Supplementary Material

Light induced cyclization of tryptamine-naphthoquinone hybrids

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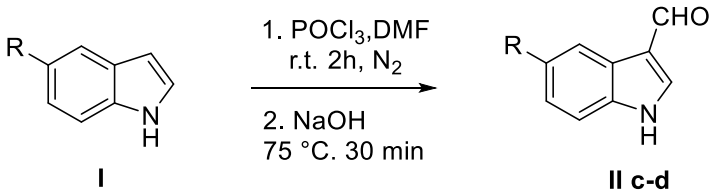
1 Experimental.

General. Reactions were carried out using glass material previously dried in the oven at 100 °C. Flash column chromatography was conducted on Whatman 60 silica gel (230-400 mesh) using gradient systems with previously distilled solvents. Reagents **II a**-**b** were obtained from the Sigma-Aldrich company and used as received. Diethylamine and dimethylformamide were dried over activated 4Å molecular sieves under a nitrogen atmosphere. Solvents were removed by evaporation under reduced pressure on a Büchi rotary evaporator. Infrared spectra were obtained on a Perkin-Elmer FT-IR Spectrum GX spectrophotometer. Melting points were measured in open capillary tubes on a Büchi Melting Point B-540 apparatus and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Ascend spectrometer using chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6). For all ^{1}H spectra TMS δ= 0.0 ppm was used as internal reference. ^{1}H NMR data are given in the following order: chemical shift δ in ppm, multiplicity, coupling constants J in Hertz, and number of hydrogens making up the signal. Microwave reactions were carried out in a CEM Discover microwave reactor. X-ray diffraction analyzes were collected on an Agilent Gemini diffractometer using Mo Kα radiation (l = 0.71073 Å). Data was integrated, scaled, classified, and averaged using the CrysAlisPro software package. The structures were solved using direct methods, SHELX 2014 and refined by full matrix least squares vs. F2.21 All non-hydrogen atoms were anisotropically refined. Position of hydrogen atoms was kept fixed with common isotropic display parameters. Crystallographic data and some details of data collection and refinement are given in Tables **1** and **2**.

2 General procedure for synthesis of compounds II c-d.



I **II c-d**

Hong, W.; Li, J.; Chang, Z.; Tan, X.; Yang, H.; Ouyang, Y.; Yang, Y.; Kaur, S.; Paterson, I.; Ngeow, Y.; Wang, H. Synthesis and biological evaluation of indole core-based derivatives with potent antibacterial activity against resistant bacterial pathogens. *The Journal of Antibiotics,* **2017**, *70*, 832-844.

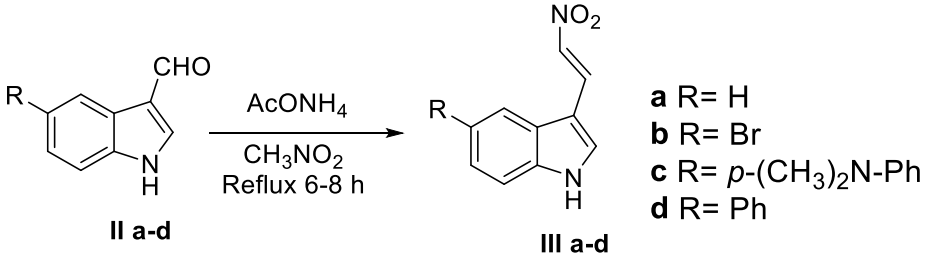
In a 100 ml round-bottom flask, equipped with a magnetic stirrer, the corresponding substituted indole **I** (2.15 mmol, 1 eq.) was added at room temperature. The flask was purged with vacuum/nitrogen cycle three times; then under a nitrogen atmosphere dry

dimethylformamide (10 ml) was added with a syringe, the mixture was left stirring in an ice bath for 10 minutes and then phosphoryl trichloride (0.4 ml, 3.44 mmol, 1.6 eq.) was added. The mixture allowed to react at room temperature for 2 hours, then was added water (20 ml) and NaOH 2M (20 mL) and the mixture was heated at 70-75 °C for 30 minutes and then it was allowed to precipitate overnight without stirring. The resulting solid was vacuum filtered through filter paper, and washed with cold water to obtain the crude indole-3-carbaldehydes **II c**-**d**.

IIc Obtained as a yellow solid, 511 mg (90% yield); **mp**: 236-238 ºC; **IR** (KBr, ν, cm^{-1}): (s, N-H indole), 1634 (vs, C=O), 798 (w, C-H_{Ar}); **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 12.00 (s, 1H), 9.93 (s, 1H), 8.25 (d, *J* = 10.2 Hz, 2H), 7.50 (dd, *J* = 11.5, 8.6 Hz, 4H), 6.80 (d, *J* = 8.3 Hz, 2H), 2.91 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 185.42, 149.93, 139.17, 136.30, 135.47, 129.33, 127.68 (2 C), 125.32, 122.58, 118.71, 117.90, 113.28 (2 C), 113.12 , 40.59 (2 C).

IId Obtained as a brown powder, 433 mg (91% yield); **mp**: 254-256 ºC; **IR** (KBr, ν, cm^{-1}): 3136 (s, N-H indole), 1635 (vs, C=O), 753 (w, C-H_{Ar}); **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 12.15 (s, 1H), 10.00 (s, 1H), 8.36 (d, *J* = 11.8 Hz, 2H), 7.69 – 7.55 (m, 4H), 7.48 (s, 2H), 7.35 (s, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 185.59, 141.66, 139.51, 137.07, 135.25, 129.39 (2 C), 127.34 (2 C), 127.27, 125.22, 123.32, 119.29, 118.87, 113.37.

3 General procedure for synthesis of compounds III a-d.



II a-d **III a-d**

Jin, H.; Zhang, P.; Bijian, K.; Ren, S.; Wan, S.; Alaoui-Jamali, M.; Jiang, T. Total Synthesis and Biological Activity of Marine Alkaloid Eudistomins Y1–Y7 and Their Analogues. *Mar. Drugs* **2013**, 11, 1427-1439.

In a 25 ml round-bottomed flask equipped with a magnetic stirrer and a condenser, were added substituted indole-3-carbaldehyde **II** (350 mg, 1.324 mmol, 1 eq.), ammonium acetate (102 mg, 1.324 mmol, 1 eq.) and nitromethane (5 ml); then the mixture was heated to reflux for 5 hours under a nitrogen atmosphere. After the reaction was complete, water was added and extracted with ethyl acetate three times. The organic phase was washed with water and brine, then dried over anhydrous sodium sulfate and

concentrated under reduced pressure. Flash chromatography using hexane-ethyl acetate 7:3 as mobile phase gave the corresponding 3-(2-nitrovinyl)-indoles **III a**-**d**.

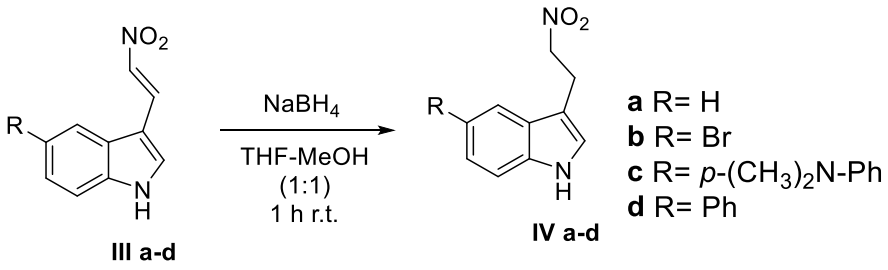
IIIa Obtained as a yellow solid, 239 mg (96% yield); **mp**: 162-164 °C; **IR** (KBr, ν, cm^{-1}): 1360, 1580 cm^{-1} (vs, NO_2), 1610 cm^{-1} (m, C=C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 8.29 (d, J = 13.5 Hz, 1H), 7.80-7.81 (m, 2H), 7.68 (d, J = 2.9 Hz, 1H), 7.48 (dd, J = 6.1, 3.0 Hz, 2H), 7.38 – 7.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 137.25, 133.34, 133.12, 132.20, 124.7, 124.33, 122.67, 120.57, 112.26, 109.79.

IIIb Obtained as a yellow solid, 338 mg (96% yield); **mp**: 200-202 °C; **IR** (KBr, ν, cm^{-1}): 1350, 1520 (vs, NO_2), 1620 (m, C=C), 1120 (w, C=C-Br); **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 12.37 (s, 1H), 8.39 (d, J = 13.5 Hz, 1H), 8.28 (s, 1H), 8.23 (d, J = 1.7 Hz, 1H), 8.10 (d, J = 13.5 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.40 (dd, J = 8.6, 1.8 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 137.11, 136.83, 134.32, 132.54, 126.95, 126.40, 123.19, 115.15, 108.21.

IIIc Obtained as a black solid, 388 mg (95% yield); **mp** >300 ºC**; IR** (KBr, ν, cm^{-1}): 3436 (s, N-H indole), 1360,1542 cm^{-1} (vs, NO_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 12.24 (s, 1H), 8.46 (d, *J* = 13.4 Hz, 1H), 8.25 (s, 1H), 8.12 (d, *J* = 13.4 Hz, 1H), 8.04 (s, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 2.94 (s, 6H) ; **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 149.99, 136.91, 136.83, 135.39, 135.17, 131.67, 129.27, 128.08 (2 C), 125.97, 122.50, 117.52, 113.54, 113.21 (2 C), 109.00, 40.63 (2 C).

IIId Orange solid, 339 mg (97% yield); **mp**: 104-106 ºC; **IR** (KBr, ν, cm^{-1}): 3247 (s, N-H indole), 1307,1566 cm^{-1} (vs, NO_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 12.31 (s, 1H), 8.47 (d, *J* = 13.4 Hz, 1H), 8.29 (s, 1H), 8.18 (s, 1H), 8.18 (d, *J* = 13.4 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.63 – 7.56 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ: 141.41, 137.64, 137.01, 134.98, 132.08, 129.2 (2 C), 127.70 (2 C), 127.23, 125.89, 123.17, 118.90, 113.68, 109.13.

General procedure for synthesis of compounds **IV a**-**d**.



Jin, H.; Zhang, P.; Bijian, K.; Ren, S.; Wan, S.; Alaoui-Jamali, M.; Jiang, T. Total Synthesis and Biological Activity of Marine Alkaloid Eudistomins Y1–Y7 and Their Analogues. *Mar. Drugs* **2013**, 11, 1427-1439.

In a 25 ml round-bottomed flask, equipped with a magnetic stirrer, 3-(2-nitrovinyl)-substituted indole **III** (150 mg, 0.8 mmol), tetrahydrofuran (2.4 ml) and methanol (0.4 ml) were added at room temperature followed by portion wise addition of sodium borohydride (60 mg, 1.6 mmol, 2 eq.) over half an hour with stirring. The mixture was stirred for an additional hour under a nitrogen atmosphere until completion of the reaction was determined by TLC. Then, water (4 ml) and hydrochloric acid (4 ml, 10% v/v) were slowly added to the reaction mixture which was extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography using hexane/ethyl acetate 7:3 as eluant to obtain the desired compounds **IVa-d**.

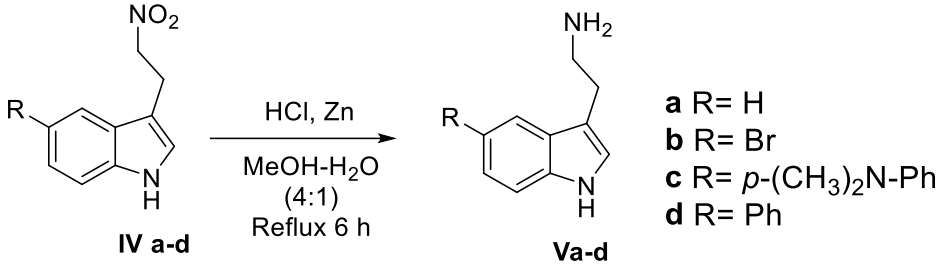
IVa Obtained as a dark brown solid, 114 mg (75% yield); **mp**: 55-56 °C; **IR** (KBr, ν, cm^{-1}): 1390, 1520 cm^{-1} (vs, NO_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.26 (td, J= 8.0, 1.0 Hz, 1H), 7.17 (td, J= 8.0, 1.0 Hz, 1H) 7.10 (d, *J* = 2.3 Hz, 1H), 4.70 (t, *J* = 7.3 Hz, 2H), 3.53 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 136.24, 126.67, 122.56, 122.53, 119.92, 118.13, 111.43, 110.09, 75.71, 23.63.

IVb Obtained as a brown solid, 118 mg (72% yield); **mp**: 90-91 °C; **IR** (KBr, ν, cm^{-1}): 1327,1540 (vs, NO_2), 1070 (m, C=C-Br); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.10 (s, 1H), 7.70 (dd J = 1.7, 0.7 Hz, 1H), 7.32 (dd, J=8.7, 1.8 Hz, 1H), 7.24 (dd, J =8.7, 0.5 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 4.65 (t, J = 7.1 Hz, 1H), 3.44 (td, J = 7.1, 0.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 134.79, 128.40, 125.76, 123.79, 120.78, 113.19, 112.86, 109.78, 75.51, 23.33.

IVc Obtained as a yellow solid, 174 mg (70% yield); **mp**: 105-107 ºC**; IR** (KBr, ν, cm^{-1}): 3395 (s, N-H indole), 1346,1542 (vs, NO_2), 796 (m, C-H_{Ar}); **^{1}H NMR**·(400 MHz, $CDCl_3$) δ: 8.05 (s, 1H), 7.73 – 7.70 (m, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.48 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.71 (t, *J* = 7.3 Hz, 2H), 3.55 (t, *J* = 7.2 Hz, 2H), 3.03 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 149.64, 135.18, 133.84, 130.65, 128.00 (2 C), 127.21, 123.00, 122.13, 115.63, 113.05 (2 C), 111.54, 110.24, 75.59, 40.77 (2 C), 23.66.

IVd Brown solid, 154 mg (72% yield); **mp**: 67-69 ºC**; IR** (KBr, ν, cm^{-1}): 3412 (s, N-H indol), 1367, 1539 cm^{-1} (vs, NO_2), 752 (w, C-H_{Ar}); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 7.81 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 3H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.08 (s, 1H), 4.72 (t, *J* = 7.2 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 142.35, 135.77, 133.62, 128.81, 127.49 (2 C), 127.23, 126.63, 123.38, 122.44, 116.65 (2 C), 111.78, 110.39, 75.77, 23.60.

4 Procedure for synthesis of tryptamines V a-d.



O. Yu. Fedorovskii, A. Yu. Volkonskii S. Golubev, Yu. Ya. Spiridonov, and N. D. Chkanikov. Synthesis of ethyl α-nitro-β-trifl uoromethyl acrylate andβ-trifl uoromethyl-substituted tryptophan analogs andtheir plant growth regulating activity. Russ., Chem. Bull., Int. Ed., Vol. 66, No. 6, June, 2017

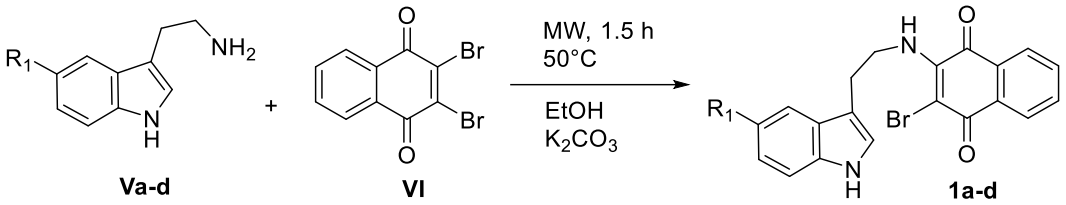
In a 25 ml round-bottom flask fitted with a magnetic stirrer, compound **IV** was added at room temperature (0.26 mmol, 1 eq.), zinc powder (170 mg, 2.6 mmol, 10 eq.), methanol (6 ml), water (1.6 ml) and concentrated hydrochloric acid (0.5 ml). The flask was covered with aluminum foil and heated to reflux for four hours. Then the reaction mixture was allowed to cool and poured in cold water (20 ml) and 30 ml of 2M sodium hydroxide solution was slowly added. Extraction with dichloromethane and concentration under reduced pressure gave crude products **Va-d**.

Va Obtained as a brown solid, 37.4 mg, (90% yield); **mp**: 91-92 °C; **IR** (KBr, ν, cm^{-1}): 3400 (vs, NH_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.17 – 7.13 (m, 1H), 7.05 (s, 1H), 3.07 (t, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 6.6 Hz, 2H), 1.74 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 136.41, 127.49, 121.99, 119.24, 118.88, 113.82, 111.12, 42.37, 29.52.

Vb Obtained as a yellow liquid, 57 mg (92% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.29-7.21 (m, 2H), 7.03 (s, 1H), 3.01 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 1.68 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 135.08, 129.33, 124.77, 123.35, 121.48, 113.42, 112.64, 112.52, 42.25, 29.27

Vc Obtained as a white solid, 61 mg (84% yield); **mp**: 96-98 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.81 (s, 1H), 7.62 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.02 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.11 (t, *J* = 6.5 Hz, 1H), 3.04 (s, 1H), 2.99 (t, *J* = 6.6 Hz, 1H), 1.50 (s, 2H ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 149.54, 135.55, 133.01, 131.20, 128.08, 128.01(2 C), 122.76, 121.50, 116.42, 113.73, 113.16 (2 C), 111.40, 42.39, 40.84 (2 C), 29.52.

5 General procedure for synthesis compounds 1a-d.



a R= H
b R= Br
c R= *p*-$(CH_3)_2$N-Ph
d R= Ph

Phutdhawong, W. S.; Ruensamran, W.; Phutdhawong, W.; Taechowisan, T. Synthesis of 1,6,7,8-tetrahydro-naphtho[2,3-d]-azepino[4,5-b] indole-9,14-diones and their inhibitory effects on pro-inflammatory cytokines. *Bioorg. Med. Chem. Let.* **2009**, *19*, 5753–5756.

In a 10 ml microwave reactor tube, fitted with a magnetic stirrer, at room temperature, was added 2,3-dibromo-2,3-dibromo-1,4-naphthoquinone (119 mg, 0.378 mmol, 1eq.), tryptamine (0.454 mmol, 1.2 eq.), potassium carbonate (105 mg, 0.756 mmol, 2 eq.), ethanol (3 ml) and allowed to react at 200 W, at 55 °C for 1.5 hours. Once the reaction was complete, the reaction mixture was concentrated under reduced pressure and the residue purified by flash chromatography using hexane/ethyl acetate 7:3 as eluant to give the desired compounds **1a-d**.

1a Obtained as a red solid, 112 mg (75% yield); **mp**: 146-148 °C; **IR** (KBr, ν, cm^{-1}): 3400 (s, N-H), 1559 (vs, C=O), 1250 (m, C=C-Br), 1072 (w, C=C-N); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 7.3 Hz, 1H), 8.06 (s, 1H), 7.96 (d, *J* = 6.4 Hz, 1H), 7.69 (td, *J* = 7.6, 1.3 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.60 (td, *J* = 7.5, 1.3 Hz, 1H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J*=1.1, 7.4 Hz, 1H), 7.17-7.12 (m, 2H), 6.16 (s, 2H), 4.22 (dd, *J* = 12.9, 6.6 Hz, 2H), 3.16 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 180.30, 175.47, 148.37, 135.40, 135.10, 132.90, 132.08, 130.40, 129.47, 126.91, 126.38, 125.46, 123.91, 121.27, 113.80, 111.63, 111.18, 107.35, 45.32, 27.03.

1b Obtained as a red solid, 125 mg (70% yield); **mp**: 170-172 °C; **IR** (KBr, ν, cm^{-1}): 3450 (s, N-H), 1575 (vs, C=O), 1280 (w, C=C-Br), 1050 (w, C=C-N); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 7.4 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.77 (s, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.15 (s, 1H), 6.11 (s, 1H), 4.21 (q, *J* = 6.6 Hz, 1H), 3.13 (t, *J* = 6.5 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 180.32, 176.58, 149.3, 135.38, 135.12, 132.93, 132.06, 130.41, 129.45, 126.91, 126.38, 125.47, 123.91, 121.26,121.11, 113.80, 111.63, 111.17, 55.34, 27.01.

1c Obtained as a red solid, 73 mg (50% yield); **mp**: 196-198 ºC; **IR** (KBr, ν, cm^{-1}): 3400 (s, N-H), 1559 (vs, C=O), 1250 (w, C=C-Br), 1072 (w, C=C-N); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.17 – 8.11 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.4

Hz, 1H), 7.15 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.20 (s, 1H), 4.26 (q, *J* = 5.9 Hz, 2H), 3.21 (t, *J* = 6.8 Hz, 2H), 3.02 (s, 6H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 183.08, 180.08, 149.56, 135.50, 134.69, 133.57, 132.27, 131.91, 130.81, 127.96 (2 C), 127.54, 126.83, 126.27, 126.19, 123.09, 122.60, 122.00, 116.21, 113.08 (2 C), 112.00, 111.46, 100.8, 42.53, 40.78 (2 C), 26.76.

1d Obtained as a red solid, 80 mg (40% yield); **mp**: 148-150 °C; **IR** (KBr, ν, cm^{-1}): 3400 (s, N-H), 1559 (vs, C=O), 1250 (m, C=C-Br), 1072 (w, C=C-N); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 8.14 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.84 – 7.83 (m, 1H), 7.72 – 7.70 (m, 1H), 7.69 – 7.66 (m, 2H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.37 – 7.32 (m, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 6.20 (s, 1H), 4.26 (q, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 183.06, 180.06, 146.75, 142.37, 136.04, 134.71, 133.40, 132.31, 129.88, 128.70 (2 C), 127.53, 127.40 (2 C), 127.32, 126.96, 126.83, 126.47, 123.79, 123.34, 122.34, 117.20, 112.20, 111.61, 45.24, 26.72.

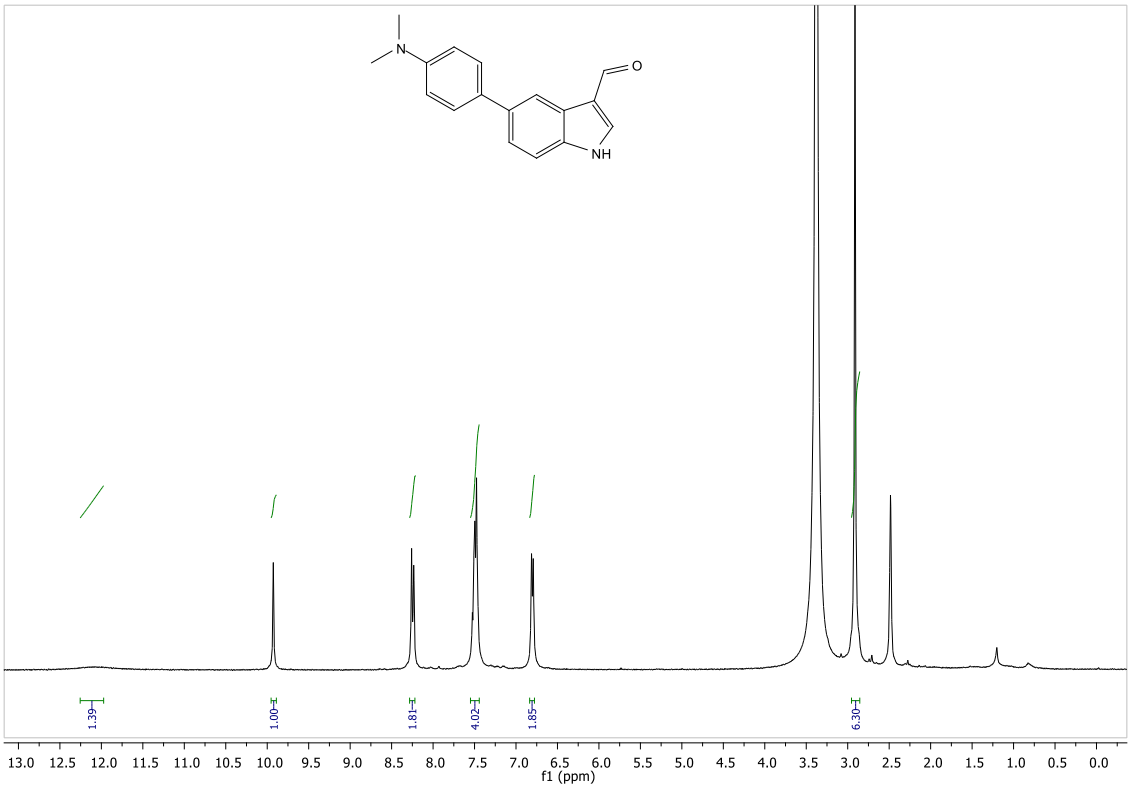
6 Table 1. Crystallographic data for compound 2a

Identification code	**dme-26**
Empirical formula	$C_{20}H_{14}N_2O_2$
Formula weight	314.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.3473(3)
b/Å	12.3544(5)
c/Å	18.6806(7)
α/°	90.00
β/°	94.227(4)
γ/°	90.00
Volume/Å^3	1460.89(11)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	0.756
F(000)	656.0
Crystal size/mm^3	0.11 × 0.09 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.58 to 155.08
Index ranges	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	18627
Independent reflections	3092 [R_{int} = 0.0555, R_{sigma} = 0.0353]
Data/restraints/parameters	3092/0/217
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0472, wR_2 = 0.1221
Final R indexes [all data]	R_1 = 0.0662, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19

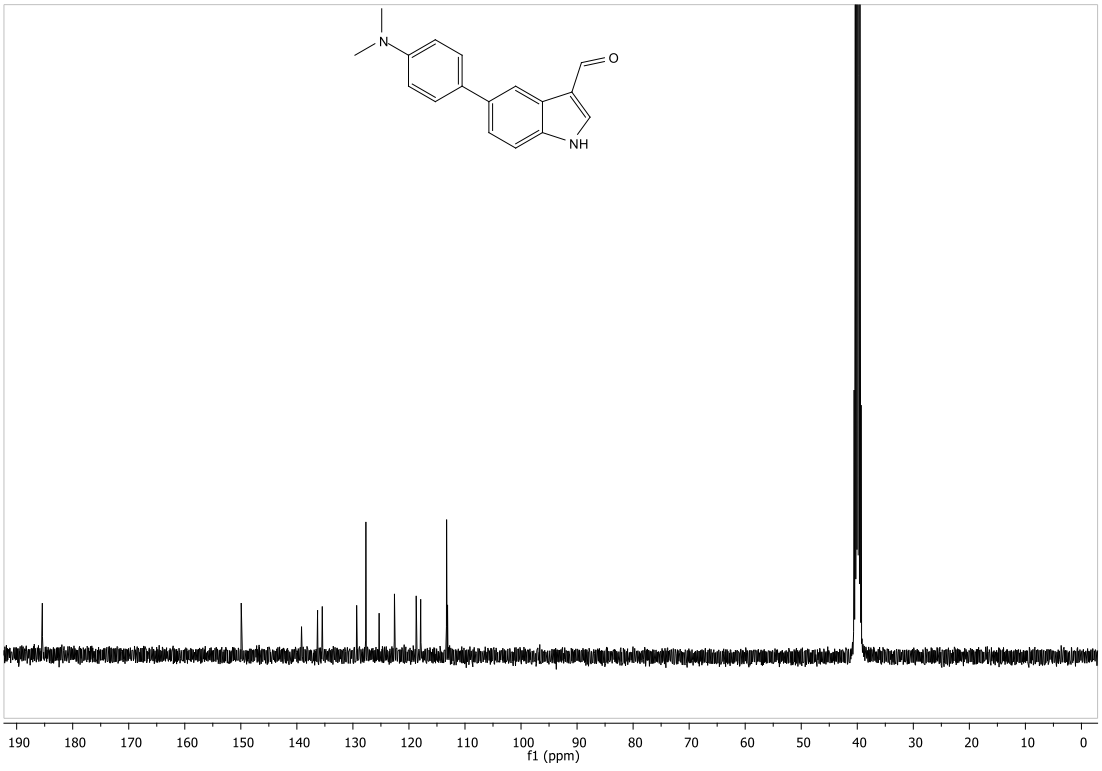
7Table 2. Crystallographic data for compound 2b

Identification code	**dme-33**
Empirical formula	$C_{20}H_{17}BrN_4O_2$
Formula weight	397.29
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.3553(16)
b/Å	7.0215(7)
c/Å	15.7962(15)
α/°	90.00
β/°	112.176(12)
γ/°	90.00
Volume/Å^3	1577.1(3)
Z	4
ρ_{calc}g/cm^3	1.673
μ/mm^{-1}	2.619
F(000)	808.0
Crystal size/mm^3	---
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.3 to 59.36
Index ranges	$-21 \le h \le 21$, $-9 \le k \le 9$, $-21 \le l \le 21$
Reflections collected	43549
Independent reflections	4274 [R_{int} = 0.0793, R_{sigma} = 0.0561]
Data/restraints/parameters	4274/0/226
Goodness-of-fit on F^2	1.006
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.0922
Final R indexes [all data]	R_1 = 0.1087, wR_2 = 0.1137
Largest diff. peak/hole / e Å^{-3}	0.39/-0.55

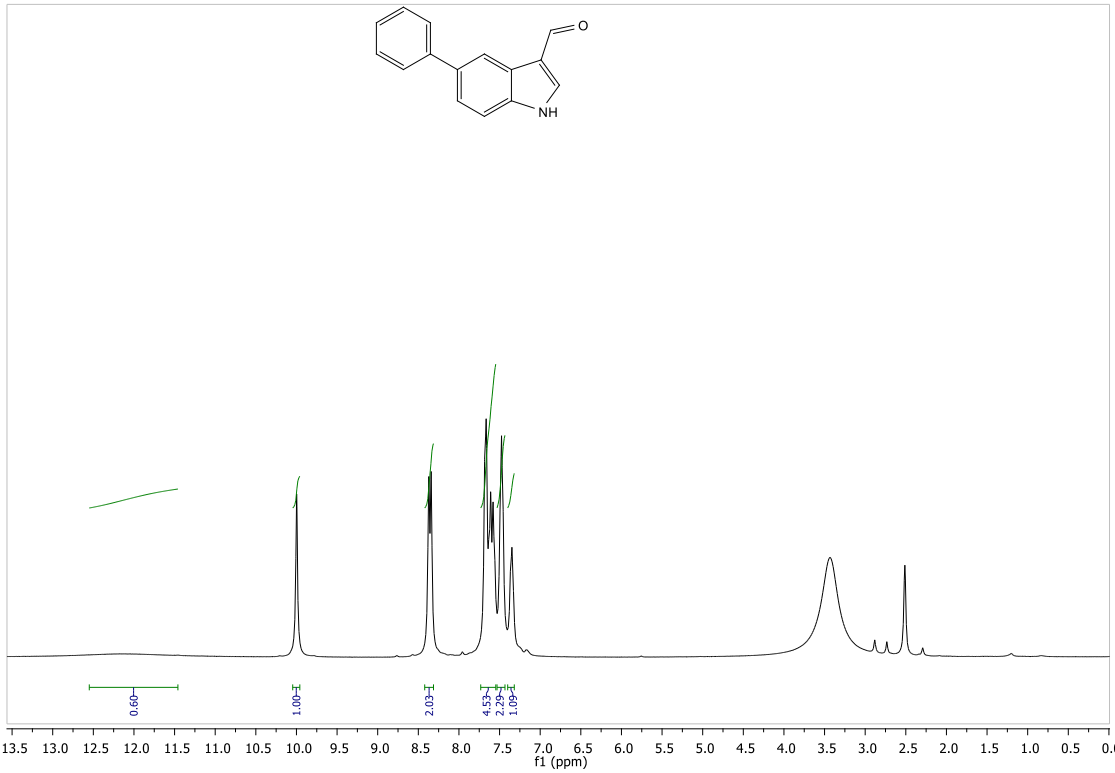
8 NMR spectra



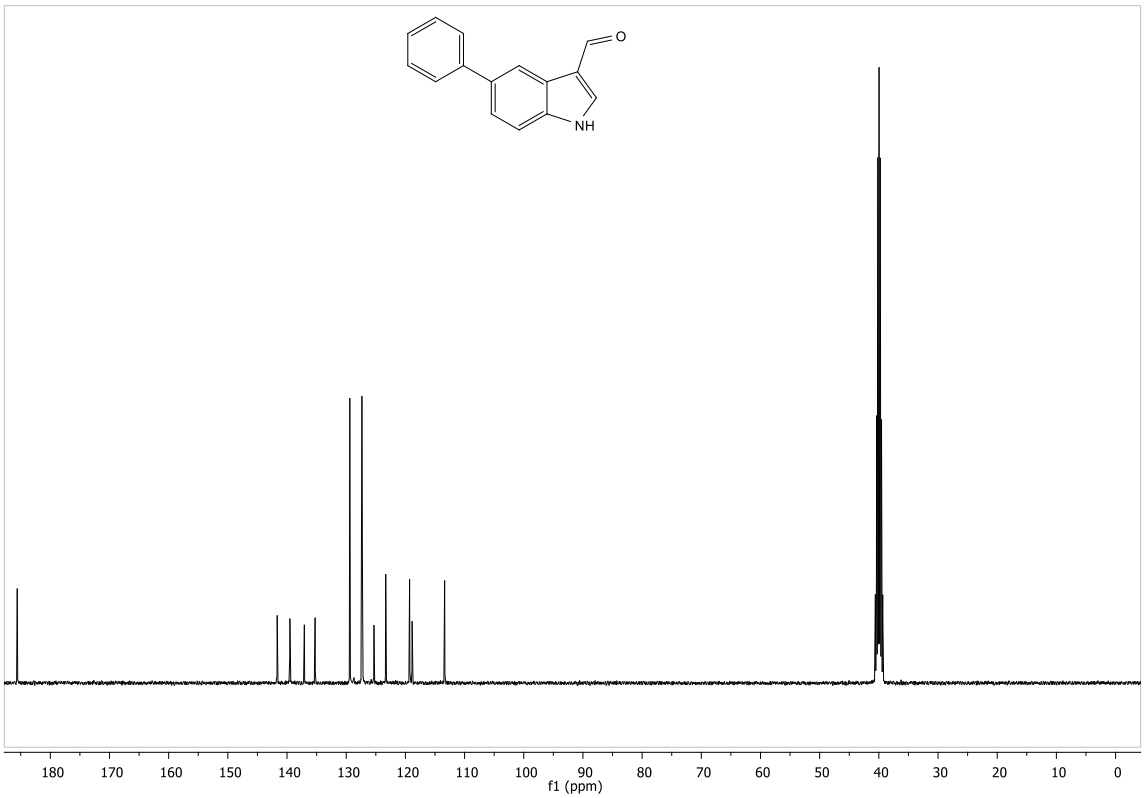
^{1}H NMR spectrum of compound IIc in DMSO-d_6



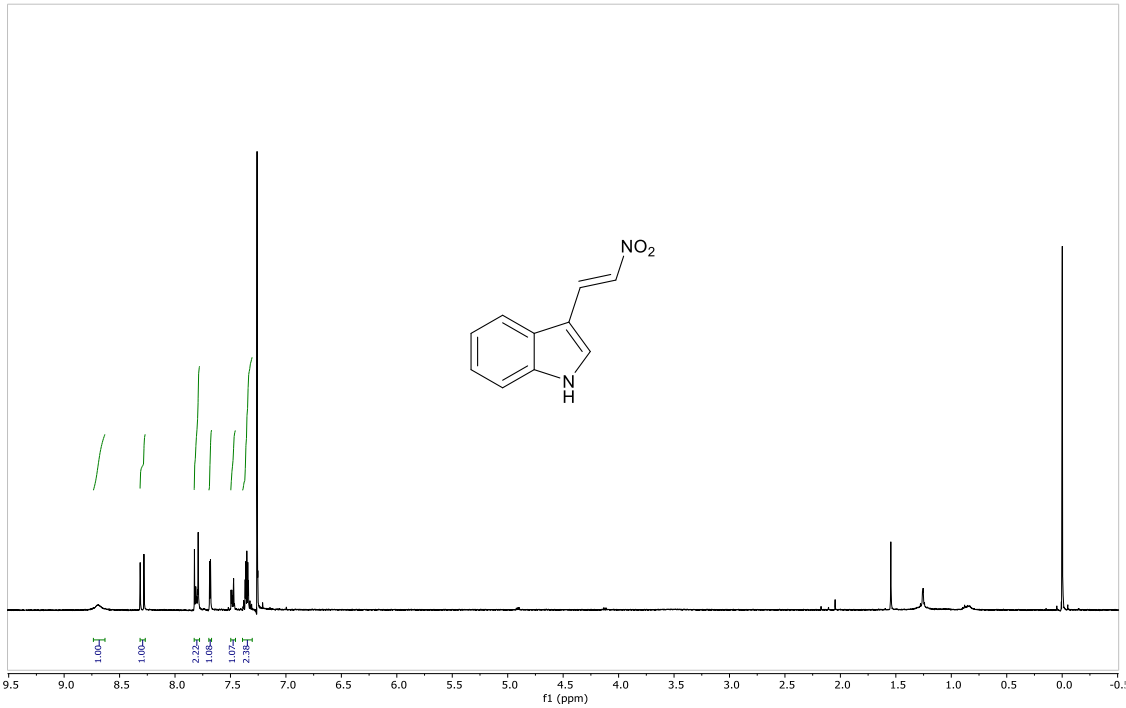
^{13}C NMR spectrum of compound IIc in DMSO-d_6



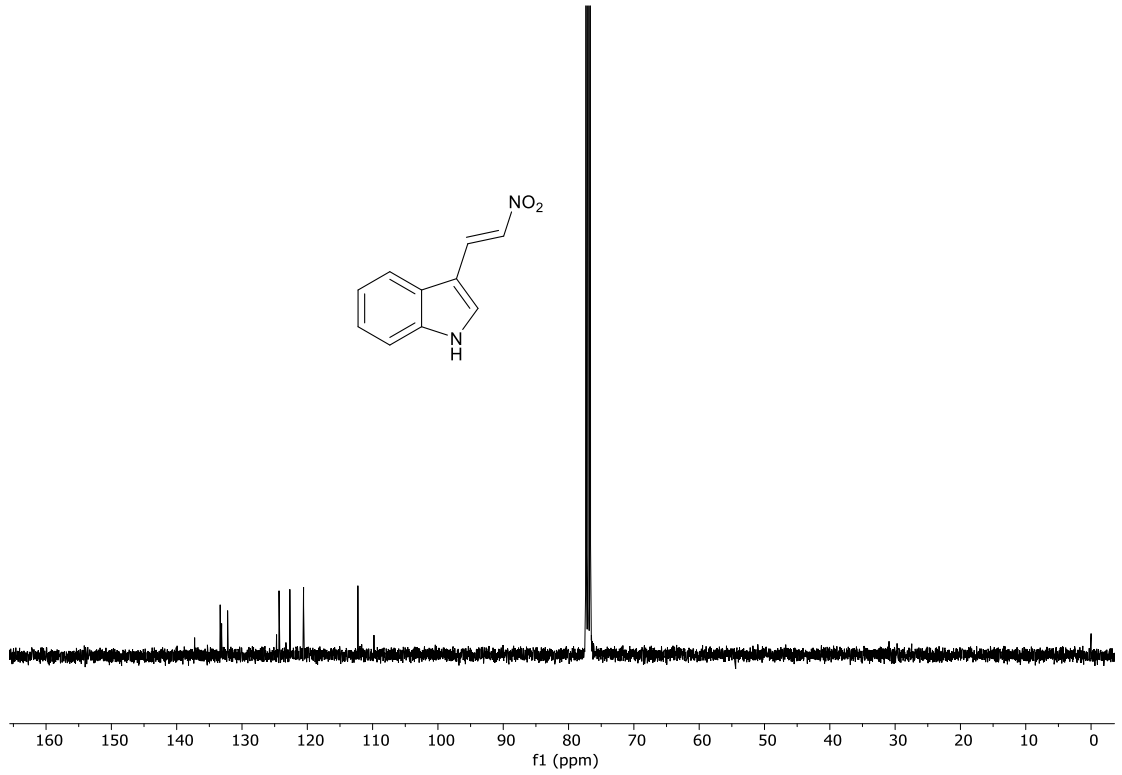
^{1}H NMR spectrum of compound IId in DMSO-d_6



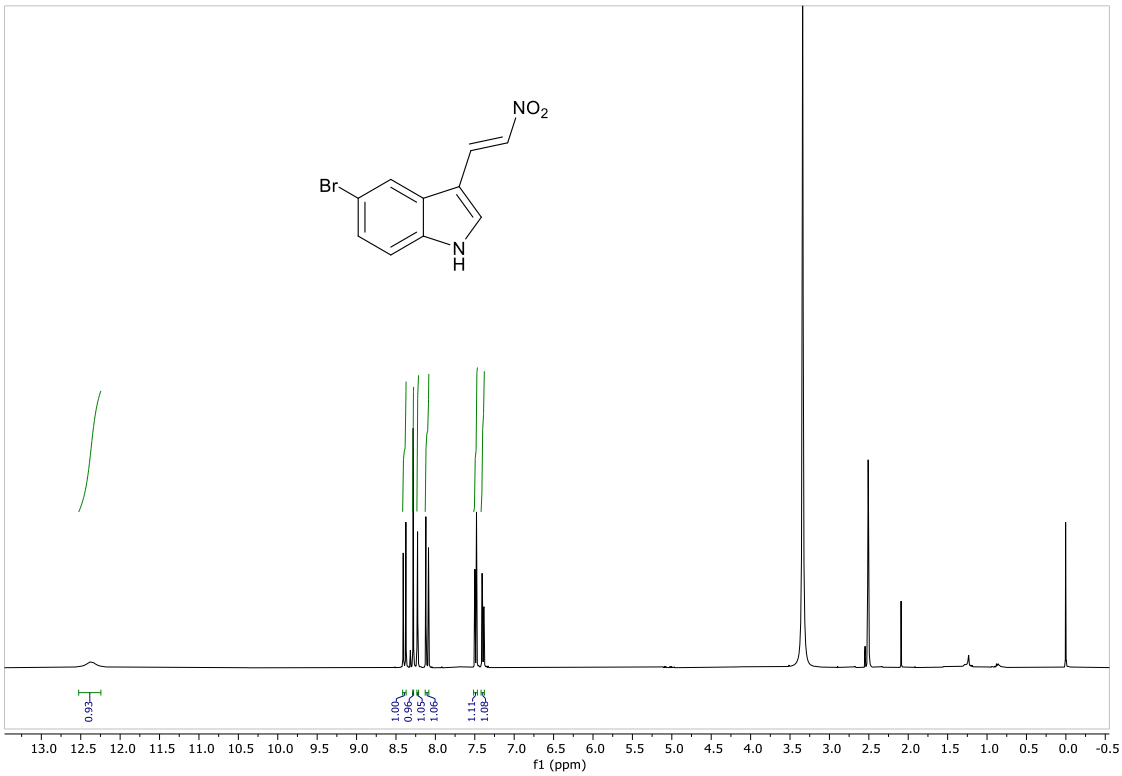
^{13}C NMR spectrum of compound IId in DMSO-d_6



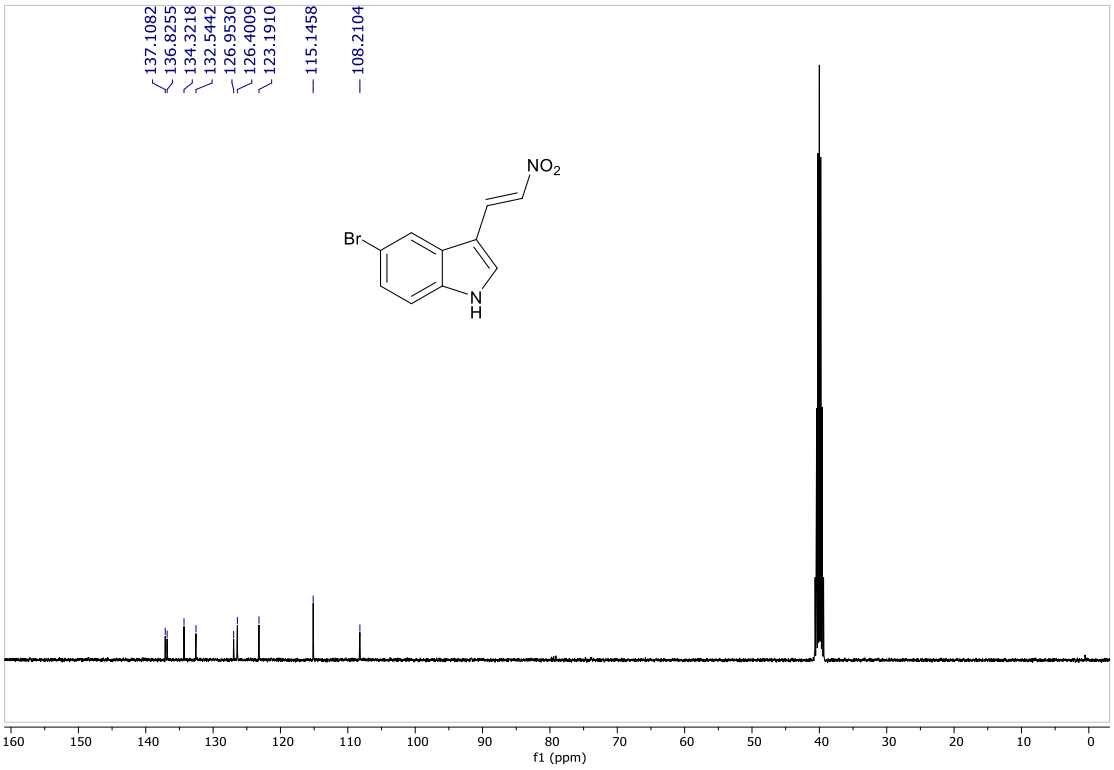
^{1}H NMR spectrum of compound IIIa in $CDCl_3$



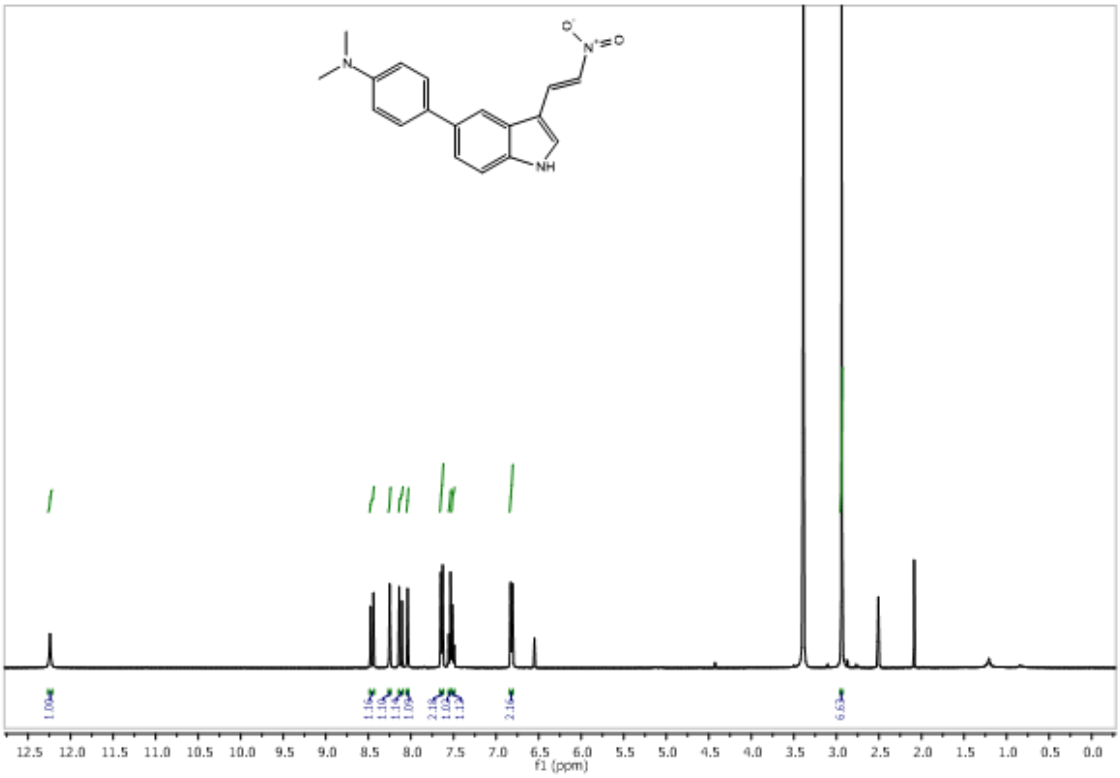
^{13}C NMR spectrum of compound IIIa in $CDCl_3$



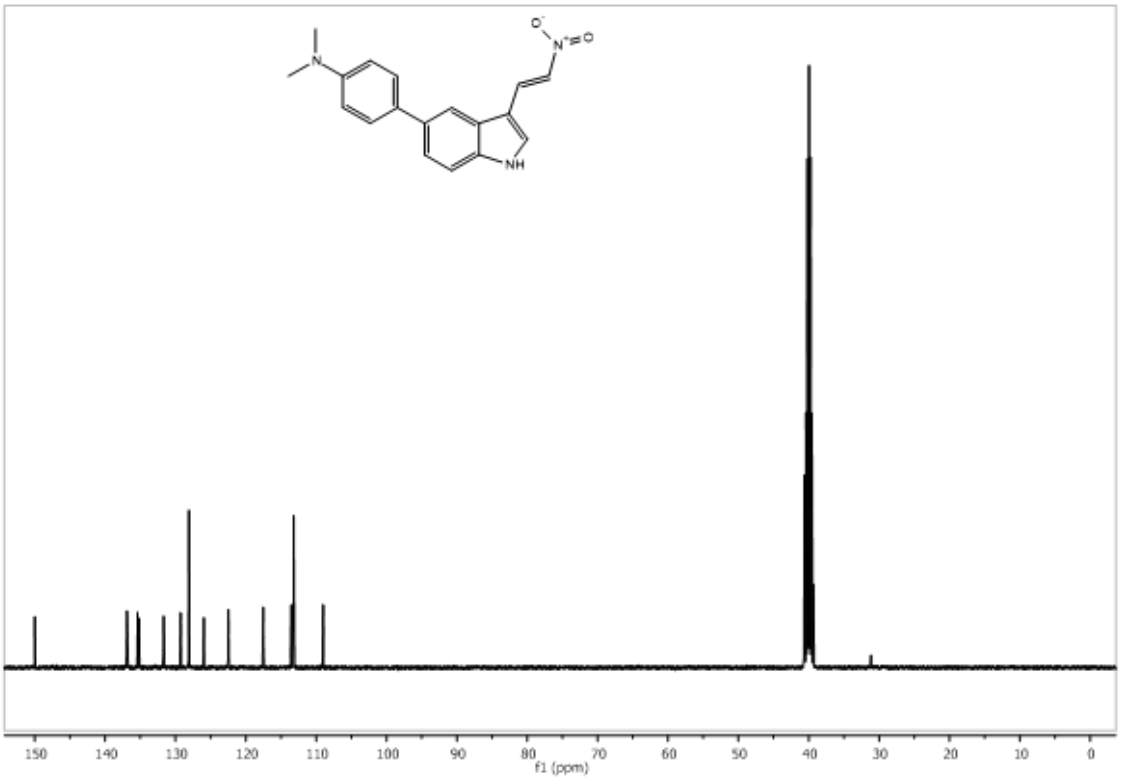
^{1}H NMR spectrum of compound IIIb in DMSO-d_6



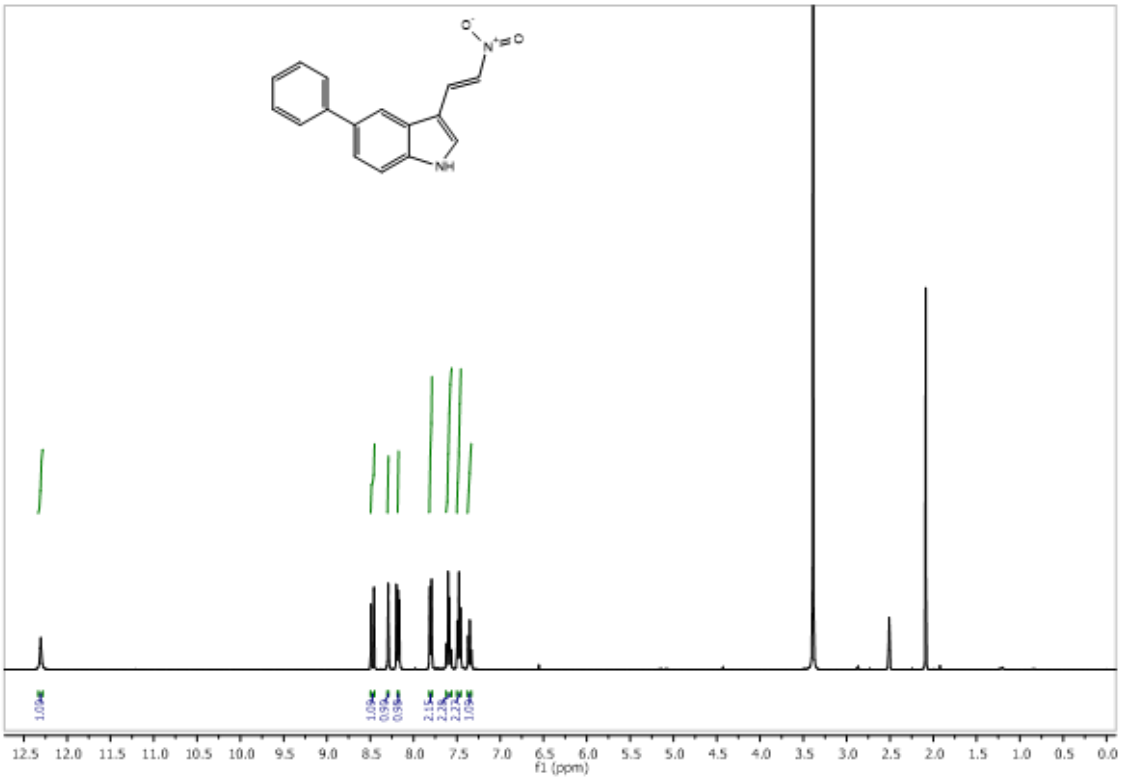
^{13}C NMR spectrum of compound IIIb in DMSO-d_6



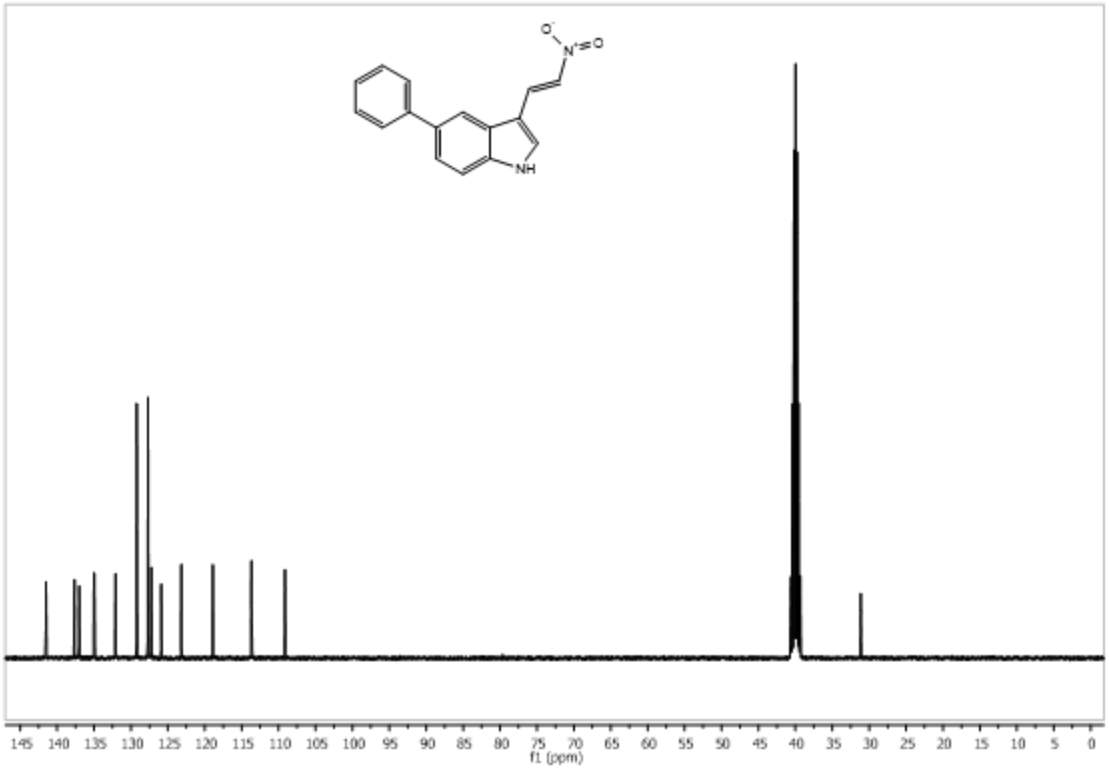
^{1}H NMR spectrum of compound IIIc in DMSO-d$_6$



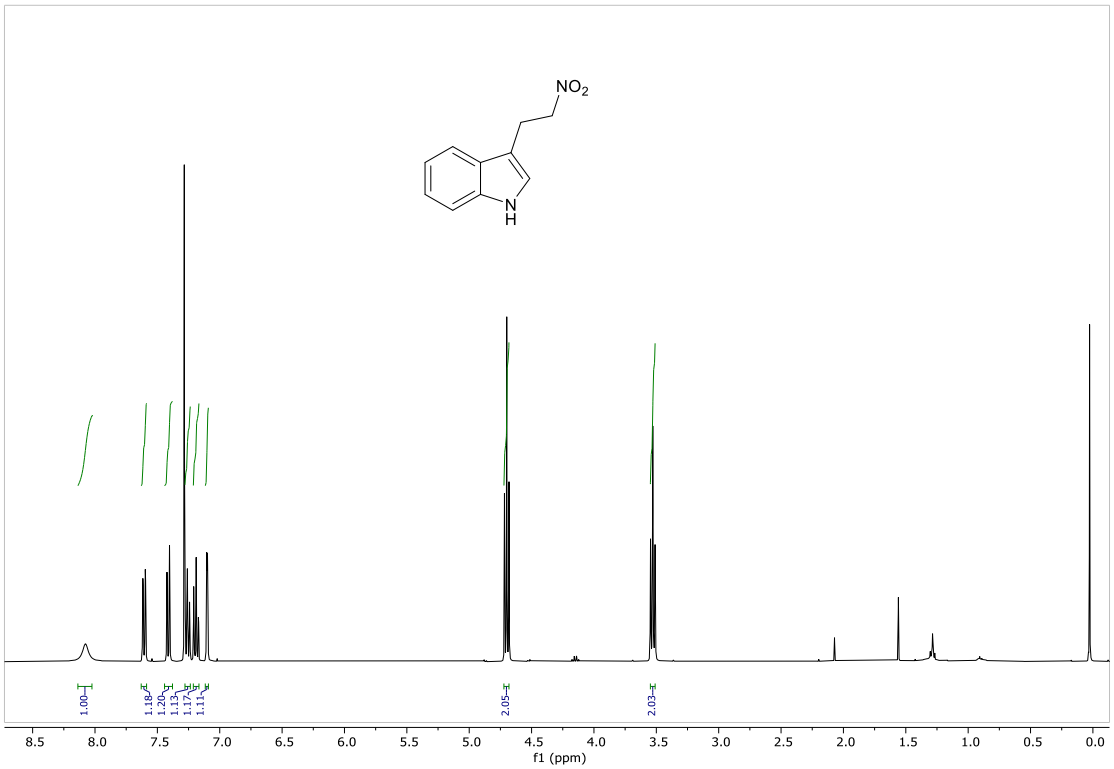
^{13}C NMR spectrum of compound IIIc in DMSO-d$_6$



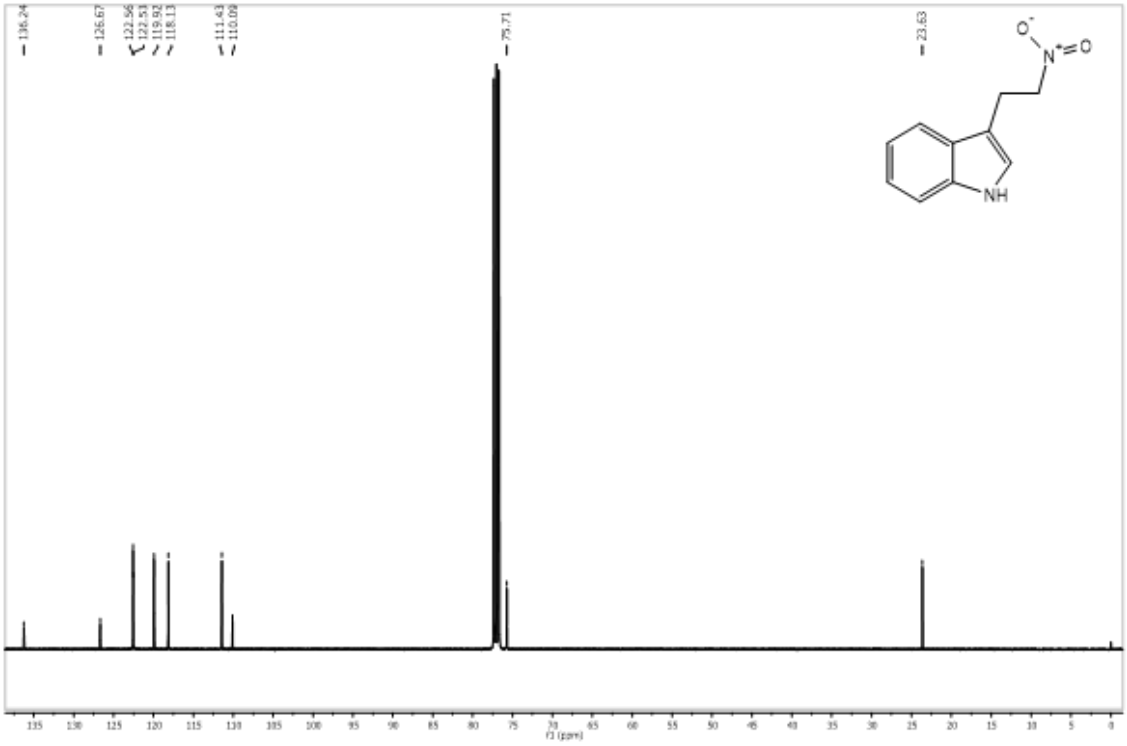
^{1}H NMR spectrum of compound IIId in DMSO-d_6



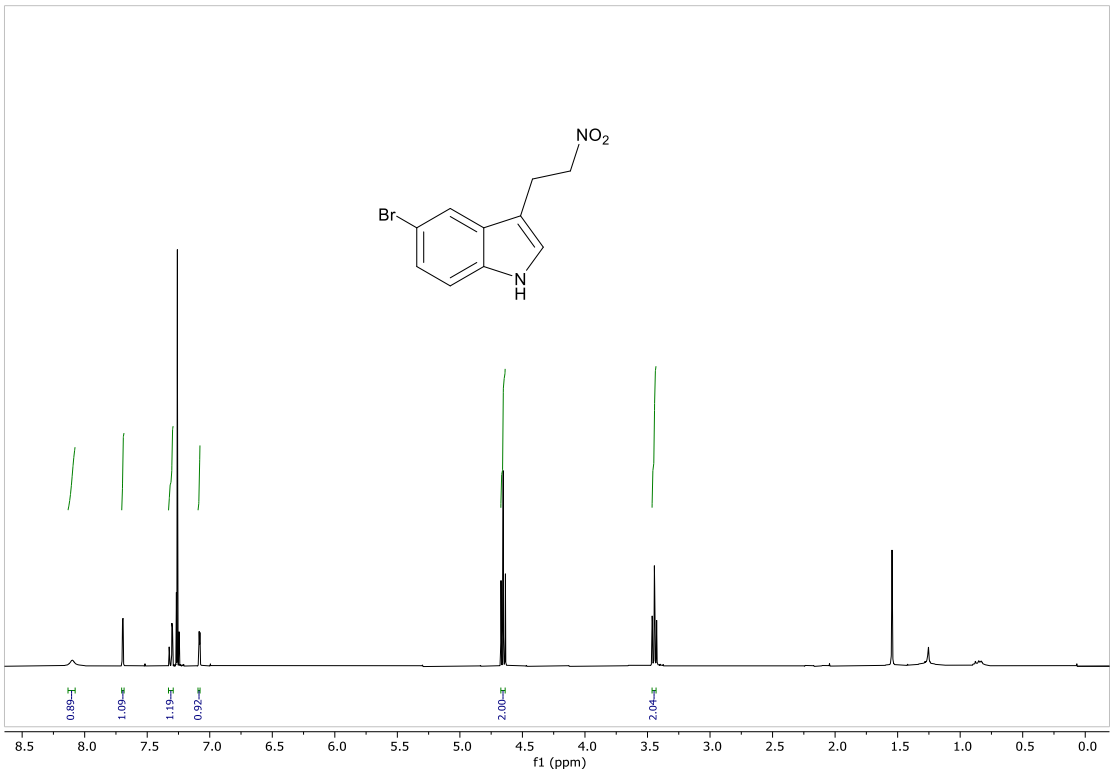
^{13}C NMR spectrum of compound IIId in DMSO-d_6



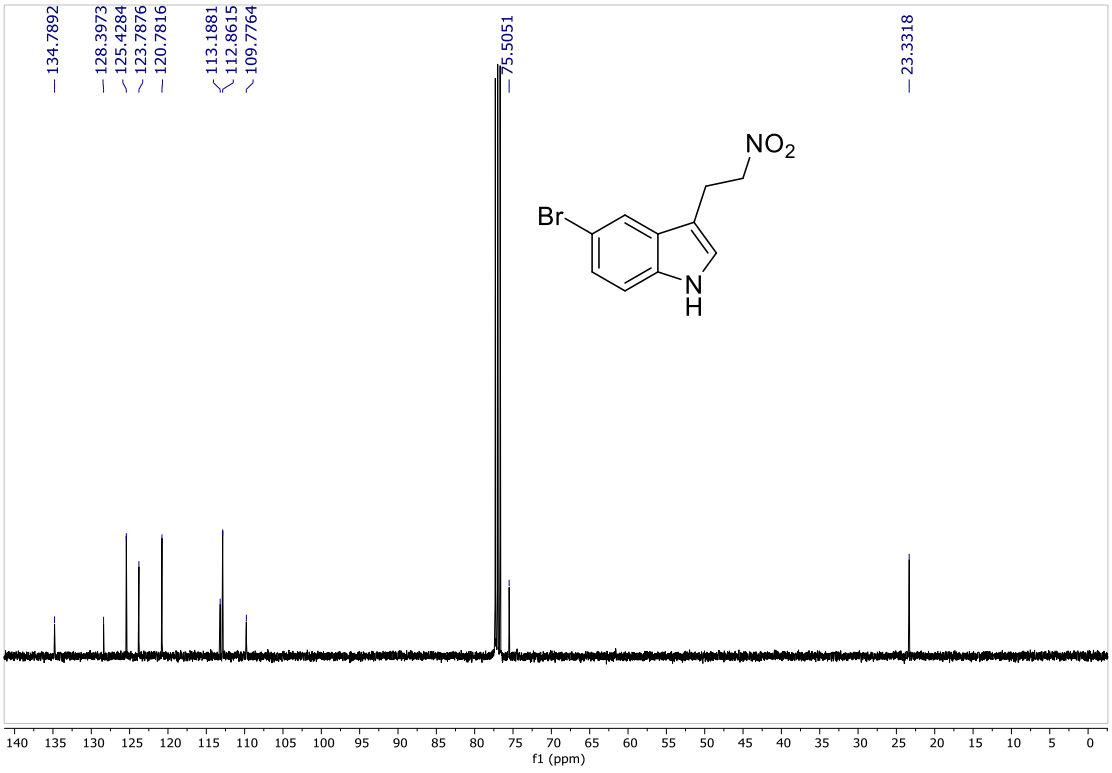
^{1}H NMR spectrum of compound IVa in $CDCl_3$



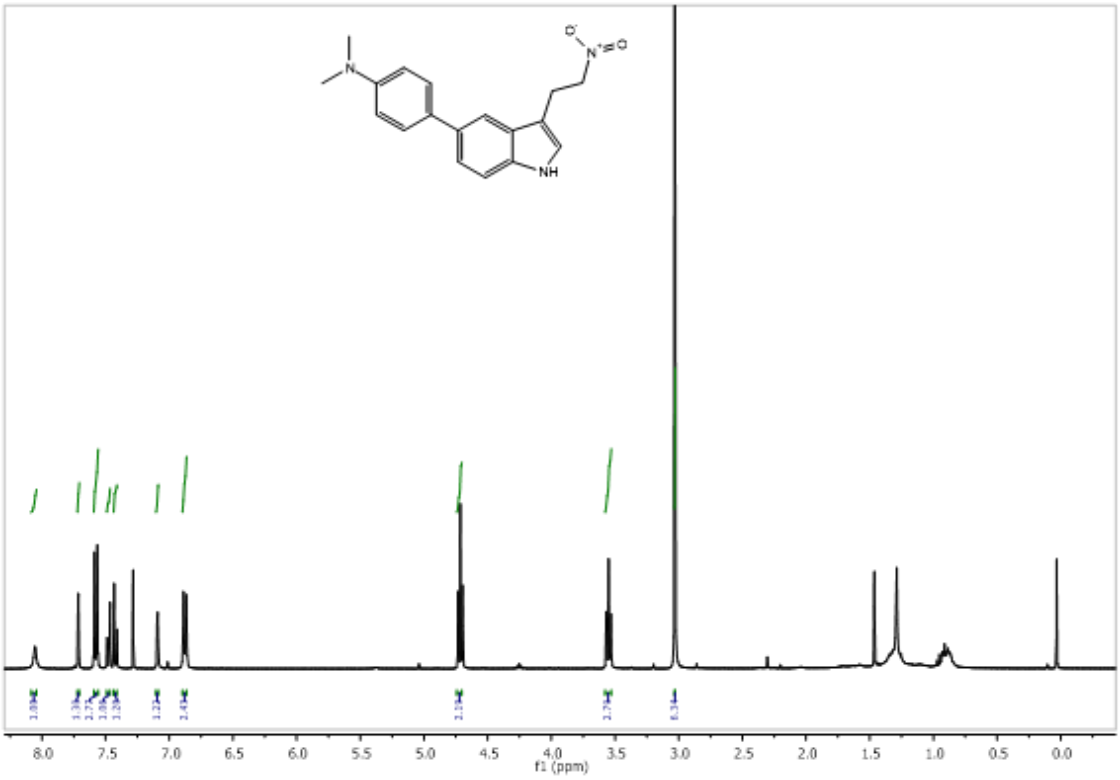
^{13}C NMR spectrum of compound IVa in $CDCl_3$



^{1}H NMR spectrum of compound IVb in$CDCl_3$



^{13}C NMR spectrum of compound IVb in $CDCl_3$



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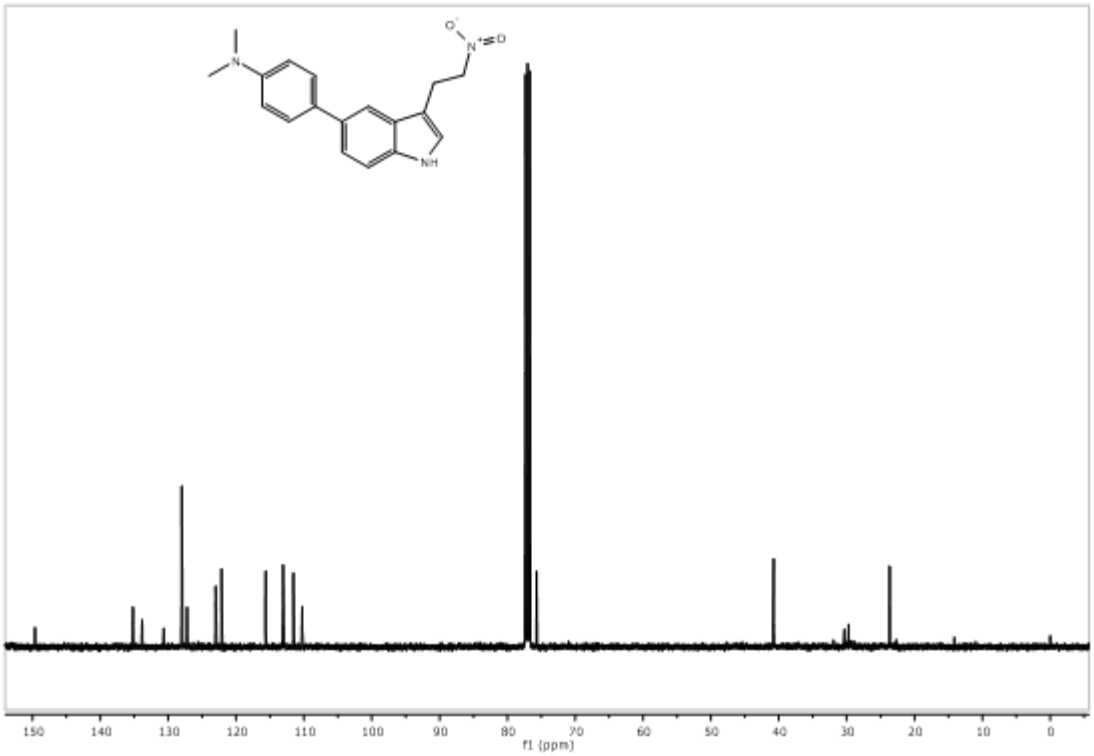
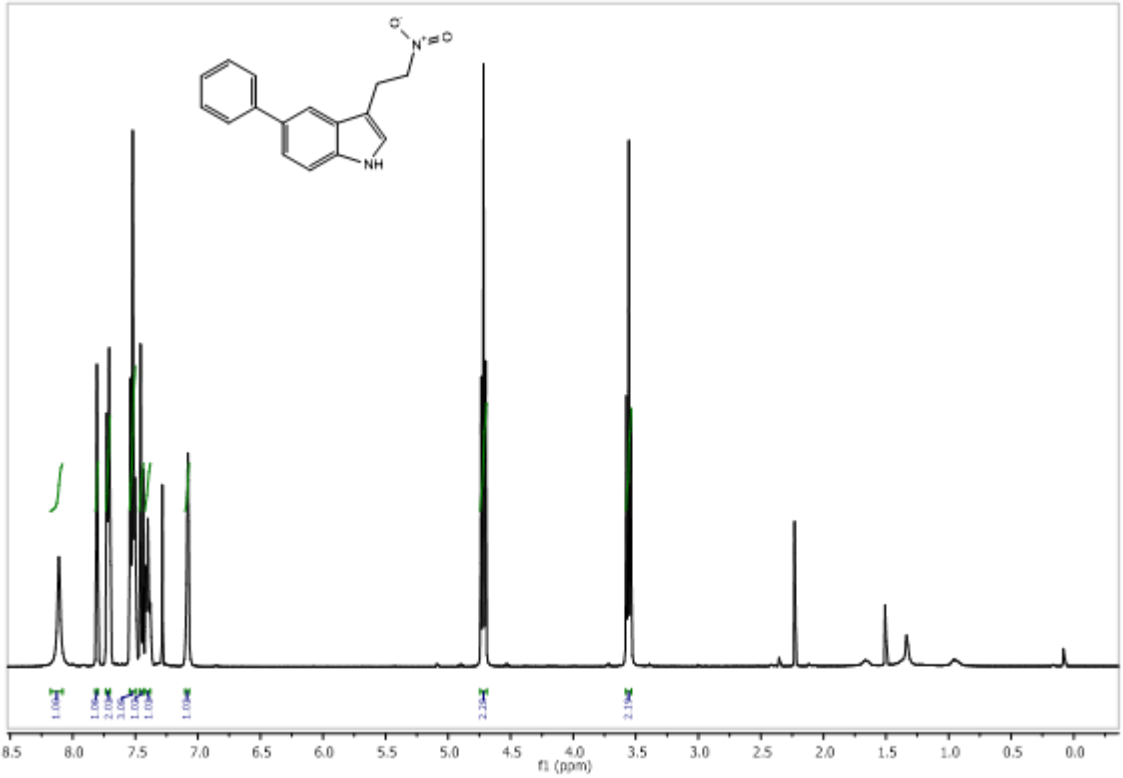
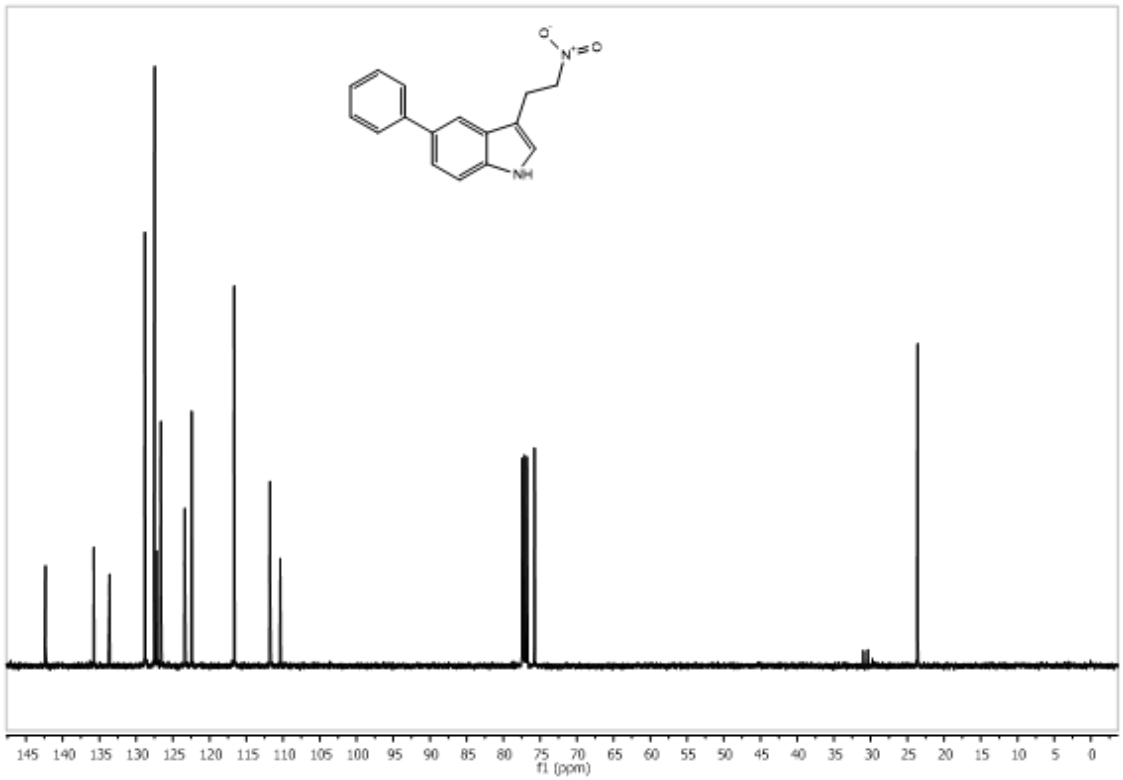


^{13}C NMR spectrum of compound IVc in $CDCl_3$



^{1}H NMR spectrum of compound IVd in $CDCl_3$



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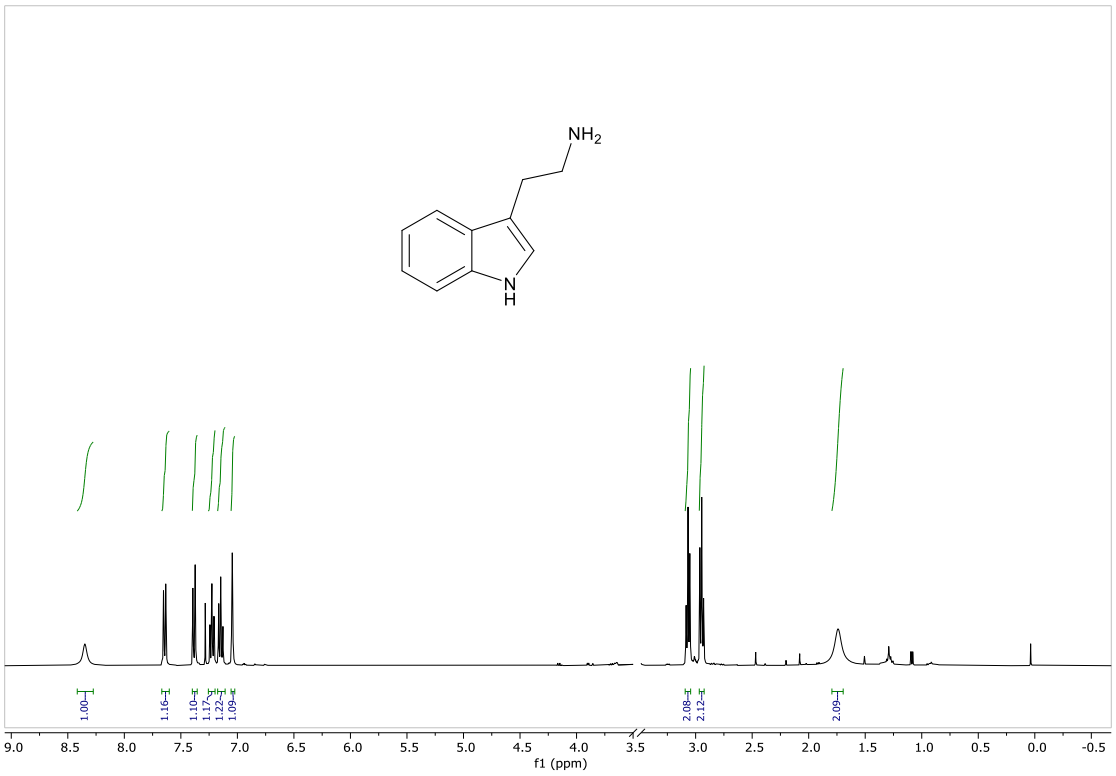
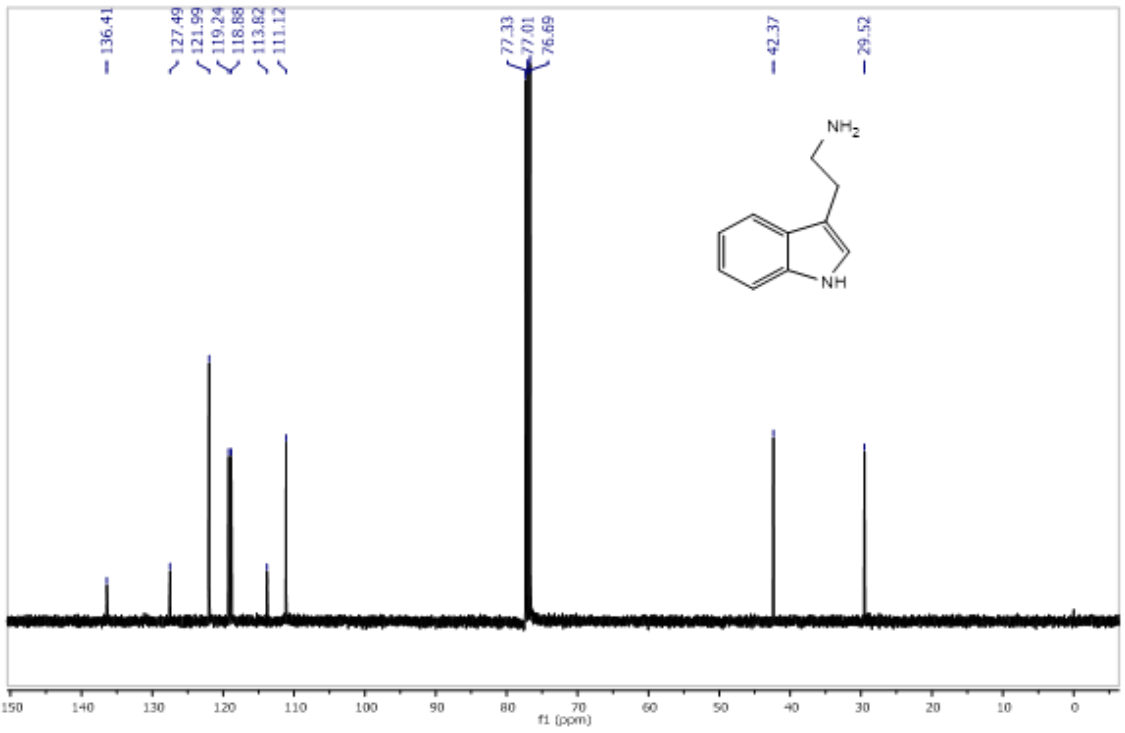
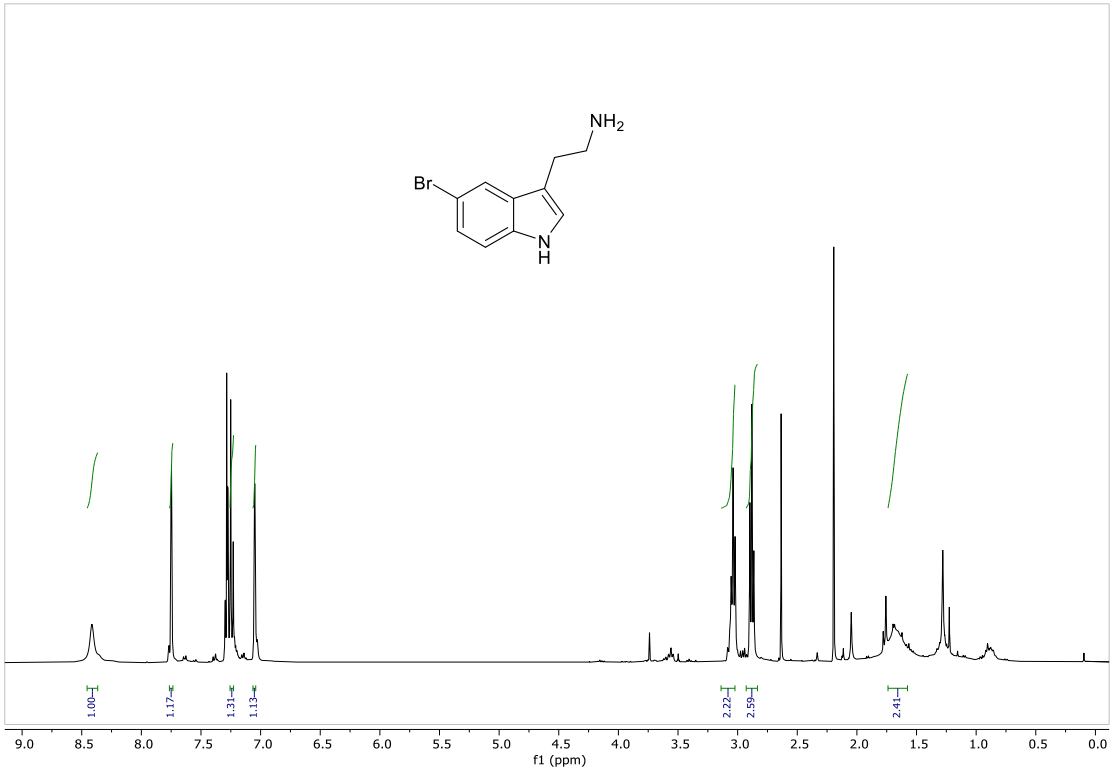


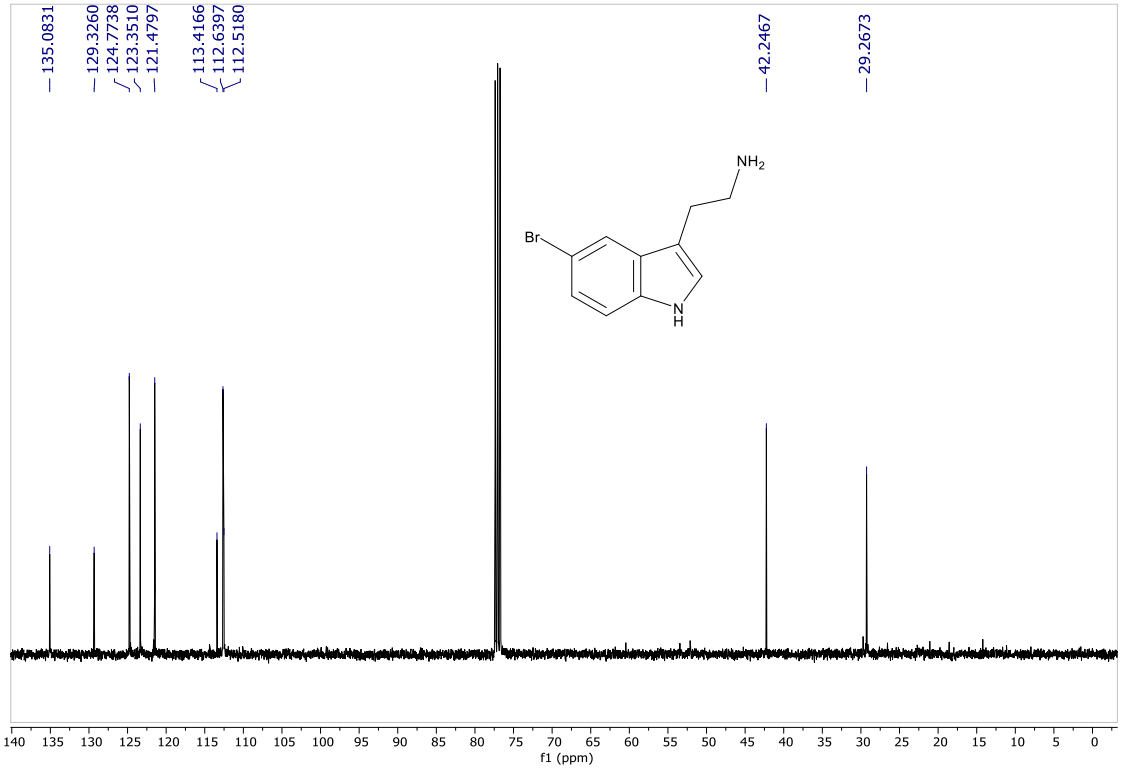
^{1}H NMR spectrum of compound Va in $CDCl_3$



^{13}C NMR spectrum of compound Va in $CDCl_3$



^{1}H NMR spectrum of compound Vb in $CDCl_3$



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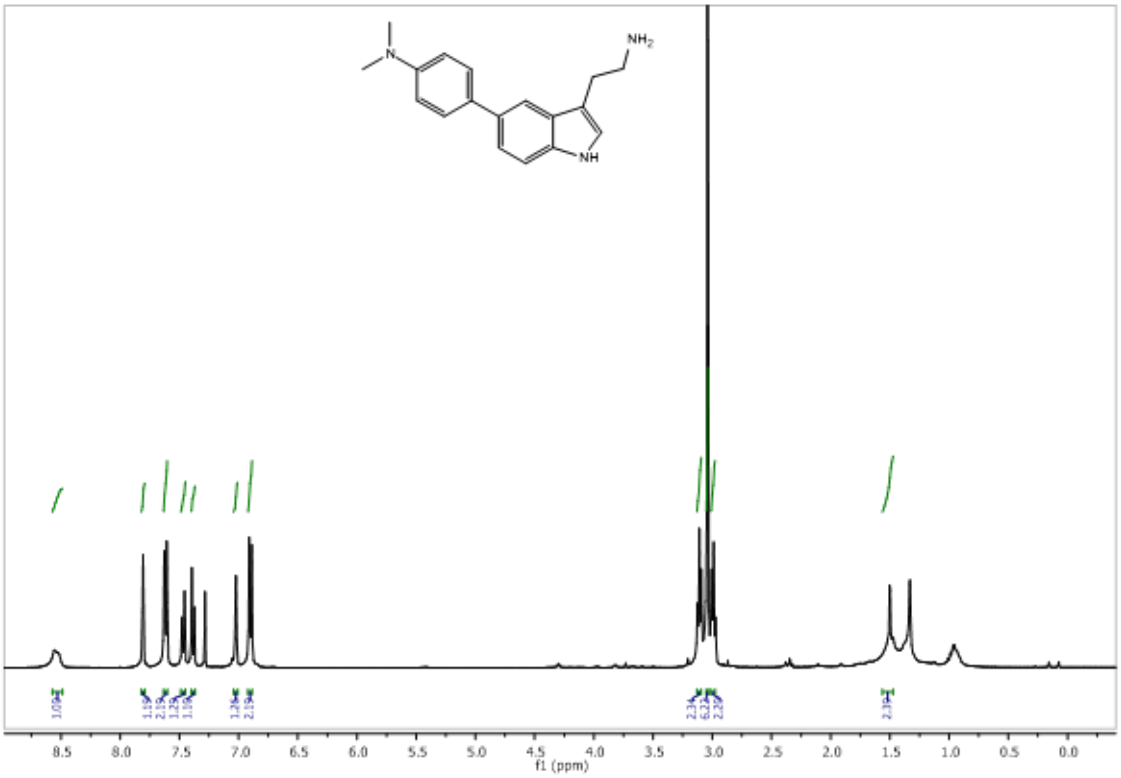

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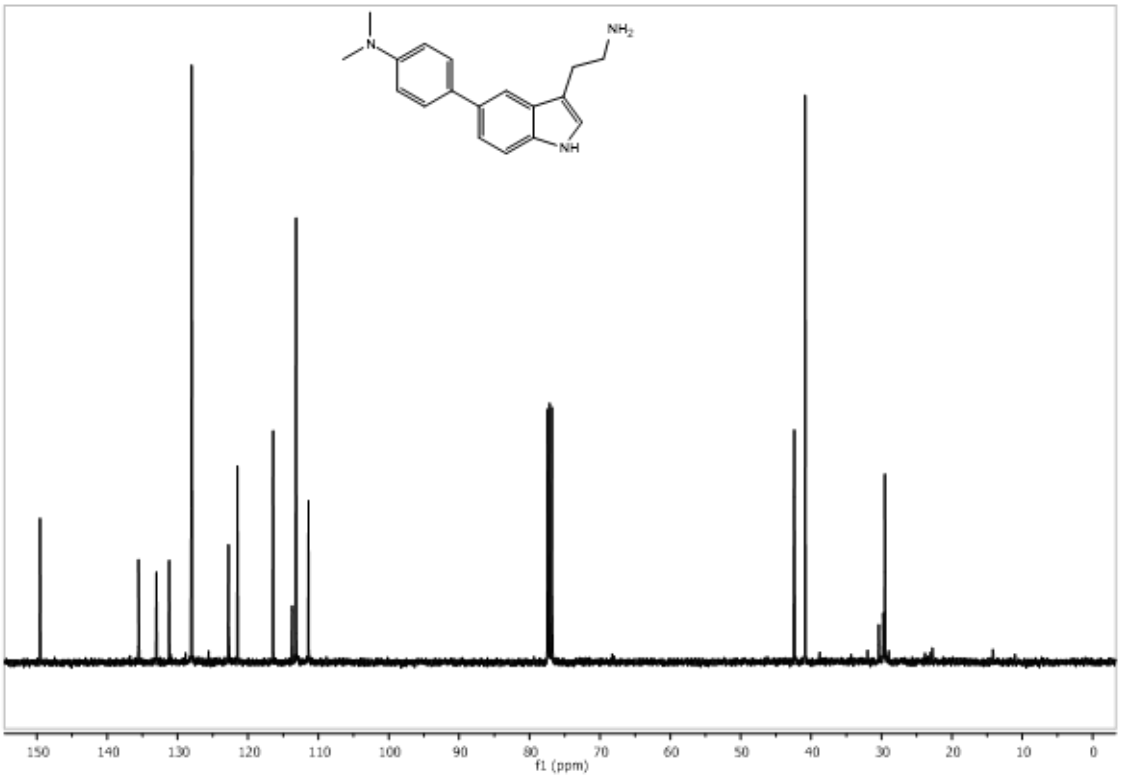
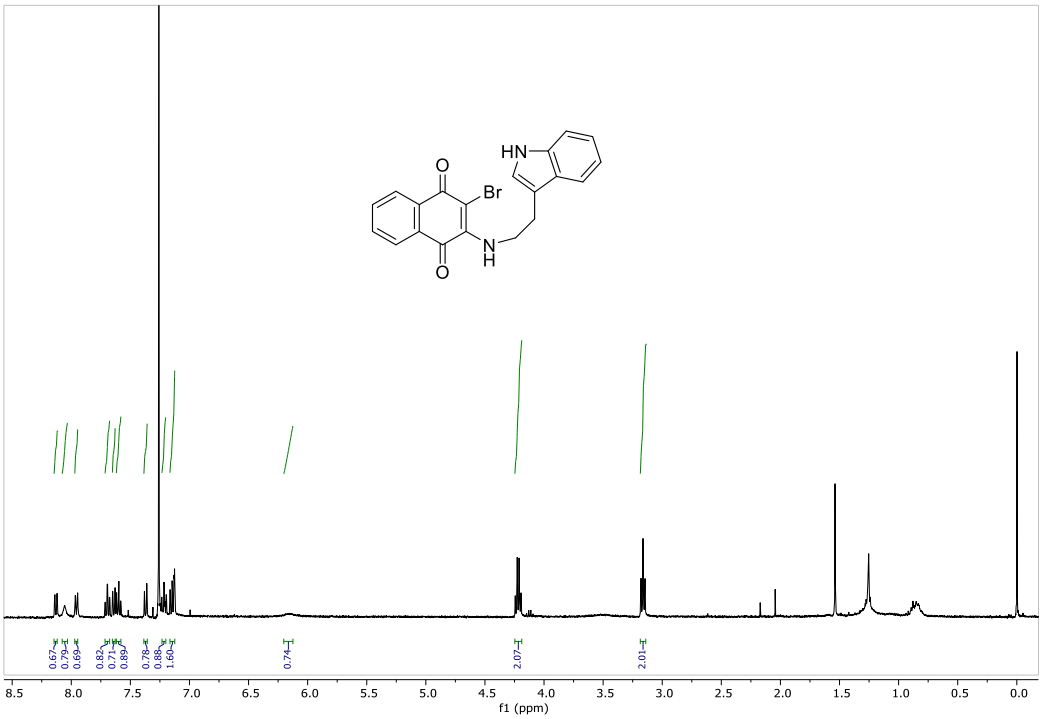
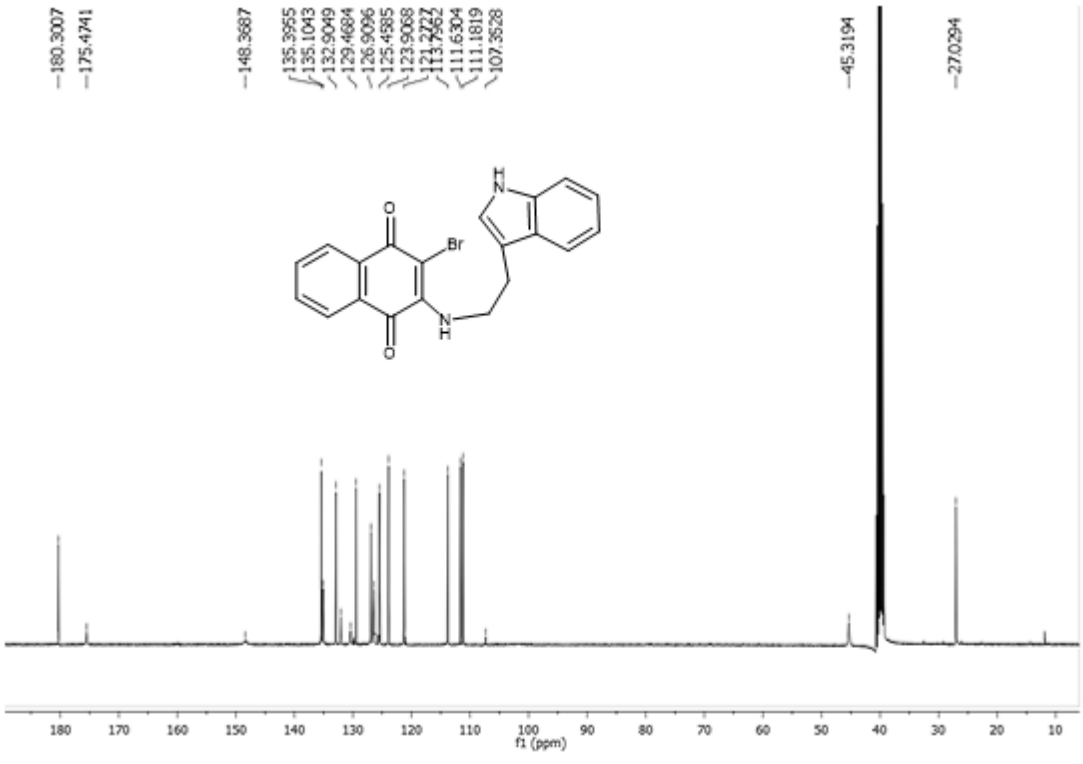


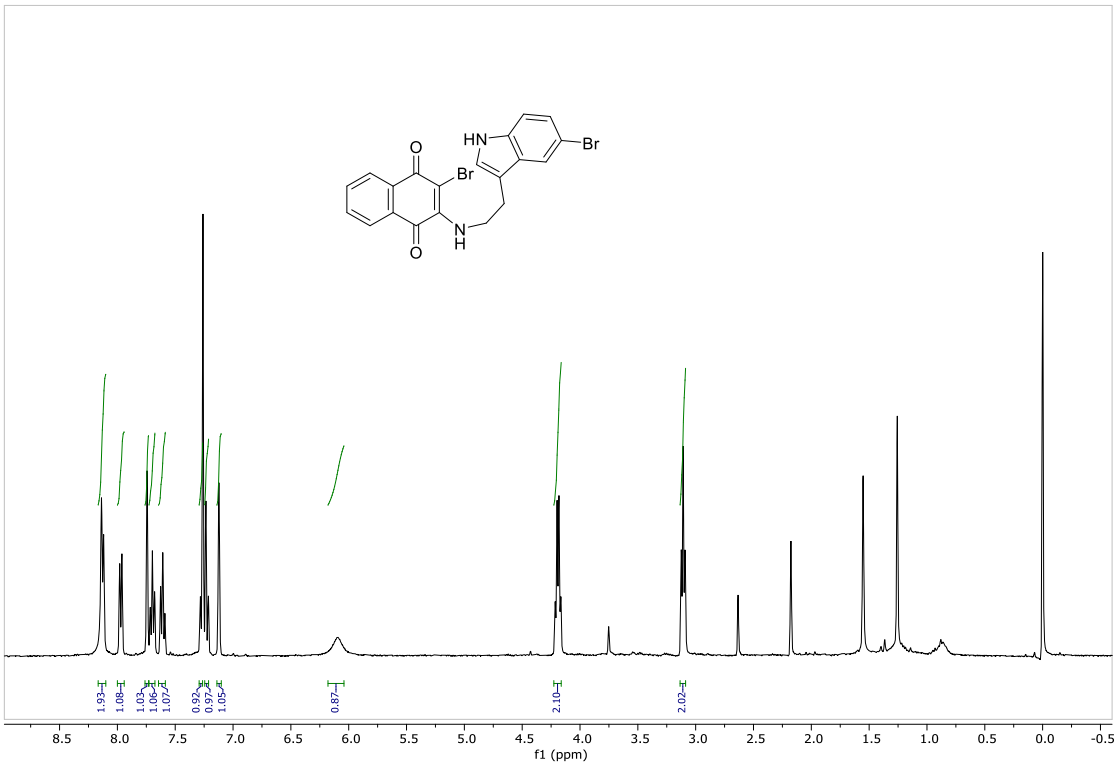
^{13}C NMR spectrum of compound Vc in $CDCl_3$



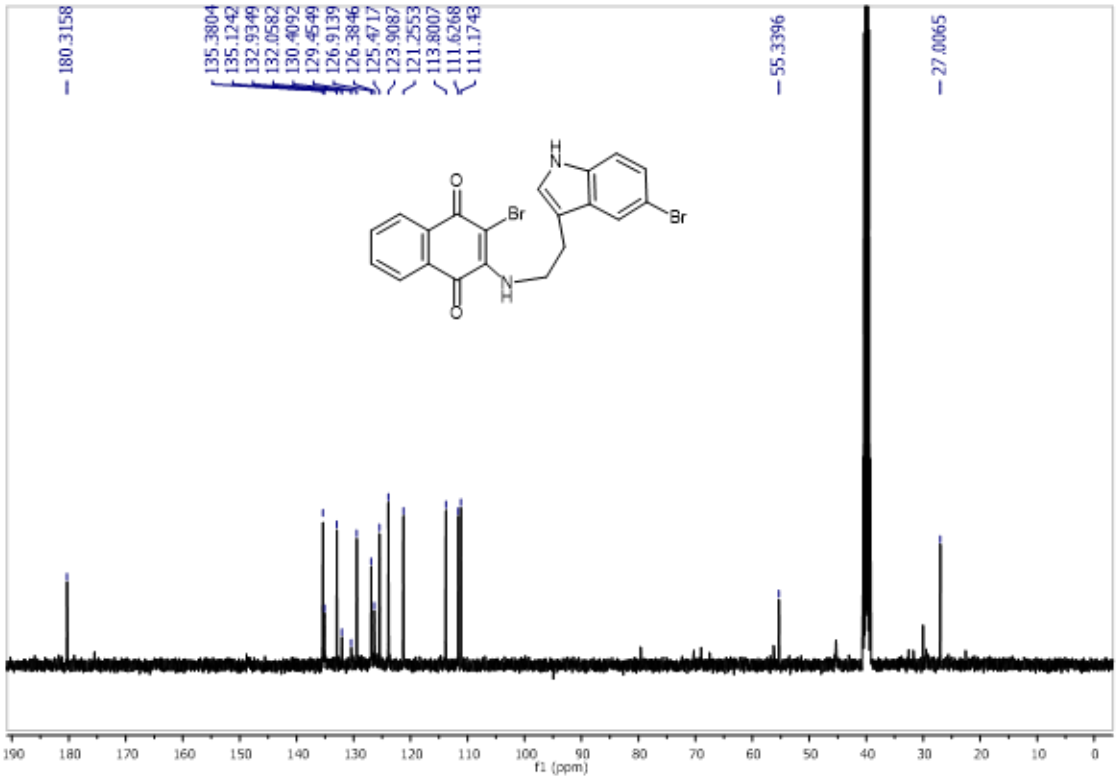
^{1}H NMR spectrum of compound 1a in DMSO-d_6



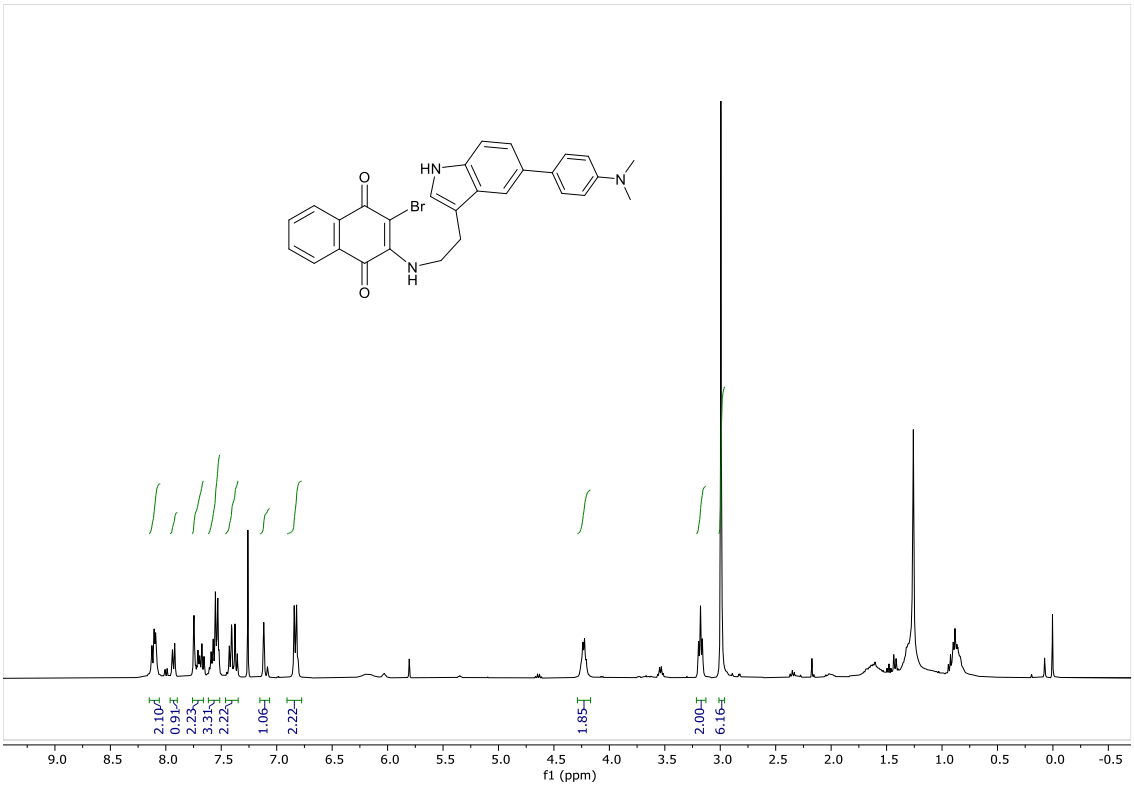
^{13}C NMR spectrum of compound 1a in DMSO-d_6



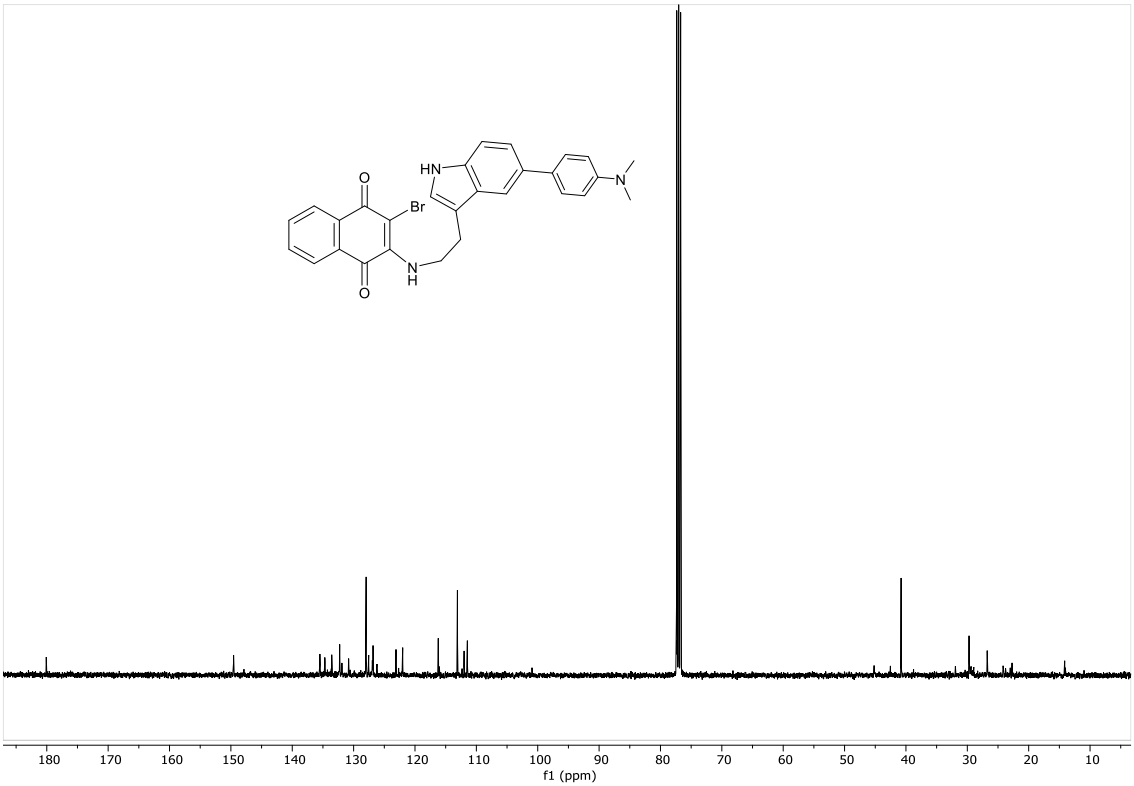
^{1}H NMR spectrum of compound 1b in DMSO-d_6



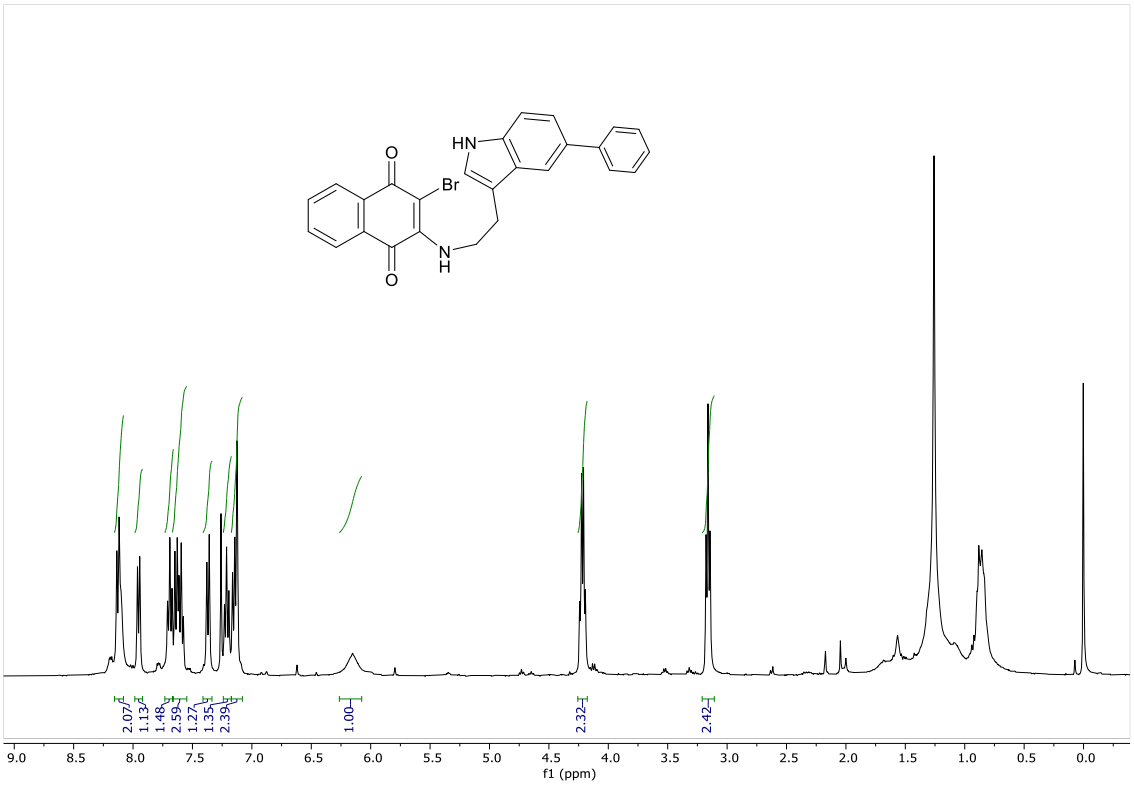
^{13}C NMR spectrum of compound 1b in DMSO-d_6



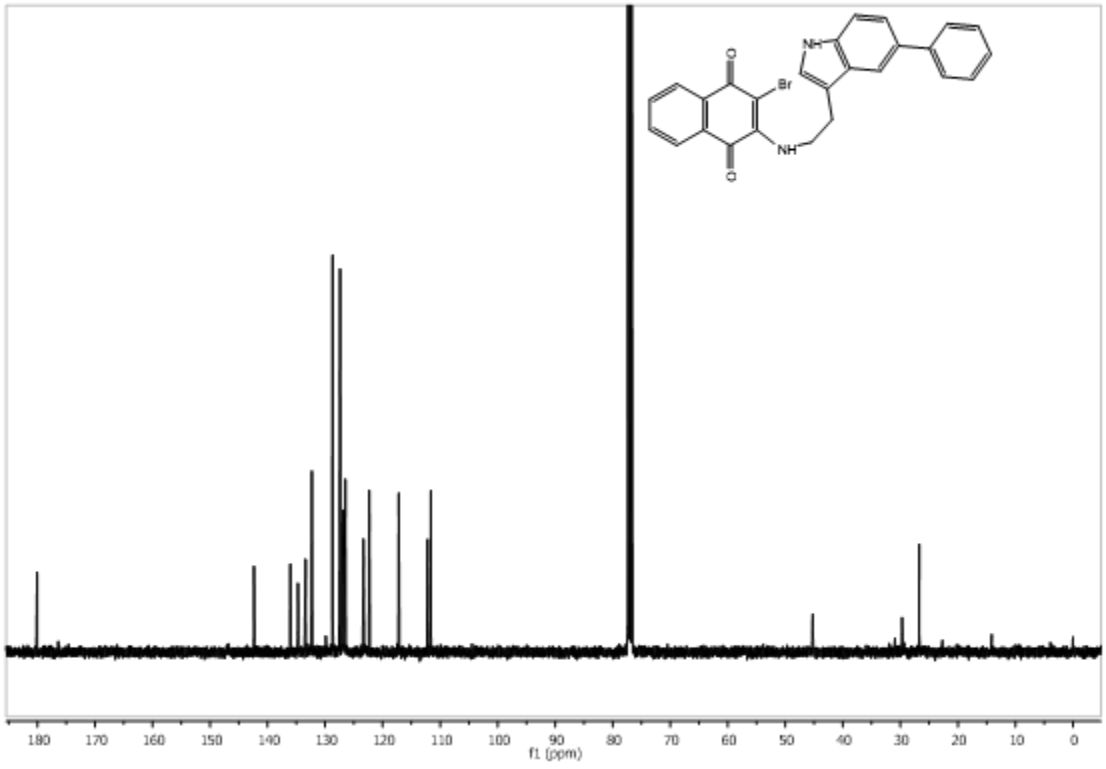
^{1}H NMR spectrum of compound 1c in $CDCl_3$



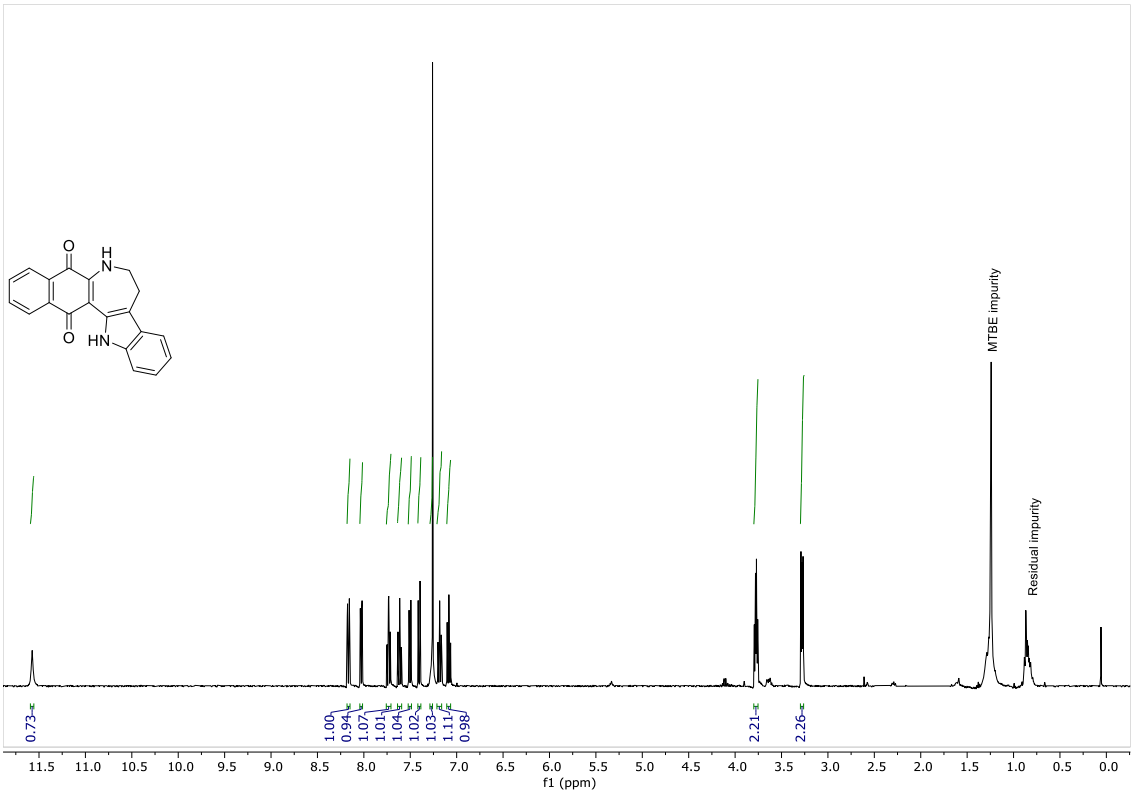
^{13}C NMR spectrum of compound 1c in $CDCl_3$



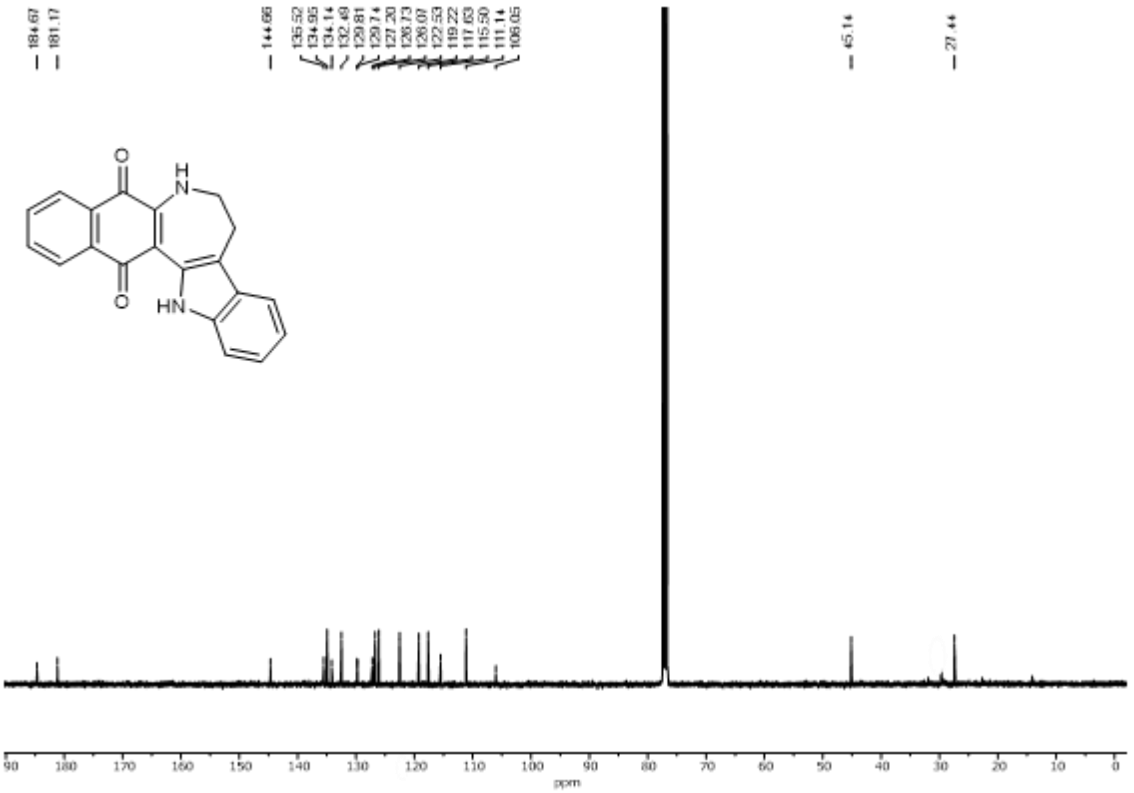
^{1}H NMR spectrum of compound 1d in $CDCl_3$



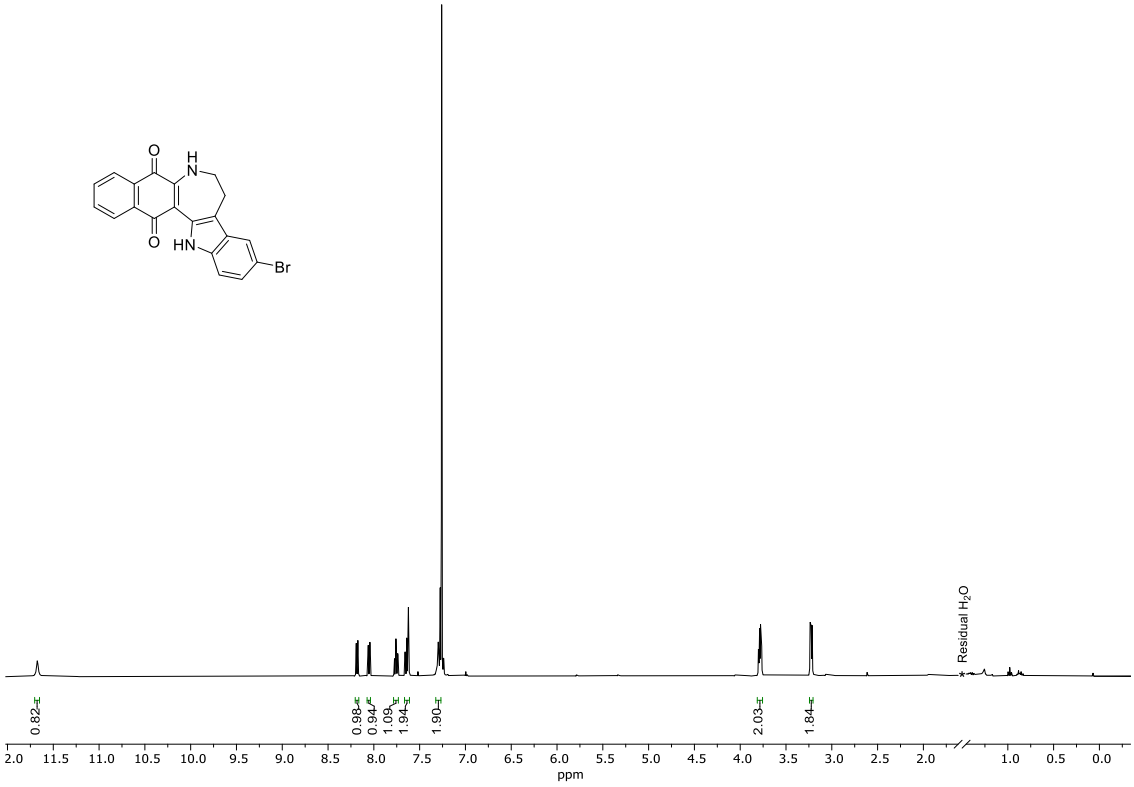
^{13}C NMR spectrum of compound 1d in $CDCl_3$



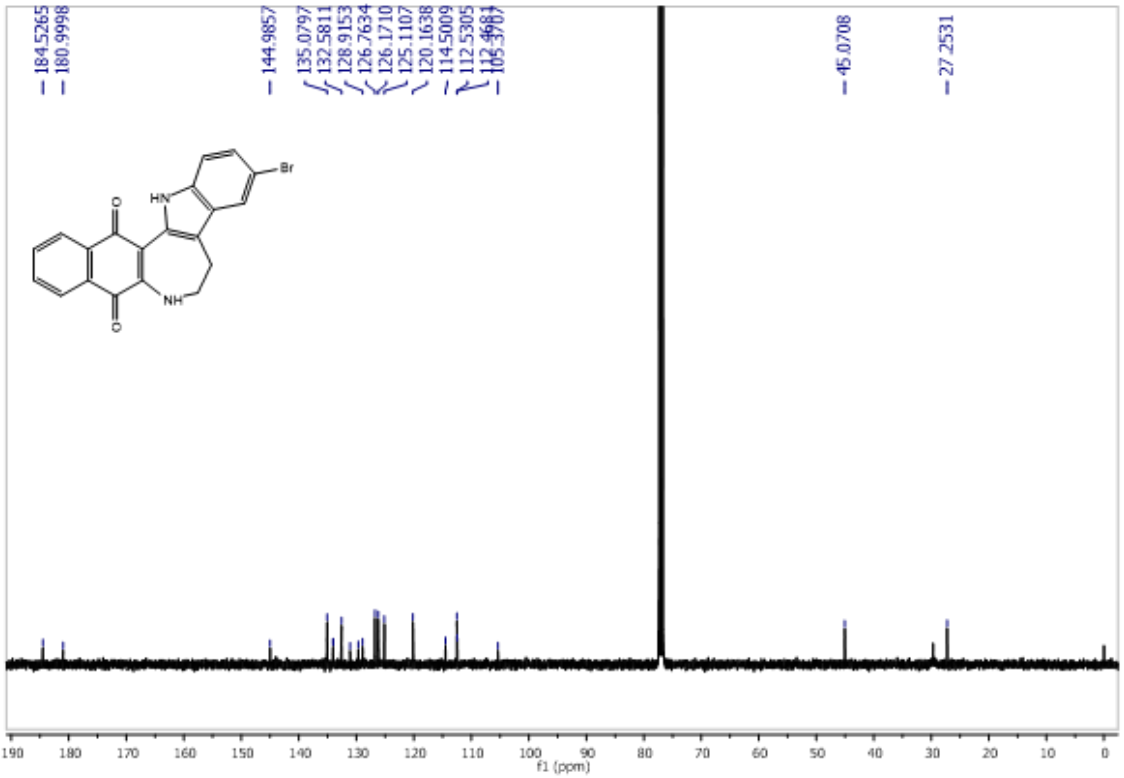
^{1}H NMR spectrum of compound 2a in $CDCl_3$



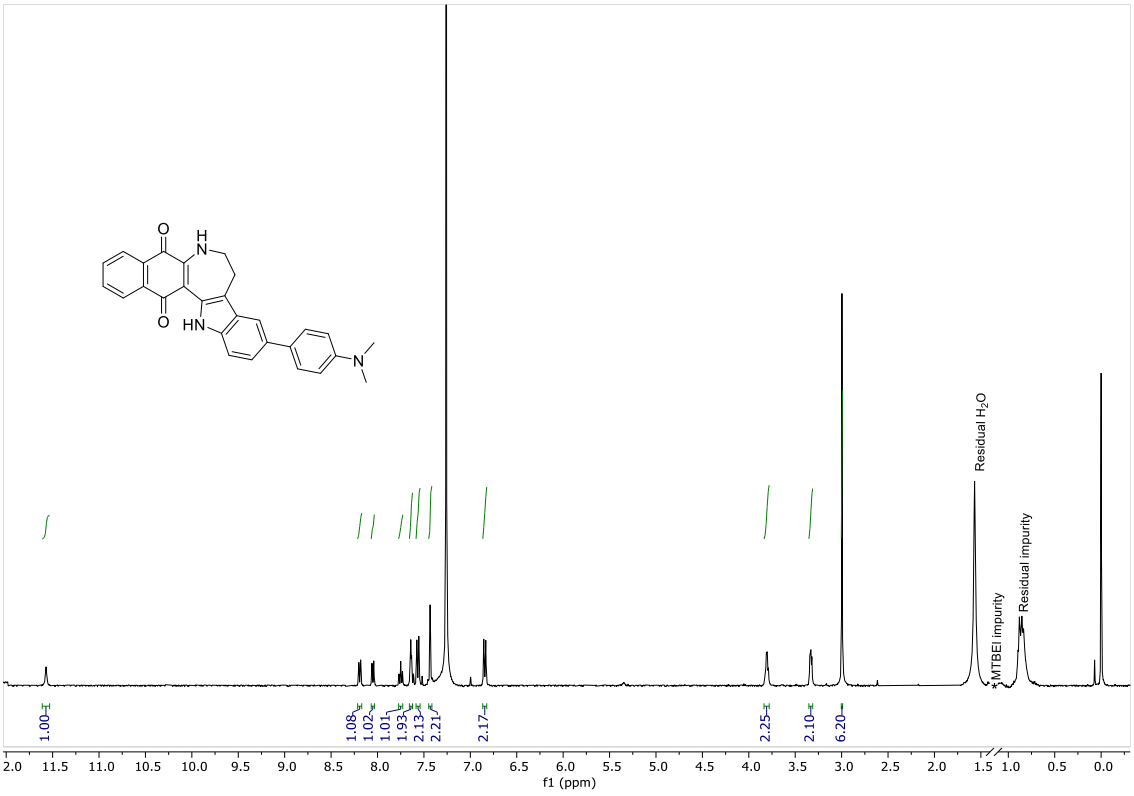
^{13}C NMR spectrum of compound 2a in $CDCl_3$



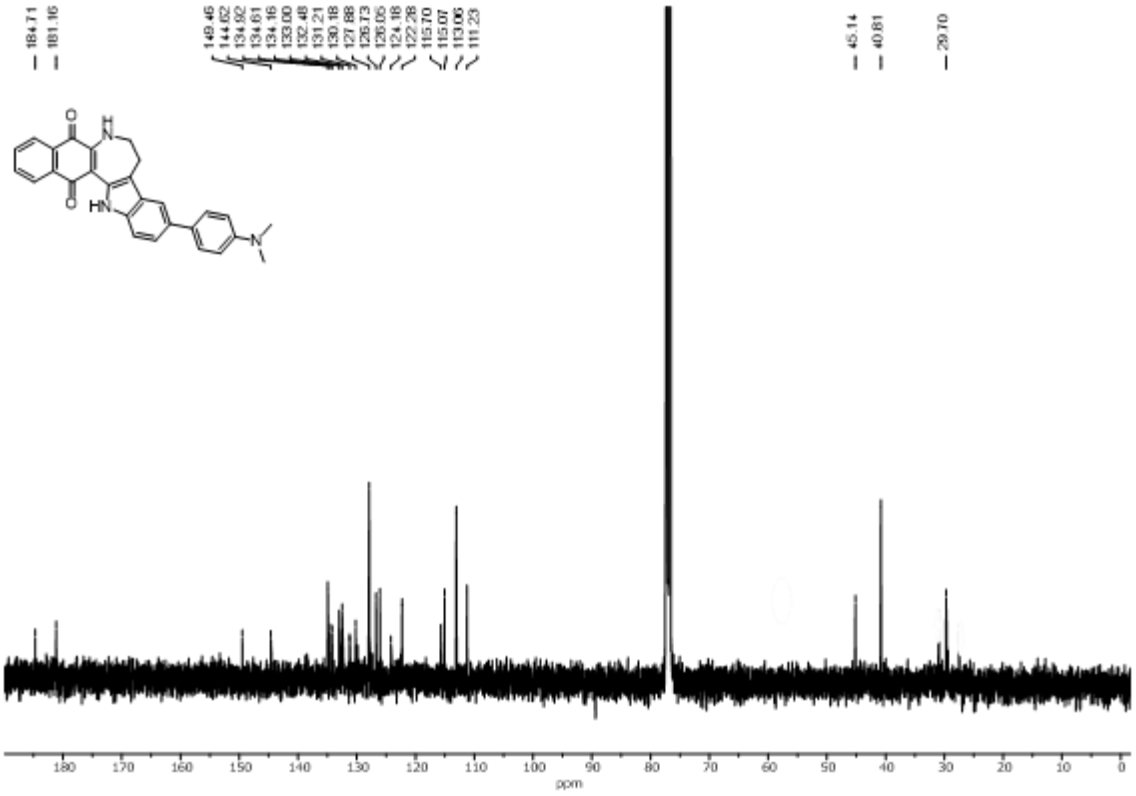
^{1}H spectrum of compound 2b in $CDCl_3$



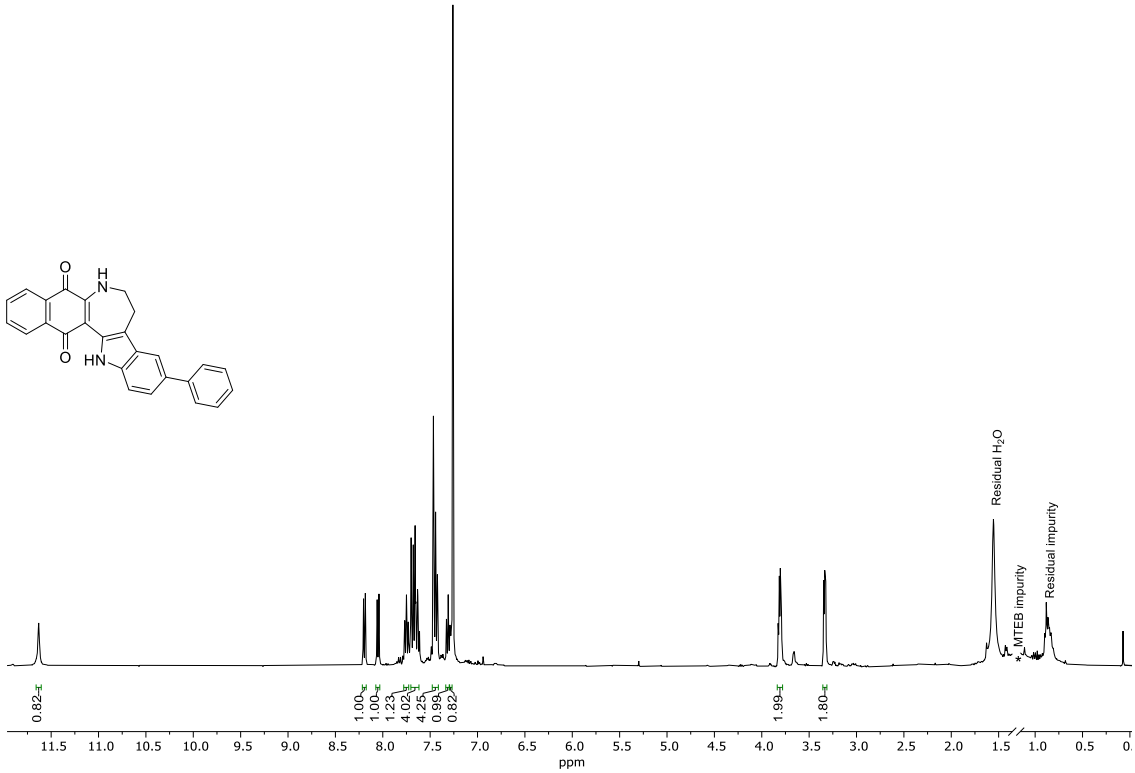
^{13}C NMR spectrum of compound 2b in $CDCl_3$



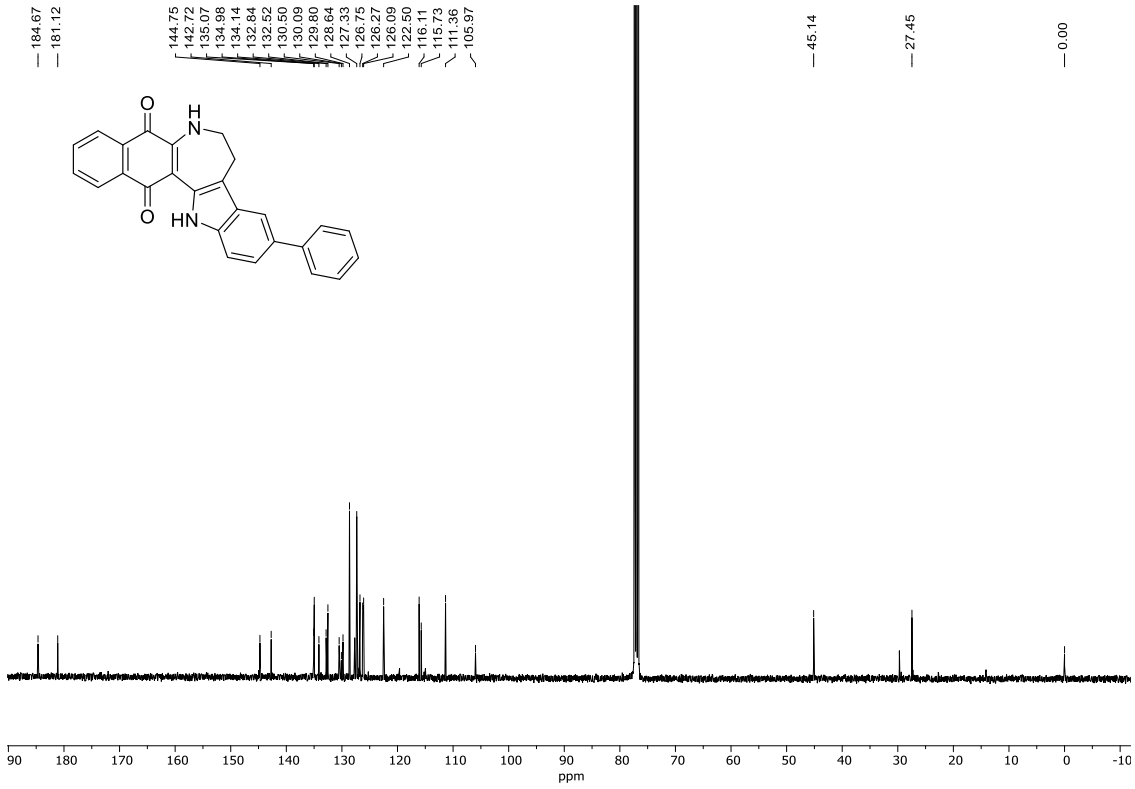
^{1}H NMR spectrum of compound 2c in $CDCl_3$



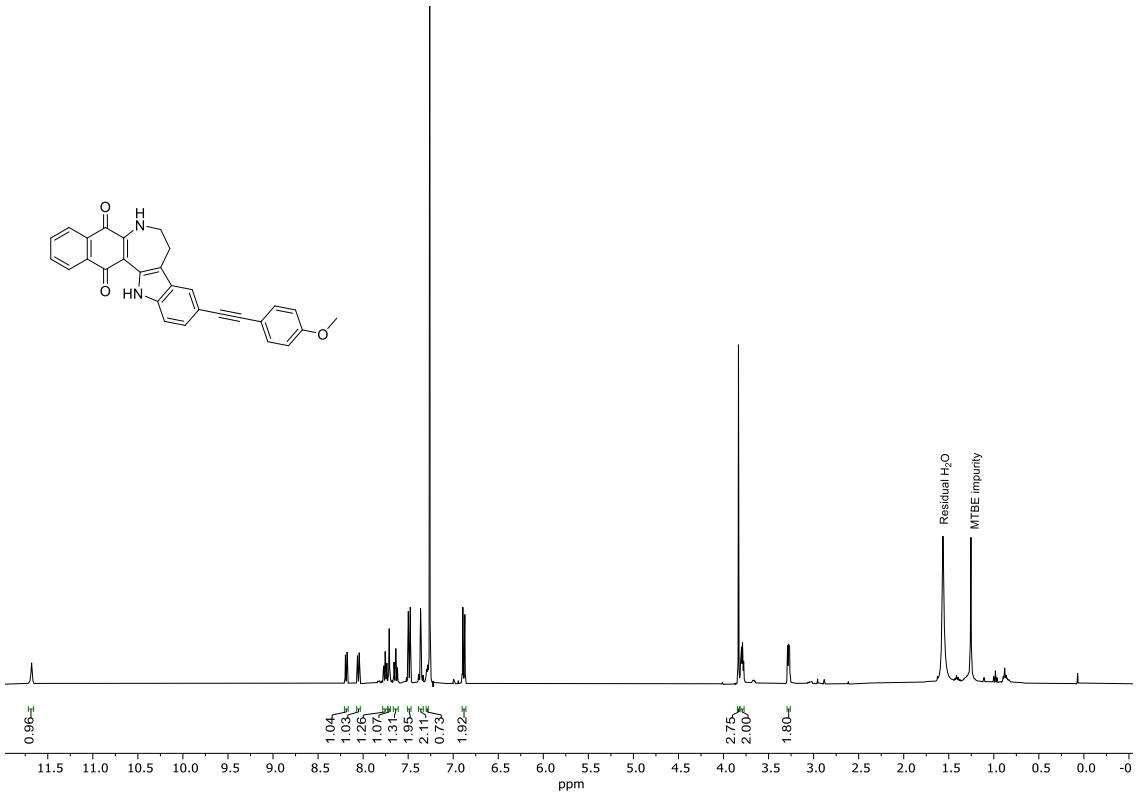
^{13}C NMR spectrum of compound 2c in $CDCl_3$



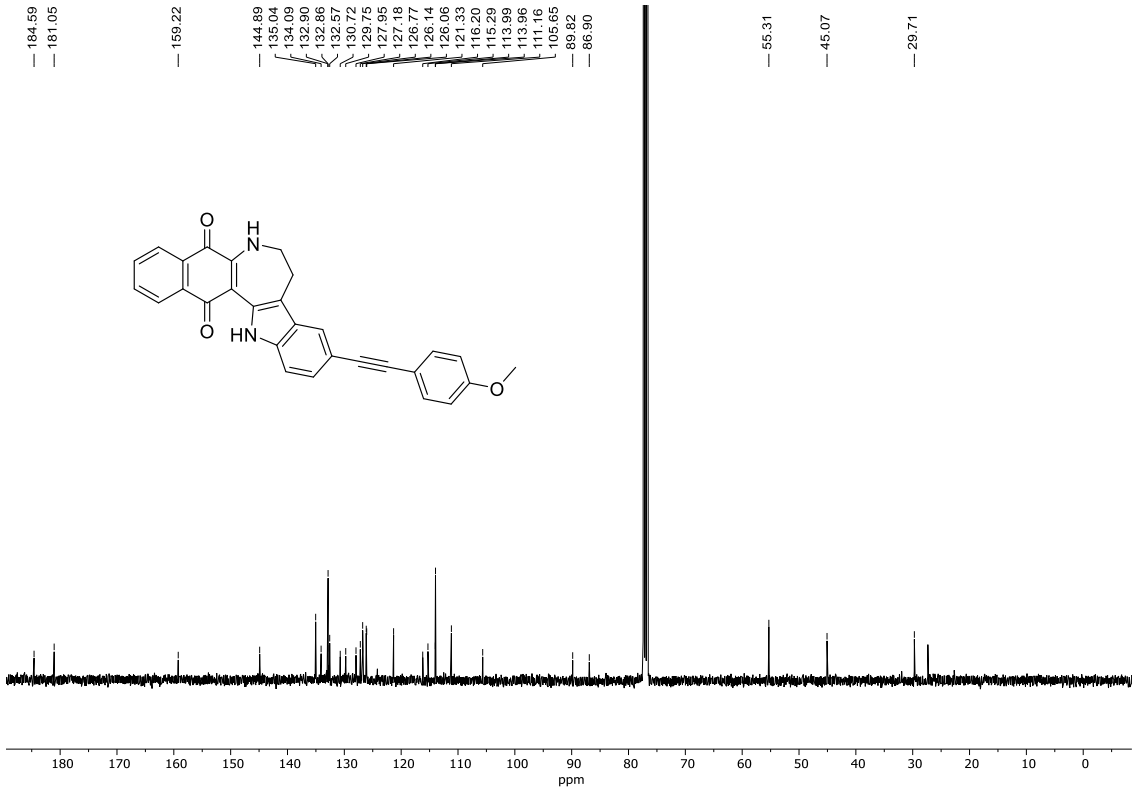
^{1}H NMR spectrum of compound 2d in $CDCl_3$



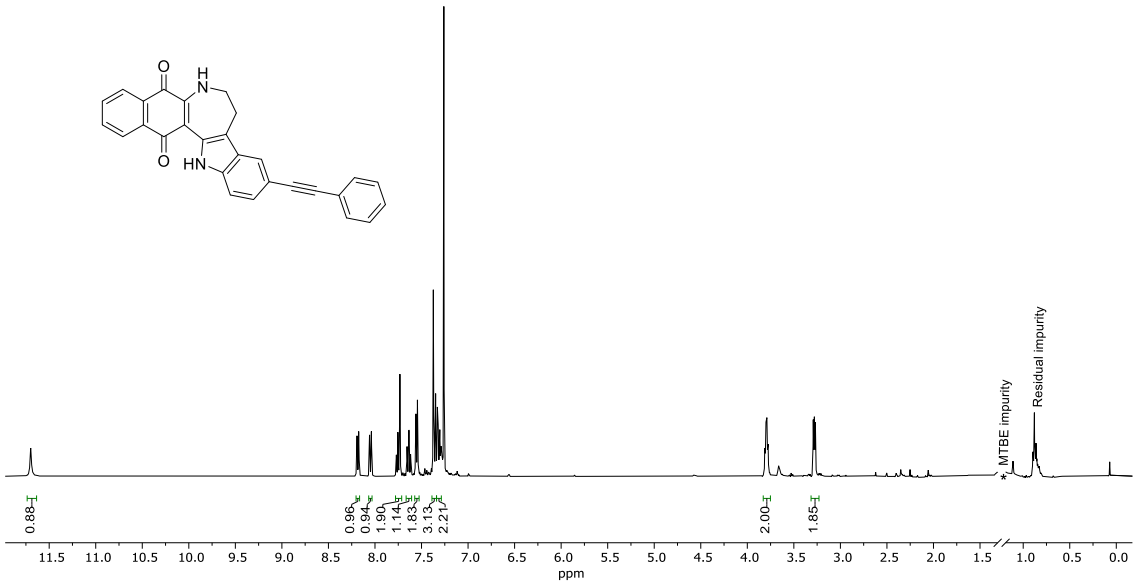
^{13}C NMR spectrum of compound 2d in $CDCl_3$



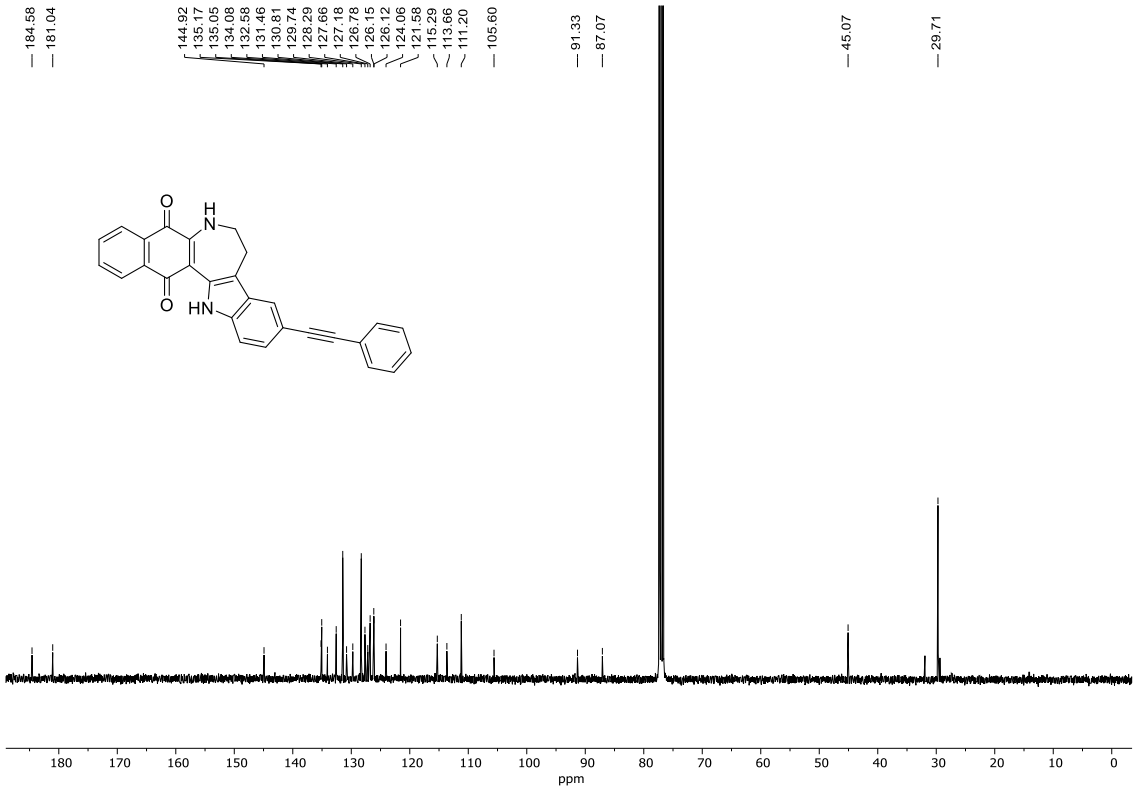
^{1}H NMR spectrum of compound 3a in $CDCl_3$



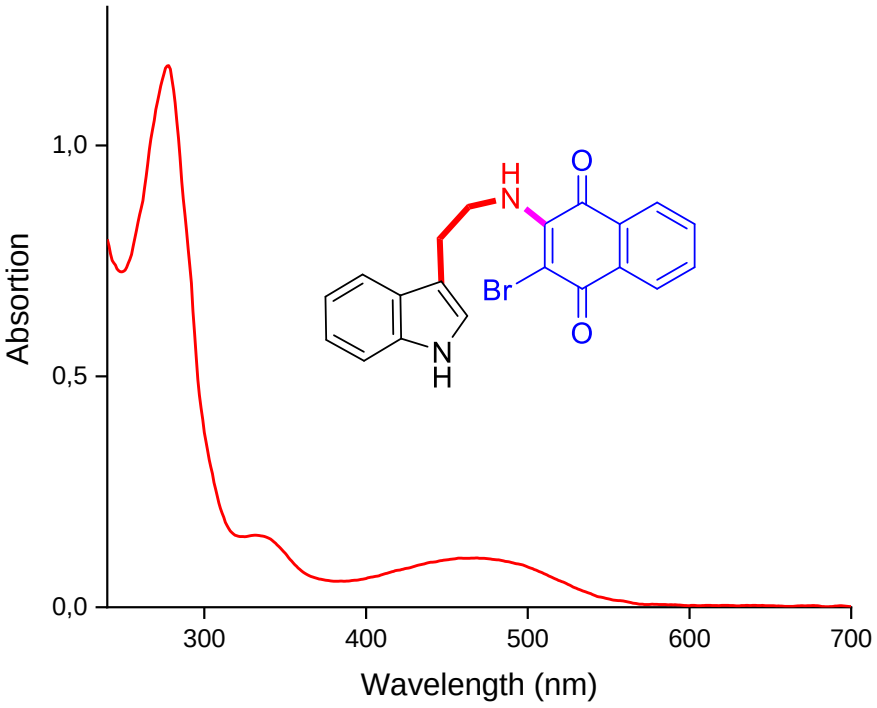
^{13}C NMR spectrum of compound 3a in $CDCl_3$



^{1}H NMR spectrum of compound 3b in $CDCl_3$



^{13}C NMR spectrum of compound 3b in $CDCl_3$



9 Figure S2. Absorption spectrum of the red compound **1a** in chloroform.