Electronic Supplementary Material (ESI)

Synthesis and properties of geometrical 4-diarylmethylene analogs of the green fluorescent protein chromophore

Masahiro Ikejiri,* Haruka Kojima, Yuumi Fugono, Aki Fujisaka, Yoshiko Chihara, and Kazuyuki Miyashita*

Faculty of Pharmacy, Osaka Ohtani University, Nishikiori-Kita 3-11-1, Tondabayashi, Osaka 584-8540, Japan.

1. Experimental section

1.1. General information

^{1}H and ^{13}C NMR spectra were recorded on a JNM-ECZ400S spectrometer at 400 and 100 MHz, respectively, and chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane or solvent signal. Mass spectra were recorded using a JEOL JMS-BU25 mass spectrometer in positive FAB mode. UV-Vis spectra were obtained on a JASCO V-730BIO spectrophotometer. IR spectra of samples in KBr were obtained on a JASCO FT/IR-6300 spectrometer by diffuse reflection. Fluorescence spectra were recorded using a JASCO FP-6200 spectrofluorometer. Fluorescence quantum yields were measured on a JASCO FP-8300 spectrometer with an integrating sphere. Photoirradiation was performed with a portable UV light (365 nm, 0.1 mW/cm^2) or a LED blue light (450–500 nm, 6.9×10^2 lux). Preparative layer chromatography (PLC) was carried out on Merck silica gel 60 F_{254}. Column chromatography was performed using Fuji Silysia PSQ 100, Teledyne Isco RediSep, or Merck Aluminum Oxide 90 active neutral.

1.2. Chemistry

Ethyl (*EZ*)-2-(((4-methoxyphenyl)(phenyl)methylene)amino)acetate (**4a**)

A solution of phenylmagnesium bromide (1.0 M in THF, 50 mL, 50 mmol) was added to a stirred solution of 4-methoxybenzonitrile (4.33 g, 32.5 mmol) in THF (30 mL); the mixture was stirred for 6 hr under reflux conditions. After the addition of MeOH (7.4 mL) at ice-water temperature, the mixture was stirred for 10 min and the solvent was evaporated under reduced pressure. The residue was diluted with ethyl acetate, washed with water and brine, dried over $MgSO_4$, and then concentrated under reduced pressure to afford a crude product of imine **3a** (7.05 g). The obtained imine **3a** (100 mg, 0.473 mmol) was treated with glycine ethyl ester hydrochloride (73 mg, 0.521 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred overnight. After dilution with ethyl acetate, the mixture was filtrated, and the filtrate was washed with water and brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/5 containing 3% Et_3N) to give **4a** (121 mg, 88% in two steps, ca. 2 : 1 inseparable mixture of diastereomers) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 7.66-7.64 (2/3H, m), 7.61 (4/3H, d, J = 9.1 Hz), 7.46-7.31 (3H, m), 7.19-7.12 (2H, m), 6.98 (2/3H, d, J = 8.7 Hz), 6.84 (4/3H, d, J = 9.1 Hz), 4.25 (2/3H, s), 4.24-4.17 (2H, m), 4.15 (4/3H, s), 3.87 (1H, s), 3.82 (2H, s), 1.28 (1H, t, J = 7.1 Hz), 1.27 (2H, t, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.7, 171.1, 170.8, 170.7, 161.5, 159.8, 139.8, 136.2, 132.1, 130.3, 130.3, 129.4, 128.8, 128.6, 128.6, 128.0, 127.6, 113.9, 113.3, 60.8, 60.8, 55.8, 55.6, 55.3, 14.2. HRMS (FAB) calcd for $C_{18}H_{20}NO_3$ $[M + H]^+$ 298.1443; found 298.1433.

Ethyl (*EZ*)-2-(((4-chlorophenyl)(4-methoxyphenyl)methylene)amino)acetate (**4b**)

A solution of (4-methoxyphenyl)magnesium bromide (0.5 M in THF, 45 mL, 22.5 mmol) was added

to a stirred solution of 4-chlorobenzonitrile (2.01 g, 14.6 mmol) in THF (14 mL), and the mixture was stirred for 5 hr under reflux conditions. After the addition of MeOH (3.4 mL) at ice-water temperature, the mixture was stirred for 10 min and the solvent was evaporated under reduced pressure. The residue was diluted with ethyl acetate, washed with water and brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The solid residue was washed with hexane to obtain a crude product of imine **3b** (3.24 g). The obtained imine **3b** (200 mg, 0.814 mmol) was treated with glycine ethyl ester hydrochloride (125 mg, 0.895 mmol) in CH_2Cl_2 (8 mL), and the mixture was stirred overnight. After dilution with Et_2O, the mixture was filtrated, and the filtrate was washed with water and brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/9 containing 3% Et_3N to 1/4 containing 3% Et_3N) to give **4b** (215 mg, 72% in two steps, ca. 2 : 1 inseparable mixture of diastereomers) as a white solid. ^{1}H-NMR ($CDCl_3$) δ: 7.60-7.57 (2H, m), 7.45 (4/3H, d, J = 8.0 Hz), 7.30 (2/3H, d, J = 8.5 Hz), 7.13 (4/3H, d, J = 8.3 Hz), 7.10 (2/3H, d, J = 8.3 Hz), 6.98 (2/3H, d, J = 8.3 Hz), 6.85 (4/3H, d, J = 8.8 Hz), 4.23 (2/3H, s), 4.22-4.17 (2H, m), 4.14 (4/3H, s), 3.87 (1H, s), 3.82 (2H, s), 1.28 (1H, t, J = 7.3 Hz), 1.27 (2H, t, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 170.6, 170.5, 170.0, 161.6, 160.0, 138.2, 136.5, 134.7, 134.4, 131.7, 130.3, 130.1, 129.3, 129.1, 128.9, 128.2, 127.4, 114.1, 113.4, 60.9, 55.7, 55.5, 55.3, 14.2. HRMS (FAB) calcd for $C_{18}H_{19}ClNO_3$ $[M + H]^+$ 332.1054; found 332.1059.

(*EZ*)-2-((4-Methoxyphenyl)(phenyl)methylene)-2,5,6,7,8,9-hexahydro-3*H*-imidazo[1,2-*a*]azepin-3-one (1a)

A mixture of imino-glycinate **4a** (500 mg, 1.68 mmol), imidate **5** (43 mg, 0.34 mmol), and acetic acid (38μL, 0.67 mmol) in toluene (1.7 mL) was stirred at room temperature for two days. After dilution of the mixture with ethyl acetate, the organic layer was washed with a saturated $NaHCO_3$ solution, water, and brine, then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/2 to 1/1) to give **1a** (68 mg, 58%, ca. 1 : 1 mixture of diastereomers).

Separation of the Z-isomer: A solution of **1a** (60 mg) in benzene (6 mL) was stirred for 2.5 hr under blue light irradiation (LED, 450–500 nm). After removal of the solvent under reduced pressure, the residue was purified by repeated recrystallization from cyclohexane (three times) in the dark to give ***Z*-1a** (29 mg, 48%) as yellow crystals. IR ν_{max}/cm^{-1}: 1599, 1701. ^{1}H-NMR ($CDCl_3$) δ: 7.61 (2H, d, J = 9.1 Hz), 7.43-7.40 (3H, m), 7.29-7.28 (2H, m), 6.87 (2H, d, J = 8.7 Hz), 3.82 (3H, s), 3.66-3.59 (2H, m), 2.81-2.76 (2H, m), 1.84-1.77 (4H, m), 1.69-1.61 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 168.1, 165.0, 160.6, 145.6, 138.3, 135.4, 134.2, 131.6, 130.1, 128.6, 128.0, 113.3, 55.3, 40.4, 31.6, 30.7, 29.0, 25.7. HRMS (FAB) calcd for $C_{22}H_{23}N_2O_2$ $[M + H]^+$ 347.1760; found 347.1753. *Separation of the E-isomer*: A solution of **1a** (46 mg) in MeOH (10 mL) was stirred for 5 hr under UV irradiation

(365 nm, 16 W). After removal of the solvent under reduced pressure, the residue was purified by repeated PLC (ethyl acetate/hexane = 1/2, repeated 8 times on one plate) in the dark to give ***E*-1a** (25 mg, 54%, purity *E*/*Z* = ca. 25) as a yellow solid. The solid was recrystallized from cyclohexane prior to measurement of the fluorescence. IR ν_{max}/cm^{-1}: 1605, 1698. ^{1}H-NMR ($CDCl_3$) δ: 7.52-7.50 (2H, m), 7.36-7.33 (3H, m), 7.27 (2H, d, *J* = 9.6 Hz), 6.92 (2H, d, *J* = 8.7 Hz), 3.85 (3H, s), 3.68-3.63 (2H, m), 2.78-2.74 (2H, m), 1.84-1.76 (4H, m), 1.70-1.65 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 168.1, 164.8, 160.4, 146.8, 139.7, 136.1, 132.4, 132.4, 130.1, 129.2, 127.6, 113.2, 55.2, 40.5, 31.4, 30.7, 29.0, 25.7. HRMS (FAB) calcd for $C_{22}H_{23}N_2O_2$ $[M + H]^+$ 347.1760; found 347.1751.

(*EZ*)-2-((4-Chlorophenyl)(4-methoxyphenyl)methylene)-2,5,6,7,8,9-hexahydro-3*H*-imidazo[1,2-*a*]azepin-3-one (1b)

A mixture of imino-glycinate **4b** (600 mg, 1.81 mmol), imidate **5** (45 mg, 0.35 mmol), and acetic acid (42 µL, 0.73 mmol) in toluene (1.8 mL) was stirred at room temperature for two days. After dilution of the mixture with ethyl acetate, the organic layer was washed with a saturated $NaHCO_3$ solution, water, and brine, then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/4 to 1/1) to give **1b** (72 mg, 53%, ca. 1.2 : 1 mixture of diastereomers).

Separation of the E-isomer: A solution of **1b** (72 mg) in benzene (8 mL) was stirred for 2 hr under blue light irradiation (LED, 450–500 nm). After removal of the solvent under reduced pressure, the residue was purified by repeated recrystallization from ethyl acetate and hexane (three times) in the dark to give ***E*-1b** (21 mg, 29%) as yellow crystals. IR ν_{max}/cm^{-1}: 1600, 1698. ^{1}H-NMR ($CDCl_3$) δ: 7.58 (2H, d, *J* = 8.7 Hz), 7.38 (2H, d, *J* = 8.7 Hz), 7.23 (2H, d, *J* = 8.2 Hz), 6.88 (2H, d, *J* = 9.1 Hz), 3.83 (3H, s), 3.66-3.60 (2H, m), 2.81-2.76 (2H, m), 1.85-1.76 (4H, m), 1.69-1.63 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 168.1, 165.3, 160.7, 144.2, 136.7, 135.6, 134.7, 134.2, 131.7, 131.3, 128.3, 113.4, 55.3, 40.5, 31.6, 30.7, 29.0, 25.7. HRMS (FAB) calcd for $C_{22}H_{22}ClN_2O_2$ $[M + H]^+$ 381.1370; found 381.1359. *Separation of the Z-isomer*: A solution of **1b** (41 mg) in benzene (6.5 mL) was stirred for 4 hr under UV irradiation (365 nm, 16 W). After removal of the solvent under reduced pressure, the residue was recrystallized from ethyl acetate and hexane to remove ***E*-1b**. After evaporation of the filtrate, the residue was purified by repeated PLC (ethyl acetate/hexane = 1/2, repeated 10 times on one plate) in the dark to give ***Z*-1b** (26 mg, 63%, purity *Z*/*E* = ca. 35) as a yellow solid. The solid was recrystallized from ethyl acetate and hexane prior to measurement of the fluorescence. IR ν_{max}/cm^{-1}: 1606, 1700. ^{1}H-NMR ($CDCl_3$) δ: 7.47 (2H, d, *J* = 8.2 Hz), 7.32 (2H, d, *J* = 8.7 Hz), 7.26 (2H, d, *J* = 8.7 Hz), 6.92 (2H, d, *J* = 8.7 Hz), 3.85 (3H, s), 3.68-3.62 (2H, m), 2.78-2.73 (2H, m), 1.84-1.76 (4H, m), 1.70-1.63 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 167.9, 165.2, 160.5, 145.1, 138.1, 136.3, 135.3, 133.8, 132.4, 129.6, 128.0, 113.3, 55.2, 40.5, 31.5, 30.7, 29.0, 25.7. HRMS (FAB) calcd for $C_{22}H_{22}ClN_2O_2$ $[M + H]^+$ 381.1370; found 381.1376.

(*EZ*)-2-(Phenyl(pyridin-2-yl)methylene)-2,5,6,7,8,9-hexahydro-3*H*-imidazo[1,2-*a*]azepin-3-one (1c)

A solution of methylamine (40% in MeOH, 7.60 g, 97.9 mmol) was added to a stirred solution of benzoylpyridine **6** (3.00 g, 16.4 mmol) in MeOH (100 mL), and the mixture was stirred for 7 hr under reflux conditions. The solvent and excess methylamine were removed under reduced pressure to give a crude product of methylimine **3c** (3.21 g). The obtained methylimine **3c** (1.00 g, 5.10 mmol) was treated with glycine ethyl ester hydrochloride (782 mg, 5.60 mmol) in CH_2Cl_2 (50 mL), and the mixture was stirred for 2 hr. After dilution of the mixture with ether, the mixture was washed with water, a saturated solution of $NaHCO_3$, and brine, then dried over $MgSO_4$ and concentrated under reduced pressure to give a crude product of imino-glycinate **4c** (1.35 g, ca. 10 : 9 mixture of diastereomers, ~99% from **6**). Since the purification of **4c** did not succeed due to its instability, the next reaction was performed with crude **4c**. A mixture of **4c** (1.35 g, ca. 5.03 mmol), imidate **5** (128 mg, 1.01 mmol), and acetic acid (172 µL, 3.00 mmol) in toluene (5.0 mL) was stirred at 50 °C for one day. After dilution of the mixture with ethyl acetate, the organic layer was extracted with 5% aqueous HCl and then re-extracted with ethyl acetate after neutralization with a saturated solution of $NaHCO_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral aluminum oxide column chromatography (ethyl acetate/hexane = 1/4 to 2/1) and then recrystallized from ethyl acetate and hexane to give **1c** (160 mg, 50%, ca. 5 : 1 mixture of diastereomers).

Separation of the E, Z-isomers: A solution of **1c** (100 mg, 0.32 mmol, *E* : *Z* = ca. 5 : 1) in MeCN (20 mL) was stirred for 6 hr under UV irradiation (365 nm, 16 W). After evaporation of the solvent, the residue was purified by silica gel column chromatography (ethyl acetate containing 3% Et_3N) to give ***E*-1c** (55 mg, 55%) and ***Z*-1c** (45 mg, 45%) as yellow solids. ***E*-1c**: IR ν_{max}/cm^{-1}: 1626, 1704. ^{1}H-NMR ($CDCl_3$) δ: 8.74 (1H, ddd, *J* = 4.6, 1.8, 0.9 Hz), 7.77 (1H, td, *J* = 7.5, 1.7 Hz), 7.70-7.67 (2H, m), 7.39-7.32 (5H, m), 3.63-3.57 (2H, m), 2.83-2.78 (2H, m), 1.84-1.76 (4H, m), 1.67-1.62 (2H, m). ^{1}H-NMR (CD_3CN) δ: 8.60 (1H, d, *J* = 4.6 Hz), 7.78 (1H, td, *J* = 7.7, 1.7 Hz), 7.59-7.56 (2H, m), 7.42 (1H, d, *J* = 7.8 Hz), 7.37-7.32 (4H, m), 3.57-3.54 (2H, m), 2.74-2.71 (2H, m), 1.83-1.72 (4H, m), 1.64-1.58 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 168.2, 167.4, 157.1, 149.8, 142.4, 137.7, 137.4, 136.1, 131.9, 129.4, 128.0, 125.0, 122.8, 40.5, 31.6, 30.6, 28.9, 25.6. HRMS (FAB) calcd for $C_{20}H_{20}N_3O$ $[M + H]^+$ 318.1606; found 318.1614. ***Z*-1c**: IR ν_{max}/cm^{-1}: 1624, 1706. ^{1}H-NMR ($CDCl_3$) δ: 8.67 (1H, ddd, *J* = 5.0, 1.8, 0.9 Hz), 7.78 (1H, dt, *J* = 8.1, 1.1 Hz), 7.72 (1H, td, *J* = 7.7, 1.7 Hz), 7.41-7.38 (3H, m), 7.36-7.32 (2H, m), 7.21 (1H, ddd, *J* = 7.4, 4.7, 1.3 Hz), 3.67-3.61 (2H, m), 2.79-2.75 (2H, m), 1.84-1.76 (4H, m), 1.70-1.63 (2H, m). ^{1}H-NMR (CD_3CN) δ: 8.50 (1H, d, *J* = 5.0 Hz), 7.89 (1H, d, *J* = 7.8 Hz), 7.79 (1H, td, *J* = 7.8, 1.8 Hz), 7.36-7.25 (6H, m), 3.61-3.57 (2H, m), 2.68-2.65 (2H, m), 1.82-1.71 (4H, m), 1.66-1.61 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 168.1, 167.1, 157.5, 149.6, 144.5, 138.3,

136.9, 135.6, 130.1, 128.8, 127.9, 127.7, 122.8, 40.5, 31.6, 30.6, 29.0, 25.5. HRMS (FAB) calcd for $C_{20}H_{20}N_3O$ $[M + H]^+$ 318.1606; found 318.1604. **4c** (ca. 10:9 dr): ^{1}H-NMR ($CDCl_3$) δ: 8.76 (9/19H, d, J = 4.6 Hz), 8.59 (10/19H, d, J = 5.0 Hz), 8.10 (10/19H, dt, J = 7.9, 1.0 Hz), 7.81 (9/19H, td, J = 7.7, 1.7 Hz), 7.74 (10/19H, td, J = 7.8, 1.8 Hz), 7.64-7.61 (1H, m), 7.50-7.21 (104/19H, m), 4.29 (20/19H, s), 4.26 (18/19H, s), 4.22 (20/19H, q, J = 7.0 Hz), 4.21 (18/19H, q, J = 7.2 Hz), 1.28 (30/19H, t, J = 7.1 Hz), 1.28 (27/19H, t, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$) δ: 171.8, 170.4, 170.3, 169.4, 156.9, 154.8, 150.0, 149.0, 138.4, 136.4, 136.3, 135.3, 130.5, 128.9, 128.6, 128.5, 128.1, 127.8, 124.4, 123.6, 123.5, 123.1, 60.9, 60.9, 55.8, 55.3, 14.2. HRMS (FAB) calcd for $C_{16}H_{17}N_2O_2$ $[M + H]^+$ 269.1290; found 269.1296.

1.3. Theoretical calculations

The theoretical calculations were performed using Spartan 14 for Windows (Wavefunction, Inc., Irvine) and Gaussian 09W 32-bit version (Gaussian, Inc., Wallingford) running with the default settings. The structures were constructed and optimized by the following three steps: 1) systematic conformational search at the molecular mechanics (MMFF) level using Spartan 14, 2) geometry optimization of the lowest-energy conformer from step 1 at the DFT/B3LYP/6-31G(d) level using Spartan 14, and 3) re-optimization of the geometry at the DFT/B3LYP/6-31G(d) or LANL2DZ (for Zn) level with a PCM solvation model (if necessary) using Gaussian 09W; frequencies were confirmed at this stage. The chemical shifts for ^{1}H NMR were calculated at the DFT/B3LYP/6-311+G(2d, p) level with an IEFPCM solvation model ($CHCl_3$) for the GIOA method using Gaussian 09W and at the DFT/EDF2/6-31G(d) level for the empirical model using Spartan 14. The chemical shifts of H and H′ calculated using the GIOA method were averaged. The absorption wavelength (λ_{max}) was calculated at the TD-DFT/6-31+G(d) level with a CPCM or an IEFPCM solvation model (CH_2Cl_2) by Gaussian 09W and several functionals were employed, namely B3LYP, CAM-B3LYP, and ωB97XD.

2. Mol2 files of DAINs 1 and 1′

For the ^{1}H-NMR study:

***Z*-1a**, opt: B3LYP/6-31G(d)/IEFPCM($CHCl_3$)
E = -1111.56275010 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 1.1445 -1.1631 -0.5141 N
2 C2 0.7632 0.1621 -0.2372 C
3 C3 2.0021 0.9892 -0.0806 C
4 N4 3.0270 0.0558 -0.2894 N
5 C5 2.4458 -1.1780 -0.5483 C
6 O6 2.1861 2.1671 0.2033 O
7 C7 -0.5325 0.5822 -0.0727 C
8 C8 4.4451 0.3893 -0.2246 C
9 C9 3.2659 -2.3943 -0.8363 C
10 C10 4.2412 -2.7869 0.2964 C
11 C11 5.4849 -1.8934 0.4236 C
12 C12 5.2270 -0.4286 0.8110 C
13 C13 -1.6707 -0.3566 -0.0033 C
14 C14 -3.9000 -2.0987 0.1287 C
15 C15 -1.5588 -1.6491 0.5589 C
16 C16 -2.9364 0.0292 -0.4832 C
17 C17 -4.0378 -0.8232 -0.4347 C
18 C18 -2.6495 -2.4993 0.6298 C
19 C19 -0.8564 2.0345 0.0204 C
20 C20 -1.5493 4.7565 0.1729 C
21 C21 -0.4856 2.9263 -0.9985 C
22 C22 -1.5925 2.5277 1.1110 C
23 C23 -1.9240 3.8799 1.1937 C
24 C24 -0.8343 4.2738 -0.9262 C
25 O25 -4.9034 -3.0094 0.2420 O
26 C26 -6.1965 -2.6597 -0.2449 C
27 H27 -2.5610 -3.4851 1.0762 H
28 H28 -0.6026 -1.9770 0.9454 H
29 H29 -4.9878 -0.4859 -0.8326 H
30 H30 -3.0617 1.0135 -0.9222 H
31 H31 -1.8947 1.8464 1.9013 H
32 H32 -2.4799 4.2469 2.0523 H
33 H33 -1.8168 5.8082 0.2309 H
34 H34 -0.5465 4.9481 -1.7283 H
35 H35 0.0709 2.5540 -1.8532 H
36 H36 2.5588 -3.2071 -1.0234 H
37 H37 3.8355 -2.2411 -1.7651 H
38 H38 4.5732 -3.8141 0.1032 H
39 H39 3.6960 -2.8112 1.2495 H
40 H40 6.0377 -1.9165 -0.5274 H
41 H41 6.1515 -2.3365 1.1744 H
42 H42 4.7030 -0.3754 1.7746 H
43 H43 6.1952 0.0683 0.9526 H
44 H44 4.8955 0.2734 -1.2196 H
45 H45 4.4730 1.4525 0.0279 H
46 H46 -6.5992 -1.7868 0.2829 H
47 H47 -6.8312 -3.5255 -0.0510 H
48 H48 -6.1760 -2.4567 -1.3224 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 44 1
14 8 45 1
15 9 10 1
16 9 36 1
17 9 37 1
18 10 11 1
19 10 38 1
20 10 39 1
21 11 12 1
22 11 40 1
23 11 41 1
24 12 42 1
25 12 43 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 25 1
31 15 18 2
32 15 28 1
33 16 17 Ar
34 16 30 1
35 17 29 1
36 18 27 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 33 1
42 21 24 Ar
43 21 35 1
44 22 23 Ar
45 22 31 1
46 23 32 1
47 24 34 1
48 25 26 1
49 26 46 1
50 26 47 1
51 26 48 1

***E*-1a**, opt: B3LYP/6-31G(d)/IEFPCM($CHCl_3$)
E = -1111.56233866 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.9148 0.8655 -0.5470 N
2 C2 -0.7412 0.1490 -0.2474 C
3 C3 -1.1029 -1.2935 -0.0586 C
4 N4 -2.4875 -1.2961 -0.2677 N
5 C5 -2.8874 0.0017 -0.5622 C
6 O6 -0.4486 -2.2841 0.2475 O
7 C7 0.4894 0.7336 -0.0825 C
8 C8 -3.3124 -2.4956 -0.1832 C
9 C9 -4.3121 0.3408 -0.8633 C
10 C10 -5.3018 -0.0006 0.2734 C
11 C11 -5.6220 -1.4951 0.4319 C
12 C12 -4.4472 -2.3960 0.8441 C
13 C13 0.6320 2.2129 -0.0431 C
14 C14 0.9695 5.0111 0.0350 C
15 C15 -0.2777 3.0302 0.6540 C
16 C16 1.7190 2.8301 -0.6916 C
17 C17 1.8794 4.2143 -0.6632 C
18 C18 -0.1054 4.4122 0.6972 C
19 C19 1.7362 -0.0564 0.0408 C
20 C20 4.1557 -1.4980 0.2661 C
21 C21 2.6978 0.2790 1.0172 C
22 C22 2.0328 -1.1194 -0.8251 C
23 C23 3.2259 -1.8325 -0.7283 C
24 C24 3.8801 -0.4344 1.1407 C
25 O25 5.3463 -2.1293 0.4575 O
26 C26 5.6749 -3.2282 -0.3880 C
27 H27 4.6094 -0.1847 1.9051 H
28 H28 2.5021 1.1027 1.6970 H
29 H29 3.4204 -2.6383 -1.4265 H
30 H30 1.3250 -1.3852 -1.6024 H
31 H31 2.4325 2.2171 -1.2333 H
32 H32 2.7178 4.6696 -1.1835 H
33 H33 1.0989 6.0897 0.0667 H
34 H34 -0.8121 5.0237 1.2519 H
35 H35 -1.1151 2.5726 1.1668 H
36 H36 4.9415 -4.0379 -0.2929 H
37 H37 5.7416 -2.9187 -1.4381 H
38 H38 6.6509 -3.5807 -0.0516 H
39 H39 -2.6193 -3.2955 0.0893 H
40 H40 -3.7180 -2.7319 -1.1761 H
41 H41 -4.0294 -2.0622 1.8032 H
42 H42 -4.8290 -3.4123 1.0050 H
43 H43 -6.4159 -1.5992 1.1824 H
44 H44 -6.0437 -1.8706 -0.5124 H
45 H45 -6.2377 0.5321 0.0657 H
46 H46 -4.9178 0.4042 1.2194 H
47 H47 -4.6261 -0.1779 -1.7816 H
48 H48 -4.3366 1.4132 -1.0754 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 39 1
14 8 40 1
15 9 10 1
16 9 47 1
17 9 48 1
18 10 11 1
19 10 45 1
20 10 46 1
21 11 12 1
22 11 43 1
23 11 44 1
24 12 41 1
25 12 42 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 33 1
31 15 18 Ar
32 15 35 1
33 16 17 Ar
34 16 31 1
35 17 32 1
36 18 34 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 Ar
43 21 28 1
44 22 23 Ar
45 22 30 1
46 23 29 1
47 24 27 1
48 25 26 1
49 26 36 1
50 26 37 1
51 26 38 1

***Z*-1b**, opt: B3LYP/6-31G(d)/IEFPCM($CHCl_3$)
E = -1571.15913068 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8384 0.8717 -0.5569 N
2 C2 -0.9142 -0.1470 -0.2634 C
3 C3 -1.6677 -1.4302 -0.0778 C
4 N4 -2.9982 -1.0398 -0.2735 N
5 C5 -3.0163 0.3182 -0.5645 C
6 O6 -1.3166 -2.5667 0.2162 O
7 C7 0.4305 0.0663 -0.0941 C
8 C8 -4.1276 -1.9582 -0.1807 C
9 C9 -4.2885 1.0492 -0.8524 C
10 C10 -5.3243 0.9980 0.2934 C
11 C11 -6.0530 -0.3453 0.4531 C
12 C12 -5.1791 -1.5429 0.8561 C
13 C13 0.9810 1.4463 -0.0596 C
14 C14 2.0791 4.0239 0.0016 C
15 C15 0.3227 2.4979 0.6048 C
16 C16 2.2112 1.7273 -0.6834 C
17 C17 2.7589 3.0079 -0.6677 C
18 C18 0.8657 3.7794 0.6442 C
19 C19 1.4067 -1.0401 0.0386 C
20 C20 3.3311 -3.0948 0.2783 C
21 C21 2.4114 -0.9876 1.0279 C
22 C22 1.4068 -2.1413 -0.8304 C
23 C23 2.3556 -3.1564 -0.7267 C
24 C24 3.3490 -2.0003 1.1582 C
25 O25 4.2998 -4.0296 0.4760 O
26 C26 4.3283 -5.1685 -0.3803 C
27 Cl27 2.7685 5.6454 0.0423 Cl
28 H28 -4.0095 2.0851 -1.0636 H
29 H29 -4.7444 0.6438 -1.7680 H
30 H30 -6.0729 1.7744 0.0946 H
31 H31 -4.8337 1.2744 1.2364 H
32 H32 -6.5699 -0.5835 -0.4884 H
33 H33 -6.8389 -0.2220 1.2092 H
34 H34 -5.8319 -2.4096 1.0204 H
35 H35 -4.6758 -1.3436 1.8116 H
36 H36 -3.6857 -2.9212 0.0876 H
37 H37 -4.5911 -2.0702 -1.1701 H
38 H38 2.4434 -0.1457 1.7130 H
39 H39 4.1099 -1.9647 1.9316 H
40 H40 0.6611 -2.1993 -1.6156 H
41 H41 2.3273 -3.9819 -1.4283 H
42 H42 5.1653 -5.7778 -0.0363 H
43 H43 4.4940 -4.8787 -1.4250 H
44 H44 3.4001 -5.7475 -0.3054 H
45 H45 2.7410 0.9353 -1.2023 H
46 H46 3.7004 3.2123 -1.1660 H
47 H47 -0.6213 2.3074 1.0996 H
48 H48 0.3543 4.5782 1.1706 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 36 1
14 8 37 1
15 9 10 1
16 9 28 1
17 9 29 1
18 10 11 1
19 10 30 1
20 10 31 1
21 11 12 1
22 11 32 1
23 11 33 1
24 12 34 1
25 12 35 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 27 1
31 15 18 Ar
32 15 47 1
33 16 17 Ar
34 16 45 1
35 17 46 1
36 18 48 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 Ar
43 21 38 1
44 22 23 Ar
45 22 40 1
46 23 41 1
47 24 39 1
48 25 26 1
49 26 42 1
50 26 43 1
51 26 44 1

***E*-1b**, opt: B3LYP/6-31G(d)/IEFPCM($CHCl_3$)
E = -1571.15940955 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8482 0.8686 -0.5530 N
2 C2 -0.9087 -0.1443 -0.2914 C
3 C3 -1.6445 -1.4364 -0.1049 C
4 N4 -2.9826 -1.0598 -0.2763 N
5 C5 -3.0200 0.3016 -0.5476 C
6 O6 -1.2736 -2.5712 0.1716 O
7 C7 0.4407 0.0641 -0.1589 C
8 C8 -4.1001 -1.9917 -0.1755 C
9 C9 -4.3051 1.0222 -0.8030 C
10 C10 -5.3192 0.9442 0.3605 C
11 C11 -6.0309 -0.4088 0.5148 C
12 C12 -5.1374 -1.6023 0.8856 C
13 C13 1.0347 1.4164 -0.1274 C
14 C14 2.2251 3.9850 -0.0763 C
15 C15 2.3191 1.6430 -0.6724 C
16 C16 0.3771 2.5169 0.4533 C
17 C17 0.9577 3.7823 0.4886 C
18 C18 2.9005 2.9005 -0.6598 C
19 C19 1.3881 -1.0816 -0.0565 C
20 C20 3.2333 -3.1745 0.1199 C
21 C21 1.4222 -2.0934 -1.0285 C
22 C22 2.3128 -1.1395 0.9993 C
23 C23 3.2274 -2.1861 1.1024 C
24 C24 2.3420 -3.1363 -0.9518 C
25 O25 2.8795 5.1764 -0.1041 O
26 C26 2.2398 6.3167 0.4639 C
27 Cl27 4.3982 -4.4938 0.2286 Cl
28 H28 -3.6428 -2.9532 0.0717 H
29 H29 -4.5801 -2.0957 -1.1577 H
30 H30 -5.7779 -2.4783 1.0491 H
31 H31 -4.6195 -1.4107 1.8348 H
32 H32 -6.8043 -0.3039 1.2863 H
33 H33 -6.5623 -0.6397 -0.4205 H
34 H34 -6.0794 1.7152 0.1858 H
35 H35 -4.8145 1.2130 1.2981 H
36 H36 -4.0414 2.0639 -1.0051 H
37 H37 -4.7730 0.6239 -1.7157 H
38 H38 -0.6037 2.3767 0.8890 H
39 H39 0.4201 4.5971 0.9595 H
40 H40 2.8582 0.8201 -1.1304 H
41 H41 3.8801 3.0694 -1.0960 H
42 H42 1.2939 6.5378 -0.0448 H
43 H43 2.9321 7.1474 0.3207 H
44 H44 2.0539 6.1775 1.5356 H
45 H45 3.9275 -2.2296 1.9298 H
46 H46 2.3109 -0.3614 1.7566 H
47 H47 0.7269 -2.0585 -1.8607 H
48 H48 2.3661 -3.9087 -1.7130 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 28 1
14 8 29 1
15 9 10 1
16 9 36 1
17 9 37 1
18 10 11 1
19 10 34 1
20 10 35 1
21 11 12 1
22 11 32 1
23 11 33 1
24 12 30 1
25 12 31 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 25 1
31 15 18 2
32 15 40 1
33 16 17 Ar
34 16 38 1
35 17 39 1
36 18 41 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 27 1
42 21 24 Ar
43 21 47 1
44 22 23 Ar
45 22 46 1
46 23 45 1
47 24 48 1
48 25 26 1
49 26 42 1
50 26 43 1
51 26 44 1

For empirical:

***Z*-1a**, opt: B3LYP/6-31G(d)
E = -1111.55342 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
M0001
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 1.135610508 -1.163620412 -0.498082450 N.2 1 M0001
2 C2 0.765282873 0.171217881 -0.255286647 C.2 1 M0001
3 C3 2.010893925 0.997380877 -0.137170630 C.2 1 M0001
4 N4 3.029697021 0.044358078 -0.322831187 N.am 1 M0001

```
      5 C5          2.434328263   -1.190434994   -0.539051616 C.2     1 M0001
      6 O6          2.212540178    2.179936137    0.093686819 O.2     1 M0001
      7 C7         -0.528567992    0.593704512   -0.085401275 C.2     1 M0001
      8 C8          4.446276040    0.371232937   -0.271483850 C.3     1 M0001
      9 C9          3.240529452   -2.425699676   -0.784087998 C.3     1 M0001
     10 C10         4.208852039   -2.783770290    0.364804789 C.3     1 M0001
     11 C11         5.462923653   -1.899301823    0.464017602 C.3     1 M0001
     12 C12         5.224514243   -0.415903542    0.791182529 C.3     1 M0001
     13 C13        -1.663977709   -0.350953680   -0.012355580 C.ar    1 M0001
     14 C14        -3.886375528   -2.098082352    0.120519098 C.ar    1 M0001
     15 C15        -1.550473179   -1.638694949    0.558466590 C.ar    1 M0001
     16 C16        -2.926476126    0.027220395   -0.503116754 C.ar    1 M0001
     17 C17        -4.025133961   -0.828970968   -0.453949414 C.ar    1 M0001
     18 C18        -2.639031354   -2.491122211    0.631171263 C.ar    1 M0001
     19 C19        -0.859115629    2.042541177    0.023905192 C.ar    1 M0001
     20 C20        -1.559774981    4.759550580    0.230875404 C.ar    1 M0001
     21 C21        -0.447588344    2.965322871   -0.949830243 C.ar    1 M0001
     22 C22        -1.639628831    2.504602415    1.097362519 C.ar    1 M0001
     23 C23        -1.975733821    3.852663903    1.207313239 C.ar    1 M0001
     24 C24        -0.799950718    4.309304753   -0.850729633 C.ar    1 M0001
     25 O25        -4.889614196   -3.012635644    0.234854404 O.3     1 M0001
     26 C26        -6.172805505   -2.671179212   -0.266214999 C.3     1 M0001
     27 H27        -2.551614173   -3.473962599    1.083920854 H       1 M0001
     28 H28        -0.593239510   -1.961895056    0.945460874 H       1 M0001
     29 H29        -4.974145131   -0.498345252   -0.860317981 H       1 M0001
     30 H30        -3.049723026    1.008116664   -0.950367366 H       1 M0001
     31 H31        -1.973399658    1.799439636    1.853168859 H       1 M0001
     32 H32        -2.566268148    4.193129622    2.053919534 H       1 M0001
     33 H33        -1.828838895    5.809595536    0.310164890 H       1 M0001
     34 H34        -0.476385895    5.007098578   -1.618493035 H       1 M0001
     35 H35         0.145998171    2.621727300   -1.790884469 H       1 M0001
     36 H36         2.522066953   -3.235084788   -0.939899531 H       1 M0001
     37 H37         3.814069622   -2.316677964   -1.717380913 H       1 M0001
     38 H38         4.531669442   -3.822017128    0.217456517 H       1 M0001
     39 H39         3.659098074   -2.763138194    1.315667633 H       1 M0001
     40 H40         6.021088745   -1.967797968   -0.482553033 H       1 M0001
     41 H41         6.121736113   -2.321103287    1.234145215 H       1 M0001
     42 H42         4.706292248   -0.315984189    1.754342798 H       1 M0001
     43 H43         6.200552642    0.072897047    0.910598274 H       1 M0001
     44 H44         4.899224519    0.219825993   -1.261546949 H       1 M0001
     45 H45         4.477181510    1.442760774   -0.054151993 H       1 M0001
     46 H46        -6.587720622   -1.795414552    0.249991617 H       1 M0001
     47 H47        -6.808544794   -3.537609637   -0.075257187 H       1 M0001
     48 H48        -6.143459618   -2.472899755   -1.345556449 H       1 M0001

@<TRIPOS>BOND
     1    1    2    1
     2    1    5    2
     3    2    3    1
     4    3    4   am
     5    4    5    1
     6    3    6    2
     7    2    7    2
     8    4    8    1
     9    5    9    1
    10    9   10    1
    11   10   11    1
    12   11   12    1
    13   12    8    1
    14   13   16   ar
    15   16   17   ar
    16   14   17   ar
    17   14   18   ar
    18   15   18   ar
    19   13   15   ar
    20    7   13    1
    21   19   22   ar
    22   22   23   ar
    23   20   23   ar
    24   20   24   ar
    25   21   24   ar
    26   19   21   ar
    27    7   19    1
    28   14   25    1
    29   25   26    1
    30   18   27    1
    31   15   28    1
    32   17   29    1
    33   16   30    1
    34   22   31    1
    35   23   32    1
    36   20   33    1
    37   24   34    1
    38   21   35    1
    39    9   36    1
    40    9   37    1
    41   10   38    1
    42   10   39    1
    43   11   40    1
    44   11   41    1
    45   12   42    1
    46   12   43    1
    47    8   44    1
    48    8   45    1
    49   26   46    1
    50   26   47    1
    51   26   48    1
```

***E*-1a**, opt:B3LYP/6-31G(d)
E = -1111.55322 A.U.
No imaginary frequencies

```
@<TRIPOS>MOLECULE
M0002
48 51
SMALL
NO_CHARGES


@<TRIPOS>ATOM
      1 N1          1.920322120   -0.856765491   -0.556506050 N.2     1 M0002
      2 C2          0.739482248   -0.139814858   -0.291216052 C.2     1 M0002
      3 C3          1.088831166    1.310400037   -0.132689862 C.2     1 M0002
      4 N4          2.483751996    1.310759190   -0.306581558 N.am    1 M0002
      5 C5          2.889972679    0.007493252   -0.565903237 C.2     1 M0002
      6 O6          0.430293359    2.308849071    0.120541039 O.2     1 M0002
      7 C7         -0.485348294   -0.732670249   -0.114047211 C.2     1 M0002
      8 C8          3.297959447    2.511607836   -0.198038652 C.3     1 M0002
      9 C9          4.321876936   -0.339688748   -0.822363878 C.3     1 M0002
     10 C10         5.276910343    0.014496271    0.339057422 C.3     1 M0002
     11 C11         5.589723933    1.511588184    0.493095344 C.3     1 M0002
     12 C12         4.401071793    2.415184372    0.863929790 C.3     1 M0002
     13 C13        -0.612770838   -2.212971675   -0.057295328 C.ar    1 M0002
     14 C14        -0.925536355   -5.011589817    0.049532372 C.ar    1 M0002
     15 C15         0.315571715   -
```

3.016355166 0.630267127 C.ar 1 M0002
16 C16 -1.704453488 -2.844325238 -0.683094157 C.ar 1 M0002
17 C17 -1.852916838 -4.228881227 -0.640442938 C.ar 1 M0002
18 C18 0.155058698 -4.398643293 0.687694352 C.ar 1 M0002
19 C19 -1.737988838 0.046067577 0.018648494 C.ar 1 M0002
20 C20 -4.159877383 1.474121110 0.286044332 C.ar 1 M0002
21 C21 -2.688984166 -0.304254801 1.000196357 C.ar 1 M0002
22 C22 -2.047797238 1.116698486 -0.831597077 C.ar 1 M0002
23 C23 -3.242927430 1.822322471 -0.713693888 C.ar 1 M0002
24 C24 -3.872611784 0.401886309 1.144536860 C.ar 1 M0002
25 O25 -5.349660959 2.103432461 0.499434847 O.3 1 M0002
26 C26 -5.686177974 3.204678200 -0.330399520 C.3 1 M0002
27 H27 -4.594097503 0.142601860 1.912961706 H 1 M0002
28 H28 -2.481751347 -1.134329974 1.668666473 H 1 M0002
29 H29 -3.444843544 2.636544871 -1.399786029 H 1 M0002
30 H30 -1.348330309 1.398724666 -1.610251328 H 1 M0002
31 H31 -2.430868339 -2.240064662 -1.217143046 H 1 M0002
32 H32 -2.695794557 -4.695893908 -1.143240573 H 1 M0002
33 H33 -1.045379998 -6.091096921 0.092594864 H 1 M0002
34 H34 0.876909847 -5.000100632 1.234123873 H 1 M0002
35 H35 1.159558270 -2.546948646 1.120040745 H 1 M0002
36 H36 -4.945553229 4.010773159 -0.249575371 H 1 M0002
37 H37 -5.777194958 2.903606331 -1.382535354 H 1 M0002
38 H38 -6.653094804 3.563697882 0.026776302 H 1 M0002
39 H39 2.590535841 3.306286998 0.055644172 H 1 M0002
40 H40 3.734217754 2.757711798 -1.176806125 H 1 M0002
41 H41 3.952373341 2.081851075 1.809108440 H 1 M0002
42 H42 4.779169918 3.431211245 1.037624601 H 1 M0002
43 H43 6.363720387 1.625356451 1.263092392 H 1 M0002
44 H44 6.035640177 1.879875382 -0.443178845 H 1 M0002
45 H45 6.220648103 -0.518898701 0.169300103 H 1 M0002
46 H46 4.863062921 -0.380271187 1.276863591 H 1 M0002
47 H47 4.667461258 0.164372914 -1.737969206 H 1 M0002
48 H48 4.345622767 -1.415312343 -1.017829111 H 1 M0002

@<TRIPOS>BOND

1	1	2	1
2	1	5	2
3	2	3	1
4	3	4	am
5	4	5	1
6	3	6	2
7	2	7	2
8	4	8	1
9	5	9	1
10	9	10	1
11	10	11	1
12	11	12	1
13	12	8	1
14	13	16	ar
15	16	17	ar
16	14	17	ar
17	14	18	ar
18	15	18	ar
19	13	15	ar
20	7	13	1
21	19	22	ar
22	22	23	ar
23	20	23	ar
24	20	24	ar
25	21	24	ar
26	19	21	ar
27	7	19	1
28	20	25	1
29	25	26	1
30	24	27	1
31	21	28	1
32	23	29	1
33	22	30	1
34	16	31	1
35	17	32	1
36	14	33	1
37	18	34	1
38	15	35	1
39	26	36	1
40	26	37	1
41	26	38	1
42	8	39	1
43	8	40	1
44	12	41	1
45	12	42	1
46	11	43	1
47	11	44	1
48	10	45	1
49	10	46	1
50	9	47	1
51	9	48	1

***Z*-1b**, opt: B3LYP/6-31G(d)
E = -1571.14997 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
M0002
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 1.828850030 -0.902879080 -0.513578022 N.2 1 M0002
2 C2 0.913536931 0.130665473 -0.248283112 C.2 1 M0002
3 C3 1.675613004 1.414347543 -0.098074671 C.2 1 M0002
4 N4 3.007697112 1.003249490 -0.281176563 N.am 1 M0002
5 C5 3.010364841 -0.361706431 -0.535569243 C.2 1 M0002
6 O6 1.340975419 2.562487607 0.152847533 O.2 1 M0002
7 C7 -0.433410102 -0.069026111 -0.080107024 C.2 1 M0002
8 C8 4.139527321 1.915693281 -0.209880474 C.3 1 M0002
9 C9 4.271594745 -1.116545022 -0.811366585 C.3 1 M0002
10 C10 5.321238462 -1.045767800 0.320557367 C.3 1 M0002
11 C11 6.057444554 0.298263679 0.446176218 C.3 1 M0002
12 C12 5.193434666 1.511538315 0.828054074 C.3 1 M0002
13 C13 -1.000703967 -1.441418615 -0.044395159 C.ar 1 M0002
14 C14 -2.131563942 -4.007444201 -0.005571707 C.ar 1 M0002
15 C15 -0.346920104 -2.511464765 0.594362674 C.ar 1 M0002
16 C16 -2.243606640 -1.698348403 -0.653131941 C.ar 1 M0002
17 C17 -2.806739909 -2.971528859 -0.648272403 C.ar 1 M0002
18 C18 -0.906593389 -3.785459198 0.622628780 C.ar 1 M0002
19 C19 -1.395814283 1.050204191 0.045937782 C.ar 1 M0002
20 C20 -3.286373956 3.135289225 0.281548796 C.ar 1 M0002
21 C21 -2.403582631 1.014932319 1.032471845 C.ar 1 M0002
22 C22 -1.375965842 2.150435767 -0.822279604 C.ar 1 M0002
23 C23 -2.308219546 3.180042258 -0.719769848 C.ar 1 M0002
24 C24 -3.325408833 2.041981963 1.160738684 C.ar 1 M0002
25 O25 -4.240600960 4.087632595 0.475182443 O.3 1

M0002
26 C26 -4.241566269 5.222855956 -0.377432926 C.3 1 M0002
27 Cl27 -2.839368953 -5.618415436 0.018936898 Cl 1 M0002
28 H28 3.973849533 -2.153907749 -0.987304086 H 1 M0002
29 H29 4.724168467 -0.747960763 -1.744634907 H 1 M0002
30 H30 6.064962556 -1.829620775 0.131446792 H 1 M0002
31 H31 4.838819690 -1.300276219 1.273985372 H 1 M0002
32 H32 6.568861668 0.513213547 -0.504549897 H 1 M0002
33 H33 6.849557964 0.189824363 1.198269518 H 1 M0002
34 H34 5.856092198 2.374700449 0.974442705 H 1 M0002
35 H35 4.692617400 1.335475627 1.789536259 H 1 M0002
36 H36 3.701044085 2.884657515 0.044993101 H 1 M0002
37 H37 4.601949380 2.012367843 -1.202591679 H 1 M0002
38 H38 -2.450340637 0.173140787 1.716966258 H 1 M0002
39 H39 -4.089227748 2.020752303 1.931720970 H 1 M0002
40 H40 -0.626558186 2.200743944 -1.604244084 H 1 M0002
41 H41 -2.258886027 4.006285628 -1.419478561 H 1 M0002
42 H42 -5.071880378 5.846957761 -0.042195323 H 1 M0002
43 H43 -4.401200902 4.939337620 -1.425989936 H 1 M0002
44 H44 -3.304732209 5.788949956 -0.295170101 H 1 M0002
45 H45 -2.769569730 -0.890851121 -1.151650381 H 1 M0002
46 H46 -3.757876759 -3.158866101 -1.135284465 H 1 M0002
47 H47 0.609625897 -2.340369914 1.071199674 H 1 M0002
48 H48 -0.398540403 -4.600290165 1.127598659 H 1 M0002

@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 3 4 am
5 4 5 1
6 3 6 2
7 2 7 2
8 4 8 1
9 5 9 1
10 9 10 1
11 10 11 1
12 11 12 1
13 12 8 1
14 13 16 ar
15 16 17 ar
16 14 17 ar
17 14 18 ar
18 15 18 ar
19 13 15 ar
20 7 13 1
21 19 22 ar
22 22 23 ar
23 20 23 ar
24 20 24 ar
25 21 24 ar
26 19 21 ar
27 7 19 1
28 20 25 1
29 25 26 1
30 14 27 1
31 9 28 1
32 9 29 1
33 10 30 1
34 10 31 1
35 11 32 1
36 11 33 1
37 12 34 1
38 12 35 1
39 8 36 1
40 8 37 1
41 21 38 1
42 24 39 1
43 22 40 1
44 23 41 1
45 26 42 1
46 26 43 1
47 26 44 1
48 16 45 1
49 17 46 1
50 15 47 1
51 18 48 1

***E*-1b**, opt: B3LYP/6-31G(d)
E = -1571.15019 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
M0001
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 1.838541313 -0.924231744 -0.546200076 N.2 1 M0001
2 C2 0.915970382 0.110614869 -0.316296679 C.2 1 M0001
3 C3 1.671463218 1.395328363 -0.153340412 C.2 1 M0001
4 N4 3.009472608 0.985388366 -0.297485873 N.am 1 M0001
5 C5 3.020147260 -0.381318055 -0.537106693 C.2 1 M0001
6 O6 1.325465164 2.542982132 0.082274457 O.2 1 M0001
7 C7 -0.437353056 -0.068289948 -0.182980662 C.2 1 M0001
8 C8 4.138722402 1.897371128 -0.189746142 C.3 1 M0001
9 C9 4.289687316 -1.138913111 -0.761750286 C.3 1 M0001
10 C10 5.294966349 -1.060210357 0.409614137 C.3 1 M0001
11 C11 6.027523774 0.284235374 0.552912863 C.3 1 M0001
12 C12 5.151096269 1.500820979 0.892286799 C.3 1 M0001
13 C13 -1.069390126 -1.402697201 -0.142570203 C.ar 1 M0001
14 C14 -2.350192634 -3.926532145 -0.064188758 C.ar 1 M0001
15 C15 -2.385861849 -1.576976832 -0.627353847 C.ar 1 M0001
16 C16 -0.423551262 -2.535469376 0.386182698 C.ar 1 M0001
17 C17 -1.048847102 -3.778665986 0.433884878 C.ar 1 M0001
18 C18 -3.012809053 -2.811640788 -0.599806591 C.ar 1 M0001
19 C19 -1.351170245 1.104564883 -0.074606100 C.ar 1 M0001
20 C20 -3.129064708 3.254661530 0.131330939 C.ar 1 M0001
21 C21 -1.377717831 2.111071397 -1.051084387 C.ar 1 M0001
22 C22 -2.246511973 1.199147680 1.003104882 C.ar 1 M0001
23 C23 -3.126111642 2.272871133 1.120562612 C.ar 1 M0001
24 C24 -2.264585683 3.180378337 -0.959784221 C.ar 1 M0001
25 O25 -3.051763152 -5.093027827 -0.068430495 O.3 1 M0001
26 C26 -2.426050391 -6.258945517 0.446850927 C.3 1 M0001
27 Cl27 -4.250336017 4.605918717 0.256682363 Cl 1 M0001
28 H28 3.691654068 2.868966550 0.039130302 H 1 M0001
29 H29 4.640033157 1.984732557 -1.164122071 H 1 M0001
30 H30 5.807972368 2.364838192 1.057567061 H 1 M0001
31 H31 4.612838562 1.332020289 1.834548457 H 1 M0001
32 H32 6.790279866 0.180087173 1.335390007 H 1 M0001
33 H33 6.575120860 0.491264461 -0.379306939 H 1 M0001
34 H34 6.044975776 -1.846298206 0.257404936 H 1 M0001
35 H35 4.775024942 -1.305714716 1.345573658 H 1 M0001

```
     36      H36              3.998068380      -
2.177483007      -0.940999969      H     1
M0001
     37      H37              4.778114199      -
0.777236649      -1.679434635      H     1
M0001
     38      H38              0.585828617      -
2.438920683       0.763715597      H     1
M0001
     39      H39             -0.515698522      -
4.619647082       0.862548026      H     1
M0001
     40      H40             -2.915906244      -
0.728611354      -1.047431474      H     1
M0001
     41      H41             -4.018963550      -
2.940709762      -0.986319301      H     1
M0001
     42      H42             -1.520507242      -
6.512716572      -0.119103724      H     1
M0001
     43      H43             -3.157040995      -
7.062173903       0.338856261      H     1
M0001
     44      H44             -2.168399048      -
6.143208638       1.507757617      H     1
M0001
     45      H45             -3.803704405
2.345592127       1.964635628      H     1
M0001
     46      H46             -2.247666765
0.425952597       1.765643486      H     1
M0001
     47      H47             -0.701296077
2.052204928      -1.897489983      H     1
M0001
     48      H48             -2.282885690
3.950274579      -1.723807684      H     1
M0001


@<TRIPOS>BOND
     1     1     2     1
     2     1     5     2
     3     2     3     1
     4     3     4    am
     5     4     5     1
     6     3     6     2
     7     2     7     2
     8     4     8     1
     9     5     9     1
    10     9    10     1
    11    10    11     1
    12    11    12     1
    13    12     8     1
    14    13    16    ar
    15    16    17    ar
    16    14    17    ar
    17    14    18    ar
    18    15    18    ar
    19    13    15    ar
    20     7    13     1
    21    19    22    ar
    22    22    23    ar
    23    20    23    ar
    24    20    24    ar
    25    21    24    ar
    26    19    21    ar
    27     7    19     1
    28    14    25     1
    29    25    26     1
    30    20    27     1
    31     8    28     1
    32     8    29     1
    33    12    30     1
    34    12    31     1
    35    11    32     1
    36    11    33     1
    37    10    34     1
    38    10    35     1
    39     9    36     1
    40     9    37     1
    41    16    38     1
    42    17    39     1
    43    15    40     1
    44    18    41     1
    45    26    42     1
    46    26    43     1
    47    26    44     1
    48    23    45     1
    49    22    46     1
    50    21    47     1
    51    24    48     1
```

For the UV-vis study:

***Z*-1a**, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1111.56592336 A.U.
No imaginary frequencies

```
@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 N1       1.1410      -1.1561      -0.5216 N
2 C2       0.7621       0.1682      -0.2365 C
3 C3       2.0026       0.9906      -0.0727 C
4 N4       3.0248       0.0585      -0.2860 N
5 C5       2.4427      -1.1729      -0.5549 C
6 O6       2.1869       2.1671       0.2222 O
7 C7      -0.5332       0.5889      -0.0710 C
8 C8       4.4449       0.3872      -0.2176 C
9 C9       3.2620      -2.3875      -0.8507 C
10 C10       4.2322      -2.7911       0.2826 C
11 C11       5.4776      -1.9018       0.4199 C
12 C12       5.2221      -0.4388       0.8151 C
13 C13      -1.6692      -0.3525      -0.0000 C
14 C14      -3.8908      -2.1036       0.1343 C
15 C15      -1.5571      -1.6344       0.5856 C
16 C16      -2.9310       0.0196      -0.5005 C
17 C17      -4.0285      -0.8379      -0.4515 C
18 C18      -2.6443      -2.4894       0.6574 C
19 C19      -0.8596       2.0405       0.0202 C
20 C20      -1.5549       4.7624       0.1685 C
21 C21      -0.4807       2.9331      -0.9956 C
22 C22      -1.6060       2.5324       1.1047 C
23 C23      -1.9385       3.8848       1.1854 C
24 C24      -0.8305       4.2806      -0.9253 C
25 O25      -4.8904      -3.0174       0.2501 O
26 C26      -6.1812      -2.6819      -0.2572 C
27 H27      -2.5558      -3.4665       1.1227 H
28 H28      -0.6048      -1.9499       0.9921 H
29 H29      -4.9754      -0.5122      -0.8659 H
30 H30      -3.0562       0.9959      -0.9571 H
31 H31      -1.9153       1.8509       1.8920 H
32 H32      -2.5026       4.2509       2.0389 H
33 H33      -1.8238       5.8138       0.2246 H
34 H34      -0.5377       4.9553      -1.7253 H
35 H35       0.0816       2.5612      -1.8467 H
36 H36       2.5552      -3.1984      -1.0475 H
37 H37       3.8356      -2.2266      -1.7755 H
38 H38       4.5619      -3.8176       0.0821 H
39 H39       3.6838      -2.8211       1.2337 H
40 H40       6.0338      -1.9206      -0.5291 H
41 H41       6.1399      -2.3509       1.1709 H
42 H42       4.6959      -0.3900       1.7779 H
43 H43       6.1909       0.0553       0.9612 H
44 H44       4.8947       0.2746      -1.2128 H
45 H45       4.4766       1.4488       0.0405 H
46 H46      -6.5934      -1.8031       0.2524 H
47 H47      -6.8131      -3.5481      -0.0565 H
48 H48      -6.1488      -2.4961      -1.3372 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 44 1
14 8 45 1
15 9 10 1
16 9 36 1
17 9 37 1
18 10 11 1
19 10 38 1
20 10 39 1
21 11 12 1
22 11 40 1
23 11 41 1
24 12 42 1
25 12 43 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 25 1
31 15 18 2
32 15 28 1
33 16 17 Ar
34 16 30 1
35 17 29 1
36 18 27 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 33 1
42 21 24 Ar
43 21 35 1
44 22 23 Ar
45 22 31 1
46 23 32 1
47 24 34 1
48 25 26 1
49 26 46 1
50 26 47 1
51 26 48 1
```

***E*-1a**, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1111.56549073 A.U.
No imaginary frequencies

```
@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 N1      -1.9136       0.8581      -0.5605 N
2 C2      -0.7408       0.1424      -0.2545 C
3 C3      -1.1039      -1.2986      -0.0611 C
4 N4      -2.4865      -1.3022      -0.2714 N
5 C5      -2.8866      -0.0062      -0.5725 C
6 O6      -0.4487      -2.2877       0.2525 O
7 C7       0.4885       0.7278      -0.0844 C
8 C8      -3.3140      -2.5007      -0.1796 C
9 C9      -4.3116       0.3306      -0.8737 C
10 C10      -5.2978      -0.0013       0.2694 C
11 C11      -5.6194      -1.4941       0.4396 C
12 C12      -4.4442      -2.3943       0.8519 C
13 C13       0.6258       2.2075      -0.0417 C
14 C14       0.9462       5.0072       0.0379 C
15 C15      -0.2765       3.0163       0.6746 C
16 C16       1.6978       2.8326      -0.7073 C
17 C17       1.8492       4.2180      -0.6785 C
18 C18      -0.1127       4.3997       0.7184 C
19 C19       1.7378      -0.0574       0.0413 C
```

20 C20 4.1649 -1.4867 0.2687 C
21 C21 2.6963 0.2825 1.0194 C
22 C22 2.0413 -1.1183 -0.8255 C
23 C23 3.2378 -1.8260 -0.7272 C
24 C24 3.8821 -0.4252 1.1442 C
25 O25 5.3581 -2.1115 0.4612 O
26 C26 5.6987 -3.2033 -0.3911 C
27 H27 4.6089 -0.1711 1.9096 H
28 H28 2.4960 1.1048 1.6995 H
29 H29 3.4387 -2.6288 -1.4270 H
30 H30 1.3366 -1.3865 -1.6051 H
31 H31 2.4054 2.2254 -1.2632 H
32 H32 2.6750 4.6803 -1.2124 H
33 H33 1.0688 6.0864 0.0696 H
34 H34 -0.8127 5.0053 1.2878 H
35 H35 -1.1005 2.5513 1.2028 H
36 H36 4.9725 -4.0198 -0.3018 H
37 H37 5.7642 -2.8863 -1.4387 H
38 H38 6.6771 -3.5486 -0.0546 H
39 H39 -2.6220 -3.3013 0.0933 H
40 H40 -3.7228 -2.7387 -1.1703 H
41 H41 -4.0224 -2.0560 1.8077 H
42 H42 -4.8265 -3.4093 1.0188 H
43 H43 -6.4091 -1.5914 1.1953 H
44 H44 -6.0465 -1.8753 -0.4999 H
45 H45 -6.2333 0.5312 0.0601 H
46 H46 -4.9101 0.4099 1.2111 H
47 H47 -4.6277 -0.1959 -1.7863 H
48 H48 -4.3376 1.4013 -1.0941 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 39 1
14 8 40 1
15 9 10 1
16 9 47 1
17 9 48 1
18 10 11 1
19 10 45 1
20 10 46 1
21 11 12 1
22 11 43 1
23 11 44 1
24 12 41 1
25 12 42 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 33 1
31 15 18 Ar
32 15 35 1
33 16 17 Ar
34 16 31 1
35 17 32 1
36 18 34 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 Ar
43 21 28 1
44 22 23 Ar
45 22 30 1
46 23 29 1
47 24 27 1
48 25 26 1
49 26 36 1
50 26 37 1
51 26 38 1

***Z*-1b**, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1571.16209066 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8362 0.8736 -0.5636 N
2 C2 -0.9133 -0.1432 -0.2602 C
3 C3 -1.6686 -1.4241 -0.0664 C
4 N4 -2.9968 -1.0358 -0.2700 N
5 C5 -3.0145 0.3198 -0.5713 C
6 O6 -1.3177 -2.5580 0.2421 O
7 C7 0.4312 0.0687 -0.0898 C
8 C8 -4.1289 -1.9518 -0.1722 C
9 C9 -4.2859 1.0479 -0.8688 C
10 C10 -5.3233 1.0089 0.2764 C
11 C11 -6.0529 -0.3323 0.4481 C
12 C12 -5.1797 -1.5269 0.8613 C
13 C13 0.9855 1.4468 -0.0562 C
14 C14 2.0898 4.0212 0.0031 C
15 C15 0.3303 2.5001 0.6091 C
16 C16 2.2161 1.7242 -0.6811 C
17 C17 2.7670 3.0036 -0.6664 C
18 C18 0.8765 3.7804 0.6475 C
19 C19 1.4038 -1.0412 0.0419 C
20 C20 3.3169 -3.1069 0.2771 C
21 C21 2.3995 -1.0026 1.0405 C
22 C22 1.4077 -2.1323 -0.8399 C
23 C23 2.3506 -3.1535 -0.7381 C
24 C24 3.3312 -2.0215 1.1689 C
25 O25 4.2788 -4.0482 0.4744 O
26 C26 4.3160 -5.1756 -0.3988 C
27 Cl27 2.7833 5.6415 0.0421 Cl
28 H28 -4.0073 2.0819 -1.0899 H
29 H29 -4.7401 0.6329 -1.7807 H
30 H30 -6.0707 1.7836 0.0678 H
31 H31 -4.8339 1.2945 1.2172 H
32 H32 -6.5702 -0.5785 -0.4910 H
33 H33 -6.8379 -0.2017 1.2037 H
34 H34 -5.8331 -2.3918 1.0320 H
35 H35 -4.6765 -1.3199 1.8152 H
36 H36 -3.6899 -2.9141 0.1026 H
37 H37 -4.5908 -2.0681 -1.1613 H
38 H38 2.4291 -0.1681 1.7347 H
39 H39 4.0851 -1.9965 1.9497 H
40 H40 0.6698 -2.1773 -1.6337 H
41 H41 2.3267 -3.9699 -1.4503 H
42 H42 5.1477 -5.7911 -0.0534 H
43 H43 4.4946 -4.8703 -1.4366 H
44 H44 3.3861 -5.7536 -0.3433 H
45 H45 2.7436 0.9310 -1.2006 H
46 H46 3.7085 3.2049 -1.1658 H
47 H47 -0.6125 2.3119 1.1073 H
48 H48 0.3679 4.5802 1.1752 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 36 1
14 8 37 1
15 9 10 1
16 9 28 1
17 9 29 1
18 10 11 1
19 10 30 1
20 10 31 1
21 11 12 1
22 11 32 1
23 11 33 1
24 12 34 1
25 12 35 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 27 1
31 15 18 Ar
32 15 47 1
33 16 17 Ar
34 16 45 1
35 17 46 1
36 18 48 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 Ar
43 21 38 1
44 22 23 Ar
45 22 40 1
46 23 41 1
47 24 39 1
48 25 26 1
49 26 42 1
50 26 43 1
51 26 44 1

***E*-1b**, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1571.16242638 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
48 51
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8438 0.8780 -0.5609 N
2 C2 -0.9081 -0.1356 -0.2889 C
3 C3 -1.6486 -1.4227 -0.0911 C
4 N4 -2.9837 -1.0452 -0.2702 N
5 C5 -3.0176 0.3138 -0.5540 C
6 O6 -1.2796 -2.5553 0.2018 O
7 C7 0.4421 0.0668 -0.1579 C
8 C8 -4.1059 -1.9721 -0.1635 C
9 C9 -4.3002 1.0344 -0.8206 C
10 C10 -5.3168 0.9722 0.3419 C
11 C11 -6.0326 -0.3769 0.5090 C
12 C12 -5.1429 -1.5691 0.8926 C
13 C13 1.0444 1.4149 -0.1285 C
14 C14 2.2521 3.9756 -0.0751 C
15 C15 2.3307 1.6328 -0.6730 C
16 C16 0.3939 2.5196 0.4528 C
17 C17 0.9826 3.7813 0.4888 C
18 C18 2.9203 2.8867 -0.6595 C
19 C19 1.3814 -1.0858 -0.0570 C
20 C20 3.2061 -3.1960 0.1150 C
21 C21 1.4145 -2.0884 -1.0388 C
22 C22 2.2970 -1.1606 1.0055 C
23 C23 3.2015 -2.2165 1.1065 C
24 C24 2.3245 -3.1405 -0.9641 C
25 O25 2.9146 5.1619 -0.1007 O
26 C26 2.2847 6.3060 0.4741 C
27 Cl27 4.3576 -4.5279 0.2220 Cl
28 H28 -3.6538 -2.9337 0.0923 H
29 H29 -4.5837 -2.0811 -1.1458 H
30 H30 -5.7860 -2.4417 1.0632 H
31 H31 -4.6256 -1.3695 1.8406 H
32 H32 -6.8058 -0.2620 1.2792 H
33 H33 -6.5638 -0.6157 -0.4242 H
34 H34 -6.0739 1.7434 0.1564 H

35 H35 -4.8133 1.2498 1.2777 H
36 H36 -4.0345 2.0734 -1.0339 H
37 H37 -4.7667 0.6262 -1.7293 H
38 H38 -0.5869 2.3856 0.8909 H
39 H39 0.4509 4.5991 0.9610 H
40 H40 2.8648 0.8068 -1.1312 H
41 H41 3.9016 3.0483 -1.0949 H
42 H42 1.3407 6.5372 -0.0329 H
43 H43 2.9843 7.1310 0.3344 H
44 H44 2.0989 6.1622 1.5450 H
45 H45 3.8944 -2.2730 1.9391 H
46 H46 2.2960 -0.3897 1.7701 H
47 H47 0.7270 -2.0391 -1.8768 H
48 H48 2.3486 -3.9052 -1.7330 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 28 1
14 8 29 1
15 9 10 1
16 9 36 1
17 9 37 1
18 10 11 1
19 10 34 1
20 10 35 1
21 11 12 1
22 11 32 1
23 11 33 1
24 12 30 1
25 12 31 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 25 1
31 15 18 2
32 15 40 1
33 16 17 Ar
34 16 38 1
35 17 39 1
36 18 41 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 27 1
42 21 24 Ar
43 21 47 1
44 22 23 Ar
45 22 46 1
46 23 45 1
47 24 48 1
48 25 26 1
49 26 42 1
50 26 43 1
51 26 44 1

1′-diH, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -997.040174785 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
44 47
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.0835 1.0865 -0.5268 N
2 C2 -0.2425 -0.0048 -0.2426 C
3 C3 -1.0954 -1.2280 -0.0741 C
4 N4 -2.3879 -0.7369 -0.2811 N
5 C5 -2.2997 0.6226 -0.5534 C
6 O6 -0.8312 -2.3881 0.2204 O
7 C7 1.1142 0.0853 -0.0803 C
8 C8 -3.5884 -1.5636 -0.2023 C
9 C9 -3.5096 1.4494 -0.8479 C
10 C10 -4.5573 1.4732 0.2886 C
11 C11 -5.3870 0.1885 0.4352 C
12 C12 -4.6082 -1.0748 0.8335 C
13 C13 1.8078 1.3963 -0.0272 C
14 C14 3.1798 3.8578 0.0739 C
15 C15 1.2560 2.5031 0.6470 C
16 C16 3.0686 1.5489 -0.6371 C
17 C17 3.7409 2.7691 -0.5980 C
18 C18 1.9384 3.7168 0.7004 C
19 C19 1.9737 -1.1256 0.0234 C
20 C20 3.6731 -3.3617 0.1946 C
21 C21 2.8939 -1.2495 1.0793 C
22 C22 1.9323 -2.1341 -0.9536 C
23 C23 2.7780 -3.2389 -0.8717 C
24 C24 3.7260 -2.3649 1.1720 C
25 H25 4.4200 -2.4515 2.0035 H
26 H26 2.9462 -0.4713 1.8353 H
27 H27 2.7395 -4.0043 -1.6421 H
28 H28 1.2409 -2.0404 -1.7851 H
29 H29 3.5134 0.7072 -1.1586 H
30 H30 4.7051 2.8679 -1.0890 H
31 H31 3.7074 4.8069 0.1137 H
32 H32 1.5008 4.5547 1.2364 H
33 H33 0.2937 2.4012 1.1337 H
34 H34 -3.2269 -2.5613 0.0591 H
35 H35 -4.0522 -1.6289 -1.1951 H
36 H36 -4.0950 -0.9204 1.7920 H
37 H37 -5.3261 -1.8899 0.9895 H
38 H38 -6.1646 0.3656 1.1890 H
39 H39 -5.9154 -0.0037 -0.5102 H
40 H40 -5.2419 2.3050 0.0848 H
41 H41 -4.0561 1.7083 1.2371 H
42 H42 -3.9863 1.0830 -1.7691 H
43 H43 -3.1514 2.4623 -1.0512 H
44 H44 4.3296 -4.2251 0.2594 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 34 1
14 8 35 1
15 9 10 1
16 9 42 1
17 9 43 1
18 10 11 1
19 10 40 1
20 10 41 1
21 11 12 1
22 11 38 1
23 11 39 1
24 12 36 1
25 12 37 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 31 1
31 15 18 Ar
32 15 33 1
33 16 17 Ar
34 16 29 1
35 17 30 1
36 18 32 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 44 1
42 21 24 Ar
43 21 26 1
44 22 23 Ar
45 22 28 1
46 23 27 1
47 24 25 1

1′-diCl, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1916.23306075 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
44 47
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8227 1.0049 -0.5124 N
2 C2 -0.9476 -0.0664 -0.2684 C
3 C3 -1.7633 -1.3190 -0.1174 C
4 N4 -3.0719 -0.8605 -0.2902 N
5 C5 -3.0264 0.5067 -0.5297 C
6 O6 -1.4577 -2.4773 0.1383 O
7 C7 0.4079 0.0564 -0.1244 C
8 C8 -4.2464 -1.7257 -0.2208 C
9 C9 -4.2637 1.3073 -0.7785 C
10 C10 -5.2910 1.2646 0.3759 C
11 C11 -6.0840 -0.0460 0.4931 C
12 C12 -5.2661 -1.2987 0.8421 C
13 C13 1.2956 -1.1358 -0.0402 C
14 C14 3.0295 -3.3236 0.0999 C
15 C15 1.2736 -2.1340 -1.0271 C
16 C16 2.2210 -1.2547 1.0104 C
17 C17 3.0799 -2.3491 1.0953 C
18 C18 2.1377 -3.2247 -0.9677 C
19 C19 1.0721 1.3815 -0.0697 C
20 C20 2.3837 3.8559 0.0297 C
21 C21 0.4882 2.4847 0.5825 C
22 C22 2.3392 1.5570 -0.6590 C
23 C23 2.9930 2.7862 -0.6241 C
24 C24 1.1372 3.7149 0.6396 C
25 Cl25 3.2061 5.4129 0.0933 Cl
26 Cl26 4.1230 -4.7038 0.1864 Cl
27 H27 3.9618 2.9091 -1.0960 H
28 H28 2.8152 0.7253 -1.1677 H
29 H29 0.6819 4.5531 1.1561 H
30 H30 -0.4802 2.3749 1.0533 H
31 H31 2.2633 -0.4889 1.7790 H
32 H32 3.7801 -2.4391 1.9186 H
33 H33 0.5807 -2.0510 -1.8577 H
34 H34 2.1196 -3.9855 -1.7405 H
35 H35 -3.8518 -2.7193 0.0054 H
36 H36 -4.7208 -1.7746 -1.2094 H
37 H37 -4.7454 -1.1602 1.7990 H
38 H38 -5.9586 -2.1385 0.9800 H
39 H39 -6.8551 0.0872 1.2623 H
40 H40 -6.6205 -0.2231 -0.4506 H
41 H41 -6.0008 2.0839 0.2113 H
42 H42 -4.7798 1.4820 1.3232 H
43 H43 -3.9377 2.3357 -0.9560 H
44 H44 -4.7448 0.9552 -1.7028 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1

13 8 35 1
14 8 36 1
15 9 10 1
16 9 43 1
17 9 44 1
18 10 11 1
19 10 41 1
20 10 42 1
21 11 12 1
22 11 39 1
23 11 40 1
24 12 37 1
25 12 38 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 26 1
31 15 18 Ar
32 15 33 1
33 16 17 Ar
34 16 31 1
35 17 32 1
36 18 34 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 Ar
43 21 30 1
44 22 23 Ar
45 22 28 1
46 23 27 1
47 24 29 1

1′-diMeO, opt: B3LYP/6-31G(d)/CPCM(CH_2Cl_2)
E = -1226.09115379 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
52 55
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 -1.8681 1.0251 -0.5225 N
2 C2 -1.0110 -0.0669 -0.2890 C
3 C3 -1.8458 -1.2977 -0.1324 C
4 N4 -3.1496 -0.8127 -0.2887 N
5 C5 -3.0816 0.5538 -0.5279 C
6 O6 -1.5691 -2.4665 0.1232 O
7 C7 0.3522 0.0383 -0.1456 C
8 C8 -4.3385 -1.6534 -0.1984 C
9 C9 -4.3064 1.3784 -0.7649 C
10 C10 -5.3213 1.3598 0.4005 C
11 C11 -6.1352 0.0635 0.5337 C
12 C12 -5.3348 -1.2022 0.8770 C
13 C13 1.2265 -1.1600 -0.1254 C
14 C14 2.9546 -3.3955 -0.1056 C
15 C15 1.1264 -2.1652 -1.1076 C
16 C16 2.2234 -1.3022 0.8526 C
17 C17 3.0727 -2.4088 0.8822 C
18 C18 1.9773 -3.2590 -1.1065 C
19 C19 1.0189 1.3537 -0.0314 C
20 C20 2.3471 3.8457 0.1747 C
21 C21 0.4421 2.4346 0.6723 C
22 C22 2.2826 1.5634 -0.6131 C
23 C23 2.9407 2.7893 -0.5293 C
24 C24 1.0934 3.6525 0.7805 C
25 O25 2.8987 5.0787 0.3325 O
26 O26 3.7357 -4.5073 -0.1879 O
27 C27 4.7493 -4.6979 0.7970 C
28 C28 4.1730 5.3326 -0.2567 C
29 H29 3.9049 2.9078 -1.0097 H
30 H30 2.7559 0.7561 -1.1625 H
31 H31 0.6523 4.4741 1.3366 H
32 H32 -0.5241 2.3046 1.1436 H
33 H33 2.3304 -0.5401 1.6189 H
34 H34 3.8165 -2.4865 1.6665 H
35 H35 1.9075 -4.0235 -1.8743 H
36 H36 0.3809 -2.0721 -1.8905 H
37 H37 5.4818 -3.8822 0.7786 H
38 H38 5.2431 -5.6354 0.5378 H
39 H39 4.3187 -4.7782 1.8022 H
40 H40 4.9410 4.6657 0.1525 H
41 H41 4.4162 6.3655 -0.0041 H
42 H42 4.1370 5.2222 -1.3469 H
43 H43 -4.7951 1.5719 1.3410 H
44 H44 -6.0196 2.1904 0.2415 H
45 H45 -3.9619 2.4001 -0.9474 H
46 H46 -4.8069 1.0367 -1.6831 H
47 H47 -6.6868 -0.1082 -0.4025 H
48 H48 -6.8944 0.2127 1.3120 H
49 H49 -4.7973 -1.0677 1.8252 H
50 H50 -6.0411 -2.0280 1.0309 H
51 H51 -3.9600 -2.6536 0.0274 H
52 H52 -4.8305 -1.6989 -1.1790 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 19 1
12 8 12 1
13 8 51 1
14 8 52 1
15 9 10 1
16 9 45 1
17 9 46 1
18 10 11 1
19 10 43 1
20 10 44 1
21 11 12 1
22 11 47 1
23 11 48 1
24 12 49 1
25 12 50 1
26 13 15 Ar
27 13 16 Ar
28 14 17 Ar
29 14 18 Ar
30 14 26 1
31 15 18 2
32 15 36 1
33 16 17 Ar
34 16 33 1
35 17 34 1
36 18 35 1
37 19 21 Ar
38 19 22 Ar
39 20 23 Ar
40 20 24 Ar
41 20 25 1
42 21 24 2
43 21 32 1
44 22 23 Ar
45 22 30 1
46 23 29 1
47 24 31 1
48 25 28 1
49 26 27 1
50 27 37 1
51 27 38 1
52 27 39 1
53 28 40 1
54 28 41 1
55 28 42 1

For the optimized structure of Z-1c:

***Z*-1c**, opt: B3LYP/6-31G(d)
E = -1013.06477039 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
43 46
SMALL
NO_CHARGES

@<TRIPOS>ATOM
1 N1 1.0599 1.2069 -0.0615 N
2 C2 0.2463 0.0615 -0.1299 C
3 C3 1.1254 -1.1291 -0.3965 C
4 N4 2.4054 -0.5521 -0.4828 N
5 C5 2.2822 0.8122 -0.2623 C
6 O6 0.8972 -2.3173 -0.5516 O
7 C7 -1.1193 0.0850 -0.0402 C
8 C8 3.6138 -1.3288 -0.7193 C
9 C9 3.4698 1.7211 -0.2337 C
10 C10 4.5330 1.3492 0.8244 C
11 C11 5.3924 0.1214 0.4842 C
12 C12 4.6505 -1.2223 0.4064 C
13 C13 -1.8618 1.3769 0.0287 C
14 C14 -3.3586 3.6764 0.2237 C
15 C15 -1.4703 2.5146 -0.6985 C
16 C16 -2.2340 3.6740 -0.5996 C
17 C17 -3.6720 2.4990 0.9060 C
18 C18 -1.9442 -1.1482 0.0174 C
19 C19 -3.5577 -3.4485 0.1209 C
20 C20 -1.6550 -2.1857 0.9158 C
21 C21 -3.0660 -1.2780 -0.8192 C
22 C22 -3.8574 -2.4230 -0.7781 C
23 C23 -2.4581 -3.3221 0.9716 C
24 H24 -4.5429 2.4556 1.5589 H
25 H25 -1.9537 4.5621 -1.1600 H
26 H26 -0.5828 2.4819 -1.3160 H
27 H27 -3.3113 -0.4778 -1.5113 H
28 H28 -4.7130 -2.5111 -1.4425 H
29 H29 -4.1805 -4.3384 0.1618 H
30 H30 -2.2224 -4.1118 1.6799 H
31 H31 -0.8032 -2.0924 1.5805 H
32 H32 3.9436 1.7390 -1.2272 H
33 H33 3.0818 2.7255 -0.0434 H
34 H34 4.0393 1.2058 1.7949 H
35 H35 5.1987 2.2133 0.9417 H
36 H36 6.1843 0.0353 1.2395 H
37 H37 5.9048 0.3000 -0.4735 H
38 H38 5.3898 -2.0182 0.2474 H
39 H39 4.1574 -1.4403 1.3631 H
40 H40 3.2662 -2.3602 -0.8262 H
41 H41 4.0614 -1.0302 -1.6775 H
42 H42 -3.9812 4.5597 0.3327 H
43 N43 -2.9608 1.3747 0.8101 N
@<TRIPOS>BOND
1 1 2 1
2 1 5 2
3 2 3 1
4 2 7 2
5 3 4 1
6 3 6 2
7 4 5 1
8 4 8 1
9 5 9 1
10 7 13 1
11 7 18 1
12 8 12 1
13 8 40 1
14 8 41 1
15 9 10 1
16 9 32 1
17 9 33 1
18 10 11 1
19 10 34 1
20 10 35 1
21 11 12 1
22 11 36 1
23 11 37 1
24 12 38 1
25 12 39 1
26 13 15 Ar

27 13 43 Ar
28 14 16 Ar
29 14 17 Ar
30 14 42 1
31 15 16 Ar
32 15 26 1
33 16 25 1
34 17 24 1
35 17 43 Ar
36 18 20 Ar
37 18 21 Ar
38 19 22 Ar
39 19 23 Ar
40 19 29 1
41 20 23 Ar
42 20 31 1
43 21 22 Ar
44 21 27 1
45 22 28 1
46 23 30 1

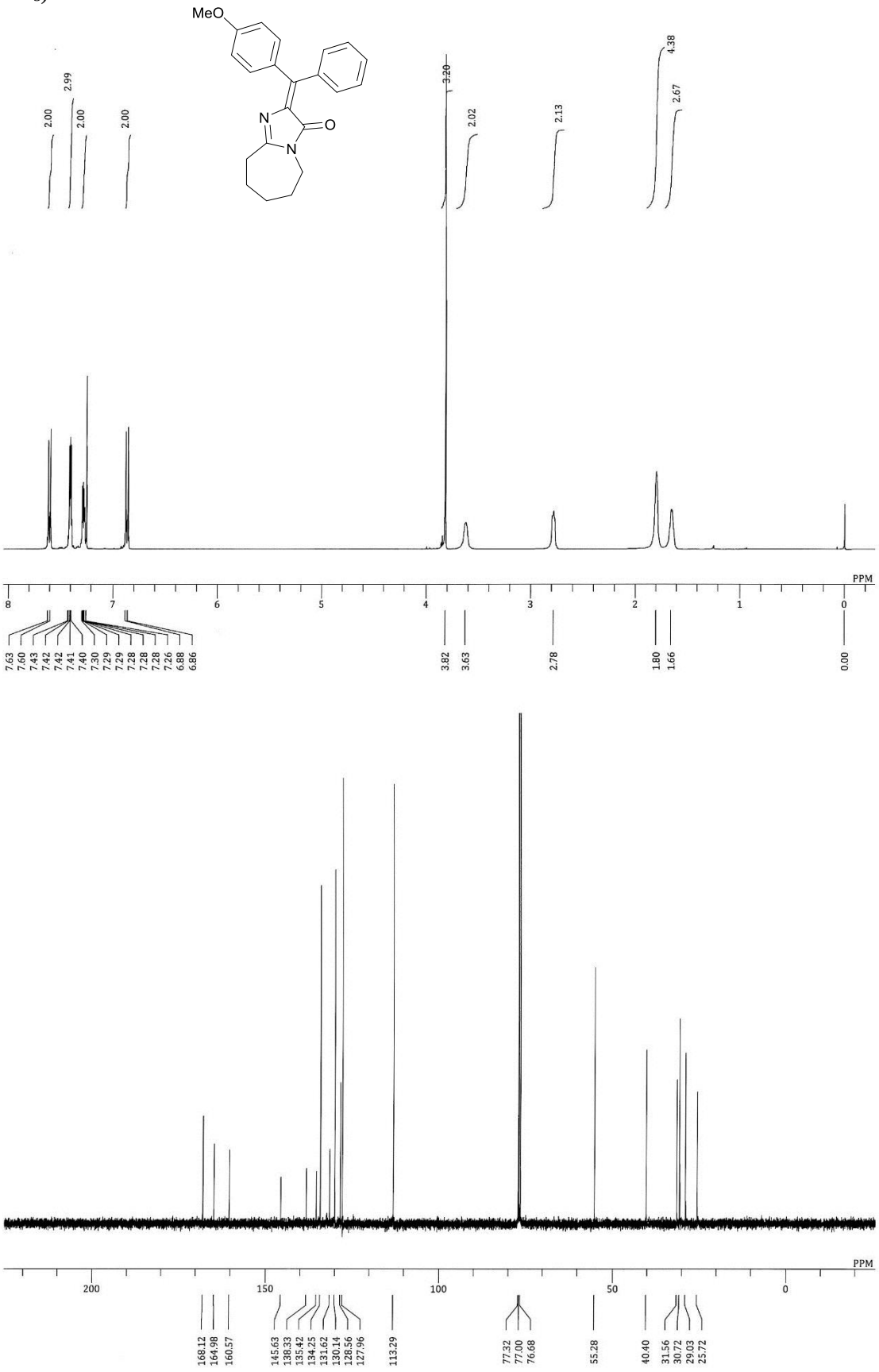
***Z*-1c** + Zn^{2+} (dihydrate), opt: 6-31G(d) for C,H,N,O and LANL2DZ for Zn
E = -1231.05453401 A.U.
No imaginary frequencies

@<TRIPOS>MOLECULE
Molecule Name
50 52
SMALL
NO_CHARGES

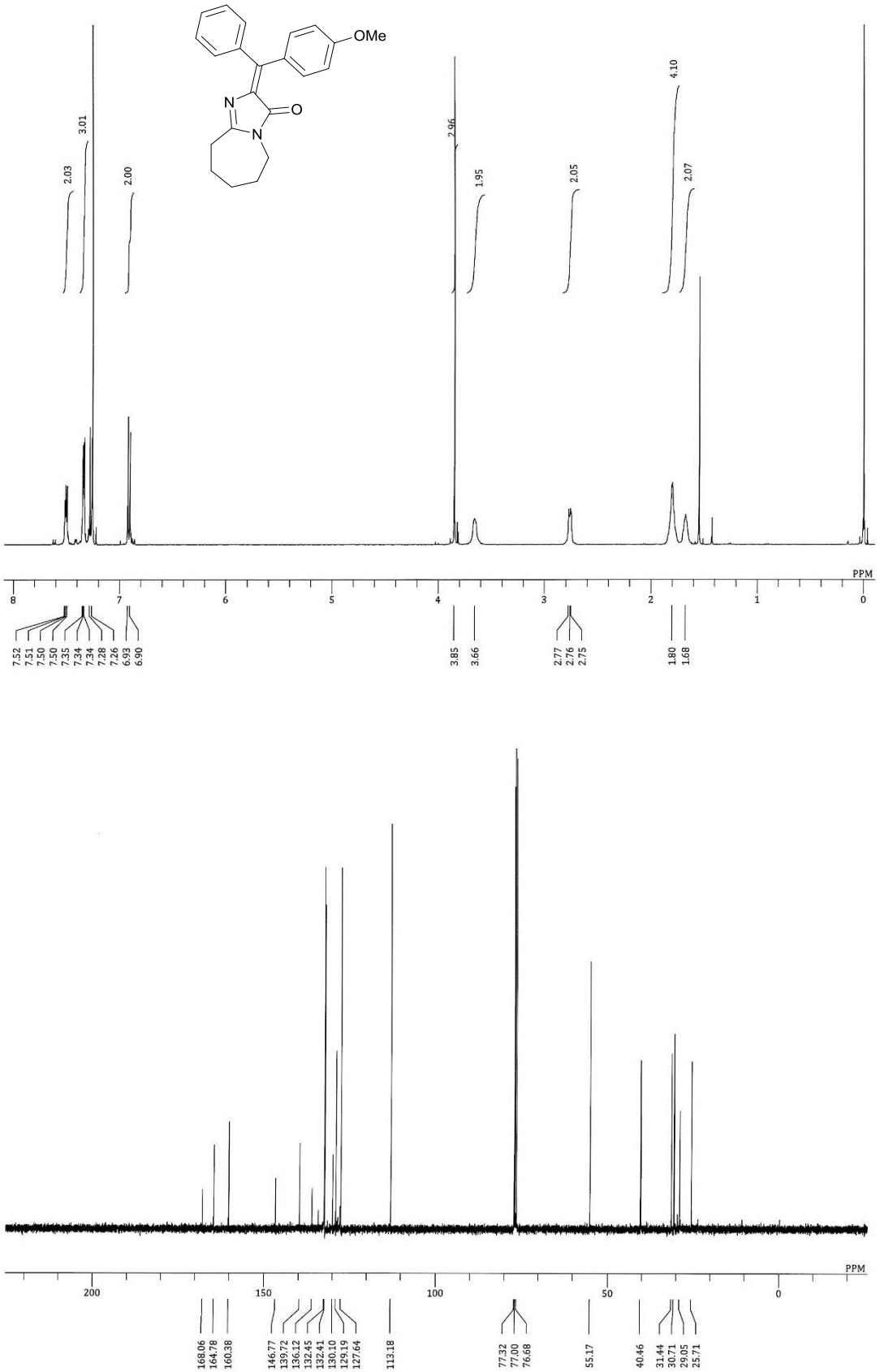
@<TRIPOS>ATOM
1 N1 -1.0805 0.2854 0.1251 N
2 C2 0.0064 -0.6214 0.1320 C
3 C3 -0.5958 -1.9903 0.3043 C
4 N4 -2.0046 -1.7326 0.3582 N
5 C5 -2.2171 -0.4144 0.2533 C
6 O6 -0.1125 -3.0886 0.3899 O
7 C7 1.3462 -0.3776 -0.0014 C
8 C8 -2.9984 -2.8148 0.5185 C
9 C9 -3.5778 0.1991 0.2588 C
10 C10 -4.5177 -0.3346 -0.8560 C
11 C11 -5.0645 -1.7508 -0.6184 C
12 C12 -4.0225 -2.8791 -0.6179 C
13 C13 2.0096 0.9417 -0.1930 C
14 C14 3.3495 3.3691 -0.5856 C
15 C15 3.3932 0.9690 -0.4488 C
16 C16 4.0636 2.1732 -0.6450 C
17 C17 1.9883 3.2957 -0.3314 C
18 C18 2.2701 -1.5621 0.0205 C
19 C19 4.0242 -3.7397 0.0539 C
20 C20 2.5321 -2.2719 -1.1601 C
21 C21 2.8956 -1.9425 1.2164 C
22 C22 3.7668 -3.0324 1.2303 C
23 C23 3.4085 -3.3571 -1.1400 C
24 H24 1.3929 4.2038 -0.2824 H
25 H25 5.1309 2.1730 -0.8435 H
26 H26 3.9351 0.0349 -0.4963 H
27 H27 2.6958 -1.3972 2.1354 H
28 H28 4.2418 -3.3288 2.1605 H
29 H29 4.7028 -4.5870 0.0675 H
30 H30 3.6065 -3.9048 -2.0563 H
31 H31 2.0499 -1.9813 -2.0900 H
32 H32 -4.0427 0.0162 1.2385 H
33 H33 -3.4614 1.2849 0.1554 H
34 H34 -3.9992 -0.2815 -1.8224 H
35 H35 -5.3609 0.3620 -0.9144 H
36 H36 -5.8016 -1.9600 -1.4013 H
37 H37 -5.6187 -1.7667 0.3307 H
38 H38 -4.5452 -3.8365 -0.5133 H
39 H39 -3.4938 -2.9208 -1.5790 H
40 H40 -2.4011 -3.7280 0.5627 H
41 H41 -3.4877 -2.6887 1.4914 H
42 H42 3.8261 4.3320 -0.7331 H
43 N43 1.3268 2.1311 -0.1369 N
44 Zn44 -0.6822 2.2278 0.1875 Zn
45 O45 -1.0263 3.3615 1.9197 O
46 O46 -1.7300 3.5270 -1.0515 O
47 H47 -1.8677 3.4015 -2.0072 H
48 H48 -1.9913 4.4408 -0.8406 H
49 H49 -0.3035 3.5832 2.5345 H
50 H50 -1.8465 3.3741 2.4450 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 Ar
3 1 44 1
4 2 3 1
5 2 7 2
6 3 4 1
7 3 6 2
8 4 5 Ar
9 4 8 1
10 5 9 1
11 7 13 1
12 7 18 1
13 8 12 1
14 8 40 1
15 8 41 1
16 9 10 1
17 9 32 1
18 9 33 1
19 10 11 1
20 10 34 1
21 10 35 1
22 11 12 1
23 11 36 1
24 11 37 1
25 12 38 1
26 12 39 1
27 13 15 Ar
28 13 43 Ar
29 14 16 Ar
30 14 17 Ar
31 14 42 1
32 15 16 Ar
33 15 26 1
34 16 25 1
35 17 24 1
36 17 43 Ar
37 18 20 Ar
38 18 21 Ar
39 19 22 Ar
40 19 23 Ar
41 19 29 1
42 20 23 Ar
43 20 31 1
44 21 22 Ar
45 21 27 1
46 22 28 1
47 23 30 1
48 43 44 1
49 45 49 1
50 45 50 1
51 46 47 1
52 46 48 1

3. ^{1}H and ^{13}C NMR spectra of compounds 1 and 4

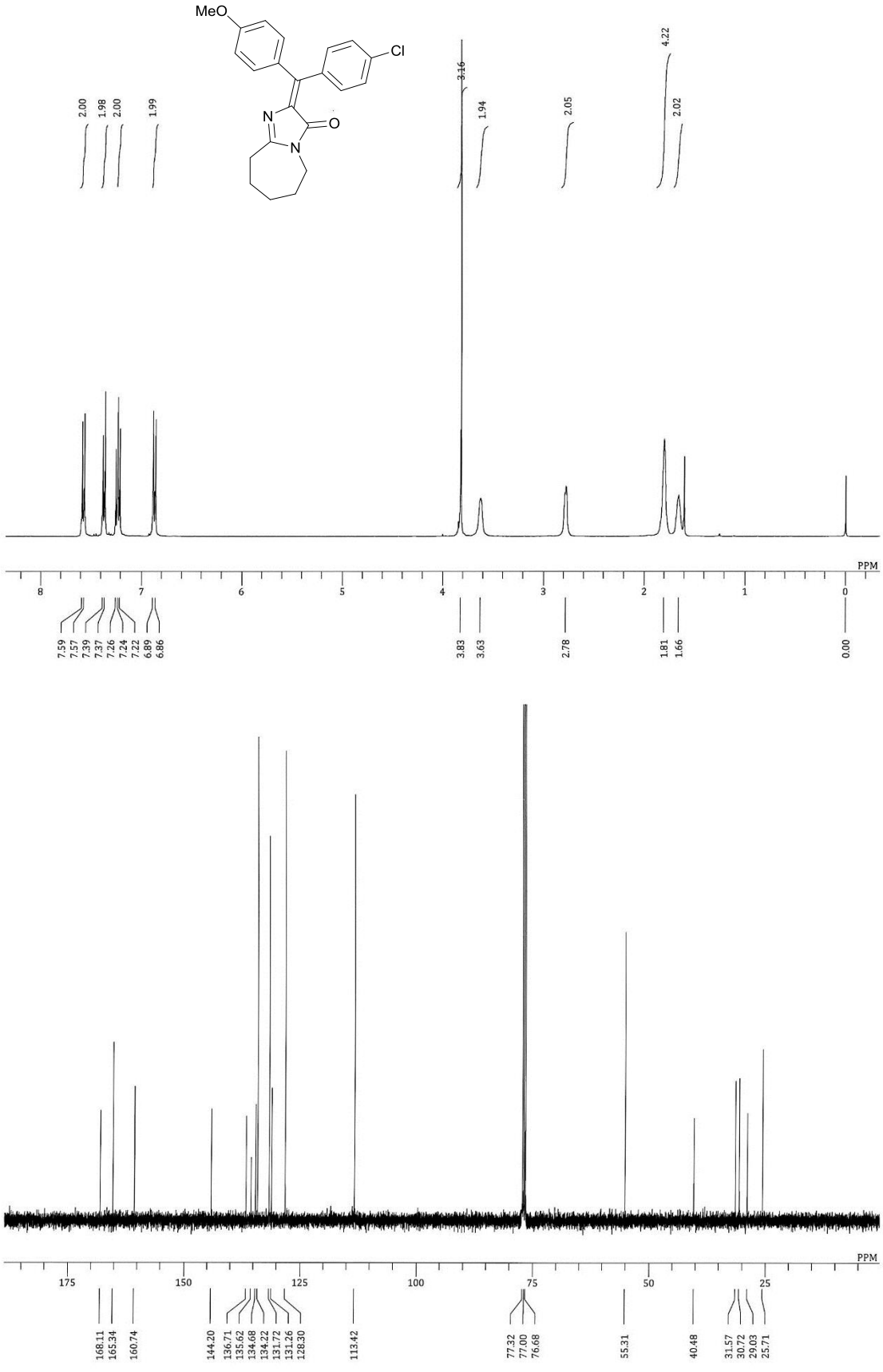
***Z*-1a** ($CDCl_3$):



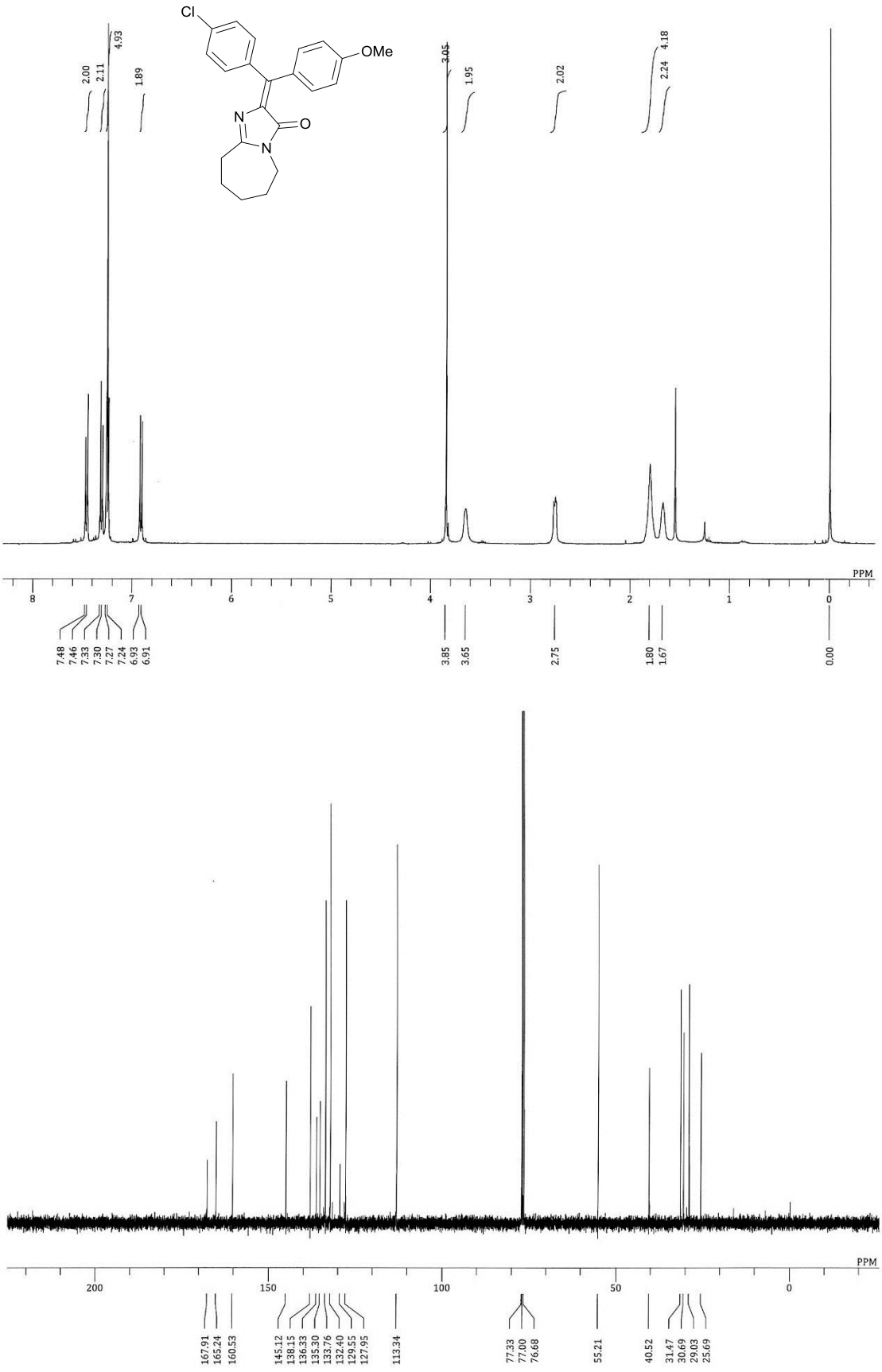
***E*-1a** ($CDCl_3$)**:**


OMe
N
O
N
2.03
3.01
2.00
2.96
1.95
2.05
4.10
2.07
PPM
8
7
6
5
4
3
2
1
0
7.52
7.51
7.50
7.50
7.35
7.34
7.34
7.28
7.26
6.93
6.90
3.85
3.66
2.77
2.76
2.75
1.80
1.68
PPM
200
150
100
50
0
168.06
164.78
160.38
146.77
139.72
136.12
132.45
132.41
130.10
129.19
127.64
113.18
77.32
77.00
76.68
55.17
40.46
31.44
30.71
29.05
25.71

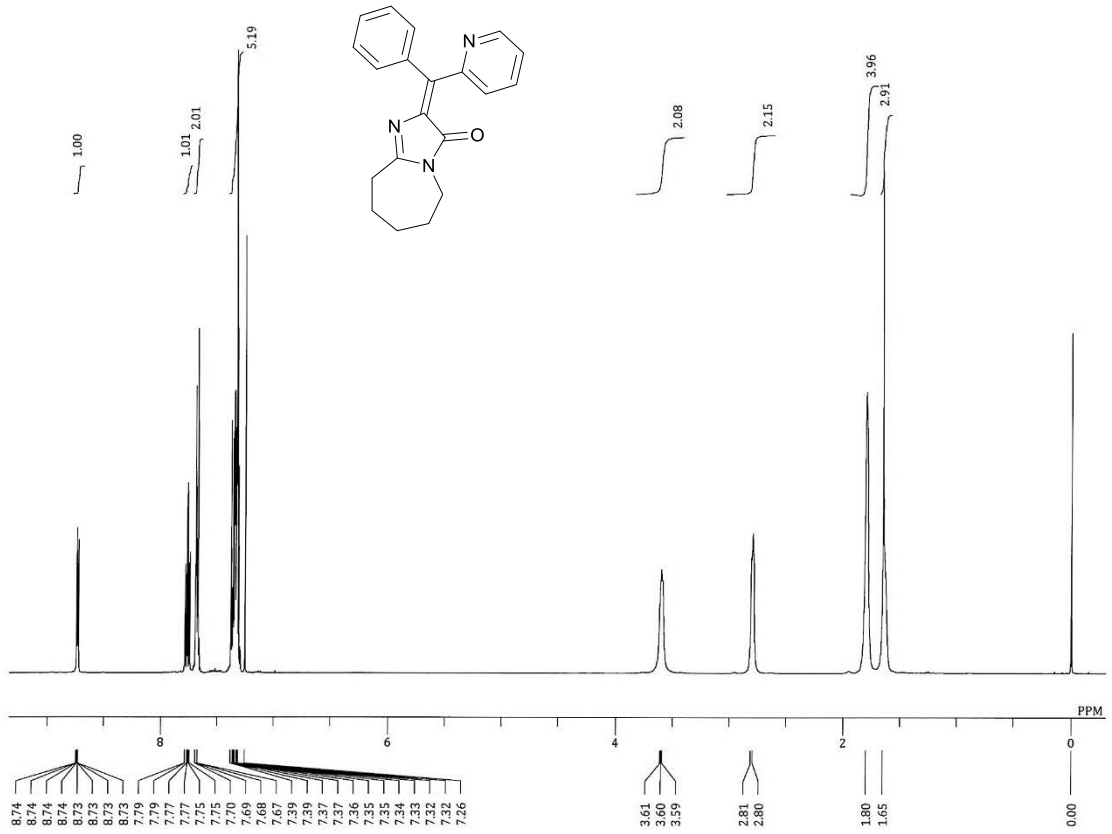
***E*-1b** ($CDCl_3$)**:**

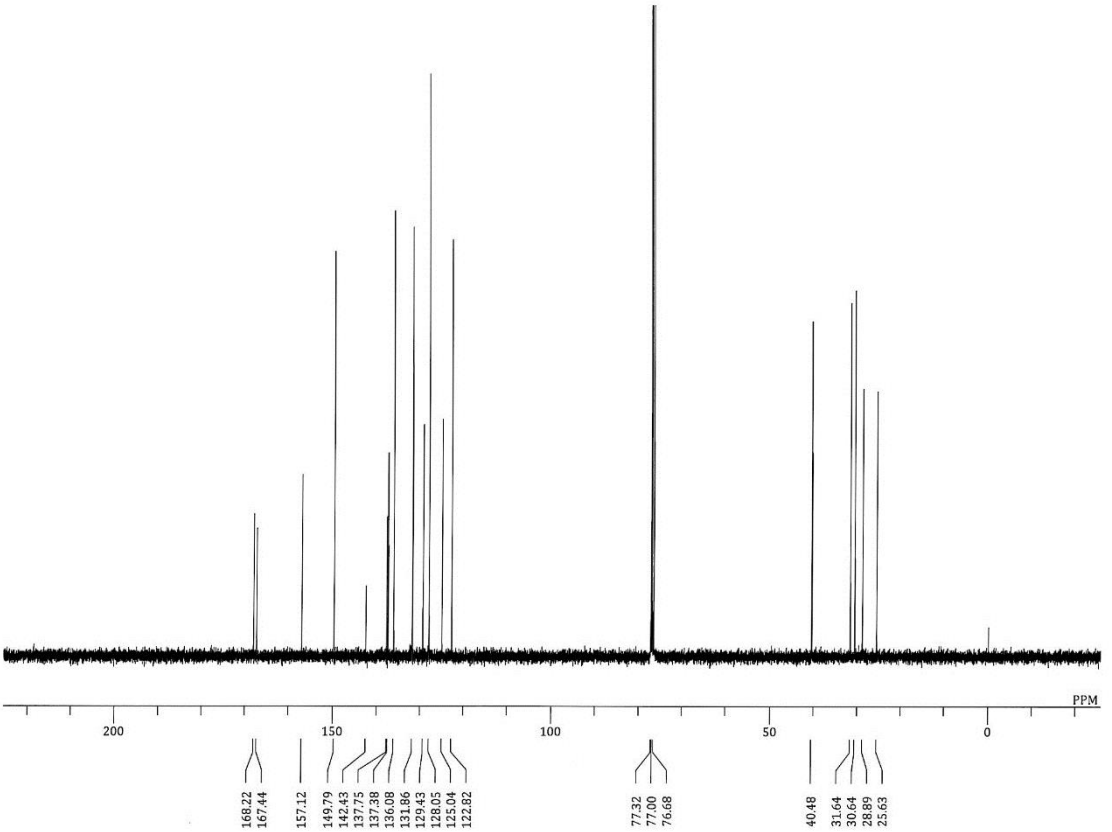

MeO
Cl
N
O
N
2.00
1.98
2.00
1.99
3.16
1.94
2.05
4.22
2.02
PPM
8
7
6
5
4
3
2
1
0
7.59
7.57
7.39
7.37
7.26
7.24
7.22
6.89
6.86
3.83
3.63
2.78
1.81
1.66
0.00
PPM
175
150
125
100
75
50
25
168.11
165.34
160.74
144.20
136.71
135.62
134.68
134.22
131.72
131.26
128.30
113.42
77.32
77.00
76.68
55.31
40.48
31.57
30.72
29.03
25.71

Z-1b ($CDCl_3$)**:**

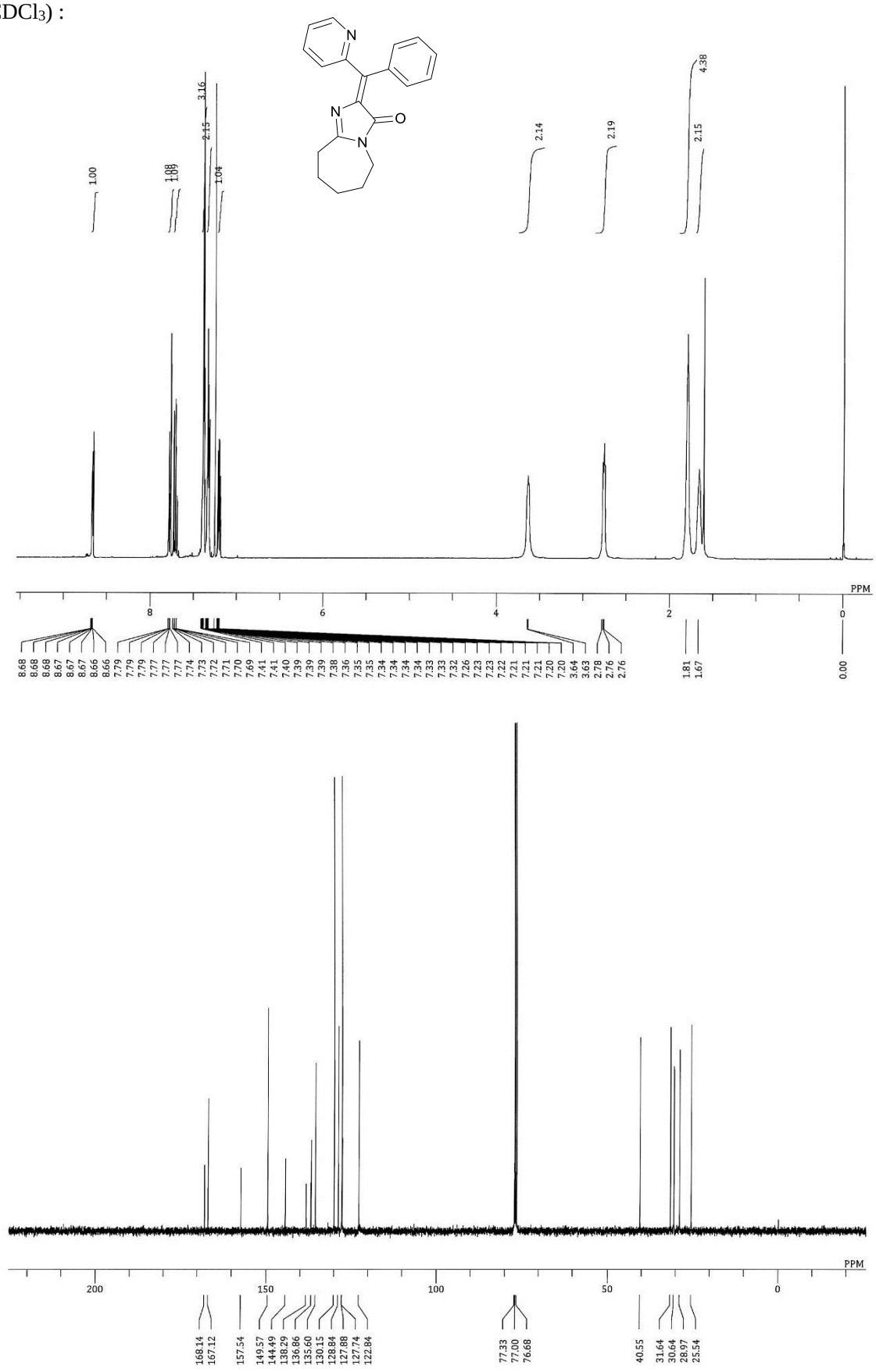

Cl
OMe
N
O
N
2.00
2.11
4.93
1.89
3.05
1.95
2.02
4.18
2.24
PPM
8
7
6
5
4
3
2
1
0
7.48
7.46
7.33
7.30
7.27
7.24
6.93
6.91
3.85
3.65
2.75
1.80
1.67
0.00
PPM
200
150
100
50
0
167.91
165.24
160.53
145.12
138.15
136.33
135.30
133.76
132.40
129.55
127.95
113.34
77.33
77.00
76.68
55.21
40.52
31.47
30.69
29.03
25.69

***E*-1c** ($CDCl_3$):

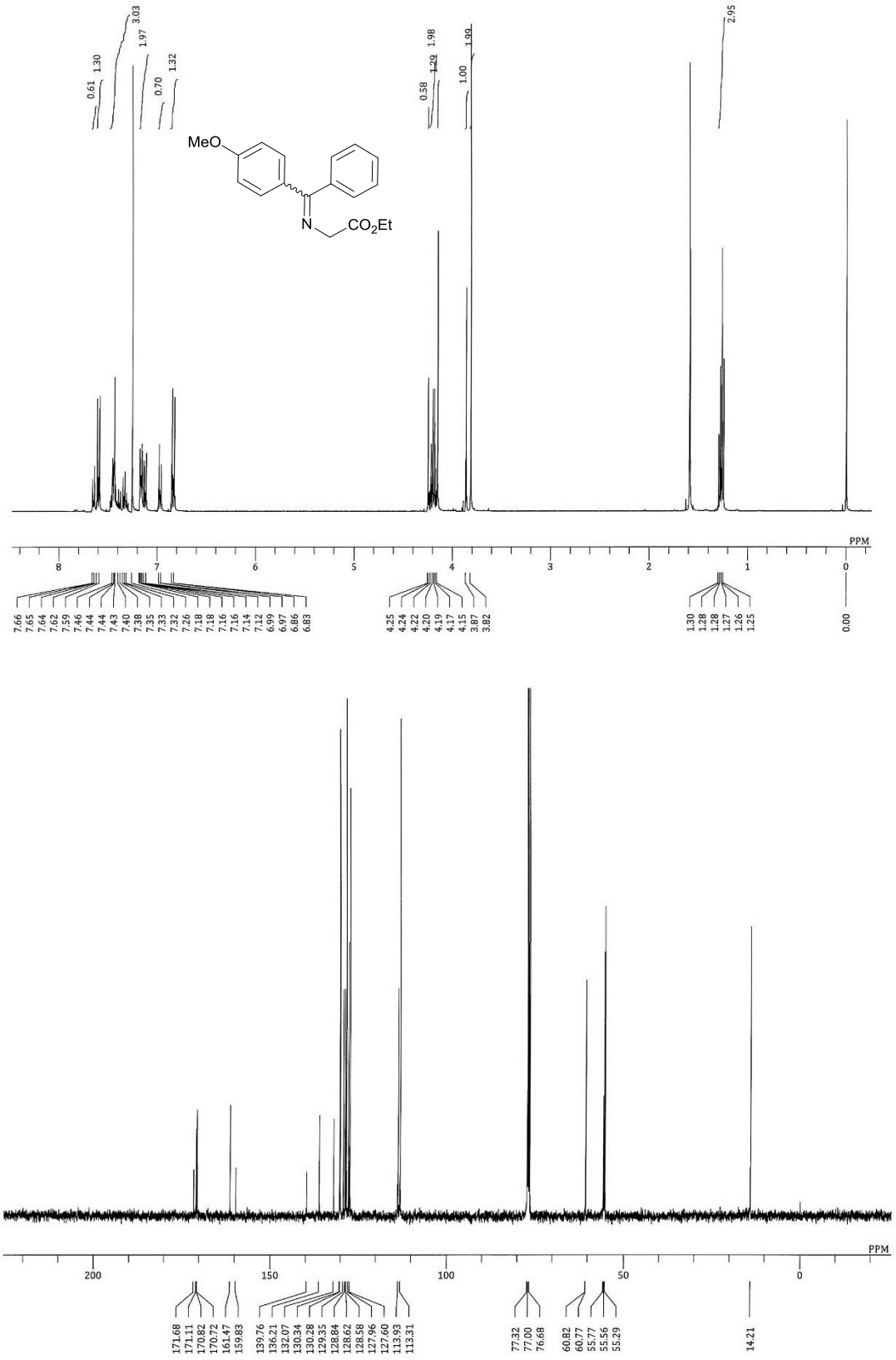

1.00
1.01
2.01
5.19
2.08
2.15
3.96
2.91
N
N
O
N
PPM
8
6
4
2
0
8.74
8.74
8.74
8.74
8.73
8.73
8.73
8.73
7.79
7.79
7.77
7.77
7.77
7.75
7.75
7.70
7.69
7.68
7.67
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.26
3.61
3.60
3.59
2.81
2.80
1.80
1.65
0.00


PPM
200
150
100
50
0
168.22
167.44
157.12
149.79
142.43
137.75
137.38
136.08
131.86
129.43
128.05
125.04
122.82
77.32
77.00
76.68
40.48
31.64
30.64
28.89
25.63

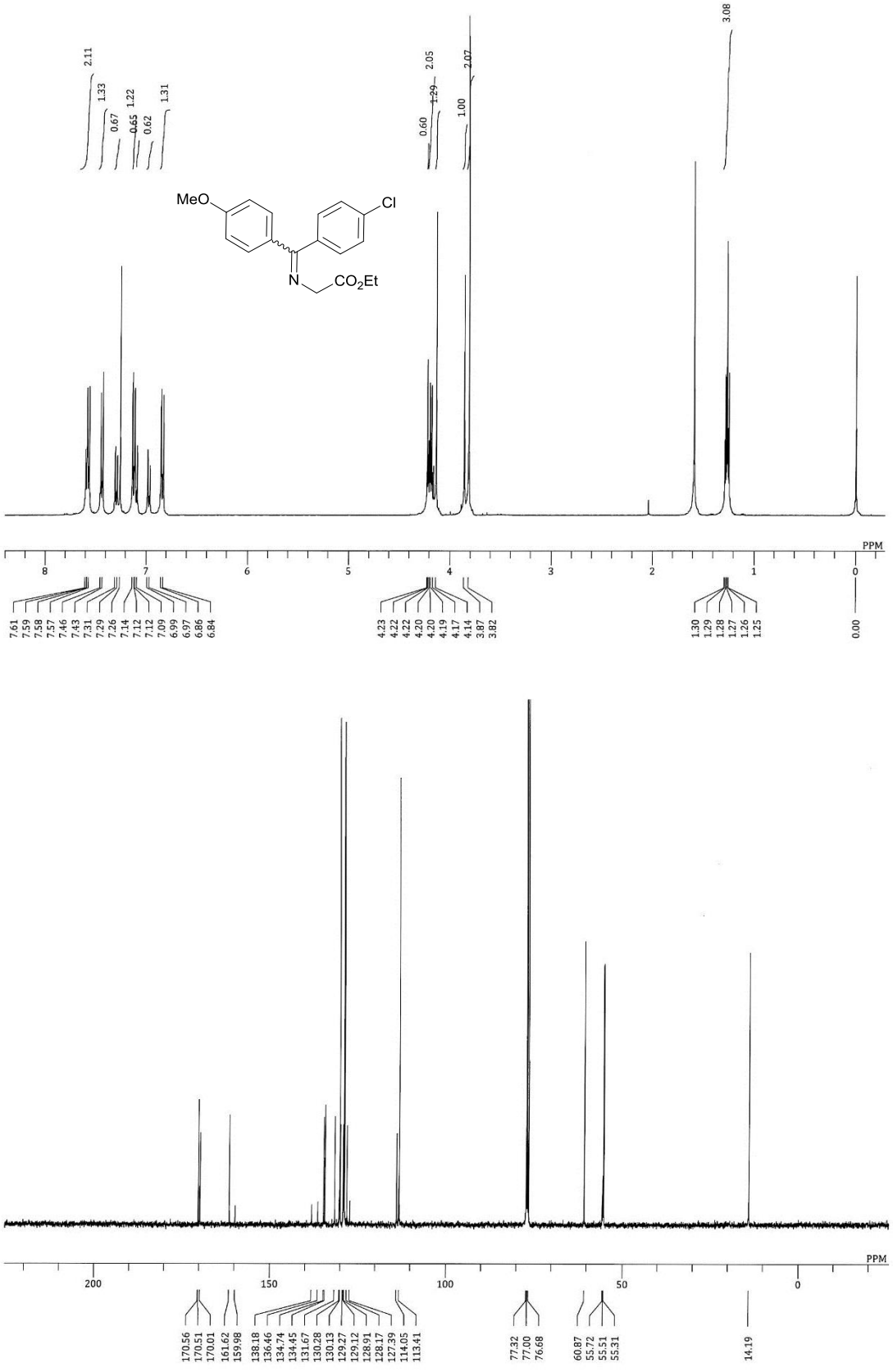
Z-1c ($CDCl_3$) :


N
N
O
N
1.00
1.08
1.00
3.16
2.15
1.04
2.14
2.19
2.15
4.38
PPM
8
6
4
2
0
8.68
8.68
8.68
8.67
8.67
8.67
8.66
8.66
7.79
7.79
7.79
7.77
7.77
7.77
7.74
7.73
7.72
7.71
7.70
7.69
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.36
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.26
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
3.64
3.63
2.78
2.76
2.76
1.81
1.67
0.00
PPM
200
150
100
50
0
168.14
167.12
157.54
149.57
144.49
138.29
136.86
135.60
130.15
128.84
127.88
127.74
122.84
77.33
77.00
76.68
40.55
31.64
30.64
28.97
25.54

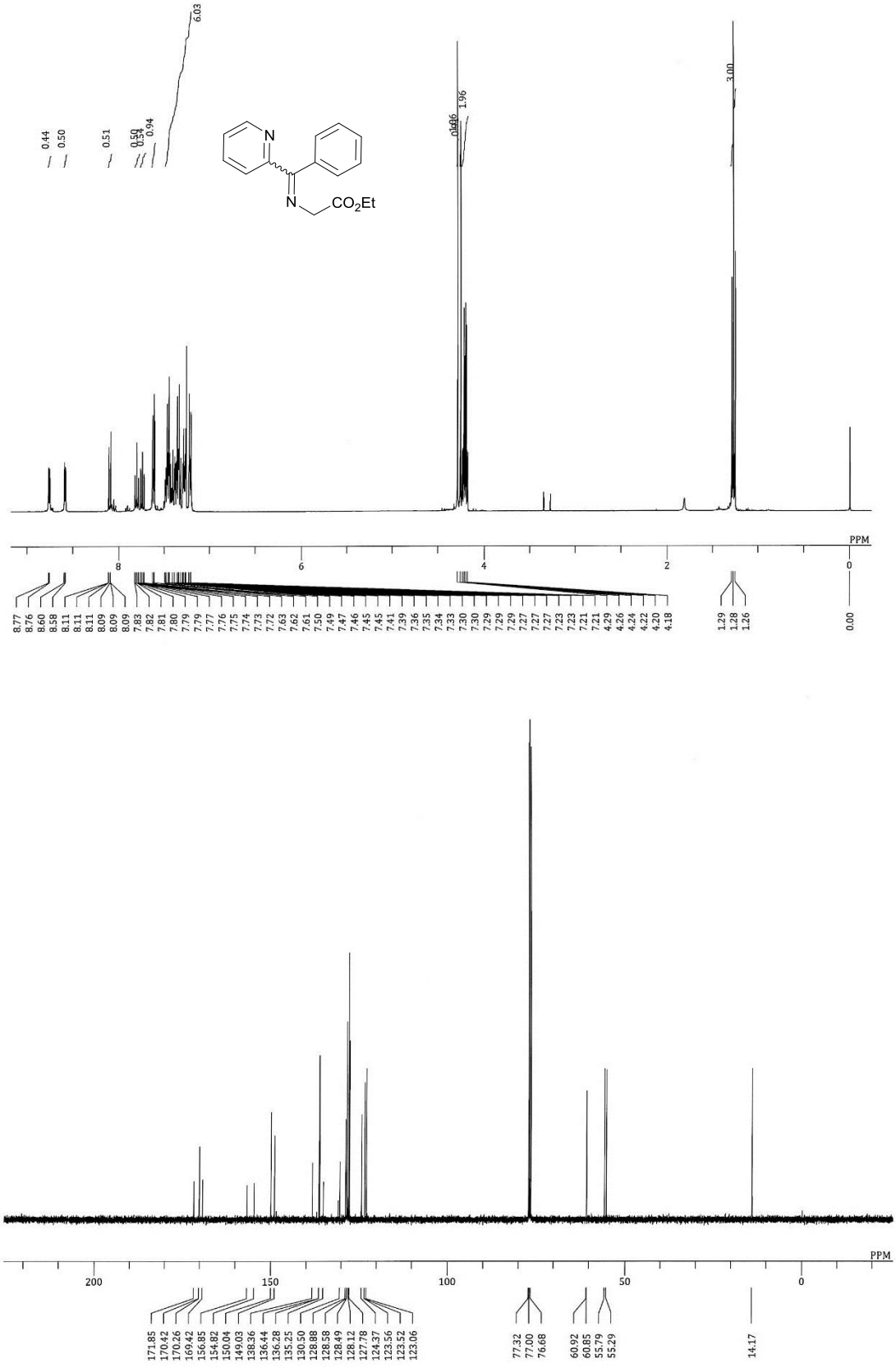
4a (2:1 mixture of diastereomers, $CDCl_3$):



4b (2:1 mixture of diastereomers, $CDCl_3$):

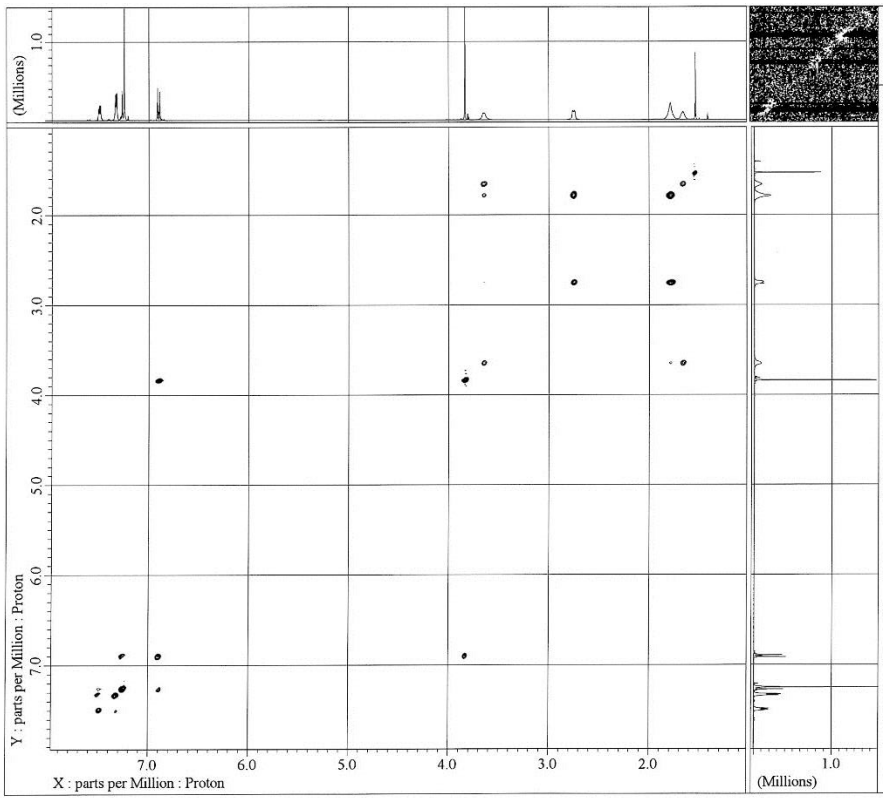


4c (10:9 crude mixture of diastereomers, $CDCl_3$):

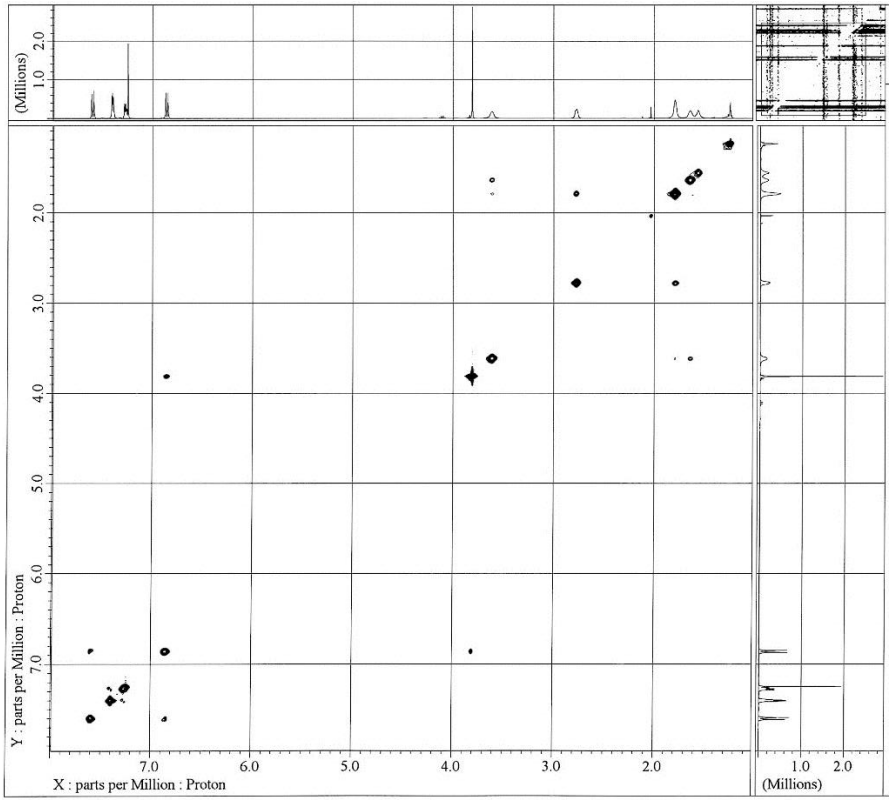


4. NOESY spectra of compounds 1a and b ($CDCl_3$)

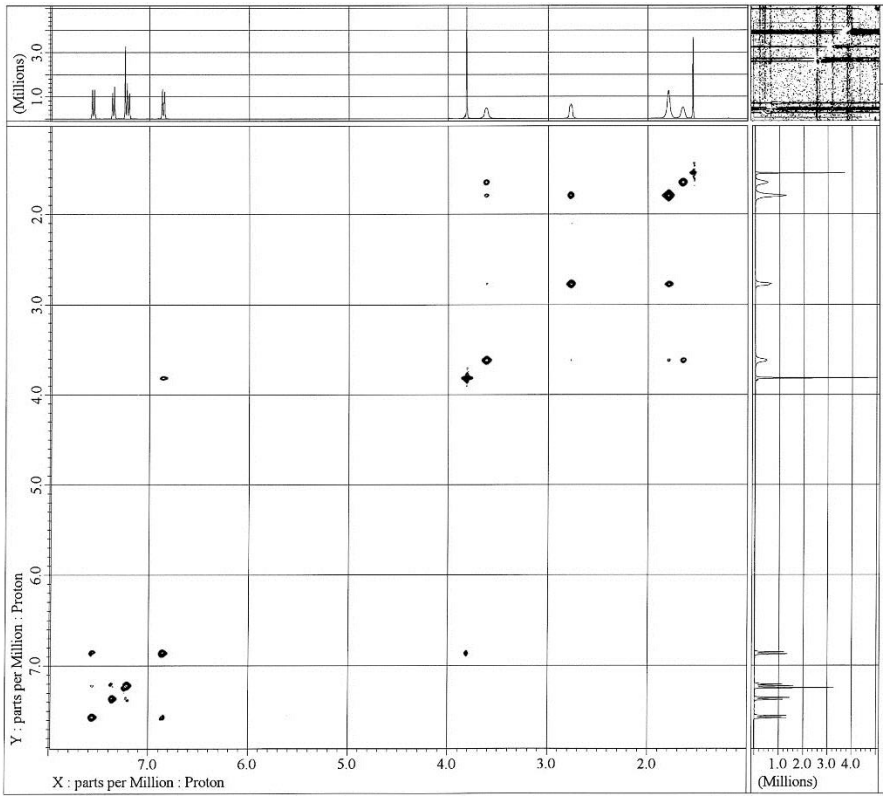
***E*-1a**



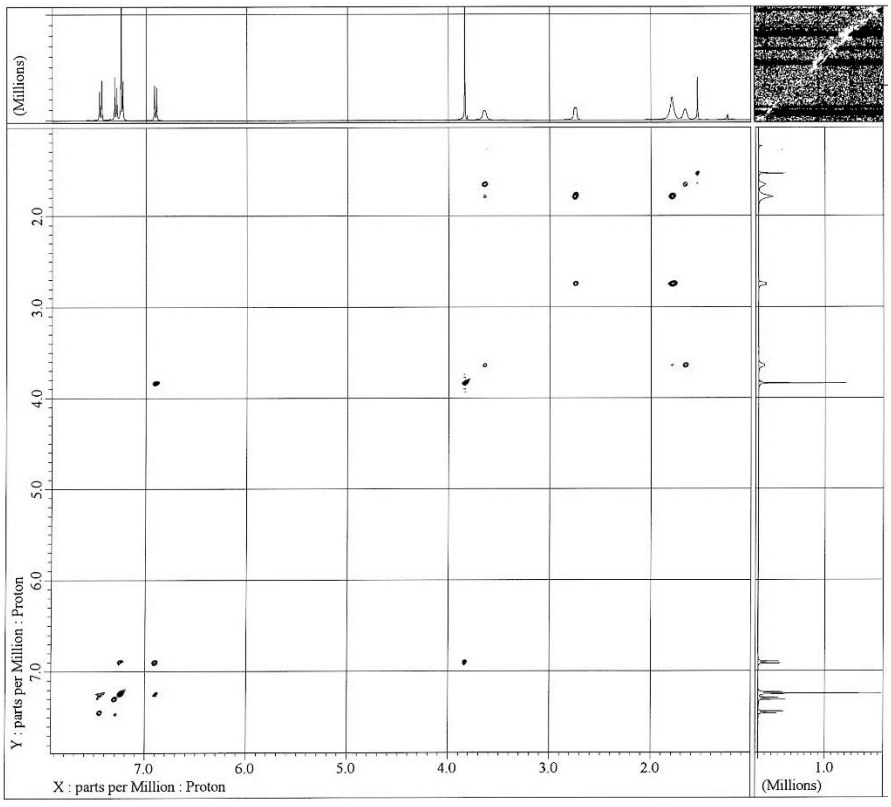
***Z*-1a**



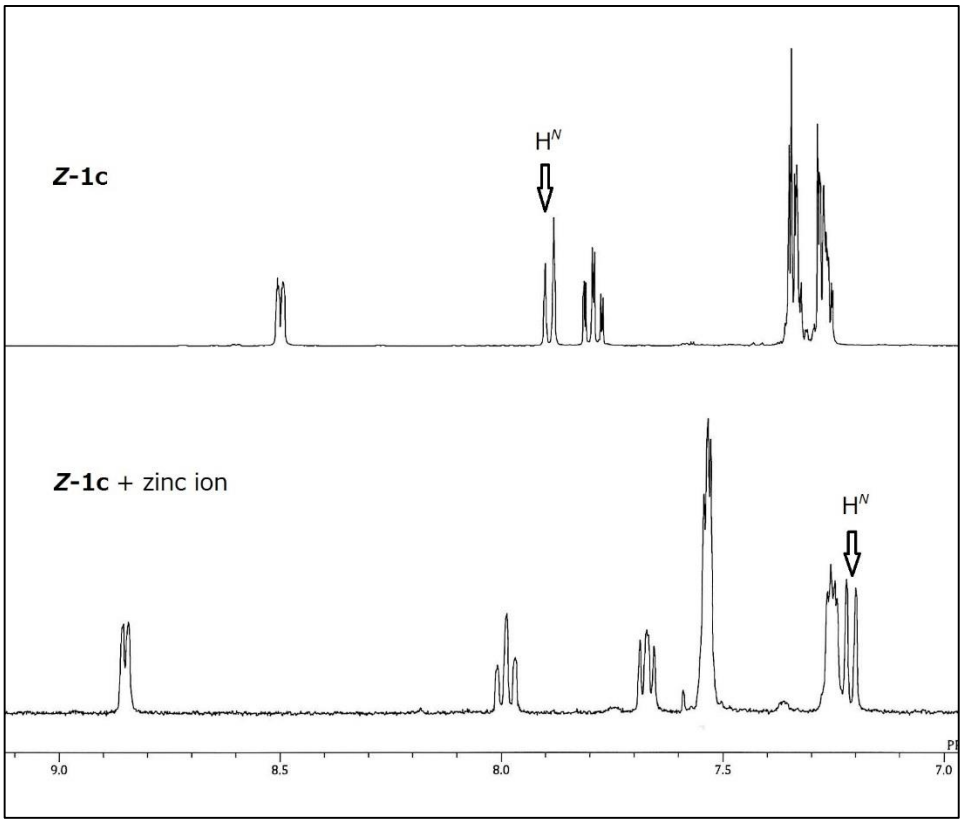
***E*-1b**

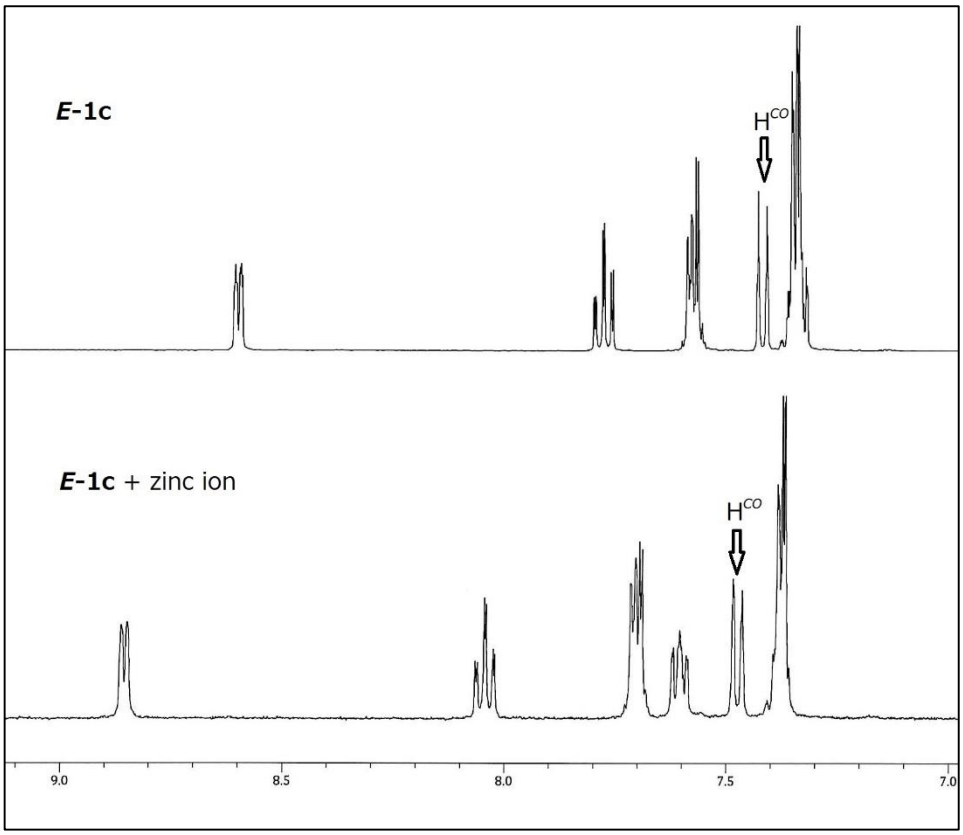

(Millions)
1.0
3.0
2.0
3.0
4.0
5.0
6.0
7.0
Y : parts per Million : Proton
7.0
6.0
5.0
4.0
3.0
2.0
X : parts per Million : Proton
1.0 2.0 3.0 4.0
(Millions)

***Z*-1b**

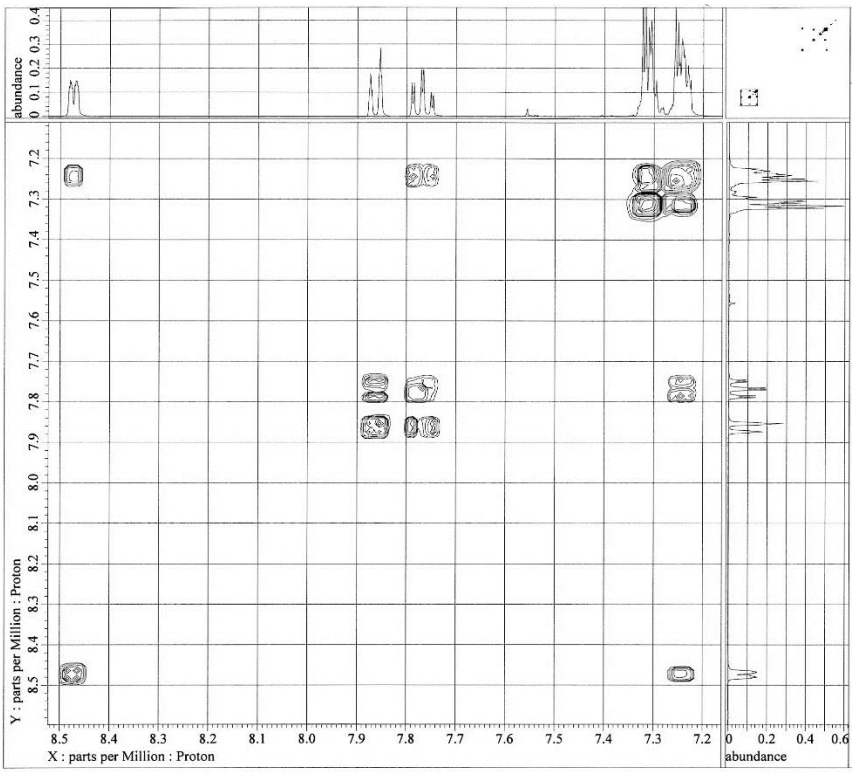

(Millions)
2.0
3.0
4.0
5.0
6.0
7.0
Y : parts per Million : Proton
7.0
6.0
5.0
4.0
3.0
2.0
X : parts per Million : Proton
1.0
(Millions)

5. ^{1}H and COSY spectra of 1c and 1c+Zn^{2+} (CD_3CN)

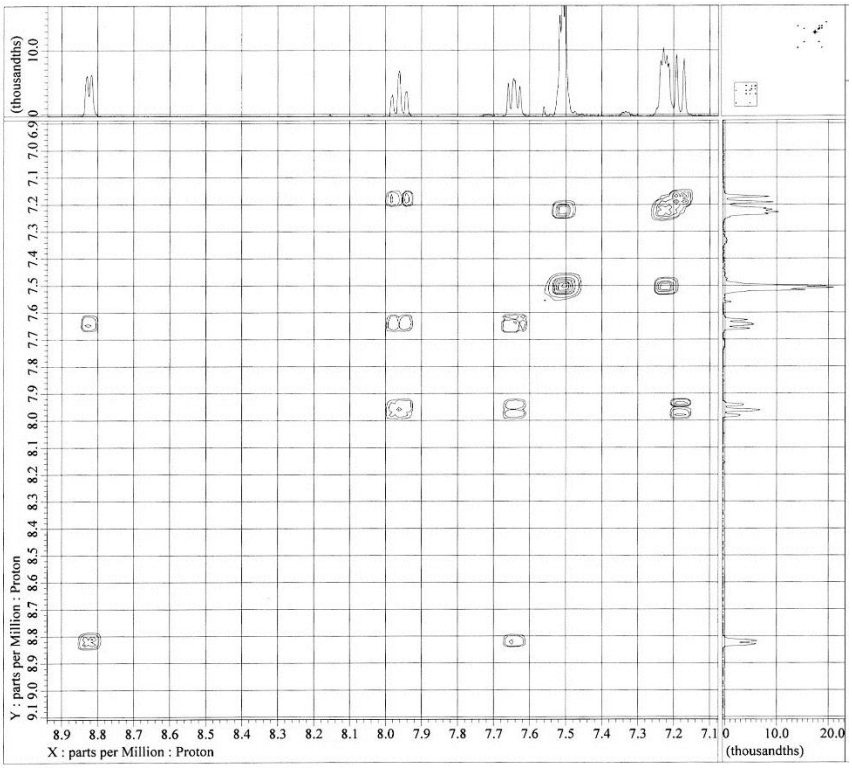




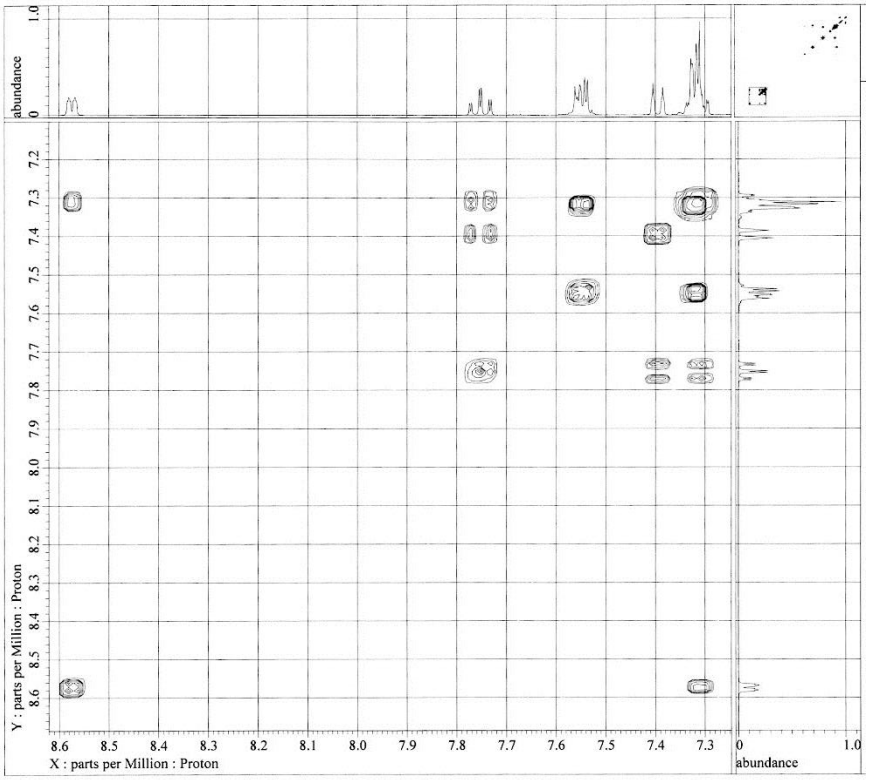
Z-1c


abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

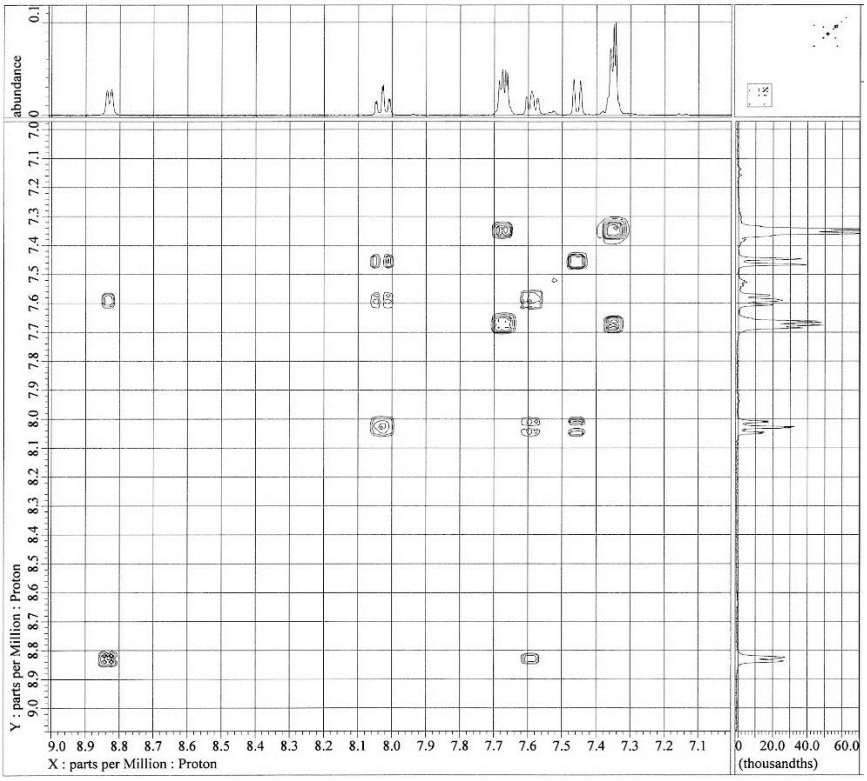
Z-1c + Zn^{2+}


(thousandths)
Y : parts per Million : Proton
X : parts per Million : Proton
(thousandths)

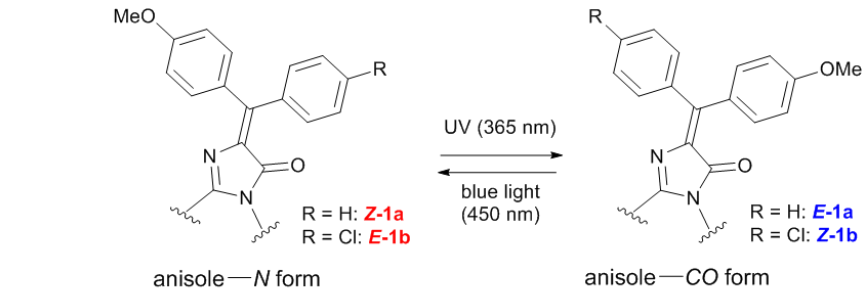
***E*-1c**

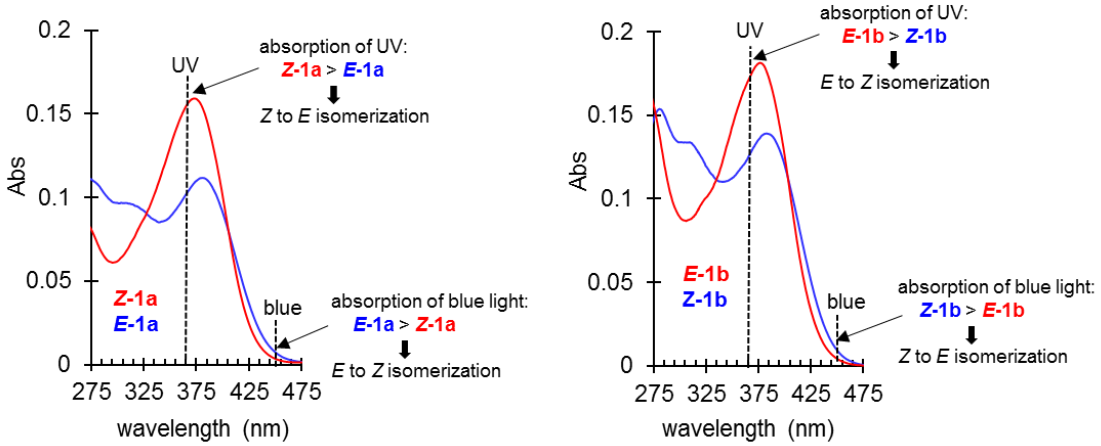

abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

***E*-1c + Zn^{2+}**


abundance
Y : parts per Million : Proton
X : parts per Million : Proton
(thousandths)

6. UV-vis spectra of compounds 1a and b





Left spectra: compound **1a** (red: *Z*-isomer, blue: *E*-isomer); right spectra: **1b** (red: *E*-isomer, blue: Z-isomer). 1.0×10^{-5} M in CH_2Cl_2