

Supporting Information

Construction of sulfonated spiro[5,5]trienones from sulfur dioxide via iron-catalyzed dearomative spirocyclization of biaryls

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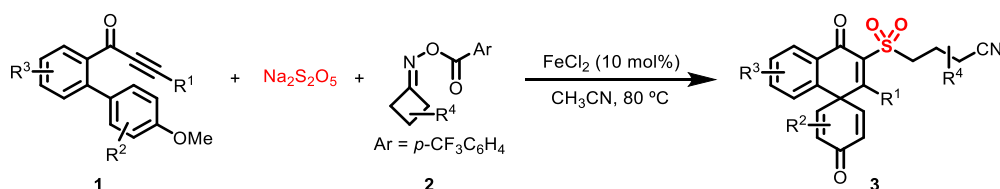
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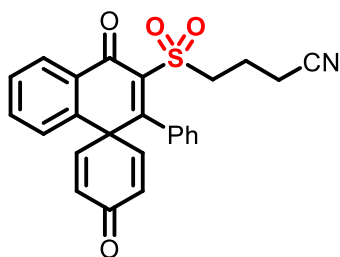
1. General Information

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrO-TOF II Instrument. X-ray single crystal diffraction data were recorded on Bruker APEX II. Biaryl ynones **1** and cycloketone oxime esters **2** were prepared according to literature procedures.^{1,2}

2. General Experimental Procedure and Characterization Data

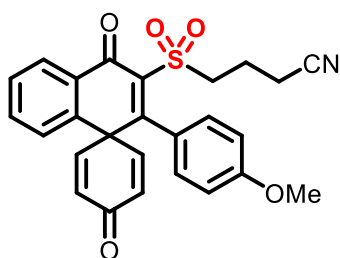


To an oven-dried flask was charged with biaryl ynones **1** (0.2 mmol), sodium metabisulfite (0.4 mmol), cycloketone oxime ester **2** (0.3 mmol) and FeCl₂ (10 mol%) under nitrogen atmosphere. Then anhydrous CH₃CN (2 mL) was added to the flask. The resulting mixture was stirred at 80 °C in an oil bath for 48 hours. After completion of reaction as monitored by TLC analysis, the mixture was cooled to room temperature, quenched with saturated aqueous NaHCO₃ (10 mL) and extracted with EA (3 × 10 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **3**.



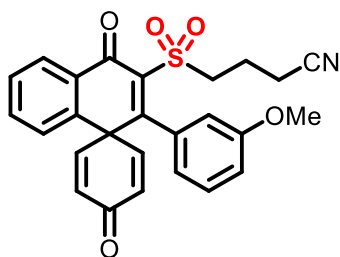
4-((4,4'-Dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3a)

Yellow solid, 86% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.20 (d, $J = 7.6$ Hz, 1H), 7.74 (t, $J = 7.1$ Hz, 1H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.31 – 7.18 (m, 6H), 7.13 (d, $J = 7.0$ Hz, 2H), 6.27 (d, $J = 9.8$ Hz, 2H), 3.62 – 3.54 (m, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.02 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.5, 180.1, 163.8, 148.4, 138.1, 137.3, 134.9, 134.4, 130.6, 130.4, 129.6, 128.8, 128.8, 127.7, 127.5, 126.7, 120.2, 54.9, 52.9, 18.7, 15.7; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{19}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 452.0932, found: 452.0934.



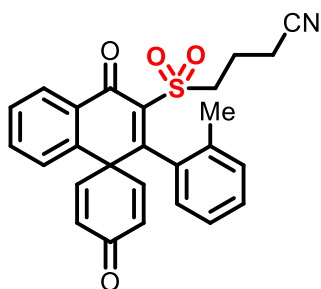
4-((2'-(4-Methoxyphenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3b)

Yellow solid, 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.65 (td, $J = 7.7, 1.5$ Hz, 1H), 7.61 – 7.56 (m, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.05 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.70 (d, $J = 10.0$ Hz, 2H), 6.38 (d, $J = 10.0$ Hz, 2H), 3.80 (s, 3H), 3.67 (t, $J = 7.3$ Hz, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.21 – 2.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.2, 179.8, 164.5, 160.7, 146.7, 138.6, 137.4, 134.7, 131.1, 129.9, 129.6, 128.5, 128.2, 128.2, 125.6, 118.4, 112.9, 55.2, 53.2, 18.5, 16.3; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 482.1038, found: 482.1034.



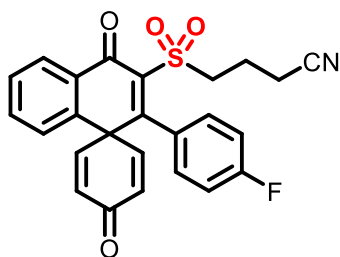
4-((2'-(3-Methoxyphenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3c)

Yellow solid, 69% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 7.7$ Hz, 1H), 7.66 (t, $J = 7.0$ Hz, 1H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.32 – 7.20 (m, 2H), 6.90 (dd, $J = 8.3, 1.8$ Hz, 1H), 6.76 – 6.60 (m, 4H), 6.38 (dd, $J = 15.9, 9.8$ Hz, 2H), 3.77 (s, 3H), 3.67 (t, $J = 7.3$ Hz, 2H), 2.55 (t, $J = 7.1$ Hz, 2H), 2.23 – 2.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.1, 179.8, 164.0, 158.4, 146.4, 138.3, 137.4, 134.7, 134.4, 131.2, 131.0, 129.9, 129.6, 128.6, 128.3, 128.2, 119.5, 118.3, 114.3, 113.7, 55.3, 55.2, 52.8, 18.5, 16.3; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 482.1038, found: 481.1037.



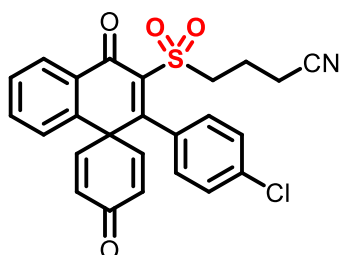
4-((4,4'-Dioxo-2'-(o-tolyl)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3d)

Light yellow solid, 43% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.69 – 7.58 (m, 2H), 7.32 – 7.23 (m, 2H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 6.88 – 6.78 (m, 2H), 6.60 (dd, $J = 9.8, 3.1$ Hz, 1H), 6.42 (dd, $J = 9.8, 1.5$ Hz, 1H), 6.27 (dd, $J = 10.1, 1.5$ Hz, 1H), 3.75 – 3.59 (m, 2H), 2.62 – 2.47 (m, 2H), 2.28 (s, 3H), 2.23 – 2.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.8, 179.8, 164.6, 147.2, 145.1, 138.5, 138.1, 134.8, 134.7, 132.3, 131.4, 131.1, 130.0, 130.0, 129.7, 129.5, 128.4, 127.7, 125.6, 124.4, 118.3, 55.0, 53.7, 21.1, 18.5, 16.3; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 466.1089, found: 466.1088.



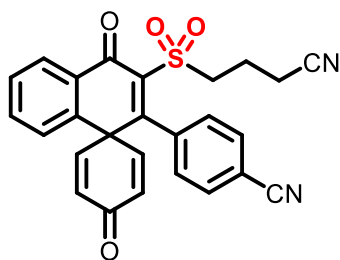
4-((2'-(4-Fluorophenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3e)

Yellow solid, 63% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.67 (td, $J = 7.7, 1.3$ Hz, 1H), 7.63 – 7.57 (m, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.12 – 7.06 (m, 2H), 7.03 (t, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 10.0$ Hz, 2H), 6.39 (d, $J = 10.0$ Hz, 2H), 3.69 (t, $J = 7.3$ Hz, 2H), 2.56 (t, $J = 7.1$ Hz, 2H), 2.22 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.8, 179.7, 163.3 (d, $J = 250.8$ Hz), 163.0, 146.2, 139.0, 137.3, 134.9, 131.4, 129.7 (d, $J = 0.9$ Hz), 129.1, 129.0, 129.0, 128.3, 128.2, 118.3, 114.8 (d, $J = 22.0$ Hz), 55.2, 52.9, 18.5, 16.4; ^{19}F NMR (376 MHz, CDCl_3) δ -110.08 – -110.25 (m); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{FNO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 470.0838, found: 470.0844.



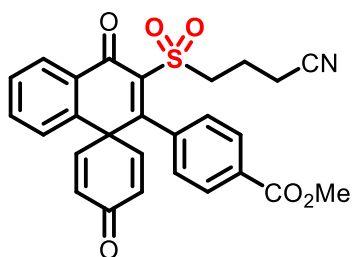
4-((2'-(4-Chlorophenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3f)

Light yellow solid, 68% yield; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.78 – 7.70 (m, 1H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.22 (d, $J = 10.0$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.31 (d, $J = 9.9$ Hz, 2H), 3.66 – 3.54 (m, 2H), 2.63 (t, $J = 7.1$ Hz, 2H), 2.03 – 1.91 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 184.5, 18.0, 162.3, 148.3, 138.0, 137.7, 134.9, 133.6, 133.2, 130.8, 130.4, 129.7, 128.8, 127.6, 126.9, 120.2, 54.9, 52.8, 18.5, 15.7; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{ClNO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 486.0543, found: 486.0544.



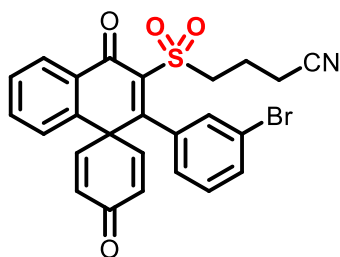
4-(3'-((3-Cyanopropyl)sulfonyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-2'-yl)benzonitrile (3g)

Yellow solid, 59% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.67 – 7.60 (m, 3H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 6.70 (d, $J = 9.7$ Hz, 2H), 6.40 (d, $J = 9.7$ Hz, 2H), 3.71 (t, $J = 7.3$ Hz, 2H), 2.57 (t, $J = 7.0$ Hz, 2H), 2.24 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.3, 179.8, 161.4, 148.0, 139.3, 137.9, 137.4, 135.1, 130.9, 130.7, 130.3, 129.8, 129.0, 128.8, 127.6, 120.2, 119.0, 111.4, 54.8, 52.4, 18.5, 15.7; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 477.0885, found: 477.0883.



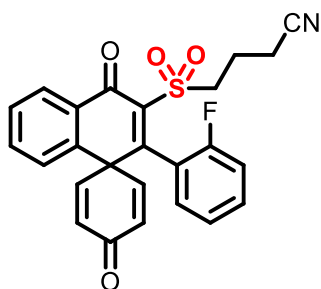
Methyl 4-(3'-((3-cyanopropyl)sulfonyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-2'-yl)benzoate (3h)

Yellow solid, 63% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.68 (td, $J = 7.7, 1.4$ Hz, 1H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.17 (d, $J = 8.3$ Hz, 2H), 6.72 (d, $J = 10.0$ Hz, 2H), 6.36 (d, $J = 10.0$ Hz, 2H), 3.91 (s, 3H), 3.67 (t, $J = 7.3$ Hz, 2H), 2.53 (t, $J = 7.1$ Hz, 2H), 2.19 – 2.10 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.6, 178.5, 165.1, 161.7, 144.9, 137.5, 136.5, 136.3, 133.9, 130.4, 129.9, 128.7, 128.7, 127.4, 127.3, 127.2, 126.2, 117.2, 54.1, 51.4, 51.3, 17.4, 15.3; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 510.0987, found: 510.0989.



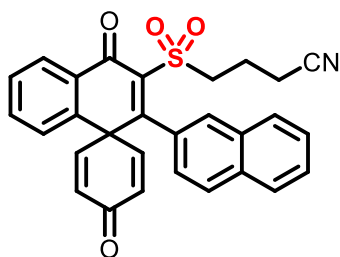
4-((2'-(3-Bromophenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3i)

Yellow solid, 66% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.74 (dd, $J = 11.0, 4.1$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.40 (s, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.26 – 7.18 (m, 3H), 7.17 – 7.12 (m, 1H), 6.38 – 6.25 (m, 2H), 3.65 – 3.54 (m, 2H), 2.68 – 2.59 (m, 2H), 2.03 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.5, 180.0, 161.5, 148.2, 138.0, 137.6, 136.4, 135.0, 131.6, 130.7, 130.4, 130.3, 129.7, 128.9, 127.6, 126.9, 120.2, 120.0, 54.9, 52.7, 18.6, 15.7; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{BrNO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 530.0038, found: 530.0031.



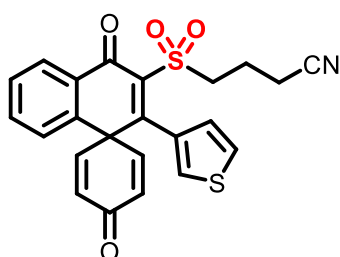
4-((2'-(2-Fluorophenyl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3j)

White solid, 62% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.22 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.76 (td, $J = 7.7, 1.4$ Hz, 1H), 7.72 – 7.66 (m, 1H), 7.41 – 7.34 (m, 1H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.27 (dd, $J = 9.9, 3.0$ Hz, 1H), 7.17 – 7.05 (m, 4H), 6.37 – 6.27 (m, 2H), 3.60 (t, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.07 – 1.88 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.3, 179.6, 158.2 (d, $J = 243.4$ Hz), 157.7, 148.0, 147.6, 138.7, 138.2, 135.0, 131.4 (d, $J = 8.2$ Hz), 130.8, 130.7, 130.2, 13.0 (d, $J = 2.0$ Hz), 129.8, 129.0, 127.6, 122.8 (d, $J = 2.7$ Hz), 121.5 (d, $J = 16.6$ Hz), 120.2, 114.9 (d, $J = 21.5$ Hz), 54.8, 53.1, 18.7, 15.6; ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -110.13 – -110.50 (m); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{FNO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 470.0838, found: 470.0845.



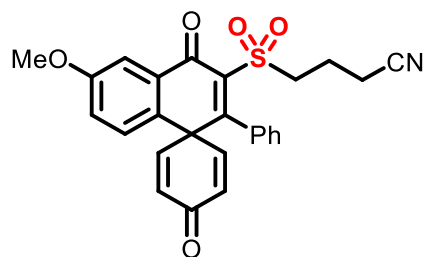
4-((2'-(Naphthalen-2-yl)-4,4'-dioxo-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3k)

Yellow solid, 72% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.25 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.94 – 7.88 (m, 1H), 7.87 – 7.82 (m, 1H), 7.80 (d, $J = 8.6$ Hz, 1H), 7.76 (td, $J = 7.7, 1.5$ Hz, 1H), 7.72 – 7.64 (m, 2H), 7.58 – 7.50 (m, 2H), 7.39 – 7.26 (m, 4H), 6.31 – 6.23 (m, 2H), 3.66 – 3.57 (m, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.06 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.5, 180.1, 163.7, 148.5, 148.5, 138.2, 137.7, 134.9, 132.9, 132.2, 131.4, 130.7, 130.6, 130.5, 129.7, 128.8, 128.6, 128.1, 127.6, 127.1, 126.9, 126.5, 126.3, 126.0, 120.2, 54.9, 53.1, 18.7, 15.7; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{32}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 502.1089, found: 502.1089.



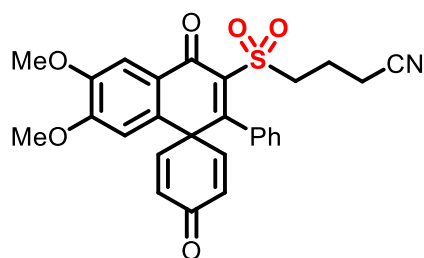
4-((4,4'-Dioxo-2'-(thiophen-3-yl)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3l)

Light yellow solid, 57% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.19 (d, $J = 7.7$ Hz, 1H), 7.77 – 7.70 (m, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 4.8, 3.0$ Hz, 1H), 7.35 – 7.26 (m, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 6.98 – 6.92 (m, 1H), 6.31 (d, $J = 9.9$ Hz, 2H), 3.68 – 3.56 (m, 2H), 2.63 (t, $J = 7.1$ Hz, 2H), 2.08 – 1.90 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.7, 179.9, 160.4, 148.3, 138.3, 138.2, 134.8, 133.7, 130.5, 130.5, 129.6, 129.0, 128.8, 127.6, 124.8, 124.6, 120.3, 54.9, 52.9, 18.6, 15.7; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_4\text{S}_2\text{Na}^+$ ($\text{M}+\text{Na}^+$): 458.0497, found: 458.0493.



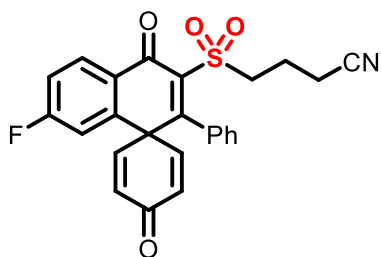
4-((6'-Methoxy-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3m)

Light yellow solid, 50% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.63 (d, $J = 2.8$ Hz, 1H), 7.33 (dd, $J = 8.8, 2.9$ Hz, 1H), 7.30 – 7.22 (m, 3H), 7.20 (d, $J = 8.8$ Hz, 1H), 7.14 (t, $J = 7.9$ Hz, 4H), 6.24 (d, $J = 10.0$ Hz, 2H), 3.88 (s, 3H), 3.57 (dd, $J = 8.8, 6.8$ Hz, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.02 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.6, 179.9, 163.9, 160.0, 148.5, 137.2, 134.4, 131.7, 130.5, 130.3, 130.2, 128.8, 127.7, 126.7, 122.7, 120.2, 109.6, 56.2, 54.9, 52.6, 18.7, 15.7; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 482.1038, found: 482.1041.



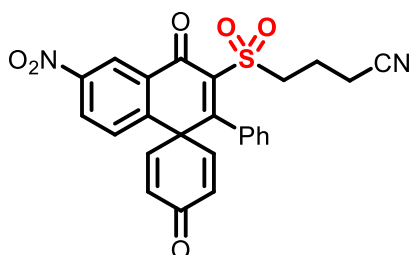
4-((6',7'-Dimethoxy-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3n)

Light yellow solid, 51% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.08 (d, $J = 7.3$ Hz, 2H), 6.69 (d, $J = 10.0$ Hz, 2H), 6.57 (s, 1H), 6.37 (d, $J = 10.0$ Hz, 2H), 4.00 (s, 3H), 3.86 (s, 3H), 3.69 (t, $J = 7.3$ Hz, 2H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.23 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.0, 178.5, 163.1, 154.8, 150.4, 146.7, 138.2, 133.1, 131.9, 131.2, 129.5, 127.2, 127.1, 123.6, 118.3, 108.8, 108.6, 56.4, 56.4, 55.2, 52.6, 18.6, 16.4; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 512.1144, found: 512.1147.



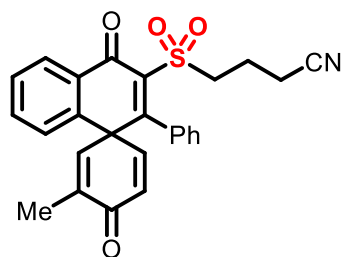
4-((7'-Fluoro-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3o)

White solid, 64% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.28 (dd, $J = 8.8, 5.9$ Hz, 1H), 7.53 (td, $J = 8.6, 2.4$ Hz, 1H), 7.32 – 7.22 (m, 3H), 7.19 (d, $J = 10.0$ Hz, 2H), 7.16 – 7.09 (m, 3H), 6.27 (d, $J = 9.9$ Hz, 2H), 3.64 – 3.52 (m, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.02 – 1.90 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 184.2, 179.1, 165.7 (d, $J = 254.8$ Hz), 164.5, 147.5, 141.7 (d, $J = 9.0$ Hz), 137.2, 134.2, 131.2, 131.1, 128.8, 127.7, 127.4 (d, $J = 2.2$ Hz), 126.7, 120.2, 117.7 (d, $J = 22.5$ Hz), 115.2 (d, $J = 23.4$ Hz), 54.9, 52.8, 18.6, 15.6; ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -103.09 – -103.25 (m); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{FNO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 470.0838, found: 470.0843.



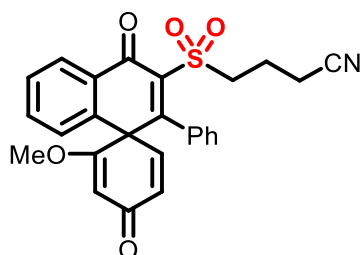
4-((6'-Nitro-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3p)

Yellow solid, 25% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.08 (d, $J = 2.3$ Hz, 1H), 8.45 (dd, $J = 8.7, 2.4$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.10 (d, $J = 7.4$ Hz, 2H), 6.71 (d, $J = 9.9$ Hz, 2H), 6.45 (d, $J = 9.9$ Hz, 2H), 3.68 (t, $J = 7.2$ Hz, 2H), 2.56 (t, $J = 7.1$ Hz, 2H), 2.23 – 2.15 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.2, 178.2, 164.6, 148.5, 144.7, 143.5, 138.4, 132.5, 132.2, 131.1, 130.3, 130.1, 128.4, 127.5, 126.9, 123.5, 118.3, 55.2, 52.7, 18.4, 16.3; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 497.0783, found: 497.0787.



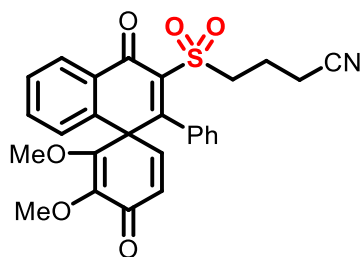
4-((3-Methyl-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3q)

White solid, 80% yield; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.19 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.72 (td, $J = 7.7, 1.4$ Hz, 1H), 7.69 – 7.62 (m, 1H), 7.31 – 7.20 (m, 4H), 7.19 – 7.10 (m, 2H), 7.07 (d, $J = 8.2$ Hz, 1H), 6.96 (dd, $J = 2.8, 1.4$ Hz, 1H), 6.23 (d, $J = 9.8$ Hz, 1H), 3.62 – 3.54 (m, 2H), 2.63 (t, $J = 7.1$ Hz, 2H), 2.02 – 1.92 (m, 2H), 1.71 (d, $J = 1.0$ Hz, 3H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 185.0, 180.2, 164.5, 148.0, 143.2, 138.9, 137.4, 137.1, 134.8, 134.3, 130.3, 129.5, 128.8, 128.6, 127.9, 127.5, 126.6, 126.4, 120.2, 54.9, 53.1, 18.7, 15.7, 15.7; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 466.1089, found: 466.1082.



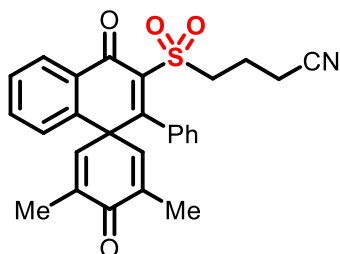
4-((2-Methoxy-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3r)

Light yellow solid, 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.64 (td, $J = 7.6, 1.4$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.42 – 7.36 (m, 1H), 7.32 (q, $J = 7.3$ Hz, 2H), 7.24 (d, $J = 7.9$ Hz, 1H), 7.14 – 7.08 (m, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.45 (d, $J = 9.7$ Hz, 1H), 6.32 (dd, $J = 9.7, 0.9$ Hz, 1H), 5.60 (s, 1H), 3.75 – 3.67 (m, 1H), 3.64 – 3.55 (m, 4H), 2.53 (t, $J = 7.1$ Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.5, 179.0, 170.6, 162.9, 140.8, 137.8, 137.0, 133.7, 131.6, 129.2, 128.9, 128.6, 128.4, 126.9, 126.5, 126.2, 126.1, 126.0, 125.5, 117.3, 104.7, 55.3, 54.3, 54.1, 17.7, 15.2; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 482.1038, found: 482.1036.



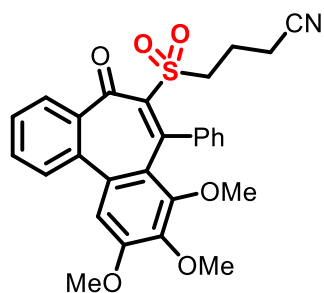
4-((2,3-Dimethoxy-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3s)

Light yellow solid, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.65 (td, $J = 7.7, 1.4$ Hz, 1H), 7.58 (t, $J = 7.1$ Hz, 1H), 7.43 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.29 – 7.25 (m, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 7.11 (d, $J = 7.7$ Hz, 1H), 6.38 (d, $J = 9.7$ Hz, 1H), 6.31 (d, $J = 9.7$ Hz, 1H), 3.84 (s, 3H), 3.75 – 3.66 (m, 1H), 3.63 – 3.54 (m, 1H), 3.45 (s, 3H), 2.53 (t, $J = 7.2$ Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.6, 180.1, 164.2, 158.4, 141.0, 140.4, 138.8, 138.2, 134.6, 132.7, 130.5, 130.3, 129.6, 129.4, 128.0, 127.4, 127.2, 127.1, 127.0, 126.8, 118.3, 61.5, 60.7, 57.2, 55.1, 18.7, 16.3; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 512.1144, found: 512.1143.



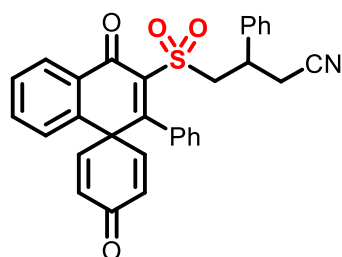
4-((3,5-Dimethyl-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)butanenitrile (3t)

White solid, 61% yield; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.20 – 8.15 (m, 1H), 7.73 – 7.67 (m, 1H), 7.63 (t, $J = 7.1$ Hz, 1H), 7.29 – 7.17 (m, 4H), 7.04 (d, $J = 6.7$ Hz, 2H), 6.90 (s, 2H), 3.62 – 3.53 (m, 2H), 2.62 (t, $J = 7.1$ Hz, 2H), 2.00 – 1.92 (m, 2H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 185.4, 180.3, 165.3, 142.8, 139.7, 137.0, 136.9, 134.8, 134.3, 130.2, 129.3, 128.8, 128.5, 127.7, 127.4, 126.2, 120.2, 54.8, 52.6, 18.79, 16.0, 15.7; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 480.1245, found: 480.1245.



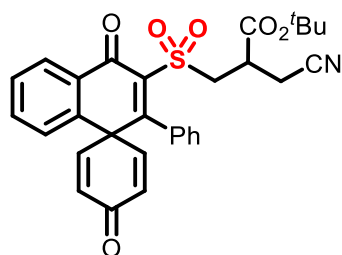
4-((8,9,10-Trimethoxy-5-oxo-7-phenyl-5H-dibenzo[*a,c*][7]annulen-6-yl)sulfonyl)butanenitrile (3u)

Yellow solid, 86% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.8$ Hz, 1H), 7.72 – 7.65 (m, 1H), 7.58 – 7.52 (m, 2H), 7.49 – 7.19 (m, 5H), 6.87 (s, 1H), 3.96 (s, 3H), 3.74 (s, 3H), 3.03 (s, 3H), 2.98 (dt, $J = 14.2, 7.2$ Hz, 1H), 2.64 (dt, $J = 14.1, 7.0$ Hz, 1H), 2.36 – 2.18 (m, 2H), 1.79 – 1.64 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.9, 155.1, 153.2, 147.4, 144.5, 141.9, 139.0, 137.9, 135.7, 134.7, 131.6, 129.2, 128.8, 127.9, 127.9, 125.4, 122.1, 118.1, 108.6, 60.6, 59.6, 56.1, 54.2, 18.7, 16.0; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 526.1300, found: 526.1298.



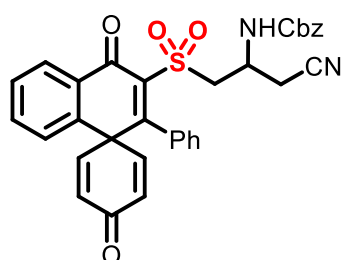
4-((4,4'-Dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)-3-phenylbutanenitrile (3aa)

Yellow solid, 56% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.66 – 7.54 (m, 2H), 7.42 – 7.35 (m, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.16 (m, 2H), 7.07 – 7.02 (m, 1H), 6.90 (d, $J = 8.5$ Hz, 1H), 6.57 (dd, $J = 10.0, 3.0$ Hz, 1H), 6.38 – 6.26 (m, 2H), 6.22 (dd, $J = 10.0, 1.4$ Hz, 1H), 4.40 (dd, $J = 14.1, 7.0$ Hz, 1H), 3.74 – 3.61 (m, 2H), 2.79 – 2.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.9, 179.8, 163.2, 146.7, 146.0, 138.5, 138.4, 137.3, 134.6, 133.0, 131.5, 130.6, 129.7, 129.6, 129.5, 129.2, 128.3, 128.2, 128.0, 127.9, 127.7, 127.4, 127.0, 126.1, 117.1, 60.0, 52.6, 37.2, 25.0; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 528.1245, found: 528.1245.



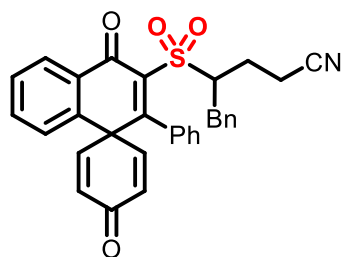
***tert*-Butyl 3-cyano-2-(((4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)methyl)propanoate (3ab)**

Yellow solid, 37% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.65 (td, $J = 7.7, 1.5$ Hz, 1H), 7.62 – 7.57 (m, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.27 (m, 3H), 7.13 – 7.05 (m, 2H), 6.76 – 6.68 (m, 2H), 6.36 (dd, $J = 18.0, 9.9$ Hz, 2H), 4.15 (dd, $J = 14.6, 5.3$ Hz, 1H), 3.67 (dd, $J = 14.6, 7.5$ Hz, 1H), 3.30 – 3.21 (m, 1H), 2.88 – 2.76 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.0, 179.7, 168.6, 163.7, 146.4, 146.3, 138.7, 137.4, 134.7, 133.1, 131.3, 131.1, 129.9, 129.6, 129.6, 128.3, 128.1, 127.4, 127.3, 127.2, 126.5, 116.7, 83.8, 56.9, 52.9, 37.3, 27.8, 19.8; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{NO}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 552.1457, found: 552.1458.



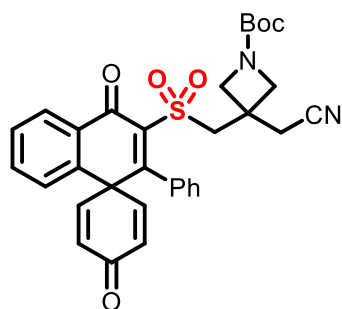
Benzyl (1-cyano-3-(((4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)propan-2-yl)carbamate (3ac)

White solid, 48% yield; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.21 (d, $J = 7.7$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.73 (t, $J = 7.0$ Hz, 1H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.39 – 7.19 (m, 8H), 7.13 (t, $J = 8.2$ Hz, 3H), 7.05 (dd, $J = 10.0, 2.7$ Hz, 1H), 6.20 (d, $J = 9.9$ Hz, 2H), 4.94 (d, $J = 12.5$ Hz, 1H), 4.76 (d, $J = 12.5$ Hz, 1H), 4.25 – 4.11 (m, 1H), 4.03 (dd, $J = 14.7, 8.8$ Hz, 1H), 3.58 (dd, $J = 14.6, 3.5$ Hz, 1H), 2.87 – 2.70 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 184.5, 179.9, 163.4, 155.7, 148.7, 147.6, 137.9, 137.7, 136.8, 134.8, 134.3, 130.9, 130.4, 130.1, 129.6, 128.8, 128.4, 128.4, 128.1, 127.6, 126.9, 126.8, 126.7, 118.3, 66.2, 58.9, 52.8, 44.4, 23.7; HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{26}\text{N}_2\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 601.1409, found: 601.1410.



4-((4,4'-Dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)-5-phenylpentanenitrile (3ad)

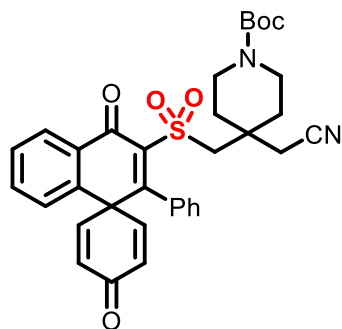
Yellow solid, 18% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 7.6$ Hz, 1H), 7.68 – 7.58 (m, 2H), 7.43 – 7.38 (m, 1H), 7.37 – 7.30 (m, 2H), 7.27 (d, $J = 7.0$ Hz, 1H), 7.25 – 7.15 (m, 5H), 7.10 (d, $J = 7.1$ Hz, 1H), 7.01 (d, $J = 8.5$ Hz, 1H), 6.65 (dd, $J = 9.9, 3.1$ Hz, 1H), 6.52 (dd, $J = 9.9, 3.1$ Hz, 1H), 6.38 (dd, $J = 9.9, 1.2$ Hz, 1H), 6.27 (dd, $J = 9.9, 1.2$ Hz, 1H), 4.62 – 4.53 (m, 1H), 3.19 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.71 (dd, $J = 14.0, 9.6$ Hz, 1H), 2.62 – 2.45 (m, 2H), 2.35 – 2.22 (m, 1H), 2.01 – 1.89 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.9, 180.0, 163.7, 146.7, 146.1, 137.6, 137.4, 135.5, 134.7, 132.9, 131.5, 130.7, 129.8, 129.6, 129.5, 129.2, 129.0, 128.3, 128.0, 127.8, 127.4, 127.3, 127.0, 126.0, 118.8, 63.9, 52.9, 35.3, 23.5, 15.4; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{25}\text{NO}_4\text{SNa}^+$ ($\text{M}+\text{Na}^+$): 542.1402, found: 542.1403.



***tert*-Butyl 3-(cyanomethyl)-3-(((4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)methyl)azetidine-1-carboxylate (3ae)**

Yellow solid, 20% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 7.5$ Hz, 1H), 7.67 (t, $J = 7.0$ Hz, 1H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.27 (m, 1H), 7.08 (d, $J = 7.4$ Hz, 2H), 6.70 (d, $J = 9.9$ Hz, 2H), 6.37 (d, $J = 9.8$ Hz, 2H), 4.10 – 3.97 (m, 4H), 3.80 (d, $J = 9.4$ Hz, 2H), 3.02 (s, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.9, 179.8, 163.9, 155.9, 146.0, 139.3, 137.4, 134.9, 132.8, 131.3, 129.8, 129.8, 129.7, 128.3, 128.2, 127.4, 126.9, 116.8, 80.5, 61.5, 52.8,

33.8, 28.3, 26.0; HRMS (ESI) calcd for $C_{32}H_{30}N_2O_6SNa^+$ ($M+Na^+$): 593.1722, found: 593.1725.



***tert*-Butyl 4-(cyanomethyl)-4-(((4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl)sulfonyl)methyl)piperidine-1-carboxylate (3af)**

Light yellow solid, 46% yield; 1H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.28 (m, 1H), 7.66 (td, $J = 7.7, 1.3$ Hz, 1H), 7.63 – 7.57 (m, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.28 (d, $J = 7.0$ Hz, 1H), 7.10 (d, $J = 7.1$ Hz, 2H), 6.72 (d, $J = 9.9$ Hz, 2H), 6.36 (d, $J = 9.9$ Hz, 2H), 3.91 – 3.71 (m, 2H), 3.69 – 3.55 (m, 2H), 3.43 – 3.31 (m, 2H), 2.75 (s, 2H), 1.88 (s, 2H), 1.62 – 1.54 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 180.0, 163.3, 154.6, 146.2, 139.7, 137.4, 134.7, 133.0, 131.3, 130.0, 129.6, 129.5, 128.3, 128.2, 127.3, 127.0, 117.3, 80.1, 59.9, 52.8, 36.5, 34.6, 28.4, 27.0; HRMS (ESI) calcd for $C_{34}H_{34}N_2O_6SNa^+$ ($M+Na^+$): 621.2035, found: 621.2034.

3. X-Ray Single Crystal Diffraction Data

The crystals of compound **3a** were grown in a mixed solution of CH₂Cl₂ and petroleum ether as the solution slowly volatilized. The X-ray crystal structure was measured on Bruker APEX II, and the data was collected by using molybdenum (Mo) irradiation source at 296.15 K. This crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2142464).

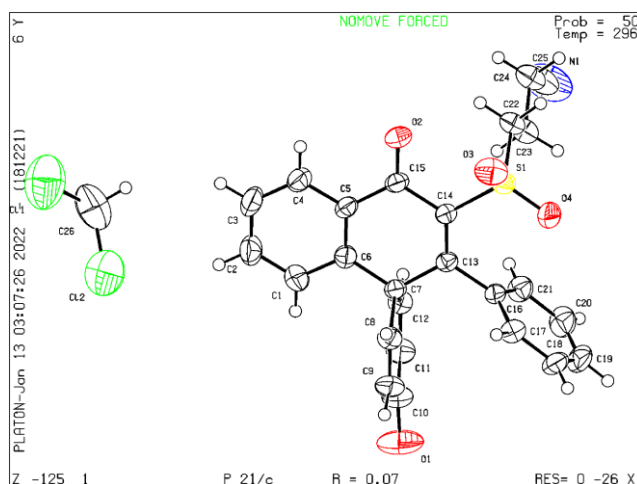


Figure S1. X-ray structure of **3a** (displacement ellipsoids are drawn at the 30% probability level).

Table S1. Crystal data and structure refinement for **3a**.

Identification code	3a
Empirical formula	C ₂₆ H ₂₁ Cl ₂ NO ₄ S
Formula weight	514.40
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.4342(12)
b/Å	23.655(3)
c/Å	11.1778(13)
α/°	90
β/°	116.254(2)
γ/°	90
Volume/Å ³	2474.4(5)
Z	4
ρ _{calc} /cm ³	1.381

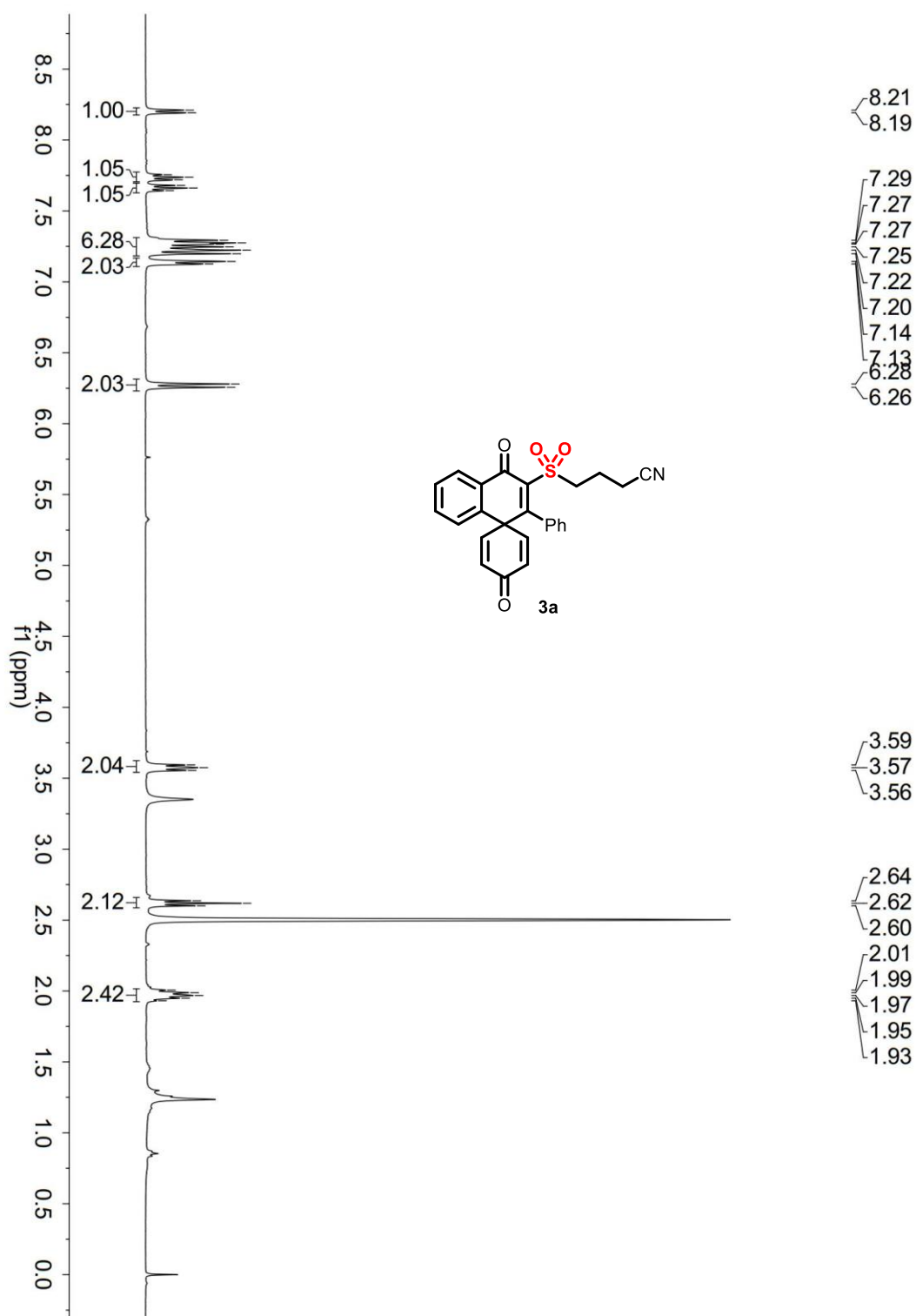
μ/mm^{-1}	0.380
F(000)	1064.0
Crystal size/ mm^3	$0.26 \times 0.24 \times 0.21$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.552 to 49.992
Index ranges	$-12 \leq h \leq 12, -27 \leq k \leq 28, -13 \leq l \leq 13$
Reflections collected	12493
Independent reflections	4345 [$R_{\text{int}} = 0.0316, R_{\text{sigma}} = 0.0347$]
Data/restraints/parameters	4345/0/307
Goodness-of-fit on F^2	1.008
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0708, wR_2 = 0.1961$
Final R indexes [all data]	$R_1 = 0.0908, wR_2 = 0.2088$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.92/-0.88

4. References

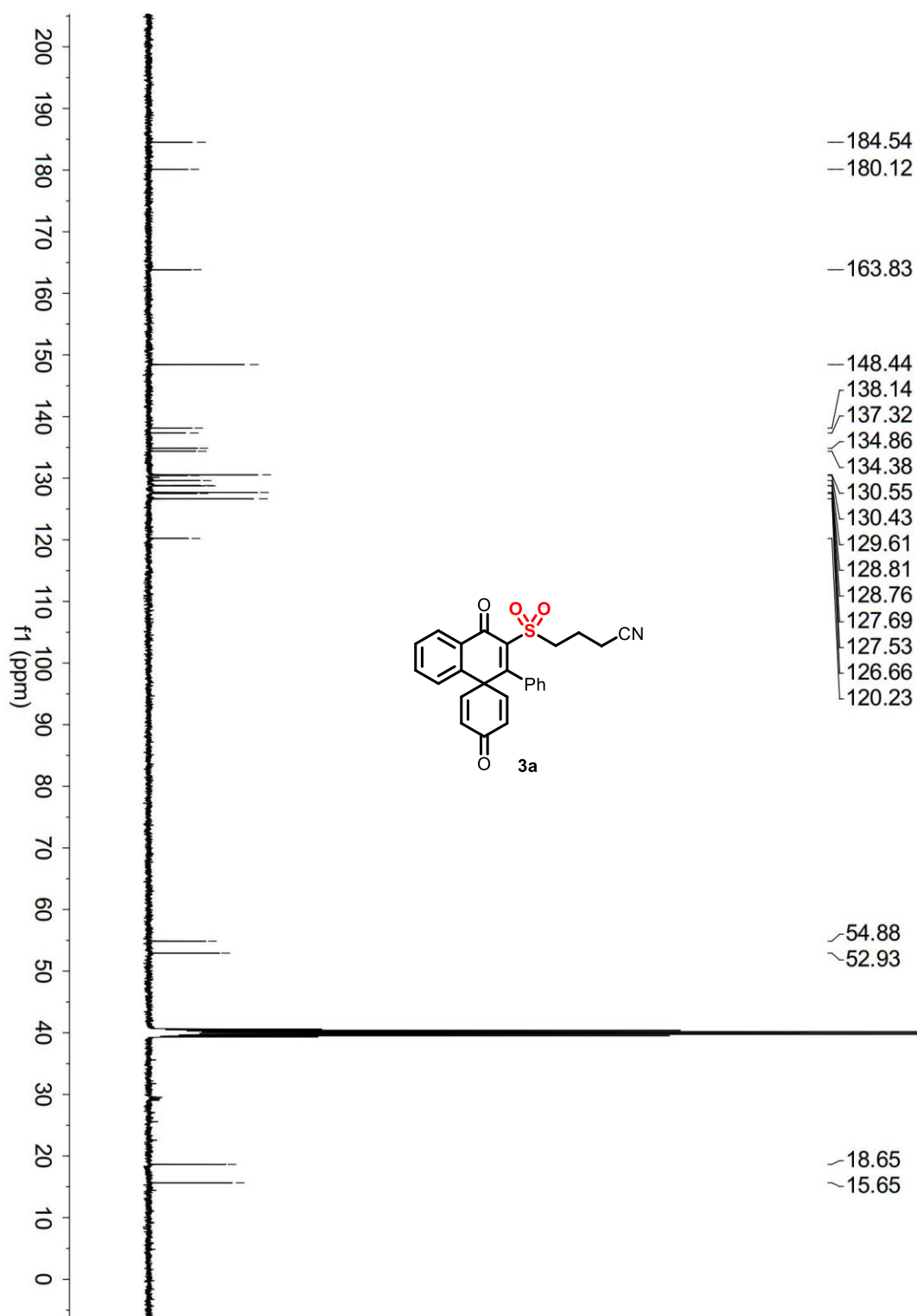
- (1) (a) Zhang, Y.; Zhang, J.; Hu, B.; Ji, M.; Ye, S.; Zhu, G. *Org. Lett.* **2018**, *20*, 2988-2992. (b) Zhang, Y.; Ma, C.; Struwe, J.; Feng, J.; Zhu, G.; Ackermann, L. *Chem. Sci.* **2021**, *12*, 10092-10096.
- (2) (a) Yu, X.-Y.; Zhao, Q.-Q.; Chen, J.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2018**, *57*, 15505-15509. (b) He, B.-Q.; Yu, X.-Y.; Wang, P.-Z.; Chen, J.-R.; Xiao, W.-J. *Chem. Commun.* **2018**, *54*, 12262-12265. (c) Zhang, J.; Li, X.; Xie, W.; Ye, S.; Wu, J. *Org. Lett.* **2019**, *21*, 4950-4954.

5. Copies of ^1H and ^{13}C NMR Spectra

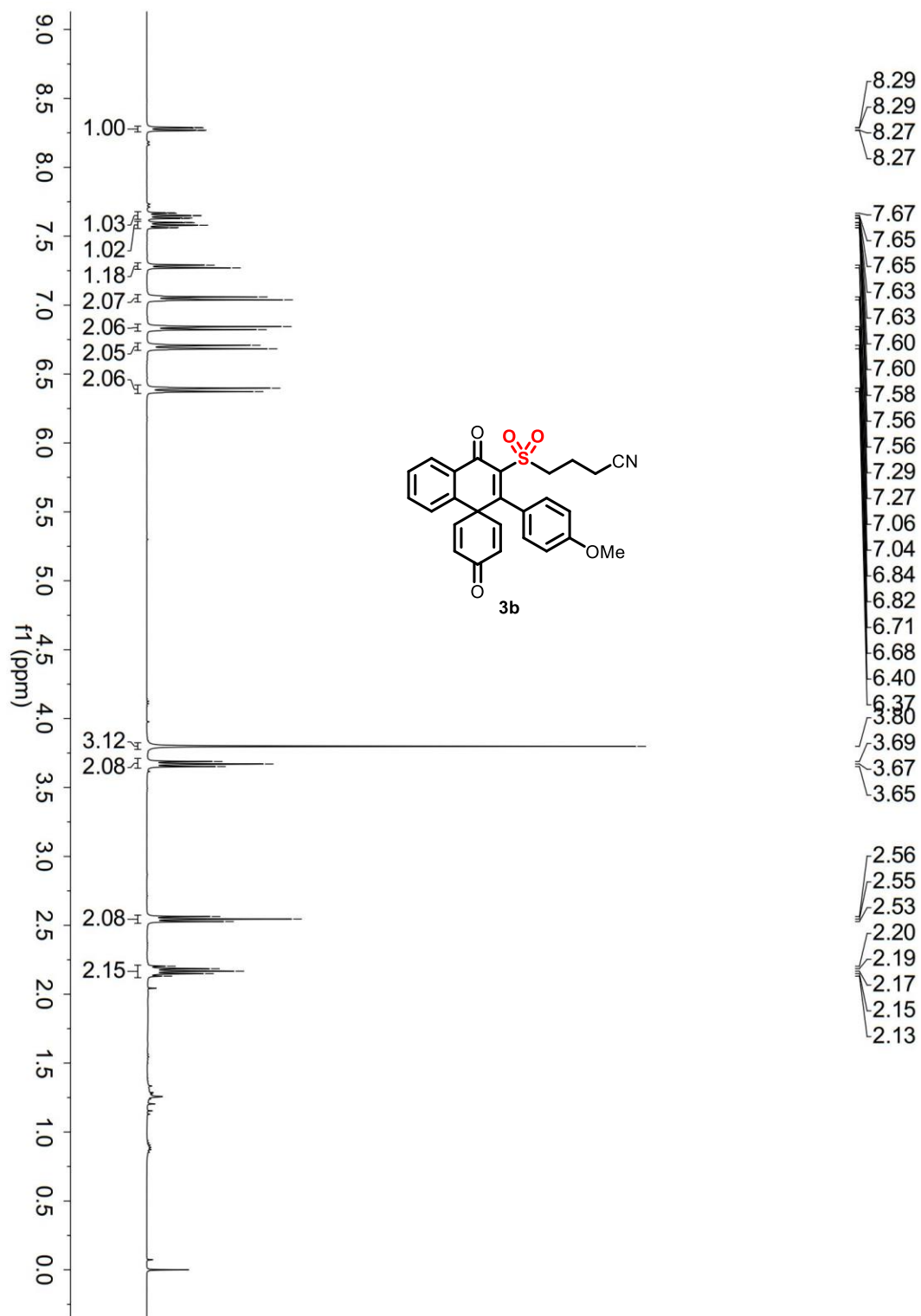
^1H NMR spectrum of compound **3a** (400 MHz, $\text{DMSO-}d_6$)



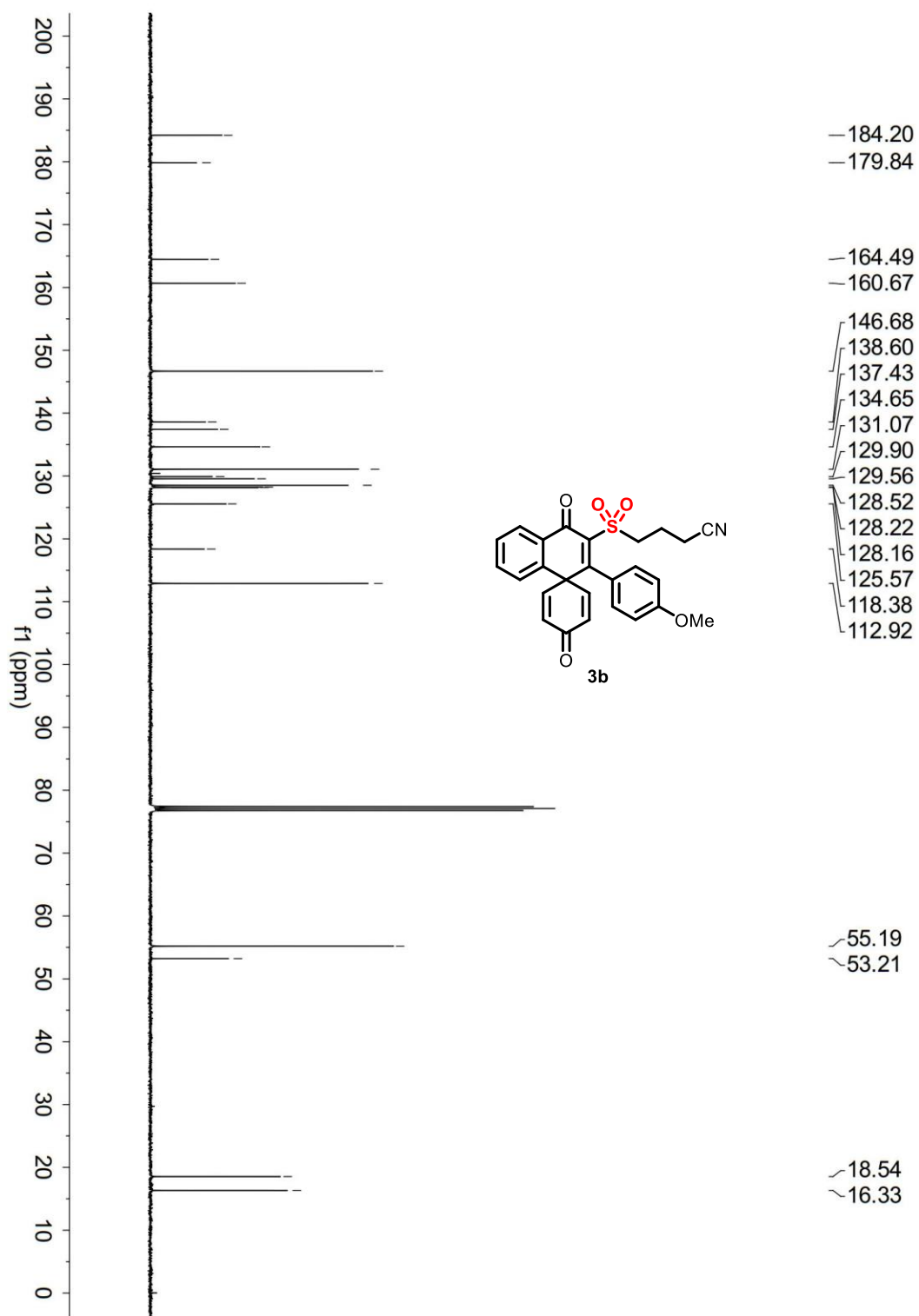
^{13}C NMR spectrum of compound **3a** (100 MHz, $\text{DMSO-}d_6$)



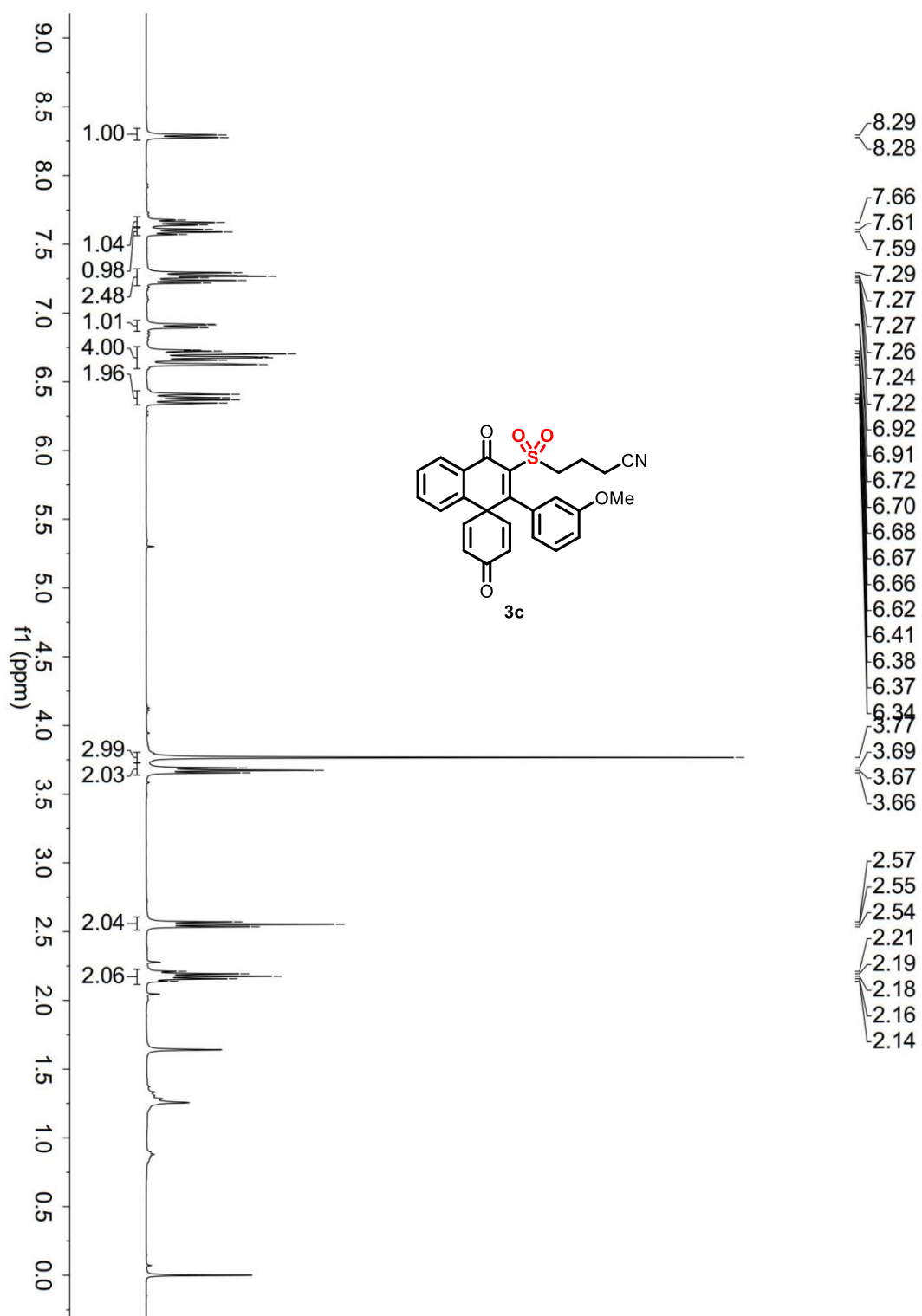
^1H NMR spectrum of compound **3b** (400 MHz, CDCl_3)



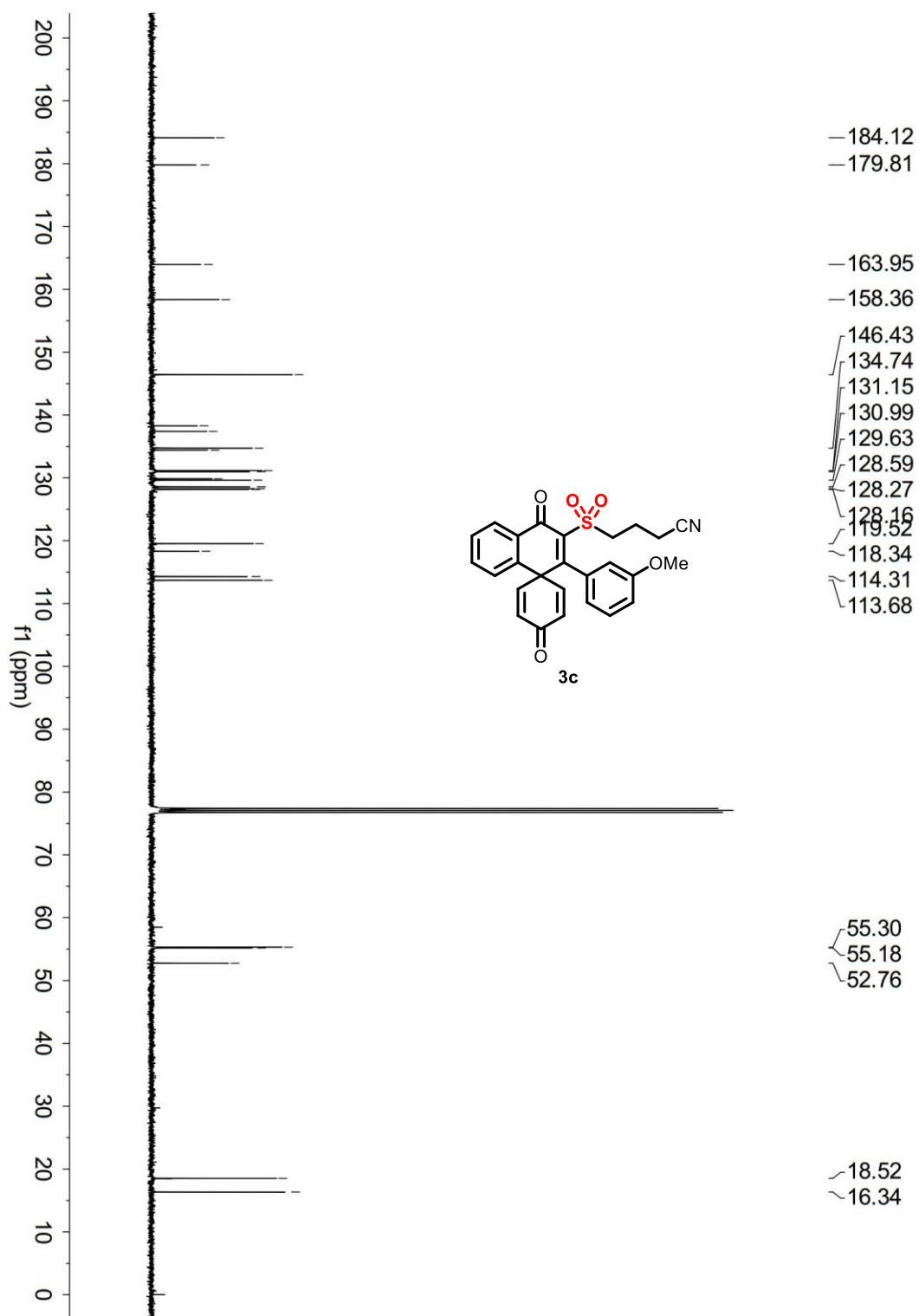
^{13}C NMR spectrum of compound **3b** (100 MHz, CDCl_3)



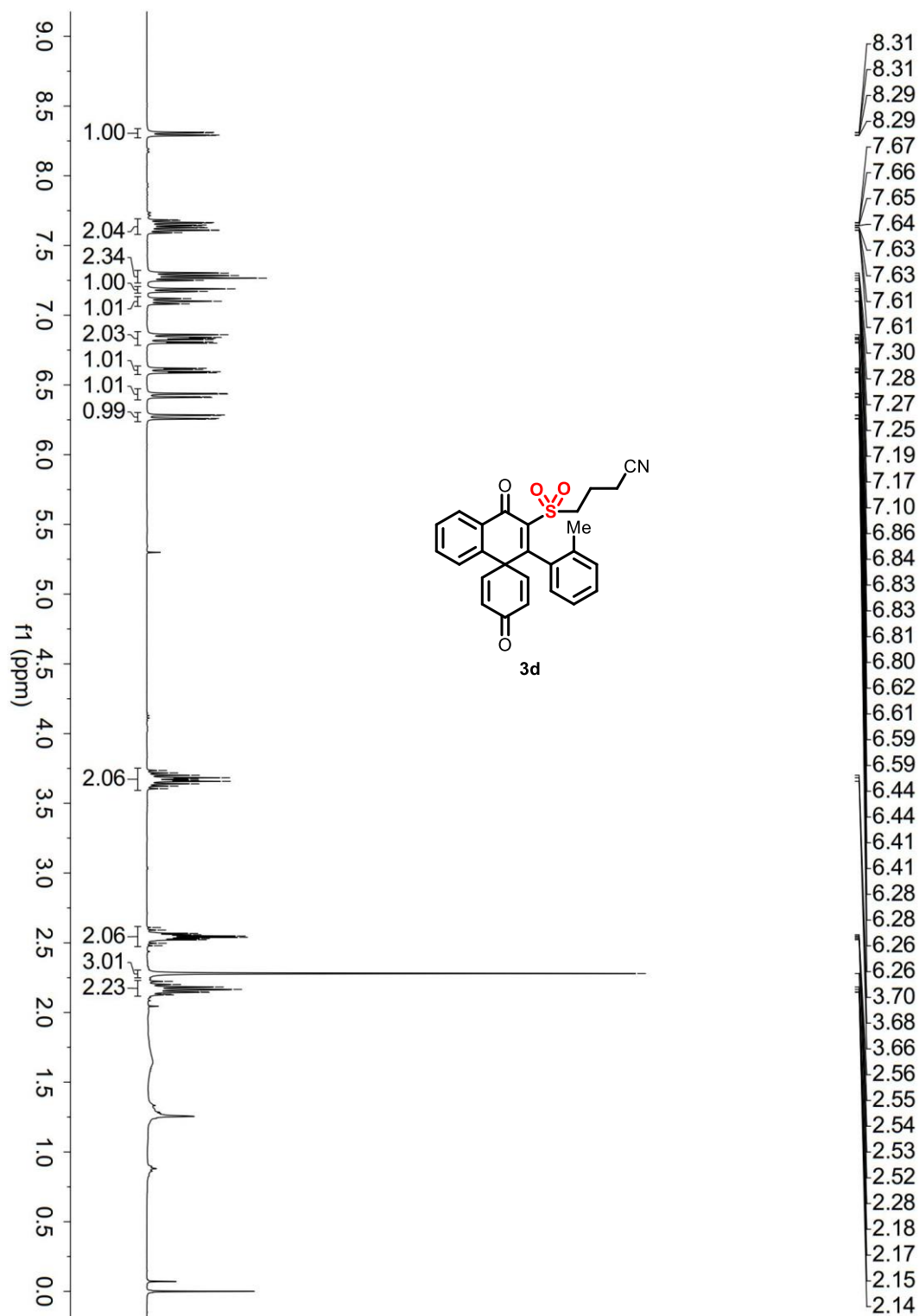
¹H NMR spectrum of compound **3c** (400 MHz, CDCl₃)



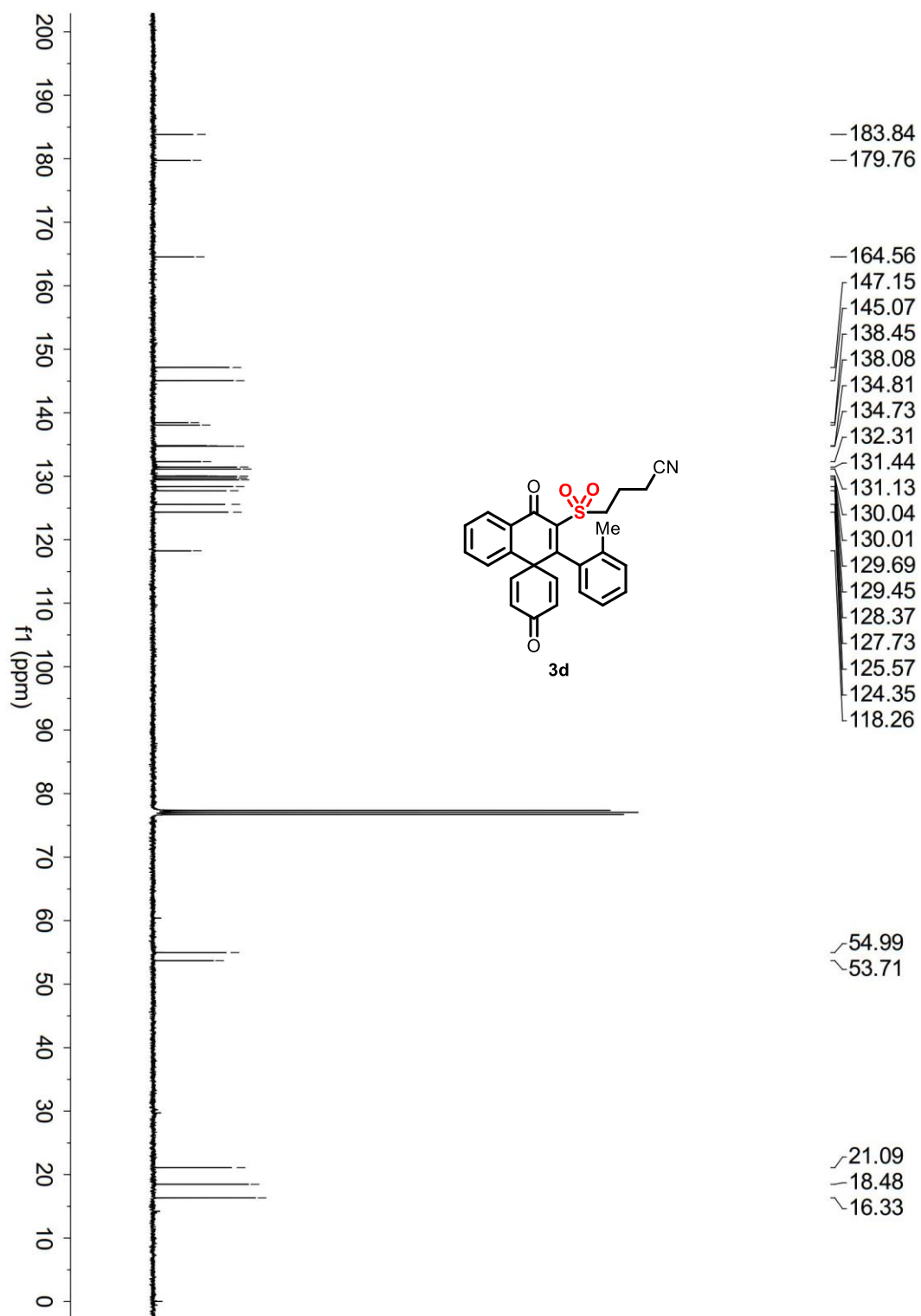
^{13}C NMR spectrum of compound **3c** (100 MHz, CDCl_3)



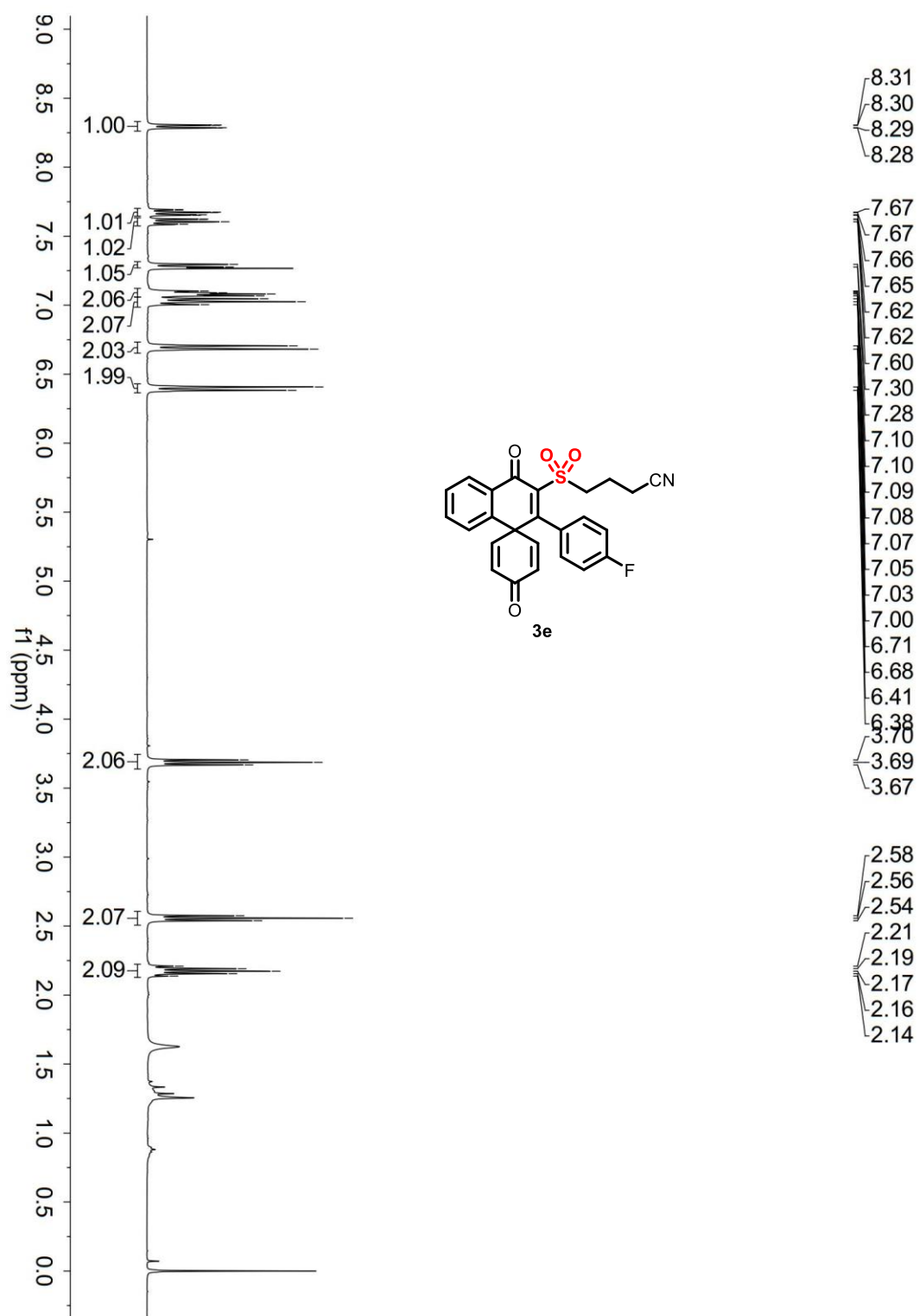
^1H NMR spectrum of compound **3d** (400 MHz, CDCl_3)



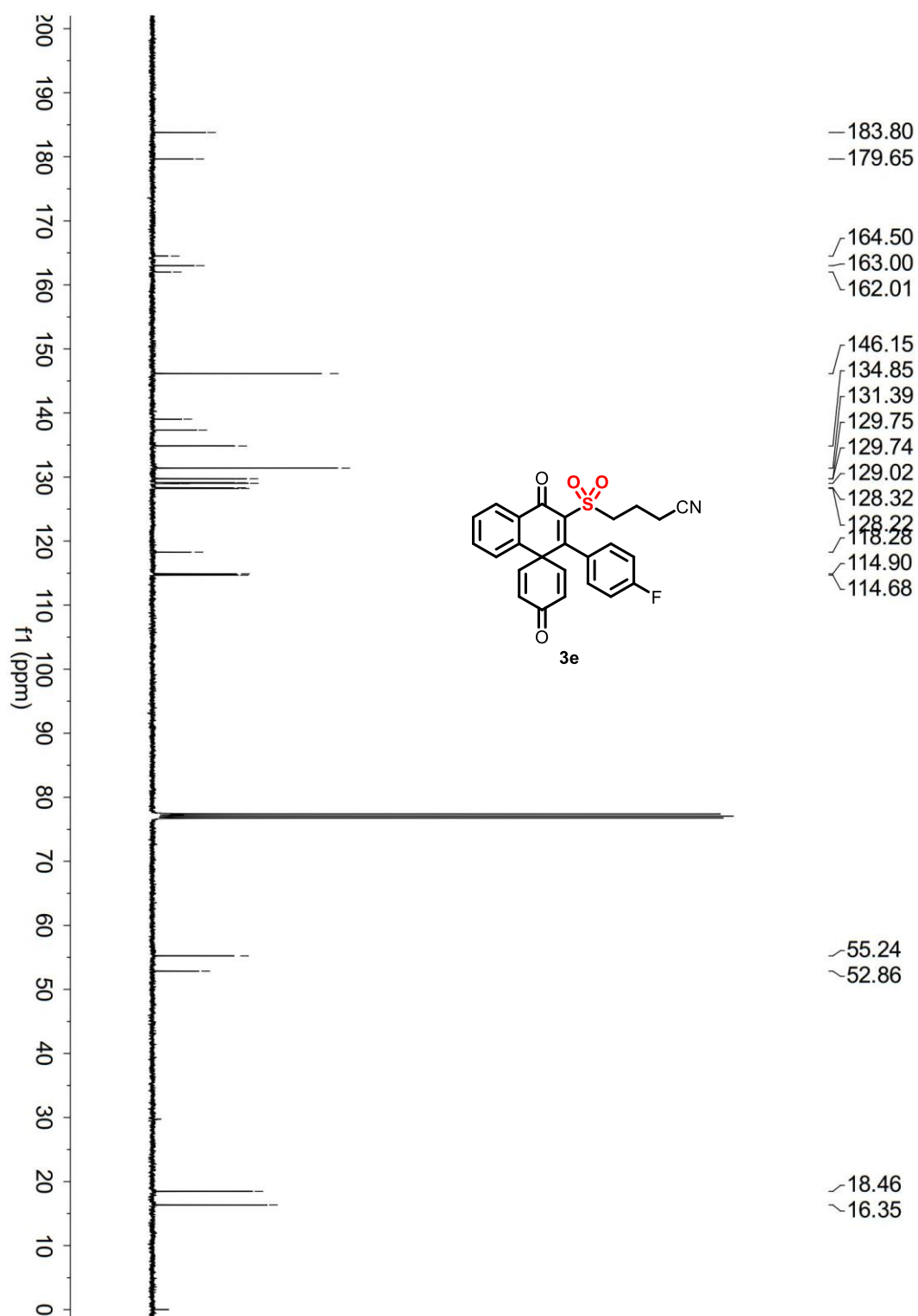
^{13}C NMR spectrum of compound **3d** (100 MHz, CDCl_3)



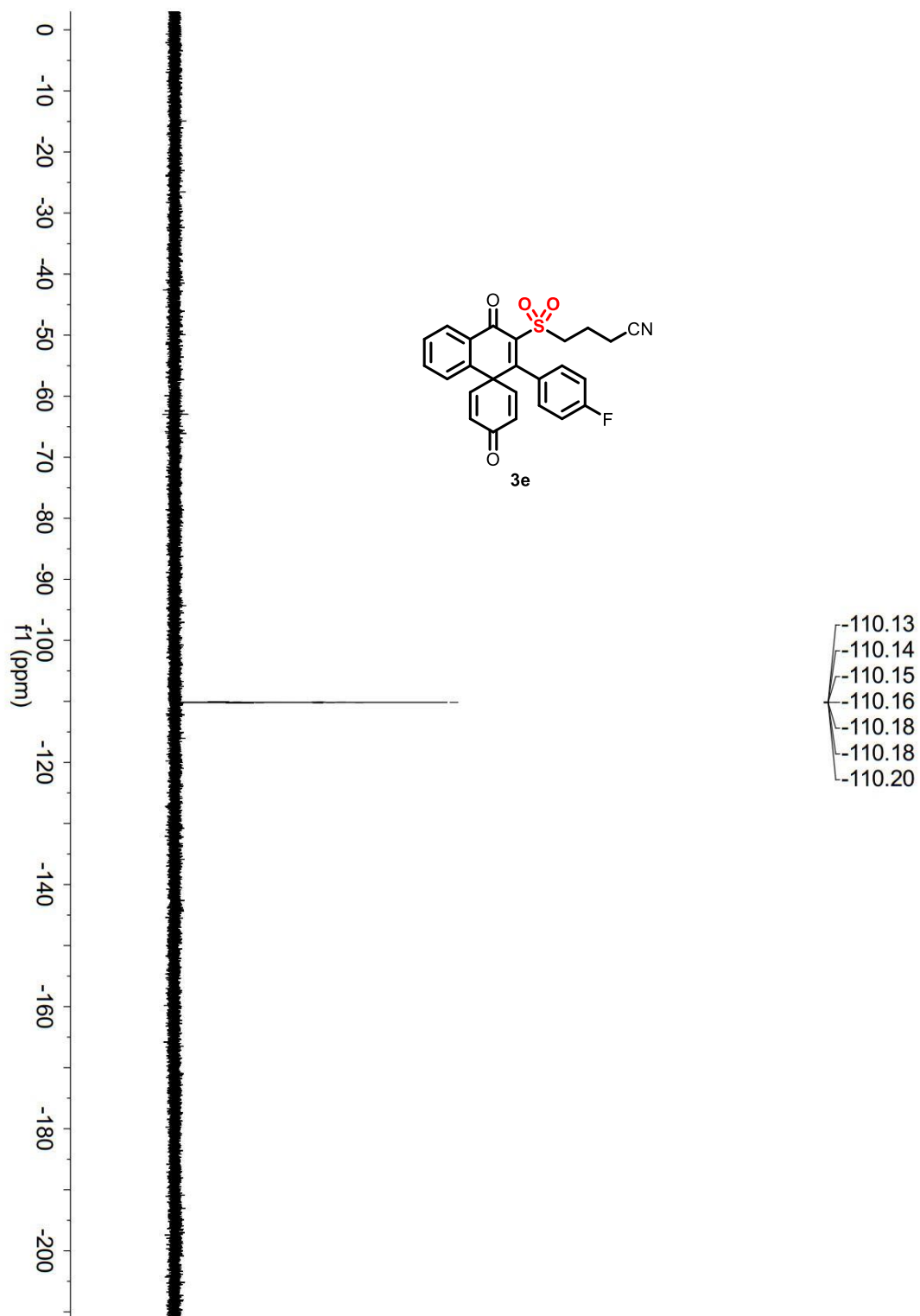
^1H NMR spectrum of compound **3e** (400 MHz, CDCl_3)



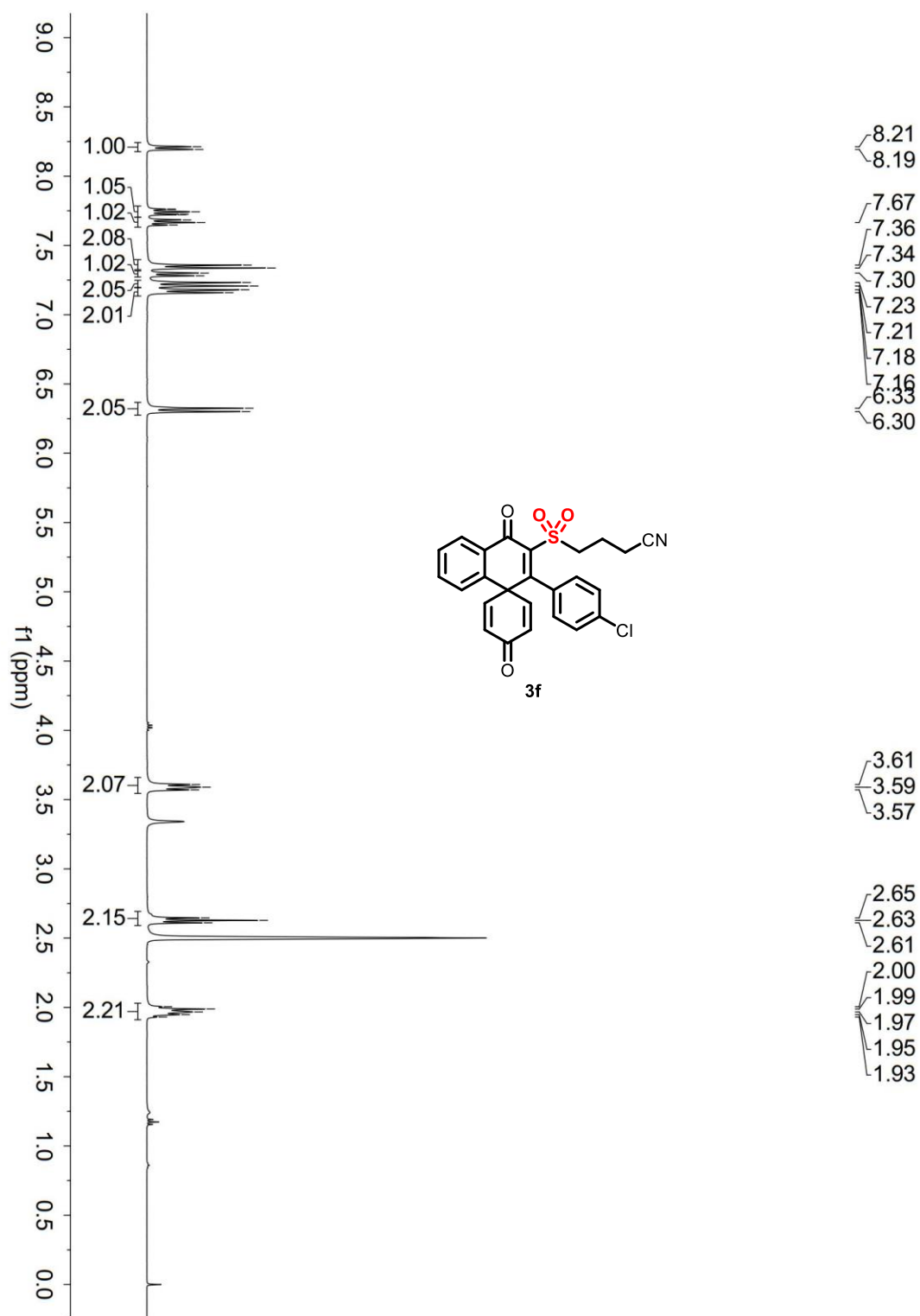
^{13}C NMR spectrum of compound **3e** (100 MHz, CDCl_3)



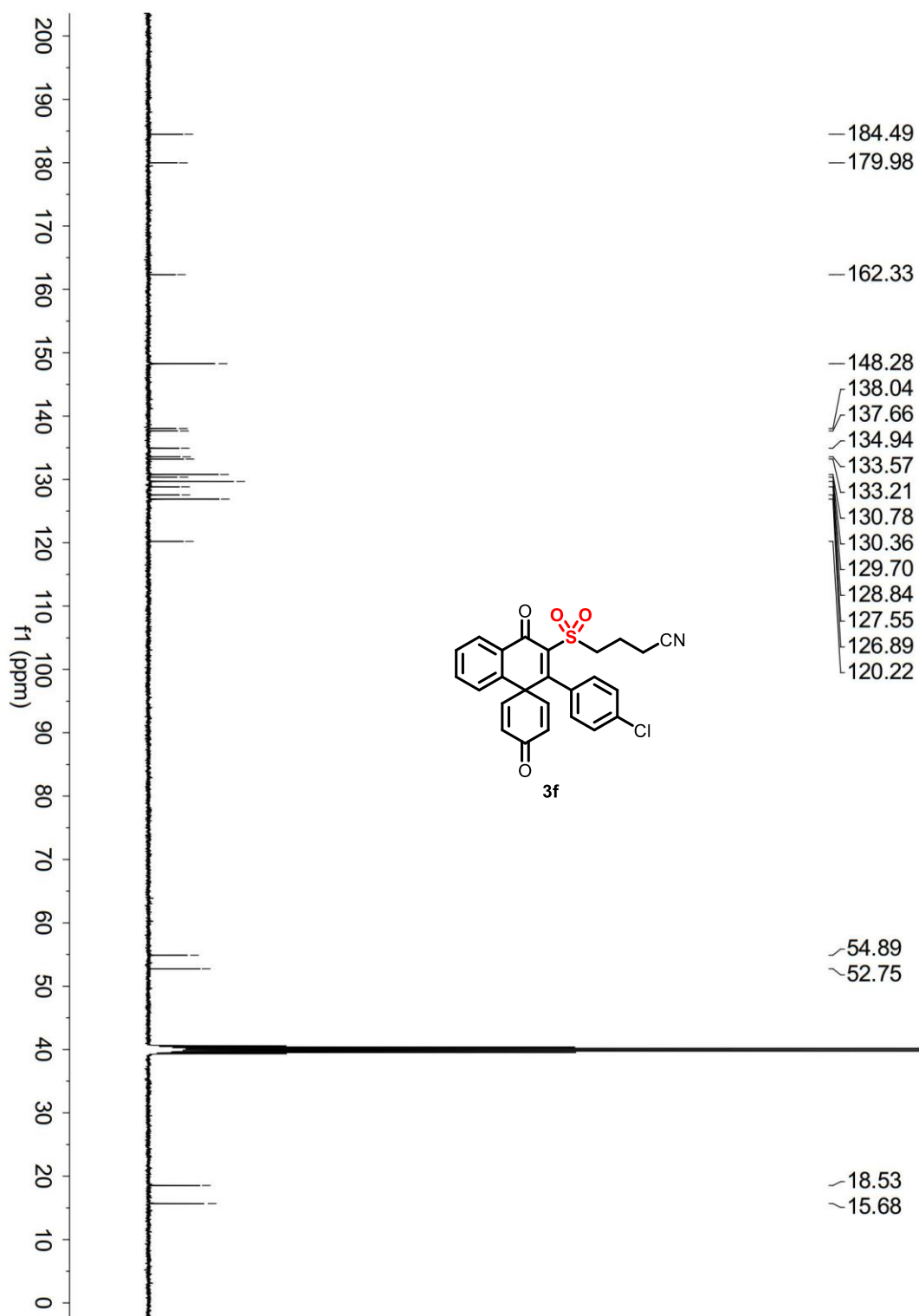
^{19}F NMR spectrum of compound **3e** (376 MHz, CDCl_3)



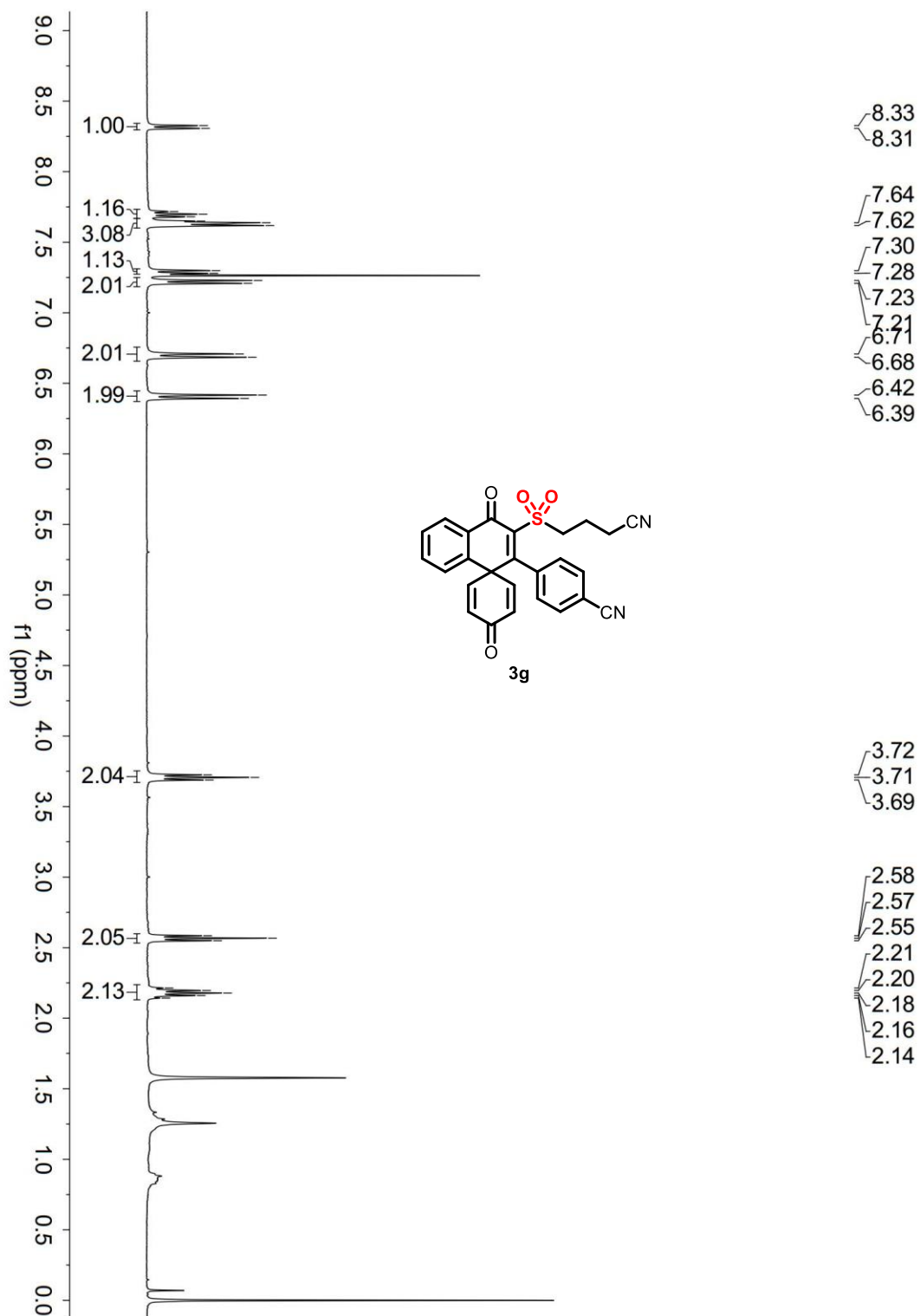
^1H NMR spectrum of compound **3f** (400 MHz, $\text{DMSO-}d_6$)



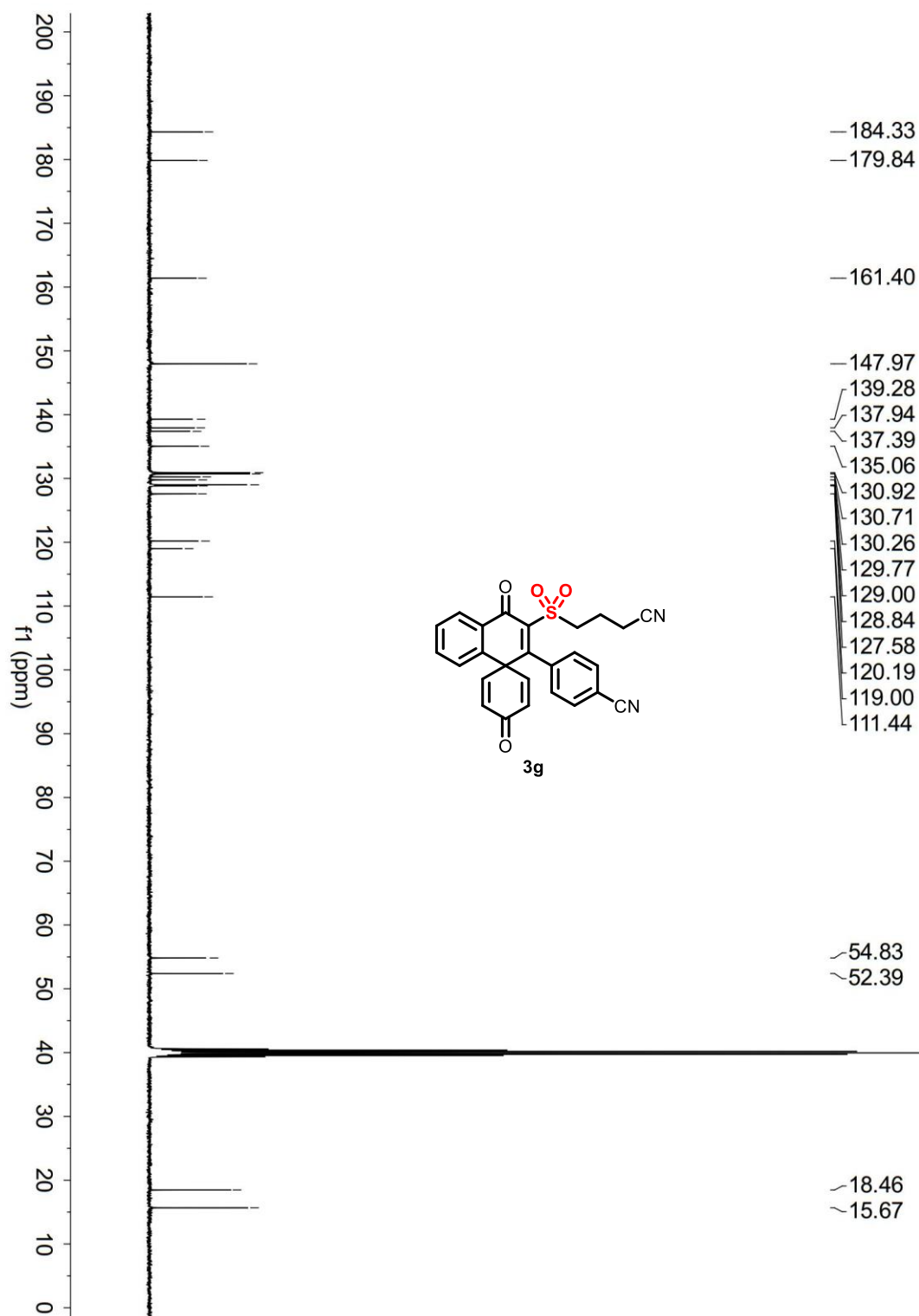
^{13}C NMR spectrum of compound **3f** (100 MHz, $\text{DMSO-}d_6$)



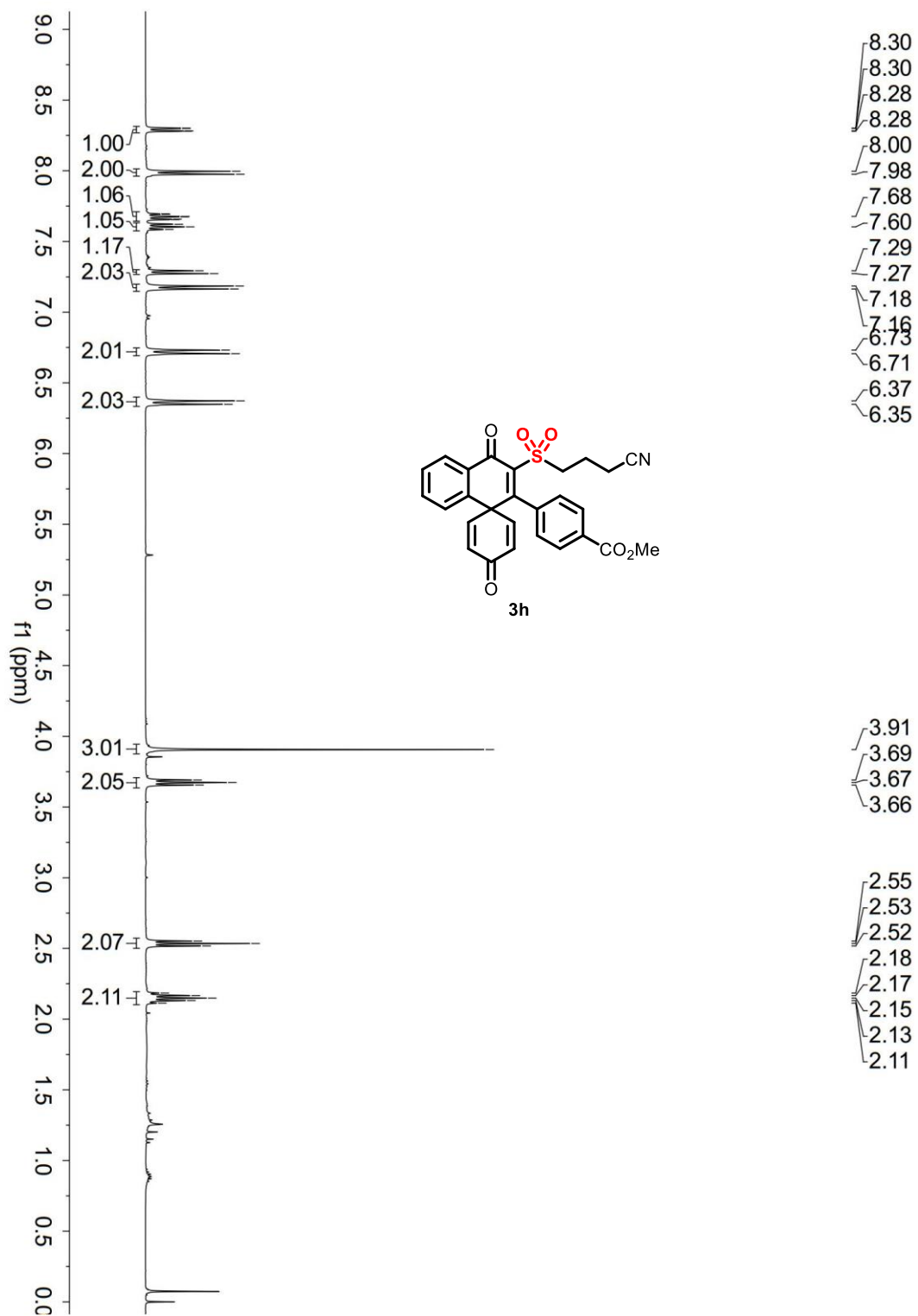
^1H NMR spectrum of compound **3g** (400 MHz, CDCl_3)



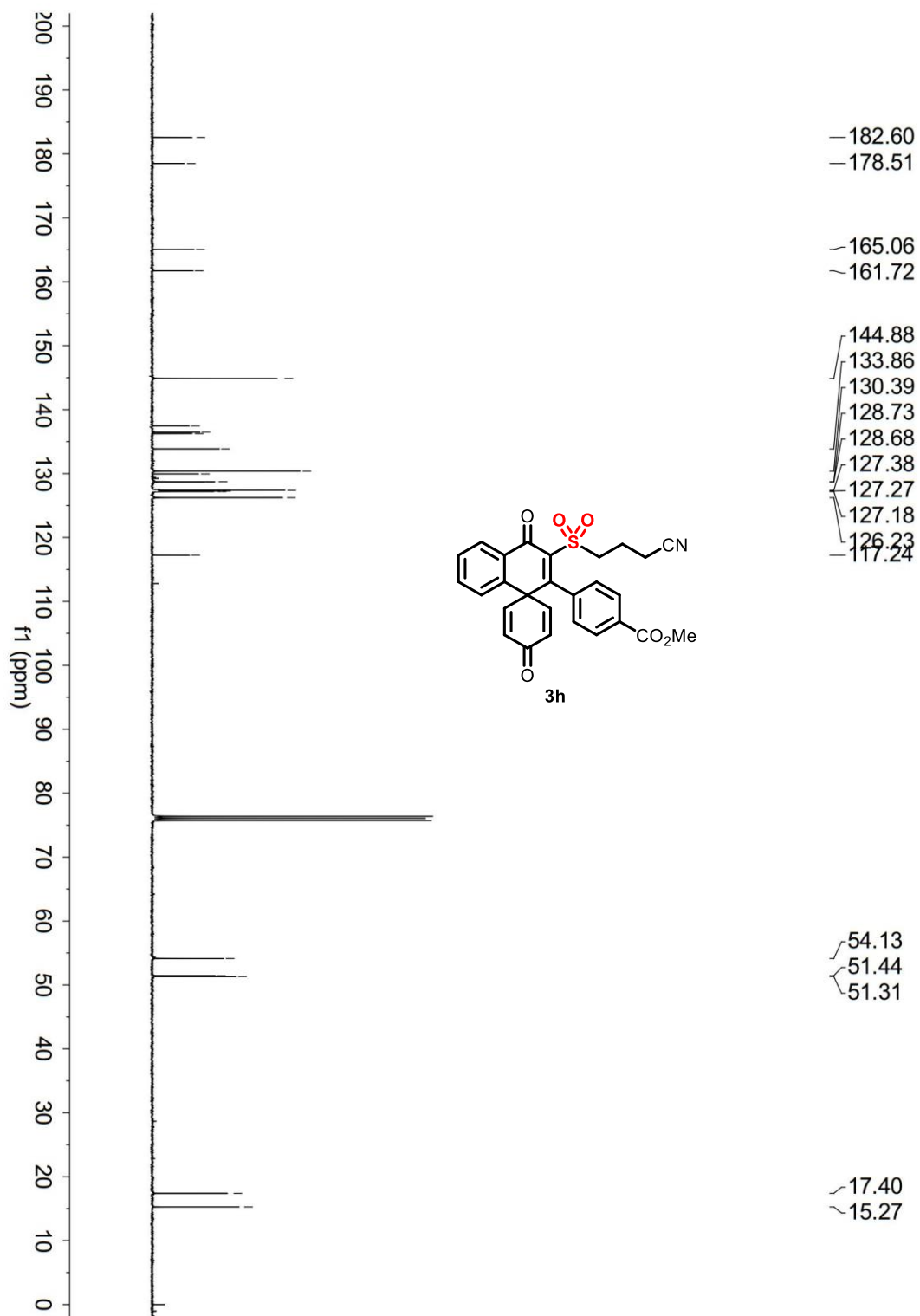
^{13}C NMR spectrum of compound **3g** (100 MHz, $\text{DMSO-}d_6$)



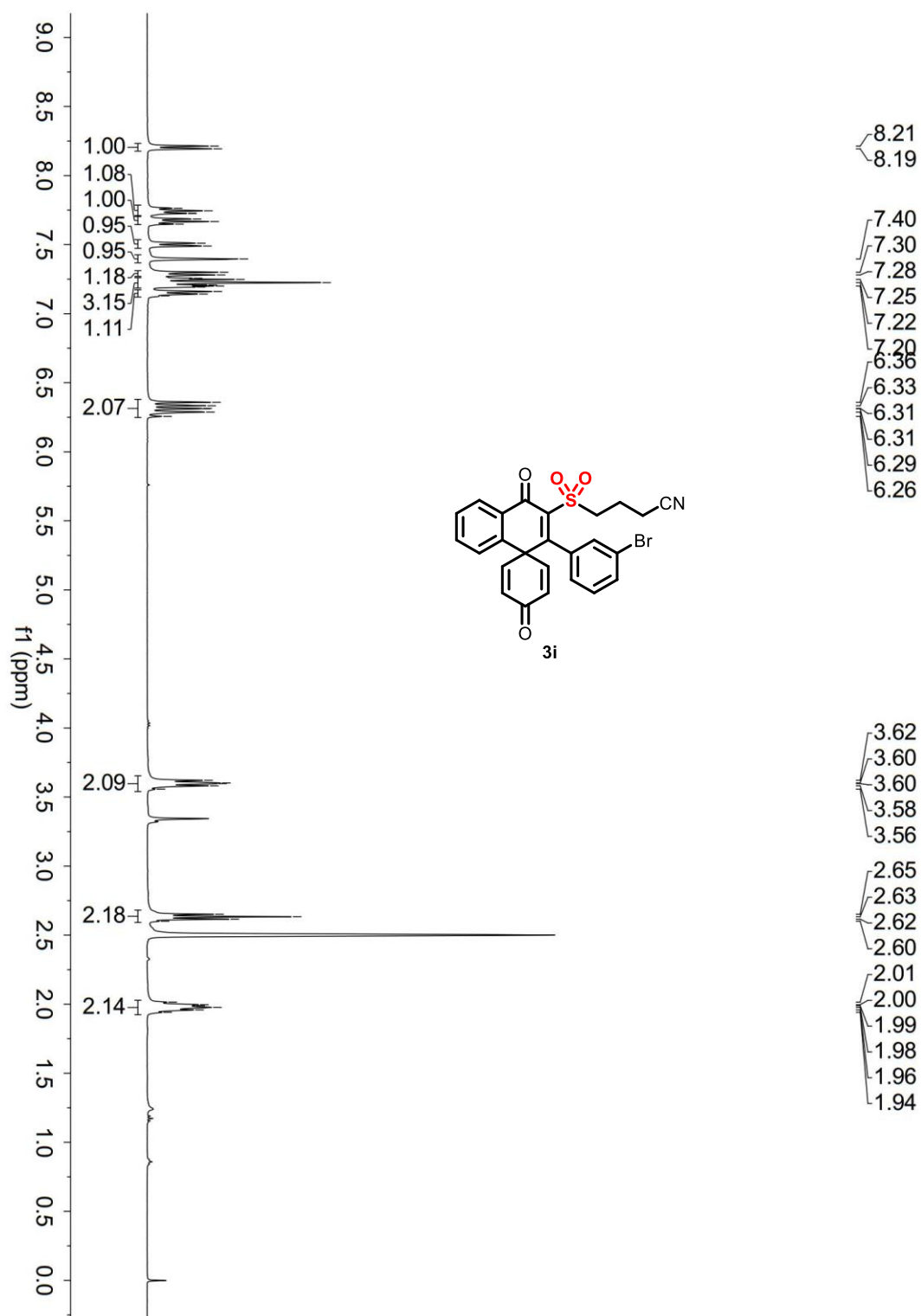
^1H NMR spectrum of compound **3h** (400 MHz, CDCl_3)



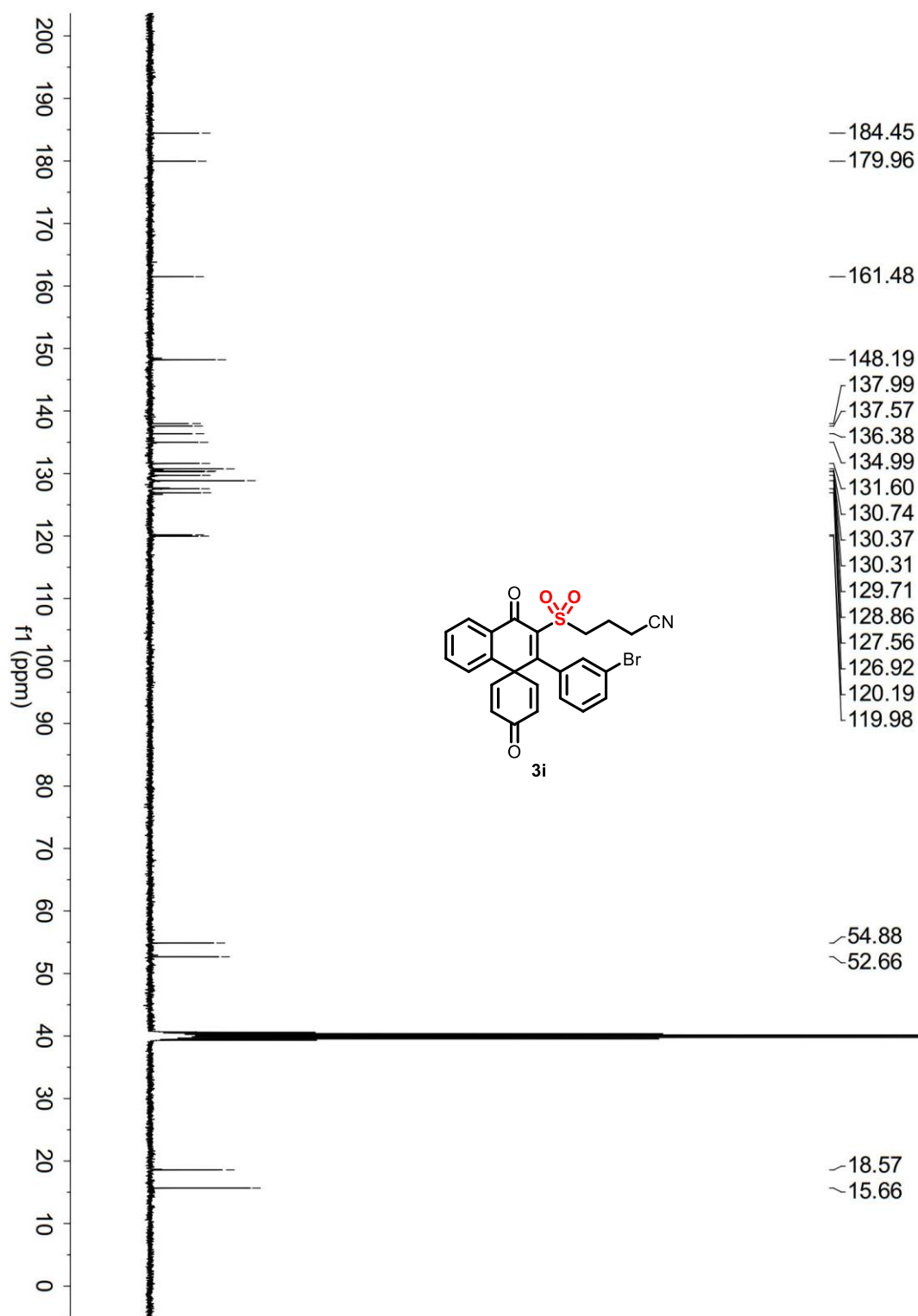
^{13}C NMR spectrum of compound **3h** (100 MHz, CDCl_3)



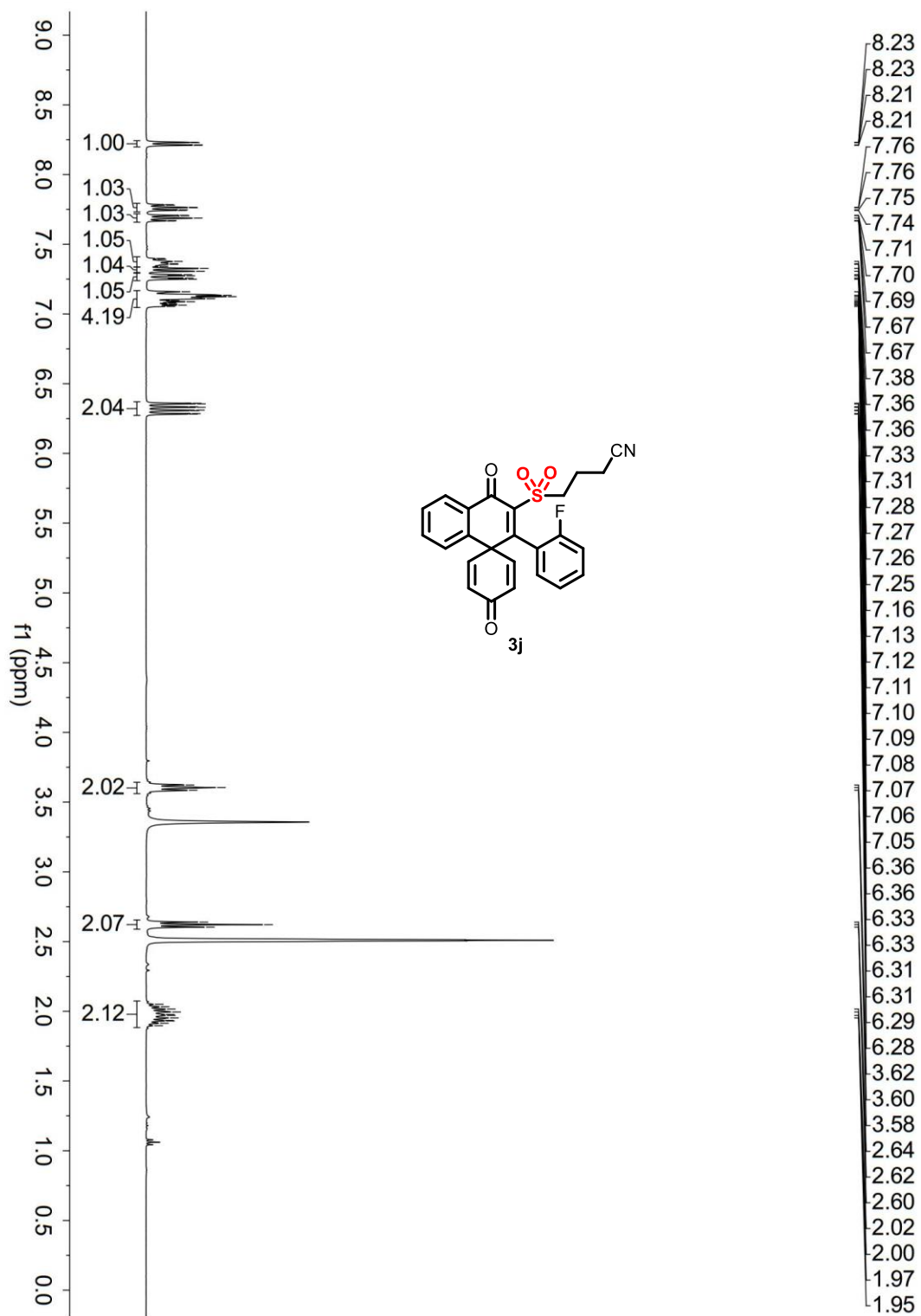
^1H NMR spectrum of compound **3i** (400 MHz, $\text{DMSO-}d_6$)



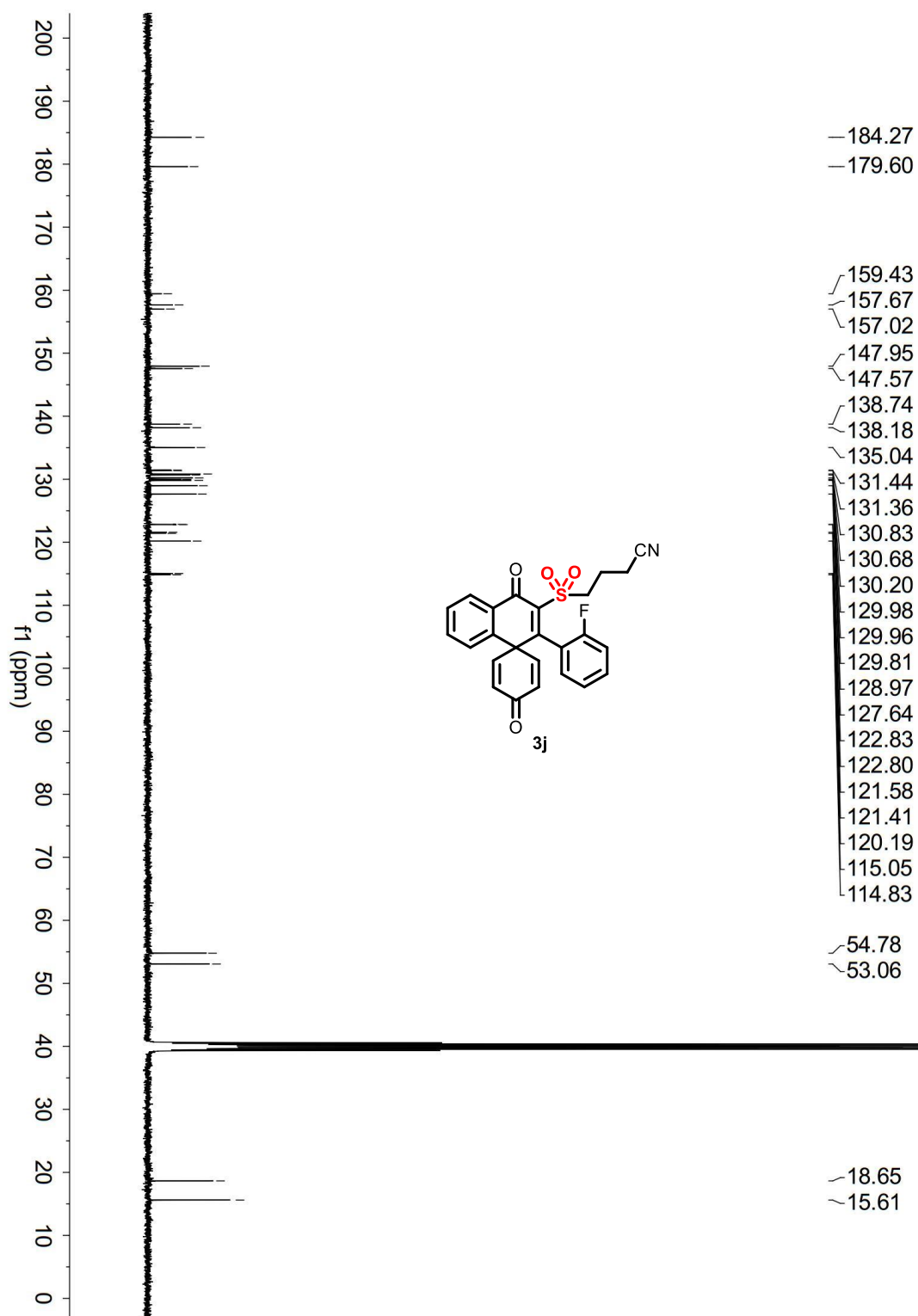
^{13}C NMR spectrum of compound **3i** (100 MHz, $\text{DMSO-}d_6$)



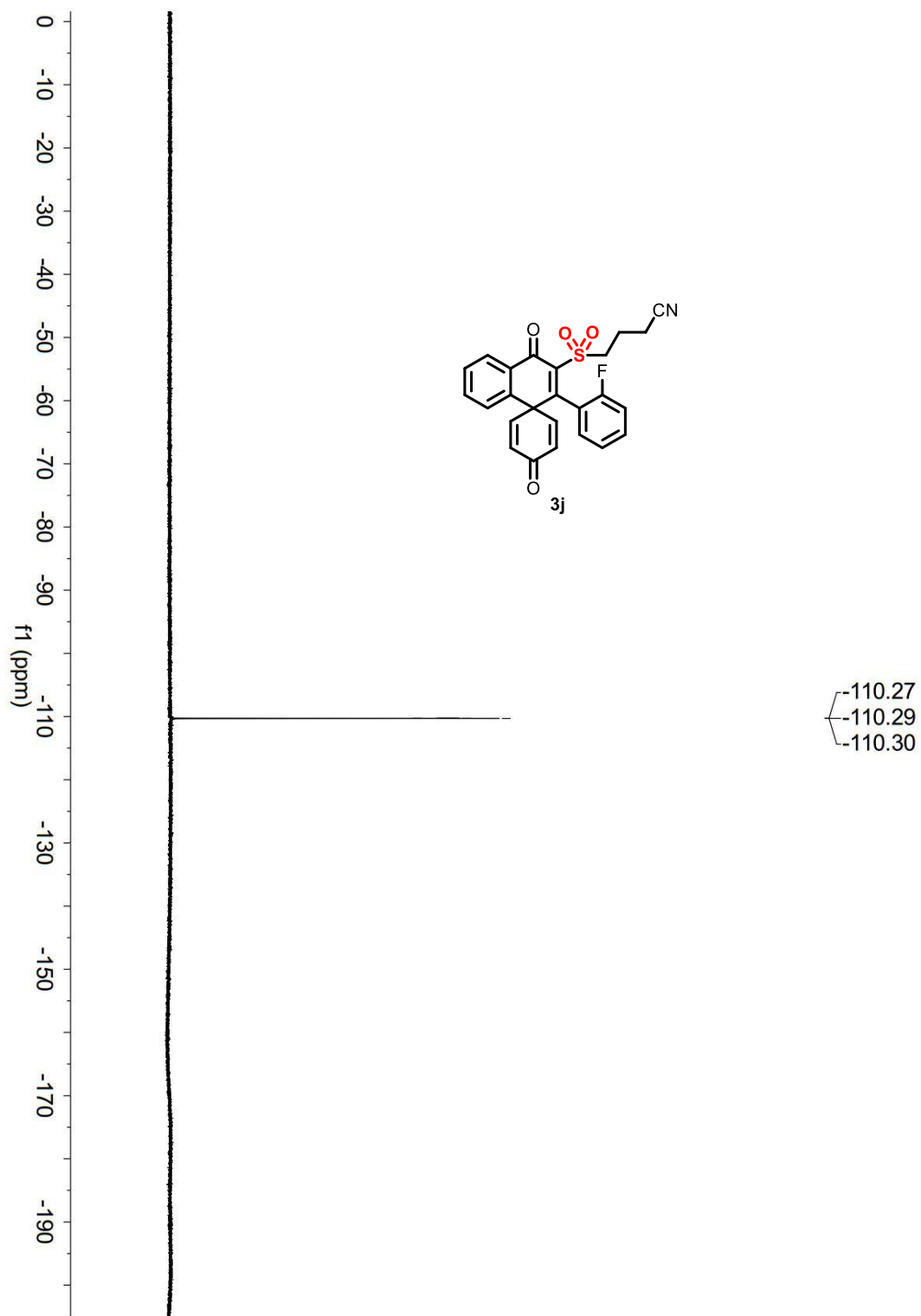
^1H NMR spectrum of compound **3j** (400 MHz, $\text{DMSO-}d_6$)



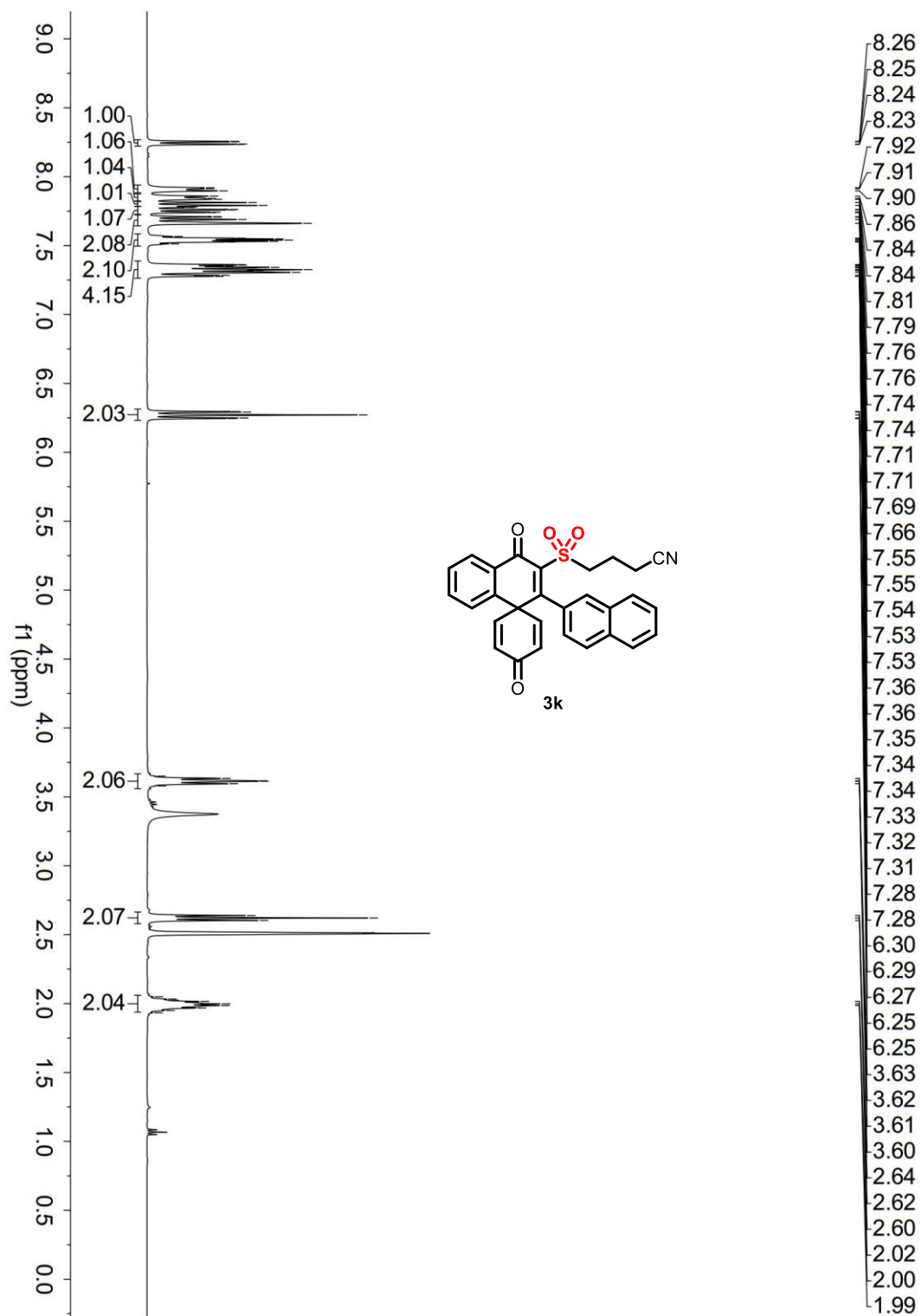
^{13}C NMR spectrum of compound **3j** (100 MHz, $\text{DMSO-}d_6$)



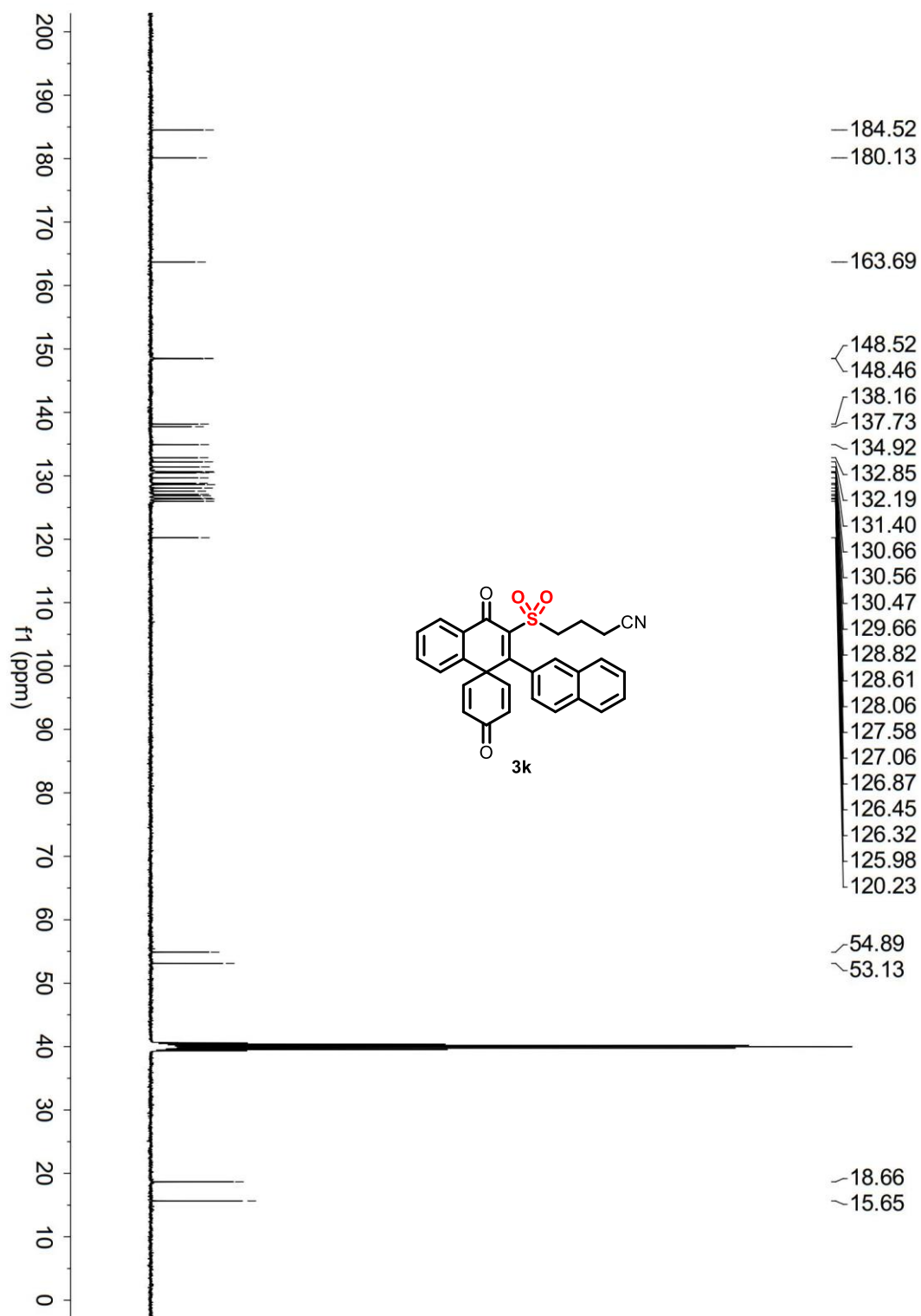
^{19}F NMR spectrum of compound **3j** (376 MHz, $\text{DMSO-}d_6$)



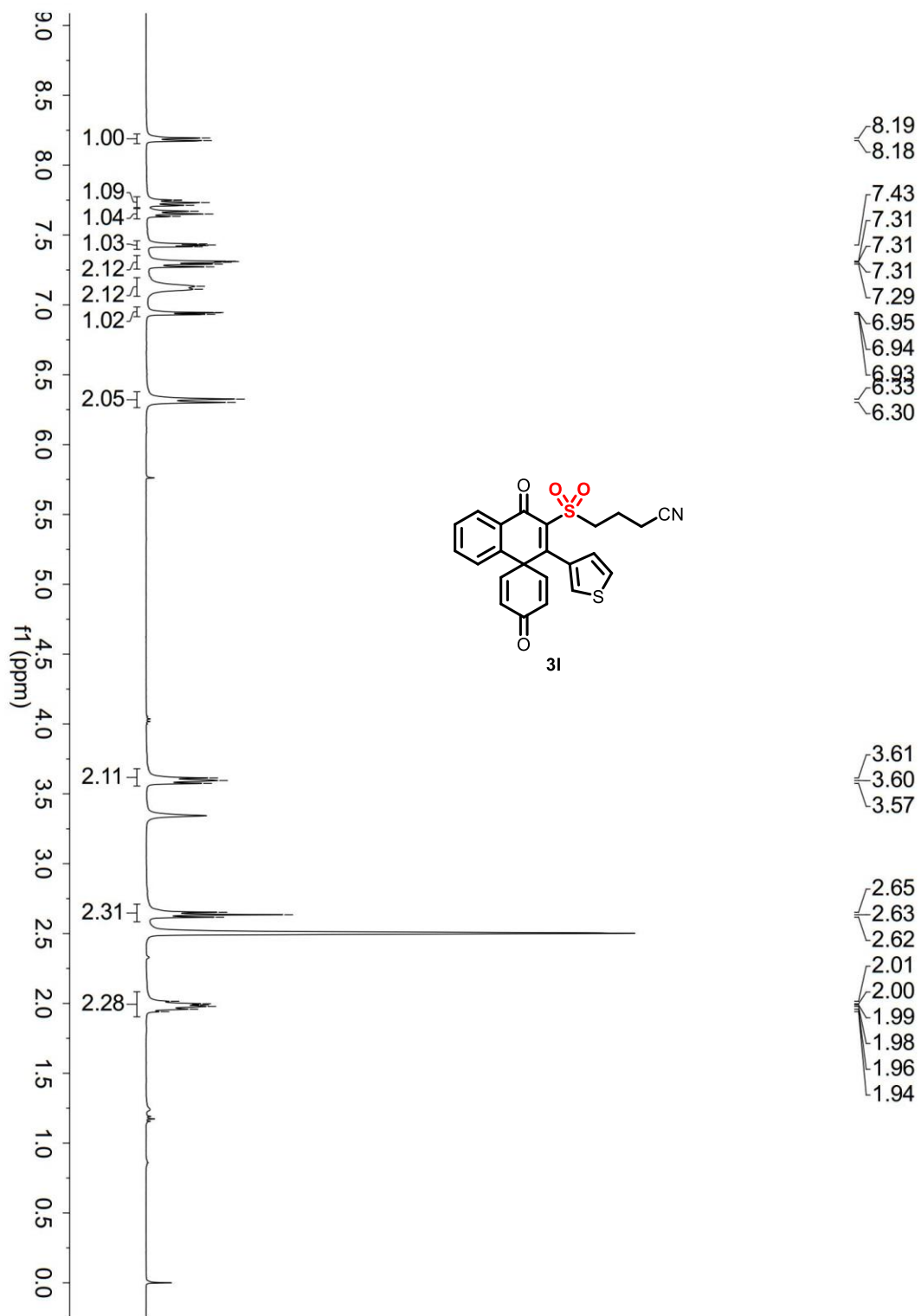
^1H NMR spectrum of compound **3k** (400 MHz, $\text{DMSO-}d_6$)



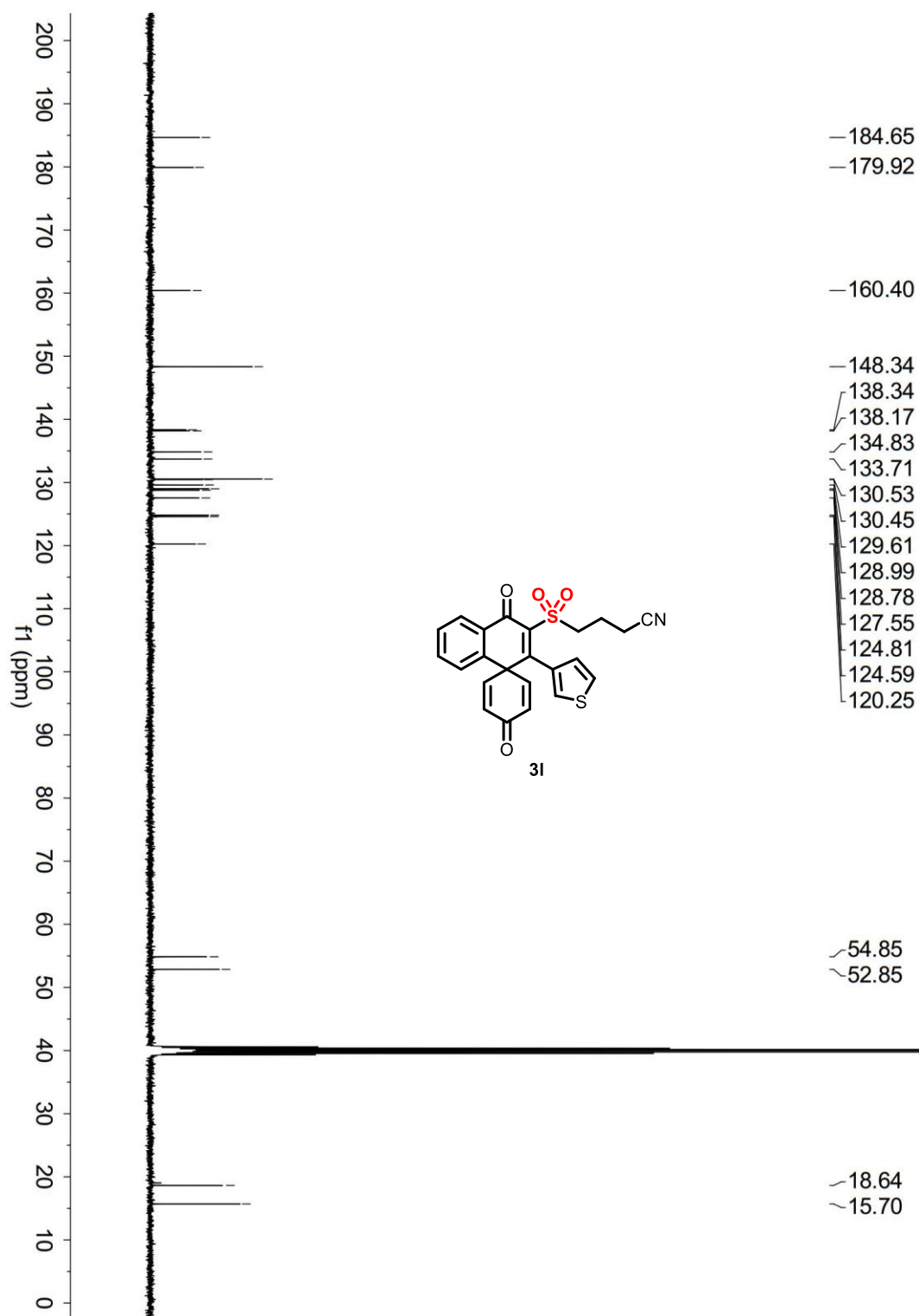
^{13}C NMR spectrum of compound **3k** (100 MHz, $\text{DMSO-}d_6$)



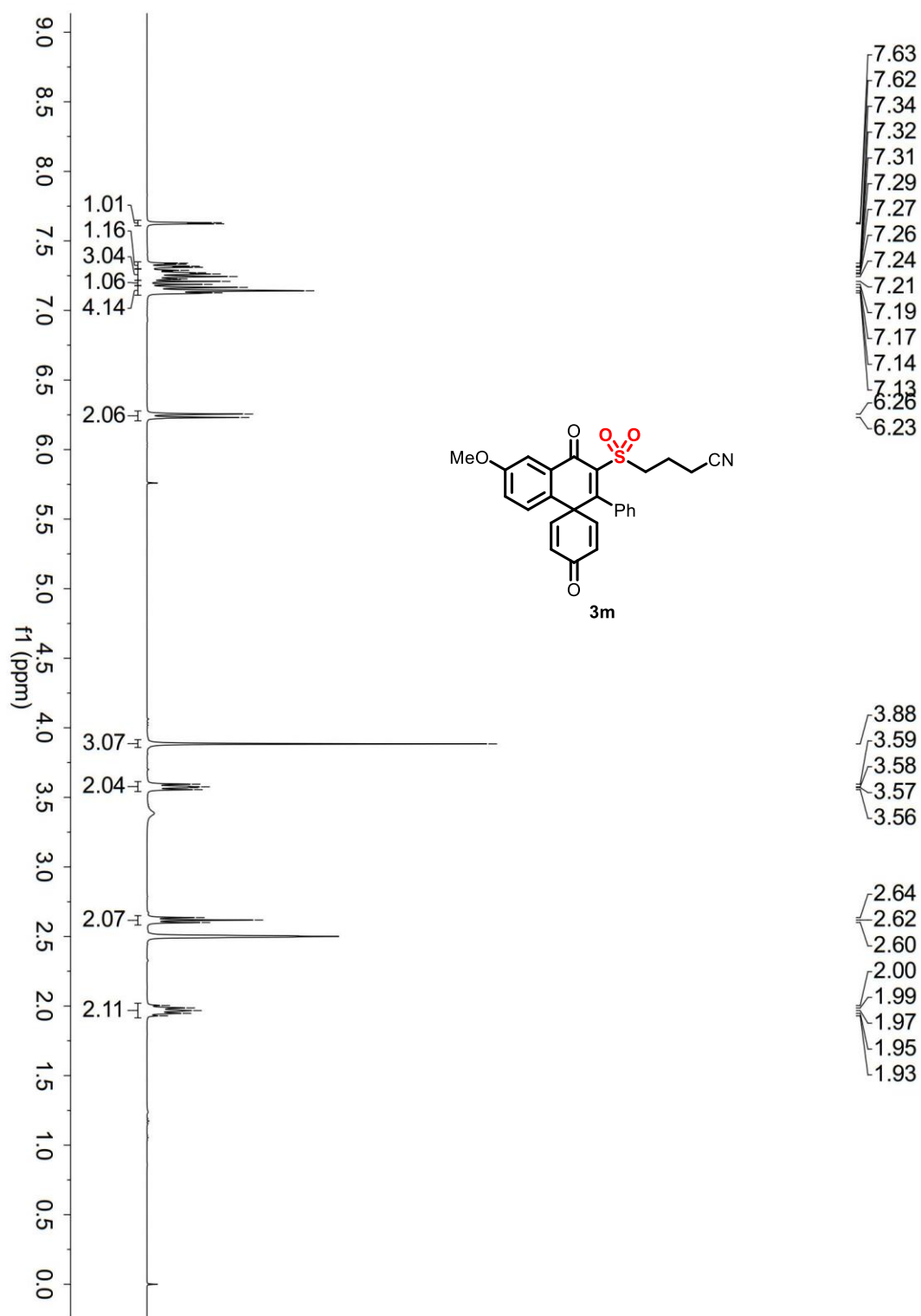
^1H NMR spectrum of compound **31** (400 MHz, $\text{DMSO-}d_6$)



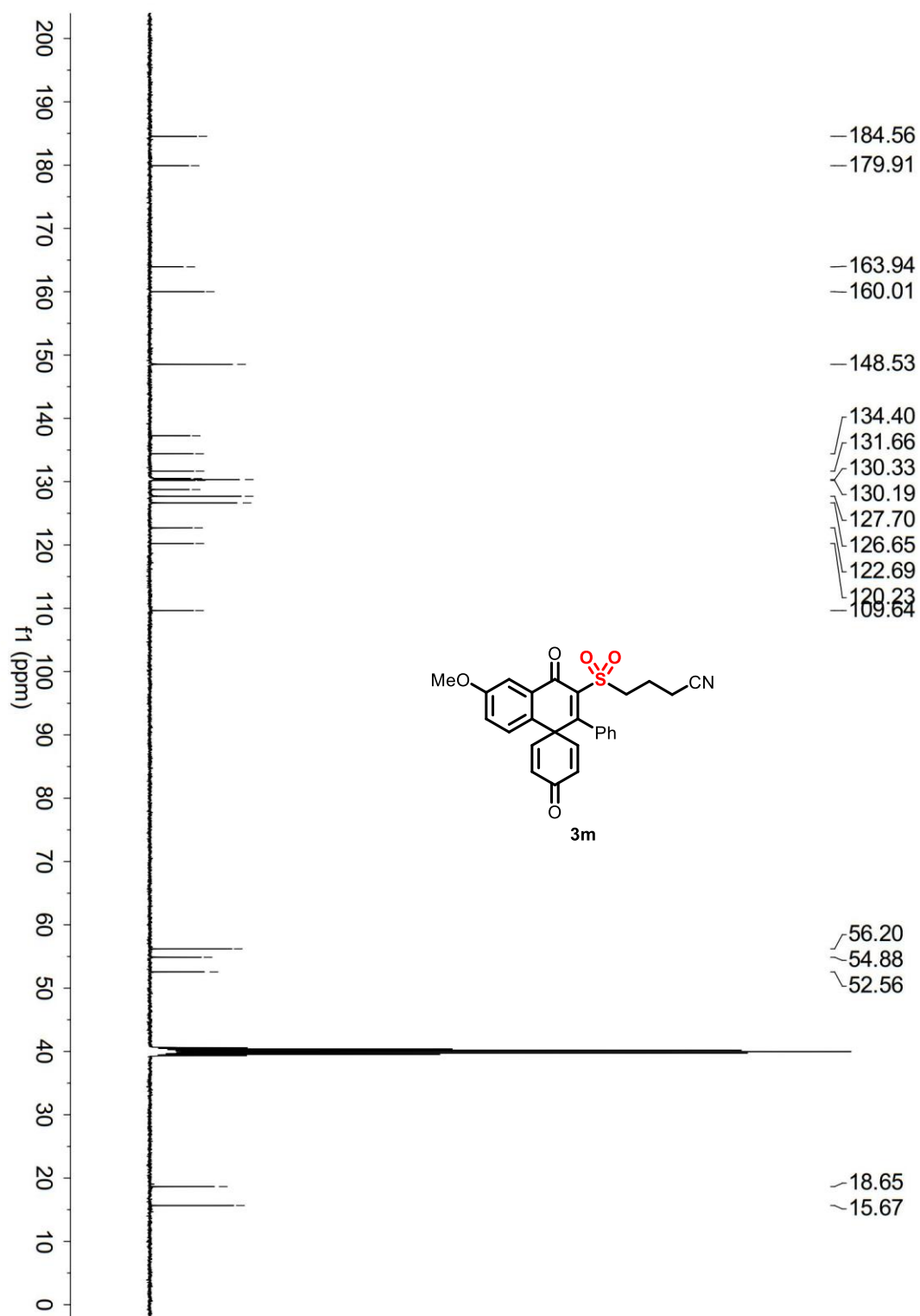
^{13}C NMR spectrum of compound **3I** (100 MHz, $\text{DMSO-}d_6$)



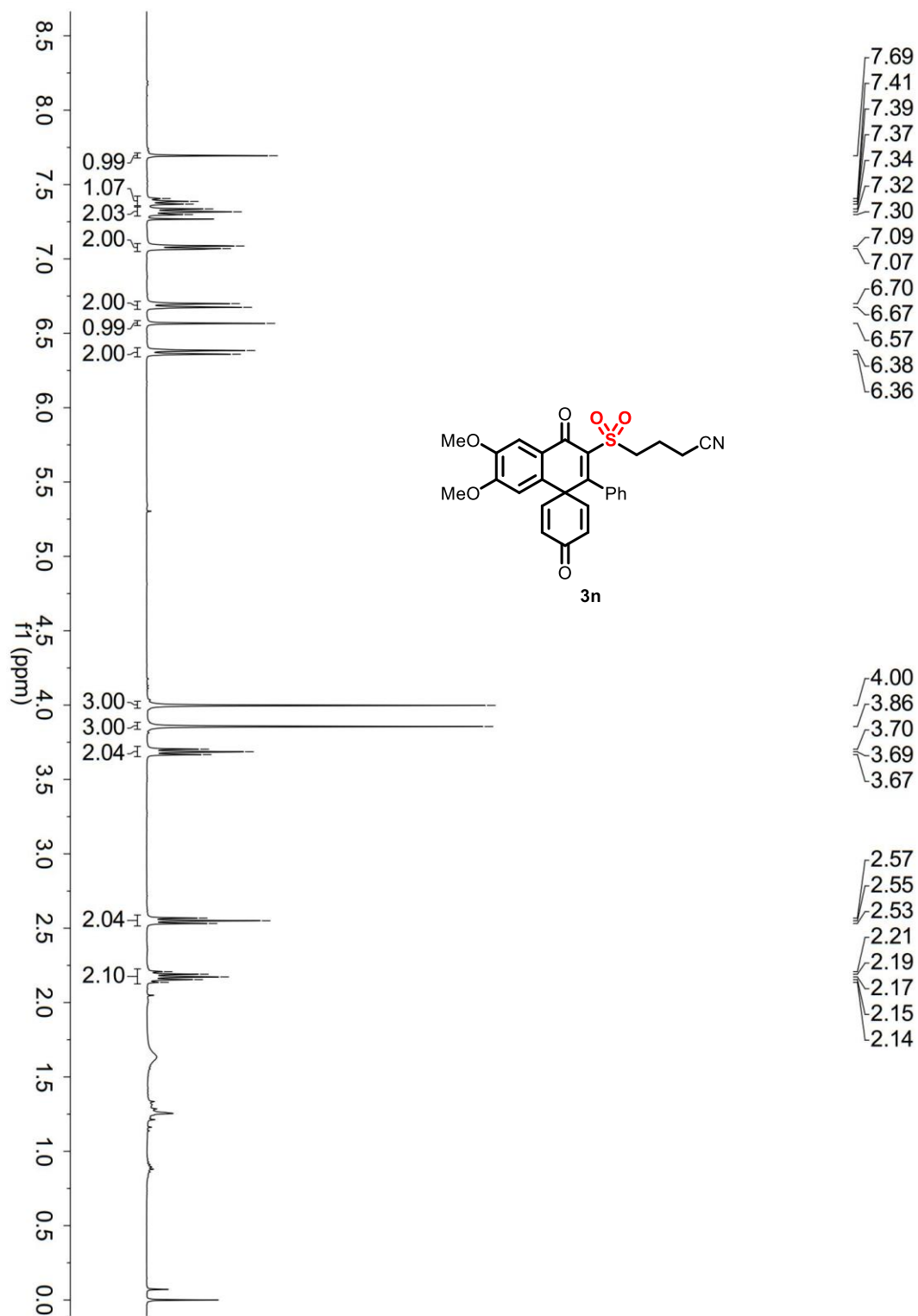
^1H NMR spectrum of compound **3m** (400 MHz, $\text{DMSO-}d_6$)



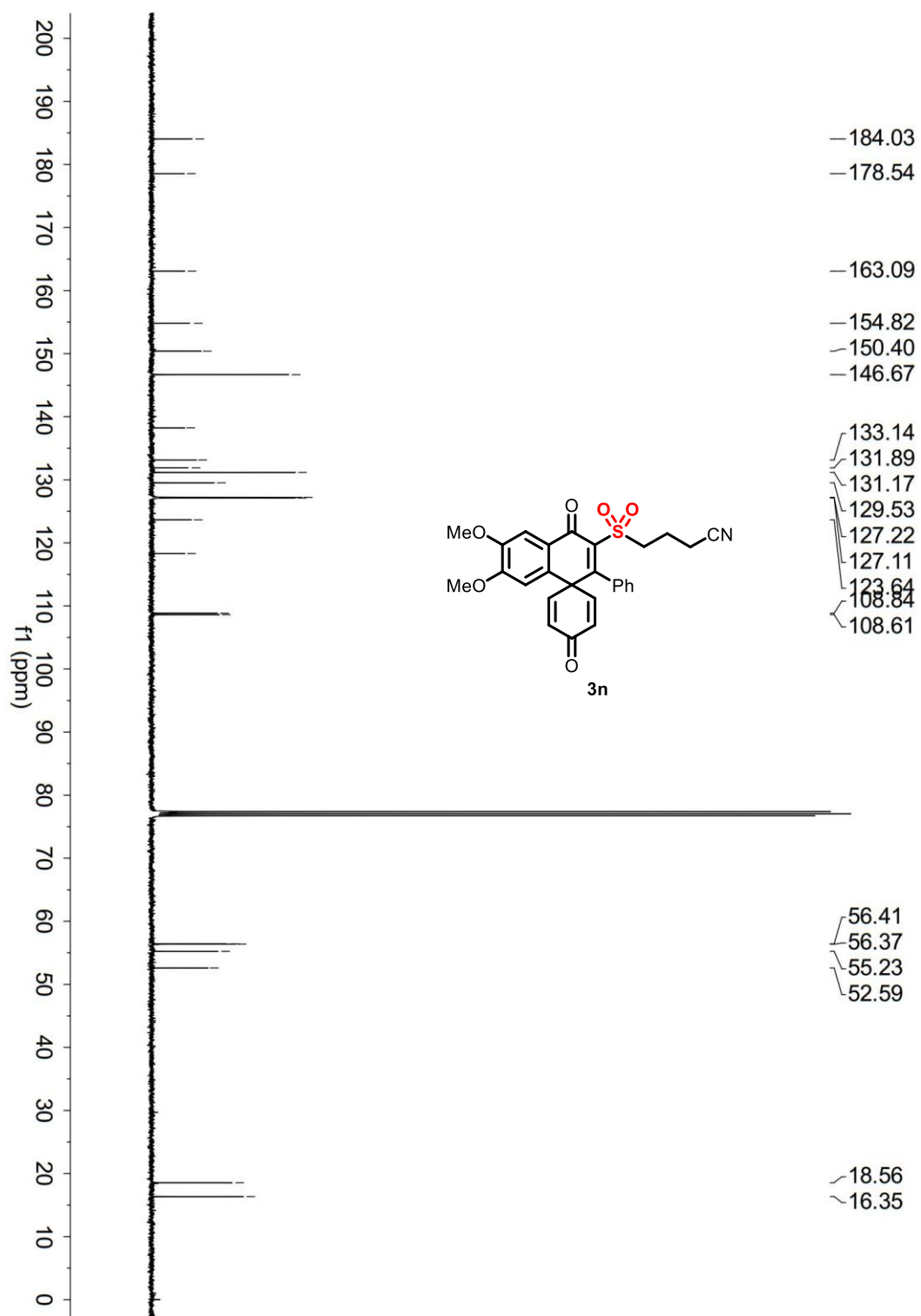
^{13}C NMR spectrum of compound **3m** (100 MHz, $\text{DMSO-}d_6$)



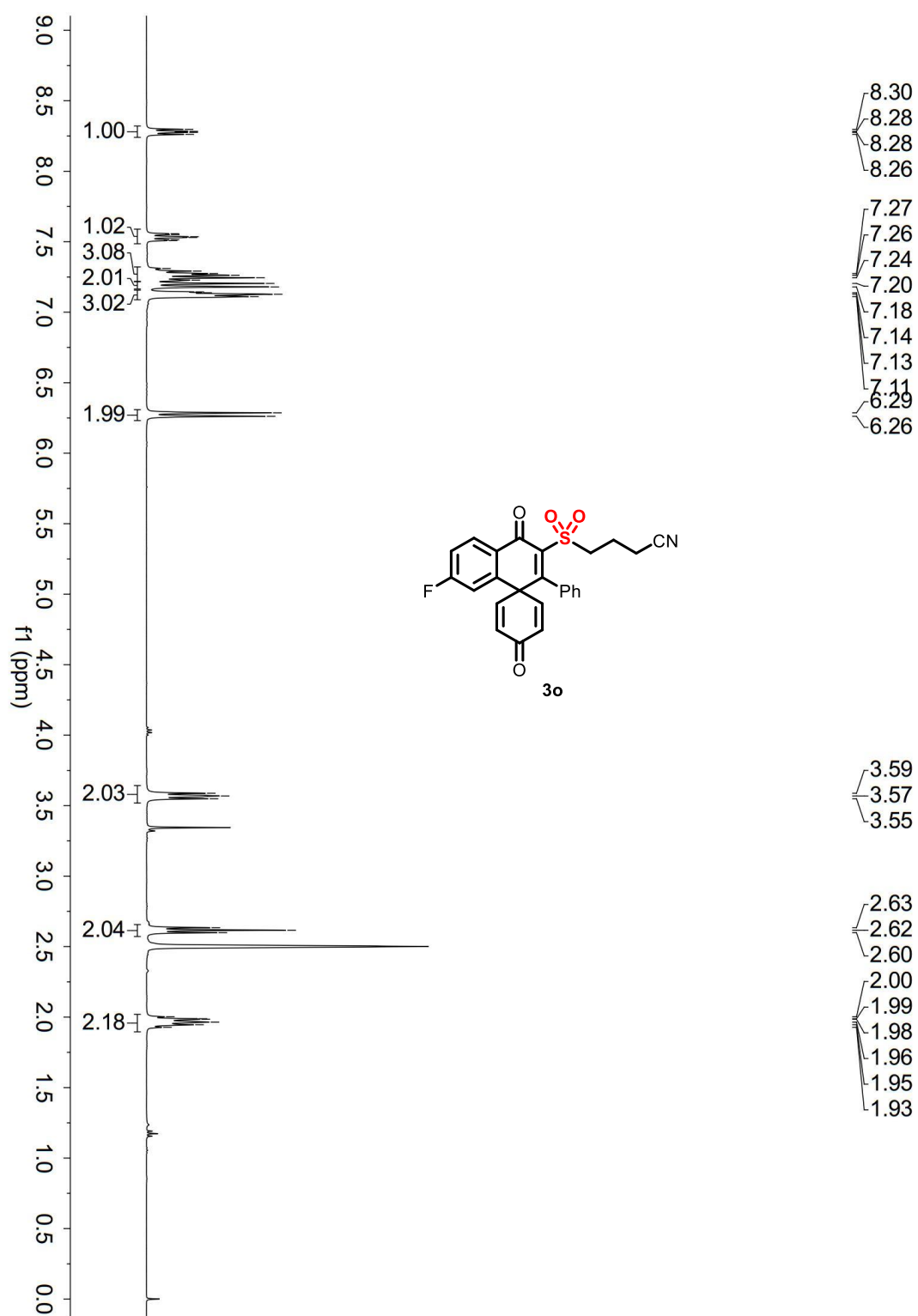
^1H NMR spectrum of compound **3n** (400 MHz, CDCl_3)



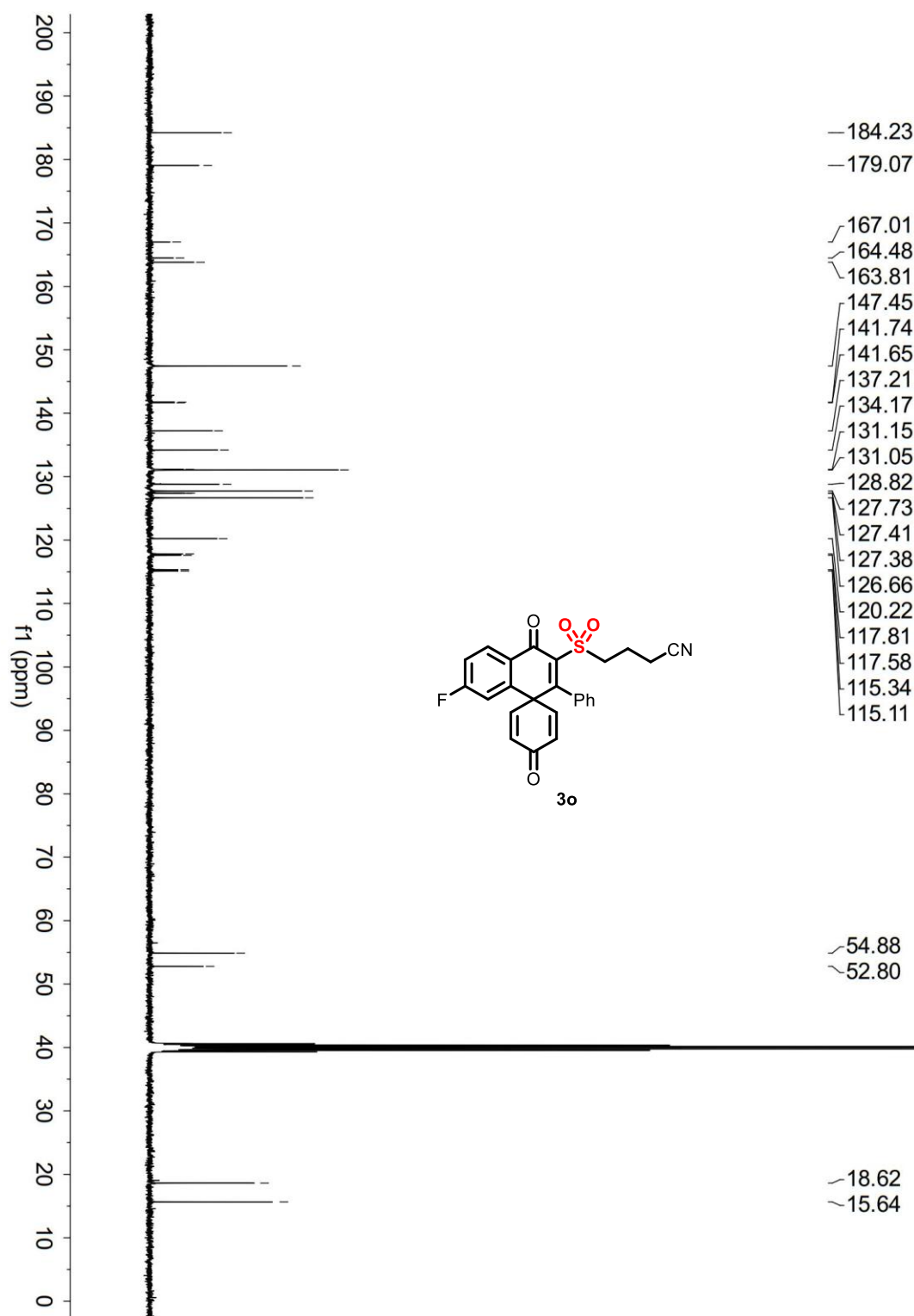
^{13}C NMR spectrum of compound **3n** (100 MHz, CDCl_3)



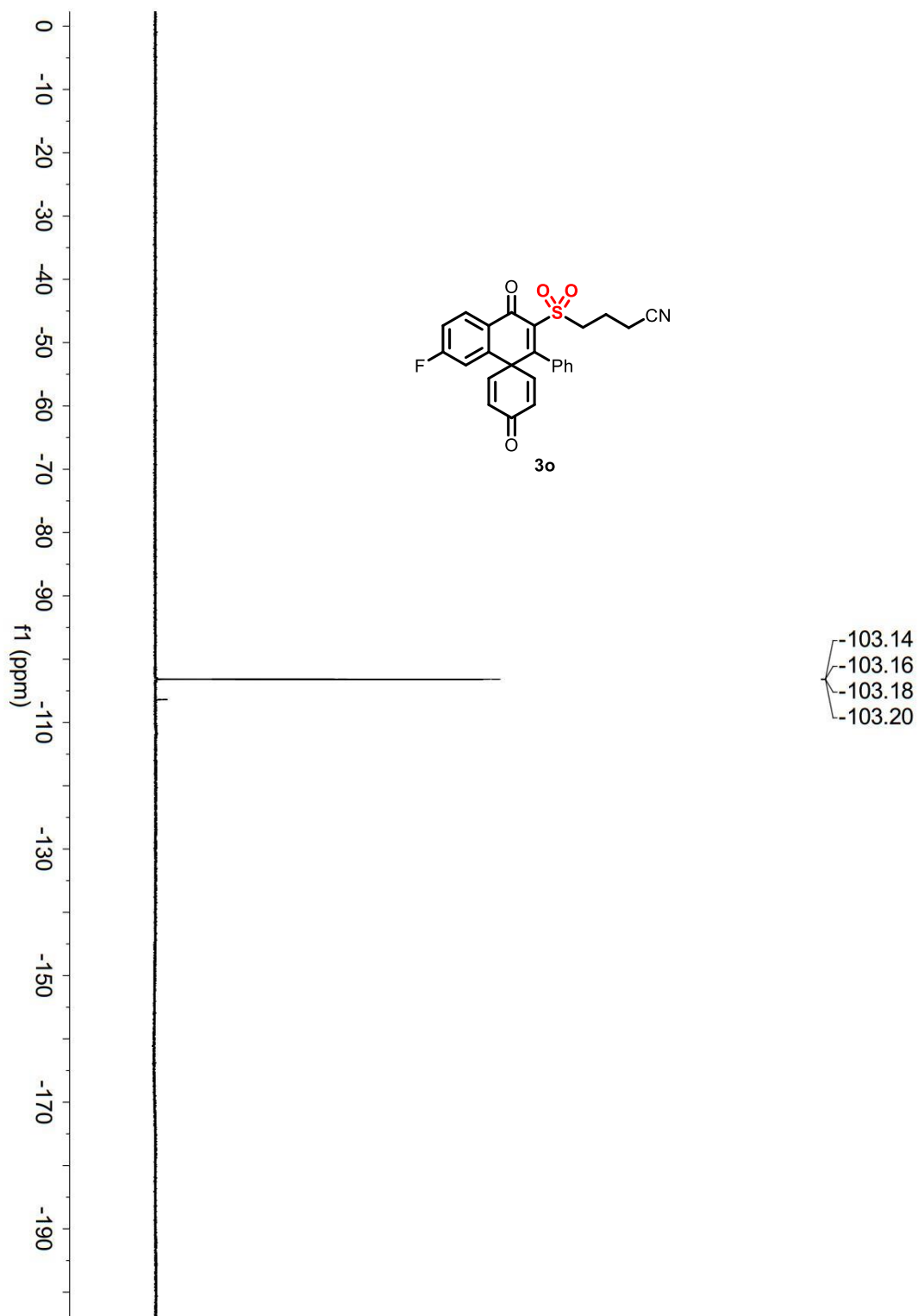
^1H NMR spectrum of compound **3o** (400 MHz, $\text{DMSO-}d_6$)



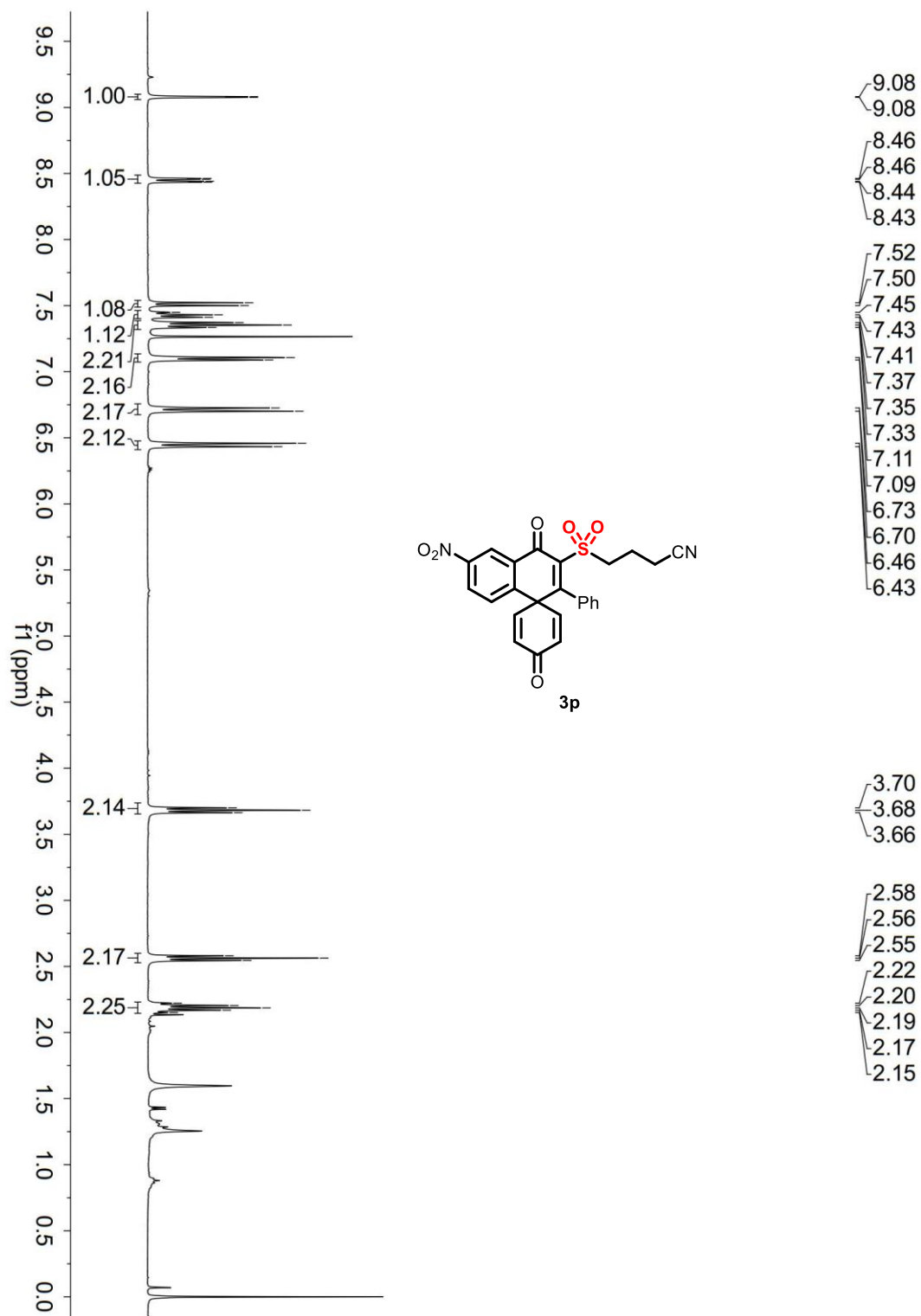
^{13}C NMR spectrum of compound **3o** (100 MHz, $\text{DMSO-}d_6$)



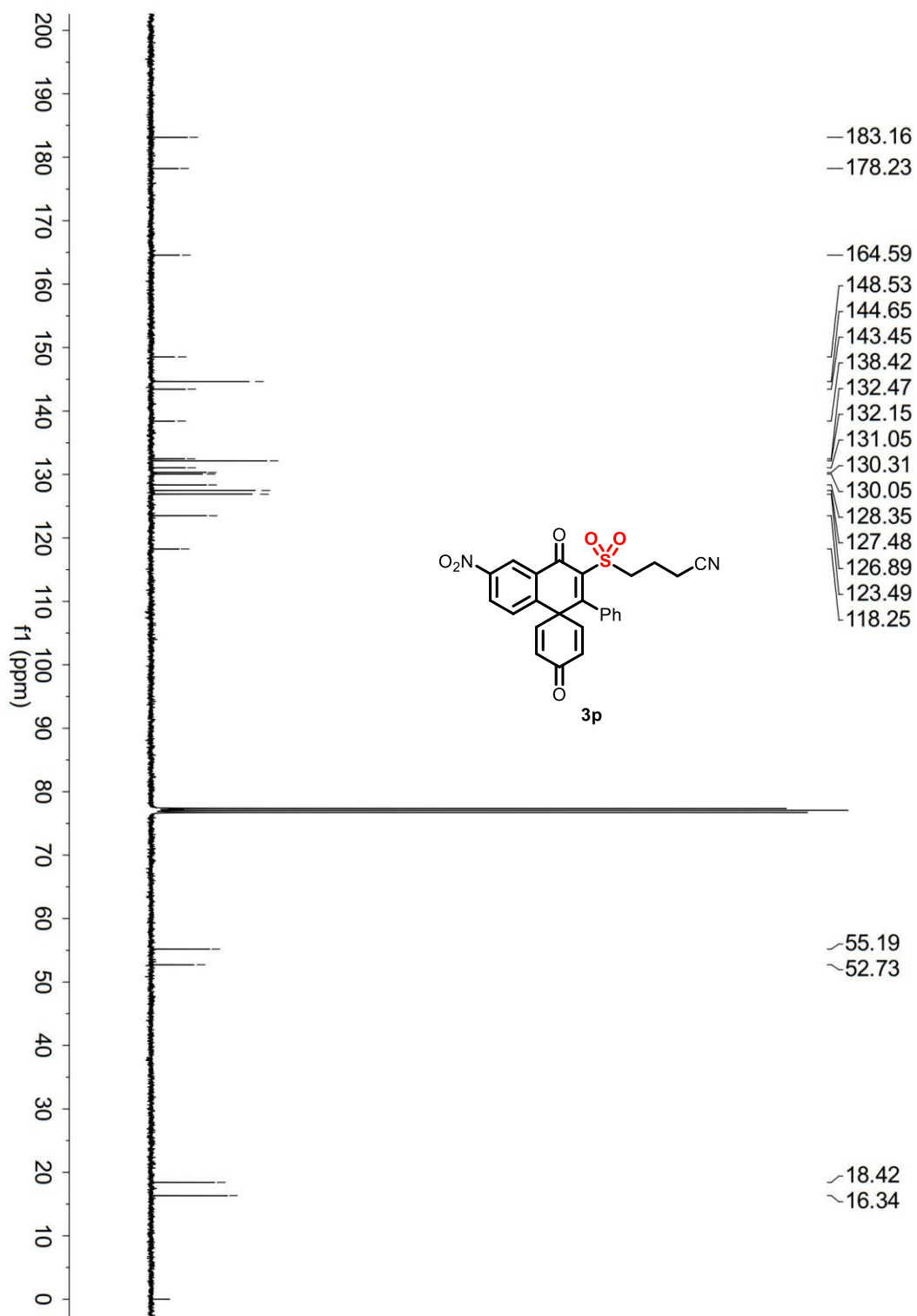
^{19}F NMR spectrum of compound **3o** (376 MHz, $\text{DMSO-}d_6$)



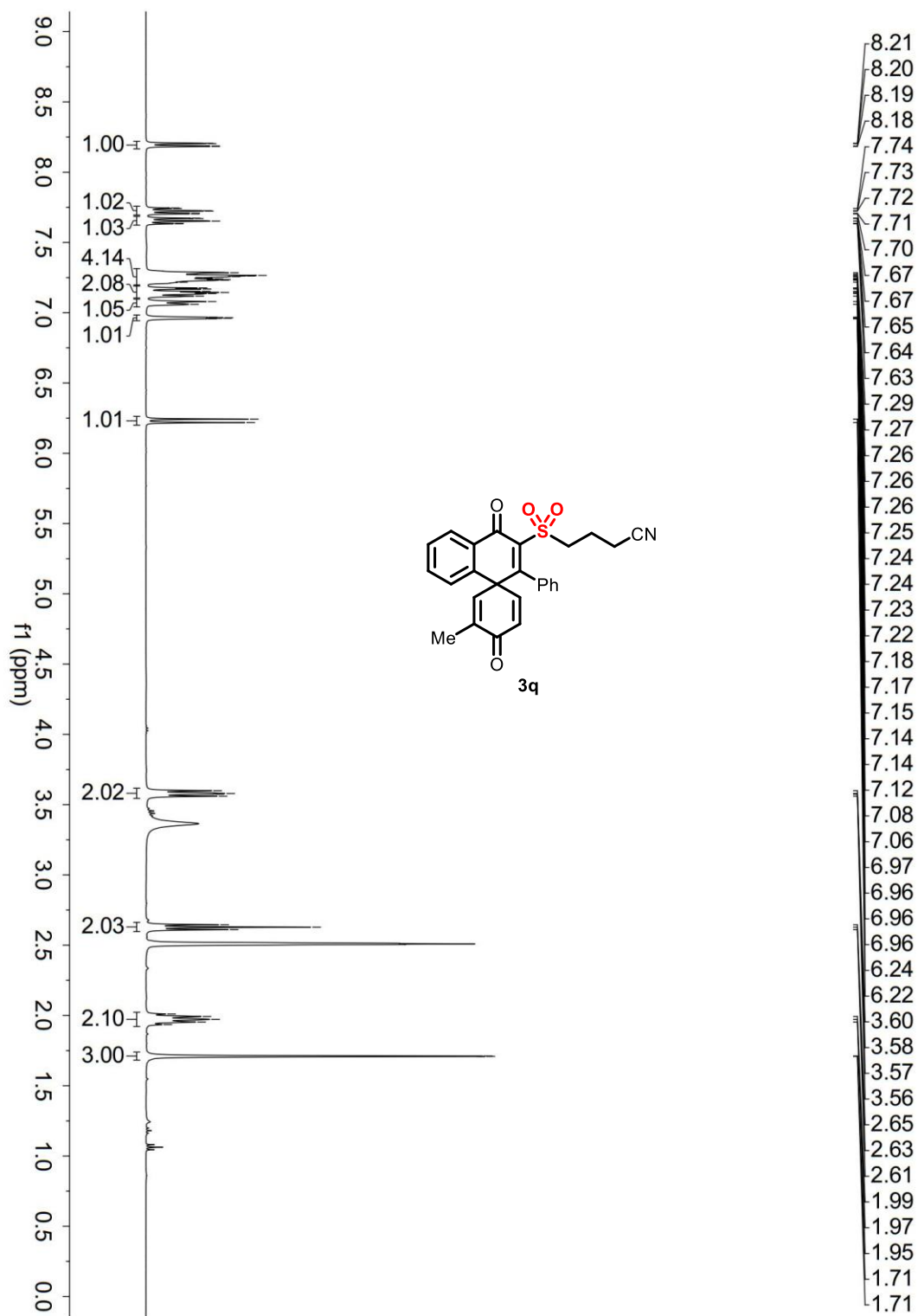
^1H NMR spectrum of compound **3p** (400 MHz, CDCl_3)



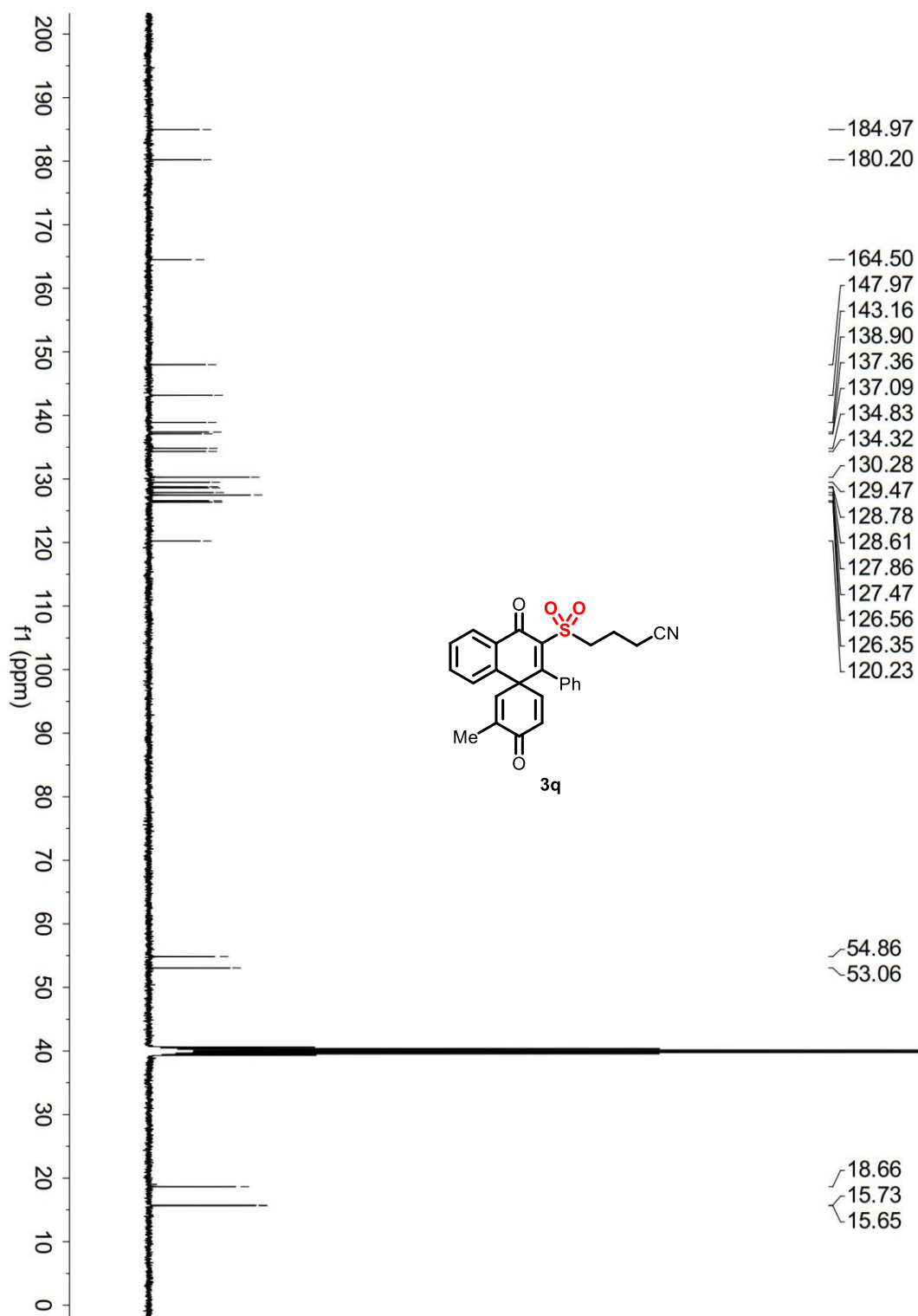
^{13}C NMR spectrum of compound **3p** (100 MHz, CDCl_3)



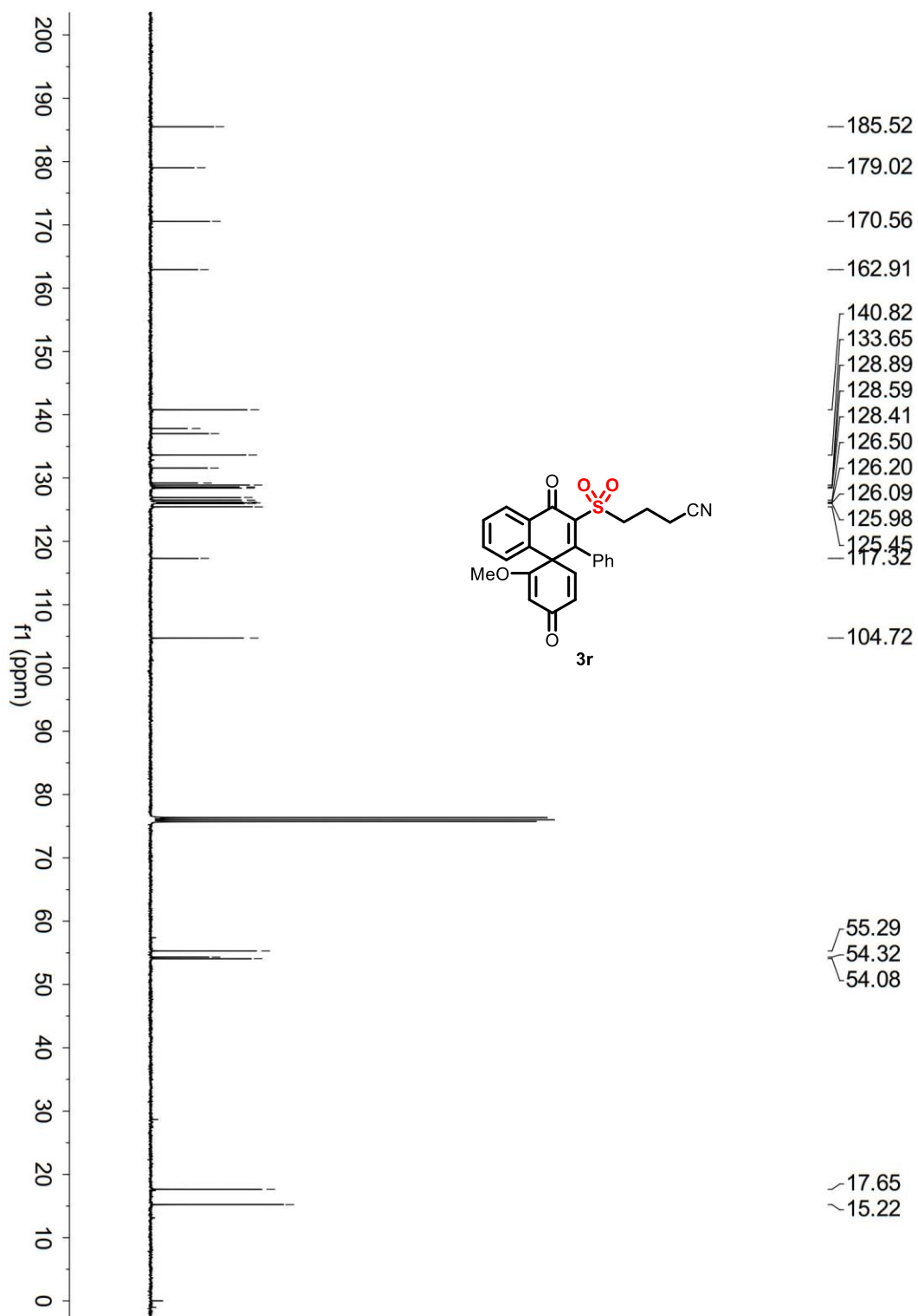
^1H NMR spectrum of compound **3q** (400 MHz, $\text{DMSO-}d_6$)



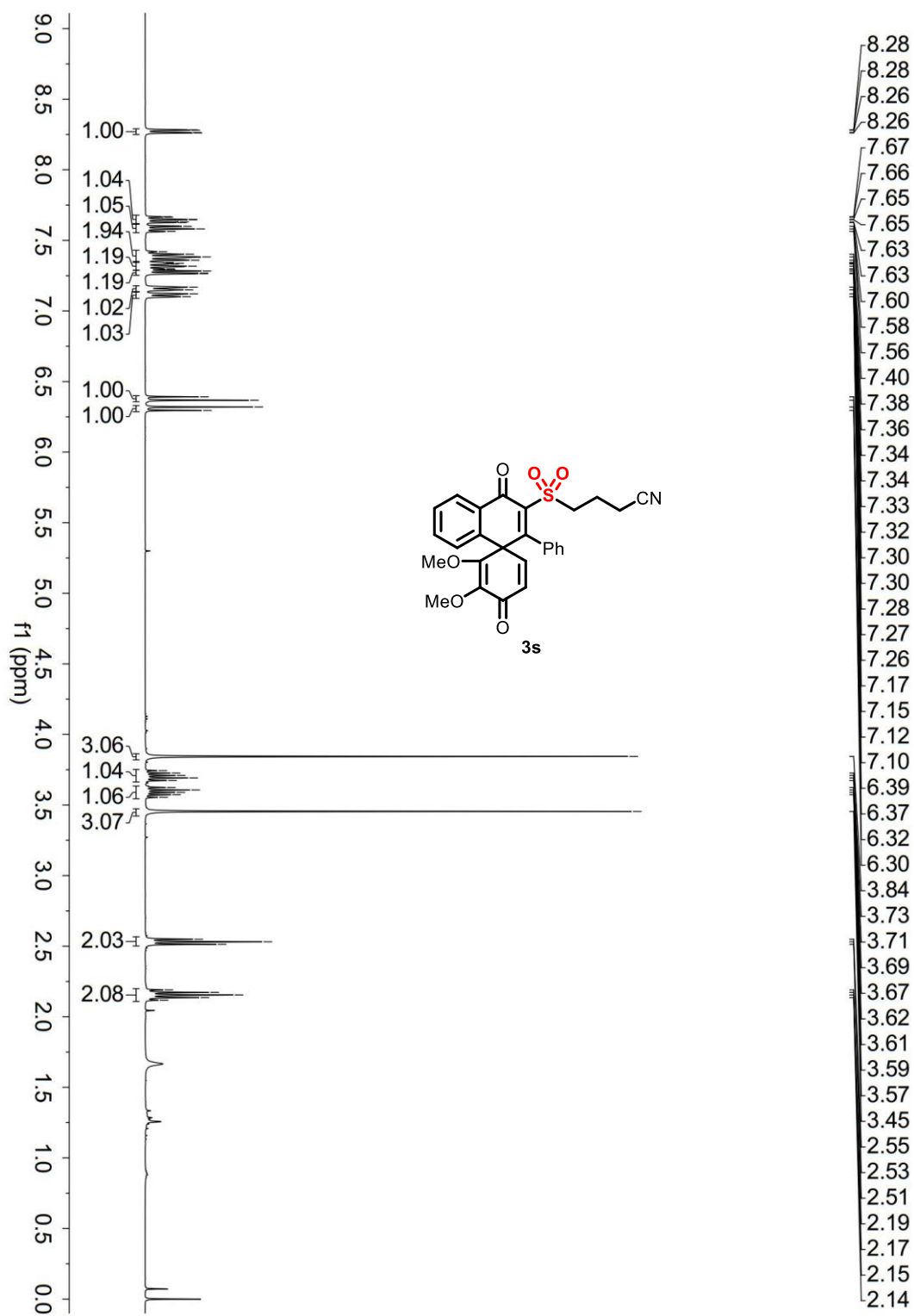
^{13}C NMR spectrum of compound **3q** (100 MHz, $\text{DMSO-}d_6$)



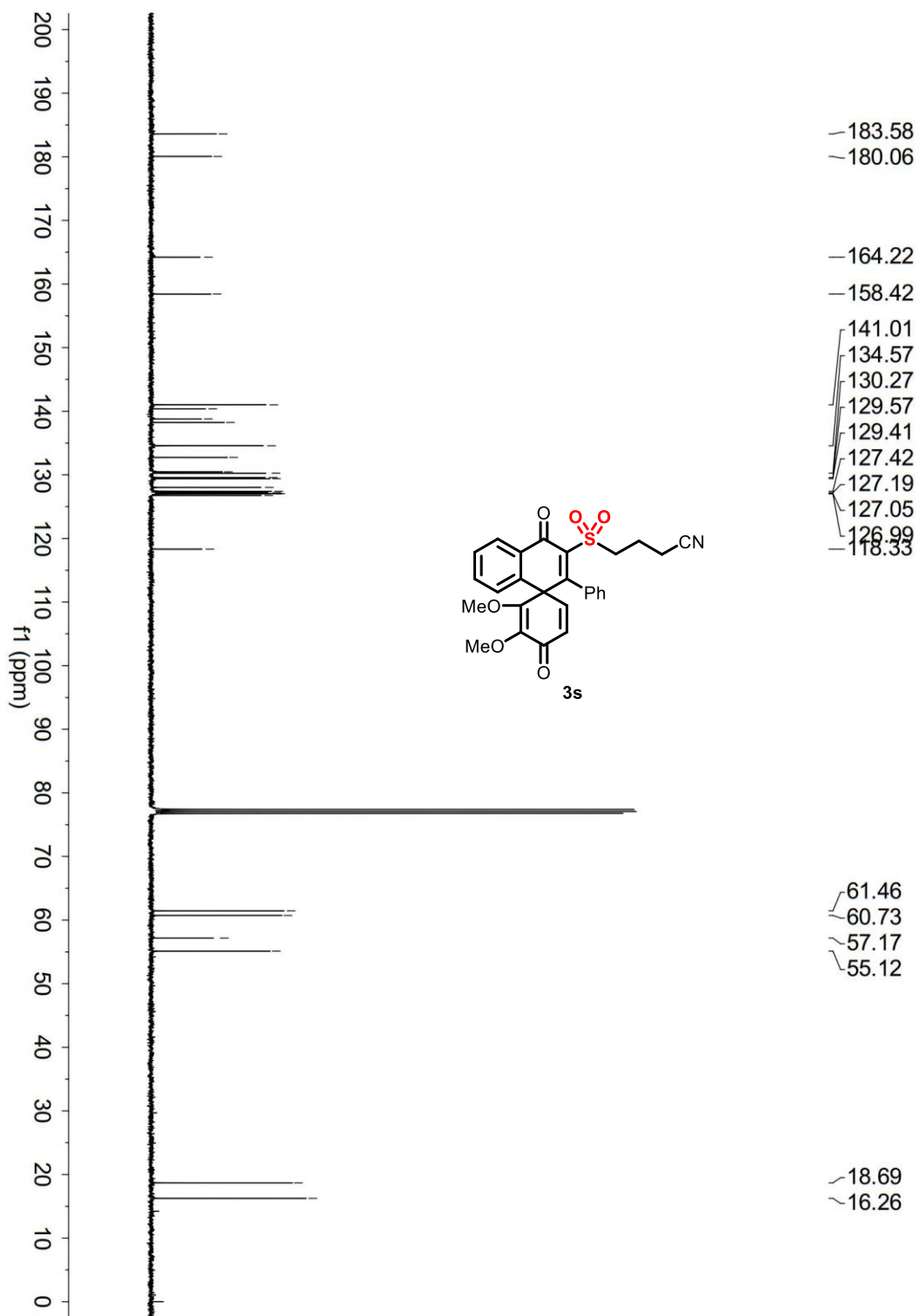
^{13}C NMR spectrum of compound **3r** (100 MHz, CDCl_3)



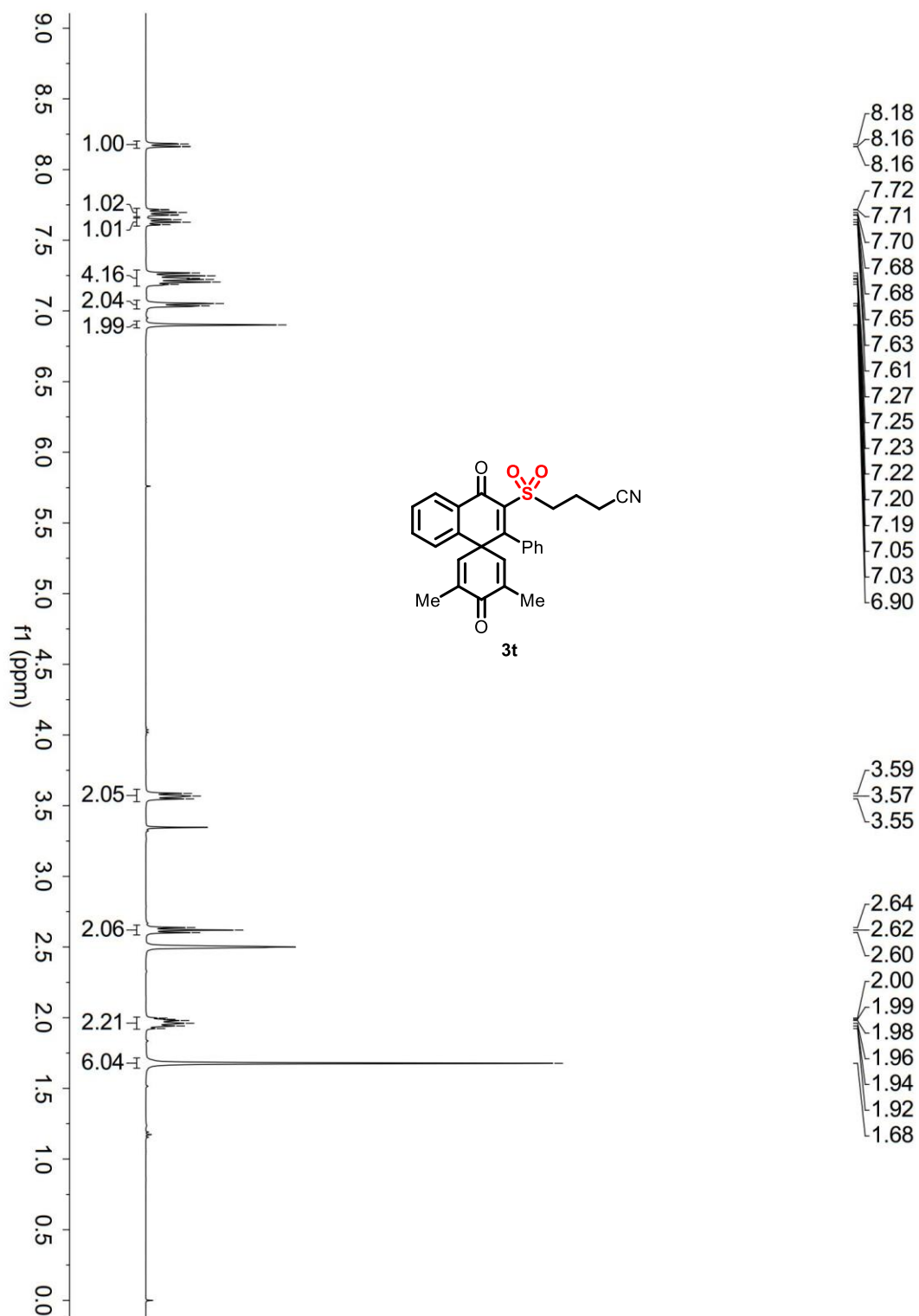
^1H NMR spectrum of compound **3s** (400 MHz, CDCl_3)



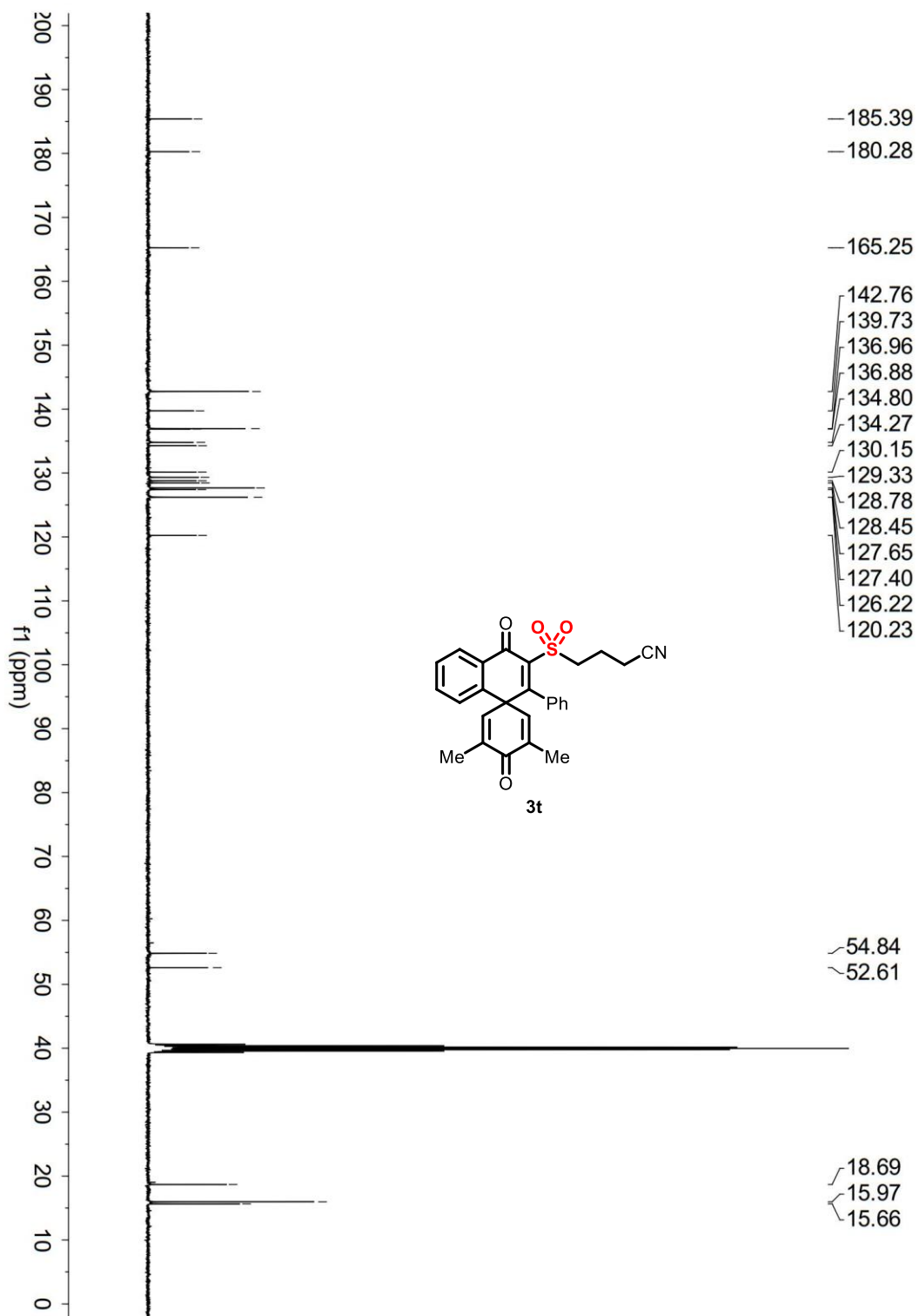
^{13}C NMR spectrum of compound **3s** (100 MHz, CDCl_3)



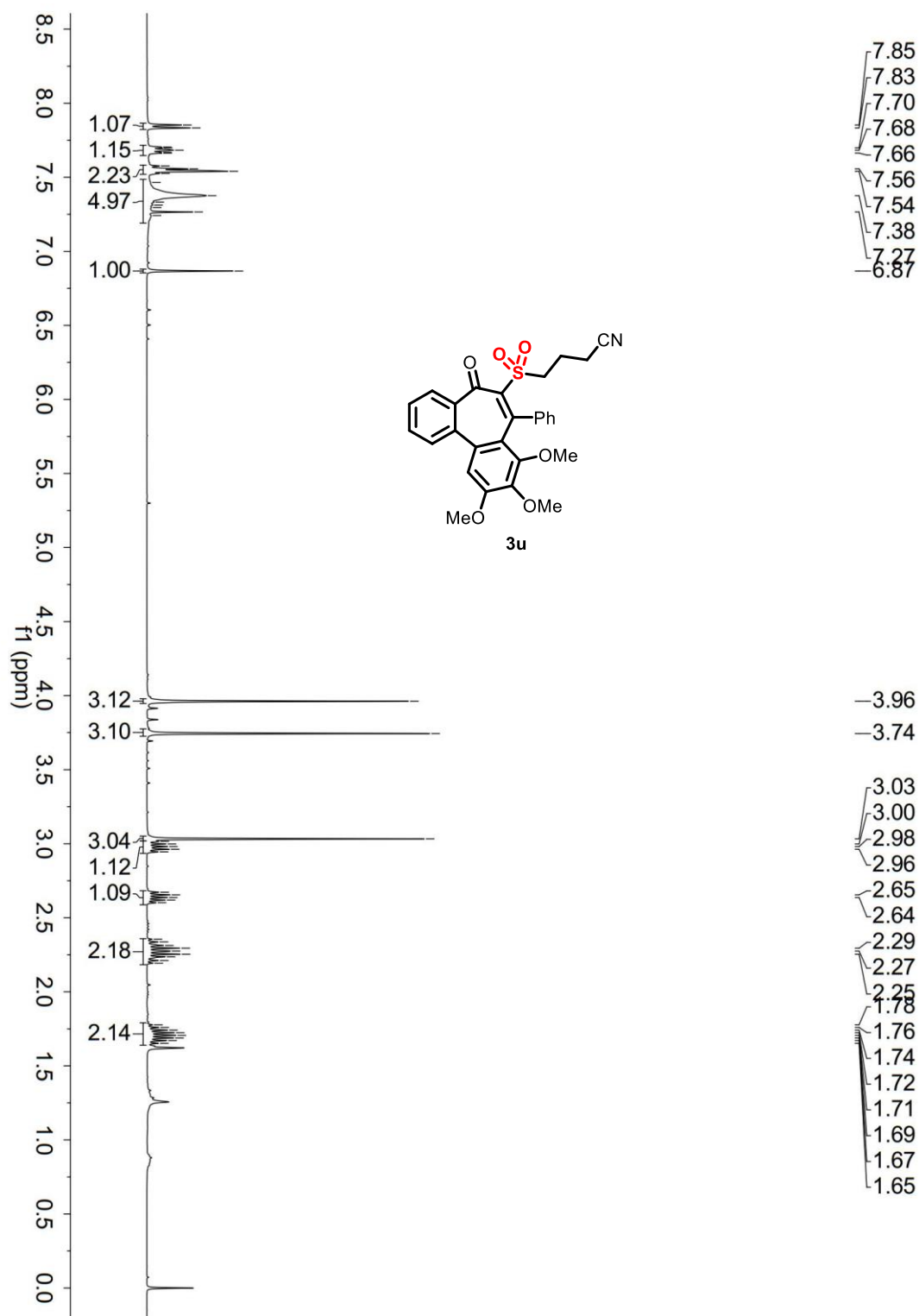
^1H NMR spectrum of compound **3t** (400 MHz, $\text{DMSO-}d_6$)



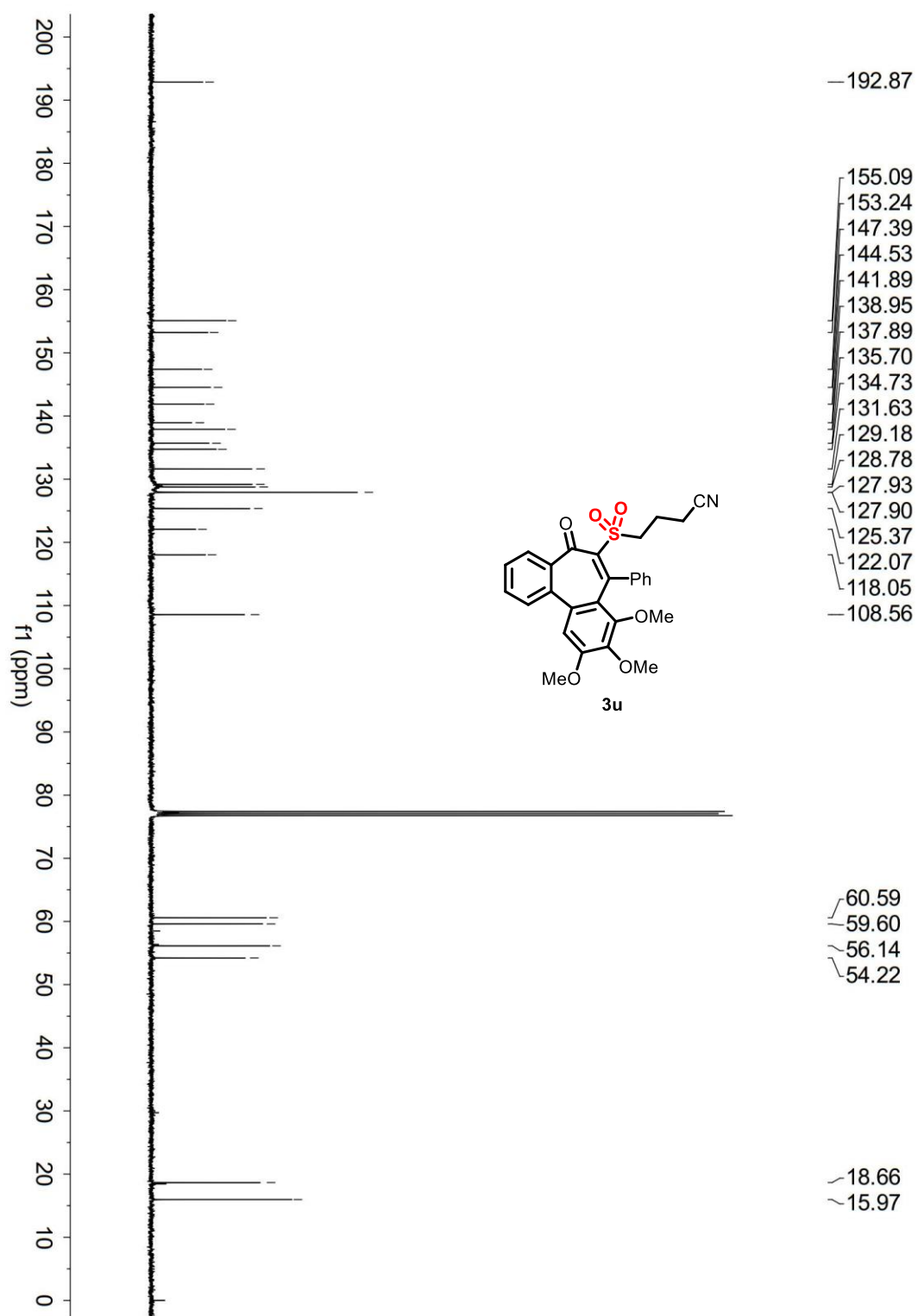
^{13}C NMR spectrum of compound **3t** (100 MHz, $\text{DMSO-}d_6$)



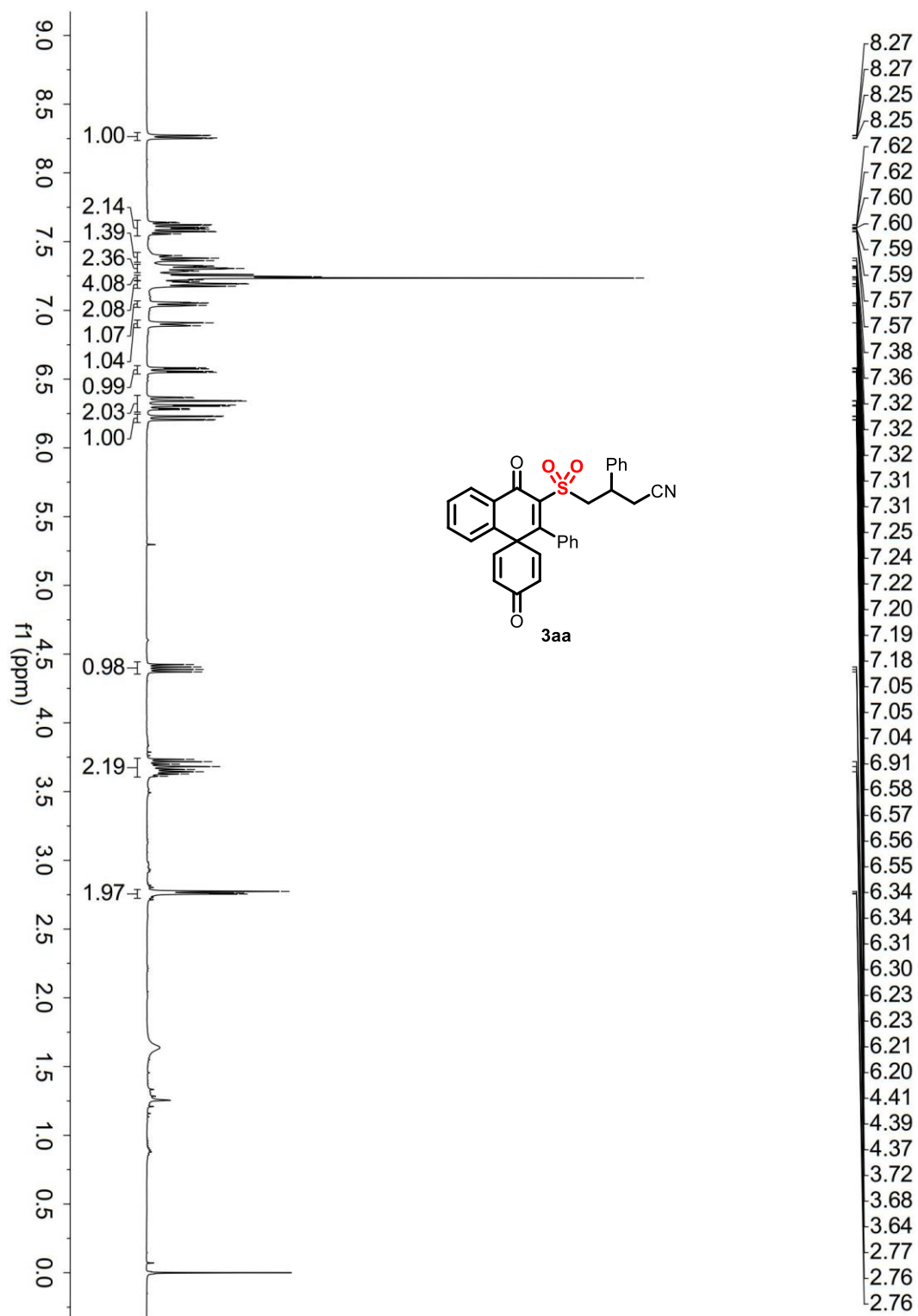
^1H NMR spectrum of compound **3u** (400 MHz, CDCl_3)



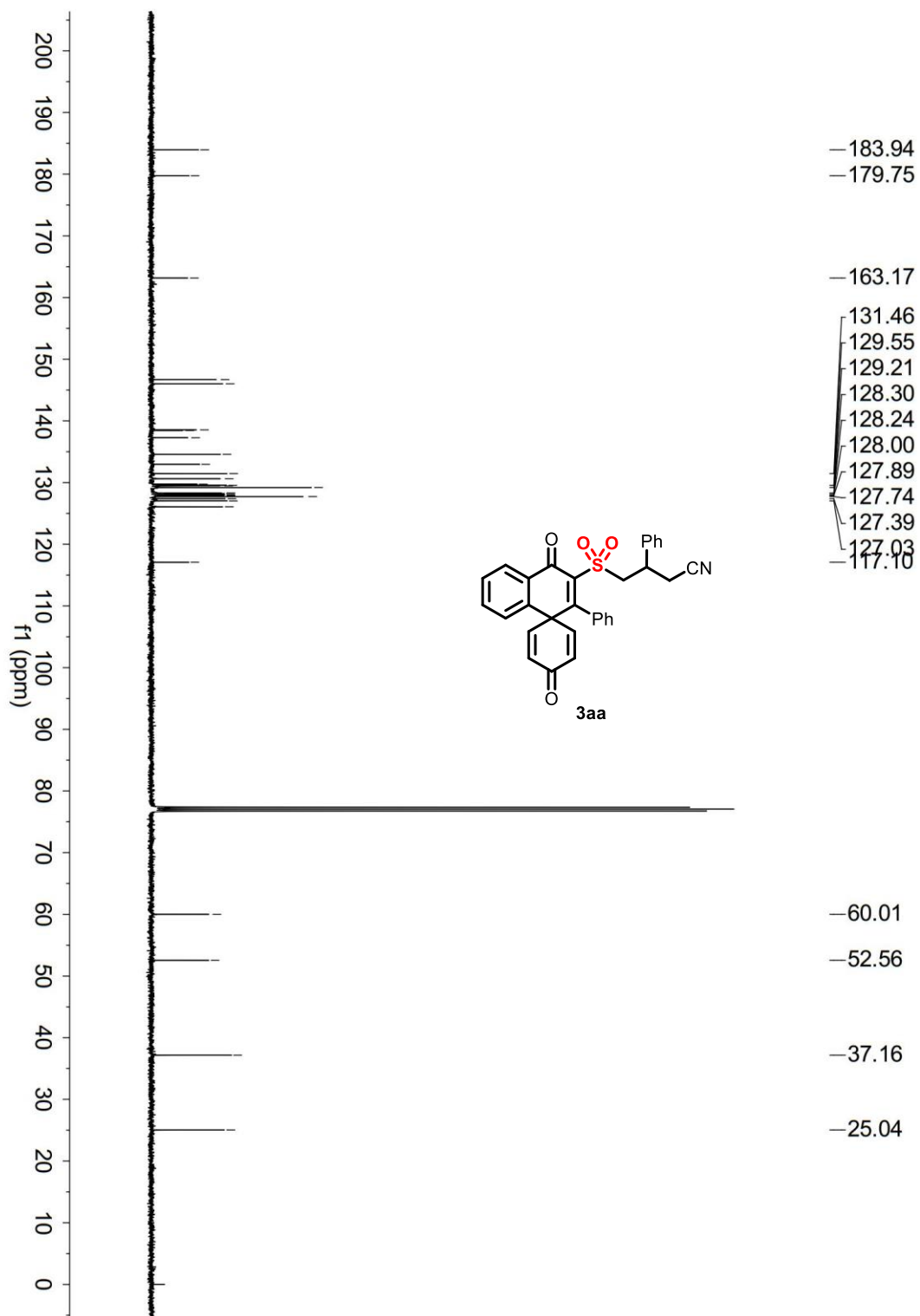
^{13}C NMR spectrum of compound **3u** (100 MHz, CDCl_3)



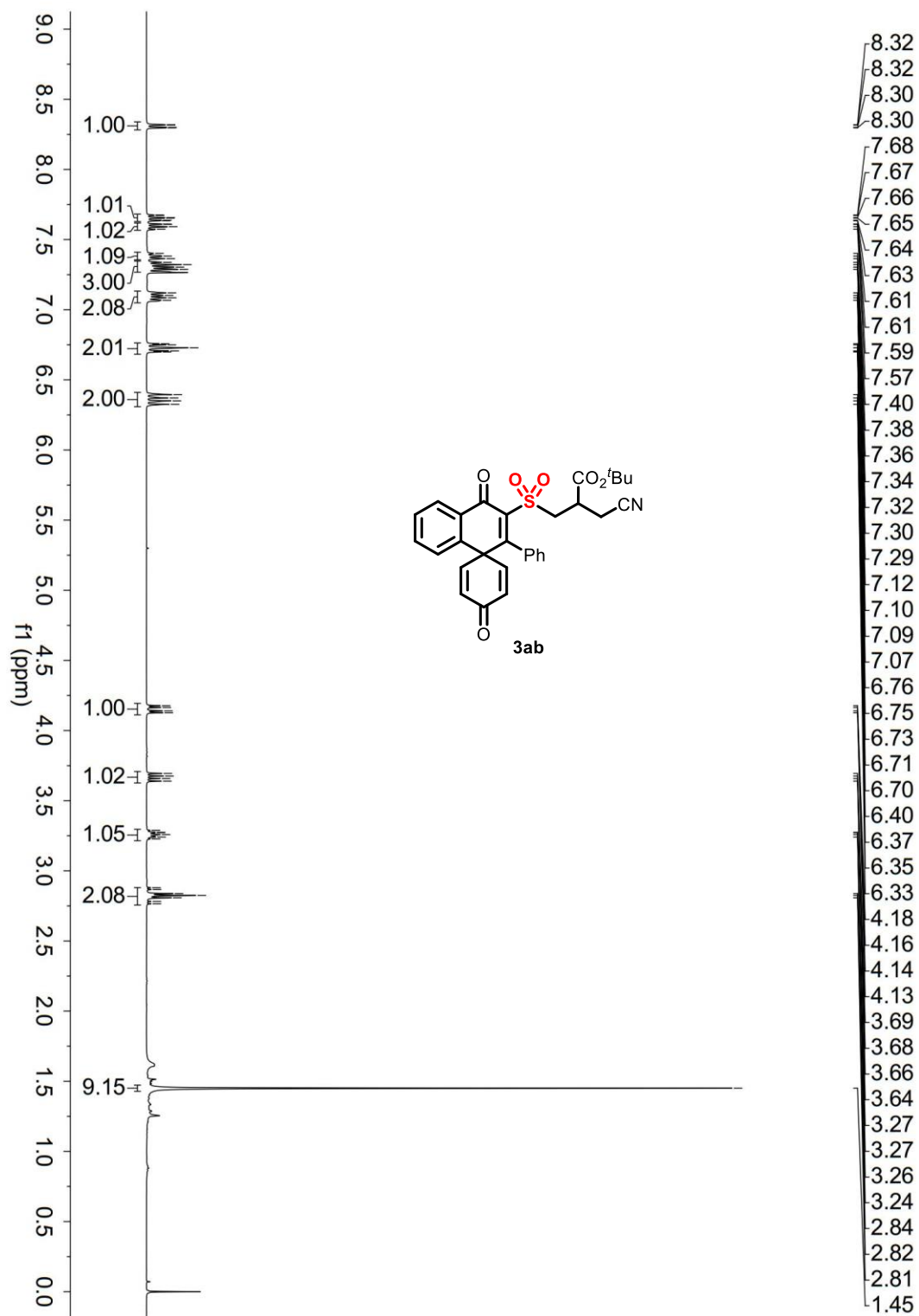
¹H NMR spectrum of compound **3aa** (400 MHz, CDCl₃)



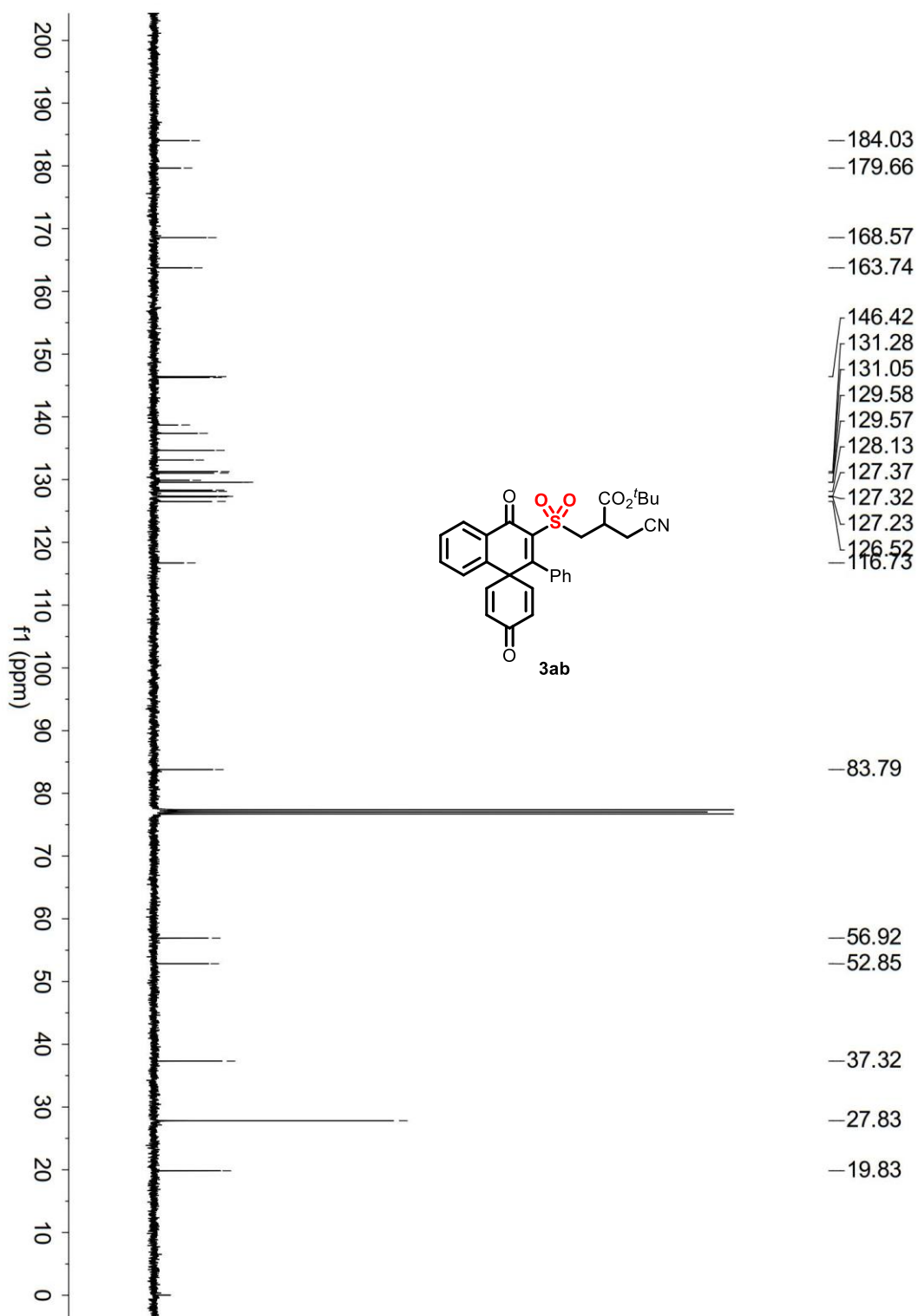
^{13}C NMR spectrum of compound **3aa** (100 MHz, CDCl_3)



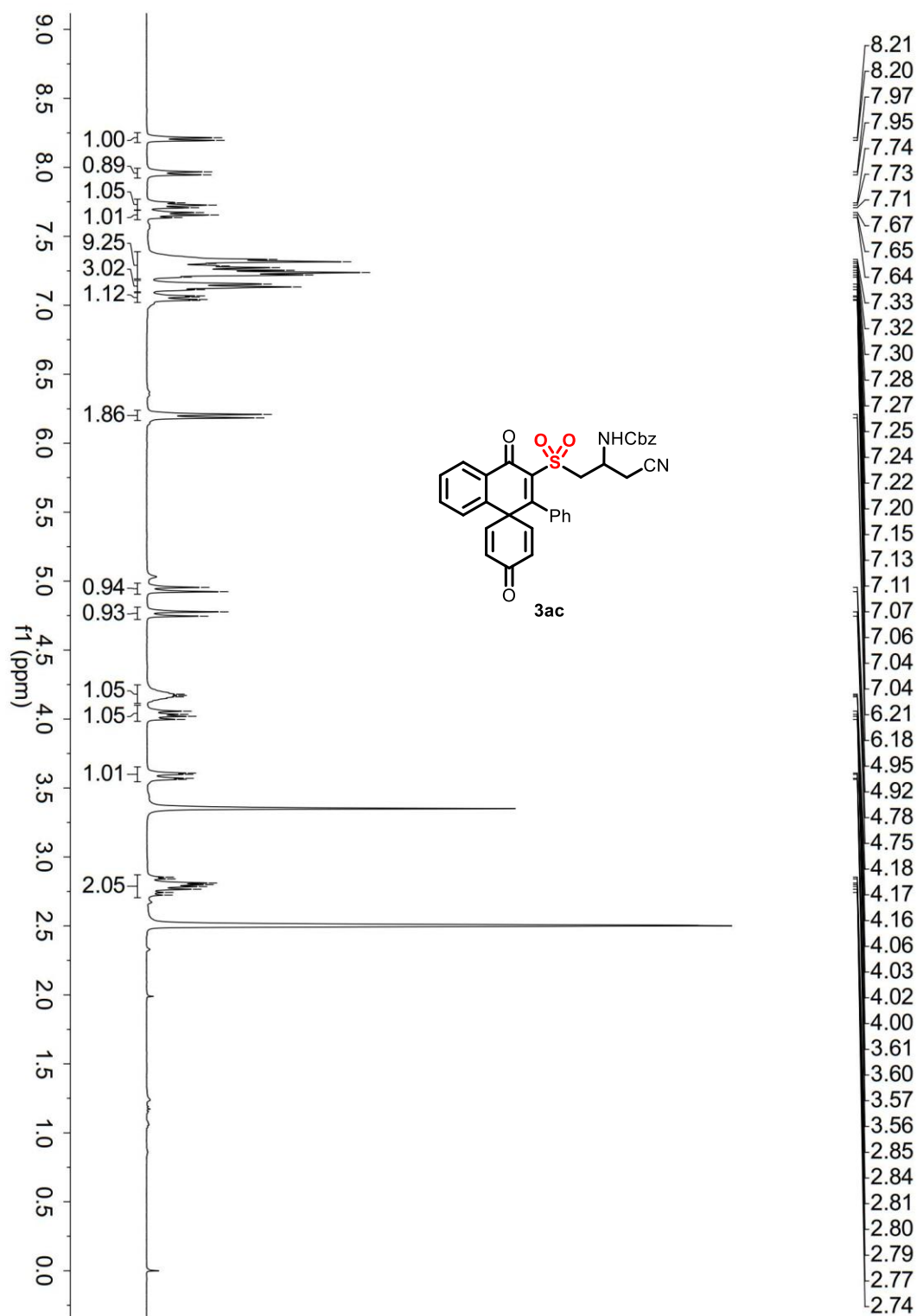
^1H NMR spectrum of compound **3ab** (400 MHz, CDCl_3)



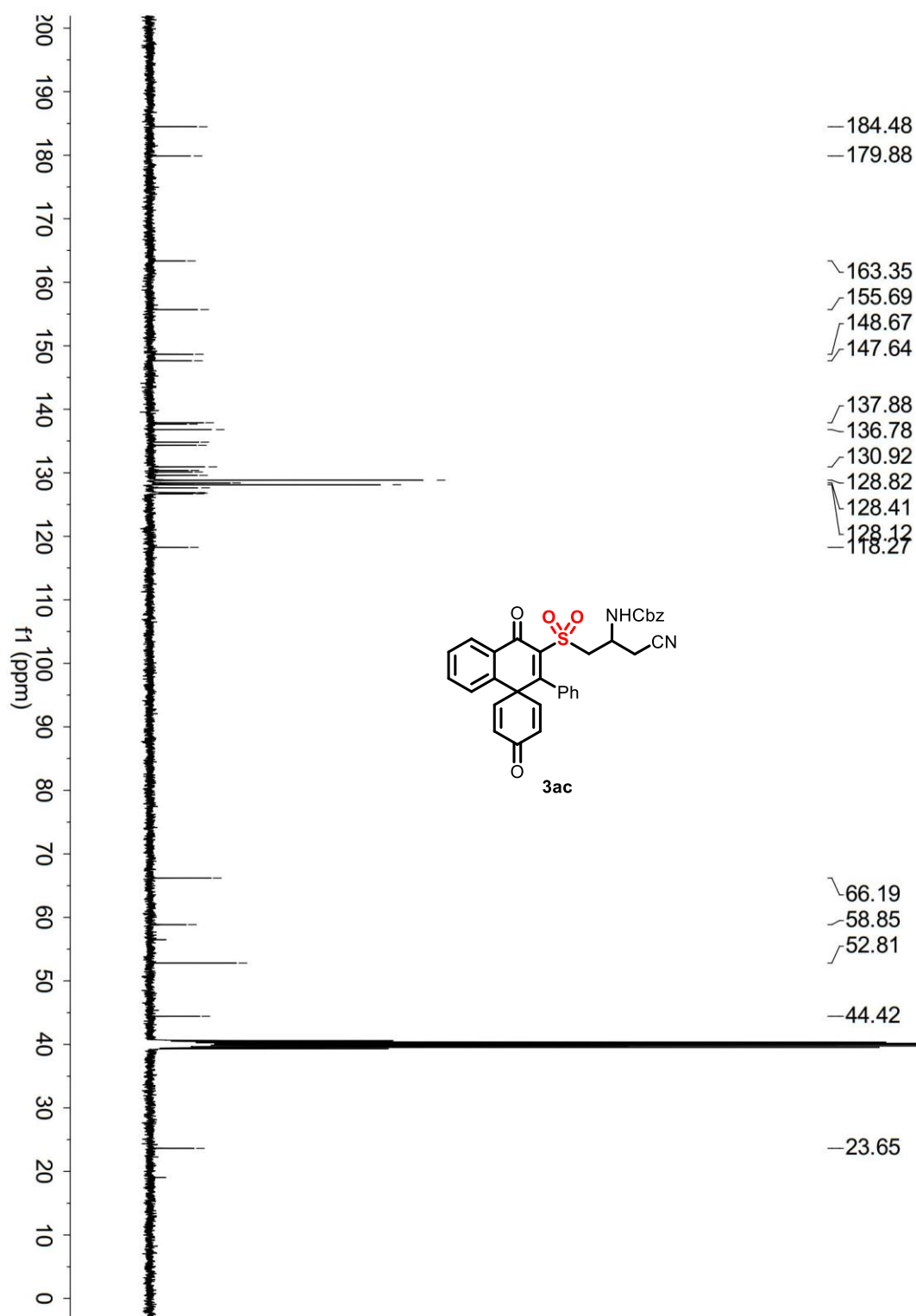
^{13}C NMR spectrum of compound **3ab** (100 MHz, CDCl_3)



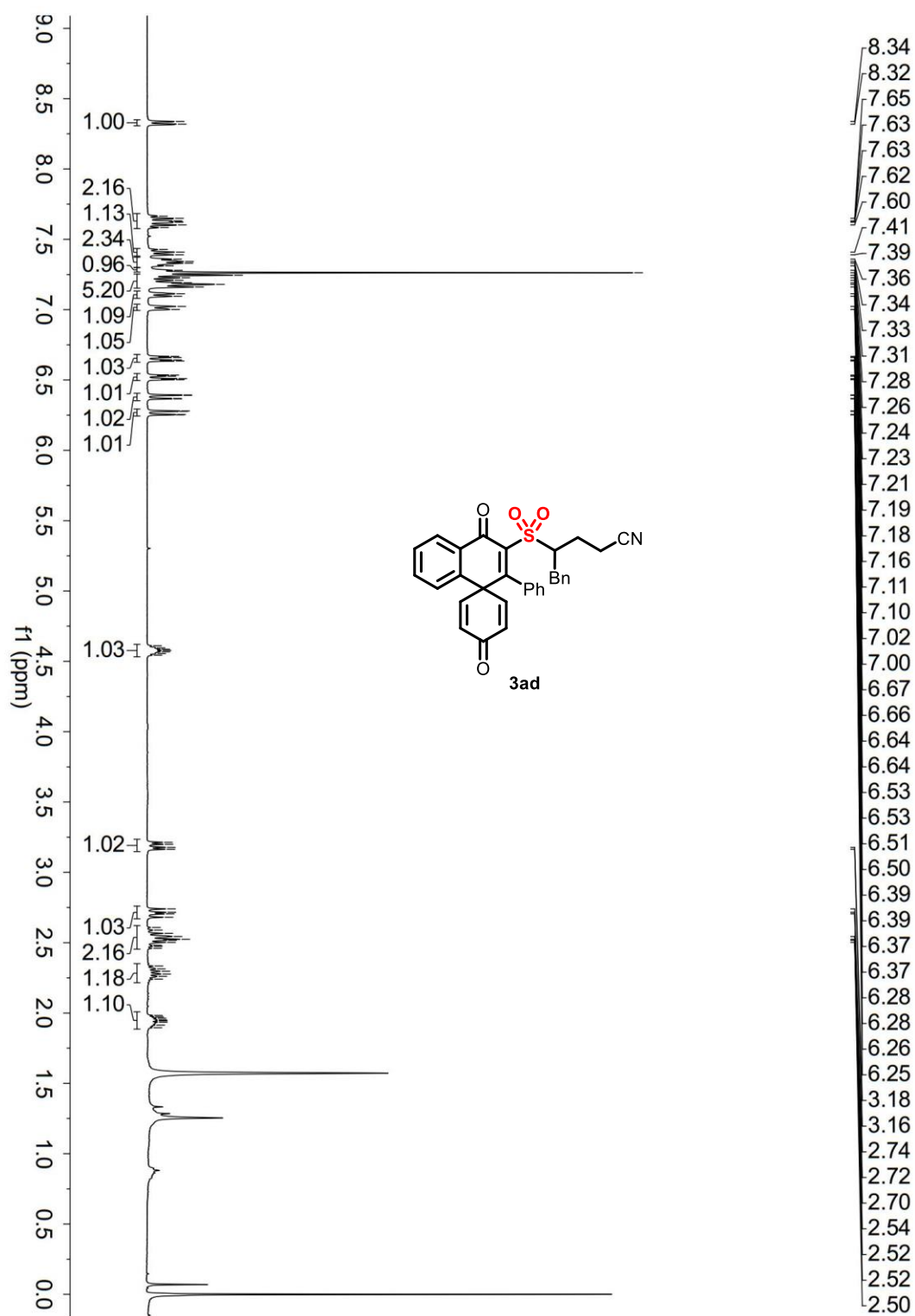
^1H NMR spectrum of compound **3ac** (400 MHz, $\text{DMSO-}d_6$)



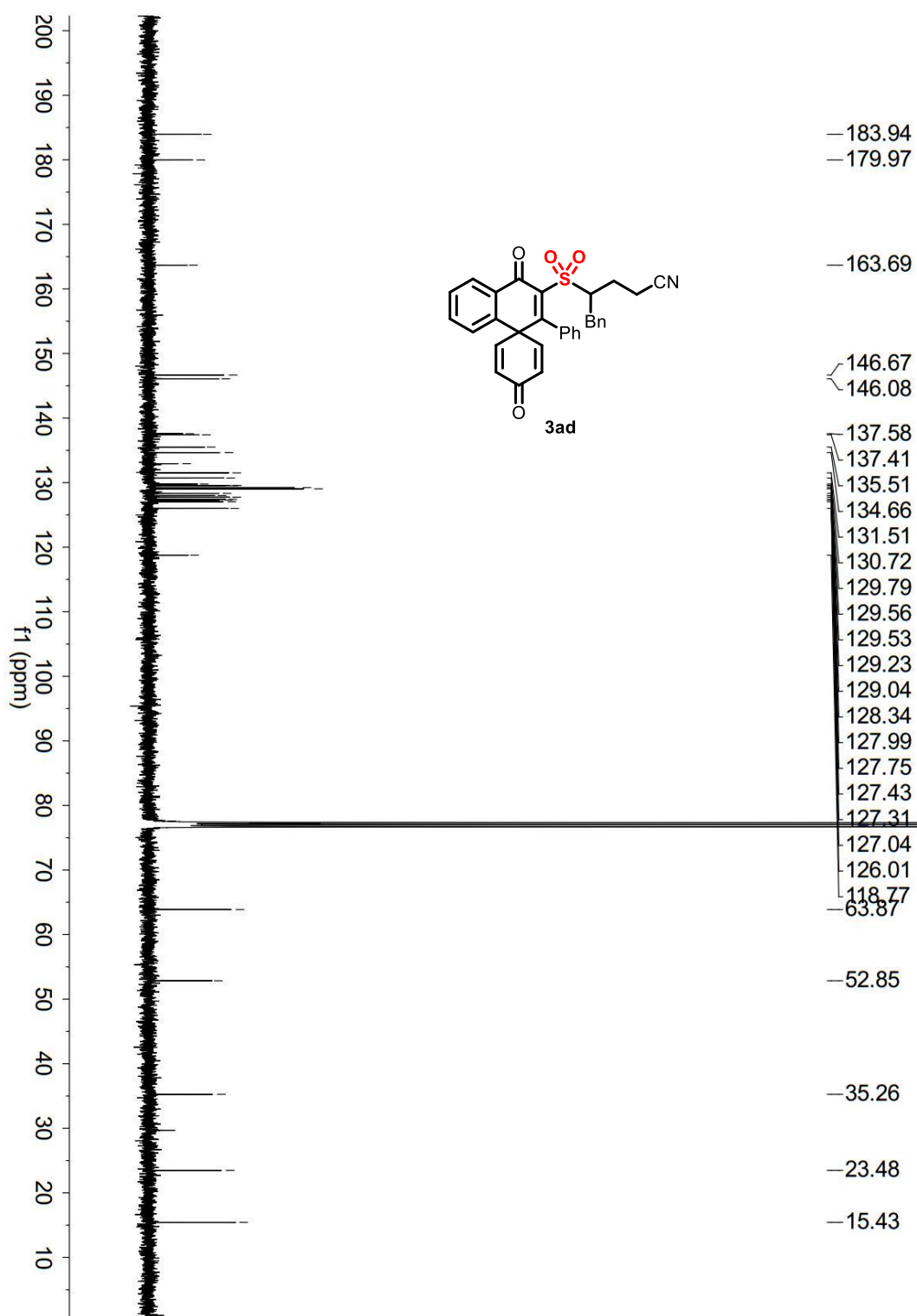
¹³C NMR spectrum of compound **3ac** (100 MHz, DMSO-*d*₆)



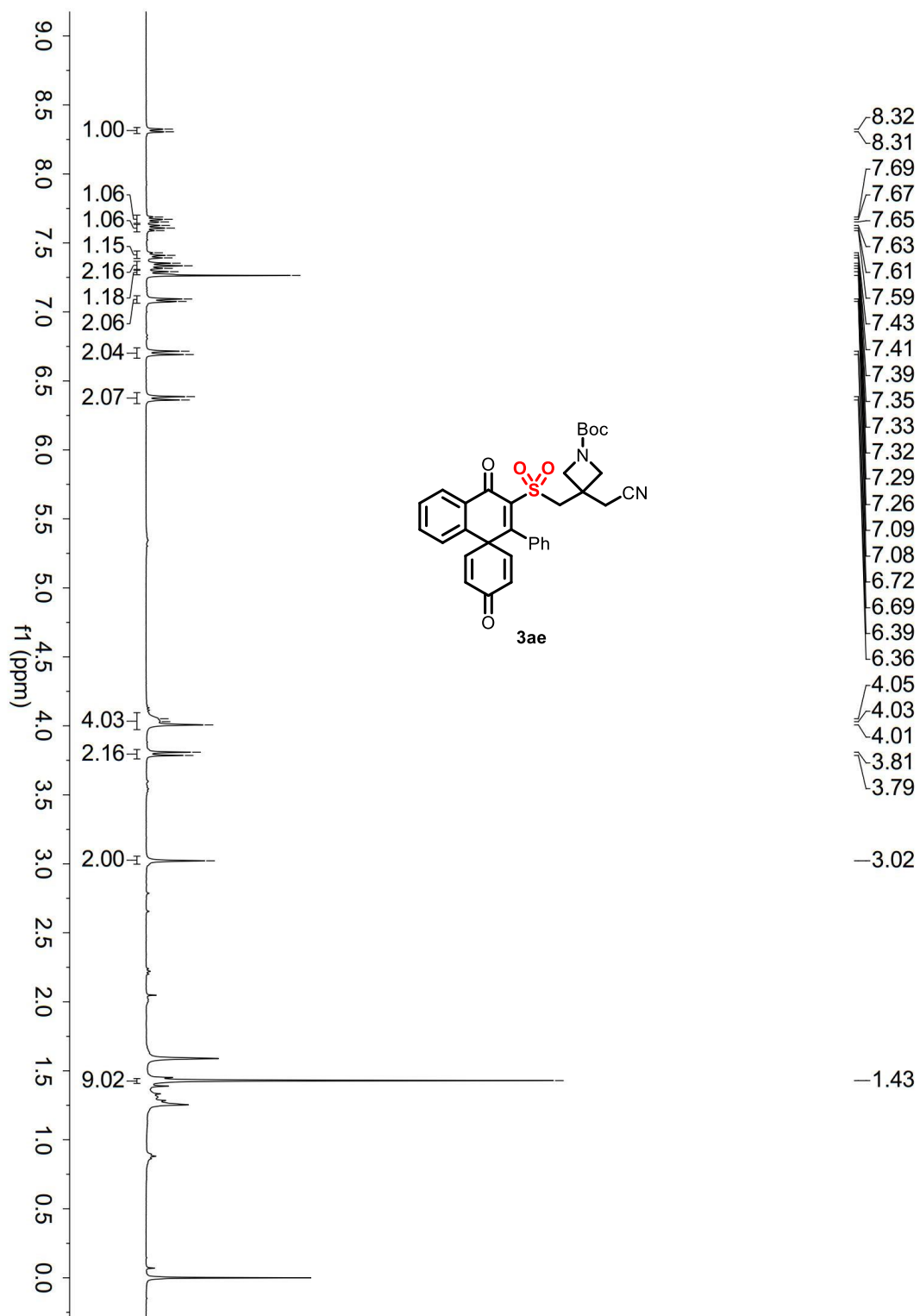
^1H NMR spectrum of compound **3ad** (400 MHz, CDCl_3)



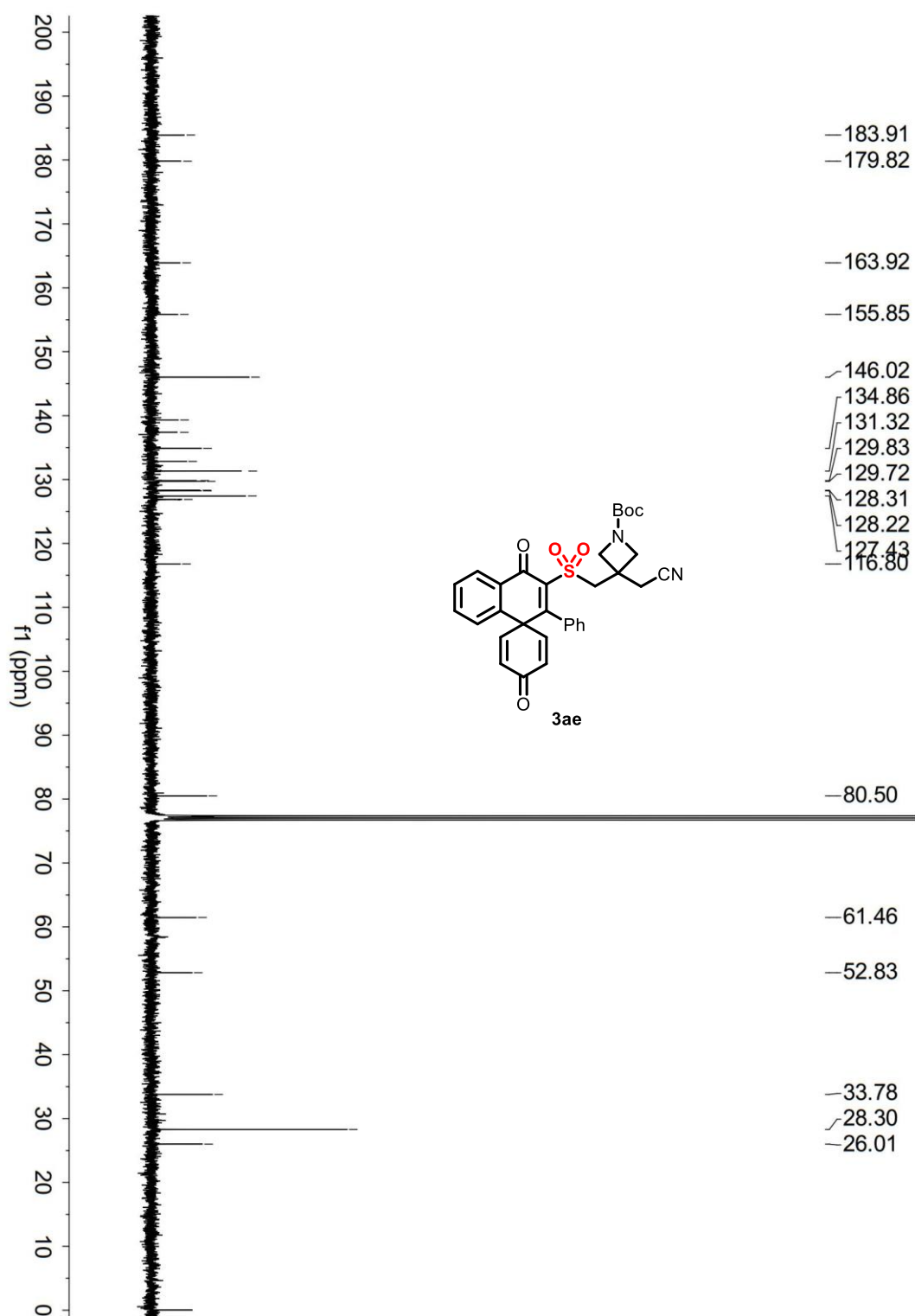
^{13}C NMR spectrum of compound **3ad** (100 MHz, CDCl_3)



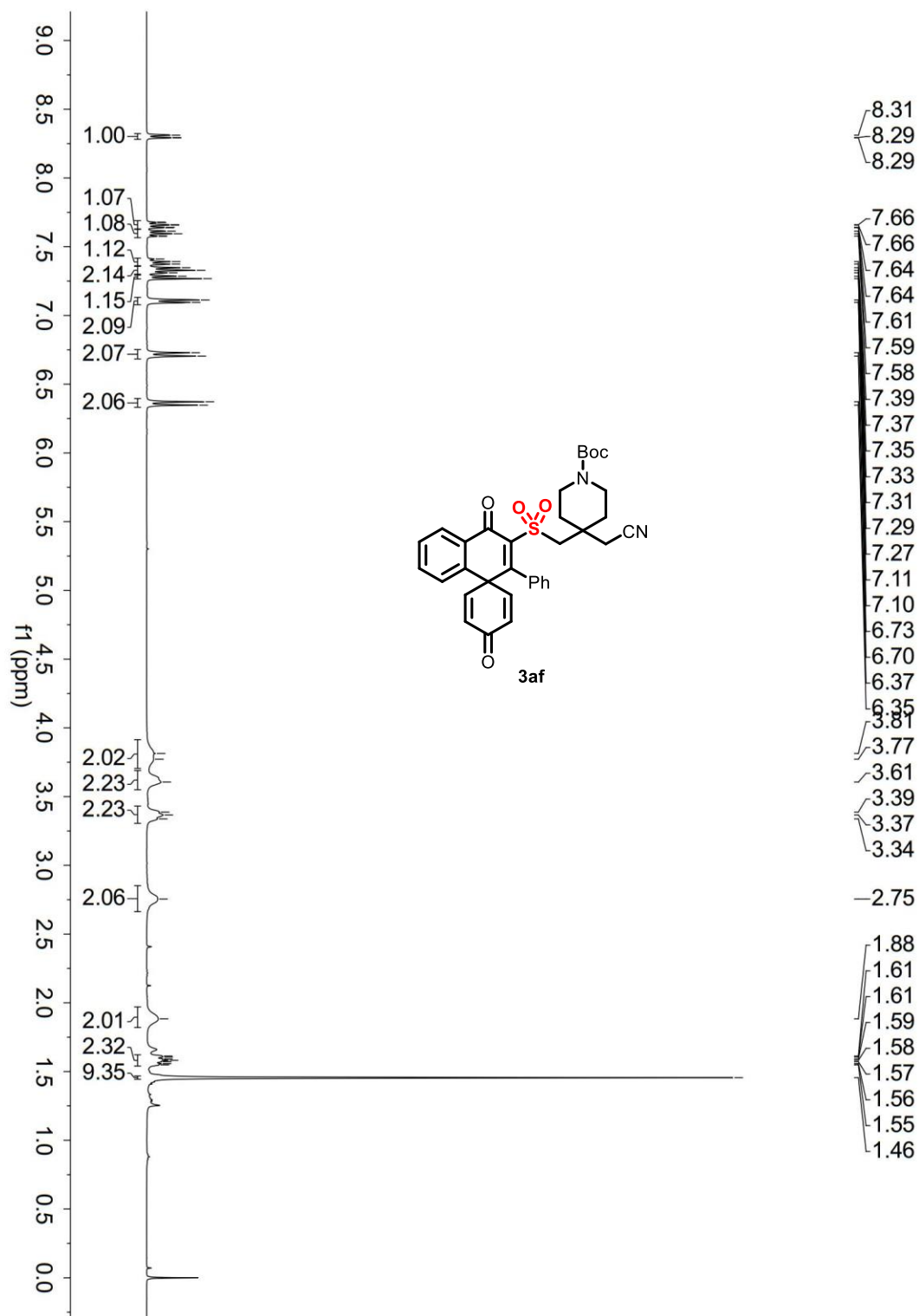
^1H NMR spectrum of compound **3ae** (400 MHz, CDCl_3)



^{13}C NMR spectrum of compound **3ae** (100 MHz, CDCl_3)



¹H NMR spectrum of compound **3af** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound **3af** (100 MHz, CDCl_3)

