Higher-order dearomative [10+2] cycloaddition of 2-nitrobenzofurans and 2-alkylidene-1-indanones to access pentacyclic scaffolds

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Supporting Information

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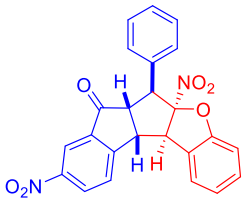
1. General Information

Unless otherwise noted, all commercial available reagents were used as received without further purification. Reactions were monitored by thin layer chromatography (TLC) with 0.2 mm silica gel-coated HSGF 254 plates visualized by UV light at 254 or 365 nm. Products were isolated and purified by column chromatography on silica gel (300−400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 or 400 MHz NMR spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. The chemical shifts (δ) were reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.51 ppm). Coupling constants (*J*) were given in Hertz (Hz). Splitting patterns of apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). All ^{13}C spectra were recorded with broadband proton decoupling. HRMS were performed on a Bruker Q-TOF mass spectrometer. Melting points were recorded on a Buchi Melting Point B-545 unit.

2. General Procedure for Synthesis of Compounds 3.

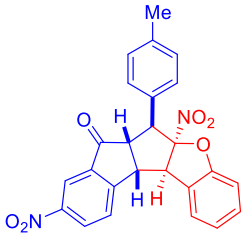
In a reaction tube equipped with a magnetic stirring bar, 2-alkylidene-1-indanones **1** (0.12 mmol, 1.2 equiv.), 2-Nitrobenzofurans **2** (0.1 mmol), Na_2CO_3 (10.6 mg, 1.0 equiv.) and catalyst TEBA (4.5 mg, 20 mol%, 0.01 mmol) were added successively, and then followed by addition CH_2Cl_2 (1.0 mL). The reaction solution was stirred at room temperature for specified time. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 1:5:0.5~ 1:6:1) to give the corresponding products **3**.

5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3aa)



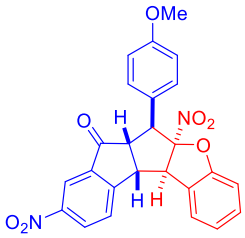
Pale yellow solid, 39 mg, 91% yield; m.p. 195.9-196.3 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.70 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.37 (d, *J* = 2.2 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.32 (m, 6H), 7.22 – 7.16 (m, 2H), 4.83 (d, *J* = 2.9 Hz, 1H), 4.32 (d, *J* = 10.8 Hz, 1H), 4.11 – 4.02 (m, 2H).;**^{13}C NMR (101 MHz, DMSO-d_6)** δ 200.8, 159.8, 157.2, 148.4, 135.7, 132.5, 130.0, 129.8, 129.6, 128.7, 128.6, 128.3, 127.1, 125.6, 123.9, 119.1, 110.6, 79.2, 57.1, 56.6, 53.8, 51.5.; **HRMS** (ESI-TOF) *m/z:* $[M + K]^+$ Calcd. for $C_{24}H_{16}N_2O_6K^+$: 467.0640; found: 467.0639.

5a,9-dinitro-6-(p-tolyl)-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ba)



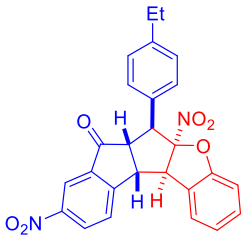
Pale yellow solid, 32.7 mg, 74% yield; m.p. 197.5-198.2 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v)= 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.45 – 8.33 (m, 2H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.36 (td, *J* = 7.8, 1.4 Hz, 1H), 7.27 – 7.14 (m, 6H), 4.81 (d, *J* = 3.3 Hz, 1H), 4.26 (d, *J* = 11.4 Hz, 1H), 4.04 (ddd, *J* = 18.7, 11.1, 7.4 Hz, 2H), 2.32 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.7, 159.8, 157.2, 148.4, 137.9, 135.6, 129.9, 129.7, 129.4, 129.3, 129.1, 128.7, 128.3, 127.1, 125.6, 123.8, 119.1, 110.5, 57.0, 56.5, 53.6, 51.4, 20.8.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_6Na^+$: 465.1057; found: 465.1062.

6-(4-methoxyphenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ca)



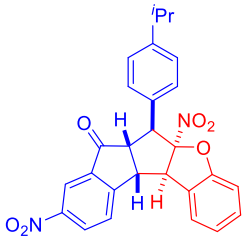
Pale yellow solid, 32 mg, 70% yield; m.p. 237.6-238.1 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.42 – 8.33 (m, 2H), 7.79 – 7.72 (m, 1H), 7.37 (td, *J* = 7.8, 1.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 6.98 – 6.92 (m, 2H), 4.81 (d, *J* = 3.2 Hz, 1H), 4.25 (d, *J* = 11.6 Hz, 1H), 4.08 – 3.95 (m, 2H), 3.78 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.1, 160.2, 159.8, 157.6, 148.8, 136.1, 131.2, 130.3, 130.2, 129.1, 128.8, 127.5, 126.0, 124.5, 124.2, 119.5, 114.4, 111.0, 57.3, 57.1, 55.6, 53.7, 51.8.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{25}H_{19}N_2O_7^+$: 459.1187; found: 459.1192.

6-(4-ethylphenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3da)



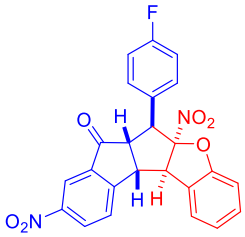
Pale yellow solid, 34.2 mg, 75% yield; m.p. 238.1-238.4 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.62 – 8.52 (m, 2H), 7.86 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.28 (td, *J* = 7.8, 1.4 Hz, 1H), 7.15 (s, 4H), 7.12 – 7.03 (m, 2H), 4.45 (d, *J* = 3.4 Hz, 1H), 4.17 (d, *J* = 11.1 Hz, 1H), 3.96 – 3.79 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 200.0, 159.0, 157.7, 149.1, 145.2, 136.2, 130.4, 130.4, 129.2, 128.6, 128.5, 127.5, 127.2, 126.8, 124.3, 120.8, 111.5, 58.3, 57.3, 54.8, 51.7, 28.6, 15.3.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{26}H_{21}N_2O_6^+$: 479.1214; found: 479.1221.

6-(4-isopropylphenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ea)



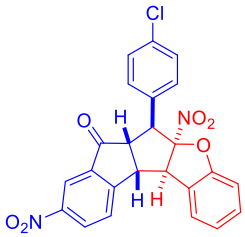
Pale yellow solid, 46.5 mg, 99% yield; m.p. 219.8-211.3 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 – 8.47 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.28 (td, *J* = 7.8, 1.4 Hz, 1H), 7.16 (d, *J* = 1.2 Hz, 4H), 7.11 – 7.03 (m, 2H), 4.44 (d, *J* = 3.4 Hz, 1H), 4.17 (d, *J* = 11.1 Hz, 1H), 3.87 (ddd, *J* = 18.5, 11.0, 7.5 Hz, 2H), 2.84 (hept, *J* = 6.9 Hz, 1H), 1.18 (dd, *J* = 7.0, 1.4 Hz, 6H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.0, 159.0, 157.7, 149.7, 149.1, 136.2, 130.4, 130.3, 129.2, 128.6, 127.5, 127.2, 127.2, 126.8, 124.3, 120.7, 111.5, 58.4, 57.4, 54.7, 51.7, 33.9, 23.9.; **HRMS** (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{27}H_{22}N_2O_6Na^+$: 493.1370; found: 493.1367.

6-(4-fluorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3fa)



Pale yellow solid, 44.2 mg, 99% yield; m.p. 209.7-210.2 °C; eluent: petroleum ether / ethyl acetate/ dichloromethane (v/v/v) = 8:1:1.; **^{1}H NMR (400 MHz, DMSO-d_6)**: δ 8.70 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.44 – 8.34 (m, 2H), 7.82 – 7.74 (m, 1H), 7.49 – 7.40 (m, 2H), 7.37 (td, *J* = 7.8, 1.4 Hz, 1H), 7.27 – 7.16 (m, 4H), 4.84 (d, *J* = 3.2 Hz, 1H), 4.37 (d, *J* = 11.3 Hz, 1H), 4.05 (ddd, *J* = 18.6, 11.0, 7.4 Hz, 2H).; **^{13}C NMR (101 MHz, DMSO-d_6):** δ 200.6, 163.5, 161.0, 159.7, 157.1, 148.4, 135.7, 131.80 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 14.5 Hz), 128.8 (d, *J* = 3.0 Hz), 128.7, 128.3, 126.9, 125.6, 123.9, 119.1, 115.5, 115.3, 110.6, 79.2, 56.9, 56.8, 52.9, 51.4.; **^{19}F NMR (376 MHz, DMSO-d_6)**: δ -113.69.; **HRMS** (ESI-TOF) *m/z:* $[M + K]^+$ Calcd. for $C_{24}H_{15}FN_2O_6K^+$: 486.0578; found: 486.0572.

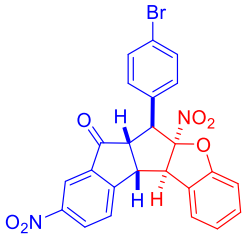
6-(4-chlorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ga)



Pale yellow solid, 45.7 mg, 99% yield; m.p. 230.1-230.5 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:1.; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.65 – 8.52 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.13 – 7.03 (m, 2H), 4.44 (d, *J* = 3.5 Hz, 1H), 4.17 (d, *J* = 11.3 Hz, 1H), 3.91 (dd, *J* = 7.6, 3.6 Hz, 1H), 3.80 (dd, *J* = 11.4, 7.5

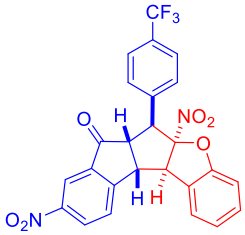
Hz, 1H).; **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 199.8, 158.9, 157.6, 149.1, 136.0, 135.3, 130.7, 130.5, 130.0, 129.3, 127.3, 127.2, 126.5, 124.5, 124.3, 120.8, 111.5, 58.4, 57.3, 54.2, 51.7.; **HRMS** (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{24}H_{15}ClN_2O_6Na^+$: 485.0511; found: 485.0519.

6-(4-bromophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ha)



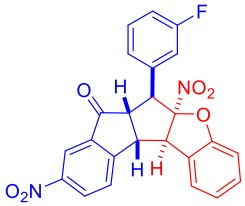
Pale yellow solid, 42.1 mg, 83% yield; m.p. 234.8-235.1 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:1.; **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.45 – 8.34 (m, 2H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.40 – 7.30 (m, 3H), 7.23 – 7.14 (m, 2H), 4.85 (d, *J* = 3.2 Hz, 1H), 4.37 (d, *J* = 11.3 Hz, 1H), 4.06 (ddd, *J* = 18.6, 10.9, 7.4 Hz, 2H).; **^{13}C NMR (101 MHz, DMSO-d_6):** δ 201.0, 160.1, 157.5, 148.8, 136.1, 132.5, 132.3, 131.9, 130.3, 130.2, 129.2, 128.7, 127.2, 126.1, 124.3, 122.5, 119.5, 111.0, 79.7, 57.4, 57.1, 53.3, 51.8.; **HRMS** (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{24}H_{15}BrN_2O_6Na^+$: 530.9989; found: 530.9981.

5a,9-dinitro-6-(4-(trifluoromethyl)phenyl)-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ia)



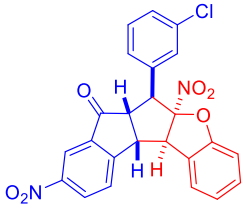
Pale yellow solid, 42.1 mg, 83% yield; m.p. 234.1-234.5 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:1.; **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.72 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.44 – 8.33 (m, 2H), 7.79 (d, *J* = 7.9 Hz, 3H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.38 (td, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.16 (m, 2H), 4.89 (d, *J* = 2.6 Hz, 1H), 4.52 (dt, *J* = 10.6, 4.2 Hz, 1H), 4.18 – 4.07 (m, 2H).; **^{13}C NMR (101 MHz, DMSO):** δ 200.6, 159.7, 157.1, 148.4, 137.5, 135.7, 130.7, 129.9, 129.8, 129.1 (q, *J* = 32.0 Hz), 128.7, 128.2, 126.7, 125.6, 125.5, 125.4 (q, *J* = 3.8 Hz), 123.9, 122.8, 119.1, 110.6, 79.2, 57.0, 56.7, 53.0, 51.4.; **^{19}F NMR (376 MHz, DMSO-d_6):** δ -61.09.; **HRMS** (ESI-TOF) *m/z:* $[M + K]^+$ Calcd. for $C_{25}H_{15}F_3N_2O_6K^+$: 535.0514; found: 535.0499.

6-(3-fluorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ja)



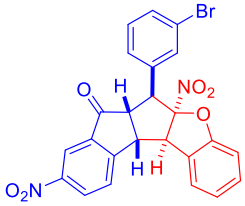
Pale yellow solid, 34 mg, 76% yield; m.p. 235.1-235.5 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.43 – 8.34 (m, 2H), 7.78 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.44 (td, *J* = 8.0, 6.2 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.27 – 7.16 (m, 4H), 4.86 (d, *J* = 2.6 Hz, 1H), 4.41 (dt, *J* = 10.9, 4.1 Hz, 1H), 4.16 – 4.04 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$)**: δ 200.6, 163.2, 160.8, 159.7, 157.1, 148.4, 135.7, 135.4 (d, *J* = 7.8 Hz), 130.4 (d, *J* = 8.5 Hz), 129.82 (d, *J* = 15.4 Hz), 128.7, 128.2, 126.8, 126.0 (d, *J* = 2.7 Hz), 125.6, 123.9, 119.1, 116.6.0 (d, *J* = 22.2 Hz), 115.5 (d, *J* = 20.8 Hz), 110.6, 79.2, 57.0, 56.7, 53.0, 51.3.; **^{19}F NMR (376 MHz, DMSO-*d*$_6$)**: δ -112.93.; **HRMS** (ESI-TOF) *m/z:* [M + K]$^+$ Calcd. for $C_{24}H_{15}FN_2O_6K^+$: 485.0546; found: 485.0546.

6-(3-chlorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ka)



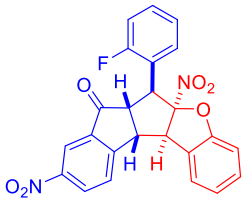
Pale yellow solid, 43 mg, 93% yield; m.p. 234.8-235.3 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.51 – 8.31 (m, 2H), 7.85 – 7.71 (m, 1H), 7.55 – 7.31 (m, 5H), 7.27 – 7.15 (m, 2H), 4.86 (d, *J* = 2.5 Hz, 1H), 4.41 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.21 – 4.03 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.6, 159.7, 157.1, 148.4, 135.7, 135.2, 133.1, 130.3, 129.9, 129.8, 129.5, 128.7, 128.6, 128.5, 128.2, 126.8, 125.6, 123.9, 119.1, 110.6, 79.2, 57.1, 56.7, 52.9, 51.3.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{24}H_{15}ClN_2O_6Na^+$: 485.0511; found: 485.0545.

6-(3-bromophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3la)



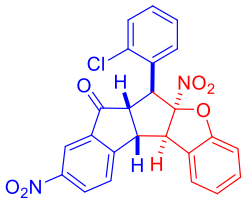
Pale yellow solid, 47.1 mg, 93% yield; m.p. 242.7-243.2 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.43 – 8.35 (m, 2H), 7.82 – 7.75 (m, 1H), 7.66 – 7.56 (m, 2H), 7.43 – 7.35 (m, 3H), 7.25 – 7.18 (m, 2H), 4.86 (d, *J* = 2.6 Hz, 1H), 4.41 (dt, *J* = 10.3, 4.2 Hz, 1H), 4.14 – 4.05 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.1, 160.1, 157.5, 148.8, 136.1, 135.9, 132.8, 131.9, 131.1, 130.3, 130.2, 129.4, 129.2, 128.7, 127.2, 126.0, 124.3, 122.2, 119.6, 111.0, 79.7, 57.5, 57.1, 53.3, 51.8.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{24}H_{15}ClN_2O_6Na^+$: 485.0511; found: 485.0545.

6-(2-fluorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ma)



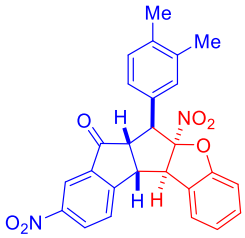
Pale yellow solid, 14.3 mg, 32% yield; m.p. 236.8-237.1 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.44 – 8.36 (m, 2H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (tdd, *J* = 7.5, 5.4, 1.7 Hz, 1H), 7.34 (dtd, *J* = 19.6, 7.7, 1.3 Hz, 2H), 7.25 – 7.15 (m, 3H), 4.90 (d, *J* = 3.0 Hz, 1H), 4.53 (d, *J* = 10.1 Hz, 1H), 4.20 – 4.12 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.4, 162.4, 160.2, 160.0, 157.4, 148.9, 135.8, 132.0 (d, *J* = 3.3 Hz), 131.1 (d, *J* = 8.7 Hz), 130.5, 130.2, 129.2, 128.4, 126.8, 126.0, 125.2 (d, *J* = 3.3 Hz), 124.3, 120.2 (d, *J* = 13.5 Hz), 119.5, 115.9 (d, *J* = 22.5 Hz), 110.9, 57.9, 56.9, 51.9, 47.9.; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -116.61.; **HRMS** (ESI-TOF) *m/z:* [M + K]$^+$ Calcd. for $C_{24}H_{15}FN_2O_6K^+$: 485.0546; found: 485.0538.

6-(2-chlorophenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3na)



Pale yellow solid, 10.2 mg, 22% yield; m.p. 233.1-233.5 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)**: δ 8.72 (dd, *J* = 8.3, 2.3 Hz, 1H), 8.45 – 8.36 (m, 2H), 7.84 – 7.75 (m, 2H), 7.47 (qd, *J* = 7.6, 1.7 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 4.89 (d, *J* = 3.8 Hz, 1H), 4.83 (d, *J* = 10.2 Hz, 1H), 4.23 (dd, *J* = 7.5, 3.8 Hz, 1H), 4.08 (dd, *J* = 10.2, 7.5 Hz, 1H).; **^{13}C NMR: (101 MHz, DMSO-*d*$_6$)**: δ 201.5, 160.3, 157.2, 149.0, 135.7, 134.5, 132.2, 131.4, 130.7, 130.6, 130.3, 129.8, 129.3, 128.3, 128.0, 126.5, 126.0, 124.4, 119.4, 111.0, 79.6, 59.1, 58.5, 51.8, 50.4.; **HRMS** (ESI-TOF) *m/z:* [M + K]$^+$ Calcd. for $C_{24}H_{15}ClN_2O_6K$: 501.0250; found: 501.0250.

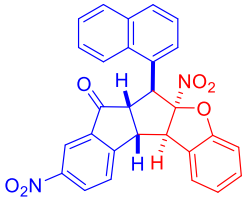
6-(3,4-dimethylphenyl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3oa)



Pale yellow solid, 34.6 mg, 76% yield; m.p. 219.7-220.2 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.64 (d, *J* = 9.1 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.30 (m, 2H), 7.25 – 6.85 (m, 5H), 4.53 (s, 1H), 4.21 (d, *J* = 10.8 Hz, 1H), 3.95 (q, *J* = 8.7, 8.0 Hz, 2H), 2.27 (s, 6H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 200.02, 159.03, 157.63, 148.96, 137.74, 137.17, 136.13, 130.43, 130.27, 130.25, 130.23, 128.50, 127.42, 127.14, 126.85, 126.56, 124.20,

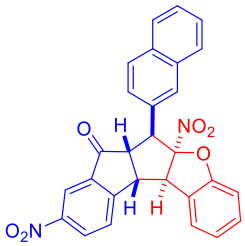
124.16, 120.62, 111.45, 58.24, 57.17, 54.75, 51.61, 20.03, 19.62.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{26}H_{20}N_2O_6Na$: 479.1214; found: 479.1216.

6-(naphthalen-1-yl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3pa)



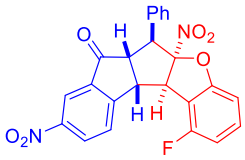
Pale yellow solid, 46.4 mg, 97% yield; m.p. 222.9-223.4 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.51 – 8.31 (m, 2H), 7.85 – 7.71 (m, 1H), 7.55 – 7.31 (m, 5H), 7.27 – 7.15 (m, 2H), 4.86 (d, *J* = 2.5 Hz, 1H), 4.41 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.21 – 4.03 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.6, 160.5, 157.4, 148.9, 136.2, 133.8, 132.5, 130.5, 130.2, 129.4, 129.3, 129.2, 128.9, 128.7, 127.3, 127.1, 126.2, 126.0, 125.9, 124.3, 122.4, 119.6, 111.1, 79.7, 59.2, 58.3, 51.8, 48.2.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{28}H_{18}N_2O_6Na^+$: 501.1057; found: 501.1044.

6-(naphthalen-2-yl)-5a,9-dinitro-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3qa)



Pale yellow solid, 47.3 mg, 99% yield; m.p. 233.2-233.6 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.72 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 2.2 Hz, 1H), 7.98 – 7.90 (m, 4H), 7.80 (d, *J* = 7.3 Hz, 1H), 7.56 (td, *J* = 5.5, 1.9 Hz, 3H), 7.38 (td, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.17 (m, 2H), 4.90 (d, *J* = 3.2 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.25 – 4.12 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.8, 159.8, 157.2, 148.4, 135.7, 132.8, 132.7, 130.1, 129.9, 129.8, 129.1, 128.7, 128.3, 128.0, 127.9, 127.6, 127.2, 127.0, 126.6, 126.5, 125.6, 123.9, 119.1, 110.6, 79.2, 57.2, 56.7, 54.0, 51.5.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{28}H_{18}N_2O_6Na^+$: 501.1057; found: 501.1052.

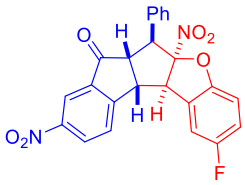
1-fluoro-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ab)



Pale yellow solid, 38.8 mg, 87% yield; m.p. 248.1-248.6 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.78 – 8.59 (m, 2H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.28 (m, 6H), 7.03 – 6.83 (m, 2H), 4.61 (d, *J* = 3.9 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H),

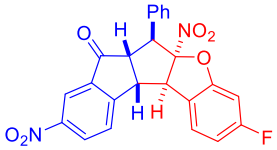
4.07 (dd, *J* = 7.8, 3.9 Hz, 1H), 3.96 (dd, *J* = 11.2, 7.7 Hz, 1H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.9, 159.5 (d, *J* = 7.5 Hz), 159.4, 158.8, 157.2, 149.2, 136.1, 132.2 (d, *J* = 8.4 Hz), 131.4, 130.7, 129.3, 129.3, 129.1, 127.6, 127.4, 120.7, 115.0 (d, *J* = 21.2 Hz), 111.1 (d, *J* = 19.6 Hz), 107.6 (d, *J* = 3.7 Hz), 57.2, 55.9, 54.5, 50.7.; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -117.03.; **HRMS** (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{24}H_{15}FN_2O_6Na^+$: 469.0806; found: 469.0818.

2-fluoro-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ac)



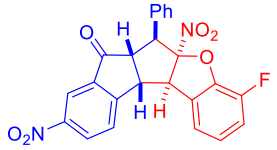
Pale yellow solid, 40.6 mg, 91% yield; m.p. 258.7-259.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) =7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.43 (d, *J* = 8.5 Hz, 2H), 7.73 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.38 (dq, *J* = 7.6, 3.7 Hz, 5H), 7.21 (dt, *J* = 6.7, 3.4 Hz, 2H), 4.83 (d, *J* = 3.3 Hz, 1H), 4.32 (d, *J* = 11.4 Hz, 1H), 4.22 – 4.04 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.0, 160.2, 160.0, 157.9, 153.7, 148.9, 136.1, 132.8, 130.4 (d, *J* = 9.7 Hz), 130.3, 130.1, 129.3, 129.0, 128.0, 119.5, 116.5 (d, *J* = 24.7 Hz), 113.5 (d, *J* = 26.2 Hz), 112.0 (d, *J* = 8.8 Hz), 111.9, 57.6, 56.9, 55.4, 54.2, 51.5.; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -119.95.; **HRMS** (ESI-TOF) *m/z:* $[M + K]^+$ Calcd. for $C_{24}H_{15}FN_2O_6K^+$: 485.0546; found: 485.0532.

3-fluoro-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ad)



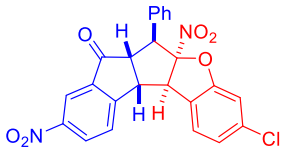
Pale yellow solid, 41.5 mg, 93% yield; m.p. 227.8-228.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.44 – 8.30 (m, 2H), 7.80 (dd, *J* = 8.4, 5.7 Hz, 1H), 7.38 (dq, *J* = 7.9, 3.8 Hz, 5H), 7.21 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.05 (td, *J* = 8.9, 8.4, 2.4 Hz, 1H), 4.83 (d, *J* = 2.5 Hz, 1H), 4.37 – 4.29 (m, 1H), 4.16 – 4.05 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.6, 164.2, 161.8, 159.6, 158.1 (d, *J* = 13.7 Hz), 148.4, 135.6, 132.3, 129.9, 129.6, 128.8, 128.5, 127.9, 126.6 (d, *J* = 10.6 Hz), 124.4, 124.4, 119.1, 110.5 (d, *J* = 22.8 Hz), 99.4 (d, *J* = 28.0 Hz), 59.8, 56.4, 56.4, 53.7, 51.4.; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -111.4.; **HRMS** (ESI-TOF) *m/z:* $[M + Na]^+$ Calcd. for $C_{24}H_{15}FN_2O_6Na^+$: 469.0806; found: 469.0805.

4-fluoro-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ae)



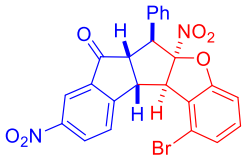
Pale yellow solid, 41 mg, 92% yield; m.p. 271.2-271.6 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.44 – 8.35 (m, 2H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.40 (s, 5H), 7.34 (dd, *J* = 10.8, 8.3 Hz, 1H), 7.22 (td, *J* = 7.9, 4.4 Hz, 1H), 4.97 (d, *J* = 2.5 Hz, 1H), 4.38 (dt, *J* = 9.9, 3.7 Hz, 1H), 4.19 – 4.10 (m, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.5, 159.4, 148.4, 147.4, 144.9, 143.5 (d, *J* = 10.7 Hz), 135.7, 132.2, 131.9 (d, *J* = 1.6 Hz), 129.9, 129.7, 128.7, 128.6, 128.6, 127.5, 125.1 (d, *J* = 5.7 Hz), 121.4 (d, *J* = 3.6 Hz), 119.1, 116.9 (d, *J* = 16.4 Hz), 79.2, 57.3, 56.5, 53.7, 51.2.; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -136.7.; **HRMS** (ESI-TOF) *m/z:* [M +K]$^+$ Calcd. for $C_{24}H_{15}FN_2O_6K^+$: 485.0546; found: 485.0545.

3-chloro-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3af)



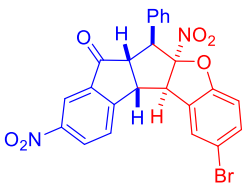
Pale yellow solid, 39.3 mg, 85% yield; m.p. 233.8-234.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.67 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.34 (m, 4H), 7.30 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.17 (d, *J* = 6.7 Hz, 2H), 4.49 (d, *J* = 3.0 Hz, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 4.05 – 3.85 (m, 2H).; **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 199.6, 158.6, 158.4, 149.2, 136.2, 136.2, 131.1, 130.5, 129.4, 129.3, 129.1, 127.2, 127.1, 126.1, 124.9, 124.6, 120.9, 112.5, 58.0, 57.2, 54.9, 51.7.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{24}H_{15}ClN_2O_6^+$: 463.0691; found: 463.0704.

1-bromo-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ag)



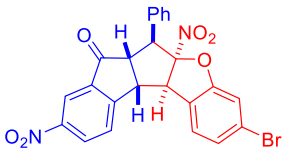
Pale yellow solid, 45.6 mg, 90% yield; m.p. 234.7-235.1 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.76 – 8.62 (m, 2H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.33 – 7.29 (m, 3H), 7.28 (d, *J* = 3.5 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.59 (d, *J* = 2.9 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 4.08 (dd, *J* = 7.3, 2.9 Hz, 1H), 3.96 (dd, *J* = 12.0, 7.2 Hz, 1H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 199.4, 158.8, 158.1, 149.2, 136.1, 132.0, 130.6, 130.4, 129.4, 129.4, 129.1, 128.2, 127.9, 127.1, 125.7, 120.7, 118.5, 110.5, 59.3, 56.6, 55.1, 50.1.; **HRMS** (ESI-TOF) *m/z:* [M + K]$^+$ Calcd. for $C_{24}H_{15}BrN_2O_6K^+$: 546.9728; found: 546.9710.

2-bromo-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ah)



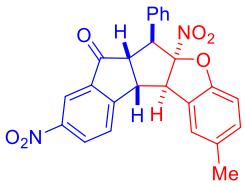
Pale yellow solid, 45.1 mg, 89% yield; m.p. 87.4-87.8 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.44 – 8.29 (m, 3H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.51 (s, 1H), 7.43 – 7.32 (m, 5H), 4.85 (s, 1H), 4.32 (t, *J* = 7.8 Hz, 1H), 4.09 (d, *J* = 8.7 Hz, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.5, 159.5, 158.1, 148.4, 135.6, 132.2, 129.9, 129.7, 128.8, 128.5, 128.0, 127.3, 126.7, 121.9, 119.1, 113.9, 79.2, 56.6, 56.5, 53.7, 51.2.; **HRMS** (ESI-TOF) *m/z:* [M + K]$^+$ Calcd. for $C_{24}H_{15}BrN_2O_6K^+$: 546.9728; found: 546.9753.

3-bromo-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ai)



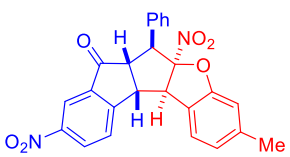
Pale yellow solid, 44.1 mg, 87% yield; m.p. 233.8-234.3 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 7:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)**: δ 8.71 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.49 – 8.28 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.46 – 7.23 (m, 6H), 4.85 (d, *J* = 2.4 Hz, 1H), 4.32 (d, *J* = 10.1 Hz, 1H), 4.09 (d, *J* = 9.2 Hz, 2H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$)**: δ 200.5, 159.5, 158.1, 148.4, 135.6, 132.2, 129.9, 129.7, 128.8, 128.5, 128.0, 127.3, 126.7, 121.9, 119.1, 113.9, 56.5, 56.5, 53.7, 51.2, 26.4.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{24}H_{15}BrN_2O_6Na^+$: 529.0006; found: 529.0009.

2-methyl-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3j)



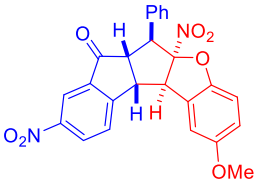
Pale yellow solid, 40.7 mg, 92% yield; m.p. 251.2-251.5 ºC; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.47 – 8.34 (m, 2H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.31 (m, 5H), 7.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 4.31 (d, *J* = 11.2 Hz, 1H), 4.11 – 3.99 (m, 2H), 2.34 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.7, 159.8, 155.2, 148.4, 135.6, 133.0, 132.5, 129.9, 129.9, 129.6, 128.7, 128.5, 128.5, 128.2, 127.2, 125.8, 119.1, 110.1, 79.2, 57.2, 56.6, 53.7, 51.3, 20.5.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_6Na^+$: 465.1057; found: 465.1062.

3-methyl-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ak)



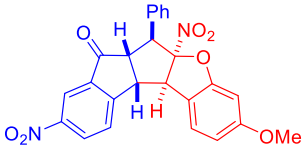
Pale yellow solid, 39.8 mg, 90% yield; m.p. 240.8-241.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.36 (t, *J* = 14.9 Hz, 2H), 7.63 (s, 1H), 7.37 (d, *J* = 14.0 Hz, 4H), 7.01 (s, 2H), 4.77 (s, 1H), 4.30 (d, *J* = 10.2 Hz, 1H), 4.04 – 4.02 (m, 2H), 2.34 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 201.2, 160.2, 157.8, 148.8, 140.3, 136.1, 132.9, 130.3, 130.1, 129.1, 129.0, 127.7, 125.7, 125.5, 124.8, 119.5, 111.5, 79.7, 57.4, 57.0, 54.2, 52.0, 21.5.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_6K^+$: 481.0796; found: 481.0806.

2-methoxy-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3al)



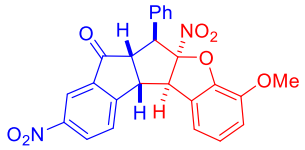
Pale yellow solid, 41.7 mg, 91% yield; m.p. 215.1-215.6 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 2.2 Hz, 1H), 7.39 (ddt, *J* = 16.5, 13.8, 3.5 Hz, 6H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.75 (d, *J* = 3.3 Hz, 1H), 4.29 (d, *J* = 11.3 Hz, 1H), 4.07 (ddd, *J* = 18.7, 11.1, 7.4 Hz, 2H), 3.79 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.8, 159.8, 156.1, 151.0, 148.4, 135.7, 132.5, 129.9, 129.6, 129.2, 128.8, 128.5, 127.5, 119.1, 114.9, 111.1, 110.9, 79.2, 57.5, 56.5, 55.9, 53.7, 51.2.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_7K^+$: 497.0746; found: 497.0757.

3-methoxy-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3am)



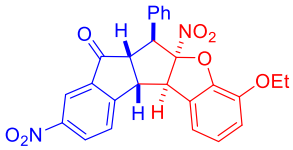
Pale yellow solid, 42.6 mg, 93% yield; m.p. 216.9-217.4 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.69 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.43 – 8.33 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.38 (q, *J* = 7.2, 6.6 Hz, 5H), 6.86 (d, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.73 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 10.5 Hz, 1H), 4.06 (d, *J* = 9.4 Hz, 2H), 3.77 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.7, 161.1, 159.8, 158.5, 148.4, 135.6, 132.4, 129.9, 129.6, 128.7, 128.5, 128.5, 127.8, 125.7, 119.8, 119.1, 109.9, 97.0, 56.7, 56.5, 55.7, 53.7, 51.6.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_7Na^+$: 481.1006; found: 481.1001.

4-methoxy-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3an)



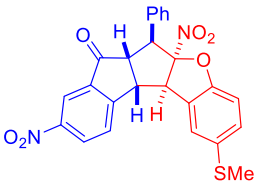
Pale yellow solid, 40.8 mg, 89% yield; m.p. 243.1-243.6 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.5, 2.2 Hz, 1H), 8.37 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.46 – 7.28 (m, 6H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 4.83 (d, *J* = 2.7 Hz, 1H), 4.41 – 4.29 (m, 1H), 4.14 – 4.05 (m, 2H), 3.85 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.7, 159.7, 148.4, 145.2, 144.1, 135.6, 132.4, 129.9, 129.6, 129.5, 128.7, 128.5, 128.5, 127.2, 124.8, 119.1, 116.9, 113.6, 57.5, 56.5, 56.0, 53.6, 51.2.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_7Na^+$: 481.1006; found: 481.1015.

4-ethoxy-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3ao)



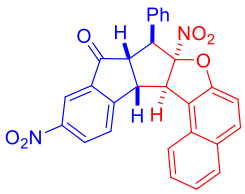
Pale yellow solid, 43 mg, 91% yield; m.p. 229.8-230.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.70 (dd, *J* = 8.5, 2.2 Hz, 1H), 8.38 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.46 – 7.32 (m, 6H), 7.15 – 7.02 (m, 2H), 4.83 (d, *J* = 2.6 Hz, 1H), 4.34 (dt, *J* = 10.3, 3.3 Hz, 1H), 4.21 – 4.07 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.7, 159.7, 148.4, 145.5, 143.2, 135.6, 132.5, 129.9, 129.8, 129.7, 128.7, 128.6, 128.5, 128.5, 127.2, 124.7, 119.1, 117.1, 115.4, 64.7, 57.5, 56.6, 53.7, 51.3, 14.8.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{26}H_{20}N_2O_7Na^+$: 495.1163; found: 495.1164.

2-(methylthio)-5a,9-dinitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (3op)



Pale yellow solid, 44.5 mg, 94% yield; m.p. 251.8-252.3 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 2.2 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.31 (m, 5H), 7.28 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.31 (d, *J* = 11.4 Hz, 1H), 4.13 (dd, *J* = 7.4, 3.3 Hz, 1H), 4.06 (dd, *J* = 11.5, 7.3 Hz, 1H), 2.52 (s, 3H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$):** δ 200.6, 159.7, 155.3, 148.4, 135.6, 132.7, 132.4, 129.8, 129.6, 129.3, 128.9, 128.5, 128.4, 127.2, 124.5, 119.0, 111.1, 57.1, 56.5, 53.7, 51.2, 16.3.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{25}H_{18}N_2O_6SNa^+$: 497.0778; found: 497.0757.

7a,11-dinitro-8-phenyl-8,8a,13b,13c-tetrahydrobenzo[5,6]pentaleno[2,1-b]naphtho[1,2-d]furan-9(7aH)-one (3aq)



Pale yellow solid, 43 mg, 90% yield; m.p. 246.9-247.4 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 6:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.77 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 2.3 Hz, 1H), 8.16 – 8.00 (m, 3H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 11.9, 8.2 Hz, 2H), 7.41 (s, 4H), 7.19 (d, *J* = 22.9 Hz, 1H), 5.46 (d, *J* = 2.9 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.19 (dd, *J* = 7.3, 2.9 Hz, 1H), 4.08 (dd, *J* = 12.1, 7.2 Hz, 1H).; **^{13}C NMR (101 MHz, DMSO):** δ 200.3, 159.4, 154.9, 148.4, 135.8, 132.1, 131.3, 130.4, 130.0, 129.7, 129.3, 129.0, 128.8, 128.6, 128.6, 128.6, 128.5, 128.1, 127.3, 124.8, 122.8, 120.2, 119.3, 111.9, 56.5, 56.0, 54.3, 50.5.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{28}H_{18}N_2O_6Na^+$: 501.1059; found: 501.1057.

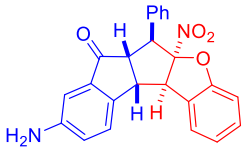
3. Gram-scale reaction for synthesis of 3aa.

In a reaction tube equipped with a magnetic stirring bar, 2-alkylidene-1-indanones **1** (3.6 mmol, 1.2 equiv.), 2-Nitrobenzofurans **2** (3.0 mmol), Na_2CO_3 (212 mg, 1.0 equiv.) and catalyst TEBA (90 mg, 20 mol%, 0.2 mmol) were added successively, and then followed by addition CH_2Cl_2 (30.0 mL). The reaction solution was stirred at room temperature for 24 h. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether / ethyl acetate/ dichloromethane 5:1:0.5~ 6:1:1) product 3aa in 85% yield with >20:1 dr.

4. Synthesis of compound 4.

To a solution of compound **3aa** (42.8 mg, 0.1 mmol) in AcOH (1.0 mL) at 0 °C was added Fe powder (16.8 mg, 3.0 equiv.). The mixture was stirred at room temperature for 48 h. The resulting mixture was then quenched with saturated $NaHCO_3$ solution and extracted with DCM three times. The combined organic layers were dried over Na_2SO_4. After evaporation of solvent, the resulting crude mixture was purified by silica gel column chromatography (petroleum ether/ ethyl acetate =2:1) to afford compound **4** in 85% yield with >20:1 dr.

9-amino-5a-nitro-6-phenyl-6,6a,11b,11c-tetrahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-7(5aH)-one (4)

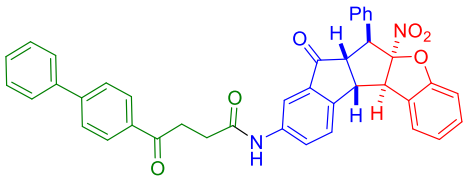


Pale yellow solid, 34 mg, 85% yield; m.p. 87.4-87.8 °C; eluent: petroleum ether/ethyl acetate/ dichloromethane (v/v/v) = 2:1:0.5.; **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 7.68 (t, *J* = 7.9 Hz, 2H), 7.42 – 7.27 (m, 6H), 7.20 – 7.04 (m, 3H), 6.79 (d, *J* = 2.4 Hz, 1H), 5.55 (s, 2H), 4.51 (d, *J* = 3.4 Hz, 1H), 4.19 (d, *J* = 11.2 Hz, 1H), 3.84 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.73 (dd, *J* = 7.3, 3.5 Hz, 1H).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$)**: δ 202.9, 157.0, 149.7, 141.9, 135.1, 133.1, 129.5, 129.5, 128.9, 128.5, 128.3, 127.7, 126.9, 125.3, 123.8, 122.7, 110.5, 106.1, 58.0, 56.5, 54.3, 50.7.; **HRMS** (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd. for $C_{24}H_{18}N_2O_4Na^+$: 421.1159; found: 421.1159.

5. Synthesis of compound 5.

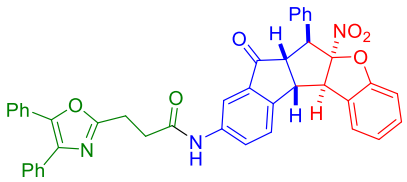
To a solution of drug moieties (0.12 mmol, 1.2 equiv.) in DCM (1.0 mL) was added EDCI (0.12 mmol, 1.2 equiv.), HOBT (0.12 mmol, 1.2 equiv.), DMAP (0.02 mmol, 0.2 equiv.) and compound **4** (0.1 mmol, 1.0 equiv.) at 0 °C. Upon completion, the reaction was quenched by saturated $NaHCO_3$ solution and the mixture was extracted with DCM. The organic phases were combined, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/EtOAc = 5/1 to 4/1) to give the corresponding product **5**

4-([1,1'-biphenyl]-4-yl)-N-(5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)-4-oxobutanamide (5a)



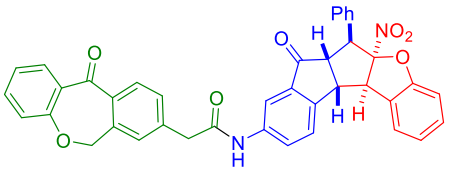
Pale yellow solid, 58.3 mg, 92% yield; m.p. 191.4-191.8 ºC; eluent: petroleum ether/ethyl acetate (v/v) = 5:1.; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.88 (s, 1H), 8.22 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 2.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.64 – 7.58 (m, 3H), 7.46 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.28 (m, 6H), 7.15 – 7.06 (m, 2H), 4.42 (d, *J* = 3.0 Hz, 1H), 4.36 – 4.26 (m, 1H), 3.84 – 3.74 (m, 2H), 3.44 (t, *J* = 6.3 Hz, 2H), 2.78 (t, *J* = 6.3 Hz, 2H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.8, 199.0, 171.3, 157.6, 149.1, 146.2, 139.7, 139.6, 135.2, 135.1, 132.3, 129.9, 129.5, 129.1, 128.8, 128.8, 128.4, 128.2, 128.1, 127.4, 127.4, 127.3, 126.3, 124.4, 124.0, 115.2, 111.2, 58.6, 57.4, 54.9, 51.4, 33.9, 31.2.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{40}H_{31}N_2O_6^+$: 635.2177; found: 635.2177.

3-(4,5-diphenyloxazol-2-yl)-N-(5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)propenamide (5b)



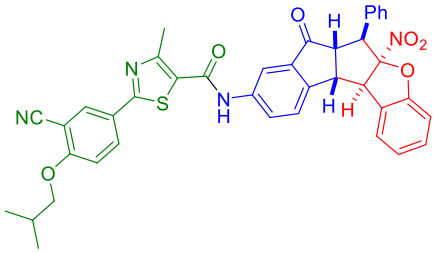
Pale yellow solid, 61.2 mg, 91% yield; m.p. 221.6-222.3 ºC; eluent: petroleum ether/ethyl acetate(v/v) = 4:1. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.32 (s, 1H), 8.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.54 – 7.51 (m, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.28 (m, 13H), 7.25 (s, 1H), 4.41 (d, *J* = 2.7 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.83 – 3.74 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 6.9 Hz, 2H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.4, 170.4, 162.8, 157.7, 149.1, 145.9, 139.6, 135.3, 134.6, 132.3, 131.9, 130.0, 129.5, 128.9, 128.8, 128.6, 128.4, 128.3, 128.1, 128.0, 127.4, 127.2, 126.5, 126.3, 125.9, 124.3, 124.0, 118.1, 115.3, 111.3, 110.7, 58.6, 57.4, 54.9, 51.4, 34.1, 24.1.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{42}H_{32}N_3O_6^+$: 674.2286; found: 674.2287.

N-5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-8-yl)acetamide (5c)



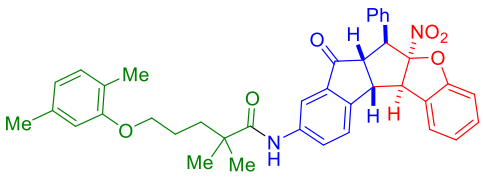
Pale yellow solid, 57.7 mg, 89% yield; m.p. 216.4-216.8 ºC; eluent: petroleum ether/ethyl acetate(v/v) = 5:1. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.89 (s, 1H), 8.39 (dd, *J* = 8.3, 2.1 Hz, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (ddt, *J* = 11.5, 5.3, 3.4 Hz, 7H), 7.14 – 7.06 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.14 (s, 2H), 4.43 (d, *J* = 3.6 Hz, 1H), 4.31 (d, *J* = 11.1 Hz, 1H), 3.93 (dd, *J* = 11.1, 7.3 Hz, 1H), 3.85 (dd, *J* = 7.5, 3.6 Hz, 1H), 3.46 (s, 2H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 203.5, 191.0, 169.9, 160.7, 157.6, 149.4, 140.3, 139.6, 136.5, 135.7, 135.0, 133.0, 132.5, 132.3, 129.9, 129.5, 129.3, 128.9, 128.9, 128.5, 128.2, 128.2, 128.0, 127.3, 126.4, 125.2, 124.4, 124.0, 121.5, 115.2, 111.2, 73.7, 58.5, 57.4, 54.8, 51.4, 43.2.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{40}H_{29}N_2O_7^+$: 671.1789; found: 671.1790.

2-(3-cyano-4-isobutoxyphenyl)-4-methyl-N-(5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)thiazole-5-carboxamide (5d)



Pale yellow solid, 66.2 mg, 95% yield; m.p. 234.1-234.5 ºC; eluent: petroleum ether/ethyl acetate(v/v) = 5:1. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.11 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.04 – 7.93 (m, 3H), 7.83 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.25 (qd, *J* = 7.6, 6.6, 2.9 Hz, 6H), 7.11 – 7.01 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 1H), 4.38 (d, *J* = 3.3 Hz, 1H), 4.22 (d, *J* = 10.5 Hz, 1H), 3.86 – 3.73 (m, 4H), 2.69 (s, 3H), 2.11 (dq, *J* = 13.3, 6.6 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 6H).; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 202.1, 165.4, 162.6, 160.2, 157.9, 157.7, 150.0, 138.7, 135.5, 132.7, 132.1, 132.0, 130.0, 129.4, 128.9, 128.7, 128.1, 127.3, 126.6, 125.7, 125.2, 124.3, 124.1, 116.2, 115.6, 112.8, 111.3, 102.9, 75.8, 58.7, 57.4, 54.9, 51.4, 28.3, 19.2, 17.7.; **HRMS** (ESI-TOF) *m/z:* [M + H]$^+$ Calcd. for $C_{40}H_{33}N_2O_6S^+$: 697.2115; found: 671.1790.

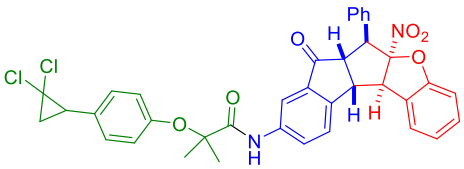
5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)pentanamide (5e)



Pale yellow solid, 53.6 mg, 85% yield; m.p. 206.8-207.3 ºC; eluent: petroleum ether/ethyl acetate(v/v) = 4:1. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.80 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.37 (dt, *J* = 6.6, 3.3 Hz, 3H), 7.35 – 7.30 (m, 3H), 7.17 – 7.10

(m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.44 (d, *J* = 2.8 Hz, 1H), 4.31 – 4.24 (m, 1H), 3.95 (t, *J* = 3.2 Hz, 2H), 3.81 (d, *J* = 9.3 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H), 1.83 (d, *J* = 3.0 Hz, 4H), 1.34 (s, 6H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.0, 176.3, 157.7, 156.9, 149.3, 139.2, 136.7, 135.4, 132.2, 130.5, 130.0, 129.5, 128.9, 128.5, 128.2, 127.3, 126.3, 124.3, 124.1, 123.6, 121.0, 115.8, 112.2, 111.3, 67.9, 58.7, 57.4, 55.0, 51.4, 43.1, 37.8, 29.8, 29.5, 27.3, 25.7, 25.3, 21.5, 16.0.; **HRMS** (ESI-TOF) *m/z:* $[M + H]^+$ Calcd. for $C_{39}H_{38}N_2O_6^+$: 631.2803; found: 631.2803.

2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methyl-N-(5a-nitro-7-oxo-6-phenyl-5a,6,6a,7,11b,11c-hexahydrobenzo[5,6]pentaleno[2,1-b]benzofuran-9-yl)propenamide (5f)



Pale yellow solid, 60.9 mg, 91% yield; m.p. 220.8-221.3 ºC; eluent: petroleum ether/ethyl acetate(v/v) = 5:1. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.82 (s, 1H), 8.14 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.30 (m, 6H), 7.22 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 7.02 – 6.95 (m, 2H), 4.46 (d, *J* = 2.8 Hz, 1H), 4.30 (d, *J* = 10.1 Hz, 1H), 3.87 – 3.78 (m, 2H), 2.87 (dd, *J* = 10.7, 8.3 Hz, 1H), 1.98 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.82 (t, *J* = 7.9 Hz, 1H), 1.61 (s, 6H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.8, 173.4, 157.7, 153.2, 149.4, 138.6, 135.5, 132.2, 130.5, 130.1, 130.0, 129.4, 128.9, 128.9, 128.2, 127.9, 127.3, 126.4, 124.3, 124.0, 121.7, 115.7, 111.3, 82.2, 60.8, 58.7, 57.3, 54.9, 51.4, 34.9, 26.0, 25.1, 25.0.; **HRMS** (ESI-TOF) *m/z:* $[M + H]^+$ Calcd. for $C_{37}H_{31}Cl_2N_2O_6^+$: 669.1554; found: 669.1565.

6. X-ray Crystal Structure of Compound 3ga.

Single crystal of compound **3ga** were prepared from the EtOH at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] Sheldrick, G. M. *Acta Cryst.* 2**008**, *A64*, 112-122.

[3] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3-8.

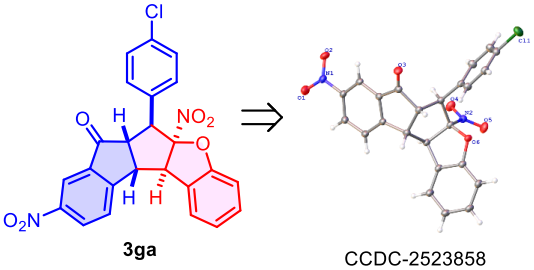


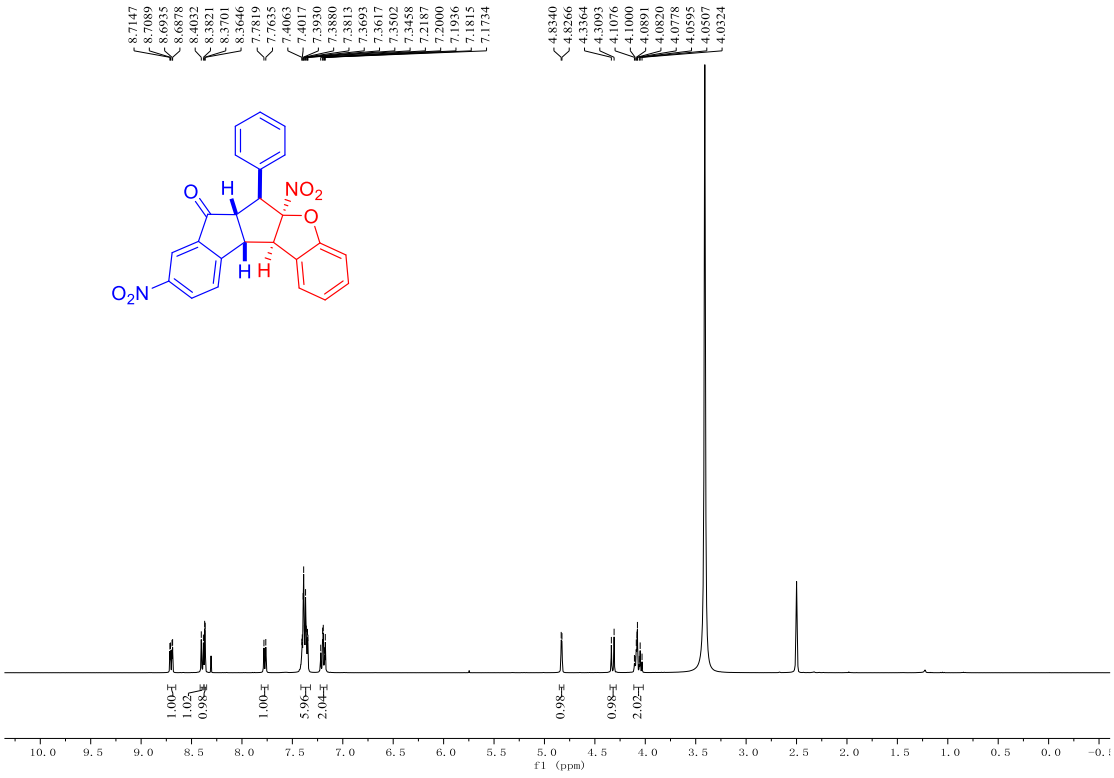
Table 1 Crystal data and structure refinement for 3ga.

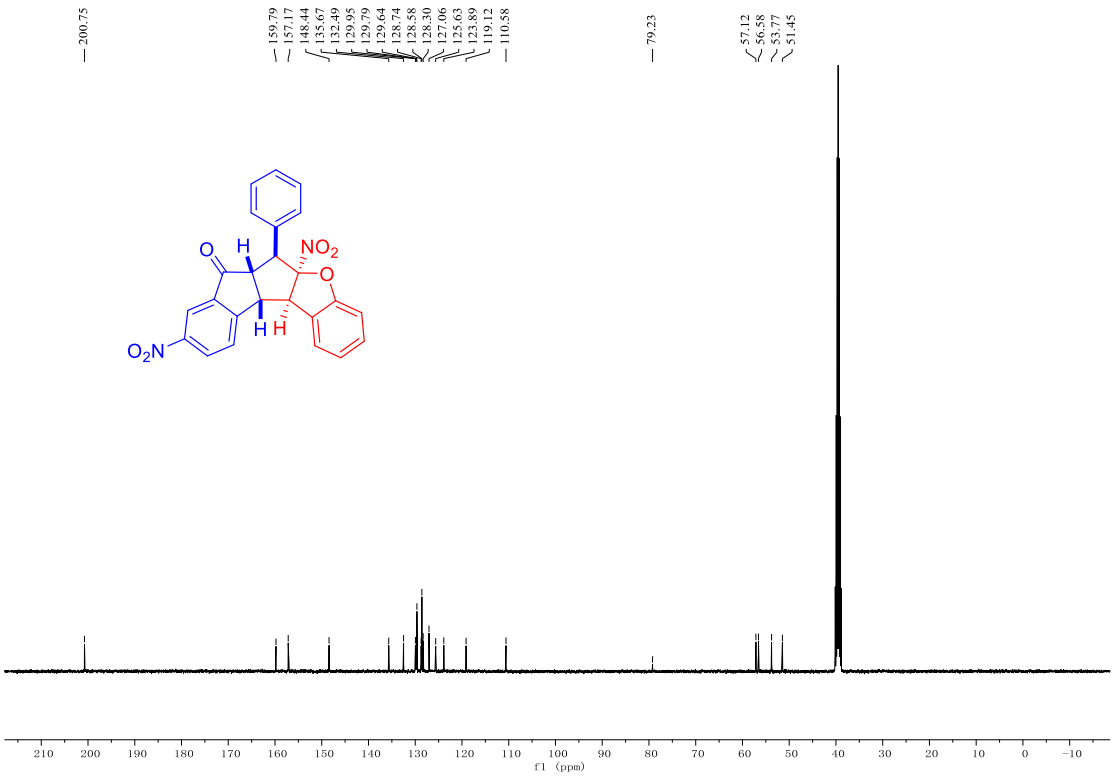
Identification code	**3ga**

Empirical formula	$C_{24}H_{15}ClN_2O_6$
Formula weight	925.66
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.8995(3)
b/Å	8.91074(8)
c/Å	17.93833(18)
α/°	90
β/°	91.6928(9)
γ/°	90
Volume/Å^3	4138.06(7)
Z	4
ρ_{calc}g/cm^3	1.486
μ/mm^{-1}	2.045
F(000)	1904.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.866 to 146.034
Index ranges	$-30 \le h \le 32$, $-8 \le k \le 10$, $-22 \le l \le 22$
Reflections collected	36653
Independent reflections	8057 [R_{int} = 0.0229, R_{sigma} = 0.0181]
Data/restraints/parameters	8057/0/596
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0854
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0894
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25

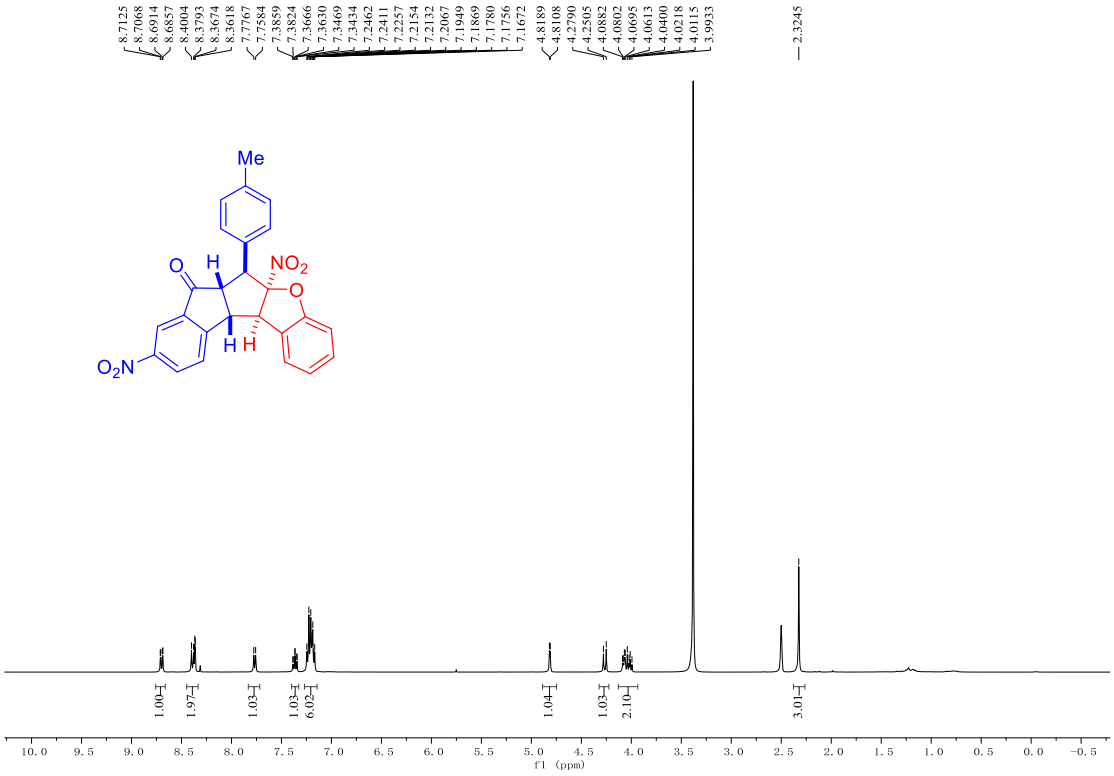
6. Copies of NMR Spectra.

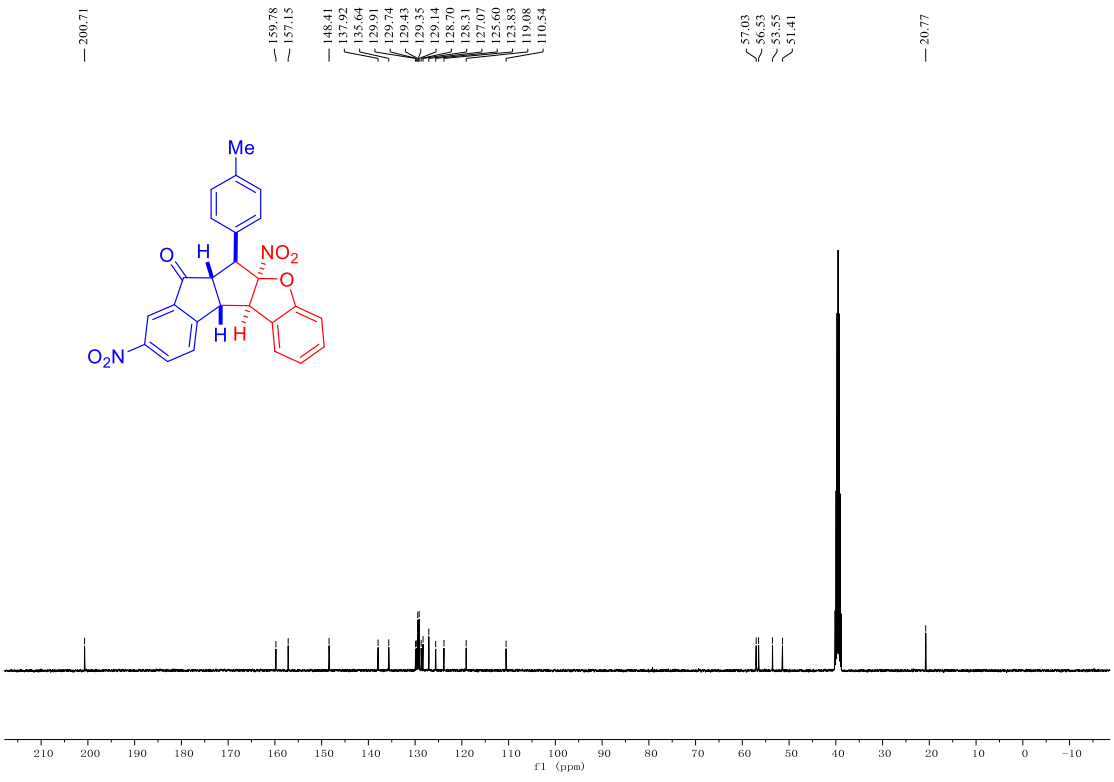
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3aa



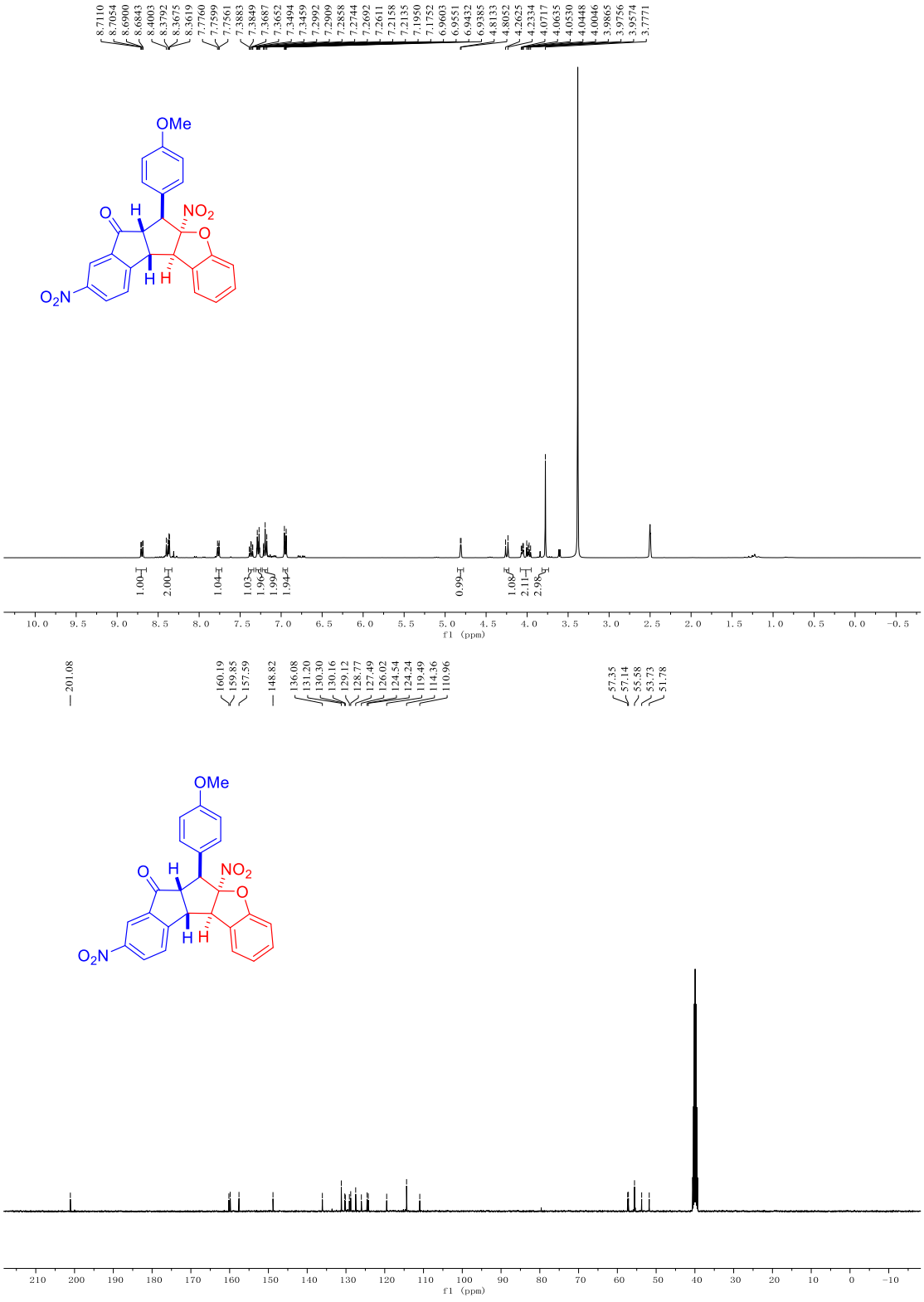


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ba

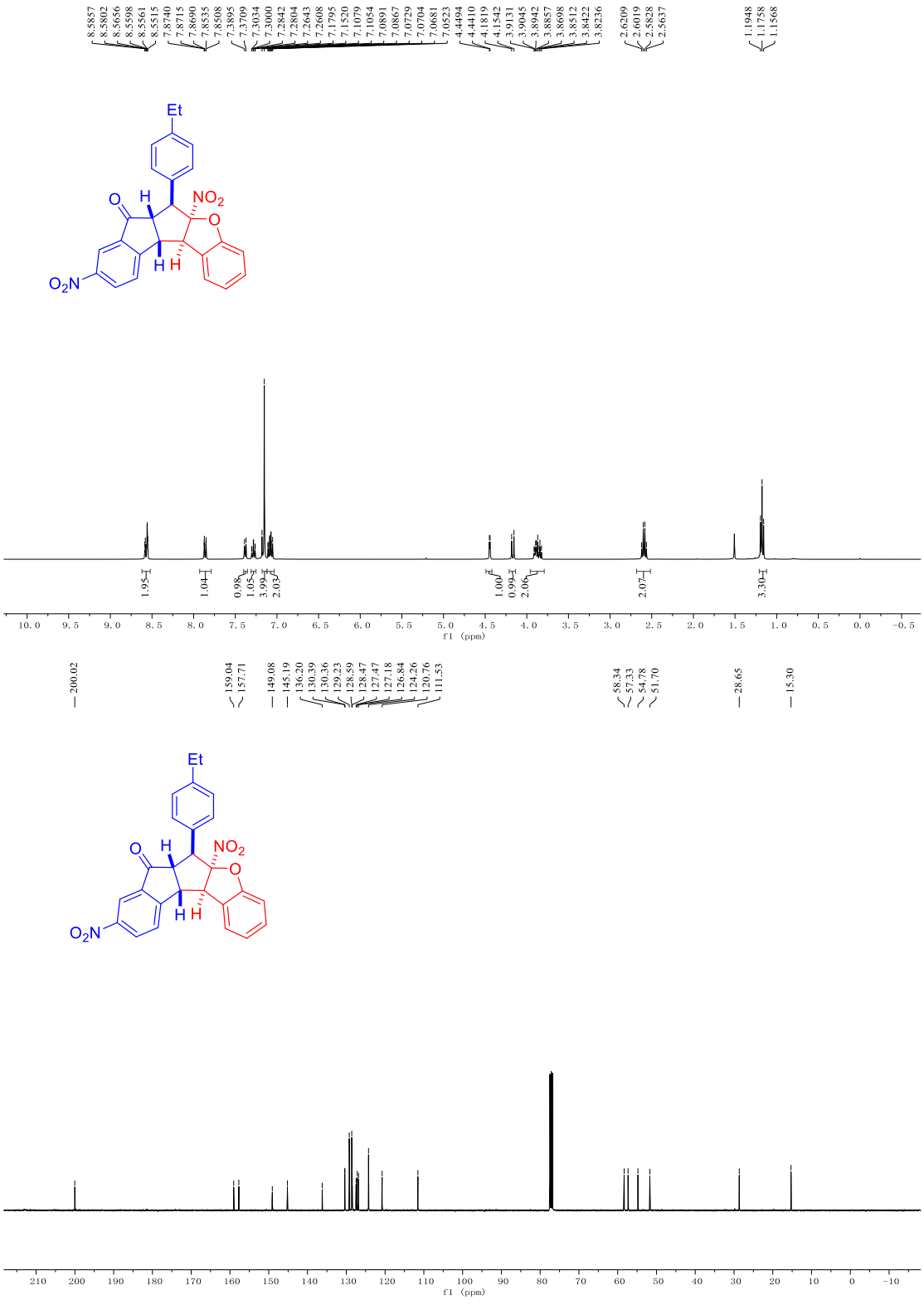




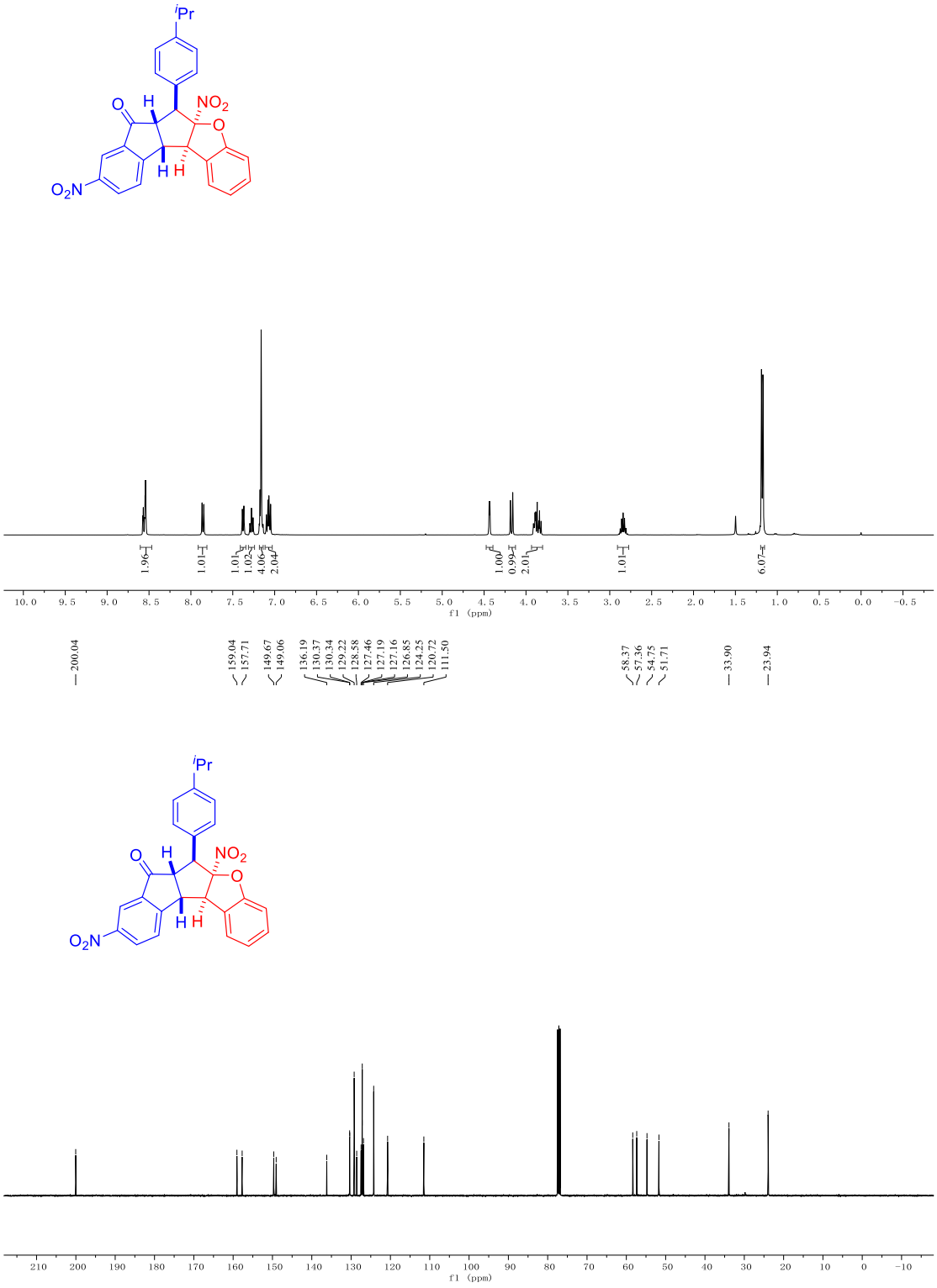
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ca



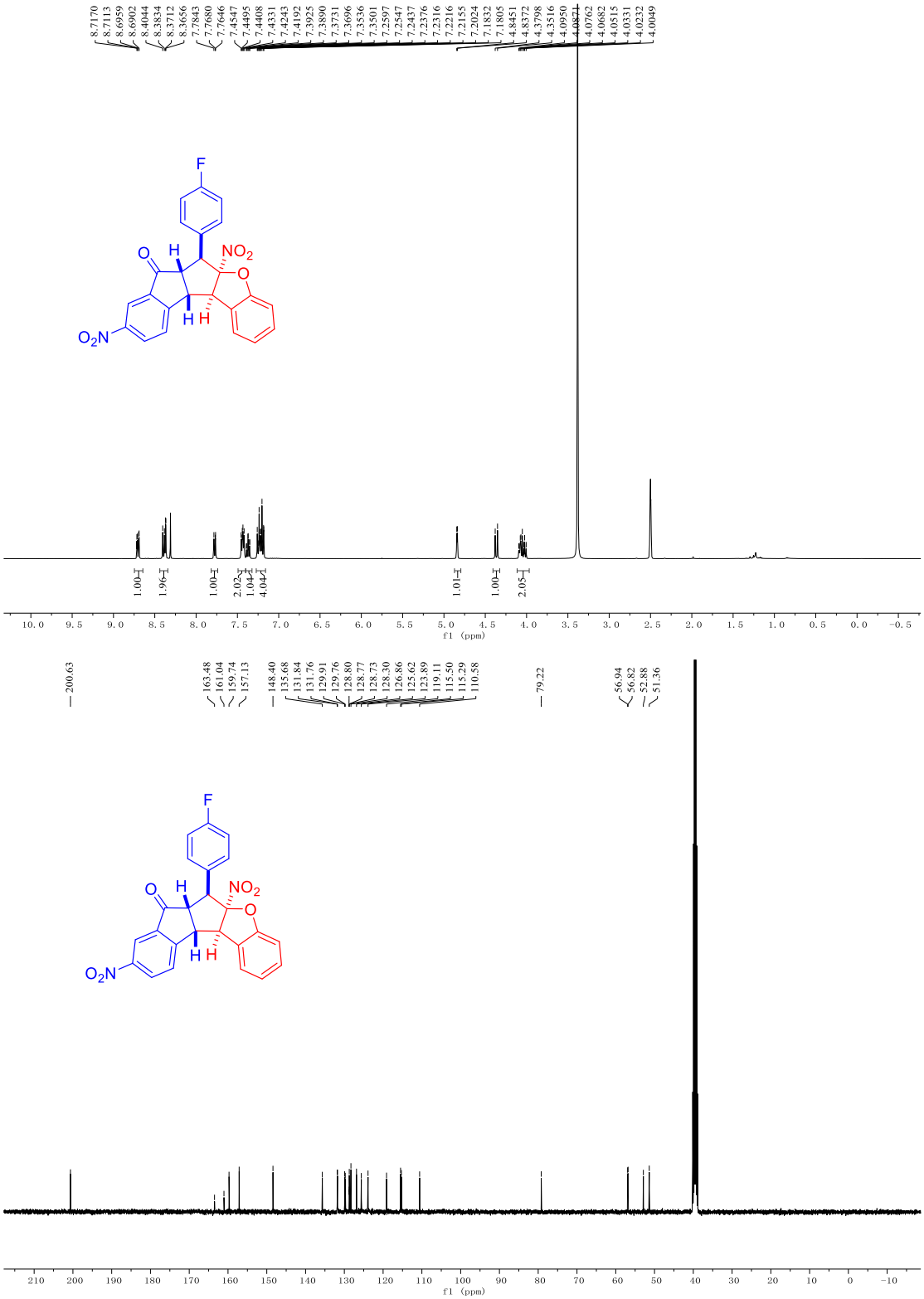
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3da



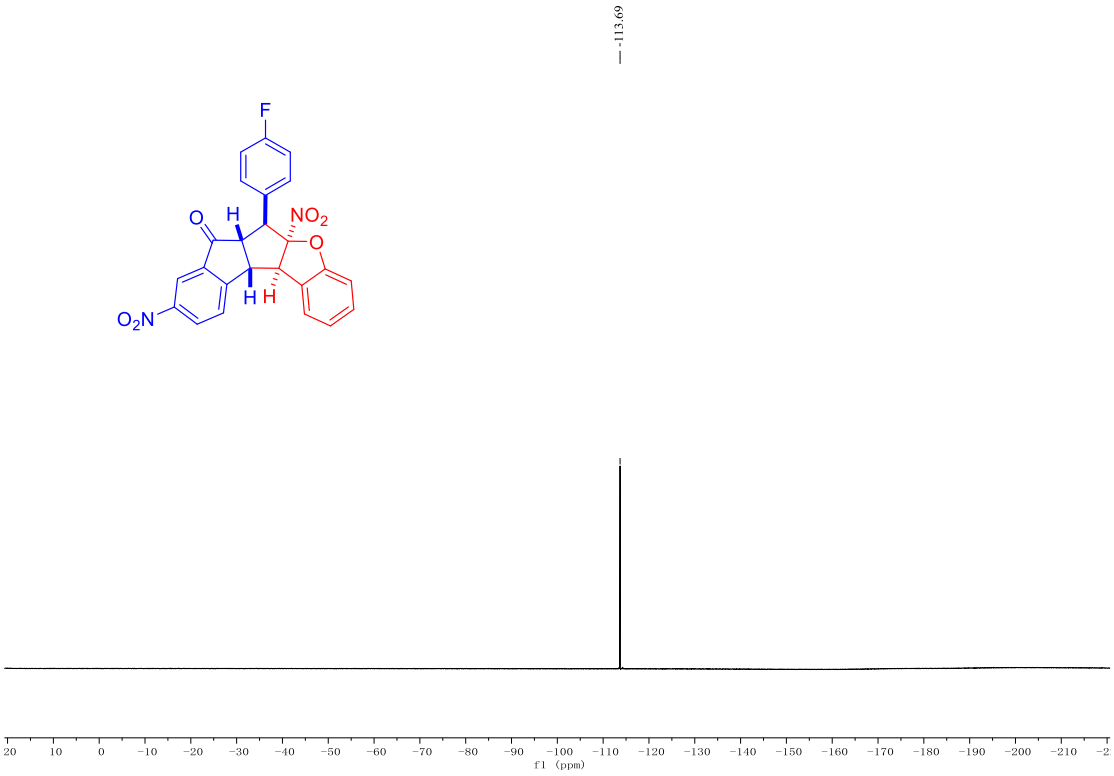
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ea



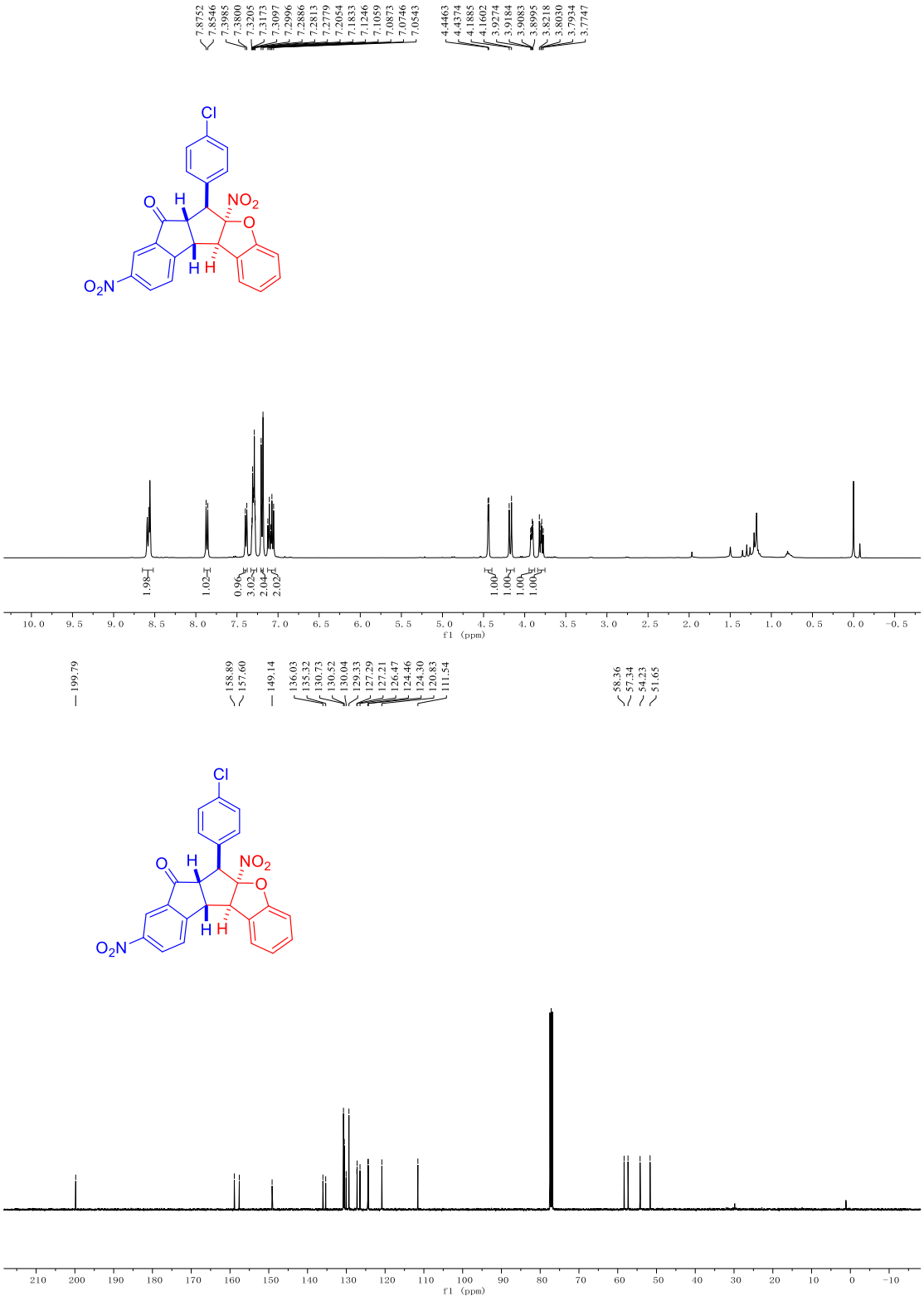
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3fa



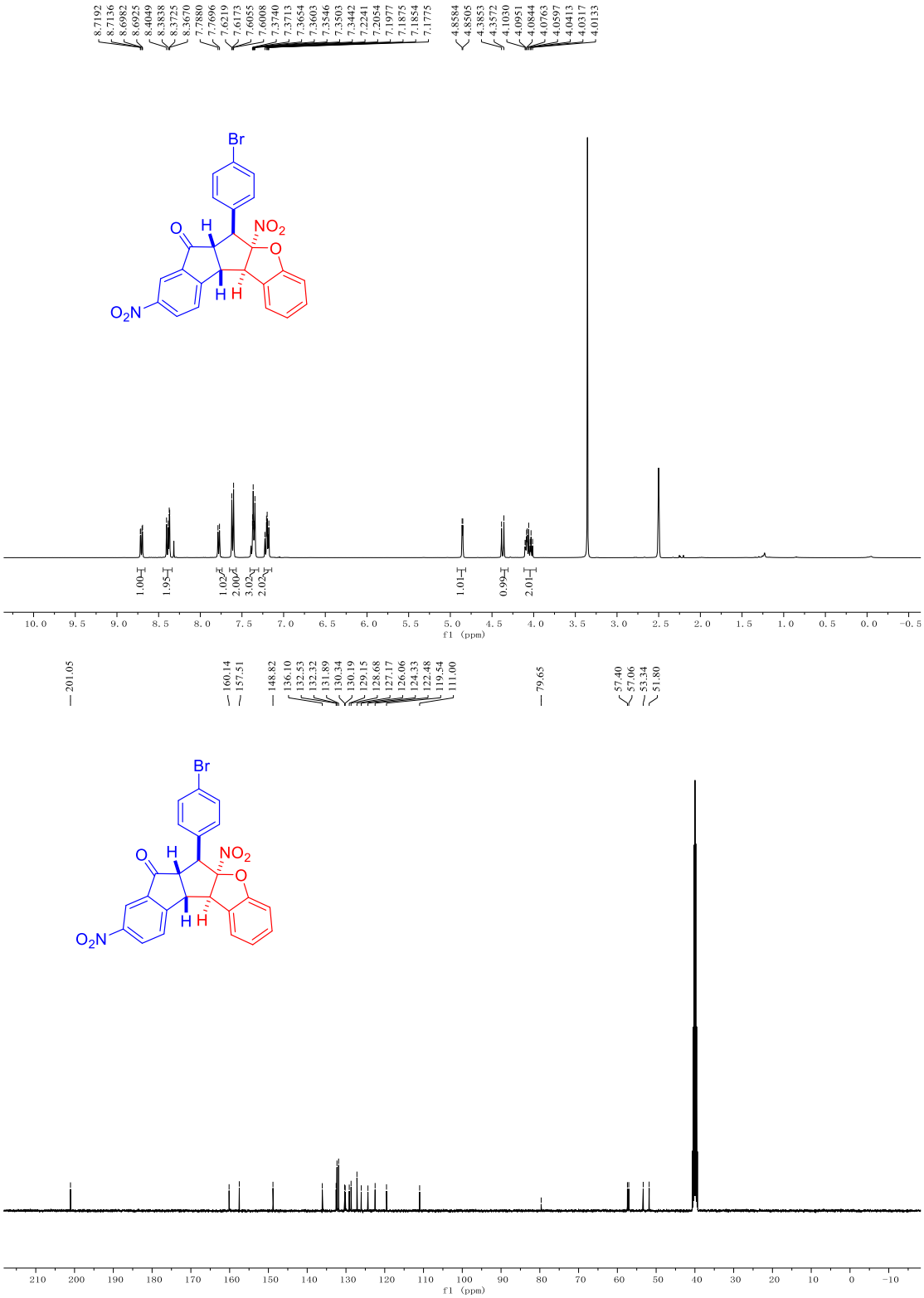
^{19}F NMR (376 MHz, DMSO-d_6) of 3fa



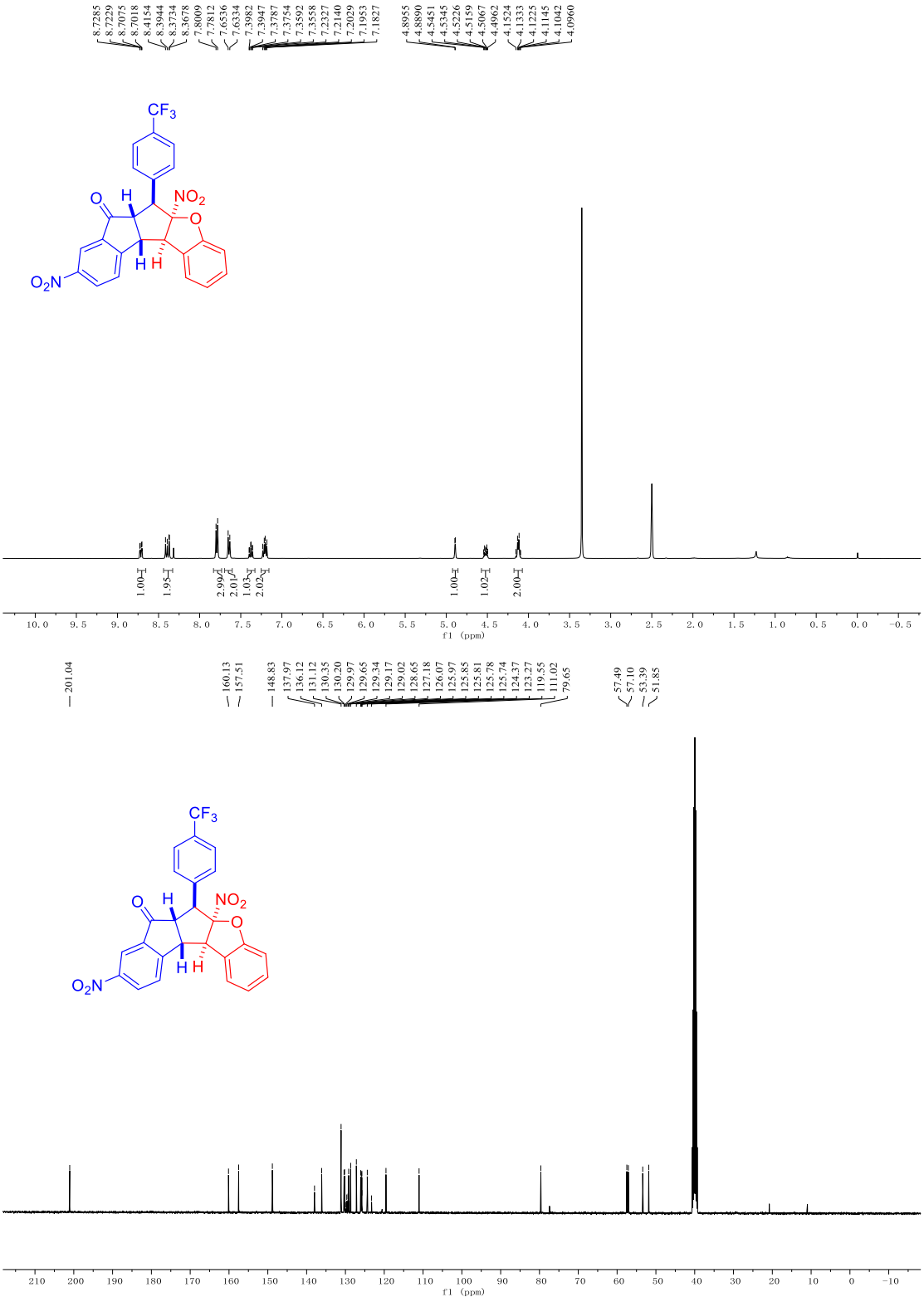
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$-d_6) of 3ga



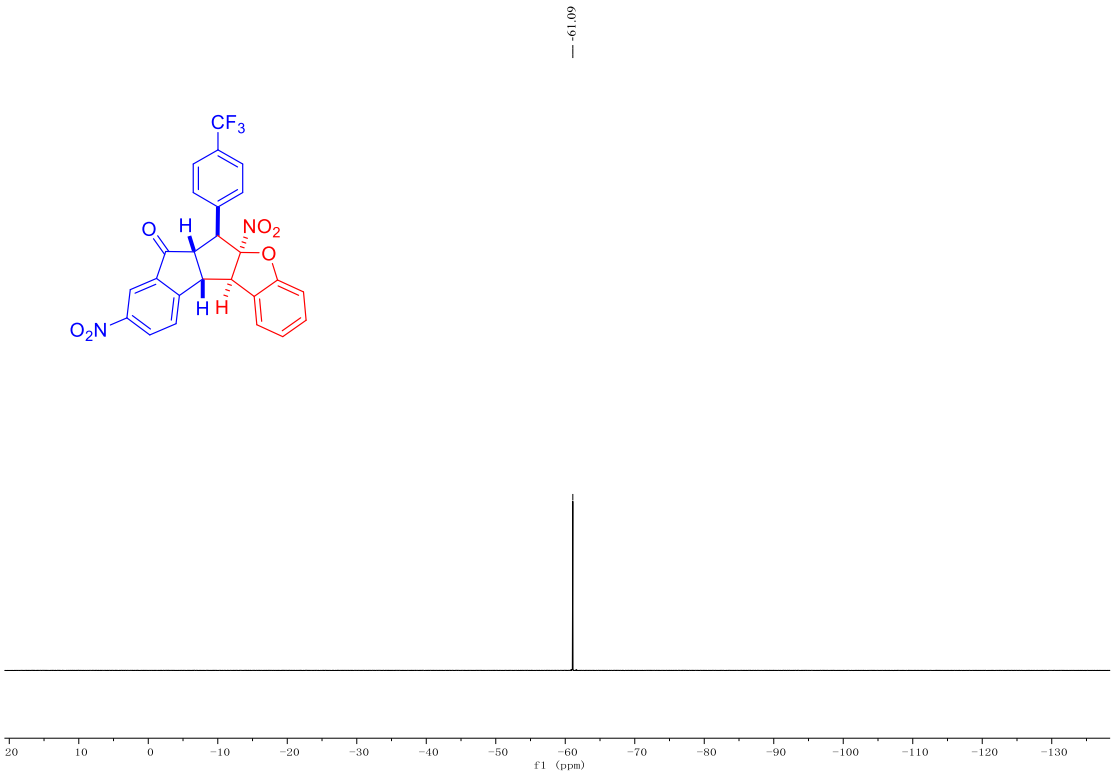
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ha



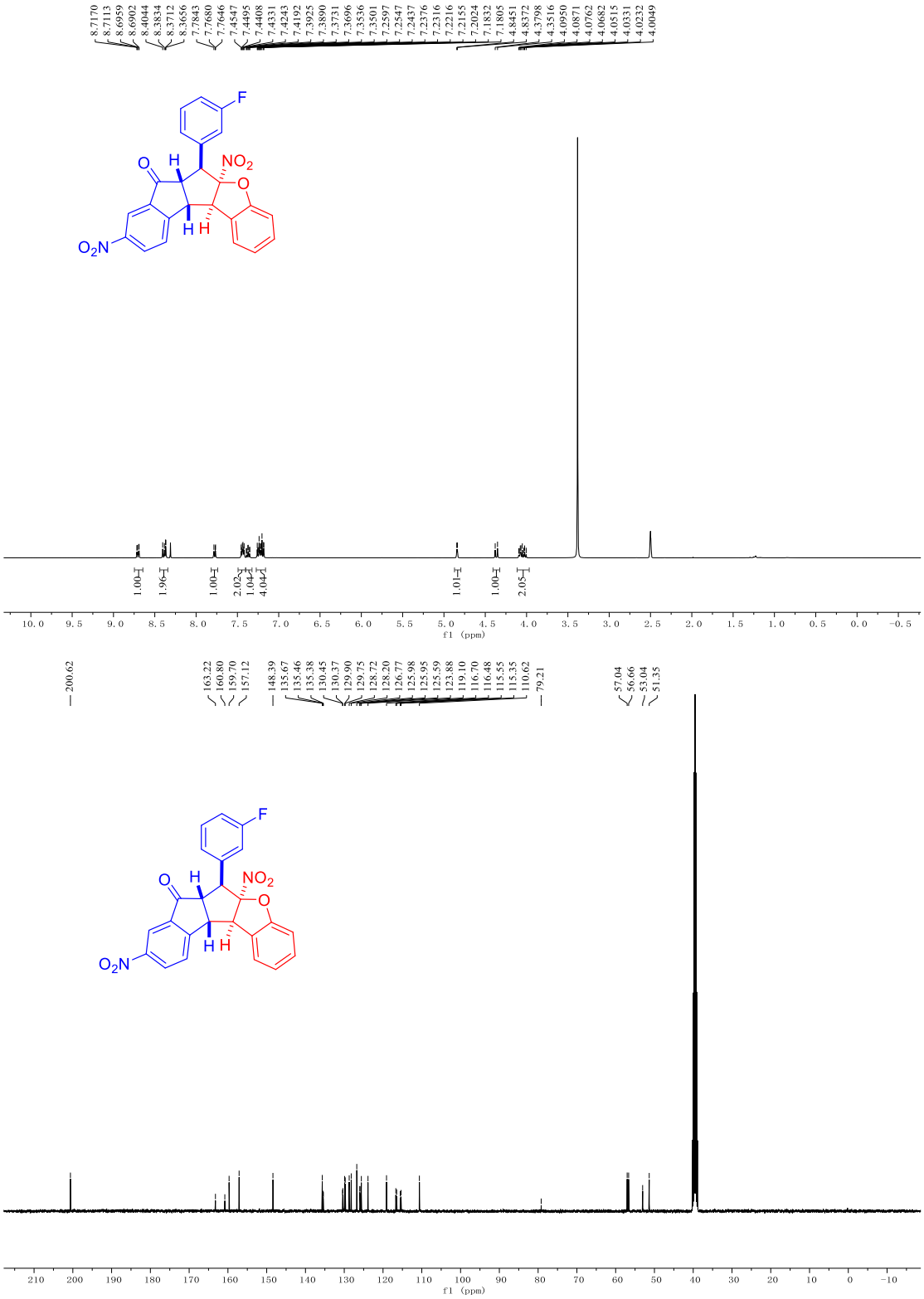
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ia



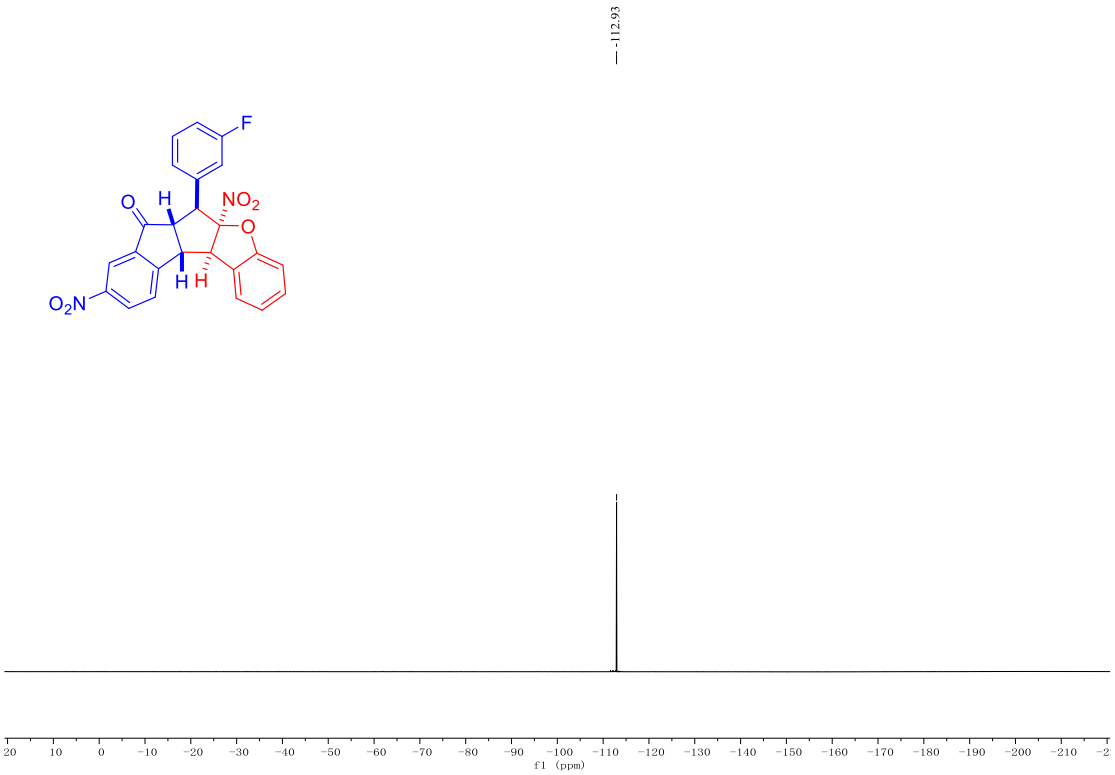
^{19}F NMR (376 MHz, DMSO-d_6) of 3ia



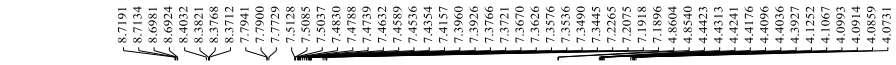
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ja

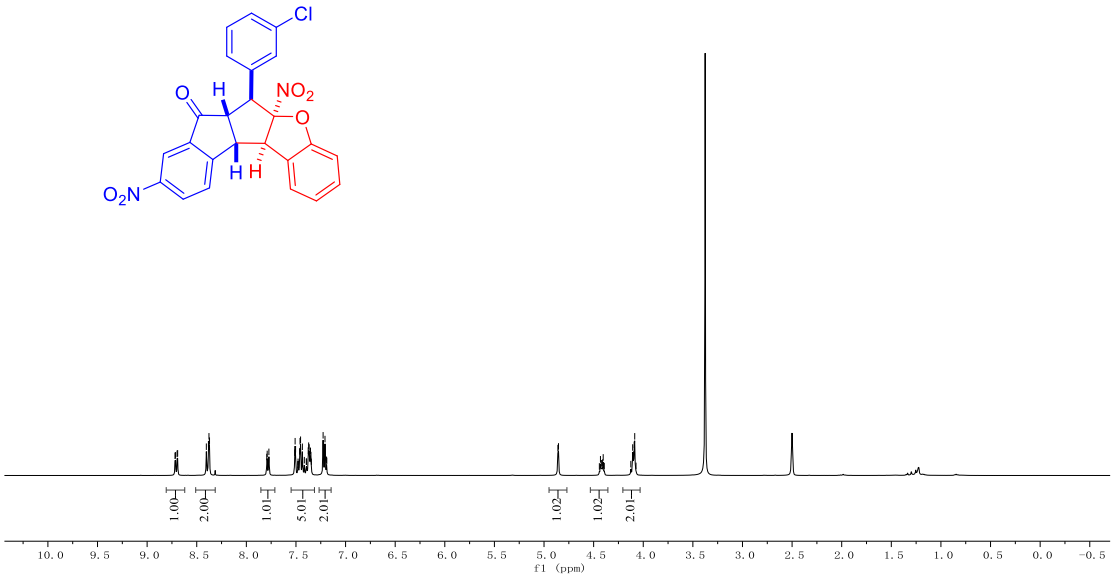


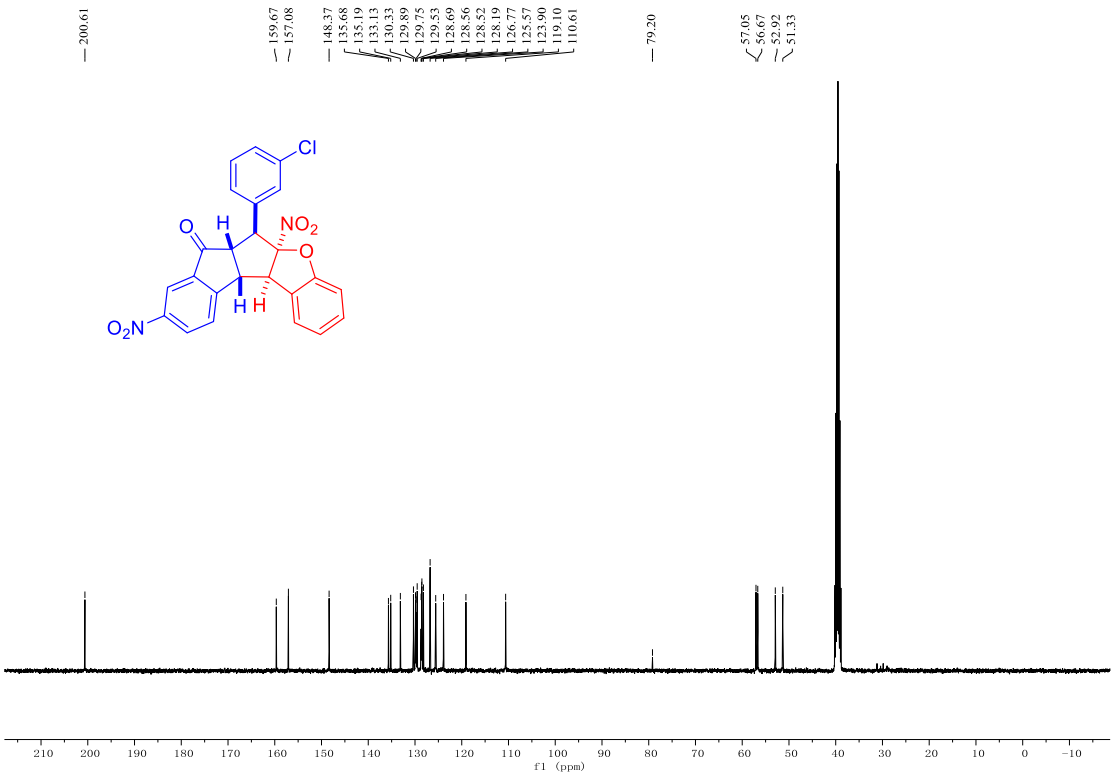
^{19}F NMR (376 MHz, DMSO-d_6) of 3ja



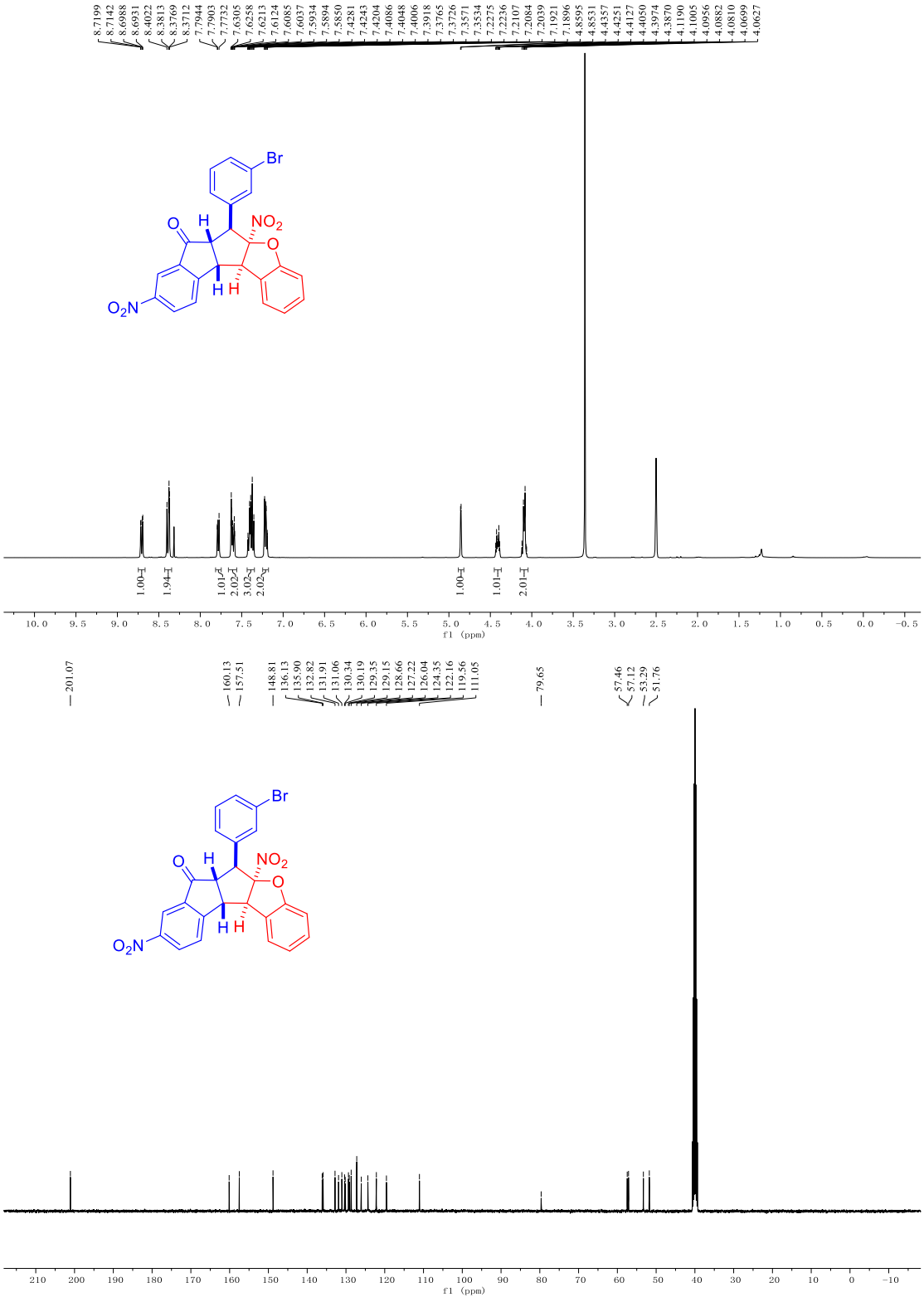
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ka



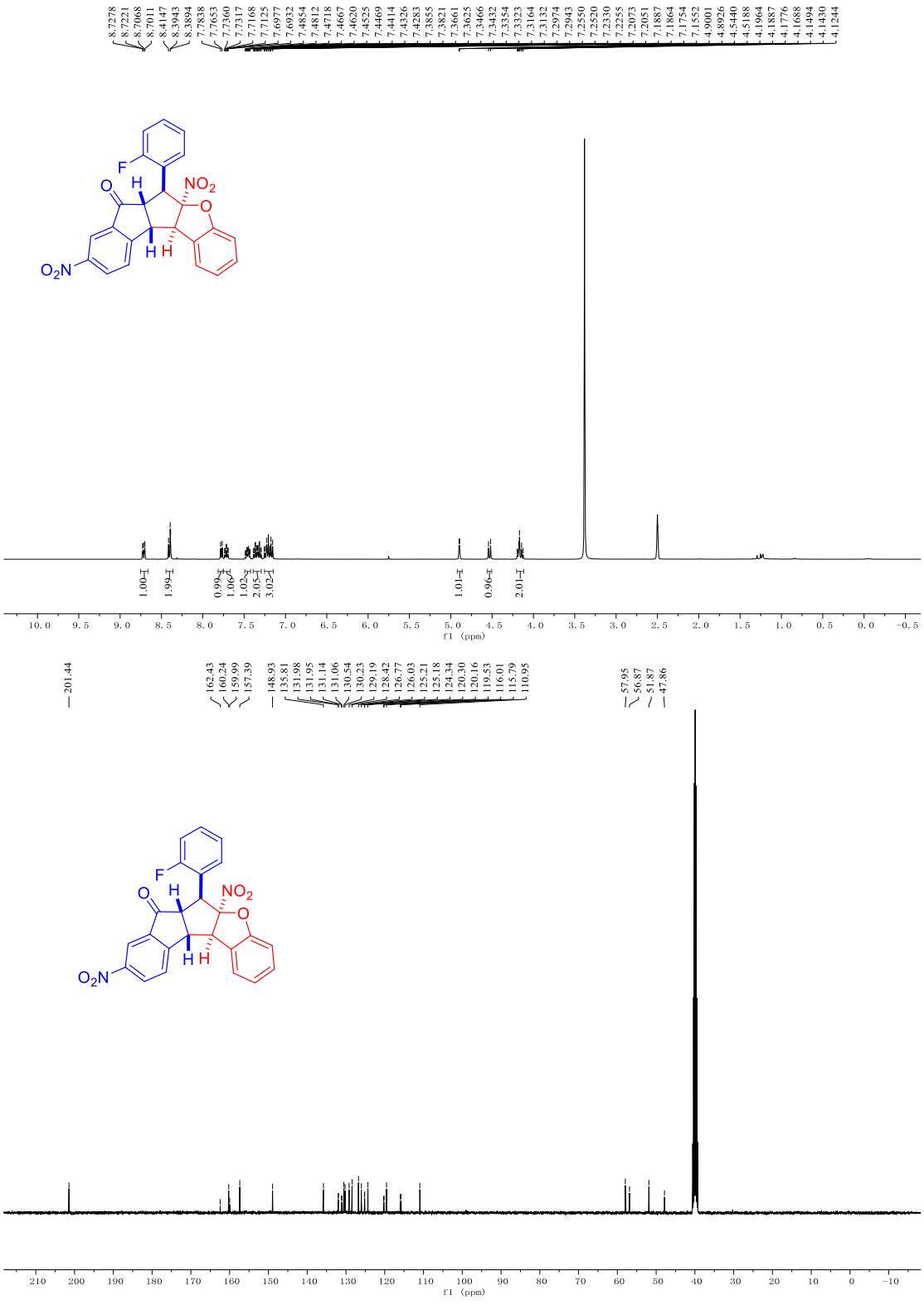




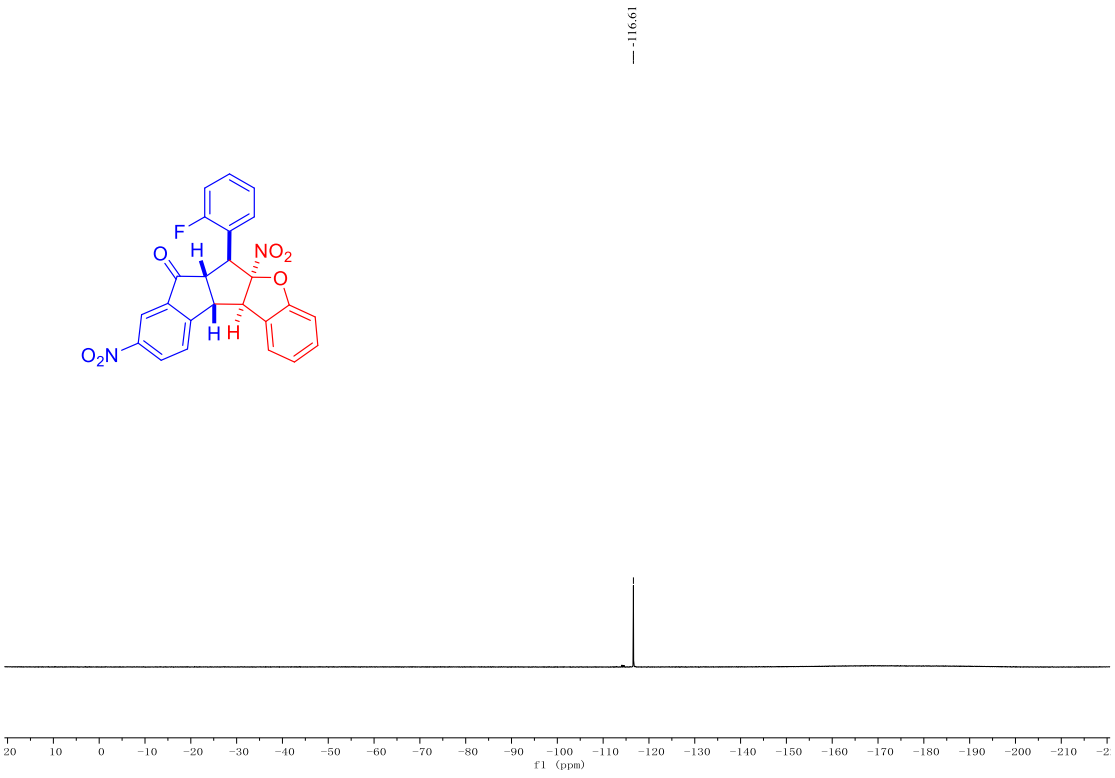
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3la



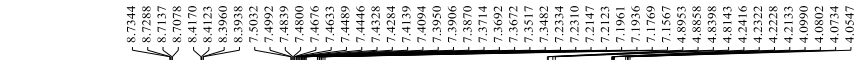
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ma

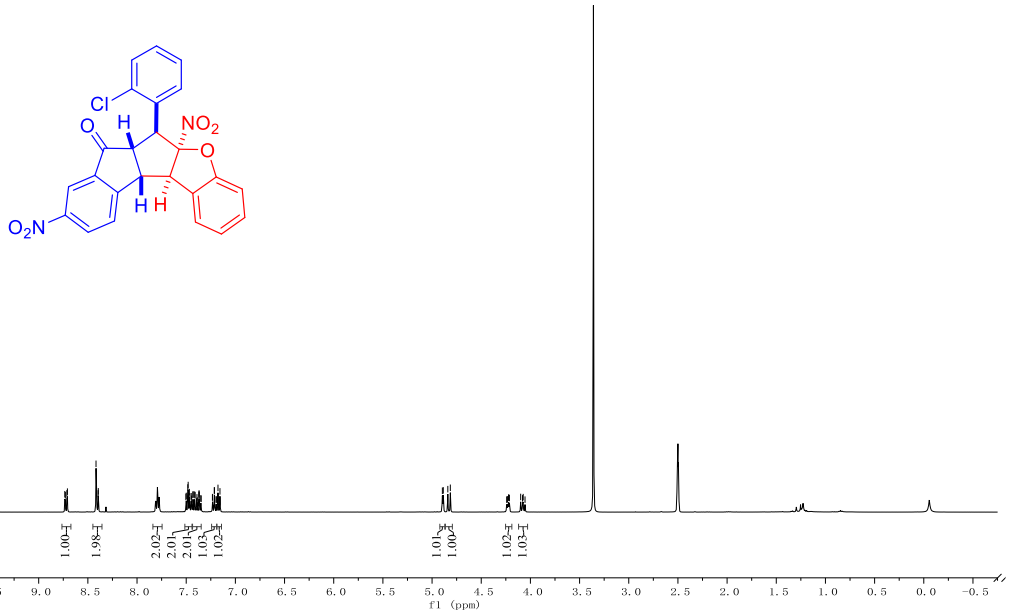


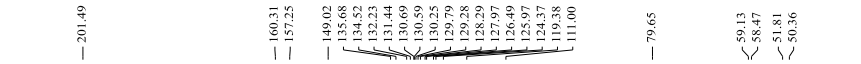
^{19}F NMR (376 MHz, DMSO-d_6) of 3ma

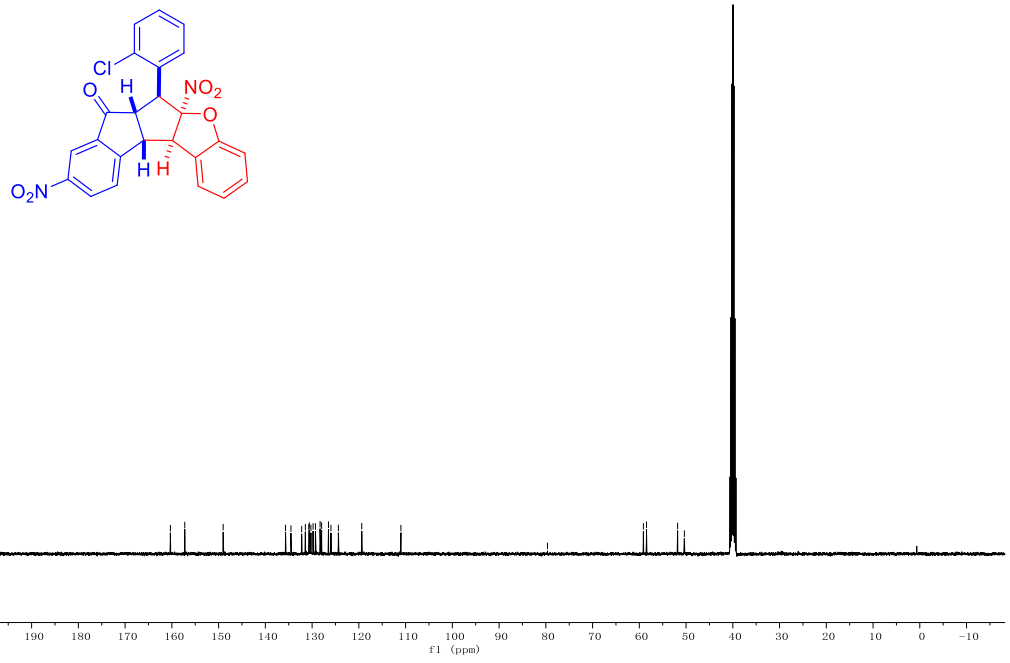


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3na

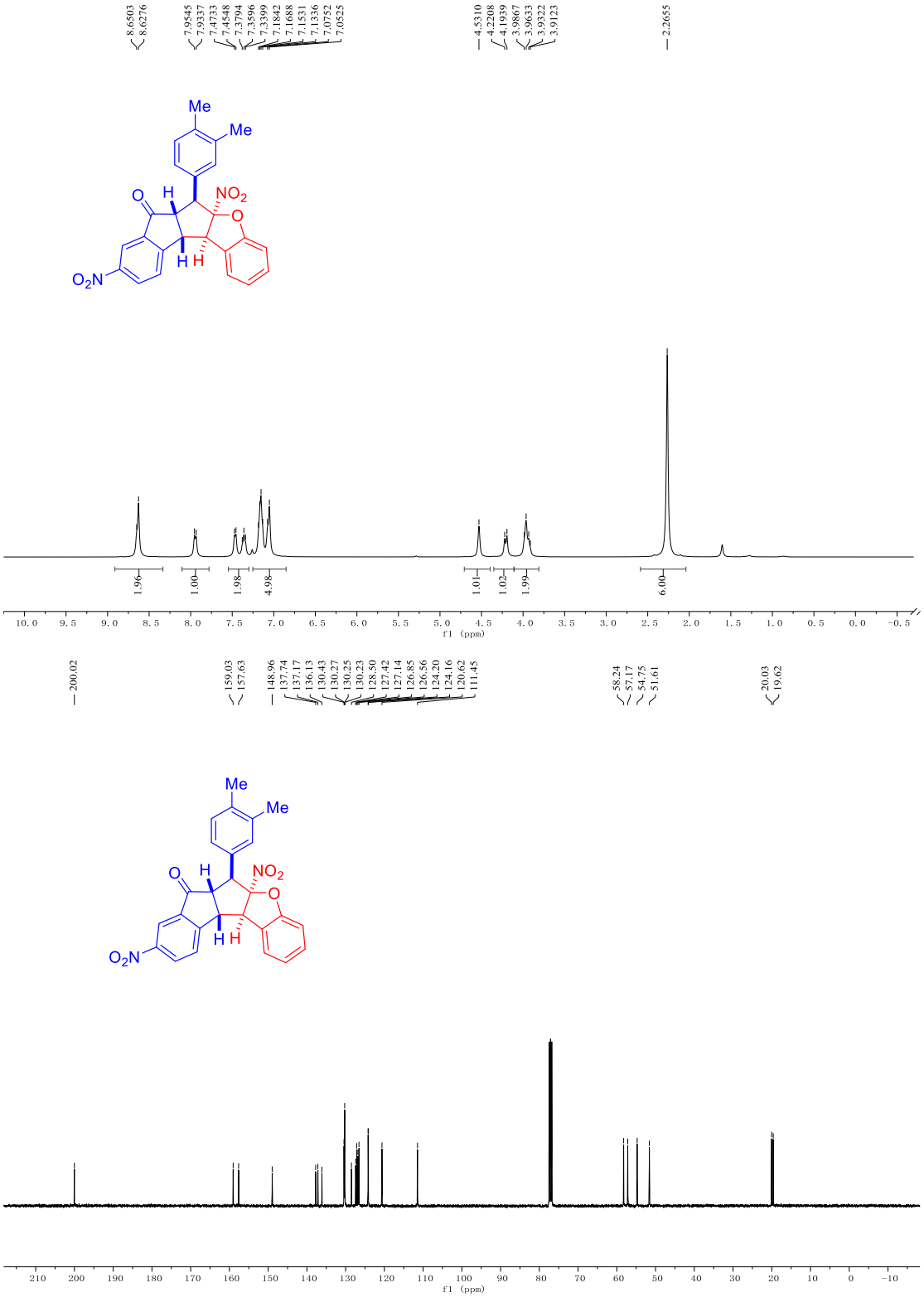




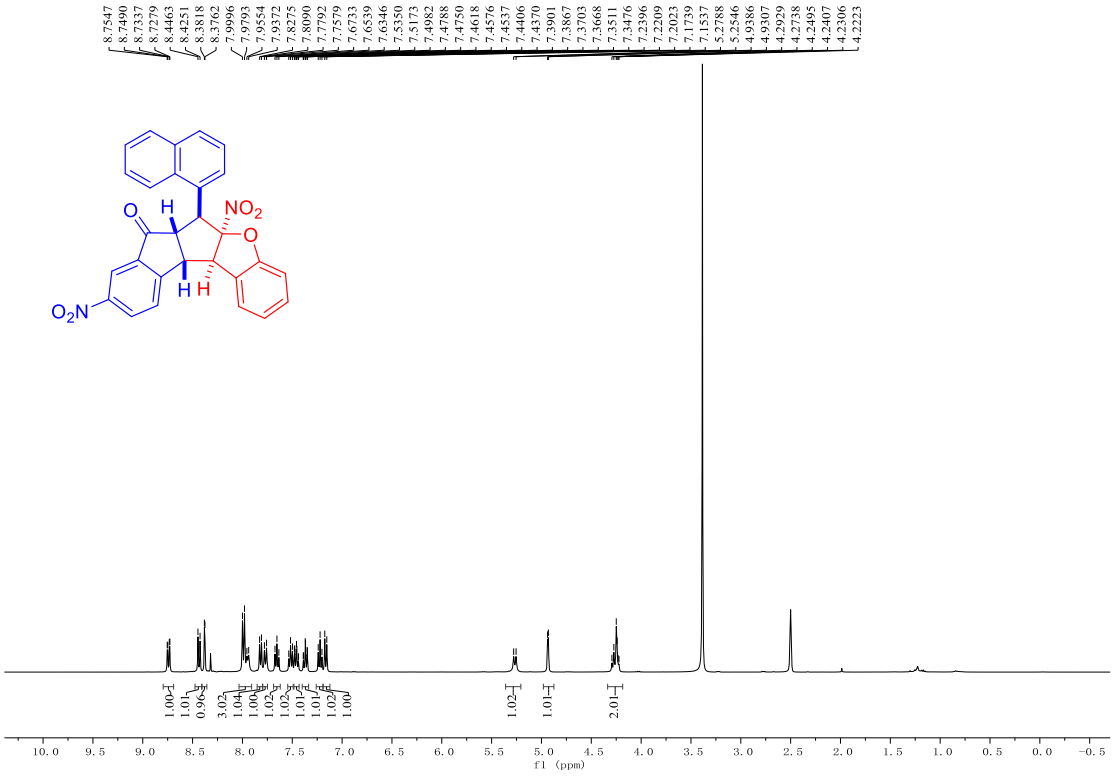


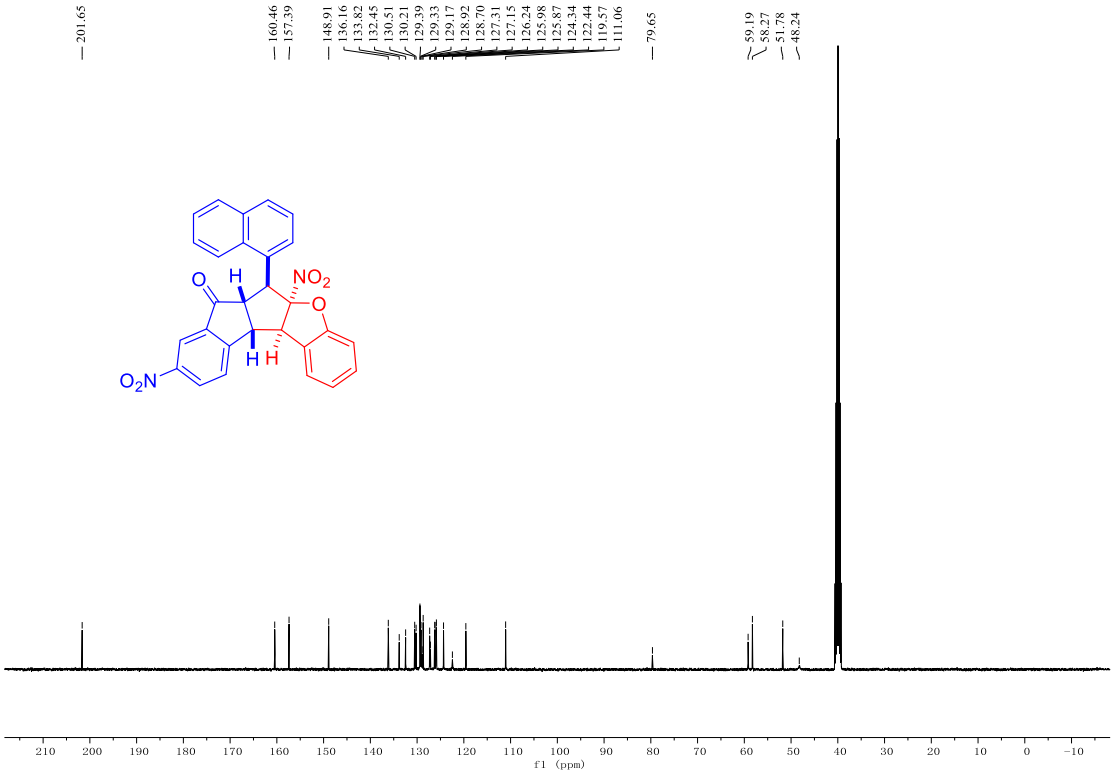


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3oa

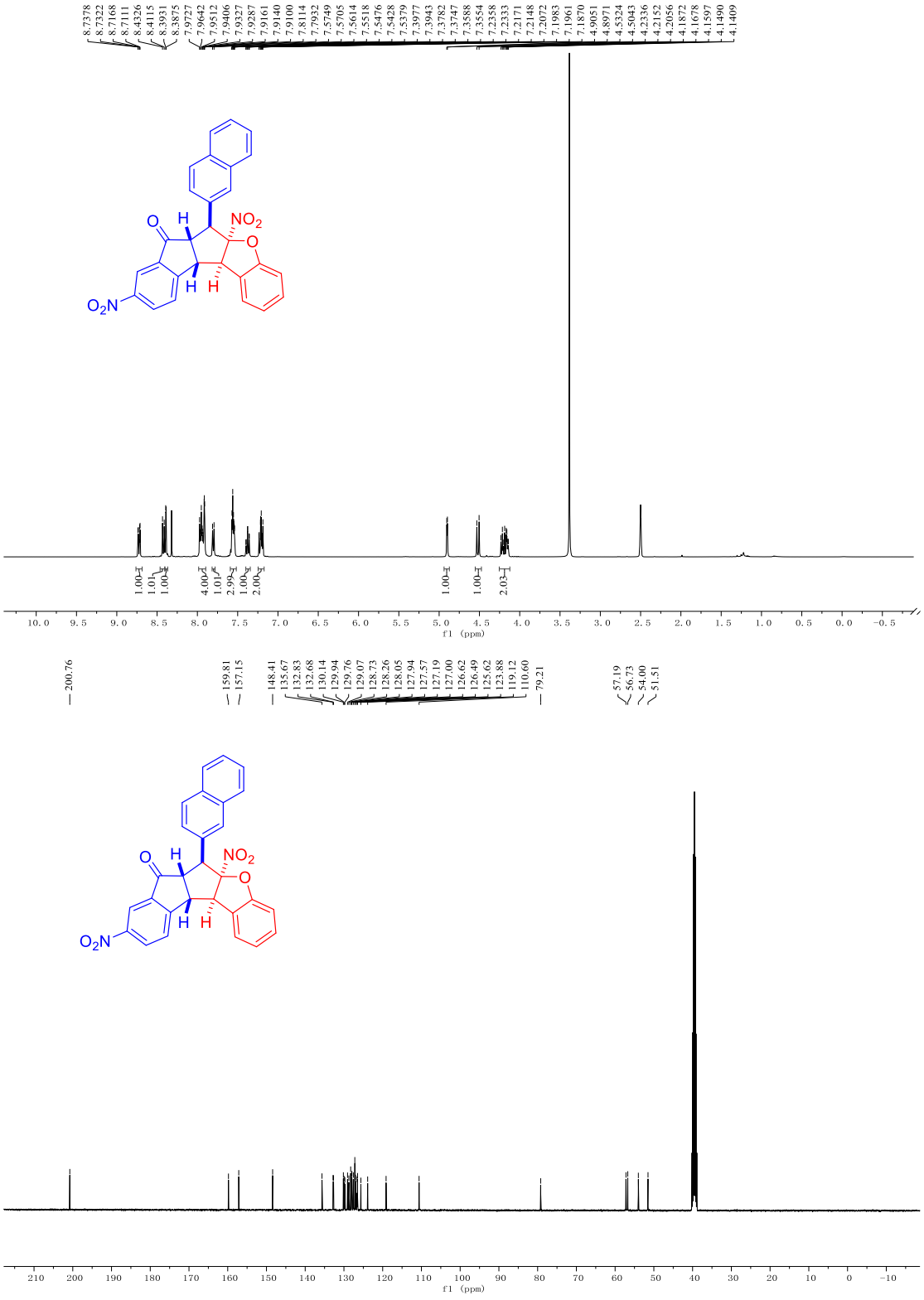


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3pa

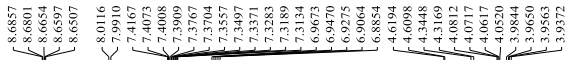


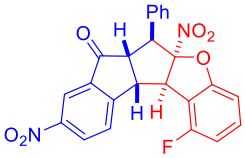


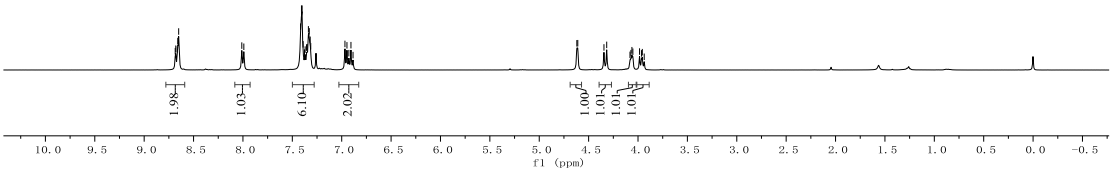
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3qa

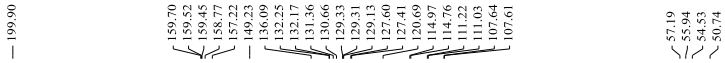


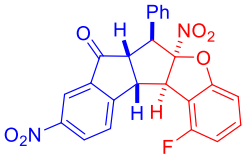
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ab

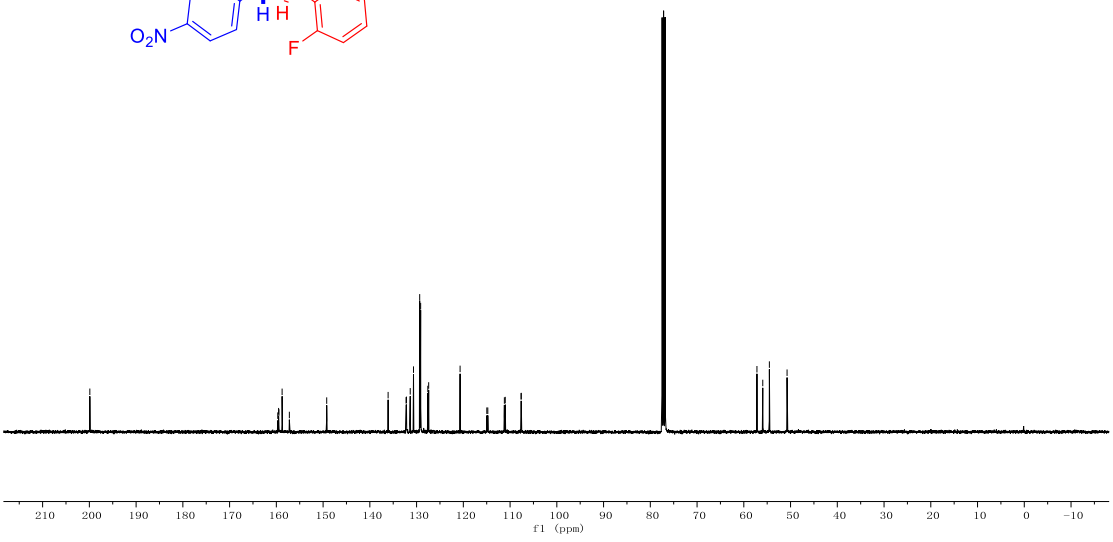




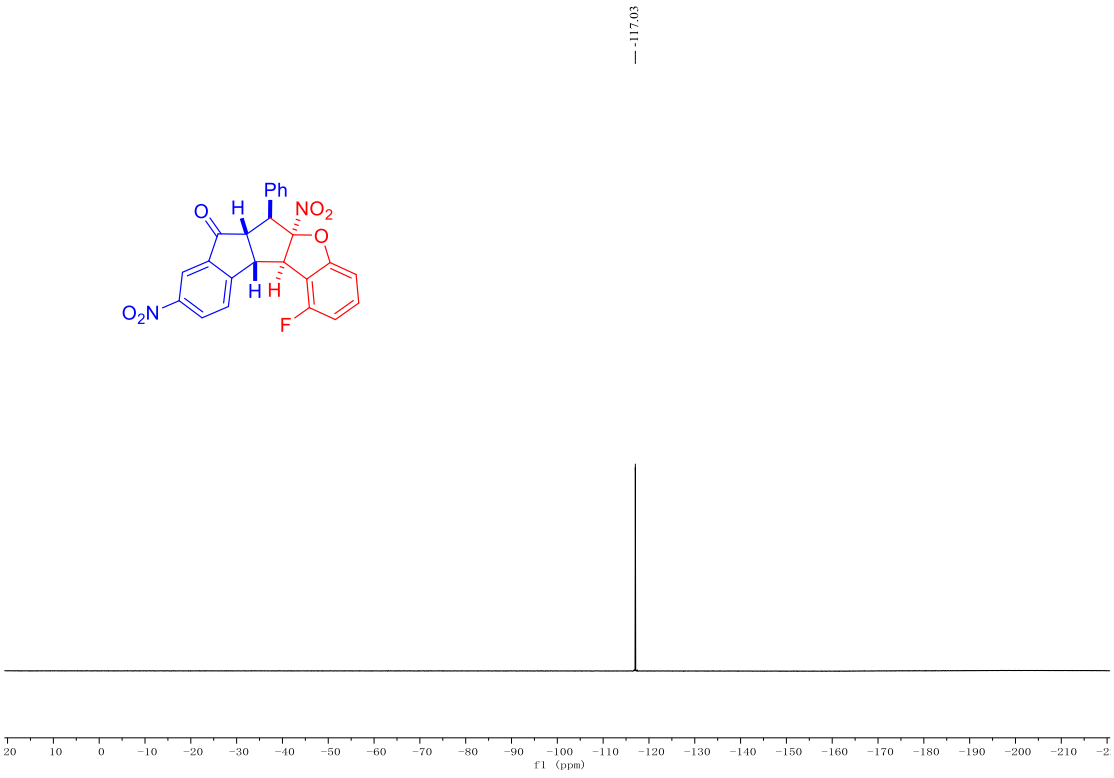




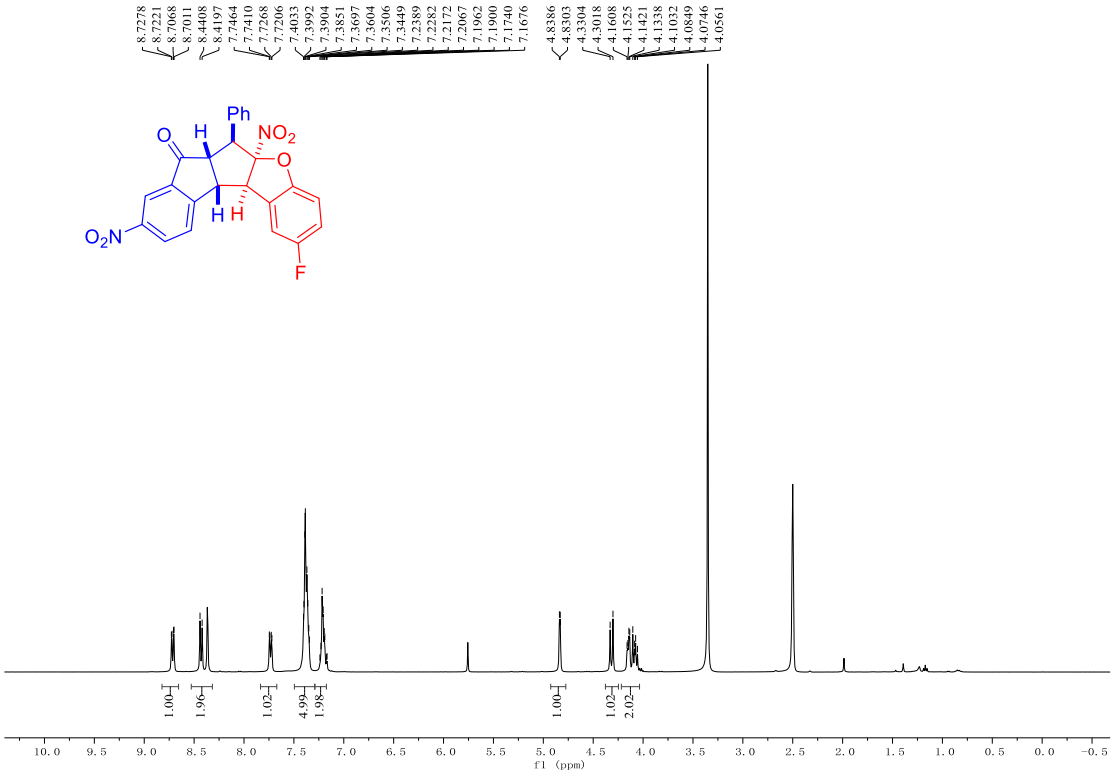


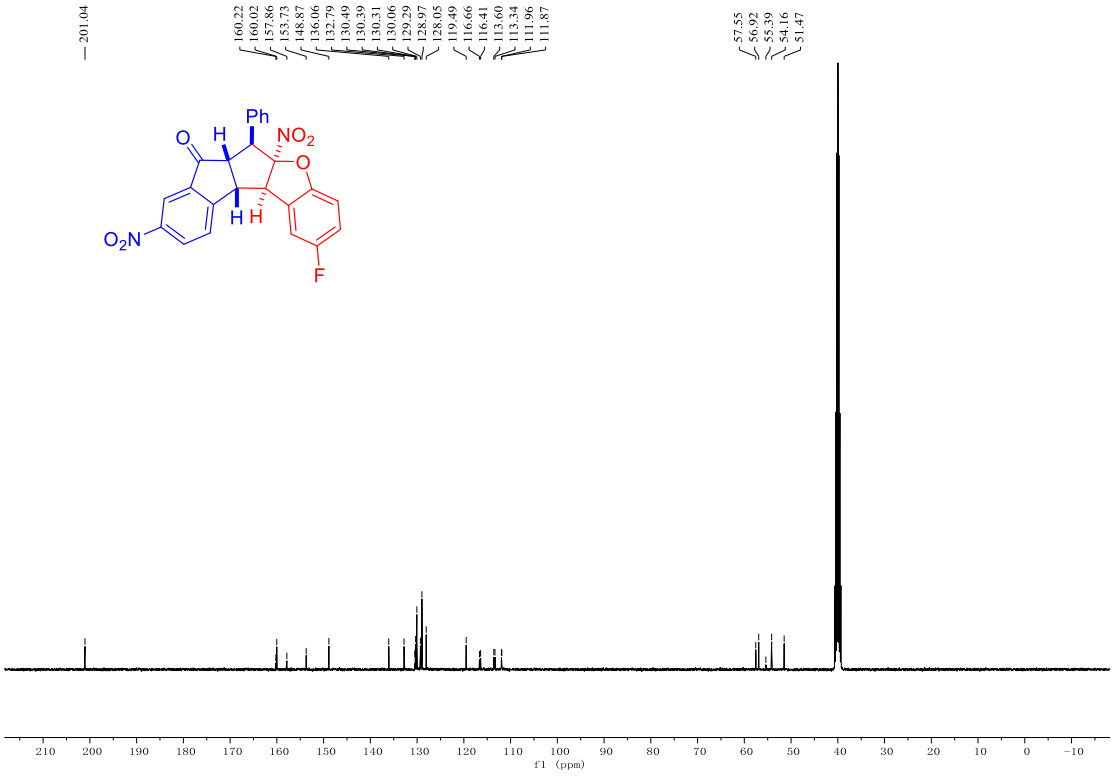


^{19}F NMR (376 MHz, DMSO-*d*$_6$) of 3ab

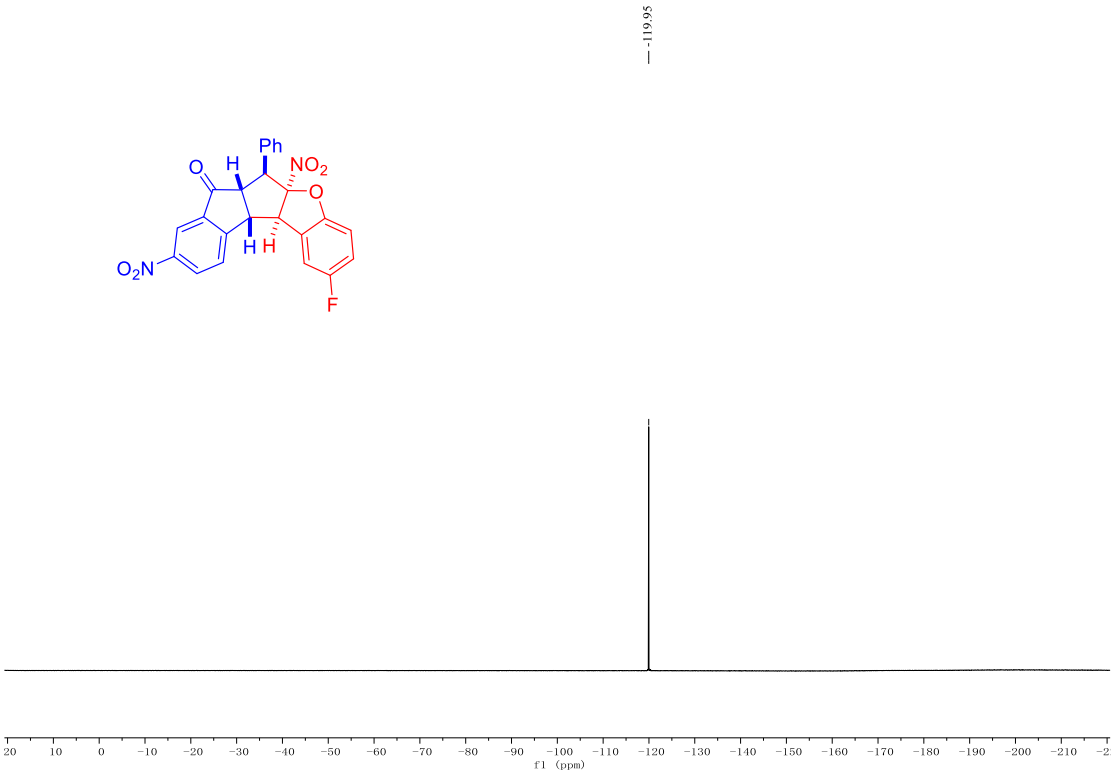


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ac

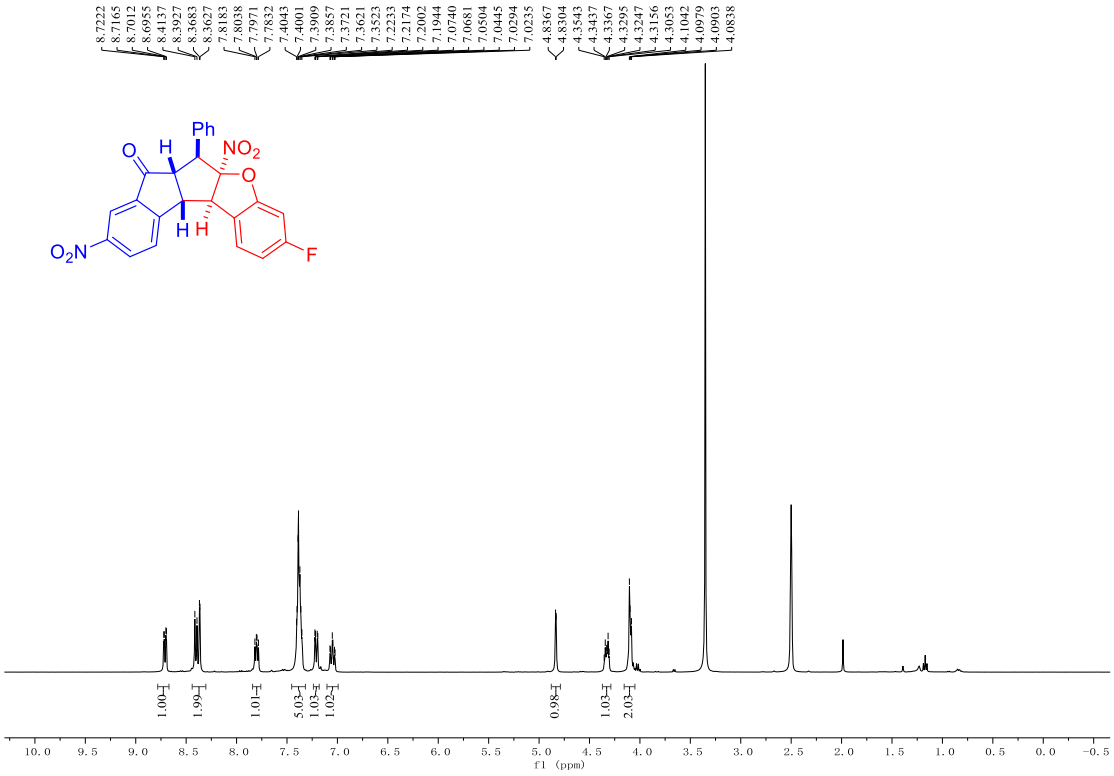


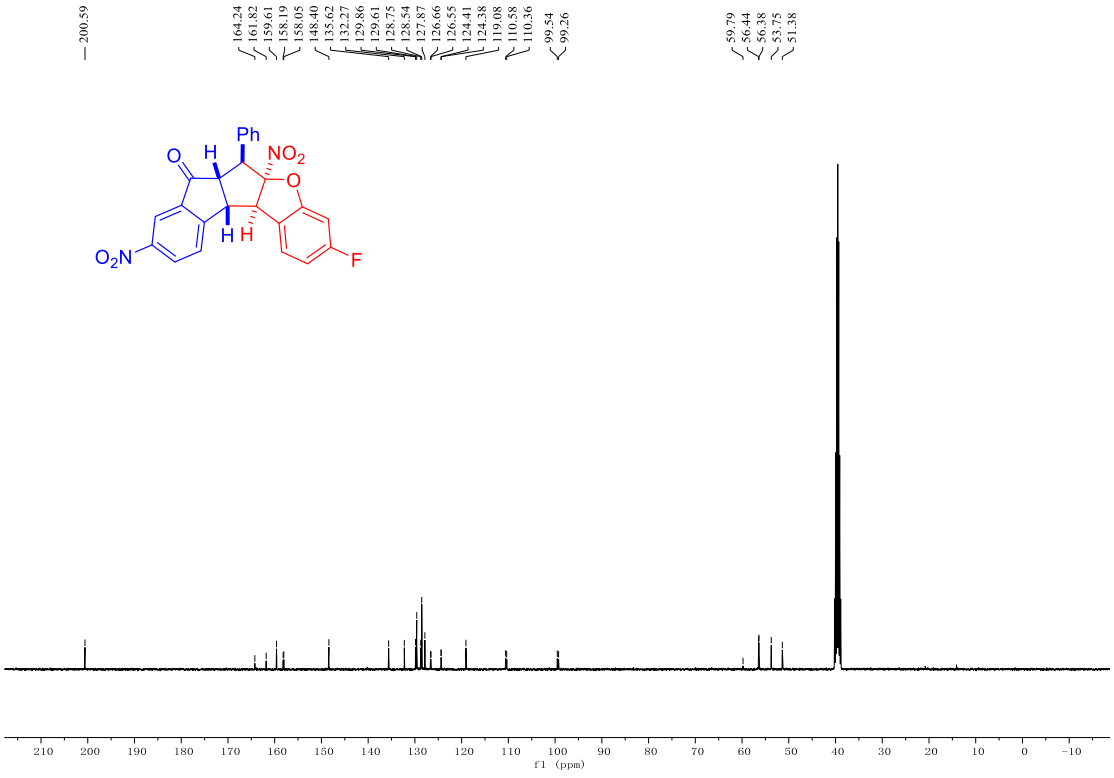


^{19}F NMR (376 MHz, DMSO-d_6) of 3ad

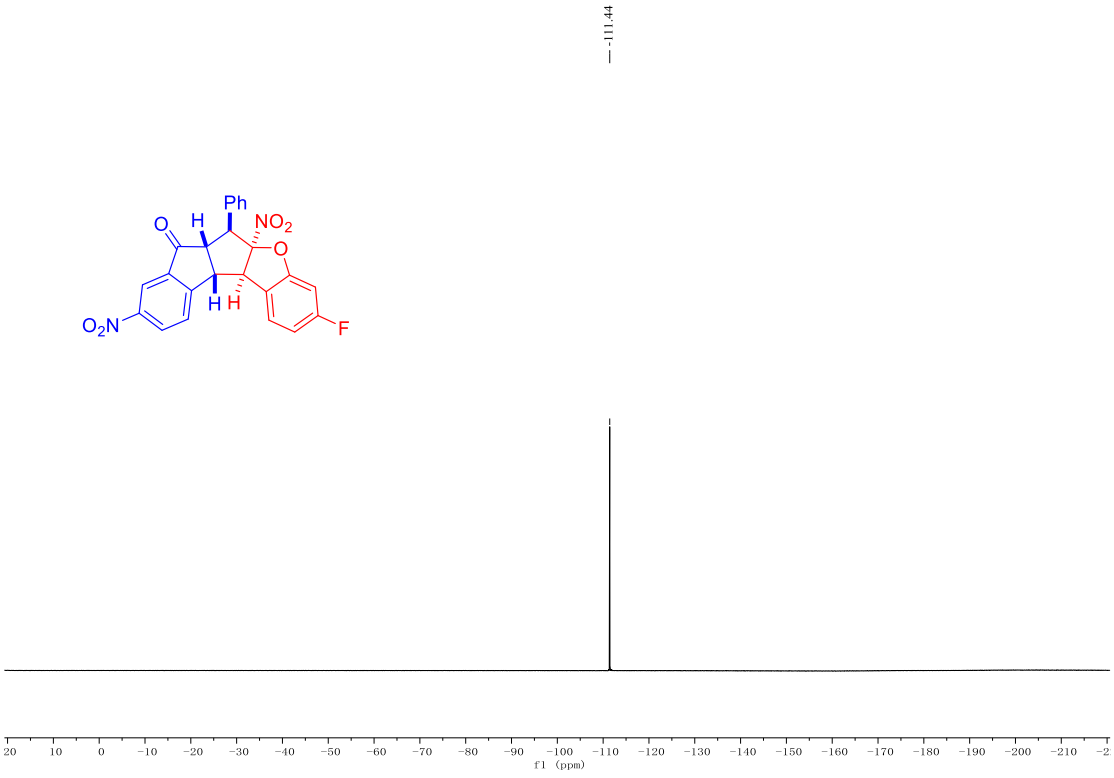


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ad

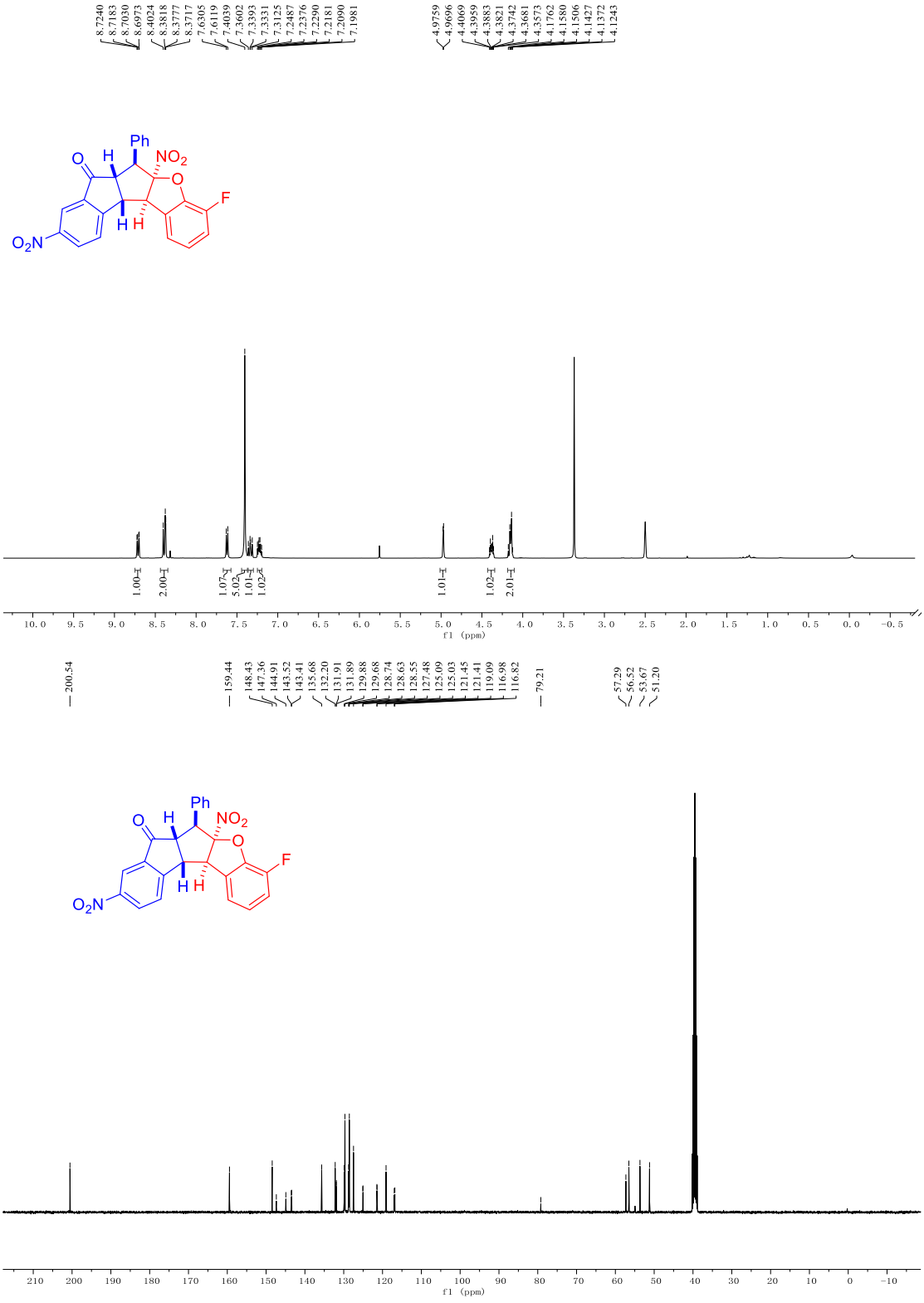




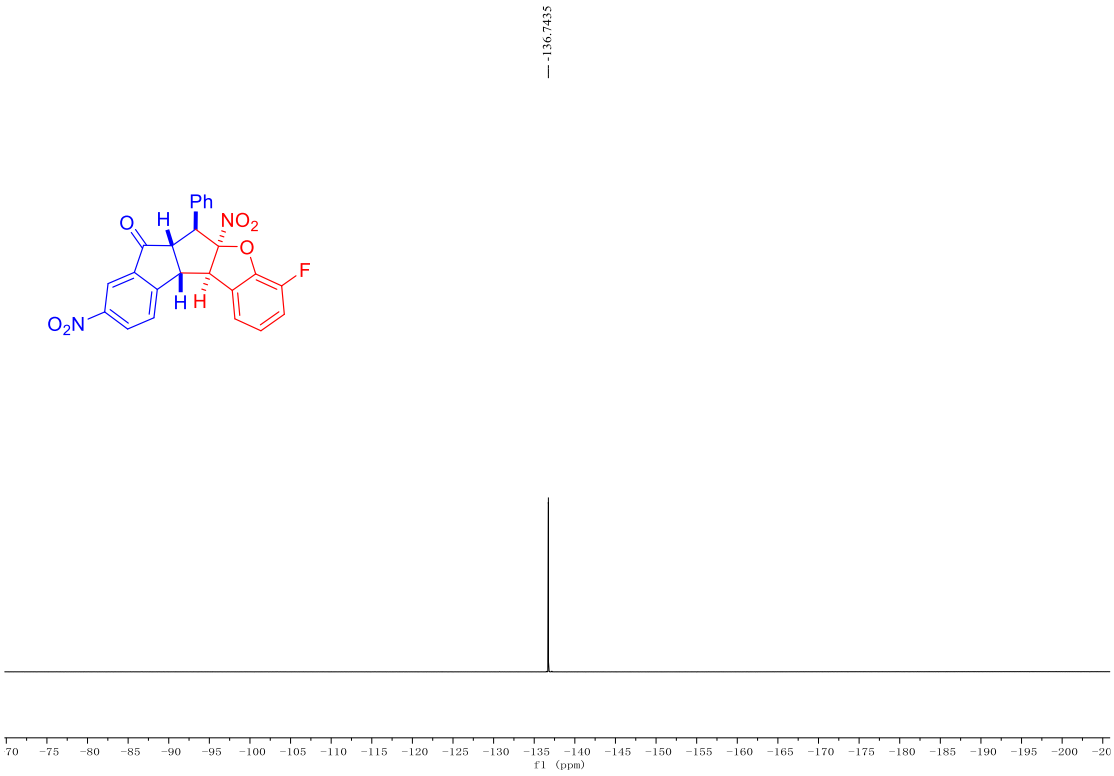
^{19}F NMR (376 MHz, DMSO-d_6) of 3ad



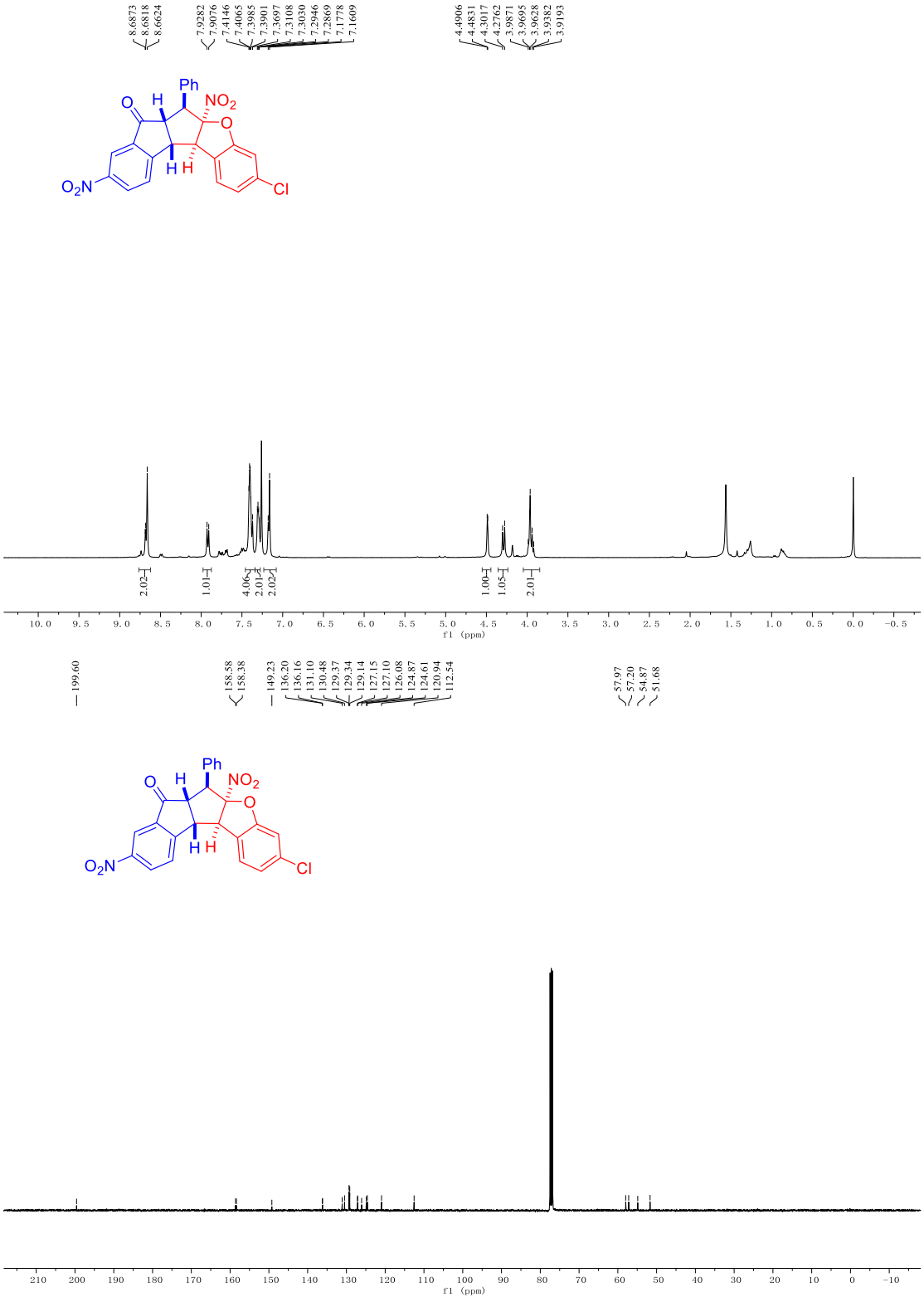
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ae



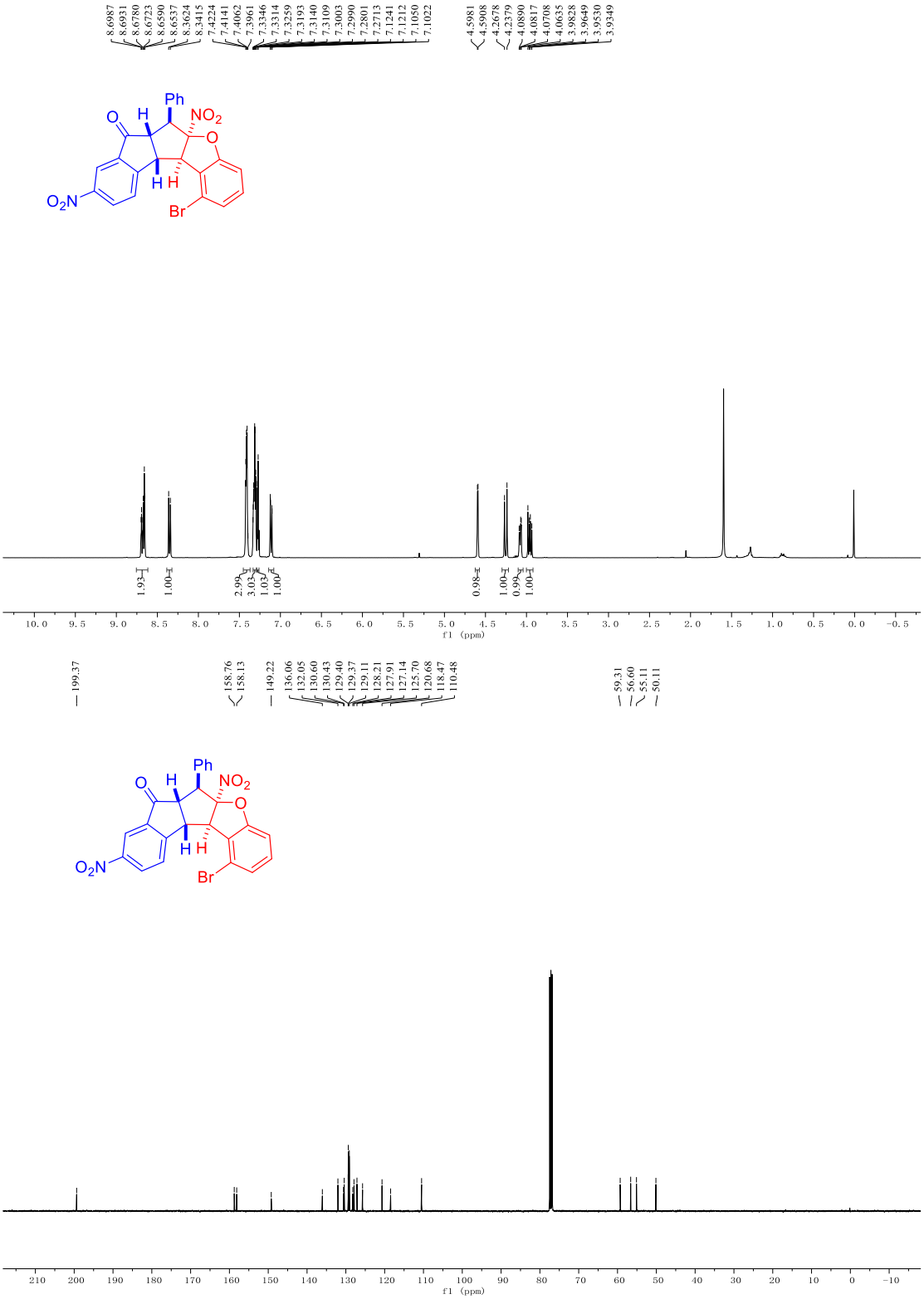
^{19}F NMR (376 MHz, DMSO-d_6) of 3ae



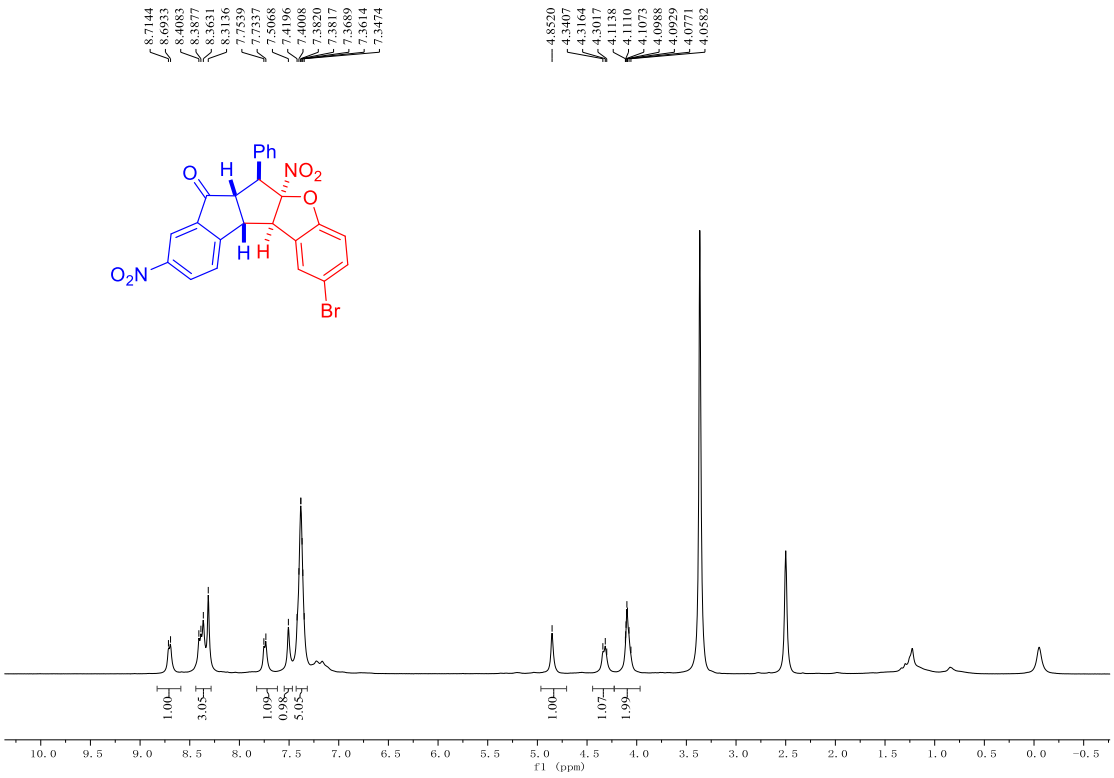
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3af

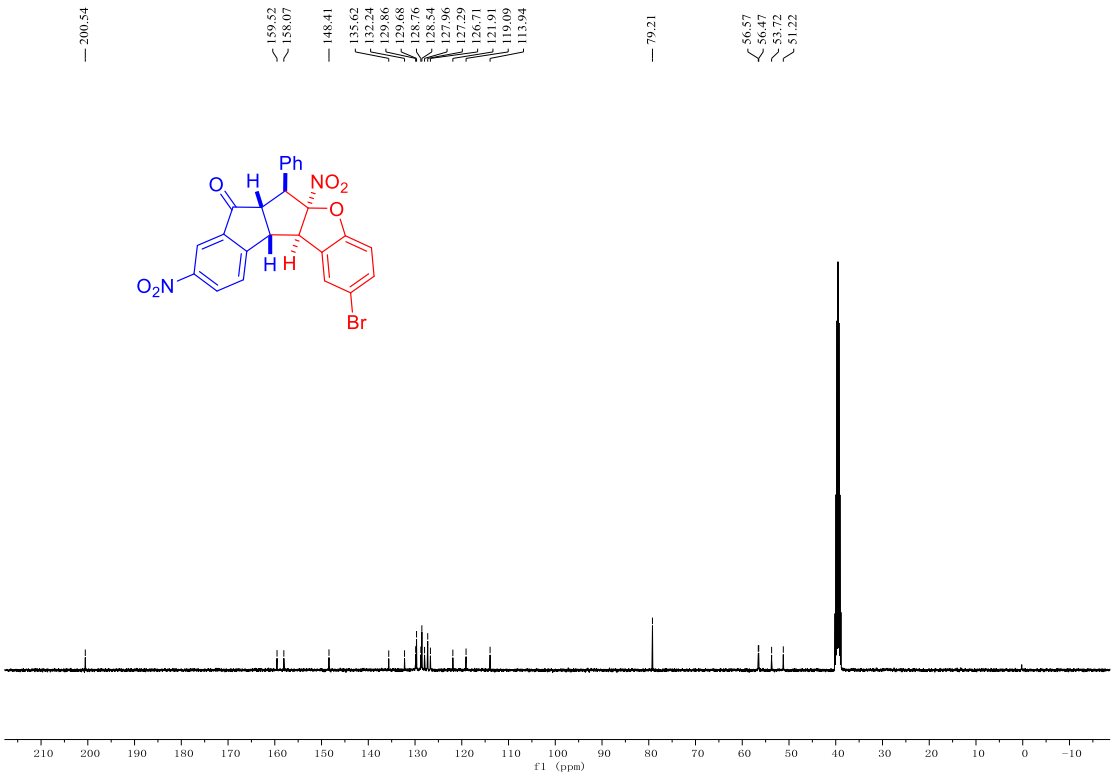


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ag

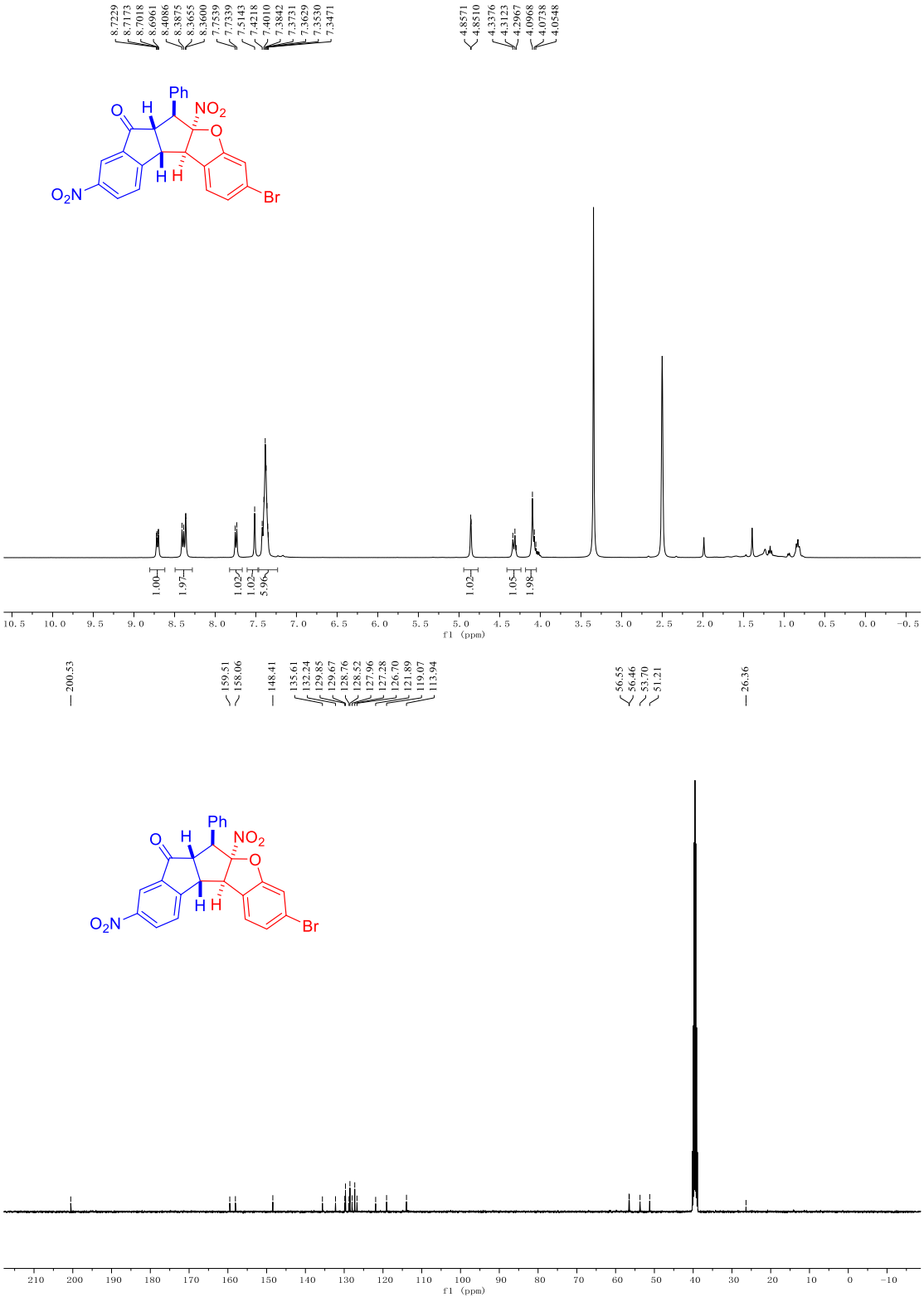


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ah

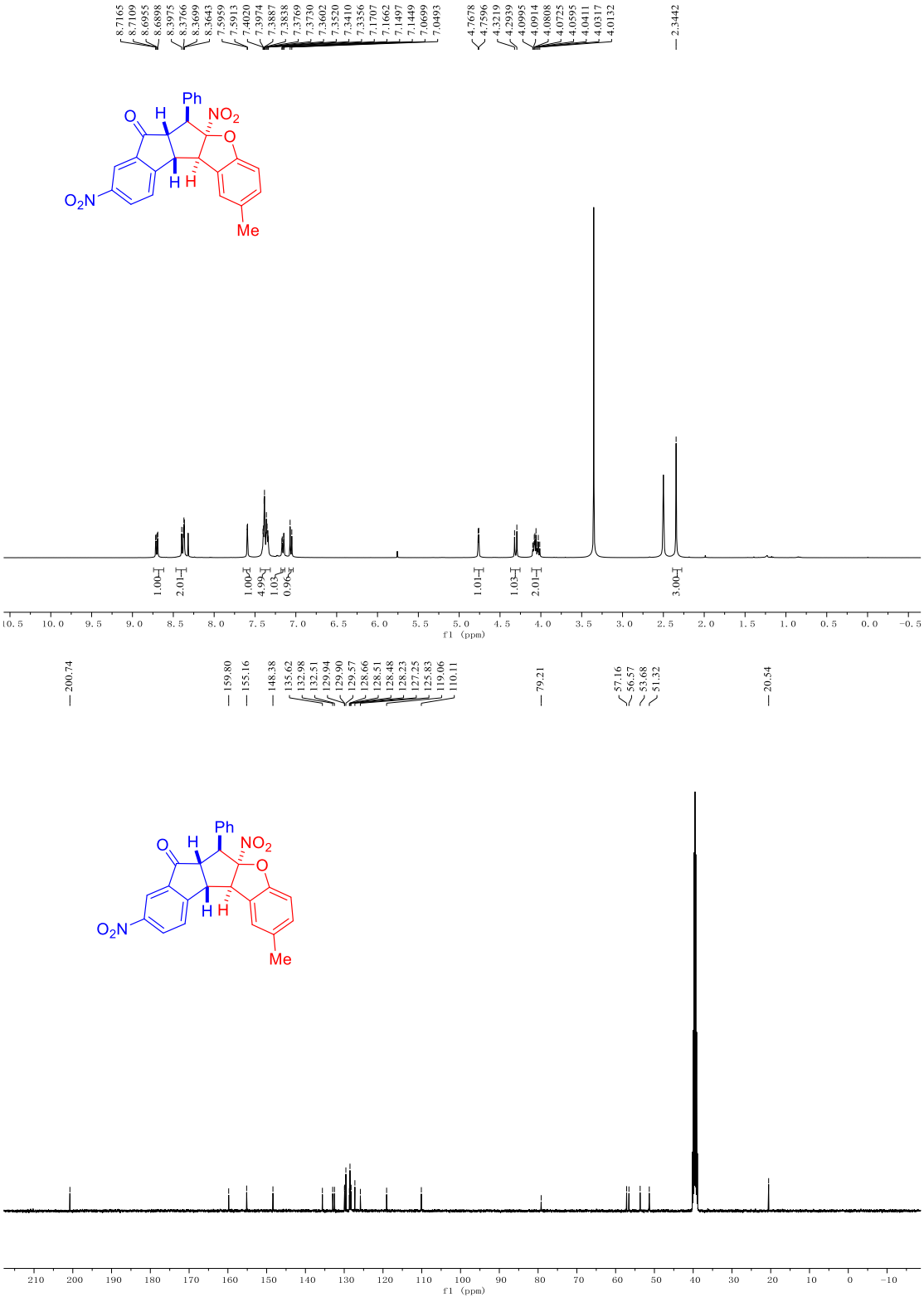




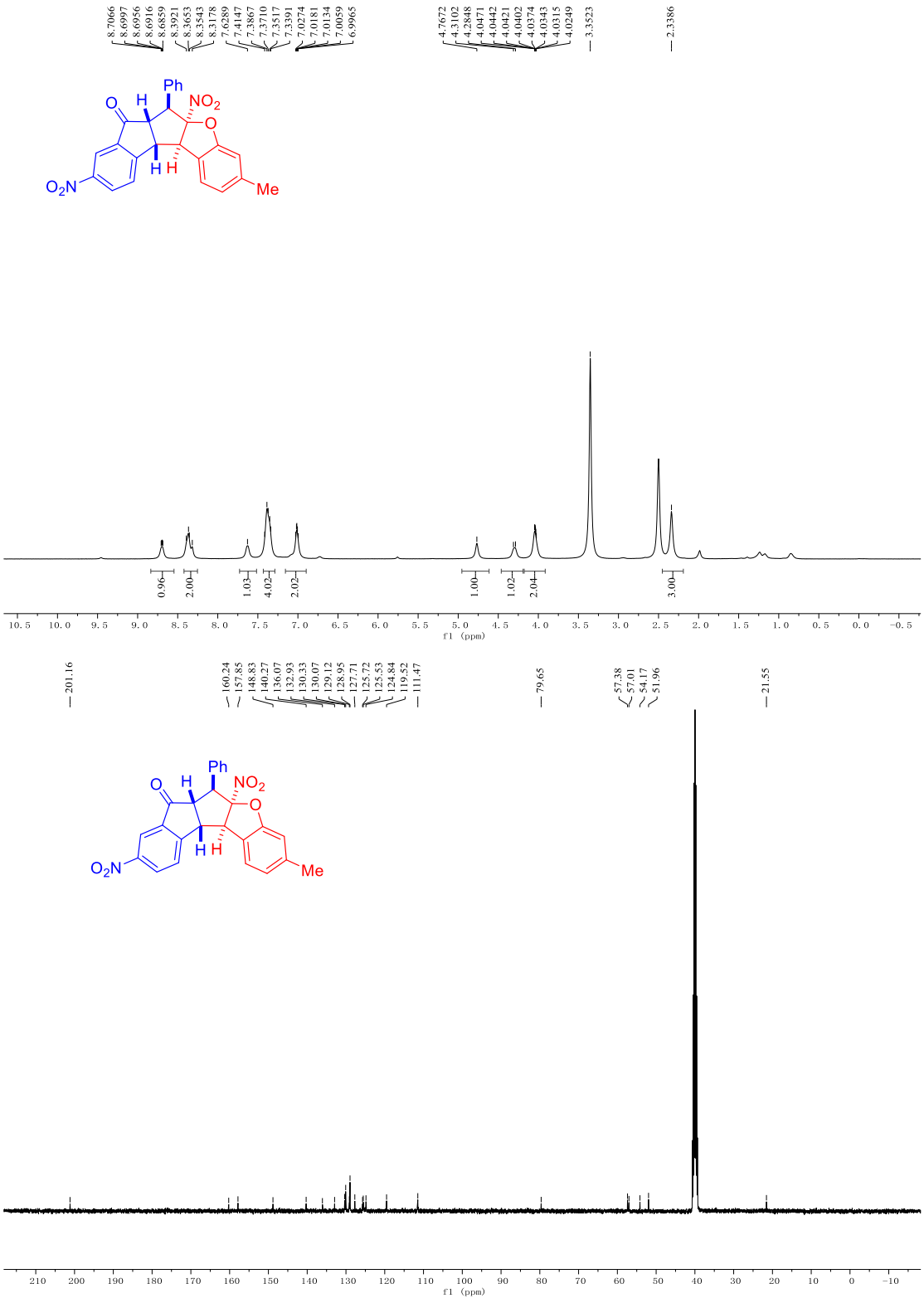
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ai



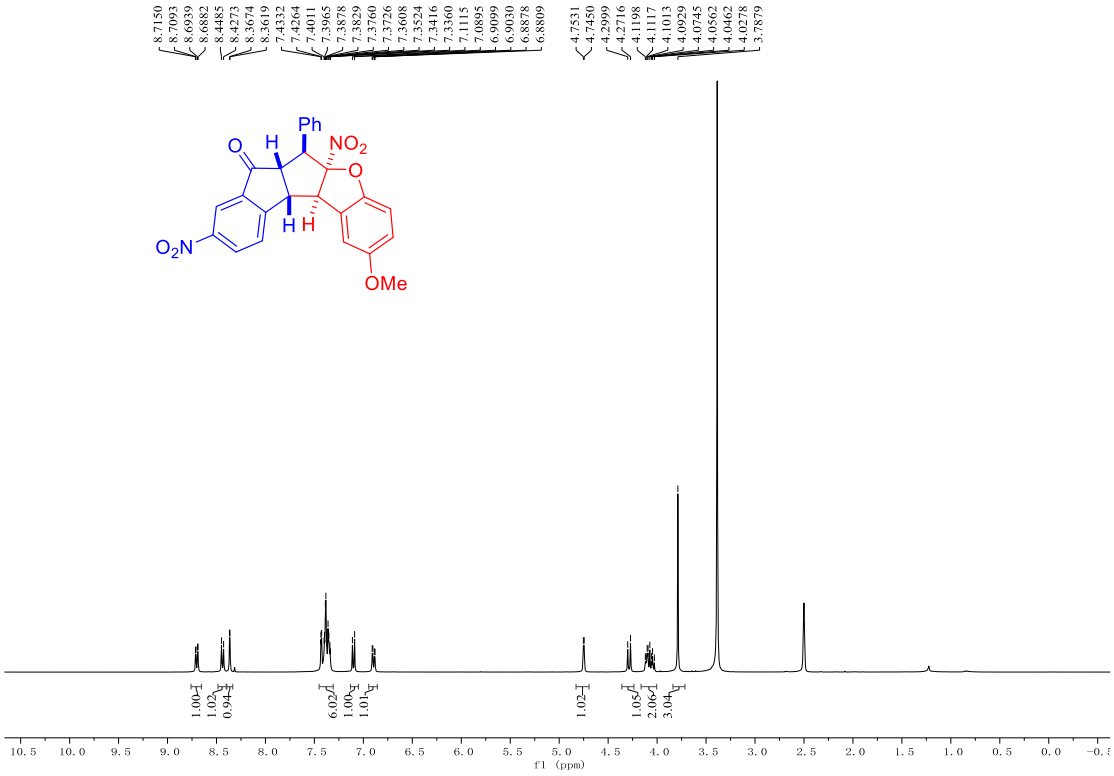
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3aj

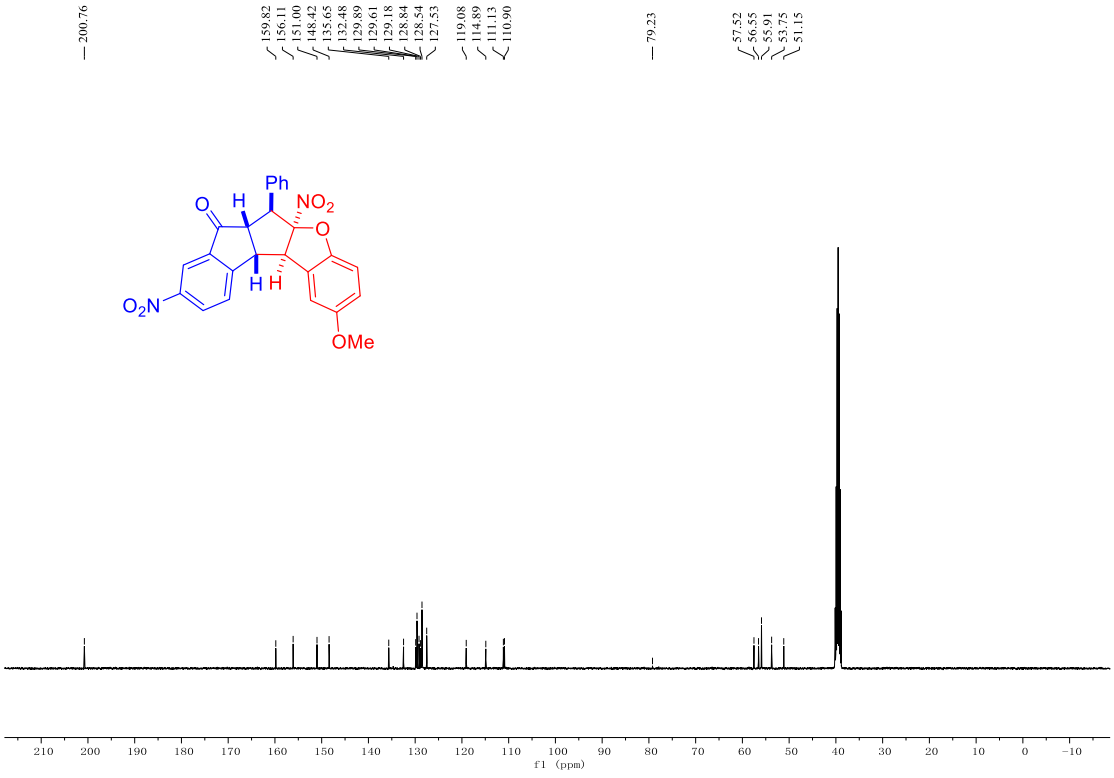


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3ak

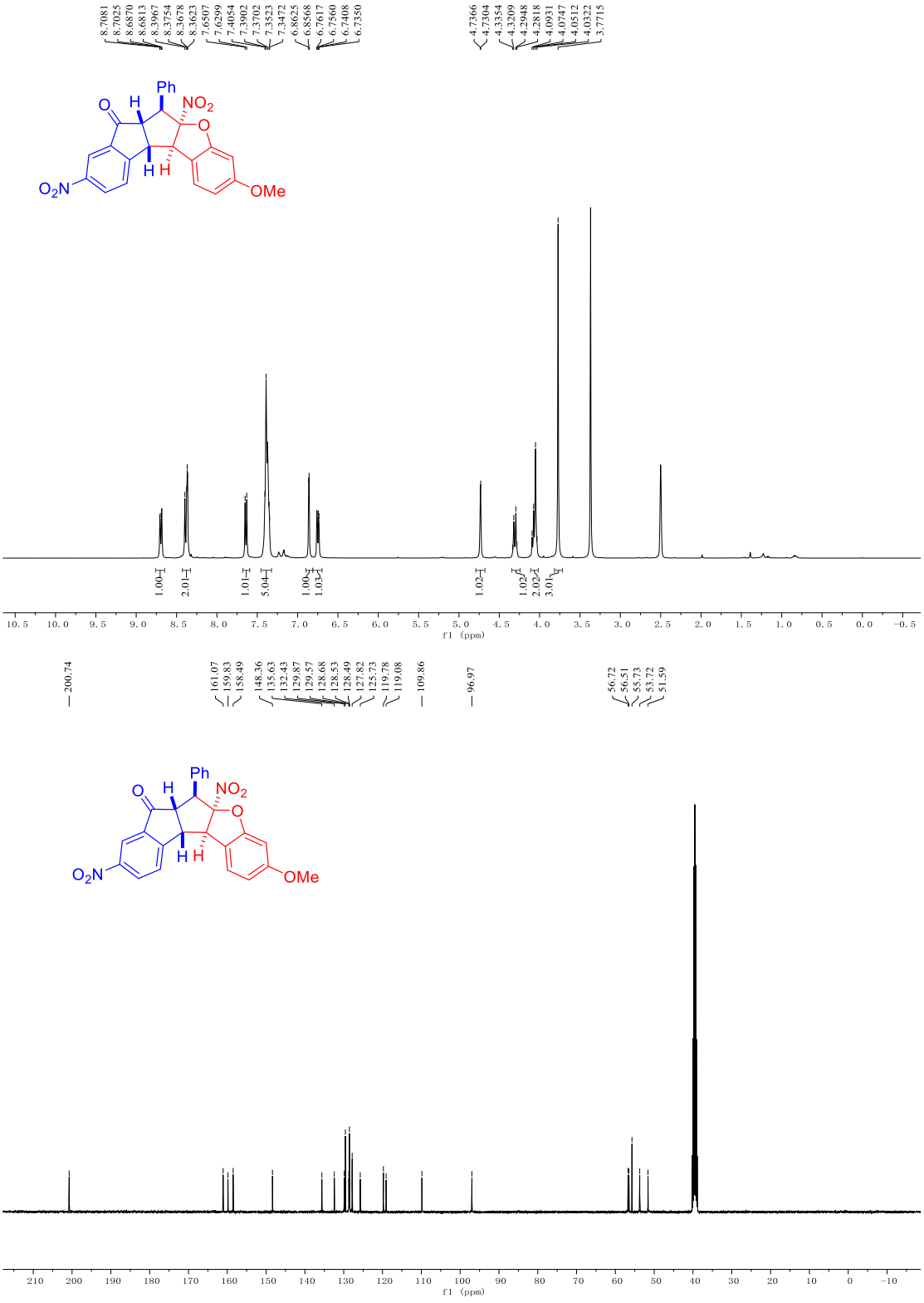


^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3al

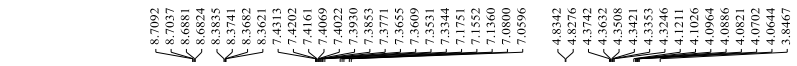


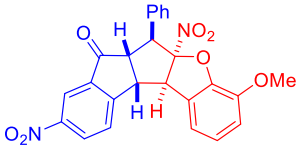


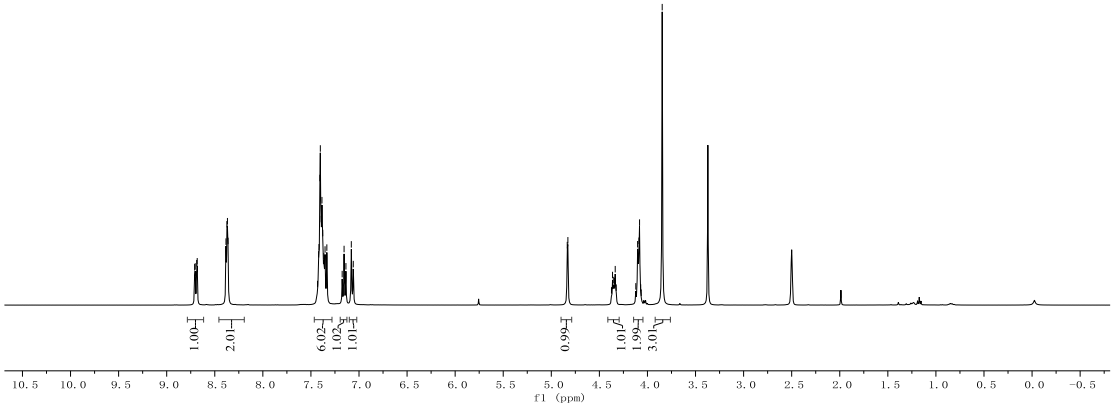
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3am

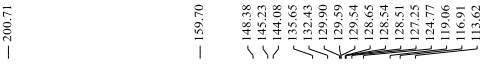


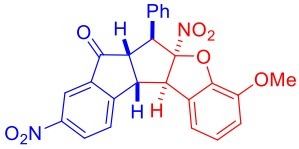
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3an

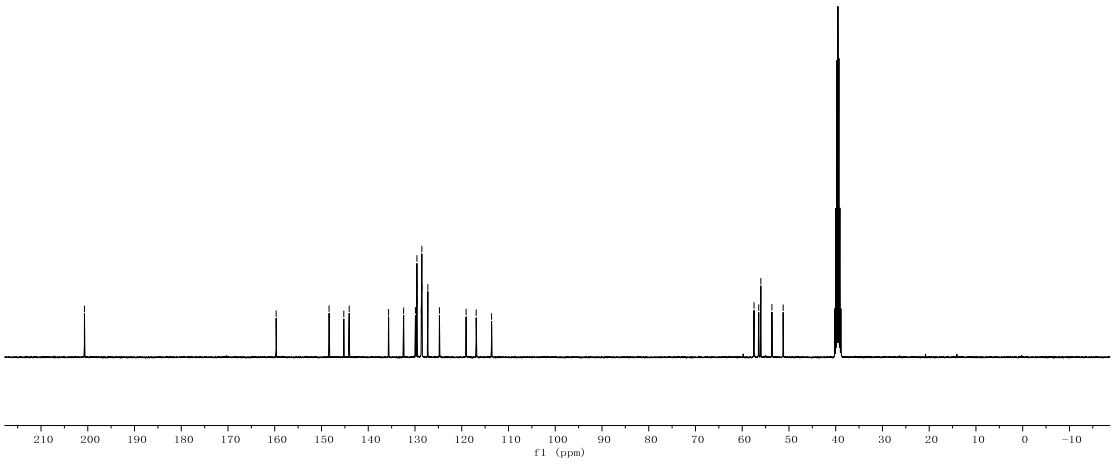




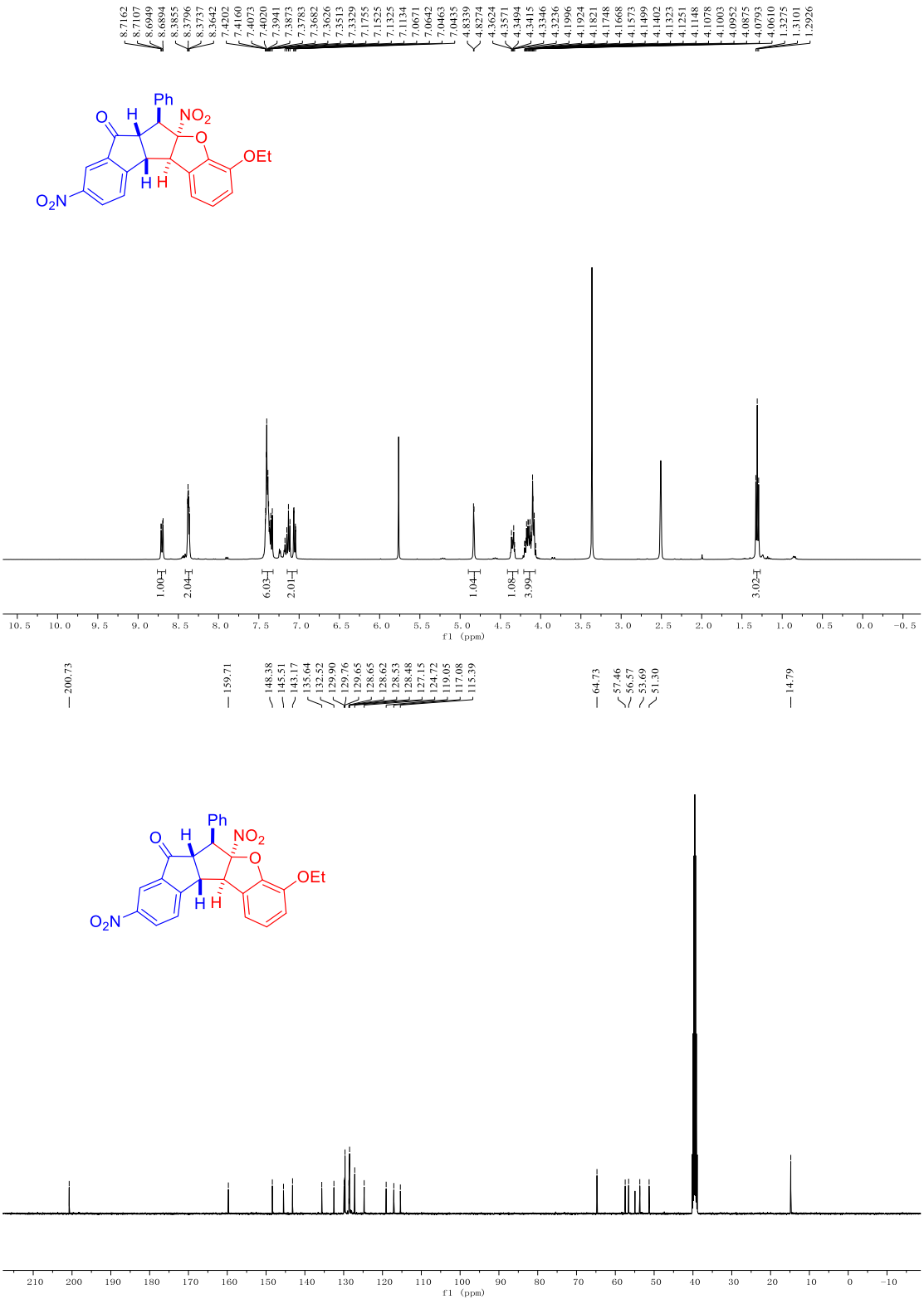




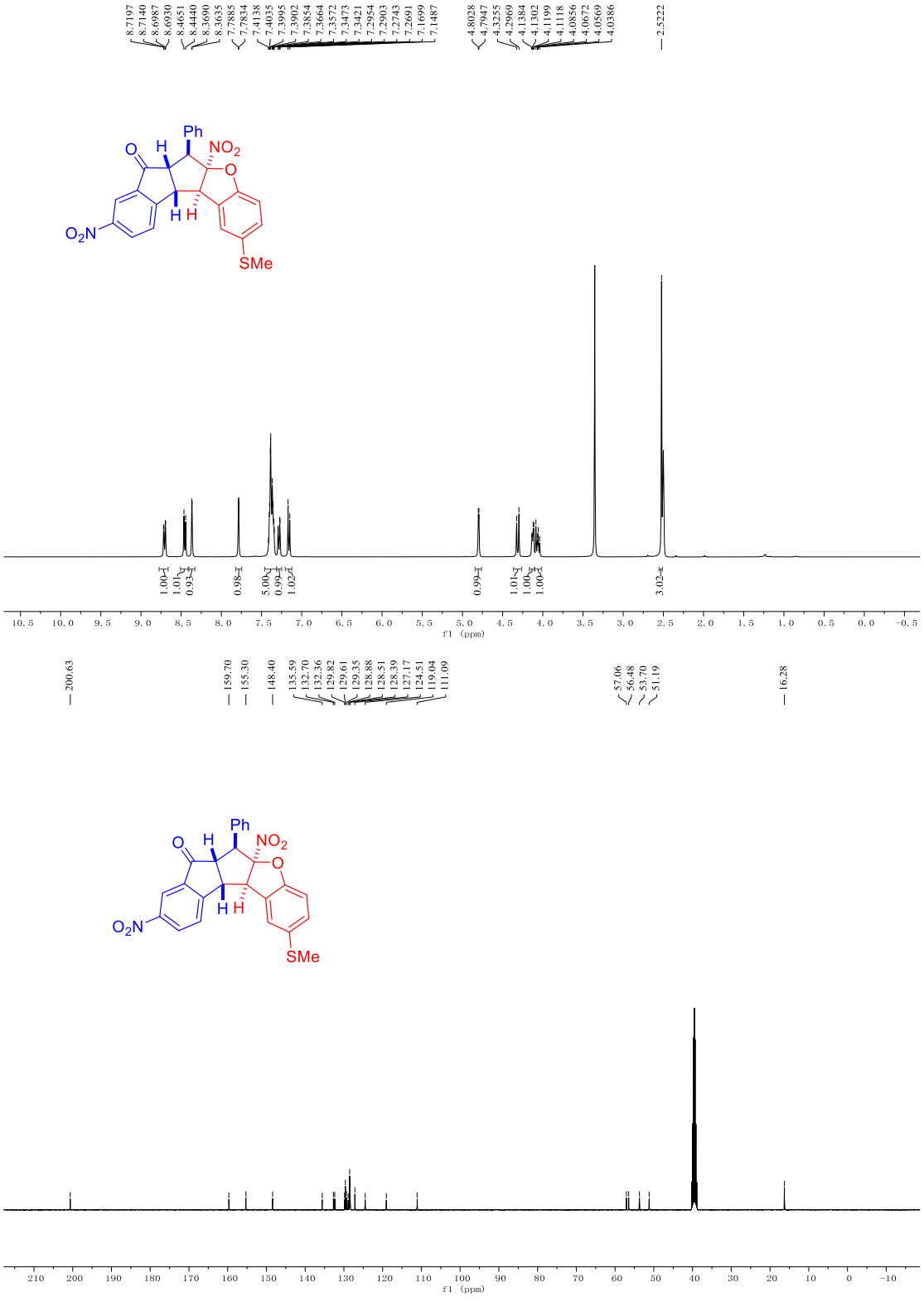




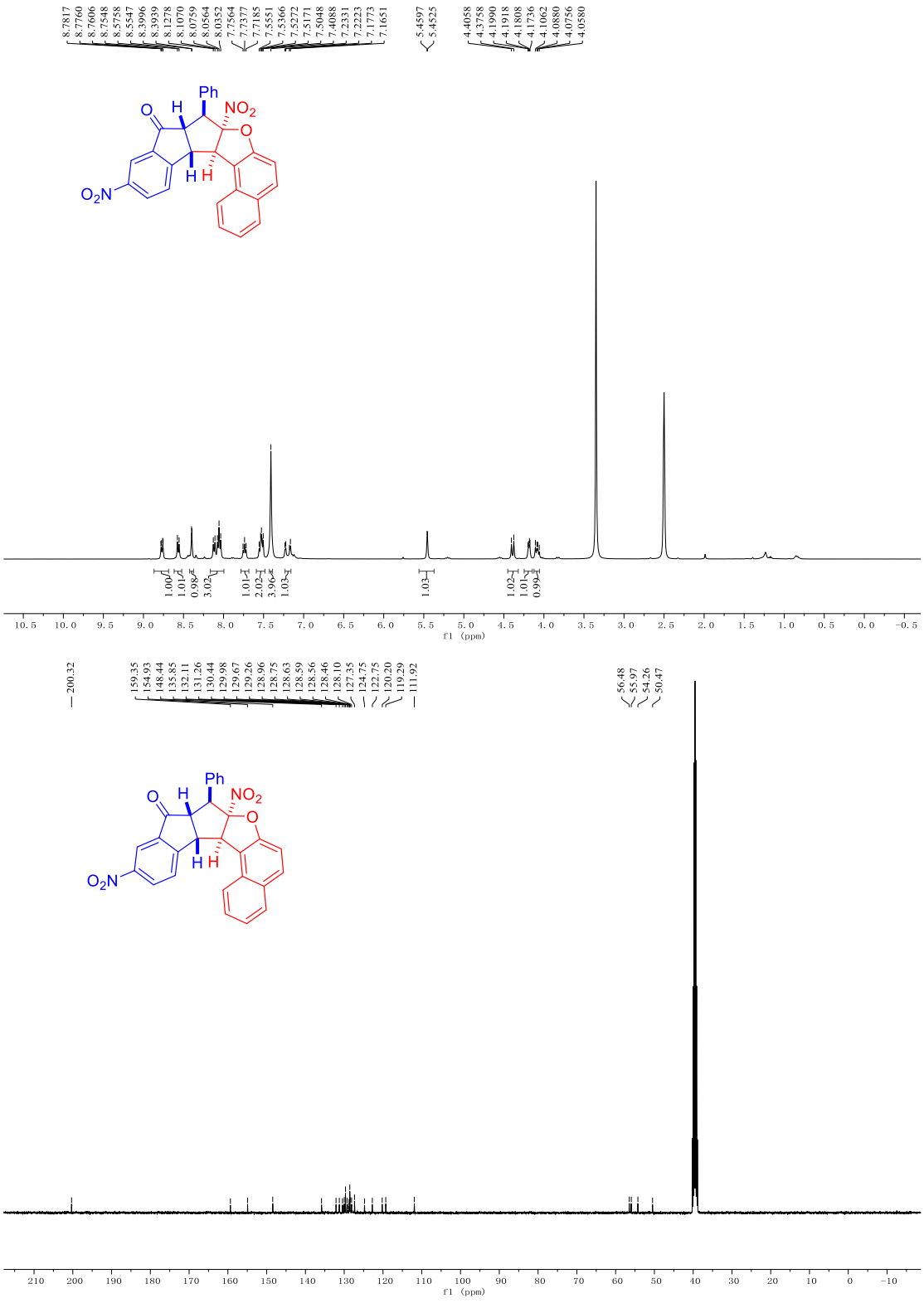
^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ao



^{1}H NMR (400 MHz, DMSO-*d*$_6$) and ^{13}C NMR (101 MHz, DMSO-*d*$_6$) of 3ap



^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) of 3aq



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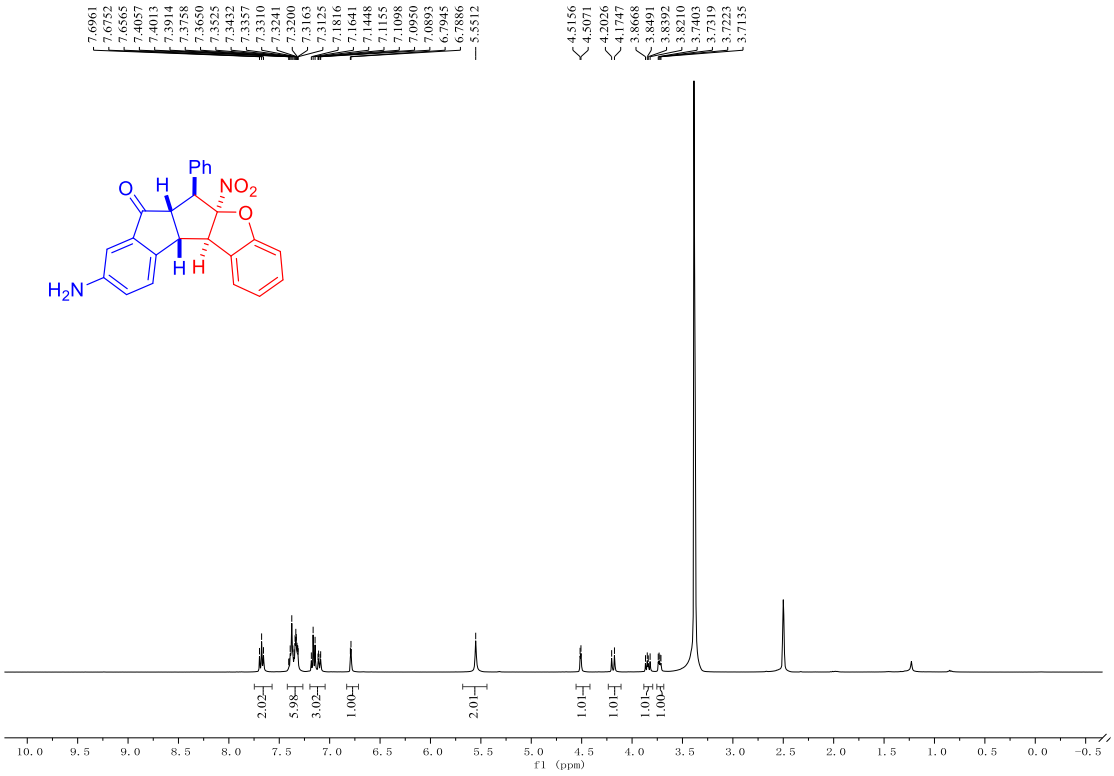
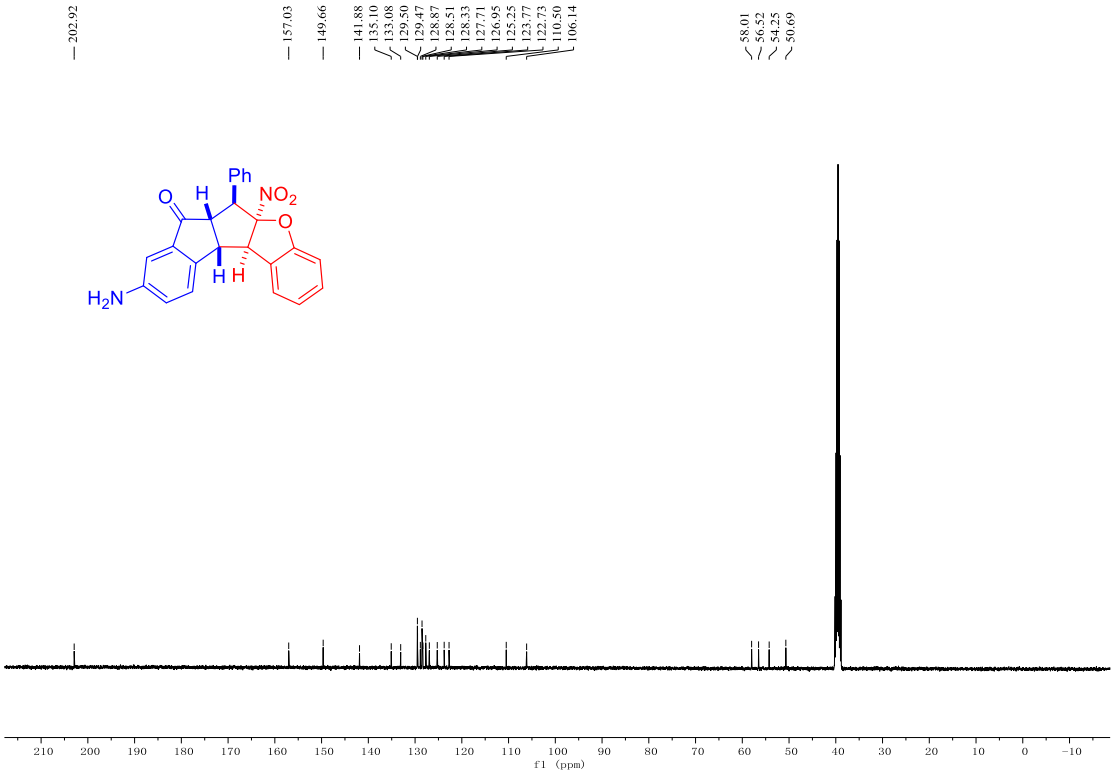
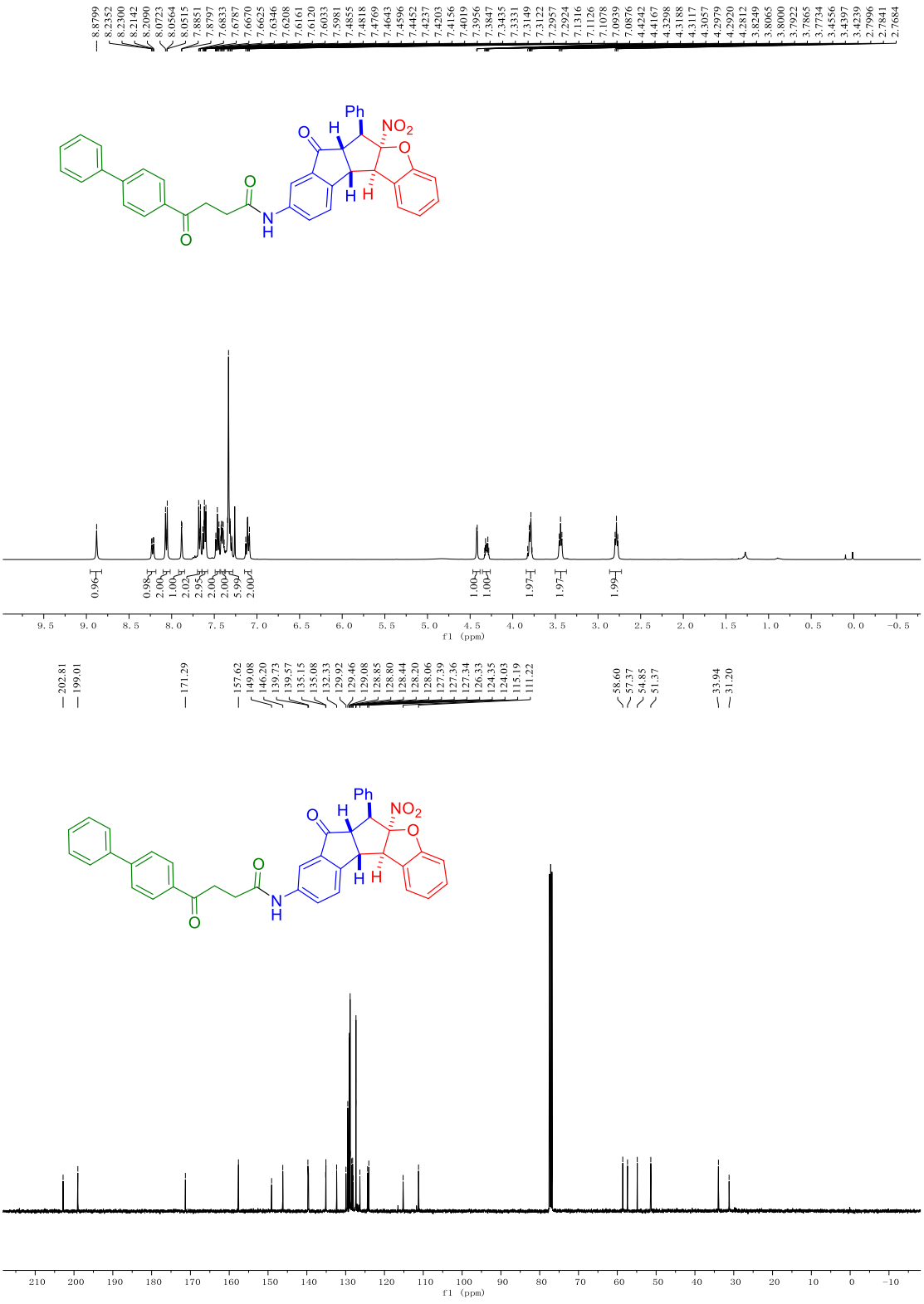
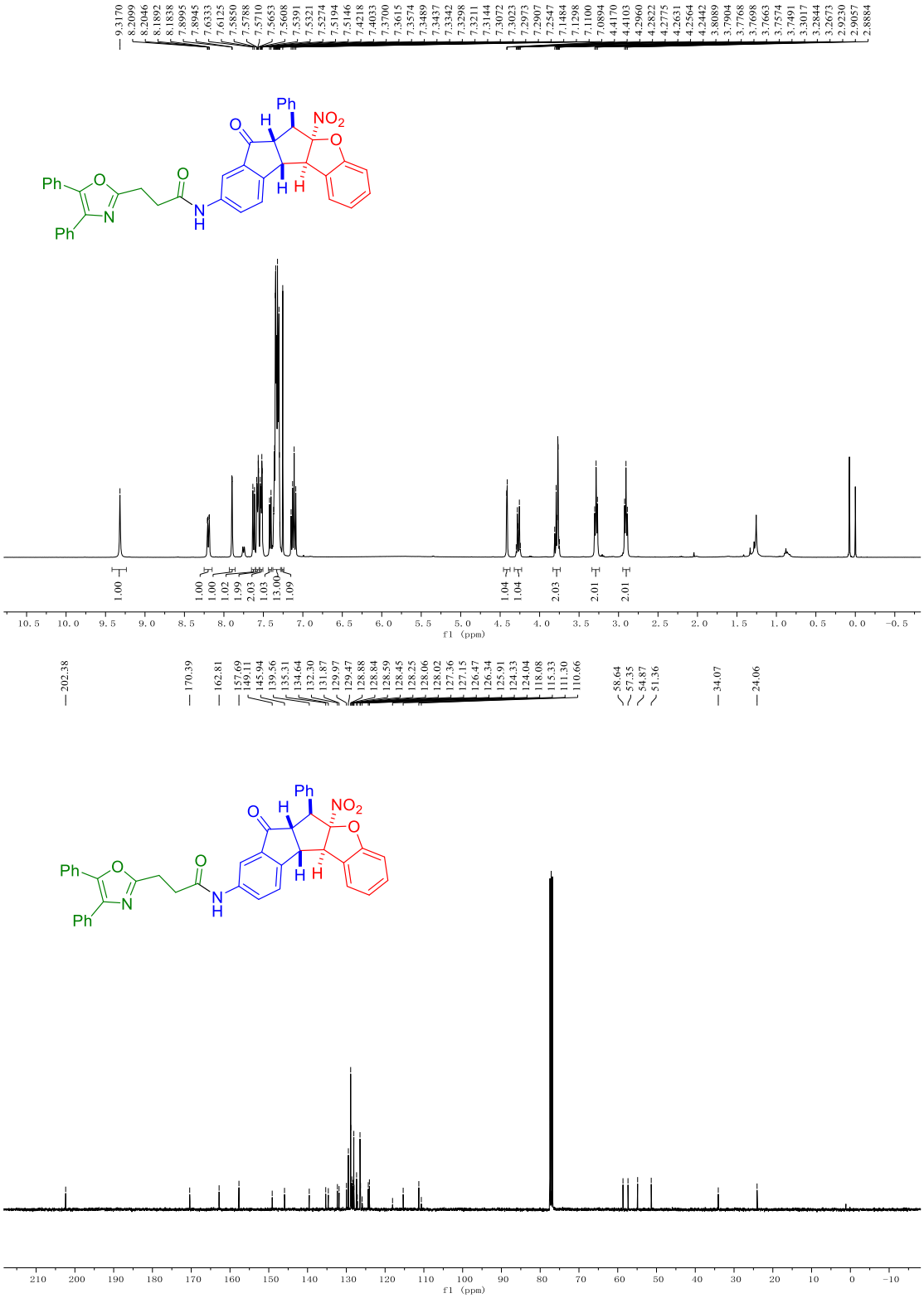




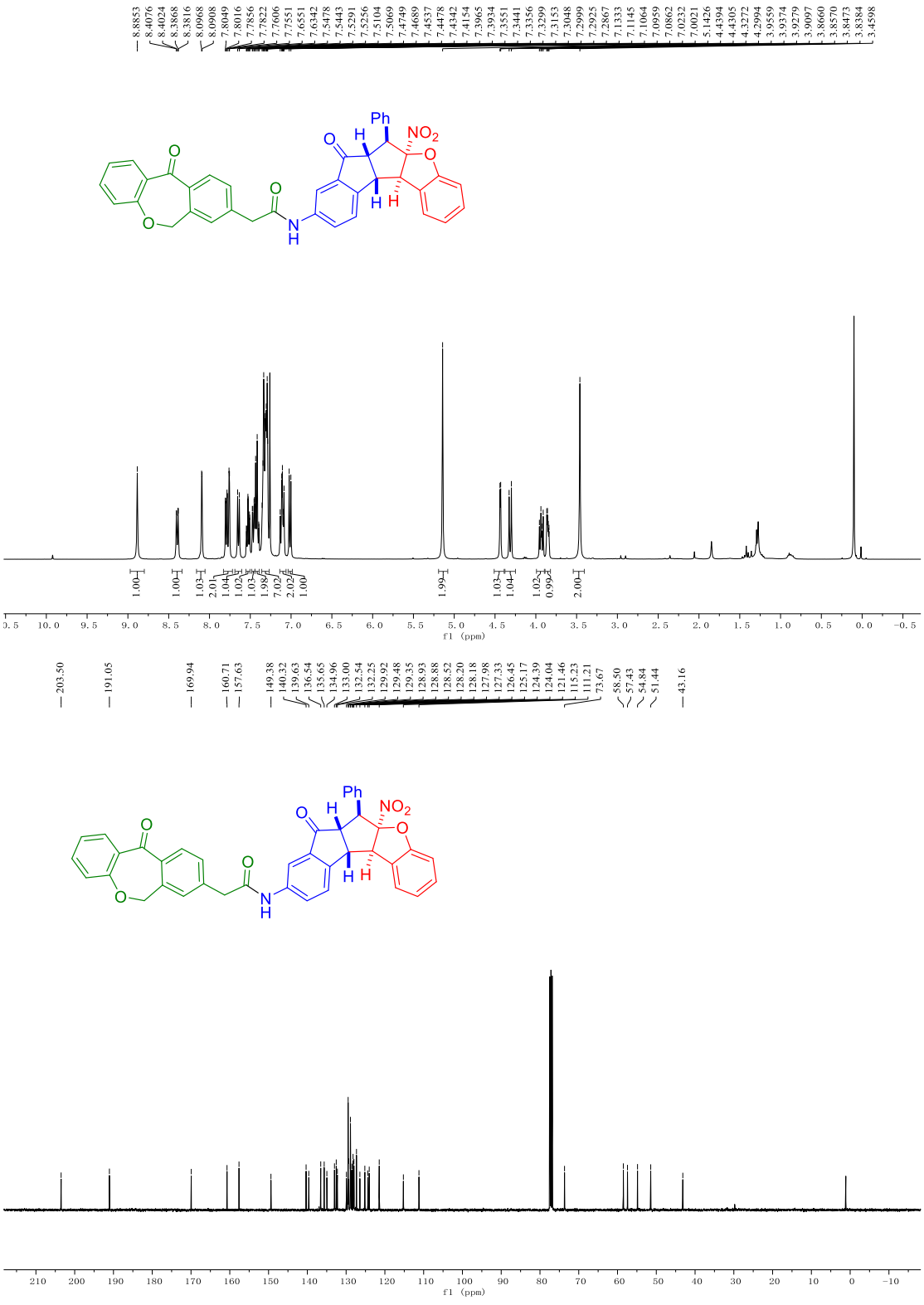
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5a



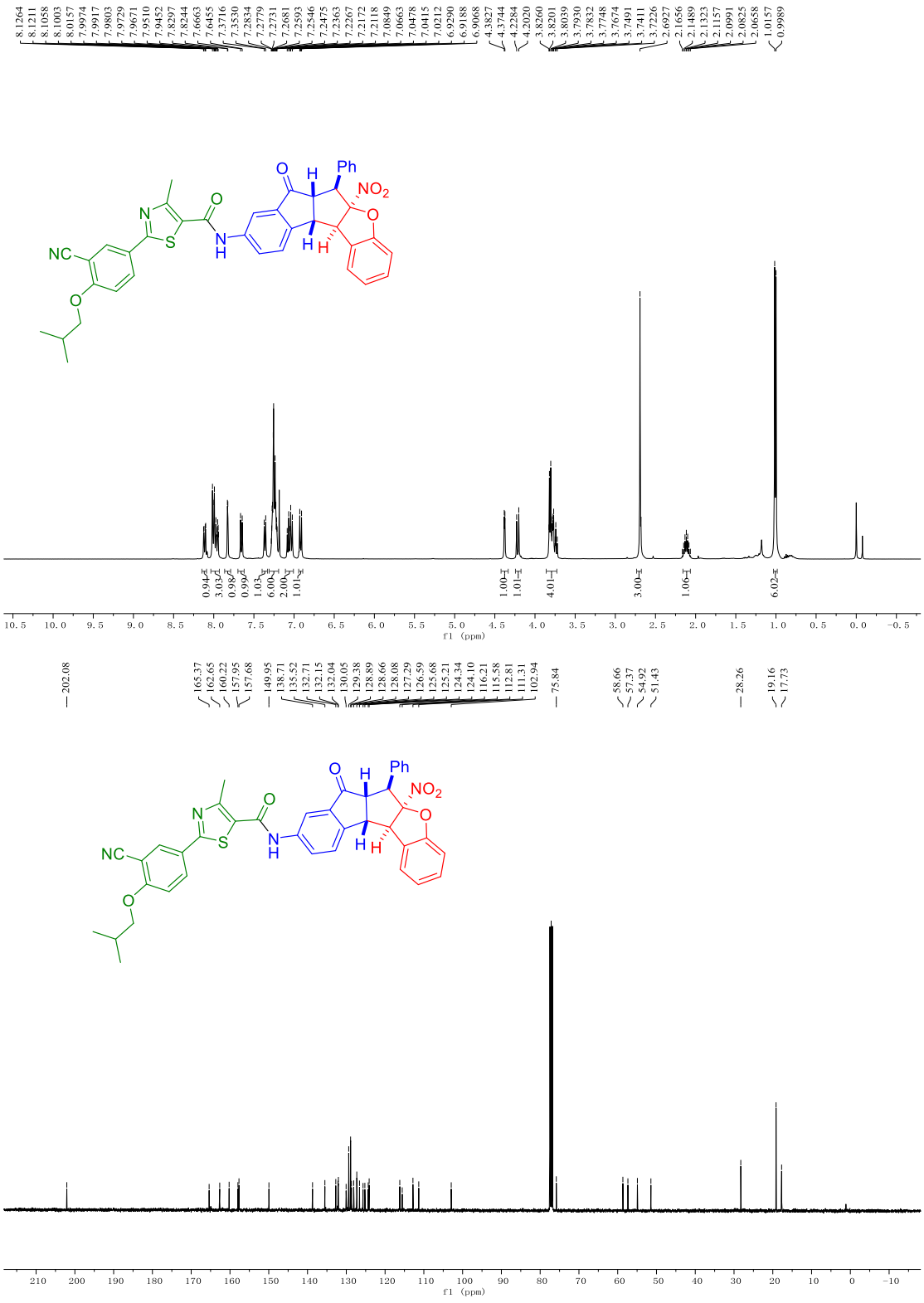
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5b



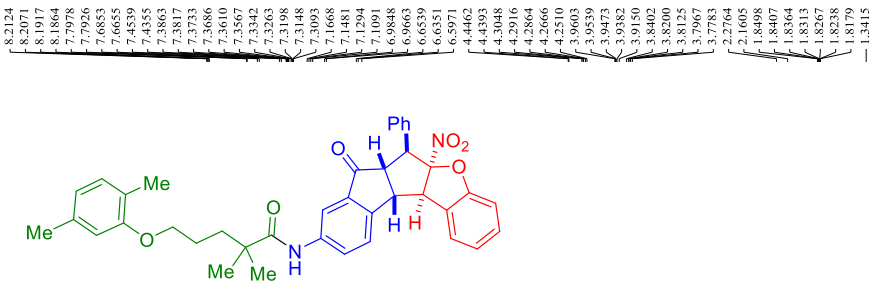
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5c

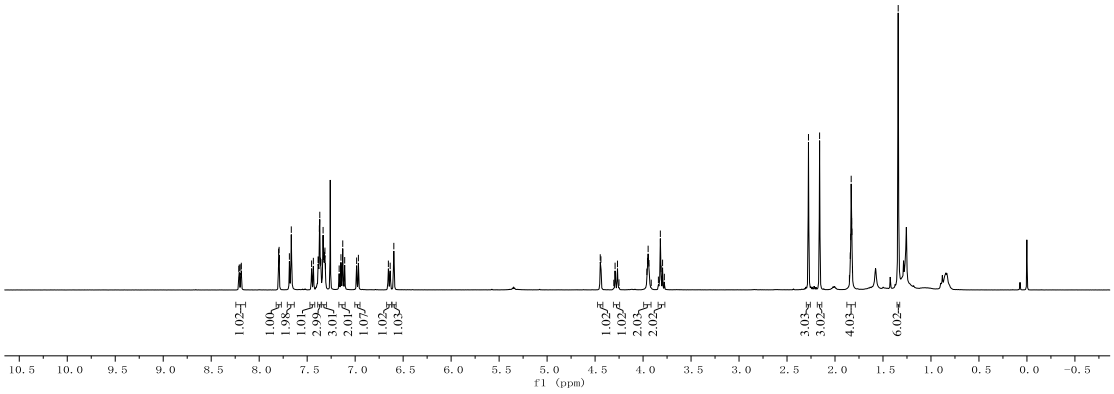


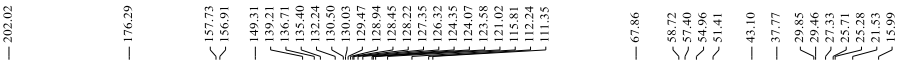
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5d

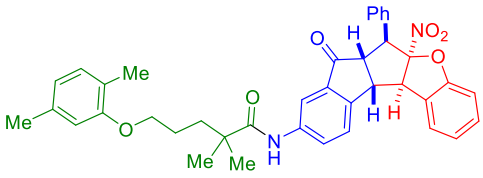


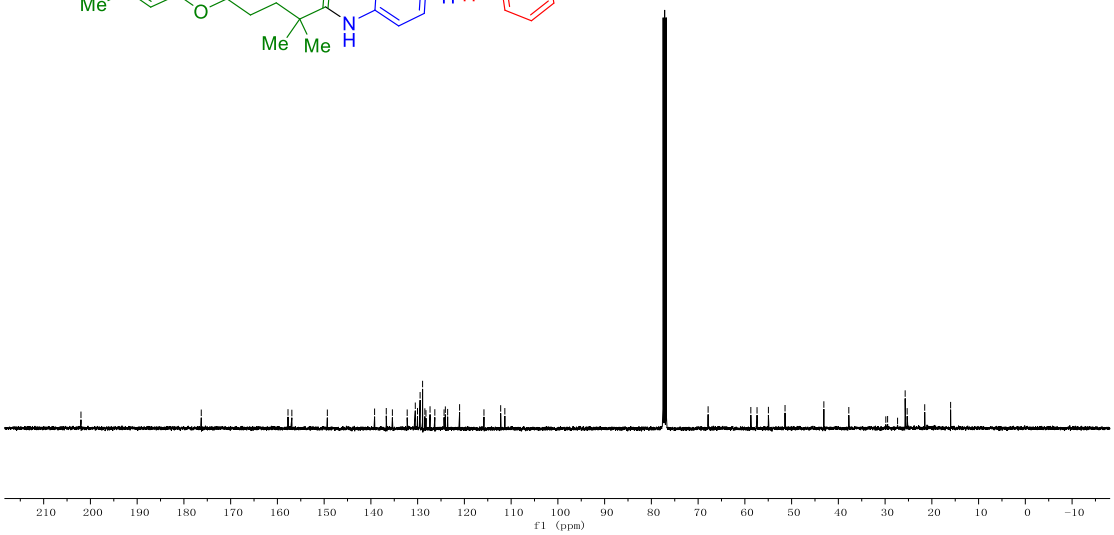
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5e











^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) of 5f