SUPPORTING INFORMATION FOR

Quinoidal Tetrazines: Formation of a Fascinating Compound Class

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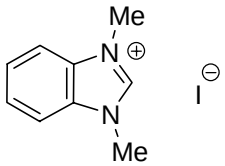
GENERAL EXPERIMENTAL

All reactions were carried out under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. Solvents were acquired from commercial sources, acetonitrile was dried over CaH_2, tetrahydrofurane over potassium and both were freshly distilled under argon before use. Reagents were either purchased from commercial sources and used without further purification, unless indicated otherwise, or prepared according to the literature. Thin layer chromatography (TLC, normal phase) was visualized by UV light (254nm) while column chromatography purification was carried out on Merck Silicagel (0.040–0.063 mm). NMR spectra were recorded on a Bruker AC 250 MHz or DRX 200 MHz spectrometer using standard Bruker sequences. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm referenced to the residual signal of the deuterated solvent. MS spectra were measured on a PE Sciex API-2000 spectrometer. Exact masses were determined on a Q-Star Pulsar (Applied Biosystems) quadrupole-time-of-flight spectrometer (ESI+, capillary 6000V, declustering potential: 20V). IR spectra were recorded on a Brucker IFS-55 spectrophotometer in KBr pastille. UV-VIS spectra were recorded on a Varian CARY 3E spectrophotometer in methanol, except for **2a**, where other solvents (methanol-water (1:1), chloroform, acetonitrile, dichloromethane) were also used. X-ray structures were analyzed on a Bruker Nonius MACH3 diffractometer. Determination of α_D values for compounds **3e**, **3f**, **3g** and **3j** cannot be achieved by optical rotation measurement due to their highly colored (violet) solutions (their absorption are in the same range as the applicable light sources). All melting points were measured on Büchi 501 apparatus and are uncorrected.

PREPARATION OF NHC PRECURSORS[1]



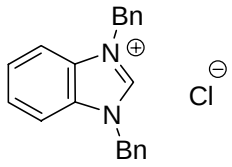
1,3-Dimethyl-benzimidazolium iodide (2h):

1.020 g (8.6 mmol) benzimidazole was dissolved in 10 ml 5N KOH solution and 5 ml MeOH, and 6 ml (96.4 mmol) MeI (99%) was added dropwise. Temperature was kept about 45°C, and

[1] NHC precursors **2a-g,** are either commercially available or were prepared according to literature procedures. For references see the manuscript.

the precipitated solid was filtered, and recrystallized from methanol-water mixture. 1.702 g **2h** was obtained as white solid (72% yield).

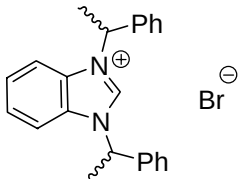
^{1}H NMR (250 MHz, d_6-DMSO) 9.66 (s, 1H); 8.04-8.00 (m, 2H); 7.72-7.68 (m, 2H); 4.08 (s, 6H). ^{13}C NMR (62.9 MHz, d_6-DMSO) 143.0; 131.5; 126.3; 113.1; 33.2. mp:190-191°C (measured); 189-192°C (literature)[2].



1,3-Dibenzyl-benzimidazolium chloride (2i):

2.000 g (16.93 mmol) benzimidazole was stirred in 6 mL benzyl chloride at 120°C for 2 days. The mixture was treated with hot ethanol, and after cooling to ambient temperature the precipitated white solid was filtered (2.385 g, 42% yield).

^{1}H NMR (250 MHz, $CDCl_3$ and d_6-DMSO) 10.50 (s, 1H); 8.03-7.96 (m, 2H); 7.65-7.29 (m, 6H); 7.45-7.36 (m, 6H); 5.85 (s, 4H). ^{13}CNMR (50.3 MHz, CD_3OD and d_6-DMSO) 142.3; 133.2; 132.1; 130.0; 129.9; 128.6; 128.1; 114.4; 51.9. mp: 210- 211°C (measured); 210-211°C (literature)[3].

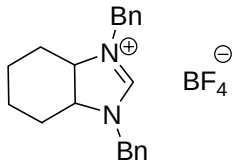


1,3-Bis(1'-phenylethyl)-benzimidazolium bromide (2j):

1.000 g (8.5 mmol) benzimidazole was stirred with 0.459 g (8.5 mmol) sodium methoxide in 6 mL toluene at 94°C. After 25 minutes, 5.26 ml (37 mmol) (1-bromoethyl)-benzene (rac.) was added. The mixture was heated for 2 days, after which it was diluted with ethanol and cooled to ambient temperature. The precipitated white solid (sodium bromide) was filtered. The filtrate was evaporated, and the mixture was purified by column chromatography using dichloromethane-methanol (9:1). **2j** was crystallized from dichloromethane-diethyl ether. Product is white solid (0.856 g, 25% yield). **2j** was obtained as a mixture of diastereoisomers. ^{1}H NMR (200 MHz, $CDCl_3$) 11.95 (d, 1H, J = 5.8 Hz); 7.54-7.50 (m, 4H); 7.42-7.33 (m, 10H); 6.33-6.30 (m, 2H); 2.33 (d, 6H, J = 6.2 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$) 141.6; 141.5;

[2] Khristich, B. I.; Bondarenko, E. V. *Chem. Heterocycl. Compd.* **1987**, *23*, 284.
[3] Starikova, O.V.; Dolgushin, G. V.; Larina, L.I.; Ushakov, P.E.; Komarova, T. N.; Lopyrev, V. A. *Russ. J. Org. Chem.* **2003**, 10, 1467.

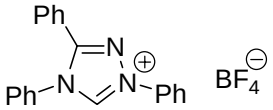
137.5; 137.5; 131.1; 131.0; 129.4; 129.0; 128.9; 128.1; 126.8; 126.7; 114.6; 59.4; 59.3; 21.2; 21.1. mp: 185- 187°C (measured).



1,3-Dibenzyl-3a,4,5,6,7,7a-hexahydro-benzimidazolium tetrafluoroborate (2k):

1.568 g (5.4 mmol) *N,N'*-dibenzyl-cyclohexane-1,2-diamine [4] and 0.567 g (5.4 mmol) ammonium tetrafluoroborate was stirred in 30 ml triethyl ortoformate at 120°C for 4 hours. The solvent was evaporated and the off-white residue was crystallized from ethanol to give 1.195 g **2k** (57% yield) as a white solid.

^{1}H NMR (250 MHz, $CDCl_3$) 8.67 (s, 1H); 7.36-7.29 (m, 10H); 4.72 (s, 4H); 3.33 (t, 2H, J = 4.3 Hz); 2.03-1.95 (m, 2H); 1.72-1.69 (m, 2H); 1.29-1.06 (m, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) 160.1; 132.8; 128.8; 128.4; 128.1; 67.3; 50.6; 27.1; 23.1. mp.:146-147°C (measured).



1,3,4-Triphenyl-4H-[1,2,4]-triazolium tetrafluoroborate (2l):

The synthetic procedure did partially deviate from the literature.[5,6] 5.740 g (0.020 mol) *N*-phenyl-benzamide phenyl-hydrazone and 2.096 g (0.020 mol) ammonium tetrafluoroborate were heated in 60 ml triethyl ortoformate at 120°C for 12 h. After cooling to room temperature the precipitated solid was filtered and washed with distilled water and diethyl ether. We obtained 5.802 g of **2l** (76% yield) as white solid.

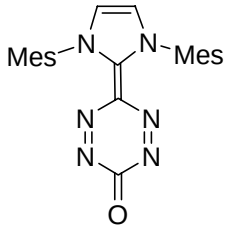
^{1}H NMR (250 MHz, d_6-DMSO) 11.38 (s, 1H); 8.11 (d, 2H, J = 7.8 Hz); 7.83-7.61 (m, 9H); 7.56-7.54 (m, 4H). ^{13}C NMR (62.9 MHz, d_6-DMSO) 153.2; 143.1; 134.8; 132.2; 132.0; 131.5; 130.8; 130.3; 130.1; 129.2; 129.2; 126.5; 122.3; 120.5. mp.: 171°C (measured).

GENERAL PROCEDURE FOR THE PREPARATION OF QUINOIDAL TETRAZINES

A glass vial was charged with the carbene precursor, potassium carbonate and dry acetonitrile as solvent, purged with argon, sealed and heated to 75-80°C for 40 min. The solution of 3,6-

[4] Denmark,S.E., Stadler, H., Dorow, R. L., Kim, J-H. *J. Org. Chem.*, **1991**, *56*, 5063.
[5] Enders D., Breuer K., Kallfass U., Ballensiefer T. *Synthesis*, **2003**, 1292.
[6] Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wielhelm, T. E.; Scholl, M.; Choi, T-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine[7] (**1**) in degassed dry acetonitrile was added to the solution of the free carbene, using a canula. The mixture was stirred at 75-80°C until the consumption of **1** by TLC (eluent: methanol-ethyl acetate (1:4) or dichloromethane-methanol (10:1)). Reaction times were ranging from a few hours in the cases of **2a-h**, to one or two days using **2i-2l** as starting material. After cooling to room temperature and removal of the solvent under reduced pressure the residue was purified by column chromatography (eluent: methanol: ethyl acetate (1:4)), except of **3h.**

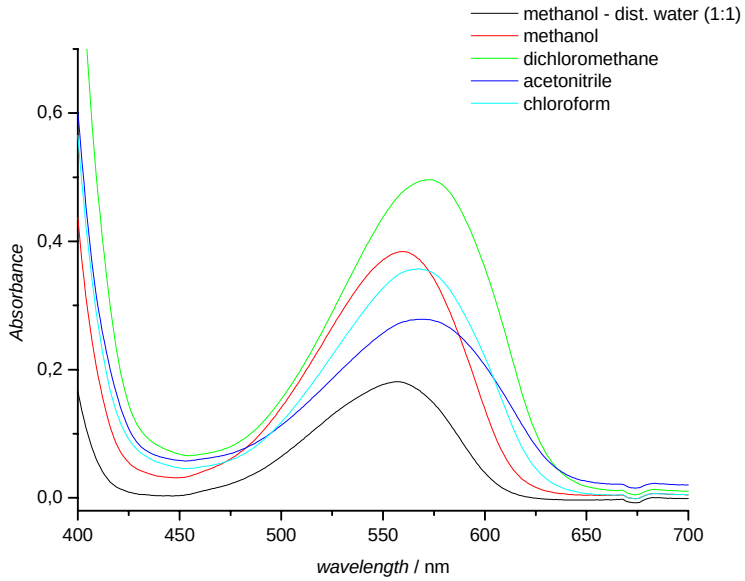


6-[1,3-Bis(mesityl)-1,3-dihydro-imidazol-2-ylidene]-6H-[1,2,4,5]tetrazine-3-one (3a):

From 196 mg (0.5 mmol) 3-bis(mesityl)-imidazolium tetrafluoroborate **(2a)**, 69 mg (0.5 mmol) dry K_2CO_3 in 3 mL acetonitrile, and 135 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine in 3 mL acetonitrile we obtained 192 mg **3a** (96% yield) as a violet solid following column chromatography.

^{1}H NMR (250 MHz, d_6-DMSO) 8.41 (s, 2H); 7.10 (s, 4H); 2.30 (s, 6H); 2.05 (s, 12H). ^{13}C NMR (62.9 MHz, $CDCl_3$) 161.2; 143.8; 143.2; 141.3; 134.4; 130.8; 129.7; 124.1; 21.1; 17.4. HRMS (ESI-QTOF) calcd for $[C_{23}H_{25}N_6O]^+$, $[MH]^+$: 401.2089 found 401.2089, difference: 0.0 ppm. MS (ESI, scan); *m/z (%)*: 401 $[MH]^+$; 330 [88%]; 145 [13%]; 119 [25%]; 91 [25%]. IR (KBr, cm^{-1}): 3165 (m), 3099 (m), 2921 (m), 2856 (m), 2142 (w), 1988 (w), 1643 (s), 1611 (s), 1564 (s), 1498 (s), 1383 (m), 1263 (m), 1233 (s), 1035 (m), 996 (m), 865 (m), 786 (m), 741 (m), 575 (m), 434 (w). UV-VIS (300 nm-800 nm, l = 1 cm): $\lambda_{max,Vis}$=560 nm, ε = 358 $dm^3*mol^{-1}*cm^{-1}$ (methanol, c= $1.07*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max,Vis}$ = 557 nm, ε = 391 $dm^3*mol^{-1}*cm^{-1}$ (methanol-water (1:1), c = $4.63*10^{-4}$ $mol*dm^{-3}$), $\lambda_{max,Vis}$ = 567 nm, ε = 405 $dm^3*mol^{-1}*cm^{-1}$ (chloroform, c = $8.81*10^{-4}$ $mol*dm^{-3}$), $\lambda_{max,Vis}$ = 568 nm, ε=362 $dm^3*mol^{-1}*cm^{-1}$ (acetonitrile, c = $7.70*10^{-4}$ $mol*dm^{-3}$), $\lambda_{max,Vis}$ = 572 nm, ε = 368 $dm^3*mol^{-1}*cm^{-1}$ (dichloromethane, c = $1.35*10^{-3}$ $mol*dm^{-3}$); $\Delta\lambda_{max,Vis}$ = 15 nm (5 solvents). mp: 253°C (decomp.).

[7] Coburn, M. D.; Buntain, G. A.; Harris, B. W.; Hiskey, M. A.; Lee;K. Y.; Ott, D. G.; *J. Heterocycl. Chem.* **1991**, *28*, 2049



UV-VIS experiments for the determination of negative solvatochromism of non-zwitter-ionic tetrazine compounds:

3,6-Bis(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine: UV-VIS (300-800nm, l=1cm): $\lambda_{max, Vis}$= 521nm, ε= 370$dm^3*mol^{-1}*cm^{-1}$ (methanol, c= 9.32 $*10^{-4}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 524nm, ε= 360 $dm^3*mol^{-1}*cm^{-1}$ (acetonitrile, c= 1.34 $*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 533 nm, ε= 405 $dm^3*mol^{-1}*cm^{-1}$ (dichloromethane, c= 1.40 $*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 535 nm, ε= 474 $dm^3*mol^{-1}*cm^{-1}$ (chloroform, c= 1.36 $*10^{-3}$ $mol*dm^{-3}$), $\Delta\lambda_{max, Vis}$ = 14 nm.

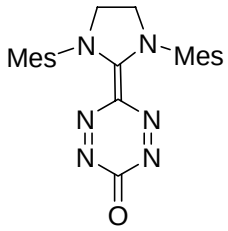
3,6-Di(pyridin-3-yl)-1,2,4,5-tetrazine: $\lambda_{max, Vis}$= 538 nm, ε= 384 $dm^3*mol^{-1}*cm^{-1}$ (methanol, c= 1.03 $*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 538 nm, ε= 369 $dm^3*mol^{-1}*cm^{-1}$ (acetonitrile, c= 1.57 $*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 548nm, ε= 317 $dm^3*mol^{-1}*cm^{-1}$ (dichloromethane, c= 1.25 $*10^{-3}$ $mol*dm^{-3}$), $\lambda_{max, Vis}$= 550 nm, ε= 474 $dm^3*mol^{-1}*cm^{-1}$ (chloroform, c= 1.17 $*10^{-3}$ $mol*dm^{-3}$), $\Delta\lambda_{max, Vis}$ = 12 nm.

Crystallographic Solution and Refinement Details

Crystallographic Characterization of 3a.

Single crystals were grown by very slow evaporation of ethanol solution of **3a.** Purple block (0.45 x 0.35 x 0.3 mm) crystals of $C_{23}H_{24}N_6O$, M = 400.48, monoclinic, a = 11.7079(10) Å, b

= 15.3735(10) Å, c = 11.8425(10) Å, β = 90.76(1), V = 2131.4(3) $Å^3$, Z = 4, space group: $P2_1/n$ (No. 14), ρ_{calc}= 1.248 g cm^{-3}. Data were collected at 293(1) K, Enraf Nonius MACH3 diffractometer, Mo Kα radiation λ = 0.71073 Å, ω-2θ motion, θ_{max} = 25.97°, 3971 measured, 2258 reflections were unique with I > 2σ(I), decay: none. The structure was solved using the SIR-92 software[8] and refined on F^2 using SHELX-97 program[9], publication material was prepared with the WINGX-97 suite[10], R(F) = 0.0629 and *w*R(F^2) = 0.2407 for 3971 reflections, 277 parameters. Residual electron density: 0.217/-0.275 e/$Å^3$. Anisotropic refinement of non hydrogen atoms. Aromatic hydrogen atoms were placed into geometric positions while orientation of methyl groups were refined using a riding model. Additional crystallographic information is provided in the deposited CIF.

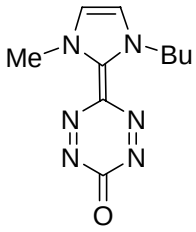


6-[1,3-Bis(mesityl)-1,3,4,5-tetrahydro-imidazol-2-ylidene]-6H-[1,2,4,5]tetrazine-3-one (3b):

From 242 mg (0.6 mmol) 1,3-bis(mesityl)-4,5-dihydro-imidazolium tetrafluoroborate **(2b)**, 84 mg (0.6 mmol) K_2CO_3 in 7 mL acetonitrile, and 162 mg (0.6 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 7 mL acetonitrile we obtained 232 mg **3b** (95% yield) as violet solid following column chromatography.

^{1}H NMR (250 MHz, $CDCl_3$ + CD_3CN) 6.88 (s, 4H); 4.41 (s, 4H); 2.29 (s, 12H); 2.24 (s, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$ + CD_3OD) 162.3; 161.4; 144.8; 140.2; 134.7; 130.9 ;129.7; 50.5; 20.6; 17.2. HRMS (ESI-QTOF) calcd for $[C_{23}H_{27}N_6O]^+$, $[MH]^+$: 403.2241, found 403.2232, difference: 2.2 ppm. MS/MS (ESI, scan): *m/z (%)*: 403 [MH^+, 45%]; 375 [4%]; 332 [100%]. IR (KBr, cm^{-1}) 2969 (w), 2917 (m), 2859 (w), 1663 (s), 1652 (s), 1633 (s), 1610 (s), 1560 (vs), 1479 (m), 1379 (m), 1292 (s), 1275 (m), 1262 (s), 1222 (m), 1016 (m), 994 (m), 855 (w), 573 (m), 429 (w). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c= 4.89*10^{-6} mol*dm^{-3}) $\lambda_{max,Vis}$ = 559 nm, ε = 385 dm^3*mol^{-1}*cm^{-1}. mp: 236-237°C (decomp.).

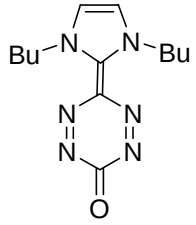
[8] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343–350.
[9] Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, **1998.**
[10] L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837-838.



6-(1-Butyl-3-methyl-1,3-dihydro-imidazol-2-ylidene)-6H-[1,2,4,5]tetrazine-3-one (3c):

From 99 mg (0.4 mmol) 1-butyl-3-methyl-imidazolium hexafluorophosphate **(2c)**, 56 mg (0.4 mmol) K_2CO_3 in 3.5 mL acetonitrile, and 107 mg (0.4 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 3.5 mL acetonitrile we obtained 93 mg **3c** (99% yield) as violet solid following column chromatography.

^{1}H NMR (250 MHz, d_6-DMSO) 7.94 (d, 1H, *J* = 2.0 Hz); 7.88 (d, 1H, *J* = 2.0 Hz); 4.33 (t, 2H, *J* = 7.3 Hz); 3.93 (s, 3H); 1.80-1.68 (m, 2H); 1.28-1.16 (m, 2H); 0.84 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (62.9 MHz, d_6-DMSO) 160.6; 144.9; 139.1; 124.2; 122.6; 48.8; 36.9; 31.5, 18.7; 13.1 HRMS (ESI-QTOF) calcd for $[C_{10}H_{15}N_6O]^+$, $[MH]^+$: 235.1301, found 235.1302, difference: 0.06 ppm. MS (ESI, scan) *m/z (%)*: 235 [MH^+, 10%]; 164 [70%]; 108 [43%]. IR (KBr, cm $^{-1}$) 3112 (m), 3083 (m), 2964 (m), 2939 (m), 2869 (s), 1987 (s), 1636 (w), 1605 (w), 1587 (w), 1526 (m), 1384 (s), 1251 (m), 991 (m), 839 (s), 796 (s), 575 (s). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = 2.15*10^{-3} mol*dm^{-3}) $\lambda_{max,Vis}$ = 556 nm, ε = 312 dm^3*mol^{-1}*cm^{-1}. mp: 185-186°C (decomp.).

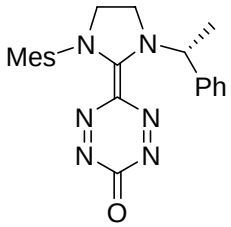


6-(1,3-Dibutyl-1,3-dihydro-imidazol-2-ylidene)-6H-[1,2,4,5]tetrazine-3-one (3d):

From 160 mg (0.6 mmol) 1,3-dibutyl-imidazolium bromide **(2d)**, 83 mg (0.6 mmol) K_2CO_3 in 7 mL acetonitrile, and 162 mg (0.6 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 7 mL acetonitrile we obtained 161 mg **3d** (97% yield) as violet waxy-solid following column chromatography.

^{1}H NMR (250 MHz, $CDCl_3$) 7.79 (s, 2H); 4.32 (t, 4H, *J* = 7.5 Hz); 1.76-1.64 (m, 4H); 1.25-1.10 (m, 4H); 0.73 (t, 6H, *J* = 7.3 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) 161.7; 144.9; 139.0; 123.0; 49.7; 31.9; 19.1; 13.0. HRMS (ESI-QTOF) calcd for $[C_{13}H_{21}N_6O]^+$, $[M+H]^+$: 277.1771, found 277.1758, difference: 4.6 ppm. MS (ESI, scan) *m/z (%)*: 277 [MH^+ 35%,]; 206 [50%]; 150 [25%]; 94 [10%]. IR (KBr, cm^{-1}) 3110 (m), 3077 (m), 2960 (s), 2933 (s), 2874 (m), 1988

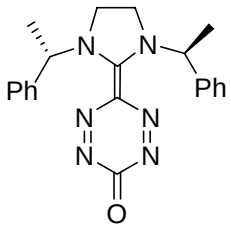
(w), 1640 (s), 1607 (s), 1580 (s), 1514 (m), 1460 (m), 1385 (m), 1253 (s), 993 (m), 837 (w), 795 (w), 574 (w). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = 1.87 mol*dm^{-3}) $\lambda_{max,Vis}$ = 557 nm, ε=245 dm^3*mol^{-1}*cm^{-1}.



6-[1–Mesityl-3-(*1'R*-1'-phenylethyl*)*-1,3,4,5-tetrahydro-imidazol-2-ylidene]-6H-[1,2,4,5]tetrazine-3-one (3e):

From 140 mg (0.37 mmol) 1-mesityl-3-(*1'R*-1'-phenylethyl)-4,5-dihydro-imidazolium tetrafluoroborate **(2e)**, 52 mg (0.37 mmol) K_2CO_3 in 5 mL acetonitrile, and 100 mg (0.37 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 5 mL acetonitrile we obtained 110 mg **3e** (77% yield) as violet solid following column chromatography.

^{1}H NMR (250 MHz, $CDCl_3$) 7.39 (s, 5H); 6.80 (s, 1H); 6.76 (s, 1H); 5.85 (q, 1H, *J* =7.3 Hz); 4.55-3.75 (m, 4H); 2.19 (s, 6H); 2.14 (s, 3H); 1.80 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) 161.0, 144.5, 139.8, 136.2, 135.2, 131.5, 129.6, 129.2, 128.9, 126.9, 55.9, 49.7, 43.9, 20.8, 17.7, 17.5, 16.4. HRMS (ESI-QTOF) calcd for $[C_{22}H_{25}N_6O]^+$, $[MH]^+$: 389.2084, 389.2076, difference: 2.3 ppm. MS (ESI, scan); *m/z (%)*: 389 [MH^+, 41%]; 285 [100%]; 214 [58%];. IR (KBr, cm^{-1}) 2978 (w), 2924 (w), 2855 (w), 2024 (w), 1656 (vs), 1608 (vs), 1566 (vs), 1484 (w), 1379 (m), 1294 (m), 1257 (m), 1015 (m), 833 (w), 760 (w), 580 (m). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = 8.73*10^{-4} mol*dm^{-3}) $\lambda_{max,Vis}$: 558 nm, ε = 319 dm^3*mol^{-1}*cm^{-1}. mp: 198-200°C (decomp.).

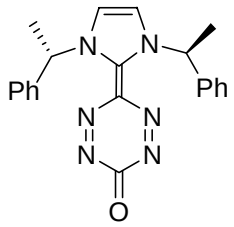


6-[1,3-Bis(*1'R*-1'-phenylethyl)-1,3,4,5-tetrahydro-imidazol-2-ylidene]-6H-[1,2,4,5]tetrazine-3-one (3f):

From 37 mg (0.1 mmol) 1,3-bis-(*1'R*-1'-phenylethyl)-4,5-dihydro-3H-imidazolium tetrafluoroborate **(2f)**, 14 mg (0.1 mmol) K_2CO_3 in 3 ml acetonitrile, and 27 mg (0.1 mmol)

3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 3 mL acetonitrile we obtained 34 mg **3f** (90%) as violet solid following column chromatography.

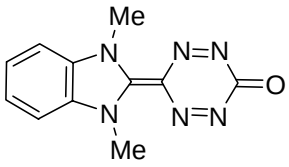
^{1}H NMR (250 MHz, $CDCl_3$) 7.32-7.16 (m, 10H); 5.48 (q, 2H, *J* = 7.0 Hz); 3.92-3.77 (m, 2H); 3.62-3.48 (m, 2H); 1.65 (d, 6H, *J* = 7.0 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) 161.2; 159.9; 144.2; 136.3; 129.3; 129.1; 127.0; 55.9; 42.8; 16.5. HRMS (ESI-QTOF) calcd for $[C_{21}H_{23}N_6O]^+$, $[MH]^+$: 375.1927, found 375.1920, difference: 2.32 ppm. MS/MS (ESI, scan); *m/z (%)*: 375 [MH^+, 41%]; 304 [100 %]. IR (KBr, cm^{-1}) 3056 (w), 2975 (w), 2929 (w), 2007 (w), 1698 (sh), 1653 (s), 1588 (s), 1575 (s), 1558 (s), 1496 (s), 1285 (s), 1254 (m), 1221 (m), 1191 (m), 1147 (m), 1026 (m), 1006 (m), 758 (m), 700 (s), 667 (m). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = $1.14*10^{-3}$ mol*dm^{-3}) $\lambda_{max,Vis}$: 556 nm, ε = 358 dm^3*mol^{-1}*cm^{-1}. mp: 198-199°C (decomp.).



6-[1,3-Bis(*1'R*-1'-phenylethyl)-1,3-dihydro-imidazol-2-ylidene]-6H-[1,2,4,5]tetrazine-3-one (3g):

From 1.500 g (4.8 mmol) 1,3-bis(*1'R*-1'-phenylethyl)-imidazolium chloride **(2g)**, 0.664 g (4.8 mmol) K_2CO_3 in 12 mL acetonitrile, and 1.300 g (4.8 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine in 12 mL acetonitrile we obtained 1.601 g **3g** (90% yield) as violet solid following column chromatography.

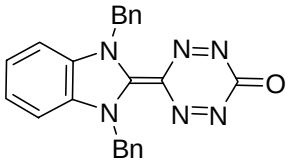
^{1}H NMR (250 MHz, $CDCl_3$) 7.63 (d, 2H, *J* = 1.5 Hz); 7.38-7.21 (m, 10H); 6.24 (q, 2H, *J* = 7.0 Hz); 1.945 (d, 6H, *J* = 7.0 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) 161.5; 144.6; 140.0; 137.4; 129.3; 129.3; 126.6; 120.1; 58.6; 20.7. HRMS (ESI-QTOF) calcd for $[C_{21}H_{21}N_6O]^+$, $[MH]^+$: 373.1771, found 373.1765, difference: -1.70 ppm. MS/MS (ESI, scan) *m/z (%)*: 373 [MH^+, 17%]; 269 [64%]; 165 [100%]. IR (KBr, cm^{-1}) 3117 (m), 2986 (m), 1992 (w), 1653 (vs), 1611 (vs), 1563 (s), 1490 (s), 1452 (s), 1383 (s), 1260 (m), 1225 (s), 1188 (m), 1104 (m), 1043 (w), 1027 (w), 823 (m), 760 (s), 741 (m), 700 (s), 611 (m), 558 (w), 525 (s), 418 (s). UV-VIS (300nm-800nm, l = 1 cm, methanol, c = $1.34*10^{-3}$ mol*dm^{-3}) $\lambda_{max,Vis}$= 557 nm, ε = 391 dm^3*mol^{-1}*cm^{-1}. CD: (l = 1, 450-700 nm, acetonitrile, c = 1 mmol*dm^{-3}) λ_{max}= 289 nm, (molar CD) Θ =20 dm^3*mol^{-1}*cm^{-1}. mp: 182-183°C (decomp.).



6-(1,3-Dimethyl-1,3-dihydro-benzimidazol-2-ylidene)-6H-[1,2,4,5]tetrazin-3-one (3h):

From 135 mg (0.5 mmol) 1,3-dimethyl-benzimidazolium iodide **(2h)**, 70 mg (0.5 mmol) K_2CO_3 in 4 mL acetonitrile, and 135 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 4 mL acetonitrile we obtained 4 mg (3% yield) **3h** as violet solid after the work-up procedure. Because of the very poor solubility of **3h** in organic solvents, the purification was different from the generally applied column chromatography. The reaction mixture was evaporated, and the solid residue was washed with dichloromethane, ethylacetate, methanol and distilled water. All of the byproducts were removed in this way, and the solution of the remaining dark violet solid (**3h**) was concentrated enough for the ^{1}H NMR measurements, but not for ^{13}C NMR.

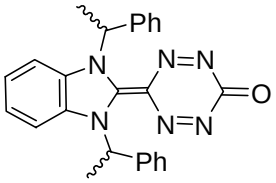
^{1}H NMR (200 MHz, CD_3CN and D_2O): 7.92-7.86 (m, 2H); 7.76-7.70 (m, 2H); 4.11 (s, 6H) HRMS (ESI-QTOF) calcd for $[C_{11}H_{11}N_6O]^+$, $[MH]^+$: 243.0989, found 243.0990, difference: 0.4 ppm. MS (ESI, scan); *m/z (%)*: 243 [MH^+, 58%]; 172 [100%]. mp: 245-246°C (decomp.).



6-(1,3-Dibenzyl-1,3-dihydro-benzimidazol-2-ylidene)-6H-[1,2,4,5]tetrazin-3-one (3i):

From 168 mg (0.5 mmol) 1,3-dibenzyl-benzimidazolium chloride **(2i)**, 70 mg (0.5 mmol) K_2CO_3 in 4 mL tetrahydrofurane, and 135 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 4 mL tetrahydrofurane we obtained 46 mg **3i** (23% yield) as violet solid following column chromatography .

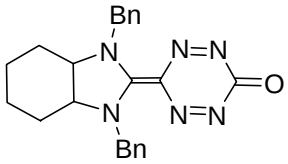
^{1}H NMR (250 MHz, d_6-DMSO) 7.92-7.86 (m, 2H), 7.67-7.62 (m, 2H), 7.34 (s, 10H), 6.01 (s, 4H) ^{13}C NMR (62.9 MHz, CD_3OD and $CDCl_3$) 161.3; 145.3; 144.3; 132.7; 131.5; 128.8; 128.5; 127.6; 126.6; 113.4; 50.3. HRMS (ESI-QTOF) calcd for $[C_{23}H_{19}N_6O]^+$, $[MH]^+$: 395.1615, found 395.1610, difference: 1.2 ppm. MS/MS (ESI, scan); *m/z (%)*: 395 [MH^+, 44%]; 352 [19%]; 324 [100%]. IR (KBr, cm^{-1}) 3062 (w), 3027 (w), 2951 (w), 2015 (w), 1647 (vs), 1610 (vs), 1524 (s), 1498 (m), 1482 (m), 1465 (s), 1394 (m), 1267 (m), 1015 (m), 767 (s), 750 (s), 708 (m), 545 (w) cm^{-1}. UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = $5.02*10^{-4}$ $mol*dm^{-3}$) $\lambda_{max,Vis}$: 558 nm, $\varepsilon = 234\ dm^3*mol^{-1}*cm^{-1}$. mp: 210-211°C (decomp.).



6-[1,3-Bis(1-phenylethyl)-1,3-dihydro-benzimidazol-2-ylidene]-6H-[1,2,4,5]tetrazin-3-one (3j):

From 204 mg (0.5 mmol) 1,3-bis(1-phenylethyl)-3H-benzimidazolium-bromide **(2j)**, 70 mg (0.5 mmol) K_2CO_3 in 5 mL acetonitrile, and 135 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 5 mL acetonitrile we obtained 110 mg **3j** (52% yield) as violet solid following column chromatography. **3j** was obtained as a mixture of diastereoisomers.

^{1}H NMR (250 MHz, $CDCl_3$ + CD_3OD) 7.26-7.23 (m, 14H), 6.13 (q, 2 H, *J* =7.0 Hz), 2.03-2.00 (d, 6H, *J* =7.0 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$ + CD_3OD) 161.9, 161.9, 145.1, 145.0, 135.4, 135.4, 130.1, 129.1, 129.0, 128.9, 127.0, 126.4, 126.4, 115.0, 57.9, 17.7, 17.6. HRMS (ESI-QTOF) calcd for $[C_{25}H_{23}N_6O]^+$, $[MH]^+$: 423.1928, found 423.1939, difference: 2.5 ppm. MS (ESI, scan); *m/z (%)*: 423 [MH^+, 100%]; 343 [15%]. IR (KBr, cm^{-1}) 3109 (w), 3057 (w), 2986 (w), 2942 (w), 2016 (w), 1653 (vs), 1643 (vs), 1523 (m), 1498 (m), 1464 (vs), 1386 (s), 1263 (m), 1241 (m), 1080 (w), 1035 (m), 755 (s), 700 (m), 582 (w). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = $8.99*10^{-4}$ mol*dm^{-3}) $\lambda_{max,Vis}$: 554 nm, ε= 327 dm^3*mol^{-1}*cm^{-1}. mp: 196-197°C (decomp.).

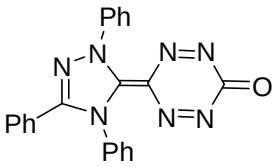


6-(1,3-Dibenzyl-1,3,3a,4,5,6,7,7a-octahydro-benzimidazol-2-ylidene)-6H-[1,2,4,5]tetrazine-3-one (3k):

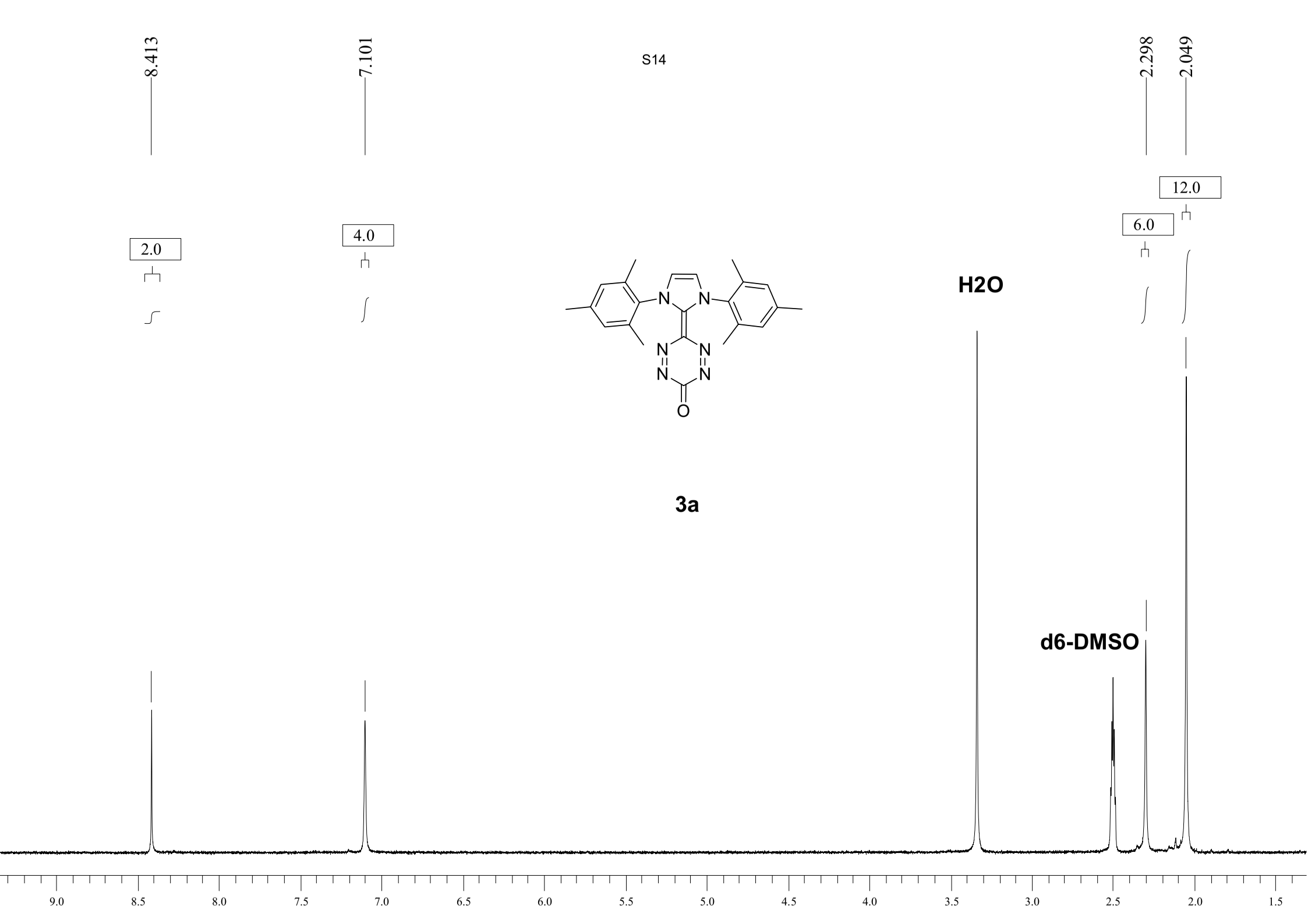
From 197 mg (0.5 mmol) 1,3-dibenzyl-3a,4,5,6,7,7a-hexahydro-benzimidazolium tetrafluoroborate **(2k)**, 70 mg (0.5 mmol) K_2CO_3 in 4 mL acetonitrile, and 136 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 4 mL acetonitrile we obtained 84 mg **3k** (42% yield) as blue solid following column chromatography.

^{1}H NMR (250 MHz, d_6-DMSO and CD_3OD) 7.42-7.31 (m, 10.0H); 5.02 (d, 2H, *J* = 16.0 Hz); 4.77 (d, 2H, *J* = 16.5 Hz); 3.72 (d, 2H, *J* = 7.5 Hz); 2.01 (d, 2H, *J* = 11.0 Hz); 1.70 (d, 2H, *J* = 8.3 Hz); 1.35-1.27 (m, 2H); 1.27-1.18 (m, 2H). ^{13}C NMR (62.9 MHz, 600 µL $C_2H_4Cl_4$ and 150 µL $CDCl_3$) 162.7; 144.95; 132.5; 129.2; 128.8; 127.3; 99.3; 66.9; 50.2; 27.6; 23.5. HRMS

(ESI-QTOF) calcd for $[C_{23}H_{25}N_6O]^+$, $[MH]^+$: 401.2084, found 401.2101, difference: 4.1 ppm. MS (ESI, scan) *m/z (%)*: 401 [MH^+, 70%,]; 330 [100%]. IR (KBr, cm^{-1}): 3027 (w), 2948 (m), 2869 (w), 2143 (w), 2004 (w), 1656 (vs), 1547 (vs), 1450 (m), 1385 (m), 1261 (s), 1180 (m), 1034 (w), 1001 (m), 818 (w), 728 (s), 691 (m), 564 (w), 465 (w). UV-VIS (300 nm-800 nm, l = 1 cm, methanol, c = $4.48*10^{-4}$ mol*dm^{-3}) $\lambda_{max,Vis}$: 558 nm, ε = 345 $dm^3*mol^{-1}*cm^{-1}$. mp: 227-228 °C (decomp.).



6-(2,4,5-Triphenyl-2,4-dihydro-[1,2,4]triazol-3-ylidene)-6H-[1,2,4,5]tetrazine-3-one (3l):
From 193 mg (0.5 mmol) 1,3,4-triphenyl-4H-[1,2,4]triazolium tetrafluoroborate **(2l)**, 70 mg (0.5 mmol) K_2CO_3 in 4 mL tetrahydrofurane, and 135 mg (0.5 mmol) 3,6-bis(3',5'-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, in 4 mL tetrahydrofurane we obtained 76 mg **3l** (39% yield) as violet solid following column chromatography.
^1H NMR (250 MHz, d_6-DMSO and CD_3CN) 7.72-7.47 (m, 15H). ^{13}C NMR (62.9 MHz, CD_3OD and $CDCl_3$) 162.7, 155.6, 148.7, 144.9, 136.7, 133.3, 132.8, 132.6, 132.2, 131.0, 130.7, 130.2, 129.9, 128.7, 126.2, 123.3. HRMS (ESI-QTOF) calcd for $[C_{22}H_{16}N_7O]^+$, $[MH]^+$: 394.1411, found 394.1414, difference: 0.7 ppm. MS/MS (ESI, scan); *m/z(%)*: 395 [MH^+, 100%]; 323 [41%]. IR (KBr, cm^{-1}): 3077 (w), 2025 (w), 1655 (vs), 1617 (s), 1540 (s), 1497 (s), 1445 (m), 1391 (s), 1269 (m), 1015 (m), 831 (w), 772 (m), 668 (s), 531 (m). UV-Vis (300 nm-800 nm, l = 1 cm, methanol, c = $6.91*10^{-4}$ mol*dm^{-3}) $\lambda_{max,Vis}$: 559 nm, ε = 278 $dm^3*mol^{-1}*cm^{-1}$. mp: 230-231°C (decomp.).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4.0
6.0
12.0
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d6-DMSO
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8.5
8.0
7.5
7.0
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4.5
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3.5
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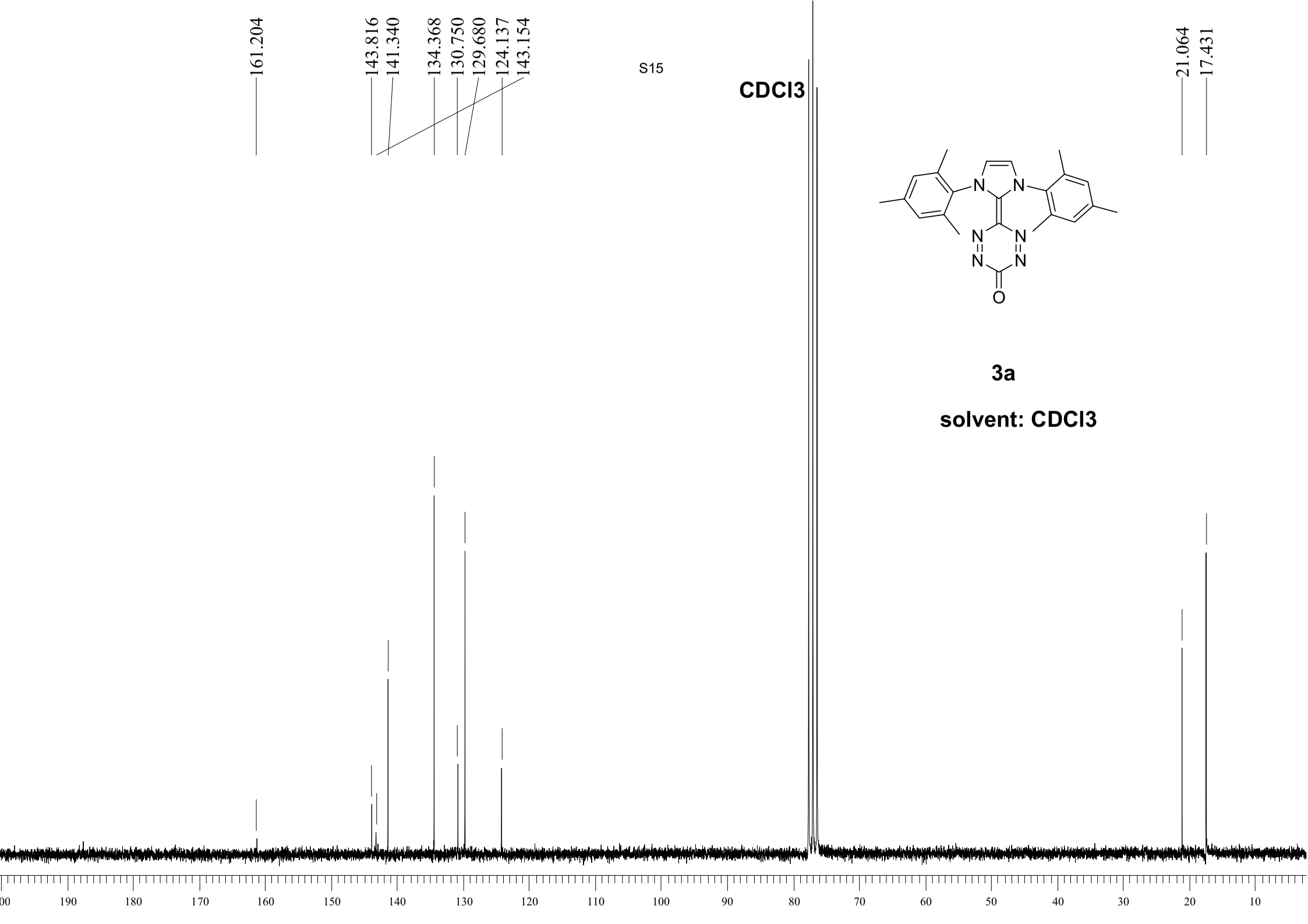
1.5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N
N
N
O
3a
solvent: CDCl3
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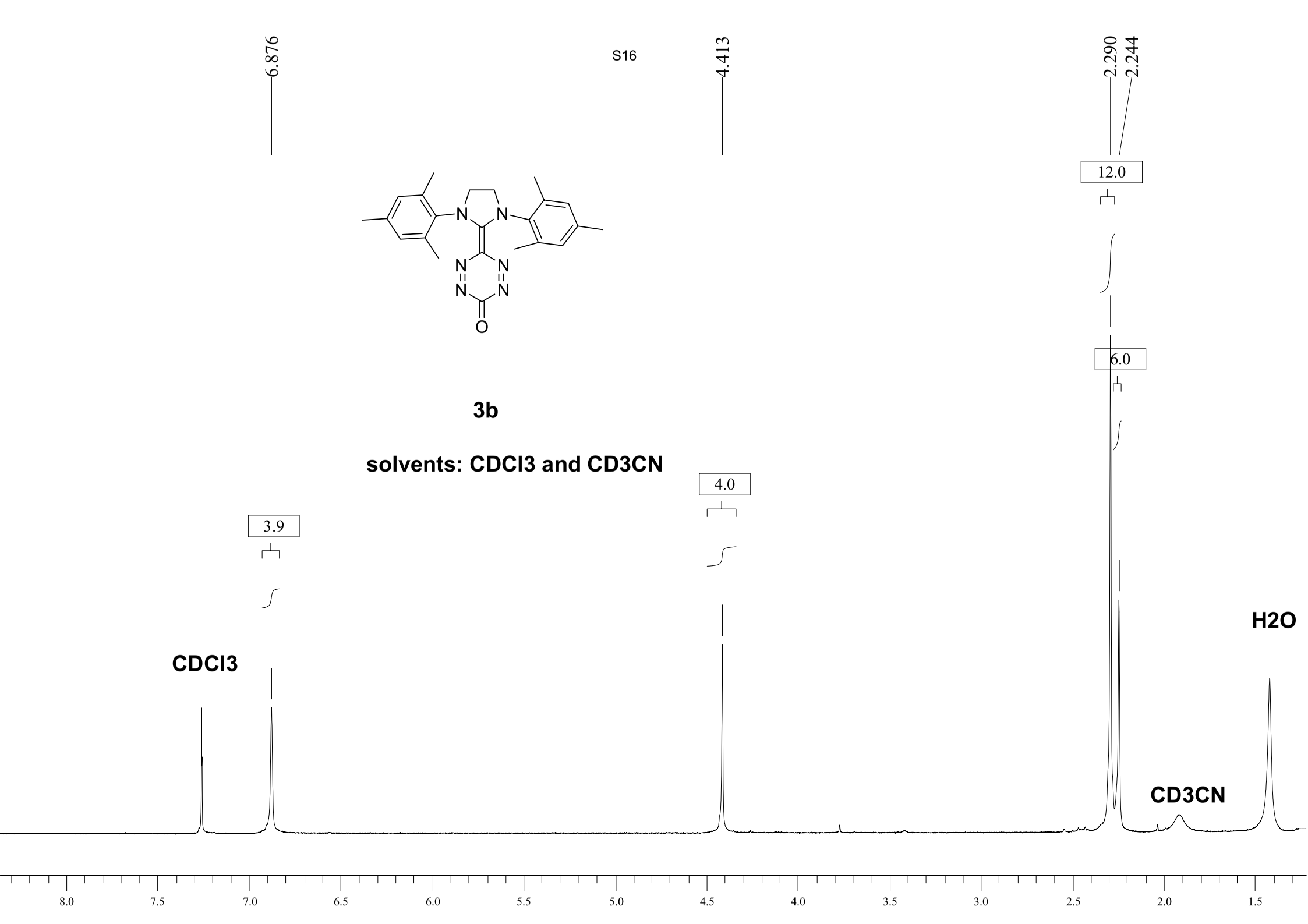
10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3b
solvents: CDCl3 and CD3CN
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CD3CN
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3.5
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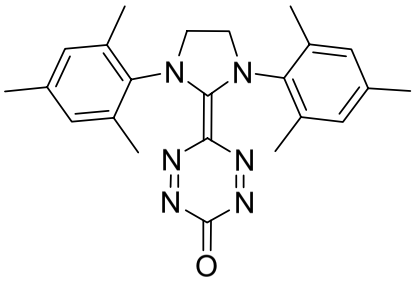
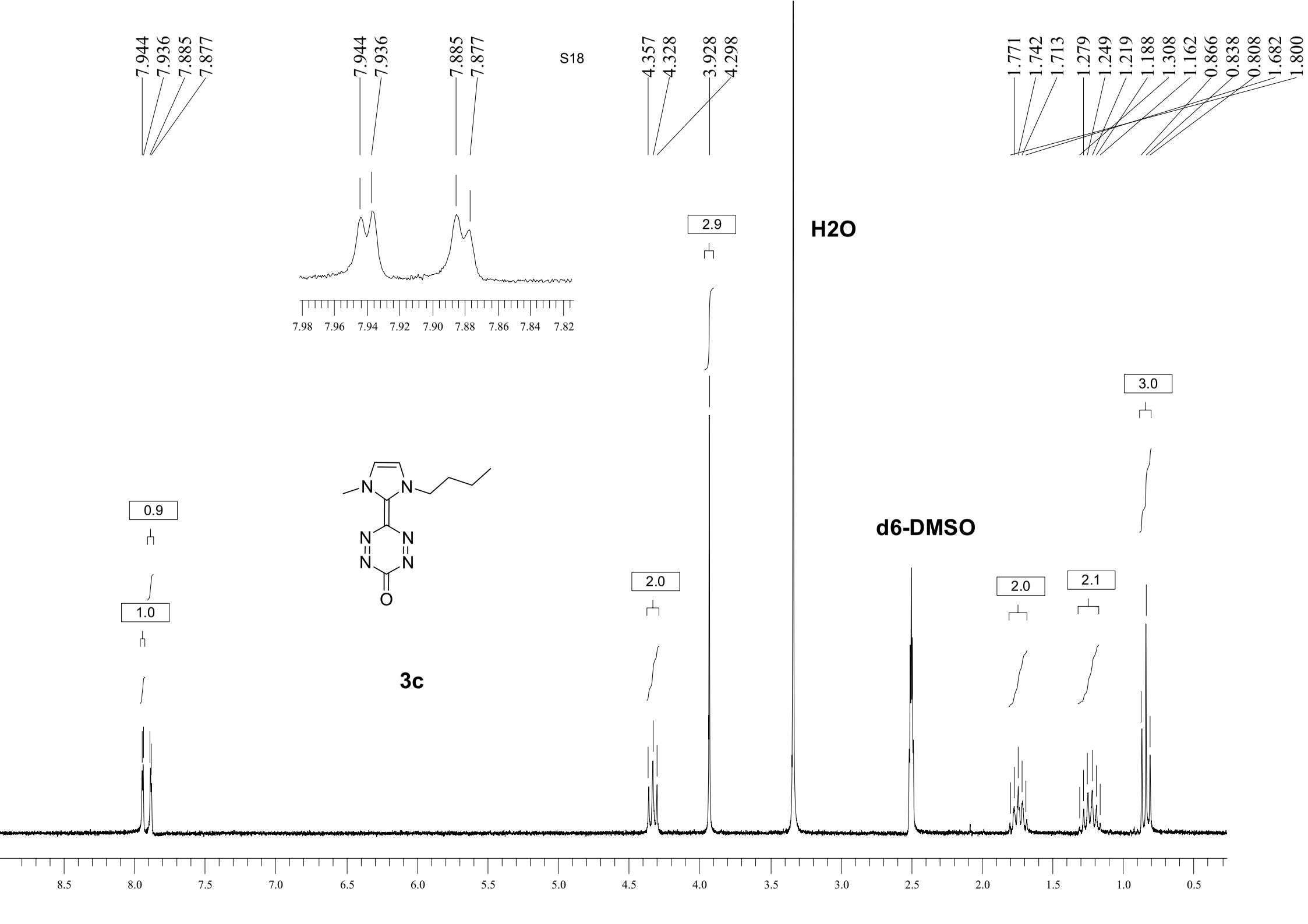


3b

Solvents: CDCl3 and CD3OD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4.328
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1.249
1.219
1.188
1.308
1.162
0.866
0.838
0.808
1.682
1.800
7.98 7.96 7.94 7.92 7.90 7.88 7.86 7.84 7.82
H2O
d6-DMSO
0.9
1.0
2.0
2.9
2.0
2.1
3.0
3c
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

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d6-DMSO
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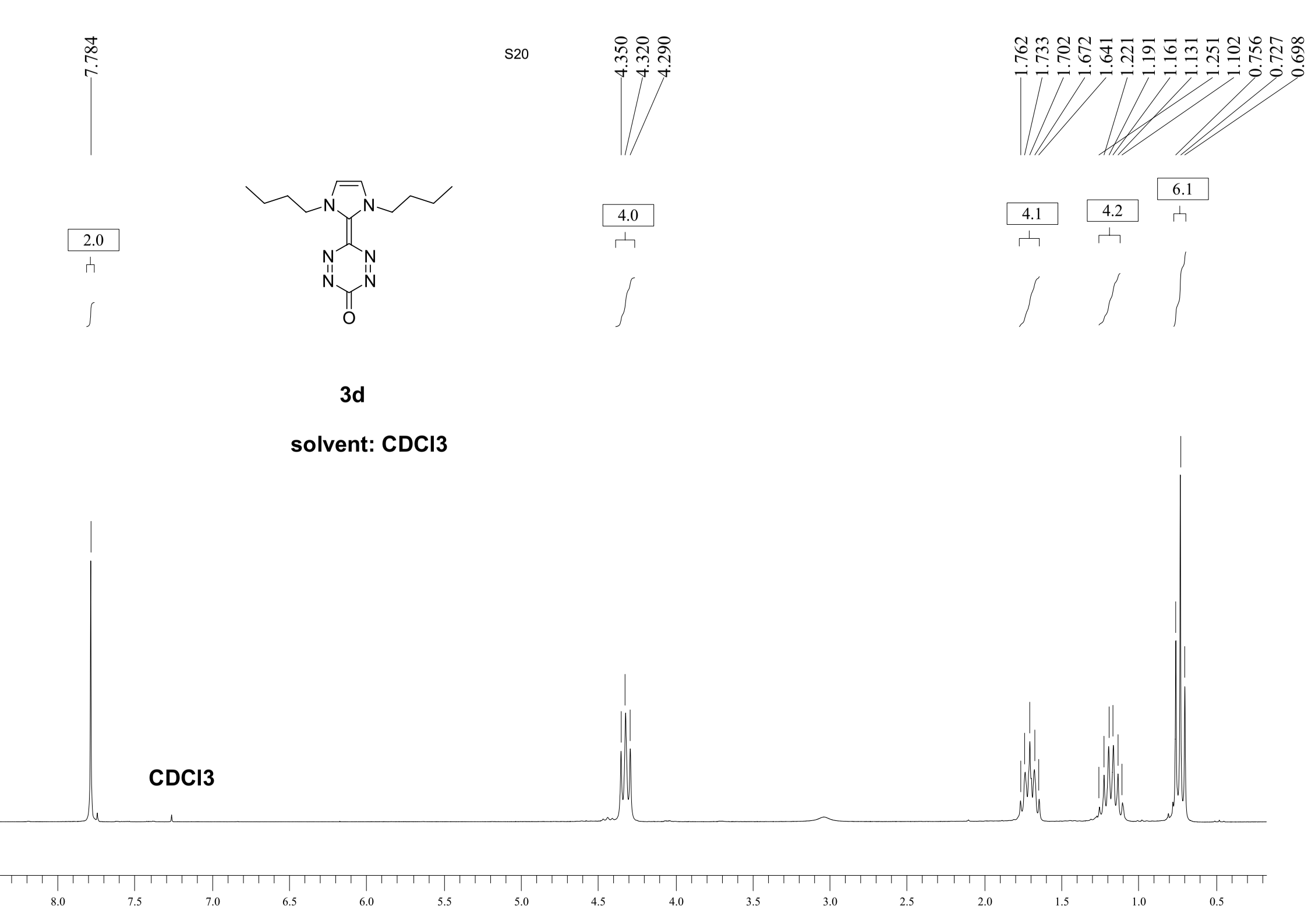
160.565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1.131
1.251
1.102
0.756
0.727
0.698
2.0
4.0
4.1
4.2
6.1
N
N
N
N
N
N
O
3d
solvent: CDCl3
CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

13.013
19.078
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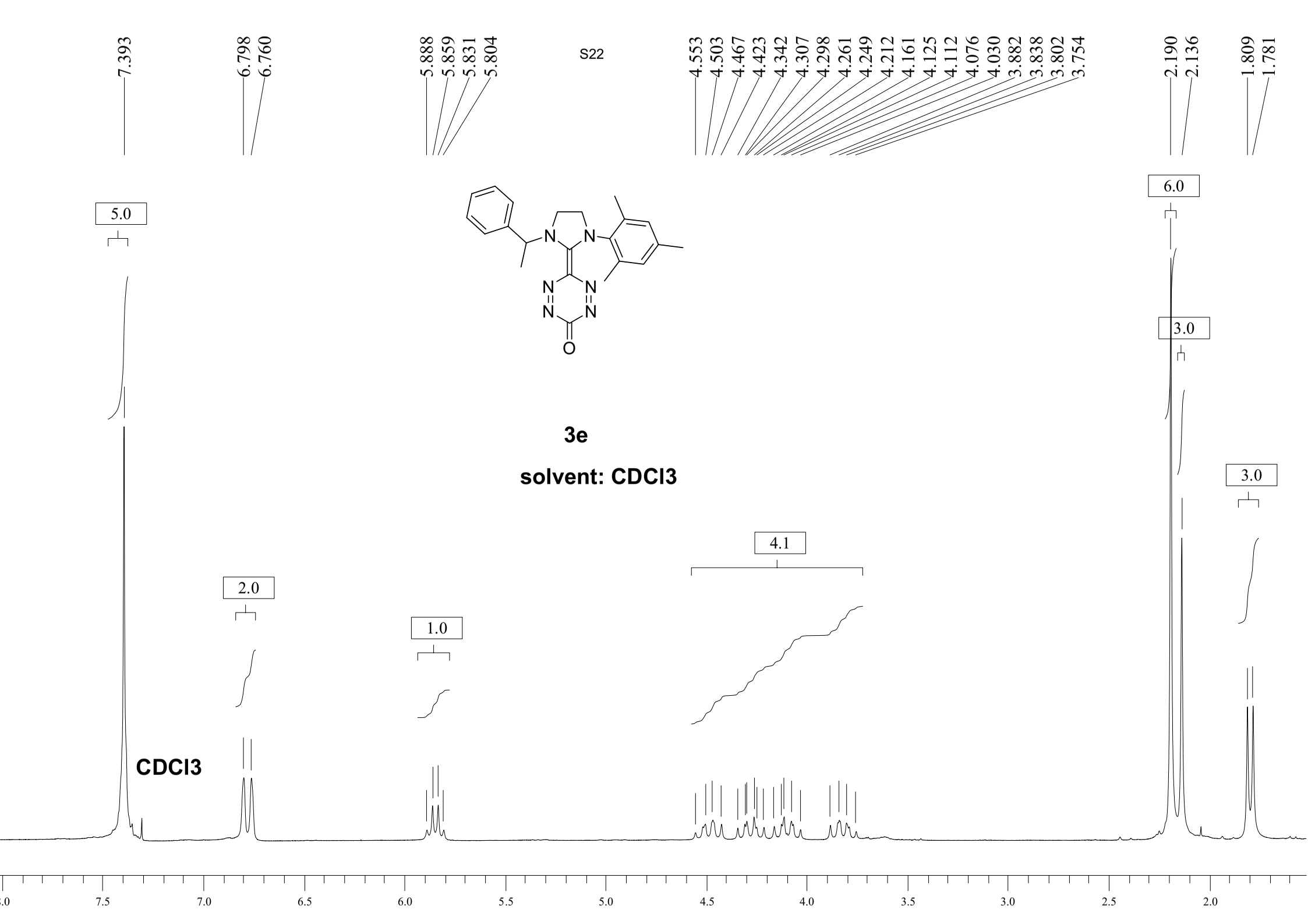
175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4.298
4.261
4.249
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4.161
4.125
4.112
4.076
4.030
3.882
3.838
3.802
3.754
2.190
2.136
1.809
1.781
5.0
2.0
1.0
4.1
6.0
3.0
3.0
N
N
N
N
N
N
O
3e
solvent: CDCl3
CDCl3
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

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160.895
144.468
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136.232
135.202
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129.588
129.573
129.150
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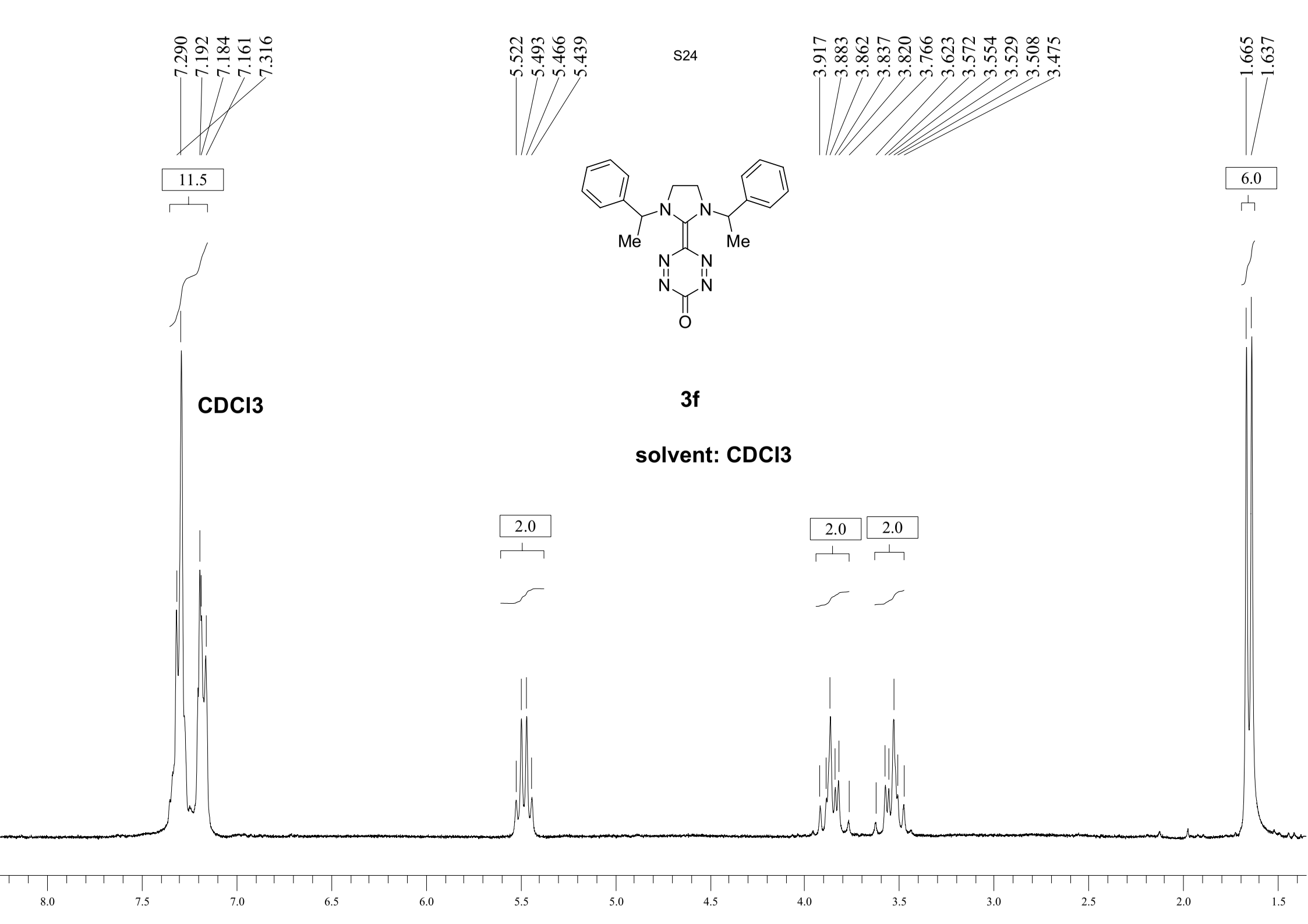
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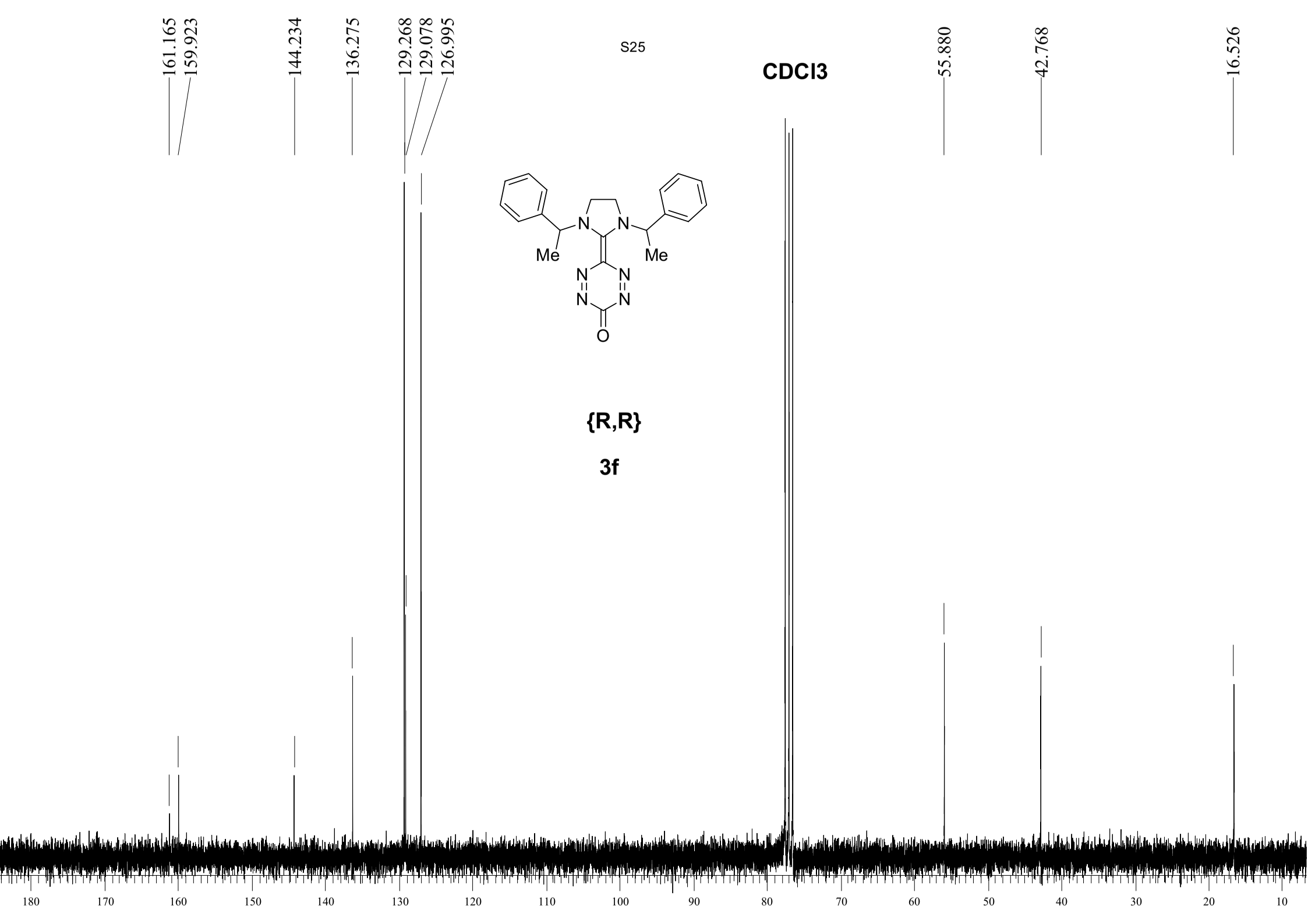
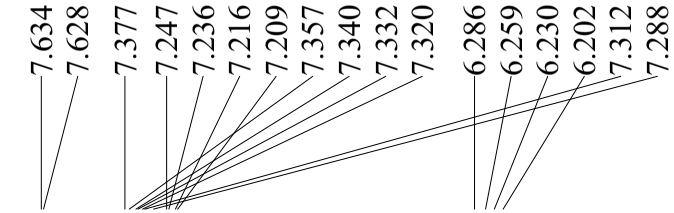
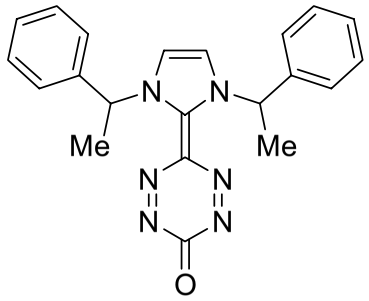
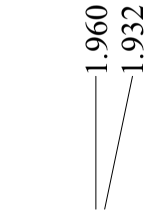
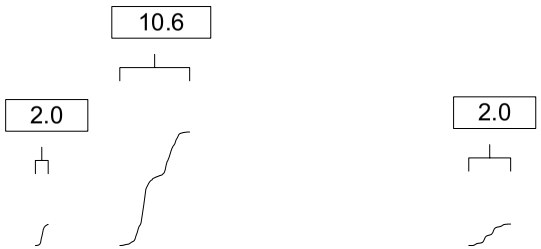
5.466
5.439
3.917
3.883
3.862
3.837
3.820
3.766
3.623
3.572
3.554
3.529
3.508
3.475
1.665
1.637
11.5
6.0
2.0
2.0
2.0
Me
Me
N
N
N
N
N
N
O
CDCl3
3f
solvent: CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

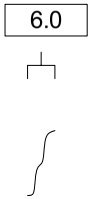

161.165
159.923
144.234
136.275
129.268
129.078
126.995
CDCl3
55.880
42.768
16.526
Me
Me
N
N
N
N
N
N
O
{R,R}
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10









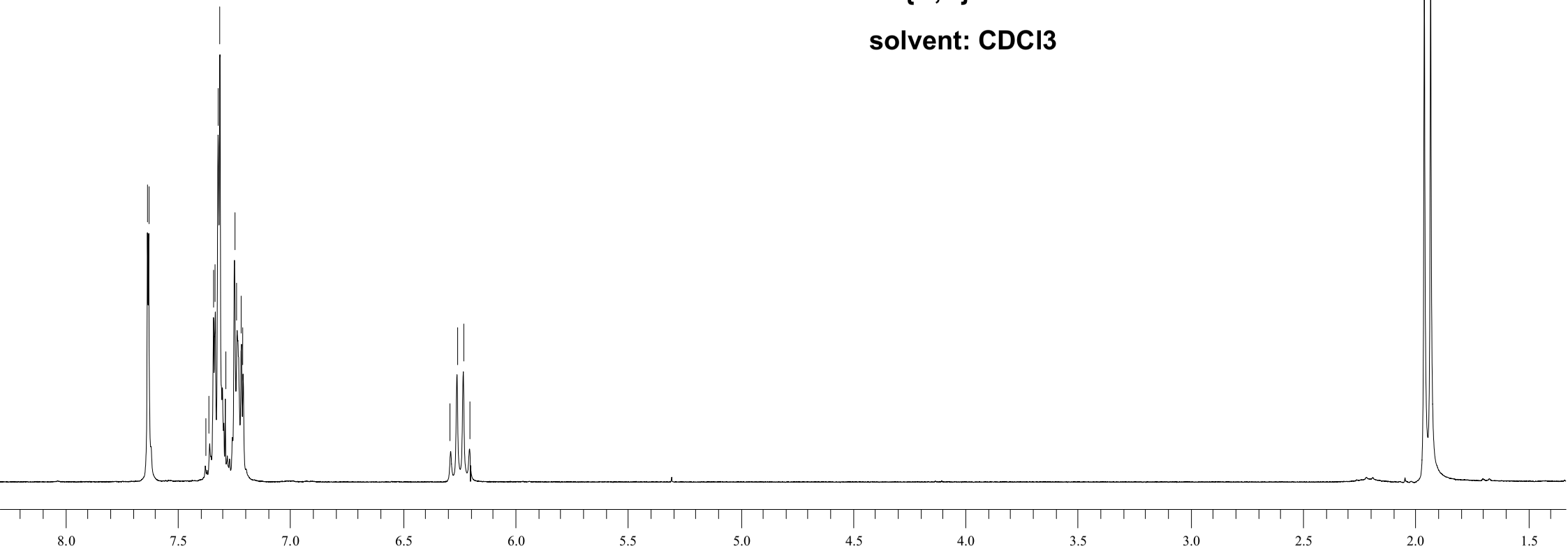


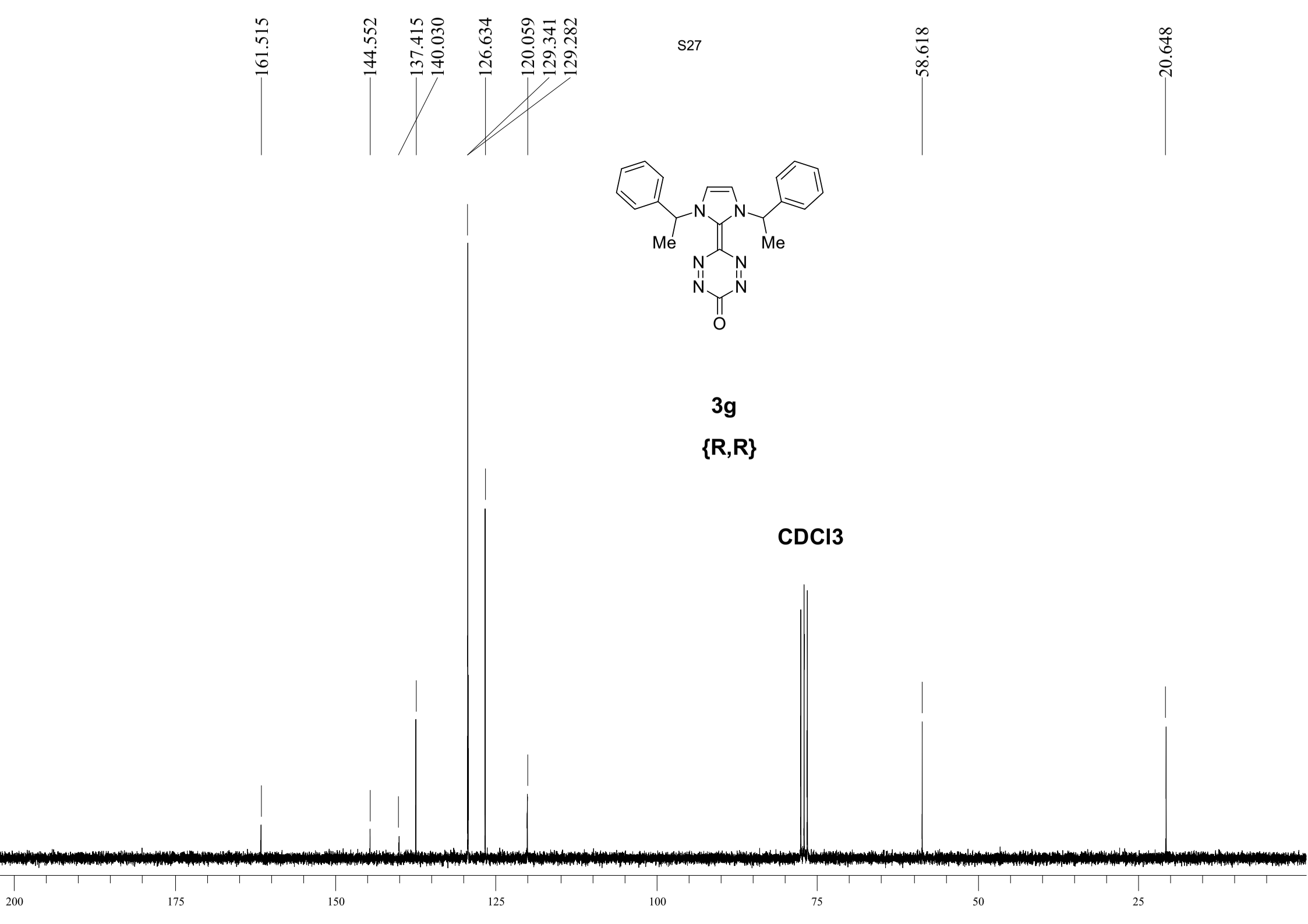
CDCl3

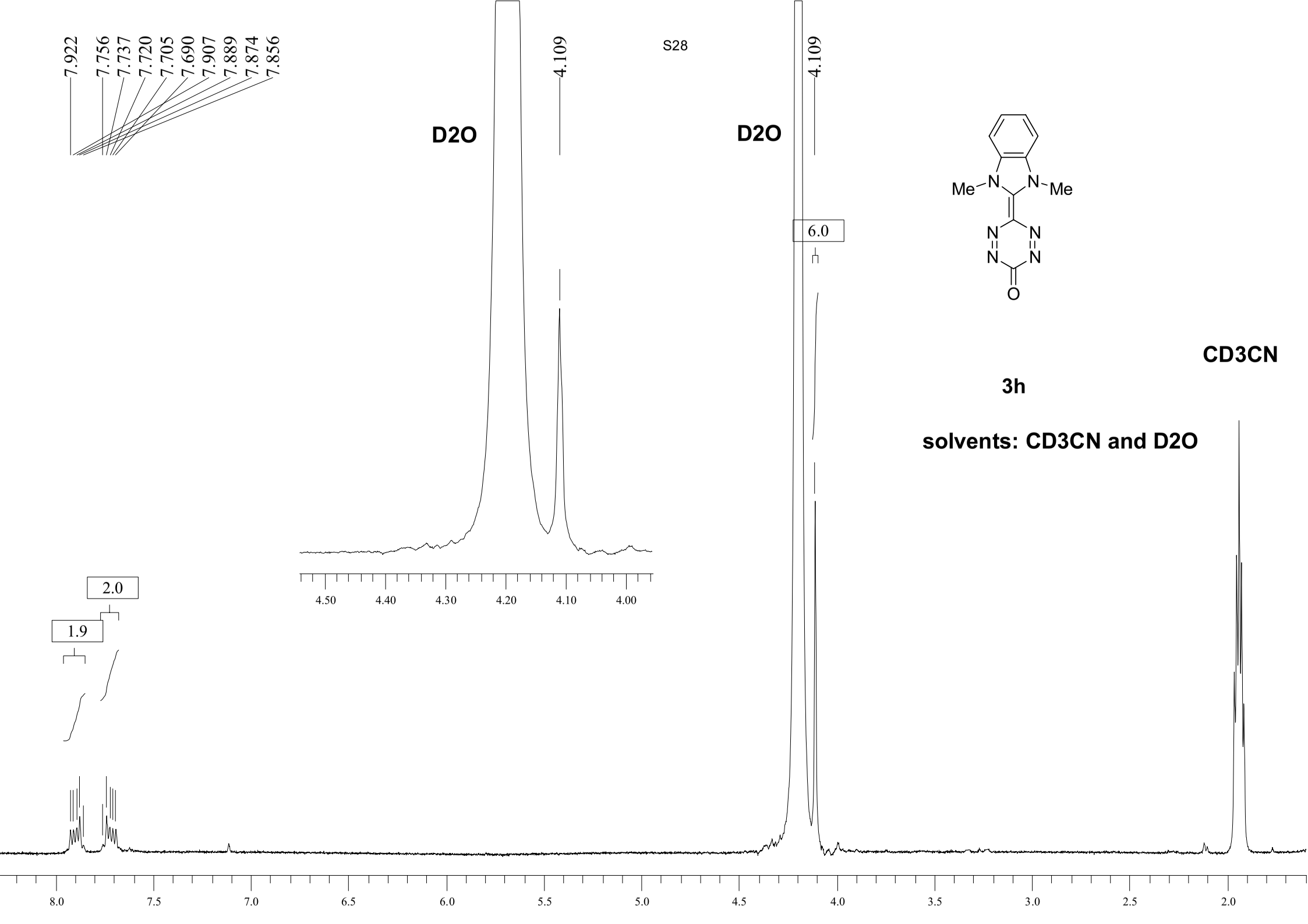
3g

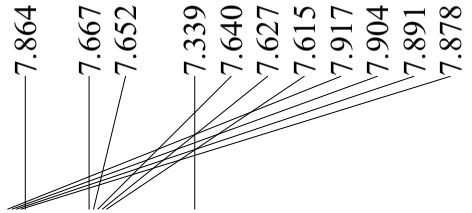
{R,R}

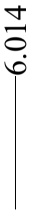
solvent: CDCl3

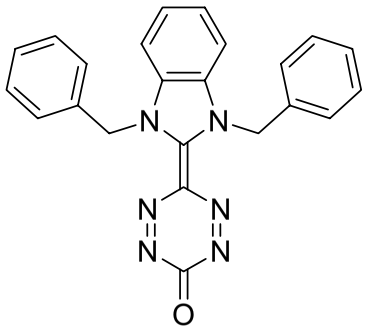



161.515
144.552
137.415
140.030
126.634
120.059
129.341
129.282
58.618
20.648
Me
Me
O
3g
{R,R}
CDCl3
200
175
150
125
100
75
50
25


7.922
7.756
7.737
7.720
7.705
7.690
7.907
7.889
7.874
7.856
4.109
D2O
4.109
D2O
6.0
Me
N
N
Me
N
N
N
N
O
CD3CN
3h
solvents: CD3CN and D2O
2.0
1.9
4.50
4.40
4.30
4.20
4.10
4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

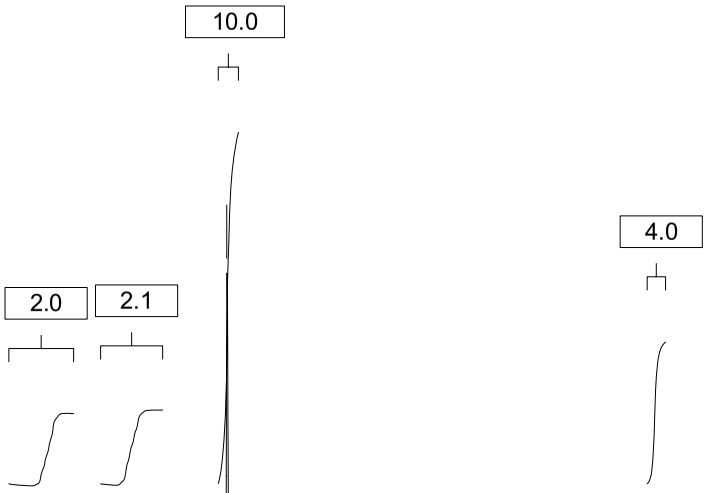






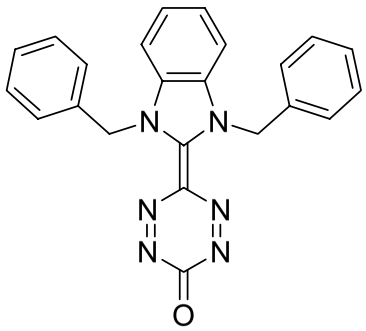
3i

solvent: d6-DMSO



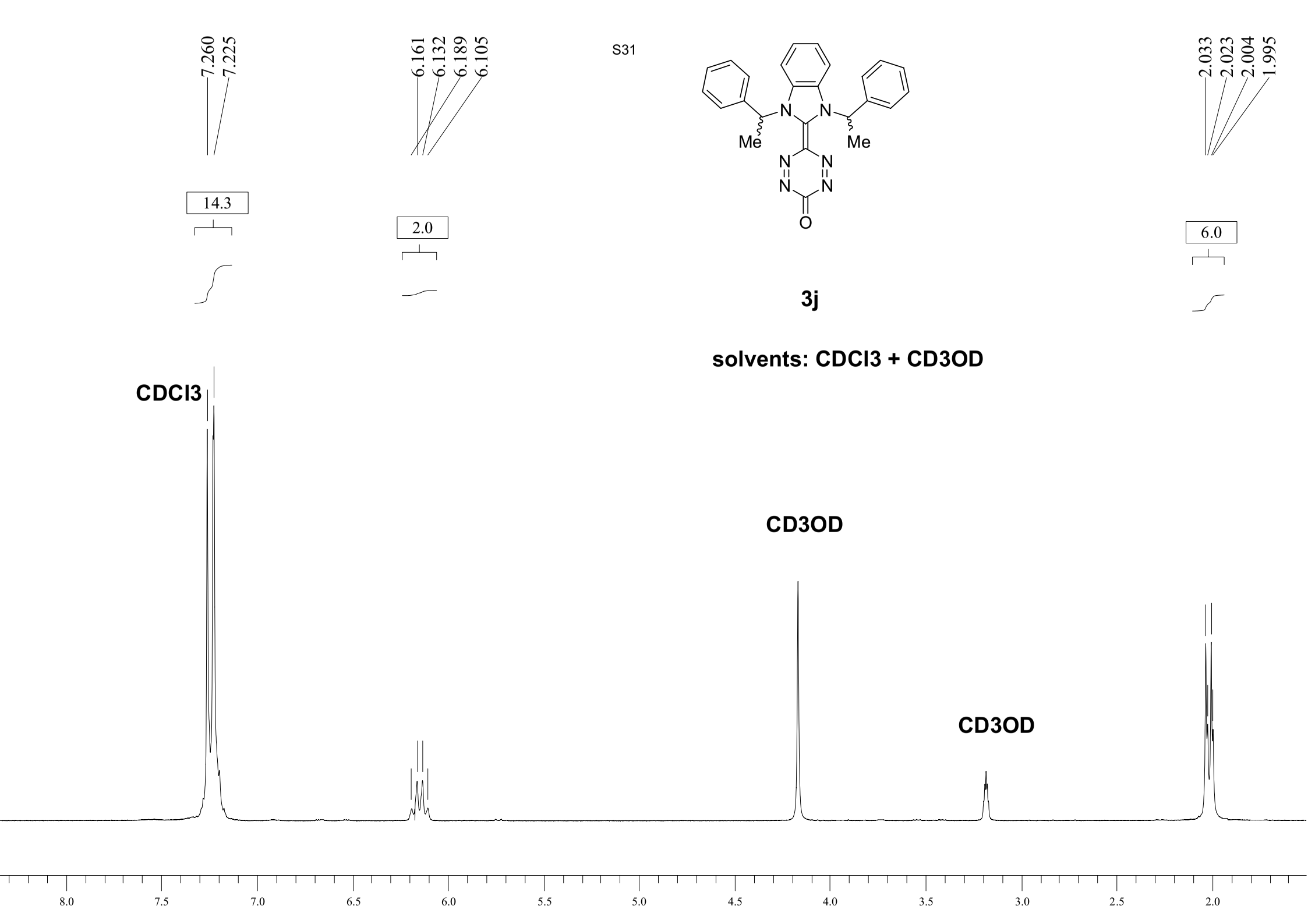
H2O

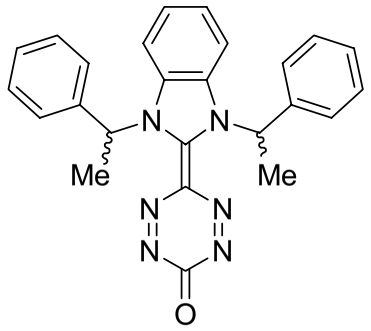
d6-DMSO



3i

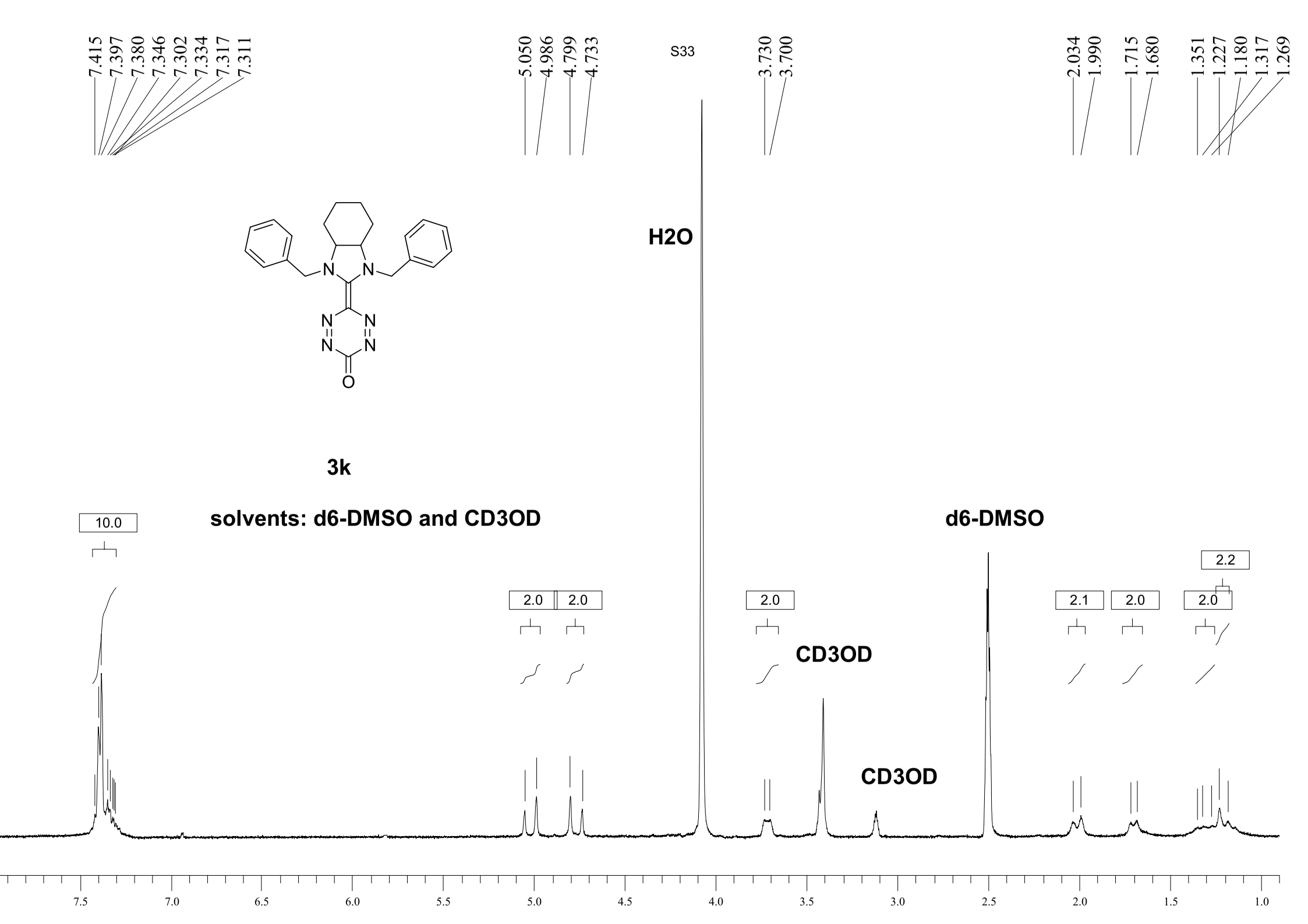
Solvents: CDCl3 + CD3OD

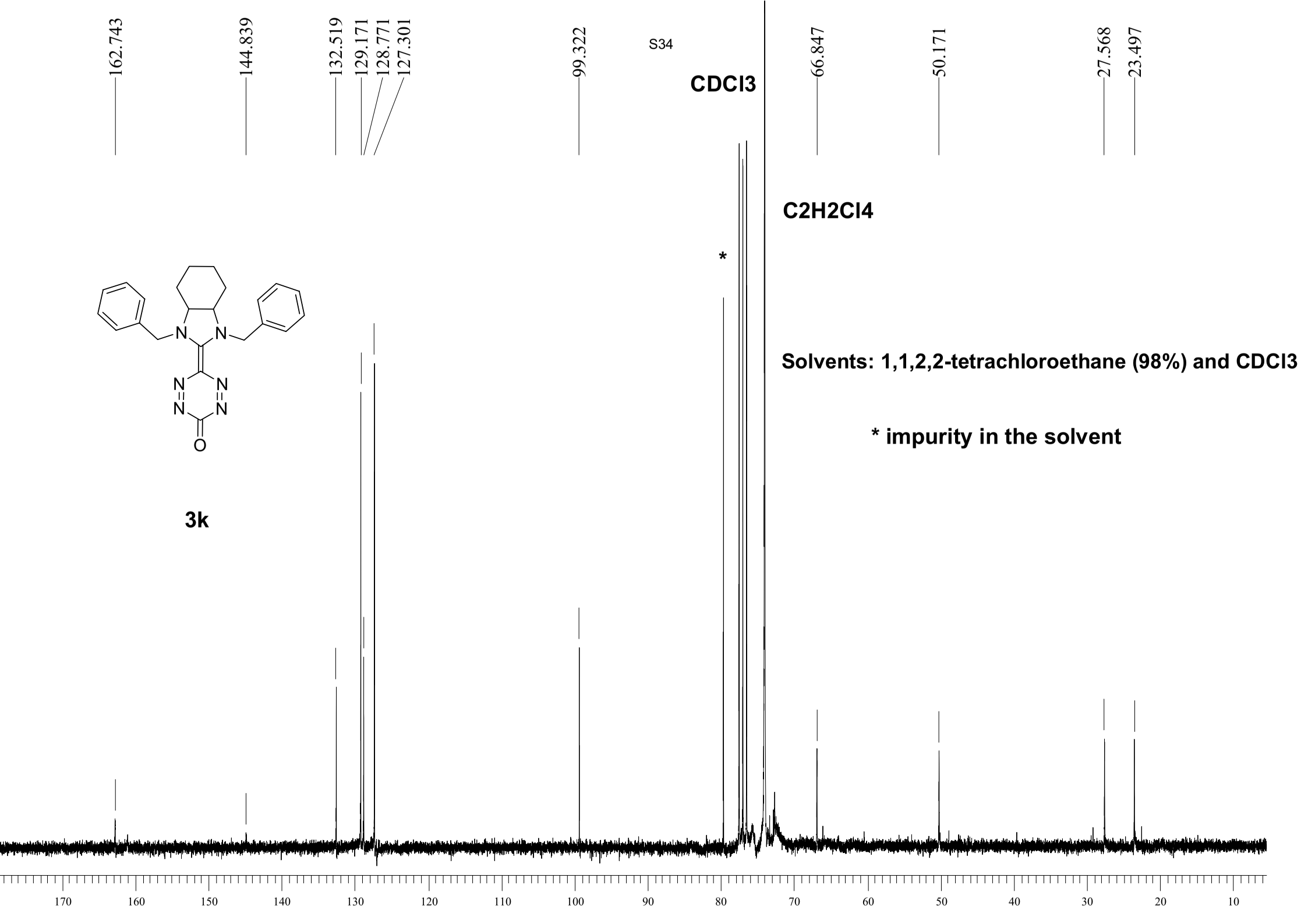

7.260
7.225
6.161
6.132
6.189
6.105
2.033
2.023
2.004
1.995
14.3
2.0
6.0
Me
Me
N
N
N
N
N
N
O
3j
solvents: CDCl3 + CD3OD
CDCl3
CD3OD
CD3OD
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

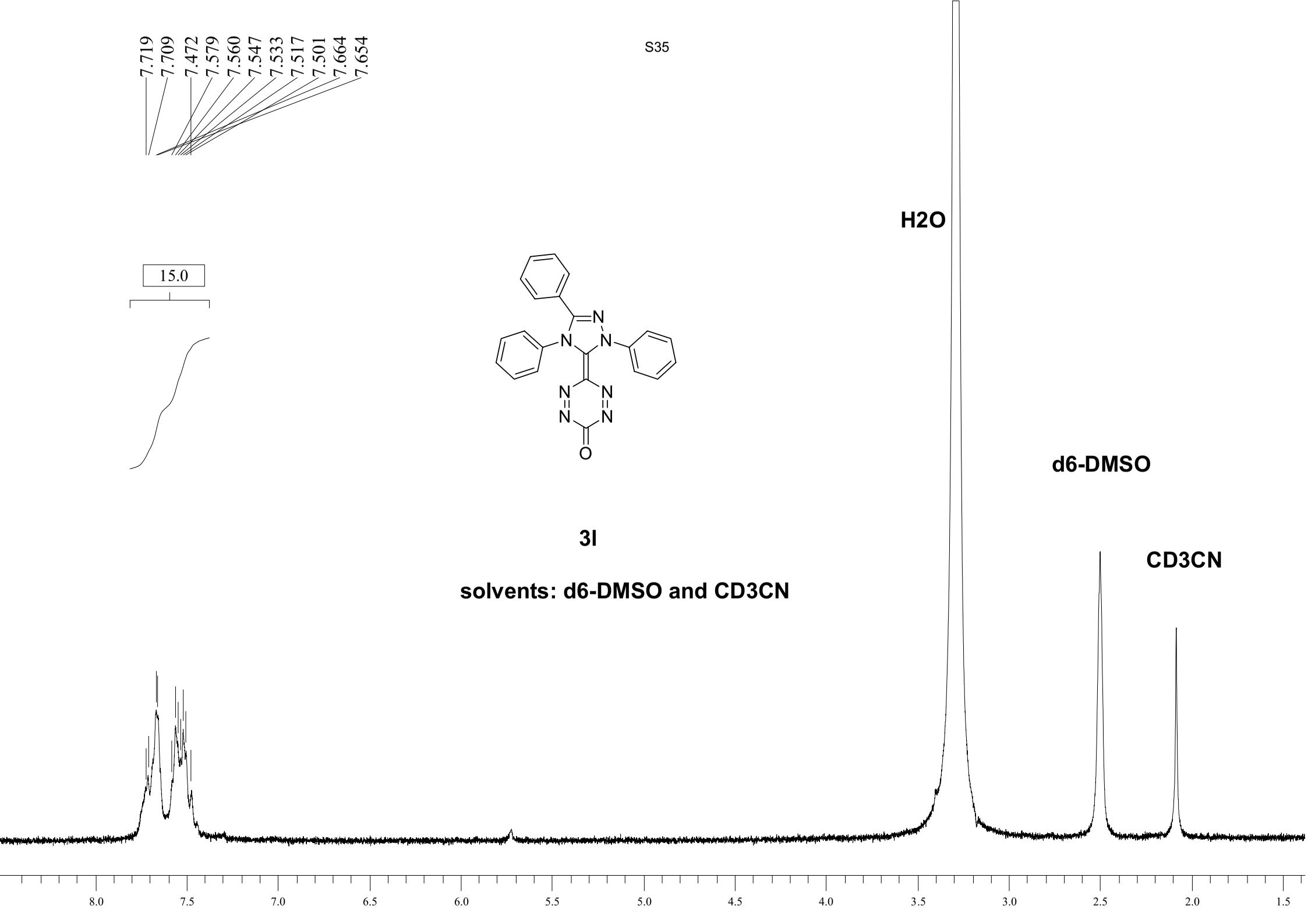


3j

solvents: CDCl3 + CD3OD

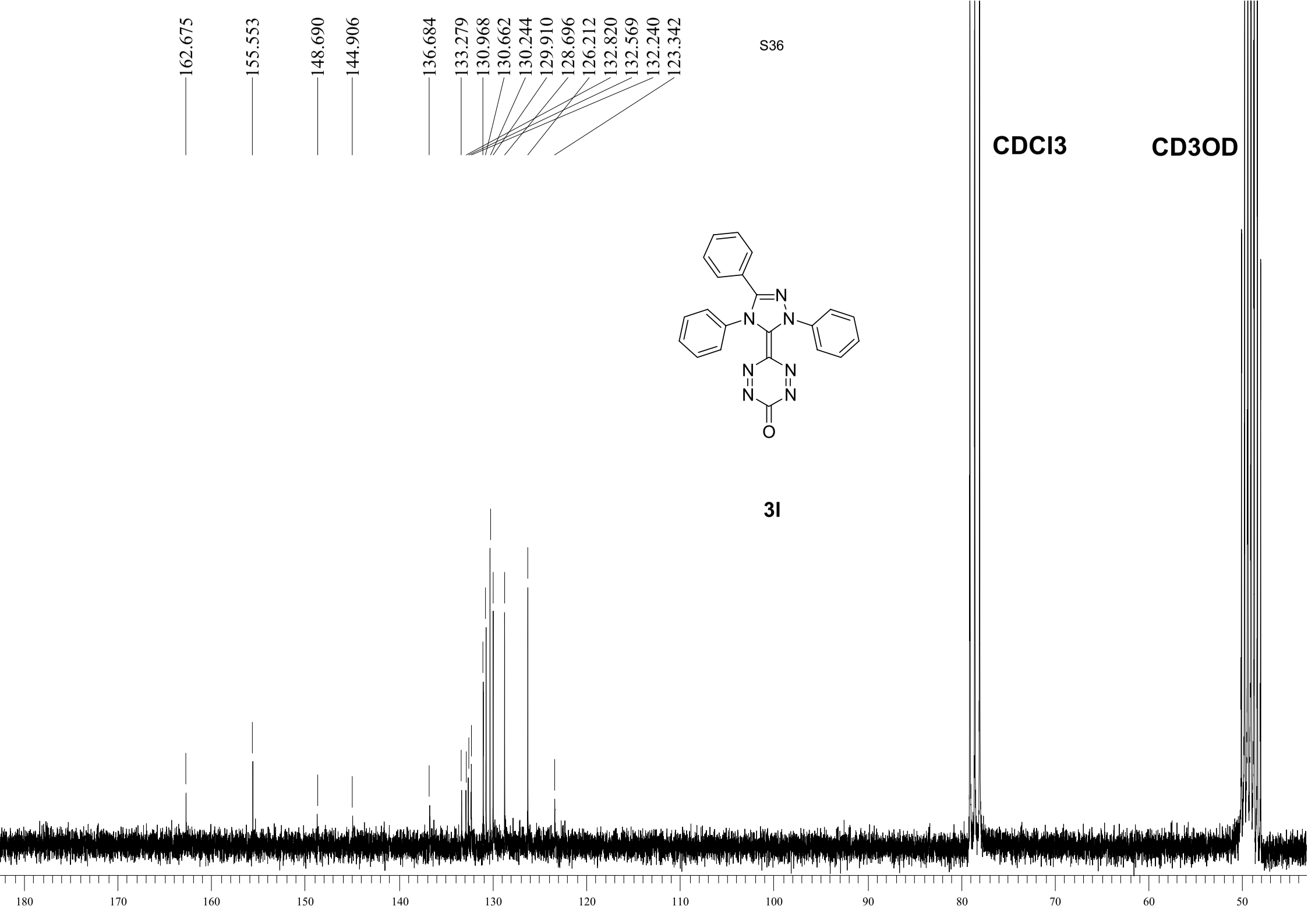

7.415
7.397
7.380
7.346
7.302
7.334
7.317
7.311
5.050
4.986
4.799
4.733
S33
3.730
3.700
2.034
1.990
1.715
1.680
1.351
1.227
1.180
1.317
1.269
H2O
3k
solvents: d6-DMSO and CD3OD
d6-DMSO
CD3OD
CD3OD
10.0
2.0
2.0
2.0
2.1
2.0
2.0
2.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


162.743
144.839
132.519
129.171
128.771
127.301
99.322
CDCl3
66.847
50.171
27.568
23.497
C2H2Cl4
*
Solvents: 1,1,2,2-tetrachloroethane (98%) and CDCl3
* impurity in the solvent
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



3l

solvents: d6-DMSO and CD3CN


162.675
155.553
148.690
144.906
136.684
133.279
130.968
130.662
130.244
129.910
128.696
126.212
132.820
132.569
132.240
123.342
CDCl3
CD3OD
N
N
N
N
N
N
N
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50

3l