Electronic Supplementary Information

Metal-free, visible-light-promoted oxidative radical cyclization of N-biarylglycine esters: one-pot construction of phenanthridine-6-carboxylates in water

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Table of Contents:

Experimental Section

General Aspects

Unless otherwise noted, all reactions were performed in a 10 mL vial in the open air atmosphere. Photoirradiation was performed with a 34 W blue LED. All commercial chemicals, reagents and precursors were purchased from commercial suppliers and used without further purification. All organic solvents were dried over 4Å molecular sieves and distilled prior to use. Water was double-distilled prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm and near UV 366 nm lights. ^{1}H NMR and ^{13}C NMR spectra were measured in deuterated DMSO (DMSO-d_6) and recorded on Brucker spectrometer. Chemical shifts are expressed in parts per million (ppm) and were calibrated using the residual protonated solvent peak. High resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF-Premier instrument. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. Melting points were determined by a PERFIT-melting point apparatus and are uncorrected. Compounds described in the literature were characterized by comparing their physical and spectroscopic data to the reported values.

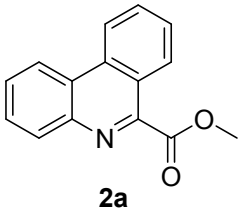
General procedure to prepare phenanthridine-6-carboxylates

To a vial (10 mL) equipped with a magnetic stir bar was charged with N-biarylglycine esters (0.3 mmol), rose bengal (5 mol%) and 3-4 mL of water. The mixture was stirred few minutes to mix well at room temperature and then vial was irradiated through the plane bottom side of the vial using a 34 W blue LED at a distance of 2 cm for 24 h. Subsequently, the reaction mixture was removed from irradiation and the organic matters were completely precipitated by cooling to 0 °C. Precipitates were isolated by filtration and purified further by recrystallization using ethanol or ethyl acetate solution. The purity of the compound was confirmed by melting point, IR, NMR and mass spectral analyses, vide infra.

Synthesis of methyl 5,6-dihydrophenanthridine-6-carboxylate (1-IV)

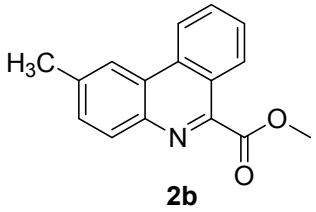
To a screw-topped Pyrex reaction tube was added methyl phenanthridine-6-carboxylate (**2a**, 1.0 mmol), isopropanol (2.0 mL) and then concentrated hydrochloric acid (5.0 mmol, 400 μL). The solution was degassed by freeze-pump-thaw method, sealed and irradiated with a LED (λ = 410 nm) at a distance of 1.0 mm for 12 hours. Afterwards, the reaction mixture was neutralized with 1.0 M aqueous sodium hydroxide solution and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by a column chromatography on neutral alumina using solution mixture of methanol-dichloromethane as eluents.

Experimental characterization data for products



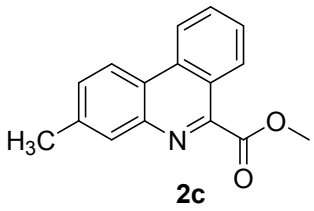
2a

Methyl phenanthridine-6-carboxylate (2a).[1-3] Pale yellow solid (67 mg, 93%): R_f 0.6 in ethyl acetate–hexane (25:75); mp = 98–100 °C (lit.[3] mp 98–100 °C); IR (neat, cm^{-1}): *v* 3056, 3017, 1743, 1724, 1620, 1609, 1566, 1483, 1446, 1390, 1327, 1248, 1136, 713, 612. ^1H NMR (300 MHz, DMSO-d_6) δ 8.69-8.55 (m, 3H), 8.31 (m, 1H), 7.89 (m, 1H), 7.79-7.73 (m, 3H), 4.15 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 150.4, 142.6, 133.4, 131.2, 131.0, 129.1, 128.7, 127.8, 127.4, 124.9, 123.6, 122.2, 122.0, 53.2. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{11}NNaO_2$ 260.0687, found 260.0685.



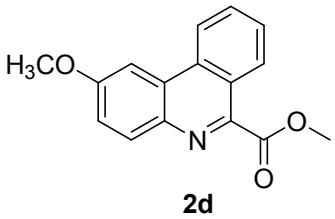
2b

Methyl 2-methylphenanthridine-6-carboxylate (2b).[1-3] Colorless solid (76 mg, 92%): R_f 0.58 in ethyl acetate–hexane (25:75); mp = 135–137 °C (lit.[3] mp 136–137 °C); IR (neat, cm^{-1}): *v* IR (neat, cm^{-1}): *v* 3058, 3023, 1742, 1723, 1620, 1611, 1567, 1483, 1447, 1392, 1327, 1248, 1131. ^1H NMR (300 MHz, DMSO-d_6) δ 8.63 (m, 2H), 8.35 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.89-7.81 (m, 1H), 7.73-7.68 (m, 1H), 7.60 (m, 1H), 4.14 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.7, 149.1, 140.9, 139.0, 133.2, 130.9, 130.8, 130.7, 127.8, 127.4, 124.8, 123.8, 122.2, 121.6, 53.1, 22.1. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_2$ 274.0844, found 274.0839.



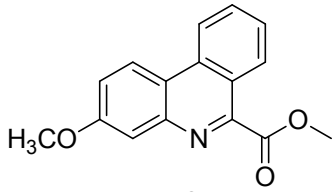
2c

Methyl 3-methylphenanthridine-6-carboxylate (2c).[1] White solid (72 mg, 88%): R_f 0.58 in ethyl acetate–hexane (25:75); mp = 82–83 °C (lit.[1] mp 81–83 °C); IR (neat, cm^{-1}): *v* 3061, 3056, 3014, 2921, 1741, 1723, 1622, 1614, 1571, 1473, 1456, 1306, 774, 752. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.61-8.55 (m, 2H), 8.41 (d, J = 8.6 Hz, 1H), 8.07 (s, 1H), 7.83 (t, J = 8.4 Hz, 1H), 7.66 (t, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 4.14 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 150.3, 142.7, 139.4, 133.5, 131.1, 130.5, 130.4, 127.6, 127.3, 123.2, 122.5, 121.9, 121.8, 53.2, 21.4. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_2$ 274.0844, found 274.0839.



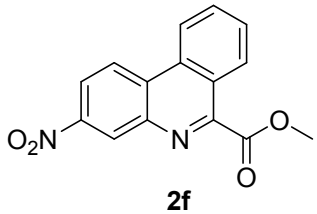
2d

Methyl 2-methoxyphenanthridine-6-carboxylate (2d). White solid (82 mg, 94%): R_f 0.52 in ethyl acetate–hexane (25:75); mp = 159–162 °C; IR (neat, cm^{-1}): *v* 3076, 3017, 1743, 1723, 1616, 1564, 1365, 1306, 1150, 771. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.67 (d, *J* = 8.6 Hz, 1H), 8.59-8.55 (m, 2H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.93 (t, J = 8.2 Hz, 1H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.75-7.71 (m, 1H), 4.17 (s, 3H), 3.94 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 150.2, 140.6, 134.6, 132.1, 131.1, 129.5, 128.3, 127.2, 125.7, 123.5, 122.1, 121.6, 55.5, 53.2. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_3$ 290.0793, found 290.0791.



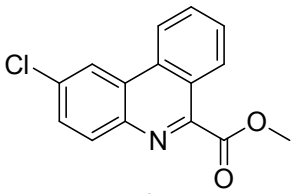
2e

Methyl 3-methoxyphenanthridine-6-carboxylate (2e).[1,2] White solid (78 mg, 90%): R_f 0.51 in ethyl acetate–hexane (25:75); mp = 111–113 °C (lit.[1] mp 110–112 °C); IR (neat, cm^{-1}): *v* 3057, 3014, 1742, 1723, 1614, 1487, 1461, 1363, 1141, 773. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.61 (d, J = 8.6 Hz, 1H), 8.57 (d, J = 8.6 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 7.2 Hz, 1H), 7.69-7.66 (m, 2H), 7.42-7.36 (m, 1H), 4.16 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 160.3, 150.4, 144.3, 133.6, 131.2, 127.4, 127.0, 123.3, 122.7, 121.5, 120.3, 119.3, 110.2, 55.7, 53.2. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_3$ 290.0793, found 290.0789.



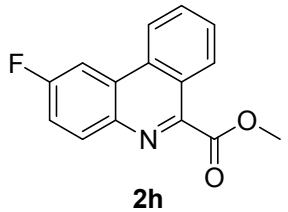
2f

Methyl 3-nitrophenanthridine-6-carboxylate (2f).[2] Pale yellow solid (52 mg, 56%): R_f 0.42 in ethyl acetate–hexane (25:75); mp = 176–178 °C; IR (neat, cm^{-1}): *v* 3064, 3019, 1744, 1722, 1620, 1607, 1561, 1521, 1479, 1476, 1362, 1347, 791, 704. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.18-9.14 (m, 1H), 8.74-8.71 (m, 2H), 8.66 (d, J = 8.4 Hz, 1H), 8.54-8.50 (m, 1H), 8.03 (t, J = 7.4 Hz, 1H), 7.89 (t, J = 7.4 Hz, 1H), 4.19 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.8, 152.7, 147.8, 142.1, 132.3, 132.2, 129.9, 129.2, 127.9, 126.6, 124.4, 123.6, 123.0, 122.2, 53.5. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{10}N_2NaO_4$ 305.0538, found 305.0532.



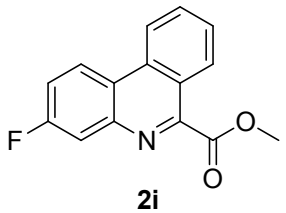
2g

Methyl 2-chlorophenanthridine-6-carboxylate (2g).[1-3] White solid (69 mg, 78%): R_f 0.59 in ethyl acetate–hexane (25:75); mp = 145–147 °C (lit.[3] mp 146–147 °C); IR (neat, cm^{-1}): ν 3094, 3059, 3018, 1743, 1723, 1617, 1562, 1489, 1366, 1143, 729. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.66 (d, J = 8.5 Hz, 1H), 8.59-8.54 (m, 2H), 8.23 (d, J = 8.8 Hz, 1H), 7.92 (t, J = 8.2 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.74-7.71 (m, 1H), 4.16 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 150.4, 150.1, 134.9, 132.5, 132.4, 131.4, 129.8, 128.6, 127.4, 126.0, 123.8, 122.3, 121.9, 53.4. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{10}ClNNaO_2$ 294.0298, found 294.0291.



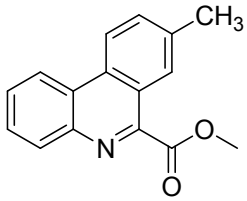
2h

Methyl 2-fluorophenanthridine-6-carboxylate (2h).[1,2] White solid (58 mg, 69%): R_f 0.60 in ethyl acetate–hexane (25:75); mp = 145–146 °C (lit.[1] mp 144–146 °C); IR (neat, cm^{-1}): ν 3057, 3021, 1741, 1724, 1618, 1560, 1491, 1363, 1143, 728. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.67 (d, J =8.6 Hz, 1H), 8.53 (d, J =8.6 Hz, 1H), 8.32-8.27 (m, 1H), 8.21-8.18 (m, 1H), 7.91 (t, J =7.7 Hz, 1H), 7.77 (t, J =7.7 Hz, 1H),7.55-7.52 (m, 1H), 4.15 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 163.5, 149.3, 139.4, 133.5, 132.9, 131.3, 128.7, 127.5, 126.6, 123.4, 122.3, 118.5, 107.2, 53.2. ^{19}F NMR (282 MHz, DMSO-d_6): δ −109.3. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{10}FNNaO_2$ 278.0593, found 278.0587.



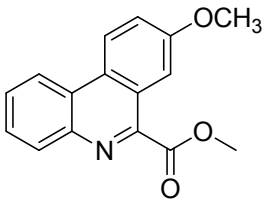
2i

Methyl 3-fluorophenanthridine-6-carboxylate (2i).[1,2] Pale yellow solid (64 mg, 77%): R_f 0.60 in ethyl acetate–hexane (25:75); mp = 129–131 °C (lit.[1] mp 128–130 °C); IR (neat, cm^{-1}): *v* 3072, 3058, 3019, 1744, 1722, 1623, 1608, 1567, 1484, 1269, 1144, 707. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62-8.58 (m, 3H), 7.94-7.89 (m, 2H), 7.76-7.73 (m, 1H), 7.53-7.49 (m, 1H), 4.16 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.3, 164.0, 151.6, 143.9, 133.4, 131.7, 130.9, 127.9, 127.6, 124.2, 123.1, 121.9, 121.7, 118.0, 115.5, 53.3. ^{19}F NMR (282 MHz, DMSO-d_6): δ −110.7. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{10}FNNaO_2$ 278.0593, found 278.0590.



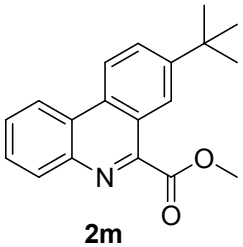
2k

Methyl 8-methylphenanthridine-6-carboxylate (2k).[1,3] Yellow solid (72 mg, 88%): R_f 0.57 in ethyl acetate–hexane (25:75); mp = 79–81 °C (lit.[1] mp 80–81 °C); IR (neat, cm^{-1}): *v* 3068, 3054, 3015, 1743, 1723, 1619, 1610, 1566, 1492, 1343, 1232, 1029, 712, 601. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57-8.51 (m, 2H), 8.39-8.36 (m, 1H), 8.28-8.23 (m, 1H), 7.76-7.68 (m, 3H), 4.16 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.8, 150.1, 142.4, 138.2, 133.0, 131.5, 131.0, 128.5, 126.6, 125.2, 123.7, 122.0, 121.9, 53.2, 21.7. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_2$ 274.0844, found 274.0839.



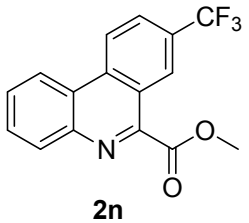
2l

Methyl 8-methoxyphenanthridine-6-carboxylate (2l).[1,3] Yellow solid (79 mg, 90%): R_f 0.52 in ethyl acetate–hexane (25:75); mp = 101–103 °C (lit.[3] mp 102–103 °C); IR (neat, cm^{-1}): *v* 3055, 3016, 1742, 1724, 1620, 1613, 1563, 1491, 1345, 1233, 1029, 713. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.56 (d, J = 8.8 Hz, 1H), 8.52-8.48 (m, 1H), 8.33-8.22 (m, 1H), 8.17 (d, J = 2.8 Hz, 1H), 7.79-7.67 (m, 2H), 7.54-7.50 (m, 1H), 4.16 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.7, 159.3, 148.6, 141.9, 131.0, 128.8, 128.2, 128.1, 125.4, 125.2, 123.9, 122.5, 121.6, 106.9, 55.6, 53.3. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}NNaO_3$ 290.0793, found 290.0786.



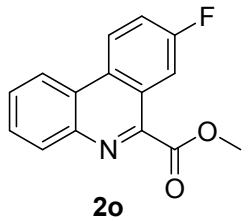
2m

Methyl 8-(tert-butyl)phenanthridine-6-carboxylate (2m).[1] Light brown liquid (88 mg, 92%): R_f 0.64 in ethyl acetate–hexane (25:75); IR (neat, cm^{-1}): *v* 3066, 3055, 3017, 1743, 1721, 1621, 1610, 1567, 1494, 1343, 1231, 1029, 714, 603. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.66-8.64 (m, 1H), 8.59-8.52 (m, 2H), 8.30-8.24 (m, 1H), 7.96-7.94 (m, 1H), 7.77-7.70 (m, 2H), 4.17 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 151.2, 150.2, 142.5, 131.4, 131.0, 129.7, 128.8, 125.0, 123.7, 122.8, 122.0, 121.9, 53.3, 35.2, 31.1. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_2$ 316.1313, found 316.1309.



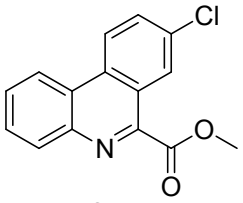
2n

Methyl 8-(trifluoromethyl)phenanthridine-6-carboxylate (2n).[1,3] White solid (88 mg, 89%): R_f 0.57 in ethyl acetate–hexane (25:75); mp = 110–112 °C (lit.[3] mp 110–112 °C); IR (neat, cm^{-1}): ν 3061, 3056, 3014, 1742, 1720, 1619, 1612, 1567, 1331, 1232, 1163, 1132, 1081, 710. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.08 (s, 1H), 8.77 (d, J = 8.8 Hz, 1H), 8.63-8.58 (m, 1H), 8.36-8.31 (m, 1H), 8.11-8.05 (m, 1H), 7.85-7.81 (m, 2H), 4.18 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.8, 149.4, 143.3, 135.6, 131.4, 130.3, 129.8 (q, J = 33.2 Hz), 129.6, 127.0 (q, J = 3.2 Hz), 125.2 (q, J = 4.4 Hz), 124.2, 124.0 (q, J = 271.2 Hz), 123.4, 123.0, 122.4, 53.5. ^{19}F NMR (282 MHz, DMSO-d_6): δ −62.5. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{16}H_{10}F_3NNaO_2$ 328.0561, found 328.0556.



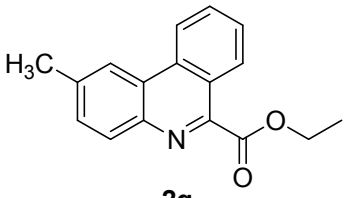
2o

Methyl 8-fluorophenanthridine-6-carboxylate (2o).[3] White solid (70 mg, 84%): R_f 0.59 in ethyl acetate–hexane (25:75); mp = 159–162 °C (lit.[3] mp 159–161 °C); IR (neat, cm^{-1}): ν 3069, 3056, 3017, 1745, 1724, 1621, 1612, 1567, 1344, 1232, 714, 607. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65-8.61 (m, 1H), 8.53-8.48 (m, 1H), 8.45-8.41 (m, 1H), 8.34-8.28 (m, 1H), 7.82-7.71 (m, 2H), 7.66-7.59 (m, 1H), 4.16 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 161.5 (d, J = 247.8 Hz), 148.6 (d, J = 4.4 Hz), 142.4, 131.3, 130.2 (d, J = 1.8 Hz), 129.4, 129.0, 124.9 (d, J = 9.0 HZ), 124.8 (d, J = 8.8 Hz), 121.8, 120.6 (d, J = 24.2 Hz), 112.3 (d, J = 23.3 Hz), 53.4. ^{19}F NMR (282 MHz, DMSO-d_6): δ −110.5. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{15}H_{10}FNNaO_2$ 278.0593, found 278.0591.



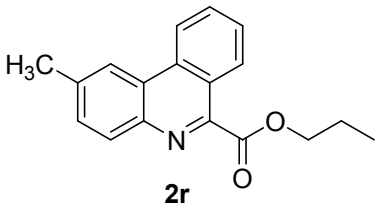
2p

Methyl 8-chlorophenanthridine-6-carboxylate (2p).[1,3] Yellow solid (77 mg, 87%): R_f 0.59 in ethyl acetate–hexane (25:75); mp = 140–142 °C (lit.[3] mp 141–143 °C); IR (neat, cm^{-1}): *v* 3061, 3055, 3016, 2931, 1744, 1723, 1613, 1532, 1496, 1464, 1363, 1257, 1173, 773, 739. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.74 (d, J = 2.4 Hz, 1H), 8.57 (d, J = 8.8 Hz, 1H), 8.56-8.49 (m, 1H), 8.31-8.26 (m, 1H), 7.86-7.73 (m, 3H), 4.16 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 148.8, 142.5, 134.3, 131.8, 131.2, 129.5, 129.3, 126.6, 124.5, 123.8, 121,9, 53.3. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{10}ClNNaO_2$ 294.0298, found 294.0293.



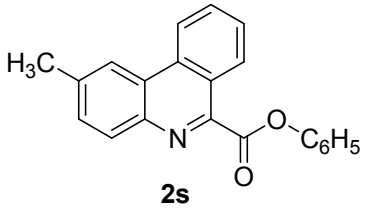
2q

Ethyl 2-methylphenanthridine-6-carboxylate (2q).[2] White solid (80 mg, 92%): R_f 0.58 in ethyl acetate–hexane (25:75); mp = 83–85 °C; IR (neat, cm^{-1}): *v* 3072, 3057, 3018, 1744, 1722, 1621, 1614, 1568, 1346, 1232, 714, 609. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65 (d, J = 8.6 Hz, 1H), 8.56 (d, J = 8.6 Hz, 1H), 8.37 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.88-7.85 (m, 1H), 7.72-7.69 (m, 1H), 7.62-7.59 (m, 1H), 4.65 (q, J =7.4 Hz, 2H), 2.65 (s, 3H), 1.54 (t, J = 8.0 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 150.1, 141.0, 138.9, 133.2, 130.9, 130.8, 130.6, 127.8, 127.2, 124.7, 123.6, 122.1, 121.6, 62.4, 22.2, 14.4. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{15}NNaO_2$ 288.1000, found 288.996.



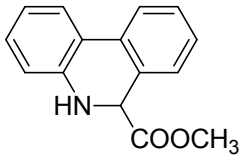
2r

Propyl 2-methylphenanthridine-6-carboxylate (2r).[2] Light yellow liquid (84 mg, 93%): R_f 0.57 in ethyl acetate–hexane (25:75); IR (neat, cm^{-1}): ν 3074, 3057, 3021, 1743, 1722, 1622, 1614, 1569, 1234, 715, 608. ^1H NMR (300 MHz, DMSO-d_6) δ 8.66 (d, J = 8.6 Hz, 1H), 8.54 (d, J = 8.6 Hz, 1H), 8.39 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.89-7.86 (m, 1H), 7.74-7.71 (m, 1H), 7.64-7.60 (m, 1H), 4.54 (t, J = 7.0 Hz, 2H), 2.65 (s, 3H), 1.94-1.89 (m, 2H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.7, 152.3, 141.2, 138.9, 133.1, 130.9, 130.8, 130.6, 127.8, 127.2, 124.6, 123.5, 122.2, 121.6, 67.8, 22.1, 22.0, 10.6. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{17}NNaO_2$ 302.1157, found 302.1151.



2s

Phenyl 2-methylphenanthridine-6-carboxylate (2s).[2] White solid (84 mg, 83%): R_f 0.55 in ethyl acetate–hexane (25:75); mp = 59–61 °C; IR (neat, cm^{-1}): ν 3068, 3057, 3019, 1744, 1723, 1621, 1614, 1568, 1346, 1234, 717, 607. ^1H NMR (300 MHz, DMSO-d_6) δ 8.78 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 8.4 Hz, 1H), 8.43 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.94-7.90 (m, 1H), 7.78-7.75 (m, 1H), 7.67-7.63 (m, 1H), 7.53-7.49 (m, 2H), 7.44-7.39 (m, 2H), 7.35-7.31 (m, 1H), 2.69 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.7, 150.9, 148.5, 141.2, 139.4, 133.3, 131.0, 130.9, 129.6, 128.0, 127.3, 126.2, 125.0, 123.9, 122.3, 121.9, 121.7, 22.2. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{15}NNaO_2$ 336.1000, found 336.997.



1-IV

Methyl 5,6-dihydrophenanthridine-6-carboxylate (1-IV).[4,5] This compound was synthesized following the literature procedure.[5] Pale yellow solid: R_f 0.12 in ethyl acetate–hexane (25:75). IR (neat, cm^{-1}): *v* 3354, 3214, 3198, 3021, 1717, 1620, 1609, 1564, 1134, 721. ^1H NMR (300 MHz, DMSO-d_6) δ 7.67-7.64 (m, 1H), 7.53-7.51 (m, 1H), 7.31-7.27 (m, 2H), 7.08-7.01 (m, 2H), 6.88 (d, J = 2.2 Hz, 1H), 6.77-6.74 (m, 1H), 6.67-6.63 (m, 1H), 5.12 (d, J = 2.2 Hz, 1H), 4.01 (s, 3H). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{14}NO_2$ 240.1019, found 240.1011.

References

(1) C. Pan, J. Han, H. Zhang, C. Zhu, *J. Org. Chem*. **2014**, *79*, 5374.

(2) G. Wang, S.-Y. Chen, X.-Q. Yu, *Tetrahedron Lett*. **2014**, *55*, 5338.

(3) X. Li, M. Fang, P. Hu, G. Hong, Y. Tang, X. Xu, *Adv. Synth. Catal*. **2014**, *356*, 2103.

(4) J. K. Augustine, A. Bombrun, P. Alagarsamy, A. Jothi, *Tetrahedron Lett*. **2012**, *53*, 6280.

(5) T. McCallum, S. P. Pitre, M. Morin, J. C. Scaiano, L. Barriault, *Chem. Sci*. **2017**, *8*, 7412.

Copies of ^{1}H, ^{13}C and ^{19}F-NMR Spectra

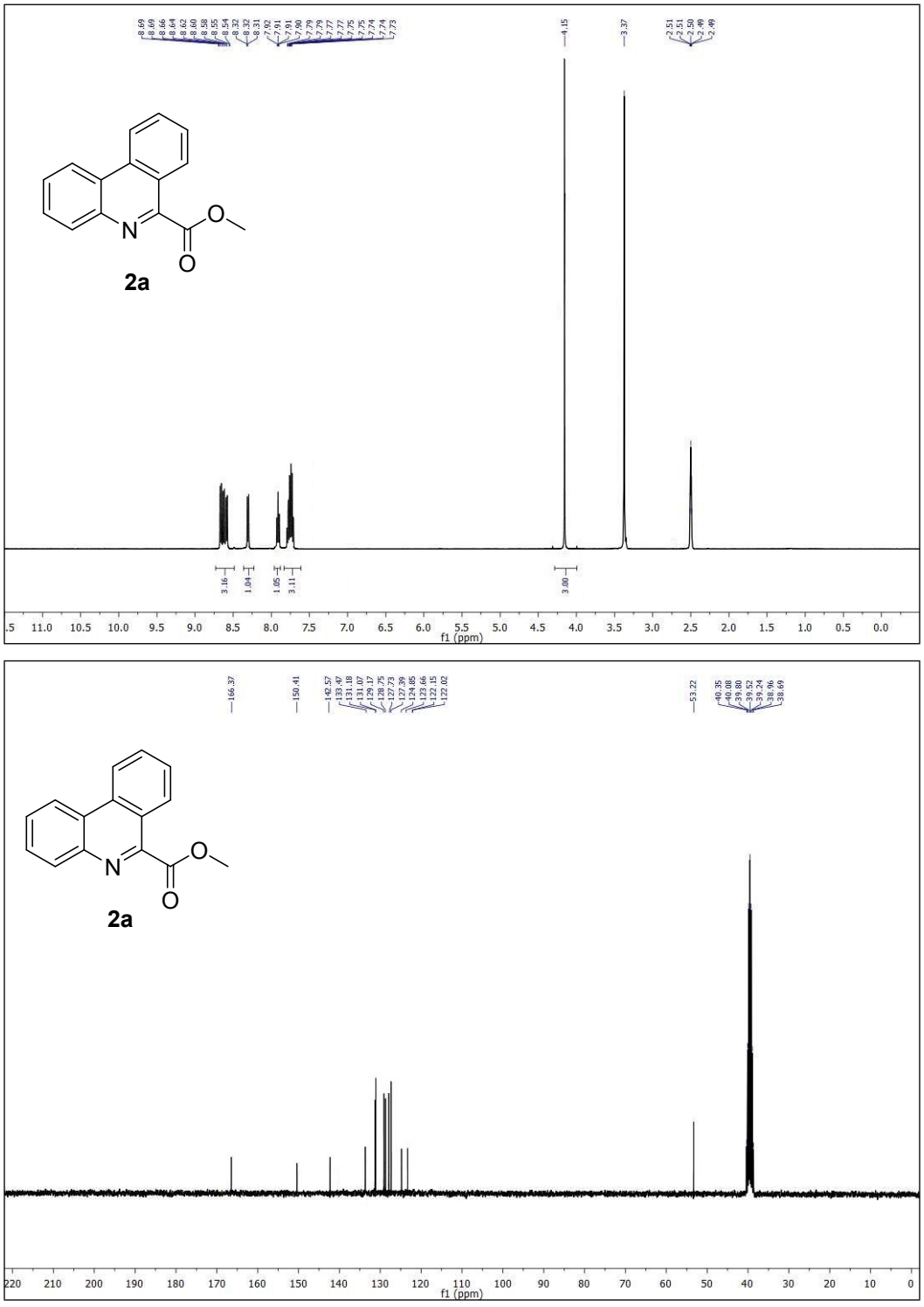


Figure S1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** in DMSO-d_6.

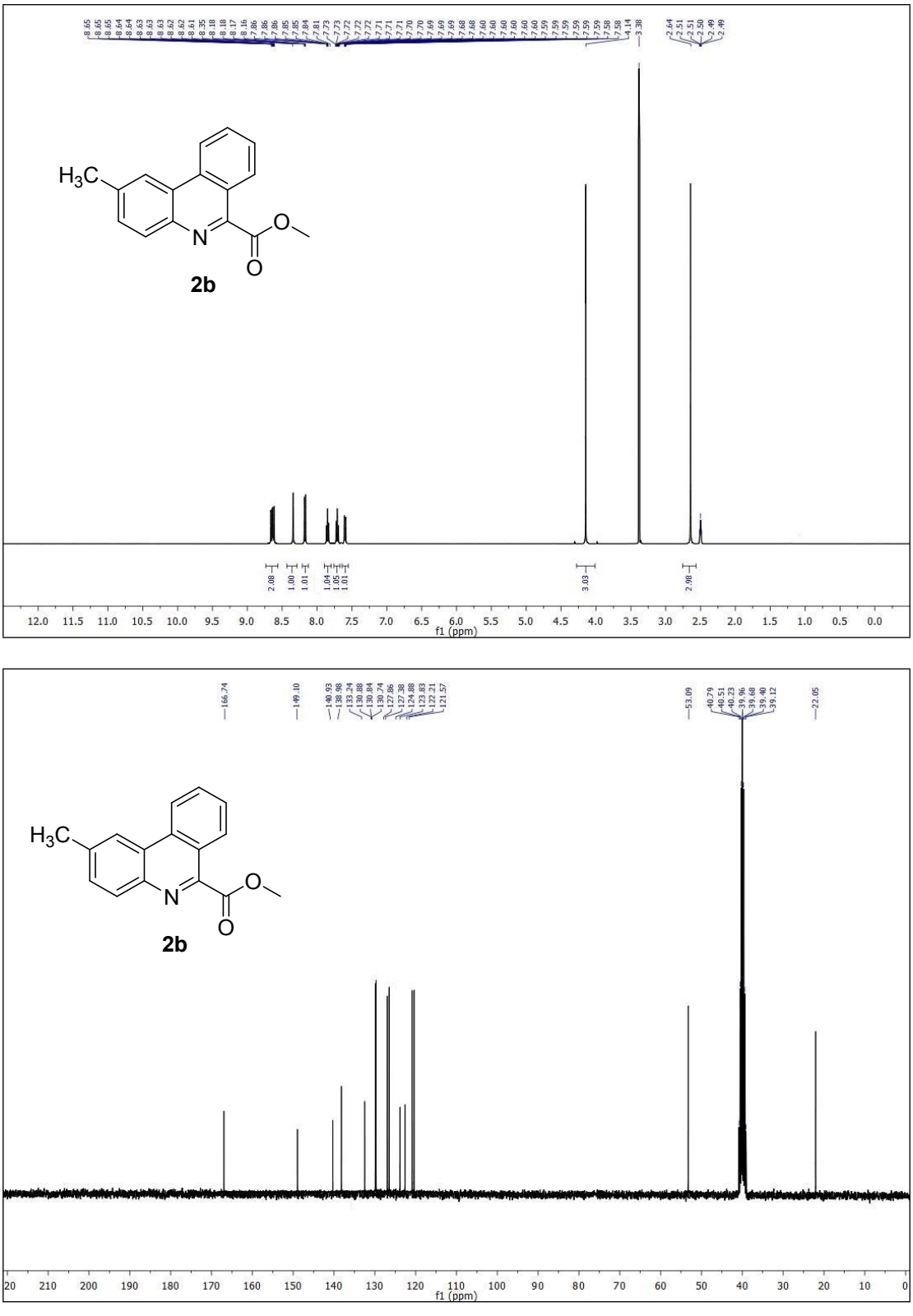


Figure S2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b** in DMSO-d_6.

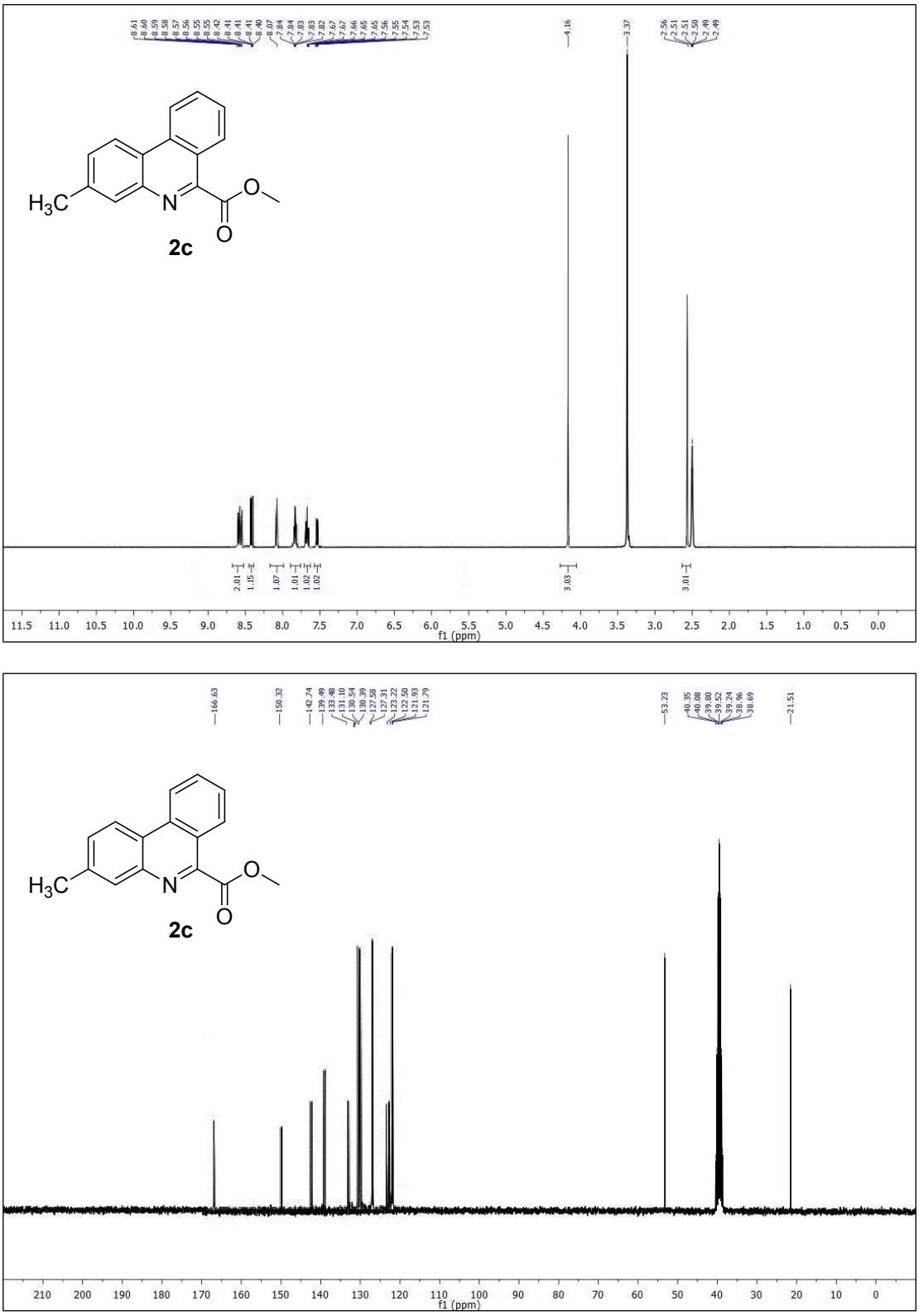


Figure S3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2c** in DMSO-d_6.

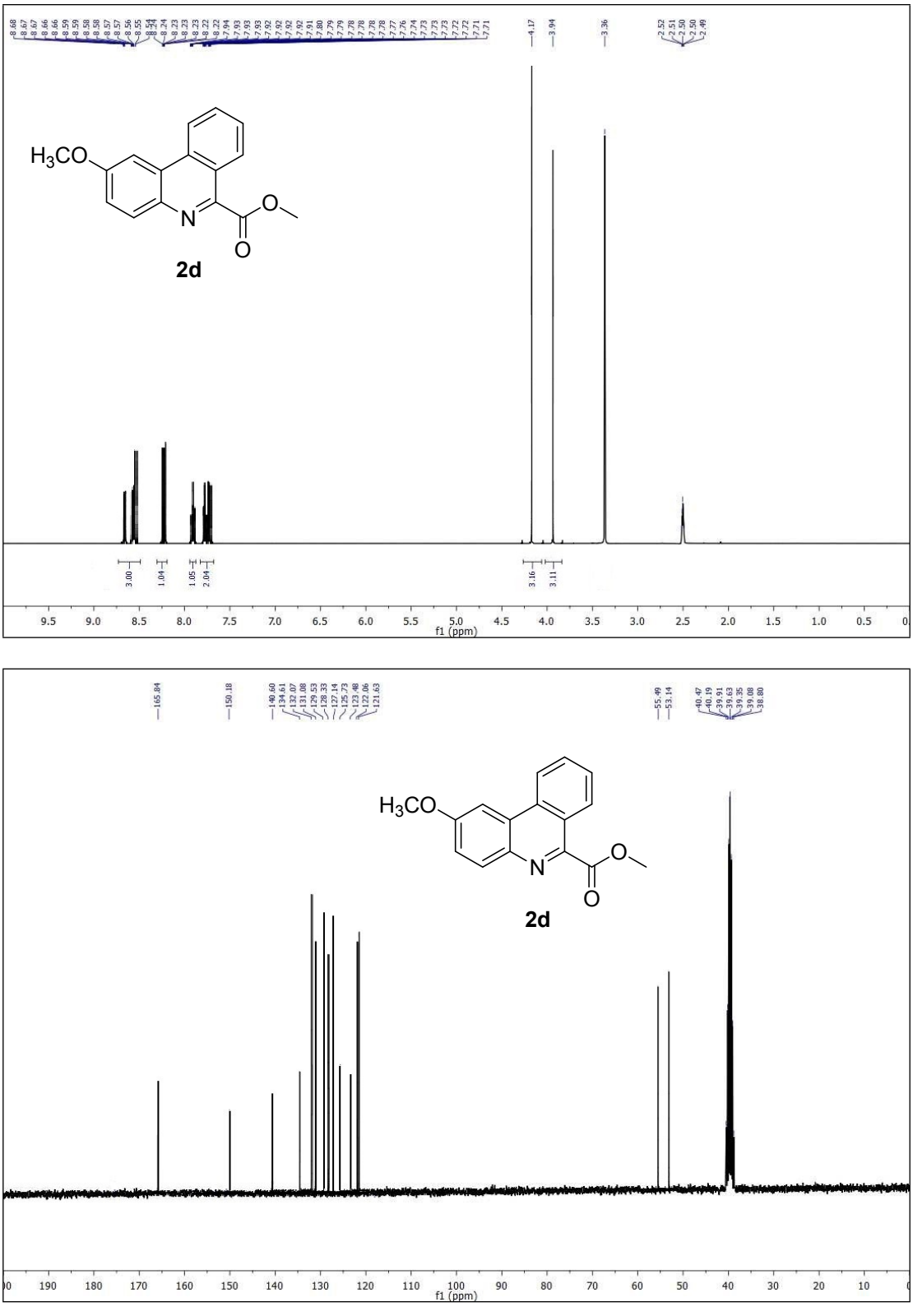


Figure S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2d** in DMSO-d_6

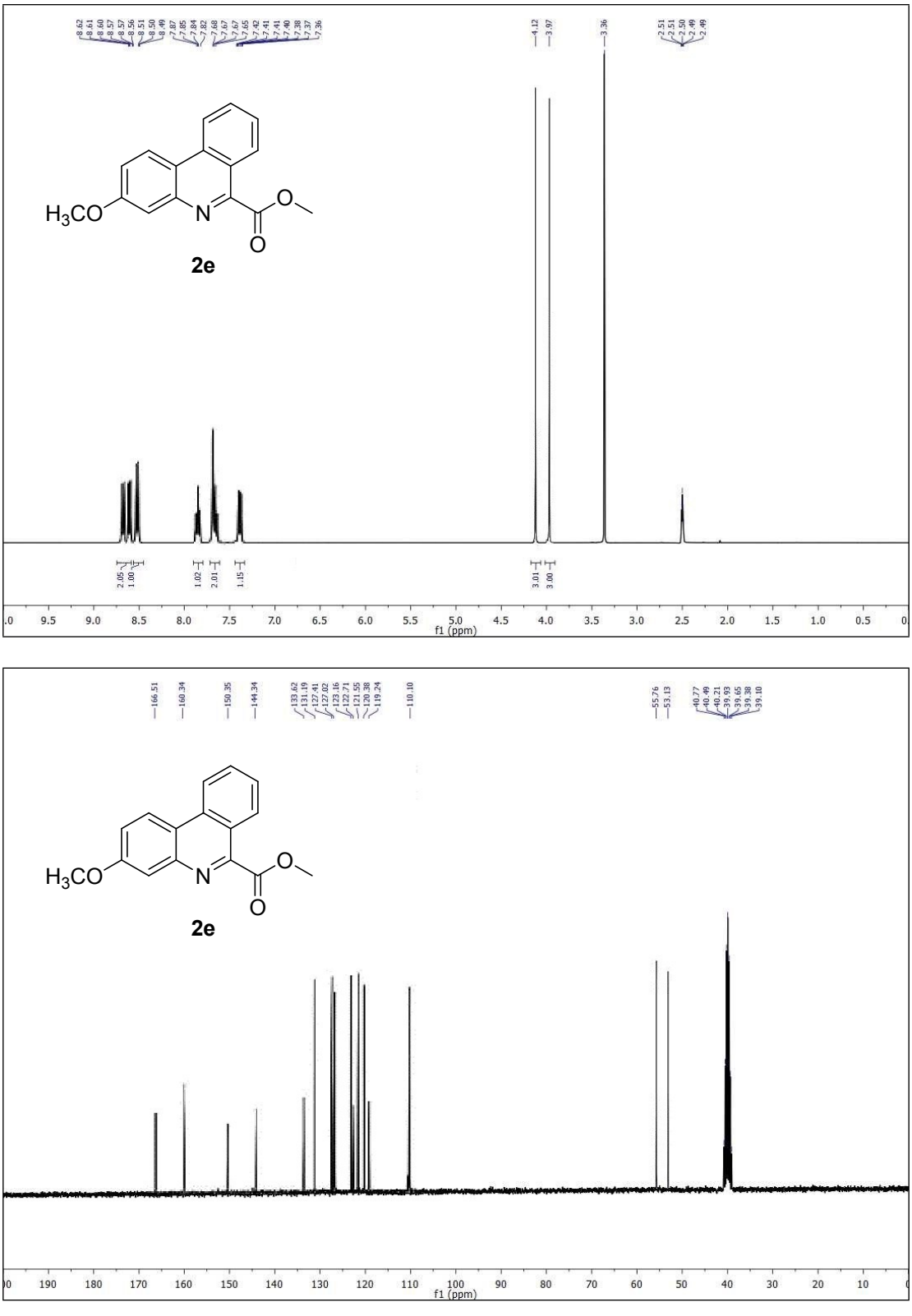


Figure S5. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2e** in DMSO-d_6

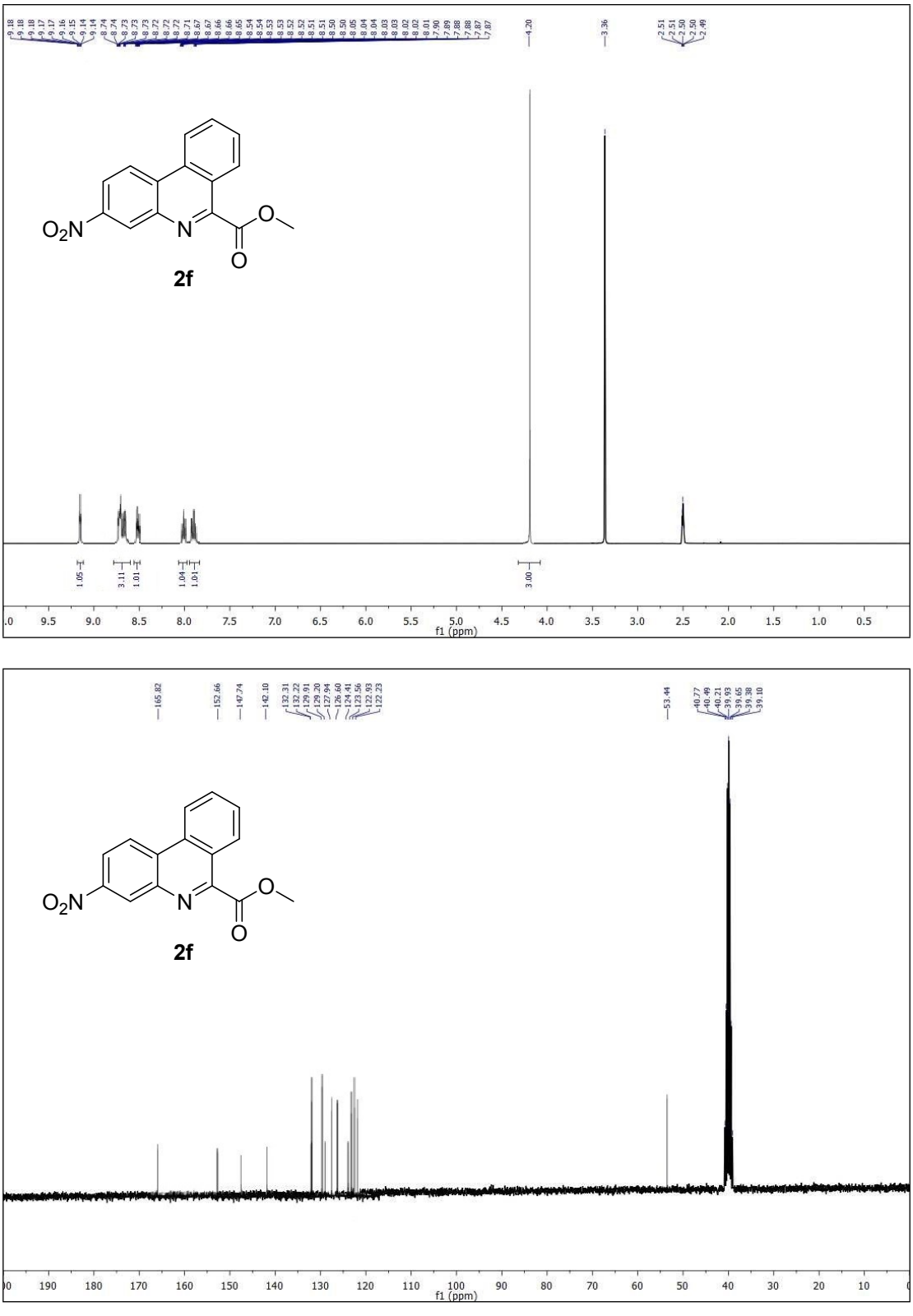


Figure S6. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2f** in DMSO-d_6

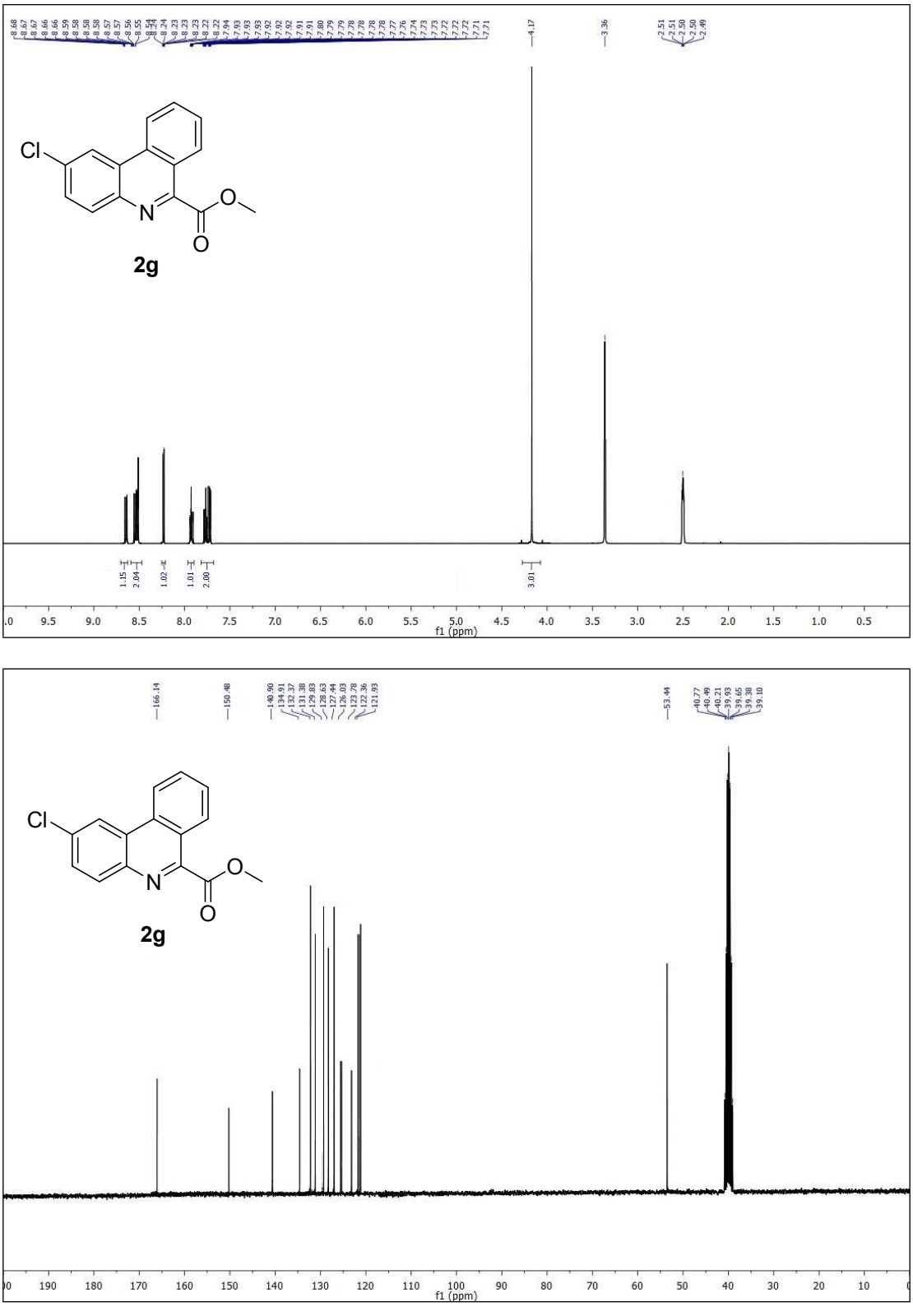
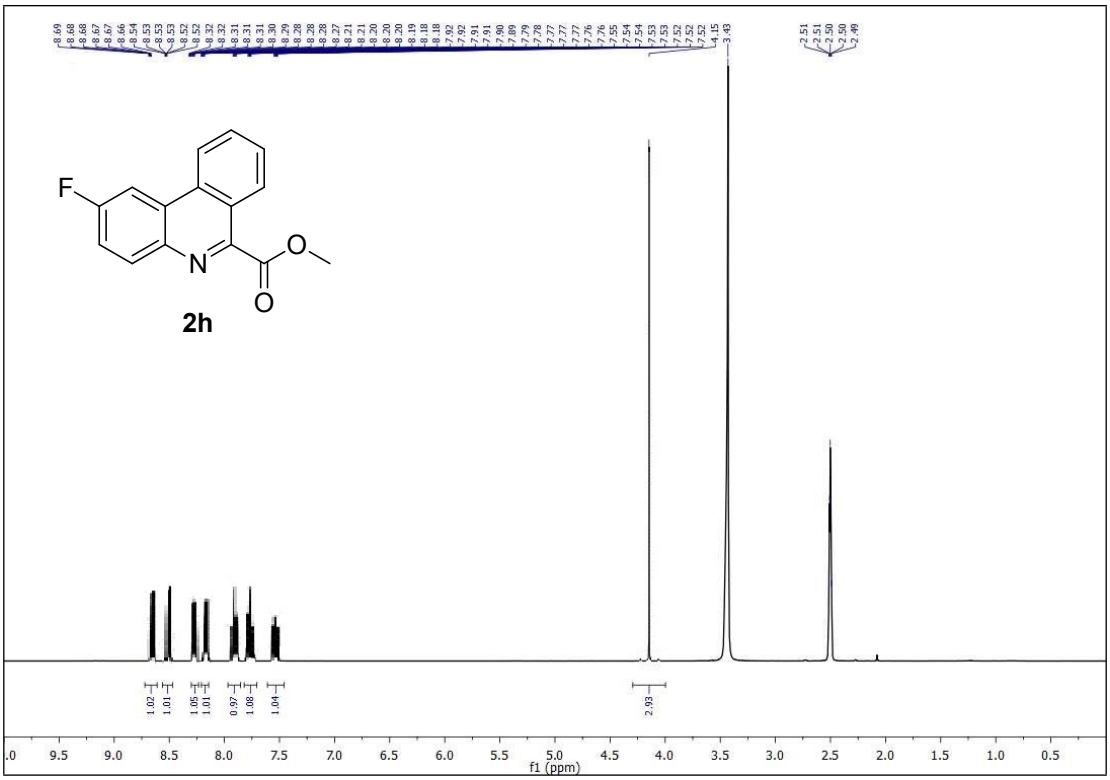


Figure S7. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2g** in DMSO-d_6



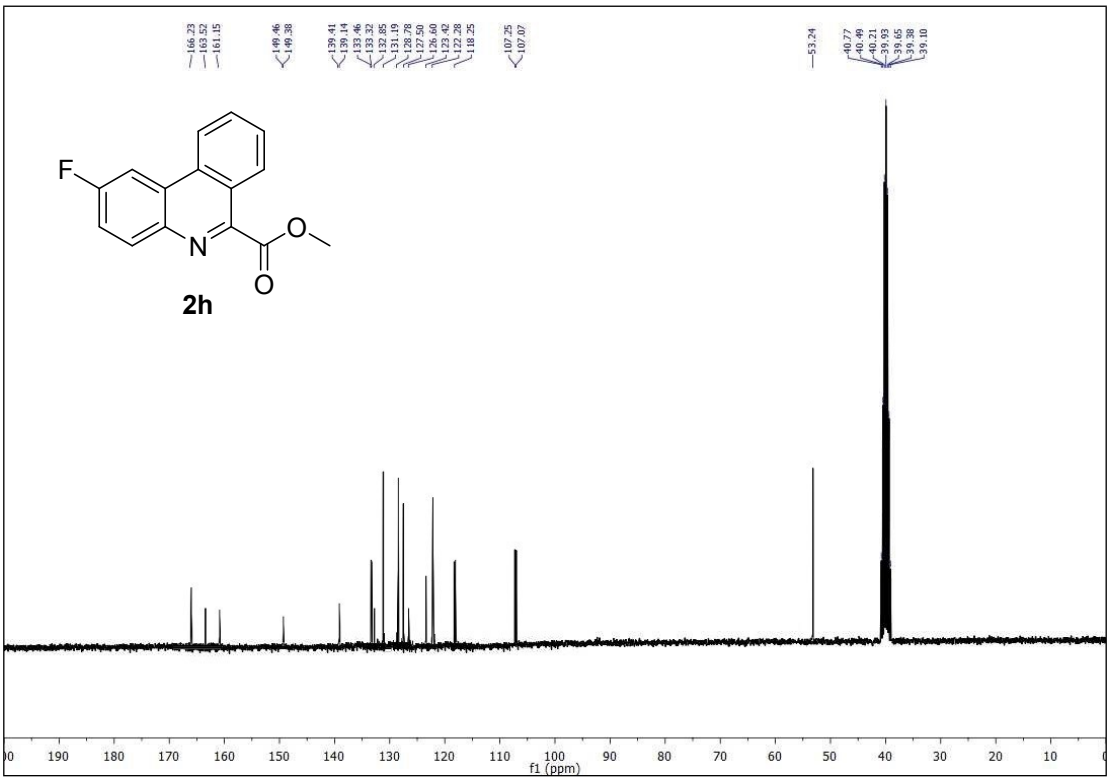


Figure S8. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2h** in DMSO-d_6

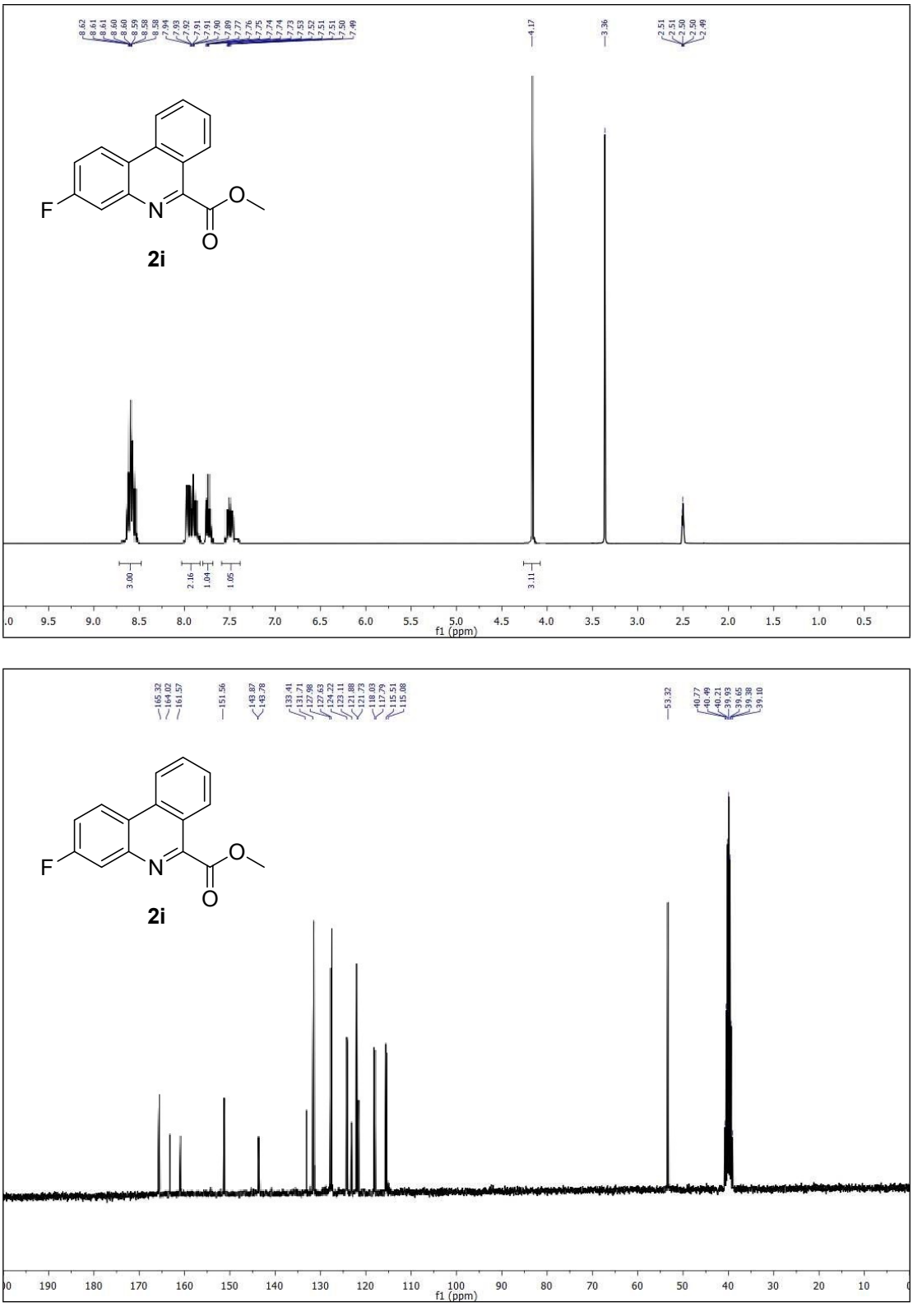


Figure S9. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2i** in DMSO-d_6

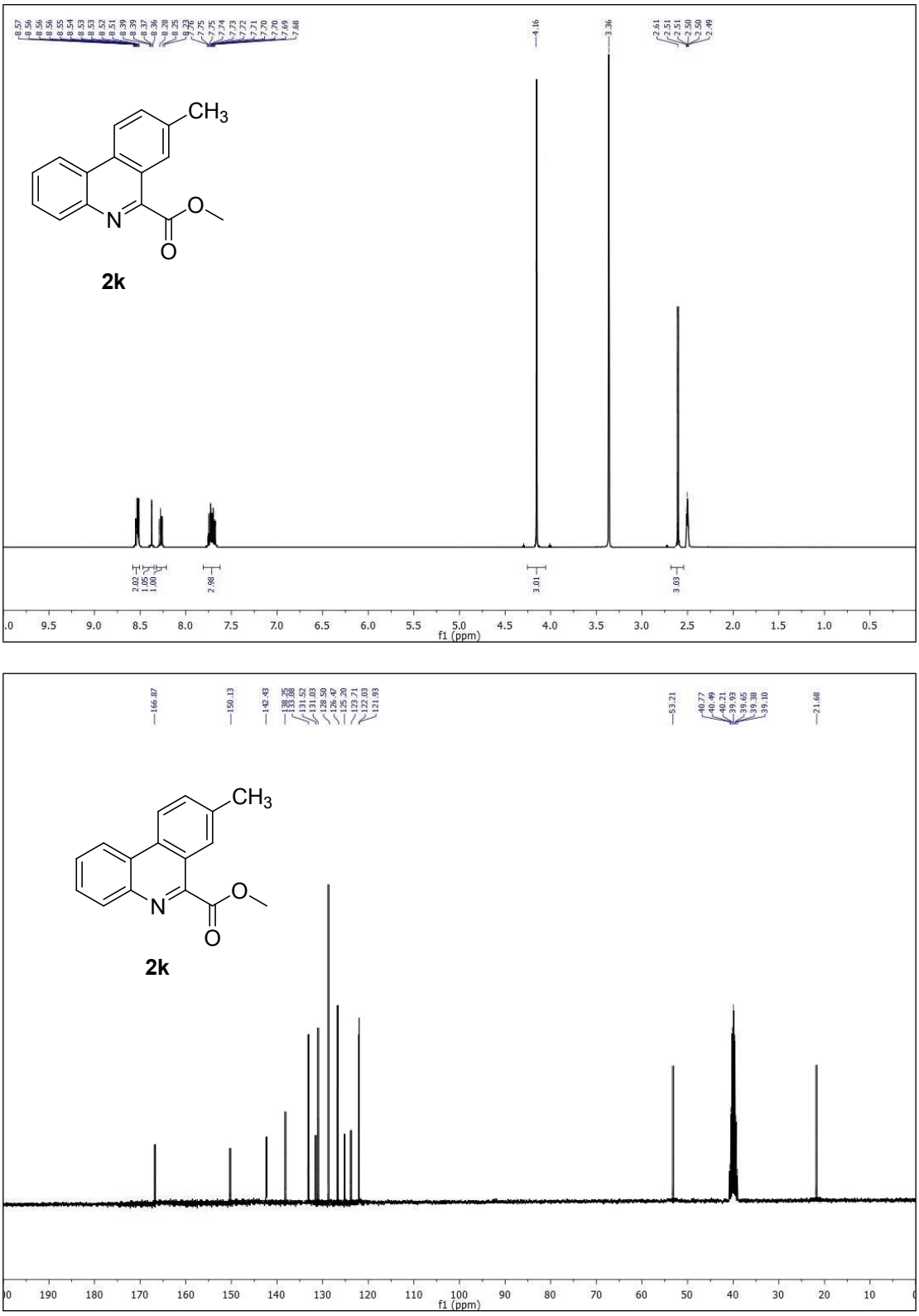


Figure S10. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2k** in DMSO-d_6

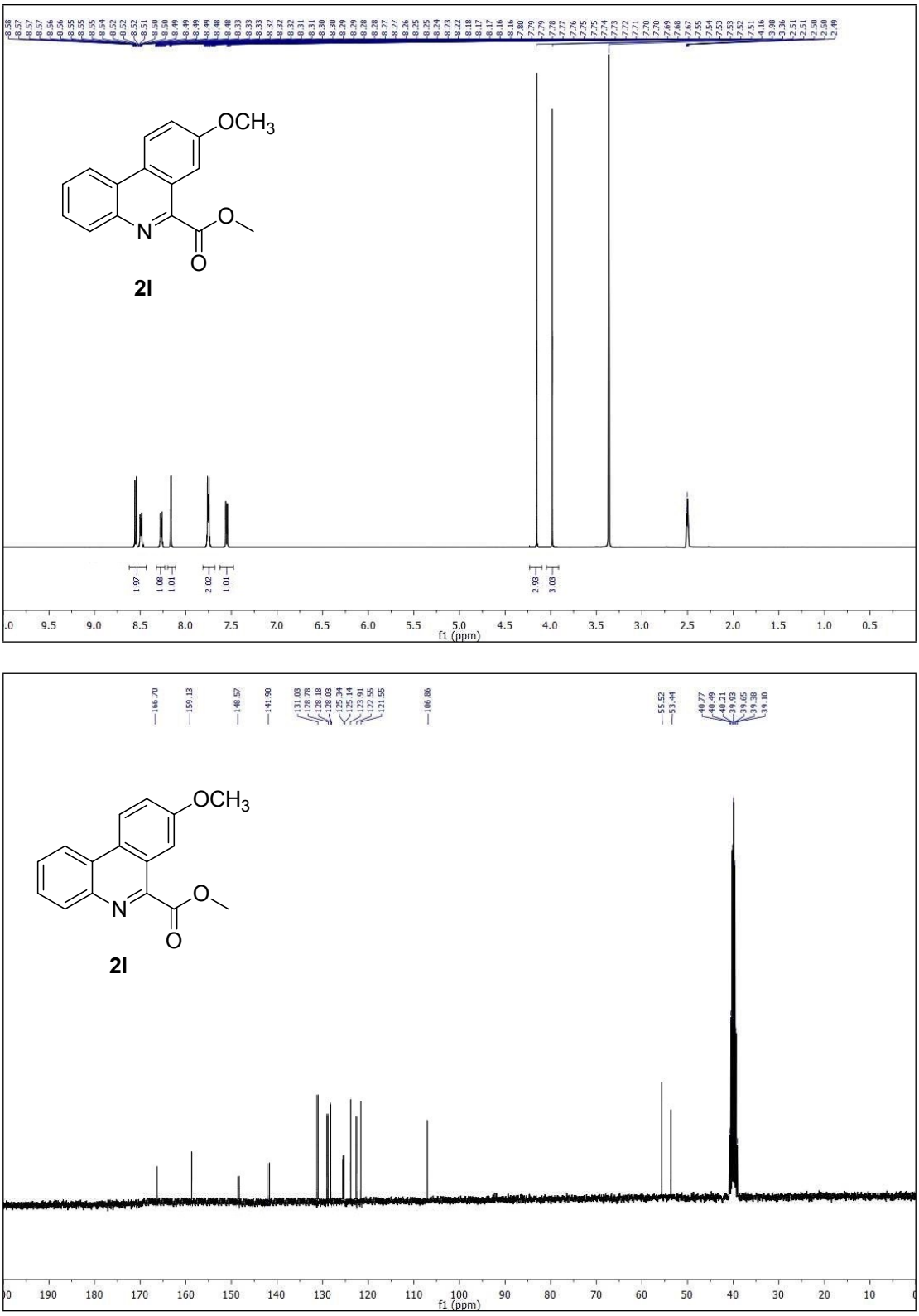


Figure S11. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2l** in DMSO-d_6

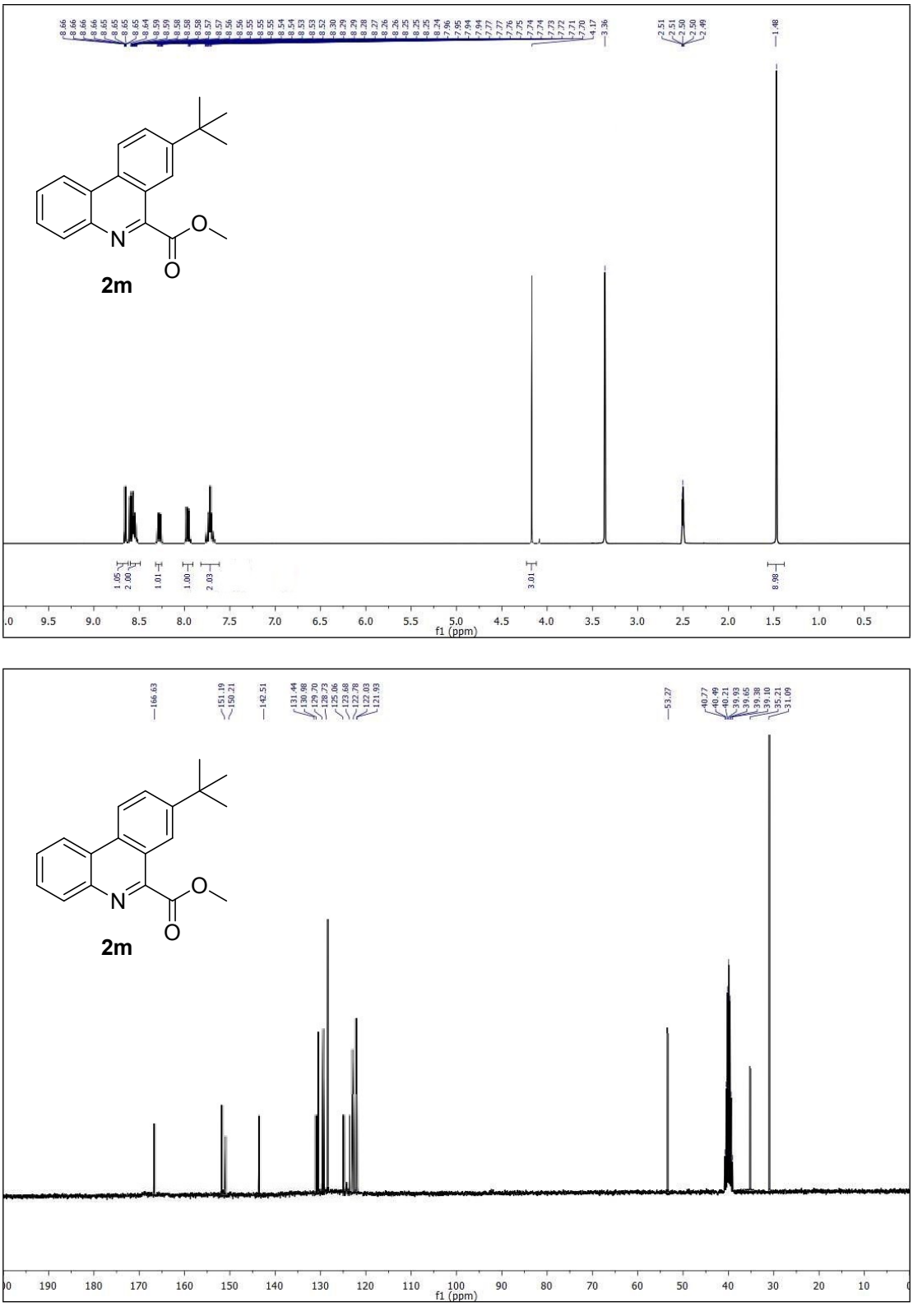


Figure S12. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2m** in DMSO-d_6

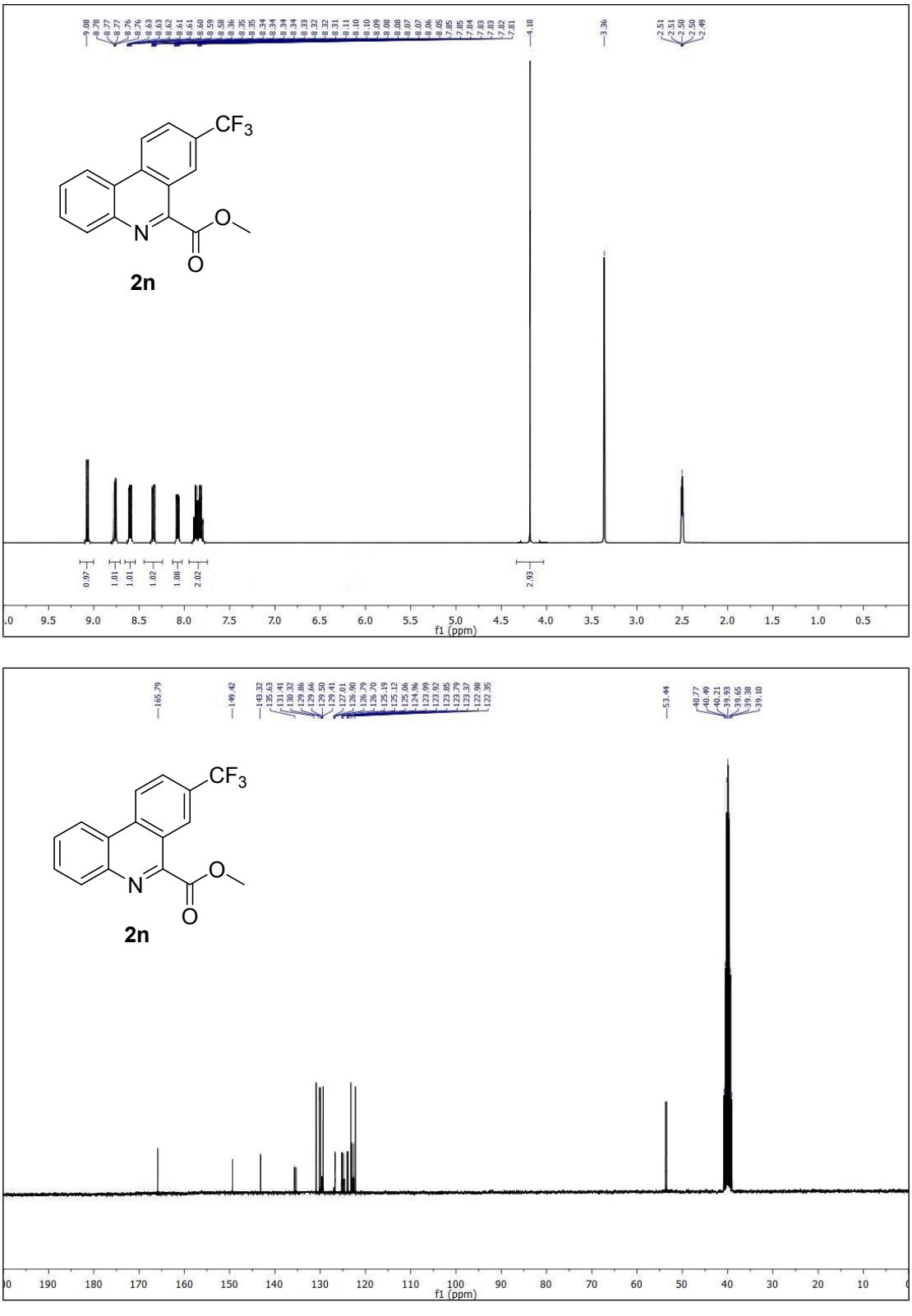


Figure S13. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2n** in DMSO-d_6

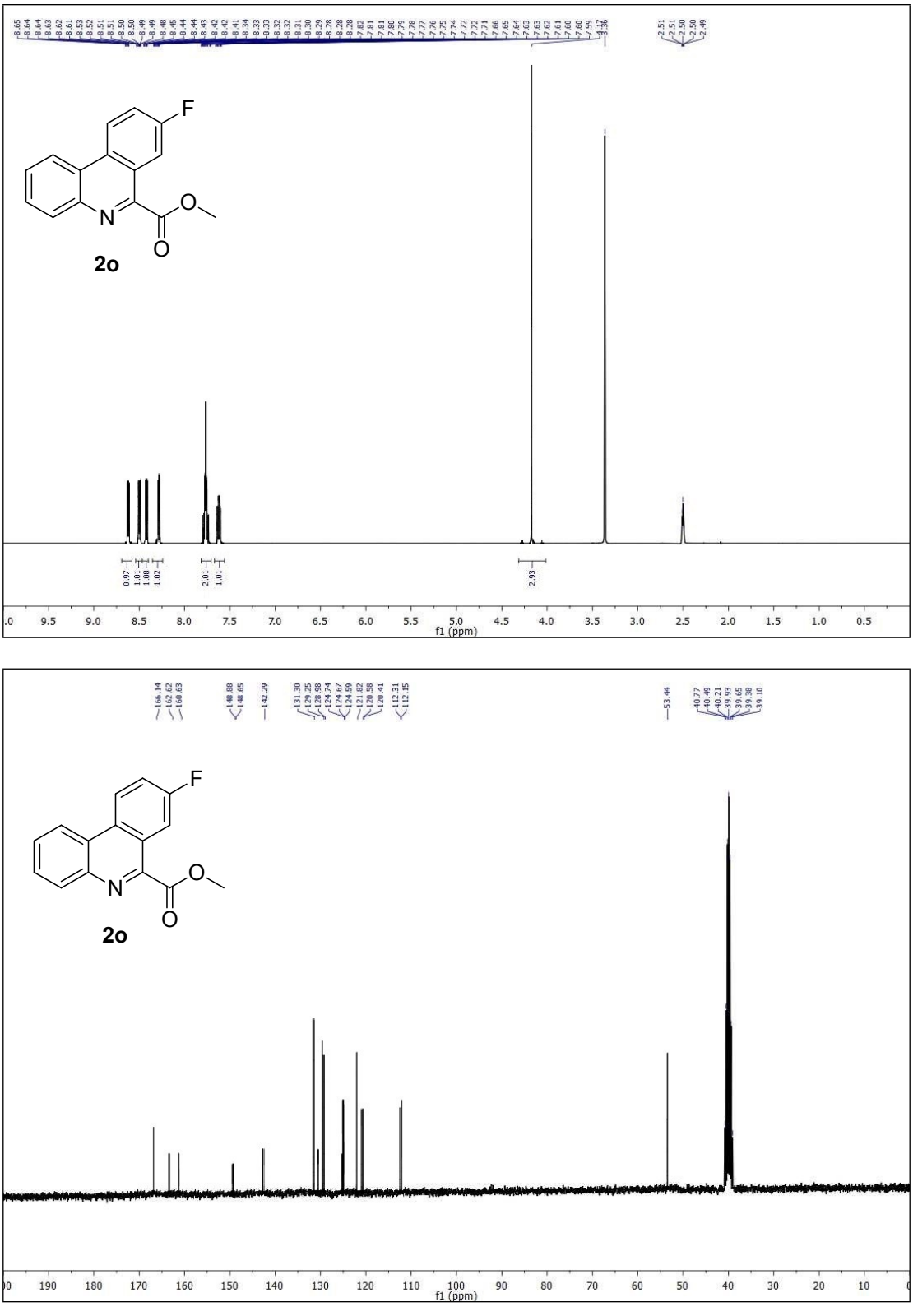


Figure S14. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2o** in DMSO-d_6

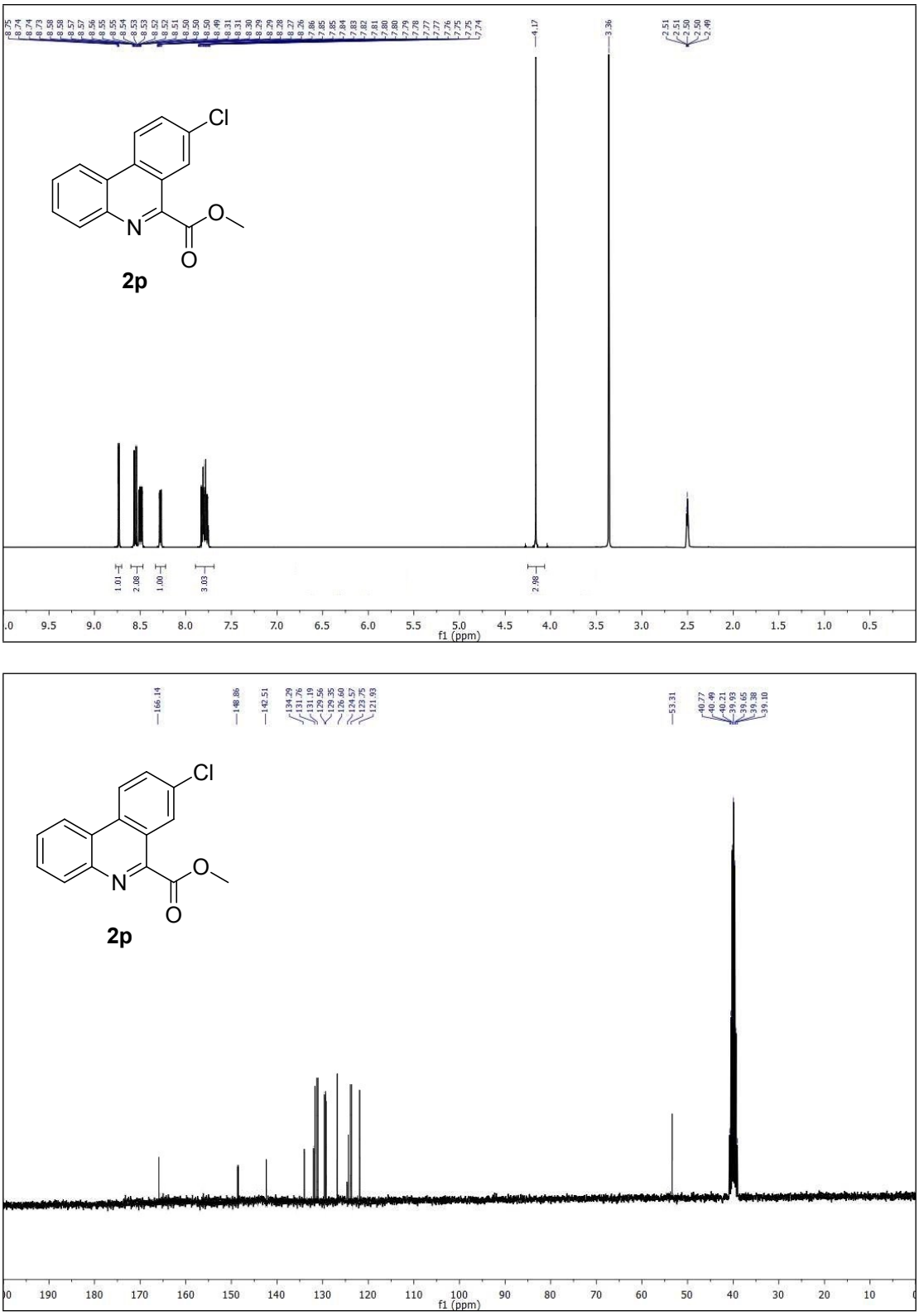


Figure S15. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2p** in DMSO-d_6

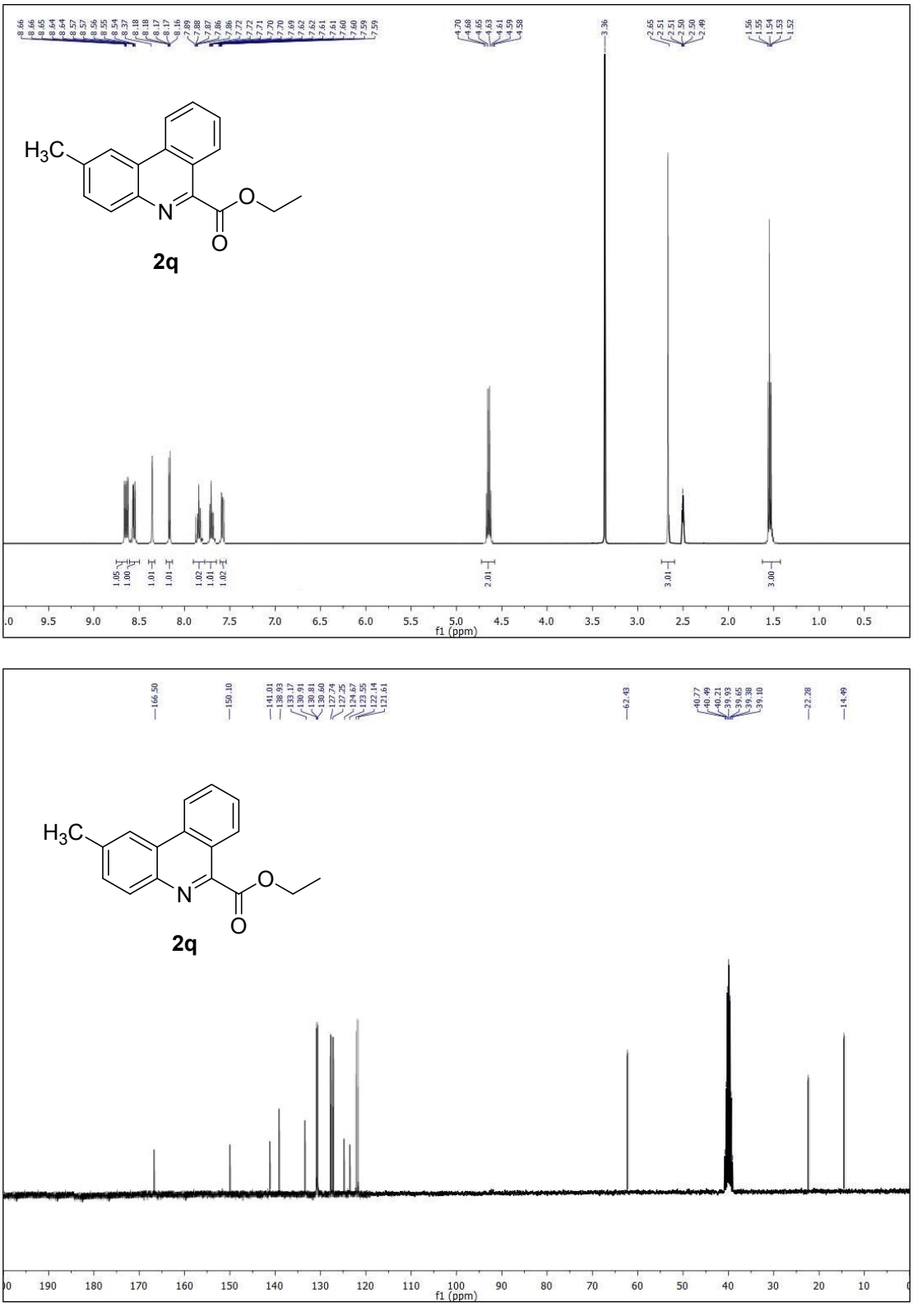


Figure S16. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2q** in DMSO-d_6

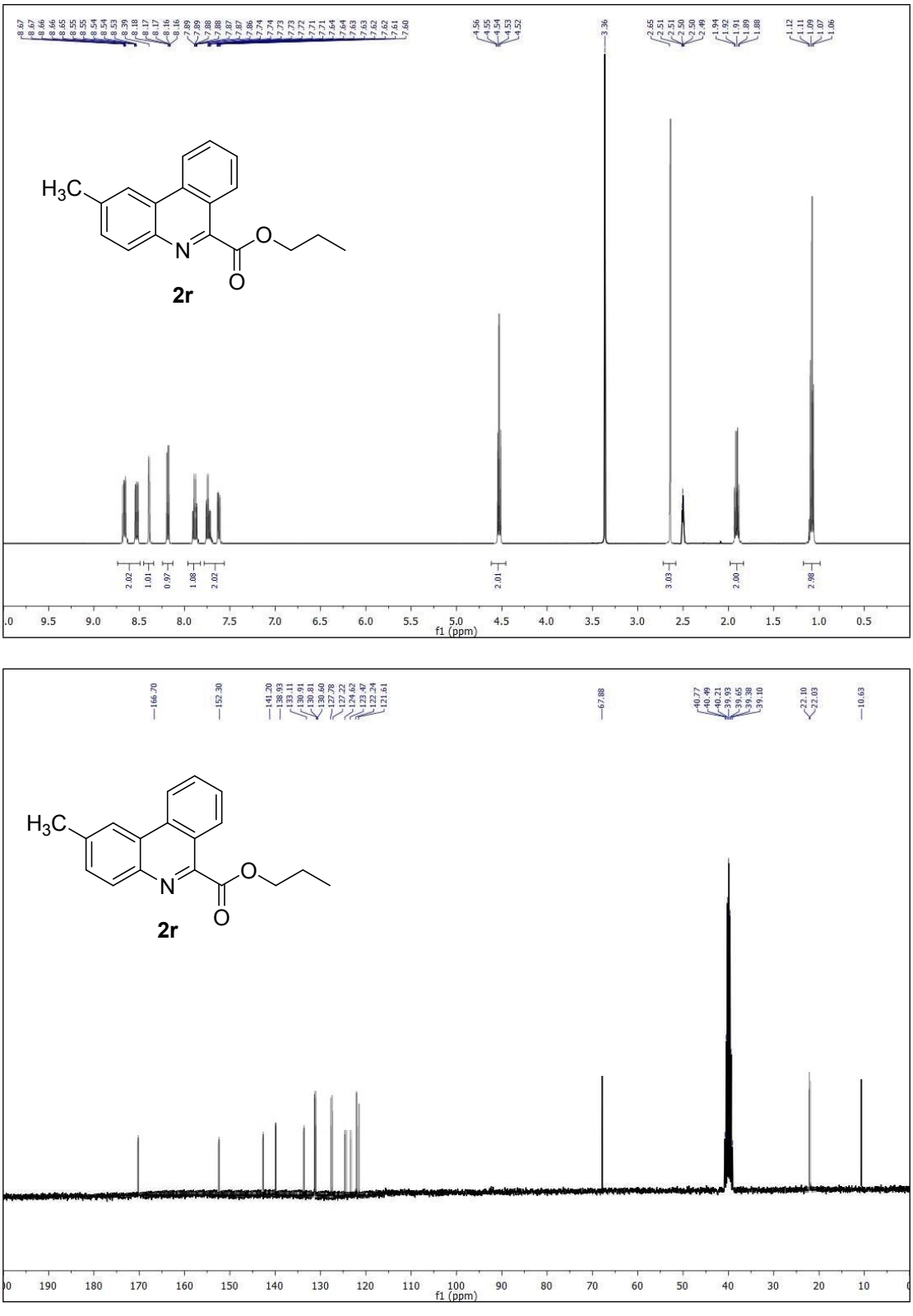


Figure S17. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2r** in DMSO-d_6

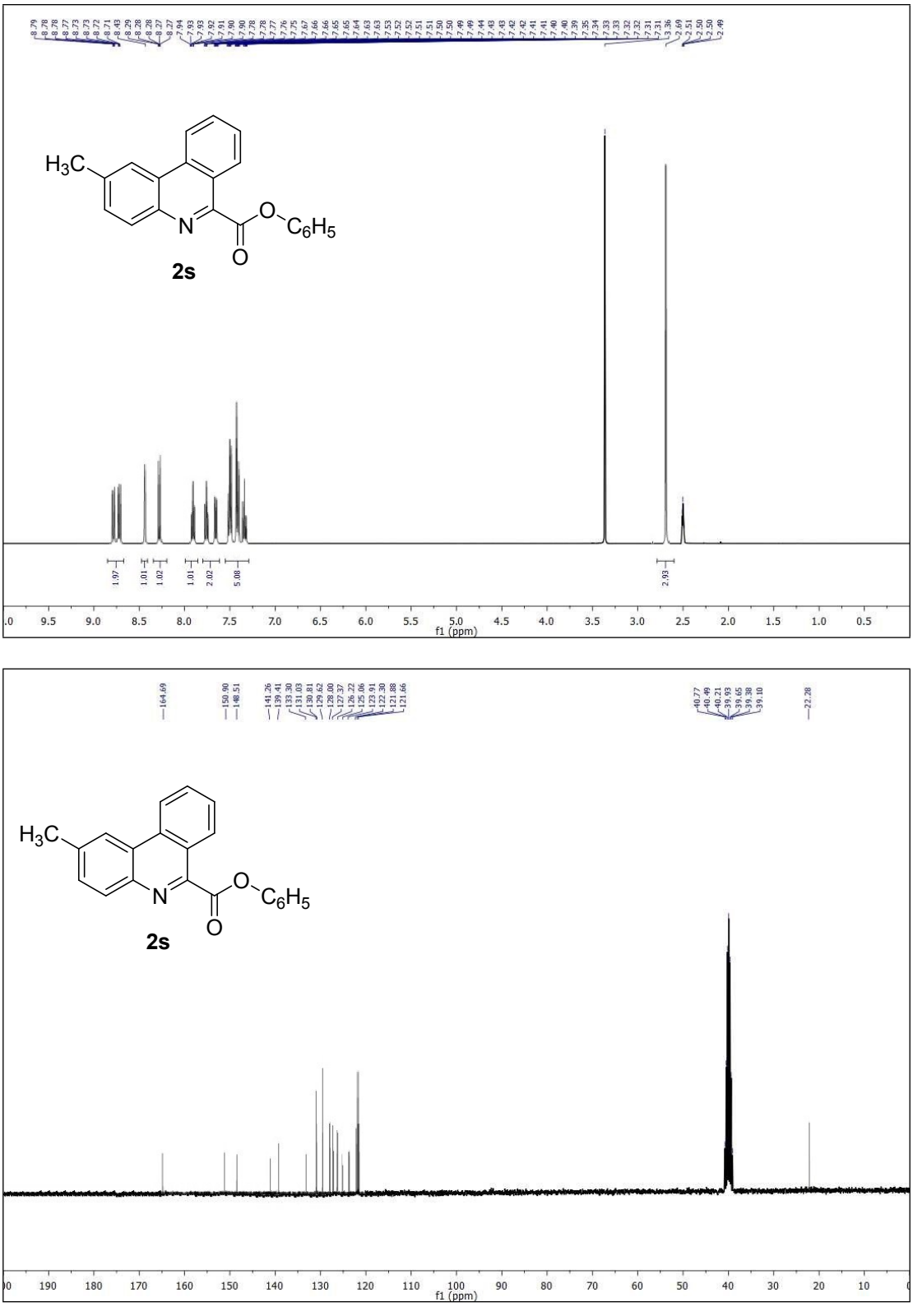


Figure S18. ^{1}H (top) and ^{13}C NMR (bottom) spectra of **2s** in DMSO-d_6

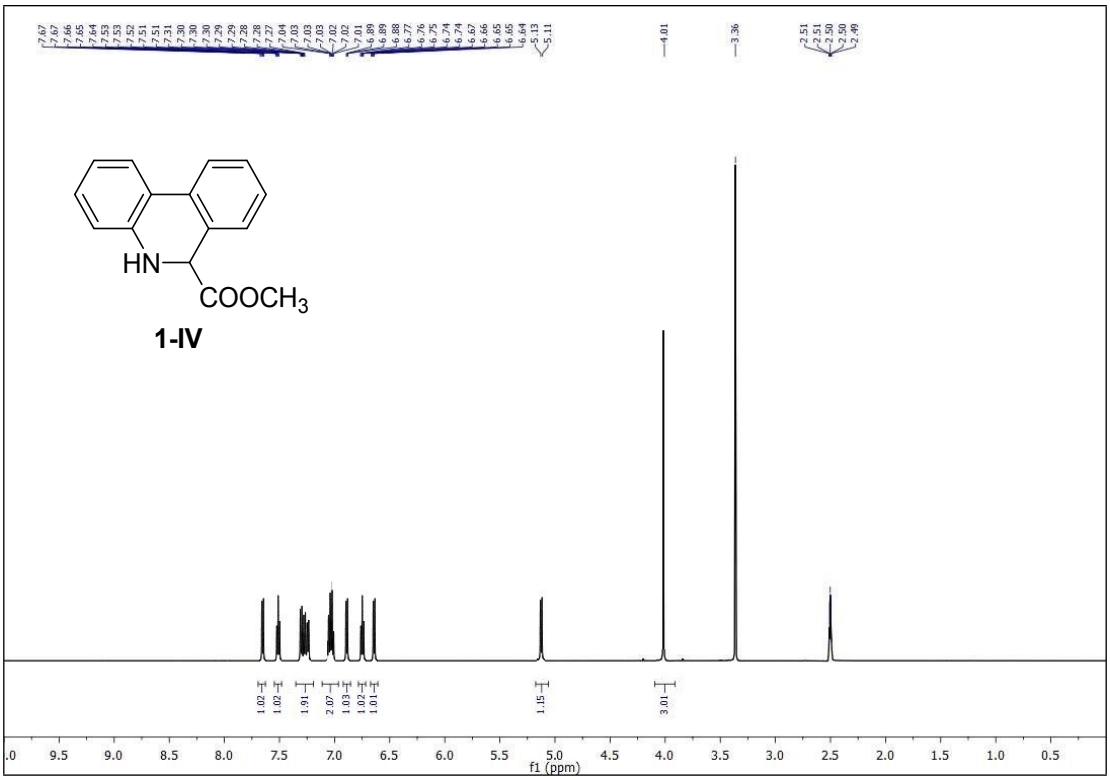
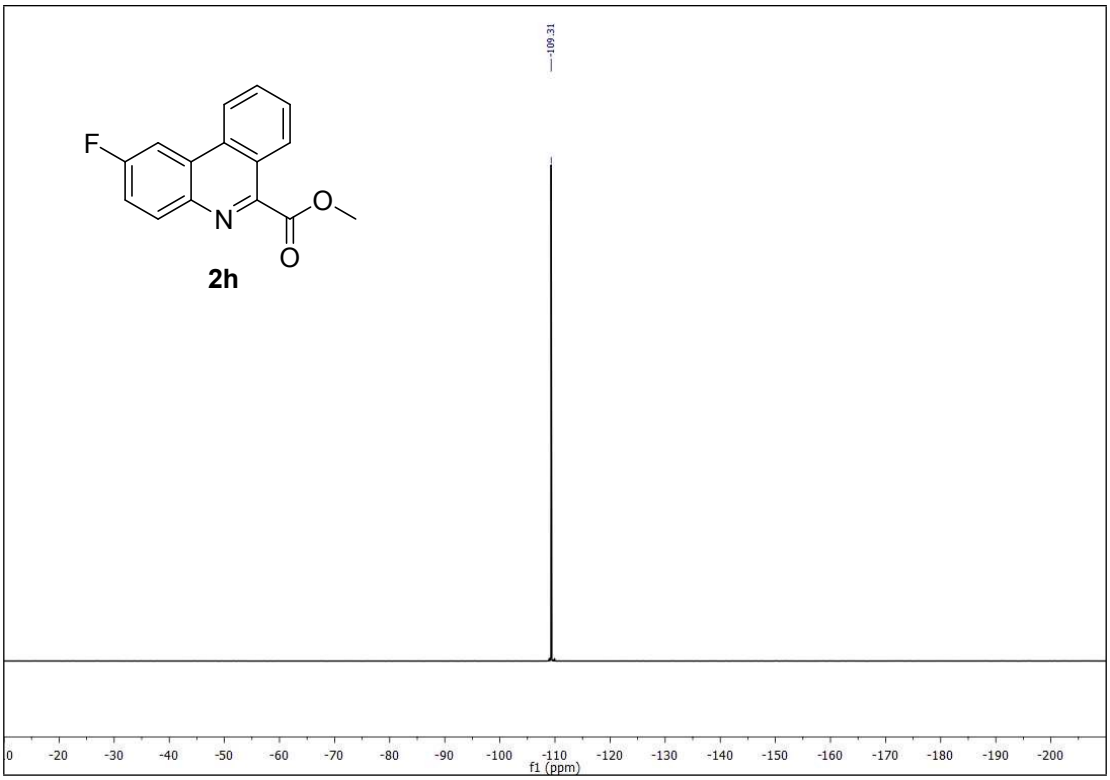


Figure S19. ^{1}H NMR spectra of **1-IV** in DMSO-d_6



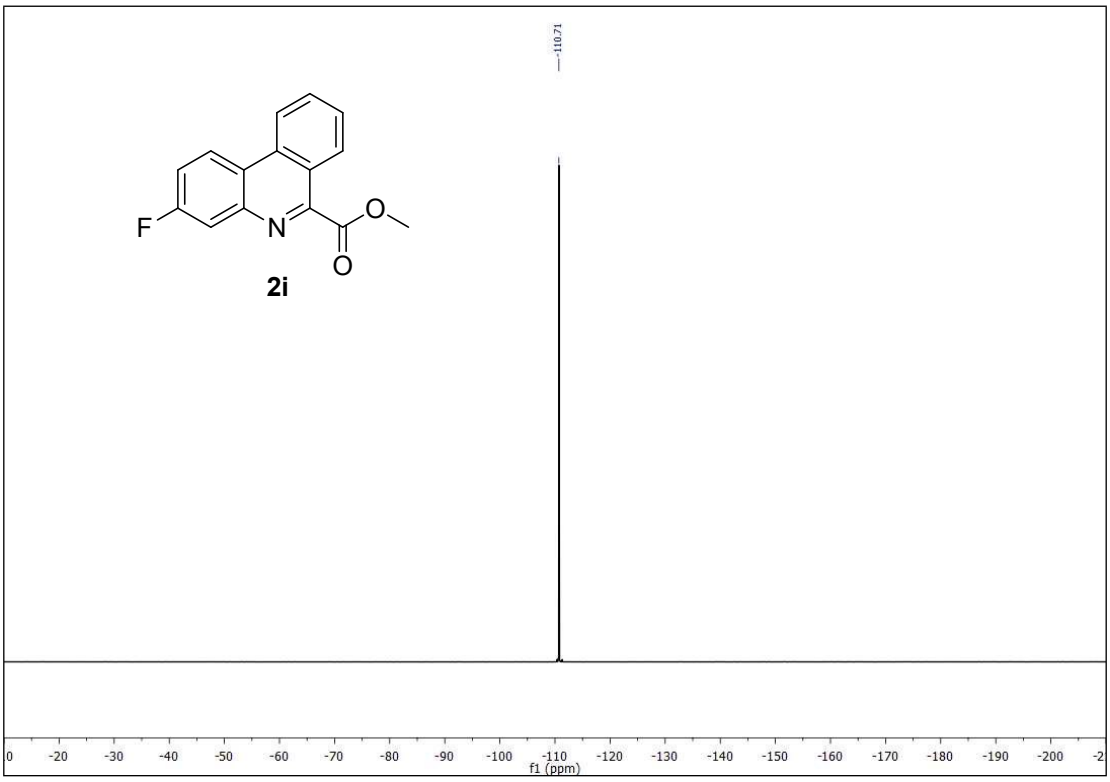


Figure S20. ^{19}F NMR spectra of **2h** (top) and **2i** (bottom) in DMSO-d_6

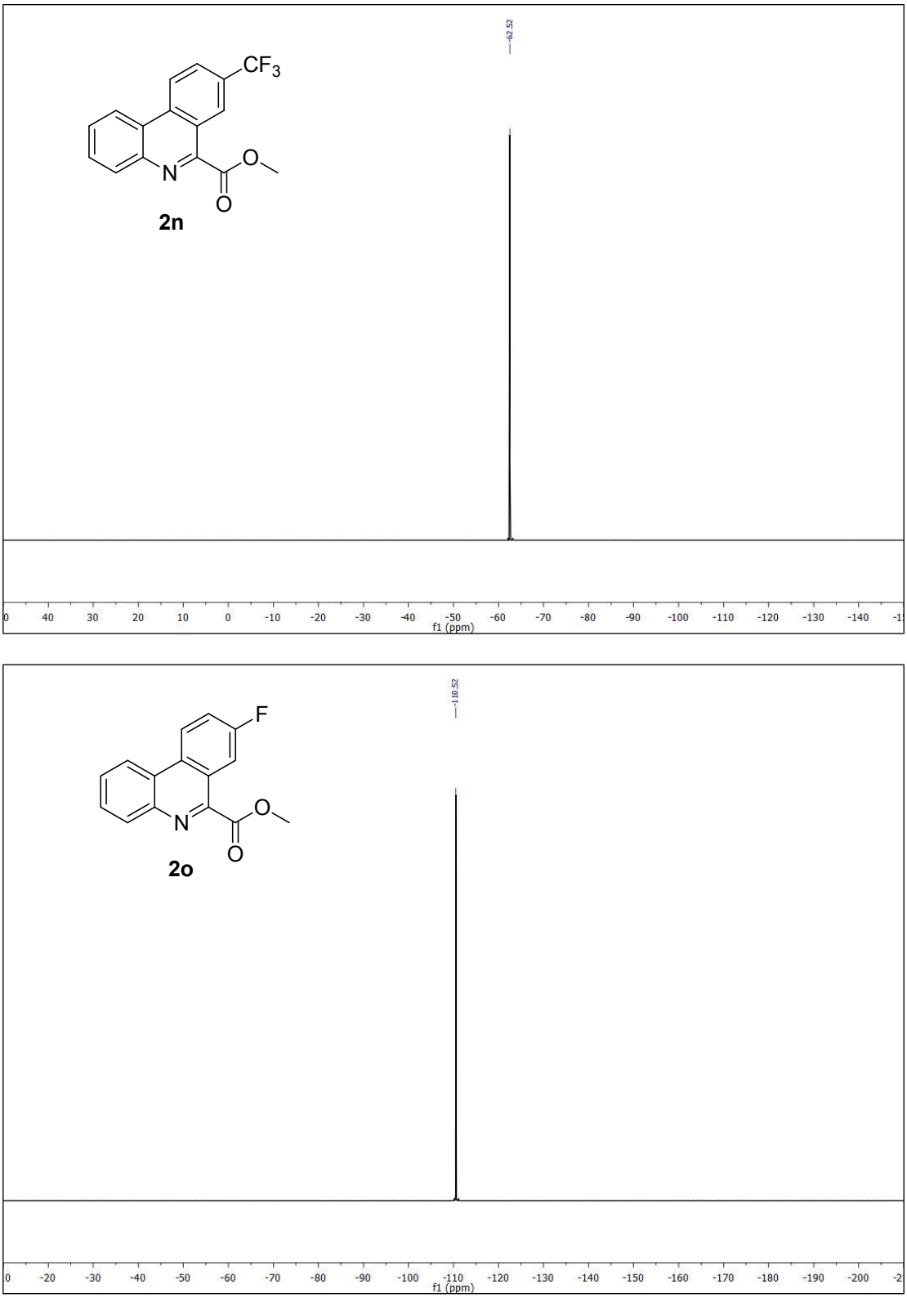


Figure S21. ^{19}F NMR spectra of **2n** (top) and **2o** (bottom) in DMSO-d_6