Supporting Information

Catalyst-free regioselective sulfonylation of phenoxazine with sulfonyl hydrazides in H_2O/HFIP

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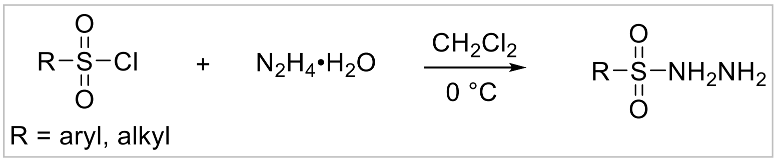
Part I Experimental Section

1.1 General information

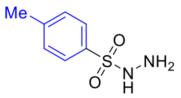
All reagents and solvents were purchased from commercial sources and used without further purification. Analytical TLC was performed with silica gel GF254 plates. Visualization was accomplished by UV light. Products were purified by flash column chromatography on 200−300 mesh silica gel. Flash chromatography was conducted eluting with PE/EA, and they were listed as volume/volume ratios. ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $(CD_3)_2SO$ (^{1}H: δ = 2.50 and $^{13}C\{^{1}H\}$: δ = 39.52 ppm) as internal standard, and coupling constants (*J*) are given in Hz. Oil baths were used as the heat source. High resolution mass spectra (HRMS) were measured on a Thermo Scientific-Orbitrap Exploris 120 mass spectrometer. The sulfonyl hydrazides **2** were synthesized according to the known literature procedures.[1]

1.2 General procedure for the preparation of substrates



To a chilled (0 °C) solution of substituted sulfonyl chloride (2.5 mmol) in CH_2Cl_2 (20 mL) was added hydrazine hydrate 99% (12.5 mmol) dropwise. The reaction mixture was stirred for 30 min, then the PH was adjusted to approximately 11 by using 10% aqueous Na_2CO_3. The solution was extracted with CH_2Cl_2 (3×20 mL) and washed with water and saturated brine, respectively. Then the combined organic phases were dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated under reduced pressure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to afford the pure products.

Sulfonylhydrazide derivatives



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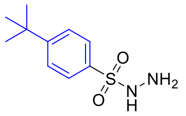

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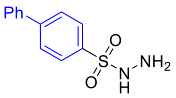

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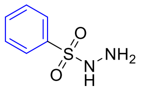

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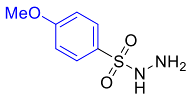

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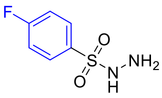

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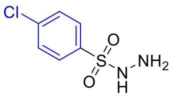

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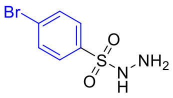

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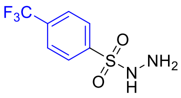

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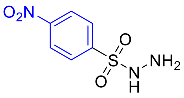

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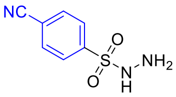

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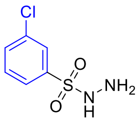

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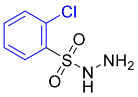

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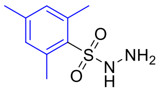

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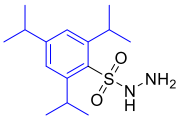

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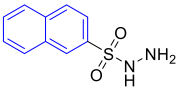

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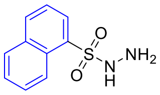

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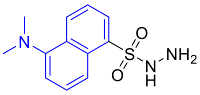

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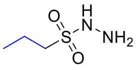
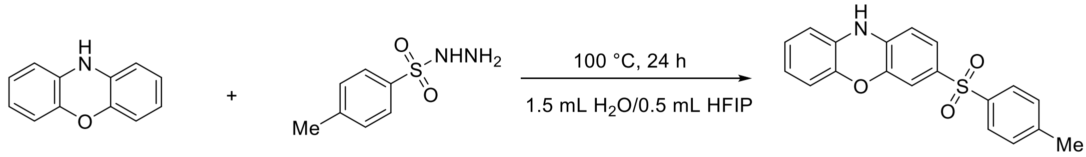


2s

1.3 General procedure for the sulfonylation reaction (**3a** as an example)



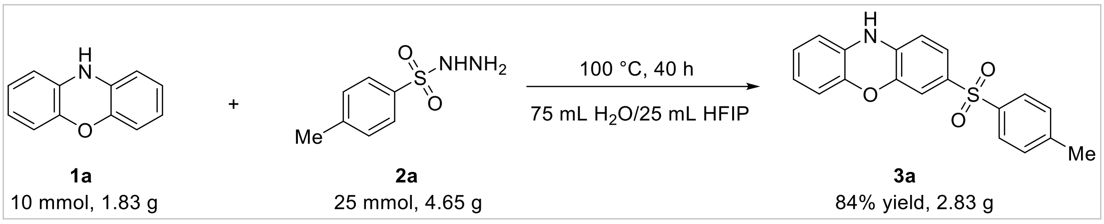
1a 0.2 mmol, 36.61 mg

2a 0.5 mmol, 93.02 mg

3a 85% yield, 57.3 mg

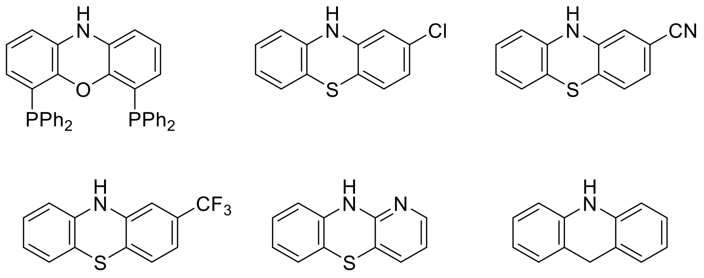
A solution of 10*H*-phenoxazine **1a** (0.2 mmol, 36.61 mg), 4-methylbenzenesulfonohydrazide **2a** (0.5 mmol, 93.02 mg) in 1.5 mL H_2O and 0.5 mL HFIP were stirred in air atmosphere at 100 °C in a Schlenk tube for 24 h in an oil bath. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) as a light-yellow solid.

1.4 Procedure for the gram-scale synthesis experiment



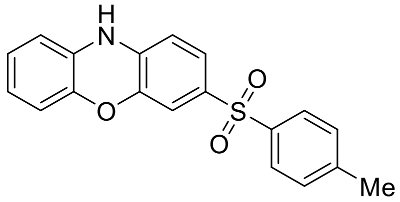
A solution of 10*H*-phenoxazine **1a** (10 mmol, 1.83 g), 4-methylbenzenesulfonohydrazide **2a** (25 mmol, 4.65 g) in 75 mL H_2O and 25 mL HFIP were stirred in air atmosphere at 100 °C in a Schlenk tube for 40 h in an oil bath. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the product **3a** was obtained by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 3:1) as a light-yellow solid.

1.5 Substrates not compatible for the reaction system



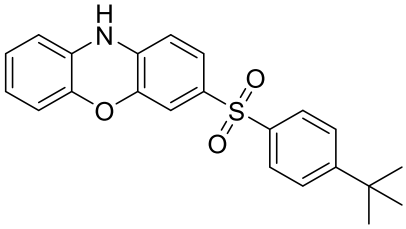
1.6 Characterization data for the products

3-tosyl-10*H*-phenoxazine (**3a**)



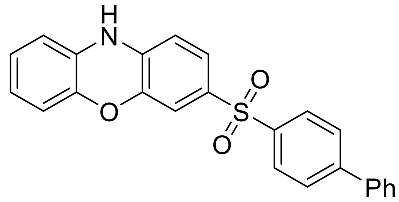
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (3/1, v/v), light yellow solid; 57.3 mg, 85% yield; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.75 (d, J = 8.4 Hz, 2H), 7.27−7.24 (m, 3H), 7.02 (d, J = 2.0 Hz, 1H), 6.72−6.68 (m, 1H), 6.64 (t, J = 7.6 Hz, 1H), 6.58−6.55 (m, 1H), 6.35 (t, J = 8.4 Hz, 2H), 5.97 (s, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR [100 MHz, $CDCl_3$] δ 143.9, 143.6, 143.0, 139.1, 136.8, 132.8, 129.9, 129.6, 127.2, 124.2, 124.1, 122.5, 115.7, 114.5, 113.8, 112.8, 21.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{15}NO_3S$ $[M-H]^-$ 336.0695, found 336.0703.

3-((4-(*tert*-butyl)phenyl)sulfonyl)-10*H*-phenoxazine (**3b**)



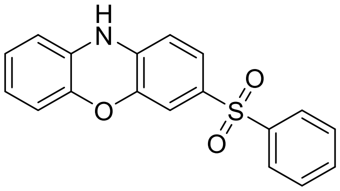
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 63.6 mg, 84% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.92 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.29−7.27 (m, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.75−6.71 (m, 1H), 6.64−6.57 (m, 2H), 6.51 (d, J = 8.0 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 156.7, 143.3, 142.8, 139.7, 138.1, 132.0, 130.8, 127.2, 126.9, 125.1, 124.9, 122.2, 115.7, 114.3, 113.9, 113.4, 35.3, 31.1. HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_3S$ [M-H]$^-$ 378.1164, found 378.1168.

3-([1,1'-biphenyl]-4-ylsulfonyl)-10*H*-phenoxazine (**3c**)



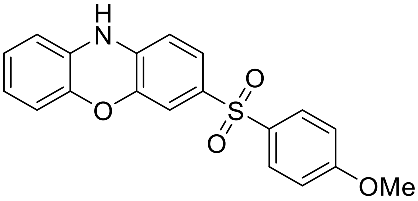
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 58.2 mg, 73% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.96 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.70−7.68 (m, 2H), 7.50−7.46 (m, 2H), 7.44−7.39 (m, 1H), 7.34−7.32 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.65−6.58 (m, 2H), 6.53 (d, J = 8.0 Hz, 1H), 6.47−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 145.2, 143.3, 142.8, 141.2, 138.8, 138.2, 131.7, 130.7, 129.6, 129.1, 128.3, 128.0, 127.6, 125.3, 124.9, 122.3, 115.7, 114.4, 114.0, 113.4. HRMS (ESI) m/z calcd for $C_{24}H_{17}NO_3S$ [M-H]$^-$ 398.0851, found 398.0858.

3-(phenylsulfonyl)-10*H*-phenoxazine (**3d**)



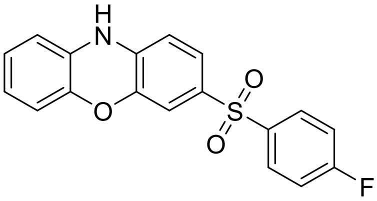
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 55.5 mg, 86% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.93 (s, 1H), 7.90−7.88 (m, 2H), 7.67−7.63 (m, 1H), 7.60−7.56 (m, 2H), 7.30−7.28 (m, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.64−6.58 (m, 2H), 6.51 (d, J = 8.0 Hz, 1H), 6.47−6.45 (m, 1H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 143.3, 142.8, 142.5, 138.2, 133.6, 131.6, 130.7, 130.0, 127.3, 125.3, 124.9, 122.3, 115.7, 114.4, 114.0, 113.4. HRMS (ESI) *m/z* calcd for $C_{18}H_{13}NO_3S$ $[M-H]^-$ 322.0538, found 322.0543.

3-((4-methoxyphenyl)sulfonyl)-10*H*-phenoxazine (**3e**)



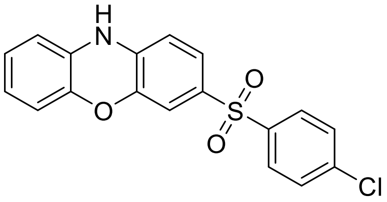
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 60.7 mg, 86% yield; ^1H NMR [400 MHz, $(CD_3)_2SO$] δ 8.89 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.26−7.24 (m, 1H), 7.09 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 2.4 Hz, 1H), 6.76−6.72 (m, 1H), 6.64−6.58 (m, 2H), 6.50 (d, J = 8.0 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 163.2, 143.2, 142.8, 137.8, 134.0, 132.6, 130.8, 129.6, 124.9, 124.8, 122.2, 115.7, 115.2, 114.3, 113.7, 113.3, 56.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_4S$ $[M-H]^-$ 352.0644, found 352.0651.

3-((4-fluorophenyl)sulfonyl)-10*H*-phenoxazine (**3f**)



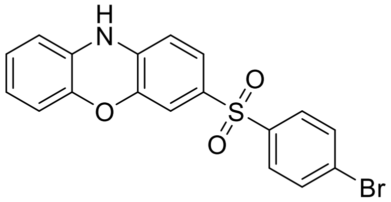
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 56.6 mg, 83% yield; ^1H NMR [400 MHz, $(CD_3)_2SO$] δ 8.94 (s, 1H), 7.98−7.95 (m, 2H), 7.41 (t, J = 8.8 Hz, 2H), 7.30−7.28 (m, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.76−6.71 (m, 1H), 6.64−6.57 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 166.3, 163.8, 143.3, 142.8, 138.94, 138.91, 138.3, 131.4, 130.7, 130.6, 130.5, 125.3, 124.9, 122.3, 117.3, 117.1, 115.6, 114.4, 114.0, 113.4. HRMS (ESI) *m/z* calcd for $C_{18}H_{12}FNO_3S$ $[M-H]^-$ 340.0444, found 340.0447.

3-((4-chlorophenyl)sulfonyl)-10*H*-phenoxazine (**3g**)



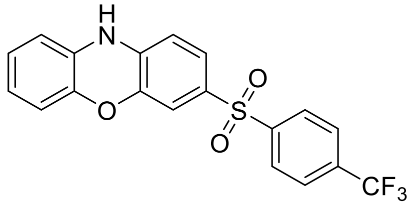
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 60.6 mg, 85% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.96 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.30−7.28 (m, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.76−6.71 (m, 1H), 6.64−6.57 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.47−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 143.3, 142.8, 141.3, 138.7, 138.4, 131.0, 130.7, 130.1, 129.3, 125.4, 124.9, 122.3, 115.6, 114.4, 114.0, 113.4. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{12}ClNO_3S$ [M-H]$^-$ 356.0148, found 356.0151.

3-((4-bromophenyl)sulfonyl)-10*H*-phenoxazine (**3h**)



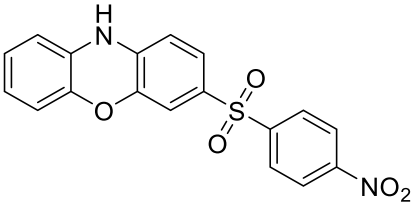
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 64.9 mg, 81% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.97 (s, 1H), 7.83−7.77 (m, 4H), 7.30−7.27 (m, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.65−6.58 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.47−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 143.3, 142.8, 141.8, 138.4, 133.1, 130.9, 130.6, 129.4, 127.7, 125.5, 124.9, 122.4, 115.7, 114.4, 114.0, 113.4. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{12}BrNO_3S$ [M-H]$^-$ 399.9643, found 399.9651.

3-((4-(trifluoromethyl)phenyl)sulfonyl)-10*H*-phenoxazine (**3i**)



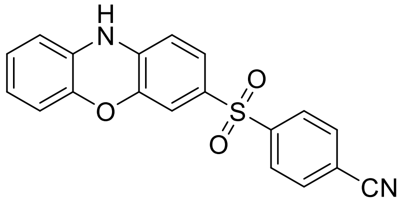
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 68.8 mg, 88% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 9.00 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.34−7.32 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.75−6.71 (m, 1H), 6.64−6.57 (m, 2H), 6.53 (d, J = 8.0 Hz, 1H), 6.48−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 146.4, 143.4, 142.9, 138.8, 133.7, 133.4, 133.1, 132.7, 130.6, 130.2, 128.3, 127.8, 127.29, 127.25, 127.21, 127.1, 125.8, 125.1, 124.9, 122.4, 119.7, 115.6, 114.4, 114.2, 113.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{12}F_3NO_3S$ [M-H]$^-$ 390.0412, found 390.0417.

3-((4-nitrophenyl)sulfonyl)-10*H*-phenoxazine (**3j**)



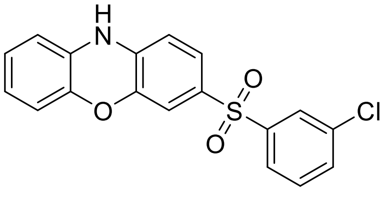
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), red solid; 63.3 mg, 86% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 9.03 (s, 1H), 8.35 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 7.35−7.32 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 6.64−6.57 (m, 2H), 6.53 (d, J = 8.0 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 150.4, 147.8, 143.4, 142.9, 138.9, 130.5, 129.7, 128.9, 126.0, 125.3, 124.9, 122.5, 115.7, 114.5, 114.2, 113.5. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{12}N_2O_5S$ $[M-H]^-$ 367.0389, found 367.0393.

4-((10*H*-phenoxazin-3-yl)sulfonyl)benzonitrile (**3k**)



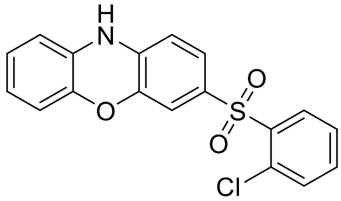
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 55.6 mg, 80% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 9.02 (s, 1H), 8.08−8.04 (m, 4H), 7.33−7.31 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.65−6.57 (m, 2H), 6.52 (d, J = 8.4 Hz, 1H), 6.47−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 146.4, 143.4, 142.9, 138.8, 134.2, 130.5, 129.9, 128.1, 125.9, 124.9, 122.5, 118.0, 116.0, 115.7, 114.4, 114.3, 113.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{12}N_2O_3S$ $[M-H]^-$ 347.0491, found 347.0494.

3-((3-chlorophenyl)sulfonyl)-10*H*-phenoxazine (**3l**)



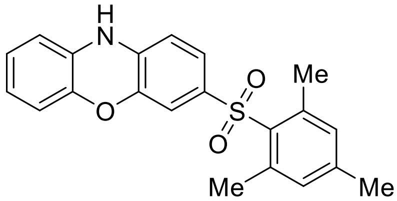
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 59.9 mg, 84% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.98 (s, 1H), 7.94 (t, J = 2.0 Hz, 1H), 7.87−7.85 (m, 1H), 7.74−7.71 (m, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.34−7.31 (m, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.76−6.72 (m, 1H), 6.65−6.58 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.47−6.45 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 144.4, 143.3, 142.9, 138.6, 134.7, 133.6, 132.1, 130.6, 126.9, 126.1, 125.7, 124.9, 122.4, 115.6, 114.4, 114.2, 113.4. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{12}ClNO_3S$ [M-H]$^-$ 356.0148, found 356.0154.

3-((2-chlorophenyl)sulfonyl)-10*H*-phenoxazine (**3m**)



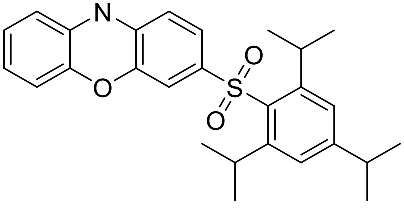
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 58.5 mg, 82% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 9.00 (s, 1H), 8.20−8.17 (m, 1H), 7.69−7.65 (m, 1H), 7.62−7.58 (m, 2H), 7.31−7.28 (m, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.76−6.72 (m, 1H), 6.64−6.57 (m, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.48−6.46 (m, 1H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 142.9, 138.8, 138.5, 135.6, 132.5, 131.6, 131.0, 130.6, 129.7, 128.6, 126.5, 124.9, 122.4, 115.7, 114.6, 114.4, 113.1. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{12}ClNO_3S$ [M-H]$^-$ 356.0148, found 356.0153.

3-(mesitylsulfonyl)-10*H*-phenoxazine (**3n**)



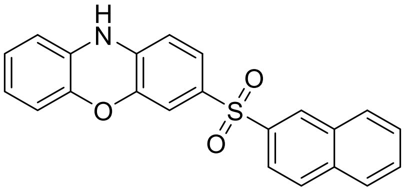
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 61.3 mg, 84% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.90 (s, 1H), 7.19−7.16 (m, 1H), 7.05 (s, 2H), 6.77−6.73 (m, 2H), 6.65−6.58 (m, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 1H), 2.52 (s, 6H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 143.4, 142.9, 142.8, 139.3, 137.7, 134.8, 133.6, 132.6, 130.9, 124.9, 123.9, 122.2, 115.7, 114.3, 113.1, 112.7, 22.7, 20.9. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{19}NO_3S$ [M-H]$^-$ 364.1008, found 364.1014.

3-((2,4,6-triisopropylphenyl)sulfonyl)-10*H*-phenoxazine (**3o**)



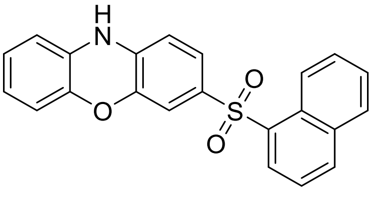
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow oil; 55.7 mg, 62% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.89 (s, 1H), 7.26 (s, 2H), 7.10−7.08 (m, 1H), 6.76−6.72 (m, 1H), 6.70 (d, J = 2.0 Hz, 1H), 6.63−6.58 (m, 2H), 6.55 (d, J = 8.4 Hz, 1H), 6.47−6.45 (m, 1H), 4.13−4.07 (m, 2H), 2.95−2.88 (m, 1H), 1.19 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.8 Hz, 12H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 153.9, 150.7, 143.0, 142.7, 137.2, 135.3, 133.3, 130.9, 124.9, 124.5, 123.1, 122.1, 115.7, 114.3, 113.3, 112.0, 33.8, 29.2, 24.8. 23.8. HRMS (ESI) *m*/*z* calcd for $C_{27}H_{31}NO_3S$ [M-H]$^-$ 448.1947, found 448.1956.

3-(naphthalen-2-ylsulfonyl)-10*H*-phenoxazine (**3p**)



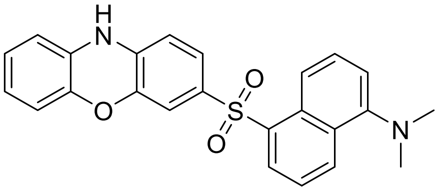
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 61.1 mg, 82% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.93 (s, 1H), 8.61 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.87−7.84 (m, 1H), 7.70−7.62 (m, 2H), 7.37−7.34 (m, 1H), 7.07 (d, J = 2.0 Hz, 1H), 6.74−6.70 (m, 1H), 6.63−6.56 (m, 2H), 6.52 (d, J = 8.4 Hz, 1H), 6.46−6.44 (m, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 143.3, 142.8, 139.4, 138.2, 134.8, 132.3, 131.6, 130.7, 130.2, 129.8, 129.6, 128.4, 128.3, 128.2, 125.4, 124.9, 122.8, 122.3, 115.6, 114.4, 114.1, 113.4. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{15}NO_3S$ [M-H]$^-$ 372.0695, found 372.0702.

3-(naphthalen-1-ylsulfonyl)-10*H*-phenoxazine (**3q**)



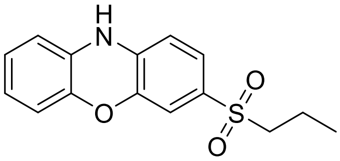
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 59.6 mg, 80% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.92 (s, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 7.2 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.73−7.68 (m, 2H), 7.62 (t, J = 8.0 Hz, 1H), 7.39−7.37 (m, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.73−6.69 (m, 1H), 6.61−6.54 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 143.1, 142.8, 138.1, 136.5, 135.4, 134.3, 131.5, 130.7, 129.8, 129.7, 128.9, 127.8, 127.5, 125.4, 125.3, 124.9, 124.2, 122.3, 115.6, 114.3, 113.8, 113.3. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{15}NO_3S$ [M-H]$^-$ 372.0695, found 372.0699.

5-((10*H*-phenoxazin-3-yl)sulfonyl)-*N,N*-dimethylnaphthalen-1-amine (**3r**)



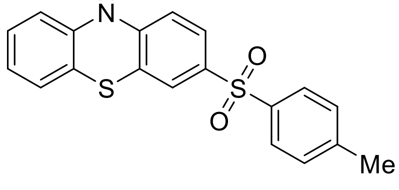
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 59.9 mg, 72% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.91 (s, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.68 (t, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 8.8 Hz, 1H), 7.37−7.35 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.73−6.69 (m, 1H), 6.60−6.53 (m, 2H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 2.75 (s, 6H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 152.1, 143.1, 142.8, 138.0, 136.8, 131.7, 131.1, 130.7, 129.7, 129.4, 128.9, 125.3, 124.9, 124.4, 122.2, 118.5, 115.7, 115.6, 114.3, 113.8, 113.2, 45.4. HRMS (ESI) *m*/*z* calcd for $C_{24}H_{20}N_2O_3S$ [M-H]$^-$ 415.1117, found 415.1122.

3-(propylsulfonyl)-10*H*-phenoxazine (**3s**)



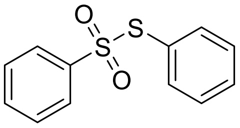
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light gray solid; 29.4 mg, 51% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 8.90 (s, 1H), 7.21−7.18 (m, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.79−6.75 (m, 1H), 6.67−6.62 (m, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.58−1.48 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2SO$] δ 143.0, 142.9, 138.1, 131.0, 129.9, 125.4, 124.9, 122.2, 115.7, 114.4, 114.3, 113.1, 56.9, 16.8, 13.0. HRMS (ESI) *m*/*z* calcd for $C_{15}H_{15}NO_3S$ [M-H]$^-$ 288.0695, found 288.0700.

3-tosyl-10*H*-phenothiazine (**3t**)



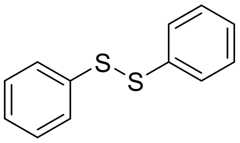
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (4/1, v/v), light yellow solid; 37.4 mg, 53% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 9.16 (s, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.49−7.46 (m, 1H), 7.38 (s, 1H), 7.36 (s, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.78 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR [100 MHz, $(CD_3)_2SO$] δ 146.8, 144.2, 140.3, 139.5, 133.9, 130.5, 128.4, 128.1, 127.4, 126.7, 125.5, 123.6, 117.9, 115.9, 115.5, 114.6, 21.4. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{15}NO_2S_2$ $[M-H]^-$ 352.0466, found 352.0474.

S-phenyl benzenesulfonothioate (**4**)



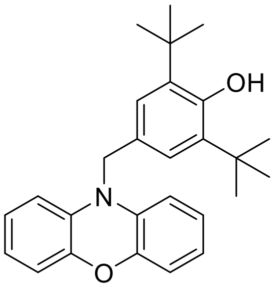
The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (20/1, v/v), white solid; 40.6 mg, 65% yield; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.59−7.54 (m, 3H), 7.49−7.45 (m, 1H), 7.44−7.39 (m, 2H), 7.37−7.31 (m, 4H).

1,2-diphenyldisulfane (**5**)



The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (40/1, v/v), white solid; 10.9 mg, 20% yield; ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.48−7.45 (m, 4H), 7.29−7.25 (m, 4H), 7.22−7.17 (m, 2H).

4-((10*H*-phenoxazin-10-yl)methyl)-2,6-di-*tert*-butylphenol (**6**)



The product was prepared according to the general working procedure (24 h) and purified by silica gel column chromatography with petroleum ether/ethyl acetate (30/1, v/v), light yellow solid; 28.7 mg, 35% yield; ^{1}H NMR [400 MHz, $(CD_3)_2SO$] δ 7.04 (s, 2H), δ 6.84 (s, 1H), 6.77−6.73 (m, 2H), 6.69−6.62 (m, 4H), 6.54−6.51 (m, 2H), 4.74 (s, 2H), 1.29 (s, 18H).

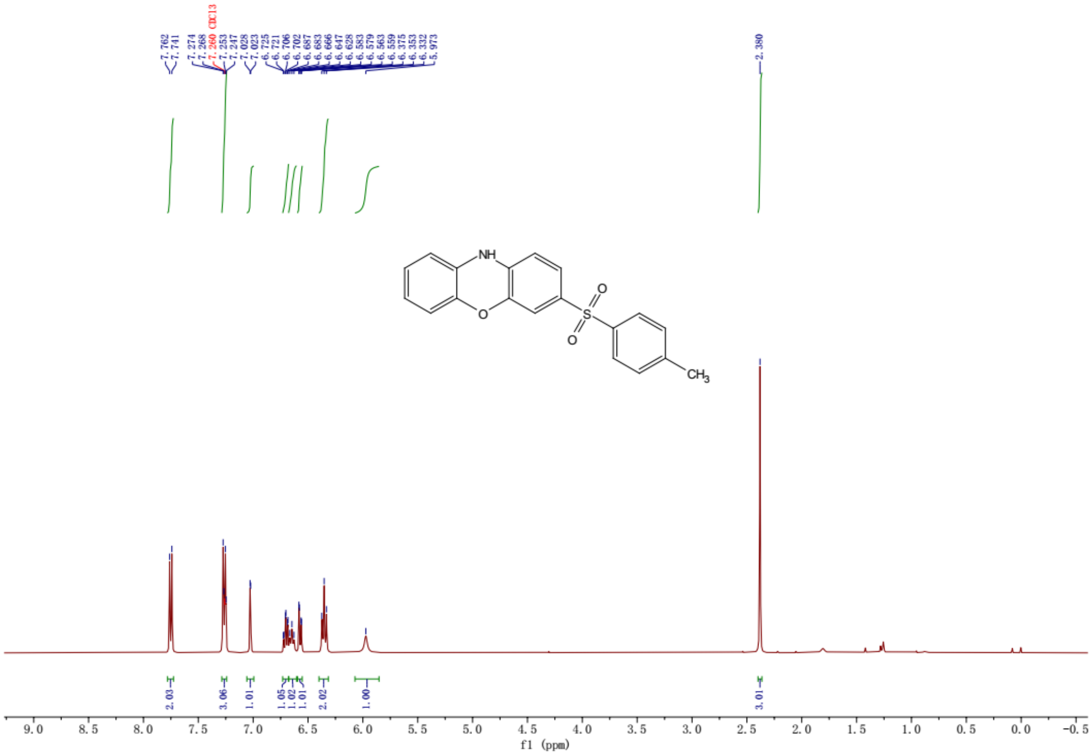
References:

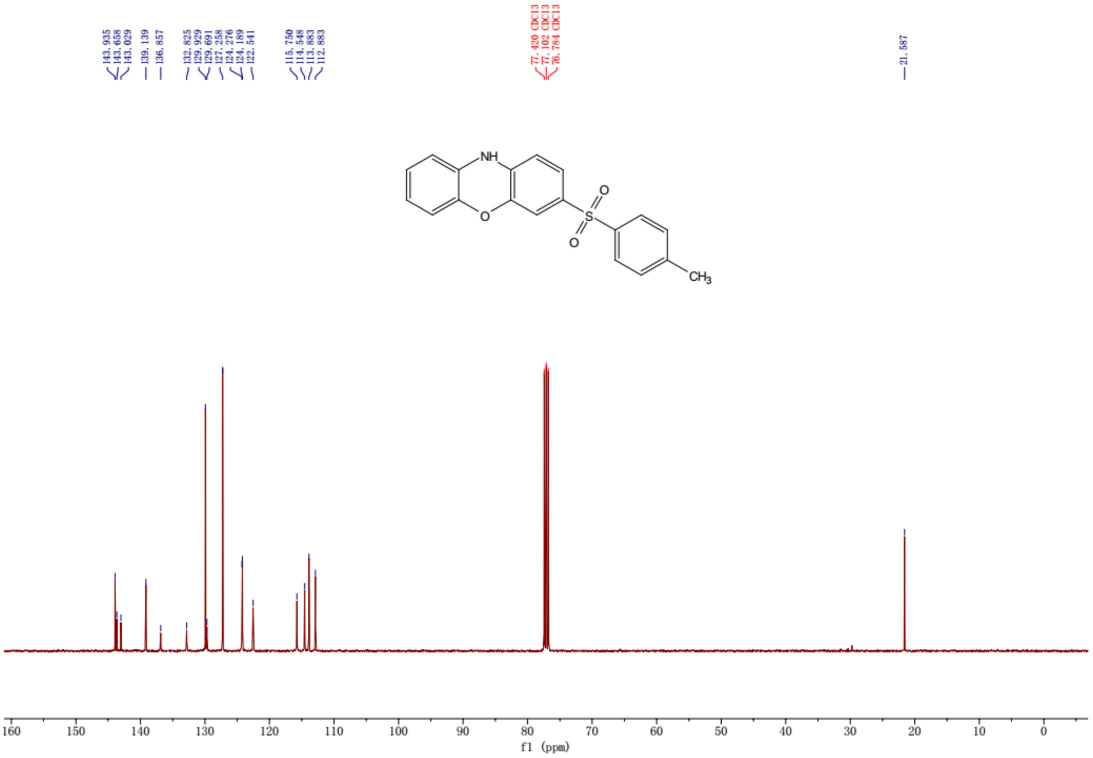
1. M. M. Shaaban, H. M. Ragab, K. Akaji, R. P. McGeary, A. E. A. Bekhit, W. M. Hussein, J. L.

Kurz, B. H. Elwakil, S. A. Bekhit, T. M. Ibrahim, M. A. Mahran, A. A. Bekhit, *Bioorg. Chem*. **2020**, *105*, 104386.

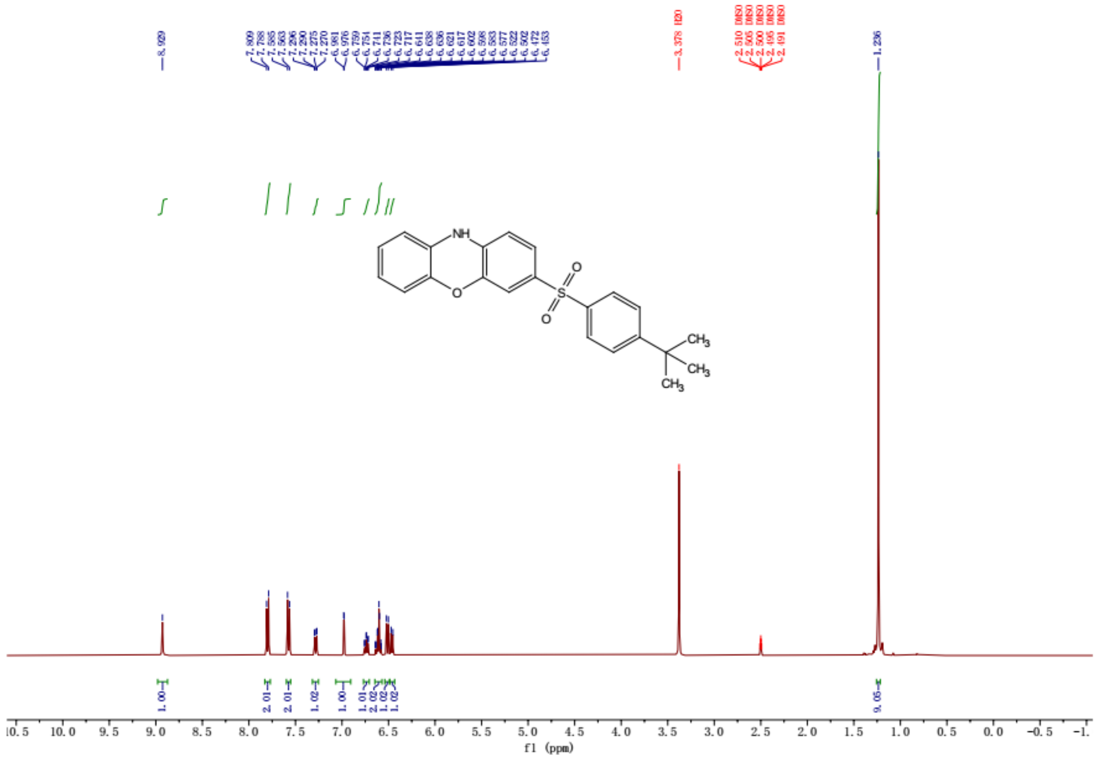
Part II NMR spectra

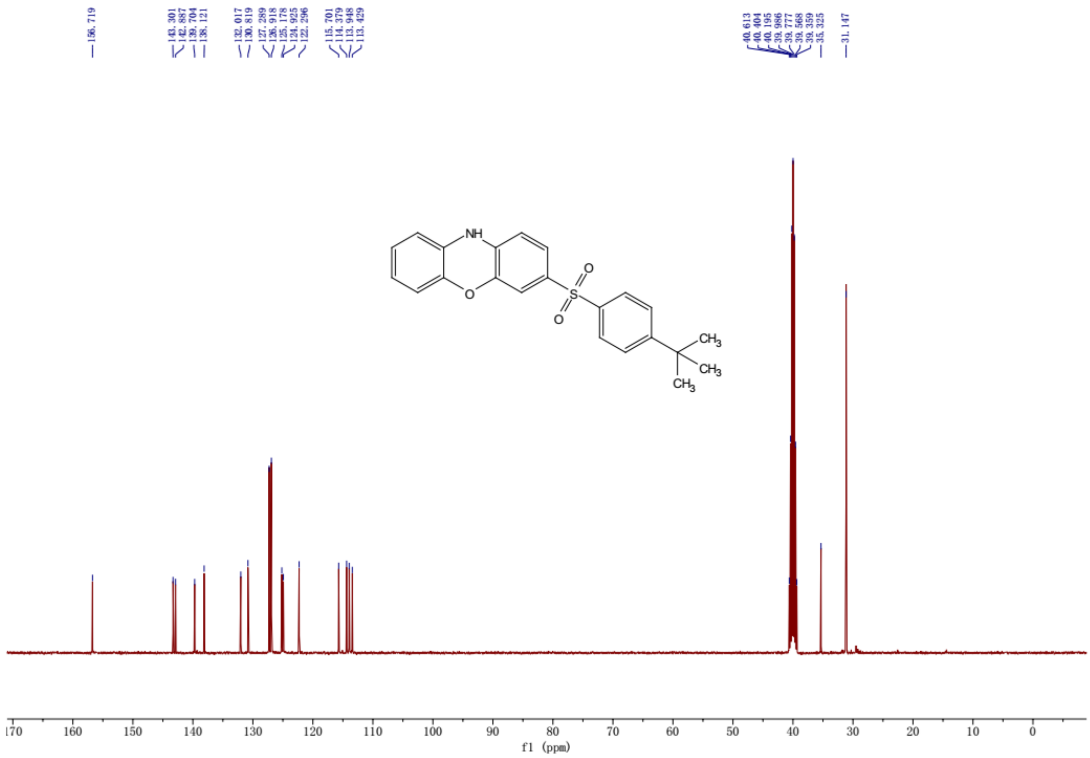
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3a**



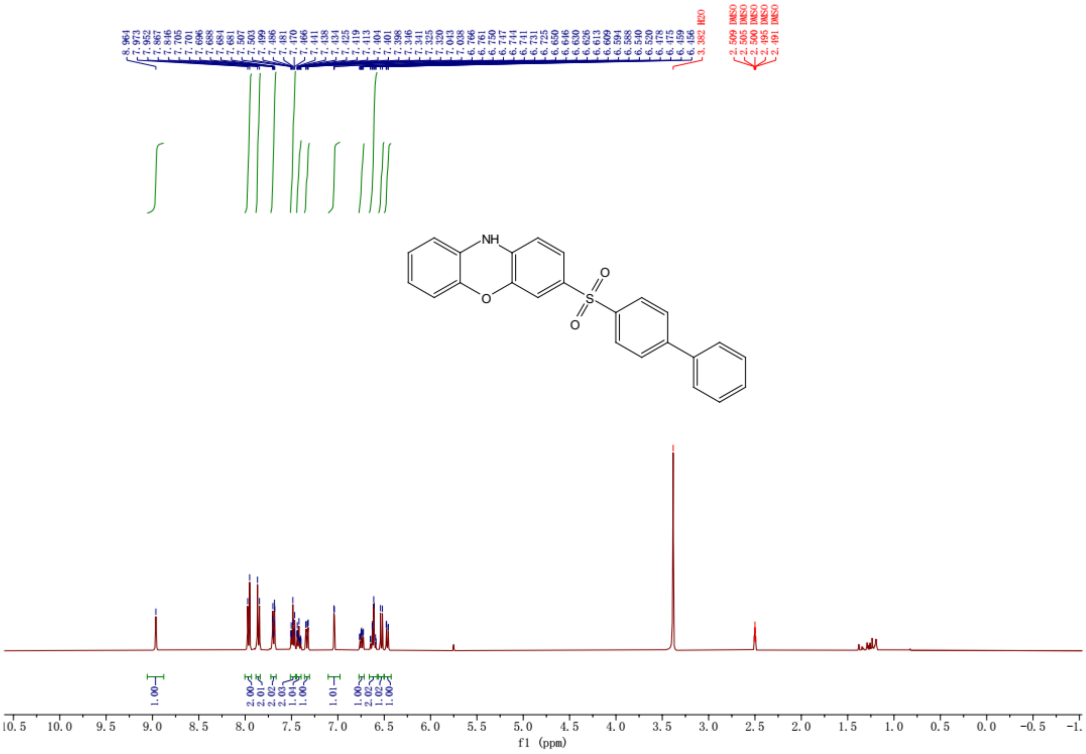


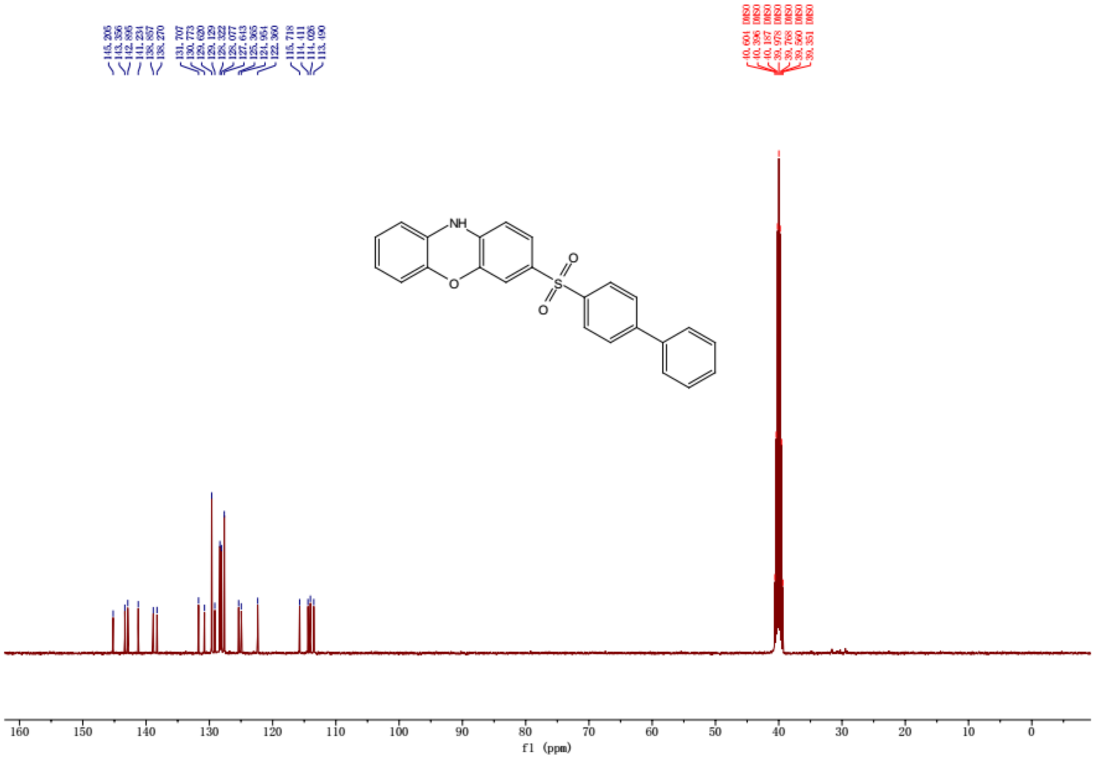
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3b**



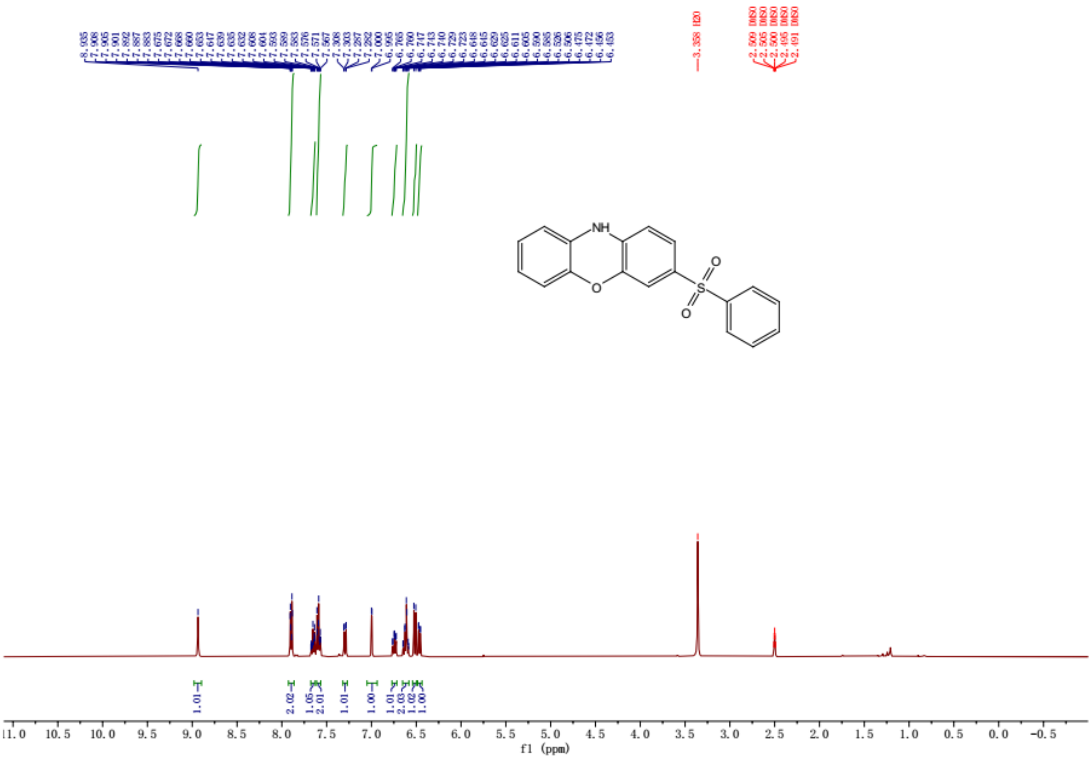


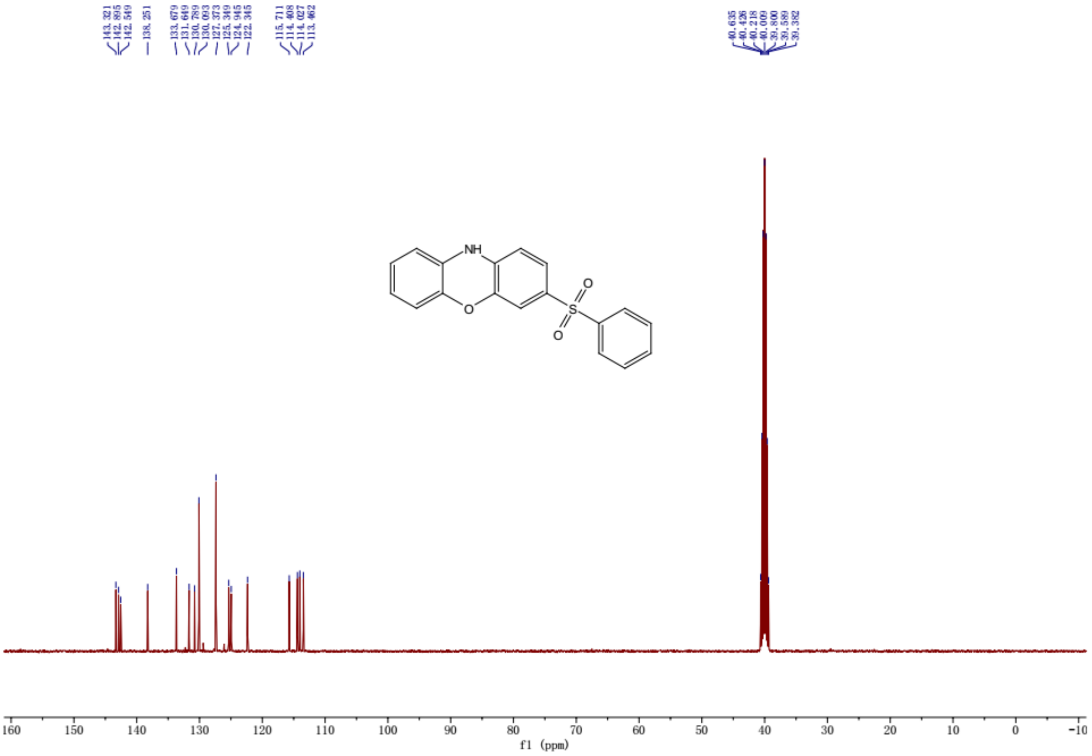
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3c**



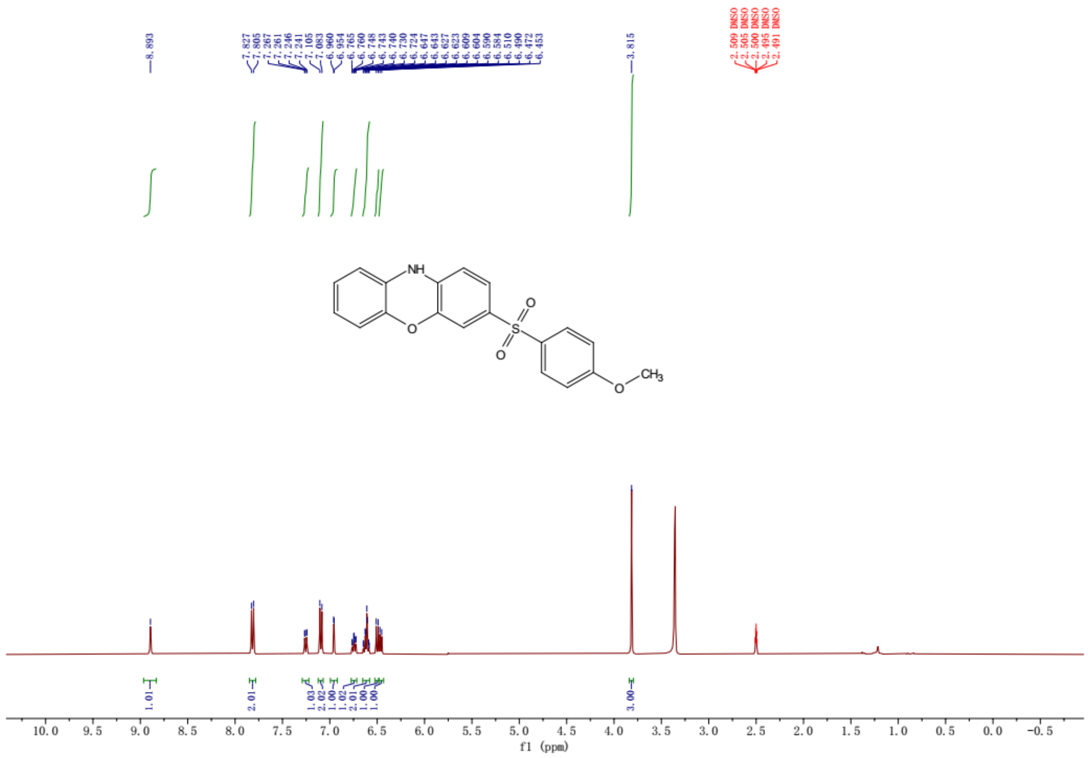


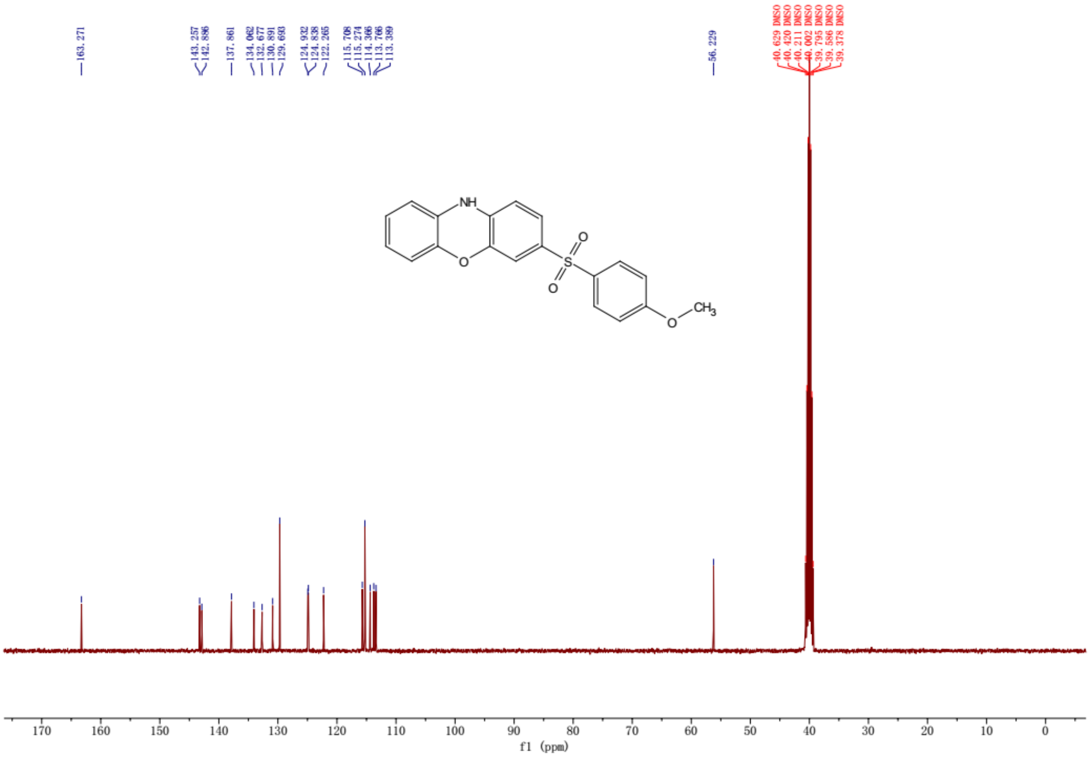
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3d**



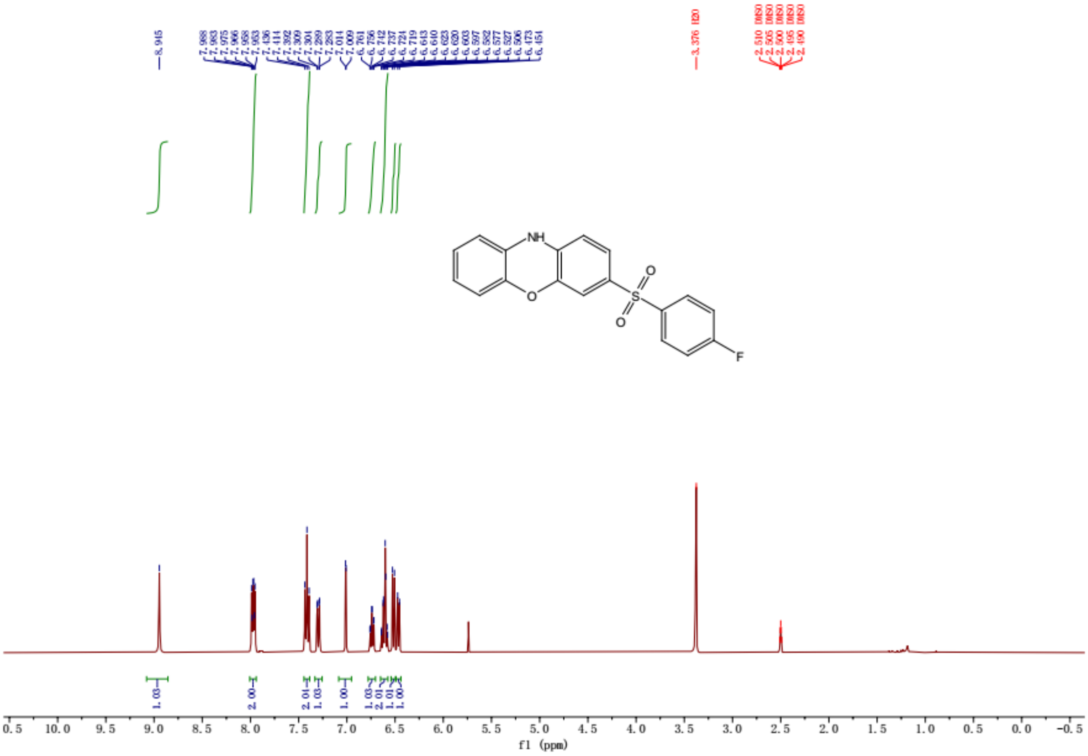


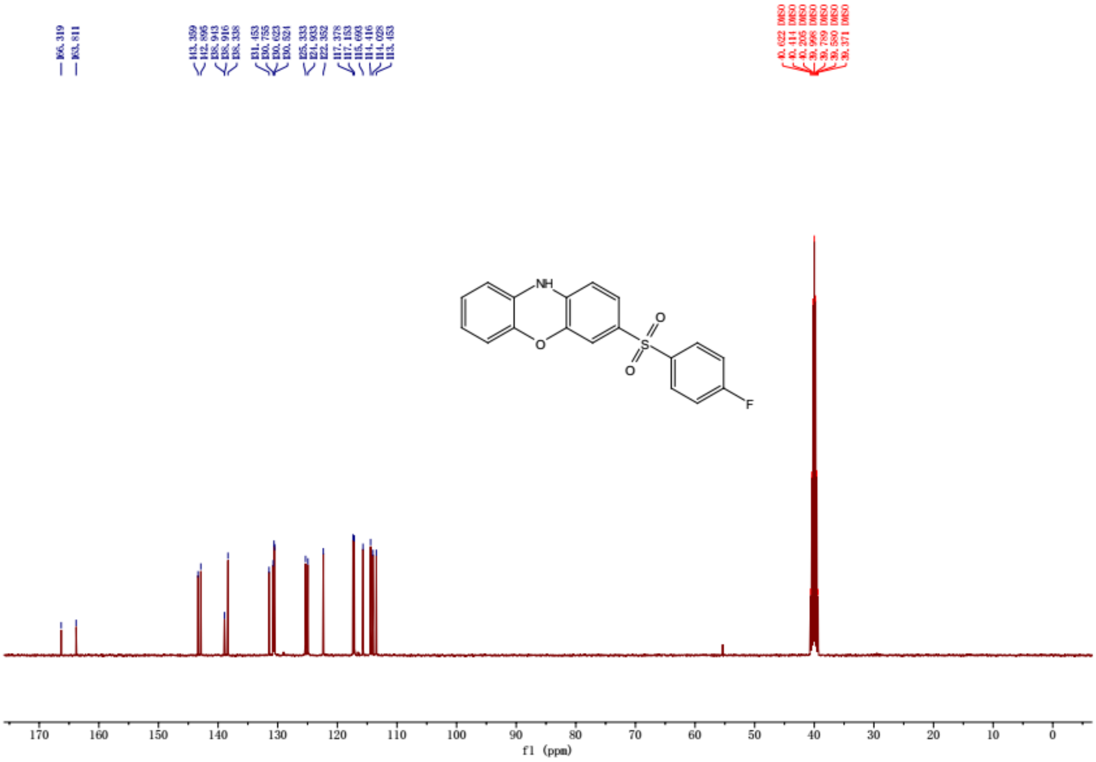
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3e**



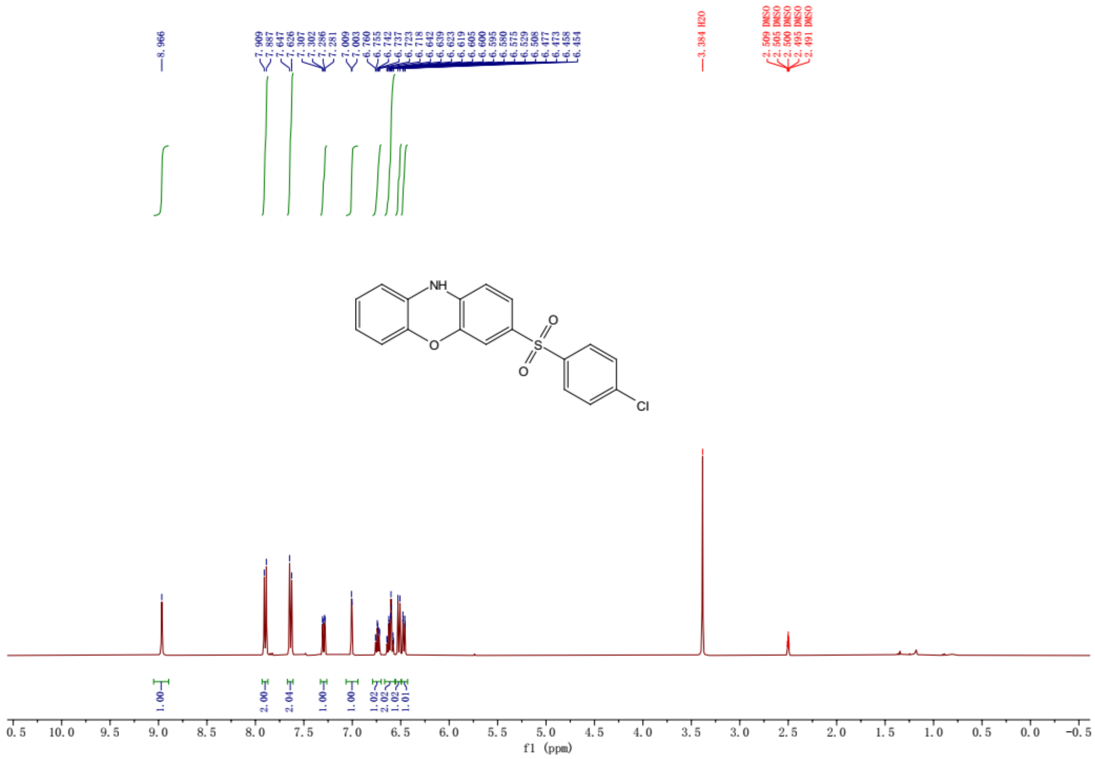


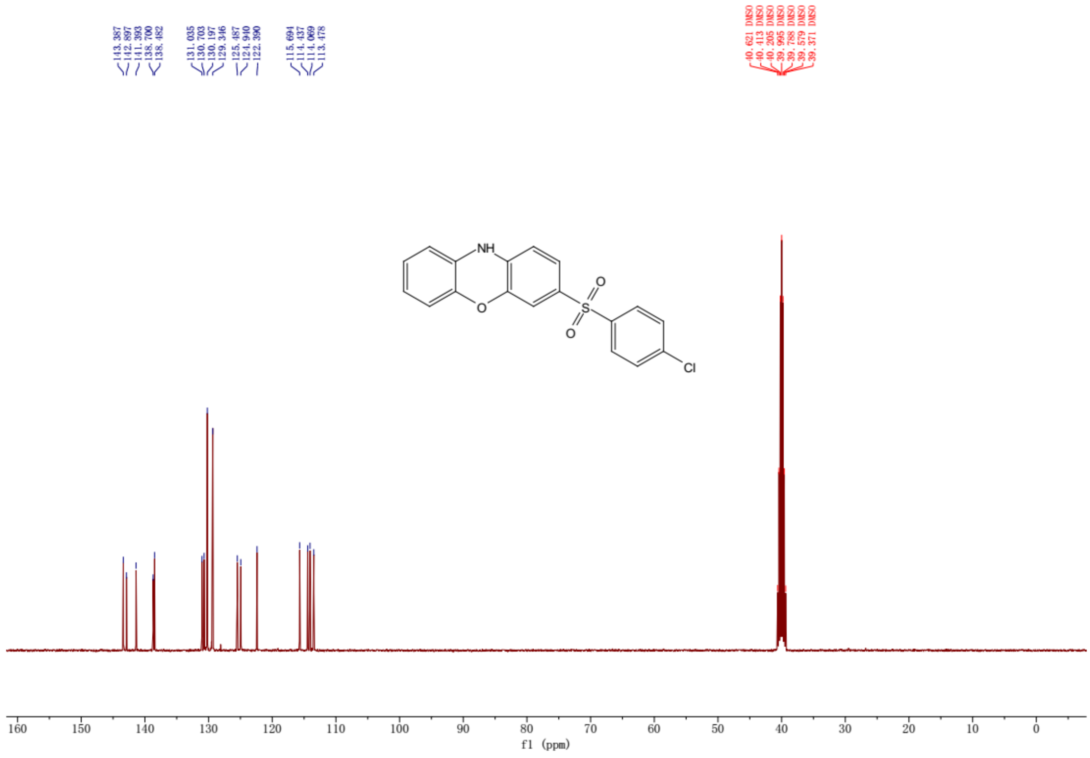
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3f**



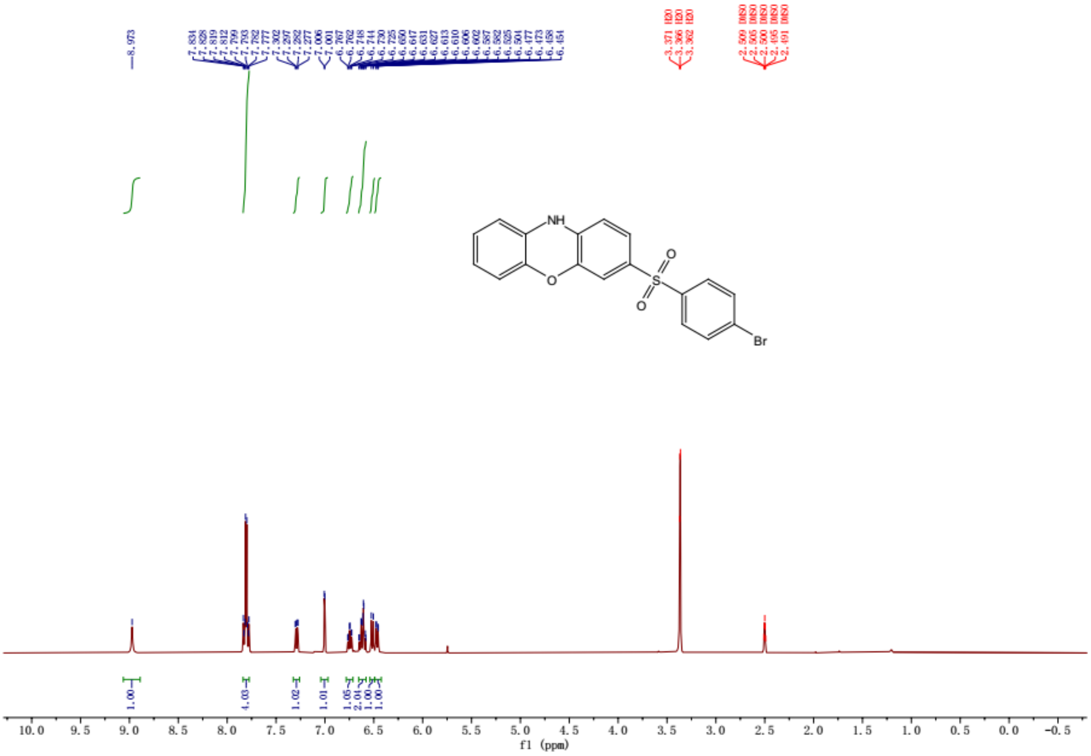


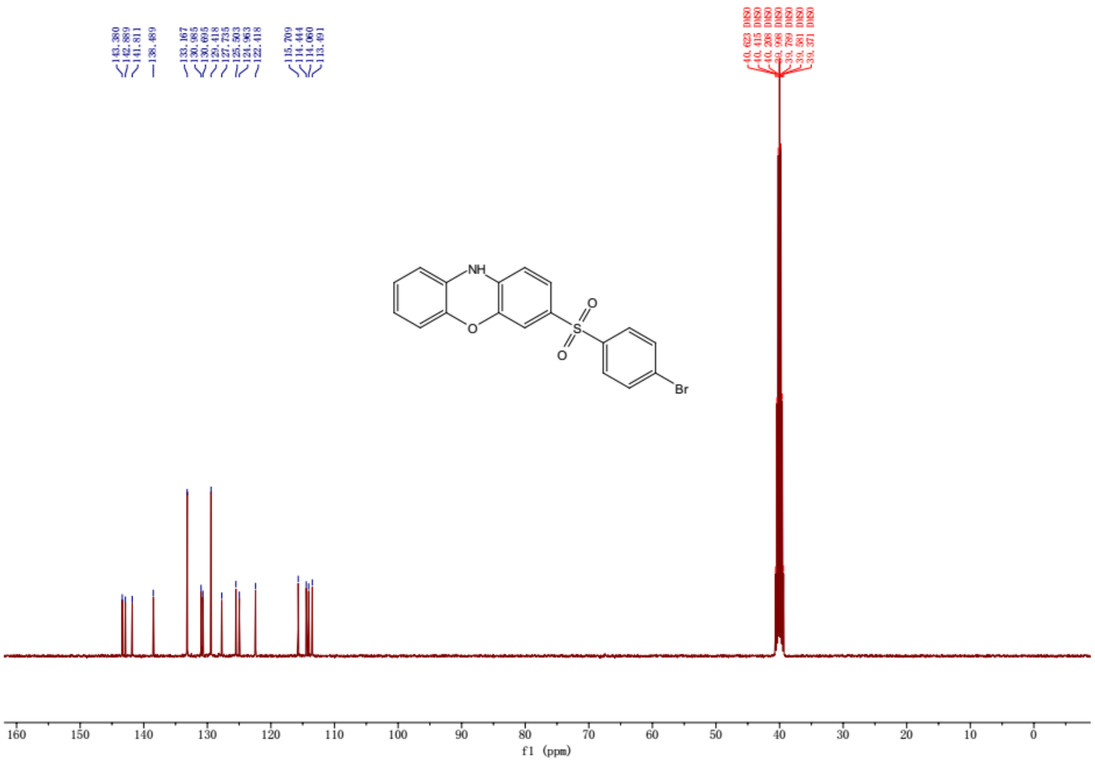
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3g**



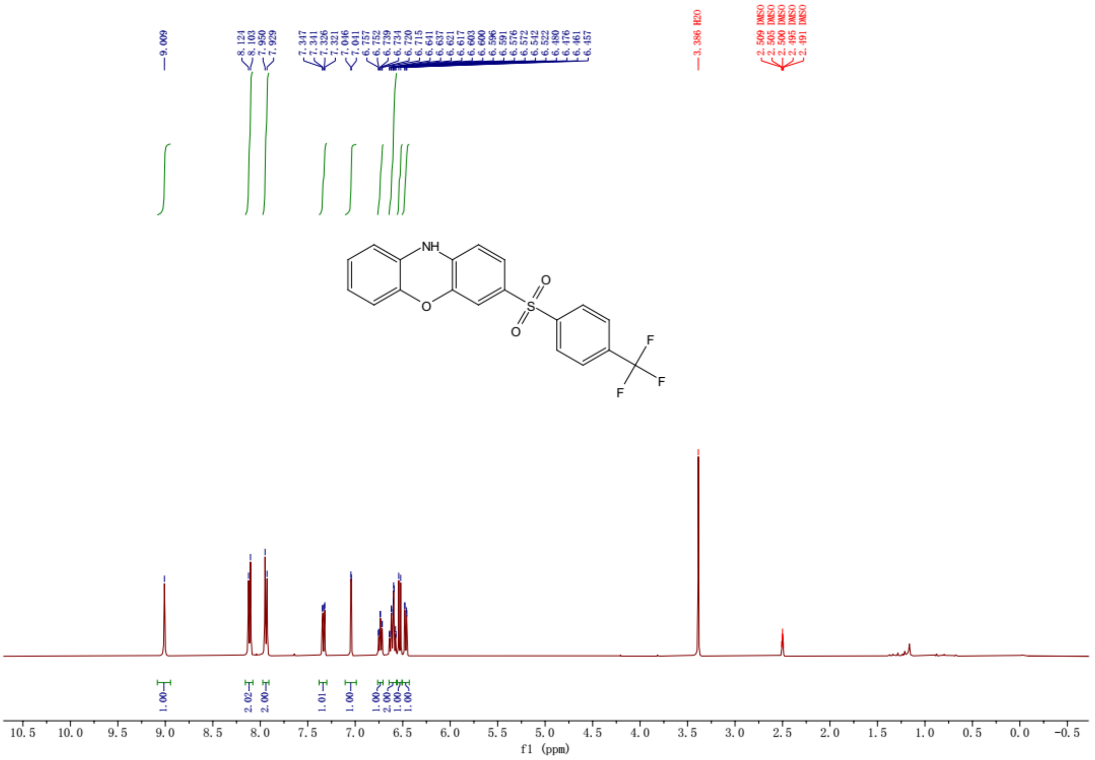


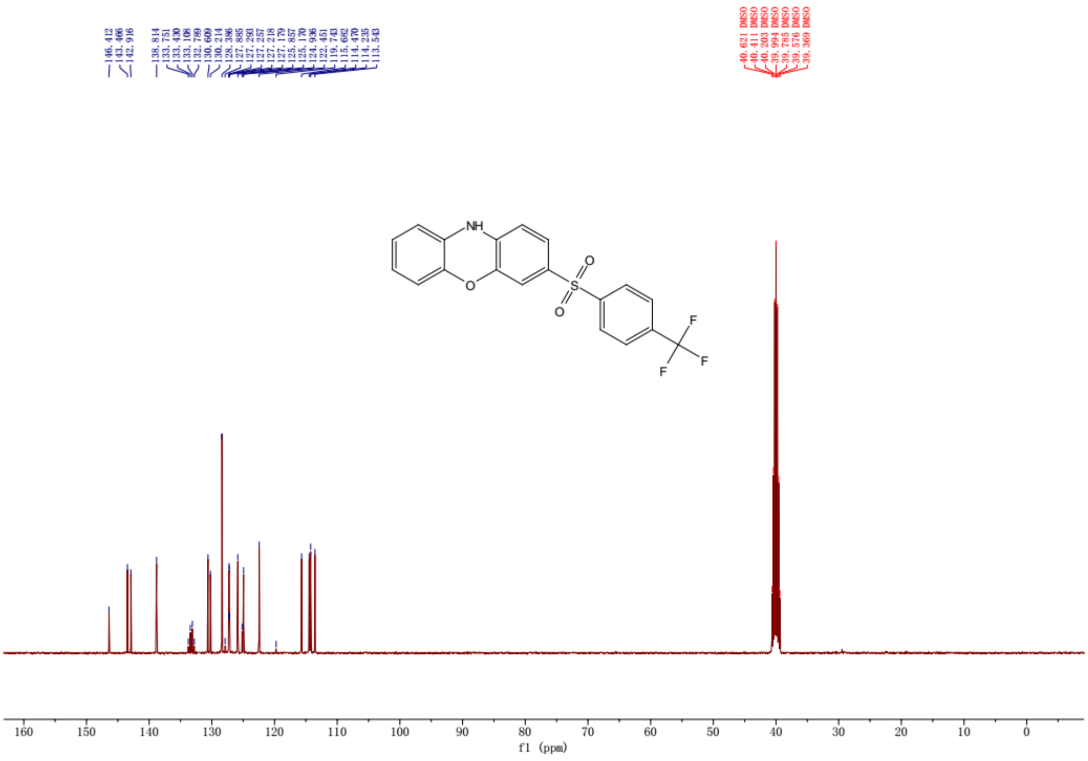
^{1}H NMR (400 MHz, DMSO-d_6) and $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **3h**



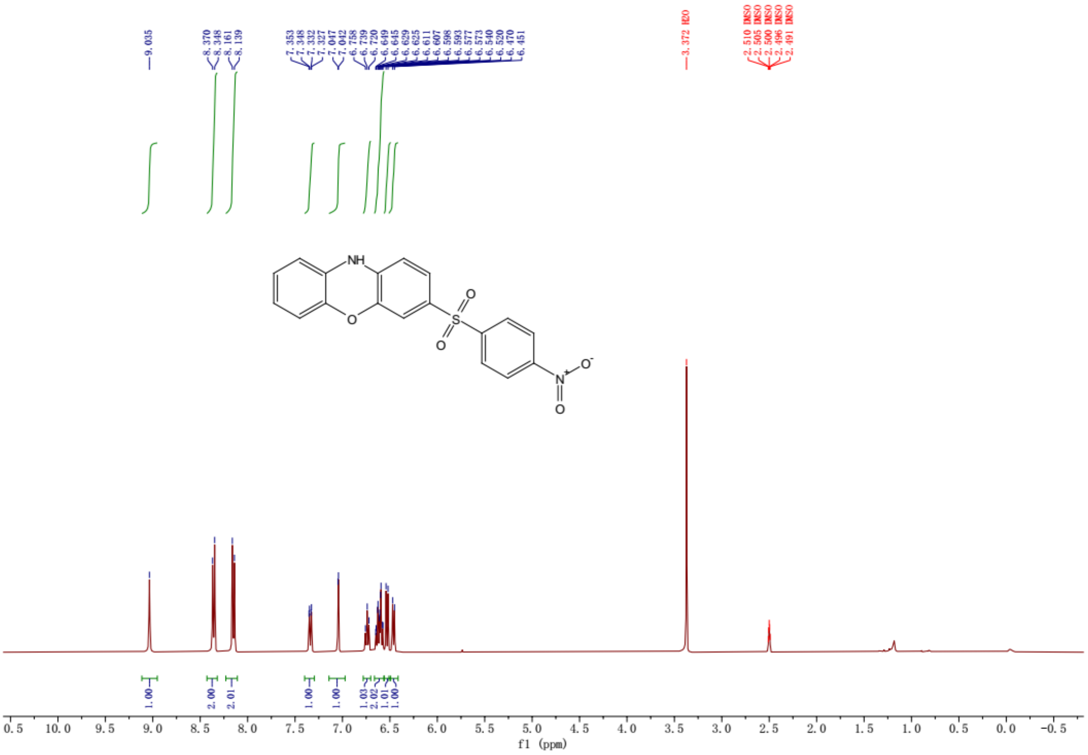


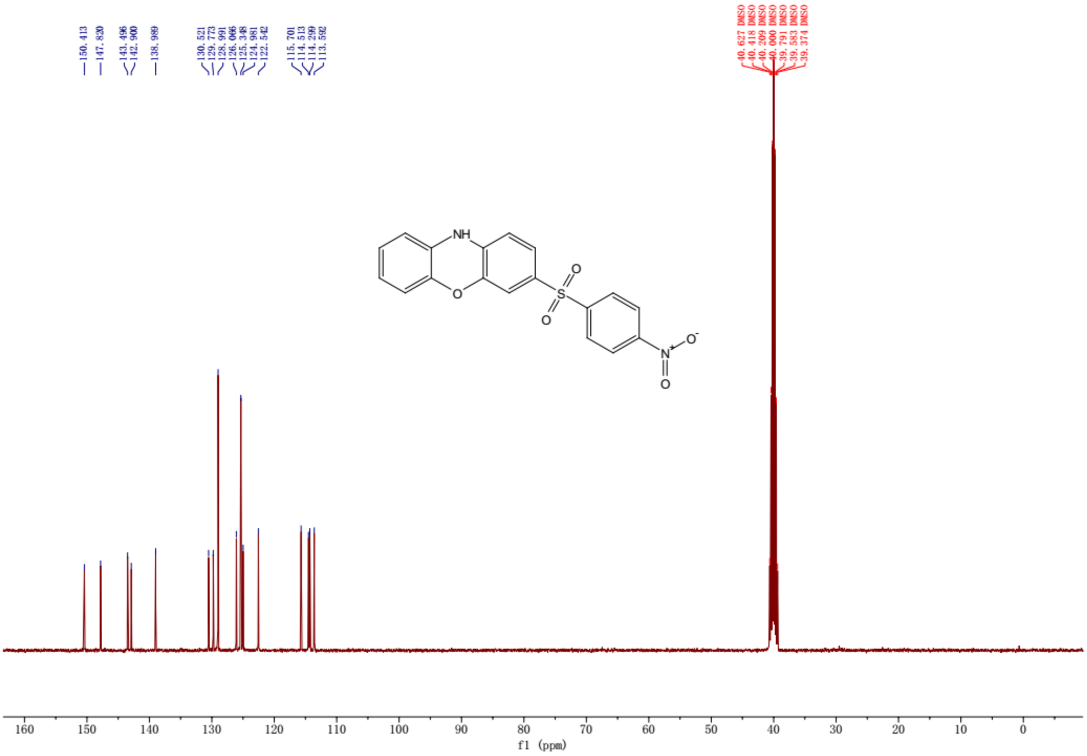
^{1}H NMR (400 MHz, DMSO-d_6) and $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **3i**



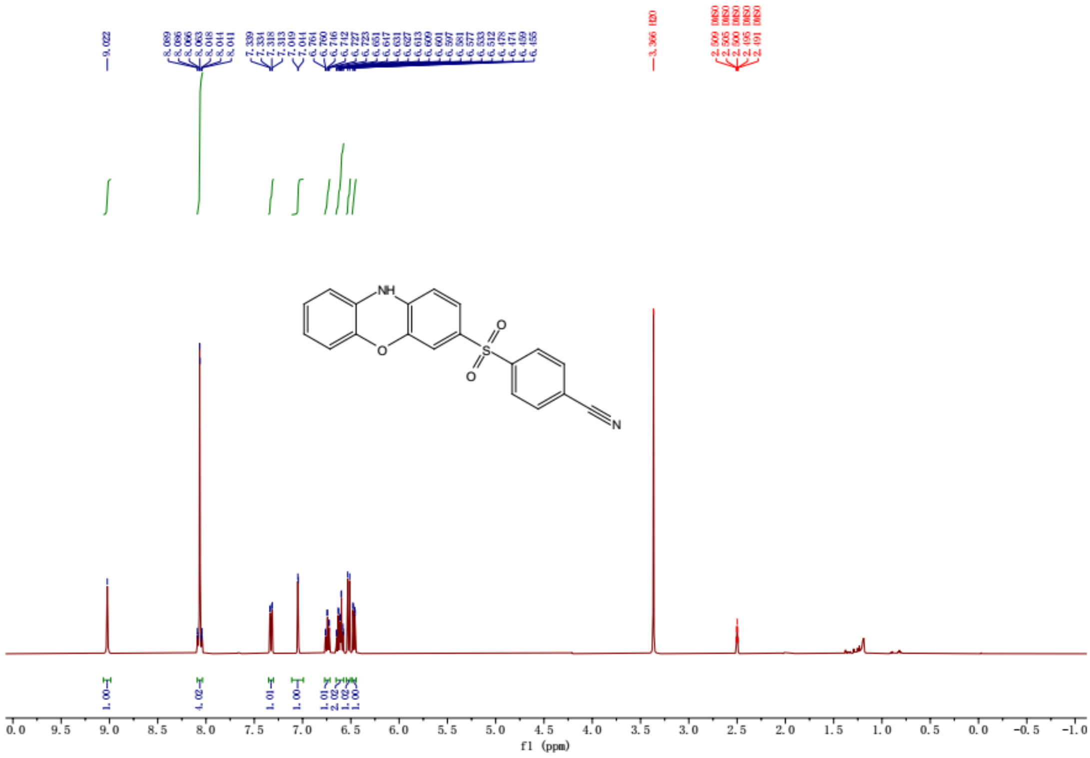


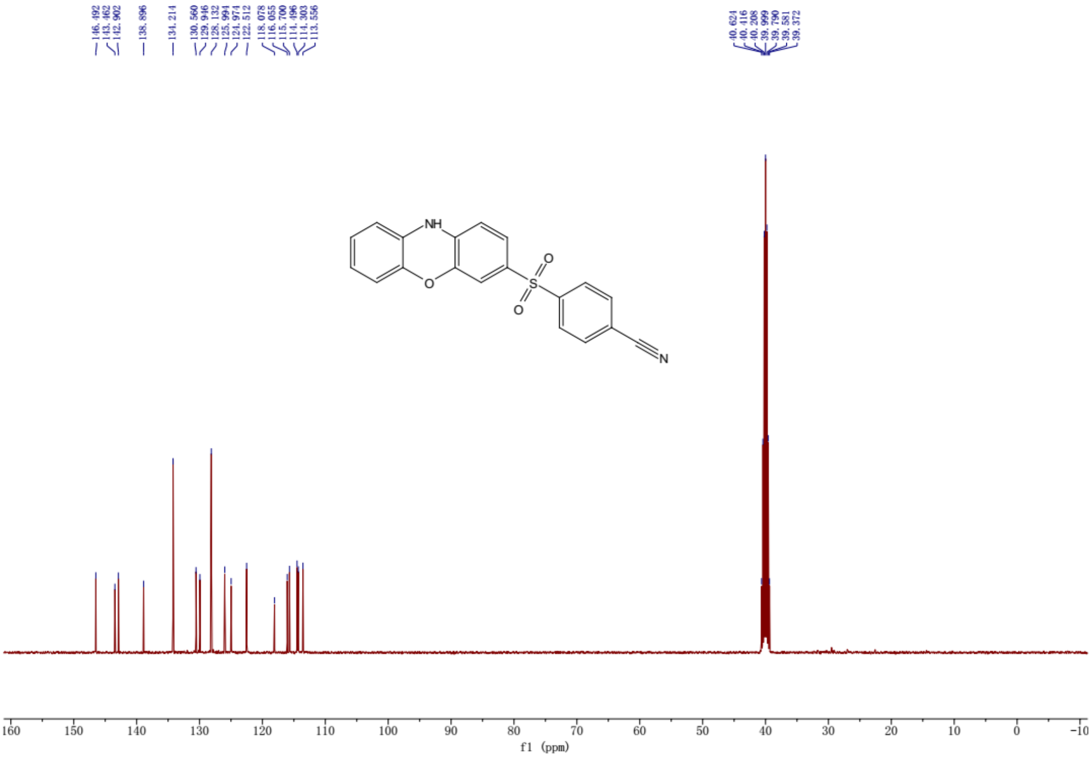
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3j**



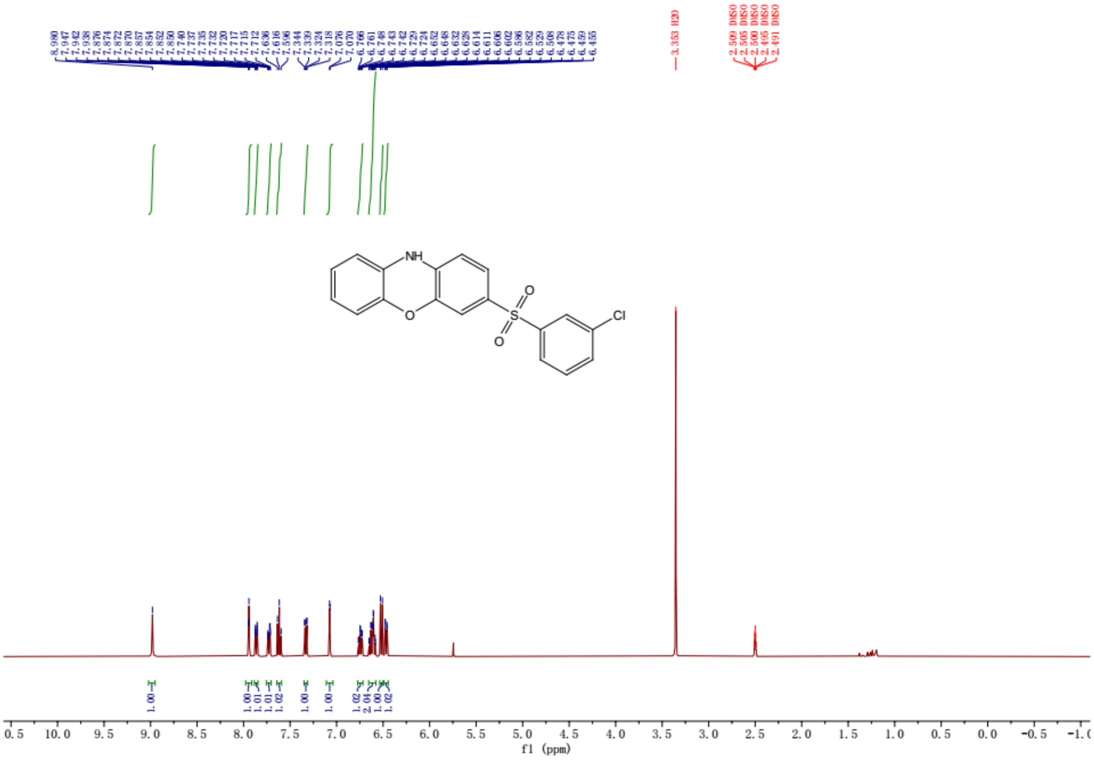


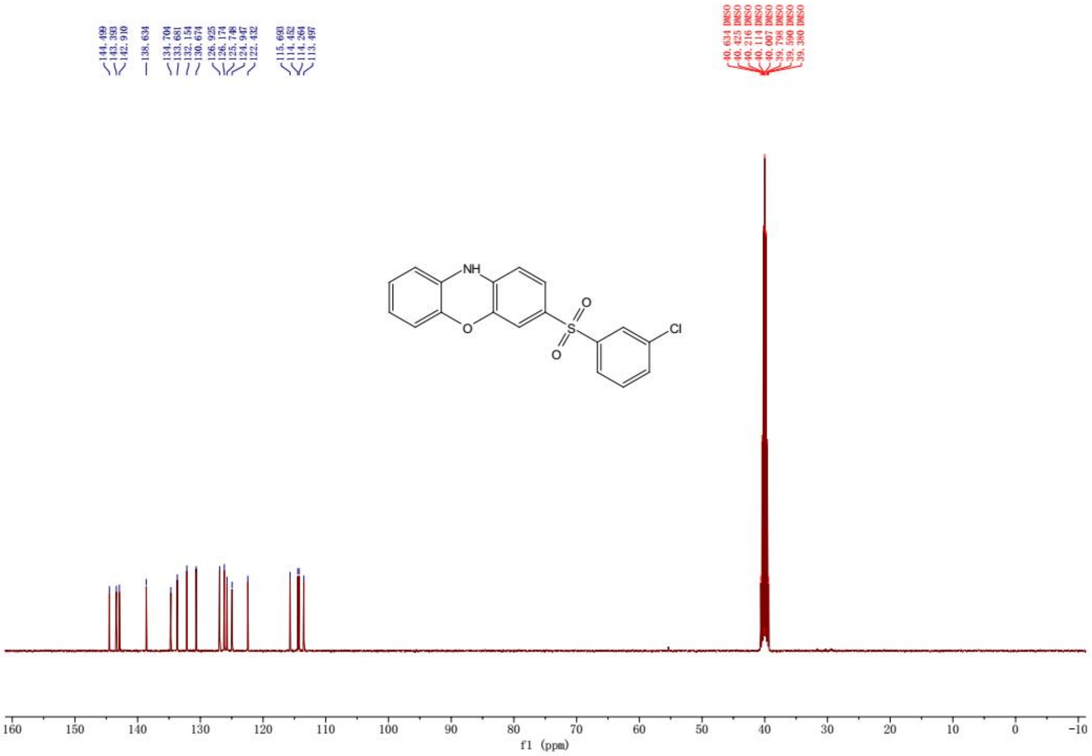
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3k**



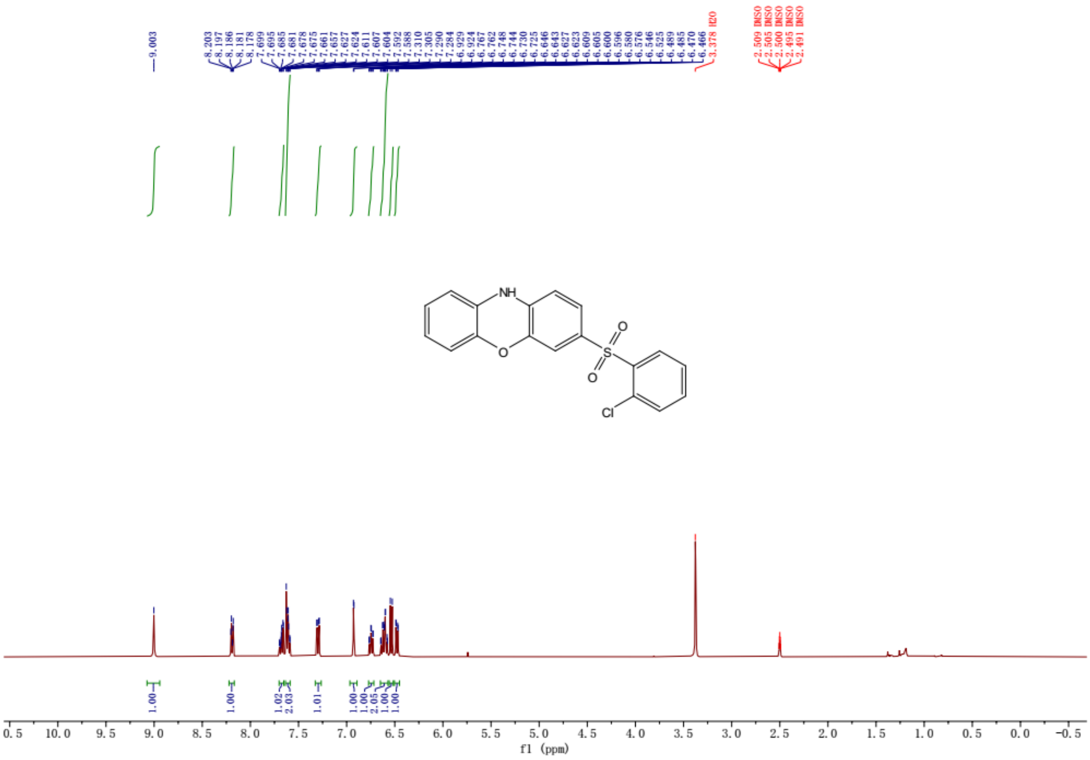


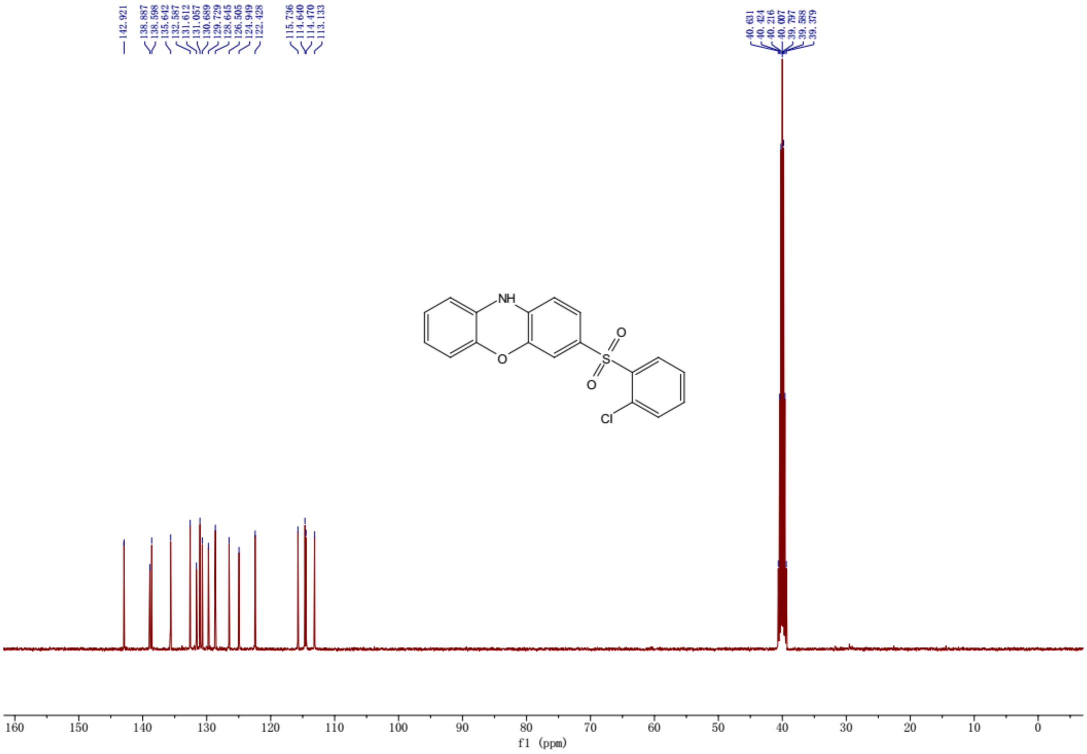
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3l**



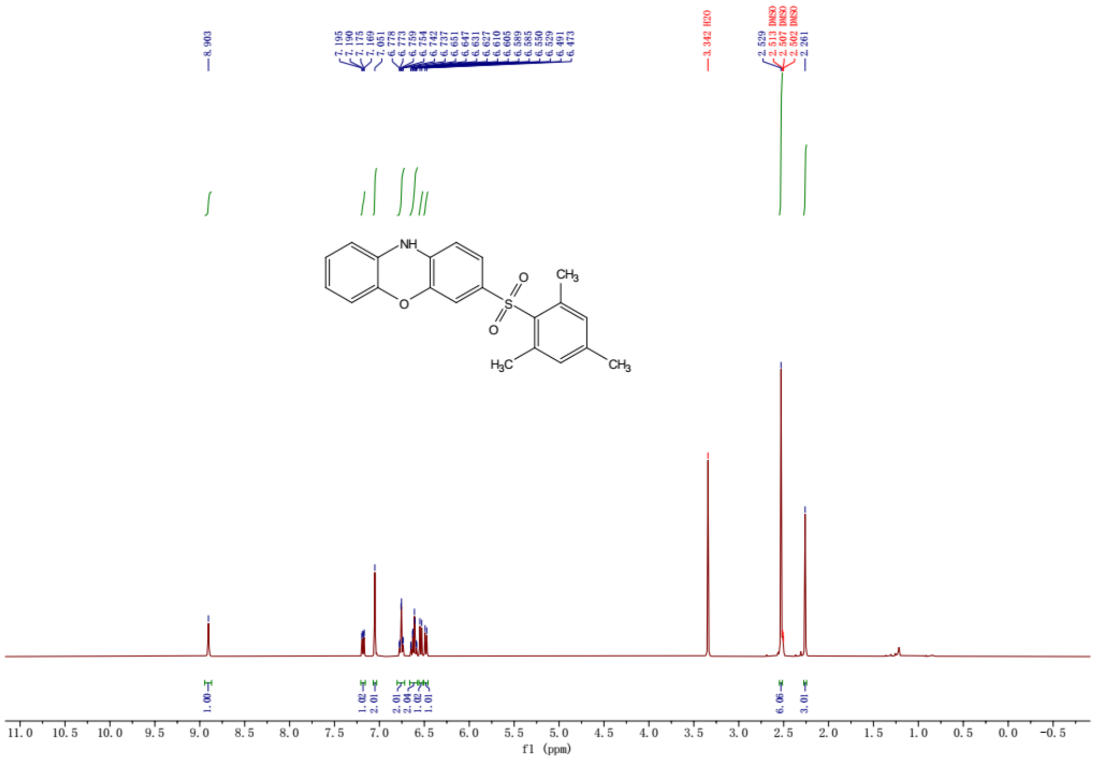


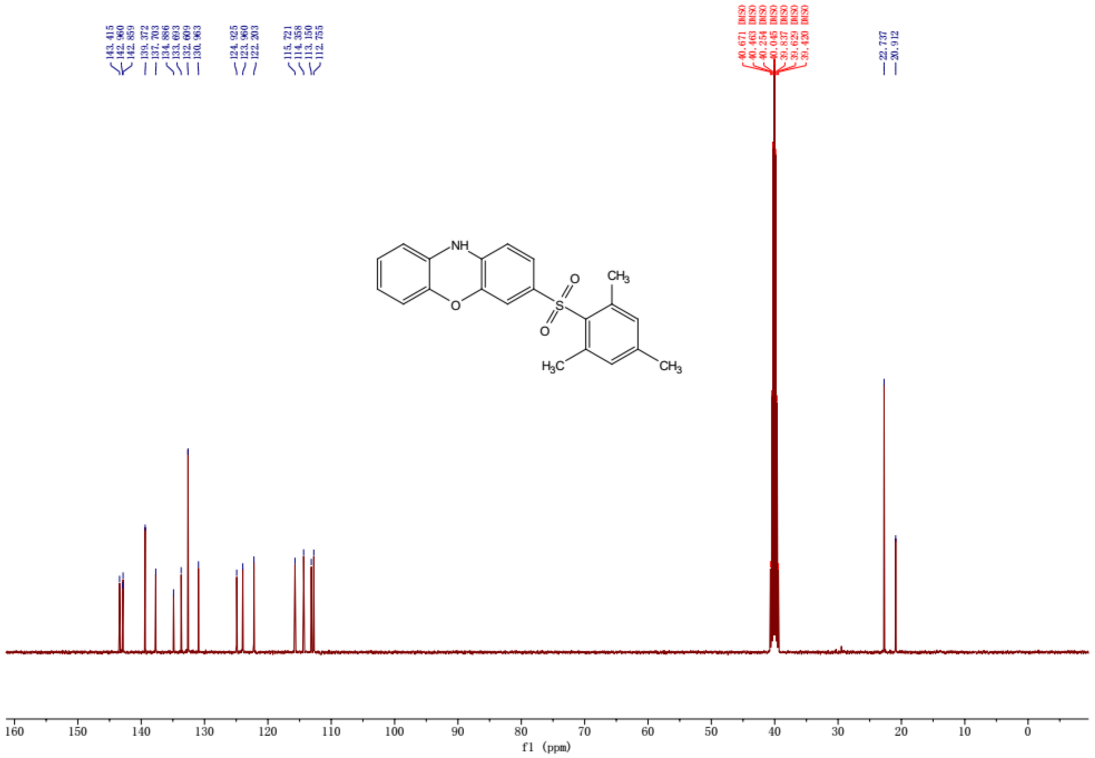
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3m**



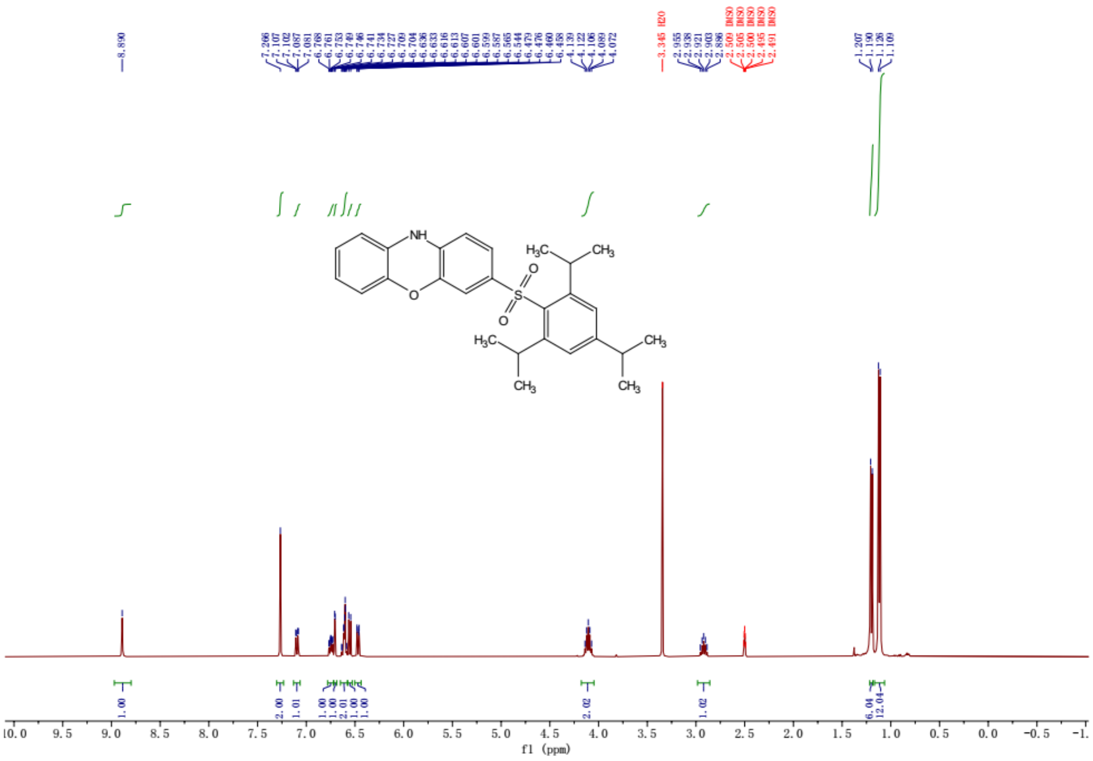


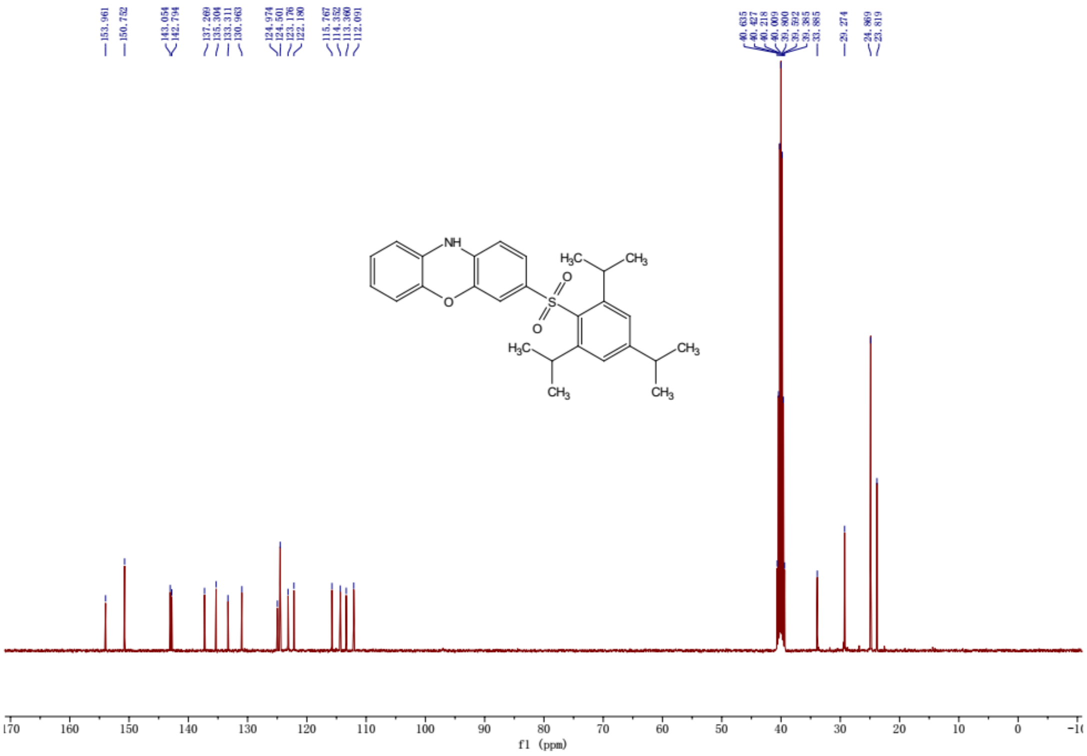
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3n**



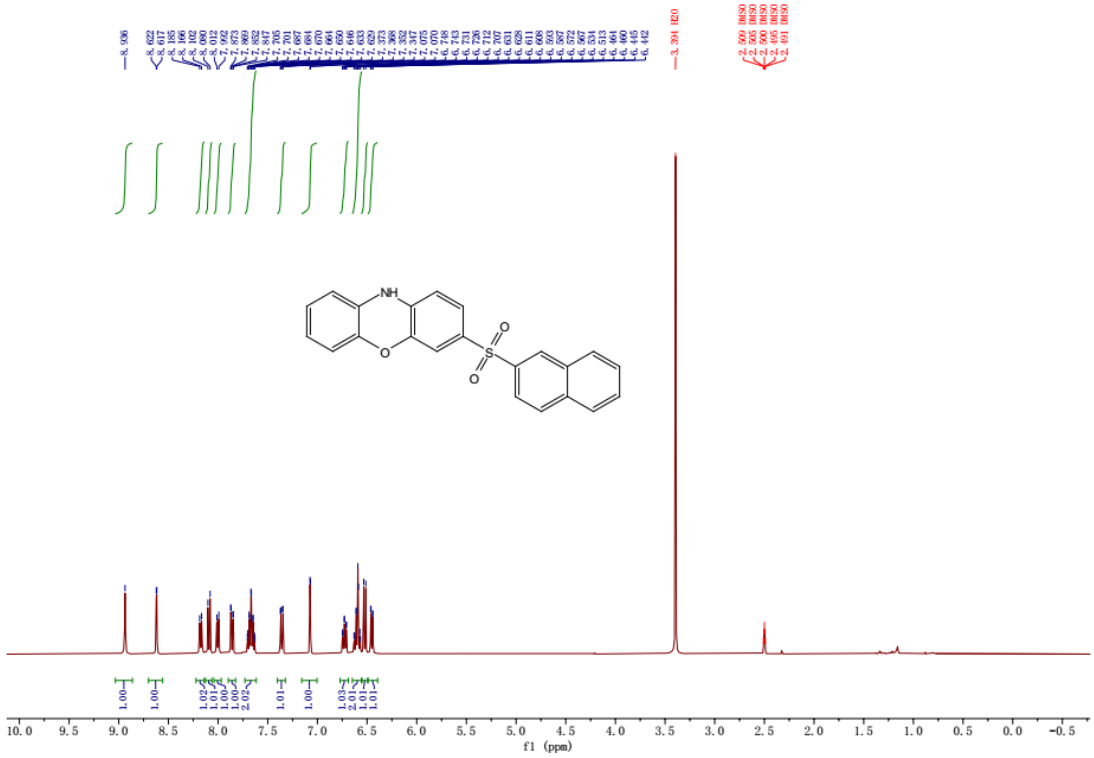


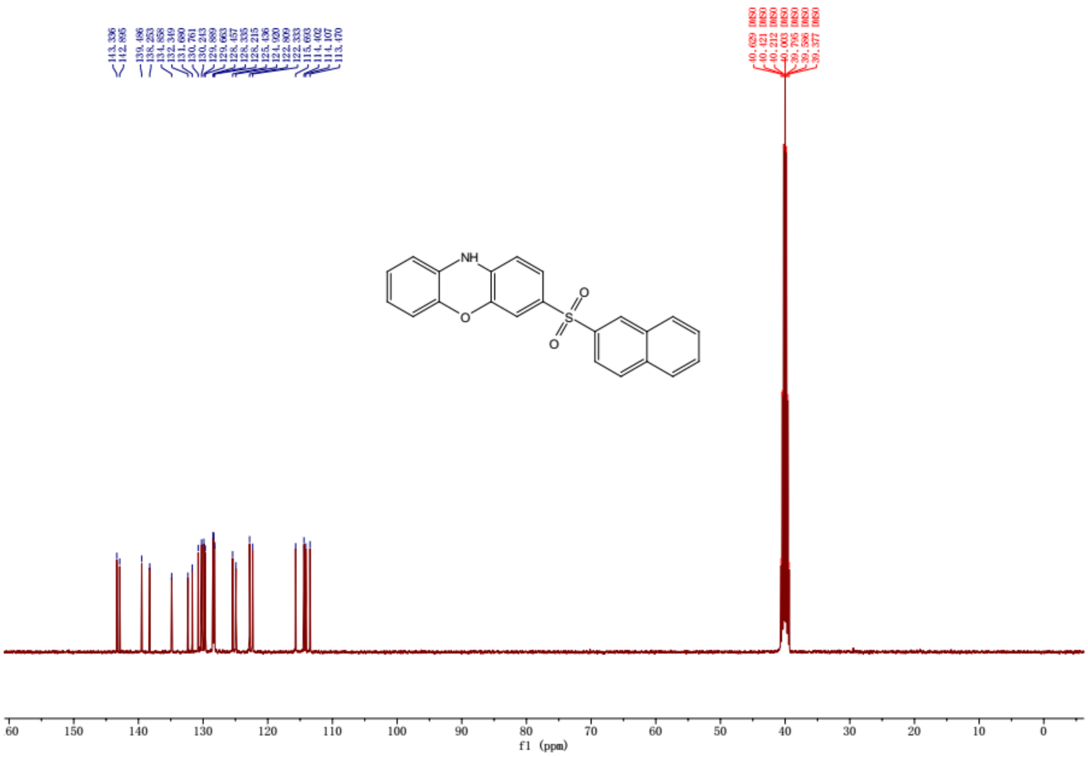
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3o**



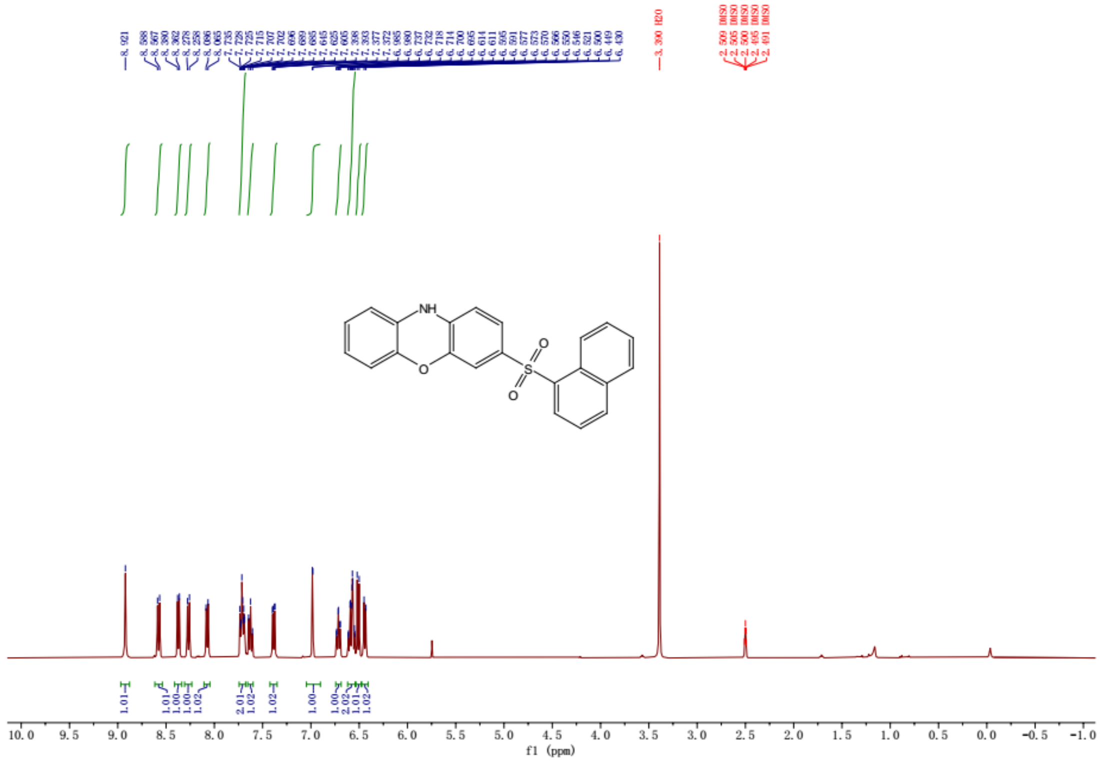


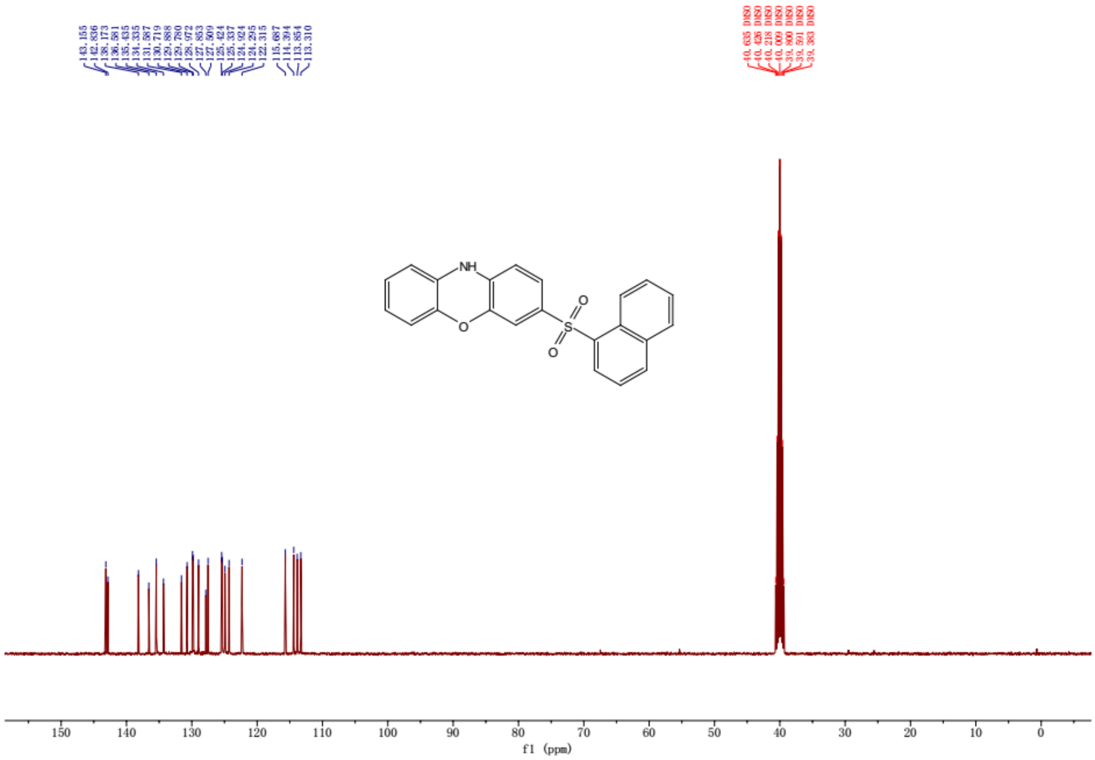
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3p**



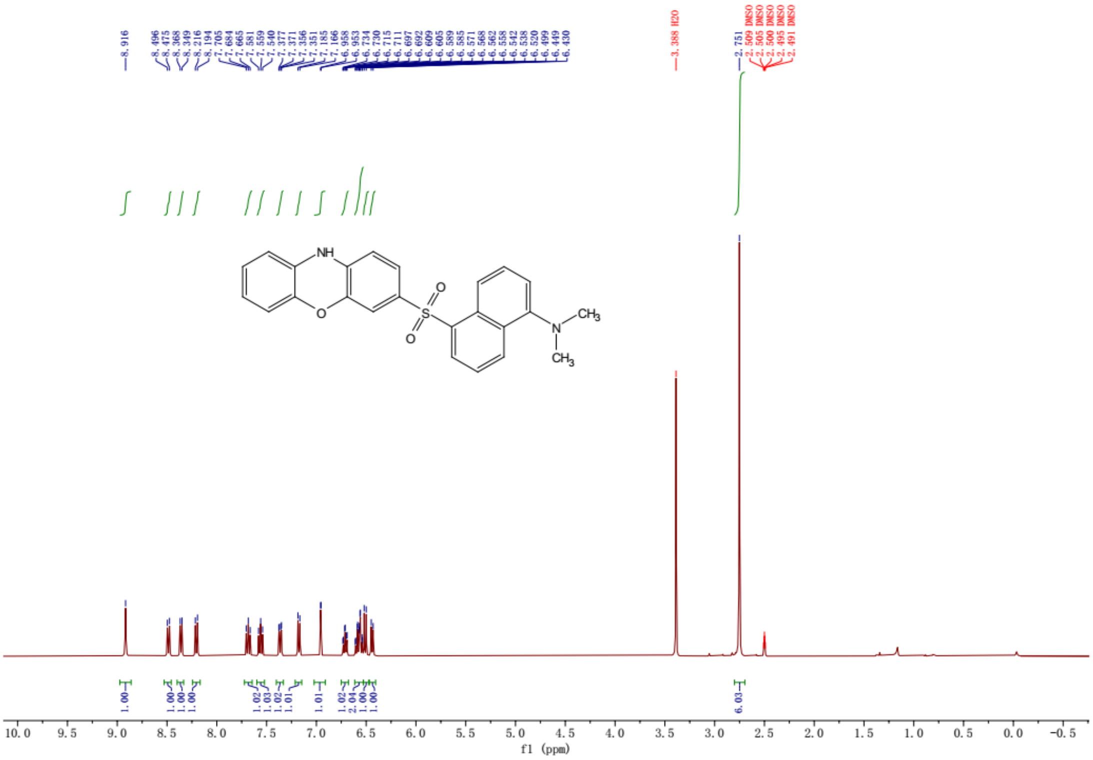


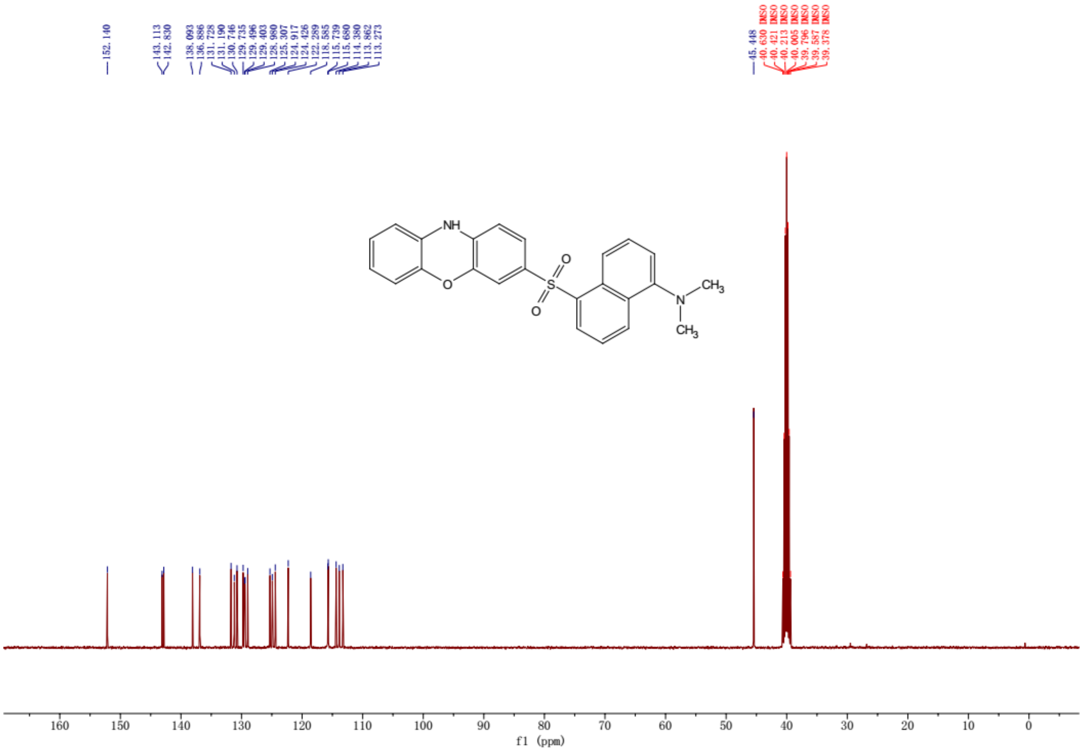
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3q**



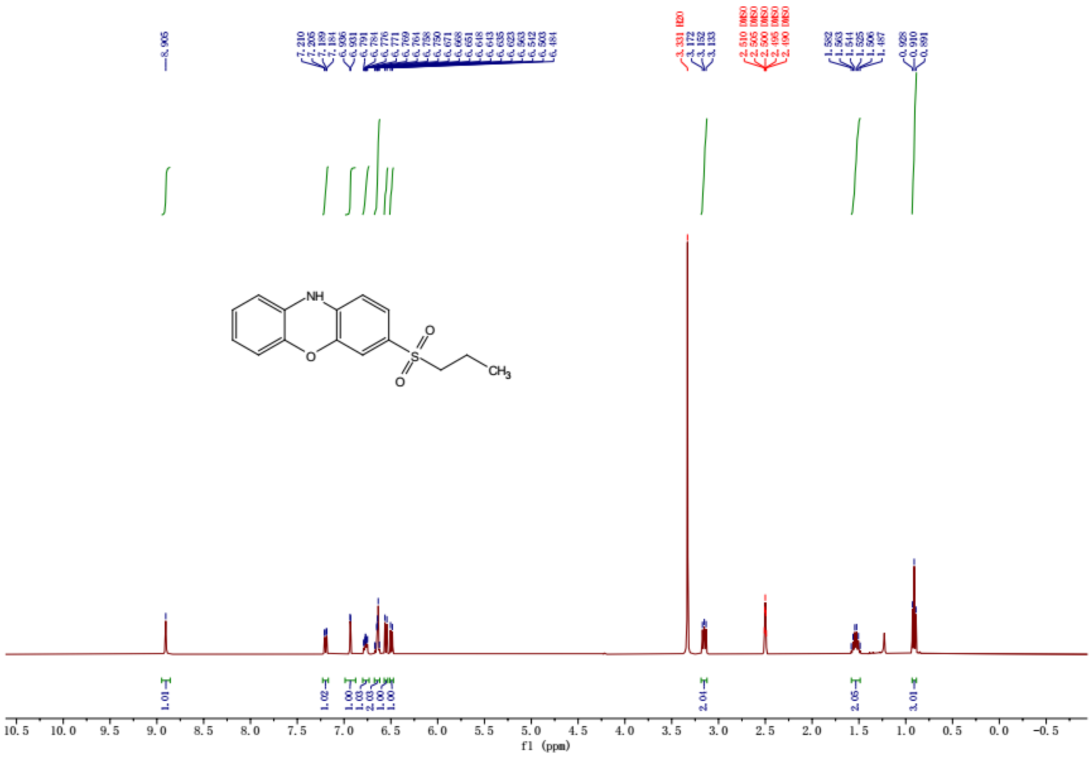


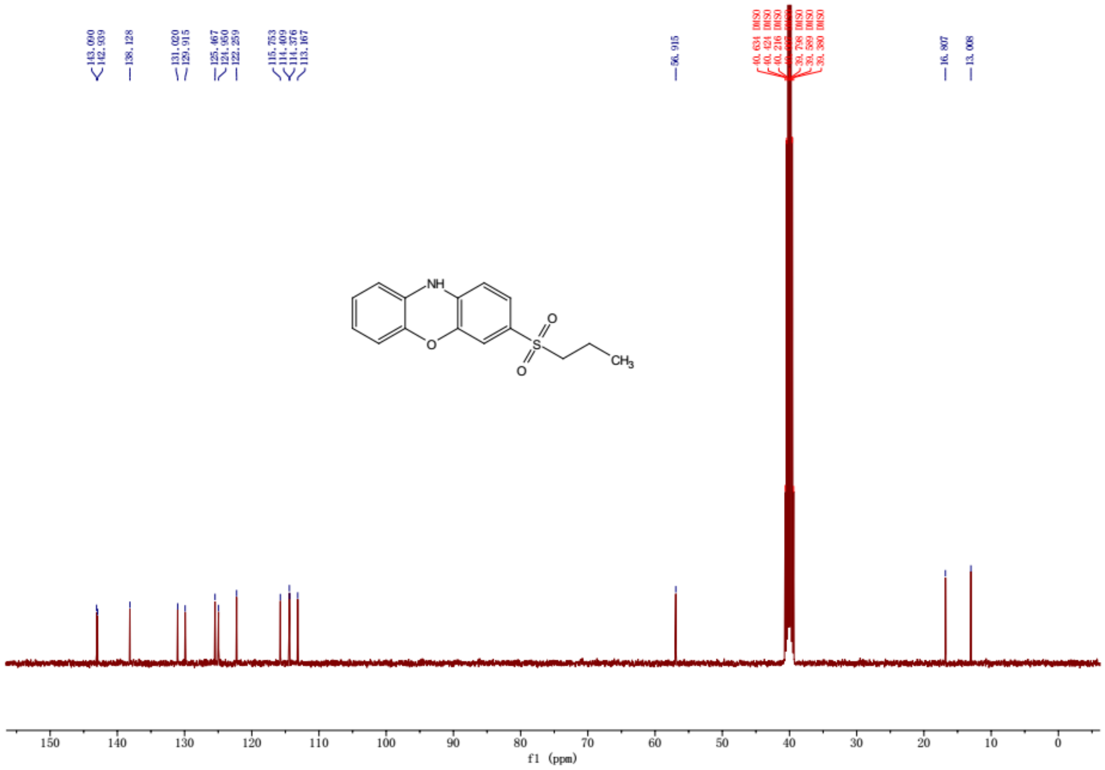
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3r**



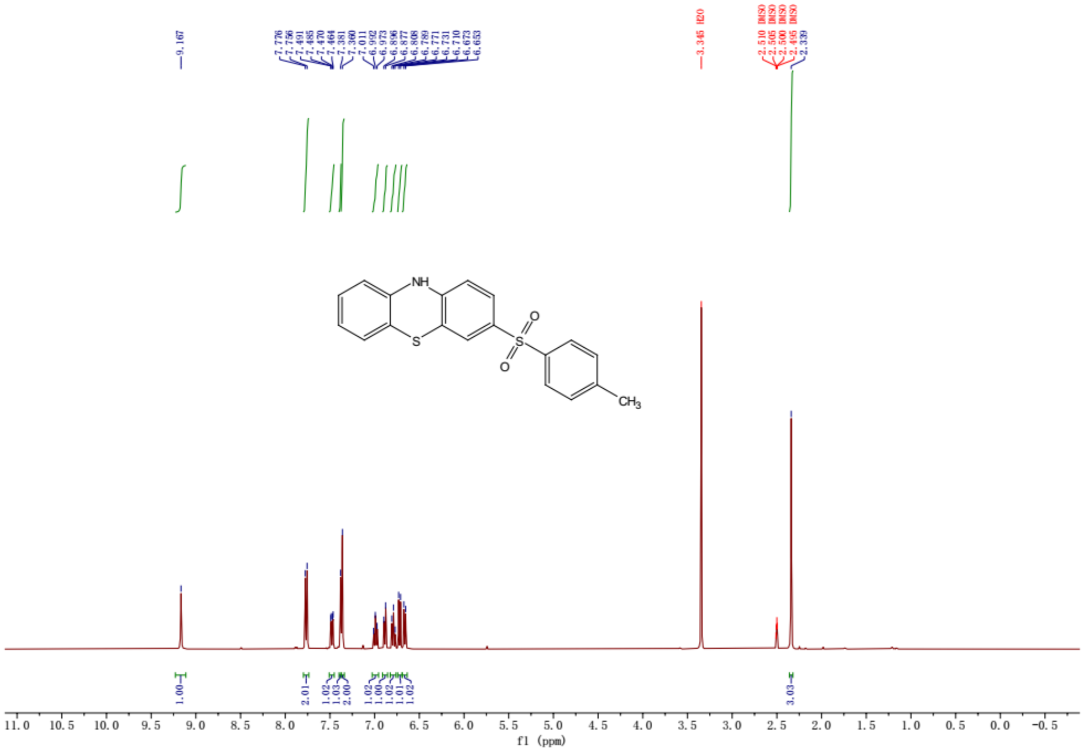


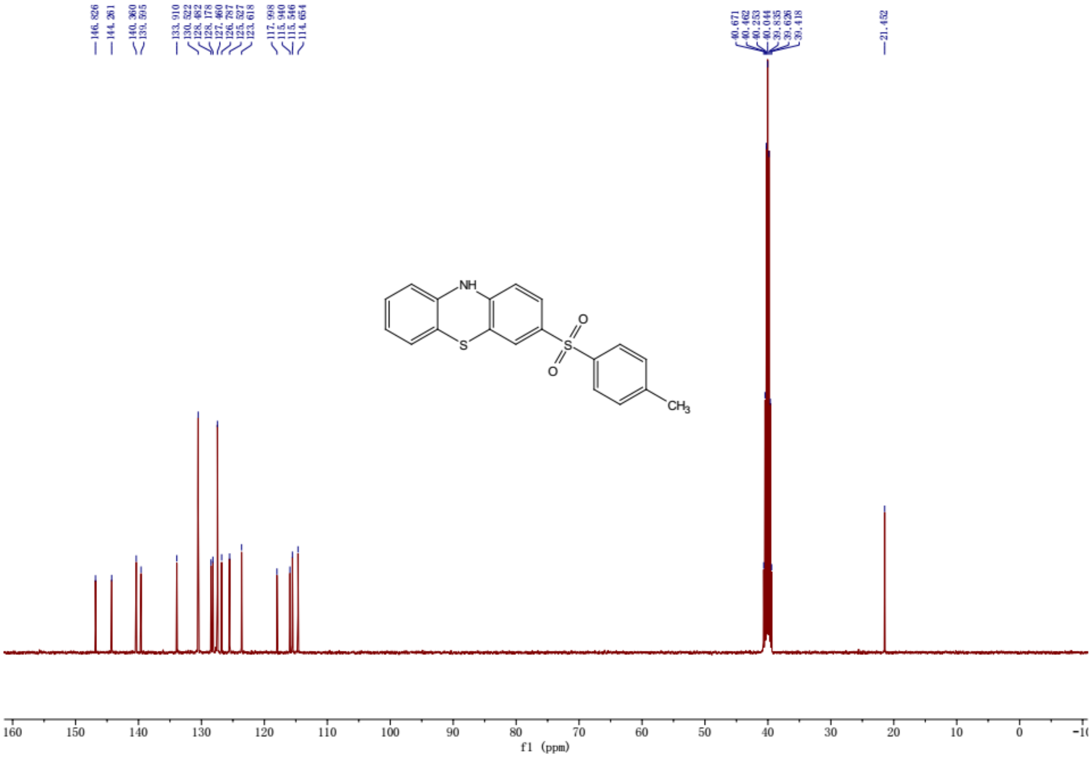
^{1}H NMR (400 MHz, DMSO-d_6) and $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of **3s**



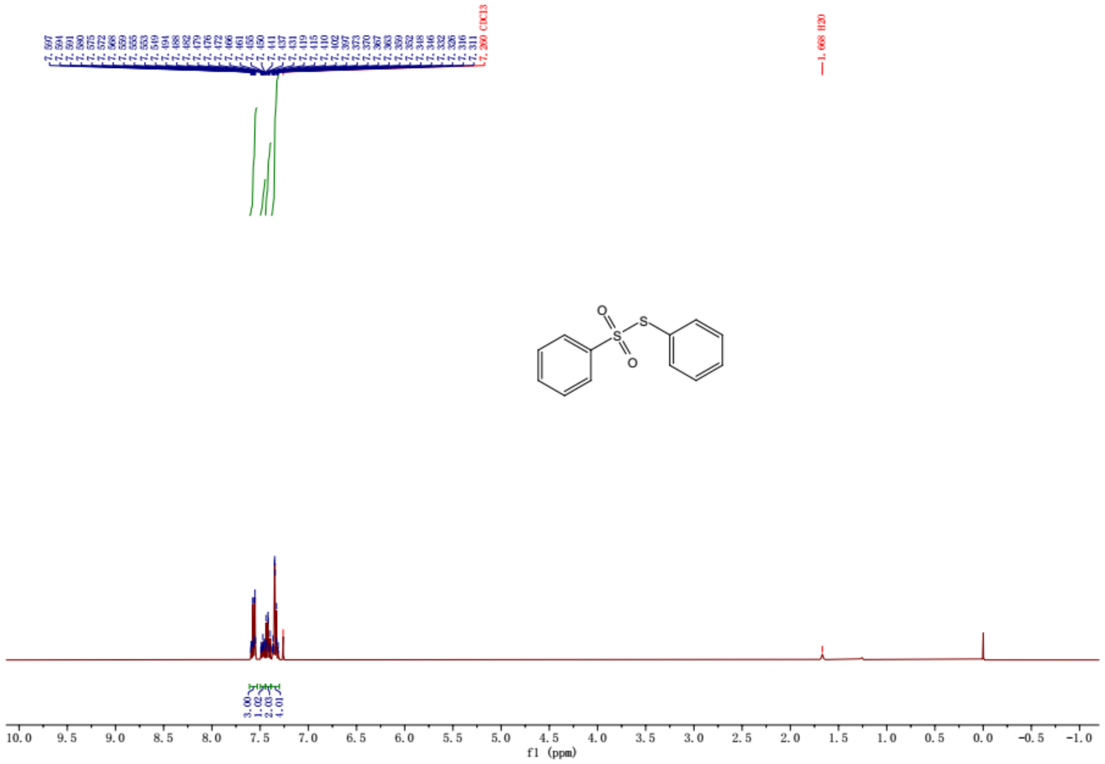


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of **3t**

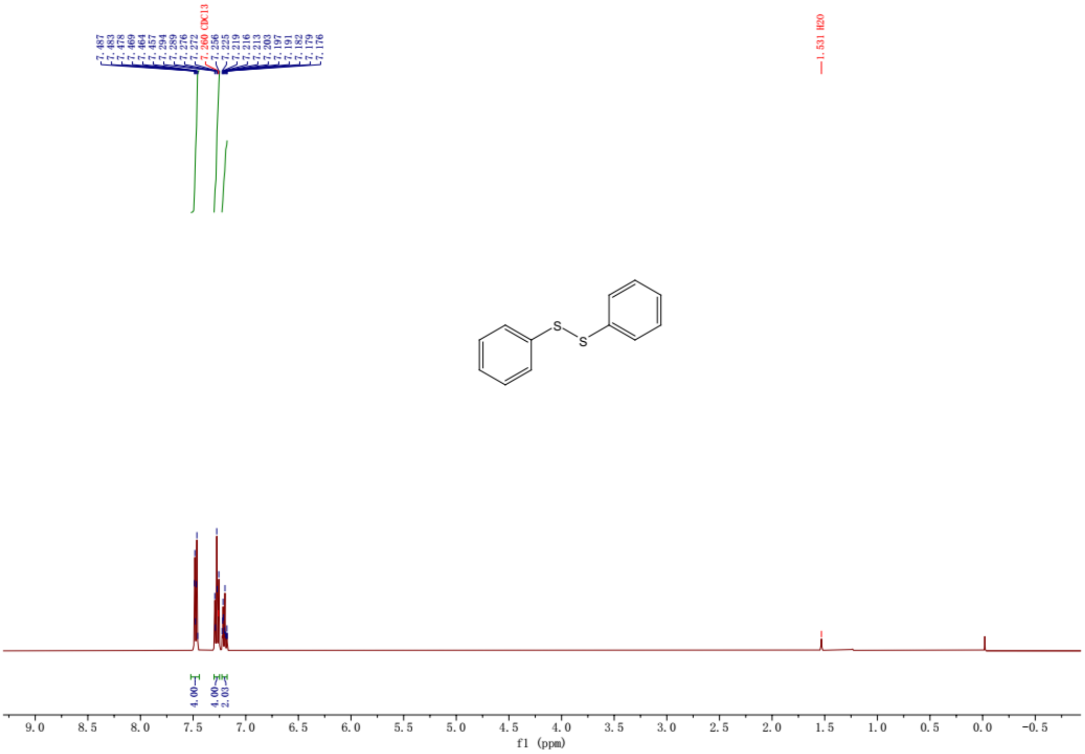




^{1}H NMR (400 MHz, $CDCl_3$) of **4**



^{1}H NMR (400 MHz, $CDCl_3$) of **5**



^{1}H NMR (400 MHz, DMSO-d_6) of **6**