

Supporting Information For

**Silver-Catalyzed Tandem C≡C bond Hydroazidation/Radical
Addition/Cyclization of Biphenyl Acetylene: One-pot Synthesis of 6-Methyl
Sulfonylated Phenanthridines**

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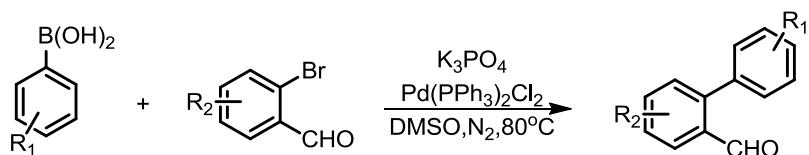
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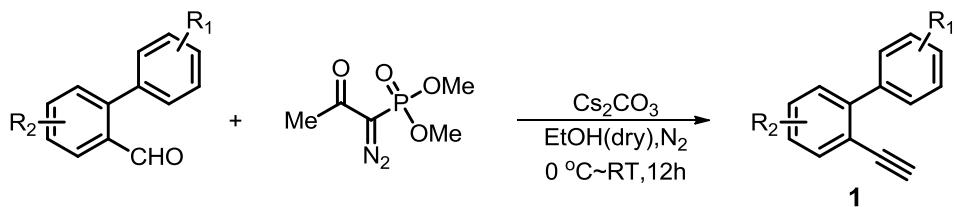
1. General Information

All the reagents were purchased from commercial sources and used without purification unless otherwise indicated. The products were purified by column chromatography over silica gel (300-400 size). NMR spectra were measured on a Varian I NOVA 500 or Bruker AV-600 spectrometer and reported in parts per million. The ¹H NMR (600 MHz) chemical shifts were measured relative to TMS, DMSO or CDCl₃ as the internal reference. The ¹³C NMR (125 MHz or 150 MHz) chemical shifts were given using CDCl₃ and DMSO as the internal standard. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Agilent 1200HPLC/MicrOTOF II) equipped with ESI ionization source. Melting points were determined with XRC-1 and are uncorrected.

2. Preparation of the Substrates^[1,2]

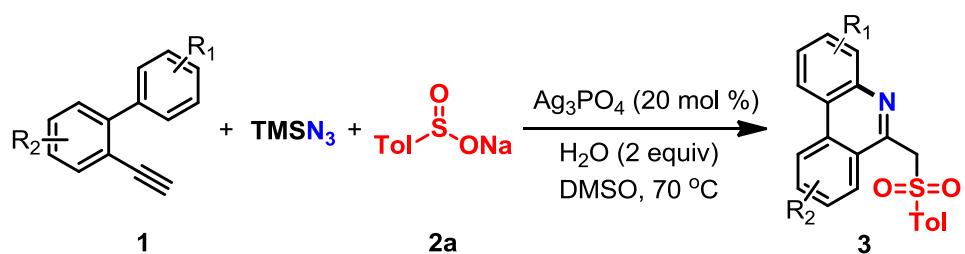


Typical synthetic procedure (with [1,1'-biphenyl]-2-carbaldehyde as an example): To a stirred solution of phenyboronic (731.6 mg, 6.0 mmol), potassium phosphate (2.1 g, 10.0 mmol) and bis(triphenylphosphine)palladium(II) chloride (175.5 mg, 0.25 mmol) in DMSO was added 2-bromobenzaldehyde (925 mg, 5.0 mmol) under nitrogen at 80 °C for 10 h. After completion, the resulting mixture was concentrated and extract with dichloromethane (3 x 15 mL), washed with brine (3 x 40 mL). The combined organic layer was dried over MgSO₄ and evaporated. Finally, the crude product was further purified by flash column chromatography (silica gel) using petroleum ether/ethyl acetate as an eluent.



Typical synthetic procedure (with **1a as an example):** To a stirred solution of aldehyde (182.2 mg, 1.0 mmol) and BOR (Bestman-Ohira Reagent) (384 mg, 2.0 mmol) in dry EtOH (10 mL) was added Cs₂CO₃ (977 mg, 3.0 mmol) at 0 °C and the resulting mixture was stirred until complete consumption of aldehyde (monitored by TLC). After complete conversion of aldehyde, solvent was evaporated under reduced pressure and the mixture was extracted with 10 mL of ethyl acetate thrice and washed with 5 mL brine. Then the combined organic phase was collected by passing through anhydrous Na₂SO₄. Organic portion was evaporated and directly used for purification using silica gel (300-400 mesh) column chromatography with petroleum ether and ethyl acetate as the eluent.

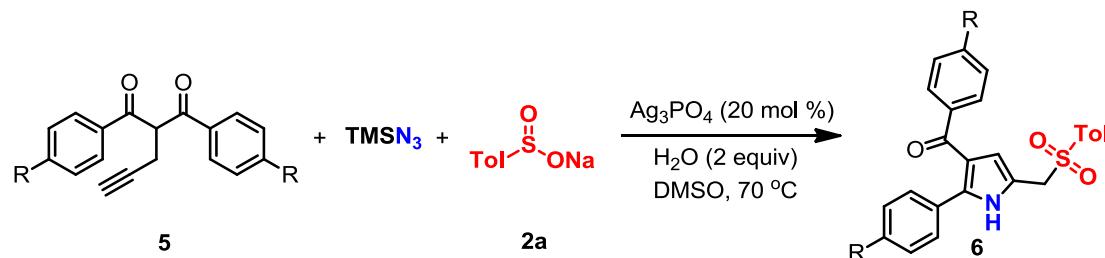
3. General Experimental Procedure for the Synthesis of Products



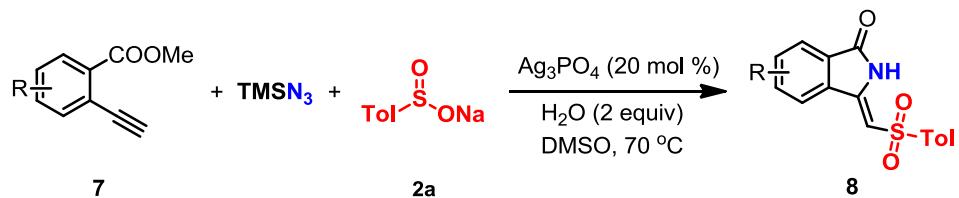
Typical synthetic procedure (with **3a as an example):** To a stirred suspension of 2-ethynyl-1,1'-biphenyl (**1a**) (89 mg, 0.5 mmol), TMSN₃ (99 μL, 0.75 mmol) and H₂O (18 μL) in DMSO (2 mL) at 70 °C, TsNa (134mg, 0.75 mmol), Ag₃PO₄(41.8 mg, 0.10 mmol) was added. Then the mixture was stirred at 70 °C for 6.0 h until the complete conversion of substrate **1a**. After completion, the resulting mixture was concentrated and extract with dichloromethane (3 x 15 mL), washed with brine (3 x 40 mL). The combined organic layer was dried over MgSO₄ and concentrated. Finally, the crude product was further purified by flash column chromatography (silica gel) using petroleum ether/ethyl acetate (3:1) as an eluent to gave pure product **3a** as a light yellow solid in 63% yield.

Typical synthetic procedure (with **3b as an example):** To a stirred suspension of 2-ethynyl-4'-methyl-1,1'-biphenyl (**1b**) (192 mg, 1 mmol), TMSN₃ (198 μL, 1.5 mmol) and H₂O (36 μL) in DMSO (5 mL) at 70 °C, TsNa (268 mg, 1.5 mmol), Ag₃PO₄(83.6 mg, 0.20 mmol) was added. Then the mixture was stirred at 70 °C for

6.0 h until the complete conversion of substrate **1b**. After completion, the resulting mixture was concentrated and extract with dichloromethane (3 x 20 mL), washed with brine (3 x 40 mL). The combined organic layer was dried over MgSO₄ and concentrated. Finally, the crude product was further purified by flash column chromatography (silica gel) using petroleum ether/ethyl acetate (3:1) as an eluent to gave pure product **3b** as a yellow solid in 52% yield (0.52 mmol, 188.3 mg).



Typical synthetic procedure (with **6a as an example):** To a solution of 1,3-diphenyl-2-(prop-2-yn-1-yl)propane-1,3-dione (**5a**) (131 mg, 0.5 mmol), TMSN₃ (99 µL, 0.75 mmol) and H₂O (18 µL) in DMSO (2 mL) at 70 °C, TsNa (134mg, 0.75 mmol), Ag₃PO₄ (41.8 mg, 0.10 mmol) was added. The mixture was then stirred for 6.0 h until substrate **5a** disappeared. The resulting mixture was concentrated and taken up by dichloromethane (3 x 15 mL). The organic layer was washed with brine (3 x 40 mL), dried over MgSO₄ and concentrated. Purification of the crude product with flash column chromatography (silica gel; petroleum ether: ethyl acetate = 4:1) gave **6a** in 57% yield as a yellow solid.



Typical synthetic procedure (with **8a as an example):** To a solution of methyl 2-ethynylbenzoate (**7a**) (80 mg, 0.5 mmol), TMSN₃ (99 µL, 0.75 mmol) and H₂O (18 µL) in DMSO (2 mL) at 70 °C, TsNa (134mg, 0.75 mmol), Ag₃PO₄ (41.8 mg, 0.10 mmol) was added. The mixture was then stirred for 6.0 h until substrate **7a** disappeared. The resulting mixture was concentrated and taken up by dichloromethane (3 x 15 mL). The organic layer was washed with brine (3 x 40 mL), dried over MgSO₄ and concentrated. Purification of the crude product with flash

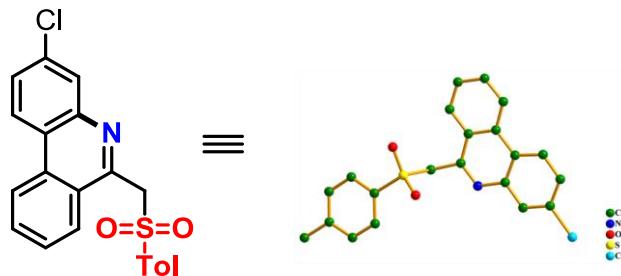
column chromatography (silica gel; petroleum ether: ethyl acetate = 3:1) gave **8a** in 72% yield as a white solid.

4. Reference

- [1] Kumar, R.; Verma, D.; Mobin, S. M.; Namboothiri, I. N. N. *Org. Lett.* **2012**, *14*, 4070- 4073.
- [2] Dutta, U.; Lupton, D. W.; Maiti, D. *Org. Lett.* **2016**, *18*, 860-863.

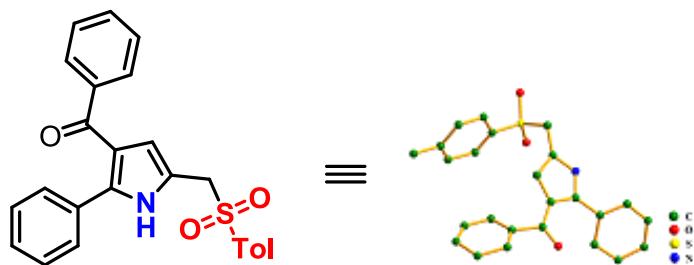
5. X-Ray Crystallographic Information

Table S1. Crystallography data and structure refinement for **3e** (CCDC 1545378)



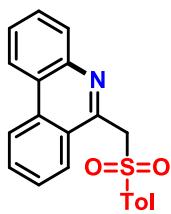
Empirical formula	C ₂₁ H ₁₆ ClN O ₂ S
Temperature	298(2)K
Wavelength	0.71073 Å
Unit cell dimensions	a = 22.262(3) Å alpha = 90 deg. b = 5.2166(7) Å beta = 100.464(2) deg. c = 15.694(2) Å gamma = 90 deg.
Volume	1792.2(4) Å ³
Z	4
Calculated density	1.415 Mg/m ³
Absorption coefficient	0.345 mm ⁻¹
F(000)	792
Crystal size	0.1 x 0.1x 0.1 m
Theta range for data collection	1.860 to 26.419 deg.
Reflections collected / unique	9687 / 3667 [R(int) = 0.0399]
Data / restraints / parameters	3667 / 0 / 235
Goodness-of-fit on F ²	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1282
R indices (all data)	R1 = 0.0735, wR2 = 0.1393

Table S2. Crystallography data and structure refinement for **6a** (CCDC 1547932)

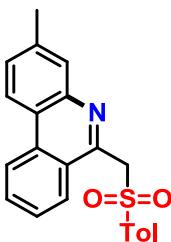


Empirical formula	C ₂₅ H ₂₁ N O ₃ S
Temperature	298(2)K
Wavelength	0.71073 Å
Unit cell dimensions	a = 14.339(3) Å alpha = 90 deg. b = 15.396(3) Å beta = 90 deg. c = 18.846(3) Å gamma = 90 deg.
Volume	4160.4(14) Å ³
Z	1
Calculated density	1.618 Mg/m ³
Absorption coefficient	0.774 mm ⁻¹
F(000)	2052
Crystal size	0.1 x 0.1x 0.1 m
Theta range for data collection	1.323 to 26.436 deg.
Reflections collected / unique	24164 / 19853 [R(int) = 0.0765]
Data / restraints / parameters	19853 / 3 / 962
Goodness-of-fit on F ²	1.017
Final R indices [I>2sigma(I)]	R1 = 0.1415, wR2 = 0.3187
R indices (all data)	R1 = 0.2529, wR2 = 0.4030

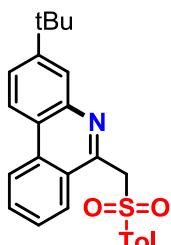
6. Spectral Data of All the Synthesized Products



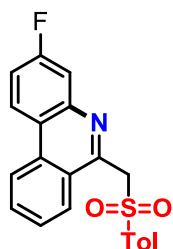
(3a) Light yellow solid (109.7 mg, 0.32 mmol, 63% yield), m.p: 195-196 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.56-8.52 (m, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.87-7.83 (m, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.69-7.64 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.15 (s, 2H), 2.37 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 149.8, 144.7, 143.2, 135.5, 133.1, 130.9, 129.8, 129.4, 128.7, 127.63, 127.61, 127.0, 125.6, 124.0, 122.3, 122.0, 62.6, 21.5; **HRMS** (ESI) m/z calcd. for C₂₁H₁₈NO₂S [M+H]⁺ 348.1053, found 348.1062.



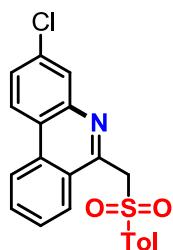
(3b) Yellow solid (108.6 mg, 0.30 mmol, 60% yield), m.p: 198-199 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.57 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 2H), 2.54 (s, 3H), 2.38 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 149.7, 144.6, 143.5, 138.8, 135.6, 133.2, 130.8, 129.44, 129.39, 128.6, 127.1, 126.9, 125.3, 122.1, 121.71, 121.67, 62.7, 21.5, 21.4; **HRMS** (ESI) m/z calcd. for C₂₂H₂₀NO₂S [M+H]⁺ 362.1209, found 362.1218.



(3c) Light yellow solid (125.3 mg, 0.31 mmol, 62% yield), m.p: 185-186 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.60 (d, *J* = 7.8 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.85-7.82 (m, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.76-7.74 (m, 1H), 7.69-7.66 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 5.13 (s, 2H), 2.38 (s, 3H), 1.43 (s, 9H); **¹³C NMR** (150 MHz, CDCl₃) δ 152.1, 149.5, 144.6, 143.3, 135.5, 133.1, 130.8, 129.4, 128.7, 127.2, 126.9, 125.9, 125.7, 125.4, 122.1, 121.6, 62.6, 34.9, 31.3, 21.5; **HRMS** (ESI) m/z calcd. for C₂₅H₂₆NO₂S [M+H]⁺ 404.1679, found 404.1687.



(3d) White solid (135.5 mg, 0.37 mmol, 74% yield), m.p: 191-192 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.49 (dd, *J* = 6.0 Hz, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.87-7.84 (m, 1H), 7.72-7.70 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 3.0 Hz, *J* = 9.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 2H), 2.39 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 162.5 (d, *J* = 247.5 Hz), 151.2, 144.8, 144.4 (d, *J* = 12.0 Hz), 135.5, 132.9, 131.3, 129.5, 128.6, 127.5, 127.2, 125.2, 124.0 (d, *J* = 9.0 Hz), 122.1, 120.7 (d, *J* = 1.5 Hz), 116.7 (d, *J* = 24.0 Hz), 114.2 (d, *J* = 19.5 Hz), 62.6, 21.6; **HRMS** (ESI) m/z calcd. for C₂₁H₁₇FNO₂S [M+H]⁺ 366.0959, found 366.0958.



(3e) Light yellow solid (101.2 mg, 0.27 mmol, 53% yield), m.p: 208-209 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.76 (t, *J* = 7.8 Hz,

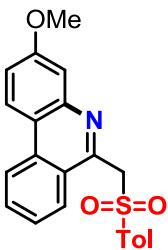
1H), 7.63-7.61 (m, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 5.13 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 151.2, 144.9, 143.9, 135.4, 134.4, 132.8, 131.4, 129.5, 129.1, 128.7, 128.2, 128.0, 127.3, 125.6, 123.4, 122.5, 122.2, 62.7, 21.6; **HRMS** (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{17}\text{ClNO}_2\text{S}$ [M+H]⁺ 382.0669, found 382.0663.



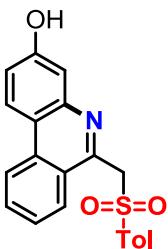
(3f) Yellow solid (114.2 mg, 0.26 mmol, 51% yield), m.p: 192-193 °C; **^1H NMR** (600 MHz, CDCl_3) δ 8.59 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 9.0 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.99 (s, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.79-7.74 (m, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.13 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 151.2, 144.9, 135.4, 132.8, 132.3, 131.4, 130.9, 129.6, 128.7, 128.1, 127.3, 125.6, 123.5, 122.9, 122.4, 122.2, 62.8, 21.7; **HRMS** (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{16}\text{BrNNaO}_2\text{S}$ [M+Na]⁺ 447.9983, found 447.9987.



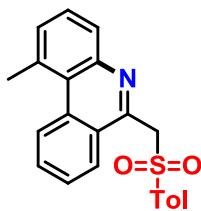
(3g) Yellow solid (143.6 mg, 0.35 mmol, 69% yield), m.p: 193-194 °C; **^1H NMR** (600 MHz, CDCl_3) δ 8.64 (t, J = 8.4 Hz, 2H), 8.41 (d, J = 8.4 Hz, 1H), 8.08 (s, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.85-7.81 (m, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.15 (s, 2H), 2.39 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 151.6, 145.0, 142.5, 135.3, 132.4, 131.5, 130.5 (q, J = 33.0 Hz), 129.6, 128.9, 128.6, 127.4 (q, J = 4.5 Hz), 127.3, 126.22, 126.18, 123.9 (q, J = 271.5 Hz), 123.4 (q, J = 3.0 Hz), 123.1, 122.7, 62.7, 21.5; **HRMS** (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{17}\text{F}_3\text{NO}_2\text{S}$ [M+H]⁺ 416.0927, found 416.0933.



(3h) Yellow solid (86.0 mg, 0.22 mmol, 43% yield), m.p: 196-197 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.83-7.79 (m, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.32-7.28 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.12 (s, 2H), 3.93 (s, 3H), 2.39 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 160.1, 150.1, 144.6, 135.6, 133.4, 131.0, 129.5, 128.7, 127.0, 126.6, 124.7, 123.2, 121.8, 118.9, 118.2, 114.6, 109.5, 62.7, 55.6, 21.6; **HRMS** (ESI) m/z calcd. for C₂₂H₁₉NNaO₃S [M+Na]⁺ 400.0978, found 400.0979.

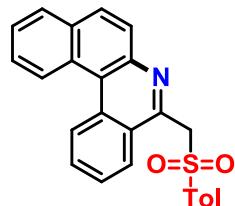


(3i) Light yellow solid (108.1 mg, 0.28 mmol, 56% yield), m.p: 225-226 °C; **¹H NMR** (600 MHz, DMSO) δ 10.12 (s, 1H), 8.69 (d, *J* = 7.8 Hz, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.67-7.60 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.13 (s, 1H), 5.38 (s, 2H), 2.40 (s, 3H); **¹³C NMR** (125 MHz, DMSO) δ 158.6, 150.9, 145.1, 144.8, 136.8, 133.4, 131.5, 130.0, 128.7, 128.2, 126.5, 124.6, 124.5, 122.2, 118.9, 116.9, 112.5, 61.6, 21.6; **HRMS** (ESI) m/z calcd. for C₂₁H₁₇NNaO₃S [M+Na]⁺ 386.0827, found 386.0828.

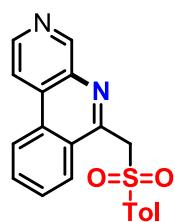


(3j) Light yellow solid (103.2 mg, 0.29 mmol, 57% yield), m.p: 205-206 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.87 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H),

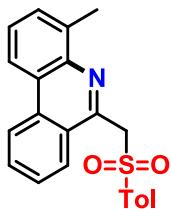
7.86-7.83 (m, 1H), 7.74-7.72 (m, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.57-7.53 (m, 3H), 7.49 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 5.14 (s, 2H), 3.09 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 149.4, 144.7, 144.6, 135.5, 134.9, 134.4, 131.8, 130.0, 129.4, 128.8, 128.7, 127.7, 127.0, 126.8, 126.7, 126.4, 123.7, 62.6, 26.7, 21.5; **HRMS** (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_2\text{S} [\text{M}+\text{H}]^+$ 362.1209, found 362.1215.



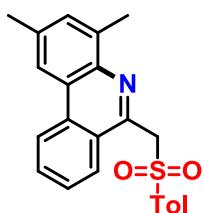
(3k) Yellow solid (125.4 mg, 0.32 mmol, 63% yield), m.p: 254-255 °C; **^1H NMR** (600 MHz, CDCl_3) δ 9.11 (d, J = 8.4 Hz, 1H), 9.05 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.91 (t, J = 7.8 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.75-7.71 (m, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 5.24 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 148.8, 144.7, 143.0, 135.5, 133.5, 133.3, 130.5, 129.6, 129.4, 129.3, 128.73, 128.69, 127.9, 127.8, 127.1, 127.0, 126.8, 126.74, 126.72, 126.68, 120.9, 62.6, 21.6; **HRMS** (ESI) m/z calcd. for $\text{C}_{25}\text{H}_{20}\text{NO}_2\text{S} [\text{M}+\text{H}]^+$ 398.1209, found 398.1202.



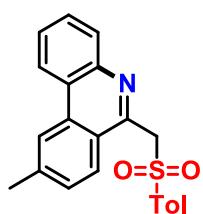
(3l) Yellow solid (129.9 mg, 0.35 mmol, 70% yield), m.p: 198-199 °C; **^1H NMR** (600 MHz, CDCl_3) δ 9.15 (s, 1H), 8.77 (d, J = 6.0 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 5.4 Hz, 1H), 7.99-7.97 (m, 1H), 7.93-7.90 (m, 1H), 7.56 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.18 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ 153.2, 151.9, 146.1, 145.1, 138.3, 135.2, 131.7, 131.3, 130.0, 129.6, 128.9, 128.7, 127.5, 127.2, 122.9, 115.1, 62.6, 21.6; **HRMS** (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{NaO}_2\text{S} [\text{M}+\text{Na}]^+$ 371.0830, found 371.0835.



(3m) Light yellow solid (110.4 mg, 0.31 mmol, 61% yield), m.p: 225-226 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.64 (d, *J* = 7.8 Hz, 1H), 8.41-8.38 (m, 2H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.51-7.46 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 2H), 2.36 (s, 3H), 2.31 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 148.2, 144.4, 141.8, 137.9, 135.4, 133.5, 130.7, 129.2, 128.8, 127.5, 127.2, 126.9, 125.3, 123.8, 122.5, 119.7, 62.6, 21.5, 17.4; **HRMS** (ESI) m/z calcd. for C₂₂H₂₀NO₂S [M+H]⁺ 362.1209, found 362.1213.

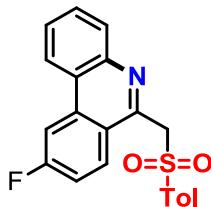


(3n) Yellow solid (122.2 mg, 0.33 mmol, 65% yield), m.p: 201-202 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.17 (s, 1H), 7.85-7.82 (m, 1H), 7.75-7.72 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.32 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 2.56 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 147.1, 144.4, 140.2, 137.6, 137.1, 135.4, 133.2, 131.1, 130.4, 129.2, 128.9, 127.4, 126.8, 125.5, 123.7, 122.5, 119.3, 62.5, 22.0, 21.5, 17.3; **HRMS** (ESI) m/z calcd. for C₂₃H₂₂NO₂S [M+H]⁺ 376.1366, found 376.1374.

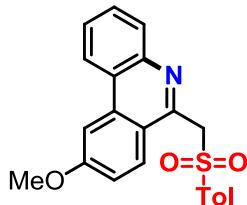


(3o) White solid (108.6 mg, 0.30 mmol, 60% yield), m.p: 188-189 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.54-8.51 (m, 1H), 8.41 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.80-7.78 (m, 1H), 7.66-7.62 (m, 2H), 7.57-7.52 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 2H), 2.64 (s, 3H), 2.37 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 149.6, 144.6, 143.5, 141.5,

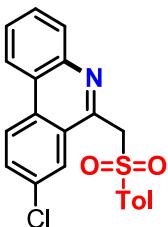
135.5, 133.3, 129.8, 129.4, 128.7, 128.5, 127.3, 126.9, 123.9, 123.8, 121.94, 121.89, 62.7, 22.3, 21.5; **HRMS** (ESI) m/z calcd. for $C_{22}H_{20}NO_2S$ [M+H]⁺ 362.1209, found 362.1211.



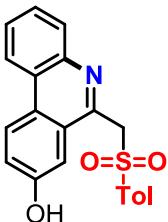
(3p) White solid (89.3 mg, 0.23 mmol, 46% yield), m.p: 184-185 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.44-8.40 (m, 2H), 8.25-8.22 (m, 1H), 7.84-7.82 (m, 1H), 7.72-7.67 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.50-7.46 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.12 (s, 2H), 2.40 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.9 (d, *J* = 252.0 Hz), 149.3, 144.8, 143.6, 135.7 (d, *J* = 10.5 Hz), 135.4, 130.2 (d, *J* = 9.0 Hz), 130.0, 129.5, 129.4, 128.7, 127.7, 123.6 (d, *J* = 4.5 Hz), 122.7, 122.2, 116.9 (d, *J* = 24.0 Hz), 107.5 (d, *J* = 22.5 Hz), 62.9, 21.6; **HRMS** (ESI) m/z calcd. for $C_{21}H_{16}FNNaO_2S$ [M+Na]⁺ 388.0778, found 388.0771.



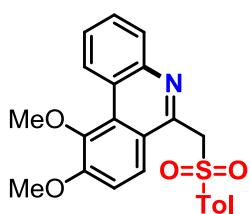
(3q) White solid (116.0 mg, 0.29 mmol, 58% yield), m.p: 175-176 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.45 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.91 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 2H), 4.03 (s, 3H), 2.37 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 161.5, 149.2, 144.6, 143.7, 135.5, 135.4, 129.8, 129.4, 129.0, 128.8, 128.7, 127.1, 123.8, 122.0, 120.6, 117.7, 103.0, 62.8, 55.6, 21.5; **HRMS** (ESI) m/z calcd. for $C_{22}H_{19}NNaO_3S$ [M+Na]⁺ 400.0978, found 400.0979.



(3r) Yellow solid (105.1 mg, 0.28 mmol, 55% yield), m.p: 212-213 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.52 (d, *J* = 8.4 Hz, 1H), 8.47-8.46 (m, 1H), 8.15 (d, *J* = 1.2 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.77-7.76 (m, 1H), 7.71-7.67 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 2H), 2.39 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 148.7, 145.0, 135.4, 133.7, 131.61, 131.56, 129.9, 129.6, 129.2, 128.7, 128.2, 126.3, 126.2, 124.0, 123.4, 121.9, 62.4, 21.6; **HRMS** (ESI) m/z calcd. for C₂₁H₁₇ClNO₂S [M+H]⁺ 382.0669, found 382.0665.

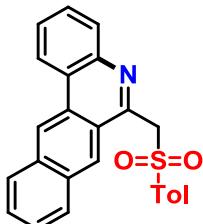


(3s) Yellow solid (125.6 mg, 0.35 mmol, 69% yield), m.p: 247-248 °C; **¹H NMR** (600 MHz, DMSO) δ 10.25 (s, 1H), 8.70 (d, *J* = 9.0 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 7.77-7.75 (m, 1H), 7.68-7.67 (m, 2H), 7.65-7.63 (m, 3H), 7.47 (dd, *J* = 2.5 Hz, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 5.28 (s, 2H), 2.39 (s, 3H); **¹³C NMR** (150MHz, DMSO) δ 157.4, 149.7, 144.8, 142.1, 136.8, 130.0, 129.7, 128.6, 128.1, 127.9, 127.6, 126.0, 124.8, 124.4, 122.4, 122.3, 111.0, 61.9, 21.6; **HRMS** (ESI) m/z calcd. for C₂₁H₁₈NO₃S [M+H]⁺ 364.1007, found 364.1005.

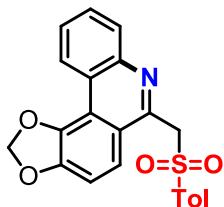


(3t) Yellow solid (146.9 mg, 0.36 mmol, 72% yield), m.p: 193-194 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.36-8.35 (m, 1H), 7.82 (s, 1H), 7.77-7.76 (m, 1H), 7.62 (s, 1H), 7.60-7.57 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.07 (s, 2H), 4.11 (s, 3H), 4.08 (s, 3H), 2.34 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 152.6, 149.6, S15

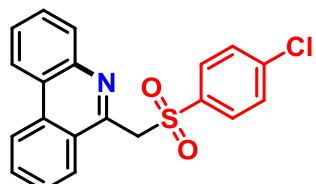
148.0, 144.6, 142.9, 135.4, 129.8, 129.3, 129.0, 128.5, 127.7, 127.0, 123.6, 121.4, 120.9, 106.7, 101.8, 63.3, 56.1, 56.0, 21.5; **HRMS** (ESI) m/z calcd. for C₂₃H₂₂NO₄S [M+H]⁺ 408.1264, found 408.1270.



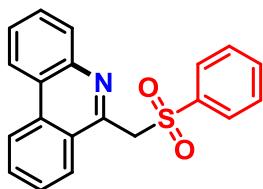
(3u) White solid (135.4 mg, 0.34 mmol, 68% yield), m.p: 187-188 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.09-9.05 (m, 1H), 8.98-8.95 (m, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.07-8.04 (m, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.92-7.89 (m, 1H), 7.76-7.72 (m, 2H), 7.72-7.68 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 2H), 2.35 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 148.8, 145.2, 144.6, 135.4, 134.7, 132.6, 129.7, 129.4, 128.8, 128.70, 128.65, 128.6, 128.5, 128.3, 128.1, 127.2, 127.1, 126.9, 124.5, 124.2, 122.9, 62.9, 21.5; **HRMS** (ESI) m/z calcd. for C₂₅H₂₀NO₂S [M+H]⁺ 398.1209, found 398.1205.



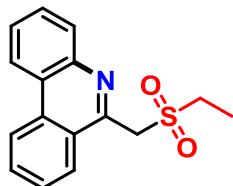
(3v) Yellow solid (123.5 mg, 0.32 mmol, 63% yield), m.p: 217-218 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.36-8.34 (m, 1H), 7.94 (s, 1H), 7.77-7.75 (m, 1H), 7.69 (s, 1H), 7.62-7.60 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.19 (s, 2H), 5.05 (s, 2H), 2.39 (s, 3H); **¹³C NMR** (125 MHz, DMSO) δ 151.7, 149.2, 148.5, 144.8, 143.1, 136.7, 131.1, 130.0, 129.6, 128.7, 127.7, 124.3, 123.3, 122.7, 105.3, 102.9, 100.8, 62.0, 21.6; **HRMS** (ESI) m/z calcd. for C₂₂H₁₈NO₄S [M+H]⁺ 392.0957, found 392.0958.



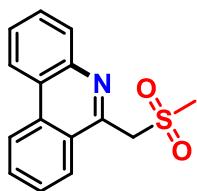
(3w) White solid (117.0 mg, 0.30 mmol, 60% yield), m.p: 182-183 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.58-8.56 (m, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.92-7.89 (m, 1H), 7.80-7.76 (m, 2H), 7.70-7.69 (m, 2H), 7.59-7.57 (m, 2H), 7.37-7.35 (m, 2H), 5.17 (s, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ 149.4, 143.2, 140.5, 136.7, 133.2, 131.1, 130.3, 129.8, 129.1, 128.9, 127.9, 127.8, 126.9, 125.5, 124.0, 122.4, 122.0, 62.4; **HRMS** (ESI) m/z calcd. for C₂₀H₁₄ClNNaO₂S [M+Na]⁺ 390.0326, found 390.0331.



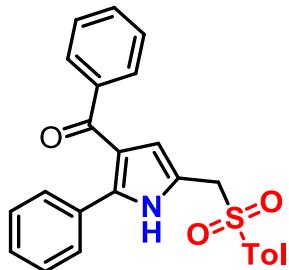
(3x) White solid (103.6 mg, 0.31 mmol, 62% yield), m.p: 188-189 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.53 (t, *J* = 5.4 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.79-7.78 (m, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.68-7.64 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 5.17 (s, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ 149.6, 143.2, 138.3, 133.6, 133.1, 130.9, 129.9, 128.8, 128.70, 128.66, 127.66, 127.65, 126.9, 125.5, 123.9, 122.3, 121.9, 62.5; **HRMS** (ESI) m/z calcd. for C₂₀H₁₆NO₂S [M+H]⁺ 334.0896, found 334.0899.



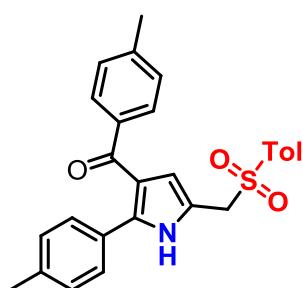
(3y) White solid (84.4 mg, 0.30 mmol, 59% yield), m.p: 190-191 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.66 (d, *J* = 7.8 Hz, 1H), 8.59 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 7.2 Hz, 1H), 7.78-7.75 (m, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 5.02 (s, 2H), 3.21 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (150MHz, CDCl₃) δ 150.4, 143.3, 133.3, 131.2, 129.9, 128.9, 127.9, 127.8, 127.1, 125.6, 124.3, 122.4, 122.1, 58.2, 46.6, 6.5; **HRMS** (ESI) m/z calcd. for C₁₆H₁₆NO₂S [M+H]⁺ 286.0896, found 286.0897.



(3z) White solid (88.4 mg, 0.33 mmol, 65% yield), m.p: 183-184 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.67 (d, *J* = 7.8 Hz, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.15-8.13 (m, 1H), 7.91-7.88 (m, 1H), 7.78-7.76 (m, 2H), 7.74-7.71 (m, 1H), 5.04 (s, 2H), 3.09 (s, 3H); **¹³C NMR** (150MHz, CDCl₃) δ 150.3, 143.3, 133.4, 131.2, 129.9, 129.0, 127.9, 126.9, 125.5, 124.3, 122.4, 122.2, 60.6, 40.4; **HRMS** (ESI) m/z calcd. for C₁₅H₁₄NO₂S [M+H]⁺ 272.0740, found 272.0746.

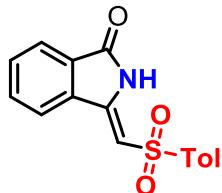


(5a) Yellow solid (118.6 mg, 0.29 mmol, 57% yield), m.p: 221-222 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.13 (s, 1H), 7.62-7.59 (m, 4H), 7.47-7.46 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.33-7.30 (m, 5H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.16 (d, *J* = 2.4 Hz, 1H), 4.38 (s, 2H), 2.46 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 191.7, 145.3, 139.2, 138.9, 134.4, 131.8, 131.2, 129.8, 129.5, 128.5, 128.43, 128.39, 127.8, 120.5, 118.2, 116.1, 55.5, 21.7; **HRMS** (ESI) m/z calcd. for C₂₅H₂₂NO₃S [M+H]⁺ 416.1320, found 416.1323.

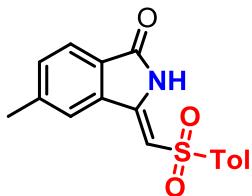


(5b) White solid (135.5 mg, 0.31 mmol, 61% yield), m.p: 235-236 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.19 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.09 (d, *J* = 2.4 Hz, 1H), 4.36 (s, 2H), 2.45 (s, 3H), 2.36 (s, 3H), 2.33 (s,

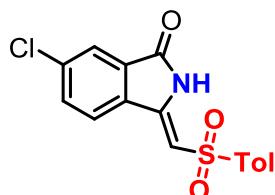
3H); **¹³C NMR** (150 MHz, CDCl₃) δ 191.5, 145.2, 142.4, 138.9, 138.4, 136.7, 134.4, 129.80, 129.79, 129.2, 128.6, 128.5, 128.2, 120.3, 117.7, 116.1, 55.6, 21.7, 21.6, 21.3; **HRMS** (ESI) m/z calcd. for C₂₇H₂₆NO₃S [M+H]⁺ 444.1633, found 444.1628.



(7a) White solid (108.0 mg, 0.36 mmol, 72% yield), m.p: 163-164 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.36 (s, 1H), 7.83-7.81 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.57-7.56 (m, 2H), 7.51-7.49 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 2.37 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 167.3, 144.9, 143.4, 138.7, 135.9, 133.1, 132.3, 130.1, 129.0, 127.2, 124.3, 121.3, 100.7, 21.6; **HRMS** (ESI) m/z calcd. for C₁₆H₁₄NO₃S [M+H]⁺ 300.0694, found 300.0692.



(7b) White solid (102.1 mg, 0.33 mmol, 65% yield), m.p: 171-172 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.35 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 3H), 6.05 (s, 1H), 2.46 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 167.5, 144.8, 144.2, 143.6, 138.7, 136.2, 133.1, 130.1, 127.1, 126.4, 124.0, 121.7, 100.2, 21.9, 21.6; **HRMS** (ESI) m/z calcd. for C₁₇H₁₆NO₃S [M+H]⁺ 314.0851, found 314.0853.

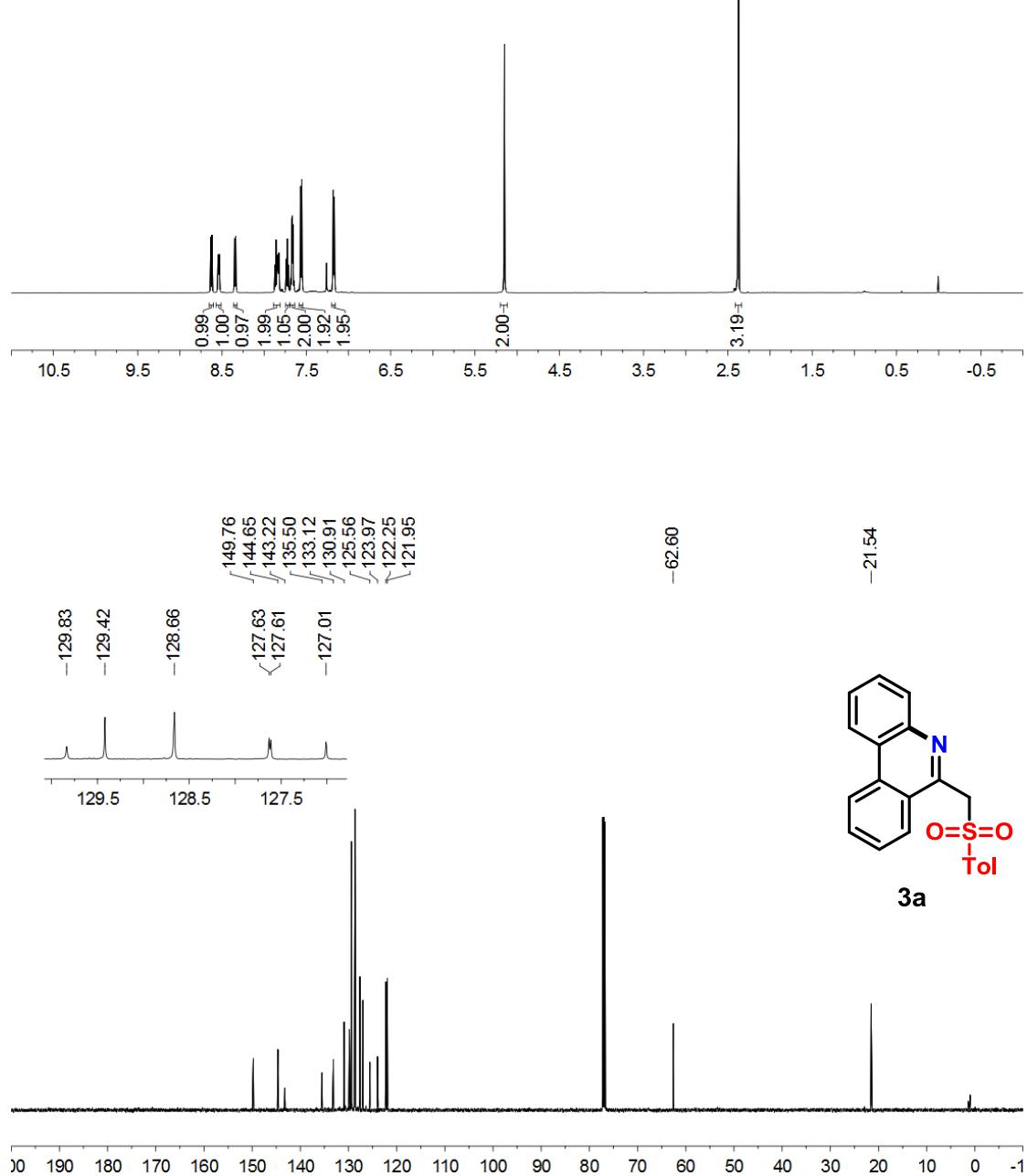
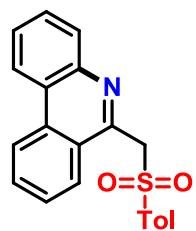


(7c) White solid (71.8 mg, 0.22 mmol, 43% yield), m.p: 185-186 °C; **¹H NMR** (600 MHz, CDCl₃) δ 9.49 (s, 1H), 7.85 (t, *J* = 8.4 Hz, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.06 (s, 1H), 2.45 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 165.9, 145.1, 142.3, 138.8, 138.3, 133.9, 133.2, 130.6, 130.2, 127.2,

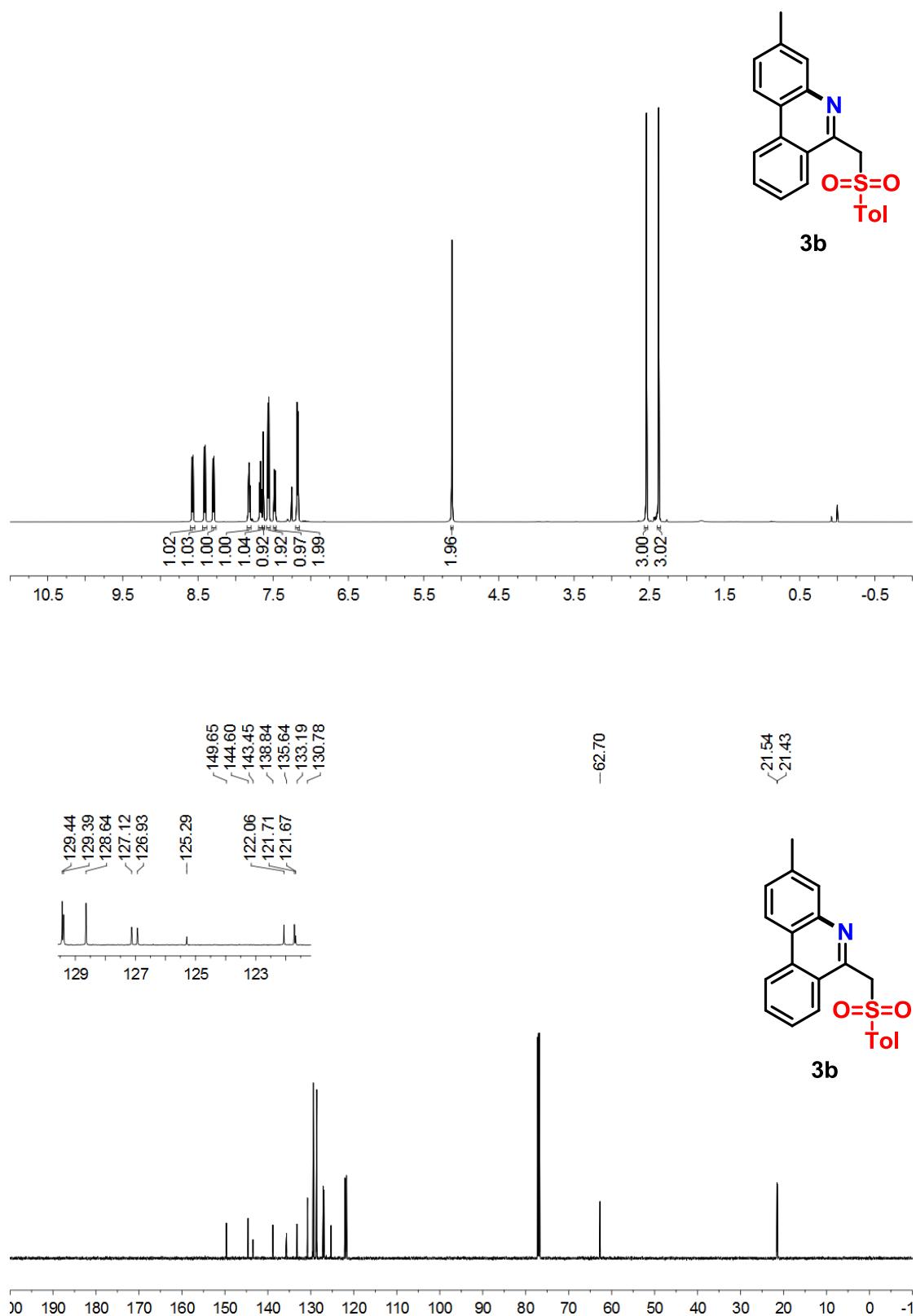
124.6, 122.5, 101.4, 21.7; **HRMS** (ESI) m/z calcd. for $C_{16}H_{13}ClNO_3S$ $[M+H]^+$ 334.0305, found 334.0312.

7. NMR Spectra Copies of All the Products

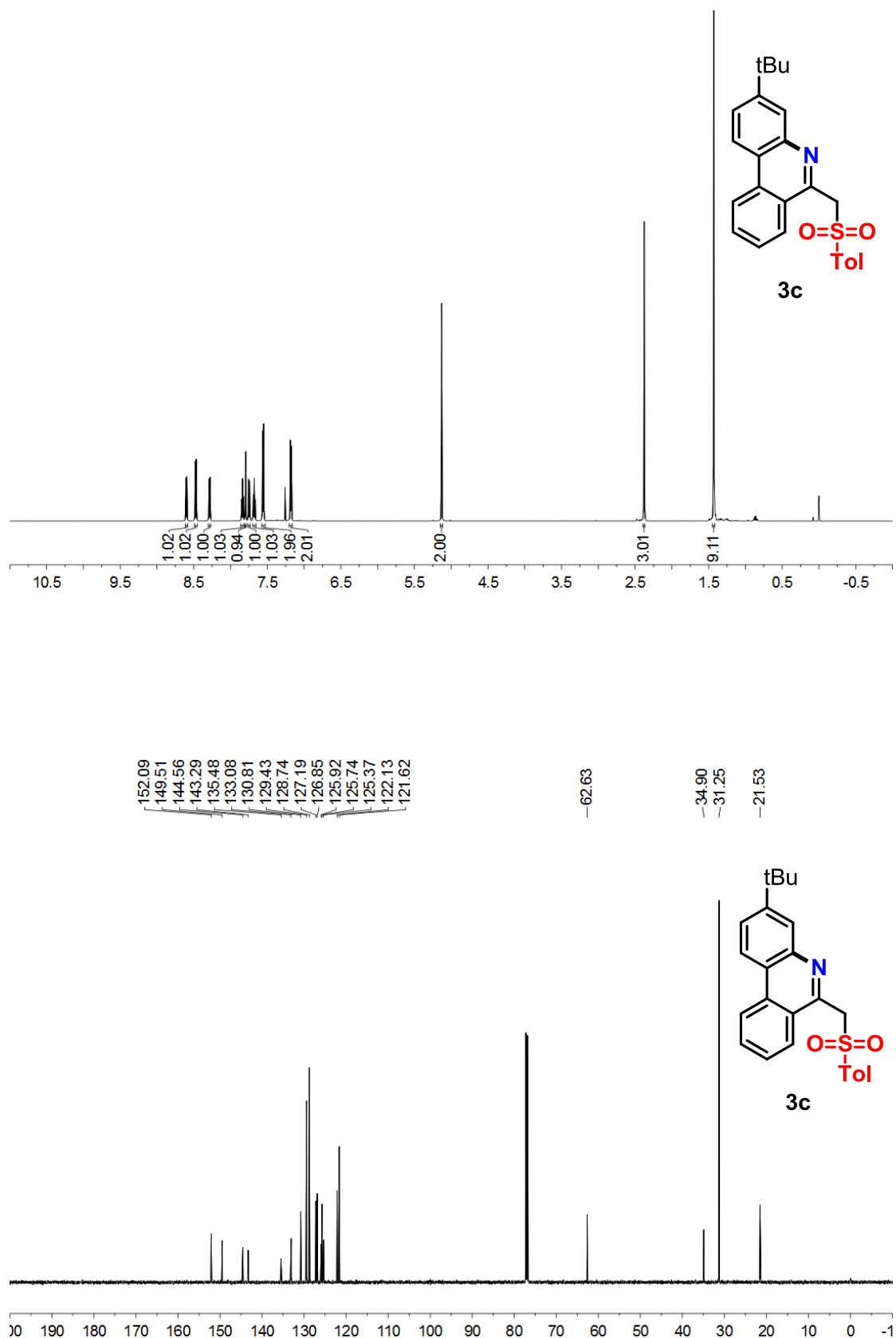
3a ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



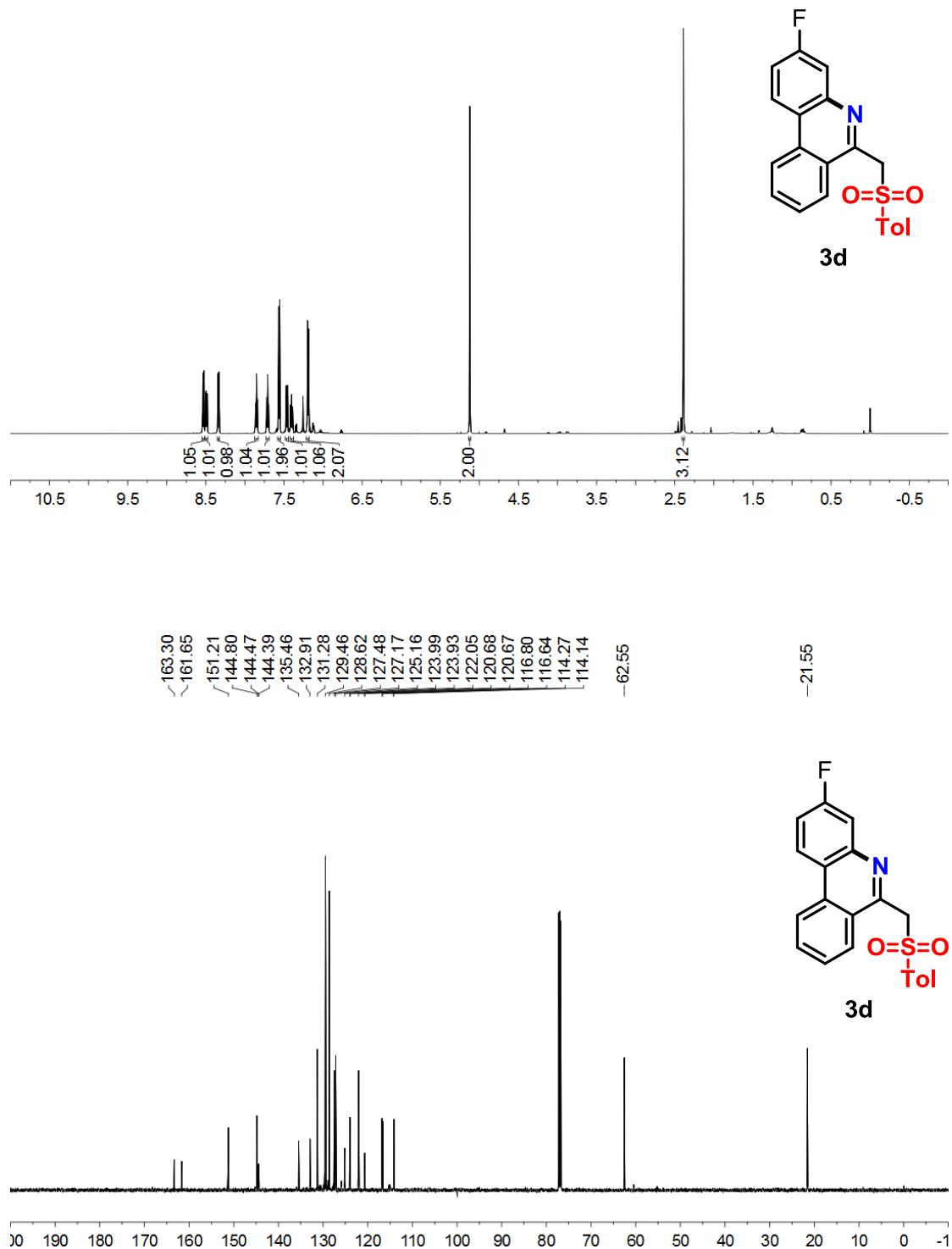
3b ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



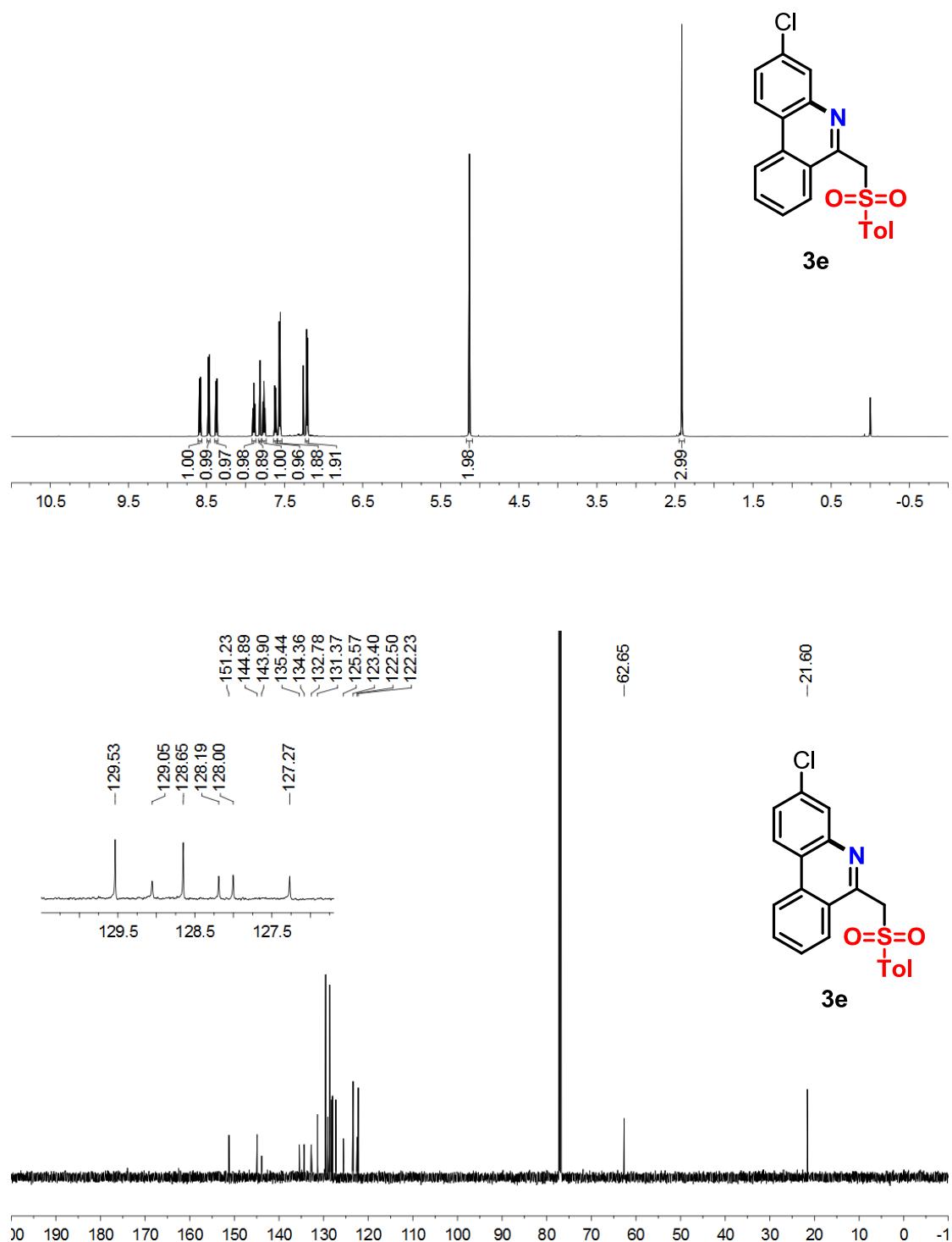
3c ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



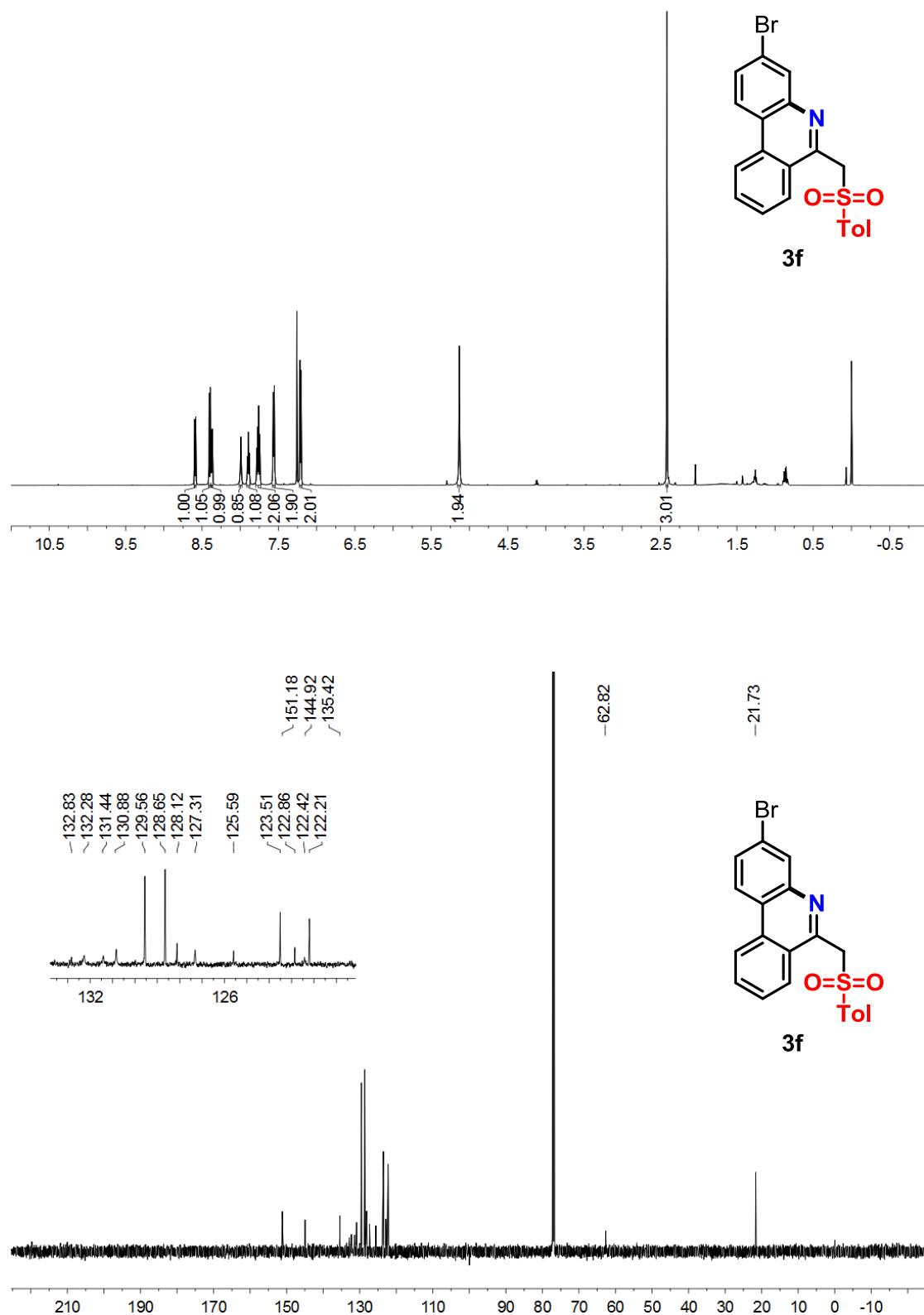
3d ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



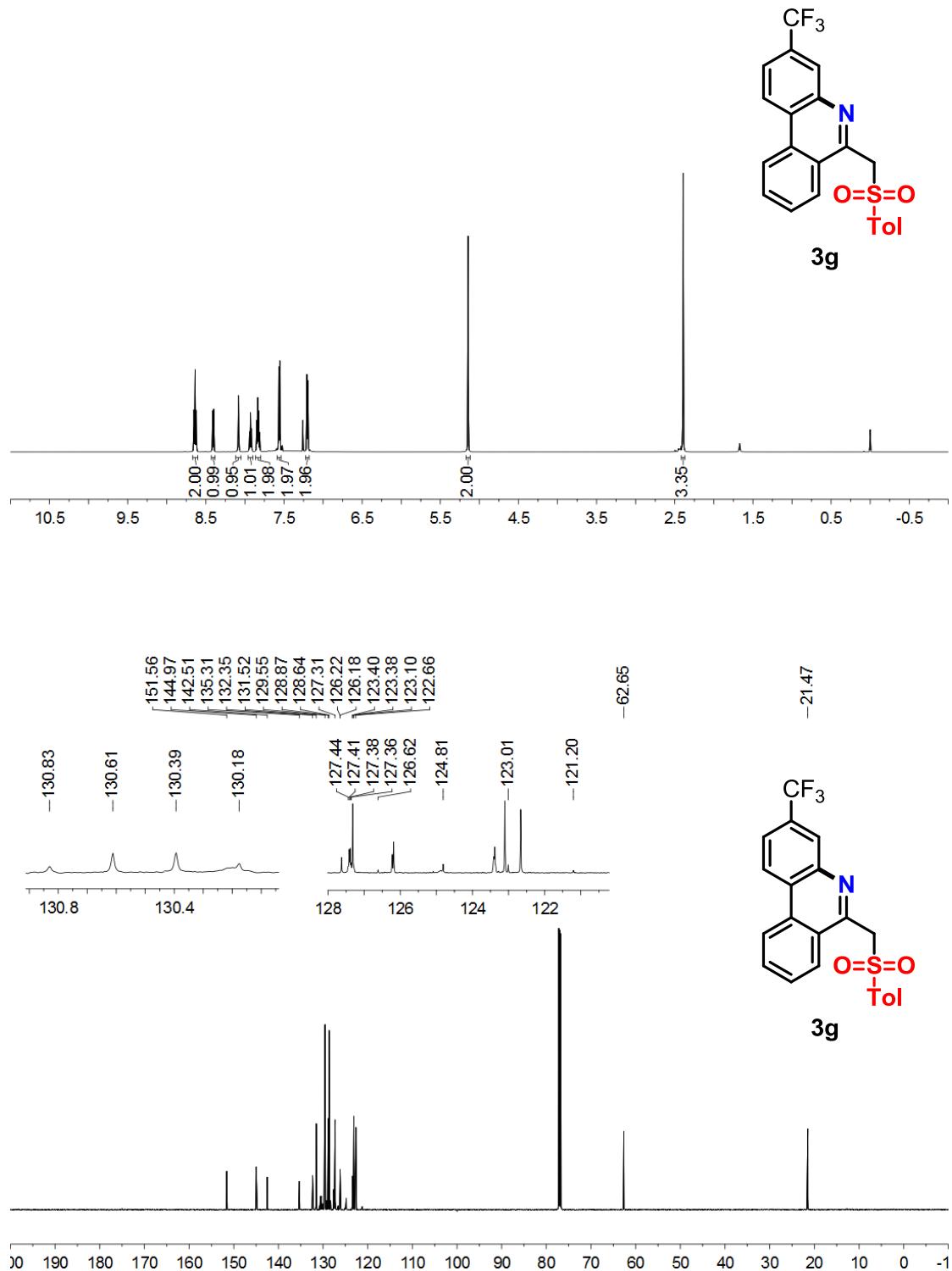
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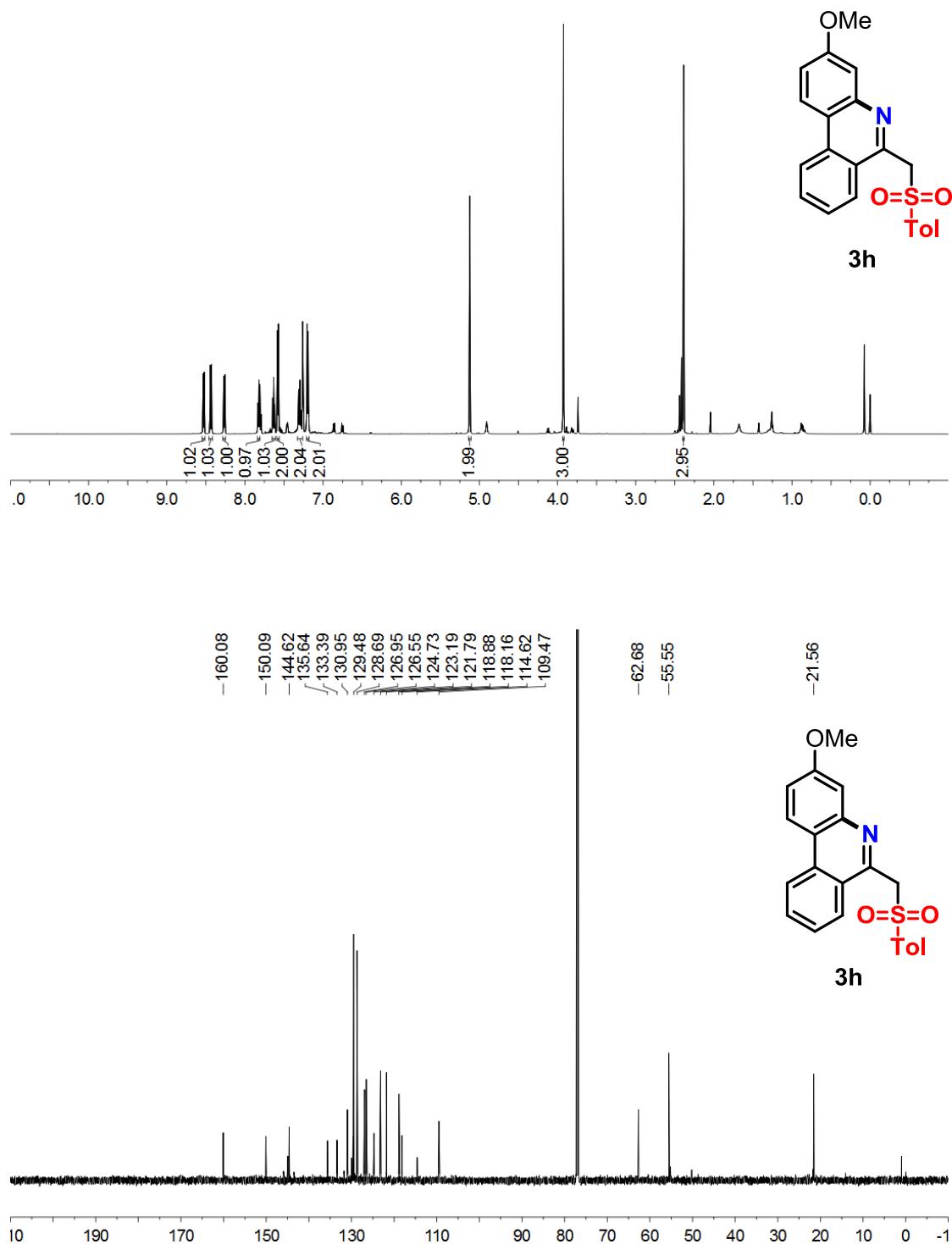
3f ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



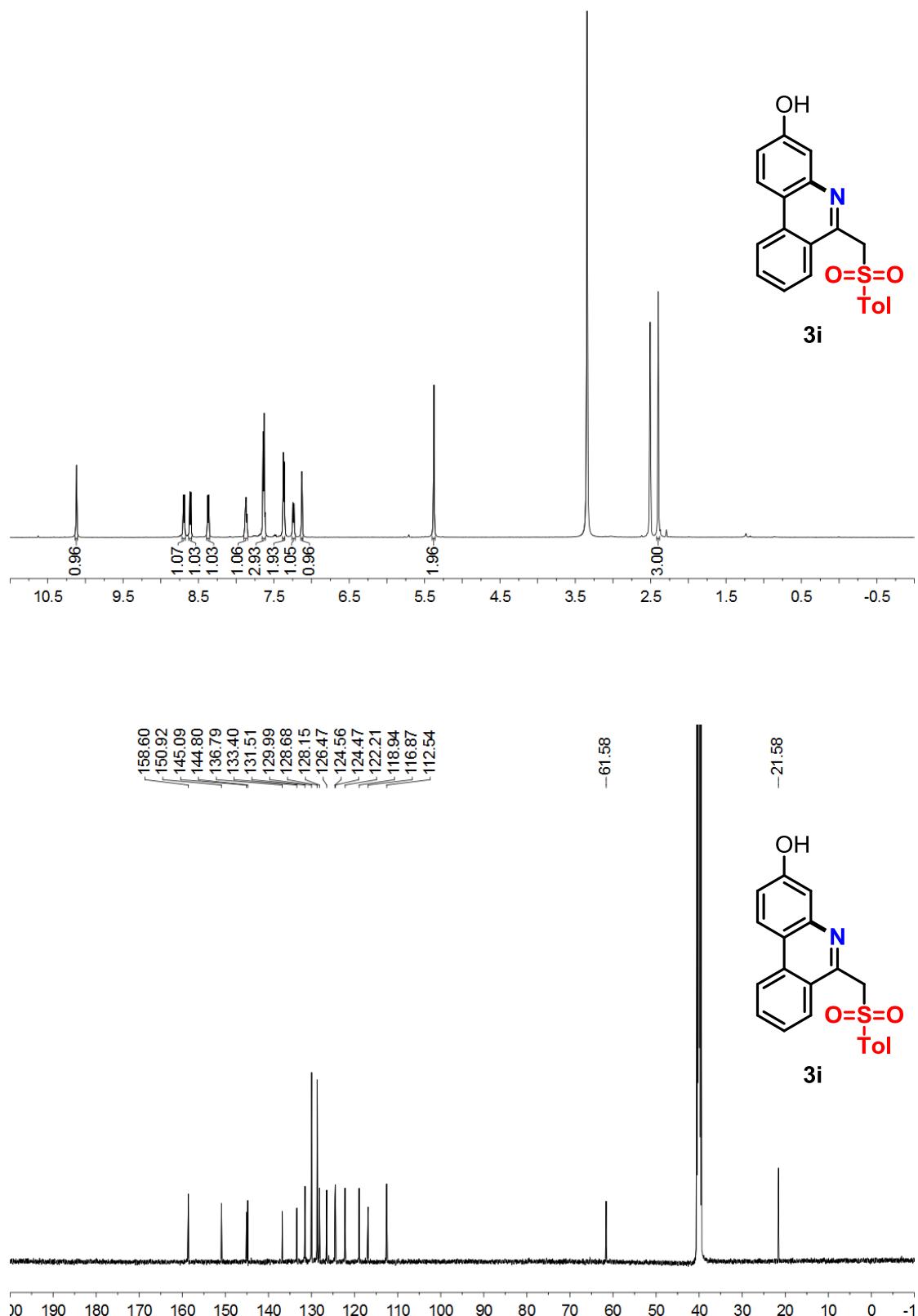
3g ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



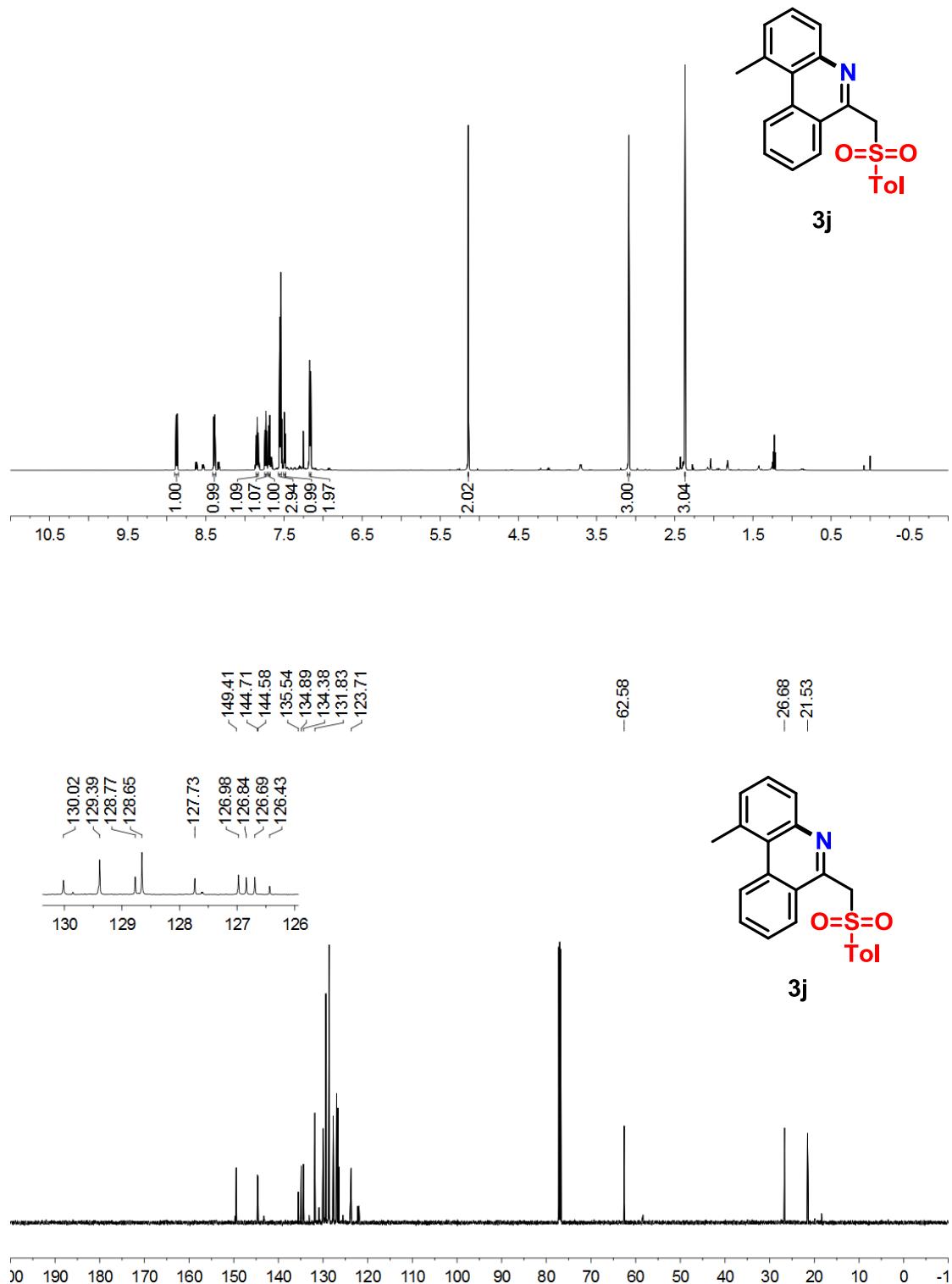
3h ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



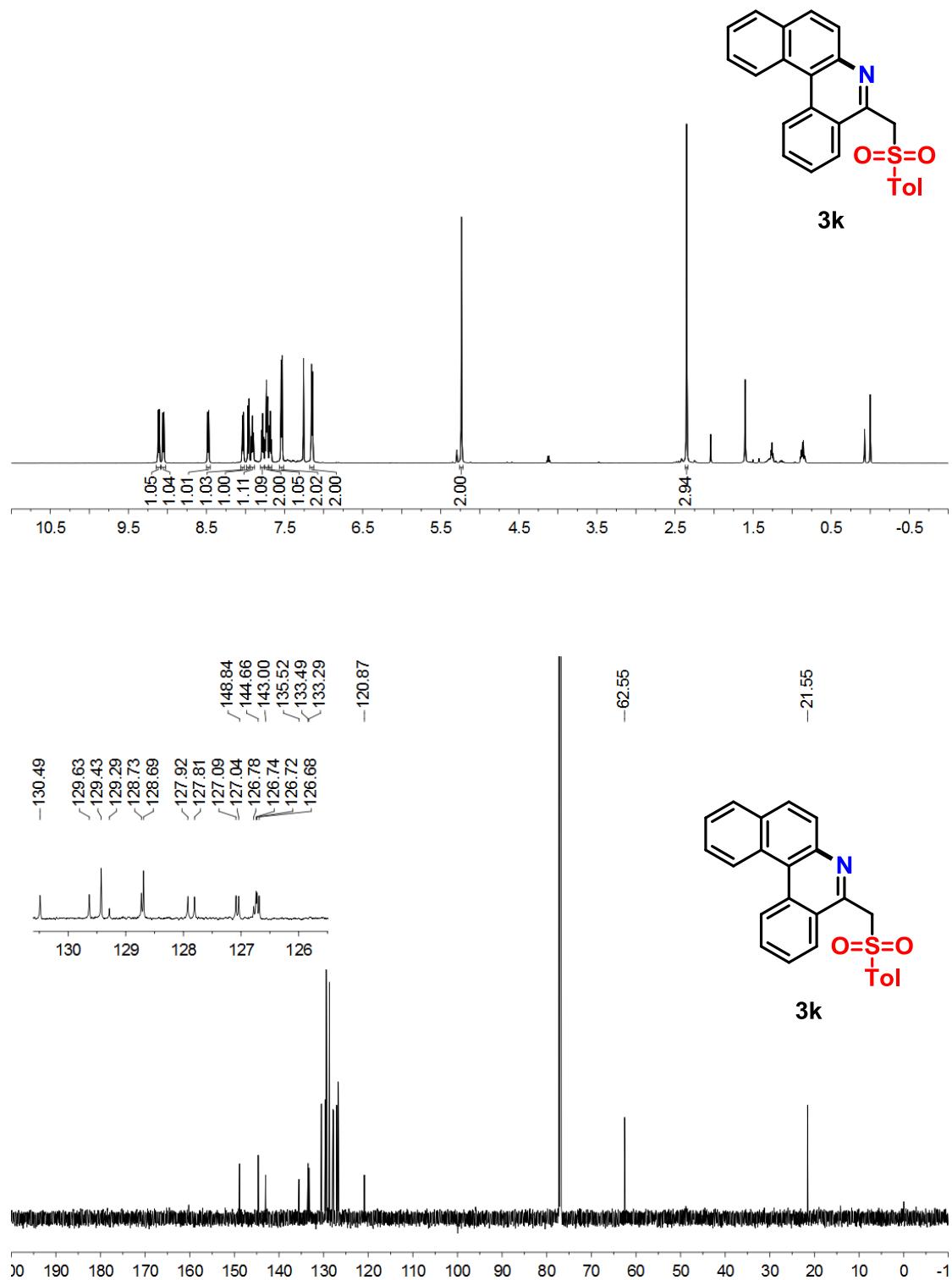
3i ^1H NMR (600 MHz, DMSO) & ^{13}C NMR (125 MHz, DMSO)



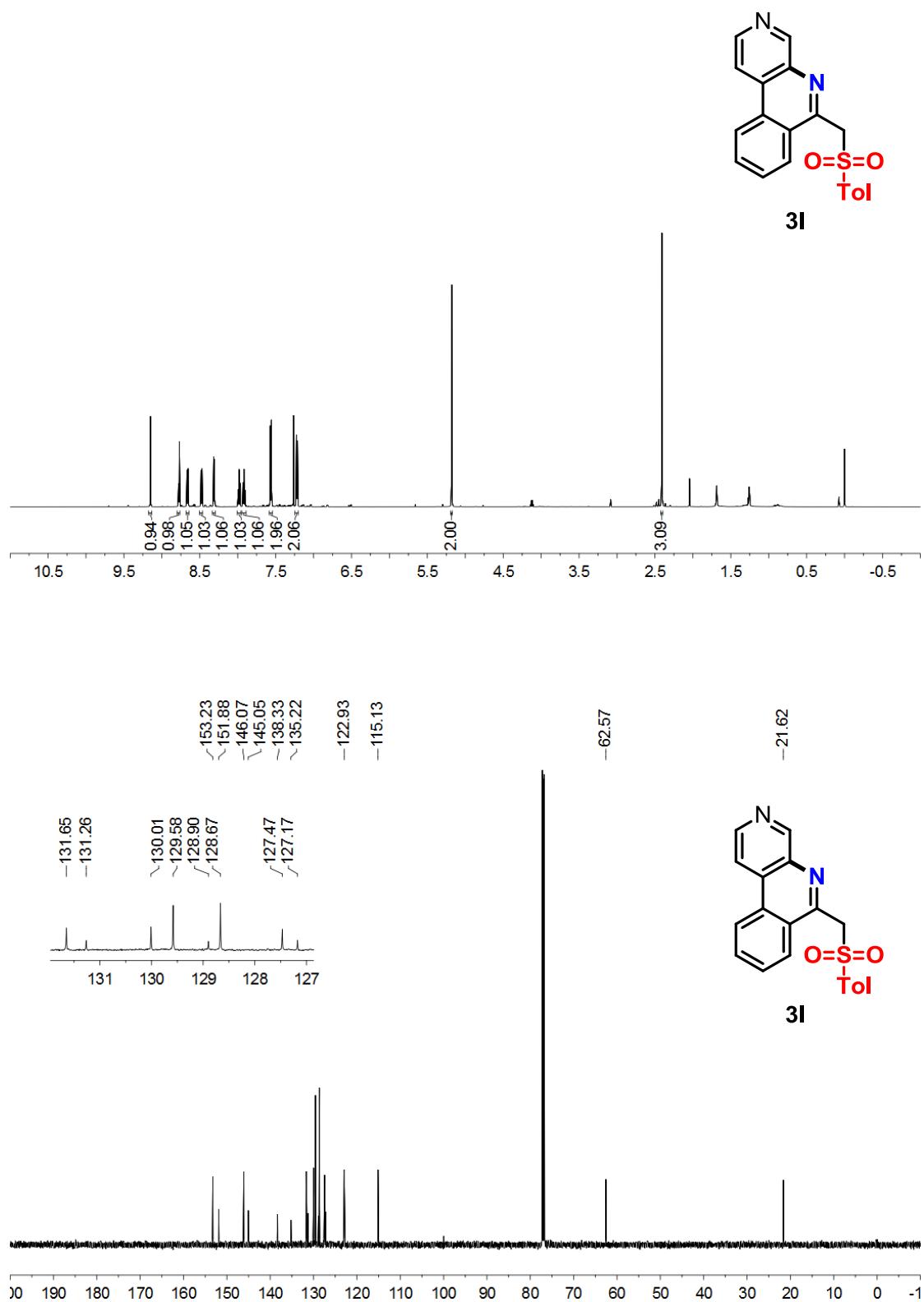
3j ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



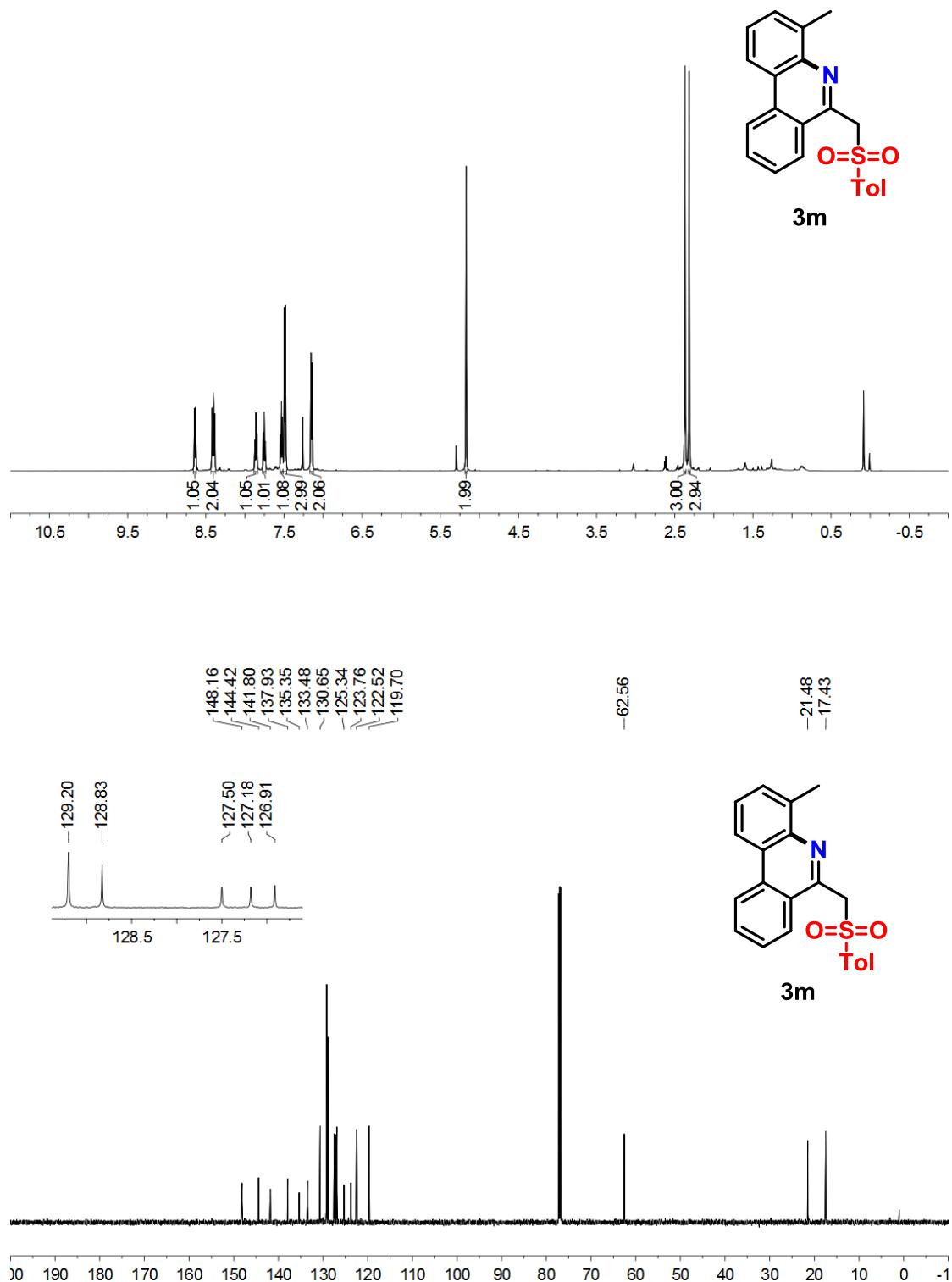
3k ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



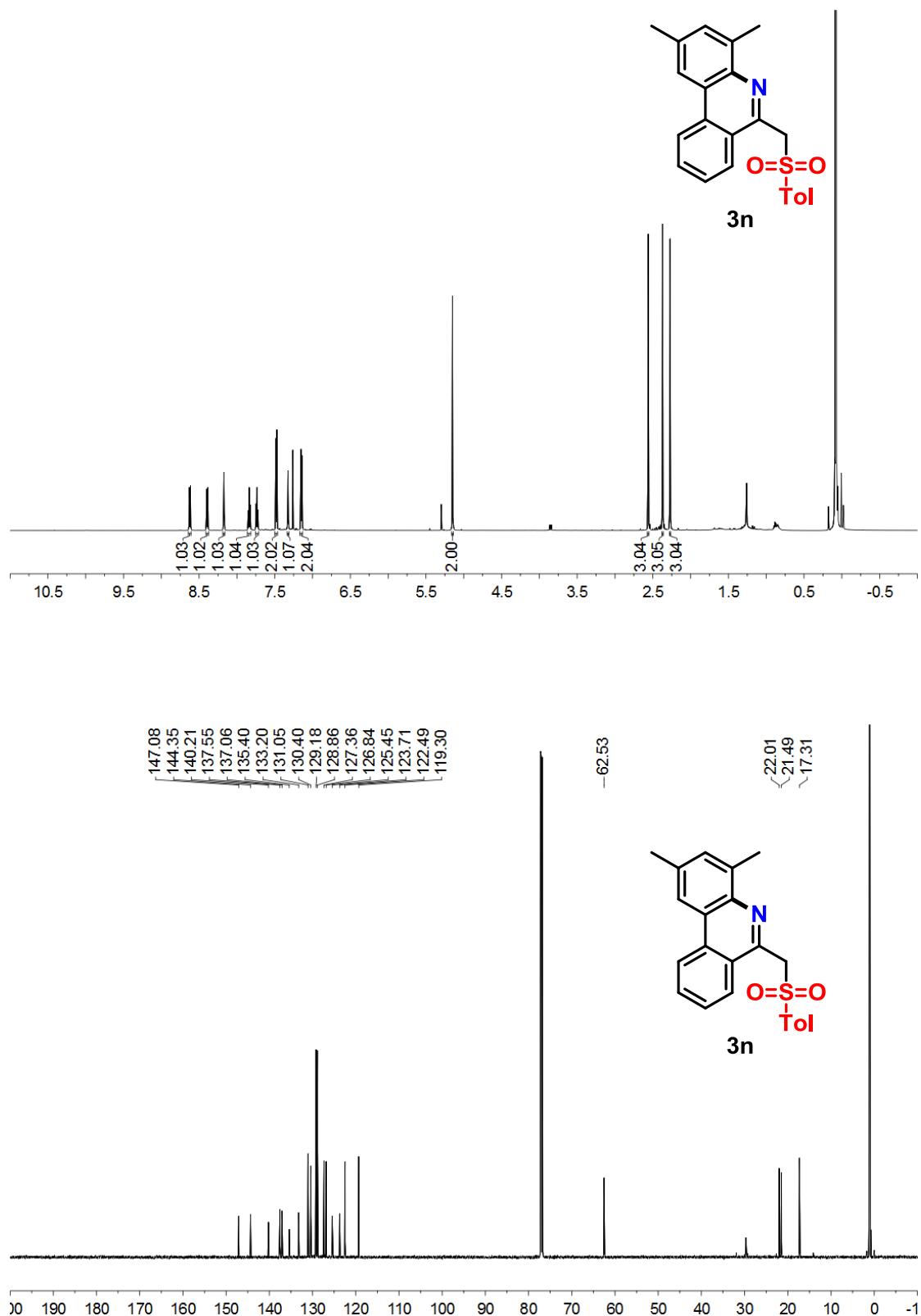
3l ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



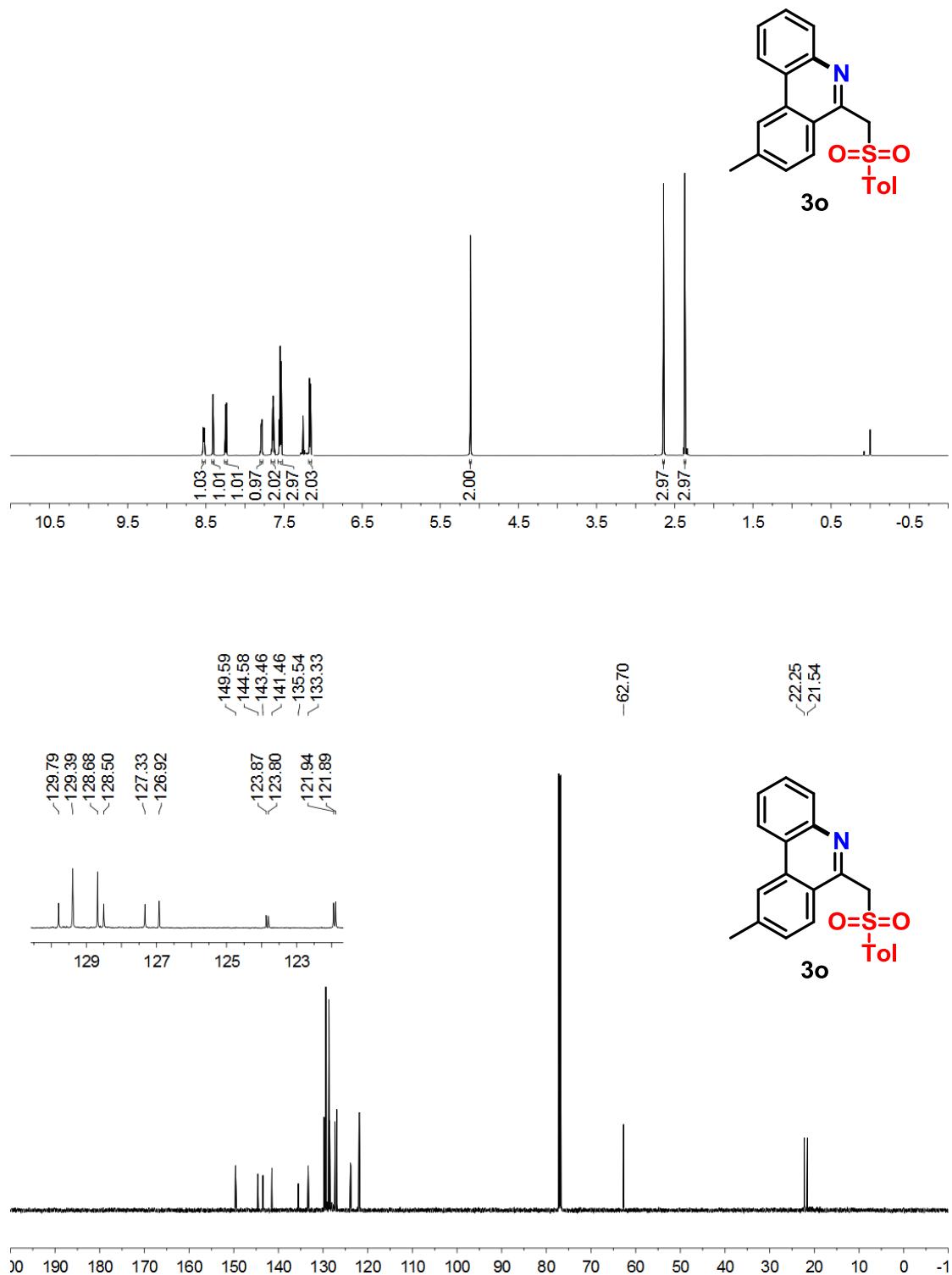
3m ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



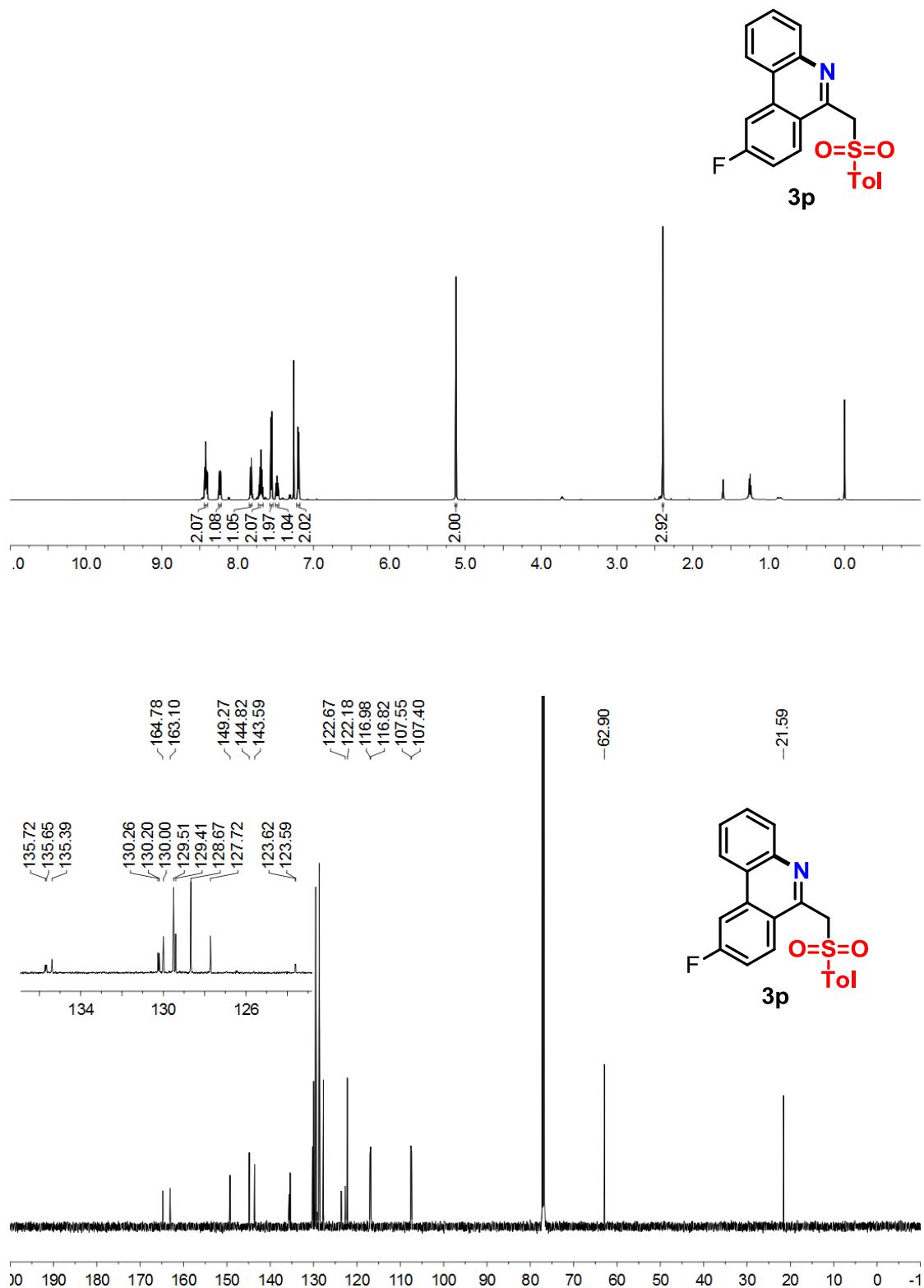
3n ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



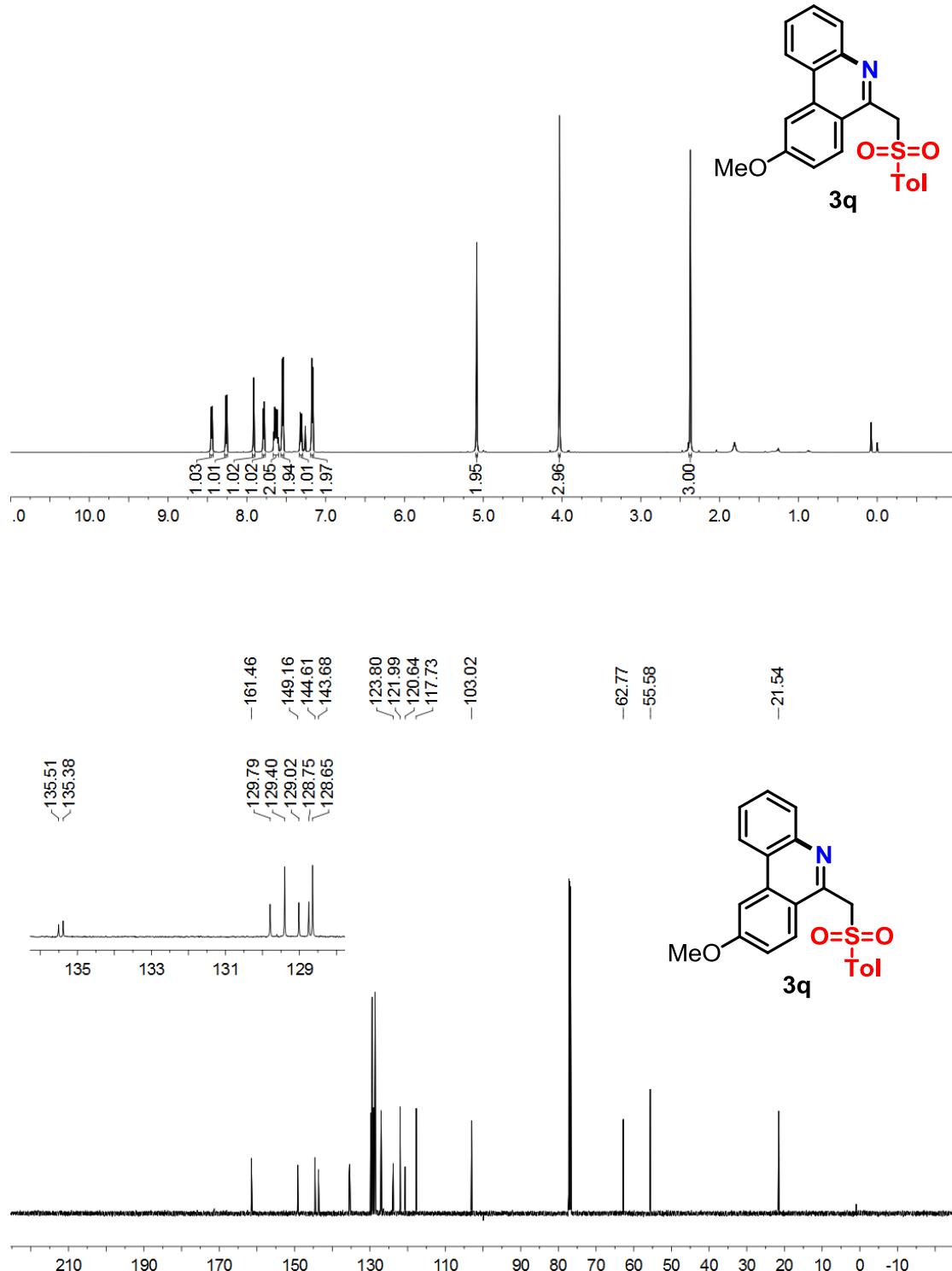
3o ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



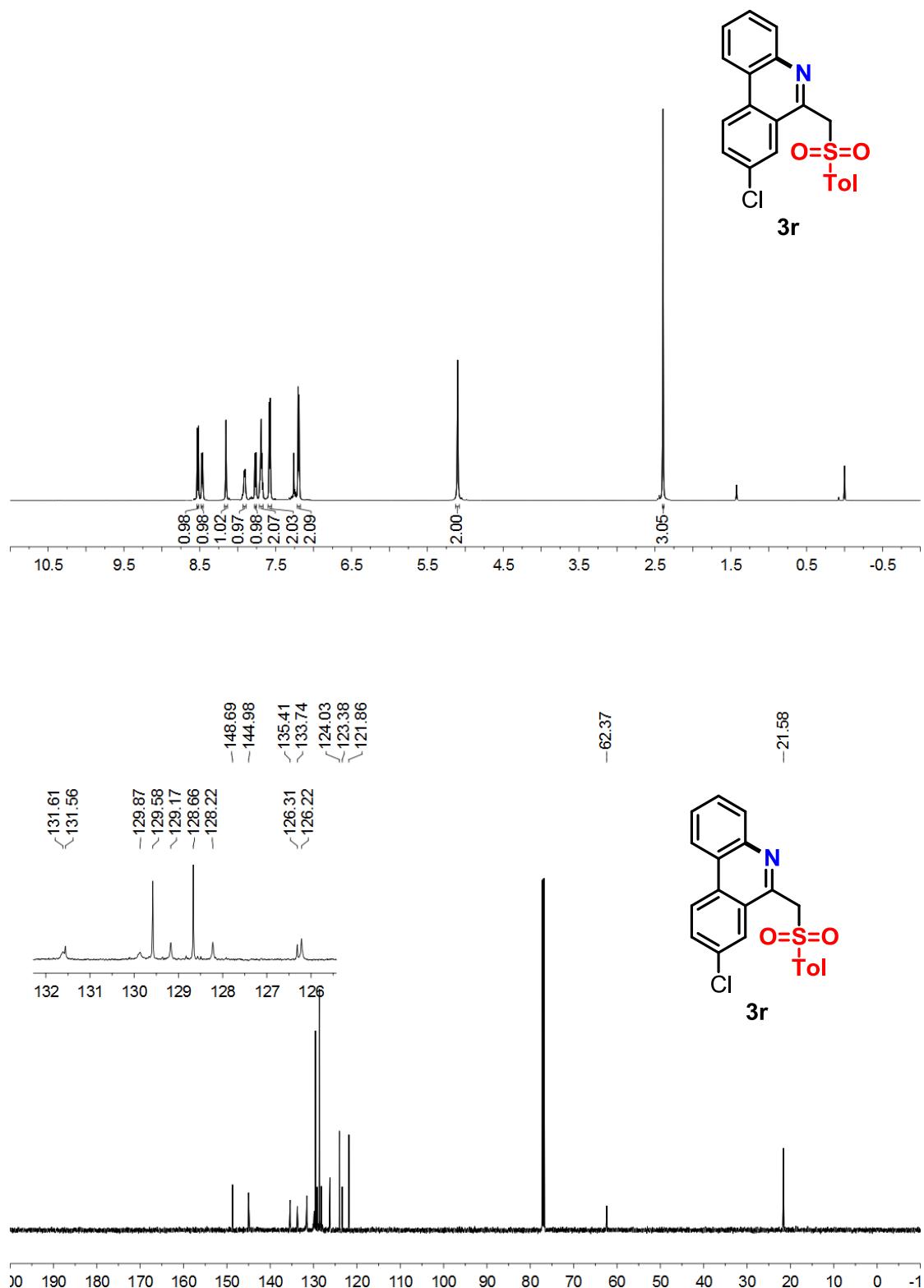
3p ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



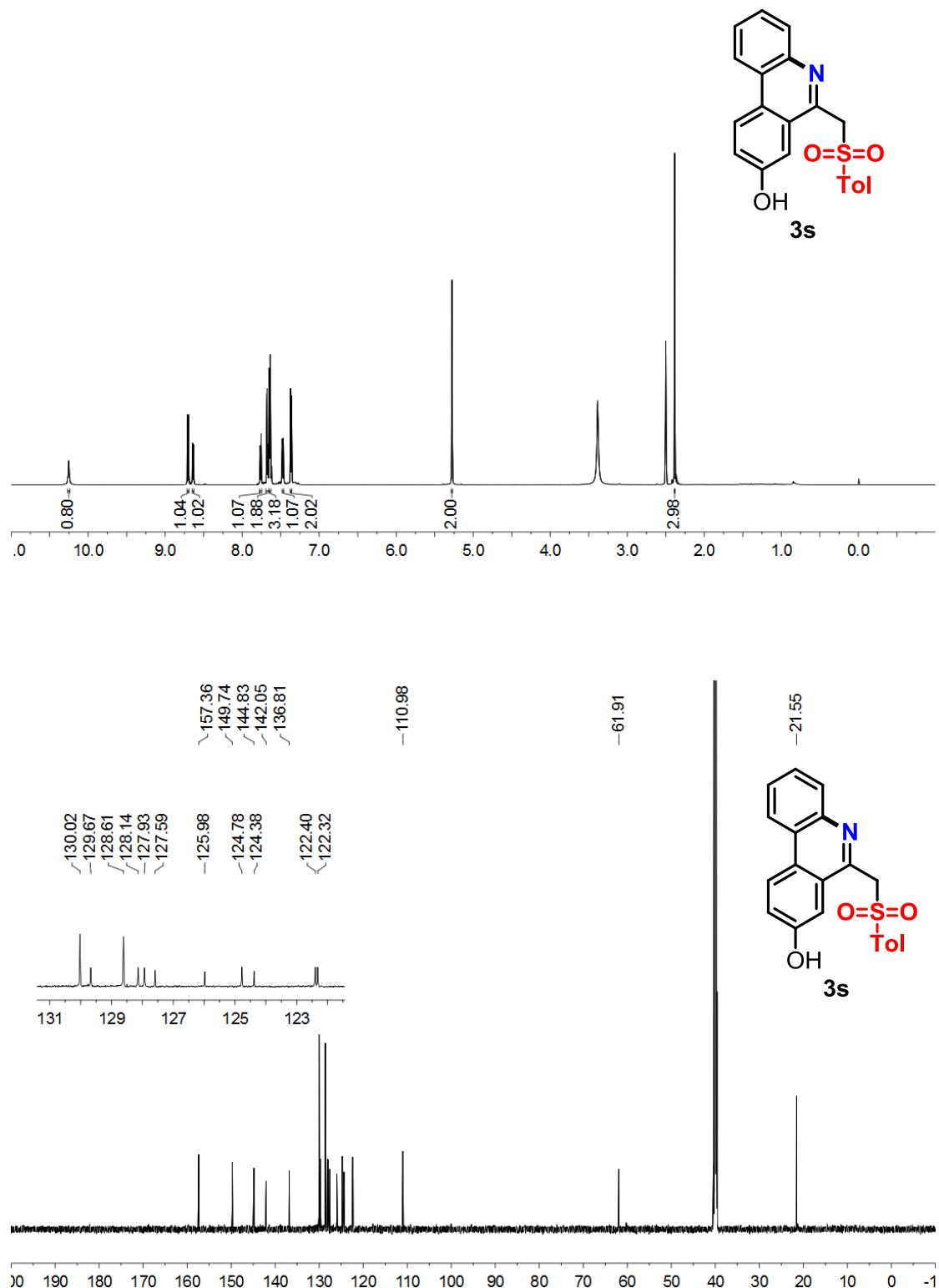
3q ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



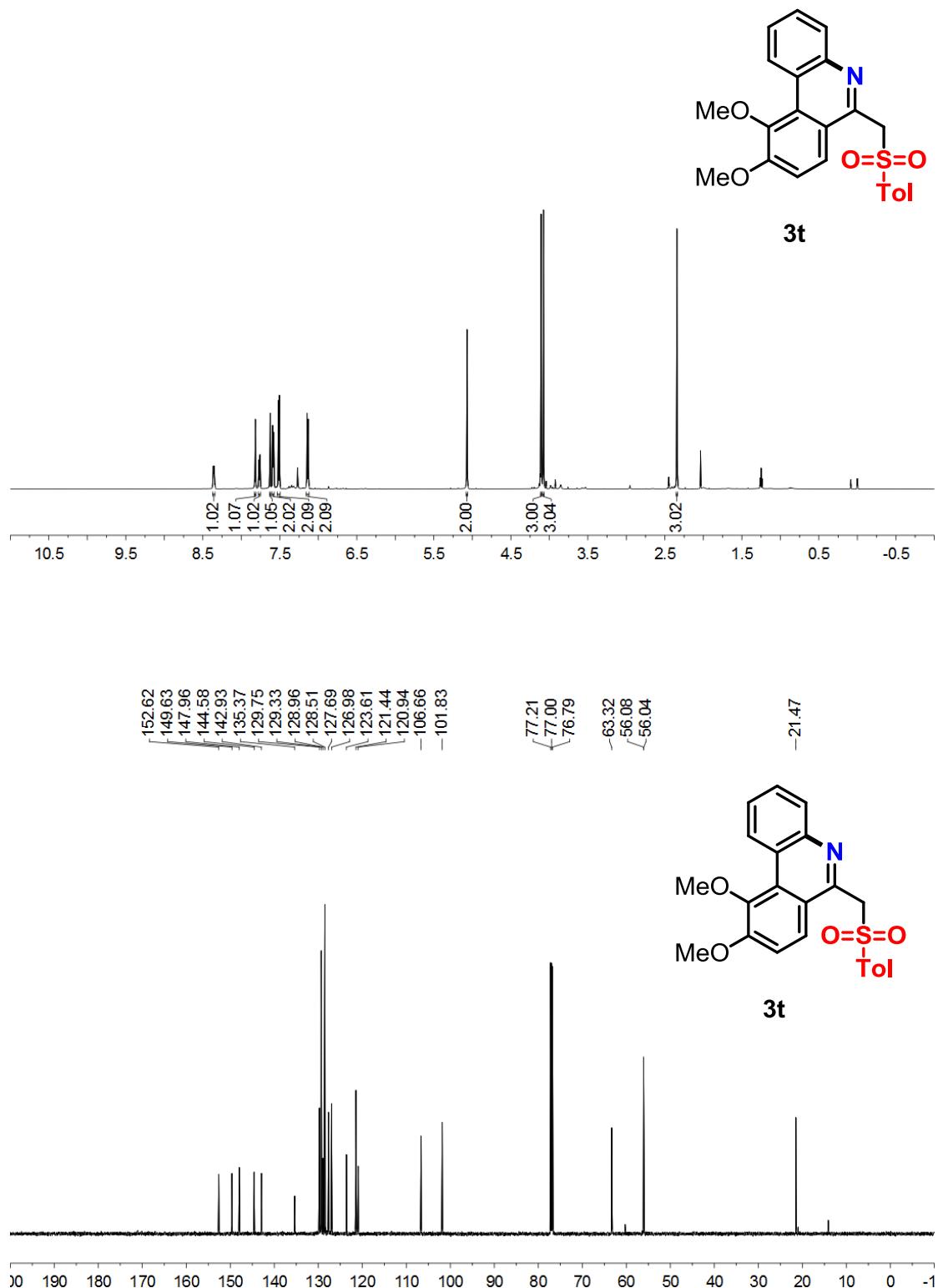
3r ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



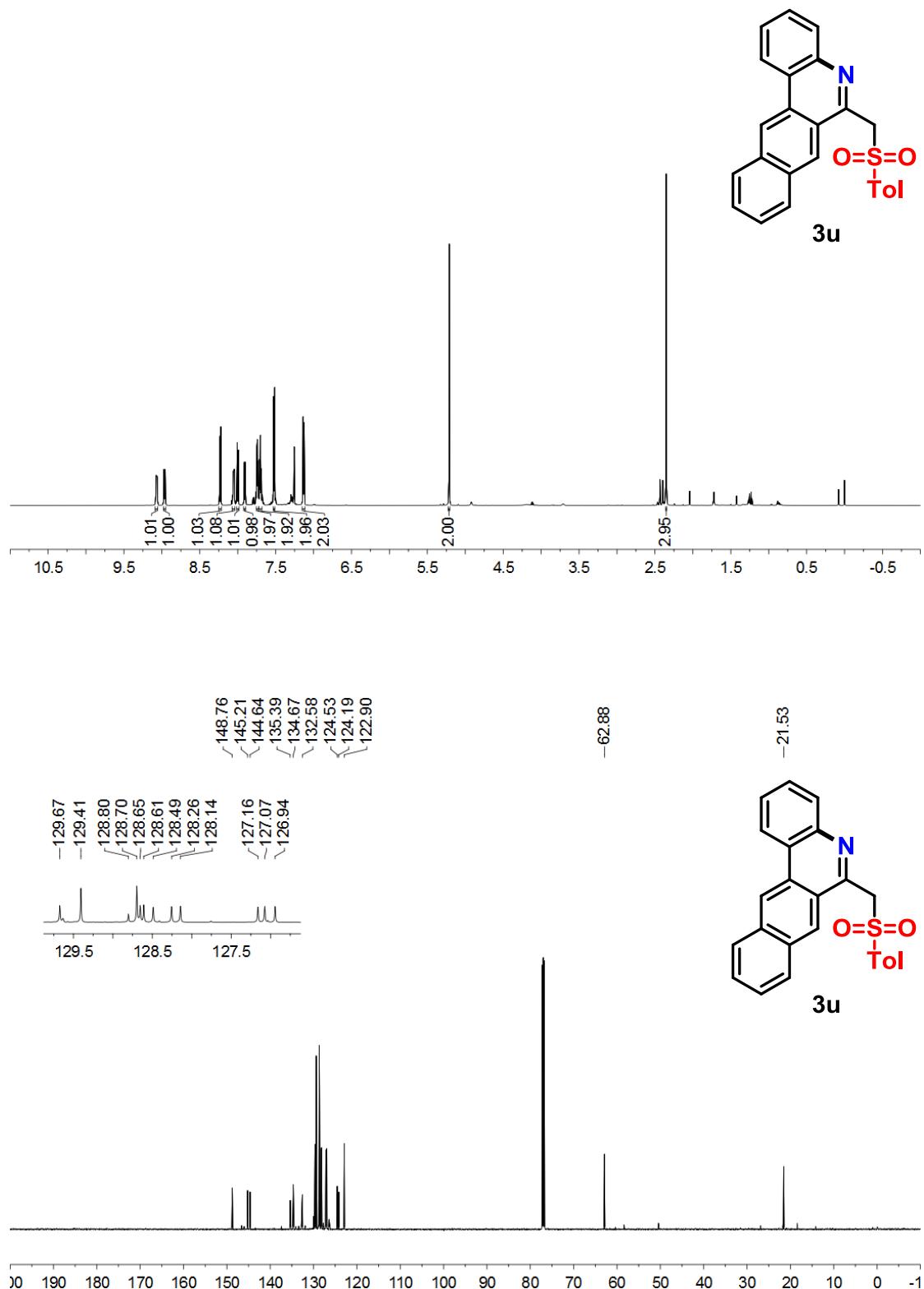
3s ^1H NMR (600 MHz, DMSO) & ^{13}C NMR (150 MHz, DMSO)



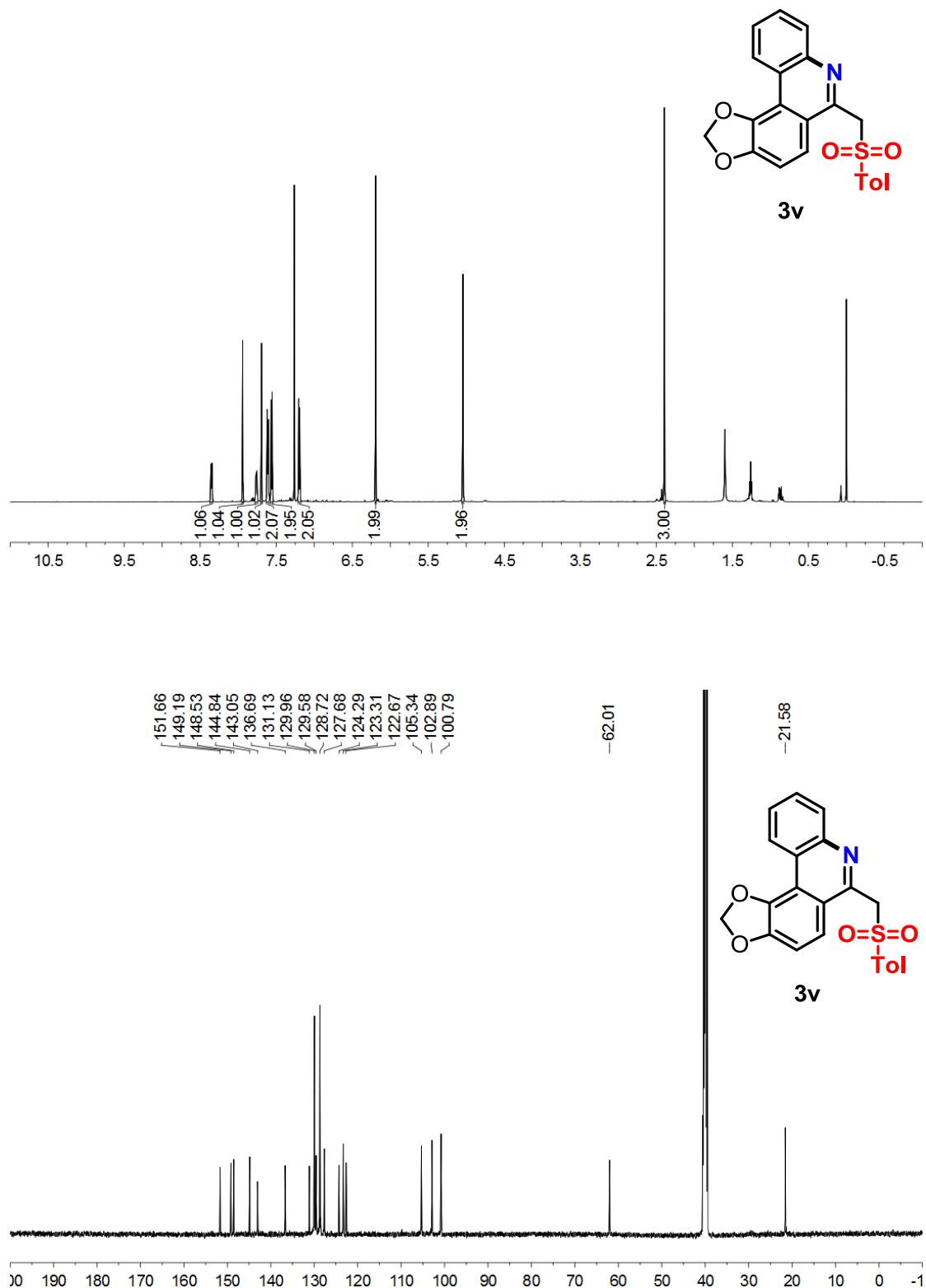
3t ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



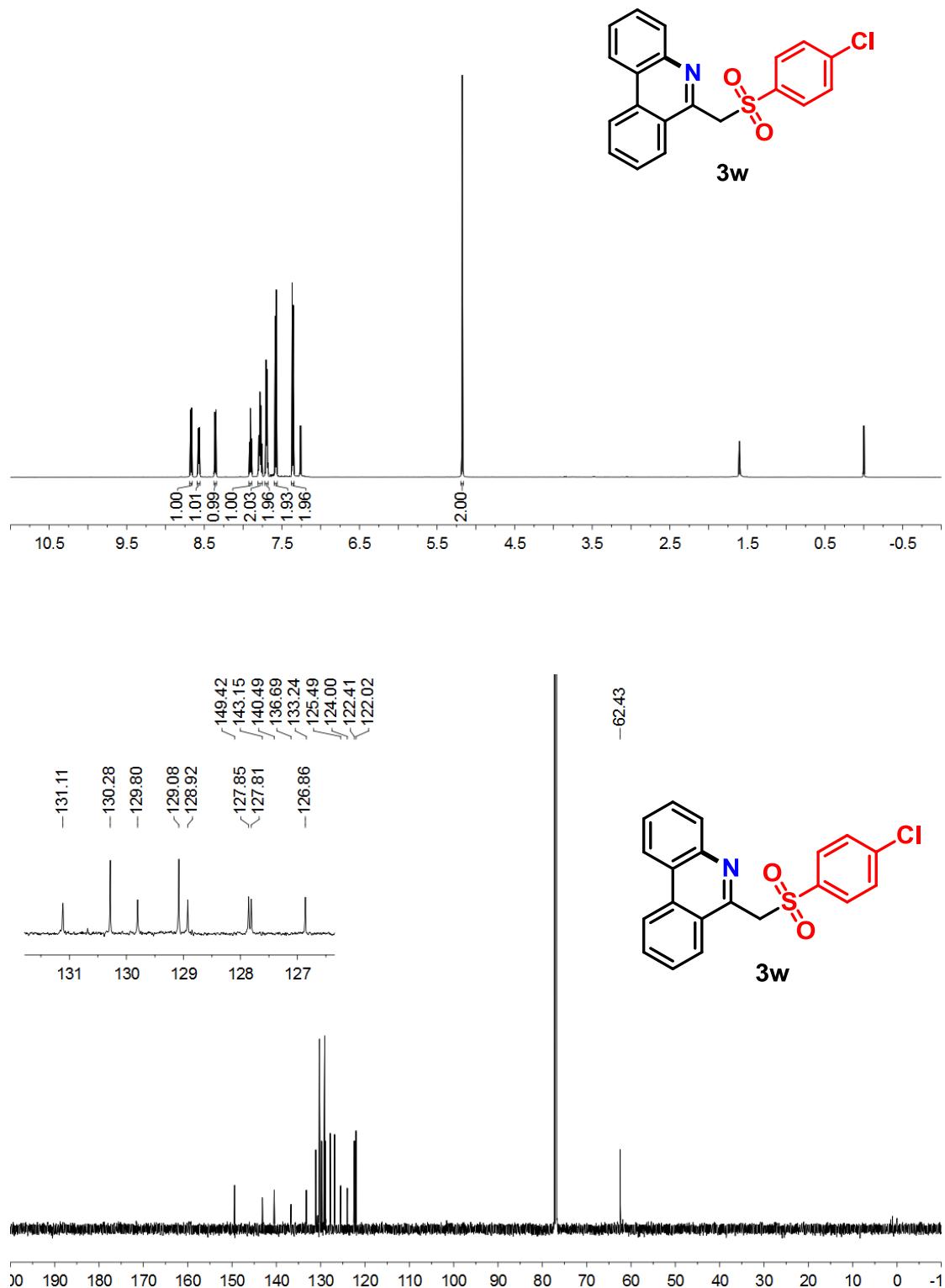
3u ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



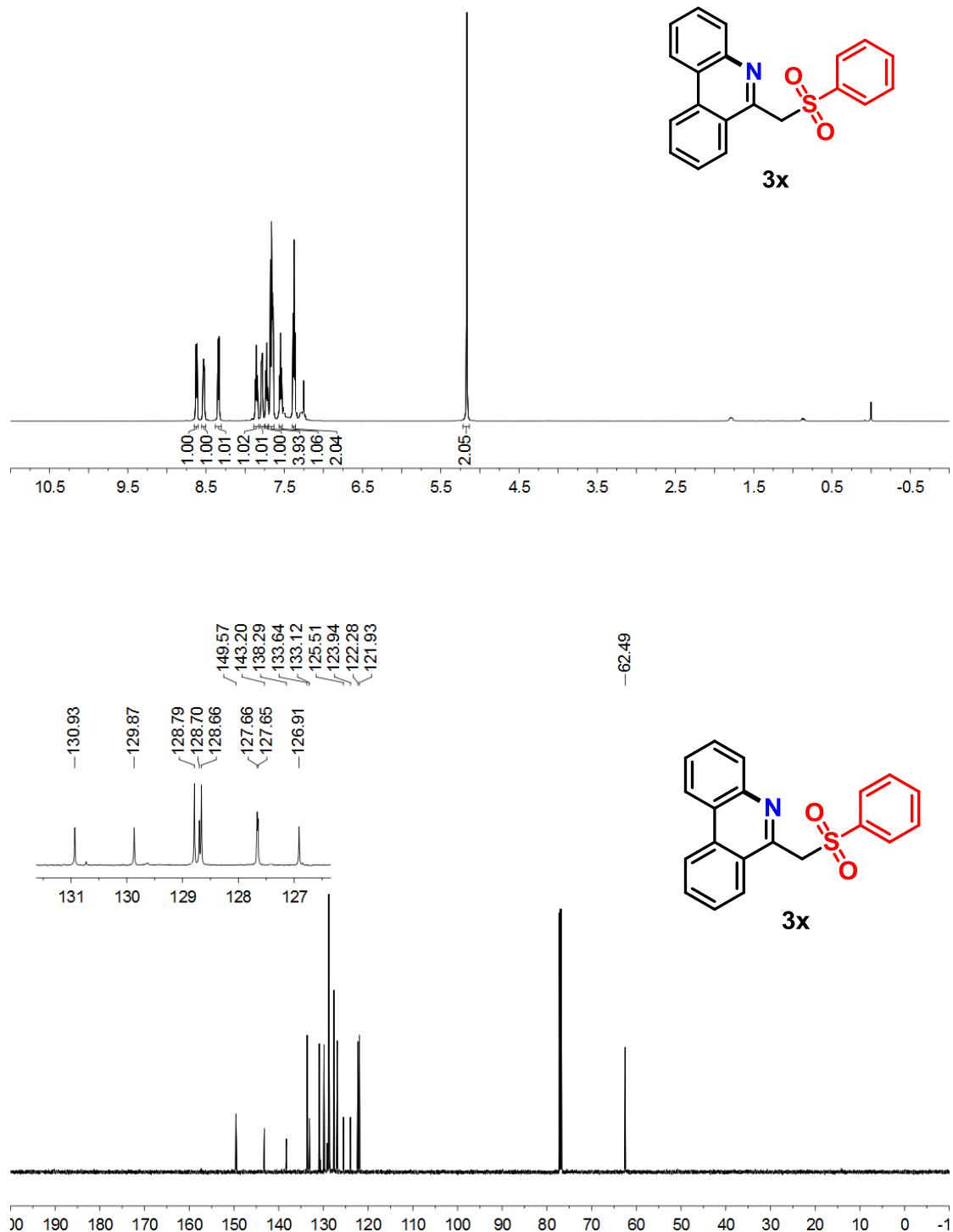
3v ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (125 MHz, DMSO)



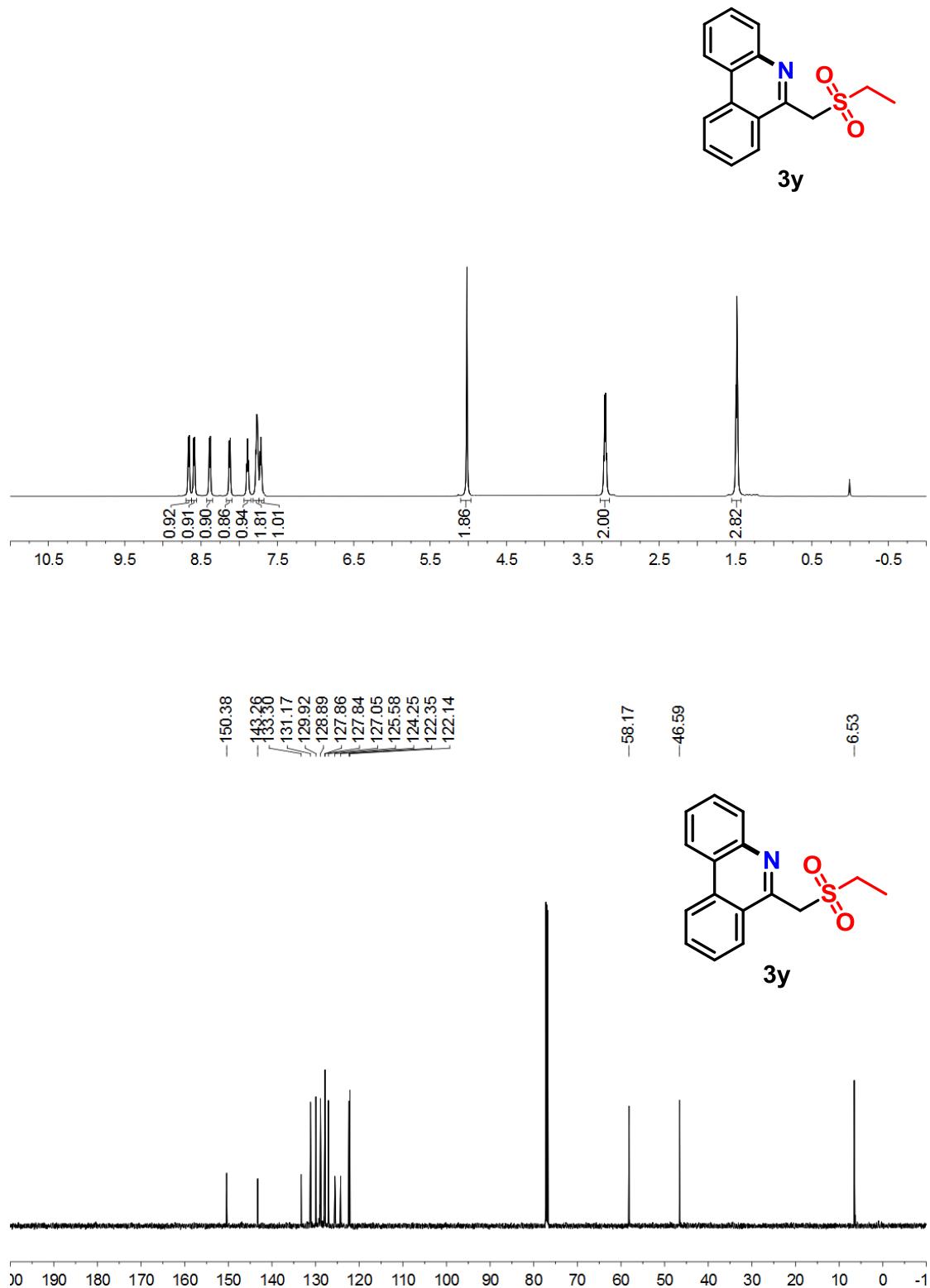
3w ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



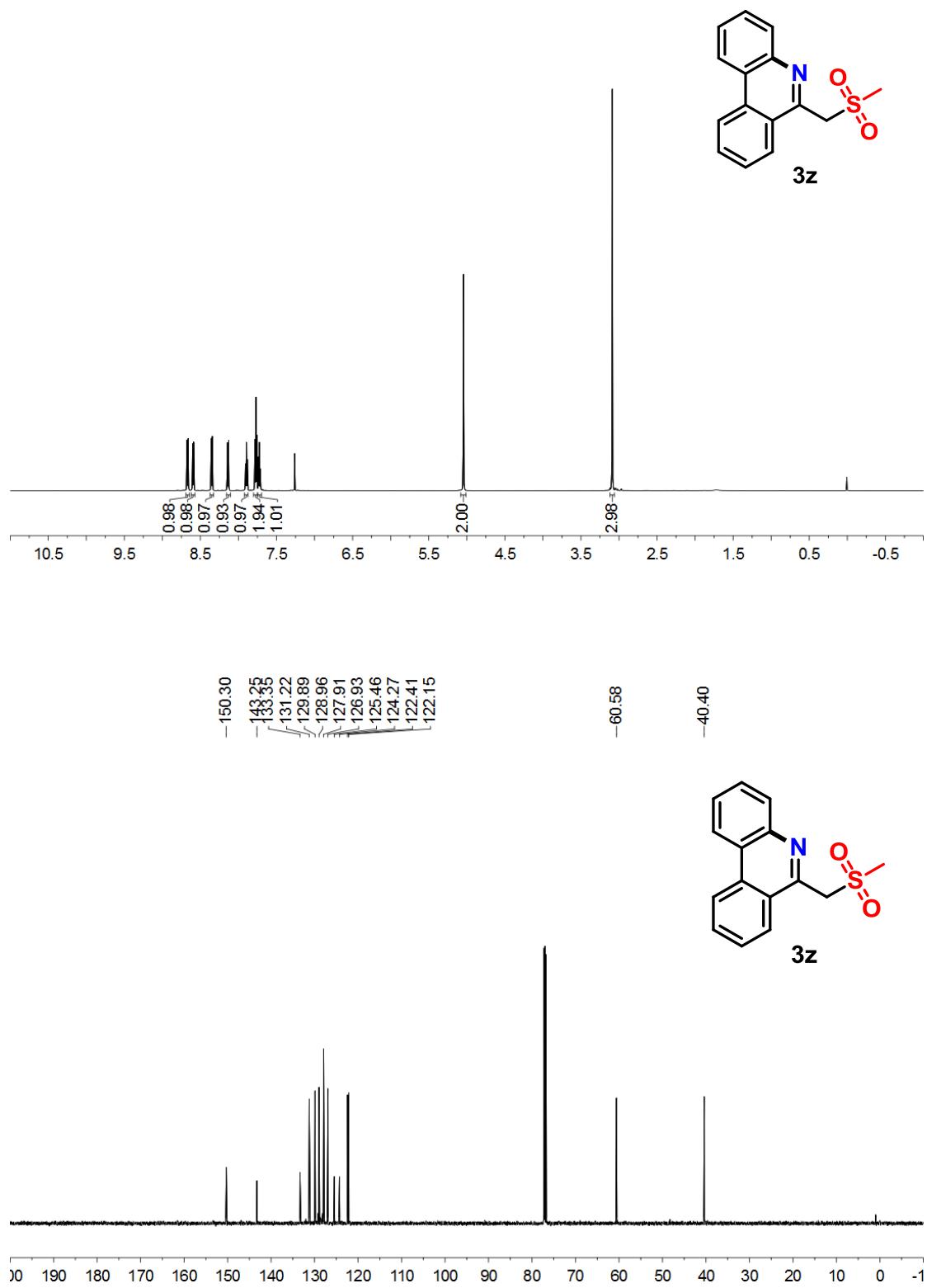
3x ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



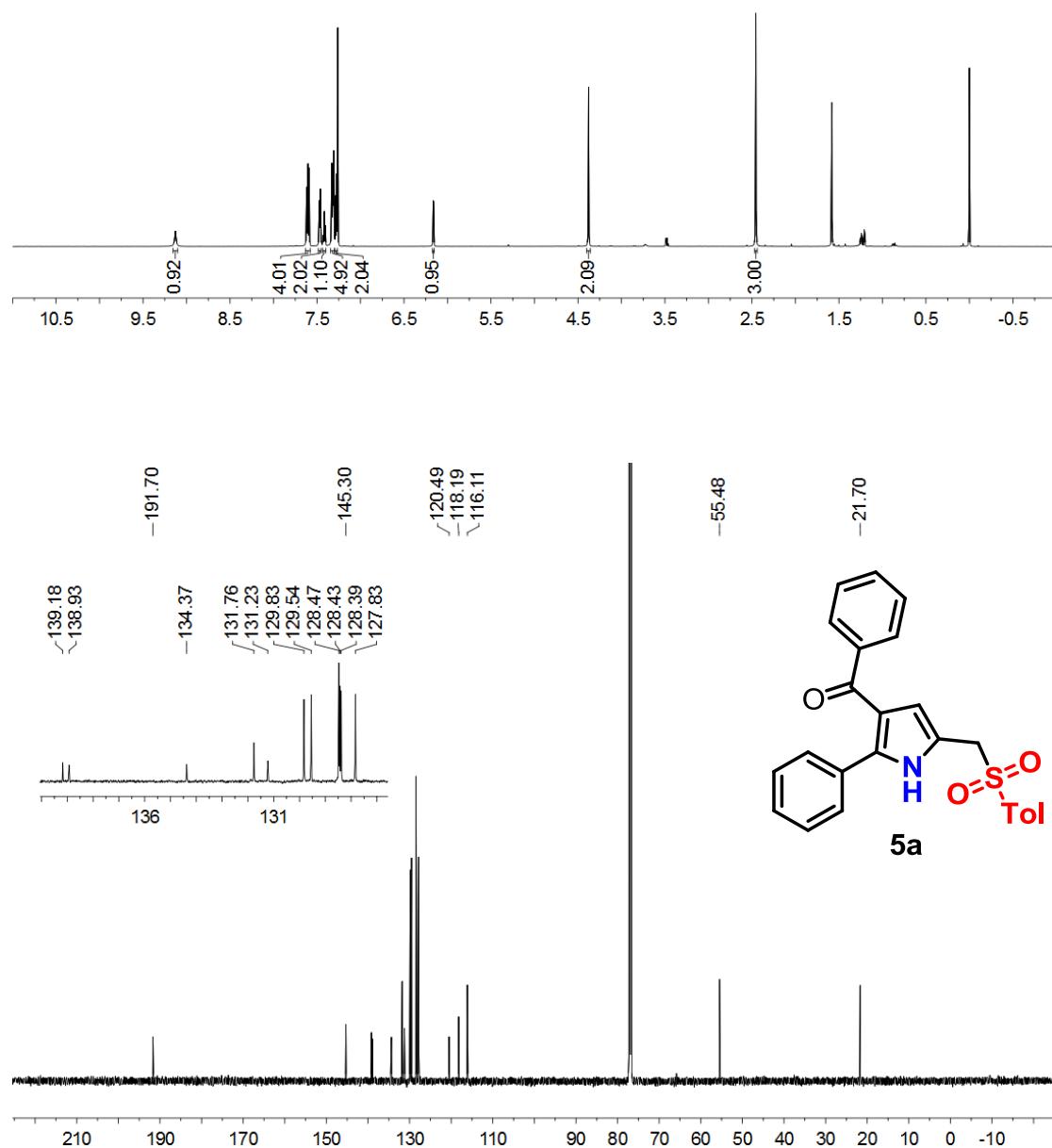
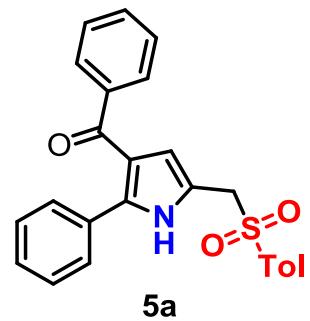
3y ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



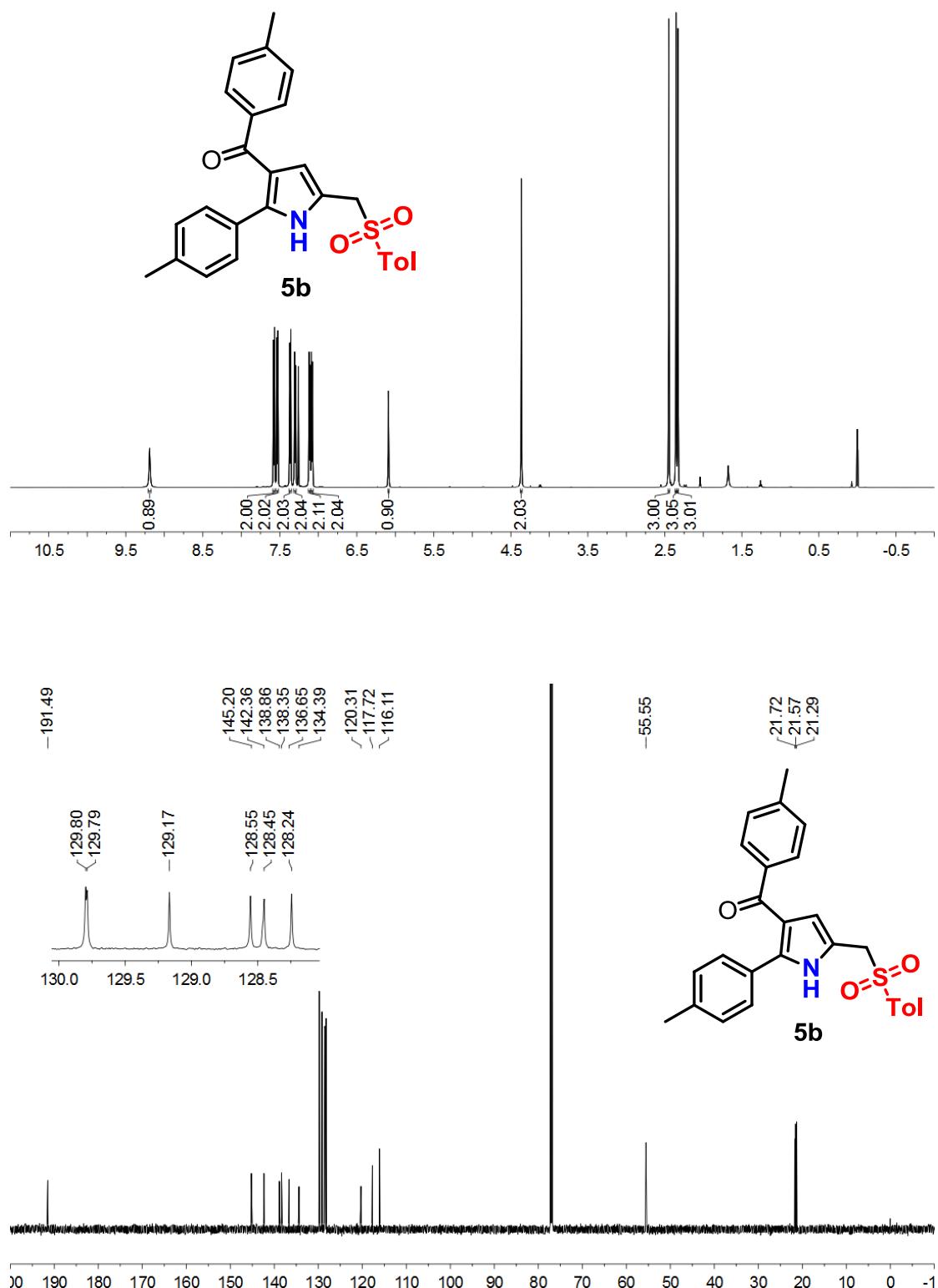
3z ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



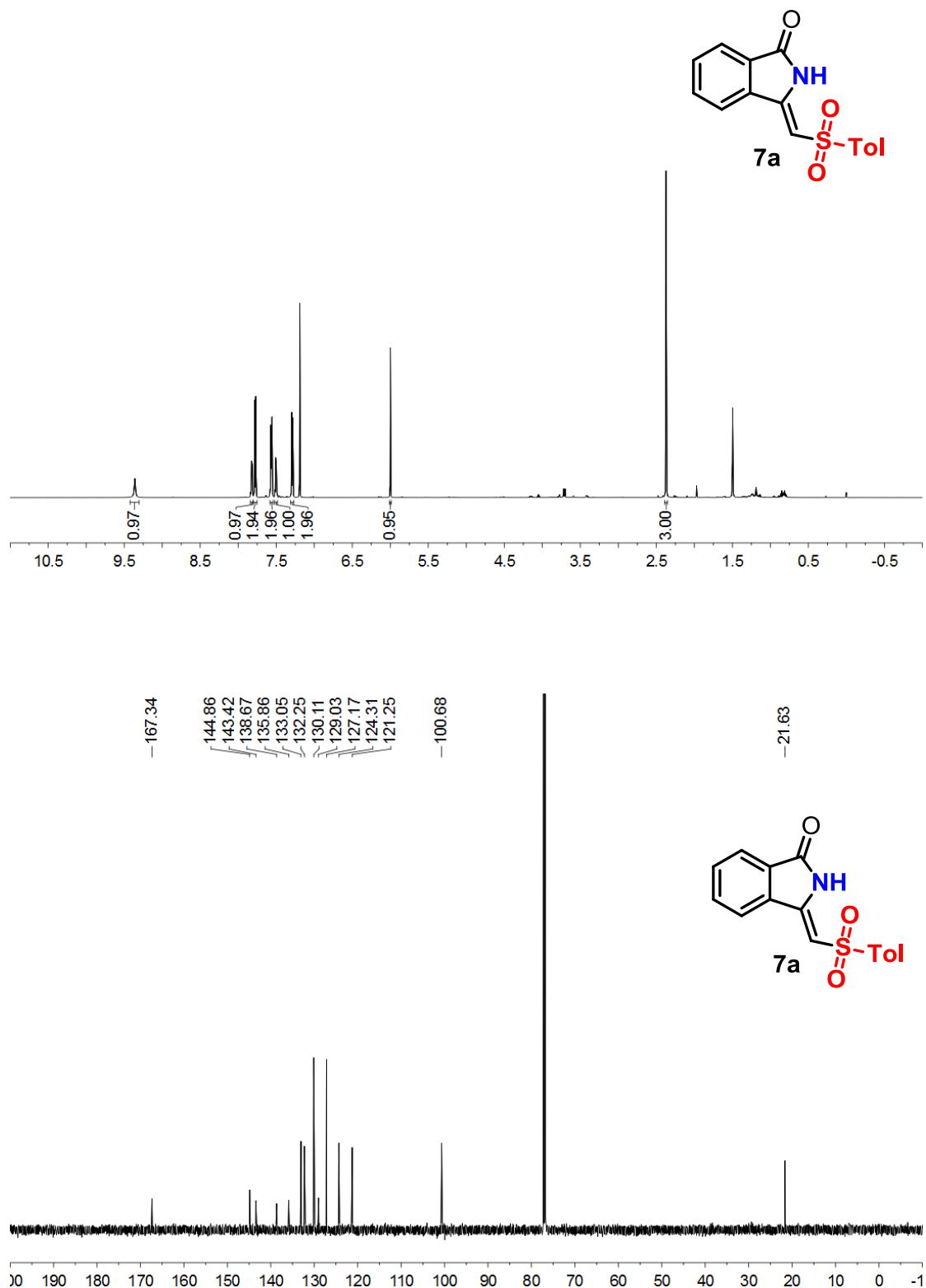
5a ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



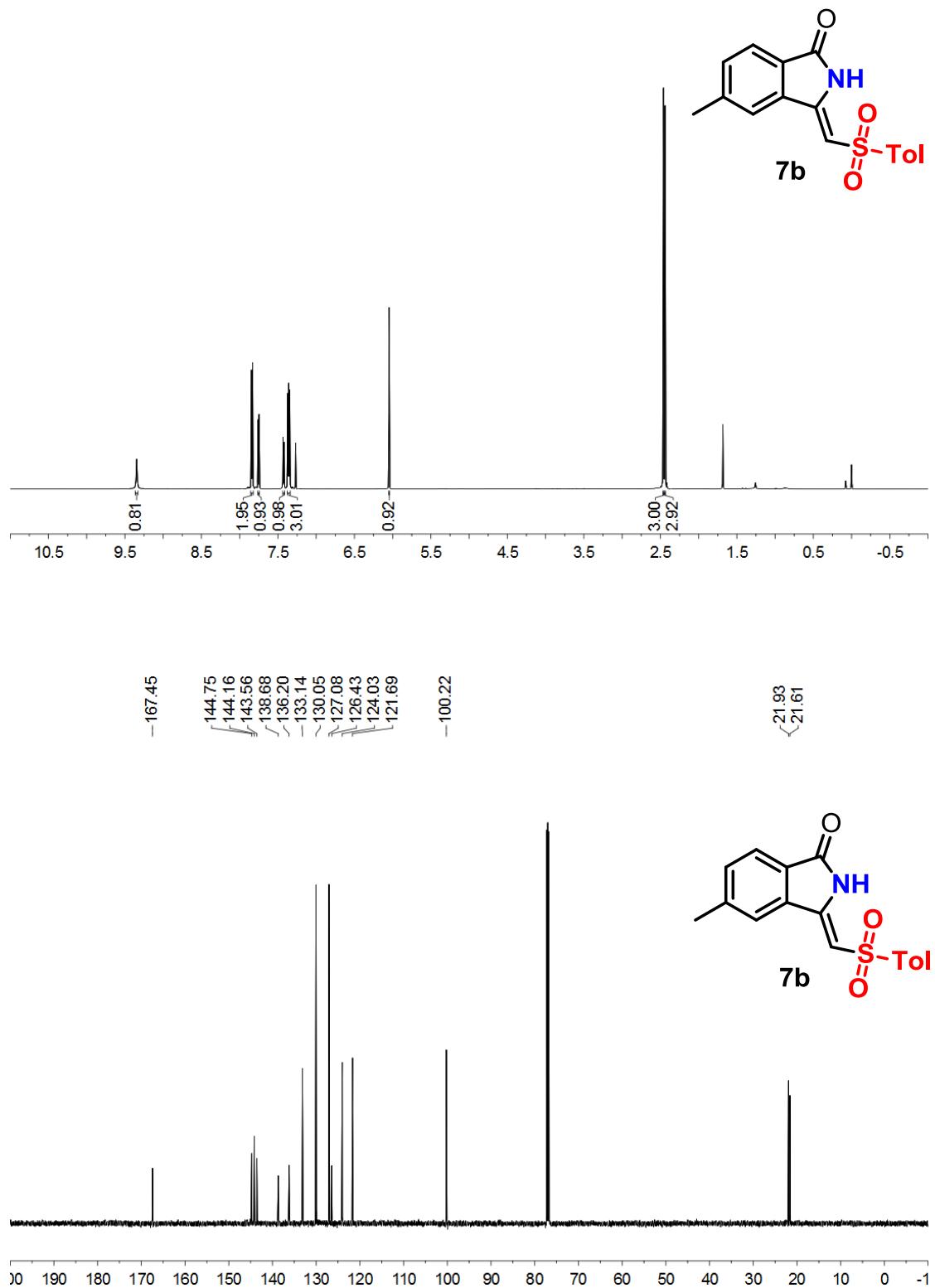
5b ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



7a ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



7b ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (150 MHz, CDCl_3)



7c ^1H NMR (600 MHz, CDCl_3) & ^{13}C NMR (125 MHz, CDCl_3)

