Divergent Synthesis of 2-Methylthioindole and 2-Unsubstituted Indole Derivatives Mediated by $SOCl_2$ and Dimethyl/diethyl Sulfoxides

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Supporting Information

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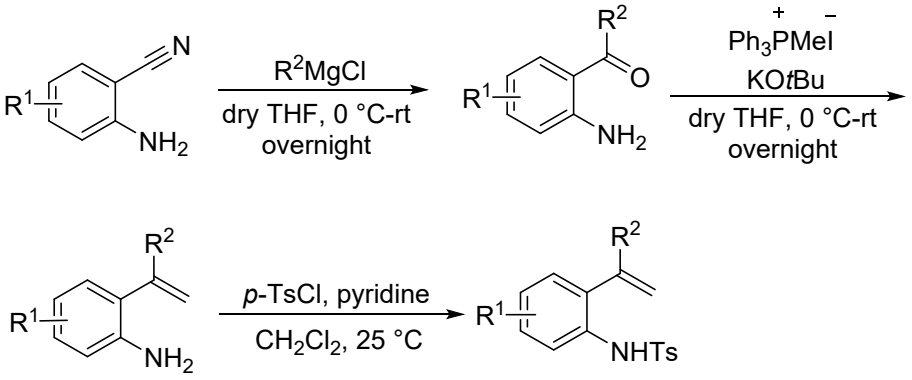
I. General Information

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 ^{o}C. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J*, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectrometer. Melting points were determined with a Micromelting point apparatus. TLC plates were visualized by exposure to ultraviolet light.

Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 ^{o}C for 3 h before used. Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE).

II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the synthesis of 1-phenylvinylaniline derivatives 1 (1a-q):[1]



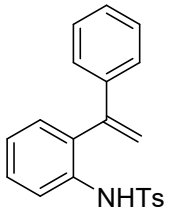
General procedure: 2-Aminobenzonitrile (1.0 equiv, 10 mmol) was added to a solution of Grignard reagent (3.0 equiv, 30 mmol) in THF (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Saturated aq. NH_4Cl (30 mL) was then cautiously added dropwise by syringe until gas evolution ceased. The reaction mixture was then extracted with CH_2Cl_2 (3 x 30 mL). The organic solvent was removed by rotary evaporator under vacuum and the residue was purified by flash column chromatography on silica gel to afford ketone intermediate.

To a stirred solution of Ph_3PMeI (1.5 equiv, 7.5 mmol) in dry THF (10 mL) was added KO^{t}Bu (1.5 equiv, 7.5 mmol) in portions under nitrogen. After the mixture was stirred at room temperature for 0.5 h, a solution of the corresponding ketone (1 equiv, 5 mmol) in THF (10 mL) was added dropwise. The reaction mixture was then stirred at room temperature under nitrogen overnight. Then the reaction mixture was quenched with water and extracted with EtOAc (25 mL x 2). The combined organic layers were washed with saturated aq. $NaHCO_3$ (25 mL) and brine (25 mL), dried over anhydrous Na_2SO_4, and concentrated on rotary evaporator under vacuum. The residue was purified by column chromatography on silica gel to give 2-alkenylaniline.

To a solution of 2-alkenylaniline (1.0 equiv, 10.0 mmol) in pyridine (20 mL) was added *p*-toluenesulfonyl chloride (1.1 equiv, 11.0 mmol) at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (3 x 30 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/PE = 1/5) to give the corresponding 1-phenylvinylaniline product.

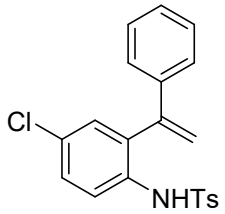
b. Spectroscopic data of 1-phenylvinylaniline derivatives 1 (1a-q):

4-Methyl-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1a)



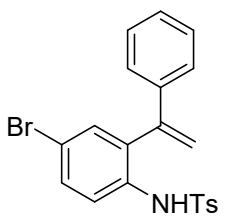
Following the general procedure, **1a** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 80%); mp: 88-90 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.10 (dd, *J* = 10.3, 4.2 Hz, 3H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.53 (s, 1H), 5.69 (s, 1H), 4.89 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 143.7, 138.7, 136.1, 134.3, 133.1, 130.5, 129.5, 128.9, 128.8, 128.6, 127.3, 126.4, 124.7, 121.1, 117.1, 21.5. HRMS (ESI) calcd for $C_{21}H_{19}NNaO_2S^+$ [M + Na^+] 372.1029, found 372.1022.

***N*-(4-Chloro-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1b)**



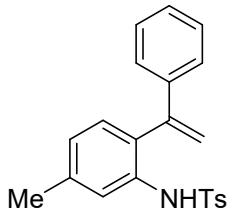
Following the general procedure, **1b** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 82%); mp: 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 7.01 (dt, *J* = 8.5, 1.8 Hz, 2H), 6.45 (s, 1H), 5.69 (d, *J* = 0.6 Hz, 1H), 4.88 (d, *J* = 0.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.99, 143.96, 137.9, 135.8, 134.8, 133.0, 130.24, 130.22, 129.6, 129.0, 128.89, 128.85, 127.2, 126.3, 122.7, 117.8, 21.8. HRMS (ESI) calcd for $C_{21}H_{18}{}^{35}ClNNaO_2S^+$ [M + Na^+] 406.0639, found 406.0635.

***N*-(4-Bromo-2-(1-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (1c)**



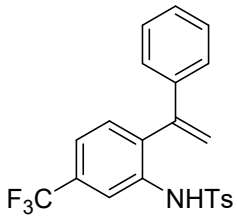
Following the general procedure, **1c** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 78%); mp: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.35 – 7.28 (m, 1H), 7.23 (dd, *J* = 8.7, 1.8 Hz, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.95 (m, 2H), 6.45 (s, 1H), 5.70 (d, *J* = 0.4 Hz, 1H), 4.89 (d, *J* = 0.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.8, 137.9, 135.7, 135.0, 133.5, 133.1, 131.8, 129.6, 129.0, 128.9, 127.2, 126.3, 122.8, 117.9, 117.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{18}{}^{79}BrNNaO_2S^+$ [M + Na^+] 450.0134, found 450.0136.

4-Methyl-*N*-(5-methyl-2-(1-phenylvinyl)phenyl)benzenesulfonamide (1d)



Following the general procedure, **1d** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 83%); mp: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.89 (m, 2H), 6.49 (s, 1H), 5.65 (s, 1H), 4.85 (s, 1H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 143.7, 139.0, 138.9, 136.1, 134.0, 130.3, 130.3, 129.5, 128.8, 128.5, 127.3, 126.4, 125.6, 121.9, 116.9, 21.6, 21.5. HRMS (ESI) calcd for $C_{22}H_{21}NNaO_2S^+$ [M + Na^+] 386.1185, found 386.1188.

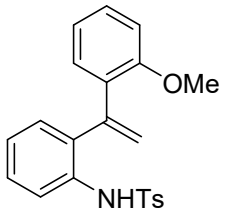
4-Methyl-*N*-(2-(1-phenylvinyl)-5-(trifluoromethyl)phenyl)benzenesulfonamide (1e)



Following the general procedure, **1e** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 75%); mp: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.2 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.33 (ddd, *J* = 7.8, 6.5, 4.6 Hz, 2H), 7.29 – 7.18 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.95 (m, 2H), 6.68 (s, 1H), 5.80 (s, 1H), 4.98 (s, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 137.7, 136.0, 135.5, 135.0,

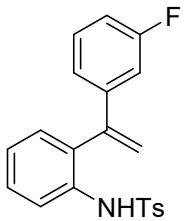
131.4 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 131.00, 130.97, 129.7, 129.0, 128.9, 127.3, 126.3, 123.7 (q, $^{1}J_{C\text{-}F}$ = 270.8 Hz), 121.1 (q, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 118.0, 117.3 (q, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 21.6. HRMS (ESI) calcd for $C_{22}H_{18}F_3NNaO_2S^+$ [M + Na^+] 440.0903, found 440.0908.

***N*-(2-(1-(3-Methoxyphenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (1f)**



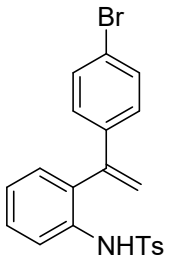
Following the general procedure, **1f** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 68%); mp: 87-89 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 24.0, 15.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 6.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 5.45 (d, *J* = 1.3 Hz, 1H), 4.87 (d, *J* = 1.3 Hz, 1H), 3.77 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 143.5, 142.4, 136.4, 134.3, 134.1, 129.9, 129.9, 129.4, 129.4, 129.3, 128.2, 127.3, 123.9, 121.6, 120.8, 119.7, 111.3, 55.6, 21.5. HRMS (ESI) calcd for $C_{22}H_{21}NNaO_3S^+$ [M + Na^+] 402.1134, found 402.1138.

***N*-(2-(1-(3-Fluorophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (1g)**



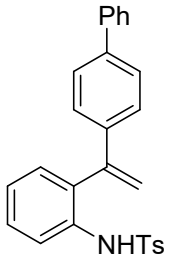
Following the general procedure, **1g** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 65%); mp: 64-66 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.20 (dd, *J* = 14.1, 7.9 Hz, 1H), 7.15 – 7.07 (m, 3H), 7.03 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.96 (td, *J* = 8.3, 2.3 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 6.52 (d, *J* = 10.2 Hz, 1H), 5.77 (s, 1H), 4.99 (s, 1H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.04 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 144.0, 143.9, 141.0 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 136.0, 134.2, 132.3, 130.4, 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 129.5, 129.1, 127.1, 124.8, 121.9, 121.1, 118.2, 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 113.4 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 21.5. HRMS (ESI) calcd for $C_{21}H_{18}FNNaO_2S^+$ [M + Na^+] 390.0934, found 390.0938.

***N*-(2-(1-(4-Bromophenyl)vinyl)phenyl)-4-methylbenzenesulfonamide (1h)**



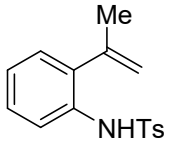
Following the general procedure, **1h** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 73%); mp: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.28 (s, 2H), 7.11 (t, *J* = 7.9 Hz, 3H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 5.76 (s, 1H), 5.00 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 143.9, 137.5, 136.0, 134.2, 132.3, 131.8, 130.4, 129.5, 129.1, 127.8, 127.1, 124.7, 122.7, 120.9, 117.7, 21.6. HRMS (ESI) calcd for $C_{21}H_{18}{}^{79}BrNNaO_2S^+$ [M + Na^+] 450.0134, found 450.0138.

***N*-(2-(1-([1,1'-Biphenyl]-4-yl)vinyl)phenyl)-4-methylbenzenesulfonamide (1i)**



Following the general procedure, **1i** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 62%); mp: 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.31 (m, 8H), 7.19 – 6.97 (m, 6H), 6.61 (s, 1H), 5.77 (d, *J* = 3.7 Hz, 1H), 4.93 (d, *J* = 3.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 143.8, 141.3, 140.2, 137.5, 136.1, 134.3, 133.0, 130.5, 129.5, 128.9, 127.7, 127.4, 127.2, 127.0, 126.8, 124.8, 121.1, 117.1, 21.5. HRMS (ESI) calcd for $C_{27}H_{23}NNaO_2S^+$ [M + Na^+] 448.1342, found 448.1346.

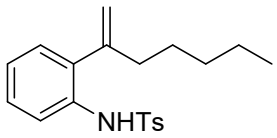
4-Methyl-*N*-(2-(prop-1-en-2-yl)phenyl)benzenesulfonamide (1j)



Following the general procedure, **1j** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 88%); mp: 74-76 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 9.5, 4.9 Hz, 3H), 7.04

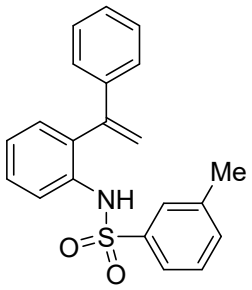
(dd, J = 8.8, 6.0 Hz, 2H), 7.01 (dd, J = 7.6, 1.6 Hz, 1H), 5.26 (s, 1H), 4.68 (s, 1H), 2.36 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 142.1, 136.4, 134.8, 132.9, 129.6, 128.0, 128.0, 127.2, 124.4, 120.6, 117.1, 24.4, 21.5. HRMS (ESI) calcd for $C_{16}H_{17}NNaO_2S^+$ [M + Na^+] 310.0872, found 310.0876.

_N_-(2-(Hept-1-en-2-yl)phenyl)-4-methylbenzenesulfonamide (1k)



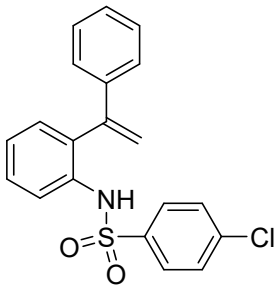
Following the general procedure, **1k** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 65%); mp: 61-63 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.21 (t, J = 8.9 Hz, 3H), 7.03 (t, J = 7.5 Hz, 1H), 7.00 – 6.94 (m, 2H), 5.23 (s, 1H), 4.69 (s, 1H), 2.36 (s, 3H), 1.97 – 1.87 (m, 2H), 1.26 – 1.18 (m, 4H), 1.18 – 1.13 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 143.8, 133.9, 133.4, 129.6, 128.3, 128.0, 127.2, 124.0, 119.8, 115.9, 37.8, 31.5, 27.1, 22.4, 21.5, 14.0. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_2S^+$ [M + Na^+] 366.1498, found 366.1494.

3-Methyl-_N_-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1l)



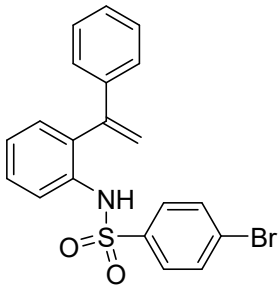
Following the general procedure, **1l** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 83%); mp: 80-82 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 8.7 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.12 (t, J = 7.4 Hz, 1H), 7.08 (dd, J = 7.4, 1.2 Hz, 1H), 7.02 (d, J = 7.5 Hz, 2H), 6.52 (s, 1H), 5.69 (s, 1H), 4.88 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 139.1, 138.9, 138.7, 134.2, 133.7, 133.3, 130.5, 128.9, 128.8, 128.7, 128.6, 127.5, 126.3, 124.9, 124.4, 121.3, 117.0, 21.2. HRMS (ESI) calcd for $C_{21}H_{19}NNaO_2S^+$ [M + Na^+] 372.1029, found 372.1026.

4-Chloro-_N_-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1m)



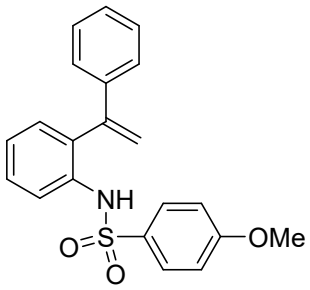
Following the general procedure, **1m** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 85%); mp: 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 7.15 (td, *J* = 7.4, 1.1 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.99 (dt, *J* = 8.5, 1.8 Hz, 2H), 6.53 (s, 1H), 5.71 (d, *J* = 0.9 Hz, 1H), 4.93 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.5, 138.5, 137.4, 133.7, 133.5, 130.7, 129.2, 129.0, 128.9, 128.7, 128.6, 126.2, 125.3, 121.7, 117.2. HRMS (ESI) calcd for $C_{20}H_{16}{}^{35}ClNNaO_2S^+$ [M + Na^+] 392.0482, found 392.0488.

4-Bromo-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1n)



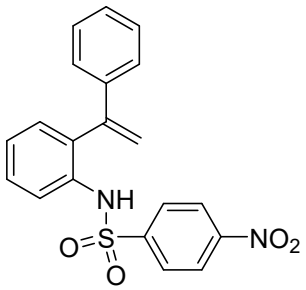
Following the general procedure, **1n** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 80%); mp: 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.28 (m, 4H), 7.25 – 7.21 (m, 2H), 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.54 (s, 1H), 5.71 (d, *J* = 0.9 Hz, 1H), 4.94 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.4, 137.9, 133.7, 133.5, 132.1, 130.7, 129.0, 128.9, 128.7, 128.6, 128.0, 126.2, 125.3, 121.7, 117.3. HRMS (ESI) calcd for $C_{20}H_{16}{}^{79}BrNNaO_2S^+$ [M + Na^+] 435.9977, found 435.9973.

4-Methoxy-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1o)



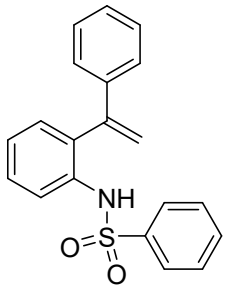
Following the general procedure, **1o** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 82%); mp: 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 7.11 (td, *J* = 7.4, 1.1 Hz, 1H), 7.07 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.80 – 6.73 (m, 2H), 6.53 (s, 1H), 5.72 (d, *J* = 0.9 Hz, 1H), 4.93 (d, *J* = 0.9 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 145.0, 138.7, 134.3, 133.1, 130.6, 130.5, 129.4, 128.9, 128.8, 128.6, 126.4, 124.7, 121.1, 117.1, 114.0, 55.6. HRMS (ESI) calcd for $C_{21}H_{19}NNaO_3S^+$ [M + Na^+] 388.0978, found 388.0971.

4-Nitro-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (1p)



Following the general procedure, **1p** was purified by silica gel chromatography (10% EtOAc/PE). A yellow solid (yield: 79%); mp: 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.74 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.39 (td, *J* = 7.9, 1.7 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.24 – 7.10 (m, 4H), 6.98 (dt, *J* = 8.5, 1.8 Hz, 2H), 6.60 (s, 1H), 5.70 (d, *J* = 0.8 Hz, 1H), 4.93 (d, *J* = 0.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 144.8, 144.5, 138.2, 133.7, 133.0, 130.8, 129.2, 128.9, 128.9, 128.3, 126.0, 125.9, 124.0, 122.2, 117.4. HRMS (ESI) calcd for $C_{20}H_{16}N_2NaO_4S^+$ [M + Na^+] 403.0723, found 403.0726.

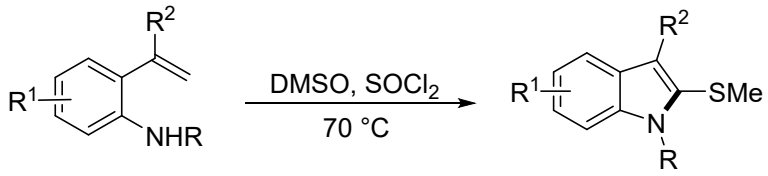
***N*-(2-(1-Phenylvinyl)phenyl)benzenesulfonamide (1q)**



Following the general procedure, **1q** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (yield: 81%); mp: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.38 – 7.31 (m, 3H), 7.32 – 7.27 (m, 1H), 7.26 – 7.21 (m, 2H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.02 (dd, *J* = 8.2, 0.9 Hz, 2H), 6.49 (s, 1H), 5.66 (s,

1H), 4.85 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 139.1, 138.6, 134.1, 133.4, 132.9, 132.9, 130.5, 128.9, 128.9, 128.7, 127.2, 126.3, 125.0, 121.4, 117.2. HRMS (ESI) calcd for $C_{20}H_{17}NNaO_2S^+$ [M + Na^+] 358.0872, found 358.0876.

c. Typical Procedure for the synthesis of 2-methylthioindole derivatives 2 (2a-o):



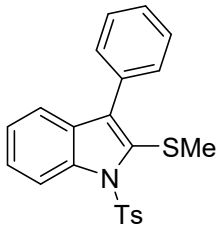
1 **2**

Method A: To a solution of substrate **1** (0.5 mmol) in DMSO (1 mL) was slowly added $SOCl_2$ (2.0 mmol, 239 mg) at 25 °C. The mixture was kept stirring at 70 °C until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and water (20 mL), extracted with EtOAc (3 x 20 mL), combined the organic phase and then evaporated the solvent, purified by flash column chromatography (2% EtOAc/PE) to afford the desired 2-methylthioindole derivatives **2**.

Method B: To a solution of substrate **1** (0.5 mmol) in DMSO (1 mL) was slowly added $SOCl_2$ (2.5 mmol, 299 mg) at 25 °C. The mixture was kept stirring at 70 °C until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and water (20 mL), extracted with EtOAc (3 x 20 mL), combined the organic phase and then evaporated the solvent, purified by flash column chromatography (2% EtOAc/PE) to afford the desired 2-methylthioindole derivatives **2**.

d. Spectroscopic data of 2-methylthioindole derivatives 2 (2a-o):

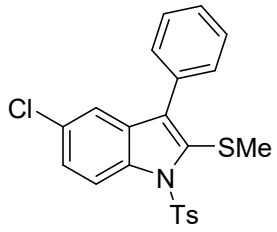
2-(Methylthio)-3-phenyl-1-tosyl-1*H*-indole (2a)



Following the general procedure **Method A**, **2a** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (157 mg, 80%); mp: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.54 –

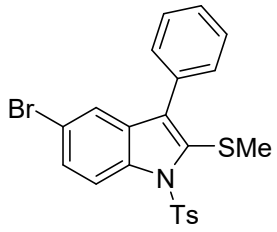
7.36 (m, 7H), 7.28 (s, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144. 8, 138.0, 136.1, 132.6, 131.6, 130.1, 129.8, 129.6, 129.5, 128.4, 127.9, 127.3, 126.0, 123.8, 120.1, 115.6, 21.7, 21.4. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_2S_2^+$ [M + Na^+] 416.0749, found 416.0755.

5-Chloro-2-(methylthio)-3-phenyl-1-tosyl-1*H*-indole (2b)



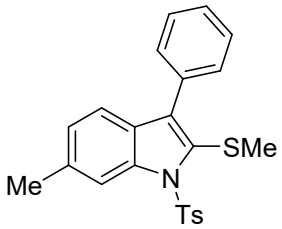
Following the general procedure **Method A**, **2b** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (139 mg, 65%); mp: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.41 (td, *J* = 5.9, 2.3 Hz, 4H), 7.36 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 136.3, 135.8, 132.0, 131.4, 130.7, 130.6, 130.0, 129.7, 129.7, 128.5, 128.1, 127.3, 126.0, 119.5, 116.7, 21.7, 21.3. HRMS (ESI) calcd for $C_{22}H_{18}{}^{35}ClNNaO_2S_2^+$ [M + Na^+] 450.0360, found 450.0366.

5-Bromo-2-(methylthio)-3-phenyl-1-tosyl-1*H*-indole (2c)



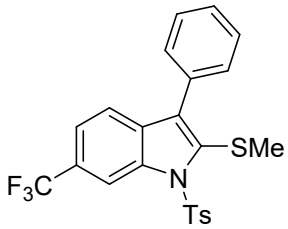
Following the general procedure **Method A**, **2c** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (172 mg, 73%); mp: 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.40 (tt, *J* = 7.8, 1.6 Hz, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 136.6, 135.8, 132.0, 131.3, 131.2, 130.5, 130.0, 129.7, 128.7, 128.5, 128.1, 127.3, 122.6, 117.4, 117.0, 21.7, 21.3. HRMS (ESI) calcd for $C_{22}H_{18}{}^{79}BrNNaO_2S_2^+$ [M + Na^+] 493.9855, found 493.9858.

6-Methyl-2-(methylthio)-3-phenyl-1-tosyl-1*H*-indole (2d)



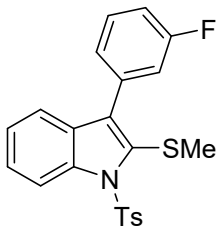
Following the general procedure **Method A**, **2d** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (179 mg, 88%); mp: 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.36 (m, 5H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 2.54 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 138.4, 136.2, 132.8, 131.7, 130.1, 129.8, 129.6, 128.9, 128.3, 127.8, 127.3, 127.1, 125.3, 119.7, 115.6, 22.2, 21.7, 21.5. HRMS (ESI) calcd for $C_{23}H_{21}NNaO_2S_2^+$ [M + Na^+] 430.0906, found 430.0902.

2-(Methylthio)-3-phenyl-1-tosyl-6-(trifluoromethyl)-1*H*-indole (2e)



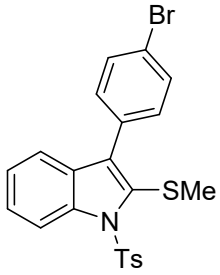
Following the general procedure **Method A**, **2e** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (70 mg, 30%); Following the general procedure **Method B**, **2e** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (113 mg, 49%); mp: 121-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.42 (dd, *J* = 5.5, 1.9 Hz, 3H), 7.25 (d, *J* = 9.6 Hz, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.09 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 137.0, 135.8, 132.9, 131.9, 131.8, 130.7, 130.0, 129.7, 128.5, 128.2, 127.8 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 127.5, 124.6 (q, $^{1}J_{C\text{-}F}$ = 270.5 Hz), 120.4, 113.0 (q, $^{4}J_{C\text{-}F}$ = 4.4 Hz), 21.6, 21.1. HRMS (ESI) calcd for $C_{23}H_{18}F_3NNaO_2S_2^+$ [M + Na^+] 484.0623, found 484.0625.

3-(3-Fluorophenyl)-2-(methylthio)-1-tosyl-1*H*-indole (2f)



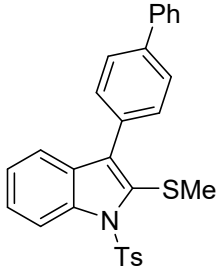
Following the general procedure **Method A**, **2f** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (146 mg, 71%); mp: 83-84 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.42 (dd, J = 15.7, 7.3 Hz, 3H), 7.28 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 8.4 Hz, 3H), 7.16 (d, J = 9.8 Hz, 1H), 7.09 (td, J = 8.4, 2.3 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.99 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 244.3 Hz), 144.9, 138.0, 136.1, 134.8 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 130.24 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 130.21, 129.8 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 129.6, 129.1, 127.3, 126.1, 125.9, 123.9, 119.8, 117.1 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 115.6, 114.7 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 21.6, 21.3. HRMS (ESI) calcd for $C_{22}H_{18}FNNaO_2S_2^+$ [M + Na^+] 434.0655, found 434.0658.

3-(4-Bromophenyl)-2-(methylthio)-1-tosyl-1*H*-indole (2g)



Following the general procedure **Method A**, **2g** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (186 mg, 79%); mp: 116-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 16.0, 7.6 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 138.0, 136.1, 131.8, 131.6, 130.4, 130.0, 129.6, 129.0, 127.3, 126.1, 123.9, 122.0, 119.8, 115.6, 21.6, 21.4. HRMS (ESI) calcd for $C_{22}H_{18}{}^{79}BrNNaO_2S_2^+$ [M + Na^+] 493.9855, found 493.9848.

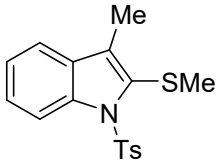
3-([1,1'-Biphenyl]-4-yl)-2-(methylthio)-1-tosyl-1*H*-indole (2h)



Following the general procedure **Method A**, **2h** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (152 mg, 65%); mp: 201-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.72 –

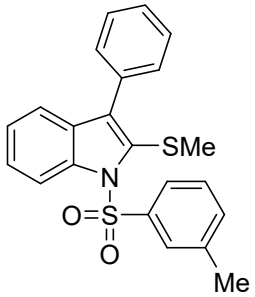
7.68 (m, 2H), 7.66 (dd, *J* = 5.2, 3.3 Hz, 1H), 7.51 (ddd, *J* = 10.3, 6.8, 1.8 Hz, 4H), 7.48 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 7.31 – 7.27 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.7, 140.6, 138.1, 136.1, 131.6, 131.2, 130.5, 129.8, 129.6, 129.5, 128.8, 127.5, 127.3, 127.1, 127.0, 126.0, 123.8, 120.1, 115.6, 21.6, 21.5. HRMS (ESI) calcd for $C_{28}H_{23}NNaO_2S_2^+$ [M + Na^+] 492.1062, found 492.1068.

3-Methyl-2-(methylthio)-1-tosyl-1*H*-indole (2i)



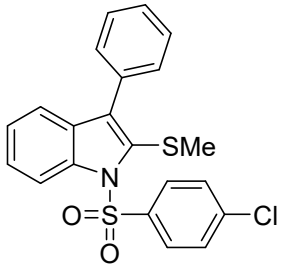
Following the general procedure **Method A**, **2i** was purified by silica gel chromatography (5% EtOAc/PE). Colorless oil (119 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.38 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.0, 136.3, 130.2, 129.5, 129.2, 127.4, 127.1, 125.8, 123.4, 119.3, 115.5, 21.6, 20.9, 10.2. HRMS (ESI) calcd for $C_{17}H_{17}NNaO_2S_2^+$ [M + Na^+] 354.0598, found 354.0599.

2-(Methylthio)-3-phenyl-1-(m-tolylsulfonyl)-1*H*-indole (2j)



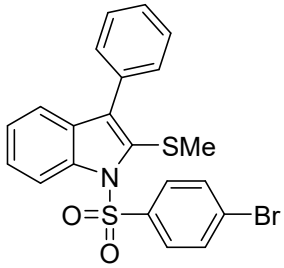
Following the general procedure **Method A**, **2j** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (159 mg, 81%); mp: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.39 (m, 7H), 7.36 – 7.24 (m, 3H), 2.36 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.9, 138.0, 134.6, 132.6, 131.7, 130.1, 129.8, 129.5, 128.8, 128.4, 127.9, 127.6, 126.0, 124.4, 123.8, 120.1, 115.5, 21.39, 21.37. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_2S_2^+$ [M + Na^+] 416.0749, found 416.0742.

1-((4-Chlorophenyl)sulfonyl)-2-(methylthio)-3-phenyl-1*H*-indole (2k)



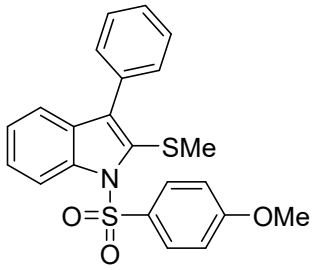
Following the general procedure **Method A**, **2k** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (147 mg, 71%); mp: 114-115 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.45 – 7.38 (m, 6H), 7.28 (t, *J* = 7.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 138.0, 137.4, 132.4, 132.2, 130.1, 129.69, 129.66, 129.3, 128.7, 128.4, 128.0, 126.2, 124.1, 120.3, 115.5, 21.3. HRMS (ESI) calcd for $C_{21}H_{16}ClNNaO_2S_2^+$ [M + Na^+] 436.0203, found 436.0208.

1-((4-Bromophenyl)sulfonyl)-2-(methylthio)-3-phenyl-1*H*-indole (2l)



Following the general procedure **Method A**, **2l** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (153 mg, 67%); mp: 114-115 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 14.1, 7.0 Hz, 3H), 7.44 – 7.39 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 137.9, 132.4, 132.3, 132.2, 130.1, 129.7, 129.0, 128.8, 128.5, 128.4, 128.0, 126.2, 124.1, 120.3, 115.5, 21.3. HRMS (ESI) calcd for $C_{21}H_{16}{}^{79}BrNNaO_2S_2^+$ [M + Na^+] 479.9698, found 479.9688.

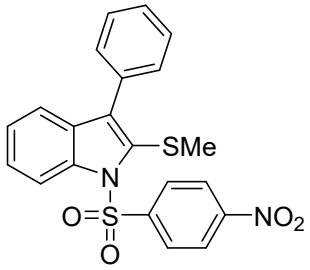
1-((4-Methoxyphenyl)sulfonyl)-2-(methylthio)-3-phenyl-1*H*-indole (2m)



Following the general procedure **Method A**, **2m** was purified by silica gel

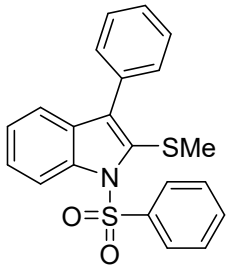
chromatography (5% EtOAc/PE). A white solid (147 mg, 72%); mp: 122-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.38 (m, 7H), 7.28 – 7.24 (d, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 138.0, 132.7, 131.5, 130.7, 130.1, 129.9, 129.56, 129.54, 128.3, 127.8, 125.9, 123.7, 120.0, 115.6, 114.1, 55.6, 21.3. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_3S_2^+$ [M + Na^+] 432.0699, found 432.0690.

2-(Methylthio)-1-((4-nitrophenyl)sulfonyl)-3-phenyl-1*H*-indole (2n)



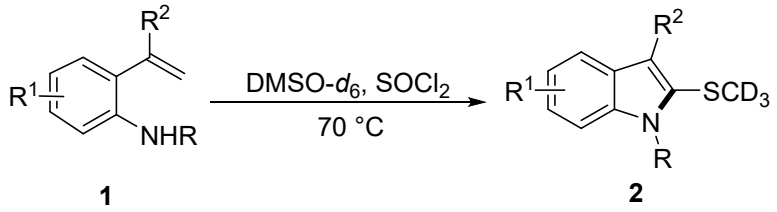
Following the general procedure **Method A**, **2n** was purified by silica gel chromatography (5% EtOAc/PE). A yellow solid (172 mg, 81%); mp: 96-98 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.7 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 4H), 7.41 (t, *J* = 7.5 Hz, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 144.2, 137.9, 132.9, 132.0, 130.0, 129.8, 129.5, 128.6, 128.5, 128.2, 126.5, 124.6, 124.2, 120.5, 115.5, 21.4. HRMS (ESI) calcd for $C_{21}H_{16}N_2NaO_4S_2^+$ [M + Na^+] 447.0444, found 447.0448.

2-(Methylthio)-3-phenyl-1-(phenylsulfonyl)-1*H*-indole (2o)



Following the general procedure **Method A**, **2o** was purified by silica gel chromatography (5% EtOAc/petroleum ether). A white solid (155mg, 82%); mp: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.96 (dd, *J* = 7.5, 0.9 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.37 (m, 9H), 7.27 (t, *J* = 7.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.1, 133.7, 132.5, 131.8, 130.1, 129.8, 129.5, 129.0, 128.4, 127.9, 127.3, 126.0, 123.9, 120.1, 115.6, 21.3. HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2S_2^+$ [M + Na^+] 402.0593, found 402.0596.

e. Typical procedure for the synthesis of 2-(d_3-methylthio) indole derivatives 2 (2p-s):

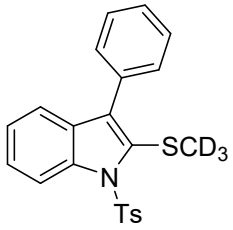


1 2

General procedure: To a solution of substrate **1** (0.5 mmol) in DMSO-d_6 (1 mL) was slowly added $SOCl_2$ (2.0 mmol, 239 mg) at 25 °C. The mixture was kept stirring at 70 °C until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and water (20 mL), extracted with EtOAc (3 x 20 mL), combined the organic phase and then evaporated the solvent, purified by flash column chromatography (2% EtOAc/PE) to afford the desired 2-(d_3-methylthio)indole derivatives **2**.

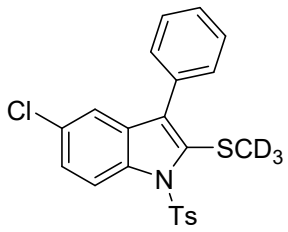
f. Spectroscopic data of 2-(d_3-methylthio) indole derivatives 2 (2p-s):

2-(d_3-Methylthio)-3-phenyl-1-tosyl-1*H*-indole (2p)



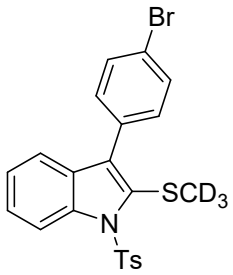
Following the general procedure, **2p** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (157 mg, 80%); mp: 116-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.49 – 7.44 (m, 5H), 7.43 – 7.39 (m, 2H), 7.26 (d, J = 15.1 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 138.1, 136.2, 132.7, 131.6, 130.1, 129.8, 129.6, 128.3, 127.8, 127.3, 125.9, 123.8, 120.0, 115.6, 21.6. HRMS (ESI) calcd for $C_{22}H_{16}D_3NNaO_2S_2^+$ [M + Na^+] 416.0749, found 416.0745.

5-Chloro-2-(d_3-methylthio)-3-phenyl-1-tosyl-1*H*-indole (2q)



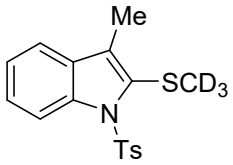
Following the general procedure, **2q** was purified by silica gel chromatography (2% EtOAc/PE). A white solid (141 mg, 66%); m.p. 150-151 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.36 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 136.3, 135.9, 132.0, 131.4, 130.8, 130.6, 130.0, 129.74, 129.65, 128.5, 128.1, 127.3, 126.0, 119.5, 116.7, 21.6. HRMS (ESI) calcd for $C_{22}H_{15}D_3ClNNaO_2S_2^+$ [M + Na^+] 450.0360, found 450.0368.

3-(4-Bromophenyl)-2-(*d*$_3$-methylthio)-1-tosyl-1*H*-indole (2r)



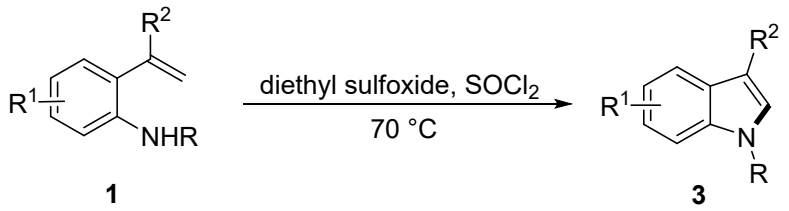
Following the general procedure, **2r** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (177 mg, 75%); mp: 117-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.41 (dd, *J* = 16.8, 8.3 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 138.0, 136.2, 131.8, 131.6, 130.4, 130.0, 129.6, 129.1, 127.3, 126.1, 123.9, 122.0, 119.8, 115.6, 21.6. HRMS (ESI) calcd for $C_{22}H_{15}D_3BrNNaO_2S_2^+$ [M + Na^+] 493.9855, found 493.9858.

3-Methyl-2-(methylthio)-1-tosyl-1*H*-indole (2s)



Following the general procedure, **2s** was purified by silica gel chromatography (5% EtOAc/PE). Colorless oil (116 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 7.81 – 7.75 (m, 2H), 7.43 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 7.38 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.28 (dd, *J* = 11.4, 4.5 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.0, 136.2, 130.2, 129.5, 129.2, 127.4, 127.1, 125.8, 123.4, 119.3, 115.5, 21.6, 10.2. HRMS (ESI) calcd for $C_{17}H_{14}D_3NNaO_2S_2^+$ [M + Na^+] 354.0593, found 354.0596.

g. Typical procedure for the synthesis of 2-unsubstituted indole derivatives 3 (3a-j):

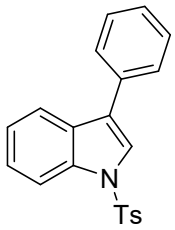


1 **3**

To a solution of substrate **1** (0.5 mmol) in diethyl sulfoxide (1 mL) was slowly added $SOCl_2$ (1.5 mmol, 179 mg) at 25 °C. The mixture was kept stirring at 70 °C until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was quenched with saturated aq. $NaHCO_3$ solution (5 mL) and water (20 mL), extracted with EtOAc (3 x 20 mL), combined the organic phase and then evaporated the solvent, purified by flash column chromatography (2% EtOAc/PE) to afford the desired 2-methylthioindole derivatives **3**.

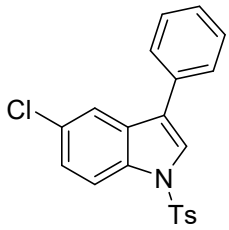
h. Spectroscopic data of 2-unsubstituted indole derivatives 3 (3a-j):

3-Phenyl-1-tosyl-1*H*-indole (3a)



Following the general procedure, **3a** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (158 mg, 91%); mp: 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 9.5 Hz, 3H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 135.6, 135.2, 133.1, 130.0, 129.3, 128.9, 127.9, 127.6, 126.9, 124.9, 124.0, 123.6, 123.0, 120.5, 113.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2S^+$ [M + Na^+] 370.0872, found 370.0878.

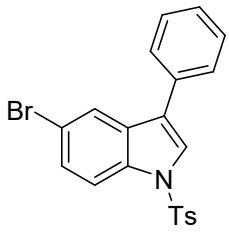
5-Chloro-3-phenyl-1-tosyl-1*H*-indole (3b)



Following the general procedure, **3b** was purified by silica gel chromatography (5%

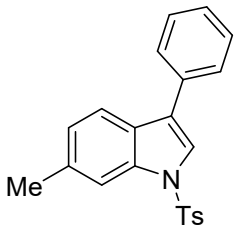
EtOAc/PE). A white solid (158 mg, 83%); mp: 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.79 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.25 (d, *J* = 9.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 134.9, 133.9, 132.4, 130.6, 130.1, 129.6, 129.1, 127.9, 126.9, 125.2, 124.2, 123.5, 120.2, 114.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{16}{}^{35}ClNNaO_2S^+$ [M + Na^+] 404.0482, found 404.0488.

5-Bromo-3-phenyl-1-tosyl-1*H*-indole (3c)



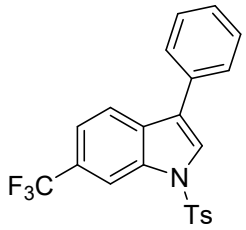
Following the general procedure, **3c** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (183 mg, 86%); mp: 132-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 134.2, 132.4, 131.1, 130.1, 129.1, 127.9, 127.9, 127.8, 126.9, 124.1, 123.4, 123.2, 117.3, 115.3, 21.6. HRMS (ESI) calcd for $C_{21}H_{16}{}^{79}BrNNaO_2S^+$ [M + Na^+] 447.9977, found 447.9973.

6-Methyl-3-phenyl-1-tosyl-1*H*-indole (3d)



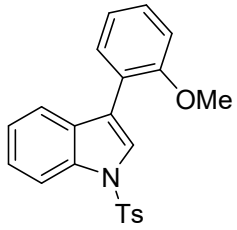
Following the general procedure, **3d** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (134 mg, 74%); mp: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.60 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 2.51 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 136.0, 135.5, 135.1, 133.3, 129.9, 128.9, 127.8, 127.5, 127.1, 126.9, 125.1, 123.9, 122.4, 120.0, 114.0, 21.9, 21.6. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_2S^+$ [M + Na^+] 384.1029, found 384.1025.

3-Phenyl-1-tosyl-6-(trifluoromethyl)-1*H*-indole (3e)



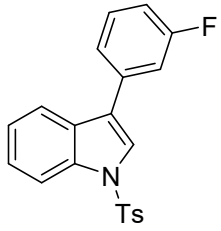
Following the general procedure, **3e** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (145 mg, 70%); mp: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.09 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 134.8, 134.6, 132.3, 131.7, 130.2, 129.1, 128.0, 127.9, 127.1 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 127.0, 125.3, 124.5 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 123.8, 121.0, 120.3 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 111.3 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 21.6. HRMS (ESI) calcd for $C_{22}H_{16}F_3NNaO_2S^+$ [M + Na^+] 438.0746, found 438.0741.

3-(2-Methoxyphenyl)-1-tosyl-1*H*-indole (3f)



Following the general procedure, **3f** was purified by silica gel chromatography (5% EtOAc/PE). Colorless oil (117 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.79 (m, 3H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.25 – 7.19 (m, 3H), 7.09 – 7.01 (m, 2H), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 144.9, 135.4, 135.0, 130.6, 130.3, 129.9, 128.8, 126.9, 125.3, 124.5, 123.2, 121.8, 121.2, 120.7, 119.5, 113.7, 111.3, 55.5, 21.6. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_3S^+$ [M + Na^+] 400.0978, found 400.0972.

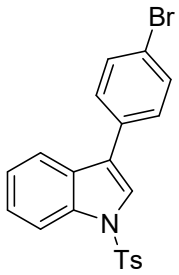
3-(3-Fluorophenyl)-1-tosyl-1*H*-indole (3g)



Following the general procedure, **3g** was purified by silica gel chromatography (5% EtOAc/PE). Colorless oil (139 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* =

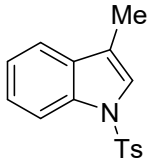
8.3 Hz, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 7.9 Hz, 1H), 7.72 (s, 1H), 7.42 (td, J = 7.9, 5.9 Hz, 1H), 7.38 (ddd, J = 6.3, 3.8, 1.2 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.09 – 7.03 (m, 1H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.58 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{C\text{-}F}$ = 244.6 Hz), 145.1, 135.5, 135.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 135.2, 130.4 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 130.0, 128.9, 126.9, 125.1, 123.7, 123.5 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 123.4, 122.8 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 120.2, 114.7 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 114.3 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 113.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{16}FNNaO_2S^+$ [M + Na^+] 388.0778, found 388.0771.

3-(4-Bromophenyl)-1-tosyl-1*H*-indole (3h)



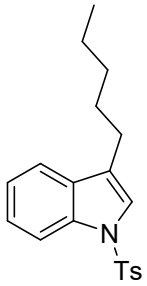
Following the general procedure, **3h** was purified by silica gel chromatography (5% EtOAc/PE). Colorless oil (159 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.9 Hz, 1H), 7.70 (s, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 135.5, 135.3, 132.1, 130.0, 129.4, 128.9, 126.9, 125.1, 123.7, 123.1, 122.8, 121.5, 120.2, 113.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{16}{}^{79}BrNNaO_2S^+$ [M + Na^+] 447.9977, found 447.9973.

3-Methyl-1-tosyl-1*H*-indole (3i)



Following the general procedure, **3i** was purified by silica gel chromatography (10% EtOAc/PE). A white solid (98 mg, 69%); mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 7.19 (d, J = 8.3 Hz, 2H), 2.32 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 135.5, 135.3, 131.8, 129.8, 126.8, 124.6, 123.1, 123.0, 119.4, 118.6, 113.7, 21.6, 9.7. HRMS (ESI) calcd for $C_{16}H_{15}NNaO_2S^+$ [M + Na^+] 308.0716, found 308.0712.

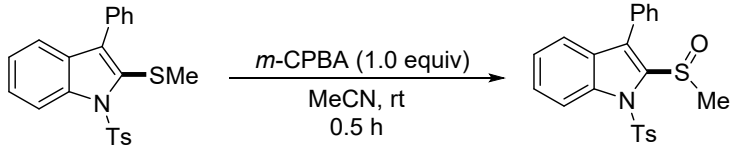
3-Pentyl-1-tosyl-1*H*-indole (3j)



Following the general procedure, **3j** was purified by silica gel chromatography (5% EtOAc/PE). A white solid (121 mg, 71%); mp: 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.21 (dd, *J* = 17.4, 8.0 Hz, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.74 – 1.63 (m, 2H), 1.39 – 1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 135.4, 135.4, 131.3, 129.8, 126.7, 124.5, 123.7, 122.9, 122.6, 119.5, 113.8, 31.6, 28.6, 24.8, 22.5, 21.5, 14.1. HRMS (ESI) calcd for $C_{20}H_{23}NNaO_2S^+$ [M + Na^+] 364.1342, found 364.1346.

i. Procedure and spectroscopic data of compounds 4-13

2-(Methylsulfinyl)-3-phenyl-1-tosyl-1*H*-indole (4)[2]

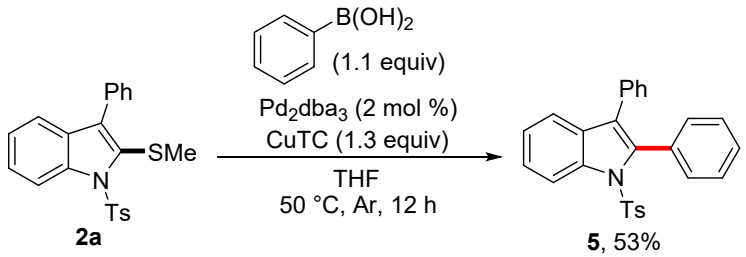


2a **4**, 91%

To a solution of compound **2a** (0.5 mmol) in MeCN (2.0 mL) was added *meta*-chloroperoxybenzoic acid (*m*-CPBA) (0.5 mmol) at 0 °C, and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the reaction, MeCN was removed *in vacuo*. The residue was admixed with DCM (30 mL) and the resultant solution was washed with water (30 mL × 3). The organic layer was further washed with aq. NaOH solution, then washed with brine, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified on silica gel (30% EtOAc/petroleum ether) to afford the corresponding sulfoxide **4** as a white solid (186 mg, 91 %), mp: 183–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.50 (ddd, *J* = 8.6, 7.2, 1.3 Hz, 1H), 7.47 – 7.40 (m, 5H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.23 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 137.4, 135.8, 134.2, 133.1, 130.7, 130.4, 130.1, 129.9, 128.7, 128.3, 127.8,

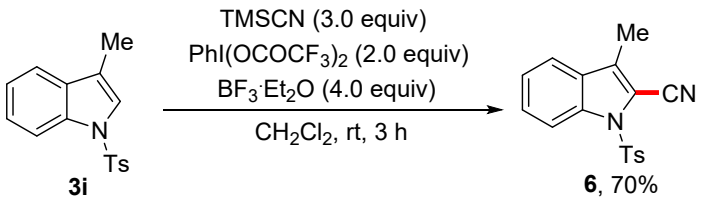
127.5, 124.5, 121.4, 115.1, 41.9, 21.7. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_3S_2^+$ [M + Na^+] 432.0699, found 432.0697.

2,3-Diphenyl-1-tosyl-1*H*-indole (5)



2-Methylthioindole (0.50 mmol), phenylboronic acid (0.55 mmol), Pd_2dba_3(0.01 mmol), and CuTC (0.65 mmol) were placed in a reaction vessel, which was flushed with argon. Then THF (5 mL) was added, and the reaction mixture was stirred at 50 °C for 12 h. When the reaction was completed (monitored by TLC), Et_2O (15 mL) was added, and then the mixture was extracted with a saturated aqueous solution of NH_4OH (3 × 20 mL). The organic layer was then dried with Na_2SO_4, and solid residues after evaporation were subjected to preparative plate silica gel chromatography (5% EtOAc/petroleum ether), giving the desired product **5** as a white solid (112 mg, 53%), mp: 145–146 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 3H), 7.29 (dd, *J* = 7.7, 2.4 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 3H), 7.20 (dd, *J* = 8.9, 6.1 Hz, 3H), 7.09 (d, *J* = 1.9 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.3, 136.9, 135.4, 132.7, 132.1, 130.9, 130.5, 129.9, 129.3, 128.5, 128.2, 127.3, 127.0, 125.2, 124.8, 124.2, 120.0, 116.3, 21.6. HRMS (ESI) calcd for $C_{27}H_{21}NNaO_2S^+$ [M + Na^+] 446.1185, found 446.1183.

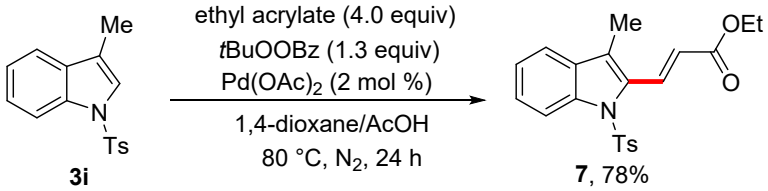
3-Methyl-1-tosyl-1*H*-indole-2-carbonitrile (6)[3]



To a stirred solution of PIFA (1.0 mmol) and $BF_3{\cdot}Et_2O$ (2.0 mmol) in CH_2Cl_2 (1 mL) added trimethylsilyl cyanide (1.5 mmol) at room temperature. After stirring 30 min, 3-methyl-1-tosyl-1*H*-indole **3i** (0.5 mmol) was added in one portion and the reaction mixture was stirred for additional 3 h under the same condition, with the reaction progress being monitored by TLC. After the completion of the reaction, saturated aq. sodium thiosulfate (5 mL) was added. The organic layer was separated

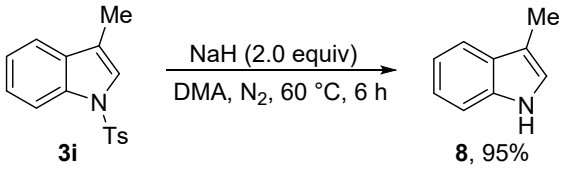
and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined extract was dried with $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (20% EtOAc/PE) to give pure **6** as a yellow powder (109 mg, 70%), mp: 162–163 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 11.4, 4.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 136.7, 134.5, 134.5, 130.2, 128.8, 128.7, 127.1, 124.4, 120.7, 114.8, 112.2, 107.1, 21.7, 10.1. HRMS (ESI) calcd for $C_{17}H_{14}N_2NaO_2S^+$ [M + Na^+] 333.0668, found 333.0662.

Ethyl (*E*)-3-(3-methyl-1-tosyl-1*H*-indol-2-yl)acrylate (7)[4]



To a solution of indole **3i** (1.0 mmol) in 1, 4-dioxane/AcOH (3:1/v:v, 4.0 mL) was added $Pd(OAc)_2$ (0.02 mmol), *tert*-butyl benzoyl peroxide (1.3 mmol) and ethyl acrylate (4.0 mmol). The resulting mixture was heated to 80 °C under N_2 atmosphere for 24 h before it was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was washed with saturated aq. $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude oil, which was purified by column chromatography (5% EtOAc/PE) to afford **7** (299 mg, 78%) as a white solid, mp: 111–112 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 14.1, 12.8 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 7.4, 3.6 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.11 (t, *J* = 6.2 Hz, 2H), 6.12 (d, *J* = 16.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.30 (d, *J* = 3.5 Hz, 6H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.9, 137.1, 134.9, 134.6, 131.8, 131.4, 129.6, 126.7, 126.5, 124.1, 123.3, 122.5, 119.8, 115.4, 60.8, 21.6, 14.4, 10.9. HRMS (ESI) calcd for $C_{21}H_{21}NNaO_4S^+$ [M + Na^+] 406.1083, found 406.1087.

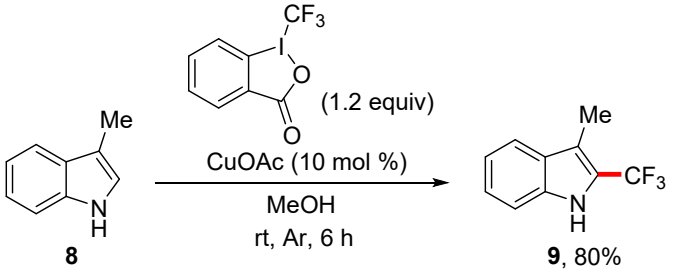
3-Methyl-1*H*-indole (8)



To a suspension solution of NaH (2.0 mmol, 2.0 equiv) in dry DMA (5.0 mL) under N_2 was added dropwise a solution of **3i** (1.0 mmol, 1.0 equiv) in dry DMA (3.0 mL) by syringe. Then the mixture was heated at 60 °C until TLC showed the

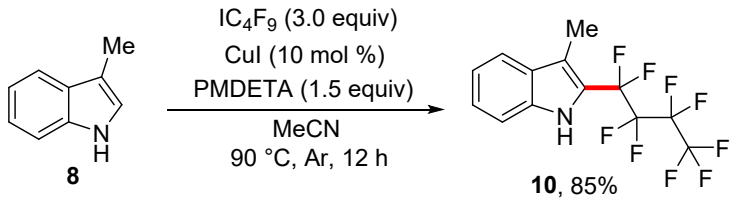
completion of the reaction. A saturated aq. solution of NH_4Cl (10 mL) was added to quench the reaction and extracted with EtOAc (20 mL) for one time. The organic layer was washed with water for three times, and the combined aqueous layers were extracted with EtOAc (20 mL) for one time. The combined organic layers were washed with brine and dried over sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography (5% EtOAc/PE) to give 3-methylindole **8** as a white solid (125 mg, 95%), mp: 93–94 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.63 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 11.0, 4.1 Hz, 1H), 7.16 (ddd, *J* = 3.1, 2.7, 1.1 Hz, 1H), 6.98 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 128.3, 121.9, 121.6, 119.2, 118.9, 111.8, 111.0, 9.7. HRMS (ESI) calcd for $C_9H_9NNa^+$ [M + Na^+] 154.0627, found 154.0623.

3-Methyl-2-(trifluoromethyl)-1*H*-indole (9)[5]



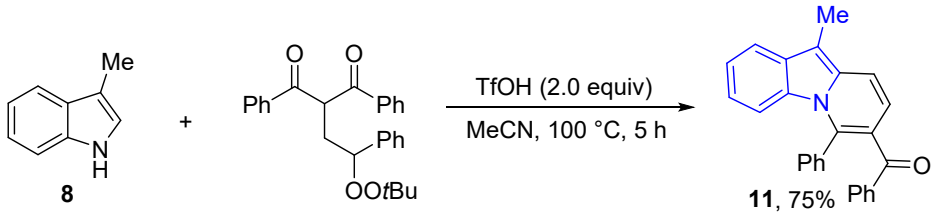
To a solution of CuOAc (0.05mmol) and Togni's reagent (0.6 mmol) in degassed MeOH (5.0 ml) was added 3-methylindole **8** (0.5 mmol) under an argon atmosphere at room temperature. The reaction mixture was stirred for 6 h, then diluted with Et_2O. To the mixture was added saturated aq. $NaHCO_3$ solution (5.0 mL), and the whole mixture was extracted with Et_2O (10 mL × 3). The combined organic layer was dried over Na_2SO_4. The solid was filtered off and the filtrate was evaporated *in vacuo*. The crude residue was purified on silica gel (10% EtOAc/PE) to give trifluoromethylated compound **9** as a colorless solid (80 mg, 80%), mp: 73–74ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 128.1, 124.8, 122.1 (q, $J_{C\text{-}F}$ = 267.0 Hz), 121.5 (q, $J_{C\text{-}F}$ = 36.7 Hz), 120.4, 120.1, 114.1 (q, $J_{C\text{-}F}$ = 2.9 Hz), 111.6, 8.35. HRMS (ESI) calcd for $C_{10}H_8F_3Na^+$ [M + Na^+] 222.0501, found 222.0506.

3-Methyl-2-(perfluorobutyl)-1*H*-indole (10)[6]



To a 25 mL of Schlenk tube was added CuI (0.1 mmol, 10 mol %) under air and then evacuated and backfilled with Ar (3 times). Acetonitrile (2 mL), PMDETA (1.5 mmol, 1.5 equiv), 3-methylindole **8** (1 mmol, 1.0 equiv) and perfluoroalkyl iodide (3.0 mmol, 3.0 equiv) were added subsequently. The reaction mixture was heated to 80 °C. After stirring for 12 h, the reaction was cooled to room temperature. Then the reaction mixture was diluted with EtOAc and filtered with a pad of Celite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (10% EtOAc/PE) to give product **10** (148 mg, 85%) as a white solid, mp: 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.24 (dt, J = 8.0, 3.4 Hz, 1H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.61 – -83.99 (m, 3F), -107.20 – -110.56 (m, 2F), -123.05 (ddd, J = 20.1, 10.0, 2.9 Hz, 2F), -124.64 – -127.77 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 128.4, 125.0, 120.4, 120.1, 119.4 (t, J = 28.4 Hz), 117.2 (t, J = 32.5 Hz), 116.8 (t, J = 3.2 Hz), 116.1 (t, J = 33.4 Hz), 114.7 (t, J = 32.7 Hz), 111.5, 8.6. HRMS (ESI) calcd for $C_{13}H_8F_9NNa^+$ [M + Na^+] 372.0405, found 372.0402.

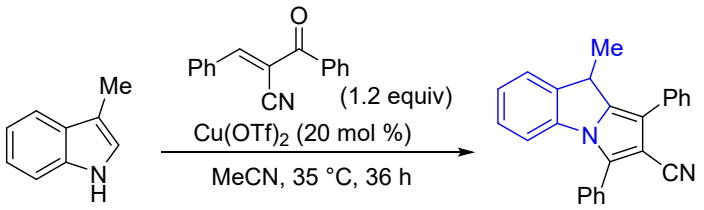
(10-Methyl-6-phenylpyrido[1,2-*a*]indol-7-yl)(phenyl)methanone (11)[7]



To a stirred solution of 3-methylindole **8** (1.5 mmol) and 4-oxo peroxide (0.5 mmol) in anhydrous MeCN (10 mL) was added TfOH (90.0 μL 1.0 mmol). The reaction tube was sealed and stirred at 100 °C for 5 h. After the mixture was cooled to room temperature, EtOAc (30.0 mL) was added and the mixture was washed with aq. $NaHCO_3$ (10 mL × 3). The organic layer was then evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (10% EtOAc/PE) to give the pure product **11** (135 mg, 75%) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.44 – 7.40 (m, 4H), 7.37 – 7.27 (m, 3H), 6.98 (d, J = 9.4 Hz, 1H), 6.89 – 6.81 (m, 1H), 6.17 (d, J = 8.7 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 141.4, 138.6, 134.3,

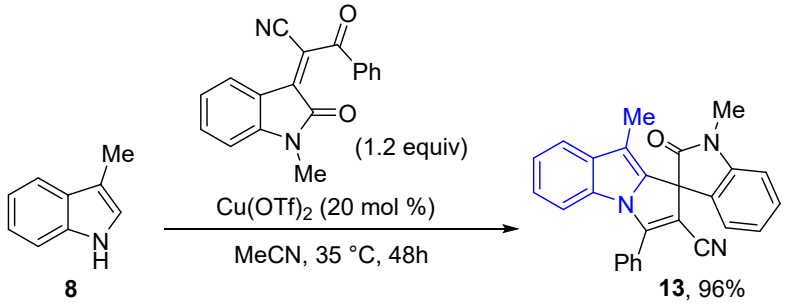
133.7, 132.6, 131.1, 130.8, 130.1, 129.7, 129.7, 129.0, 128.2, 122.6, 121.0, 120.6, 119.9, 118.4, 115.9, 115.3, 8.2. HRMS (ESI) calcd for $C_{26}H_{19}NNaO^+$ [M + Na^+] 384.1359, found 384.1356.

9-Methyl-1,3-diphenyl-9H-pyrrolo[1,2-*a*]indole-2-carbonitrile (12)[8]



To a 5.0 mL vial were successively added 3-methylindole **8** (0.5 mmol), benzaldehyde-derived oxodiene (0.6 mmol), $Cu(OTf)_2$ (0.1 mmol), and MeCN (2.0 mL). The resulting mixture was stirred at 35 °C until the full consumption of substrate **8** monitored by TLC. Then the precipitate was generated, and only a simple filtration was needed to purify product **12** (147 mg, 85%) as a white solid, mp: 173–174 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 6.5 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.20 (td, *J* = 7.4, 1.2 Hz, 1H), 7.15 (td, *J* = 7.7, 1.0 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 139.1, 138.4, 135.1, 132.3, 129.8, 129.6, 129.0, 128.9, 128.9, 127.6, 127.5, 127.2, 125.3, 125.0, 120.4, 117.1, 112.7, 96.1, 36.0, 16.9. HRMS (ESI) calcd for $C_{25}H_{18}N_2Na^+$ [M + Na^+] 369.1362, found 369.1366.

1,9'-Dimethyl-2-oxo-3'-phenylspiro[indoline-3,1'-pyrrolo[1,2-*a*]indole]-2'-carbonitrile (13)[8]



To a 5.0 mL vial were successively added 3-methylindole 8 (0.5 mmol), isatin-derived *α*,*β*-unsaturated ketone (0.6 mmol), $Cu(OTf)_2$ (0.1 mmol), and 2.0 mL of MeCN. The resulting mixture was stirred at 35 °C until almost full consumption of 3-methylindole 8 as monitored by TLC, and the precipitate was generated, and only a simple filtration was needed to purify the product **13** (193 mg, 96%) as a white solid,

mp: 212–213 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.7 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.07 (m, 4H), 7.01 (d, *J* = 7.9 Hz, 1H), 3.40 (s, 3H), 1.86 (s, 3H). ^{13}C N MR (151 MHz, $CDCl_3$) δ 172.3, 156.0, 144.4, 138.0, 134.8, 131.8, 131.7, 130.1, 129.2, 129.1, 127.0, 125.7, 124.4, 123.7, 123.5, 121.9, 119.8, 111.8, 111.3, 108.9, 96.2, 57.6, 27.2, 7.8. HRMS (ESI) calcd for $C_{27}H_{19}N_3NaO^+$ [M + Na^+] 424.1420, found 424.1425.

III. References:

1 H.-D. Xia, Y.-D. Zhang, Y.-H. Wang and C. Zhang. *Org. Lett.*, 2018, **20**, 4052-4056.

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5 R. Shimizu, H. Egami, T. Nagi, J. Chae, Y. Hamashima and M. Sodeoka. *Tetrahedron Lett.*, 2010, **51**, 5947-5949.

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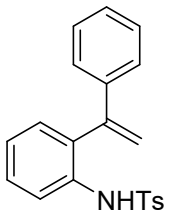
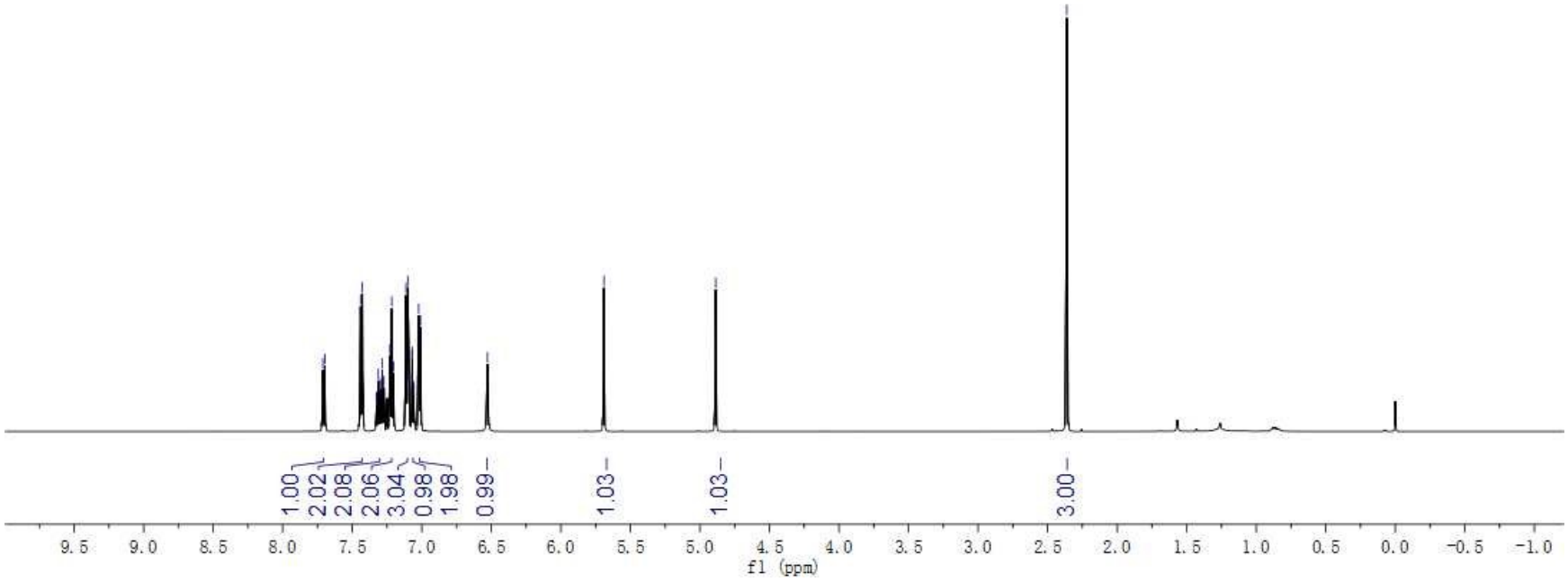
7 X. Wang, C. Lou, L. Lv and Z. Li. *Org. Lett.*, 2021, **23**, 5978-5982.

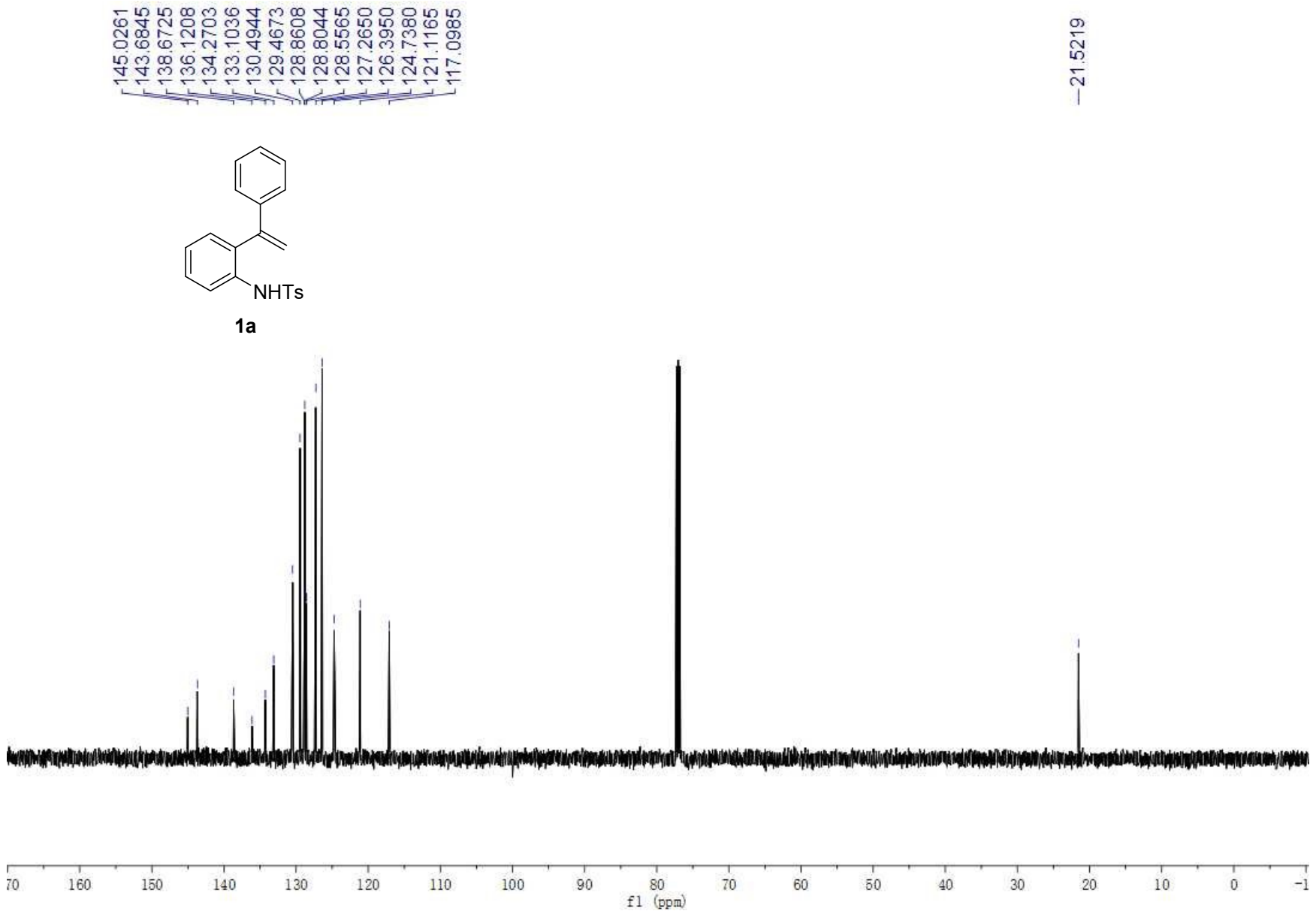
8 Y.-S. Zhu, B.-B. Yuan, J.-M. Guo, S.-J. Jin, H.-H. Dong, Q.-L. Wang and Z.-W. Bu. *J. Org. Chem.*, 2017, **82**, 5669-5677.

IV. ^{1}H and ^{13}C NMR Spectra:



1a

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134.2703
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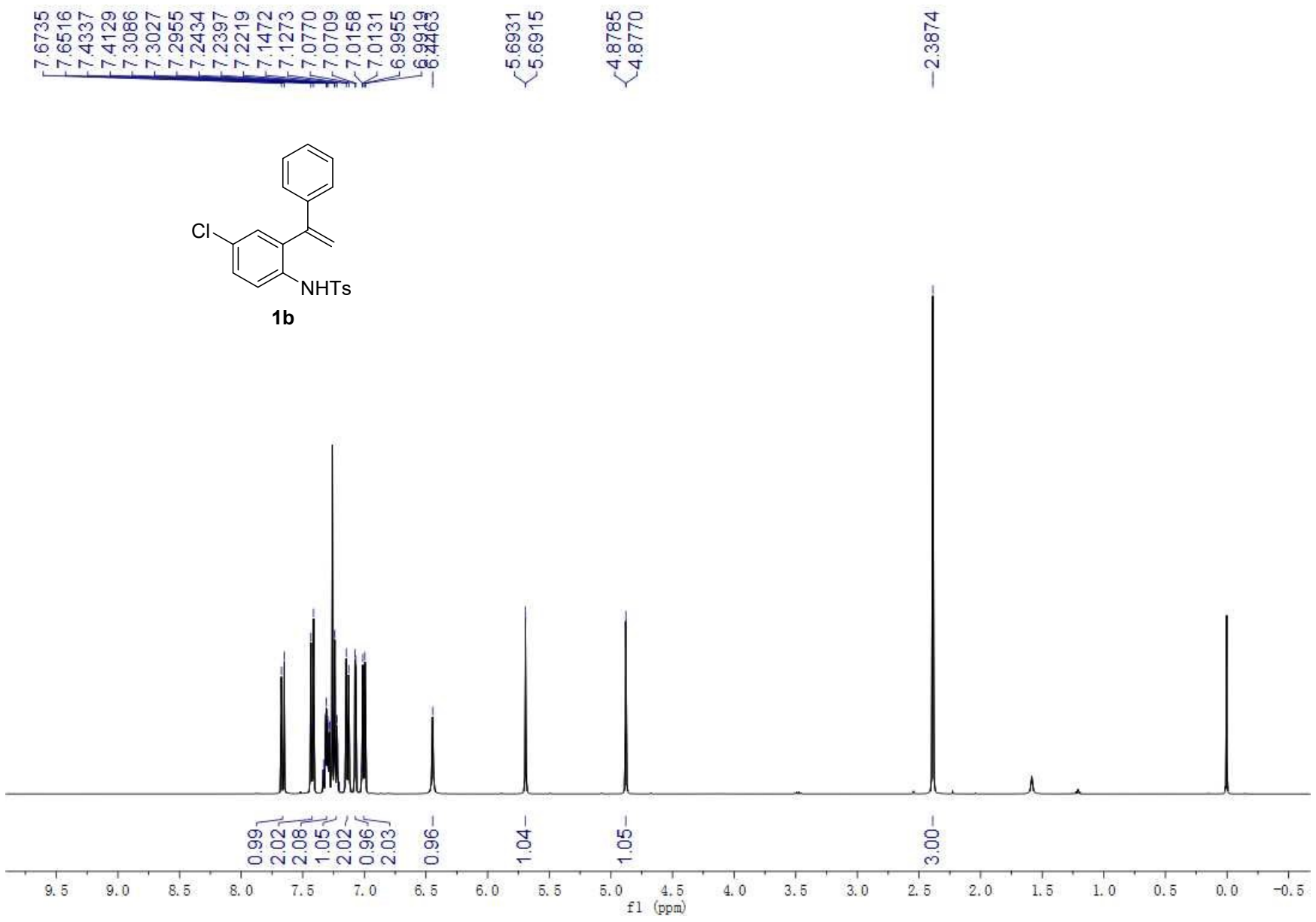
128.8608
128.8044
128.5565
127.2650
126.3950
124.7380
121.1165
117.0985
21.5219
NHTs
1a
f1 (ppm)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7.4337
7.4129
7.3086
7.3027
7.2955
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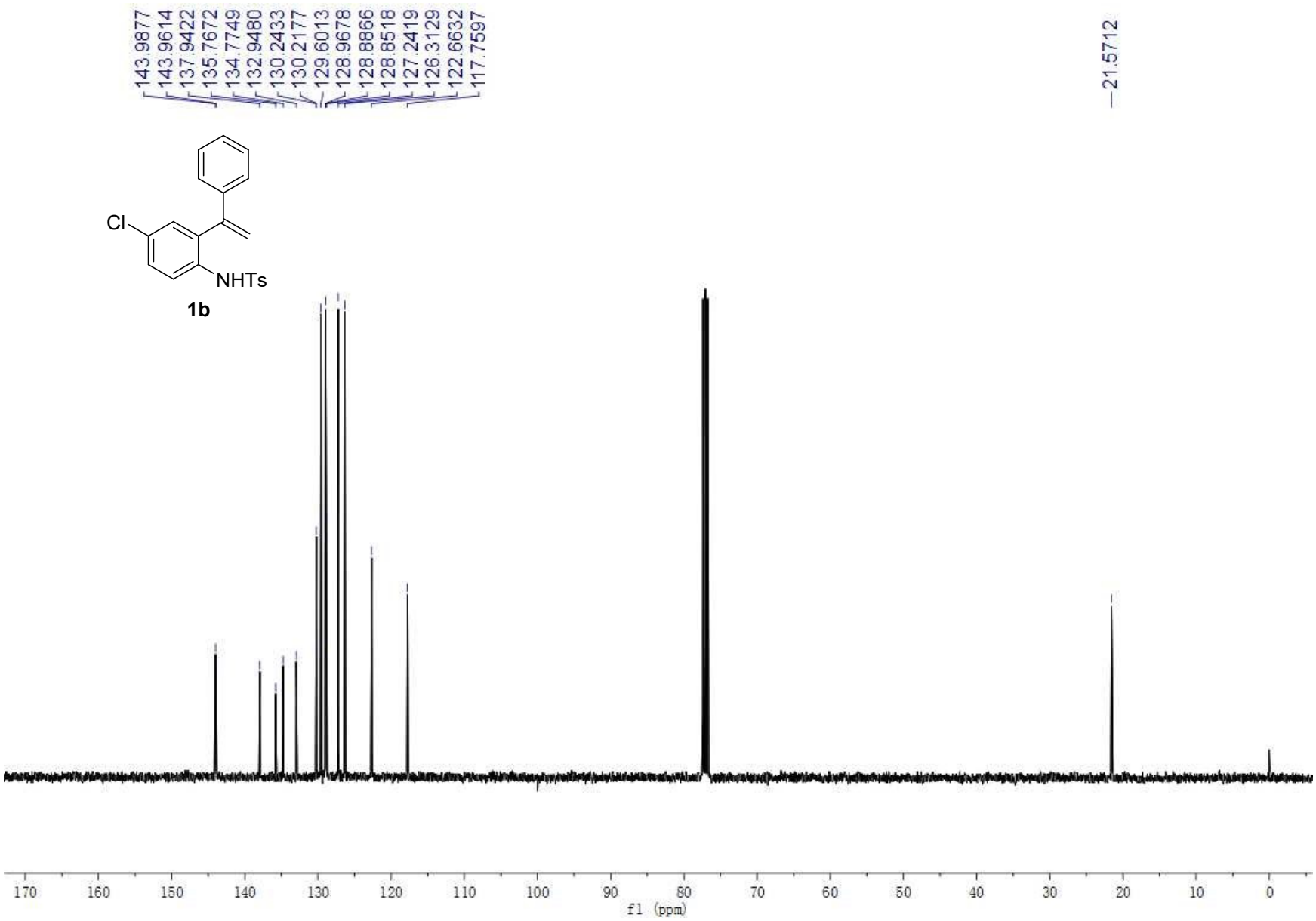
7.2397
7.2219
7.1472
7.1273
7.0770
7.0709
7.0158
7.0131
6.9955
5.6931
5.6915
4.8785
4.8770
2.3874
Cl
NHTs
1b
0.99
2.02
2.08
1.05
2.02
0.96
2.03
0.96
1.04
1.05
3.00
f1 (ppm)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137.9422
135.7672
134.7749
132.9480
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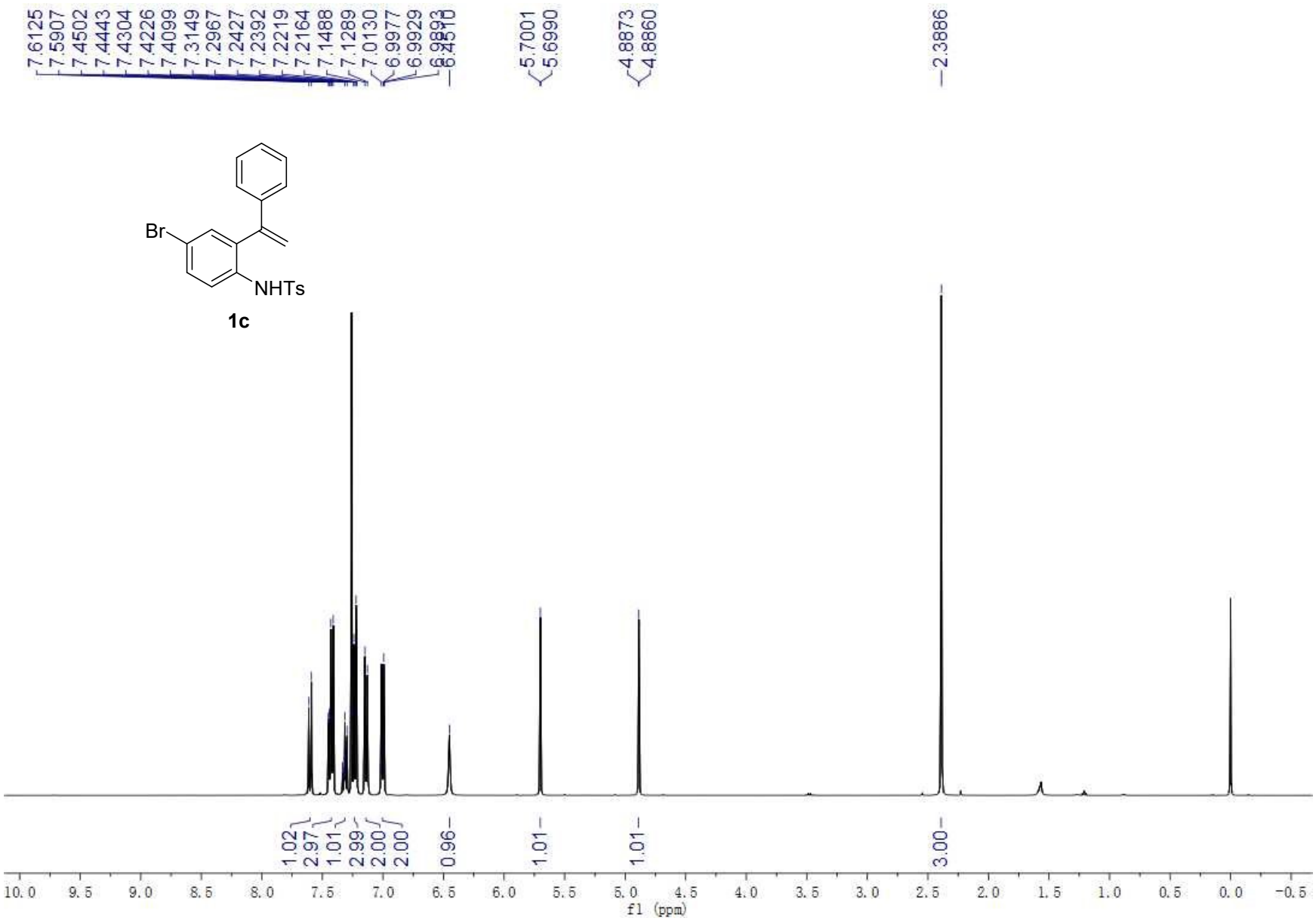
129.6013
128.9678
128.8866
128.8518
127.2419
126.3129
122.6632
117.7597
21.5712
Cl
NHTs
1b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4502
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7.4226
7.4099
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7.2967
7.2427
7.2392
7.2219
7.2164
7.1488
7.1289
7.0130
6.9977
6.9929
5.7001
5.6990
4.8873
4.8860
2.3886
Br
NHTs
1c
1.02
2.97
1.01
2.99
2.00
2.00
0.96
1.01
1.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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0.5
0.0
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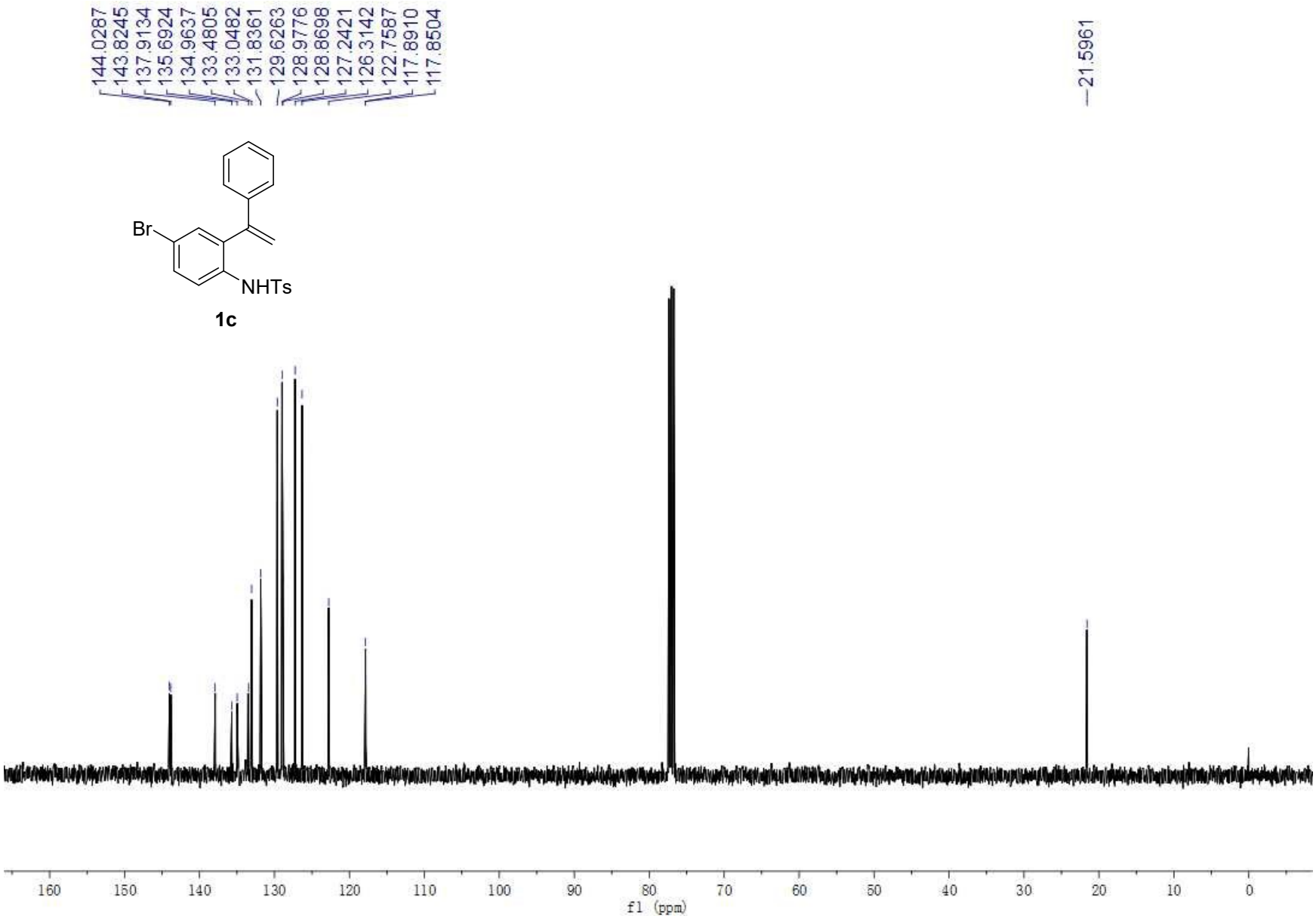
f1 (ppm)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133.0482
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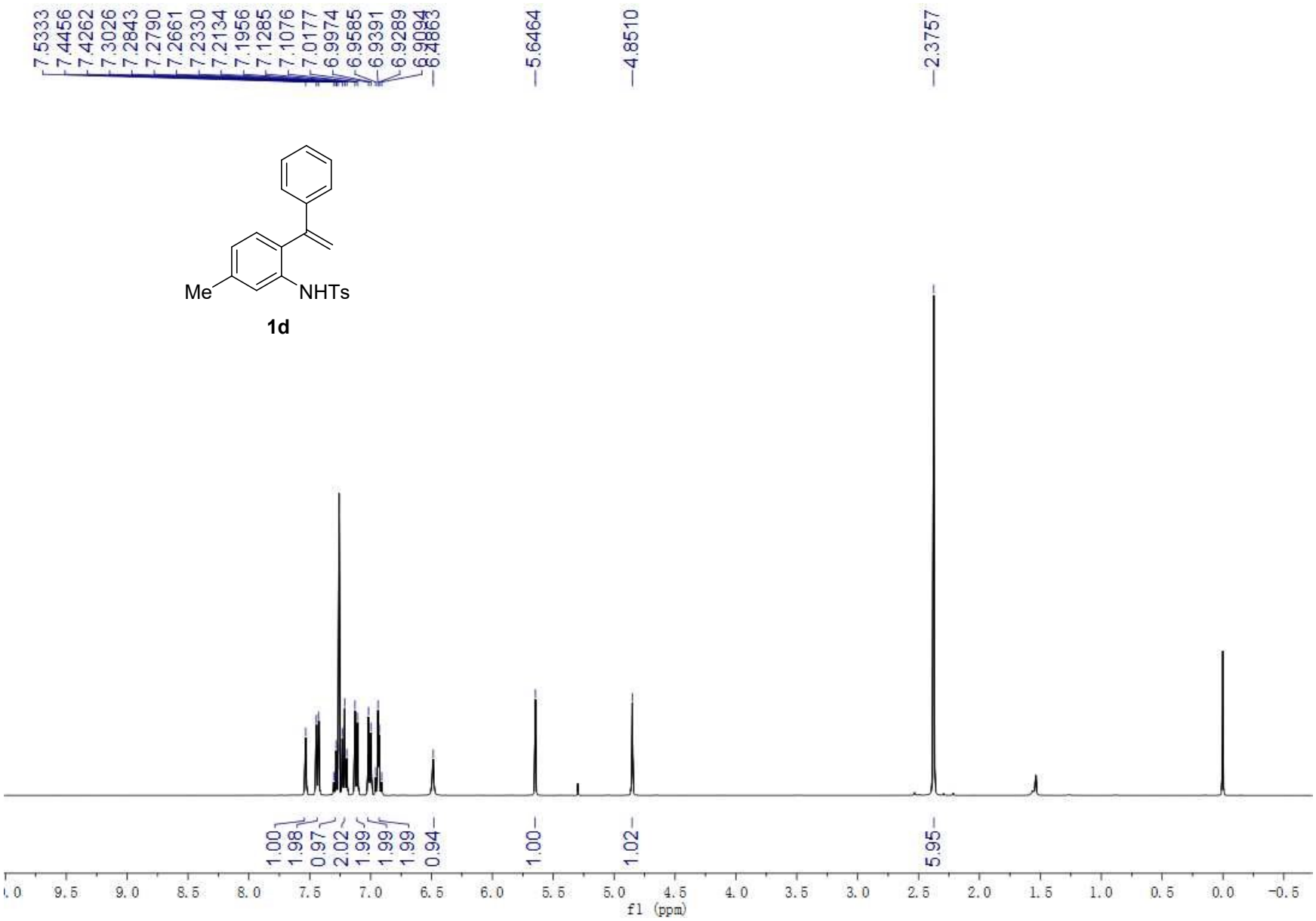
129.6263
128.9776
128.8698
127.2421
126.3142
122.7587
117.8910
117.8504
21.5961
Br
NHTs
1c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2134
7.1956
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7.1076
7.0177
6.9974
6.9585
6.9391
6.9289
5.6464
4.8510
2.3757
Me
NHTs
1d
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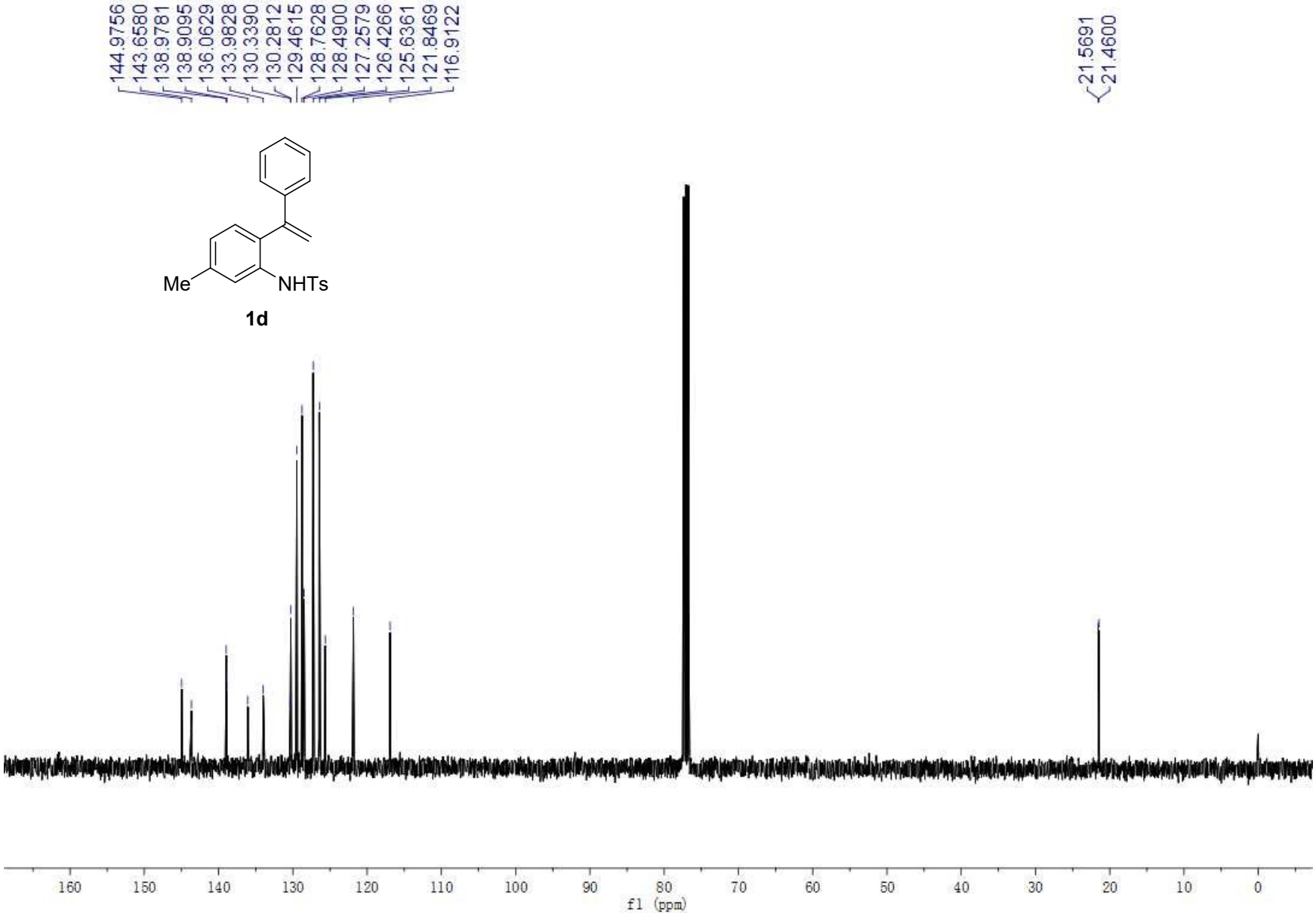
1.98
0.97
2.02
1.99
1.99
1.99
0.94
1.00
1.02
5.95
f1 (ppm)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127.2579
126.4266
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21.5691
21.4600
Me
NHTs
1d
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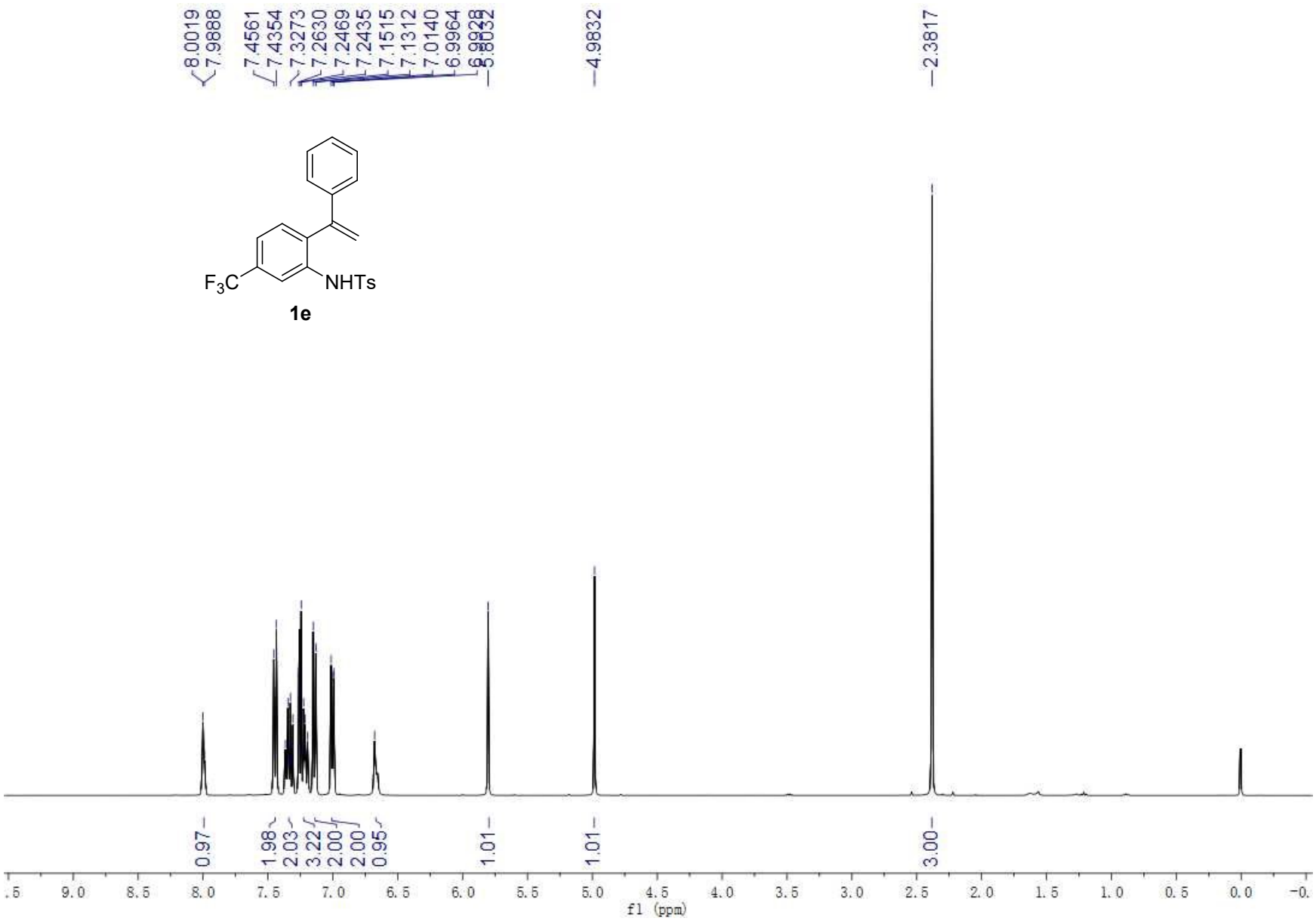
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.1515
7.1312
7.0140
6.9964
4.9832
2.3817
F3C
NHTs
1e
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2.03
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2.00
2.00
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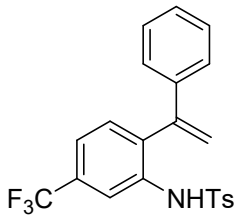
1.01
1.01
3.00
f1 (ppm)


F3C
NHTs

1e

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-10
-20
-30
-40
-50
-60
-70
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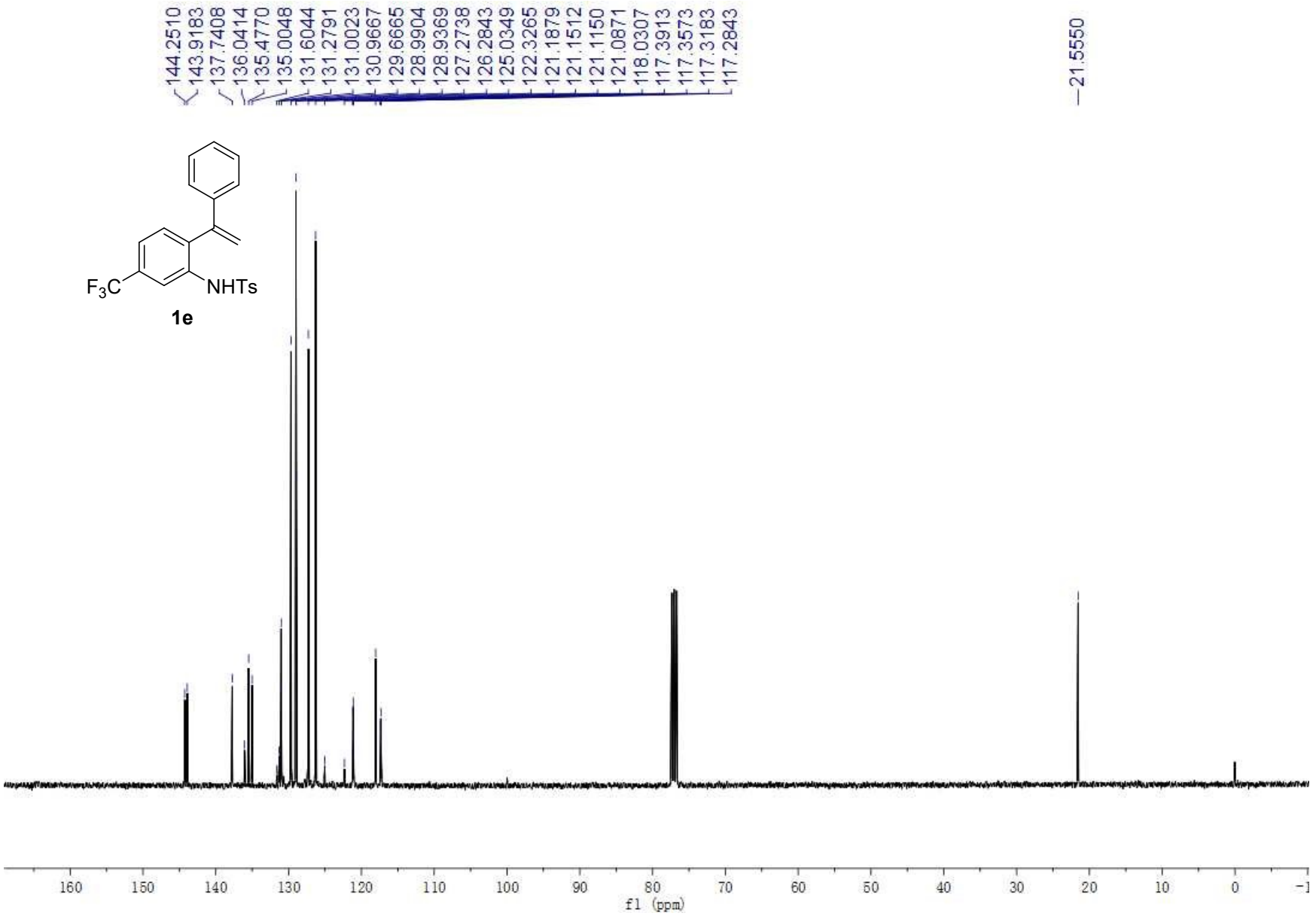
-140
-150
-160
-170
-180
f1 (ppm)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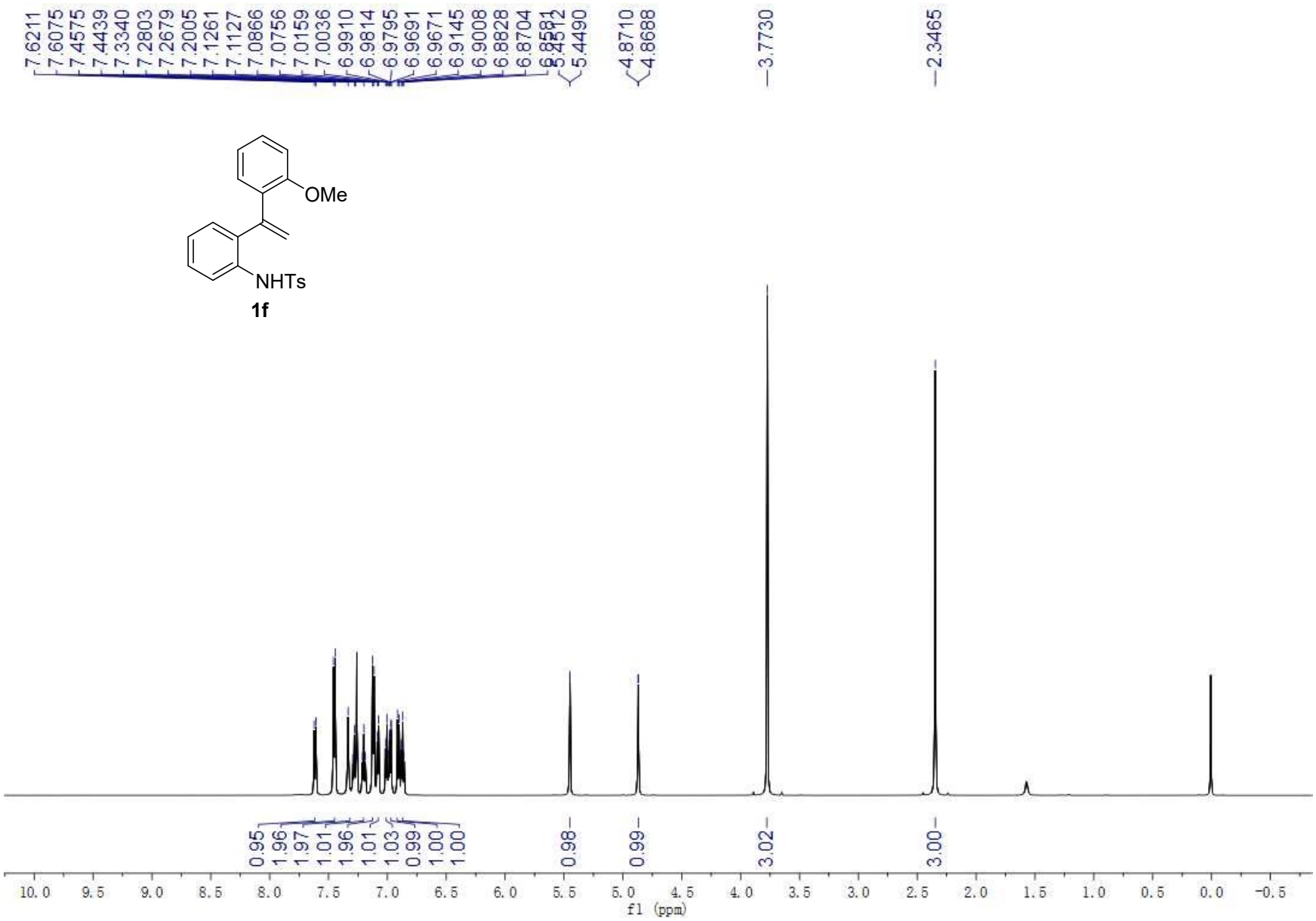
122.3265
121.1879
121.1512
121.1150
121.0871
118.0307
117.3913
117.3573
117.3183
117.2843
21.5550
F3C
NHTs
1e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.0866
7.0756
7.0159
7.0036
6.9910
6.9814
6.9795
6.9691
6.9671
6.9145
6.9008
6.8828
6.8704
5.4490
4.8710
4.8688
3.7730
2.3465
OMe
NHTs
1f
0.95
1.96
1.97
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1.00
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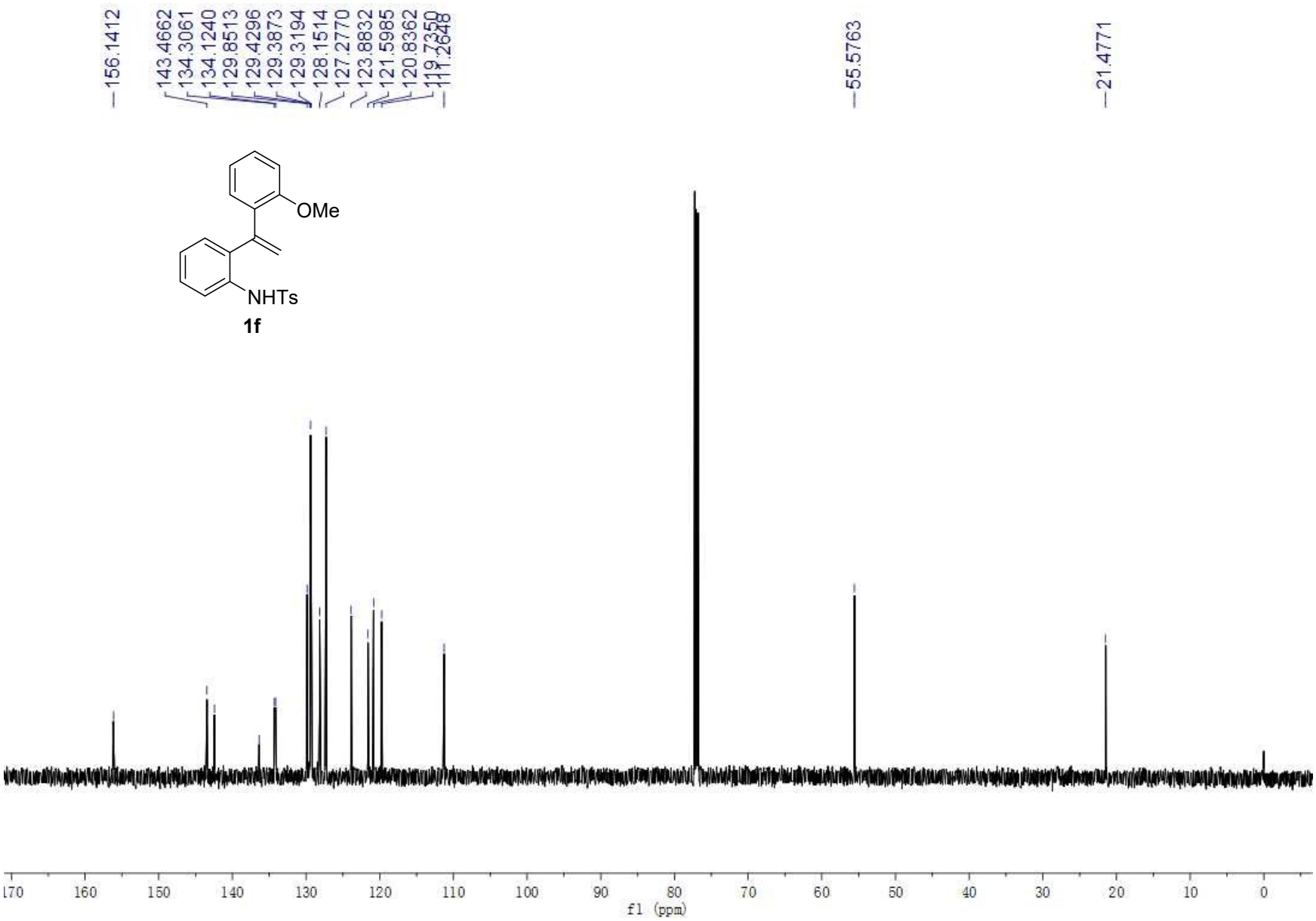
3.00
f1 (ppm)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119.7350
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OMe
NHTs
1f
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130
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80
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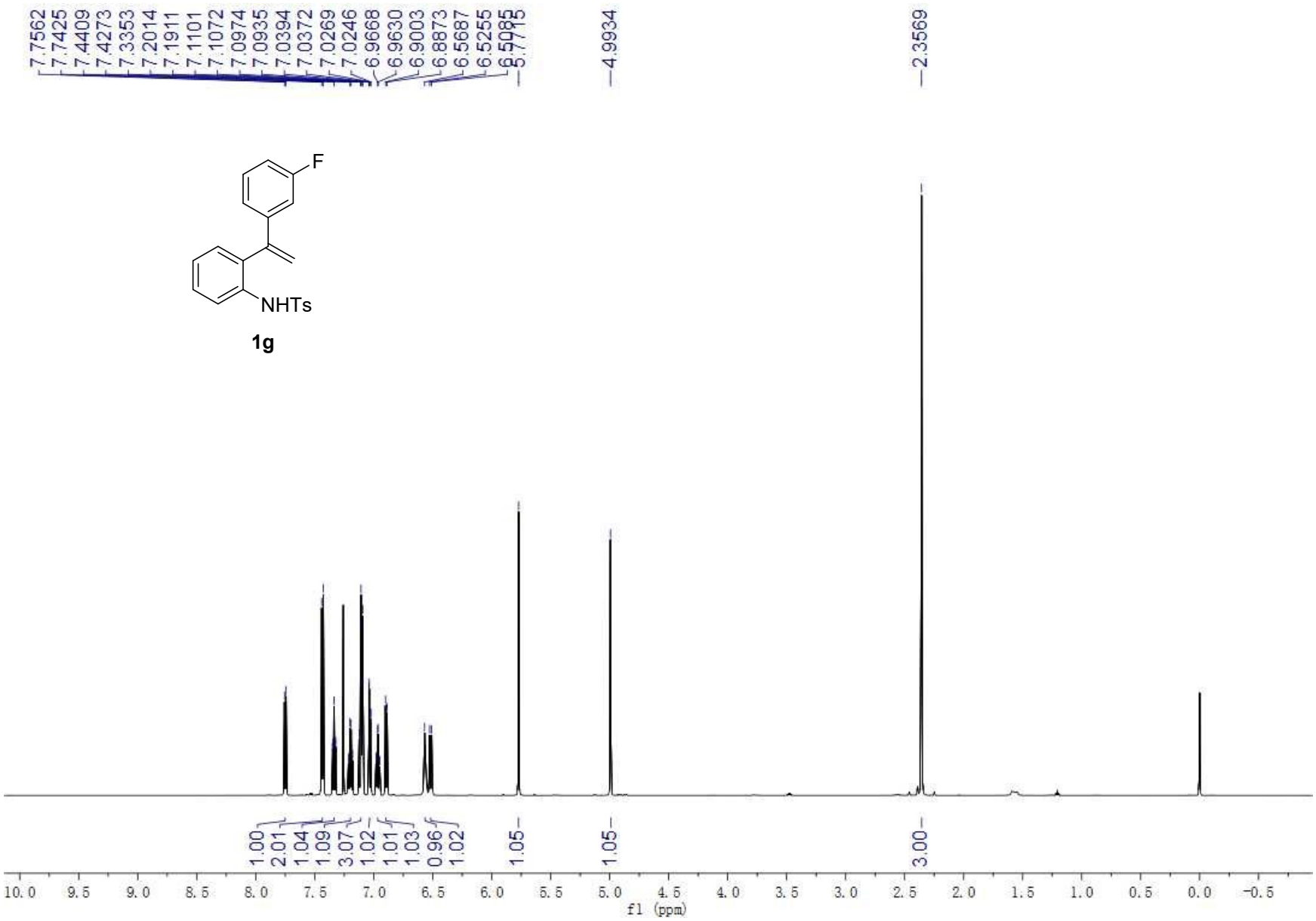
50
40
30
20
10
0
f1 (ppm)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6.9630
6.9003
6.8873
6.5687
6.5255
6.5085
5.7715
4.9934
2.3569
F
NHTs
1g
1.00
2.01
1.04
1.09
3.07
1.02
1.01
1.03
0.96
1.02
1.05
1.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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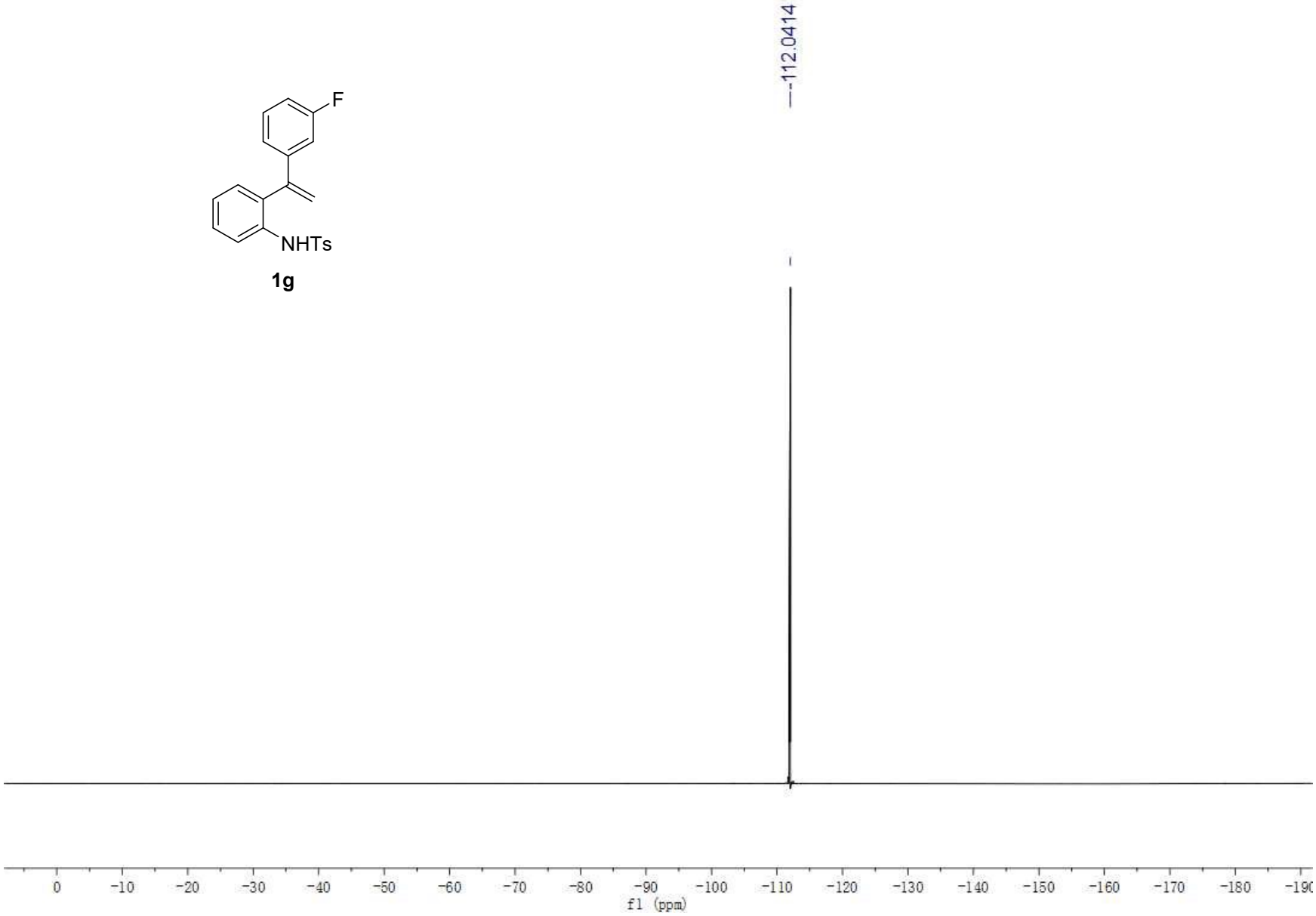
-0.5
f1 (ppm)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-10
-20
-30
-40
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-60
-70
-80
-90
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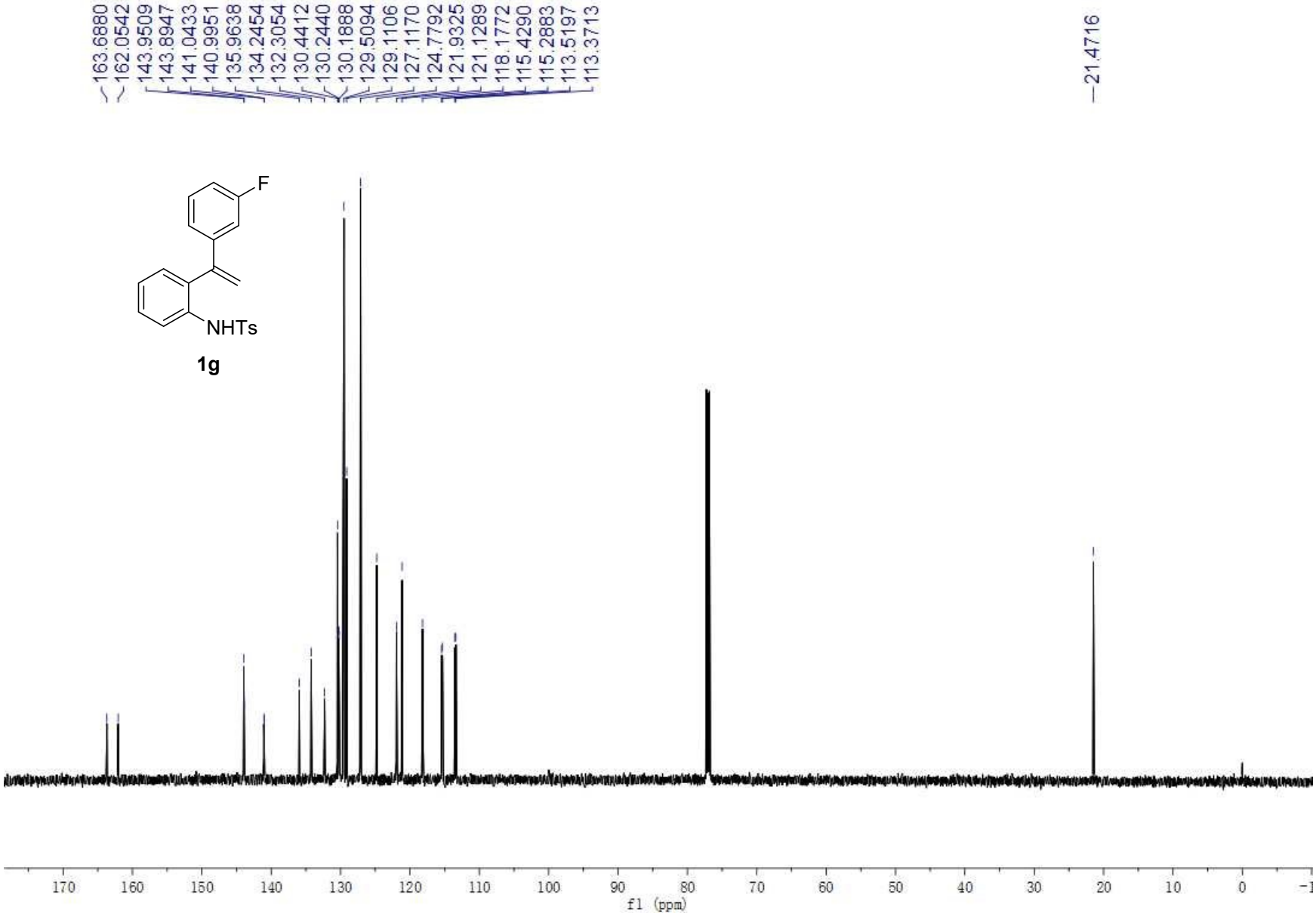
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

1g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130.2440
130.1888
129.5094
129.1106
127.1170
124.7792
121.9325
121.1289
118.1772
115.4290
115.2883
113.5197
113.3713
21.4716
F
NHTs
1g
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130
120
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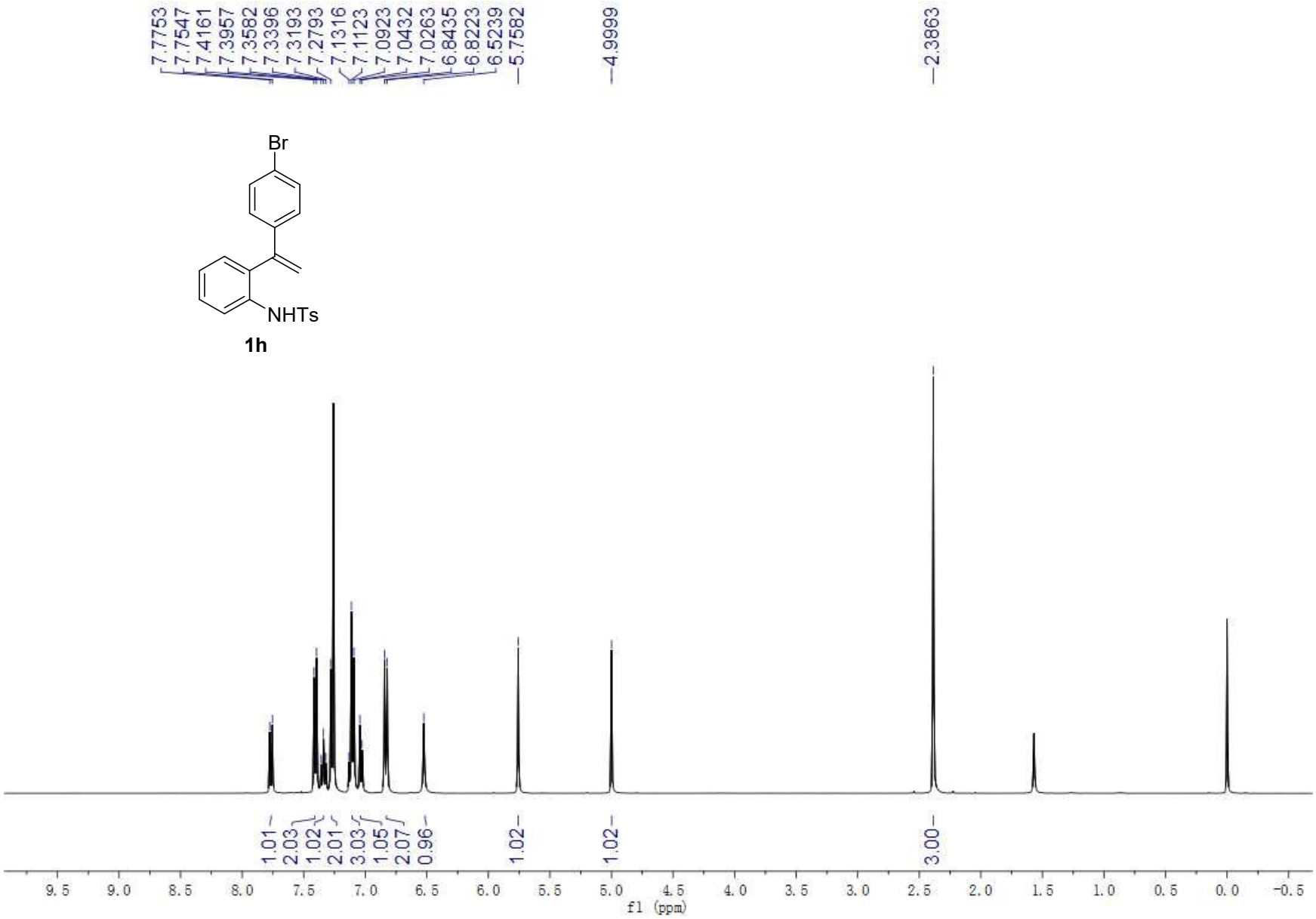
60
50
40
30
20
10
0
f1 (ppm)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7.0923
7.0432
7.0263
6.8435
6.8223
6.5239
5.7582
4.9999
2.3863
Br
NHTs
1h
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1.02
2.01
3.03
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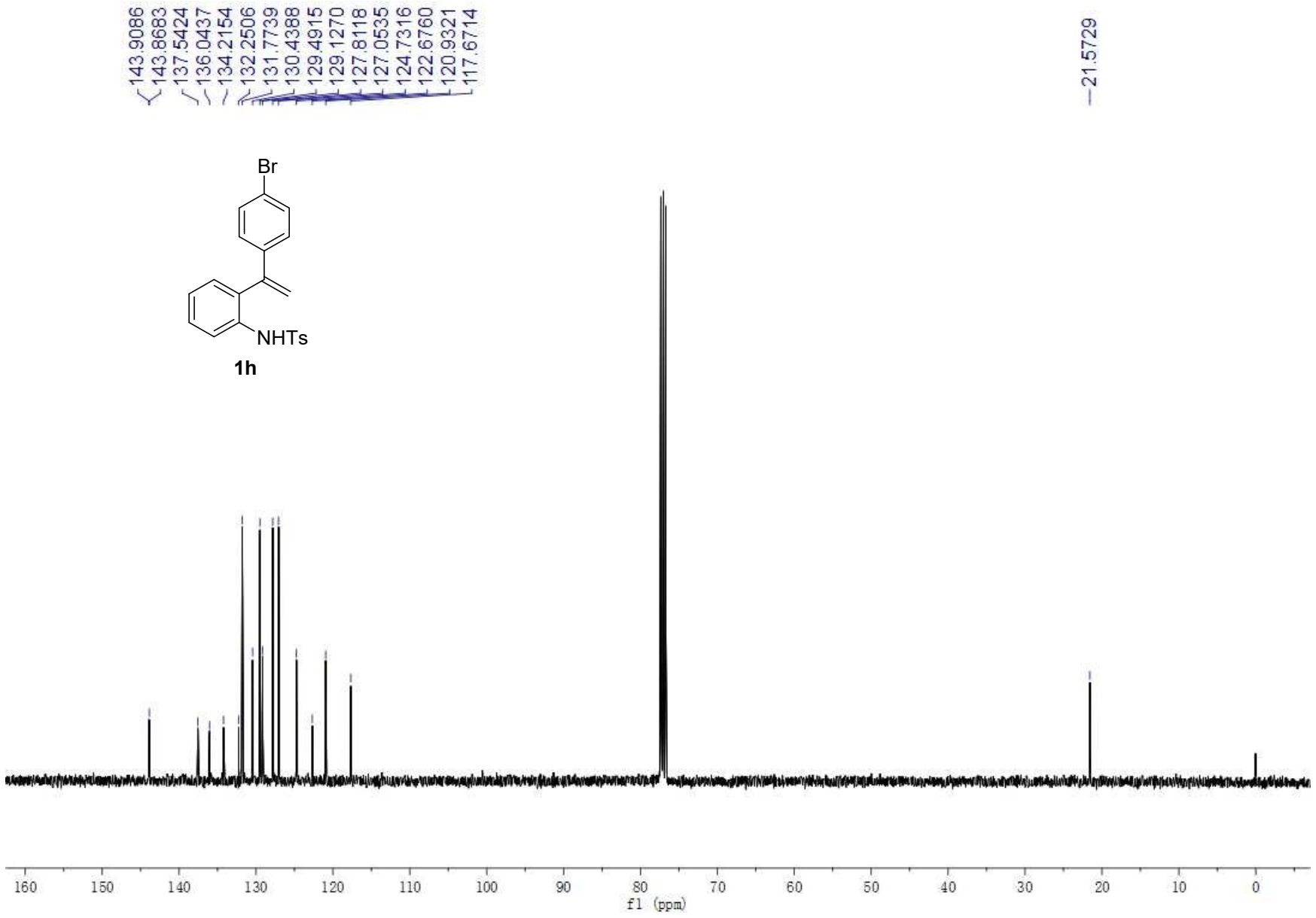
3.00
f1 (ppm)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127.0535
124.7316
122.6760
120.9321
117.6714
21.5729
Br
NHTs
1h
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140
130
120
110
100
90
80
70
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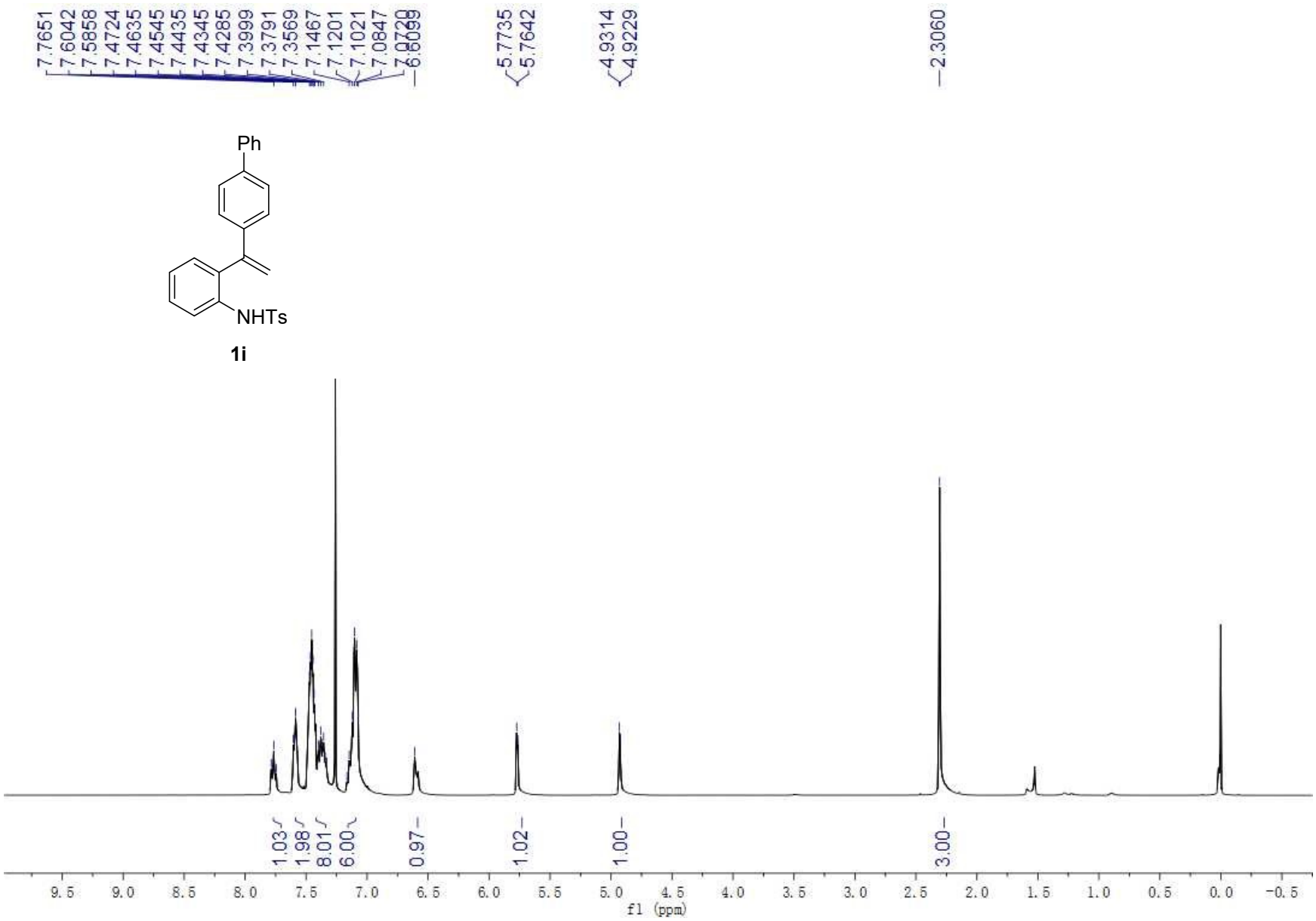
50
40
30
20
10
0
f1 (ppm)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7.1467
7.1201
7.1021
7.0847
5.7735
5.7642
4.9314
4.9229
2.3060
Ph
NHTs
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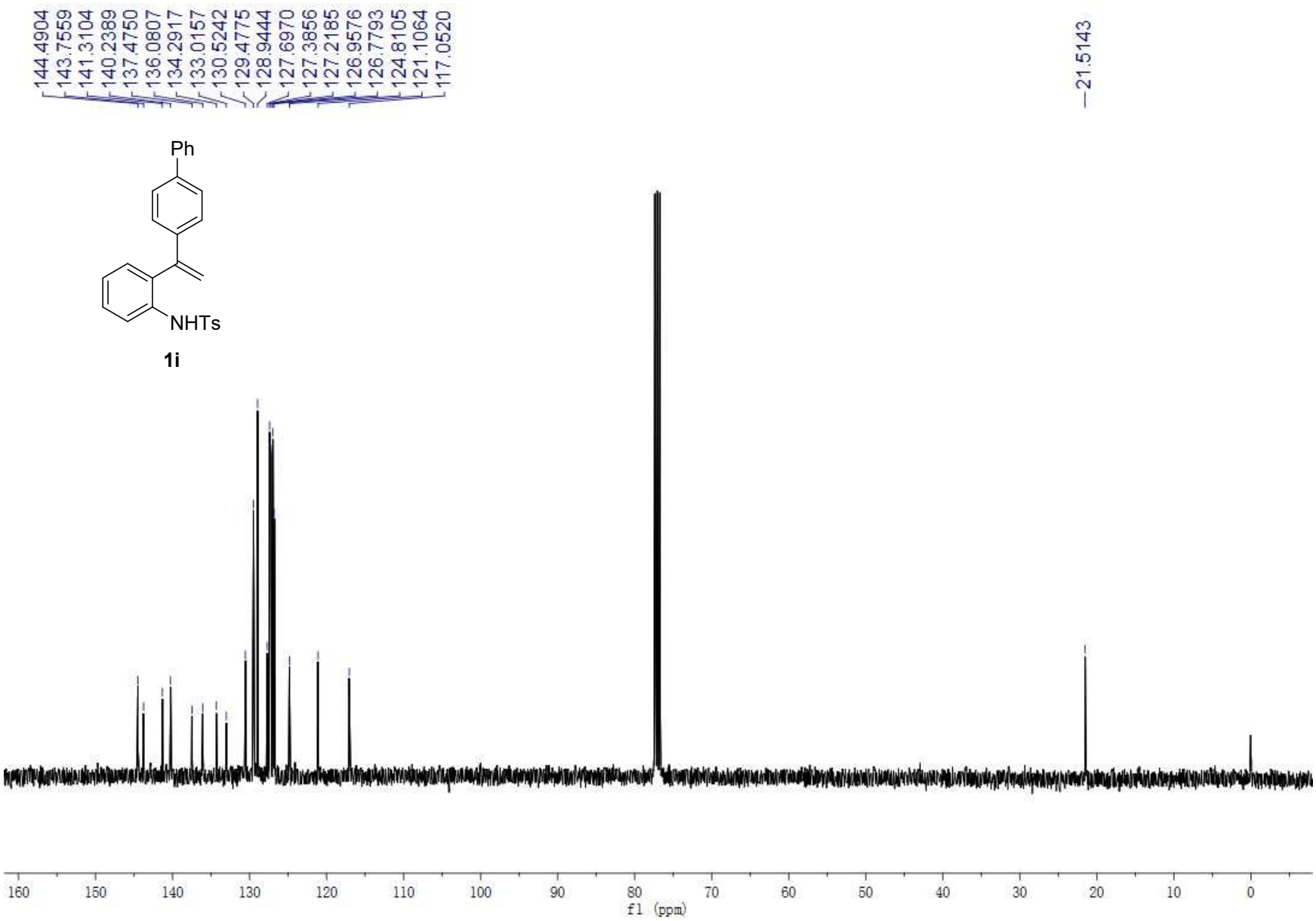
1.00
3.00
f1 (ppm)

1i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127.6970
127.3856
127.2185
126.9576
126.7793
124.8105
121.1064
117.0520
21.5143
Ph
NHTs
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150
140
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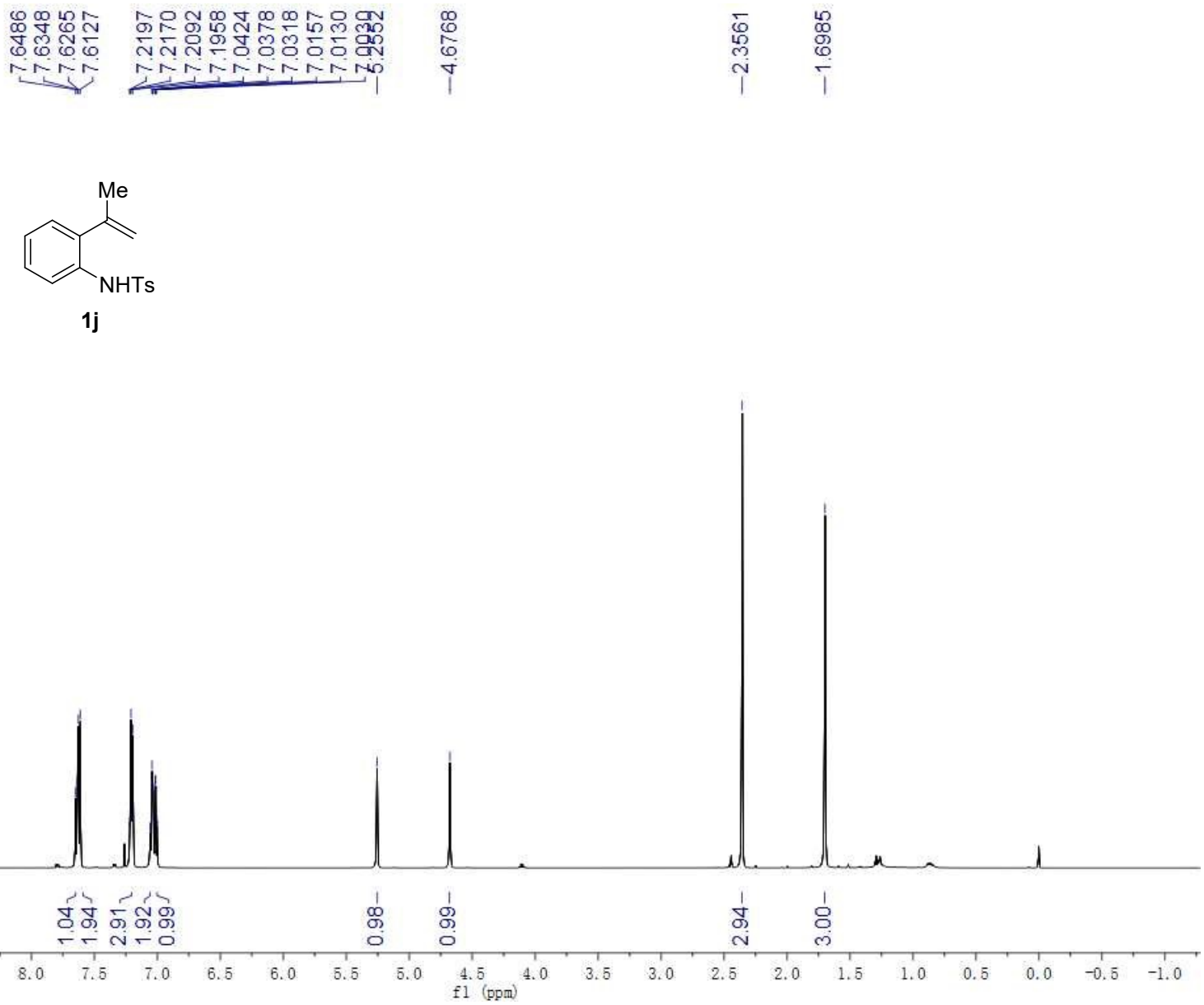
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1i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7.0318
7.0157
7.0130
5.2552
4.6768
2.3561
1.6985
Me
NHTs
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1.94
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1.92
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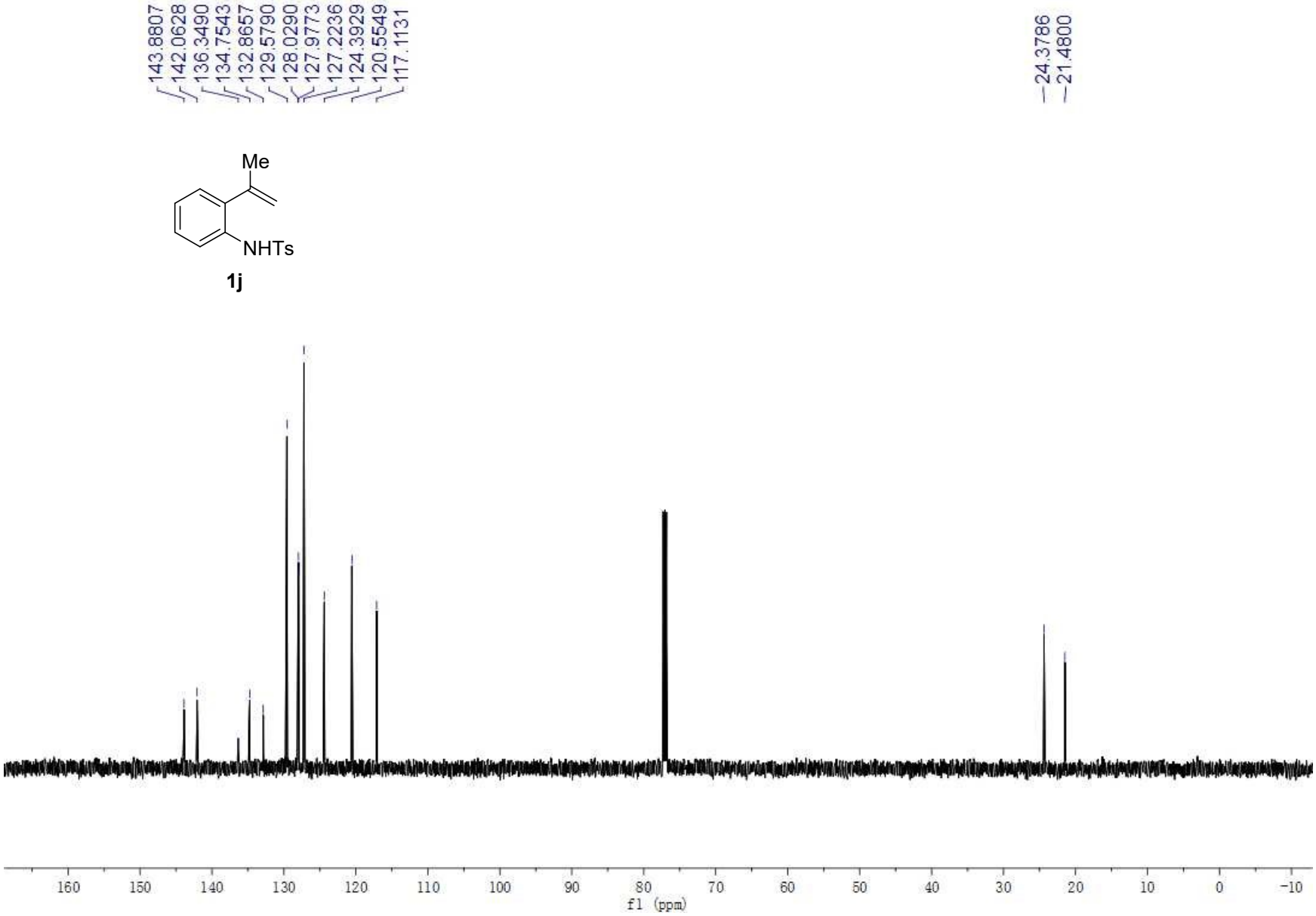
0.98
0.99
2.94
3.00
f1 (ppm)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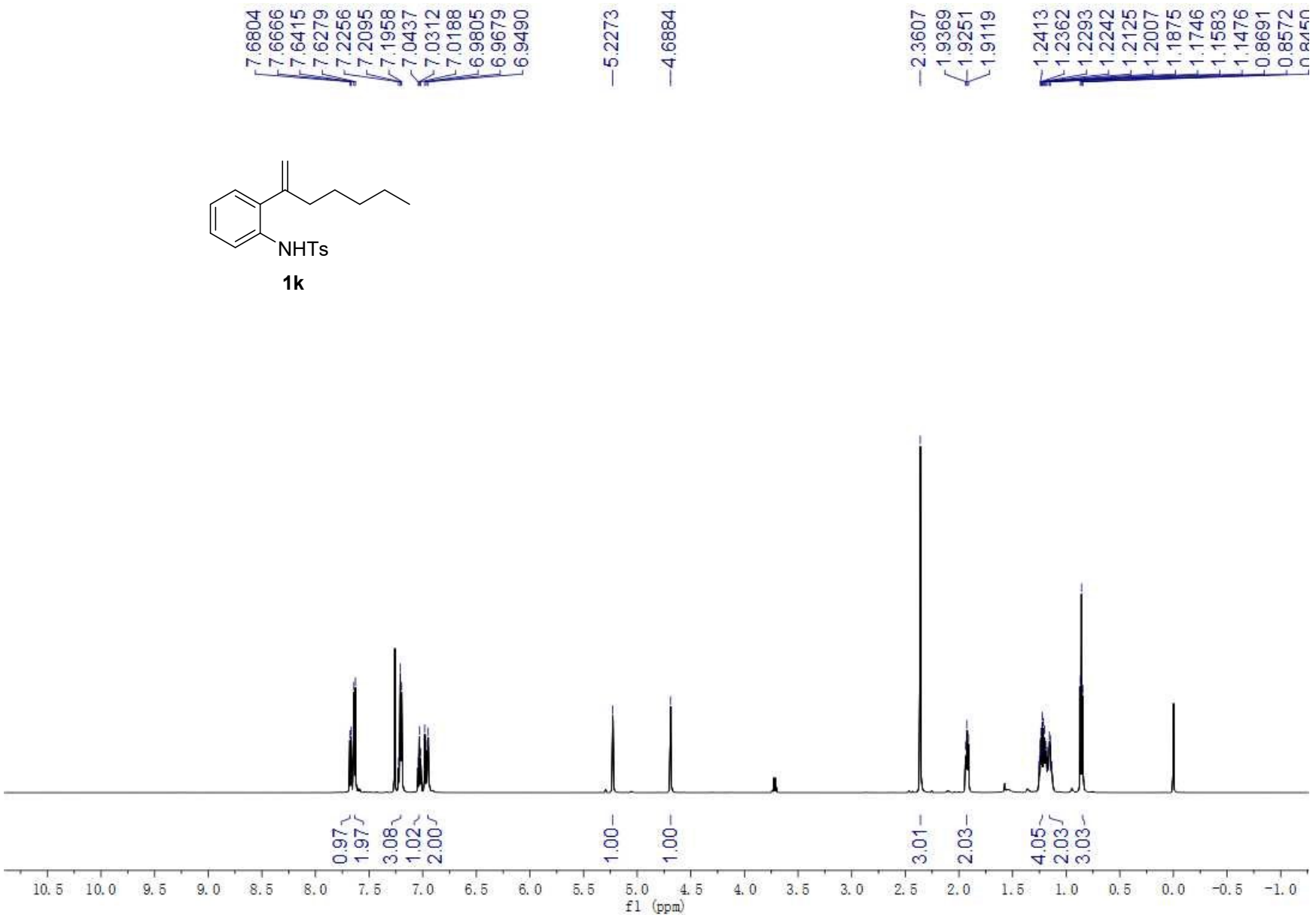
127.2236
124.3929
120.5549
117.1131
24.3786
21.4800
Me
NHTs
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

1j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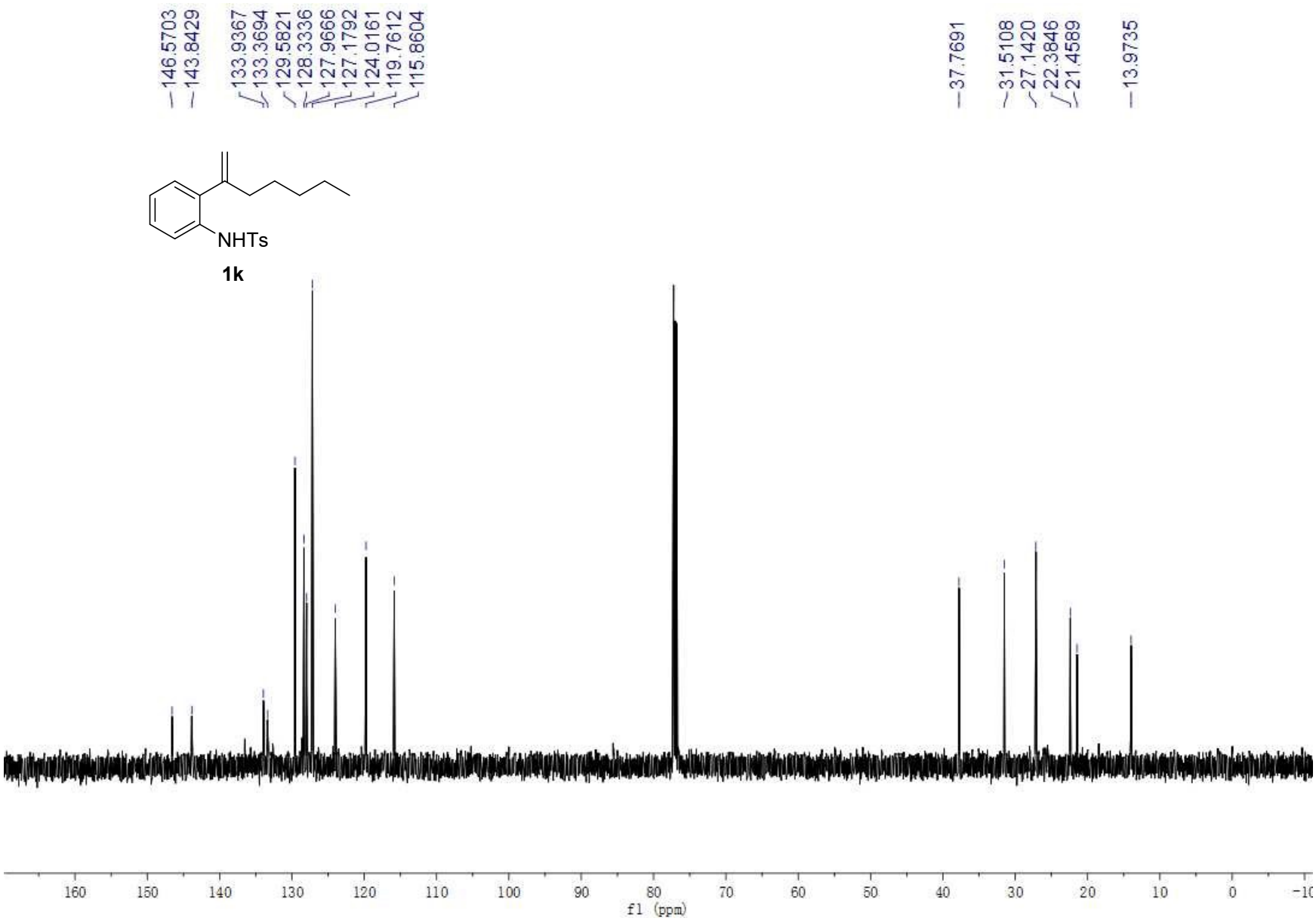
7.2095
7.1958
7.0437
7.0312
7.0188
6.9805
6.9679
6.9490
5.2273
4.6884
2.3607
1.9369
1.9251
1.9119
1.2413
1.2362
1.2293
1.2242
1.2125
1.2007
1.1875
1.1746
1.1583
1.1476
0.8691
0.8572
NHTs
0.97
1.97
3.08
1.02
2.00
1.00
1.00
3.01
2.03
4.05
2.03
3.03
f1 (ppm)

1k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133.9367
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129.5821
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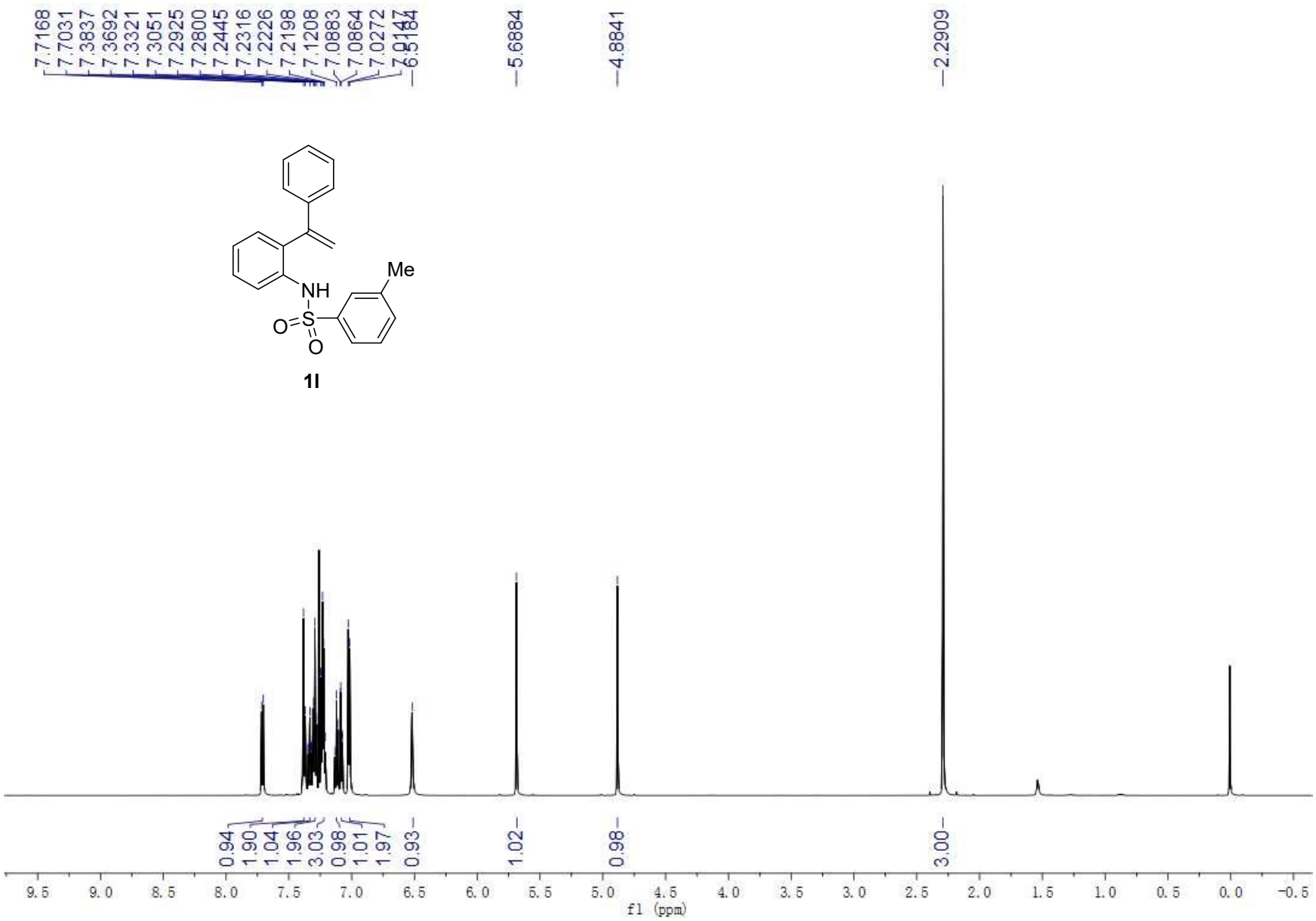
127.9666
127.1792
124.0161
119.7612
115.8604
37.7691
31.5108
27.1420
22.3846
21.4589
13.9735
NHTs
1k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2925
7.2800
7.2445
7.2316
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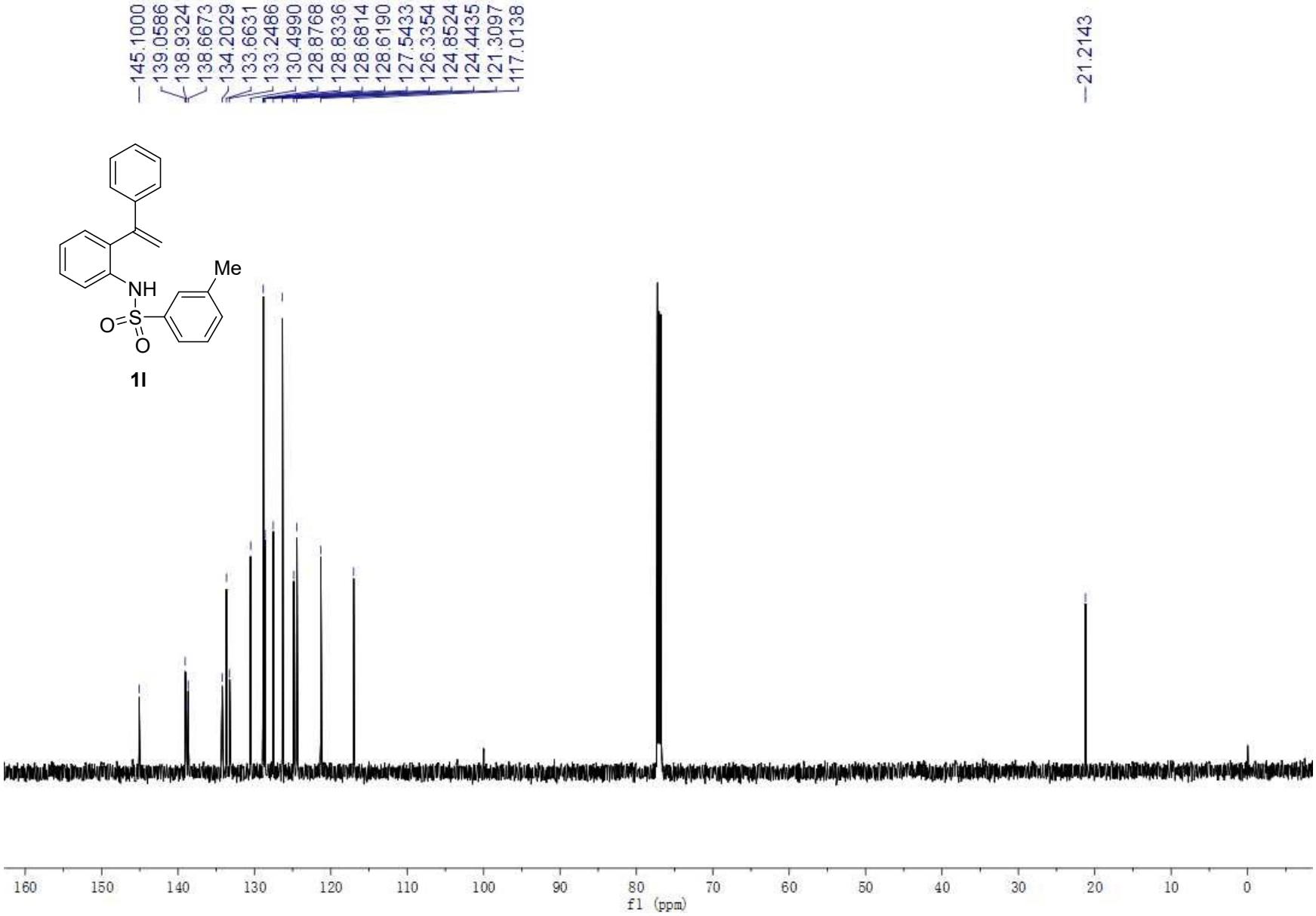
7.2198
7.1208
7.0883
7.0864
7.0272
6.9184
5.6884
4.8841
2.2909
Me
NH
O=S=O
0.94
1.90
1.04
1.96
3.03
0.98
1.01
1.97
0.93
1.02
0.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1l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138.9324
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133.6631
133.2486
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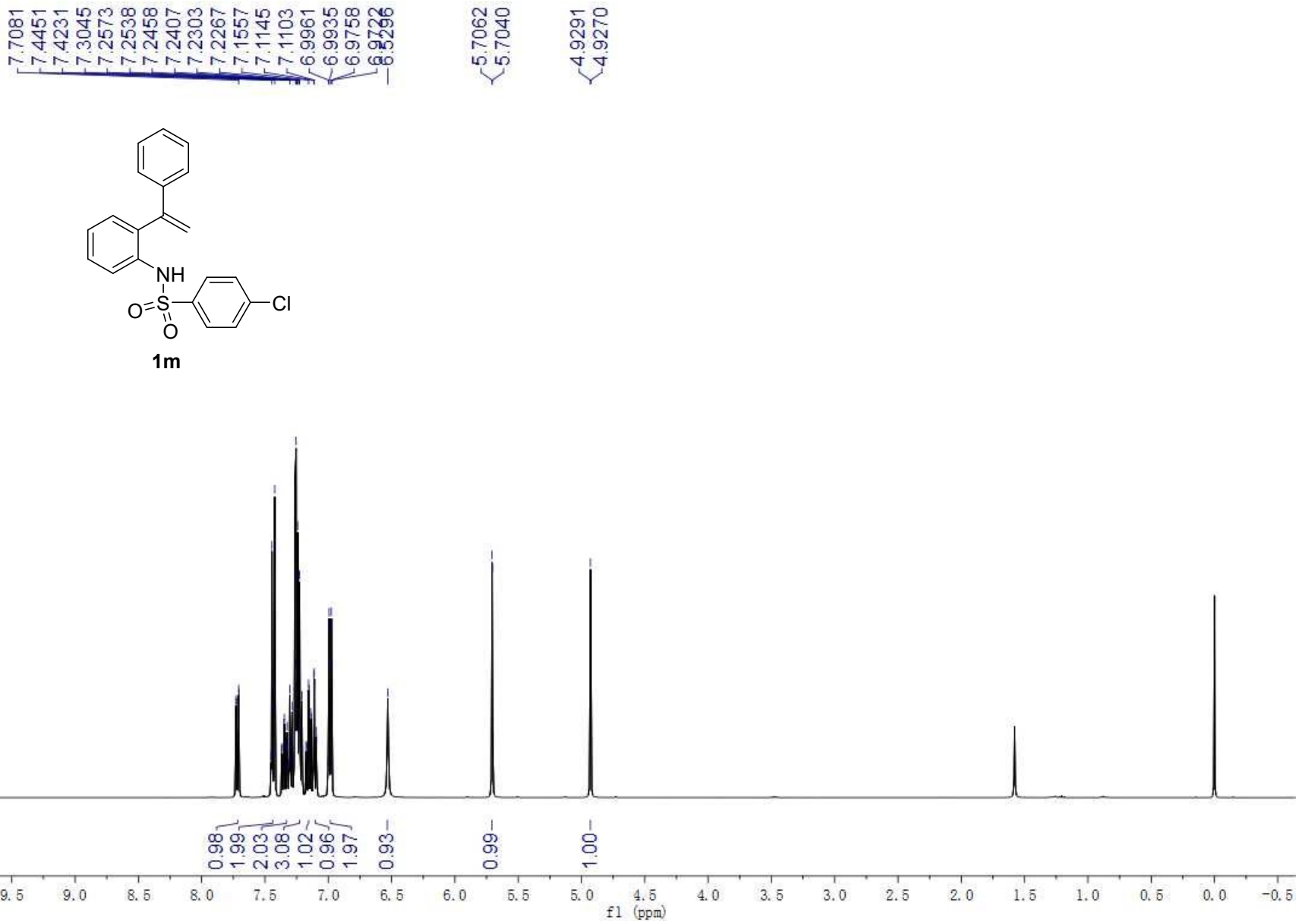
128.8768
128.8336
128.6814
128.6190
127.5433
126.3354
124.8524
124.4435
121.3097
117.0138
21.2143
Me
NH
O
S
O
1l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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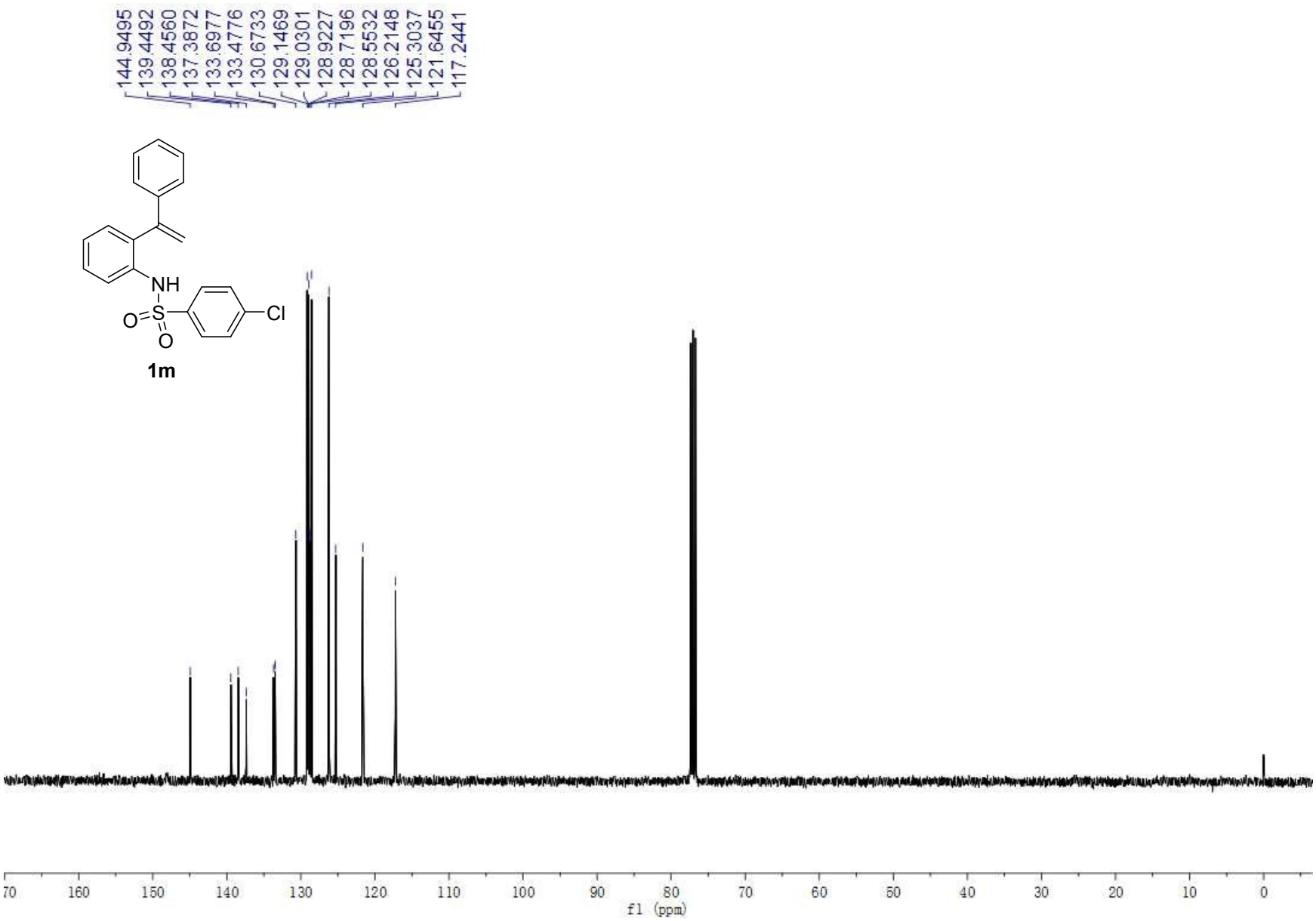
7.4231
7.3045
7.2573
7.2538
7.2458
7.2407
7.2303
7.2267
7.1557
7.1145
7.1103
6.9961
6.9935
6.9758
5.7062
5.7040
4.9291
4.9270
NH
O
S
O
Cl
1m
0.98
1.99
2.03
3.08
1.02
0.96
1.97
0.93
0.99
1.00
f1 (ppm)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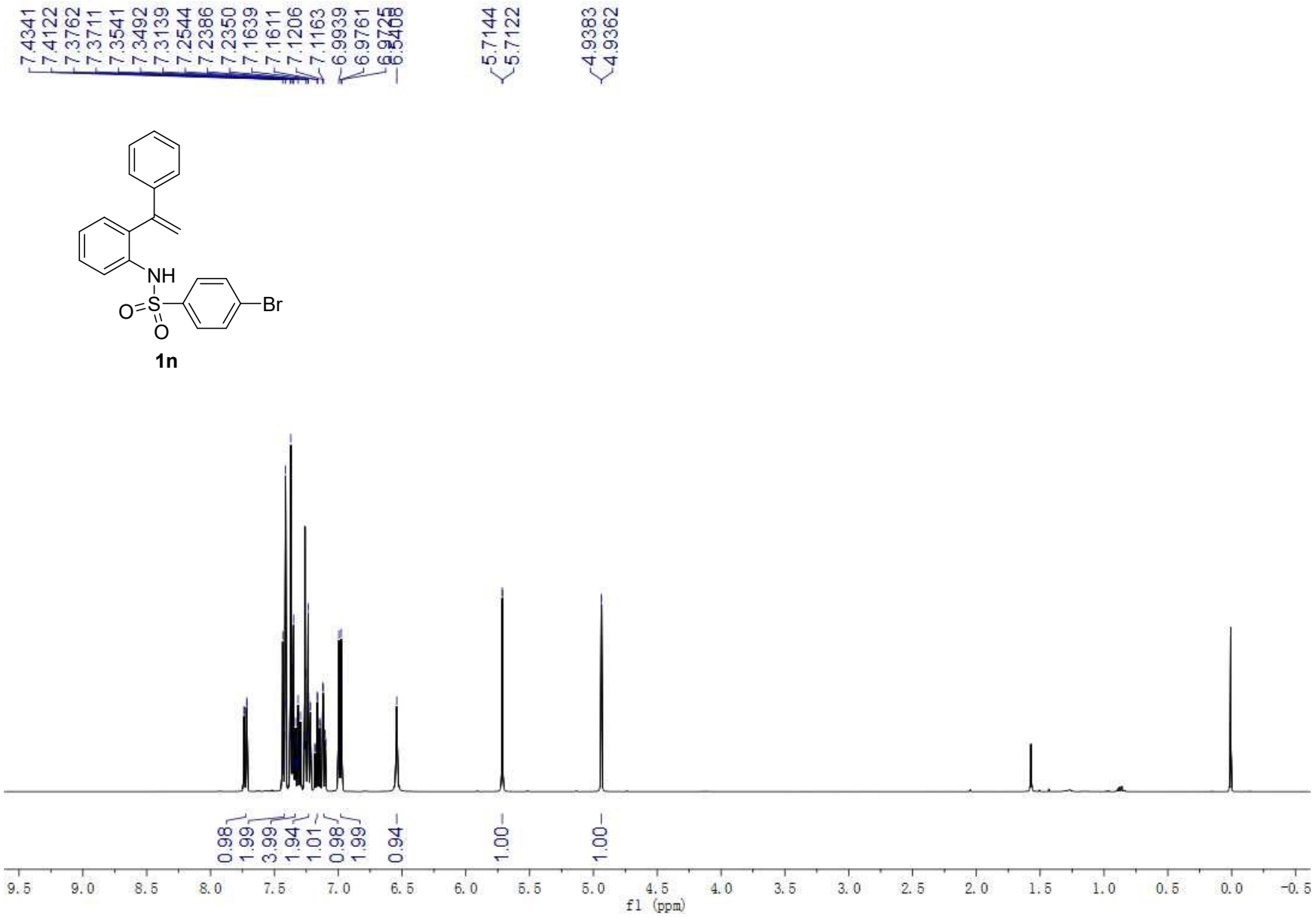
138.4560
137.3872
133.6977
133.4776
130.6733
129.1469
129.0301
128.9227
128.7196
128.5532
126.2148
125.3037
121.6455
117.2441
NH
O=S
O
Cl
1m
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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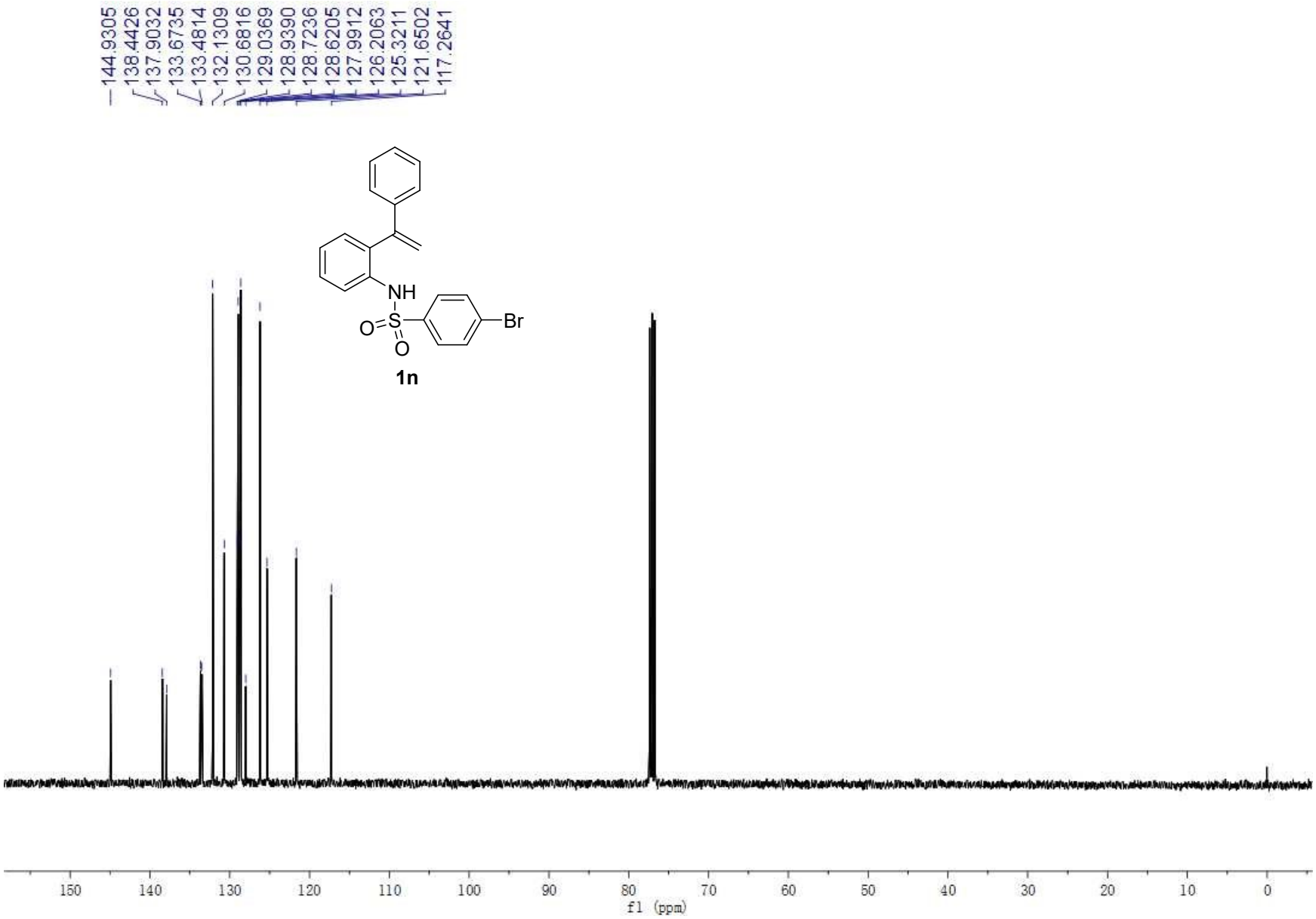
7.4122
7.3762
7.3711
7.3541
7.3492
7.3139
7.2544
7.2386
7.2350
7.1639
7.1611
7.1206
7.1163
6.9939
6.9761
5.7144
5.7122
4.9383
4.9362
NH
O
S
O
Br
1n
0.98
1.99
3.99
1.94
1.01
0.98
1.99
0.94
1.00
1.00
f1 (ppm)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137.9032
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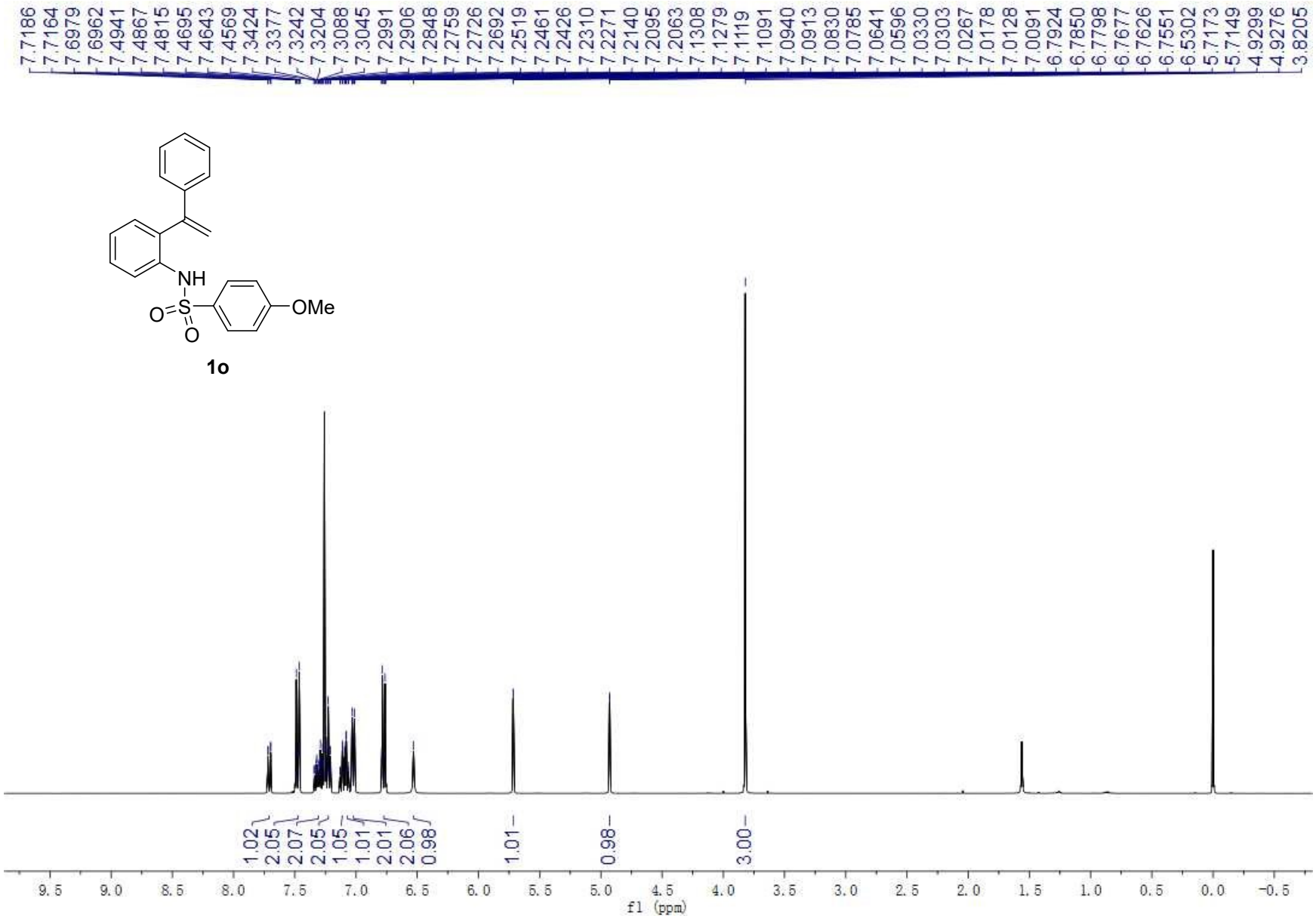
132.1309
130.6816
129.0369
128.9390
128.7236
128.6205
127.9912
126.2063
125.3211
121.6502
117.2641
NH
O=S
O
Br
1n
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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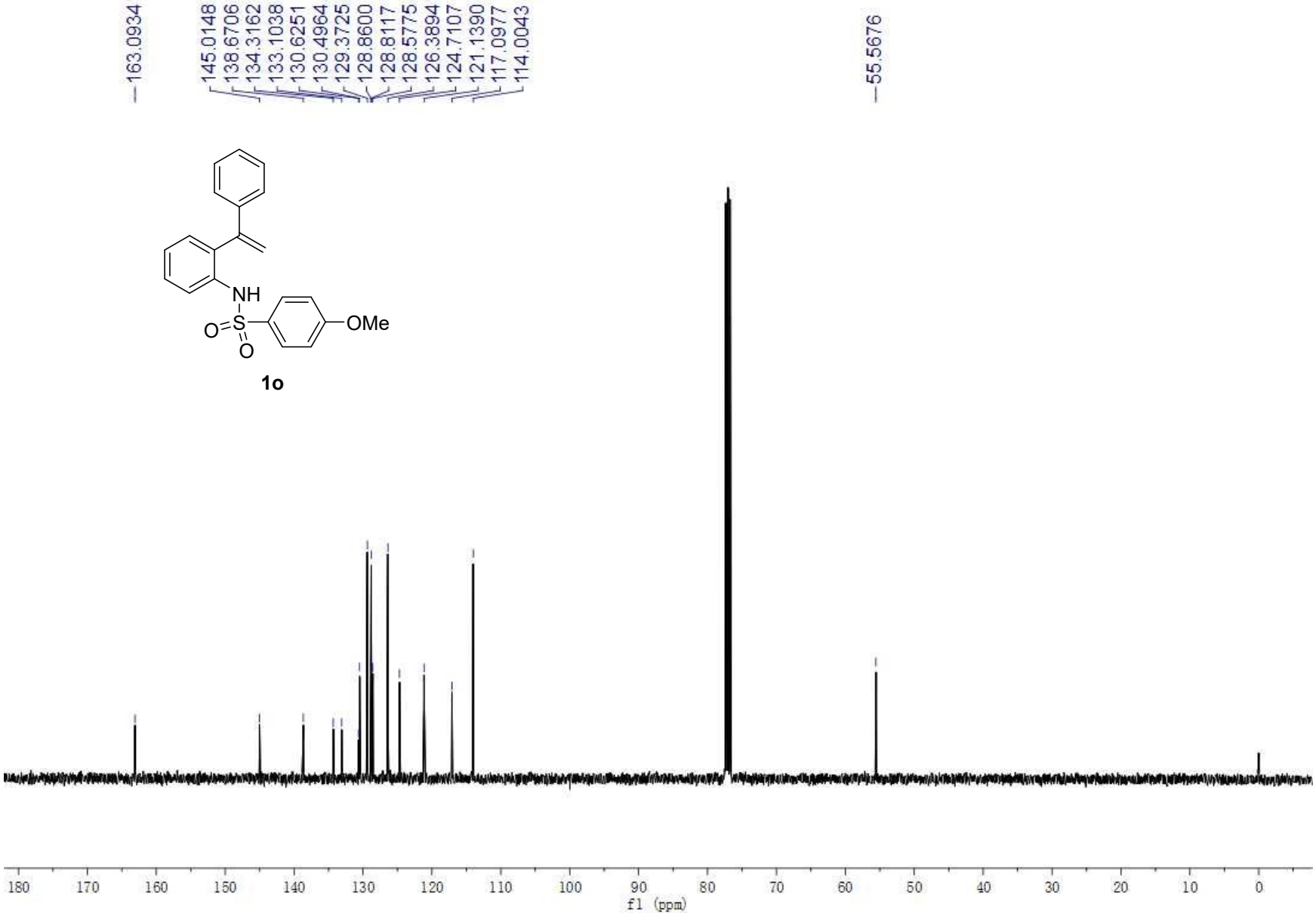
7.4941
7.4867
7.4815
7.4695
7.4643
7.4569
7.3424
7.3377
7.3242
7.3204
7.3088
7.3045
7.2991
7.2906
7.2848
7.2759
7.2726
7.2692
7.2519
7.2461
7.2426
7.2310
7.2271
7.2140
7.2095
7.2063
7.1308
7.1279
7.1119
7.1091
7.0940
7.0913
7.0830
7.0785
7.0641
7.0596
7.0330
7.0303
7.0267
7.0178
7.0128
7.0091
6.7924
6.7850
6.7798
6.7677
6.7626
6.7551
6.5302
5.7173
5.7149
4.9299
4.9276
3.8205
NH
O
S
O
OMe
1o
1.02
2.05
2.07
2.05
1.05
1.01
2.01
2.06
0.98
1.01
0.98
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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133.1038
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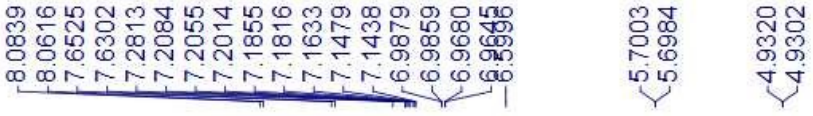
126.3894
124.7107
121.1390
117.0977
114.0043
55.5676
NH
O=S
O
OMe
1o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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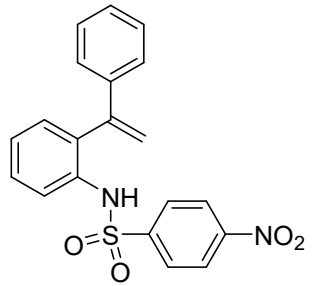
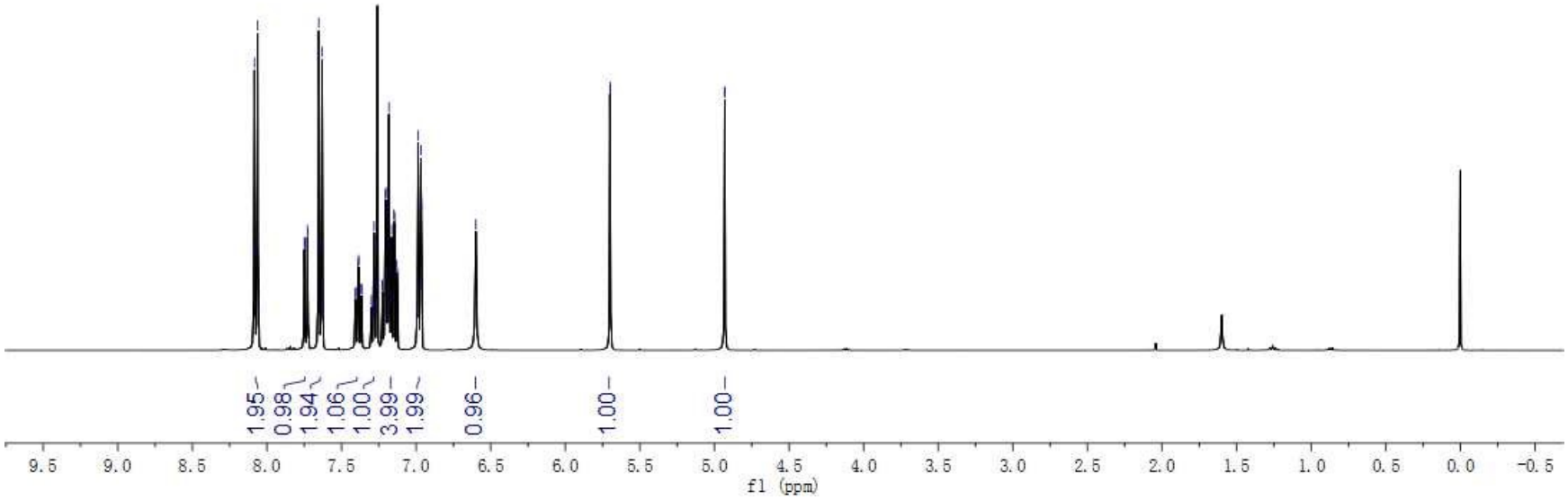
7.6525
7.6302
7.2813
7.2084
7.2055
7.2014
7.1855
7.1816
7.1633
7.1479
7.1438
6.9879
6.9859
6.9680
5.7003
5.6984
4.9320
4.9302


NH
O=S
O
NO2

1p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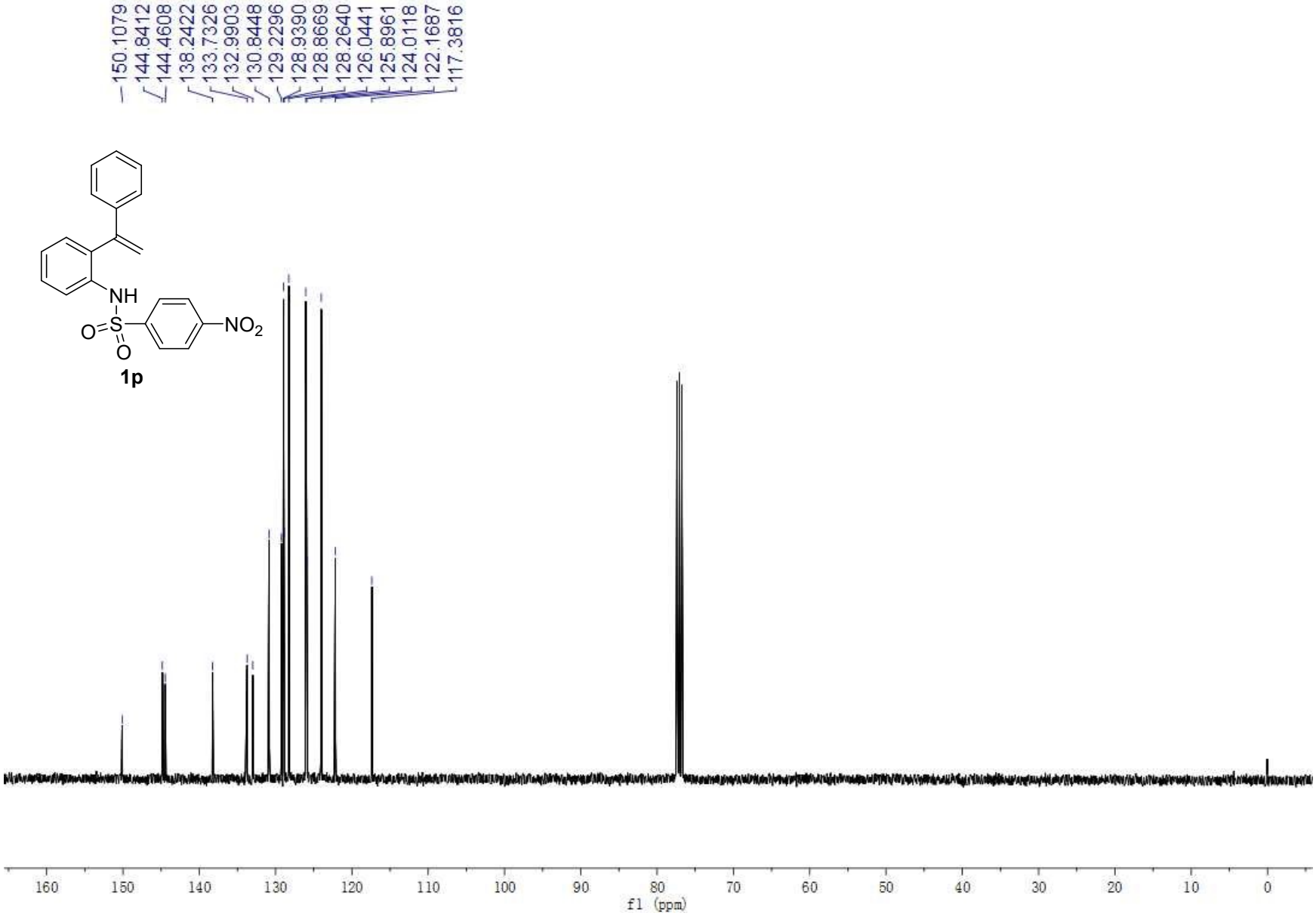
1.94
1.06
1.00
3.99
1.99
0.96
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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144.4608
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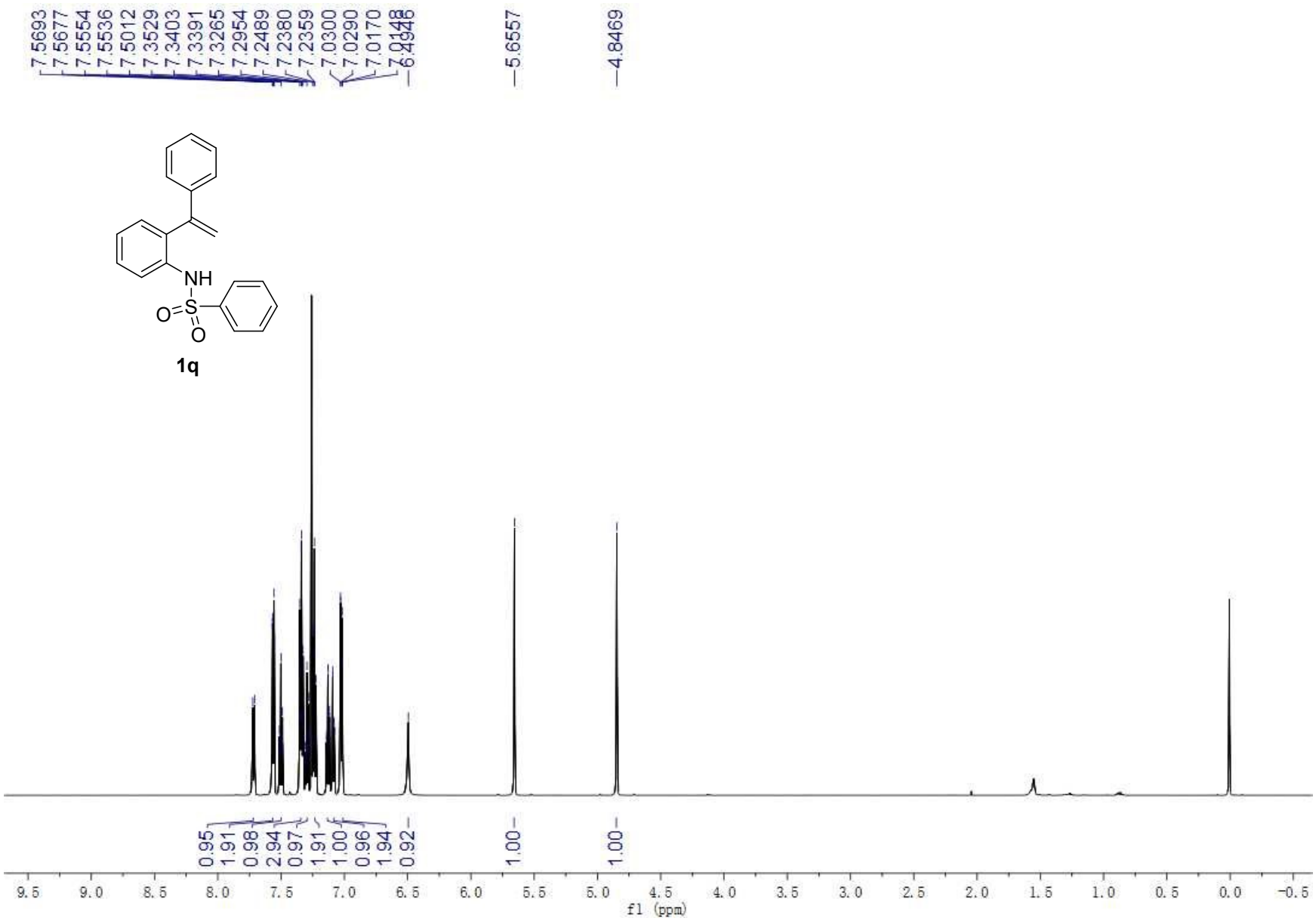
133.7326
132.9903
130.8448
129.2296
128.9390
128.8669
128.2640
126.0441
125.8961
124.0118
122.1687
117.3816
NH
O=S=O
NO2
1p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3403
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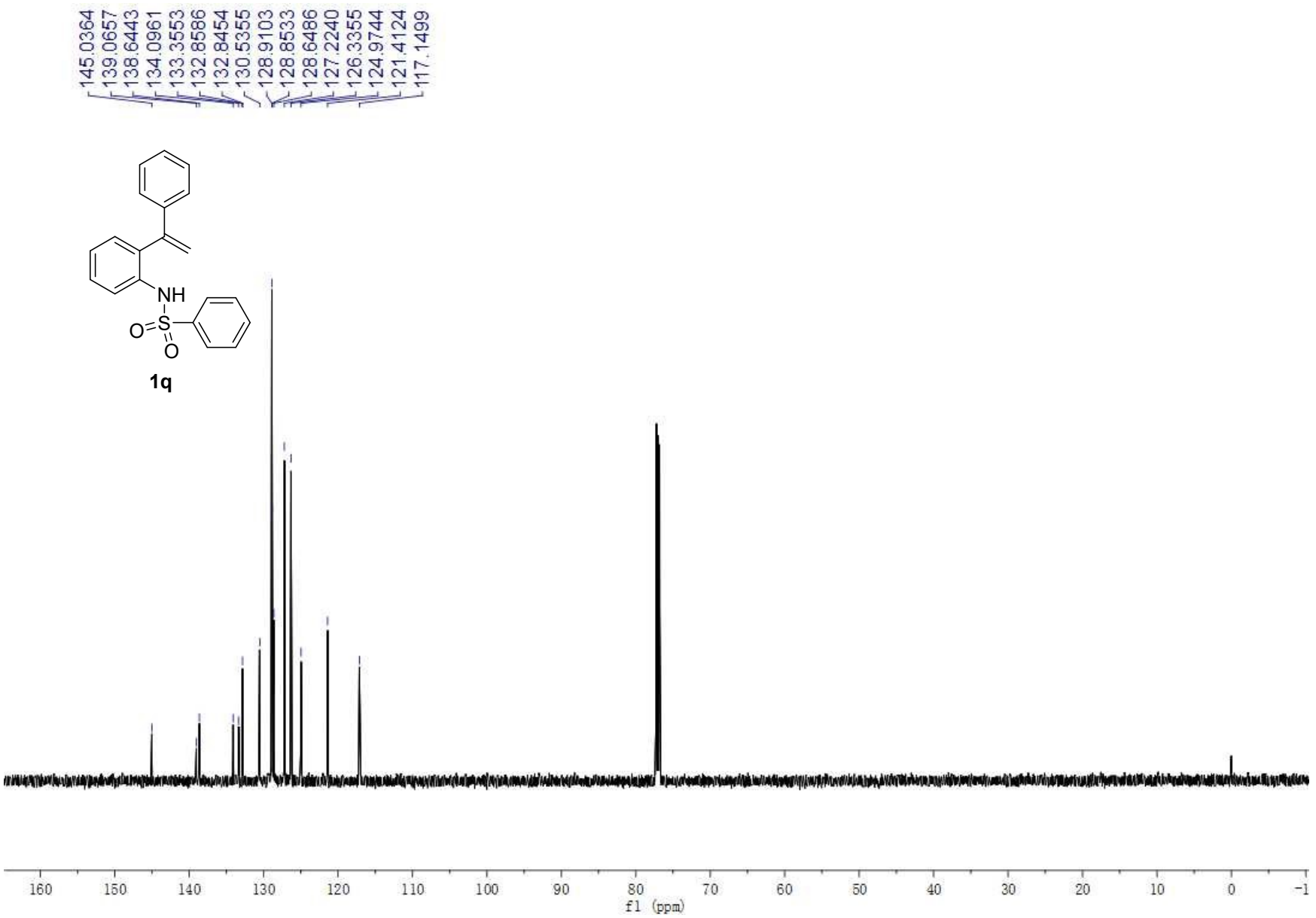
7.3265
7.2954
7.2489
7.2380
7.2359
7.0300
7.0290
7.0170
7.0148
6.4948
5.6557
4.8469
NH
O=S=O
1q
0.95
1.91
0.98
2.94
0.97
1.91
1.00
0.96
1.94
0.92
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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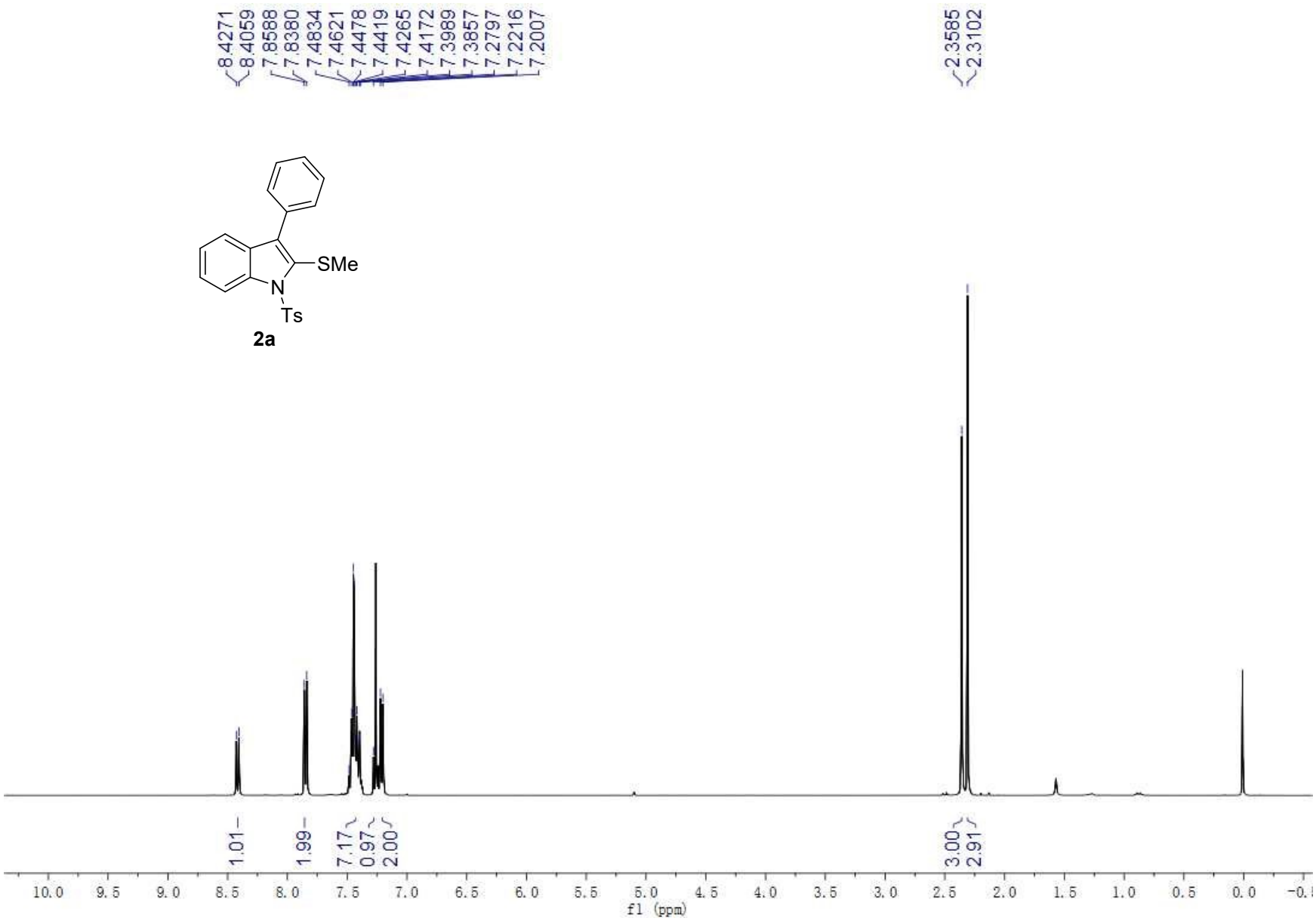
128.9103
128.8533
128.6486
127.2240
126.3355
124.9744
121.4124
117.1499
NH
O=S=O
1q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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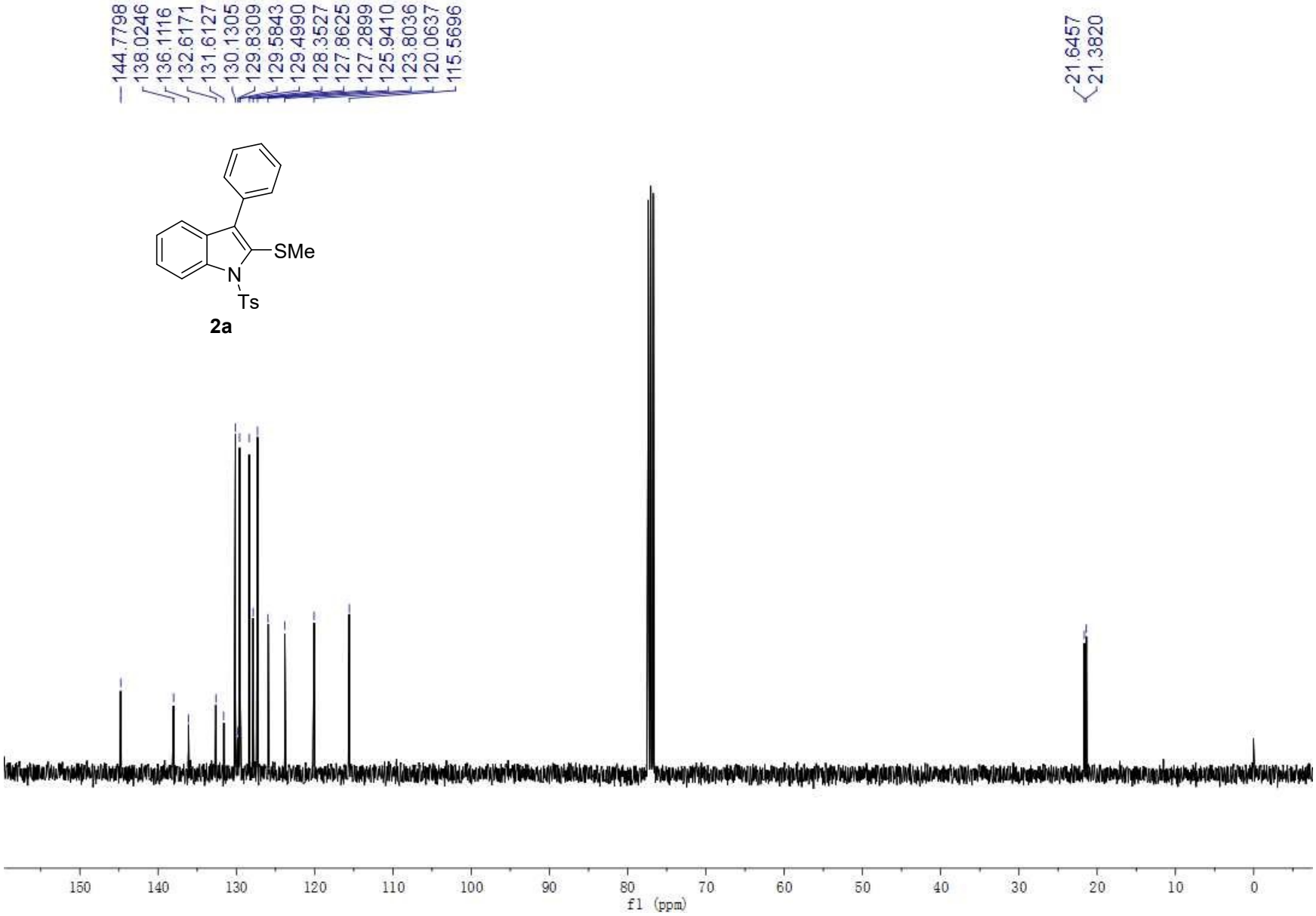
7.4265
7.4172
7.3989
7.3857
7.2797
7.2216
7.2007
2.3585
2.3102
SMe
N
Ts
2a
1.01
1.99
7.17
0.97
2.00
3.00
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.2899
125.9410
123.8036
120.0637
115.5696
21.6457
21.3820
SMe
N
Ts
2a
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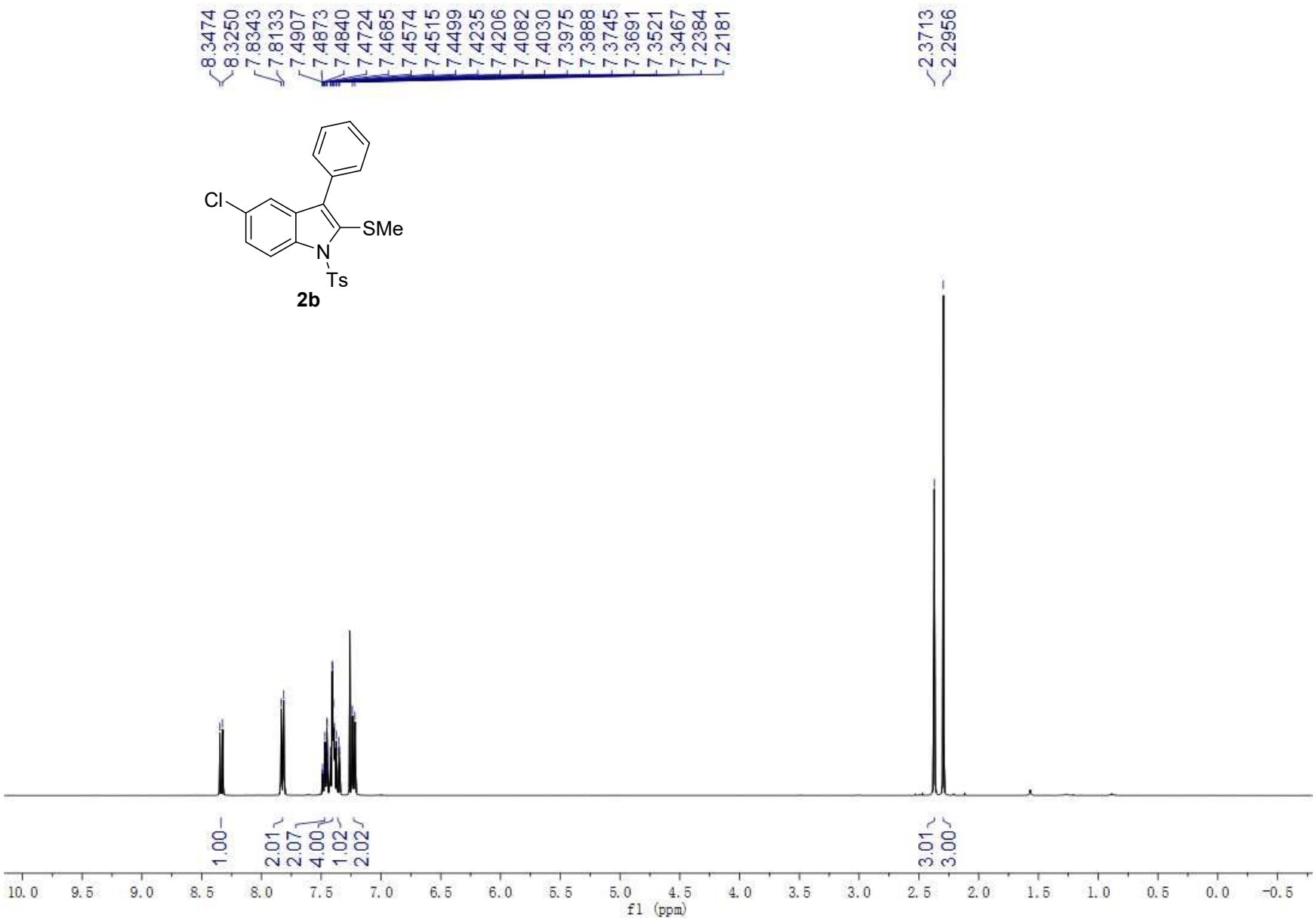
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4840
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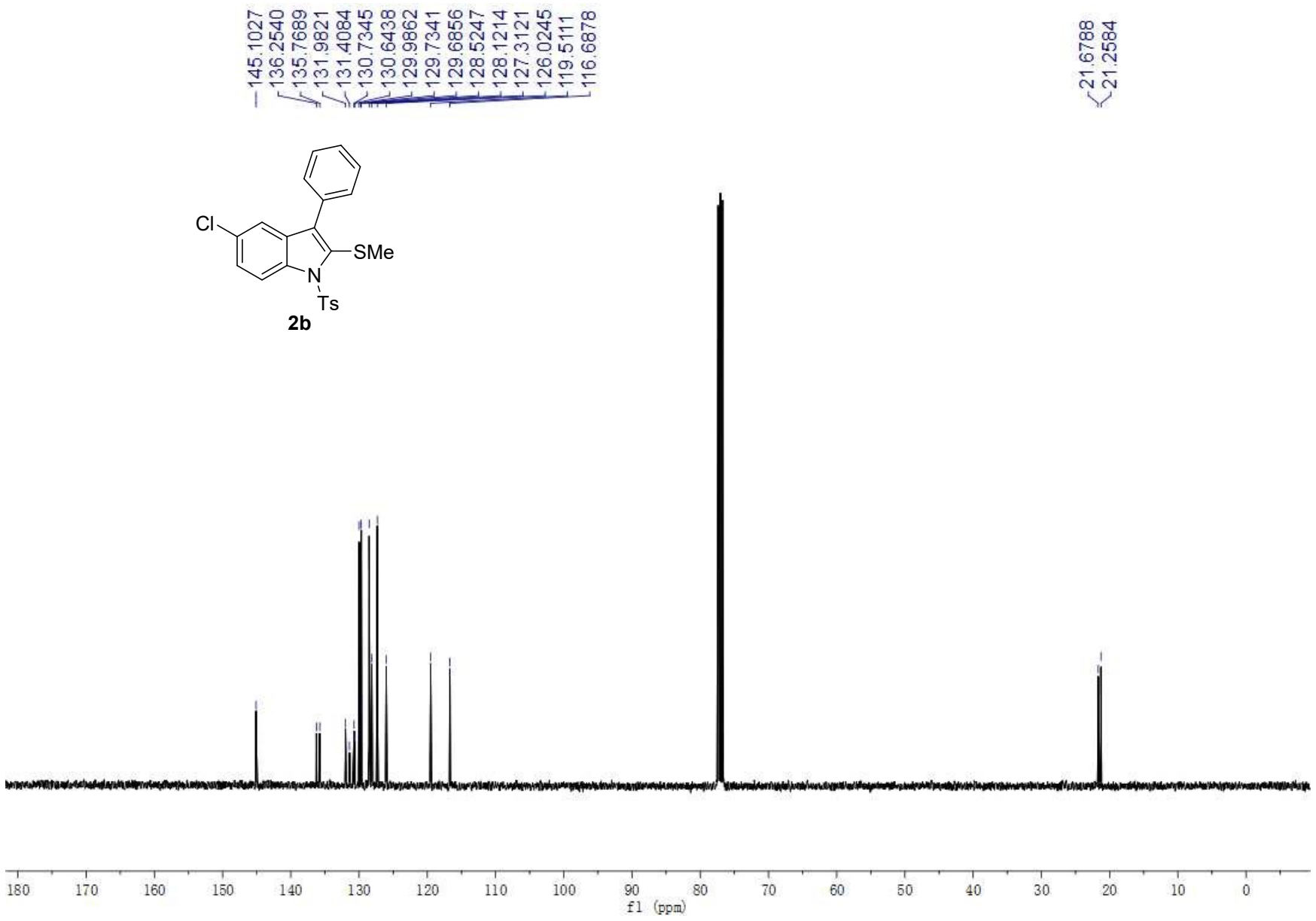
7.4499
7.4235
7.4206
7.4082
7.4030
7.3975
7.3888
7.3745
7.3691
7.3521
7.3467
7.2384
7.2181
2.3713
2.2956
Cl
SMe
N
Ts
2b
1.00
2.01
2.07
4.00
1.02
2.02
3.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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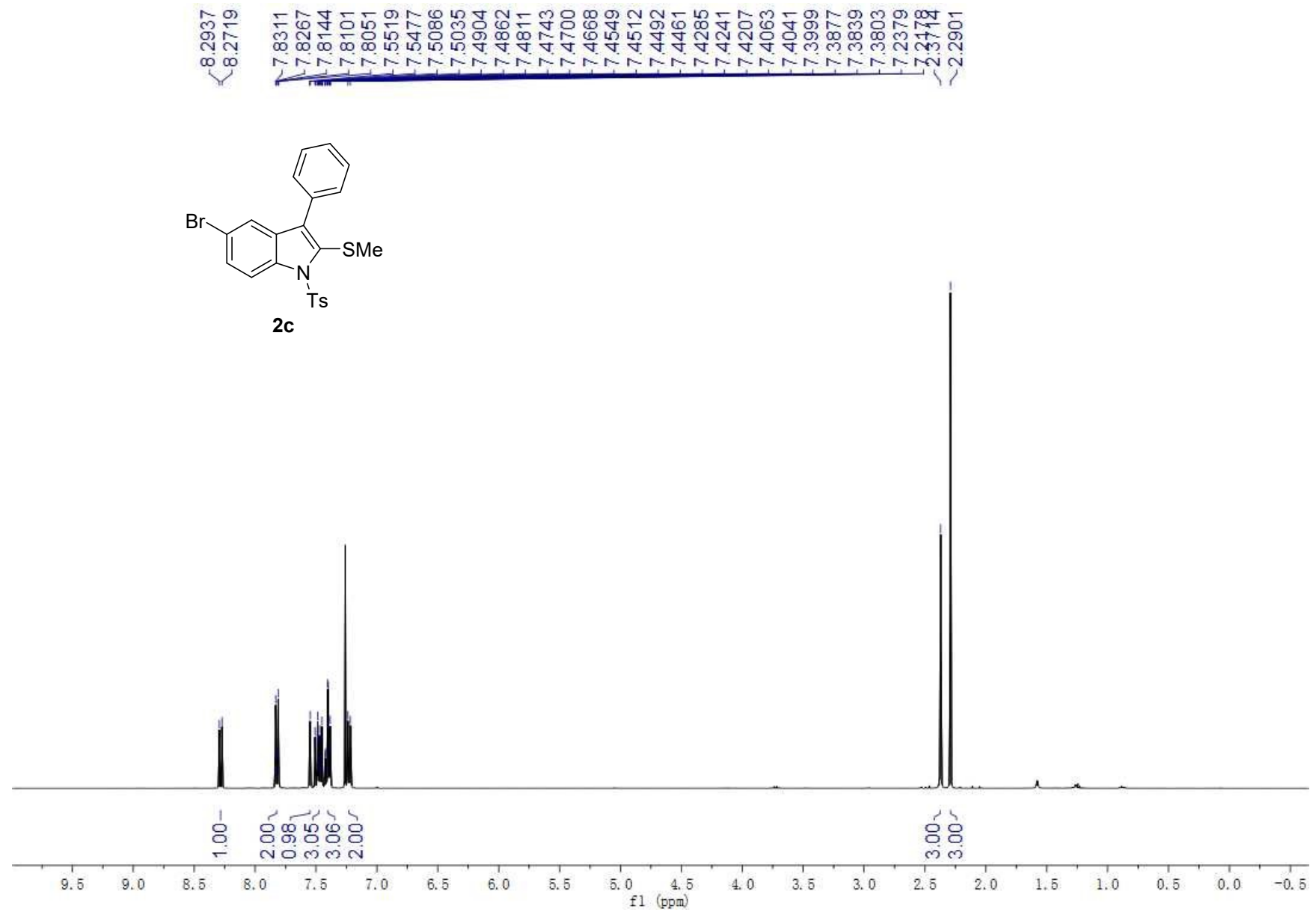
129.6856
128.5247
128.1214
127.3121
126.0245
119.5111
116.6878
21.6788
21.2584
Cl
SMe
N
Ts
2b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.5477
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7.4904
7.4862
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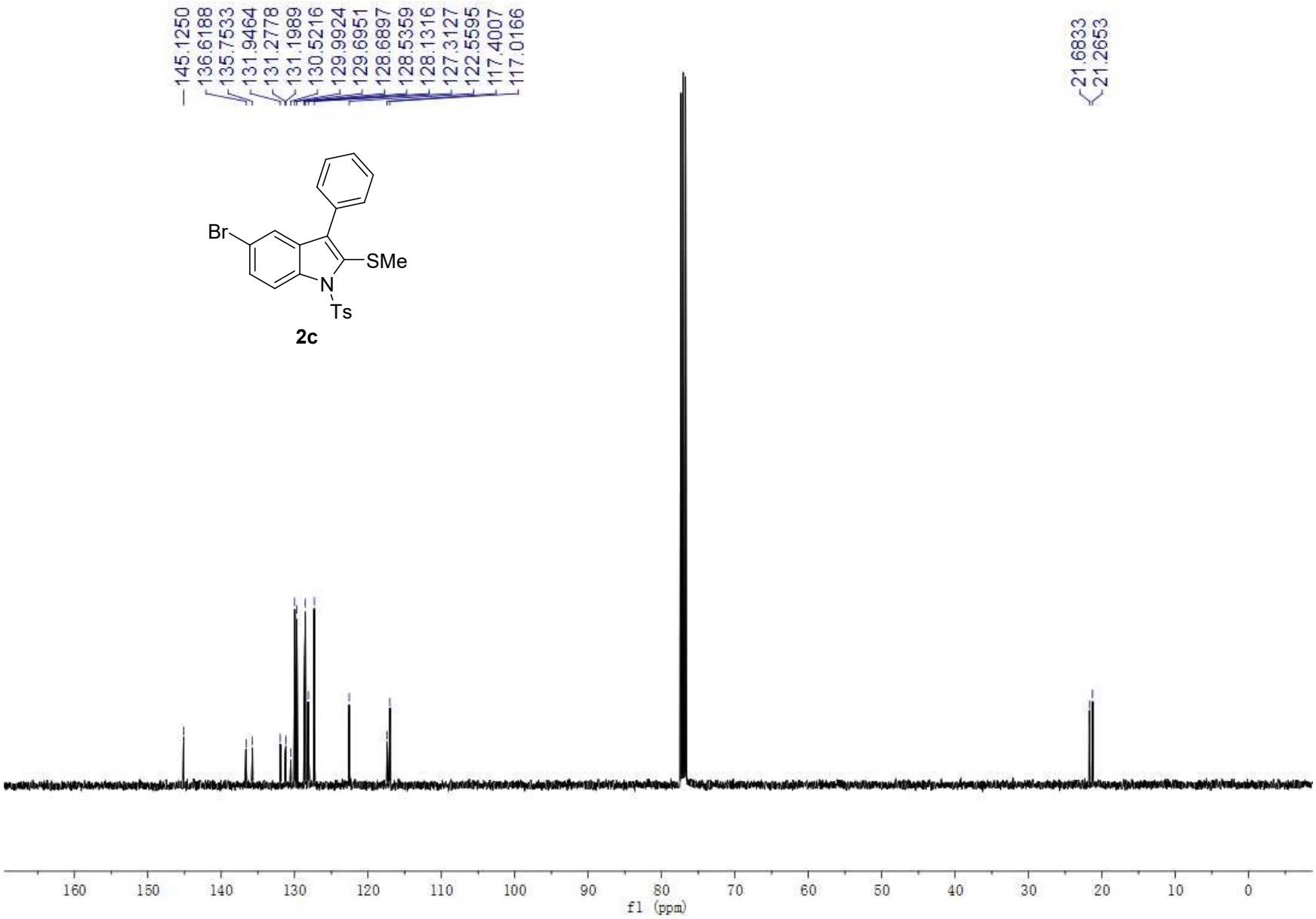
7.4743
7.4700
7.4668
7.4549
7.4512
7.4492
7.4461
7.4285
7.4241
7.4207
7.4063
7.4041
7.3999
7.3877
7.3839
7.3803
7.2379
2.3714
2.2901
Br
SMe
N
Ts
2c
1.00
2.00
0.98
3.05
3.06
2.00
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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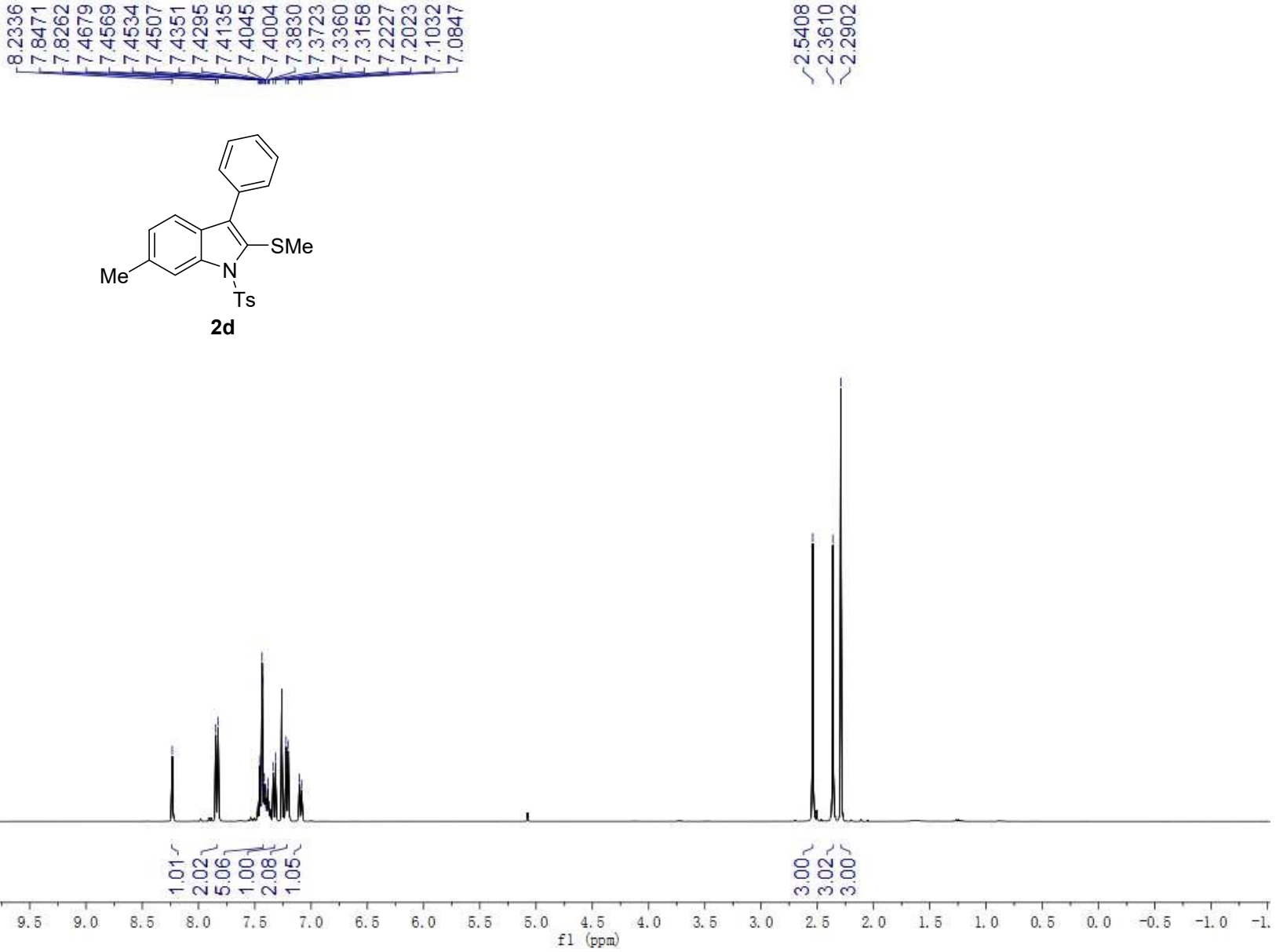
128.5359
128.1316
127.3127
122.5595
117.4007
117.0166
21.6833
21.2653
Br
SMe
N
Ts
2c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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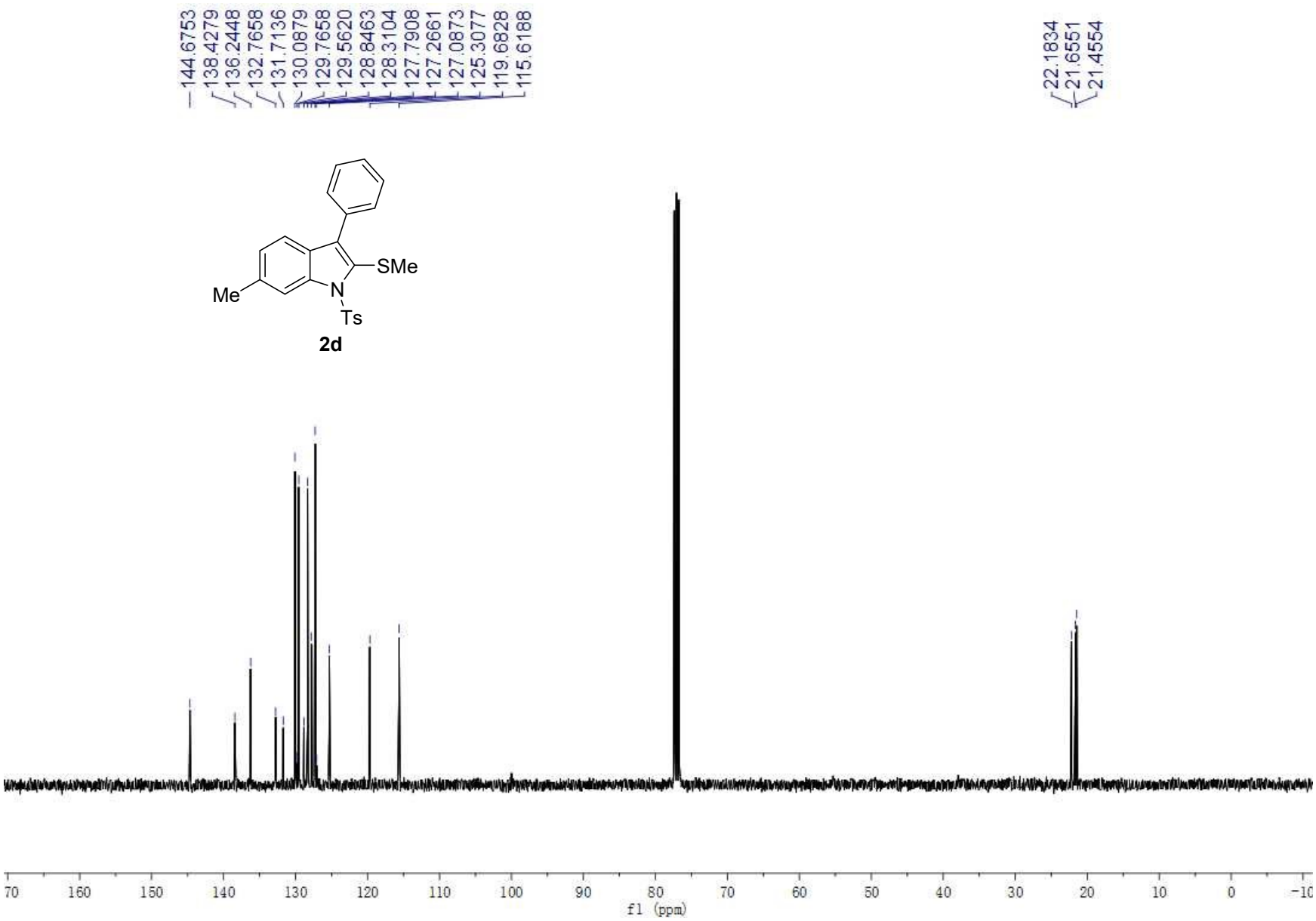
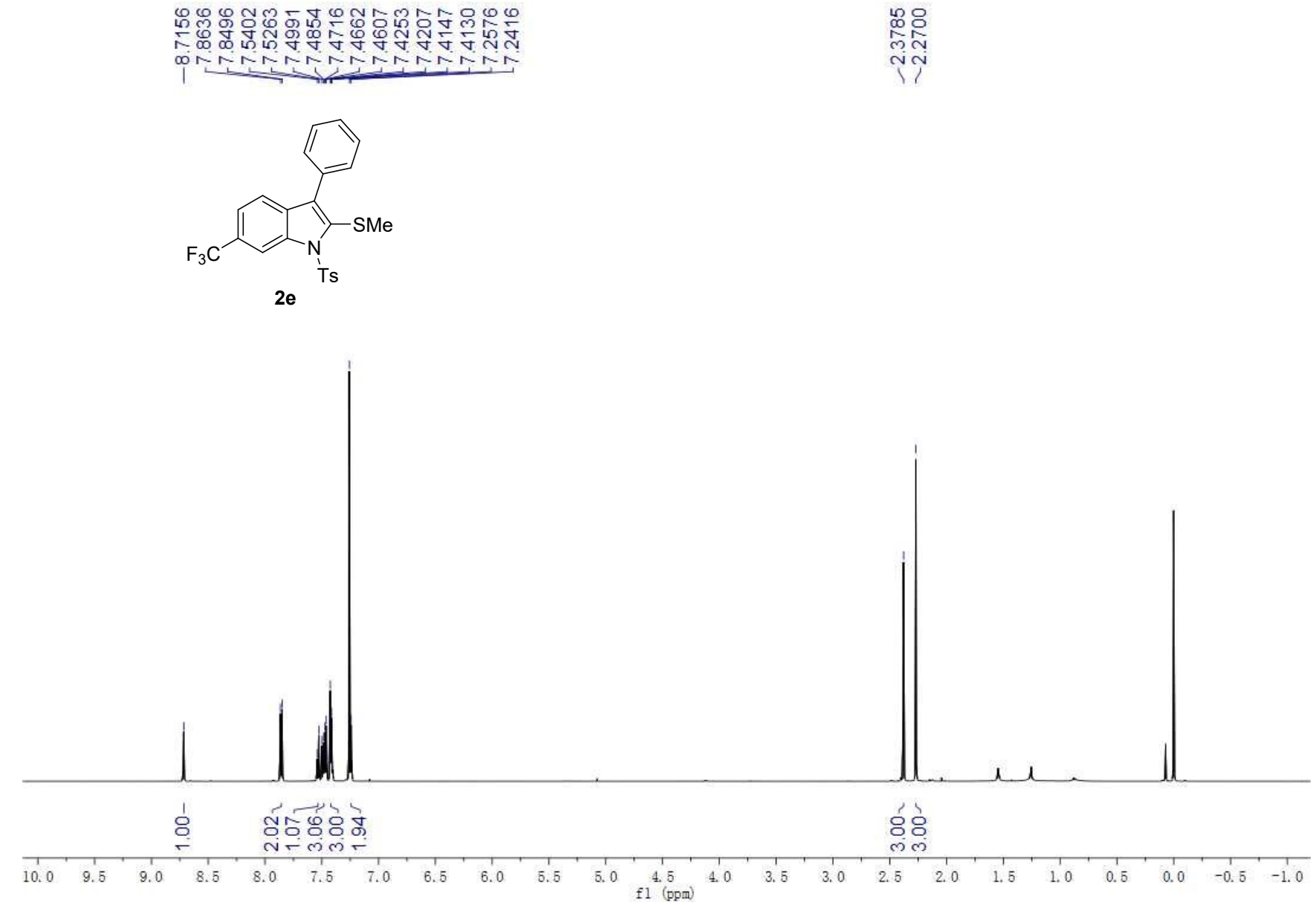
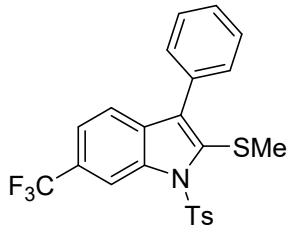
7.4045
7.4004
7.3830
7.3723
7.3360
7.3158
7.2227
7.2023
7.1032
7.0847
2.5408
2.3610
2.2902
SMe
Me
N
Ts
1.01
2.02
5.06
1.00
2.08
1.05
3.00
3.02
3.00
f1 (ppm)

2d

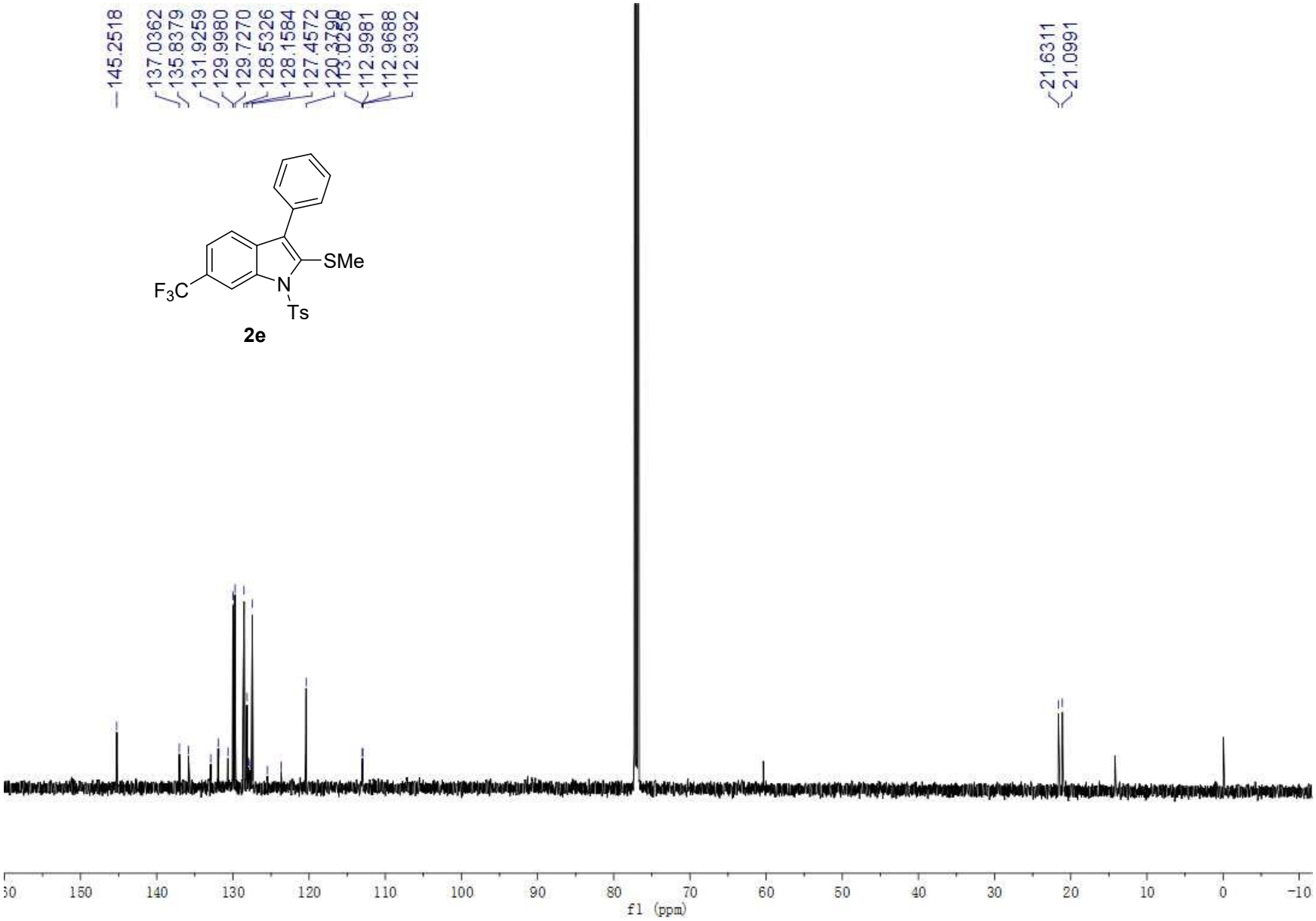

144.6753
138.4279
136.2448
132.7658
131.7136
130.0879
129.7658
129.5620
128.8463
128.3104
127.7908
127.2661
127.0873
125.3077
119.6828
115.6188
22.1834
21.6551
21.4554
SMe
Me
N
Ts
2d
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.7156
7.8636
7.8496
7.5402
7.5263
7.4991
7.4854
7.4716
7.4662
7.4607
7.4253
7.4207
7.4147
7.4130
7.2576
7.2416
2.3785
2.2700
SMe
F3C
N
Ts
2e
1.00
2.02
1.07
3.06
3.00
1.94
3.00
3.00
10.0
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)


SMe
F3C
N
Ts

2e

-61.0948
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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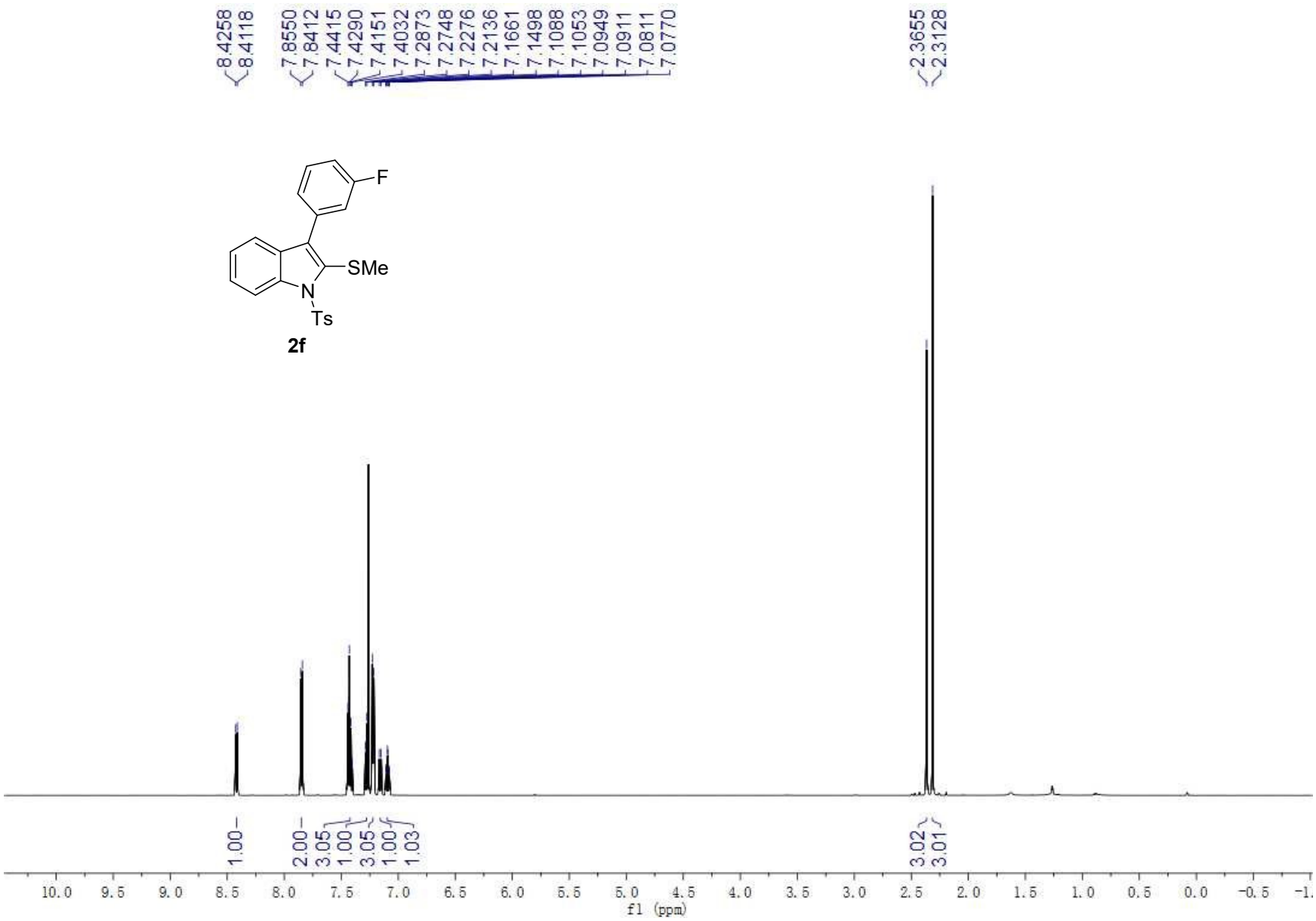
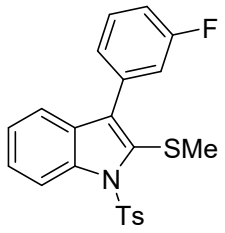
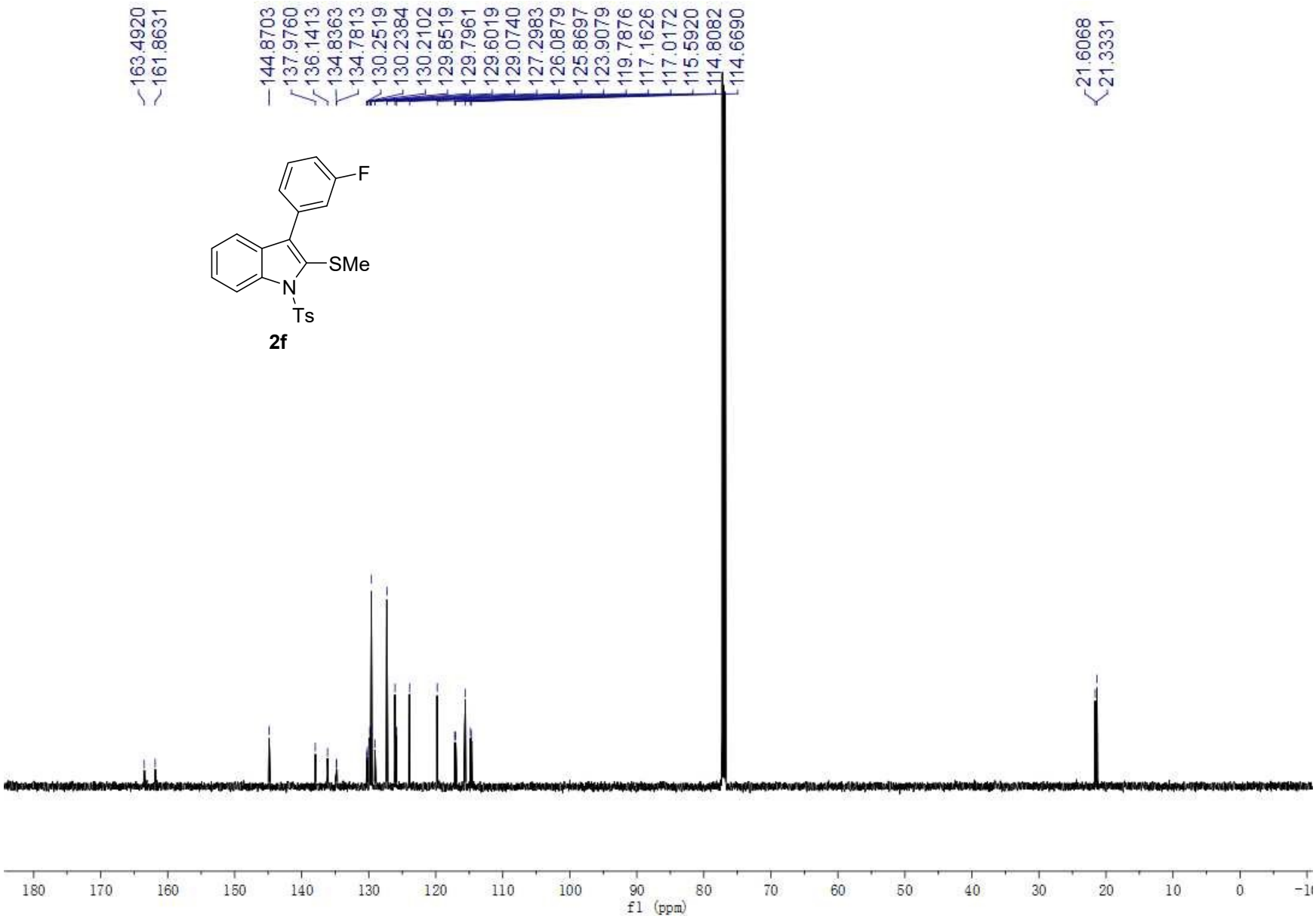
137.0362
135.8379
131.9259
129.9980
129.7270
128.5326
128.1584
127.4572
120.3790
113.0258
112.9981
112.9688
112.9392
21.6311
21.0991
SMe
F3C
N
Ts
2e
f1 (ppm)


8.4258
8.4118
7.8550
7.8412
7.4415
7.4290
7.4151
7.4032
7.2873
7.2748
7.2276
7.2136
7.1661
7.1498
7.1088
7.1053
7.0949
7.0911
7.0811
7.0770
2.3655
2.3128
F
SMe
N
Ts
2f
1.00
2.00
3.05
1.00
3.05
1.00
1.03
3.02
3.01
10.0
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
f1 (ppm)


F
SMe
N
Ts

2f

-112.9931
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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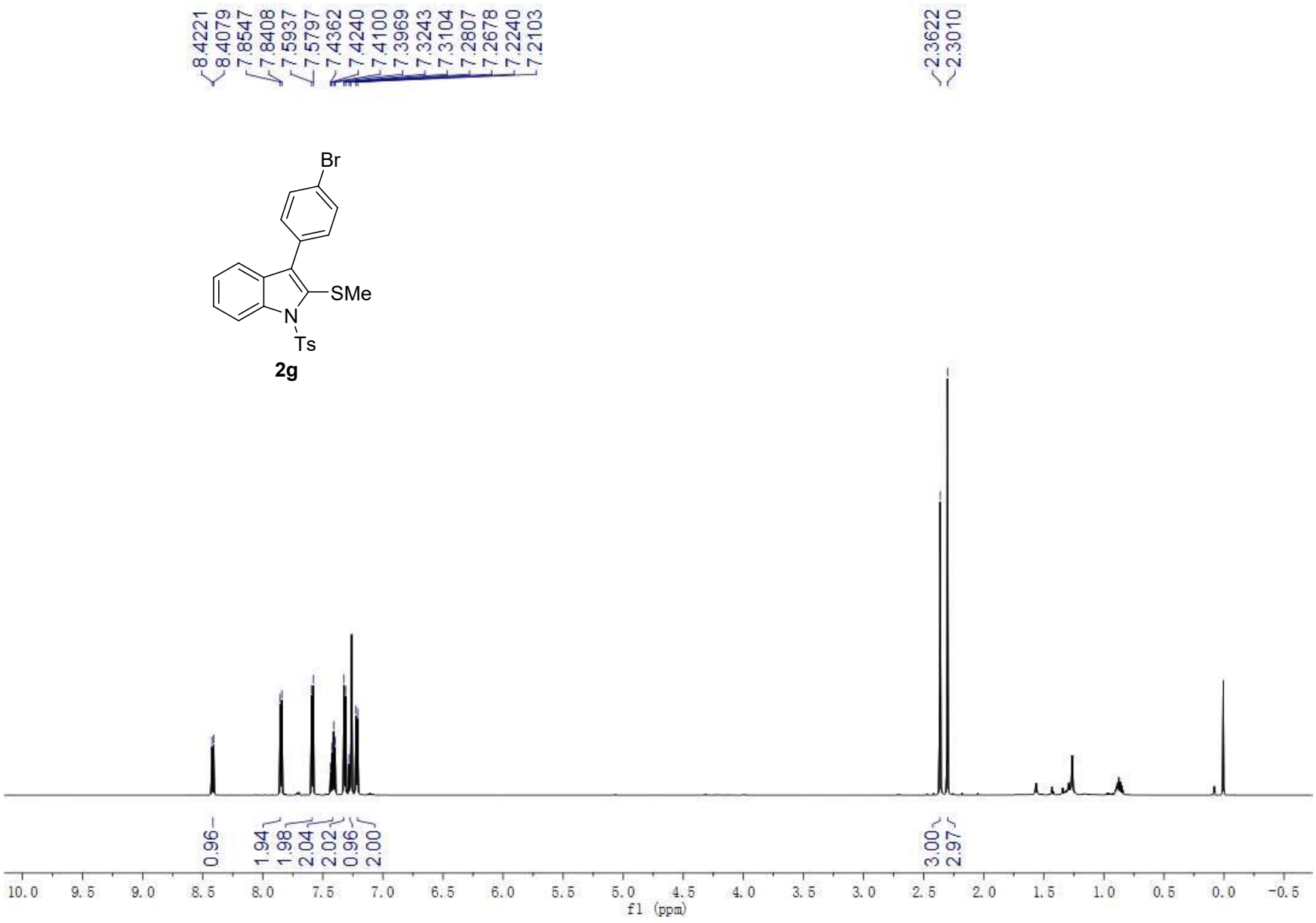
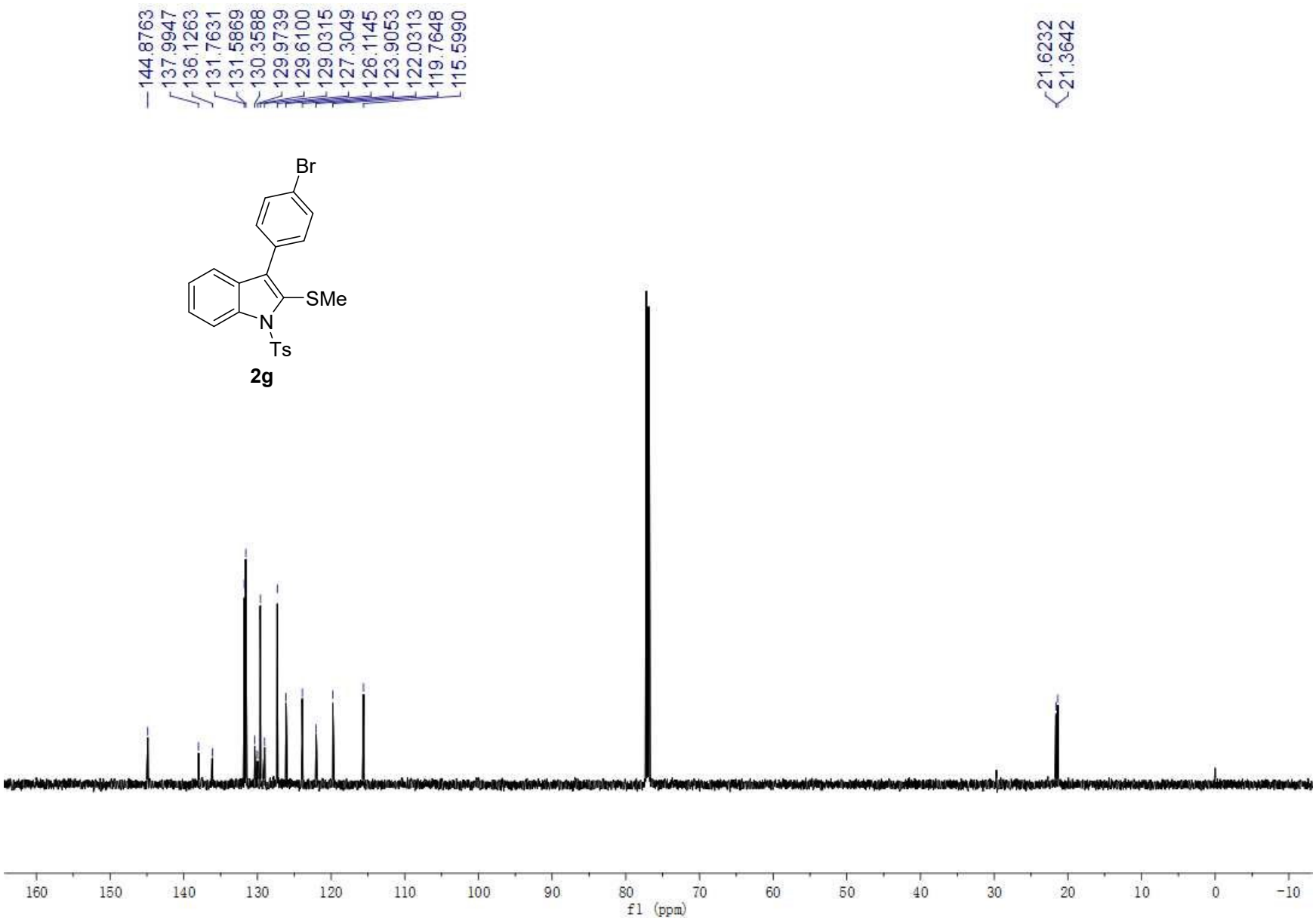
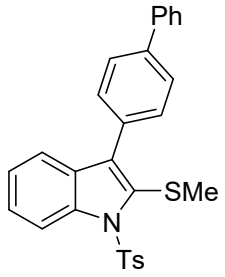
161.8631
144.8703
137.9760
136.1413
134.8363
134.7813
130.2519
130.2384
130.2102
129.8519
129.7961
129.6019
129.0740
127.2983
126.0879
125.8697
123.9079
119.7876
117.1626
117.0172
115.5920
114.8082
114.6690
21.6068
21.3331
F
SMe
N
Ts
2f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

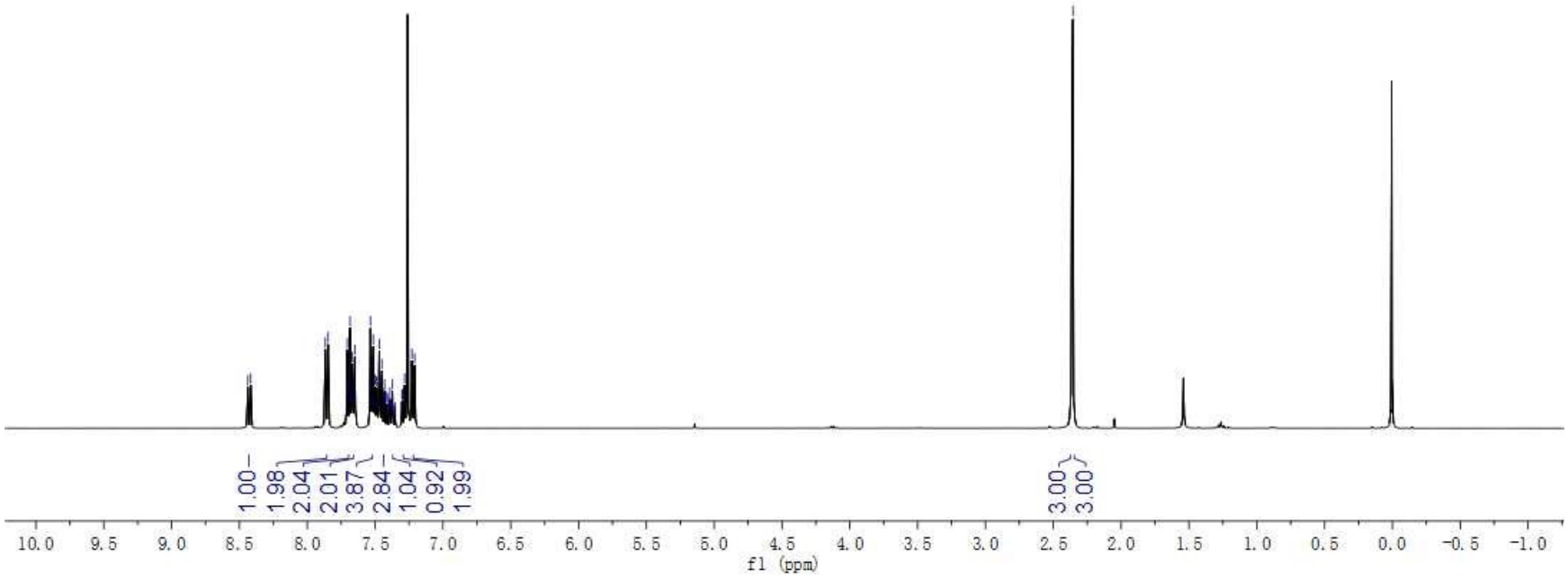

8.4221
8.4079
7.8547
7.8408
7.5937
7.5797
7.4362
7.4240
7.4100
7.3969
7.3243
7.3104
7.2807
7.2678
7.2240
7.2103
2.3622
2.3010
Br
SMe
N
Ts
2g
0.96
1.94
1.98
2.04
2.02
0.96
2.00
3.00
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

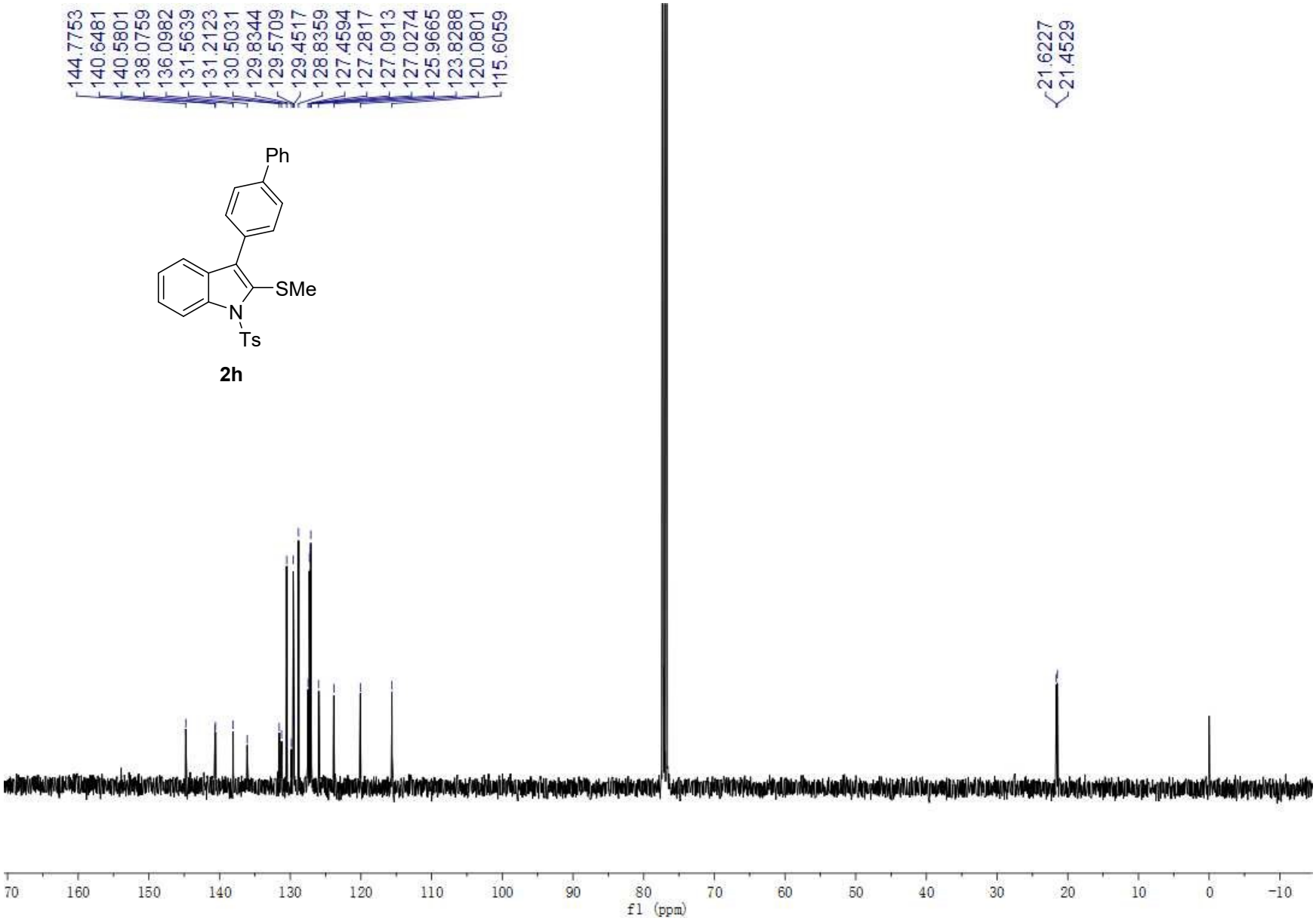

144.8763
137.9947
136.1263
131.7631
131.5869
130.3588
129.9739
129.6100
129.0315
127.3049
126.1145
123.9053
122.0313
119.7648
115.5990
21.6232
21.3642
Br
SMe
N
Ts
2g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.4380
8.4167
7.8671
7.8461
7.7055
7.7009
7.6892
7.6846
7.6801
7.6709
7.6675
7.6497
7.5344
7.5297
7.5184
7.5136
7.5009
7.4875
7.4692
7.4497
7.4331
7.4300
7.4119
7.3900
7.3717
7.3020
7.3001
7.2822
7.2287
2.3637
2.3554


Ph
SMe
N
Ts

2h


1.00
1.98
2.04
2.01
3.87
2.84
1.04
0.92
1.99
3.00
3.00
10.0
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)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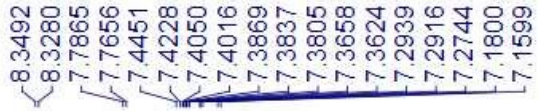
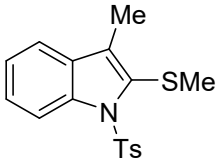
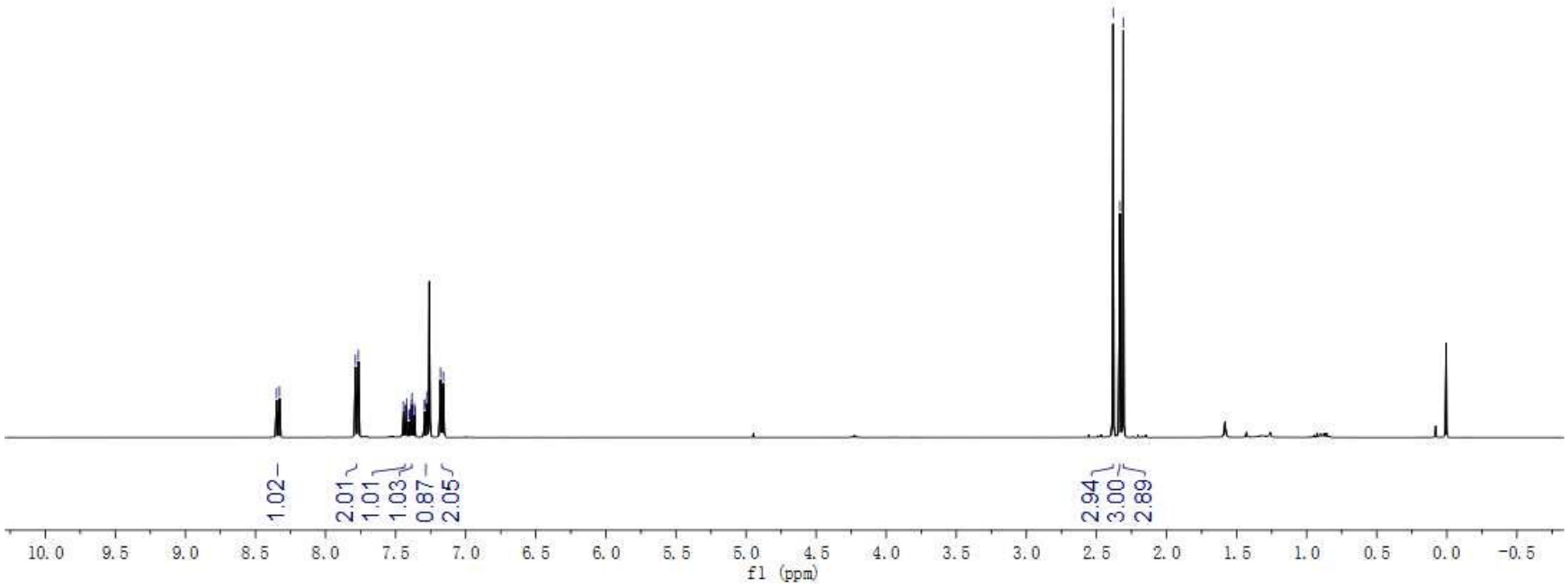
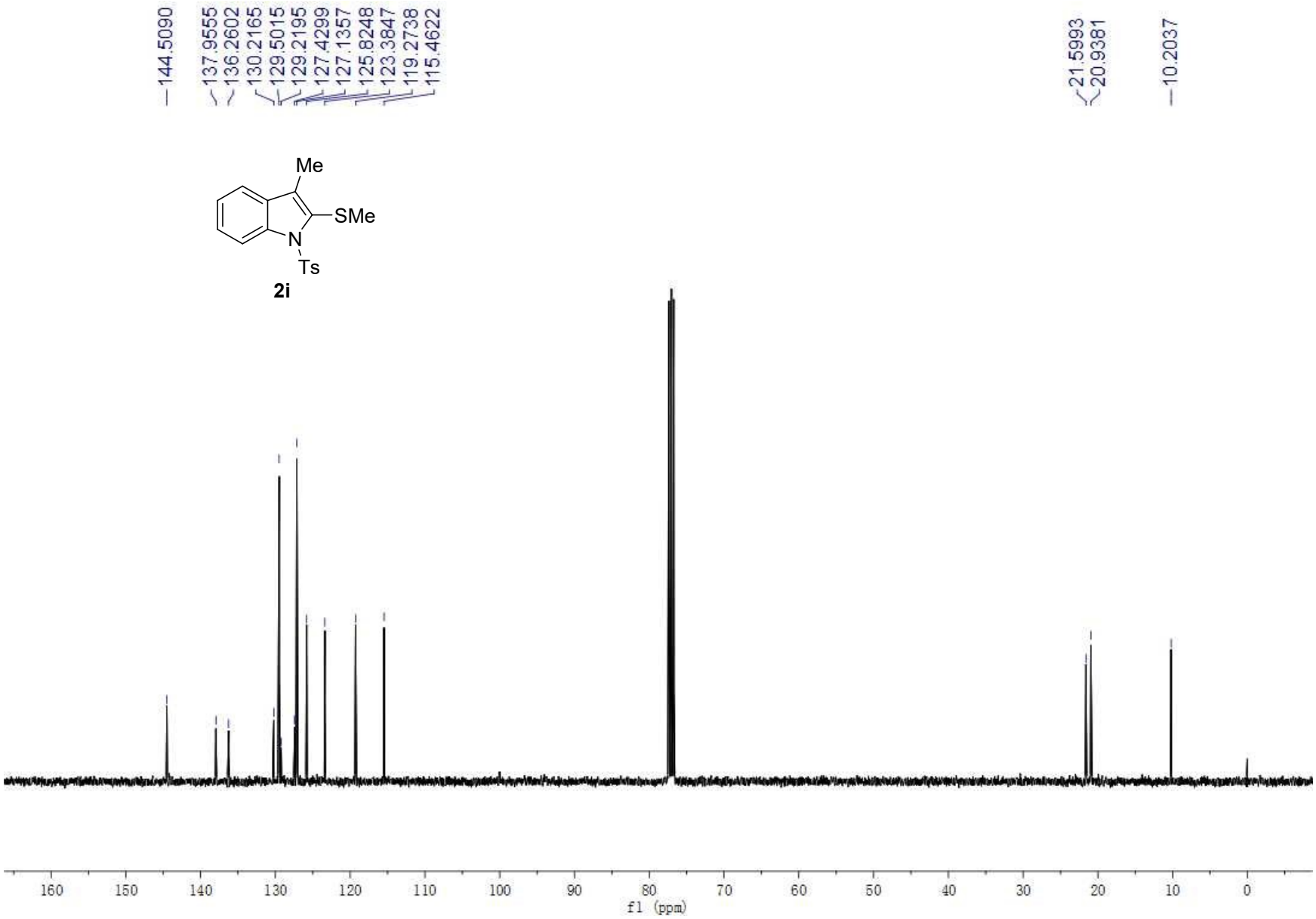
140.6481
140.5801
138.0759
136.0982
131.5639
131.2123
130.5031
129.8344
129.5709
129.4517
128.8359
127.4594
127.2817
127.0913
127.0274
125.9665
123.8288
120.0801
115.6059
21.6227
21.4529
Ph
SMe
N
Ts
2h
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.3492
8.3280
7.7865
7.7656
7.4451
7.4228
7.4050
7.4016
7.3869
7.3837
7.3805
7.3658
7.3624
7.2939
7.2916
7.2744
7.1800
7.1599
2.3810
2.3328
2.3085


Me
SMe
N
Ts

2i


1.02
2.01
1.01
1.03
0.87
2.05
2.94
3.00
2.89
10.0
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
f1 (ppm)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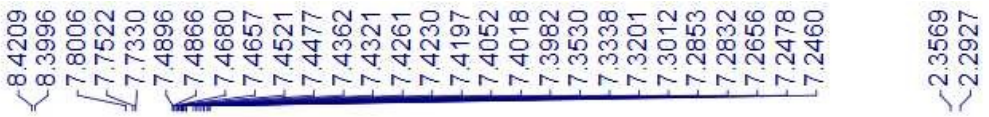
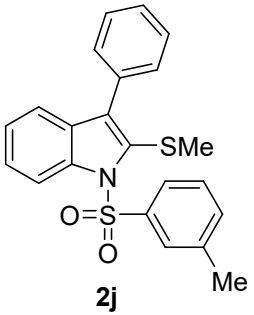
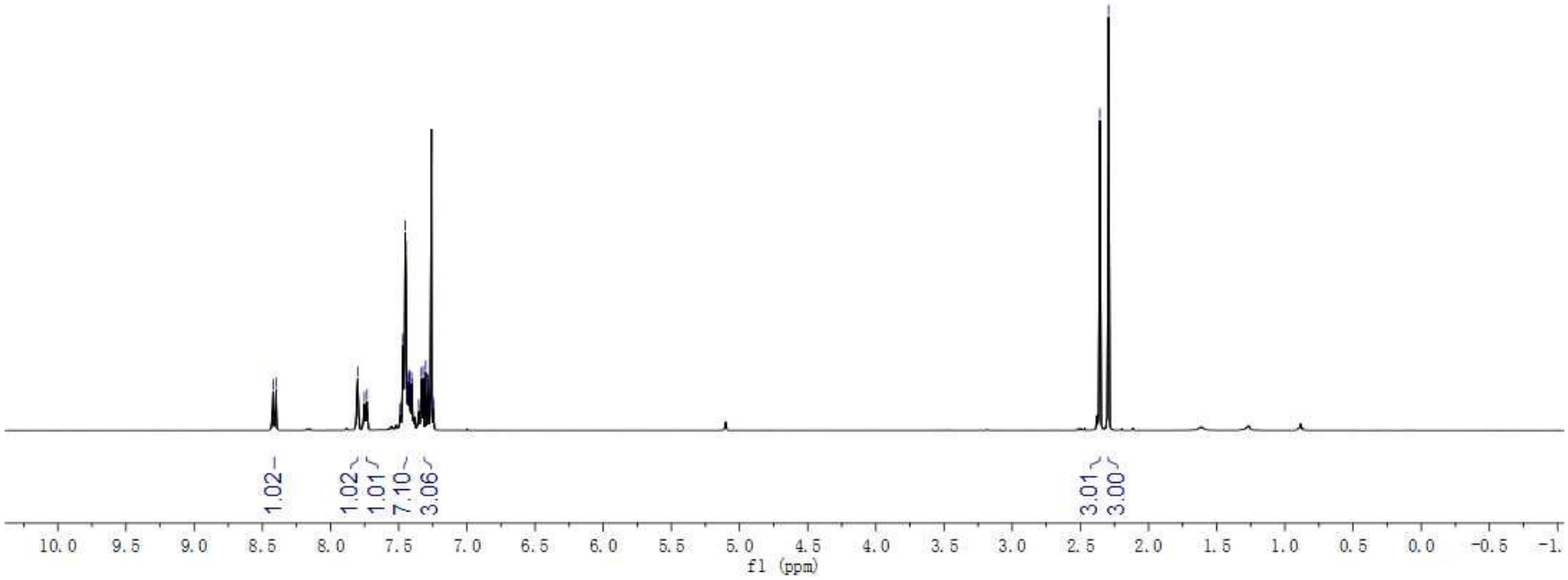
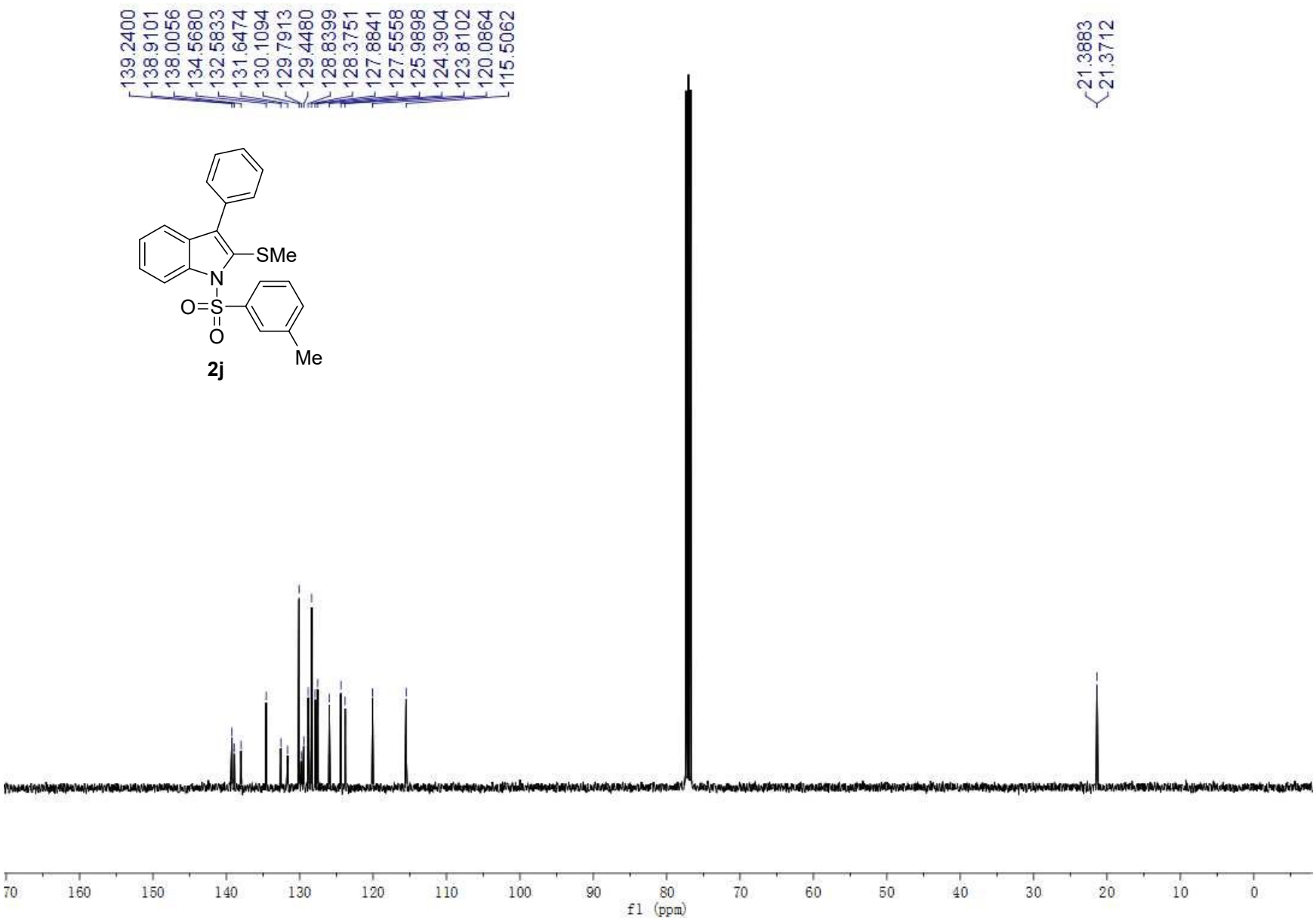
136.2602
130.2165
129.5015
129.2195
127.4299
127.1357
125.8248
123.3847
119.2738
115.4622
21.5993
20.9381
10.2037
Me
SMe
N
Ts
2i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.4209
8.3996
7.8006
7.7522
7.7330
7.4896
7.4866
7.4680
7.4657
7.4521
7.4477
7.4362
7.4321
7.4261
7.4230
7.4197
7.4052
7.4018
7.3982
7.3530
7.3338
7.3201
7.3012
7.2853
7.2832
7.2656
7.2478
7.2460
2.3569
2.2927


SMe
N
O=S=O
Me

2j


1.02
1.02
1.01
7.10
3.06
3.01
3.00
10.0
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.
f1 (ppm)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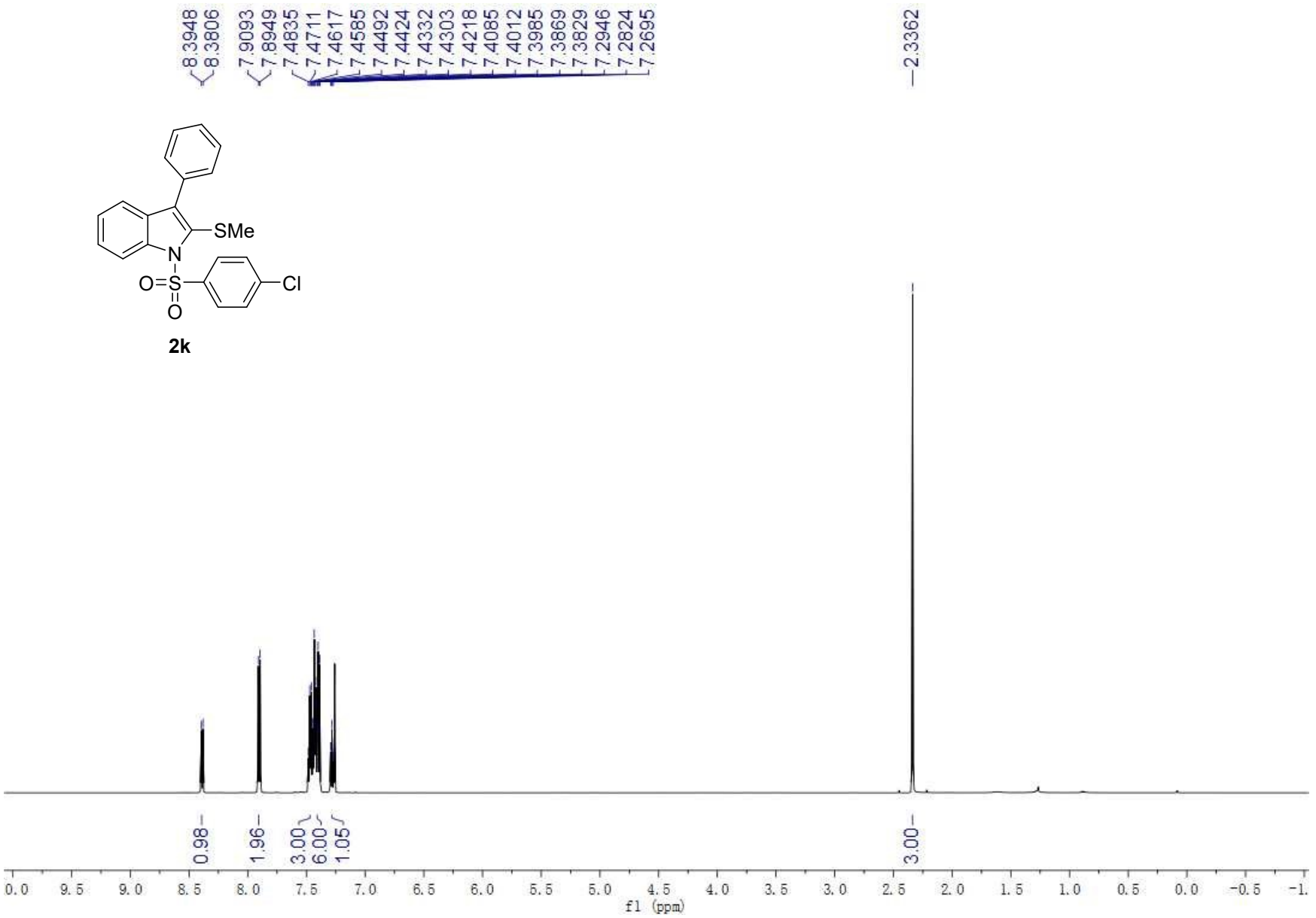
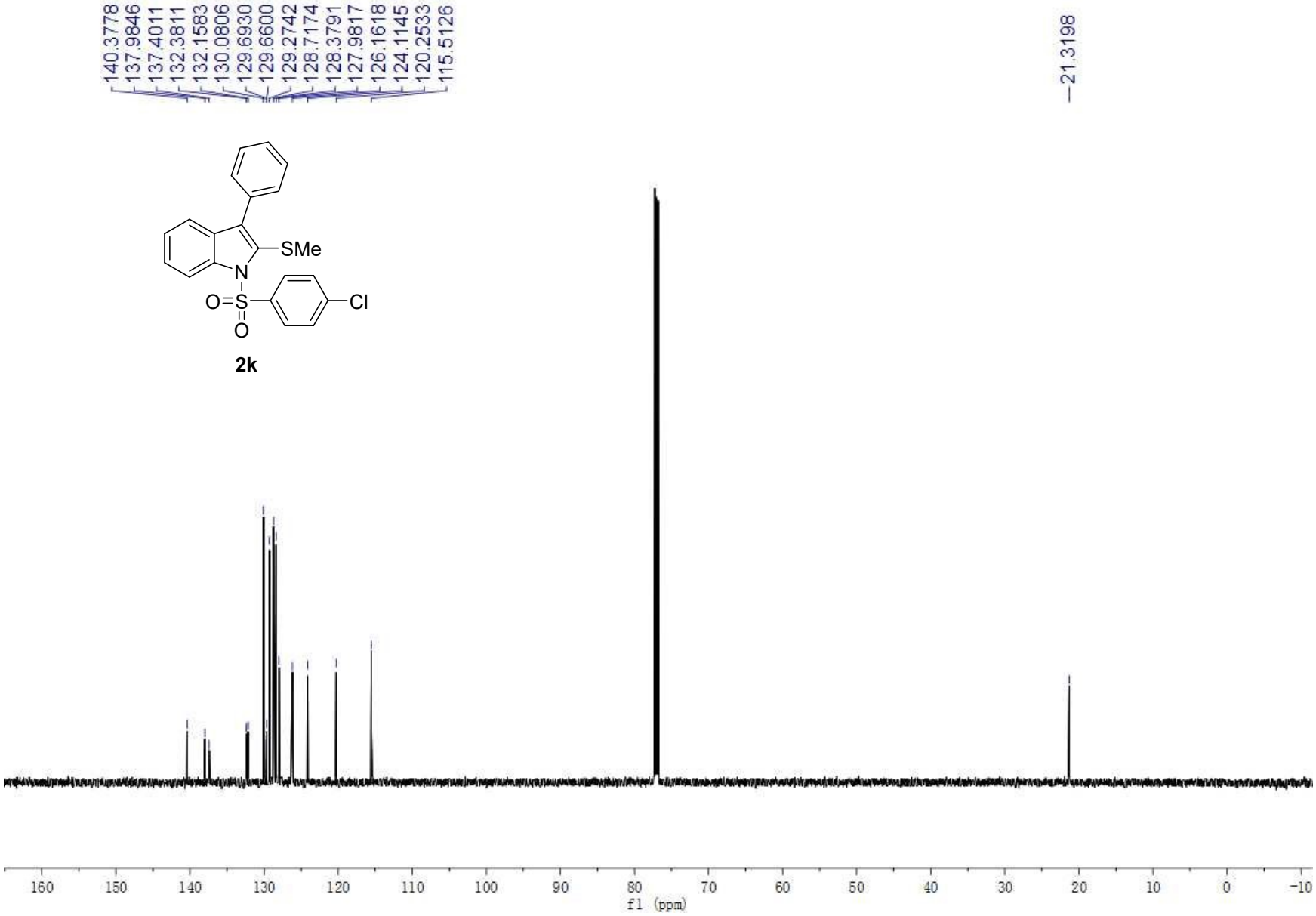
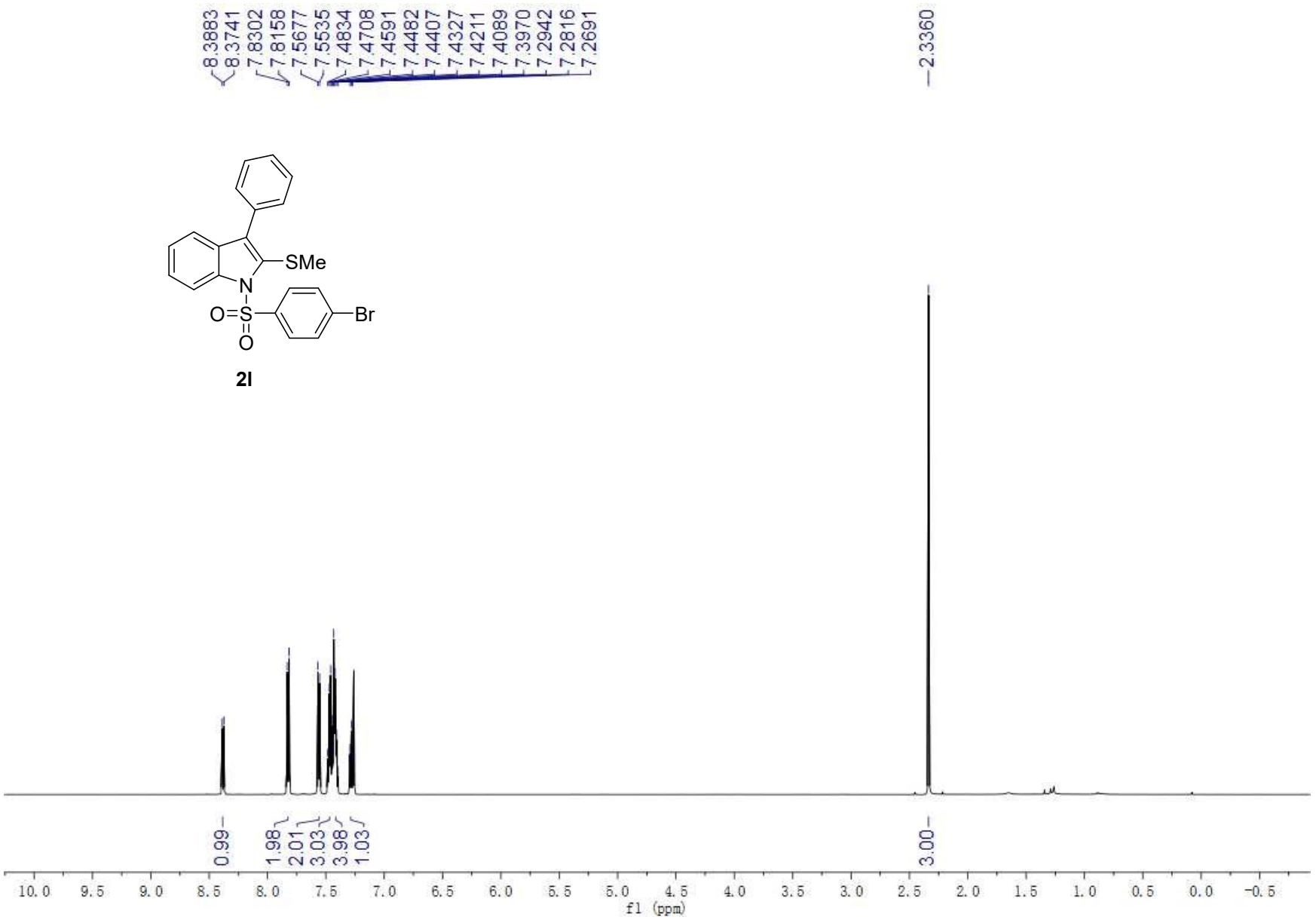
138.9101
138.0056
134.5680
132.5833
131.6474
130.1094
129.7913
129.4480
128.8399
128.3751
127.8841
127.5558
125.9898
124.3904
123.8102
120.0864
115.5062
21.3883
21.3712
SMe
N
O=S
O
Me
2j
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

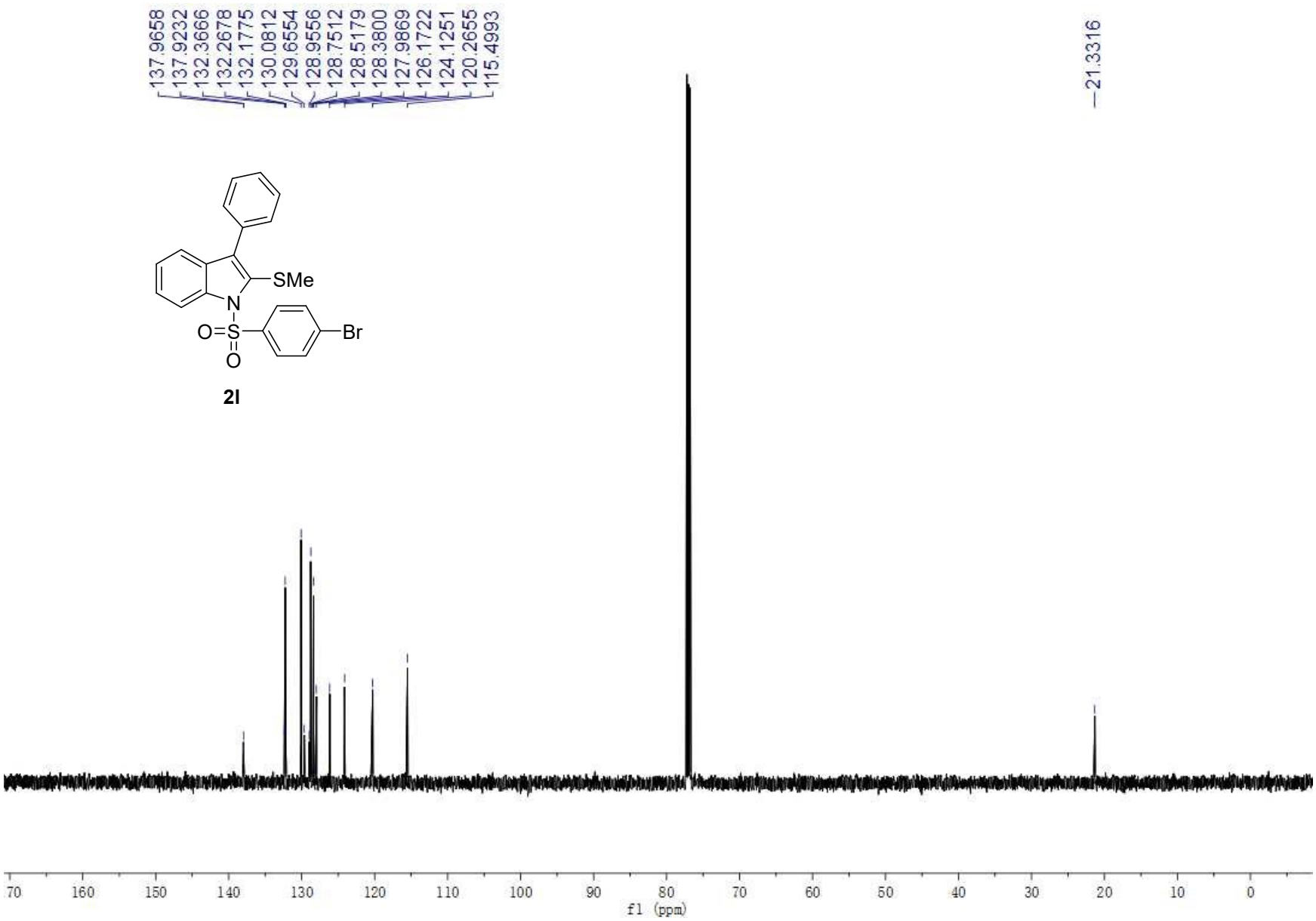

8.3948
8.3806
7.9093
7.8949
7.4835
7.4711
7.4617
7.4585
7.4492
7.4424
7.4332
7.4303
7.4218
7.4085
7.4012
7.3985
7.3869
7.3829
7.2946
7.2824
7.2695
2.3362
SMe
N
O=S
O
Cl
0.98
1.96
3.00
6.00
1.05
3.00
f1 (ppm)

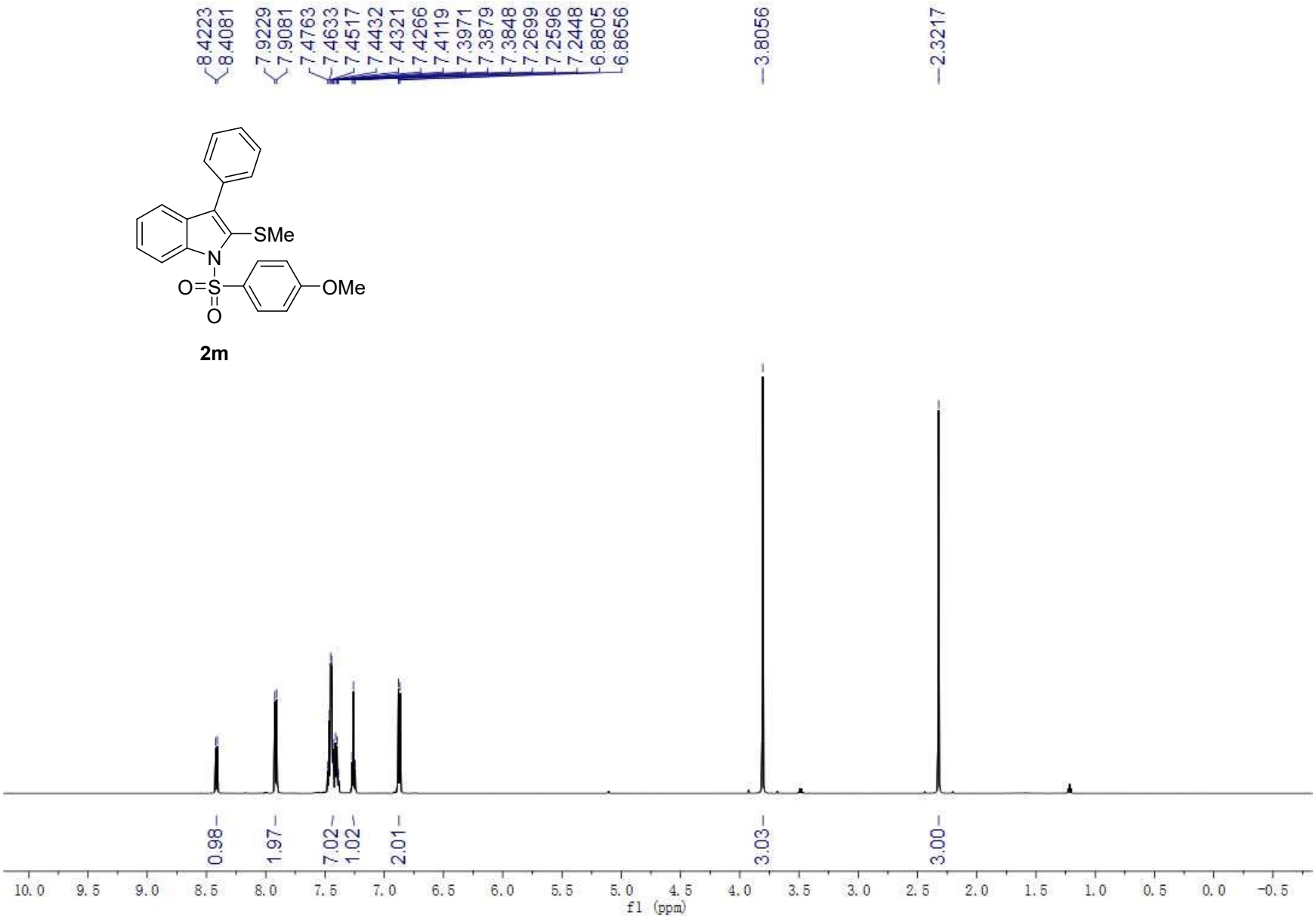
2k


140.3778
137.9846
137.4011
132.3811
132.1583
130.0806
129.6930
129.6600
129.2742
128.7174
128.3791
127.9817
126.1618
124.1145
120.2533
115.5126
21.3198
SMe
N
O=S
O
Cl
2k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

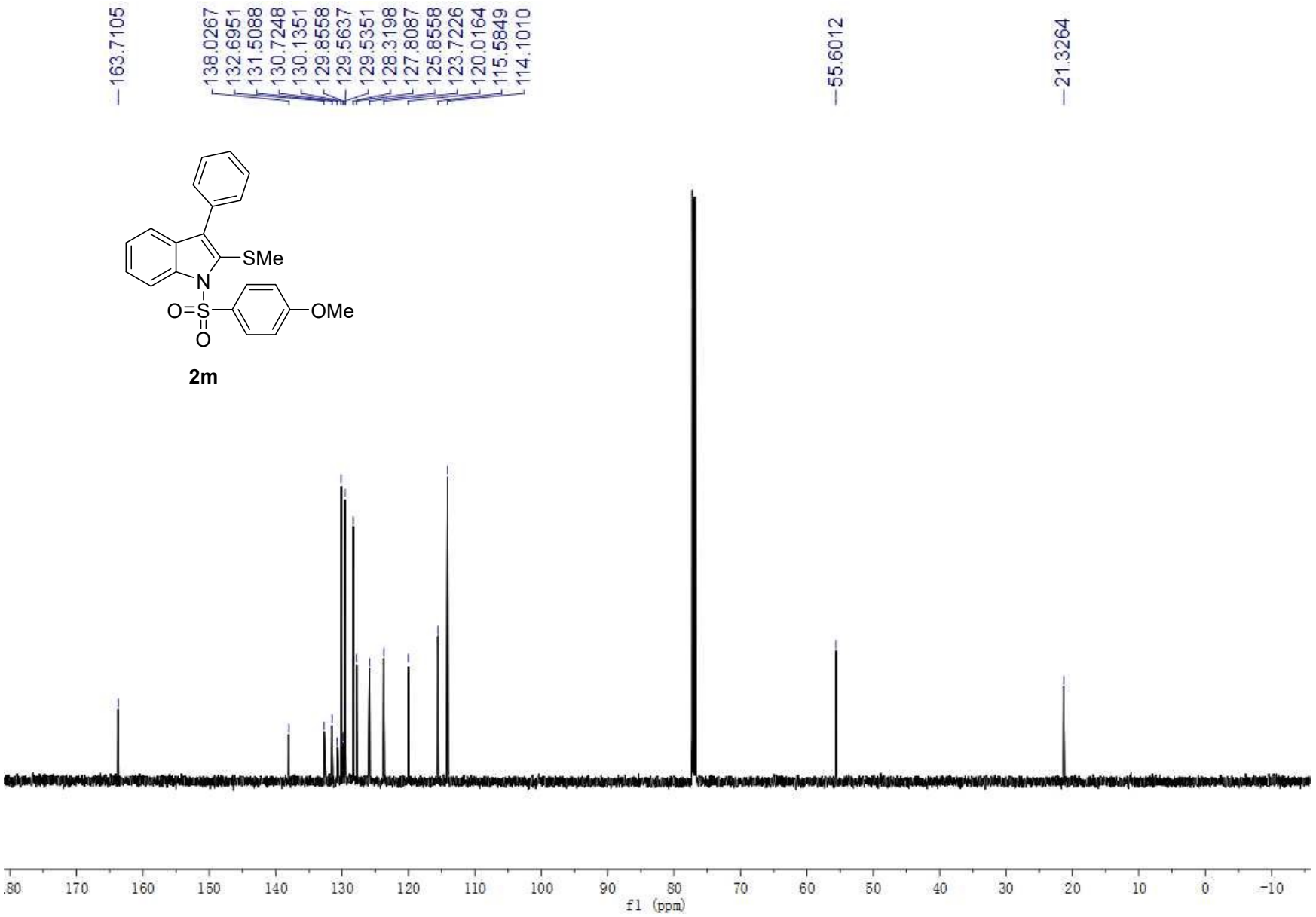

8.3883
8.3741
7.8302
7.8158
7.5677
7.5535
7.4834
7.4708
7.4591
7.4482
7.4407
7.4327
7.4211
7.4089
7.3970
7.2942
7.2816
7.2691
2.3360
SMe
N
O=S
O
Br
0.99
1.98
2.01
3.03
3.98
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

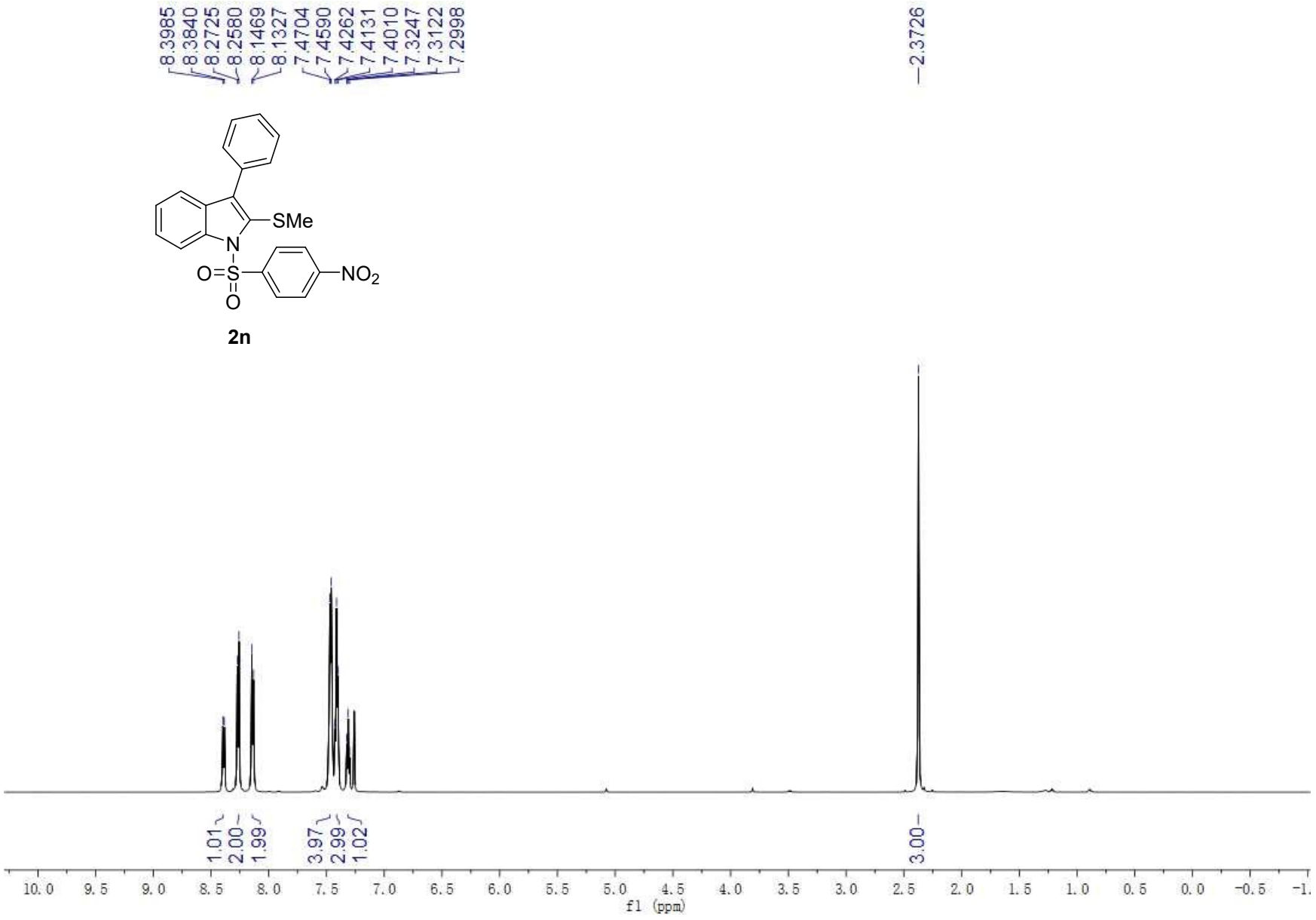
2l


137.9658
137.9232
132.3666
132.2678
132.1775
130.0812
129.6554
128.9556
128.7512
128.5179
128.3800
127.9869
126.1722
124.1251
120.2655
115.4993
21.3316
SMe
N
O=S
O
Br
2l
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.4223
8.4081
7.9229
7.9081
7.4763
7.4633
7.4517
7.4432
7.4321
7.4266
7.4119
7.3971
7.3879
7.3848
7.2699
7.2596
7.2448
6.8805
6.8656
3.8056
2.3217
SMe
N
O=S=O
OMe
0.98
1.97
7.02
1.02
2.01
3.03
3.00
10.0 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
f1 (ppm)

2m


163.7105
138.0267
132.6951
131.5088
130.7248
130.1351
129.8558
129.5637
129.5351
128.3198
127.8087
125.8558
123.7226
120.0164
115.5849
114.1010
55.6012
21.3264
SMe
N
O=S=O
OMe
2m
f1 (ppm)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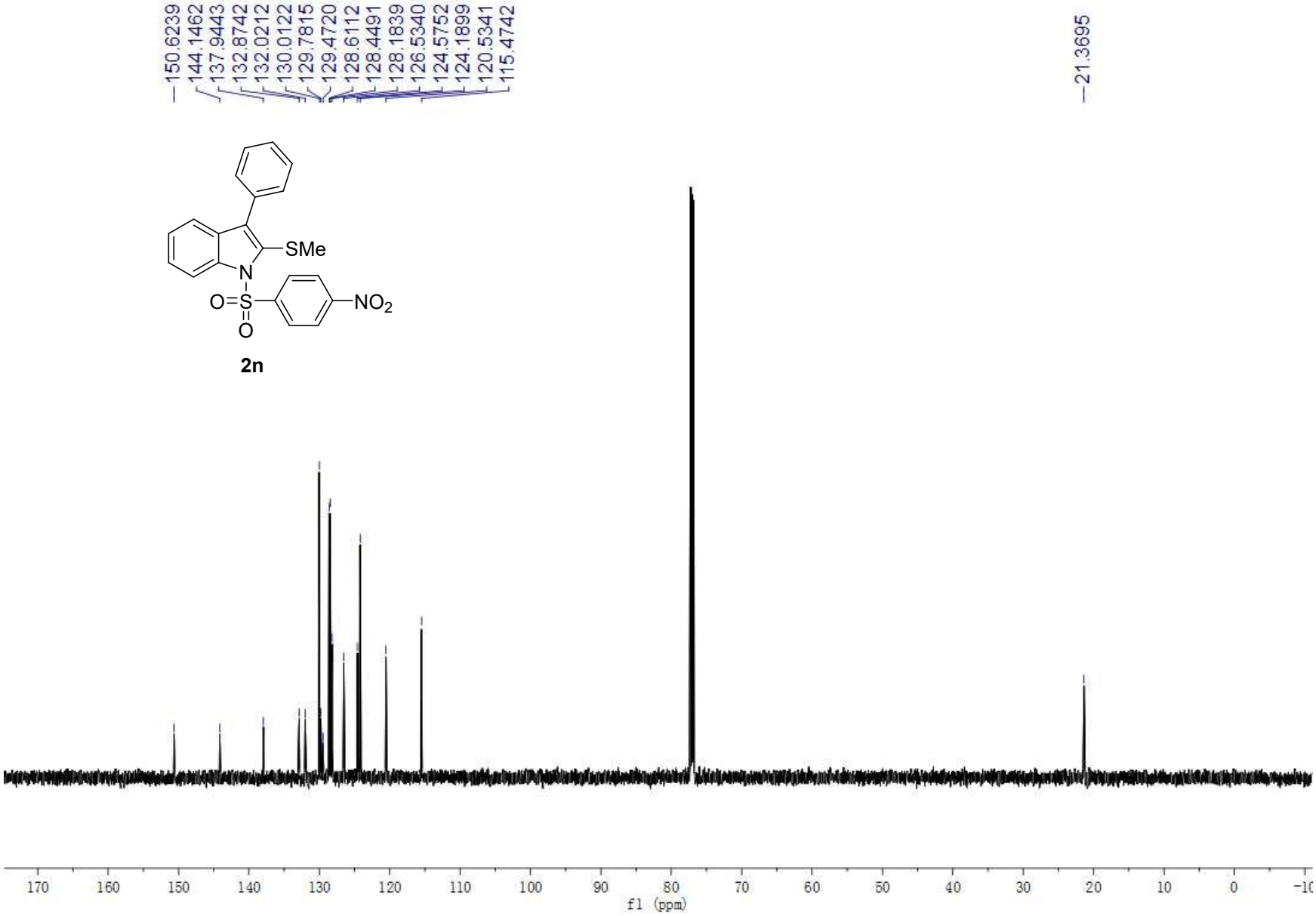
8.2725
8.2580
8.1469
8.1327
7.4704
7.4590
7.4262
7.4131
7.4010
7.3247
7.3122
7.2998
2.3726
SMe
N
O=S=O
NO2
1.01
2.00
1.99
3.97
2.99
1.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

2n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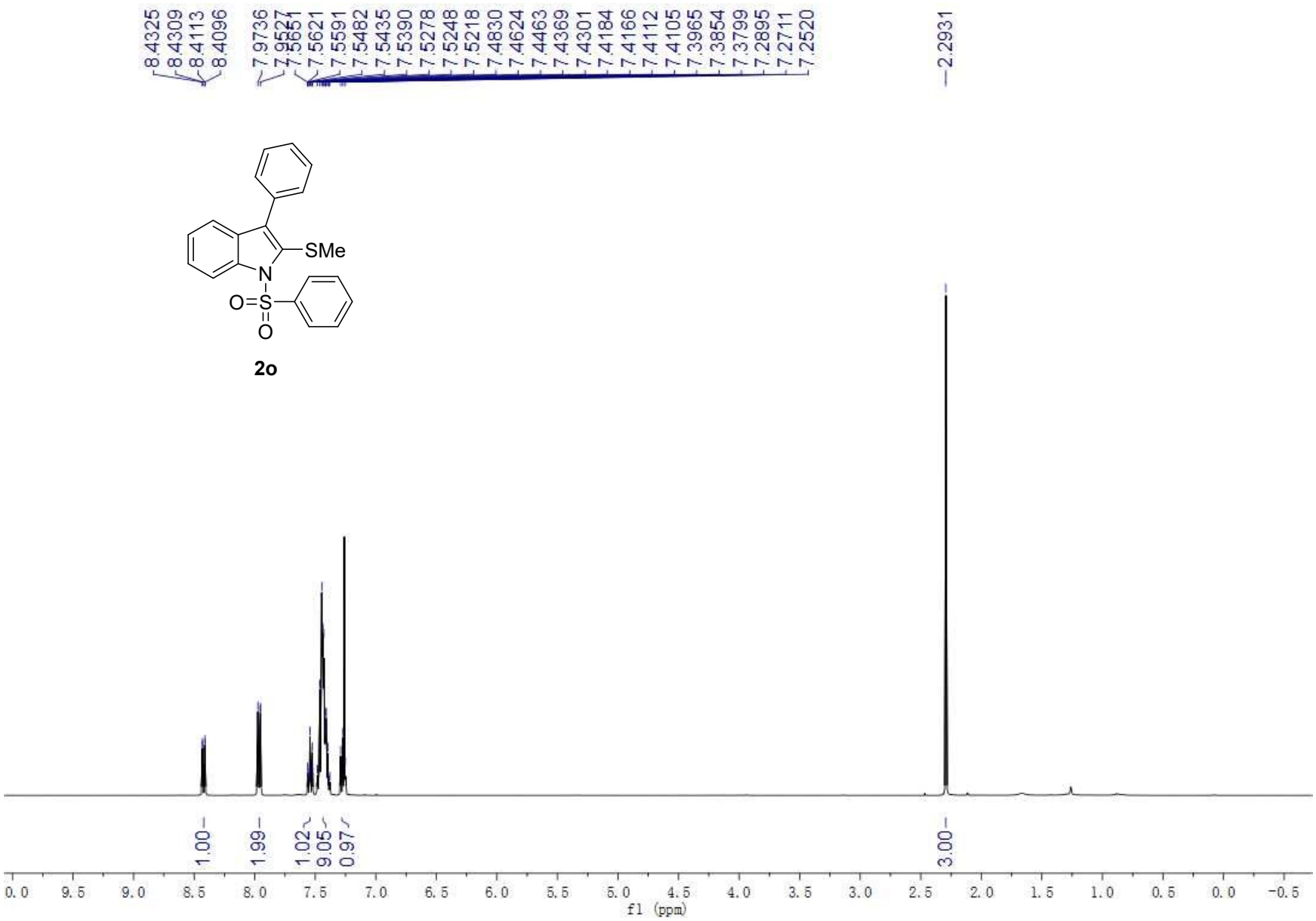
132.8742
132.0212
130.0122
129.7815
129.4720
128.6112
128.4491
128.1839
126.5340
124.5752
124.1899
120.5341
115.4742
21.3695
SMe
N
O=S=O
NO2
2n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.4113
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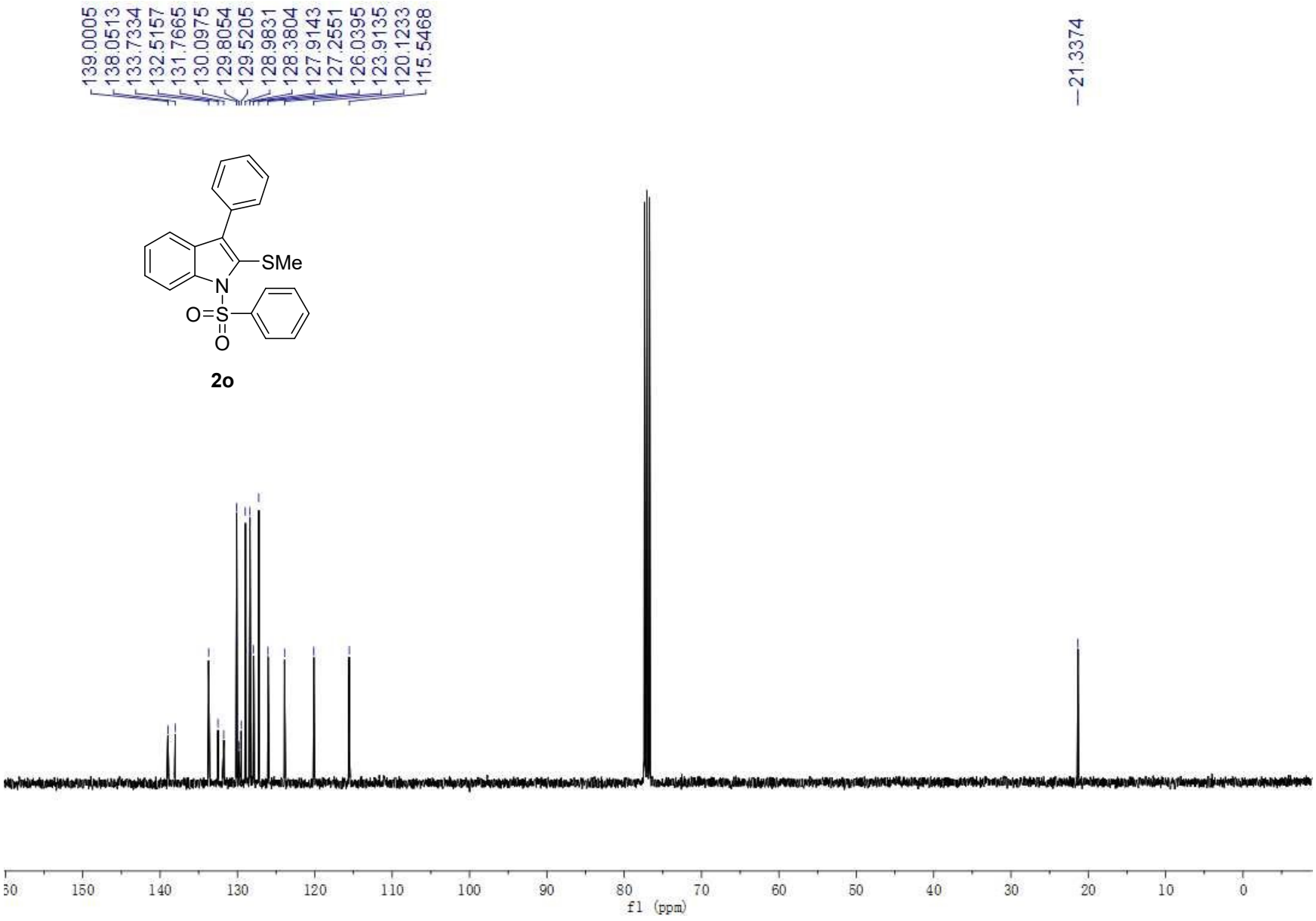
7.9351
7.5621
7.5591
7.5482
7.5435
7.5390
7.5278
7.5248
7.5218
7.4830
7.4624
7.4463
7.4369
7.4301
7.4184
7.4166
7.4112
7.4105
7.3965
7.3854
7.3799
7.2895
7.2711
7.2520
2.2931
SMe
N
O=S
O
1.00
1.99
1.02
9.05
0.97
3.00
f1 (ppm)

2o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127.9143
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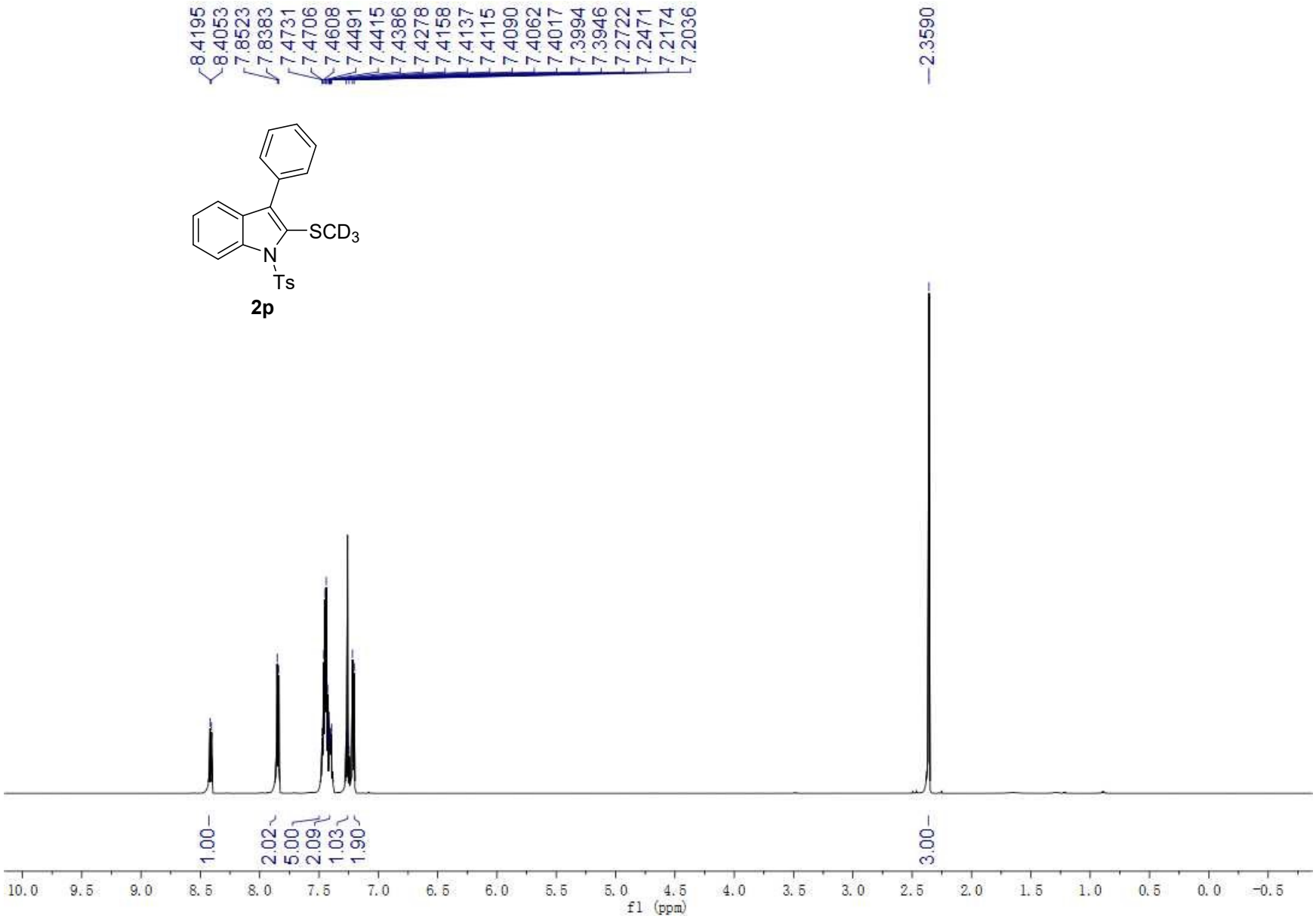
126.0395
123.9135
120.1233
115.5468
21.3374
SMe
N
O=S
O
2o
f1 (ppm)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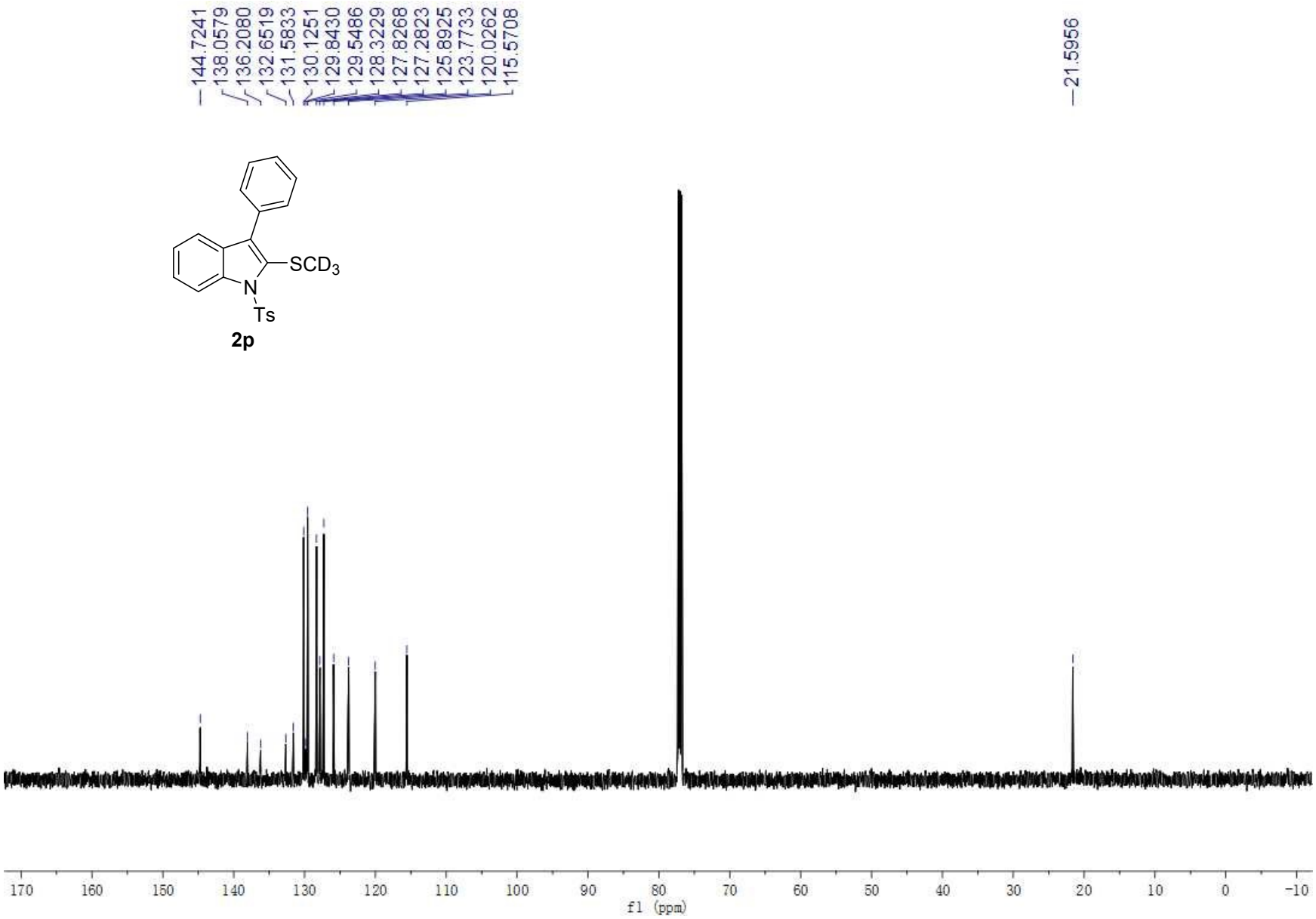
8.4053
7.8523
7.8383
7.4731
7.4706
7.4608
7.4491
7.4415
7.4386
7.4278
7.4158
7.4137
7.4115
7.4090
7.4062
7.4017
7.3994
7.3946
7.2722
7.2471
7.2174
7.2036
2.3590
SCD3
N
Ts
2p
1.00
2.02
5.00
2.09
1.03
1.90
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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136.2080
132.6519
131.5833
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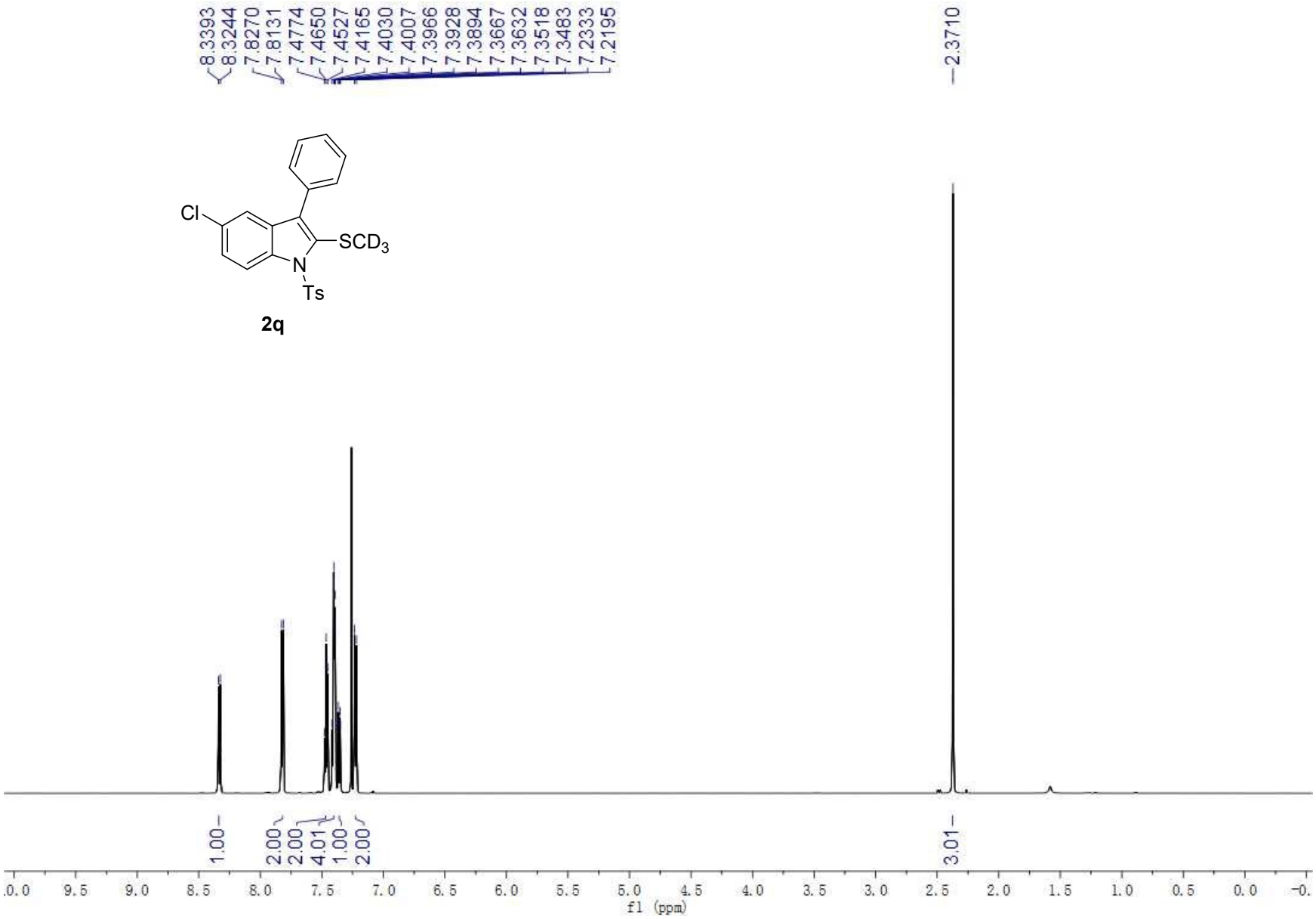
129.8430
129.5486
128.3229
127.8268
127.2823
125.8925
123.7733
120.0262
115.5708
21.5956
SCD3
N
Ts
2p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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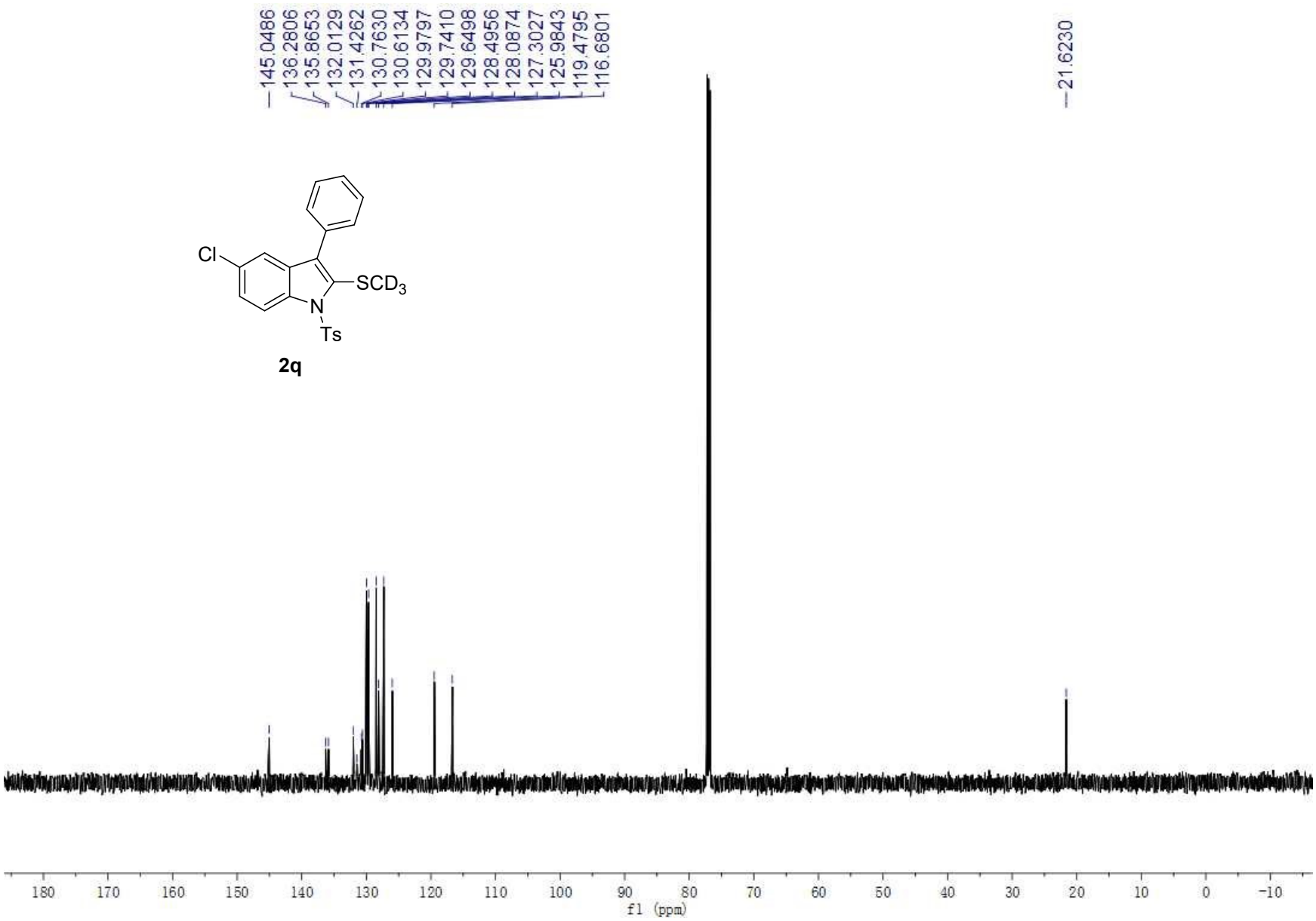
7.8270
7.8131
7.4774
7.4650
7.4527
7.4165
7.4030
7.4007
7.3966
7.3928
7.3894
7.3667
7.3632
7.3518
7.3483
7.2333
7.2195
2.3710
Cl
SCD3
N
Ts
2q
1.00
2.00
2.00
4.01
1.00
2.00
3.01
f1 (ppm)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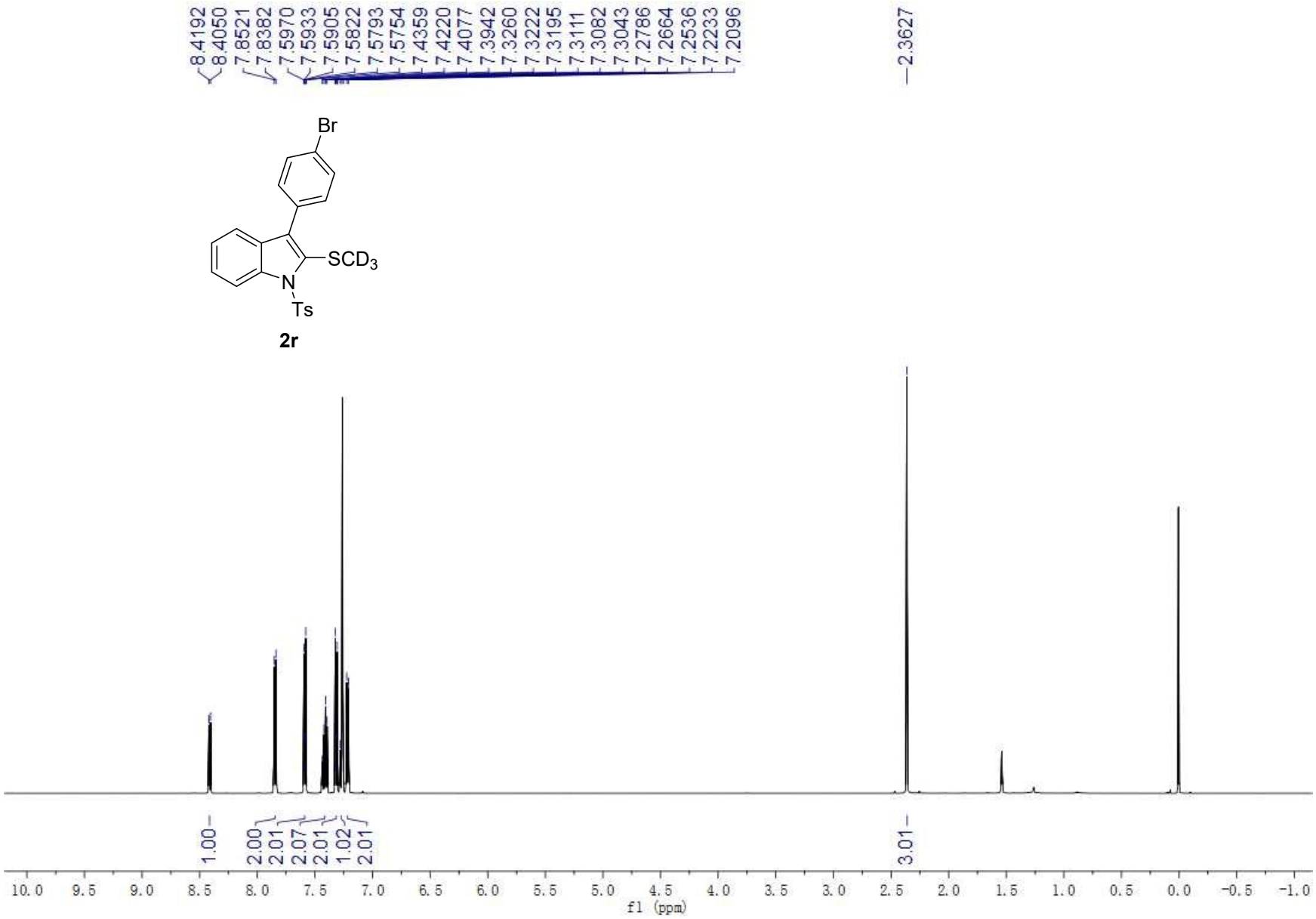
132.0129
131.4262
130.7630
130.6134
129.9797
129.7410
129.6498
128.4956
128.0874
127.3027
125.9843
119.4795
116.6801
21.6230
Cl
SCD3
N
Ts
2q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.8382
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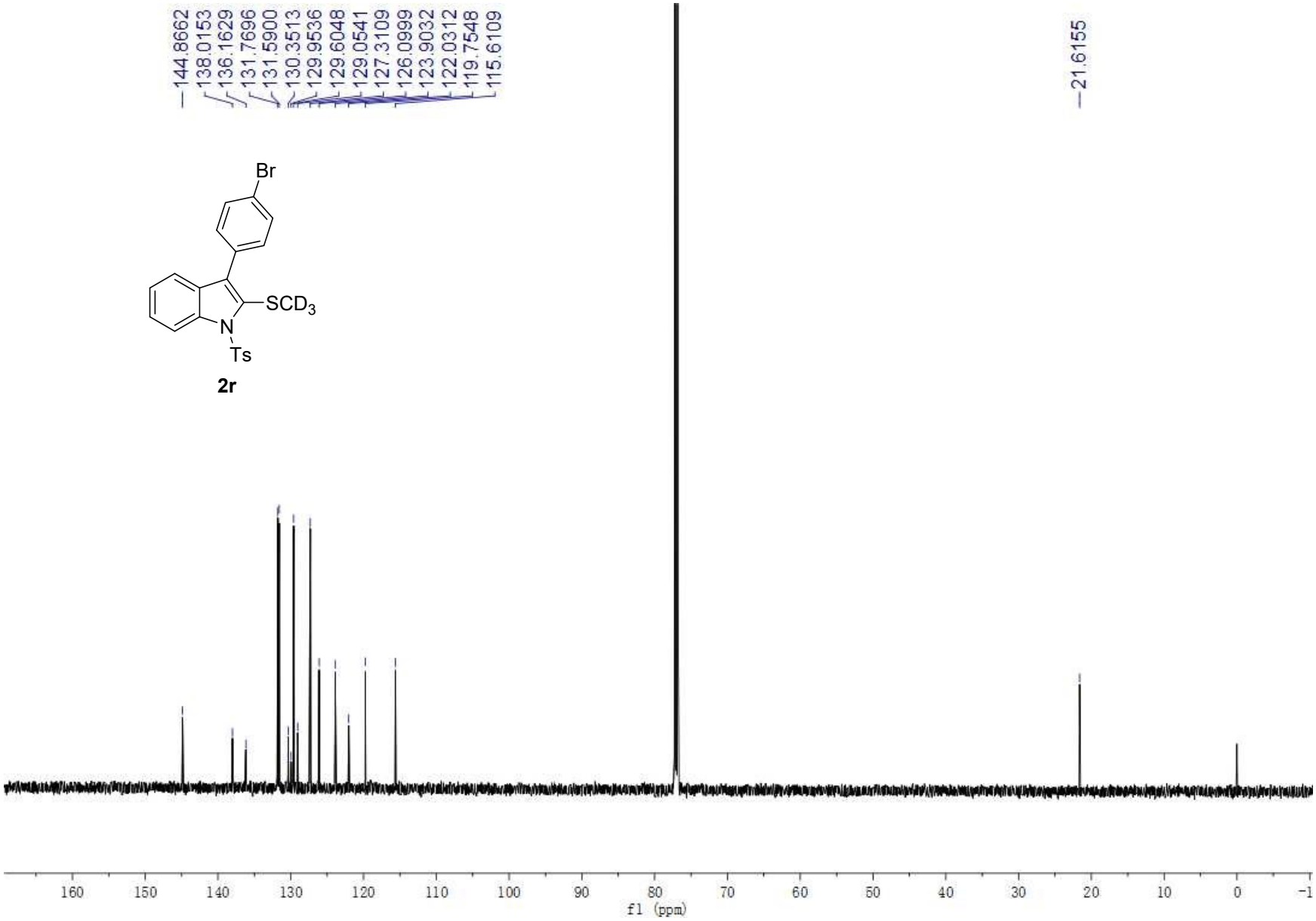
7.5933
7.5905
7.5822
7.5793
7.5754
7.4359
7.4220
7.4077
7.3942
7.3260
7.3222
7.3195
7.3111
7.3082
7.3043
7.2786
7.2664
7.2536
7.2233
7.2096
2.3627
Br
SCD3
N
Ts
2r
1.00
2.00
2.01
2.07
2.01
1.02
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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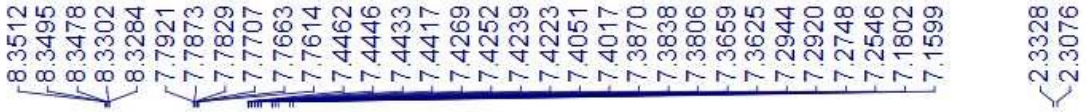
136.1629
131.7696
131.5900
130.3513
129.9536
129.6048
129.0541
127.3109
126.0999
123.9032
122.0312
119.7548
115.6109
21.6155
Br
SCD3
N
Ts
2r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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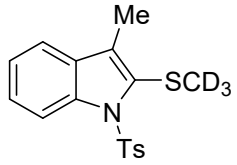
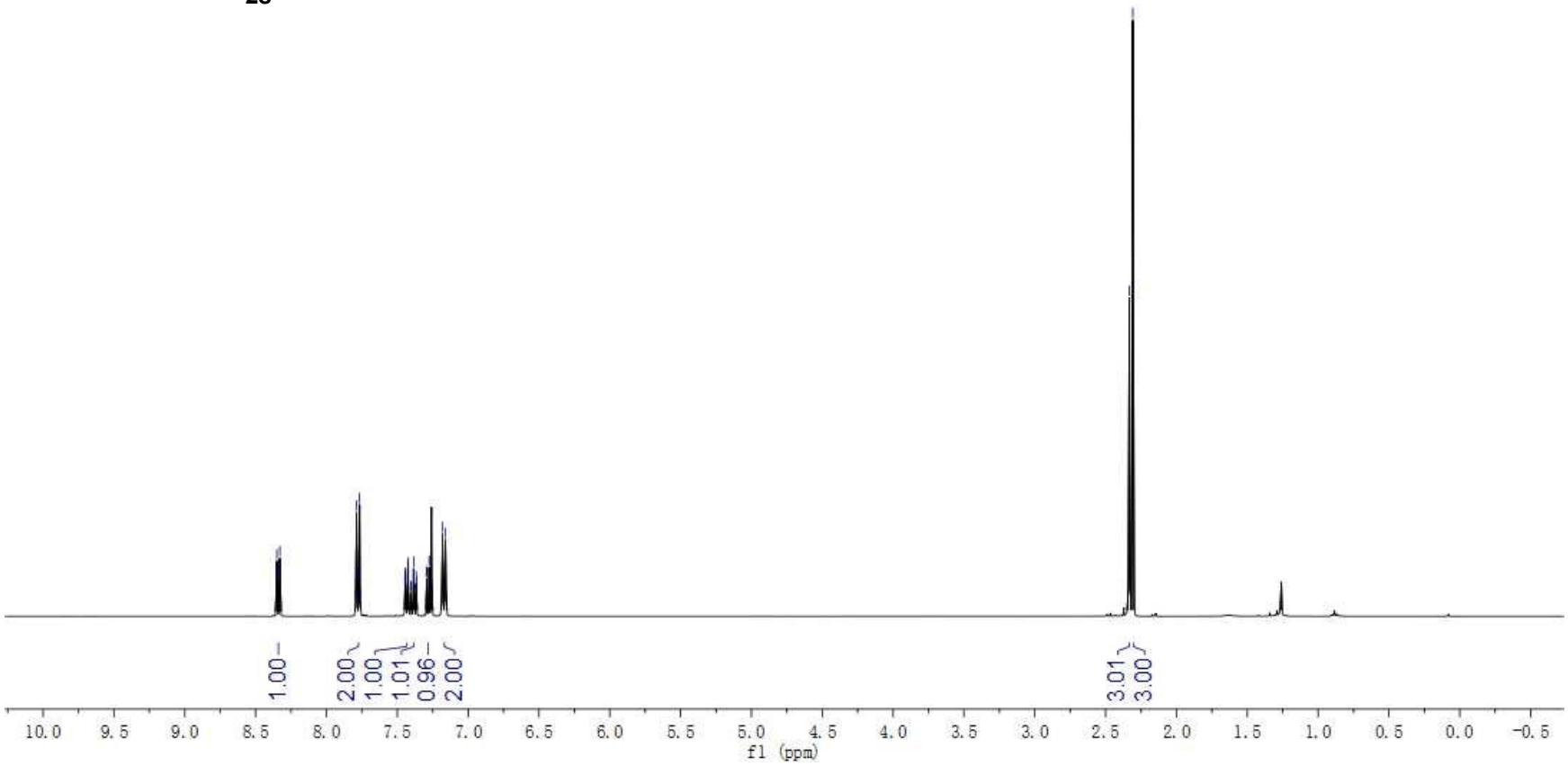
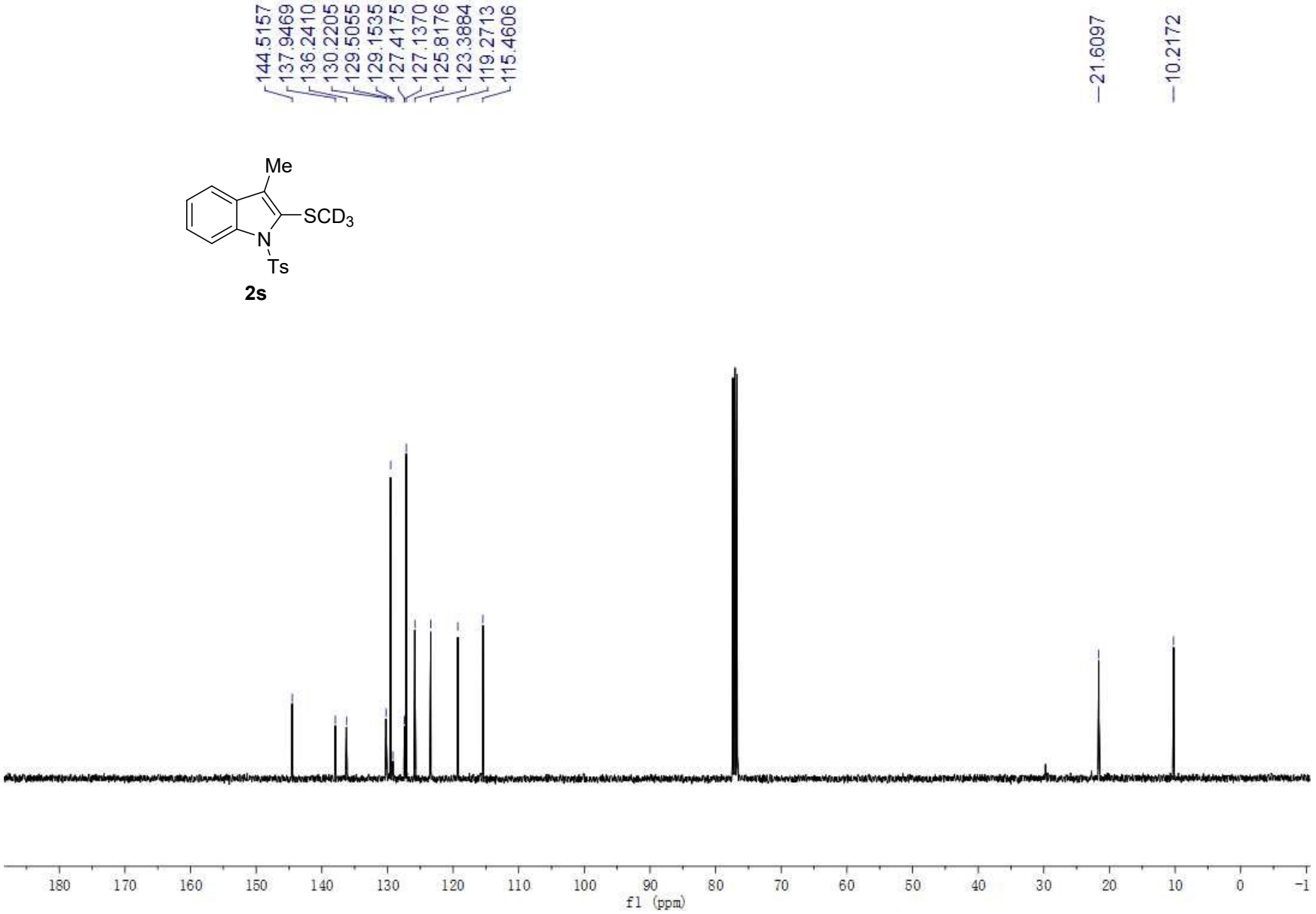
8.3478
8.3302
8.3284
7.7921
7.7873
7.7829
7.7707
7.7663
7.7614
7.4462
7.4446
7.4433
7.4417
7.4269
7.4252
7.4239
7.4223
7.4051
7.4017
7.3870
7.3838
7.3806
7.3659
7.3625
7.2944
7.2920
7.2748
7.2546
7.1802
7.1599
2.3328
2.3076


Me
SCD3
N
Ts

2s


1.00
2.00
1.00
1.01
0.96
2.00
3.01
3.00
10.0
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
f1 (ppm)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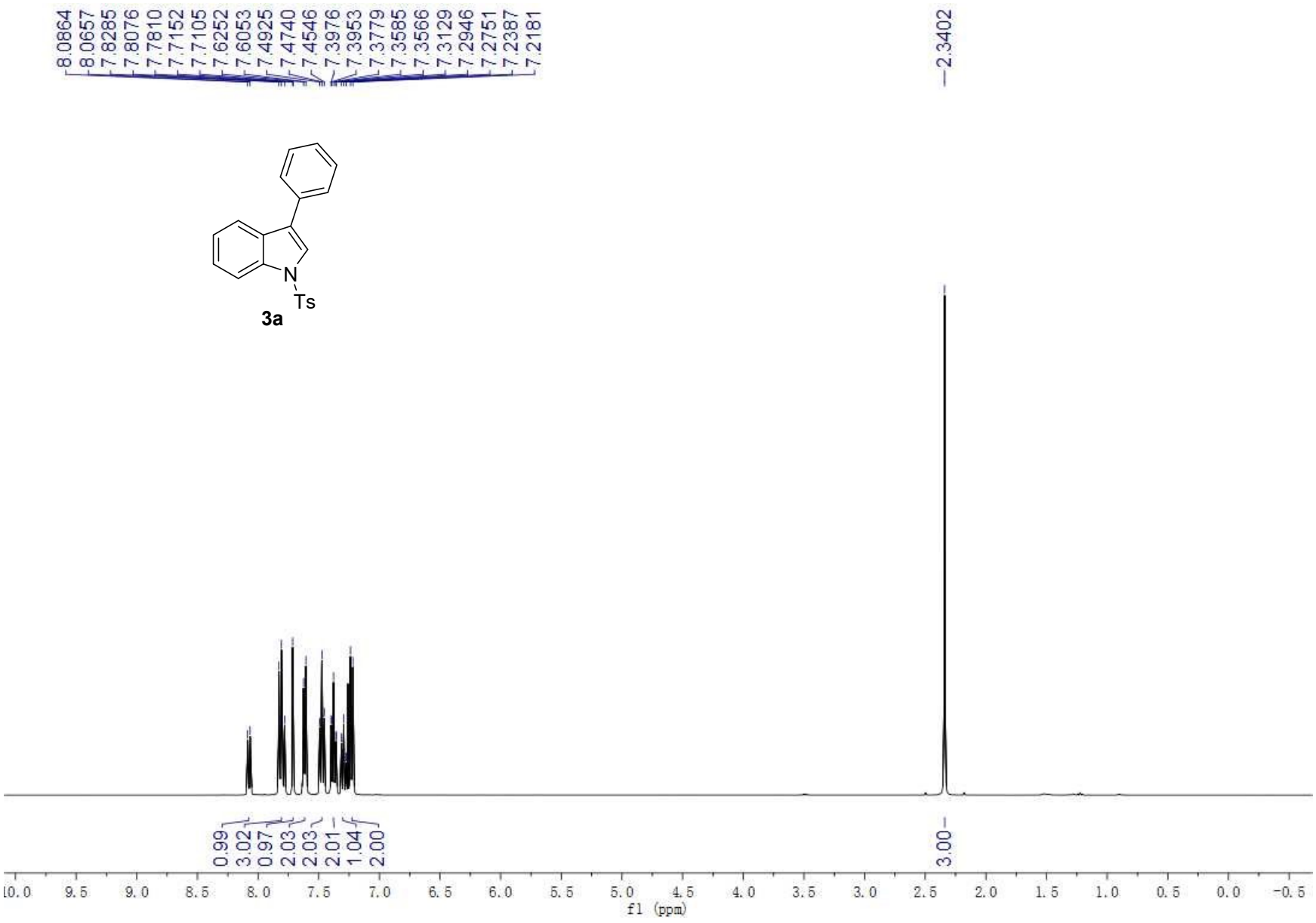
129.1535
127.4175
127.1370
125.8176
123.3884
119.2713
115.4606
21.6097
10.2172
Me
SCD3
N
Ts
2s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.8076
7.7810
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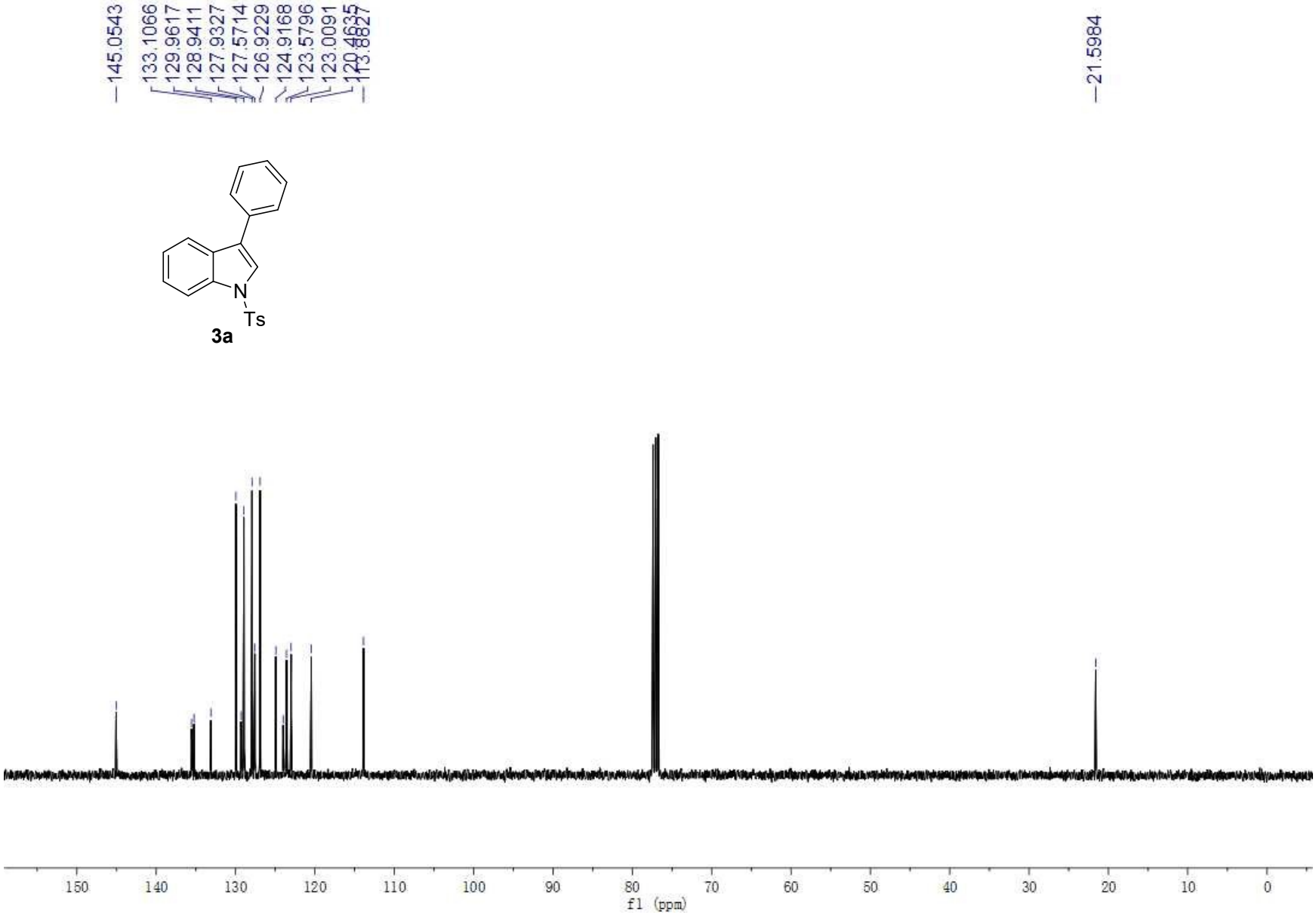
7.7105
7.6252
7.6053
7.4925
7.4740
7.4546
7.3976
7.3953
7.3779
7.3585
7.3566
7.3129
7.2946
7.2751
7.2387
7.2181
2.3402
N
Ts
3a
0.99
3.02
0.97
2.03
2.03
2.01
1.04
2.00
3.00
f1 (ppm)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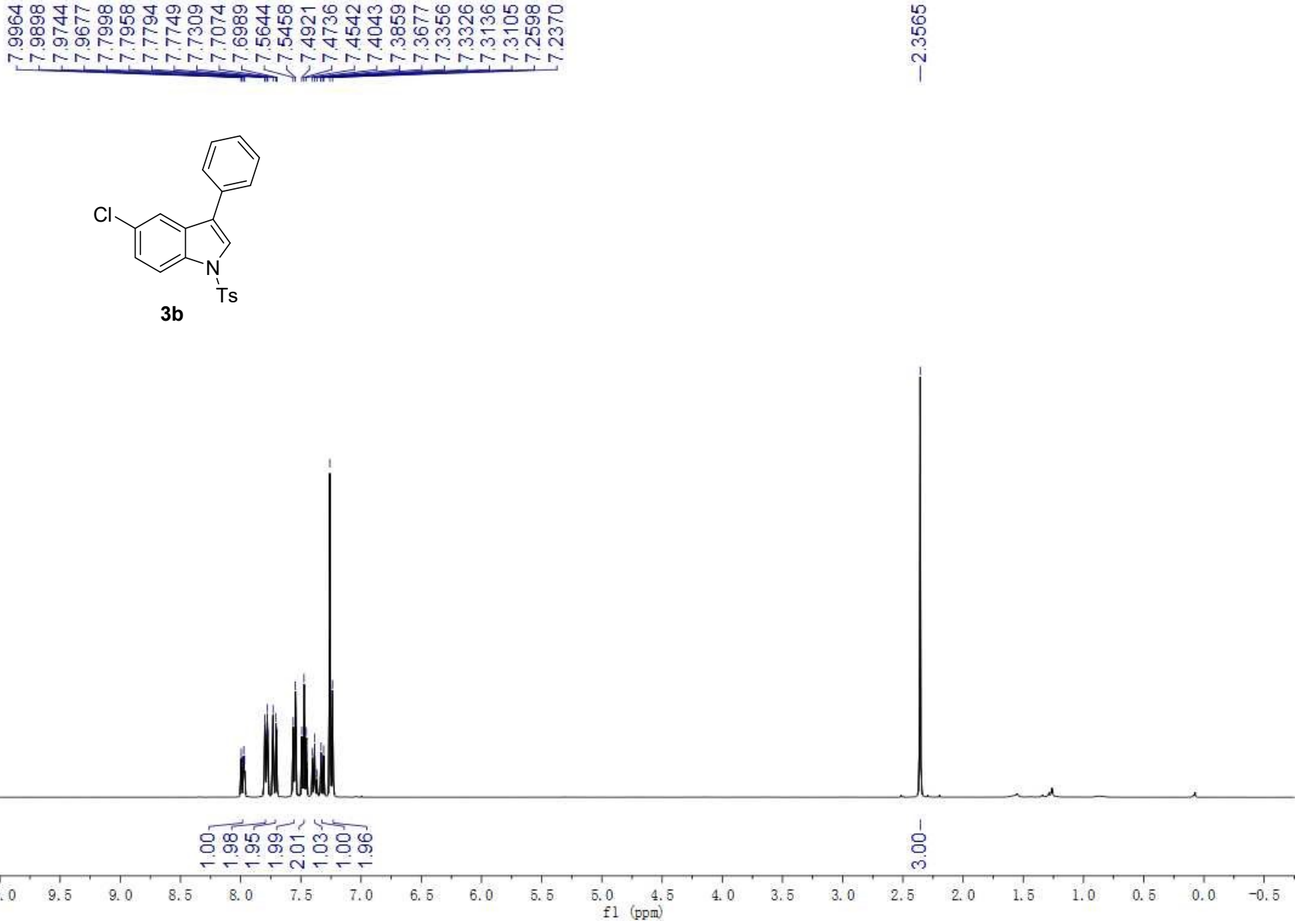
127.5714
126.9229
124.9168
123.5796
123.0091
120.4635
113.8827
21.5984
N
Ts
3a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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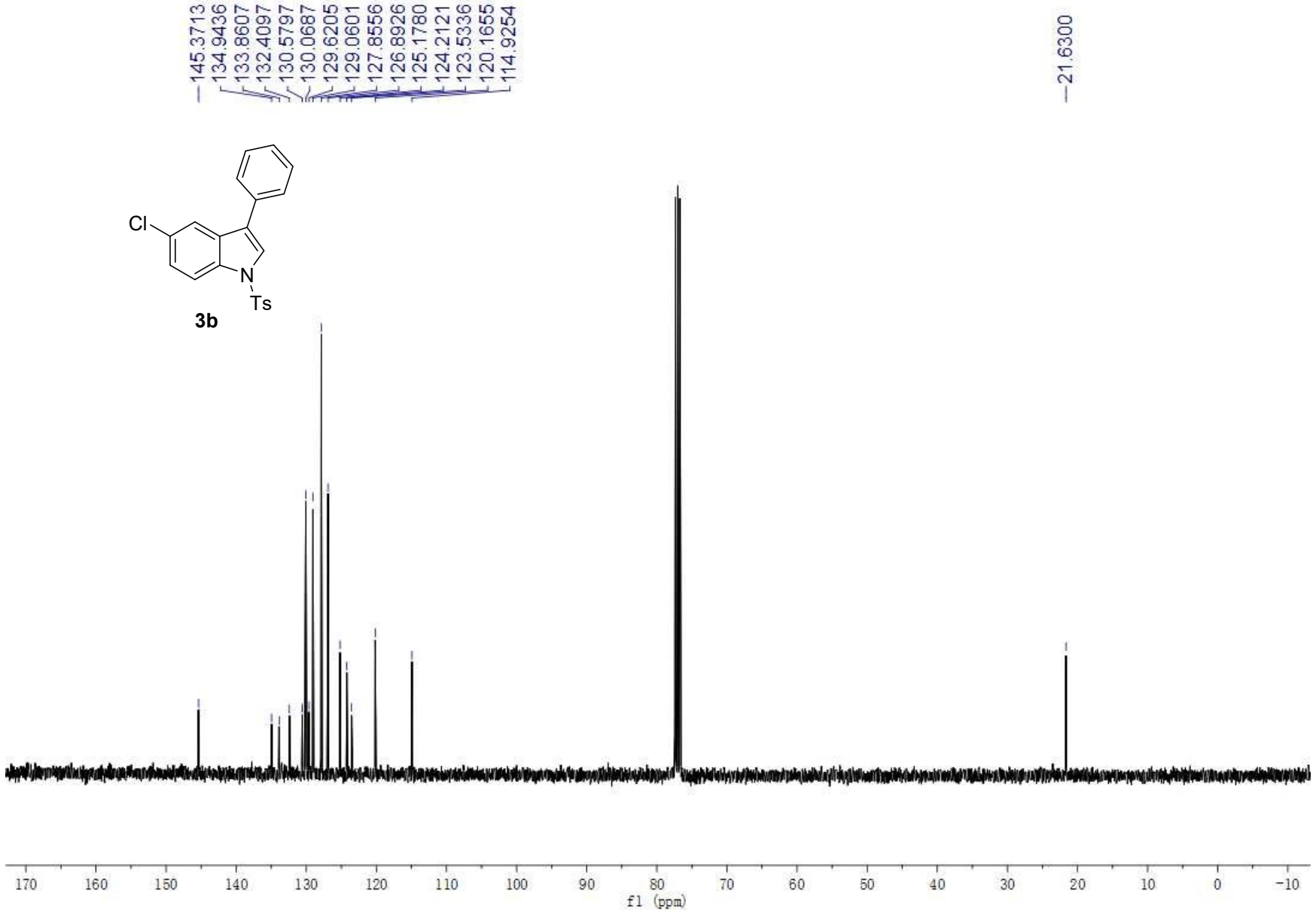
7.7998
7.7958
7.7794
7.7749
7.7309
7.7074
7.6989
7.5644
7.5458
7.4921
7.4736
7.4542
7.4043
7.3859
7.3677
7.3356
7.3326
7.3136
7.3105
7.2598
7.2370
2.3565
Cl
N
Ts
3b
1.00
1.98
1.95
1.99
2.01
1.03
1.00
1.96
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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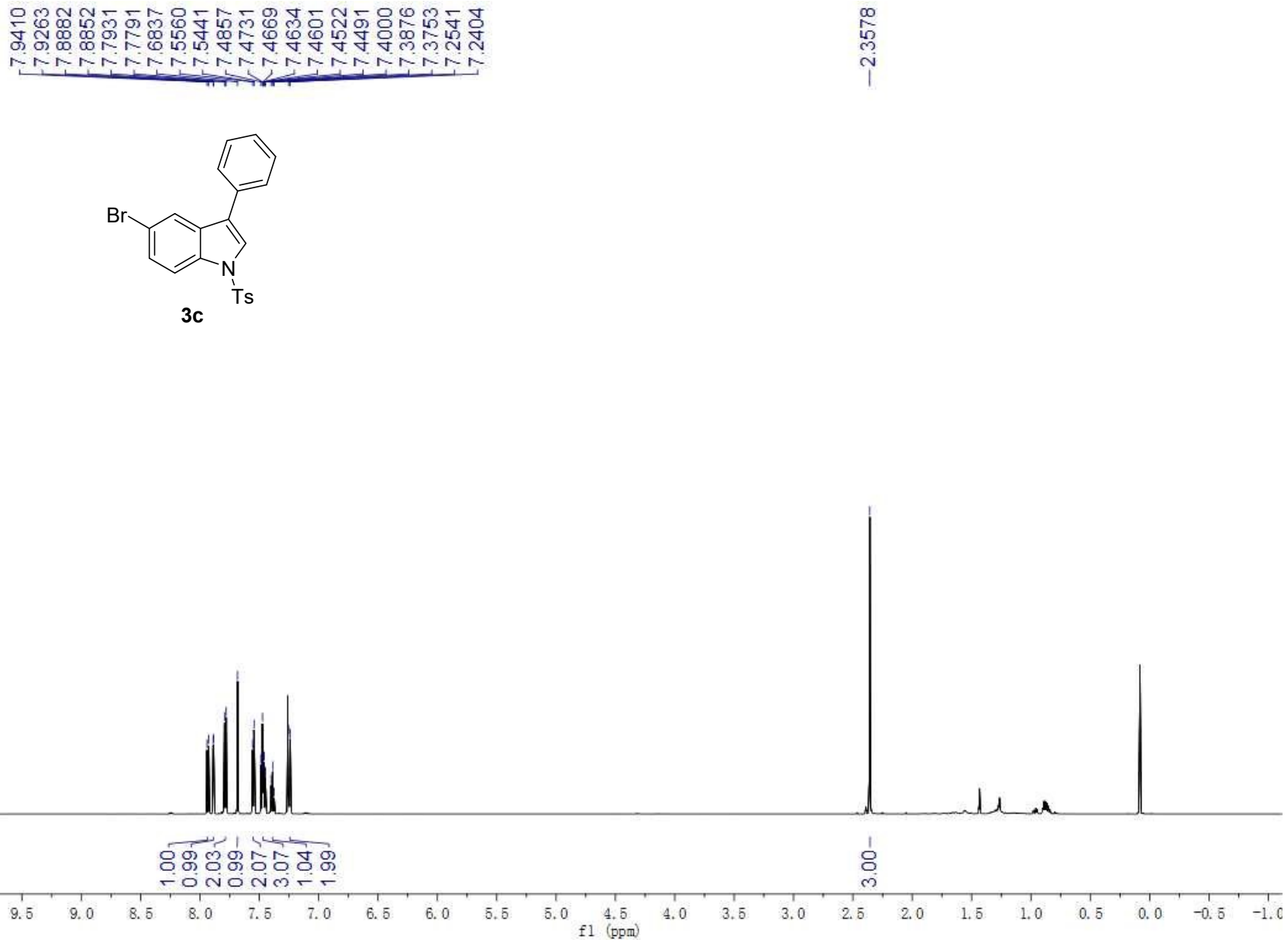
127.8556
126.8926
125.1780
124.2121
123.5336
120.1655
114.9254
21.6300
Cl
N
Ts
3b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.8882
7.8852
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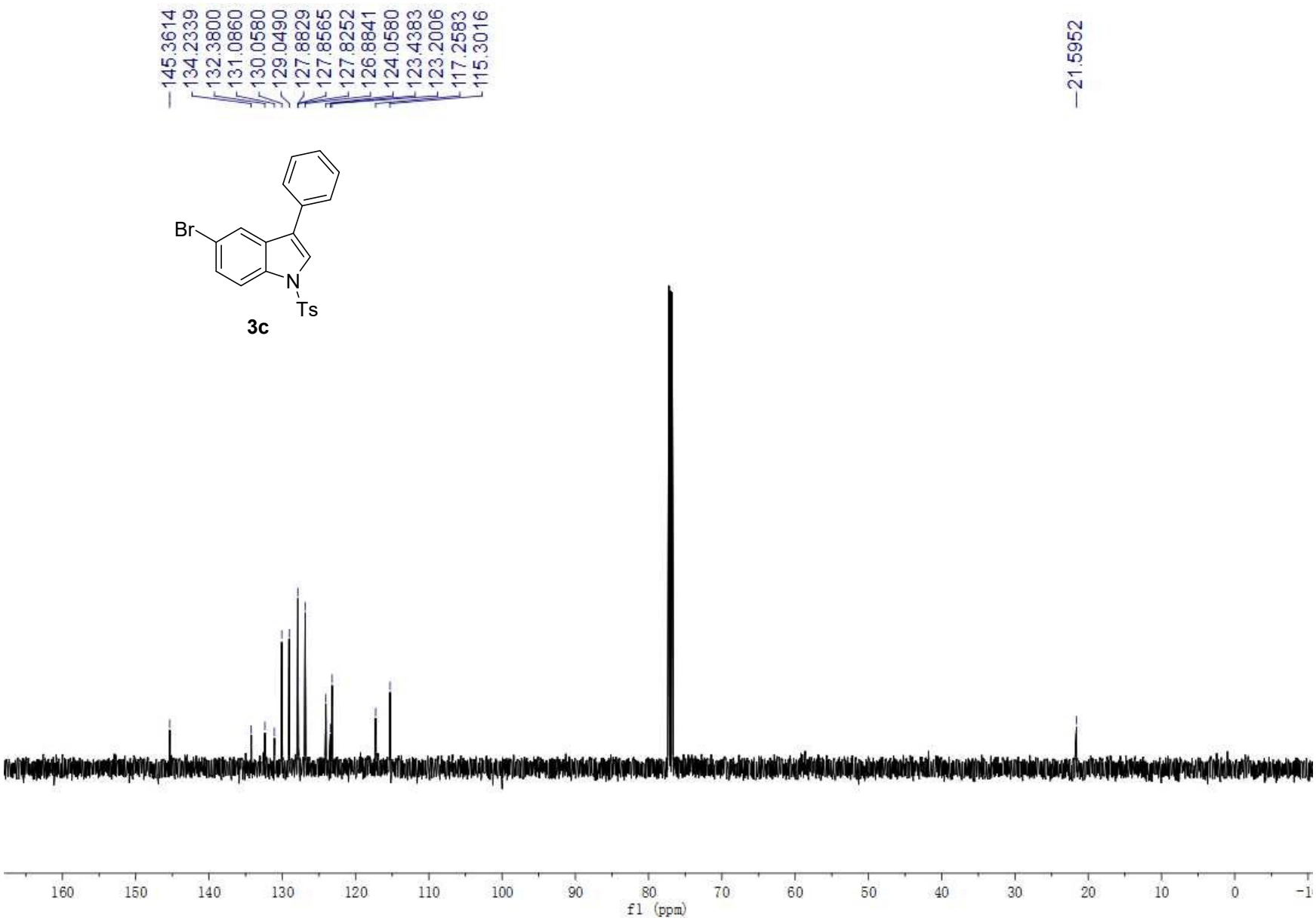
7.7791
7.6837
7.5560
7.5441
7.4857
7.4731
7.4669
7.4634
7.4601
7.4522
7.4491
7.4000
7.3876
7.3753
7.2541
7.2404
2.3578
Br
N
Ts
3c
1.00
0.99
2.03
0.99
2.07
3.07
1.04
1.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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124.0580
123.4383
123.2006
117.2583
115.3016
21.5952
Br
N
Ts
3c
160
150
140
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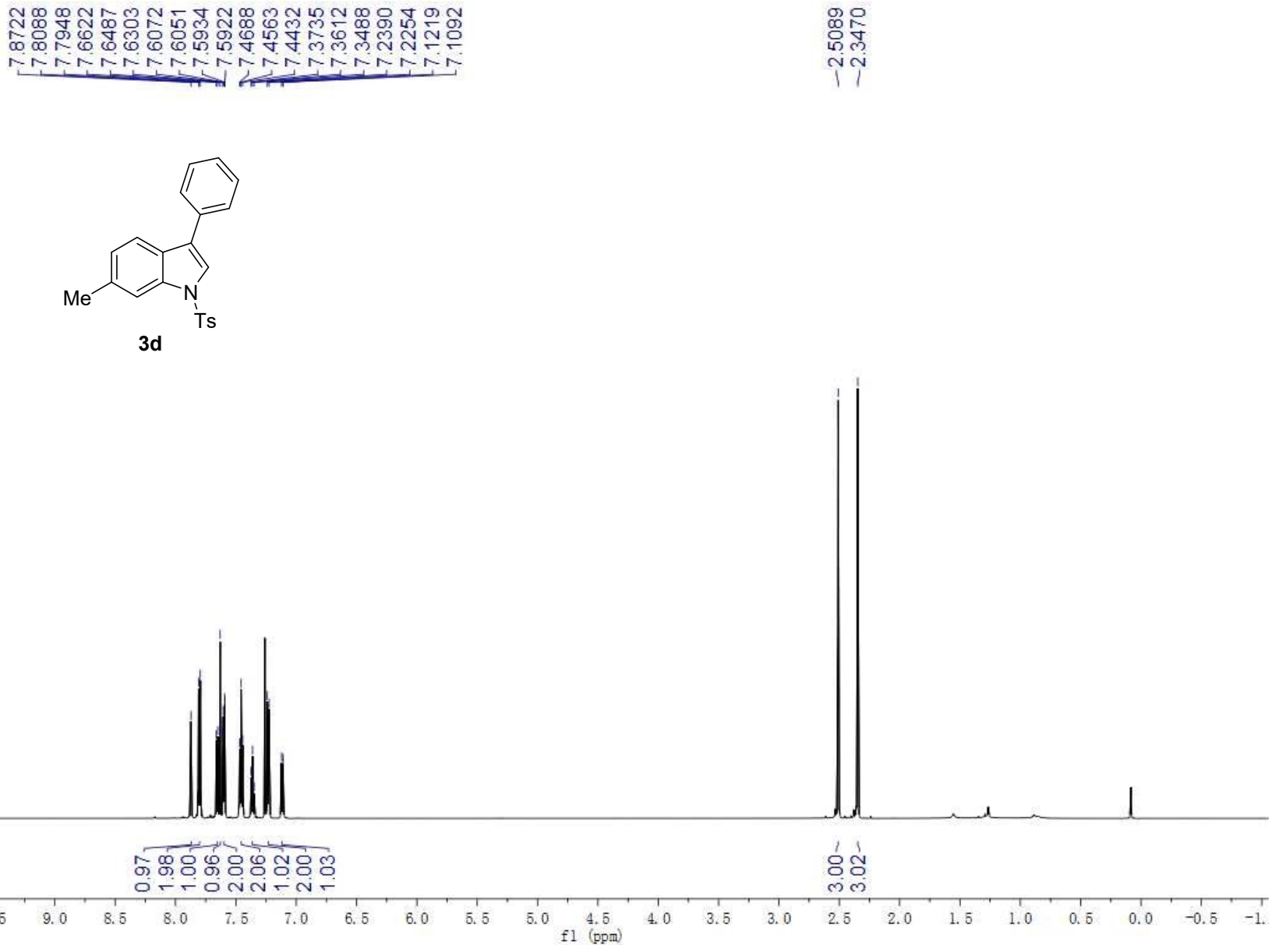
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.6072
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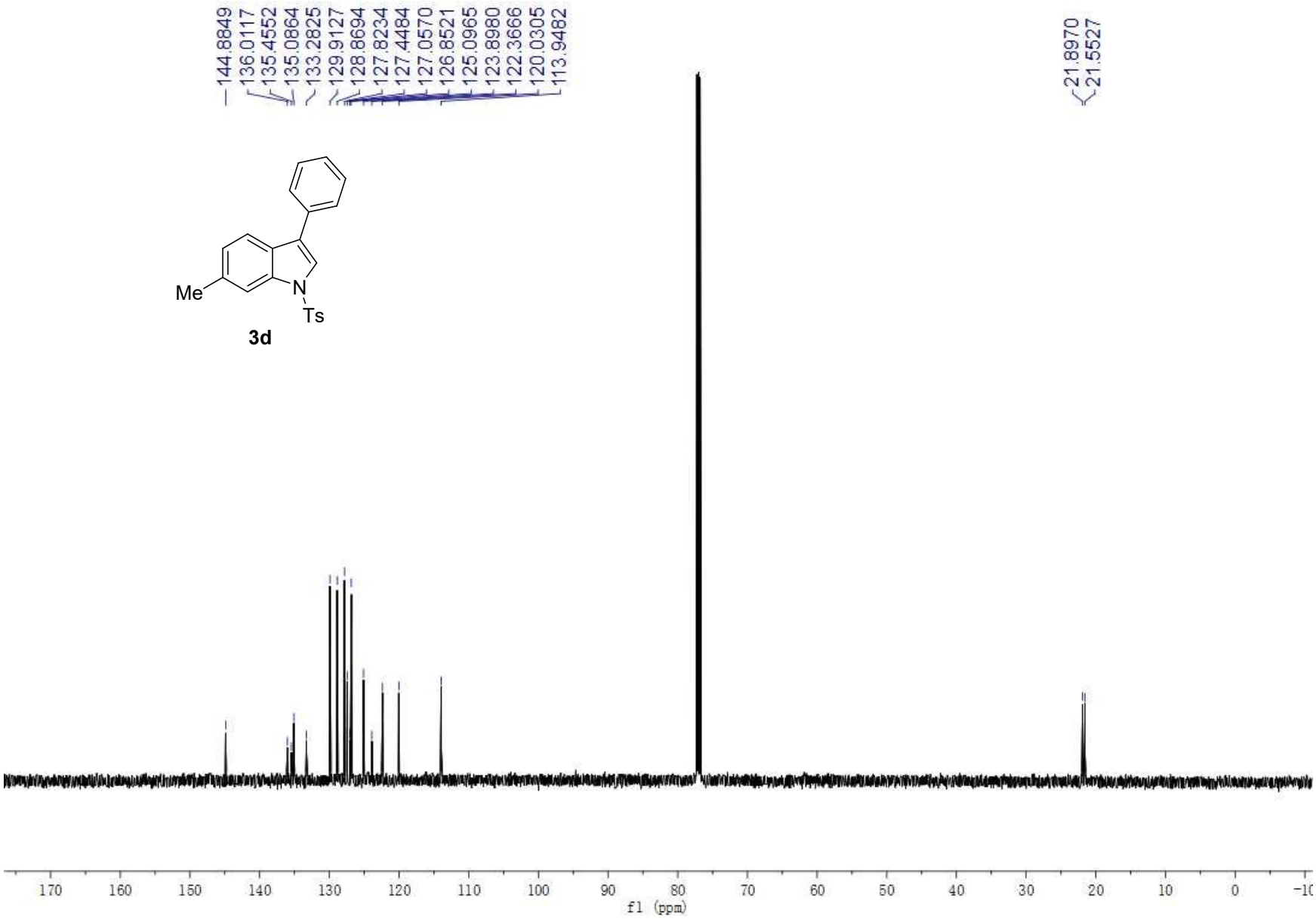
7.5934
7.5922
7.4688
7.4563
7.4432
7.3735
7.3612
7.3488
7.2390
7.2254
7.1219
7.1092
2.5089
2.3470
Me
N
Ts
3d
0.97
1.98
1.00
0.96
2.00
2.06
1.02
2.00
1.03
3.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)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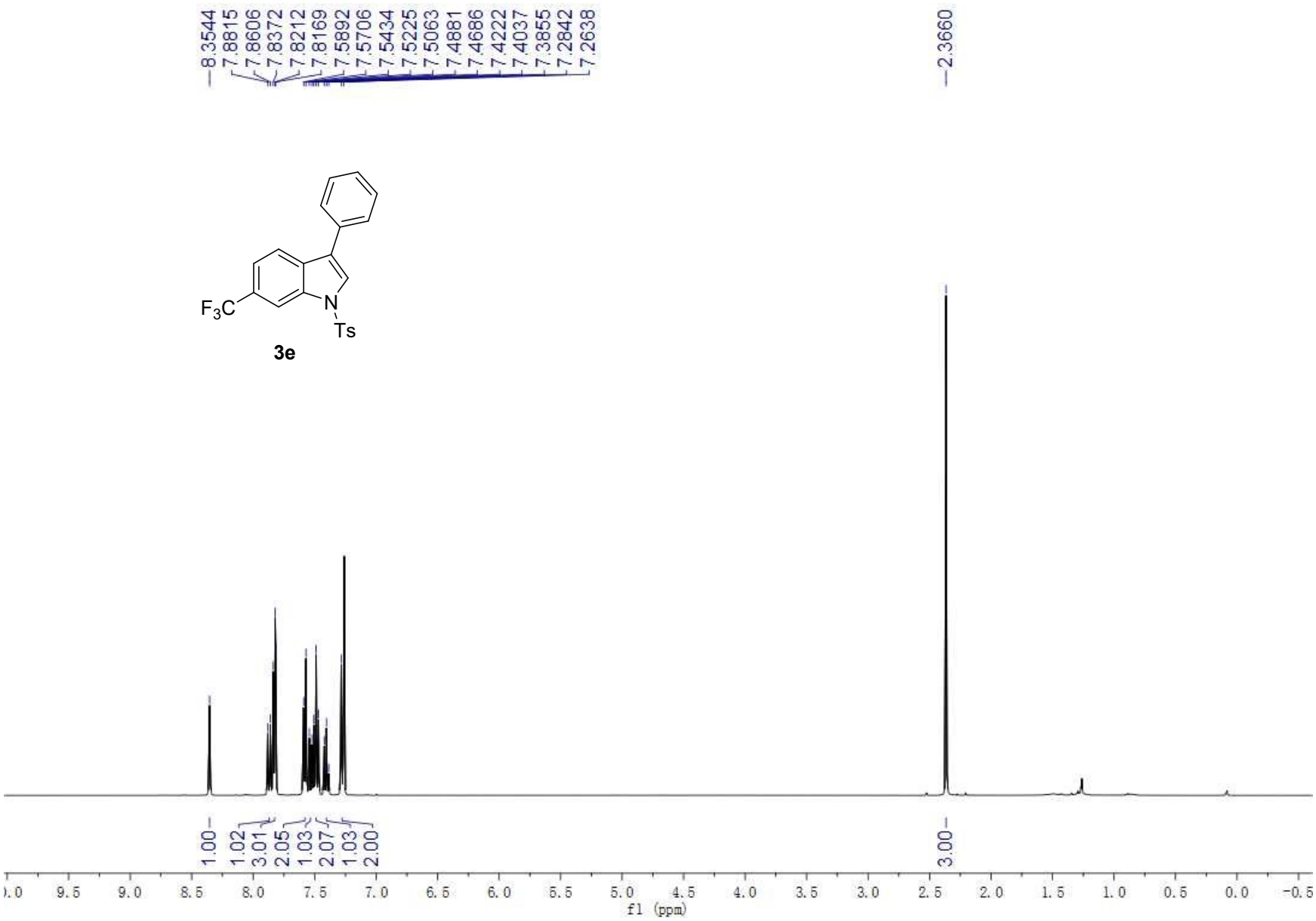
127.0570
126.8521
125.0965
123.8980
122.3666
120.0305
113.9482
21.8970
21.5527
Me
N
Ts
3d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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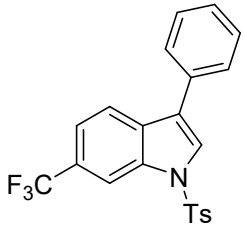
7.5063
7.4881
7.4686
7.4222
7.4037
7.3855
7.2842
7.2638
2.3660
F3C
N
Ts
3e
1.00
1.02
3.01
2.05
1.03
2.07
1.03
2.00
3.00
f1 (ppm)


F3C
N
Ts

3e

-61.0877
0
-10
-20
-30
-40
-50
-60
-70
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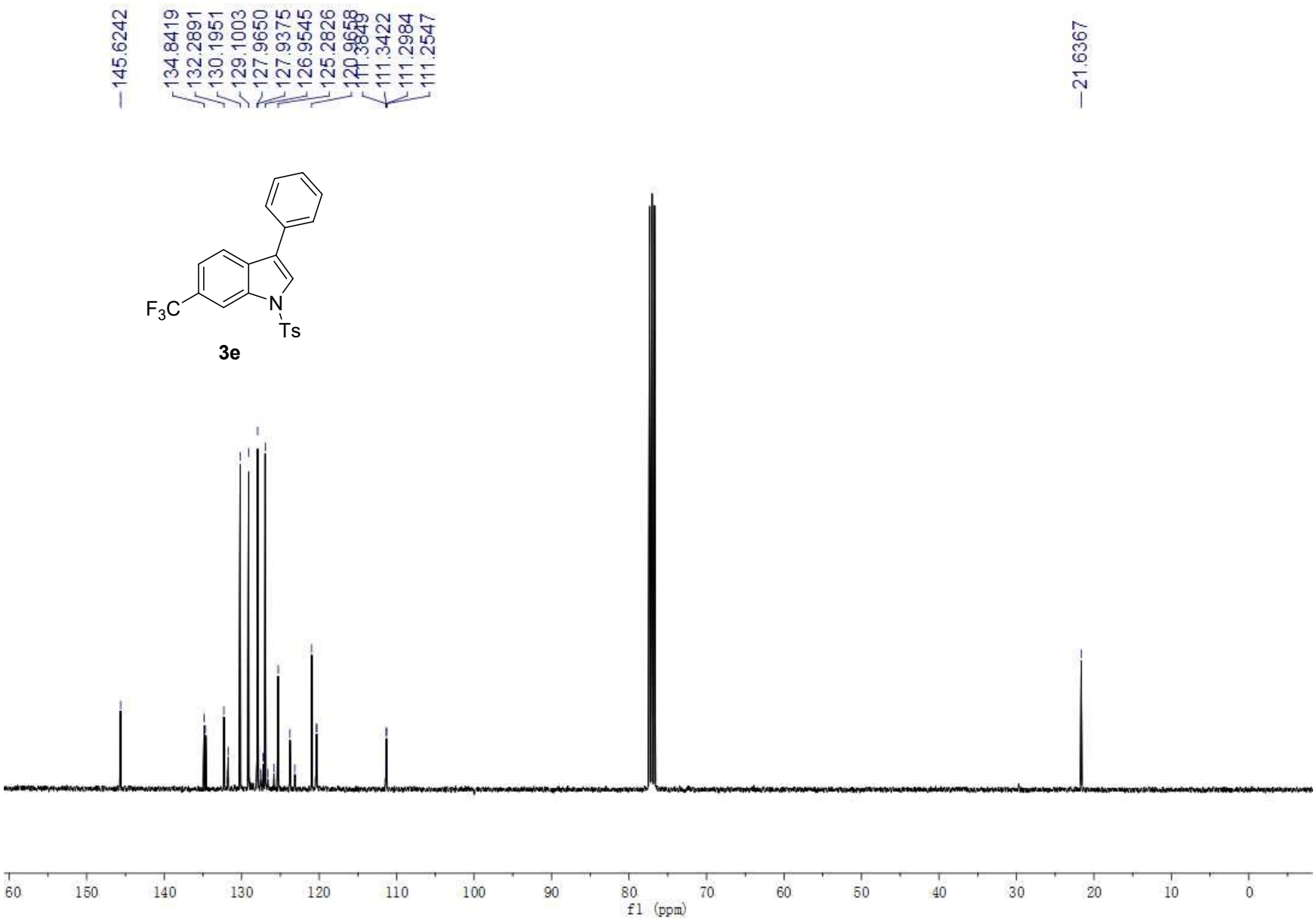
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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132.2891
130.1951
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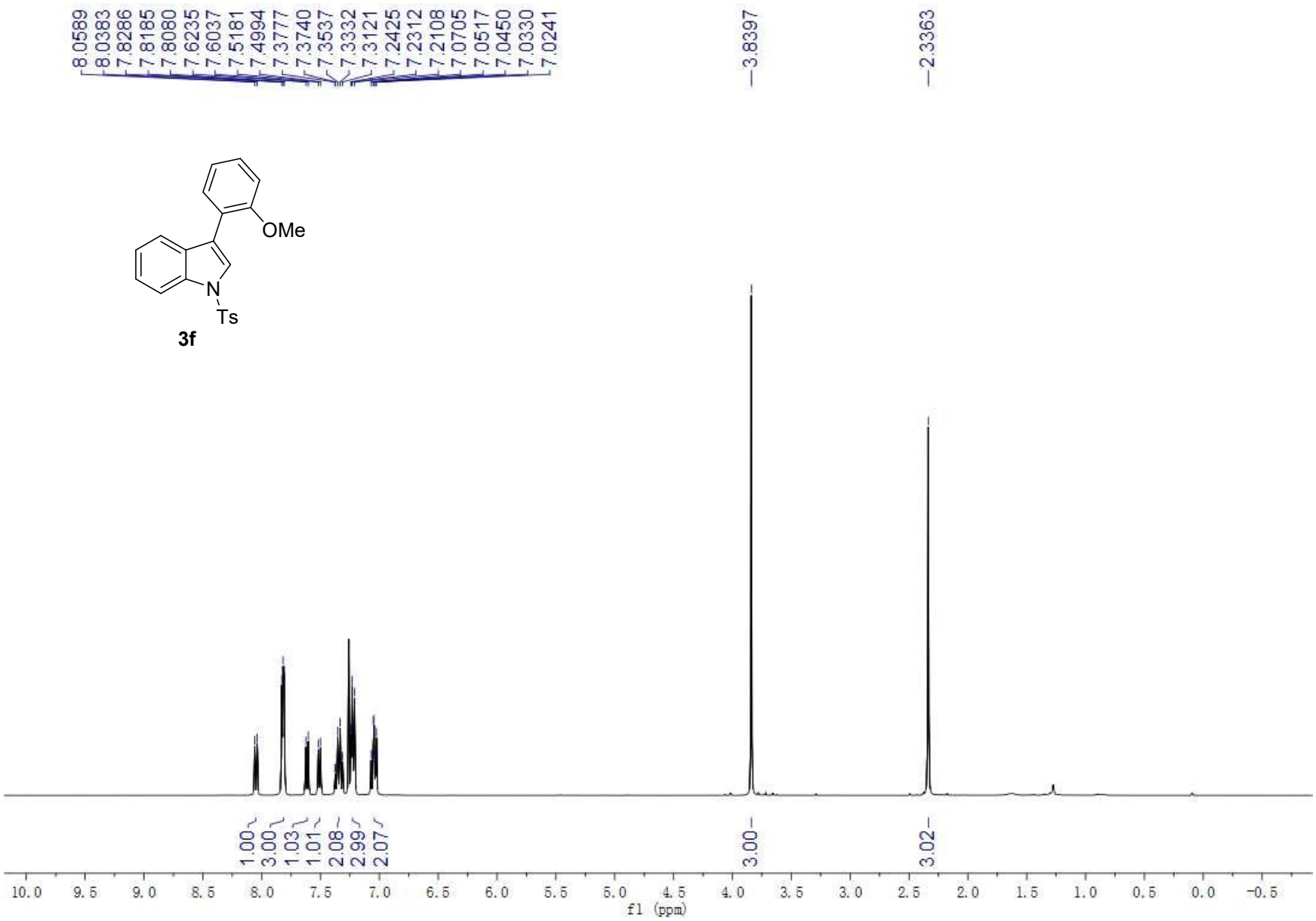
127.9650
127.9375
126.9545
125.2826
111.3422
111.2984
111.2547
21.6367
F3C
N
Ts
3e
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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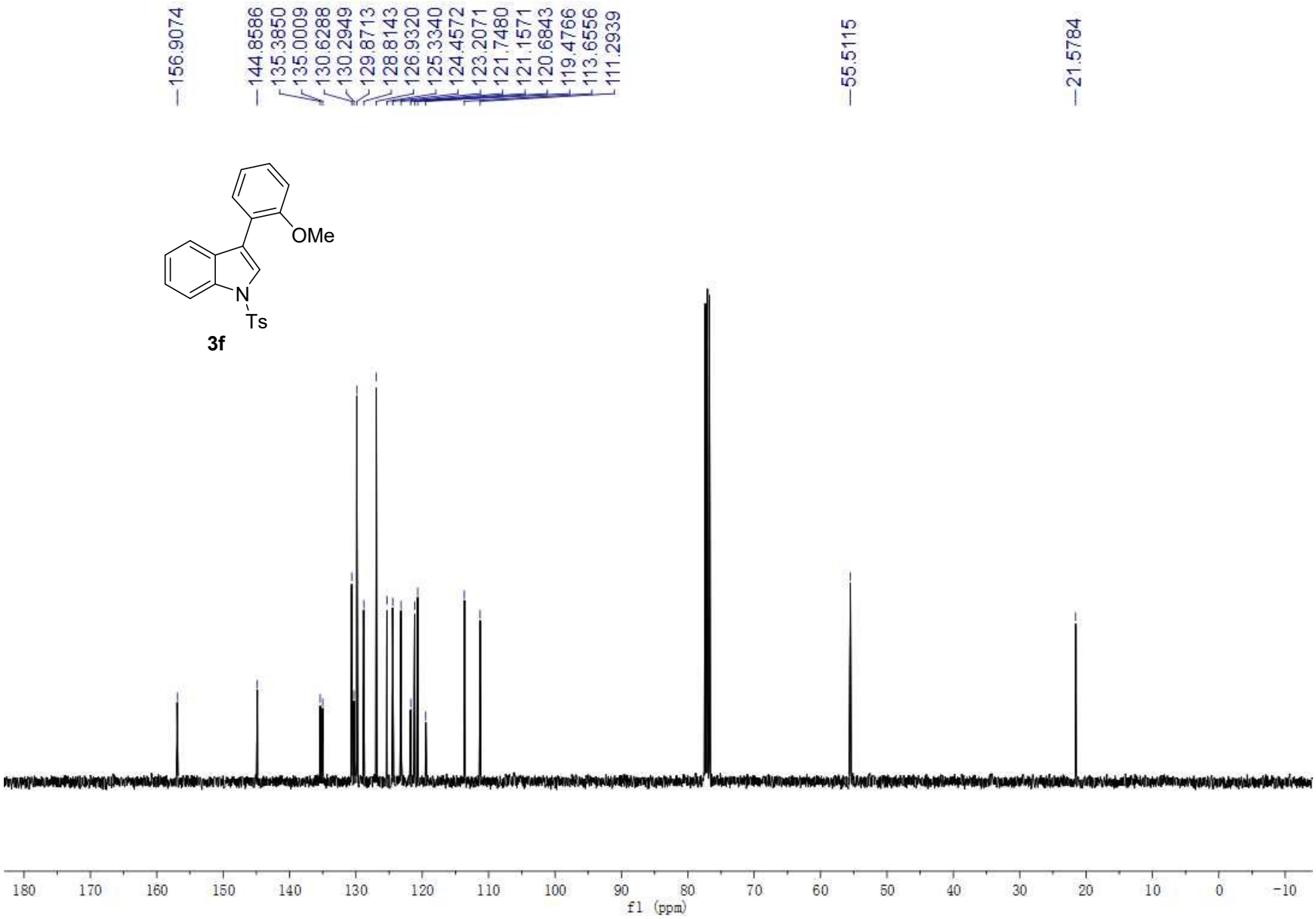
8.0383
7.8286
7.8185
7.8080
7.6235
7.6037
7.5181
7.4994
7.3777
7.3740
7.3537
7.3332
7.3121
7.2425
7.2312
7.2108
7.0705
7.0517
7.0450
7.0330
7.0241
3.8397
2.3363
OMe
N
Ts
3f
1.00
3.00
1.03
1.01
2.08
2.99
2.07
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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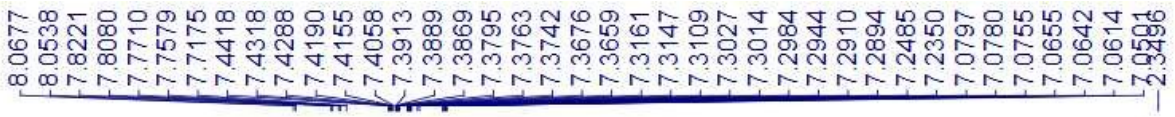
130.6288
130.2949
129.8713
128.8143
126.9320
125.3340
124.4572
123.2071
121.7480
121.1571
120.6843
119.4766
113.6556
111.2939
55.5115
21.5784
OMe
N
Ts
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.7579
7.7175
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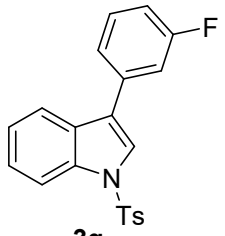
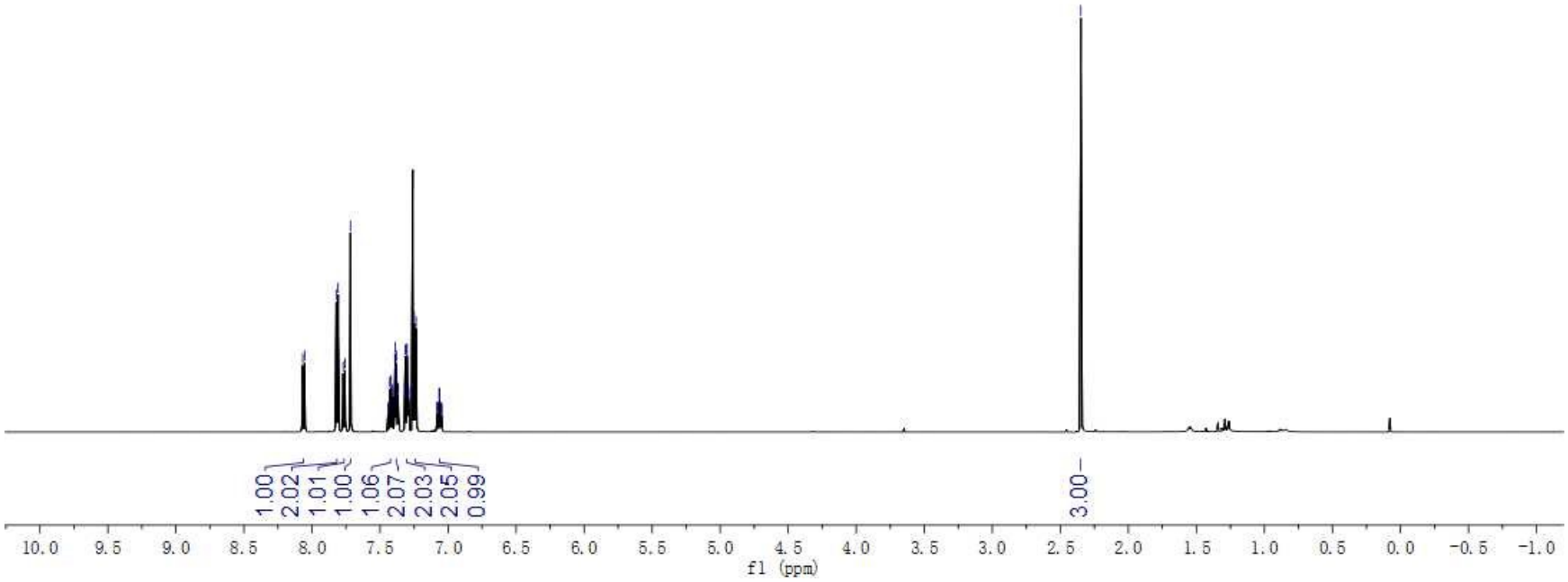
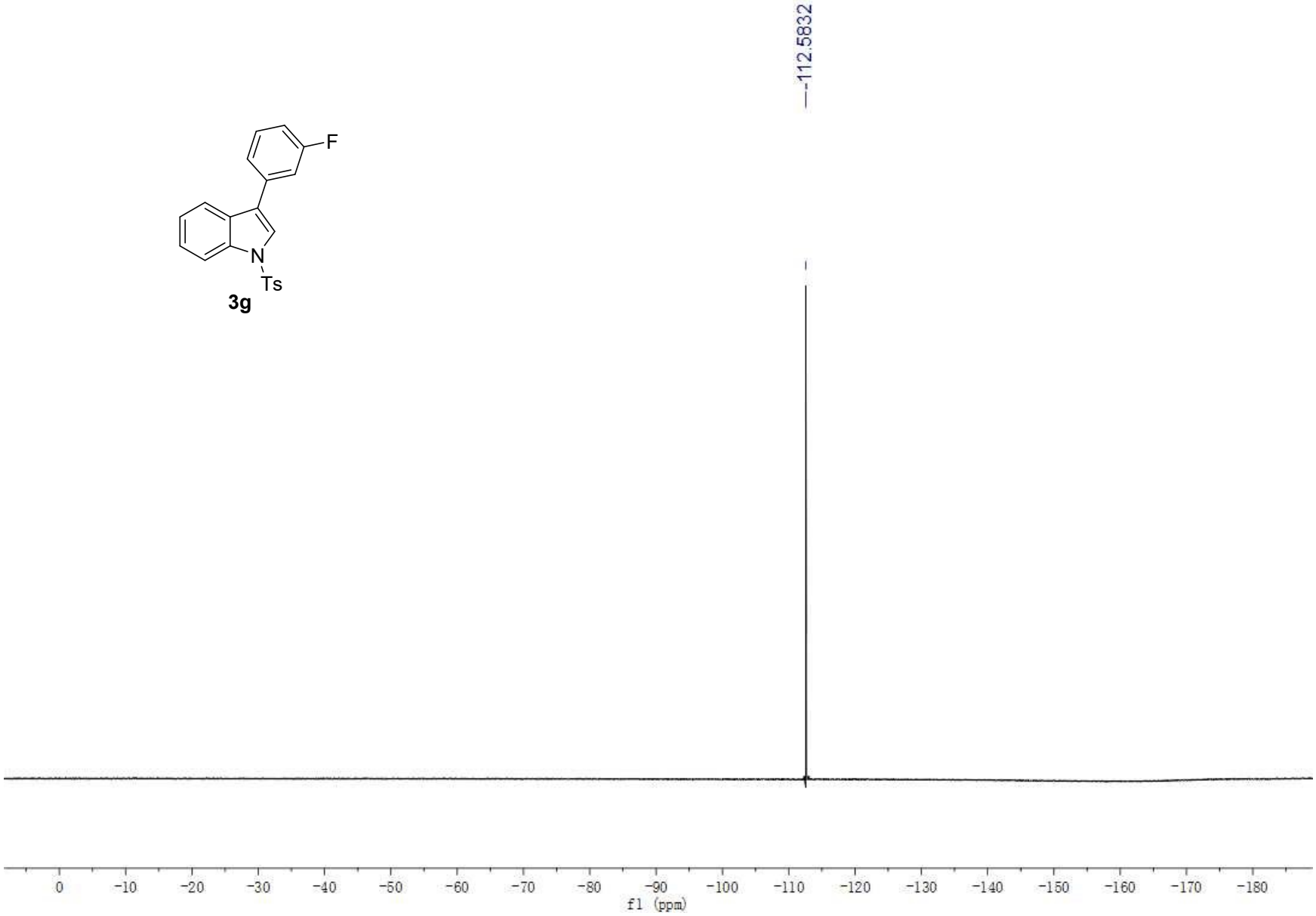
7.4318
7.4288
7.4190
7.4155
7.4058
7.3913
7.3889
7.3869
7.3795
7.3763
7.3742
7.3676
7.3659
7.3161
7.3147
7.3109
7.3027
7.3014
7.2984
7.2944
7.2910
7.2894
7.2485
7.2350
7.0797
7.0780
7.0755
7.0655
7.0642
7.0614


F
N
Ts

3g


1.00
2.02
1.01
1.00
1.06
2.07
2.03
2.05
0.99
3.00
10.0
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)


-112.5832
F
N
Ts
3g
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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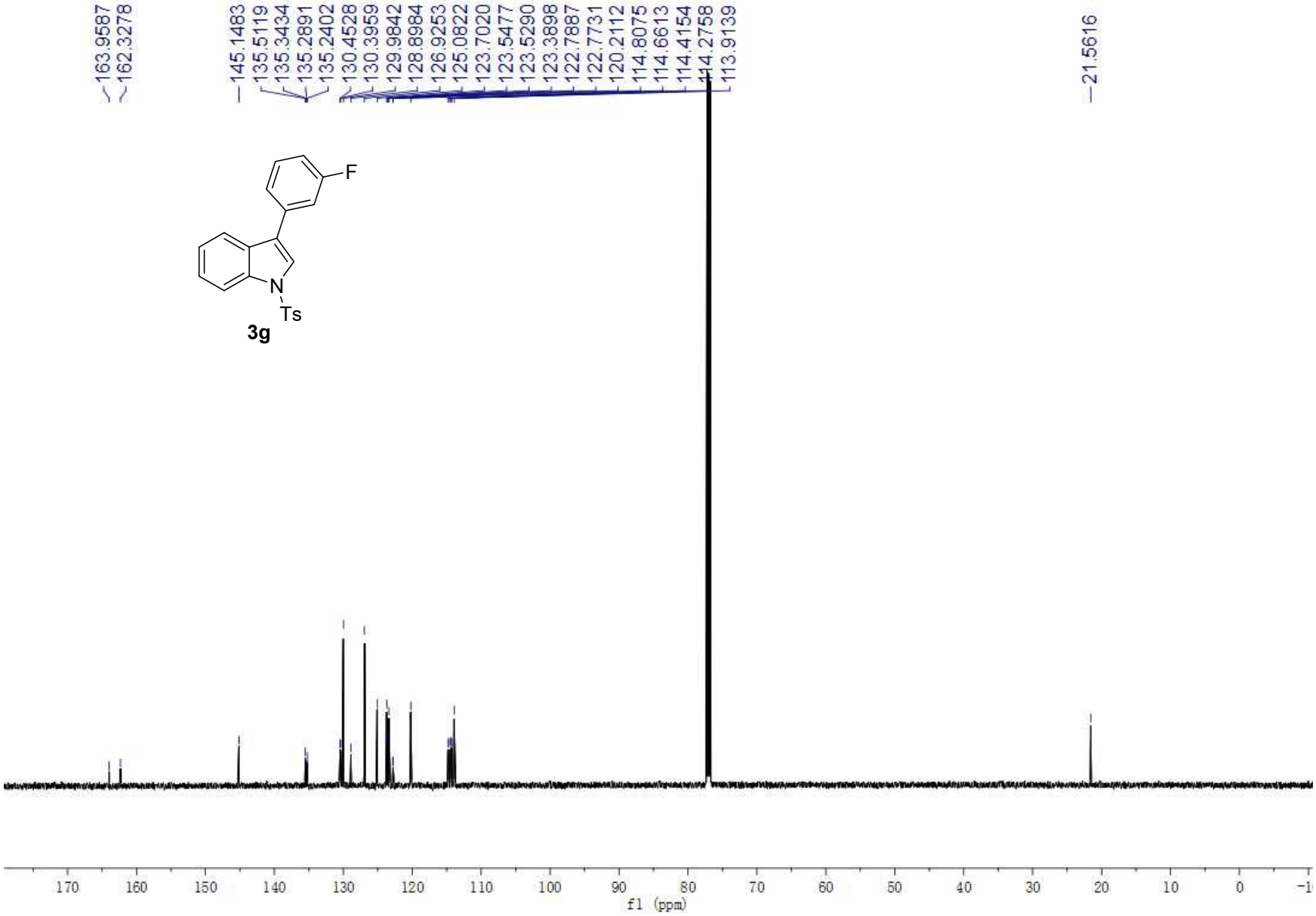
-130
-140
-150
-160
-170
-180
f1 (ppm)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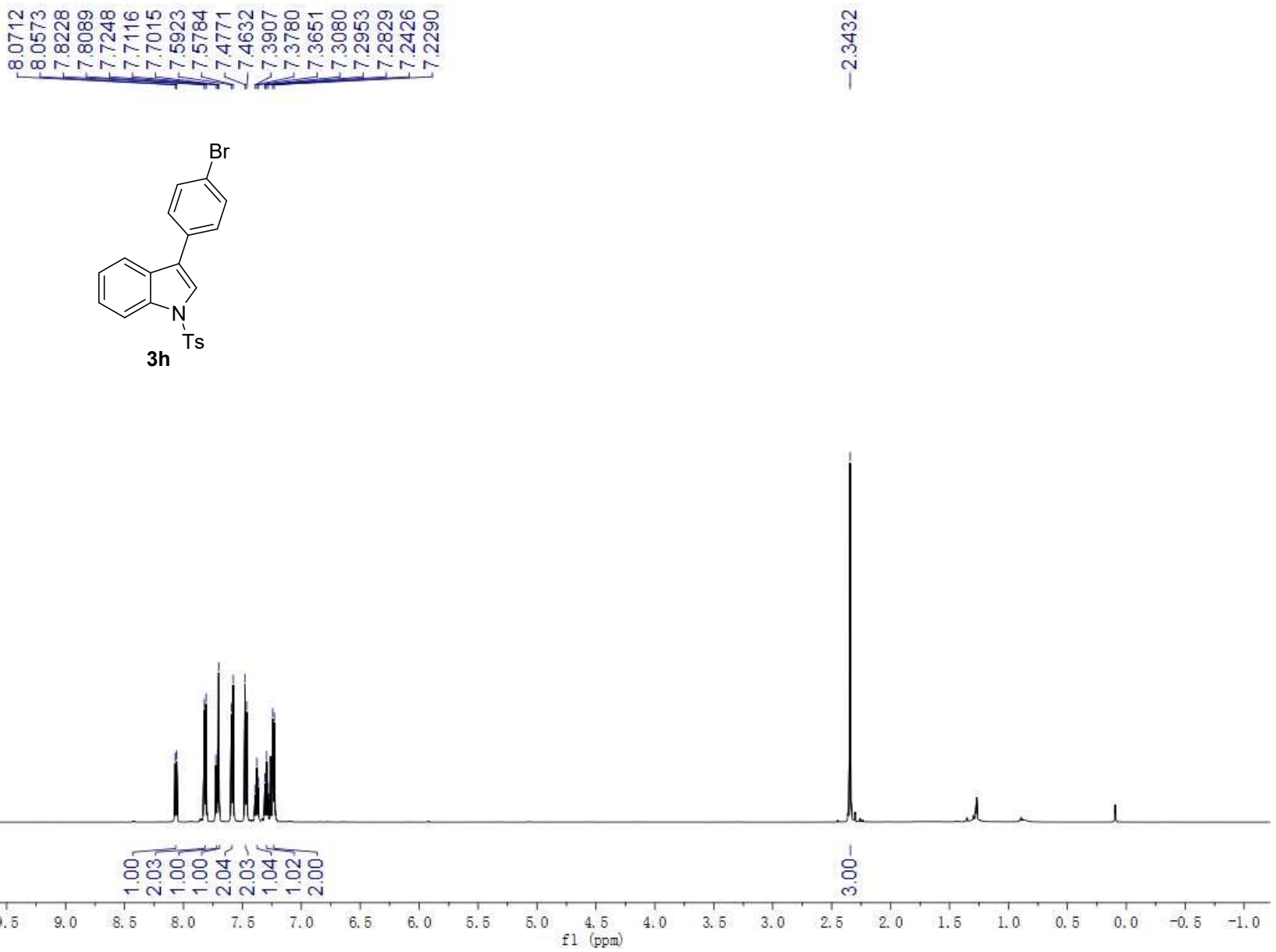
130.3959
129.9842
128.8984
126.9253
125.0822
123.7020
123.5477
123.5290
123.3898
122.7887
122.7731
120.2112
114.8075
114.6613
114.4154
114.2758
113.9139
21.5616
F
N
Ts
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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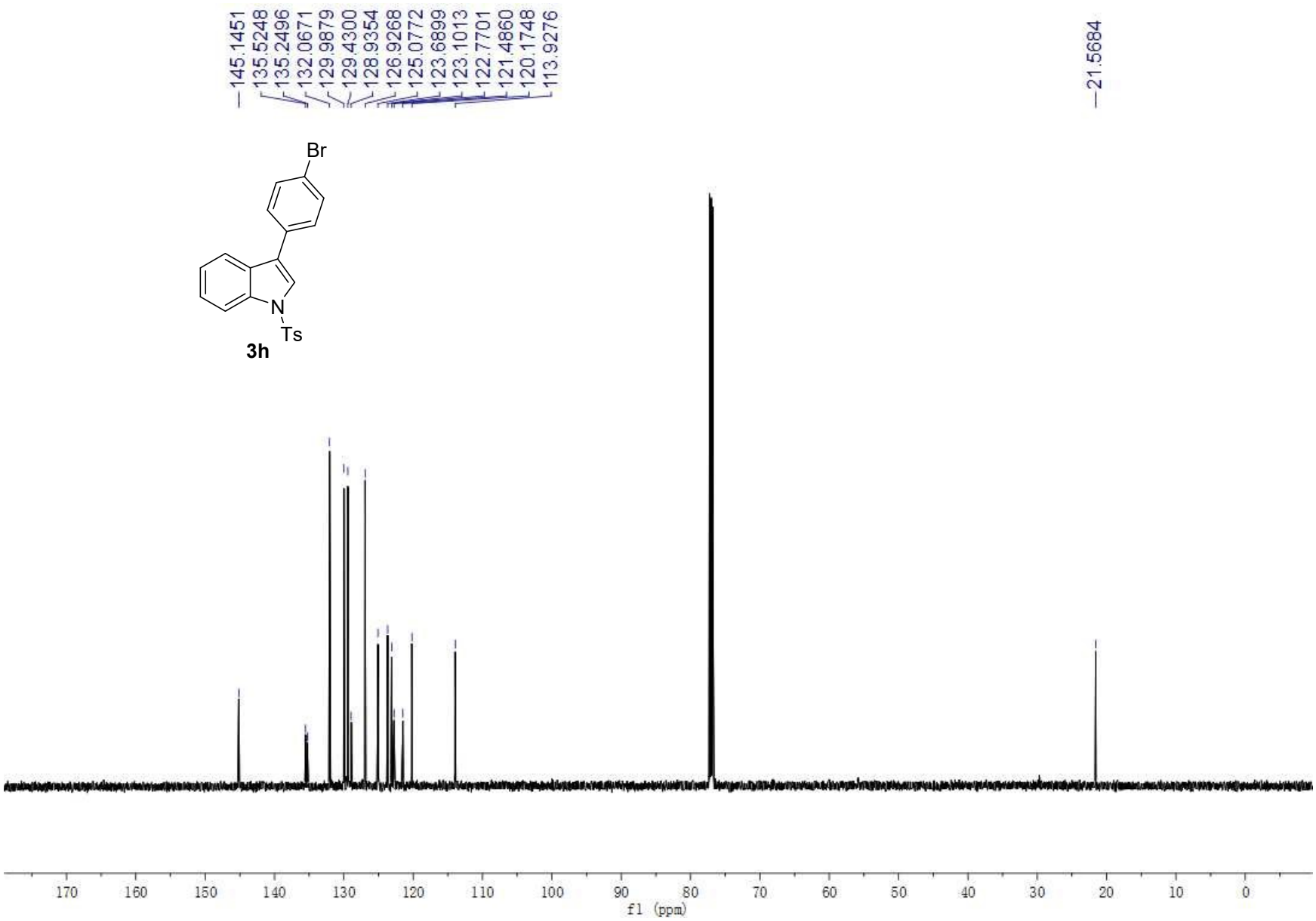
8.0573
7.8228
7.8089
7.7248
7.7116
7.7015
7.5923
7.5784
7.4771
7.4632
7.3907
7.3780
7.3651
7.3080
7.2953
7.2829
7.2426
7.2290
2.3432
Br
N
Ts
3h
1.00
2.03
1.00
1.00
2.04
2.03
1.04
1.02
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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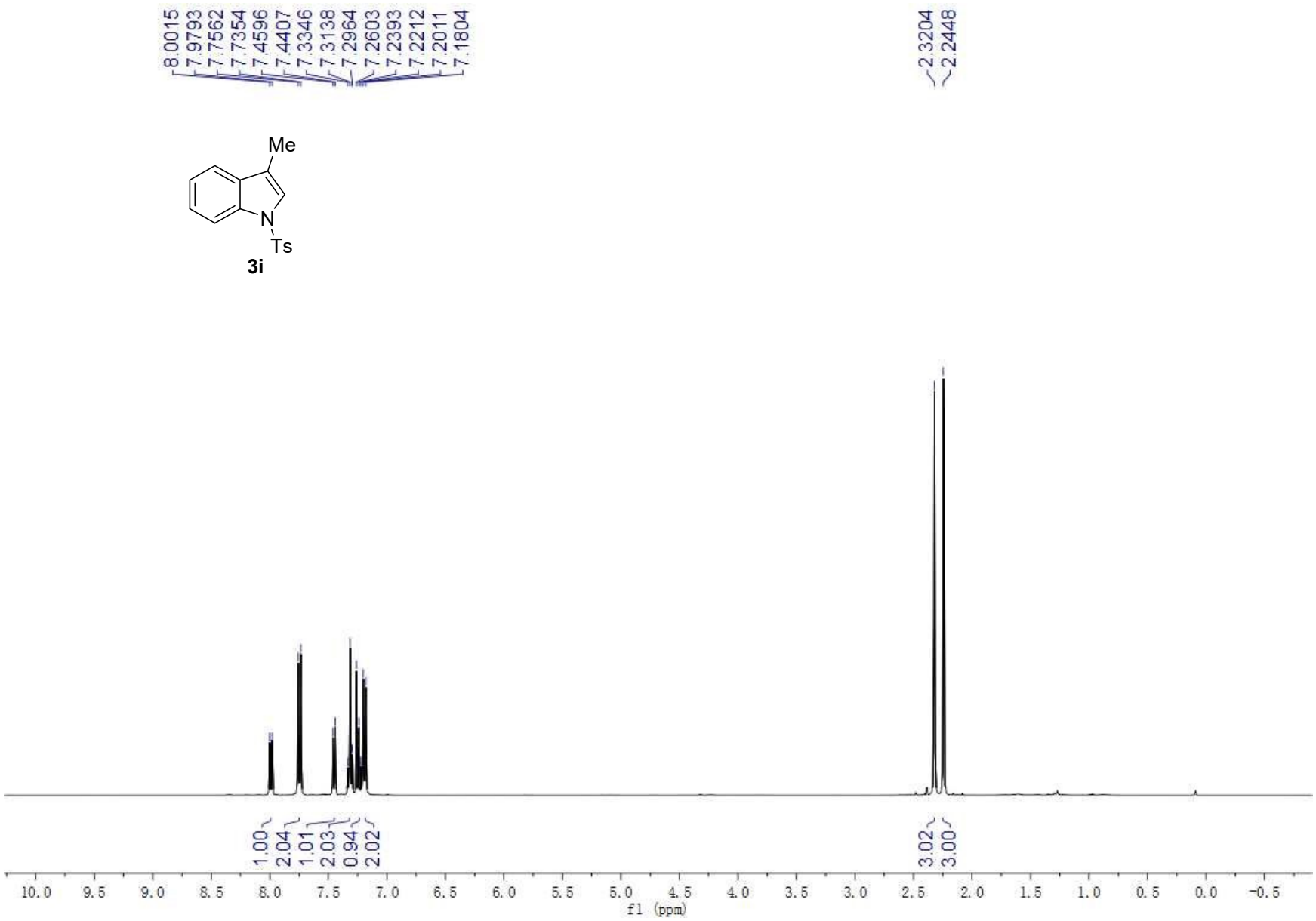
135.5248
135.2496
132.0671
129.9879
129.4300
128.9354
126.9268
125.0772
123.6899
123.1013
122.7701
121.4860
120.1748
113.9276
21.5684
Br
N
Ts
3h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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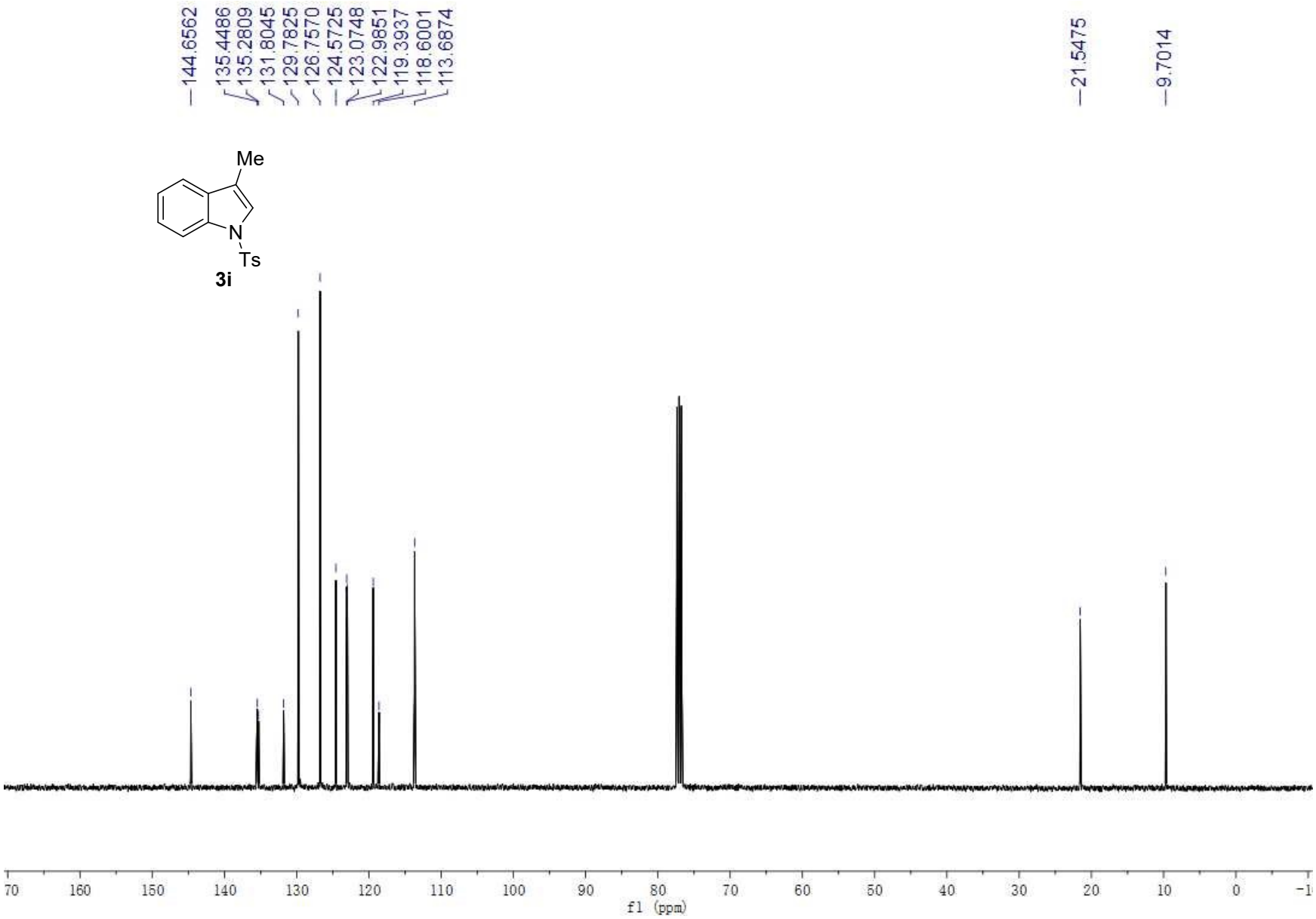
7.7562
7.7354
7.4596
7.4407
7.3346
7.3138
7.2964
7.2603
7.2393
7.2212
7.2011
7.1804
2.3204
2.2448
Me
N
Ts
1.00
2.04
1.01
2.03
0.94
2.02
3.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3i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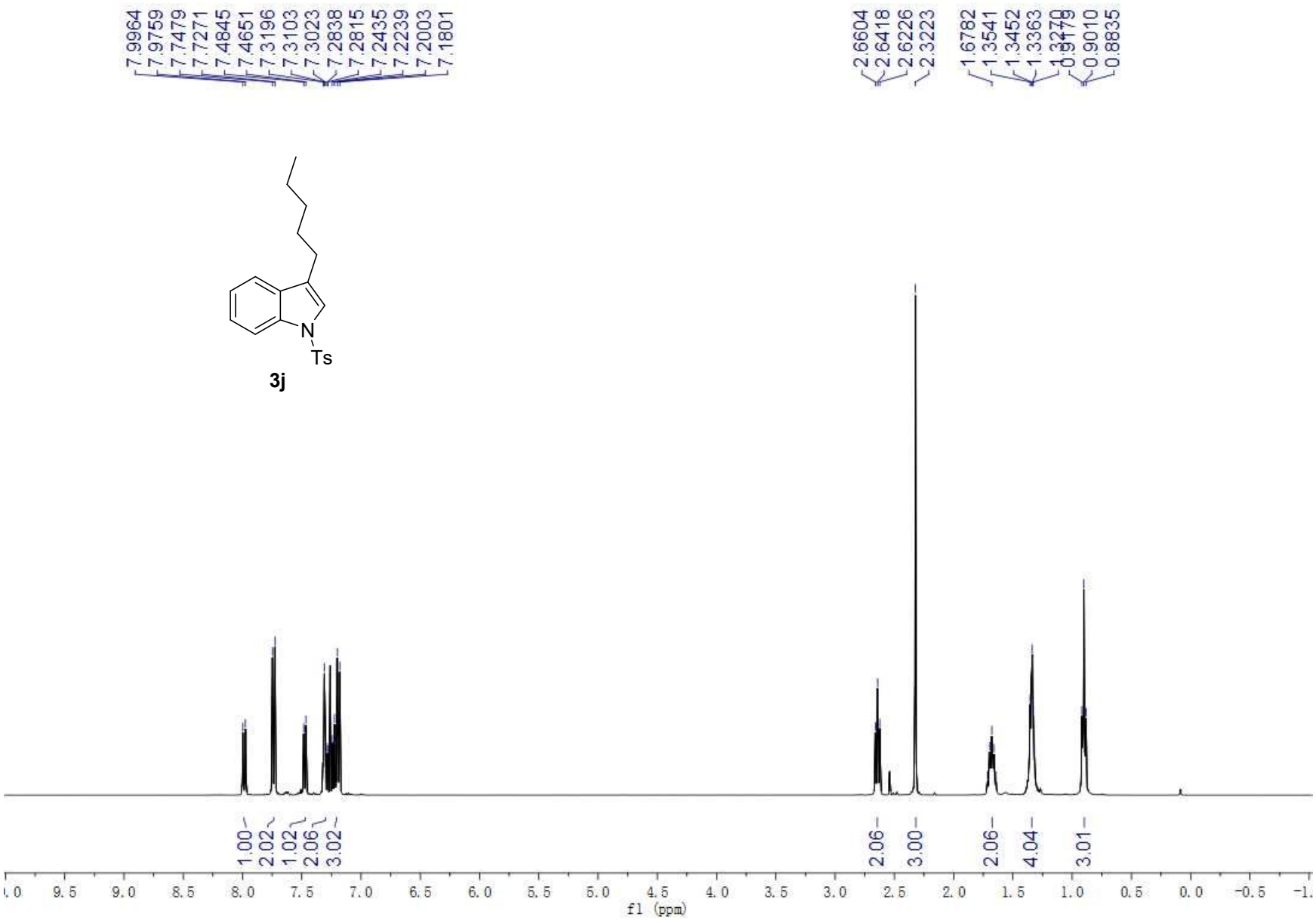
135.4486
135.2809
131.8045
129.7825
126.7570
124.5725
123.0748
122.9851
119.3937
118.6001
113.6874
21.5475
9.7014
Me
N
Ts
3i
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.9759
7.7479
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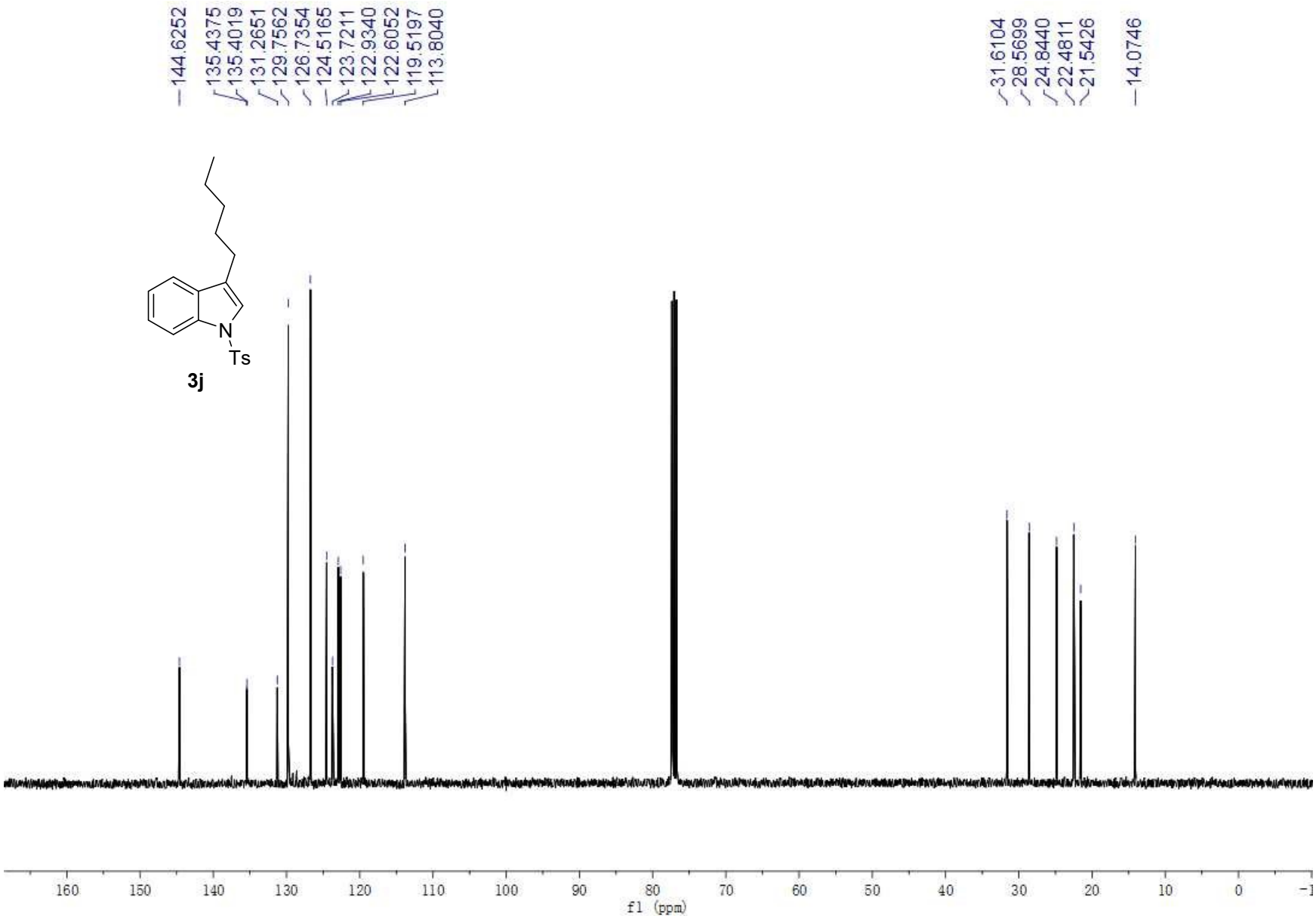
7.4845
7.4651
7.3196
7.3103
7.3023
7.2838
7.2815
7.2435
7.2239
7.2003
7.1801
2.6604
2.6418
2.6226
2.3223
1.6782
1.3541
1.3452
1.3363
0.9179
0.9010
0.8835
N
Ts
1.00
2.02
1.02
2.06
3.02
2.06
3.00
2.06
4.04
3.01
f1 (ppm)

3j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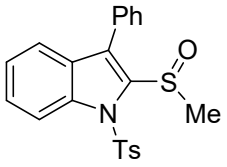
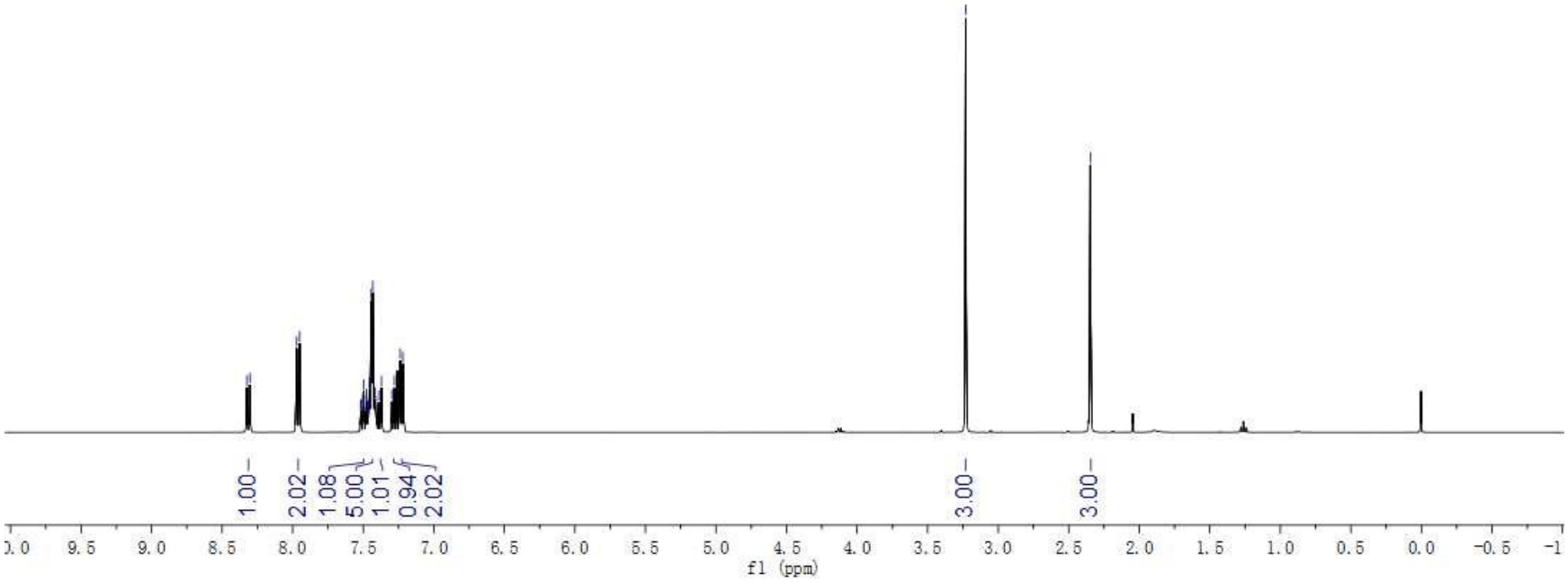
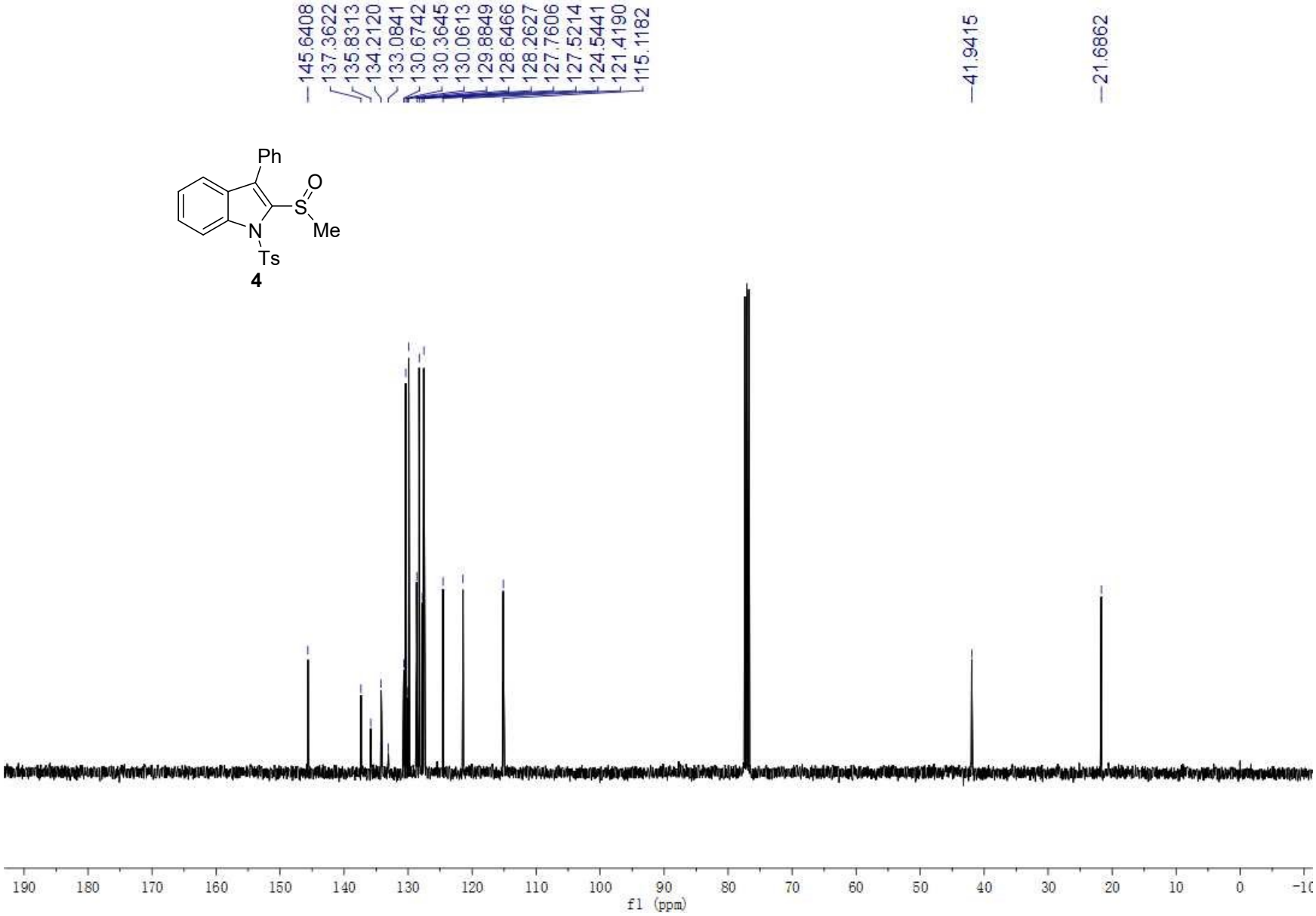
135.4375
135.4019
131.2651
129.7562
126.7354
124.5165
123.7211
122.9340
122.6052
119.5197
113.8040
31.6104
28.5699
24.8440
22.4811
21.5426
14.0746
N
Ts
3j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.3246
8.3033
7.9717
7.9508
7.5196
7.5164
7.5017
7.4984
7.4951
7.4803
7.4770
7.4625
7.4613
7.4555
7.4437
7.4384
7.4320
7.4166
7.4116
7.3895
7.3702
7.2969
7.2790
7.2385
7.2182
3.2298
2.3468


Ph
O
S
Me
N
Ts

4


1.00
2.02
1.08
5.00
1.01
0.94
2.02
3.00
3.00
f1 (ppm)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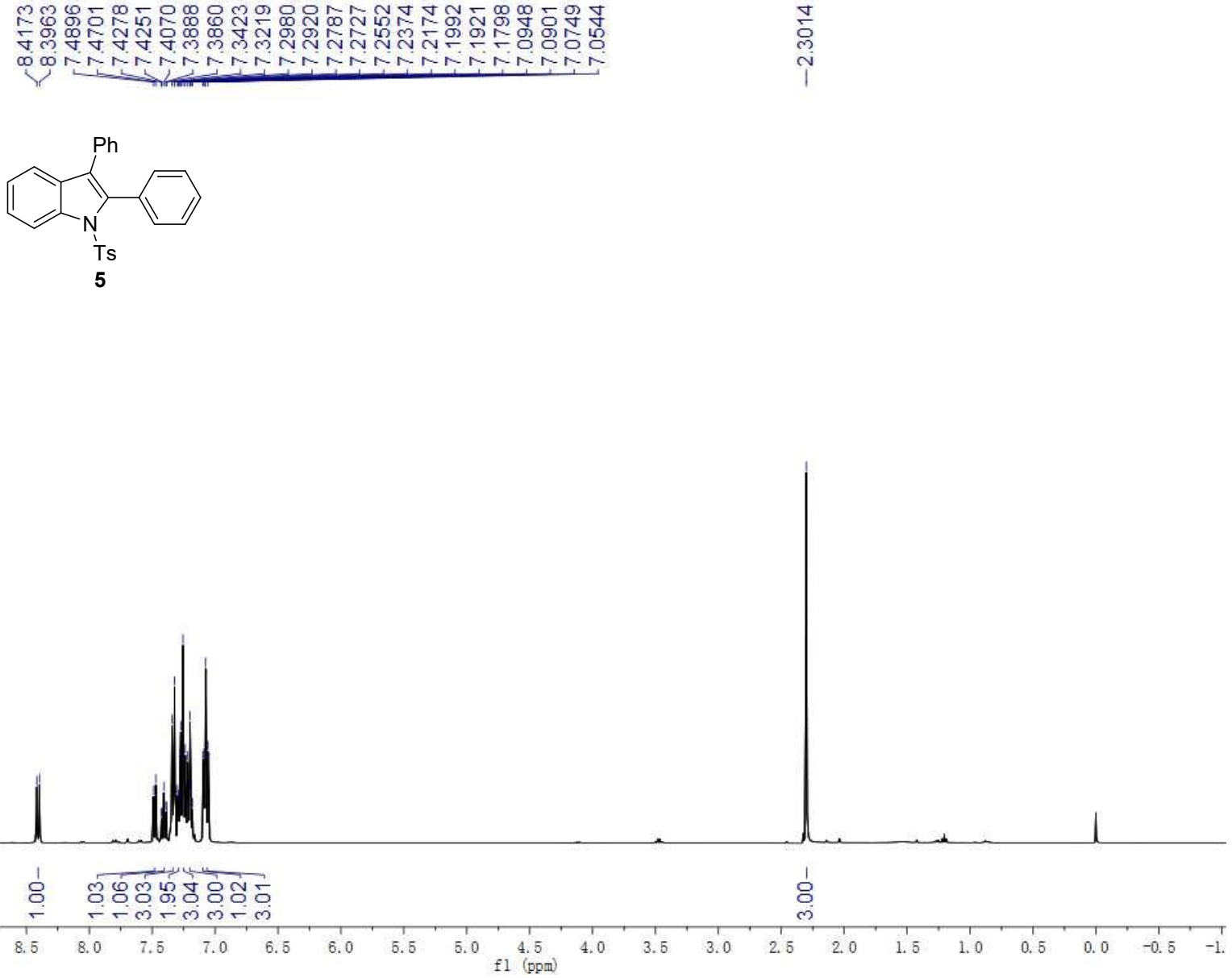
130.6742
130.3645
130.0613
129.8849
128.6466
128.2627
127.7606
127.5214
124.5441
121.4190
115.1182
41.9415
21.6862
Ph
O
S
Me
N
Ts
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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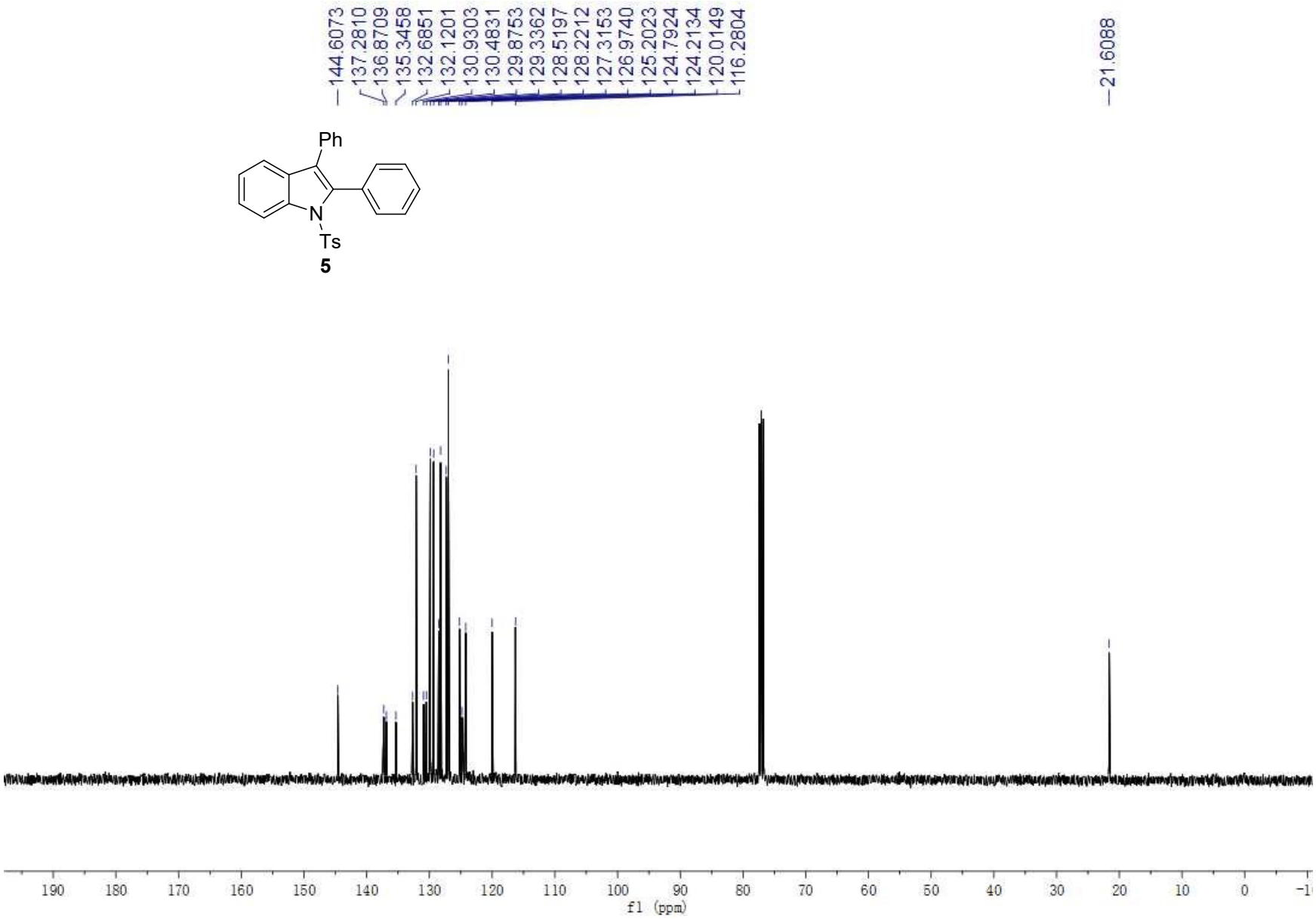
7.4896
7.4701
7.4278
7.4251
7.4070
7.3888
7.3860
7.3423
7.3219
7.2980
7.2920
7.2787
7.2727
7.2552
7.2374
7.2174
7.1992
7.1921
7.1798
7.0948
7.0901
7.0749
7.0544
2.3014
Ph
N
Ts
1.00
1.03
1.06
3.03
1.95
3.04
3.00
1.02
3.01
3.00
f1 (ppm)

5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136.8709
135.3458
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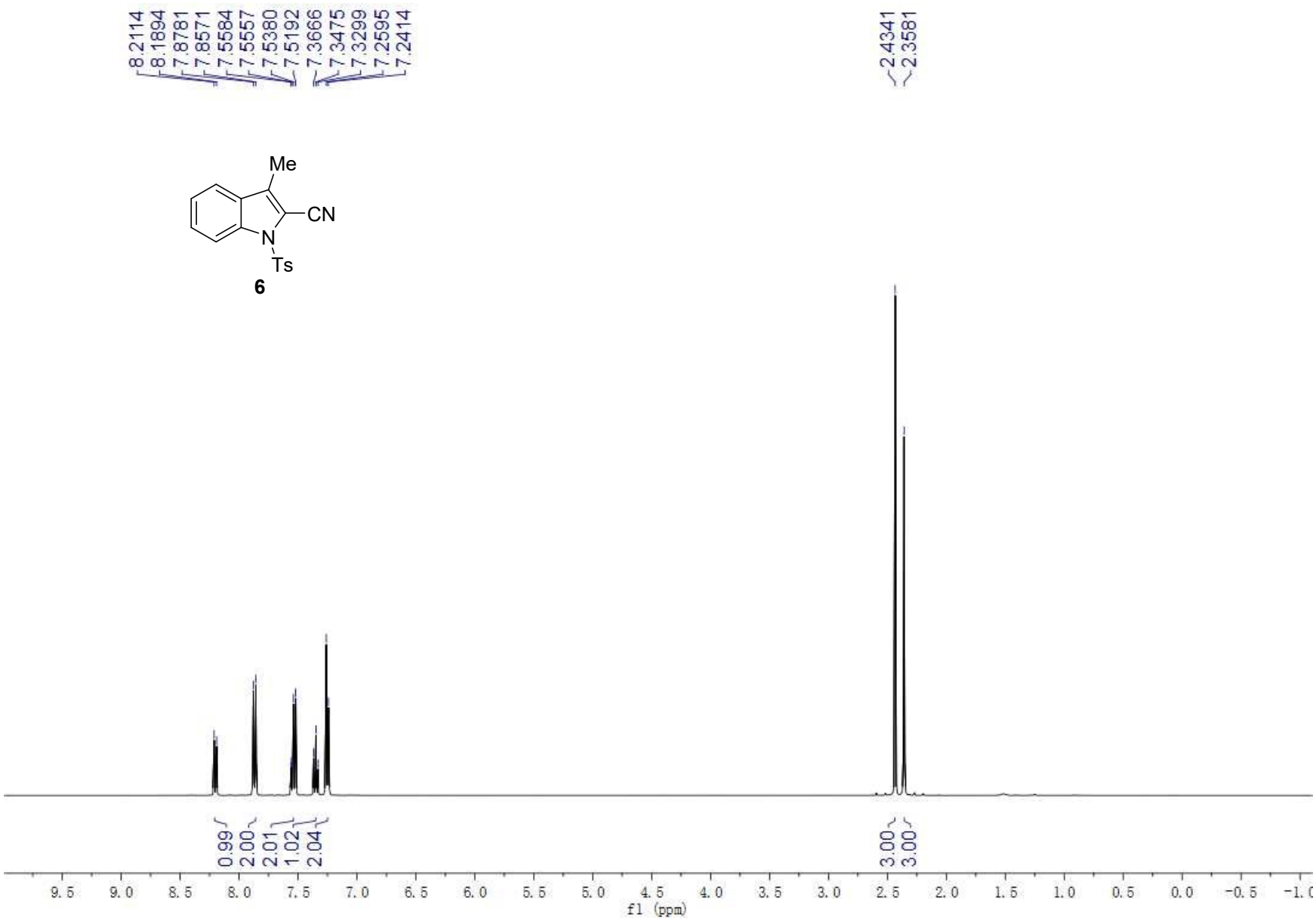
132.1201
130.9303
130.4831
129.8753
129.3362
128.5197
128.2212
127.3153
126.9740
125.2023
124.7924
124.2134
120.0149
116.2804
21.6088
Ph
N
Ts
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.5584
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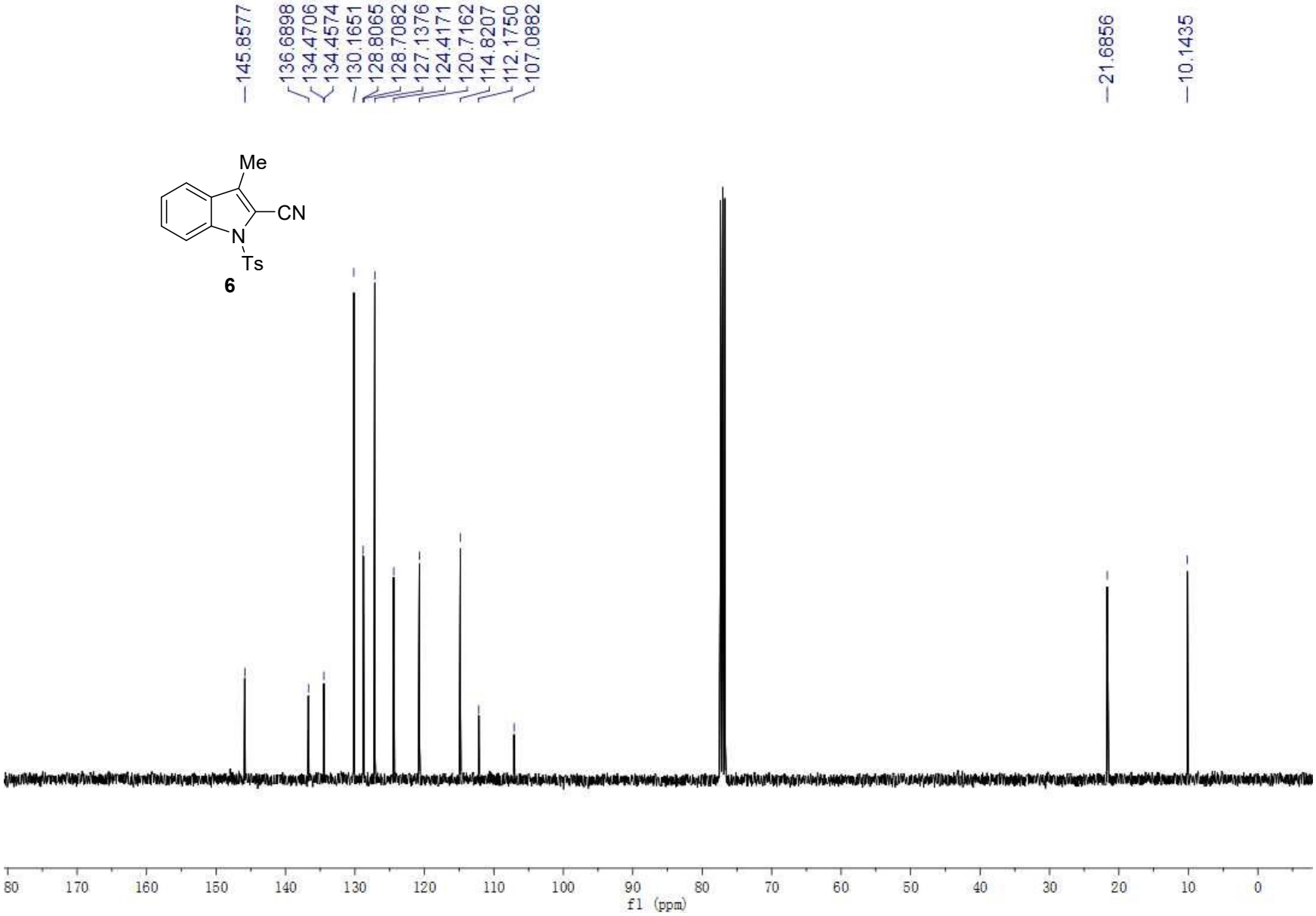
7.5380
7.5192
7.3666
7.3475
7.3299
7.2595
7.2414
2.4341
2.3581
Me
CN
N
Ts
6
0.99
2.00
2.01
1.02
2.04
3.00
3.00
f1 (ppm)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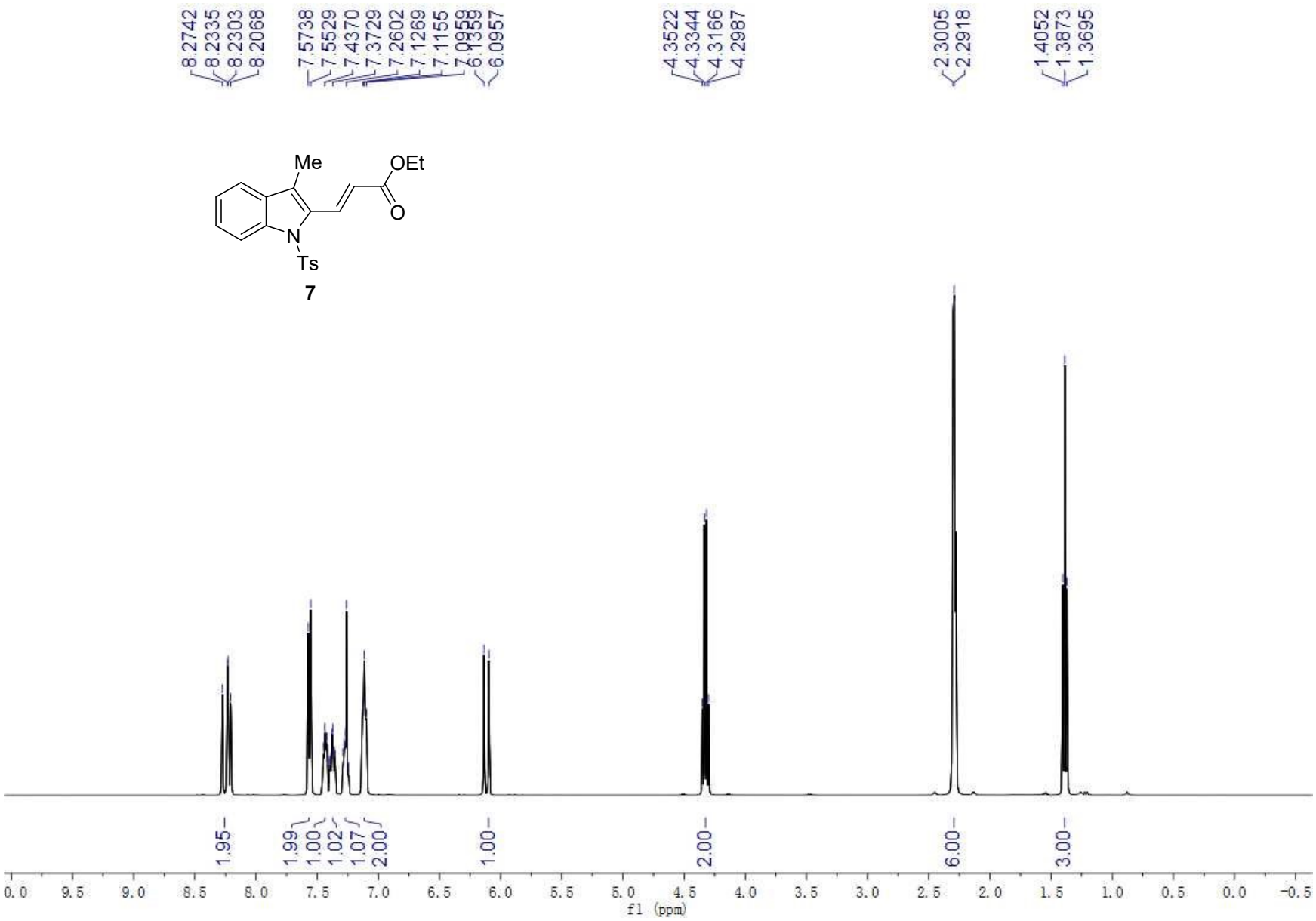
128.7082
127.1376
124.4171
120.7162
114.8207
112.1750
107.0882
21.6856
10.1435
Me
CN
N
Ts
6
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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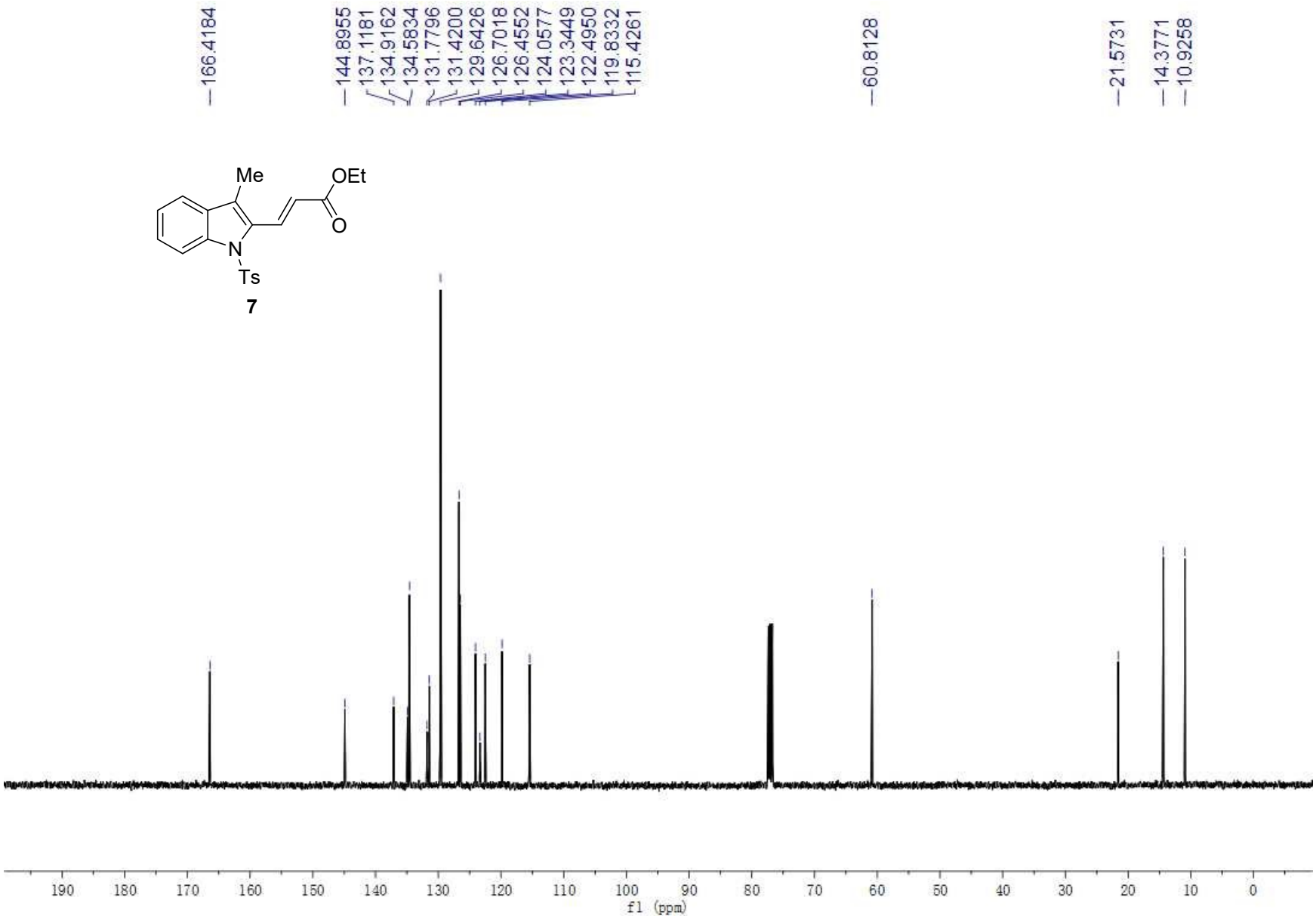
8.2335
8.2303
8.2068
7.5738
7.5529
7.4370
7.3729
7.2602
7.1269
7.1155
7.0959
7.0958
6.1359
6.0957
4.3522
4.3344
4.3166
4.2987
2.3005
2.2918
1.4052
1.3873
1.3695
Me
OEt
O
N
Ts
7
1.95
1.99
1.00
1.02
1.07
2.00
1.00
2.00
6.00
3.00
f1 (ppm)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134.5834
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131.4200
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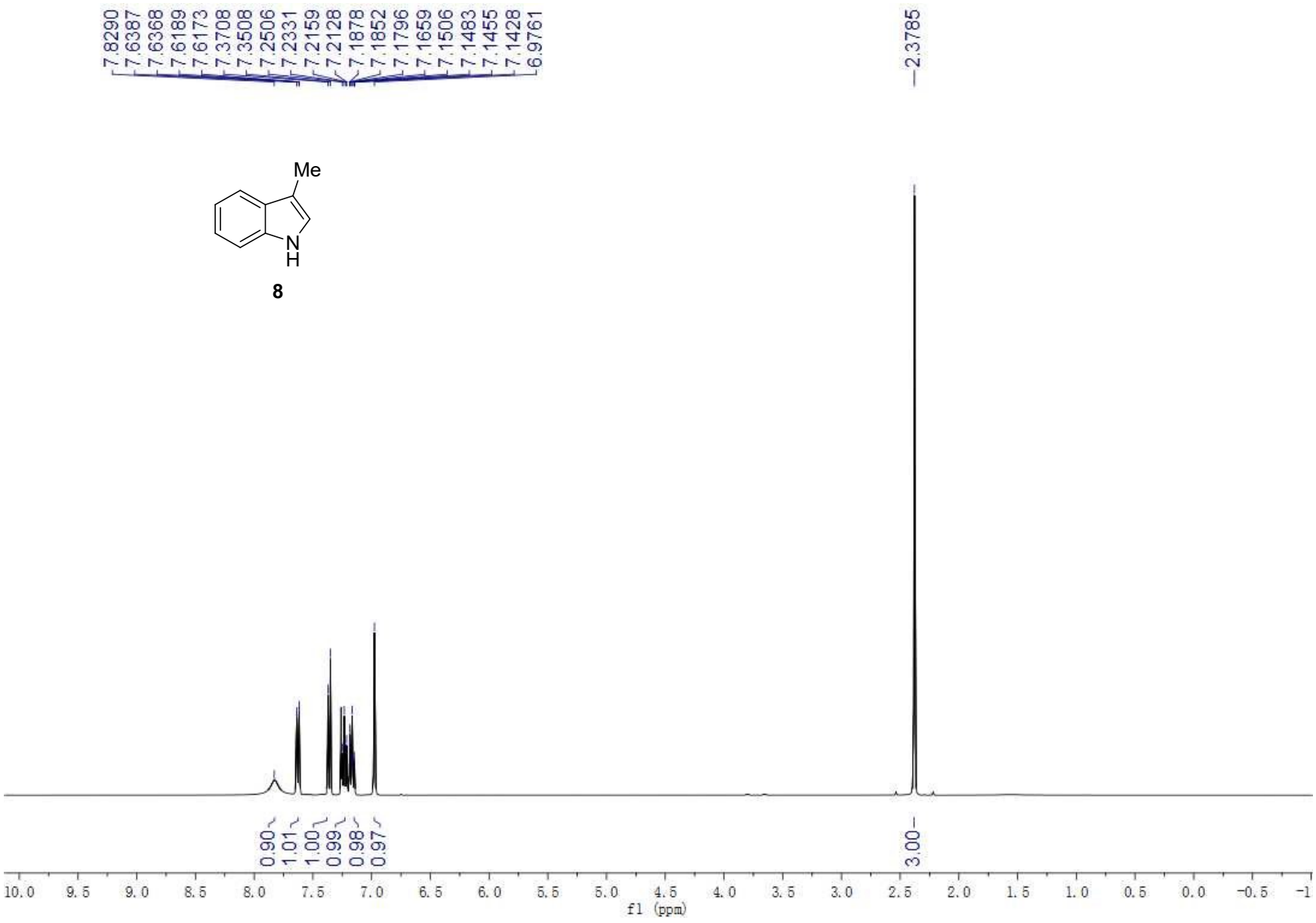
126.7018
126.4552
124.0577
123.3449
122.4950
119.8332
115.4261
60.8128
21.5731
14.3771
10.9258
Me
OEt
O
N
Ts
7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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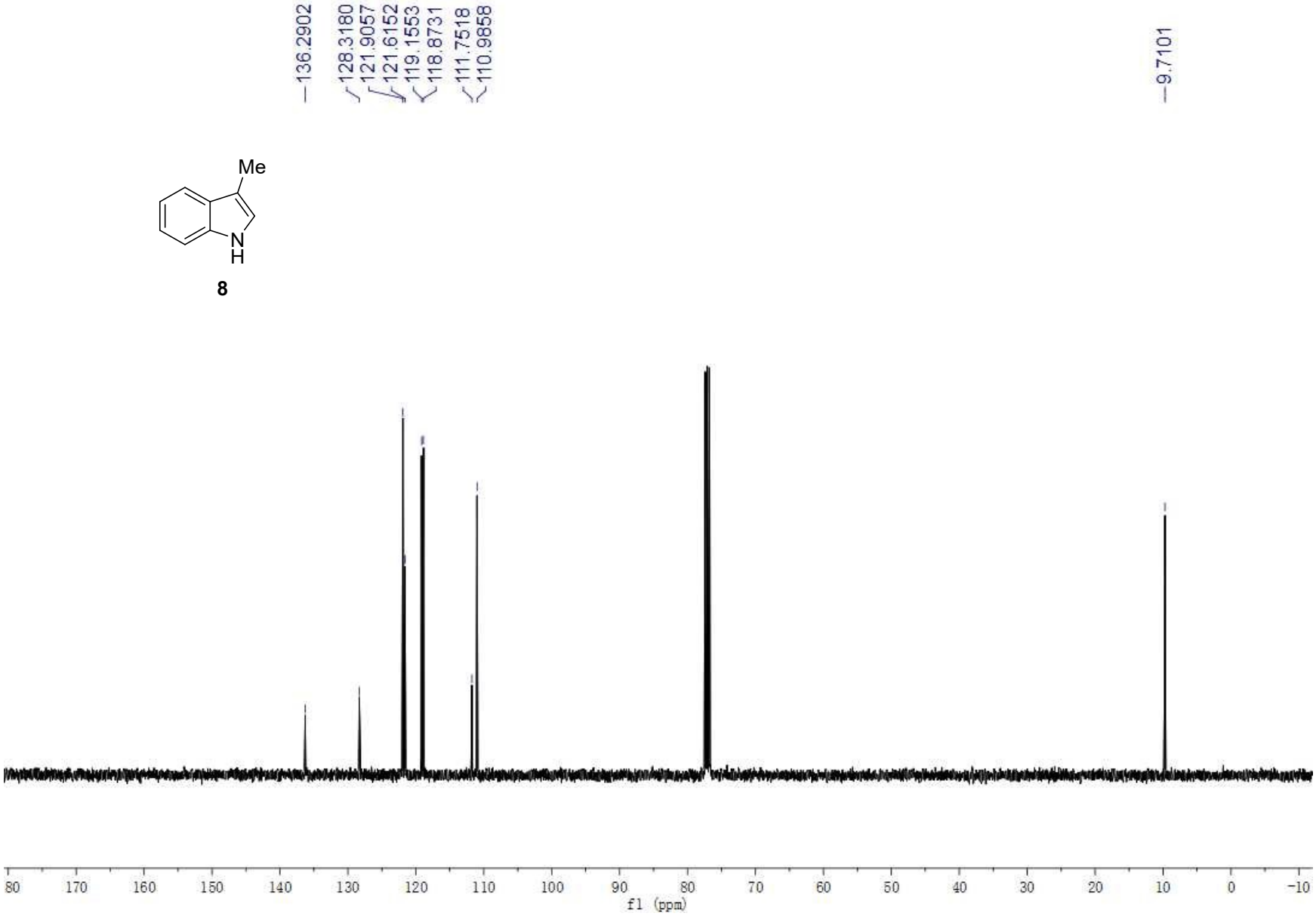
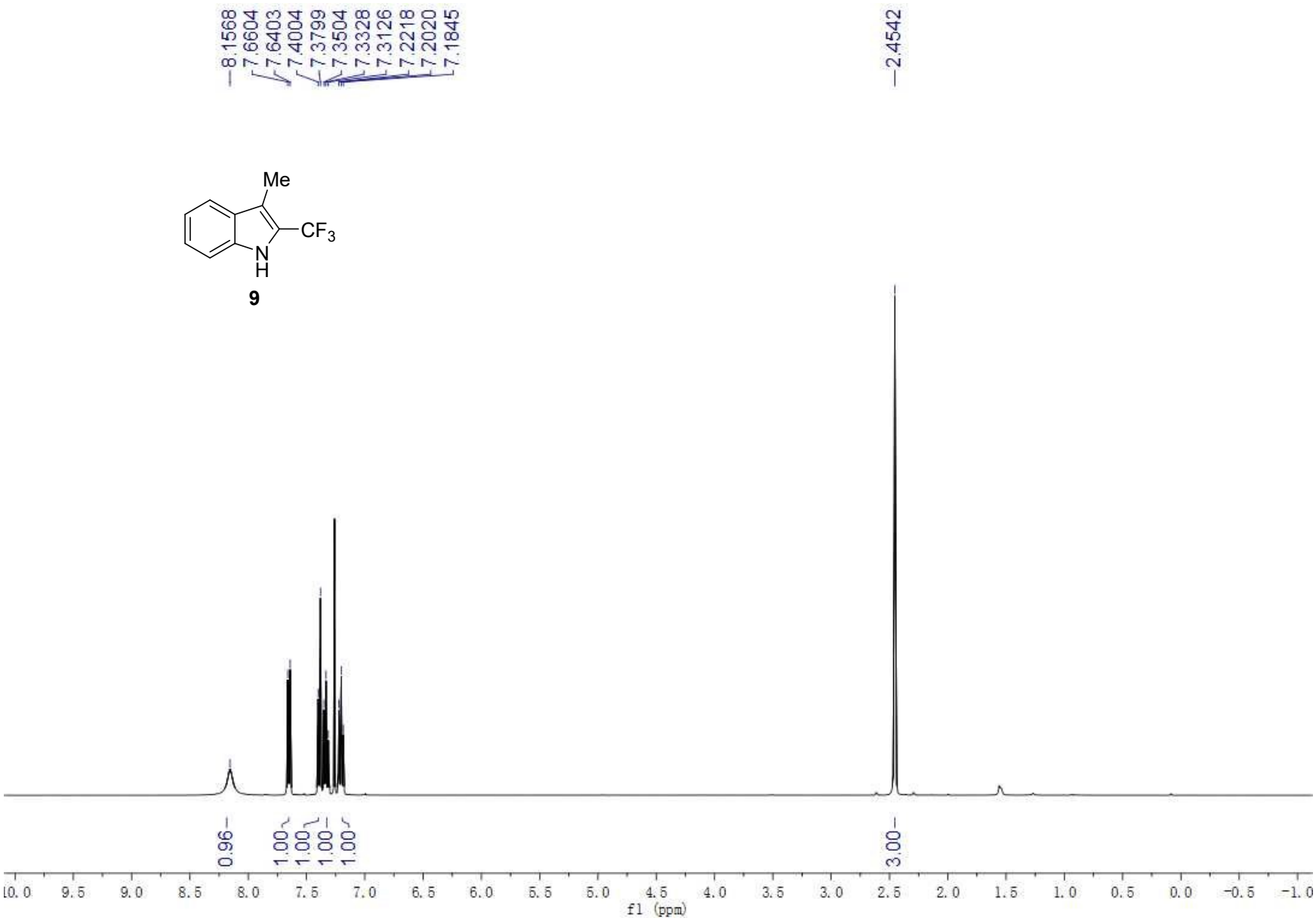
7.6368
7.6189
7.6173
7.3708
7.3508
7.2506
7.2331
7.2159
7.2128
7.1878
7.1852
7.1796
7.1659
7.1506
7.1483
7.1455
7.1428
6.9761
2.3785
Me
N
H
0.90
1.01
1.00
0.99
0.98
0.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

8


136.2902
128.3180
121.9057
121.6152
119.1553
118.8731
111.7518
110.9858
9.7101
Me
N
H
8
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.6403
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7.3799
7.3504
7.3328
7.3126
7.2218
7.2020
7.1845
2.4542
Me
CF3
N
H
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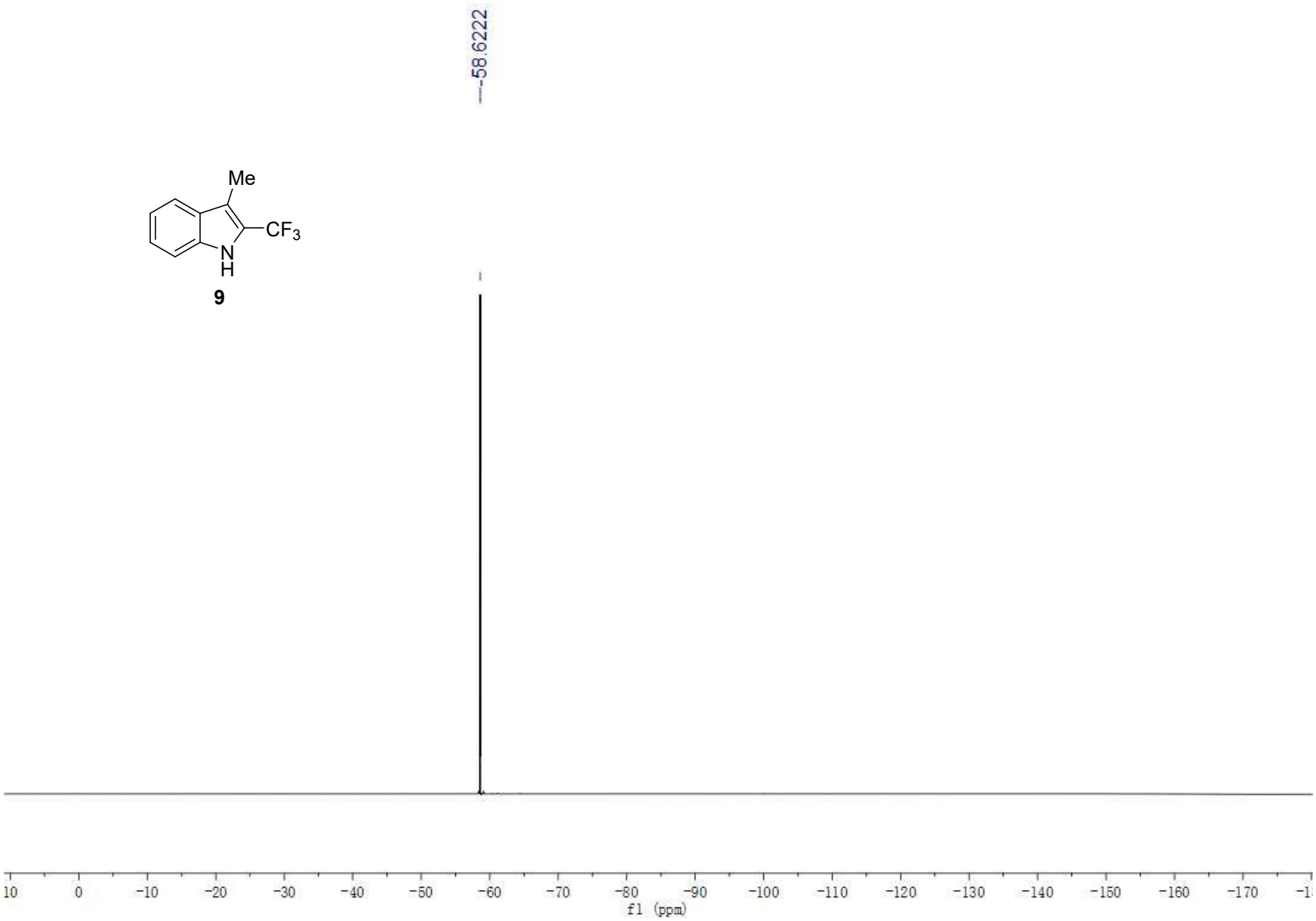
1.00
1.00
1.00
1.00
3.00
f1 (ppm)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CF3
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H
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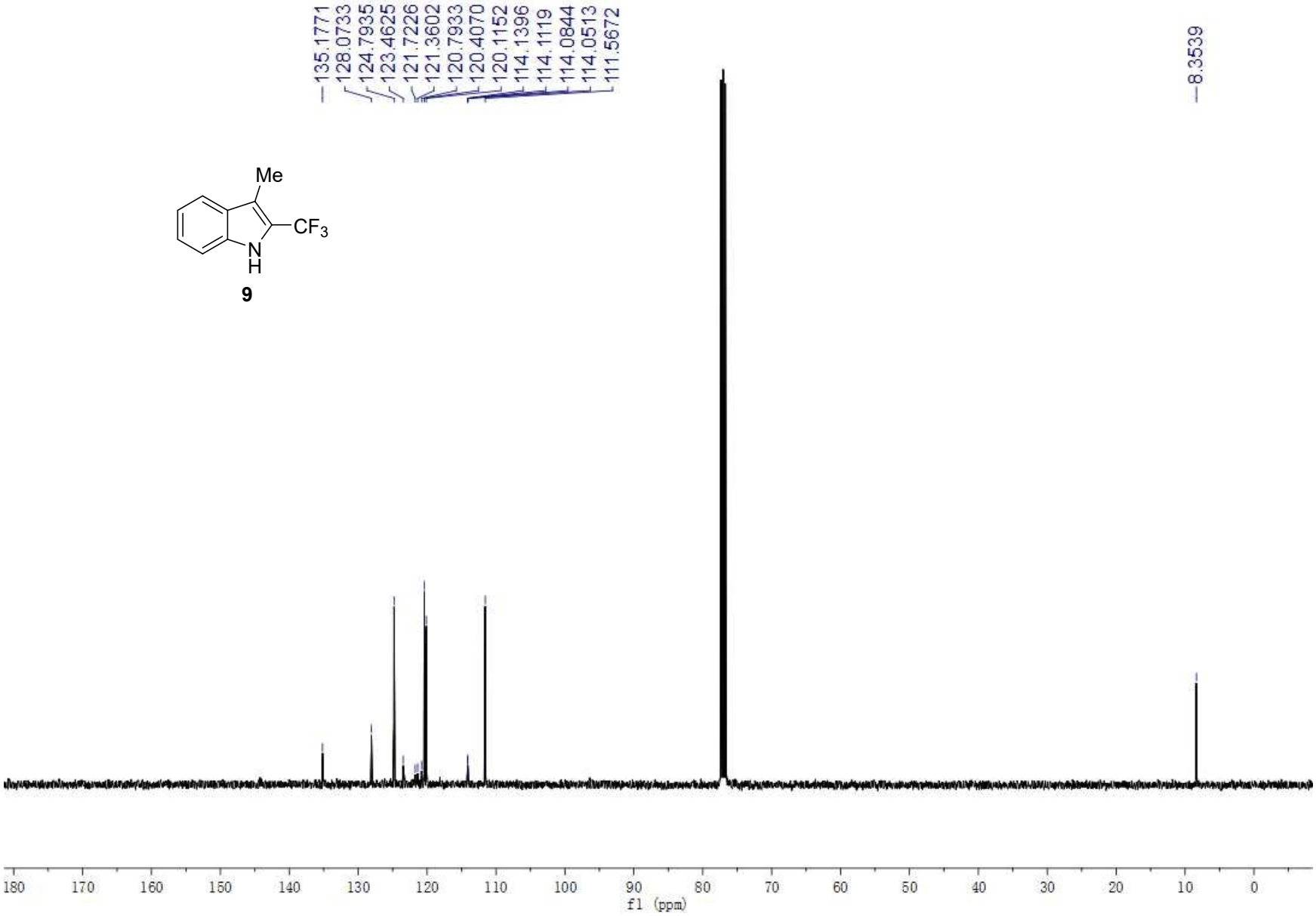
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

9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121.3602
120.7933
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120.1152
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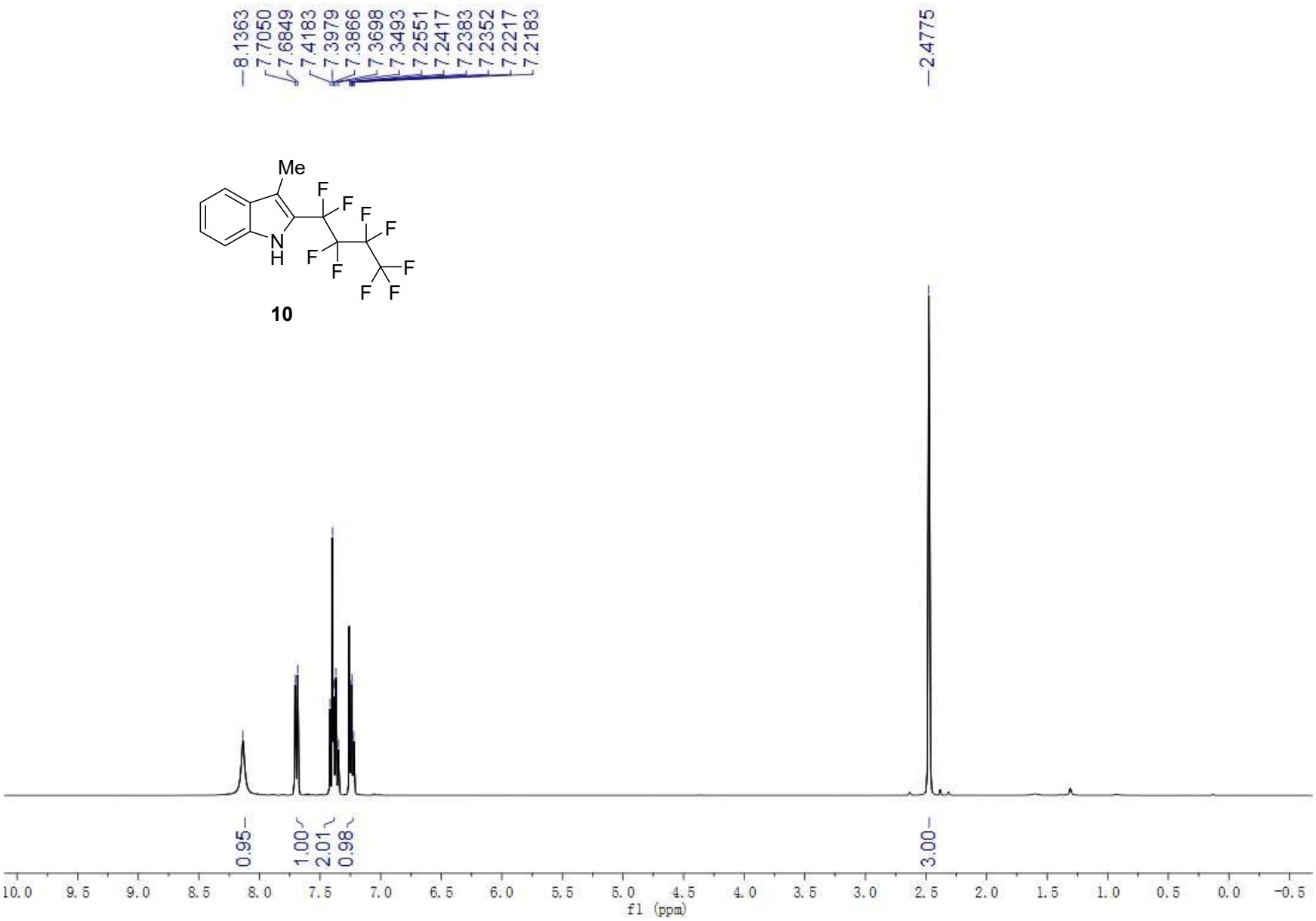
114.1119
114.0844
114.0513
111.5672
8.3539
Me
CF3
N
H
9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3979
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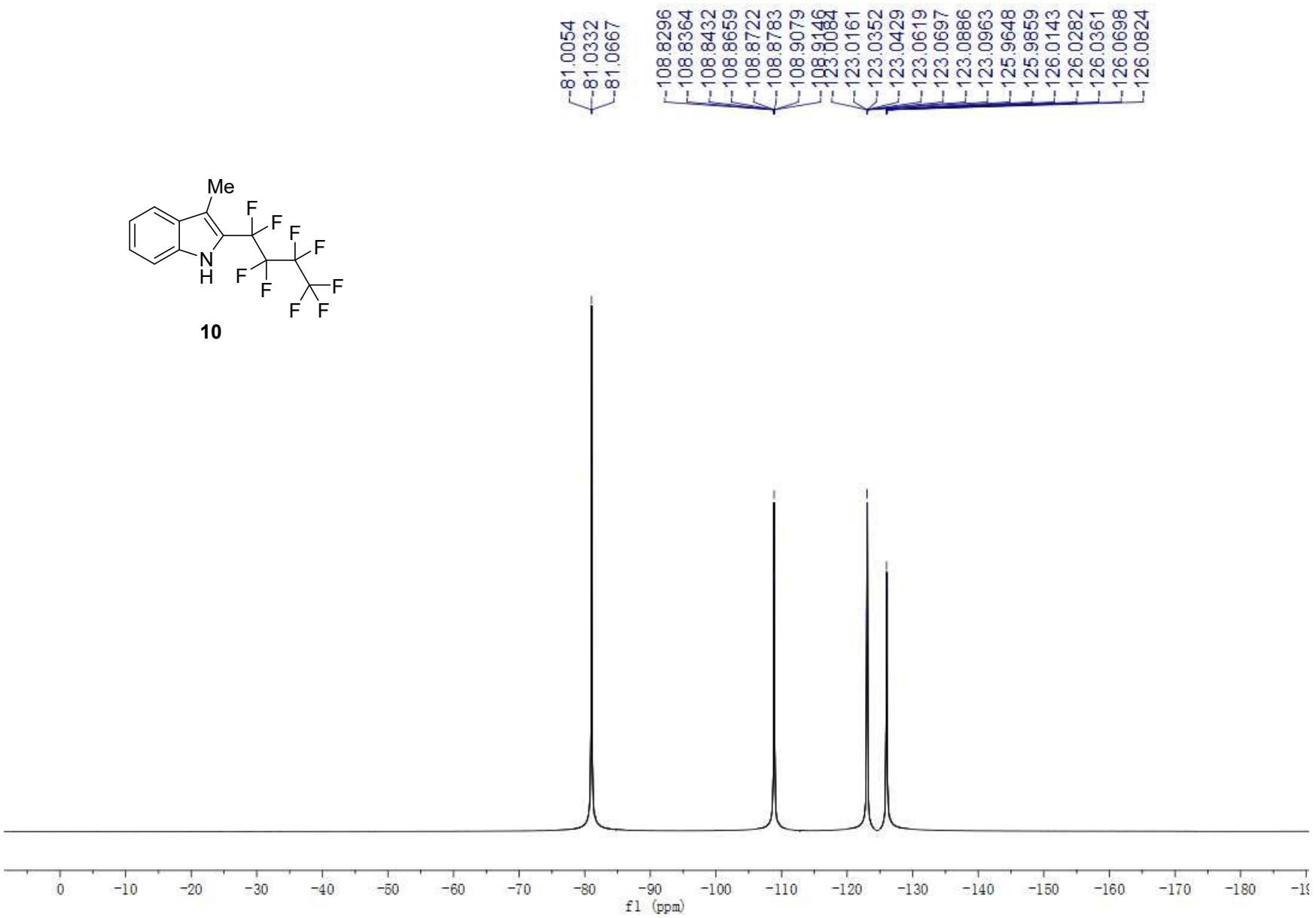
7.3698
7.3493
7.2551
7.2417
7.2383
7.2352
7.2217
7.2183
2.4775
Me
F
F
F
F
F
F
F
F
F
F
N
H
0.95
1.00
2.01
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

10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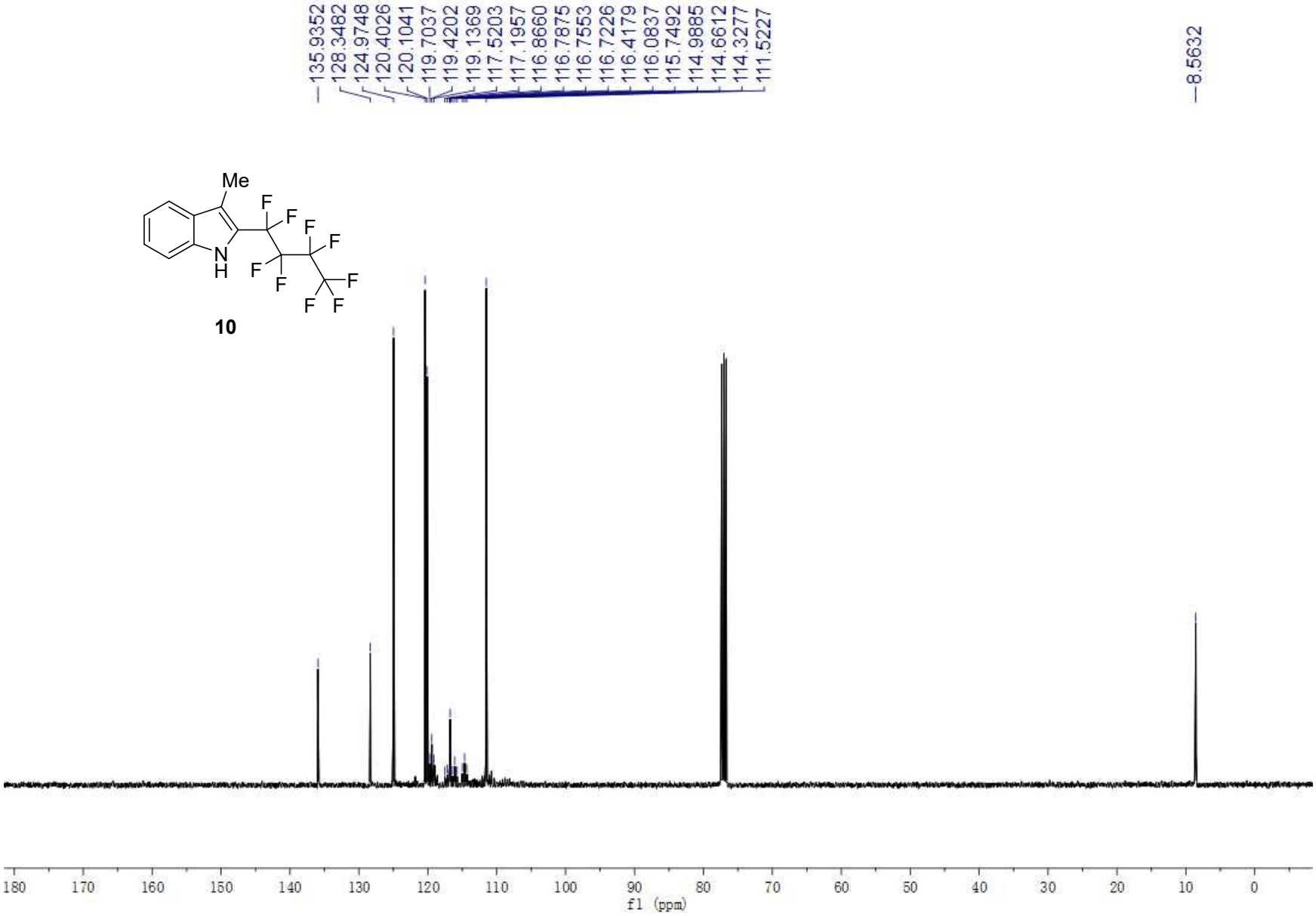
-81.0332
-81.0667
-108.8296
-108.8364
-108.8432
-108.8659
-108.8722
-108.8783
-108.9079
-123.0084
-123.0161
-123.0352
-123.0429
-123.0619
-123.0697
-123.0886
-123.0963
-125.9648
-125.9859
-126.0143
-126.0282
-126.0361
-126.0698
-126.0824
Me
F
F
F
F
F
F
F
F
F
N
H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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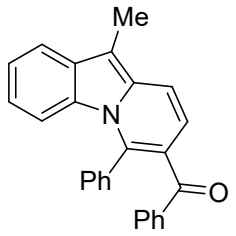
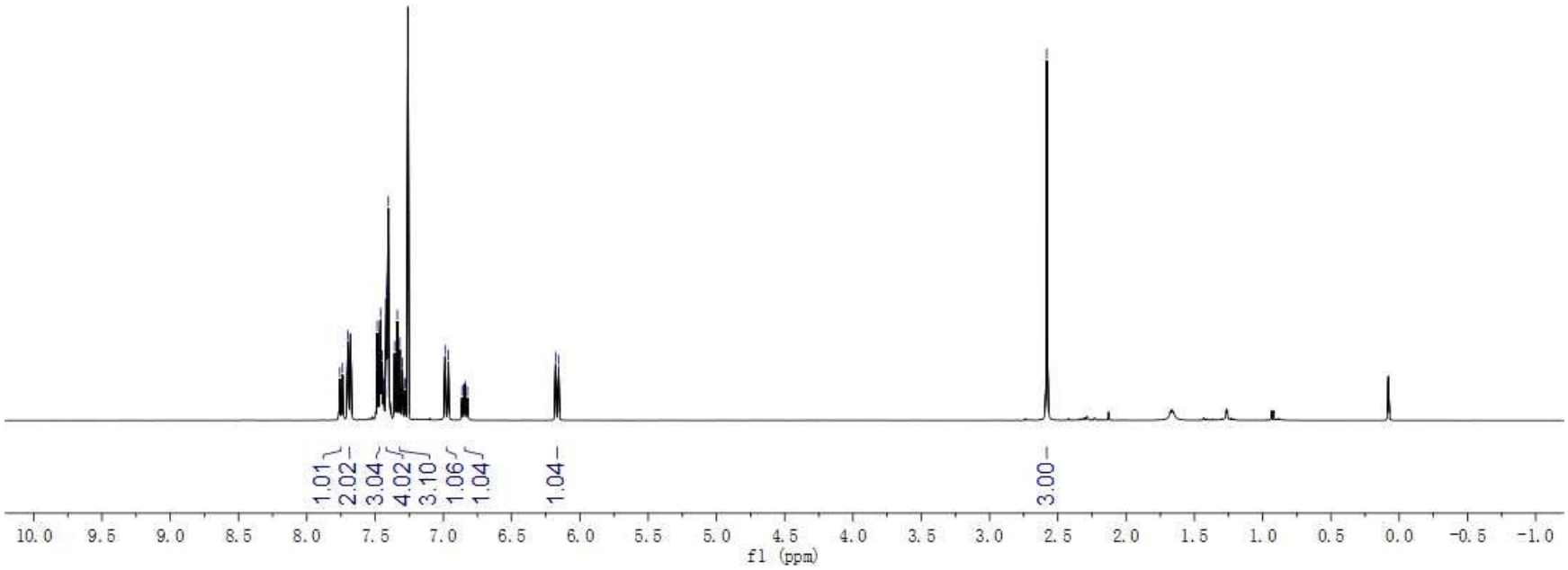
124.9748
120.4026
120.1041
119.7037
119.4202
119.1369
117.5203
117.1957
116.8660
116.7875
116.7553
116.7226
116.4179
116.0837
115.7492
114.9885
114.6612
114.3277
111.5227
8.5632
Me
F
F
F
F
F
F
F
F
F
N
H
10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7585
7.7384
7.6979
7.6769
7.4838
7.4656
7.4601
7.4522
7.4466
7.4175
7.4091
7.4028
7.3565
7.3369
7.3182
7.2994
7.2797
6.9873
6.9637
6.1782
6.1563

2.5809


Me
N
Ph
O
Ph

11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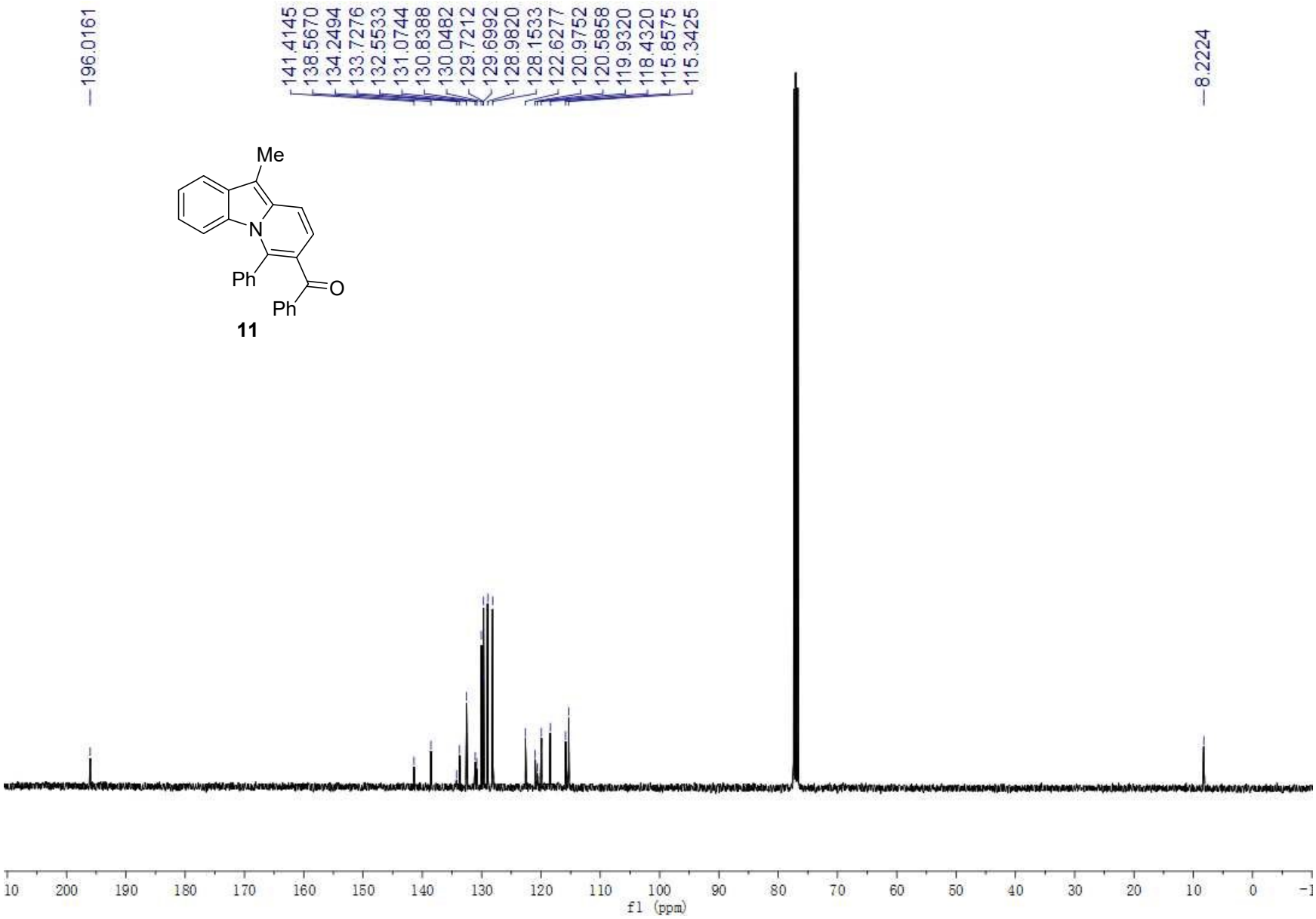
2.02
3.04
4.02
3.10
1.06
1.04
1.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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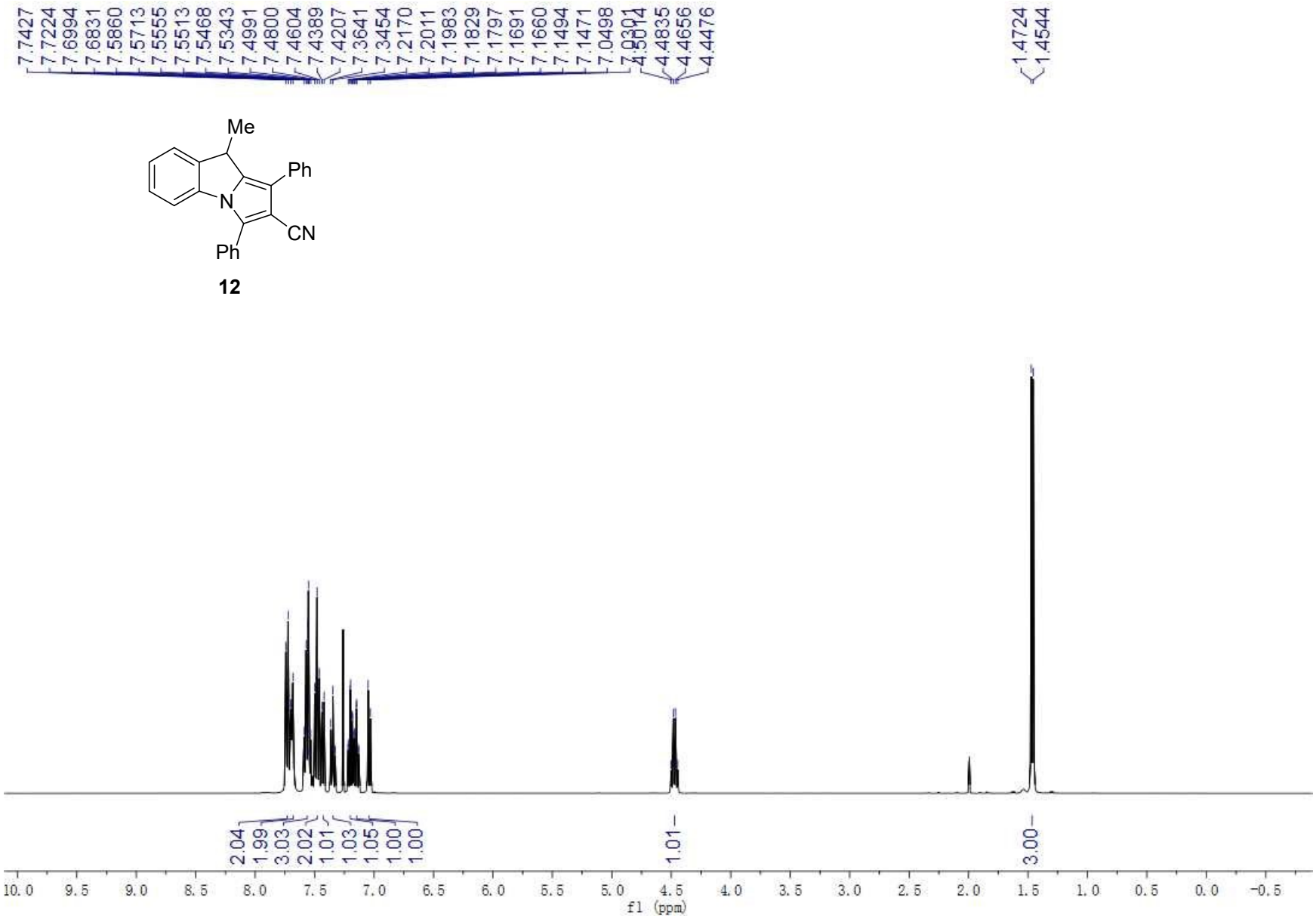
138.5670
134.2494
133.7276
132.5533
131.0744
130.8388
130.0482
129.7212
129.6992
128.9820
128.1533
122.6277
120.9752
120.5858
119.9320
118.4320
115.8575
115.3425
8.2224
Me
N
Ph
O
Ph
11
f1 (ppm)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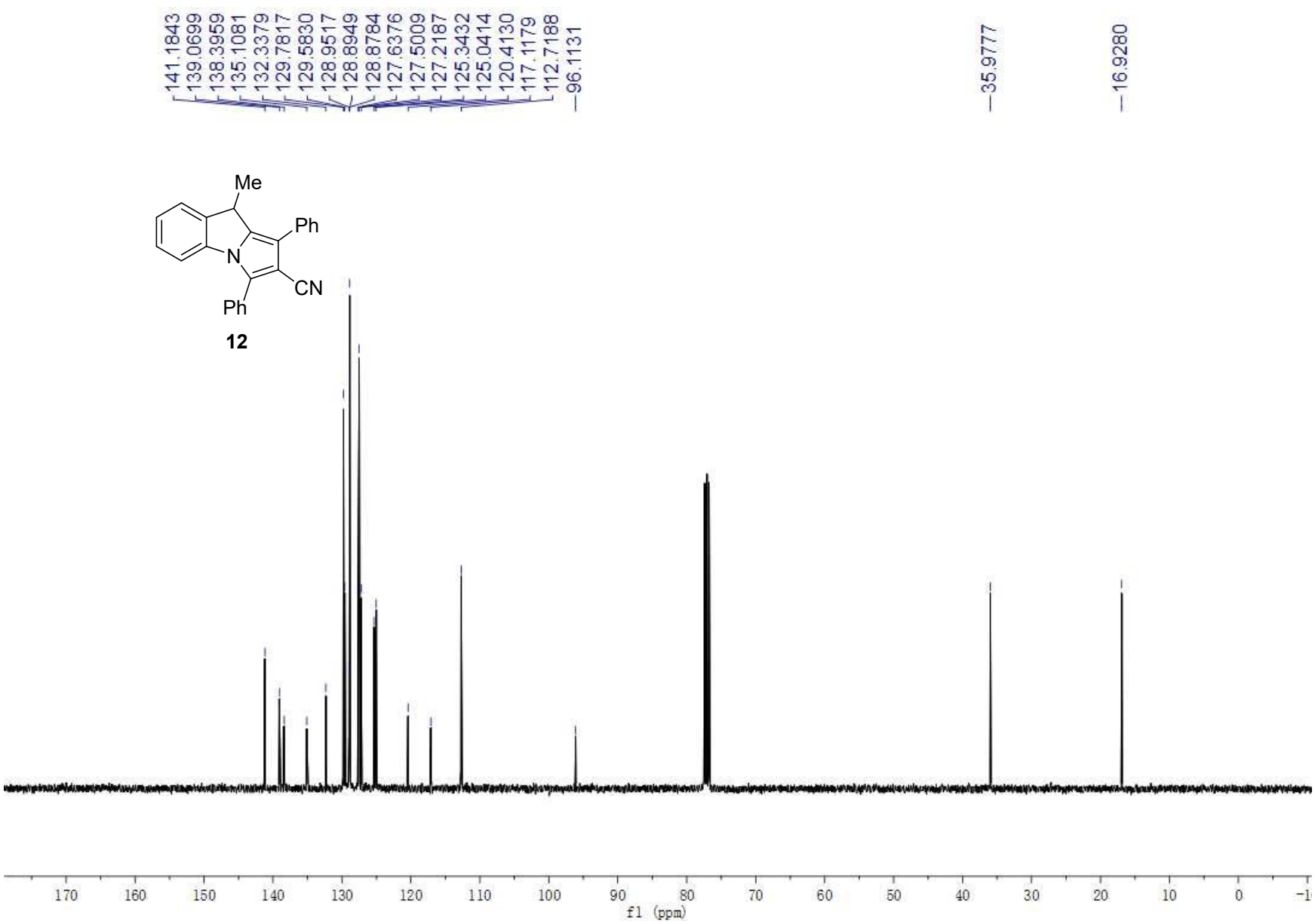
7.7224
7.6994
7.6831
7.5860
7.5713
7.5555
7.5513
7.5468
7.5343
7.4991
7.4800
7.4604
7.4389
7.4207
7.3641
7.3454
7.2170
7.2011
7.1983
7.1829
7.1797
7.1691
7.1660
7.1494
7.1471
7.0498
4.4835
4.4656
4.4476
1.4724
1.4544
Me
Ph
N
CN
Ph
12
2.04
1.99
3.03
2.02
1.01
1.03
1.05
1.00
1.00
1.01
3.00
10.0
9.5
9.0
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
f1 (ppm)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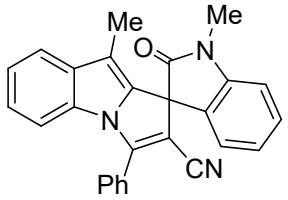
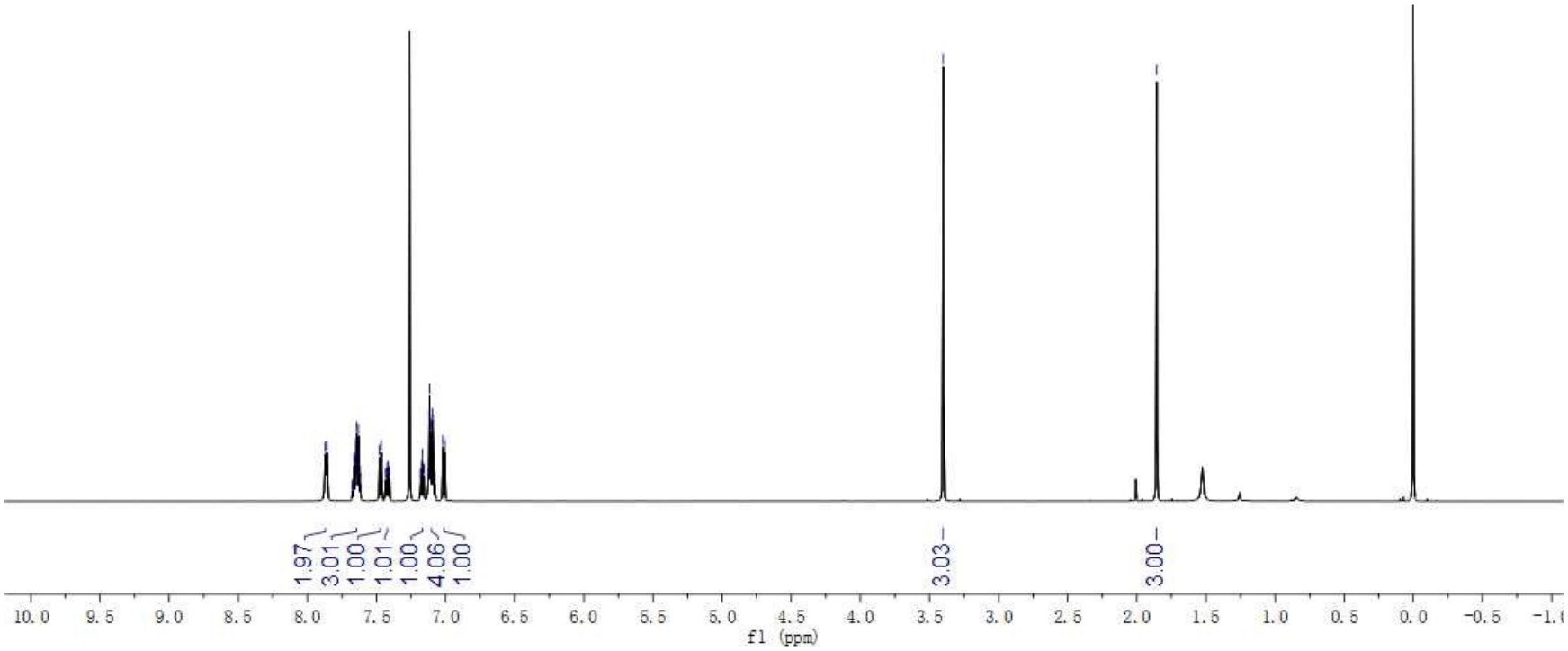
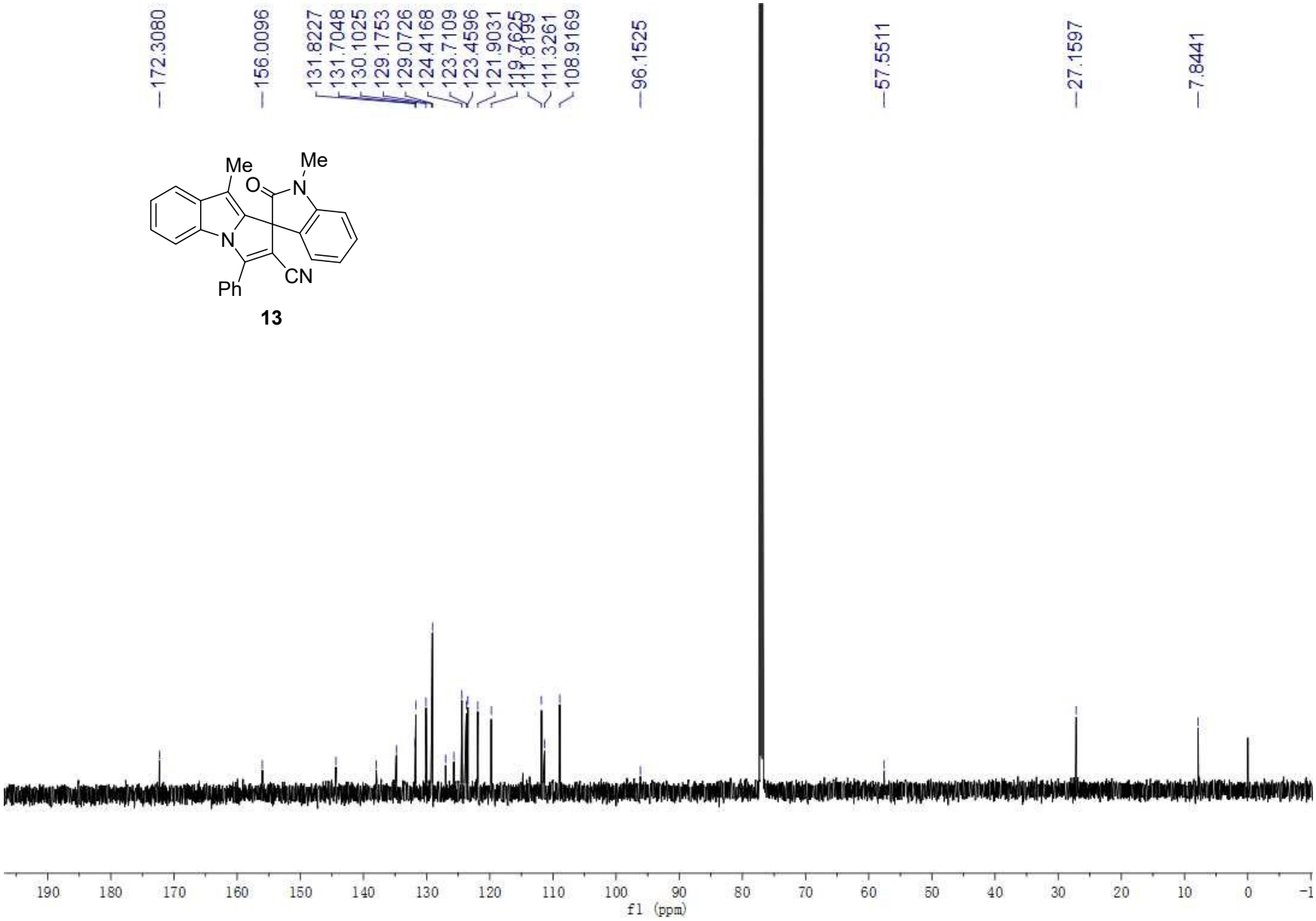
138.3959
135.1081
132.3379
129.7817
129.5830
128.9517
128.8949
128.8784
127.6376
127.5009
127.2187
125.3432
125.0414
120.4130
117.1179
112.7188
96.1131
35.9777
16.9280
Me
Ph
N
CN
Ph
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.8703
7.8591
7.6609
7.6518
7.6493
7.6463
7.6430
7.6301
7.6195
7.6160
7.4779
7.4649
7.4328
7.4294
7.4212
7.4166
7.4082
7.4049
7.1820
7.1794
7.1709
7.1686
7.1580
7.1553
7.1271
7.1182
7.1150
7.1067
7.1045
7.0935
7.0909
7.0785
7.0193
1.8555


Me
O
N
Me
N
CN
Ph

13


1.97
3.01
1.00
1.01
1.00
4.06
1.00
3.03
3.00
10.0
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
f1 (ppm)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131.8227
131.7048
130.1025
129.1753
129.0726
124.4168
123.7109
123.4596
121.9031
119.7625
111.8199
111.3261
108.9169
96.1525
57.5511
27.1597
7.8441
Me
O
Me
N
N
Ph
CN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

13