

Supporting Online Material for

CuX Dual Catalysis: Constructions of Oxazolo[2,3-*b*][1,3] oxazines via Tandem CuAAC/Ring Cleavage/[4+2+3] Annulation Reaction

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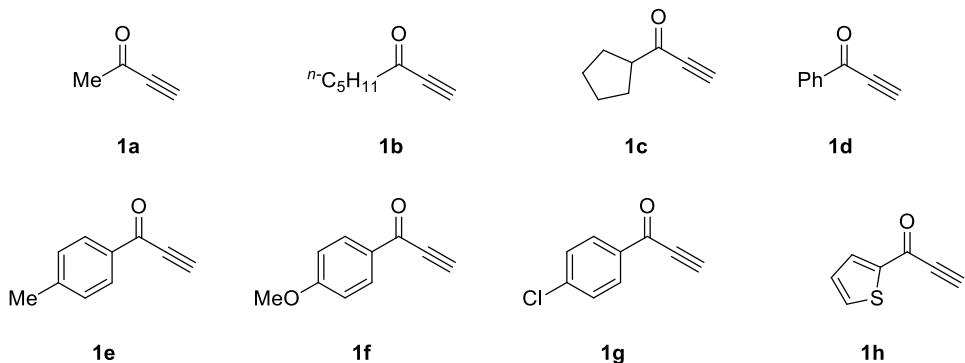
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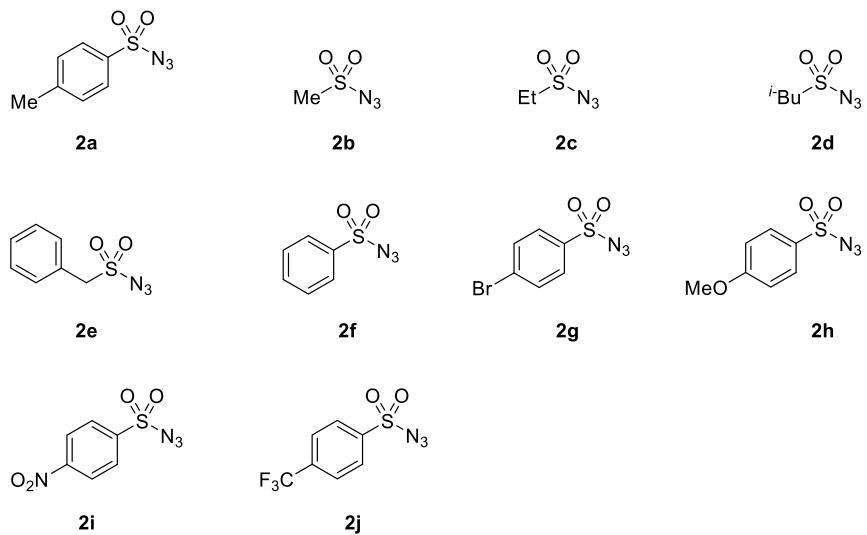
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1. The structures of starting materials of 1a-1l, 2a-2j and 3a-3h

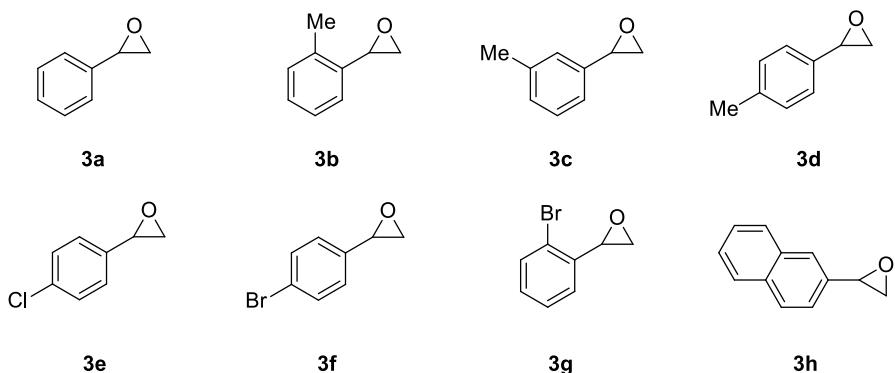
1.1 Structures of starting material of 1a-1h



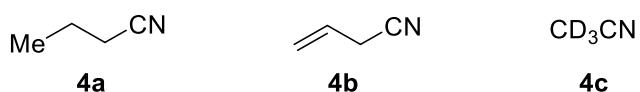
1.2 Structures of starting material of 2a-2j



1.3 Structures of starting material of 3a-3h



1.3 Structures of starting material of 4a-4c



All the starting materials of **1a–1h**, **2a–2j**, **3a–3h**, and **4a–4c** are known compounds. Terminal yrones (**1a–1h**) were prepared by purchase (**1a**) or literature methods,¹ sulfonyl azides (**2a–2j**) were prepared by literature methods², oxiranes (**3a–3h**) prepared by purchase (**3a**) or literature methods,³ and all nitriles (**4a–4c**) were prepared by purchase.

References

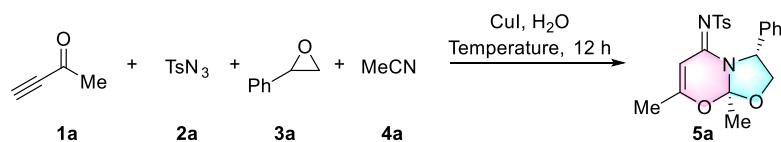
- (1) D. Chernyak, S. B. Gadamsetty, V. Gevorgyan. *Org Lett.* **2008**, *10*, 2307–2310.
- (2) D. Das and R. Samanta, *Adv. Synth. Catal.* **2018**, *360*, 379–384.
- (3) X. Ma, S. Pan, H. Wang, W. Chen. *Org Lett.* **2014**, *16*, 4554–4557.
- (4) G. Sabitha, R. Satheesh Babu, M. Rajkumar, Ch. Srinivas Reddy, J. S. Yadav. *Tetrahedron Lett.* **2001**, *42*, 3955–3958.

2. General information

All melting points were determined on a Yanaco melting point apparatus and were uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. All spectra of ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) were recorded on a Bruker AVANCE NEO 400 MHz spectrometer in DMSO-*d*₆ or CDCl₃ (otherwise as indicated) with TMS was used as an internal reference and J values are given in Hz. High resolution mass spectra (HRMS) **5a-5z**, **5aa** and **6** were recorded on Thermo Scientific Q Exactive Focus Orbitrap LC-MS/MS spectrometer. Single crystal X-ray diffraction analyses were recorded on Bruker SMART APEX II.

3. Optimization of catalytic conditions

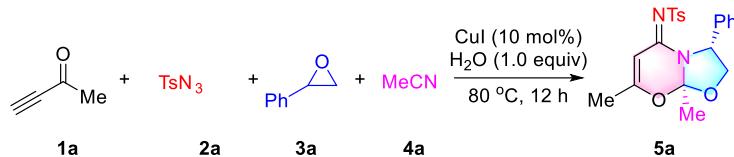
Table S1 The effect of changing the amount of Cat., H₂O and substrates, and temperature.^a



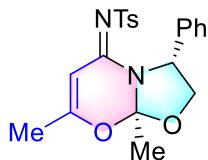
Entry	1a (mmol)	2a (mmol)	3a (mmol)	CuI (mmol)	H ₂ O (mmol)	Temperature (°C)	4a Yield ^b (%)
1	0.75	0.75	0.5	0.05	0.5	80	78
2	0.5	0.5	0.5	0.05	0.5	80	67
3	1.0	1.0	0.5	0.05	0.5	80	78
4	0.5	0.5	0.75	0.05	0.5	80	53
5	0.75	0.75	0.5	0.025	0.5	80	74
6	0.75	0.75	0.5	0.1	0.5	80	57
7	0.75	0.75	0.5	0.05	0.25	80	65
8	0.75	0.75	0.5	0.05	1.0	80	76
9	0.75	0.75	0.5	0.05	2.0	80	66
10	0.75	0.75	0.5	0.05	0.5	60	69
11	0.75	0.75	0.5	0.05	0.5	90	76
12	0.75	0.75	0.5	0.05	0.5	100	47

^a Reaction conditions: **1a** (1.5 equiv), CuI, H₂O in the solvent (**4a** as the solvent, 3 mL) was added with **3a** and **2a** in order under stirring at corresponding temperature for 12 h. ^b Isolated yields.

4. Preparation and characterizations of compounds **5a–5z** and **5aa**.



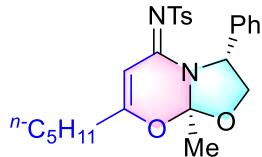
The general procedure preparation of compounds **5a** was as below: To solution of styrene oxides (**3a**, 0.5 mmol, 1.0 equiv., 60.1 mg), CuI (0.05 mmol, 0.1 equiv., 9.5 mg) in nitriles (**4a**, 3 mL) was added, then added the terminal yrones (**1a**, 0.75 mmol, 1.5 equiv., 51.1 mg) and sulfonyl azides (**2a**, 0.75 mmol, 1.5 equiv., 147.9 mg). After the reaction mixture stirring at 80 °C in an oil bath for 12 hours, and cooled at room temperature, the solvent removed by evaporating in vacuum. The residue purified by a flash chromatography [silica gel, 20%–50% EtOAc in petroleum ether (60–90 °C)] to give the corresponding products **5a** (78%, 155.4 mg), (R_f = 0.3 in 1:4 v/v ethyl acetate/60-90 petroleum ether). Unless otherwise specified, the synthesis steps of products **5b–5z** are the same as **5a**.



Chemical Formula: C₂₁H₂₂N₂O₄S
Molecular Weight: 398.4754

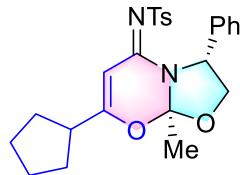
N-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5a). Preparation of compounds **5a** with **5 mmol scale**: To solution of styrene oxide (**3a**, 5.0 mmol, 1.0 equiv., 600.5 mg), CuI (0.50 mmol, 95.0 mg) in MeCN (**4a**, 30.0 mL) was added, Then added the but-3-yn-2-one (**1a**, 7.5 mmol, 1.5 equiv., 510.0 mg) and tosyl azide (**1a**, 7.5 mmol, 1.5 equiv., 1479.0 mg). After the reaction mixture stirring at 80 °C in an oil bath for 24 hours, and cooled at room temperature, the solvent removed by evaporating in vacuum. The residue purified by a flash chromatography [silica gel, 20% EtOAc in petroleum ether (60–90 °C)] to give the corresponding products **5a** (1499.0 mg, 70%), a white solid, m.p. = 159.7–160.9 °C (R_f = 0.3 in 1:4 v/v ethyl acetate/60-90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.32–7.26

(m, 5H), 7.22 (d, J = 7.6 Hz, 2H), 6.51 (s, 1H), 5.40 (s, 1H), 4.41 (d, J = 8.4 Hz, 1H), 4.36–4.33 (m, 1H), 2.39 (s, 3H), 2.07 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 155.7, 142.2, 140.4, 137.8, 129.0 (2C), 128.6 (2C), 128.0, 126.8 (2C), 126.3 (2C), 112.5, 95.0, 71.7, 61.8, 22.6, 21.4, 20.3; IR ν_{max} (KBr) 3356, 3257, 1604, 1514, 1331, 1455, 1143 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 399.1373, found 399.1367.



Chemical Formula: C₂₅H₃₀N₂O₄S
Molecular Weight: 454.5817

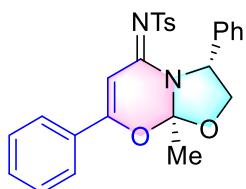
4-Methyl-N-(8a-methyl-7-pentyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5b) (159.1 mg, 70%), colorless liquid, (R_f = 0.3 in 1:5 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.8 Hz, 2H), 7.37–7.26 (m, 5H), 7.22 (d, J = 7.9 Hz, 2H), 6.49 (s, 1H), 5.41 (d, J = 5.7 Hz, 1H), 4.41 (d, J = 8.5 Hz, 1H), 4.34–4.32 (m, 1H), 2.39 (s, 3H), 2.29 (t, J = 7.7 Hz, 2H), 1.67 (s, 3H), 1.58 (p, J = 6.7 Hz, 2H), 1.35–1.30 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 155.9, 142.1, 140.4, 137.7, 129.0(2C), 128.6(2C), 128.0, 126.7(2C), 126.2(2C), 112.4, 94.3, 71.6, 61.8, 33.9, 31.2, 25.7, 22.6, 22.2, 21.4, 13.8; IR ν_{max} (KBr) 3649, 2930, 1612, 1520, 1279, 1144, 1082 cm^{-1} . HRMS (ESI) m/z calcd for C₂₅H₃₁N₂O₄S⁺ [M+H]⁺ 455.1999, found 455.1992.



Chemical Formula: C₂₅H₂₈N₂O₄S
Molecular Weight: 452.5658

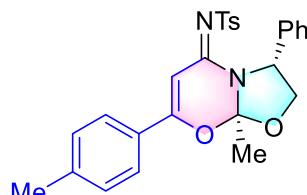
N-(7-Cyclopentyl-8a-methyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5c) (162.9 mg, 72%), a white solid, m.p. = 137.6–139.1 °C (R_f = 0.3 in 1:5 v/v ethyl acetate/60-90 petroleum ether). ^1H

NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.33–7.27 (m, 5H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.51 (s, 1H), 5.41 (s, 1H), 4.41 (d, *J* = 8.2 Hz, 1H), 4.37–4.34 (m, 1H), 2.74–2.71 (m, 1H), 2.39 (s, 3H), 1.90–1.89 (m, 2H), 1.74–1.71 (m, 3H), 1.66–1.64 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 156.1, 142.1, 140.5, 137.8, 129.0 (2C), 128.6 (2C), 128.0, 126.7 (2C), 126.3 (2C), 112.4, 93.2, 71.7, 61.7, 43.8, 30.3, 29.9, 25.6 (2C), 22.5, 21.4; IR ν_{max} (KBr) 3681, 3198, 2957, 1605, 1528, 1452, 1273, 1144 cm⁻¹. HRMS (ESI) m/z calcd for C₂₅H₂₉N₂O₄S⁺ [M+H]⁺ 453.1843, found 453.1836.



Chemical Formula: C₂₆H₂₄N₂O₄S
Molecular Weight: 460.5448

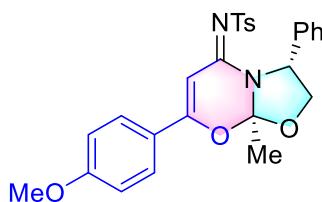
4-Methyl-N-(8a-methyl-3,7-diphenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5d) (172.7 mg, 75%), a white solid, m.p. = 142.0–142.9 °C, (R_f = 0.3 in 1:5 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 12.0, 8.4 Hz, 4H), 7.54–7.51 (m, 1H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.40–7.38 (m, 2H), 7.35–7.29 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 1H), 5.47 (s, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.43–4.40 (m, 1H), 2.38 (s, 3H), 1.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 156.5, 142.2, 140.4, 137.8, 132.3, 130.9, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.0, 127.2 (2C), 126.7 (2C), 126.3 (2C), 112.9, 92.5, 71.9, 62.0, 22.3, 21.4; IR ν_{max} (KBr) 3649, 3050, 1572, 1510, 1450, 1285, 1148 cm⁻¹. HRMS (ESI) m/z calcd for C₂₆H₂₅N₂O₄S⁺ [M+H]⁺ 461.1530, found 461.1523.



Chemical Formula: C₂₇H₂₆N₂O₄S
Molecular Weight: 474.5713

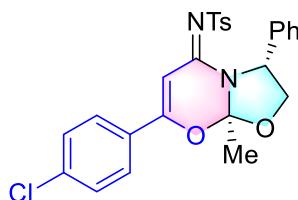
4-Methyl-N-(8a-methyl-3-phenyl-7-(p-tolyl)-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5e) (194.6 mg, 82%), a white solid, m.p. = 186.5–187.3 °C, (R_f = 0.3 in 1:5 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR

(400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 6.1 Hz, 2H), 7.33–7.31 (m, 3H), 7.26–7.22 (m, 4H), 7.11 (s, 1H), 5.47 (s, 1H), 4.47–4.42 (m, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 156.7, 143.2, 142.2, 140.5, 137.9, 129.5 (2C), 129.1 (2C), 128.6 (2C), 128.1, 128.0, 127.3 (2C), 126.7 (2C), 126.3 (2C), 112.9, 91.8, 72.0, 62.0, 22.3, 21.6, 21.4; IR ν_{max} (KBr) 3650, 2918, 1597, 1517, 1450, 1280, 1146 cm⁻¹. HRMS (ESI) m/z calcd for C₂₇H₂₇N₂O₄S⁺ [M+H]⁺ 475.1686, found 475.1679.



Chemical Formula: C₂₇H₂₆N₂O₅S
Molecular Weight: 490.5707

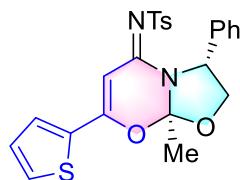
***N*-(7-(4-Methoxyphenyl)-8a-methyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5f)** (188.9 mg, 77%), a white solid, m.p. = 202.9–203.6 °C, (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 6.7 Hz, 2H), 7.36–7.30 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.03 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 5.46 (s, 1H), 4.47–4.40 (m, 2H), 3.87 (s, 3H), 2.39 (s, 3H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 162.0, 156.9, 142.2, 140.6, 138.0, 129.2 (2C), 129.1 (2C), 128.6 (2C), 128.0, 126.8 (2C), 126.3 (2C), 123.28, 114.3 (2C), 112.9, 90.8, 72.0, 62.0, 55.5, 22.3, 21.4; IR ν_{max} (KBr) 3648, 2922, 1593, 1514, 1429, 1146, 1103, 1080 cm⁻¹. HRMS (ESI) m/z calcd for C₂₇H₂₇N₂O₅S⁺ [M+H]⁺ 491.1635, found 491.1628.



Chemical Formula: C₂₆H₂₃ClN₂O₄S
Molecular Weight: 494.9898

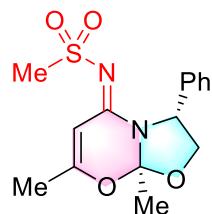
***N*-(7-(4-Chlorophenyl)-8a-methyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5g)** (183.1 mg, 74%), a white

solid, m.p. = 173.7–174.0 °C, (R_f = 0.3 in 1:5 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.42 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 6.4 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.23 (d, J = 7.5 Hz, 2H), 7.15 (s, 1H), 5.47 (s, 1H), 4.47 (d, J = 8.4 Hz, 1H), 4.43–4.40 (m, 1H), 2.38 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 156.2, 142.3, 140.3, 138.5, 137.6, 129.4, 129.1 (4C), 128.6 (2C), 128.4 (2C), 128.1, 126.7 (2C), 126.2 (2C), 113.0, 92.7, 72.0, 62.0, 22.3, 21.4; IR ν_{max} (KBr) 3685, 2986, 1595, 1508, 1429, 1281, 1148 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{ClN}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 495.1140, found 495.1133.



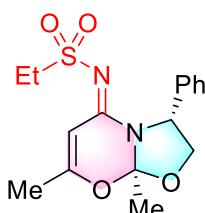
Chemical Formula: $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$
Molecular Weight: 466.5725

4-Methyl-N-(8a-methyl-3-phenyl-7-(thiophen-2-yl)-2,3-dihydrooxazolo[2,3-b] [1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5h) (182.0 mg, 78%), a white solid, m.p. = 166.3–166.9 °C, (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 4.4 Hz, 1H), 7.58 (t, J = 3.8 Hz, 1H), 7.38 (d, J = 7.4 Hz, 2H), 7.35–7.29 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (q, J = 4.0 Hz, 1H), 7.01 (s, 1H), 5.46 (s, 1H), 4.47–4.40 (m, 2H), 2.38 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.1, 156.5, 142.2, 140.3, 137.8, 134.8, 131.6, 130.0, 129.1 (2C), 128.6 (2C), 128.5, 128.0, 126.7 (2C), 126.3 (2C), 113.0, 91.0, 72.1, 62.0, 22.2, 21.4; IR ν_{max} (KBr) 3698, 2980, 1589, 1528, 1429, 1286, 1148, 1080 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4\text{S}_2^+$ [M+H] $^+$ 467.1094, found 467.1086.



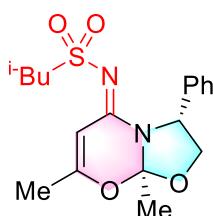
Chemical Formula: $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 322.3794

**N-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-yli
dene)methanesulfonamide (5i)** (103.2 mg, 64%), colorless liquid ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.28 (m, 5H), 6.39 (s, 1H), 5.40 (s, 1H), 4.44–4.35 (m, 2H), 2.99 (s, 3H), 2.07 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 156.0, 138.0, 128.7 (2C), 128.1, 126.5 (2C), 112.5, 95.0, 71.9, 62.0, 43.1, 22.6, 20.3; IR ν_{max} (KBr) 3647, 2920, 1620, 1537, 1452, 1275, 1126 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 323.1060, found 323.1055.



Chemical Formula: $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 336.4060

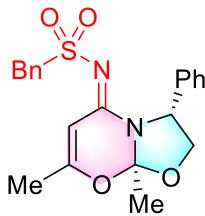
**N-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-yli
dene)ethanesulfonamide (5j)** (114.4 mg, 68%), colorless liquid ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.31 (m, 5H), 6.41 (s, 1H), 5.38 (s, 1H), 4.42–4.36 (m, 2H), 3.06–3.00 (m, 2H), 2.07 (s, 3H), 1.71 (s, 3H), 1.32 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 156.3, 138.2, 128.7 (2C), 128.1, 126.5 (2C), 112.6, 95.3, 72.0, 62.1, 49.3, 22.7, 20.3, 8.5; IR ν_{max} (KBr) 3649, 2924, 1620, 1537, 1450, 1271, 1123 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 337.1217, found 337.1209.



Chemical Formula: $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 364.4592

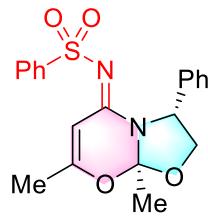
**N-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-yli
dene)-2-methylpropane-1-sulfonamide (5k)** (114.8 mg, 63%), colorless liquid ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ

7.37–7.30 (m, 5H), 6.42 (s, 1H), 5.37 (s, 1H), 4.38 (d, $J = 3.3$ Hz, 2H), 2.96–2.88 (m, 2H), 2.31–2.21 (m, 1H), 2.06 (s, 3H), 1.71 (s, 3H), 1.02–0.98 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 156.0, 138.2, 128.6 (2C), 128.0, 126.4 (2C), 112.6, 95.2, 72.0, 62.7, 62.2, 24.8, 22.6, 22.6 (2C), 20.3; IR ν_{max} (KBr) 3649, 3294, 2961, 1724, 1555, 1229, 1121 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 365.1530, found 365.1525.



Chemical Formula: $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 398.4754

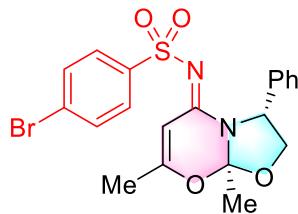
***N*-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-yli-dene)-1-phenylmethanesulfonamide (5l)** (139.5 mg, 70%), a white solid, m.p. = 160.1–161.2 °C ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.42–7.35 (m, 3H), 7.30 (d, $J = 6.7$ Hz, 2H), 7.26–7.22 (m, 1H), 7.16 (t, $J = 3.5$ Hz, 4H), 6.28 (s, 1H), 5.27 (s, 1H), 4.34–4.28 (m, 2H), 4.20 (s, 2H), 1.99 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 156.7, 138.1, 130.9 (2C), 130.2, 128.7 (2C), 128.2 (2C), 128.0, 127.9, 126.2 (2C), 112.5, 95.1, 72.25, 62.3, 60.7, 22.4, 20.2; IR ν_{max} (KBr) 3649, 2920, 1618, 1520, 1452, 1288, 1121 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 399.1373, found 399.1367.



Chemical Formula: $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 384.4488

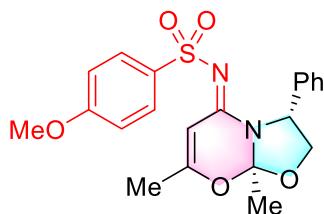
***N*-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-yli-dene)benzenesulfonamide (5m)** (140.3 mg, 73%), a white solid, m.p. = 160.3–161.3 °C ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.7$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.5$

Hz, 2H), 7.33–7.26 (m, 5H), 6.51 (s, 1H), 5.39 (d, J = 5.7 Hz, 1H), 4.42 (d, J = 8.5 Hz, 1H), 4.35 (dd, J = 8.7, 5.8 Hz, 1H), 2.07 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 155.8, 143.2, 137.7, 131.6 (2C), 128.6 (2C), 128.4, 128.1 (2C), 126.7 (2C), 126.2, 112.5, 95.0, 71.7, 61.9, 22.6, 20.3; IR ν_{max} (KBr) 3496, 2924, 1620, 1503, 1456, 1283, 1146 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 385.1217, found 385.1211.



Chemical Formula: $\text{C}_{20}\text{H}_{19}\text{BrN}_2\text{O}_4\text{S}$
Molecular Weight: 463.3449

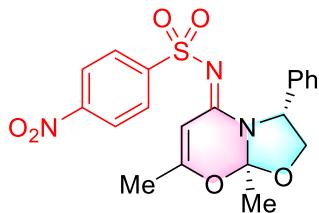
4-Bromo-N-(7,8a-dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5n) (180.7 mg, 78%), a white solid, m.p. = 179.1–180.2 °C (R_f = 0.3 in 1:5 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.34–7.27 (m, 5H), 6.48 (s, 1H), 5.37 (d, J = 5.6 Hz, 1H), 4.41 (d, J = 8.5 Hz, 1H), 4.36 (dd, J = 8.7, 5.6 Hz, 1H), 2.09 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 156.0, 142.4, 137.7, 131.7 (2C), 128.7 (2C), 128.2, 128.0 (2C), 126.7 (2C), 126.4, 112.7, 95.0, 71.9, 62.0, 22.6, 20.4; IR ν_{max} (KBr) 3649, 2945, 1626, 1522, 1458, 1269, 1141 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{BrN}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 463.0322, found 463.0317.



Chemical Formula: $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$
Molecular Weight: 414.4748

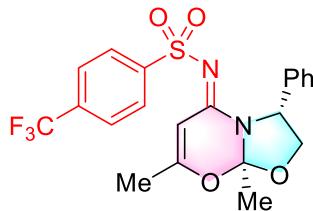
N-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methoxybenzenesulfonamide (5o) (157.5 mg, 76%), a white solid, m.p. =

156.8-157.1 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.5 Hz, 2H), 7.34–7.28 (m, 5H), 6.89 (d, J = 8.5 Hz, 2H), 6.50 (s, 1H), 5.39 (s, 1H), 4.38 (dd, J = 23.8, 7.6 Hz, 2H), 3.83 (s, 3H), 2.06 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 162.1, 155.7, 137.9, 135.4, 128.7 (2C), 128.3 (2C), 128.1, 126.8 (2C), 113.6 (2C), 112.6, 95.0, 61.9, 55.5, 22.7, 20.4; IR ν_{max} (KBr) 3647, 2957, 1630, 1526, 1458, 1269, 1250, 1139 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_5\text{S}^+$ [M+H] $^+$ 415.1322, found 415.1317.



Chemical Formula: $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_6\text{S}$
Molecular Weight: 429.4464

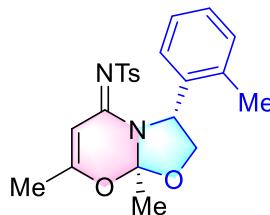
***N*-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)-4-nitrobenzenesulfonamide (5p)** (154.6 mg, 72%), a white solid, m.p. = 160.0-161.4 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.33–7.27 (m, 5H), 6.48 (s, 1H), 5.37 (t, J = 3.8 Hz, 1H), 4.40 (d, J = 3.7 Hz, 2H), 2.12 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 156.3, 149.5, 148.8, 137.5, 128.8 (2C), 128.4, 127.6 (2C), 126.5 (2C), 123.8 (2C), 112.8, 95.0, 72.1, 62.2, 22.5, 20.4; IR ν_{max} (KBr) 3649, 2950, 1601, 1508, 1454, 1287, 1144 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_6\text{S}^+$ [M+H] $^+$ 430.1067, found 430.1062.



Chemical Formula: $\text{C}_{21}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 452.4468

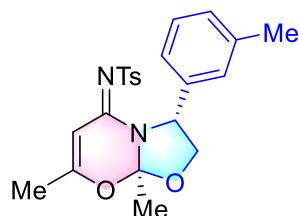
***N*-(7,8a-Dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)-4-(trifluoromethyl)benzenesulfonamide (5q)** (176.5 mg, 78%), a white solid, m.p. = 161.6-163.0 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60-90 petroleum ether). ^1H

NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.30–7.26 (m, 5H), 6.50 (s, 1H), 5.38 (d, *J* = 5.0 Hz, 1H), 4.43–4.36 (m, 2H), 2.10 (s, 3H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 156.1, 146.6, 137.5, 133.3 (q, *J* = 32.8 Hz), 128.8 (2C), 128.3, 126.8 (2C), 126.7 (2C), 125.6 (q, *J* = 3.8 Hz, 2C), 123.5 (q, *J* = 272.9 Hz), 119.39, 112.70, 95.0, 71.9, 62.1, 22.6, 20.4; IR ν_{max} (KBr) 3649, 2980, 1618, 1533, 1464, 1317, 1281, 1132 cm⁻¹. HRMS (ESI) m/z calcd for C₂₁H₂₀F₃N₂O₄S⁺ [M+H]⁺ 453.1090, found 453.1085.



Chemical Formula: C₂₂H₂₄N₂O₄S
Molecular Weight: 412.5020

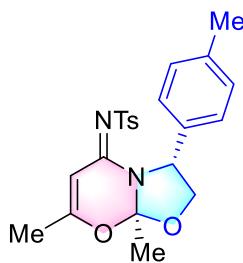
***N*-(7,8a-Dimethyl-3-(*o*-tolyl)-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)-4-methylbenzenesulfonamide (5r)** (148.5 mg, 72%), a white solid, m.p. = 139.1–139.8 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.22–7.19 (m, 4H), 6.36 (s, 1H), 5.45 (d, *J* = 6.3 Hz, 1H), 4.47 (t, *J* = 7.6 Hz, 1H), 4.11 (d, *J* = 8.5 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H), 1.83 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.9, 156.8, 142.1, 140.3, 137.0, 134.8, 130.8, 129.3 (2C), 127.6, 126.0, 125.9 (2C), 125.0, 112.8, 94.5, 72.5, 60.7, 21.9, 21.0, 20.0, 18.9; IR ν_{max} (KBr) 3649, 3356, 3258, 2922, 1526, 1300, 1153 cm⁻¹. HRMS (ESI) m/z calcd for C₂₂H₂₅N₂O₄S⁺ [M+H]⁺ 413.1530, found 413.1524.



Chemical Formula: C₂₂H₂₄N₂O₄S
Molecular Weight: 412.5020

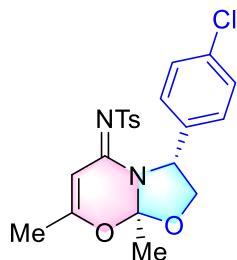
***N*-(7,8a-Dimethyl-3-(*m*-tolyl)-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)-4-methylbenzenesulfonamide (5s)** (158.8 mg, 77%), a white solid, m.p. =

167.5–168.1 °C ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.9$ Hz, 2H), 7.26–7.21 (m, 2H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.13 (d, $J = 9.4$ Hz, 2H), 7.08 (d, $J = 7.4$ Hz, 1H), 6.51 (s, 1H), 5.35 (d, $J = 5.8$ Hz, 1H), 4.41 (d, $J = 8.5$ Hz, 1H), 4.34–4.31 (m, 1H), 2.39 (s, 3H), 2.25 (s, 3H), 2.07 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.3, 155.5, 142.1, 140.5, 138.2, 137.7, 129.0 (2C), 128.7, 128.5, 127.9, 126.2 (2C), 123.5, 112.5, 95.0, 71.6, 61.8, 22.7, 21.4, 21.3, 20.2; IR ν_{max} (KBr) 3649, 2951, 1602, 1514, 1439, 1285, 1142 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 413.1530, found 413.1523.



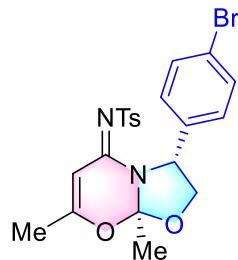
Chemical Formula: $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 412.5020

N-(7,8a-Dimethyl-3-(p-tolyl)-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-yliene)-4-methylbenzenesulfonamide (5t) (171.2 mg, 83%), a white solid, m.p. = 167.5–168.1 °C ($R_f = 0.3$ in 1:3 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.64 (d, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.20 (d, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 7.4$ Hz, 2H), 6.30 (s, 1H), 5.34 (s, 1H), 4.35 (d, $J = 8.4$ Hz, 1H), 4.30–4.27 (m, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.05 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 166.9, 156.4, 142.5, 140.5, 137.3, 135.5, 129.6 (2C), 129.3 (2C), 126.5 (2C), 126.2 (2C), 112.6, 94.3, 72.7, 61.8, 22.5, 21.2, 20.9, 20.2; IR ν_{max} (KBr) 3649, 2924, 1614, 1531, 1456, 1275, 1142 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 413.1530, found 413.1522.



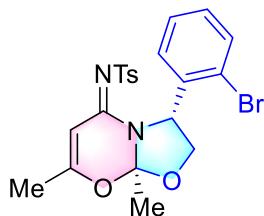
Chemical Formula: C₂₁H₂₁ClN₂O₄S
Molecular Weight: 432.9204

N-(3-(4-Chlorophenyl)-7,8a-dimethyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5u) (168.8 mg, 78%), a white solid, m.p. = 106.2-107.3 °C (Rf = 0.3 in 1:3 v/v ethyl acetate/60-90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.7 Hz, 2H), 7.26–7.23 (m, 6H), 6.50 (s, 1H), 5.35 (s, 1H), 4.38–4.31 (m, 2H), 2.40 (s, 3H), 2.07 (s, 3H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 155.7, 142.4, 140.3, 136.4, 134.0, 129.1 (2C), 128.8 (2C), 128.3 (2C), 126.3 (2C), 112.4, 95.0, 71.4, 61.3, 22.7, 21.5, 20.3; IR ν_{max} (KBr) 3649, 3356, 3259, 1628, 1526, 1456, 1302, 1144 cm⁻¹. HRMS (ESI) m/z calcd for C₂₁H₂₂ClN₂O₄S⁺ [M+H]⁺ 433.0983, found 433.0979.



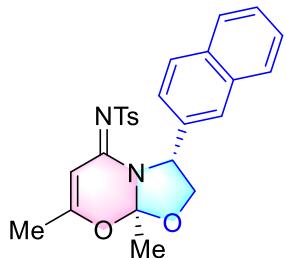
Chemical Formula: C₂₁H₂₁BrN₂O₄S
Molecular Weight: 477.3714

N-(3-(4-Bromophenyl)-7,8a-dimethyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5v) (181.4 mg, 76%), a white solid, m.p. = 188.3-191.0 °C (Rf = 0.3 in 1:3 v/v ethyl acetate/60-90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.27–7.20 (m, 4H), 6.50 (s, 1H), 5.33 (d, J = 5.4 Hz, 1H), 4.37–4.31 (m, 2H), 2.41 (s, 3H), 2.07 (s, 3H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.7, 155.8, 142.4, 140.3, 136.9, 131.8 (2C), 129.2 (2C), 128.6 (2C), 126.3 (2C), 122.1, 112.5, 95.0, 71.4, 61.4, 22.8, 21.5, 20.4; IR ν_{max} (KBr) 3649, 2953, 1618, 1530, 1454, 1269, 1142 cm⁻¹. HRMS (ESI) m/z calcd for C₂₁H₂₂BrN₂O₄S⁺ [M+H]⁺ 477.0478, found 477.0473.



Chemical Formula: C₂₁H₂₁BrN₂O₄S
Molecular Weight: 477.3714

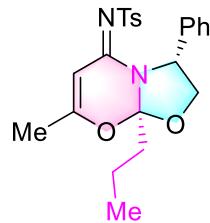
N-(3-(2-Bromophenyl)-7,8a-dimethyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5w) (167.1 mg, 70%), a white solid, m.p. = 128.7–129.1 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (t, *J* = 8.4 Hz, 3H), 7.31–7.22 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.55 (s, 1H), 5.51 (s, 1H), 4.51 (t, *J* = 7.2 Hz, 1H), 4.28 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H), 2.10 (s, 3H), 1.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 156.8, 142.1, 140.2, 137.4, 133.2, 129.4, 129.0 (2C), 127.4, 127.0, 126.1 (2C), 121.5, 113.3, 95.3, 72.6, 63.6, 22.3, 21.4, 20.4; IR ν_{max} (KBr) 3649, 2952, 1618, 1531, 1452, 1269, 1141 cm⁻¹. HRMS (ESI) m/z calcd for C₂₁H₂₂BrN₂O₄S⁺ [M+H]⁺ 477.0478, found 477.0473.



Chemical Formula: C₂₅H₂₄N₂O₄S
Molecular Weight: 448.5341

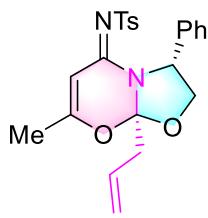
N-(7,8a-Dimethyl-2-(naphthalen-2-yl)-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5x) (168.2 mg, 75%), a white solid, m.p. = 165.3–165.9 °C (R_f = 0.3 in 1:5 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.93–7.91 (m, 2H), 7.85–7.81 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.54–7.50 (m, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.40 (s, 1H), 5.57 (d, *J* = 5.7 Hz, 1H), 4.52 (d, *J* = 8.9 Hz, 1H), 4.42 (dd, *J* = 9.1, 5.9 Hz, 1H), 2.34 (s, 3H), 2.10 (s, 3H), 1.69 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.6, 156.2, 142.1, 140.4, 135.9, 132.6, 132.4, 129.3 (2C), 128.3, 127.9, 127.6, 126.5, 126.3, 126.0 (2C), 125.2, 124.5,

112.5, 94.2, 72.2, 62.0, 22.4, 21.0, 20.0; IR ν_{max} (KBr) 3649, 2950, 1626, 1522, 1456, 1271, 1141, 1107 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 449.1530, found 449.1523.



Chemical Formula: $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 426.5285

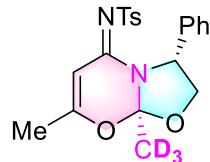
4-Methyl-N-(7-methyl-3-phenyl-8a-propyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)benzenesulfonamide (5y) (132.2 mg, 62%), a white solid, m.p. = 114.3–114.9 °C (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.9 Hz, 2H), 7.36–7.28 (m, 5H), 7.22 (d, J = 7.9 Hz, 2H), 6.51 (s, 1H), 5.39 (d, J = 5.8 Hz, 1H), 4.44 (d, J = 8.7 Hz, 1H), 4.36–4.33 (m, 1H), 2.39 (s, 3H), 2.27 (t, J = 9.9 Hz, 1H), 2.08 (s, 3H), 1.56–1.38 (m, 3H), 0.85 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 165.2, 156.2, 142.2, 140.4, 137.8, 129.0 (2C), 128.5 (2C), 128.0, 126.9 (2C), 126.3 (2C), 113.9, 95.4, 71.3, 61.9, 37.4, 21.4, 20.2, 16.4, 13.8; IR ν_{max} (KBr) 3649, 2964, 1632, 1526, 1454, 1271, 1140, 1078 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4\text{S}^+ [\text{M}+\text{H}]^+$ 427.1686, found 427.1679.



Chemical Formula: $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 424.5127

N-(8a-Allyl-7-methyl-3-phenyl-2,3-dihydrooxazolo[2,3-b][1,3]oxazin-5(8aH)-ylidene)-4-methylbenzenesulfonamide (5z) (138.0 mg, 65%), colorless liquid (R_f = 0.3 in 1:3 v/v ethyl acetate/60–90 petroleum ether). ¹H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.7 Hz, 2H), 7.39–7.33 (m, 2H), 7.31–7.26 (m, 3H), 7.22 (d, J = 7.9 Hz, 2H), 6.53 (s, 1H), 5.80–5.70 (m, 1H), 5.42 (d, J = 5.9 Hz, 1H), 5.09 (t, J = 11.5 Hz,

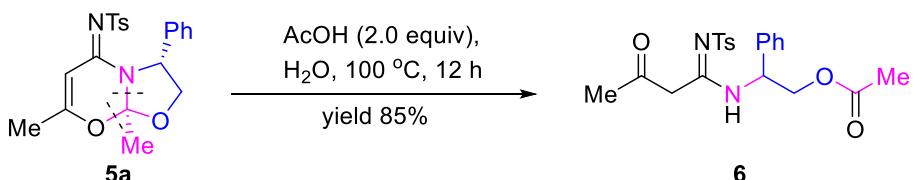
2H), 4.46 (d, J = 8.6 Hz, 1H), 4.38–4.34 (m, 1H), 3.03–2.98 (m, 1H), 2.39–2.33 (m, 4H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 156.0, 142.3, 140.4, 137.6, 129.7, 129.1 (2C), 128.6 (2C), 128.1, 127.0 (2C), 126.3 (2C), 120.0, 112.81, 95.7, 71.5, 61.9, 40.5, 21.5, 20.1; IR ν_{max} (KBr) 3649, 2920, 1620, 1522, 1449, 1278, 1142, 1082 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 425.1530, found 425.1524.



Chemical Formula: $\text{C}_{21}\text{H}_{19}\text{D}_3\text{N}_2\text{O}_4\text{S}$
Molecular Weight: 401.4939

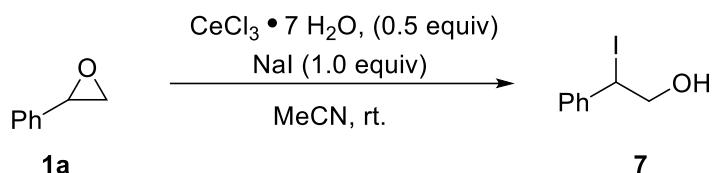
4-Methyl-N-(7-methyl-8a-methyl-d₃-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)benzenesulfonamide (5aa) (156.6 mg, 78%), a white solid, m.p. = 159.4–160.1 °C (R_f = 0.3 in 1:4 v/v ethyl acetate/60–90 petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.7 Hz, 2H), 7.32–7.29 (m, 5H), 7.22 (d, J = 7.5 Hz, 2H), 6.51 (s, 1H), 5.39 (s, 1H), 4.41 (d, J = 8.5 Hz, 1H), 4.36–4.32 (m, 1H), 2.39 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 155.7, 142.2, 140.4, 137.8, 129.0 (2C), 128.6 (2C), 128.0, 126.7 (2C), 126.2 (2C), 112.5, 95.0, 71.7, 61.8, 21.4, 20.3 (the signal of -CD₃ obscured or overlapping). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{D}_3\text{N}_2\text{O}_4\text{S}^+$ [M+H] $^+$ 402.1568, found 402.1548.

5. Hydrolysis of 5a



A magnetically stirred solution of *N*-(7,8a-dimethyl-3-phenyl-2,3-dihydrooxazolo[2,3-*b*][1,3]oxazin-5(8a*H*)-ylidene)-4-methylbenzenesulfonamide (**5a**) (398.5 mg, 1.0 mmol, 1.0 equiv.) and AcOH (aq., 1 mmol·L⁻¹ × 2 mL, 2 equiv.) stirred at 100 °C in an oil bath for 12 hours, then cooled and diluted with water (30 mL). The resulting mixture was extracted with ethyl acetate (3 × 20 mL) and the combined organic phases then dried (Na₂SO₄) and filtered before being concentrated under reduced pressure. The residue thus obtained was subjected flash chromatography (silica gel, 1:2 v/v ethyl acetate/60–90 petroleum ether) to give 2-(3-oxo-*N*^t-tosylbutanimidamido)-2-phenylethyl acetate (**6**) (354 mg, 85%) as a white solid, m.p. = 145.9–146.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.30–7.23 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.27–5.23 (m, 1H), 4.34 (m, 1H), 4.26 (dd, *J* = 11.8, 4.4 Hz, 1H), 4.10–3.98 (m, 2H), 2.37 (s, 3H), 2.25 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 203.1, 171.3, 160.7, 142.2, 140.1, 137.1, 129.1 (2C), 128.8 (2C), 128.1, 126.9 (2C), 126.0 (2C), 65.6, 55.3, 45.3, 30.9, 21.5, 20.8; IR ν_{max} (KBr) 3521, 3462, 1610, 1454, 1252, 1103 cm⁻¹. HRMS (ESI) m/z calcd for C₂₁H₂₅N₂O₅S⁺ [M+H]⁺ 417.1479, found 417.1473.

6. Preparation of 2-iodo-2-phenylethan-1-ol 7^[4]



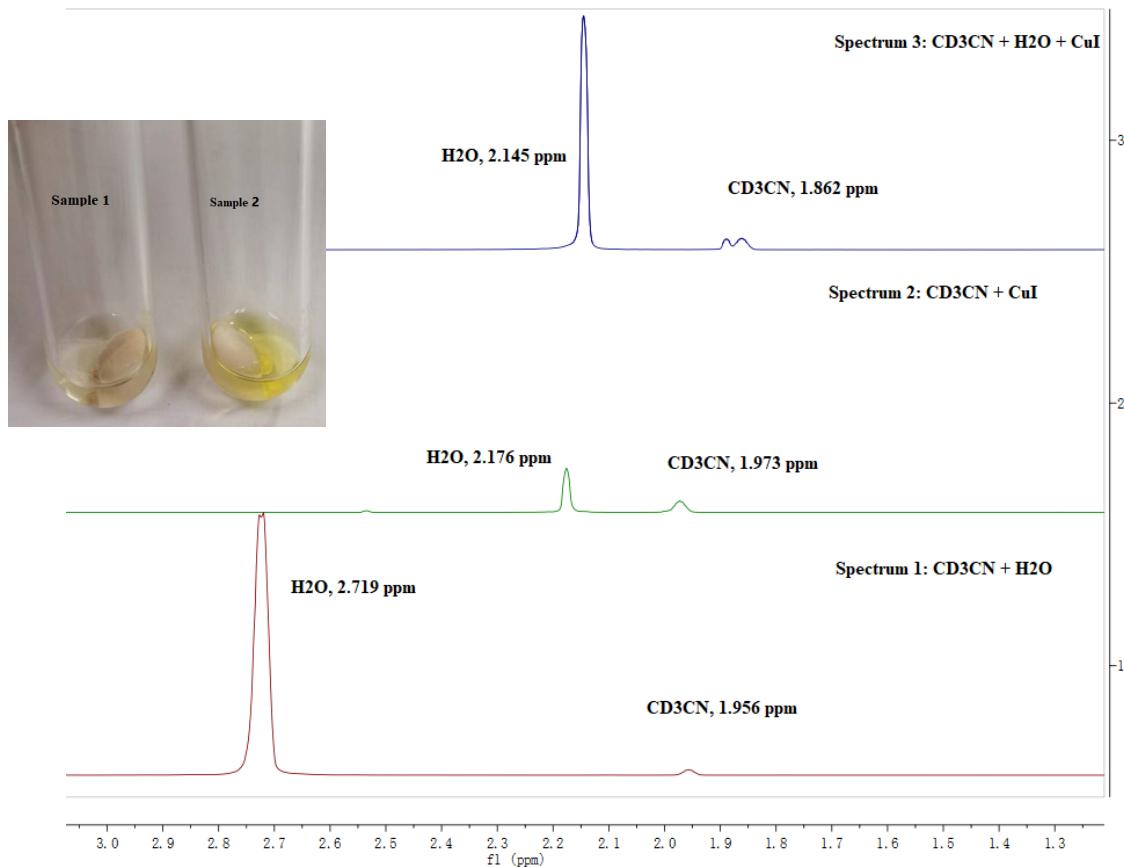
A magnetically stirred solution of Styrene oxide (**1a**) (120.1 mg, 1.0 mmol, 1.0 equiv.), Cerous chloride heptahydrate (186.3 mg, 0.5 mmol, 0.5 equiv.) and Sodium iodide (149.9 mg, 1.0 mmol, 1.0 equiv.) stirred at room temperature for 10 minutes until **1a** was completely consumed detected by TLC. The resulting mixture was filtration with diatomite before being concentrated under reduced pressure. The residue thus obtained was subjected flash chromatography (silica gel, 10:1 v/v ethyl acetate/60–90 petroleum ether) to give 2-iodo-2-phenylethanol (**6**) (235.6 mg, 95%) as a white solid, ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 7.0 Hz, 2H), 7.34–7.25 (m, 3H), 5.18 (t, J = 6.9 Hz, 1H), 4.10–4.04 (m, 1H), 3.91–3.85 (m, 1H), 2.21 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.0, 128.9 (2C), 128.5, 127.9 (2C), 68.5, 35.6.

7. Experiment of H₂O and MeCN promoted the dissociation of the polymer CuI.

Contrast test:

- (1) **Blank sample:** Mixture of H₂O (0.2 mmol, 2.0 equiv., 3.6 mg) and CD₃CN (1 mL) (**Spectrum 1**)
- (2) **Sample 1:** CuI (0.1 mmol, 1.0 equiv., 19.1 mg) and CD₃CN (1 mL) stirred at 80 °C in an oil bath for 12 hours, then centrifuge, Take the supernatant for ¹H NMR (**Spectrum 2**).
- (3) **Sample 2:** CuI (0.1 mmol, 1.0 equiv., 19.1 mg.), H₂O (0.2 mmol, 2.0 equiv., 3.6 mg) and CD₃CN (1 mL) stirred at 80 °C in an oil bath for 12 hours, then centrifuge, Take the pale yellow supernatant for ¹H NMR (**Spectrum 3**).

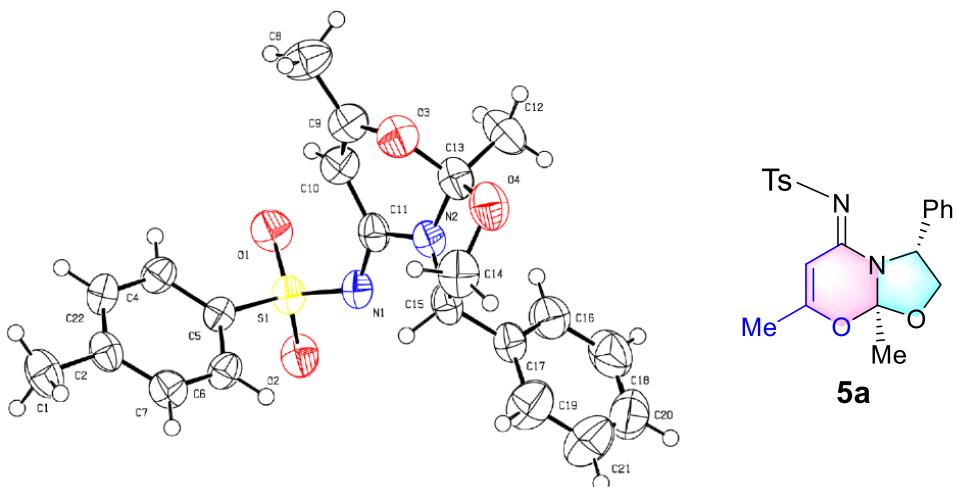
Conclusion: The CD₃CN and H₂O in Spectrum 3 have moved to the higher field relative to Spectrum 1 and Spectrum 2, indicating that the CD₃CN and H₂O coordination degree with CuI in sample 2 was relatively high than sample 1. Besides, due to the high dissociation, the sample 2's yellow color is darker than sample 1.



8.1 X-ray Crystallographic Data for Compound 5a (CCDC deposition number 2121237)

Single crystal preparation: Single crystal of compound **5a** was obtained by recrystallization from mixed solvents of ethyl acetate and petroleum ether. To a 50 mL round-bottom flask, compound **5a** (50 mg) was completely dissolved in ethyl acetate (15 mL), one third of petroleum ether (5 mL) was added successively at room temperature. The resulting solution was left open at room temperature until the white crystals precipitated. The crystallographic analysis of **5a** has shown a cis configuration of Me and Ph.

Table S2. Crystal date and strucrure refinement for product **5a**.



The ellipsoid contour percent probability level is 50%.

Identification code	5a		
Empirical formula	C21 H22 N2 O4 S		
Formula weight	398.46		
Temperature	296.15 K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P 1 21/c 1		
Unit cell dimensions	a = 20.3842(12) Å	α= 90°.	
	b = 8.7882(5) Å	β=	
106.1270(10)°.	c = 11.5351(7) Å	γ = 90°.	

Volume	1985.1(2) Å ³
Z	4
Density (calculated)	1.333 Mg/m ³
Absorption coefficient	0.193 mm ⁻¹
F(000)	840
Crystal size	0.13 x 0.12 x 0.1 mm ³
Theta range for data collection	2.958 to 25.015°.
Index ranges	-24<=h<=24, -10<=k<=10, -13<=l<=13
Reflections collected	40488
Independent reflections	3486 [R(int) = 0.1013]
Completeness to theta = 25.015°	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3486 / 0 / 256
Goodness-of-fit on F ²	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.0981
R indices (all data)	R1 = 0.1026, wR2 = 0.1205
Extinction coefficient	n/a
Largest diff. peak and hole	0.178 and -0.305 e.Å ⁻³

Check Cif Report:

Bond precision: C-C = 0.0046 Å Wavelength=0.71073

Cell: a=20.3842(12) b=8.7882(5) c=11.5351(7)
 alpha=90 beta=106.127(1) gamma=90

Temperature: 296 K

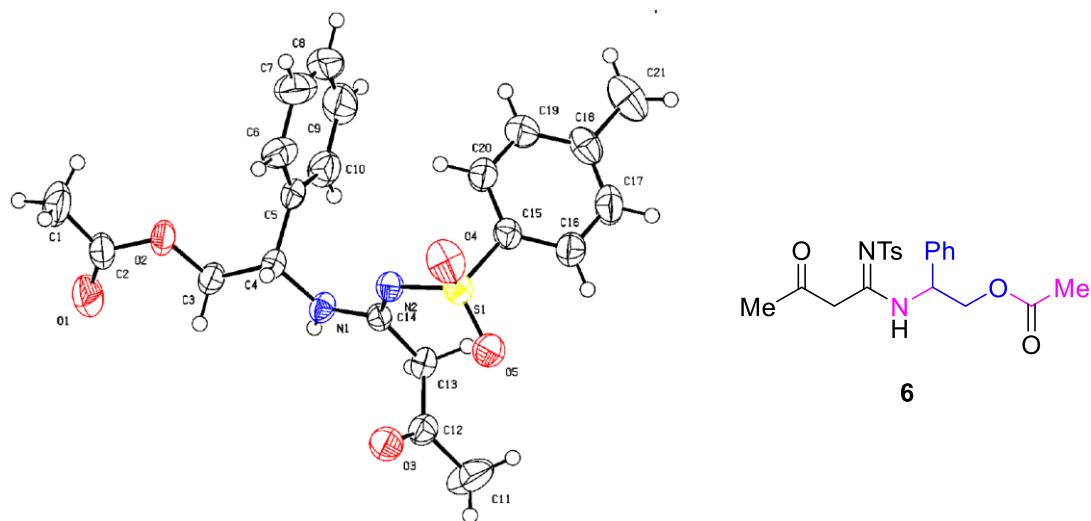
	Calculated	Reported
Volume	1985.1(2)	1985.1(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H22 N2 O4 S	C21 H22 N2 O4 S
Sum formula	C21 H22 N2 O4 S	C21 H22 N2 O4 S
Mr	398.47	398.46
Dx,g cm ⁻³	1.333	1.333

Z	4	4
Mu (mm-1)	0.193	0.193
F000	840.0	840.0
F000'	840.87	
h,k,lmax	24,10,13	24,10,13
Nref	3505	3486
Tmin,Tmax	0.975,0.981	
Tmin'	0.975	
Correction method=	Not given	
Data completeness=	0.995	Theta(max)= 25.015
R(reflections)=	0.0502(2149)	wR2(reflections)= 0.1205(3486)
S =	1.051	Npar= 256

8.2 X-ray Crystallographic Data for Compound 7 (CCDC deposition number 2189784)

Single crystal preparation: Single crystal of compound 7 was obtained by recrystallization from mixed solvents of ethyl acetate and petroleum ether. To a 50 mL round-bottom flask, compound 7 (50 mg) was completely dissolved in ethyl acetate (15 mL), one third of petroleum ether (5 mL) was added successively at room temperature. The resulting solution was left open at room temperature until the white crystals precipitated.

Table S3. Crystal date and strucrure refinement for product 6.



The ellipsoid contour percent probability level is 50%.

Identification code	6	
Empirical formula	C ₂₁ H ₂₄ N ₂ O ₅ S	
Formula weight	416.48	
Temperature	273.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.4022(6) Å	α = 90°.
	b = 9.6458(6) Å	β = 96.804(2)°.
	c = 19.7304(9) Å	γ = 90°.
Volume	2154.7(2) Å ³	

Z	4
Density (calculated)	1.284 Mg/m ³
Absorption coefficient	0.184 mm ⁻¹
F(000)	880
Crystal size	0.13 x 0.12 x 0.1 mm ³
Theta range for data collection	2.353 to 25.436°.
Index ranges	-13<=h<=13, -11<=k<=11, -23<=l<=23
Reflections collected	60680
Independent reflections	3960 [R(int) = 0.1117]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6208
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3960 / 0 / 265
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1096
R indices (all data)	R1 = 0.0807, wR2 = 0.1234
Extinction coefficient	n/a
Largest diff. peak and hole	0.249 and -0.318 e.Å ⁻³

Check Cif Report:

Bond precision: C-C = 0.0039 Å Wavelength=0.71073

Cell: a=11.4022(6) b=9.6458(6) c=19.7304(9)

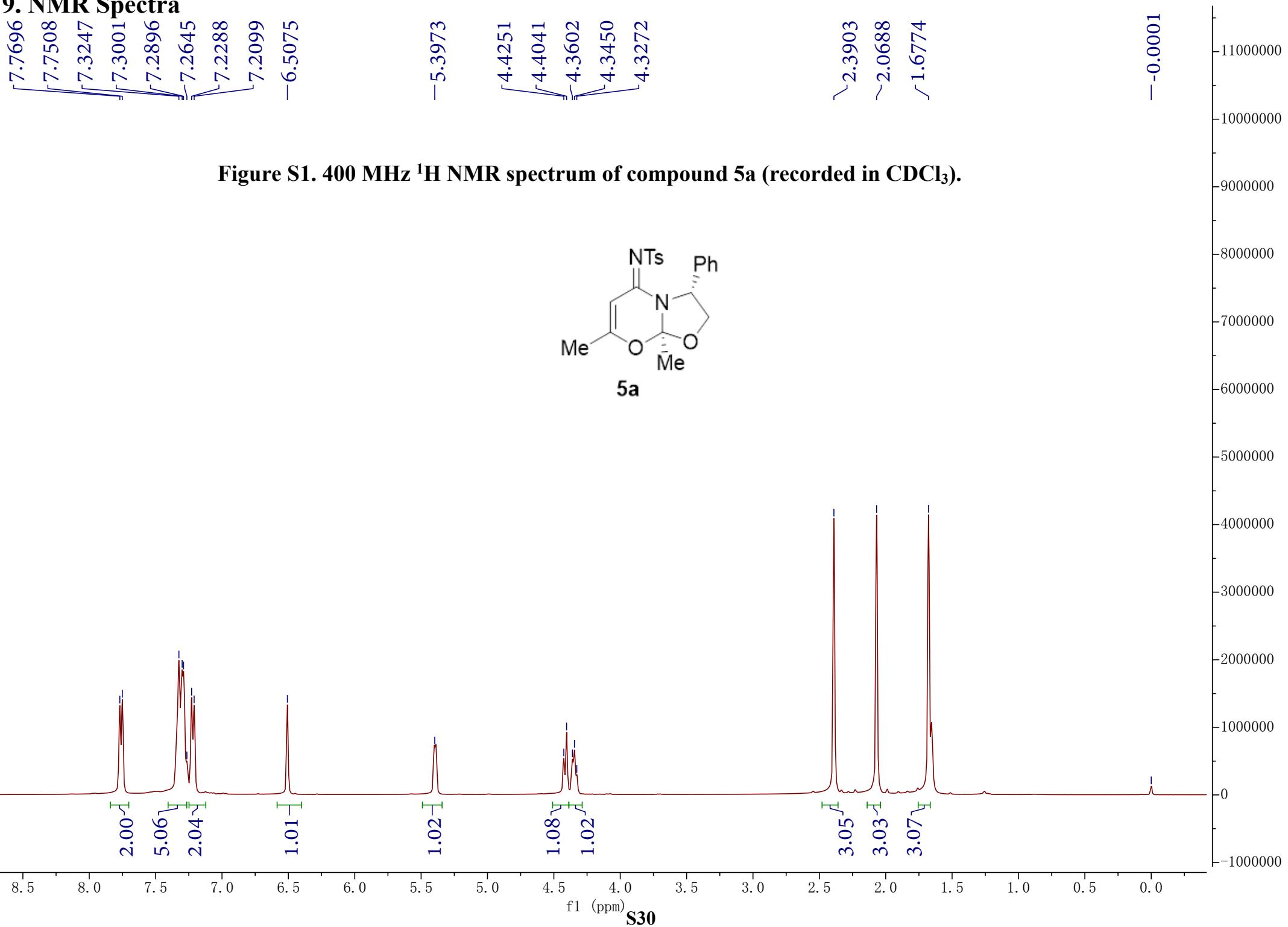
 alpha=90 beta=96.804(2) gamma=90

Temperature: 273 K

	Calculated	Reported
Volume	2154.7(2)	2154.7(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H24 N2 O5 S	C21 H24 N2 O5 S
Sum formula	C21 H24 N2 O5 S	C21 H24 N2 O5 S
Mr	416.48	416.48
Dx,g cm ⁻³	1.284	1.284
Z	4	4

Mu (mm-1)	0.184	0.184
F000	880.0	880.0
F000'	880.91	
h,k,lmax	13,11,23	13,11,23
Nref	3982	3960
Tmin,Tmax	0.976,0.982	0.621,0.745
Tmin'	0.976	
Correction method=	# Reported T Limits:	Tmin=0.621 Tmax=0.745
AbsCorr =	MULTI-SCAN	
Data completeness=	0.994	Theta(max)= 25.436
R(reflections)=	0.0499(2840)	wR2(reflections)= 0.1234(3960)
S =	1.049	Npar= 265

9. NMR Spectra



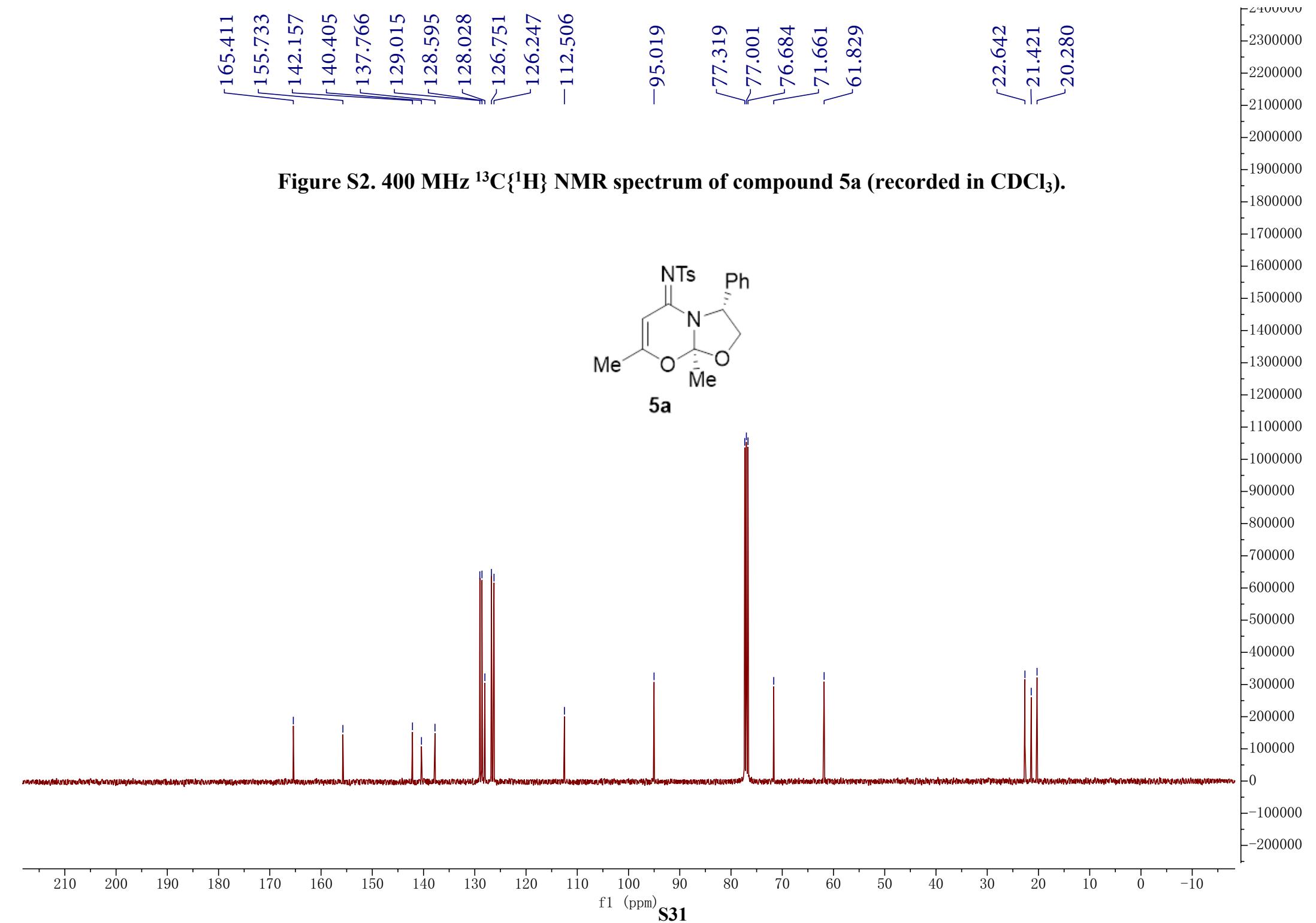
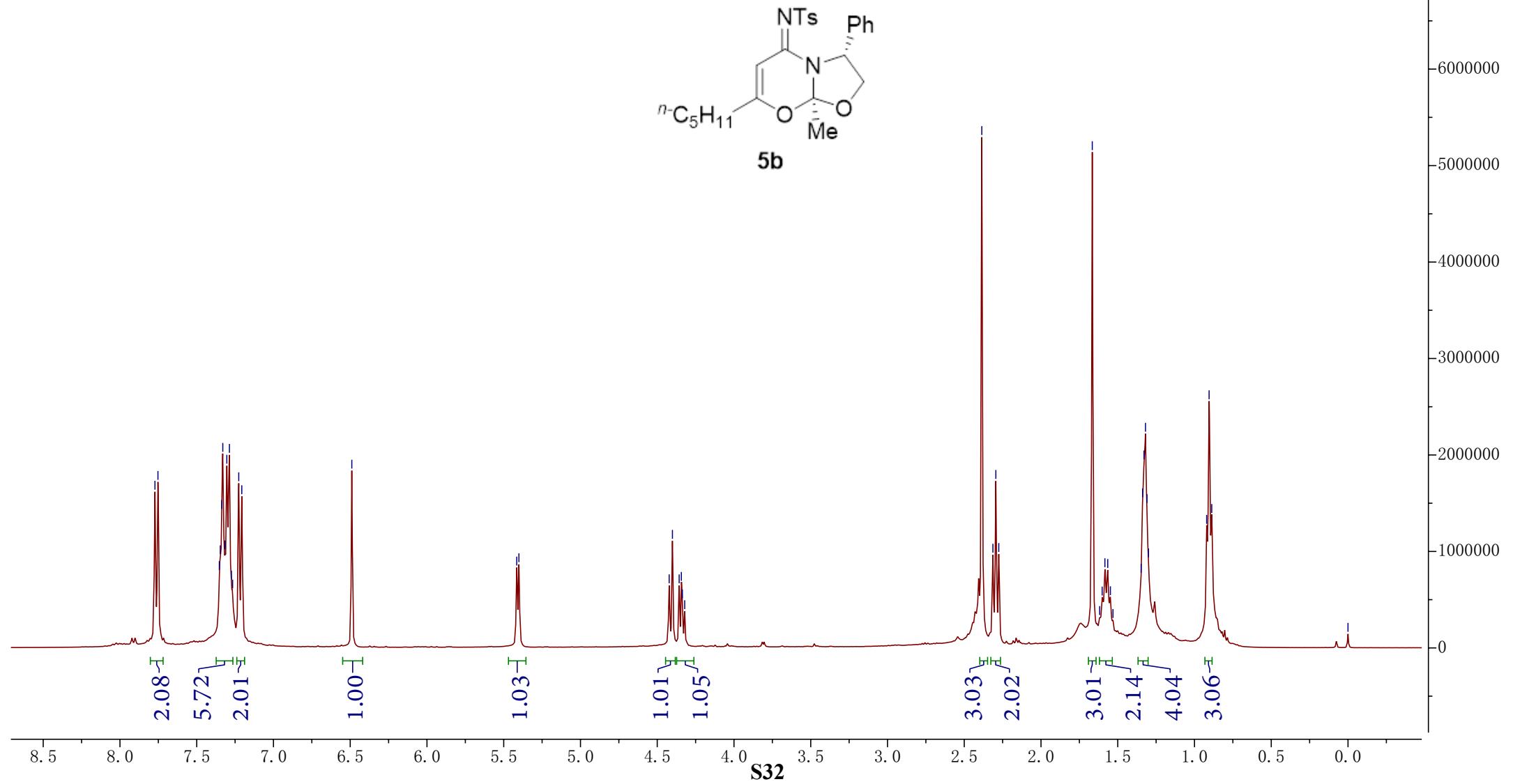
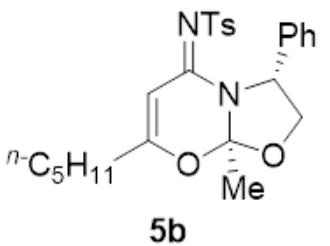
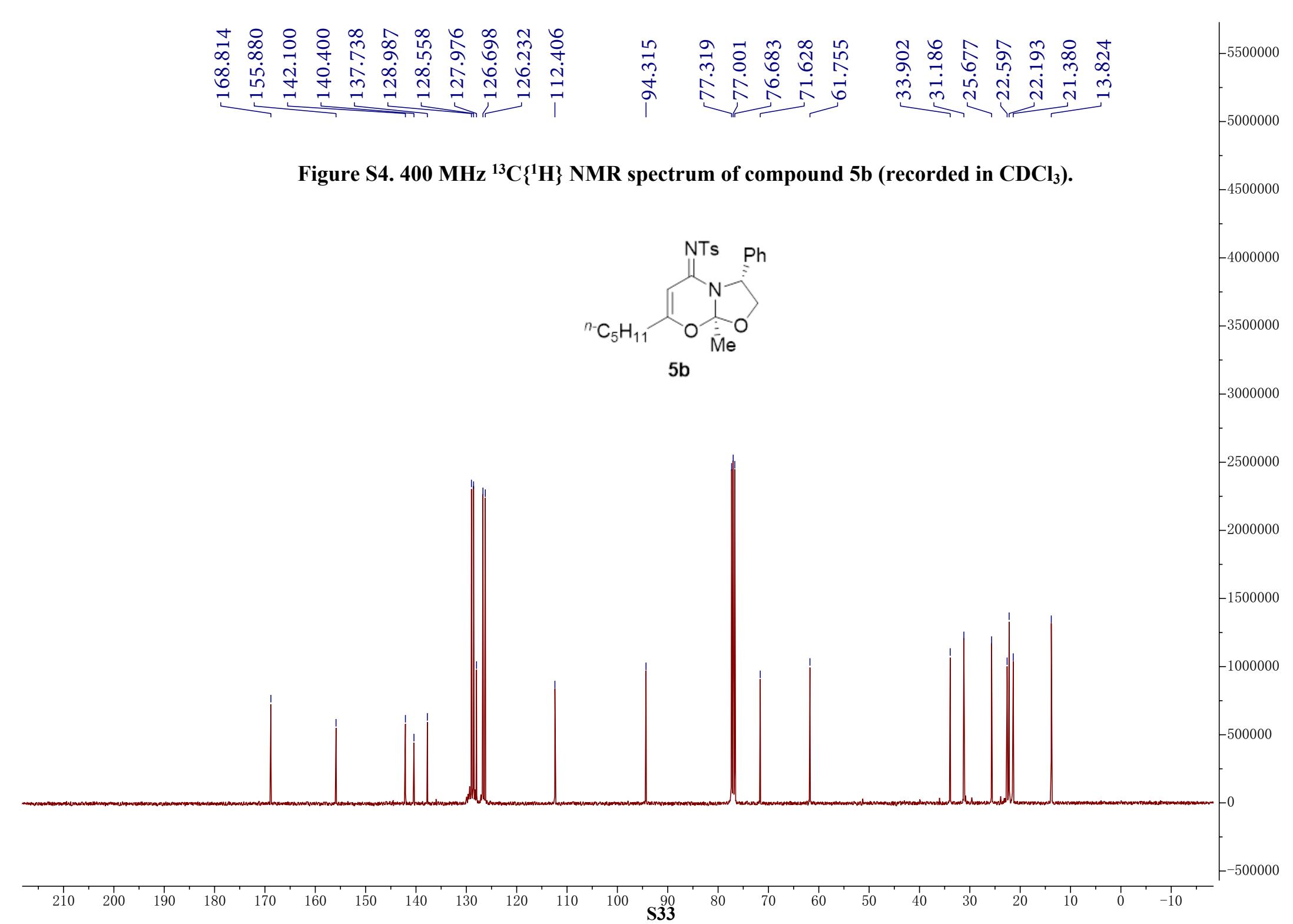




Figure S3. 400 MHz ^1H NMR spectrum of compound **5b** (recorded in CDCl_3).





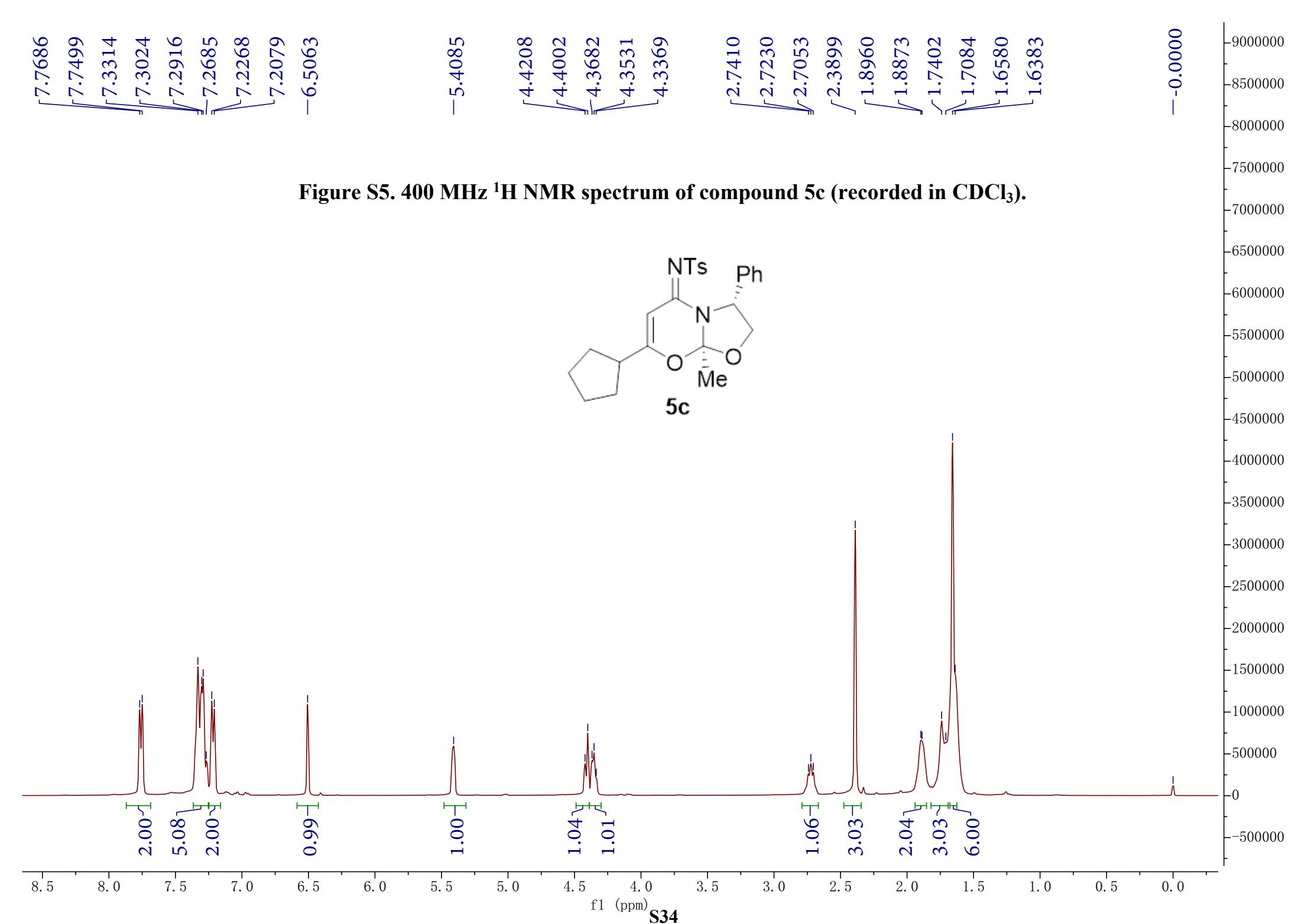
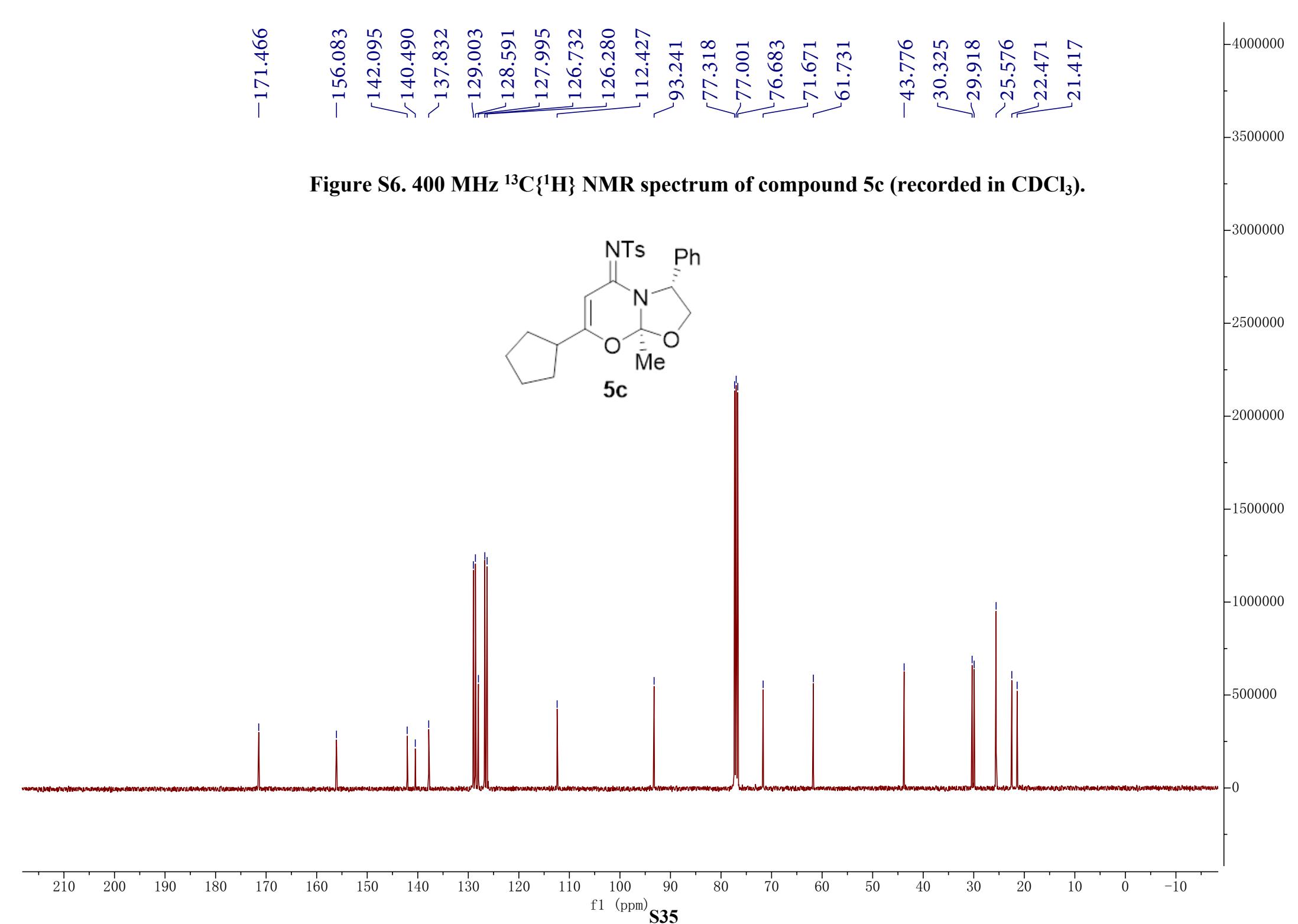
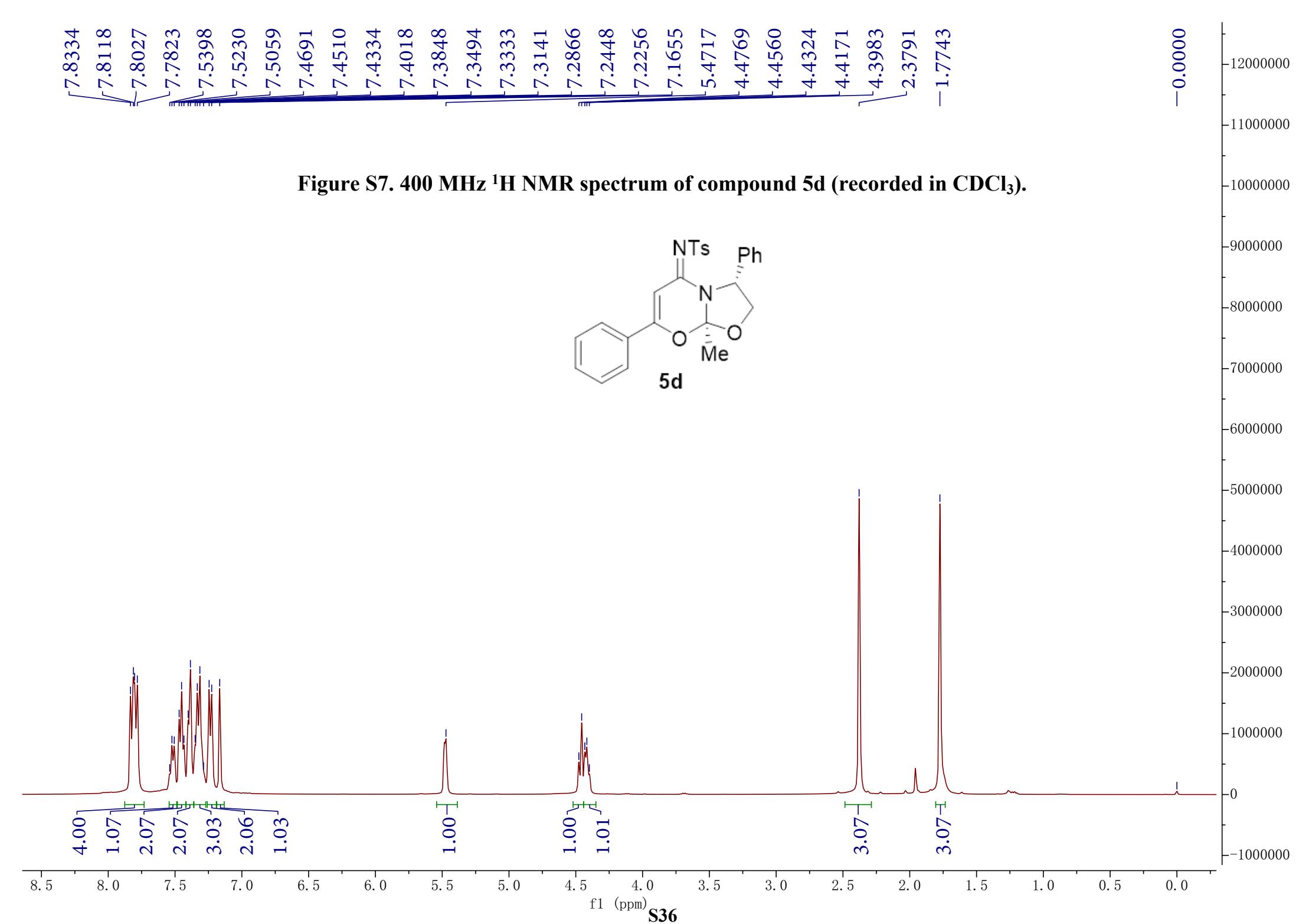
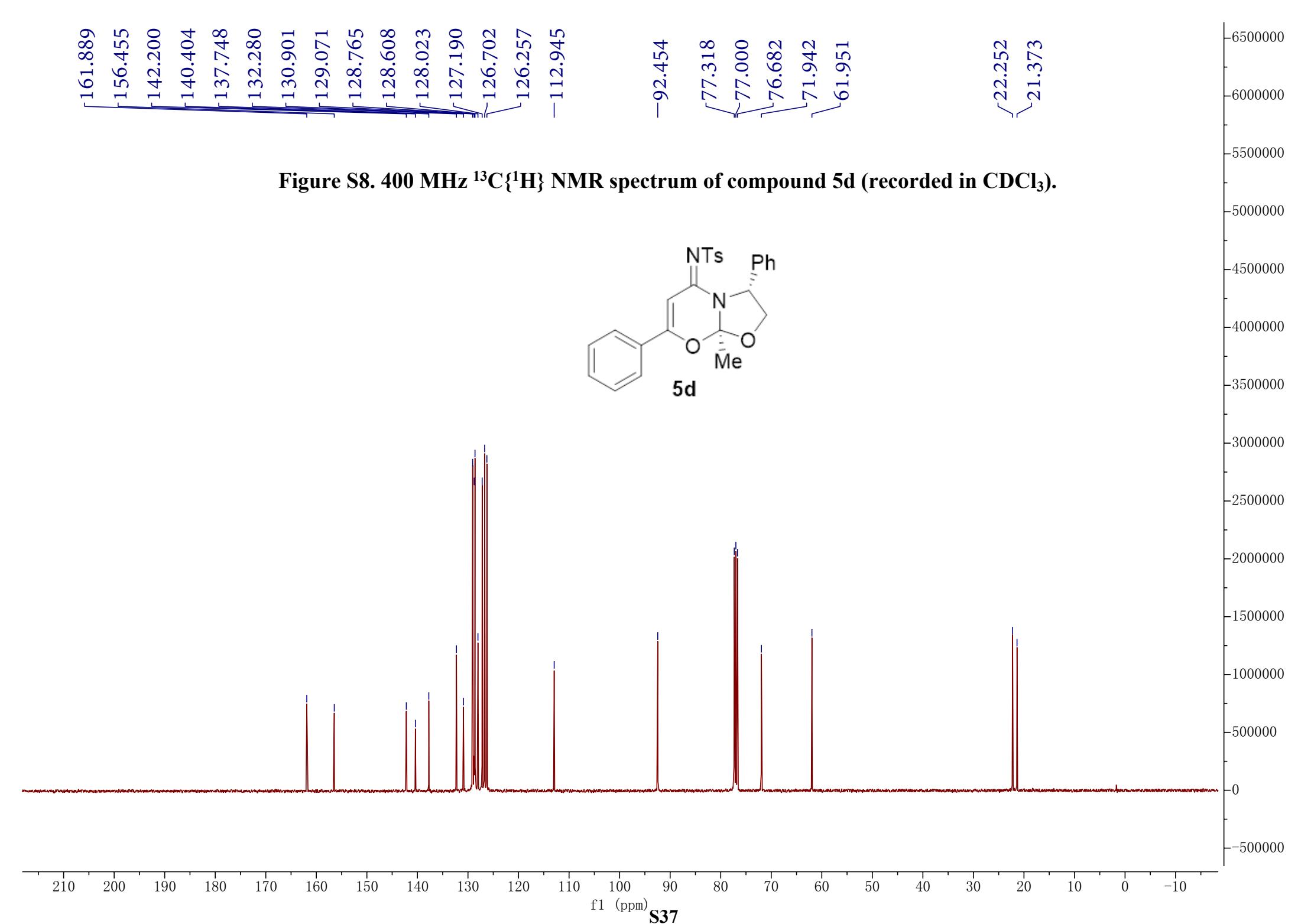
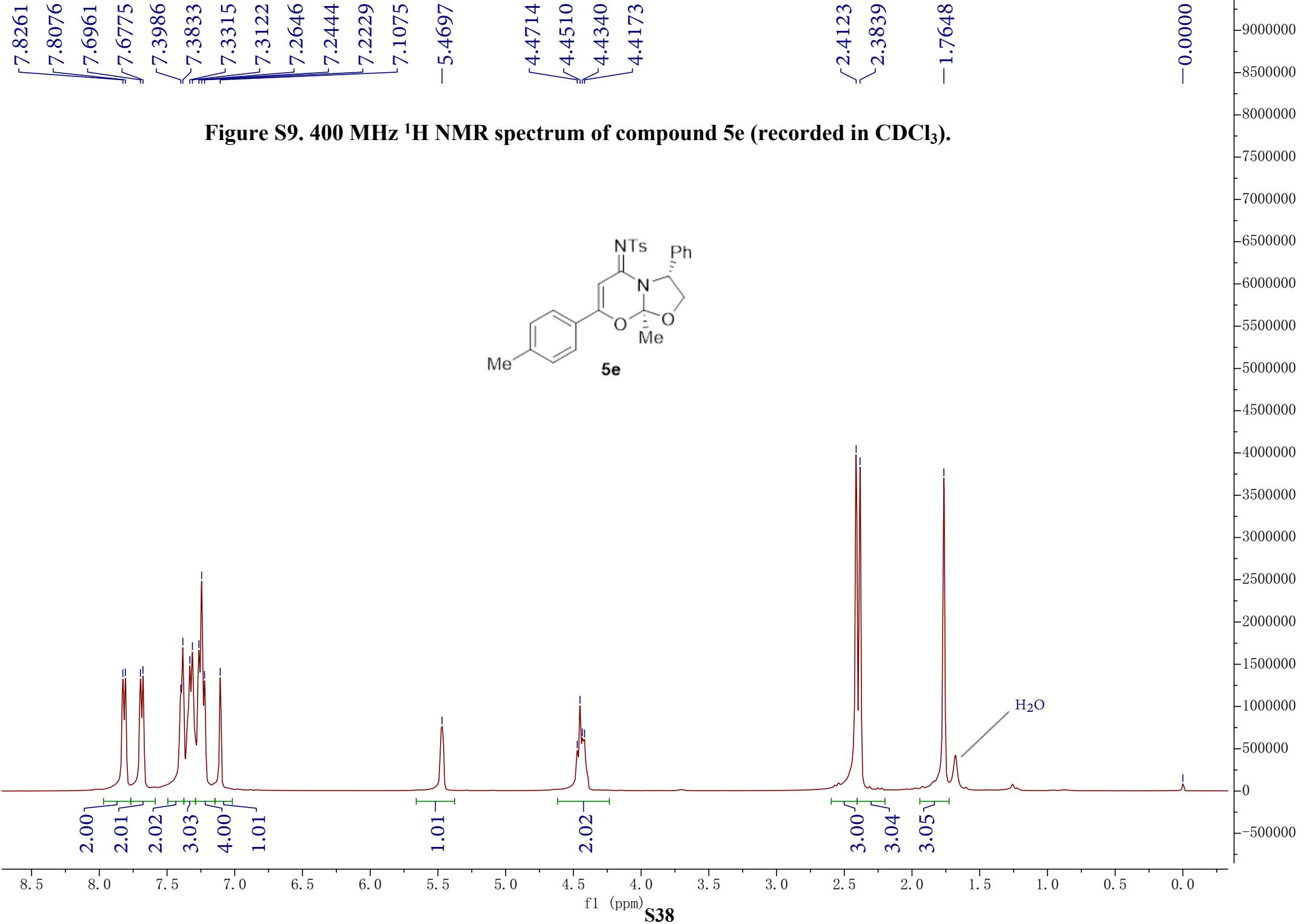


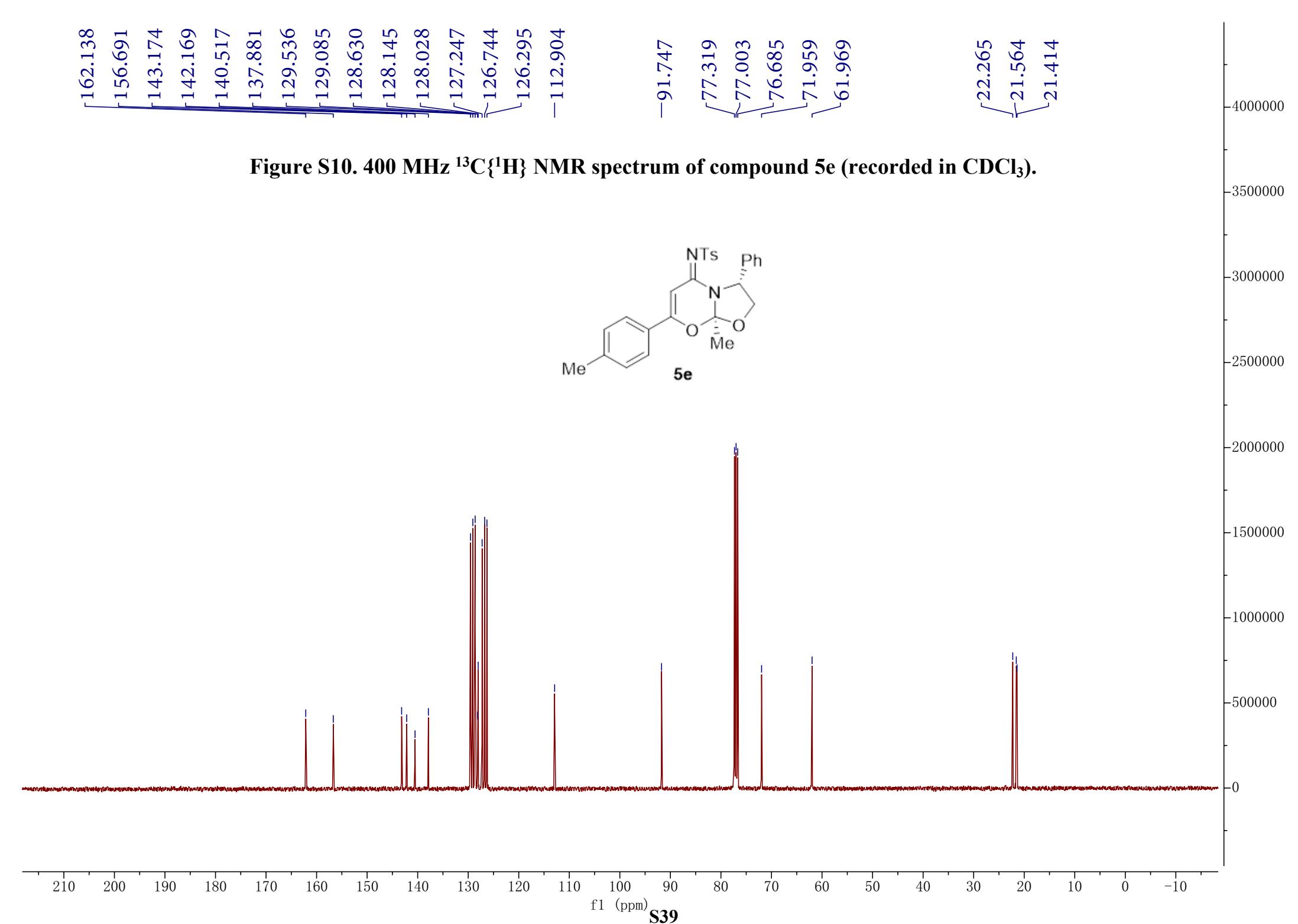
Figure S5. 400 MHz ^1H NMR spectrum of compound 5c (recorded in CDCl_3).

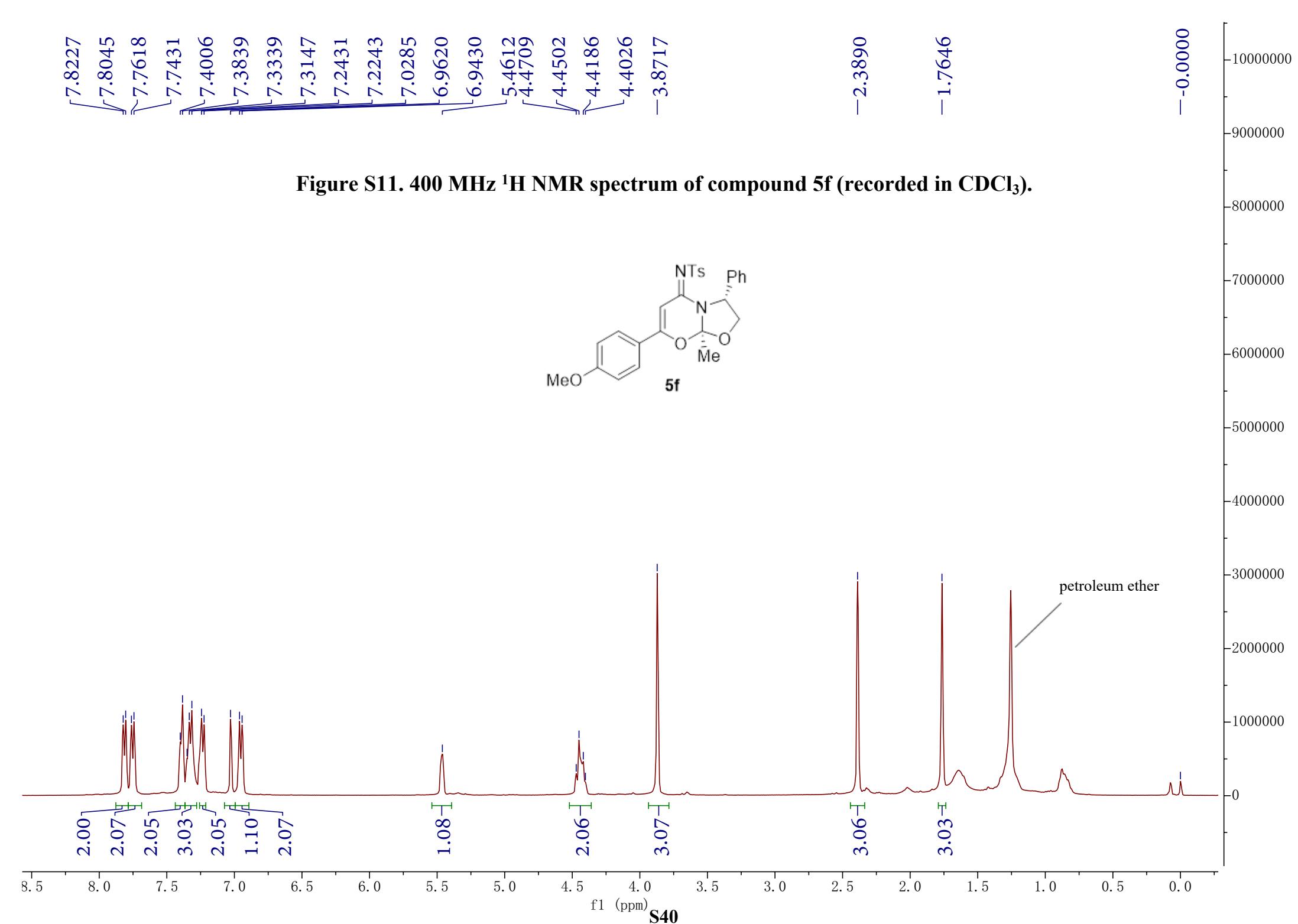


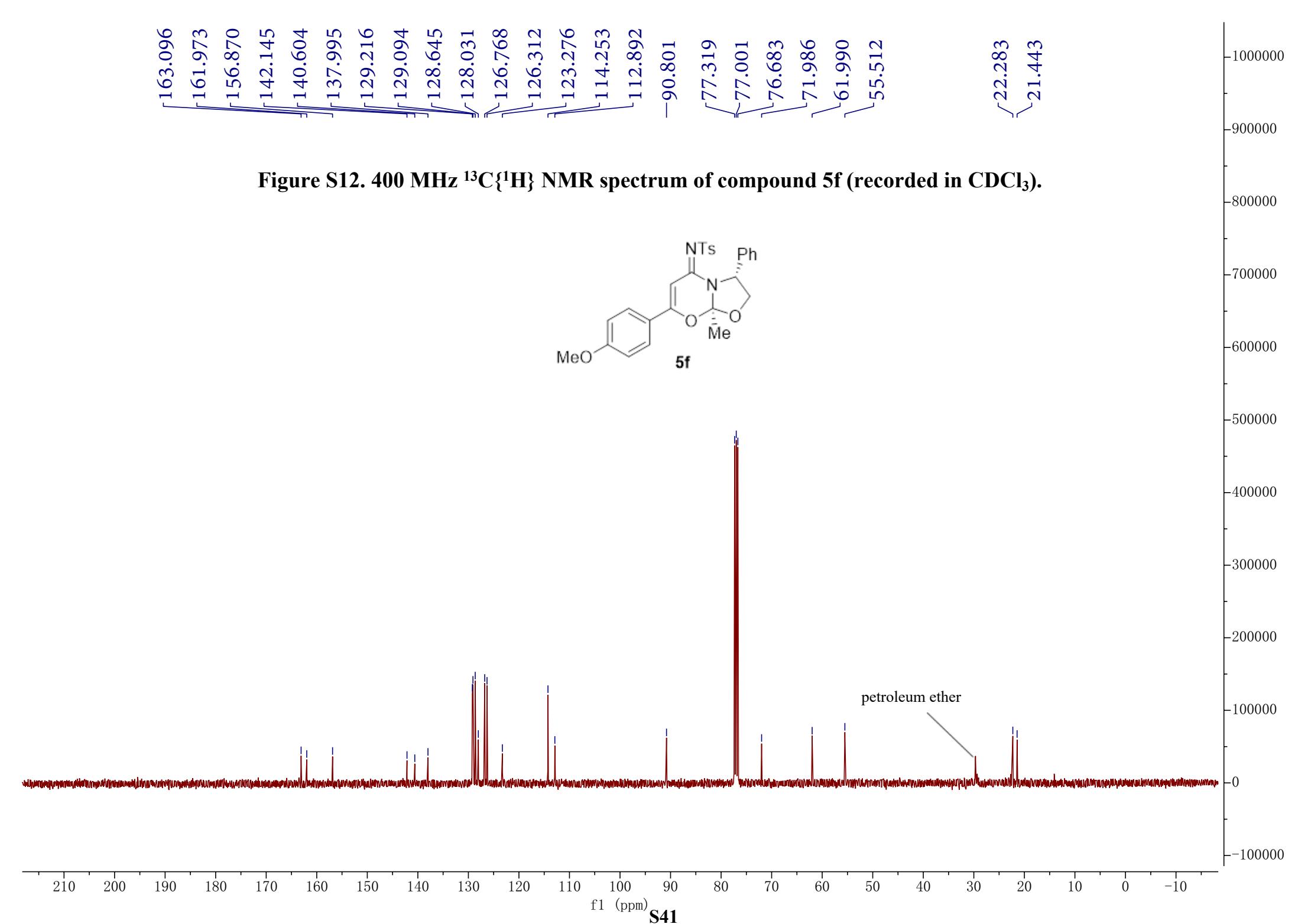


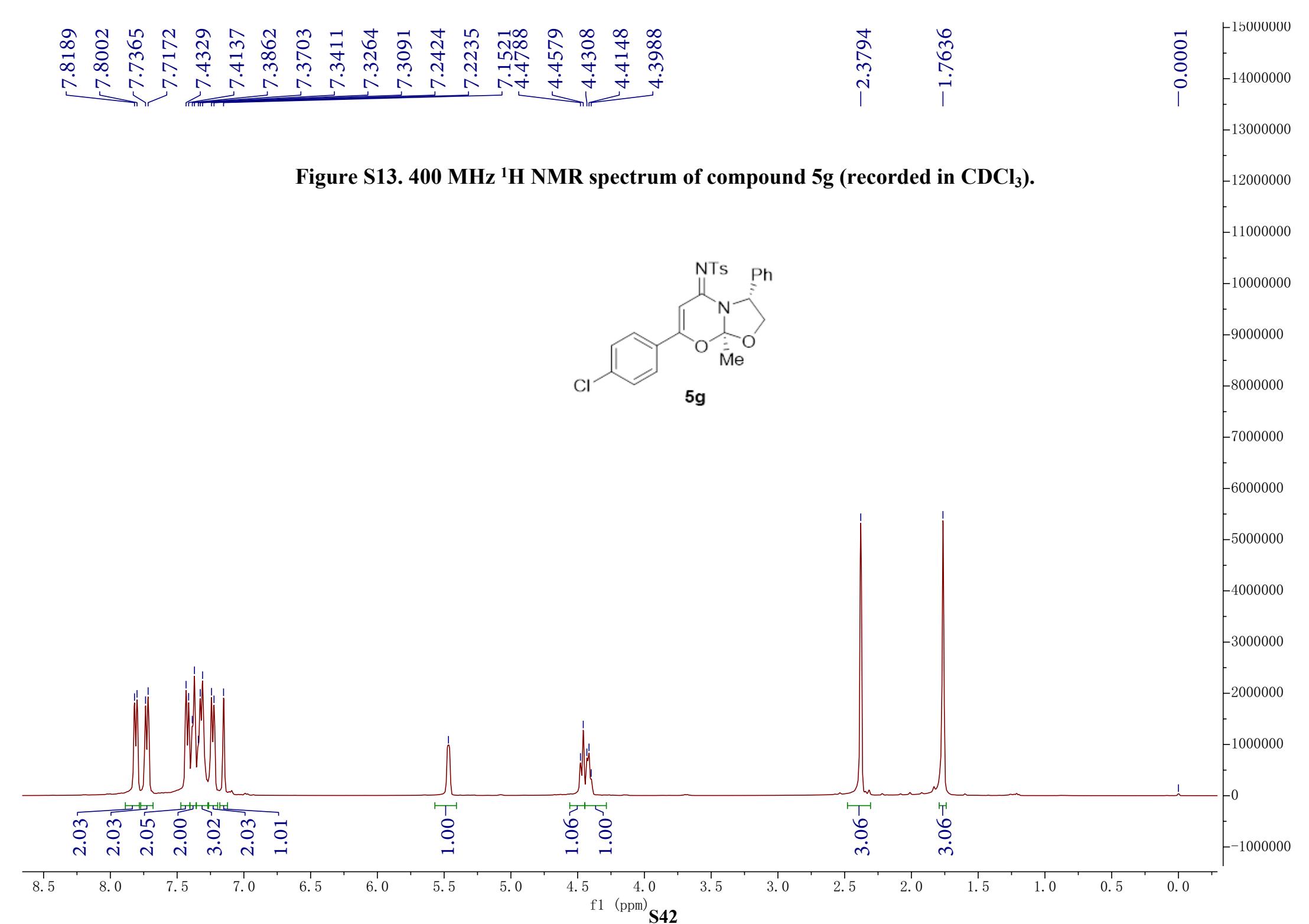


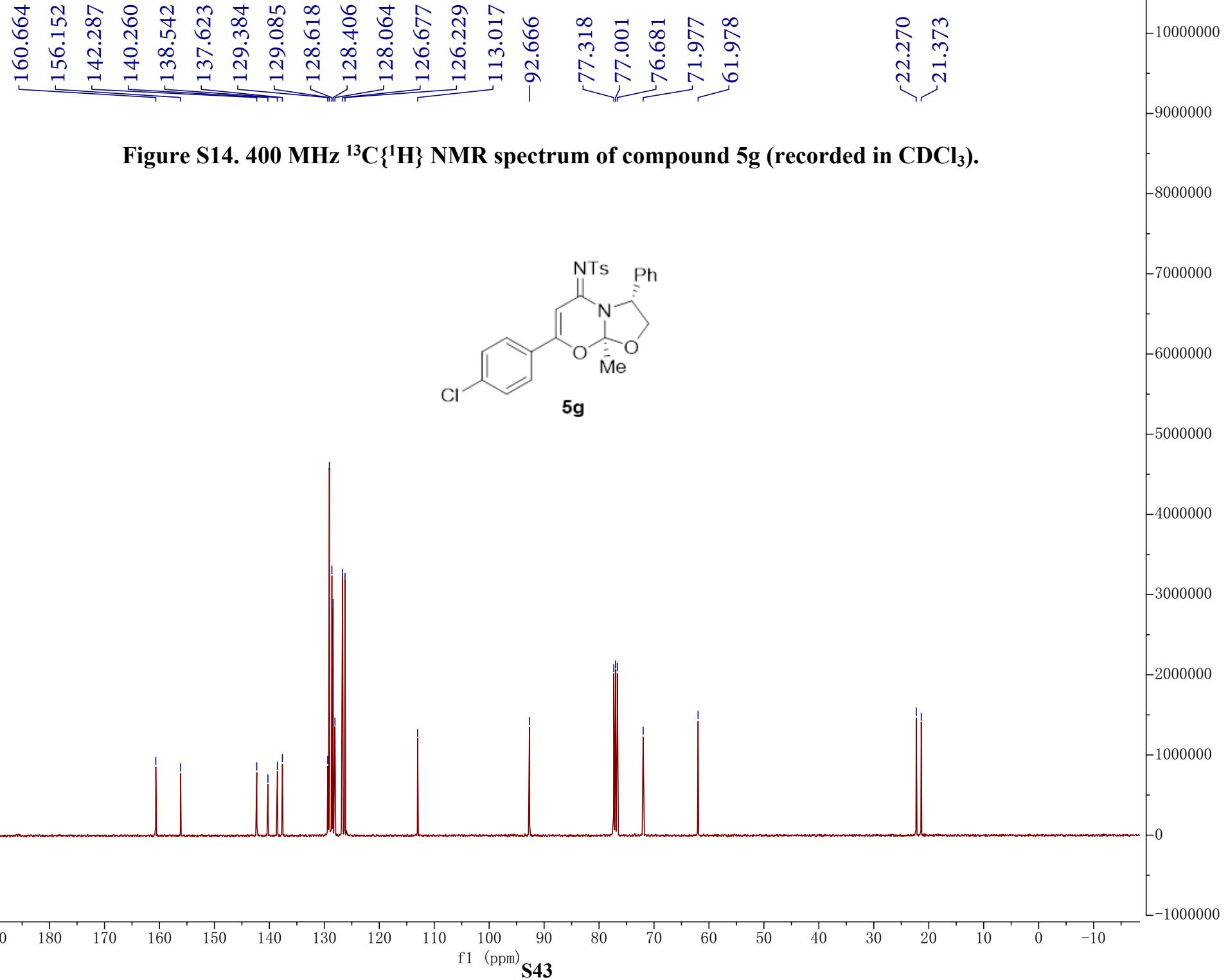


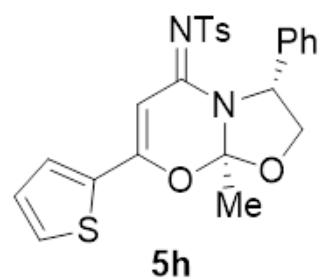
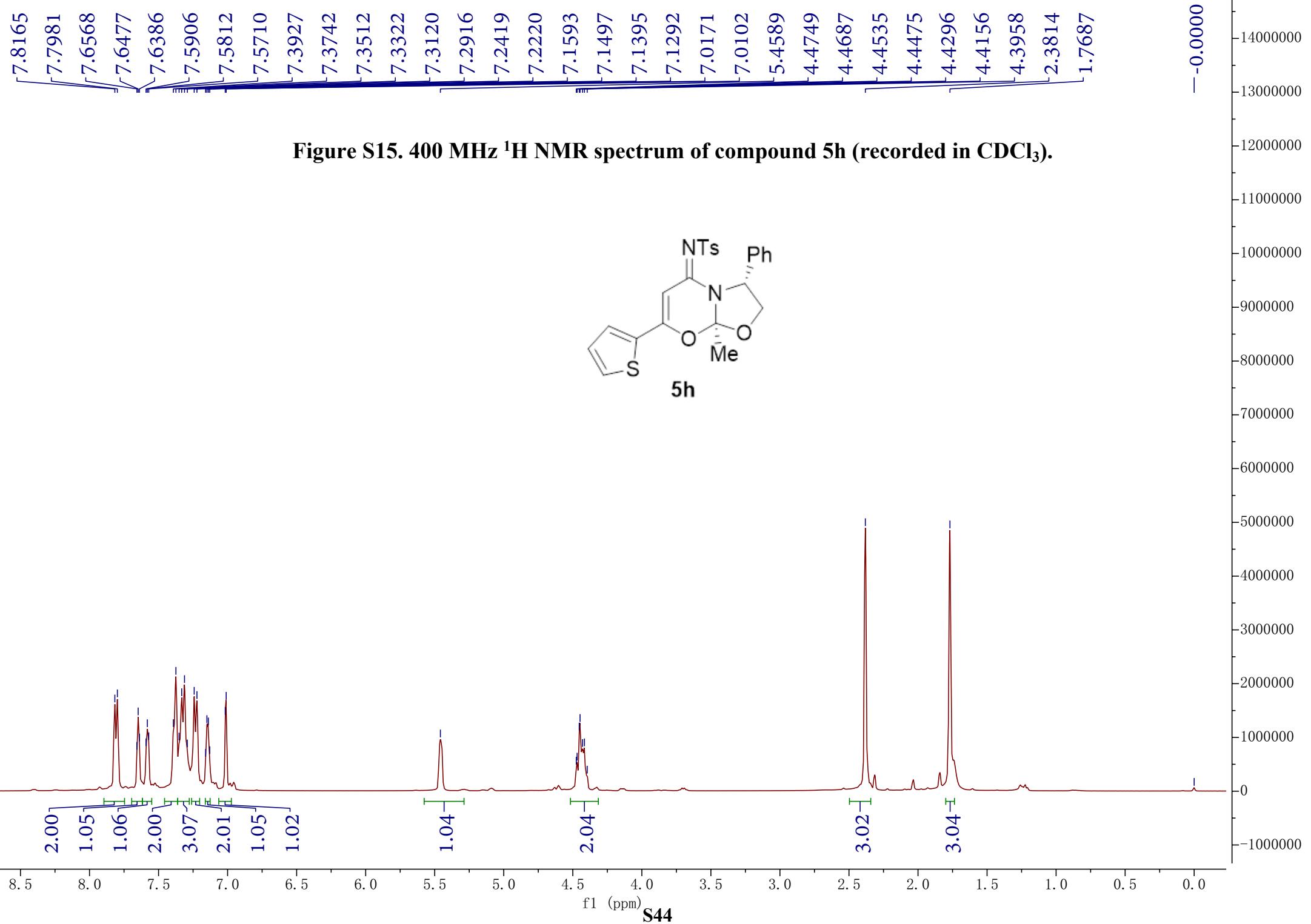












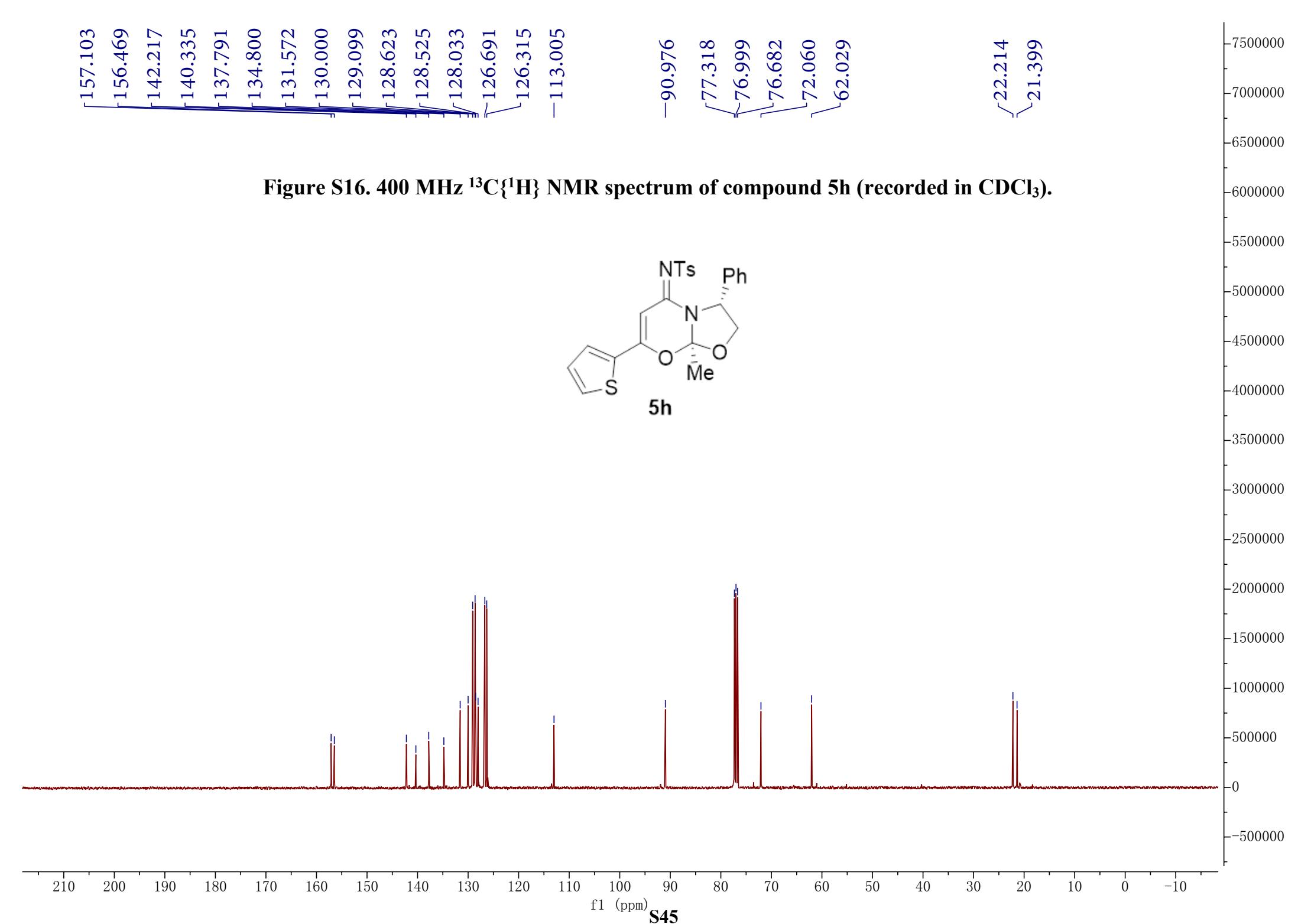
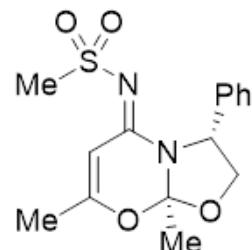
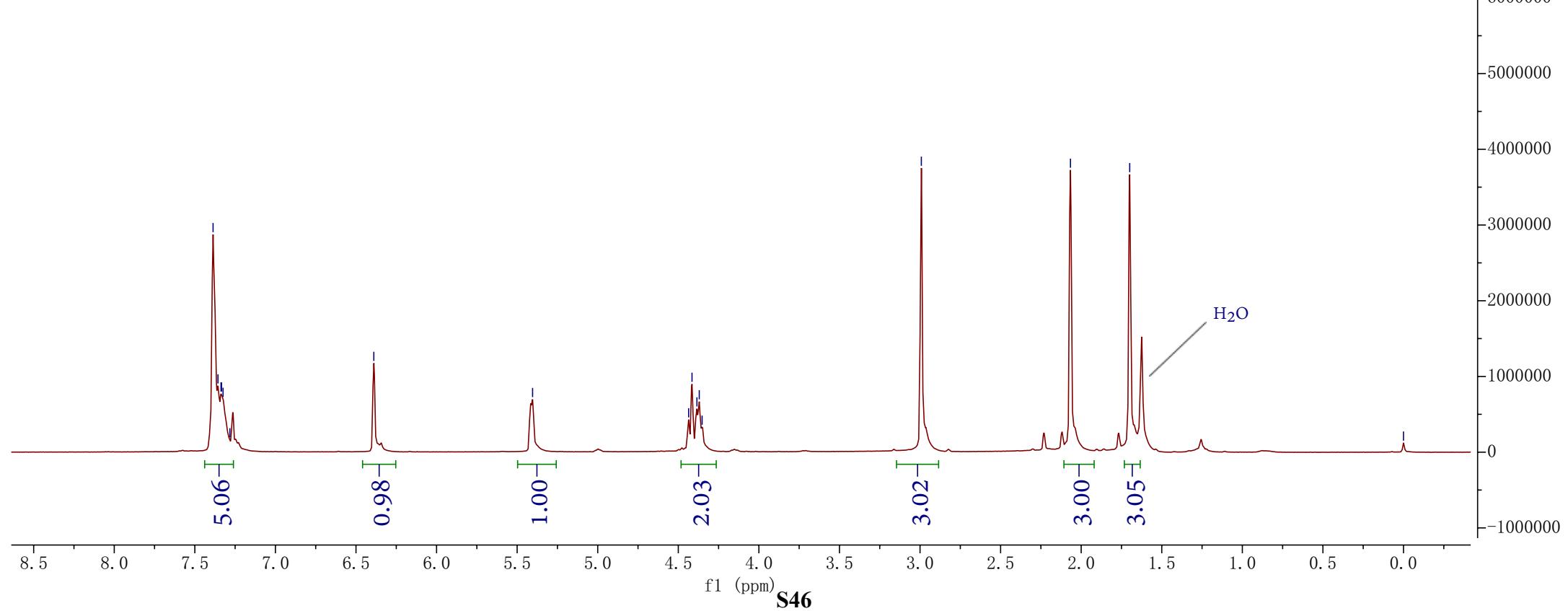


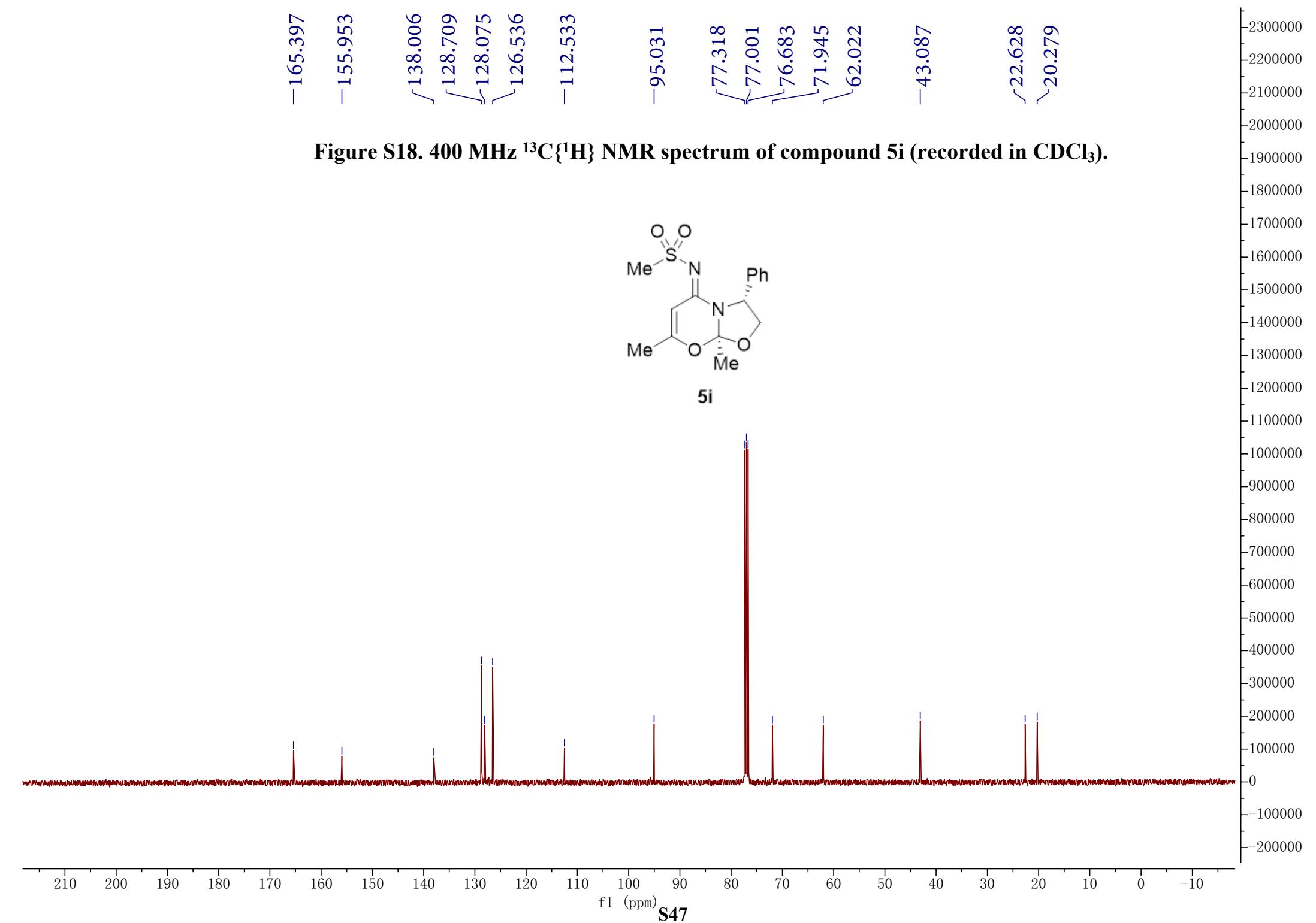


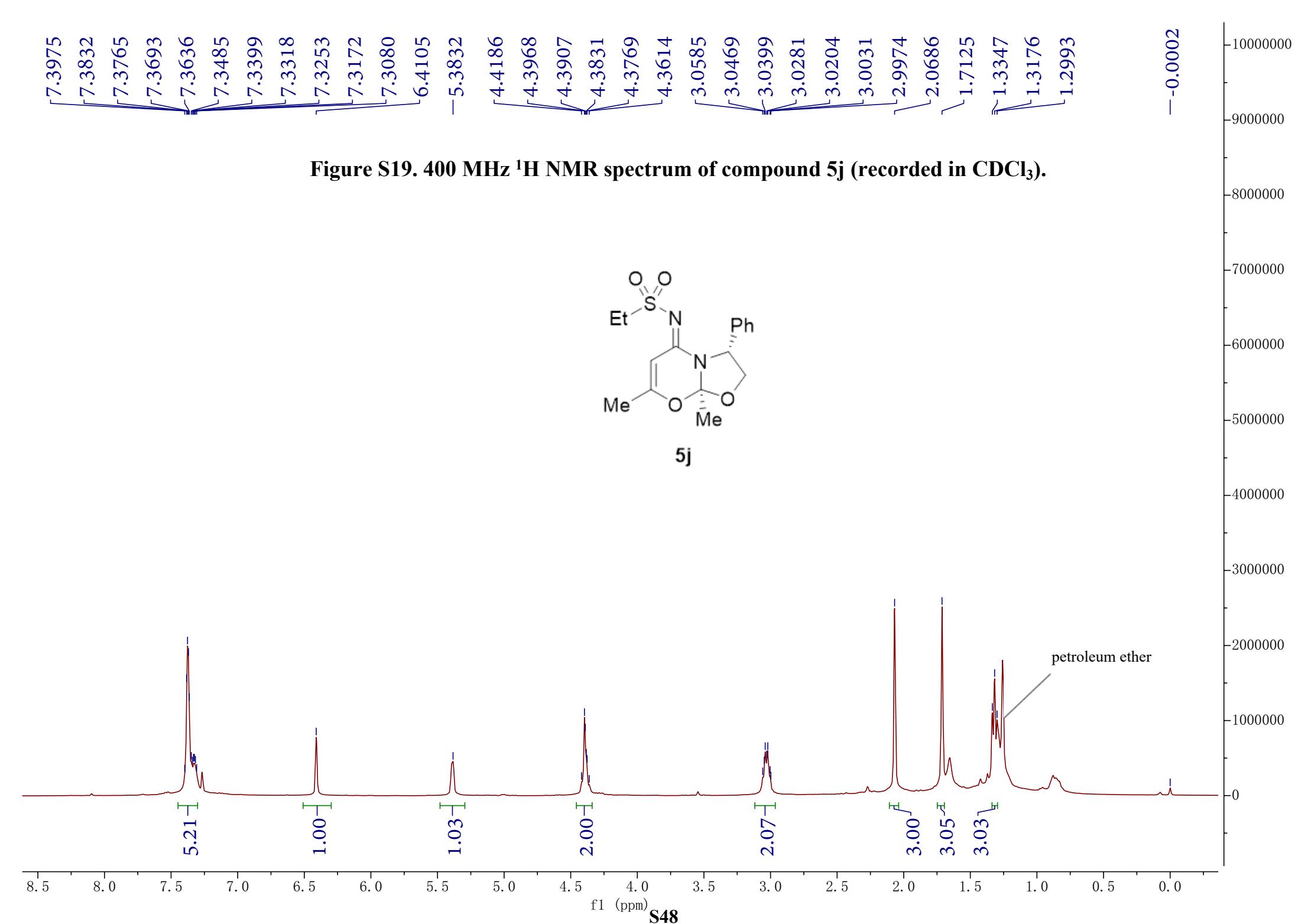
Figure S17. 400 MHz ¹H NMR spectrum of compound **5i** (recorded in CDCl₃).

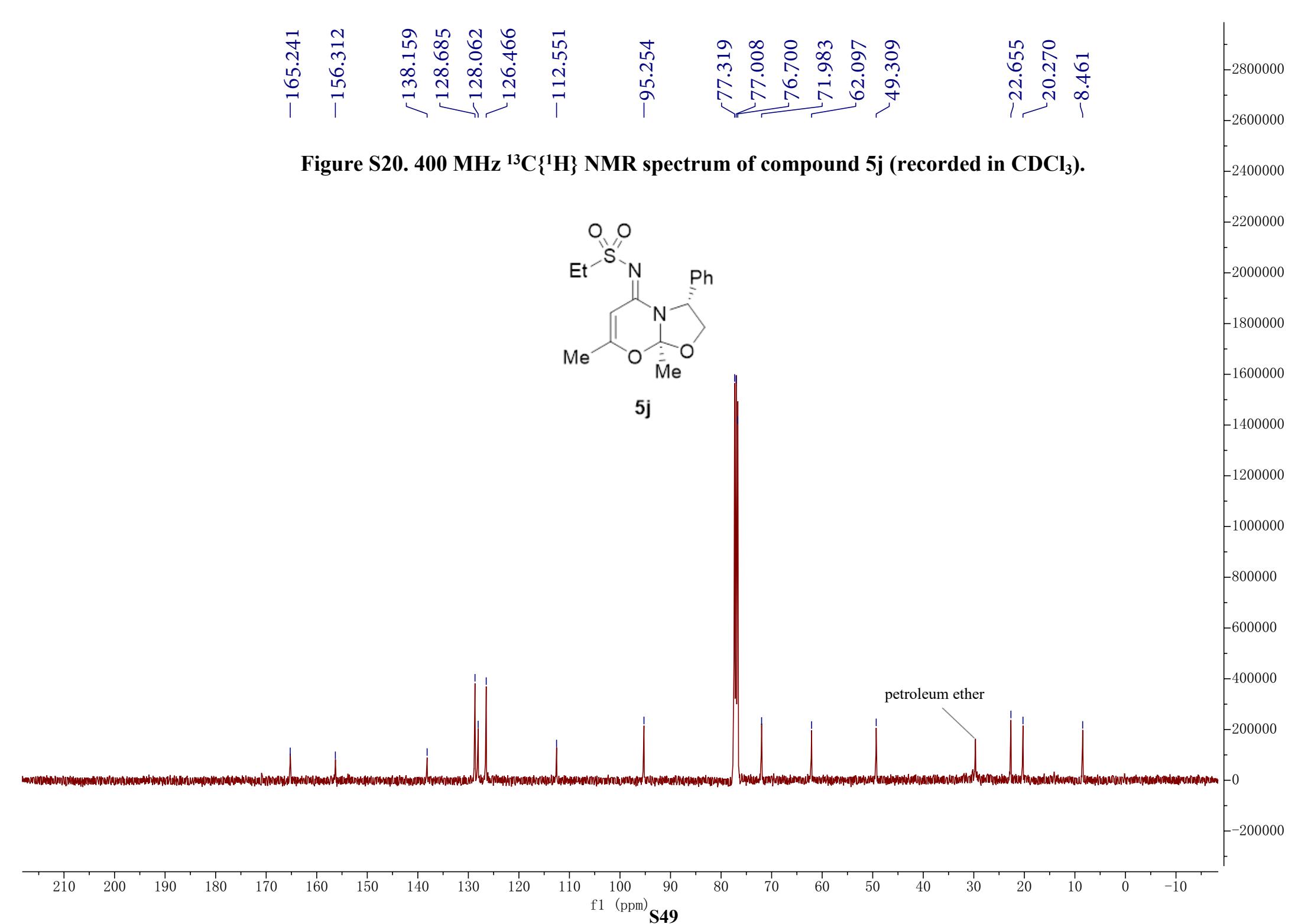


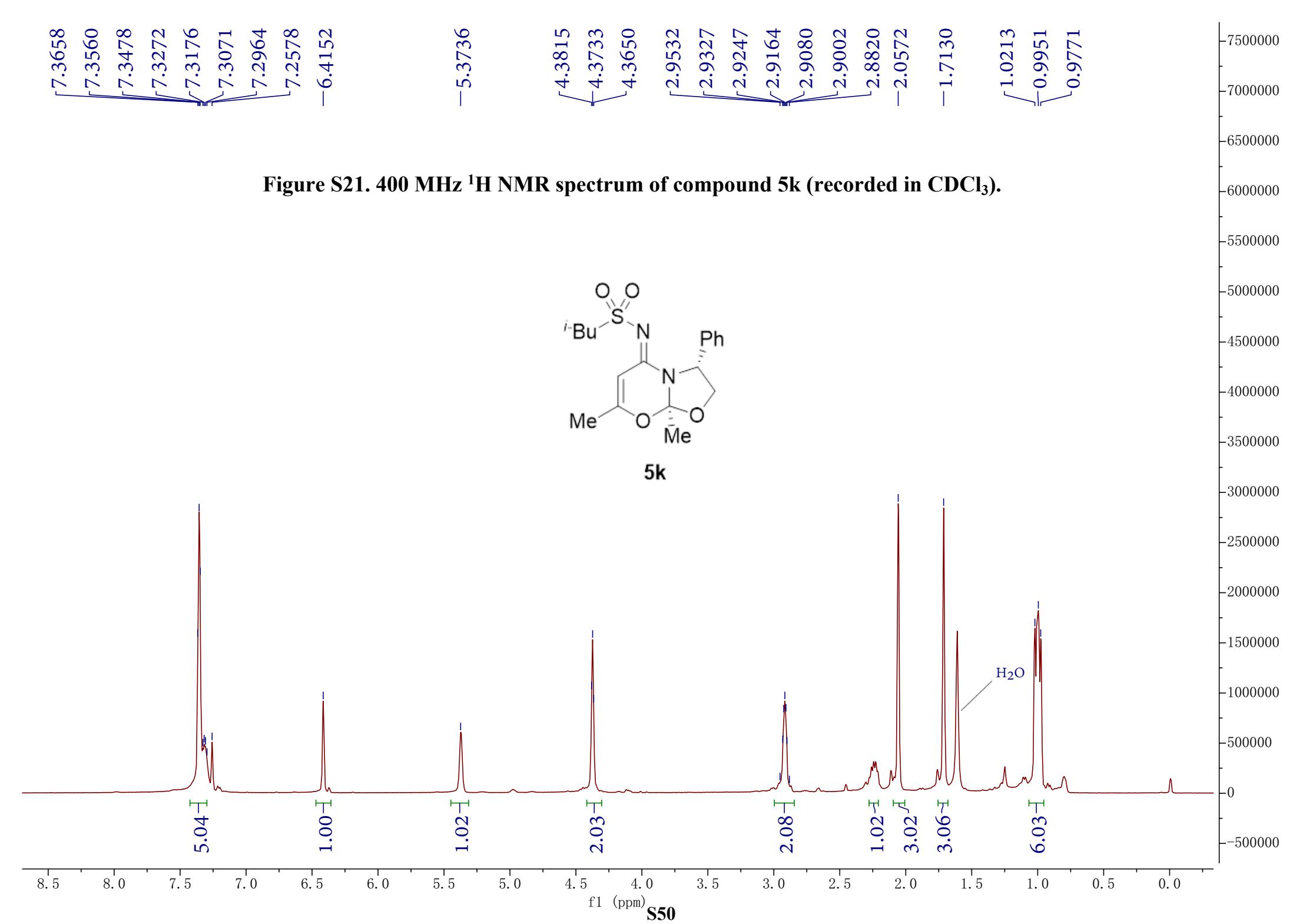
5i





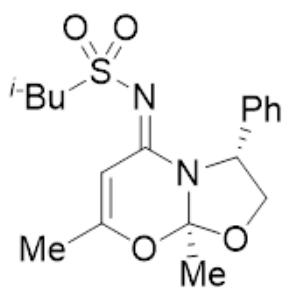




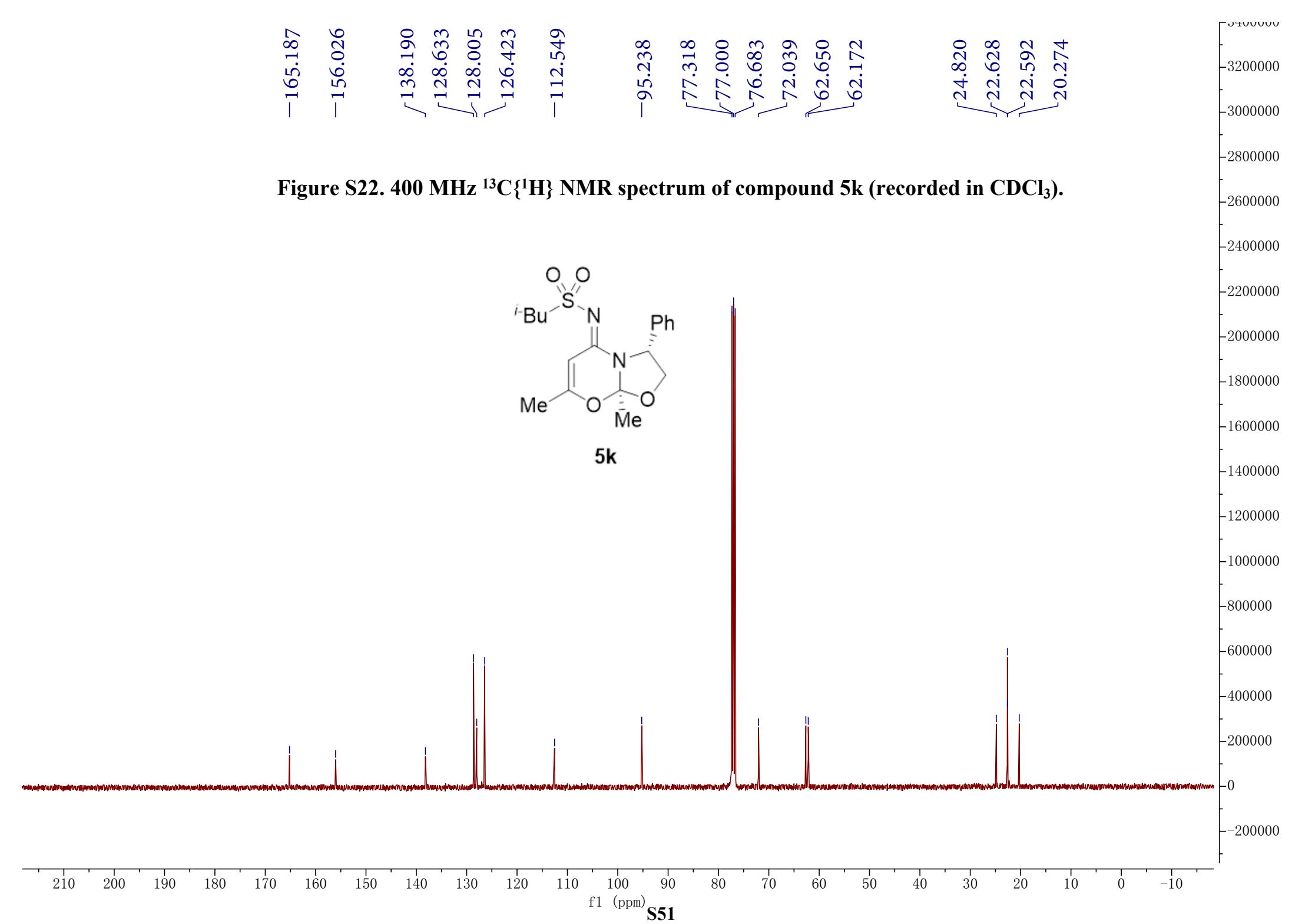


-165.187
 -156.026
 / 138.190
 \ 128.633
 \ 128.005
 \ 126.423
 -112.549
 -95.238
 [77.318
 \ 77.000
 \ 76.683
 \ 72.039
 \ 62.650
 \ 62.172
 24.820
 \ 22.628
 \ 22.592
 \ 20.274

Figure S22. 400 MHz $^{13}\text{C}\{\text{H}\}$ NMR spectrum of compound **5k** (recorded in CDCl_3).



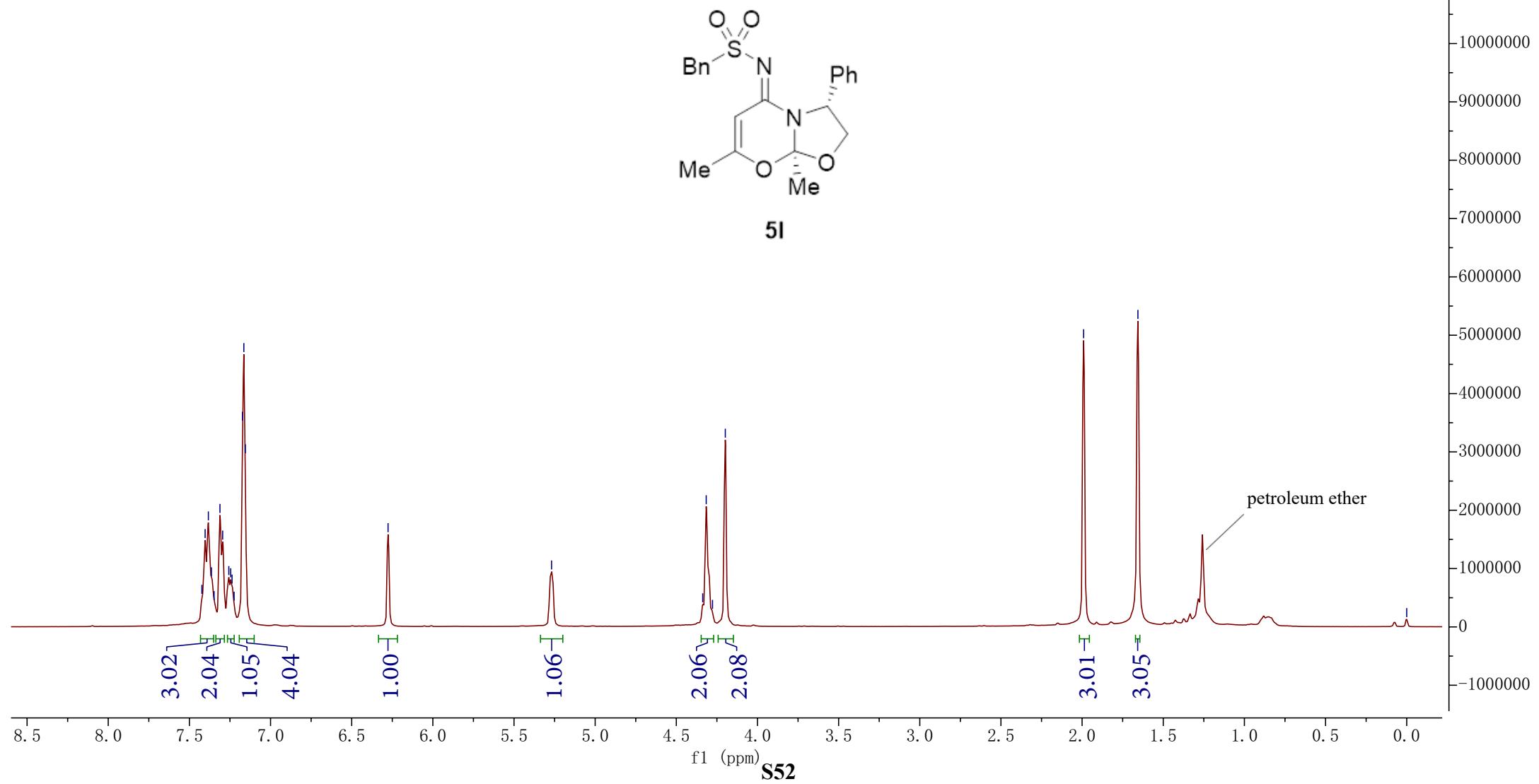
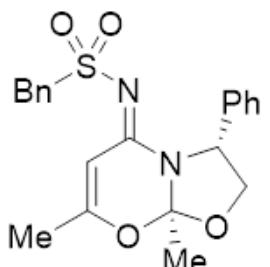
5k

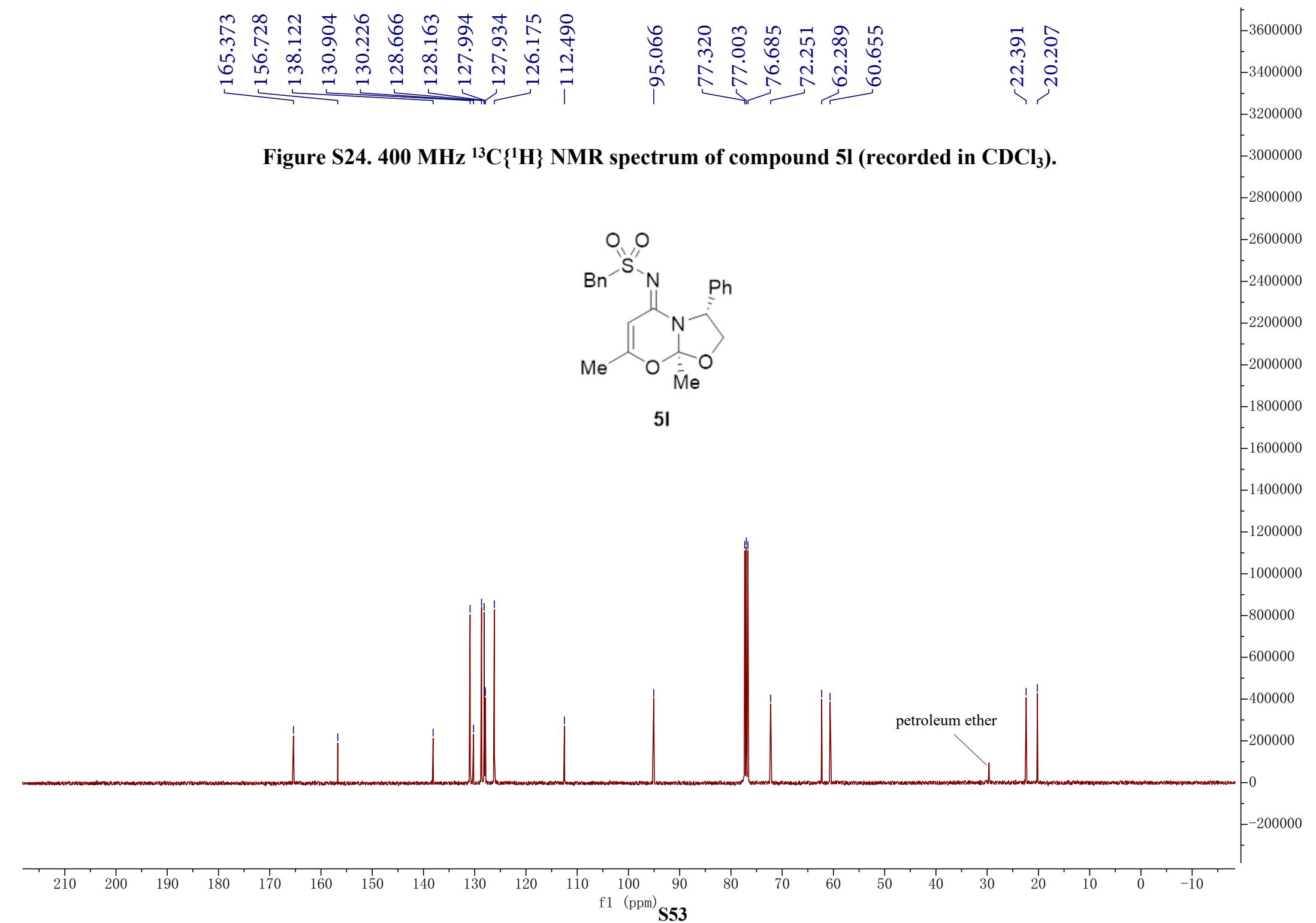


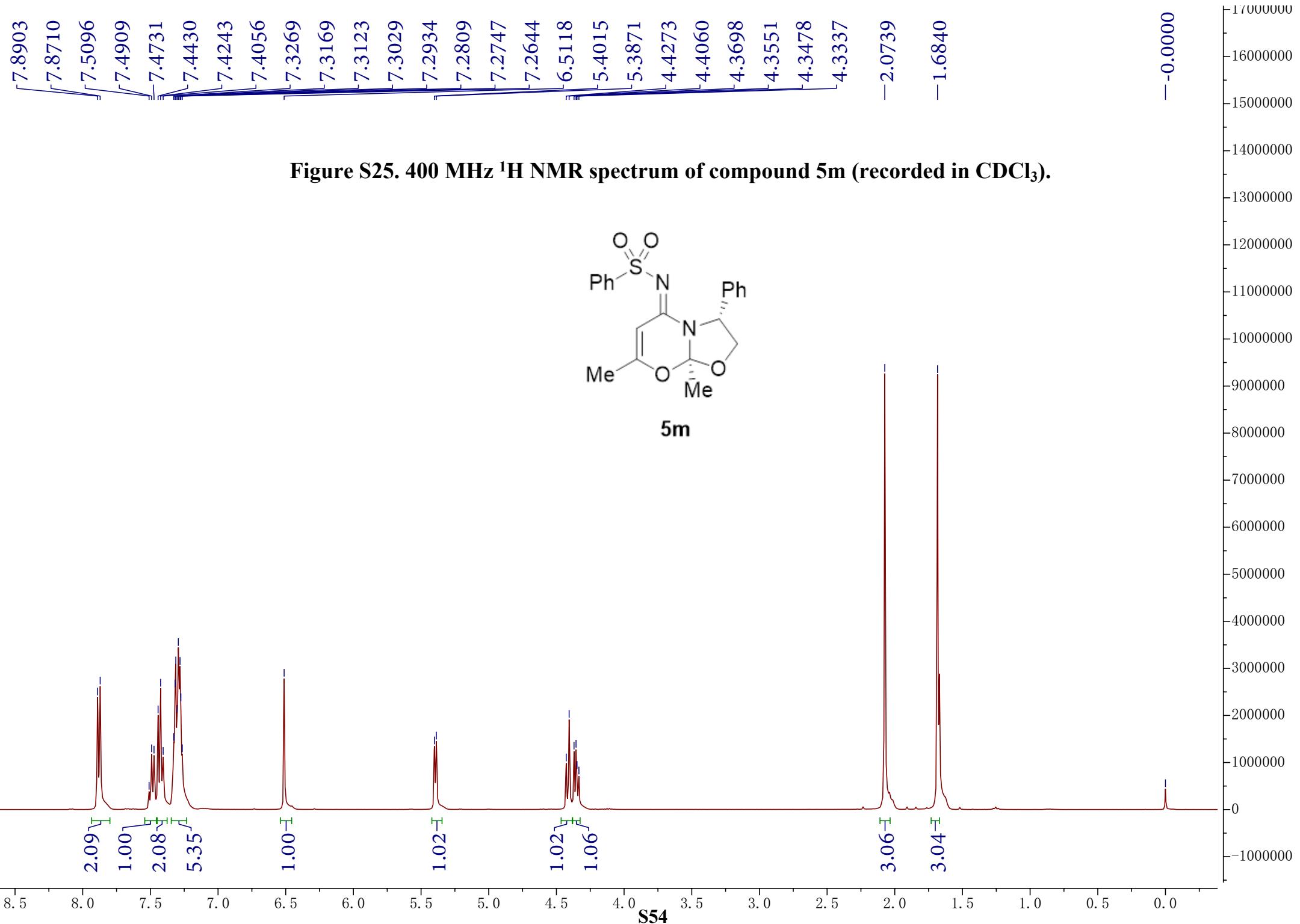
S51



Figure S23. 400 MHz ^1H NMR spectrum of compound **5l** (recorded in CDCl_3).







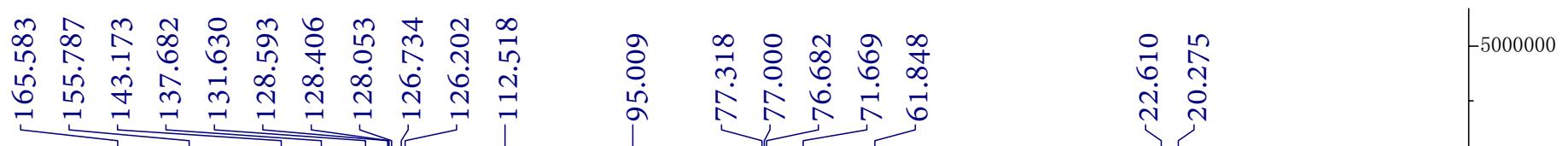
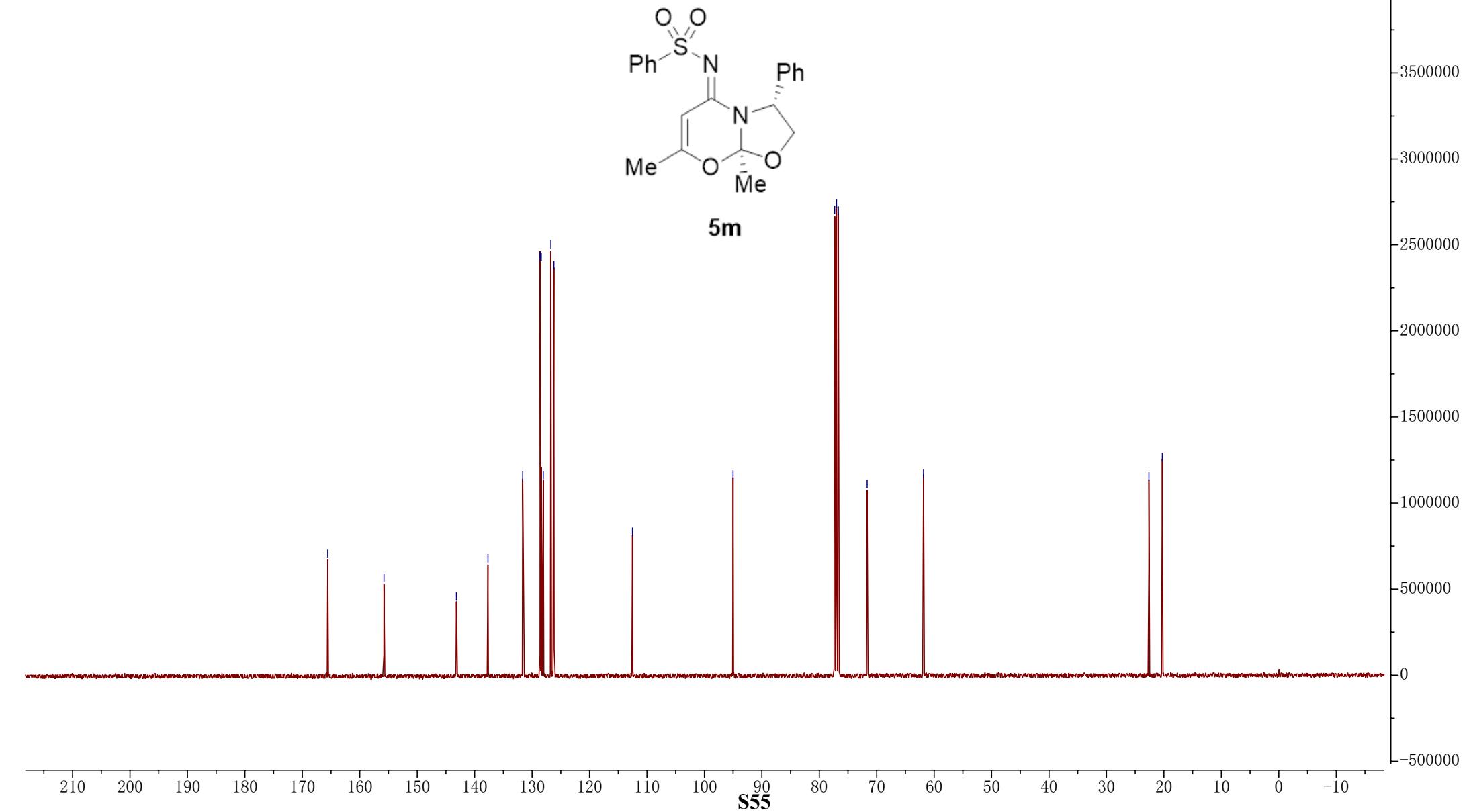
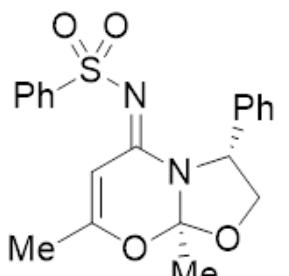


Figure S26. 400 MHz $^{13}\text{C}\{\text{H}\}$ NMR spectrum of compound **5m** (recorded in CDCl_3).



7.7296
7.7091
7.5561
7.5358
7.3409
7.3056
7.2667
-6.4795

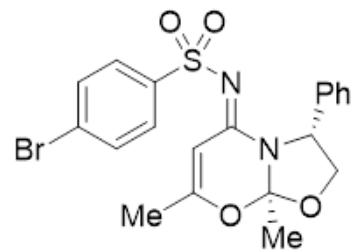
5.3769
5.3629
4.4197
4.3986
4.3809
4.3663
4.3587
4.3451

-2.0858

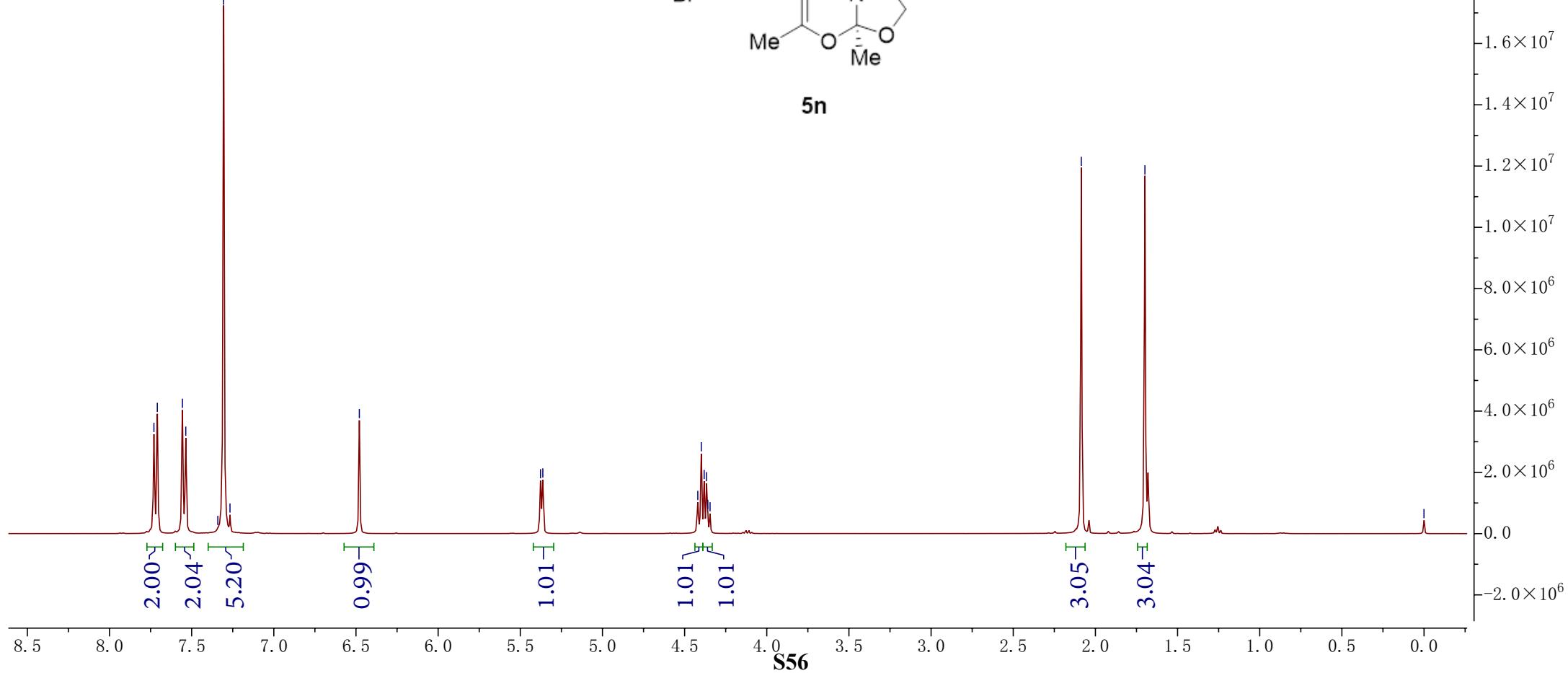
-1.6986

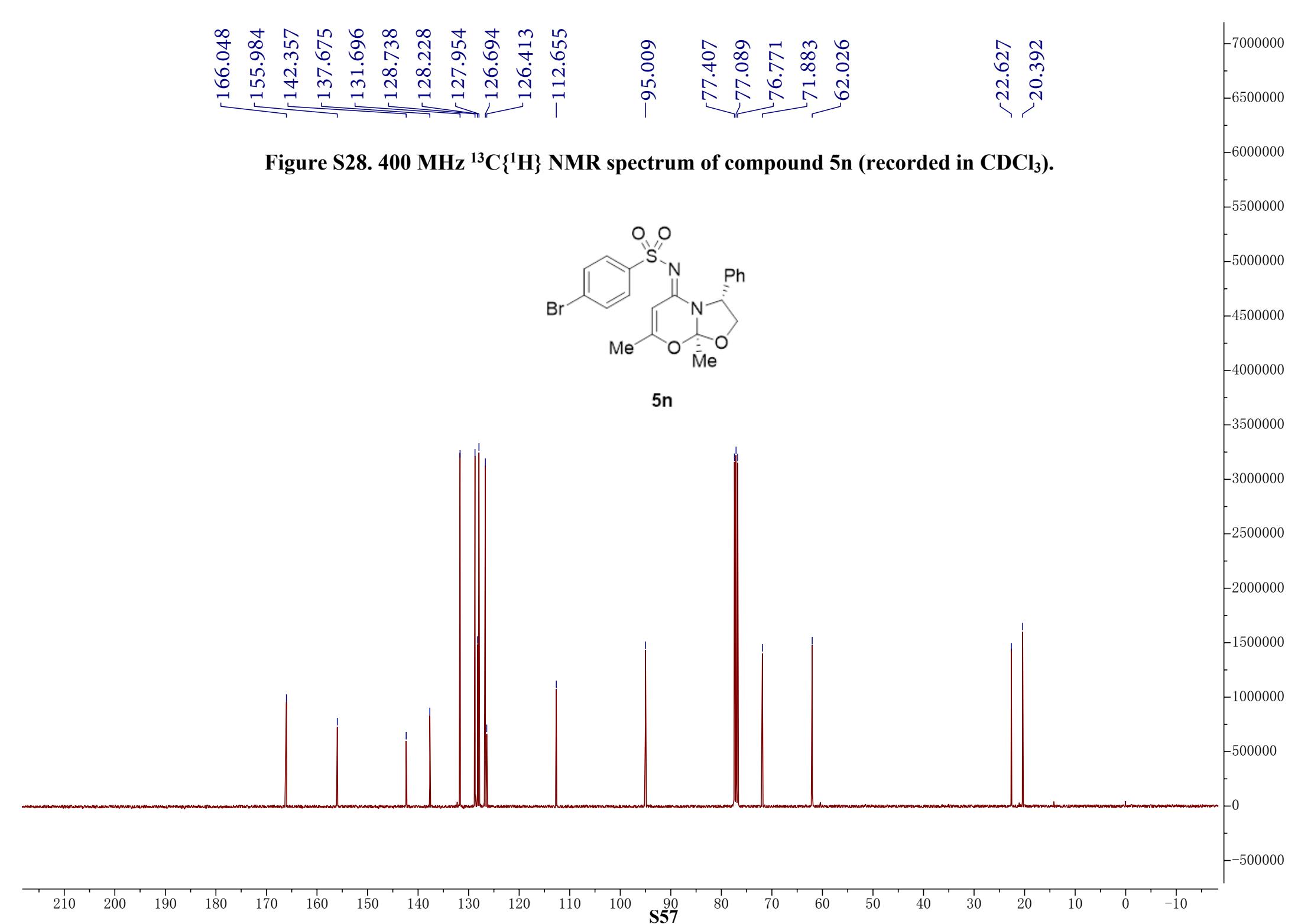
-0.0005
 3.0×10^7
 2.8×10^7
 2.6×10^7
 2.4×10^7
 2.2×10^7
 2.0×10^7
 1.8×10^7
 1.6×10^7
 1.4×10^7
 1.2×10^7
 1.0×10^7
 8.0×10^6
 6.0×10^6
 4.0×10^6
 2.0×10^6
0.0
 -2.0×10^6

Figure S27. 400 MHz ^1H NMR spectrum of compound **5n** (recorded in CDCl_3).



5n





7.8175
7.7964
7.3400
7.3209
7.2988
7.2822
6.9055
6.8843
6.5041

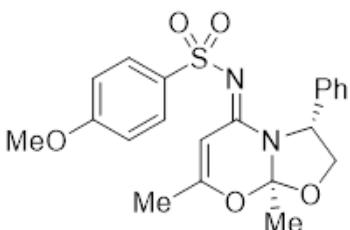
-5.3926

4.4187
4.3975
4.3571
4.3402
-3.8306

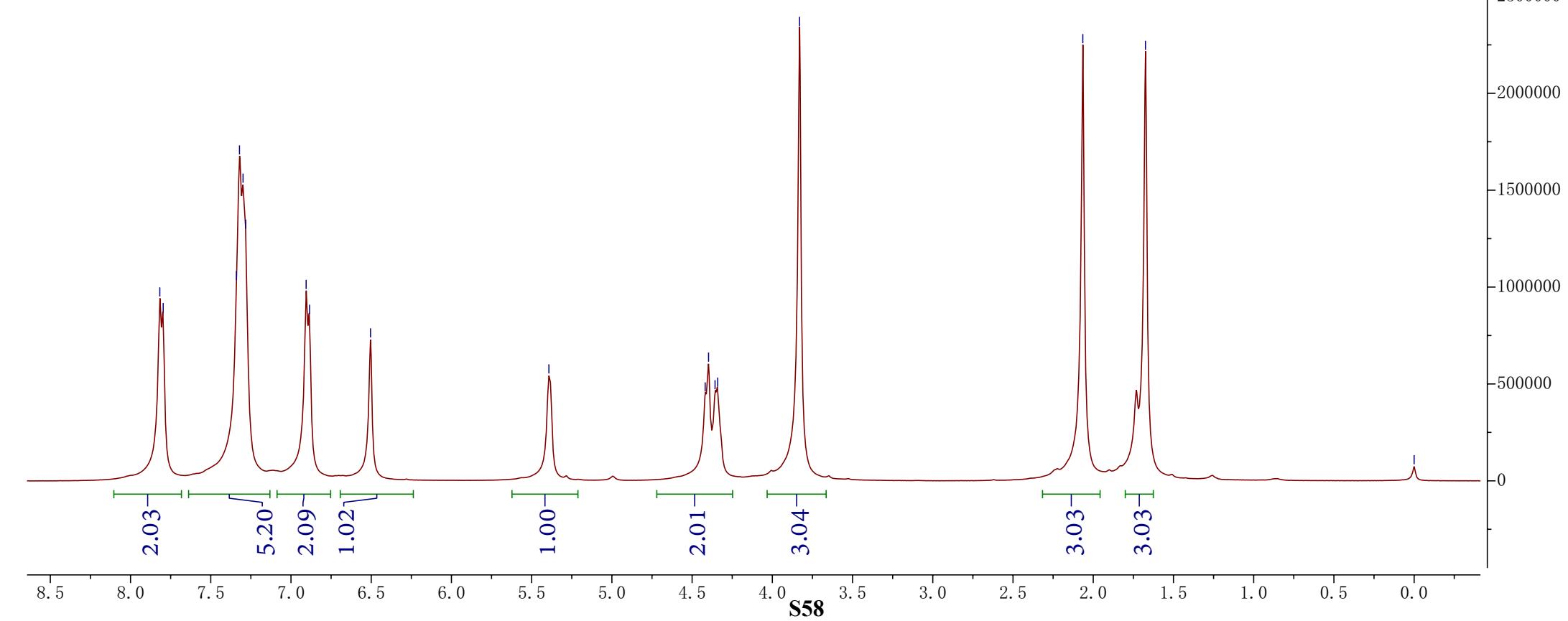
-2.0650
-1.6745

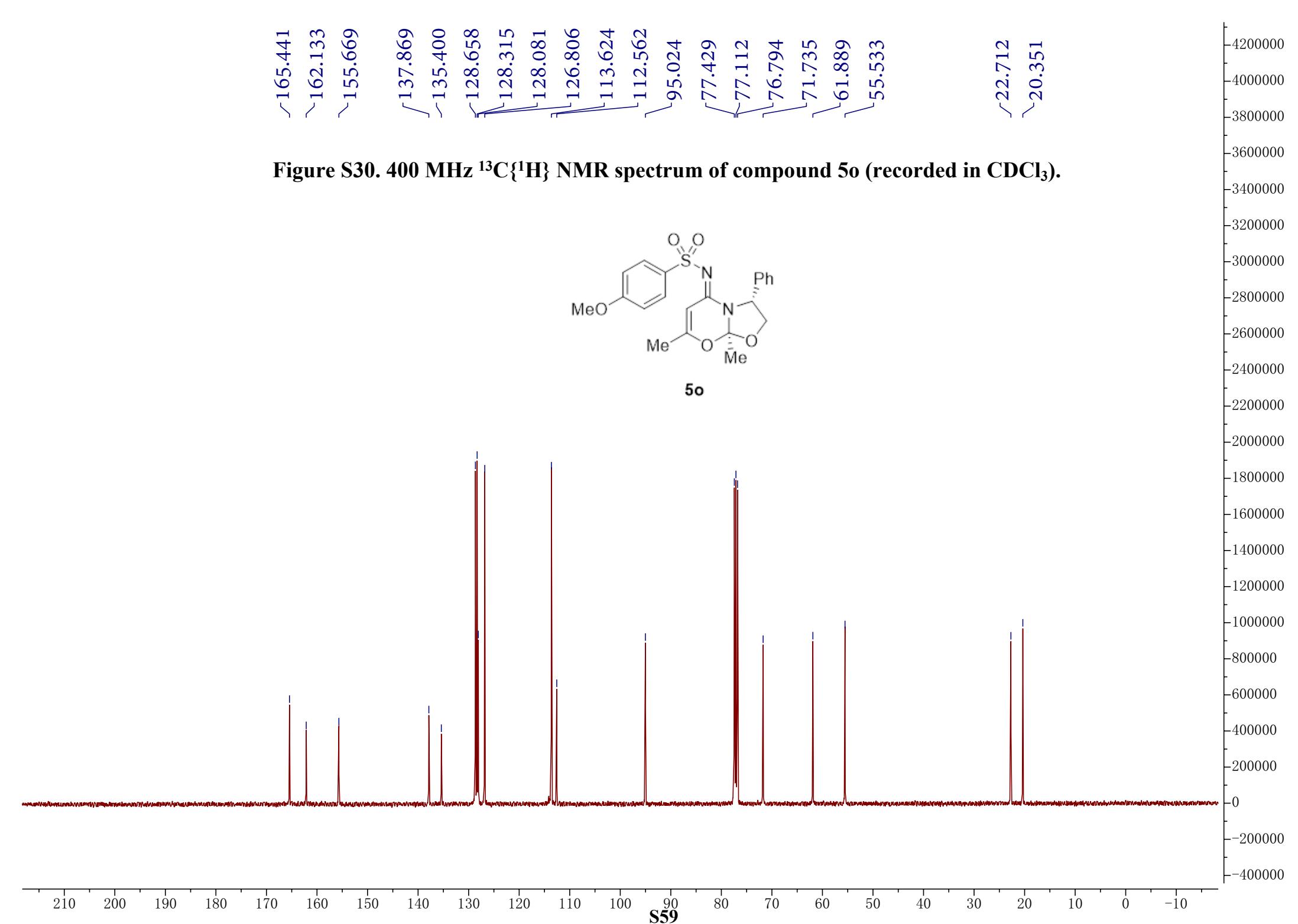
-0.0001

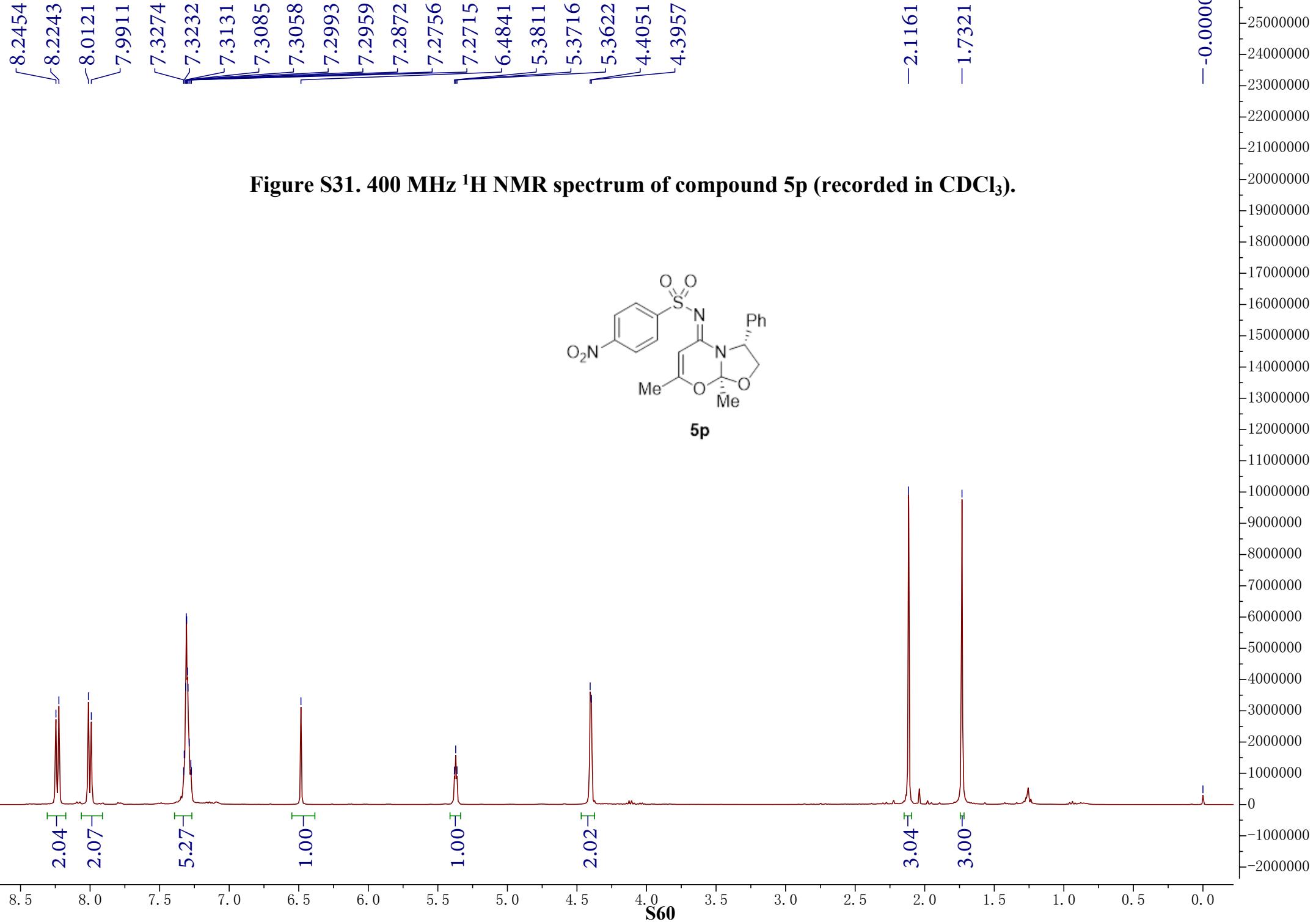
Figure S29. 400 MHz ^1H NMR spectrum of compound **5o** (recorded in CDCl_3).



5o







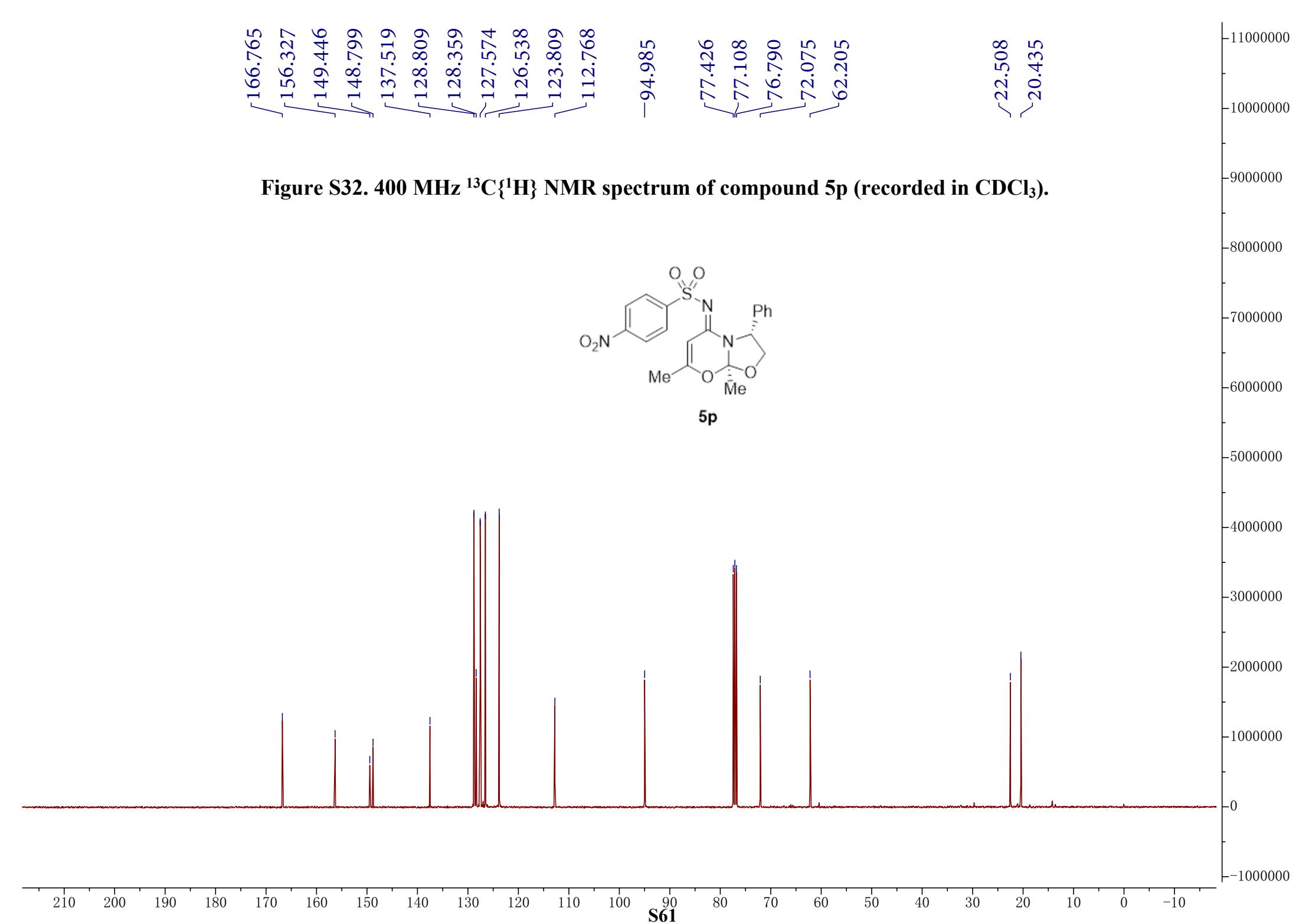
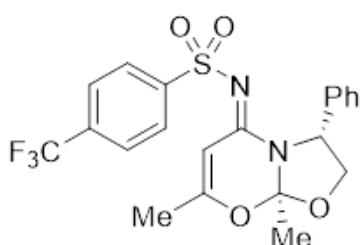




Figure S33. 400 MHz ^1H NMR spectrum of compound **5q** (recorded in CDCl_3).



5q

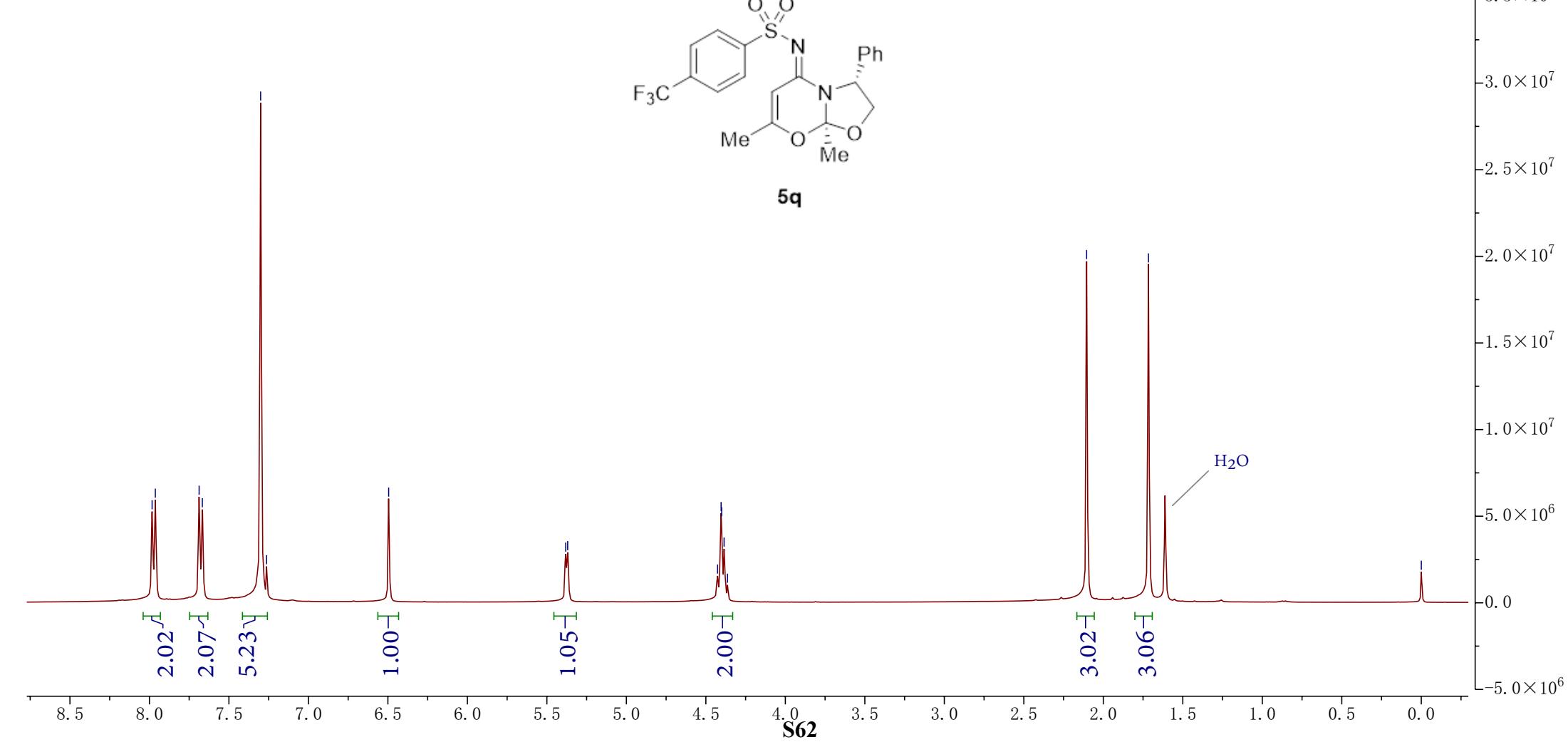
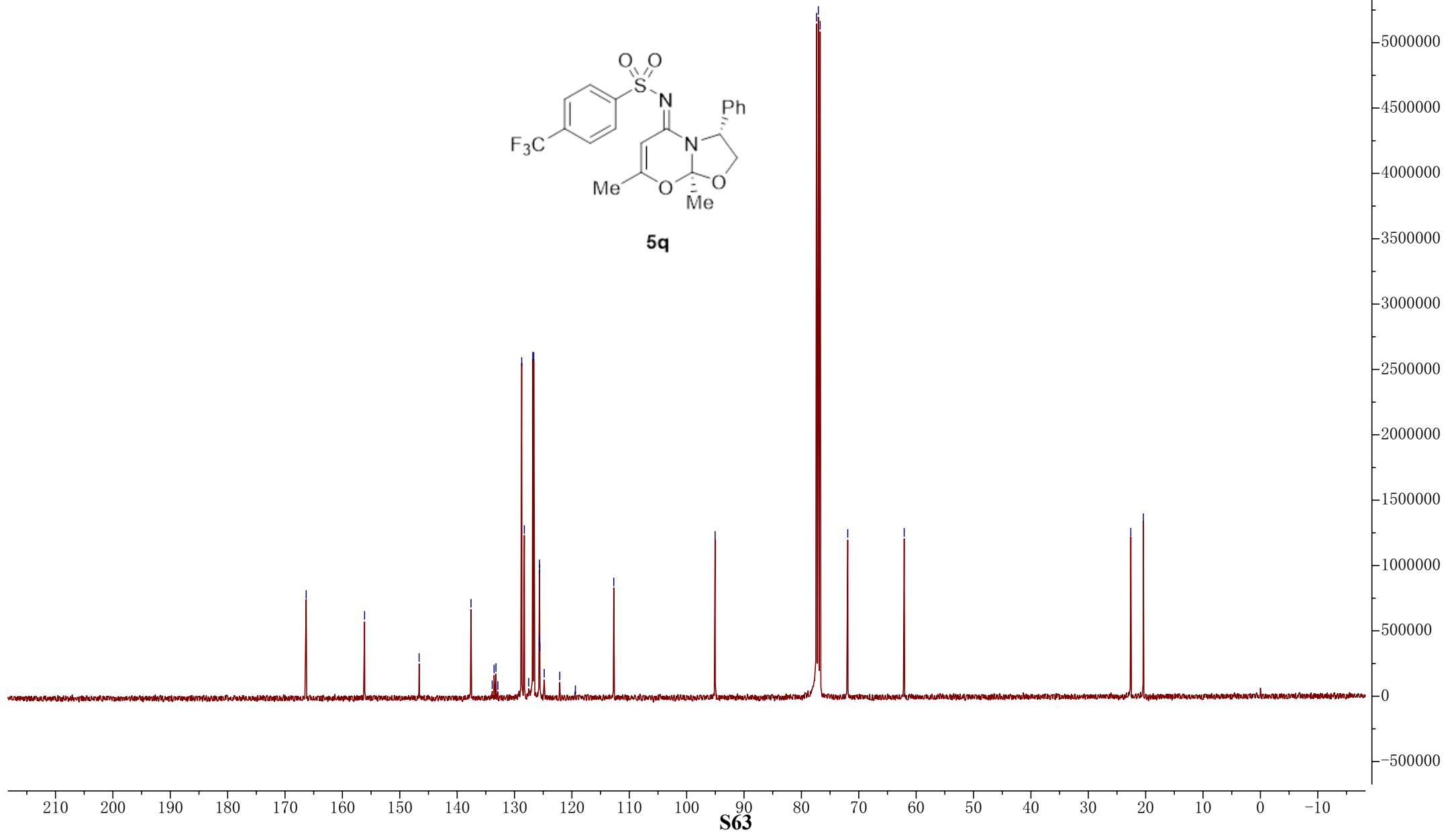
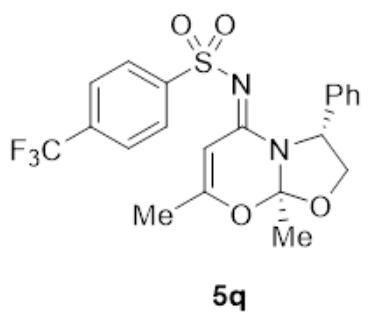
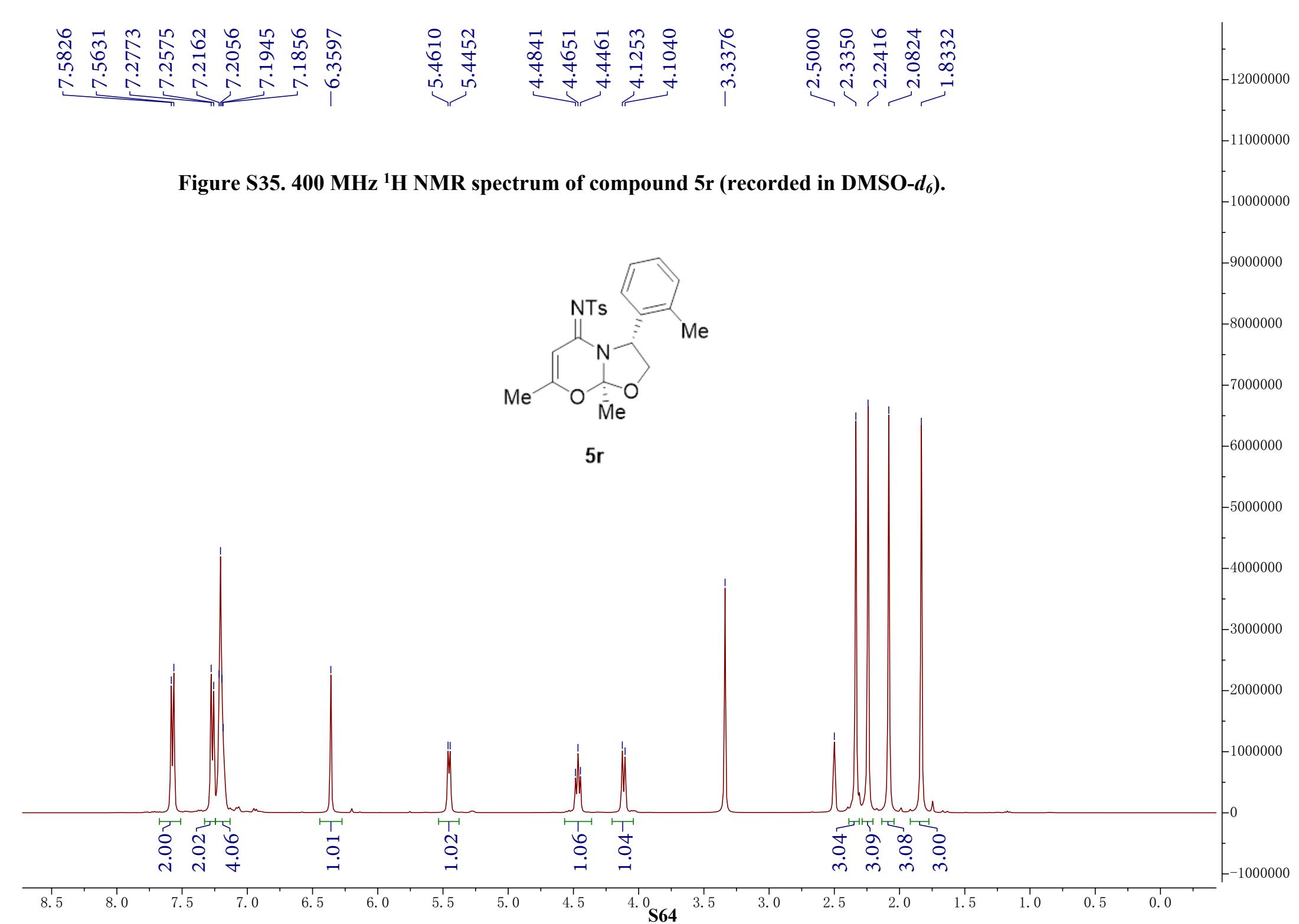
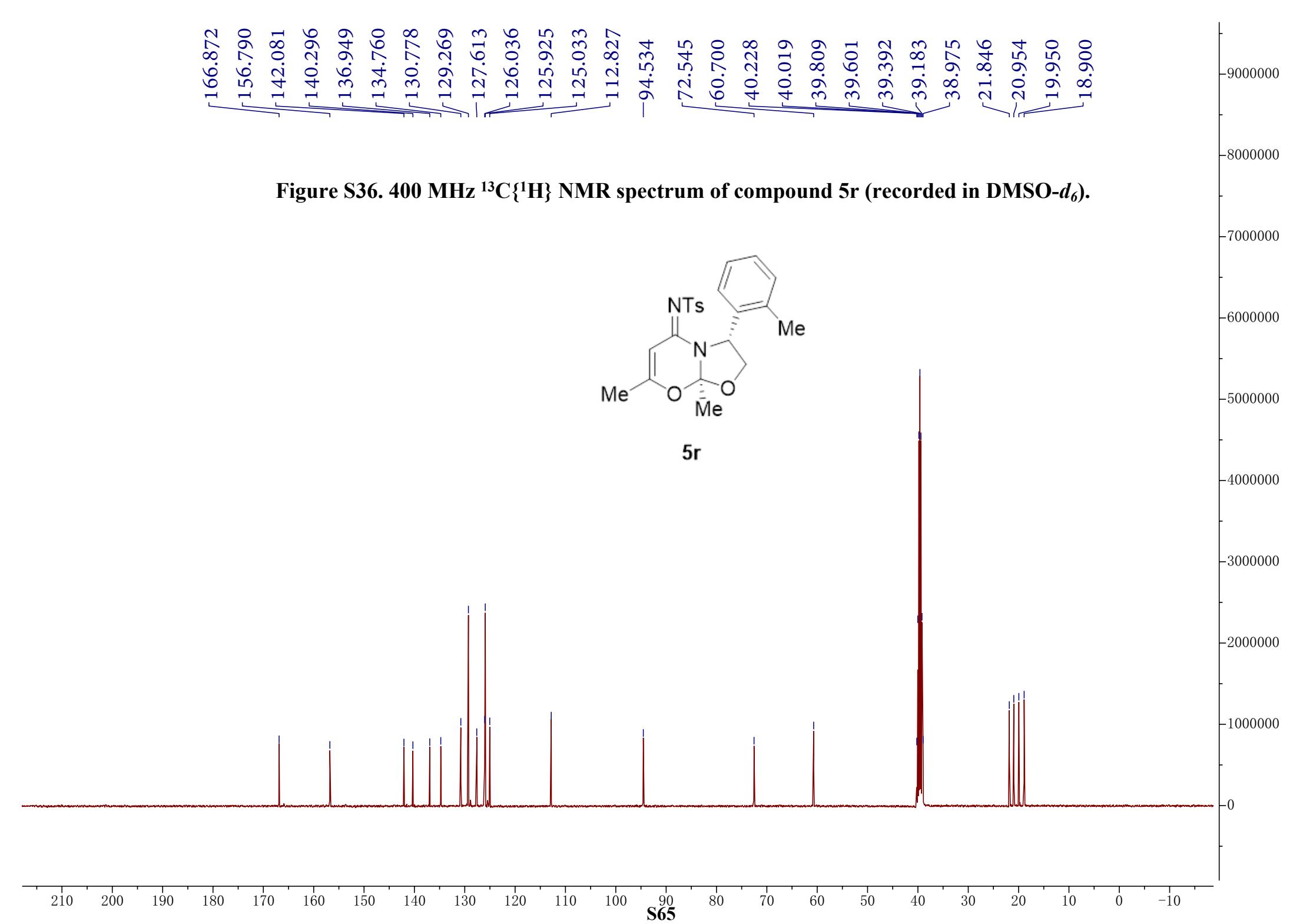




Figure S34. 400 MHz $^{13}\text{C}\{\text{H}\}$ NMR spectrum of compound **5q** (recorded in CDCl_3).







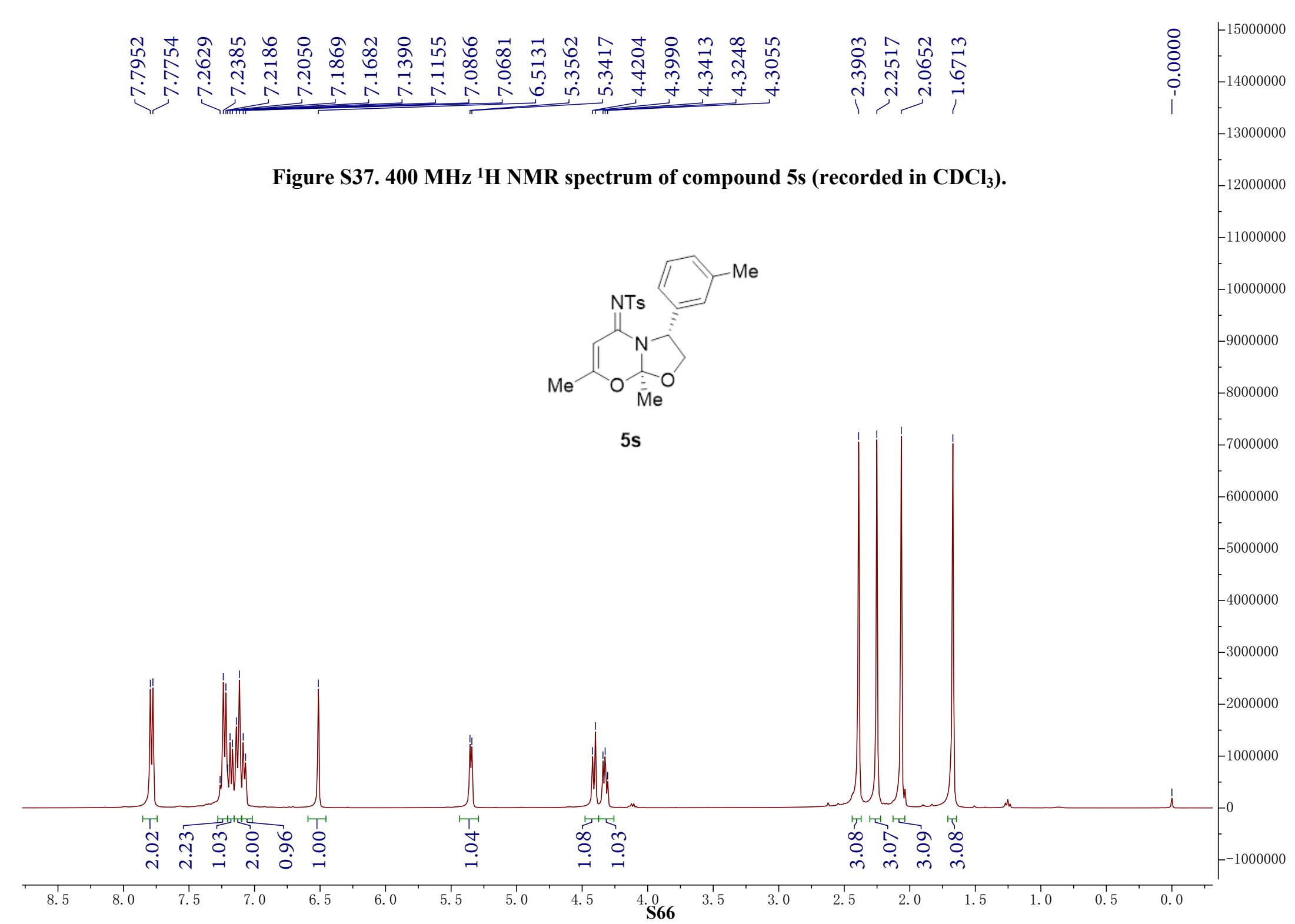
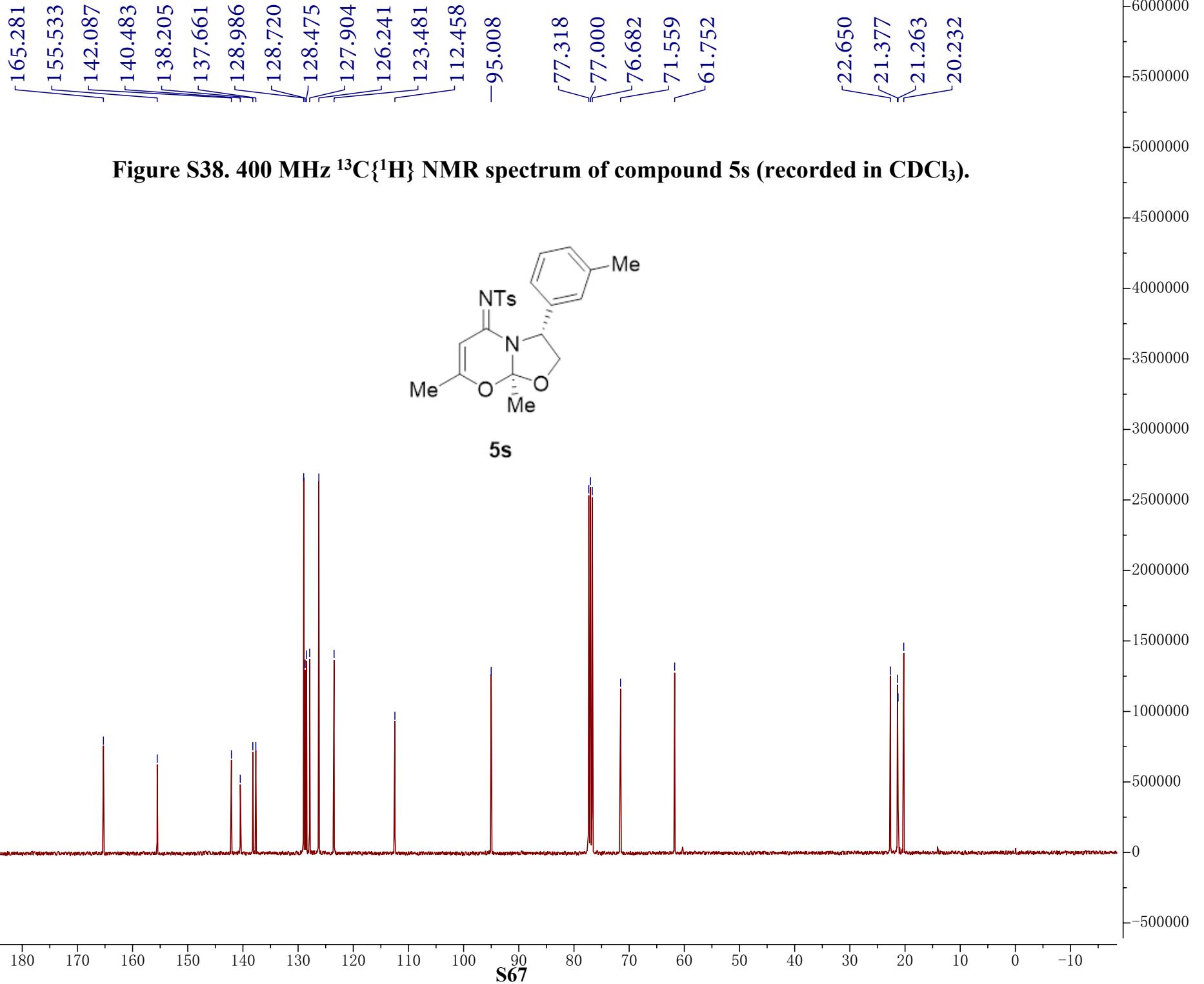
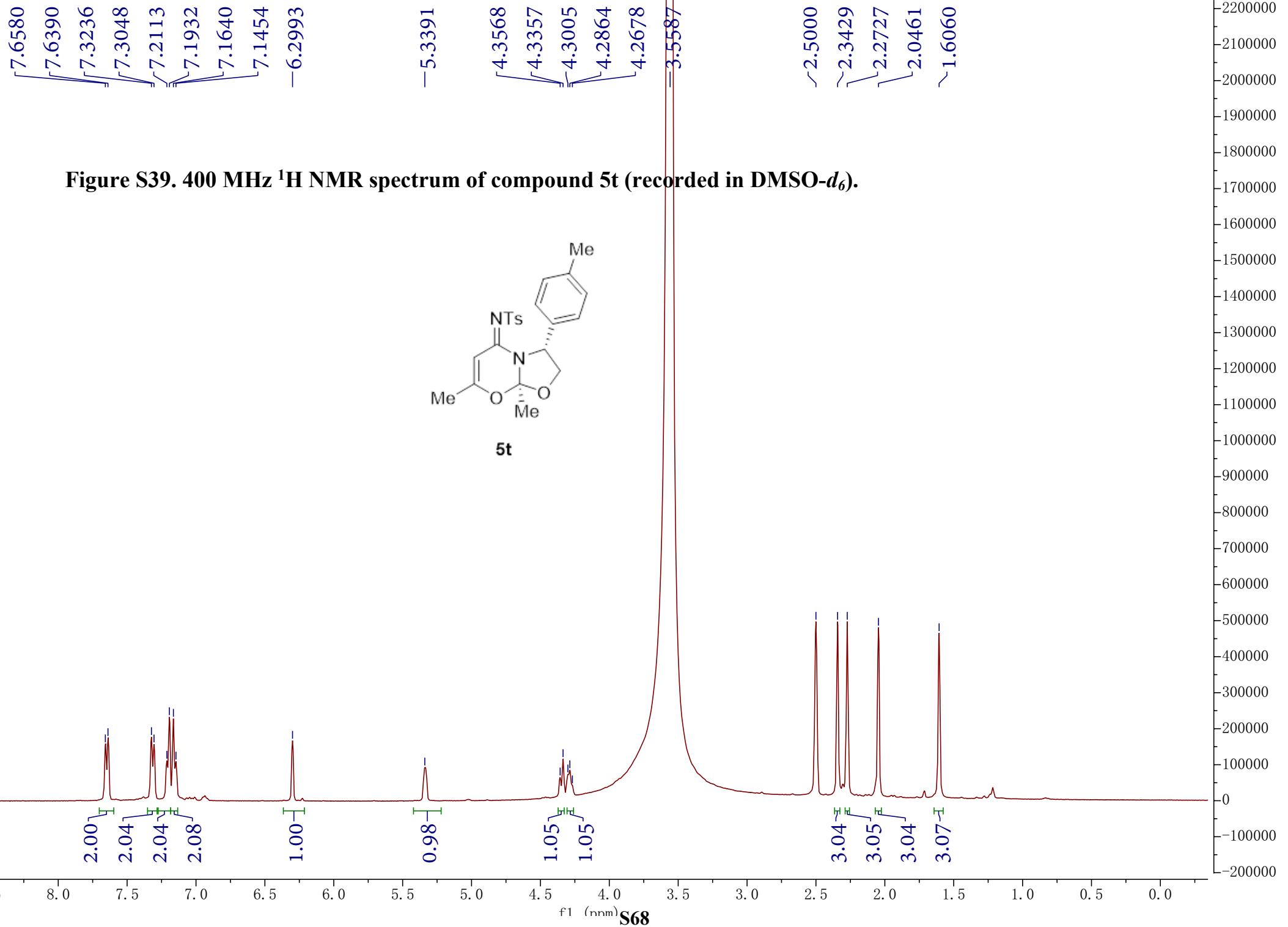


Figure S37. 400 MHz ^1H NMR spectrum of compound 5s (recorded in CDCl_3).





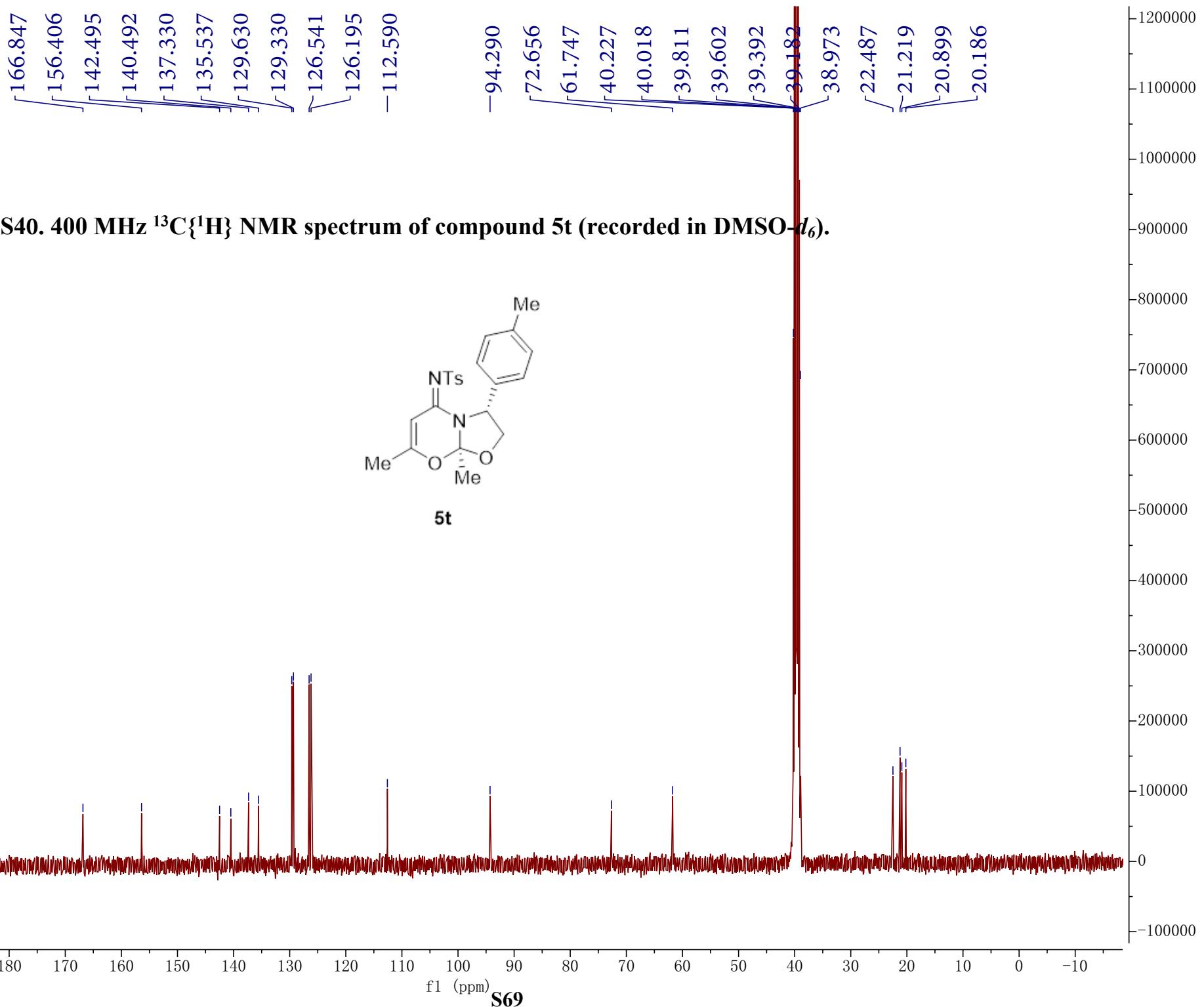
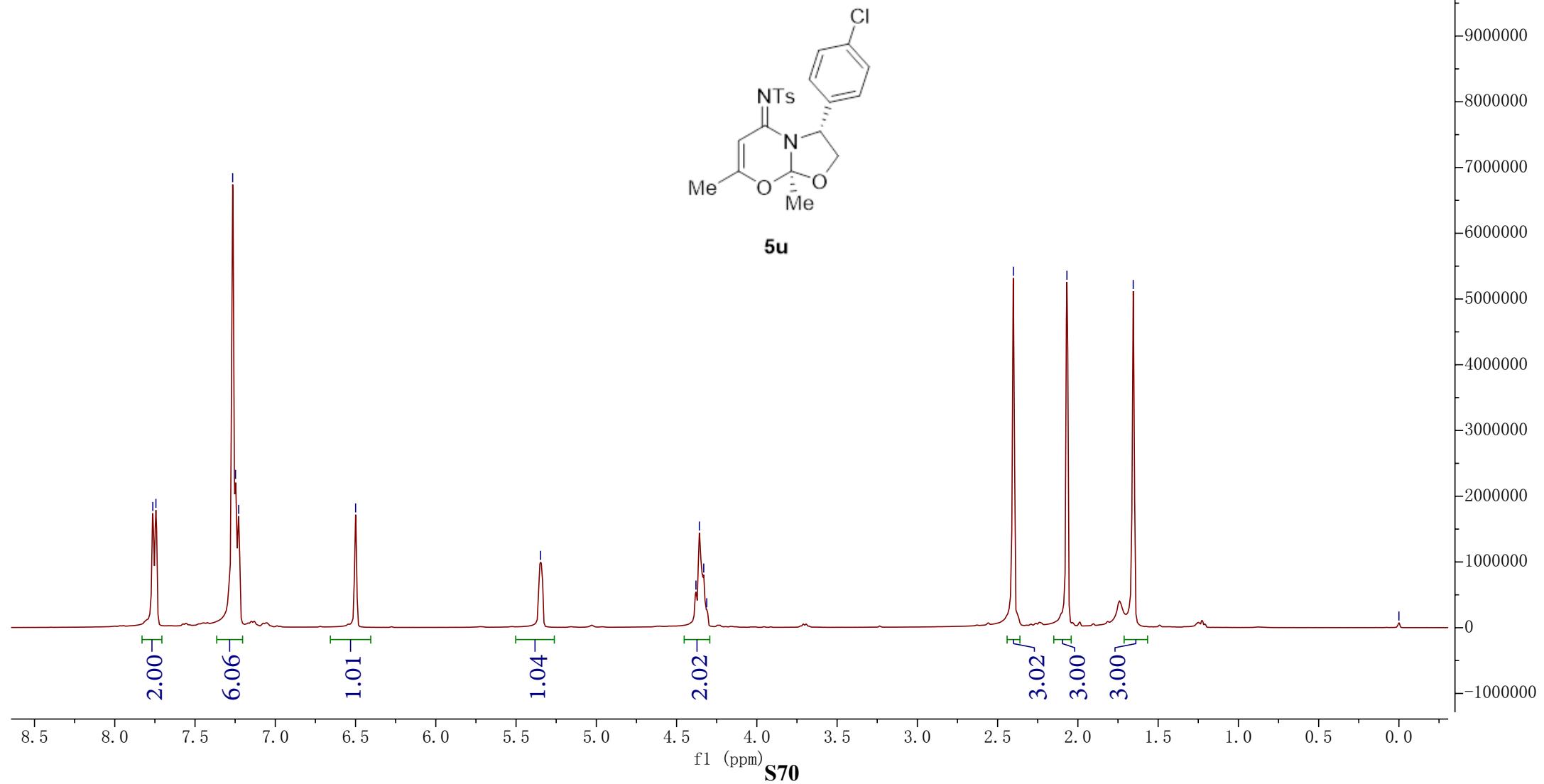
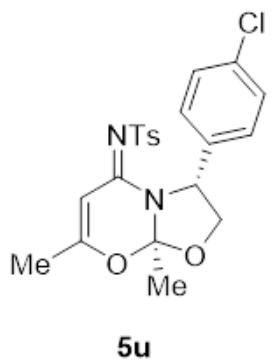
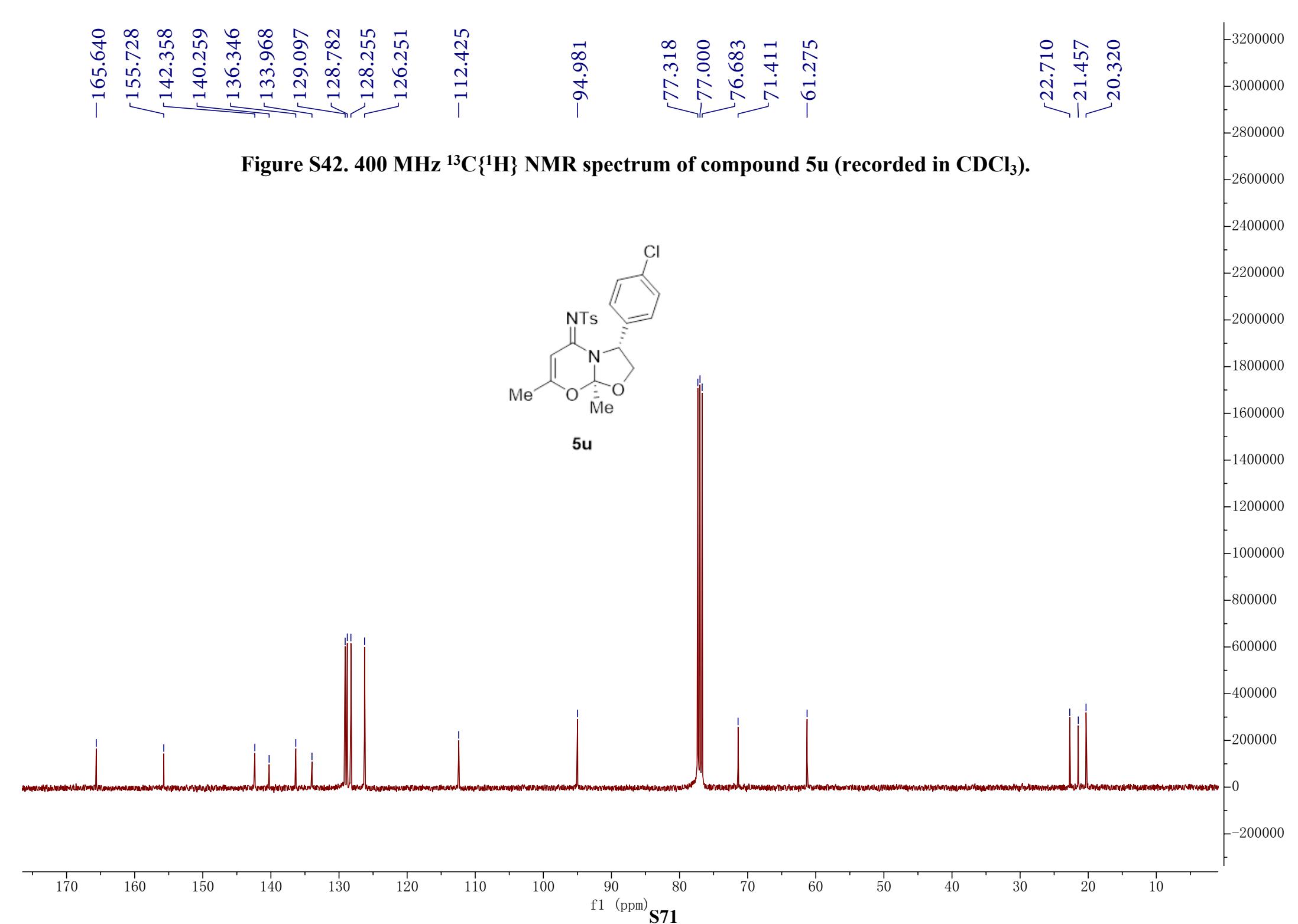
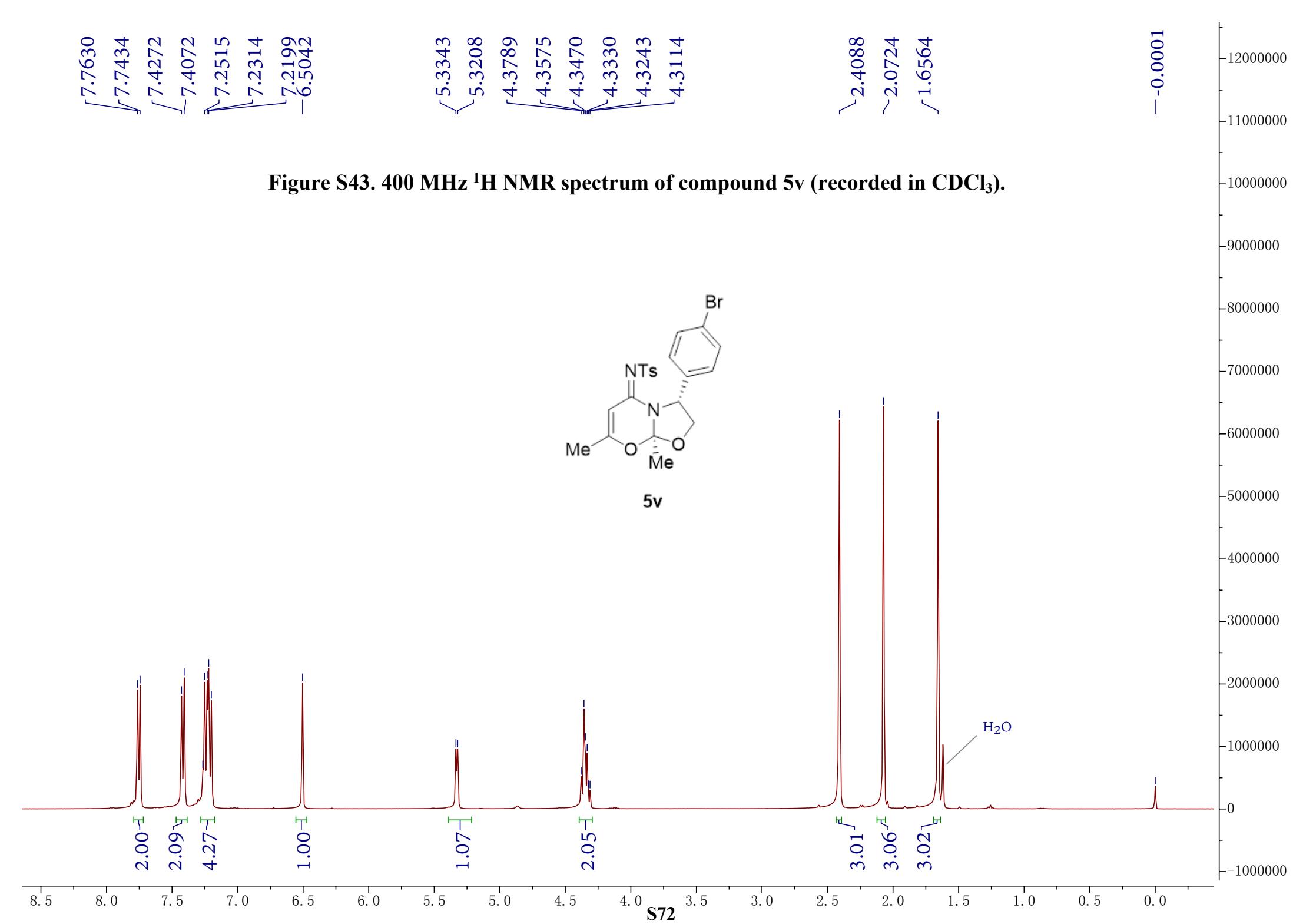


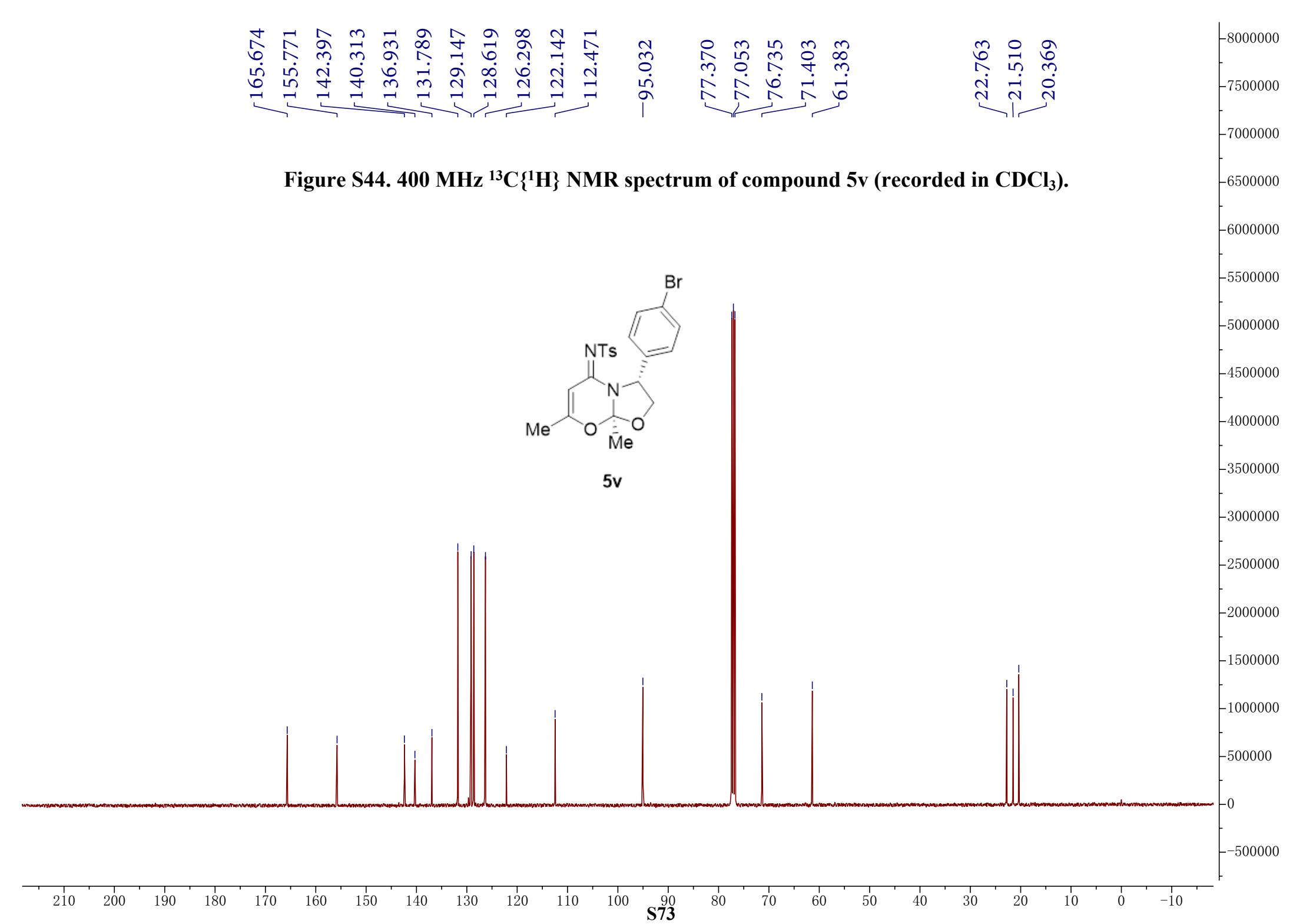


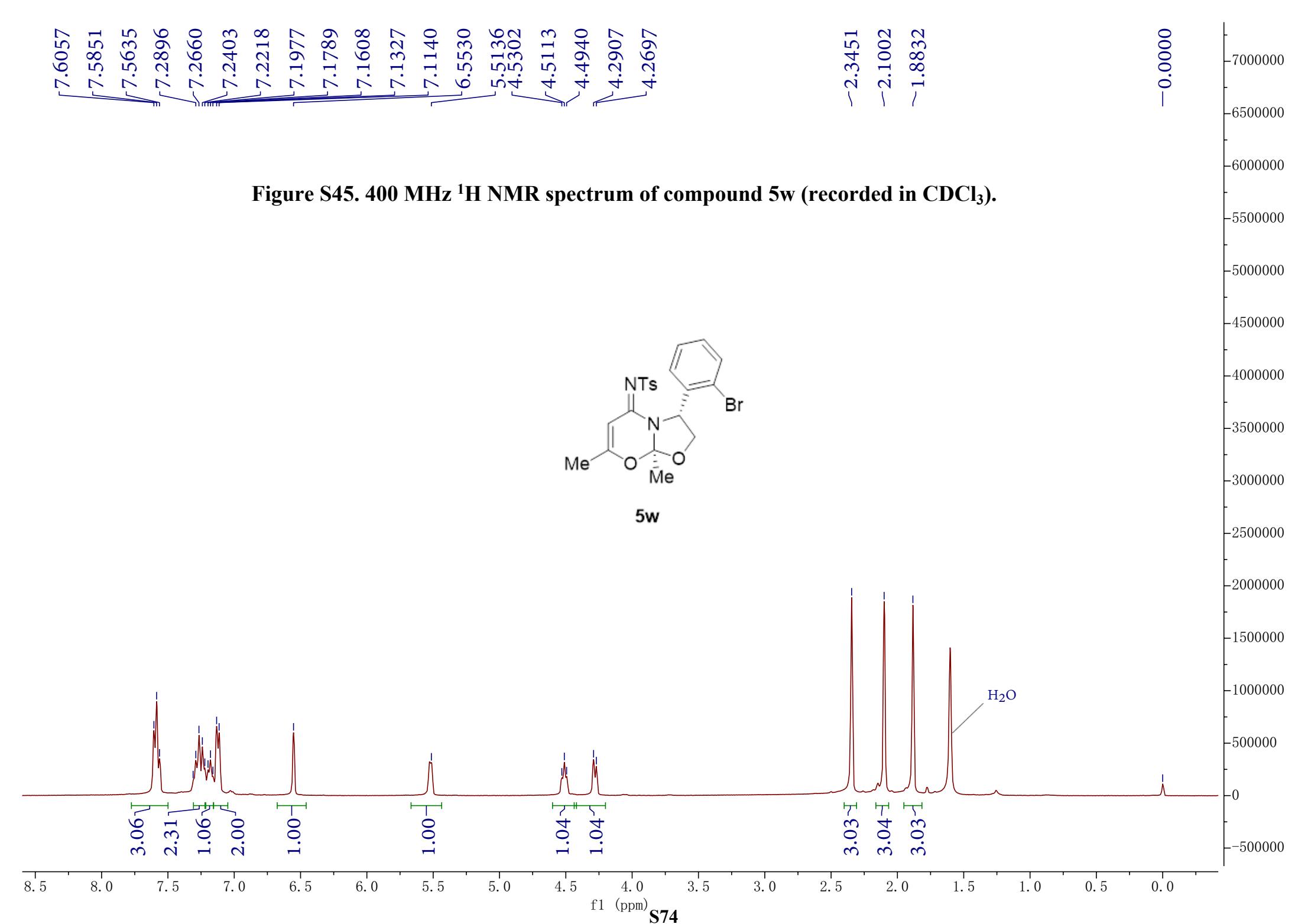
Figure S41. 400 MHz ^1H NMR spectrum of compound **5u** (recorded in CDCl_3).

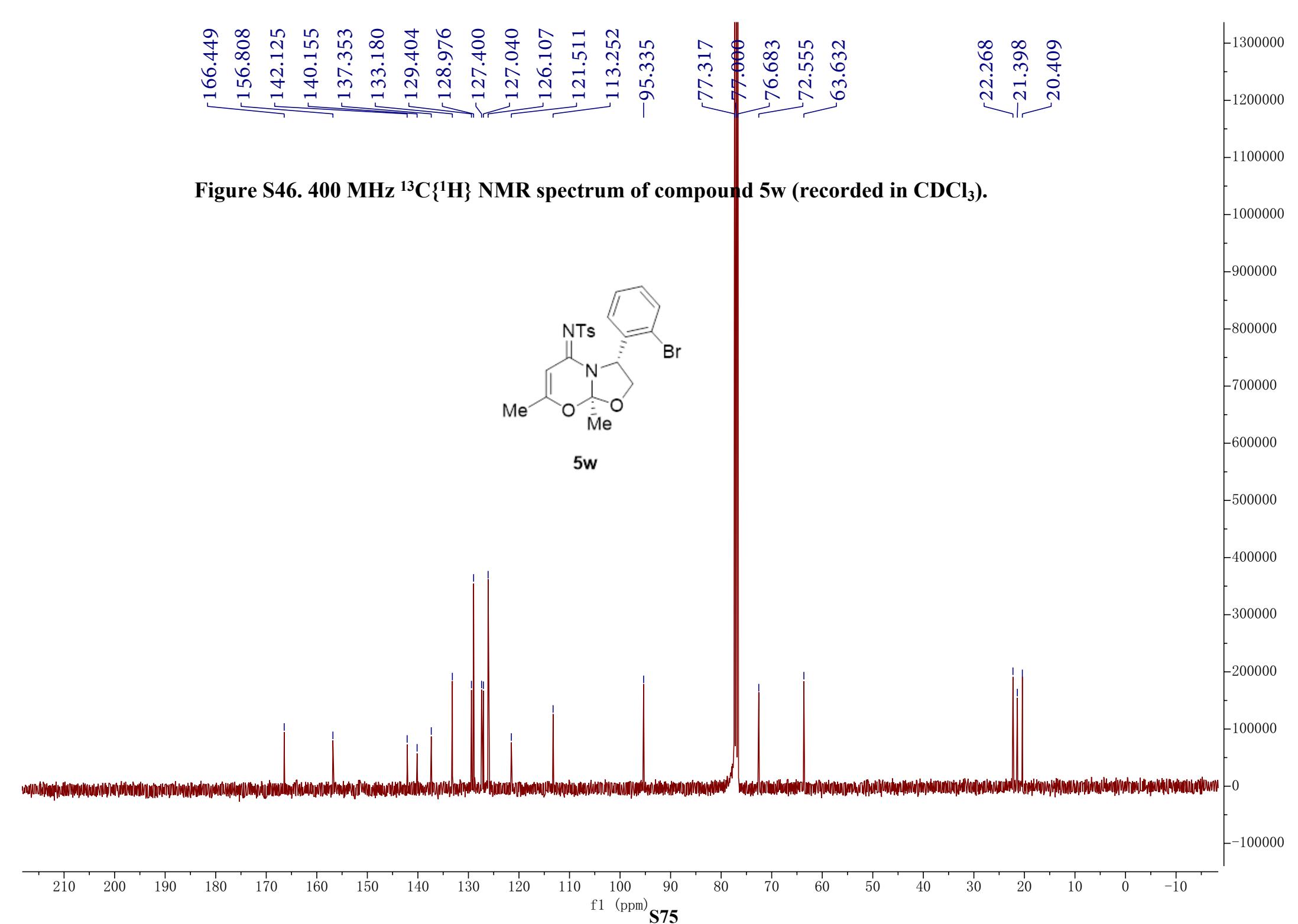


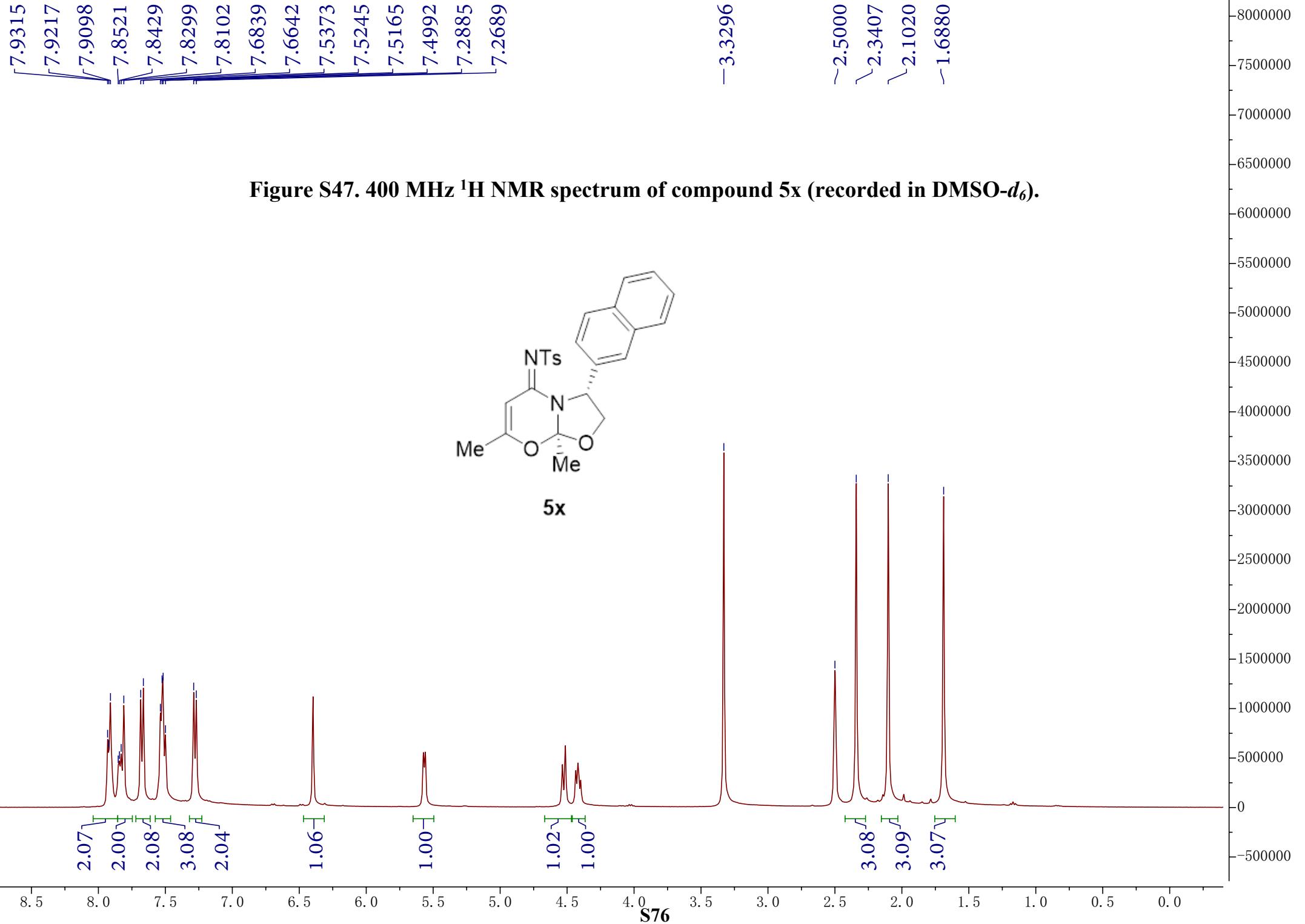


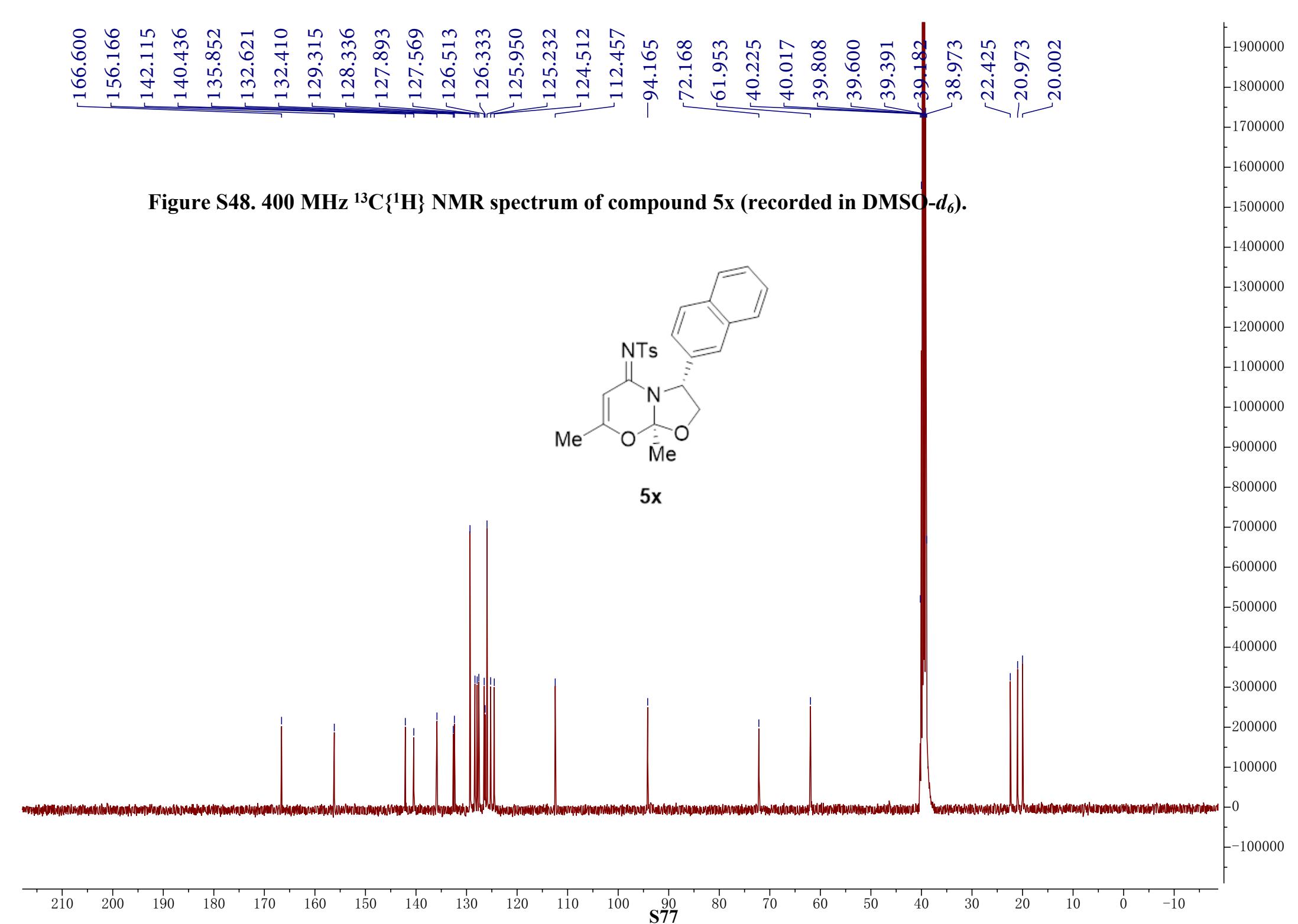








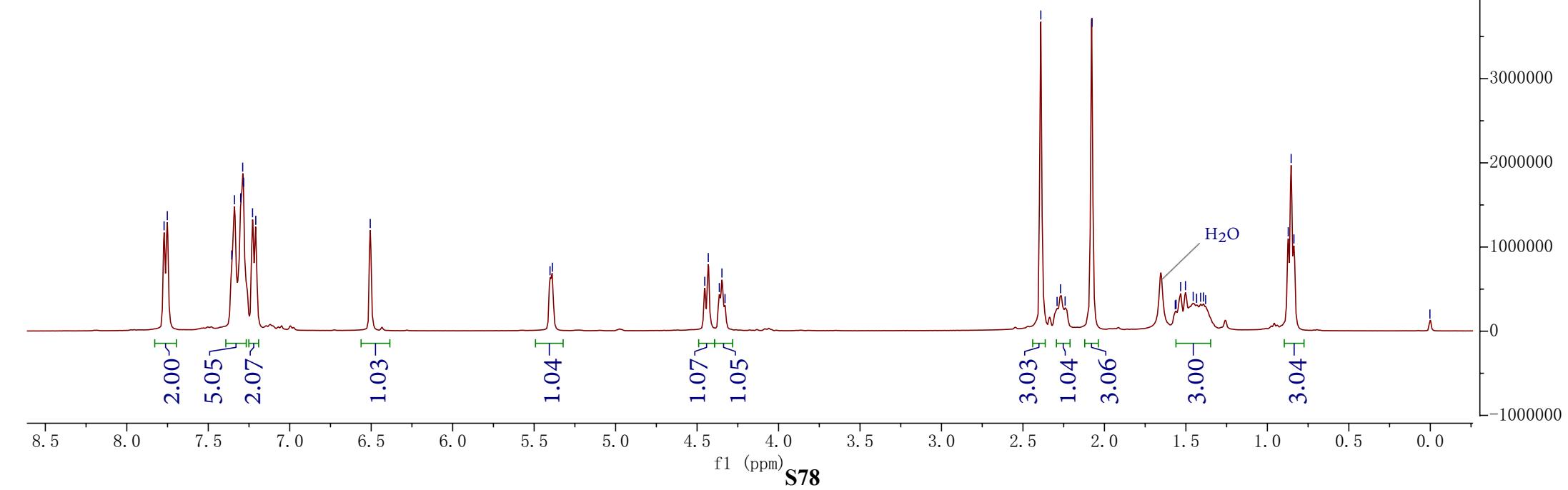
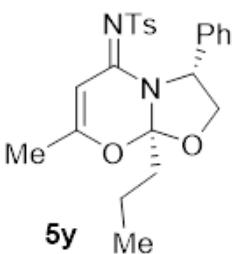


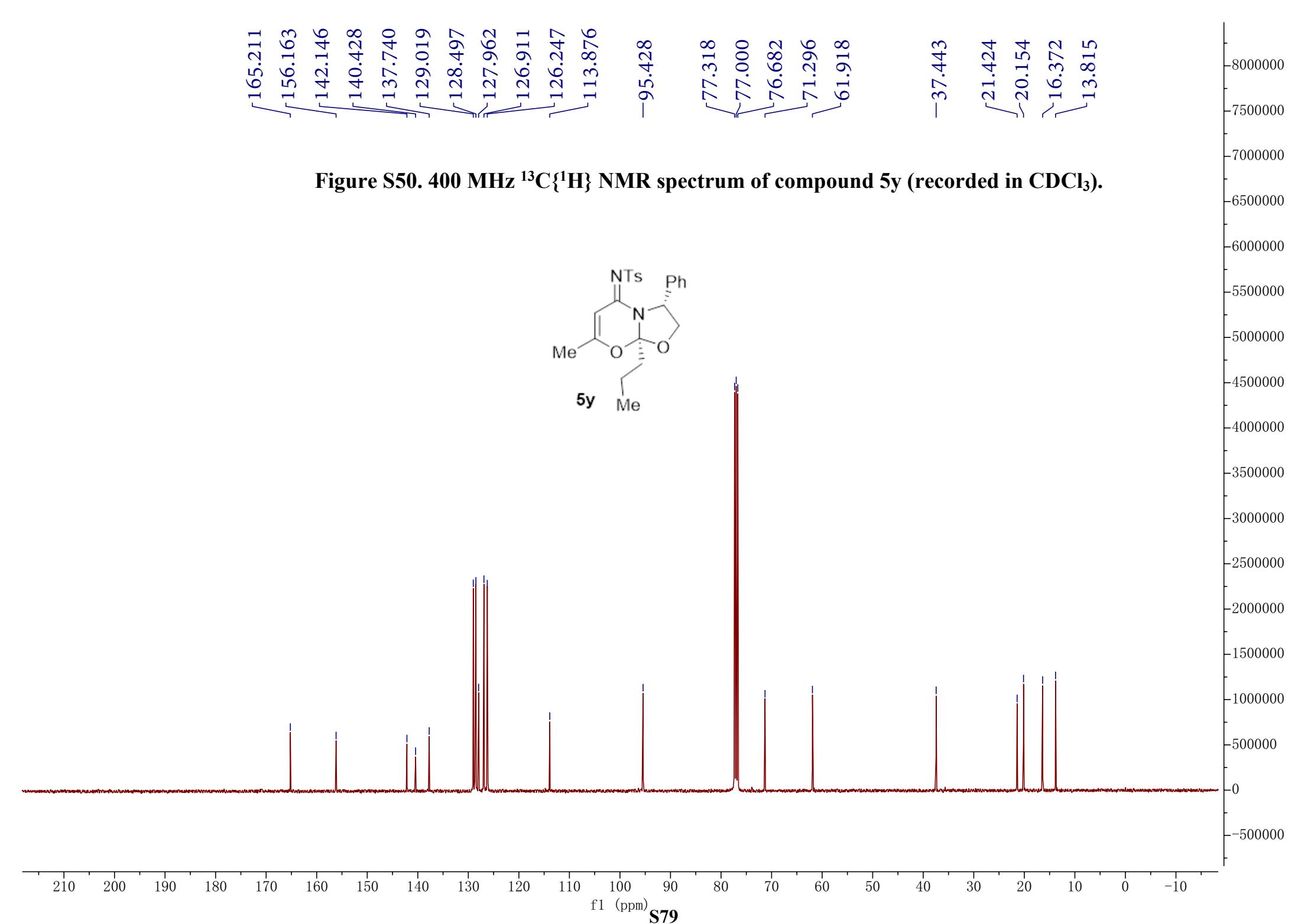


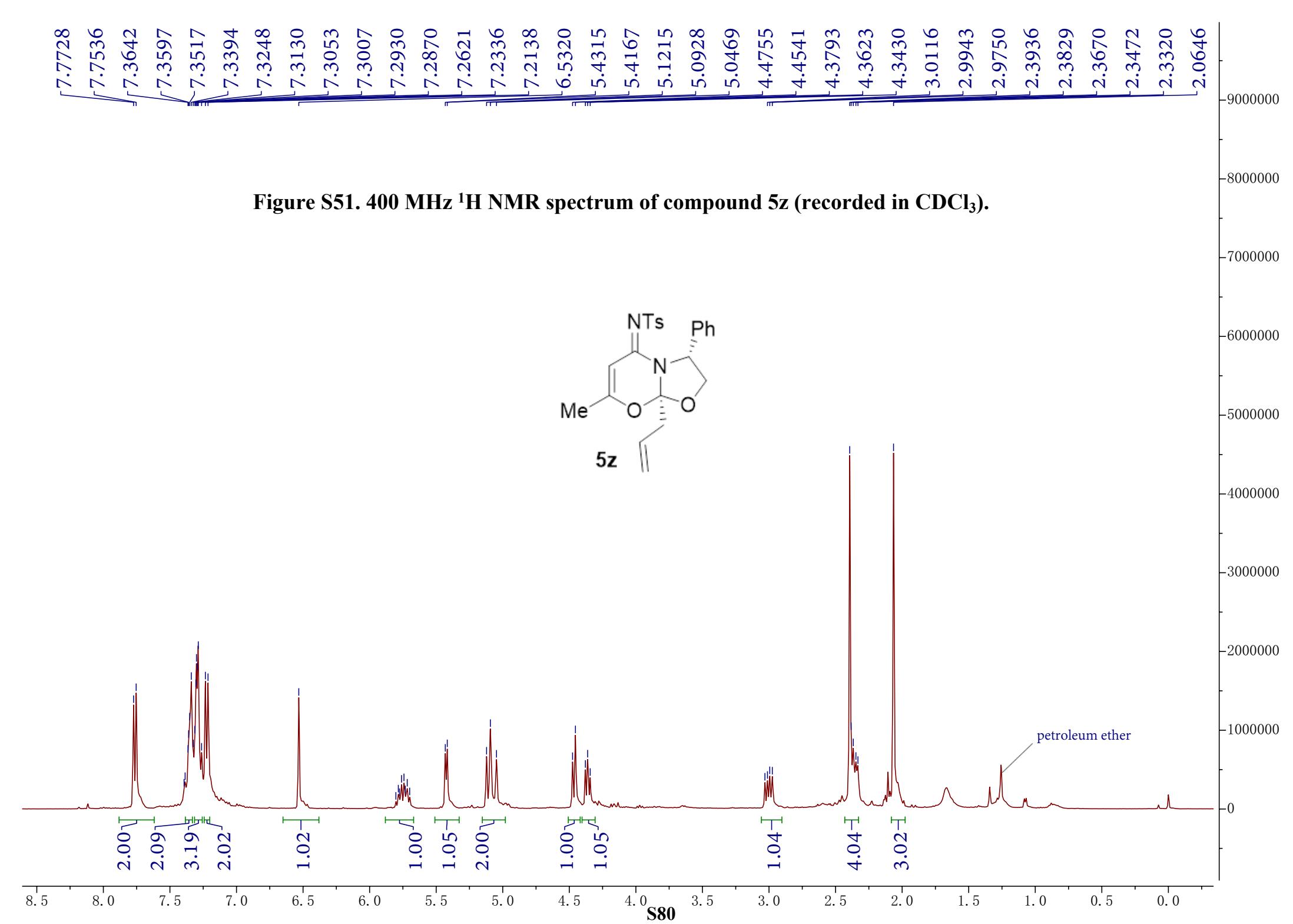
7.7514
7.3391
7.3012
7.2887
7.2832
7.2282
7.2084
6.5059

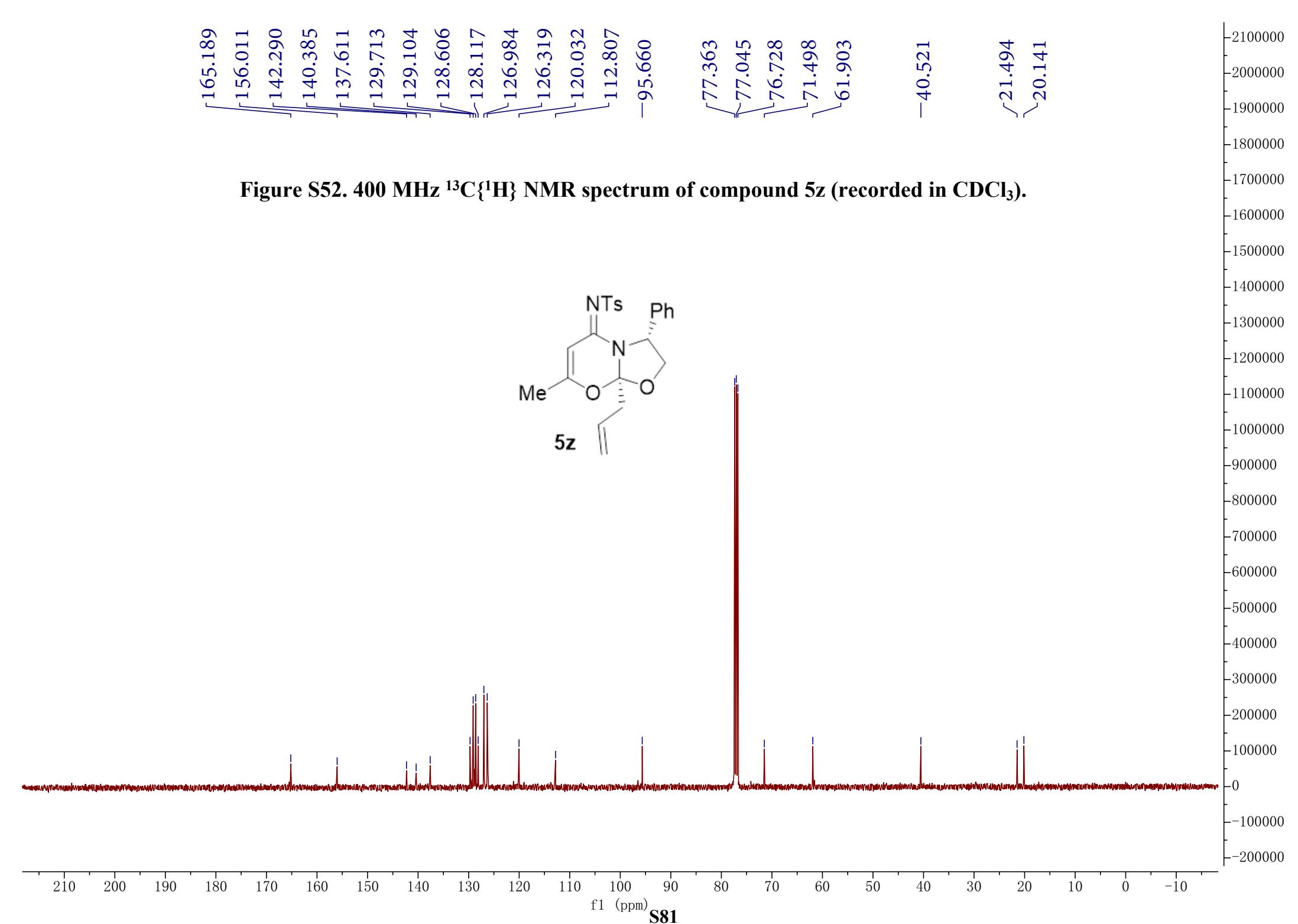
5.4026
5.3881
4.4530
4.4313
4.3634
4.3475
4.3285
2.3904
2.2907
2.2692
2.2413
2.0762
1.5653
1.5604
1.5323
1.5028
1.4552
1.4343
1.4095
1.3915
1.3789
0.8720
0.8540
0.8370
0.0024

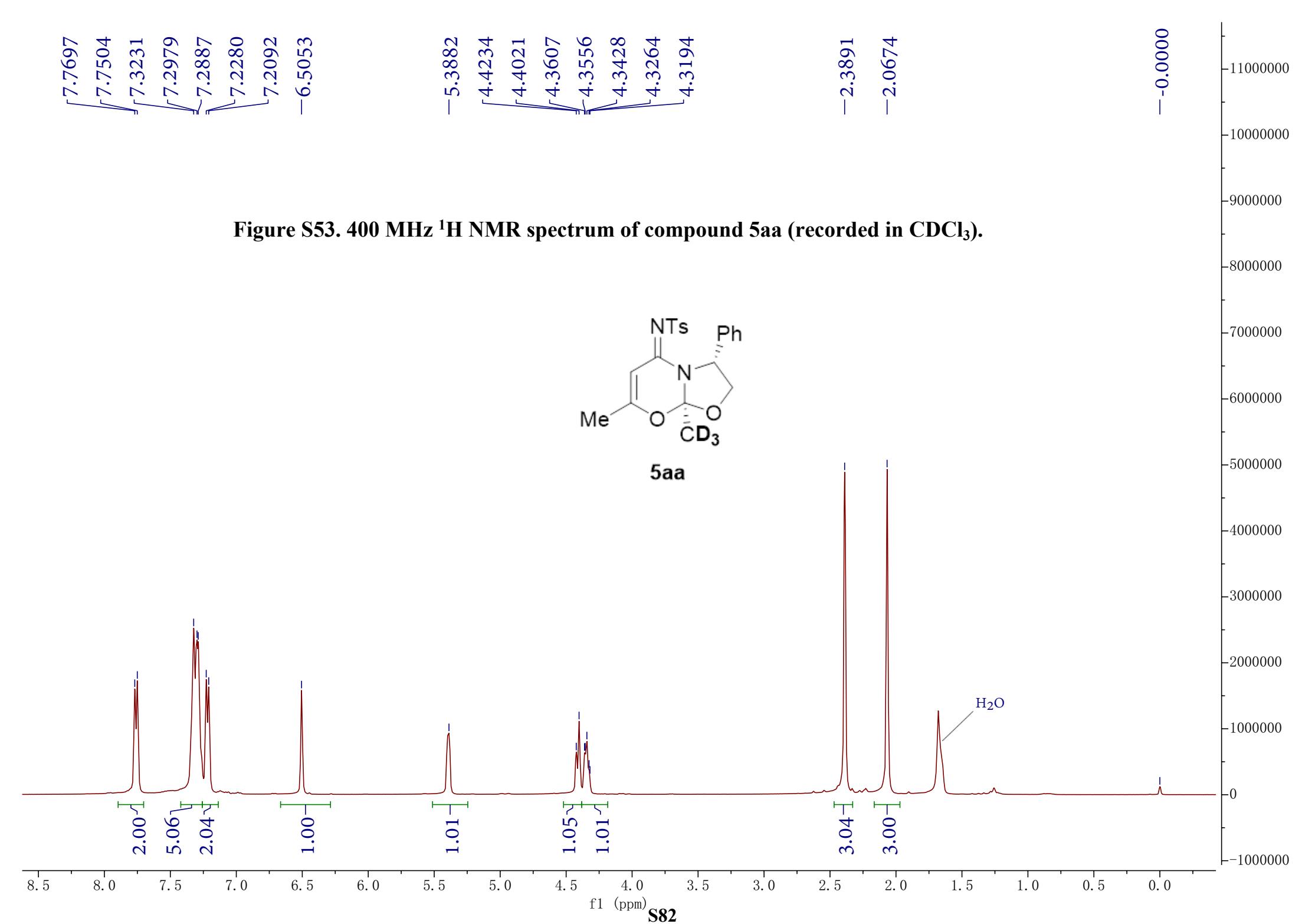
Figure S49. 400 MHz ^1H NMR spectrum of compound **5y** (recorded in CDCl_3).

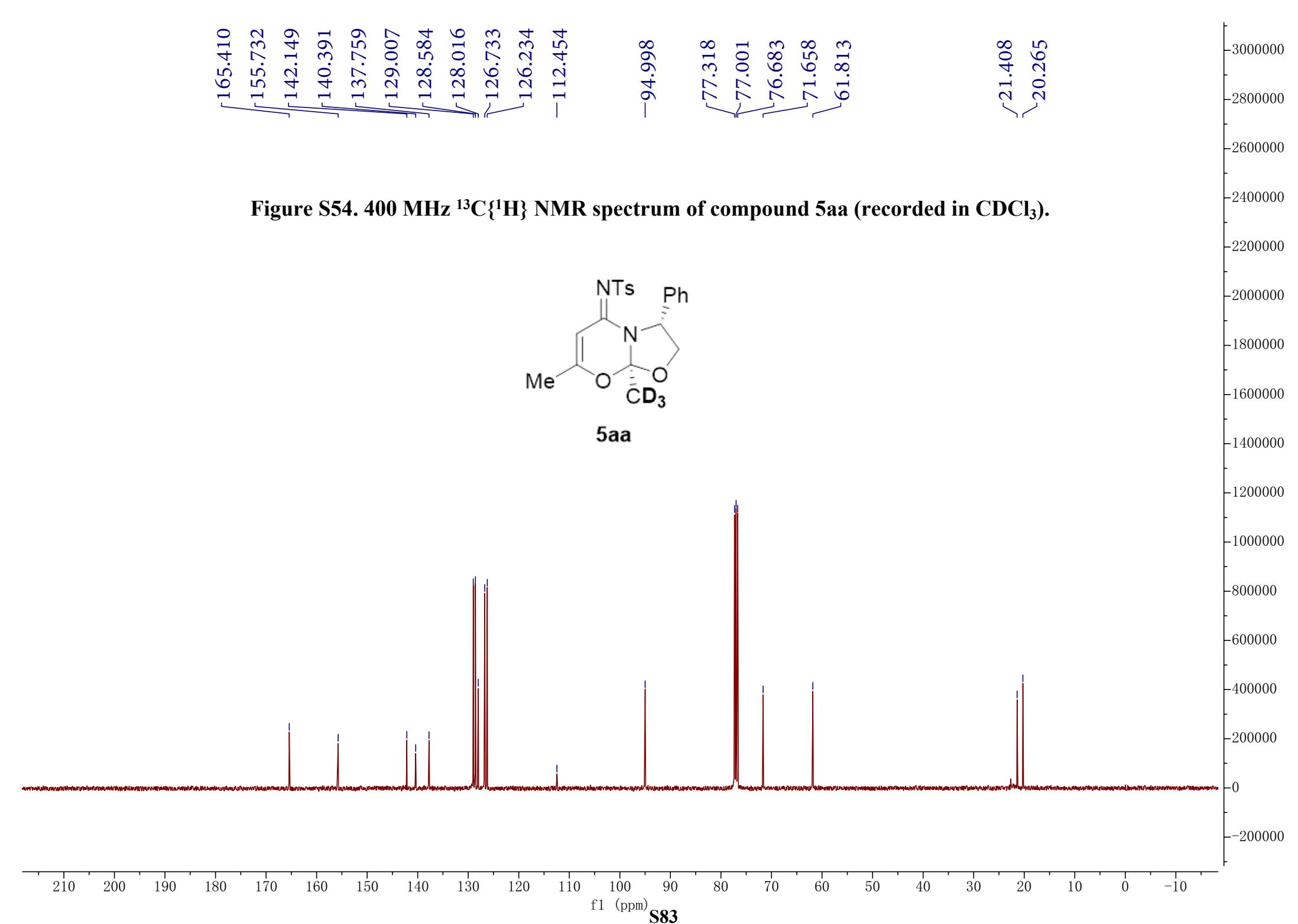


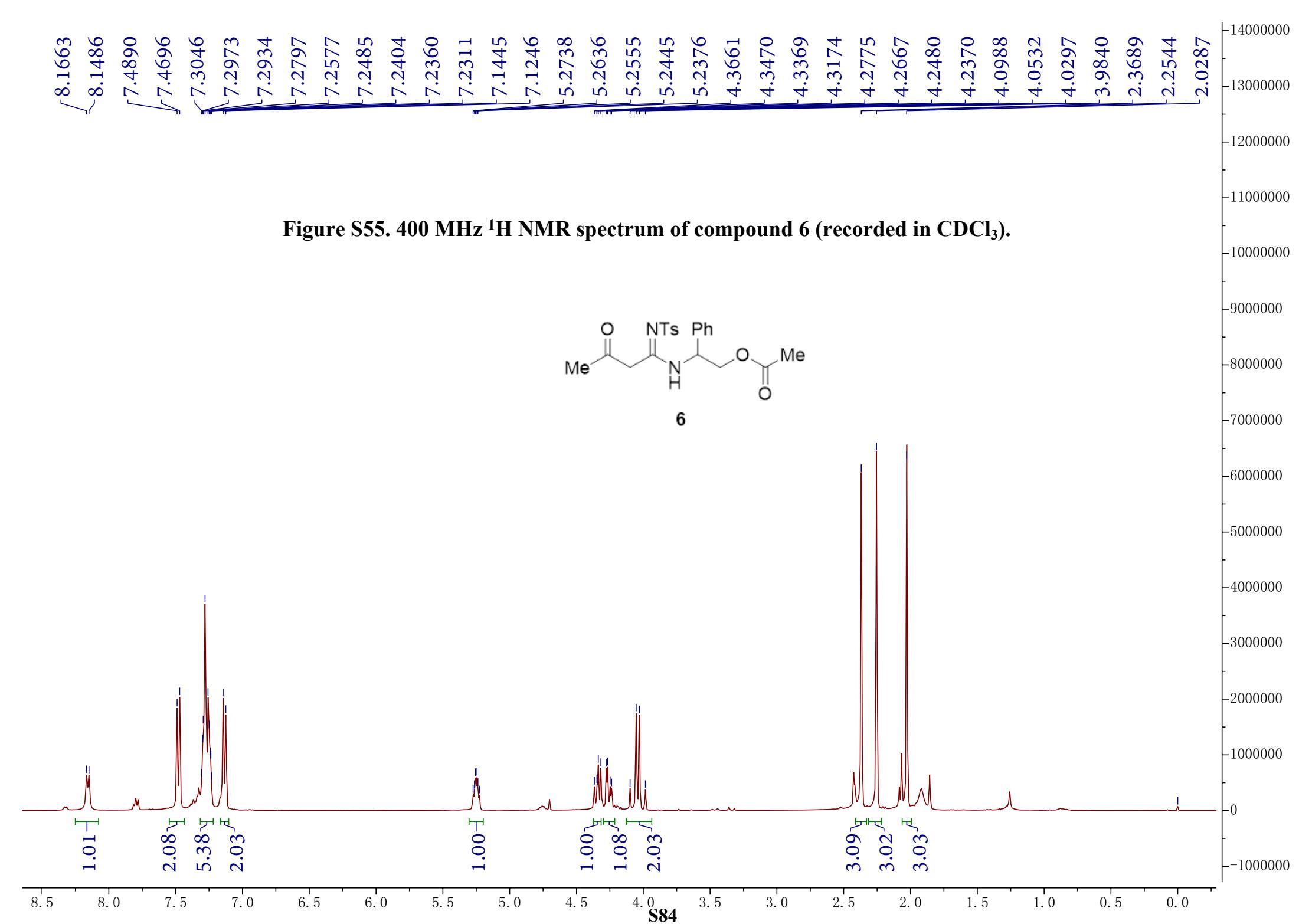












-203.072

-171.300

-160.743

142.234

140.056

137.086

129.056

128.749

128.083

126.918

126.009

77.423

77.106

76.787

65.604

55.272

~45.319

~30.883

21.462

20.769

Figure S56. 400 MHz $^{13}\text{C}\{\text{H}\}$ NMR spectrum of compound **6** (recorded in CDCl_3).

