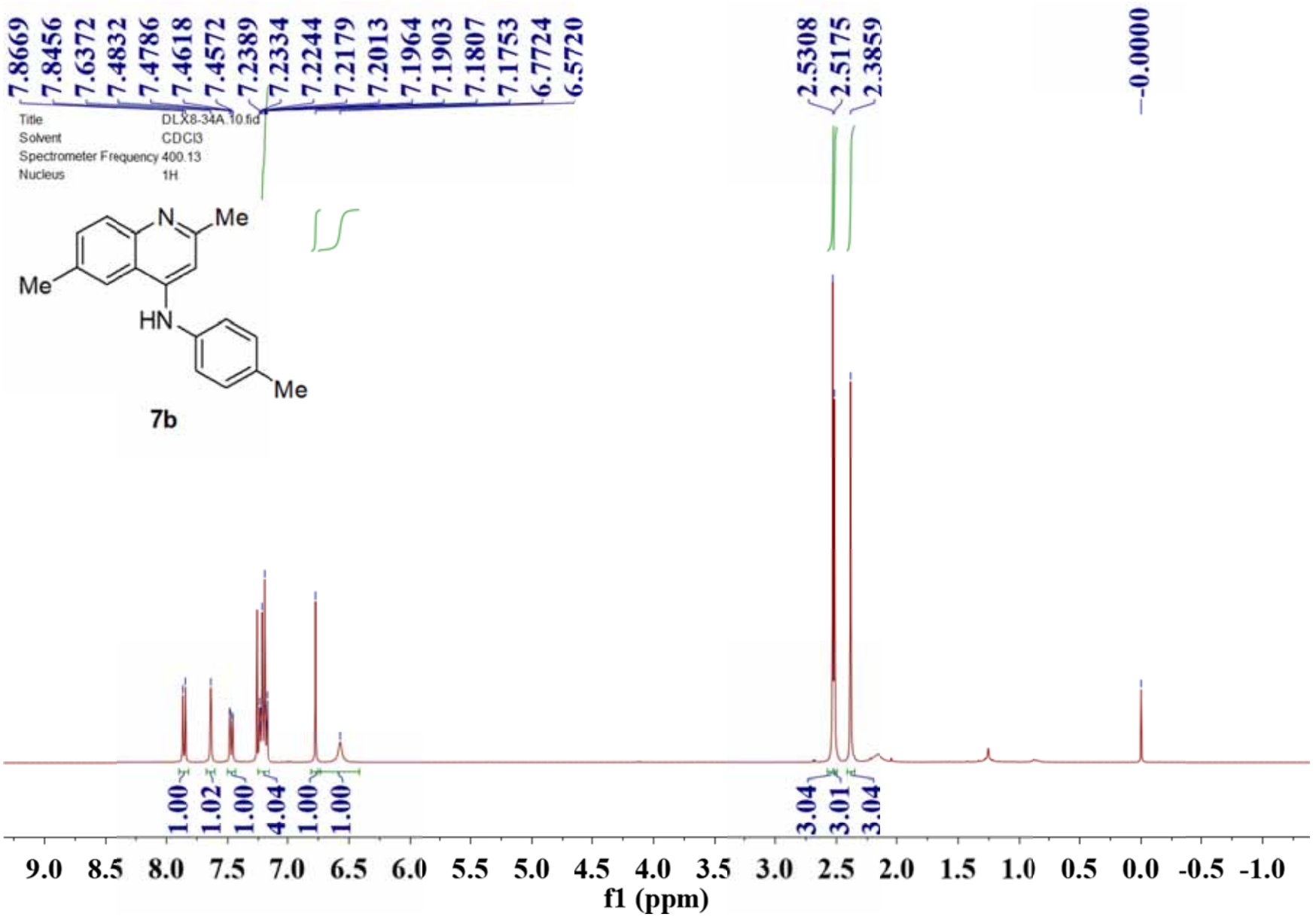

8.0938
8.0820
8.0789
8.0737
8.0599
7.7357
7.6348
7.3129
7.2960
7.2916
7.2780
7.2733
7.2344
7.2148
7.1380
3.3485
3.0201
2.9301
1.3352
1.3061
1.2851
1.2558
1.2177
1.2098
1.2015
1.1832
1.1611
1.1436
1.1263
1.1120
1.1002
1.0872
1.0711
0.8413
0.8336
0.8251
0.8166
0.8089
0.7985
0.0000
Title DLX7-97-2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
n-hex
Ms
n-hex
Ms
6s (minor)
2.05
1.04
1.02
2.02
2.03
1.06
1.00
3.05
2.08
3.04
1.04
1.04
16.07
6.06
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)

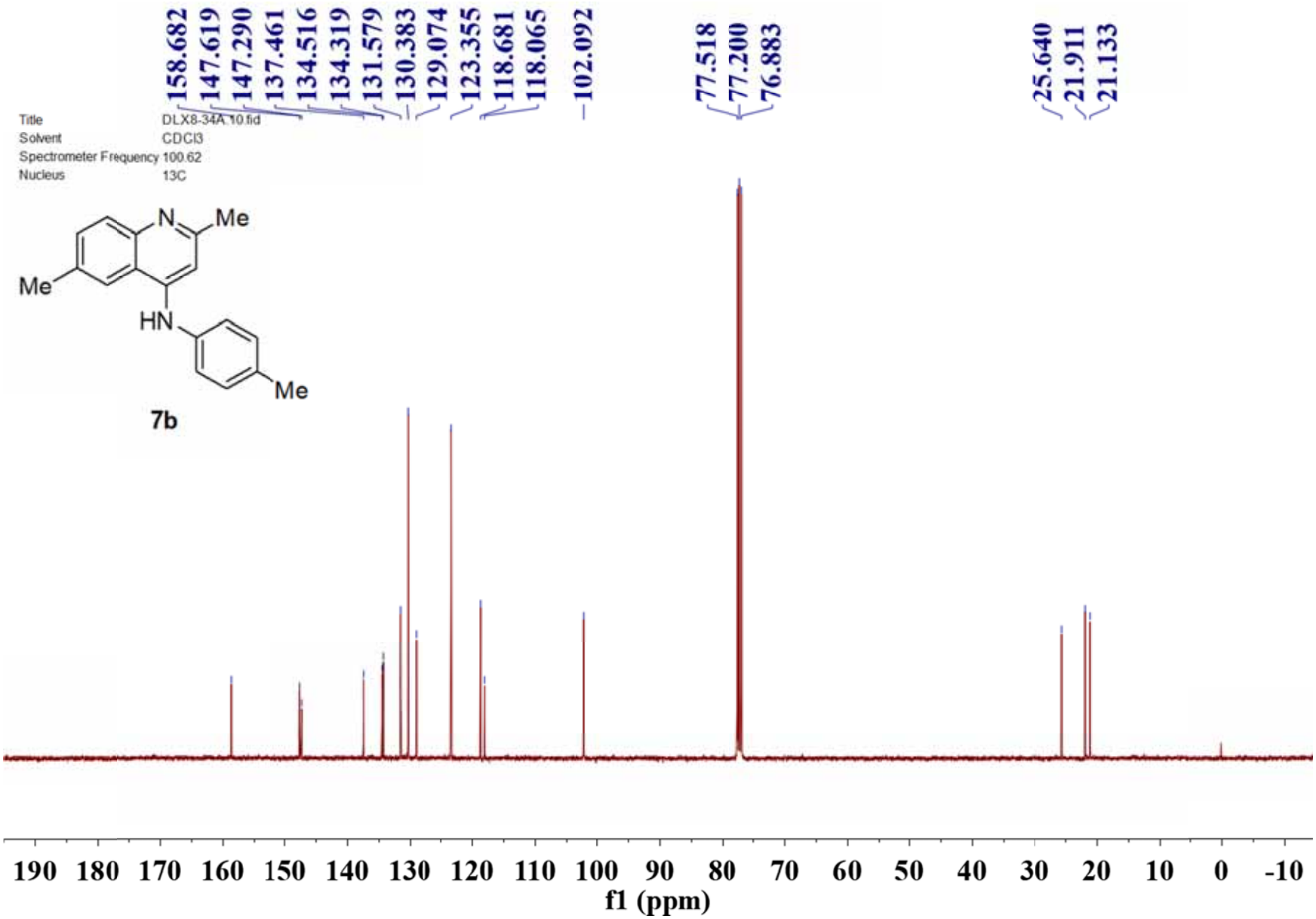

155.153
147.623
142.684
141.896
137.528
129.754
129.725
128.609
128.133
124.975
124.714
120.826
77.517
77.200
76.882
68.246
41.018
36.634
31.557
31.521
30.274
30.135
29.501
29.355
29.012
27.627
22.631
22.572
14.158
Title DLX7-97-2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
n-hex
N
Ms
n-hex
Ms
N
6s (minor)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

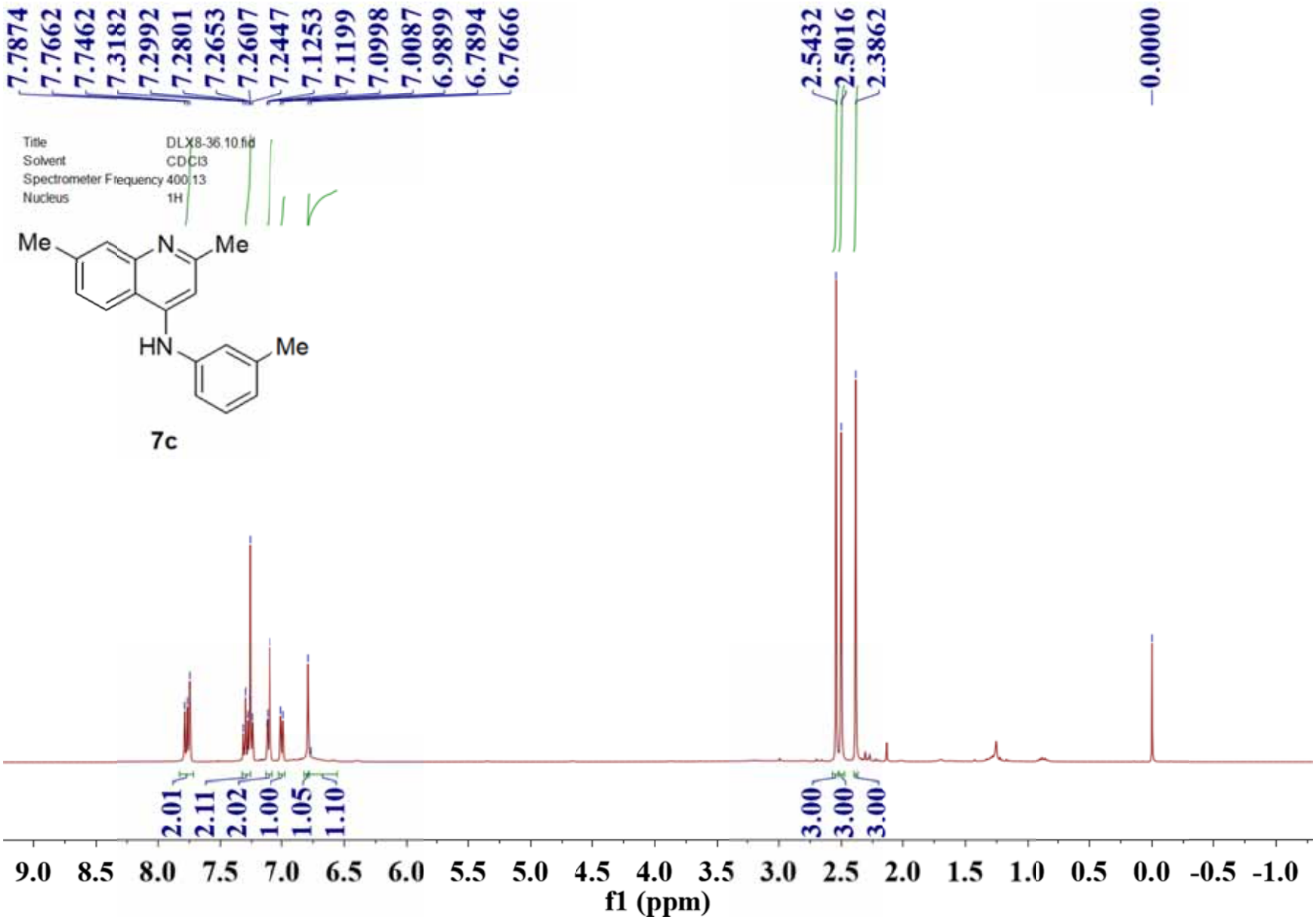
^{1}H NMR and ^{13}C NMR Spectra of 4-Aminoquinolines 7.

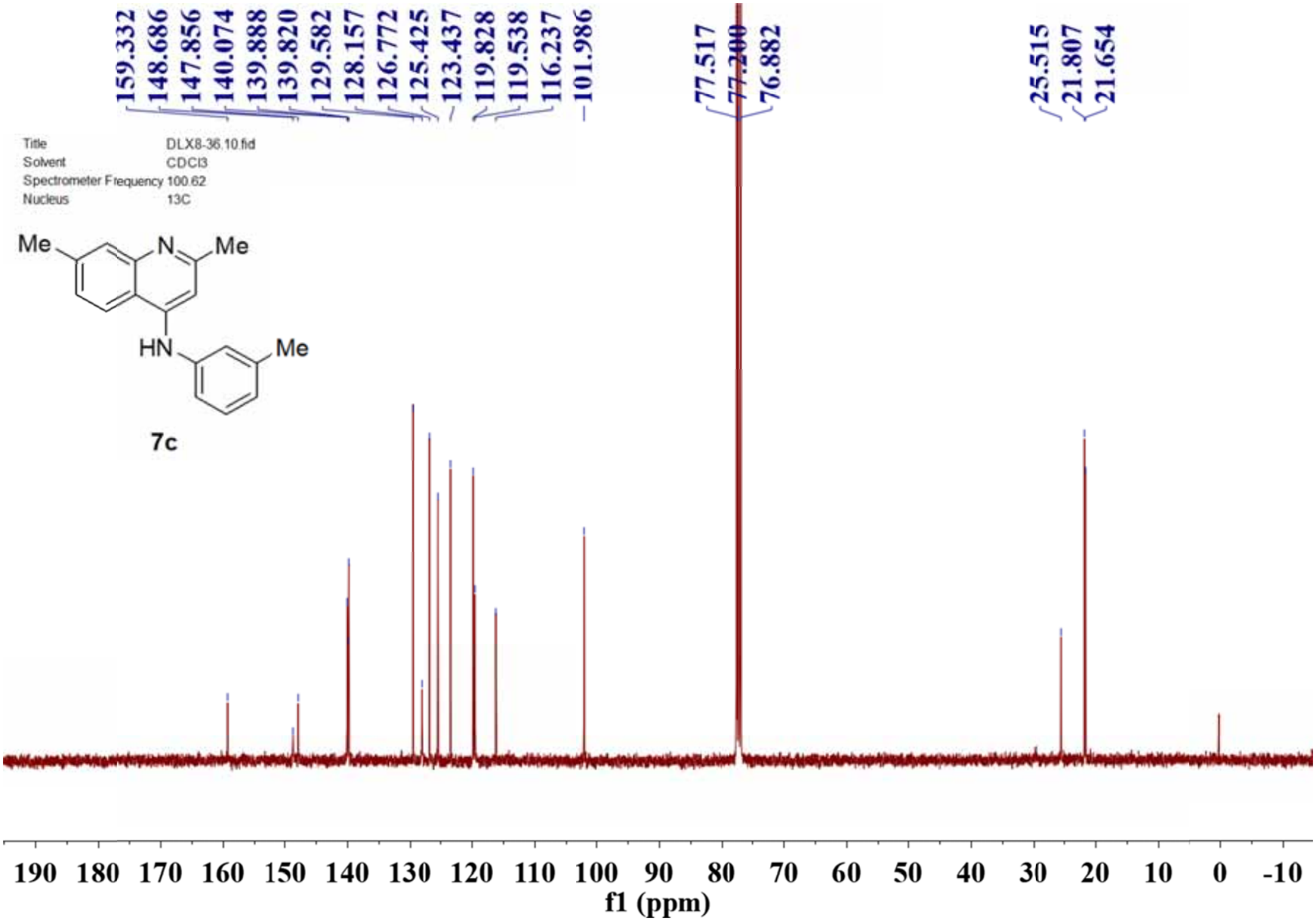


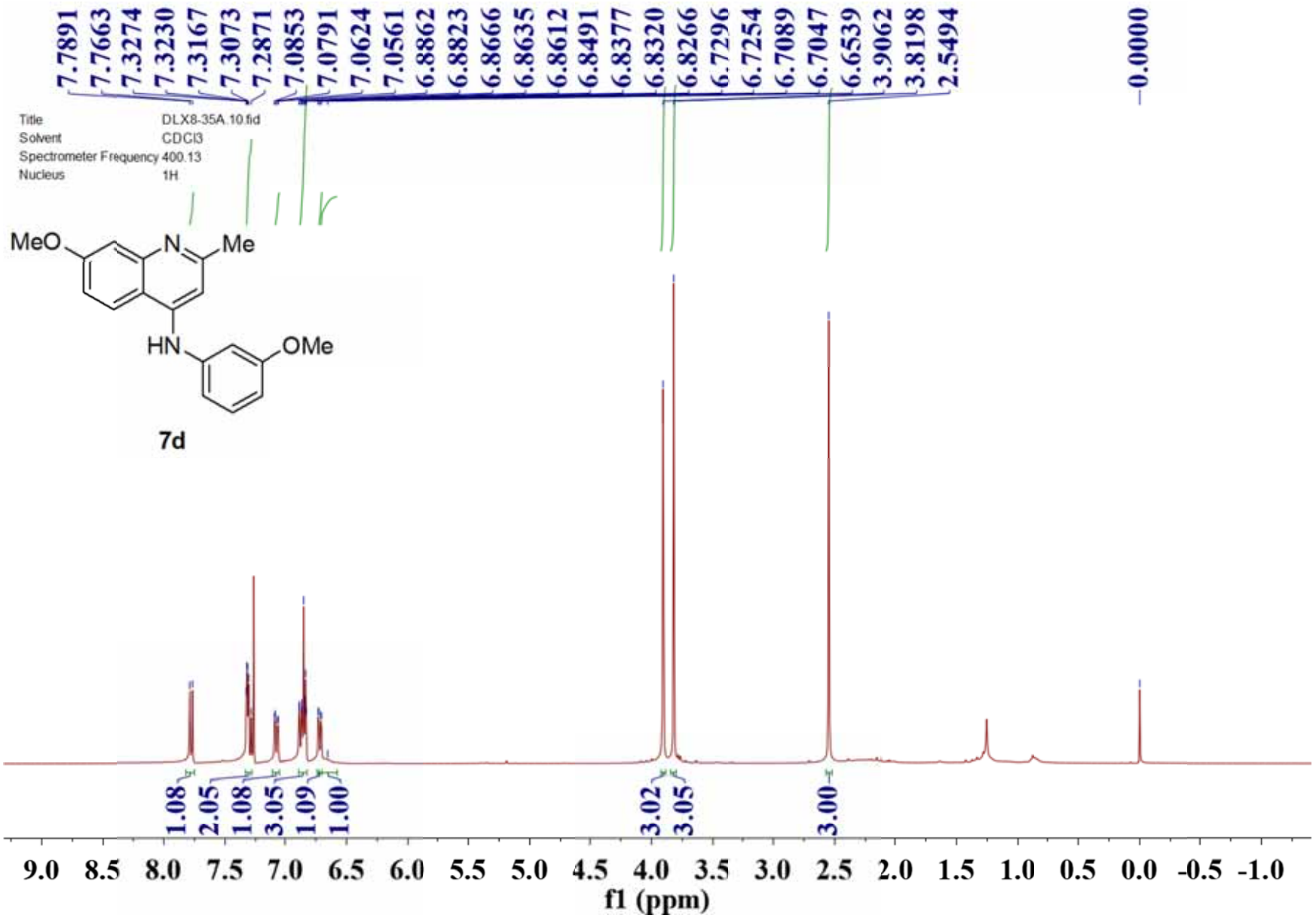

159.490
148.632
147.856
140.140
129.803
129.654
129.028
124.700
124.603
122.816
119.865
118.402
102.496
77.518
77.200
76.882
25.582
Title DLX7-77A1.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
HN
7a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

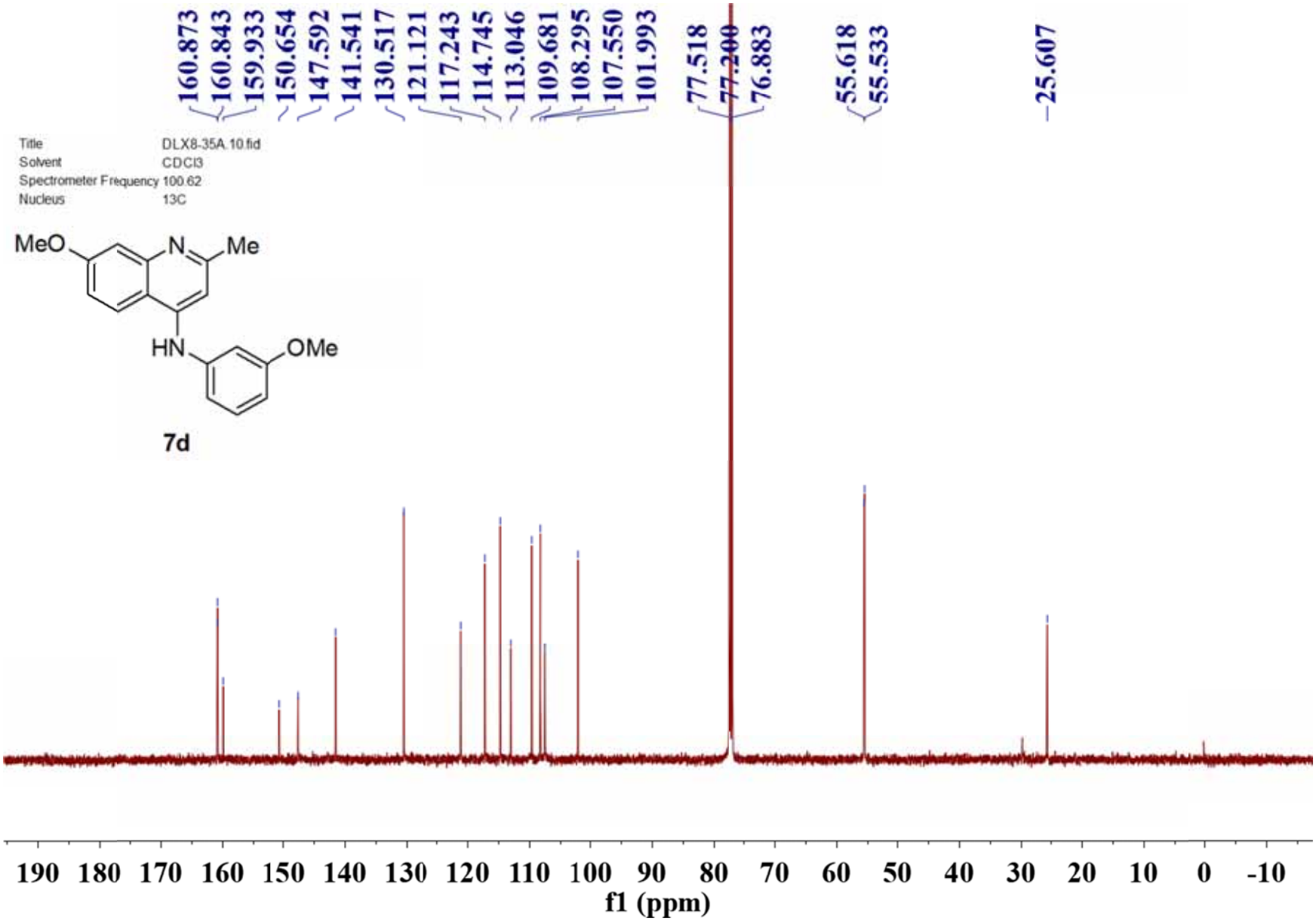

7.8669
7.8456
7.6372
7.4832
7.4786
7.4618
7.4572
7.2389
7.2334
7.2244
7.2179
7.2013
7.1964
7.1903
7.1807
7.1753
6.7724
6.5720
2.5308
2.5175
2.3859
-0.0000
Title DLX8-34A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Me
Me
HN
Me
7b
1.00
1.02
1.00
4.04
1.00
1.00
3.04
3.01
3.04
9.0 8.5 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)

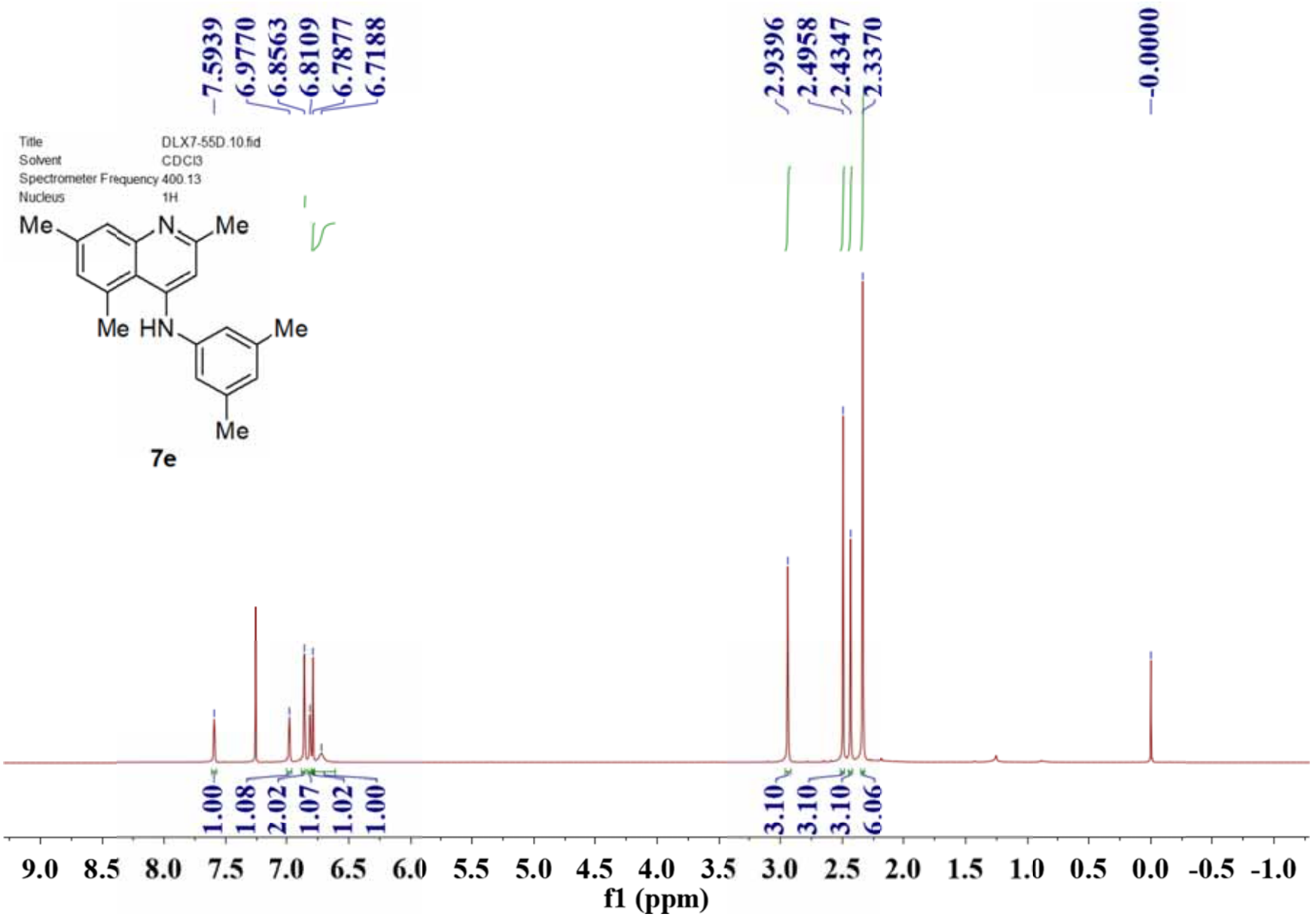

158.682
147.619
147.290
137.461
134.516
134.319
131.579
130.383
129.074
123.355
118.681
118.065
102.092
77.518
77.200
76.883
25.640
21.911
21.133
Title DLX8-34A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
Me
HN
Me
7b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

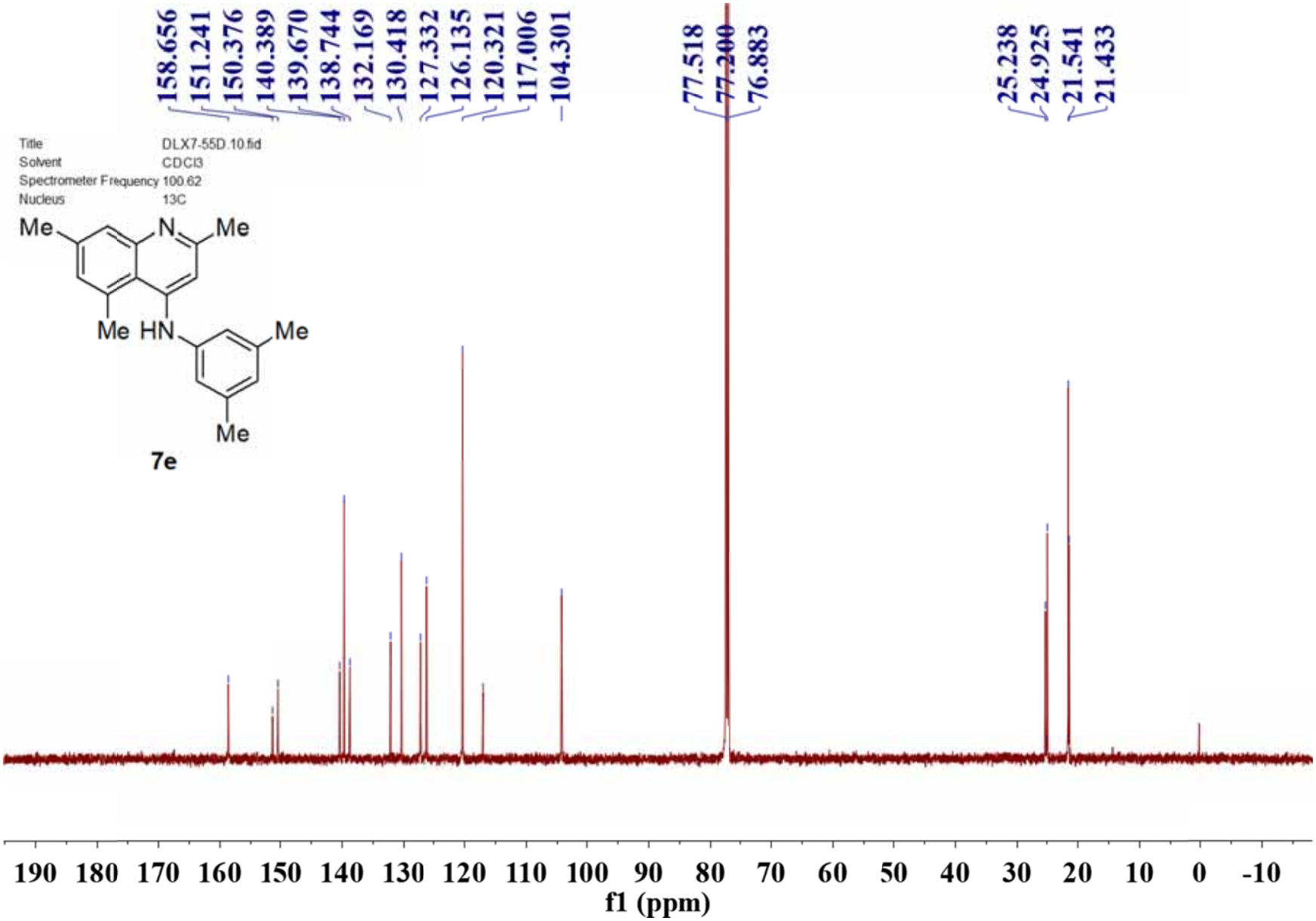

7.7874
7.7662
7.7462
7.3182
7.2992
7.2801
7.2653
7.2607
7.2447
7.1253
7.1199
7.0998
7.0087
6.9899
6.7894
6.7666
2.5432
2.5016
2.3862
0.0000
Title DLX8-36.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
HN
Me
7c
2.01
2.11
2.02
1.00
1.05
1.10
3.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 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)

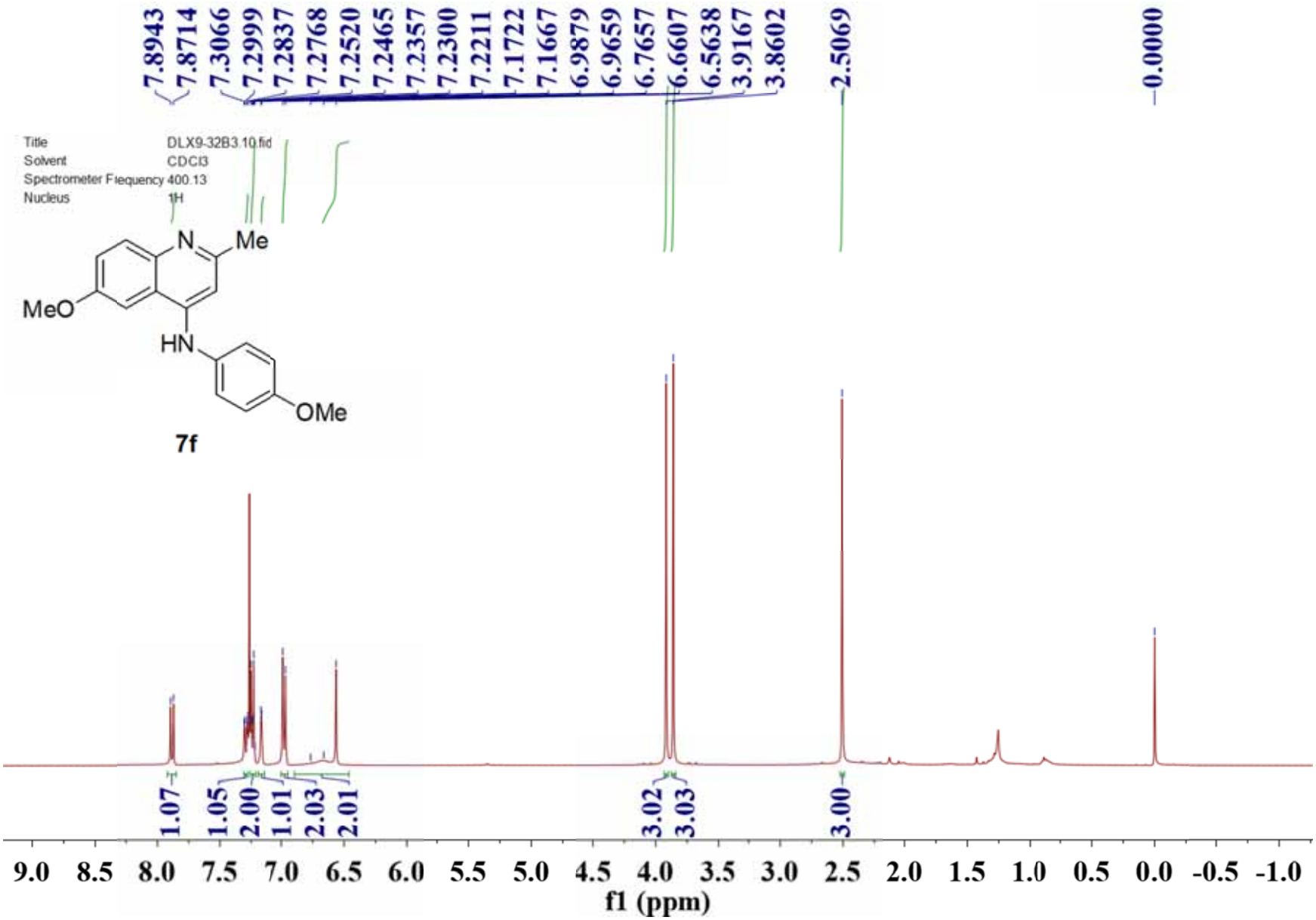

159.332
148.686
147.856
140.074
139.888
139.820
129.582
128.157
126.772
125.425
123.437
119.828
119.538
116.237
101.986
77.517
77.200
76.882
25.515
21.807
21.654
Title DLX8-36.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
HN
Me
7c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

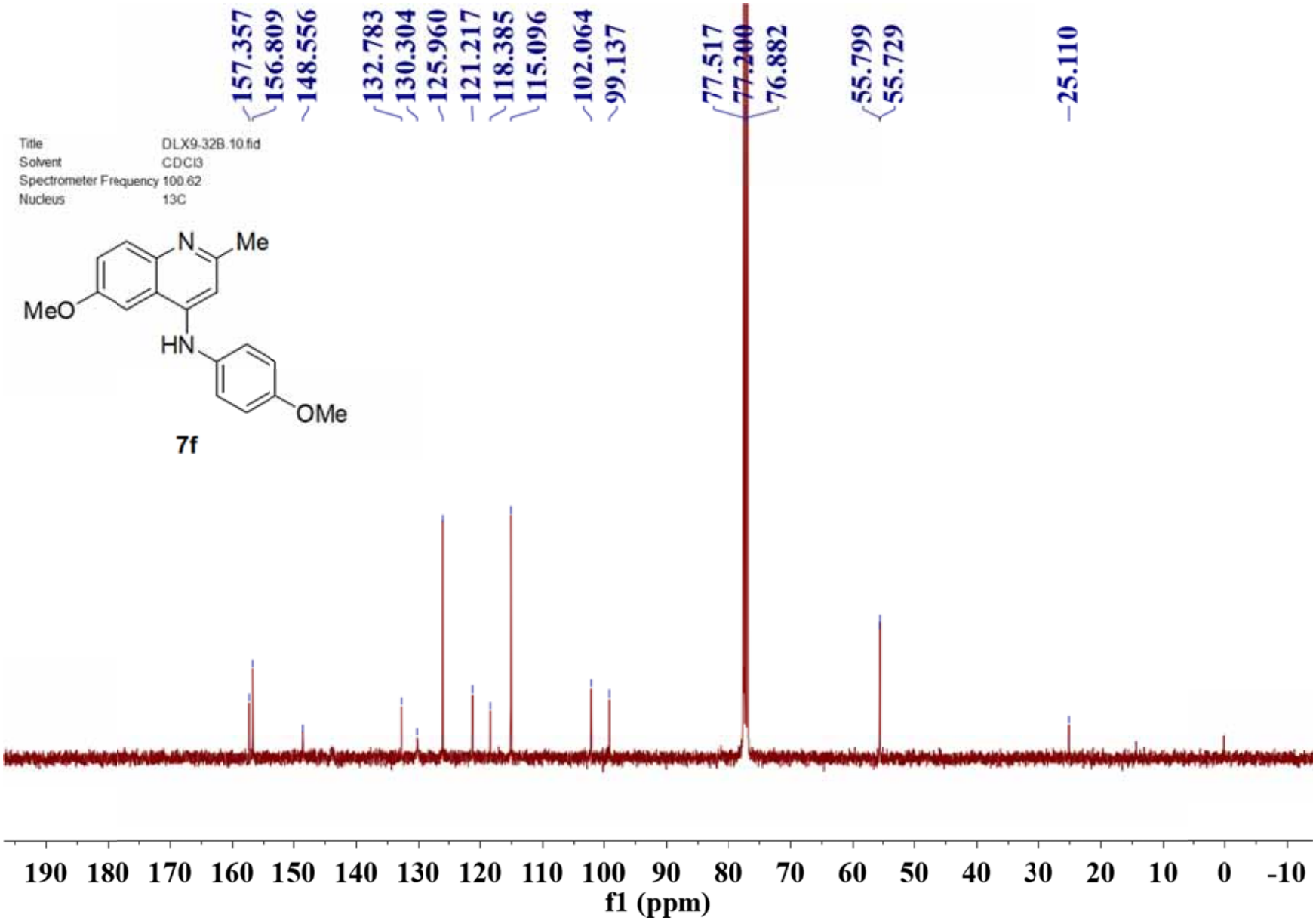

7.7891
7.7663
7.3274
7.3230
7.3167
7.3073
7.2871
7.0853
7.0791
7.0624
7.0561
6.8862
6.8823
6.8666
6.8635
6.8612
6.8491
6.8377
6.8320
6.8266
6.7296
6.7254
6.7089
6.7047
6.6539
3.9062
3.8198
2.5494
0.0000
Title DLX8-35A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
MeO
N
Me
HN
OMe
7d
1.08
2.05
1.08
3.05
1.09
1.00
3.02
3.05
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)

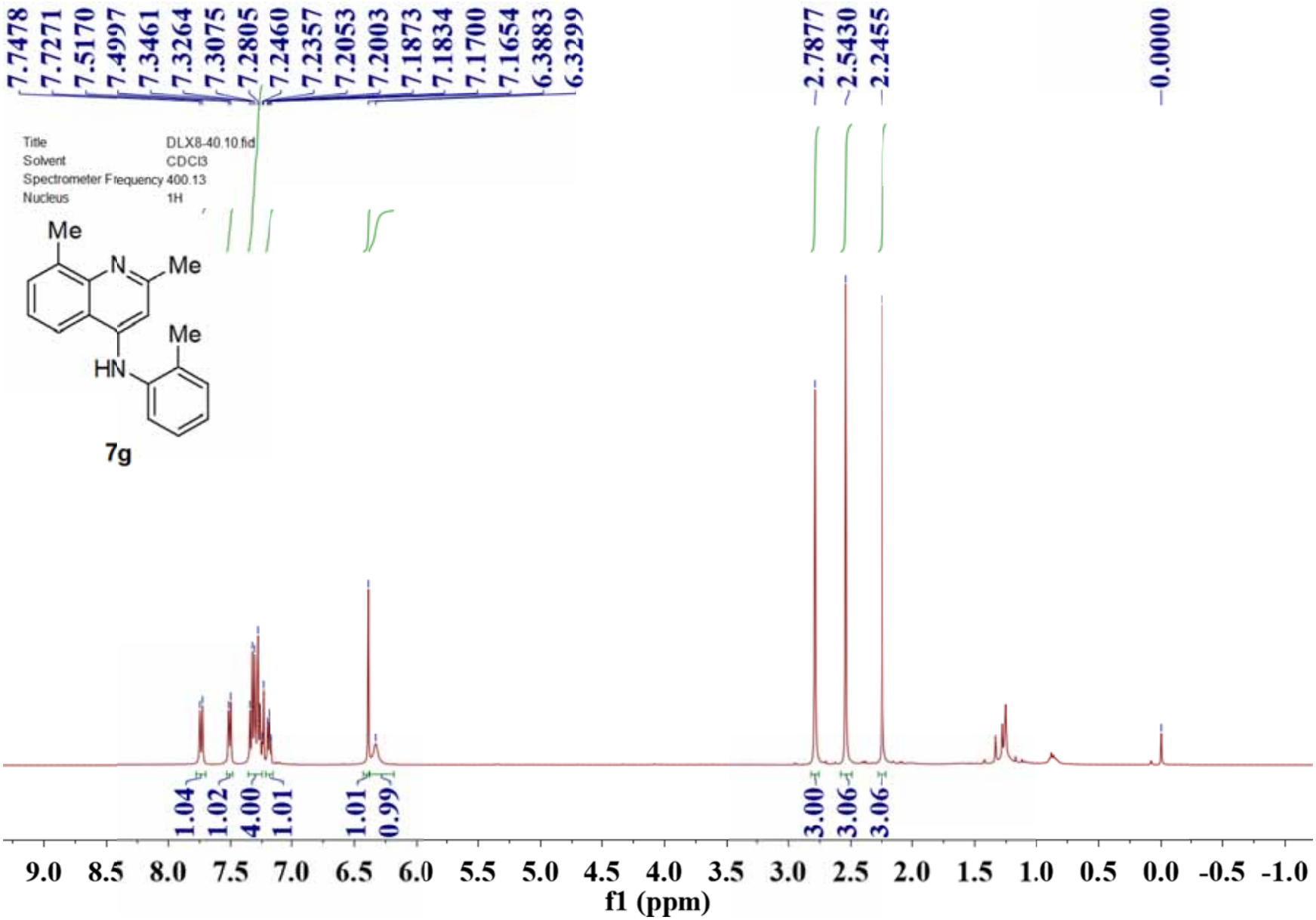

160.873
160.843
159.933
150.654
147.592
141.541
130.517
121.121
117.243
114.745
113.046
109.681
108.295
107.550
101.993
77.518
77.200
76.883
55.618
55.533
25.607
Title DLX8-35A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
MeO
N
Me
HN
OMe
7d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

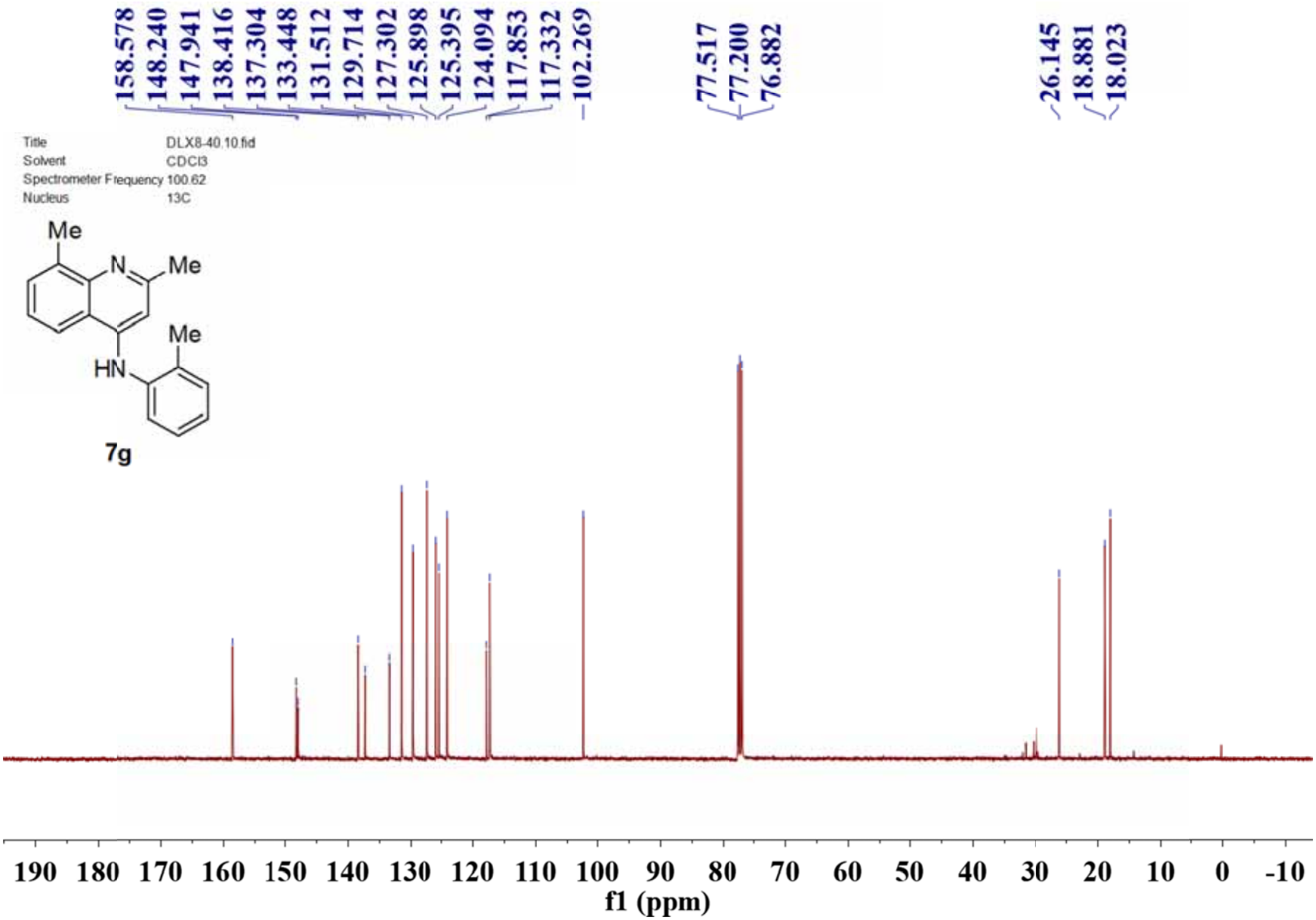

7.5939
6.9770
6.8563
6.8109
6.7877
6.7188
2.9396
2.4958
2.4347
2.3370
-0.0000
Title DLX7-55D.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
HN
Me
Me
7e
1.00
1.08
2.02
1.07
1.02
1.00
3.10
3.10
3.10
6.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

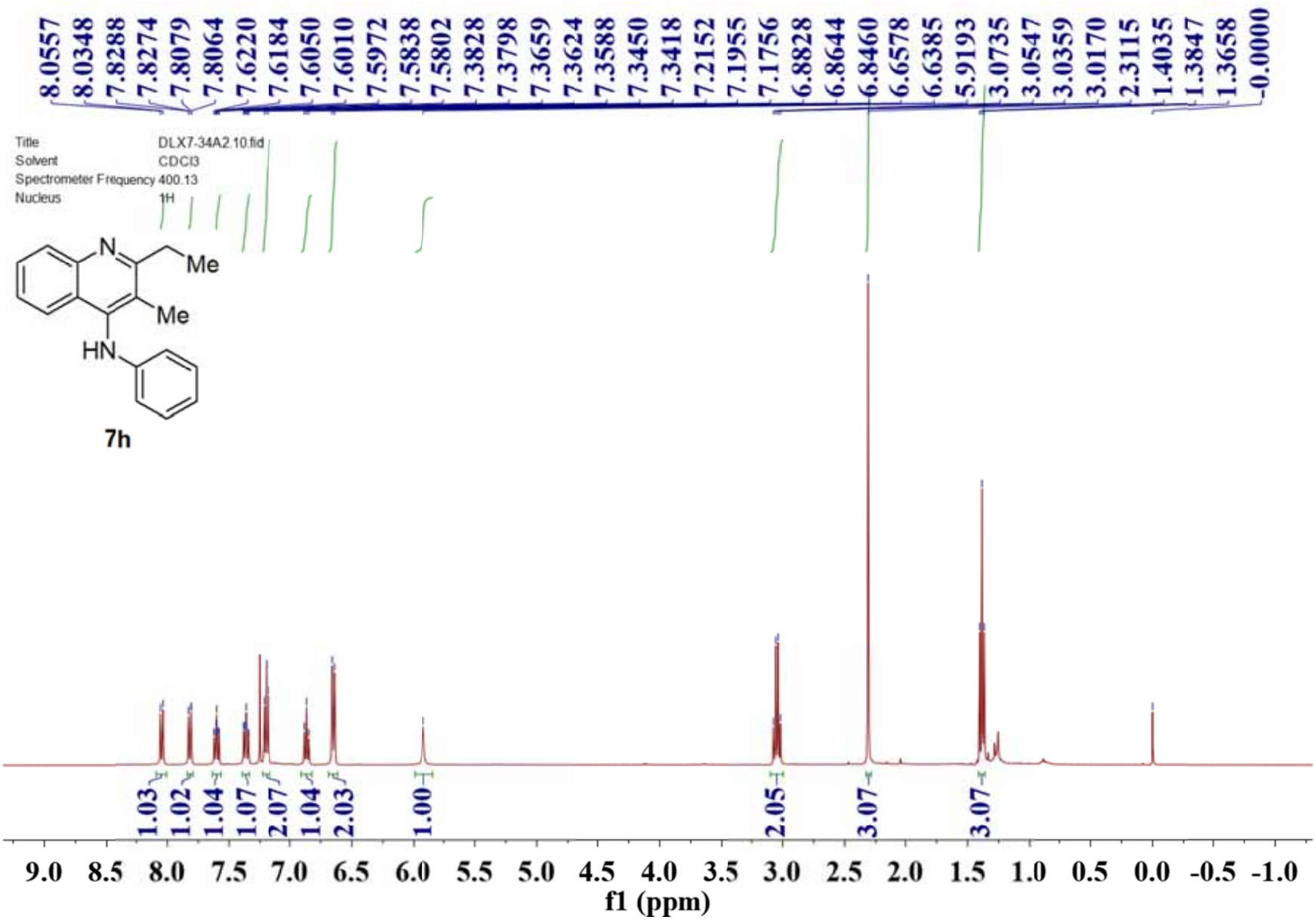

158.656
151.241
150.376
140.389
139.670
138.744
132.169
130.418
127.332
126.135
120.321
117.006
104.301
77.518
77.200
76.883
25.238
24.925
21.541
21.433
Title DLX7-55D.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
HN
Me
Me
7e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

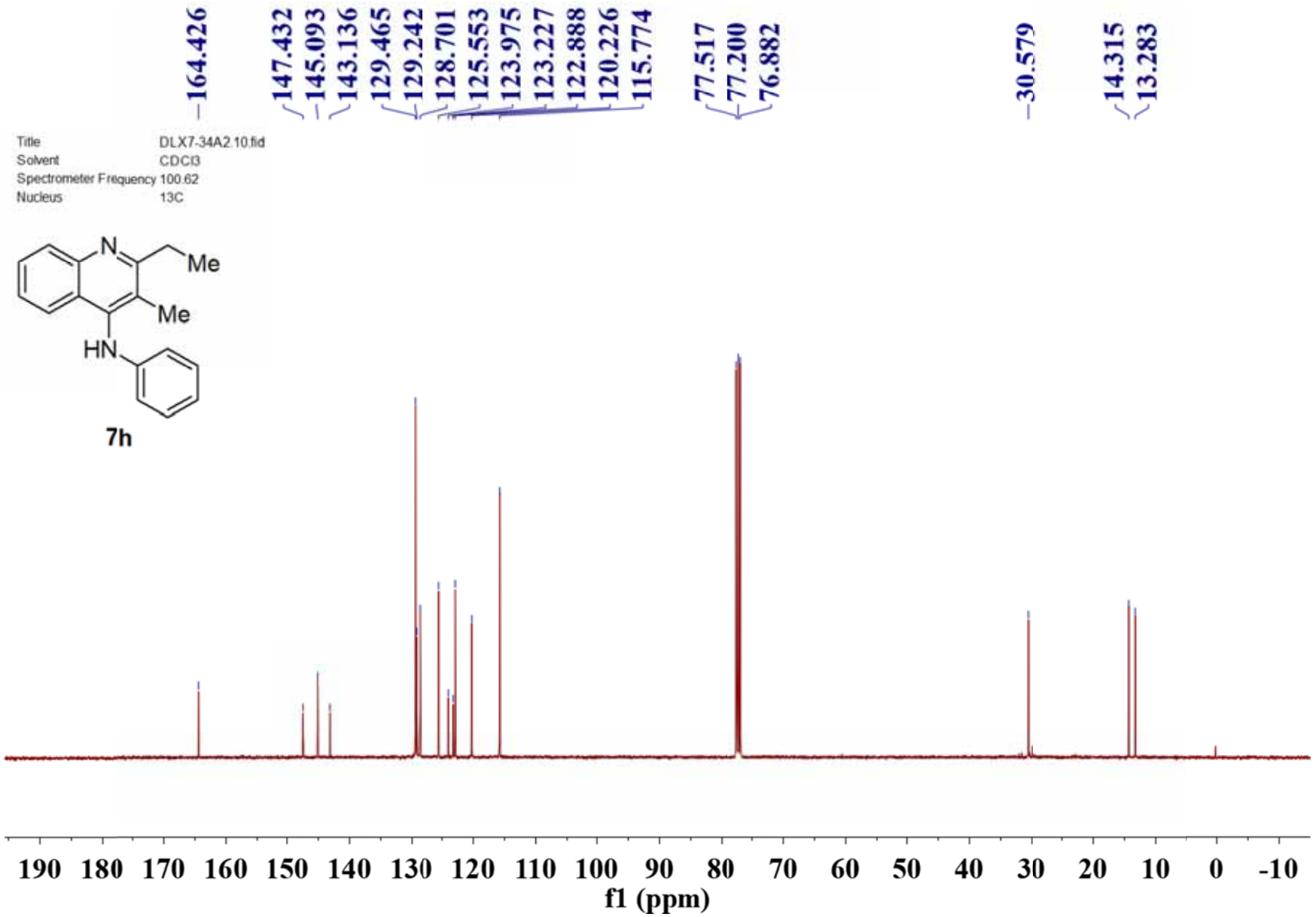

7.8943
7.8714
7.3066
7.2999
7.2837
7.2768
7.2520
7.2465
7.2357
7.2300
7.2211
7.1722
7.1667
6.9879
6.9659
6.7657
6.6607
6.5638
3.9167
3.8602
2.5069
0.0000
Title DLX9-32B3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Me
MeO
HN
OMe
7f
1.07
1.05
2.00
1.01
2.03
2.01
3.02
3.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

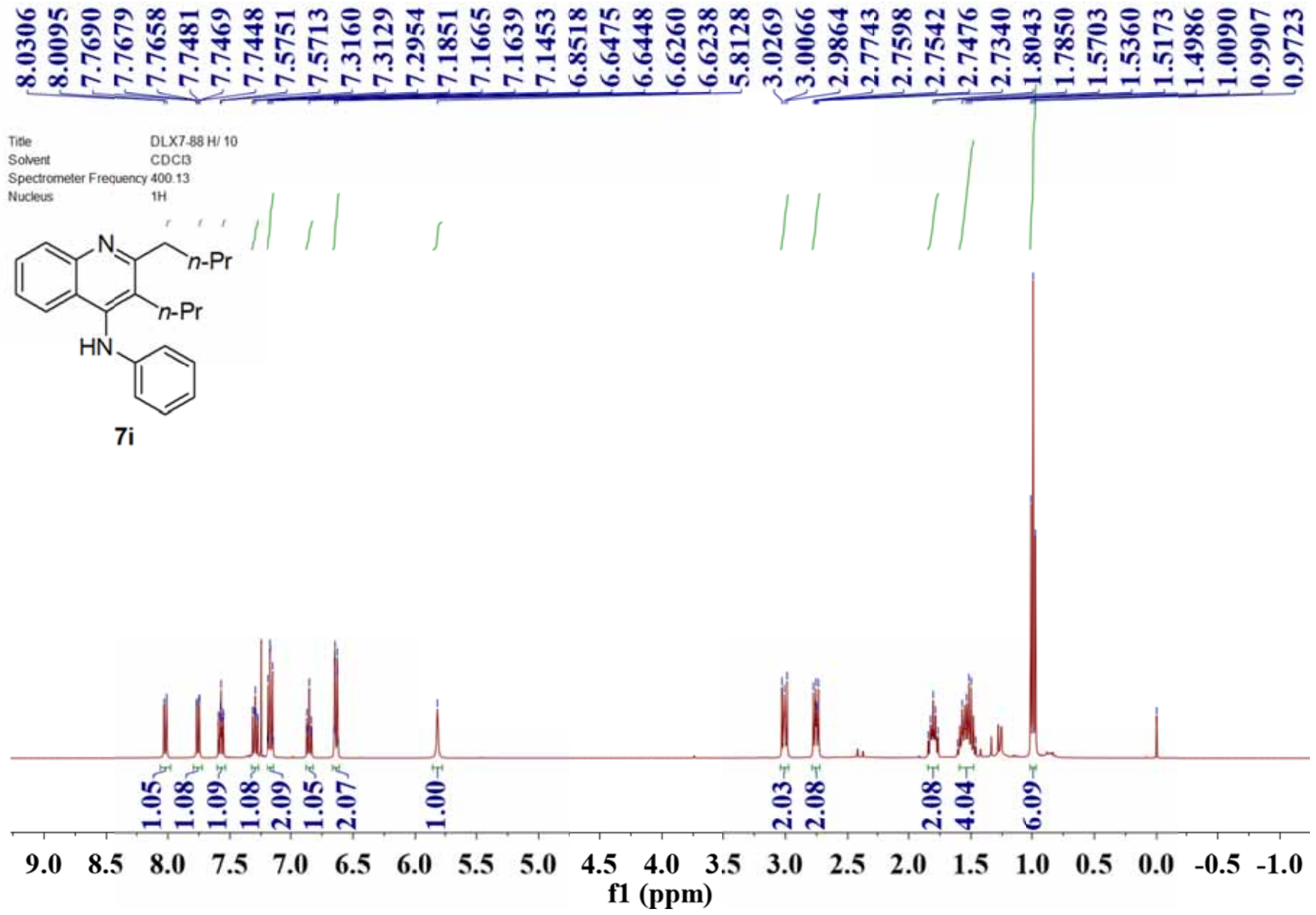

157.357
156.809
148.556
132.783
130.304
125.960
121.217
118.385
115.096
102.064
99.137
77.517
77.200
76.882
55.799
55.729
25.110
Title DLX9-32B.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
MeO
HN
OMe
7f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

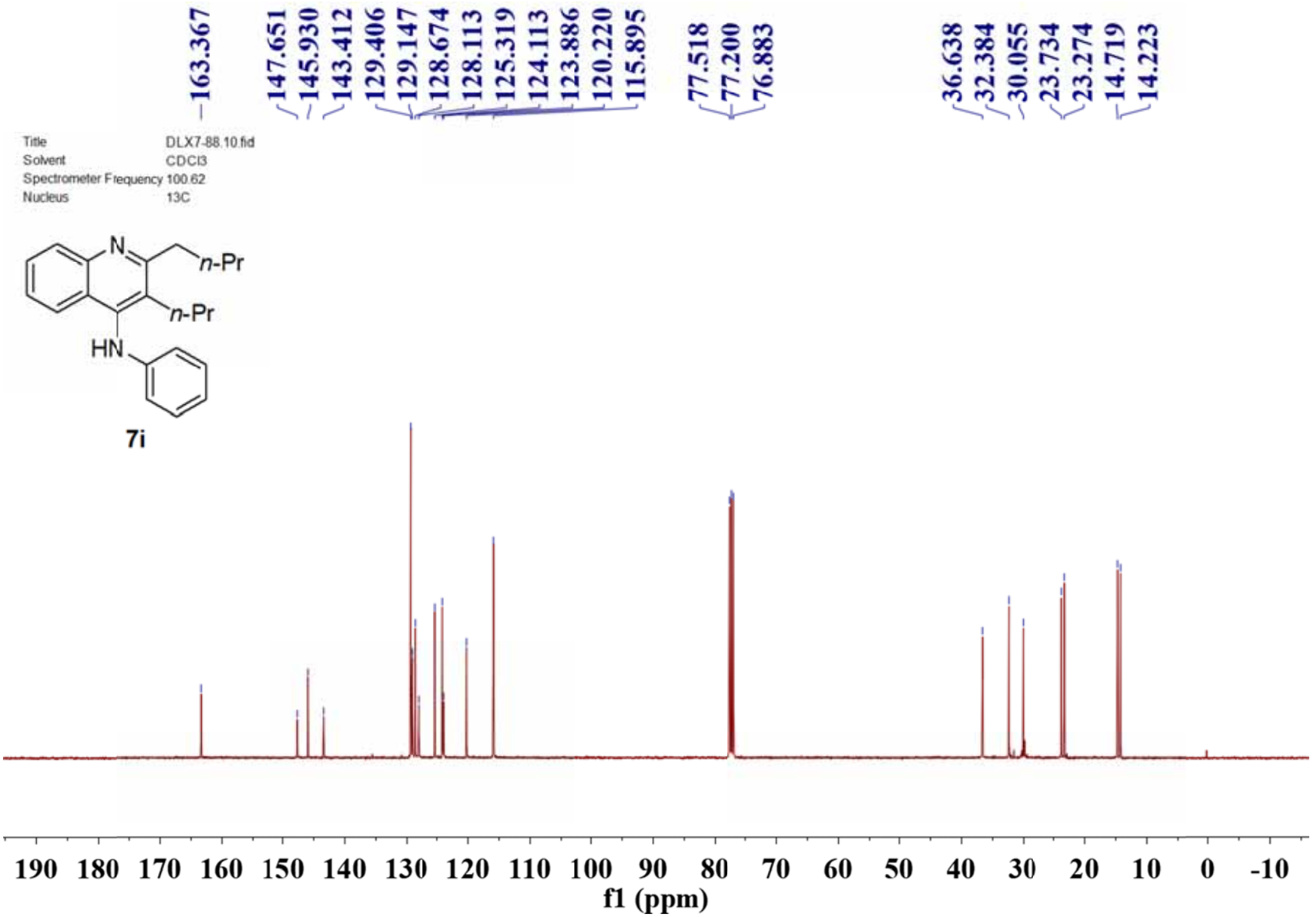

7.7478
7.7271
7.5170
7.4997
7.3461
7.3264
7.3075
7.2805
7.2460
7.2357
7.2053
7.2003
7.1873
7.1834
7.1700
7.1654
6.3883
6.3299
2.7877
2.5430
2.2455
0.0000
Title DLX8-40.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
HN
7g
1.04
1.02
4.00
1.01
1.01
0.99
3.00
3.06
3.06
9.0 8.5 8.0 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)

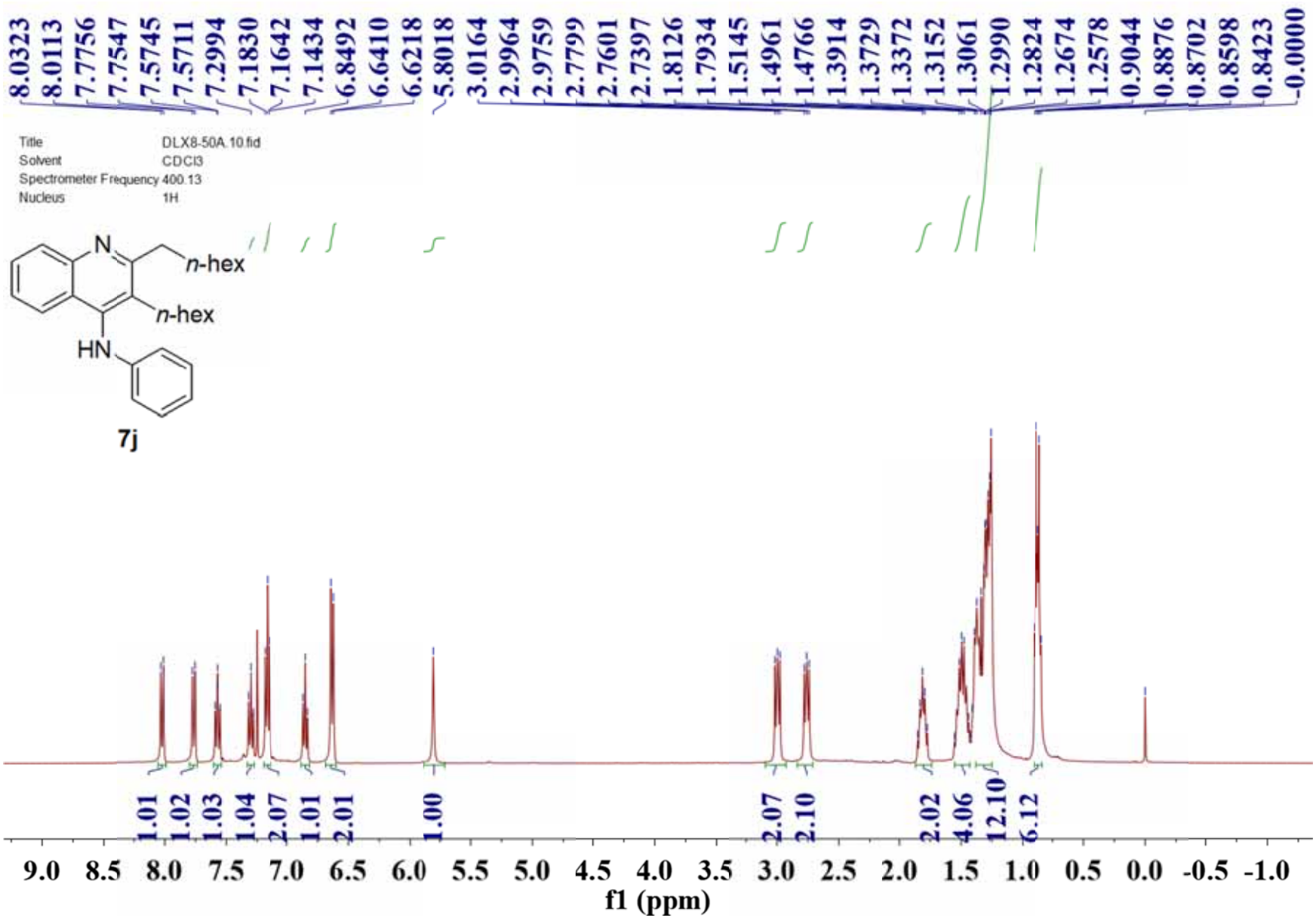

158.578
148.240
147.941
138.416
137.304
133.448
131.512
129.714
127.302
125.898
125.395
124.094
117.853
117.332
102.269
77.517
77.200
76.882
26.145
18.881
18.023
Title DLX8-40.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
HN
7g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

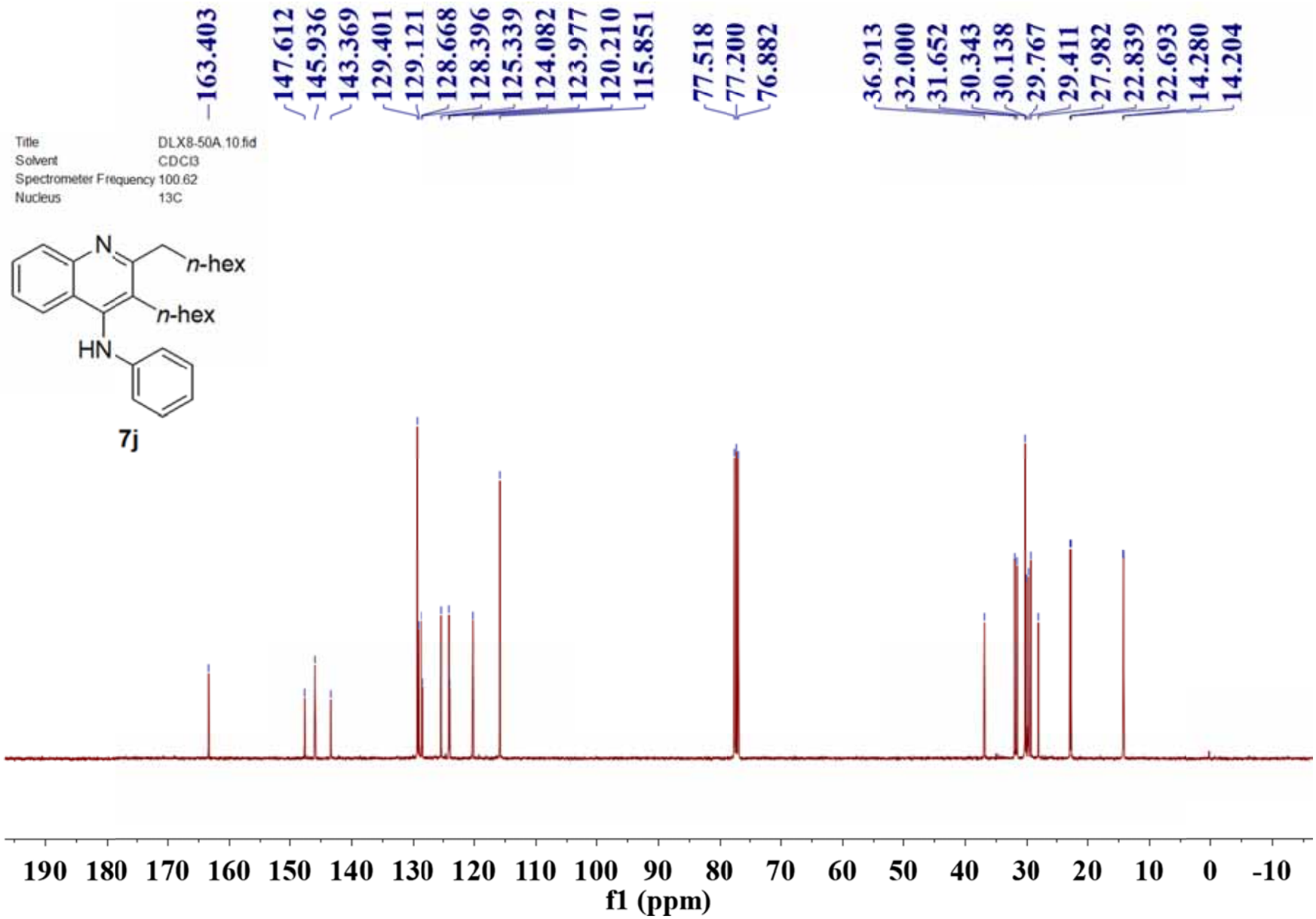

8.0557
8.0348
7.8288
7.8274
7.8079
7.8064
7.6220
7.6184
7.6050
7.6010
7.5972
7.5838
7.5802
7.3828
7.3798
7.3659
7.3624
7.3588
7.3450
7.3418
7.2152
7.1955
7.1756
6.8828
6.8644
6.8460
6.6578
6.6385
5.9193
3.0735
3.0547
3.0359
3.0170
2.3115
1.4035
1.3847
1.3658
-0.0000
Title DLX7-34A2.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Me
Me
HN
7h
1.03
1.02
1.04
1.07
2.07
1.04
2.03
1.00
2.05
3.07
3.07
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)

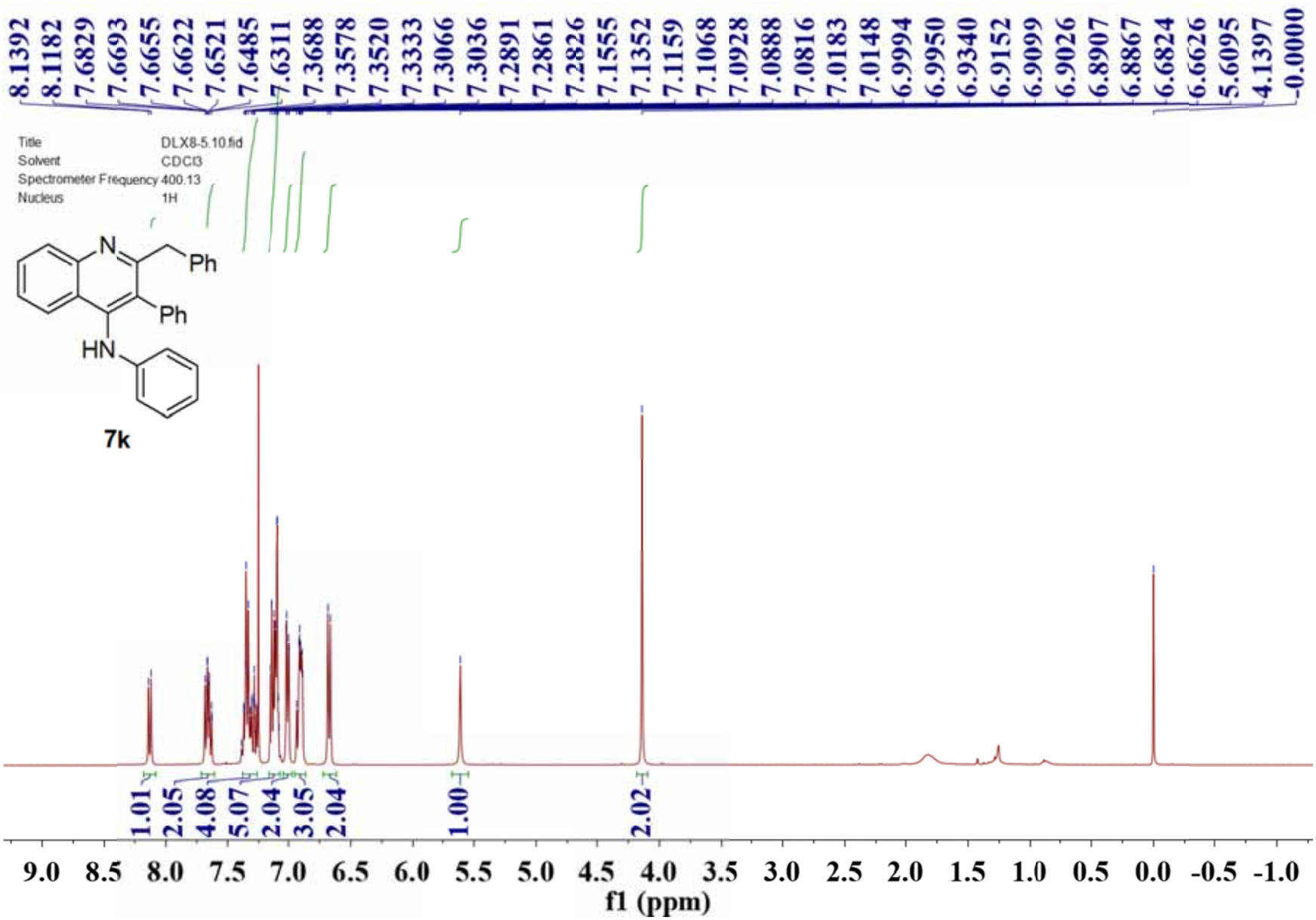

164.426
147.432
145.093
143.136
129.465
129.242
128.701
125.553
123.975
123.227
122.888
120.226
115.774
77.517
77.200
76.882
30.579
14.315
13.283
Title DLX7-34A2.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
Me
HN
7h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

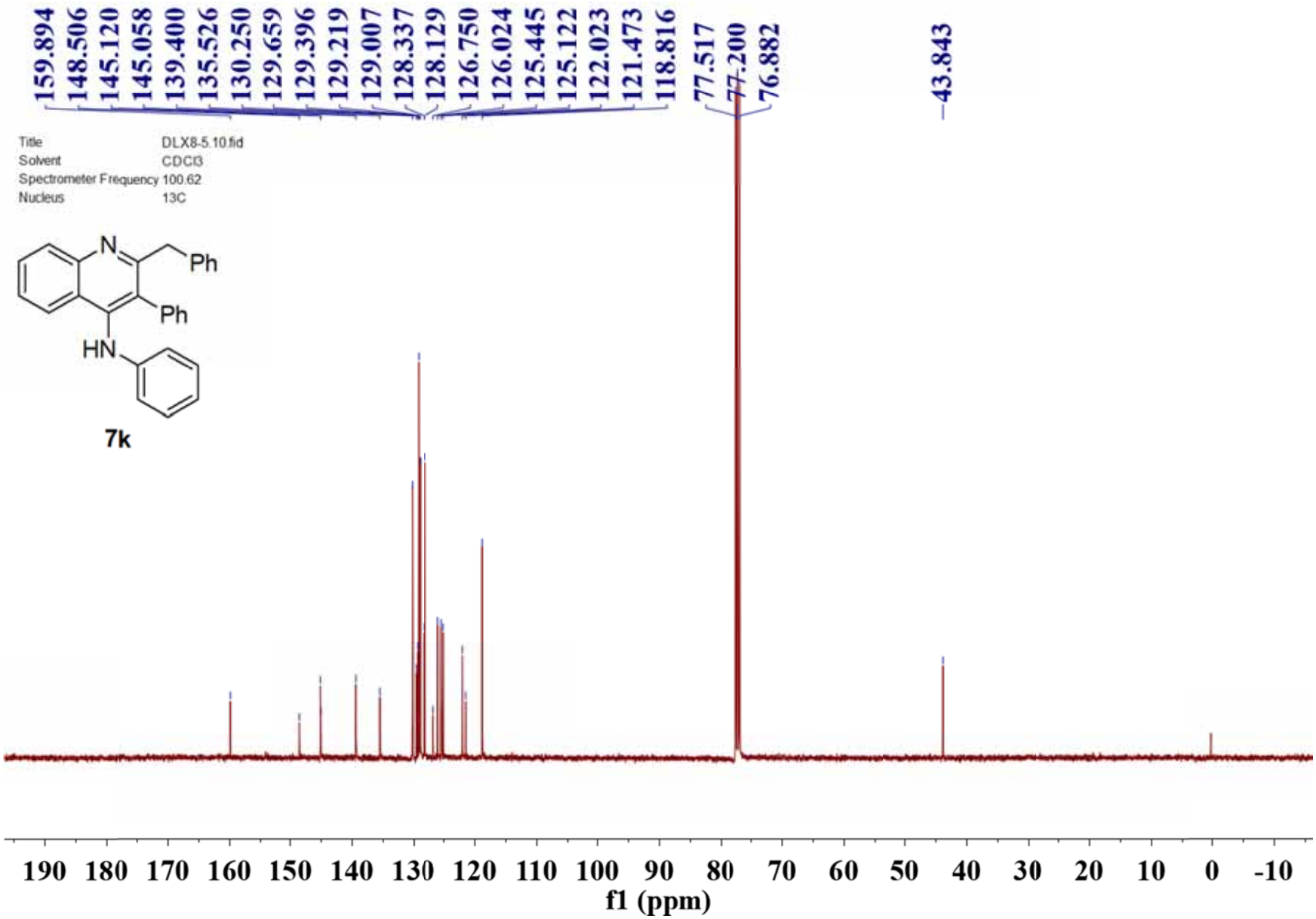

8.0306
8.0095
7.7690
7.7679
7.7658
7.7481
7.7469
7.7448
7.5751
7.5713
7.3160
7.3129
7.2954
7.1851
7.1665
7.1639
7.1453
6.8518
6.6475
6.6448
6.6260
6.6238
5.8128
3.0269
3.0066
2.9864
2.7743
2.7598
2.7542
2.7476
2.7340
1.8043
1.7850
1.5703
1.5360
1.5173
1.4986
1.0090
0.9907
0.9723
Title DLX7-88 H/ 10
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
n-Pr
n-Pr
HN
7i
1.05
1.08
1.09
1.08
2.09
1.05
2.07
1.00
2.03
2.08
2.08
4.04
6.09
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)

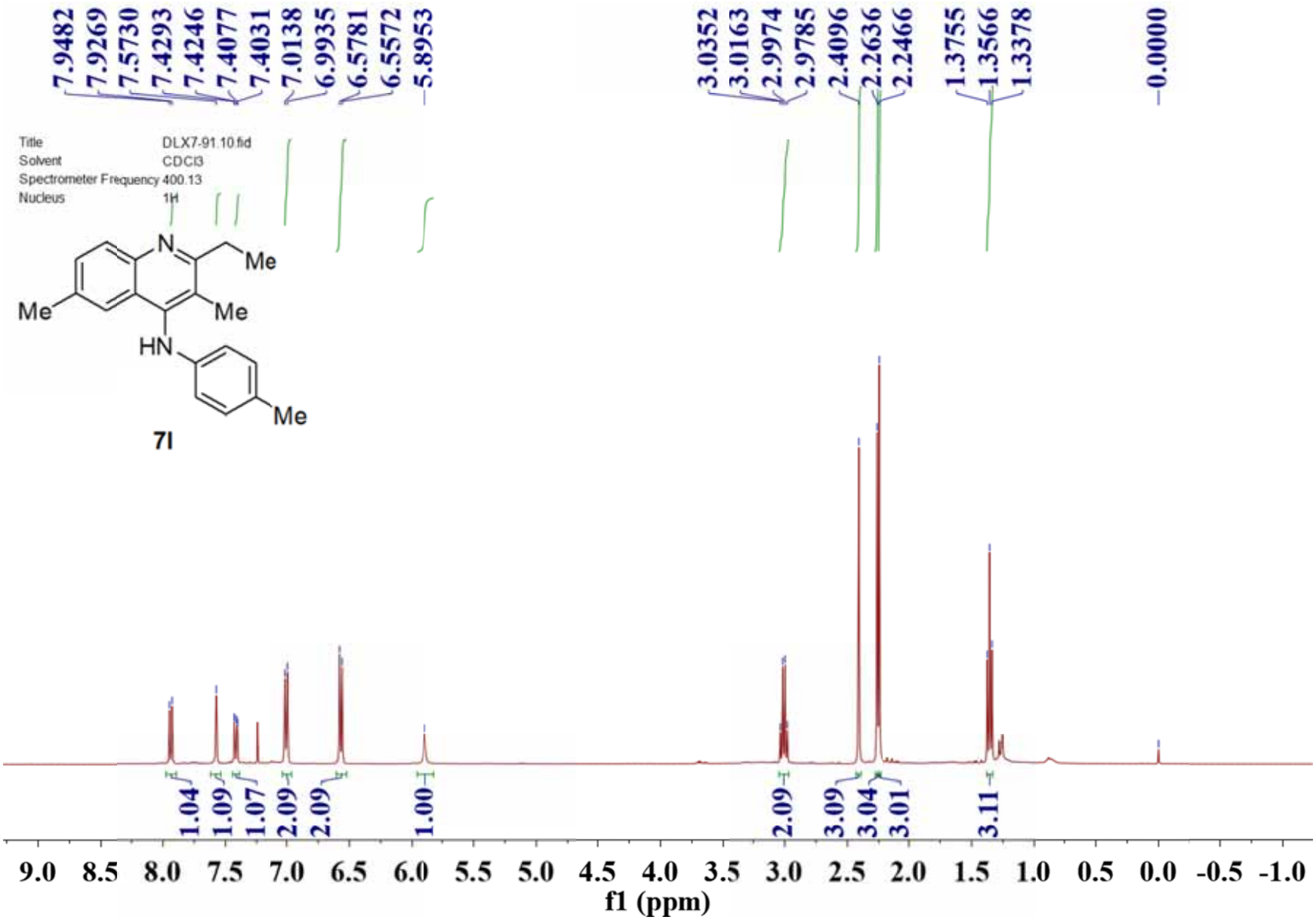

163.367
147.651
145.930
143.412
129.406
129.147
128.674
128.113
125.319
124.113
123.886
120.220
115.895
77.518
77.200
76.883
36.638
32.384
30.055
23.734
23.274
14.719
14.223
Title DLX7-88.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
n-Pr
n-Pr
HN
7i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

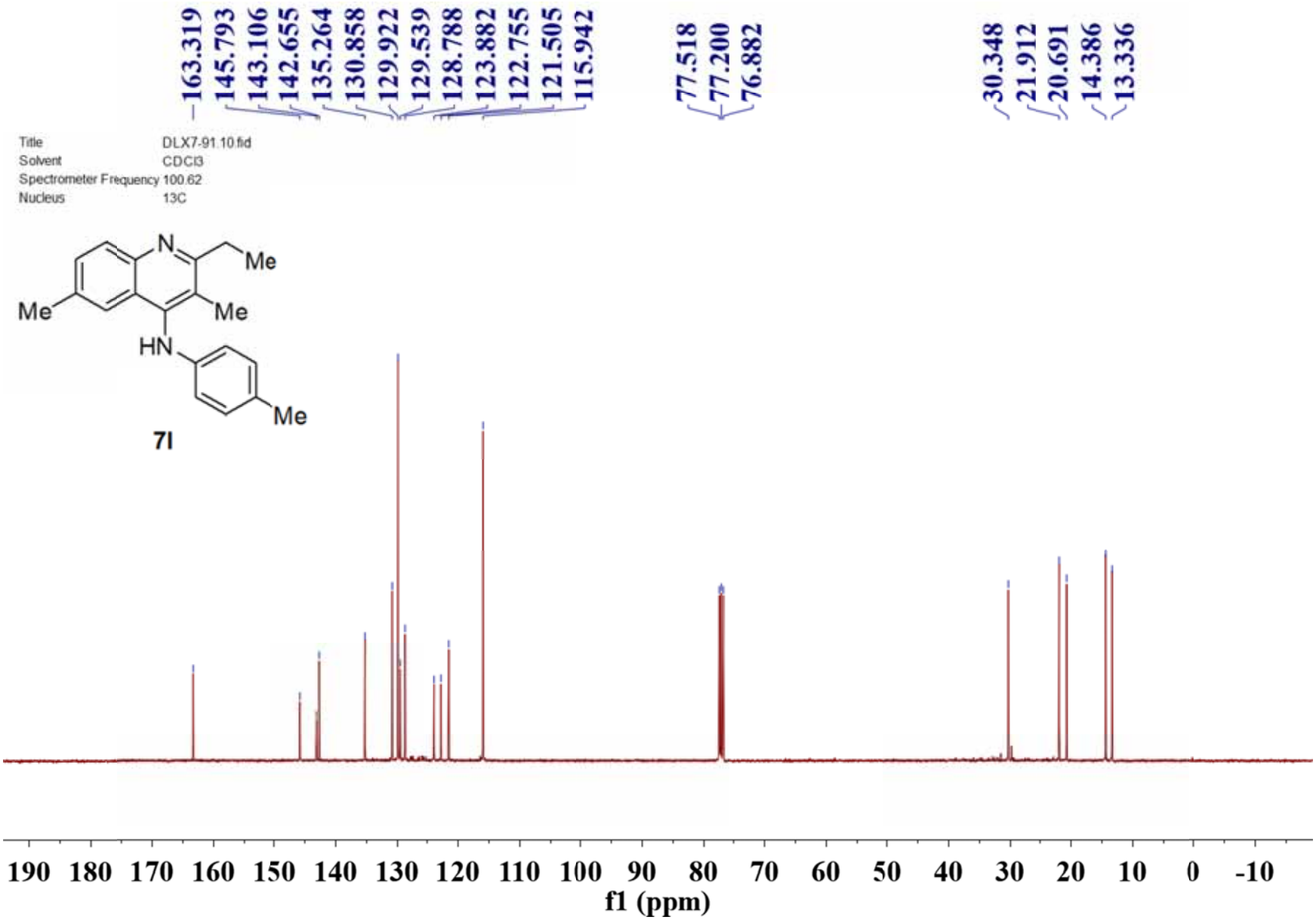

8.0323
8.0113
7.7756
7.7547
7.5745
7.5711
7.2994
7.1830
7.1642
7.1434
6.8492
6.6410
6.6218
5.8018
3.0164
2.9964
2.9759
2.7799
2.7601
2.7397
1.8126
1.7934
1.5145
1.4961
1.4766
1.3914
1.3729
1.3372
1.3152
1.3061
1.2990
1.2824
1.2674
1.2578
0.9044
0.8876
0.8702
0.8598
0.8423
-0.0000
Title DLX8-50A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
n-hex
n-hex
HN
7j
1.01
1.02
1.03
1.04
2.07
1.01
2.01
1.00
2.07
2.10
2.02
4.06
12.10
6.12
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)

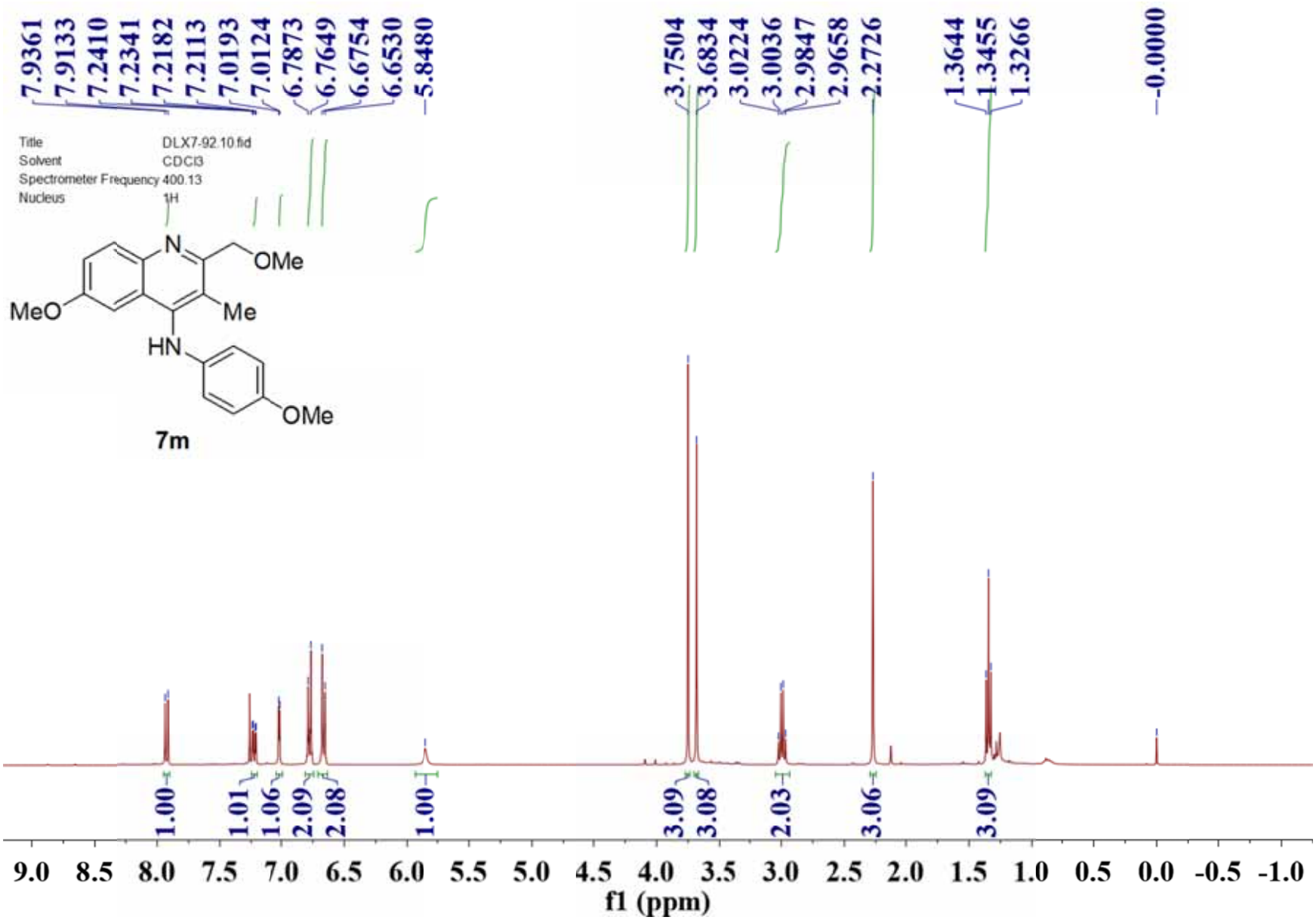

163.403
147.612
145.936
143.369
129.401
129.121
128.668
128.396
125.339
124.082
123.977
120.210
115.851
77.518
77.200
76.882
36.913
32.000
31.652
30.343
30.138
29.767
29.411
27.982
22.839
22.693
14.280
14.204
Title DLX8-50A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
n-hex
n-hex
HN
7j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

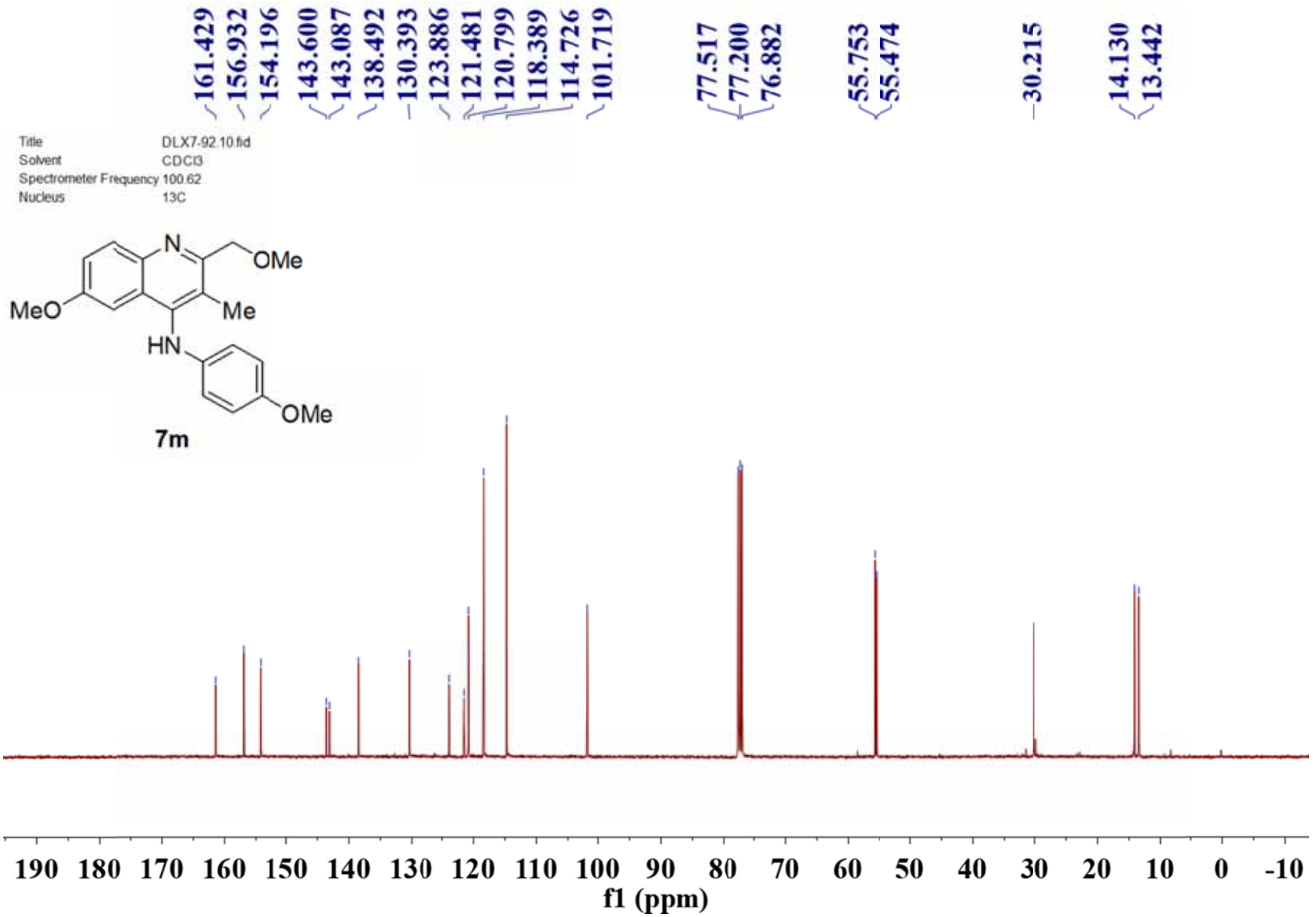

8.1392
8.1182
7.6829
7.6693
7.6655
7.6622
7.6521
7.6485
7.6311
7.3688
7.3578
7.3520
7.3333
7.3066
7.3036
7.2891
7.2861
7.2826
7.1555
7.1352
7.1159
7.1068
7.0928
7.0888
7.0816
7.0183
7.0148
6.9994
6.9950
6.9340
6.9152
6.9099
6.9026
6.8907
6.8867
6.6824
6.6626
5.6095
4.1397
-0.0000
Title DLX8-5.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Ph
Ph
HN
7k
1.01
2.05
4.08
5.07
2.04
3.05
2.04
1.00
2.02
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)

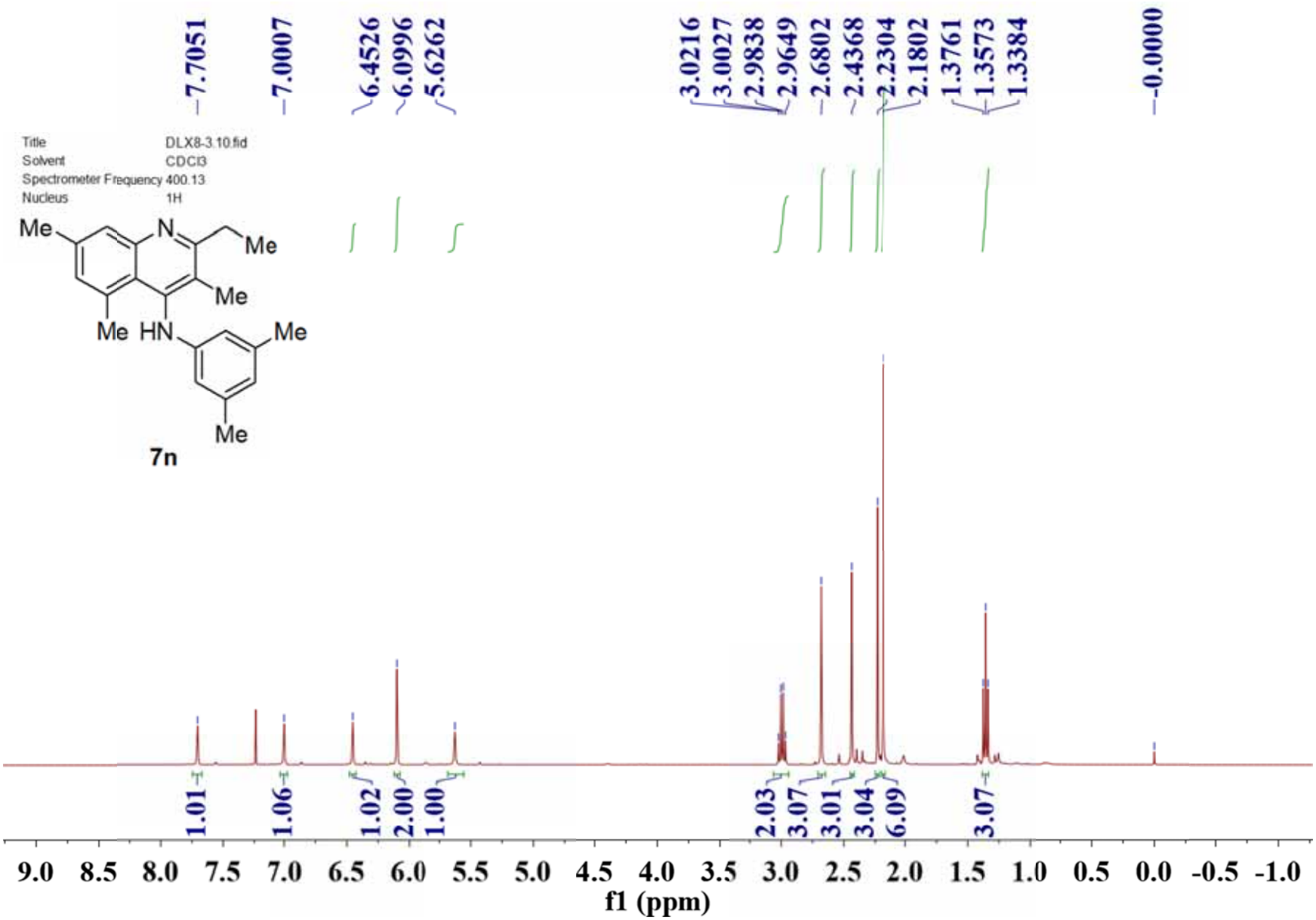

159.894
148.506
145.120
145.058
139.400
135.526
130.250
129.659
129.396
129.219
129.007
128.337
128.129
126.750
126.024
125.445
125.122
122.023
121.473
118.816
77.517
77.200
76.882
43.843
Title DLX8-5.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Ph
Ph
HN
7k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

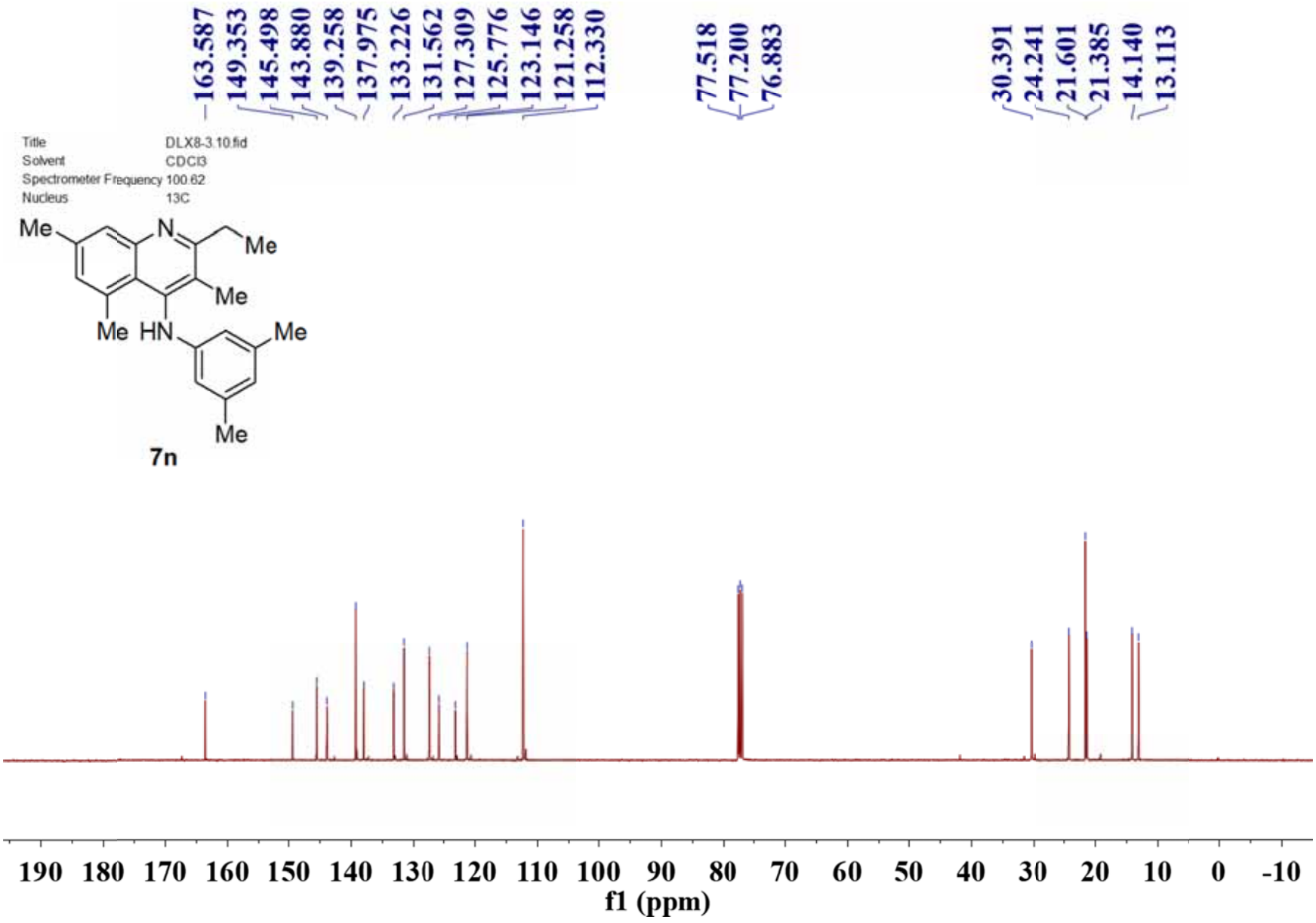

7.9482
7.9269
7.5730
7.4293
7.4246
7.4077
7.4031
7.0138
6.9935
6.5781
6.5572
5.8953
3.0352
3.0163
2.9974
2.9785
2.4096
2.2636
2.2466
1.3755
1.3566
1.3378
0.0000
Title DLX7-91.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Me
Me
Me
HN
Me
7l
1.04
1.09
1.07
2.09
2.09
1.00
2.09
3.09
3.04
3.01
3.11
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)

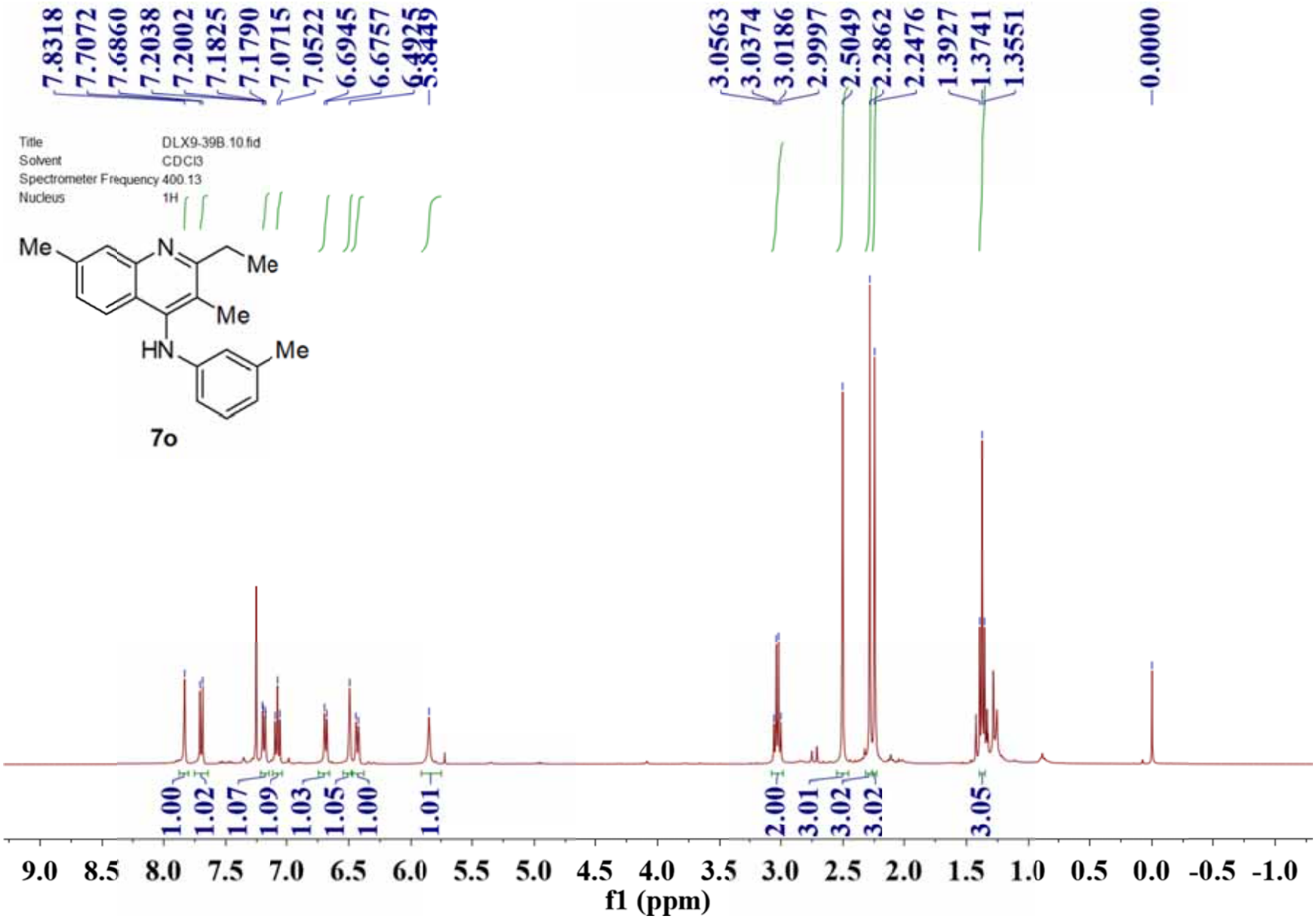

163.319
145.793
143.106
142.655
135.264
130.858
129.922
129.539
128.788
123.882
122.755
121.505
115.942
77.518
77.200
76.882
30.348
21.912
20.691
14.386
13.336
Title DLX7-91.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
Me
Me
HN
Me
7l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

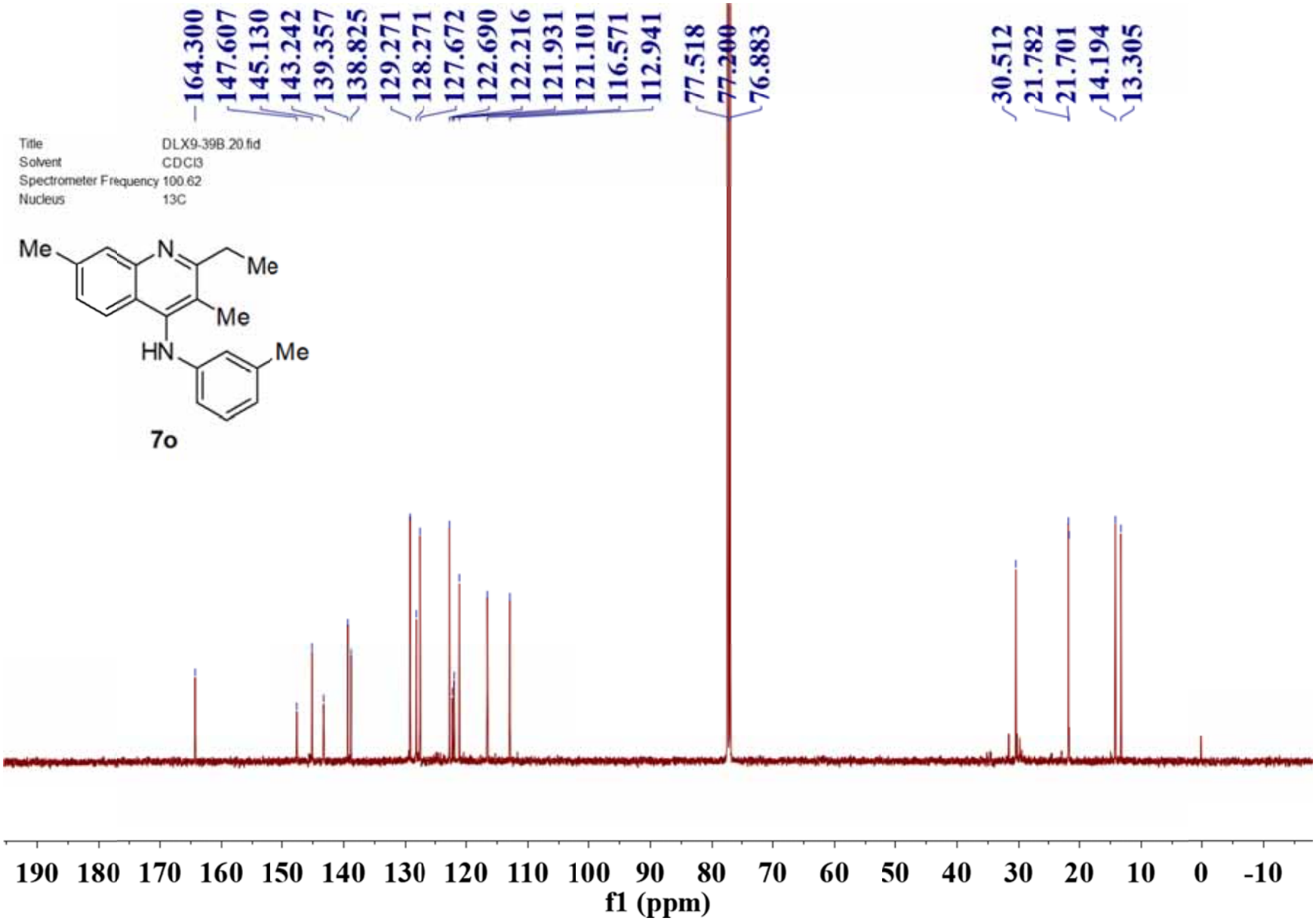

7.9361
7.9133
7.2410
7.2341
7.2182
7.2113
7.0193
7.0124
6.7873
6.7649
6.6754
6.6530
5.8480
3.7504
3.6834
3.0224
3.0036
2.9847
2.9658
2.2726
1.3644
1.3455
1.3266
0.0000
Title DLX7-92.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
OMe
MeO
Me
HN
OMe
7m
1.00
1.01
1.06
2.09
2.08
1.00
3.09
3.08
2.03
3.06
3.09
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)

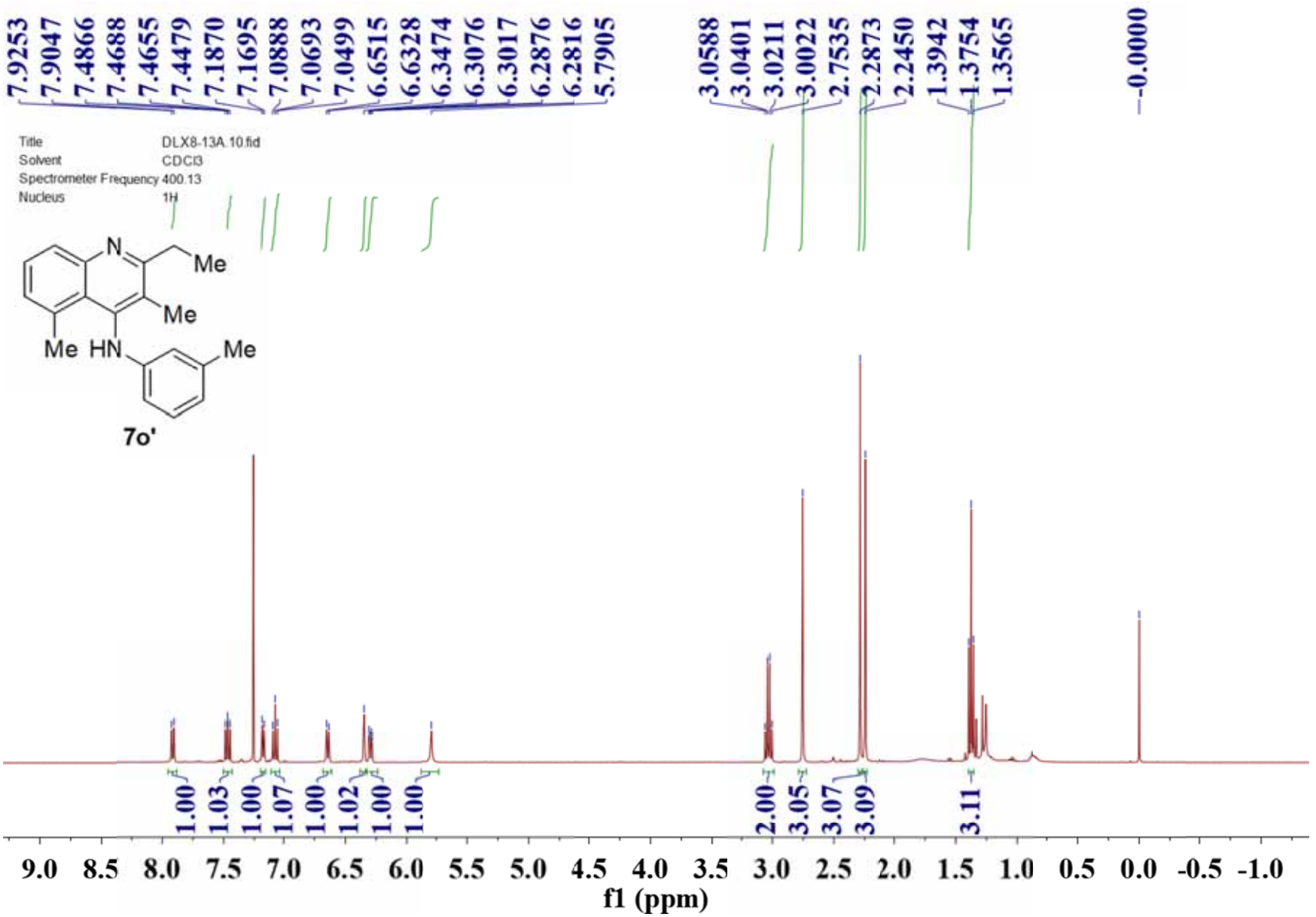

161.429
156.932
154.196
143.600
143.087
138.492
130.393
123.886
121.481
120.799
118.389
114.726
101.719
77.517
77.200
76.882
55.753
55.474
30.215
14.130
13.442
Title DLX7-92.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
OMe
MeO
Me
HN
OMe
7m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

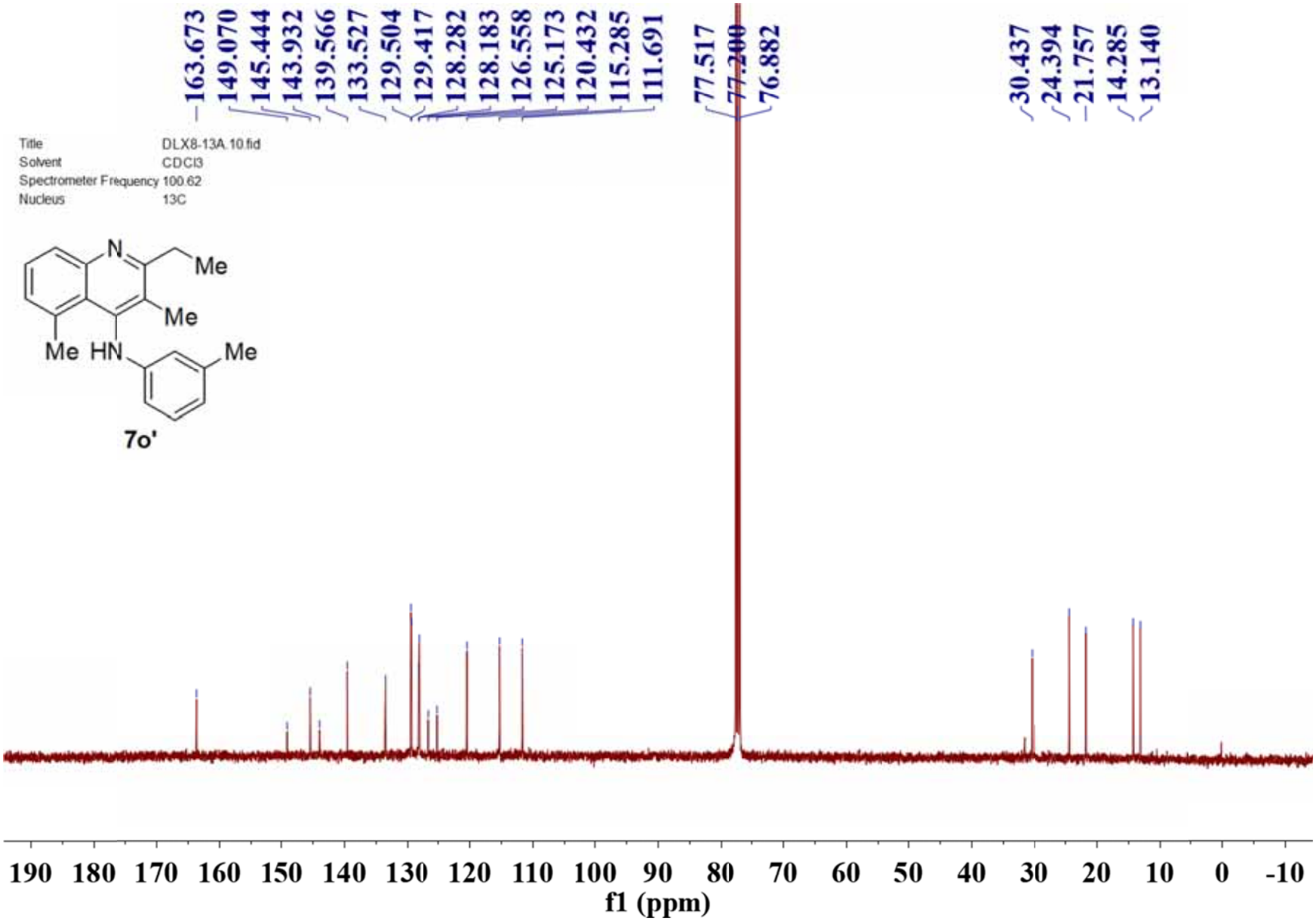

7.7051
7.0007
6.4526
6.0996
5.6262
3.0216
3.0027
2.9838
2.9649
2.6802
2.4368
2.2304
2.1802
1.3761
1.3573
1.3384
0.0000
Title DLX8-3.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
Me HN
Me
Me
7n
1.01
1.06
1.02
2.00
1.00
2.03
3.07
3.01
3.04
6.09
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)


163.587
149.353
145.498
143.880
139.258
137.975
133.226
131.562
127.309
125.776
123.146
121.258
112.330
77.518
77.200
76.883
30.391
24.241
21.601
21.385
14.140
13.113
Title DLX8-3.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
Me HN
Me
Me
7n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.8318
7.7072
7.6860
7.2038
7.2002
7.1825
7.1790
7.0715
7.0522
6.6945
6.6757
6.4925
5.8449
3.0563
3.0374
3.0186
2.9997
2.5049
2.2862
2.2476
1.3927
1.3741
1.3551
0.0000
Title DLX9-39B.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
Me
N
Me
Me
HN
Me
7o
1.00
1.02
1.07
1.09
1.03
1.05
1.00
1.01
2.00
3.01
3.02
3.02
3.05
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)


164.300
147.607
145.130
143.242
139.357
138.825
129.271
128.271
127.672
122.690
122.216
121.931
121.101
116.571
112.941
77.518
77.200
76.883
30.512
21.782
21.701
14.194
13.305
Title DLX9-39B.20.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
Me
N
Me
Me
HN
Me
7o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.9253
7.9047
7.4866
7.4688
7.4655
7.4479
7.1870
7.1695
7.0888
7.0693
7.0499
6.6515
6.6328
6.3474
6.3076
6.3017
6.2876
6.2816
5.7905
3.0588
3.0401
3.0211
3.0022
2.7535
2.2873
2.2450
1.3942
1.3754
1.3565
-0.0000
Title DLX8-13A.10.fid
Solvent CDCl3
Spectrometer Frequency 400.13
Nucleus 1H
N
Me
Me
Me HN
Me
7o'
1.00
1.03
1.00
1.07
1.00
1.02
1.00
1.00
2.00
3.05
3.07
3.09
3.11
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)


163.673
149.070
145.444
143.932
139.566
133.527
129.504
129.417
128.282
128.183
126.558
125.173
120.432
115.285
111.691
77.517
77.200
76.882
30.437
24.394
21.757
14.285
13.140
Title DLX8-13A.10.fid
Solvent CDCl3
Spectrometer Frequency 100.62
Nucleus 13C
N
Me
Me
Me HN
Me
7o'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)