Supporting Information

Copper-Mediated Reduction of Azides under Seemingly Oxidising Conditions: Catalytic and Computational Studies

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1. GENERAL CONSIDERATIONS

All chemicals were obtained from commercial sources (Aldrich, Fisher, Fluorochem, and VWR) and used without further purification. Air and moisture sensitive manipulations were performed using standard Schlenk line techniques. Anhydrous solvents were dried passing them through columns of molecular sieves in a solvent purification system. Column chromatography and TLC were performed on silica gel (Kieselgel 60), using UV light and phosphomolybdic acid, $KMnO_4$, or $Ce(SO_4)_2$ dip to visualise the products. NMR spectra were measured on Bruker AVANCE 400 spectrometers (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz, ^{31}P: 101 MHz) at 20 °C unless stated otherwise. The chemical shifts (δ) are given in ppm relatively to a tetramethylsilane standard or the residual solvent signal. The multiplicity is given in br, s, d, t, q, sept, and m for broad, singlet, doublet, triplet, quartet, septet, and multiplet. Mass spectra (MS) were recorded on a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using EI or ESI techniques at the Mass Spectroscopy Service of Imperial College London. Infrared spectra were recorded using a Perkin Elmer 100 series FT-IR spectrometer, equipped with a beam-condensing accessory, and samples were sandwiched between diamond compressor cells. Melting points (uncorrected) were determined on an Electrothermal Gallenhamp apparatus. Single crystal X-ray diffraction were collected using Agilent Xcalibur PX Ultra A and Xcalibur 3 E diffractometers, and the structures were refined using the SHELXTL, and SHELX-2013 program systems.

[Cu(DAB)][1] and [Cu(NHC)][2] complexes, DAB^{3MeO},[3] DAB^{DMA},[4] $^{Me}DAB^{DMA}$,[5] $ImPy^{DMA}$,[6] $ImPy^{Anis}$,[7] $ImPy^{Ad}$,[7] and $ImPy^{Dipp}$ [8] were prepared following the procedures reported in the literature.

1-Azido-4-nitrobenzene,[9] 3-azido-3-nitrobenzene,[9] 4-azidobenzonitrile,[10] 1-azido-4-(trifluoromethyl)benzene,[11] ethyl 4-azidobenzoate,[12] 4-azidoacetophenone,[13] 4-azido-7-nitrobenzo[c][1,2,5]oxadiazole,[14] tosylazide,[15] 4-azidopyridine,[16] and methyl 3-azidothiophene-2-carboxylate[17] were prepared following the procedures reported in the literature.

2. PREPARATION OF COPPER(I) COMPLEXES

General procedure for the preparation of $[Cu(DAB^R)_2]BF_4$: $[Cu(NCMe)_4]BF_4$ (1 equiv) and DAB^R (2 equiv) were suspended in dry, degassed DCM under a N_2 atmosphere and stirred at room temperature for 16 h. The reaction mixture was then filtered through celite and concentrated to ~one third of the original volume under reduced pressure, followed by the addition of petroleum ether. The formed precipitate was collected, washed with petroleum ether, and dried under reduced pressure to give the expected $[Cu(DAB^R)_2]BF_4$ complex.

Bis(*N*,*N*'-bis(3,4,5-trimethoxyphenyl)-1,4-diazabuta-1,3-diene)copper(I) tetrafluoroborate $[Cu(DAB^{3MeO})_2]BF_4$ (2): Following the general procedure from $[Cu(NCMe)_4]BF_4$ (41 mg, 0.13 mmol), DAB^{3MeO} (100 mg, 0.26 mmol), and DCM (50 mL), $[Cu(DAB^{3MeO})_2]BF_4$ **2** was isolated as a black solid (102 mg, 75%).

Mp: 166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 4H), 6.82 (s, 8H), 3.86–3.78 (m, 36H). $^{13}C\{^{1}H\}$ NMR could not be measured due to low solubility of the title compound in acetone-d6, $CDCl_3$, CD_3CN, or DMSO-d6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -153.3 (s). IR: 2943 (C−H st), 1588 (C–N asym st), 1499 1604, 1459, 1420, 1337 (C–N sym st), 1232, 1225, 999, 826 cm^{-1}. HRMS calcd for $C_{40}H_{48}N_4CuO_{12}$ 839.2559, found 839.2564 ($[Cu(DAB^{3MeO})_2]^+$.

Bis(*N*,*N*'-bis(4-*N*,*N*-dimethylaminophenyl)-1,4-diazabuta-1,3-dien)copper(I) tetrafluoroborate [Cu(DAB^{DMA})$_2$]BF$_4$ (3): Following the general procedure from $[Cu(NCMe)_4]BF_4$ (315 mg, 1 mmol), DAB^{DMA} (588 mg, 2 mmol), and DCM (60 mL), $[Cu(DAB^{DMA})_2]BF_4$ **3** was isolated as a light green solid (663 mg, 90%).
Mp: 293 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 8.95 (s, 4H), 7.51 (d, *J* = 9.0 Hz, 8H), 6.66 (d, *J* = 9.0 Hz, 8H), 2.92 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d6): δ 151.7, 147.3, 135.4, 124.9, 112.7, 40.2. ^{19}F NMR (377 MHz, DMSO-d6): δ -148.3 (s). IR: 2857 (C−H st), 2803 (C−H st), 1600, 1554 (C–N asym st), 1515, 1439, 1358 (C–N sym st), 1297, 1165, 1047 (BF_4^-), 945, 812, 635 cm^{-1}. HRMS calcd for $C_{36}H_{44}N_8Cu$ 651.2985, found 651.2984 ($[Cu(DAB^{DMA})_2]^+$).

Bis(*N*,*N*'-bis(4-*N*,*N*-dimethylaminophenyl)-1,4-diaza-2,3-dimethylbuta-1,3-diene)copper(I) tetrafluoroborate [Cu(^{Me}DAB^{DMA})$_2$]BF$_4$ (4): Following the general procedure from $[Cu(NCMe)_4]BF_4$ (97 mg, 0.31 mmol), $^{Me}DAB^{DMA}$ (200 mg, 0.62 mmol), and DCM (50 mL), $[Cu(^{Me}DAB^{DMA})_2]BF_4$ **4** was isolated as a black solid (150 mg, 61%).
Mp: 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (s, 16H) 2.99 (s, 24H), 2.21 (s, 12H). ^{13}C NMR could not be measured due to low solubility of the title compound in acetone-d6, $CDCl_3$, CD_3CN, or DMSO-d6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -152.9 (s). IR: 2803 (C−H st), 1604, 1511 (C–N asym st), 1442, 1352 (C–N sym st), 1225, 1122, 1050 (BF_4^-), 944, 826 cm^{-1}. HRMS calcd for $C_{40}H_{52}N_8Cu$ 707.3605, found 707.3578 ($[Cu(^{Me}DAB^{DMA})_2]^+$)

General procedure for the preparation of [Cu(ImPy^{R})$_2$]OTf: $[Cu(OTf)]_2\cdot$toluene (1 equiv) and ImPy^{R} (2 equiv) were suspended in dry, degassed toluene under N_2 atmosphere and stirred at room temperature for 16 h. The reaction mixture was then filtered and the precipitate was washed with toluene and dried under reduced pressure to obtain the expected $[Cu(ImPy^R)_2]OTf$ complex.

Bis(2-(4-*N*,*N*-dimethylaminophenyliminomethyl)pyridine)copper(I) trifluoromethanesulfonate [Cu(ImPy^{DMA})$_2$]OTf (5): Following the general procedure from $[Cu(OTf)]_2\cdot$toluene (126 mg, 0.5 mmol), $ImPy^{DMA}$ (226 mg, 1.0 mmol), and toluene (5 mL), $[Cu(ImPy^{DMA})_2]OTf$ **5** was isolated as a black solid (341 mg, 97%).
Spectroscopic data were consistent with previously reported data for this compound.[18]
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (br s, 2H), 8.42 (br s, 2H), 8.05 (br s, 4H), 7.48 (br s, 6H), 6.59 (br s, 4H), 2.96 (s, 12H). ^{13}C NMR could not be measured due to low solubility of the title compound in acetone-d6, $CDCl_3$, CD_3CN, or DMSO-d6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -77.2 (s).

IR: 1595, 1519 (C–N st), 1222, 1153, 1026, 634, 516 cm^{-1}. HRMS calcd. for $C_{28}H_{30}N_6Cu$ 513.1828, found 513.1818 ($[Cu(ImPy^{DMA})_2]^+$).

Bis(2-(4-methoxyphenyliminomethyl)pyridine)copper(I) trifluoromethanesulfonate [Cu(ImPy^{Anis})$_2$]OTf (6): Following the general procedure from $[Cu(OTf)]_2$·toluene (126 mg, 0.5 mmol), $ImPy^{Anis}$ (213 mg, 1.0 mmol), and toluene (5 mL), $[Cu(ImPy^{Anis})_2]OTf$ **6** was isolated as a black solid (142 mg, 45%).
Spectroscopic data were consistent with previously reported data for this compound.[19]
Mp: 120 °C. ^1H NMR (400 MHz, acetone-d6): δ 9.46 (s, 2H), 8.76 (br s, 2H), 8.37–8.20 (m, 4H), 7.83 (br t, *J* = 6.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.4 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR could not be measured due to low solubility of the title compound in acetone-d6, $CDCl_3$, CD_3CN, or DMSO-d6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -77.1 (s). IR: 2937, 2841, 2015, 1596 (C–N st), 1506, 1466, 1444, 1363, 1246, 1223, 1152, 1112, 1055, 1026, 833, 772, 744, 718 cm^{-1}. HRMS calcd for $C_{28}H_{24}N_4CuO_2$ 487.1195, found 487.1193 ($[Cu(ImPy^{Anis})_2]^+$).

Bis(2-(adamantyliminomethyl)pyridine)copper(I) trifluoromethanesulfonate [Cu(ImPy^{Ad})$_2$] OTf (7): Following the general procedure from $[Cu(OTf)]_2$·toluene (126 mg, 0.5 mmol), $ImPy^{Ad}$ (241 mg, 1.0 mmol), and toluene (5 mL), $[Cu(ImPy^{Ad})_2]OTf$ **7** was isolated as a brown solid (290 mg, 84%). Single crystals suitable for X-ray diffraction were grown from DCM/petroleum ether.
Mp: 211 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 2H), 8.39 (br s, 2H), 8.11–8.02 (m, 2H), 8.02–7.91 (m, 2H), 7.65–7.54 (m, 2H), 2.14 (s, 6H), 1.84–1.64 (m, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 156.2, 151.4, 148.5, 138.4, 127.9, 127.7, 60.1, 43.8, 35.9, 29.3. ^{19}F NMR (377 MHz, $CDCl_3$): δ -77.9 (s). IR: 2905, 2851, 1647 (C–N st), 1593, 1519, 1474, 1441, 1372, 1263, 1222, 1138, 1102, 1087, 1030, 984, 1050, 771, 743, 697 cm^{-1}. HRMS calcd for $C_{32}H_{40}N_4Cu$ 543.2549, found 543.2545 ($[Cu(ImPy^{Ad})_2]^+$).

Bis(2-(2,6-bis(1-methylethyl)phenyliminomethyl)pyridine)copper(I) trifluoromethanesulfo-sulfonate [Cu(ImPy^{Dipp})$_2$]OTf (8): Following the general procedure from $[Cu(OTf)]_2$·toluene (126 mg, 0.5 mmol), $ImPy^{Dipp}$ (266 mg, 1.0 mmol), and toluene (5 mL), $[Cu(ImPy^{Dipp})_2]OTf$ **8** was isolated as a brown solid (356 mg, 96%). Single crystals suitable for X-ray diffraction were grown from DCM/petroleum ether.
Mp: 239 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.58–8.49 (m, 2H), 8.47–8.42 (m, 2H), 8.23 (s, 2H), 8.15–7.98 (m, 2H), 7.87 (br s, 2H), 7.22–7.03 (m, 6H), 2.87 (br s, 4H), 1.11 (br s, 12H), 0.53 (br s, 12H). ^1H NMR (400 MHz, acetone-d6): 8.90 (s, 2H), 8.80 (br s, 2H), 8.42–8.25 (m, 4H), 7.98 (br t, *J* = 6.0 Hz, 2H), 7.17 (br s, 6H), 3.21–2.84 (m, 4H), 1.11 (br s, 12H), 0.60 (br s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d6): δ 164.6, 150.1, 149.2, 145.6, 139.2, 138.8, 129.5, 128.5, 126.6, 123.6, 68.3, 27.8. ^{19}F NMR (377 MHz, acetone-d_6): δ -77.9 (s). IR: 2960, 2868, 1637, 1616, 1602, 1590, 1564, 1463, 1446, 1387, 1365, 1310, 1271, 1254, 1223, 1209, 1156, 1101, 1029, 1015, 935, 910, 779, 759, 752, 708 cm^{-1}. HRMS calcd for $C_{36}H_{44}N_4Cu$ 595.2862, found 595.2834 ($[Cu(ImPy^{Dipp})_2]^+$).

3. CRYSTALLOGRAPHIC DATA

X-Ray crystal structure of (3)

Crystal data for **3**: $[C_{36}H_{44}CuN_8](BF_4)\cdot CH_2Cl_2$, M = 824.07, monoclinic, $P2_1/c$ (no. 14), a = 20.808(3), b = 31.071(2), c = 12.2164(11) Å, β = 90.694(11)°, V = 7897.6(15) Å^3, Z = 8 [two independent molecules], D_c = 1.386 g cm^{-3}, μ(Cu-Kα) = 2.504 mm^{-1}, T = 173 K, dark red needles, Agilent Xcalibur PX Ultra A diffractometer; 15216 independent measured reflections (R_{int} = 0.0662), F^2 refinement,[20,21] R_1(obs) = 0.2039, wR_2(all) = 0.5109, 10628 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 153°], 1014 parameters. CCDC 1583789.

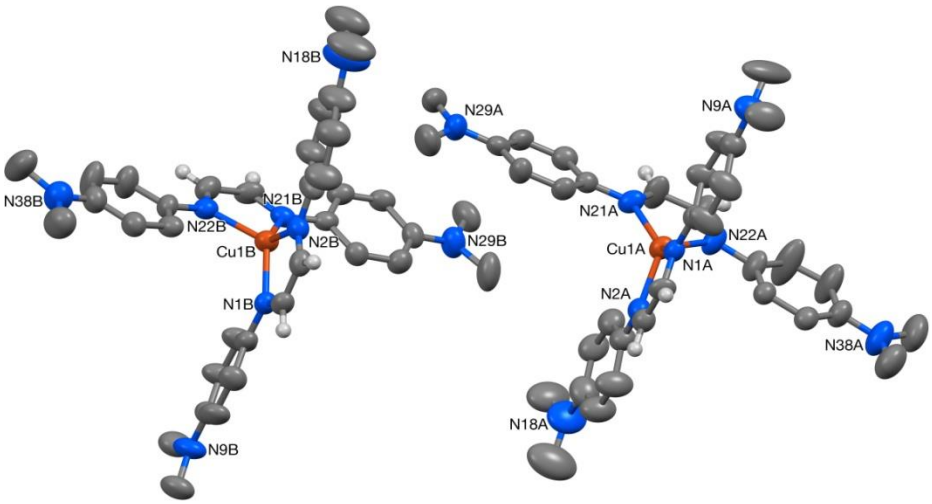


Figure S1: Structure of the two independent cations, **3-A** (right) and **3-B** (left), present in the crystal of **3** (50% probability ellipsoids).Most hydrogen atoms are omitted for clarity.

The initial diffraction images for crystals of **3** showed slightly streaky spots, but the elongated tails of the spots were of substantially lower intensity than the main peaks so this was not expected to be a major issue. The spots indexed well to a monoclinic unit cell with a sensible volume (though with a beta angle quite close to 90°), and so a 0.84 Å resolution unique monoclinic data set was collected. The data collection ran for *ca*. 89 hours, but gave a weaker than expected data set with a mean I/σ of *ca*. 5.4.

Close inspection of reciprocal space plots showed the data set to be badly twinned, with the initial indexing using only *ca*. 52% of the observed spots. Unfortunately, despite numerous efforts no attempts at modelling the twinning gave any noticeable improvement over the standard, non-twin, data processing. These efforts included investigating the possibility of the near 90° beta angle causing the data set to emulate orthorhombic symmetry. The best that could be achieved was to process the data using every available crystal movement option (moderate and significant wobbling, as well as sudden discontinuous changes of sample orientation) despite no evidence that the crystal in any way moved independently of the goniometer. This "best", however, is still very poor with R_1 in excess of 0.20 and wR_2 more than 0.50 in the final refinement. Numerous syntheses and recrystallisations were tried over a *ca*. 4 year period to get a better structure, with four samples reaching a diffractometer though only two complete data sets were collected. The results presented here are the best we were able to obtain. Despite the evident issues, the structure derived from this

data clearly reveals the nature of the complex to be a CuL_2 species, and so we feel that it still has some worth.

The structure contains two independent copper cations (**3-A** and **3-B**), two independent BF_4 anions, and two independent included dichloromethane solvent molecules. The N9B-based dimethylamido group in complex **3-B**, the B20-based tetrafluoroborate anion, and the C50-based included dichloromethane solvent molecule were all found to be disordered, and in each case, two orientations were identified, of *ca*. 85:15, 55:45 and 76:24% occupancy respectively. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

X-Ray crystal structure of (7)

Crystal data for **7**: $C_{32}H_{40}CuN_4 \cdot CF_3O_3S \cdot 0.5(CH_2Cl_2)$, M = 735.75, monoclinic, $P2_1/n$ (no. 14), a = 12.3905(3), b = 19.0233(5), c = 14.4810(3) Å, β = 102.996(2)°, V = 3325.85(14) Å^3, Z = 4, D_c = 1.469 g cm^{-3}, μ(Cu-Kα) = 2.744 mm^{-1}, T = 173 K, red platy needles, Agilent Xcalibur PX Ultra A diffractometer; 6376 independent measured reflections (R_{int} = 0.0316), F^2 refinement,[1,2] R_1(obs) = 0.0397, wR_2(all) = 0.1092, 4921 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 148°], 479 parameters. CCDC 1583790.

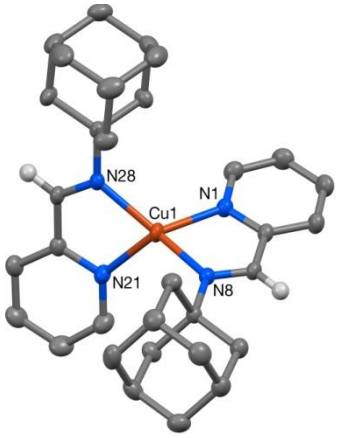


Figure S2: Structure of the cation present in the crystal of **7** (50% probability ellipsoids). Most hydrogen atoms are omitted for clarity.

The triflate anion and the included dichloromethane solvent molecule in the structure of **7** were both found to be disordered, the latter across a centre of symmetry. For the triflate anion two orientations were identified of *ca*. 91 and 9% occupancy, whilst for the dichloromethane solvent molecule two unique orientations of *ca*. 42 and 8% were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

X-Ray crystal structure of (8)

Crystal data for **8**: $C_{36}H_{44}CuN_4 \cdot CF_3O_3S$, M = 745.36, triclinic, P-1 (no. 2), a = 9.1002(5), b = 10.9858(6), c = 19.3481(7) Å, α = 89.693(4), β = 79.192(4), γ = 82.793(4)°, V = 1884.64(16) Å^3, Z = 2, D_c = 1.313 g cm^{-3}, μ(Mo-Kα) = 0.689 mm^{-1}, T = 233 K (the crystals were found to shatter in the low temperature stream at both 173K and 203K, and so the temperature was raised to 233 K), red-brown blocks, Agilent Xcalibur 3 E diffractometer; 7408 independent measured reflections (R_{int} = 0.0215), F^2 refinement,[1,2] R_1(obs) = 0.0504, wR_2(all) = 0.1271, 5713 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 483 parameters. CCDC 1583791.

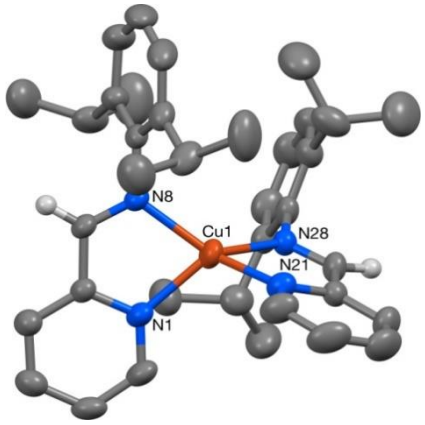


Figure S3: Structure of the cation present in the crystal of **8** (50% probability ellipsoids). Most hydrogen atoms are omitted for clarity.

The S50-based triflate anion in the structure of **8** was found to be disordered. Two orientations were identified of *ca*. 75 and 25% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

4. REDUCTION OF AZIDES

General procedure: In a microwave vial azide (0.5 mmol) and [Cu(DAB^{DMA})$_2$]BF$_4$ **3** (37 mg, 10 mol%) were suspended in a microwave vial in toluene (0.33 mL) and water (0.66 mL) and sealed using a crimped cap. This mixture was heated to 100 °C for 20 h before being cooled and filtered through celite and washed with EtOAc. The organic filtrate was washed with saturated, aqueous Na$_4$EDTA (3×10 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. Reported yields are isolated yields, and are the average of at least two independent runs.

4-Nitroaniline (1a): Following the general procedure, from 1-azido-4-nitrobenzene (82 mg, 0.5 mmol), **1a** was isolated as a brown solid (60 mg, 89%) after purification by column chromatography (silica, petroleum ether/EtOAc = 1:2, R_f = 0.3).

Spectroscopic data were consistent with previously reported data for this compound.[22]
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 4.39 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 152.4, 139.8, 126.4, 113.4.

3-Nitroaniline (1b): Following the general procedure from 3-azido-3-nitrobenzene (72 mg, 0.5 mmol), **1b** was isolated as a brown solid (55 mg, 91%) without further purification necessary.
Spectroscopic data were consistent with previously reported data for this compound.[23]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.55 (m, 1H), 7.52–7.47 (m, 1H), 7.31–7.23 (m, 1H) 6.98–6.92 (m, 1H), 4.00 (s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 149.2, 147.4, 129.9, 120.6, 113.2, 109.0.

4-Aminobenzonitrile (1c): Following the general procedure from 4-azidobenzonitrile (82 mg, 0.5 mmol), **1c** was isolated as a light brown solid (45 mg, 65%) after purification by column chromatography (silica, petroleum ether/EtOAc = 1:2, R_f = 0.2).
Spectroscopic data were consistent with previously reported data for this compound.[24]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.91 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 150.6, 133.8, 120.2, 114.4, 99.9.

4-(Trifluoromethyl)aniline (1d): Following the general procedure from 1-azido-4-(trifluoromethyl)benzene (94 mg, 0.5 mmol), **1d** was isolated as a black oil (54 mg, 64%) after purification by column chromatography (silica, petroleum ether/EtOAc = 1:2, R_f = 0.6).
Spectroscopic data were consistent with previously reported data for this compound.[22]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.92 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 149.4, 126.7 (q, *J* = 3.9 Hz), 124.9 (q, *J* = 270.4 Hz), 120.1 (q, *J* = 32.4 Hz), 114.2. ^{19}F NMR (377 MHz, $CDCl_3$): δ -61.1 (s).

Ethyl 4-aminobenzoate (1e): Following the general procedure from ethyl 4-azidobenzoate (89 mg, 0.5 mmol) **1e** was isolated as a yellow solid (68 mg, 89%) after purification by column chromatography (silica, petroleum ether/EtOAc = 1:2, R_f = 0.5).
Spectroscopic data were consistent with previously reported data for this compound.[22]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.78 (m, 2H), 6.67–6.56 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.09 (br s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 166.7, 150.8, 131.5, 120.0, 113.8, 60.3, 14.4.

4-Aminoacetophenone (1f): Following the general procedure from 4-azidoacetophenone (81 mg, 0.5 mmol), **1f** was isolated as an orange solid (53 mg, 78%) after purification by column chromatography (silica, petroleum ether/EtOAc = 1:1, R_f = 0.3).
Spectroscopic data were consistent with previously reported data for this compound.[22]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.67 (m, 2H), 6.72–6.53 (m, 2H), 4.25 (br s, 2H), 2.50 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 196.6, 151.3, 130.8, 127.7, 113.7, 26.1.

7-Nitrobenzo[*c*][1,2,5]oxadiazol-4-amine (1g): Following the general procedure from 4-azido-7-nitrobenzo[c][1,2,5]oxadiazole (103 mg, 0.5 mmol), **1g** was isolated as a brown solid (50 mg, 55%) without further purification necessary.
Spectroscopic data were consistent with previously reported data for this compound.[14]
^{1}H NMR (400 MHz, DMSO-d6): δ 8.89 (br s, 2H), 8.54–8.42 (m, 1H), 6.39 (d, *J* = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6): δ 147.8, 144.8, 144.6, 138.5, 121.0, 103.1.

Tosyl amine (1h): Following the general procedure from tosyl azide (99 mg, 0.5 mmol), **1h** was isolated as an off-white solid (62 mg, 73%) without further purification necessary.
Spectroscopic data were consistent with previously reported data for this compound.[25]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.02 (br s, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 143.6, 139.0, 129.7, 126.4, 21.5.

4-Aminopyridine (1i): Following the general procedure from 4-azidopyridine (60 mg, 0.5 mmol), **1i** was isolated as a red oil (22 mg, 45%) after purification by column chromatography (silica, petroleum ether/EtOAc/NEt_3 = 1:2:0.02, R_f = 0.3).
Spectroscopic data were consistent with previously reported data for this compound.[26]
^{1}H NMR (400 MHz, DMSO-d6): δ 7.97 (dd, *J* = 4.8; 1.5 Hz, 2H), 6.46 (dd, *J* = 4.8; 1.5 Hz, 2H), 5.98 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d6): δ 154.6, 149.9, 109.3.

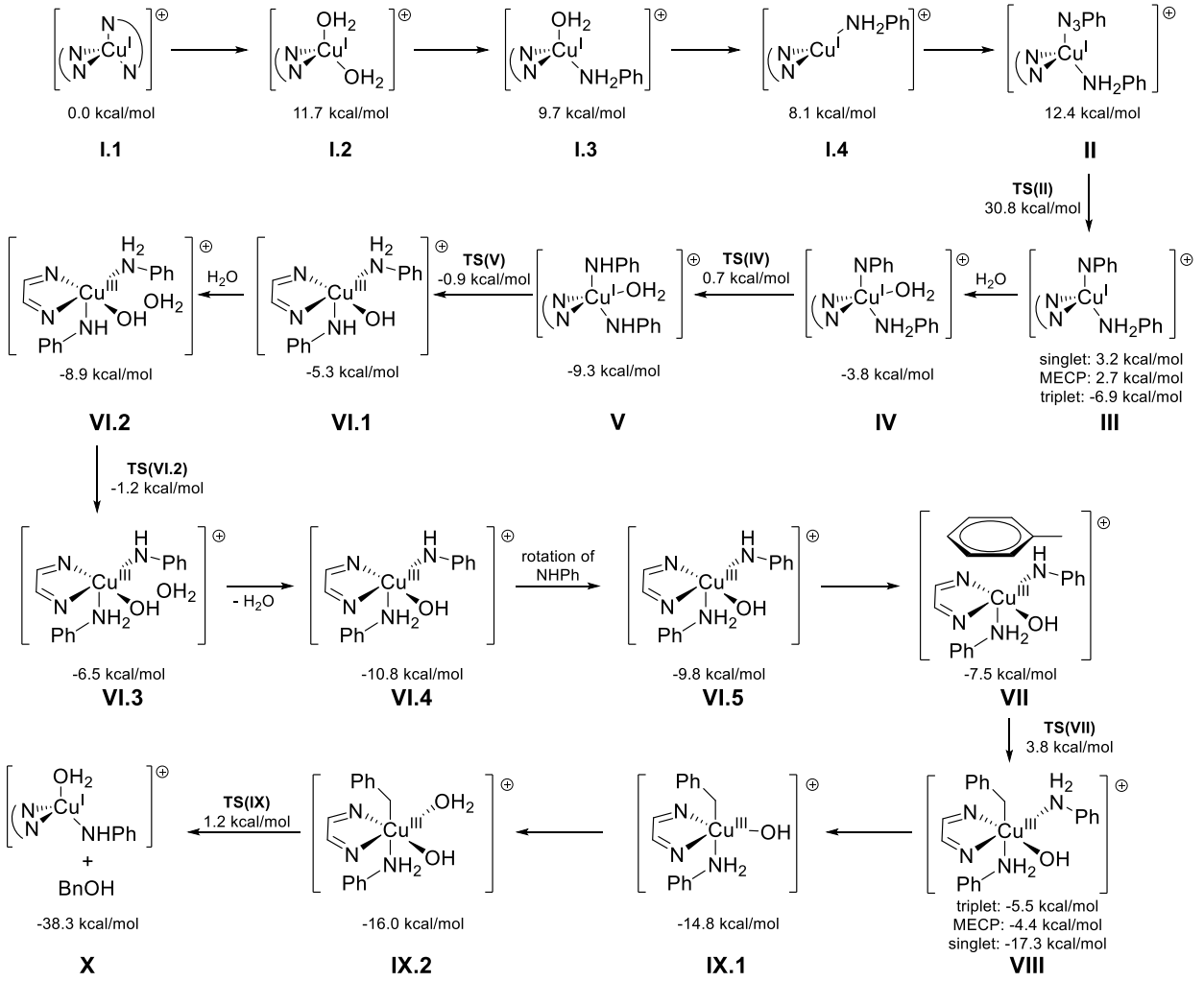
Methyl-3-azidothiophene-2-carboxylate (1j): Following the general procedure from methyl 3-azidothiophene-2-carboxylate (81 mg, 0.5 mmol), **1j** was isolated as a yellow solid (31 mg, 69%) after purification by column chromatography (silica, petroleum ether/EtOAc = 5:1 R_f = 0.4).
Spectroscopic data were consistent with previously reported data for this compound.[27]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H) 5.48 (br s), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.0, 154.0, 131.5, 119.8, 101.2, 51.2.

5. COMPUTATIONAL DATA

All calculations were carried out with the Gaussian09 program package[28] using the methods of the Density functional Theory (DFT). The selected functional was BP86[29] with empirical dispersion correction of Grimme (BP86-D3).[30] The selected basis set was 6-31G(d) for C, N, O and H,[31] and SDD for Cu with the corresponding electron core potentials.[32] The validity of the description was confirmed by benchmarking with a variety of functionals, see Table S4. Solvent effects were considered with the use of a continuum model, namely SMD.[33] We considered water as computational solvent because reaction in water gives higher yields than in toluene, although experimentally toluene/water (1:1) or (1:2) mixtures give better results. Optimizations of all species presented were carried out in solution without symmetry restrictions. We confirmed the nature of all computed stationary points as minima or transition states through vibrational

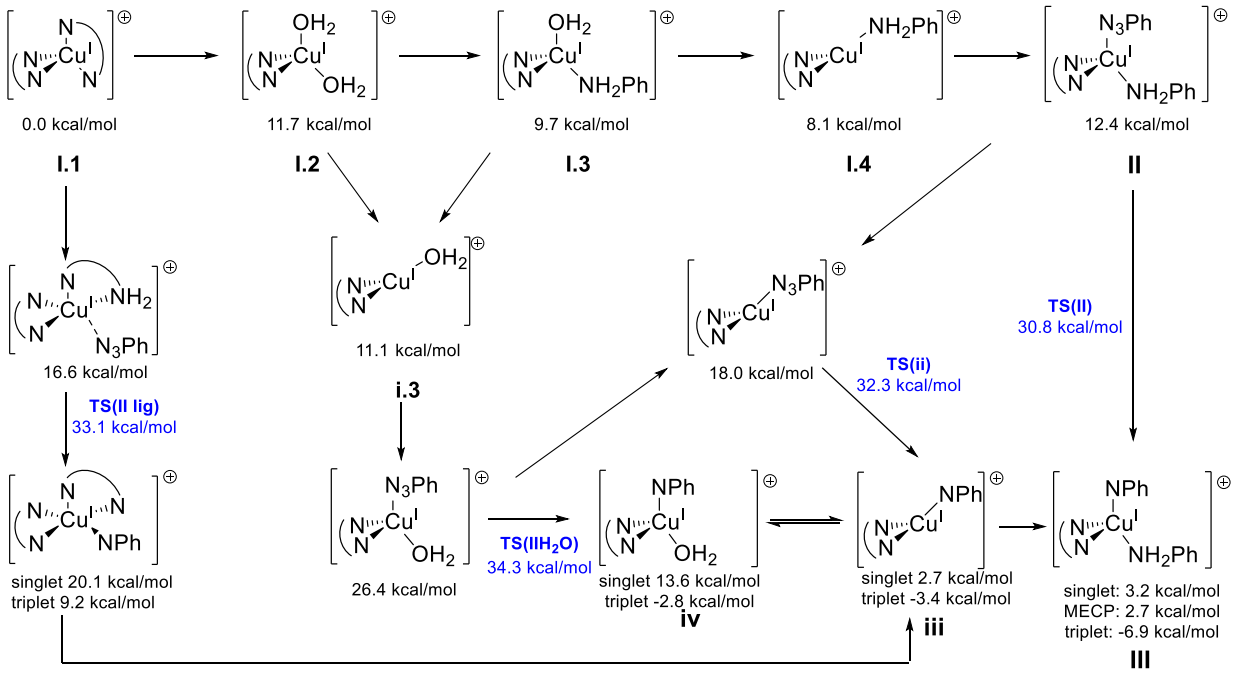
frequency calculations. Systematic conformation analyses were carried out for all steps and therefore only results with the most stable conformers are discussed. Free energy corrections were initially calculated at 298.15 K and 105 Pa pressure, including zero point energy corrections (ZPE). Frequencies were later re-evaluated with the GoodVibes[34] program changing the temperature to 373.15 K and the reference state to 1M. Grimme's correction for low frequency modes[35] (below 100 cm^{-1}) was applied to all species. Minimum energy crossing points (MECP) were computed with the program supplied by Harvey.[36] Reported MECP free energies correspond to an average of those for the two intervening states.

A summary of the computational results, including the full reaction cycle (Scheme S.1) and the obtained potential and free energies are given in Table S.1 (intermediates) and Table S.2 (transition states and MECPs). The energeticsfor the transition state for the nitrogen extrusion of the 4-nitrophenyl azide are presented in Table S3. The relative energies were calculated with respect to $[Cu(DAB^{Me})]^+$ and PhN_3.



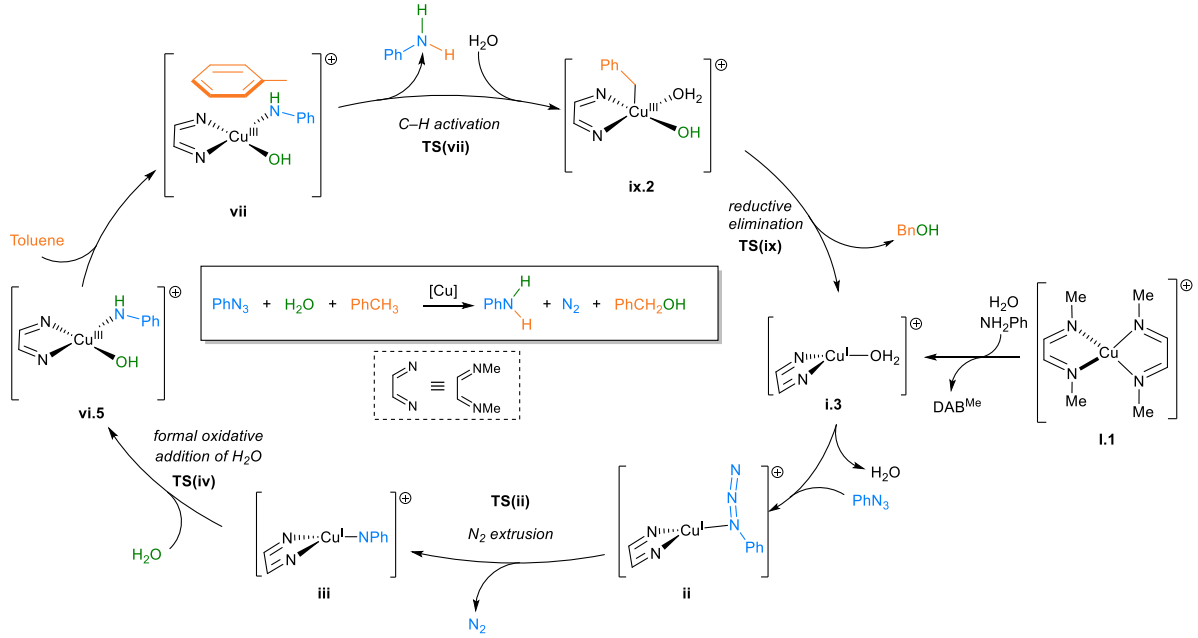
Scheme S1. Full computed reaction cycle. Energies correspond to free energies in solution at 373.15 K.

Alternative active species in the rate limiting step (nitrogen extrusion)



Scheme S2. Some of the computed active species in the nitrogen extrusion step. Energies correspond to free energies in solution at 373.15 K.

Alternative catalytic cycle: Reaction pathway without aniline coordination



Scheme S3. Overview of the alternative catalytic cycle, without aniline coordination, with selected intermediates. Lowercase roman numbers notation is used for equivalent species in the main text with uppercase roman numbers but without aniline as ligand.

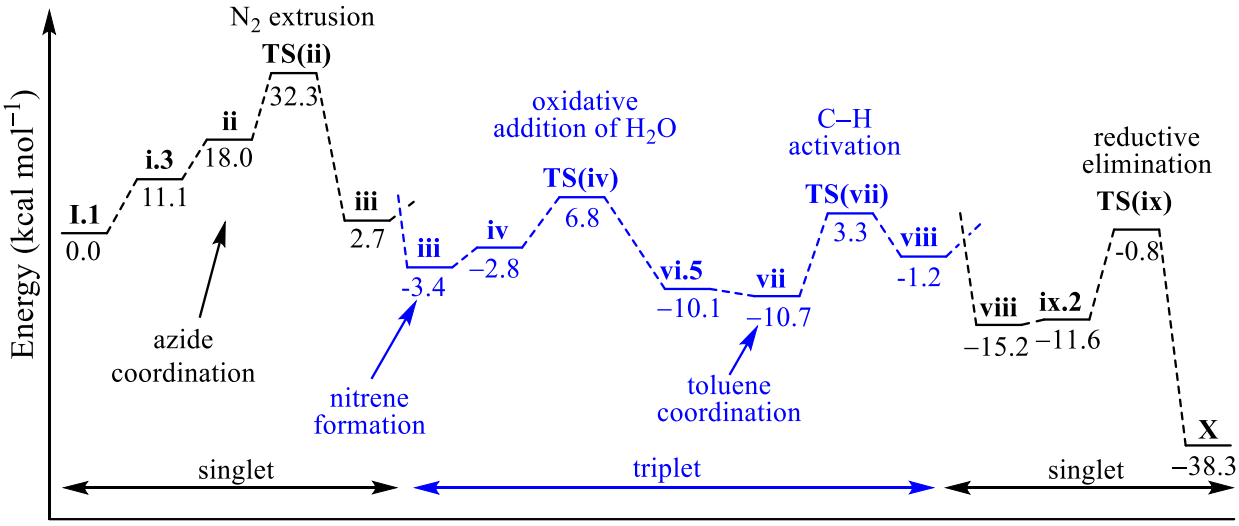


Figure S4. Free energy diagram for the alternative catalytic cycle without aniline coordination, with selected intermediates at 373.15 K and in kcal mol^{-1}. Lowercase roman numbers notation is used for equivalent species in the main text with uppercase roman numbers but without aniline as ligand.

Table S1. Calculated energies for all reaction intermediates. E = potential energy, G = free energy in solution.

label	E [Hartree]	G 298K [Hartree]	G 373K[a] [Hartree]	ΔE [kcal mol^{-1}]	ΔG 298K [kcal mol^{-1}]	ΔG 373K[a] [kcal mol^{-1}]
I.1	-730.85034	-730.65759	-730.66694	0.0	0.0	0.0
I.2	-616.97057	-616.84572	-616.85460	4.8	13.0	11.7
I.3	-828.16787	-827.95468	-827.96451	-2.4	9.3	9.7
I.4	-751.72990	-751.53853	-751.54717	8.7	8.0	8.1
II	-1147.60619	-1147.32392	-1147.33497	-3.2	10.0	12.4
III	-1038.07780	-1037.80046	-1037.81113	-0.3	1.6	3.2
	-1038.09184	-1037.81624	-1037.82722	-9.1	-8.3	-6.9
IV	-1114.52569	-1114.23089	-1114.24212	-17.6	-6.1	-3.8
V	-1114.53305	-1114.24004	-1114.25100	-22.3	-11.8	-9.3
VI.1	-1114.53077	-1114.23348	-1114.24454	-20.8	-7.7	-5.3
VI.2	-1190.97590	-1190.65876	-1190.67011	-36.4	-12.1	-8.9
VI.3	-1190.97001	-1190.65496	-1190.66626	-32.7	-9.7	-6.5
VI.4	-1114.53756	-1114.24200	-1114.25335	-25.1	-13.0	-10.8
VI.5	-1114.53717	-1114.24032	-1114.25169	-24.9	-12.0	-9.8
VII	-1386.11821	-1385.70410	-1385.71689	-39.2	-12.2	-7.5
VIII	-1386.13884	-1385.72040	-1385.73254	-52.2	-22.4	-17.3
	-1386.11792	-1385.70026	-1385.71374	-39.0	-9.8	-5.5

Table S1. cont						
IX.1	-1098.50418	-1098.18989	-1098.20189	-34.3	-16.5	-14.8
IX.2	-1174.94569	-1174.61175	-1174.62378	-47.6	-18.8	-16.0
Aniline	-287.60613	-287.52116	-287.52655			
Benzyl azide	-395.85732	-395.78870	-395.79456			
Benzyl alcohol	-346.77132	-346.67356	-346.67933			
DAB-Me	-266.71272	-266.62751	-266.63334			
H_2O	-76.42027	-76.41821	-76.41984			
N_2	-109.52378	-109.53689	-109.53842			
Toluene	-271.55813	-271.46346	-271.46879			

[a] Free energy at 373.15 K with Grimme corrections for low frequencies and change of the state of reference to 1 M.

Table S2. Calculated energies for all transition states and MECPs.

label	**E** [Hartree]	**G 298K** [Hartree]	**G 373K[a]** [Hartree]	**ΔE** [kcal mol^{-1}]	**ΔG 298K** [kcal mol^{-1}]	**ΔG 373K[a]** [kcal mol^{-1}]
TS(II)	-1147.57524	-1147.29515	-1147.30570	16.2	28.1	30.8
TS(IV)	-1114.51578	-1114.22406	-1114.23494	-11.4	-1.8	0.7
TS(V)	-1114.51817	-1114.22639	-1114.23751	-12.9	-3.2	-0.9
TS(VI.2)	-1190.95957	-1190.64568	-1190.65790	-26.2	-3.9	-1.2
TS(VII)	-1386.09726	-1385.68586	-1385.69886	-26.1	-0.7	3.8
TS(IX)	-1174.91477	-1174.58452	-1174.59624	-28.2	-1.7	1.2
MECP III	-1038.07589	-1037.80125	-1037.81151	0.9	1.1	3.0
singlet/triplet	-1038.07588	-1037.80234	-1037.81249	0.9	0.4	2.4
MECP VIII	-1386.11442	-1385.69870	-1385.71100	-36.9	-8.8	-3.8
singlet/triplet	-1386.11442	-1385.69995	-1385.71280	-36.8	-9.6	-4.9

[a] Free energy at 373.15 K with Grimme corrections for low frequencies and change of the state of reference to 1 M.

Table S3. Calculated energies considering nitrophenyl azide.

label	**E** [Hartree]	**G 298K** [Hartree]	**G 373K[a]** [Hartree]	**ΔE** [kcal mol^{-1}]	**ΔG 298K** [kcal mol^{-1}]	**ΔG 373K[a]** [kcal mol^{-1}]
4-Nitrophenylazide	-600.38860	-600.32209	-600.32875			
TS(II)	-1352.11864	-1351.83912	-1351.85050	8.6	21.5	24.1

[a] Free energy at 373.15 K with Grimme corrections for low frequencies and change of the state of reference to 1 M.

Benchmarking of computational method:

Table S4. Calculated frequencies (cm^{-1}) for C=N stretching with different functionals for complex **1**, $[Cu(DAB^{Me})_2]^+$ (species optimized in gas phase). Experimental data corresponding to complex $[Cu(DAB^{tBu})_2]BF_4$ are 1541 for the symmetric stretching and 1627 cm^{-1} for the asymmetric stretching.

Method	**M06**	**ωB97x-D**	**B3lyp-D3**	**BP86-D3**	**BP86-D3**	**BP86-D3**	**BP86-D3**
Basis Set	*sdd & 6-31g(d)*	*sdd & 6-31g(d)*	*sdd & 6-31g(d)*	*sdd & 6-31g(d)*	*cc-pVTZ*	*cc-pVQZ*	*sdd & cc-pVTZ*
sym	1678	1707	1644	1552	1529	1527	1531
C=N	1680	1707	1644	1555	1534	1532	1536
asym	1748	1775	1726	1630	1610	1610	1614
C=N	1748	1775	1726	1630	1610	1610	1614

Cartesian Coordinates and for All Computed Structures

Small Minima (organic)

N_2

Energy (POTENTIAL) = -109.523780034 Eh

	Atom	X	Y	Z
1	N	-1.5008	1.2933	0.0000
2	N	-2.6179	1.2933	0.0000

nitrophenylazide

Energy (POTENTIAL) = -600.388598025 Eh

	Atom	X	Y	Z
1	N	-0.4851	-3.6713	0.9706
2	N	-1.1041	-4.6390	0.4834
3	N	-1.5829	-5.5049	-0.1100
4	C	-0.7690	-3.2711	2.2955
5	C	-0.0306	-2.1635	2.7704
6	C	-1.7214	-3.9102	3.1243
7	C	-0.2392	-1.6941	4.0657
8	H	0.7006	-1.6822	2.1154
9	C	-1.9325	-3.4407	4.4193
10	H	-2.2928	-4.7686	2.7576
11	C	-1.1895	-2.3380	4.8788
12	H	0.3226	-0.8396	4.4486
13	H	-2.6644	-3.9207	5.0723
14	N	-1.4097	-1.8499	6.2362
15	O	-2.2737	-2.4178	6.9423
16	O	-0.7250	-0.8825	6.6393

H_2O

Energy (POTENTIAL) =

	Atom	X	Y	Z
1	H	0.0441	0.0000	0.0389
2	O	-0.0227	0.0000	1.0159
3	H	0.9182	0.0000	1.2872

Toluene

Energy (POTENTIAL) = -271.558127933 Eh

	Atom	X	Y	Z
1	C	-2.4781	-1.3432	0.0427
2	C	-1.0718	-1.3425	0.0507
3	C	-0.3456	-0.1343	0.0091
4	C	-1.0682	1.0785	-0.0391
5	C	-2.4724	1.0834	-0.0474
6	C	-3.1843	-0.1295	-0.0065
7	H	-3.0216	-2.2944	0.0775
8	H	-0.5270	-2.2937	0.0917
9	H	-0.5190	2.0277	-0.0693
10	H	-3.0133	2.0361	-0.0830
11	H	-4.2800	-0.1270	-0.0105
12	C	1.1678	-0.1282	0.0010
13	H	1.5605	0.1778	-0.9875
14	H	1.5731	0.5867	0.7402
15	H	1.5787	-1.1271	0.2279

phenylazide

Energy (POTENTIAL) = -395.857319138 Eh

	Atom	X	Y	Z
1	N	-0.3776	-3.7352	0.9904
2	N	-0.9759	-4.6996	0.4842
3	N	-1.4350	-5.5782	-0.1138
4	C	-0.7622	-3.2841	2.2894
5	C	-0.0421	-2.1845	2.7959
6	C	-1.7932	-3.8766	3.0479
7	C	-0.3573	-1.6780	4.0652
8	H	0.7543	-1.7380	2.1924
9	C	-2.0965	-3.3584	4.3153
10	H	-2.3520	-4.7316	2.6520
11	C	-1.3836	-2.2604	4.8300
12	H	0.2040	-0.8226	4.4559
13	H	-2.8978	-3.8190	4.9030
14	H	-1.6271	-1.8616	5.8201

benzylalcohol

Energy (POTENTIAL) = -346.771318955 Eh

	Atom	X	Y	Z
1	C	-2.4657	-1.3421	0.0252
2	C	-1.0604	-1.3382	0.0560
3	C	-0.3451	-0.1251	0.0296
4	C	-1.0620	1.0887	-0.0176
5	C	-2.4658	1.0879	-0.0388
6	C	-3.1728	-0.1284	-0.0201
7	H	-3.0083	-2.2939	0.0473
8	H	-0.5110	-2.2864	0.1033
9	H	-0.5114	2.0356	-0.0317
10	H	-3.0105	2.0383	-0.0719
11	H	-4.2684	-0.1290	-0.0366
12	C	1.1697	-0.1226	0.0123
13	H	1.5250	0.0578	-1.0247
14	H	1.5503	-1.1215	0.3136
15	O	1.6604	0.9091	0.8920
16	H	2.6036	1.0417	0.6602

aniline

Energy (POTENTIAL) = -287.606134639 Eh

	Atom	X	Y	Z
1	C	-0.4593	0.5306	-0.0696
2	C	0.9513	0.5626	0.0680
3	C	1.5915	1.8243	0.1579
4	C	0.8411	3.0084	0.1169
5	C	-0.5595	2.9719	-0.0155
6	C	-1.1989	1.7216	-0.1090
7	H	-0.9676	-0.4386	-0.1443
8	H	2.6828	1.8651	0.2600
9	H	1.3610	3.9712	0.1855
10	H	-1.1407	3.8994	-0.0483
11	H	-2.2886	1.6697	-0.2180
12	N	1.6858	-0.6243	0.1807
13	H	1.2419	-1.4326	-0.2629
14	H	2.6649	-0.5400	-0.1042

PhCH2CH2Ph

Energy (POTENTIAL) = -541.925064860 Eh

	Atom	X	Y	Z
1	C	-3.2652	-0.5856	0.0529
2	C	-1.8601	-0.5898	0.0776
3	C	-1.1319	0.6180	0.0408
4	C	-1.8466	1.8329	-0.0293
5	C	-3.2512	1.8423	-0.0552
6	C	-3.9659	0.6317	-0.0138
7	H	-3.8138	-1.5337	0.0884
8	H	-1.3164	-1.5411	0.1298
9	H	-1.2918	2.7788	-0.0611
10	H	-3.7892	2.7960	-0.1044
11	H	-5.0615	0.6372	-0.0305
12	C	0.3821	0.6106	0.0061

13	H	0.7836	1.4959	0.5341
14	H	0.7752	-0.2849	0.5223
15	C	0.9213	0.6201	-1.4530
16	H	0.5192	-0.2628	-1.9839
17	H	0.5281	1.5179	-1.9659
18	C	2.4353	0.6138	-1.4888
19	C	3.1527	-0.5987	-1.5618
20	C	3.1610	1.8199	-1.3849
21	C	4.5579	-0.6075	-1.5394
22	H	2.6008	-1.5435	-1.6401
23	C	4.5656	1.8163	-1.3609
24	H	2.6146	2.7693	-1.3248
25	C	5.2695	0.6011	-1.4388
26	H	5.0979	-1.5591	-1.6035
27	H	5.1118	2.7635	-1.2851
28	H	6.3651	0.5965	-1.4240

H_2O_2

Energy (POTENTIAL) = -151.550686192 Eh

	Atom	X	Y	Z
1	O	-3.0530	2.3974	-0.1927
2	O	-4.3724	1.7127	-0.1927
3	H	-4.9458	2.5134	-0.1927
4	H	-2.4797	1.5967	-0.1927

PhC(=O)H

Energy (POTENTIAL) = -345.574589447 Eh

	Atom	X	Y	Z
1	C	-0.3222	-0.2398	0.0000
2	C	1.0799	-0.2325	0.0006
3	C	1.7789	0.9951	0.0001
4	C	1.0657	2.2168	-0.0010
5	C	-0.3326	2.2058	-0.0015
6	C	-1.0263	0.9781	-0.0010
7	H	-0.8677	-1.1891	0.0004
8	H	1.6431	-1.1736	0.0013
9	H	1.6250	3.1585	-0.0013
10	H	-0.8899	3.1485	-0.0023
11	H	-2.1218	0.9733	-0.0014
12	C	3.2542	0.9835	0.0007
13	O	3.9685	1.9967	0.0004
14	H	3.7172	-0.0356	0.0016

O_2

Energy (POTENTIAL) = -150.327271826 Eh

	Atom	X	Y	Z
1	O	-3.0416	1.8063	-0.1927
2	O	-4.2720	1.8063	-0.1927

DAB-Me

Energy (POTENTIAL) = -266.712719175 Eh

	Atom	X	Y	Z
1	C	-1.6066	1.5049	0.0035
2	H	-2.1304	2.4824	-0.0014
3	C	-0.1407	1.5503	0.0057
4	H	0.3831	0.5728	0.0106
5	C	1.9352	2.6282	0.0059
6	H	2.3561	1.6023	0.0104
7	H	2.3176	3.1680	-0.8795
8	H	2.3140	3.1739	0.8891
9	C	-3.6825	0.4270	0.0036
10	H	-4.1035	1.4528	-0.0009
11	H	-4.0615	-0.1187	-0.8796
12	H	-4.0649	-0.1128	0.8889
13	N	0.4782	2.6844	0.0026
14	N	-2.2256	0.3708	0.0066

Large Minima (complexes)

I.1

Energy (POTENTIAL) = -730.850341693 Eh

	Atom	X	Y	Z
1	Cu	5.8909	2.1753	4.7454
2	N	5.6810	0.1555	4.7173
3	C	6.8326	-0.4504	4.6202
4	H	6.9251	-1.5463	4.6179
5	C	8.0211	0.3893	4.5148
6	H	9.0151	-0.0657	4.3944
7	N	7.8451	1.6808	4.5821
8	C	4.4590	-0.6290	4.8473
9	C	8.9944	2.5736	4.4896
10	N	4.9924	3.5214	3.5345
11	C	4.3433	4.4311	4.2089
12	H	3.8087	5.2589	3.7210
13	C	4.3434	4.3094	5.6630
14	H	3.7836	5.0278	6.2795
15	N	5.0251	3.3239	6.1800
16	C	5.0265	3.5900	2.0782
17	C	5.0447	3.1426	7.6267
18	H	4.6460	-1.7181	4.8626
19	H	3.9457	-0.3258	5.7762
20	H	3.7856	-0.3793	4.0091
21	H	4.6060	2.6542	1.6711
22	H	6.0794	3.6406	1.7507
23	H	4.4693	4.4554	1.6760
24	H	8.8374	3.2614	3.6406
25	H	9.9506	2.0348	4.3619
26	H	9.0353	3.1921	5.4031
27	H	4.6647	2.1326	7.8595
28	H	4.4434	3.8983	8.1638
29	H	6.0910	3.1829	7.9758

I.2

Energy (POTENTIAL) = -616.970565543 Eh

	Atom	X	Y	Z
1	C	-0.9916	0.8678	-0.6429
2	H	-1.7103	1.6309	-0.9768
3	C	0.3596	1.2436	-0.2660
4	H	0.7811	2.2073	-0.5885
5	C	-2.6945	-0.8002	-0.7711
6	H	-3.0827	-1.2313	0.1693
7	H	-3.3471	0.0392	-1.0759
8	H	-2.7309	-1.5981	-1.5326
9	C	2.4469	0.6684	0.7360
10	H	2.7807	1.6473	0.3447
11	H	2.6192	0.6253	1.8254
12	H	3.0582	-0.1298	0.2791
13	N	-1.3050	-0.4029	-0.5550
14	N	1.0395	0.3877	0.4597
15	Cu	0.0955	-1.4158	0.5190
16	H	-1.8990	-2.5646	1.6532
17	H	-0.9311	-2.1056	2.7655
18	H	1.3278	-3.6009	0.9242
19	H	1.3500	-3.3743	-0.6031
20	O	-0.9542	-2.6097	1.9219
21	O	1.5612	-2.9272	0.2466

I.3

Energy (POTENTIAL) = -828.167872685 Eh

	Atom	X	Y	Z
1	C	-0.5935	1.0729	-0.5212
2	H	-1.2485	1.8952	-0.8504
3	C	0.7921	1.0386	-0.9671
4	H	1.1227	1.6881	-1.7911
5	C	-2.3681	0.1877	0.7817
6	H	-2.3160	0.3504	1.8730
7	H	-2.9631	1.0010	0.3244
8	H	-2.8761	-0.7788	0.6267
9	C	2.9655	0.0587	-0.8815
10	H	3.1821	0.7355	-1.7286
11	H	3.6883	0.2371	-0.0674
12	H	3.0954	-0.9885	-1.2079
13	N	-1.0087	0.1111	0.2590
14	N	1.6064	0.2097	-0.3637
15	Cu	0.7029	-0.9894	0.9377
16	H	0.1707	-3.5281	0.7789
17	H	0.6395	-3.0774	-0.6211
18	O	0.9116	-3.0704	0.3230
19	N	0.6168	-1.4846	2.9256
20	H	0.9487	-2.4586	2.9869
21	H	1.2603	-0.9057	3.4830
22	C	-0.7314	-1.3744	3.4239
23	C	-1.1220	-0.2415	4.1611
24	C	-1.6715	-2.3755	3.1136
25	C	-2.4563	-0.1115	4.5819
26	H	-0.3839	0.5340	4.3956
27	C	-3.0004	-2.2377	3.5409
28	H	-1.3580	-3.2502	2.5317
29	C	-3.4012	-1.1055	4.2734
30	H	-2.7543	0.7732	5.1549
31	H	-3.7268	-3.0204	3.2968
32	H	-4.4400	-1.0008	4.6032

I.4

Energy (POTENTIAL) = -751.729896739 Eh

	Atom	X	Y	Z
1	C	-0.6321	-0.5334	-0.8117
2	H	-1.2771	-0.3850	-1.6960
3	C	0.1337	0.6295	-0.3350
4	H	-0.0971	1.6176	-0.7596
5	C	-1.2512	-2.8141	-0.7023
6	H	-1.8817	-3.2308	0.1027
7	H	-1.8778	-2.5968	-1.5900
8	H	-0.5137	-3.5982	-0.9541
9	C	1.7871	1.6857	1.0210
10	H	1.4246	2.6091	0.5360
11	H	1.6586	1.7610	2.1141
12	H	2.8639	1.5544	0.8241
13	N	-0.5326	-1.6608	-0.1908
14	N	1.0732	0.4934	0.5550
15	Cu	1.4529	-1.2065	1.3233
16	N	2.0850	-2.8698	2.1543
17	H	1.8206	-2.9016	3.1511
18	H	3.1160	-2.8960	2.1198
19	C	1.5308	-4.0127	1.4459
20	C	0.3989	-4.6728	1.9528
21	C	2.1048	-4.4148	0.2263
22	C	-0.1596	-5.7418	1.2328
23	H	-0.0418	-4.3463	2.9016
24	C	1.5408	-5.4856	-0.4845
25	H	2.9799	-3.8804	-0.1606
26	C	0.4066	-6.1526	0.0139
27	H	-1.0416	-6.2547	1.6307
28	H	1.9903	-5.7965	-1.4336
29	H	-0.0326	-6.9850	-0.5456

II

Energy (POTENTIAL) = -1147.60619471 Eh

	Atom	X	Y	Z
1	C	0.5930	0.8807	1.5432

2	H	-0.1079	1.6705	1.8566
3	C	1.8641	0.7239	2.2649
4	H	2.1073	1.4123	3.0882
5	C	-0.9306	0.1137	-0.1239
6	H	-1.3976	-0.8861	-0.0734
7	H	-1.6247	0.8731	0.2832
8	H	-0.7331	0.3183	-1.1911
9	C	3.9137	-0.4352	2.6395
10	H	4.0440	0.2801	3.4720
11	H	3.9370	-1.4683	3.0272
12	H	4.7539	-0.3365	1.9305
13	N	0.3397	0.0547	0.5778
14	N	2.6626	-0.2412	1.9117
15	N	0.9302	-3.1712	1.3704
16	N	1.2433	-4.2826	0.8895
17	N	1.7078	-5.2339	0.4212
18	C	-0.4604	-2.9216	1.6541
19	C	-0.7295	-1.9600	2.6430
20	C	-1.5009	-3.5403	0.9366
21	C	-2.0592	-1.5984	2.9010
22	H	0.1011	-1.4929	3.1796
23	C	-2.8274	-3.1770	1.2156
24	H	-1.2778	-4.2833	0.1647
25	C	-3.1108	-2.2023	2.1889
26	H	-2.2714	-0.8421	3.6637
27	H	-3.6406	-3.6533	0.6583
28	H	-4.1479	-1.9169	2.3927
29	Cu	1.9493	-1.3436	0.3915
30	N	2.3579	-2.1164	-1.4402
31	H	2.6097	-3.1146	-1.3829
32	H	3.1618	-1.6293	-1.8619
33	C	1.1662	-1.9283	-2.2404
34	C	1.0173	-0.7659	-3.0196
35	C	0.1280	-2.8764	-2.1816
36	C	-0.1801	-0.5479	-3.7206
37	H	1.8310	-0.0326	-3.0582
38	C	-1.0683	-2.6452	-2.8765
39	H	0.2601	-3.7891	-1.5924
40	C	-1.2307	-1.4798	-3.6466
41	H	-0.2906	0.3594	-4.3241
42	H	-1.8744	-3.3843	-2.8156
43	H	-2.1658	-1.3015	-4.1875

III_triplet

Energy (POTENTIAL) = -1038.09183999 Eh

Atom		X	Y	Z
1	C	-0.7643	0.9388	-0.7167
2	H	-0.8783	1.7995	-1.3909
3	C	0.4493	0.8088	0.1056
4	H	1.2320	1.5800	0.0475
5	C	-2.8426	0.0303	-1.4666
6	H	-3.7422	-0.0264	-0.8296
7	H	-2.8895	0.9281	-2.1083
8	H	-2.8310	-0.8784	-2.0951
9	C	1.7585	-0.4651	1.6388
10	H	2.4318	0.4113	1.6486
11	H	1.4819	-0.7449	2.6689
12	H	2.2906	-1.3255	1.1958
13	N	-1.6611	0.0067	-0.6160
14	N	0.5489	-0.2347	0.8659
15	N	-1.2428	-3.0298	1.4969
16	C	-0.5210	-4.0677	1.9340
17	C	0.8940	-4.1704	1.6613
18	C	-1.1361	-5.1216	2.7036
19	C	1.6299	-5.2562	2.1280
20	H	1.3614	-3.3702	1.0798
21	C	-0.3776	-6.1972	3.1611
22	H	-2.2078	-5.0533	2.9178
23	C	1.0049	-6.2761	2.8800
24	H	2.7019	-5.3172	1.9098
25	H	-0.8601	-6.9890	3.7446
26	H	1.5905	-7.1261	3.2444
27	Cu	-0.9856	-1.6085	0.4074
28	N	-0.1743	-2.5394	-1.3955
29	H	-0.9704	-2.6343	-2.0395
30	H	0.1343	-3.4738	-1.0950
31	C	0.8854	-1.7552	-1.9428
32	C	0.5928	-0.7050	-2.8378
33	C	2.2099	-1.9571	-1.5050
34	C	1.6198	0.1507	-3.2688
35	H	-0.4359	-0.5619	-3.1861
36	C	3.2264	-1.0956	-1.9408
37	H	2.4342	-2.7823	-0.8210
38	C	2.9375	-0.0330	-2.8171
39	H	1.3816	0.9662	-3.9600
40	H	4.2521	-1.2577	-1.5925
41	H	3.7343	0.6396	-3.1509

III_singlet

Energy (POTENTIAL) = -1038.07780368 Eh

Atom		X	Y	Z
1	C	-0.6972	0.6148	-0.1564
2	H	-0.9023	1.6644	-0.4066
3	C	0.5743	0.2281	0.4536
4	H	1.3195	0.9874	0.7304
5	C	-2.8050	-0.0520	-1.0752
6	H	-3.6520	-0.4015	-0.4607
7	H	-2.9224	1.0221	-1.3019
8	H	-2.8211	-0.6336	-2.0139
9	C	1.9988	-1.5551	1.2125
10	H	2.6713	-0.7492	1.5576
11	H	1.7502	-2.2216	2.0573
12	H	2.5076	-2.1671	0.4475
13	N	-1.5585	-0.3386	-0.3781
14	N	0.7667	-1.0431	0.6409
15	N	-0.6493	-3.9044	0.3006
16	C	-0.2303	-4.4275	1.4674
17	C	-0.3301	-3.7370	2.7374
18	C	0.3402	-5.7555	1.4829
19	C	0.1474	-4.3125	3.9103
20	H	-0.7837	-2.7389	2.7348
21	C	0.7697	-6.3423	2.6711
22	H	0.4170	-6.2881	0.5287
23	C	0.6875	-5.6193	3.8817
24	H	0.0856	-3.7700	4.8596
25	H	1.1880	-7.3542	2.6694
26	H	1.0410	-6.0783	4.8111
27	Cu	-0.8099	-2.1429	-0.0468
28	N	-0.2857	-2.2919	-2.2547
29	H	-1.1420	-2.1053	-2.7892
30	H	-0.0117	-3.2774	-2.3433
31	C	0.7634	-1.3748	-2.5180
32	C	0.4664	-0.0491	-2.9021
33	C	2.1022	-1.7488	-2.2733
34	C	1.5014	0.8929	-3.0176
35	H	-0.5734	0.2372	-3.0966
36	C	3.1257	-0.7988	-2.3882
37	H	2.3255	-2.7792	-1.9735
38	C	2.8331	0.5284	-2.7547
39	H	1.2592	1.9201	-3.3115
40	H	4.1603	-1.0988	-2.1890
41	H	3.6359	1.2679	-2.8398

IV

Energy (POTENTIAL) = -1114.52569421 Eh

Atom		X	Y	Z
1	C	-0.9493	1.0114	-0.2462
2	H	-1.1119	2.0629	-0.5247
3	C	0.3306	0.6066	0.3562
4	H	1.1139	1.3607	0.5287
5	C	-3.0961	0.4290	-1.1055
6	H	-3.9335	0.1339	-0.4493
7	H	-3.1724	1.5013	-1.3571
8	H	-3.1712	-0.1807	-2.0233
9	C	1.7407	-1.1477	1.1729
10	H	2.4465	-0.3412	1.4438
11	H	1.5305	-1.7840	2.0490
12	H	2.2007	-1.7982	0.4073
13	N	-1.8430	0.0939	-0.4458
14	N	0.4850	-0.6456	0.6440
15	N	-1.4153	-3.2654	1.0152
16	C	-0.5814	-4.1658	1.5604
17	C	-0.9658	-4.9113	2.7325
18	C	0.7174	-4.4294	0.9863
19	C	-0.0911	-5.8376	3.2967
20	H	-1.9520	-4.7245	3.1698
21	C	1.5709	-5.3646	1.5652
22	H	1.0052	-3.8720	0.0894
23	C	1.1785	-6.0719	2.7234
24	H	-0.3936	-6.3890	4.1937
25	H	2.5540	-5.5502	1.1186
26	H	1.8566	-6.8031	3.1749
27	Cu	-1.1796	-1.7890	-0.0163
28	N	-0.4591	-2.3995	-1.9300
29	H	-0.7741	-3.3927	-1.9855
30	H	0.5644	-2.3502	-1.8437
31	C	-0.9674	-1.5846	-2.9861
32	C	-2.1454	-1.9657	-3.6607
33	C	-0.3498	-0.3534	-3.2877
34	C	-2.6988	-1.1166	-4.6319
35	H	-2.6254	-2.9177	-3.4111
36	C	-0.9176	0.4917	-4.2520
37	H	0.5571	-0.0591	-2.7470
38	C	-2.0928	0.1168	-4.9292
39	H	-3.6130	-1.4218	-5.1527
40	H	-0.4369	1.4501	-4.4766
41	H	-2.5321	0.7801	-5.6815
42	O	-1.7689	-4.9263	-1.4781
43	H	-1.8705	-4.4669	-0.6080
44	H	-2.6086	-4.7056	-1.9362

V

Energy (POTENTIAL) = -1114.53305168 Eh

Atom		X	Y	Z
1	C	-0.2259	0.5036	1.0750
2	H	-0.4649	1.5612	1.2592
3	C	0.7377	-0.1978	1.9305
4	H	1.1616	0.3081	2.8100
5	C	-1.7058	0.4356	-0.8108
6	H	-2.6642	-0.1096	-0.7560
7	H	-1.8697	1.5076	-0.6016
8	H	-1.3147	0.3098	-1.8355
9	C	1.9625	-2.1881	2.4379
10	H	2.4642	-1.5654	3.1999
11	H	1.3863	-2.9839	2.9414
12	H	2.7100	-2.6781	1.7927
13	N	-0.7679	-0.1803	0.1144
14	N	1.0529	-1.4143	1.6026
15	C	-0.1466	-4.5192	1.3219
16	C	-1.1066	-3.9762	2.2336
17	C	0.7128	-5.5651	1.7789
18	C	-1.1736	-4.4345	3.5489
19	H	-1.7793	-3.1932	1.8647
20	C	0.6303	-6.0190	3.0970
21	H	1.4506	-5.9849	1.0851
22	C	-0.3040	-5.4550	3.9923

23	H	-1.9083	-4.0045	4.2383
24	H	1.3028	-6.8128	3.4401
25	H	-0.3592	-5.8131	5.0254
26	Cu	0.0999	-2.0185	-0.1226
27	N	0.5386	-2.1184	-2.0297
28	H	0.2619	-2.9830	-2.5202
29	C	1.0015	-1.1710	-2.8843
30	C	1.0549	-1.3931	-4.3028
31	C	1.4606	0.0885	-2.3691
32	C	1.5352	-0.3991	-5.1515
33	H	0.7086	-2.3544	-4.6995
34	C	1.9345	1.0706	-3.2332
35	H	1.4309	0.2511	-1.2865
36	C	1.9748	0.8375	-4.6271
37	H	1.5705	-0.5773	-6.2313
38	H	2.2812	2.0279	-2.8306
39	H	2.3511	1.6140	-5.3007
40	N	-0.0822	-3.9963	0.0522
41	H	0.5928	-4.5157	-0.5309
42	O	-2.6350	-3.1996	-0.9939
43	H	-1.7560	-3.5541	-0.6758
44	H	-2.7412	-2.4176	-0.4124

VI.1

Energy (POTENTIAL) = -1114.53076775 Eh

Atom		X	Y	Z
1	C	0.1884	0.3549	0.0330
2	H	0.1670	1.4515	-0.0421
3	C	1.3722	-0.3236	0.5804
4	H	2.2566	0.2619	0.8667
5	C	-1.9834	0.1838	-0.9608
6	H	-2.8699	-0.1920	-0.4233
7	H	-1.9664	1.2877	-0.9422
8	H	-2.0548	-0.1598	-2.0075
9	C	2.4835	-2.3582	1.1526
10	H	3.3501	-1.7035	1.3490
11	H	2.2140	-2.9094	2.0694
12	H	2.7439	-3.1023	0.3804
13	N	-0.7894	-0.3935	-0.3634
14	N	1.3219	-1.6135	0.6939
15	C	-0.2853	-4.6425	1.7194
16	C	-1.6043	-4.4169	2.1638
17	C	0.7128	-5.0434	2.6278
18	C	-1.9184	-4.5957	3.5178
19	H	-2.3622	-4.0910	1.4429
20	C	0.3887	-5.2107	3.9839
21	H	1.7298	-5.2327	2.2663
22	C	-0.9241	-4.9884	4.4341
23	H	-2.9443	-4.4233	3.8605
24	H	1.1670	-5.5252	4.6872
25	H	-1.1728	-5.1226	5.4919
26	Cu	-0.2968	-2.4139	-0.2411
27	N	0.8930	-2.6201	-2.2210
28	H	0.0427	-2.9876	-2.6886
29	C	1.1163	-1.3538	-2.6740
30	C	0.1984	-0.6494	-3.5295
31	C	2.2892	-0.6554	-2.2242
32	C	0.4107	0.6889	-3.8509
33	H	-0.6953	-1.1783	-3.8817
34	C	2.4951	0.6802	-2.5658
35	H	3.0088	-1.1963	-1.6009
36	C	1.5528	1.3658	-3.3659
37	H	-0.3125	1.2207	-4.4782
38	H	3.3880	1.2030	-2.2071
39	H	1.7119	2.4195	-3.6163
40	N	0.0324	-4.4099	0.3395
41	H	0.9884	-4.7057	0.1008
42	O	-1.8365	-3.0752	-1.1534
43	H	-0.6320	-4.8702	-0.2999
44	H	-2.0938	-2.3512	-1.7646

VI.2

Energy (POTENTIAL) = -1190.97590447 Eh

Atom		X	Y	Z
1	C	0.0291	0.4198	-0.0953
2	H	0.0436	1.5101	-0.2350
3	C	1.1809	-0.2614	0.5123
4	H	2.0651	0.3188	0.8101
5	C	-2.1315	0.2596	-1.1097
6	H	-3.0395	-0.0879	-0.5894
7	H	-2.0973	1.3630	-1.1214
8	H	-2.1764	-0.1113	-2.1489
9	C	2.2297	-2.2745	1.2327
10	H	3.0942	-1.6166	1.4282
11	H	1.9095	-2.7594	2.1704
12	H	2.5119	-3.0733	0.5270
13	N	-0.9664	-0.3199	-0.4604
14	N	1.1018	-1.5444	0.6765
15	C	-0.3175	-4.6485	1.6709
16	C	-1.5518	-4.4428	2.3228
17	C	0.7967	-5.1162	2.3963
18	C	-1.6663	-4.7063	3.6945
19	H	-2.4044	-4.0698	1.7436
20	C	0.6734	-5.3697	3.7714
21	H	1.7461	-5.2857	1.8772
22	C	-0.5546	-5.1673	4.4254
23	H	-2.6272	-4.5482	4.1961
24	H	1.5413	-5.7356	4.3306
25	H	-0.6471	-5.3689	5.4977
26	Cu	-0.5377	-2.3444	-0.2482
27	N	0.6589	-2.5160	-2.3059
28	H	-0.2136	-2.8059	-2.7810
29	C	1.0222	-1.2703	-2.7124
30	C	0.2004	-0.4586	-3.5681
31	C	2.2499	-0.7138	-2.2150
32	C	0.5639	0.8535	-3.8572
33	H	-0.7312	-0.8868	-3.9557
34	C	2.6042	0.5981	-2.5229
35	H	2.8874	-1.3420	-1.5843
36	C	1.7606	1.3936	-3.3319
37	H	-0.0802	1.4714	-4.4915
38	H	3.5367	1.0169	-2.1310
39	H	2.0376	2.4283	-3.5572
40	N	-0.2012	-4.3470	0.2785
41	H	0.7216	-4.6157	-0.1447
42	O	-2.0941	-2.9966	-1.1326
43	H	-0.9675	-4.7592	-0.2737
44	H	-2.4037	-2.2621	-1.7055
45	O	2.1829	-4.5448	-1.2383
46	H	1.9599	-5.2825	-1.8458
47	H	1.6937	-3.7537	-1.6490

VI.3

Energy (POTENTIAL) = -1190.97000581 Eh

Atom		X	Y	Z
1	C	-0.2271	0.5187	-0.1206
2	H	-0.0822	1.5699	-0.4105
3	C	0.8326	-0.1905	0.6113
4	H	1.7043	0.3549	0.9972
5	C	-2.3343	0.4321	-1.2422
6	H	-3.3062	0.3306	-0.7298
7	H	-2.1389	1.4926	-1.4832
8	H	-2.3947	-0.1541	-2.1756
9	C	1.6958	-2.2698	1.4523
10	H	2.5718	-1.6675	1.7509
11	H	1.2350	-2.7253	2.3454
12	H	2.0060	-3.0894	0.7829
13	N	-1.2973	-0.1540	-0.4106
14	N	0.6901	-1.4708	0.7703
15	C	-0.2520	-5.1297	1.3154
16	C	-1.2739	-4.4170	2.0480
17	C	0.8998	-5.6011	2.0433
18	C	-1.1266	-4.1746	3.4100
19	H	-2.1527	-4.0591	1.4994
20	C	1.0233	-5.3599	3.4072
21	H	1.6782	-6.1319	1.4853
22	C	0.0181	-4.6423	4.0987
23	H	-1.8998	-3.6209	3.9532
24	H	1.9057	-5.7164	3.9487
25	H	0.1265	-4.4482	5.1706
26	Cu	-0.7909	-2.2114	-0.2950
27	N	0.4947	-2.4837	-2.0324
28	H	-0.1858	-2.8724	-2.6982
29	C	1.0593	-1.2599	-2.4659
30	C	0.3432	-0.4185	-3.3466
31	C	2.2986	-0.8299	-1.9394
32	C	0.8681	0.8311	-3.7012
33	H	-0.6247	-0.7513	-3.7373
34	C	2.8158	0.4226	-2.3051
35	H	2.8437	-1.4812	-1.2475
36	C	2.1055	1.2592	-3.1837
37	H	0.3060	1.4758	-4.3853
38	H	3.7791	0.7441	-1.8951
39	H	2.5114	2.2372	-3.4621
40	N	-0.3044	-5.3502	-0.0151
41	H	1.2124	-5.0440	-0.7777
42	O	-2.1922	-3.1290	-1.1127
43	H	-1.1481	-4.8862	-0.4081
44	H	-2.9978	-2.7408	-0.7040
45	O	2.0704	-4.6490	-1.1585
46	H	2.1834	-5.1277	-2.0079
47	H	1.1854	-3.2240	-1.7397

VI.4

Energy (POTENTIAL) = -1114.53756269 Eh

Atom		X	Y	Z
1	C	-0.0653	0.5635	-0.2774
2	H	-0.0079	1.6100	-0.6084
3	C	1.1567	-0.1606	0.0958
4	H	2.1279	0.3528	0.0958
5	C	-2.4228	0.5259	-0.6516
6	H	-3.1627	0.4631	0.1639
7	H	-2.2814	1.5786	-0.9542
8	H	-2.8206	-0.0523	-1.5025
9	C	2.1765	-2.2384	0.7061
10	H	3.1177	-1.6605	0.7081
11	H	2.0308	-2.7247	1.6860
12	H	2.2326	-3.0409	-0.0507
13	N	-1.1816	-0.0924	-0.2169
14	N	1.0192	-1.4111	0.4109
15	N	-0.3765	-4.0042	0.3550
16	C	-0.2384	-4.6116	1.5501
17	C	-0.6593	-3.9210	2.7414
18	C	0.3271	-5.9303	1.6742
19	C	-0.5135	-4.5228	3.9851
20	H	-1.0934	-2.9204	2.6330
21	C	0.4626	-6.5136	2.9286
22	H	0.6480	-6.4537	0.7666
23	C	0.0450	-5.8192	4.0888
24	H	-0.8338	-3.9944	4.8887
25	H	0.8942	-7.5155	3.0200
26	H	0.1547	-6.2875	5.0720
27	Cu	-0.8812	-2.1046	0.0316
28	N	0.0203	-2.2566	-2.2724
29	H	-0.7875	-2.7303	-2.6885
30	H	0.8080	-2.8986	-2.1413

31	C	0.3515	-1.0259	-2.8602
32	C	-0.6464	-0.2465	-3.4923
33	C	1.6574	-0.4960	-2.7223
34	C	-0.3405	1.0335	-3.9685
35	H	-1.6596	-0.6523	-3.5922
36	C	1.9524	0.7889	-3.2128
37	H	2.4358	-1.1019	-2.2446
38	C	0.9590	1.5629	-3.8321
39	H	-1.1251	1.6253	-4.4529
40	H	2.9690	1.1814	-3.1005
41	H	1.1899	2.5651	-4.2074
42	O	-2.7531	-2.5094	-0.1106
43	H	-0.0371	-4.5763	-0.4334
44	H	-2.7827	-3.4722	0.0794

VI.5

Energy (POTENTIAL) = -1114.53717283 Eh

Atom		X	Y	Z
1	C	0.0231	0.6666	-0.4943
2	H	0.2264	1.7146	-0.7562
3	C	1.1283	-0.2300	-0.1354
4	H	2.1526	0.1575	-0.0535
5	C	-2.2987	0.9436	-0.9742
6	H	-2.6989	0.4709	-1.8869
7	H	-3.0945	0.9125	-0.2113
8	H	-2.0216	1.9904	-1.1914
9	C	1.8796	-2.4525	0.3179
10	H	1.6236	-3.0423	1.2137
11	H	1.9181	-3.1488	-0.5400
12	H	2.8698	-1.9803	0.4470
13	N	-1.1680	0.1553	-0.5154
14	N	0.8316	-1.4767	0.0665
15	N	-0.9282	-3.8282	0.0344
16	C	-1.6691	-4.5976	0.8601
17	C	-1.4130	-6.0069	1.0095
18	C	-2.7417	-4.0040	1.6149
19	C	-2.2058	-6.7733	1.8558
20	H	-0.5928	-6.4568	0.4388
21	C	-3.5207	-4.7895	2.4564
22	H	-2.9165	-2.9289	1.5056
23	C	-3.2631	-6.1748	2.5817
24	H	-2.0109	-7.8453	1.9623
25	H	-4.3338	-4.3332	3.0299
26	H	-3.8805	-6.7864	3.2472
27	Cu	-1.1167	-1.9039	-0.4225
28	N	-0.0966	-2.0043	-2.6823
29	H	-0.9565	-2.3054	-3.1506
30	H	0.5734	-2.7715	-2.5757
31	C	0.4439	-0.7989	-3.1516
32	C	-0.3917	0.1733	-3.7530
33	C	1.8070	-0.4912	-2.9233
34	C	0.1313	1.4202	-4.1154
35	H	-1.4492	-0.0592	-3.9206
36	C	2.3204	0.7623	-3.2998
37	H	2.4577	-1.2459	-2.4672
38	C	1.4892	1.7259	-3.8921
39	H	-0.5285	2.1622	-4.5787
40	H	3.3790	0.9800	-3.1205
41	H	1.8906	2.7030	-4.1800
42	O	-2.9299	-2.0659	-1.0232
43	H	-0.1601	-4.3515	-0.4141
44	H	-3.1053	-3.0315	-1.0083

VII

Energy (POTENTIAL) = -1386.11820996 Eh

Atom		X	Y	Z
1	C	-0.0083	0.3847	-0.3227
2	H	0.1257	1.4746	-0.3017
3	C	1.1355	-0.5008	-0.0655
4	H	2.1193	-0.0724	0.1700
5	C	-2.2971	0.6128	-0.9661
6	H	-2.5053	0.4553	-2.0389
7	H	-3.1686	0.2510	-0.3987
8	H	-2.1411	1.6896	-0.7756
9	C	2.0385	-2.7114	-0.0186
10	H	1.8411	-3.3948	0.8256
11	H	2.0998	-3.3248	-0.9356
12	H	3.0024	-2.1972	0.1454
13	N	-1.1352	-0.1813	-0.6091
14	N	0.9325	-1.7768	-0.1577
15	N	-0.8502	-4.0708	-0.1088
16	C	-1.6260	-4.6477	0.8373
17	C	-1.1877	-5.8145	1.5563
18	C	-2.8936	-4.0594	1.1794
19	C	-1.9669	-6.3349	2.5838
20	H	-0.2234	-6.2630	1.2930
21	C	-3.6610	-4.6014	2.2044
22	H	-3.2201	-3.1809	0.6133
23	C	-3.2035	-5.7338	2.9177
24	H	-1.6201	-7.2127	3.1386
25	H	-4.6202	-4.1435	2.4661
26	H	-3.8082	-6.1486	3.7304
27	Cu	-0.9788	-2.2142	-0.7909
28	N	0.2045	-2.0061	-2.9763
29	H	-0.5720	-2.3416	-3.5542
30	H	0.9640	-2.6911	-2.9267
31	C	0.6098	-0.6884	-3.2464
32	C	-0.3109	0.2409	-3.7842
33	C	1.9020	-0.2450	-2.8766
34	C	0.0501	1.5860	-3.9271
35	H	-1.3117	-0.1031	-4.0696
36	C	2.2548	1.1064	-3.0348
37	H	2.6231	-0.9652	-2.4731
38	C	1.3331	2.0314	-3.5516
39	H	-0.6775	2.2943	-4.3391
40	H	3.2595	1.4329	-2.7439
41	H	1.6090	3.0845	-3.6667
42	O	-2.7231	-2.3541	-1.5908
43	H	0.0354	-4.5810	-0.2481
44	H	-2.8862	-3.3212	-1.6359
45	C	0.2264	-0.1130	2.9202
46	C	-0.1640	1.2129	2.6647
47	C	-1.5118	1.5144	2.3933
48	C	-2.4575	0.4778	2.3688
49	C	-2.0591	-0.8500	2.6109
50	C	-0.7150	-1.1649	2.8986
51	H	1.2780	-0.3387	3.1344
52	H	0.5850	2.0125	2.6811
53	H	-1.8172	2.5476	2.1964
54	H	-3.5091	0.6976	2.1540
55	H	-2.8022	-1.6554	2.5884
56	C	-0.2791	-2.5909	3.1467
57	H	-1.1331	-3.2438	3.3949
58	H	0.2018	-3.0098	2.2445
59	H	0.4595	-2.6506	3.9660

VIII_triplet

Energy (POTENTIAL) = -1386.11791525 Eh

Atom		X	Y	Z
1	C	0.0497	1.7622	0.8074
2	H	-0.0911	2.6791	1.3959
3	C	1.3948	1.2241	0.5913
4	H	2.2634	1.7112	1.0543
5	C	-2.3007	1.5944	0.4007
6	H	-2.9175	0.8288	0.9030
7	H	-2.3563	2.5371	0.9744
8	H	-2.7101	1.7508	-0.6129
9	C	2.8182	-0.3791	-0.4424
10	H	3.6127	0.1272	0.1341
11	H	2.8130	-1.4552	-0.1983
12	H	3.0276	-0.2753	-1.5202
13	N	-0.9372	1.1071	0.2838
14	N	1.5052	0.1822	-0.1737
15	Cu	-0.2892	-0.5072	-0.8041
16	N	0.4552	-2.1190	-1.9781
17	H	-0.4043	-2.6862	-1.9869
18	H	1.1934	-2.6285	-1.4749
19	C	0.8595	-1.7133	-3.2905
20	C	-0.1206	-1.2742	-4.2059
21	C	2.2205	-1.6853	-3.6486
22	C	0.2693	-0.7759	-5.4579
23	H	-1.1769	-1.3090	-3.9170
24	C	2.5997	-1.1836	-4.9047
25	H	2.9737	-2.0624	-2.9488
26	C	1.6309	-0.7171	-5.8094
27	H	-0.4965	-0.4288	-6.1596
28	H	3.6610	-1.1607	-5.1738
29	H	1.9317	-0.3208	-6.7845
30	O	-2.0220	-1.1835	-1.2699
31	H	-2.6286	-0.8015	-0.6004
32	C	-0.2384	-1.2086	2.2988
33	C	0.8103	-0.4921	2.9627
34	C	0.5164	0.4755	3.9285
35	C	-0.8222	0.7602	4.2716
36	C	-1.8704	0.0521	3.6425
37	C	-1.5894	-0.9145	2.6777
38	H	1.8504	-0.7056	2.6911
39	H	1.3330	1.0183	4.4174
40	H	-1.0467	1.5238	5.0235
41	H	-2.9113	0.2704	3.9057
42	H	-2.4030	-1.4430	2.1672
43	C	0.0404	-2.1111	1.2401
44	H	1.0718	-2.3847	0.9973
45	H	-0.7606	-2.7107	0.7958
46	C	0.8092	2.3624	-2.3426
47	C	2.0914	2.0353	-2.8493
48	C	3.2038	2.8056	-2.4911
49	C	3.0691	3.9189	-1.6365
50	C	1.7945	4.2599	-1.1546
51	C	0.6679	3.4936	-1.5007
52	H	2.2001	1.1614	-3.5027
53	H	4.1900	2.5327	-2.8837
54	H	3.9456	4.5139	-1.3595
55	H	1.6678	5.1282	-0.4983
56	H	-0.3271	3.7631	-1.1285
57	N	-0.2727	1.5191	-2.5803
58	H	-1.2059	1.9111	-2.4439
59	H	-0.2011	0.8960	-3.3902

VIII_singlet

Energy (POTENTIAL) = -1386.13884354 Eh

Atom		X	Y	Z
1	C	0.3324	2.0649	1.2271
2	H	0.4956	2.8886	1.9434
3	C	1.5257	1.3218	0.7804
4	H	2.5155	1.6797	1.0981
5	C	-1.9808	2.5248	1.1598
6	H	-2.7982	1.8366	1.4335
7	H	-1.7825	3.2231	1.9960
8	H	-2.3278	3.0984	0.2784
9	C	2.5999	-0.4525	-0.4311
10	H	3.5335	0.0613	-0.1453
11	H	2.5843	-1.4691	-0.0016
12	H	2.5447	-0.5536	-1.5276
13	N	-0.8237	1.7457	0.7574
14	N	1.4232	0.2736	0.0284

15	Cu	-0.2977	-0.2760	-0.6134
16	N	0.3329	-2.8116	-2.4189
17	H	-0.5567	-2.3932	-2.0923
18	H	0.9673	-2.9074	-1.6184
19	C	0.8992	-2.0785	-3.4706
20	C	0.0682	-1.3818	-4.3868
21	C	2.3006	-2.0548	-3.6824
22	C	0.6264	-0.6813	-5.4687
23	H	-1.0192	-1.4067	-4.2451
24	C	2.8456	-1.3575	-4.7710
25	H	2.9550	-2.5917	-2.9854
26	C	2.0177	-0.6610	-5.6718
27	H	-0.0382	-0.1448	-6.1554
28	H	3.9327	-1.3514	-4.9098
29	H	2.4501	-0.1106	-6.5134
30	O	-1.8450	-0.9340	-1.4076
31	H	-2.3558	-1.4379	-0.7385
32	C	-0.5358	-1.0749	2.0962
33	C	0.5664	-0.7194	2.9185
34	C	0.3729	0.0397	4.0787
35	C	-0.9239	0.4505	4.4461
36	C	-2.0296	0.0799	3.6567
37	C	-1.8390	-0.6747	2.4944
38	H	1.5749	-1.0262	2.6193
39	H	1.2321	0.3170	4.6987
40	H	-1.0720	1.0542	5.3478
41	H	-3.0383	0.3958	3.9431
42	H	-2.6887	-0.9301	1.8506
43	C	-0.3307	-1.7578	0.8223
44	H	0.6482	-2.2372	0.6794
45	H	-1.1586	-2.3911	0.4761
46	C	0.8109	2.0812	-2.3355
47	C	2.0587	1.7835	-2.9175
48	C	3.0809	2.7432	-2.8964
49	C	2.8692	3.9989	-2.2992
50	C	1.6170	4.2939	-1.7305
51	C	0.5869	3.3411	-1.7463
52	H	2.2175	0.8067	-3.3871
53	H	4.0476	2.5068	-3.3543
54	H	3.6712	4.7444	-2.2832
55	H	1.4370	5.2719	-1.2713
56	H	-0.3876	3.5629	-1.2984
57	N	-0.1995	1.0732	-2.2802
58	H	-1.1497	1.4666	-2.2672
59	H	-0.1215	0.4058	-3.0680

IX.1

Energy (POTENTIAL) = -1098.50417907 Eh

	Atom	X	Y	Z
1	C	0.8984	0.7583	-0.5084
2	H	1.1658	1.8265	-0.5885
3	C	2.0091	-0.2083	-0.4998
4	H	3.0263	0.1662	-0.6836
5	C	-1.3866	1.3050	-0.3909
6	H	-1.9158	1.1926	0.5732
7	H	-1.0465	2.3527	-0.5066
8	H	-2.1132	1.0590	-1.1857
9	C	2.9280	-2.4148	-0.3291
10	H	3.8919	-1.9055	-0.4987
11	H	2.9659	-2.9932	0.6092
12	H	2.7296	-3.1246	-1.1514
13	N	-0.3126	0.3301	-0.4257
14	N	1.8185	-1.4680	-0.2660
15	Cu	0.0537	-2.2093	-0.1112
16	N	-0.0132	-2.4581	-2.2623
17	H	-0.9541	-2.8560	-2.3870
18	H	0.6875	-3.1850	-2.4653
19	C	0.1924	-1.2789	-3.0428
20	C	-0.9021	-0.4521	-3.3597
21	C	1.4999	-0.8885	-3.3914
22	C	-0.6834	0.7773	-3.9959
23	H	-1.9133	-0.7663	-3.0780
24	C	1.7091	0.3484	-4.0231
25	H	2.3452	-1.5431	-3.1511
26	C	0.6226	1.1897	-4.3198
27	H	-1.5384	1.4198	-4.2320
28	H	2.7288	0.6526	-4.2821
29	H	0.7907	2.1551	-4.8082
30	O	-1.6014	-3.0217	-0.0500
31	H	-1.8960	-3.1186	0.8795
32	C	-0.2067	-0.9815	2.4596
33	C	0.7028	0.0906	2.6637
34	C	0.2534	1.3287	3.1343
35	C	-1.1126	1.5224	3.4197
36	C	-2.0260	0.4653	3.2364
37	C	-1.5805	-0.7712	2.7570
38	H	1.7626	-0.0612	2.4298
39	H	0.9655	2.1479	3.2810
40	H	-1.4644	2.4932	3.7848
41	H	-3.0874	0.6127	3.4629
42	H	-2.2904	-1.5910	2.5997
43	C	0.2595	-2.2641	1.9394
44	H	1.3346	-2.4607	2.0543
45	H	-0.3546	-3.1392	2.1971

IX.2

Energy (POTENTIAL) = -1174.94568574 Eh

	Atom	X	Y	Z
1	C	-0.8998	1.1083	-2.0134
2	H	-1.4800	1.3819	-2.9061
3	C	0.4503	1.6713	-1.8391
4	H	0.8011	2.3956	-2.5943
5	C	-2.7306	-0.2688	-1.2878
6	H	-3.3952	0.1472	-0.5105
7	H	-3.1470	-0.0587	-2.2873
8	H	-2.6656	-1.3567	-1.1253
9	C	2.4732	1.8530	-0.6323
10	H	2.7753	2.5788	-1.4127
11	H	2.5026	2.3384	0.3609
12	H	3.1988	1.0186	-0.5984
13	N	-1.3983	0.3058	-1.1287
14	N	1.1496	1.2978	-0.8246
15	Cu	-0.2917	-0.3441	0.3035
16	H	0.0404	-2.7519	1.3802
17	H	0.3001	-0.9336	2.5480
18	O	-0.2987	-3.6031	0.9402
19	O	0.6481	-1.2091	1.6736
20	N	0.7129	-1.7530	-1.0119
21	H	0.4106	-2.6193	-0.5093
22	H	1.7033	-1.5556	-0.8196
23	C	0.4025	-1.7498	-2.3987
24	C	1.1624	-0.9764	-3.3016
25	C	-0.7362	-2.4453	-2.8560
26	C	0.7648	-0.8810	-4.6447
27	H	2.0514	-0.4455	-2.9442
28	C	-1.1255	-2.3412	-4.1983
29	H	-1.3121	-3.0539	-2.1502
30	C	-0.3841	-1.5525	-5.0978
31	H	1.3575	-0.2741	-5.3375
32	H	-2.0141	-2.8809	-4.5433
33	H	-0.6958	-1.4693	-6.1441
34	C	-0.4492	2.0481	1.7734
35	C	-0.6775	3.1786	0.9428
36	C	0.1236	4.3192	1.0539
37	C	1.1693	4.3574	1.9976
38	C	1.4099	3.2450	2.8285
39	C	0.6147	2.0995	2.7147
40	H	-1.4830	3.1351	0.2014
41	H	-0.0627	5.1830	0.4070
42	H	1.7968	5.2508	2.0838
43	H	2.2222	3.2746	3.5625
44	H	0.8051	1.2267	3.3491
45	C	-1.2811	0.8560	1.6421
46	H	-2.2639	1.0125	1.1787
47	H	0.4547	-4.2230	1.0397
48	H	-1.3368	0.2013	2.5241

Transition States

TS_II

Energy (POTENTIAL) = -1147.57523784 Eh

	Atom	X	Y	Z
1	C	0.3040	0.6800	0.0772
2	H	-0.2492	1.4905	-0.4191
3	C	1.7343	0.8417	0.3716
4	H	2.2529	1.7627	0.0695
5	C	-1.6562	-0.6964	0.1222
6	H	-2.1904	-0.8655	1.0736
7	H	-2.1285	0.1366	-0.4285
8	H	-1.7304	-1.6258	-0.4666
9	C	3.7749	-0.0623	1.2169
10	H	4.2111	0.9014	0.8992
11	H	3.9716	-0.2310	2.2897
12	H	4.2602	-0.8870	0.6653
13	N	-0.2532	-0.4425	0.4113
14	N	2.3389	-0.1334	0.9822
15	N	0.2598	-3.3721	1.3835
16	N	0.9574	-4.8713	1.4909
17	N	1.8039	-5.3735	0.8948
18	C	-0.9630	-3.3081	2.0589
19	C	-1.1232	-2.3945	3.1361
20	C	-2.0920	-4.0367	1.5952
21	C	-2.3908	-2.1589	3.6827
22	H	-0.2383	-1.8574	3.4978
23	C	-3.3480	-3.8258	2.1710
24	H	-1.9608	-4.7444	0.7696
25	C	-3.5028	-2.8773	3.2042
26	H	-2.5132	-1.4308	4.4916
27	H	-4.2181	-4.3814	1.8054
28	H	-4.4925	-2.7052	3.6405
29	Cu	1.1768	-1.7917	1.0086
30	N	2.1695	-2.5517	-0.8108
31	H	1.9343	-3.5468	-0.9058
32	H	3.1871	-2.4473	-0.7189
33	C	1.6198	-1.7515	-1.8566
34	C	2.2772	-0.5737	-2.2670
35	C	0.3585	-2.0786	-2.3961
36	C	1.6631	0.2771	-3.2023
37	H	3.2575	-0.3258	-1.8445
38	C	-0.2434	-1.2224	-3.3280
39	H	-0.1511	-2.9872	-2.0558
40	C	0.4012	-0.0382	-3.7331
41	H	2.1790	1.1923	-3.5124
42	H	-1.2263	-1.4809	-3.7369
43	H	-0.0758	0.6297	-4.4577

TS_IV

Energy (POTENTIAL) = -1114.51577857 Eh

	Atom	X	Y	Z
1	C	-0.1185	0.4937	0.4817
2	H	-0.3459	1.5674	0.5492
3	C	0.9753	-0.0794	1.2850
4	H	1.5925	0.5735	1.9198
5	C	-1.8979	0.1694	-1.0849
6	H	-2.7914	-0.4268	-0.8311
7	H	-2.0986	1.2427	-0.9237
8	H	-1.6757	-0.0118	-2.1498

9	C	2.2308	-2.0160	1.9385
10	H	2.8260	-1.3100	2.5439
11	H	1.7845	-2.7889	2.5875
12	H	2.8811	-2.5360	1.2137
13	N	-0.7844	-0.3128	-0.2819
14	N	1.1651	-1.3559	1.2025
15	N	0.0060	-4.1217	0.2967
16	C	-0.2513	-4.7026	1.4837
17	C	-0.6149	-3.9441	2.6547
18	C	-0.1518	-6.1376	1.6099
19	C	-0.8255	-4.5812	3.8735
20	H	-0.7225	-2.8582	2.5548
21	C	-0.3688	-6.7553	2.8375
22	H	0.1035	-6.7169	0.7159
23	C	-0.6989	-5.9860	3.9769
24	H	-1.0944	-3.9928	4.7573
25	H	-0.2828	-7.8440	2.9219
26	H	-0.8630	-6.4794	4.9404
27	Cu	-0.1421	-2.2562	-0.1444
28	N	-0.3803	-2.7371	-2.1860
29	H	-1.2547	-2.3502	-2.5658
30	H	-0.3647	-3.8319	-2.1928
31	C	0.7762	-2.1594	-2.7790
32	C	0.6953	-0.9993	-3.5799
33	C	2.0388	-2.7461	-2.5187
34	C	1.8645	-0.4280	-4.1020
35	H	-0.2839	-0.5583	-3.7959
36	C	3.1990	-2.1685	-3.0491
37	H	2.0896	-3.6456	-1.8958
38	C	3.1202	-1.0055	-3.8392
39	H	1.7924	0.4711	-4.7236
40	H	4.1716	-2.6293	-2.8453
41	H	4.0299	-0.5556	-4.2500
42	O	-0.1422	-5.3756	-1.8778
43	H	0.0402	-4.8222	-0.6687
44	H	-1.0728	-5.6761	-1.7850

TS_V

Energy (POTENTIAL) = -1114.51816584 Eh

Atom		X	Y	Z
1	C	-0.3211	0.7622	0.8211
2	H	-0.4300	1.8499	0.9436
3	C	0.5313	-0.0051	1.7357
4	H	1.0824	0.5119	2.5342
5	C	-1.7326	0.7558	-1.1251
6	H	-2.7085	0.2440	-1.1709
7	H	-1.8727	1.8325	-0.9222
8	H	-1.2467	0.6217	-2.1083
9	C	1.4573	-2.0849	2.4331
10	H	2.0927	-1.4566	3.0821
11	H	0.8164	-2.7303	3.0582
12	H	2.0853	-2.7478	1.8158
13	N	-0.9107	0.1009	-0.1229
14	N	0.6094	-1.2896	1.5538
15	C	-0.2210	-4.6277	1.3142
16	C	-1.1671	-4.3730	2.3458
17	C	0.9272	-5.4100	1.6101
18	C	-0.9570	-4.8763	3.6326
19	H	-2.0484	-3.7641	2.1161
20	C	1.1225	-5.9130	2.9010
21	H	1.6588	-5.6023	0.8167
22	C	0.1889	-5.6462	3.9215
23	H	-1.6903	-4.6694	4.4197
24	H	2.0131	-6.5133	3.1170
25	H	0.3497	-6.0364	4.9317
26	Cu	-0.4159	-1.8981	-0.1334
27	N	0.2064	-2.0975	-2.0216
28	H	-0.2427	-2.8464	-2.5730
29	C	0.9034	-1.2447	-2.8087
30	C	0.9497	-1.3941	-4.2386
31	C	1.6234	-0.1552	-2.2074
32	C	1.6672	-0.4892	-5.0149
33	H	0.4052	-2.2268	-4.6983
34	C	2.3333	0.7396	-3.0004
35	H	1.5988	-0.0560	-1.1179
36	C	2.3605	0.5821	-4.4058
37	H	1.6944	-0.6072	-6.1031
38	H	2.8777	1.5673	-2.5342
39	H	2.9229	1.2895	-5.0235
40	N	-0.4310	-4.0845	0.0539
41	H	0.2057	-4.4461	-0.6673
42	O	-2.3818	-2.7183	-0.5383
43	H	-1.5398	-3.6458	-0.2602
44	H	-2.8854	-2.5988	0.2971

TS_VI

Energy (POTENTIAL) = -1190.95957074 Eh

Atom		X	Y	Z
1	C	-0.0115	0.5041	-0.0800
2	H	0.0301	1.5880	-0.2628
3	C	1.1497	-0.1786	0.5105
4	H	2.0387	0.4059	0.7852
5	C	-2.1949	0.3665	-1.0329
6	H	-3.0985	0.1170	-0.4502
7	H	-2.1088	1.4619	-1.1439
8	H	-2.3039	-0.0937	-2.0310
9	C	2.2395	-2.1669	1.2255
10	H	3.1012	-1.4944	1.3792
11	H	1.9533	-2.6281	2.1852
12	H	2.5071	-2.9788	0.5290
13	N	-1.0367	-0.2212	-0.3810
14	N	1.0873	-1.4609	0.6857
15	C	-0.2651	-4.7056	1.5162
16	C	-1.5548	-4.7272	2.1173
17	C	0.8746	-4.9825	2.3173
18	C	-1.6912	-4.9933	3.4827
19	H	-2.4282	-4.5045	1.4942
20	C	0.7247	-5.2502	3.6827
21	H	1.8609	-5.0096	1.8440
22	C	-0.5538	-5.2494	4.2755
23	H	-2.6883	-4.9981	3.9364
24	H	1.6093	-5.4711	4.2897
25	H	-0.6644	-5.4545	5.3454
26	Cu	-0.5588	-2.3049	-0.1951
27	N	0.5571	-2.5336	-2.1309
28	H	-0.2487	-2.9098	-2.6499
29	C	1.0288	-1.3201	-2.6111
30	C	0.2134	-0.5020	-3.4406
31	C	2.3089	-0.8571	-2.1996
32	C	0.6639	0.7607	-3.8279
33	H	-0.7713	-0.8713	-3.7471
34	C	2.7477	0.4070	-2.6002
35	H	2.9335	-1.5005	-1.5719
36	C	1.9279	1.2245	-3.4064
37	H	0.0309	1.3923	-4.4594
38	H	3.7331	0.7627	-2.2829
39	H	2.2754	2.2174	-3.7089
40	N	-0.1075	-4.3896	0.1618
41	H	0.9787	-4.5207	-0.4193
42	O	-2.1836	-2.9587	-0.9225
43	H	-0.9225	-4.6882	-0.3947
44	H	-2.7094	-2.1729	-1.1882
45	O	2.0375	-4.4351	-1.1479
46	H	1.9401	-5.1699	-1.7920
47	H	1.2834	-3.3175	-1.7864

TS_VII

Energy (POTENTIAL) = -1386.09725987 Eh

Atom		X	Y	Z
1	C	-0.0939	1.0452	-0.4817
2	H	-0.0322	2.1199	-0.7059
3	C	1.0805	0.3314	0.0354
4	H	2.0409	0.8547	0.1410
5	C	-2.3948	0.9700	-1.1195
6	H	-2.7350	0.4382	-2.0231
7	H	-3.1711	0.8398	-0.3448
8	H	-2.2647	2.0451	-1.3404
9	C	2.0730	-1.6935	0.8020
10	H	1.8299	-2.1872	1.7578
11	H	2.2796	-2.4847	0.0579
12	H	2.9759	-1.0709	0.9304
13	N	-1.1711	0.3516	-0.6478
14	N	0.9306	-0.9163	0.3486
15	N	-0.6094	-3.3734	0.9904
16	C	-1.5313	-4.4344	0.9812
17	C	-1.1895	-5.7044	0.4515
18	C	-2.8391	-4.2203	1.4910
19	C	-2.1470	-6.7257	0.4079
20	H	-0.1761	-5.8677	0.0661
21	C	-3.7817	-5.2545	1.4566
22	H	-3.0882	-3.2411	1.9118
23	C	-3.4445	-6.5083	0.9100
24	H	-1.8785	-7.6996	-0.0155
25	H	-4.7865	-5.0830	1.8574
26	H	-4.1869	-7.3127	0.8802
27	Cu	-0.9320	-1.6350	-0.1120
28	N	0.0224	-2.5613	-2.0123
29	H	-0.7303	-3.1848	-2.3226
30	H	0.8616	-3.0905	-1.7544
31	C	0.2588	-1.4525	-2.8580
32	C	-0.8011	-0.9109	-3.6184
33	C	1.5114	-0.8006	-2.8434
34	C	-0.6144	0.2822	-4.3290
35	H	-1.7737	-1.4150	-3.6128
36	C	1.6859	0.3945	-3.5593
37	H	2.3321	-1.2227	-2.2523
38	C	0.6255	0.9480	-4.2989
39	H	-1.4479	0.6980	-4.9058
40	H	2.6592	0.8968	-3.5327
41	H	0.7649	1.8834	-4.8507
42	O	-2.7229	-2.0364	-0.6597
43	H	0.3332	-3.7265	0.7572
44	H	-2.7837	-3.0136	-0.5863
45	C	0.7513	-0.2241	3.4879
46	C	0.8233	1.1406	3.1986
47	C	-0.2968	1.8157	2.6660
48	C	-1.4932	1.1108	2.4328
49	C	-1.5664	-0.2586	2.7076
50	C	-0.4472	-0.9565	3.2542
51	H	1.6215	-0.7489	3.8977
52	H	1.7529	1.6894	3.3848
53	H	-0.2352	2.8844	2.4360
54	H	-2.3586	1.6265	2.0031
55	H	-2.4873	-0.8153	2.4987
56	C	-0.5111	-2.3946	3.4627
57	H	-1.4937	-2.8098	3.7397
58	H	-0.4852	-2.8878	2.2210
59	H	0.3312	-2.8573	3.9969

TS_IX

Energy (POTENTIAL) = -1174.91477106 Eh

Atom		X	Y	Z
1	C	-1.0011	1.0423	-2.1890
2	H	-1.4928	1.3737	-3.1205
3	C	0.3755	1.5090	-1.9444

4	H	0.8272	2.2192	-2.6532
5	C	-2.9091	-0.2231	-1.6021
6	H	-3.5720	0.0778	-0.7698
7	H	-3.3331	0.1358	-2.5607
8	H	-2.8860	-1.3277	-1.6058
9	C	2.3958	1.5162	-0.6655
10	H	2.4569	1.9171	0.3612
11	H	3.0537	0.6295	-0.7137
12	H	2.7400	2.2768	-1.3899
13	N	-1.5672	0.2626	-1.3314
14	N	1.0272	1.0812	-0.9094
15	Cu	0.2576	-0.2947	0.2220
16	H	-0.3070	-2.8951	1.0612
17	H	0.4081	-1.3240	2.3554
18	O	-0.0985	-3.7901	0.6556
19	O	-0.3540	-1.2980	1.7320
20	N	1.1545	-1.9075	-1.1326
21	H	0.8437	-2.7509	-0.6077
22	H	2.1685	-1.7652	-1.0714
23	C	0.6484	-1.8237	-2.4492
24	C	1.2829	-1.0083	-3.4129
25	C	-0.5639	-2.4697	-2.7798
26	C	0.6961	-0.8252	-4.6758
27	H	2.2243	-0.5089	-3.1565
28	C	-1.1418	-2.2779	-4.0420
29	H	-1.0541	-3.1003	-2.0298
30	C	-0.5219	-1.4500	-4.9975
31	H	1.1961	-0.1835	-5.4100
32	H	-2.0875	-2.7779	-4.2797
33	H	-0.9787	-1.3002	-5.9813
34	C	-0.0305	1.8157	2.0522
35	C	-0.3327	2.8477	1.1184
36	C	0.4389	4.0102	1.0779
37	C	1.5360	4.1642	1.9517
38	C	1.8494	3.1498	2.8767
39	C	1.0700	1.9878	2.9348
40	H	-1.1690	2.7068	0.4257
41	H	0.1932	4.8012	0.3616
42	H	2.1439	5.0741	1.9096
43	H	2.6985	3.2723	3.5573
44	H	1.3025	1.1960	3.6560
45	C	-0.8917	0.6476	2.1691
46	H	-1.8224	0.6384	1.5914
47	H	0.7036	-4.0607	1.1526
48	H	-0.9738	0.2217	3.1706

MECPs

SP_MECP_III_singlet

Energy (POTENTIAL) = -1038.07588574 Eh

Atom		X	Y	Z
1	C	-0.2309	0.5831	0.1204
2	H	-0.2255	1.6703	-0.0346
3	C	0.9381	-0.1030	0.6690
4	H	1.8102	0.4653	1.0234
5	C	-2.4424	0.4152	-0.7919
6	H	-3.3056	0.2732	-0.1182
7	H	-2.3172	1.4872	-1.0212
8	H	-2.6562	-0.1479	-1.7172
9	C	1.9877	-2.1907	1.2286
10	H	2.7750	-1.5654	1.6878
11	H	1.6047	-2.9149	1.9682
12	H	2.4128	-2.7680	0.3879
13	N	-1.2601	-0.1615	-0.1699
14	N	0.8790	-1.4002	0.7251
15	N	-1.1518	-3.8667	0.1397
16	C	-0.9989	-4.5900	1.2617
17	C	-0.8793	-4.0077	2.5836
18	C	-0.9654	-6.0332	1.1713
19	C	-0.6960	-4.8066	3.7070
20	H	-0.9214	-2.9147	2.6599
21	C	-0.8442	-6.8238	2.3114
22	H	-1.0576	-6.4848	0.1778
23	C	-0.6951	-6.2154	3.5774
24	H	-0.5817	-4.3519	4.6966
25	H	-0.8412	-7.9156	2.2283
26	H	-0.5825	-6.8401	4.4697
27	Cu	-0.8674	-2.0977	-0.0400
28	N	-0.3523	-2.0467	-2.2940
29	H	-1.2493	-1.9898	-2.7895
30	H	0.0553	-2.9808	-2.4139
31	C	0.5406	-0.9950	-2.6315
32	C	0.0508	0.2199	-3.1563
33	C	1.9158	-1.1235	-2.3414
34	C	0.9287	1.2911	-3.3821
35	H	-1.0167	0.3213	-3.3801
36	C	2.7851	-0.0481	-2.5741
37	H	2.2892	-2.0635	-1.9189
38	C	2.2991	1.1656	-3.0931
39	H	0.5343	2.2286	-3.7896
40	H	3.8499	-0.1608	-2.3421
41	H	2.9809	2.0042	-3.2693

SP_MECP_III_triplet

Energy (POTENTIAL) = -1038.07588453 Eh

Atom		X	Y	Z
1	C	-0.2309	0.5831	0.1204
2	H	-0.2255	1.6703	-0.0346
3	C	0.9381	-0.1030	0.6690
4	H	1.8102	0.4653	1.0234
5	C	-2.4424	0.4152	-0.7919
6	H	-3.3056	0.2732	-0.1182
7	H	-2.3172	1.4872	-1.0212
8	H	-2.6562	-0.1479	-1.7172
9	C	1.9877	-2.1907	1.2286
10	H	2.7750	-1.5654	1.6878
11	H	1.6047	-2.9149	1.9682
12	H	2.4128	-2.7680	0.3879
13	N	-1.2601	-0.1615	-0.1699
14	N	0.8790	-1.4002	0.7251
15	N	-1.1518	-3.8667	0.1397
16	C	-0.9989	-4.5900	1.2617
17	C	-0.8793	-4.0077	2.5836
18	C	-0.9654	-6.0332	1.1713
19	C	-0.6960	-4.8066	3.7070
20	H	-0.9214	-2.9147	2.6599
21	C	-0.8442	-6.8238	2.3114
22	H	-1.0576	-6.4848	0.1778
23	C	-0.6951	-6.2154	3.5774
24	H	-0.5817	-4.3519	4.6966
25	H	-0.8412	-7.9156	2.2283
26	H	-0.5825	-6.8401	4.4697
27	Cu	-0.8674	-2.0977	-0.0400
28	N	-0.3523	-2.0467	-2.2940
29	H	-1.2493	-1.9898	-2.7895
30	H	0.0553	-2.9808	-2.4139
31	C	0.5406	-0.9950	-2.6315
32	C	0.0508	0.2199	-3.1563
33	C	1.9158	-1.1235	-2.3414
34	C	0.9287	1.2911	-3.3821
35	H	-1.0167	0.3213	-3.3801
36	C	2.7851	-0.0481	-2.5741
37	H	2.2892	-2.0635	-1.9189
38	C	2.2991	1.1656	-3.0931
39	H	0.5343	2.2286	-3.7896
40	H	3.8499	-0.1608	-2.3421
41	H	2.9809	2.0042	-3.2693

SP_MECP_VIII_singlet

Energy (POTENTIAL) = -1386.11442410 Eh

Atom		X	Y	Z
1	C	0.1051	1.8575	1.1014
2	H	0.0198	2.6906	1.8159
3	C	1.4268	1.3044	0.7832
4	H	2.3252	1.7227	1.2579
5	C	-2.2541	1.8320	0.6976
6	H	-2.9114	0.9935	0.9862
7	H	-2.3068	2.6289	1.4633
8	H	-2.6247	2.2174	-0.2707
9	C	2.7772	-0.2468	-0.4322
10	H	3.6109	0.2183	0.1238
11	H	2.7556	-1.3315	-0.2308
12	H	2.9315	-0.1056	-1.5155
13	N	-0.9102	1.3320	0.5003
14	N	1.4924	0.3264	-0.0689
15	Cu	-0.2789	-0.2927	-0.7371
16	N	0.4527	-1.9957	-2.0368
17	H	-0.4882	-2.4125	-2.0524
18	H	1.0910	-2.5722	-1.4770
19	C	0.9587	-1.6798	-3.3212
20	C	0.0703	-1.2586	-4.3376
21	C	2.3463	-1.7111	-3.5742
22	C	0.5749	-0.8371	-5.5766
23	H	-1.0090	-1.2655	-4.1432
24	C	2.8379	-1.2923	-4.8197
25	H	3.0307	-2.0663	-2.7968
26	C	1.9603	-0.8399	-5.8215
27	H	-0.1210	-0.5059	-6.3547
28	H	3.9167	-1.3192	-5.0061
29	H	2.3511	-0.5046	-6.7874
30	O	-2.0239	-0.9204	-1.2063
31	H	-2.4979	-0.8955	-0.3464
32	C	-0.3765	-1.1966	2.2103
33	C	0.7008	-0.6407	2.9683
34	C	0.4526	0.1653	4.0838
35	C	-0.8718	0.4435	4.4778
36	C	-1.9507	-0.1073	3.7514
37	C	-1.7123	-0.9171	2.6401
38	H	1.7295	-0.8512	2.6547
39	H	1.2926	0.5852	4.6480
40	H	-1.0644	1.0836	5.3451
41	H	-2.9804	0.1086	4.0563
42	H	-2.5478	-1.3243	2.0587
43	C	-0.1227	-1.9338	1.0139
44	H	0.9009	-2.2652	0.8051
45	H	-0.9314	-2.5125	0.5547
46	C	0.7324	2.2547	-2.3984
47	C	1.9502	1.9480	-3.0452
48	C	3.0542	2.7982	-2.8984
49	C	2.9623	3.9632	-2.1134
50	C	1.7426	4.2768	-1.4869
51	C	0.6284	3.4343	-1.6281
52	H	2.0241	1.0369	-3.6499
53	H	3.9938	2.5449	-3.4030
54	H	3.8297	4.6208	-1.9958
55	H	1.6524	5.1859	-0.8809
56	H	-0.3208	3.6780	-1.1374
57	N	-0.3338	1.3281	-2.4428
58	H	-1.2583	1.7367	-2.2690
59	H	-0.3433	0.7547	-3.2955

SP_MECP_VIII_triplet

Energy (POTENTIAL) = -1386.11441752 Eh

Atom		X	Y	Z
1	C	0.1051	1.8575	1.1014
2	H	0.0198	2.6906	1.8159
3	C	1.4268	1.3044	0.7832

4	H	2.3252	1.7227	1.2579
5	C	-2.2541	1.8320	0.6976
6	H	-2.9114	0.9935	0.9862
7	H	-2.3068	2.6289	1.4633
8	H	-2.6247	2.2174	-0.2707
9	C	2.7772	-0.2468	-0.4322
10	H	3.6109	0.2183	0.1238
11	H	2.7556	-1.3315	-0.2308
12	H	2.9315	-0.1056	-1.5155
13	N	-0.9102	1.3320	0.5003
14	N	1.4924	0.3264	-0.0689
15	Cu	-0.2789	-0.2927	-0.7371
16	N	0.4527	-1.9957	-2.0368
17	H	-0.4882	-2.4125	-2.0524
18	H	1.0910	-2.5722	-1.4770
19	C	0.9587	-1.6798	-3.3212
20	C	0.0703	-1.2586	-4.3376
21	C	2.3463	-1.7111	-3.5742
22	C	0.5749	-0.8371	-5.5766
23	H	-1.0090	-1.2655	-4.1432
24	C	2.8379	-1.2923	-4.8197
25	H	3.0307	-2.0663	-2.7968
26	C	1.9603	-0.8399	-5.8215
27	H	-0.1210	-0.5059	-6.3547
28	H	3.9167	-1.3192	-5.0061
29	H	2.3511	-0.5046	-6.7874
30	O	-2.0239	-0.9204	-1.2063
31	H	-2.4979	-0.8955	-0.3464
32	C	-0.3765	-1.1966	2.2103
33	C	0.7008	-0.6407	2.9683
34	C	0.4526	0.1653	4.0838
35	C	-0.8718	0.4435	4.4778
36	C	-1.9507	-0.1073	3.7514
37	C	-1.7123	-0.9171	2.6401
38	H	1.7295	-0.8512	2.6547
39	H	1.2926	0.5852	4.6480
40	H	-1.0644	1.0836	5.3451
41	H	-2.9804	0.1086	4.0563
42	H	-2.5478	-1.3243	2.0587
43	C	-0.1227	-1.9338	1.0139
44	H	0.9009	-2.2652	0.8051
45	H	-0.9314	-2.5125	0.5547
46	C	0.7324	2.2547	-2.3984
47	C	1.9502	1.9480	-3.0452
48	C	3.0542	2.7982	-2.8984
49	C	2.9623	3.9632	-2.1134
50	C	1.7426	4.2768	-1.4869
51	C	0.6284	3.4343	-1.6281
52	H	2.0241	1.0369	-3.6499
53	H	3.9938	2.5449	-3.4030
54	H	3.8297	4.6208	-1.9958
55	H	1.6524	5.1859	-0.8809
56	H	-0.3208	3.6780	-1.1374
57	N	-0.3338	1.3281	-2.4428
58	H	-1.2583	1.7367	-2.2690
59	H	-0.3433	0.7547	-3.2955

Effect of nitro group

nitrophenylazide

Energy (POTENTIAL) = -600.388598025 Eh

Atom		X	Y	Z
1	N	-0.4851	-3.6713	0.9706
2	N	-1.1041	-4.6390	0.4834
3	N	-1.5829	-5.5049	-0.1100
4	C	-0.7690	-3.2711	2.2955
5	C	-0.0306	-2.1635	2.7704
6	C	-1.7214	-3.9102	3.1243
7	C	-0.2392	-1.6941	4.0657
8	H	0.7006	-1.6822	2.1154
9	C	-1.9325	-3.4407	4.4193
10	H	-2.2928	-4.7686	2.7576
11	C	-1.1895	-2.3380	4.8788
12	H	0.3226	-0.8396	4.4486
13	H	-2.6644	-3.9207	5.0723
14	N	-1.4097	-1.8499	6.2362
15	O	-2.2737	-2.4178	6.9423
16	O	-0.7250	-0.8825	6.6393

TSII_nitro

Energy (POTENTIAL) = -1352.11863773 Eh

Atom		X	Y	Z
1	C	0.8801	0.9520	-0.8122
2	H	0.4063	1.7826	-1.3539
3	C	2.3263	0.9751	-0.5376
4	H	2.9171	1.8693	-0.7830
5	C	-1.2196	-0.1991	-0.6417
6	H	-1.7394	-0.2831	0.3282
7	H	-1.6159	0.6569	-1.2138
8	H	-1.3931	-1.1410	-1.1877
9	C	4.2568	-0.1375	0.3306
10	H	4.8031	0.7653	0.0068
11	H	4.3463	-0.2486	1.4267
12	H	4.7024	-1.0355	-0.1313
13	N	0.2082	-0.0723	-0.3929
14	N	2.8440	-0.0871	-0.0105
15	N	-0.0825	-2.7964	0.5929
16	N	-0.2002	-4.1678	-0.3249
17	N	0.5006	-4.5081	-1.1734
18	C	-0.9208	-2.8363	1.6670
19	C	-0.9088	-1.7208	2.5800
20	C	-1.7977	-3.9314	1.9813
21	C	-1.6395	-1.7455	3.7545
22	H	-0.2649	-0.8611	2.3759
23	C	-2.5330	-3.9446	3.1539
24	H	-1.8665	-4.7724	1.2874
25	C	-2.4493	-2.8626	4.0603
26	H	-1.5875	-0.9039	4.4486
27	H	-3.1740	-4.7980	3.3887
28	Cu	1.3722	-1.4774	0.4600
29	N	2.5397	-2.7453	1.5734
30	H	3.5119	-2.4102	1.5028
31	H	2.4907	-3.6692	1.1194
32	C	2.1117	-2.8150	2.9495
33	C	1.3955	-3.9346	3.4082
34	C	2.3524	-1.7188	3.7987
35	C	0.9047	-3.9491	4.7224
36	H	1.2043	-4.7724	2.7293
37	C	1.8610	-1.7453	5.1113
38	H	2.9054	-0.8517	3.4201
39	C	1.1296	-2.8548	5.5754
40	H	0.3308	-4.8132	5.0722
41	H	2.0429	-0.8910	5.7718
42	H	0.7334	-2.8627	6.5959
43	O	-3.0749	-1.9285	6.0914
44	O	-3.9022	-3.9026	5.5457
45	N	-3.1793	-2.8990	5.2889

6. REACTION ORDER IN CATALYST

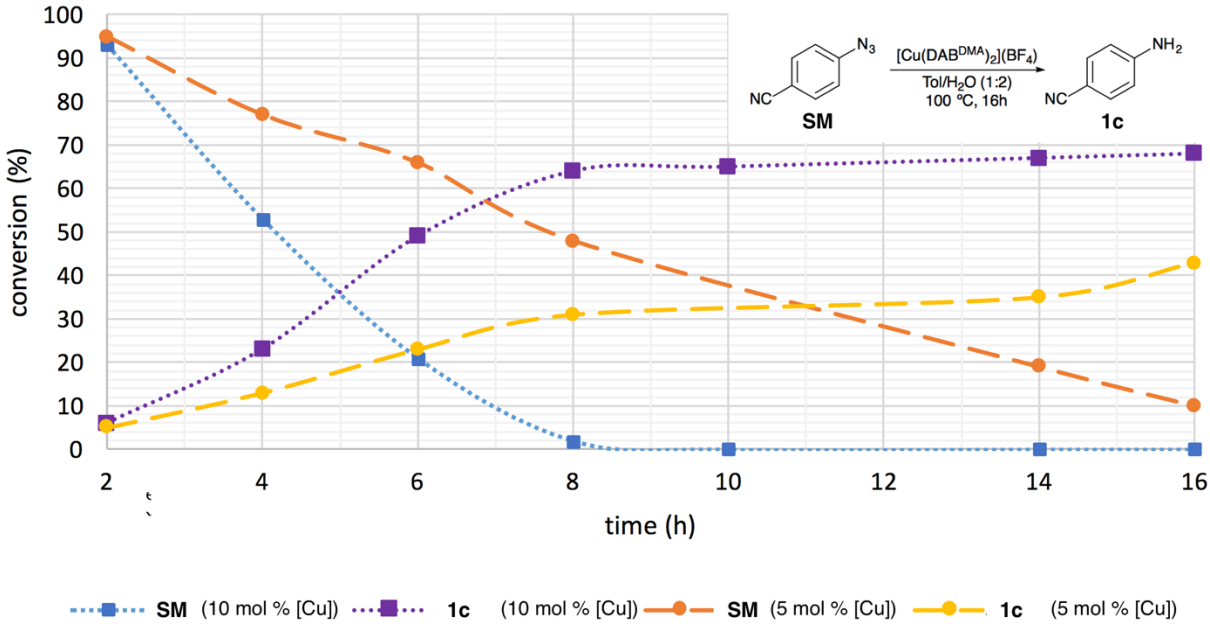


Figure S5. ^{1}H NMR conversion over time. ^{1}H NMR conversions are the average of two independent reactions and are calculated with respect to 1,3,5-trimethoxybenzene as internal standard.

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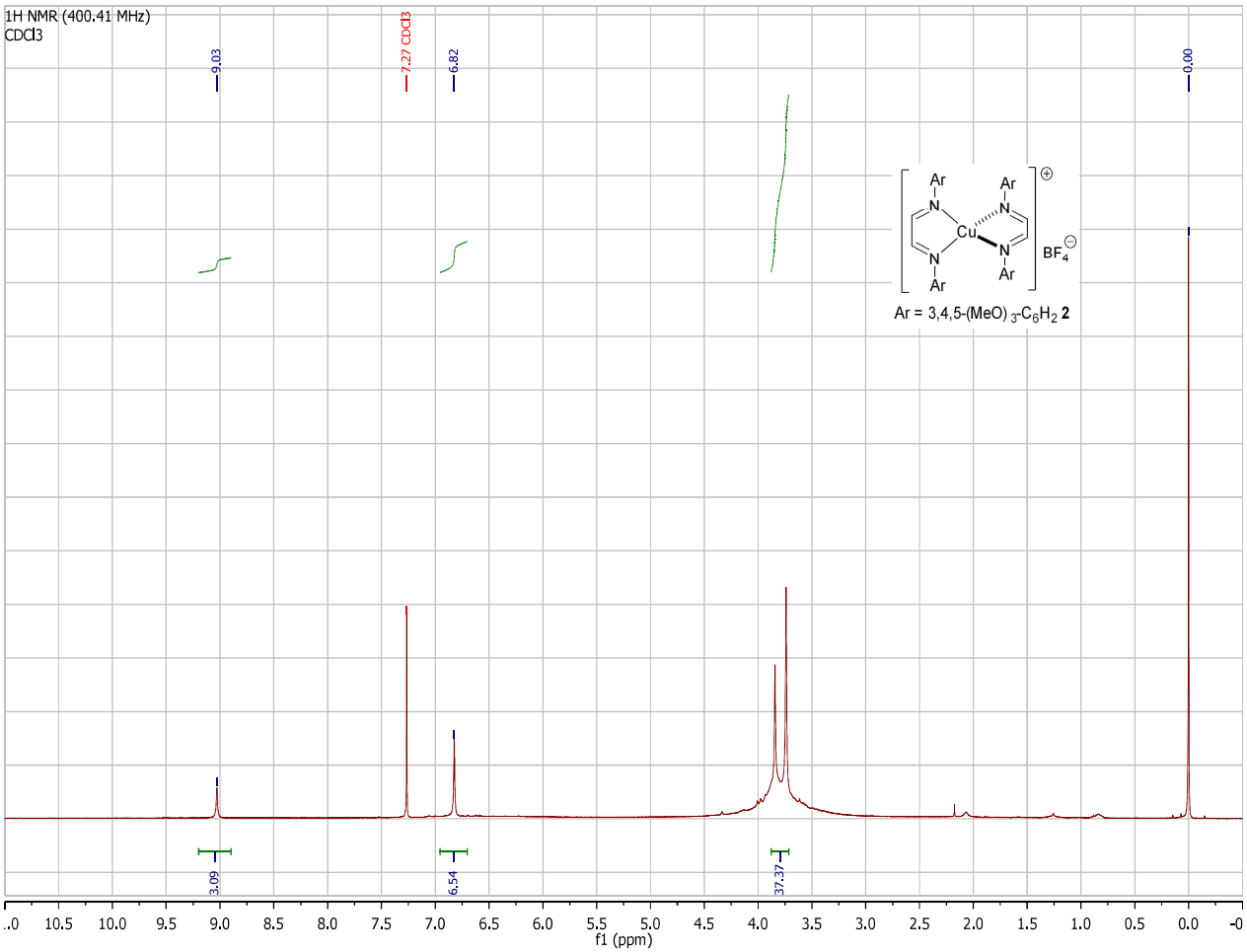
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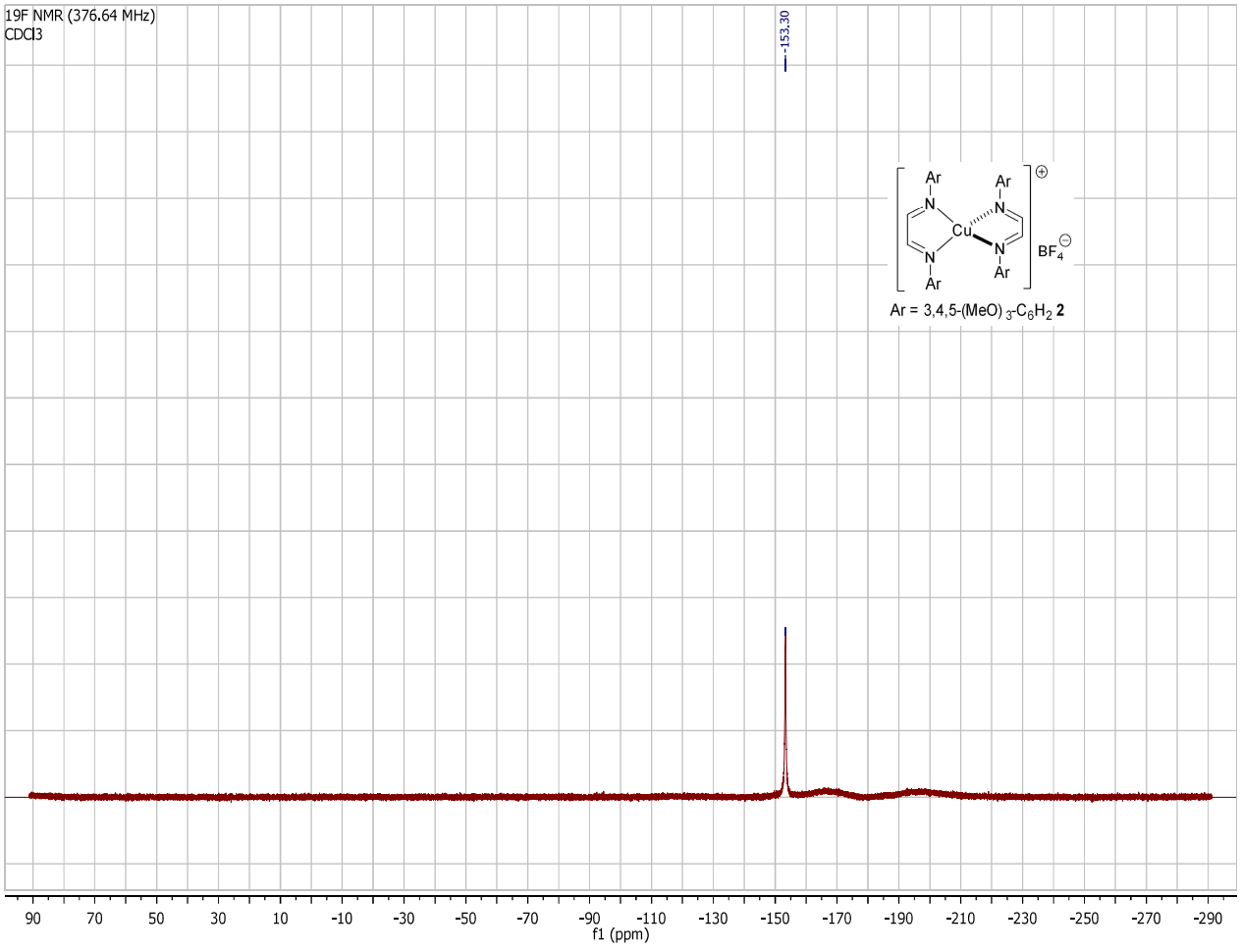
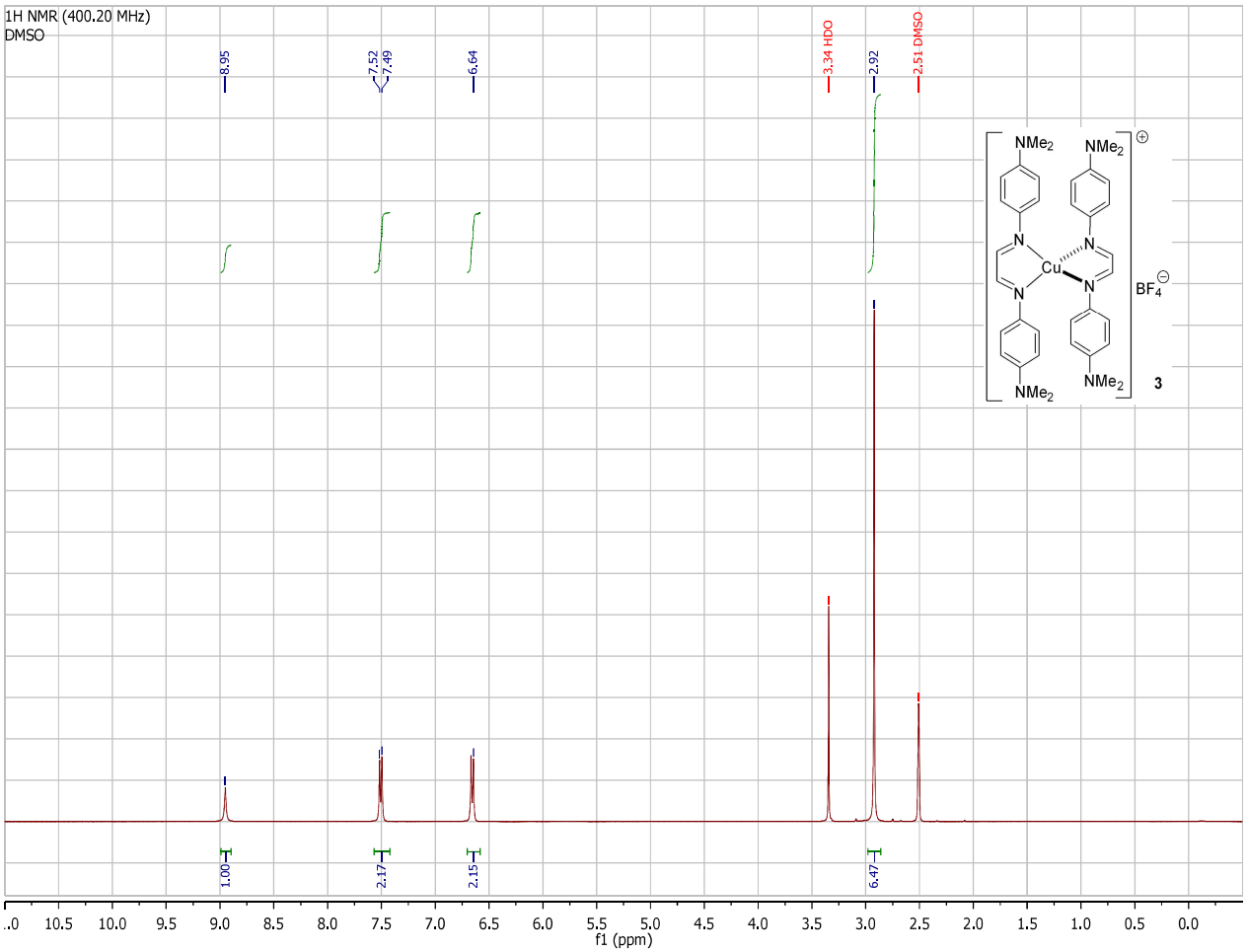
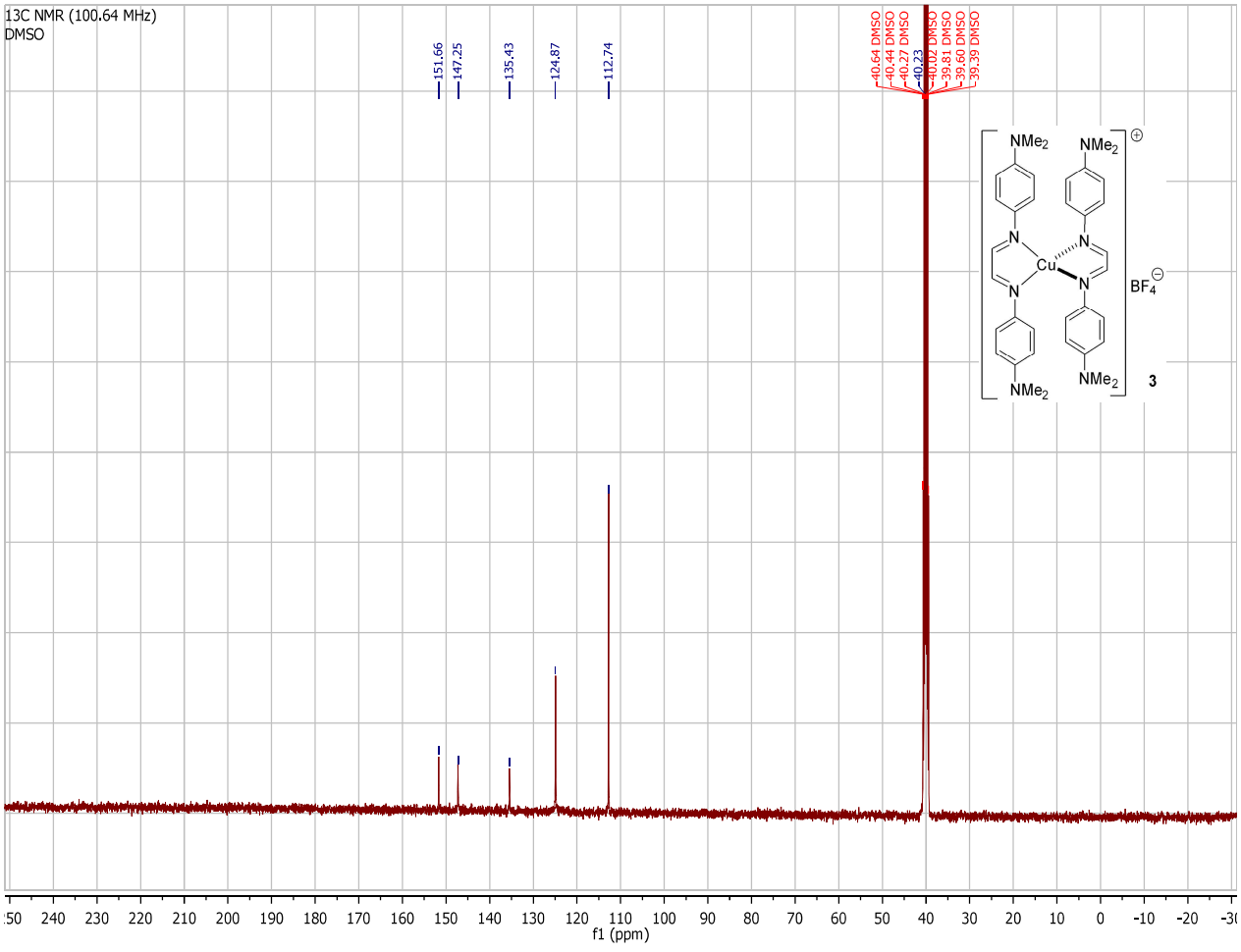
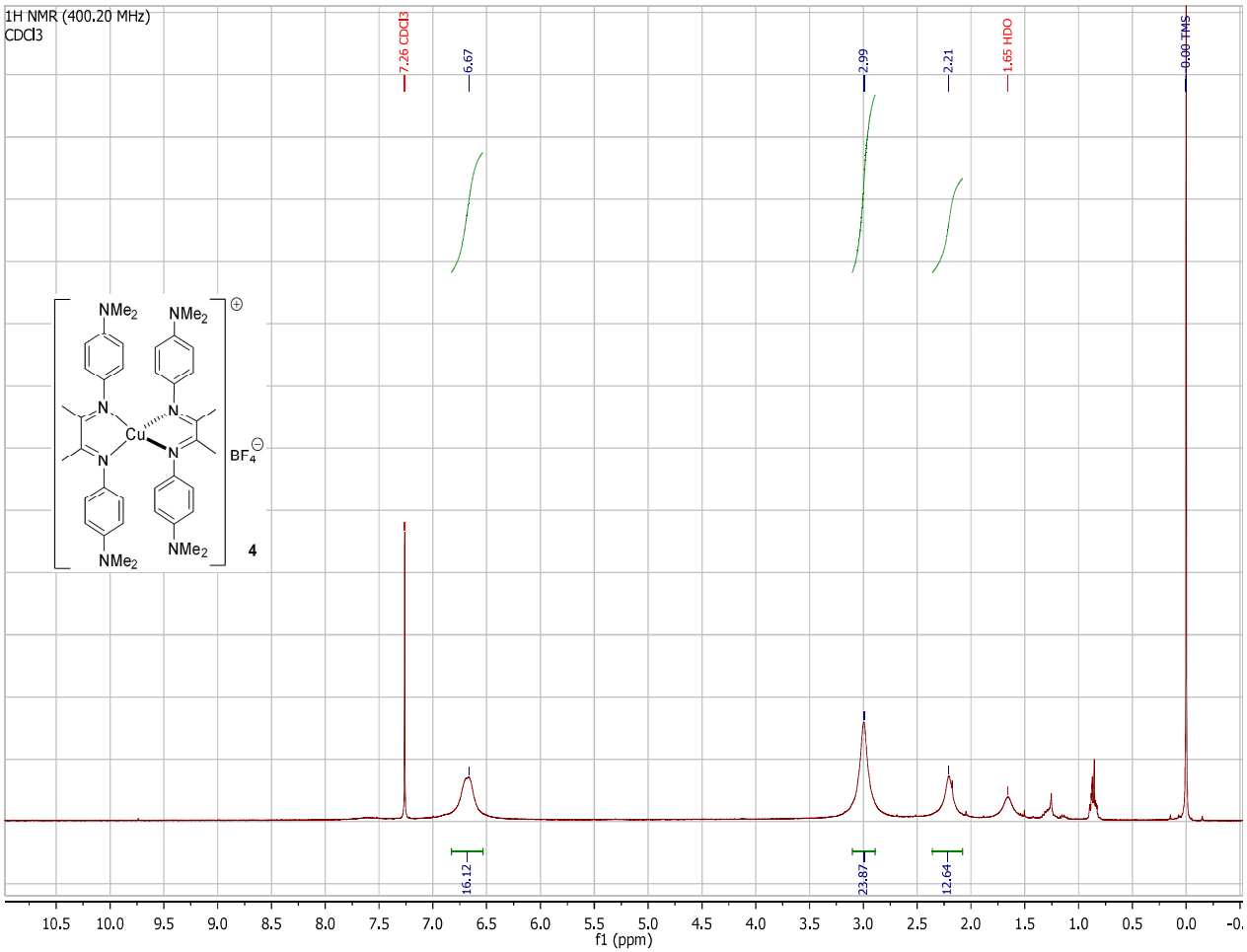
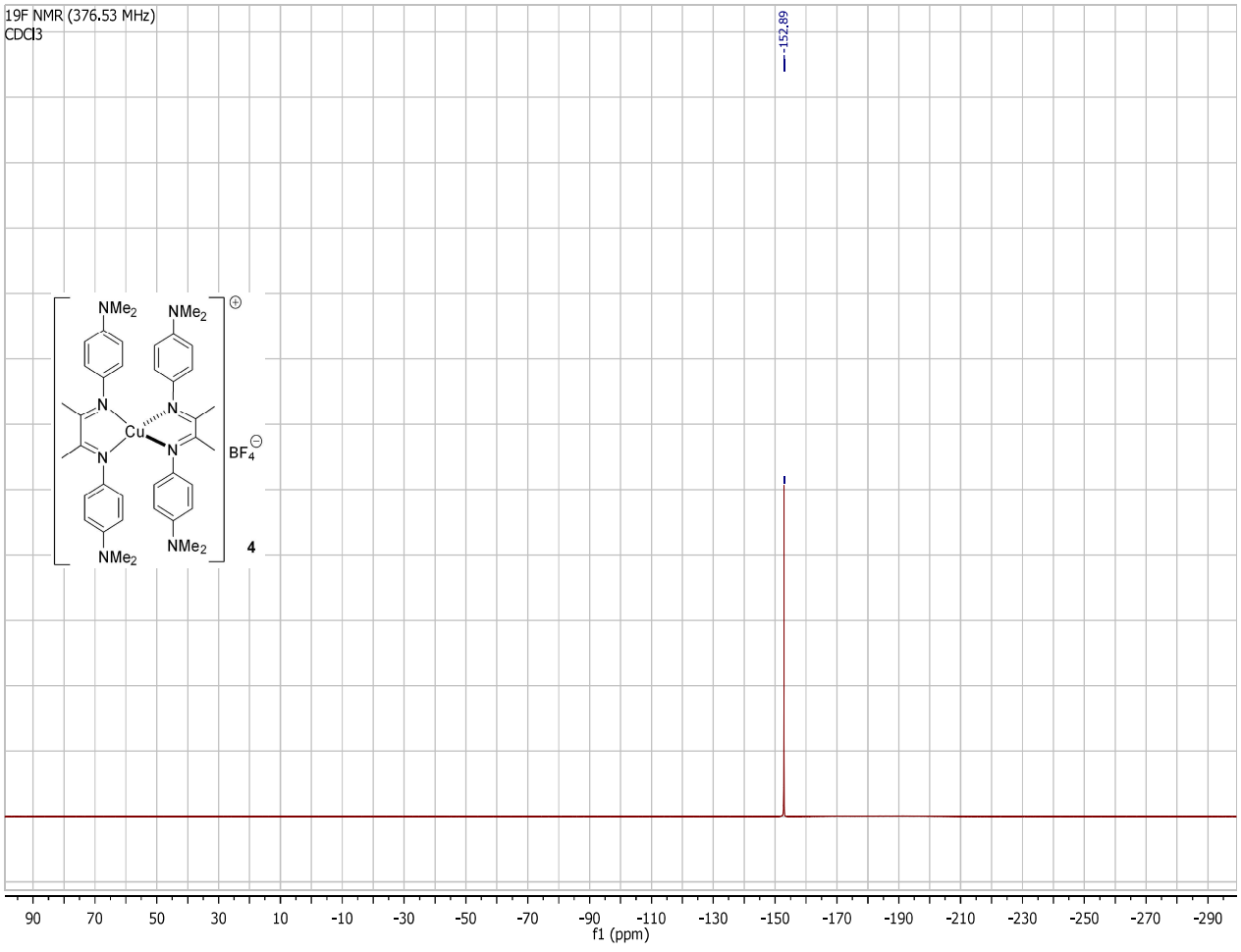
CDCl3
9.03
7.27 CDCl3
6.82
0.00
3.09
6.54
37.37
f1 (ppm)
Ar = 3,4,5-(MeO) 3-C6H2 2

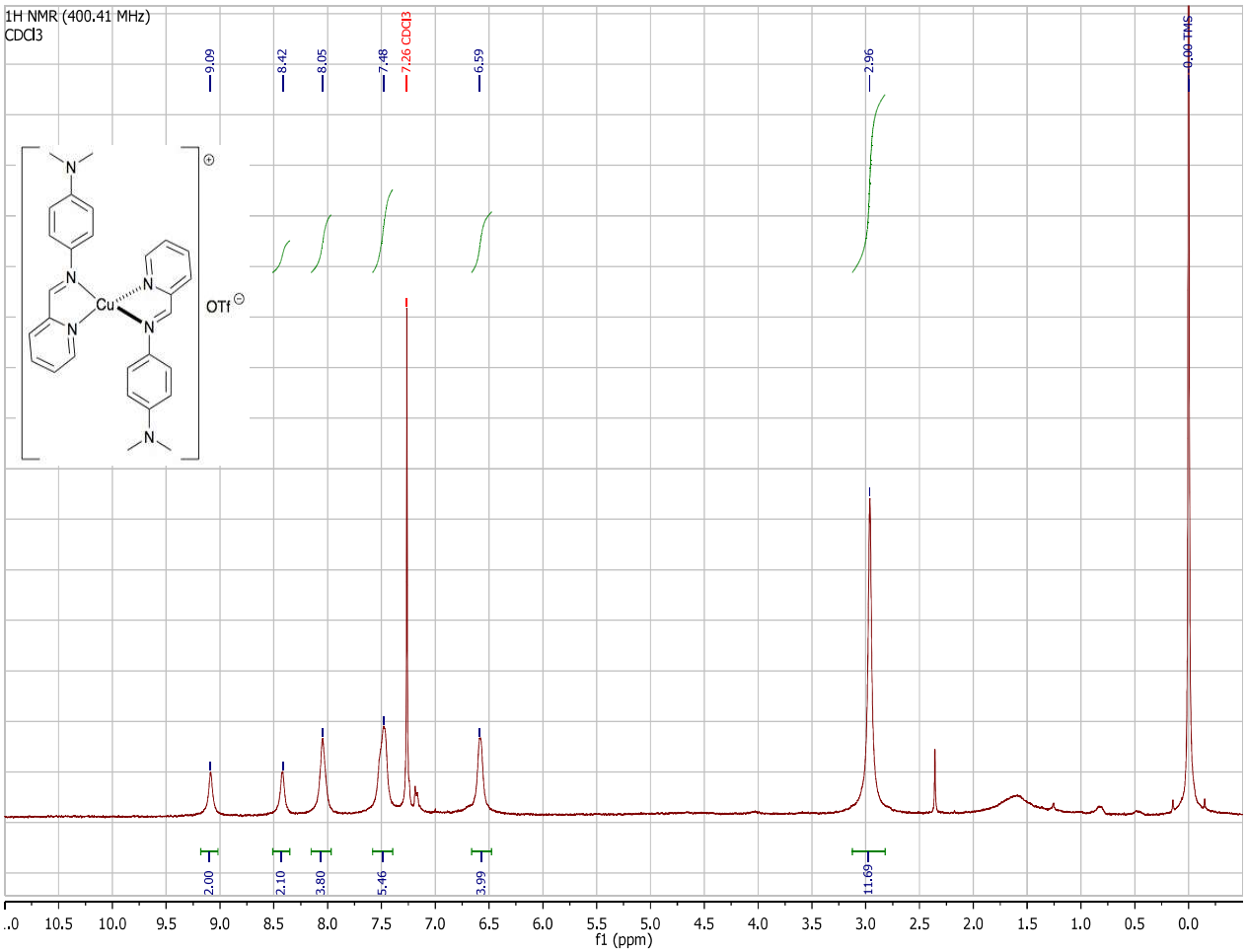

19F NMR (376.64 MHz)
CDCl3
-153.30
f1 (ppm)
Ar = 3,4,5-(MeO) 3-C6H2 2

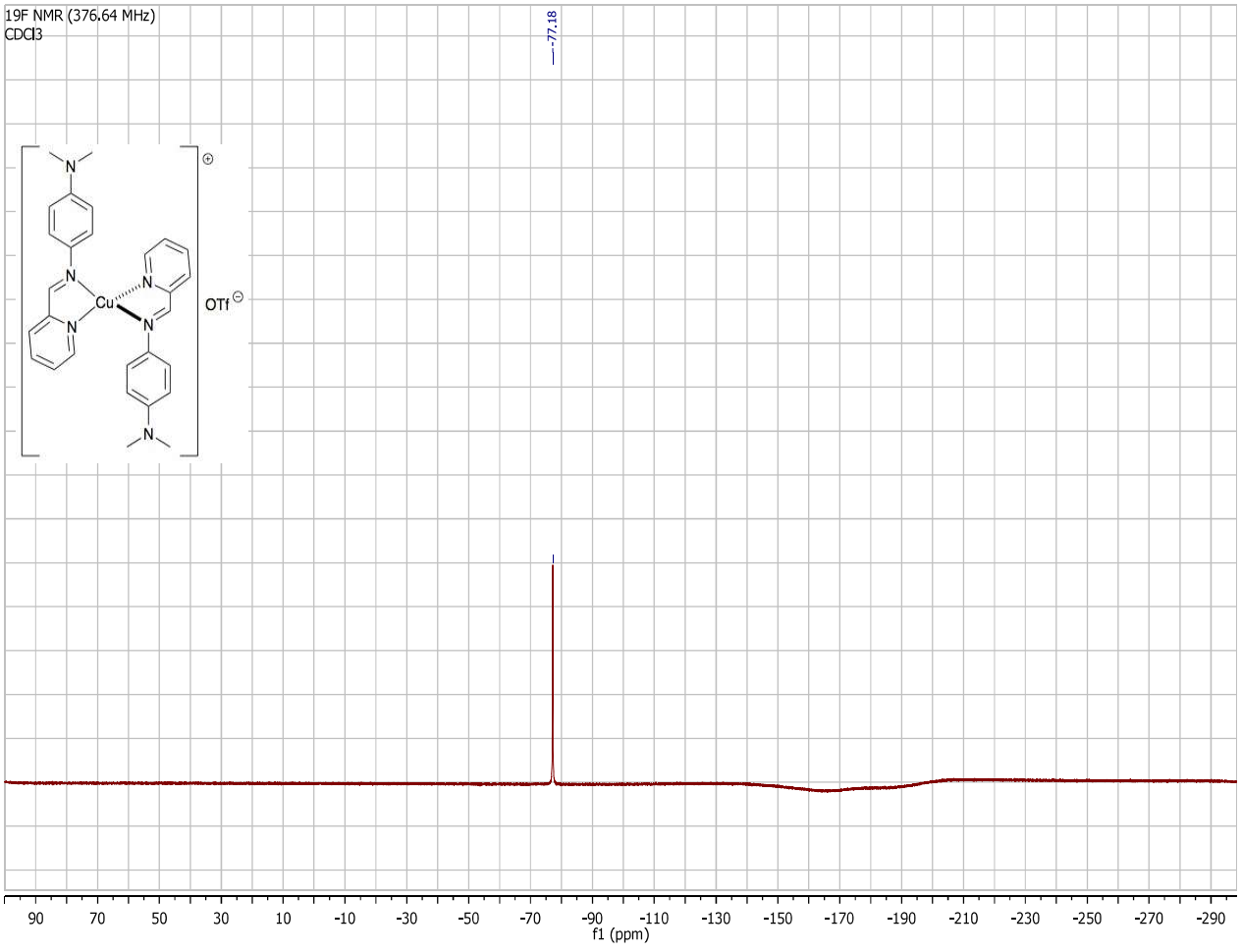

1H NMR (400.20 MHz)
DMSO
8.95
7.52
7.49
6.64
3.34 HDO
2.92
2.51 DMSO
1.00
2.17
2.15
6.47
f1 (ppm)
NMe2
Cu
BF4
3

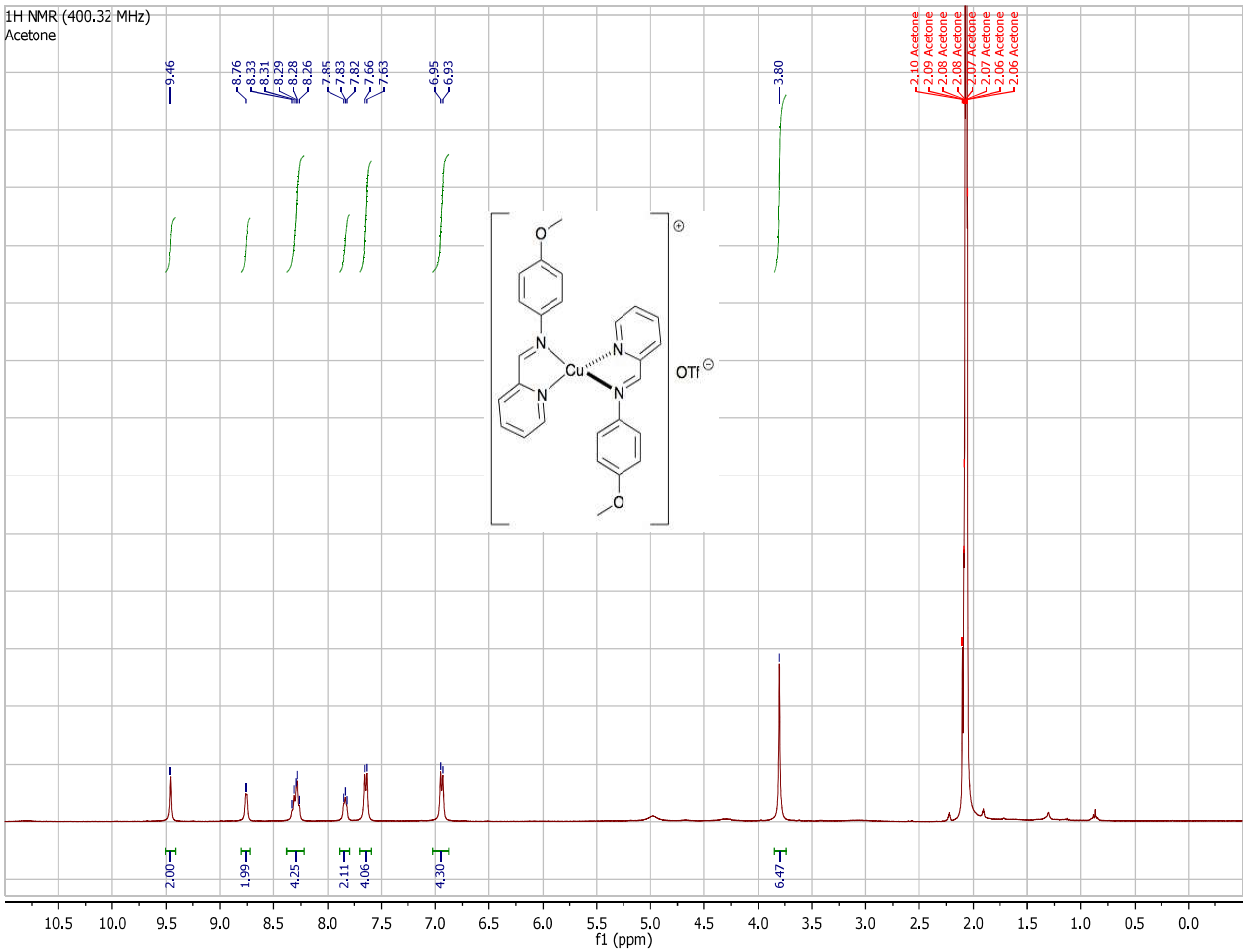

13C NMR (100.64 MHz)
DMSO
151.66
147.25
135.43
124.87
112.74
40.64 DMSO
40.44 DMSO
40.27 DMSO
40.23
40.07 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO
f1 (ppm)
NMe2
Cu
BF4
3

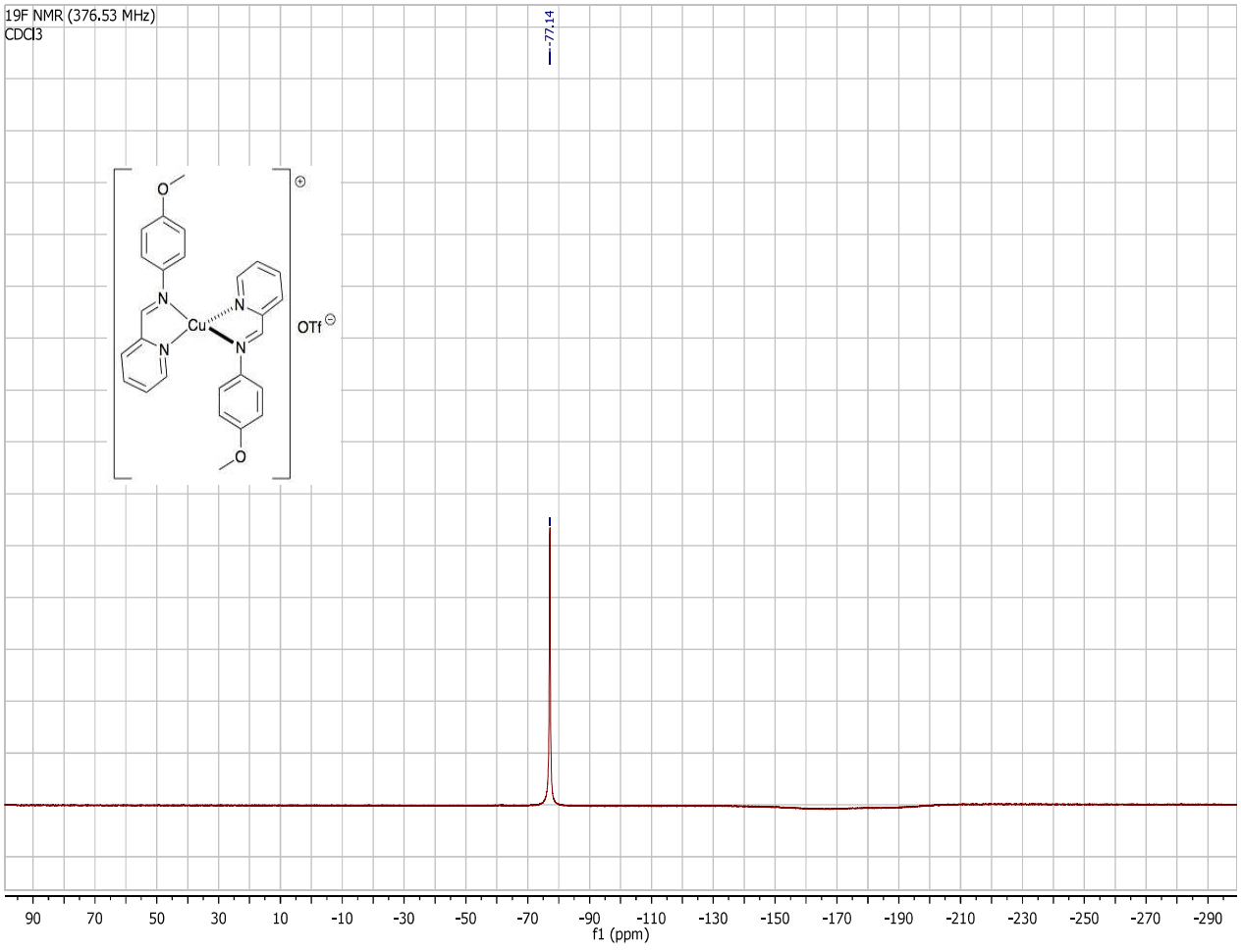

1H NMR (400.20 MHz)
CDCl3
7.26 CDCl3
6.67
2.99
2.21
1.65 HDO
0.00 TMS
16.12
23.87
12.64
f1 (ppm)
4

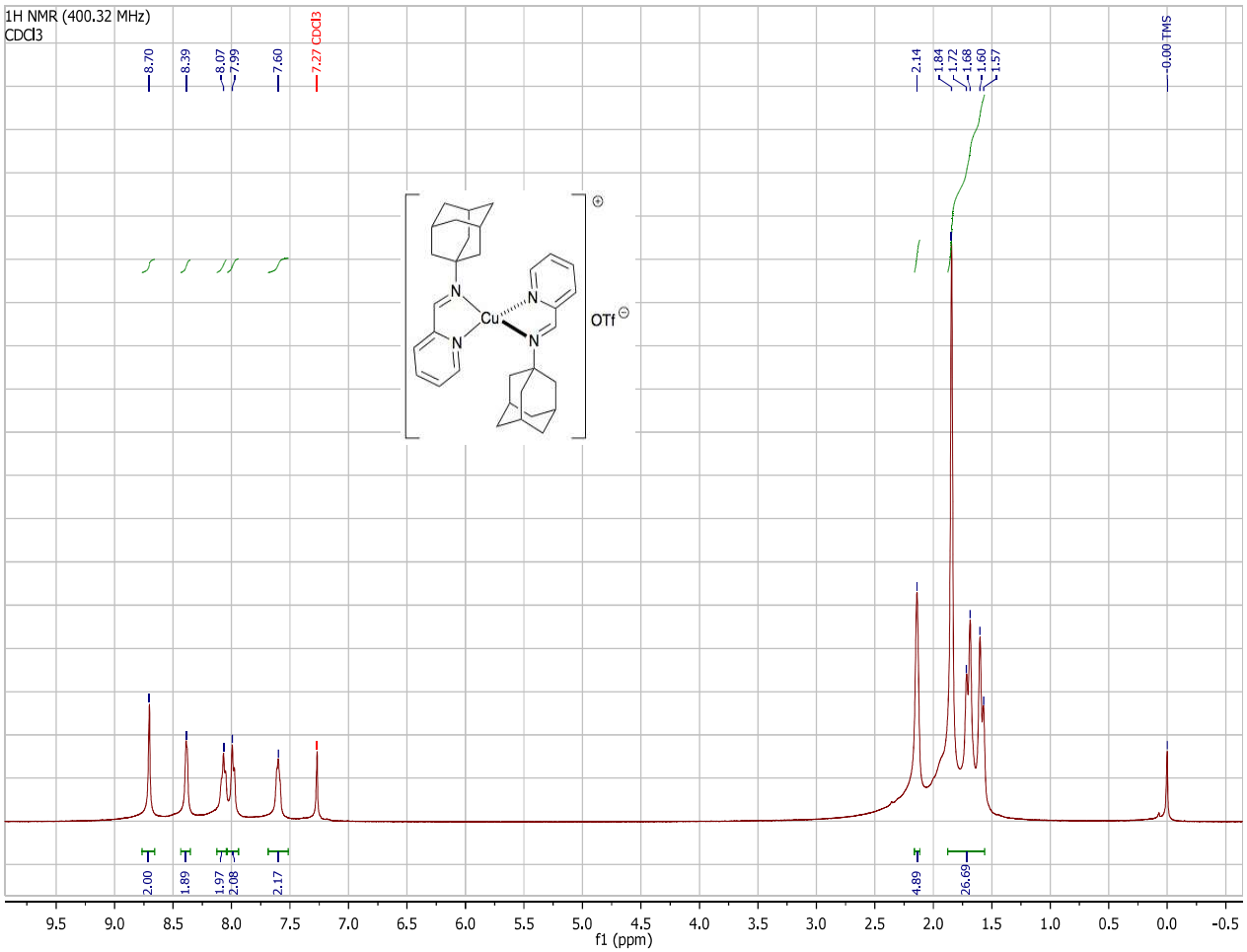

19F NMR (376.53 MHz)
CDCl3
-152.89
f1 (ppm)
4

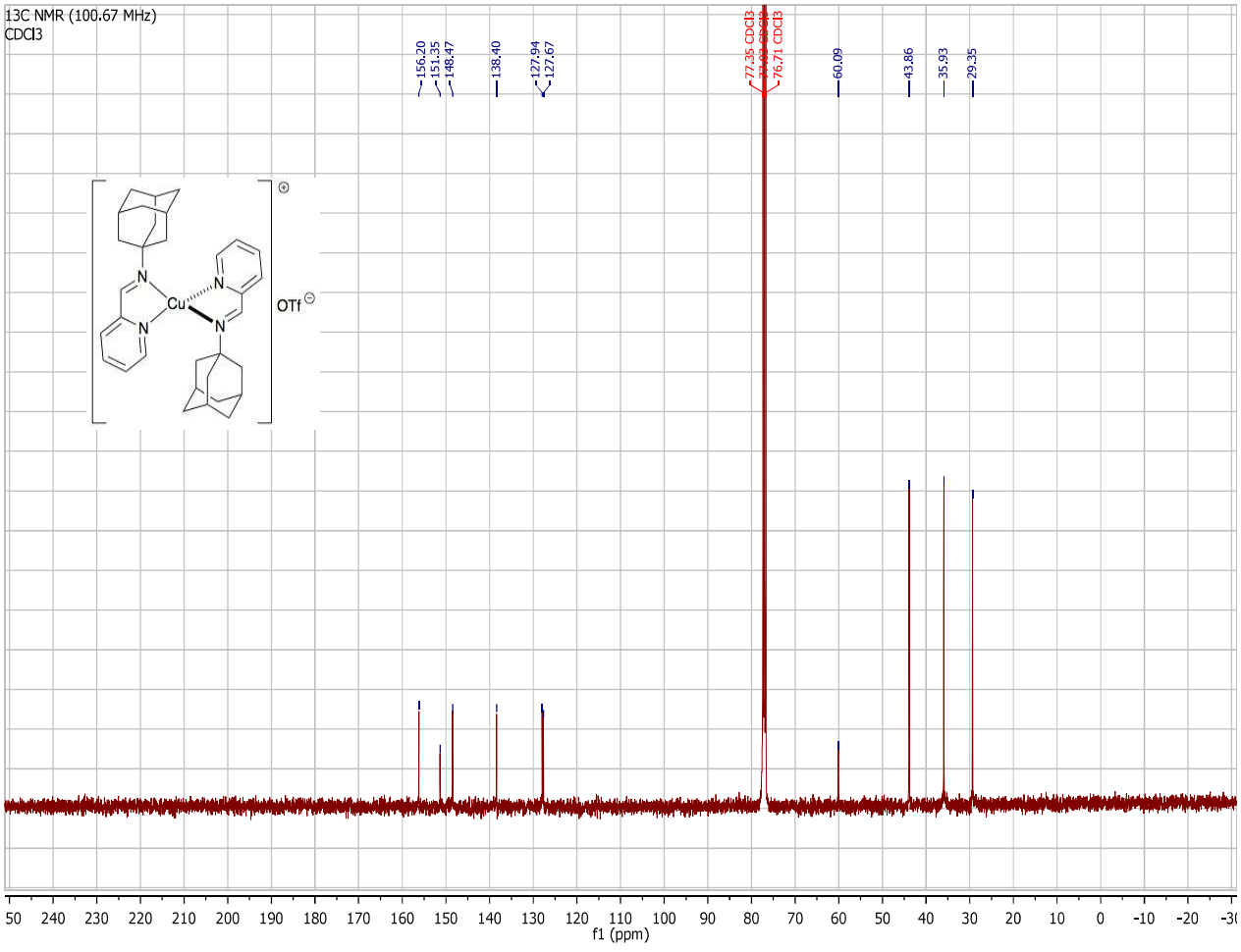

1H NMR (400.41 MHz)
CDCl3
9.09
8.42
8.05
7.48
7.26 CDCl3
6.59
2.96
0.00 TMS
OTf
2.00
2.10
3.80
5.46
3.99
11.69
f1 (ppm)

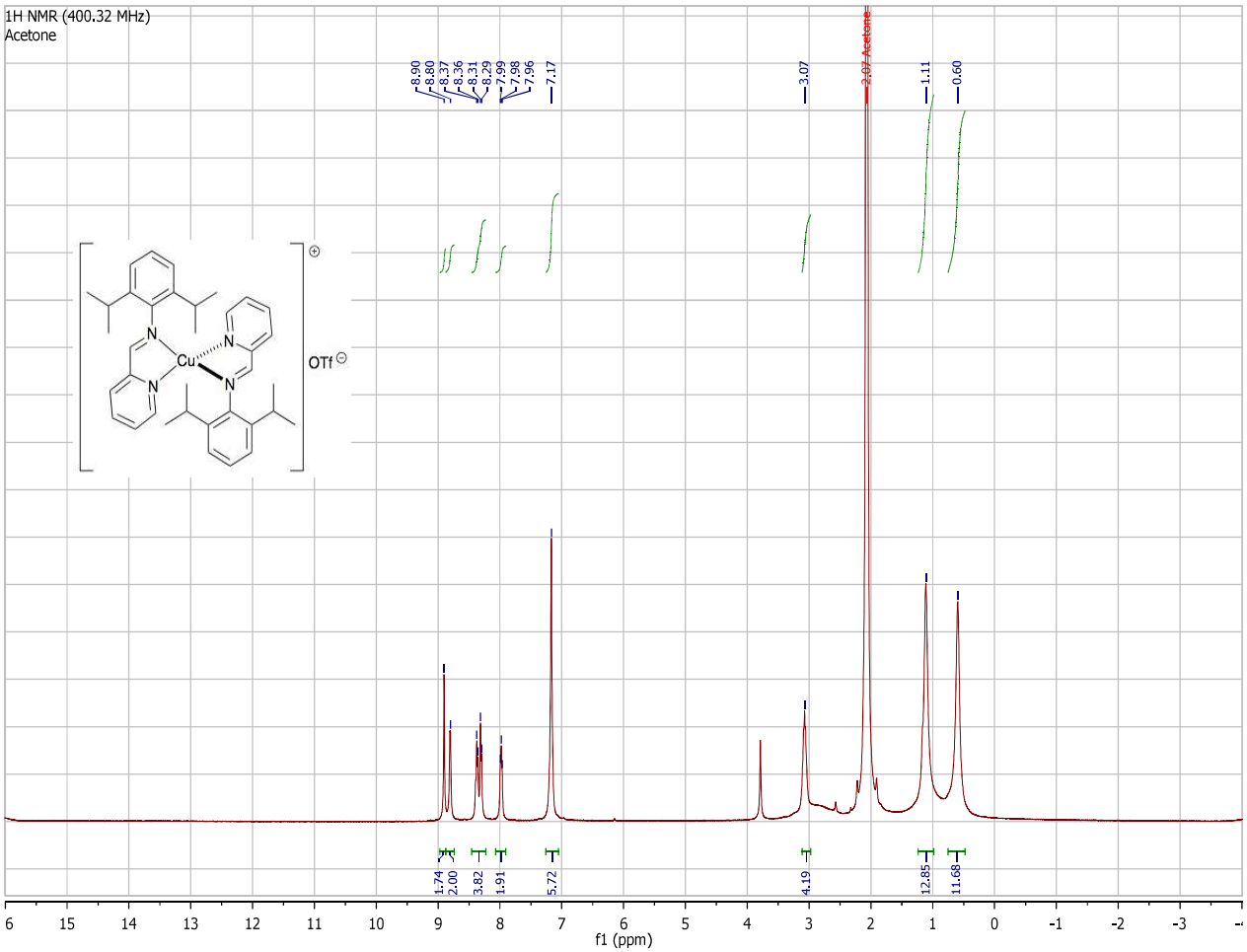

19F NMR (376.64 MHz)
CDCl3
-77.18
OTf
f1 (ppm)

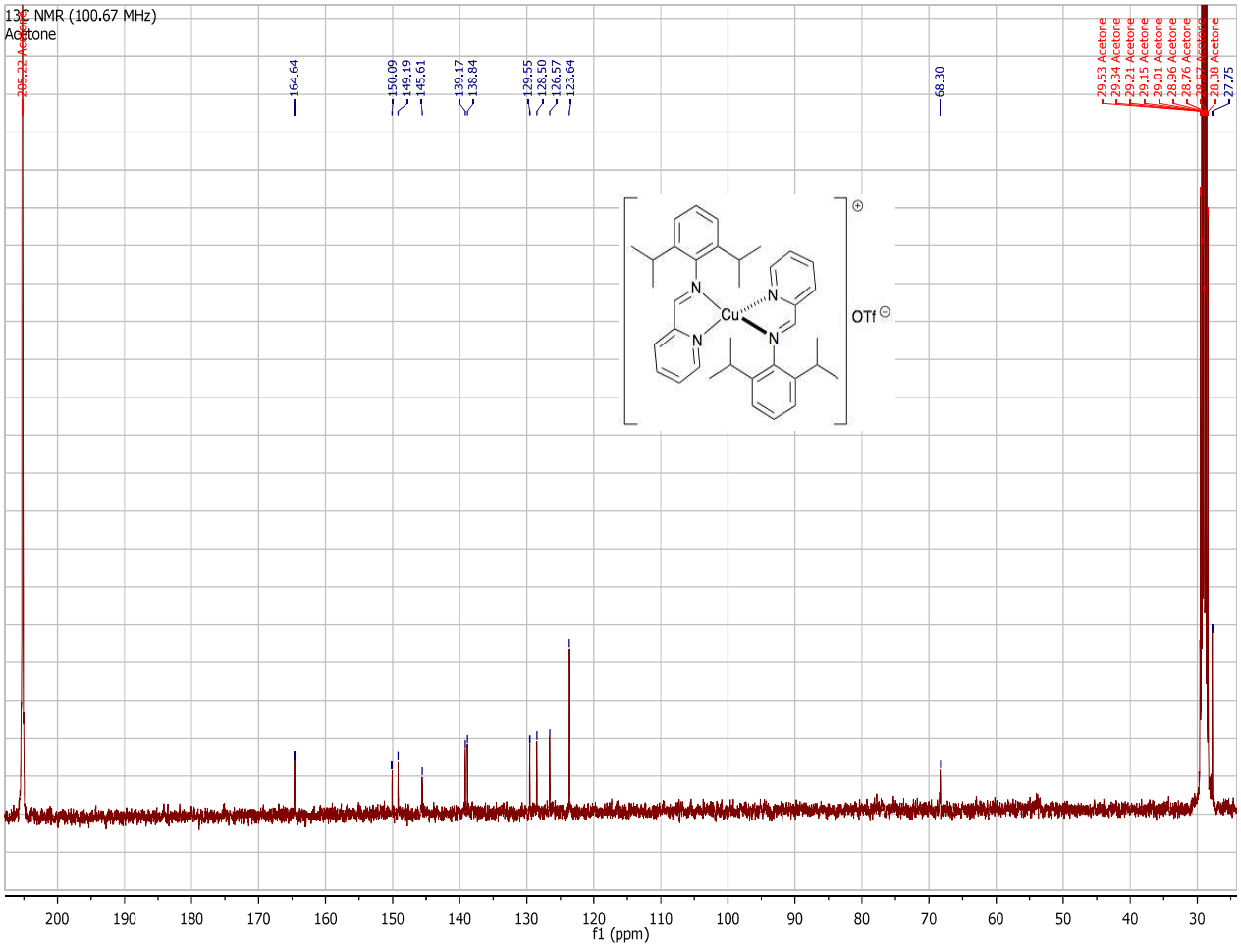

1H NMR (400.32 MHz)
Acetone
9.46
8.76
8.33
8.31
8.29
8.28
8.26
7.85
7.83
7.82
7.66
7.63
6.95
6.93
3.80
2.10 Acetone
2.09 Acetone
2.08 Acetone
2.08 Acetone
2.07 Acetone
2.07 Acetone
2.06 Acetone
2.06 Acetone
OTf
2.00
1.99
4.25
2.11
4.06
4.30
6.47
f1 (ppm)

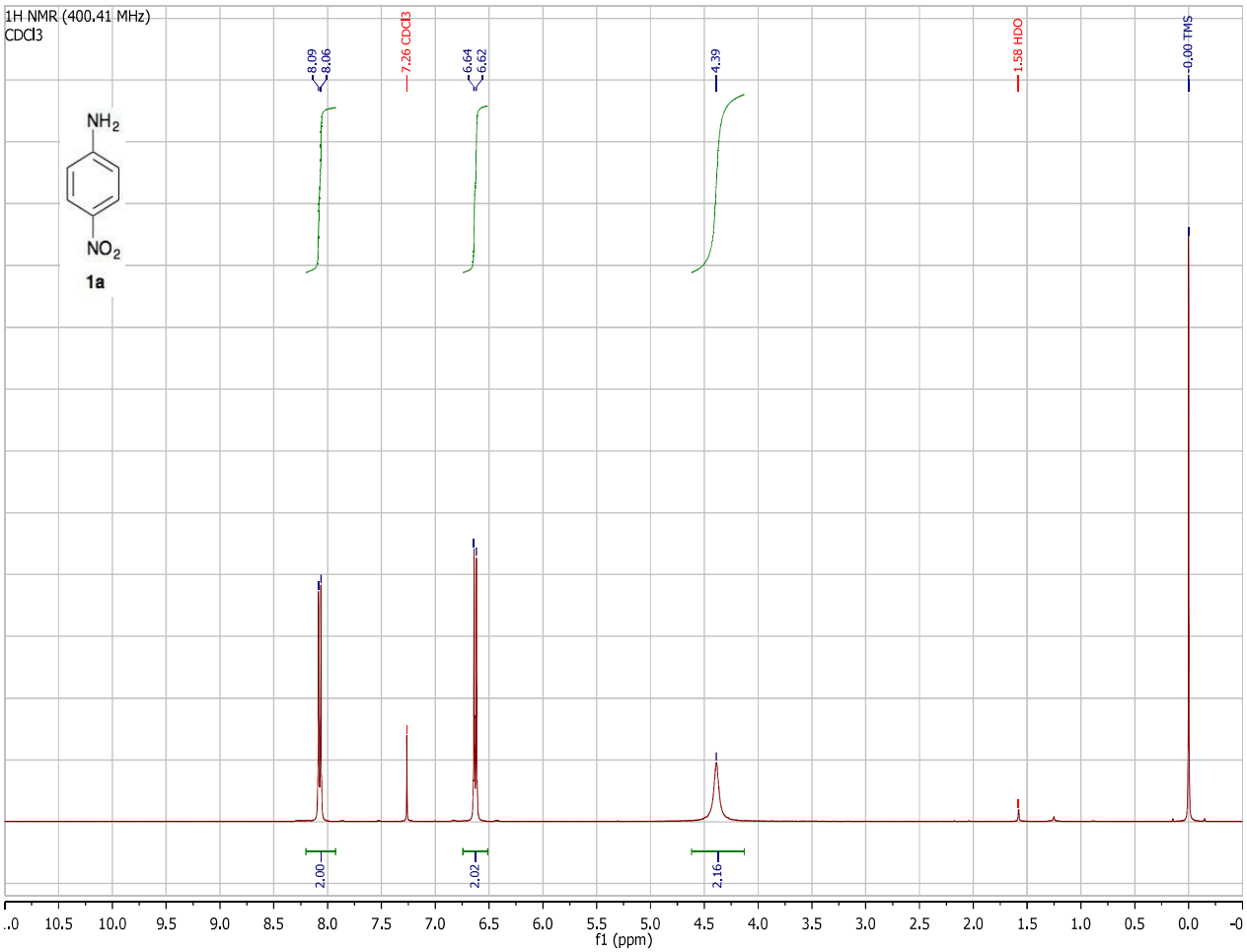

19F NMR (376.53 MHz)
CDCl3
-77.14
OTf
f1 (ppm)

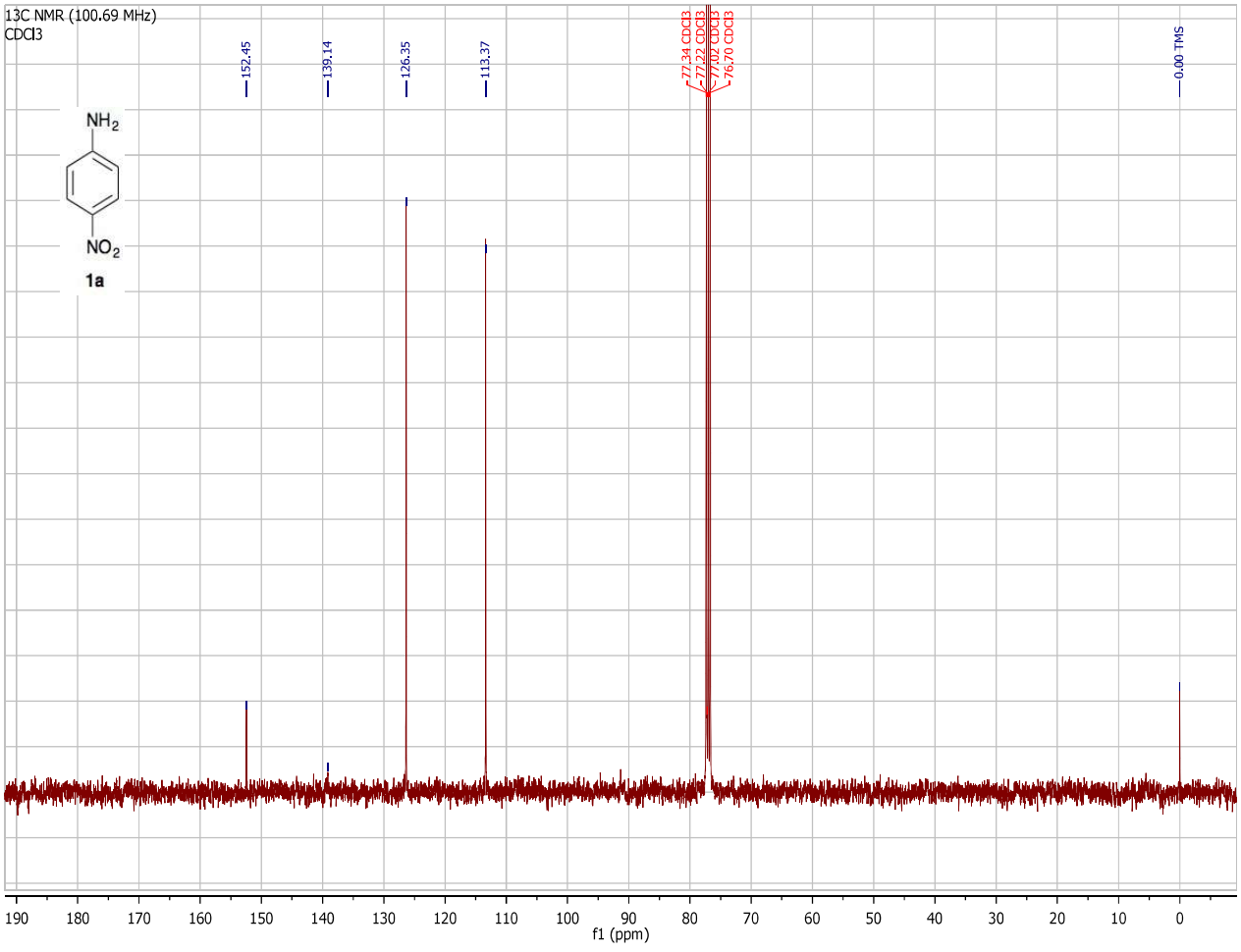

1H NMR (400.32 MHz)
CDCl3
8.70
8.39
8.07
7.99
7.60
7.27 CDCl3
2.14
1.84
1.72
1.68
1.60
1.57
0.00 TMS
OTf
2.00
1.89
1.97
2.08
2.17
4.89
26.69
f1 (ppm)

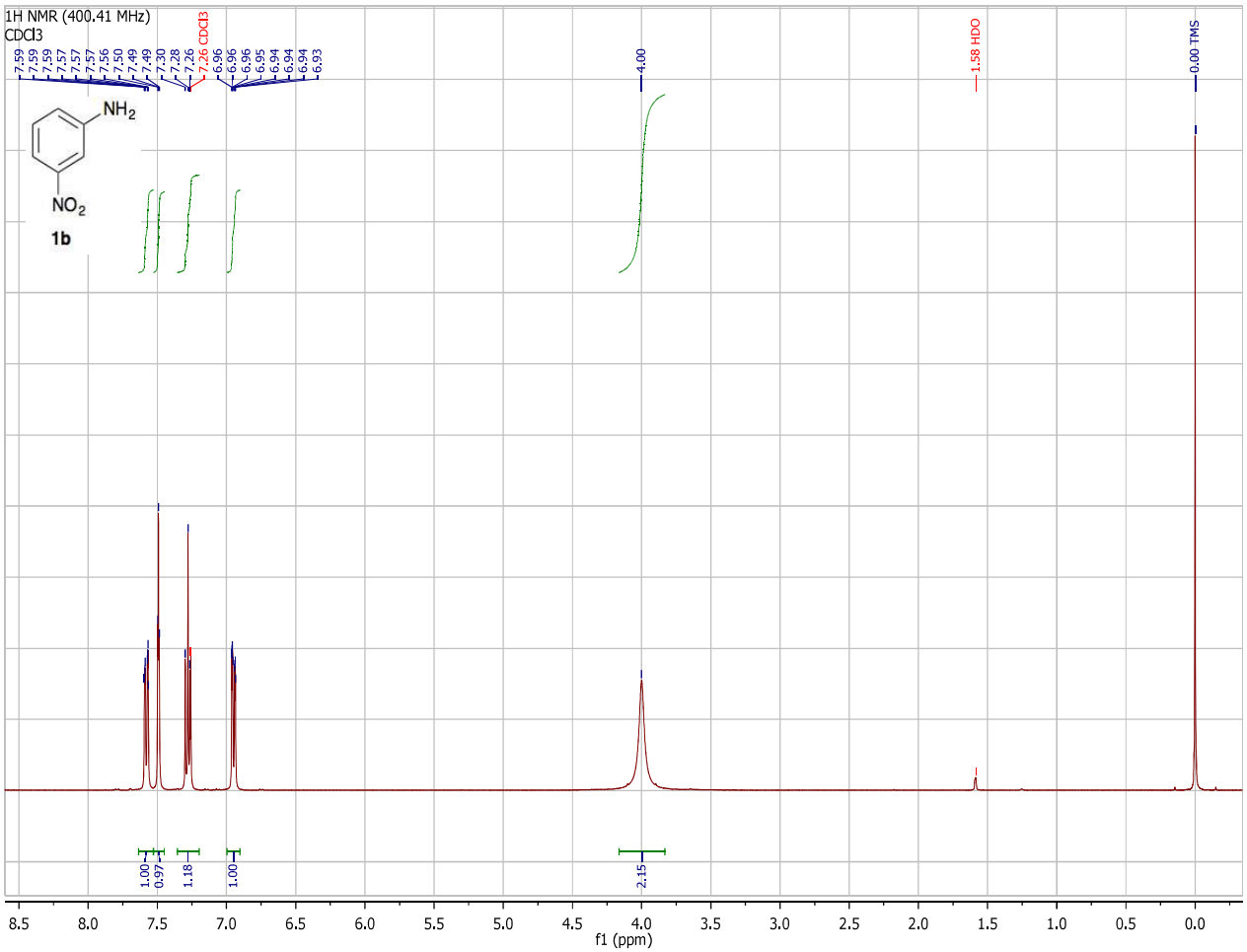

13C NMR (100.67 MHz)
CDCl3
156.20
151.35
148.47
138.40
127.94
127.67
77.35 CDCl3
76.71 CDCl3
60.09
43.86
35.93
29.35
OTf
f1 (ppm)

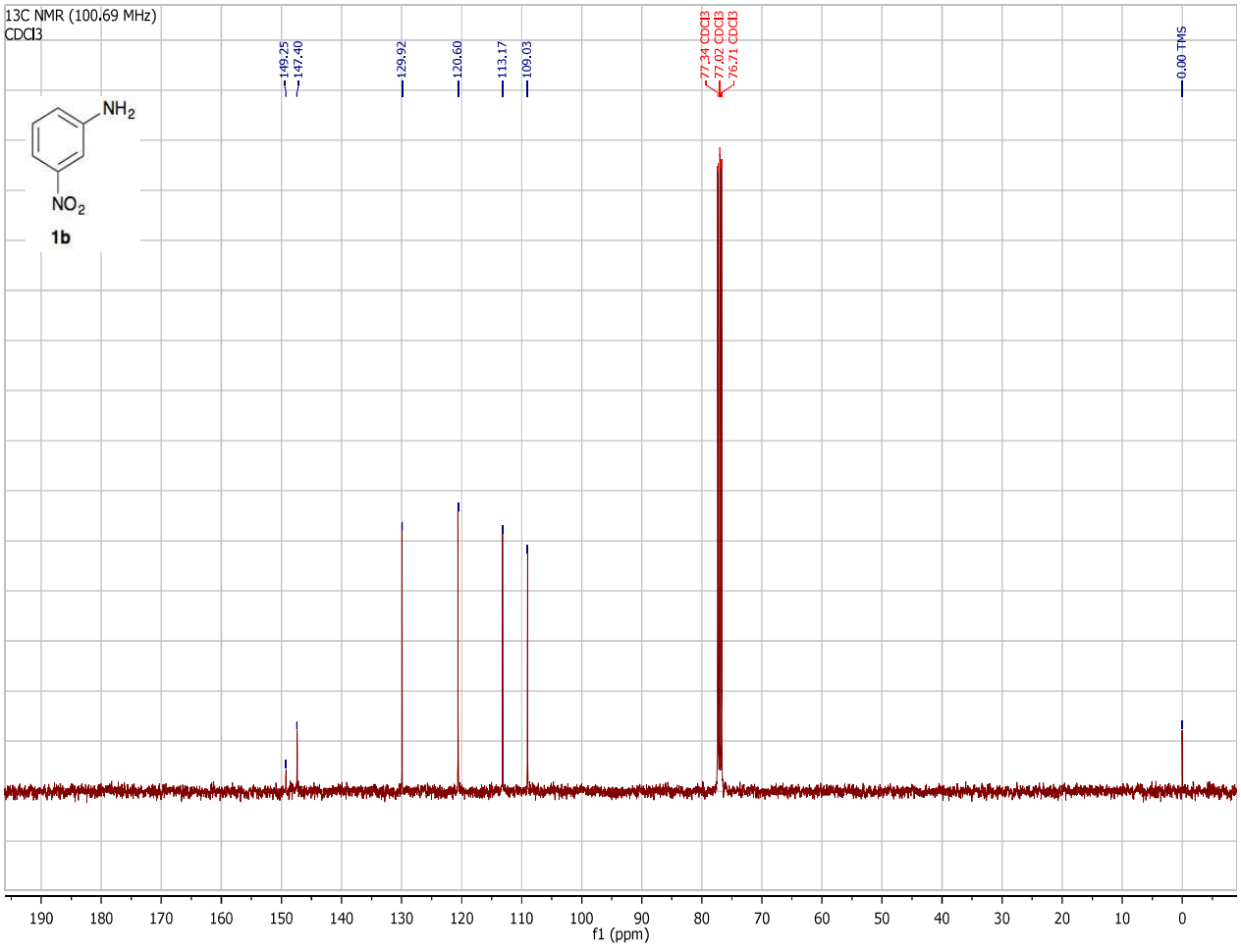

1H NMR (400.32 MHz)
Acetone
8.90
8.80
8.37
8.36
8.31
8.29
7.99
7.98
7.96
7.17
3.07
2.07 Acetone
1.11
0.60
OTf
1.74
2.00
3.82
1.91
5.72
4.19
12.85
11.68
f1 (ppm)

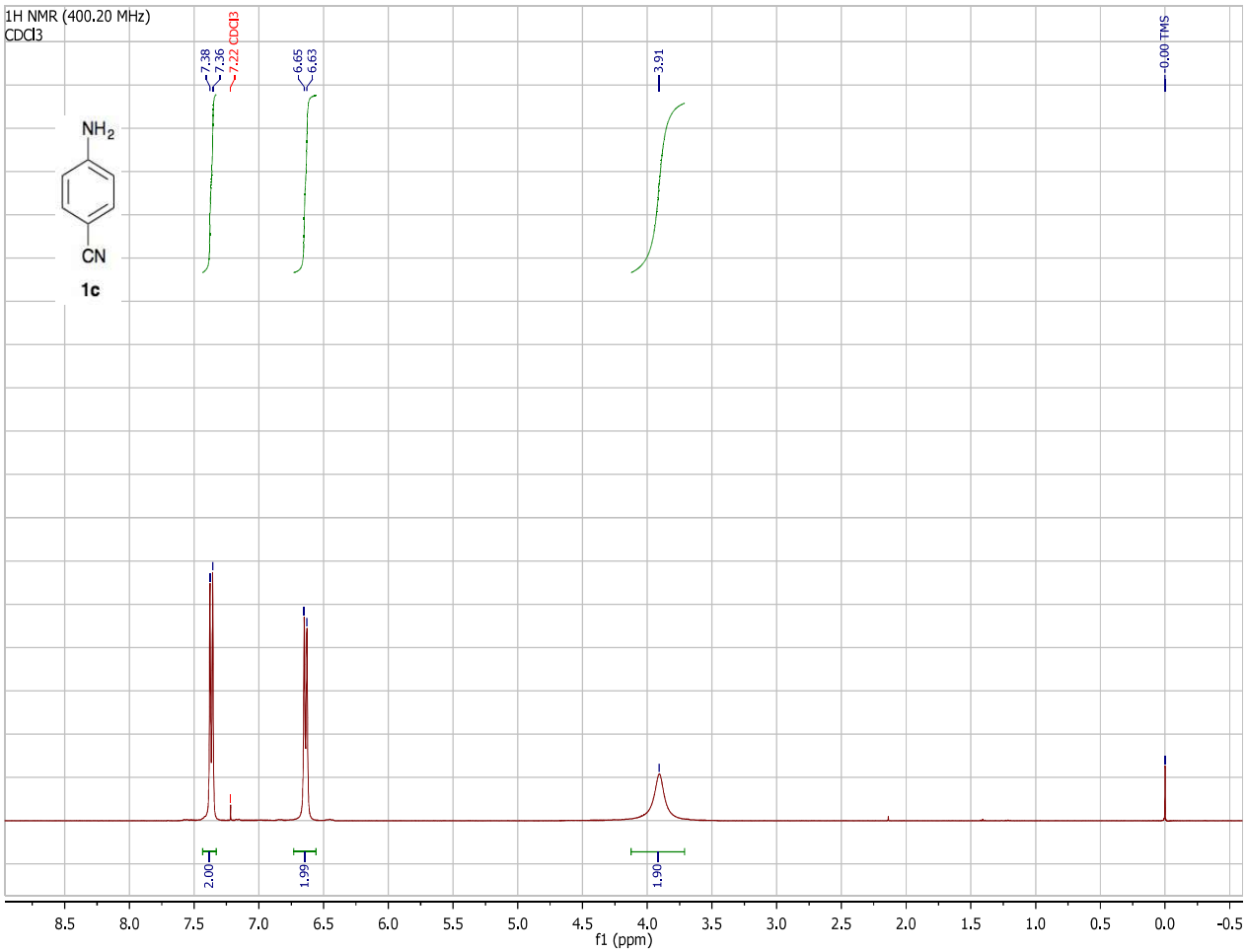

13C NMR (100.67 MHz)
Acetone
205.22 Acetone
164.64
150.09
149.19
145.61
139.17
138.84
129.55
128.50
126.57
123.64
68.30
29.53 Acetone
29.34 Acetone
29.21 Acetone
29.15 Acetone
29.01 Acetone
28.96 Acetone
28.76 Acetone
28.38 Acetone
27.75
OTf
f1 (ppm)

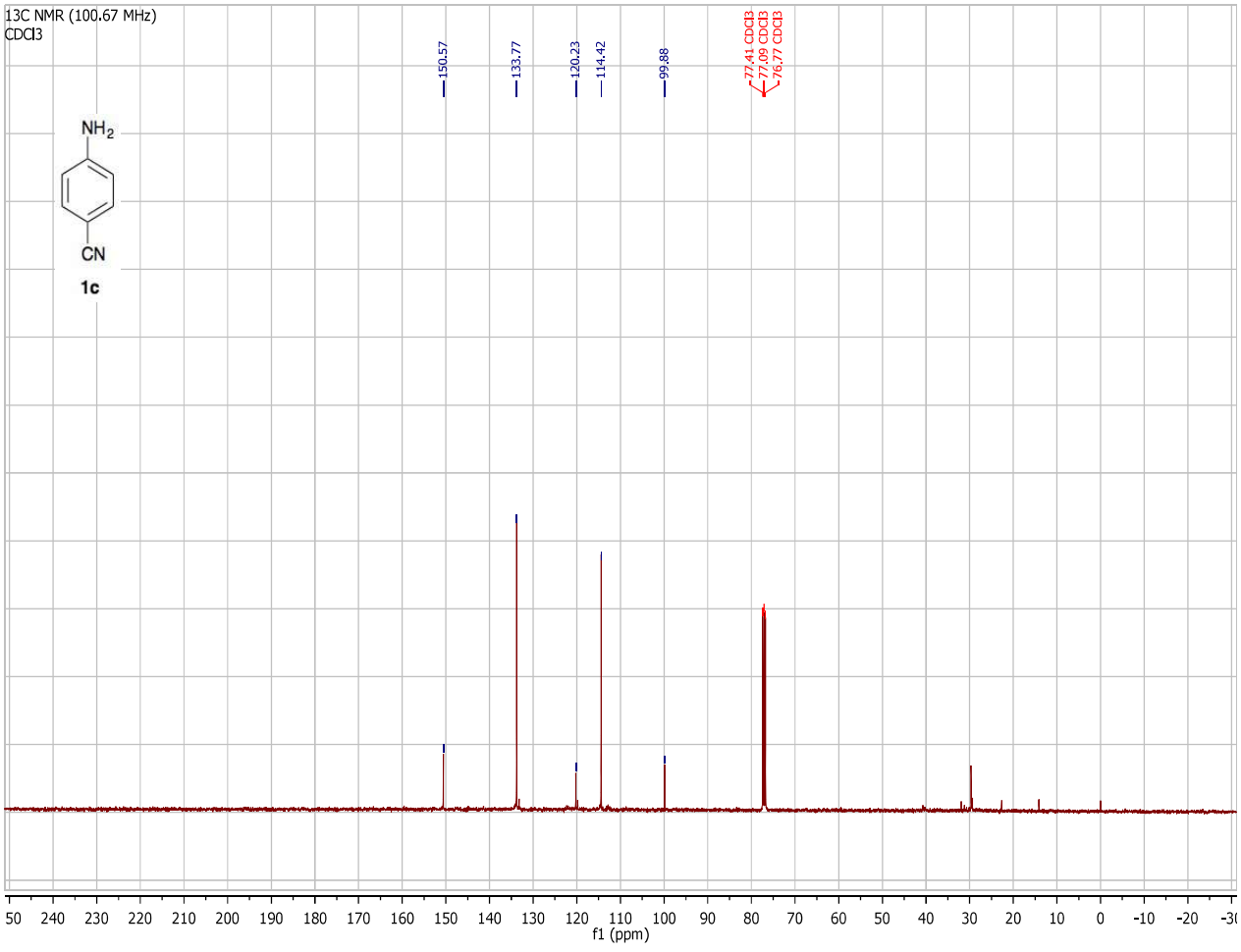

1H NMR (400.41 MHz)
CDCl3
8.09
8.06
7.26 CDCl3
6.64
6.62
4.39
1.58 HDO
0.00 TMS
NH2
NO2
1a
2.00
2.02
2.16
f1 (ppm)

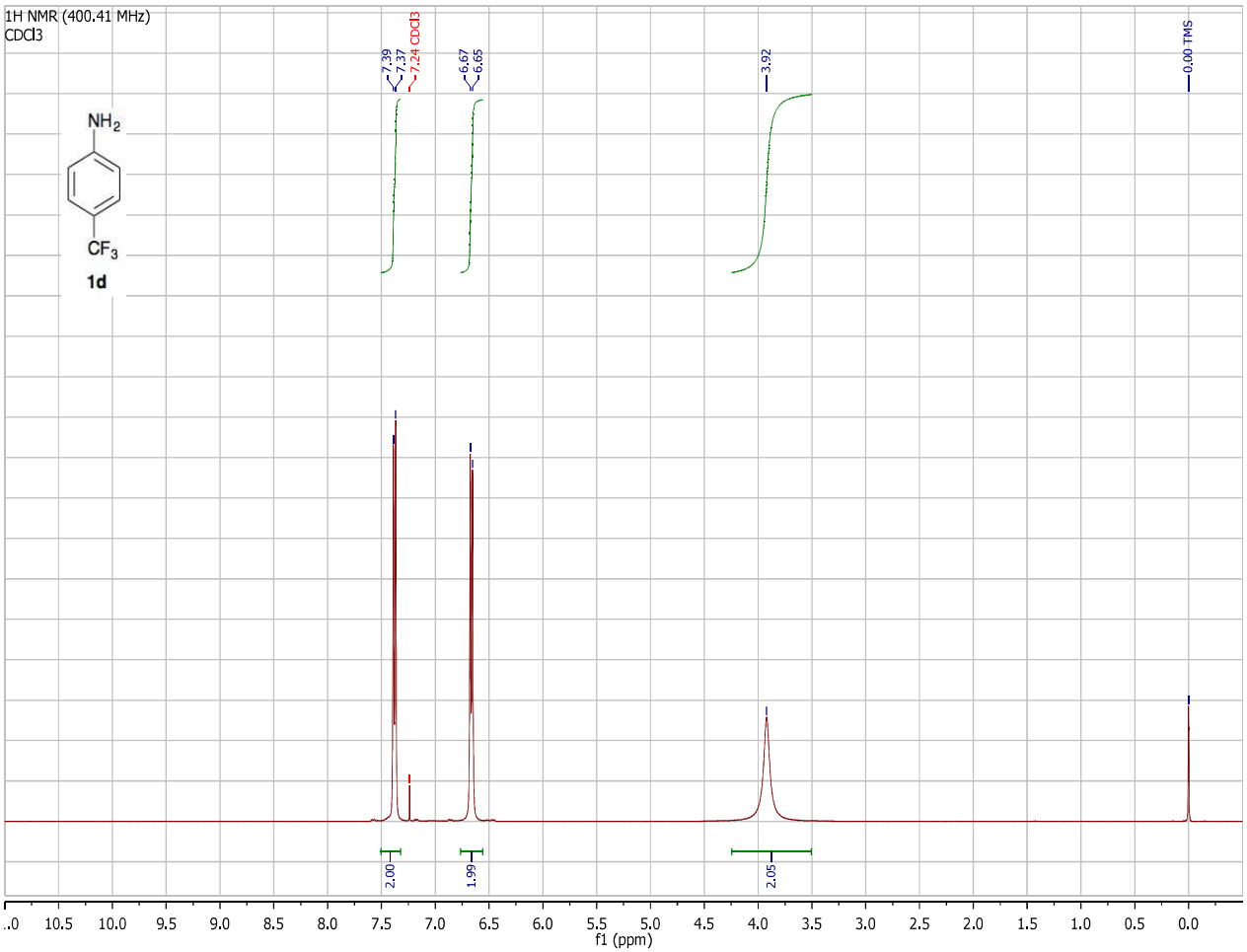

13C NMR (100.69 MHz)
CDCl3
152.45
139.14
126.35
113.37
77.34 CDCl3
77.22 CDCl3
77.02 CDCl3
76.70 CDCl3
0.00 TMS
NH2
NO2
1a
f1 (ppm)

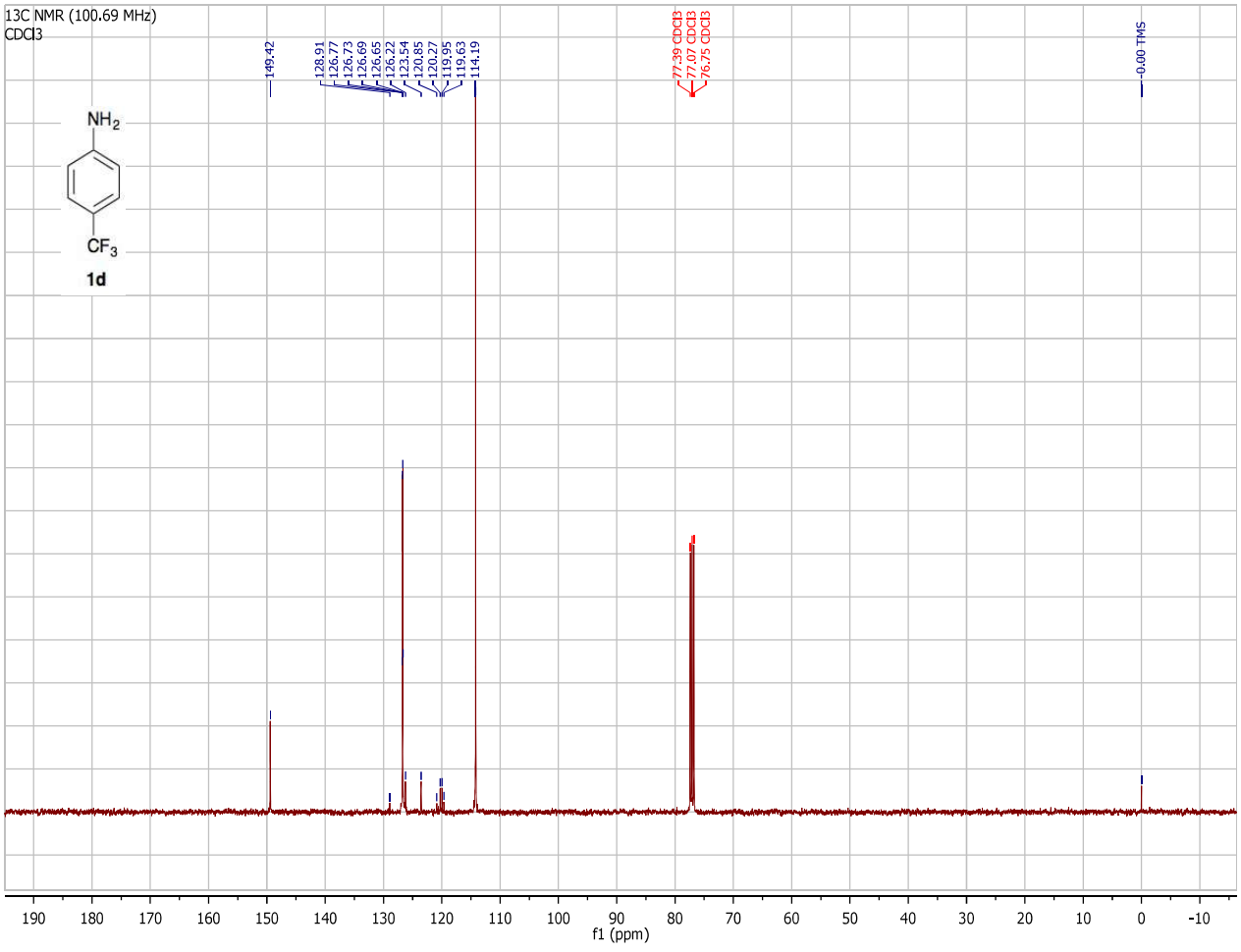

1H NMR (400.41 MHz)
CDCl3
7.59
7.59
7.59
7.57
7.57
7.57
7.56
7.50
7.49
7.49
7.30
7.28
7.26
7.26 CDCl3
6.96
6.96
6.96
6.95
6.94
6.94
6.94
6.93
4.00
1.58 HDO
0.00 TMS
NH2
NO2
1b
1.00
0.97
1.18
1.00
2.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

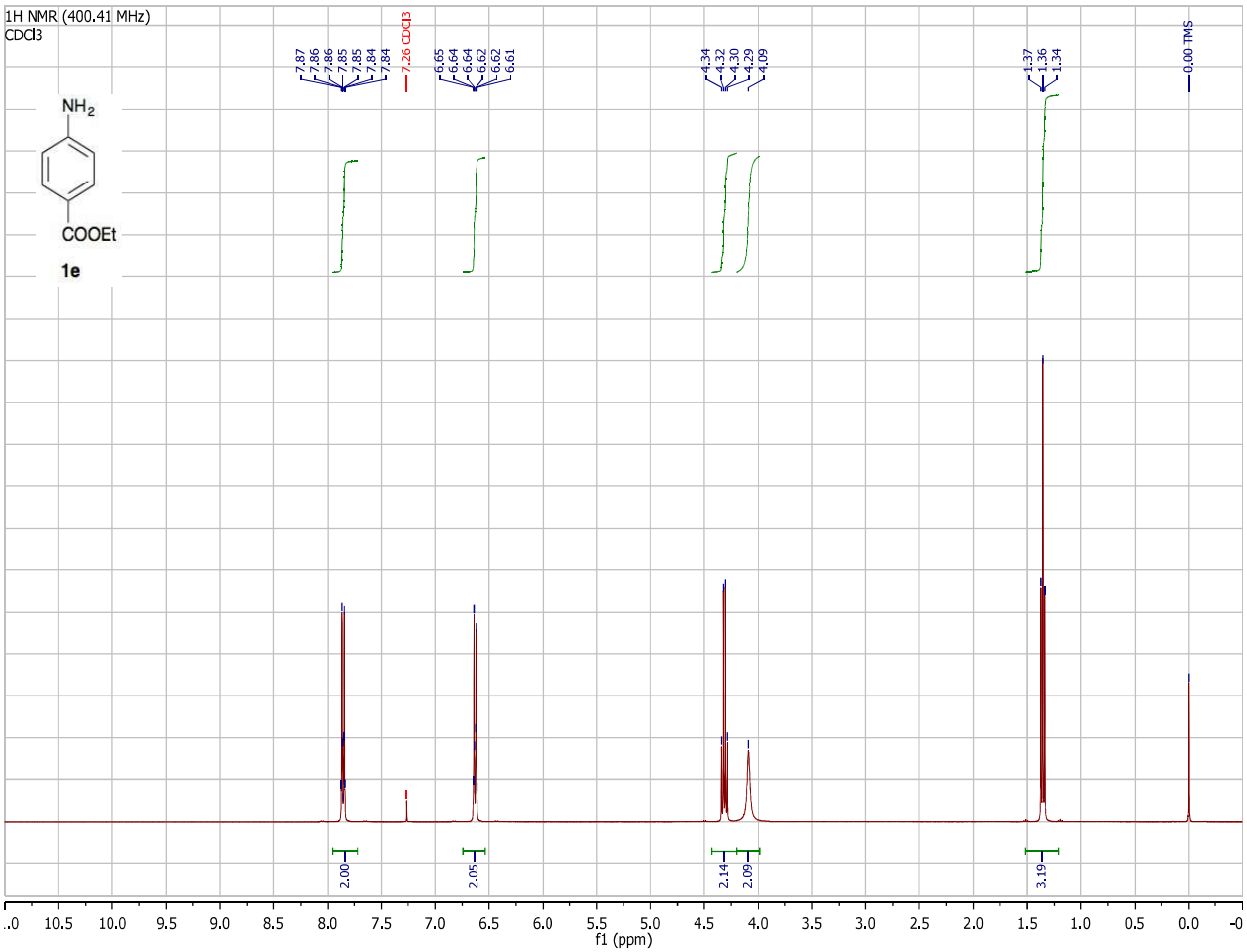

13C NMR (100.69 MHz)
CDCl3
149.25
147.40
129.92
120.60
113.17
109.03
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
0.00 TMS
NH2
NO2
1b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

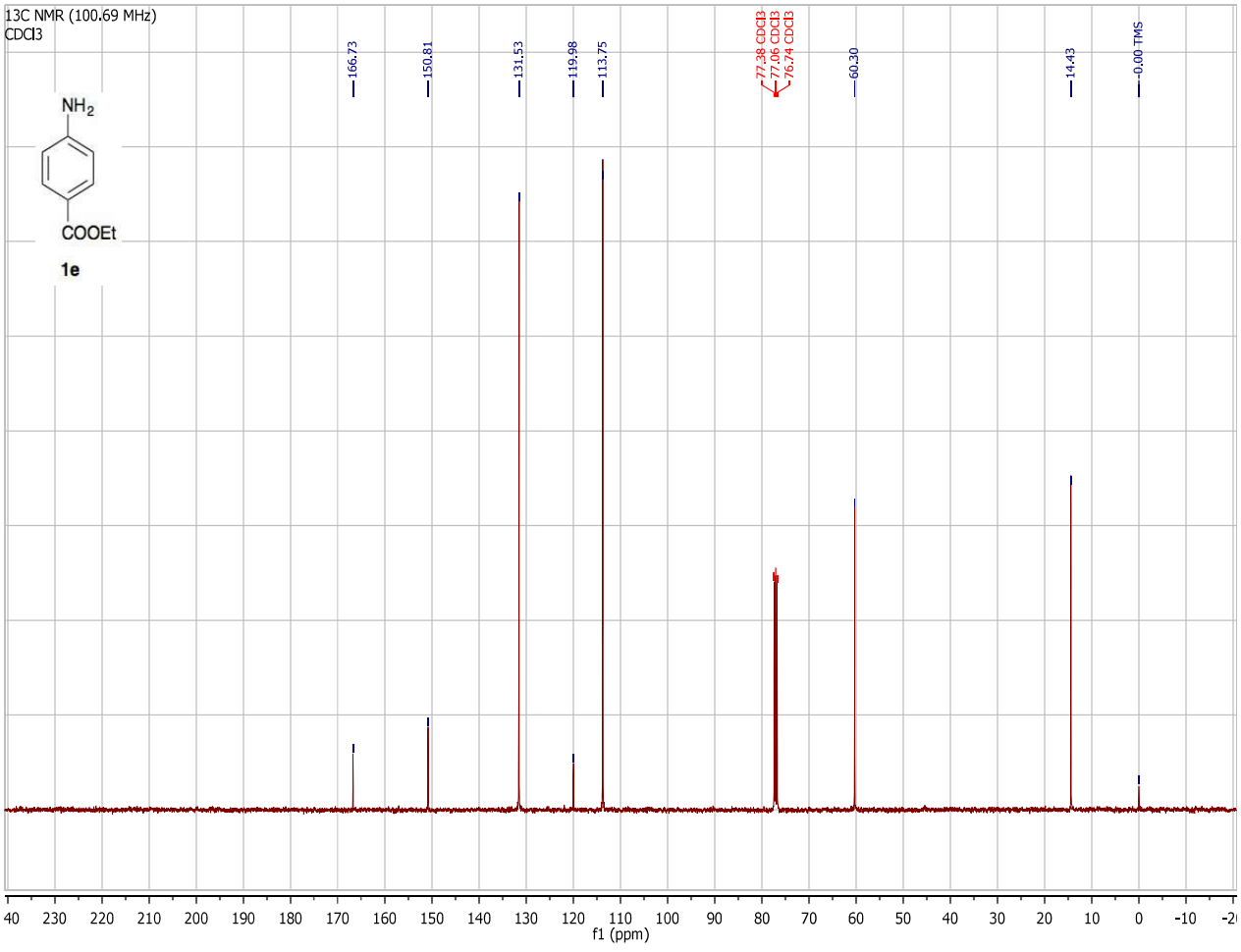

1H NMR (400.20 MHz)
CDCl3
7.38
7.36
7.22 CDCl3
6.65
6.63
3.91
0.00 TMS
NH2
CN
1c
2.00
1.99
1.90
f1 (ppm)

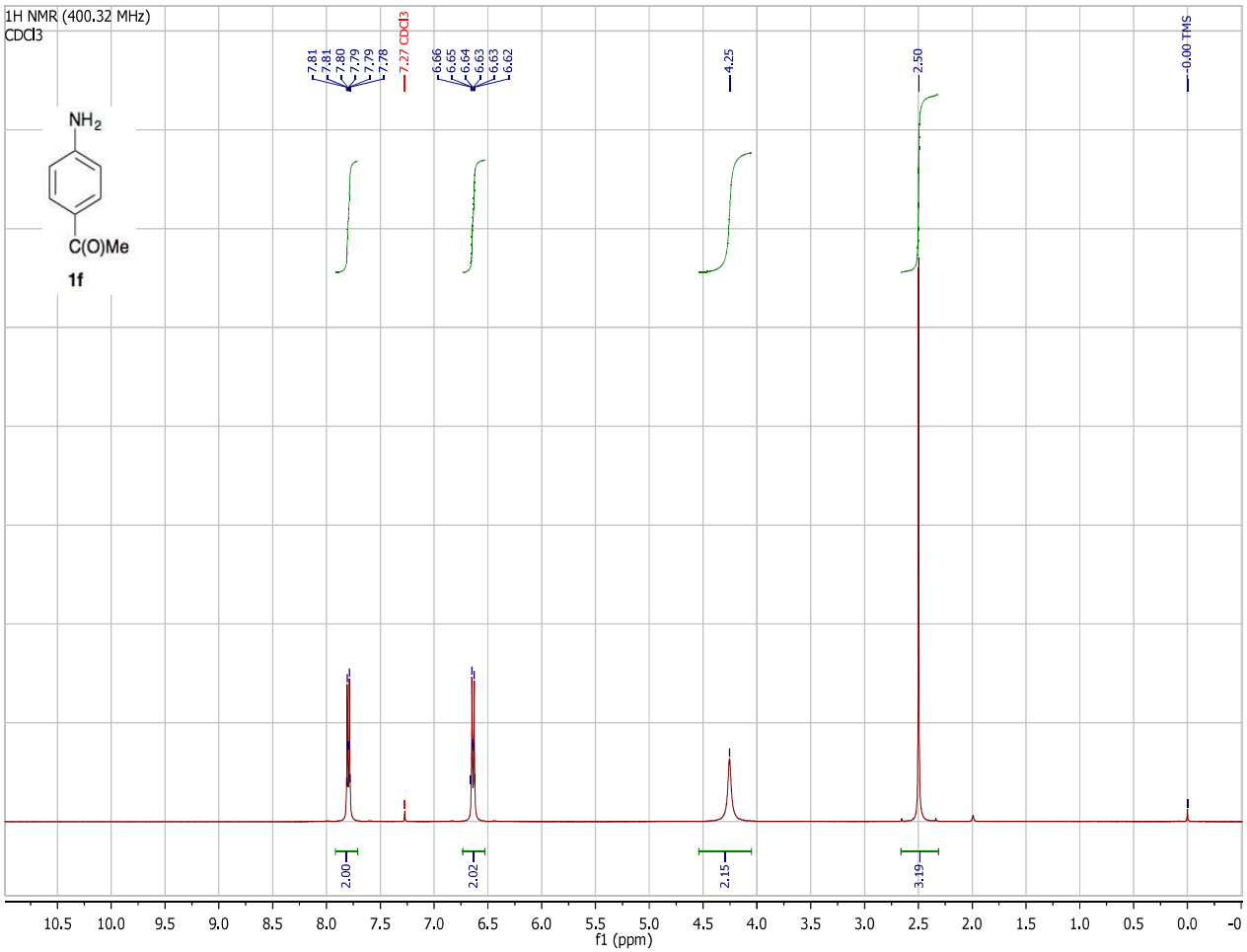

13C NMR (100.67 MHz)
CDCl3
150.57
133.77
120.23
114.42
99.88
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
NH2
CN
1c
f1 (ppm)

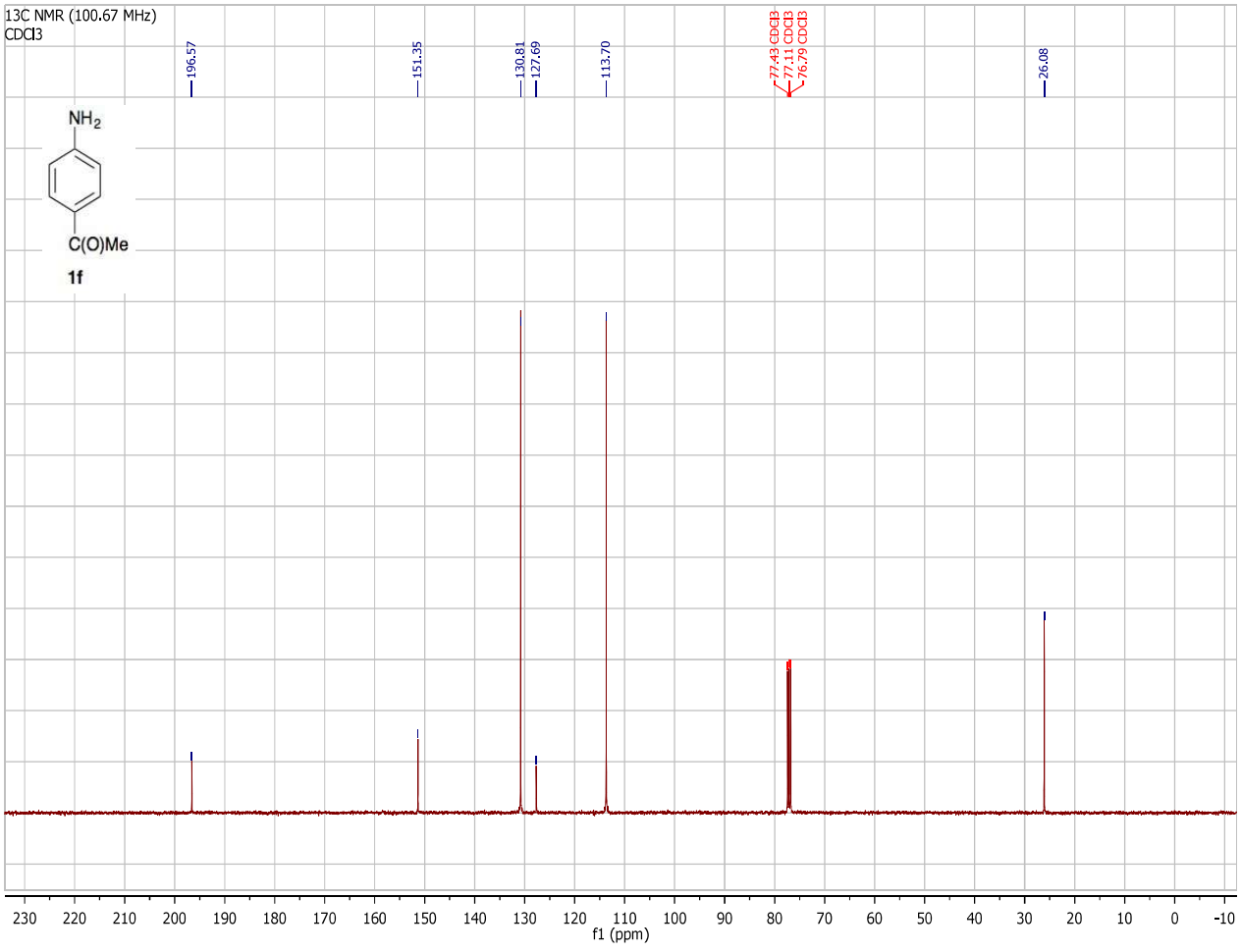

1H NMR (400.41 MHz)
CDCl3
7.39
7.37
7.24 CDCl3
6.67
6.65
3.92
0.00 TMS
NH2
CF3
1d
2.00
1.99
2.05
f1 (ppm)

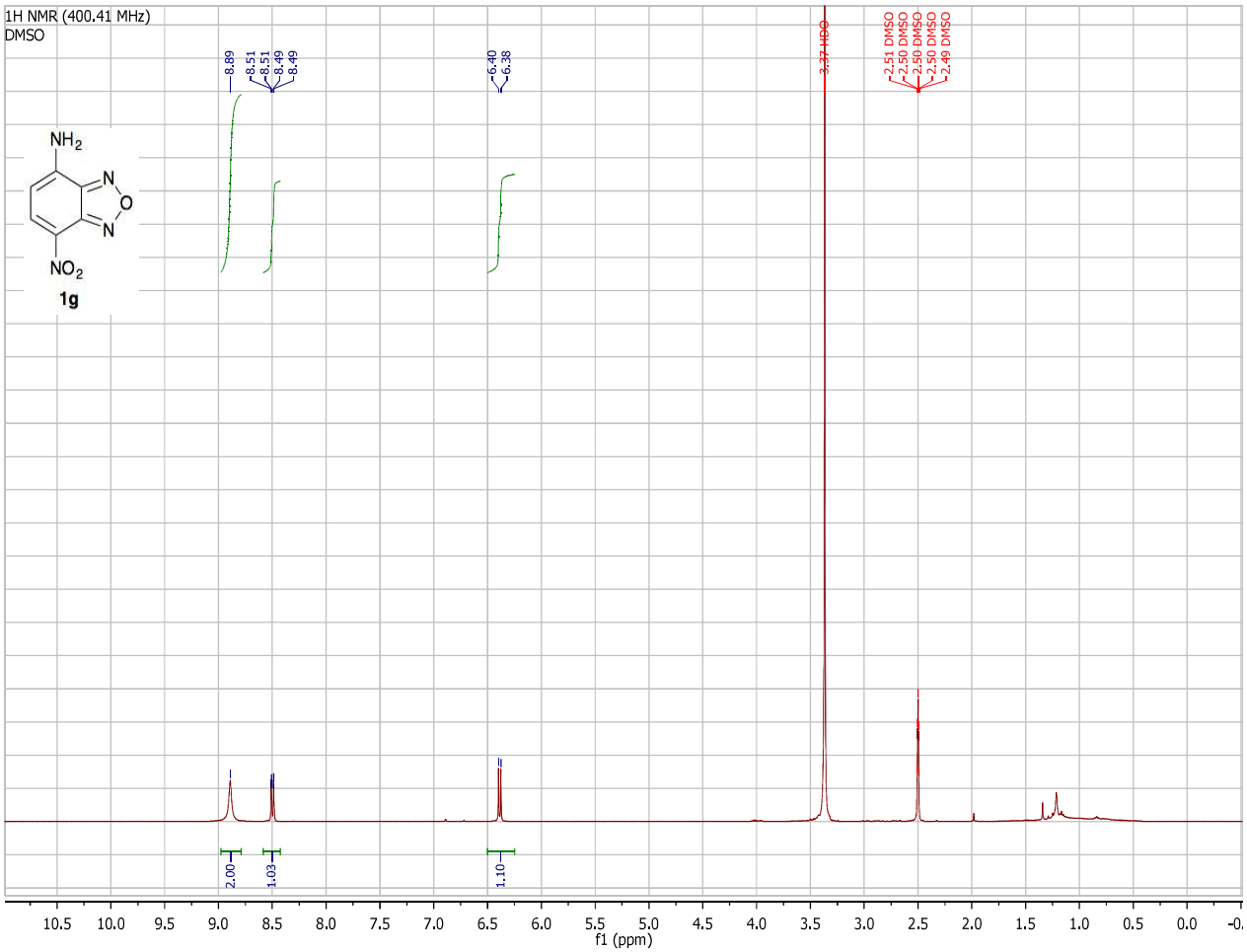

13C NMR (100.69 MHz)
CDCl3
149.42
128.91
126.77
126.73
126.69
126.65
126.22
123.54
120.85
120.27
119.95
119.63
114.19
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
0.00 TMS
NH2
CF3
1d
f1 (ppm)

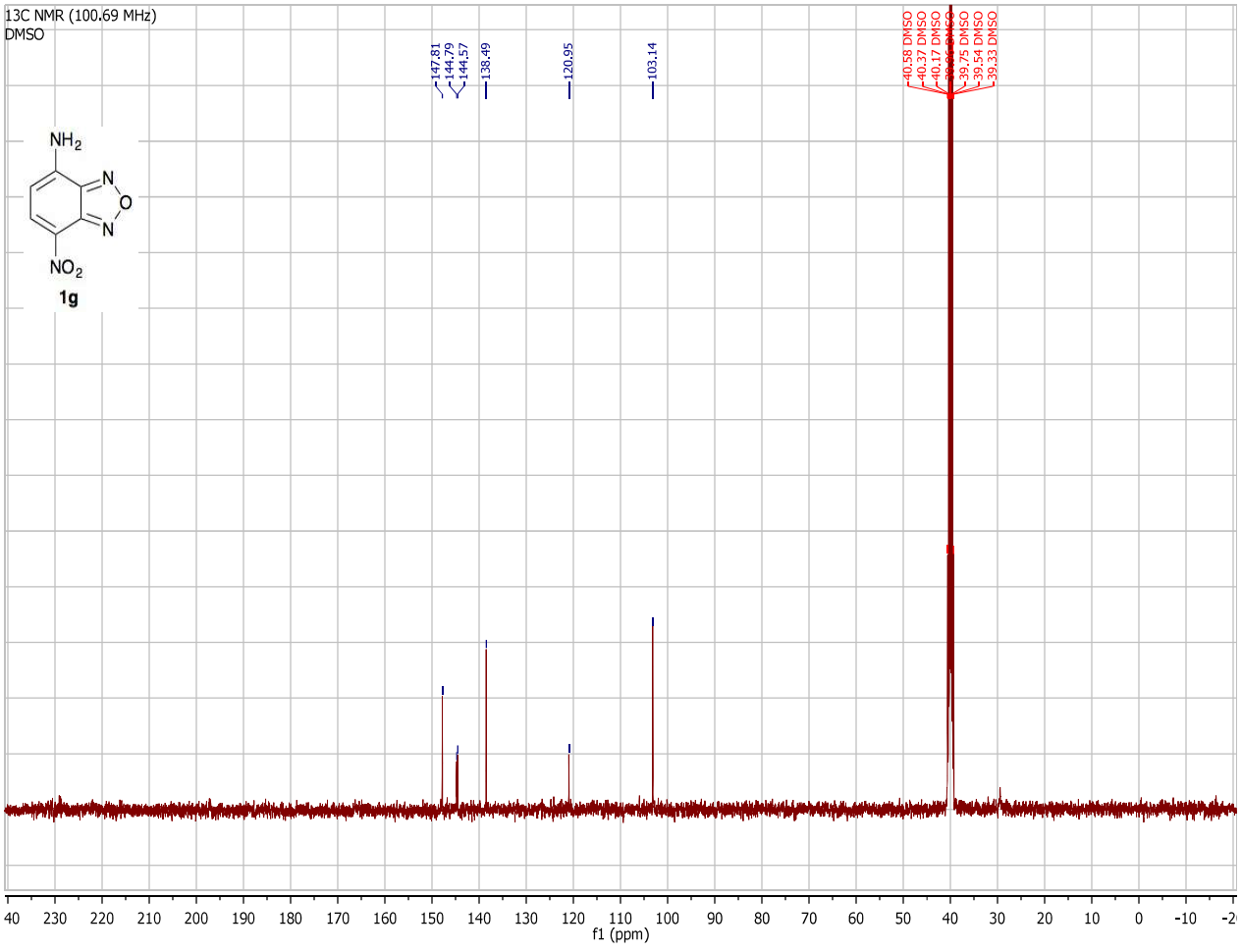

1H NMR (400.41 MHz)
CDCl3
NH2
COOEt
1e
7.87
7.86
7.86
7.85
7.85
7.84
7.84
7.26 CDCl3
6.65
6.64
6.64
6.62
6.62
6.61
4.34
4.32
4.30
4.29
4.09
1.37
1.36
1.34
0.00 TMS
2.00
2.05
2.14
2.09
3.19
f1 (ppm)

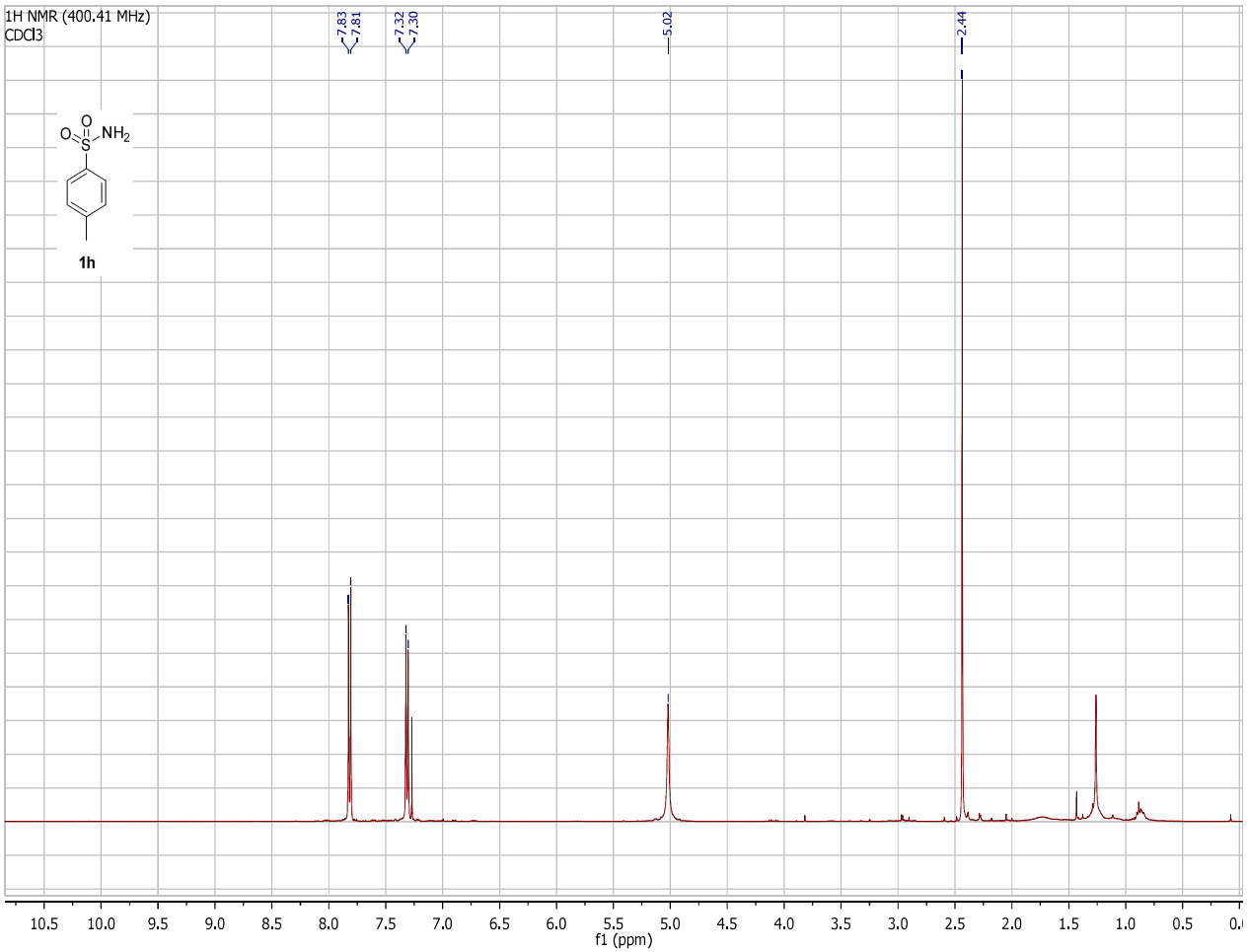

13C NMR (100.69 MHz)
CDCl3
NH2
COOEt
1e
166.73
150.81
131.53
119.98
113.75
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
60.30
14.43
-0.00 TMS
f1 (ppm)

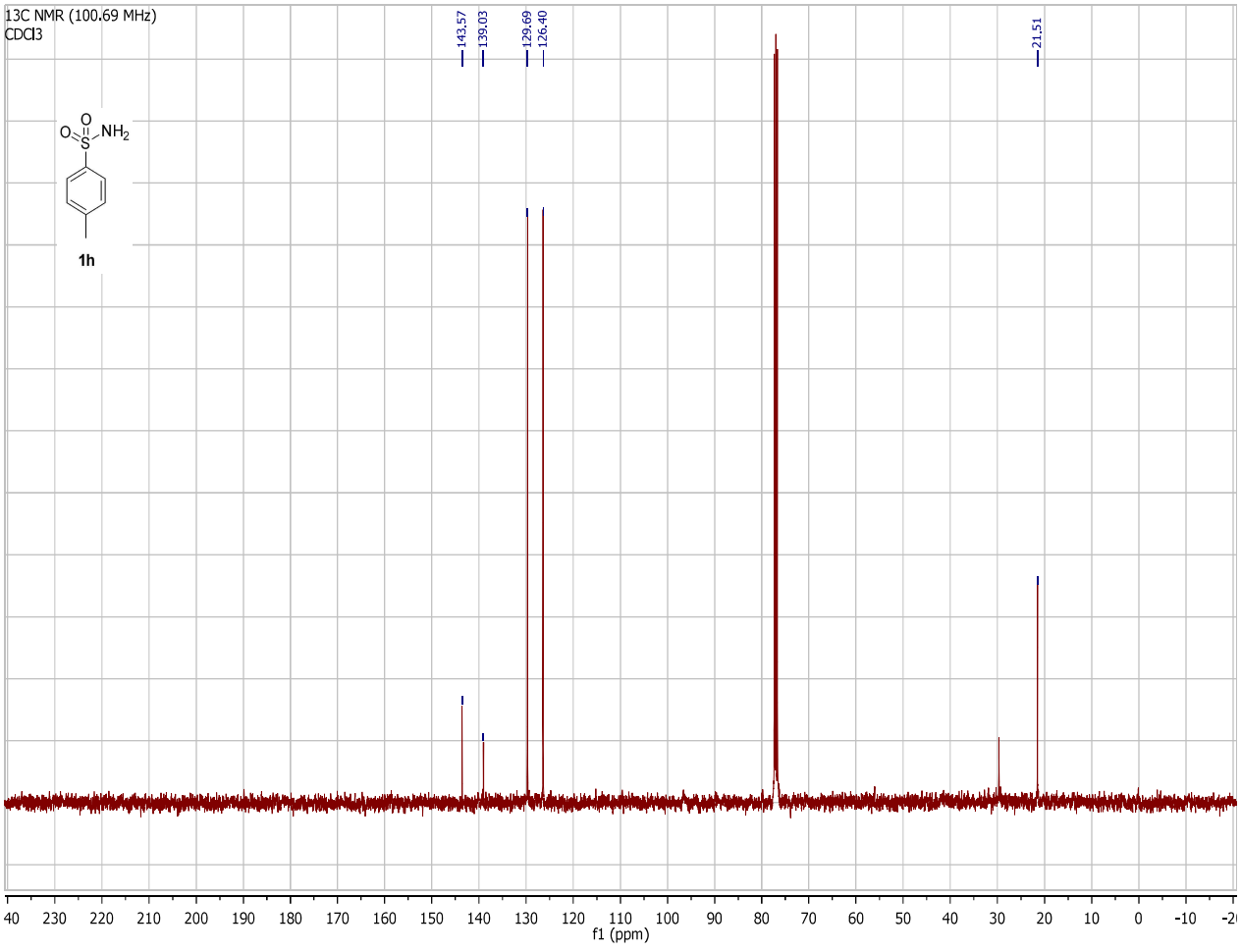

1H NMR (400.32 MHz)
CDCl3
NH2
C(O)Me
1f
7.81
7.81
7.80
7.79
7.79
7.78
7.27 CDCl3
6.66
6.65
6.64
6.63
6.63
6.62
4.25
2.50
0.00 TMS
2.00
2.02
2.15
3.19
f1 (ppm)

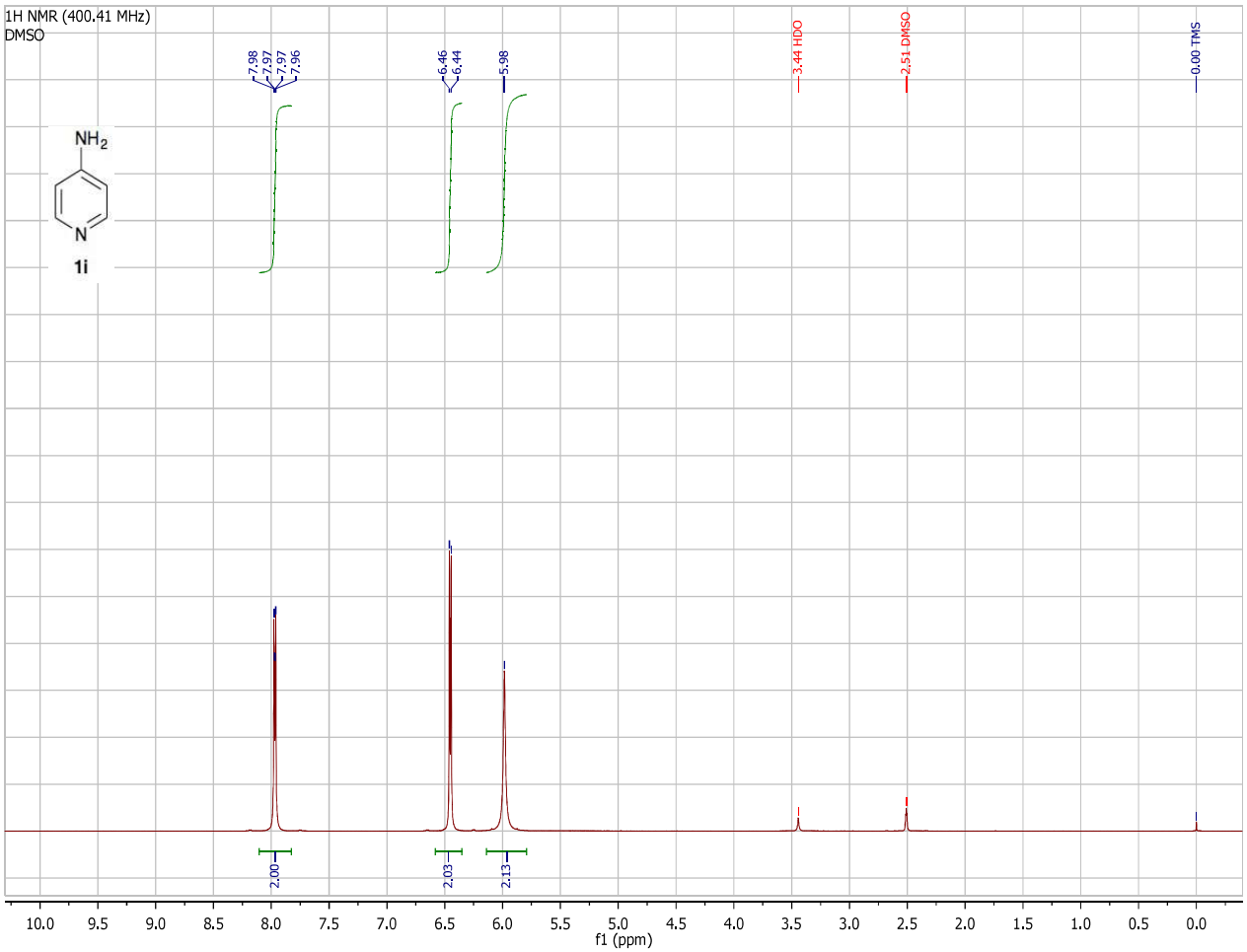

13C NMR (100.67 MHz)
CDCl3
NH2
C(O)Me
1f
196.57
151.35
130.81
127.69
113.70
77.43 CDCl3
77.11 CDCl3
76.79 CDCl3
26.08
f1 (ppm)

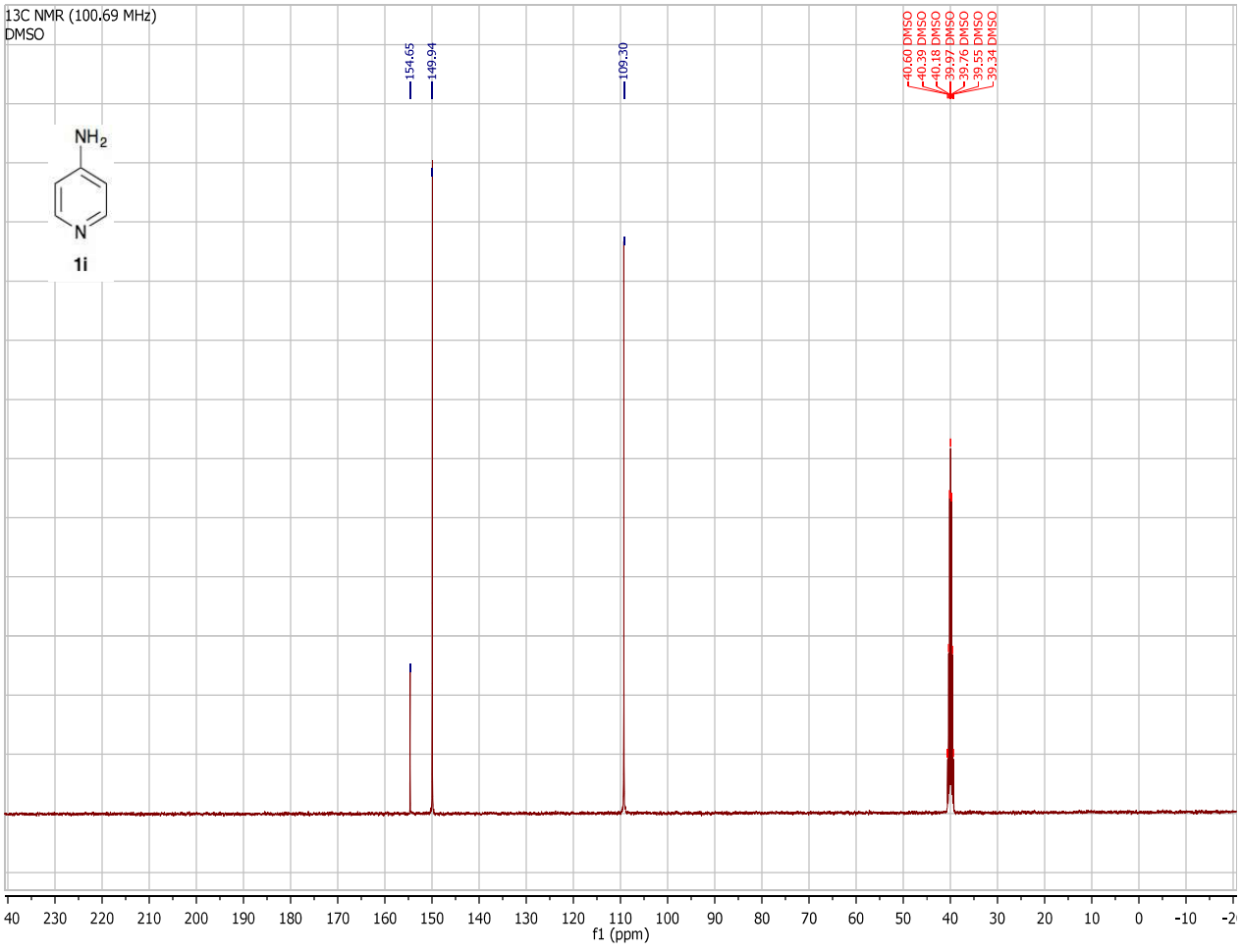

1H NMR (400.41 MHz)
DMSO
8.89
8.51
8.51
8.49
8.49
6.40
6.38
3.37 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
NH2
NO2
1g
2.00
1.03
1.10
f1 (ppm)

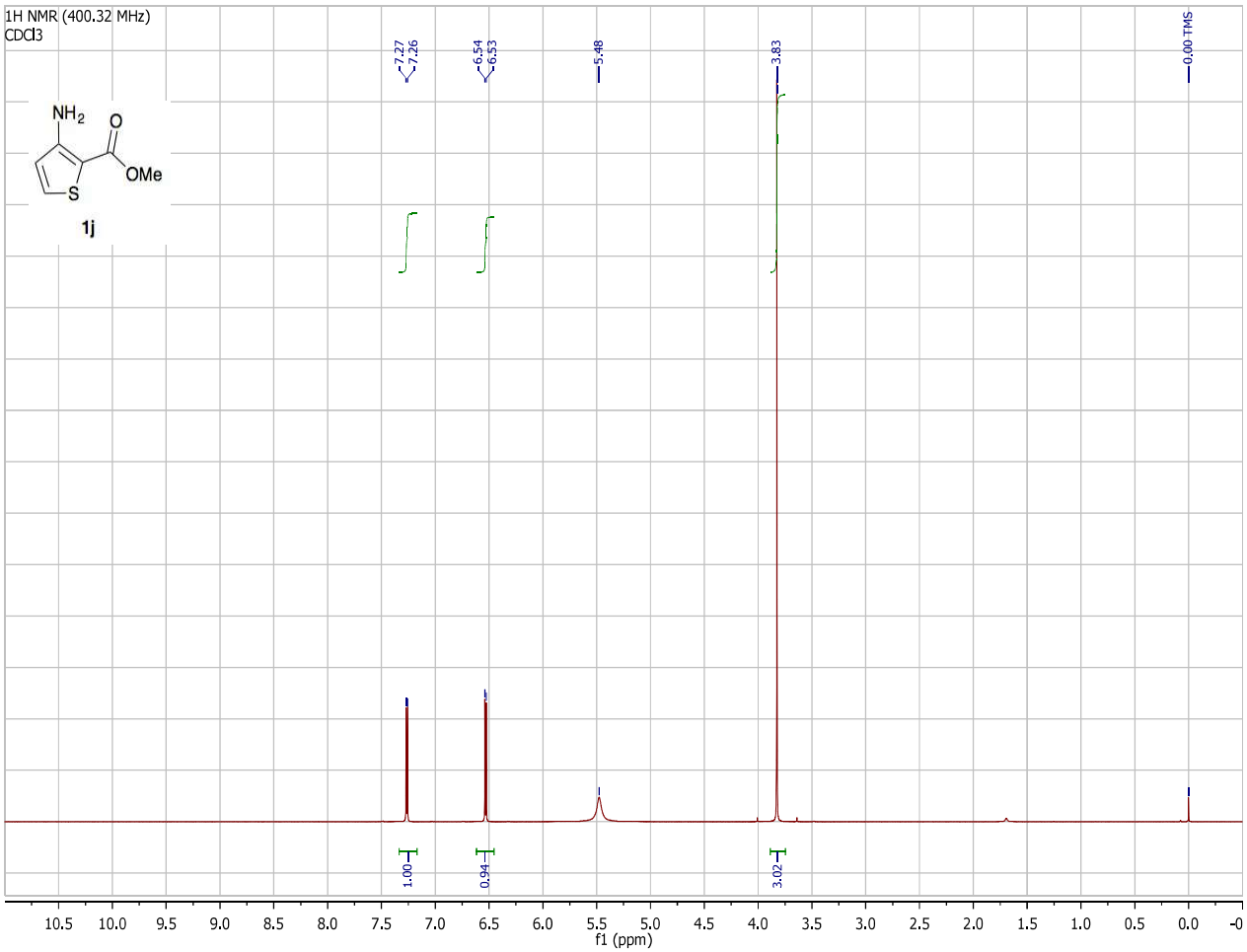

13C NMR (100.69 MHz)
DMSO
147.81
144.79
144.57
138.49
120.95
103.14
40.58 DMSO
40.37 DMSO
40.17 DMSO
39.75 DMSO
39.54 DMSO
39.33 DMSO
NH2
NO2
1g
f1 (ppm)

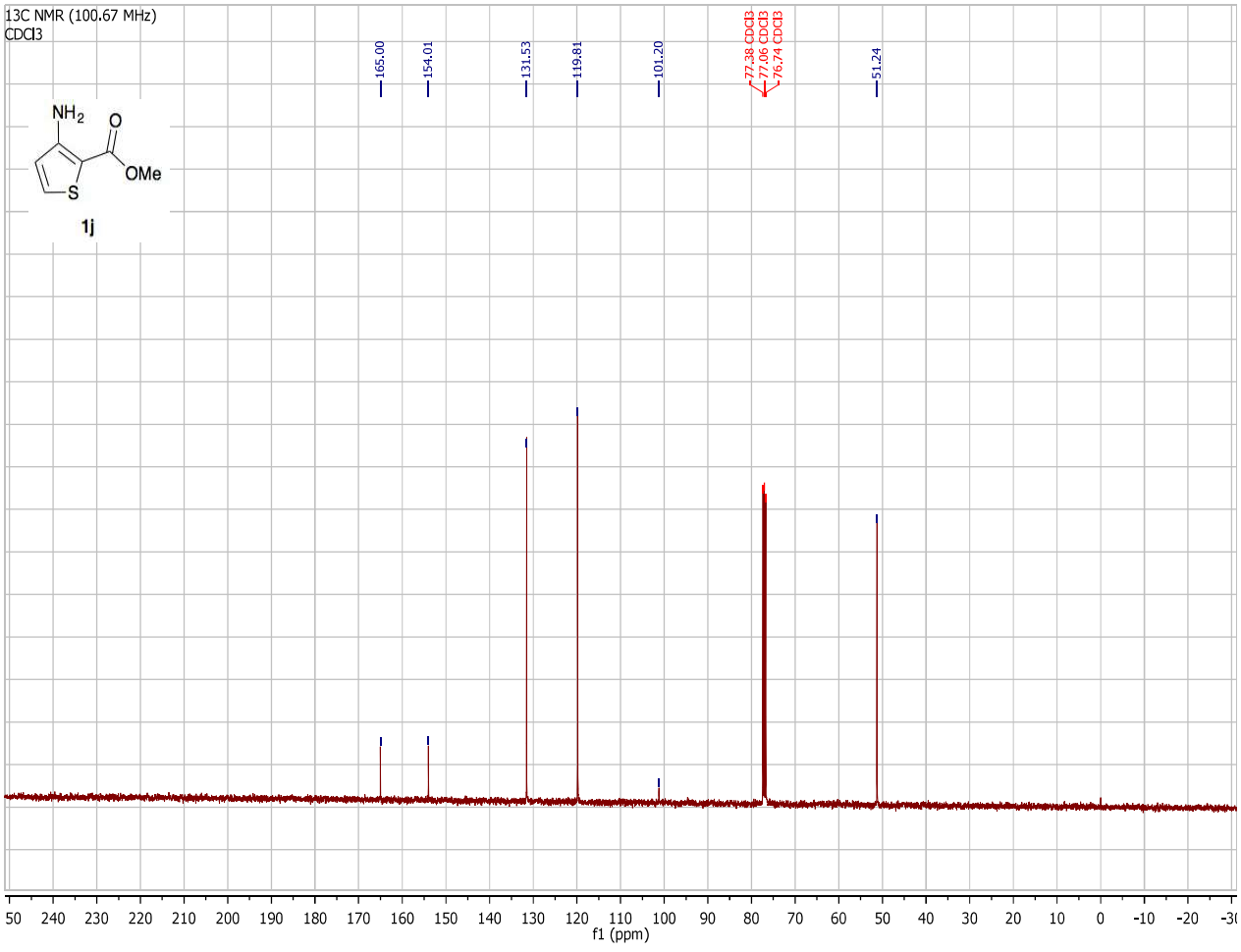

1H NMR (400.41 MHz)
CDCl3
7.83
7.81
7.32
7.30
5.02
2.44
O
O=S-NH2
1h
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


13C NMR (100.69 MHz)
CDCl3
143.57
139.03
129.69
126.40
21.51
O
O=S-NH2
1h
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1H NMR (400.41 MHz)
DMSO
7.98
7.97
7.97
7.96
6.46
6.44
5.98
3.44 HDO
2.51 DMSO
0.00 TMS
NH2
N
1i
2.00
2.03
2.13
10.0 9.5 9.0 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 0.0
f1 (ppm)


13C NMR (100.69 MHz)
DMSO
154.65
149.94
109.30
40.60 DMSO
40.39 DMSO
40.18 DMSO
39.97 DMSO
39.76 DMSO
39.55 DMSO
39.34 DMSO
NH2
N
1i
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1H NMR (400.32 MHz)
CDCl3
NH2
O
OMe
S
1j
7.27
7.26
6.54
6.53
5.48
3.83
0.00 TMS
1.00
0.94
3.02
f1 (ppm)


13C NMR (100.67 MHz)
CDCl3
NH2
O
OMe
S
1j
165.00
154.01
131.53
119.81
101.20
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
51.24
f1 (ppm)