Supplementary Material (ESI) for Chemical Communications

Electrophilic Aromatic Substituted Luciferins as Bioluminescent Probes for Glutathione *S*-Transferase Assays

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Supporting Information

I. Materials and general methods

2-Cyano-6-hydroxyquinoline was prepared by the reported method (Branchini, B. R.; Hayward, M. M.; Bamford, S.; Brennan, P. M.; Lajiness, E. J. Photochem. Photobiol. **1989**, 49, 689-95). 2-Cyano-6-hydroxybenzothiazole was provided by *Promega Biosciences, Inc.* All other reagents and solvents for chemical syntheses were purchased from *Aldrich*, *Sigma*, and *Fisher* and were used without further purification. Nuclear Magnetic Resonance (NMR) and mass spectra were recorded on a Varian-300 and Fisions VG Platform II spectrometers. UV-Vis absorption spectra were recorded on Beckman DU 650. The purity and free luciferin analyses were performed on Agilent 1100 HPLC with monitoring absorbance at 254 nm and 330 nm. The products for GST reactions were analyzed by Aligent 1100-Brucker Esquire 4000 LC-MS.

II. GST assays protocol and Kinetic Parameter determination

Step1: GST reaction. Generally, 1 μg of human glutathione *S*-transferase A1-1, M1-1 or P1-1 protein (Sigma) was incubated with 100 μM compound **1-3** or **5-11** and 2.0 mM GSH in 125 mM Hepes buffer in a final volume of 100 μl for 30 minutes at room temperature.

Step 2: detection of luciferin. To each Step 1 reaction, 100 μl of a proprietary luciferin detection reagent were added and the luminescent signal was measured after 20 minutes on a Veritas microplate luminometer (Turner Biosystems).

The apparent K_m values for substrate **9** were measured by varying the substrate concentrations (0-50 μM) while GSH concentration (2.0 mM) and GST enzyme concentration were held constant.

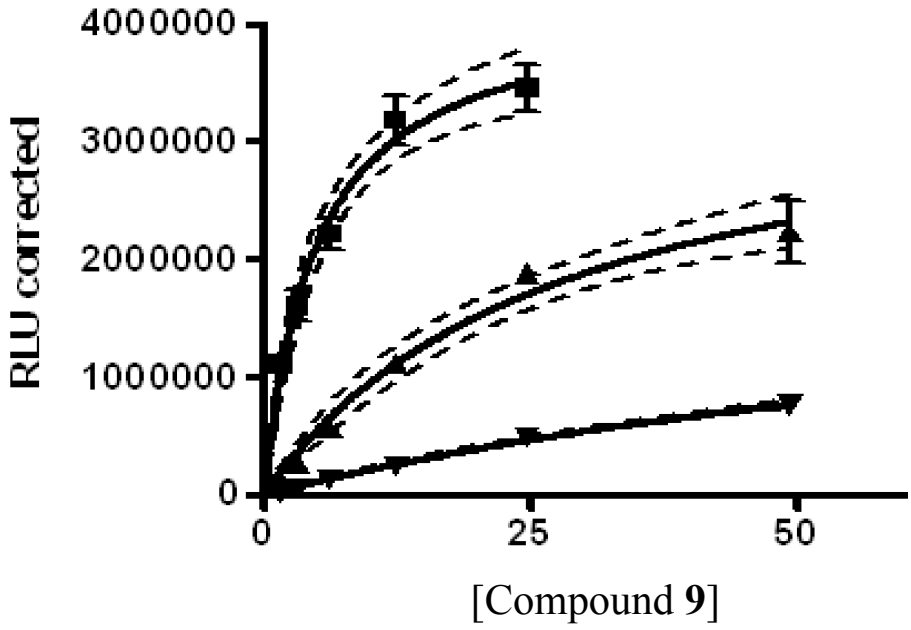


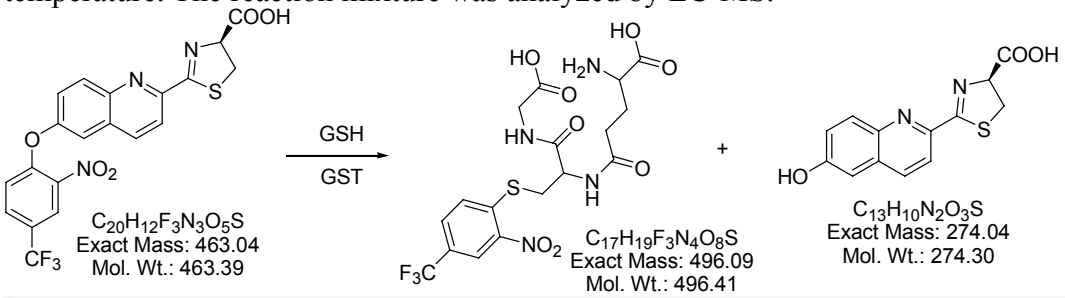
FIGURE S1 Kinetic curves for compound **9** with human GSTs in the presence of 2.0 mM GSH (A1-1 ■; M1-1 ▲; P1-1 ▼)

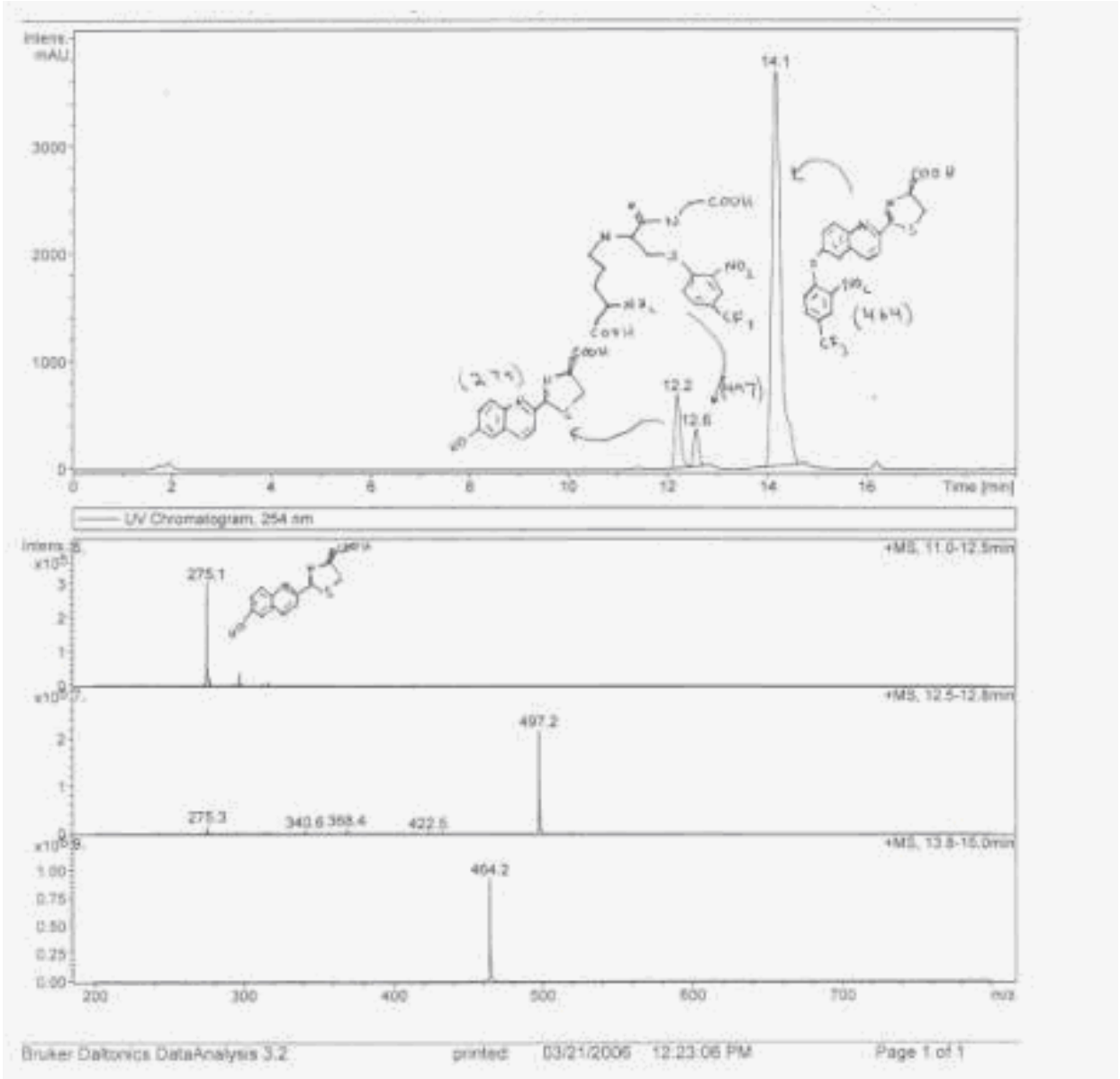
Table S1 Apparent Km values for compound **9** with human GST A1-1, M1-1 and P1-1

GST Enzymes	V_{max} x 10^{-6}	K_m (μM)
A1-1	4.21 ± 0.25	4.85 ± 0.81
M1-1	3.63 ± 0.45	27.81 ± 6.81
P1-1	2.20 ± 0.31	91.80 ± 18.22

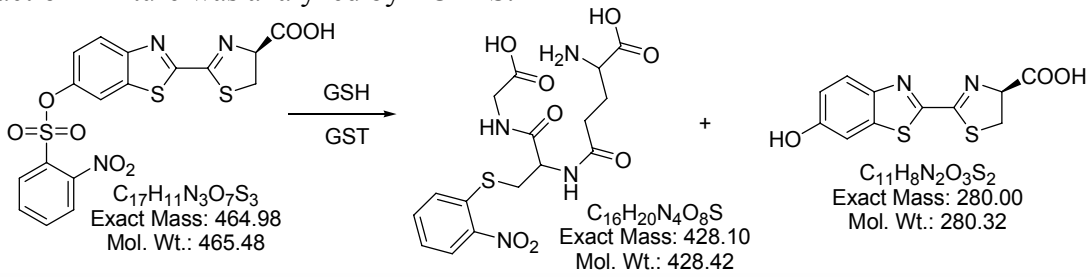
III. Product analyses for GST reactions

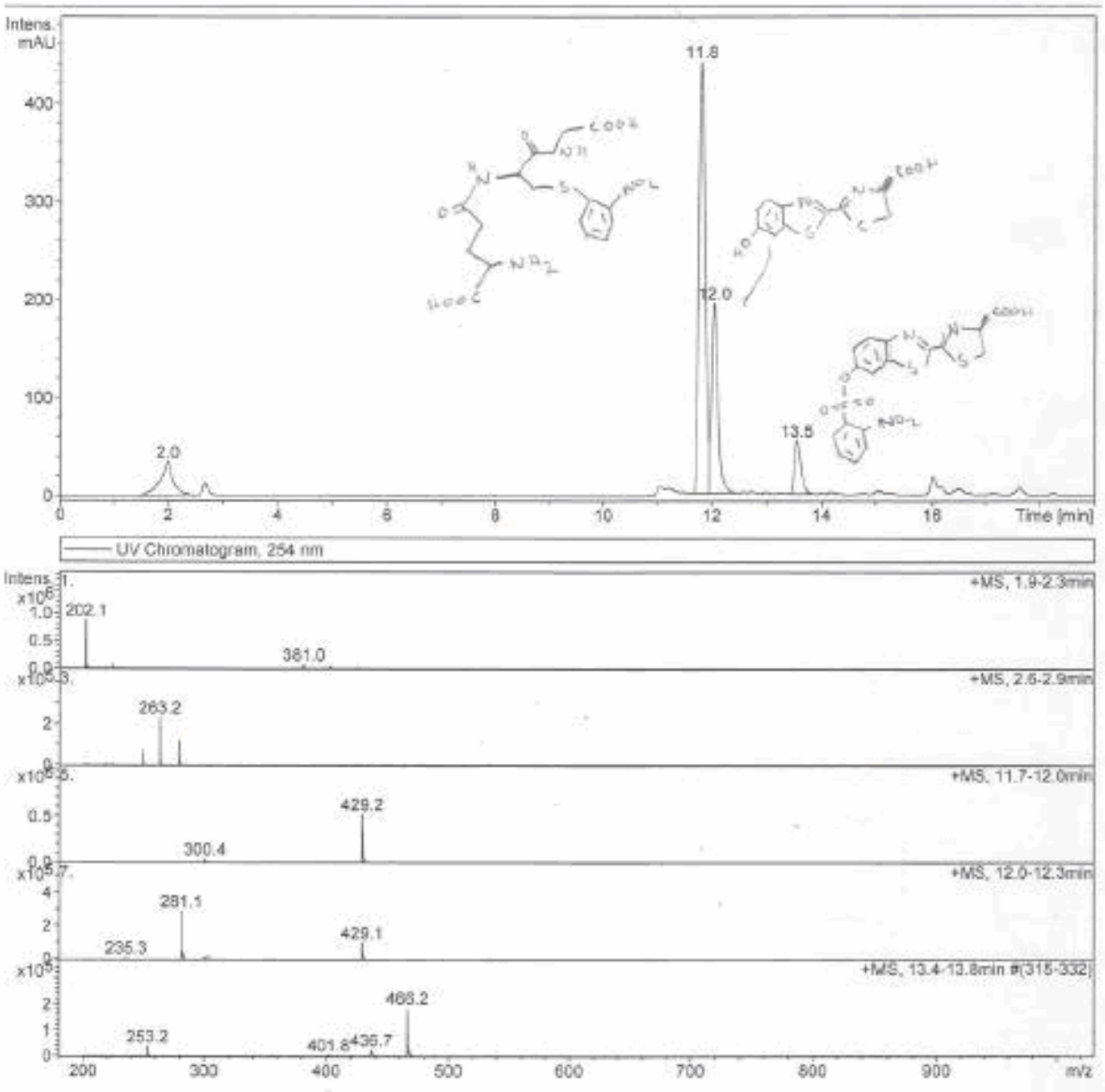
Compound **2** (100 μM) and GSH (1.0 mM) were incubated with12 μg of human glutathione *S*-transferase M1-1 in 400 μl of Hepes buffer (125 mM) for 2 hours at room temperature. The reaction mixture was analyzed by LC-MS.





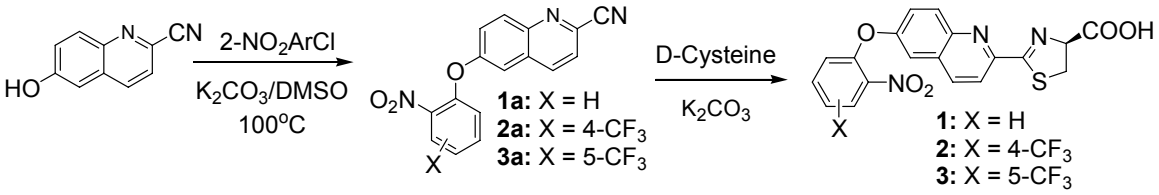
Compound **5** (100 µM) and GSH (2.0 mM) were incubated with 4 µg of *S. japonicum* in 400 µl of Hepes buffer (125 mM) for 1 hour at room temperature. The reaction mixture was analyzed by LC-MS.





IV. Syntheses of compounds 1-3 and 5-11

3.1 Syntheses of compounds 1-3



General procedure for the preparations of compounds 1a-3a: The mixture of 2-cyano-6-hydroxyquinoline (0.50 g, 2.94 mmol), 1-choloro-2-nitrobenzne derivatives (2.94 mmol) and potassium carbonate (0.41 g, 2.97 mmol) in 30 ml of DMSO was stirred and heated 100°C for 30 minutes. Upon cooling to room temperature, the mixture was poured into cold water (30 ml) and extracted three times with methylene chloride. The combined organic layer was washed with water and dried over magnesium sulfate. After removal of the solvent, the product was purified by flash chromatography using heptane and methylene chloride as solvent.

2-Cyano-6-(2-nitrophenoxy)quinoline (1a) (yield 31%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.20 (d, J = 9.6 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 8.08 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.65-7.75 (m, 3H), 7.43 (td, J = 8.5 Hz, J = 1.2 Hz, 1H), 7.29 (dd, J = 8.7 Hz, J = 1.5 Hz, 1H), 7.25 (d, J = 2.7 Hz, 1H). MS (ES) m/e (M+1): 292.

2-Cyano-6-(2-nitro-4-trifluoromethylphenoxy)quinoline (2a) (yield 35%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.36 (d, J = 2.4 Hz, 1H), 8.26 (d, J = 9.0Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 8.7 Hz, J = 3.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.67 (dd, J = 9.0 Hz, J = 2.7 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H). MS (ES) m/e (M+1): 360.

2-Cyano-6-(2-nitro-5-trifluoromethylphenoxy)quinoline (3a) (yield 52%):^{1}H NMR (CD_2Cl_2) δ(ppm): 8.25 (d, J = 9.0Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.18 (dd, J = 8.4 Hz, J = 1.0 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.62-7.69 (m, 2H), 7.49 (d, J = 1.8 Hz, 1H), 7.37 (d, J = 2.7 Hz, 1H). MS (ES) m/e (M+1): 360.

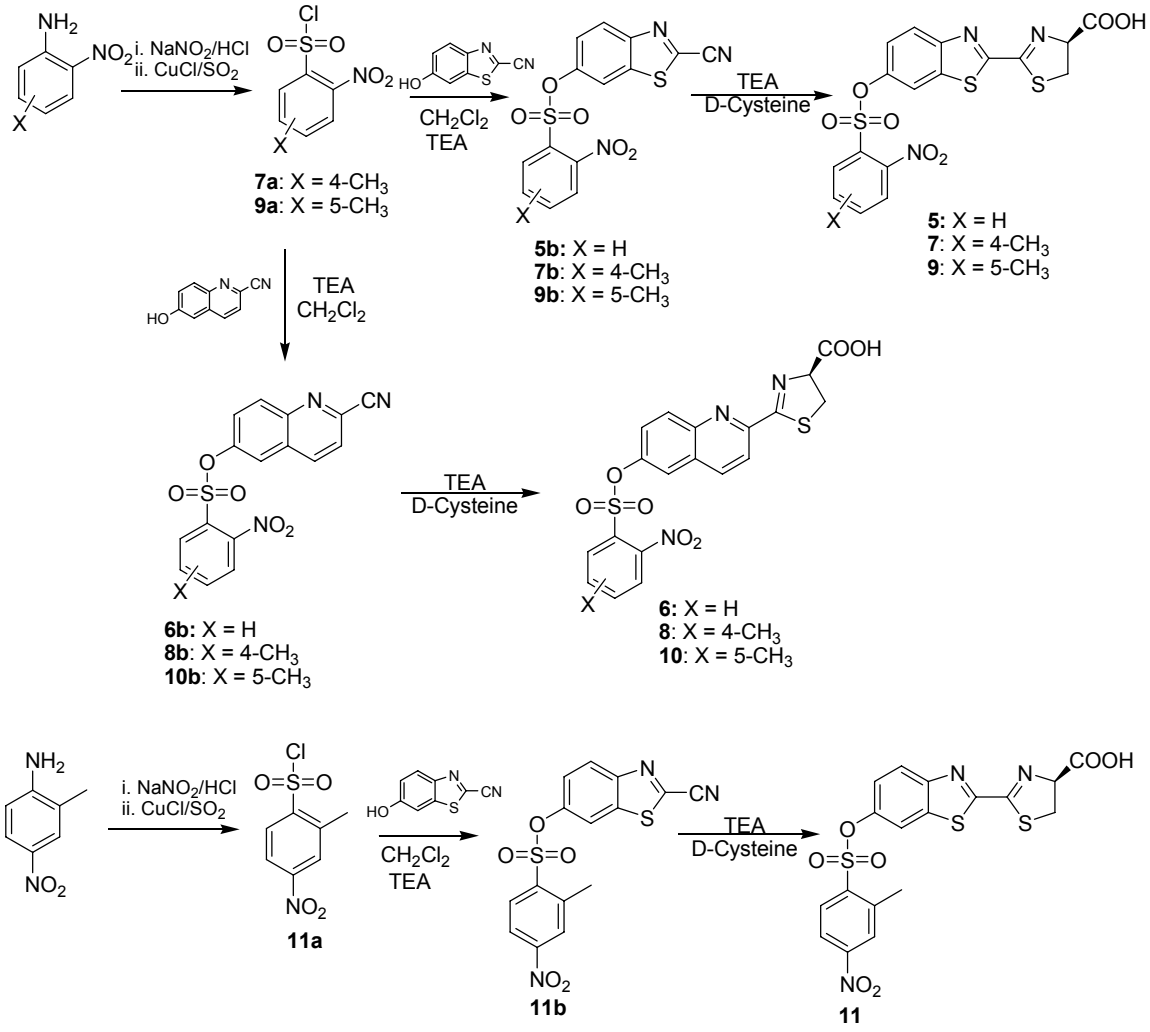
General procedure for the preparations of compounds 1-3: To the solution of 2-Cyano-6-(2-nitrophenoxy)quinoline derivative (1.50 mmol) and D-cystine (2.25 mmol) in methanol (40ml), CH_2Cl_2 (20 ml) and H_2O (10 ml) was added K_2CO_3 (1.5 mmol). The mixture was stirred at room temperature for 1 hour and then neutralized to slightly acidic with acidic acid. After removal of organic solvent, the solid was collected by filtration, washed three times with water and purified by flash chromatography using methylene chloride/methanol (90/10) as eluent. The product was solidified in cold ether, and the white powder collected by filtration and dried under vacuum.

2-Cyano-6-(2-nitrophenoxy)quinolinyl luciferin (1) (yield 56%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.39 (d, J = 8.4 Hz, 1H), 8.13 (m, 3H), 7.78 (t, J = 8.7 Hz, 1H), 7.63 (dd, J = 9.0 Hz, J = 2.7 Hz, 1H), 7.56 (s, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 8.10 Hz, 1H), 5.37 (t, J = 8.5 Hz, 1H, CHCOO), 3.59 (m, 2H, CH_2). MS (ES) m/e (M+1): 396. λ_{max} (nm) / ε_{max} ($cm^{-1}M^{-1}$): 323/10,400; 327/9,500 in MeOH.

2-Cyano-6-(2-nitro-4-trifluoromethylphenoxy)quinolinyl luciferin (2) (yield 20%): ^{1}H NMR (d_6-DMSO): 8.54 (d, J = 2.1 Hz, 1H), 8.42 (d, J = 8.5 Hz, 1H), 8.10-8.20 (m, 2H), 8.07 (dd, J = 9.5 Hz, J = 2.4 Hz, 1H), 7.82 (d, J = 2.7 Hz, 1H), 7.72 (dd, J = 9.3 Hz, J = 3.0 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 5.44 (dd, J = 8.7 Hz, J = 8.4 Hz, 1H, CHCOO), 3.45-3.75 (m, 2H, CH_2). MS (ES) m/e (M+1): 464. λ_{max} (nm) / ε_{max} ($cm^{-1}M^{-1}$): 322/12,300, 328/9,900 in MeOH.

2-Cyano-6-(2-nitro-5-trifluoromethylphenoxy)quinolinyl luciferin (3) (yield 66%): ^{1}H NMR (d_6-DMSO): 8.42 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.7 Hz, 1H), 8.10-8.20 (m, 2H), 7.87 (d, J = 8.7 Hz, 1H), 7.82 (s, br, 1H), 7.65-7.75 (m, 2H), 5.43 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H, CHCOO), 3.50-3.70 (m, 2H, CH_2). MS (ES) m/e (M+1): 464. λ_{max} (nm)/ε_{max} ($cm^{-1}M^{-1}$): 321/10,400; 328/8,300 in MeOH.

3.2 Syntheses of compounds 5-11



General procedure for the preparations of compounds (7a, 9a and 11a): To the mixture of concentrated HCl (30 ml) and acetic acid (10 ml) was added aromatic amine (10.0 g, 65.7 mmol) in one portion with stirring at room temperature. The white

hydrochloride salt was formed immediately and the resultant mixture was cooled to -15°C. A solution of sodium nitrite (5.44 g, 78.9 mmol) in 15 ml of water was added dropwise while the temperature was kept at -5°C to -10°C, and the resultant mixture was then stirred for 45 minutes at this temperature range. Sulfur dioxide was bubbled through acidic acid (70 ml) for 30 minutes at 0°C. To the solution was added copper (I) chloride (1.65 g), the mixture was continued to bubbling sulfur dioxide at 0°C till the solution appeared slightly blue color (about another 30 minutes). The above diazonium solution was added to this sulfur dioxide solution at 0°C and stirred for 10 minutes at 0°C. The mixture was then poured into ice-water and extracted three times with ether. The combined organic layer was washed with brine and dried with magnesium sulfate. After removal of the solvent, the product was purified by flash chromatography using heptane/methylene chloride (7/3 to 6/4) as eluent.

2-Nitro-4-methylbenzenesulfonyl chloride (7a) (yield 53%): ^{1}H NMR ($CDCl_3$) δ(ppm): 8.13 (d, J = 8.4 Hz, 1H), 7.67 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H).

2-Nitro-5-methylbenzenesulfonyl chloride (9a) (yield 33%): ^{1}H NMR (CD_2Cl_2) δ(ppm): ^{1}H NMR ($CDCl_3$) δ(ppm): 8.05 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H).

4-Nitro-2-methylbenzenesulfonyl chloride (7a) (yield 29%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.12 (d, J = 8.1 Hz, 1H), 7.67 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H).

General procedure for the preparations of compounds (5b to 11b): To the solution of benzene sulfonyl choloride derivative (0.7 g, 2.98 mmol) and 2-cyano-6-hydroxoylbenzothiazole or 2-cyano-6-hydroxyquinoline (2.84 mmol) in 10 ml of dry methylene chloride was added triethylamine (0.58 g, 5.68 mmol) at room temperature and the resultant mixture was stirred for 3 hours. The product was purified by flash chromatography using heptane/methylene chloride (1/2) as eluent.

2-Cyanobenzothiazol-6-yl 2-nitrobenzenesulfonate (5b) (yield 55%): ^{1}H NMR ($CDCl_3$) δ(ppm): 8.19 (d, J = 9.3 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 2.4 Hz, 1H), 7.85-7.95 (m, 2H), 7.73 (m, 1H), 7.51 (dd, J = 8.7 Hz, J = 2.4 Hz, 1 H). MS (ES) m/e (M+1): 362.

2-Cyanoquinolin-6-yl 2-nitrobenzenesulfonate (6b) (yield 63%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.34 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.83-7.93 (m, 2H), 7.62-7.82 (m, 4H). MS (ES) m/e (M+1): 356.

2-Cyanobenzothiazol-6-yl 2-nitro-4-methylbenzenesulfonate (7b) (yield 67%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.23 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 2.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.5 -7.6 (m, 2H), 2.58 (s, 3H, CH_3). MS (ES) m/e (M+1): 376.

2-Cyanoquinolin-6-yl 2-nitro-4-methylbenzenesulfonate (8b) (yield 40%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.34 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 9.3 Hz, 1H), 7.82 (d, J = 2.7 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.69 (s, 1H), 7.66 (dd, J = 9.0 Hz, J = 2.7 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 2.52 (s, CH_3, 3H). MS (ES) m/e (M+1): 370.

2-Cyanobenzothiazol-6-yl 2-nitro-5-methylbenzenesulfonate (9b) (yield 85%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.21 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 2.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.52 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 2.46 (s, CH_3, 3H). MS (ES) m/e (M+1): 376.

2-Cyanoquinolin-6-yl 2-nitro-5-methylbenzenesulfonate (10b) (yield 56%): ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.34 (d, J = 8.1 Hz, 1H), 8.18 (d, J = 9.3 Hz, 1H), 7.80-7.86 (m,

3H), 7.78 (d, J = 8.7 Hz, 1H), 7.69 (dd, J = 9.6 Hz, J = 2.7 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 2.58 (s, CH_3, 3H). MS (ES) m/e (M+1): 370.

2-Cyanobenzothiazol-6-yl 2-methyl-4-nitrobenzenesulfonate (11b) (yield 85%): ^{1}H NMR ($CDCl_3$) δ(ppm): 8.30 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 9.3 Hz, 1H), 8.13 (dd, J = 8.7 Hz, J = 2.0 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 2.4 Hz, 1H), 7.27 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 2.95 (s, 3H, CH_3). MS (ES) m/e (M+1): 376.

General procedure for the preparations of compounds 5-11: To the solution of nitrobenzene sulfonate derivative (1.07 mmol) and D-cystine (1.28 mmol) in methanol (20ml), CH_2Cl_2 (10 ml) and H_2O (5 ml) was added triethylamine (1.6 mmol). The mixture was stirred at room temperature for 30-60 minutes and then neutralized to slightly acidic with acidic acid. After removal of organic solvent under vacuum, the solid was collected by filtration, washed three times with water and purified by flash chromatography using methylene chloride/methanol (90/10) as eluent. The product was solidified in cold ether, and the white powder collected by filtration and dried under vacuum.

Luciferin 2-nitrobenzenesulfonate (5) (yield 55%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.15-8.25 (m, 3 H), 8.05 (td, J = 7.5 Hz, J = 1.3 Hz, 1H), 7.99 (dd, J = 8.0 Hz, Hz, J = 1.2 Hz, 1H), 7.85 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.34 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 5.44 (dd, J = 8.7, J = 8.7 Hz, 1H, C**H**-COOH), 3.6-3.9 (m, 2H, CH_2). MS (ES): m/e (M+1), 466. λ_{max} 292 nm, ε_{max} 19,100 $cm^{-1}M^{-1}$ in MeOH.

Quinolinyl-luciferin 2-nitrobenzenesulfonate (6) (yield 36%): ^{1}H NMR (d_6-DMSO): 8.54 (d, J = 8.4 Hz, 1H), 8.16-8.26 (m, 2H), 8.10 (d, J = 9.3 Hz, 1H), 8.07 (td, J = 7.5 Hz, J = 1.2 Hz, 1H), 8.01 (dd, J = 7.8, J = 1.2 Hz, 1H), 7.98 (d, J = 2.7, 1H), 7.85 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.57 (dd, J = 9.3, J = 2.7 Hz, 1H), 5.41 (dd, J = 8.7 Hz, J = 8.7 Hz, 1H, C**H**-COOH), 3.5-3.7 (m, 2H, CH_2). MS (ES): m/e (M+1), 460. λ_{max} 285 nm, ε_{max} 9,010 $cm^{-1}M^{-1}$ in MeOH.

Luciferin 2-nitro-4-methylbenzenesulfonate (7) (yield 62%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.18 (d, J = 9.0 Hz, 1 H), 8.16 (d, J = 2.4 Hz, 1H), 8.06 (s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.33 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 5.44 (dd, J = 8.7, J = 8.7 Hz, 1H, C**H**-COOH), 3.6-3.9 (m, 2H, CH_2), 2.48 (s, CH_3, 3H, overlap with DMSO). MS (ES): m/e (M+1), 480. λ_{max} 292 nm, ε_{max} 20,500 $cm^{-1}M^{-1}$ in MeOH.

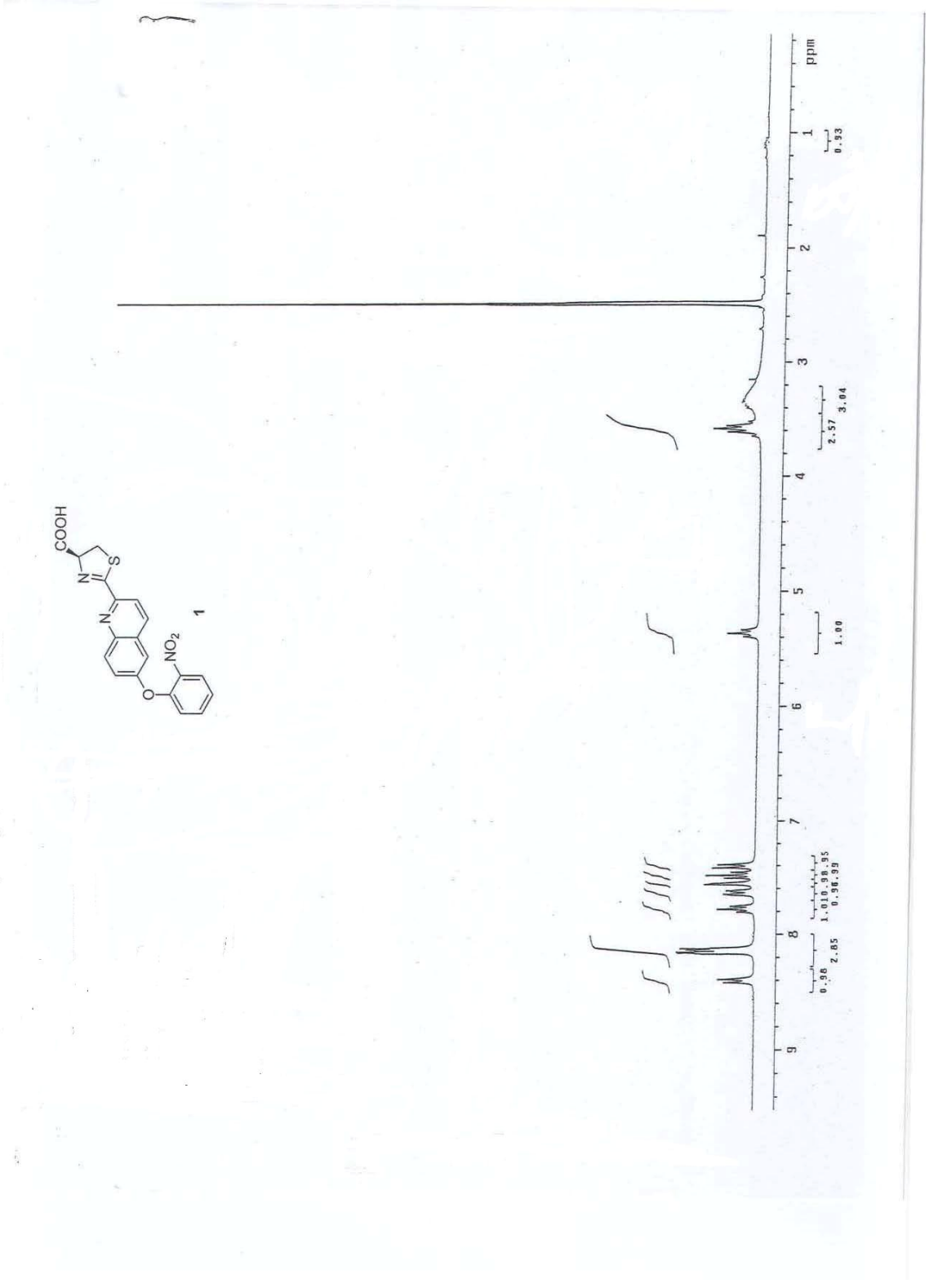
Quinolinyl-luciferin 2-nitro-4-methylbenzenesulfonate (8) (yield 55%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.55 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1 H), 8.07 (s, 1H), 7.98 (d, J = 3.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.33 (dd, J = 9.3 Hz, J = 3.4 Hz, 1H), 5.45 (dd, J = 8.7, J = 8.7 Hz, 1H, C**H**-COOH), 3.5-3.8 (m, 2H, CH_2), 2.48 (s, CH_3, 3H, overlap with DMSO). MS (ES): m/e (M+1), 474. λ_{max} 286 nm, ε_{max} 11,500 $cm^{-1}M^{-1}$ in MeOH.

Luciferin 2-nitro-5-methylbenzenesulfonate (9) (yield 48%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.18-8.22 (m, 2H), 8.11 (d, J = 8.4 Hz, 1H), 7.80-7.98 (m, 2H), 7.36 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H), 5.44 (dd, J = 8.7, J = 8.7 Hz, 1H, C**H**-COOH), 3.6-3.9 (m, 2H, CH_2), 2.42 (s, CH_3, 3H). MS (ES): m/e (M+1), 480. λ_{max} 292 nm, ε_{max} 19,700 $cm^{-1}M^{-1}$ in MeOH.

Quinolinyl-luciferin 2-nitro-5-methylbenzenesulfonate (10) (yield 42%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.56 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 8.15 (d, J = 9.3 Hz, 1 H), 8.11 (d, J = 8.4 Hz, 1H), 8.0 (d, J = 2.7 Hz, 1H), 7.89 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.59 (dd, J = 9.3 Hz, J = 2.7 Hz, 1H), 5.45 (dd, J = 8.7, J = 8.7 Hz, 1H, C**H**-

COOH), 3.5-3.8 (m, 2H, CH_2), 2.49 (s, CH_3, 3H). MS (ES): m/e (M+1), 474. λ_{max} 285 nm, ε_{max} 11,600 $cm^{-1}M^{-1}$ in MeOH.

Luciferin 2-methyl-4-nitrobenzenesulfonate (11) (yield 62%): ^{1}H NMR (d_6-DMSO) δ(ppm): 8.48 (s, 1H), 8.1-8.2 (m, 2H), 8.08 (d, J = 2.4 Hz, 1 H), 8.01 (d, J = 8.7 Hz, 1H), 7.27 (dd, J = 8.7 Hz, J = 2.4 Hz, 1H), 5.453 (t, J = 8.7, 1H, C**H**-COOH), 3.6-3.9 (m, 2H, CH_2), 2.84 (s, CH_3, 3H). MS (ES): m/e (M+1), 480. λ_{max} 293 nm, ε_{max} 19,700 $cm^{-1}M^{-1}$ in MeOH.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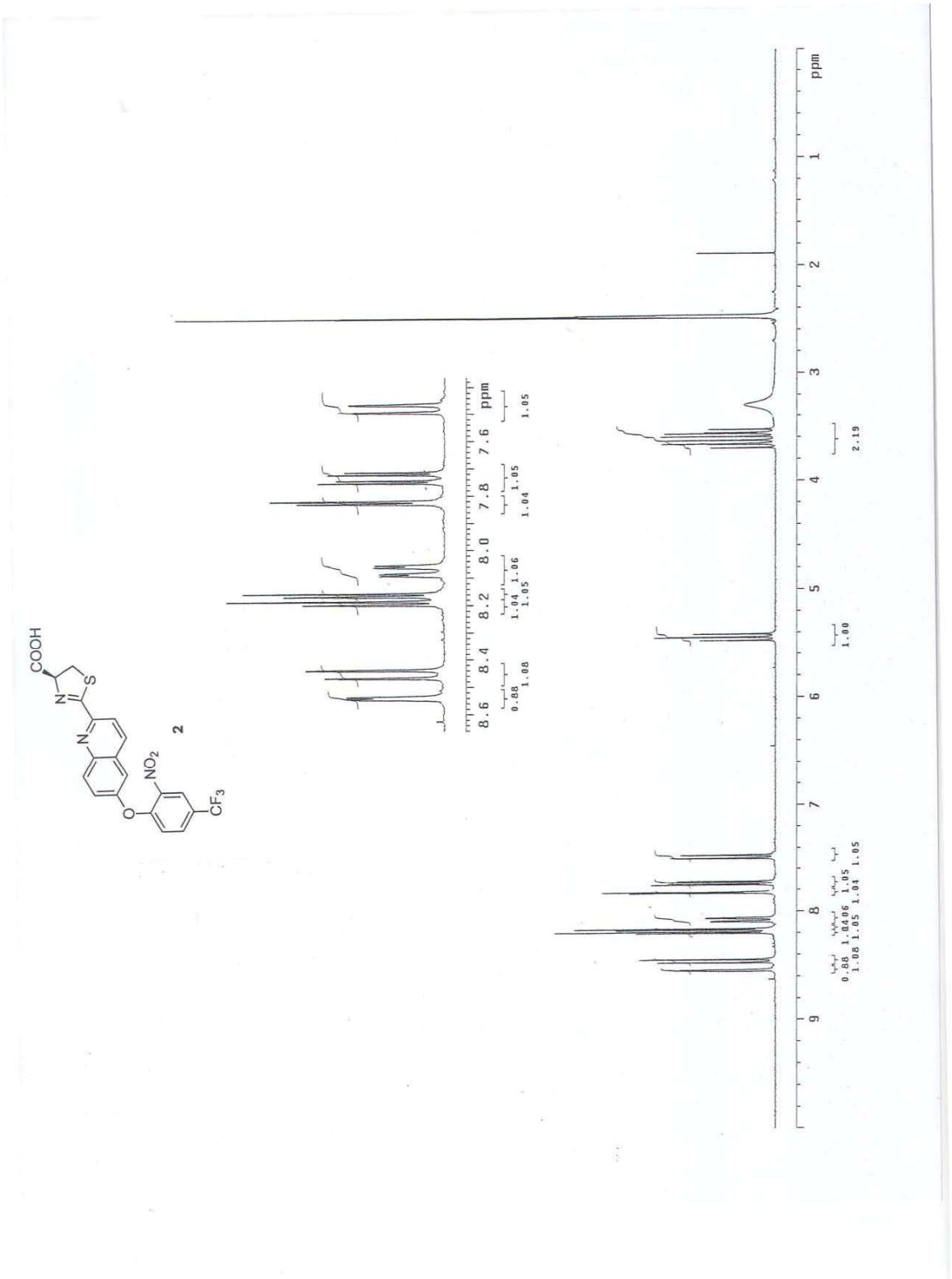
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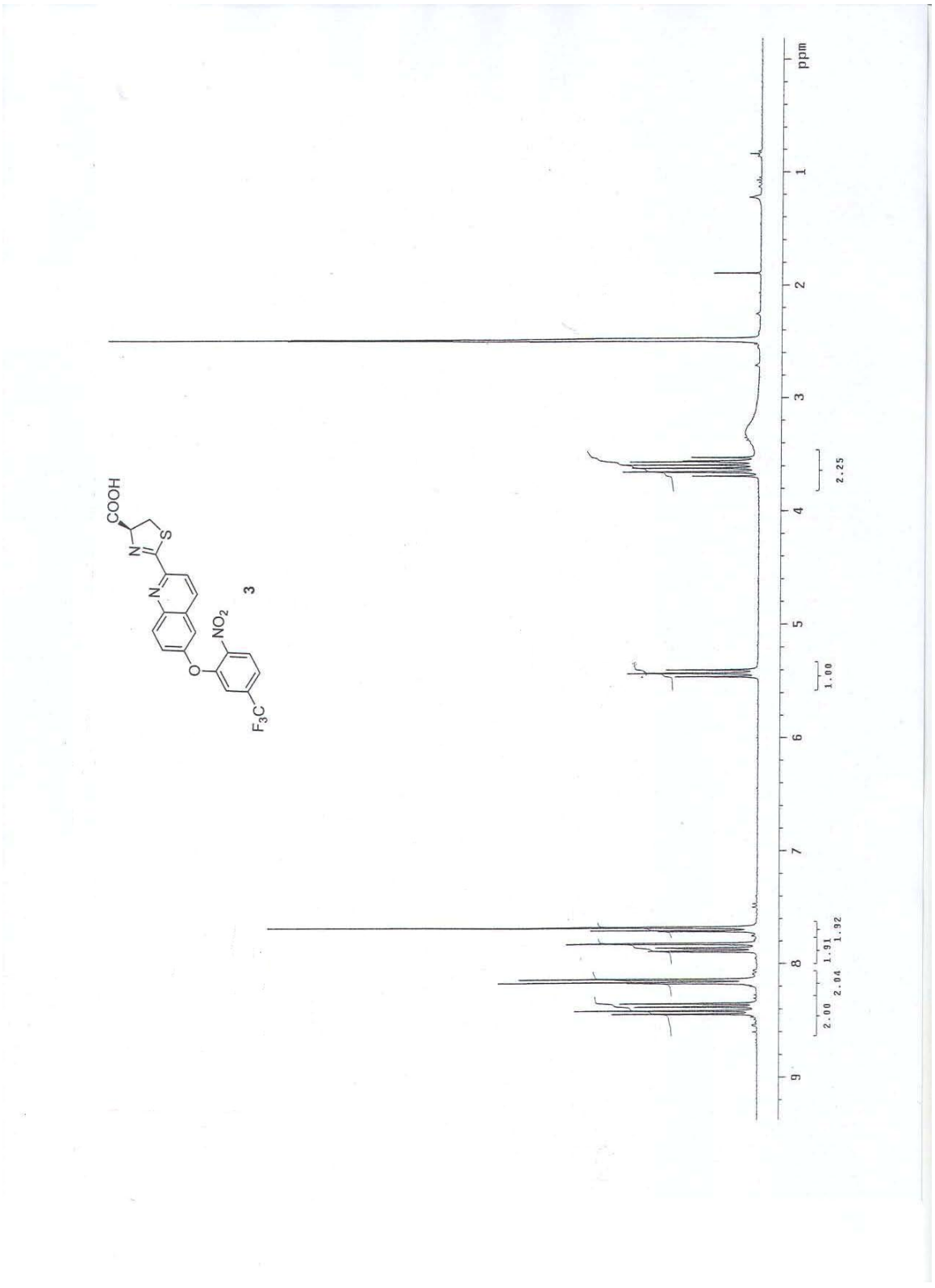
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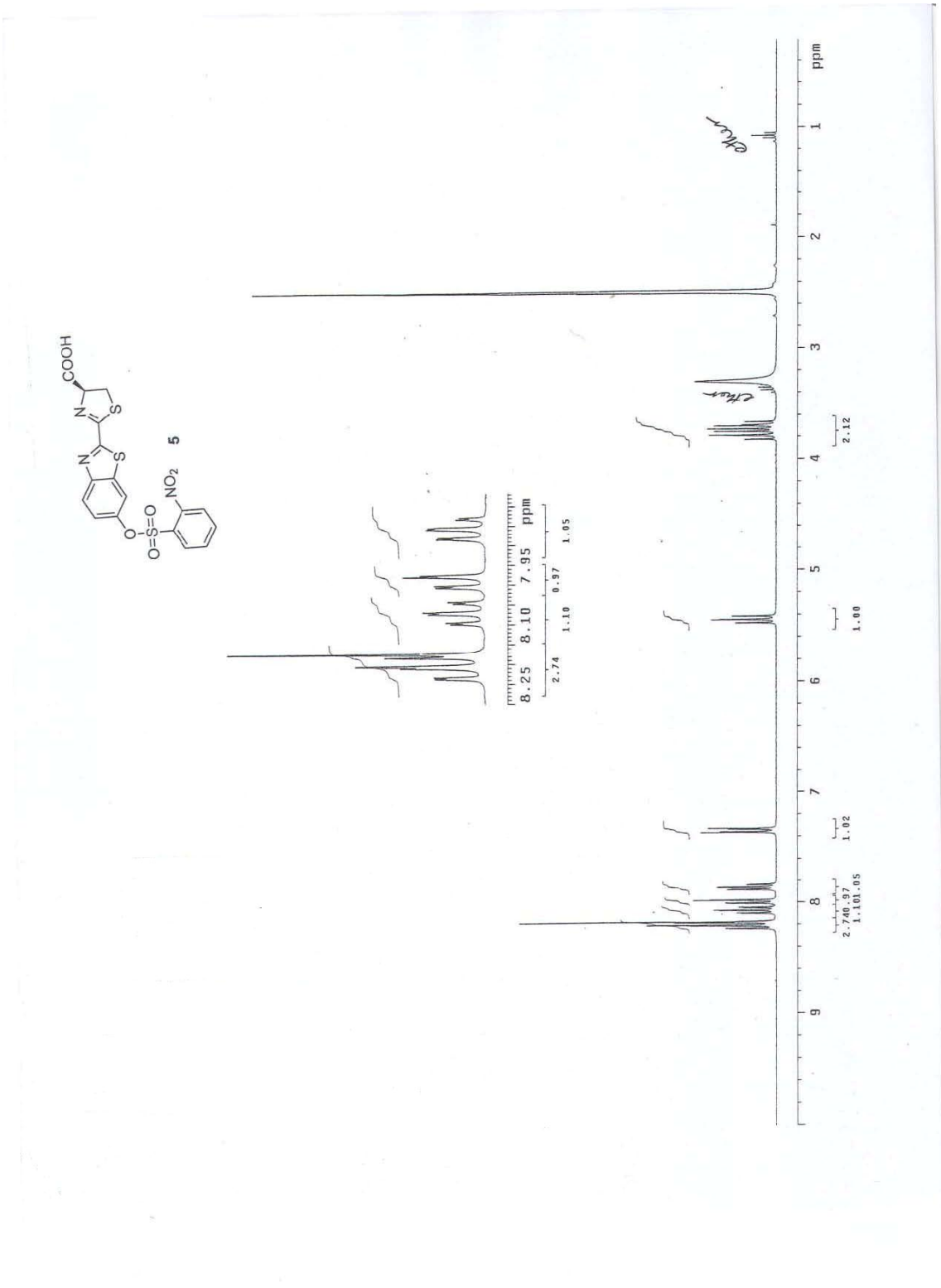
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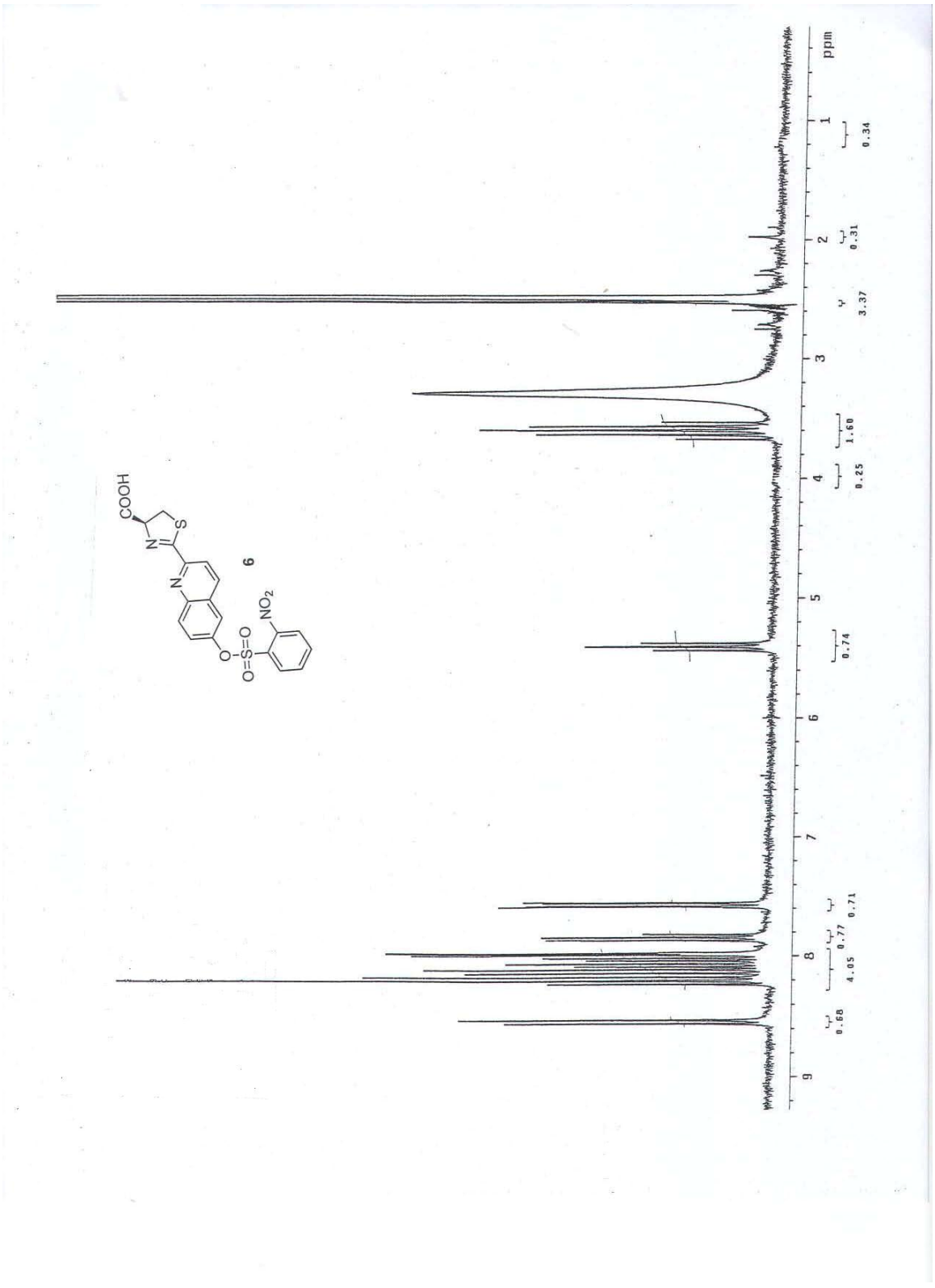
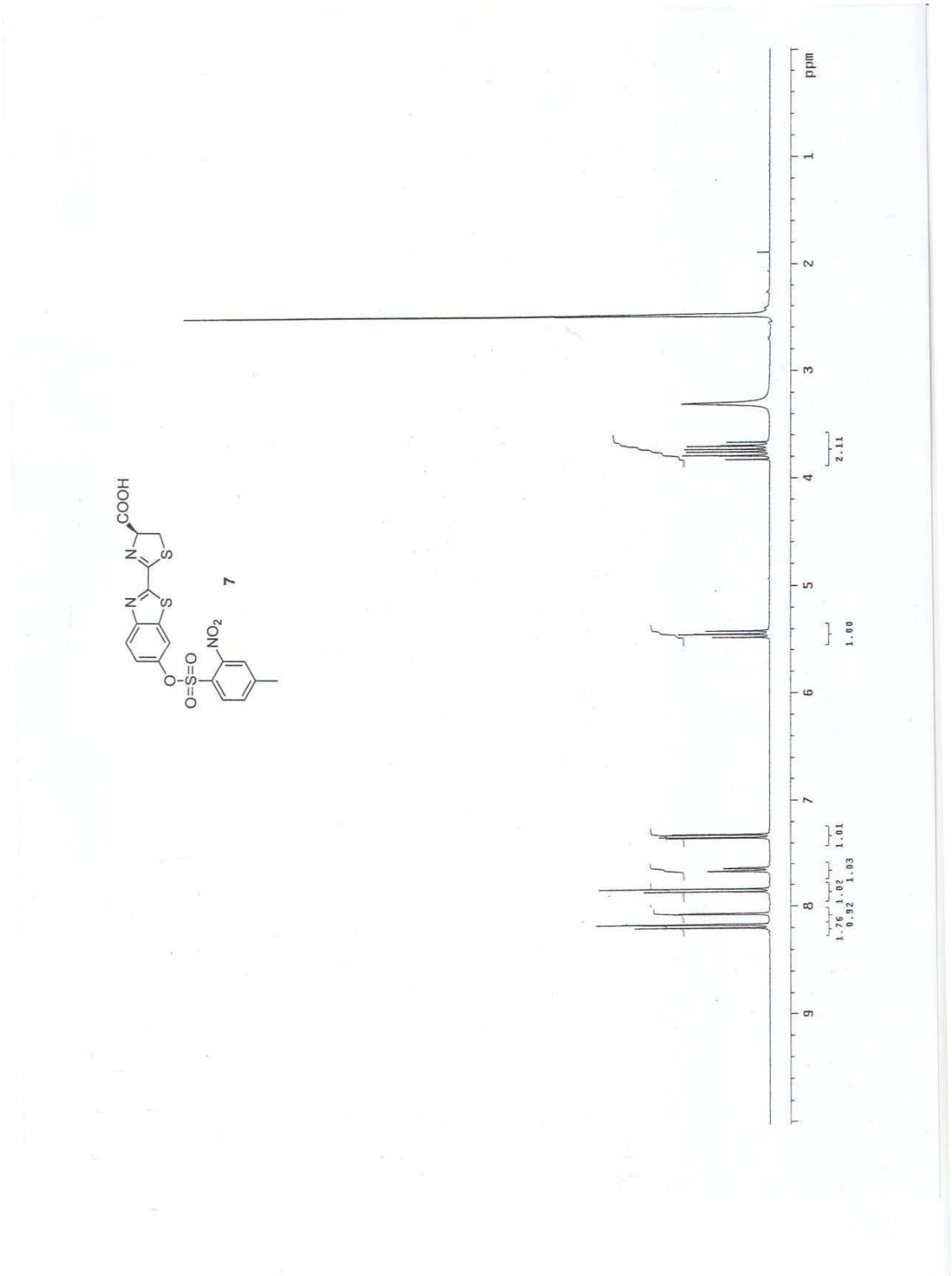
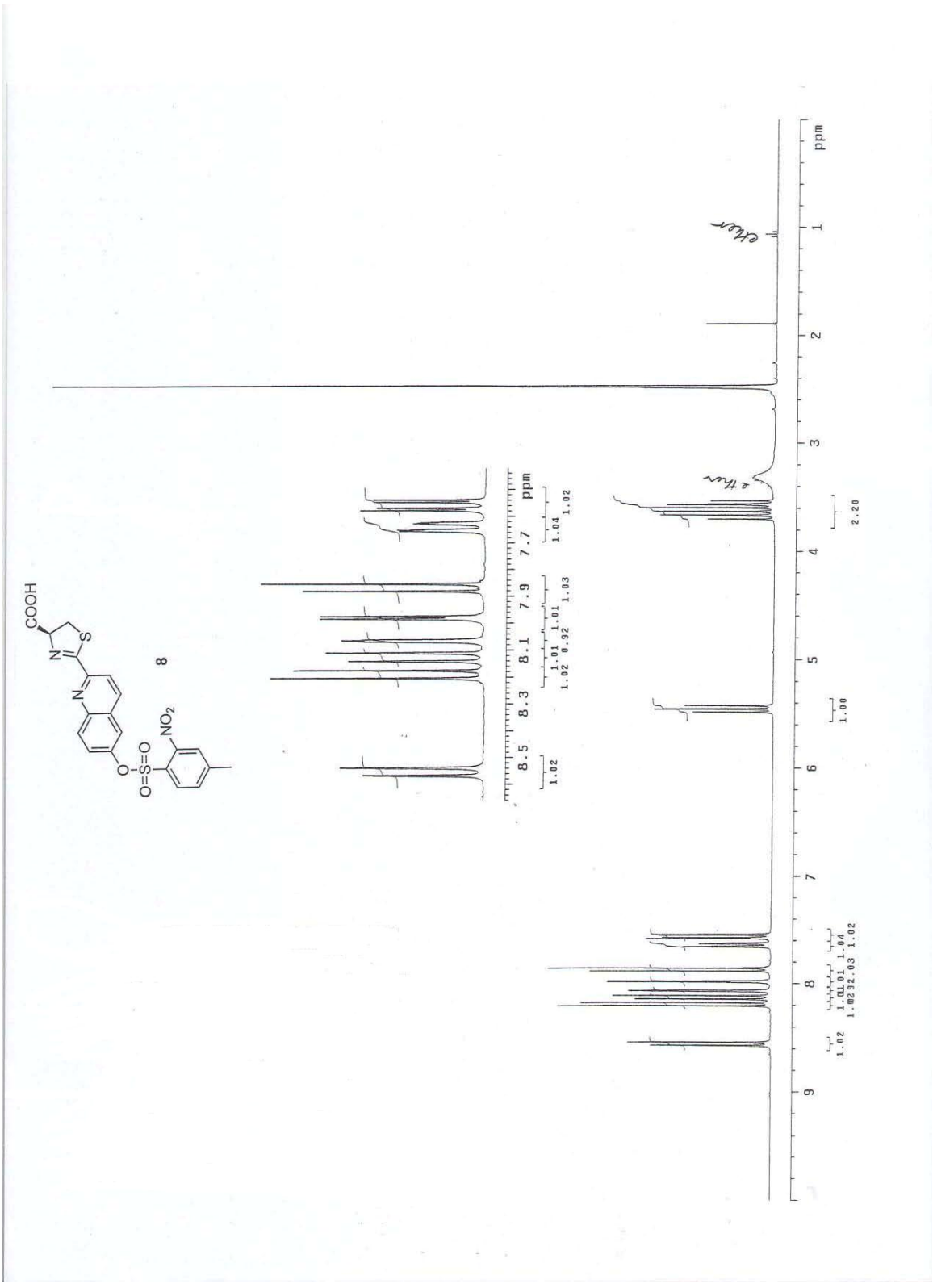
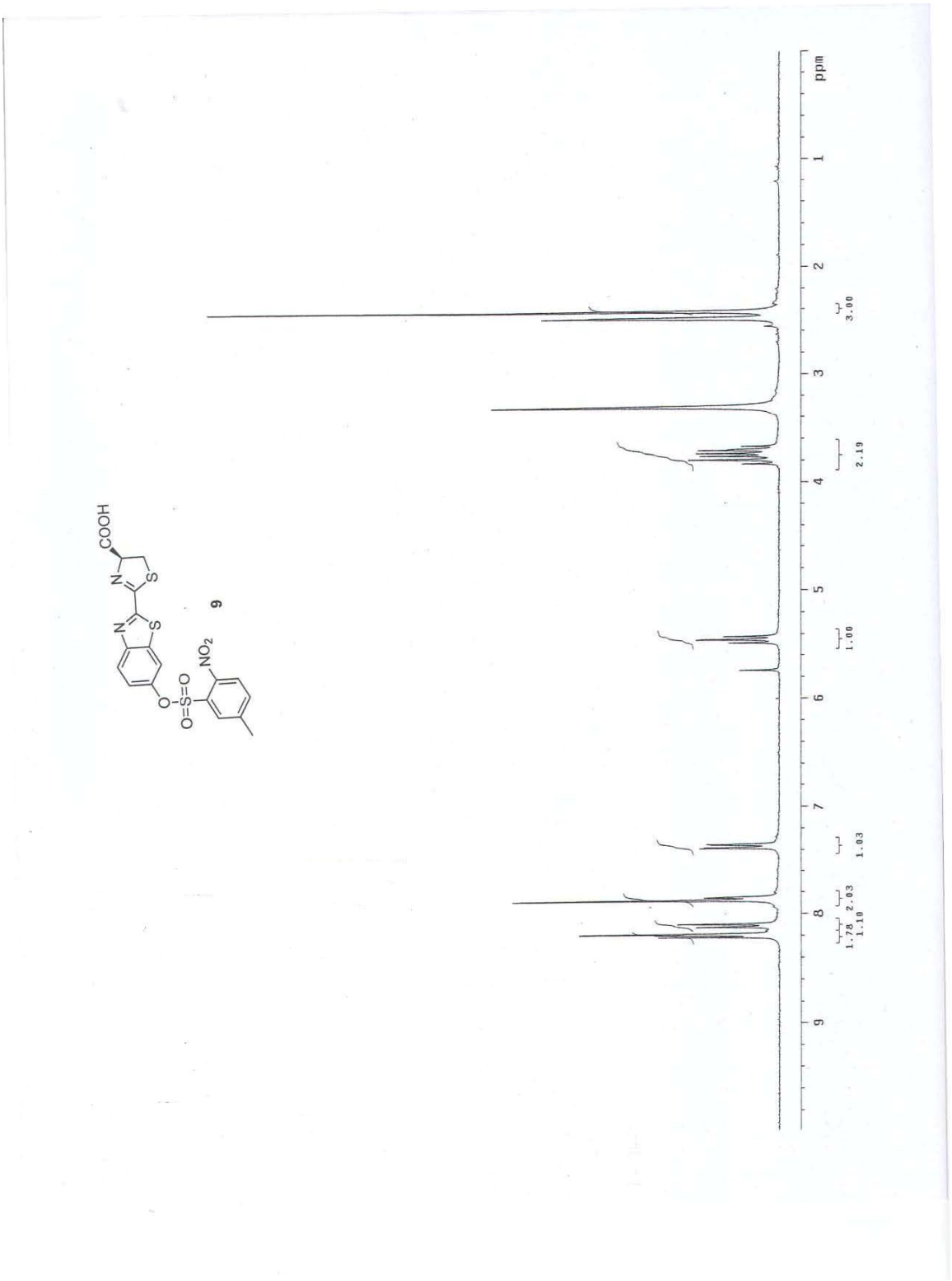
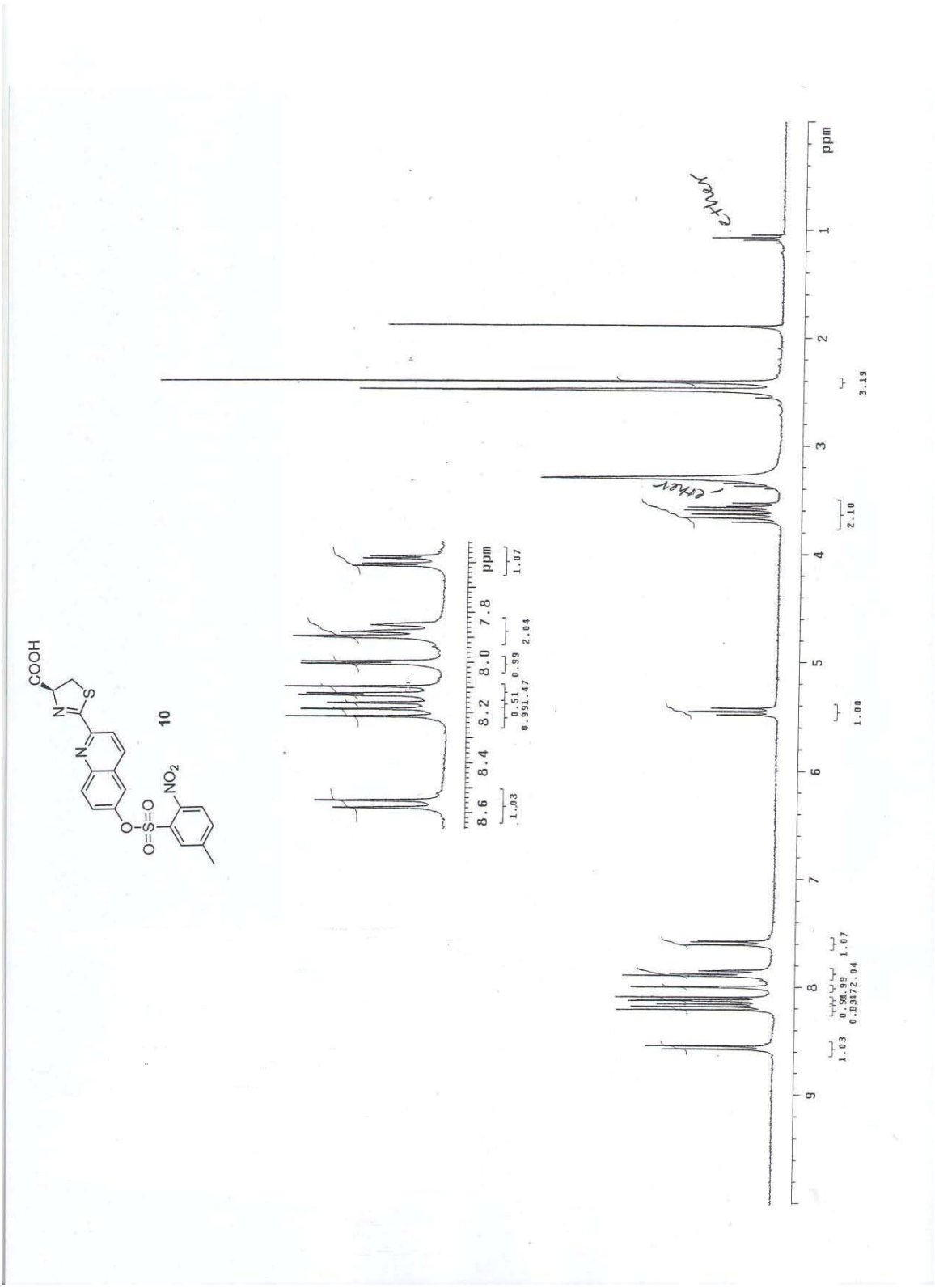
ppm

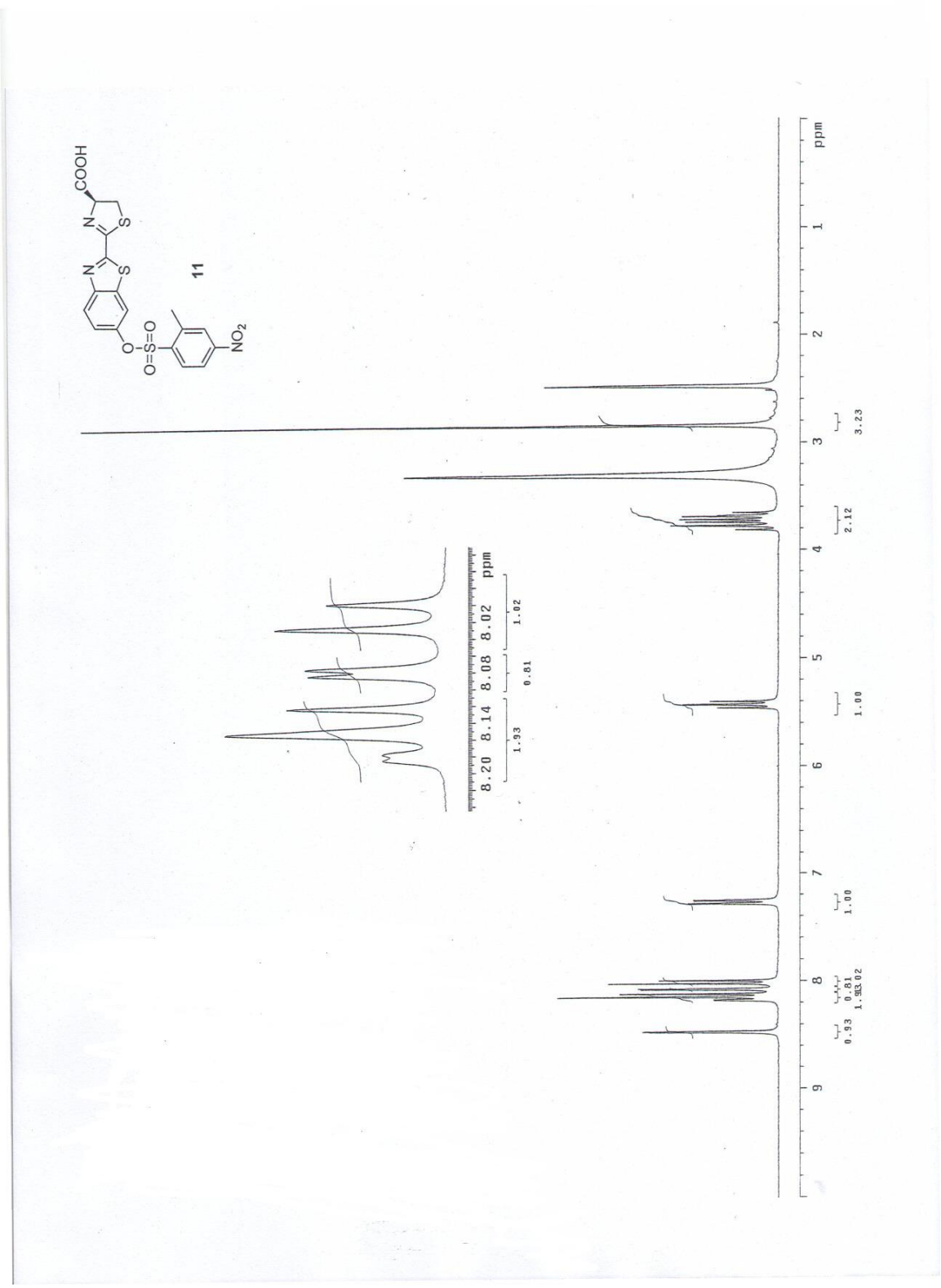

COOH
N
S
N
O
O=S=O
NO2
6
ppm
1
2
3
4
5
6
7
8
9
0.34
0.31
3.37
1.60
0.25
0.74
0.71
0.77
4.05
0.68


COOH
N
S
N
S
O
O=S=O
NO2
7
ppm
1
2
3
4
5
6
7
8
9
2.11
1.00
1.01
1.03
1.02
1.76
0.92


COOH
N
S
N
O
O=S=O
NO2
8
ethanol
ppm


COOH
N
S
N
S
O
O=S=O
NO2
9
ppm
1
2
3
4
5
6
7
8
9
3.00
2.19
1.00
1.03
2.03
1.78
1.10


COOH
N
S
N
O
O=S=O
NO2
10
ppm
8.6 8.4 8.2 8.0 7.8
1.03
0.51 0.99 2.04
0.99 1.47
1.07
ppm
1 2 3 4 5 6 7 8 9
1.03
0.58 0.99
0.89 4.04
1.07
2.10
1.00
3.19


COOH
N
S
N
S
O
O=S=O
NO2
11
ppm
8.20 8.14 8.08 8.02 ppm
1.93
0.81
1.02
2.12
3.23
1.00
0.93
0.81
1.00