Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light-induced Sulfonylation/Cyclization of Vinyl Azides: One-Pot Construction of 6-(Sulfonylmethyl)phenanthridines

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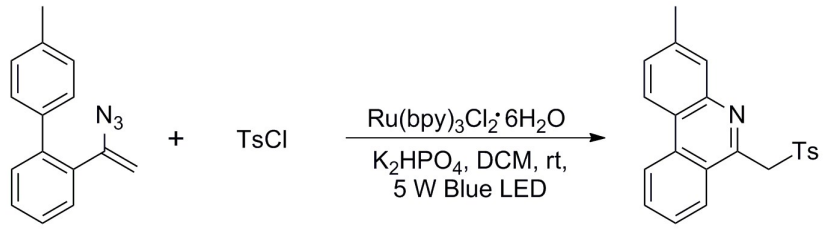
Contents:

Ⅰ. General Methods and Materials

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard (DMSO-d_6 δ = 2.5 for ^{1}H NMR, or δ = 40.0 for ^{13}C NMR). ^{31}P and ^{19}F NMR spectra were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Substrates were prepared according to published literature methods.[S1]

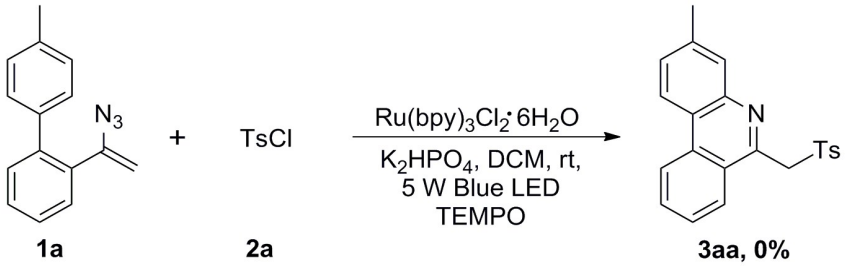
2. The General Procedure for the Synthesis of 3.



To a Schlenk tube were added vinyl azides **1** (0.26 mmol, 1.3 equiv.), sulfonyl chlorides (0.2 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2$•$6H_2O$ (2 mol%), K_2HPO_4 (0.24 mmol, 1.2 equiv) and charged with argon for three times. CH_2Cl_2 (2.0 mL) was added and the mixture was then irradiated by blue LED strips at room temperature for 18 h. After substrate was consumed (monitored by TLC), the reaction was concentrated in vacuo, and the resulting residue was purified by column chromatography using a mixture of petroleum ether / acetone as eluent to give the desired sulfonylated phenanthridine derivatives **3**.

3. Preliminary mechanistic studies.

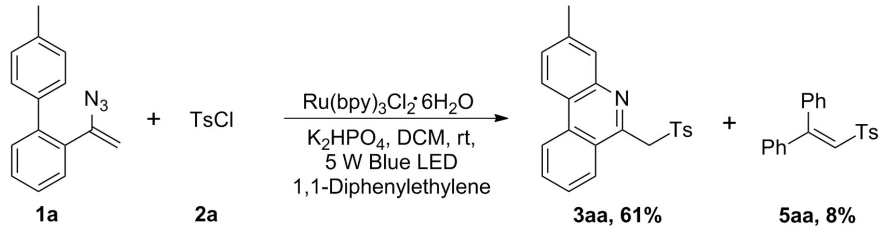
3.1 Radicals Trapping Experiments using TEMPO



In a Schlenk tube, 2-(1-azidovinyl)-4'-methyl-1,1'-biphenyl **1a** (0.26 mmol, 1.3 equiv), *p*-toluene sulfonyl chloride **2a** (0.2 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2$•$6H_2O$ (2 mol%), K_2HPO_4 (0.24 mmol, 1.2 equiv) and TEMPO (1.3 equiv) were added and charged with Ar three times. Then, CH_2Cl_2

(2.0 mL) were added and the mixture was then irradiated by blue LED strips at room temperature for 18 h (monitored by TLC). However, no desired product **3aa** is generated.

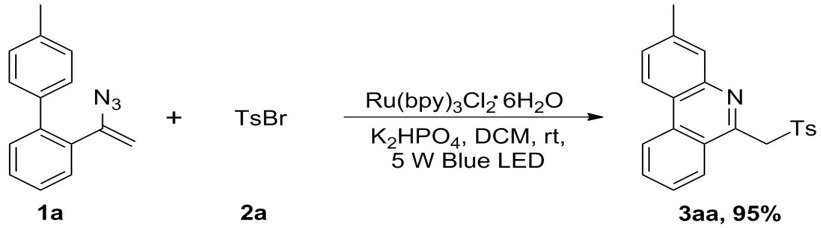
3.2 Radicals Trapping Experiments using 1,1-Diphenylethylene



In a Schlenk tube, 2-(1-azidovinyl)-4'-methyl-1,1'-biphenyl **1a** (0.26 mmol, 1.3 equiv), *p*-toluene sulfonyl chloride **2a** (0.2 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2$•$6H_2O$ (2 mol%), K_2HPO_4 (0.24 mmol, 1.2 equiv) and 1,1-Diphenylethylene (1.3 equiv) were added and charged with Ar three times. Then, CH_2Cl_2 (2.0 mL) were added and the mixture was then irradiated by blue LED strips at room temperature for 18 h, After substrate was consumed (monitored by TLC), the reaction was concentrated in vacuo, and the resulting residue was purified by column chromatography to give **3aa** and **5aa** in 61% and 8% yield, respectively.

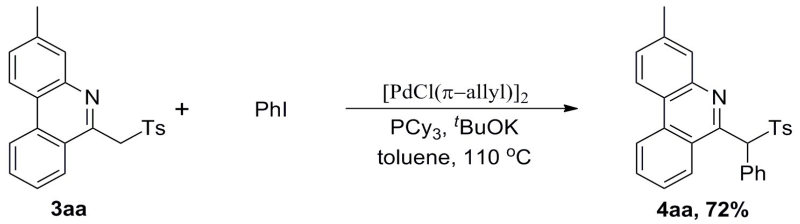
4. Application Studies

4.1 *p*-Toluene Sulfonyl Bromide as Sulfonylation Reagent[S2]



To a Schlenk tube were added 2-(1-azidovinyl)-4'-methyl-1,1'-biphenyl **1a** (0.26 mmol, 1.3 equiv.), *p*-toluene sulfonyl bromide (0.2 mmol, 1.0 equiv.), $Ru(bpy)_3Cl_2$•$6H_2O$ (2 mol%), K_2HPO_4 (0.24 mmol, 1.2 equiv) and charged with argon for three times. CH_2Cl_2 (2.0 mL) was added and the mixture was then irradiated by blue LED strips at room temperature for 18 h. After substrate was consumed (monitored by TLC), the reaction was concentrated in vacuo, and the resulting residue was purified by column chromatography using a mixture of petroleum ether / acetone as eluent to give the 3-methyl-6-(tosylmethyl)phenanthridine **3aa** with 95% yield.

4.2 Palladium-catalyzed Benzylic Direct Arylation of 3aa[S3]



To a Schlenk tube were added ^{t}BuOK (68 mg, 2.0 equiv), $[PdCl(\pi\text{-allyl})]_2$ (2.5 mol%), PPy_3 (10 mol%), 3-methyl-6-(tosylmethyl)phenanthridine **3aa** (109 mg, 0.3 mmol), iodobenzene (40 uL, 1.2 equiv) and charged with argon for three times. Toluene (3 mL) was added and the mixture was then heated at reflux for 10 h. After the mixture was cooled to room temperature, a saturated NH_4Cl aq. (5 mL) was added. The product was extracted with ethyl acetate three times. The

combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Silica gel column purification (PE/EA=5:1) gave 3-methyl-6-(phenyl(tosyl)methyl)phenanthridine **4aa** (94 mg, 0.21 mmol) in 72% yield.

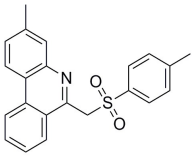
5. References

[S1] (a) Y.-F. Wang, G. H. Lonca, M. L. Runigo and S. Chiba, *Org. Lett.* 2014, **16**, 4272. (b) E. G. Mackay and A. Studer, *Chem. Eur. J.* 2016, **22**, 13455. (c) J.-C. Yang, J.-J. Zhang and L.-N. Guo, *Org. Biomol. Chem.*, 2016, **14**, 9806 (d) H,-T. Qin, S.-W. Wu, J.-L. Liu and F. Liu, *Chem. Commun.,* 2017, **53**, 1696. (e) A. Hassner and F. W. Fowler, *Tetrahedron Lett.* 1967, **8**, 1545.

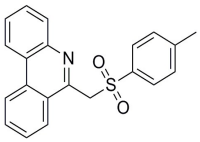
[S2] A. Lennartson. M. Quant and K. Moth-Poulsen**,** *Synlett,* 2015**, 26***,* 1501.

[S3] T. Niwa, H. Yorimitsu and K. Oshima, *Tetrahedron*, 2009, **65**, 1971.

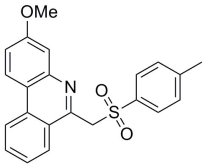
6. Characterization data of products



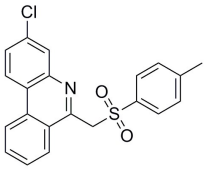
3-methyl-6-(tosylmethyl)phenanthridine (3aa) (92%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.76 (m, 1H), 7.70 – 7.61 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 2H), 2.53 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.65, 144.59, 143.45, 138.83, 135.67, 133.18, 130.76, 129.43, 129.38, 128.63, 127.10, 126.92, 125.29, 122.05, 121.70, 121.66, 62.69, 21.52, 21.41. **MS (ESI)**: found $[M+H]^+$ 362.0..



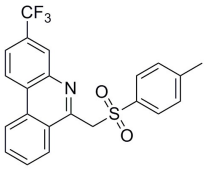
6-(tosylmethyl)phenanthridine (3ab) (87%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (d, *J* = 8.3 Hz, 1H), 8.59 – 8.50 (m, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 7.84 (m, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.67 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.76, 144.61, 143.25, 135.54, 133.10, 130.85, 129.86, 129.39, 128.64, 127.59, 127.58, 126.98, 125.56, 123.95, 122.23, 121.93, 62.63, 21.50. **MS (ESI)**: found $[M+H]^+$ 348.0.



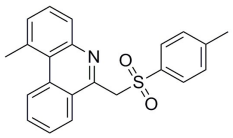
3-methoxy-6-(tosylmethyl)phenanthridine (3ac) (82%) light yellow solid; **^{1}H NMR (400 MHz, DMSO)** δ 8.71 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 8.5 Hz, 1H), 8.38 (d, *J* = 7.5 Hz, 1H), 7.88 (s, 1H), 7.64 (d, *J* = 6.9 Hz, 3H), 7.35 (d, *J* = 6.9 Hz, 3H), 7.26 (s, 1H), 5.38 (s, 2H), 3.90 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 160.22, 151.12, 144.98, 144.84, 136.76, 133.19, 131.60, 130.02, 128.67, 128.08, 126.89, 126.01, 124.82, 124.45, 122.43, 118.77, 117.97, 109.94, 61.78, 55.91, 21.49. **MS (ESI)**: found $[M+H]^+$ 378.1.



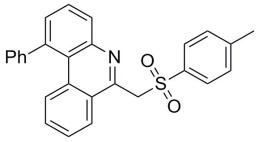
3-chloro-6-(tosylmethyl)phenanthridine (3ad) (84%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 7.3 Hz, 1H), 7.76 (dd, *J* = 19.0, 11.5 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 2H), 5.12 (s, 2H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.22, 144.86, 143.89, 135.49, 134.33, 132.75, 131.33, 129.51, 129.04, 128.63, 128.15, 127.96, 127.23, 125.54, 123.37, 122.47, 122.20, 62.66, 21.58. **MS (ESI)**: found $[M+H]^+$ 382.0.



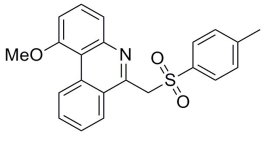
6-(tosylmethyl)-3-(trifluoromethyl)phenanthridine (3ae) (74%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 (dd, *J* = 8.0, 5.7 Hz, 2H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.08 (s, 1H), 7.92 (t, *J* = 7.4 Hz, 1H), 7.82 (dd, *J* = 12.4, 5.5 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 2H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.54, 144.96, 142.49, 135.33, 132.32, 131.51, 130.48 (q, *J* = 33.4 Hz), 129.55, 128.85, 128.62, 127.41 (q, *J* = 4.2 Hz), 127.29, 126.20, 126.16, 123.94 (d, *J* = 272.3 Hz), 123.40 (q, *J* = 3.3 Hz), 123.09, 122.64, 62.64, 21.47. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -62.91. **MS (ESI)**: found $[M+H]^+$ 416.1.



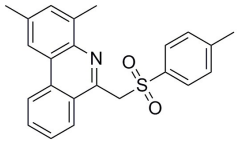
1-methyl-6-(tosylmethyl)phenanthridine (3af) (82%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 (d, *J* = 8.6 Hz, 1H), 8.39 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.75 – 7.65 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 3H), 7.50 – 7.45 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 2H), 3.09 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.44, 144.74, 144.57, 135.61, 134.89, 134.40, 131.83, 130.01, 129.39, 128.80, 128.67, 127.73, 126.99, 126.84, 126.70, 126.46, 123.73, 62.62, 26.67, 21.53. **MS (ESI)**: found $[M+H]^+$ 362.1.



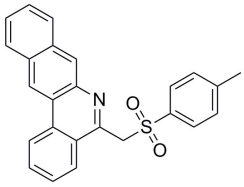
1-phenyl-6-(tosylmethyl)phenanthridine (3ag) (79%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.82 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73 – 7.58 (m, 4H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.48 (dt, *J* = 11.1, 4.6 Hz, 4H), 7.41 – 7.35 (m, 2H), 7.31 (dd, *J* = 11.5, 4.1 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.96, 144.61, 144.42, 143.86, 139.85, 135.72, 133.23, 131.27, 129.66, 129.42, 129.20, 129.07, 128.86, 128.64, 127.50, 127.27, 127.01, 126.57, 126.53, 122.27, 62.60, 21.53. **MS (ESI)**: found $[M+H]^+$ 424.2.



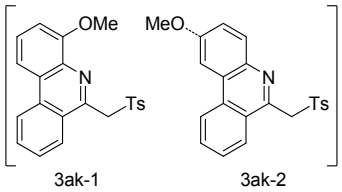
1-methoxy-6-(tosylmethyl)phenanthridine (3ah) (72%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.59 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 18.3, 8.1 Hz, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 3H), 5.14 (s, 2H), 4.12 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.93, 150.38, 145.31, 144.61, 135.61, 133.23, 130.74, 129.43, 128.74, 128.13, 126.94, 126.46, 125.90, 122.74, 114.81, 108.70, 62.72, 55.93, 21.58. **MS (ESI)**: found $[M+H]^+$ 378.1..



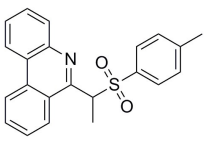
2,4-dimethyl-6-(tosylmethyl)phenanthridine (3ai) (80%) yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.15 (s, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 2H), 2.54 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.05, 144.32, 140.18, 137.53, 137.03, 135.40, 133.17, 131.02, 130.37, 129.16, 128.83, 127.32, 126.80, 125.41, 123.68, 122.46, 119.28, 62.52, 21.99, 21.47, 17.30. **MS (ESI)**: found $[M+H]^+$ 376.1.



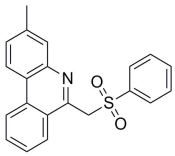
5-(tosylmethyl)benzo[b]phenanthridine (3aj) (93%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (d, *J* = 8.2 Hz, 1H), 8.53 – 8.27 (m, 3H), 8.01 – 7.80 (m, 3H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.51 (dd, *J* = 17.7, 7.7 Hz, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.21 (s, 2H), 2.22 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.12, 144.50, 139.87, 135.19, 133.35, 132.99, 131.35, 130.67, 129.31, 128.81, 128.34, 127.45, 127.33, 126.69, 126.40, 126.03, 124.63, 122.63, 120.93, 119.55, 62.35, 21.37. **MS (ESI)**: found $[M+H]^+$ 398.1.



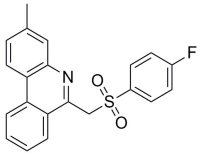
2-methoxy-6-(tosylmethyl)phenanthridine (3ak-1):4-methoxy-6-(tosylmethyl)phenanthridine (3ak-2) = 5:1 (81%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (dd, *J* = 22.7, 8.3 Hz, 1H), 8.34 (dd, *J* = 18.5, 8.3 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.84 (dd, *J* = 15.3, 7.4 Hz, 1H), 7.72 (dd, *J* = 16.3, 8.3 Hz, 1H), 7.64 – 7.44 (m, 3H), 7.16 (t, *J* = 12.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 52.0 Hz, 2H), 3.97 (d, *J* = 28.9 Hz, 3H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.91, 148.31, 144.28, 135.66, 134.45, 133.10, 130.80, 130.41, 129.39, 129.29, 128.79, 128.67, 127.89, 127.79, 126.92, 125.78, 125.33, 122.79, 122.27, 113.86, 108.64, 102.60, 62.53, 56.16, 55.62, 21.54. **MS (ESI)**: found $[M+H]^+$ 378.1.



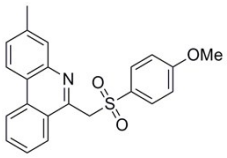
6-(1-tosylethyl)phenanthridine (3al) (89%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (d, *J* = 8.3 Hz, 1H), 8.58 – 8.46 (m, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 2H), 7.77 – 7.56 (m, 3H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.52 (q, *J* = 6.8 Hz, 1H), 2.37 (s, 3H), 1.90 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.43, 144.53, 143.02, 133.20, 133.08, 130.57, 130.17, 130.09, 128.99, 128.59, 127.53, 126.14, 125.82, 123.89, 122.42, 121.96, 62.60, 21.60, 15.24. **MS (ESI)**: found $[M+H]^+$ 362.1..



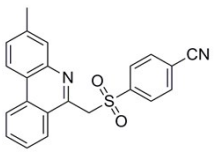
3-methyl-6-((phenylsulfonyl)methyl)phenanthridine (3an) (90%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.67 (dd, *J* = 11.1, 7.6 Hz, 3H), 7.60 (s, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 5.14 (s, 2H), 2.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.54, 143.48, 138.95, 138.56, 133.66, 133.26, 130.87, 129.49, 129.44, 128.86, 128.69, 127.20, 126.90, 125.30, 122.14, 121.76, 121.71, 62.64, 21.48. **MS (ESI)**: found $[M+H]^+$ 348.0.



6-(((4-fluorophenyl)sulfonyl)methyl)-3-methylphenanthridine (3ao) (91%) white solid; **^{1}H NMR (400 MHz, DMSO)** δ 8.74 (d, *J* = 7.9 Hz, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 7.1 Hz, 1H), 7.77 (s, 2H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 2H), 5.46 (s, 2H), 2.47 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 165.59 (d, *J* = 252.6 Hz), 150.57, 143.42, 139.24, 135.81 (d, *J* = 2.6 Hz), 133.02, 132.03, 131.93, 131.60, 129.92, 129.13, 128.01, 127.60, 125.36, 122.85 (d, *J* = 15.4 Hz), 121.64, 116.71 (d, *J* = 22.8 Hz), 61.44, 21.48. **^{19}F NMR (282 MHz, DMSO)** δ -105.47. **MS (ESI)**: found $[M+H]^+$ 366.1.

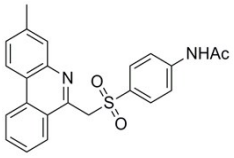


6-(((4-methoxyphenyl)sulfonyl)methyl)-3-methylphenanthridine (3ap) (91%) white solid; **^{1}H NMR (400 MHz, DMSO)** δ 8.74 (d, *J* = 8.1 Hz, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 7.86 (t, *J* = 7.3 Hz, 1H), 7.77 – 7.57 (m, 4H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 2H), 5.34 (s, 2H), 3.77 (s, 3H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 163.82, 150.85, 143.50, 139.16, 132.98, 131.51, 131.09, 130.91, 129.84, 129.25, 128.09, 127.54, 125.41, 122.91, 122.72, 121.65, 114.77, 62.02, 56.24, 21.48. **MS (ESI)**: found $[M+H]^+$ 378.1..

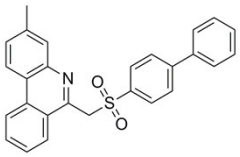


4-(((3-methylphenanthridin-6-yl)methyl)sulfonyl)benzonitrile (3aq) (75%) white solid; **^{1}H NMR (400 MHz, DMSO)** δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.01

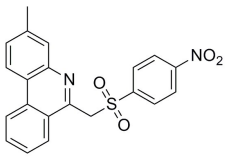
(d, *J* = 8.3 Hz, 2H), 7.97 – 7.83 (m, 3H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 10.5 Hz, 2H), 5.57 (s, 2H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 150.23, 143.52, 143.28, 139.31, 133.55, 133.05, 131.72, 130.01, 129.62, 129.02, 127.92, 127.71, 125.33, 122.96, 122.85, 121.62, 118.06, 116.56, 60.77, 21.47. **MS (ESI)**: found $[M+H]^+$ 373.1.



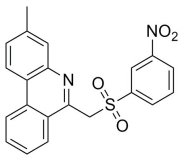
N-(4-(((3-methylphenanthridin-6-yl)methyl)sulfonyl)phenyl)acetamide (3ar) (80%) white solid; **^{1}H NMR (400 MHz, DMSO)** δ 10.32 (s, 1H), 8.72 (d, *J* = 6.7 Hz, 1H), 8.58 (d, *J* = 6.9 Hz, 1H), 8.36 (d, *J* = 6.6 Hz, 1H), 7.85 (s, 1H), 7.76 – 7.56 (m, 6H), 7.50 (s, 1H), 5.33 (s, 2H), 2.45 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.20, 150.35, 144.11, 143.10, 138.77, 132.62, 131.14, 129.51, 128.87, 127.73, 127.15, 125.03, 122.52, 122.32, 121.25, 118.45, 61.48, 24.26, 21.09. **MS (ESI)**: found $[M+H]^+$ 405.1.



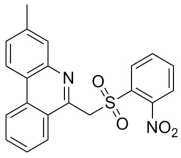
6-(([1,1'-biphenyl]-4-ylsulfonyl)methyl)-3-methylphenanthridine (3as) (78%) light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.60 – 7.34 (m, 9H), 5.16 (s, 2H), 2.47 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.57, 146.57, 143.40, 139.29, 138.88, 136.79, 133.18, 130.81, 129.43, 129.33, 129.18, 128.94, 128.47, 127.40, 127.30, 127.15, 126.84, 125.22, 122.08, 121.70, 121.61, 62.72, 21.36. **MS (ESI)**: found $[M+H]^+$ 424.2.



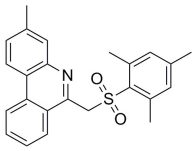
3-methyl-6-(((4-nitrophenyl)sulfonyl)methyl)phenanthridine (3at) (80%) light yellow solid; ^{1}H NMR (400 MHz, DMSO) δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.89 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.39 (m, 2H), 5.60 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 150.53, 149.81, 144.51, 142.87, 138.94, 132.68, 131.37, 130.24, 129.64, 128.62, 127.53, 127.36, 124.94, 124.25, 122.59, 122.49, 121.24, 60.38, 21.05. **MS (ESI)**: found $[M+H]^+$ 393.1.



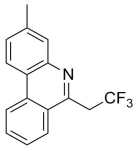
3-methyl-6-(((3-nitrophenyl)sulfonyl)methyl)phenanthridine (3au) (52%) light yellow solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.51 (s, 1H), 8.42 (t, *J* = 6.9 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 15.7, 7.6 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.64 – 7.40 (m, 3H), 5.22 (s, 2H), 2.52 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 148.86, 147.97, 143.12, 140.28, 139.33, 134.37, 133.36, 131.20, 129.96, 129.84, 128.96, 128.00, 127.44, 126.48, 125.04, 124.40, 122.37, 121.86, 121.69, 62.09, 21.45. **MS (ESI)**: found $[M+H]^+$ 393.1.



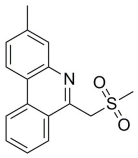
3-methyl-6-(((2-nitrophenyl)sulfonyl)methyl)phenanthridine (3av) (72%) light yellow solid; ^{1}H NMR (400 MHz, DMSO) δ 8.74 (d, *J* = 6.1 Hz, 1H), 8.60 (s, 1H), 8.41 (d, *J* = 6.0 Hz, 1H), 8.05 (s, 1H), 7.88 (s, 2H), 7.80 – 7.57 (m, 3H), 7.49 (s, 2H), 5.68 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 149.68, 148.58, 142.92, 138.93, 135.94, 132.80, 132.75, 132.12, 131.37, 129.69, 128.74, 127.43, 127.31, 125.06, 122.58, 122.53, 121.37, 61.33, 21.07. **MS (ESI)**: found $[M+H]^+$ 393.0.



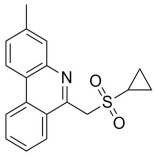
6-((mesitylsulfonyl)methyl)-3-methylphenanthridine (3aw) (84%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (d, *J* = 8.3 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.78 (m, 1H), 7.73 – 7.65 (m, 1H), 7.63 (s, 1H), 7.49 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.29 (d, *J* = 5.5 Hz, 1H), 6.85 (s, 2H), 5.16 (s, 2H), 2.56 (s, 3H), 2.39 (s, 6H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.87, 143.52, 143.17, 140.45, 138.72, 133.02, 132.71, 131.93, 130.67, 129.73, 129.48, 129.29, 129.02, 128.15, 127.07, 126.90, 125.47, 122.01, 121.66, 121.53, 62.61, 22.81, 21.39, 20.90. **MS (ESI)**: found $[M+H]^+$ 390.1.



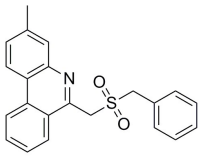
3-methyl-6-(2,2,2-trifluoroethyl)phenanthridine (3ax) (46%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 7.84 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 4.19 (q, *J* = 10.4 Hz, 2H), 2.59 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.08 (q, J = 3.2 Hz), 143.57, 139.12, 133.27, 130.68, 129.67, 129.26, 127.10, 126.17, 125.64 (q, J = 276.1 Hz), 125.21, 122.33, 121.74, 121.70, 40.49 (q, *J* = 29.1 Hz), 21.47. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -63.12, -63.16, -63.19. **MS (ESI)**: found $[M+H]^+$ 275.9.



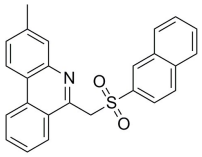
3-methyl-6-((methylsulfonyl)methyl)phenanthridine (3ay) (26%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.96 (s, 1H), 7.90 (t, *J* = 7.4 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 8.4, 1.4 Hz, 1H), 5.06 (s, 2H), 3.10 (s, 3H), 2.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.26, 143.48, 139.26, 133.49, 131.17, 129.73, 129.42, 127.47, 126.91, 125.22, 122.27, 122.03, 121.97, 60.69, 40.42, 21.51. **MS (ESI)**: found $[M+H]^+$ 286.0.



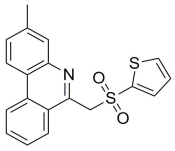
6-((cyclopropylsulfonyl)methyl)-3-methylphenanthridine (3az) (37%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.94 – 7.82 (m, 1H), 7.82 – 7.69 (m, 1H), 7.57 (dd, *J* = 8.4, 1.5 Hz, 1H), 5.13 (s, 2H), 2.73 – 2.48 (m, 4H), 1.13 (tt, *J* = 5.7, 3.0 Hz, 2H), 1.06 – 0.86 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.23, 143.58, 139.16, 133.36, 131.04, 129.57, 129.51, 127.34, 127.07, 125.30, 122.19, 121.94, 60.45, 29.73, 21.52, 5.21. **MS (ESI)**: found $[M+H]^+$ 312.0.



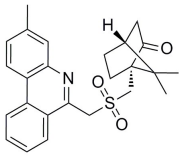
6-((benzylsulfonyl)methyl)-3-methylphenanthridine (3ba) (28%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.06 (s, 1H), 7.97 – 7.83 (m, 1H), 7.83 – 7.67 (m, 3H), 7.60 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.53 – 7.37 (m, 3H), 4.93 (s, 2H), 4.56 (s, 2H), 2.67 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.49, 143.47, 139.24, 133.47, 131.49, 131.11, 129.69, 129.42, 128.96, 128.90, 128.22, 127.44, 126.80, 125.55, 122.28, 122.02, 58.05, 56.30, 21.55. **MS (ESI)**: found $[M+H]^+$ 362.1.



3-methyl-6-((naphthalen-2-ylsulfonyl)methyl)phenanthridine (3bb) (60%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 (d, *J* = 8.2 Hz, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.28 (s, 1H), 7.84 (m, 4H), 7.75 – 7.62 (m, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.37 (m, 2H), 5.24 (s, 2H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.53, 143.38, 138.82, 135.44, 135.32, 133.25, 132.03, 130.81, 130.69, 129.39, 129.36, 129.07, 128.98, 127.78, 127.29, 127.14, 126.84, 125.33, 123.33, 122.10, 121.64, 62.65, 21.33. **MS (ESI)**: found $[M+H]^+$ 398.1.

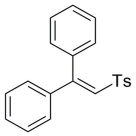


3-methyl-6-((thiophen-2-ylsulfonyl)methyl)phenanthridine (3bc) (90%) light yellow solid; **^{1}H NMR (400 MHz, DMSO)** δ 8.75 (d, *J* = 8.1 Hz, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 4.3 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 1H), 7.79 – 7.57 (m, 3H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 3.8 Hz, 1H), 5.50 (s, 2H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 150.14, 143.08, 139.48, 138.80, 135.74, 135.09, 132.58, 131.16, 129.54, 128.88, 128.21, 127.44, 127.18, 124.95, 122.50, 122.35, 121.27, 62.61, 21.08. **MS (ESI)**: found $[M+H]^+$ 354.0.

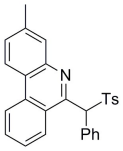


(1S,4R)-7,7-dimethyl-1-((((3-methylphenanthridin-6-yl)methyl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (3bd) (69%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 7.93 (s, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 5.34 (d, *J* = 14.1 Hz,

1H), 5.18 (d, *J* = 14.1 Hz, 1H), 4.08 (d, *J* = 15.0 Hz, 1H), 3.20 (d, *J* = 15.0 Hz, 1H), 2.61 (s, 3H), 2.51 – 2.29 (m, 2H), 2.12 (d, *J* = 4.1 Hz, 1H), 2.09 – 2.02 (m, 1H), 2.01 – 1.90 (m, 2H), 1.52 – 1.39 (m, 1H), 1.04 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 214.63, 150.47, 143.48, 139.00, 133.35, 130.88, 129.44, 127.27, 126.94, 125.49, 122.13, 121.88, 121.83, 61.36, 59.22, 50.23, 48.40, 42.64, 27.07, 25.41, 21.49, 19.82. **MS (ESI)**: found $[M+H]^+$ 422.3.

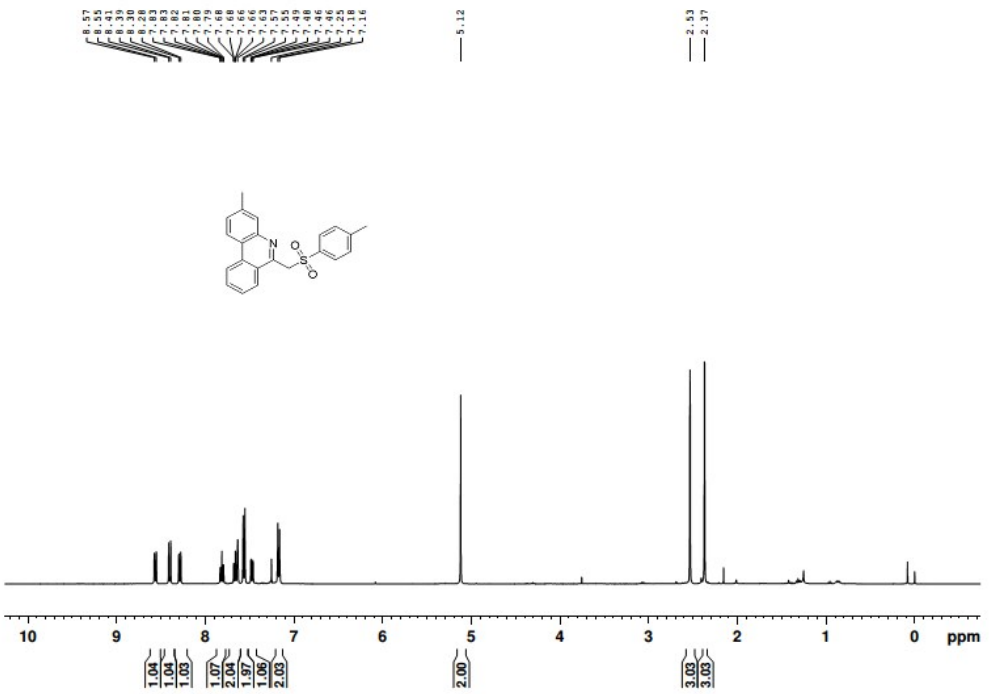


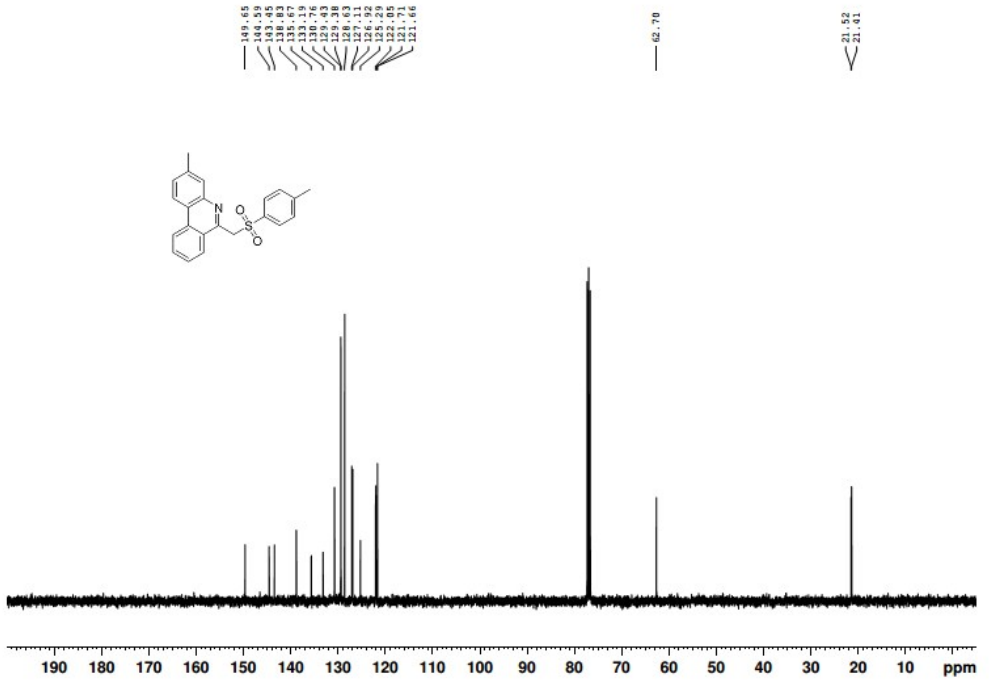
(2-tosylethene-1,1-diyl)dibenzene (5aa) (8%) white solid; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 (s, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.34 (m, 1H), 7.32 (s, 1H), 7.30 (d, *J* = 2.1 Hz, 2H), 7.27 (t, *J* = 1.7 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.16 (s, 1H), 7.13 (s, 1H), 7.11 – 7.10 (m, 1H), 7.08 (d, *J* = 1.6 Hz, 1H), 6.99 (s, 1H), 2.37 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.65, 143.70, 139.19, 138.57, 135.53, 130.17, 129.73, 129.28, 128.92, 128.79, 128.52, 128.15, 127.75, 127.65, 21.52. **MS (ESI)**: found $[M+H]^+$ 335.1.

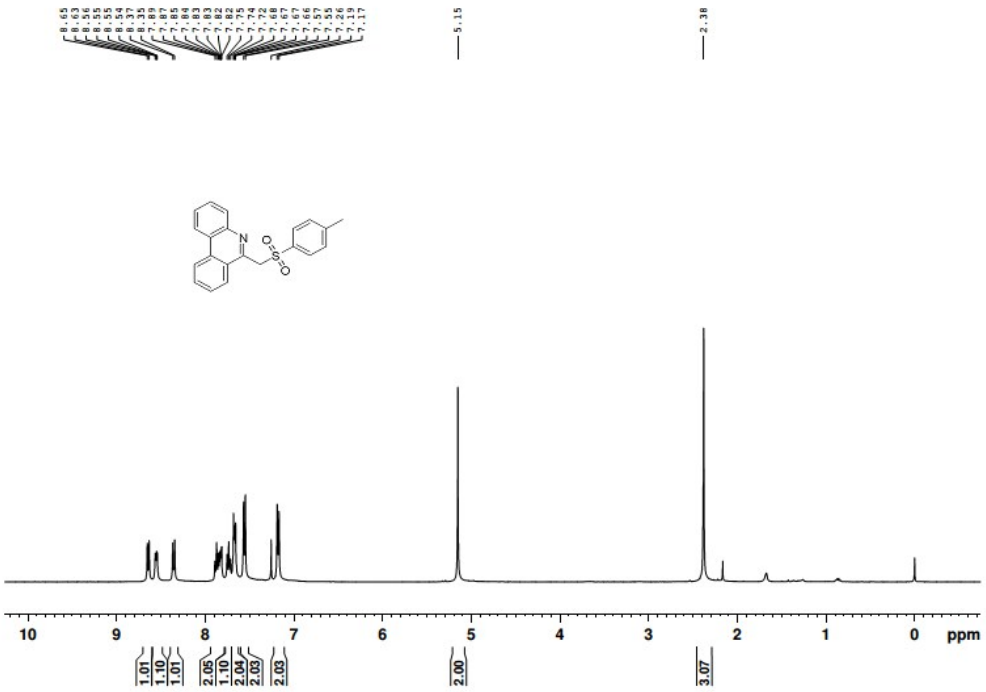


3-methyl-6-(phenyl(tosyl)methyl)phenanthridine (4aa) (72%) white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.96 (s, 1H), 7.72 – 7.65 (m, 1H), 7.64 – 7.58 (m, 4H), 7.54 – 7.49 (m, 1H), 7.46 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 2.59 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.17, 144.17, 142.90, 138.84, 135.33, 133.30, 132.12, 130.93, 130.83, 130.35, 129.52, 129.21, 128.97, 128.41, 128.25, 127.09, 124.81, 124.54, 122.44, 121.71, 121.31, 73.40, 21.57, 21.49. **MS (ESI)**: found $[M+H]^+$ 438.1.

7. Copies of NMR spectra



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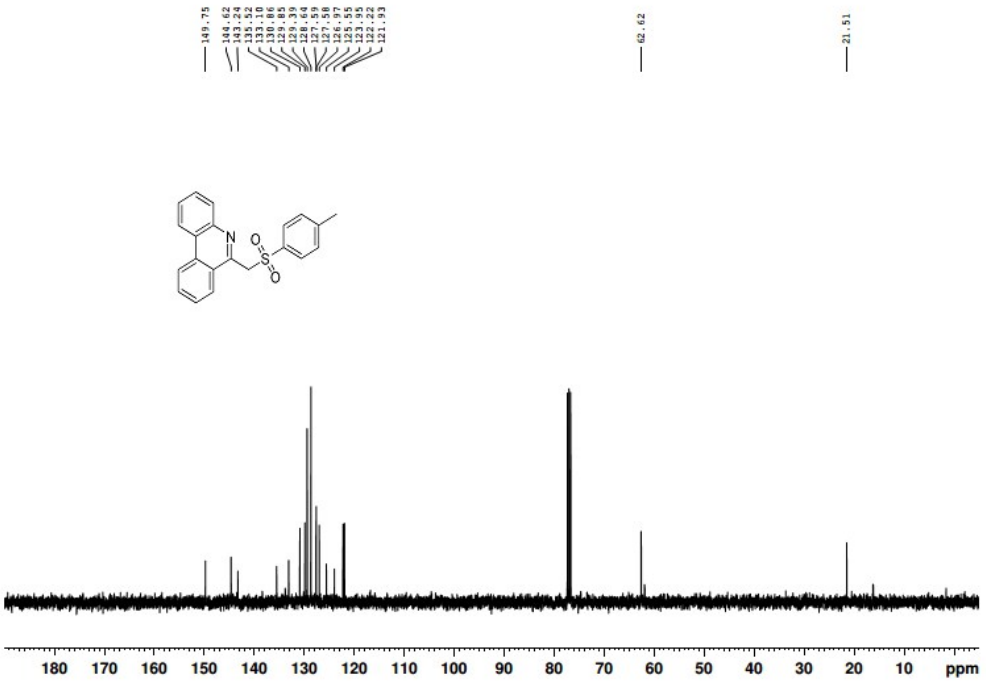
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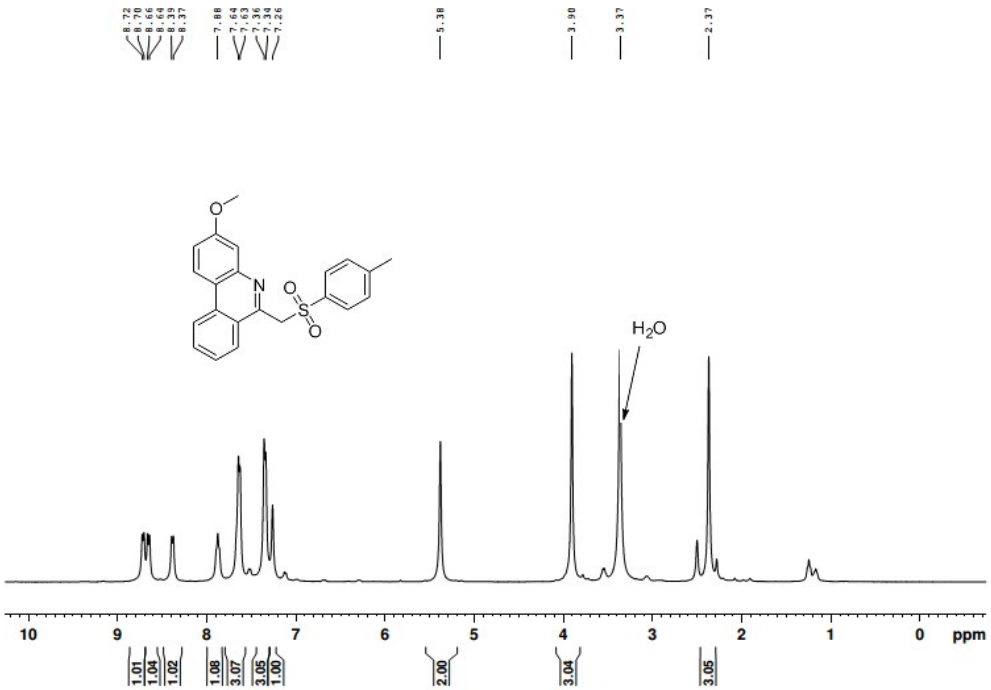
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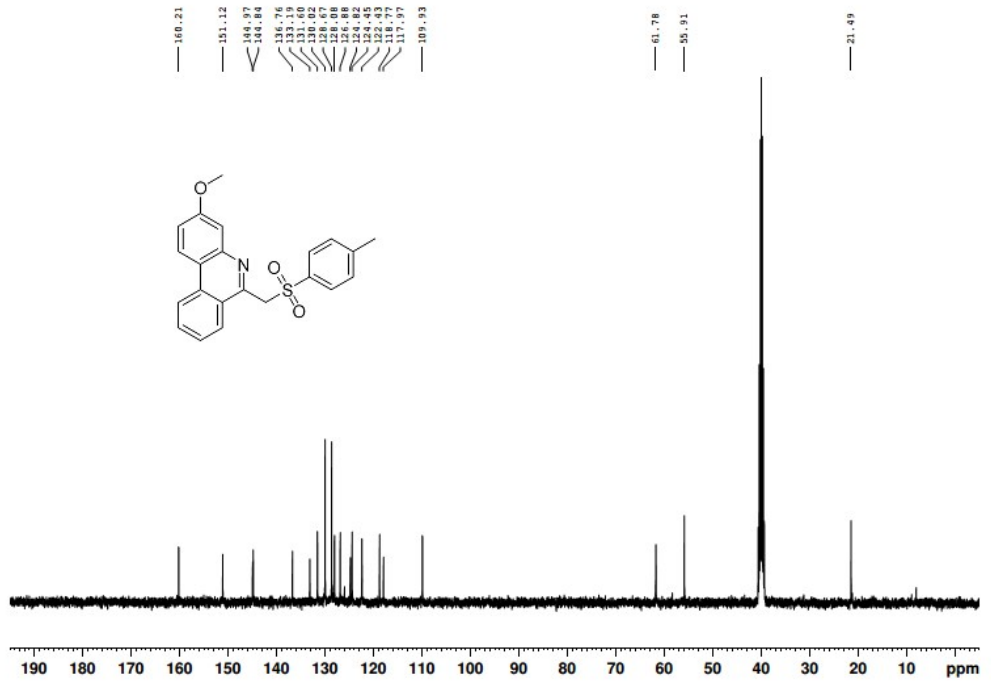
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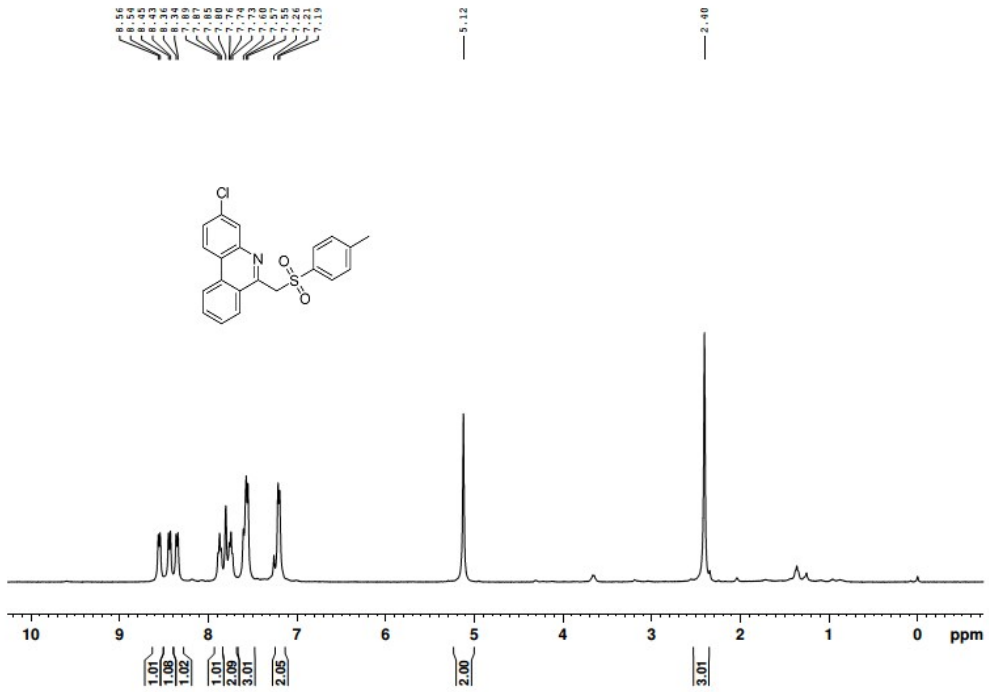
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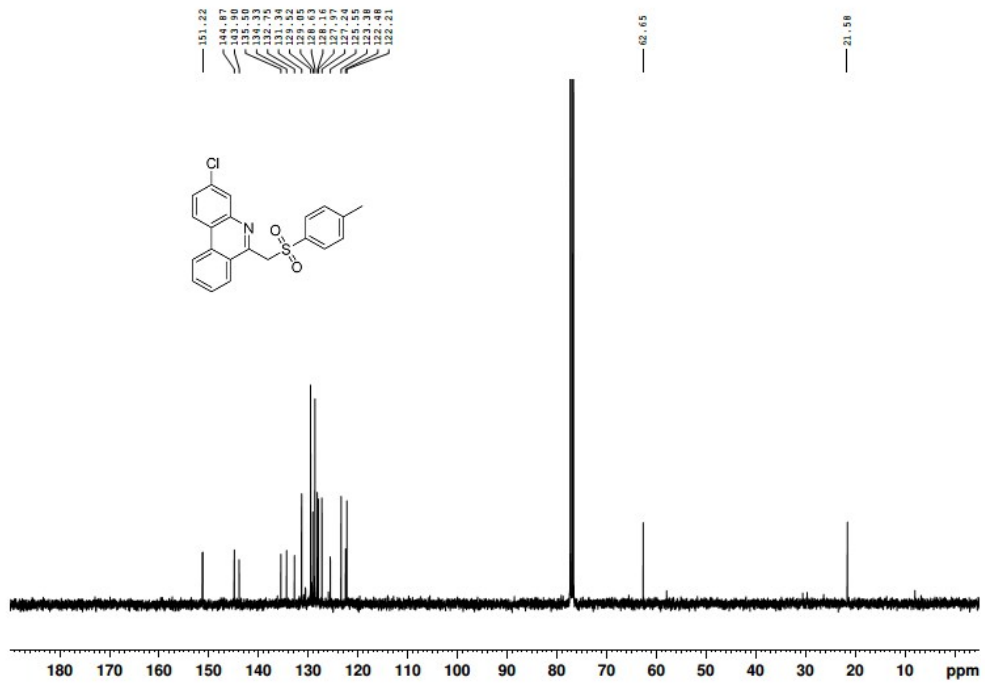
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122.21
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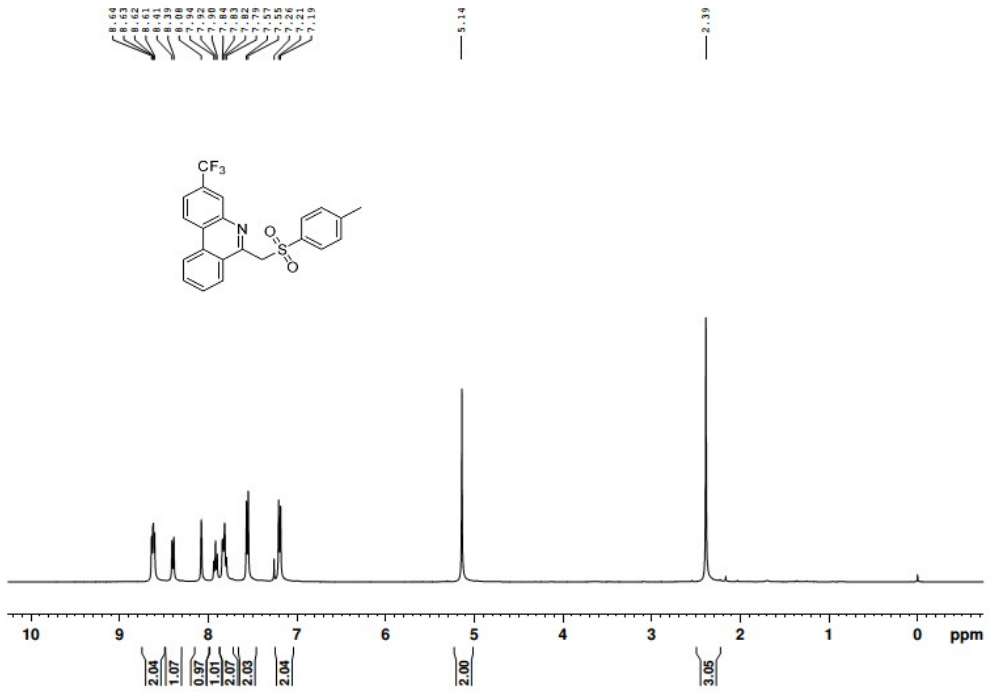
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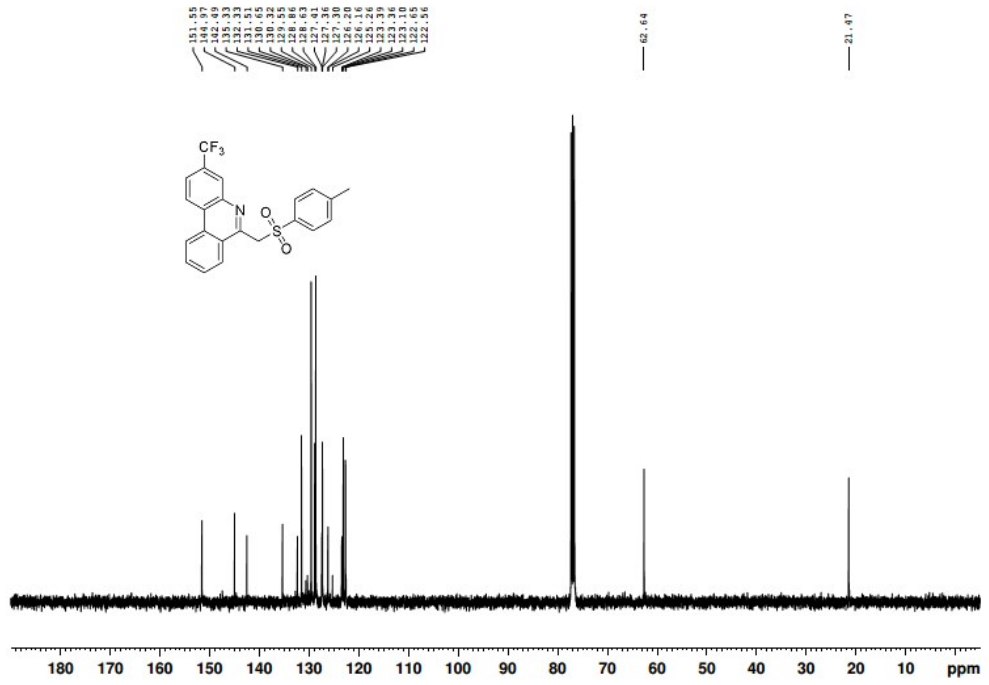
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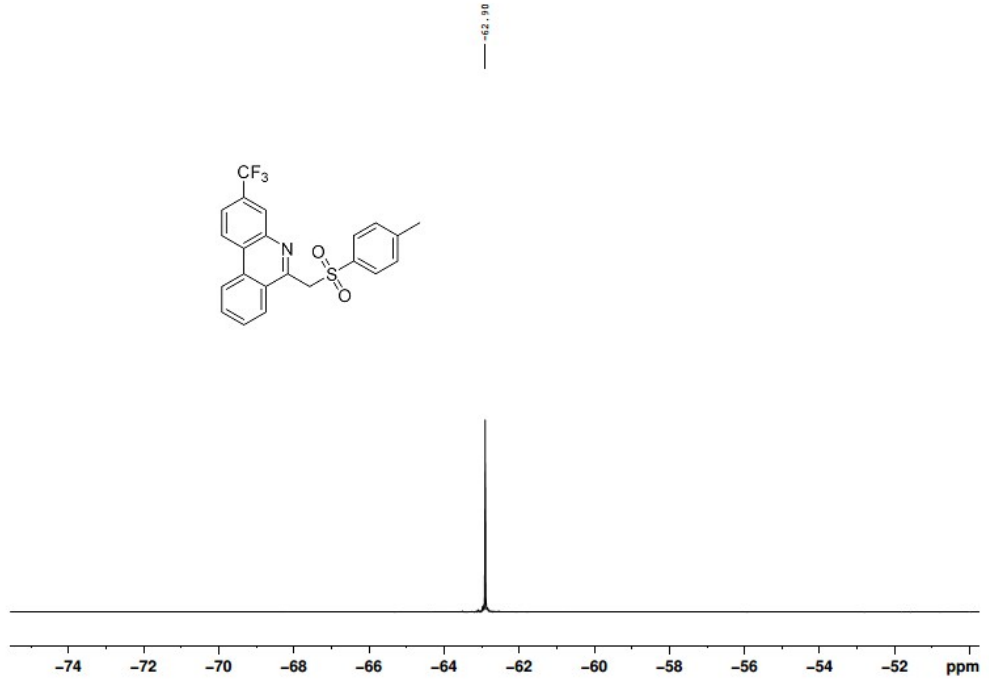
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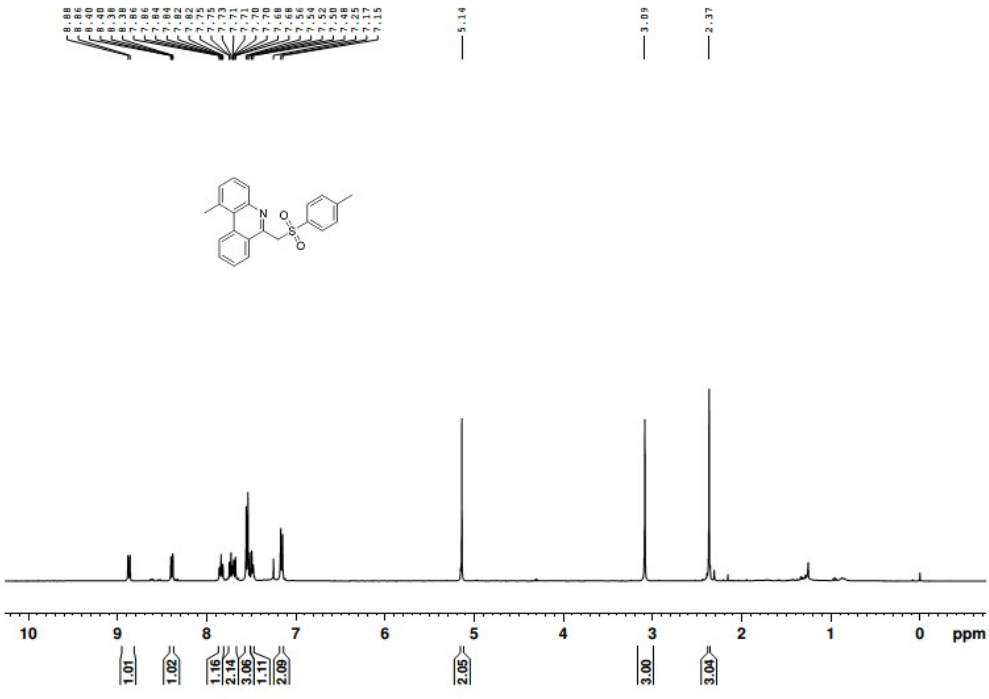
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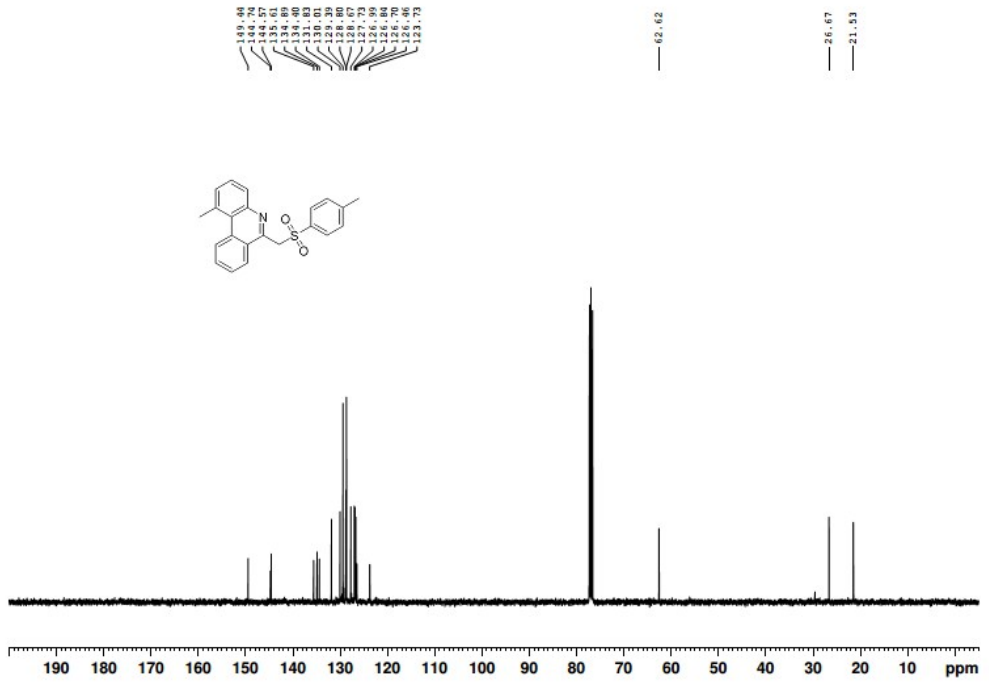
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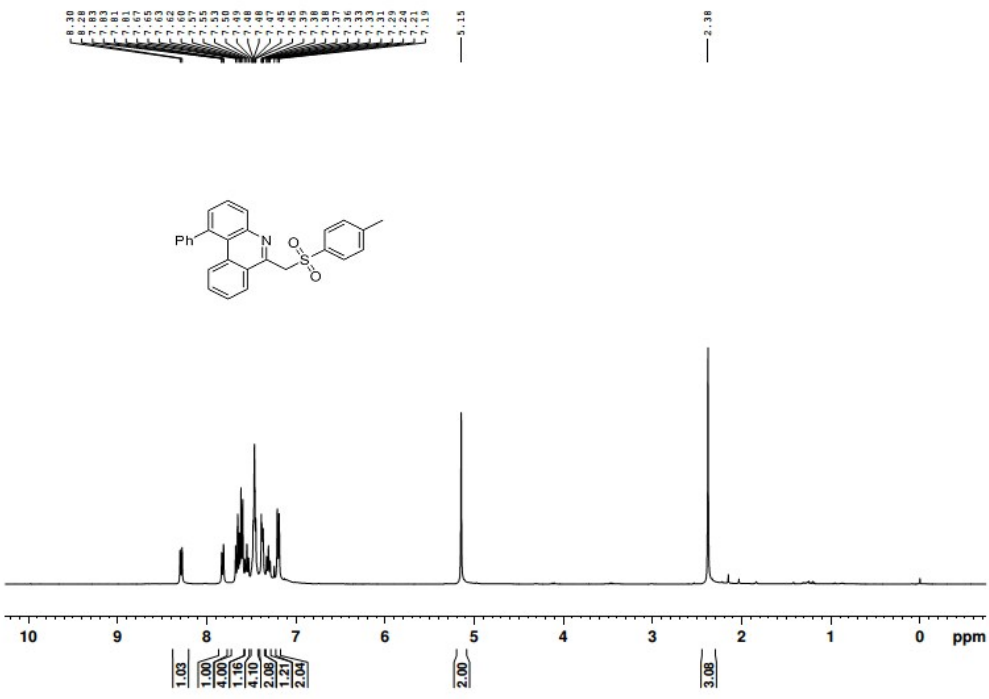
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7.31
7.29
7.24
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7.19
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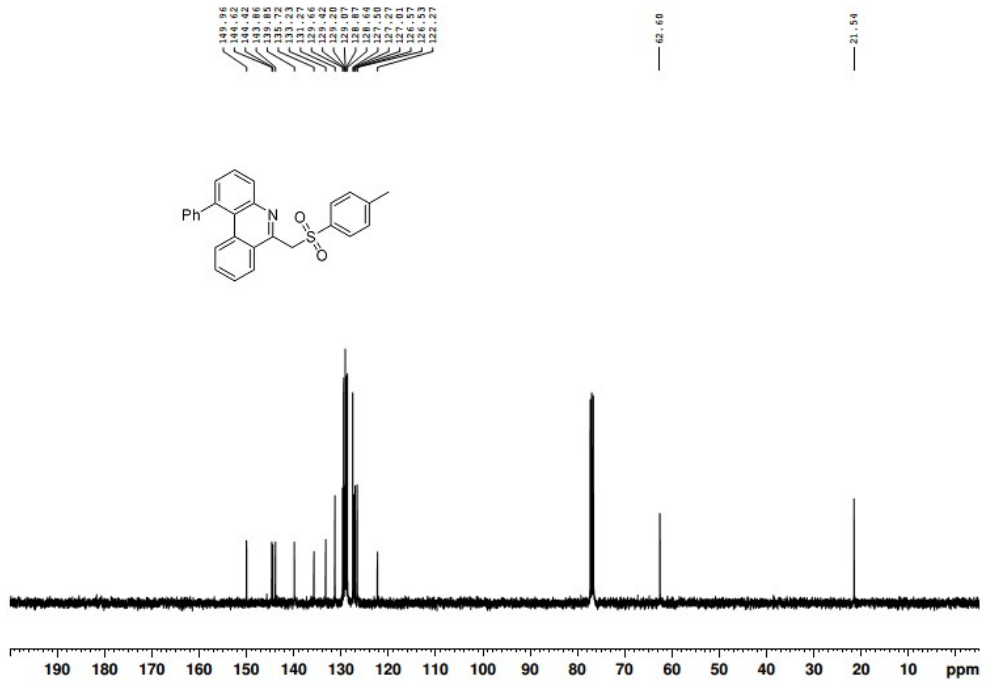
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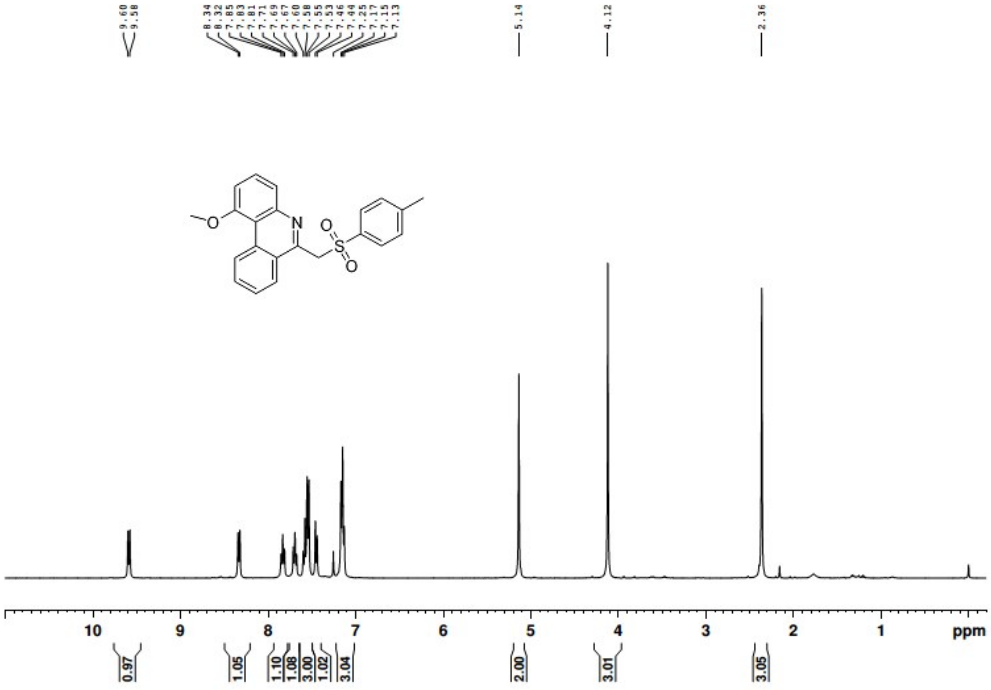
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S
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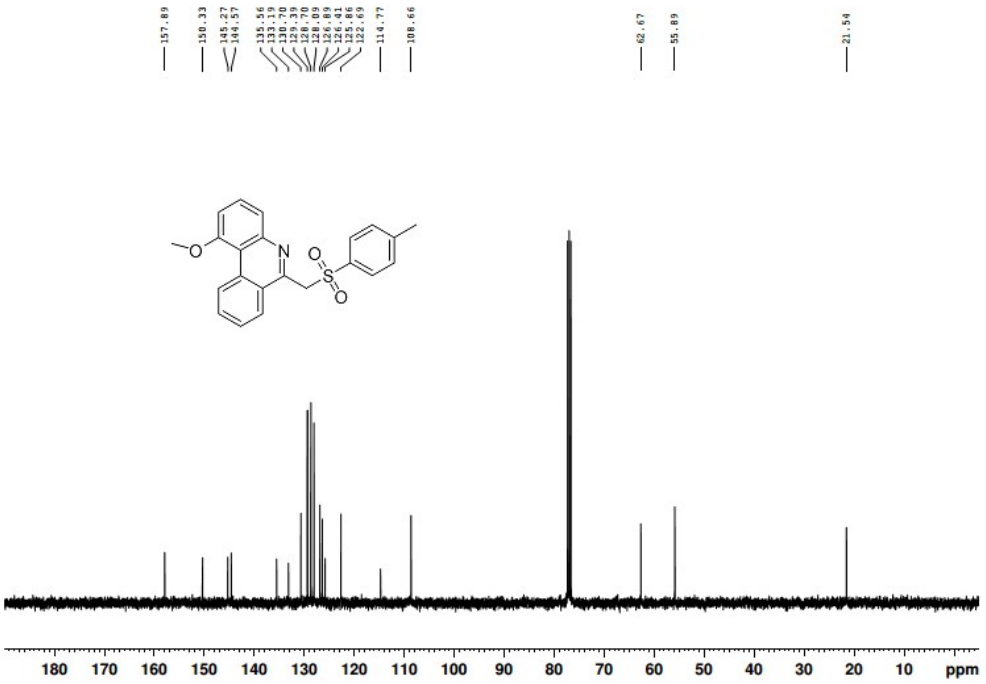
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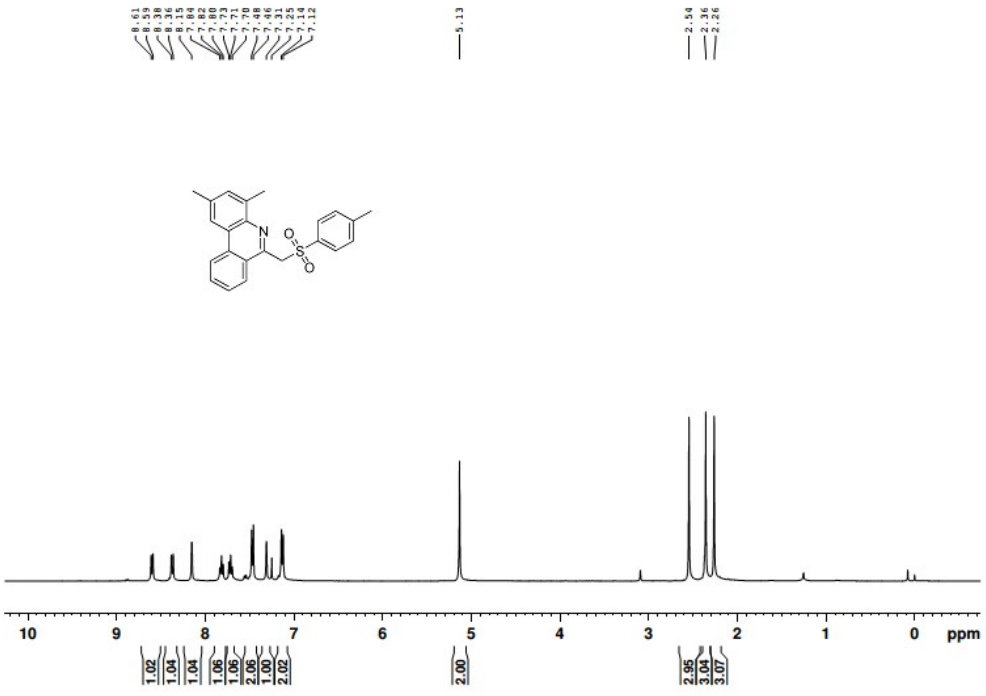
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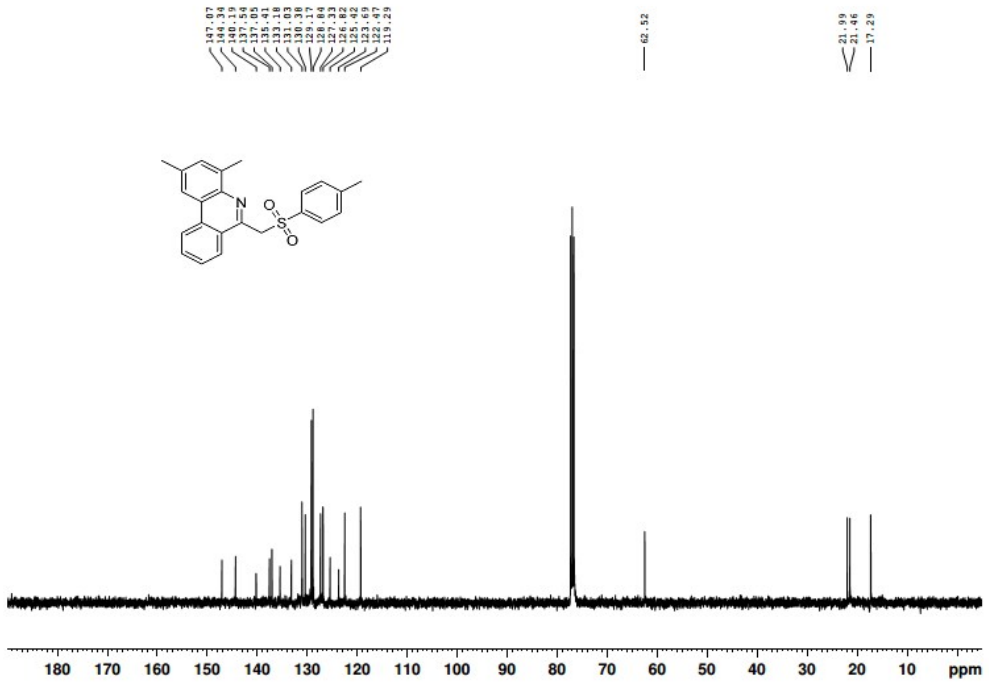
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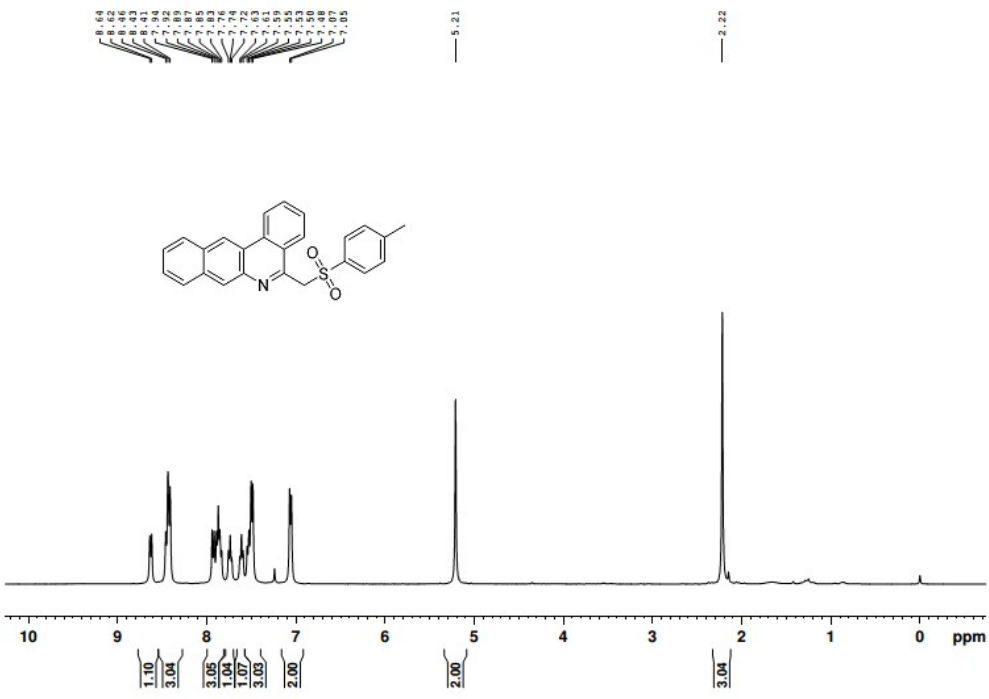
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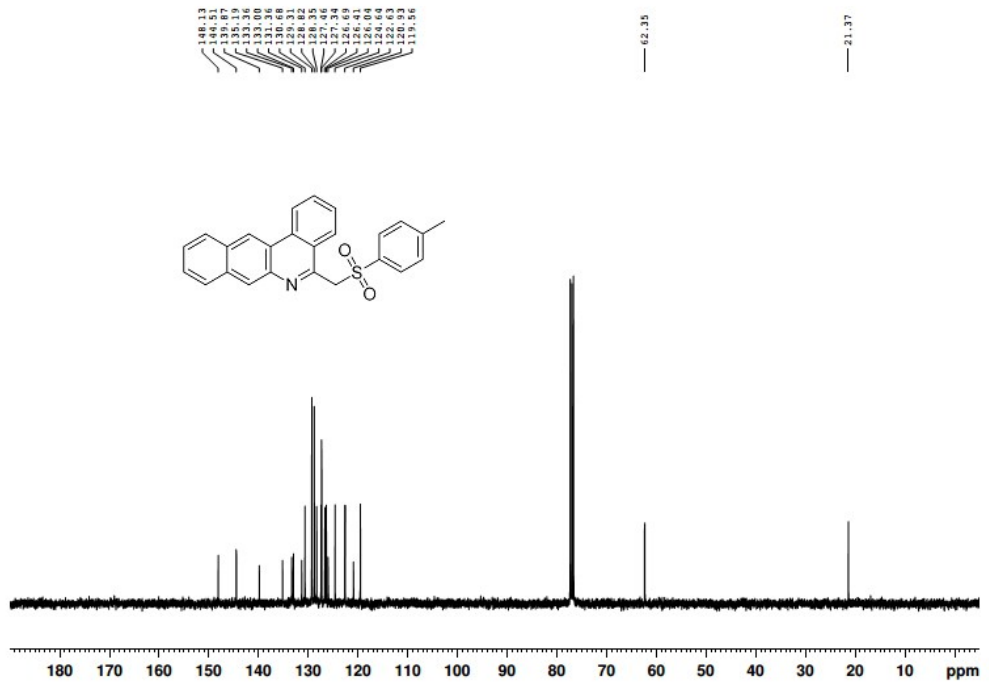
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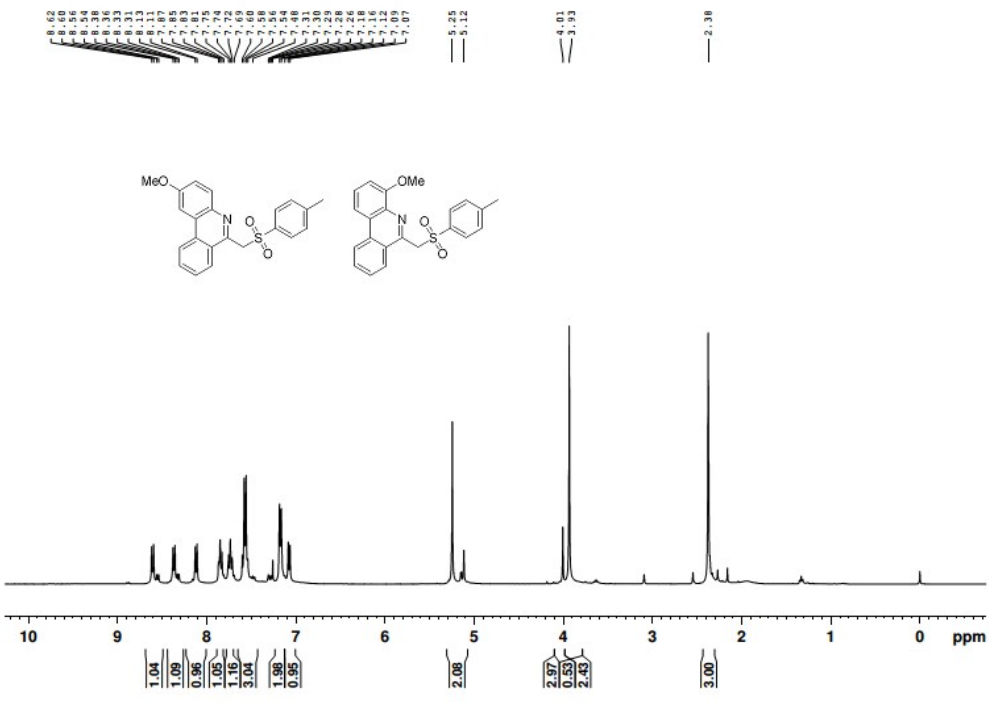
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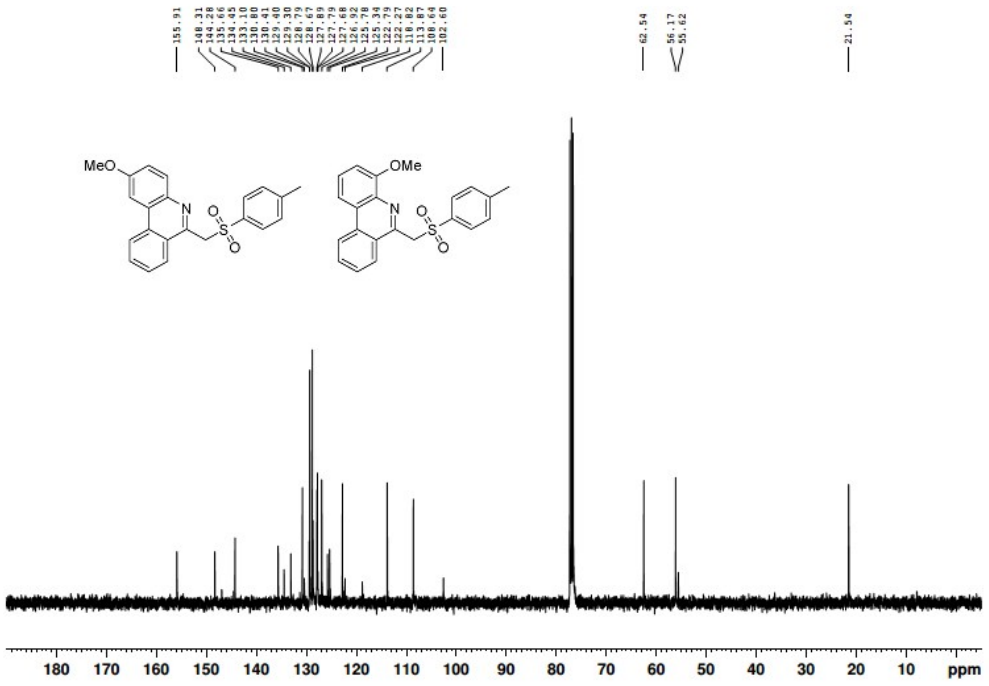
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21.54
MeO
OMe
N
O
S
O
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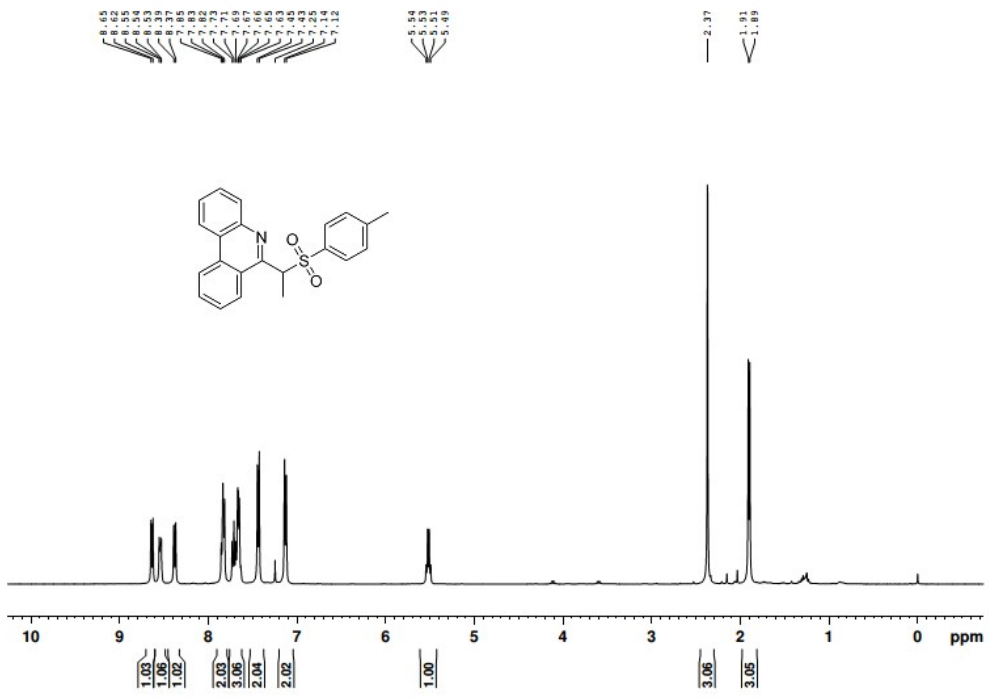
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8.54
8.53
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7.82
7.73
7.71
7.69
7.67
7.66
7.65
7.63
7.45
7.43
7.25
7.14
7.12
5.54
5.53
5.51
5.49
2.37
1.91
1.89
N
O
S
O
10 9 8 7 6 5 4 3 2 1 0 ppm
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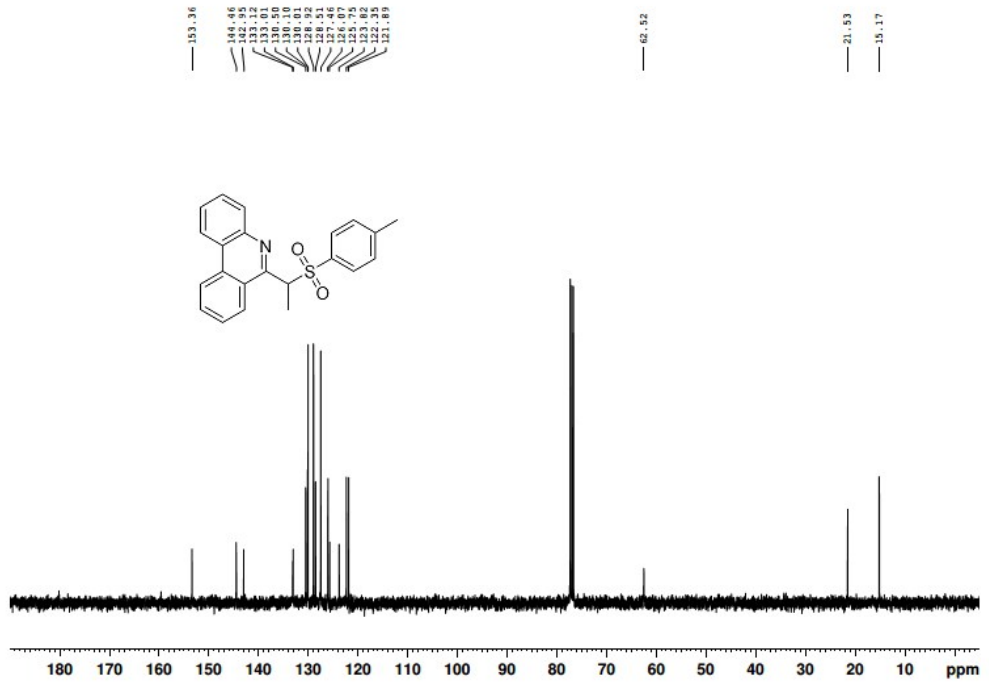
1.06
1.02
2.03
3.06
2.04
2.02
1.00
3.06
3.05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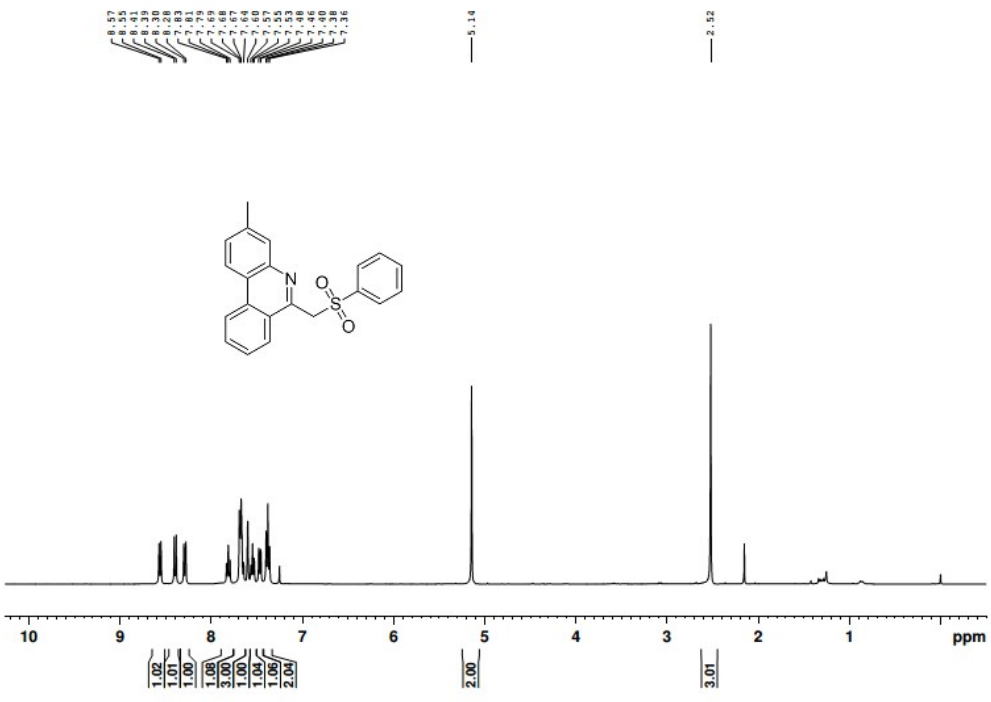
133.01
130.50
130.10
130.01
128.92
128.51
127.46
126.07
125.75
123.02
122.35
121.89
62.52
21.53
15.17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.55
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8.33
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8.28
7.83
7.81
7.79
7.69
7.68
7.67
7.66
7.60
7.57
7.55
7.53
7.48
7.46
7.40
7.38
7.36
5.14
2.52
10 9 8 7 6 5 4 3 2 1 ppm
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1.00
1.08
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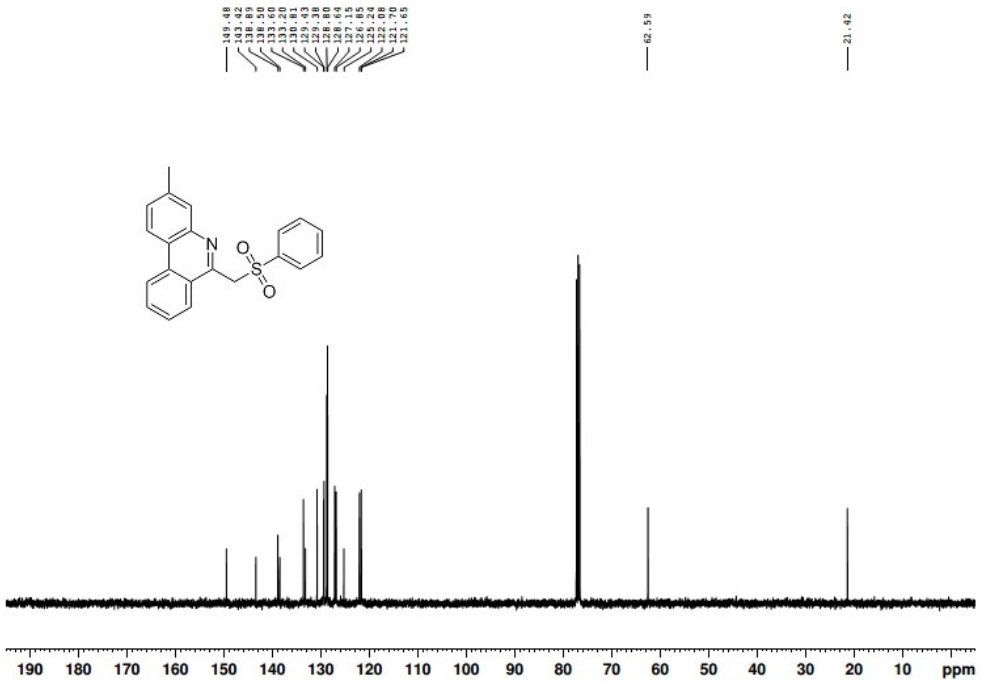
1.00
1.04
1.06
2.04
2.00
3.01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130.81
129.43
129.38
128.60
128.06
127.15
126.05
125.24
123.08
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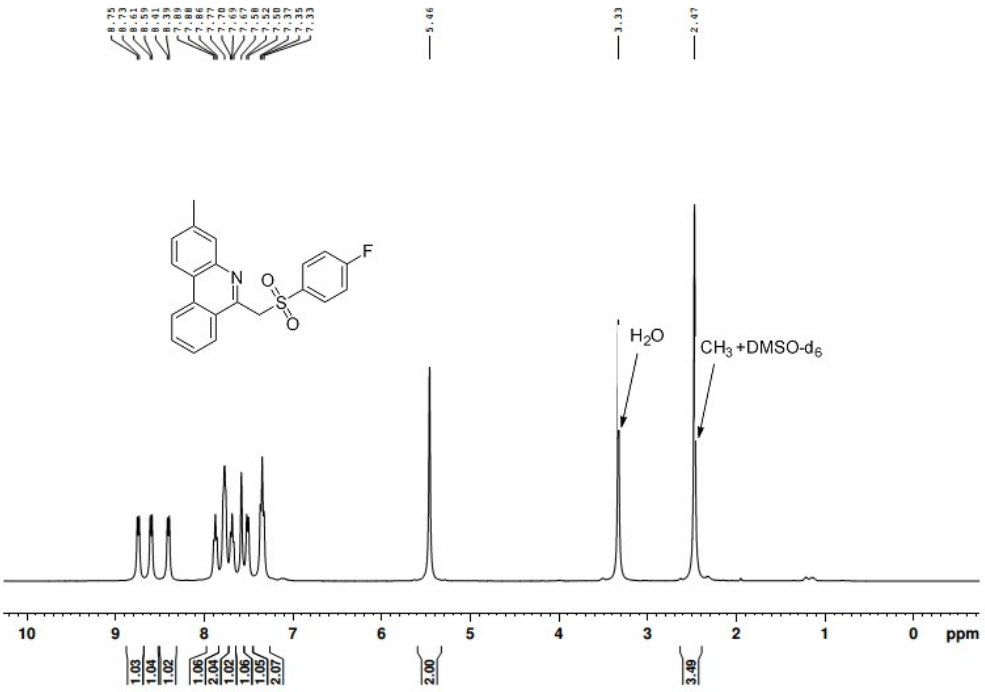
121.65
62.59
21.42
N
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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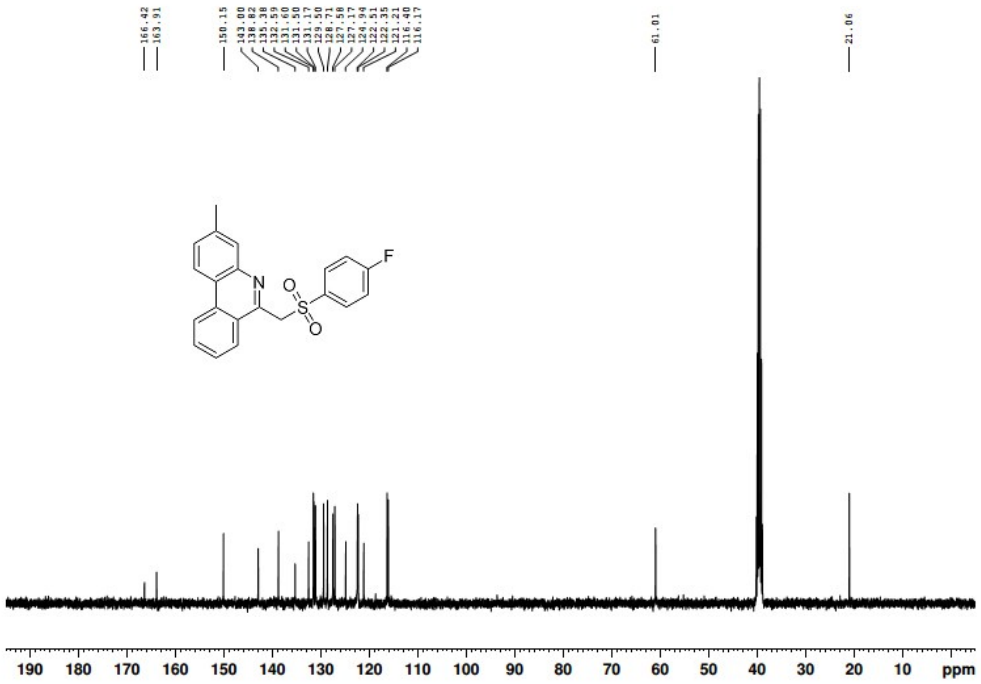
8.73
8.61
8.45
8.41
8.39
7.89
7.88
7.86
7.77
7.70
7.69
7.67
7.58
7.52
7.50
7.37
7.35
7.33
5.46
3.33
2.47
N
O
S
O
F
H2O
CH3 +DMSO-d6
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.04
1.02
1.06
2.04
1.02
1.06
1.05
2.07
2.00
3.49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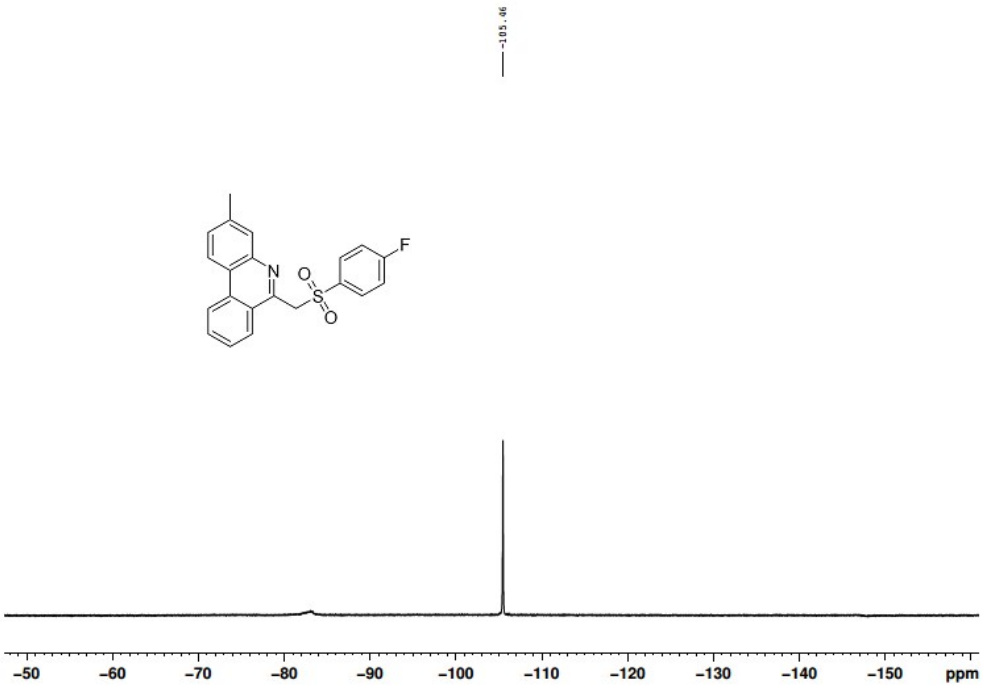
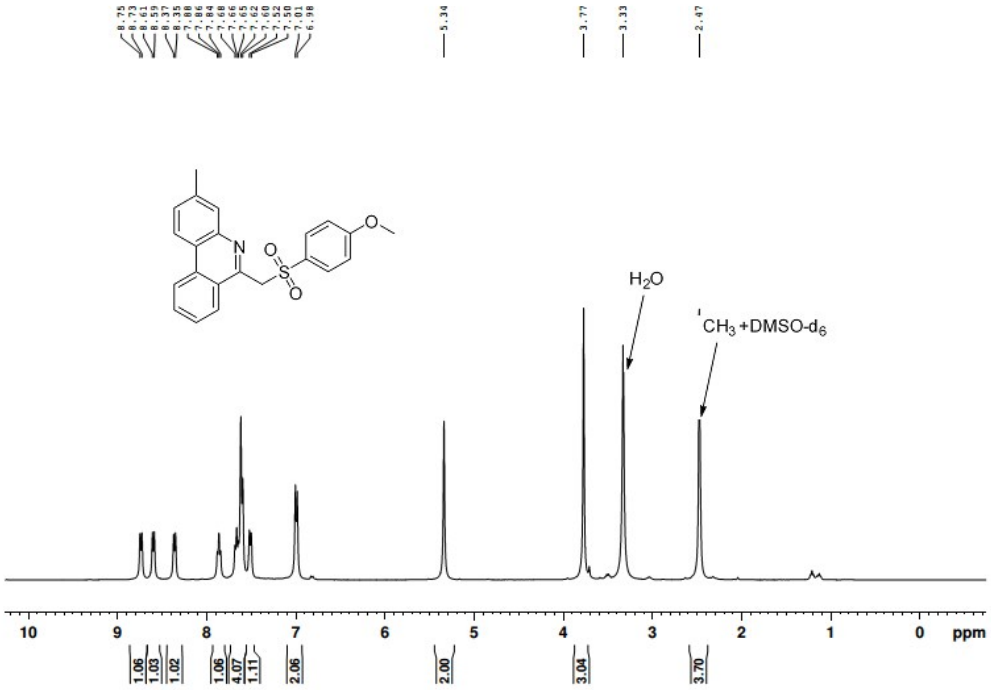
132.59
131.60
131.30
131.17
129.50
128.71
128.58
127.17
124.94
122.51
122.35
122.21
116.40
116.17
61.01
21.06
F
N
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-105.06
F
N
O
S
O
−50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 ppm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8.73
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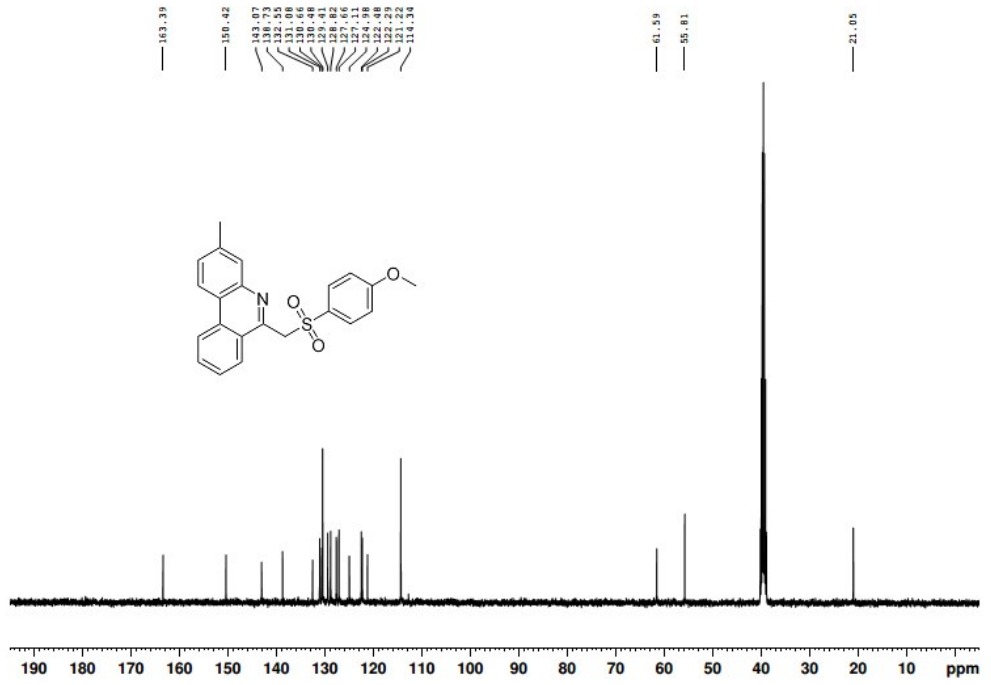
8.59
8.37
8.35
7.86
7.84
7.68
7.66
7.65
7.62
7.60
7.52
7.50
7.01
6.98
5.34
3.77
3.33
2.47
H2O
CH3 +DMSO-d6
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.03
1.02
1.06
4.07
1.11
2.06
2.00
3.04
3.70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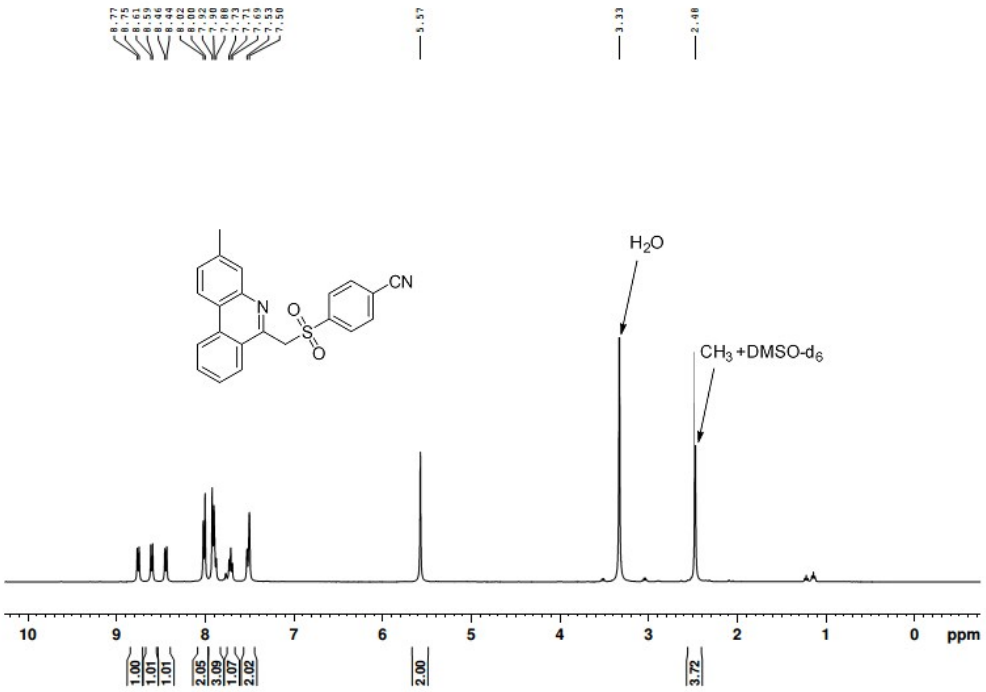
131.00
130.66
130.48
129.41
128.82
128.66
127.11
124.98
122.48
122.29
121.22
114.34
61.59
55.81
21.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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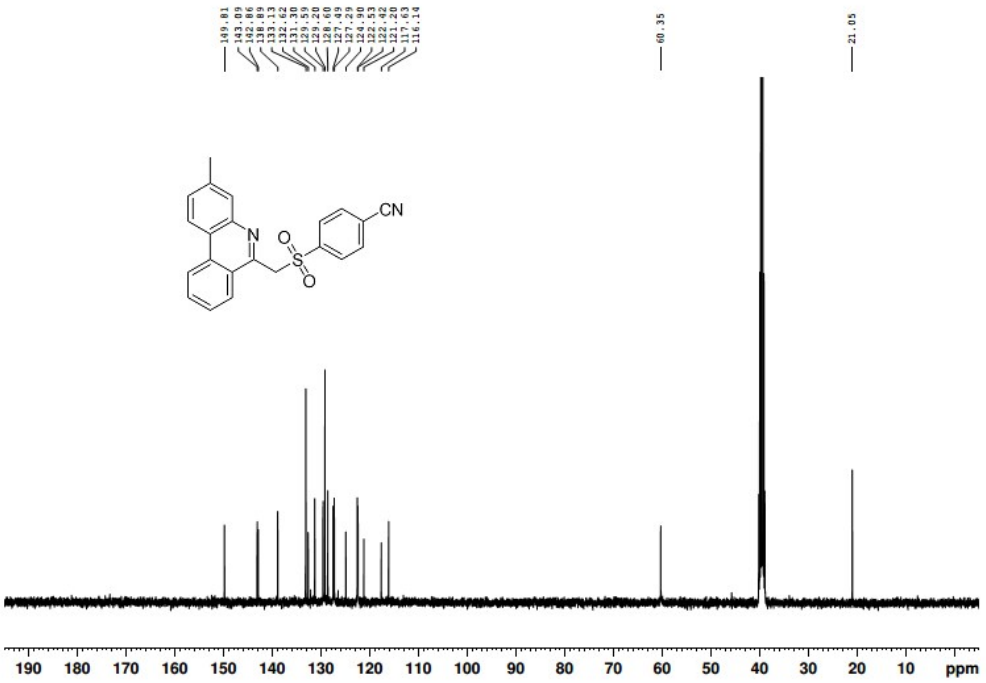
8.75
8.61
8.59
8.46
8.44
8.02
8.00
7.92
7.90
7.88
7.73
7.71
7.69
7.53
7.50
5.57
3.33
2.48
CN
N
O
S
O
H2O
CH3 +DMSO-d6
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.01
2.05
3.09
1.07
2.02
2.00
3.72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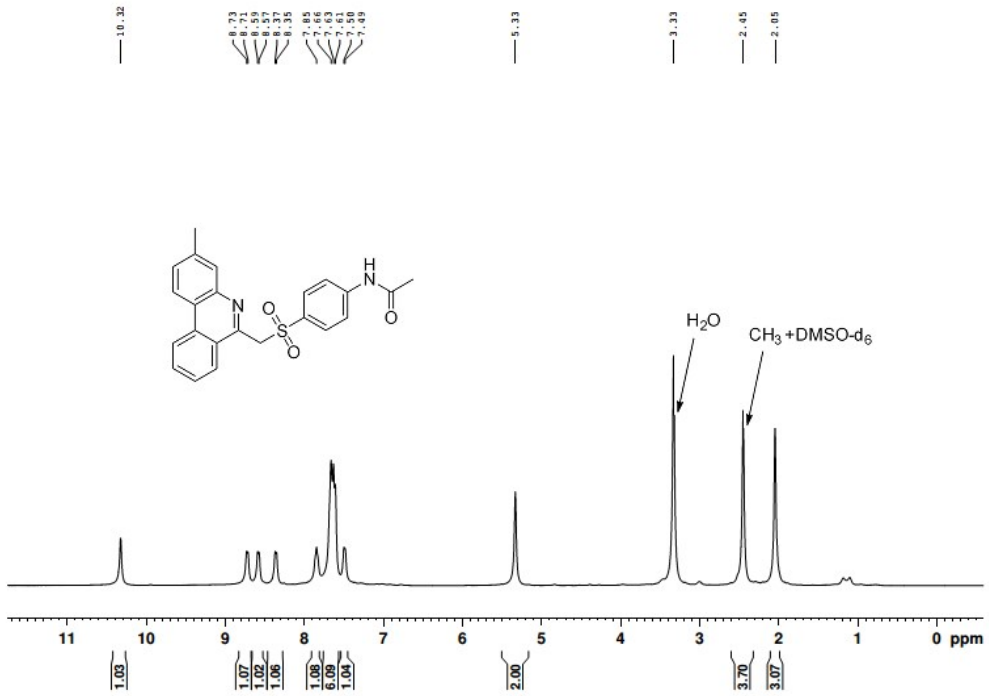
143.09
142.86
138.89
133.13
132.42
131.30
129.59
129.20
128.60
127.49
127.29
124.90
122.53
122.42
121.26
117.63
116.14
60.35
21.05
CN
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.71
8.59
8.57
8.37
8.35
7.85
7.66
7.63
7.61
7.50
7.49
5.33
3.33
2.45
2.05
H2O
CH3 +DMSO-d6
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.03
1.07
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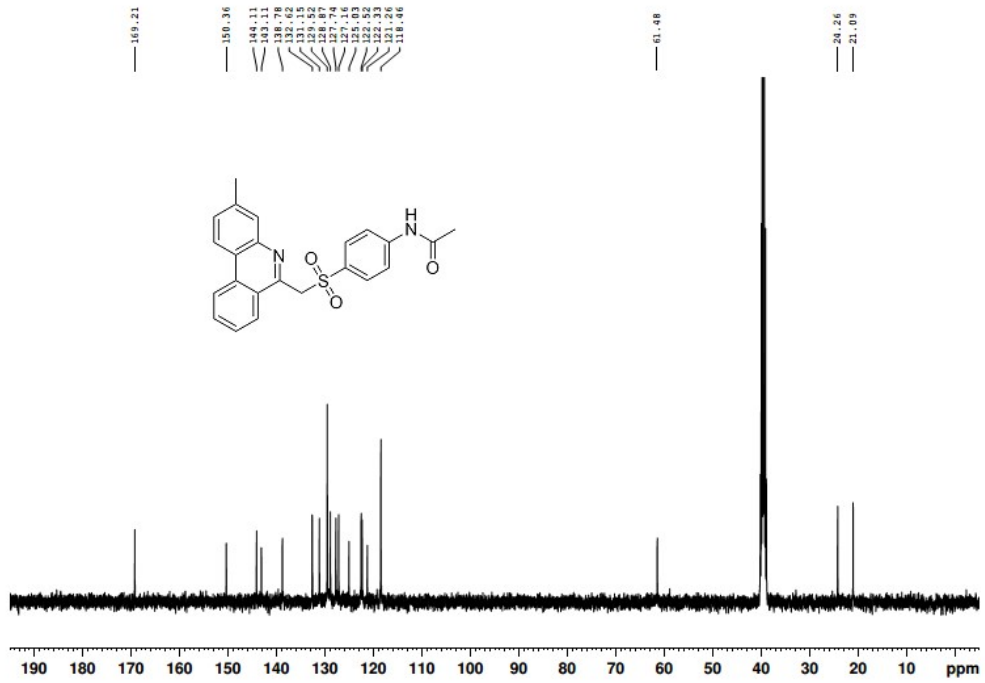
1.08
6.09
1.04
2.00
3.70
3.07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129.52
128.87
127.74
127.16
125.03
122.52
122.33
121.26
118.46
61.48
24.26
21.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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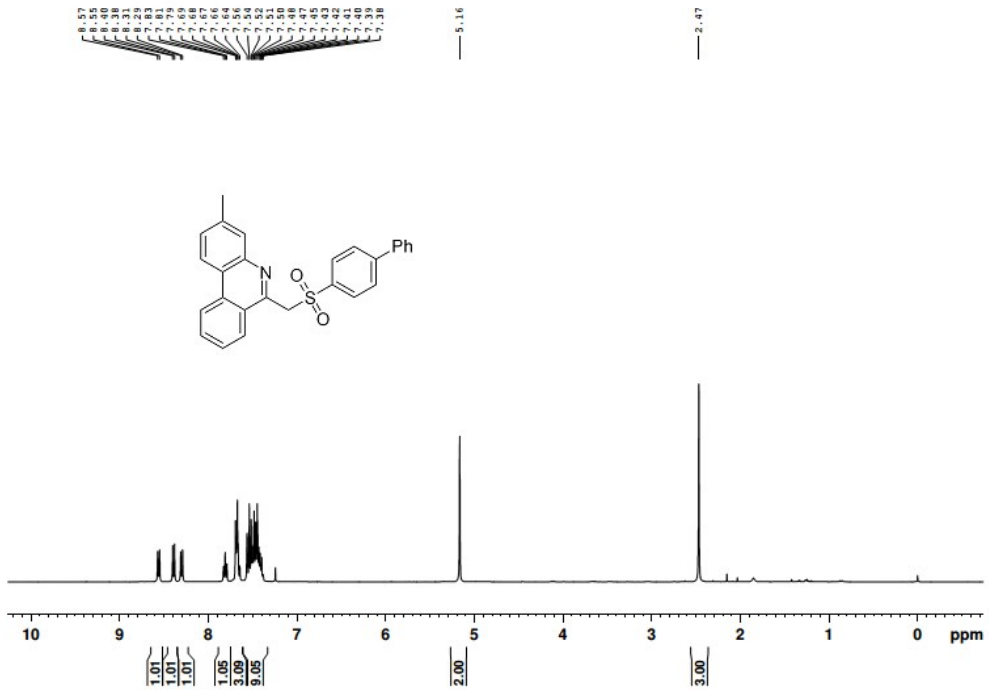
30
20
10
ppm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7.79
7.69
7.68
7.67
7.66
7.64
7.56
7.54
7.52
7.51
7.50
7.48
7.47
7.45
7.43
7.42
7.41
7.40
7.39
7.38
5.16
2.47
Ph
N
O
S
O
10
9
8
7
6
5
4
3
2
1
0
ppm
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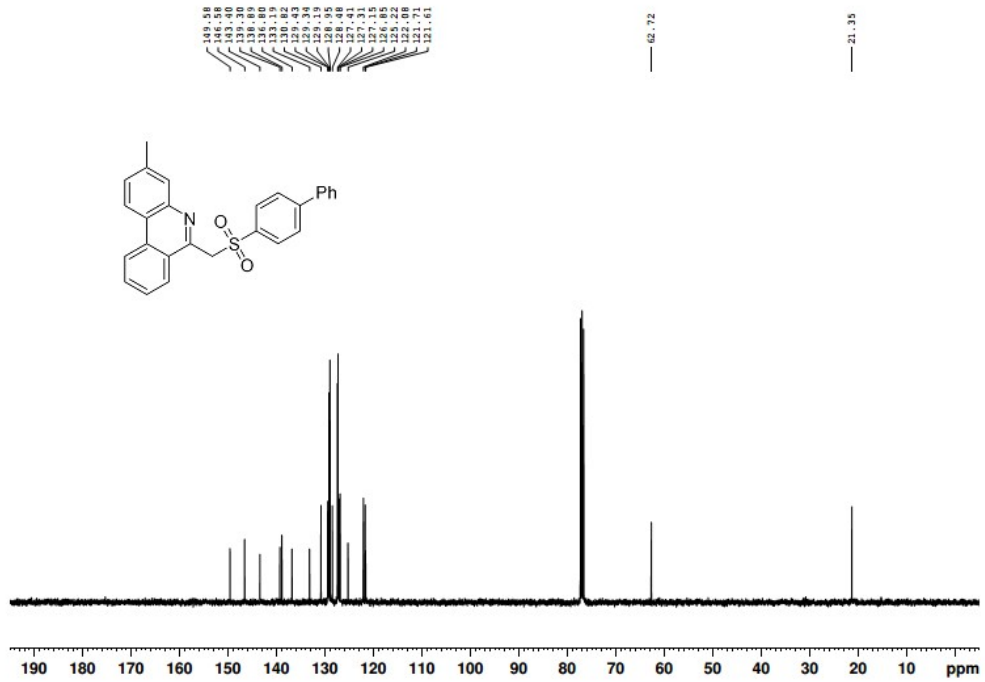
1.01
1.01
1.05
3.09
9.05
2.00
3.00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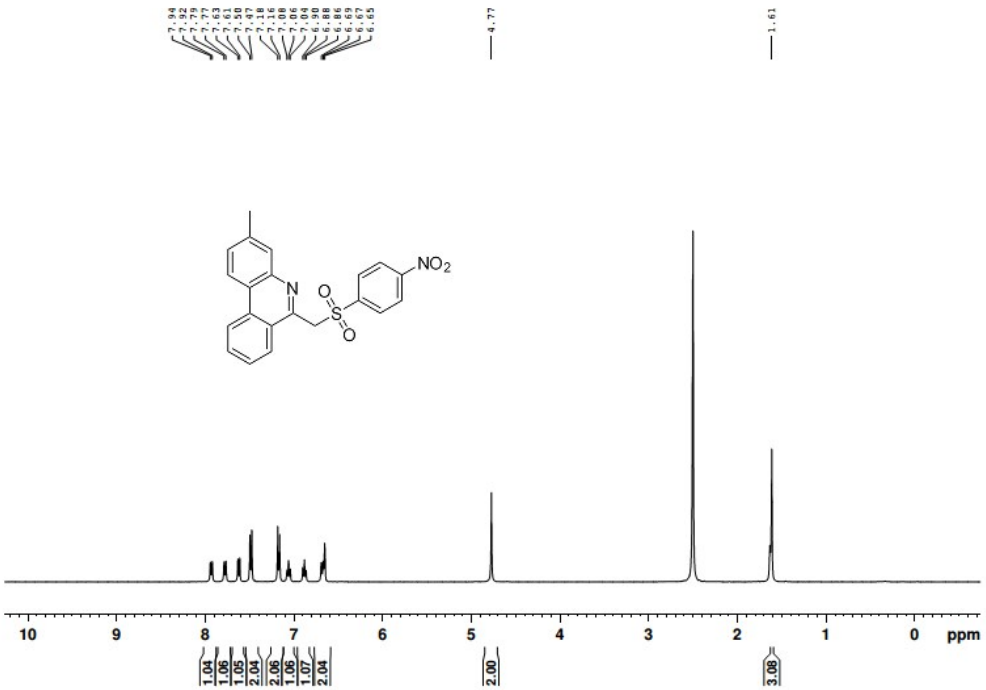
136.80
133.19
130.82
129.43
129.34
129.19
128.95
128.48
127.41
127.31
127.15
126.85
125.22
122.08
121.71
121.61
62.72
21.35
Ph
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.92
7.79
7.77
7.63
7.61
7.50
7.47
7.18
7.16
7.08
7.06
7.04
6.90
6.88
6.86
6.69
6.67
6.65
4.77
1.61
NO2
N
O
S
O
10
9
8
7
6
5
4
3
2
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ppm
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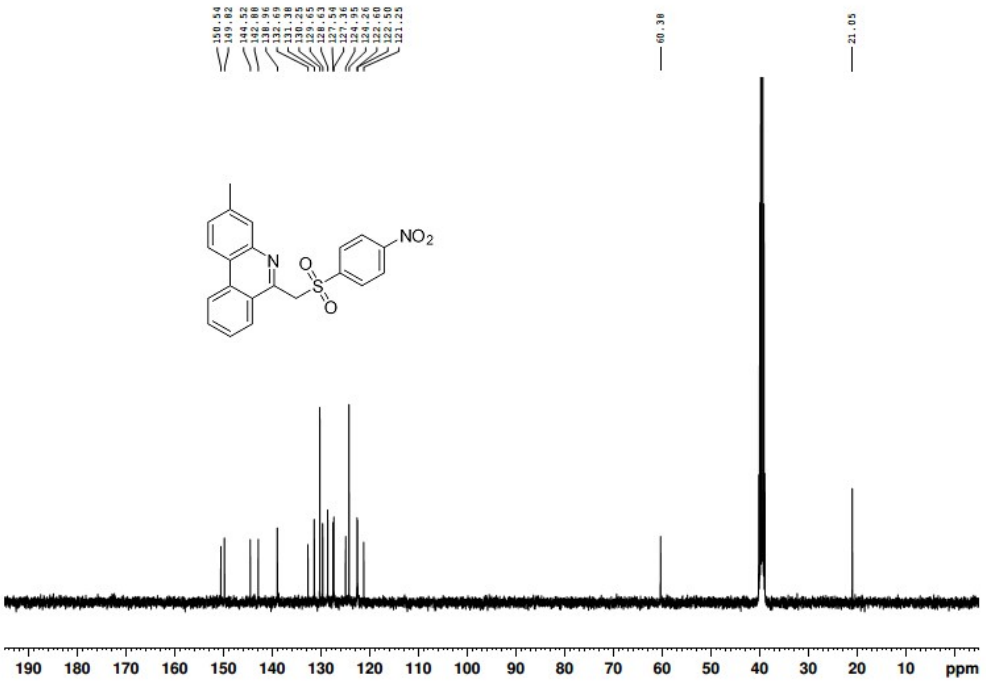
1.06
1.05
2.04
2.06
1.06
1.07
2.04
2.00
3.08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131.38
130.75
129.65
128.63
127.54
127.36
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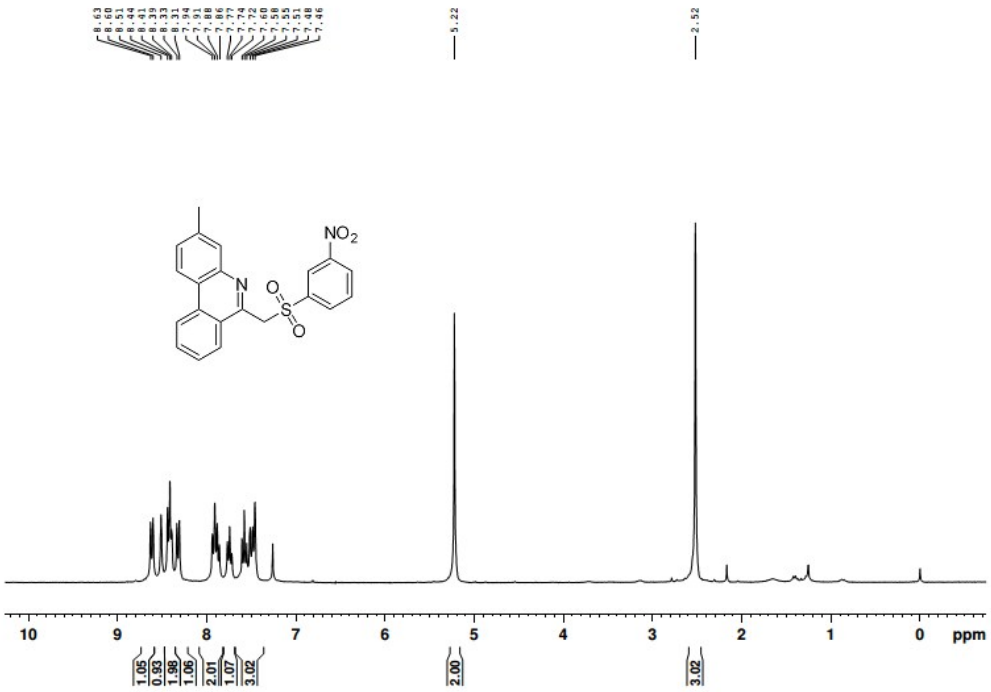
124.26
122.60
122.50
121.25
60.38
21.05
NO2
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.44
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8.33
8.31
7.94
7.91
7.88
7.86
7.77
7.74
7.72
7.60
7.58
7.55
7.51
7.48
7.46
5.22
2.52
NO2
N
O
S
O
10
9
8
7
6
5
4
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ppm
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1.06
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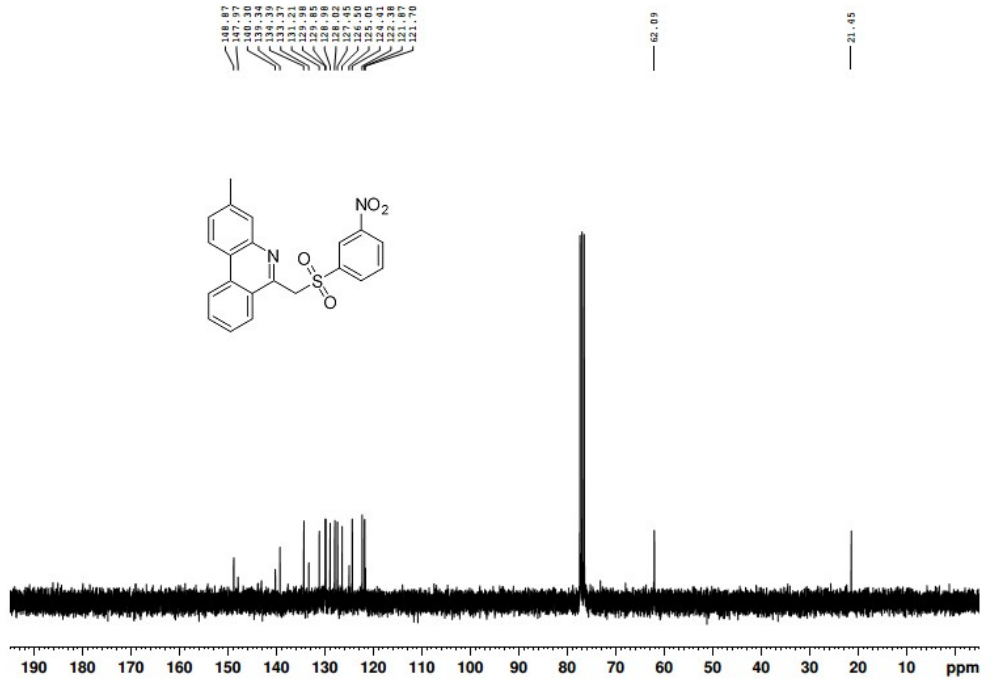
1.07
3.02
2.00
3.02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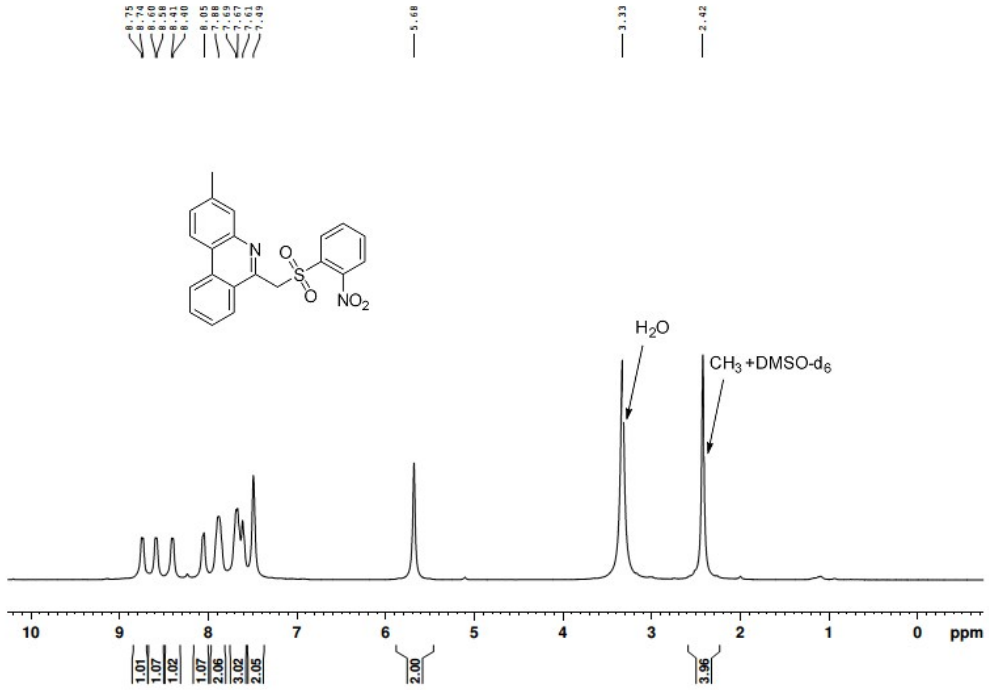
129.86
129.85
128.98
128.02
127.45
126.68
125.05
124.41
122.38
121.97
121.70
62.09
21.45
NO2
N
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.74
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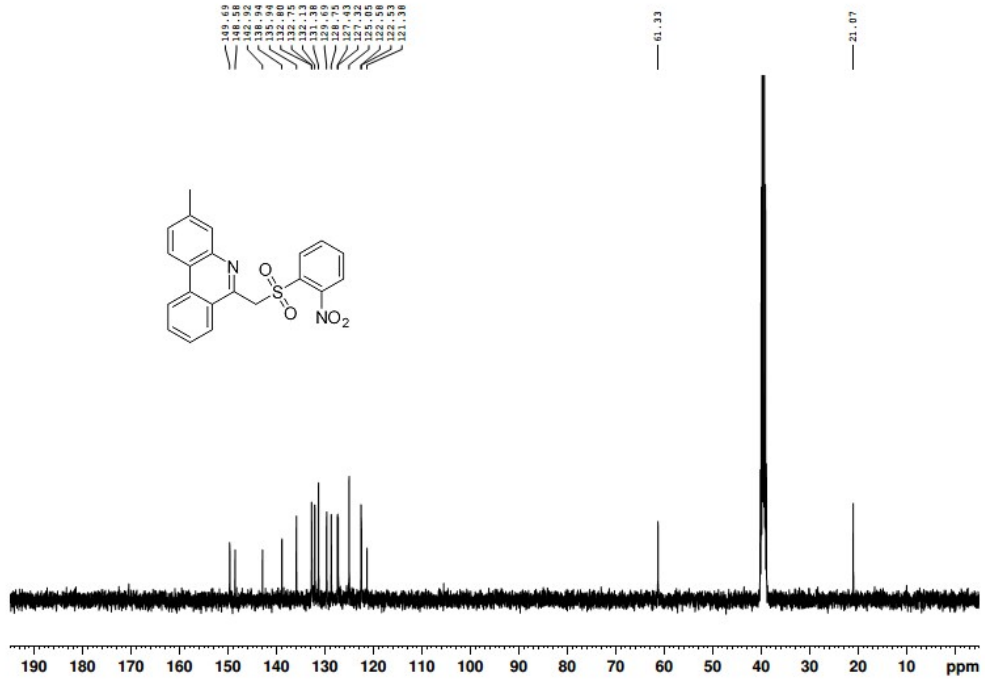
8.58
8.41
8.40
8.05
7.88
7.69
7.67
7.61
7.49
5.68
3.33
2.42
N
O
S
O
NO2
H2O
CH3 +DMSO-d6
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.07
1.02
1.07
2.06
3.02
2.05
2.00
3.96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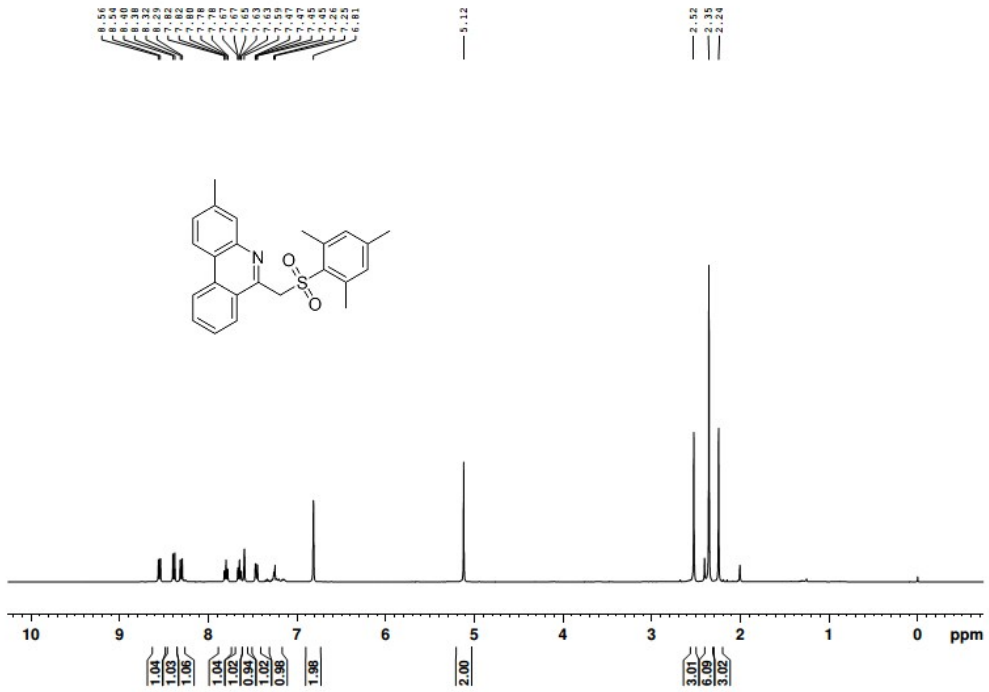
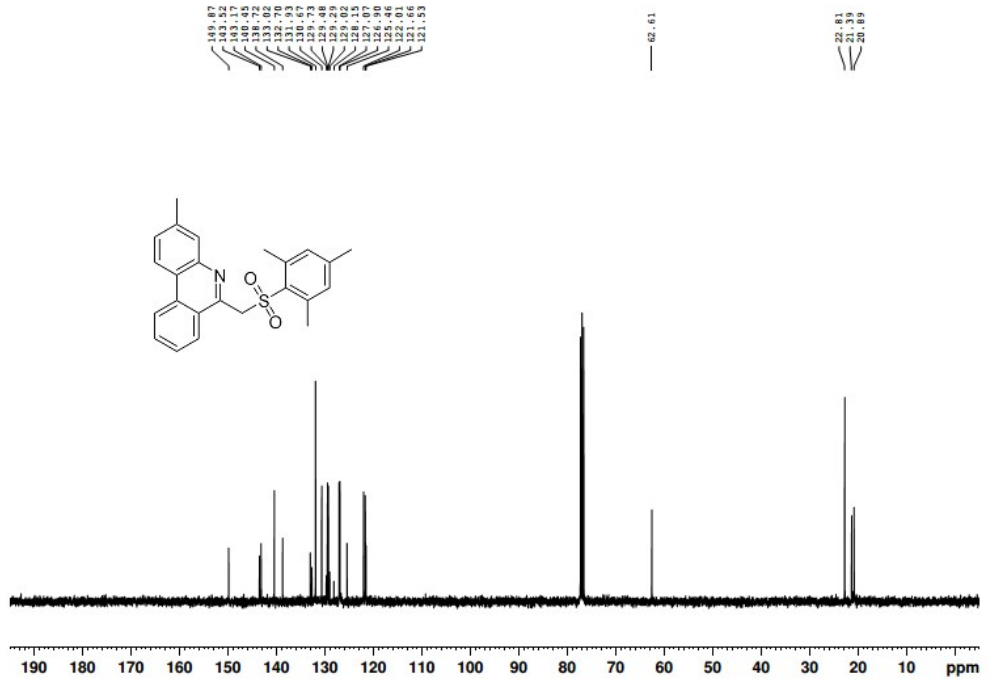
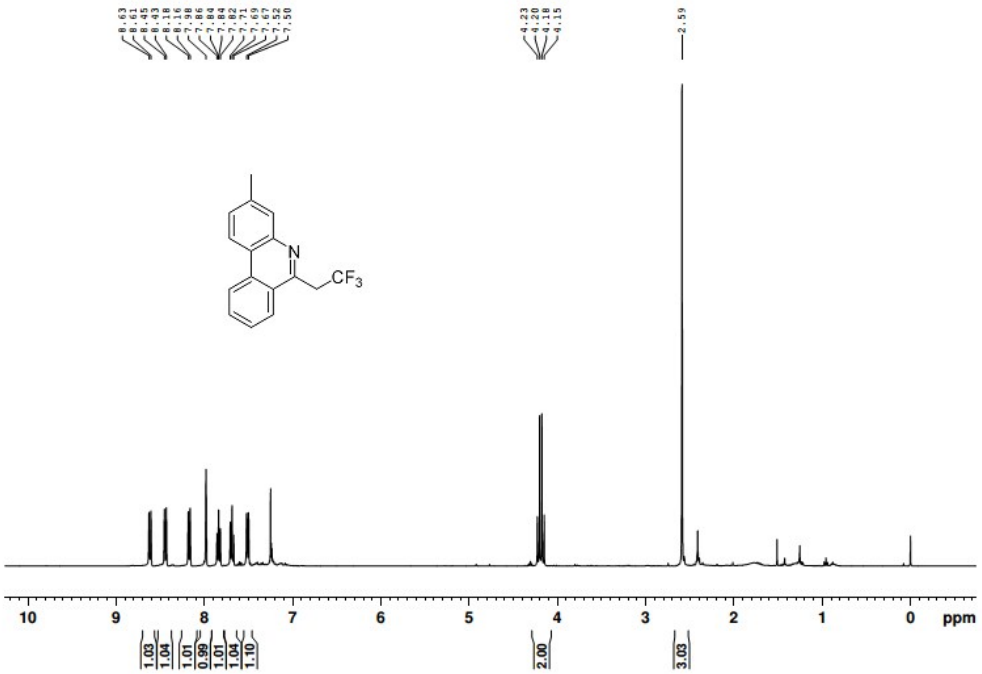
132.13
131.38
129.69
128.75
127.43
127.32
125.05
122.58
122.53
121.38
61.33
21.07
N
O
S
O
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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8.61
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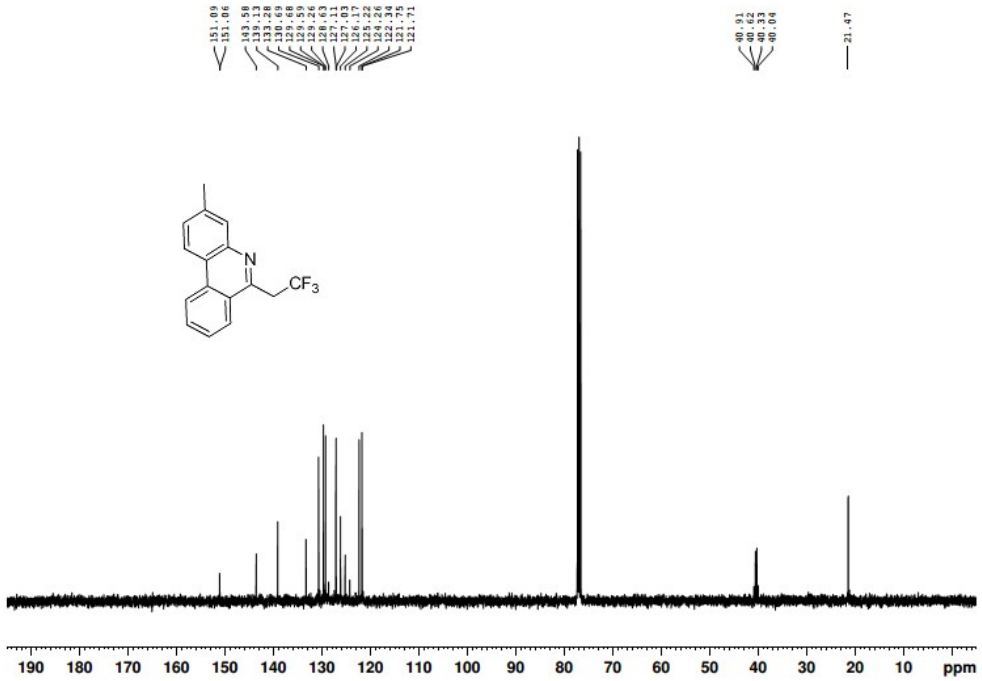
8.43
8.18
8.16
7.98
7.86
7.84
7.82
7.71
7.69
7.67
7.52
7.50
4.23
4.20
4.18
4.15
2.59
N
CF3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.04
1.01
0.99
1.01
1.04
1.10
2.00
3.03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151.06
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139.13
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130.69
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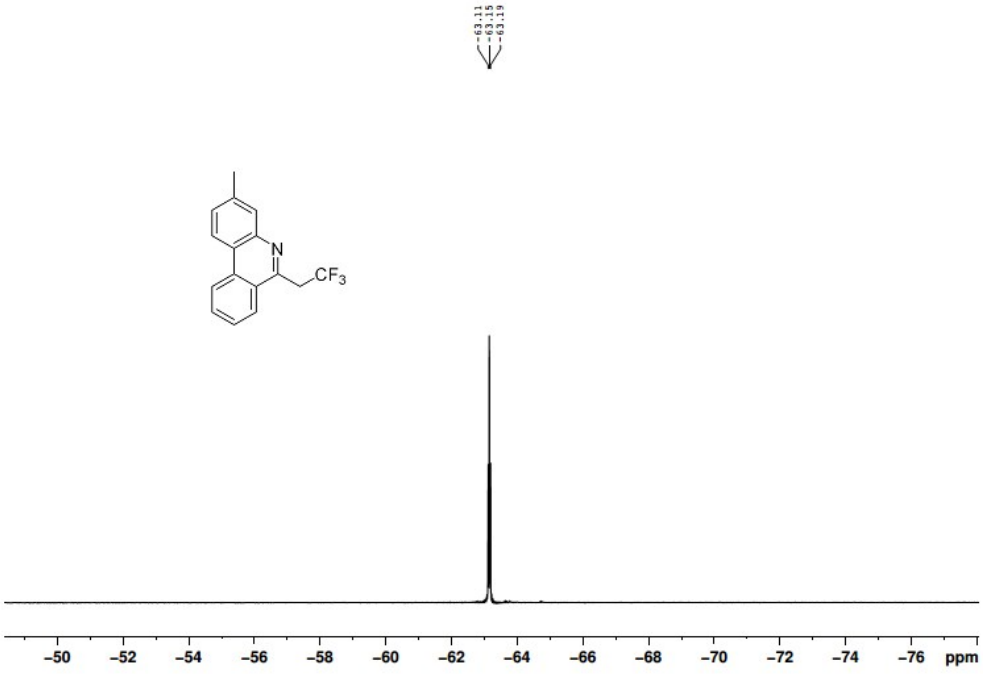
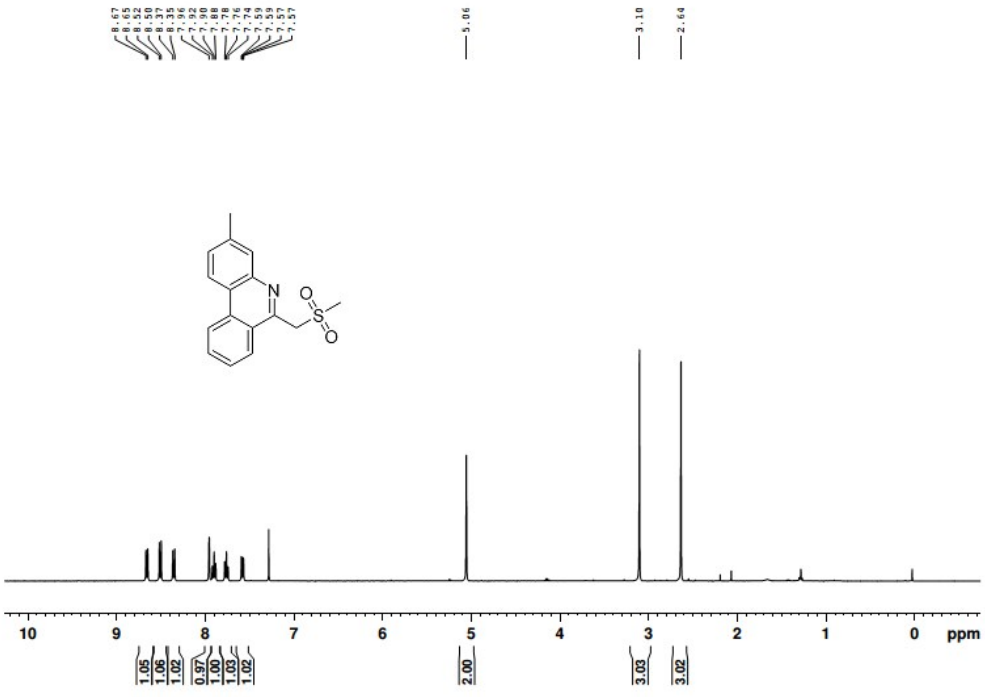
129.59
128.96
128.63
127.11
127.03
126.77
126.22
124.26
122.34
121.75
121.71
40.91
40.62
40.33
40.04
21.47
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-63.11
-63.15
-63.19
N
CF3
−50 −52 −54 −56 −58 −60 −62 −64 −66 −68 −70 −72 −74 −76 ppm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8.50
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8.35
7.96
7.92
7.90
7.88
7.78
7.76
7.74
7.59
7.59
7.57
7.57
5.06
3.10
2.64
N
O
S
O
10 9 8 7 6 5 4 3 2 1 0 ppm
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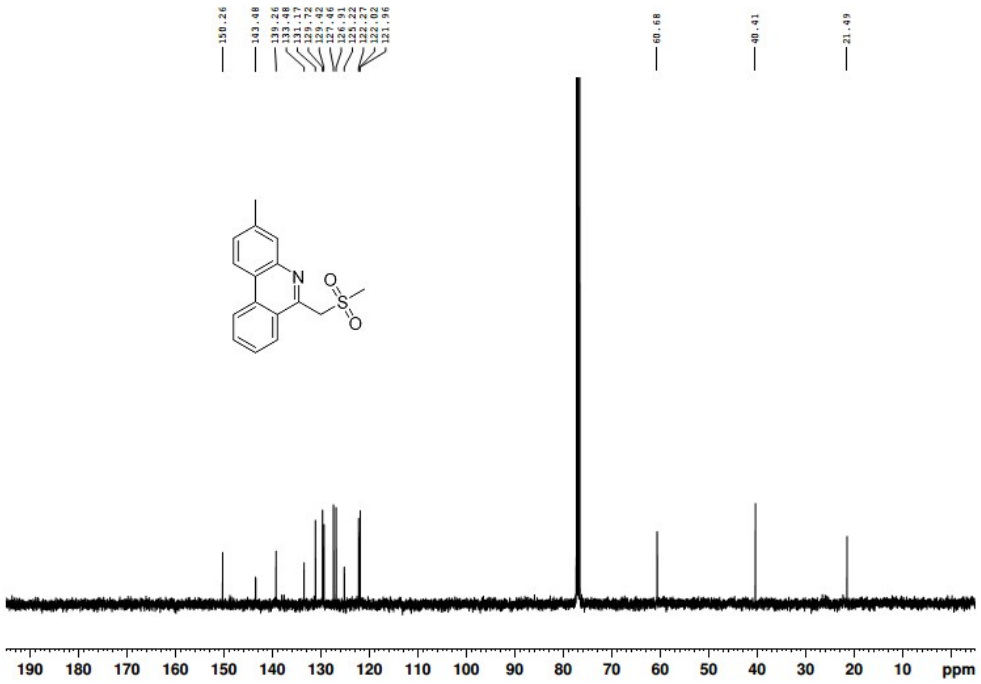
1.06
1.02
0.97
1.00
1.03
1.02
2.00
3.03
3.02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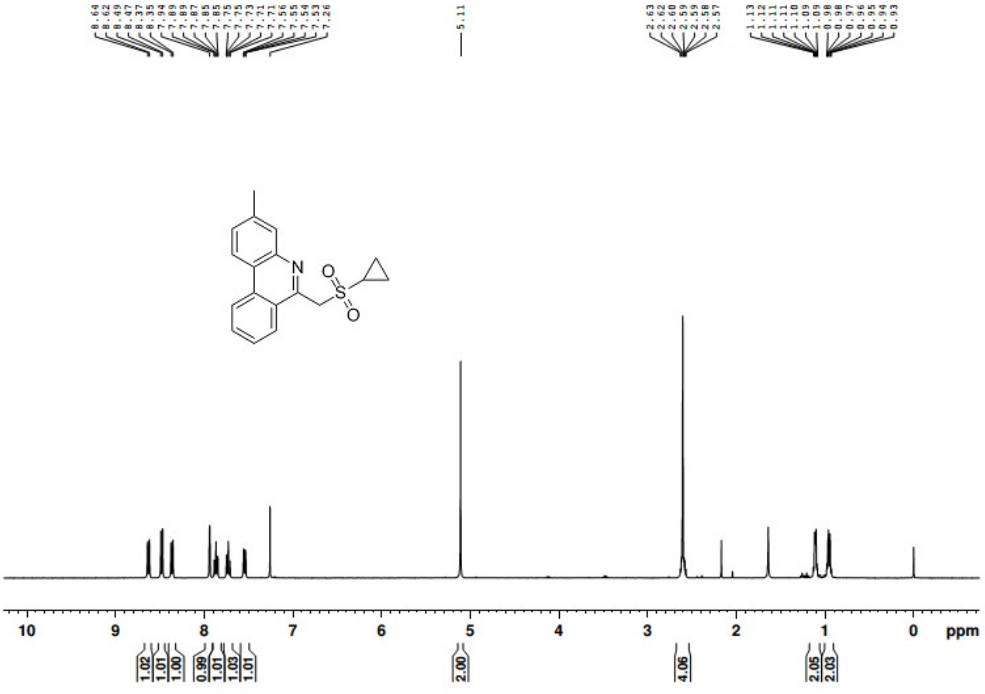
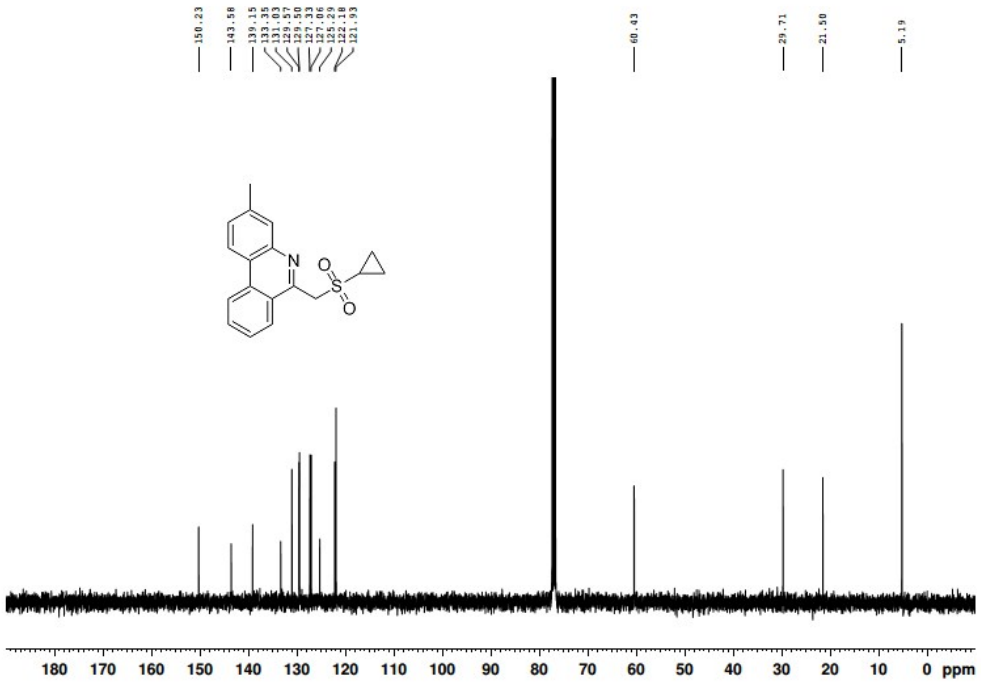
133.48
131.17
129.72
129.42
127.46
126.91
125.22
122.27
122.02
121.96
60.68
40.41
21.49
N
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.64
8.62
8.49
8.47
8.37
8.35
7.94
7.89
7.88
7.87
7.85
7.85
7.75
7.73
7.71
7.71
7.56
7.55
7.54
7.53
7.26
5.11
2.63
2.62
2.60
2.59
2.59
2.58
2.57
1.13
1.12
1.11
1.11
1.10
1.09
1.09
1.08
0.98
0.97
0.96
0.95
0.94
0.93
N
O
S
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
1.01
1.00
0.99
1.01
1.03
1.01
2.00
4.06
2.05
2.03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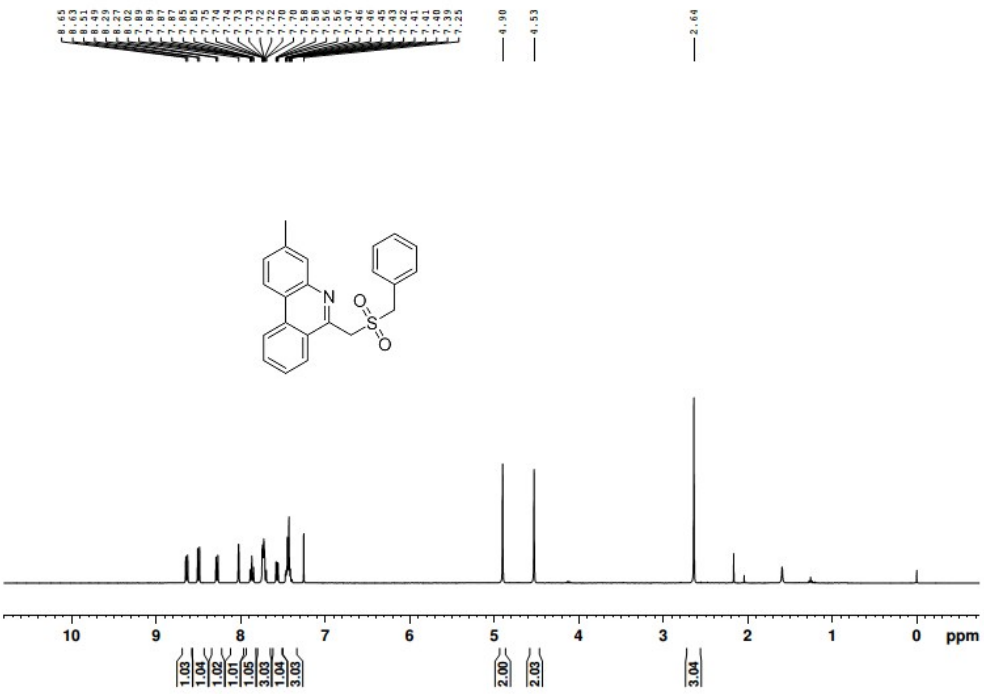
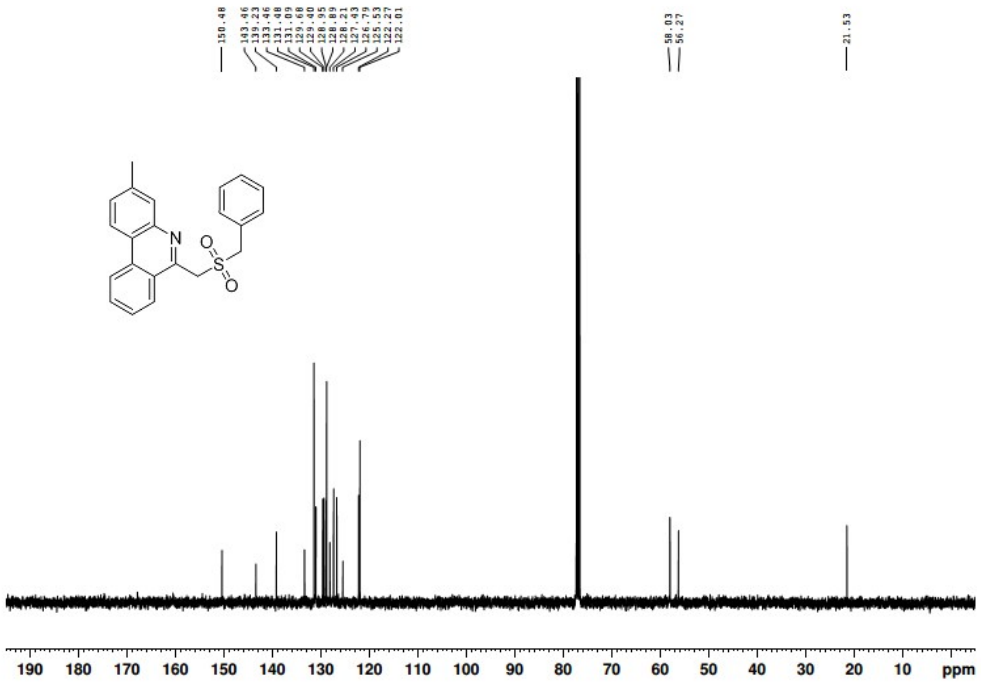
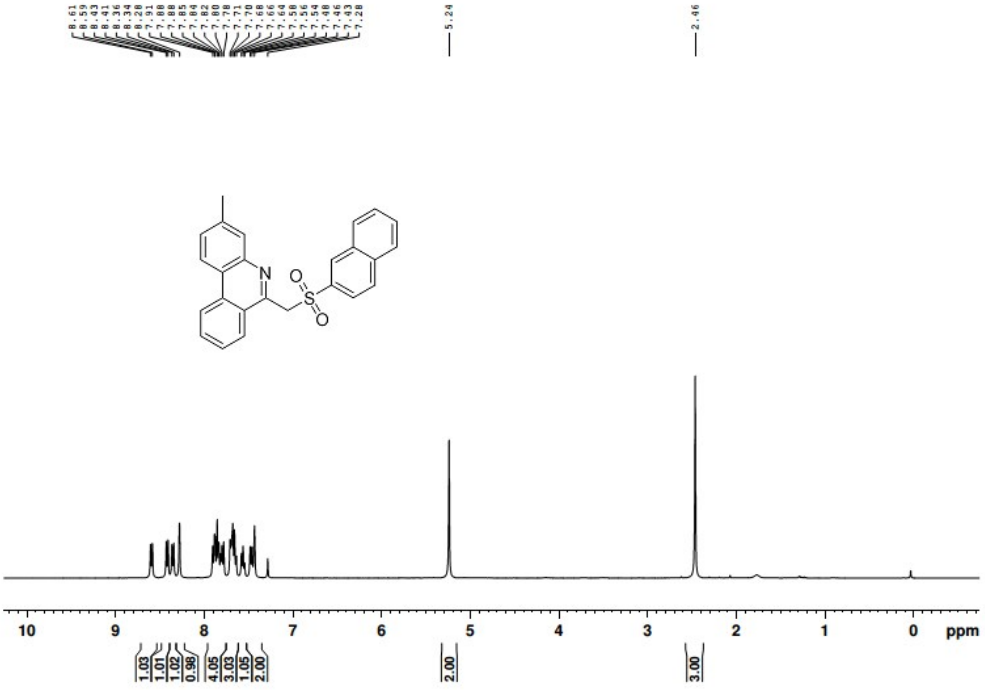
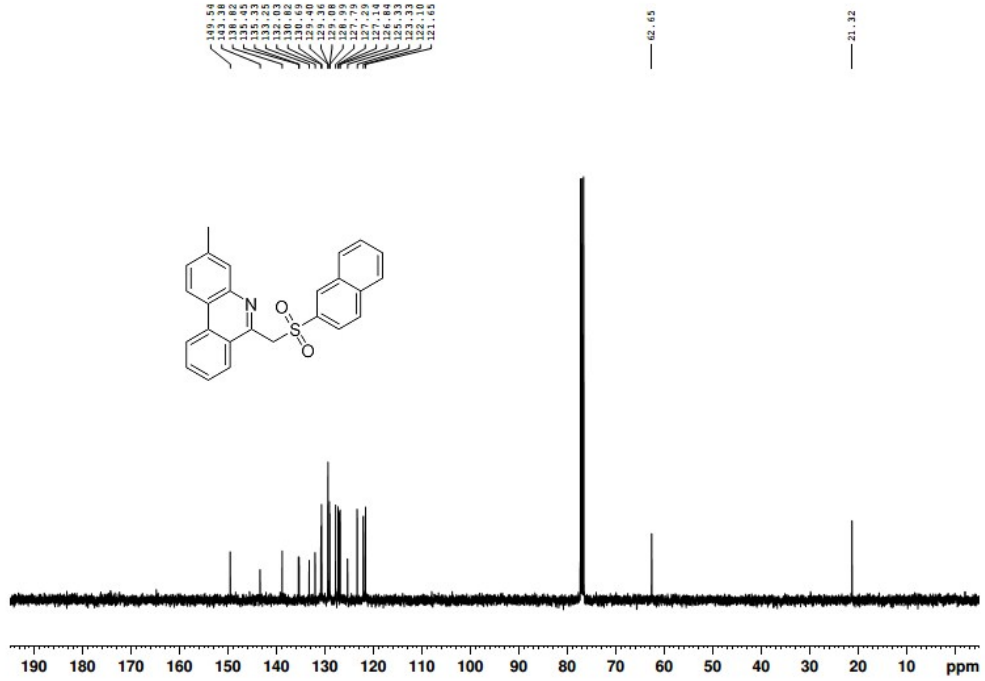
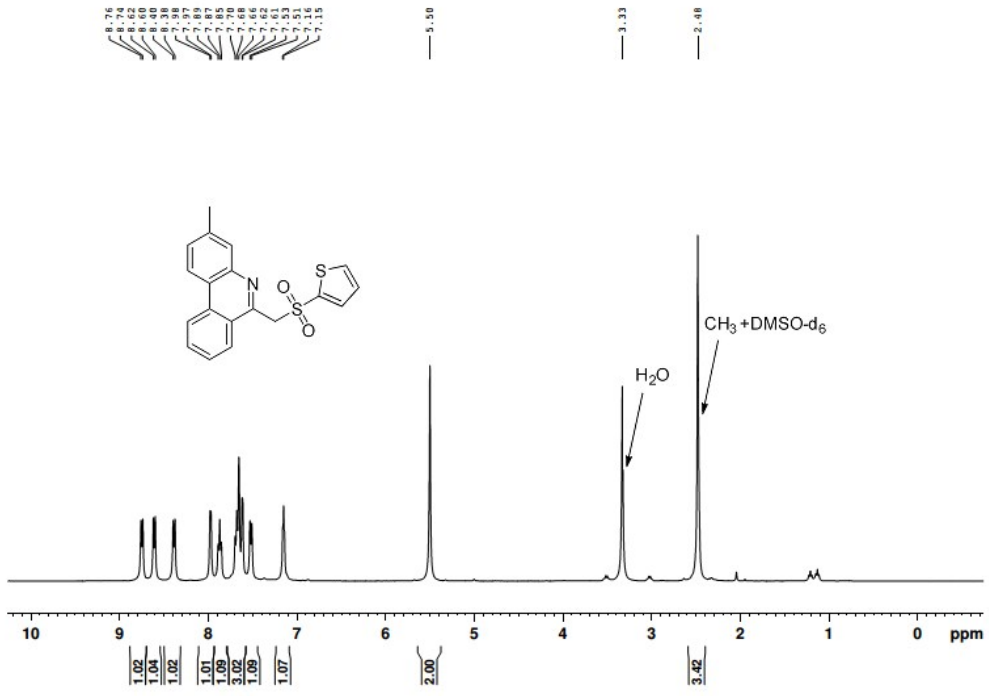
143.58
139.15
133.35
131.03
129.57
129.50
127.33
127.06
125.29
122.18
121.93
60.43
29.71
21.50
5.19
N
O
S
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

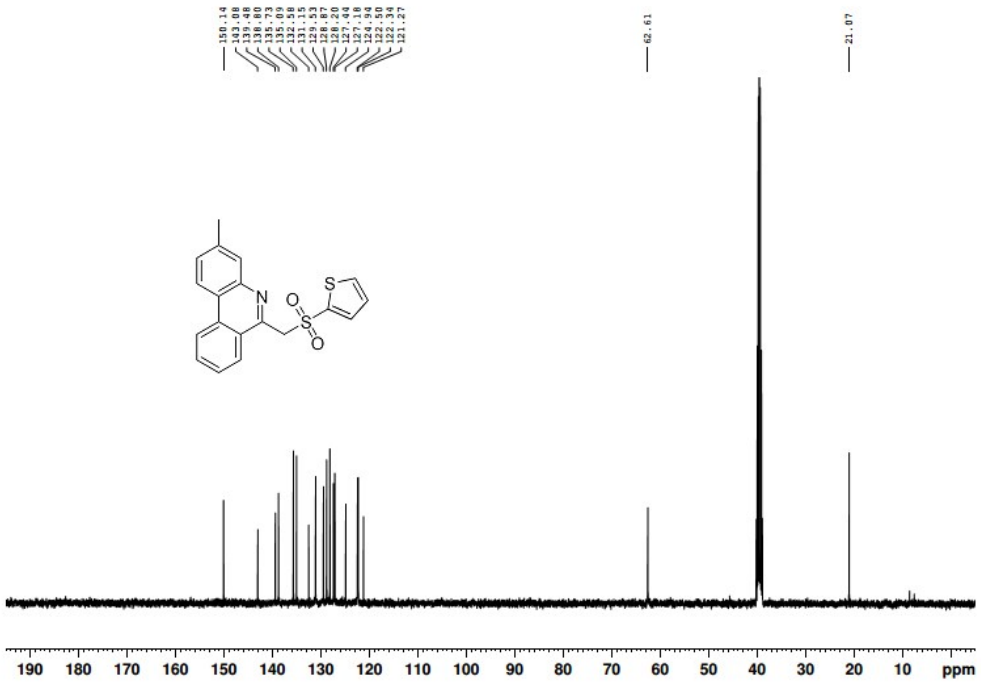

8.65
8.53
8.51
8.49
8.29
8.27
8.02
7.89
7.89
7.87
7.87
7.85
7.85
7.75
7.74
7.74
7.73
7.73
7.72
7.72
7.70
7.70
7.58
7.58
7.56
7.56
7.47
7.46
7.46
7.45
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.25
4.90
4.53
2.64
N
O
S
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.04
1.02
1.01
1.05
3.03
1.04
3.03
2.00
2.03
3.04

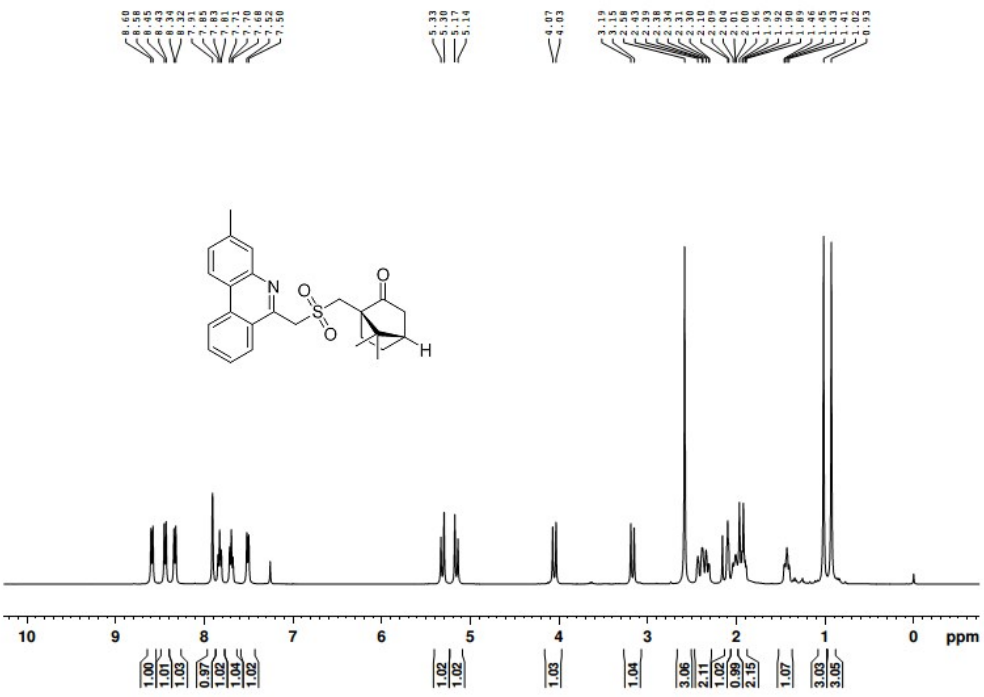

150.48
143.46
139.23
133.46
131.48
131.09
129.68
129.60
128.95
128.89
128.21
127.43
127.13
125.53
122.27
122.01
58.03
56.27
21.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

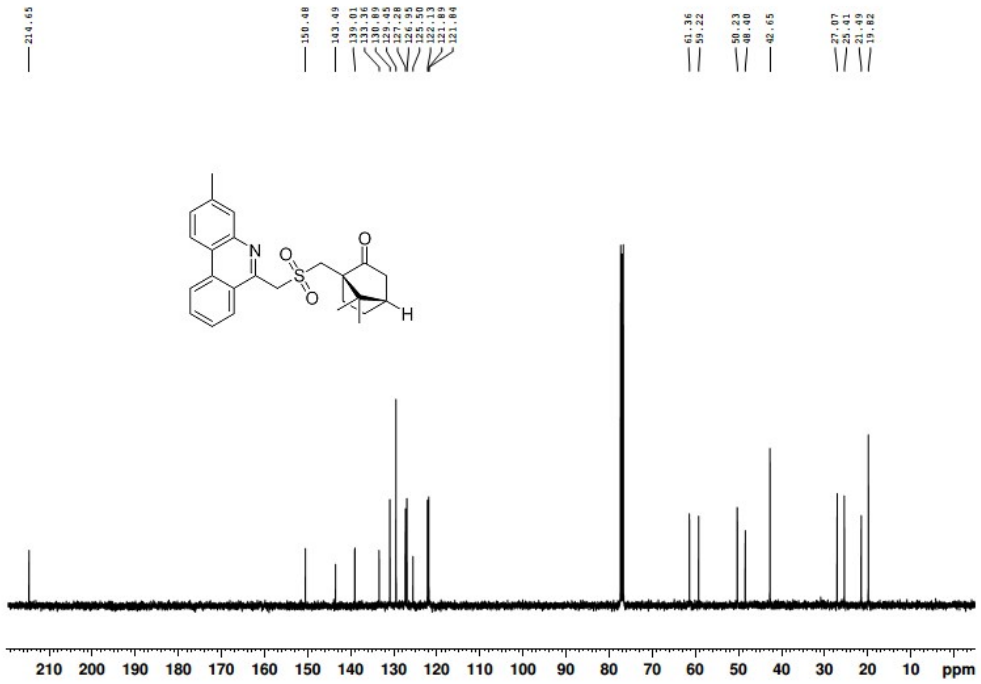

8.61
8.59
8.43
8.41
8.36
8.34
8.28
7.91
7.88
7.88
7.85
7.84
7.82
7.80
7.79
7.71
7.70
7.68
7.66
7.60
7.58
7.56
7.54
7.48
7.46
7.43
7.28
5.24
2.46
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
1.01
1.02
0.96
4.05
3.03
1.05
2.00
2.00
3.00

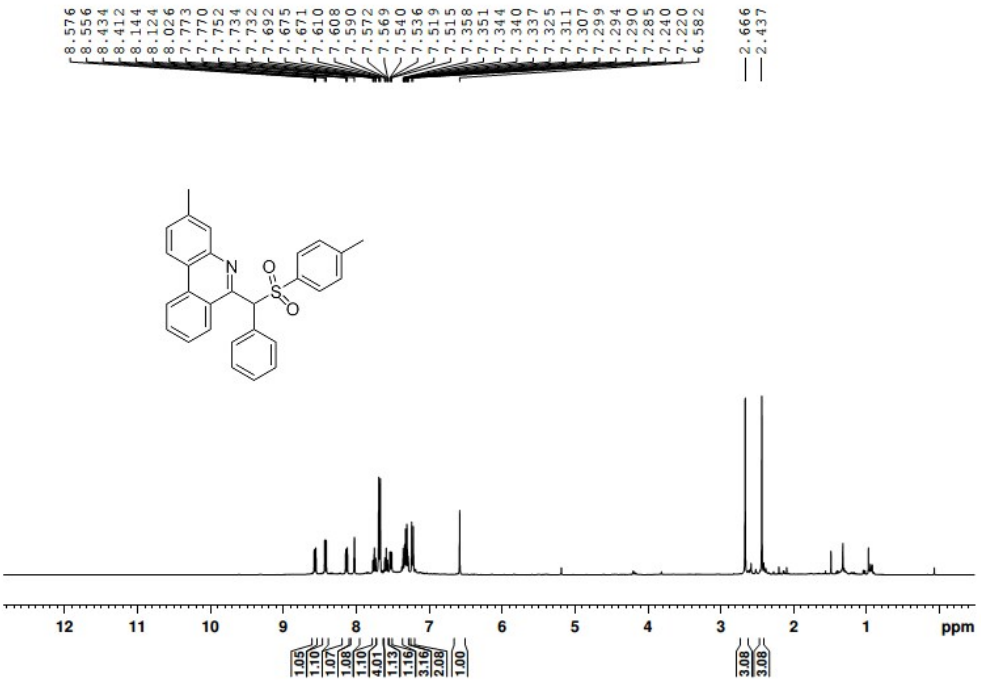

149.54
143.38
138.02
136.45
135.33
133.25
132.03
130.62
130.62
129.40
129.36
129.08
128.99
127.79
127.29
127.14
126.84
126.53
123.33
122.10
121.65
62.65
21.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

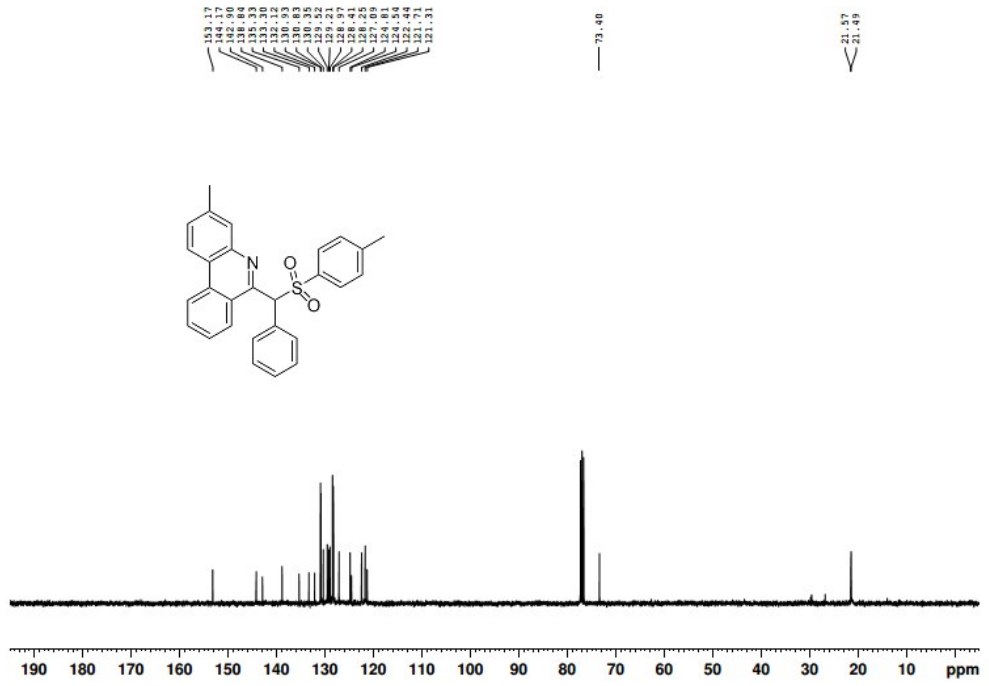

8.76
8.74
8.62
8.60
8.40
8.38
8.08
7.97
7.89
7.87
7.85
7.70
7.68
7.66
7.62
7.61
7.53
7.51
7.16
7.15
5.50
3.33
2.48
H2O
CH3 +DMSO-d6
10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
1.04
1.02
1.01
1.09
3.02
1.09
1.07
2.00
3.42

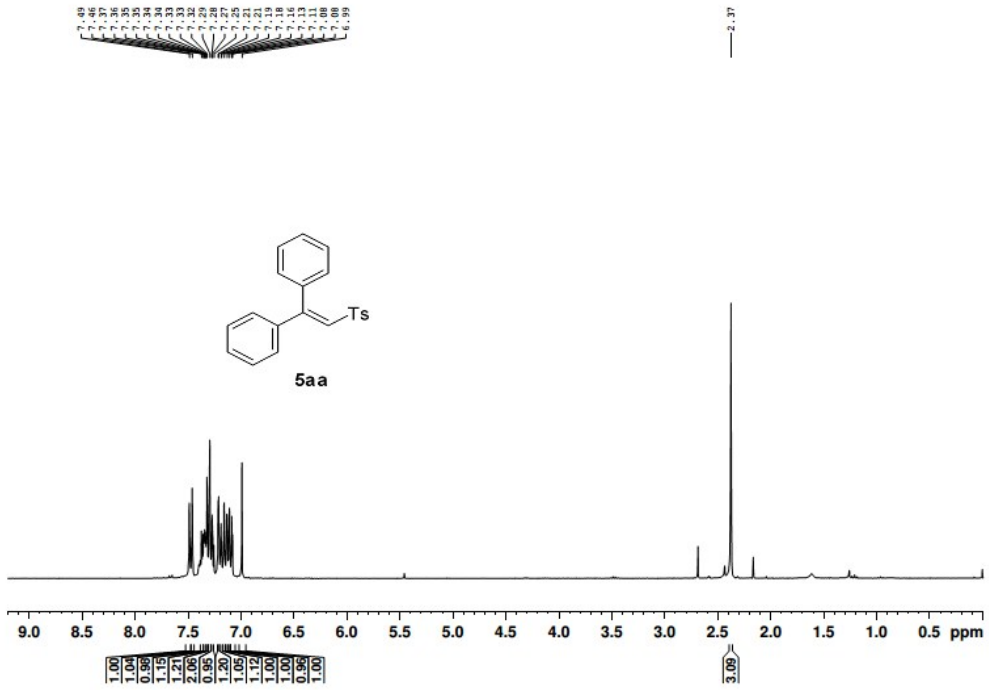

150.14
143.08
139.48
136.60
135.73
135.09
132.58
131.15
129.53
128.87
128.20
127.44
127.18
126.94
122.50
122.34
121.27
62.61
21.07
N
O
S
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

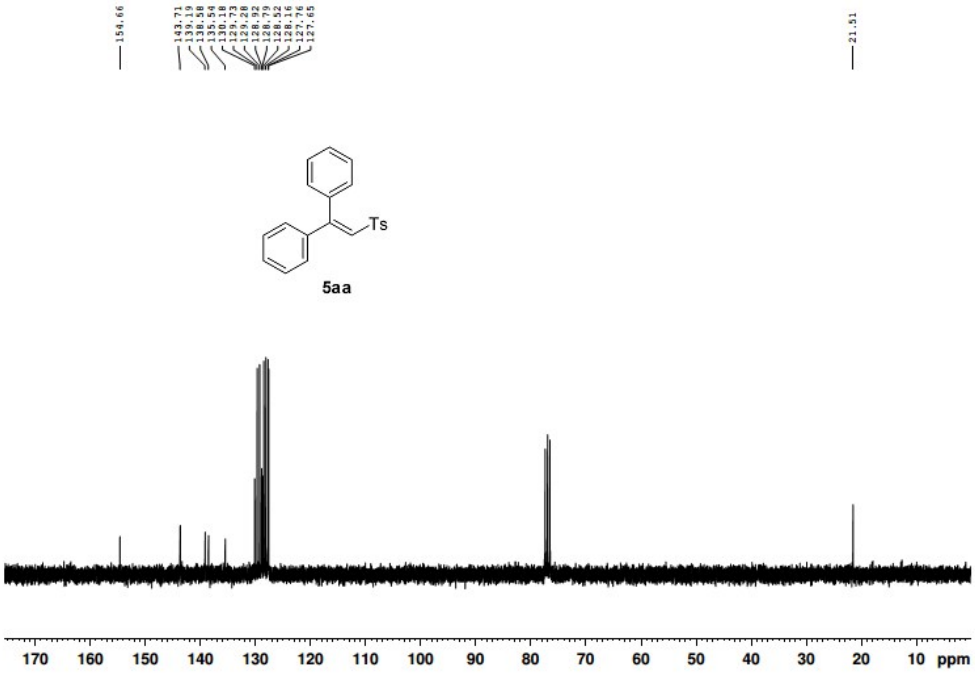

8.60
8.58
8.45
8.43
8.34
8.32
7.91
7.85
7.83
7.81
7.71
7.70
7.68
7.62
7.50
5.33
5.30
5.17
5.14
4.07
4.03
3.19
3.15
2.58
2.43
2.38
2.34
2.31
2.18
2.10
2.09
2.04
2.01
2.00
1.96
1.93
1.92
1.90
1.88
1.46
1.45
1.43
1.41
1.02
0.93
N
O
S
O
O
H
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.01
1.03
0.97
1.02
1.04
1.02
1.02
1.02
1.03
1.04
3.06
2.11
1.02
0.99
2.15
1.07
3.03
3.05


214.65
150.48
143.49
139.01
133.36
130.89
129.45
127.28
126.95
125.50
122.13
121.89
121.84
61.36
59.22
50.23
48.40
42.65
27.07
25.41
21.49
19.82
N
O
S
O
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.576
8.556
8.434
8.412
8.144
8.124
8.026
7.773
7.770
7.752
7.734
7.732
7.692
7.675
7.671
7.610
7.608
7.590
7.572
7.569
7.540
7.536
7.519
7.515
7.358
7.351
7.344
7.340
7.337
7.325
7.311
7.307
7.299
7.294
7.290
7.285
7.240
7.220
6.582
2.666
2.437
N
O
S
O
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.05
1.10
1.07
1.08
1.10
4.01
1.13
1.16
3.16
2.08
1.00
3.08
3.08


153.17
142.77
142.00
138.84
135.33
133.10
132.13
130.93
130.83
130.35
129.52
129.21
128.97
128.41
128.25
127.09
126.81
124.54
122.44
121.71
121.31
73.40
21.57
21.49
N
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.49
7.46
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.29
7.28
7.27
7.25
7.21
7.21
7.19
7.18
7.16
7.13
7.11
7.08
7.08
6.99
2.37
Ts
5aa
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.04
0.98
1.15
1.21
2.06
0.96
1.20
1.05
1.12
1.00
1.00
0.98
1.00
3.09


154.66
143.71
139.19
138.88
135.54
130.18
129.73
129.60
128.92
128.79
128.52
128.16
127.76
127.65
21.51
Ts
5aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm