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SUPPORTING INFORMATION

Photocontrol of Antibacterial Activity: Shifting from UV to Red Light Activation

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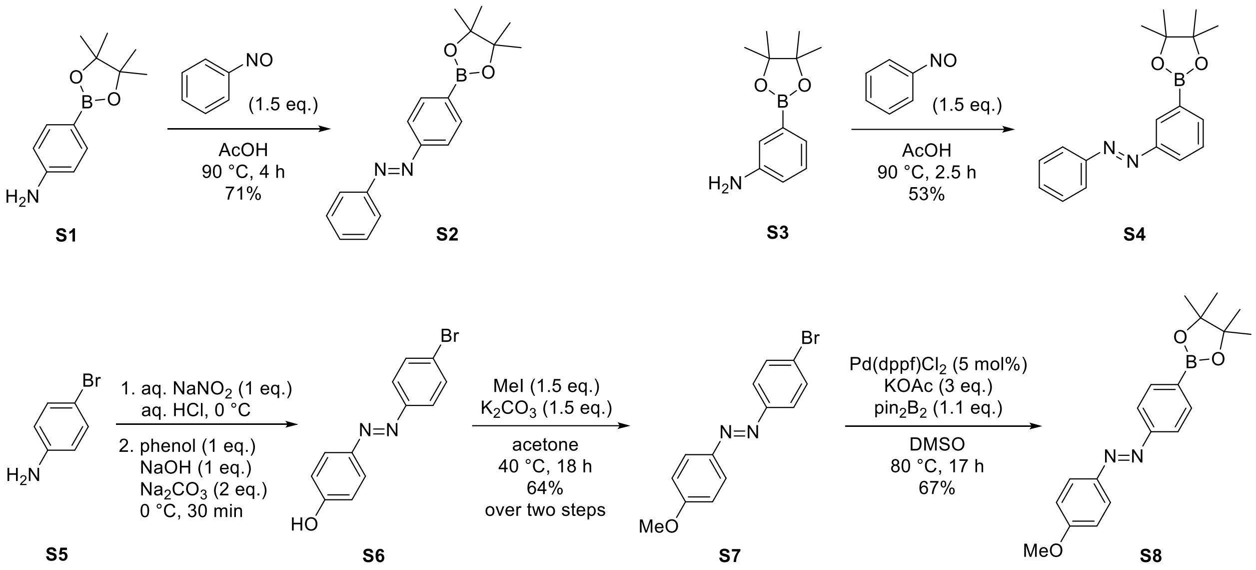
General experimental details

Synthesis. All commercially available chemicals were used without further purification. Moisture sensitive reactions were performed in flame-dried glassware under an atmosphere of nitrogen. Dichloromethane (DCM) and tetrahydrofuran (THF) were dried using an M. Braun SPS-800 solvent purification system. Flash chromatography was performed with Macherey-Nagel Silica 60 M (40−63 µm); the employed eluent is reported in parentheses (volumetric ratios, P = pentane). Thin-layer chromatography (TLC) was performed on precoated silica gel plates with fluorescence-indicator UV$_{254}$ (Merck Kieselgel 60 F254), and components were visualized by observation under UV light or by treating the plates with $KMnO_4$ solution or CAM (cerium ammonium molybdate in diluted sulfuric acid) followed by heating. NMR spectra were obtained on Varian AMX400 and Agilent Technologies 400-MR spectrometers operating at 400 MHz for ^{1}H NMR spectra; ^{13}C NMR spectra were recorded at 101 MHz. Chemical shifts are reported in ppm relative to residual solvent signals (δ_H 7.26 and δ_C 77.16 for $CDCl_3$, δ_H 2.50 and δ_C 39.52 for DMSO-d$_6$). Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc. High resolution mass spectra were obtained on a Thermo scientific LTQ Orbitrap XL (ESI ionization). Melting points were determined using a Buchi melting point B-545 apparatus.

Irradiation experiments. Photochemical experiments were carried out at 20 °C unless stated otherwise. UV-Vis absorption spectra were recorded on Hewlet-Packard HP 8453 and Jasco V-630 spectrophotometers in 10 mm quartz cuvettes using DMSO (J.T.Baker, Baker Analyzed), aqueous buffer solution (a mixture of Bis-TRIS, TRIS, MES and sodium acetate, 2 mM each, pH adjusted to 7.4) and LB growth medium (see details for experiments on bacteria). Irradiation was performed using Spectroline ENB-280C/FE UV lamps (365 nm), a Thorlabs model M365F1 LED (365 nm, 4.1 mW), a Sahlmann Photochemical Solution LED system (400 nm: 3 × 330 mW, FWHM 13.5 nm; 527 nm: 3 × 270 mW, FWHM 35.1 nm; 652 nm: 3 × 400 mW, FWHM 26.4 nm) and a Thorlabs OSL1-EC Fiber Illuminator (white light), also used in combination with a filter cutting off wavelength below 530 nm (white light ≥ 530 nm). UHPLC-MS analysis was conducted on a ThermoFischer Scientific Vanquish UHPLC System (RP column: Acquity UPLC HSS T3 1.8 µm, 2.1 × 150 mm; eluent: 0.1% aqueous formic acid [A] and acetonitrile with 0.1% formic acid [B] using a linear gradient of 5% B to 90% B over 8 min) in combination with an LCQ Fleet mass spectrometer.

Synthesis of diaminopyrimidines 2a-j



Scheme S1 Synthesis of boronic esters **S2**, **S4** and **S8**.

(*E*)-1-Phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (S2):[1]

Aniline **S1** (657 mg, 3.00 mmol, 1 eq.) was added to a solution of nitrosobenzene (482 mg, 4.50 mmol, 1.5 eq.) in 15 mL glacial acetic acid under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 4 h, before it was allowed to cool to room temperature and poured into water. After the addition of a small amount of brine, the aqueous layer was repeatedly extracted with dichloromethane and the combined organic layers were successively washed with water, saturated aqueous $NaHCO_3$ solution, water and brine, and dried over Na_2SO_4. Concentration of the organic layer under reduced pressure and purification by flash chromatography (DCM) gave azobenzene **S2** as a red crystalline solid (658 mg, 2.14 mmol, 71%).

TLC: R_f = 0.79 (DCM/P 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 – 7.88 (m, 6H), 7.56 – 7.45 (m, 3H), 1.38 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 152.8, 135.8, 131.3, 129.2, 123.1, 122.1, 84.2, 25.1.

The spectroscopic data is in accordance with the literature.[1]

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[1] J. H. Harvey, B. K. Butler, D. Trauner, *Tetrahedron Lett.* **2007**, *48*, 1661.

(*E*)-1-Phenyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (S4)

was prepared analogously to **S2**: Reaction of aniline **S3** (1.10 g, 5.00 mmol, 1 eq.) with nitrosobenzene (803 mg, 7.50 mmol, 1.5 eq.) gave **S4** as a red oil that crystallized upon standing in the freezer (810 mg, 2.63 mmol, 53%).

TLC: R_f = 0.76 (DCM/P 7:3). **Mp**: 108 – 112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.02 (ddd, *J* = 8.0, 2.2, 1.3 Hz, 1H), 7.97 – 7.91 (m, 3H), 7.56 – 7.45 (m, 4H), 1.39 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.8, 152.2, 137.4, 131.0, 129.4, 129.2, 128.7, 125.5, 123.0, 84.2, 25.1. **HRMS** (ESI): *m/z* 309.1780 [309.1769 calcd. for $C_{18}H_{22}BN_2O_2^+$ (M+H$^+$)].

(*E*)-1-(4-Bromophenyl)-2-(4-methoxyphenyl)diazene (S7):

Initially following a previously reported procedure for the synthesis of azobenzene **S6**,[2] 4-bromoaniline (**S5**, 1.72 g, 10.0 mmol, 1 eq.) was dissolved in 13 mL 2 N aqueous HCl and cooled to 0 °C before a solution of $NaNO_2$ (690 mg, 10.0 mmol, 1 eq.) in 10 mL water was added dropwise from a dropping funnel. In a separate flask, phenol (941 mg, 10.0 mmol, 1 eq.) dissolved in 200 mL of water was treated with NaOH (400 mg, 10.0 mmol, 1 eq.) and Na_2CO_3 (2.12 g, 20.0 mmol, 2 eq.) and the resulting solution was cooled to 0 °C. To this, the diazonium solution was carefully added via dropping funnel, and upon complete addition stirring at 0 °C was continued for 30 min. After acidifying the reaction mixture with 2 N aqueous HCl, the orange precipitate was filtered off, washed with water and dried in vacuo. The thus obtained crude azobenzene **S6** was dissolved in acetone, and iodomethane (0.93 mL, 2.13 g, 15.0 mmol, 1.5 eq.) and K_2CO_3 (2.07 g, 15 mmol, 1.5 eq.) were added to the solution. The reaction mixture was stirred at 40 °C for 18 h, before the solvent was removed under reduced pressure and the residue was partitioned between DCM and water (60 mL each). The aqueous layer was extracted with DCM (1 × 60 mL), the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (P/EtOAc 100:0 → 99:1 → 98:2 → 95:5) yielded azobenzene **S7** as an orange solid (1.87 g, 6.42 mmol, 64% over two stpes).

TLC: R_f = 0.59 (P/EtOAc 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.5, 151.6, 147.0, 132.4, 125.1, 124.7, 124.2, 114.4, 55.8.
The spectroscopic data is in accordance with the literature.[3]

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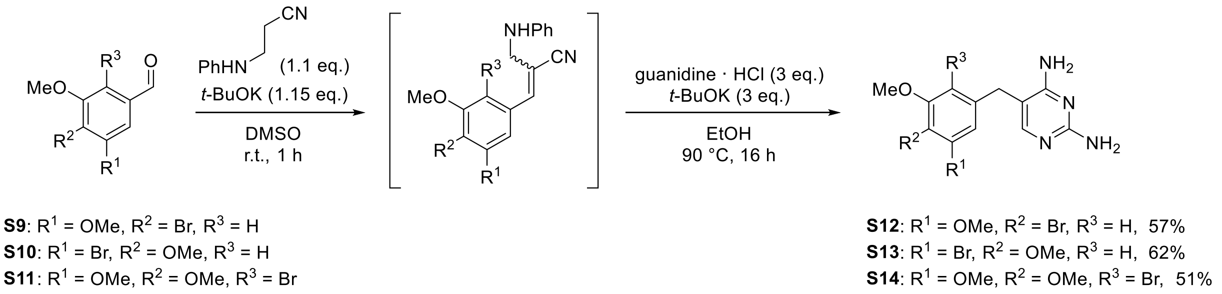
[2] O. K. Rasheed, J. Raftery, P. Quayle, *Synlett* **2015**, *26*, 2806.

[3] P. Sarkara, C. Mukhopadhyay, *Green Chem.* **2016**, *18*, 442.

(*E*)-1-(4-Methoxyphenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (S8):

A suspension of bromide **S7** (349 mg, 1.20 mmol, 1 eq.), bis(pinacolato)diboron (335 mg, 1.32 mmol, 1.1 eq.) and KOAc (353 mg, 3.60 mmol, 3 eq.) in 2.5 mL dry DMSO was purged with argon for 1 h, before Pd(dppf)Cl_2 (43.0 mg, 60.0 μmol, 5 mol%) was added and the resulting reaction mixture stirred at 80 °C for 17 h. Having cooled to room temperature, the reaction mixture was partitioned between EtOAc and diluted aqueous $NaHCO_3$ solution (30 mL each). The aqueous layer was extracted with EtOAc (1 × 30 mL), the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (P/EtOAc 95:5 → 90:10) gave boronic ester **S8** as a red-orange solid (271 mg, 0.801 mmol, 67%)

TLC: R_f = 0.38 (P/EtOAc 9:1). **Mp**: 122 – 125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 – 7.91 (m, 4H), 7.88 – 7.84 (m, 2H), 7.04 – 6.99 (m, 2H), 3.90 (s, 3H), 1.37 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.4, 154.6, 147.2, 135.8, 125.1, 121.9, 114.4, 84.2, 55.7, 25.1. **HRMS** (ESI): *m/z* 339.1884 [339.1875 calcd. for $C_{19}H_{24}BN_2O_3^+$ (M+H^+)].



Scheme S2 Synthesis of diaminopyrimidines **S12-14**.

5-(4-Bromo-3,5-dimethoxybenzyl)pyrimidine-2,4-diamine (S12):

Following a previously reported, modified procedure,[4] 3-anilinopropionitrile (1.61 g, 11.0 mmol, 1.1 eq.) and subsequently KO*t*-Bu (1.29 g, 11.5 mmol, 1.15 eq.) were added to a solution of 4-bromo-3,5-benzaldehyde (**S9**, 2.45 g, 10.0 mmol, 1 eq.) in 25 mL dry DMSO. The reaction mixture was stirred at room temperature for 1 h and then partitioned between EtOAc and water (250 mL each). The aqueous layer was extracted with EtOAc (2 × 100 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. A guanidine solution was prepared separately by dissolving guanidine hydrochloride

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[4] C. Tahtaoui, A. Demailly, C. Guidemann, C. Joyeux, P. Schneider, *J. Org. Chem.* **2010**, *75*, 3781.

(2.87 g, 30.0 mmol, 3 eq.) in 30 mL dry EtOH under nitrogen atmosphere and treating it with KO*t*-Bu (3.37 g, 30.0 mmol, 3 eq.). This mixture was allowed to stir for 30 min at room temperature, before it was filtered over a glass filter and the filter cake washed with another 30 mL of EtOH. The obtained filtrate was then added to the crude intermediate of the first step under nitrogen and stirred under reflux for 16 h. Upon cooling, the product crystallized from the reaction mixture. It was filtered off, washed successively with ice-cooled water and water/EtOH (1:1) and dried in vacuo, after which diaminopyrimidine **S12** was obtained as a yellow powder (1.92 g, 5.66 mmol, 57% over two steps).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.54 (s, 1H), 6.64 (s, 2H), 6.11 (bs, 2H), 5.70 (bs, 2H), 3.78 (s, 6H), 3.58 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.3, 162.2, 156.3, 155.8, 141.6, 105.4, 105.3, 97.1, 56.2, 33.1.
The spectroscopic data is in accordance with the literature.[5]

5-(3-Bromo-4,5-dimethoxybenzyl)pyrimidine-2,4-diamine (S13)

was prepared analogously to **S12**: Reacting 3-bromo-4,5-dimethoxybenzaldehyde (**S10**, 2.00 g, 8.16 mmol, 1 eq.) following the two-step procedure gave diaminopyrimidine **S13** as a yellow crystalline solid (1.72 g, 5.07 mmol, 62% over two steps).

Mp: 203 – 205 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.58 (s, 1H), 7.00 – 6.95 (m, 2H), 6.16 (bs, 2H), 5.77 (bs, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 3.56 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.4, 162.1, 156.1, 153.1, 143.8, 138.2, 123.4, 116.3, 112.9, 105.2, 60.0, 56.0, 32.0. **HRMS** (ESI): *m/z* 339.0460 [339.0451 calcd. for $C_{13}H_{16}BrN_4O_2^+$ (M+H$^+$)].

5-(2-Bromo-3,4,5-trimethoxybenzyl)pyrimidine-2,4-diamine (S14)

was prepared analogously to **S12**: Reacting 2-bromo-3,4,5-trimethoxybenzaldehyde[6] (**S11**, 2.50 g, 9.09 mmol, 1 eq.) following the two-step procedure gave diaminopyrimidine **S14** as an off-white solid (1.71 g, 4.63 mmol, 51% over two steps).

Mp: 194 – 196 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.12 (s, 1H), 6.76 (s, 1H), 6.24 (bs, 2H), 5.75 (bs, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.61 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.3, 162.2, 155.0, 152.4, 150.3, 141.1, 134.2, 110.2, 110.1, 103.6, 60.7, 60.7, 56.0, 33.7. **HRMS** (ESI): *m/z* 369.0565 [369.0557 calcd. for $C_{14}H_{18}BrN_4O_3^+$ (M+H$^+$)].

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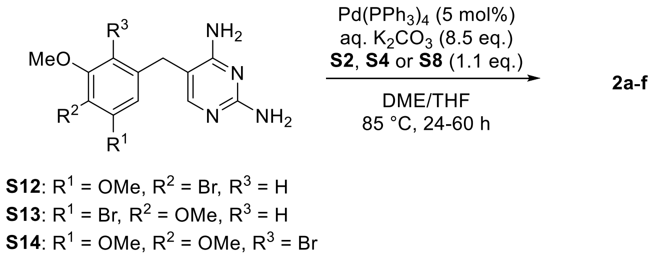
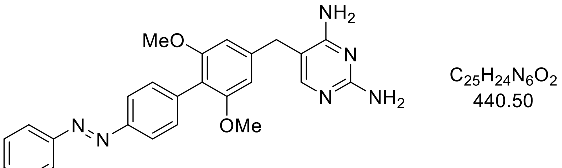
[5] I. Kompis, A. Wick, *Helv. Chim. Acta* **1977**, *60*, 3025.
[6] G. A. Molander, K. M. George, L. G. Monovich, *J. Org. Chem.* **2003**, *68*, 9533.



Scheme S3 Synthesis of diaminopyrimidines **2s-f** by *Suzuki* cross-coupling.

(*E*)-5-((2,6-Dimethoxy-4'-(phenyldiazenyl)-[1,1'-biphenyl]-4-yl)methyl)pyrimidine-2,4-diamine (2a):

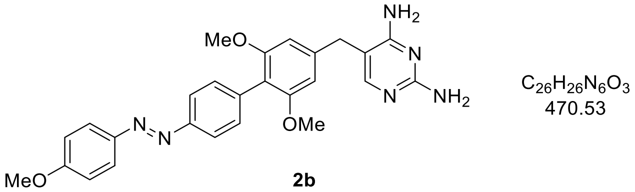


2a

All solvents were separately purged with argon before use. Bromide **S12** (321 mg, 0.947 mmol, 1 eq.) was added to a suspension of $Pd(PPh_3)_4$ (55.0 mg, 47.4 µmol, 5 mol%) in 7.3 mL 1,2-dimethoxyethane under nitrogen atmosphere and the resulting mixture stirred for 15 min at room temperature. Subsequently, boronic ester **S2** (321 mg, 1.04 mmol, 1.1 eq.) dissolved in 1 mL THF was added to the reaction mixture (an additional 1 mL THF was used to rinse the boronic ester vessel), followed by the addition of 4 mL of a 2 N aqueous K_2CO_3 solution (1.11 g, 8.05 mmol, 8.5 eq.). The biphasic reaction mixture was then vigorously stirred at 85 °C for 44 h. After cooling to room temperature, the mixture was partitioned between water and EtOAc, the separated aqueous layer extracted with EtOAc (2 × 20 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. After purification by flash chromatography (DCM/MeOH 98:2 → 95:5), diaminopyrimidine **2a** was obtained as an orange powder (206 mg, 0.468 mmol, 48%).

TLC: R_f = 0.45 (DCM/MeOH 8:1). **Mp**: 232 – 234 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.93 – 7.83 (m, 4H), 7.65 – 7.52 (m, 4H), 7.48 – 7.40 (m, 2H), 6.69 (s, 2H), 6.16 (bs, 2H), 5.72 (bs, 2H), 3.68 – 3.63 (m, 8H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.3, 162.2, 156.8, 155.8, 152.1, 150.4, 142.3, 137.9, 132.0, 131.3, 129.4, 122.5, 121.7, 115.3, 105.5, 104.8, 55.7, 33.3. **HRMS** (ESI): *m/z* 441.2033 [441.2034 calcd. for $C_{25}H_{25}N_6O_2^+$ (M+H$^+$)].

(*E*)-5-((2,6-Dimethoxy-4'-((4-methoxyphenyl)diazenyl)-[1,1'-biphenyl]-4-yl)methyl)-pyrimidine-2,4-diamine (2b):

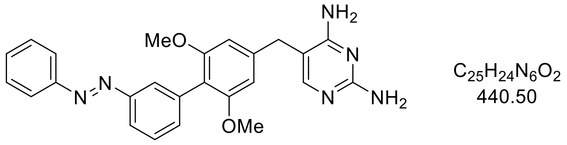


2b

In a procedure analogous to the preparation of **2a**, coupling of bromide **S12** (236 mg, 0.696 mmol, 1 eq.) with boronic ester **S8** (259 mg, 0.766 mmol, 1.1 eq.) for 48 h gave diaminopyrimidine **2b** as a bright orange solid (213 mg, 0.453 mmol, 65%).

TLC: $R_f = 0.42$ (DCM/MeOH 8:1). **Mp**: 244 – 246 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.92 – 7.87 (m, 2H), 7.84 – 7.79 (m, 2H), 7.61 (s, 1H), 7.42 – 7.38 (m, 2H), 7.17 – 7.11 (m, 2H), 6.69 (s, 2H), 6.15 (bs, 2H), 5.70 (bs, 2H), 3.87 (s, 3H), 3.65 (s, 6H), 3.64 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.3, 162.2, 161.9, 156.9, 155.9, 150.5, 146.3, 142.2, 137.1, 131.9, 124.5, 121.4, 115.4, 114.6, 105.5, 104.8, 55.7, 55.6, 33.3. **HRMS** (ESI): *m/z* 471.2137 [471.2139 calcd. for $C_{26}H_{27}N_6O_3^+$ (M+H$^+$)].

(*E*)-5-((2,6-Dimethoxy-3'-(phenyldiazenyl)-[1,1'-biphenyl]-4-yl)methyl)pyrimidine-2,4-diamine (2c):

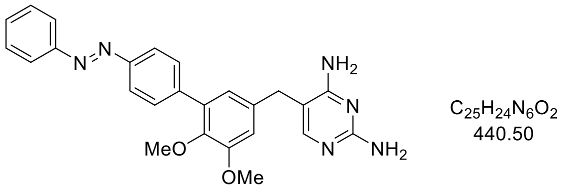


2c

In a procedure analogous to the preparation of **2a**, coupling of bromide **S12** (339 mg, 1.00 mmol, 1 eq.) with boronic ester **S4** (339 mg, 1.10 mmol, 1.1 eq.) for 48 h gave diaminopyrimidine **2c** as an orange crystalline solid (92.5 mg, 0.210 mmol, 21%).

TLC: $R_f = 0.46$ (DCM/MeOH 8:1). **Mp**: 218 – 220 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.91 – 7.86 (m, 2H), 7.82 – 7.77 (m, 1H), 7.72 – 7.70 (m, 1H), 7.62 (s, 1H), 7.61 – 7.53 (m, 4H), 7.39 (d, J = 7.5 Hz, 1H), 6.70 (s, 2H), 6.19 (bs, 2H), 5.75 (bs, 2H), 3.67 – 3.63 (m, 8H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.3, 162.2, 156.9, 155.7, 151.9, 151.6, 142.1, 135.6, 134.1, 131.4, 129.4, 128.6, 125.0, 122.5, 120.7, 115.3, 105.6, 104.8, 55.7, 33.3. **HRMS** (ESI): *m/z* 441.2033 [441.2034 calcd. for $C_{25}H_{25}N_6O_2^+$ (M+H$^+$)].

(*E*)-5-((5,6-Dimethoxy-4'-(phenyldiazenyl)-[1,1'-biphenyl]-3-yl)methyl)pyrimidine-2,4-diamine (2d):

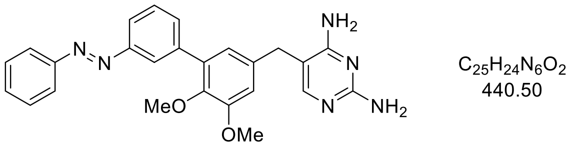


2d

In a procedure analogous to the preparation of **2a**, coupling of bromide **S13** (339 mg, 1.00 mmol, 1 eq.) with boronic ester **S2** (339 mg, 1.10 mmol, 1.1 eq.) for 60 h gave diaminopyrimidine **2d** as a red crystalline solid (426 mg, 0.967 mmol, 97%).

TLC: $R_f = 0.37$ (DCM/MeOH 8:1). **Mp**: 98 – 101 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.95 (d, J = 8.3 Hz, 2H), 7.93 – 7.89 (m, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.02 (d, J = 1.9 Hz, 1H), 6.88 (d, J = 1.9 Hz, 1H), 6.16 (bs, 2H), 5.72 (bs, 2H), 3.83 (s, 3H), 3.63 (s, 2H), 3.55 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.2, 162.2, 155.7, 152.5, 152.0, 150.7, 144.2, 141.2, 136.5, 133.4, 131.5, 130.0, 129.5, 122.5, 122.4, 121.6, 113.2, 105.7, 60.2, 55.8, 32.4. **HRMS** (ESI): *m/z* 441.2031 [441.2034 calcd. for $C_{25}H_{25}N_6O_2^+$ (M+H$^+$)].

(*E*)-5-((5,6-Dimethoxy-3'-(phenyldiazenyl)-[1,1'-biphenyl]-3-yl)methyl)pyrimidine-2,4-diamine (2e):

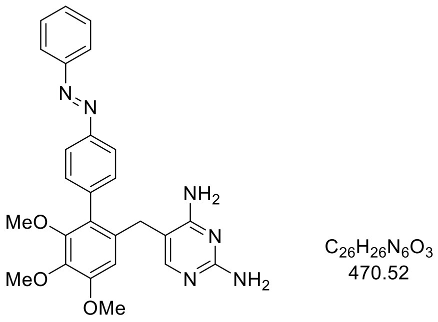


2e

In a procedure analogous to the preparation of **2a**, coupling of bromide **S13** (339 mg, 1.00 mmol, 1 eq.) with boronic ester **S4** (339 mg, 1.10 mmol, 1.1 eq.) gave diaminopyrimidine **2e** as an orange foam (320 mg, 0.726 mmol, 73%).

TLC: $R_f = 0.55$ (DCM/MeOH 8:1). **Mp**: 98 – 101 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.95 (s, 1H), 7.94 – 7.85 (m, 3H), 7.67 – 7.55 (m, 6H), 7.02 (d, J = 1.9 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H), 6.19 (bs, 2H), 5.74 (bs, 2H), 3.83 (s, 3H), 3.62 (s, 2H), 3.55 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.2, 162.2, 155.7, 152.5, 151.9, 151.8, 144.1, 139.2, 136.5, 133.5, 132.0, 131.6, 129.5, 129.3, 123.1, 122.6, 121.7, 121.1, 113.0, 105.7, 60.2, 55.8, 32.4. **HRMS** (ESI): *m/z* 441.2034 [441.2034 calcd. for $C_{25}H_{25}N_6O_2^+$ (M+H$^+$)].

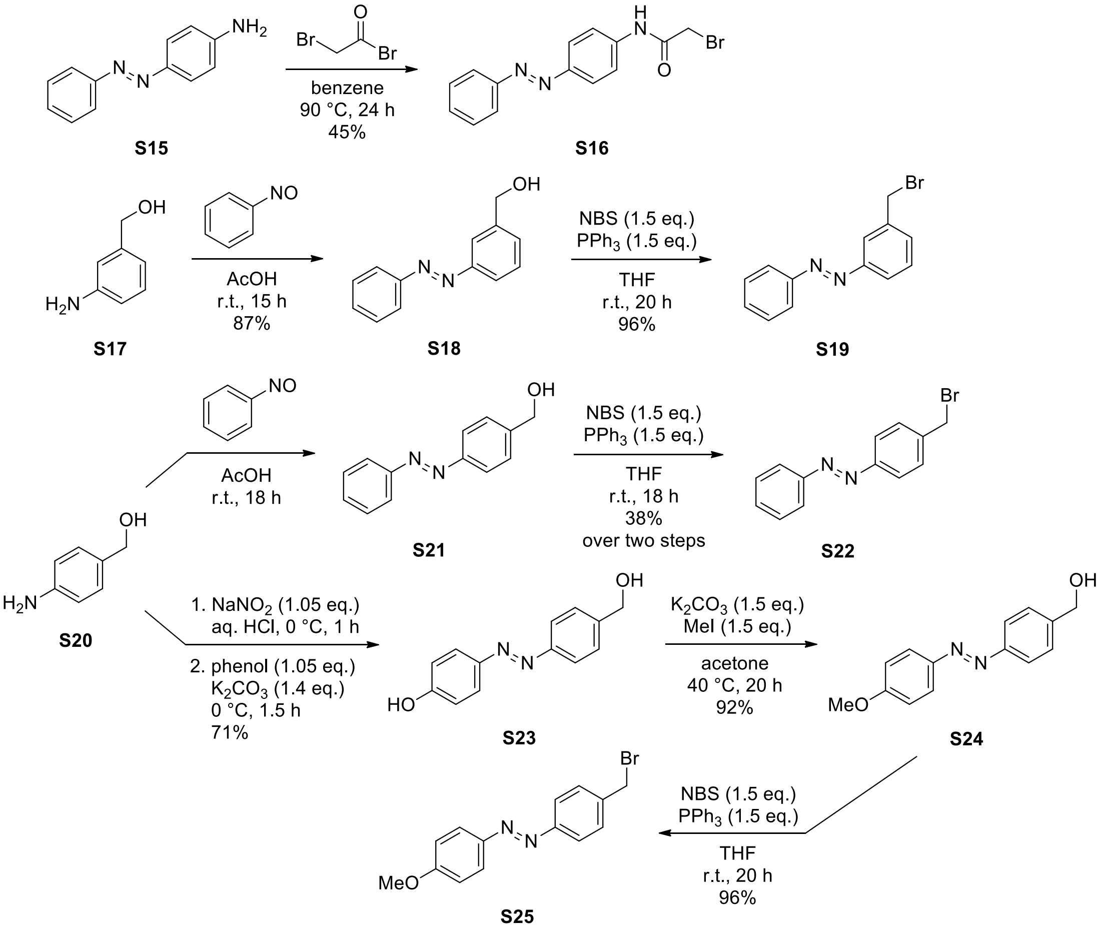
(*E*)-5-((4,5,6-Trimethoxy-4'-(phenyldiazenyl)-[1,1'-biphenyl]-2-yl)methyl)pyrimidine-2,4-diamine (2f):



2f

In a procedure analogous to the preparation of **2a**, coupling of bromide **S14** (369 mg, 1.00 mmol, 1 eq.) with boronic ester **S2** (339 mg, 1.10 mmol, 1.1 eq.) gave diaminopyrimidine **2f** as a red-orange foam (348 mg, 0.740 mmol, 74%).

TLC: R_f = 0.58 (DCM/MeOH 8:1). **Mp**: 56 – 59 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.94 – 7.85 (m, 4H), 7.64 – 7.55 (m, 3H), 7.39 (d, J = 8.1 Hz, 2H), 6.98 (s, 1H), 6.72 (s, 1H), 6.00 (bs, 2H), 5.66 (bs, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.55 (s, 3H), 3.34 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.0, 161.9, 154.9, 152.6, 152.0, 150.8, 150.6, 140.2, 140.2, 132.6, 131.4, 131.1, 129.5, 127.7, 122.5, 122.1, 109.3, 105.1, 60.7, 60.4, 55.9, 30.9. **HRMS** (ESI): *m/z* 471.2138 [471.2139 calcd. for $C_{26}H_{27}N_6O_3^+$ (M+H$^+$)].



Scheme S4 Synthesis of bromides **S16**, **S19**, **S22** and **S25**.

(*E*)-2-Bromo-*N*-(4-(phenyldiazenyl)phenyl)acetamide (S16):[7]

2-Bromoacetyl bromide (0.5 mL, 1.16 g, 5.74 mmol, 1 eq.) was added dropwise over 30 min to a solution of 4-aminoazobenzene (**S15**, 1.25 g, 6.31 mmol, 1.1 eq.) in 50 mL dry benzene, and the resulting reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, the newly formed brownish precipitate was filtered off and recrystallized from EtOH to give acylated aminoazobenzene **S16** as a red crystalline solid (816 mg, 2.56 mmol, 45%).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 10.76 (s, 1H), 7.94 – 7.89 (m, 2H), 7.89 – 7.79 (m, 4H), 7.62 – 7.50 (m, 3H), 4.10 (s, 2H).

The spectroscopic data is in accordance with the literature.[7]

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[7] E. A. Yushkova, E. N. Zaikov, I. I. Stoikov, I. S. Antipin, *Russ. Chem. Bull. Int. Ed.* **2009**, *58*, 101.

(*E*)-(3-(Phenyldiazenyl)phenyl)methanol (S18):[8]

Nitrosobenzene (0.957 g, 8.93 mmol, 1.1 eq.) was added to a solution of 3-aminobenzyl alcohol (**S17**, 1.00 g, 8.12 mmol, 1 eq.) in 40 mL glacial acetic acid under nitrogen atmosphere, and the reaction mixture was stirred at room temperature. After 15 h, acetic acid was removed under reduced pressure, the residue was taken up in EtOAc and washed with water. The aqueous layer was extracted with EtOAc (2 × 30 mL) and the combined organic layers were successively washed with saturated, aqueous $NaHCO_3$ solution, water and brine, and dried over Na_2SO_4. After purification by flash chromatography (P/EtOAc 90:10 → 80:10 → 70:30), azobenzene **S18** was obtained as a red oil that crystallized upon standing in the fridge (1.50 g, 7.07 mmol, 87%).

TLC: R_f = 0.57 (P/EtOAc 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 3H), 7.89 – 7.81 (m, 1H), 7.56 – 7.44 (m, 5H), 4.79 (s, 2H), 2.07 (s, 1H).
The spectroscopic data is in accordance with the literature.[9]

(*E*)-1-(4-(Bromomethyl)phenyl)-2-phenyldiazene (S19):[9]

A solution of alcohol **S18** (1.47 g, 6.92 mmol, 1 eq.) in 35 mL dry THF under nitrogen atmosphere was cooled to 0 °C and alternatingly treated with portions of *N*-bromosuccinimide (1.85 g, 10.4 mmol, 1.5 eq.) and triphenylphosphine (2.73 g, 10.4 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature for 20 h, before it was filtered over a short plug of silica and the filtrate was concentrated under reduced pressure. Purification of the residue by flash chromatography (P/EtOAc 99:1 → 98:2), gave bromide **S19** as a red oil that crystallized upon standing in the fridge (1.82 g, 6.61 mmol, 96%).

TLC: R_f = 0.75 (P/EtOAc 8:2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 – 7.91 (m, 3H), 7.93 – 7.83 (m, 1H), 7.58 – 7.47 (m, 5H), 4.59 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.0, 152.7, 139.0, 131.5, 131.4, 129.7, 129.3, 123.5, 123.1, 123.0, 32.9.
The spectroscopic data is in accordance with the literature.[9]

(*E*)-1-(4-(Bromomethyl)phenyl)-2-phenyldiazene (S22)

was prepared analogously to **S19** in a two-step procedure starting from 4-aminobenzyl alcohol (**S20**, 1.23 g, 10.0 mmol, 1 eq.) via azobenzene **S21**, bromination of which yielded **S22** as an orange solid (1.04 g, 3.78 mmol, 38% over two steps).

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[8] P. Stawski, M. Sumser, D. Trauner, *Angew. Chem. Int. Ed.* **2012**, *51*, 5748.

[9] P. Fatás, E. Longo, F. Rastrelli, M Crisma, C Toniolo, A I. Jiménez, C Cativiela, A. Moretto, *Chem. Eur. J.* **2011**, *17*, 12606.

TLC: R_f = 0.72 (P/EtOAc 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.96 – 7.86 (m, 4H), 7.57 – 7.46 (m, 5H), 4.56 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 152.7, 152.5, 140.7, 131.4, 130.0, 129.3, 123.4, 123.1, 32.9.

The spectroscopic data is in accordance with the literature.[9]

(*E*)-4-((4-(Hydroxymethyl)phenyl)diazenyl)phenol (S23):[10]

A suspension of 4-aminobenzyl alcohol (**S20**, 2.00 g, 16.2 mmol, 1 eq.) in 30 mL water at 0 °C was treated with 3.4 mL concentrated aqueous HCl, followed by the slow addition of an ice-cooled solution of $NaNO_2$ (1.17 g, 17.0 mmol, 1.05 eq.) in 8 mL water. After 1 h of stirring under continued cooling, a separately prepared solution of phenol (1.60 g, 17.0 mmol, 1.05 eq.) and K_2CO_3 (3.14 g, 22.7 mmol, 1.4 eq.) in 25 mL water was added dropwise over 10 min, after which stirring was continued for a further 1.5 h. Diluted aqueous acetic acid was then used to acidify the reaction mixture to a pH of 4-5, before the obtained precipitate was filtered off and washed with water and small amounts of MeOH. Drying in vacuo gave azobenzene **S23** as a yellow solid (2.63 g, 11.5 mmol, 71%).

^{1}H NMR (400 MHz, DMSO-d_6): *δ* 10.25 (bs, 1H), 7.83 – 7.76 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.98 – 6.91 (m, 2H), 5.34 b(s, 1H), 4.59 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): *δ* 160.8, 151.0, 145.2, 145.2, 127.1, 124.7, 121.9, 115.9, 62.5.

The spectroscopic data is in accordance with the literature.[10]

(*E*)-(4-((4-Methoxyphenyl)diazenyl)phenyl)methanol (S24):[11]

Iodomethane (0.53 mL, 1.21 g, 8.54 mmol, 1.5 eq.) and K_2CO_3 (1.18 g, 8.54 mmol, 1.5 eq.) were added to a solution of azobenzene **S23** (1.30 g, 5.70 mmol, 1 eq.) in 100 mL acetone. The reaction mixture was stirred at 40 °C for 20 h, before the solvent was removed under reduced pressure and the residue partitioned between DCM and water (100 mL each). The aqueous layer was extracted with DCM (2 × 80 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (P/EtOAc 70:30 → 60:40) yielded azobenzene **S24** as an orange crystalline solid (1.27 g, 5.24 mmol, 92%).

TLC: R_f = 0.60 (P/EtOAc 6:4). **^{1}H NMR** (400 MHz, DMSO-d_6): *δ* 7.89 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 5.37 (t, *J* = 5.7 Hz, 1H),

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[10] J.-H. Kim, M. E. El-Khouly, Y. Araki, O. Ito, K.-Y. Kay, *Chem. Lett.* **2008**, *37*, 544.

[11] D. M. Junge, D. V. McGrath, *J. Am. Chem. Soc.* **1999**, *121*, 4912.

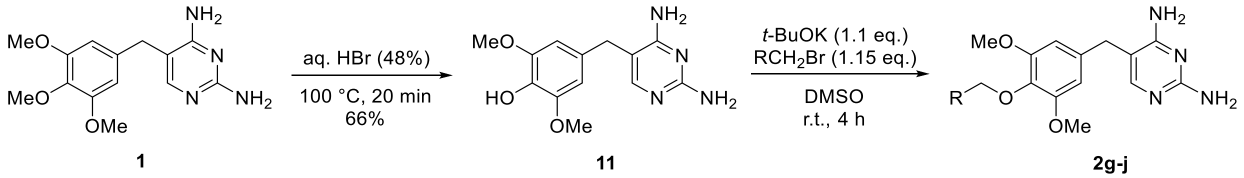
4.60 (d, *J* = 5.5 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): *δ* 161.9, 150.9, 146.2, 145.7, 127.1, 124.5, 122.1, 114.6, 62.5, 55.6.

The spectroscopic data is in accordance with the literature.[11]

(*E*)-1-(4-(Bromomethyl)phenyl)-2-(4-methoxyphenyl)diazene (S25)

was prepared analogously to **S19**: Reaction of alcohol **S24** (1.28 g, 5.30 mmol, 1 eq.) with *N*-bromosuccinimide and triphenylphosphine gave bromide **S25** as an orange solid (1.56 g, 5.11 mmol, 96%).

TLC: R$_f$ = 0.59 (P/EtOAc 6:4). **Mp**: 114 – 117 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): *δ* 7.93 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.56 (s, 2H), 3.90 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): *δ* 162.4, 152.6, 147.1, 139.9, 130.0, 125.0, 123.1, 114.4, 55.8, 33.1. **HRMS** (ESI): *m/z* 305.0291 [305.0284 calcd. for $C_{14}H_{14}BrN_2O^+$ (M+H$^+$)].



Scheme S5 Synthesis of diaminopyrimidines **2g-j** by alkylation of phenol **11**.

4-((2,4-Diaminopyrimidin-5-yl)methyl)-2,6-dimethoxyphenol (11):[12]

Trimethoprim (10.0 g, 34.4 mmol) was dissolved in 120 mL 48% aqueous HBr preheated to 90 °C. The resulting solution was stirred at 100 °C for 30 min and subsequently quenched by careful addition of 25 mL 50% aqueous NaOH. After standing overnight in the fridge, the formed crystals were filtered off, washed with ice-cooled water and then dissolved in boiling water. The hot solution was neutralized with 25% aqueous ammonia, upon which the product recrystallized. After standing in the fridge for another night, the crystals were filtered off and dried in vacuo, resulting in phenol **11** as an off-white crystalline solid (6.24 g, 22.6 mmol, 66%).

^{1}H NMR (400 MHz, DMSO-d_6): *δ* 8.16 (bs, 1H), 7.46 (s, 1H), 6.49 (s, 2H), 6.08 (bs, 2H), 5.71 (bs, 2H), 3.70 (s, 6H), 3.47 (s, 2H).

The spectroscopic data is in accordance with the literature.[13]

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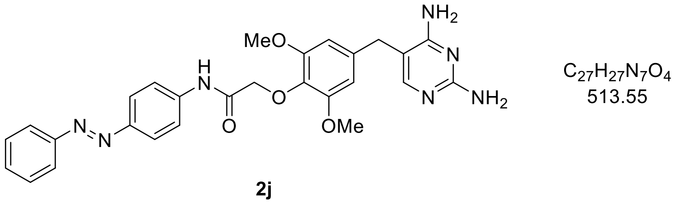
[12] P. Liu, A. Calderon, G. Konstantinidis, J. Hou, S. Voss, X. Chen, F Li, S. Banerjee, J.-E. Hoffmann, C. Theiss, L. Dehmelt, Y.-W. Wu, *Angew. Chem. Int. Ed.* **2014**, *53*, 10049.

(*E*)-2-(4-((2,4-Diaminopyrimidin-5-yl)methyl)-2,6-dimethoxyphenoxy)-N-(4-(phenyldiazenyl)phenyl)acetamide (2j):

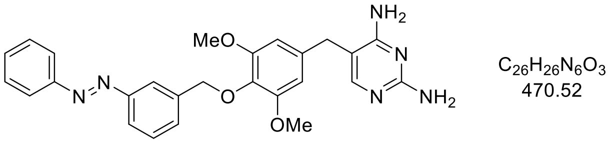


2j

Following a modified procedure previously reported for the preparation of a different product,[12] KO*t*-Bu (15.6 mg, 0.139 mmol, 1.1 eq.) was added to a solution of phenol **11** (34.8 mg, 0.126 mmol, 1 eq.) in 0.83 mL dry DMSO under nitrogen atmosphere and the resulting mixture stirred for 30 min at room temperature. Subsequently bromide **S16** (44.1 mg, 0.139 mmol, 1.1 eq.) was added to the reaction, and stirring at room temperature was continued for 4 h. The reaction mixture was then partitioned between water and EtOAc, the separated aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. After purification by flash chromatography (DCM/MeOH 95:5 → 90:10), diaminopyrimidine **2j** was obtained as an orange solid (26.2 mg, 51.0 μmol, 40%).

TLC: $R_f = 0.53$ (DCM/MeOH 6:1). **Mp**: 211 – 214 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 7.96 – 7.83 (m, 6H), 7.62 – 7.52 (m, 3H), 7.49 (s, 1H), 6.67 (s, 2H), 6.57 (bs, 2H), 6.37 (bs, 2H), 4.53 (s, 2H), 3.81 (s, 6H), 3.57 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 167.9, 162.6, 160.4, 152.0, 151.9, 151.7, 147.9, 141.1, 136.0, 134.4, 131.1, 129.4, 123.7, 122.4, 119.7, 106.3, 106.0, 72.2, 56.1, 32.8. **HRMS** (ESI): *m/z* 514.2195 [514.2197 calcd. for $C_{27}H_{28}N_7O_4^+$ (M+H$^+$)].

(*E*)-5-(3,5-Dimethoxy-4-(3-(phenyldiazenyl)benzyloxy)benzyl)pyrimidine-2,4-diamine (2g):



2g

In a procedure analogous to the preparation of **2j**, reaction of phenol **1** (111 mg, 0.400 mmol, 1 eq.) with bromide **S19** (121 mg, 0.440 mmol, 1.1 eq.) and purification by flash chromatography

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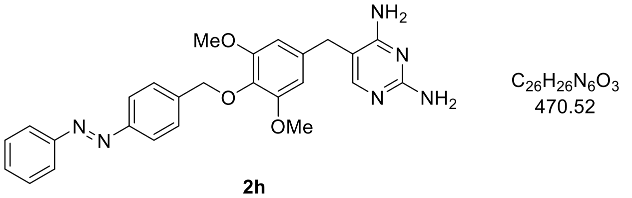
[13] W. Liu, F. Li, X. Chen, J. Hou, L. Yi, Y.-W. Wu, *J. Am. Chem. Soc.* **2014**, *136*, 4468.

(DCM/MeOH 98:2 → 95:5) gave diaminopyrimidine **2g** as a red-orange crystalline solid (140 mg, 0.298 mmol, 75%).

TLC: R_f = 0.37 (DCM/MeOH 8:1). **Mp**: 161 – 163 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.03 (s, 1H), 7.92 (d, J = 7.4 Hz, 2H), 7.86 (d, J = 7.5 Hz, 1H), 7.66 – 7.55 (m, 5H), 7.52 (s, 1H), 6.59 (s, 2H), 6.10 (bs, 2H), 5.70 (bs, 2H), 4.98 (s, 2H), 3.75 (s, 6H), 3.54 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.2, 162.2, 155.6, 152.8, 151.9, 151.8, 139.7, 136.2, 134.5, 131.5, 130.6, 129.5, 129.2, 122.7, 122.5, 120.9, 105.8, 105.8, 73.5, 55.9, 33.0. **HRMS** (ESI): *m/z* 471.2141 [471.2139 calcd. for $C_{26}H_{27}N_6O_3^+$ (M+H$^+$)].

(*E*)-5-(3,5-Dimethoxy-4-(4-(phenyldiazenyl)benzyloxy)benzyl)pyrimidine-2,4-diamine (2h):

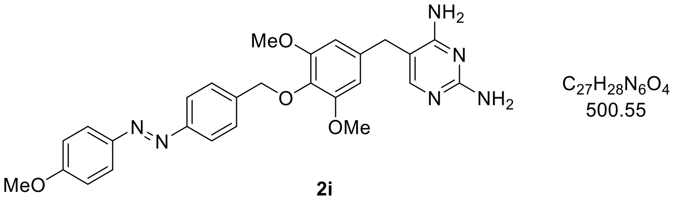


2h

In a procedure analogous to the preparation of **2j**, reaction of phenol **11** (111 mg, 0.400 mmol, 1 eq.) with bromide **S22** (121 mg, 0.440 mmol, 1.1 eq.) and purification by flash chromatography (DCM/MeOH 98:2 → 95:5) gave diaminopyrimidine **2h** as an orange solid (105 mg, 0.223 mmol, 56%).

TLC: R_f = 0.36 (DCM/MeOH 8:1). **Mp**: 204 – 206 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.93 – 7.87 (m, 4H), 7.67 (d, J = 8.3 Hz, 2H), 7.64 – 7.56 (m, 3H), 7.53 (s, 1H), 6.60 (s, 2H), 6.11 (bs, 2H), 5.71 (bs, 2H), 4.96 (s, 2H), 3.75 (s, 6H), 3.55 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.2, 162.2, 155.5, 152.8, 151.9, 151.3, 141.7, 136.2, 134.5, 131.5, 129.5, 128.6, 122.5, 122.4, 105.8, 105.8, 73.4, 55.9, 33.0. **HRMS** (ESI): *m/z* 471.2139 [471.2139 calcd. for $C_{26}H_{27}N_6O_3^+$ (M+H$^+$)].

(*E*)-5-(3,5-Dimethoxy-4-(4-((4-methoxyphenyl)diazenyl)benzyloxy)benzyl)pyrimidine-2,4-diamine (2i):

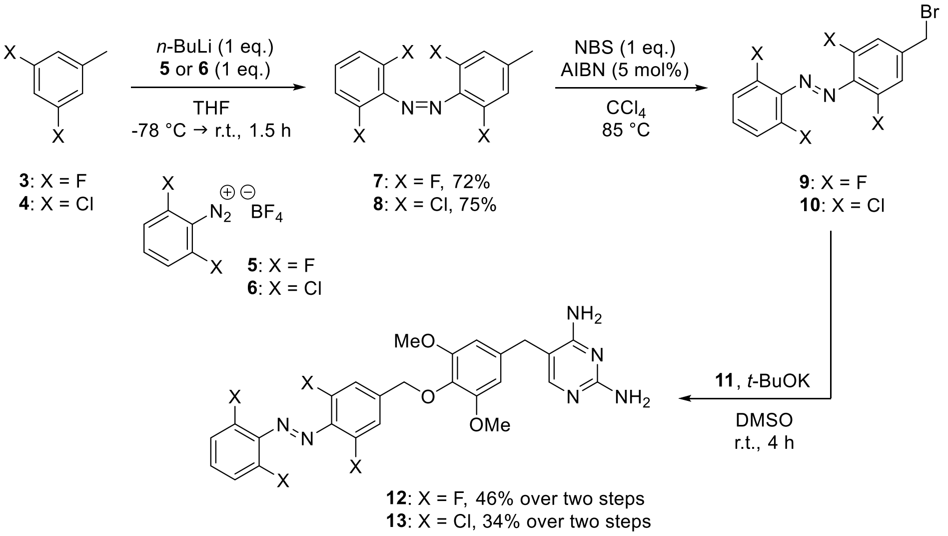


2i

In a procedure analogous to the preparation of **2j**, reaction of phenol **11** (100 mg, 0.362 mmol, 1 eq.) with bromide **S25** (121 mg, 0.398 mmol, 1.1 eq.) and purification by flash chromatography (DCM/MeOH 98:2 → 95:5) gave diaminopyrimidine **2i** as an orange solid (66.6 mg, 0.133 mmol, 37%).

TLC: R_f = 0.47 (DCM/MeOH 8:1). **Mp**: 209 – 211 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.90 (d, J = 8.9 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.53 (s, 1H), 7.14 (d, J = 9.0 Hz, 2H), 6.59 (s, 2H), 6.15 (bs, 2H), 5.75 (bs, 2H), 4.94 (s, 2H), 3.87 (s, 3H), 3.75 (s, 6H), 3.55 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 162.2, 162.0, 162.0, 155.2, 152.8, 151.4, 146.2, 140.9, 136.1, 134.5, 128.6, 124.5, 122.0, 114.6, 105.8, 105.8, 73.5, 55.9, 55.6, 33.0. **HRMS** (ESI): *m/z* 501.2242 [501.2245 calcd. for $C_{27}H_{29}N_6O_4^+$ (M+H$^+$)].

Synthesis of red-shifted diaminopyrimidines 12 and 13



Scheme S6 Synthesis of diaminopyrimidines **12** and **13**.

(*Z*)-1-(2,6-Difluoro-4-methylphenyl)-2-(2,6-difluorophenyl)diazene (7):

Following our previously reported procedure in a slightly modified way,[14] 3,5-difluorotoluene (512 mg, 4.00 mmol, 1 eq.) dissolved in 8 mL dry THF at -78 °C was slowly treated with a solution of *n*-BuLi (1.6 M in hexane, 2.5 mL, 4.00 mmol, 1 eq.), after which stirring was continued at -78 °C for 1 h. Solid 2,6-difluorobenzenediazonium tetrafluoroborate[14] (**5**, 912 mg, 4.00 mmol, 1 eq.) was then at once added to the reaction mixture, which was subsequently allowed to warm to room temperature over 1.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. After purification by flash chromatography (P/EtOAc 100:0 → 99:1 → 98:2), azobenzene **7** was obtained as a dark-red crystalline solid (766 mg, 2.86 mmol, 72%) consisting mainly of the *cis* isomer, which was used in the next step without thermal adaptation.

TLC: $R_f = 0.38$ (P/EtOAc 95:5). **Mp**: 85 – 87 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.65 – 7.54 (m, 1H), 7.35 (t, J = 9.6 Hz, 2H), 7.22 (d, J = 11.6 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 159.0 (dd, J = 7.7, 4.7 Hz), 156.4 (dd, J = 6.8, 4.6 Hz), 148.38 (t, J = 10.6 Hz), 135.8 (t, J = 10.6 Hz), 133.9 (t, J = 10.3 Hz), 131.5 (t, J = 9.7 Hz), 116.7 (dd, J = 20.0, 3.2 Hz), 116.3 (dd, J = 20.6, 2.9 Hz), 24.3. **^{19}F NMR** (376 MHz, DMSO-d_6): δ -122.0 (d, J = 10.8 Hz), -122.3 (dd, J = 10.0, 6.1 Hz). **HRMS** (ESI): *m/z* 269.0701 [269.0696 calcd. for $C_{13}H_9F_4N_2^+$ $(M+H^+)$].

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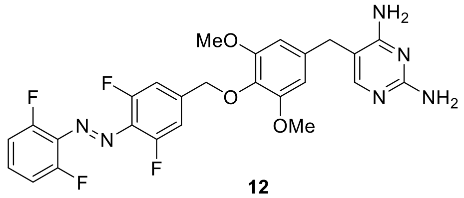
[14] M. J. Hansen, M. M. Lerch, W. Szymanski, B. L. Feringa, *Angew. Chem. Int. Ed.* **2016**, *55*, 13514.

(*Z*)-1-(2,6-Ddichloro-4-methylphenyl)-2-(2,6-dichlorophenyl)diazene (8):

In a procedure analogous to the preparation of **7**, reaction of 3,5-dichlorotoluene (593 mg, 3.68 mmol, 1 eq.) with *n*-BuLi and 2,6-dichlorobenzenediazonium tetrafluoroborate[14] (**6**, 961 mg, 3.68 mmol, 1 eq.) gave azobenzene **8** as a dark-red crystalline solid (916 mg, 2.74 mmol, 75%) consisting mainly of the *cis* isomer, which was used in the next step without thermal adaptation.

TLC: $R_f = 0.55$ (P/EtOAc 95:5). **Mp**: 121 – 124 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.69 (d, J = 8.1 Hz, 2H), 7.55 (s, 2H), 7.50 (t, J = 8.1 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 146.8, 143.9, 142.4, 130.9, 130.3, 129.8, 126.2, 125.8, 20.2. **HRMS** (ESI): *m/z* 334.9490 [334.9485 calcd. for $C_{13}H_9Cl_4N_2^+$ (M+H$^+$)].

(*E*)-5-(4-(4-((2,6-Difluorophenyl)diazenyl)-3,5-difluorobenzyloxy)-3,5-dimethoxybenzyl)-pyrimidine-2,4-diamine (12):



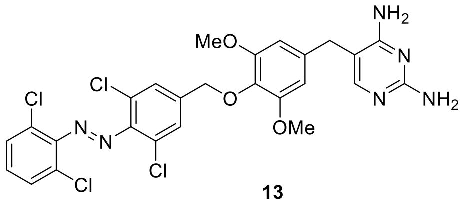
12

$C_{26}H_{22}F_4N_6O_3$
542.48

Azobenzene **7** (268 mg, 1.00 mmol, 1 eq.), *N*-bromosuccinimide (178 mg, 1.00 mmol, 1 eq.) and AIBN (33.0 mg, 0.200 mmol, 20 mol%) were dissolved in 10 mL carbon tetrachloride under nitrogen atmosphere. The resulting mixture was heated to 85 °C with stirring for 60 h. After cooling to room temperature, the solvent was then removed under reduced pressure and the product purified by flash chromatography (P/EtOAc 98:2 → 96:4) to yield bromide **9** as a dark red solid (166 mg, 0.478 mmol, 48%). KO*t*-Bu (49.3 mg, 0.440 mmol, 1.1 eq.) was added to a solution of phenol **11** (111 mg, 0.400 mmol, 1 eq.) in 1.3 mL dry DMSO under nitrogen atmosphere and the resulting mixture was stirred for 30 min at room temperature. Subsequently bromide **9** (153 mg, 0.440 mmol, 1.1 eq.) was added to the reaction, and stirring at room temperature was continued for 4 h. The reaction mixture was then partitioned between water and EtOAc, the separated aqueous layer was extracted with EtOAc (3 × 30 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. After purification by flash chromatography (DCM/MeOH 98:2 → 95:5), diaminopyrimidine **12** was obtained as a red-orange crystalline solid (207 mg, 0.382 mmol, 95%).

TLC: R$_f$ = 0.36 (DCM/MeOH 8:1). **Mp**: 183 – 185 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.63 (tt, *J* = 8.4, 6.1 Hz, 1H), 7.53 (s, 1H), 7.46 (d, *J* = 10.9 Hz, 2H), 7.37 (t, *J* = 9.3 Hz, 2H), 6.61 (s, 2H), 6.12 (bs, 2H), 5.71 (bs, 2H), 4.99 (s, 2H), 3.76 (s, 6H), 3.55 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.2, 162.1, 155.9 (dd, *J* = 10.8, 4.3 Hz), 155.5, 153.3 (dd, *J* = 11.2, 4.4 Hz), 152.5, 145.1 (t, *J* = 9.9 Hz), 136.5, 134.3, 133.1 (t, *J* = 10.8 Hz), 130.7 (t, *J* = 10.0 Hz), 129.5 (t, *J* = 10.1 Hz), 113.2 (dd, *J* = 20.1, 3.4 Hz), 111.3 (dd, *J* = 21.1, 3.2 Hz), 105.7, 105.7, 72.5, 55.9, 33.0. **^{19}F NMR** (376 MHz, DMSO-d$_6$): δ -121.4 (d, *J* = 10.8 Hz), -122.0 (dd, *J* = 10.0, 6.1 Hz). **HRMS** (ESI): *m/z* 543.1762 [543.1762 calcd. for $C_{26}H_{23}F_4N_6O_3^+$ (M+H$^+$)].

(*E*)-5-(4-(3,5-Dichloro-4-((2,6-dichlorophenyl)diazenyl)benzyloxy)-3,5-dimethoxybenzyl)-pyrimidine-2,4-diamine (13):



13

$C_{26}H_{22}Cl_4N_6O_3$
608.30

In a two-step procedure analogous to the preparation of **12**, reacting azobenzene **8** (305 mg, 0.913 mmol, 1 eq.) with *N*-bromosuccinimide (162 mg, 0.913 mmol, 1 eq.) and AIBN (16.0 mg, 45.7 µmol, 10 mol%) at 85 °C for 22 h first gave bromide **10** as a dark red solid (198 mg, 0.480 mmol, 53%). Bromide **10** (182 mg, 0.440 mmol, 1.1 eq.) was subsequently reacted with phenol **11** (111 mg, 0.400 mmol, 1 eq.) and KO*t*-Bu, after which purification by flash chromatography (DCM/MeOH 98:2 → 95:5) gave diaminopyrimidine **13** as an reddish brown solid (159 mg, 0.261 mmol, 65%).

TLC: R$_f$ = 0.43 (DCM/MeOH 8:1). **Mp**: 215 – 217 °C. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 7.80 (s, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.49 (m, 2H), 6.61 (s, 2H), 6.13 (bs, 2H), 5.72 (bs, 2H), 4.99 (s, 2H), 3.76 (s, 6H), 3.54 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d$_6$): δ 162.2, 162.2, 155.7, 152.5, 146.6, 145.3, 142.4, 136.5, 134.2, 131.2, 129.9, 128.4, 126.0, 125.9, 105.7, 105.7, 72.2, 55.9, 33.0. **HRMS** (ESI): *m/z* 609.0552 [609.0551 calcd. for $C_{26}H_{23}Cl_4N_6O_3^+$ (M+H$^+$)].

Photoisomerization of diaminopyrimidines 2a-2j

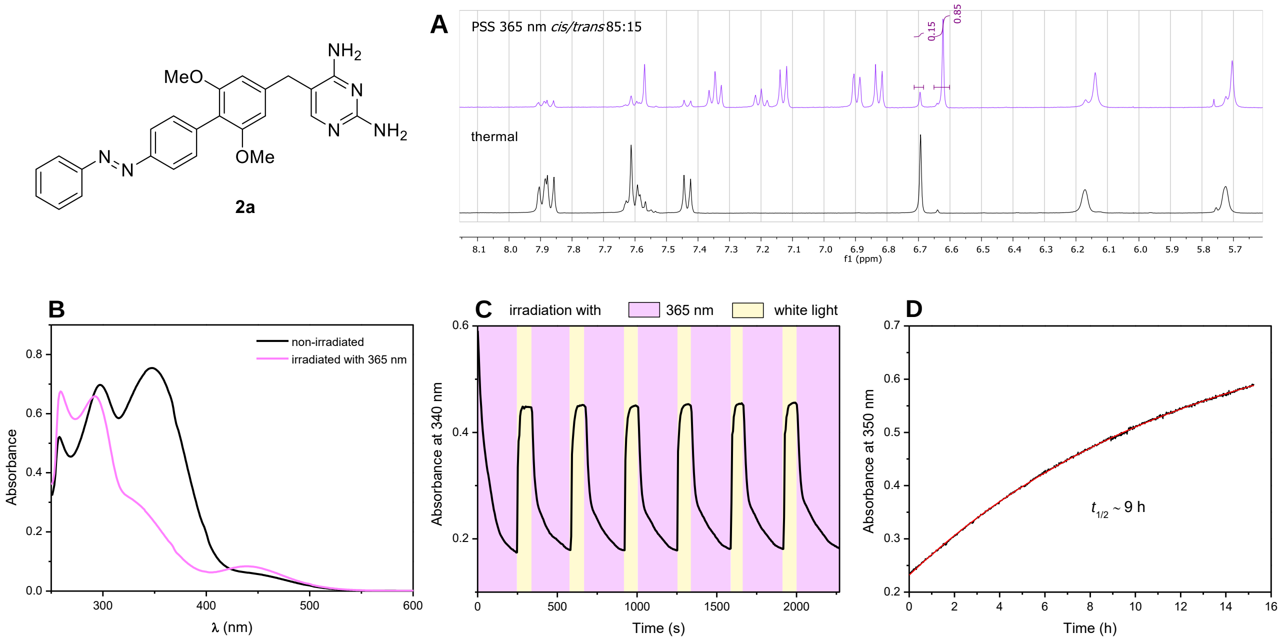


Figure S1 Photochemistry of compound **2a** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

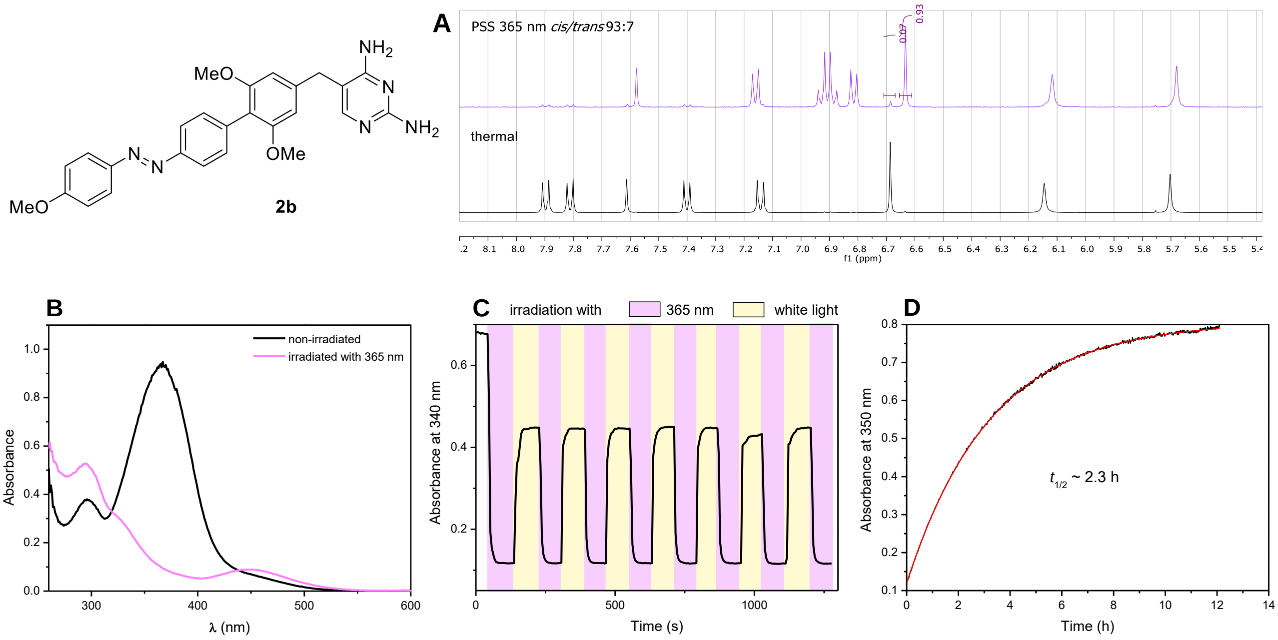


Figure S2 Photochemistry of compound **2b** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

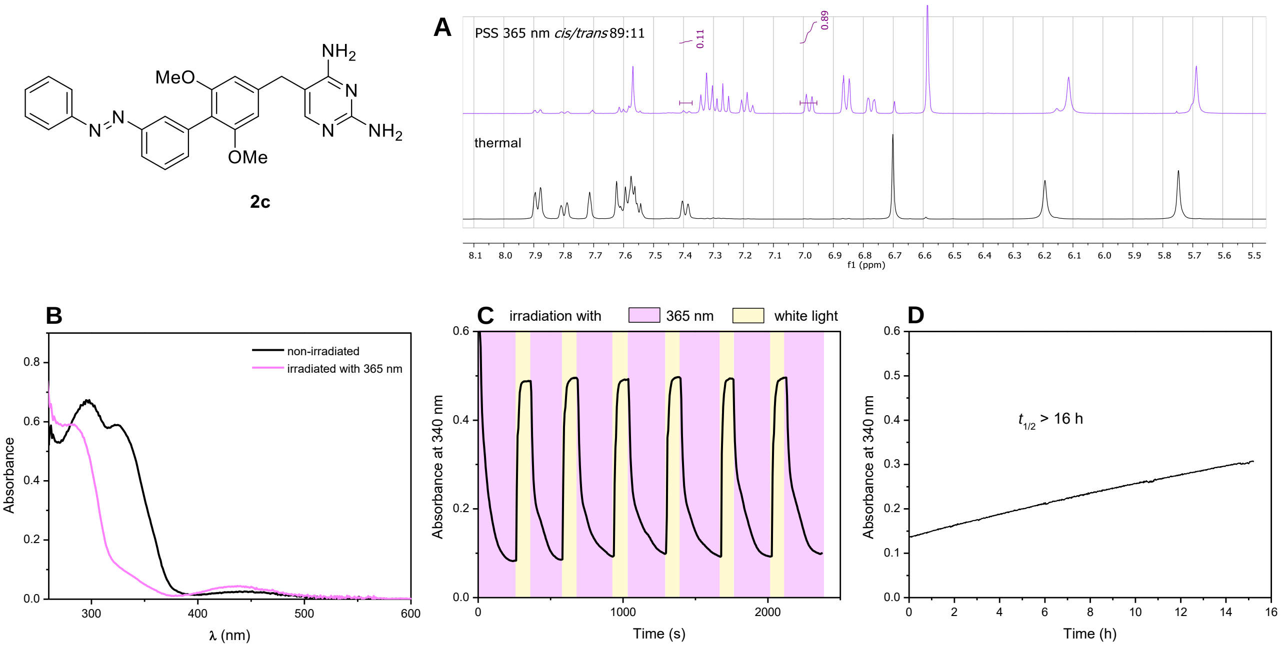


Figure S3 Photochemistry of compound **2c** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 μM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

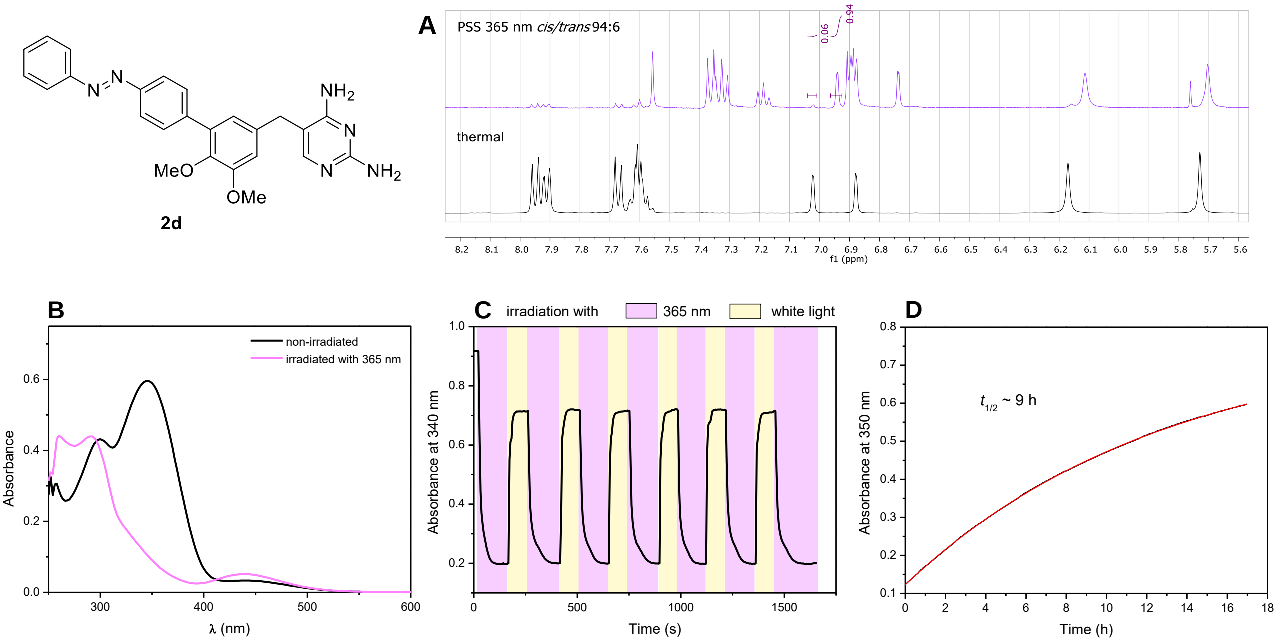


Figure S4 Photochemistry of compound **2d** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 μM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

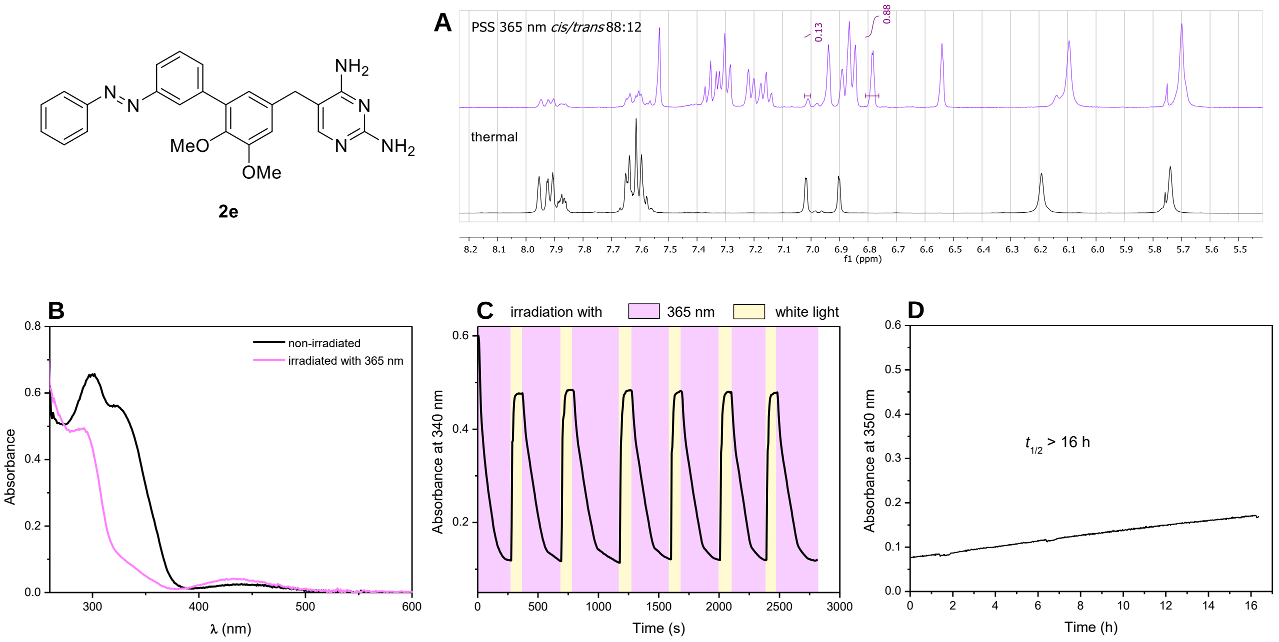

2e

Figure S5 Photochemistry of compound **2e** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

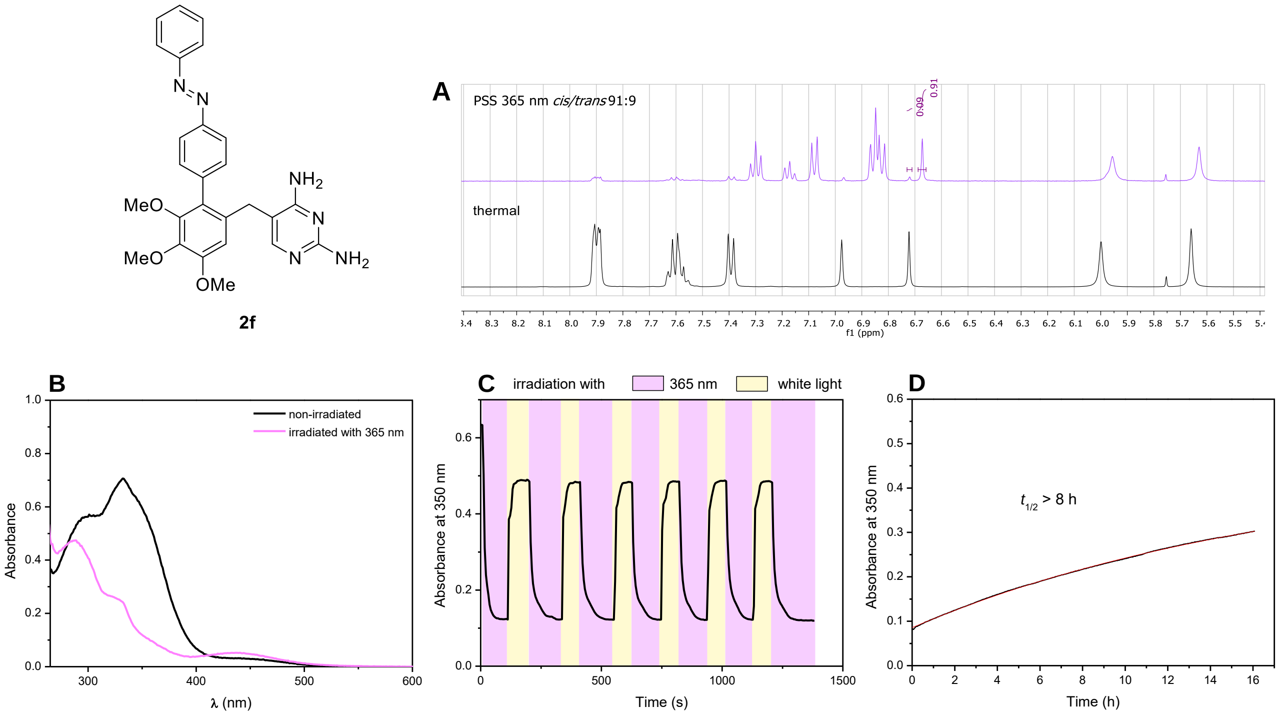

2f

Figure S6 Photochemistry of compound **2f** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

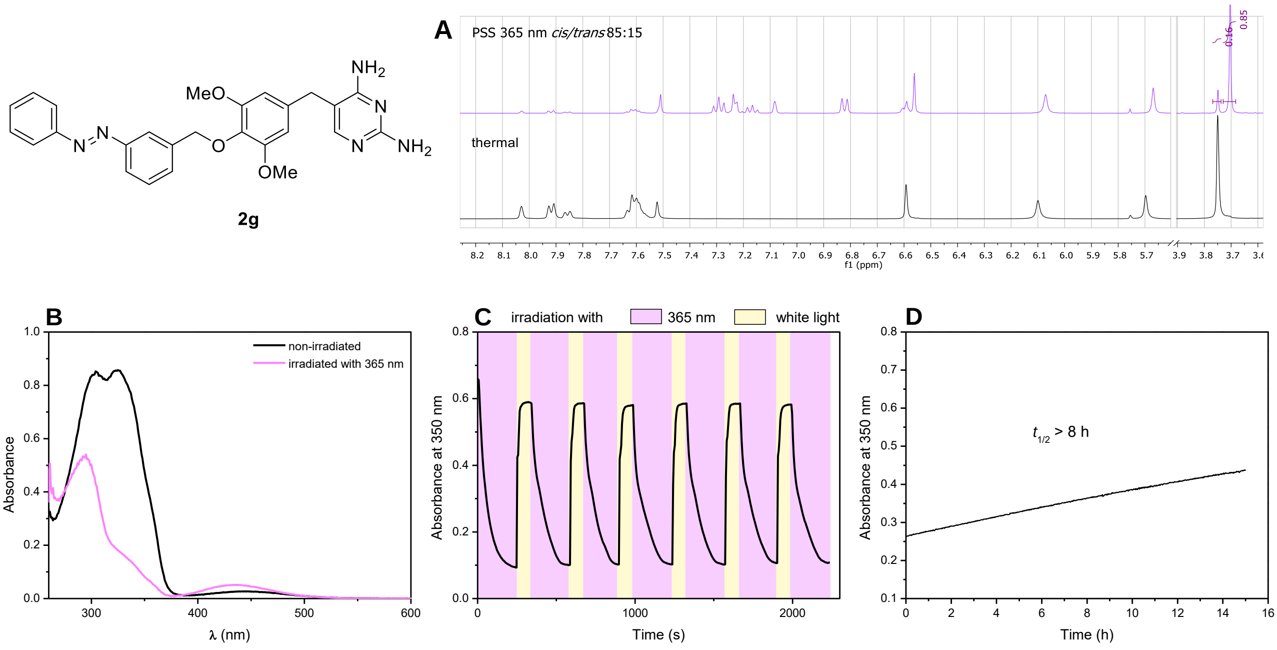


Figure S7 Photochemistry of compound **2g** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

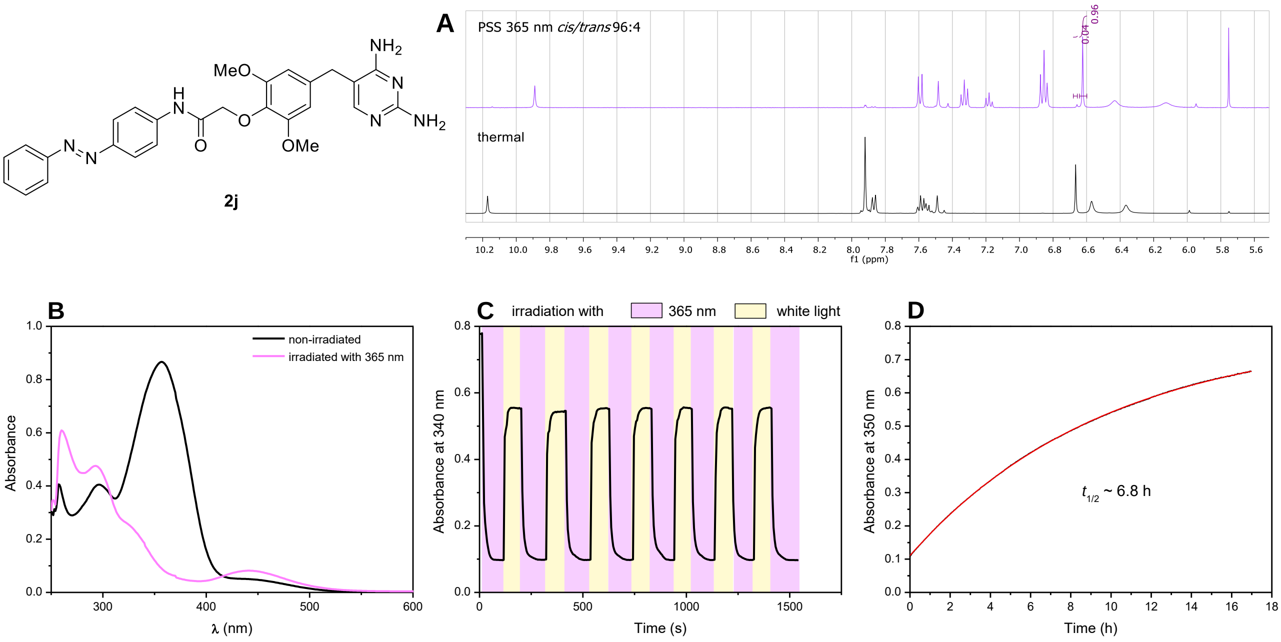
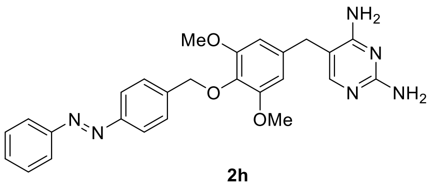


Figure S8 Photochemistry of compound **2j** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 µM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.



2h

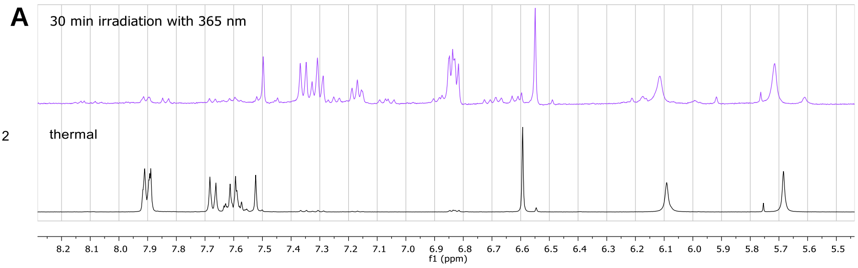
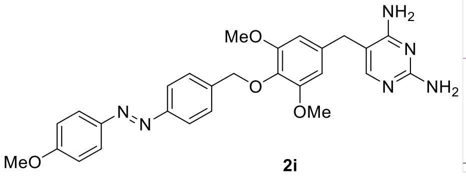
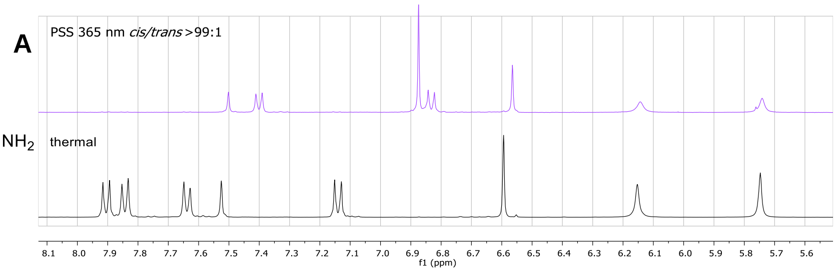


Figure S9 A) Extract from ^{1}H NMR spectra of compound **2h** before and after irradiation with UV light at λ = 365 nm in DMSO-d$_6$ (c ≈ 2 mM) that shows degradation occurring upon irradiation besides photoisomerization.



2i



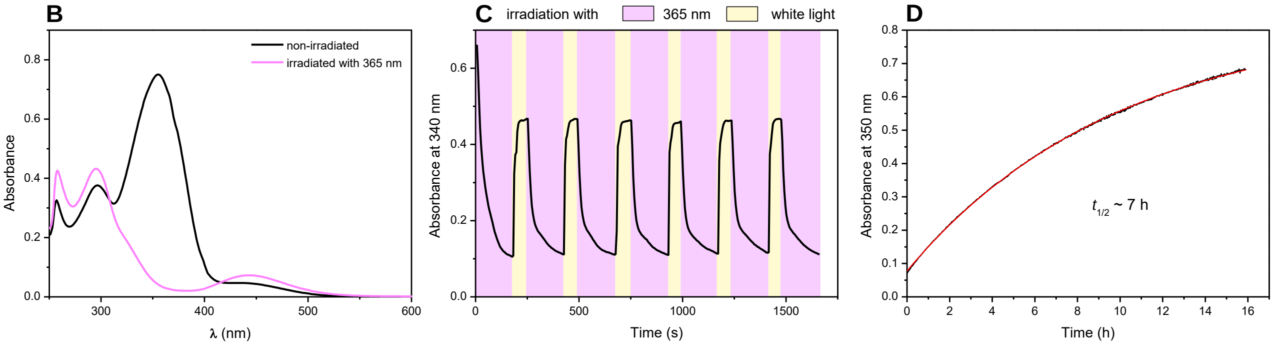


Figure S10 Photochemistry of compound **2i** in DMSO: A) Extract from ^{1}H NMR spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 2 mM). B) UV-Vis absorption spectra before and after irradiation with UV light at λ = 365 nm (c ≈ 30 μM). C) Reversible photochromism. D) Thermal *cis-trans* isomerization at 37 °C.

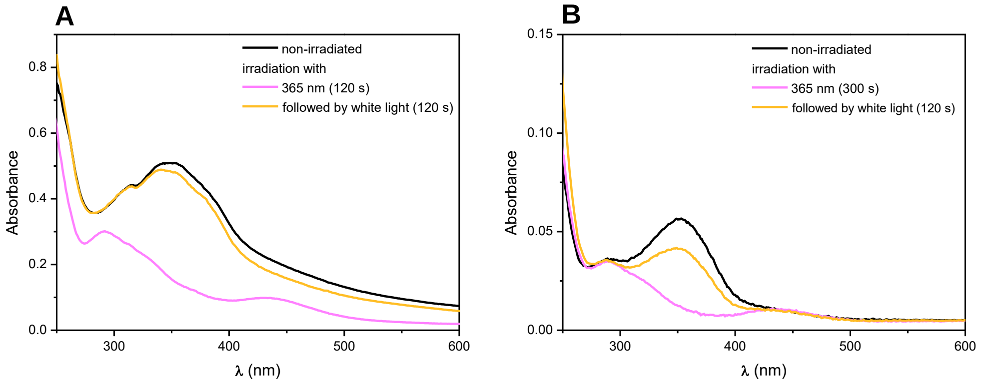


Figure S11 A) UV-Vis absorption spectra of compound **2i** in aqueous buffer at pH = 7.4 with 1.5 vol% DMSO before and after successive irradiation with UV light at λ = 365 nm and white light (c ≈ 30 μM). Light scattering evident in the spectra indicates a degree of aggregation of the compound in its *trans* form that is dissolved upon photoisomerization with UV light at λ = 365 nm and reestablished upon *cis-trans* isomerization with white light. B) UV-Vis absorption spectra of compound **2j** in aqueous buffer at pH = 7.4 with 0.25 vol% DMSO before irradiation and after successive irradiation with UV light at λ = 365 nm and white light (c ≈ 5 μM). Effects of aggregation are no longer evident here at lower concentration.

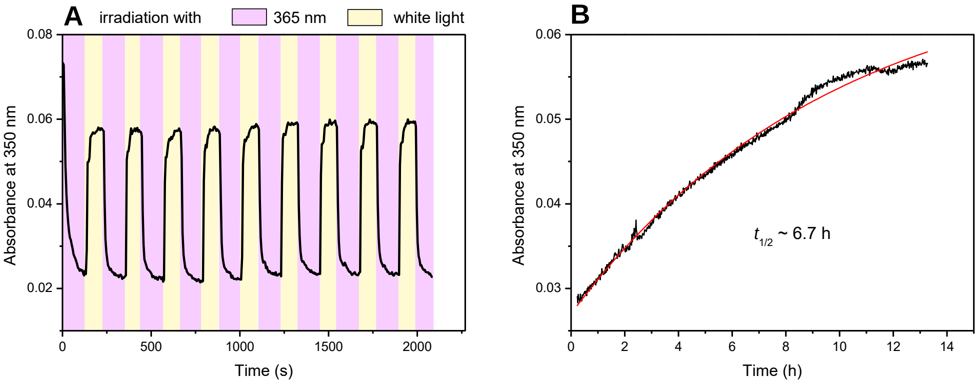


Figure S12 A) Reversible photochromism of compound **2i** in aqueous buffer at pH = 7.4 with 0.25 vol% DMSO at 37 °C and c ≈ 5 µM. B) Thermal *cis-trans* isomerization of **2i** under the same conditions.

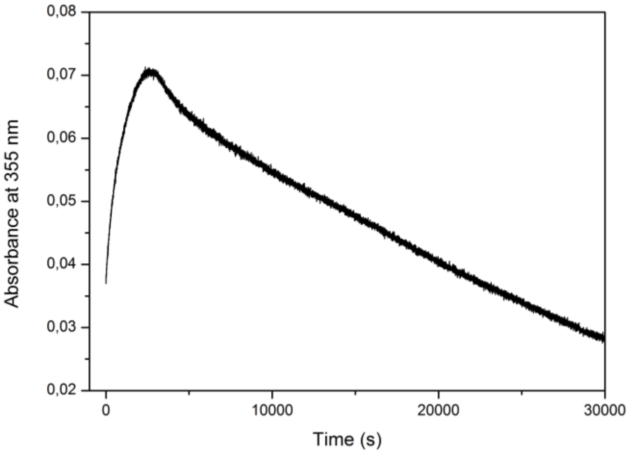


Figure S13 Further attempt at half-life determination of **2i** in aqueous buffer at pH = 7.4 with 1 vol% DMSO at 37 °C and c ≈ 10 µM. After partial thermal *cis-trans* isomerization compound **2i** starts to aggregate/precipitate which makes the measurement of a reliable half-life difficult, especially at c > 5 µM.

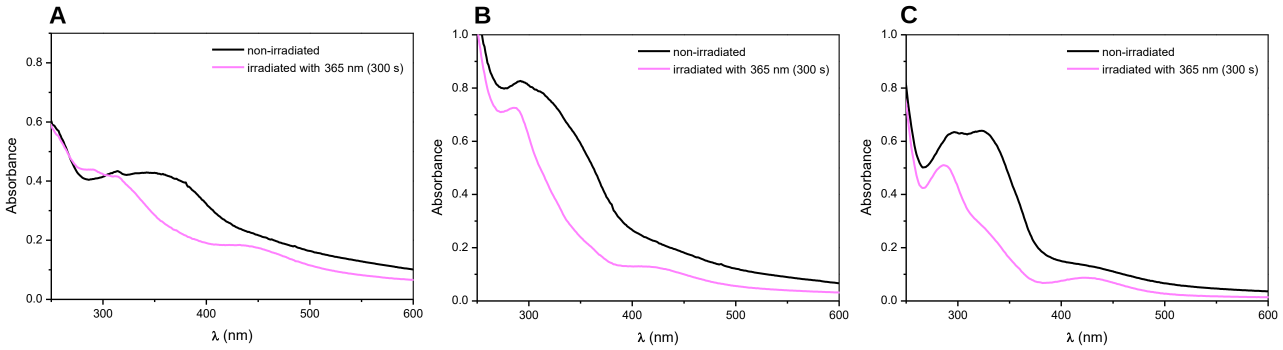


Figure S14 UV/Vis absorption spectra of selected compounds **2b** (A) **2e** (B) and **2g** (C) in aqueous buffer at pH = 7.4 with 1.5 vol% DMSO (c ≈ 30 µM) before and after irradiation with UV light at λ = 365 nm, showing light scattering likely due to aggregation, especially of the *trans* isomers.

Photoisomerization of red-shifted diaminopyrimidines 12 and 13

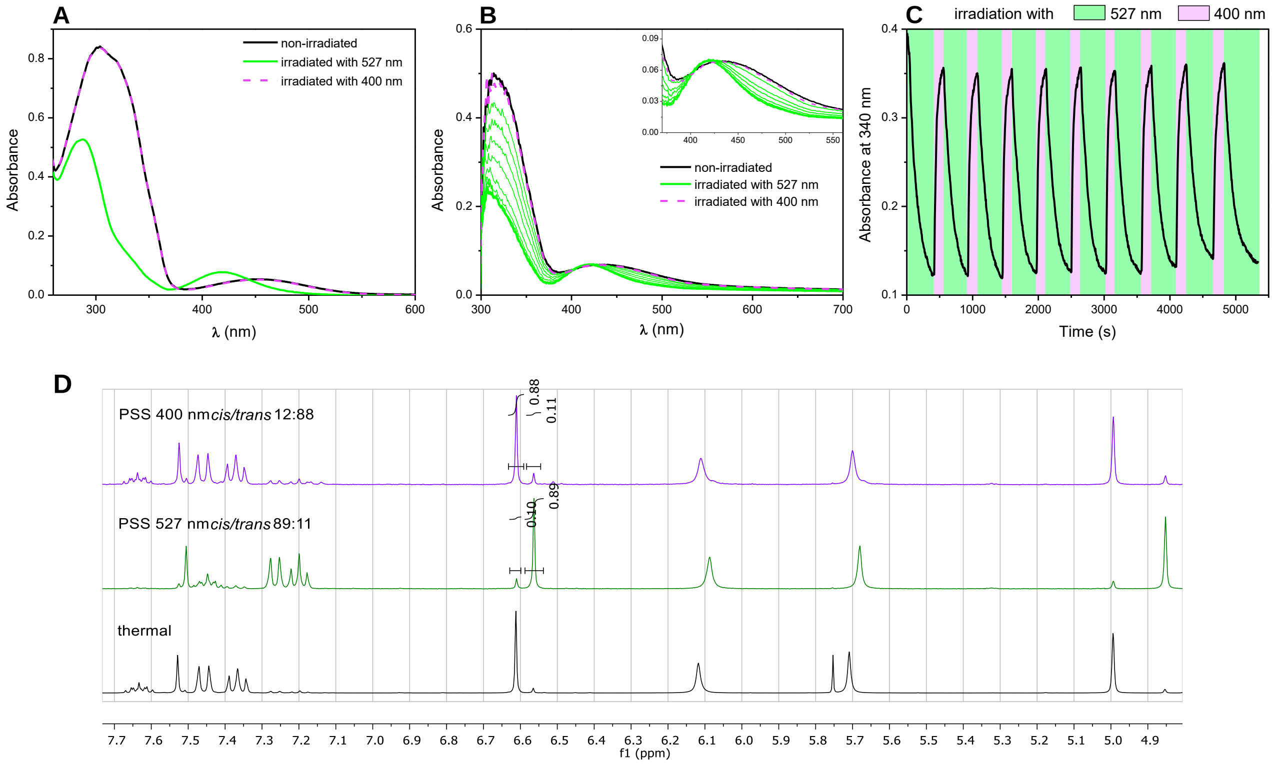


Figure S15 Photoisomerization of compound **12**: A) UV-Vis absorption spectra before and after irradiation with green light at λ = 527 nm (2 min) and violet light at λ = 400 nm (2 min) in DMSO (c ≈ 30 µM). B) UV-Vis absorption spectra before and after irradiation with green light at λ = 527 nm (over 6 min) and violet light at λ = 400 nm (2 min) in aqueous LB broth with 1.5 vol% DMSO (c ≈ 30 µM). C) Reversible photochromism in aqueous LB broth with 1.5 vol% DMSO at 37 °C (c ≈ 30 µM). D) Extract from ^{1}H NMR spectra before and after irradiation with green light at λ = 527 nm and violet light at λ = 400 nm for 30 min, respectively, in DMSO-d$_6$ (c ≈ 2 mM).

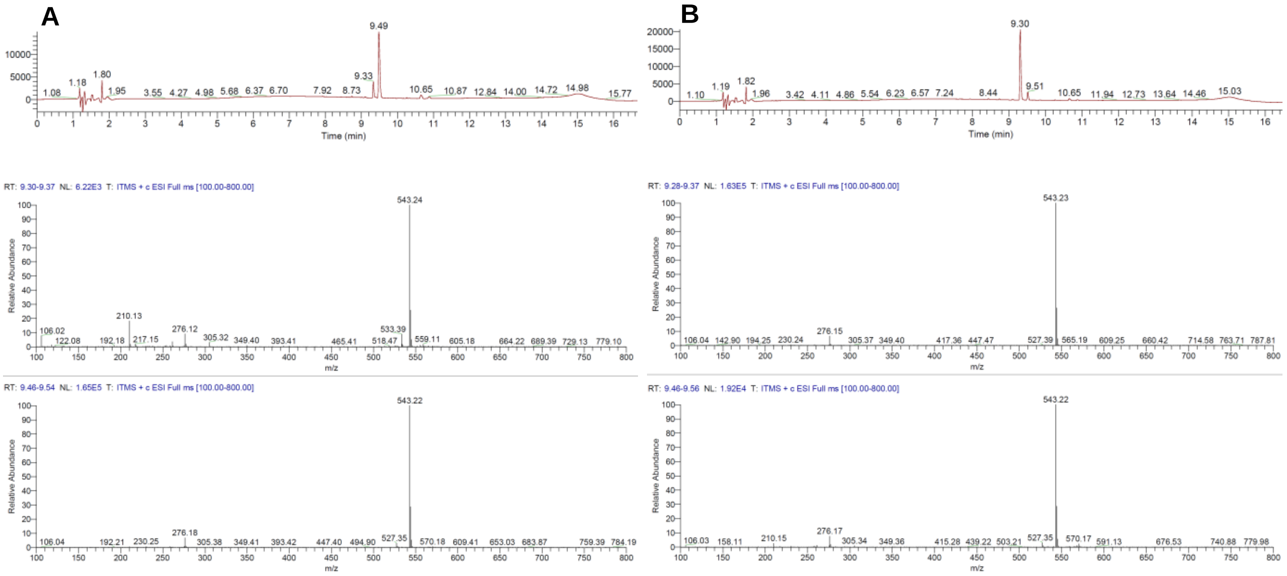


Figure S16 UHPLC-MS analysis of compound **12** before (A) and after (B) irradiation with green light at λ = 527 nm for 30 min in aqueous buffer at pH = 7.4 with 0.5 vol% DMSO at c ≈ 80 µM. Chromatograms show detection by UV-Vis absorption trace at λ = 425 nm. MS traces correspond to signals at: 9.33 min and 9.49 min (A), 9.30 min and 9.51 min (B).

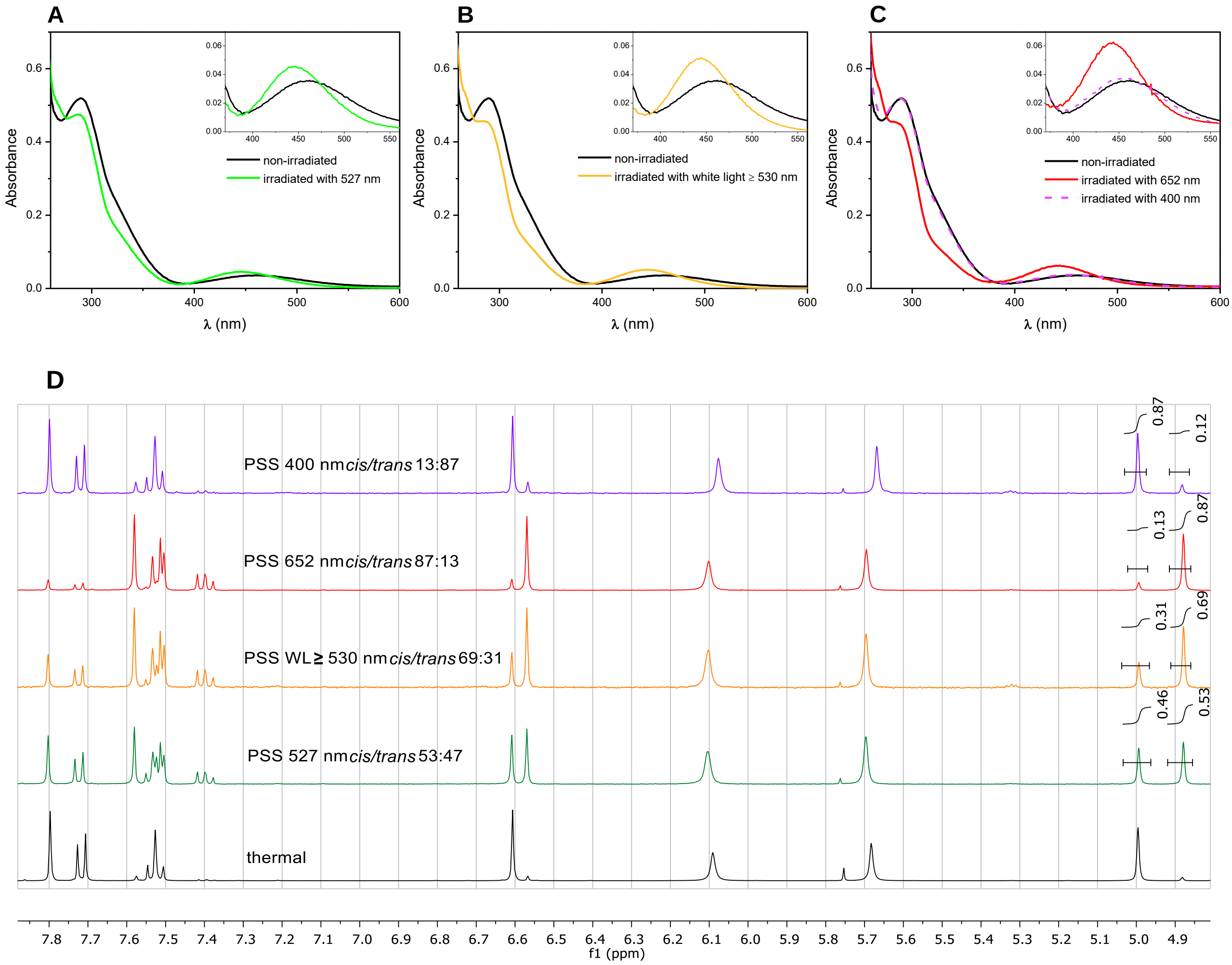


Figure S17 Photoisomerization of compound **13** in DMSO: UV-Vis absorption spectra before and after irradiation with A) green light at λ = 527 nm for 10 min; B) white light at λ ≥ 530 nm for 10 min; C) red light at λ = 652 nm for 2 h (c ≈ 40 µM). D) Extract from ^{1}H NMR spectra before and after irradiation with various light sources (λ = 527 nm: 1 h, white light at λ ≥ 530 nm: 1 h, λ = 652 nm: 3 h, λ = 400 nm: 30 min) in DMSO-d_6 (c ≈ 2 mM).

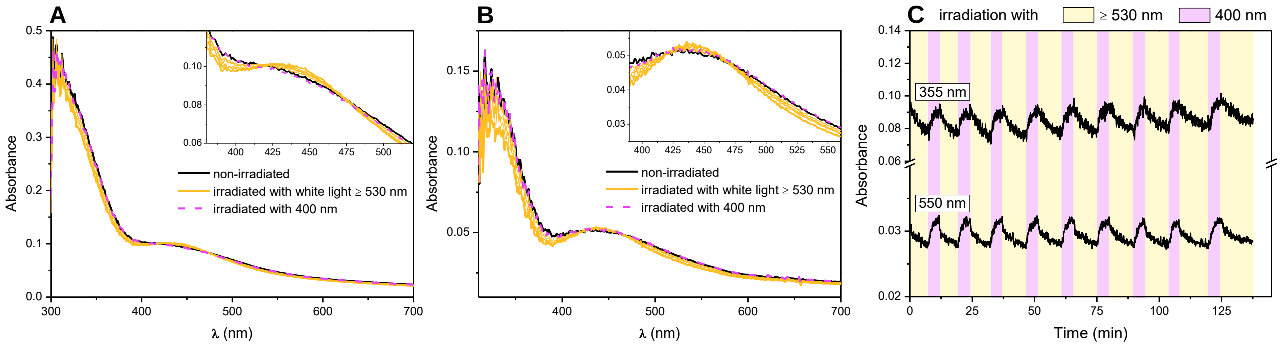


Figure S18 Photoisomerization of compound **13** in aqueous LB broth: UV-Vis absorption spectra before and after irradiation with white light at λ ≥ 530 nm over 10 min and violet light at λ = 400 nm for 5 min at A) c ≈ 40 µM (2 vol% DMSO) and B) c ≈ 15 µM (0.75 vol% DMSO). C) Reversible photochromism at 37 °C (c ≈ 15 µM, 0.75 vol% DMSO).

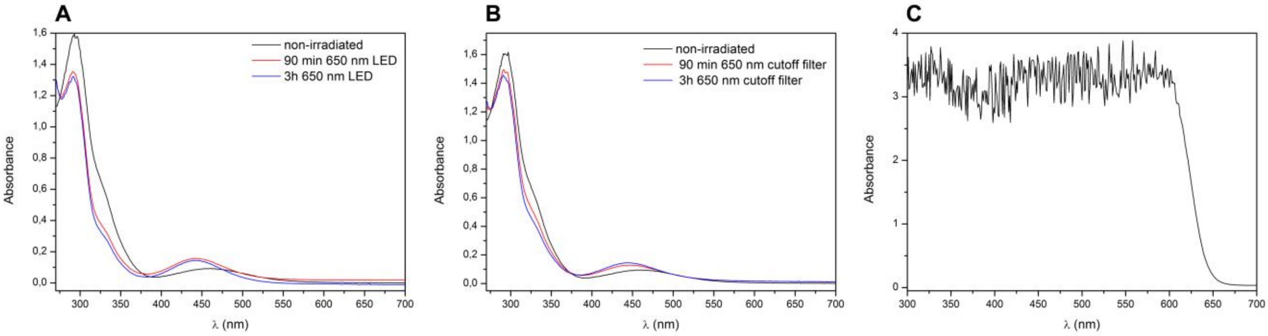


Figure S19 Photoisomerization of compound **13** in DMSO and c ≈ 100 μM: UV-Vis absorption spectra before and after irradiation with A) red light at λ = 652 nm and B) with white light using a 650 nm cutoff filter. C) Absorbance spectrum of the 650 nm cutoff filter showing no significant absorption below 650 nm.

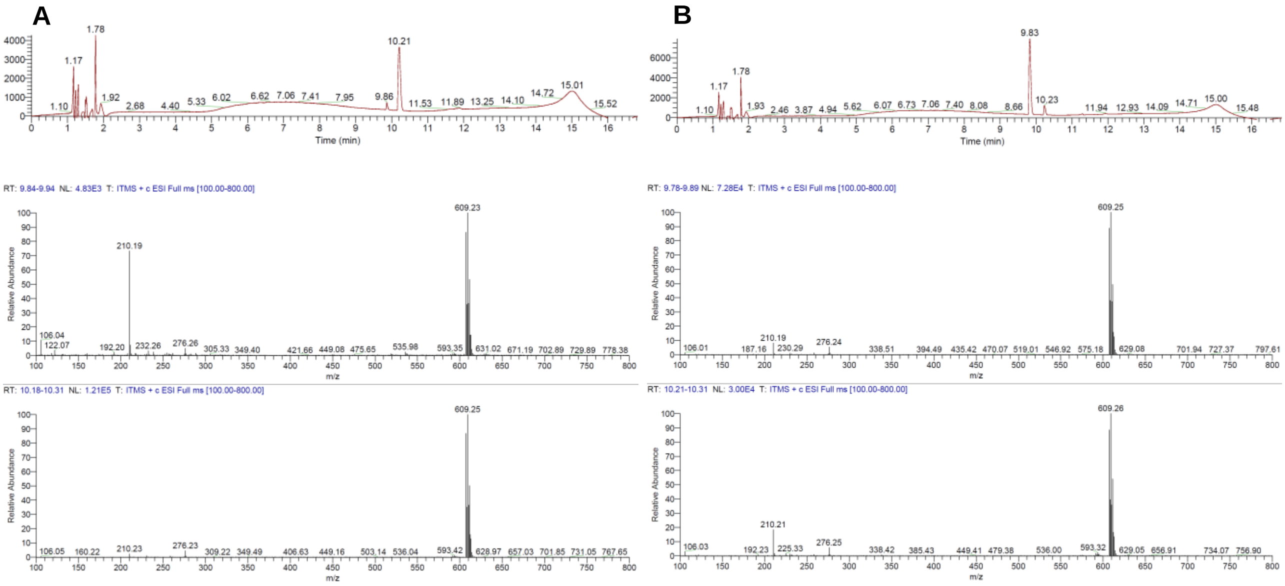


Figure S20 UHPLC-MS analysis of compound **13** before (A) and after (B) irradiation with red light at λ = 652 nm for 2.5 h in aqueous buffer at pH = 7.4 at c ≈ 80 μM with 0.5 vol% DMSO. Chromatograms show detection by UV-Vis absorption trace at λ = 405 nm. MS traces correspond to signals at: 9.86 min and 10.21 min (A), 9.83 min and 10.23 min (B).

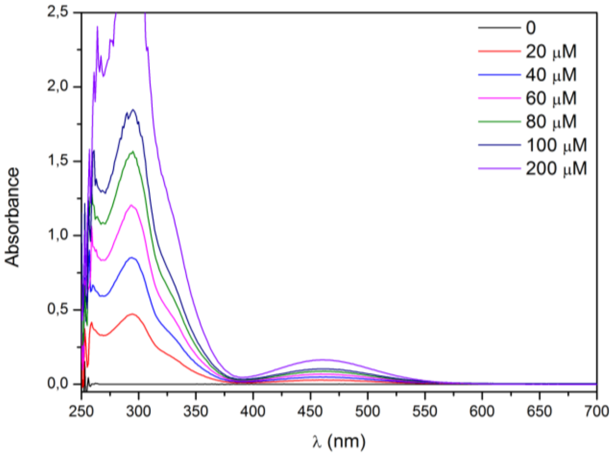


Figure S21 Increasing concentrations of compound **13** (20 °C, aqueous buffer, pH = 7.4) showing absorbance up to 575 nm.

Thermal half-lifes of *cis*-12 and *cis*-13: Because of the high thermal stability of the *cis* isomers of diaminopyrimidines **12** and **13**, an approximation of its thermal half-life *via* UV-Vis was not feasible. UHPLC-MS analysis of a sample of **12** that was irradiated with green light at λ = 527 nm in aqueous buffer at pH = 7.4 and subsequently left standing at room temperature in the dark for a day confirmed a half-life of well over 24 h in water (figure S22). The same could be shown for **13** after irradiation with red light at λ = 652 nm (figure S23).

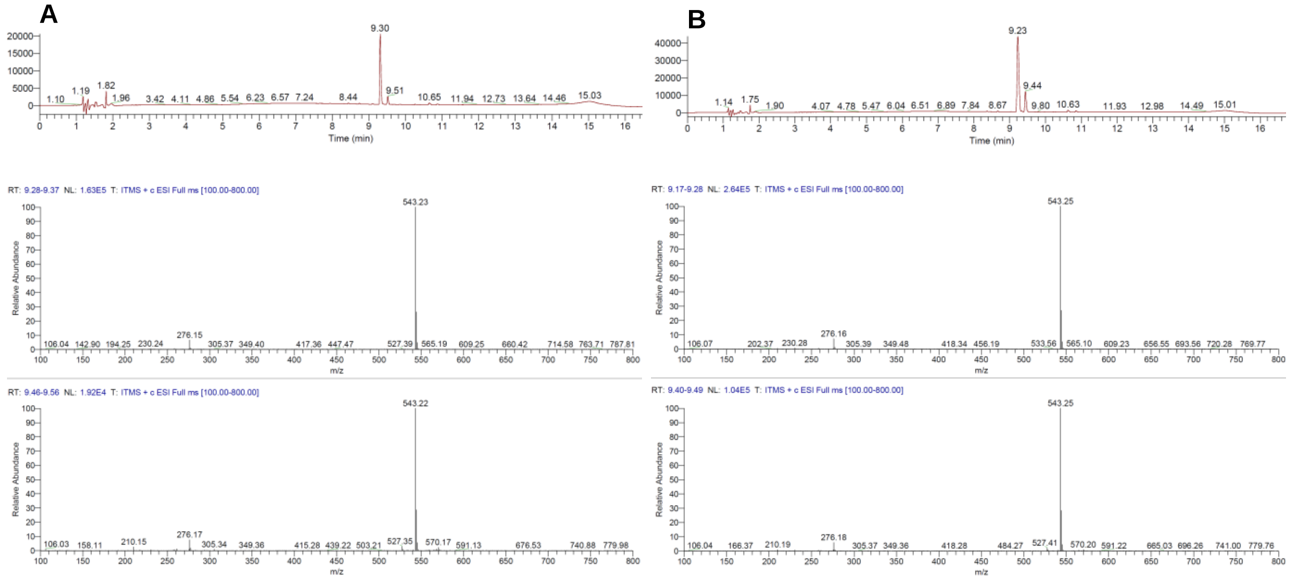


Figure S22 UHPLC-MS analysis of A) compound **12** after irradiation with green light at λ = 527 nm for 30 min in aqueous buffer at pH = 7.4 with 0.5 vol% DMSO at c ≈ 80 µM and B) the same sample after standing for 24 h at room temperature in the dark. Chromatograms show detection by UV-Vis absorption trace at λ = 425 nm. MS traces correspond to signals at: 9.30 min and 9.51 min (A), 9.23 min and 9.44 min (B).

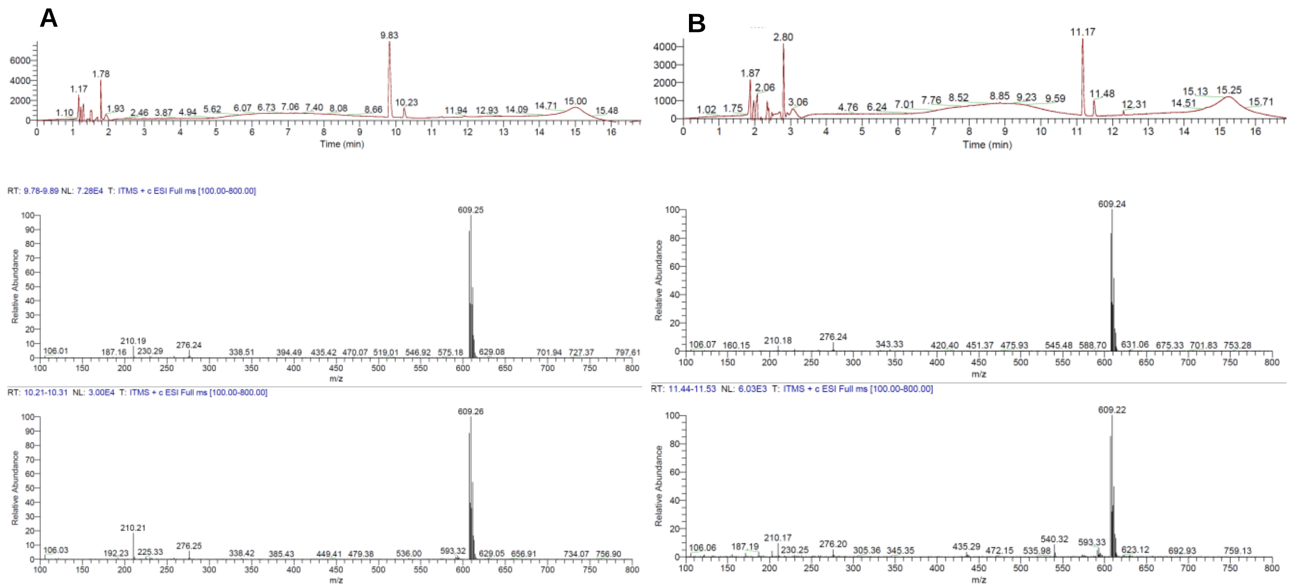


Figure S23 UHPLC-MS analysis of A) compound **13** after irradiation with red light at λ = 652 nm for 2.5 h in aqueous buffer at pH = 7.4 with 0.5 vol% DMSO at c ≈ 80 µM and B) the same sample after standing for 24 h at room temperature in the dark. Chromatograms show detection by UV-Vis absorption trace at λ = 405 nm. MS traces correspond to signals at: 9.83 min and 10.23 min (A), 11.17 min and 11.46 min (B).

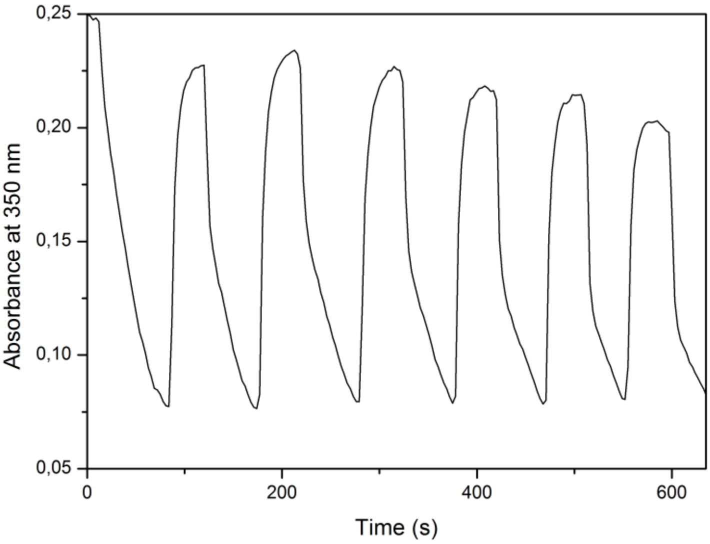


Figure S24 Reversible photosisomerization of **2i** (37 °C, buffer with 1 vol% DMSO at pH = 7.4, 20 μM) in the presence of 10 mM glutathione (GSH). 5 cycles of 365 nm/white light irradiation could be performed without the observation of significant fatigue or reduction.

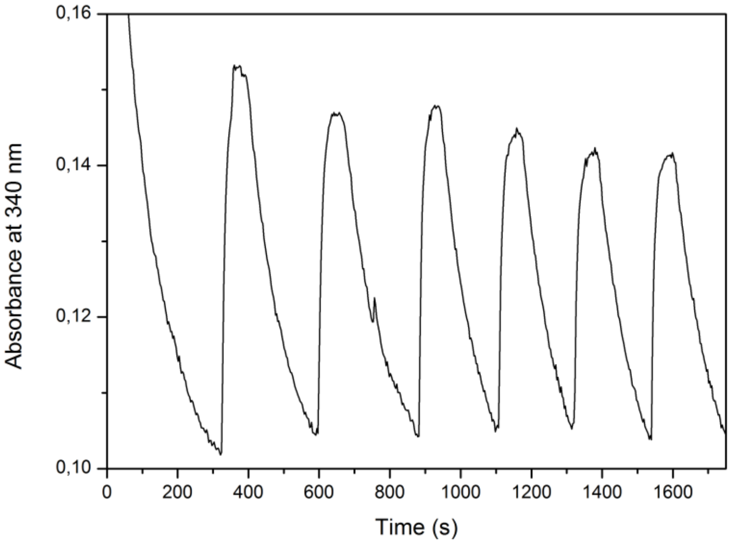
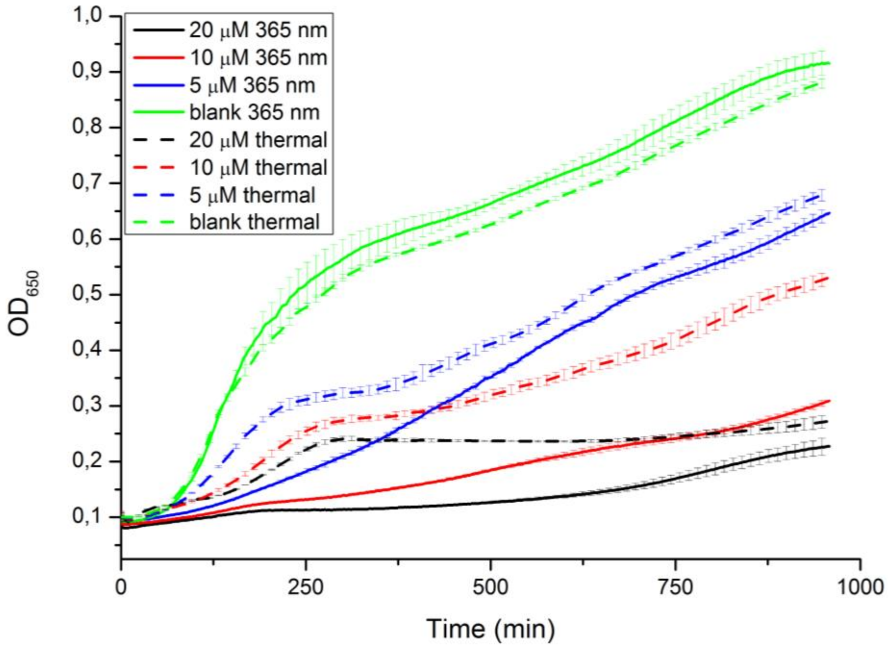


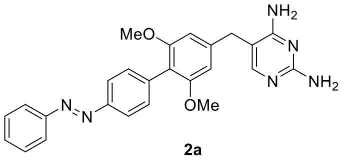
Figure S25 Reversible photosisomerization of **12** (37 °C, buffer with 1 vol% DMSO at pH=7.4, 20 μM) in the presence of 10 mM glutathione (GSH). 5 cycles of 530 nm/400 nm irradiation could be performed without the observation of significant fatigue or reduction.

Antibiotics Assays

Bacterial strain and growth conditions. *E. coli* CS1562 was grown in Luria Bertani (LB) medium (5 g/L yeast extract; 10 g/L tryptone; 5 g/L NaCl) supplemented with tetracycline (10 µg/mL) at 37 °C .

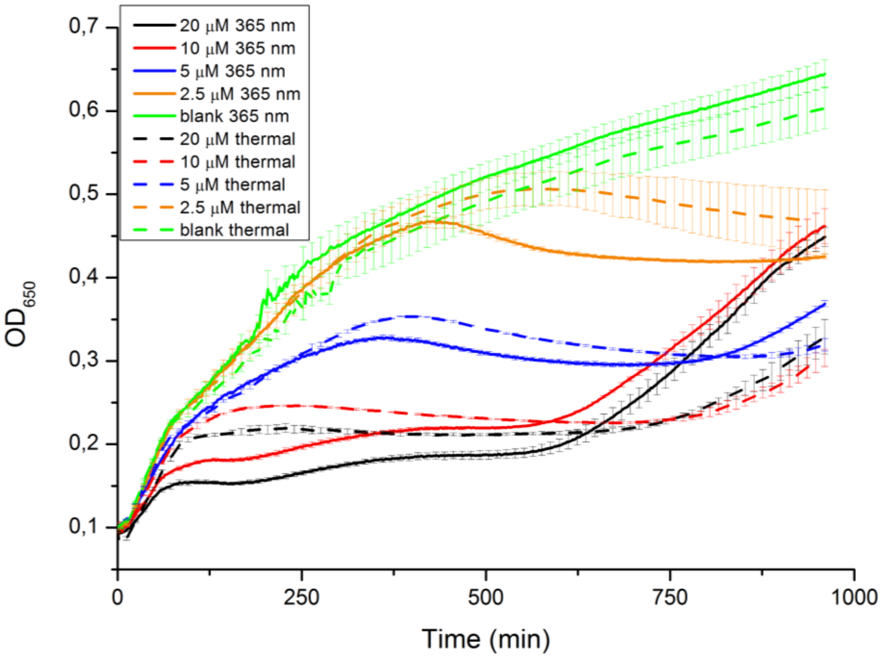
Antibacterial activity and bacterial growth curves. Overnight cultures of *E. coli* CS1562 were diluted to an OD_{650} of 0.1 and 100 µl of this cell suspension was added to 100 µl medium containing antibiotics at the given concentrations. To determine the antibacterial activity after photoisomerization, the solutions were first irradiated with UV light at $\lambda = 365$ nm for 15 min (compounds **2a-j**) or with green light at $\lambda = 527$ nm for 30 min (red-shifted derivative **12**) prior to adding the cell suspension. In case of diaminopyrimidine **12** irradiation was also performed *in situ* after addition of the cell suspension. For red-shifted derivative **13**, a 16 mM stock solution in DMSO was divided into two halves and one of them irradiated with red light at $\lambda = 652$ nm for 2.5 h. Cells were grown in a microtiter plate at 37 °C and cell density ($\lambda = 650$ nm) was measured every 2 min for 16 h, with a 10 s shaking step before each measurement, in a microplate reader (Synergy H1, BioTek). Graphs were background-corrected by subtracting the OD_{650} at time 0. MIC values were calculated by plotting the OD_{650} against the concentrations of the used antibiotics in a two-fold dilution series. The MIC_{90} values were determined after 16 h incubation and represent the concentration at which the OD_{650} is < 10% of the blank sample.

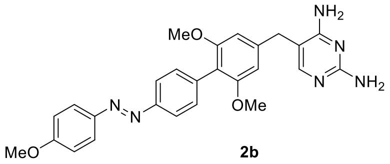




2a

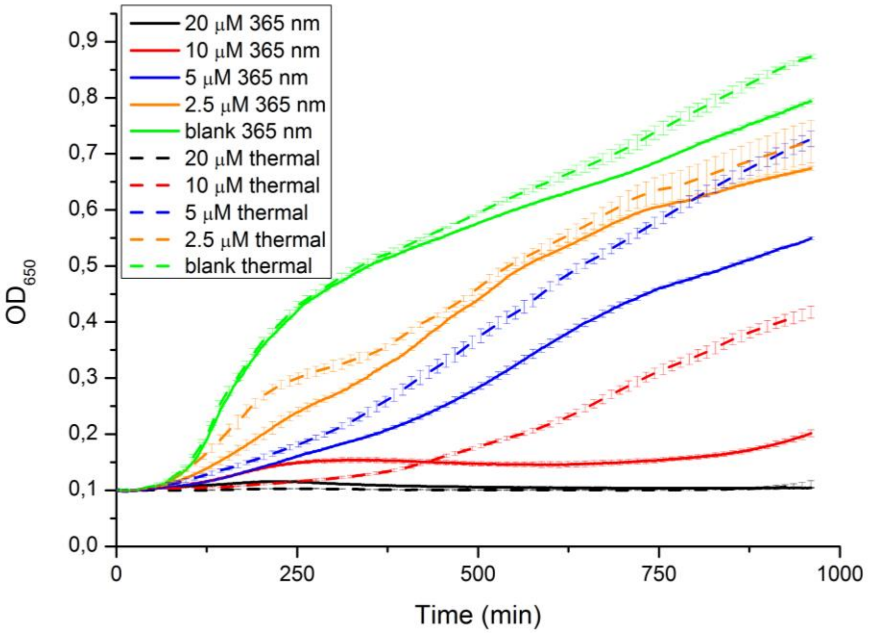
Figure S26 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2a**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

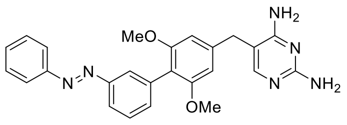




2b

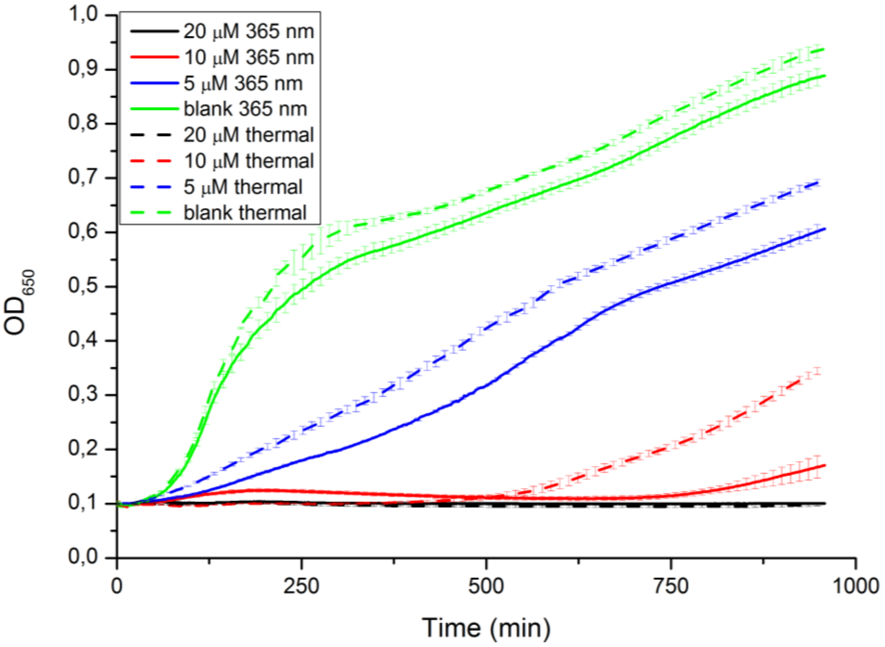
Figure S27 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2b**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

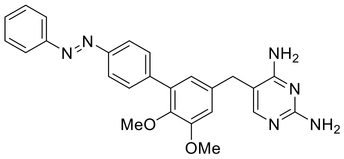




2c

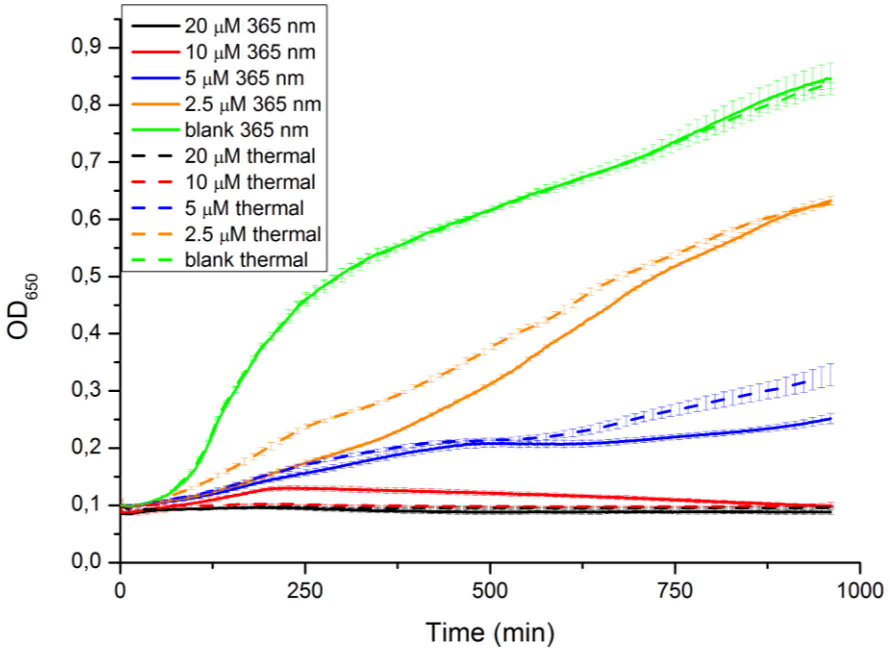
Figure S28 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2c**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

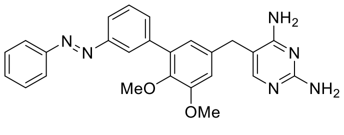




2d

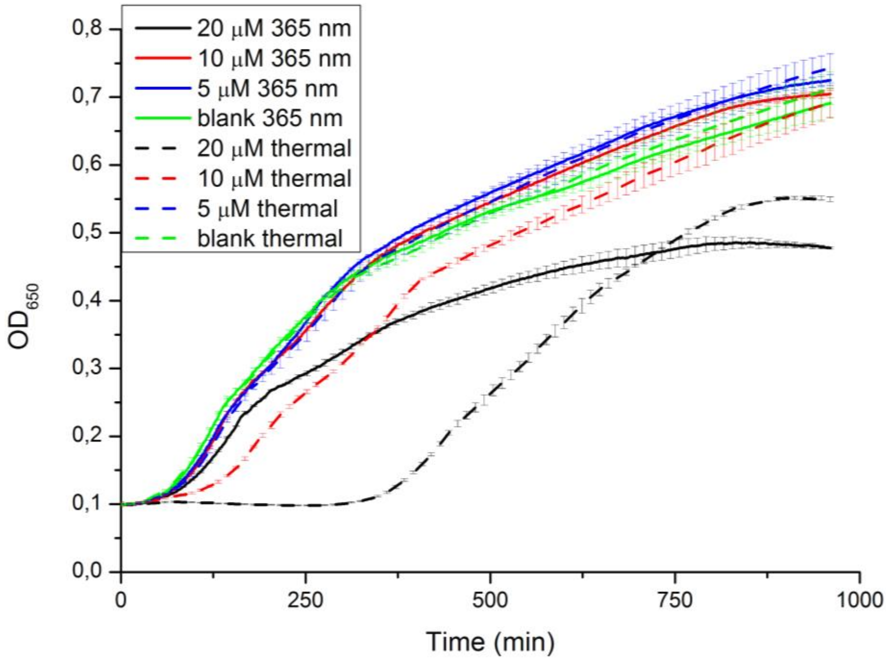
Figure S29 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2d**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

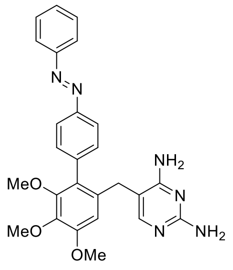




2e

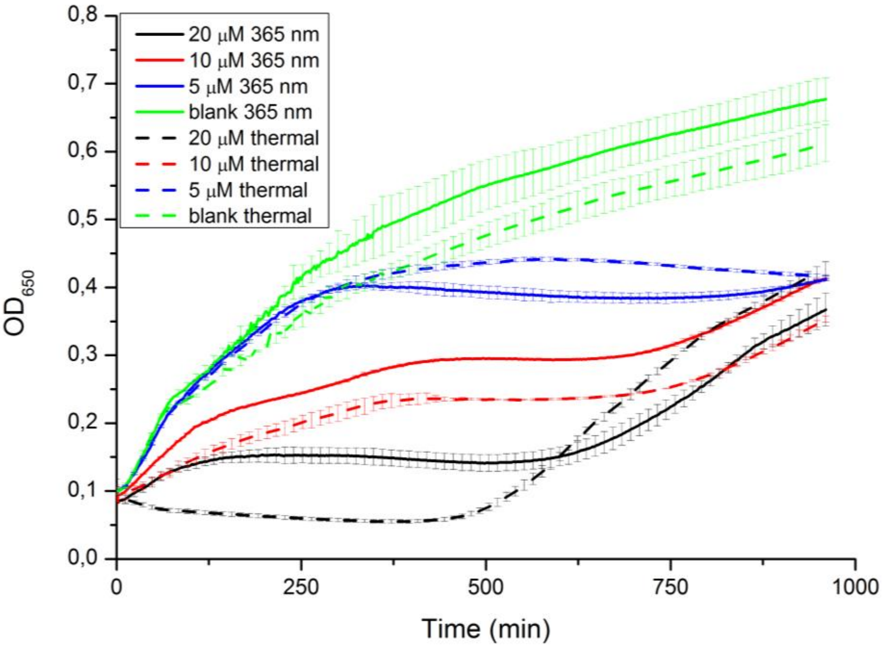
Figure S30 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2e**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

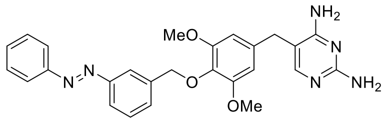




2f

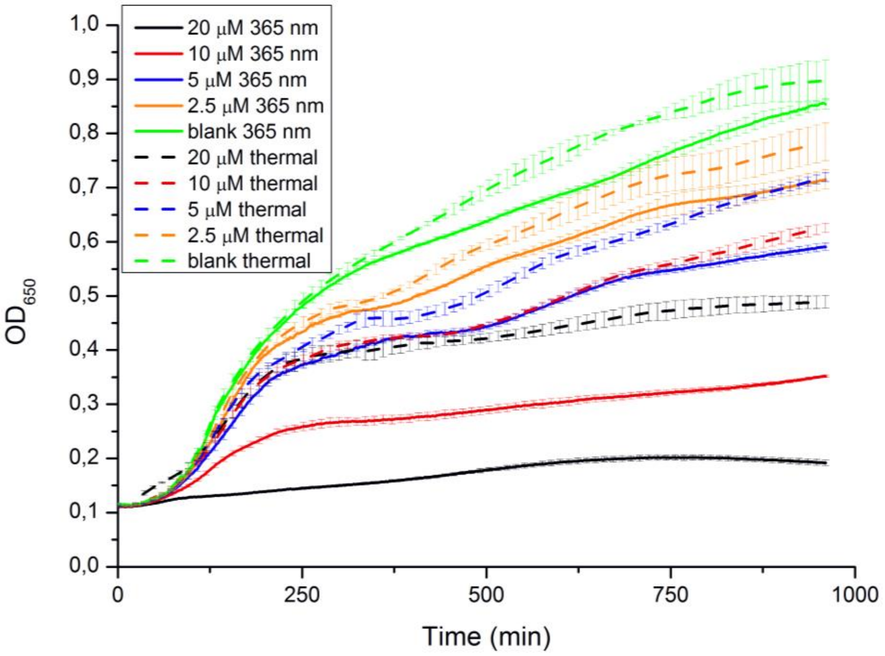
Figure S31 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2f**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

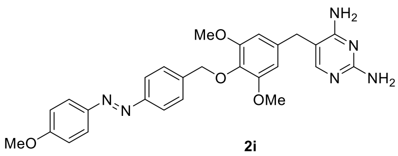




2g

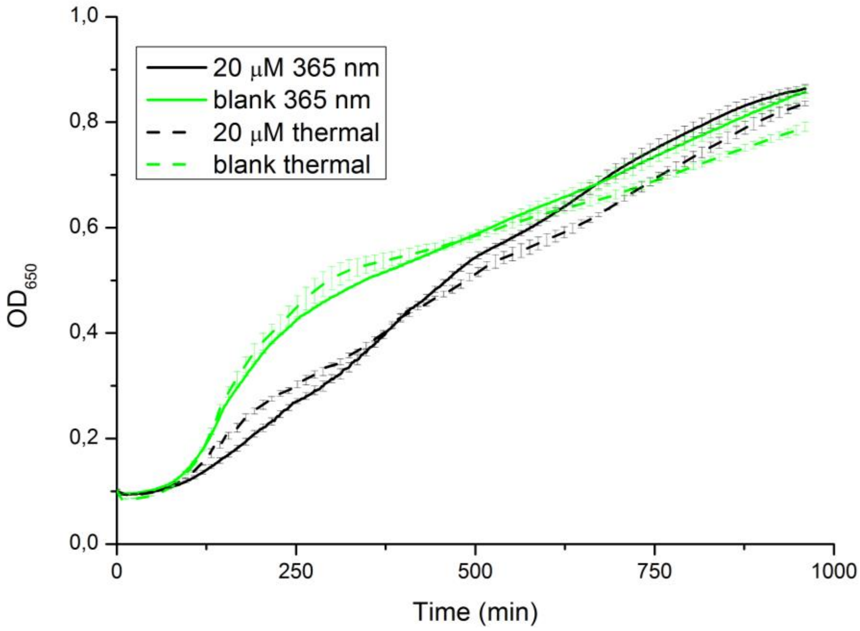
Figure S32 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2g**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

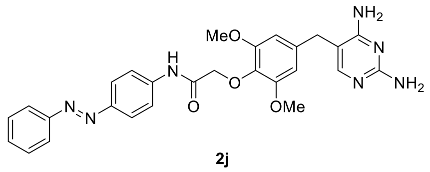




2i

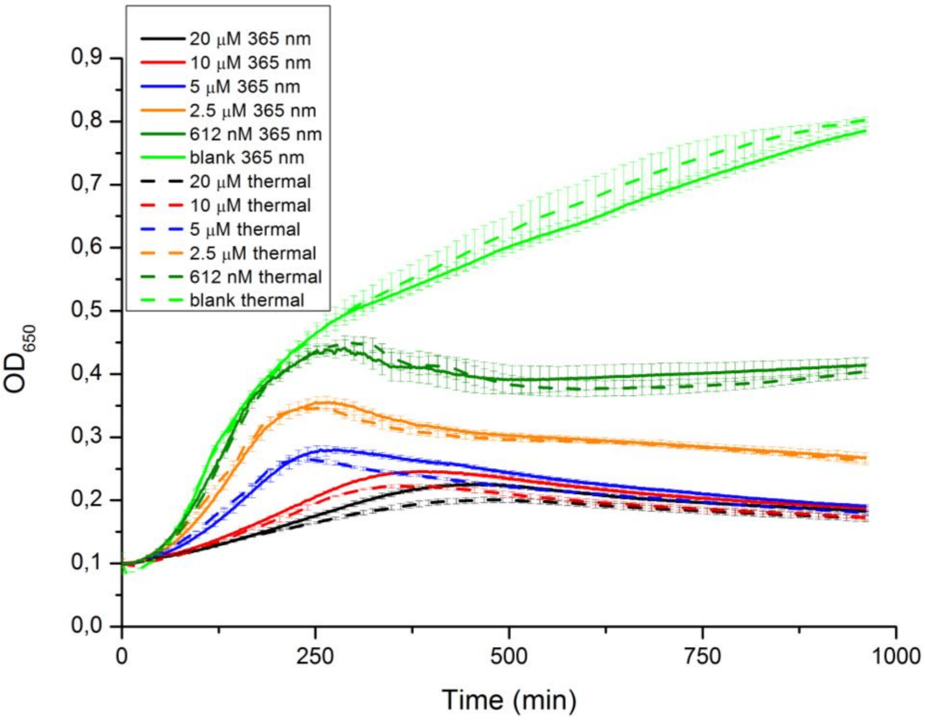
Figure S33 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2i**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

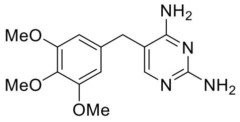




2j

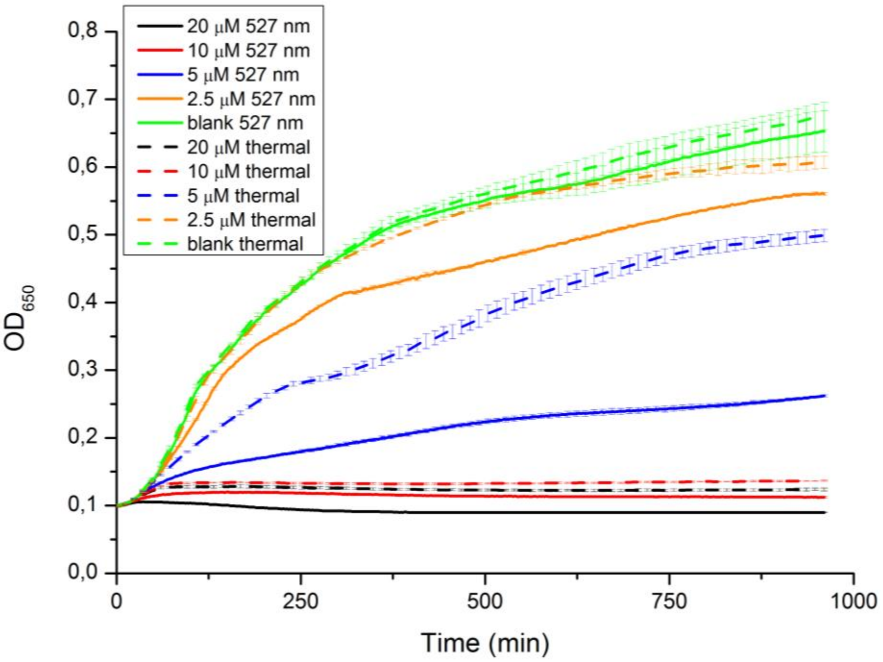
Figure S34 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **2j**. Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

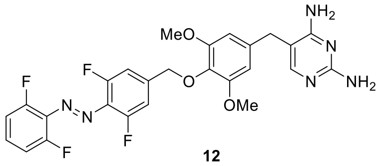




trimethoprim (**1**)

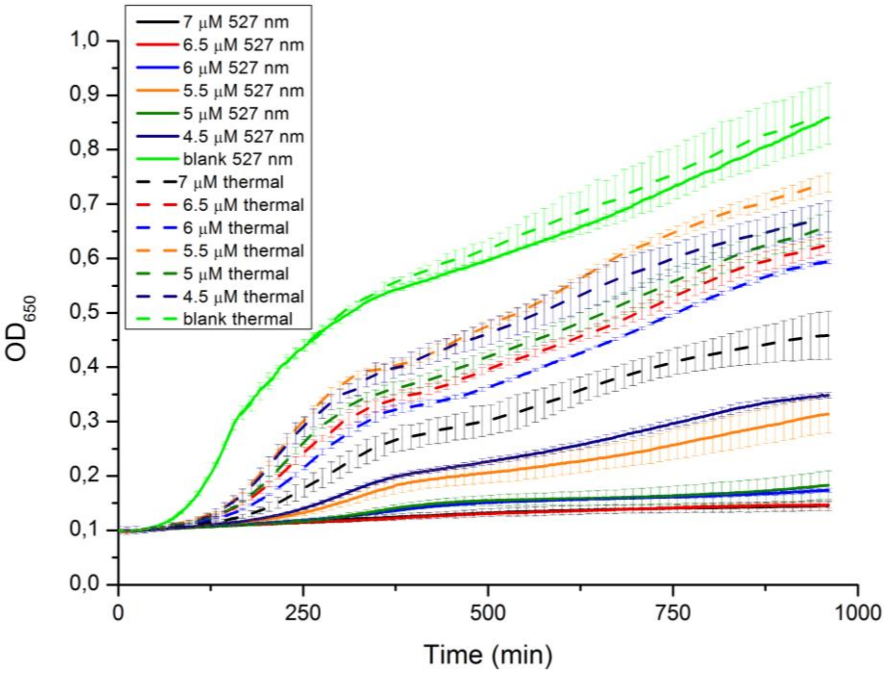
Figure S35 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of trimethoprim (**1**). Samples after irradiation with UV light at λ = 365 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

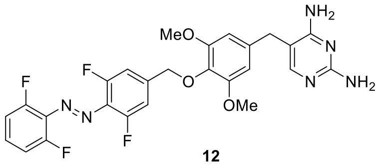




12

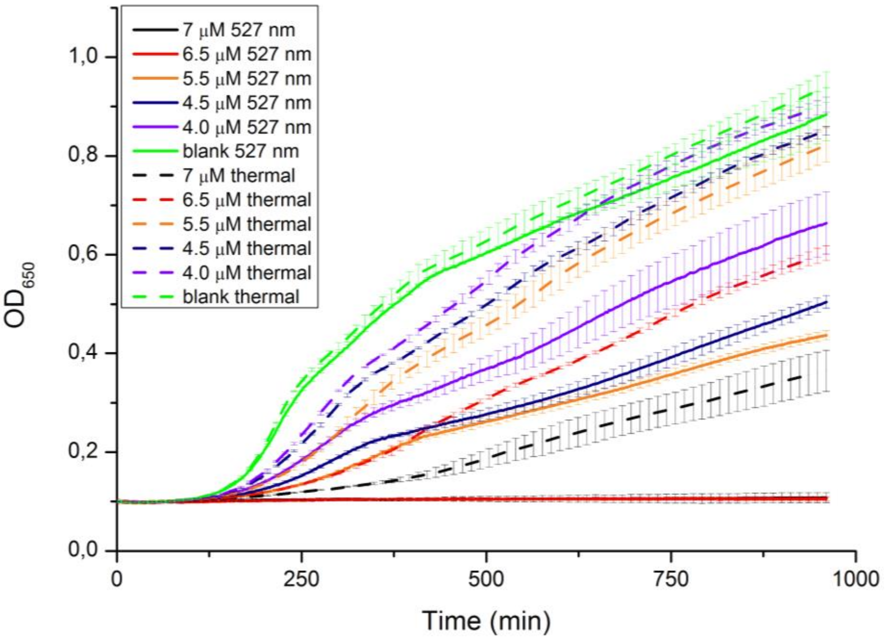
Figure S36 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **12**. Samples after irradiation with green light at λ = 527 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

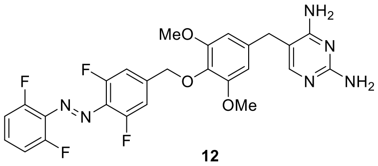




12

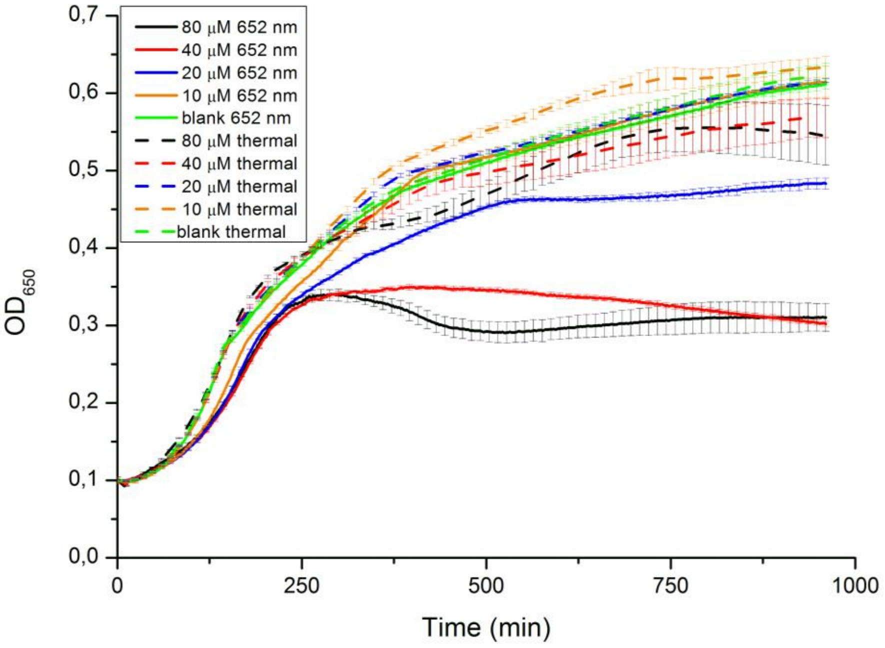
Figure S37 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations (narrowed concentration window) of **12**. Samples after irradiation with green light at λ = 527 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

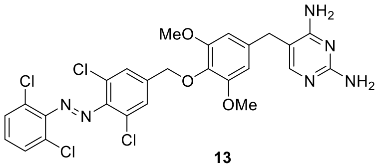




12

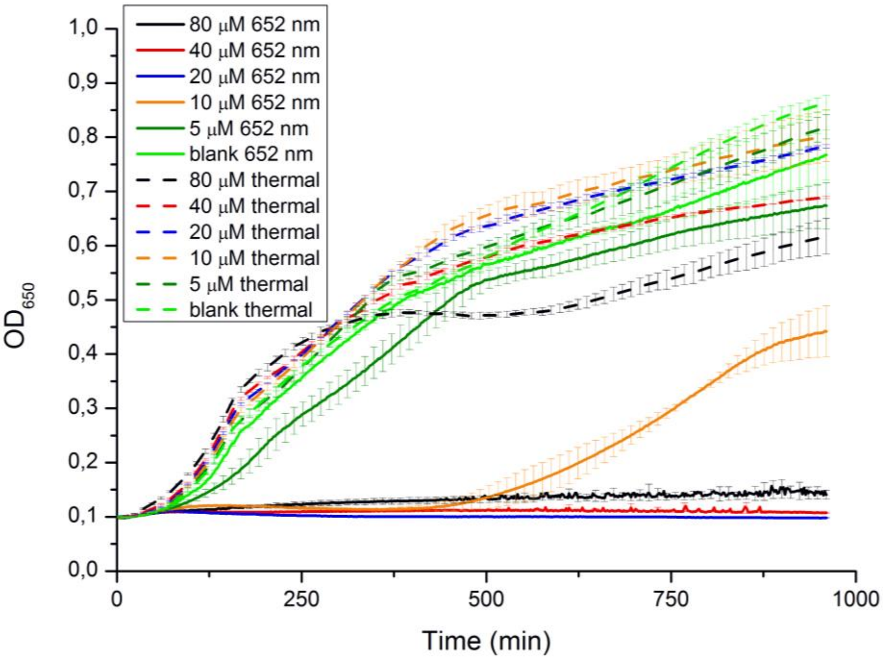
Figure S38 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations (narrowed concentration window) of **12**. Irradiation was performed *in situ* in the presence of bacteria. Samples after irradiation with green light at λ = 527 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

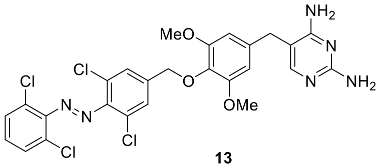




13

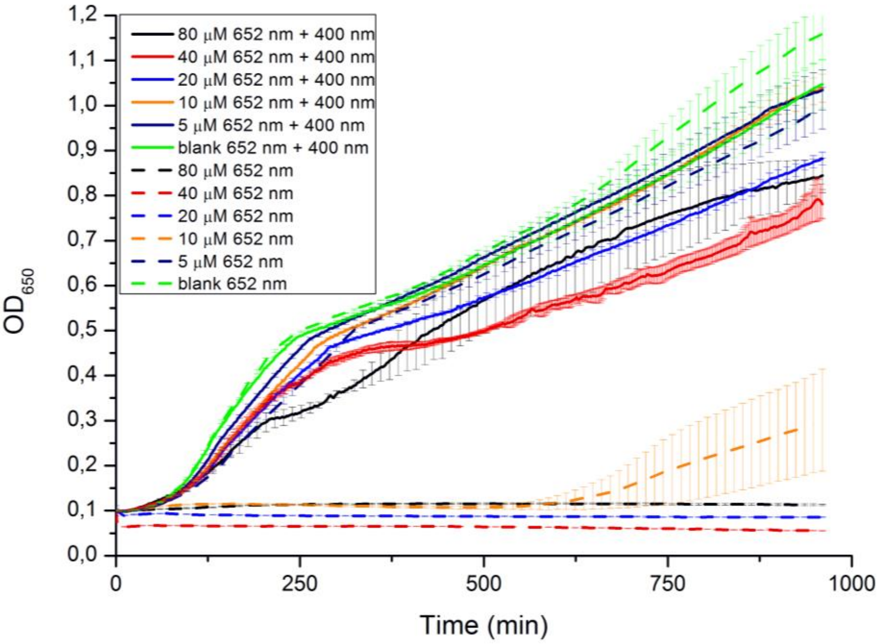
Figure S39 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **13**. Samples after irradiation with red light at λ = 652 nm are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

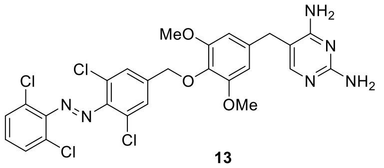




13

Figure S40 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **13**. Irradiation was performed on a 16 mM solution in DMSO for 2.5 h with red light at λ = 652 nm before a twofold dilution series in LB was made. Samples after irradiation are presented as solid lines. Samples after thermal adaptation are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.





13

Figure S41 Bacterial growth curves of *E. coli* CS1562 at increasing concentrations of **13**. Irradiation was performed on a 16 mM solution in DMSO for 3 h with red light at λ = 652 nm before a two-fold dilution series in LB was made. Subsequently, after inoculation with bacteria, half of the 96-well plate was covered and irradiated with λ = 400 nm for 30 min. OD_{650} was measured every 2 minutes for 16 h at 37 °C. Samples after irradiation with violet light at λ = 400 nm are presented as solid lines. Samples not irradiated with violet light are presented as dashed lines. Error bars show s.d. calculated from measurements in triplicate.

Chemical actinometry and quantum yield determination

An aqueous 0.05 M H_2SO_4 solution containing 6 mM, 12 mM and 150 mM $K_3[Fe(C_2O_4)_3]$ (2 or 3 mL, 1 cm quartz cuvette), respectively for 365, 400 and 527 nm, was irradiated at 20 °C for a given period of time in the dark with the respective wavelength. A volume of 20, 10, 20 μL was taken respectively for 365, 400 and 527 nm and diluted to 2.0 mL with an aqueous 0.5 M H_2SO_4 solution containing phenanthroline (1 g/L) and NaOAc (122.5 g/L). The absorption at $\lambda = 517$ nm was measured and compared to an identically prepared non-irradiated sample. The concentration of $[Fe(phenanthroline)_3]^{2+}$ complex was calculated using its molar absorptivity ($\mathcal{E} = 11100$ m^{-1} cm^{-1}). This concentration corresponded to the concentration of Fe^{2+} ions that had formed upon irradiation divided by 100, 200, 100 respectively for 365, 400 and 527 nm. For 527 nm the probabililty factor at $\lambda = 527$ nm was taken into account[15] and the theoretical concentration of Fe^{2+} formed upon irradiation at all given time-points was calculated (probability factor = $1\text{-}10^{-Abs(527nm)}$). The Fe^{2+} ion concentration was plotted versus time and the following slope, obtained by linear fitting to the equation y = ax + b using Origin software (S42-S44), equals the rate of formation for the given wavelengths at standardized conditions. These rates can be converted in light doses by taking into account the quantum yield and area of irradiation which is 2, 3 and 3 cm^2 respectively for 365, 400 and 530 nm. Subsequently, the energy per moles of photons at a given wavelength ($E_{\text{mole of photons}} = N_A \times h \times \nu = N_A \times h \times c / \lambda$) is taken to convert this into J s^{-1} cm^{-2}.

A solution of (*trans*)-**2i** was irradiated with the Thorlab model F365F1 high-power LED under identical standardized conditions as with the actinometry at concentrations high enough to absorb all incident light (absorbance at 365 ≥ 2). The absorbance decrease at $\lambda = 385$ nm was monitored over time by UV-Vis spectroscopy. The molar absorptivities at $\lambda = 365$ nm [(*trans*)-**2i**, $\mathcal{E}_{trans} = 18111$ m^{-1} cm^{-1}; for (*cis*)-**2i**, $\mathcal{E}_{cis} = 1282$ m^{-1} cm^{-1}] were used to calculate the concentration increase of (*cis*)-**2i** according to $\Delta c = \Delta abs/(\mathcal{E}_{trans} + \mathcal{E}_{cis})$. The initial concentration increase was plotted versus time (S45) and the slope, the rate of formation of *cis* isomer over time, was obtained by linear fitting to the equation y = ax + b using Origin software. The photochemical quantum yield for **2i** ($\phi_{\text{trans-cis}}$) was calculated by comparison of the rate of formation of (*cis*)-**2i** with the rate of Fe^{2+} ion formation at identical conditions upon 365 nm irradiation from potassium ferrioxalate using the known quantum yield for the ferrioxalate at the given wavelength ($\phi = 1.21$).[16,17]

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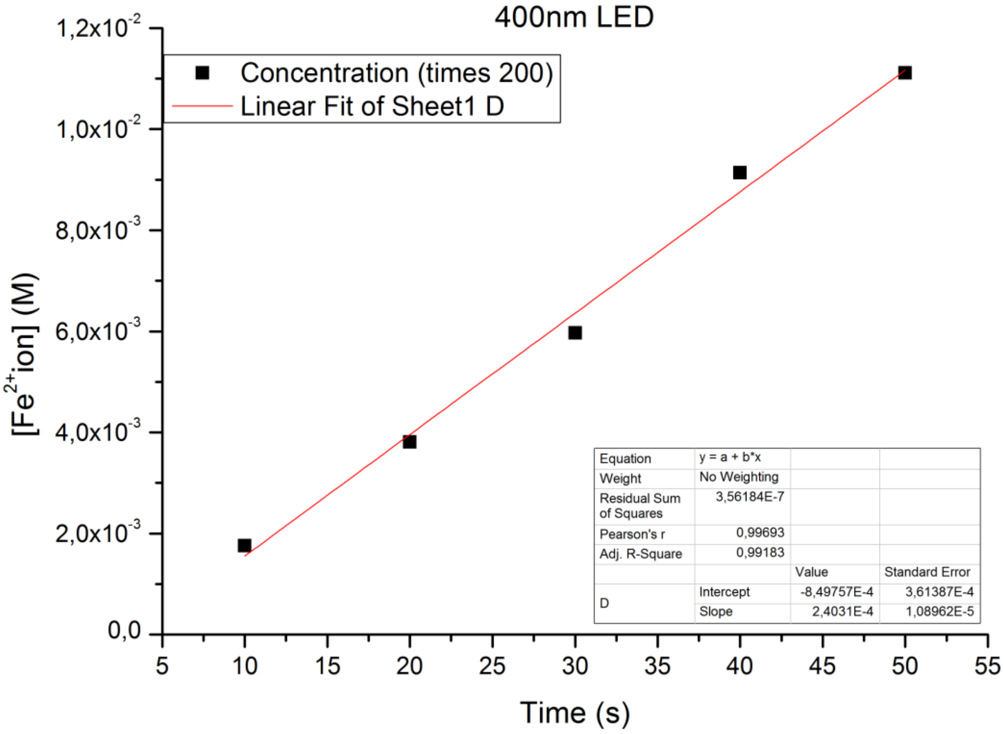
[15] S. L. Hopkins, Siewert, S. H. C. Askes, P. Veldhuizen, R. Zwier, Michal Hegerc, Sylvestre Bonnet, *Photochem. Photobiol. Sci.* **2016**, *15*, 644.

[16] C. G. Hatchard, C. A. Parker, *Proc. R Soc. Lond. A Math. Phys. Eng. Sci.* **1956**, *235*, 518.

Calculation of the quantum yield for the reverse reaction at 365 nm can be performed following $\phi_{cis\text{-}trans} = \phi_{trans\text{-}cis} * \mathcal{E}_{trans}*[2i_{trans}]/(\mathcal{E}_{cis}*[2i_{cis}])$ where the concentrations of **2i** are taken at given PSS (1:99, *trans:cis*).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3,56184E-7		
Pearson's r	0,99693		
Adj. R-Square	0,99183		
		Value	Standard Error
D	Intercept	-8,49757E-4	3,61387E-4
	Slope	2,4031E-4	1,08962E-5

Figure S42 Concentration of Fe^{2+} ions measured after five different irradiation times (10, 20, 30, 40, 50 s) with 400 nm light. The slope of the plot corresponds to the rate of Fe^{2+} ion formation: 2.40×10^{-4} M s^{-1} ± 1.08×10^{-5} M s^{-1} = 7.20×10^{-7} mole s^{-1} ± 3.24 x 10-8 mole s^{-1}. Following ϕ(ferrioxalate at 400 nm) = 1.14 and the area of irradiation = 3 cm^2 and $E_{\text{(mole of photons at 400 nm)}} = 2.99 \times 10^5$ this gives the light dose at 400 nm of 6.29×10^{-3} J s^{-1} cm^{-2}.

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[17] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry*, Third Edition, (CRC Press, 2006).

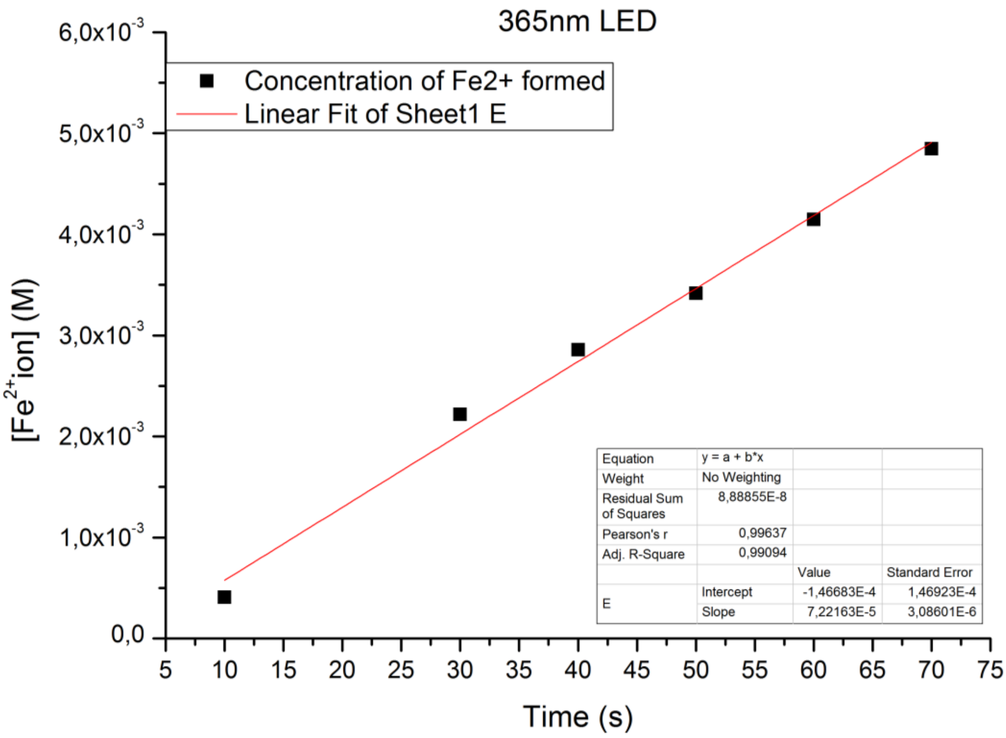


Figure S43 Concentration of Fe^{2+} ions measured after six different irradiation times (10, 30, 40, 50, 60, 70 s) with 365 nm light. The slope of the plot corresponds to the rate of Fe^{2+} ion formation: 7.22×10^{-5} M s^{-1} ± 3.08×10^{-6} M s^{-1} = 1.44×10^{-7} mole s^{-1} ± 6.16×10^{-9} mole s^{-1}. Following ϕ(ferrioxalate at 365 nm)= 1.21 and the area of irradiation = 2 cm^2 and $E_{\text{(mole of photons at 365 nm)}}$ = 3.28×10^5 this gives the light dose at 365 nm of 1.95×10^{-3} J s^{-1} cm^{-2}.

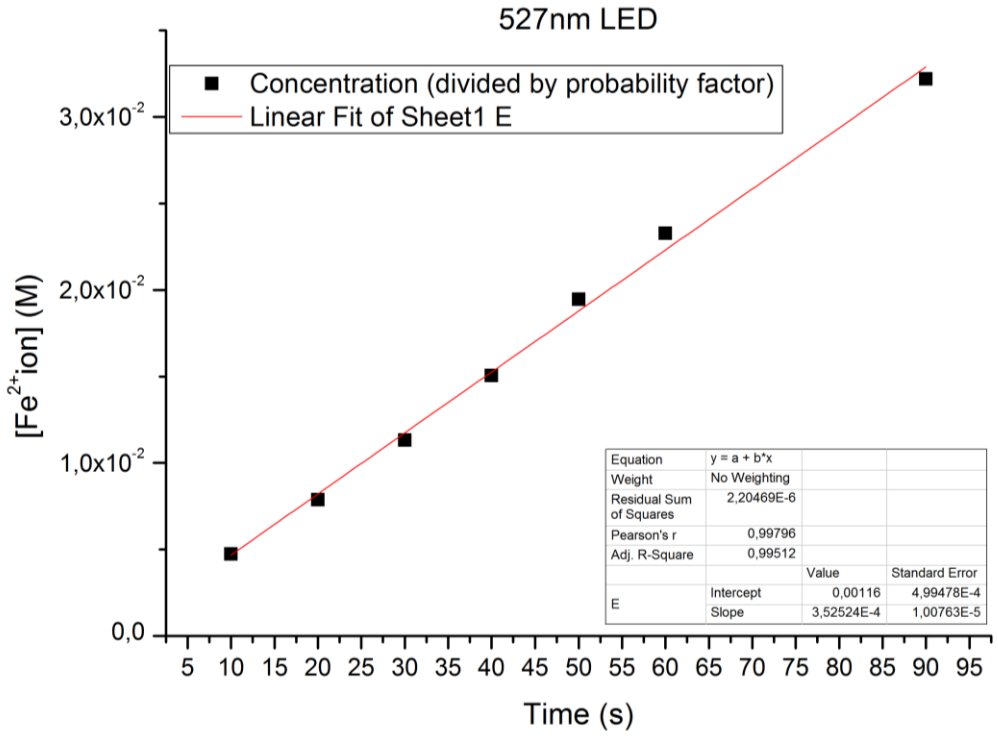
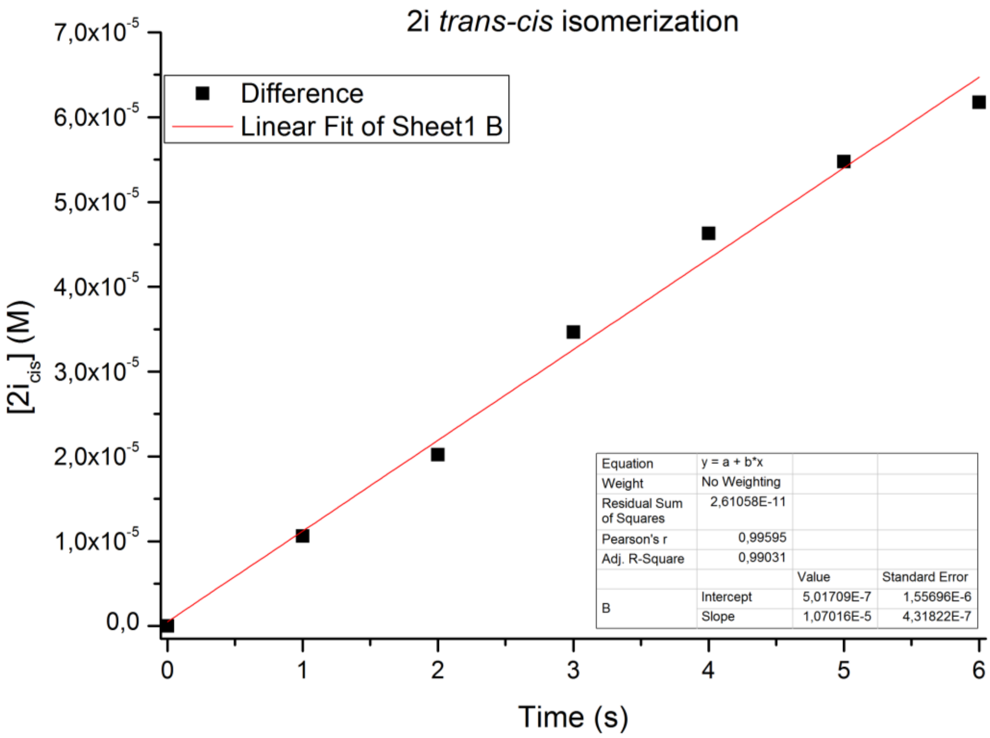


Figure S44 Concentration of Fe^{2+} ions measured after seven different irradiation times (10, 20, 30, 40, 50, 60, 90 s) with 527 nm light. The slope of the plot corresponds to the rate of Fe^{2+} ion formation: 3.52×10^{-4} M s^{-1} ± 1.00×10^{-5} M s^{-1} = 1.05×10^{-6} mole s^{-1} ± 3×10^{-8} mole s^{-1}. Following ϕ(ferrioxalate at 527 nm)= 0.53 and the area of irradiation = 3 cm^2 and $E_{\text{(mole of photons at 527 nm)}}$ = 2.27×10^5 this gives the light dose at 527 nm of 1.49×10^{-1} J s^{-1} cm^{-2}.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2,61058E-11		
Pearson's r	0,99595		
Adj. R-Square	0,99031		
		Value	Standard Error
B	Intercept	5,01709E-7	1,55696E-6
	Slope	1,07016E-5	4,31822E-7

Figure S45 Plot of the concentration of (*cis*)-**2i** as a function of time during λ_{max} = 365 nm irradiation of a solution of (*trans*)-**2i** in DMSO (c = 1.33×10^{-4} M, 1 cm quartz cuvette) obtained by monitoring the absorption decrease at λ = 385 nm. The slope of the plot corresponds to the *trans-cis* isomerisation rate: 1.07×10^{-5} M s^{-1} ± 4.31×10^{-7} M s^{-1} = 3.21×10^{-8} mole s^{-1} ± 1.29×10^{-9} mole s^{-1}. Correlation of this rate to the rate of ferrioxalate consumption at these standardized conditions with 365 nm and the ferrioxalate quantum yield at the given wavelength gives a quantum yield of 18% for *trans-cis* isomerization and logically a quantum yield of 2.5% for *cis-trans* isomerization.

Sahlmann
Photochemical
Solutions

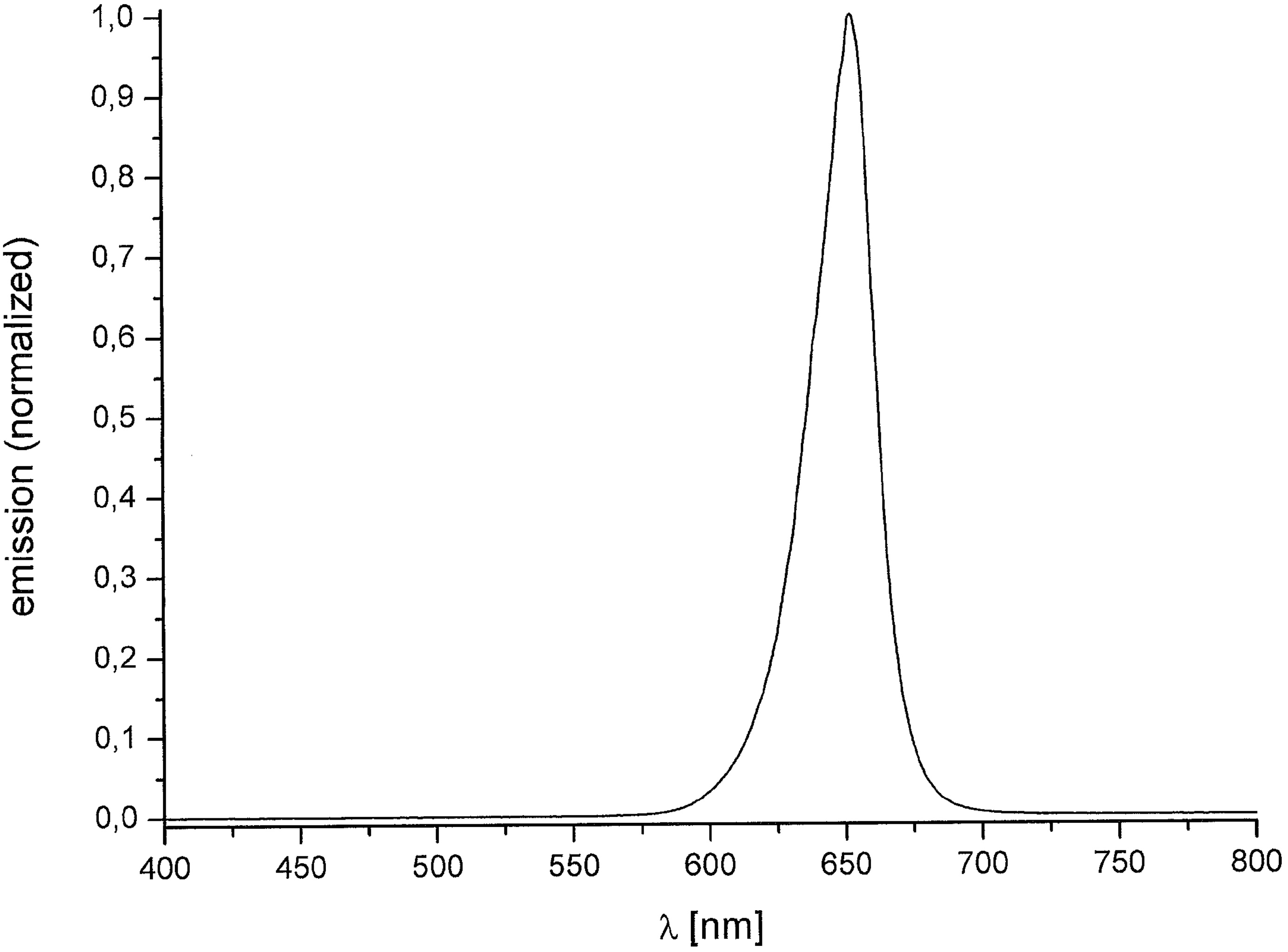
LED light source 3x 627 nm

LED type: 3x LXML PD01
rank: 0040
typ. optical power: 1200 mW

emission characteristics:

spectrometer: Ocean Optics USB 4000
peak wavelenght: 652 nm
FWHM: 26.4 nm

spectral distribution:



Sahlmann
Photochemical
Solutions

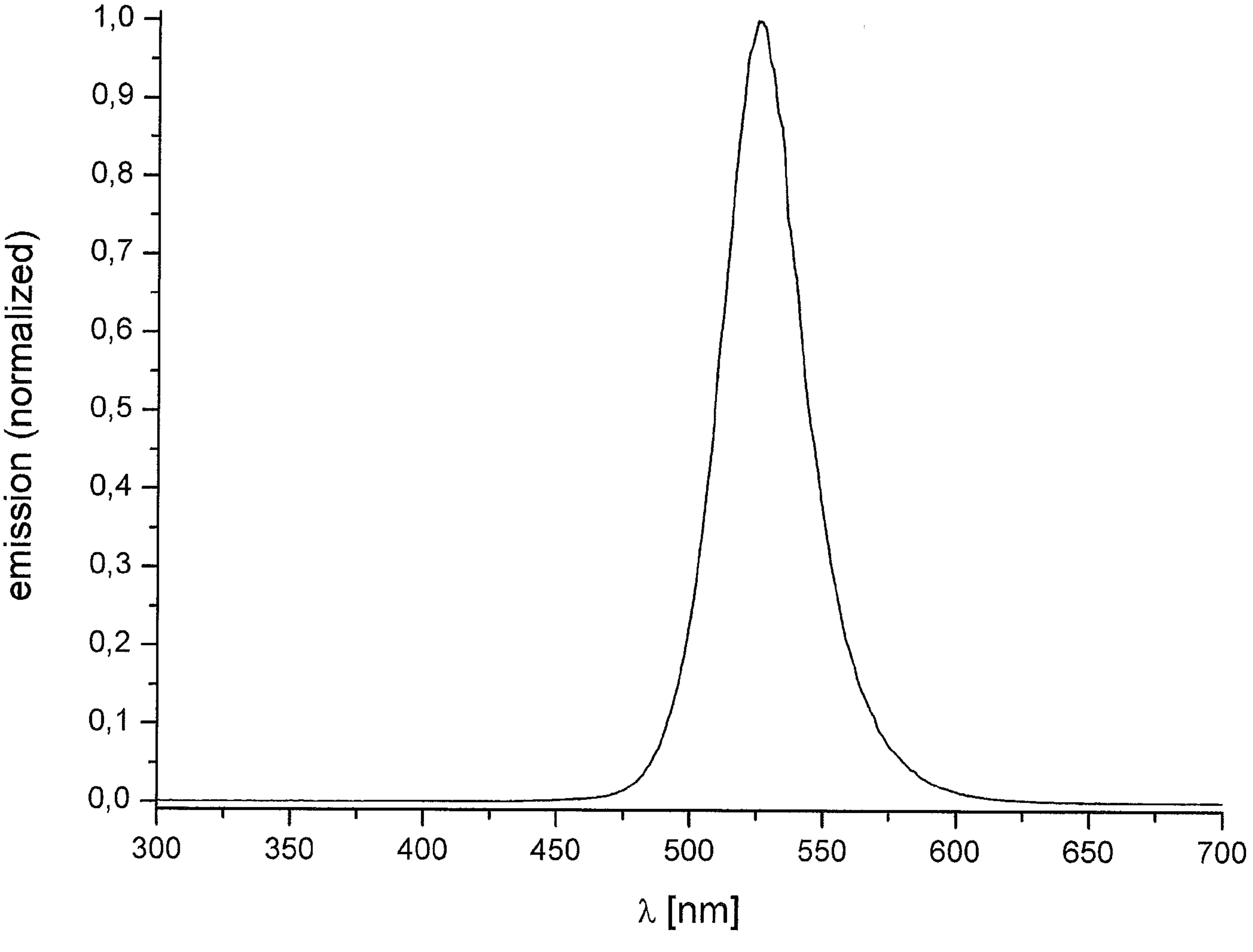
LED light source 3x 530 nm

LED type: 3x LXML PM01
rank: 0100
typ. optical power: 810 mW

emission characteristics:

spectrometer: Ocean Optics USB 4000
peak wavelenght: 526 nm
FWHM: 35.1 nm

spectral distribution:



Sahlmann Photochemical Solutions

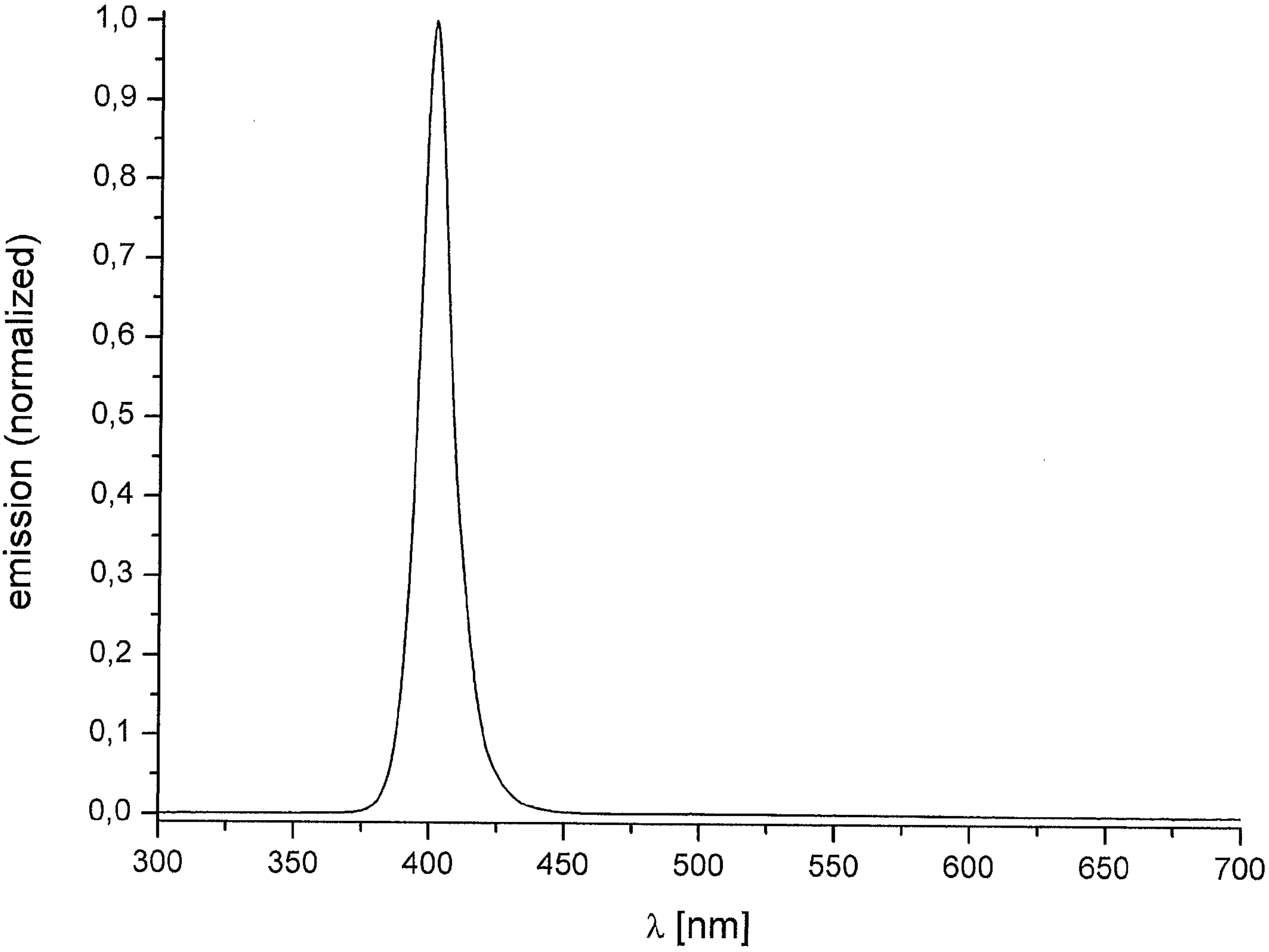
LED light source 3x 400 nm

LED type: 3x Roithner VL-400-Emitter
rank: n.a.
typ. optical power: 1000 mW

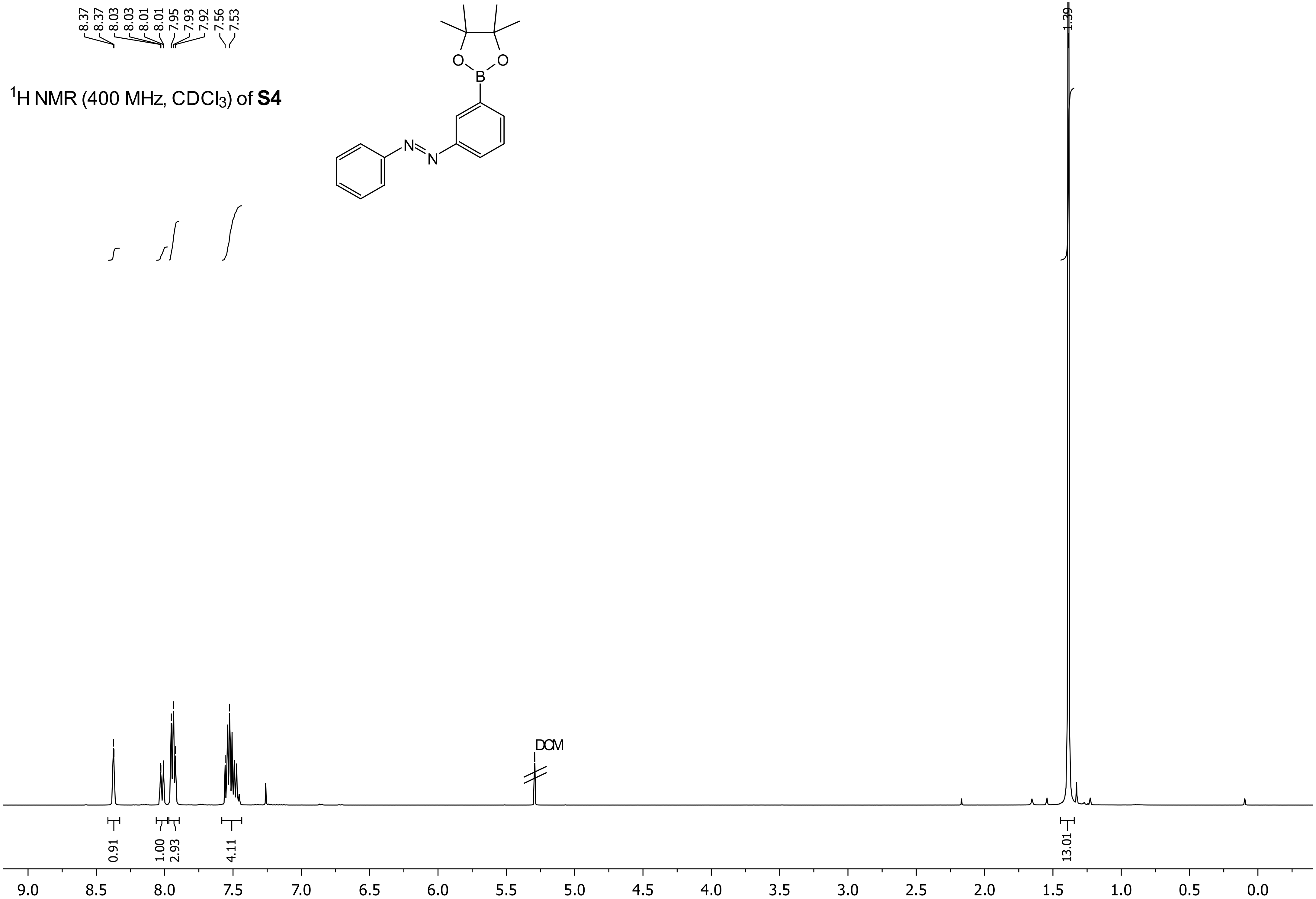
emission characteristics:

spectrometer: Ocean Optics USB 4000
peak wavelenght: 401 nm
FWHM: 13.5 nm

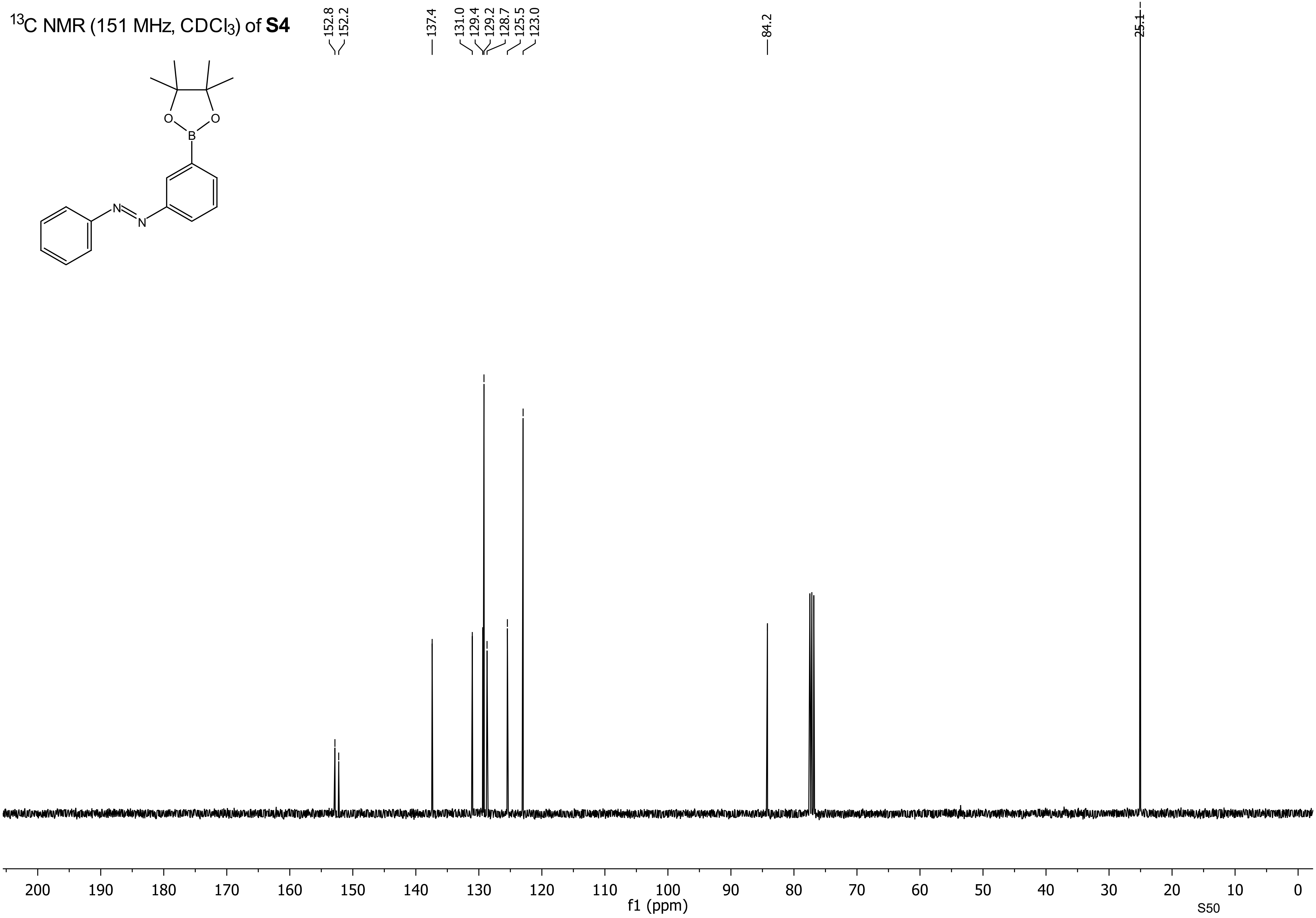
spectral distribution:



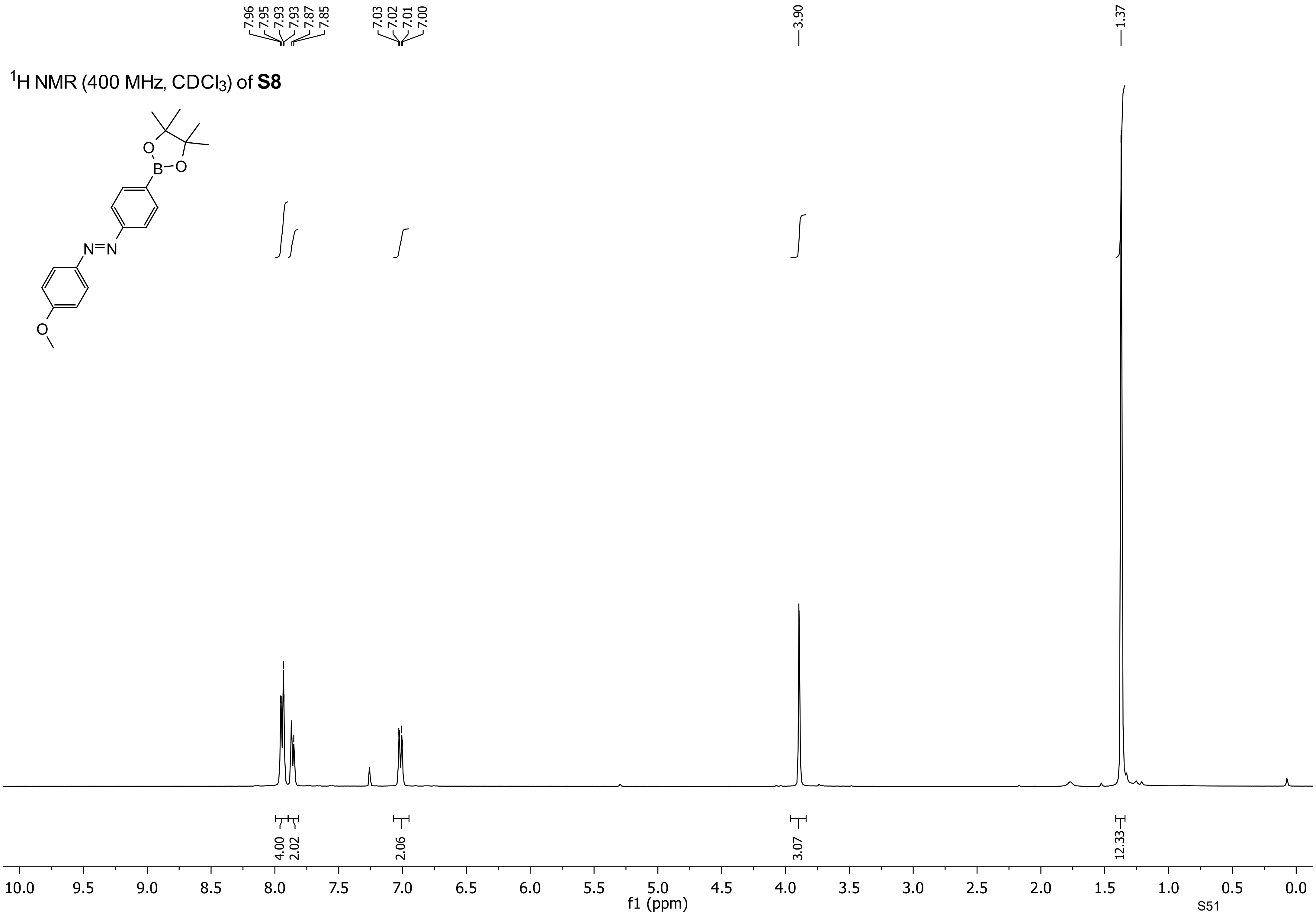
^1H NMR (400 MHz, $CDCl_3$) of **S4**



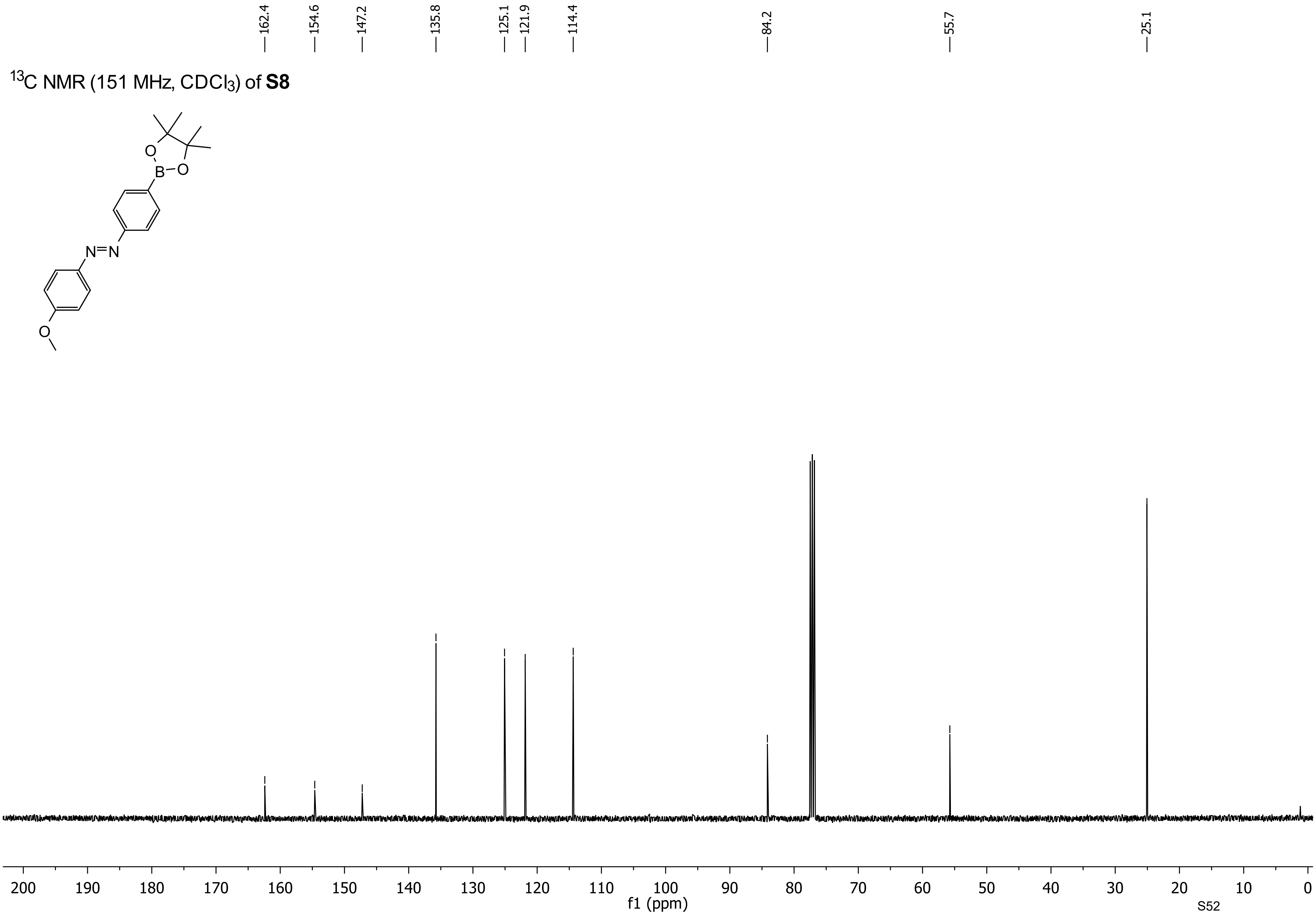
^{13}C NMR (151 MHz, CDCl$_3$) of **S4**



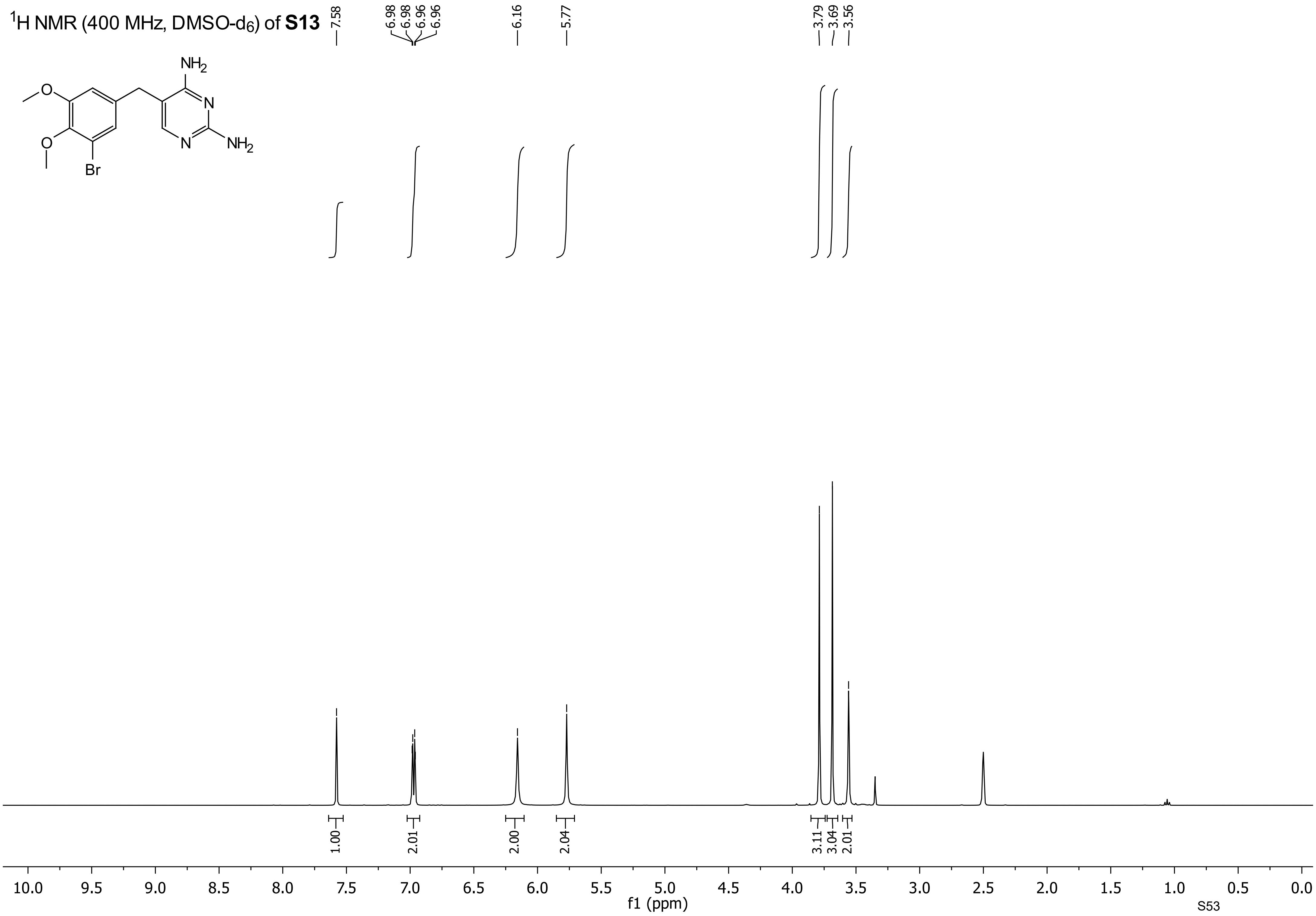
^{1}H NMR (400 MHz, CDCl$_3$) of **S8**



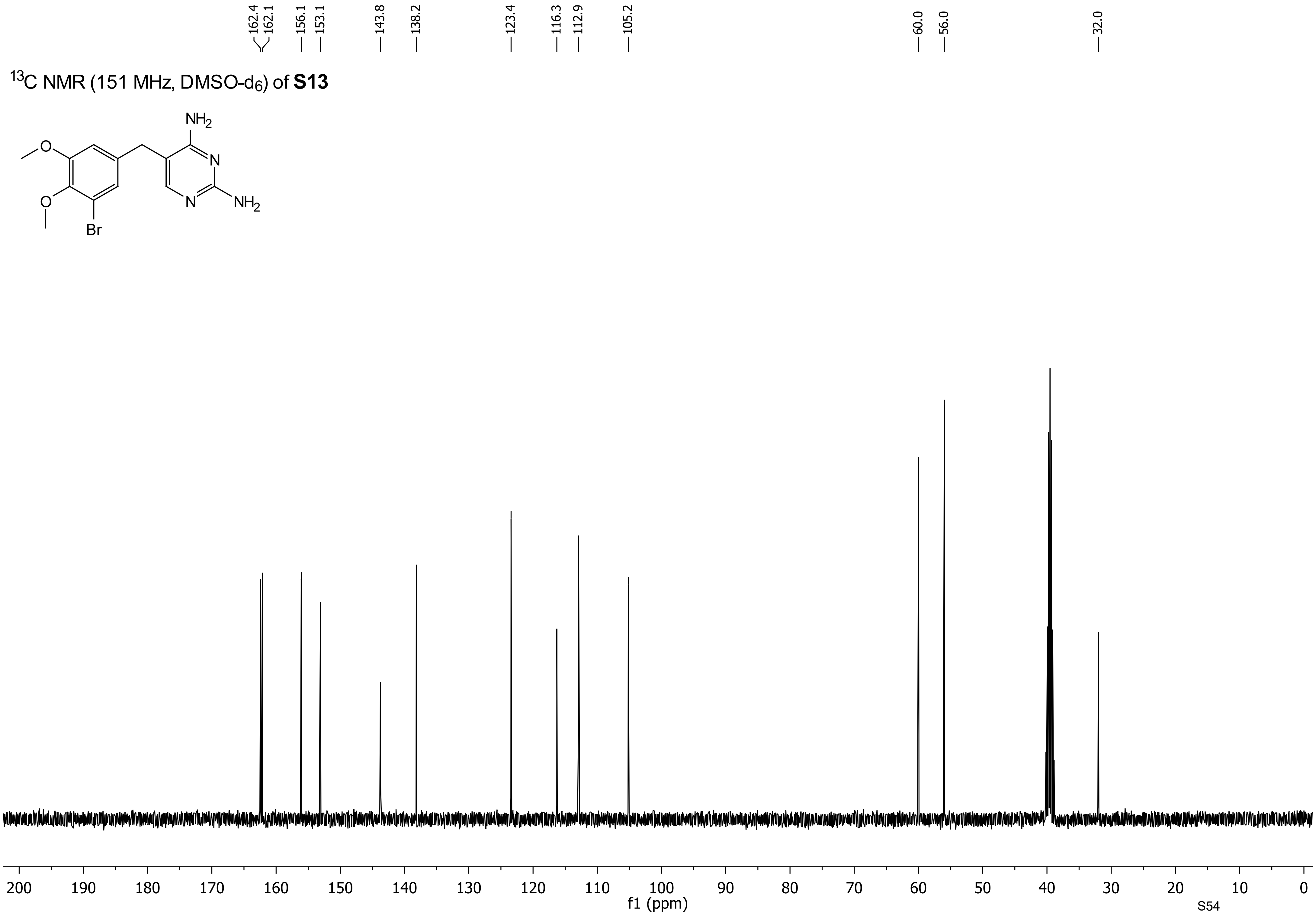
^{13}C NMR (151 MHz, $CDCl_3$) of **S8**



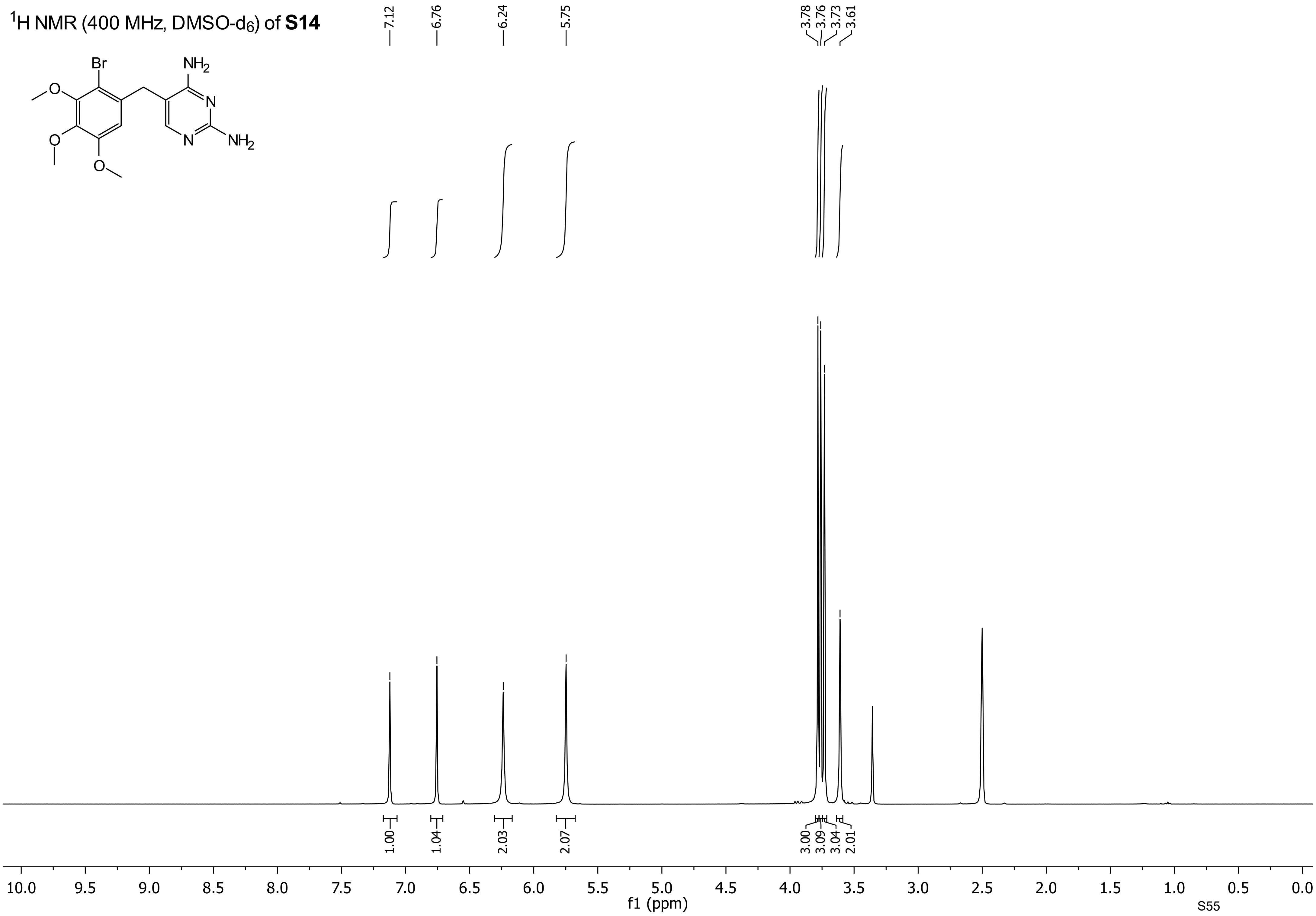
^{1}H NMR (400 MHz, DMSO-d_6) of **S13**



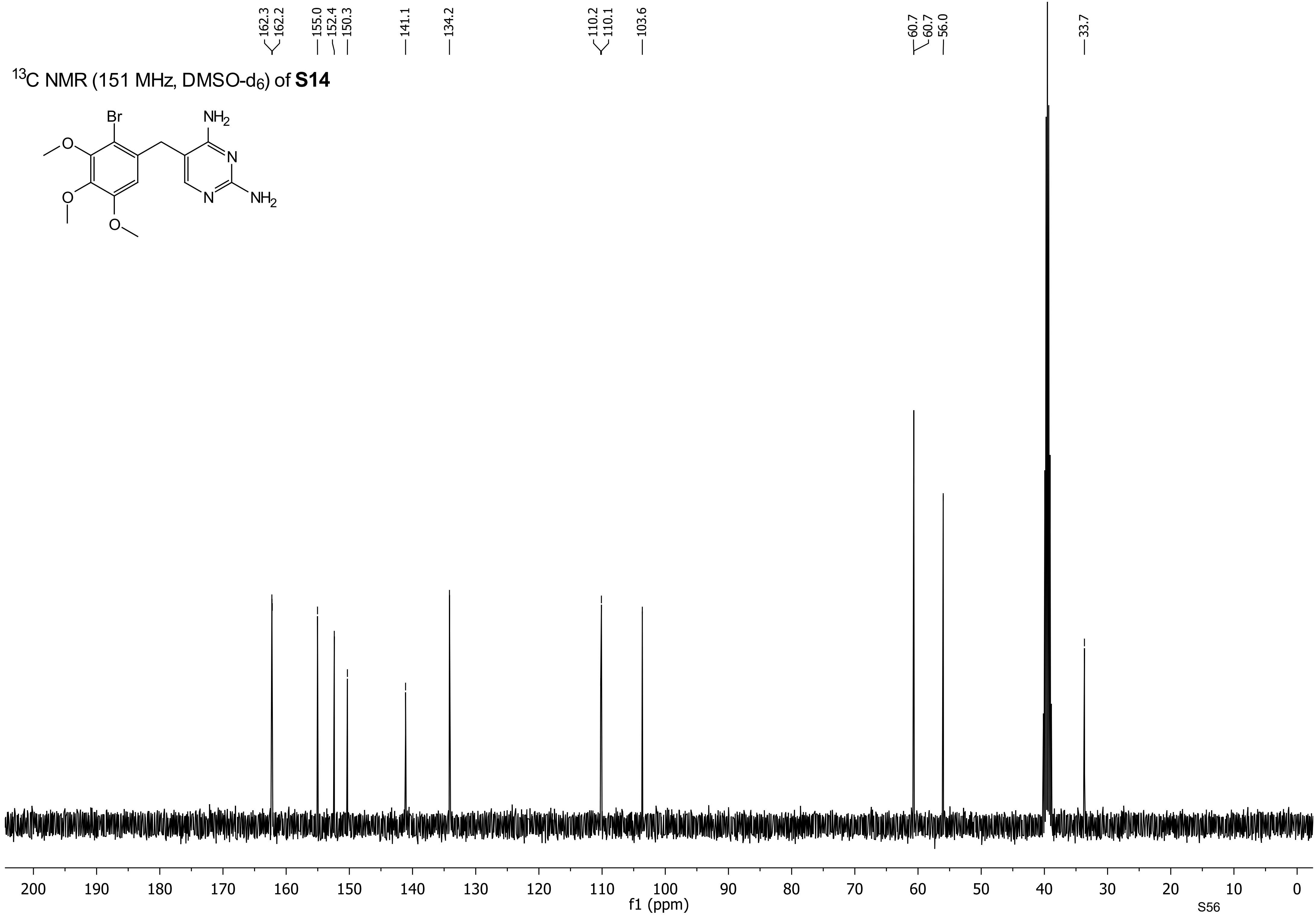
^{13}C NMR (151 MHz, DMSO-d$_6$) of **S13**



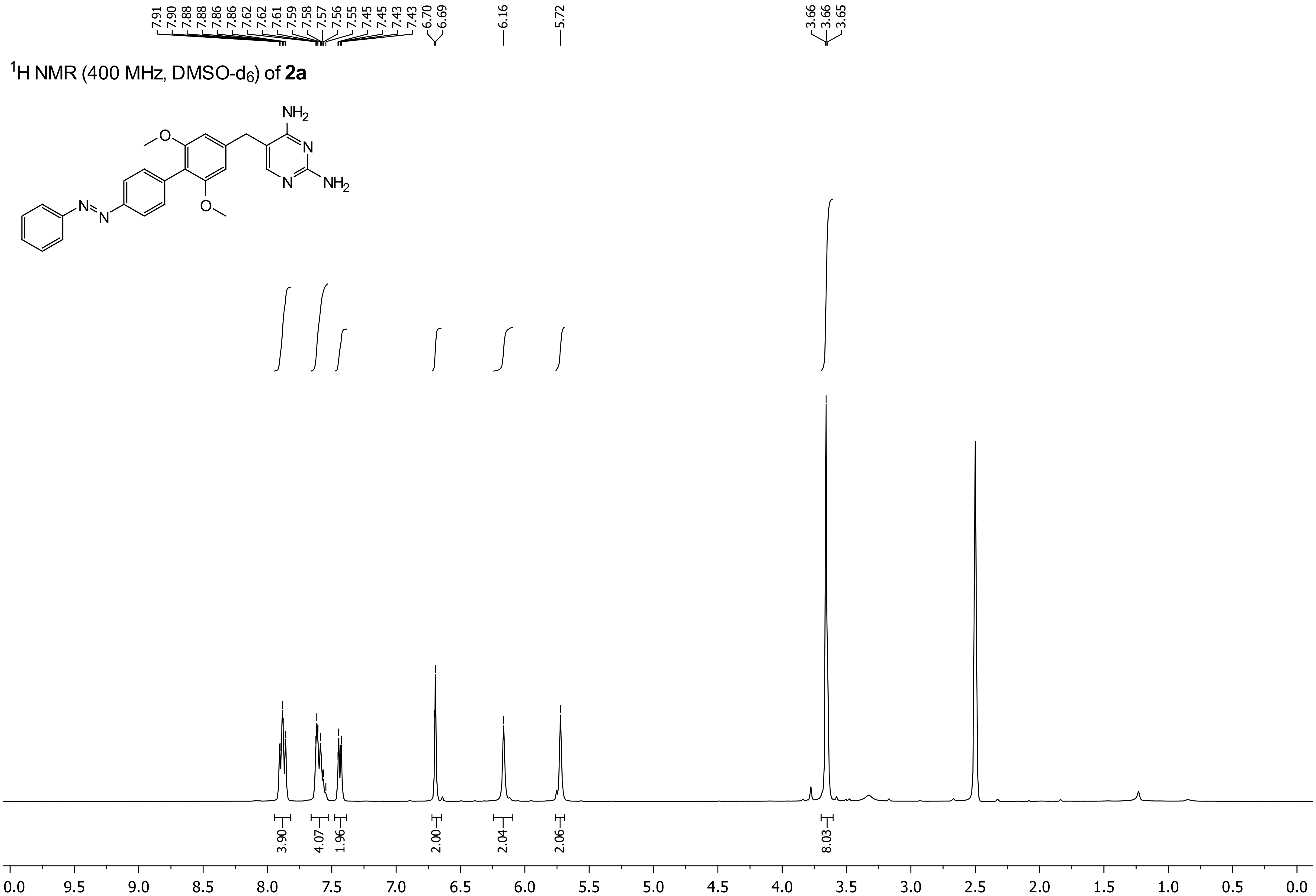
^{1}H NMR (400 MHz, DMSO-d$_6$) of **S14**



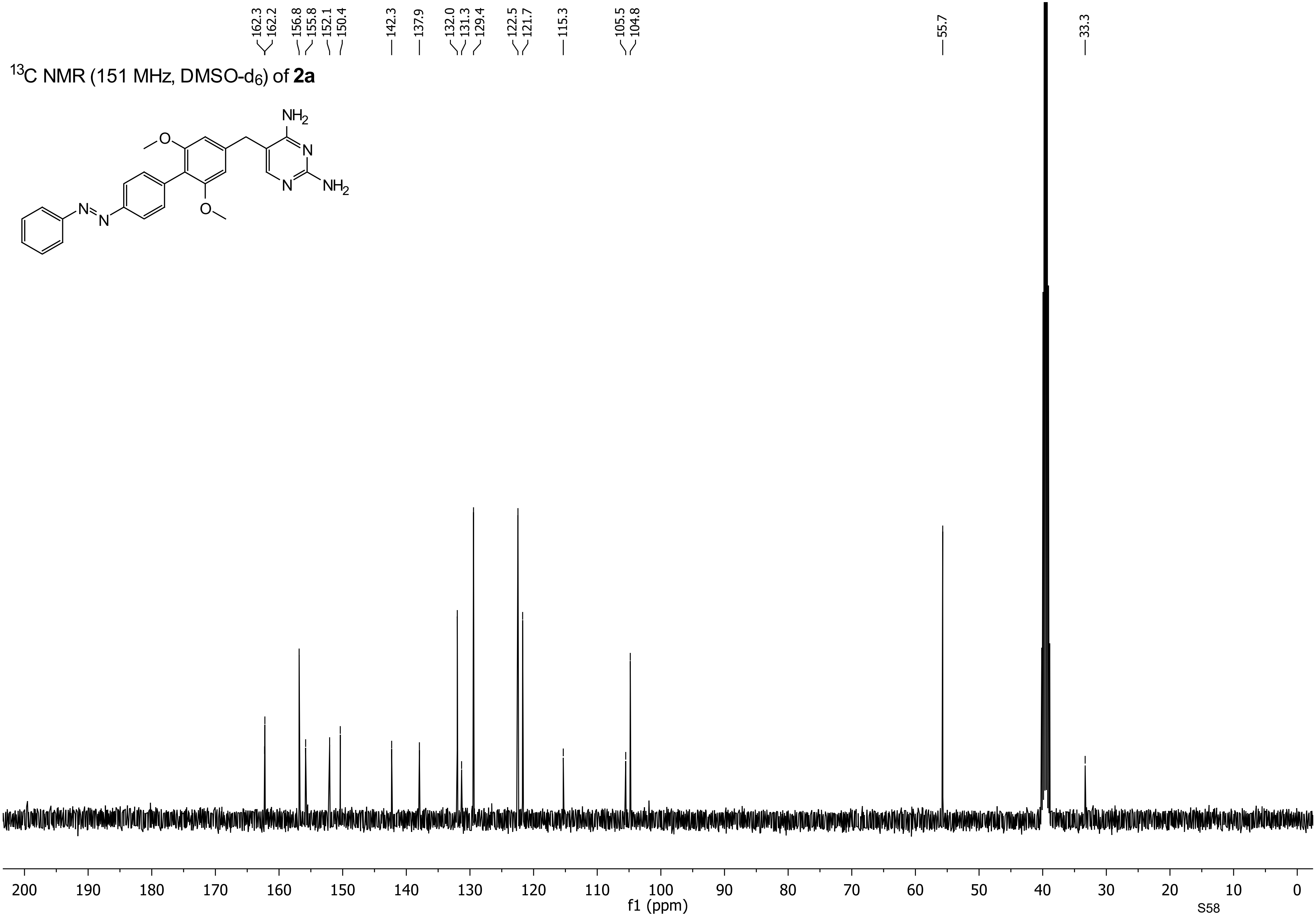
^{13}C NMR (151 MHz, DMSO-d_6) of **S14**



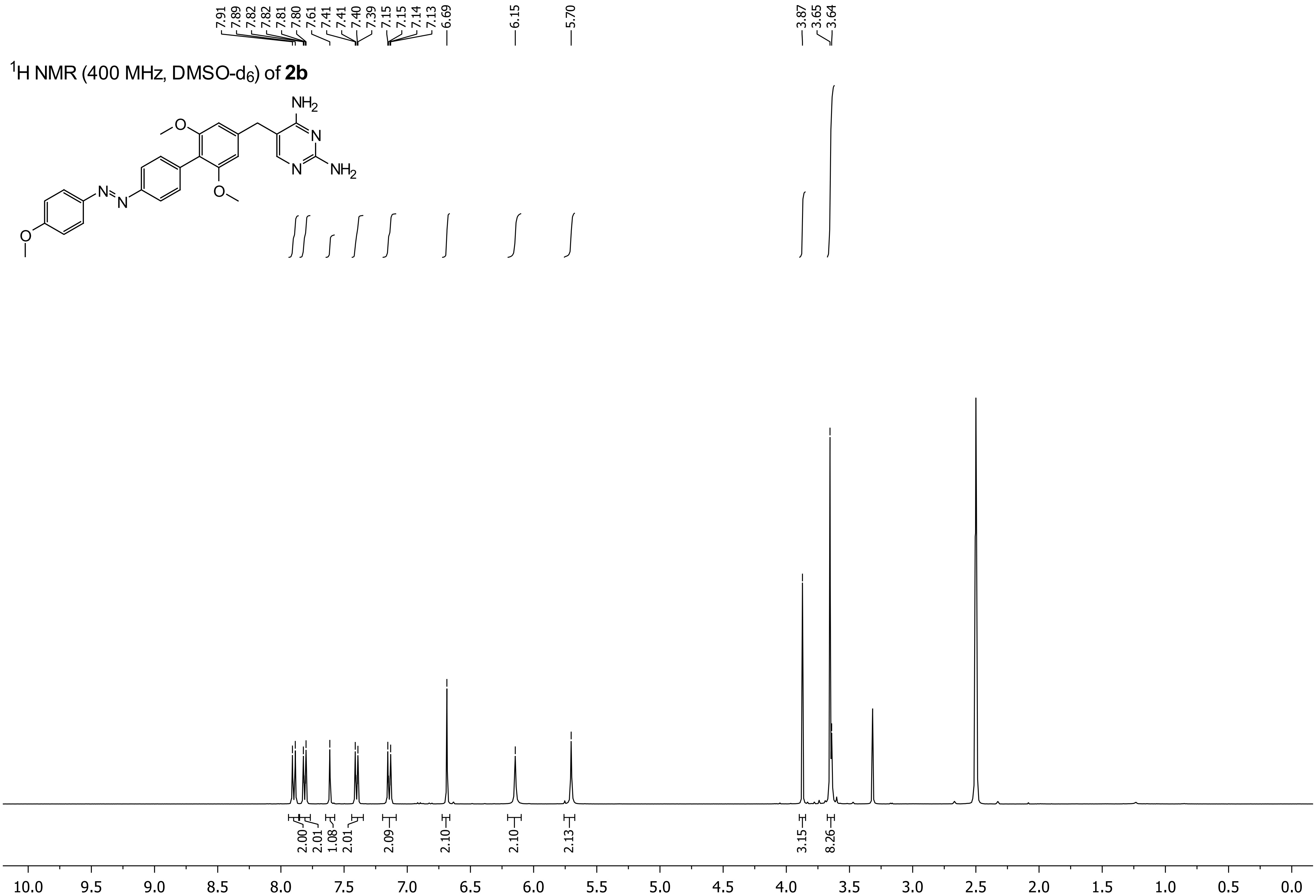
^{1}H NMR (400 MHz, DMSO-d$_6$) of **2a**



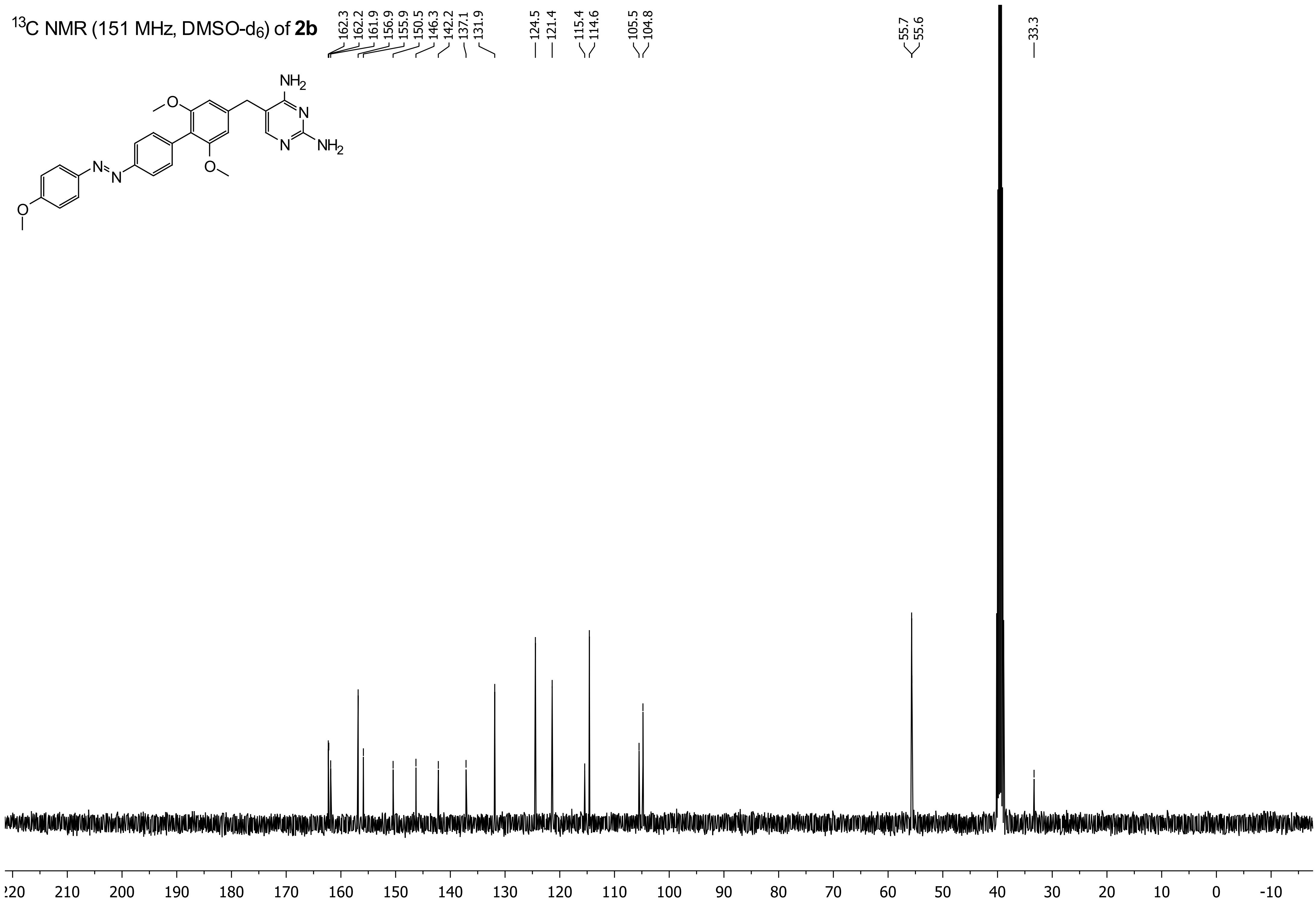
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2a**



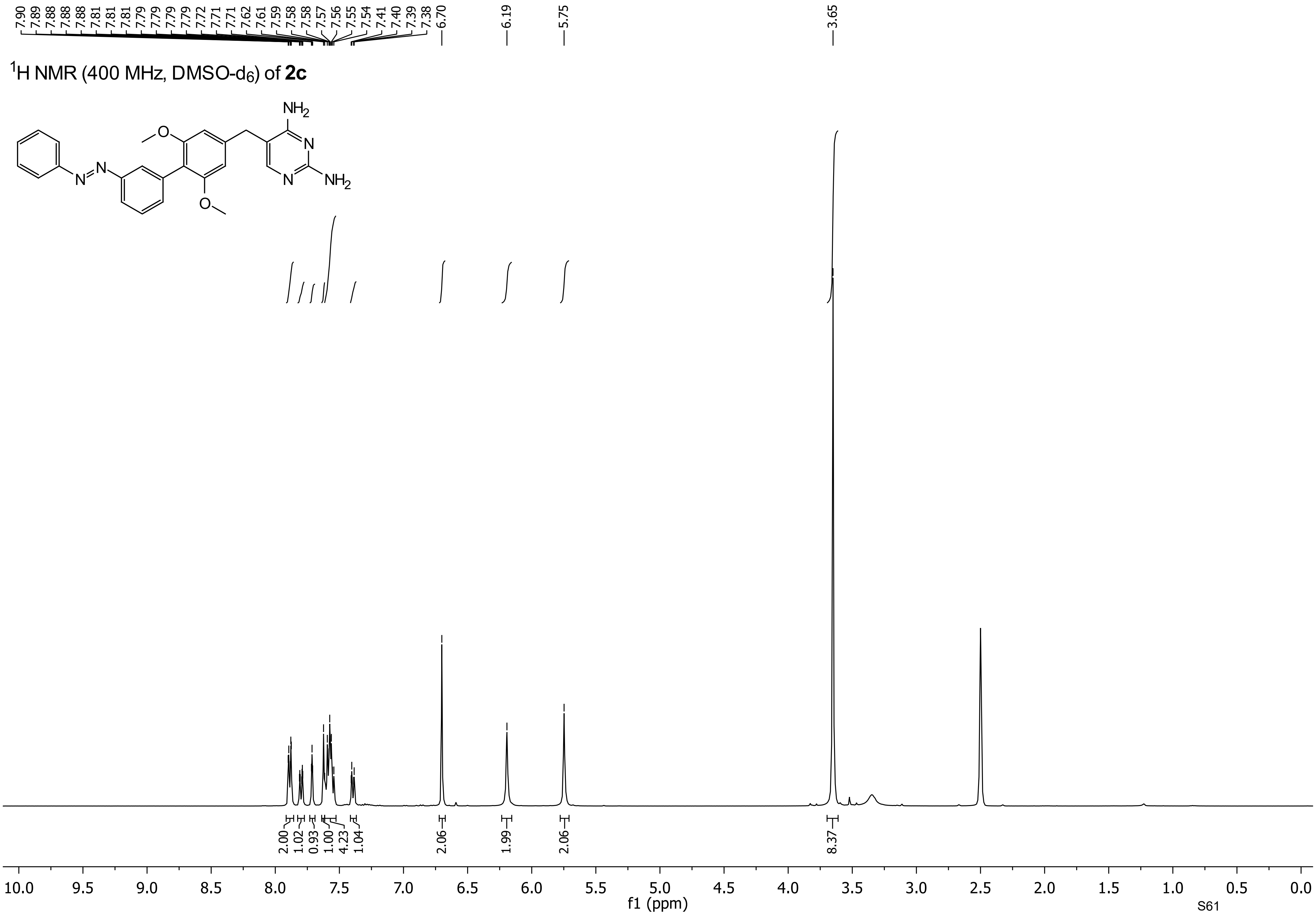
^{1}H NMR (400 MHz, DMSO-d$_6$) of **2b**



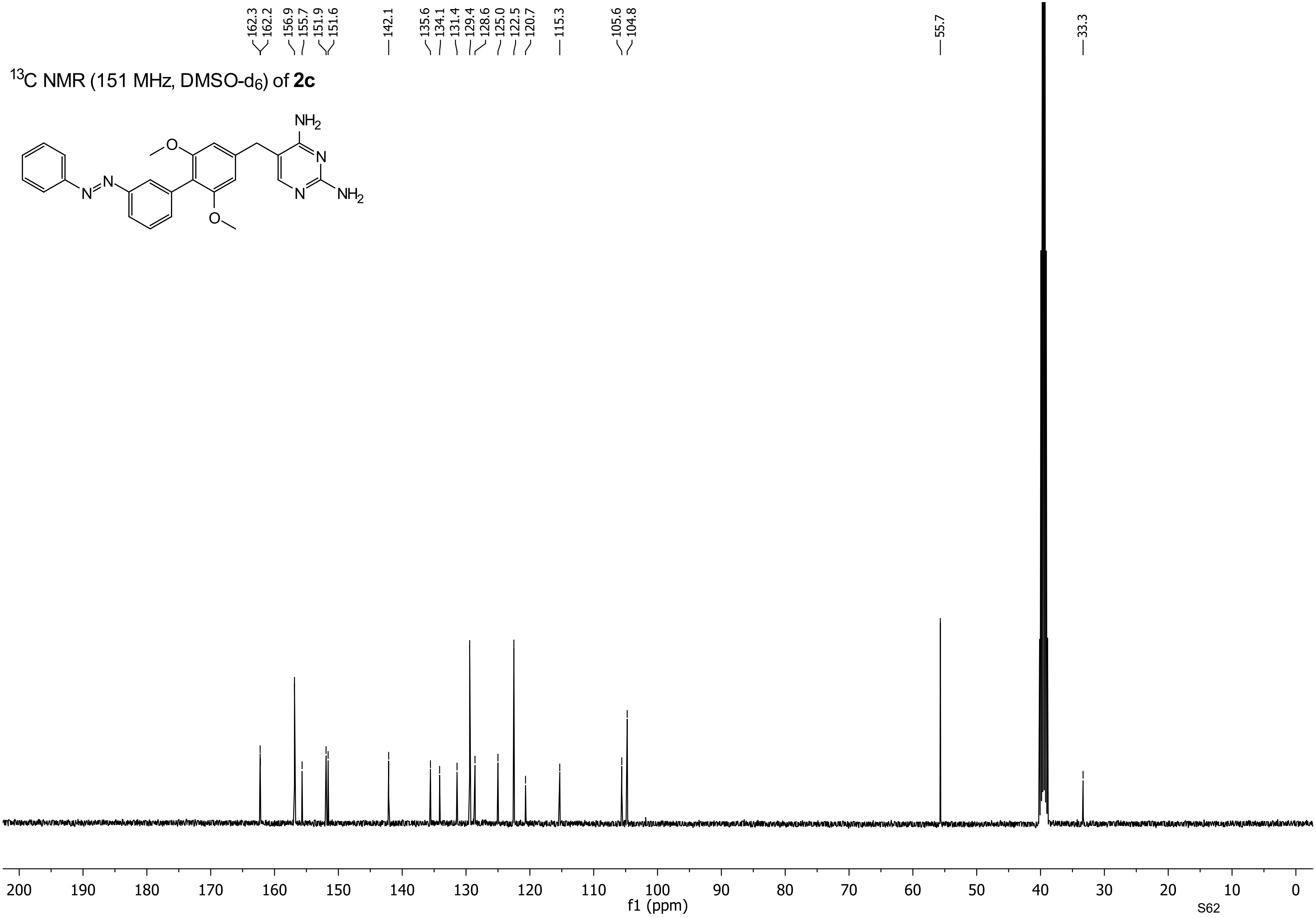
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2b**

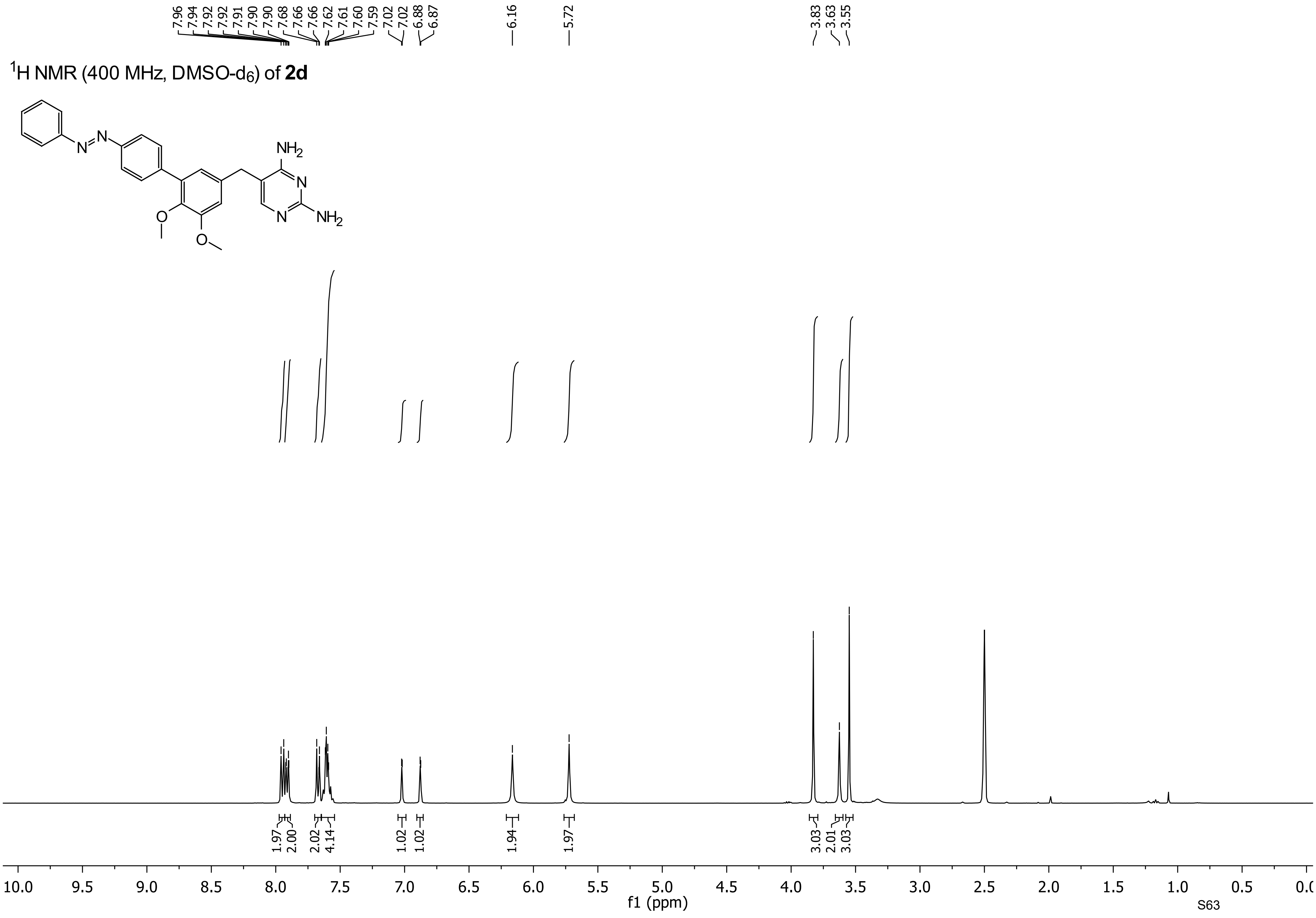


^{1}H NMR (400 MHz, DMSO-d_6) of **2c**



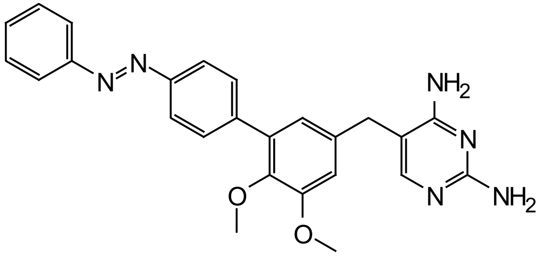
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2c**

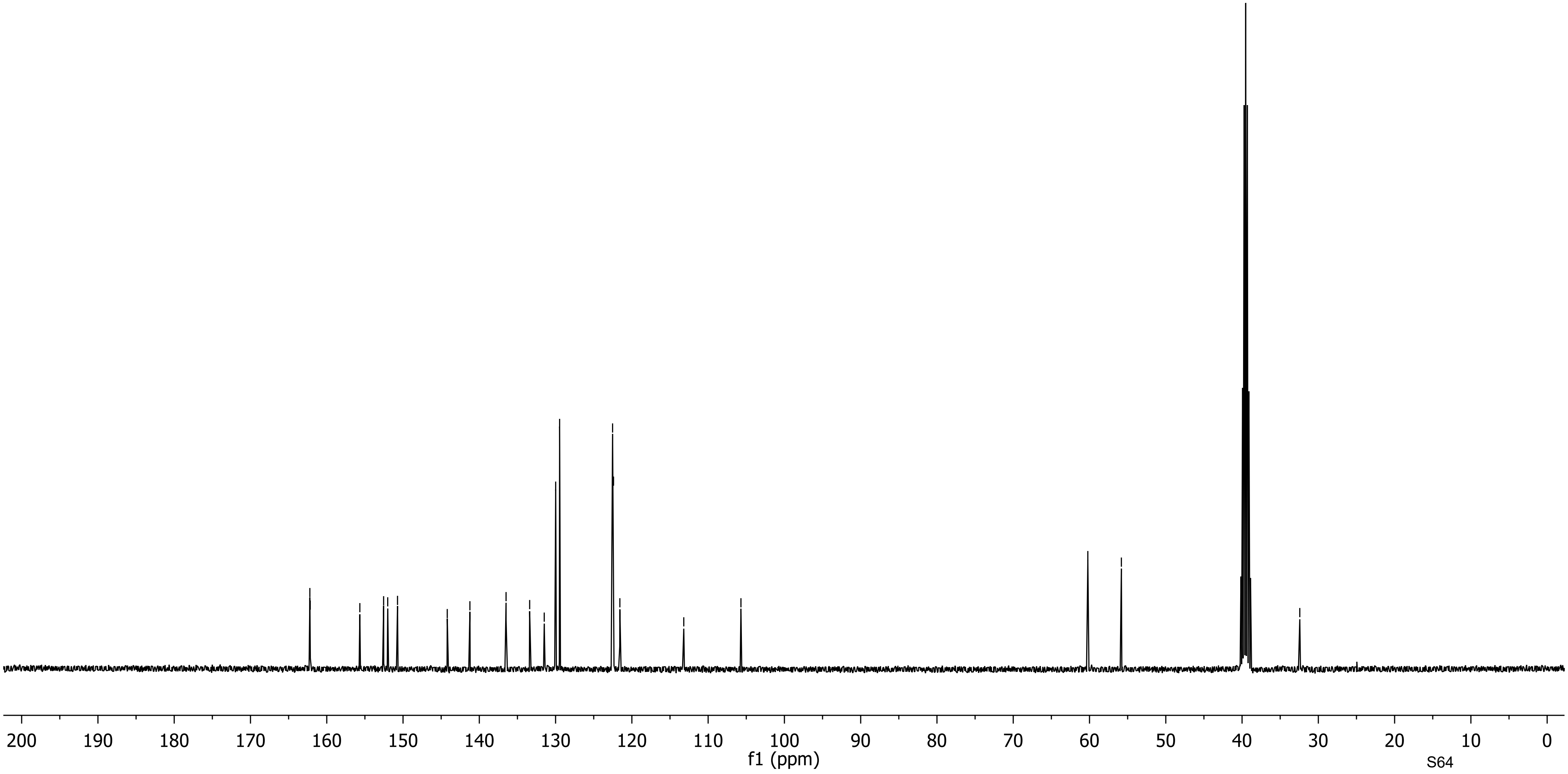


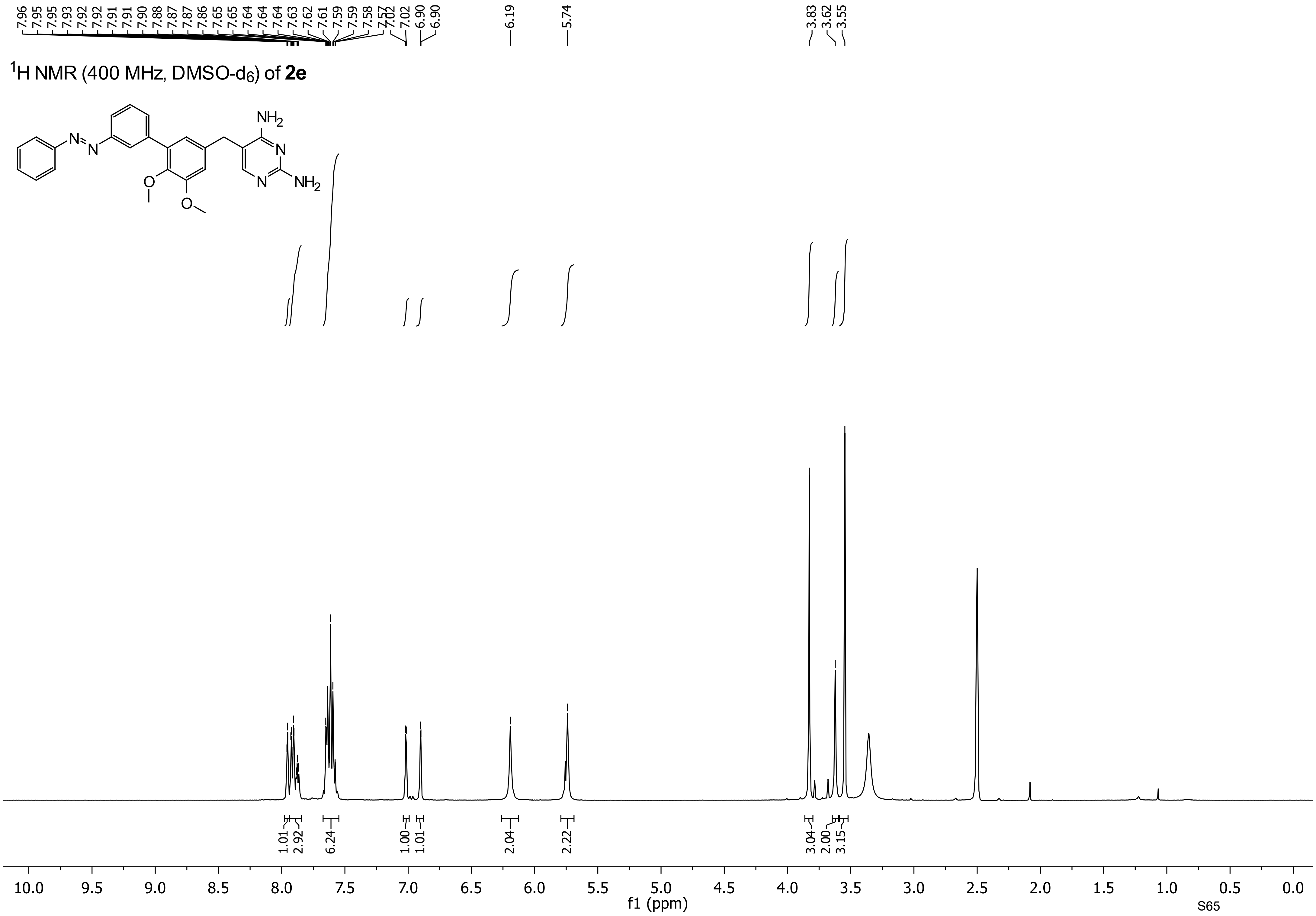


^{1}H NMR (400 MHz, DMSO-d$_6$) of **2d**

^{13}C NMR (151 MHz, DMSO-d_6) of **2d**

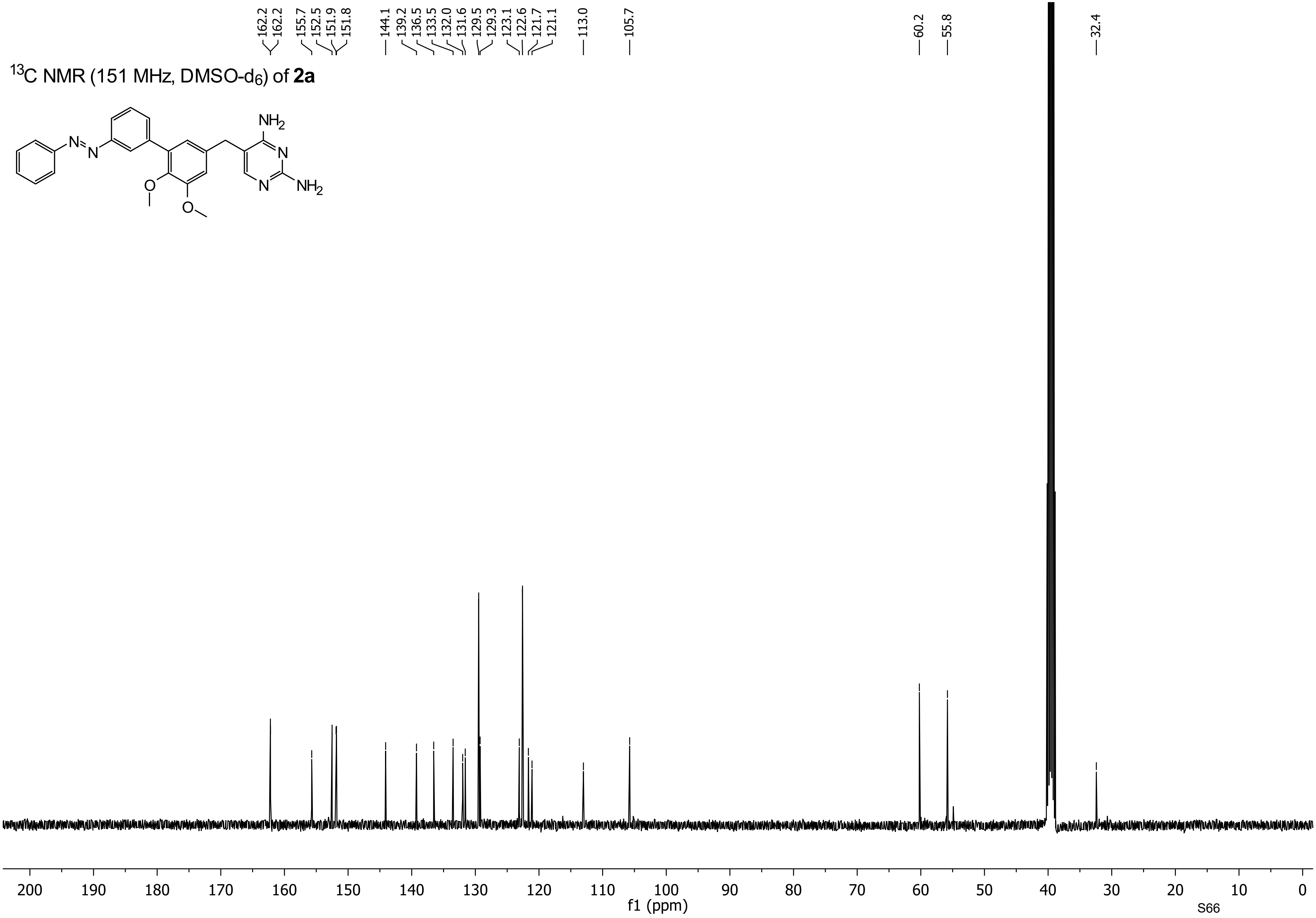




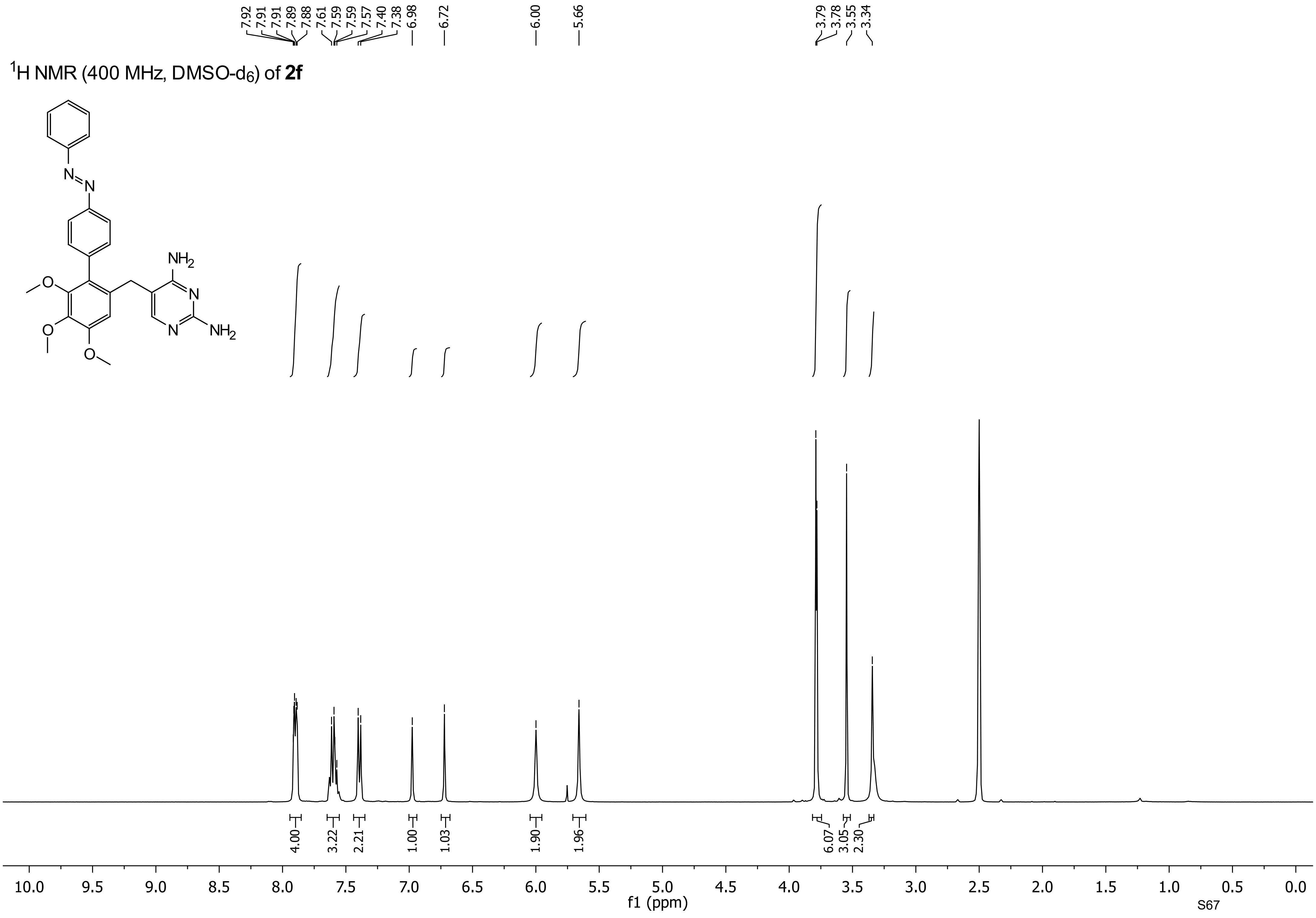


^{1}H NMR (400 MHz, DMSO-d$_6$) of **2e**

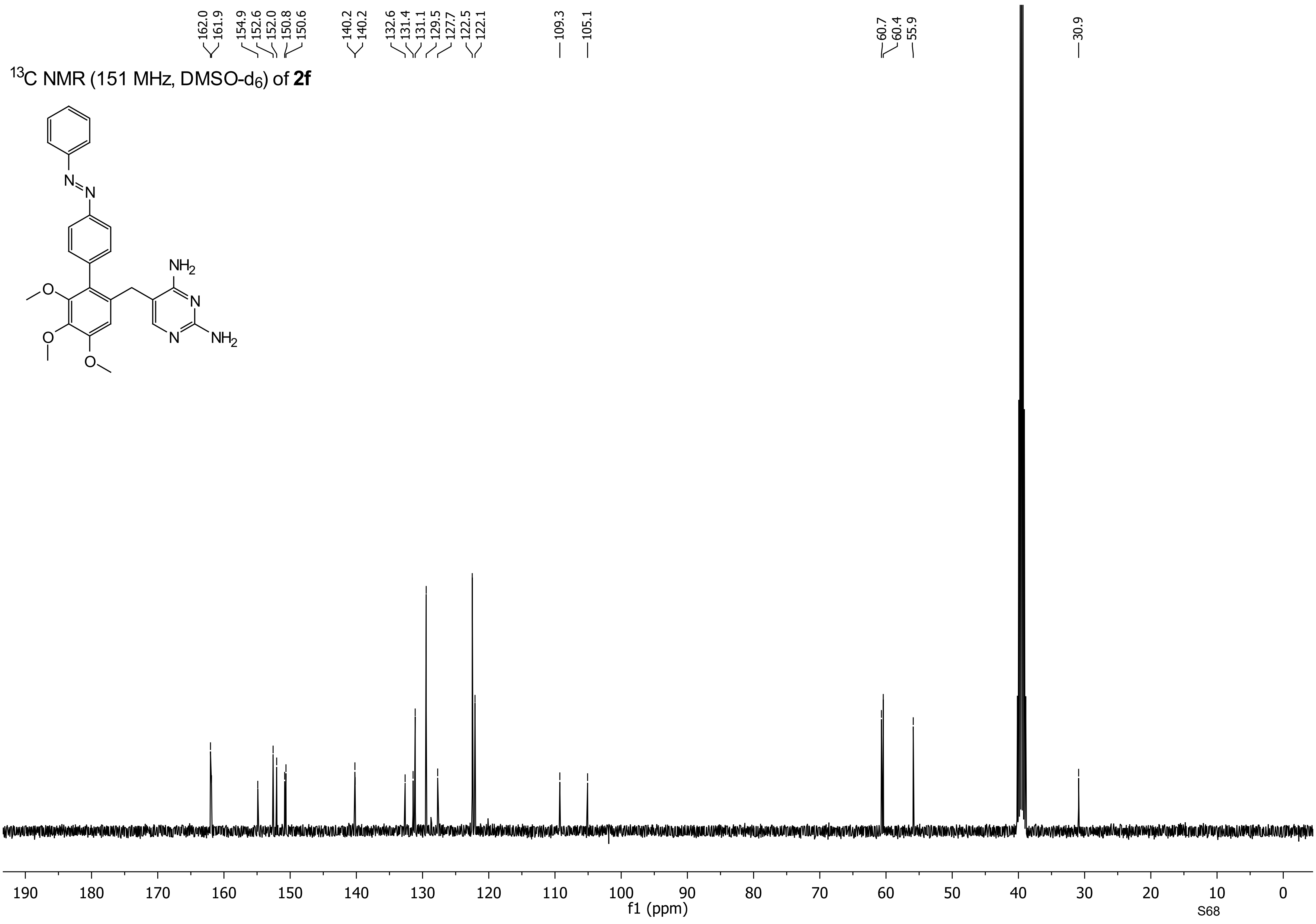
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2a**



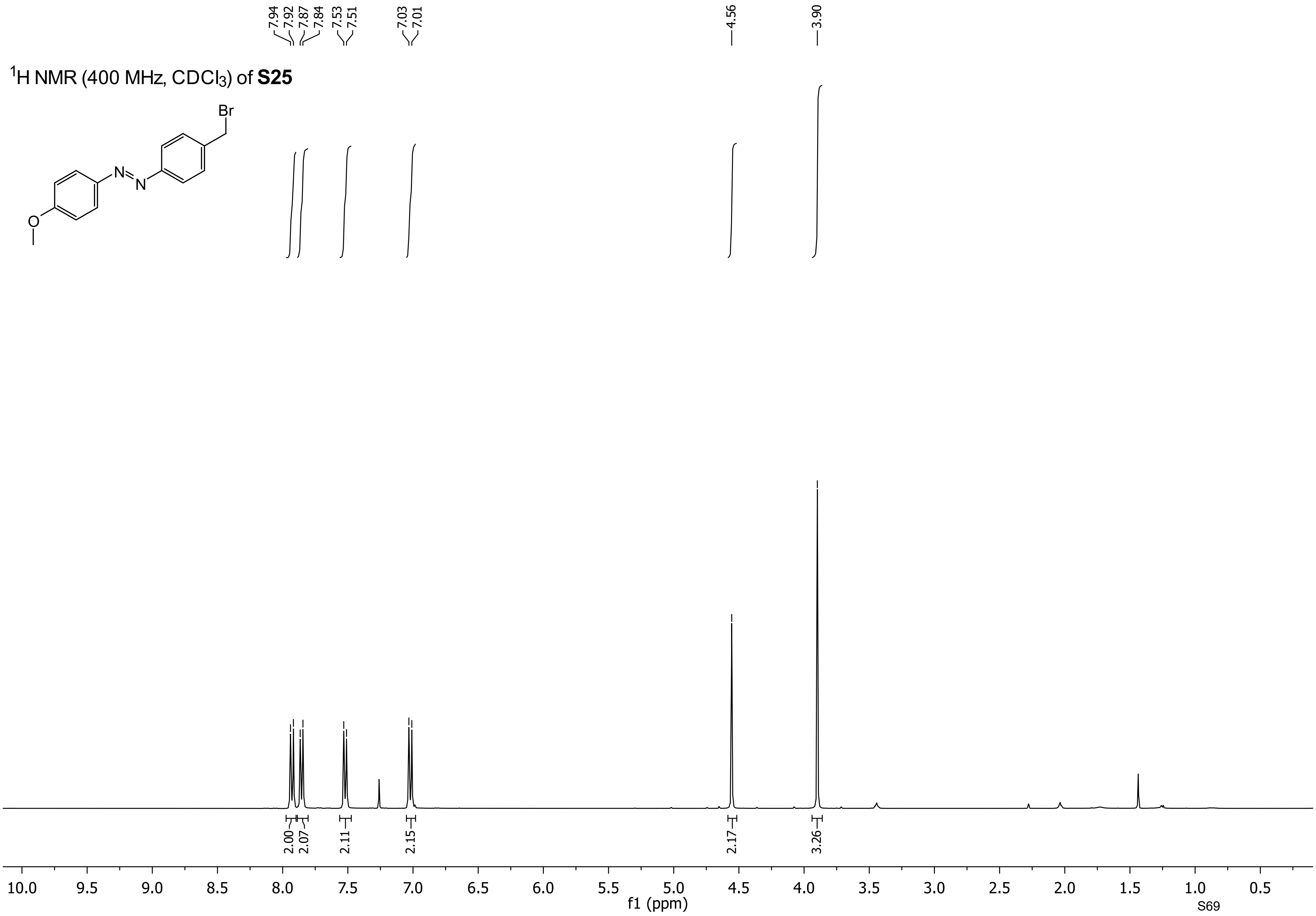
^{1}H NMR (400 MHz, DMSO-d$_6$) of **2f**



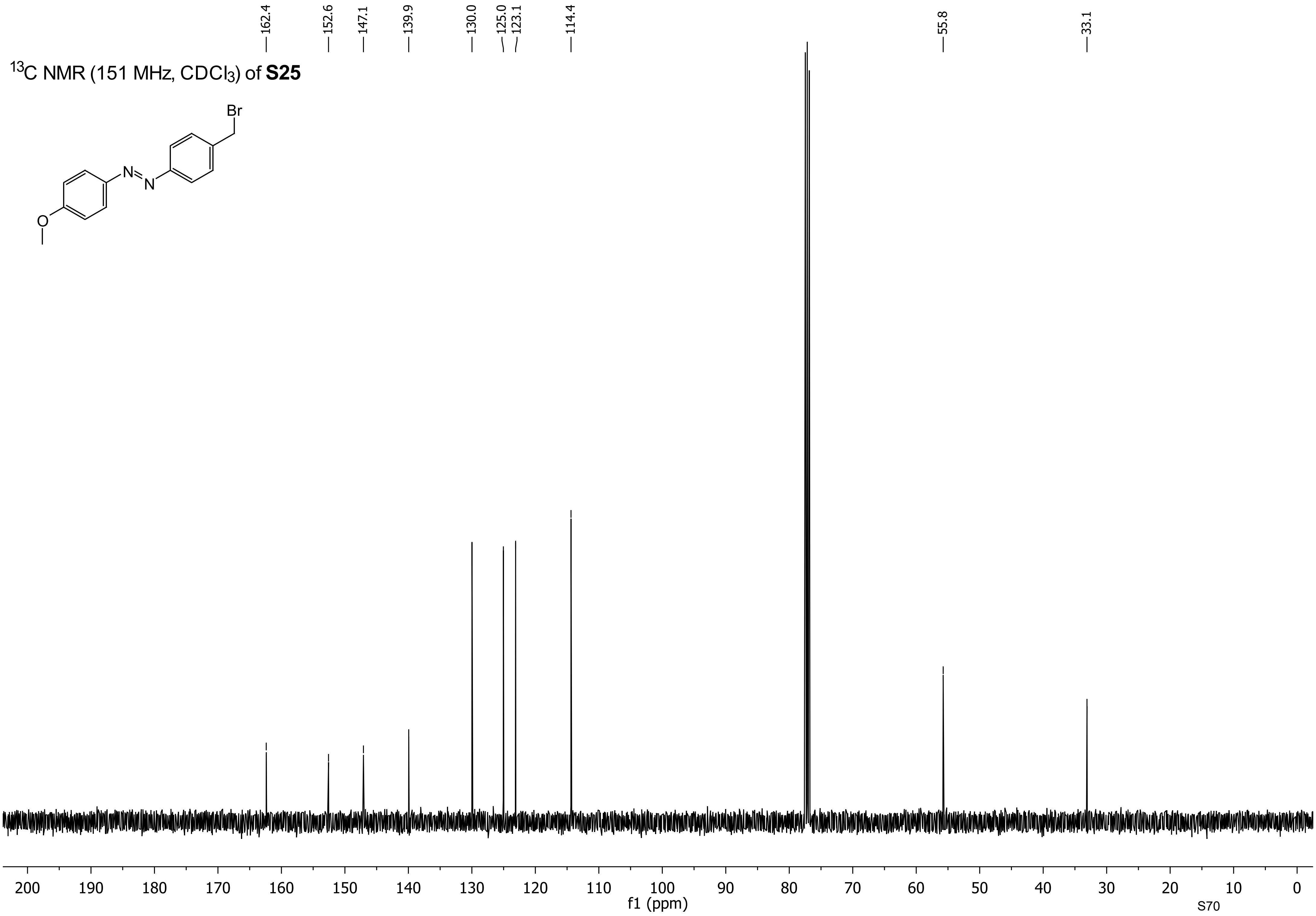
^{13}C NMR (151 MHz, DMSO-d_6) of **2f**



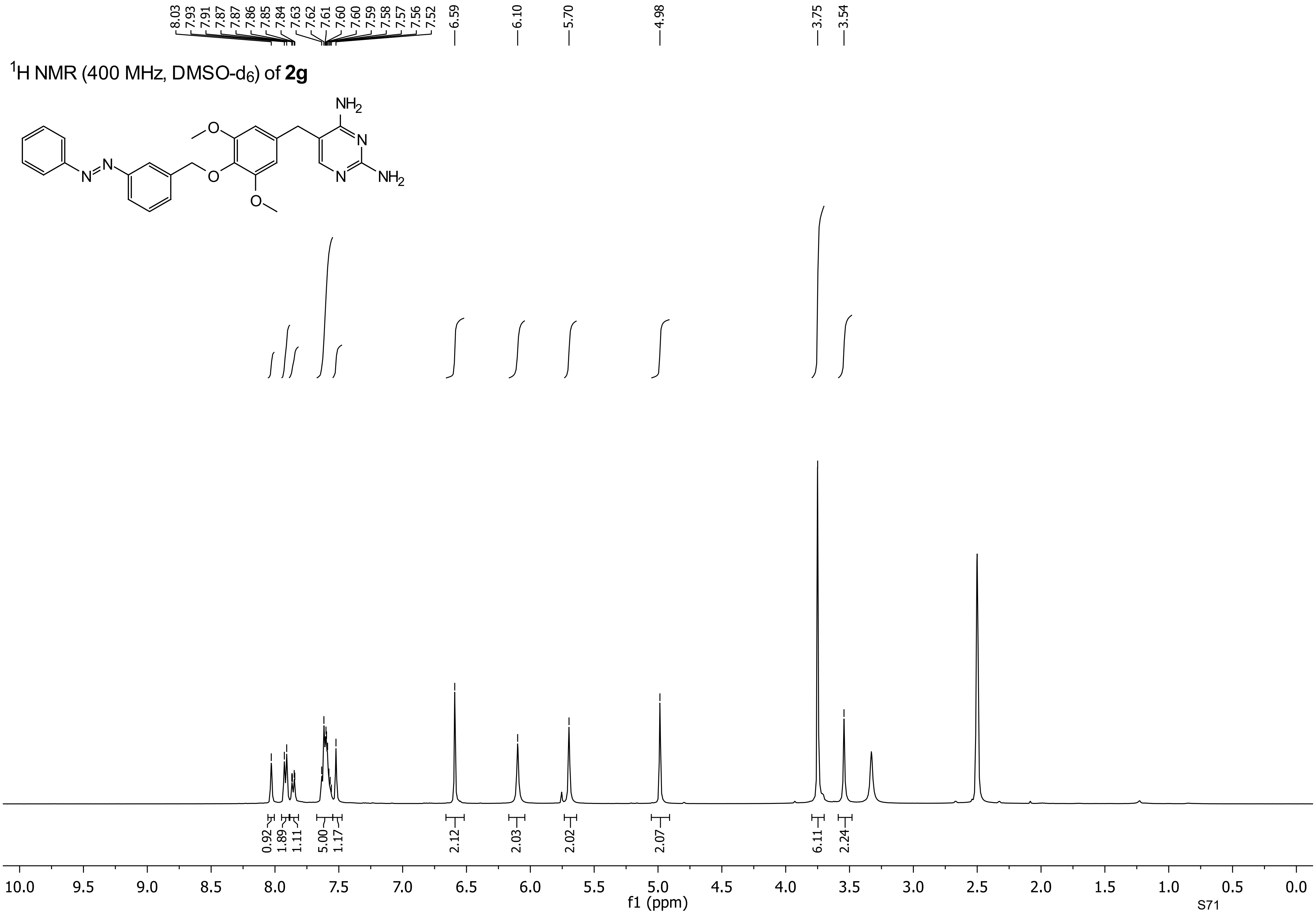
^{1}H NMR (400 MHz, $CDCl_3$) of **S25**



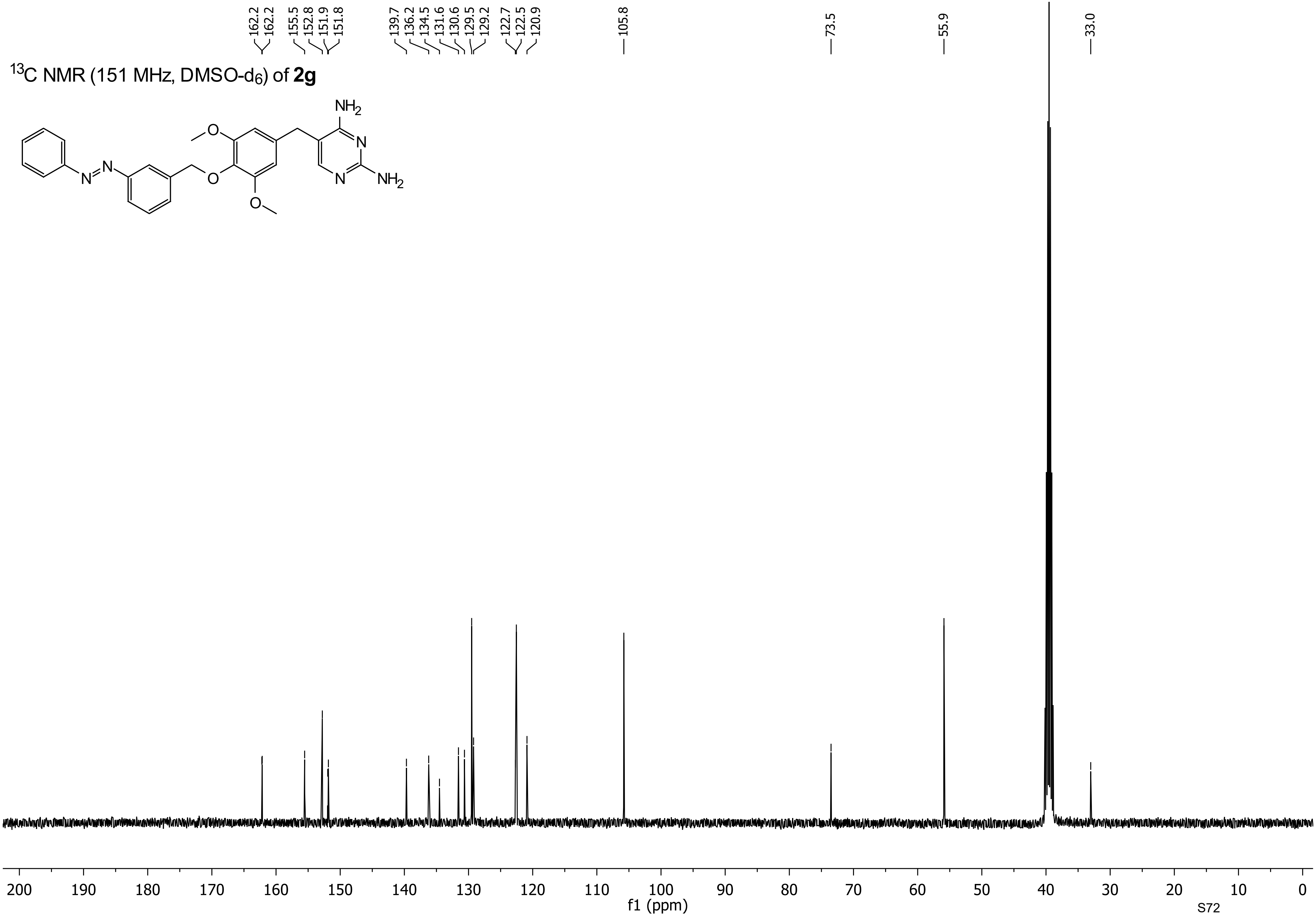
^{13}C NMR (151 MHz, CDCl$_3$) of **S25**



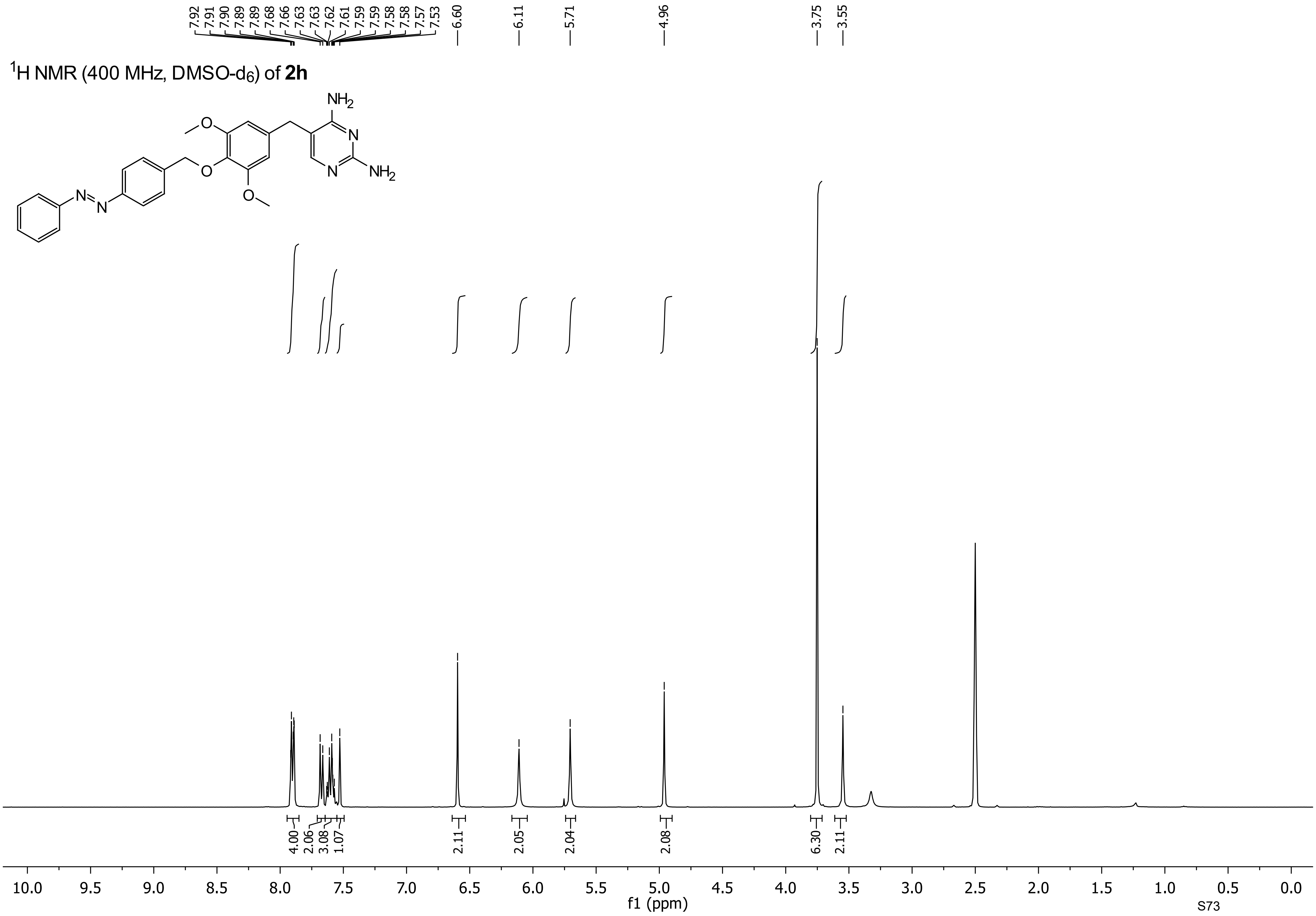
^{1}H NMR (400 MHz, DMSO-d$_6$) of **2g**



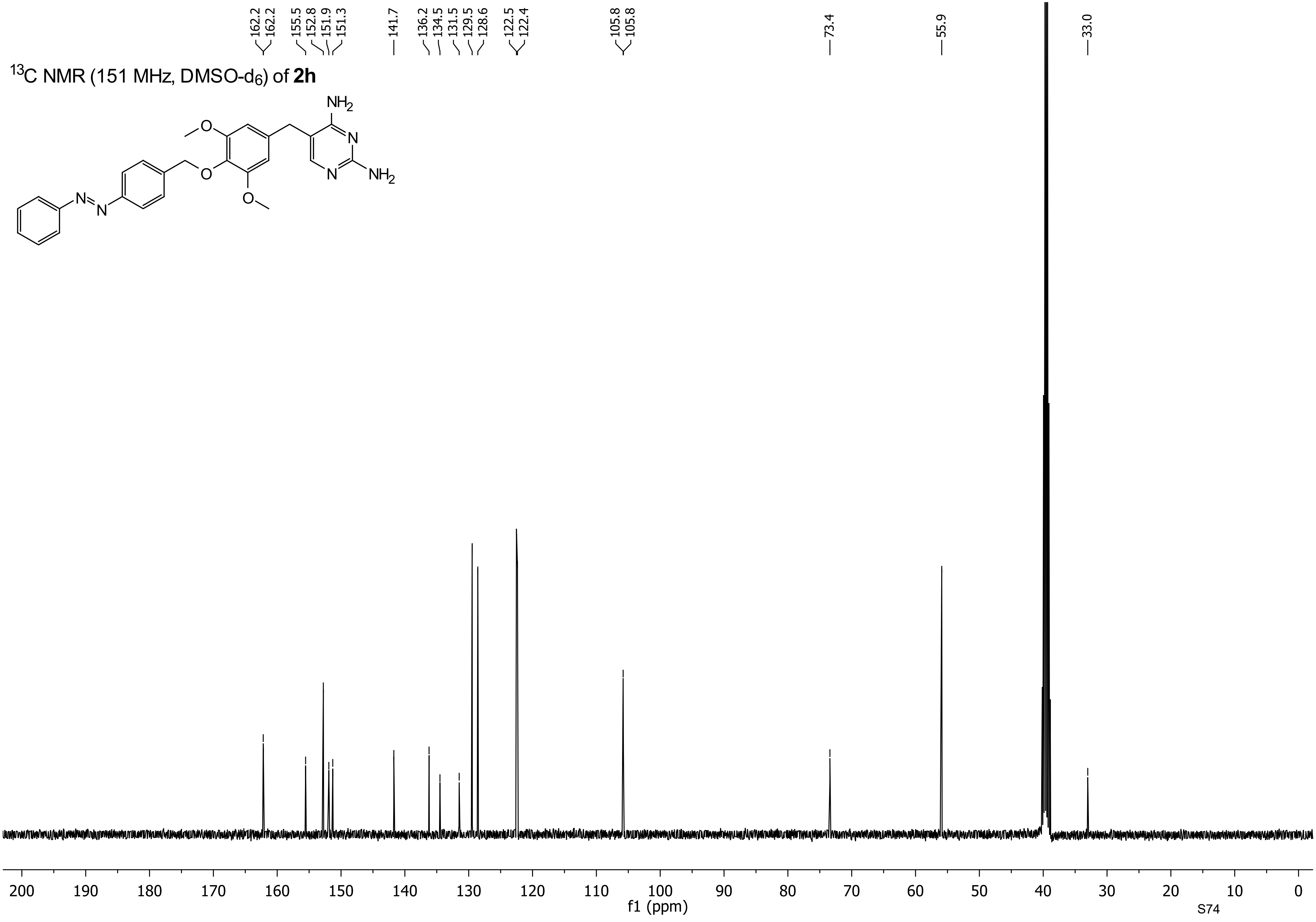
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2g**



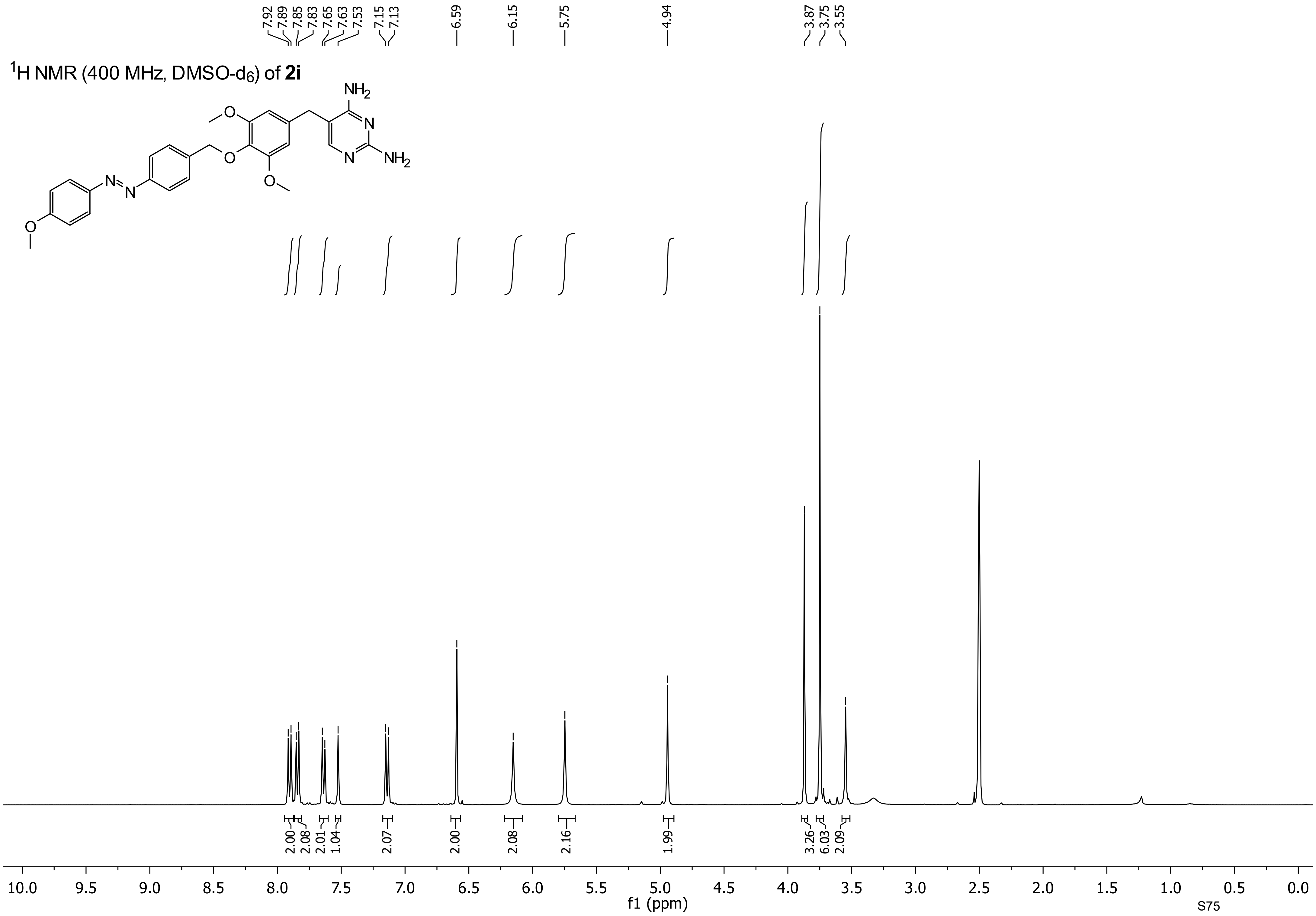
^{1}H NMR (400 MHz, DMSO-d_6) of **2h**



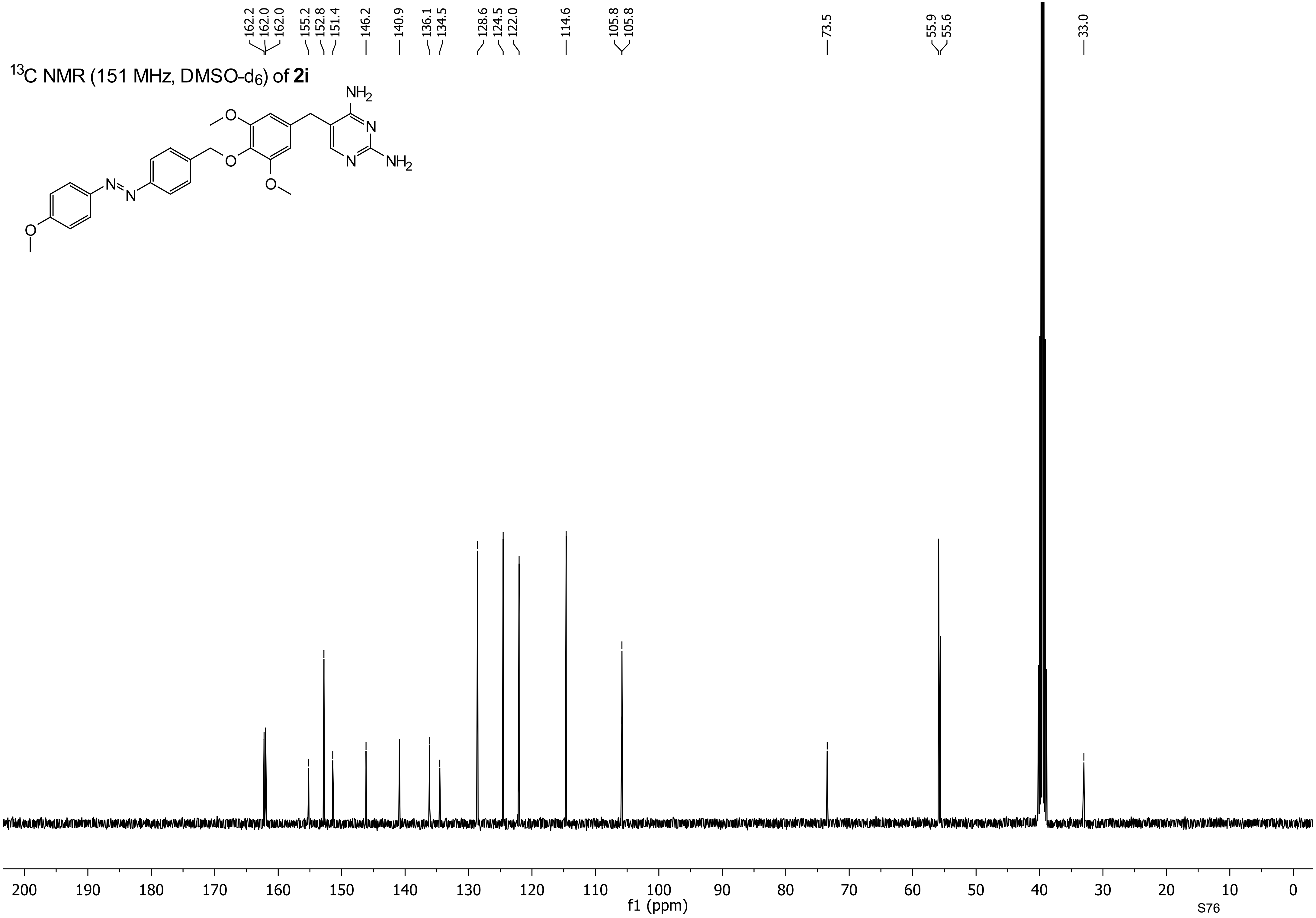
^{13}C NMR (151 MHz, DMSO-d$_6$) of **2h**

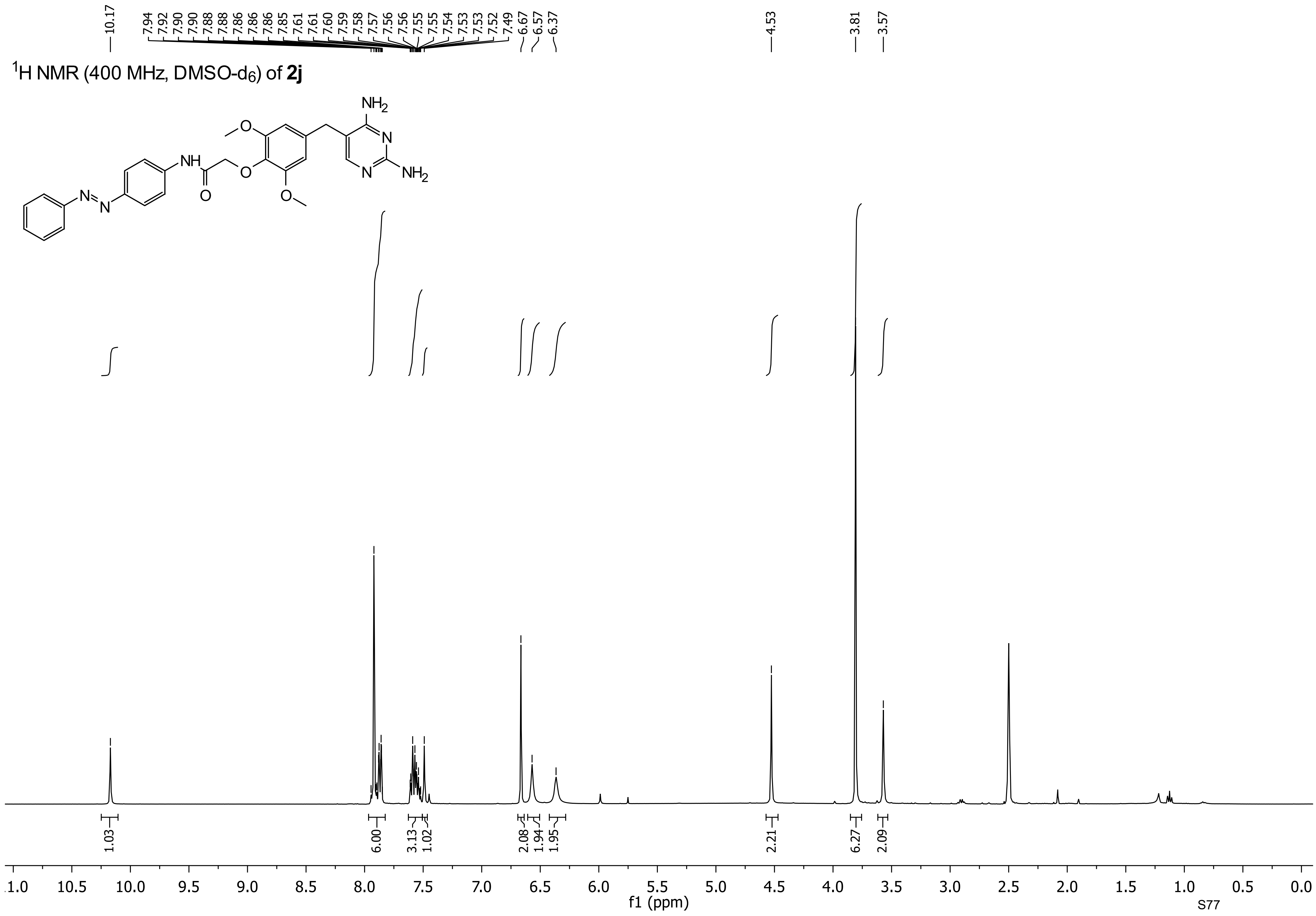


^{1}H NMR (400 MHz, DMSO-d_6) of **2i**

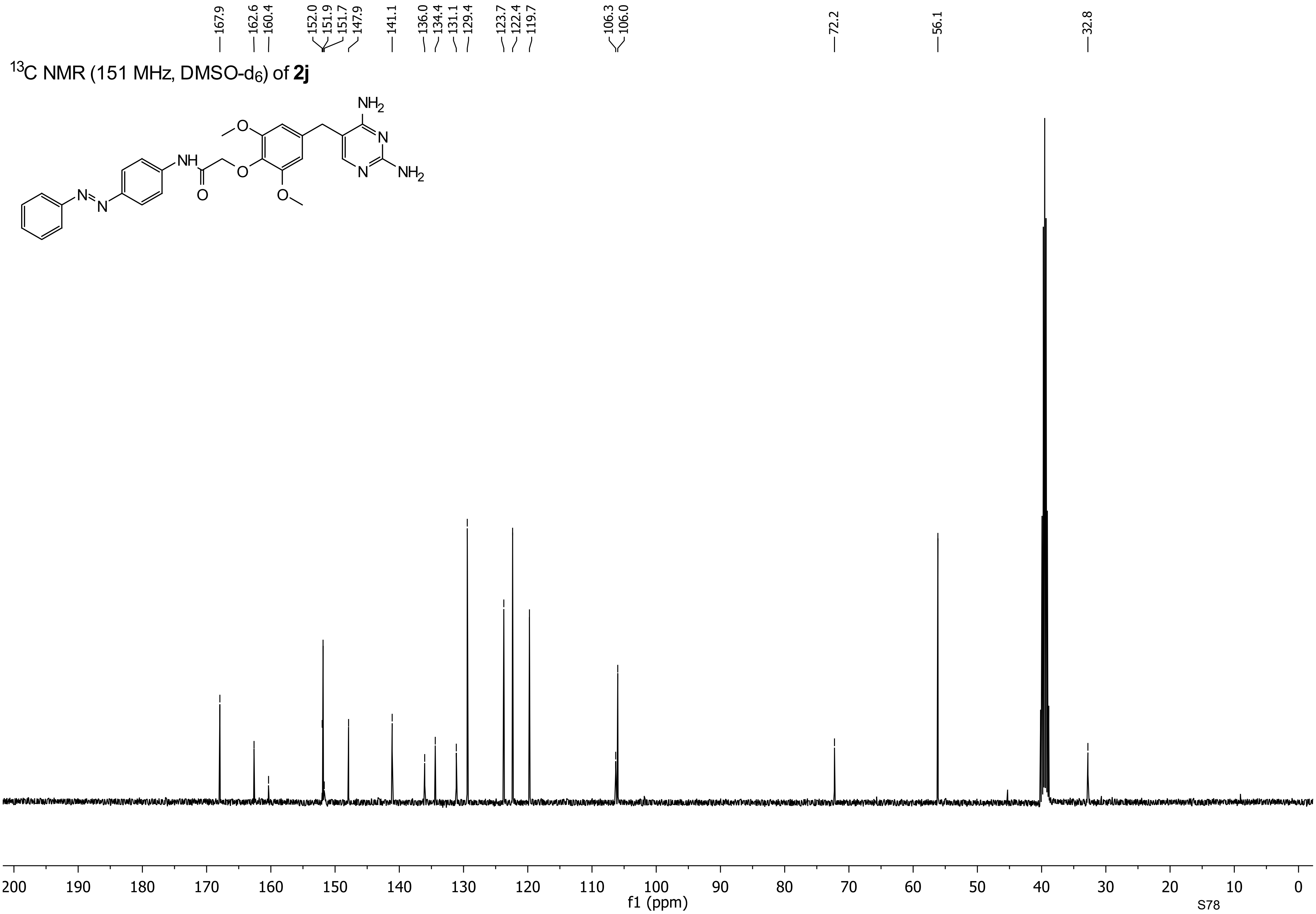


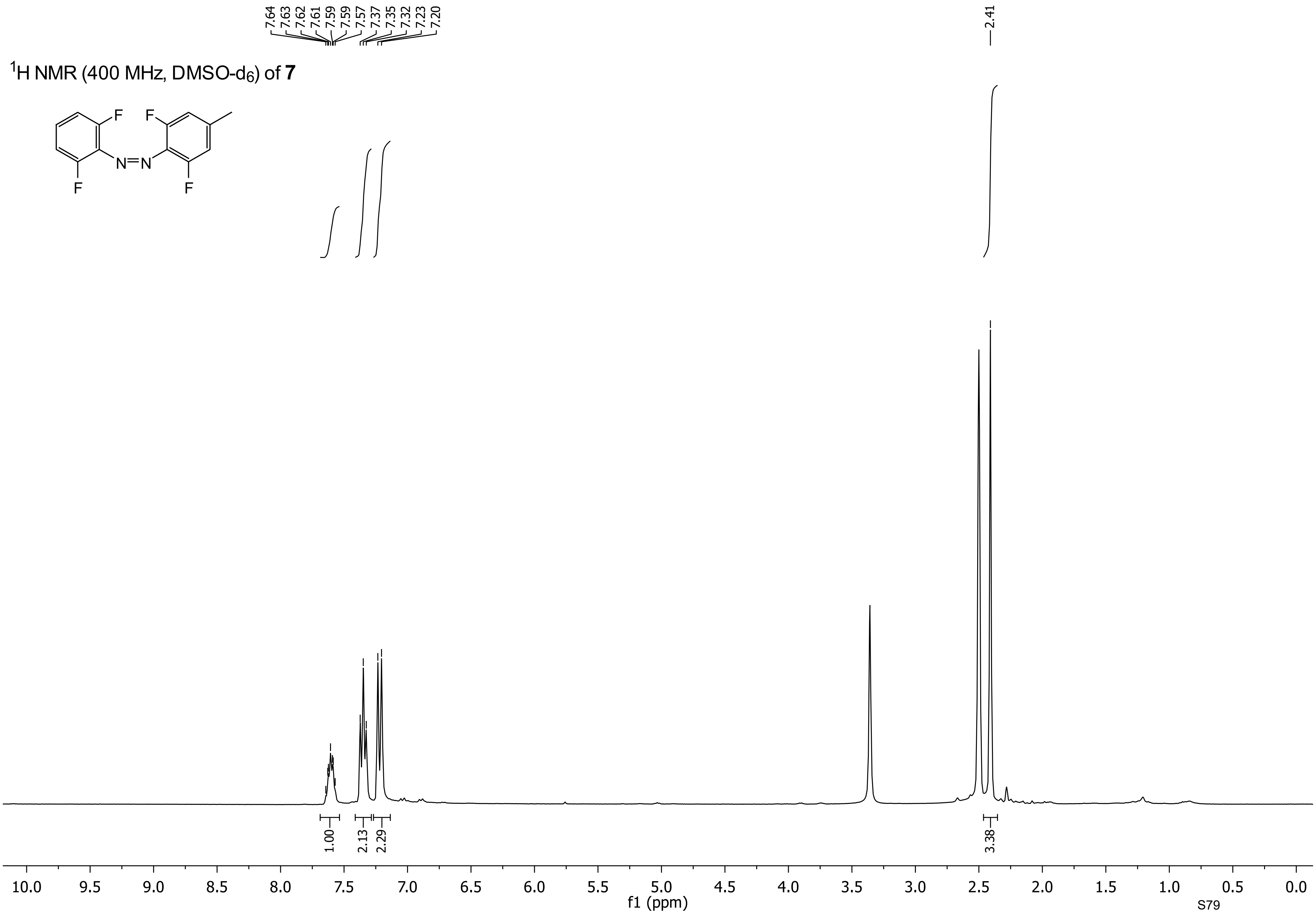
^{13}C NMR (151 MHz, DMSO-d_6) of **2i**




^{1}H NMR (400 MHz, DMSO-d_6) of **2j**

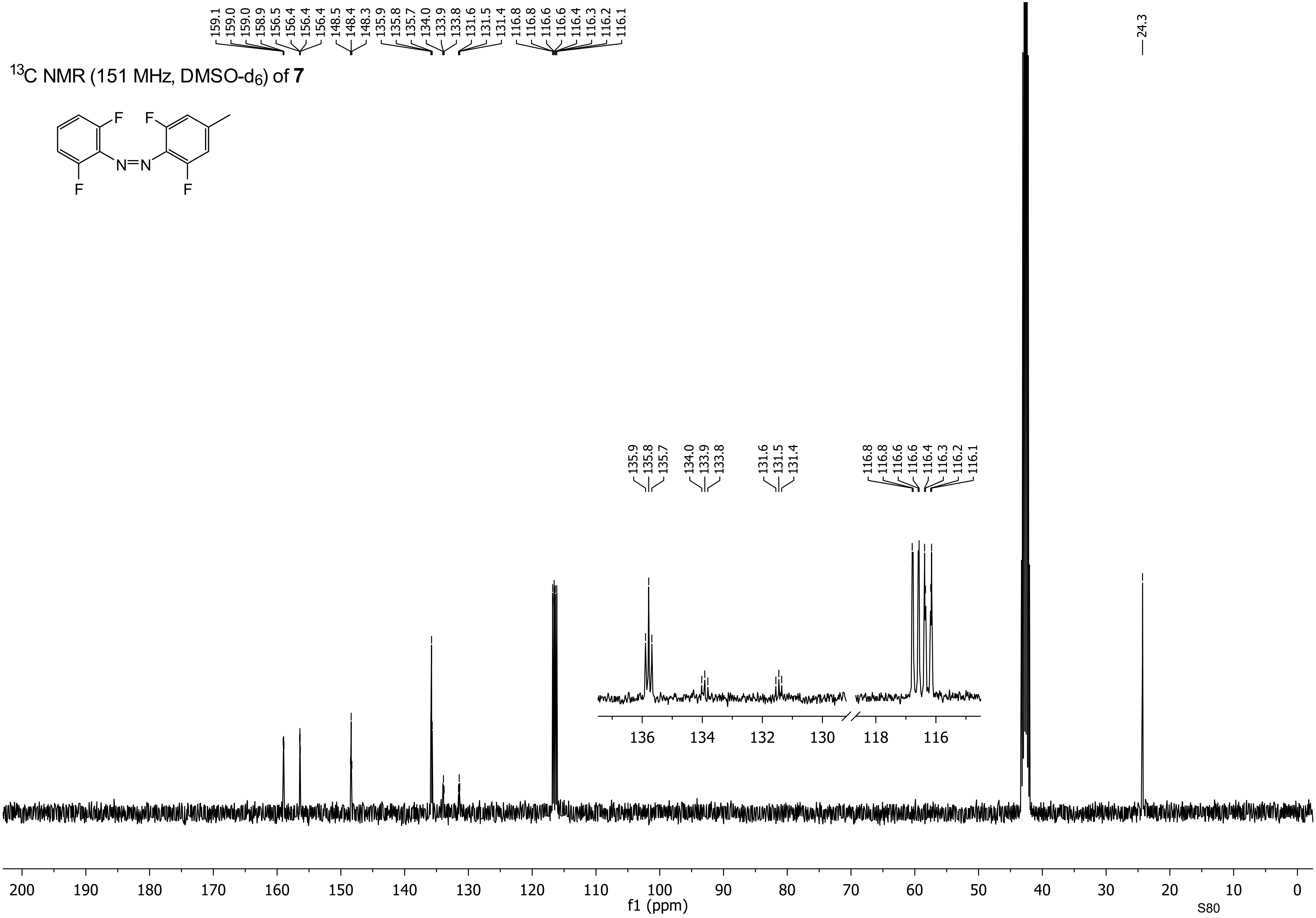
^{13}C NMR (151 MHz, DMSO-d_6) of **2j**



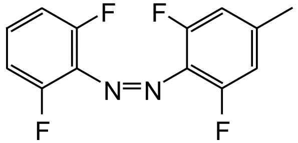


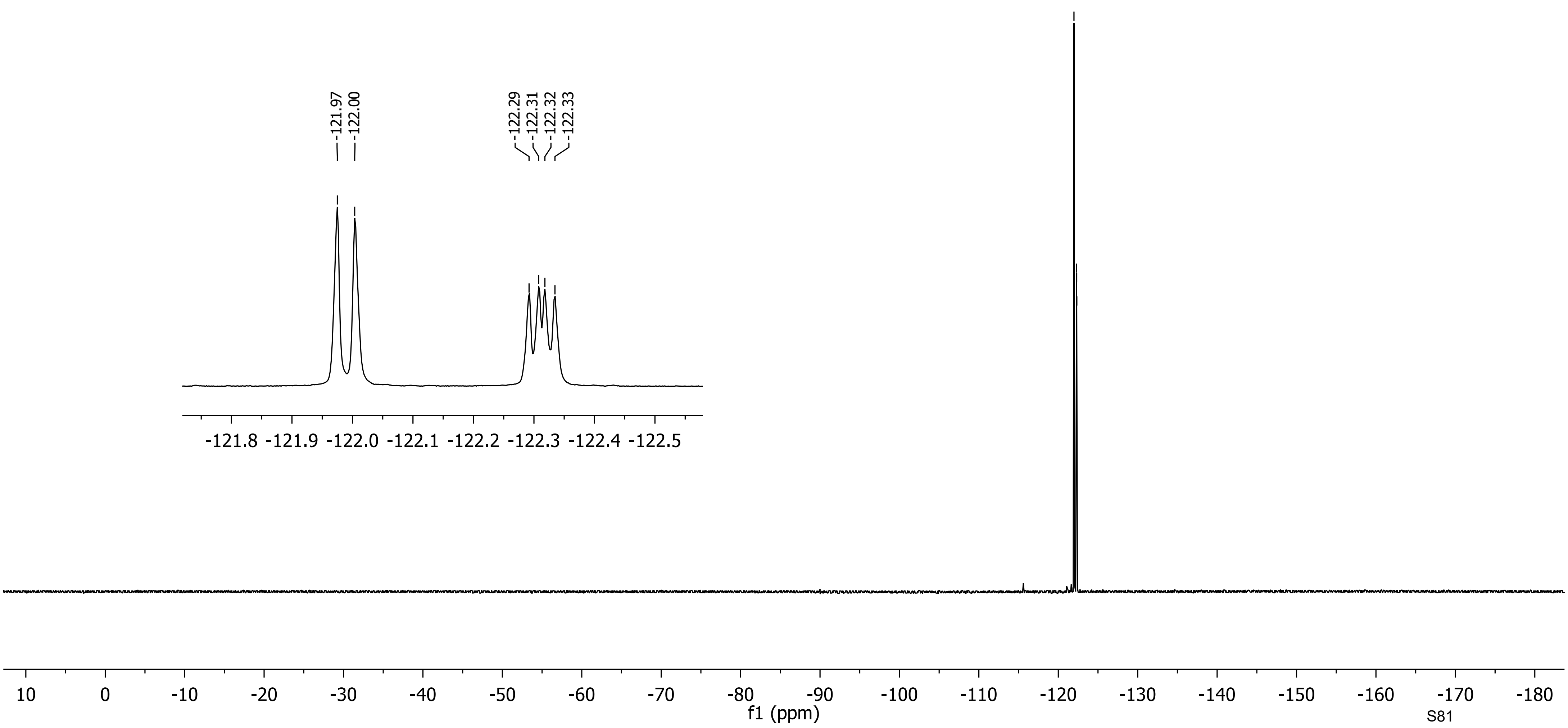
^{1}H NMR (400 MHz, DMSO-d$_6$) of **7**

^{13}C NMR (151 MHz, DMSO-d_6) of **7**

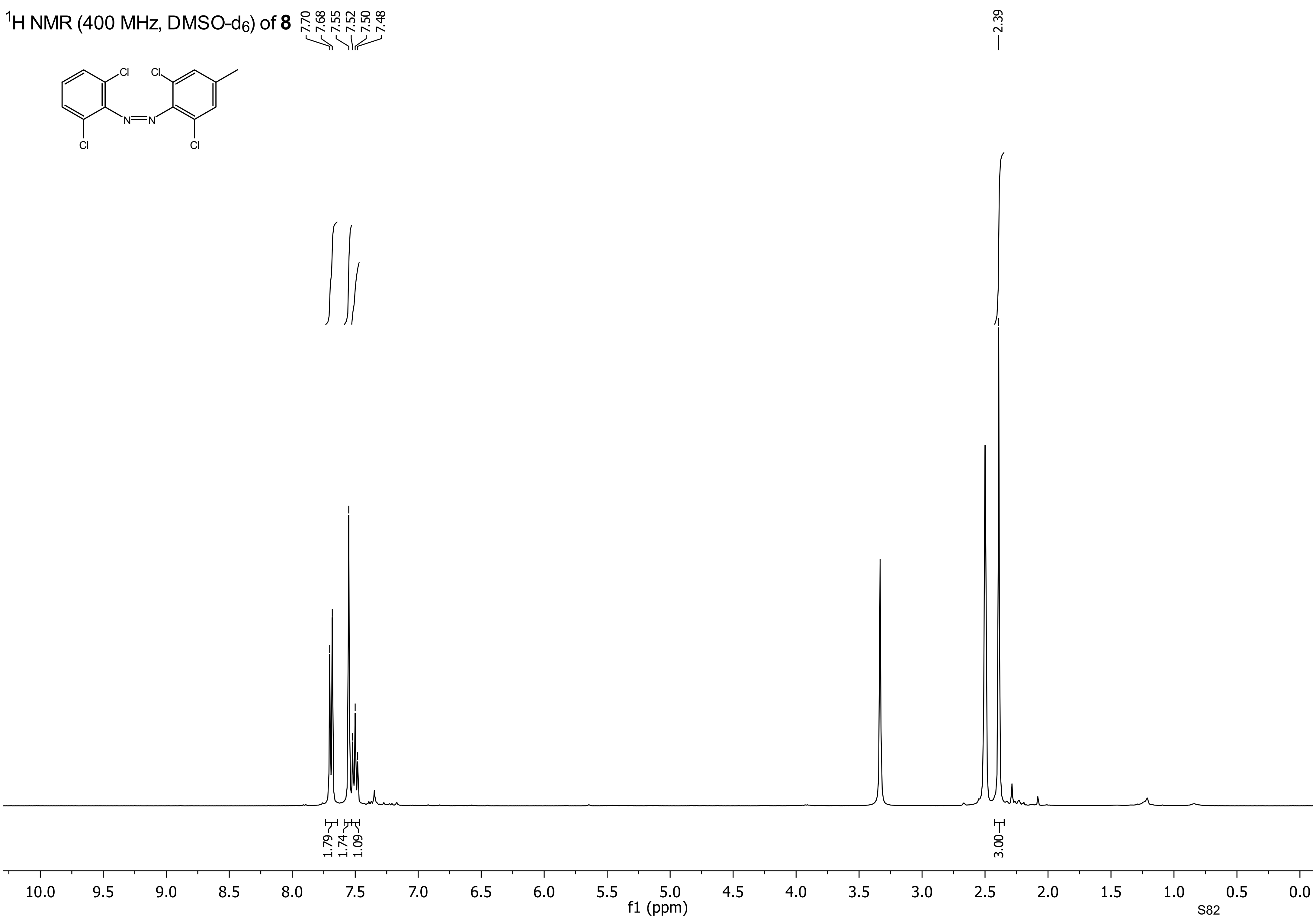


^{19}F NMR (376 MHz, DMSO-d$_6$) of **7**

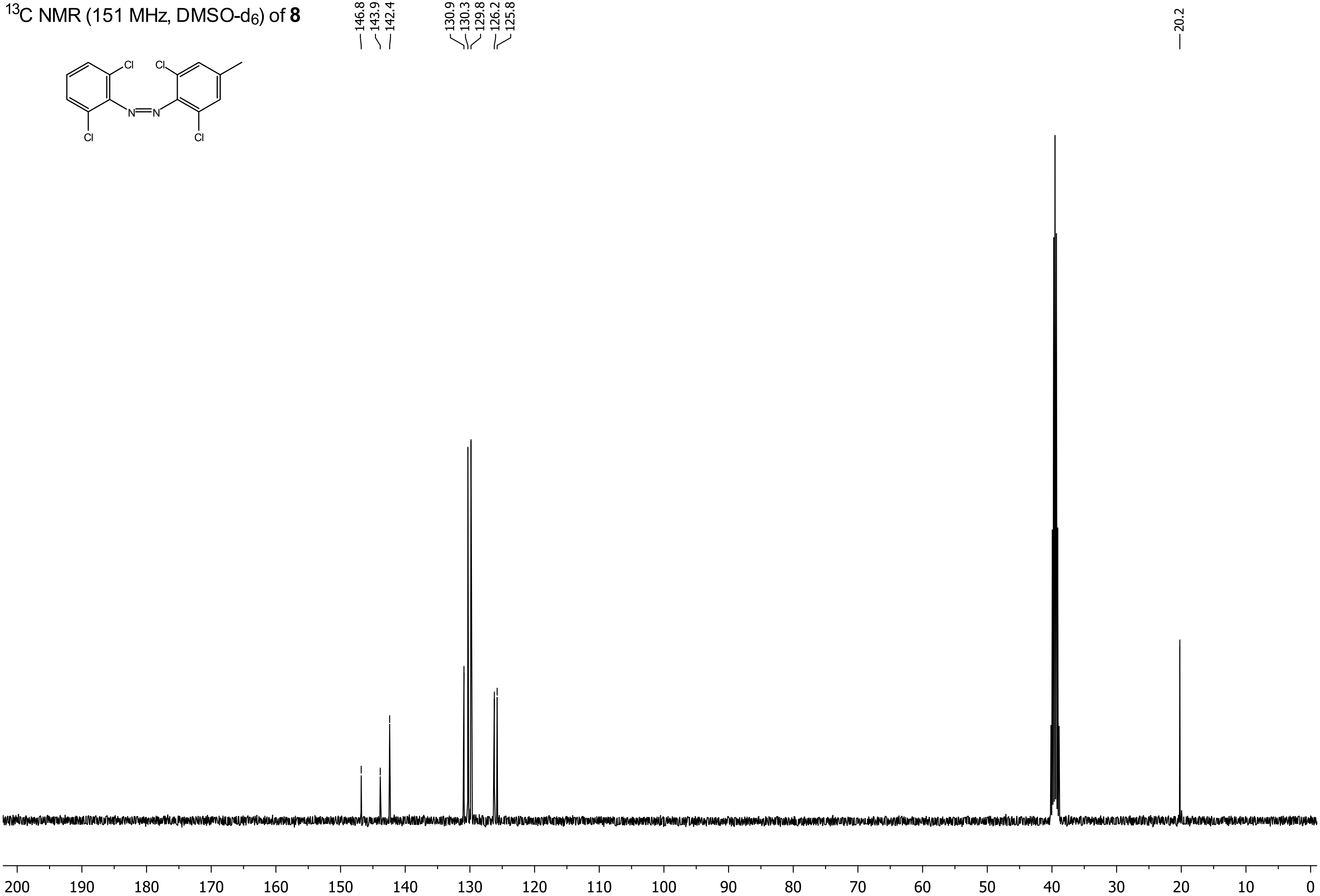




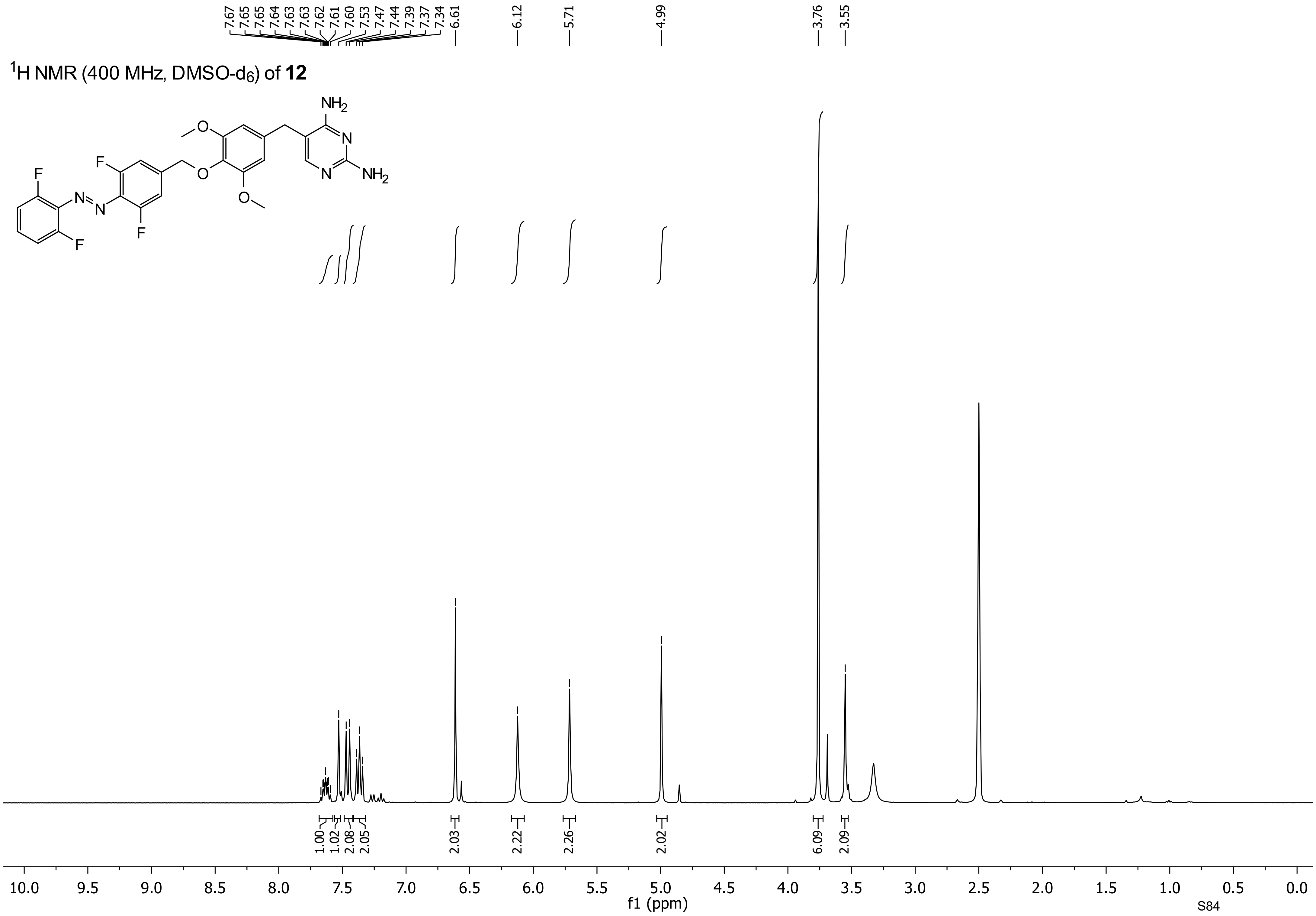
^{1}H NMR (400 MHz, DMSO-d$_6$) of **8**



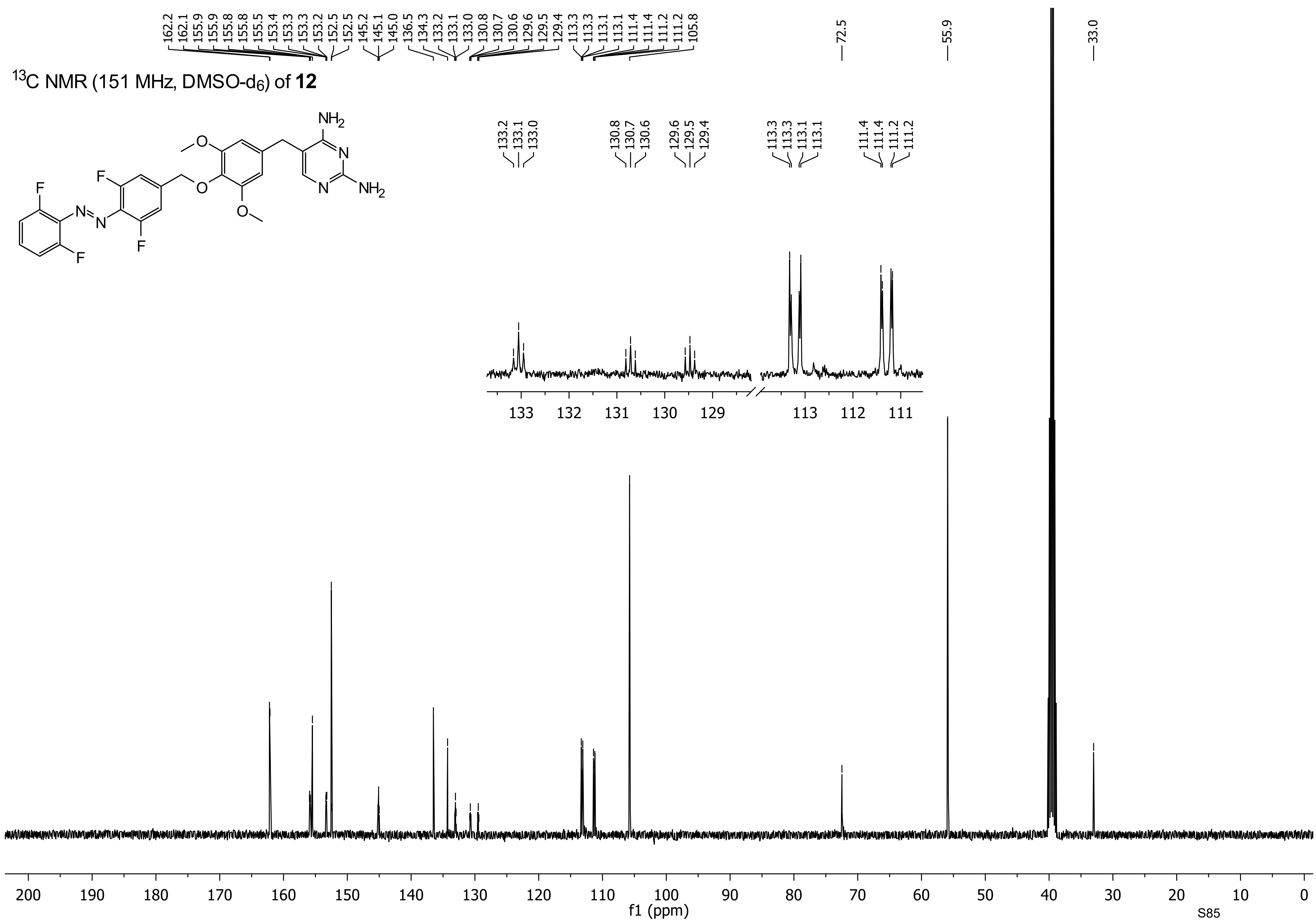
^{13}C NMR (151 MHz, DMSO-d$_6$) of **8**



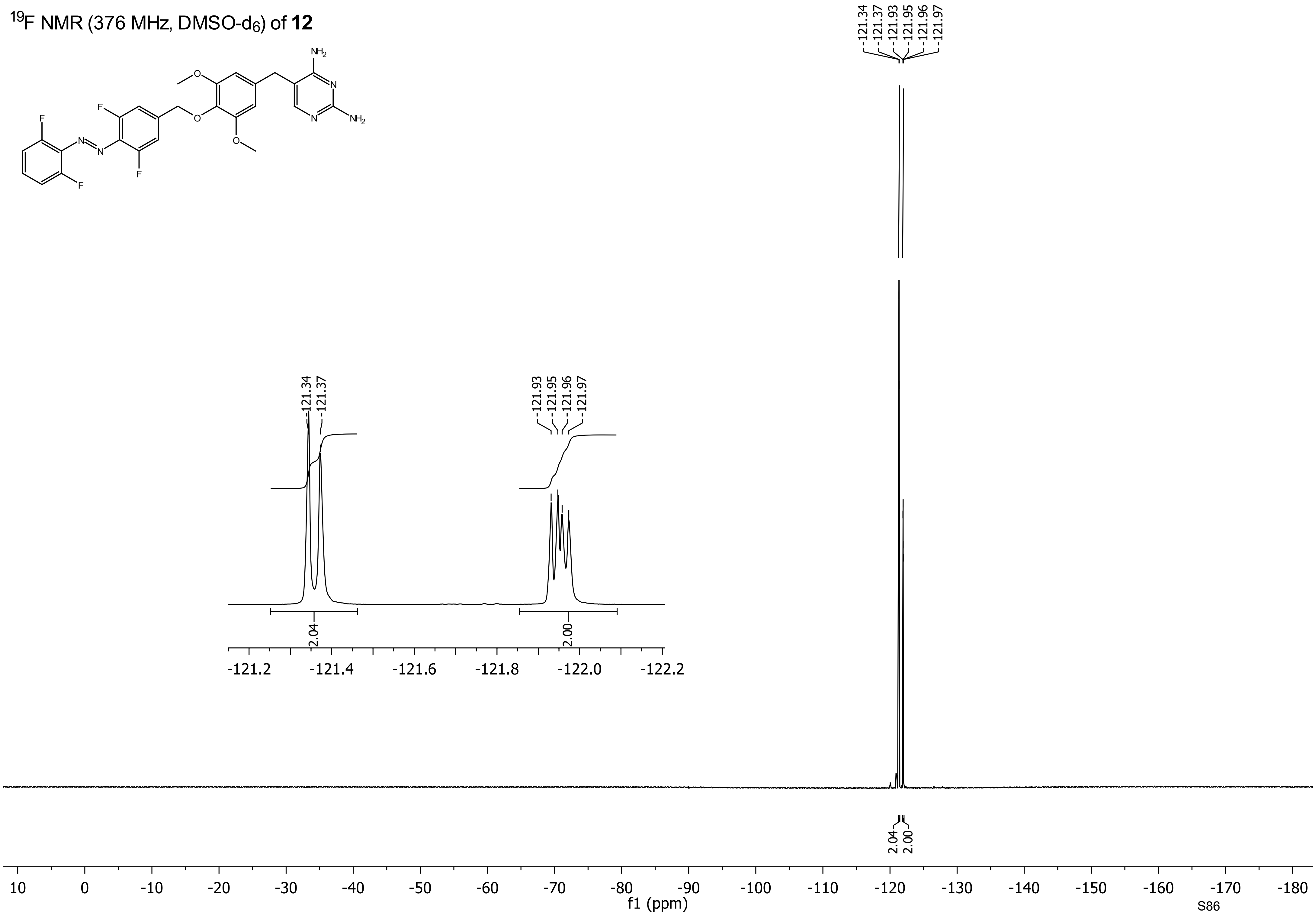
^{1}H NMR (400 MHz, DMSO-d_6) of **12**



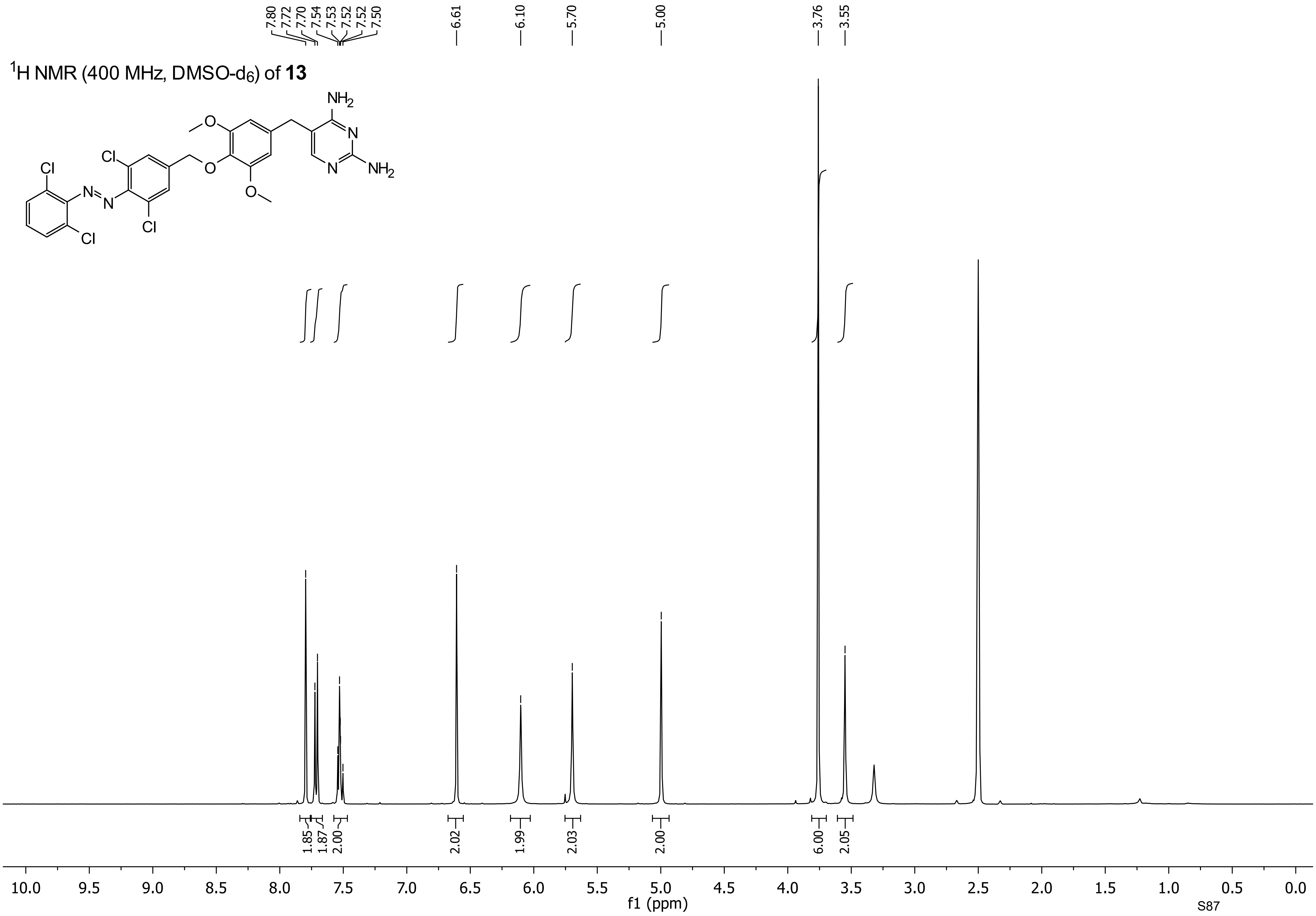
^{13}C NMR (151 MHz, DMSO-d_6) of **12**



^{19}F NMR (376 MHz, DMSO-d$_6$) of **12**



^{1}H NMR (400 MHz, DMSO-d$_6$) of **13**



^{13}C NMR (151 MHz, DMSO-d_6) of **13**