Supporting Information for

(3+2)-Annulation of *p*-Quinamine and Aryne : A Strategy to Construct the Multisubstituted Hydrocarbazoles

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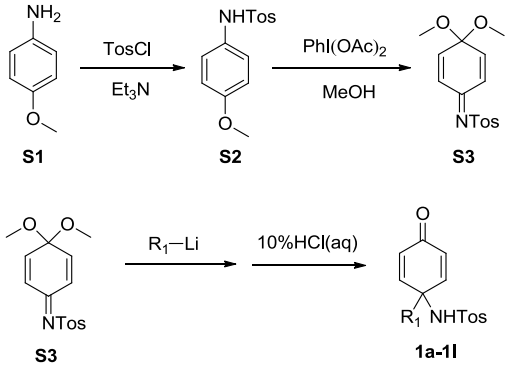
TABLE OF CONTENTS

1. General information.

Solvents were purified and dried by standard methods prior to use. Molecular sieves were activated prior to use by heating under the reduced pressure and commercially available 18-crown-6 was recrystallized from anhydrous MeCN. Other commercially available reagents were used without further purification unless otherwise noted. All syntheses of complex were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined with a digital Koffer apparatus and were uncorrected. ^{1}H and ^{13}C NMR data were recorded on a 400 MHz spectrometer using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High-resolution mass spectra (HRMS) were obtained on a FT-ICR spectrometer.

2. Preparation of starting materials.

1) *p*-quinamine **1a-1l** were prepared according to the previously reported procedure.[1]



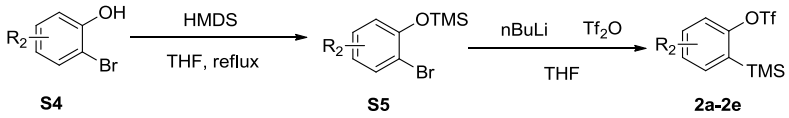
To a solution of *p*-anisidine **S1** (10 mmol, 1.0 equiv.) in DCM (100 mL) was added 4-toluene sulfonyl chloride (12 mmol, 1.2 equiv.) and Et_3N (12 mmol, 1.2 equiv.), at 0 ℃, then the reaction system was moved to the room temperature and stirred for 20 hours. After the reaction was complete, the mixture was added saturated NH_4Cl. The aqueous layer was extracted with DCM for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give sulfamide **S2** (2.50g, 90%) as a white solid.

To an oven-dried two necked flask, **S2** (2.50g, 9 mmol, 1.0 equiv.) and MeOH (100mL)

were added under N_2 atmosphere and cooled to 0 ℃. (Diacetoxyiodo)benzene (2.90g, 9 mmol, 1.0 equiv.) was added to this solution over 5 minutes, and keep the stirring for 1 hour. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and extracted with DCM three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give the residue which was purified by a silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give sulfimide **S3** (2.50g, 90%) as a pink solid.

To an oven-dried three necked flask, bromide (2.2 mmol, 1.1 equiv.) in THF (10 ml), were added under N_2 atmosphere. 0.8 ml of nBuLi (2.5M in hexane) was added to the system dropwise at -78 ℃, keeping stirring for about 1 hour, **S3** (2 mmol, 1.0 equiv.) in THF (10 mL), was added dropwise at -78 ℃, the mixture was stirred for another 2 hours at -78 ℃. Then, the mixture was quenched by solution of 10% HCl and stirred for 10 hours. The mixture was extracted with CH_2Cl_2 three times, dried over $MgSO_4$ and evaporated under reduced pressure. The compound was purified by column chromatography (petroleum ether /EtOAc = 10/1) to give **1a-1l**.

2) ortho-silyl aryltriflates **2a-2e** were prepared according to the previously reported procedure.[2]



S4 **S5** **2a-2e**

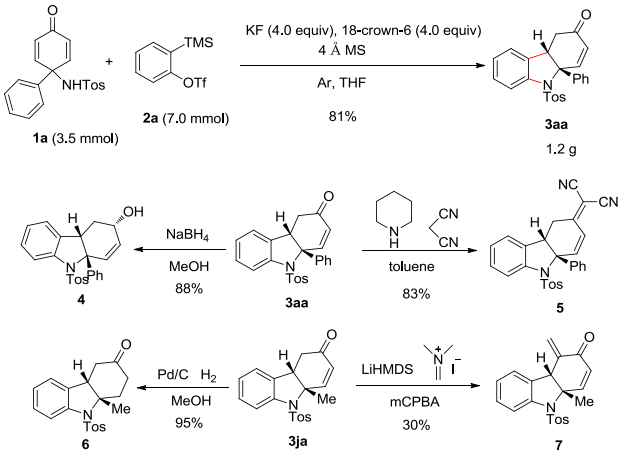
To an oven-dried two necked flask, 2-Bromophenol **S4** (20 mmol, 1.0 equiv) in THF (50 ml), HMDS (22 mmol 1.1 equiv) were added under N_2 atmosphere. After refluxing for 3 h, the system concentrated under reduced pressur, the crude product **S5** was obtained to try the next step without further purification.

THF (30.0 mL), and **S5** (10.0 mmol, 1.0 equiv.) were added to an oven-dried two necked flask under N_2 atmosphere and cooled to -78 ℃. 4 ml of nBuLi (2.5M in hexane) was added dropwise and the mixture was stirred for 2 hours at -78 ℃. Then trifluoromethanesulfonic anhydride (11 mmol, 1.1 equiv.) was added dropwise and the mixture was stirred for another 1h at -78 ℃. Then the mixture was quenched by sat. $NaHCO_3$ and stirred for another 4h at room temperature. The mixture was extracted with EtOAc three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to give **2a-2e**.

3. General procedure for the (3+2)-annulation.

The mixture of *p*-quinamine (0.2 mmol, 1.0 equiv.), KF (46mg, 0.8 mmol, 4.0 equiv.), 18-crown-6 (211 mg, 0.8 mmol, 4.0 equiv.) and activated 4 Å molecular sieve (50 mg) in a flash was evacuated and backfilled with Ar. for 3 times. Then northo-silyl aryltriflate's (0.6 mmol, 3.0 equiv.) in THF (5 mL) was added to the above system and stirred at ambient temperature for 10 hours. Then the reaction mixture was directly concentrated with evaporator and the residue was purified by silica gel column chromatography, affording the desire hydrocarbazoles products.

4. Scale-up and Transformation of Hydrocarbazole 3aa and 3ja.



1) The procedure of scale-up transformation of **3aa**

The mixture of *p*-quinamine (1.19 g, 3.5 mmol, 1.0 equiv), KF (813mg, 14 mmol, 4.0 euqiv.), 18-crown-6 (3.70 g, 14 moml, 4.0 euqiv.) and activated 4 Å molecular sieve (0.50 g) in a flash was evacuated and backfilled with Ar. for 3 times. Then northo-silyl aryltriflate's (2.10 g, 7 mmol, 2.0 equiv.) in THF (100 mL) was added to the above system and stirred at ambient temperature for 10 hours. After the reaction was complete (monitored by TLC), the reaction mixture was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1) to afford 1.20 g hydrocarbazole **3aa** in 81% yield.

2) The procedure of getting product **4.**

Hydrocarbazole **3aa** (120 mg, 0.3 mmol, 1.0 equiv.) was dissolved in MeOH (15 mL) and was added $NaBH_4$ (11 mg, 0.33 mmol, 1.1 equiv) at 0 ℃, then the reaction system was moved to the room temperature and stirred for 2 hours (monitored by TLC). After the reaction

was complete, the mixture was quenched with saturated NH_4Cl. The aqueous layer was extracted with DCM for 3 times (10 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 2:1) to give product **4** (110 mg, 88%) as a white solid.

3) The procedure of getting product **5.**

Hydrocarbazole **3aa** (200 mg, 0.5 mmol, 1.0 equiv.) in toluene (50 mL), piperidine (82 mg, 1 mmol, 2.0 equiv.) and malononitrile (95 mg, 1.5 mmol, 3.0 equiv.) were added to a Dean–Stark apparatus, under Ar. atmosphere. After refluxing for 20 h , the system concentrated under reduced pressure , the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 4:1) to give product **5** (184 mg, 83%) as a green solid.

4) The procedure of getting product **6.**

To a stirred solution of Hydrocarbazole **3ja** (176mg 0.5 mmol, 1.0 equiv.) in methanol (20 mL) was added palladium (10%) on carbon (10 mg). Then the reaction mixture was stirred under an atmosphere of H_2 at room temperature for 10 h. The reaction mixture was then filtered on a silica pad and rinsed with EtOAc. After evaporation of solvent, the residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 2:1) to give product **6** (170 mg, 95%) as colourless oil.

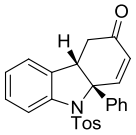
5) The procedure of getting product **7.**

Hydrocarbazole **3ja** (71mg, 0.2 mmol, 1.0 equiv.) in THF (30mL) was added to an oven-dried two necked flask under Ar. atmosphere and cooled to -78 ℃. 0.4 mL LiHMDS (1M in hexane) was added dropwise and the mixture was stirred for 5min at -78 ℃, then elevated the temperature to 0 ℃ and stirred for 1 hour. After that, Eschenmoser salt's (110 mg, 0.6 mmol, 3.0 equiv.) in THF solvent was added dropwise at -78 ℃ and the mixture was stirred for another 1 hour at room temperature. Then the mixture was quenched by sat. $NaHCO_3$. The mixture was extracted with EtOAc three times, dried over Na_2SO_4 and concentracted under reduced pressure. The crude product was obtained to try the next step without further purification.

The crude product's DCM/sat.$NaHCO_3$ (2:1) solvent was added the mCPBA (80 mg 0.4 mmol, 2.0 equiv.) (85%) and the mixture was stirred violently. 20 Minutes later, 1M NaOH

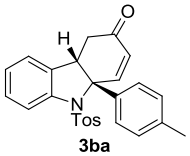
(aq) was added to the system, then the mixture was extracted with EtOAc three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 5:1) to give product **7** (22 mg, 30%) as a white solid.

5. Characterization data for all products.



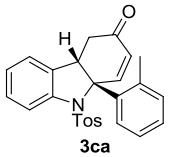
3aa

Compound **3aa** (72 mg 86%) was obtained as a white solid according to the general procedure. Mp: 203−206 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.41 – 7.32 (m, 3H), 7.28 (dd, J = 11.8, 4.6 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.10 – 7.00 (m, 2H), 6.25 (d, J = 10.4 Hz, 1H), 3.82 (t, J = 6.2 Hz, 1H), 2.51 (dd, J = 16.5, 5.5 Hz, 1H), 2.38 (s, 3H), 2.27 (dd, J = 16.5, 7.1 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.2, 144.7, 144.2, 141.1, 140.8, 137.5, 130.8, 130.0, 129.5, 129.0, 128.6, 128.3, 126.8, 126.6, 124.0, 123.5, 114.8, 74.6, 51.3, 38.1, 21.5. **HRMS** (ESI): m/z $[M+NH_4]^+$ calculated for $C_{25}H_{25}N_2O_3S$: 433.1580, found: 433.1581.



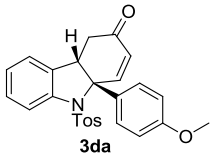
3ba

Compound **3ba** (86 mg 94%) was obtained as a white solid according to the general procedure. Mp: 239−245 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.43 (dd, J = 10.4, 0.5 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.08 – 6.98 (m, 2H), 6.23 (d, J = 10.4 Hz, 1H), 3.80 (t, J = 6.2 Hz, 1H), 2.51 (dd, J = 16.5, 5.5 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.27 (dd, J = 16.5, 7.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 144.9, 144.2, 140.8, 138.1, 138.1, 137.5, 130.8, 129.8, 129.4, 129.2, 128.9, 126.9, 126.5, 123.9, 123.5, 114.8, 74.5, 51.2, 38.1, 21.5, 21.0. **HRMS** (ESI): m/z $[M+NH_4]^+$ calculated for $C_{26}H_{27}N_2O_3S$: 447.1737, found: 447.1738.



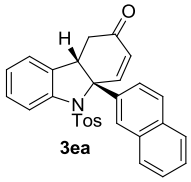
3ca

Compound **3ca** (65 mg 76%) was obtained as a white solid according to the general procedure. Mp: 251−254 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 1H), 7.52 (dd, J = 10.0, 4.1 Hz, 3H), 7.47 (d, J = 7.5 Hz, 1H), 7.28 (dt, J = 16.0, 6.4 Hz, 3H), 7.19 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.17 (d, J = 10.5 Hz, 1H), 4.09 (t, J = 4.7 Hz, 1H), 2.71 – 2.54 (m, 2H), 2.39 (s, 3H), 2.03 (d, J = 5.4 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.2, 145.3, 144.2, 140.3, 137.7, 137.5, 136.3, 133.2, 130.0, 129.5, 129.1, 129.1, 128.7, 128.2, 126.9, 126.1, 123.7, 123.6, 114.5, 75.4, 47.5, 36.9, 21.5, 21.0. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{26}H_{24}NO_3S$: 430.1471, found: 430.1464.



3da

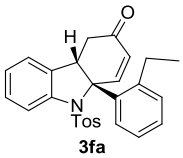
Compound **3da** (76 mg 85%) was obtained as a white solid according to the general procedure. Mp: 82−86 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 10.4 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.04 (dt, J = 14.6, 7.2 Hz, 2H), 6.89 – 6.80 (m, 2H), 6.22 (d, J = 10.4 Hz, 1H), 3.79 (d, J = 10.2 Hz, 4H), 2.50 (dd, J = 16.5, 5.4 Hz, 1H), 2.38 (s, 3H), 2.29 (dd, J = 16.5, 6.9 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 159.4, 145.1, 144.2, 140.8, 137.6, 132.8, 130.8, 129.7, 129.4, 129.0, 128.0, 126.8, 123.9, 123.5, 114.9, 113.9, 74.3, 55.3, 51.2, 38.0, 21.5. **HRMS** (ESI): m/z $[M+NH_4]^+$ calculated for $C_{26}H_{27}N_2O_4S$: 463.1686, found: 463.1687.



3ea

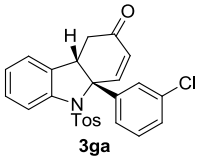
Compound **3ea** (81 mg 87%) was obtained as a white solid according to the general procedure. Mp: 114−120 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 1.4 Hz, 1H), 7.82 (dd, J = 13.8, 6.1 Hz, 2H), 7.79 – 7.70 (m, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.57 – 7.47 (m, 4H), 7.28 (dd, J = 11.4, 4.1 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.04 (dt, J = 14.5, 7.3 Hz, 2H), 6.31 (d, J = 10.4 Hz, 1H), 3.93 (t, J = 5.8 Hz, 1H), 2.54 (dd, J = 16.5, 5.5 Hz, 1H), 2.43 – 2.35 (m, 4H). **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 196.1, 144.6, 144.2, 140.9, 138.0, 137.5, 132.9, 132.8, 130.6, 130.3, 129.4, 129.0, 128.5, 128.3, 127.6, 126.9, 126.6, 126.6, 126.0, 124.1, 123.9, 123.4, 114.8, 75.1, 51.0, 37.6, 21.5. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{29}H_{24}NO_3S$: 466.1471, found: 466.1465.



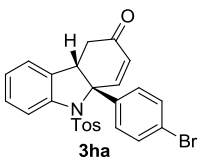
3fa

Compound **3fa** (67 mg 76%) was obtained as a white solid according to the general procedure. Mp: 214−217 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 1H), 7.51 (dd, J = 13.7, 4.3 Hz, 4H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.12 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.15 (d, J = 10.5 Hz, 1H), 4.02 (s, 1H), 2.54 (ddd, J = 21.6, 15.8, 6.4 Hz, 3H), 2.38 (s, 3H), 2.20 (s, 1H), 1.09 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.2, 145.6, 144.2, 142.5, 140.4, 137.9, 137.1, 131.1, 130.3, 129.5, 129.1, 128.8, 128.1, 126.8, 125.8, 123.8, 123.7, 114.7, 75.3, 48.6, 37.4, 25.0, 21.5, 15.6. **HRMS** (ESI): m/z $[M+NH_4]^+$ calculated for $C_{27}H_{29}N_2O_3S$: 461.1893, found: 461.1892.



3ga

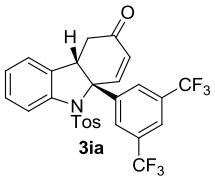
Compound **3ga** (64 mg 72%) was obtained as a white solid according to the general procedure. Mp: 82−86 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.41 (dd, J = 10.4, 0.7 Hz, 1H), 7.37 (ddd, J = 6.0, 2.7, 2.0 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.32 – 7.27 (m, 3H), 7.23 (d, J = 8.1 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.27 (d, J = 10.4 Hz, 1H), 3.79 (s, 1H), 2.52 (dd, J = 16.6, 5.5 Hz, 1H), 2.42 – 2.33 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 144.5, 143.8, 143.1, 140.6, 137.3, 134.6, 130.5, 130.3, 129.9, 129.6, 129.2, 128.6, 127.0, 126.8, 124.9, 124.1, 123.4, 114.7, 74.3, 51.3, 37.5, 21.6. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{25}H_{20}ClNO_3SNa$: 472.0745, found: 472.0742.



3ha

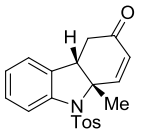
Compound **3ha** (75 mg 76%) was obtained as a white solid according to the general procedure. Mp: 86−90 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 1H), 7.60 (dd, J

= 8.6, 1.9 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.39 (d, *J* = 10.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 6.6, 0.7 Hz, 2H), 6.25 (d, *J* = 10.4 Hz, 1H), 3.74 (t, *J* = 6.3 Hz, 1H), 2.50 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.39 (s, 3H), 2.25 (dd, *J* = 16.5, 7.3 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 144.5, 144.0, 140.7, 140.5, 137.3, 131.7, 130.5, 130.3, 129.6, 129.1, 128.3, 126.8, 124.2, 123.5, 122.4, 114.9, 74.0, 51.2, 38.2, 21.6. **HRMS** (ESI): m/z $[M+H]^+$ calculated for $C_{25}H_{21}BrNO_3S$: 494.0420, found: 494.0411.



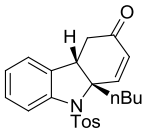
3ia

Compound **3ia** (75 mg 68%) was obtained as a white solid according to the general procedure. Mp: 116−124 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 14.6 Hz, 3H), 7.62 (dd, *J* = 14.4, 8.3 Hz, 3H), 7.44 (dd, *J* = 10.4, 1.0 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.29 – 7.21 (m, 2H), 7.16 – 7.05 (m, 2H), 6.36 (d, *J* = 10.5 Hz, 1H), 3.79 (t, *J* = 5.4 Hz, 1H), 2.52 (dd, *J* = 5.6, 2.3 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9, 145.0, 144.4, 142.3, 140.5, 137.0, 132.1(q, J= 33 Hz), 131.7, 129.9, 129.6, 129.5, 126.8, 124.4, 124.3, 123.5, 122.6, 121.6, 114.7, 74.4, 51.5, 37.0, 21.5.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.73. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{27}H_{19}F_6NO_3SNa$: 574.0882, found: 574.0870.



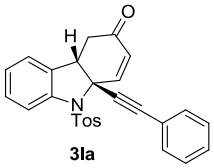
3ja

Compound **3ja** (47 mg 67%) was obtained as a white solid according to the general procedure. Mp: 153−156 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.24 (dd, *J* = 12.0, 6.7 Hz, 3H), 7.17 – 7.08 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.97 (d, *J* = 10.4 Hz, 1H), 3.40 (t, *J* = 6.1 Hz, 1H), 2.63 (dd, *J* = 16.6, 5.7 Hz, 1H), 2.46 – 2.31 (m, 4H), 1.82 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.9, 146.9, 144.1, 140.5, 138.3, 131.2, 129.7, 128.9, 128.6, 126.5, 123.9, 123.6, 115.3, 69.1, 48.0, 38.1, 25.2, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{20}H_{19}NO_3SNa$: 376.0978, found: 376.0971.



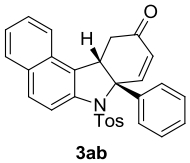
3ka

Compound **3ka** (41 mg 52%) was obtained as a white solid according to the general procedure. Mp: 90−95 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 10.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.2 Hz, 1H), 7.05 (td, J = 7.4, 0.6 Hz, 1H), 6.11 (d, J = 10.5 Hz, 1H), 3.43 (dd, J = 10.5, 5.8 Hz, 1H), 2.42 (dd, J = 16.3, 5.7 Hz, 1H), 2.33 (s, 3H), 2.12 – 2.00 (m, 1H), 1.97 – 1.83 (m, 1H), 1.76 – 1.61 (m, 1H), 1.31 (tdd, J = 10.9, 9.6, 5.0 Hz, 4H), 0.87 (t, J = 7.1 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 145.6, 144.1, 140.33, 137.4, 132.9, 130.0, 129.5, 128.7, 126.6, 124.2, 124.0, 116.2, 70.8, 45.2, 40.8, 39.7, 26.3, 22.8, 21.5, 13.9. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{23}H_{25}NO_3SNa$: 418.1447, found: 418.1438.



3la

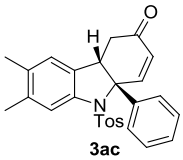
Compound **3la** (49 mg 56%) was obtained as colorless oil according to the general procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.1 Hz, 1H), 7.46 – 7.32 (m, 5H), 7.26 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.14 – 7.09 (m, 2H), 7.05 (td, J = 7.4, 0.7 Hz, 1H), 6.01 (d, J = 10.1 Hz, 1H), 4.00 (t, J = 4.2 Hz, 1H), 3.04 (dd, J = 16.7, 5.6 Hz, 1H), 2.92 (dd, J = 16.7, 3.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9, 144.0, 143.4, 139.9, 137.9, 131.9, 129.6, 129.5, 129.3, 129.2, 128.4, 128.1, 127.1, 124.1, 123.3, 121.5, 115.1, 89.0, 84.2, 64.3, 49.3, 36.2, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{27}H_{21}NO_3SNa$: 462.1134, found: 462.1125.



3ab

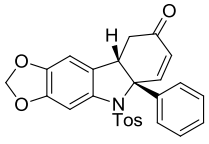
Compound **3ab** (79 mg 85%) was obtained as a white solid according to the general procedure. Mp: 204−208 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 9.0 Hz, 1H), 7.84 (dd, J = 14.9, 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.1

Hz, 1H), 7.42 – 7.32 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.18 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.28 (d, *J* = 10.4 Hz, 1H), 4.13 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.72 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.28 (s, 3H), 1.39 (dd, *J* = 16.2, 12.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 145.0, 144.4, 143.0, 138.5, 136.8, 131.4, 129.9, 129.5, 129.0, 128.9, 128.8, 128.8, 128.1, 127.2, 127.0, 126.5, 126.1, 125.0, 122.6, 116.6, 72.6, 49.7, 40.9, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{29}H_{23}NO_3SNa$: 488.1291, found: 488.1283.



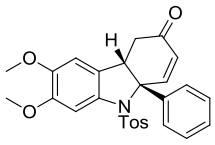
3ac

Compound **3ac** (53 mg 60%) was obtained as a white solid according to the general procedure. Mp: 210−214 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.45 – 7.36 (m, 3H), 7.35 – 7.28 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 6.22 (d, *J* = 10.4 Hz, 1H), 3.79 – 3.68 (m, 1H), 2.47 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.19 – 2.10 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 144.9, 144.0, 141.5, 138.8, 137.7, 137.4, 132.41, 129.7, 129.4, 128.5, 128.4, 128.1, 126.8, 126.5, 124.5, 116.2, 74.3, 51.1, 38.7, 21.5, 20.5, 19.4. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{27}H_{25}NO_3SNa$: 466.1447, found: 466.1438.



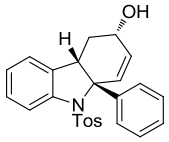
3ad

Compound **3ad** (50 mg 55%) was obtained as a white solid according to the general procedure. Mp: 214−217 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.33 (dd, *J* = 9.2, 3.7 Hz, 4H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.48 (s, 1H), 6.22 (d, *J* = 10.4 Hz, 1H), 5.93 (dd, *J* = 12.3, 1.2 Hz, 2H), 3.65 (dd, *J* = 8.9, 5.4 Hz, 1H), 2.47 – 2.34 (m, 4H), 1.83 (dd, *J* = 16.3, 8.9 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 148.1, 144.7, 144.5, 144.3, 141.7, 137.1, 134.8, 129.5, 128.6, 128.2, 126.8, 126.4, 124.1, 104.1, 101.6, 98.8, 74.1, 50.7, 39.5, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{26}H_{21}NO_5SNa$: 482.1033, found: 482.1024.



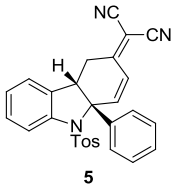
3ae

Compound **3ae** (52 mg 55%) was obtained as a white solid in according to the general procedure. Mp: 106−110 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.52 – 7.40 (m, 3H), 7.37 – 7.23 (m, 4H), 7.17 (d, J = 8.2 Hz, 2H), 6.55 (s, 1H), 6.21 (d, J = 10.4 Hz, 1H), 3.95 (s, 3H), 3.77 (d, J = 3.9 Hz, 3H), 3.69 (dd, J = 9.0, 5.5 Hz, 1H), 2.44 (dd, J = 16.3, 5.5 Hz, 1H), 2.36 (s, 3H), 1.80 (dd, J = 16.3, 9.1 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 149.5, 146.4, 144.6, 144.2, 141.9, 137.3, 134.1, 129.4, 128.5, 128.1, 126.7, 126.4, 123.0, 106.8, 100.9, 73.7, 56.3, 56.2, 50.9, 39.6, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{27}H_{25}NO_5SNa$: 498.1346, found: 498.1338.



4

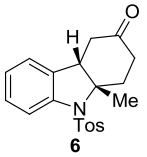
Compound **4** (110 mg 88%) was obtained as a white solid according to the procedure. Mp: 99−103 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.40 (dd, J = 5.5, 3.6 Hz, 2H), 7.30 – 7.16 (m, 6H), 7.05 – 6.93 (m, 2H), 6.52 (dd, J = 10.3, 1.9 Hz, 1H), 6.16 – 6.07 (m, 1H), 4.42 – 4.24 (m, 1H), 3.28 (dd, J = 12.0, 4.3 Hz, 1H), 2.35 (s, 3H), 2.03 – 1.92 (m, 1H), 0.86 (td, J = 12.4, 9.7 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 143.8, 141.1, 137.8, 134.8, 132.7, 129.1, 128.5, 128.4, 128.0, 127.4, 127.2, 125.9, 124.2, 123.9, 115.4, 73.6, 65.5, 50.1, 37.6, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{25}H_{23}NO_3SNa$: 440.1291, found: 440.1282.



5

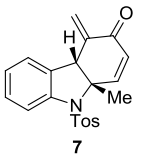
Compound **5** (184 mg 83%) was obtained as a green solid according to the procedure. Mp: 120−125 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.23 (dd, J = 14.7, 4.8 Hz, 3H), 7.07 (d, J = 4.4 Hz, 2H), 7.00 (d, J = 10.1 Hz, 1H), 3.71 – 3.57 (m, 1H), 2.78 (dd, J = 16.8, 5.1 Hz, 1H), 2.55 (dd, J = 16.8, 7.0 Hz,

1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 144.5, 142.5, 140.9, 140.5, 137.3, 129.7, 129.5, 129.4, 128.7, 128.5, 126.8, 126.5, 125.6, 124.2, 123.4, 115.2, 111.8, 111.0, 83.6, 74.4, 49.6, 30.5, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{28}H_{21}N_3O_2SNa$: 486.1247, found: 486.1237.



6

Compound **6** (170 mg 95%) was obtained as colorless oil according to the procedure. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.17 (t, J = 7.7 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 3.42 (t, J = 6.0 Hz, 1H), 2.86 – 2.65 (m, 2H), 2.58 (dd, J = 16.1, 6.3 Hz, 1H), 2.39 (s, 3H), 2.36 – 2.17 (m, 3H), 1.76 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.1, 143.9, 141.6, 138.6, 130.4, 129.7, 128.7, 126.7, 124.3, 123.2, 113.6, 70.9, 48.0, 41.9, 35.5, 32.8, 27.9, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{20}H_{21}NO_3SNa$: 378.1134, found: 378.1129.



7

Compound **7** (22 mg 30%) was obtained as a white solid according to the procedure. Mp: 157−161 ℃ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.31 – 7.19 (m, 3H), 7.08 (dd, J = 10.3, 1.4 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.31 (d, J = 1.4 Hz, 1H), 6.04 (d, J = 10.3 Hz, 1H), 5.47 (s, 1H), 4.07 (s, 1H), 2.40 (s, 3H), 1.87 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 148.6, 144.1, 140.9, 138.9, 138.3, 129.8, 129.7, 129.2, 128.5, 126.4, 125.7, 124.3, 123.7, 114.8, 71.4, 56.0, 24.1, 21.5. **HRMS** (ESI): m/z $[M+Na]^+$ calculated for $C_{21}H_{19}NO_3SNa$: 388.0978, found: 388.0971.

Reference:

[1] Jia, P.; Zhang, Q.; Jin, H.; Huang, Y. *Org. Lett.* **2017**, *19*, 412.

[2] Ueta, Y.; Mikami, K.; Ito, S. *Angew. Chem. Int. Ed.* **2016**, *55,* 7525.

6. X-ray crystallographic structure of product 3aa

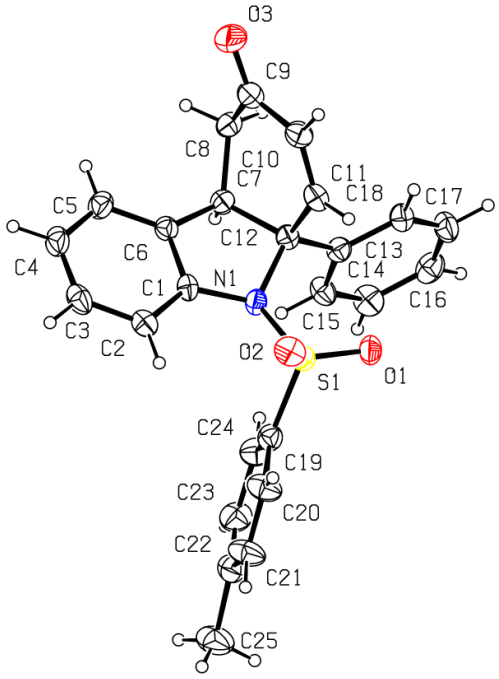
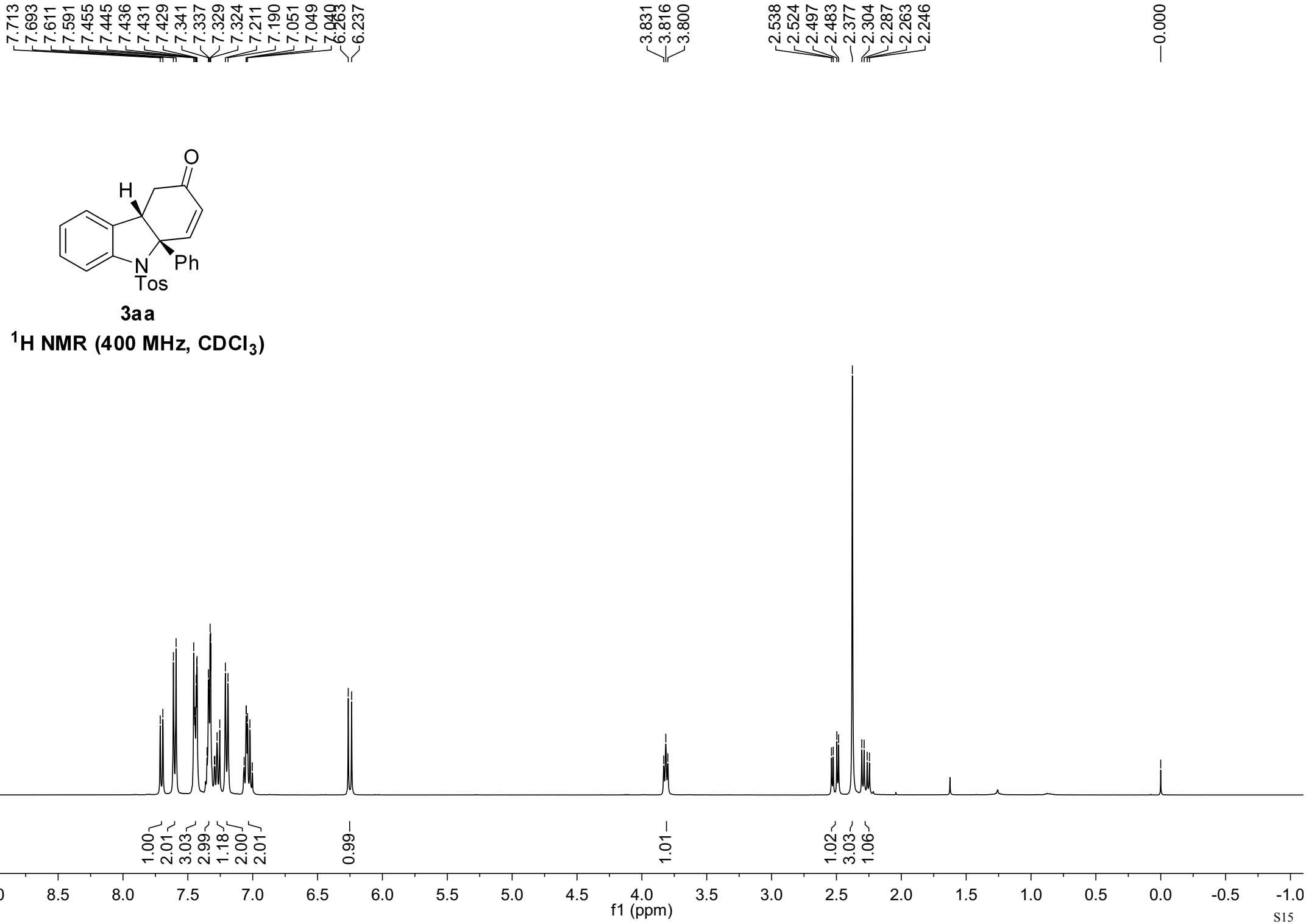
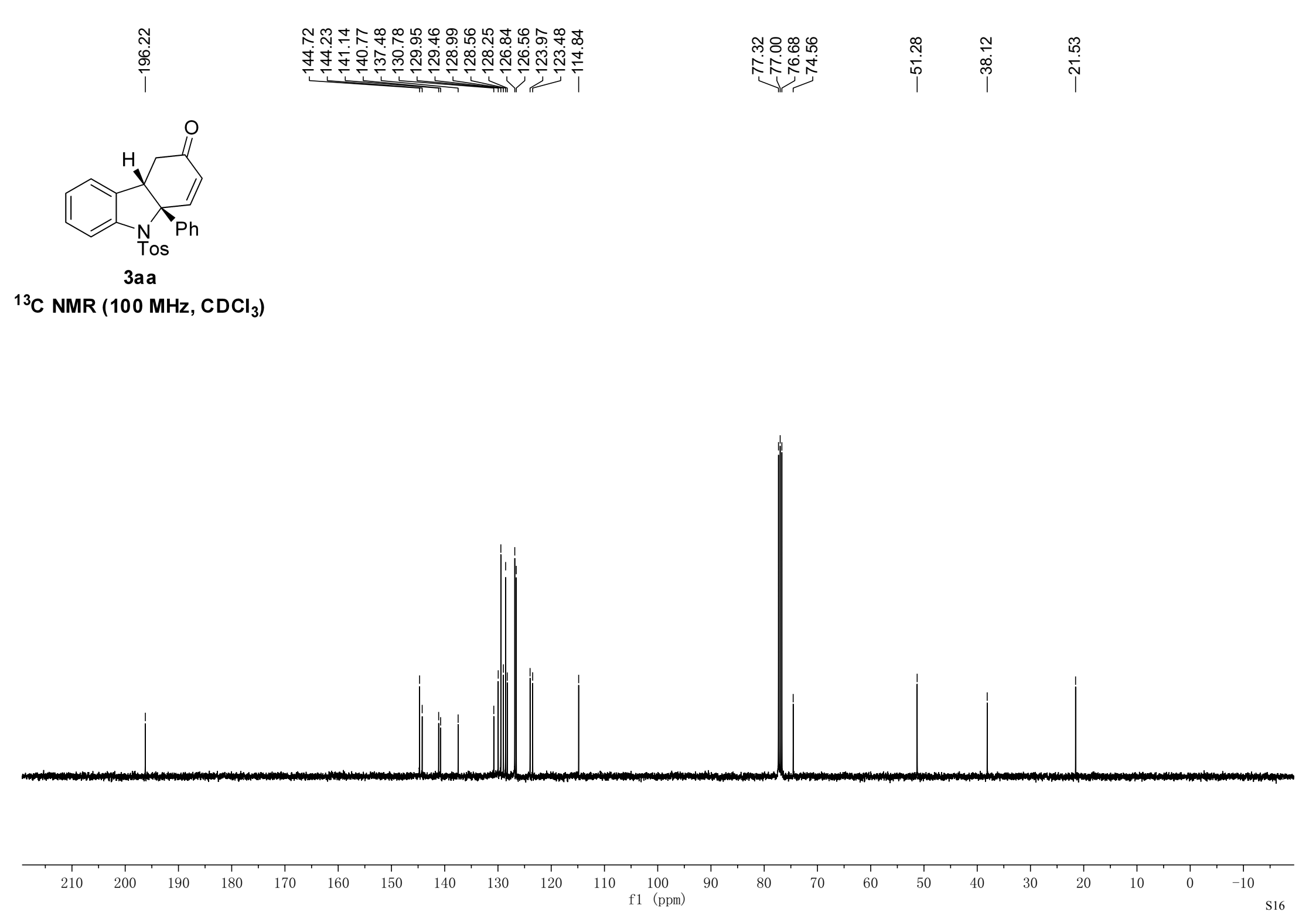


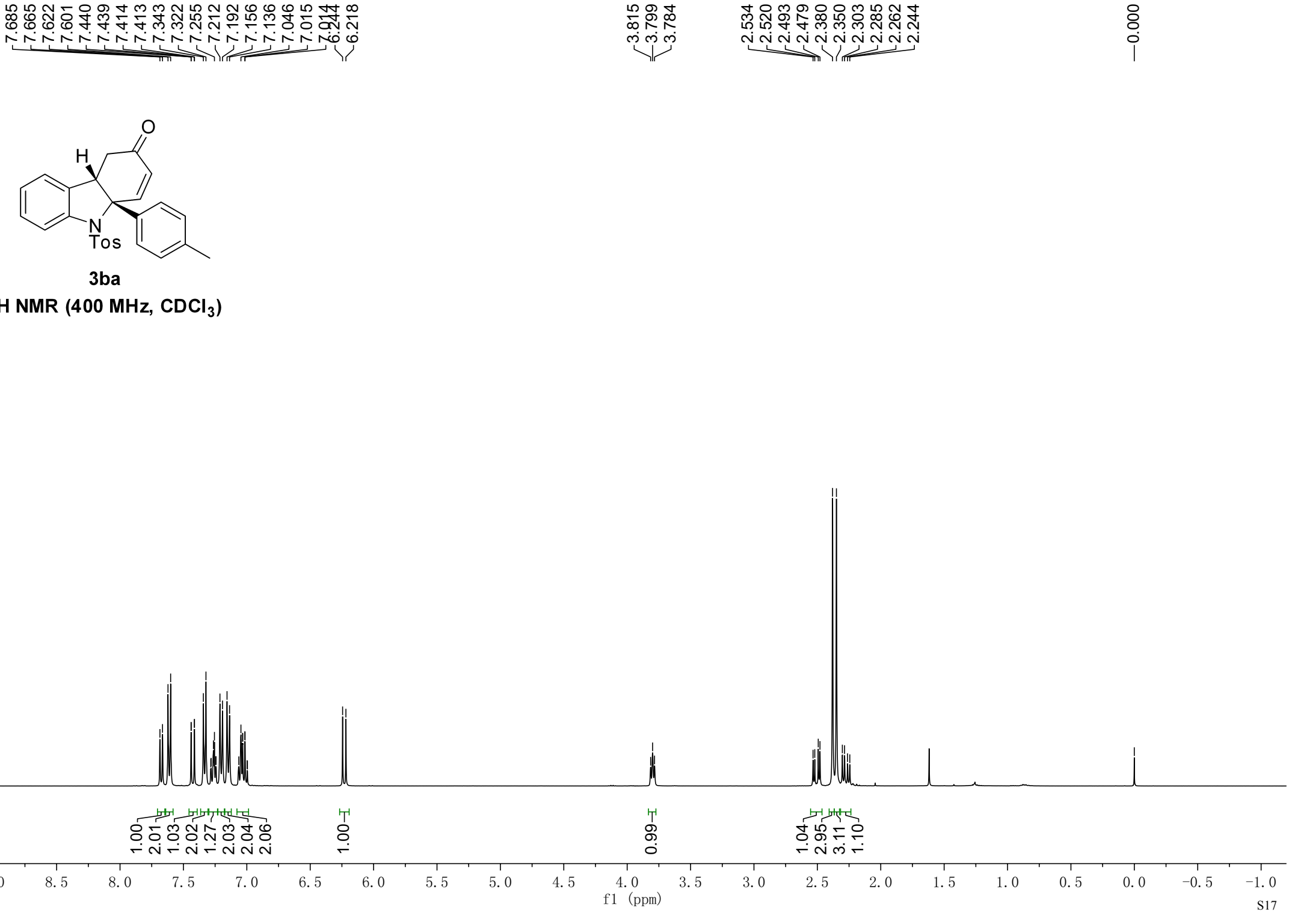
Figure S1: X-ray crystallographic structure of compound **3aa** (CCDC 1551379). Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.



3aa

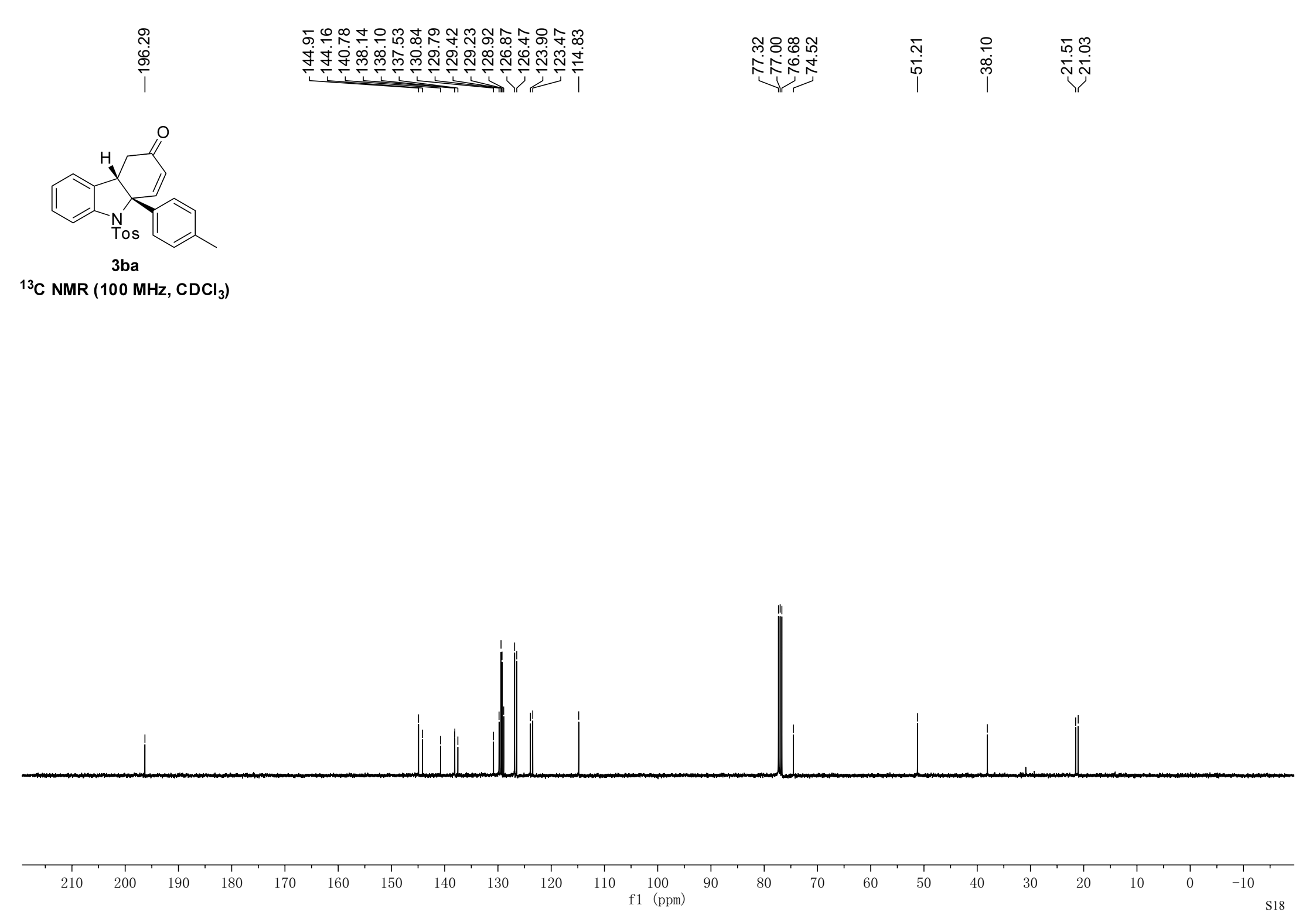
^{1}H NMR (400 MHz, $CDCl_3$)

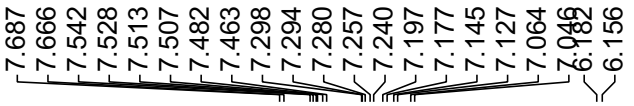

196.22
144.72
144.23
141.14
140.77
137.48
130.78
129.95
129.46
128.99
128.56
128.25
126.84
126.56
123.97
123.48
114.84
77.32
77.00
76.68
74.56
51.28
38.12
21.53
O
H
N
Ph
Tos
3aa
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

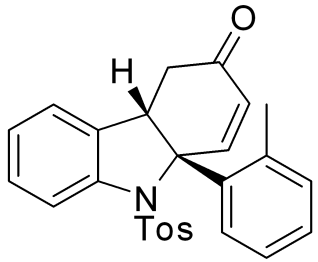


3ba

^{1}H NMR (400 MHz, $CDCl_3$)

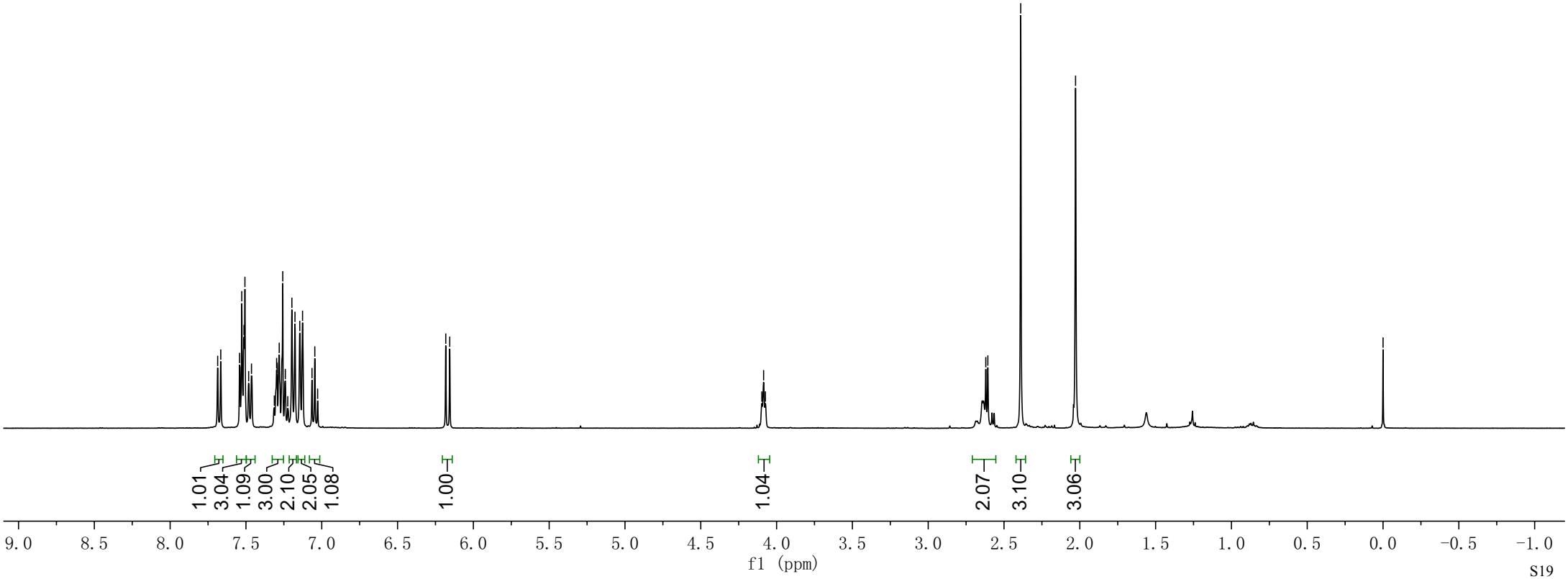

196.29
144.91
144.16
140.78
138.14
138.10
137.53
130.84
129.79
129.42
129.23
128.92
126.87
126.47
123.90
123.47
114.83
77.32
77.00
76.68
74.52
51.21
38.10
21.51
21.03
O
H
N
Tos
3ba
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

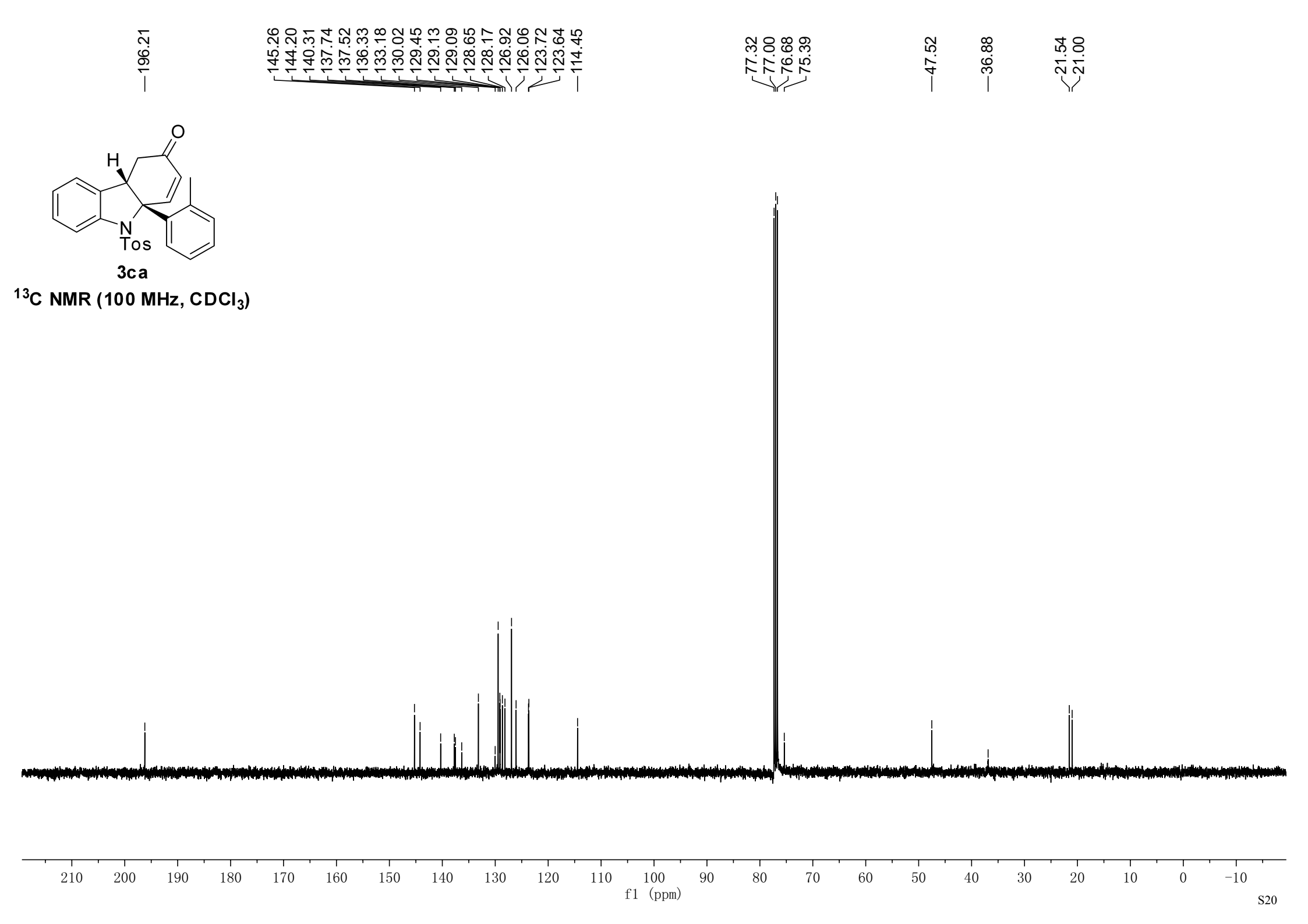


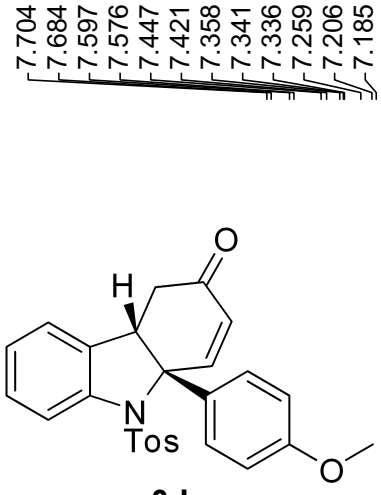


3ca

^{1}H NMR (400 MHz, $CDCl_3$)

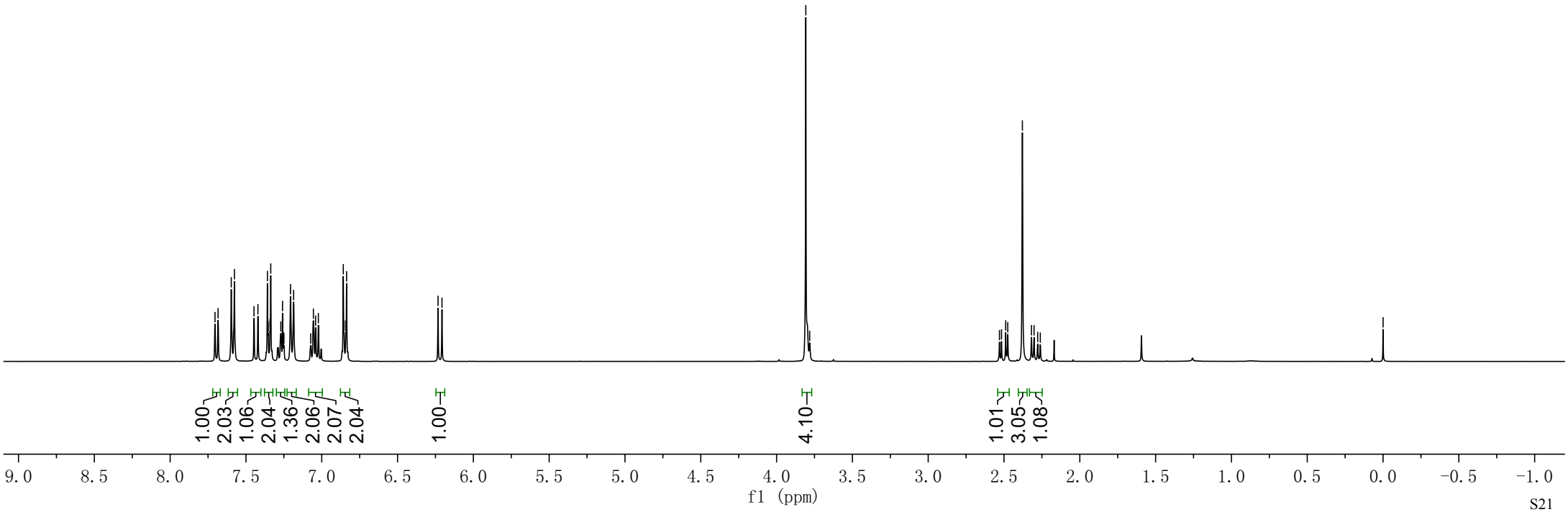


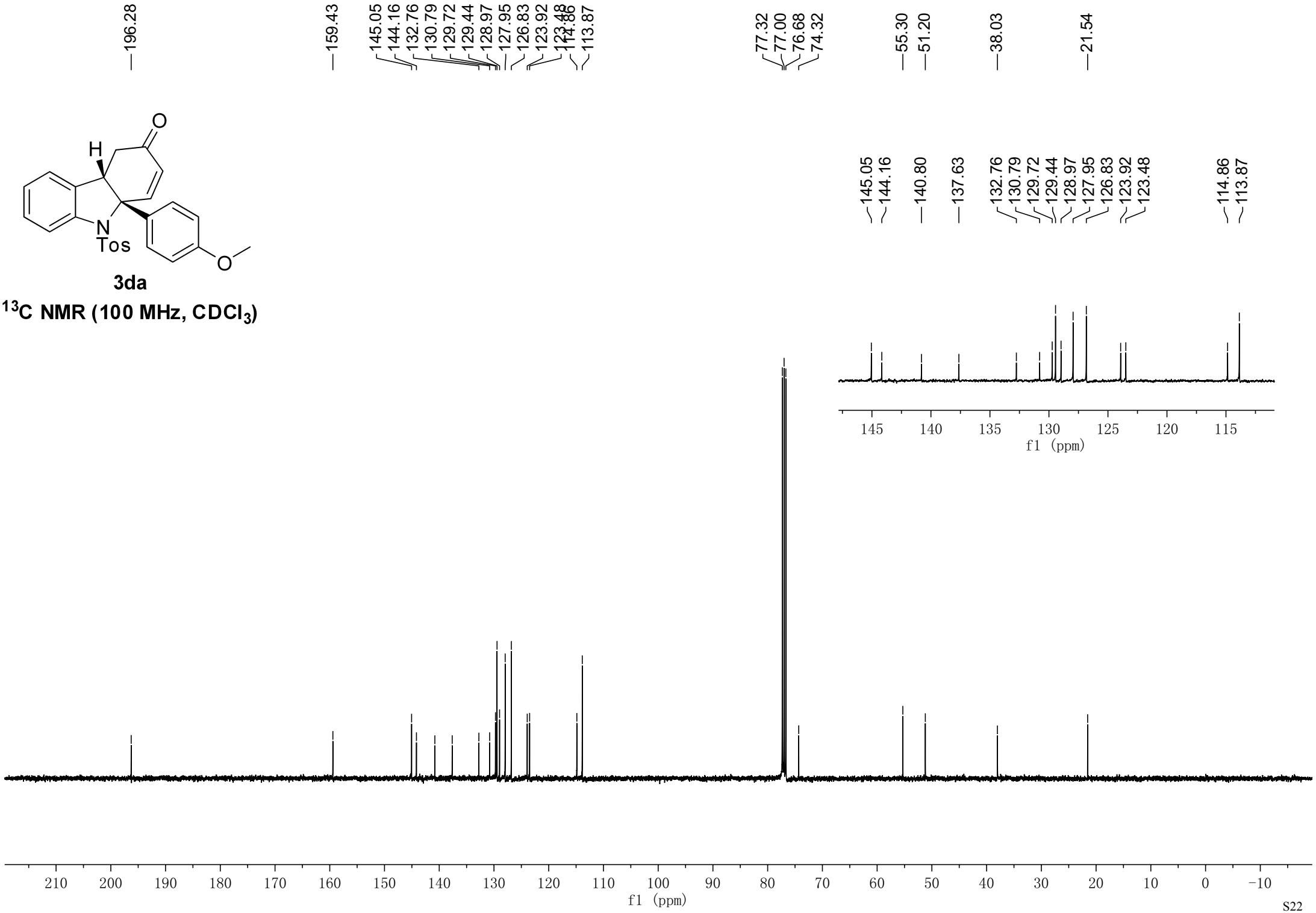

196.21
145.26
144.20
140.31
137.74
137.52
136.33
133.18
130.02
129.45
129.13
129.09
128.65
128.17
126.92
126.06
123.72
123.64
114.45
77.32
77.00
76.68
75.39
47.52
36.88
21.54
21.00
O
H
N
Tos
3ca
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

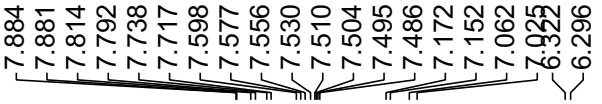


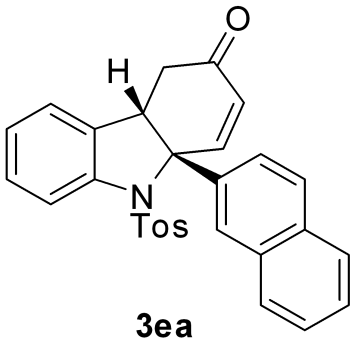
3da

^{1}H NMR (400 MHz, $CDCl_3$)



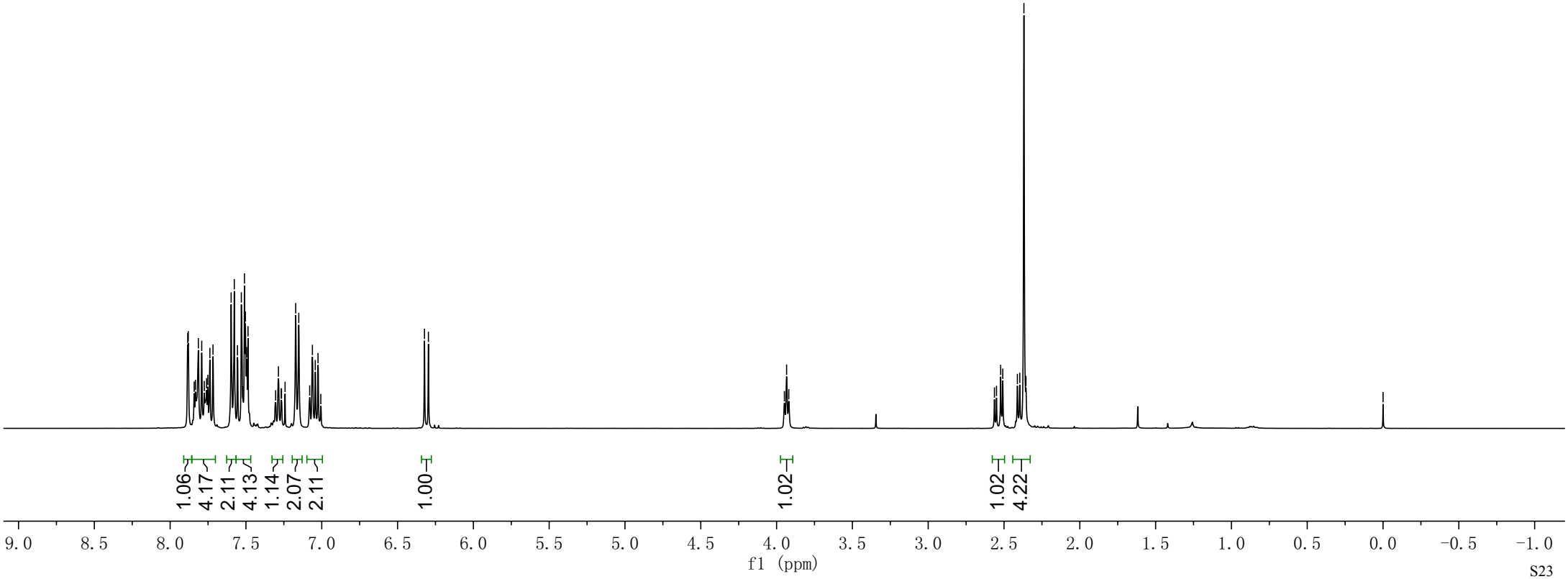

196.28
159.43
145.05
144.16
132.76
130.79
129.72
129.44
128.97
127.95
126.83
123.92
123.48
114.86
113.87
77.32
77.00
76.68
74.32
55.30
51.20
38.03
21.54
O
H
N
Tos
O
3da
13C NMR (100 MHz, CDCl3)
145.05
144.16
140.80
137.63
132.76
130.79
129.72
129.44
128.97
127.95
126.83
123.92
123.48
114.86
113.87
145
140
135
130
125
120
115
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

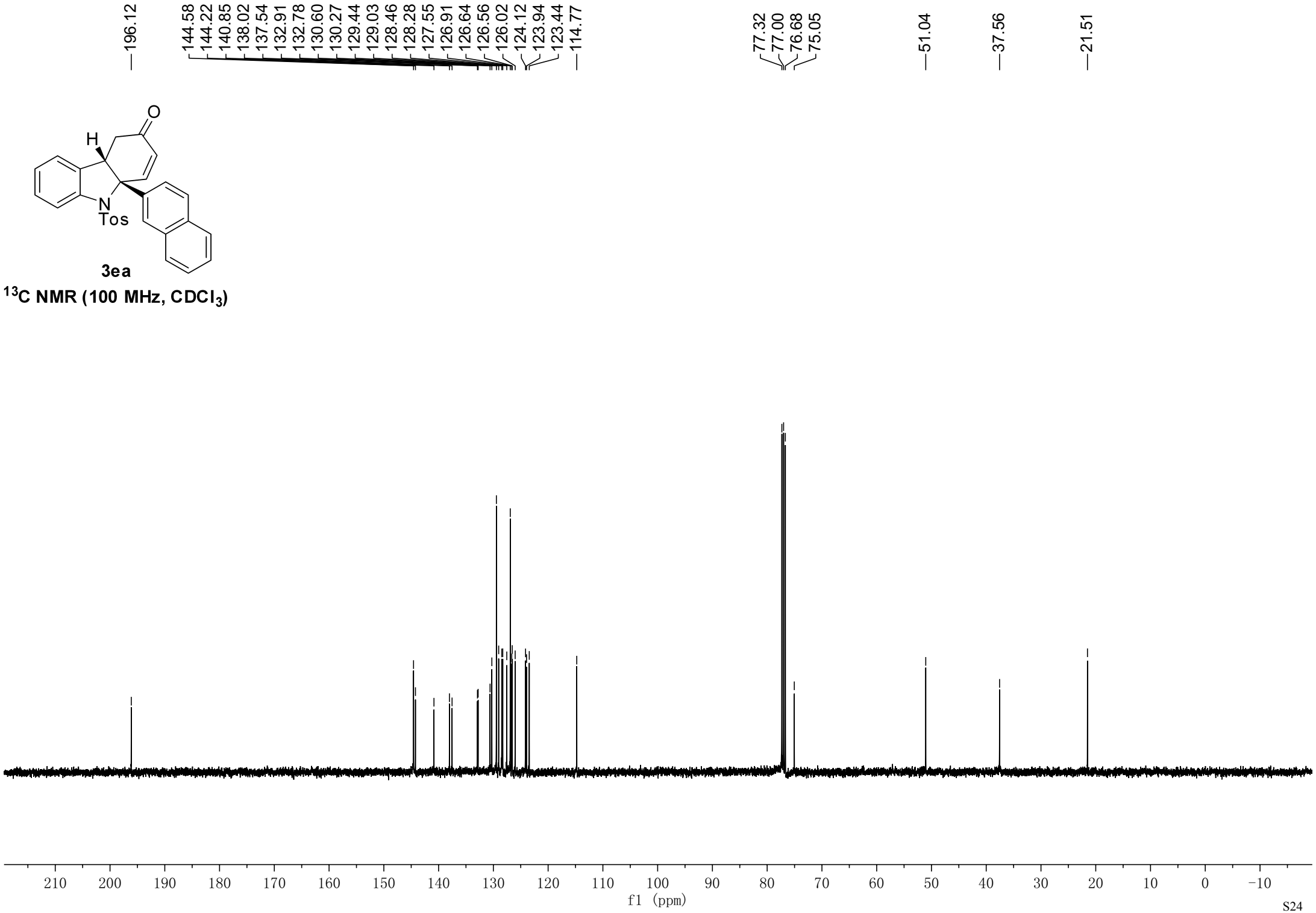


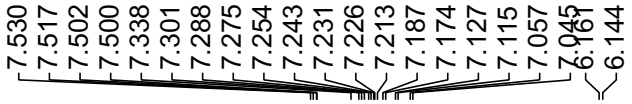


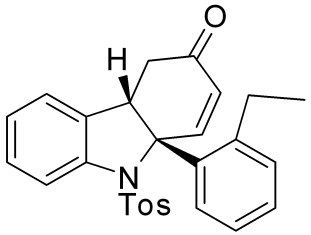
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



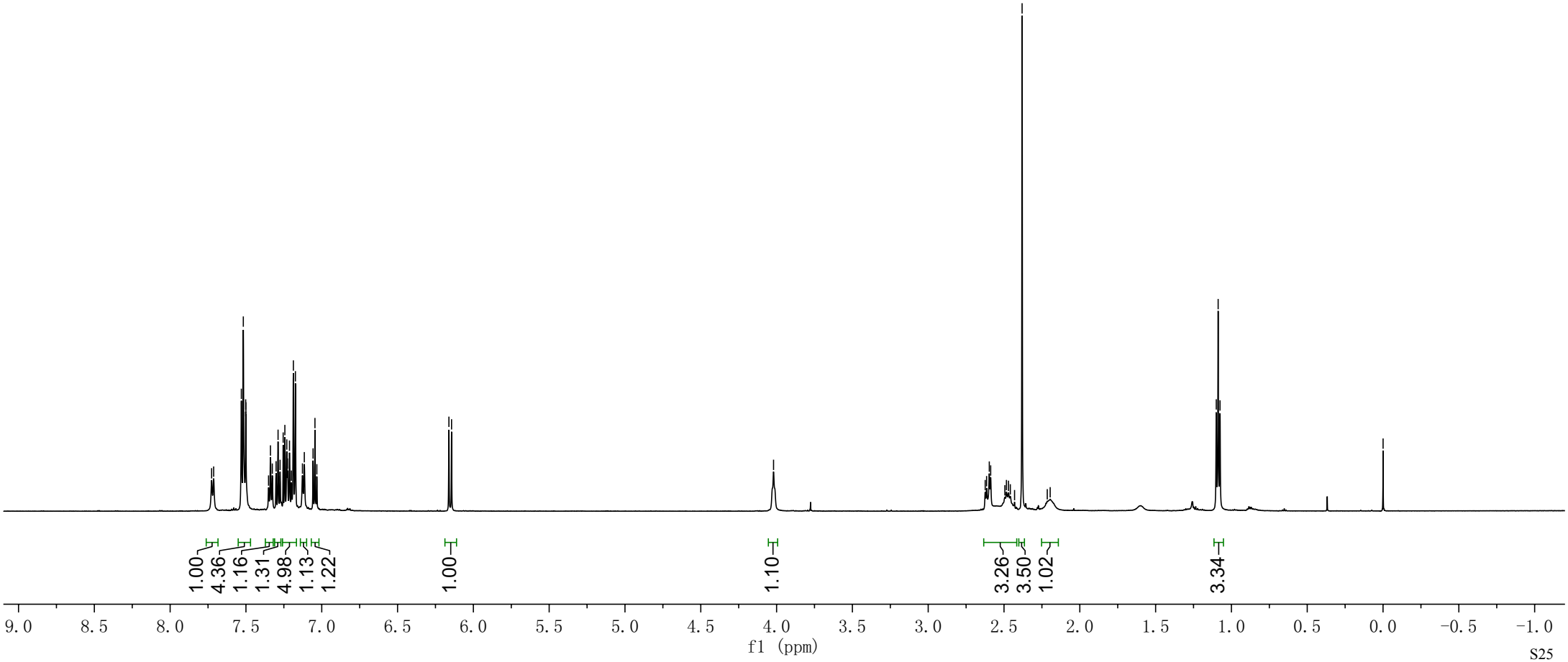

196.12
144.58
144.22
140.85
138.02
137.54
132.91
132.78
130.60
130.27
129.44
129.03
128.46
128.28
127.55
126.91
126.64
126.56
126.02
124.12
123.94
123.44
114.77
77.32
77.00
76.68
75.05
51.04
37.56
21.51
O
H
N
Tos
3ea
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

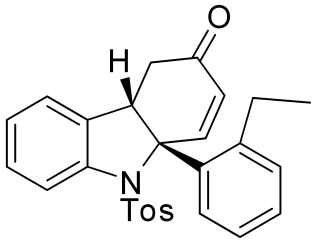




3fa

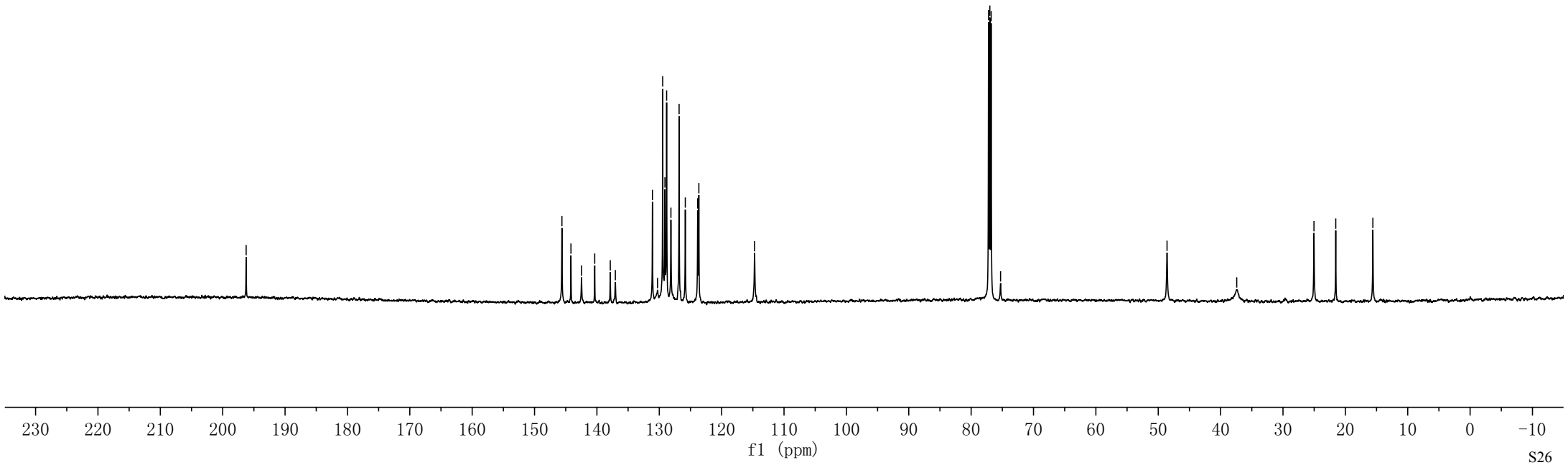
^{1}H NMR (600 MHz, $CDCl_3$)

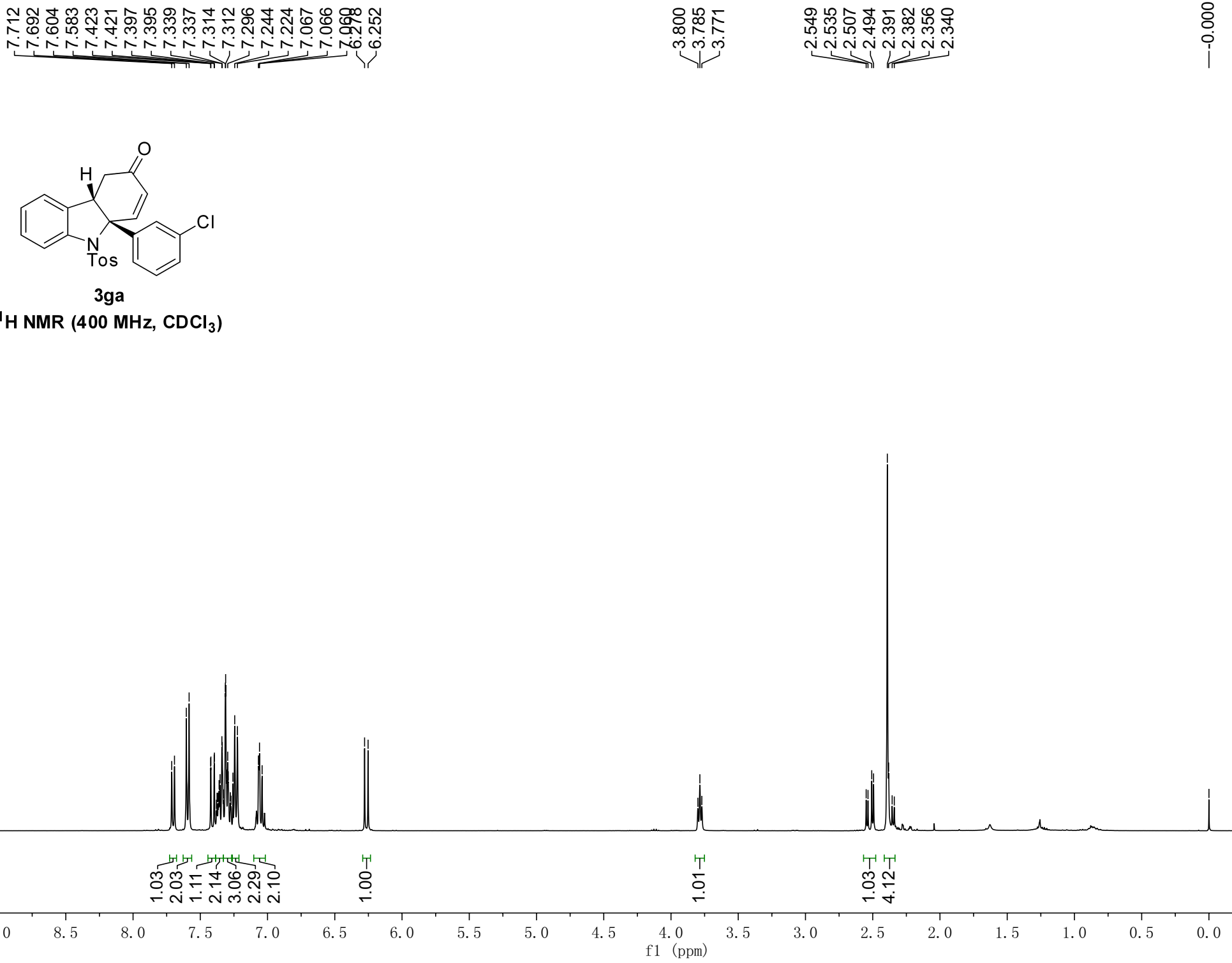




3fa

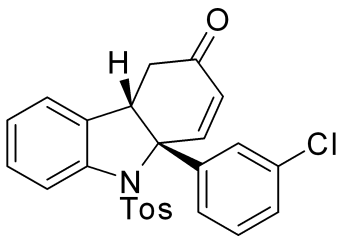
^{13}C NMR (150 MHz, $CDCl_3$)





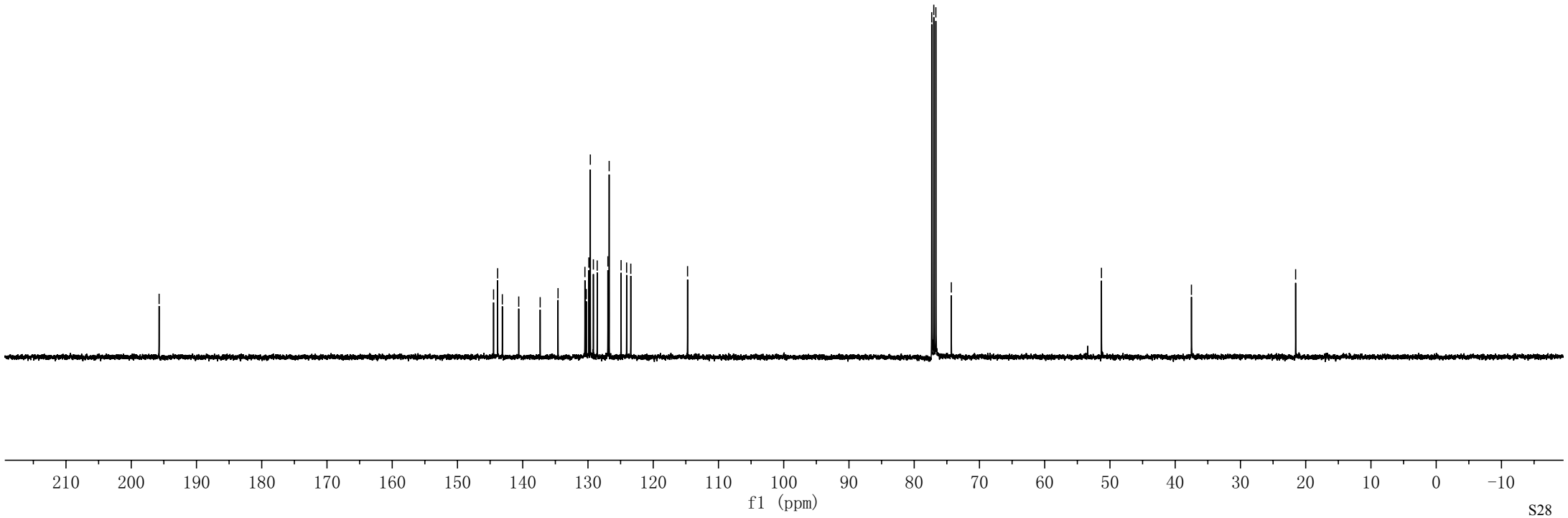
3ga

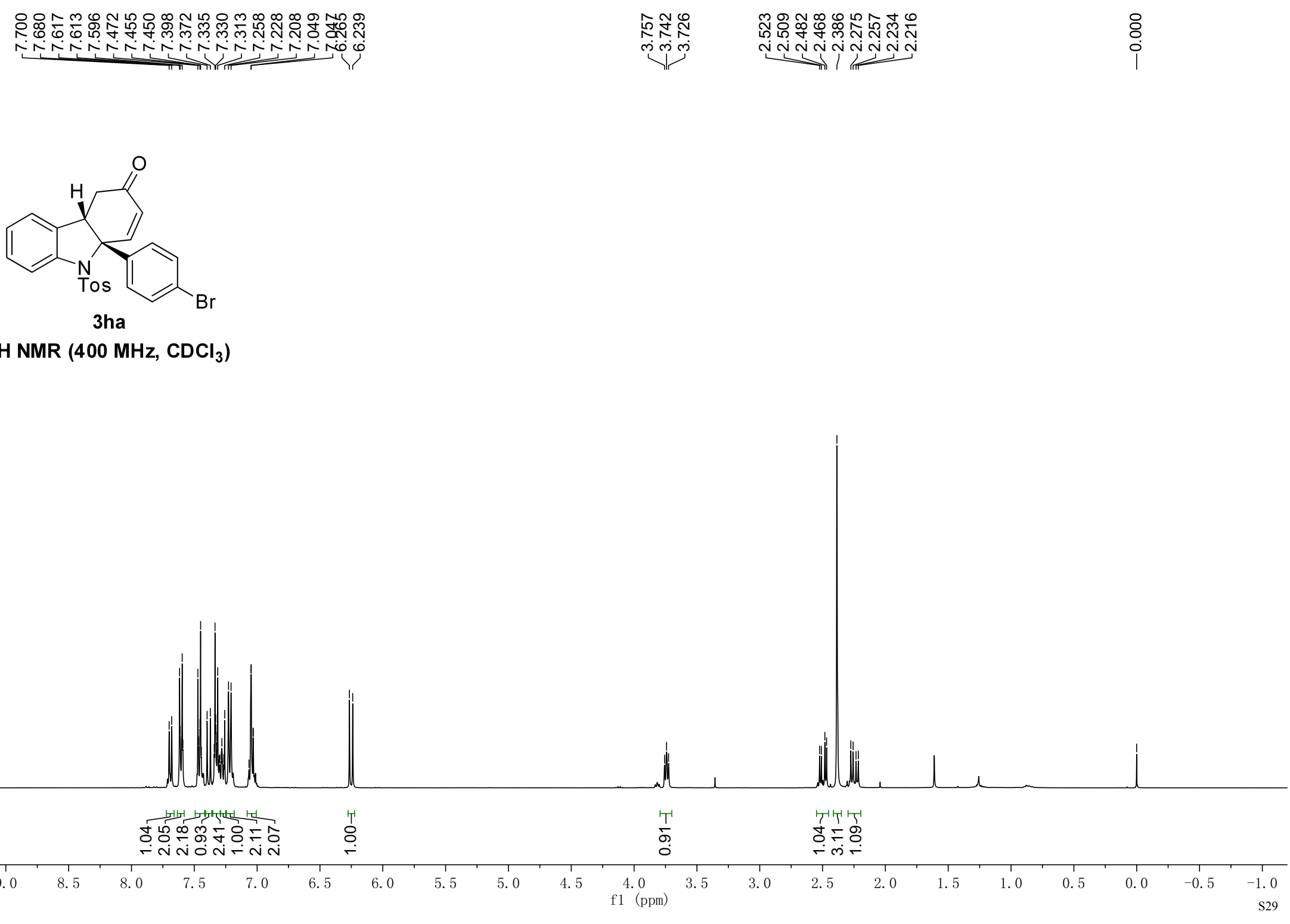
^{1}H NMR (400 MHz, $CDCl_3$)



3ga

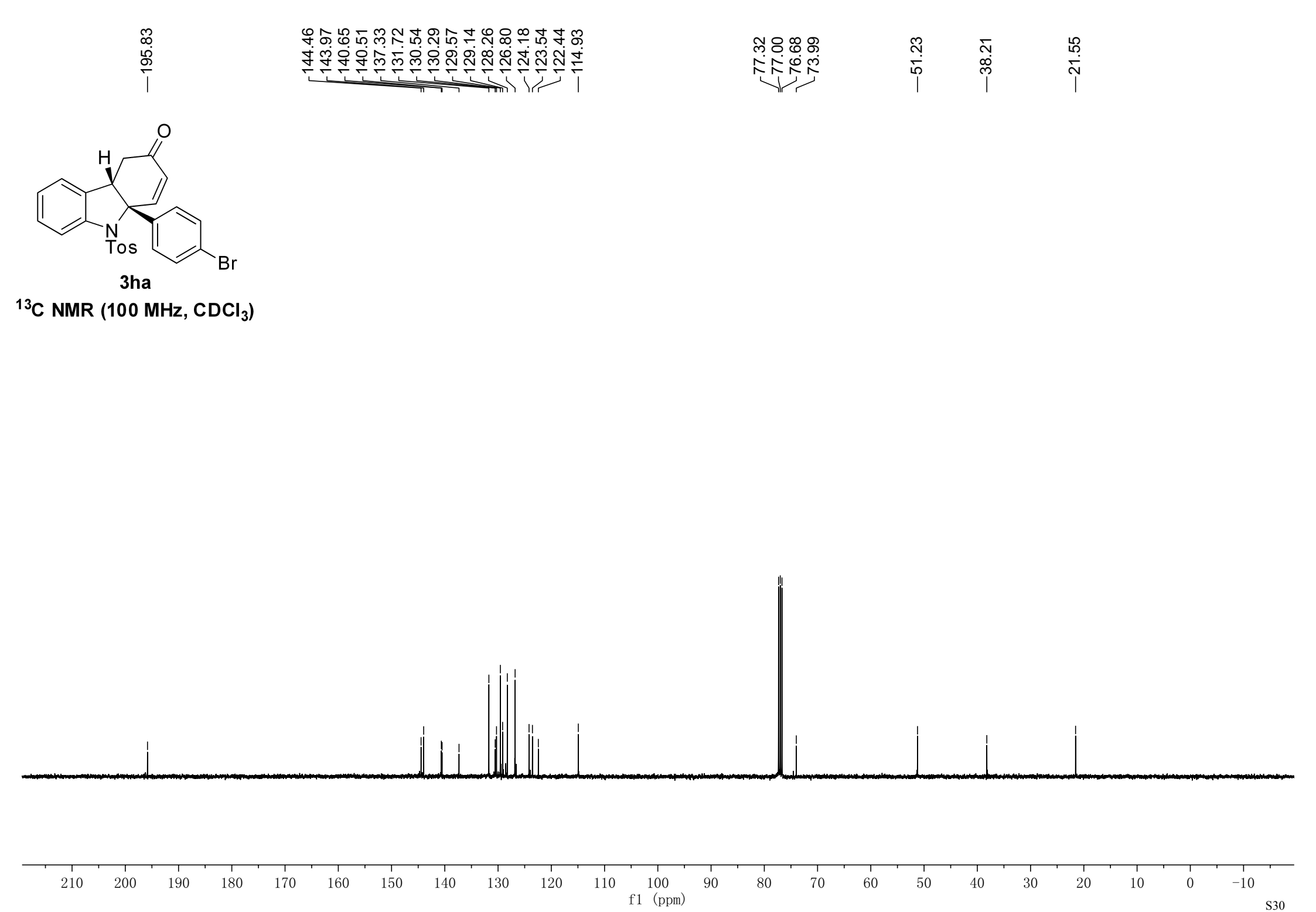
^{13}C NMR (100 MHz, $CDCl_3$)





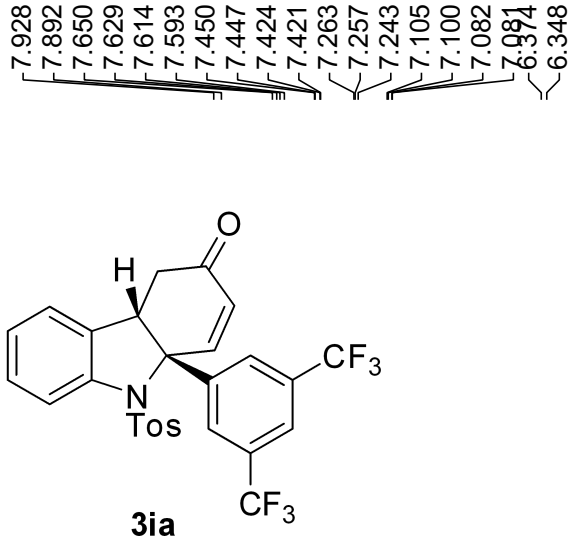
3ha

^{1}H NMR (400 MHz, $CDCl_3$)



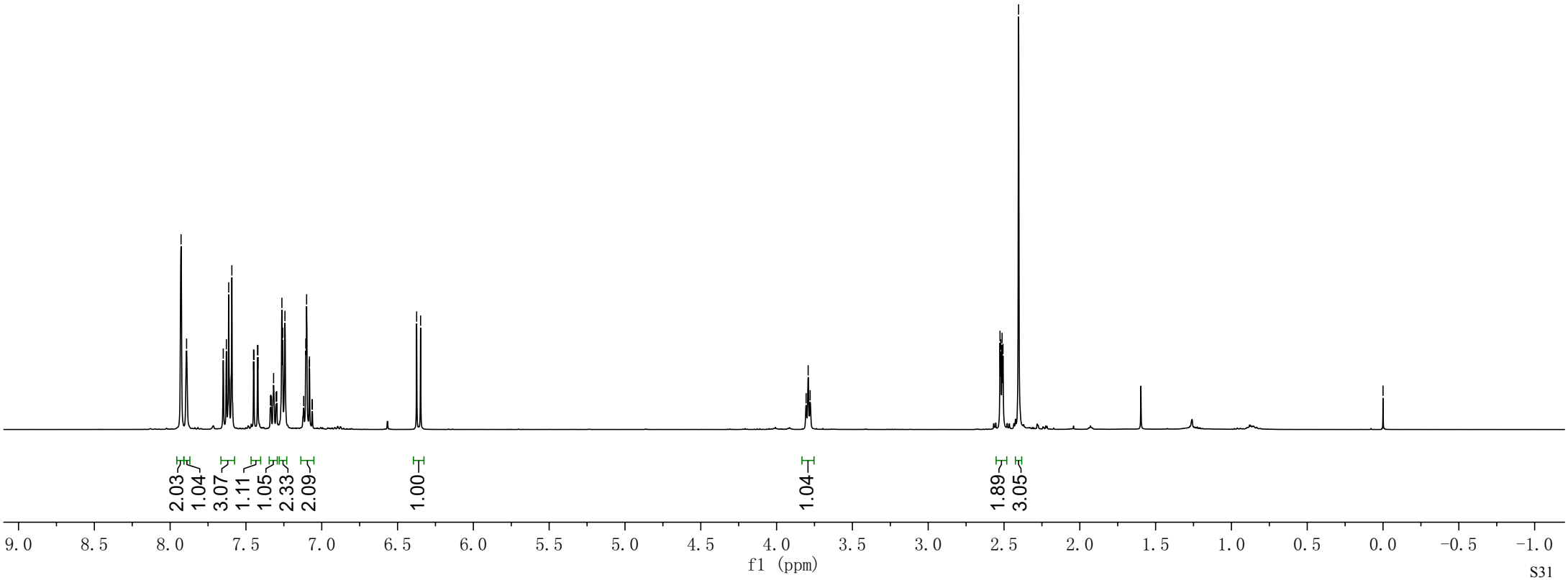
3ha

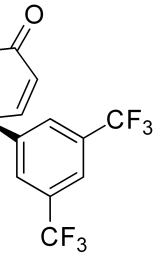
^{13}C NMR (100 MHz, $CDCl_3$)



3ia

^{1}H NMR (400 MHz, $CDCl_3$)

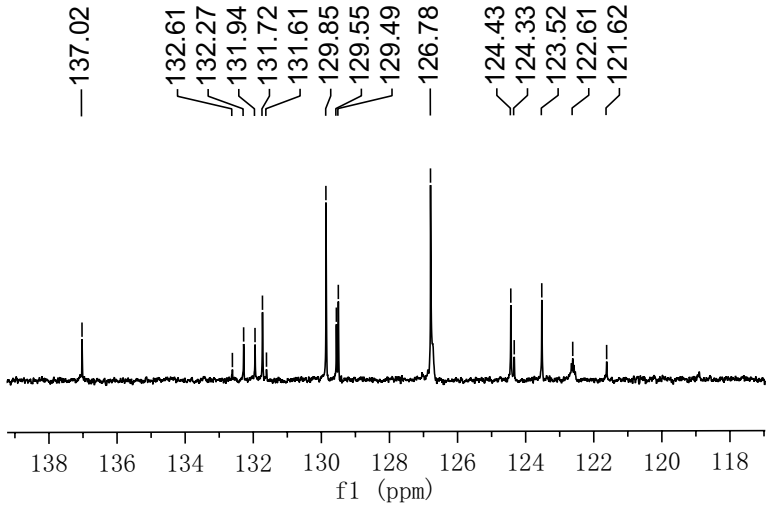


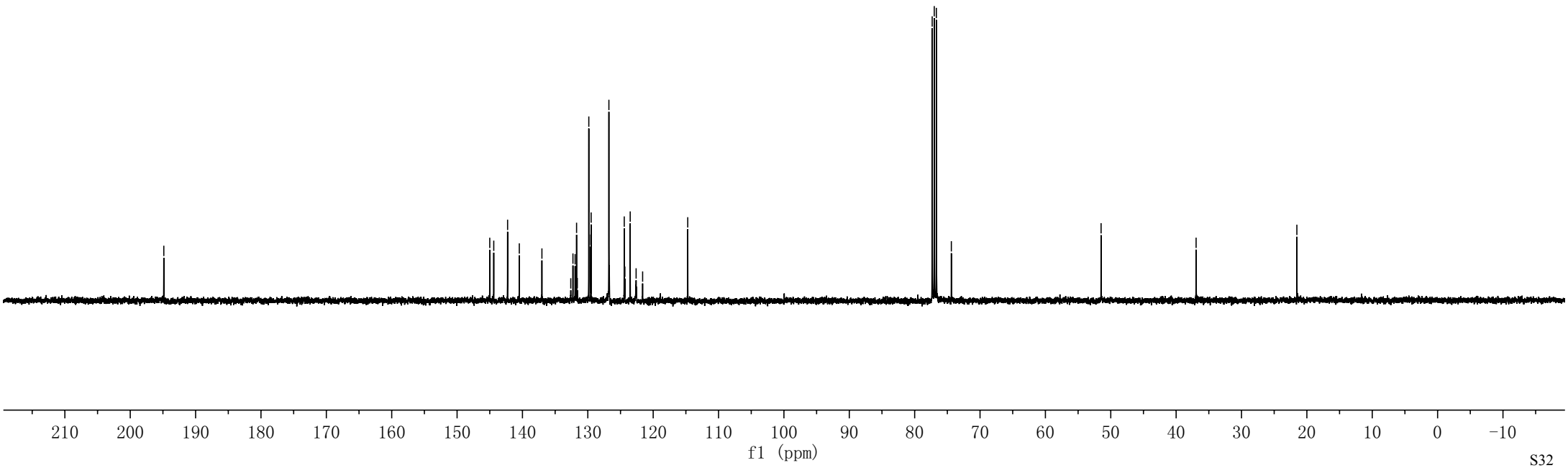


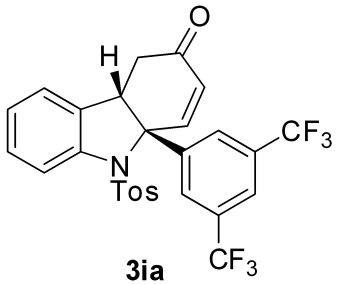
3ia

^{13}C NMR (100 MHz, $CDCl_3$)

194.86
145.00
144.39
142.27
140.48
137.02
132.61
132.27
131.94
131.72
131.61
129.85
129.55
129.49
126.78
124.43
124.33
123.52
122.61
121.62
114.71
77.32
77.00
76.68
74.39
51.48
36.95
21.53

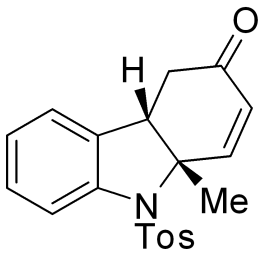






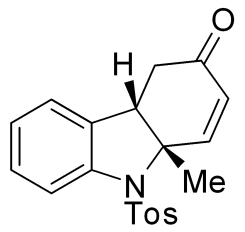
3ia

^{19}F NMR (376 MHz, $CDCl_3$)



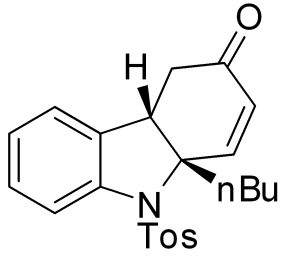
3ja

^{1}H NMR (400 MHz, $CDCl_3$)



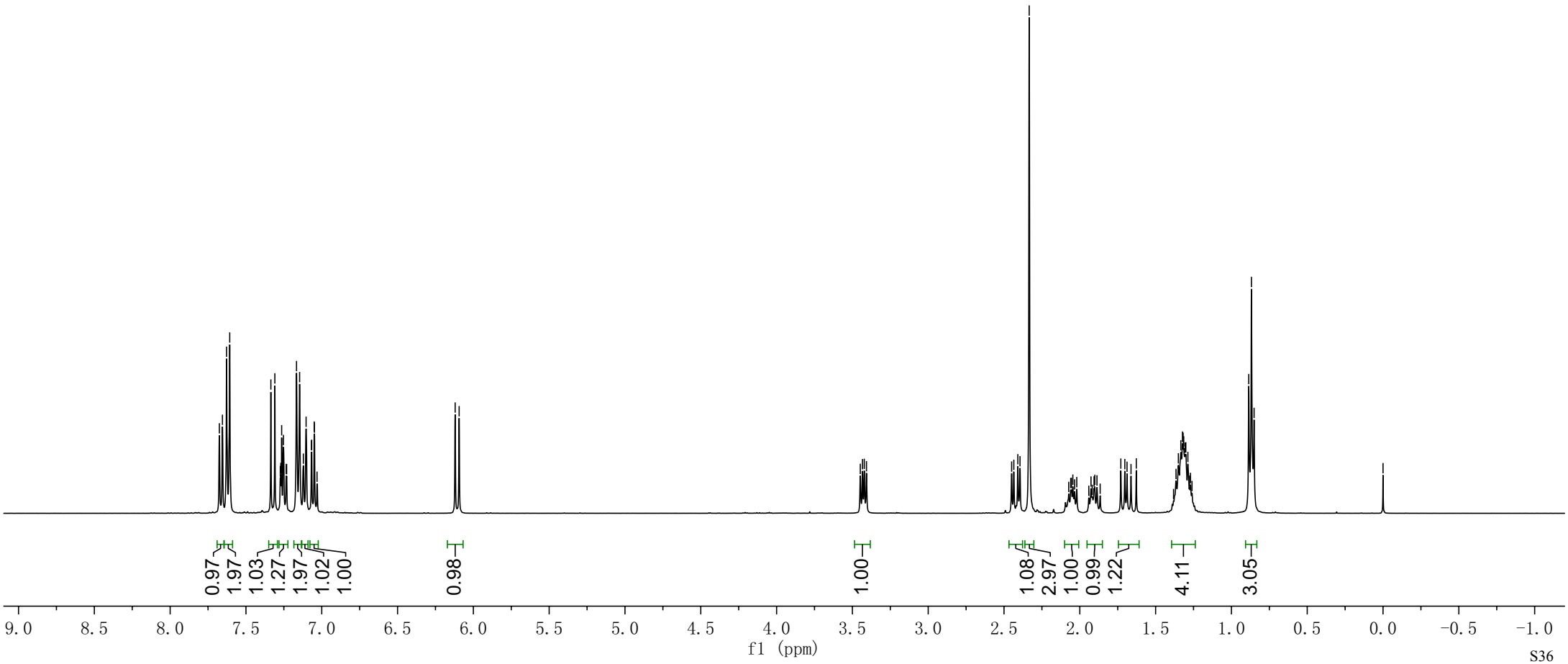
3ja

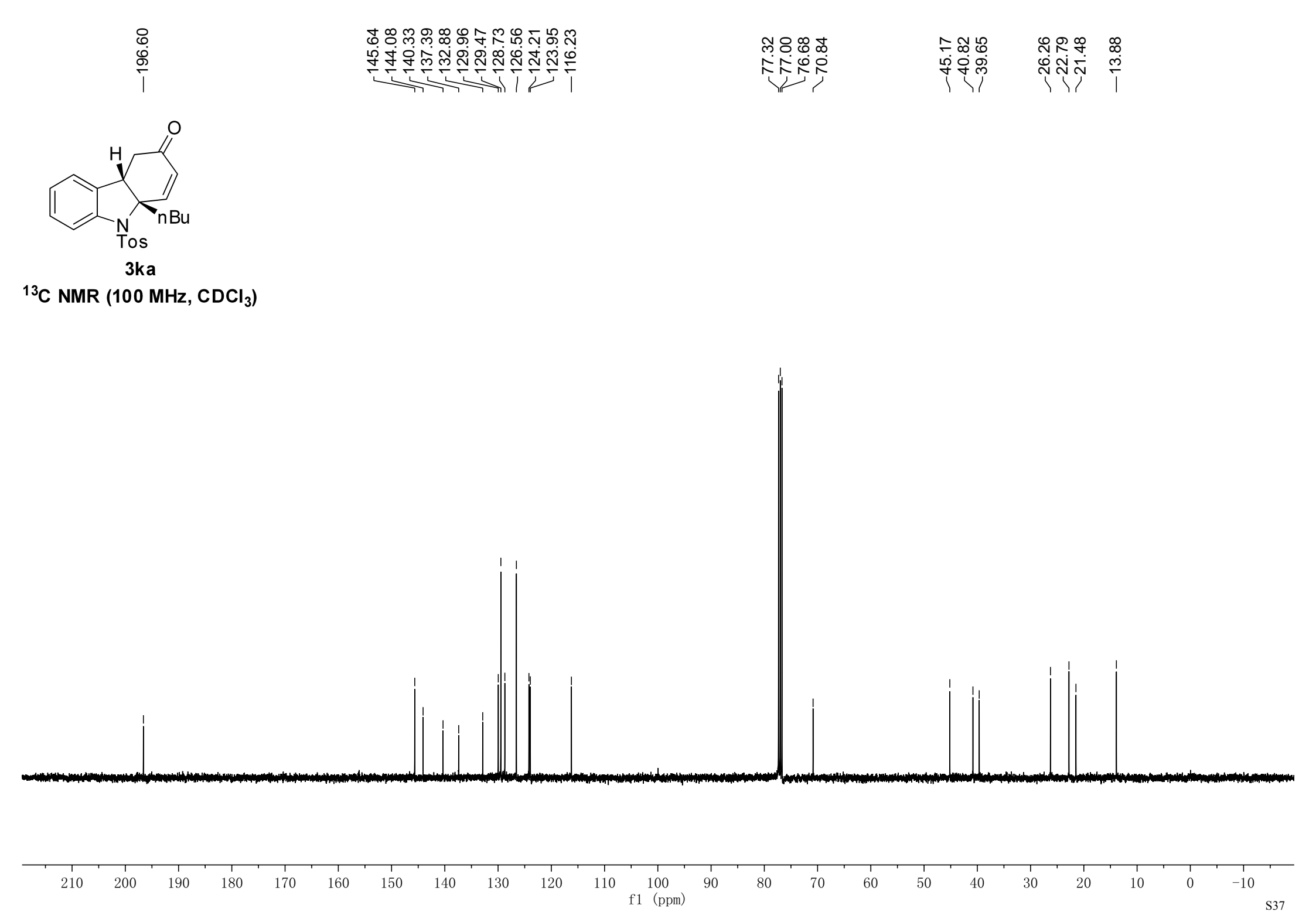
^{13}C NMR (100 MHz, $CDCl_3$)

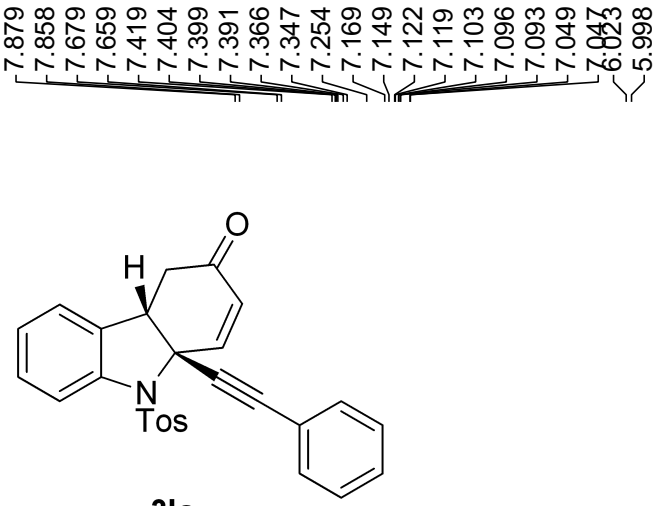


3ka

^{1}H NMR (400 MHz, $CDCl_3$)

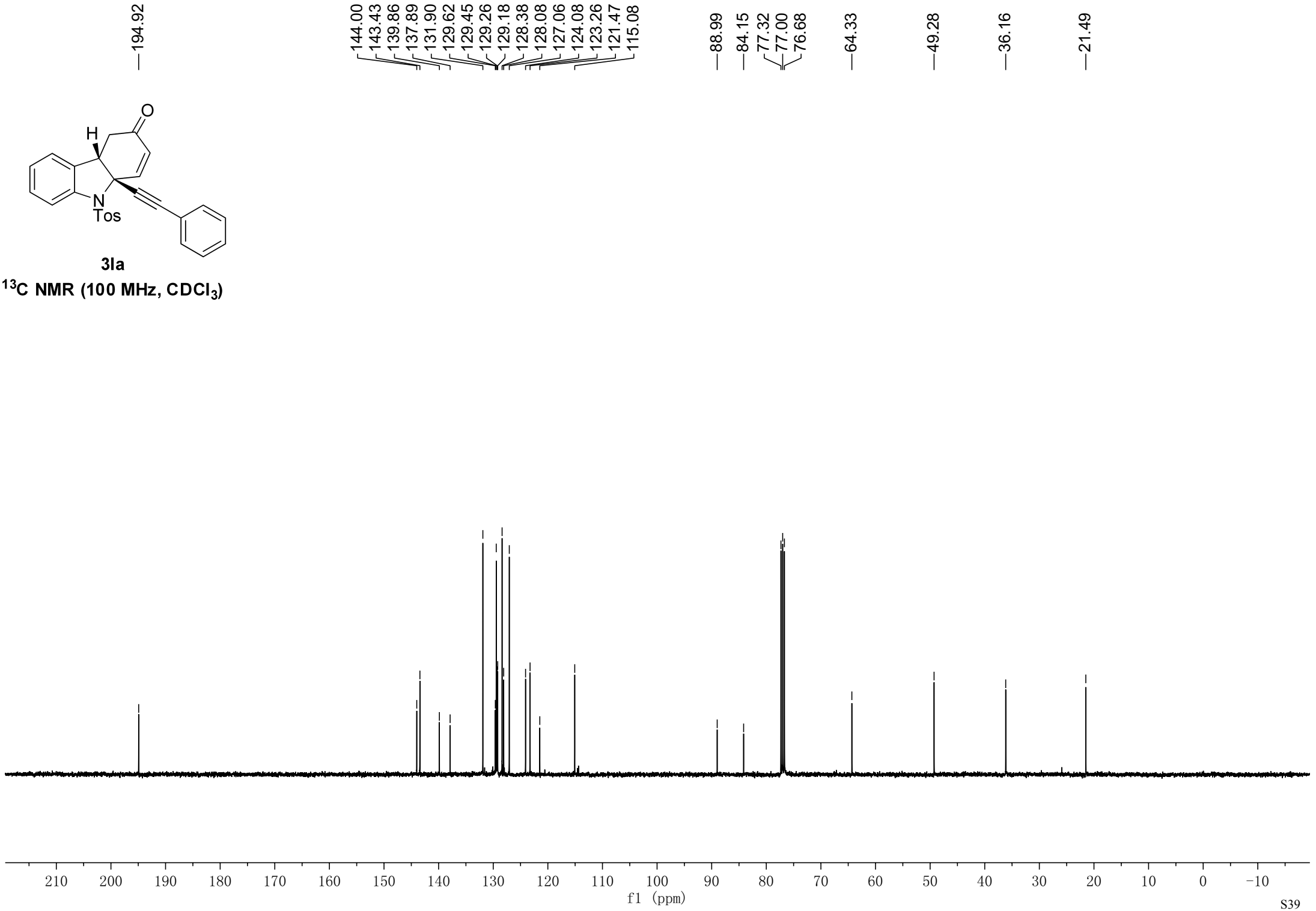


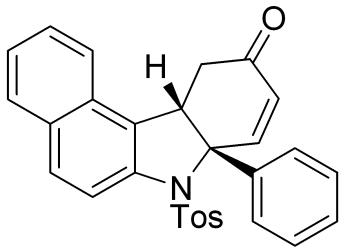

196.60
145.64
144.08
140.33
137.39
132.88
129.96
129.47
128.73
126.56
124.21
123.95
116.23
77.32
77.00
76.68
70.84
45.17
40.82
39.65
26.26
22.79
21.48
13.88
O
H
N
Tos
nBu
3ka
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3la

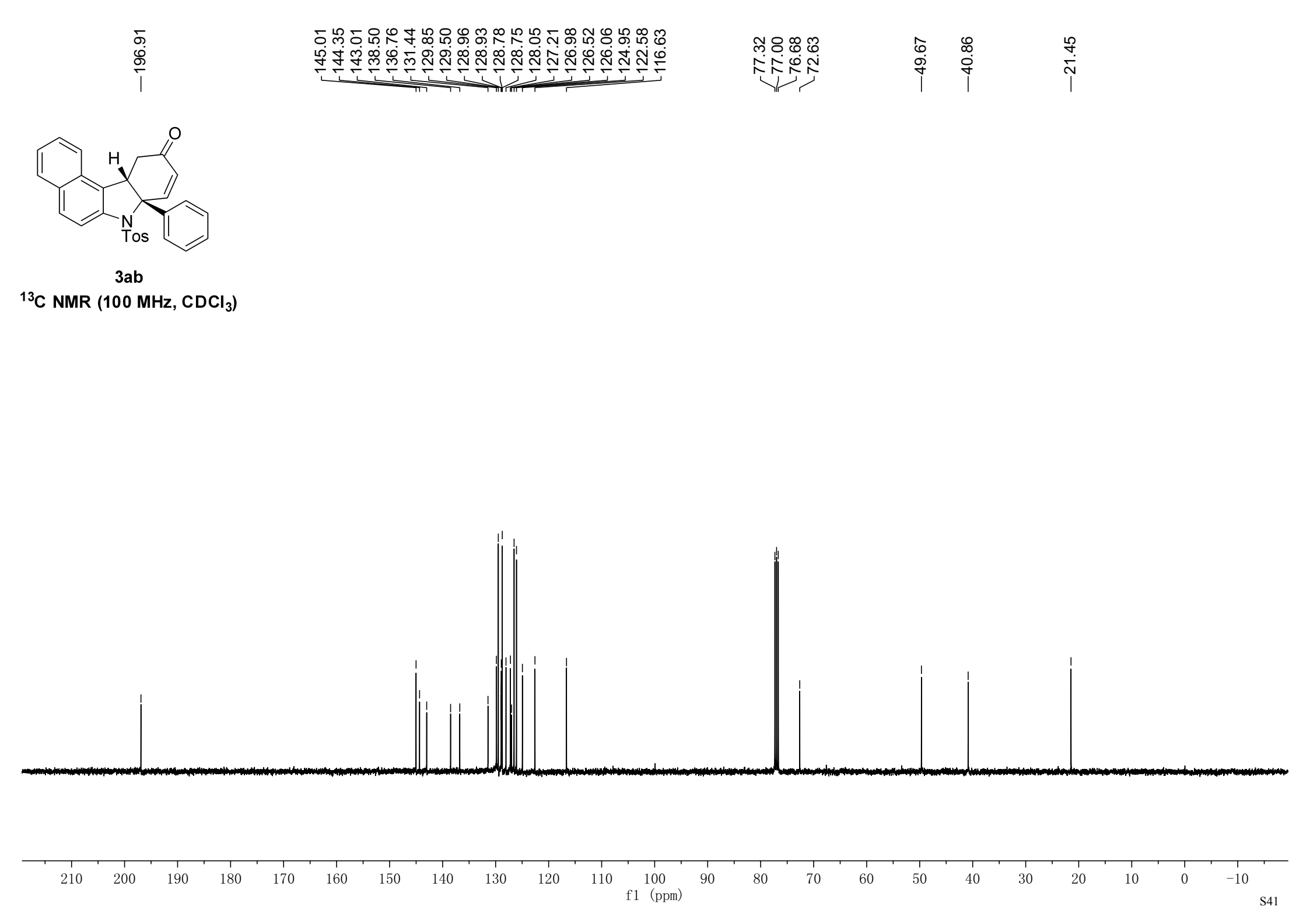
^{1}H NMR (400 MHz, $CDCl_3$)


194.92
144.00
143.43
139.86
137.89
131.90
129.62
129.45
129.26
129.18
128.38
128.08
127.06
124.08
123.26
121.47
115.08
88.99
84.15
77.32
77.00
76.68
64.33
49.28
36.16
21.49
O
H
N
Tos
3la
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3ab

^{1}H NMR (400 MHz, $CDCl_3$)

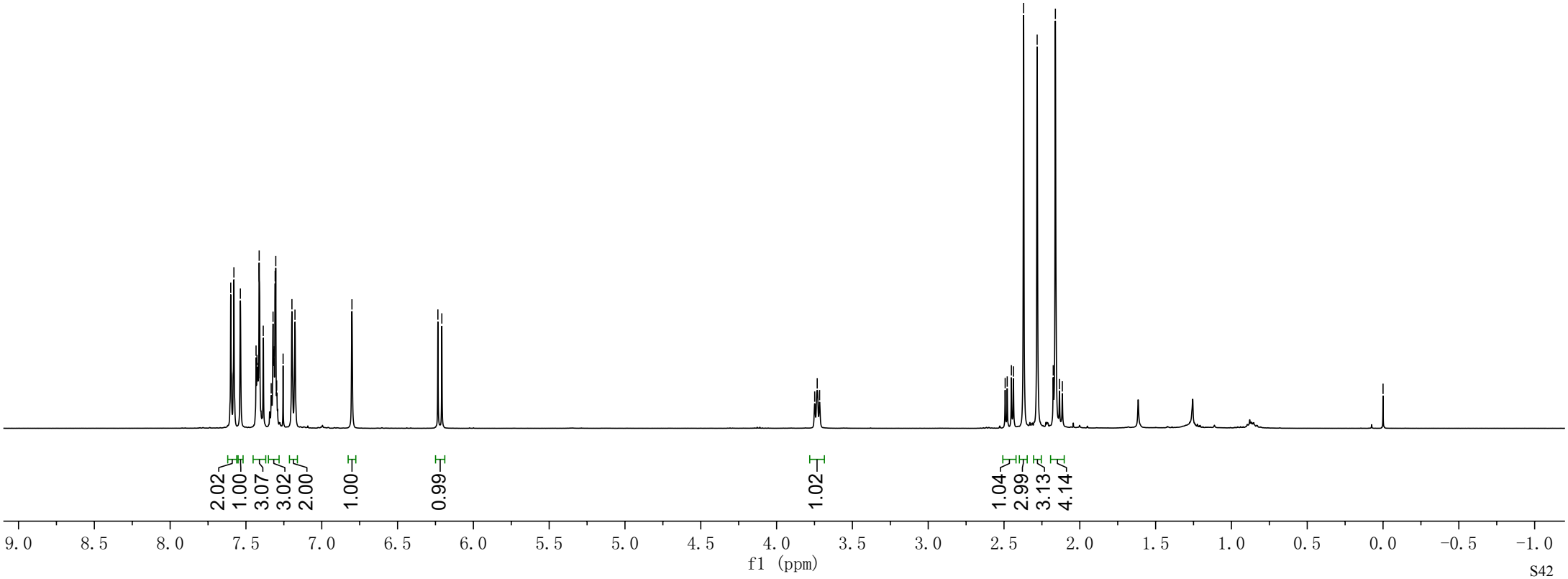


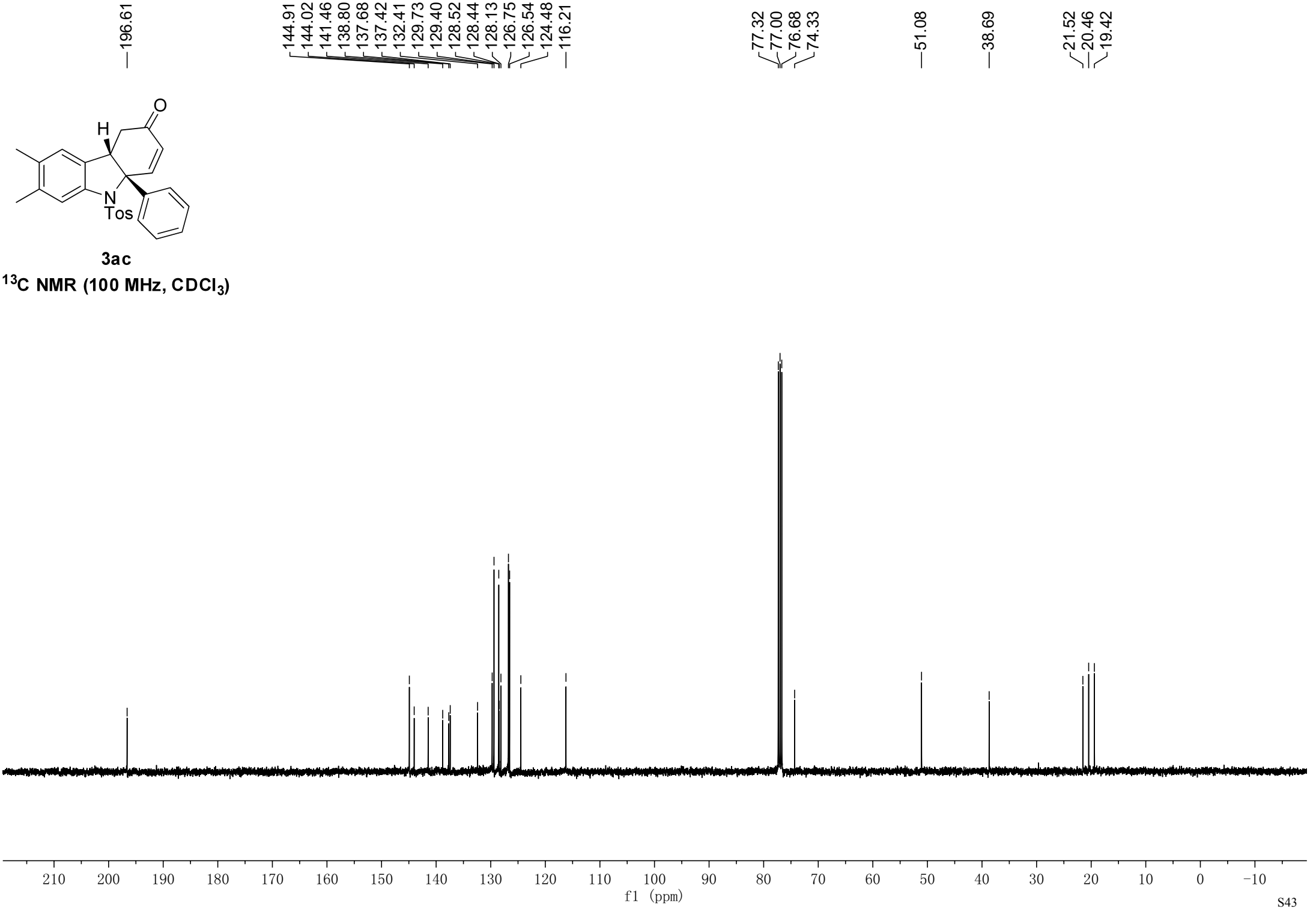
3ab

^{13}C NMR (100 MHz, $CDCl_3$)

3ac

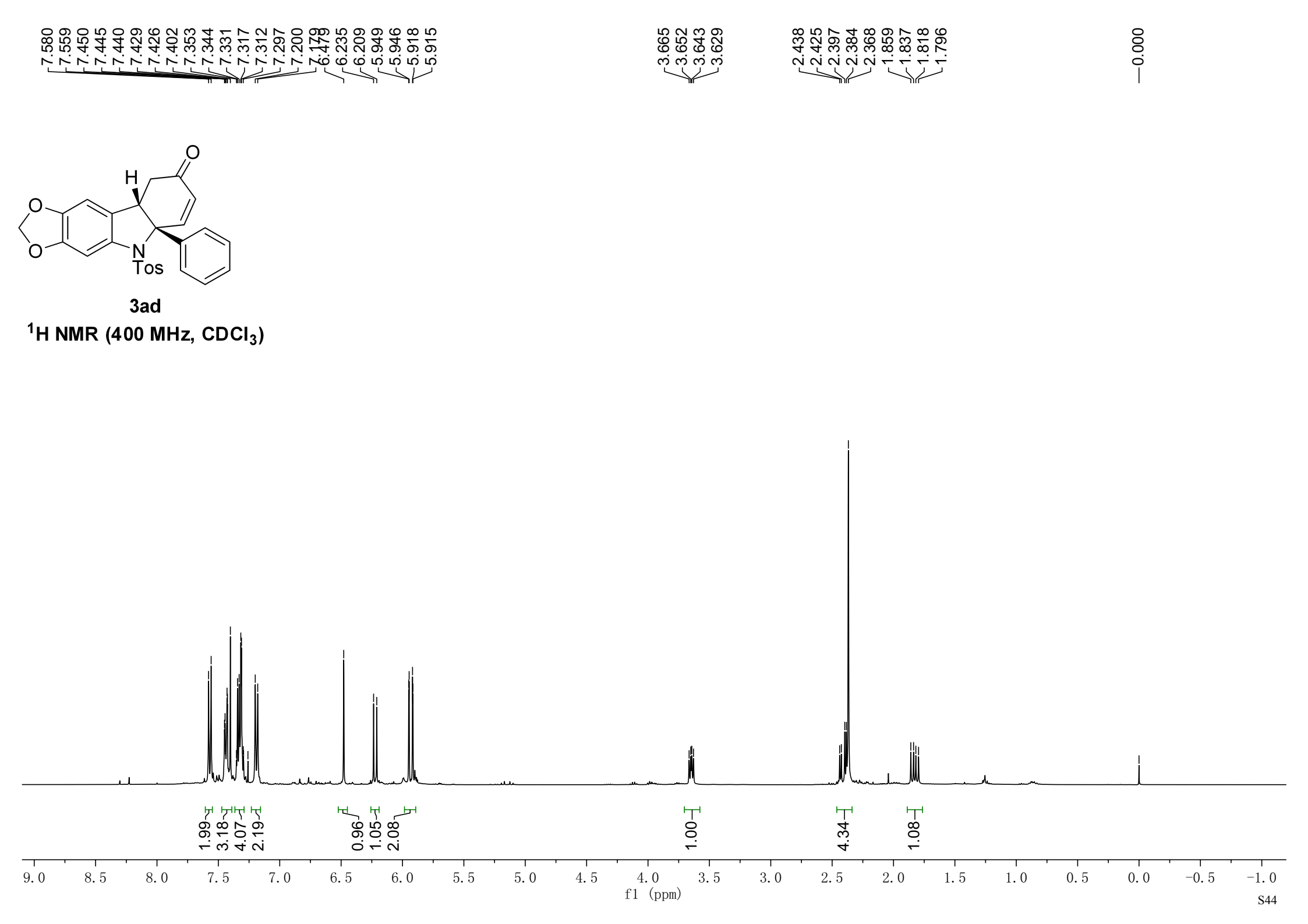
^{1}H NMR (400 MHz, $CDCl_3$)





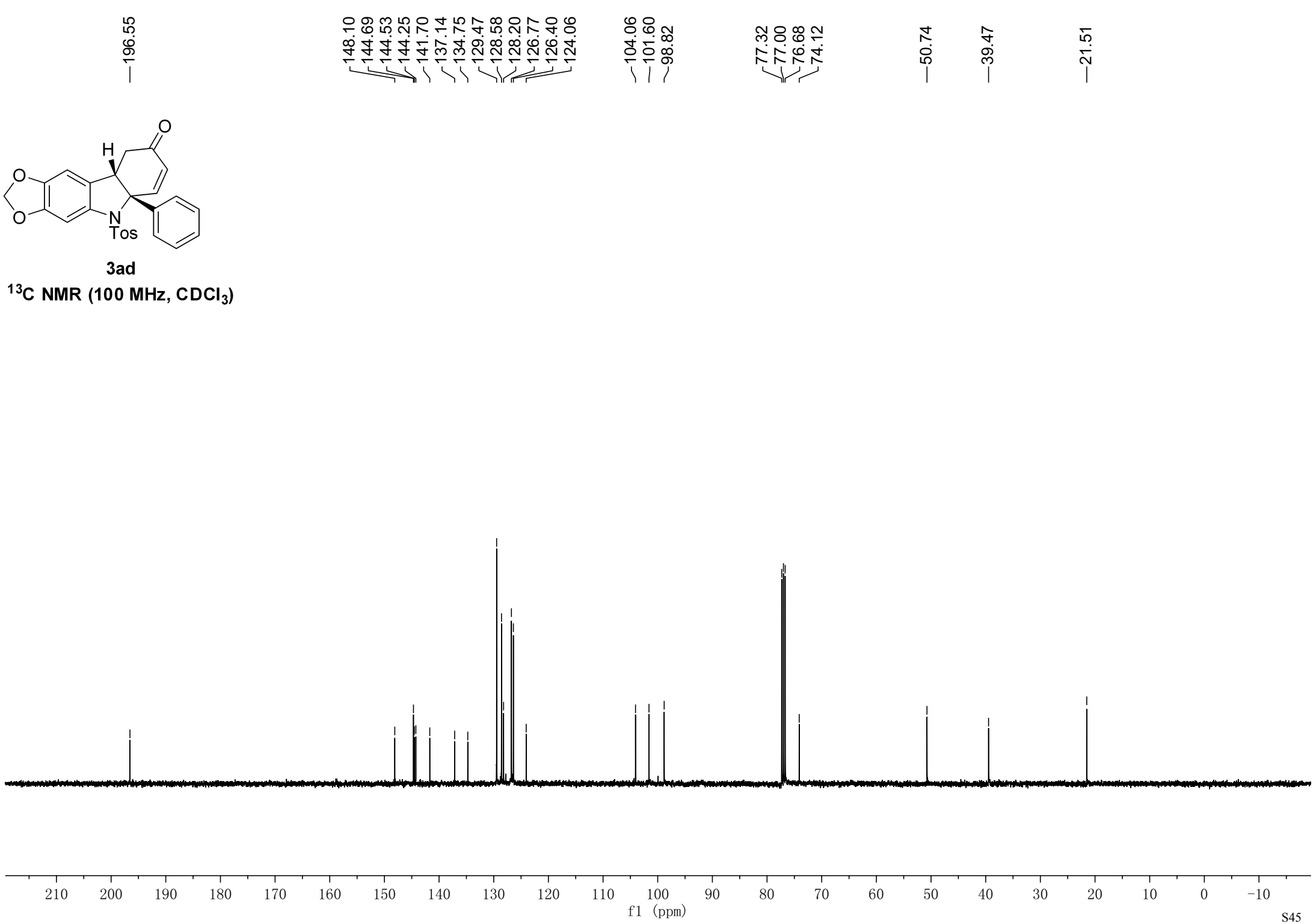
3ac

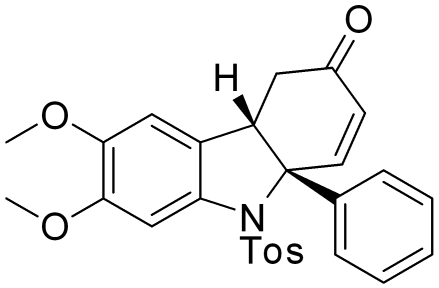
^{13}C NMR (100 MHz, $CDCl_3$)



3ad

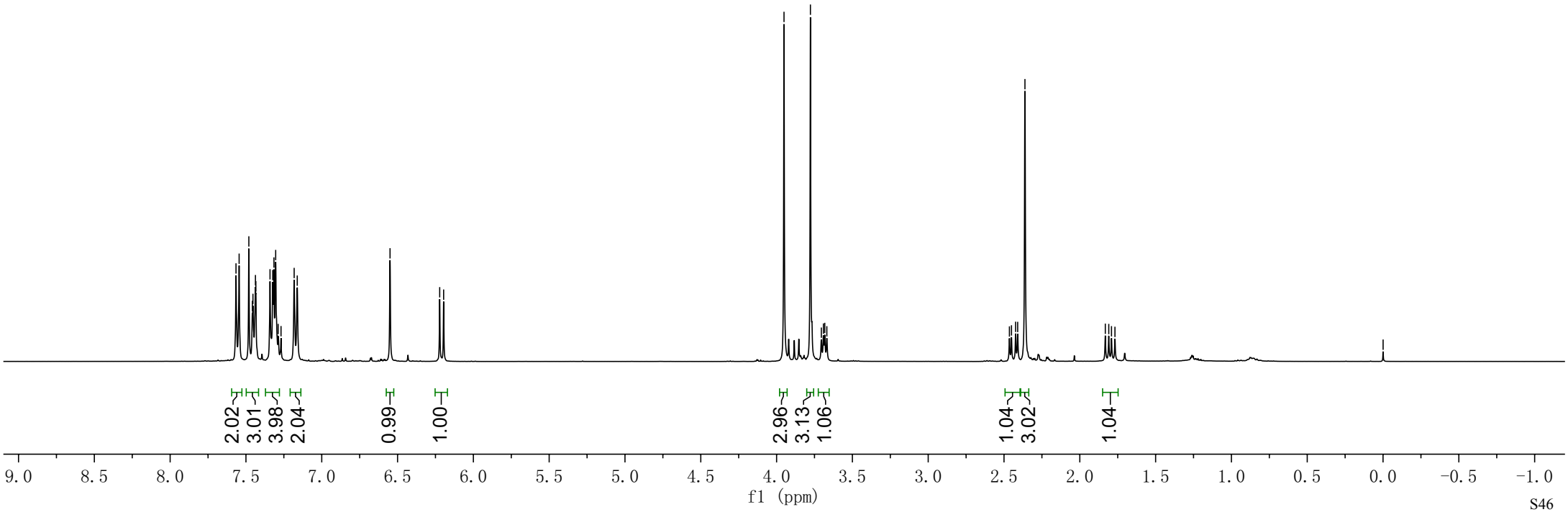
^{1}H NMR (400 MHz, $CDCl_3$)

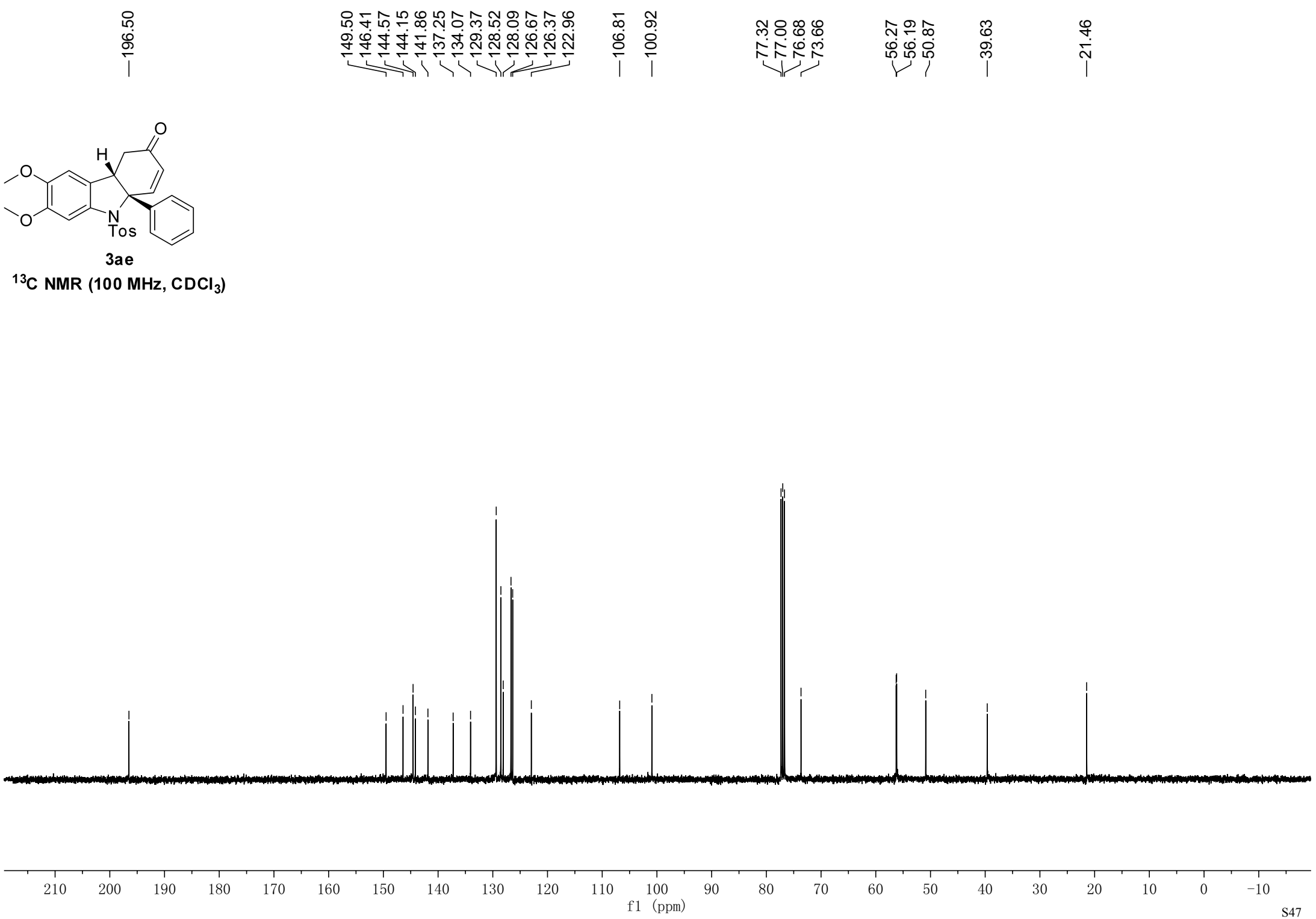

196.55
148.10
144.69
144.53
144.25
141.70
137.14
134.75
129.47
128.58
128.20
126.77
126.40
124.06
104.06
101.60
98.82
77.32
77.00
76.68
74.12
50.74
39.47
21.51
O
H
O
O
N
Tos
3ad
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

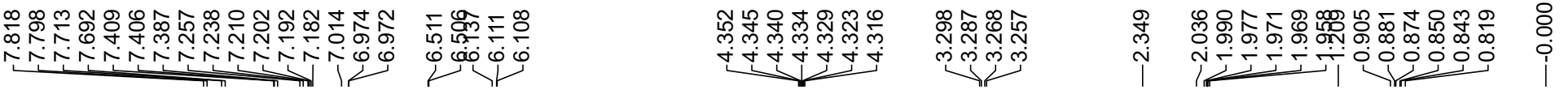


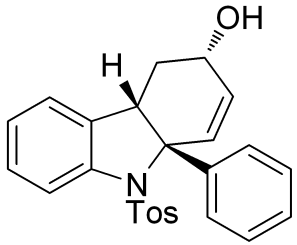
3ae

^{1}H NMR (400 MHz, $CDCl_3$)



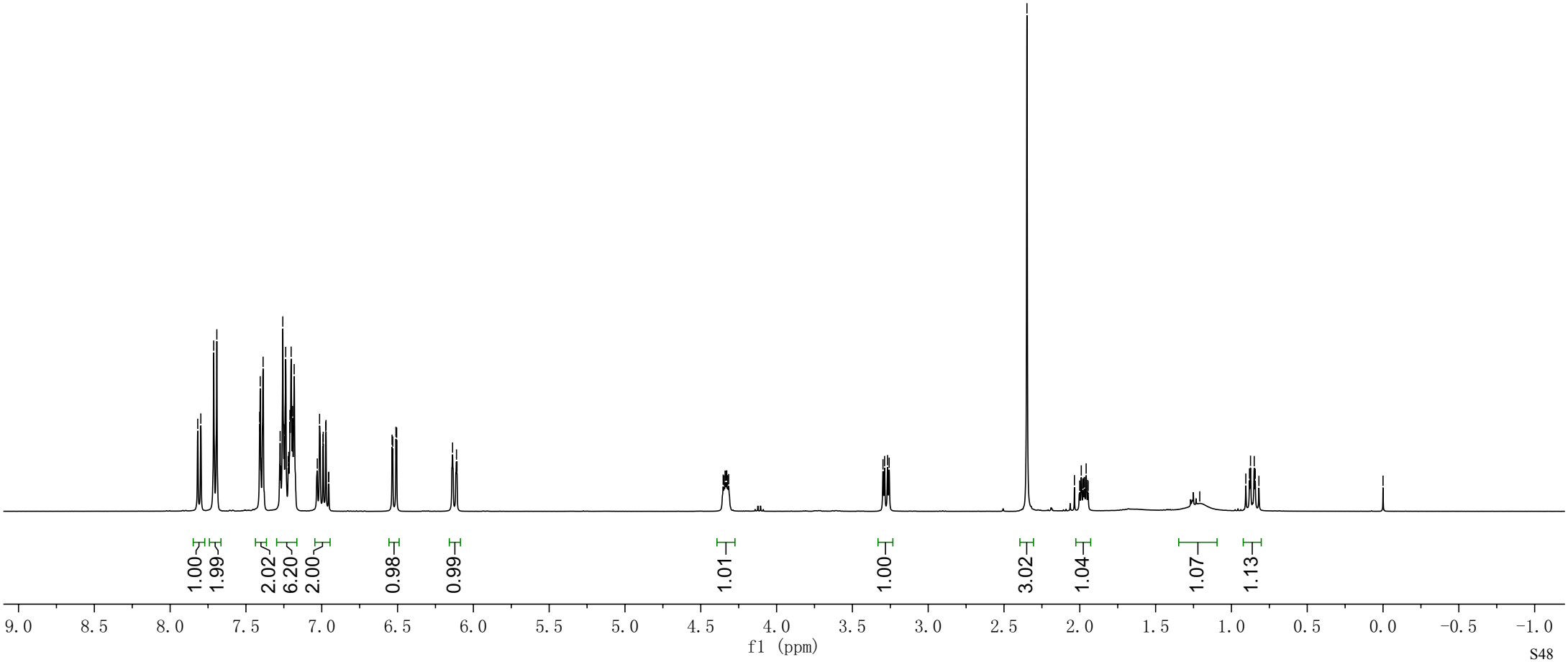

196.50
149.50
146.41
144.57
144.15
141.86
137.25
134.07
129.37
128.52
128.09
126.67
126.37
122.96
106.81
100.92
77.32
77.00
76.68
73.66
56.27
56.19
50.87
39.63
21.46
O
H
O
O
N
Tos
3ae
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

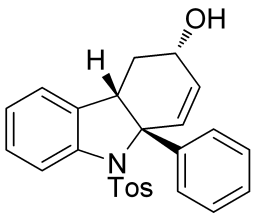




4

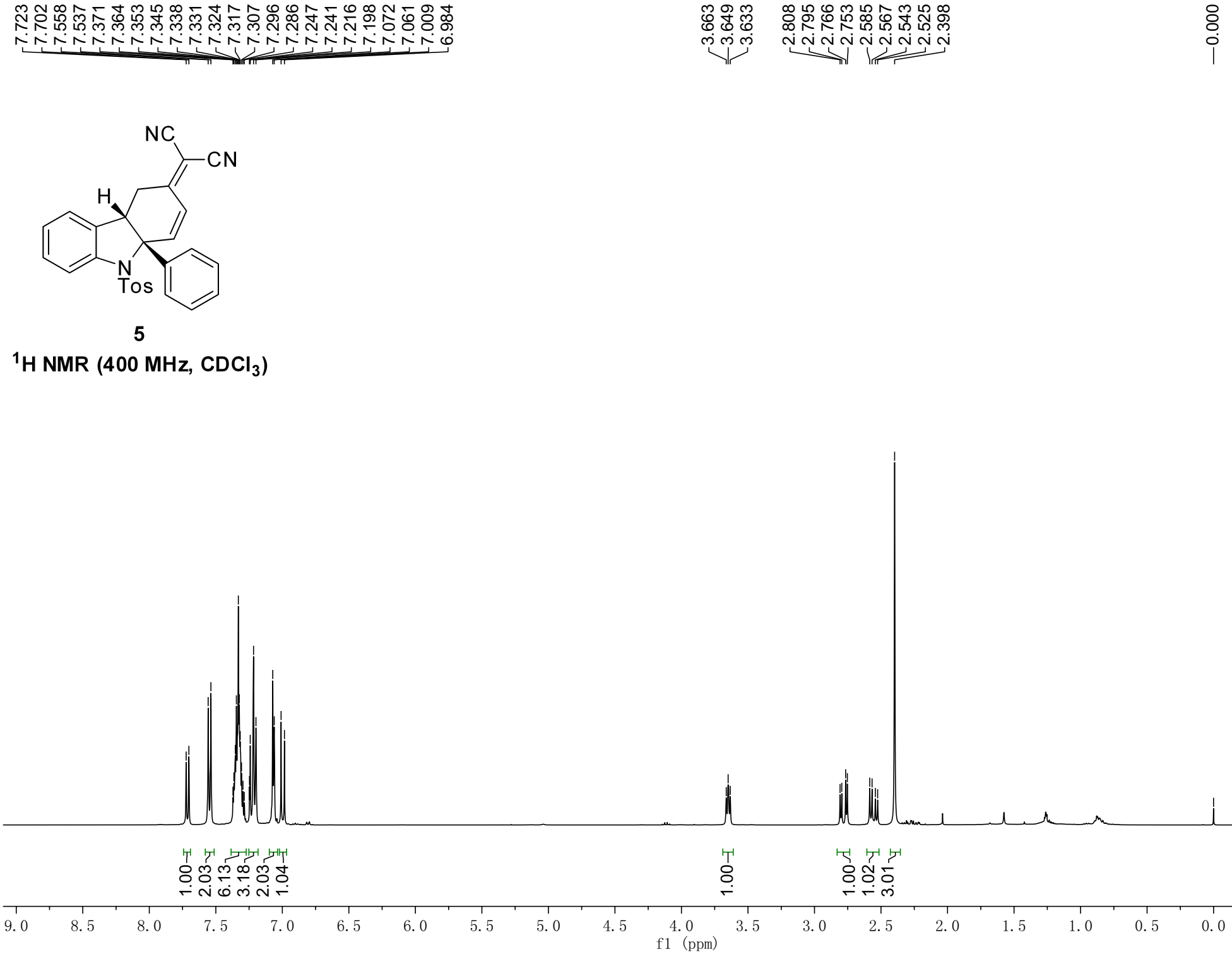
^{1}H NMR (400 MHz, $CDCl_3$)





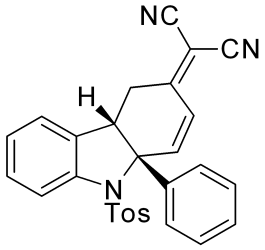
4

^{13}C NMR (100 MHz, $CDCl_3$)



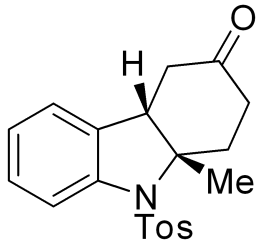
5

^{1}H NMR (400 MHz, $CDCl_3$)



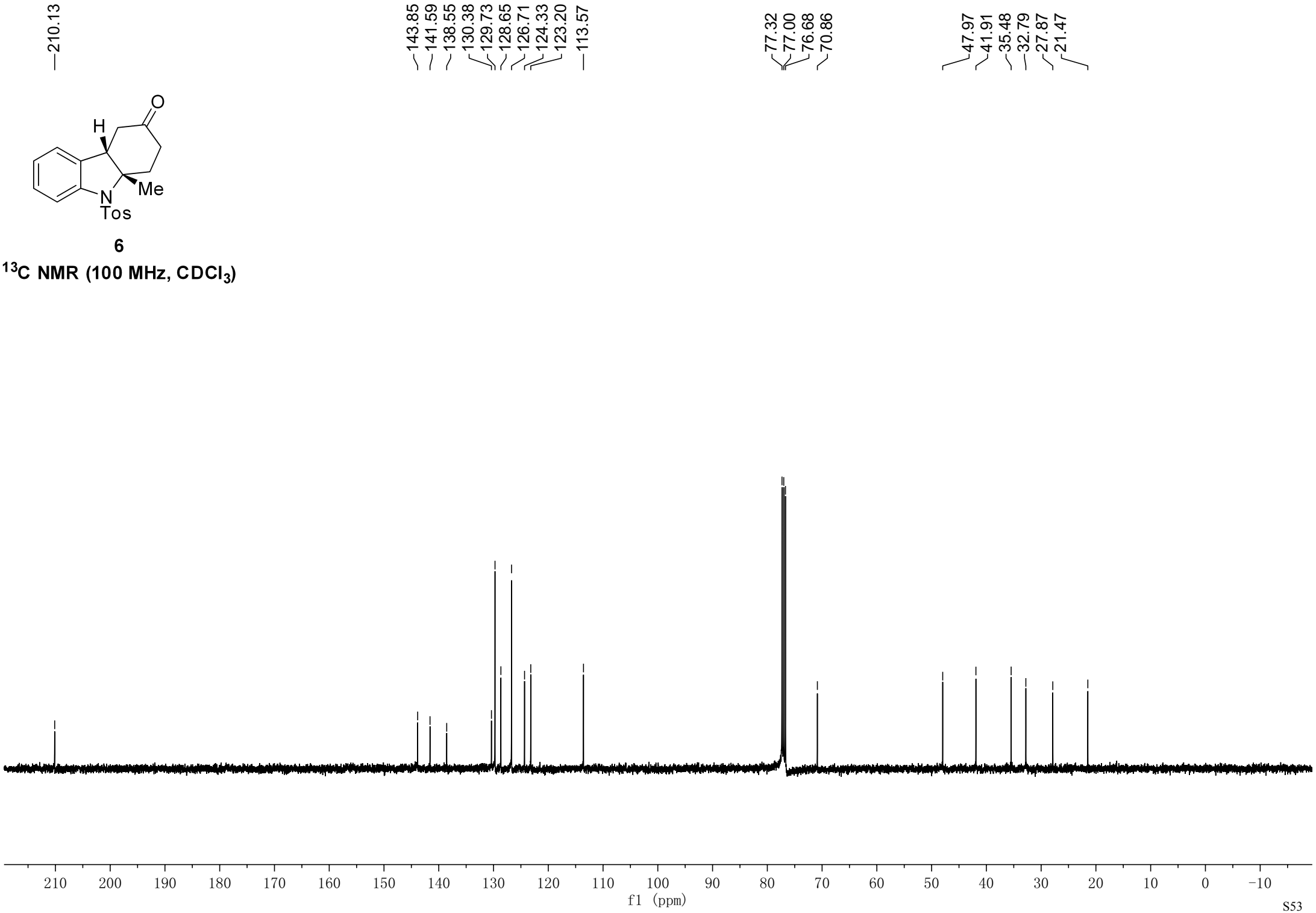
5

^{13}C NMR (100 MHz, $CDCl_3$)



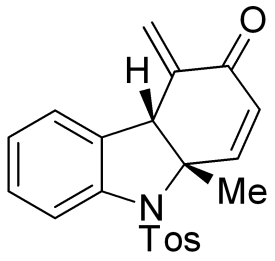
6

^{1}H NMR (400 MHz, $CDCl_3$)



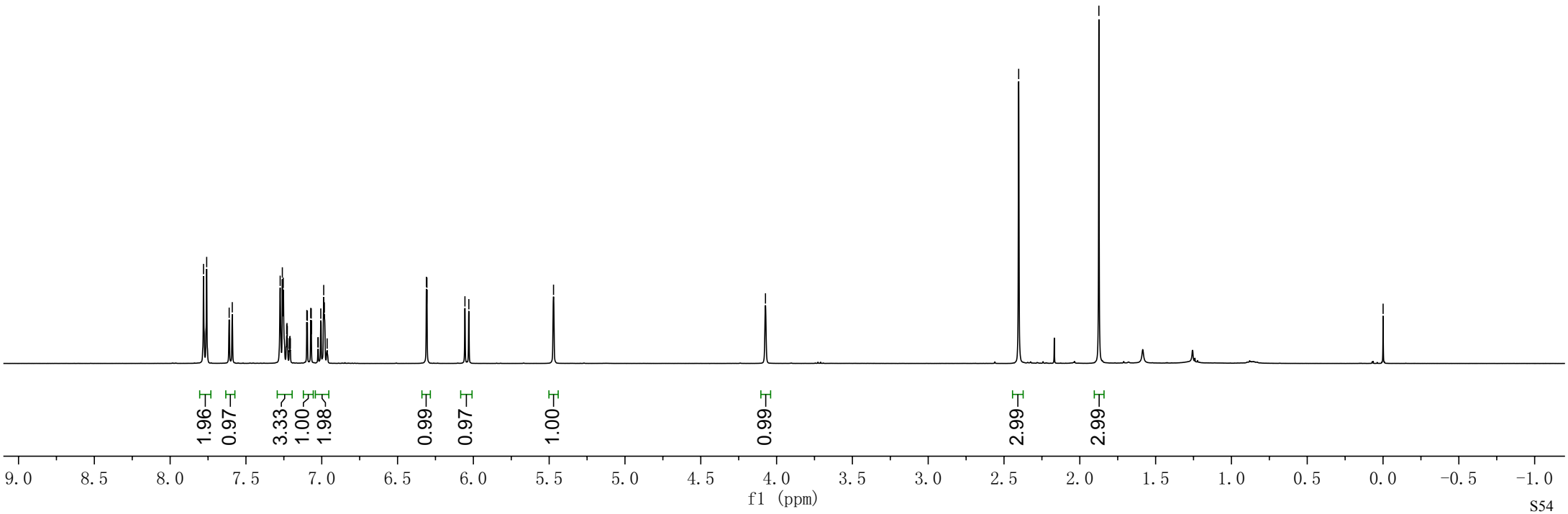
6

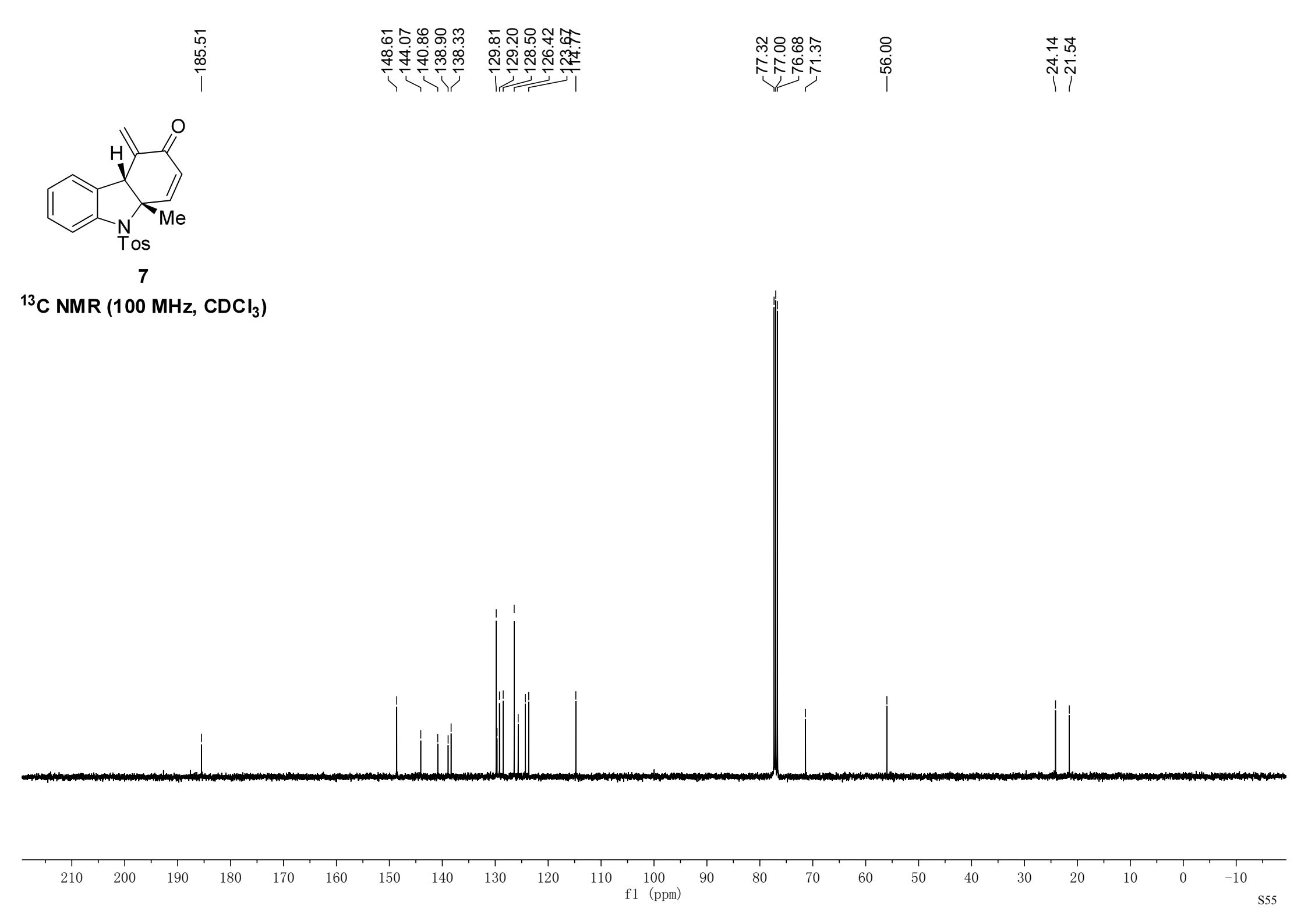
^{13}C NMR (100 MHz, $CDCl_3$)



7

^{1}H NMR (400 MHz, $CDCl_3$)




185.51
148.61
144.07
140.86
138.90
138.33
129.81
129.20
128.50
126.42
123.67
114.77
77.32
77.00
76.68
71.37
56.00
24.14
21.54
O
H
Me
N
Tos
7
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)