"Turn-on" FRET-based Luminescent Iridium(III) Probes for the Detection of Cysteine and Homocysteine

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Supporting Information

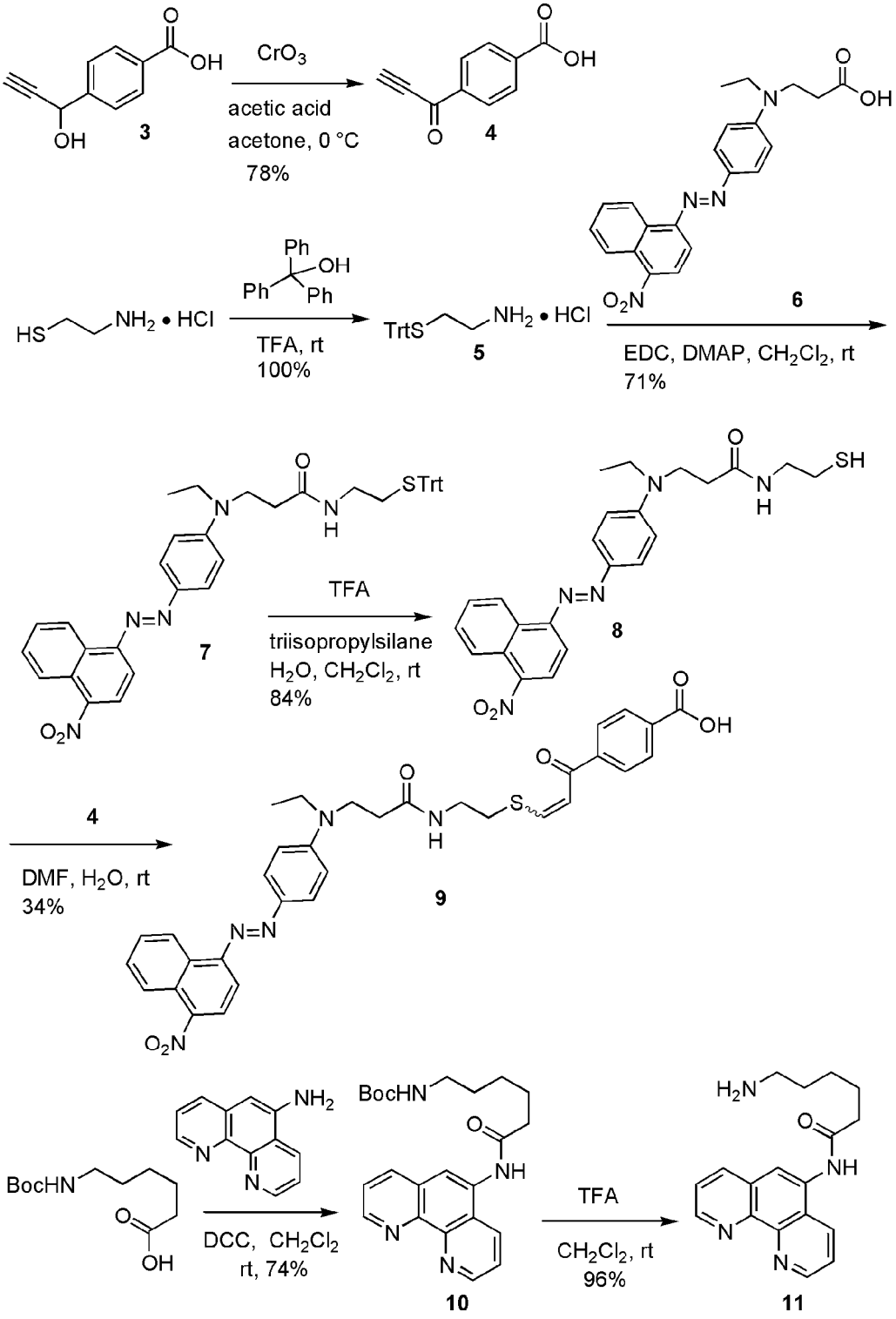
General

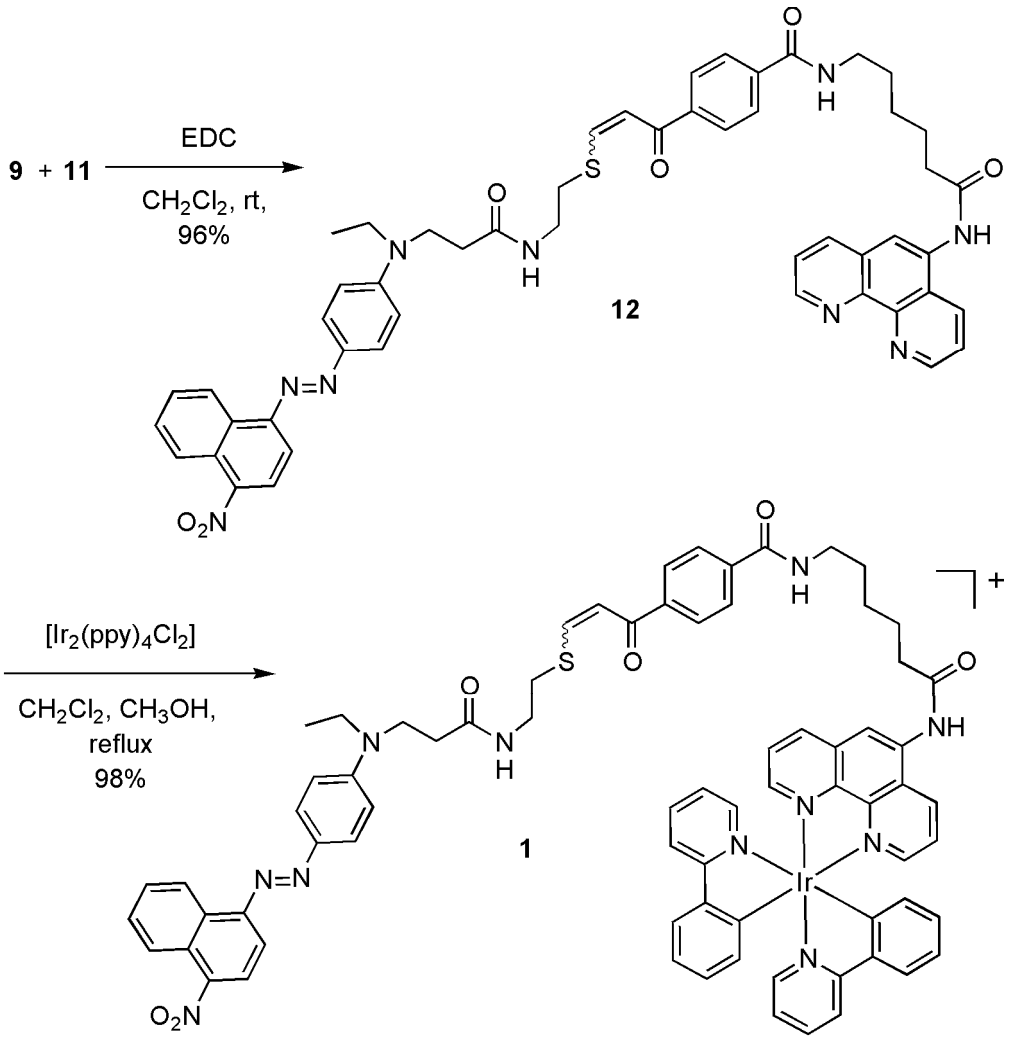
Chemicals purchased from commercial sources were used without further purification. Stock solutions of analytes for analyses were freshly prepared prior use. TLC analyses were performed on silica gel plates and flash column chromatography was conducted over silica gel 60 (230–400 mesh ASTM) with ethyl acetate/*n*-hexane or methanol/dichloromethane as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 or DPX-400 spectrometer. Chemical shifts (ppm) are referenced to TMS. Mass spectra were measured by Finnigan MAT 95 or LCQ mass spectrometer.

General Spectral Measurements

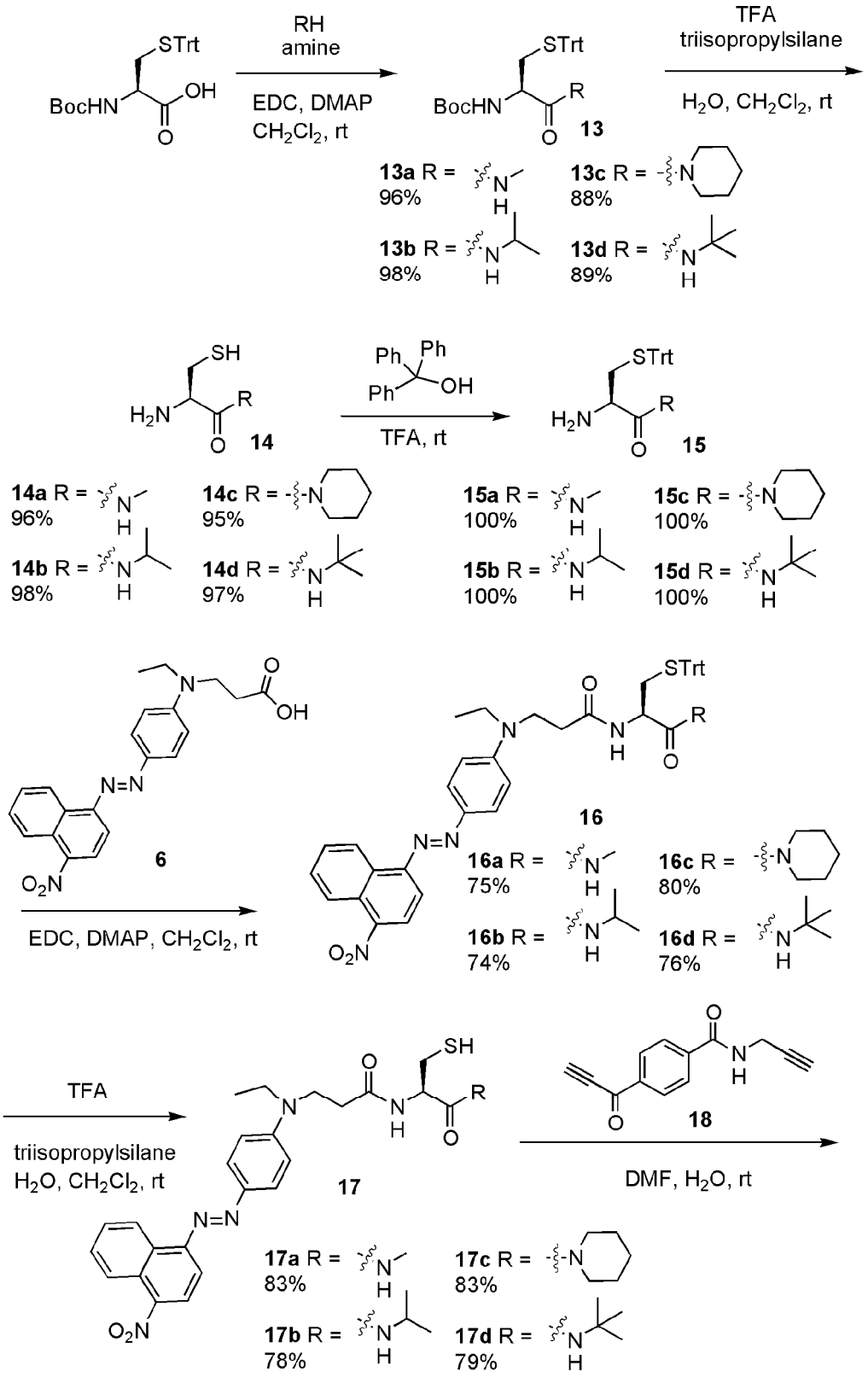
Electronic absorption spectra were recorded with a HP Agilent 8453 UV/Vis spectrophotometer. The emission spectra were measured on a SPEX Fluorolog-3-21 spectrofluorometer.

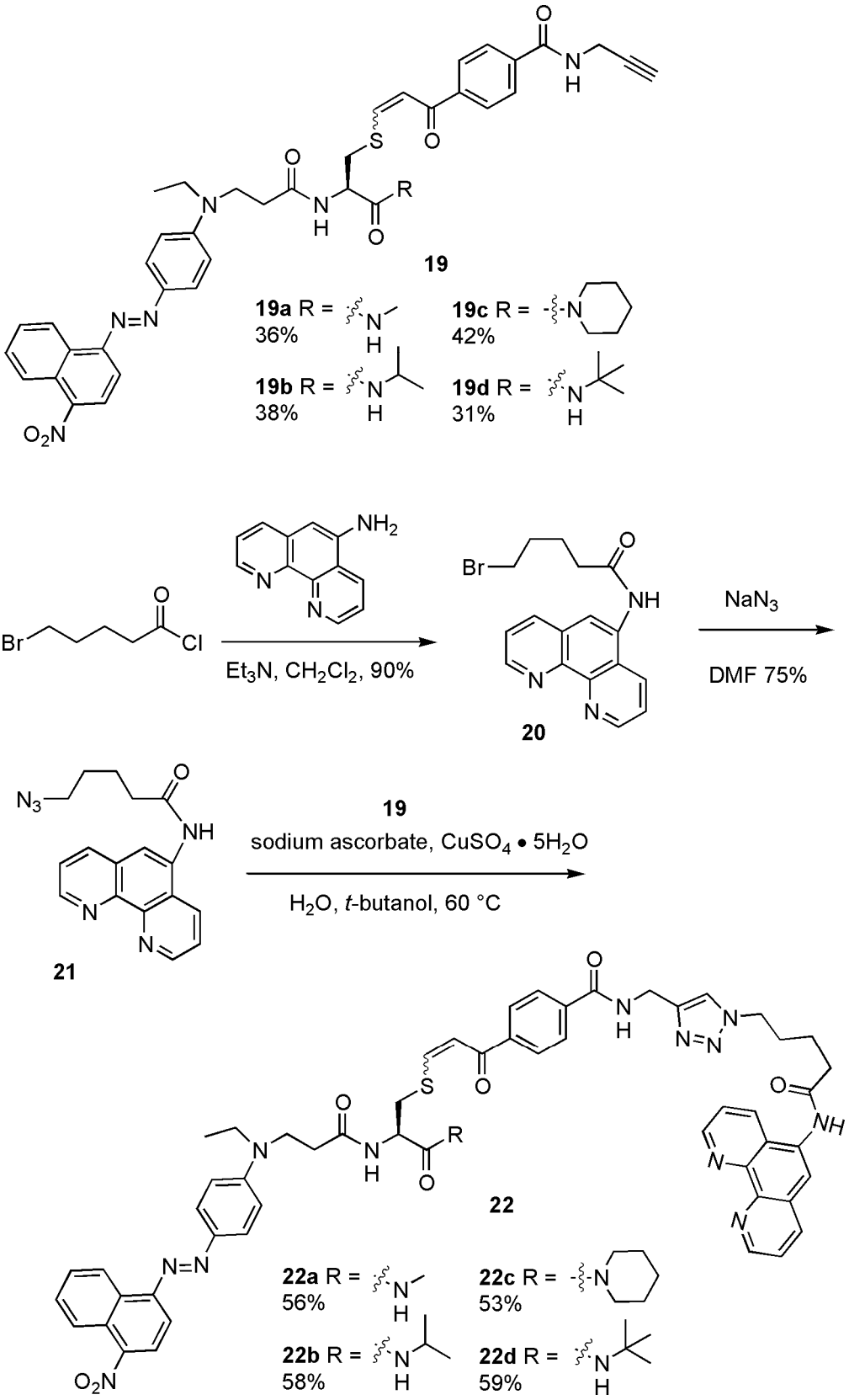
Synthesis of 1

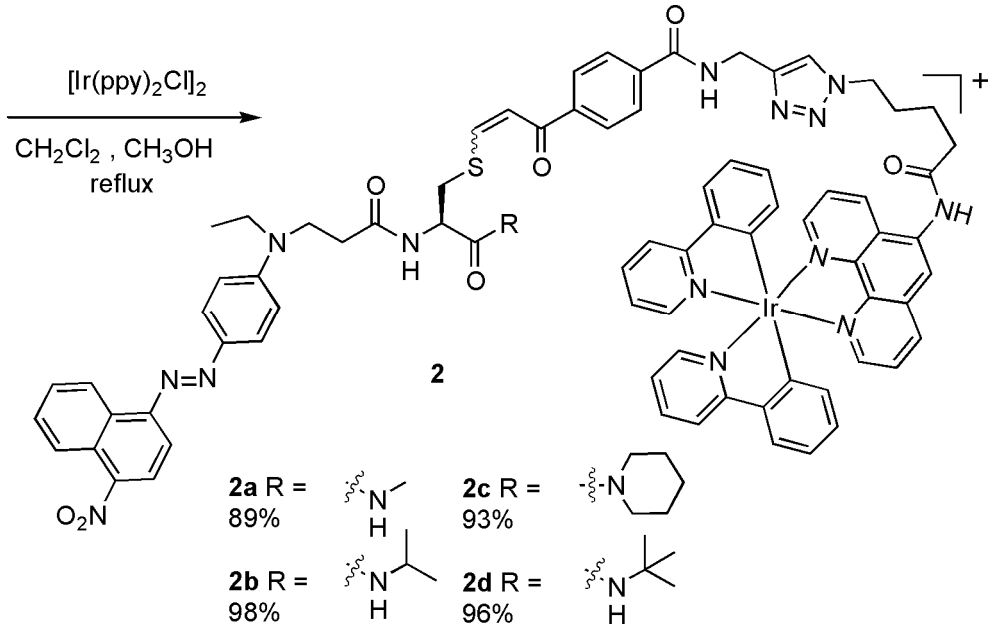



9 + 11
EDC
CH2Cl2, rt,
96%
12
[Ir2(ppy)4Cl2]
CH2Cl2, CH3OH,
reflux
98%
1
+

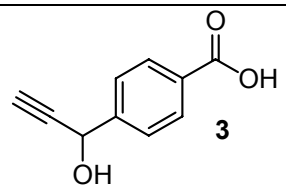
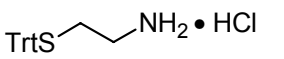
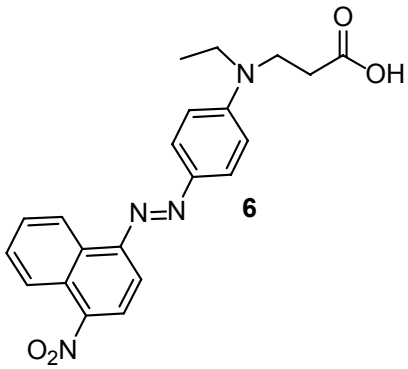
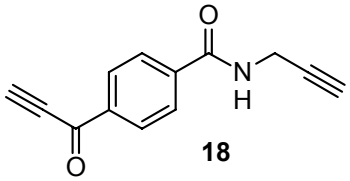
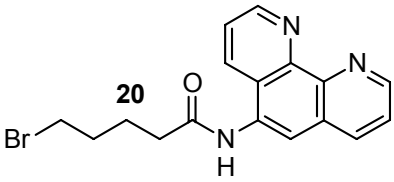
Synthesis of 2a–d



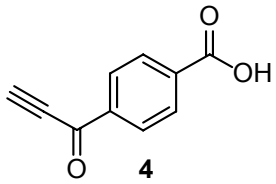

19
19a R = 36%
19b R = 38%
19c R = 42%
19d R = 31%
Et3N, CH2Cl2, 90%
20
NaN3
DMF 75%
21
19
sodium ascorbate, CuSO4 • 5H2O
H2O, t-butanol, 60 °C
22
22a R = 56%
22b R = 58%
22c R = 53%
22d R = 59%


[Ir(ppy)2Cl]2
CH2Cl2 , CH3OH
reflux
2
2a R = 89%
2b R = 98%
2c R = 93%
2d R = 96%

Literature Reference of Known Compounds 3, 5, 6, 18, 20 and $[Ir_2(ppy)_4Cl_2]$

 **3**	H.-Y. Shiu, T.-C. Chan, C.-M. Ho, Y. Liu, M.-K. Wong, C.-M. Che, *Chem. Eur. J.* **2009**, *15*, 3839–3850.
 **5**	Commercial available
 **6**	H.-Y. Shiu, H.-C. Chong, Y.-C. Leung, M.-K. Wong, C.-M. Che, *Chem. Eur. J.* **2010**, *16*, 3308–3313.
 **18**	H.-Y. Shiu, T.-C. Chan, C.-M. Ho, Y. Liu, M.-K. Wong, C.-M. Che, *Chem. Eur. J.* **2009**, *15*, 3839–3850.
 **20**	H. Sho, H. Li, C. Han, P. Wang, *Chem. Res. Chin. Univ.* **2004**, *20*, 149–151.
$[Ir_2(ppy)_4Cl_2]$	S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.

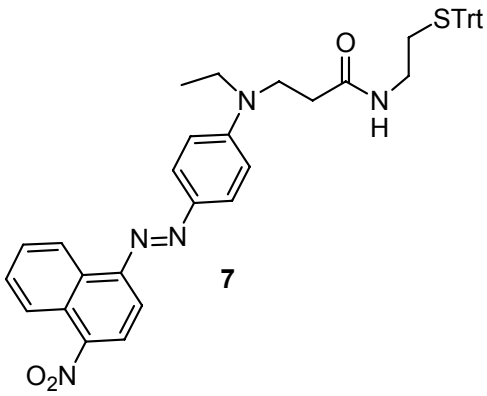
Preparation and Characterization of 4, 7, 8, 9, 10, 11, 12 and 1



4

4: **3** (200 mg, 1.1 mmol), chromium(VI) oxide (227 mg, 2.2 mmol) and acetic acid (0.6 mL, 11 mmol) in 10 mL of acetone was stirred at 0 °C for 3 h. After evaporation of solvent, the residue was purified by flash column chromatography (70% EtOAc in *n*-hexane) to give product **4** (154 mg, 78% isolated yield).

4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 6.4 Hz, 2H), 8.14 (d, J = 6.8 Hz, 2H), 4.05 (s, 1H); ^{13}C NMR δ 177.8, 166.8, 140.2, 136.2, 130.6, 120.6, 120.0, 84.2, 80.5 (125 MHz, $CDCl_3$); EIMS: *m/z* = 174 (M^+); HRMS (EI) for $C_{10}H_6O_3$, calcd 174.0317, found 174.0313.

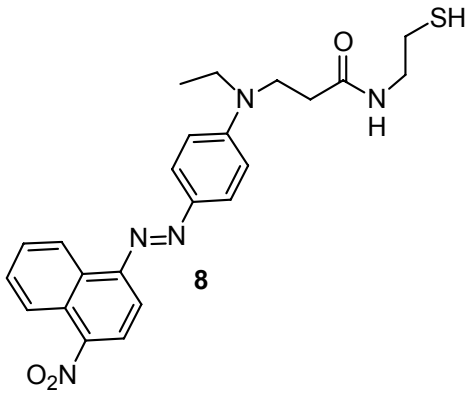


7

7: **5** (29 mg, 0.09 mmol), **6** (30 mg, 0.08 mmol), 1-(3-dimethyl aminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (17.6 mg, 0.09 mmol), 4-di(methylamino)pyridine (DMAP) (1 mg, catalytic amount) and triethylamine (9.3 mg, 0.09 mmol) in 2 mL of anhydrous dimethylformamide (DMF) was stirred at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (2% MeOH in CH_2Cl_2) to give product **7** (38 mg, 71% isolated yield).

7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 8.2 Hz, 1H), 8.68 (d, J = 8.4 Hz,

1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.78–7.70 (m, 3H), 7.40–7.38 (m, 6H), 7.29–7.20 (m, 9H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 3.76 (t, *J* = 6.8 Hz, 2H), 3.49 (q, *J* = 7.1 Hz, 2H), 3.10 (q, *J* = 6.2 Hz, 2H), 2.45–2.42 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 152.1, 150.8, 145.9, 144.7, 144.6, 131.5, 129.5, 128.0, 127.9, 127.2, 126.9, 126.4, 125.0, 124.6, 123.2, 111.5, 109.8, 67.0, 46.7, 45.8, 38.3, 34.6, 31.9, 31.8, 29.7, 29.7, 29.4, 22.7, 14.1, 12.4; ESIMS *m/z* 694 ($[M + H]^+$); HRMS (ESI) for $C_{42}H_{40}N_5O_3S$, calcd 694.2852, found 694.2850.

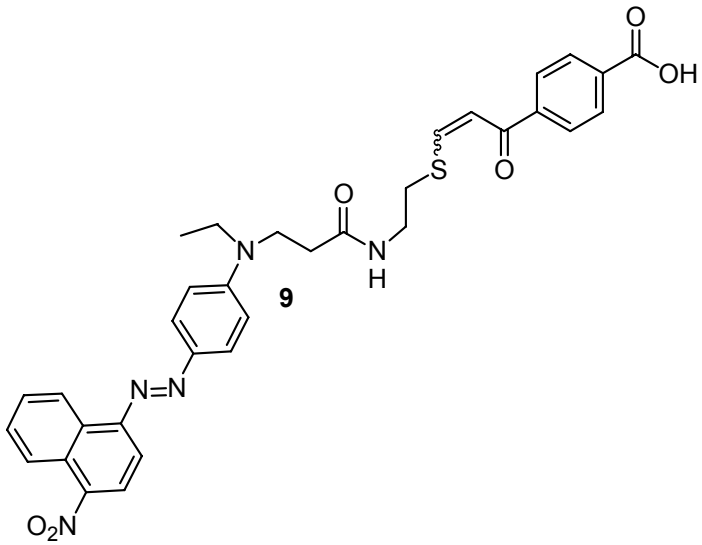


8

8: **7** (43.6 mg, 0.063 mmol), triisopropylsilane (0.12 mL), trifluoroacetic acid (1.3 mL) and H_2O (0.05 mL) was stirred in 0.5 mL of CH_2Cl_2 at room temperature for 1 h. After evaporation of solvent, the residue was purified by flash column chromatography (2% MeOH in CH_2Cl_2) to give product **8** (23.8 mg, 84% isolated yield).

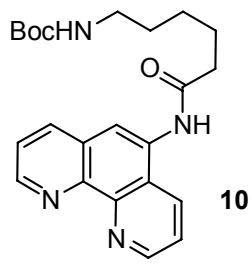
8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.78–7.70 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.91 (s, 1H), 3.83 (t, *J* = 6.8 Hz, 2H), 3.56 (q, *J* = 7.1 Hz, 2H), 3.46 (q, *J* = 6.2 Hz, 2H), 2.67 (d, *J* = 8.4 Hz, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 152.0, 150.8, 145.9, 144.7, 131.5, 129.5, 127.2, 126.6, 126.4, 125.0, 124.6, 123.2, 111.5, 109.8, 46.7, 45.8, 42.4, 34.7, 31.9, 29.7, 29.4, 24.6, 22.7, 14.1, 12.4; ESIMS *m/z* 452 ([M

+ H]$^+$); HRMS (ESI) for $C_{23}H_{26}N_5O_3S$, calcd 452.1756, found 452.1751.



9: **8** (20.2 mg, 0.05 mmol), **4** (9.4 mg, 0.05 mmol) and H_2O (1.5 mL) was stirred in 0.5 mL of DMF at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (5% MeOH in CH_2Cl_2) to give product **9** (9.6 mg, 34% isolated yield, *Z*/*E* = 4/6).

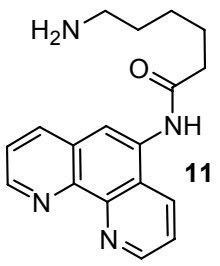
9: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93–8.97 (m, 1H), 8.66–8.62 (m, 1H), 8.31–8.25 (m, 1H), 8.12–8.10 (m, 1H), 8.04–8.01 (m, 2H), 7.97–7.95 (m, 1H), 7.92–7.86 (m, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.70–7.61 (m, 2H), 7.36 (d, *J* = 9.6 Hz, 0.4H), 7.14 (d, *J* = 14.8 Hz, 0.6H), 6.78 (t, *J* = 9.8 Hz, 2H) 6.95 (d, *J* = 9.7 Hz, 0.4H), 6.35 (t, *J* = 5.8 Hz, 0.6H), 6.29 (t, *J* = 5.7 Hz, 0.4H), 3.83 (t, *J* = 6.2 Hz, 2H), 3.73 (q, *J* = 7.0 Hz, 1H), 3.52–3.50 (m, 2H), 3.55–3.50 (m, 2H), 3.11 (t, *J* = 6.7 Hz, 1H), 3.00–2.97 (m, 1H), 2.63–2.58 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 184.3, 171.4, 168.0, 151.9, 150.8, 148.6, 141.7, 132.4, 131.5, 130.9, 130.4, 130.3, 129.6, 128.8, 128.4, 128.1, 127.9, 127.2, 126.6, 126.4, 125.0, 123.1, 118.7, 111.5, 109.8, 85.2, 85.1, 83.3, 83.0, 79.3, 79.0, 77.6, 68.2, 46.8, 46.7, 45.8, 38.8, 38.7, 34.6, 31.9, 31.8, 30.9, 30.4, 29.7, 29.3, 28.9, 23.8, 23.3, 23.2, 23.0, 22.7, 16.5, 14.1, 12.4, 11.0; ESIMS *m/z* 626 ([M + H]$^+$); HRMS (ESI) for $C_{33}H_{32}N_5O_6S$, calcd 626.2073, found 626.2071.



10

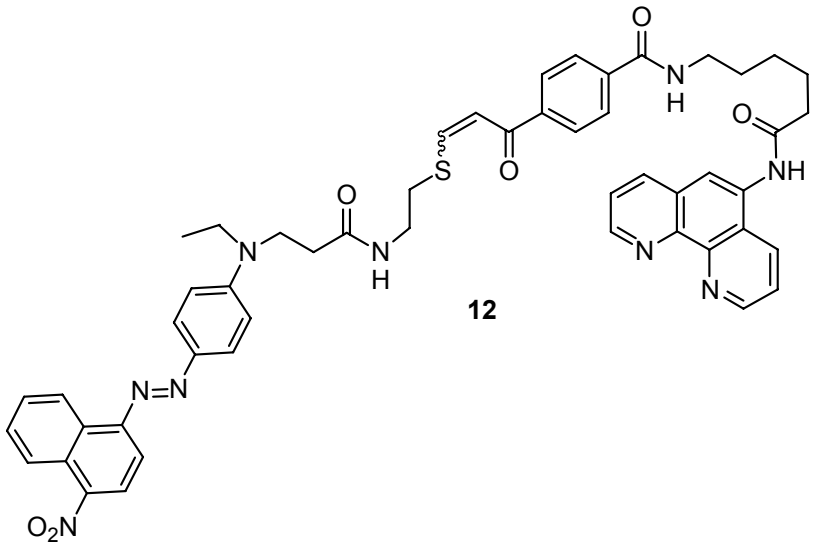
10: A solution of 6-*tert*-butoxycarbonylamino-hexanoic acid (1060 mg, 4.6 mmol) and *N*,*N'*-Dicyclohexylcarbodiimide (DCC) (473 mg, 2.3 mmol) in acetonitrile (30 mL) was stirred at room temperature for 1 h and filtered to remove the dicyclohexylurea (DCU) precipitate. The resulting anhydride was used without further purification and added to a solution of 5-amino-1,10-phenanthroline (70.8 mg, 0.36 mmol) and triethylamine (255 mg, 2.5 mmol) in acetonitrile (30 mL). The solution was stirred at room temperature for 6 days under argon. After evaporation of solvent, the residue was purified by flash column chromatography on Al_2O_3 (2% MeOH in CH_2Cl_2) to give product **10** (107.8 mg, 74% isolated yield).

10: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, J = 3.0 Hz, 1H), 9.08 (d, J = 2.5 Hz, 1H), 8.51 (s, 1H), 8.46 (d, J = 8.2 Hz, 1H), 8.21 (s, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.59 (m, 2H), 4.64 (s, 1H), 3.08–3.07 (m, 2H), 2.49–2.46 (m, 2H), 1.74–1.65 (m, 2H), 1.42 (m, 11H), 1.33–1.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 172.6, 156.2, 156.1, 150.1, 149.8, 146.5, 144.5, 135.9, 130.9, 130.3, 128.4, 124.4, 123.4, 122.8, 122.3, 120.0, 105.6, 79.3, 79.2, 78.2, 78.0, 77.9, 53.4, 40.3, 40.2, 37.2, 37.1, 36.4, 29.8, 29.7, 29.7, 28.6, 28.6, 28.5, 28.5, 28.5, 28.4, 28.3, 26.3, 26.2, 25.3, 25.1; ESIMS *m/z* 409 ($[M + H]^+$); HRMS (ESI) for $C_{23}H_{29}N_4O_3$, calcd 409.2240, found 409.2241.



11

11: **10** (100 mg, 0.25 mmol) and trifluoroacetic acid (1 mL) was stirred in 0.5 mL of CH_2Cl_2 at room temperature for 30 min. After evaporation of solvent, the crude mixture **11** was used for synthesis without further purification (75 mg, 96% yield).

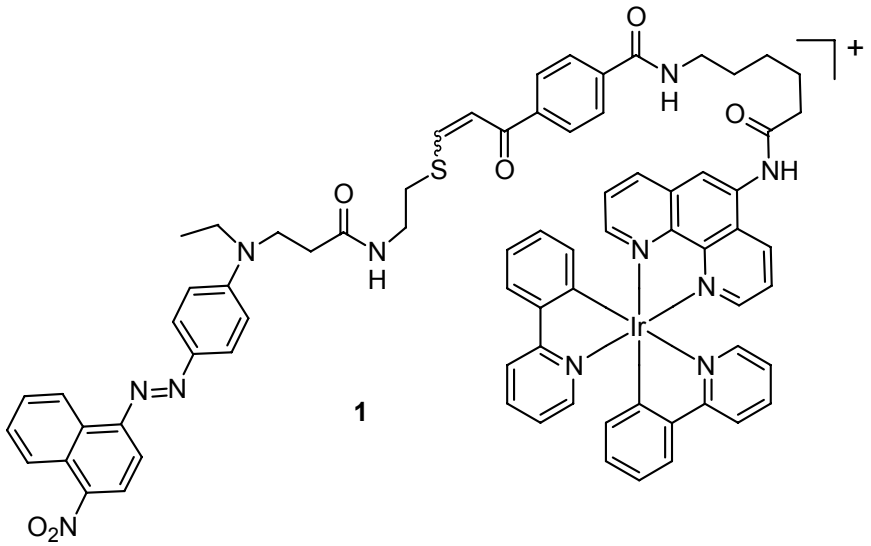


12

12: **9** (40 mg, 0.064 mmol), **11** (70.3 mg, 0.23 mmol), 1-(3-dimethyl aminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (49 mg, 0.26 mmol), 4-di(methylamino)pyridine (DMAP) (1 mg, catalytic amount) and triethylamine (33 mg, 0.32 mmol) in 2 mL of anhydrous dimethylformamide (DMF) was stirred at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (2% MeOH in CH_2Cl_2) to give product **12** (56 mg, 96% isolated yield).

12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13–9.06 (m, 2H), 9.05–9.00 (m, 3H), 8.62 (d, J = 8.6 Hz, 1H), 8.53–8.49 (m, 2H), 8.33–8.29 (m, 2H), 8.24–8.21 (m, 1H), 8.11–8.10 (m, 1H), 8.08–8.05 (m, 1H), 8.01–7.98 (m, 1H), 7.97–7.95 (m, 1H), 7.94–7.93 (m, 1H), 7.90–7.83 (m, 3H), 7.80–7.74 (m, 1H), 7.72–7.68 (m, 4H),

7.67–7.63 (m, 1H), 7.09 (d, *J* = 14.8 Hz, 0.5H), 7.05 (d, *J* = 9.7 Hz, 0.5H), 6.88–6.83 (m, 2H), 6.55 (d, *J* = 6.4 Hz, 0.5H), 3.81–3.80 (m, 2H), 3.58–3.50 (m, 4H), 3.46–3.45 (m, 2H), 3.10–3.08 (m, 1H), 3.04 (s, 1H), 2.95 (t, *J* = 6.8 Hz, 1H), 2.63–2.58 (m, 5H), 1.90–1.87 (m, 2H), 1.75–1.72 (m, 2H), 1.62–1.57 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ESIMS *m/z* 916 ($[M + H]^+$); HRMS (ESI) for $C_{51}H_{50}N_9O_6S$, calcd 916.3605, found 916.3604.



1

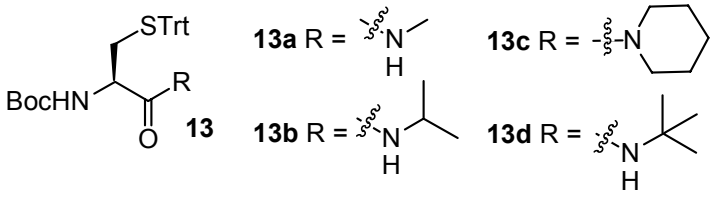
1: A mixture of $[Ir_2(ppy)_4Cl_2]$ (7.5 mg, 0.007 mmol) and **12** (12.7 mg, 0.014 mmol) in 30 mL MeOH/CH_2Cl_2 = 1:1 (v/v) was refluxed under an inert atmosphere of N_2 in the dark for 4 h. The solution was then evaporated to dryness and the solid was dissolved in CH_2Cl_2 and purified by column chromatography on Al_2O_3 (8% MeOH in CH_2Cl_2) to give product **1** (9.7 mg, 98% isolated yield).

1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.38–11.23 (m, 1H), 9.66–9.53 (m, 1H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.7 Hz, 1H), 8.54 (m, 1H), 8.32–8.28 (m, 2H), 8.21–8.18 (m, 1H), 8.14–8.11 (m, 1H), 8.10–8.06 (m, 1H), 8.01–7.90 (m, 6H), 7.86–7.79 (m, 3H), 7.77–7.68 (m, 8H), 7.63–7.60 (m, 1H), 7.29–7.26 (m, 2H), 7.11–7.07 (m, 2H), 7.02–6.96 (m, 3H), 6.87–6.82 (m, 2H), 6.80–6.76 (m, 2H), 6.42–6.36 (m, 2H), 3.80 (q, *J* = 6.4 Hz, 2H), 3.54–3.47 (m, 6H), 3.26–3.24 (m, 0.5H), 3.19–3.16 (m, 0.5H), 3.05 (t, *J* = 6.8 Hz, 1H), 3.01–2.93 (m, 3H), 2.56 (t, *J*

= 6.6 Hz, 2H), 2.36 (s, 1H), 1.98–1.93 (m, 2H), 1.84–1.79 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ESIMS *m/z* 1416 ($[M + H]^+$).

Preparation and Characterization of 13a–d, 14a–d, 15a–d, 16a–d, 17a–d, 19a–d, 21, 22a–d, 2a–d

General Procedure for 13a–d



Boc-Cys(Trt)-OH (100 mg, 0.22 mmol), amine, 1-(3-dimethyl aminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (50 mg, 0.26 mmol), 4-di(methylamino)pyridine (DMAP) (1 mg, catalytic amount) and triethylamine (26 mg, 0.26 mmol) in 2 mL of anhydrous dimethylformamide (DMF) was stirred at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (50–80% EtOAc in *n*-hexane) to give product **13**.

13a: According to the general procedure for **13a**–**d** using methylamine hydrochloride (17.5 mg, 0.26 mmol), **13a** was obtained (100.5 mg, 96% isolated yield).

13a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.40 (m, 7H), 7.28–7.25 (m, 4H), 7.25–7.20 (m, 4H), 6.13 (s, 1H), 4.96 (d, J = 7.8 Hz, 1H), 3.88 (s, 1H), 2.72–2.65 (m, 4H), 2.53 (dd, J = 12.8, 5.2 Hz, 1H), 1.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 144.4, 129.5, 128.0, 126.8, 100.3, 80.2, 67.1, 53.5, 34.0, 28.3, 26.2; EIMS *m/z* 476 (M^+); HRMS (EI) for $C_{28}H_{32}N_2O_3S$, calcd 476.2134, found 476.2132.

13b: According to the general procedure for **13a**–**d** using isopropylamine (15 mg, 0.26 mmol), **13b** was obtained (88 mg, 80% yield).

13b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.40 (m, 7H), 7.28–7.25 (m, 4H), 7.25–7.20 (m, 4H), 5.75 (d, *J* = 7.2 Hz, 1H), 4.82 (s, 1H), 4.02–3.93 (m, 1H), 3.78 (s, 1H), 2.68 (dd, *J* = 12.4, 6.6 Hz, 1H), 2.50 (dd, *J* = 12.8, 5.0 Hz, 1H), 1.41 (s, 9H), 1.10–1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 155.4, 129.9, 129.6, 129.3, 128.8, 128.3, 128.0, 127.8, 127.0, 126.8, 80.1, 67.1, 53.7, 41.5, 34.0, 30.2, 28.3, 22.6; EIMS *m/z* 504 (M^+); HRMS (EI) for $C_{30}H_{36}N_2O_3S$, calcd 504.2447, found 504.2445.

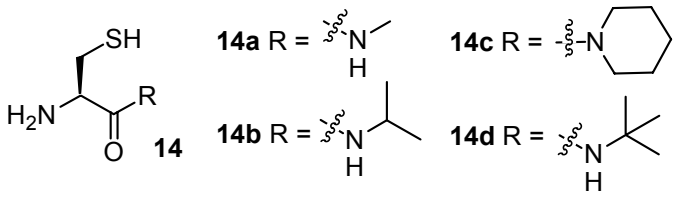
13c: According to the general procedure for **13a**–**d** using piperidine (22 mg, 0.26 mmol), **13c** was obtained (103 mg, 88% yield).

13c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.39 (m, 7H), 7.28–7.25 (m, 4H), 7.25–7.18 (m, 4H), 5.39 (d, *J* = 8.6 Hz, 1H), 4.56 (s, 1H), 3.88 (s, 1H), 3.48–3.46 (m, 2H), 3.14–3.13 (m, 1H), 3.07–3.05 (m, 1H), 2.48–2.46 (m, 1H), 2.35 (dd, *J* = 16.2, 9.9 Hz, 1H), 1.56–1.54 (m, 2H), 1.47 (m, 2H), 1.43 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 129.6, 127.9, 126.7, 49.3, 46.4, 43.3, 35.2, 28.3, 26.3, 25.4, 24.4; EIMS *m/z* 476 (M^+); HRMS (EI) for $C_{32}H_{38}N_2O_3S$, calcd 530.2603, found 530.2601.

13d: According to the general procedure for **13a**–**d** using *t*-butylamine (19 mg, 0.26 mmol), **13d** was obtained (101 mg, 89% yield).

13d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 7H), 7.31–7.24 (m, 4H), 7.23–7.21 (m, 4H), 5.84 (s, 1H), 4.79 (s, 1H), 3.72 (s, 1H), 2.65–2.64 (m, 1H), 2.46 (dd, *J* = 7.5, 5.3 Hz, 1H), 1.47 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 144.4, 129.6, 128.0, 127.9, 126.8, 67.1, 53.9, 51.3, 33.8, 31.7, 28.6, 28.2, 22.6, 14.1; EIMS *m/z* 518 (M^+); HRMS (EI) for $C_{31}H_{38}N_2O_3S$, calcd 518.2603, found 518.2601.

General Procedure for 14a–d



13, triisopropylsilane (0.12 mL), trifluoroacetic acid (1.3 mL) and H_2O (0.05 mL) was stirred in 0.5 mL of CH_2Cl_2 at room temperature for 0.5 h. After evaporation of solvent, CH_2Cl_2 (30 mL) was added to the resulting residues. The organic layer was extracted with H_2O (10 mL). The aqueous layer was then evaporated to give the transparent oil product. The crude mixture **14** was used for synthesis without further purification.

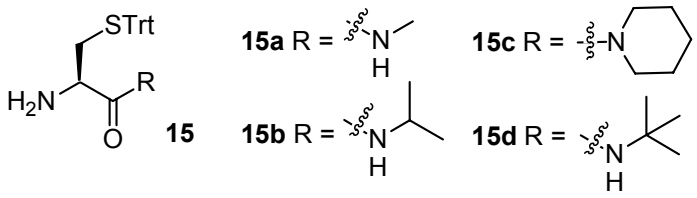
14a: According to the general procedure for **14a**–**d** using **13a** (50 mg, 0.11 mmol), **14a** was obtained (14 mg, 96% yield).

14b: According to the general procedure for **14a**–**d** using **13b** (50 mg, 0.10 mmol), **14b** was obtained (16 mg, 98% yield).

14c: According to the general procedure for **14a**–**d** using **13c** (50 mg, 0.094 mmol), **14c** was obtained (16.8 mg, 95% yield).

14d: According to the general procedure for **14a**–**d** using **13d** (50 mg, 0.097 mmol), **14d** was obtained (17.0 mg, 97% yield).

General Procedure for 15a–d



14, triphenylmethanol in 2 mL of trifluoroacetic acid was stirred at room temperature for 3 h. After evaporation of solvent, the crude mixture was washed by hexane for several times to give product **15**.

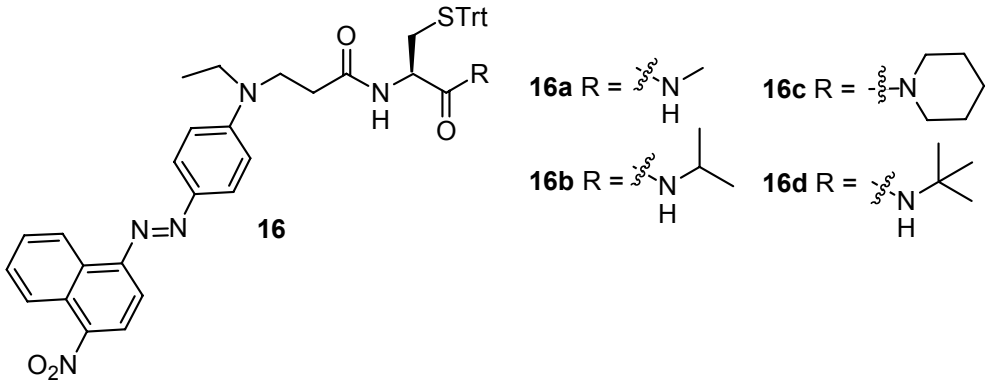
15a: According to the general procedure for **15a**–**d** using **14a** (15 mg, 0.112 mmol) and triphenylmethanol (29 mg, 0.112 mmol), **15a** was obtained (42.1 mg, 100% yield).

15b: According to the general procedure for **15a**–**d** using **14b** (15 mg, 0.093 mmol) and triphenylmethanol (24 mg, 0.093 mmol) was used, **15b** was obtained (37.8 mg, 100% yield).

15c: According to the general procedure for **15a**–**d** using **14c** (15 mg, 0.079 mmol) and triphenylmethanol (21 mg, 0.079 mmol) was used, **15c** was obtained (34.0 mg, 100% yield).

15d: According to the general procedure for **15a**–**d** using **14d** (15 mg, 0.085 mmol) and triphenylmethanol (22 mg, 0.085 mmol), **15d** was obtained (35.5 mg, 100% yield).

General Procedure for 16a–d



16a–d: **15, 6** (30 mg, 0.08 mmol), 1-(3-dimethyl aminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (61.4 mg, 0.32 mmol), 4-di(methylamino)pyridine (DMAP) (1 mg, catalytic amount) and triethylamine (40.4 mg, 0.40 mmol) in 2 mL of anhydrous dimethylformamide (DMF) was stirred at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (2–6% MeOH in CH_2Cl_2) to give product **16**.

16a: According to the general procedure for **16a–d** using **15a** (90 mg, 0.24 mmol)**, 16a** was obtained (45 mg, 75% isolated yield).

16a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.78–7.70 (m, 3H), 7.40–7.38 (m, 6H), 7.29–7.20 (m, 9H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.04 (d, *J* = 7.6 Hz, 1H), 5.89–5.87 (m, 1H), 4.13–4.08 (m, 1H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.46 (q, *J* = 7.1 Hz, 2H), 2.75–2.71 (m, 0.6 H), 2.70 (m, 3H), 2.69 – 2.65 (m, 1H), 2.68 (dd, *J* = 13.3, 7.6 Hz, 1H), 2.60 (dd, *J* = 13.3, 5.6 Hz, 1H), 2.46–2.45 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 150.7, 144.6, 144.3, 131.5, 129.6, 129.5, 128.1, 127.9, 127.9, 127.2, 126.9, 126.8, 126.6, 126.4, 125.0, 124.6, 123.1, 111.5, 109.8, 52.3, 46.5, 45.6, 34.4, 33.5, 26.3, 14.2, 12.3; ESIMS

m/z 751 ([M + H]$^+$); HRMS (ESI) for $C_{44}H_{43}N_6O_4S$, calcd 751.3066, found 751.3065.

16b: According to the general procedure for **16a**–**d** using **15b** (97 mg, 0.24 mmol)**,** **16b** was obtained (46.1 mg, 74% isolated yield).

16b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.78–7.70 (m, 3H), 7.40–7.38 (m, 6H), 7.29–7.20 (m, 9H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 7.8 Hz, 1H), 5.70 (d, *J* = 7.8 Hz, 1H), 4.03–3.98 (m, 1H), 3.96–3.88 (m, 1H), 3.77–3.68 (m, 2H), 3.46–3.41 (m, 2H), 2.68–2.63 (m, 1H), 2.55–2.50 (m, 1H), 2.49–2.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 168.9, 150.8, 144.6, 144.4, 131.5, 129.6, 129.6, 129.5, 128.1, 128.0, 127.2, 126.9, 126.6, 126.4, 125.1, 124.6, 123.1, 111.4, 109.7, 67.2, 60.4, 54.1, 52.5, 46.5, 45.6, 41.8, 41.0, 37.5, 34.4, 34.0, 31.5, 30.9, 30.1, 29.7, 22.7, 22.6, 21.1, 14.2, 12.3; ESIMS *m/z* 779 ([M + H]$^+$); HRMS (ESI) for $C_{46}H_{47}N_6O_4S$, calcd 779.3379, found 779.3380.

16c: According to the general procedure for **16a**–**d** using **15c** (103.2 mg, 0.24 mmol), **16c** was obtained (51.4 mg, 80% isolated yield).

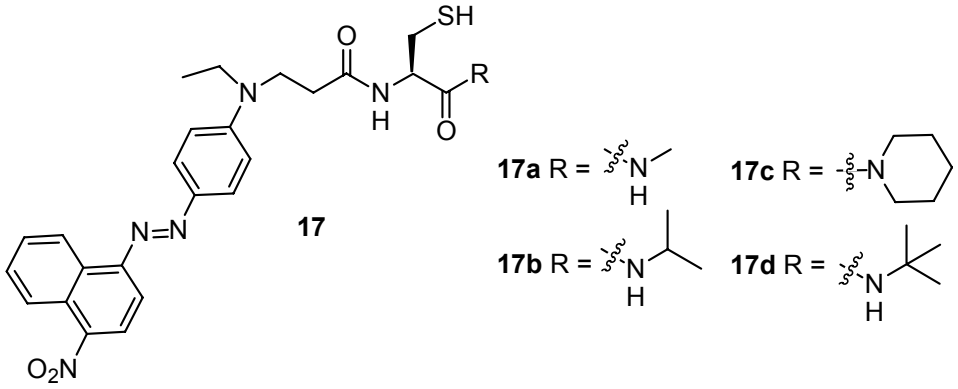
16c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.75–7.73 (m, 3H), 7.39–7.37 (m, 6H), 7.29–7.21 (m, 9H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.93–4.92 (m, 1H), 3.80–3.77 (m, 2H), 3.51–3.47 (m, 3H), 3.42–3.41 (m, 1H), 3.12–3.08 (m, 1H), 3.02–2.99 (m, 1H), 2.59–2.52 (m, 3H), 2.46–2.43 (m, 1H), 1.67 (m, 2H), 1.56 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.0, 152.1, 150.9, 145.7, 144.6, 144.4, 131.4, 130.0, 129.6, 129.5, 129.3, 128.0, 127.7, 127.2, 127.0, 126.8, 126.6, 126.4, 125.1, 124.6, 123.1,

111.5, 111.2, 109.8, 66.9, 60.4, 47.9, 46.6, 46.4, 45.6, 43.4, 34.8, 34.5, 31.5, 30.8, 30.1, 29.7, 26.3, 25.6, 25.4, 25.4, 24.3, 14.2, 12.4; ESIMS *m/z* 805 ($[M + H]^+$); HRMS (ESI) for $C_{48}H_{49}N_6O_4S$, calcd 805.3536, found 805.3533.

16d: According to the general procedure for **16a**–**d** using **15d** (100.3 mg, 0.24 mmol), **16d** was obtained (48.2 mg, 76% isolated yield).

16d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.75–7.73 (m, 3H), 7.42–7.40 (m, 6H), 7.31–7.22 (m, 9H), 6.74 (d, *J* = 9.2 Hz, 2H), 5.97 (d, *J* = 7.7 Hz, 1H), 5.61 (s, 1H), 3.94–3.92 (m, 1H), 3.74–3.71 (m, 2H), 3.46–3.43 (m, 2H), 2.62 (dd, *J* = 7.2, 5.8 Hz, 1H), 2.51–2.46 (m, 1H), 2.45–2.43 (m, 1H), 1.25 (s, 9H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.8, 150.7, 144.6, 144.4, 132.6, 129.6, 128.1, 128.0, 127.2, 126.9, 126.6, 126.4, 125.0, 124.6, 123.1, 111.5, 109.8, 52.8, 51.7, 46.5, 45.6, 34.5, 33.9, 28.6, 12.3, 5.6; ESIMS *m/z* 793 ($[M + H]^+$); HRMS (ESI) for $C_{47}H_{49}N_6O_4S$, calcd 793.3536, found 793.3533.

General Procedure for 17a–d



17a–**d**: **16**, triisopropylsilane (0.12 mL), trifluoroacetic acid (1.3 mL) and H_2O (0.05 mL) was stirred in 0.5 mL of CH_2Cl_2 at room temperature for 1 h. After evaporation of solvent, the residue was purified by flash column chromatography

(2–6% MeOH in CH_2Cl_2) to give product **17**.

17a: According to the general procedure for **17a**–**d** using **16a** (50 mg, 0.067 mmol), **17a** was obtained (28.1 mg, 83% isolated yield).

17a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.80–7.70 (m, 3H), 7.05–7.02 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 4.53–4.48 (m, 1H), 3.80 (t, *J* = 6.9 Hz, 2H), 3.54 (t, *J* = 7.1 Hz, 2H), 2.90–2.80 (m, 1H), 2.74–2.64 (m, 1H), 2.78–2.76 (m, 3H), 2.62–2.58 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.3, 152.0, 150.8, 145.8, 144.6, 131.4, 129.5, 127.2, 126.6, 126.3, 125.0, 124.5, 123.1, 111.5, 109.8, 54.6, 54.5, 50.1, 49.9, 49.7, 49.5, 49.3, 46.6, 45.5, 34.5, 34.4, 30.8, 29.7, 26.4, 26.3, 26.2, 12.3; ESIMS *m/z* 509 ([M + H]$^+$); HRMS (ESI) for $C_{25}H_{29}N_6O_4S$, calcd 509.1971, found 509.1970.

17b: According to the general procedure for **17a**–**d** using **16b** (50 mg, 0.064 mmol), **17b** was obtained (26.9 mg, 78% isolated yield).

18b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.75–7.73 (m, 3H), 6.83 (d, *J* = 9.3 Hz, 2H), 4.41 (dd, *J* = 6.7, 5.8Hz, 1H), 4.06–3.96 (m, 1H), 3.82–3.78 (m, 2H), 3.57–3.52 (m, 2H), 2.79–2.76 (m, 2H), 2.64–2.60 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19–1.15 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 168.7, 152.0, 150.9, 145.8, 144.6, 131.4, 129.5, 127.2, 126.6, 126.3, 125.0, 124.5, 123.1, 111.5, 109.8, 54.7, 50.0, 49.8, 49.6, 49.4, 49.2, 49.0, 48.8, 46.6, 45.4, 41.7, 34.4, 26.4, 22.4, 22.2, 12.3; ESIMS *m/z* 537 ([M + H]$^+$); HRMS (ESI) for $C_{27}H_{33}N_6O_4S$, calcd 537.2284, found 537.2283.

17c: According to the general procedure for **17a**–**d** using **16c** (50 mg, 0.062

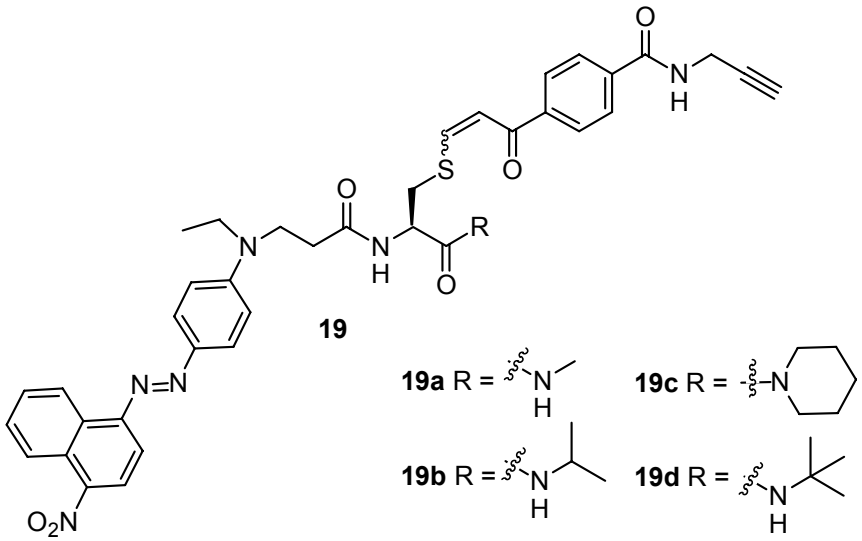
mmol), **17c** was obtained (29.0 mg, 83% isolated yield).

17c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.75–7.72 (m, 3H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.77 (m, 1H), 5.13–5.11 (m, 1H), 3.81 (t, *J* = 7.0 Hz, 2H), 3.57–3.52 (m, 3H), 3.51–3.48 (m, 3H), 2.94–2.87 (m, 1H), 2.76–2.70 (m, 1H), 2.62–2.59 (m, 2H), 1.65–1.45 (m, 6H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 167.5, 152.0, 150.9, 145.8, 144.6, 131.5, 129.5, 127.2, 126.6, 126.4, 125.0, 124.6, 123.1, 111.5, 111.3, 109.8, 50.1, 46.9, 46.6, 45.6, 45.4, 43.6, 42.7, 34.6, 30.7, 29.7, 26.5, 25.5, 24.4, 24.3, 14.1, 12.4; ESIMS *m/z* 563 ($[M + H]^+$); HRMS (ESI) for $C_{29}H_{35}N_6O_4S$, calcd 563.2440, found 563.2442.

17d: According to the general procedure for **17a**–**d** using **16d** (50 mg, 0.063 mmol), **17d** was obtained (27.4 mg, 79% isolated yield).

17d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.2 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 9.1 Hz, 2H), 7.75–7.71 (m, 3H), 6.80 (d, *J* = 9.1 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.02 (s, 1H), 4.41–4.39 (m, 1H), 3.83–3.78 (m, 2H), 3.53 (q, *J* = 7.0 Hz, 2H), 2.93–2.91 (m, 1H), 2.70–2.66 (m, 1H), 2.61 (t, *J* = 6.8 Hz, 2H) , 1.27 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 168.4, 152.0, 150.8, 145.9, 144.7, 131.5, 129.5, 127.2, 126.6, 126.3, 125.0, 124.6, 123.1, 111.5, 109.8, 55.0, 52.0, 46.6, 45.6, 34.6, 30.9, 29.7, 28.7, 26.8, 12.4; ESIMS *m/z* 793 ($[M + H]^+$); HRMS (ESI) for $C_{28}H_{35}N_6O_4S$, calcd 551.2440, found 551.2443.

General Procedure for 19a–d



19a–**d**: **17**, **18** and H_2O (1.5 mL) was stirred in 0.5 mL of DMF at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography (5–10% MeOH in CH_2Cl_2) to give product **19**.

19a: According to the general procedure for **19a**–**d** using **17a** (20 mg, 0.039 mmol), **18** (8.2 mg, 0.039 mmol), **19a** was obtained (10.1 mg, 36% isolated yield, *Z*/*E* = 1/1).

19a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03–9.00 (m, 1H), 8.67–8.62 (m, 1H), 8.34–8.28 (m, 1H), 8.03–7.97 (m, 2H), 7.95–7.93 (m, 1H), 7.90–7.88 (m, 1H), 7.87–7.85 (m, 1H), 7.80–7.78 (m, 1H), 7.75–7.69 (m, 2H), 7.48 (d, *J* = 9.7 Hz, 0.5H), 7.12 (d, *J* = 15.0 Hz, 0.5H), 7.07 (d, *J* = 9.7 Hz, 0.5H), 6.86–6.80 (m, 2H), 4.22–4.17 (m, 2H), 3.79 (q, *J* = 7.2 Hz, 2H), 3.54 (q, *J* = 7.2 Hz, 2H), 3.22 (dd, *J* = 17.4, 6.8 Hz, 1H), 3.08 (dd, *J* = 14.5, 6.8 Hz, 1H), 2.84–2.77 (m, 3H), 2.77–2.64 (m, 2H), 2.31 (t, *J* = 2.5 Hz, 1H), 1.26–1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 186.6, 171.5, 170.0, 153.5, 152.0, 150.8, 149.3, 145.7, 139.9, 131.3, 129.5, 128.5, 128.0, 127.6, 127.5, 127.5, 127.2, 126.5, 126.2, 124.9, 124.5, 123.0, 118.7, 116.8, 111.6, 109.7, 71.5, 53.2, 52.1, 49.7, 49.5, 49.3, 49.1, 48.8, 48.6, 48.4,

46.5, 45.3, 34.2, 29.6, 29.5, 26.1, 12.1; ESIMS *m/z* 720 ($[M + H]^+$); HRMS (ESI) for $C_{38}H_{38}N_7O_6S$, calcd 720.2604, found 720.2601.

19b: According to the general procedure for **19a**–**d** using **17b** (20 mg, 0.037 mmol) and **18** (7.8 mg, 0.037 mmol), **19b** was obtained (10.5 mg, 38% isolated yield, *Z*/*E* = 1/1).

19b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03–9.00 (m, 1H), 8.66 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.03–7.99 (m, 3H), 7.96–7.88 (m, 3.5H), 7.82–7.79 (m, 1H), 7.74–7.71 (m, 2H), 7.52 (d, *J* = 9.7 Hz, 0.5 H), 7.13 (d, *J* = 14.9 Hz, 0.5H), 7.08 (d, *J* = 9.7 Hz, 0.5H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.65 (t, *J* = 6.5 Hz, 0.5H), 4.58 (t, *J* = 6.7 Hz, 0.5H), 4.00–3.95 (m, 1H), 3.81–3.80 (m, 4H), 3.56–3.54 (m, 2H), 3.30–3.25 (m, 0.5H), 3.21–3.11 (m, 1H), 3.06–3.04 (m, 0.5H), 2.64–2.63 (m, 2H), 2.35 (t, *J* = 2.5 Hz, 1H), 1.26–1.23 (m, 3H), 1.16–1.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 190.7, 175.7, 172.4, 171.0, 157.9, 156.0, 155.0, 153.6, 149.6, 148.4, 143.9, 141.3, 141.1, 135.3, 133.5, 132.4, 131.9, 131.5, 131.2. 130.4, 130.2, 128.9, 128.4, 126.9, 122.6, 120.6, 115.4, 113.6, 83.1, 75.1, 57.2, 56.1, 50.5, 49.2, 45.7, 45.6, 42.6, 38.5, 38.1, 33.5, 33.3, 25.9, 16.0; ESIMS *m/z* 748 ($[M + H]^+$); HRMS (ESI) for $C_{40}H_{42}N_7O_6S$, calcd 748.2917, found 748.2919.

19c: According to the general procedure for **19a**–**d** using **17c** (20 mg, 0.036 mmol) and **18** (7.6 mg, 0.036 mmol), **19c** was obtained (11.7 mg, 42% isolated yield, *Z*/*E* = 3/2).

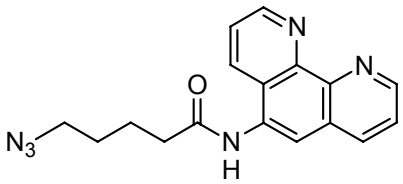
19c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02–8.99 (m, 1H), 8.66 (d, *J* = 8.7 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.01–7.96 (m, 2H), 7.90–7.84 (m, 2H), 7.79–7.76 (m, 2H), 7.74–7.68 (m, 2H), 7.33 (d, *J* = 9.7 Hz, 0.6H), 7.25 (d, *J* = 13.9 Hz, 0.4H), 6.99–6.94 (m, 2H), 6.83–6.80 (m, 2H), 6.45–6.44 (m,

0.4H), 6.42–6.40 (m, 0.6H), 5.25–5.23 (m, 0.4H), 5.23–5.21 (m, 0.6H), 4.26–4.22 (m, 2H), 3.85–3.78 (m, 2H), 3.55–3.51 (m, 3H), 3.49–3.47 (m, 3H), 3.24–3.21 (m, 1H), 3.12–3.03 (m, 2H), 2.63–2.59 (m, 2H), 2.30–2.29 (m, 1H), 1.71 (m, 4H) 1.62–1.56 (m, 6H), 1.26–1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 185.6, 170.4, 170.2, 167.6, 167.4, 166.2, 166.1, 153.3, 151.9, 150.9, 150.9, 148.4, 145.8, 144.6, 140.1, 140.1, 137.2, 137.0, 131.4, 129.6, 128.8, 128.1, 127.4, 127.3, 127.2, 126.6, 126.3, 125.0, 124.5, 123.1, 118.5, 116.8, 111.6, 111.5, 109.8, 79.1, 76.7, 72.1, 48.6, 47.4, 47.2, 46.5, 45.4, 43.7, 43.6, 39.6, 34.9, 34.6,. 34.5, 29.9, 29.7, 26.4, 26.3, 25.3, 24.2, 12.4, 12.3; ESIMS *m/z* 774 ($[M + H]^+$); HRMS (ESI) for $C_{42}H_{44}N_7O_6S$, calcd 774.3074, found 774.3071.

19d: According to the general procedure for **19a**–**d** using **17d** (20 mg, 0.036 mmol) and **18** (7.6 mg, 0.036 mmol), was used, **19d** was obtained (8.6 mg, 31% isolated yield, *Z*/*E* = 3/2).

19d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99–8.96 (m, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.29–8.27 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.48 (d, *J* = 9.7 Hz, 0.6H), 7.12 (d, *J* = 13.8 Hz, 0.4H), 7.00–6.97 (m, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 6.31 (d, *J* = 7.4 Hz, 1H), 4.25–4.23 (m, 2H), 3.82–3.77 (m, 2H), 3.54–3.51 (m, 2H), 3.32–2.95 (m, 2H), 2.63–2.62 (m, 2H), 2.31–2.29 (m, 1H), 2.04 (m, 1H), 1.33 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 188.0, 185.7, 170.9, 168.3, 168.0, 166.4, 166.3, 166.1, 162.6, 153.1, 151.9, 150.9, 147.7, 145.8, 144.6, 140.0, 138.5, 137.7, 137.3, 137.1, 131.9, 131.5, 129.6, 128.8, 128.5, 128.1, 127.6, 127.5, 127.4, 127.3, 126.6, 126.3, 125.0, 124.6, 123.1, 118.8, 117.1, 116.5, 111.6, 109.9, 109.8, 79.3, 79.2, 72.2, 72.1, 60.4, 54.1, 52.6, 52.5, 52.2, 52.0, 46.6, 45.5, 39.0, 36.5, 34.6, 34.3, 34.1, 31.5, 30.1, 30.0, 29.9, 29.7, 28.7, 28.6, 21.1, 14.2, 12.4; ESIMS *m/z* 793 ($[M + H]^+$); HRMS (ESI) for $C_{41}H_{44}N_7O_6S$, calcd 762.3074, found

762.3074.

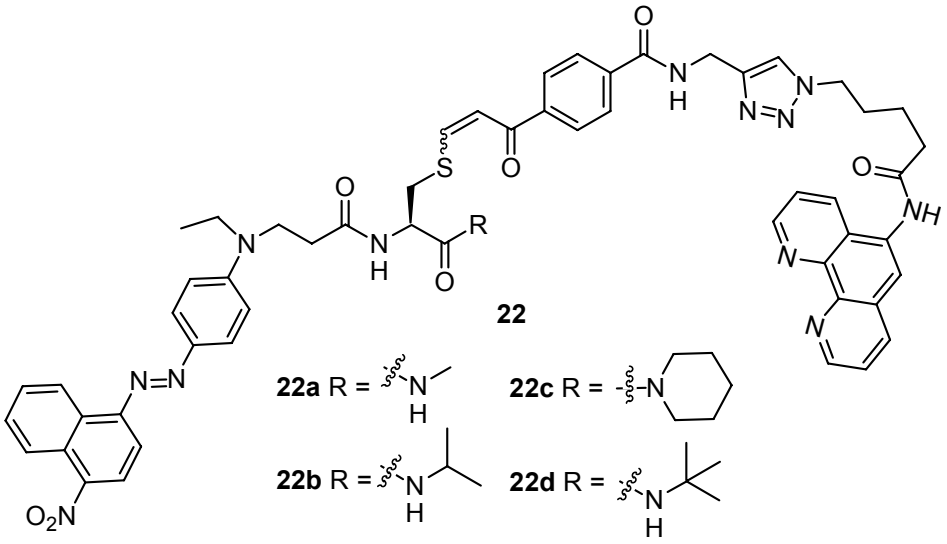


21

21: **20** (100 mg, 0.28 mmol) and sodium azide (268.9 mg, 0.84 mmol) was stirred in 2 mL of DMF at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography on Al_2O_3 (1% MeOH in CH_2Cl_2) to give product **21** (67.2 mg, 75% isolated yield).

21: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.92 (d, *J* = 7.7 Hz, 2H), 8.31 (d, *J* = 8.2 Hz), 7.94 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H), 7.48–7.45 (m, 1H), 7.35–7.32 (m, 1H), 3.26 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 6.9 Hz, 2H), 1.82–1.75 (m, 2H), 1.64–1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 149.6, 149.4, 148.7, 146.0, 144.1, 135.8, 130.9, 130.7, 128.1, 124.6, 123.3, 122.5, 120.5, 106.6, 51.1, 36.1, 28.3, 22.7; EIMS *m/z* 476 (M^+); HRMS (EI) for $C_{17}H_{16}N_6O$, calcd 320.1386, found 320.1386.

General Procedure for 22a–d



22: **19**, **21**, sodium ascorbate, $CuSO_4 \cdot 5H_2O$, was stirred in a solvent mixture of 1 mL of H_2O and 2 mL of DMF at room temperature for 24 h. After evaporation of solvent, the residue was purified by flash column chromatography on Al_2O_3 (5–10% MeOH in CH_2Cl_2) to give product **22**.

22a: According to the general procedure for **22a**–**d** using **19a** (40 mg, 0.056 mmol), **21** (17.9 mg, 0.056 mmol), sodium ascorbate (1.1 mg, 0.0056 mmol), $CuSO_4 \cdot 5H_2O$ (0.14 mg, 0.00056 mmol), **22a** was obtained (32.6 mg, 56% isolated yield).

22a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (m, 2H), 9.07 (m, 2H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.59–8.57 (m, 1H), 8.49–8.43 (m, 2H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.29–8.25 (m, 2H), 8.17–8.12 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 2H), 7.95–7.90 (m, 2H), 7.86 (s, 3H), 7.82 (s, 2H), 7.79–7.74 (m, 1H), 7.72–7.67 (m, 6H), 7.47 (d, *J* = 9.6 Hz, 1H), 7.00 (d, J = 9.7 Hz, 1H), 6.84 (d, *J* = 9.2 Hz, 2H), 4.63 (t, *J* = 5.7 Hz, 3H), 4.48–4.45 (m, 2H), 4.04–4.03 (m, 2H), 3.81–3.78 (m, 3H), 3.55–3.53 (m, 2H), 3.43–3.41 (m, 3H), 3.22–3.19 (m, 2H), 3.17–3.11 (m, 1H), 3.07–3.01 (m, 1H), 2.99 (m, 1H), 2.77–2.76 (m, 2H), 2.66–2.60 (m, 6H),

2.12–2.08 (m, 3H), 1.95–1.91 (m, 3H), 1.83–1.77 (m, 5H), 1.45–1.35 (m, 4H), 1.24 (m, 3H); ESIMS *m/z* 1040 ($[M + H]^+$); HRMS (ESI) for $C_{55}H_{54}N_{13}O_7S$, calcd 1040.3990, found 1040.3991.

22b: According to the general procedure for **22a**–**d** using **19b** (40 mg, 0.054 mmol), **21** (17.3 mg, 0.054 mmol), sodium ascorbate (1.07 mg, 0.0054 mmol), $CuSO_4 \cdot 5H_2O$ (0.14 mg, 0.00054 mmol) was used, **22b** was obtained (33.4 mg, 58% isolated yield).

22b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14–9.12 (m, 2H), 9.06–9.00 (m, 3H), 8.65–8.63 (d, *J* = 8.8 Hz, 1H), 8.50–8.46 (m, 2H), 8.33–8.31 (m, 1H), 8.28–8.27 (m, 2H), 8.13–8.12 (m, 2H), 8.02–8.00 (m, 2H), 7.90–7.77 (m, 7H), 7.74–7.66 (m, 6H), 7.49 (d, *J* = 9.8 Hz, 0.5H), 7.06 (d, *J* = 14.9 Hz, 0.5 H), 7.02 (d, *J* = 9.8 Hz, 0.5H), 6.85 (d, *J* = 9.2 Hz, 2H), 5.69 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 7.1 Hz, 3H), 4.60–4.56 (m, 1H), 4.47 (t, *J* = 6.8 Hz, 3H), 4.03–3.98 (m, 1H), 3.97–3.86 (m, 1H), 3.86–3.80 (m, 4H), 3.65 (q, *J* = 7.0, 3H), 3.57–3.52 (m, 2H), 2.63–2.61 (m, 6H), 2.09 (t, *J* = 7.3Hz, 4H), 1.91–1.79 (m, 4H), 1.26–1.23 (m, 3H), 1.16–1.13 (m, 6H); ESIMS *m/z* 1068 ($[M + H]^+$); HRMS (ESI) for $C_{57}H_{58}N_{13}O_7S$, calcd 1068.4303, found 1068.4300.

22c: According to the general procedure for **22a**–**d** using **19c** (40 mg, 0.052 mmol), **21** (16.6 mg, 0.052 mmol), sodium ascorbate (1.03 mg, 0.0052 mmol), $CuSO_4 \cdot 5H_2O$ (0.13 mg, 0.00052 mmol) was used, **22c** was obtained (30.1 mg, 53% isolated yield).

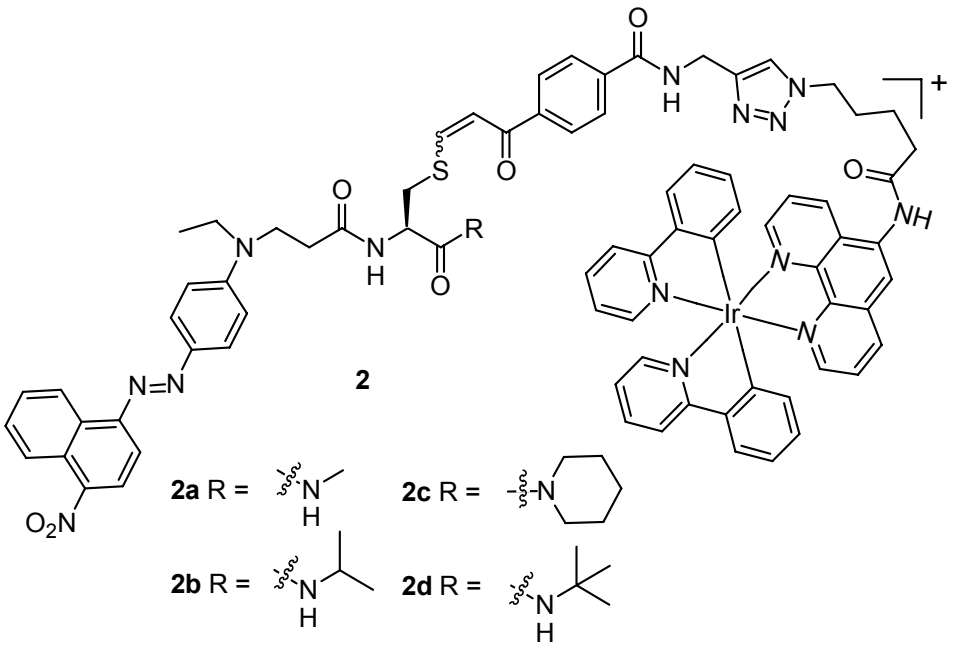
22c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20–9.17 (m, 0.3H), 9.10–9.07 (m, 2H), 9.04–9.00 (m, 1H), 8.92–8.86 (m, 0.5H), 8.68–8.61 (m, 1H), 8.63–8.61 (m, 1H), 8.44–8.27 (m, 2H), 8.19–8.11 (m, 3H), 8.03–7.97 (m, 2H), 7.83–7.78 (m, 4H),

7.75 (m, 2H), 7.73–7.62 (m, 5H), 7.61 (m, 3H), 7.18–7.16 (m, 0.4H), 6.86 (d, *J* = 9.6 Hz, 0.6H), 6.80 (d, *J* = 9.2 Hz, 2H), 5.61 (m, 1H), 4.72–4.65 (m, 3H), 4.38 (m, 3H), 4.06–4.00 (m, 0.5H), 3.88–3.81 (m, 2H), 3.71 (q, *J* = 7.0 Hz, 2H), 3.64 (m, 1H), 3.57–3.46 (m, 2H), 3.04–2.88 (m, 7H), 2.88–2.85 (m, 2H), 2.61–2.58 (m, 2H), 2.57–2.53 (m, 3H), 2.09–1.97 (m, 3H), 1.91–1.79 (m, 3H), 1.71 (m, 15H), 1.66 (m, 6H), 1.55 (m, 6H); ESIMS *m/z* 1094 ($[M + H]^+$); HRMS (ESI) for $C_{59}H_{60}N_{13}O_7S$, calcd 1094.4459, found 1094.4461.

22d: According to the general procedure for **22a**–**d** using **19d** (40 mg, 0.053 mmol), **21** (17.0 mg, 0.053 mmol), sodium ascorbate (1.05 mg, 0.0053 mmol), $CuSO_4 \cdot 5H_2O$ (0.13 mg, 0.00053 mmol) was used, **22d** was obtained (33.8 mg, 59% isolated yield).

22d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15–9.03 (m, 2H), 9.02–8.98 (m, 1H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.41–8.38 (m, 1H), 8.34–8.30 (m, 1H), 8.23–8.16 (m, 1H), 8.13–8.11 (m, 1H), 8.00–7.95 (m, 2H), 7.90–7.84 (m, 3H), 7.81–7.72 (m, 4H), 7.71–7.68 (m, 2H), 7.62–7.58 (m, 2H), 7.49–7.44 (m, 1H), 7.00–6.93 (m, 2H), 6.83–6.79 (m, 2H), 4.62 (m, 2H), 4.55–4.50 (m, 1H), 4.46–4.42 (m, 2H), 4.35–4.31 (m, 1H), 3.80–3.75 (m, 2H), 3.66–3.65 (m, 0.6H), 3.55–3.51 (m, 2H), 3.43–3.40 (m, 2H), 3.20–3.19 (m, 1H), 3.06–3.03 (m, 1H), 2.63–2.54 (m, 3H), 2.09–2.06 (m, 2H), 1.84–1.80 (m, 2H), 1.68–1.65 (m, 3H), 1.32 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ESIMS *m/z* 1082 ($[M + H]^+$); HRMS (ESI) for $C_{58}H_{60}N_{13}O_7S$, calcd 1082.4459, found 1082.4455.

General Procedure for 2a–d



2a–**d**: A mixture of $[Ir_2(ppy)_4Cl_2]$ (7.5 mg, 0.007 mmol) and **22** in 30 mL MeOH/CH_2Cl_2 = 1:1 (v/v) was refluxed under an inert atmosphere of N_2 in the dark for 4 h. The solution was then evaporated to dryness and the solid was dissolved in CH_2Cl_2 and purified by column chromatography on Al_2O_3 (8% MeOH in CH_2Cl_2) to give product **2**.

2a: According to the general procedure for **2a**–**d** using **22a** (14.5 mg, 0.014 mmol), **2a** was obtained (9.6 mg, 89% isolated yield).

2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, J = 8.7 Hz, 0.3H), 9.05–9.00 (m, 0.5H), 8.70–8.64 (m, 1H), 8.58–8.53 (m, 0.3H), 8.45–8.28 (m, 1H), 8.22 – 8.19 (m, 1H), 8.12–8.11 (m, 1H), 7.98–7.96 (m, 1H), 7.93–7.89 (m, 3H), 7.85–7.82 (m, 2H) 7.73–7.70 (m, 6H), 7.66–7.64 (m, 2H), 7.33–7.30 (m, 1H), 7.09–7.07 (m, 2H), 7.00–6.95 (m, 2H), 6.86–6.79 (m, 4H), 6.40–6.37 (m, 2H), 4.73–4.62 (m, 1H), 4.73–4.62 (m, 1H), 4.11–4.01 (m, 0.2H), 3.85–3.75 (m, 1H), 3.73–3.71 (m, 0.6H), 3.66–3.64 (m, 1H), 3.54–3.49 (m, 2H), 3.35 (t, *J* = 6.8 Hz, 1H), 3.27–2.99 (m,

1H), 2.94–2.90 (m, 1H), 2.76–2.72 (m, 2H), 2.62 (s, 1H), 2.24–2.17 (m, 0.4H), 2.08–2.04 (m, 1H), 1.93–1.86 (m, 1H), 1.81–1.76 (m, 2H), 1.24 (m, 3H); ESIMS *m/z* 1539 ($[M + H]^+$).

2b: According to the general procedure for **2a**–**d** using **22b** (14.9 mg, 0.014 mmol), **2b** was obtained (10.7 mg, 98% isolated yield).

2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60–9.51 (m, 1H), 9.00 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.7 Hz, 1H), 8.55–8.52 (m, 1H), 8.40–8.35 (m, 1H), 8.28–8.26 (m, 1H), 8.19–8.18 (m, 1H), 8.12–8.11 (m, 1H), 7.96–7.89 (m, 6H), 7.87–7.83 (m, 2H), 7.75–7.69 (m, 7H), 7.67–7.63 (m, 2H), 7.32–7.30 (m, 1H), 7.09–7.05 (m, 2H), 6.97–6.94 (m, 2H), 6.86–6.77 (m, 4H), 6.40–6.37 (m, 2H), 5.68–5.65 (m, 0.3H), 4.74–4.69 (m, 2H), 4.48–4.44 (m, 2H), 4.06–4.01 (m, 2H), 4.00–3.94 (m, 0.4H), 3.77–3.76 (m, 1H), 3.50–3.48 (m, 1H), 3.21–3.14 (m, 1H), 3.09–3.01 (m, 1H), 2.95–2.88 (m, 3H), 2.66–2.63 (m, 1H), 2.12–2.05 (m, 2H), 1.88–1.84 (m, 2H), 1.68–1.64 (m, 2H), 1.44–1.39 (m, 2H), 1.26–1.22 (m, 3H), 1.20–1.13 (m, 3H), 1.12–1.09 (m, 3H); ESIMS *m/z* 1567 ($[M + H]^+$).

2c: According to the general procedure for **2a**–**d** using **22c** (15.3 mg, 0.014 mmol) was used, **2c** was obtained (10.0 mg, 93% isolated yield).

2c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56–9.54 (m, 1H), 9.02 (d, *J* = 8.2 Hz, 1H), 8.67–8.57 (m, 2H), 8.41–8.30 (m, 2H), 8.19–8.12 (m, 2H), 8.02–7.97 (m, 5H), 7.92–7.85 (m, 6H), 7.85–7.75 (m, 3H), 7.77–7.69 (m, 6H), 7.65–7.63 (m, 1H), 7.54–7.52 (m, 1H), 7.32–7.26 (m, 2H), 7.09–7.07 (m, 2H), 7.00–6.96 (m, 3H), 6.86–6.77 (m, 6H), 6.41–6.36 (m, 2H), 5.22–5.17 (m, 1H), 4.76–4.75 (m, 2H), 4.49–4.46 (m, 2H), 4.25–4.22 (m, 1H), 4.11 (m, 1H), 4.06–4.03 (m, 2H), 3.91–3.88 (m, 0.6H), 3.86–3.79 (m, 3H), 3.75–3.70 (m, 2H), 3.65 (m, 5H),

3.59–3.48 (m, 8H), 3.08–3.05 (m, 2H), 2.88–2.83 (m, 2H), 2.62–2.59 (m, 3H), 2.24–2.20 (m, 2H), 2.17–2.09 (m, 2H), 1.89–1.85 (m, 3H), 1.42–1.32 (m, 6H); ESIMS *m/z* 1539 ($[M + H]^+$).

2d: According to the general procedure for **2a**–**d** using **22d** (15.1 mg, 0.014 mmol) was used, **2d** was obtained (10.6 mg, 96% isolated yield).

2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56–9.54 (m, 1H), 9.02–9.00 (m, 1H), 8.65–8.63 (m, 1H), 8.56–8.53 (m, 1H), 8.45–8.37 (m, 1H), 8.33–8.28 (m, 1H), 8.24–8.19 (m, 2H), 8.13–8.12 (m, 1H), 7.98–7.91 (m, 7H), 7.87–7.82 (m, 2H), 7.78–7.75 (m, 2H), 7.73–7.69 (m, 6H), 7.68–7.65 (m, 1H), 7.64–7.61 (m, 1H), 7.45–7.39 (m, 1H), 7.31–7.30 (m, 2H), 7.26 (m, 1H), 7.09–7.06 (m, 2H), 6.98–6.96 (m, 2H), 6.93–6.90 (m, 1H), 6.85–6.75 (m, 4H), 6.46–6.36 (m, 2H), 4.80–4.75 (m, 1H), 4.71–4.65 (m, 1H), 4.59–4.53 (m, 1H), 4.92–4.46 (m, 2H), 3.80–3.78 (m, 2H), 3.54–3.49 (m, 2H), 3.24–3.09 (m, 1H), 3.06–2.97 (m, 1H), 2.93–2.90 (m, 2H), 2.65–2.61 (m, 2H), 2.65–2.61 (m, 2H), 2.12–2.09 (m, 2H), 1.93–1.86 (m, 2H), 1.31 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ESIMS *m/z* 1581 ($[M + H]^+$).

Time Course of the Reaction between 1 and Hcy/Cys

Stock solutions of Hcy and Cys were freshly prepared in double distilled water (100 mM). Probe **1** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mM). 10 μL of the probe stock and 5 μL of Hcy or Cys stock were added in a solvent mixture of 5 μL H_2O, 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. The resulting solution was shaken well before the emission spectra were recorded. The excitation wavelength was at 590 nm and the excitation and emission slit widths were 3.5 nm. The emission intensity of the reaction mixture was monitored for 30 min. (Fig. S1)

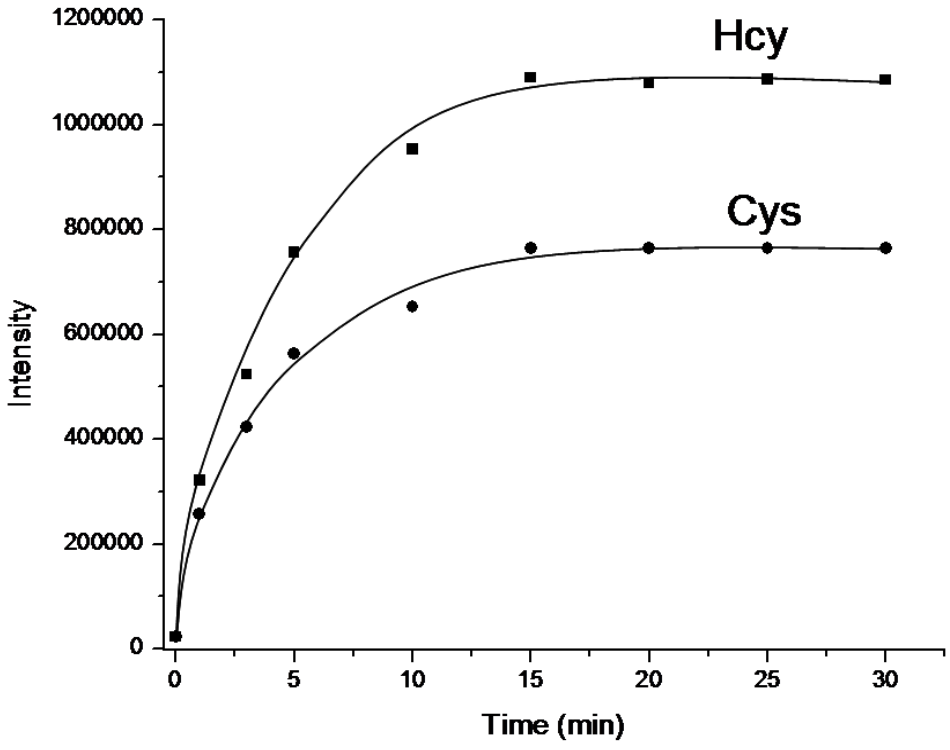


Fig. S1 Time course of the reaction between **1** and Hcy and Cys in a molar ratio of 1:50

Titration Curve for the Detection of Hcy by 1

Two stock solutions of Hcy were freshly prepared in double distilled water (1.4 mg in 1 mL H_2O, 10 mM) and (14 mg in 1 mL H_2O, 100 mM). Probe **1** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock, 80 μL of pH 8.1 PBS buffer, appropriate aliquots of Hcy stock were mixed with different volumes of H_2O, (for details, see Table S1). The resulting solution was diluted with 300 μL of CH_3CN and was shaken well. After 15 min, the emission spectra were recorded. The excitation wavelength was 590 nm and the excitation and emission slit widths were 3.5 nm. Different concentrations of Hcy (0–2.5 mM) were prepared in order to obtain an overlaid emission spectrum. A titration curve of the emission intensity against different concentrations of Hcy was obtained, with correlation coefficient R = 0.99 (Fig. S2).

Table S1 Various conditions for setting a titration curve of Hcy and **1**

[Hcy]	Hcy stock (10 mM)	H_2O
0 mM	0 μL	10 μL
0.025 mM	1 μL	9 μL
0.075 mM	3 μL	7 μL
0.125 mM	5 μL	5 μL
0.175 mM	7 μL	3 μL
0.25 mM	10 μL	0 μL
[Hcy]	Hcy stock (100 mM)	H_2O
0.75 mM	3 μL	7 μL
1.25 mM	5 μL	5 μL
1.75 mM	7 μL	3 μL
2.25 mM	9 μL	1 μL
2.5 mM	10 μL	0 μL

The above procedures were followed to obtain a titration curve of Hcy and **2d**

(Fig. S3).

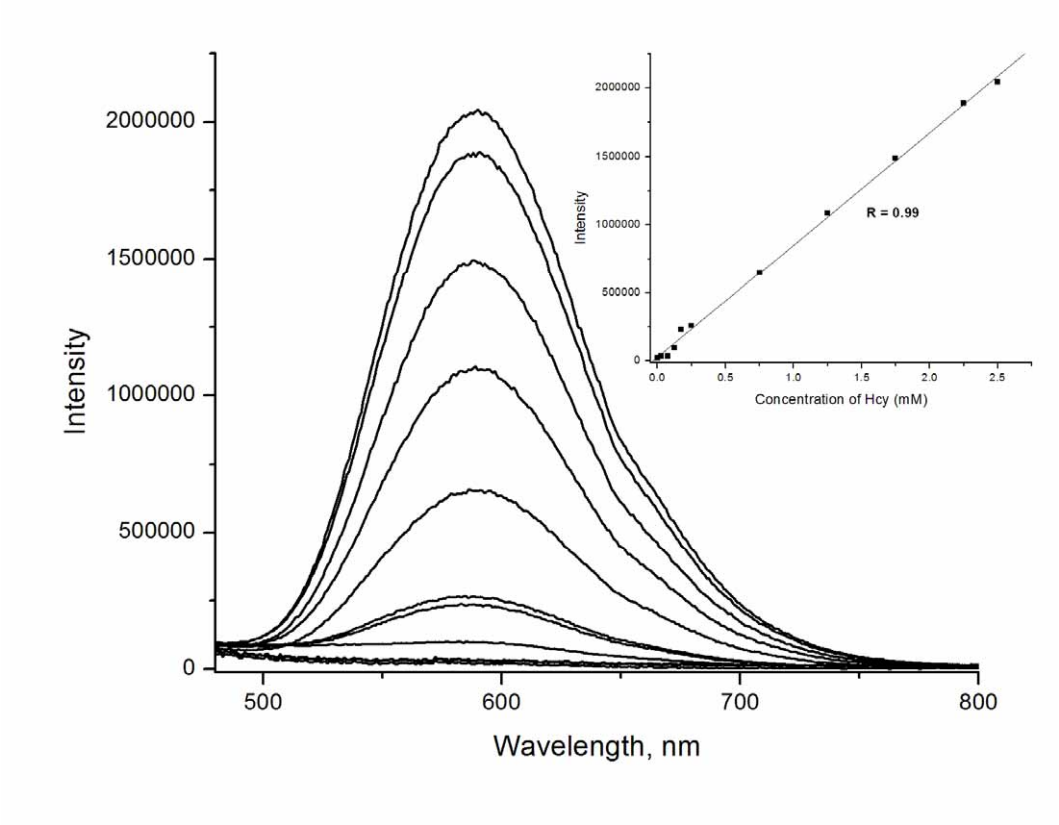


Fig. S2 Emission spectral traces of **1** (25 μM) in CH_3CN/PBS buffer with [Hcy]/[**1**] ratios from 0 to 100 at room temperature. Each spectrum was acquired 15 mins after Hcy addition. (Detection limit: 0.13 mM)

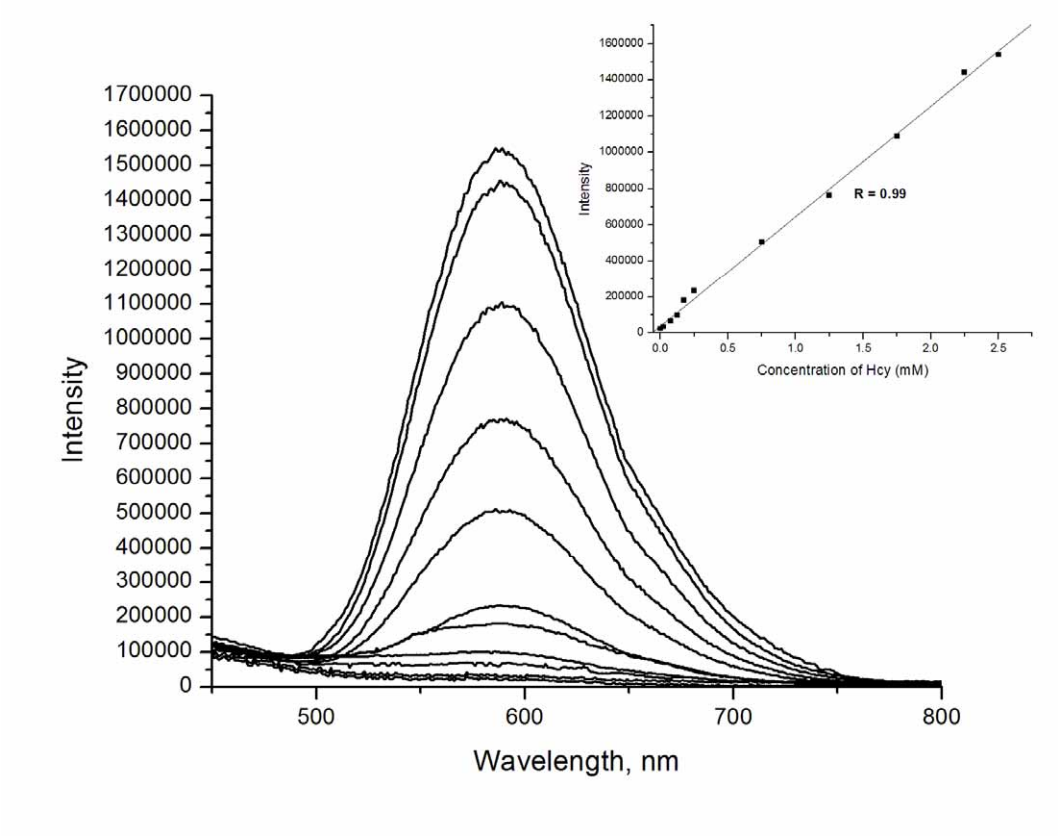


Fig. S3 Emission spectral traces of **2d** (25 μM) in CH_3CN/PBS buffer with [Hcy]/[**2d**] ratios from 0 to 100 at room temperature. Each spectrum was acquired 15 mins after Hcy addition. (Detection limit: 0.12 mM)

Titration Curve for the Detection of Cys by 1

Two stock solutions of Cys were freshly prepared in double distilled water (1.2 mg in 1 mL H_2O, 10 mM) and (12 mg in 1 mL H_2O, 100 mM). Probe **1** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock, 80 μL of pH 8.1 PBS buffer, appropriate aliquots of Cys stock were mixed with different volumes of H_2O, (for details, see Table S2). The resulting solution was diluted with 300 μL of CH_3CN and was shaken well. After 15 min, the emission spectra were recorded. The excitation wavelength was 590 nm and the excitation and emission slit widths were 3.5 nm. Different concentrations of Cys (0–2.5 mM) were prepared in order to obtain an overlaid emission spectrum. A titration curve of the emission intensity against different concentrations of Cys was obtained, with correlation coefficient R = 0.99 (Fig. S4).

Table S2 Various conditions for setting a titration curve of Cys and **1**

[Cys]	Cys stock (10 mM)	H_2O
0 mM	0 μL	10 μL
0.025 mM	1 μL	9 μL
0.075 mM	3 μL	7 μL
0.125 mM	5 μL	5 μL
0.175 mM	7 μL	3 μL
0.25 mM	10 μL	0 μL
[Cys]	Cys stock (100 mM)	H_2O
0.75 mM	3 μL	7 μL
1.25 mM	5 μL	5 μL
1.75 mM	7 μL	3 μL
2.25 mM	9 μL	1 μL
2.5 mM	10 μL	0 μL

The above procedures were followed to obtain a titration curve of Cys and **2d** (Fig. S5).

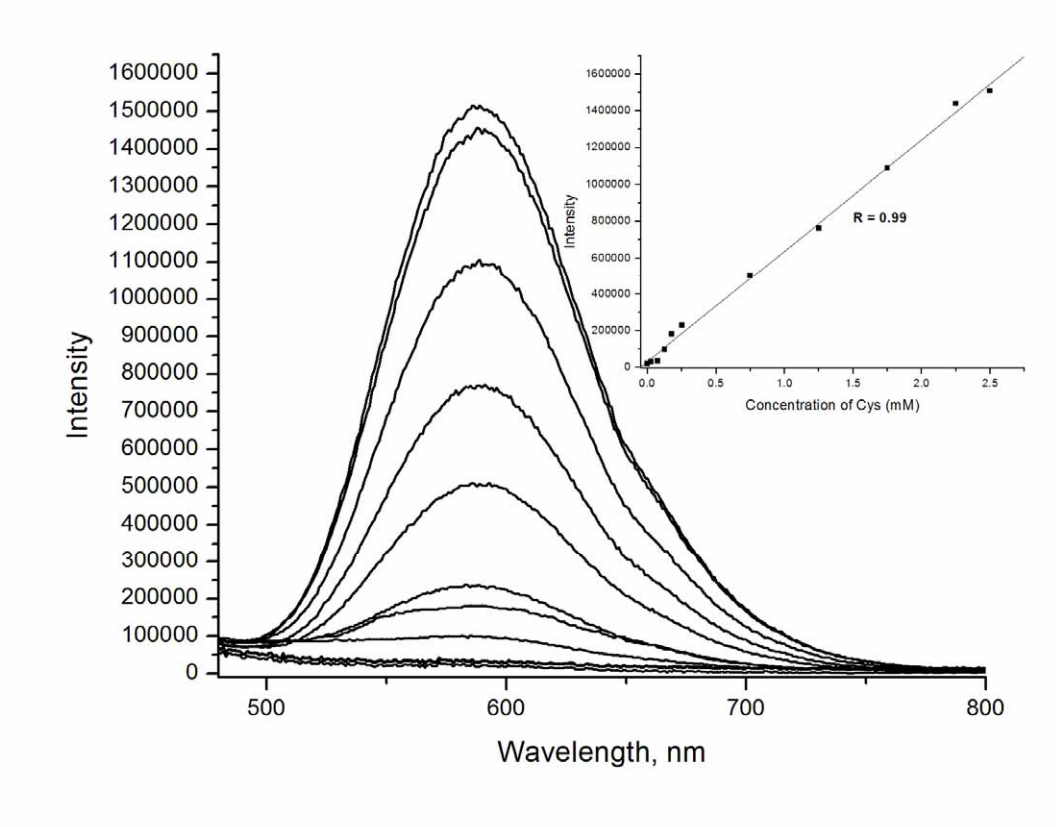


Fig. S4 Emission spectral traces of **1** (25 μM) in CH_3CN/PBS buffer with [Cys]/[**1**] ratios from 0 to 100 at room temperature. Each spectrum was acquired 15 mins after Cys addition. (Detection limit: 0.15 mM)

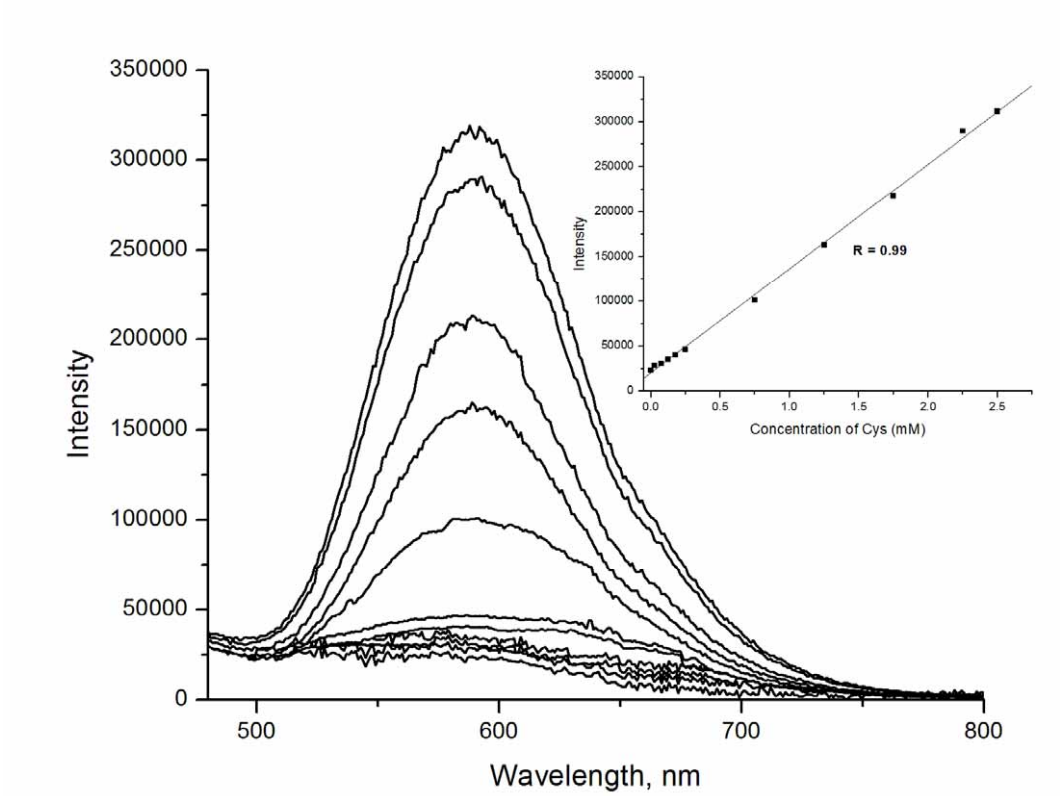


Figure S5 Emission spectral traces of **2d** (25 μM) in CH_3CN/PBS buffer with [Cys]/[**2d**] ratios from 0 to 100 at room temperature. Each spectrum was acquired 15 mins after Cys addition. (Detection limit: 0.15 mM)

Mass Spectrometry Analysis of the Mixtures of Probes 1, 2a–d and Hcy/Cys

A stock solution of Hcy was freshly prepared in double distilled water (1.4 mg in 1 mL H_2O, 10 mM). Probe **1** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock and 10 μL of Hcy stock were added to a solvent mixture 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. After 15 min, the reaction mixture was analyzed by ESI-MS (Fig. S6)

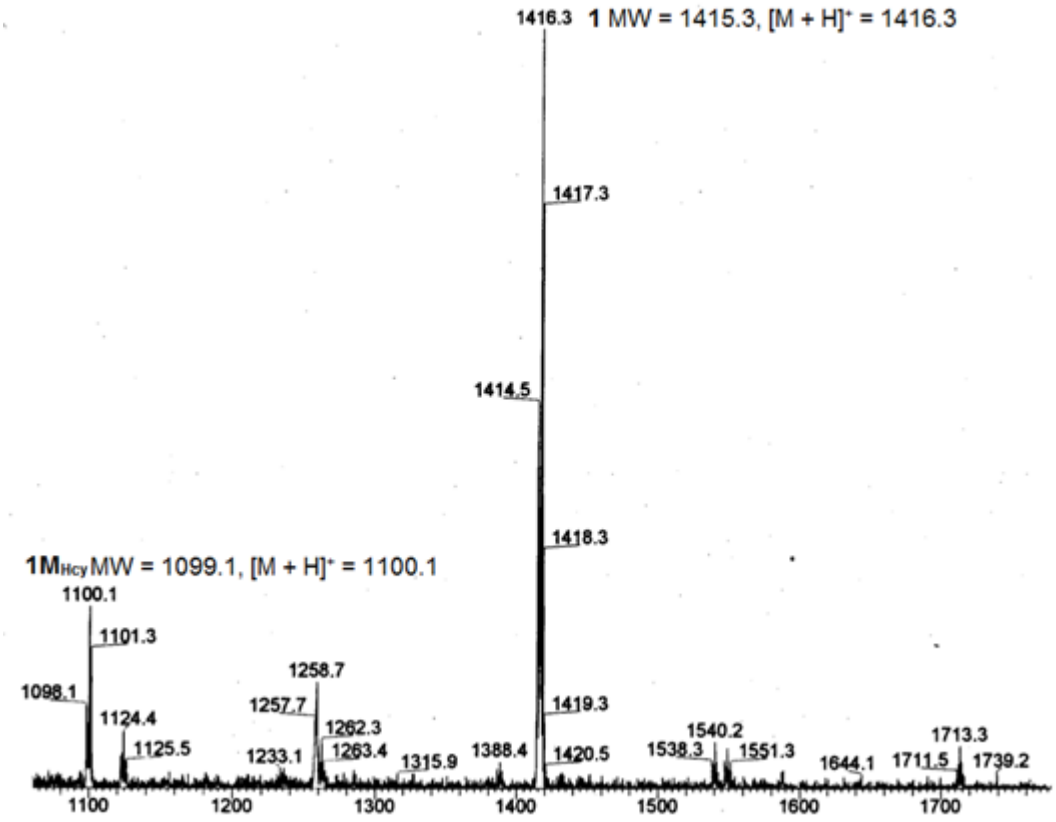


Fig S6 ESI-MS of the reaction mixture upon addition of Hcy to **1** in CH_3CN/PBS buffer

Mass spectrometry analyses of the reaction mixture of **2a**–**d** and Hcy followed the same procedures (Fig. S7–S10).

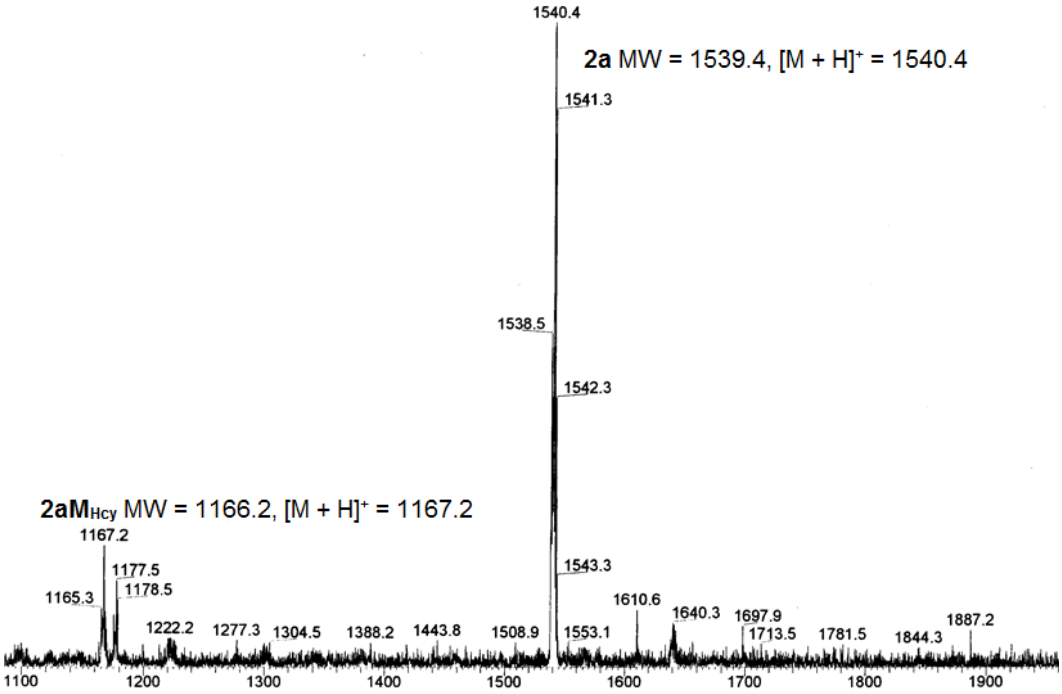


Fig. S7 ESI-MS of a reaction mixture containing Hcy and **2a** in CH_3CN/PBS buffer

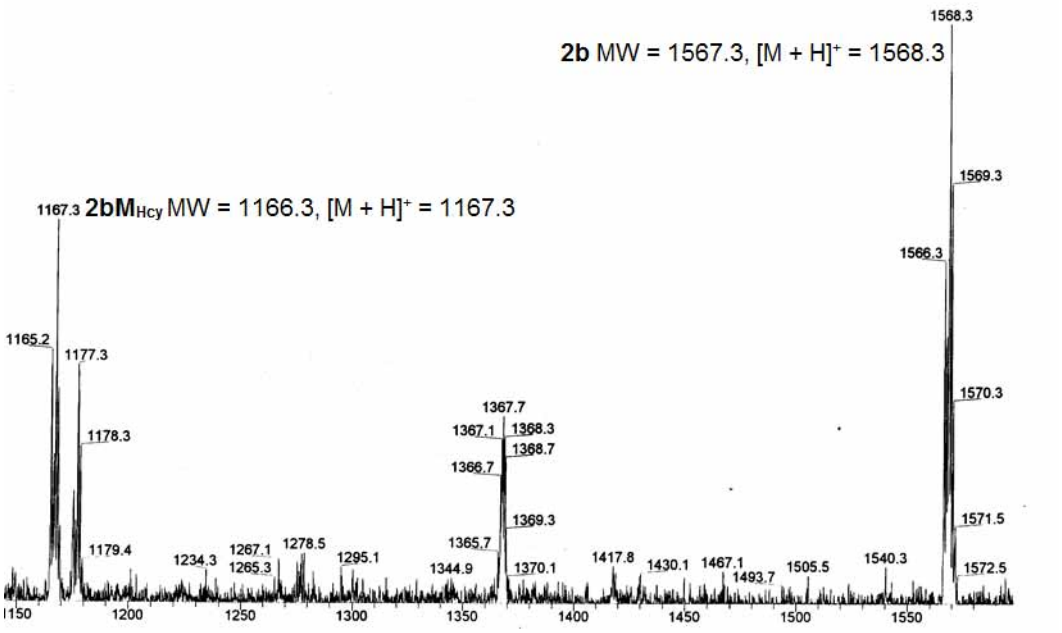


Fig. S8 ESI-MS of a reaction mixture containing Hcy and **2b** in CH_3CN/PBS buffer

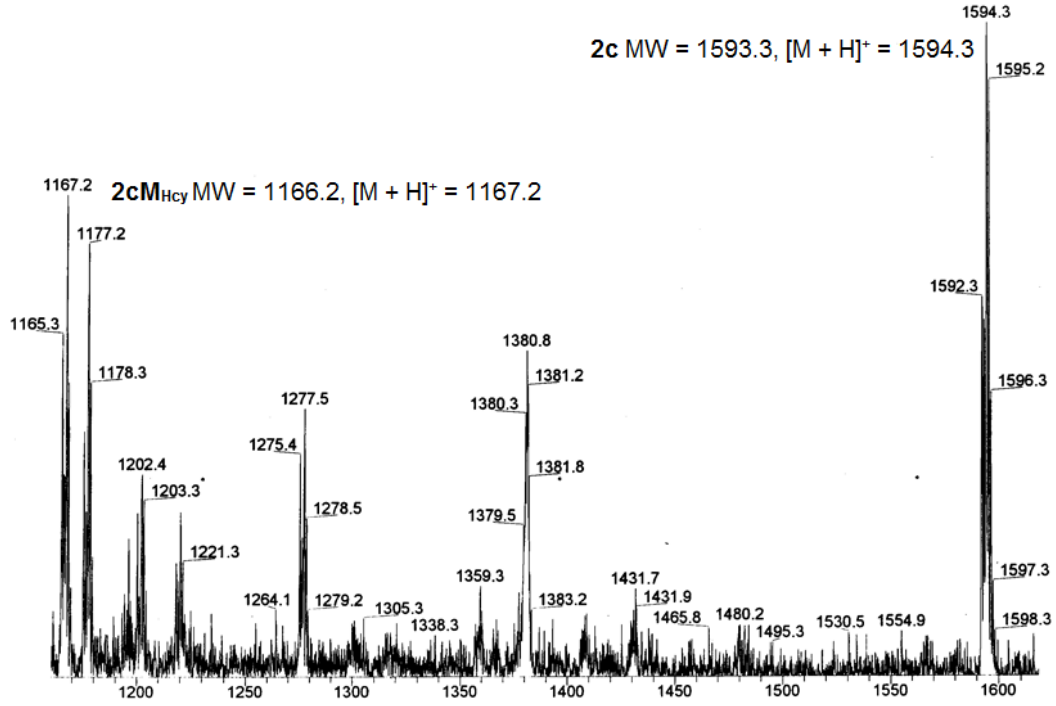


Fig. S9 ESI-MS of a reaction mixture containing Hcy and **2c** in CH_3CN/PBS buffer

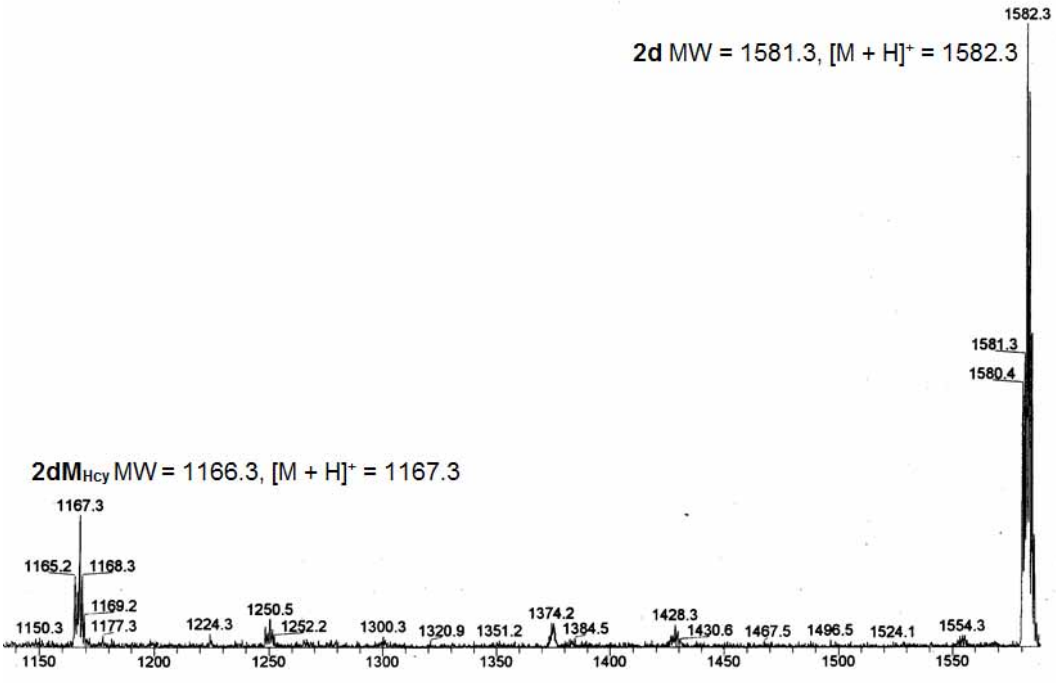


Fig. S10 ESI-MS of a reaction mixture containing Hcy and **2d** in CH_3CN/PBS buffer

A stock solution of Cys was freshly prepared in double distilled water (1.2 mg in 1 mL H_2O, 10 mM). Probe **1** was respectively dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock and 10 μL of Cys stock were added to a solvent mixture 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. After 15 min, the reaction mixture was analyzed by ESI-MS (Fig. S11).

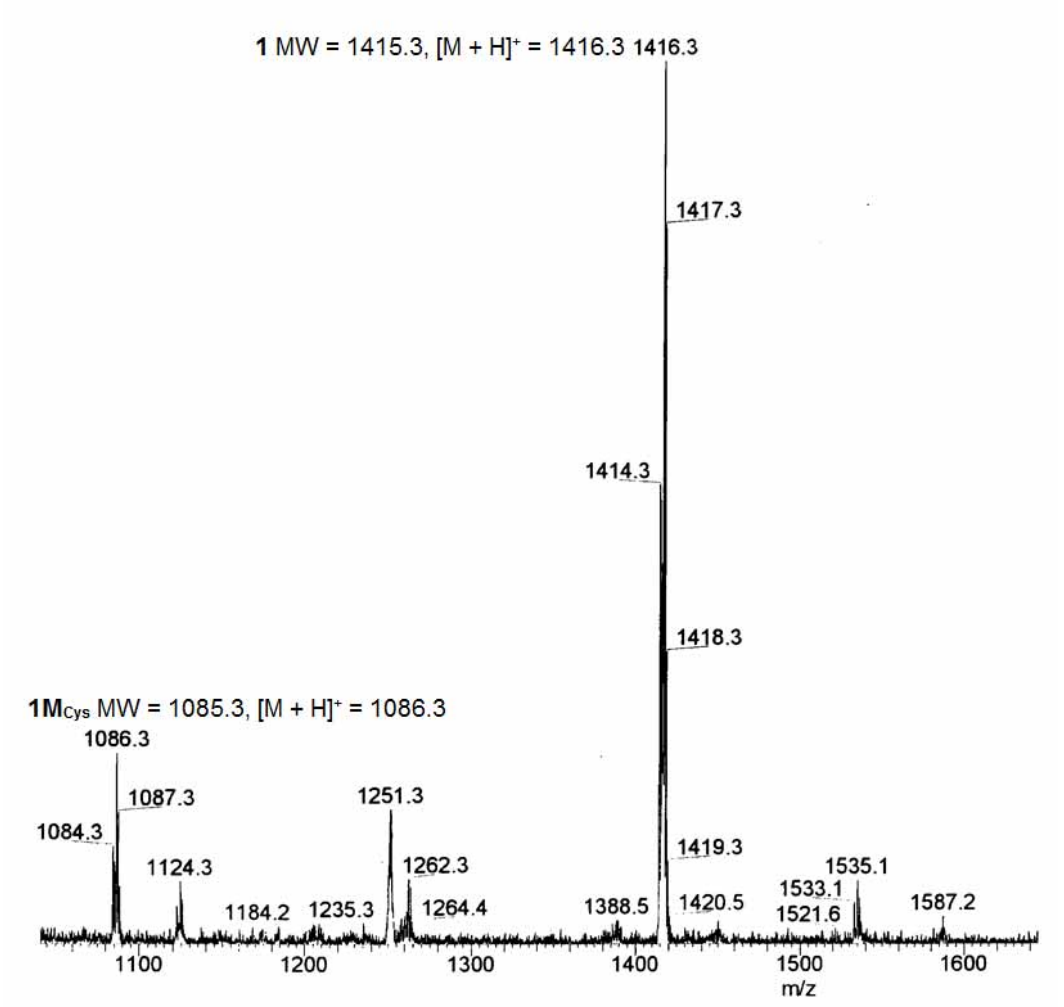


Fig. S11 ESI-MS of the reaction mixture upon addition of Cys to **1** in CH_3CN/PBS buffer

Mass spectrometry analyses of the reaction mixture of **2a**–**d** and Cys followed the same procedures (Fig. S12–S15).

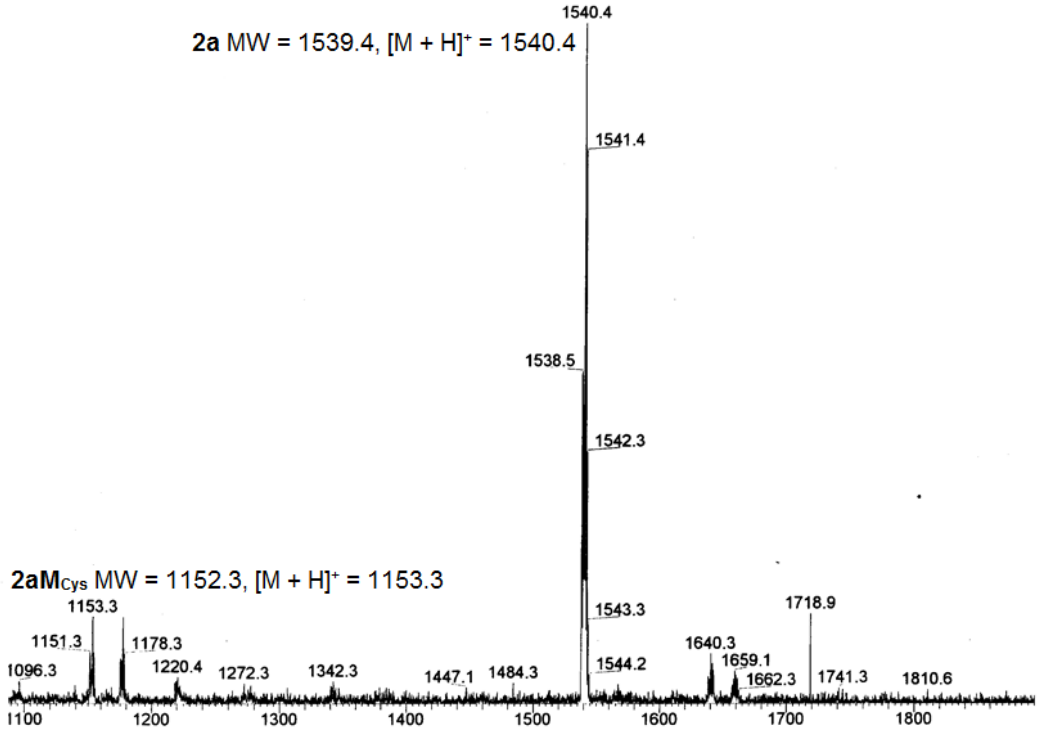


Fig. S12 ESI-MS of a reaction mixture containing Cys and **2a** in CH_3CN/PBS buffer

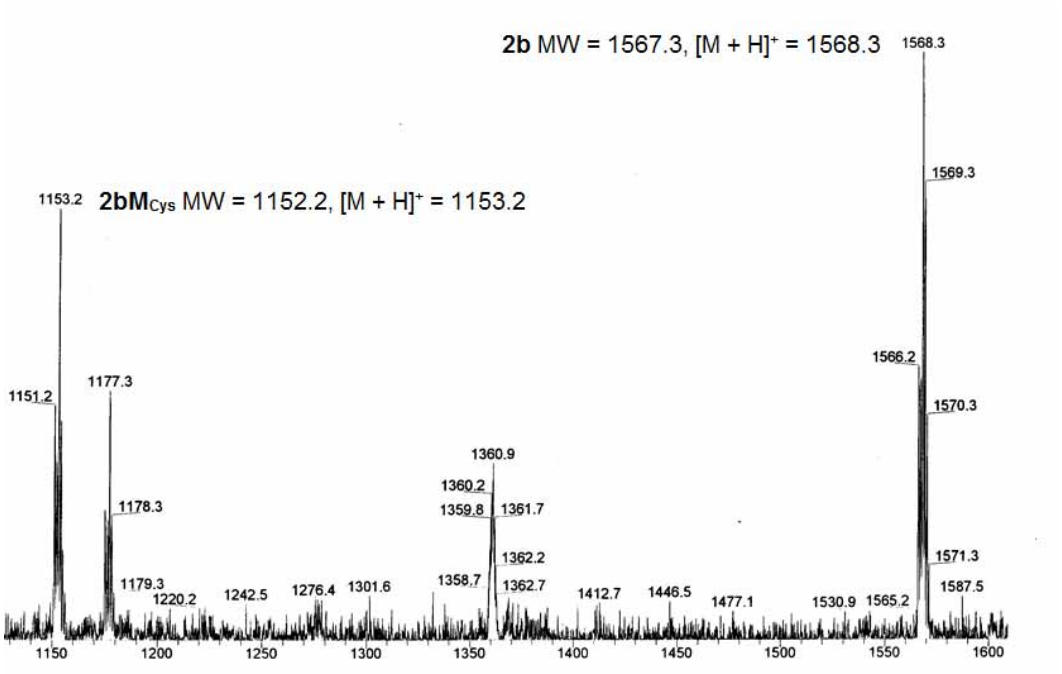


Fig. S13 ESI-MS of a reaction mixture containing Cys and **2b** in CH_3CN/PBS buffer

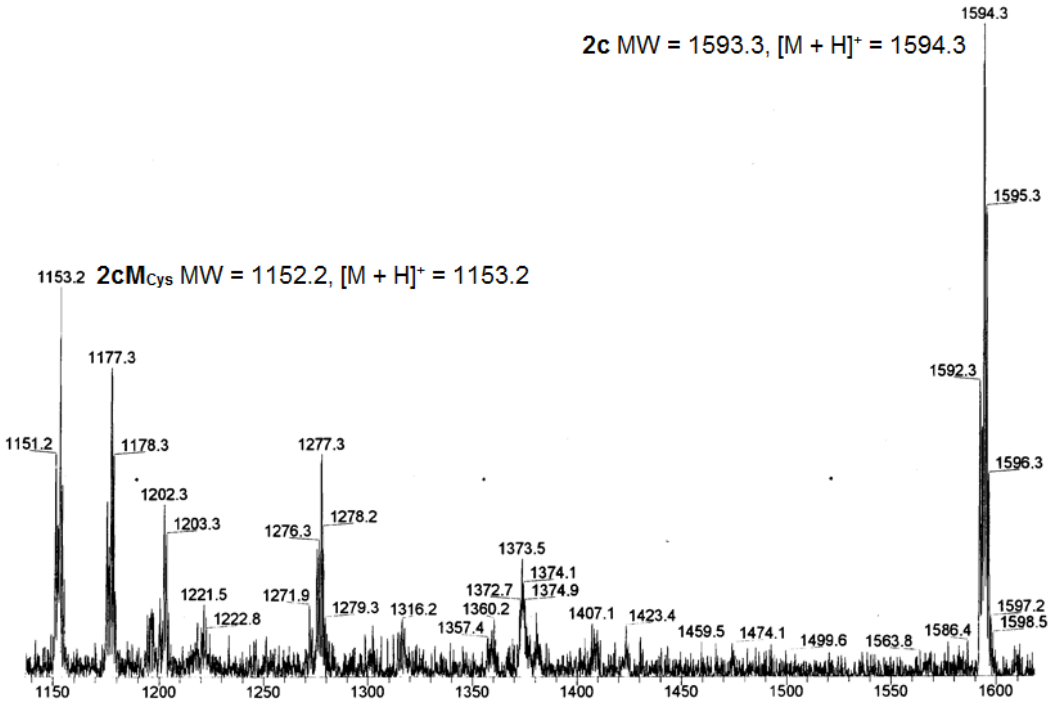


Fig. S14 ESI-MS of a reaction mixture containing Cys and **2c** in CH_3CN/PBS buffer

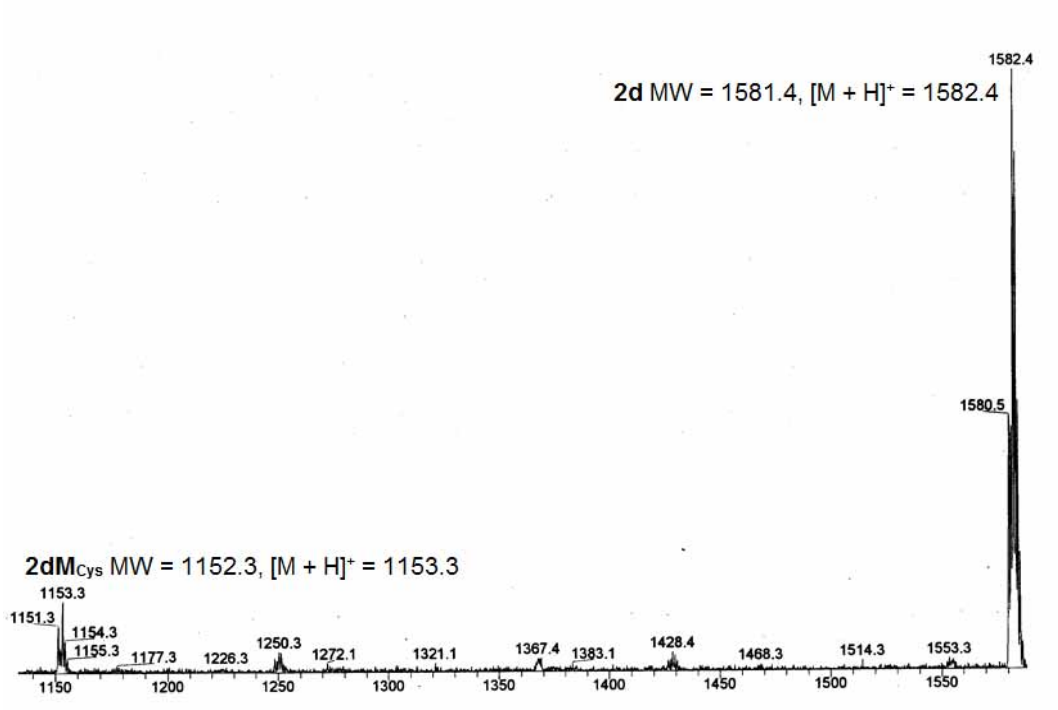


Fig. S15 ESI-MS of a reaction mixture containing Cys and **2d** in CH_3CN/PBS buffer

Mass Spectrometry Analysis of the Mixtures of Probe 2d and BSA

A stock solution of Bovine Serum Albumin (BSA) was freshly prepared in double distilled water (66 mg in 1 mL H_2O, 1 mM). Probe **2d** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock and 10 μL of BSA stock were added to a solvent mixture 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. As a control, probe **2d** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock was added to a solvent mixture of 10 μL of H_2O, 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. After 15 min, the reaction mixtures were analyzed by LC-MS (Fig. S16). BSA is a protein (MW = 66 kDa) which contains a single and surface-exposed cysteine residue. This experiment demonstrated that the probe is not able to react with steric bulk cysteine-containing biomacromolecules.

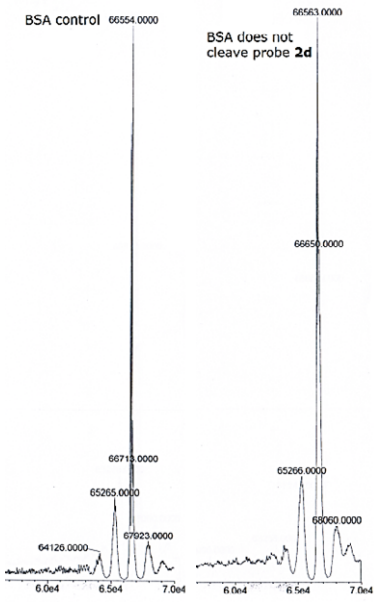


Fig. S16 LC-MS of a reaction mixture containing (a) BSA only (b) BSA and probe **2d**

Emission Intensity Enhancement in the Detection of Different Analytes by Probe 1

The amino acids (Cys, Hcy, Ala, Arg, Asn, Asp, Glu, Gln, Gly, His, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, Val) and GSH stock solutions were freshly prepared in double distilled water (100 mM). Probe **1** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mM). 10 μL of the probe stock and 5 μL of analyte stock were added to a solvent mixture of 5 μL H_2O, 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. The resulting solution was shaken well. After 15 min, the emission spectra were recorded. For all the measurement, the excitation wavelength was 590 nm and the excitation and emission slit widths were 3.5 nm. The emission intensity obtained after reacting **1** with each analyte in the aforementioned conditions was measured and compared (Fig. S17).

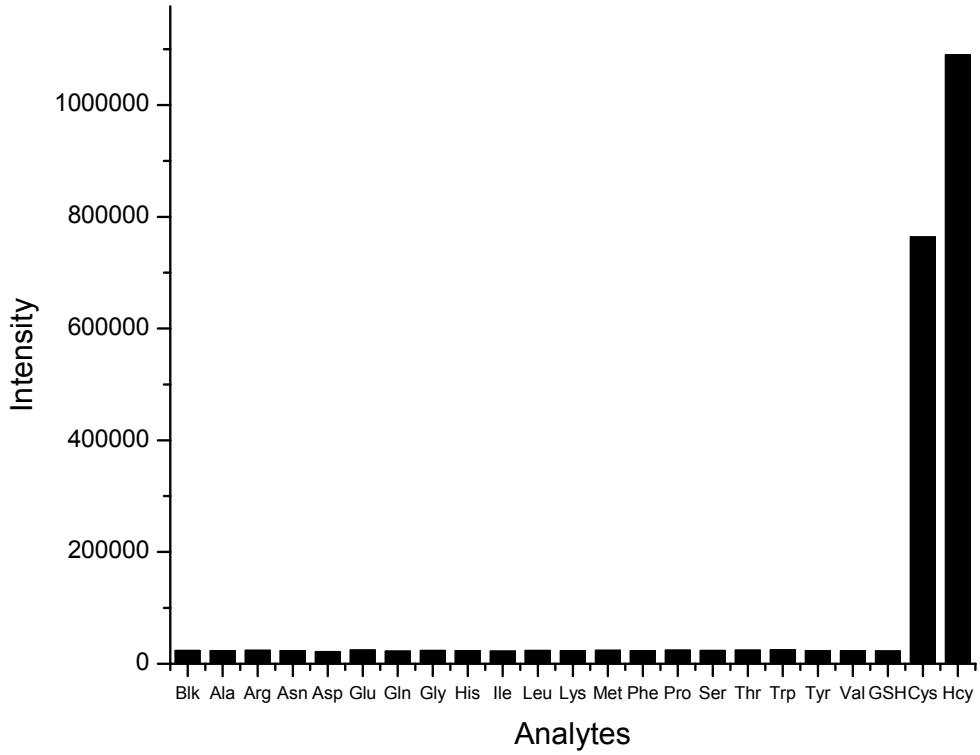


Fig. S17 Enhancement of emission intensity in the detection of different analytes by probe **1**

Quantum Yield Determination

Williams *et al.*[1] stated the comparative method for recording Φ_F. The relative quantum yield of sample was related to that of a solution of a standard by the equation

$$\Phi_{F(sample)} = \left(\frac{A_{standard}}{A_{sample}}\right)\left(\frac{F_{sample}}{F_{standard}}\right)\left(\frac{n_{sample}}{n_{standard}}\right)^2 \Phi_{F(standard)} \qquad (1)$$

Φ_F is the fluorescence quantum yield, A is the absorbance, F is the area under the corrected emission curve and n is the refractive index. The concentration of standard was adjusted so that the absorbance of the sample at the wavelength of excitation was equal to that of the standard, which made the absorbance ratio to be

equal to 1. Acetonitrile was used for both the standard and the sample solution; the refractive index ratio was therefore also equal to 1.

So equation (1) is reduced to

$$\Phi_{F(sample)} = \left(\frac{F_{sample}}{F_{standard}} \right) \Phi_{F(standard)} \qquad (2)$$

Here, $[Ru(bipy)_3]Cl_2$ was used as the standard; the quantum yield of $[Ru(bipy)_3]Cl_2$ in acetonitrile[2] is 0.062. The quantum yield of **1** was calculated to be 0.0028.

Literature reference for quantum yield determination:

1. A. T. R. Williams, S. A. Winfield, J. N. Miller, *Analyst* **1983**, *108*, 1067–1071.

2. S. D. Bergman, D. Gut, M. Kol, C. Sabatini, A. Barbieri, F. Barigelletti, *Inorg. Chem.* **2005**, *44*, 7943–7950.

Emission Intensity Enhancement in the Detection of Hcy/Cys by Probes 1, 2a–d

A stock solution of Hcy was freshly prepared in double distilled water (14 mg in 10 mL H_2O, 100 mM). Cys stock was freshly prepared in the same way (12 mg in 10 mL H_2O, 100mM). Probe **1**, **2a**–**d** was respectively dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mg in 1 mL CH_3CN, 1 mM). 10 μL of the probe stock and 7 μL of Hcy or Cys stock were added to a solvent mixture of 3 μL of H_2O, 80 μL of pH 8.1 PBS buffer and 300 μL of CH_3CN. After 15 min, the emission spectra were recorded. The excitation

wavelength was 590 nm and the excitation and emission slit widths were 3.5 nm. The emission intensity obtained after reacting **1**, **2a**–**d** with either Hcy or Cys in the aforementioned conditions was measured and compared (Fig. S18).

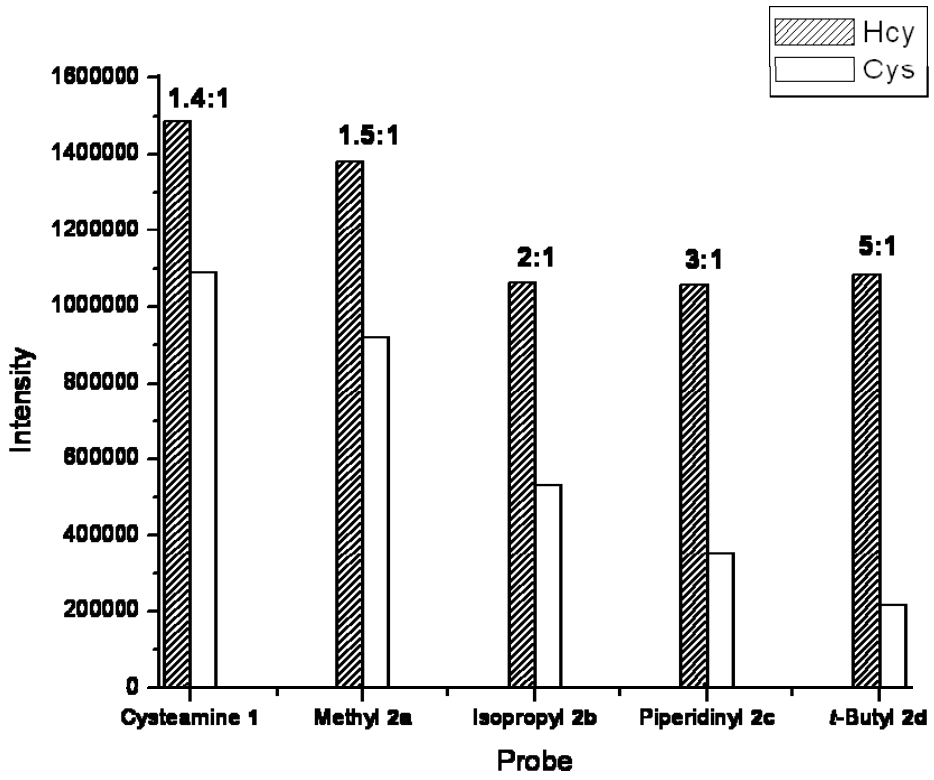


Fig. S18 Emission intensity enhancement in the detection of Hcy/Cys by probes **1**, **2a**–**d**

Detection of Hcy and Cys in Human Blood Plasma by Probe 2d

Probe **2d** was dissolved in CH_3CN at room temperature to afford the probe stock solution (1 mM). Commercial lyophilized human blood plasma is reconstituted with distilled water (5.0 mL). The thiols assay of human blood plasma requires prior reduction of disulfides to free thiols. This can be accomplished by using *tris*[2-carboxyethyl]phosphine hydroxide (TCEP) (1.5 mM). This is followed by deproteinization upon addition of MeOH which contains triphenylphosphine (PPh_3) (1.5 mM) at room temperature for 30 min. After centrifugation (5.0 min, 3000*g*) the supernatant is used for the analysis.

Literature reference for preparation of human blood plasma sample:

1. W. Wang, J. O. Escobedo, C. M. Lawrence, R. M. Strongin *J. Am. Chem. Soc.* **2004**, *126*, 3400–3401

The amount of thiols in the reduced human blood plasma was estimated by using the standard addition method with Hcy (10 mM stock) as the standard. Different volumes of the freshly prepared Hcy stock (0, 1, 3, 5, 7 or 10 μL) was added directly to 10 μL of probe **2d** (25 μM) and 50 μL of reduced human blood plasma in a solvent mixture of 30 μL of pH 8.1 PBS buffer and appropriate volume of H_2O (for details, see Table S3). The resulting solution was shaken well and diluted with 300 μL of CH_3CN. After 15 min, the emission at 590 nm was recorded. A titration curve of the emission intensity against different volumes of Hcy was obtained, with correlation coefficient R = 0.99 (Fig. S19). The

concentration of thiols in the reduced human blood plasma sample detected by **2d** was found to be 0.31 mM, using the equation:

$$C_X = X\frac{C_S}{V_X}$$

where C_X is the concentration of the sample; C_S is the concentration of the standard, i.e. 10 mM; V_X is the volume of the sample aliquot, i.e. 50 μL; X is the absolute value of x-intercept, i.e. 1.5 μL.

Table S3 Various conditions for setting a titration curve of Hcy and **2d**

Hcy stock (10 mM)	H_2O
0 μL	10 μL
1 μL	9 μL
3 μL	7 μL
5 μL	5 μL
7 μL	3 μL
10 μL	0 μL

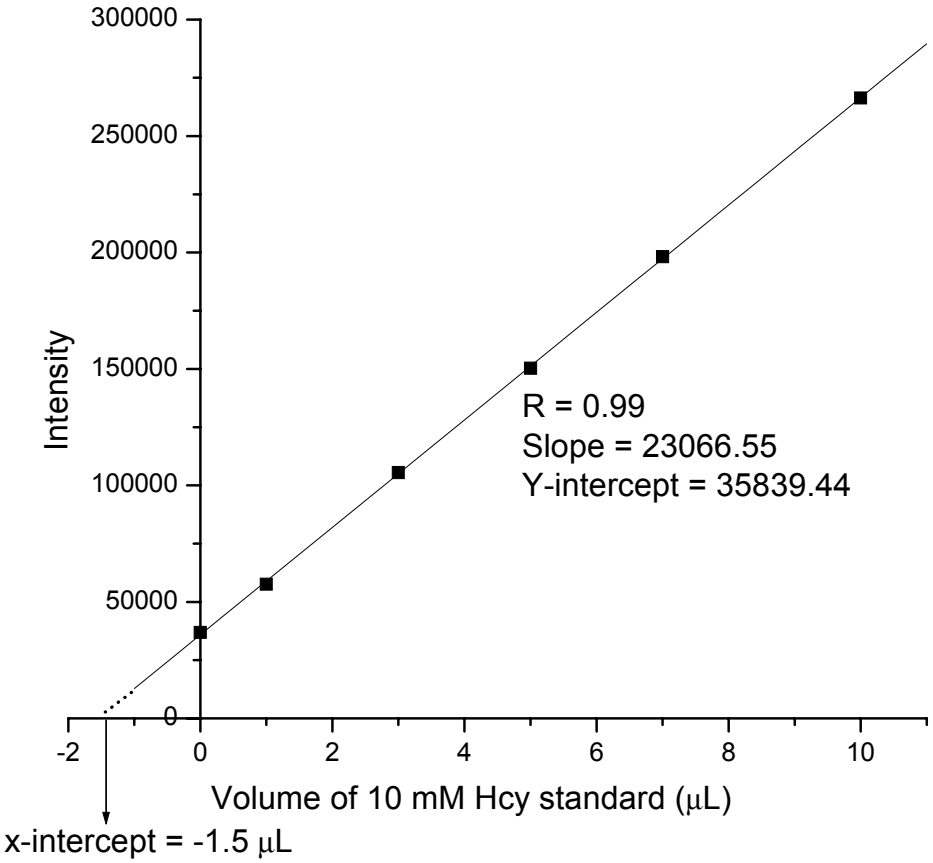


Fig. S19 Titration curve obtained when **2d** (25 μM) reacts with 50 μL of the reduced human blood plasma including different volumes (0, 1, 3, 5, 7, 10 μL) of standard Hcy stock (10 mM)

Lifetime Determination

FRET is the energy transfer from a donor luminophore to an acceptor which may not have to re-emit in the case of dark quenching. The FRET efficiency relates to the lifetimes of the donor molecule in the presence and absence of an acceptor: $E = 1 - \frac{\tau'_D}{\tau_D}$, where τ'_D and τ_D are the donor fluorescence lifetimes in the presence and absence of an acceptor. In order to validate our Ir(III) probe is built on a FRET-based system, the metal part was synthesized and the corresponding

lifetime was measured as τ_D whereas the lifetime of probe **1** was measured as τ'_D . The lifetime of the metal part τ_D was measured as 0.6 μs; τ'_D was too short to be measured by our instrument. The reduction in lifetime of the quenched probe **1** can be considered as the result of energy transfer from the Ir(III) complex to the diarylazo quencher.

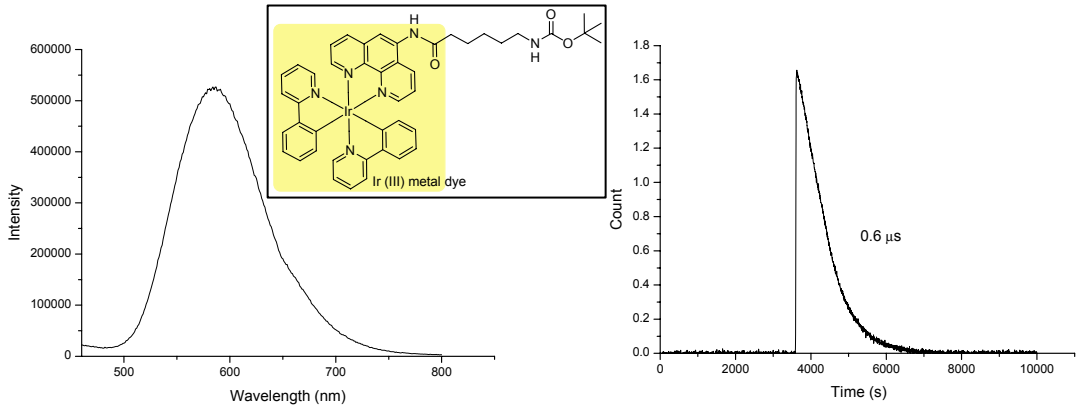


Fig. S20 Luminescence emission spectrum (left) and lifetime (right) spectrum of the metal part (inset)

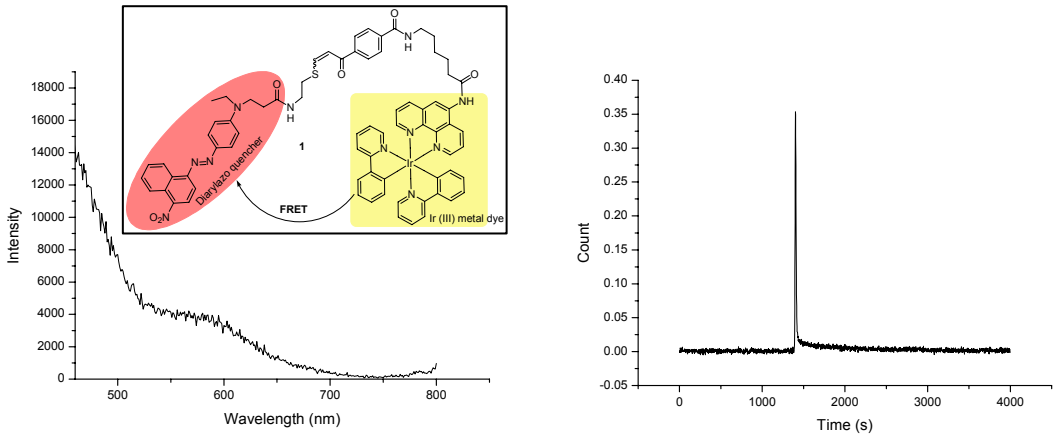
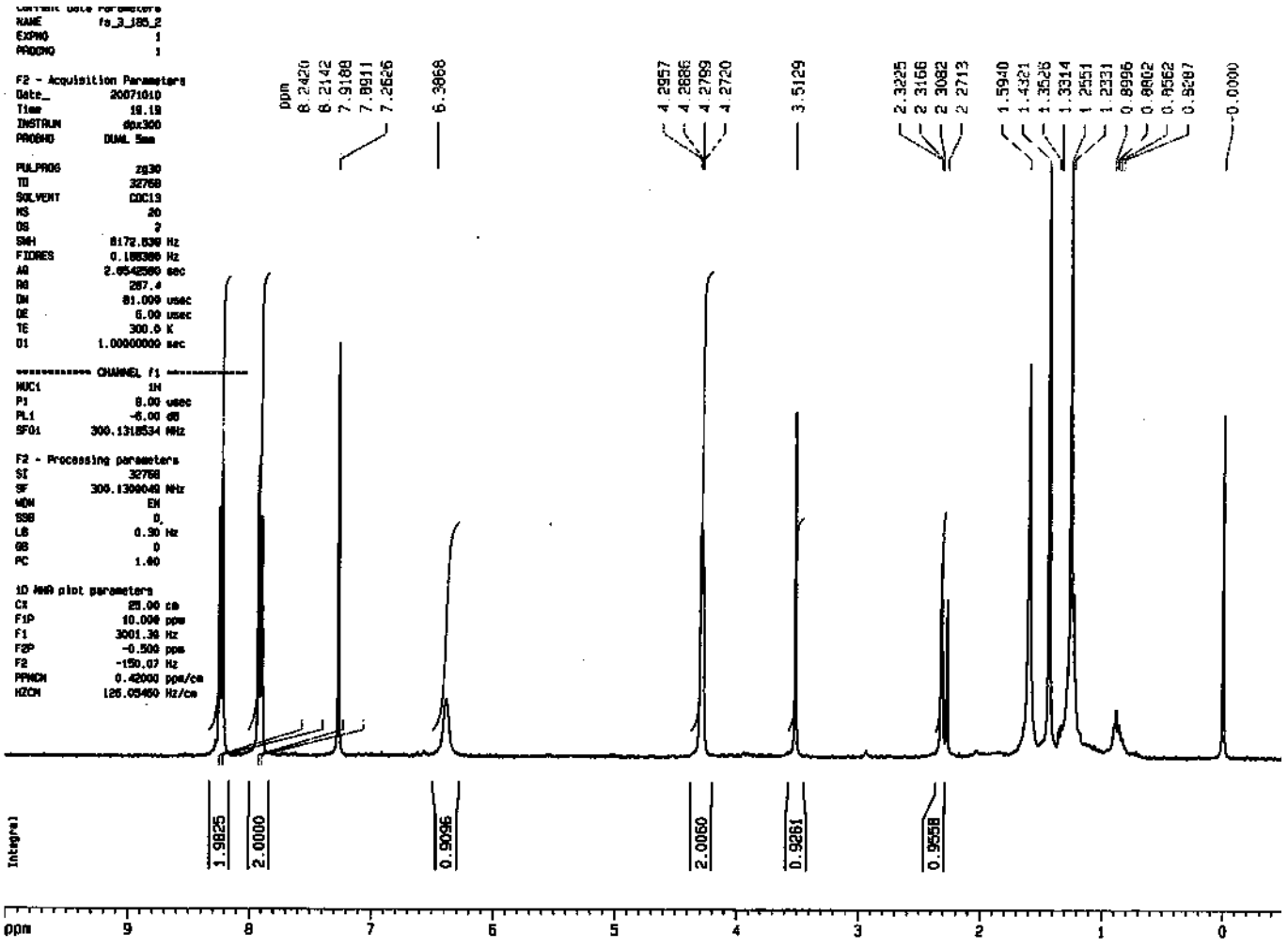


Fig. S21 Luminescence emission spectrum (left) and lifetime (right) spectrum of probe **1** (inset)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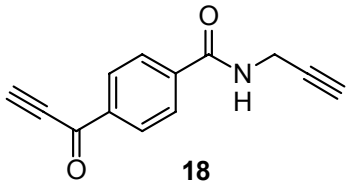
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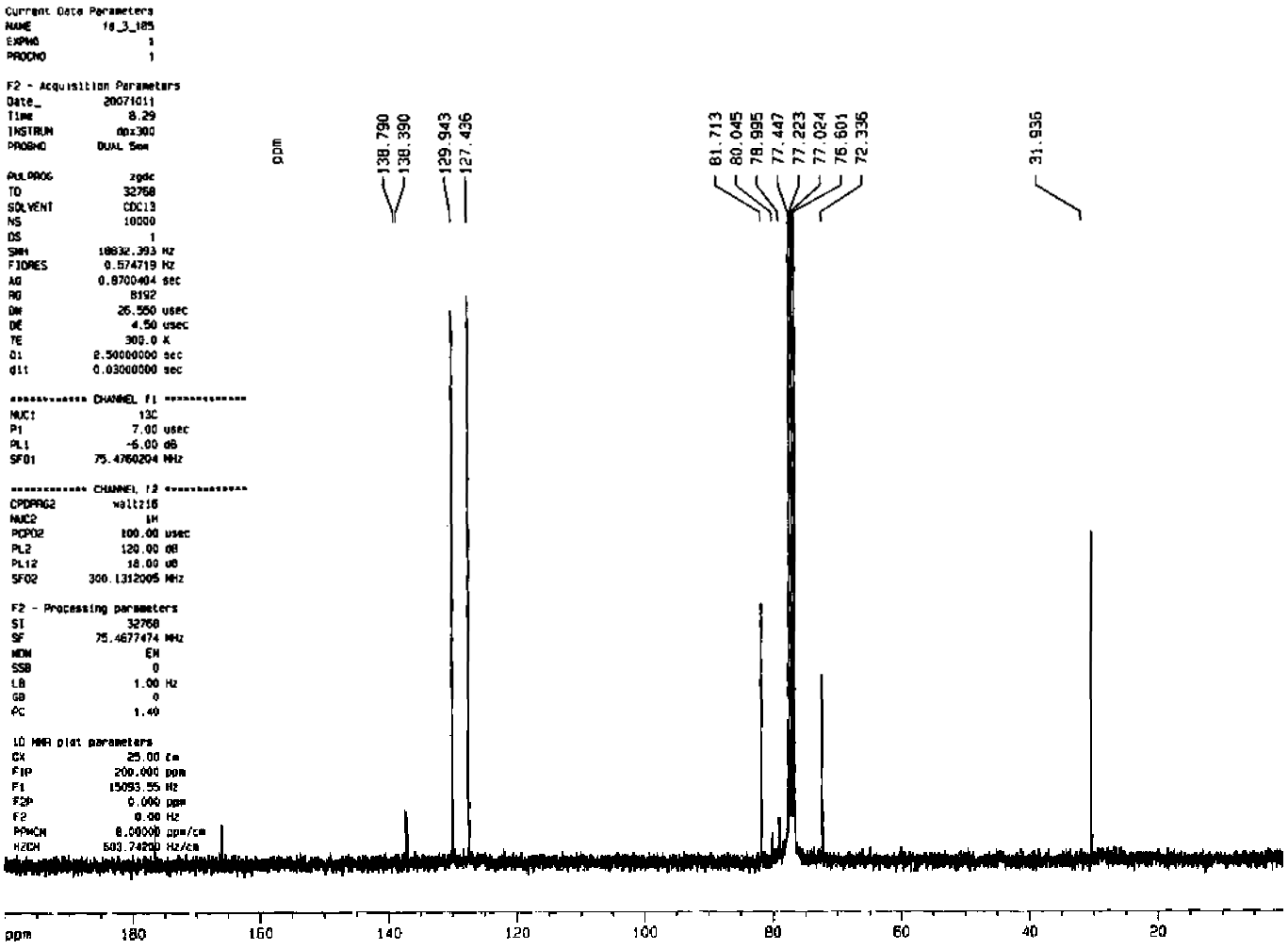
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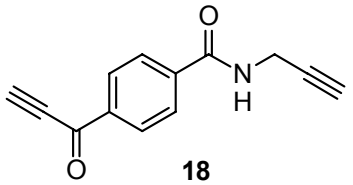
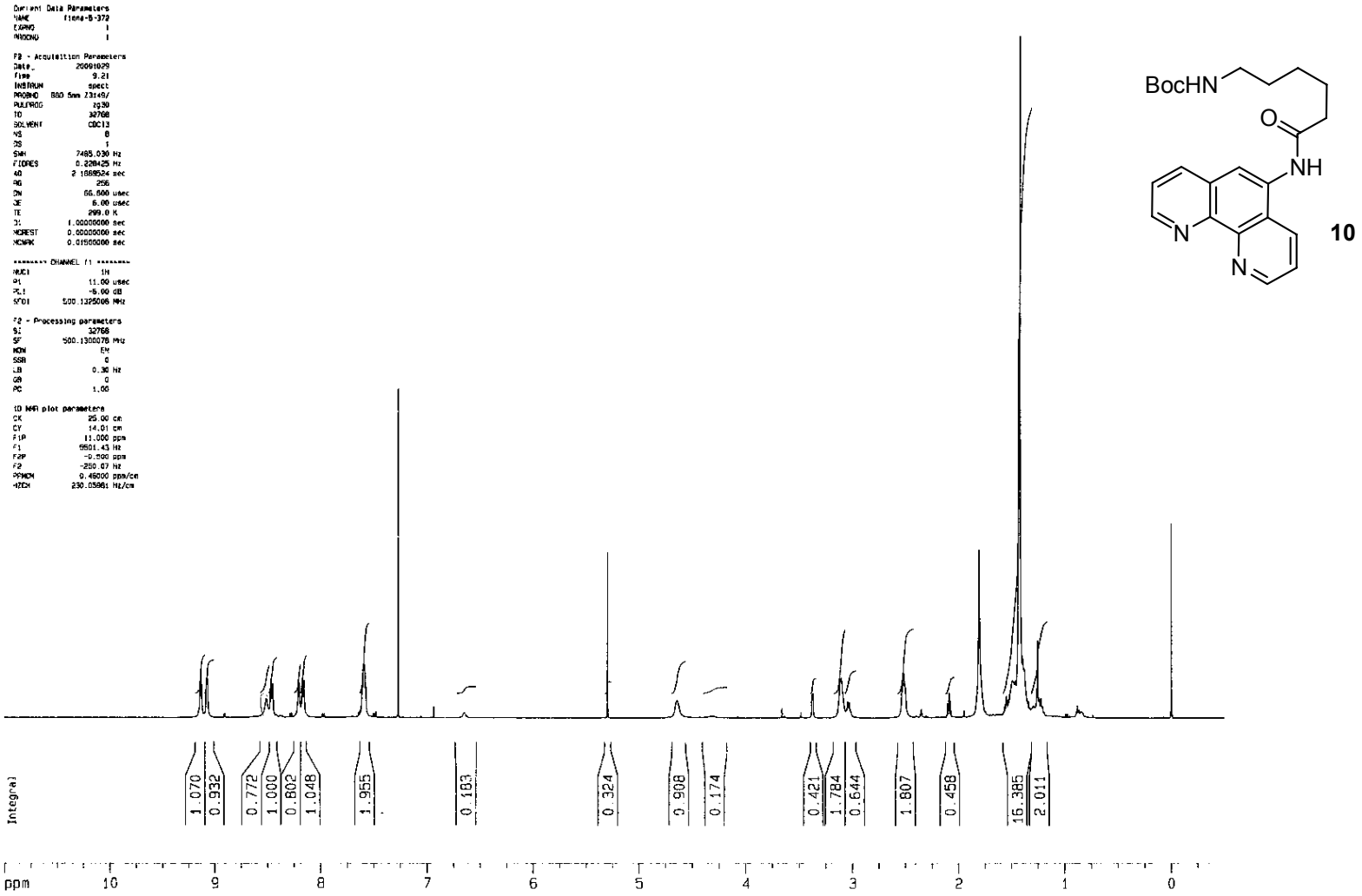
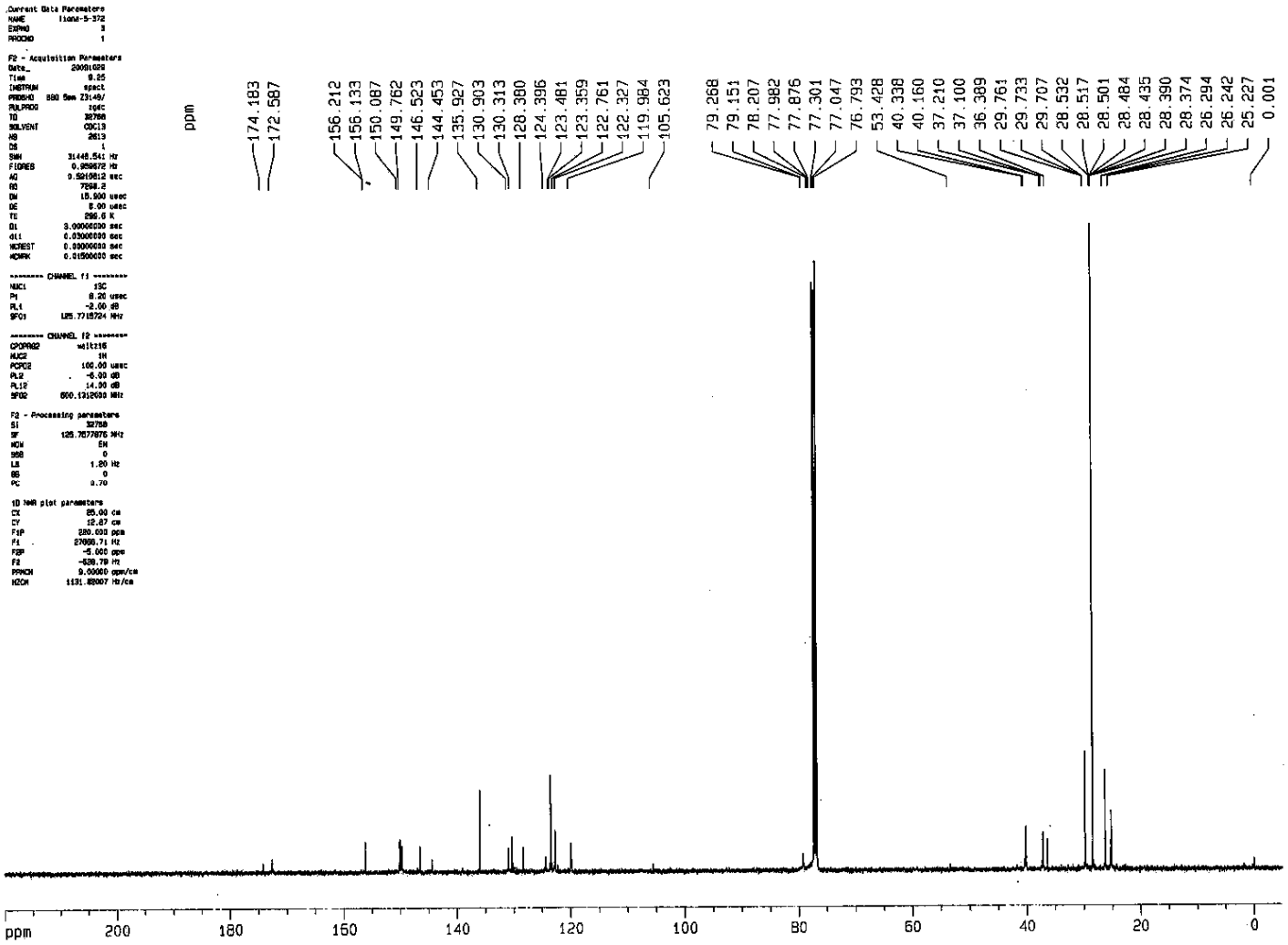
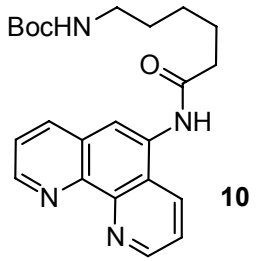
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.00000 ppm/cm
HZCM 603.74200 Hz/cm
ppm
138.790
138.390
129.943
127.436
81.713
80.045
78.995
77.447
77.223
77.024
76.601
72.336
31.936
ppm
180
160
140
120
100
80
60
40
20


O
N
H
O

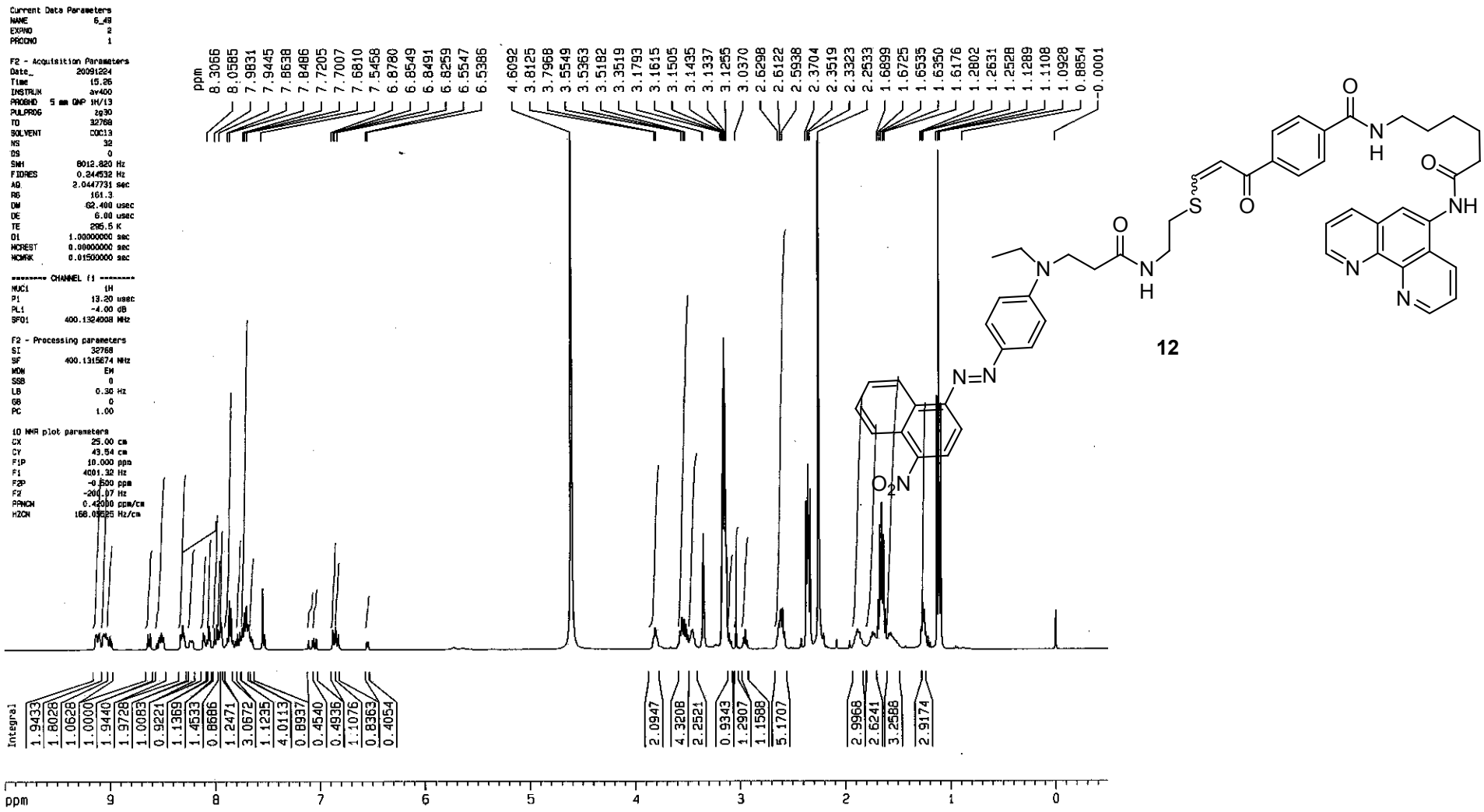
18


Current Data Parameters
NAME fiona-5-372
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091029
Time 9.21
INSTRUM spect
PROBHD BBO 5mm Z3z+6/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 1
SWH 7485.030 Hz
FIDRES 0.228425 Hz
AQ 2.1868524 sec
RG 256
DW 66.800 usec
DE 6.00 usec
TE 299.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -5.00 dB
SFO1 500.1325006 MHz
F2 - Processing parameters
SI 32768
SF 500.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 14.01 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.46000 ppm/cm
HZCM 230.05961 Hz/cm
BocHN
O
NH
N
N
10
Integral
1.070
0.932
0.772
1.000
0.802
1.048
1.955
0.183
0.324
0.908
0.174
0.421
1.784
0.644
1.807
0.458
16.385
2.011
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
174.183
172.587
156.212
156.133
150.087
149.762
146.523
144.453
135.927
130.903
130.313
128.380
124.396
123.481
123.359
122.761
122.327
119.984
105.623
79.268
79.151
78.207
77.982
77.876
77.301
77.047
76.793
53.428
40.338
40.160
37.210
37.100
36.389
29.761
29.733
29.707
28.532
28.517
28.501
28.484
28.435
28.390
28.374
26.294
26.242
25.227
0.001
ppm
200
180
160
140
120
100
80
60
40
20
0

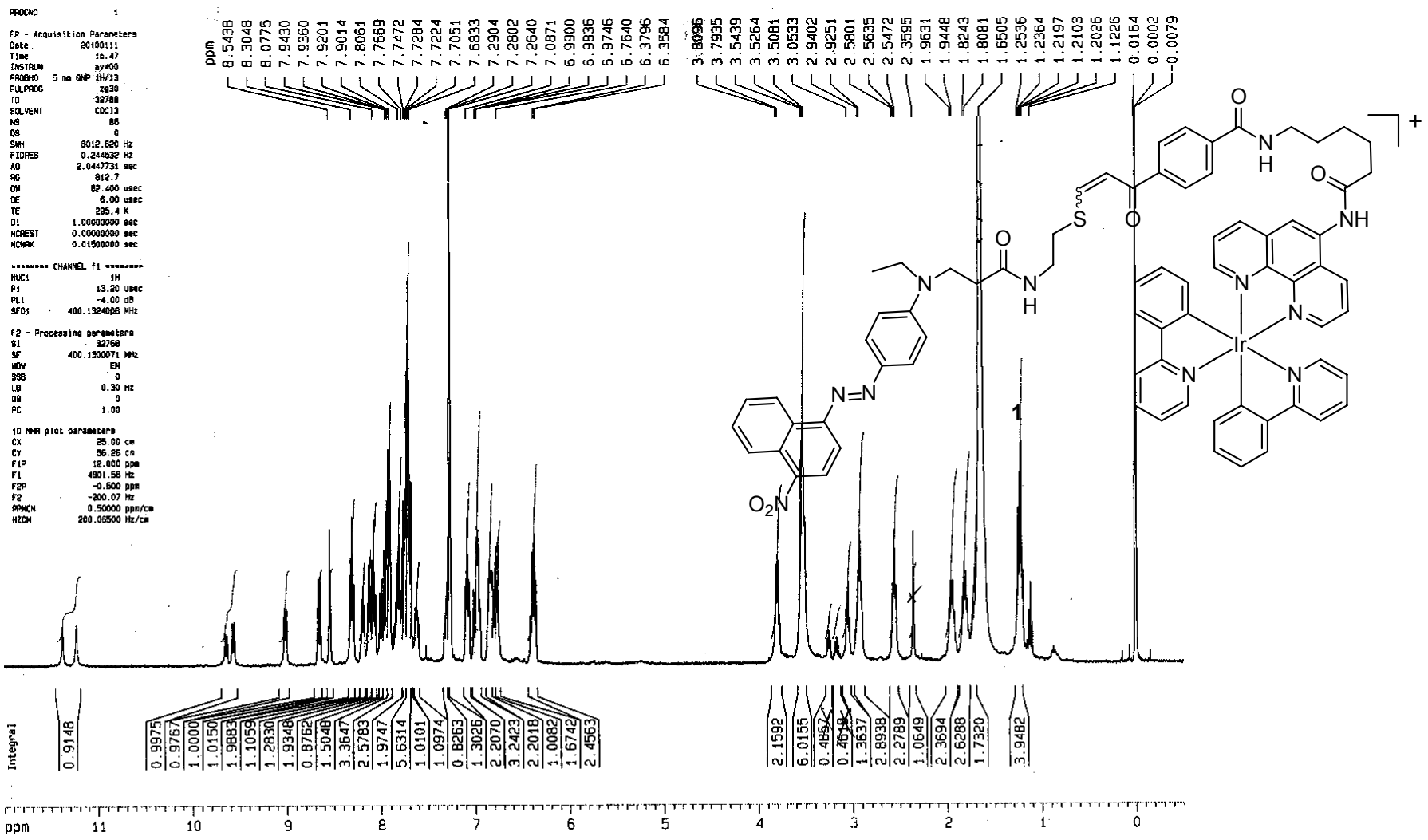

BocHN
O
NH
N
N

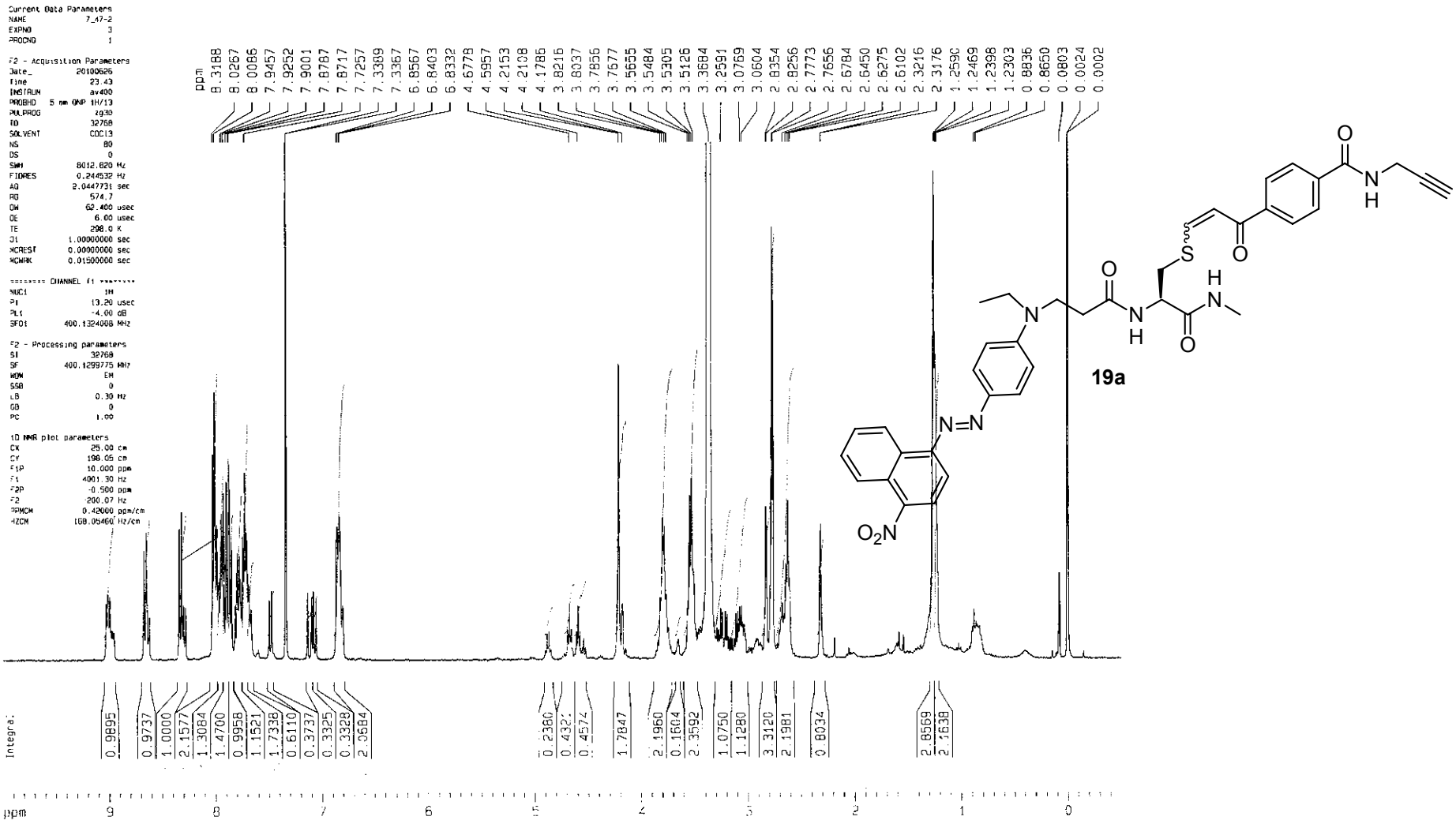
10

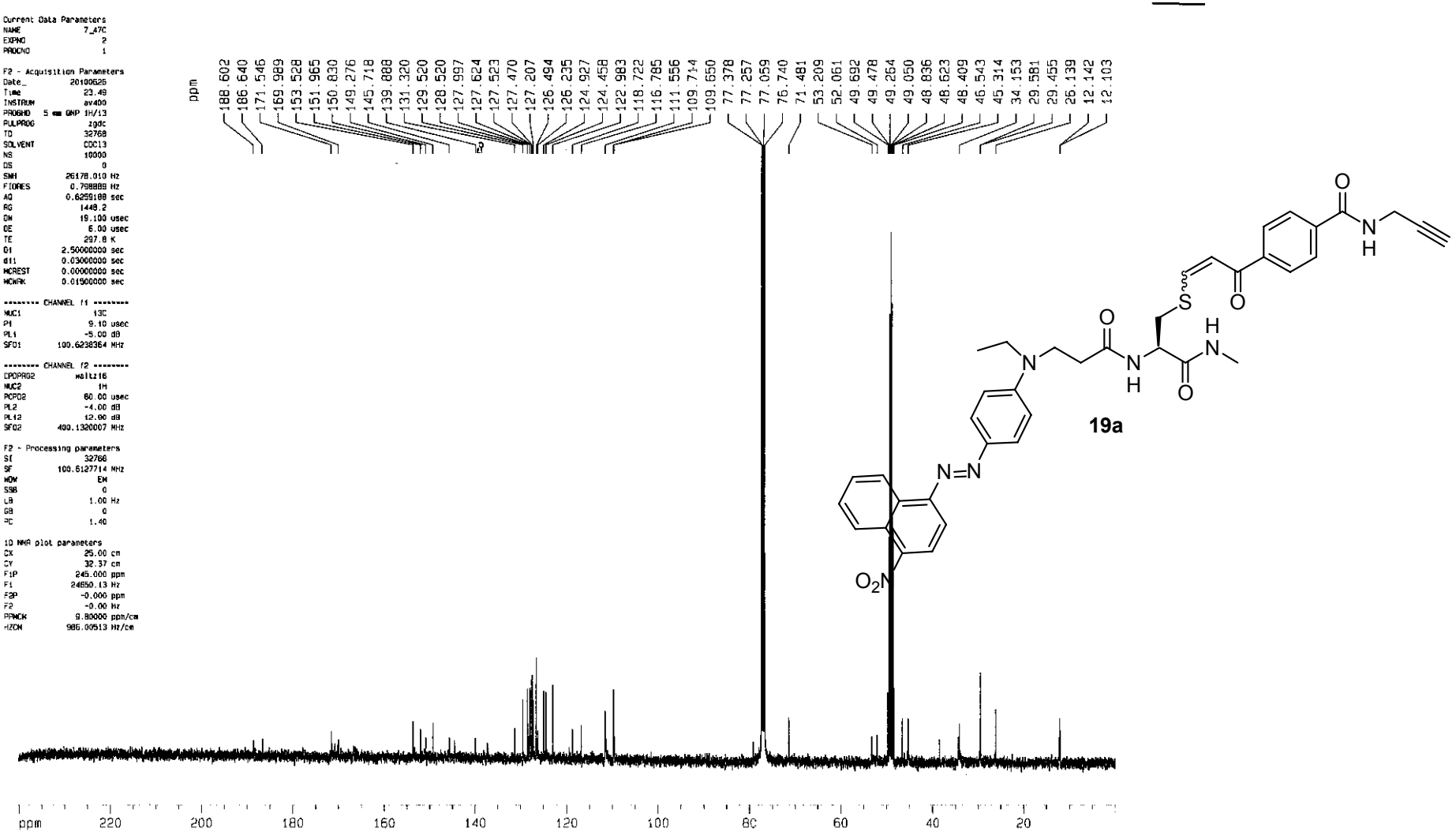

Current Data Parameters
NAME 6_48
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091224
Time 15.26
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 295.5 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1315674 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 43.54 cm
F1P 10.000 ppm
F1 4001.32 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05525 Hz/cm
ppm
8.3066
8.0585
7.9831
7.9445
7.8638
7.8486
7.7205
7.7007
7.6810
7.5458
7.8780
6.8549
6.8491
6.8259
6.5547
6.5386
4.6092
3.8125
3.7968
3.5549
3.5363
3.5182
3.3519
3.1793
3.1615
3.1505
3.1435
3.1337
3.1255
3.0370
2.6298
2.6122
2.5938
2.3704
2.3519
2.3323
2.2533
1.6899
1.6725
1.6535
1.6350
1.6176
1.2802
1.2631
1.2528
1.1289
1.1108
1.0928
0.8854
-0.0001
Integral
1.9433
1.8028
1.0628
1.0000
1.9440
1.9728
1.0083
0.9221
1.1369
1.4533
0.8686
1.2471
3.0672
1.1235
4.0113
0.8937
0.4540
0.4936
1.1076
0.8363
0.4054
2.0947
4.3208
2.2521
0.9343
1.2907
1.1588
5.1707
2.9968
2.6241
3.2588
2.9174
ppm
9
8
7
6
5
4
3
2
1
0

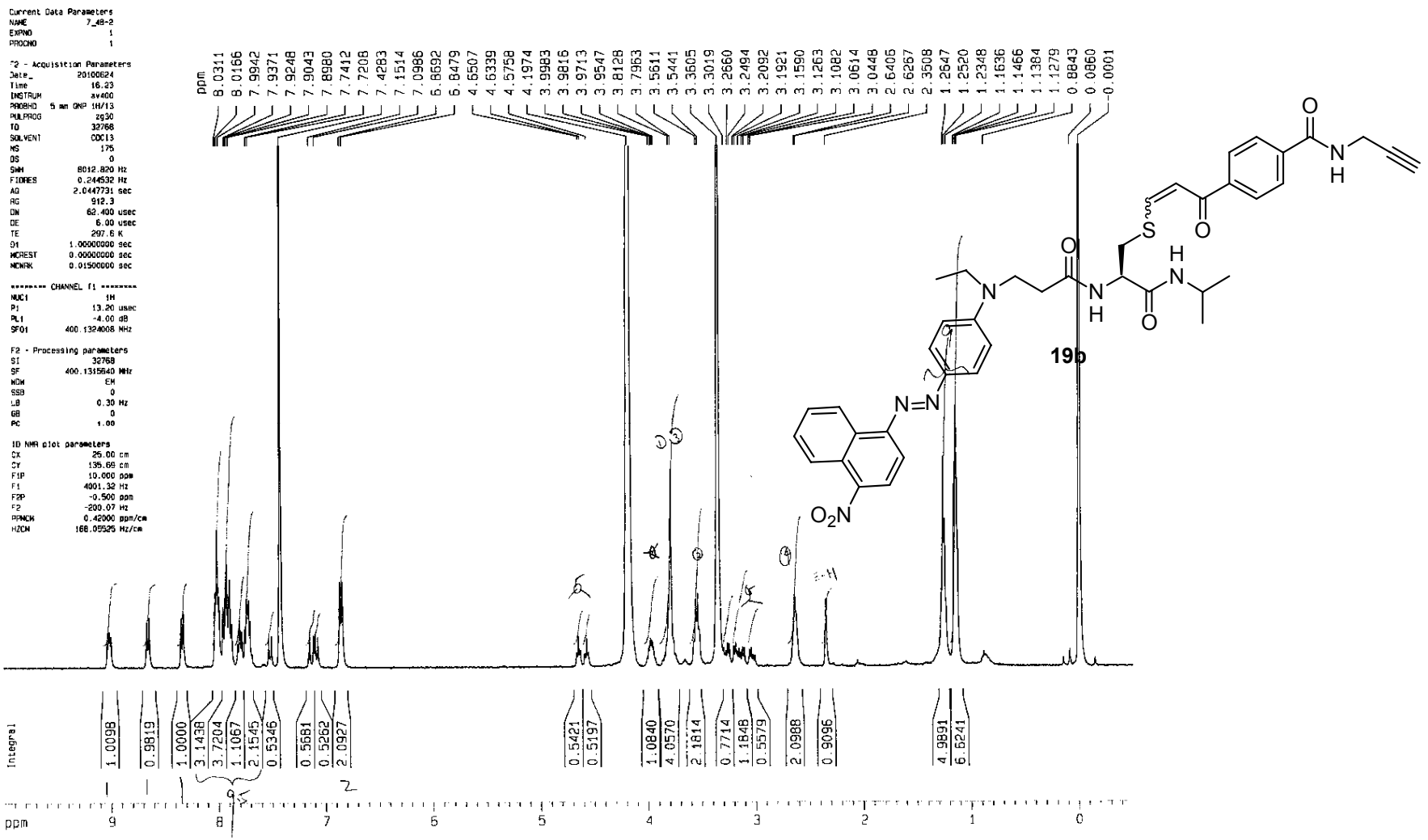
O
N
H
O
NH
S
O
O
N
N
H
N=N
O2N
N
N
N

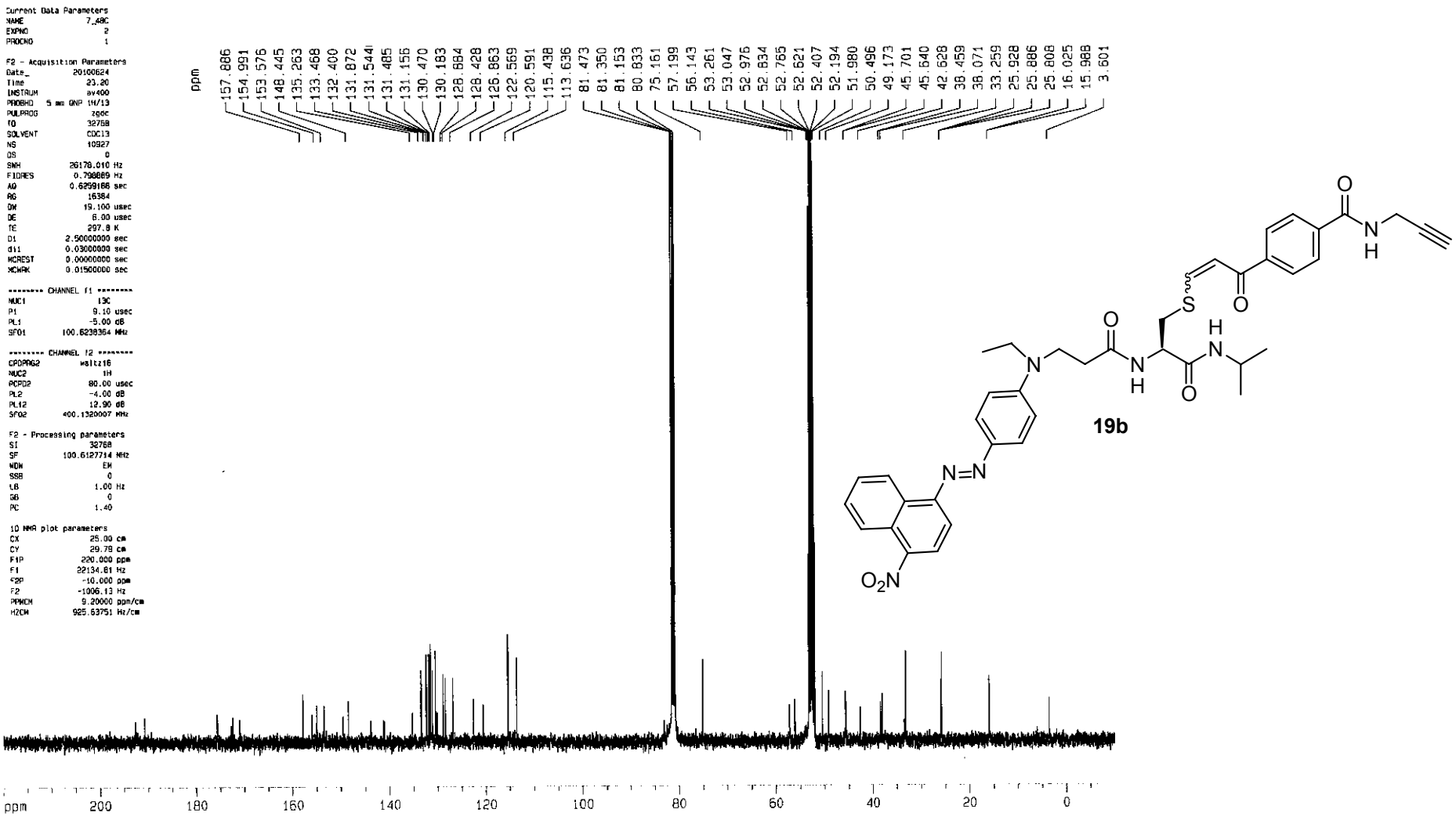
12

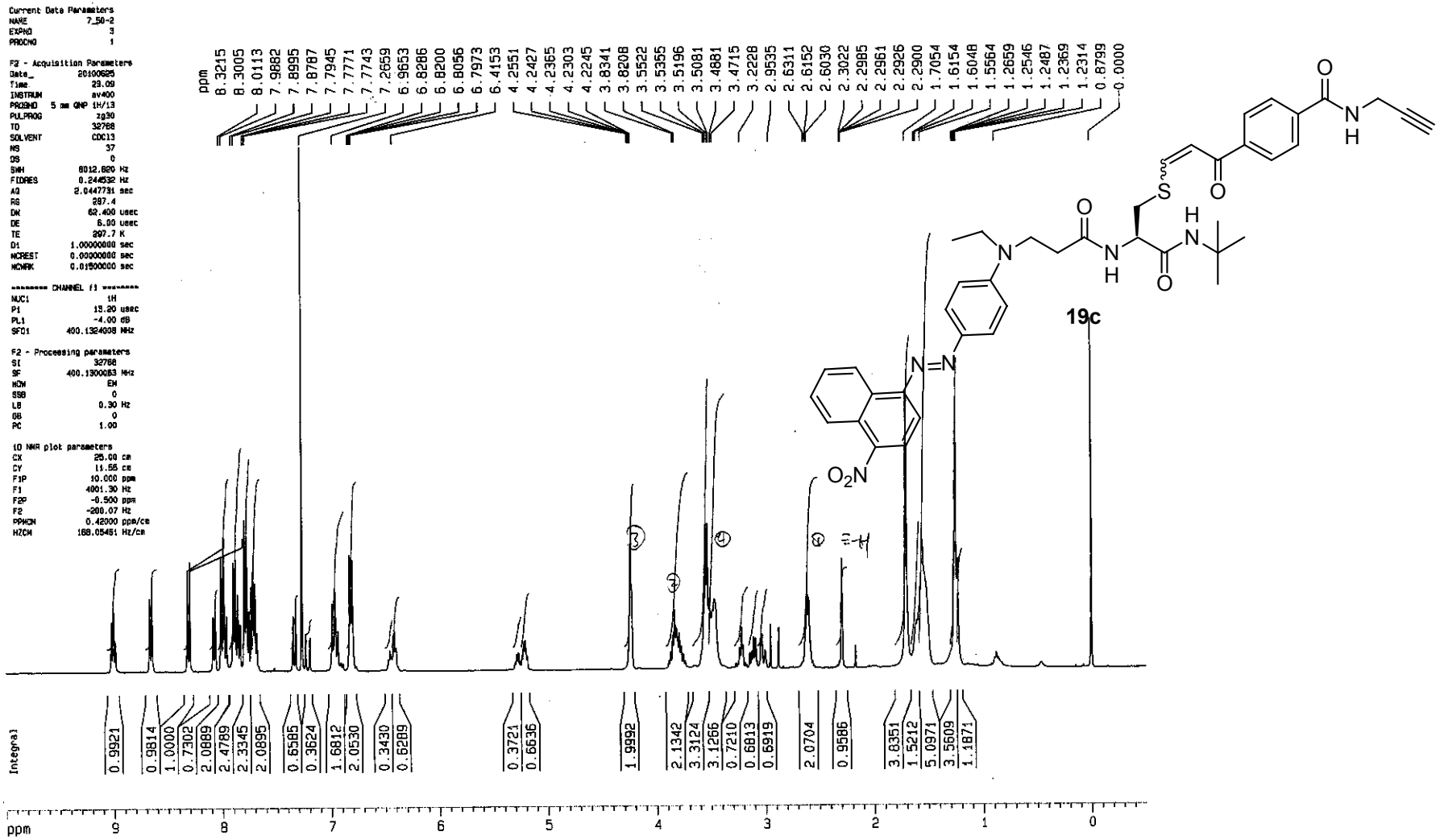

PROCNO 1
F2 - Acquisition Parameters
Date_ 20100111
Time 15.47
INSTRUM ay400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 88
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 812.7
DW 62.400 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324006 MHz
F2 - Processing parameters
SI 32768
SF 400.1300071 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 56.25 cm
F1P 12.000 ppm
F1 4801.56 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm
ppm
8.5438
8.3048
8.0775
7.9430
7.9360
7.9201
7.9014
7.8061
7.7669
7.7472
7.7284
7.7224
7.7051
7.6833
7.2904
7.2802
7.2640
7.0871
6.9900
6.9836
6.9746
6.7640
6.3796
6.3584
3.7935
3.5439
3.5264
3.5081
3.0533
2.9402
2.9251
2.5801
2.5635
2.5472
2.3595
1.9631
1.9448
1.8243
1.8081
1.6505
1.2536
1.2364
1.2197
1.2103
1.2026
1.1226
0.0164
0.0002
-0.0079
Integral
0.9148
0.9975
0.9767
1.0000
1.0150
1.9883
1.1059
1.2830
1.9348
0.8762
1.5048
3.3647
2.5783
1.9747
5.6314
1.0101
1.0974
0.8263
1.3026
2.2070
3.2423
2.2018
1.0082
1.6742
2.4563
2.1592
6.0155
0.4857
0.4618
1.3637
2.8938
2.2789
1.0649
2.3694
2.6288
1.7320
3.9482
ppm
11
10
9
8
7
6
5
4
3
2
1
0
O2N
N=N
Ir
NH
S
O

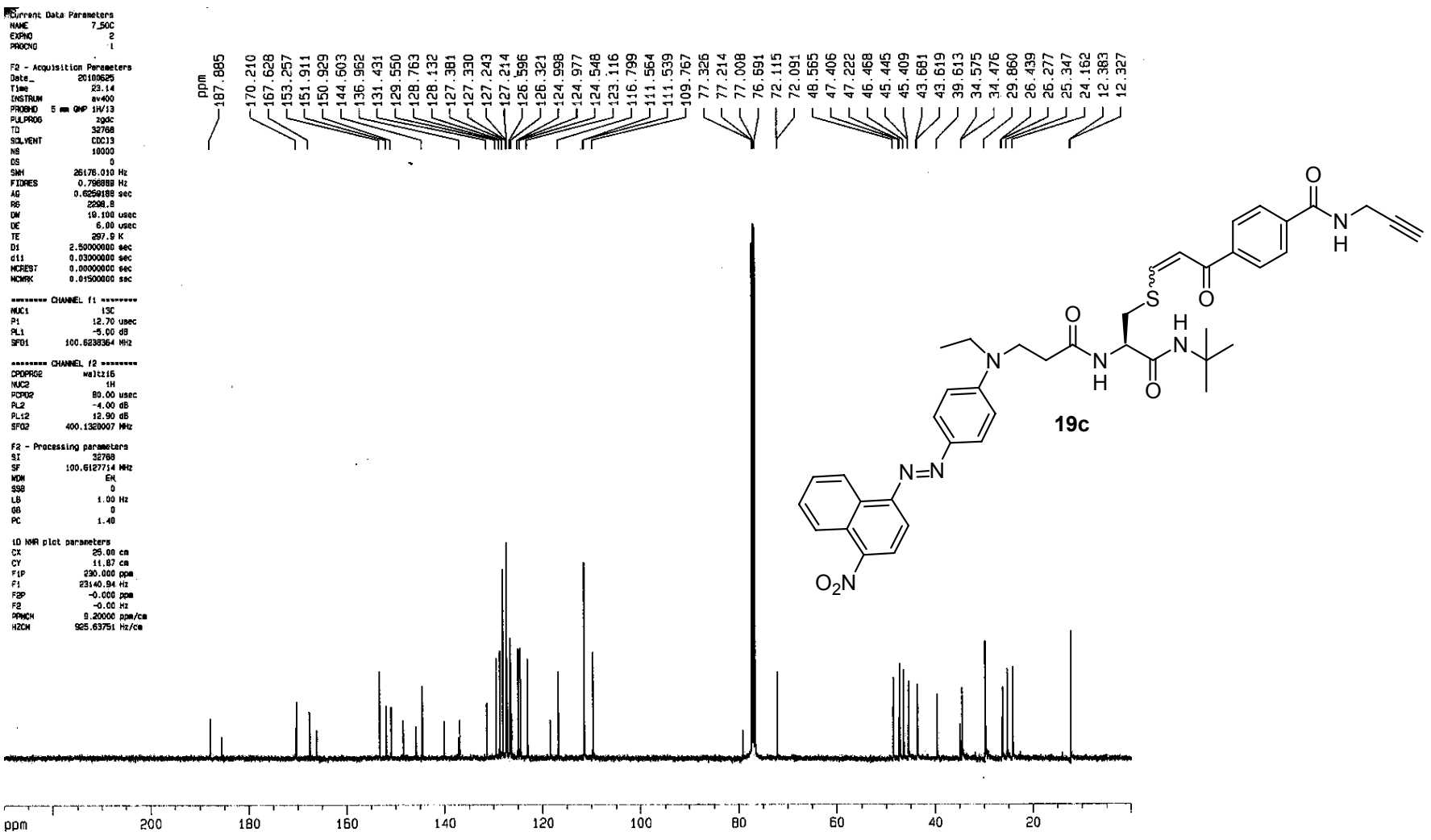

Current Data Parameters
NAME 7_47-2
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100626
Time 23.43
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 80
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 574.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1299775 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 198.05 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05460 Hz/cm
ppm
8.3188
8.0267
8.0086
7.9457
7.9252
7.9001
7.8787
7.8717
7.7257
7.3389
7.3367
6.8567
6.8403
6.8332
4.6778
4.5957
4.2153
4.2138
4.1785
3.8216
3.8037
3.7856
3.7677
3.5655
3.5484
3.5305
3.5126
3.3684
3.2591
3.0769
3.0604
2.8354
2.8256
2.7773
2.7656
2.6784
2.6450
2.6275
2.6102
2.3216
2.3176
1.2590
1.2469
1.2398
1.2303
0.8836
0.8650
0.0803
0.0024
0.0002
Integral
0.9895
0.9737
1.0000
2.1577
1.3084
1.4700
0.9958
1.1521
1.7338
0.6110
0.3737
0.3325
0.3328
2.0684
0.2386
0.4327
0.4574
1.7847
2.1960
0.1604
2.3592
1.0750
1.1280
3.3120
2.1981
0.8034
2.8569
2.1638
ppm
9
8
7
6
5
4
3
2
1
0
N=N
O_2N
O
N
H
S
19a

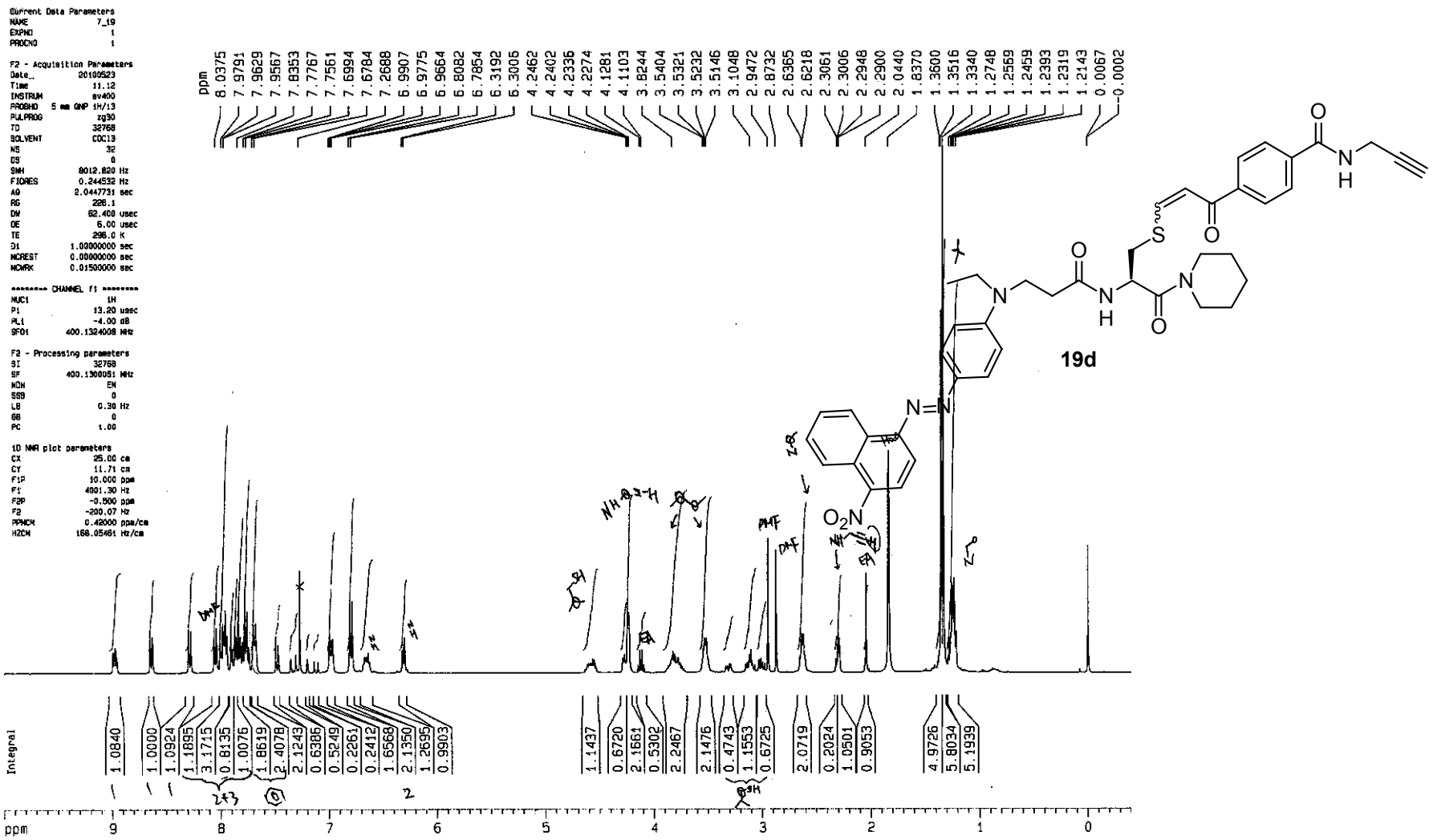

Current Data Parameters
NAME 7_47C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100625
Time 23.49
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 10000
DS 0
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 1448.2
DW 19.100 usec
DE 6.00 usec
TE 297.8 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 9.10 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL2 -4.00 dB
PL12 12.00 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 32.37 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 9.80000 ppm/cm
HZCM 986.00513 Hz/cm
ppm
188.602
186.640
171.546
169.989
153.528
151.965
150.830
149.276
145.718
139.888
131.320
129.520
128.520
127.997
127.624
127.523
127.470
127.207
126.494
126.235
124.927
124.458
122.983
118.722
116.785
111.556
109.714
109.650
77.378
77.257
77.059
76.740
71.481
53.209
52.061
49.692
49.478
49.264
49.050
48.836
48.623
48.409
46.543
45.314
34.153
29.581
29.455
26.139
12.142
12.103
19a
ppm
220
200
180
160
140
120
100
80
60
40
20

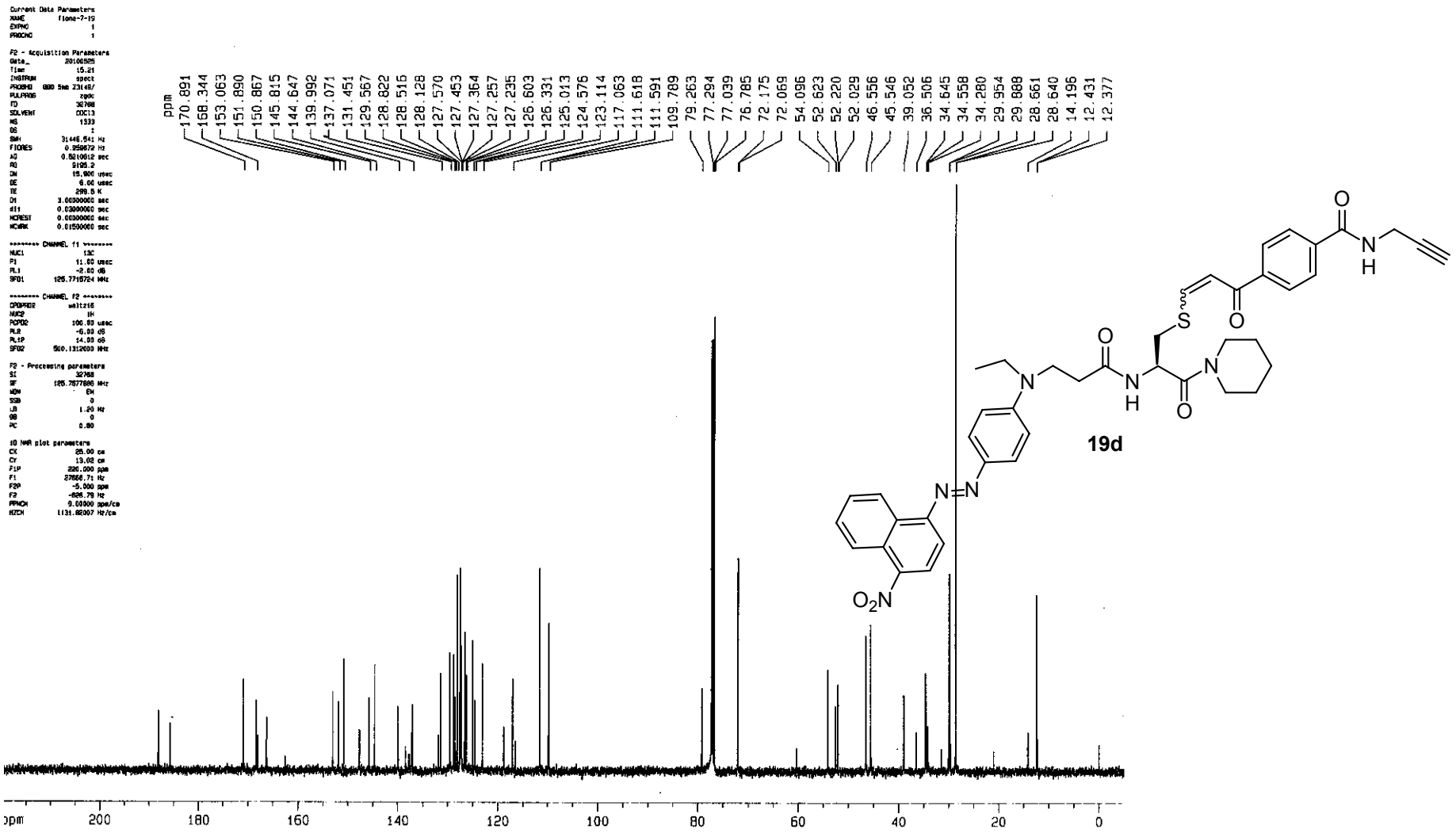

Current Data Parameters
NAME 7_48-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100624
Time 16.23
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 176
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 912.3
DW 62.400 usec
DE 6.00 usec
TE 297.6 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1315540 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 135.69 cm
F1P 10.000 ppm
F1 4001.32 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05525 Hz/cm
ppm
8.0311
8.0166
7.9942
7.9371
7.9248
7.9043
7.8980
7.7412
7.7208
7.4283
7.1514
7.0986
6.8692
6.8479
4.6507
4.6339
4.5758
4.1974
3.9983
3.9816
3.9713
3.9547
3.8128
3.7963
3.5611
3.5441
3.3505
3.3019
3.2660
3.2494
3.2092
3.1921
3.1590
3.1263
3.1082
3.0614
3.0448
2.6406
2.6267
2.3508
1.2647
1.2520
1.2348
1.1636
1.1466
1.1384
1.1279
0.8843
0.0860
-0.0001
Integral
1.0098
0.9819
1.0000
3.1438
3.7204
1.1067
2.1545
0.5346
0.5681
0.5262
2.0927
0.5421
0.5197
1.0840
4.0570
2.1814
0.7714
1.1848
0.5579
2.0988
0.9096
4.9891
6.6241
ppm
9
8
7
6
5
4
3
2
1
0
19b

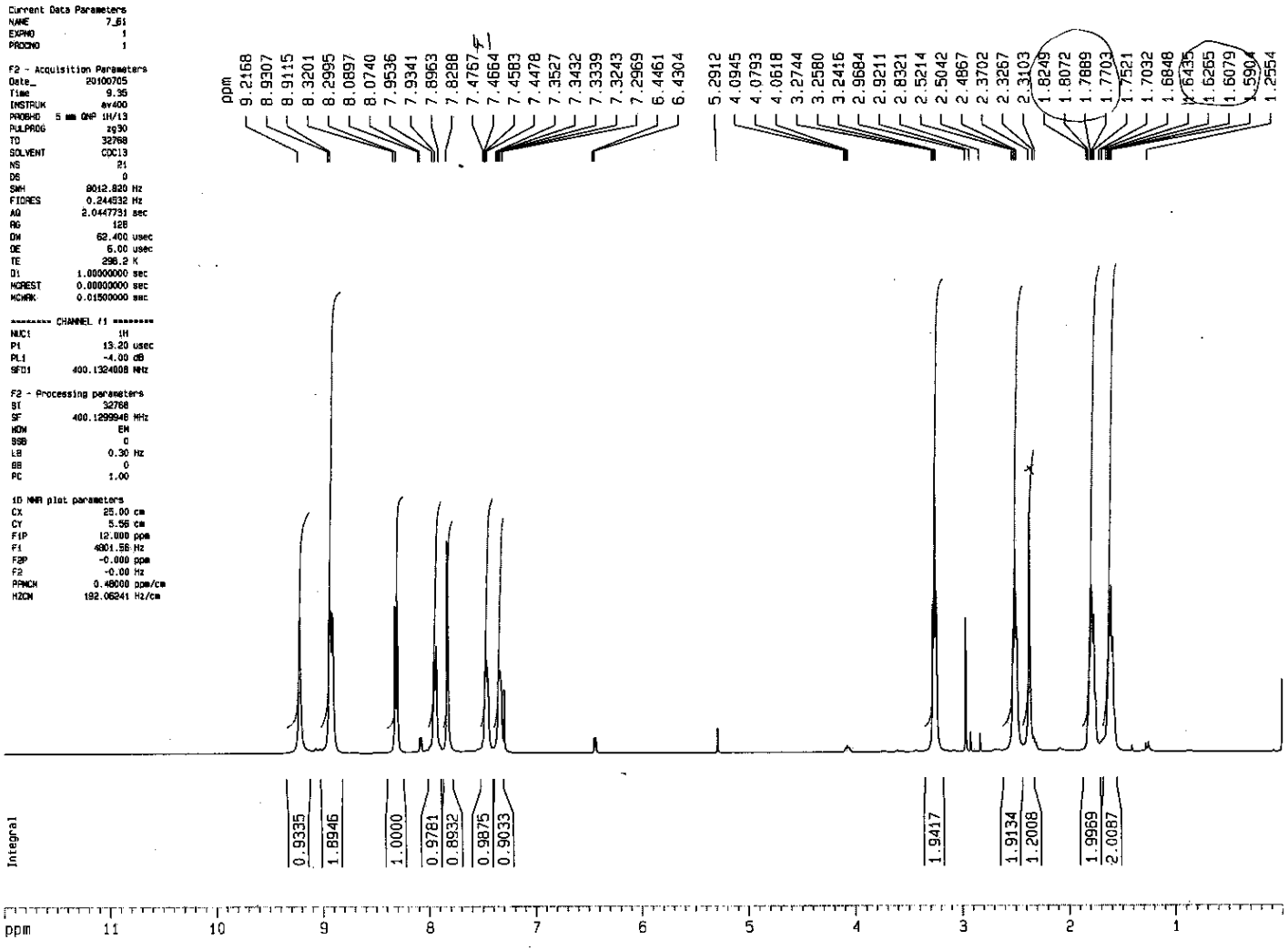

Current Data Parameters
NAME 7_48C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100624
Time 23.20
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 10927
DS 0
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259166 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 297.8 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 9.10 usec
PL1 -5.00 dB
SF01 100.6238364 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SF02 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 20.79 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.20000 ppm/cm
HZCM 925.63751 Hz/cm
ppm
157.886
154.991
153.576
148.445
135.263
133.468
132.400
131.872
131.544
131.485
131.156
130.470
130.183
128.884
128.428
125.863
122.569
120.591
115.438
113.636
81.473
81.350
81.153
80.833
75.161
57.199
56.143
53.261
53.047
52.976
52.834
52.765
52.621
52.407
52.194
51.980
50.496
49.173
45.701
45.640
42.628
38.459
38.071
33.259
25.928
25.886
25.808
16.025
15.988
3.601
19b
ppm
200
180
160
140
120
100
80
60
40
20
0

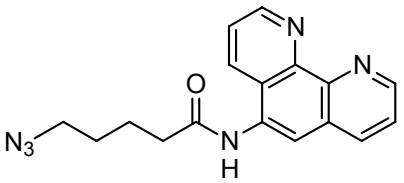

Current Data Parameters
NAME 7_50-2
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100625
Time 23.09
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 37
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 287.4
DW 62.400 usec
DE 6.00 usec
TE 297.7 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 11.55 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05451 Hz/cm
ppm
8.3215
8.3005
8.0113
7.9882
7.8995
7.8787
7.7945
7.7771
7.7743
7.2659
6.9653
6.8286
6.8200
6.8056
6.7973
6.4153
4.2551
4.2427
4.2365
4.2303
4.2245
3.8341
3.8208
3.5522
3.5355
3.5196
3.5081
3.4881
3.4715
3.2228
2.9535
2.6311
2.6152
2.6030
2.3022
2.2985
2.2961
2.2926
2.2900
1.7054
1.6154
1.6048
1.5564
1.2659
1.2546
1.2487
1.2369
1.2314
0.8799
0.0000
19c
Integral
0.9921
0.9814
1.0000
0.7302
2.0889
2.4789
2.3345
2.0895
0.6585
0.3624
1.6812
2.0530
0.3430
0.6289
0.3721
0.6636
1.9992
2.1342
3.3124
3.1266
0.7210
0.6813
0.6919
2.0704
0.9586
3.8351
1.5212
5.0971
3.5609
1.1871
ppm
9
8
7
6
5
4
3
2
1
0


Current Data Parameters
NAME 7_50C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100625
Time 23.14
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 10000
DS 0
SWH 26178.010 Hz
FIDRES 0.798888 Hz
AQ 0.6259188 sec
RG 2298.8
DW 19.100 usec
DE 6.00 usec
TE 297.9 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 11.87 cm
F1P 230.000 ppm
F1 23140.94 Hz
F2P -0.008 ppm
F2 -0.00 Hz
PPMCM 9.20000 ppm/cm
HZCM 925.63751 Hz/cm
ppm
187.885
170.210
167.628
153.257
151.911
150.929
144.603
136.962
131.431
129.550
128.763
128.132
127.381
127.330
127.243
127.214
126.596
126.321
124.998
124.977
124.548
123.116
116.799
111.564
111.539
109.767
77.326
77.214
77.008
76.691
72.115
72.091
48.565
47.406
47.222
46.468
45.445
45.409
43.681
43.619
39.613
34.575
34.476
29.860
26.439
26.277
25.347
24.162
12.383
12.327
19c
ppm
200
180
160
140
120
100
80
60
40
20

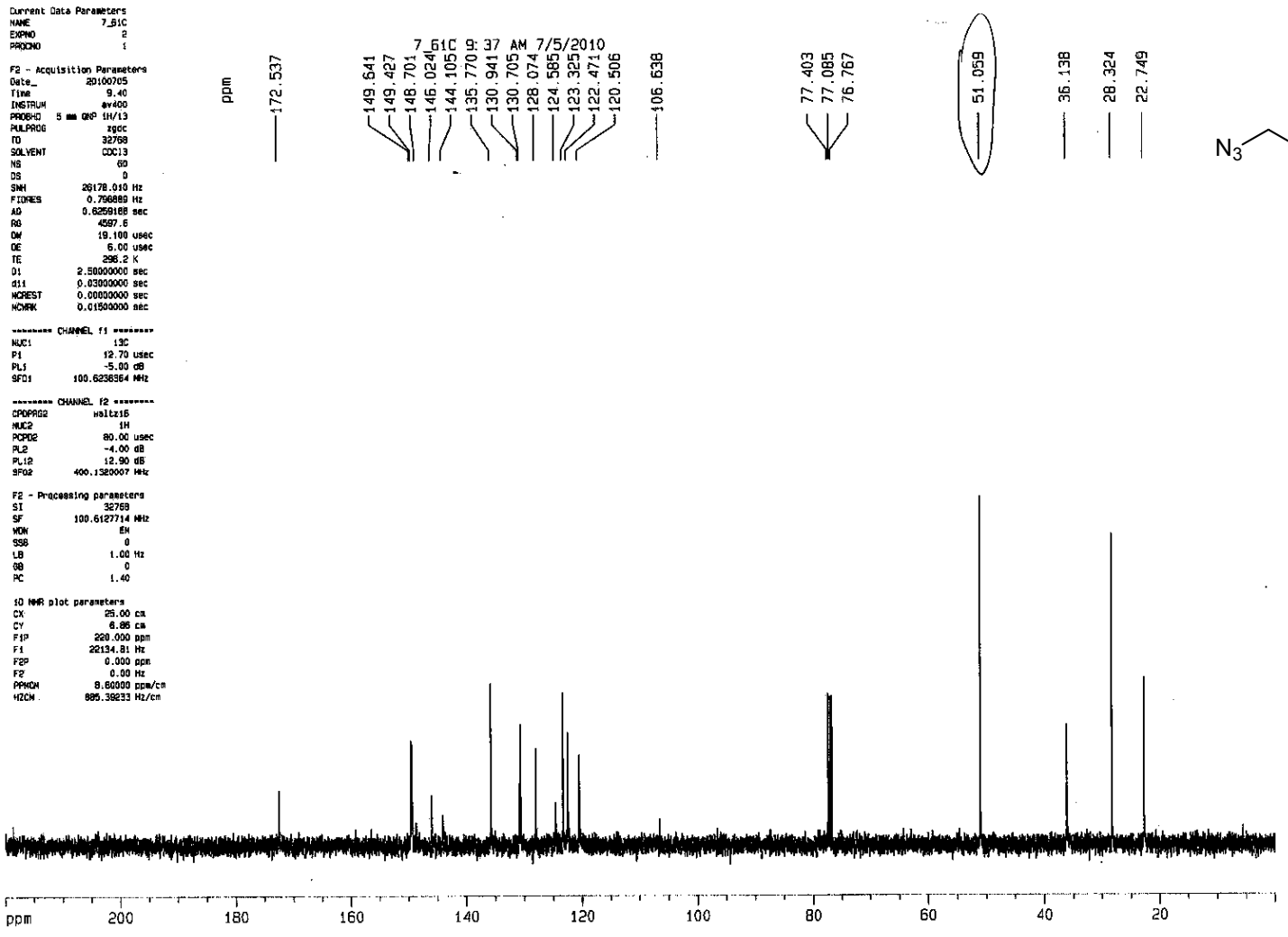

Current Data Parameters
NAME 7_19
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100523
Time 11.12
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 228.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 11.71 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05461 Hz/cm
ppm
8.0375 7.9791 7.9629 7.9567 7.8353 7.7767 7.7561 7.6994 7.6784 7.2688 6.9907 6.9775 6.9664 6.8082 6.7854 6.3192 6.3005 4.2462 4.2402 4.2336 4.2274 4.1281 4.1103 3.8244 3.5404 3.5321 3.5232 3.5146 3.1048 2.9472 2.8732 2.6365 2.6218 2.3061 2.3006 2.2948 2.2900 2.0440 1.8370 1.3600 1.3516 1.3340 1.2748 1.2569 1.2459 1.2393 1.2319 1.2143 0.0067 -0.0002
Integral
1.0840 1.0000 1.0924 1.1895 3.1715 0.8135 1.0076 1.8619 2.4078 2.1243 0.6386 0.5249 0.2261 0.2412 1.6568 2.1350 1.2695 0.9903 1.1437 0.6720 2.1661 0.5302 2.2467 2.1476 0.4743 1.1553 0.6725 2.0719 0.2024 1.0501 0.9053 4.9726 5.8034 5.1939
ppm
9 8 7 6 5 4 3 2 1 0
19d


Current Data Parameters
NAME fiona-7-19
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100505
Time 15.21
INSTRUM spect
PROBHD 5mm Z31487
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 1333
DS 2
SWH 31446.541 Hz
FIDRES 0.959572 Hz
AQ 0.5210612 sec
RG 9195.2
DW 15.900 usec
DE 6.00 usec
TE 299.5 K
D1 3.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SFO1 125.7715724 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 14.50 dB
SFO2 500.1312000 MHz
F2 - Processing parameters
SI 32768
SF 125.7577886 MHz
WDW EM
SSB 0
LB 1.20 Hz
GB 0
PC 0.80
1D NMR plot parameters
CX 25.00 cm
CY 13.02 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P -5.000 ppm
F2 -626.79 Hz
PPMCM 9.00000 ppm/cm
HZCM 1131.88907 Hz/cm
ppm
170.891
168.344
153.063
151.890
150.867
145.815
144.647
139.992
137.071
131.451
129.567
128.822
128.515
128.128
127.570
127.453
127.364
127.257
127.235
126.603
126.331
125.013
124.576
123.114
117.063
111.618
111.591
109.789
79.263
77.294
77.039
76.785
72.175
72.069
54.096
52.623
52.220
52.029
46.556
45.546
39.052
36.506
34.645
34.558
34.280
29.954
29.888
28.661
28.540
14.196
12.431
12.377
19d
ppm
200
180
160
140
120
100
80
60
40
20
0


Current Data Parameters
NAME 7_61
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100705
Time 9.35
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 21
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1299946 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 5.56 cm
F1P 12.000 ppm
F1 4801.56 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 0.48000 ppm/cm
HZCM 192.06241 Hz/cm
ppm
9.2168
8.9307
8.9115
8.3201
8.2995
8.0897
8.0740
7.9536
7.9341
7.8963
7.8288
7.4767
7.4664
7.4583
7.4478
7.3527
7.3432
7.3339
7.3243
7.2969
6.4461
6.4304
5.2912
4.0945
4.0793
4.0618
3.2744
3.2580
3.2416
2.9684
2.9211
2.8321
2.5214
2.5042
2.4867
2.3702
2.3267
2.3103
1.8249
1.8072
1.7889
1.7703
1.7521
1.7032
1.6848
1.6435
1.6265
1.6079
1.5904
1.2554
Integral
0.9335
1.8946
1.0000
0.9781
0.8932
0.9875
0.9033
1.9417
1.9134
1.2008
1.9969
2.0087
ppm
11
10
9
8
7
6
5
4
3
2
1


N
N
O
N
H
N3

21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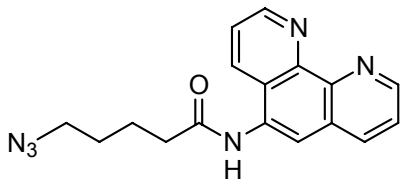
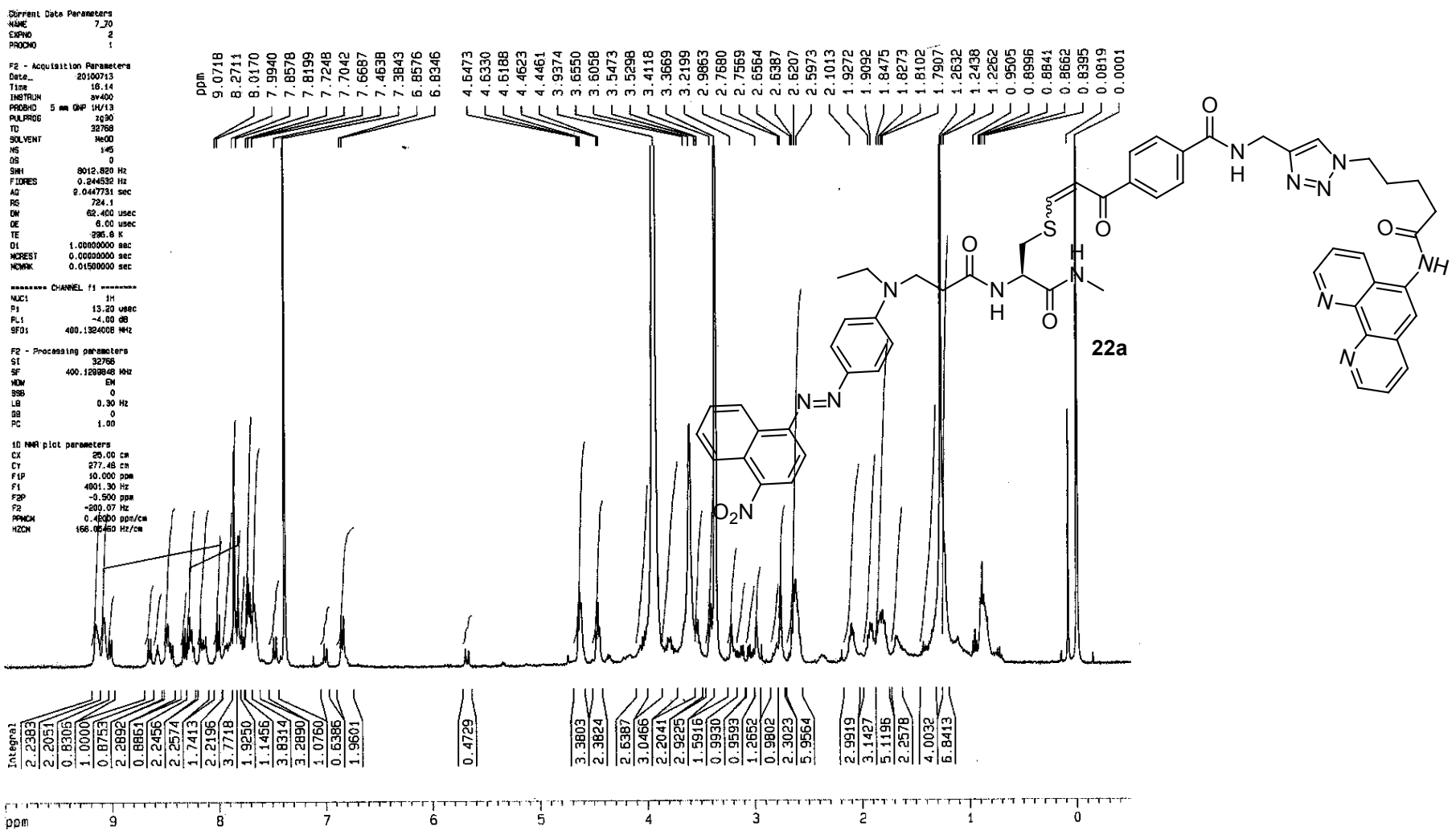
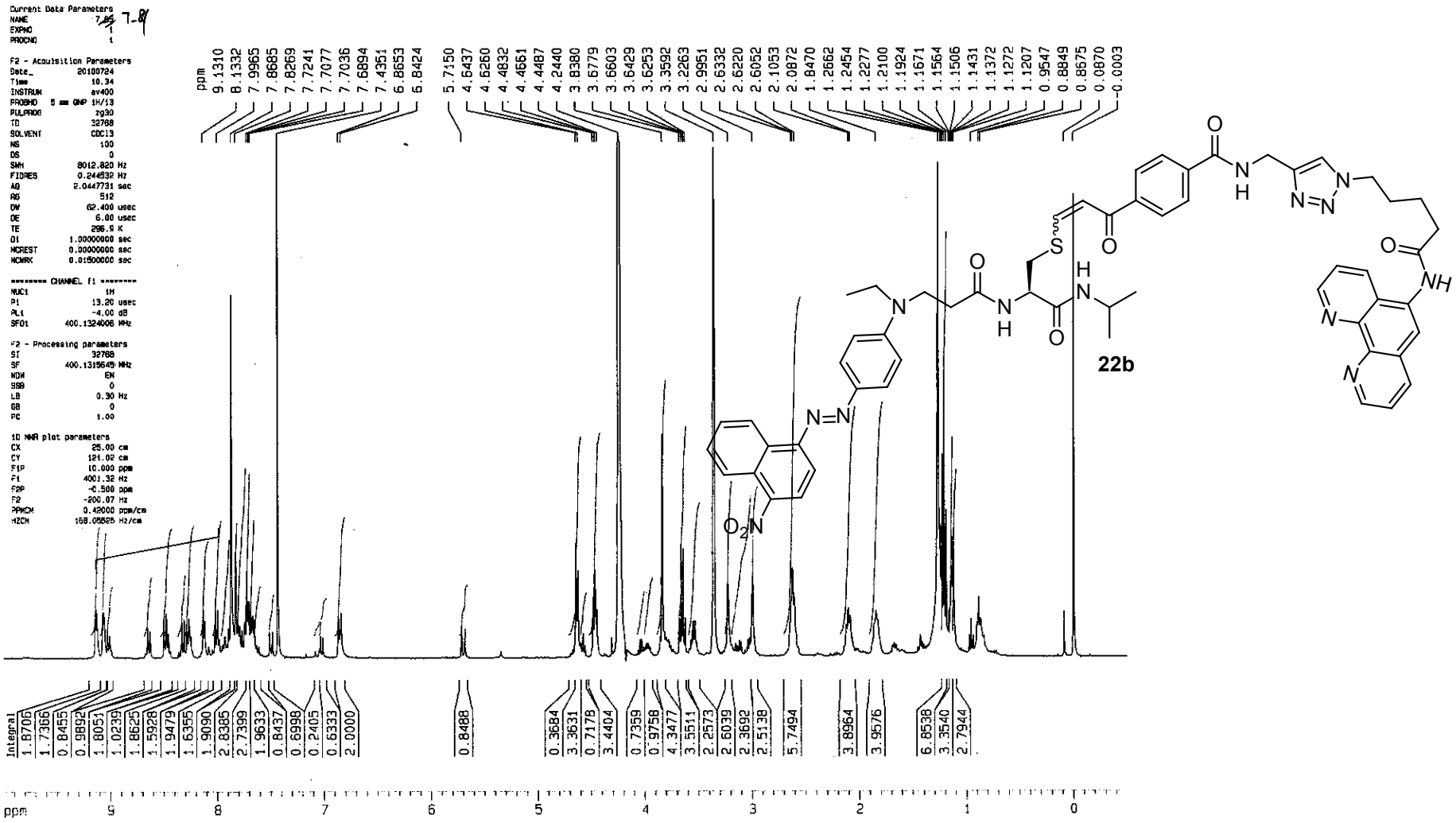
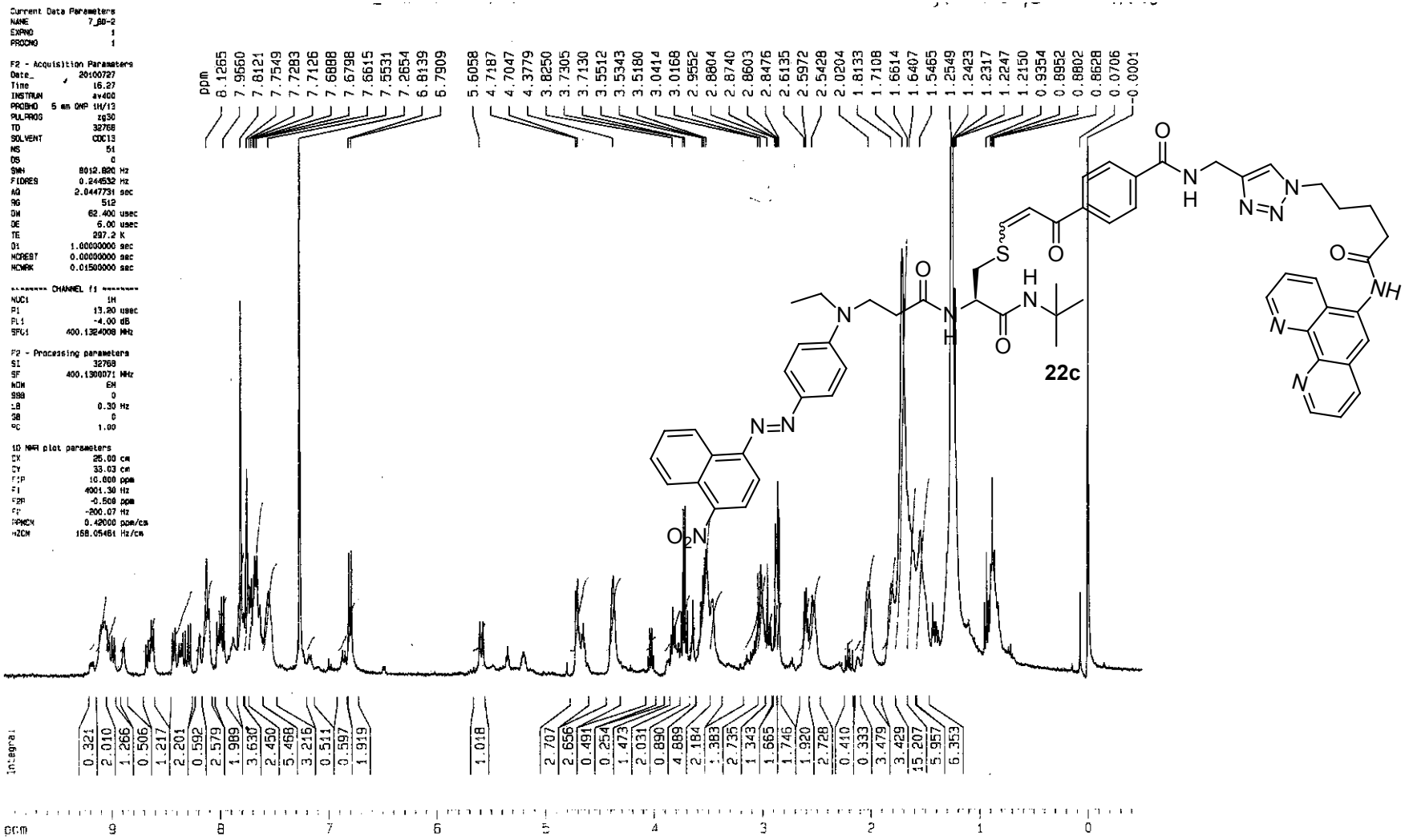
NAME 7_61C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100705
Time 9.40
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 60
DS 0
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 4597.6
DW 19.100 usec
DE 6.00 usec
TE 298.2 K
D1 2.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 12.70 usec
PL1 -5.00 dB
SFO1 100.6238364 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.90 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 25.00 cm
CY 6.86 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.80000 ppm/cm
HZCM 885.38233 Hz/cm
7_61C 9:37 AM 7/5/2010
ppm
172.537
149.641
149.427
148.701
146.024
144.105
135.770
130.941
130.705
128.074
124.585
123.325
122.471
120.506
106.638
77.403
77.085
76.767
51.059
36.138
28.324
22.749
ppm
200
180
160
140
120
100
80
60
40
20

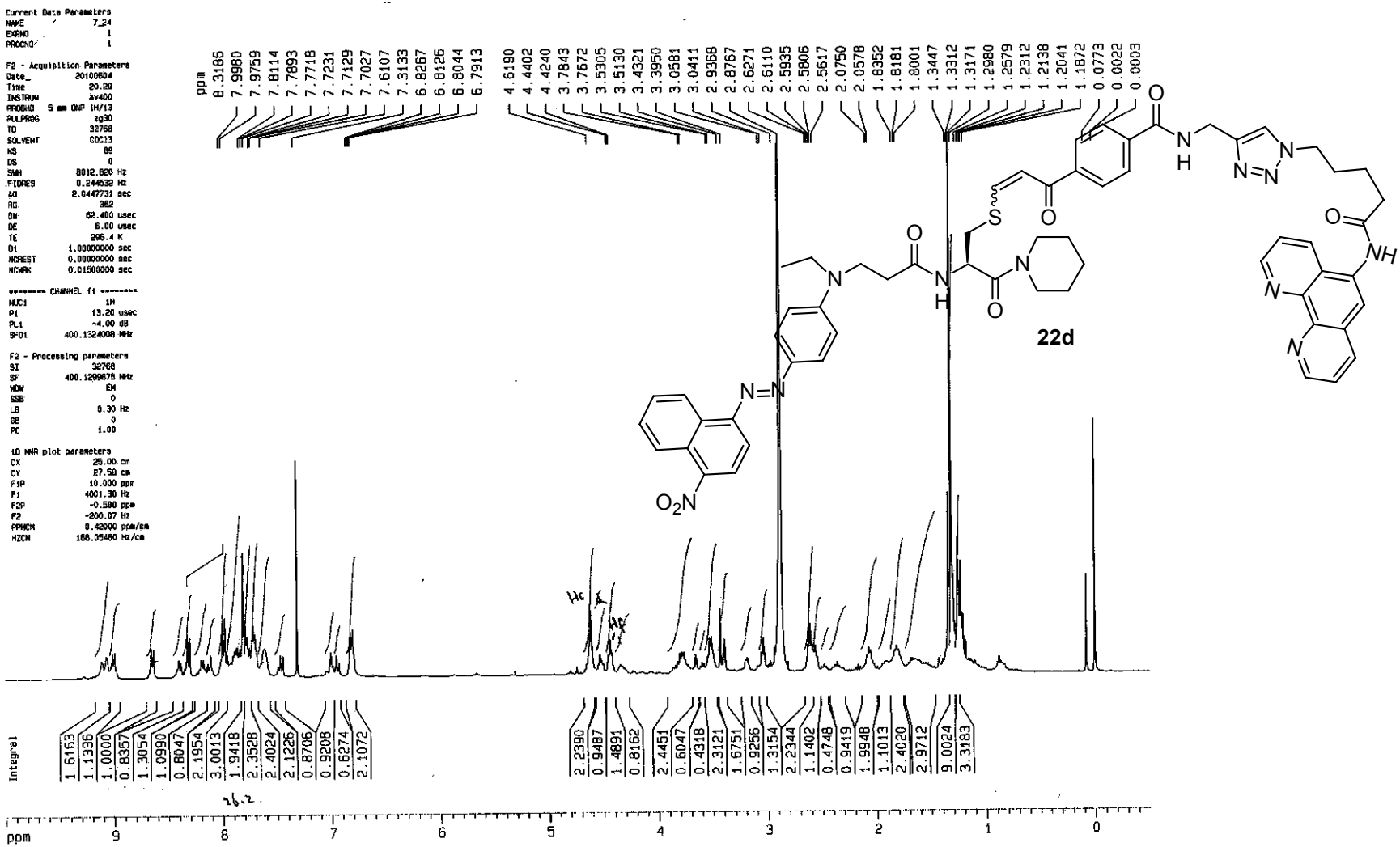

N
N
O
N
H
N3

21


22a


22b


Current Data Parameters
NAME 7_80-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100727
Time 16.27
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 512
DW 62.400 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300071 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 33.03 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05461 Hz/cm
ppm
8.1265
7.9560
7.8121
7.7549
7.7283
7.7126
7.6888
7.6798
7.6615
7.5531
7.2654
6.8139
6.7909
5.6058
4.7187
4.7047
4.3779
3.8250
3.7305
3.7130
3.5512
3.5343
3.5180
3.0414
3.0168
2.9552
2.8804
2.8740
2.8603
2.8476
2.6135
2.5972
2.5428
2.0204
1.8133
1.7108
1.6614
1.6407
1.5465
1.2549
1.2423
1.2317
1.2247
1.2150
0.9354
0.8952
0.8802
0.8628
0.0706
-0.0001
Integral
0.321
2.010
1.266
0.506
1.217
2.201
0.592
2.579
1.989
3.630
2.450
5.468
3.215
0.511
0.597
1.919
1.018
2.707
2.656
0.491
0.254
1.473
2.031
0.890
4.889
2.184
1.383
2.735
1.343
1.665
1.746
1.920
2.728
0.410
0.333
3.479
3.429
15.207
5.957
6.353
ppm
9
8
7
6
5
4
3
2
1
0
22c


Current Data Parameters
NAME 7_24
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100604
Time 20.20
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 88
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 362
DW 62.400 usec
DE 6.00 usec
TE 296.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1299875 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 26.00 cm
CY 27.58 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.580 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05460 Hz/cm
ppm
8.3186
7.9980
7.9759
7.8114
7.7893
7.7718
7.7231
7.7129
7.7027
7.6107
7.3133
6.8267
6.8126
6.8044
6.7913
4.6190
4.4402
4.4240
3.7843
3.7672
3.5305
3.5130
3.4321
3.3950
3.0581
3.0411
2.9368
2.8767
2.6271
2.6110
2.5935
2.5806
2.5617
2.0750
2.0578
1.8352
1.8181
1.8001
1.3447
1.3312
1.3171
1.2980
1.2579
1.2312
1.2138
1.2041
1.1872
0.0773
0.0022
0.0003
22d
Integral
1.6163
1.1336
1.0000
0.8357
1.3054
1.0990
0.8047
2.1954
3.0013
1.9418
2.3528
2.4024
2.1226
0.8706
0.9208
0.6274
2.1072
2.2390
0.9487
1.4891
0.8162
2.4451
0.6047
0.4318
2.3121
1.6751
0.9256
1.3154
2.2344
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0.9419
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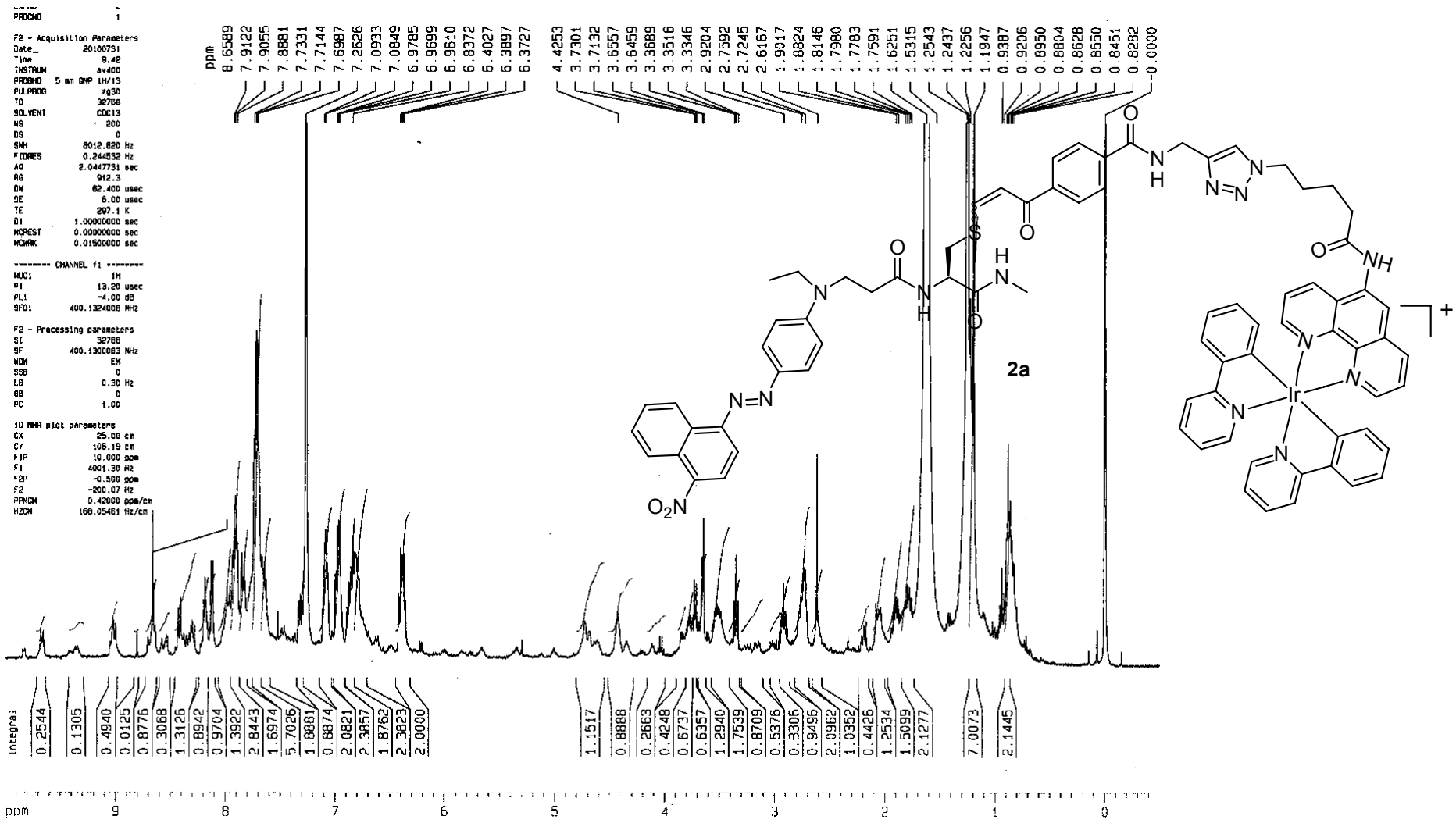
2.9712
9.0024
3.3183
ppm


2a
ppm
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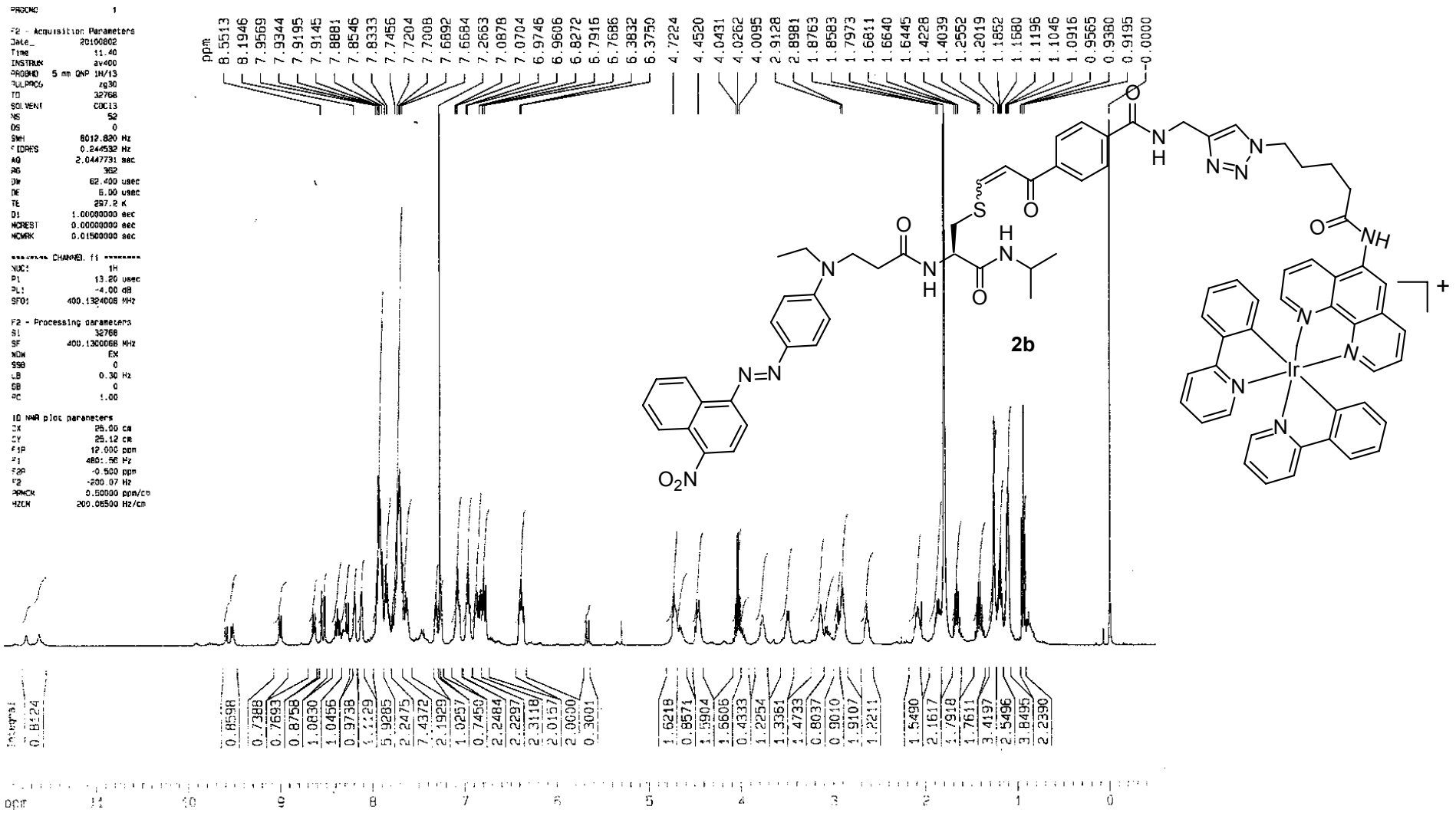
7.9122
7.9055
7.8881
7.7331
7.7144
7.6987
7.2626
7.0933
7.0849
6.9785
6.9699
6.9610
6.8372
6.4027
6.3897
6.3727
4.4253
3.7301
3.7132
3.6557
3.6459
3.3689
3.3516
3.3346
2.9204
2.7592
2.7245
2.6167
1.9017
1.8824
1.8146
1.7980
1.7783
1.7591
1.6251
1.5315
1.2543
1.2437
1.2256
1.1947
0.9387
0.9206
0.8950
0.8804
0.8628
0.8550
0.8451
0.8282
-0.0000
Integral
0.2544
0.1305
0.4940
0.0125
0.8776
0.3068
1.3126
0.8942
0.9704
1.3922
2.8443
1.6974
5.7026
1.8881
0.8874
2.0821
2.3857
1.8762
2.3823
2.0000
1.1517
0.8888
0.2663
0.4248
0.6737
0.6357
1.2940
1.7539
0.8709
0.5376
0.3306
0.9496
2.0962
1.0352
0.4426
1.2534
1.5099
2.1277
7.0073
2.1445
ppm
9
8
7
6
5
4
3
2
1
0


PROBHD 5 mm QNP 1H/13
SOLVENT CDCl3
SFO1 400.1324008 MHz
ppm
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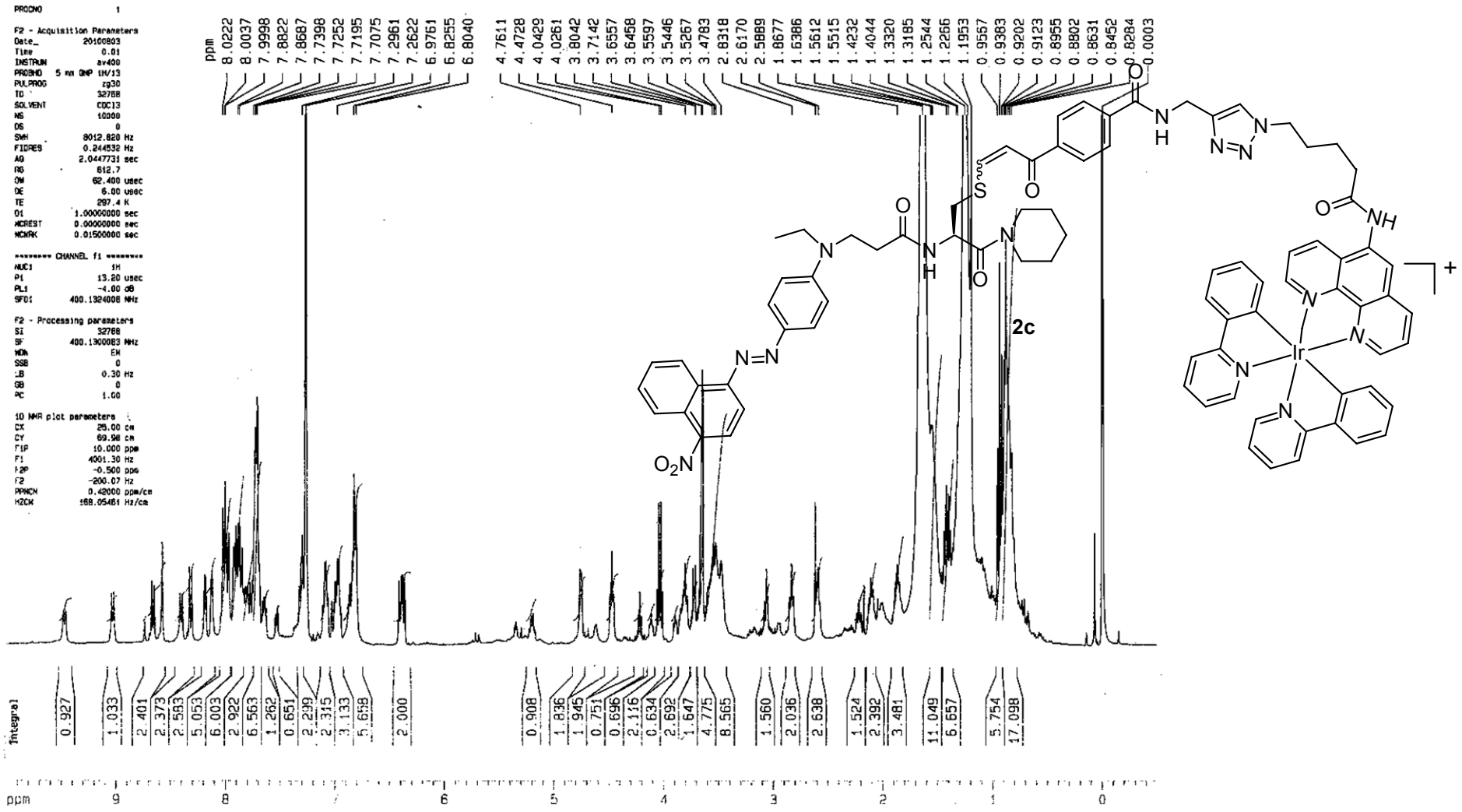
7.9195
7.9145
7.8881
7.8546
7.8333
7.7456
7.7204
7.7008
7.6892
7.6684
7.2663
7.0878
7.0704
6.9746
6.9606
6.8272
6.7916
6.7686
6.3832
6.3750
4.7224
4.4520
4.0431
4.0262
4.0095
2.9128
2.8981
1.8763
1.8583
1.7973
1.6811
1.6640
1.6445
1.4228
1.4039
1.2552
1.2019
1.1852
1.1680
1.1196
1.1046
1.0916
0.9565
0.9380
0.9195
-0.0000
2b
Ir
N=N
O2N
NH
+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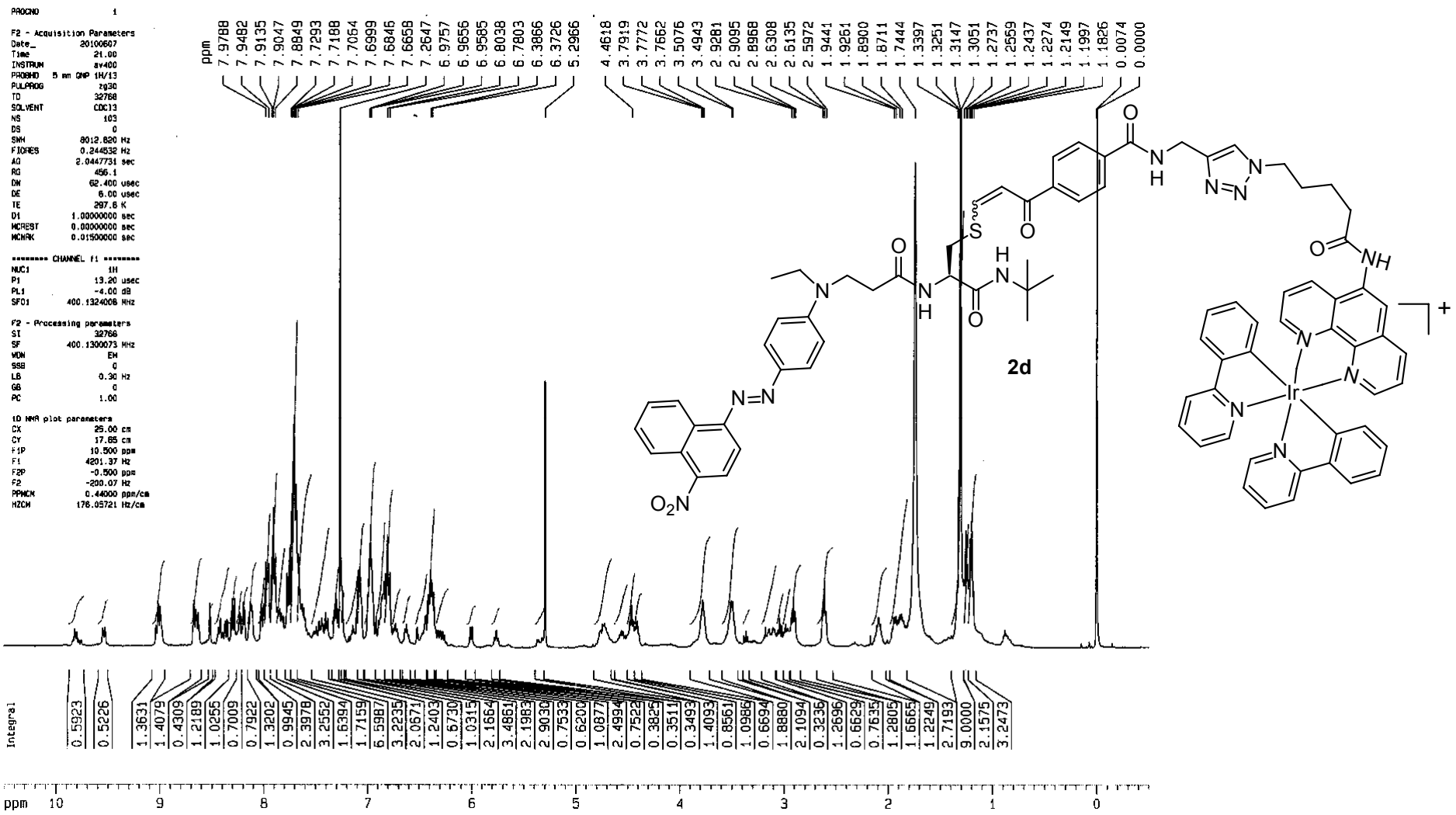
Date_ 20100803
Time 0.01
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 10000
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 812.7
DW 62.400 usec
DE 6.00 usec
TE 297.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300083 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 69.98 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42000 ppm/cm
HZCM 168.05461 Hz/cm
ppm
8.0222 8.0037 7.9998 7.8822 7.8687 7.7398 7.7252 7.7195 7.7075 7.2961 7.2622 6.9761 6.8255 6.8040
4.7611 4.4728 4.0429 4.0261 3.8042 3.7142 3.6557 3.6458 3.5597 3.5446 3.5267 3.4783 2.8318 2.6170 2.5889 1.8677 1.6386 1.5612 1.5515 1.4232 1.4044 1.3320 1.3185 1.2544 1.2266 1.1953 0.9567 0.9383 0.9202 0.9123 0.8955 0.8802 0.8631 0.8452 0.8284 -0.0003
2c
Integral
0.927 1.033 2.401 2.373 2.583 5.053 6.003 2.922 6.563 1.262 0.651 2.299 2.315 3.133 5.658 2.000
0.908 1.836 1.945 0.751 0.696 2.116 0.634 2.692 1.647 4.775 8.565 1.560 2.036 2.638 1.524 2.392 3.481 11.049 6.657 5.754 17.098
ppm 9 8 7 6 5 4 3 2 1 0


PROCNO 1
F2 - Acquisition Parameters
Date_ 20100607
Time 21.00
INSTRUM av400
PROBHD 5 mm GNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 103
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 456.1
DW 62.400 usec
DE 6.00 usec
TE 297.6 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1324006 MHz
F2 - Processing parameters
SI 32768
SF 400.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 25.00 cm
CY 17.65 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.44000 ppm/cm
HZCM 176.05721 Hz/cm
ppm
7.9788 7.9482 7.9135 7.9047 7.8849 7.7293 7.7188 7.7054 7.6999 7.6846 7.6658 7.2647 6.9757 6.9656 6.9585 6.8038 6.7803 6.3866 6.3726 5.2966 4.4618 3.7919 3.7772 3.7662 3.5076 3.4943 2.9281 2.9095 2.8968 2.6308 2.6135 2.5972 1.9441 1.9261 1.8900 1.8711 1.7444 1.3397 1.3251 1.3147 1.3051 1.2737 1.2559 1.2437 1.2274 1.2149 1.1997 1.1826 0.0074 0.0000
2d
Integral
0.5923 0.5226 1.3631 1.4079 0.4309 1.2189 1.0255 0.7009 0.7922 1.3202 0.9945 2.3978 3.2552 1.6394 1.7159 6.5987 3.2235 2.0671 1.2403 0.6730 1.0315 2.1664 3.4861 2.1983 2.9030 0.7533 0.6200 1.0877 2.4994 0.7522 0.3825 0.3511 0.3493 1.4093 0.8561 1.0986 0.6694 1.8880 2.1094 0.3236 1.2696 0.6629 0.7635 1.2805 1.6665 1.2249 2.7193 9.0000 2.1575 3.2473
ppm 10 9 8 7 6 5 4 3 2 1 0