Sulfur-stabilised copper nanoparticles for the aerobic oxidation of amines to imines under ambient conditions

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Supplementary Information

General

Anhydrous copper(II) chloride (97%, Sigma-Aldrich), lithium powder (MEDALCHEMY S.L.), DTBB (4,4'-di-*tert*-butylbiphenyl, Sigma-Aldrich), and all other reagents (Sigma-Aldrich, Acros, Alfa Aesar, Fluorochem) were commercially available of the best grade and were used without further purification. THF was dried in a Sharlab PS-400-3MD solvent purification system using an alumina column. All reactions were carried out on a multireactor apparatus using the corresponding reactor tubes.

Field Emission Scanning Electron Microscopy (FE-SEM) was conducted on a Zeiss Merlin VP Compact apparatus, equipped with an EDX microanalysis system Quantax 400 from Bruker. Scanning electron microscopy (SEM) was conducted on a Hitachi S3000N apparatus, equipped with an X-ray detector Bruker XFlash 3001 for microanalysis (EDS) and mapping. The Transmission Electron microscopy (TEM) images were recorded on a JEOL JEM-2010 microscope, equipped with a lanthanum hexaboride filament operated at an acceleration voltage of 200 kV. Cryogenic Electron Microscopy (Cryo-EM) samples were analysed in a Talos Arctica Cryo-EM with a X field emission gun operating at 200 kV; the samples (3 μL, in ethanol) were applied to one side of Quantifoil Lacey Carbon film Cu/Rh lacey carbon grids, blotted, and plunged into liquid ethane in a FEI Vitrobot Mark IV; the images were acquired with the EPU Software (ThermoFisher Scientific®) installed on a Falcon III direct electron detector and recorded under low-dose conditions at a nominal magnification of 17500, 45000 and 150000 (0.60, 0.23 and 0.07 nm/pixel sampling rate, respectively). The X-Ray Photoelectron Spectroscopy (XPS) spectra were measured with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatized and Al-Kα radiation source of 300 W and a hemispheric electron analyser equipped with 9 channeltron electron multipliers. The intensities of the different contributions were obtained by means of the calculation of the integral of each peak, after having eliminated the baseline with S form and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. All the binding energies were referred to the C 1s line at 284.4 eV, obtaining values with a precision of ± 0.2 eV. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analyses were performed with a Perkin Elmer Optima 4300 DV (dual vision) apparatus. The powder X-ray Diffraction (XRD) diagram was collected in the θ–θ mode using a Bruker D8 Advance X-ray diffractometer: Cu $K\alpha_1$ irradiation, λ = 1.5406 Å; 25 ºC, 2θ = 4–80. The BET surface area was determined with an Autosorb-6 apparatus (Quantachrome Instruments), after sample degasification (40 ºC, 12 h, in vacuo) with an Autosorb Degasser Materprep (Quantachrome Instruments).

Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. Infrared analysis was performed with a Jasco 4100LE (Pike MIRacle ATR) spectrophotometer; wavenumbers ($\tilde{\upsilon}$) are given in cm^{-1}. NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers (300 and 400 MHz for ^{1}H NMR; 75 and 101 MHz for ^{13}C NMR); chemical shifts are given in (δ) parts per million (ppm) and coupling constants (*J*) in Hertz. Mass spectra (EI) were obtained at 70 eV on an Agilent 5763 (GC) spectrometer; fragment ions in m/z with relative intensities (%) in parentheses. High Resolution Mass Spectrometry (HRMS) analyses (EI) were also carried out at 70 eV on an Agilent 7200 (Q-TOF) spectrometer. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with a Youling 6100 instrument equipped with a flame ionisation detector and a HP-5MS 30 m capillary column (0.25 mm diameter, 0.25 μm film thickness), using nitrogen (1 mL/min) as a carrier gas, $T_{injector}$ 270 ºC, T_{column} 80 ºC (3 min) and 80–270 ºC (15 ºC/min); retention times (t_R) are given in min. Analytical thin-layer chromatography (TLC) was carried out on TLC plastic sheets with silica gel 60 F254 (Merck). Column and preparative chromatography were performed using silica gel 60 of 40–60 microns and P/UV254, respectively (hexane/EtOAc as eluent).

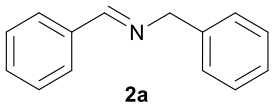
General procedure for the preparation of CuNPs/support. Dry THF (2 mL) was added dropwise to a mixture of lithium powder (14 mg, 2.0 mmol) and 4,4'-di-*tert*-butylbiphenyl (DTBB, 27 mg, 0.1 mmol), under an argon atmosphere. Then, anhydrous $CuCl_2$ (134 mg, 1.0 mmol) was added to the green suspension, which rapidly turned black upon the formation of CuNPs. This suspension was diluted with THF (18 mL), followed by the addition of the corresponding support (1.28 g) (Table 1, entries 3–11). The resulting mixture was stirred for 1 h at room temperature, filtered, and the solid was successively washed with THF (20 mL) and MeOH (20 mL), and dried under vacuum.

General procedure for the preparation of Cu_2ONPs/S_8. Anhydrous $CuCl_2$ (134 mg, 1.0 mmol) was dissolved in dry EtOH (15 mL) and S_8 (1.28 g) was added to the resulting solution. The mixture was stirred, followed by the addition of $NaBH_4$ (4 equiv.). The resulting mixture was stirred for 1 h at rt, filtered, and the solid was successively washed with water (20 mL), EtOH (10 mL) and THF (10 mL), and dried under vacuum.

General procedure for the aerobic oxidation of amines. The amine **1** (1.0 mmol) was added to a reactor tube containing Cu_2ONPs/S_8 (20 mg, 0.3 mol%; Table 2) and the mixture was stirred at room temperature for 24 h without any solvent. The resulting mixture was diluted with EtOAc,

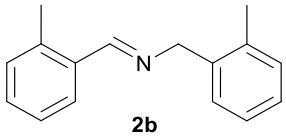
filtered through a pad of neutral alumina, celite and $MgSO_4$, and the filtrate was analysed by GLC and GC-MS and concentrated under vacuum. The imines **2** were generally purified by recrystallisation from hexane. Imines **2a**, **2g** and **2l** were obtained in quantitative conversion and did not require any further purification; imines **2c**, **2am** and **2an** were purified by column chromatography (basic alumina, hexane-EtOAc); the very sensitive imine **2f** was purified by bulb-to-bulb distillation.

Characterisation of imines 2



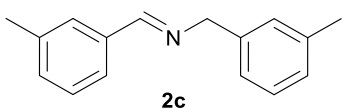
2a

(*E*)-*N*-Benzyl-1-phenylmethanimine (2a).[1] Yellow oil (82 mg, 84%); R_f 0.89 (9:1, hexane-EtOAc); t_R 13.28; IR (neat) $\tilde{\upsilon}$ 3061, 3027, 1644, 1580, 1495, 1452, 1131, 1026, 752 and 694; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (d, J = 1.3, 2H), 7.25–7.29 (m, 1H), 7.32–7.36 (m, 4H), 7.40–7.44 (m, 3H), 7.76–7.81 (m, 2H) and 8.40 (t, J = 1.3, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 65.2, 127.1, 128.1, 128.4, 128.6, 128.7, 130.9, 136.3, 139.4 and 162.2; MS (EI) *m/z* (%) 195 (50) $[M]^+$, 194 (51), 117 (12), 92 (31), 91 (100), 89 (10) and 65 (14).



2b

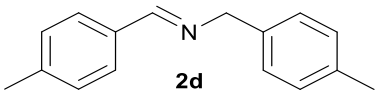
(*E*)-*N*-(2-Methylbenzyl)-1-(*o*-tolyl)methanimine (2b).[2] Yellow oil (106 mg, 95%); R_f 0.93 (9:1, hexane-EtOAc); t_R 14.75; IR (neat) $\tilde{\upsilon}$ 3020, 1639, 1602, 1460 and 753; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.50 (s, 3H), 4.82 (d, J = 1.0, 2H), 7.15–7.19 (m, 4H), 7.22–7.32 (m, 3H) 7.90–7.95 (m, 1H) and 8.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.4, 19.5, 63.4, 126.2, 126.3, 128.4, 127.2, 127.8, 130.2, 130.4, 130.9, 134.4, 136.2, 137.4, 137.9 and 160.7; MS (EI) *m/z* (%) 224 (12) $[M^+ + 1]$, 223 (71) $[M^+]$, 222 (32), 208 (19), 206 (15), 205 (13), 132 (14), 118 (24), 106 (13), 105 (100), 104 (57), 103 (20), 91 (11), 79 (16) and 77 (22).



2c

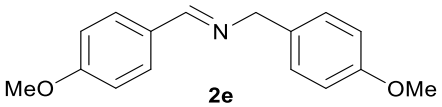
(*E*)-*N*-(3-Methylbenzyl)-1-(*m*-tolyl)methanimine (2c).[3] Yellow oil (89 mg, 80%); R_f 0.72 (8:2, hexane-EtOAc); t_R 12.16; IR (neat) $\tilde{\upsilon}$ 3024, 2920, 2854, 1643, 1608, 1485, 1450, 1037, 779 and

694; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.39 (s, 3H), 4.78 (s, 2H), 7.06–7.14 (m, 4H), 7.21–7.26 (m, 1H), 7.28–7.33 (m, 1H), 7.53–7.55 (m, 1H), 7.65 (s, 1H) and 8.36–8.37 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 21.5, 65.2, 125.2, 125.9, 127.9, 128.5, 128.6, 128.9, 131.7, 136.2, 138.2, 138.4, 139.2 and 162.3; MS (EI) *m/z* (%) 223 (45) [M^+], 222 (32), 208 (20), 207 (19), 106 (48), 105 (100), 103 (16), 91 (15), 79 (13) and 77 (20).



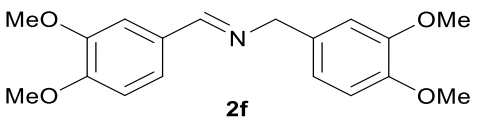
2d

(*E*)-*N*-(4-Methylbenzyl)-1-(*p*-tolyl)methanimine (2d).[4] Yellow solid (79 mg, 71%); mp 76–78 ºC (from hexane) [lit.,[4] 83–84 ºC (from MeOH)]; R_f 0.92 (9:1, hexane-EtOAc); t_R 15.03; IR (neat) $\tilde{\upsilon}$ 3020, 2917, 2852, 1645, 1514 and 796; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.37 (s, 3H), 4.76 (s, 2H), 7.14 (d, *J* = 7.6, 2H), 7.19–7.23 (m, 4H), 7.64–7.68 (d, *J* = 6.8, 2H) and 8.33 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.2, 21.6, 64.9, 128.1, 128.4, 129.3, 129.4, 133.8, 136.5, 136.6, 141.1, and 161.8; MS (EI) *m/z* (%) 223 (48) [M^+], 222 (22), 106 (20), 105 (100), 103 (10) and 77 (12).



2e

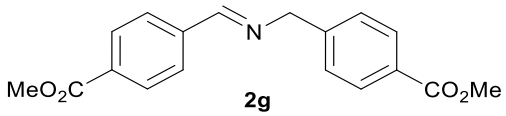
(*E*)-*N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl)methanimine (2e).[5] Yellow oil (122 mg, 96%); R_f 0.91 (9:1, hexane-EtOAc); t_R 17.32; IR (neat) $\tilde{\upsilon}$ 3002, 2955, 2939, 2835, 1644, 1605, 1578, 1511, 1463, 1441, 1421, 1302, 1248, 1166, 1108, 1033 and 832; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H), 3.83 (s, 3H), 4.72 (s, 2H), 6.88, 6.92 (AA'BB' system, *J* = 8.0, 4H), 7.24, 7.71 (AA'XX' system, *J* = 8.0, 4H) and 8.29 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.4, 55.5, 64.5, 114.0, 114.1, 129.3, 129.9, 131.8, 158.8, 161.0 and 161.8; MS (EI) *m/z* (%) 255 (17) [$M]^+$, 121 (100).



2f

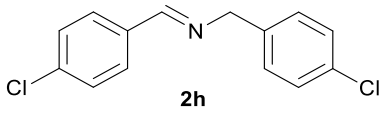
(*E*)-*N*-(3,4-Dimethoxybenzyl)-1-(3,4-dimethoxyphenyl)methanimine (2f).[6] Yellow oil (151 mg, 96%); R_f 0.22 (9:1, hexane-EtOAc); t_R 20.94; IR (neat) $\tilde{\upsilon}$ 3009, 2925, 2841, 1635, 1509, 1261 and 804; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86, 3.88, 3.90, 3.92 (4 s, 12H), 4.73 (s, 2H), 6.83–6.88 (m, 4H), 7.19 (d, *J* = 8.2, 1H), 7.47 (s, 1H), and 8.28 (s, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 55.6, 55.7, 64.5, 108.6, 110.2, 111.0, 111.2, 120.0, 123.1, 129.2, 131.8, 147.1, 148.8, 149.1, 151.3 and 161.1; MS (EI) *m/z* (%) 315 (100) $[M]^+$, 316 (32), 314 (11), 152 (43), 151 (100), 107 (19) and 106 (10).



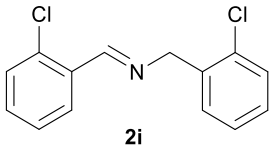
2g

Methyl (*E*)-4-{[(4-(Methoxycarbonyl)benzyl]imino}methyl) benzoate (2g).[7] Yellow solid (148 mg, 95%); mp 118–123 ºC (from hexane); R_f 0.37 (9:1, hexane-EtOAc); t_R 21.18; IR (neat) $\tilde{\upsilon}$ 2953, 2922, 2853, 1717, 1642, 1433, 1272, 1105, 854 and 816; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91, 3.94 (2 s, 6H), 4.90 (s, 2H), 7.42, 8.02 (AA'XX' system, J = 9.0, 4H), 7.85, 8.09 (AA'XX' system, J = 9.0, 4H) and 8.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.0, 52.3, 64.7, 126.9, 127.8, 128.2, 128.9, 129.9, 132.1, 139.7, 144.2, 161.6, 166.6 and 166.9; MS (EI) *m/z* (%) 311 (40) $[M]^+$, 310 (27), 296 (15), 280 (18), 252 (21), 188 (11), 150 (40), 149 (100), 121 (30), 90 (19), 124 (16), 86 (16) and 91 (12); HRMS (EI) calcd. for $C_{18}H_{17}NO_4$ 311.1158, found 311.1149.



2h

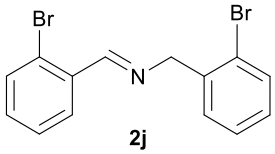
(*E*)-*N*-(4-Chlorobenzyl)-1-(4-chlorophenyl)methanimine (2h).[8a] Yellow solid (85 mg, 64%); mp 58.5–61.0 ºC (from hexane) (lit.,[8b] 58–60 ºC); R_f 0.86 (9:1, hexane-EtOAc); t_R 16.38; IR (neat) $\tilde{\upsilon}$ 2851, 2817, 1641, 1592, 1488, 1090, 1046, 1012, 825, 810 and 798; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 (s, 2H), 7.25, 7.32 (AA'BB' system, J = 4.0, 4H), 7.40, 7.70 (AA'XX', J = 8.0, 4H) and 8.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 64.3, 128.8, 129.1, 129.4, 129.6, 133.0, 134.6, 137.0, 137.4, 161.0; MS (EI) *m/z* (%) 265 (25) $[M]^+$, 264 (19), 236 (38), 262 (20), 151 (13), 127 (40), 126 (15), 125 (100) and 89 (23).



2i

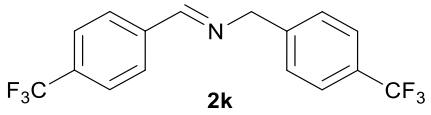
(*E*)-*N*-(2-Chlorobenzyl)-1-(2-chlorophenyl)methanimine (2i).[9] Yellow oil (111 mg, 84%); R_f 0.95 (9:1, hexane-EtOAc); t_R 15.86; IR (neat) $\tilde{\upsilon}$ 3067, 2921, 1639, 1470, 1443, 1052, 751 and 430; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.95 (s, 2H), 7.19–7.45 (m, 7H), 8.11 (dd, J = 7.6, 1.6, 1H) and 8.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 137.0, 135.4, 133.6, 133.3, 131.9, 130.0,

129.8, 129.5, 128.6, 128.4, 127.1, 127.0 and 62.3; MS (EI) *m/z* (%) 265 (22) $[M]^+$, 264 (21), 263 (33), 262 (24), 228 (12), 151 (10), 127 (34), 126 (17), 125 (100) and 89 (23).



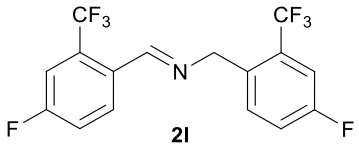
2j

(*E*)-*N*-(2-Bromobenzyl)-1-(2-bromophenyl)methanimine (2j).[10] Yellow oil (148 mg, 84%); R_f 0.90 (9:1, hexane-EtOAc); t_R 17.27; IR (neat) $\tilde{\upsilon}$ 3062, 2890, 1637, 1590, 1566, 1466, 1439, 1373, 1043, 1026, 750, 683 and 660; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.93 (s, 2H), 7.14 (t, *J* = 8.0, 1H), 7.24–7.38 (m, 3H), 7.40–7.44 (m, 2H), 7.58 (d, *J* = 8.0, 2H), 8.11 (dd, *J* = 7.7, 1.9, 1H) and 8.81 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.5, 123.8, 125.4, 127.7, 127.8, 128.7, 129.1, 130.0, 132.1, 132.8, 133.2, 134.6, 138.6 and 162.1; MS (EI) *m/z* (%) 355 (25), 354 (25), 353 (49) $[M^+]$, 352 (40), 351 (25), 350 (19), 274 (19), 272 (19), 172 (18), 171 (98), 170 (19), 169 (100), 165 (10), 91 (31), 90 (35), 89 (38) and 63 (11).



2k

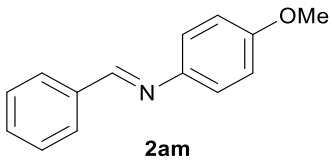
(*E*)-*N*-[4-(Trifluoromethyl)benzyl]-1-[4-(trifluoromethyl)phenyl]methanimine (2k).[11] Yellow oil (156 mg, 94%); R_f 0.93 (9:1, hexane-EtOAc); t_R 13.25; IR (neat) $\tilde{\upsilon}$ 2853, 1650, 1583, 1418, 1376, 1325, 1165, 1125, 1066, 1045, 1019 and 836; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.90 (s, 2H), 7.47, 7.61 (AA'XX' system, *J* = 8.0, 4H), 7.68, 7.90 (d, *J* = 8.0, 2H) and 8.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.5, 124.0 (q, *J* = 271.9), 124.4 (q, *J* = 271.9), 125.6 (q, *J* = 3.9), 125.8 (q, *J* = 3.9), 129.6 (q, *J* = 32.3), 132.7 (q, *J* = 32.6), 139.1, 143.1 and 161.2; MS (EI) *m/z* (%) 331 (48) $[M]^+$, 330 (44), 312 (14), 185 (13), 160 (21), 159 (100) and 109 (16).



2l

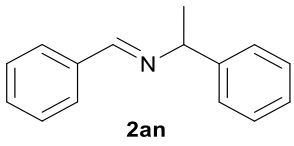
(*E*)-*N*-[4-Fluoro-2-(trifluoromethyl)benzyl]-1-[4-fluoro-2-(trifluoromethyl)phenyl]-methanimine (2l). Yellow solid (178 mg, 97%); mp 49–52 ºC (from hexane); R_f 0.37 (9:1, hexane-EtOAc); t_R 21.18; IR (neat) $\tilde{\upsilon}$ 3094, 1646, 1612, 1491, 1430, 1314, 1267, 1160, 874 and 821; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.97 (s, 2H), 7.21–7.42 (m, 4H), 7.57 (dd, *J* = 8.7, 5.7, 1H), 8.31 (dd, *J* = 8.7, 5.7, 1H) and 8.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.4 (*J* = 1.6), 113.5,

114.4–112.5 (m), 119.1 (dq, *J* = 274.0, 2.3), 123.5 (dq, *J* = 274.0, 2.5), 125.3, 129.7 (q, *J* = 31.7), 129.8 (q, *J* = 31.6), 131.0, 133.2, 160.7, and 163.9; MS (EI) *m/z* (%) 368 (12) $[M+1]^+$, 367 (73) $[M]^+$, 366 (54), 348 (11), 204 (13), 203 (16), 190 (10), 178 (41), 177 (100), 127 (51) and 107 (14); HRMS (EI) calcd. for $C_{16}H_9F_8N$ 367.0607, found 367.0606.



2am

(*E*)-*N*-(4-Methoxyphenyl)-1-phenylmethanimine (2am).[12] Yellow solid (91 mg, 86%); mp 69–70 ºC (from hexane) [lit.,[12] 70.0–70.5 ºC (from hexane)]; R_f 0.62 (8:2, hexane-EtOAc); t_R 13.63; IR (neat) $\tilde{\upsilon}$ 2923, 2854, 1620, 1577, 1496, 1292, 1238, 1184, 1292, 1030, 833, 752 and 686; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.95, 7.26 (AA'XX' system, *J* = 9.0, 4H), 7.47–7.49 (m, 3H), 7.89–7.92 (m, 2H) and 8.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 114.5, 122.3, 128.7, 128.9, 131.2, 136.6, 145.1, 158.4 and 158.5; MS (EI) *m/z* (%) 211 (94) $[M^+]$, 210 (15), 197 (15), 196 (100) and 167 (22).



2an

(*E*)-1-Phenyl-*N*-(1-phenylethyl)methanimine (2an).[13] Yellow oil (63 mg, 60%); R_f 0.57 (8:2, hexane-EtOAc); t_R 12.07; IR (neat) $\tilde{\upsilon}$ 3028, 2923, 2854, 1450, 1022, 752 and 694; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (d, *J* = 6.6, 3H), 4.45 (q, *J* = 6.6, 1H), 7.14–7.25 (m, 3H), 7.27–7.35 (m, 5H), 7.67–7.71 (m, 2H) and 8.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.8, 69.7, 126.6, 126.8, 128.3, 128.4, 128.5, 130.6, 136.4, 145.2 and 159.5; MS (EI) *m/z* (%) 209 (23) $[M^+]$, 208 (18), 195 (24), 194 (46), 106 (12), 105 (100), 104 (11), 103 (11), 92 (20), 91 (68) and 65 (12).

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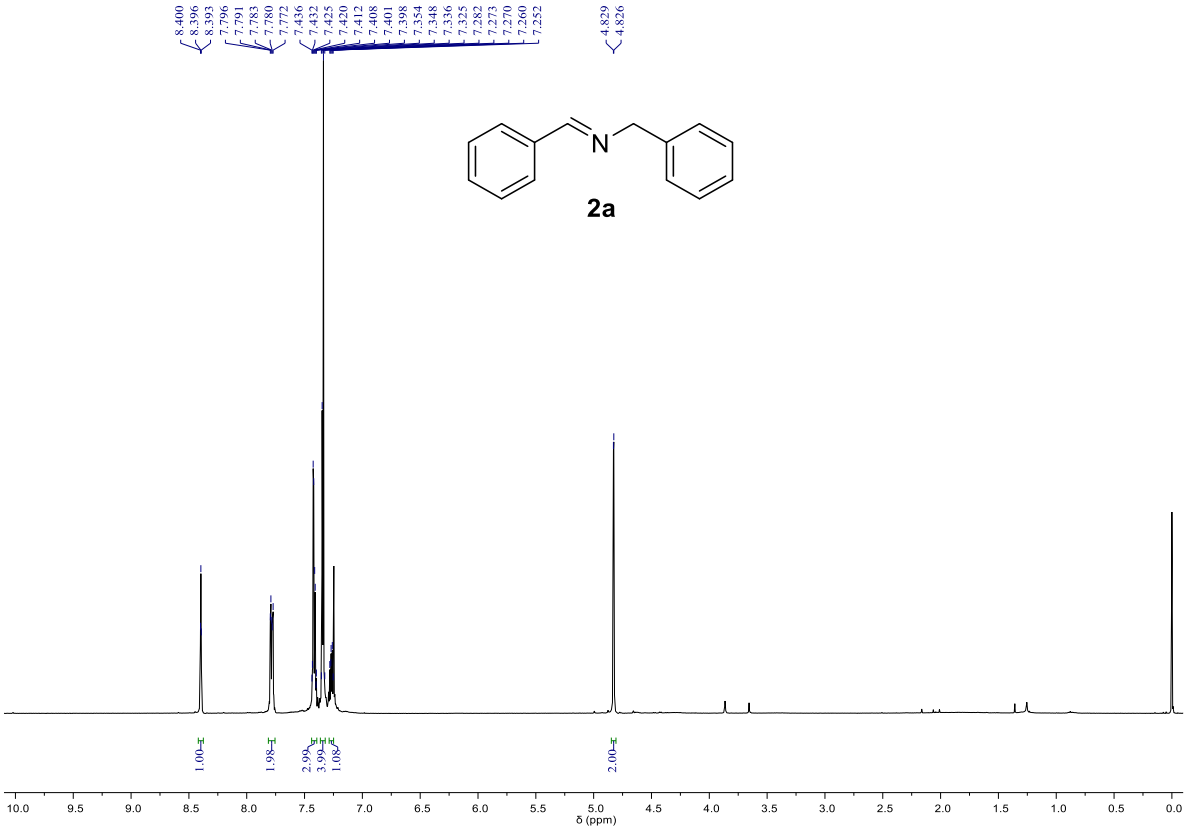
NMR spectra of the imines 2



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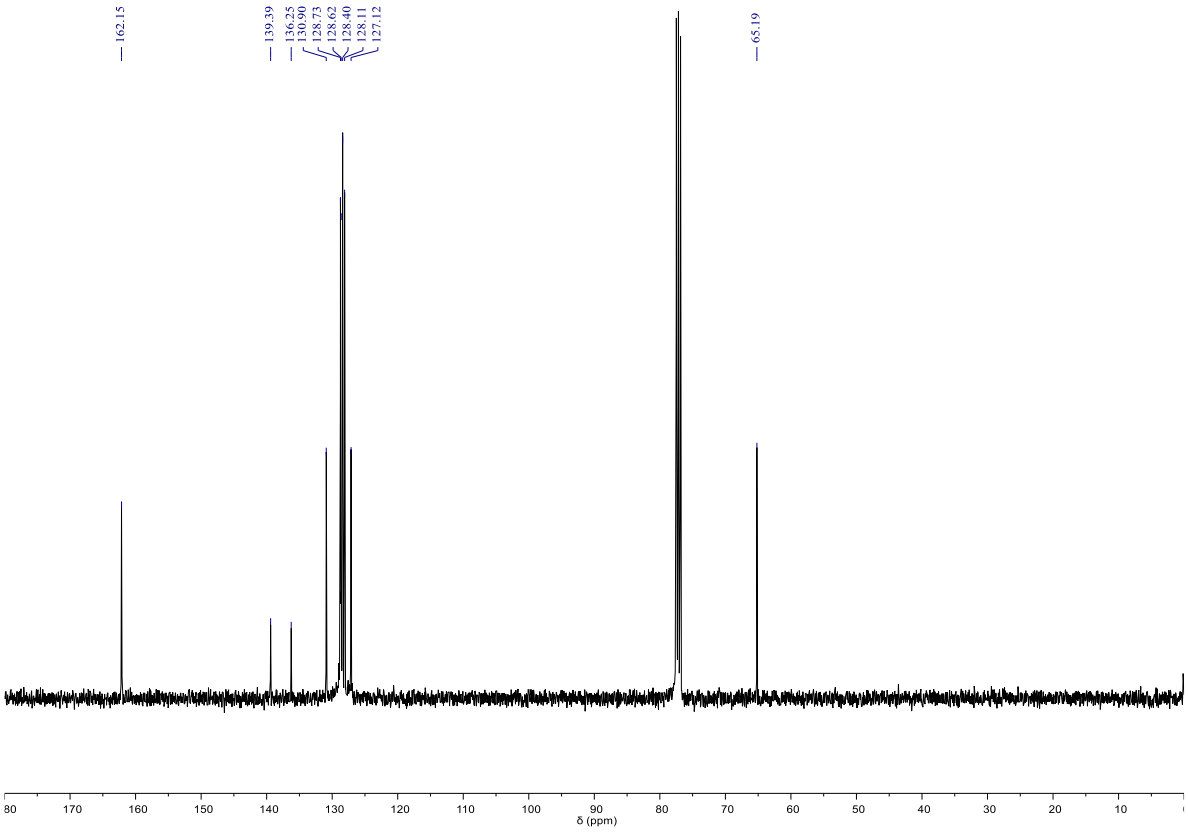

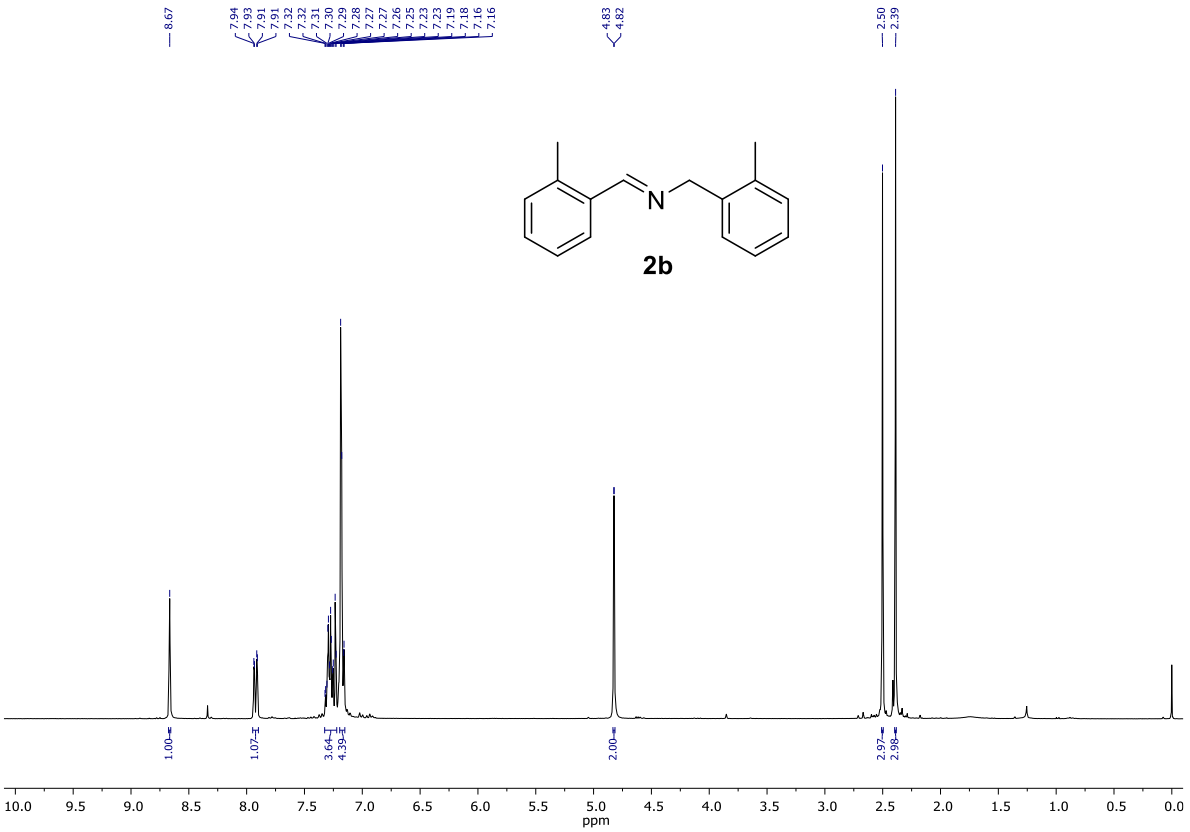

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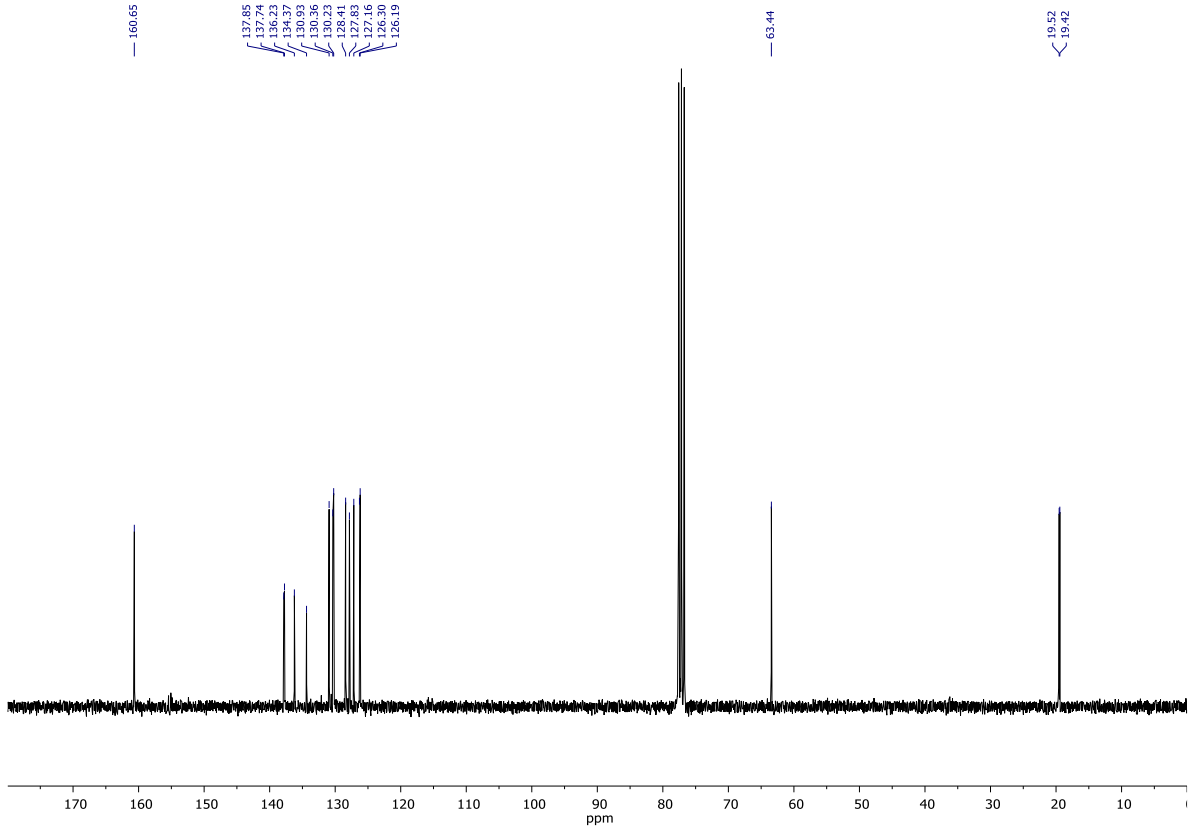

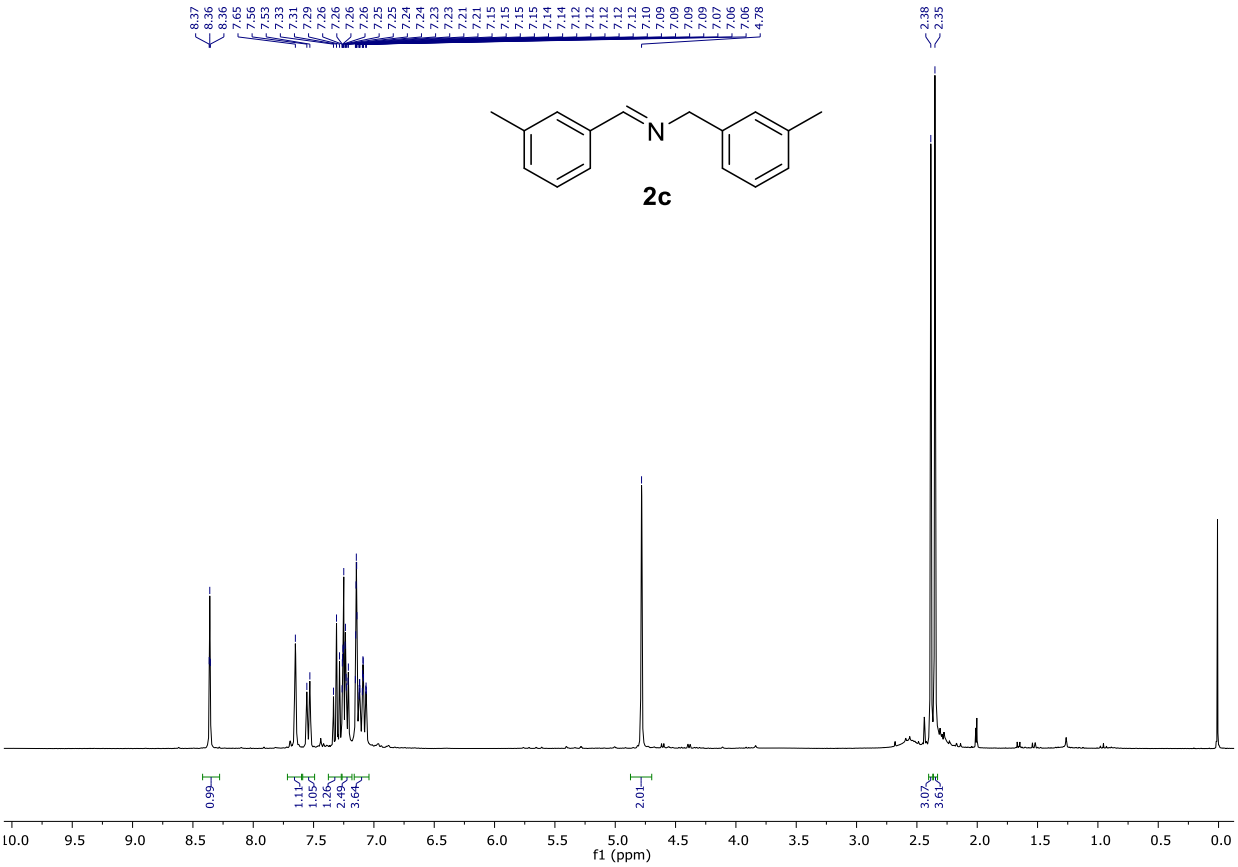

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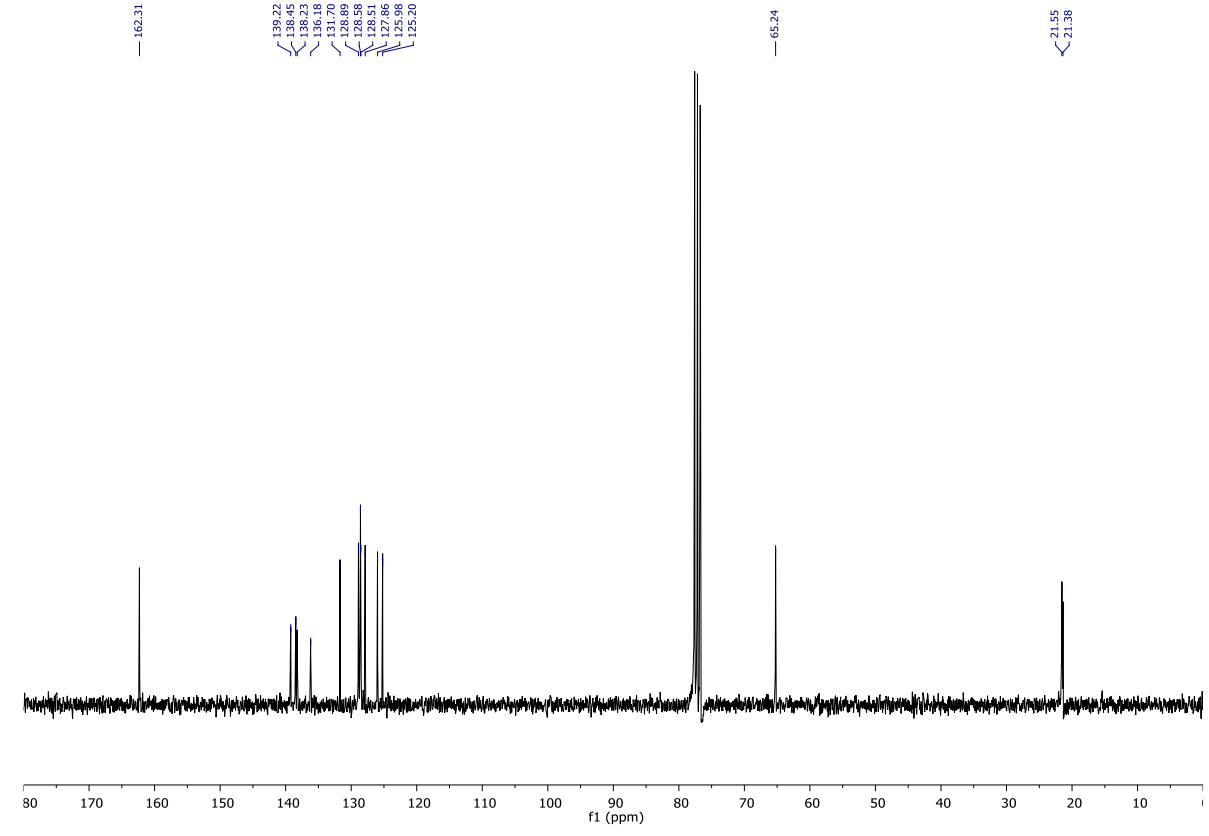

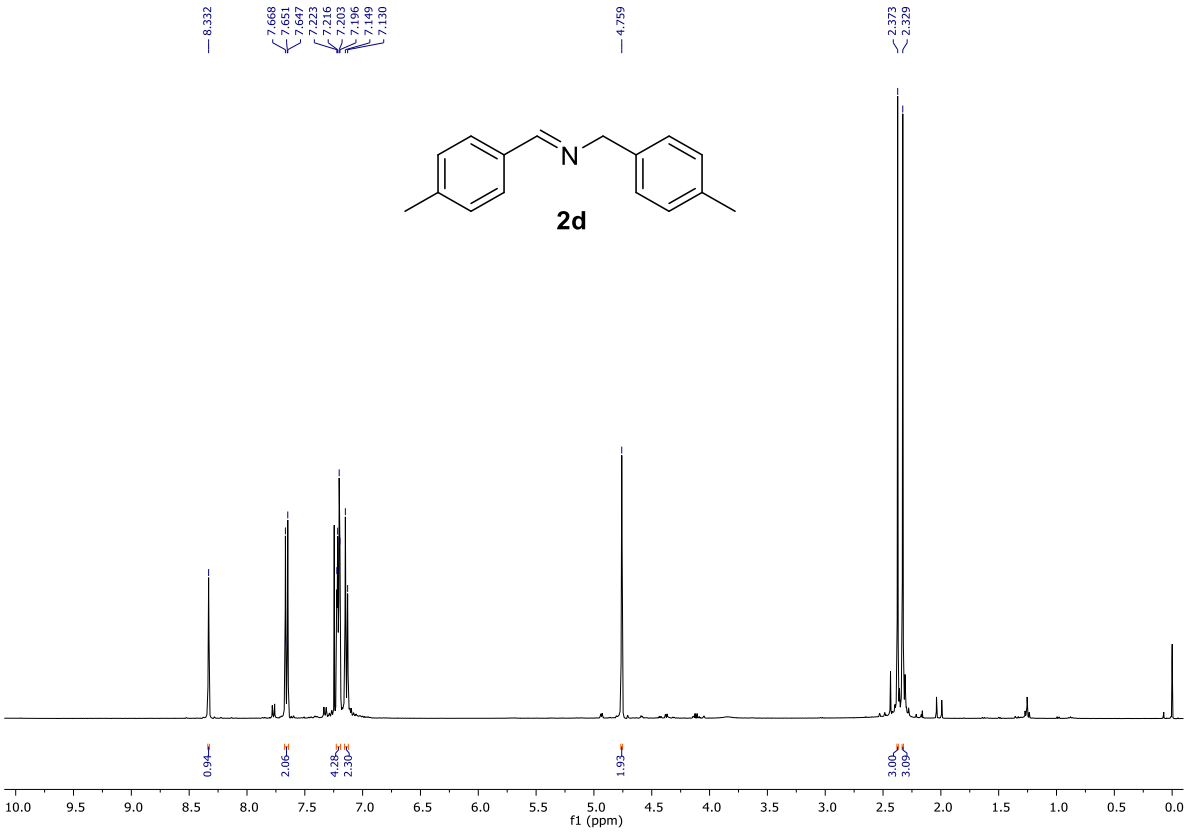

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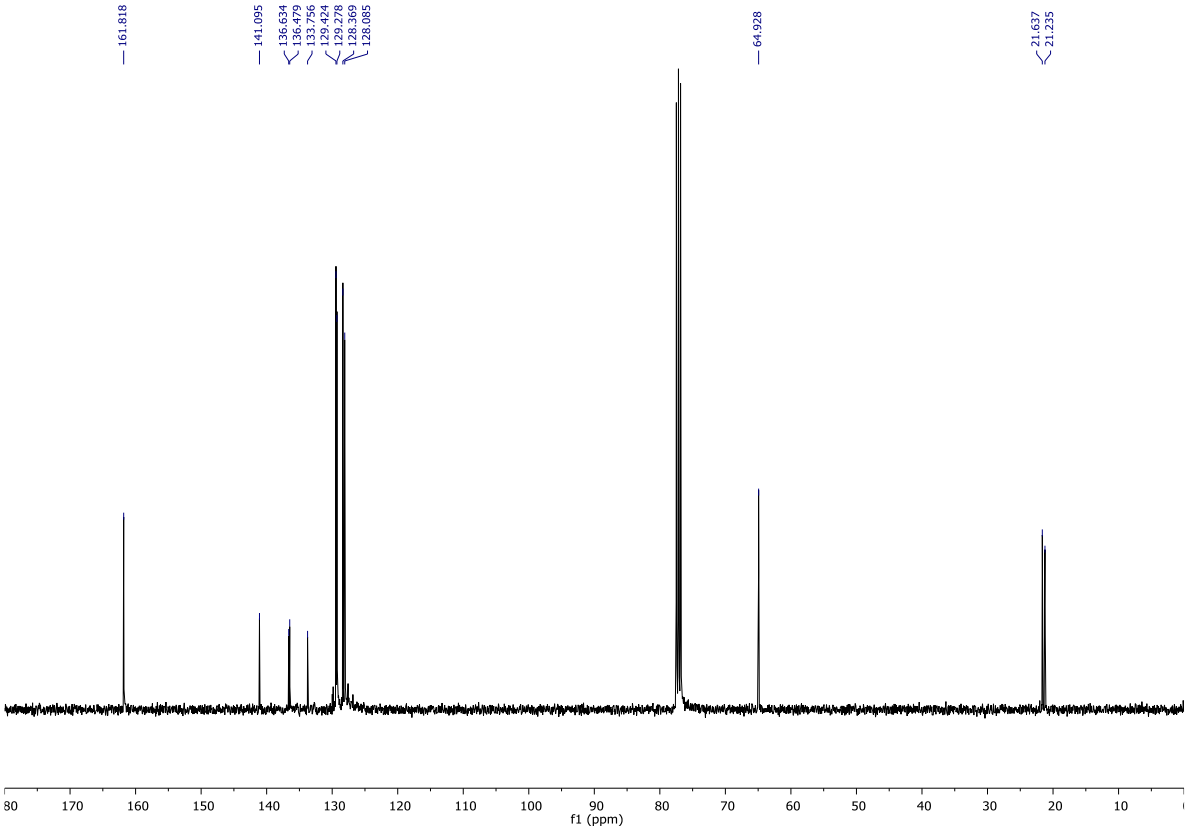

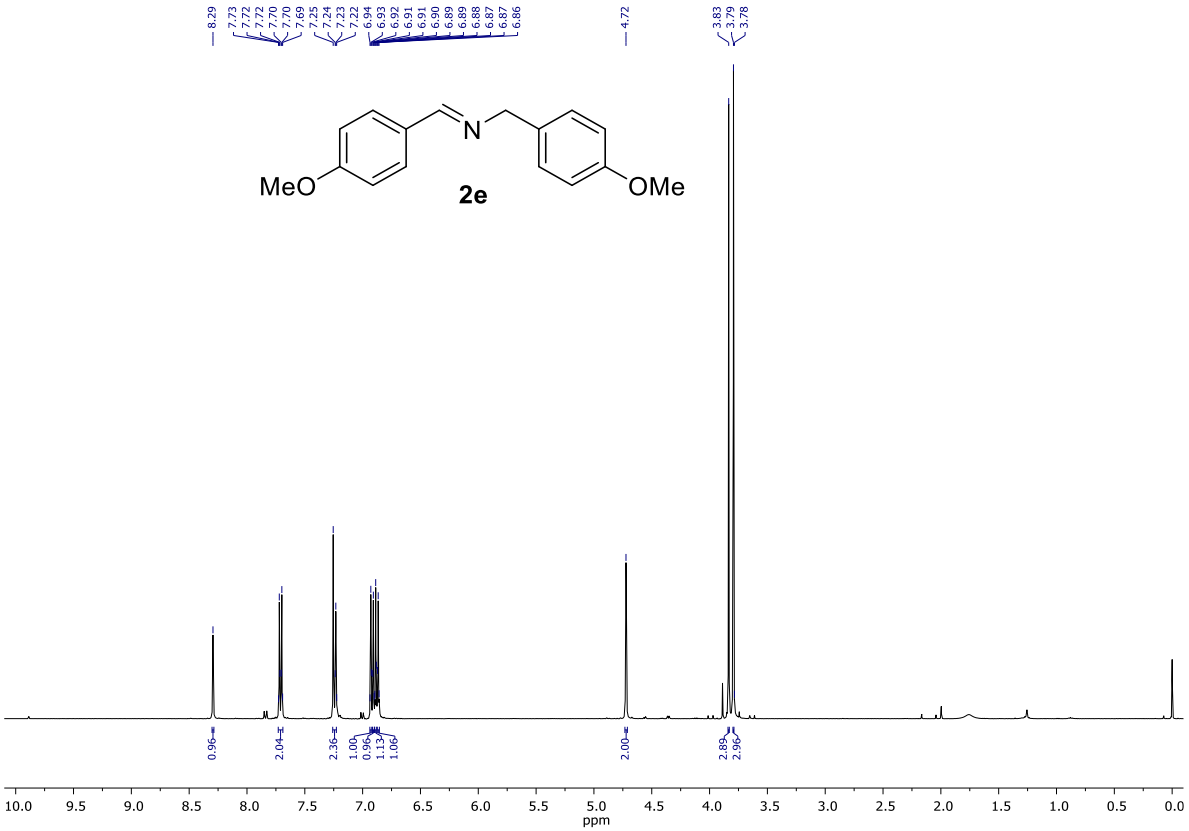

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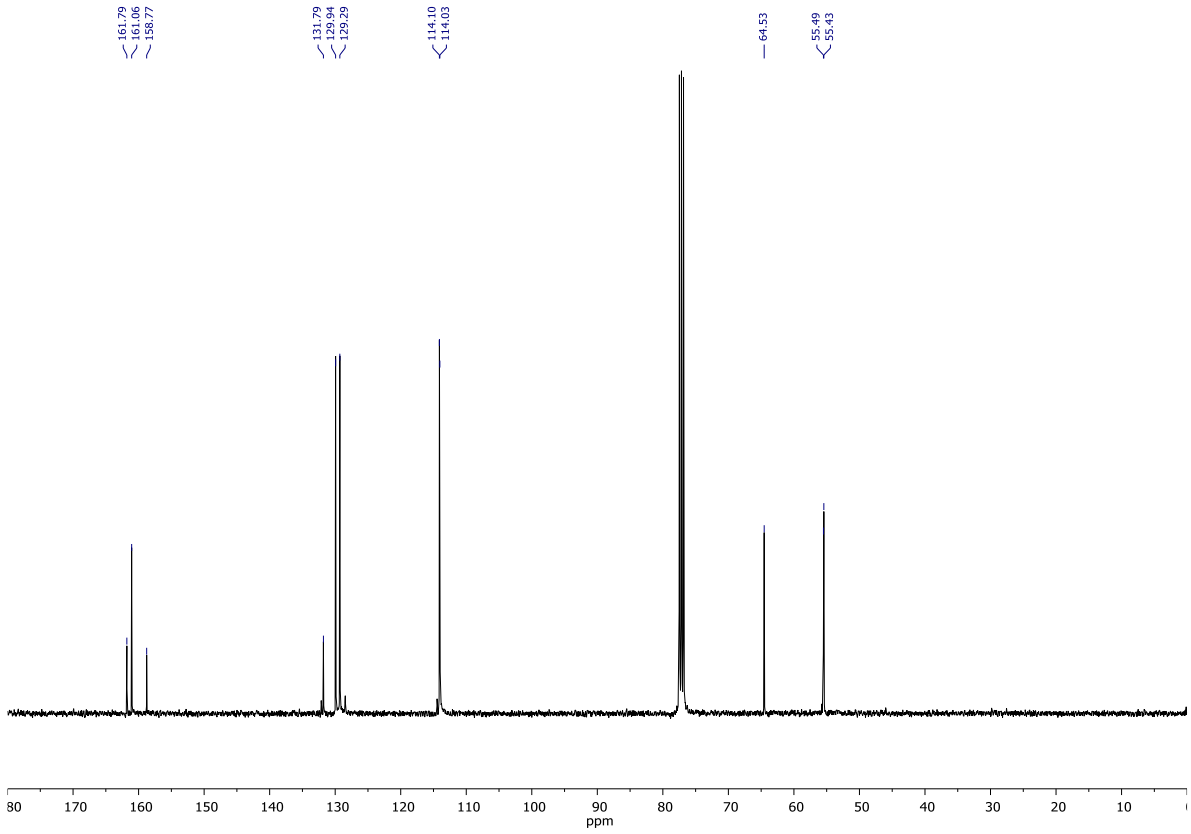

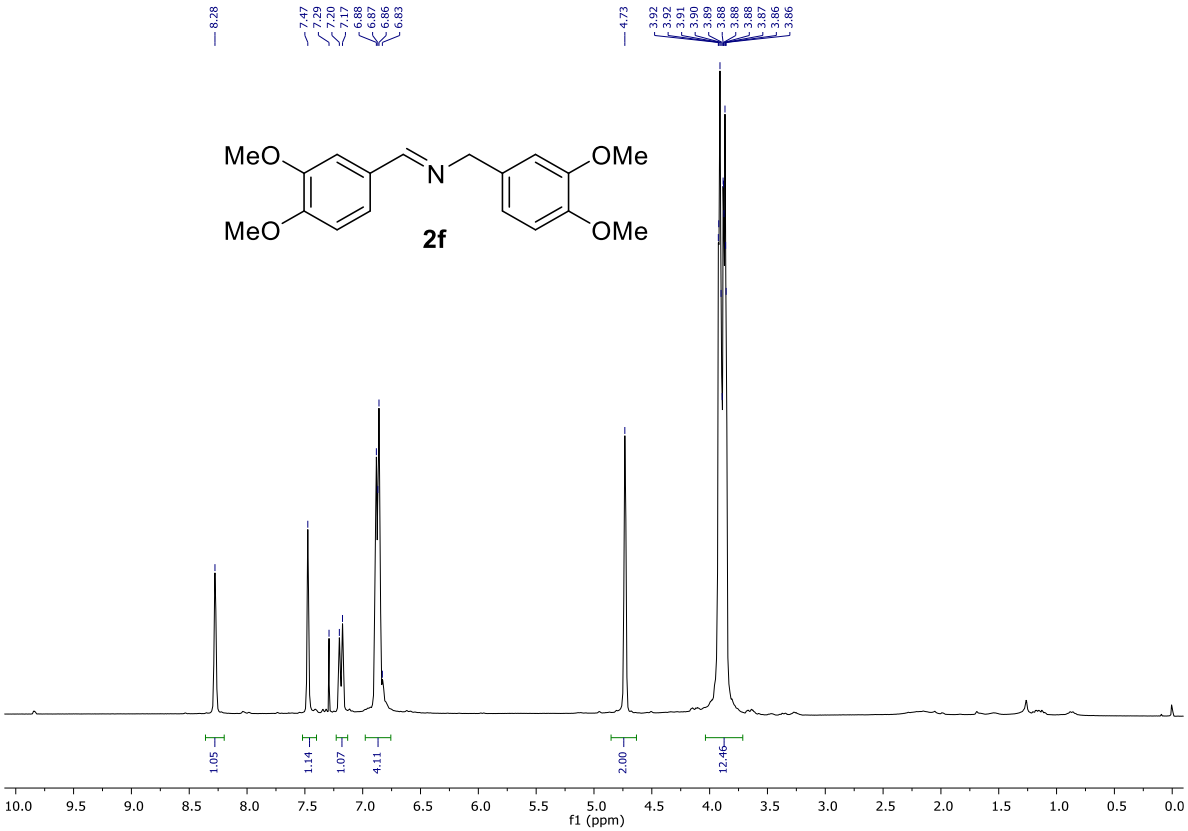

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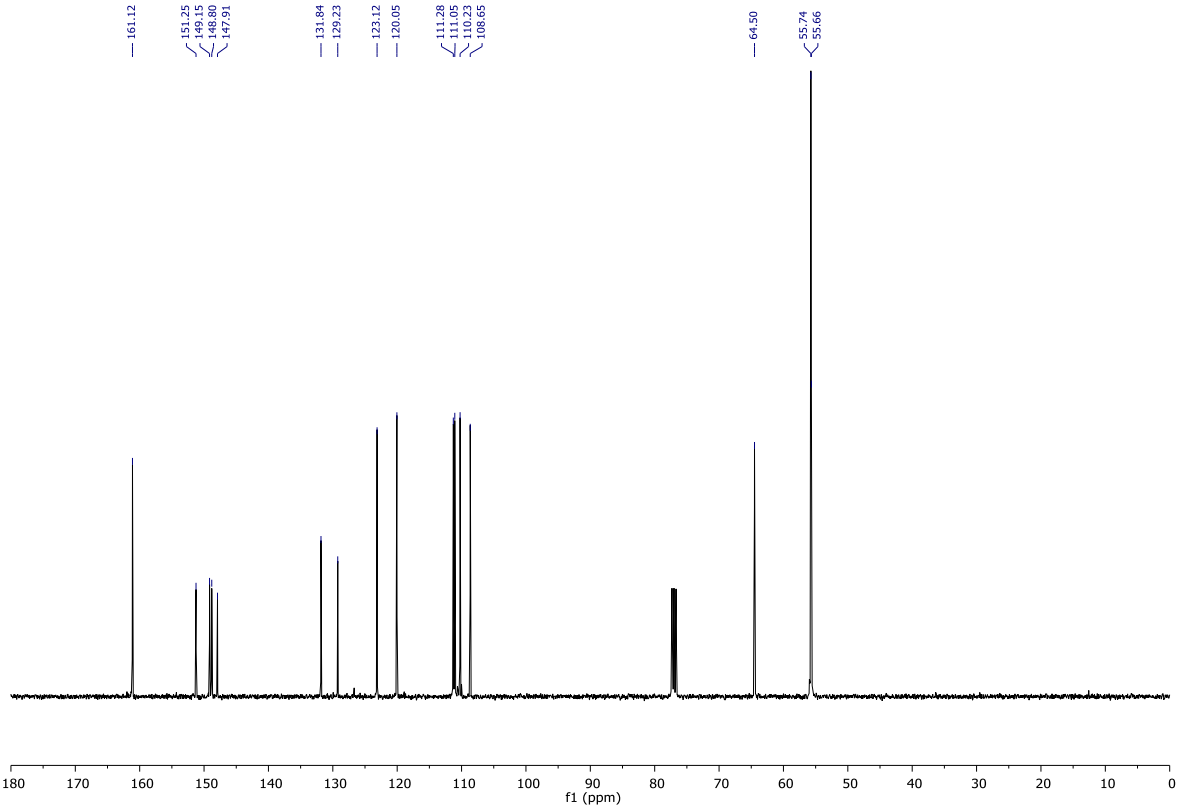

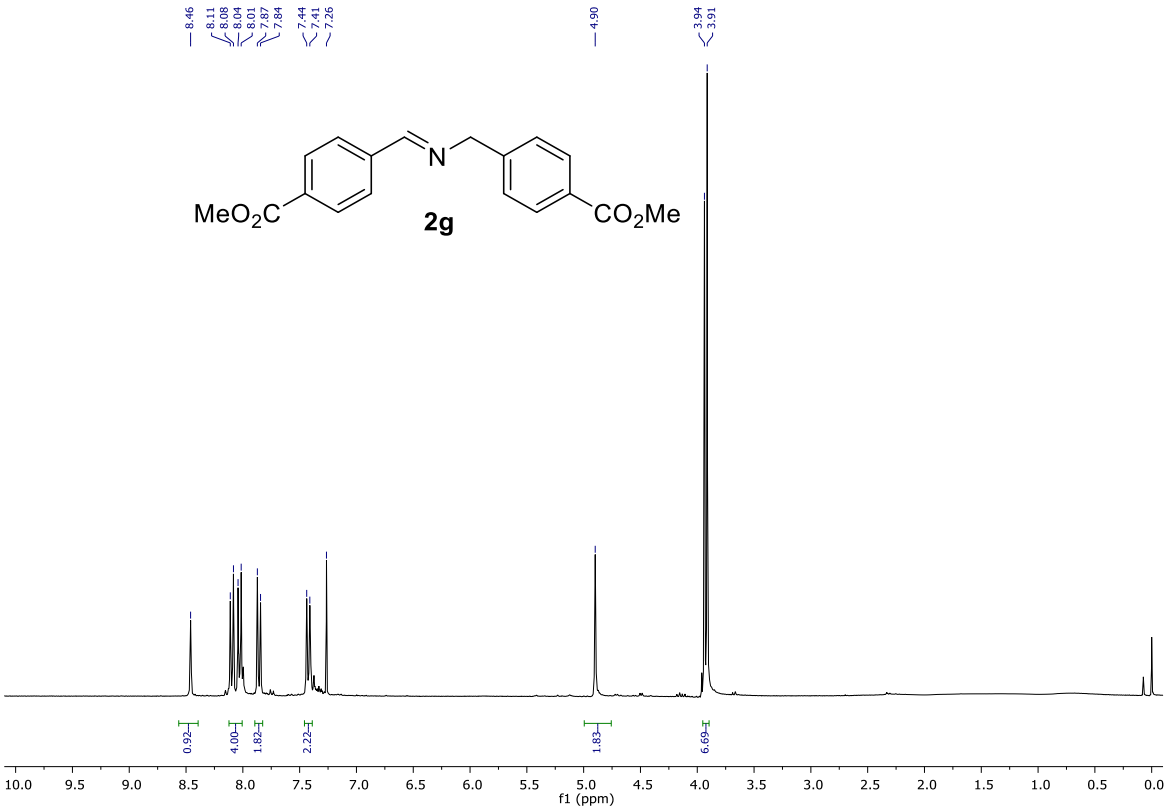

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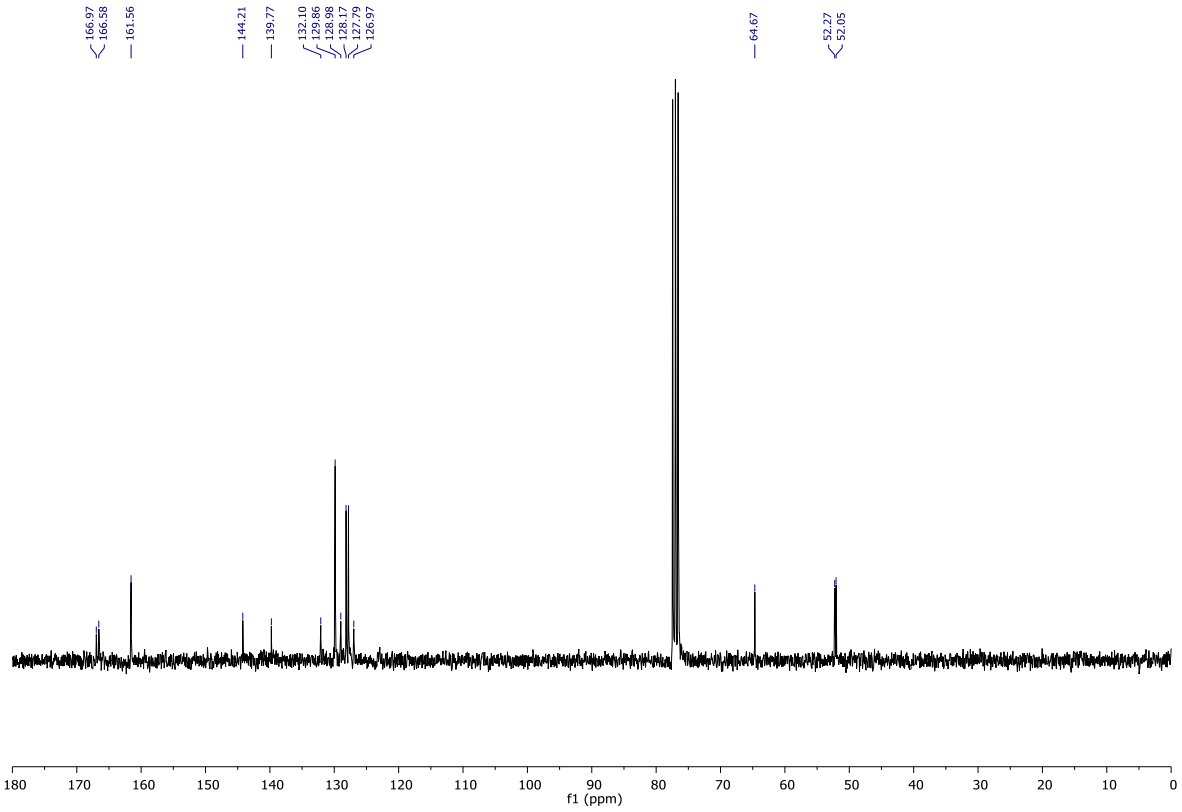

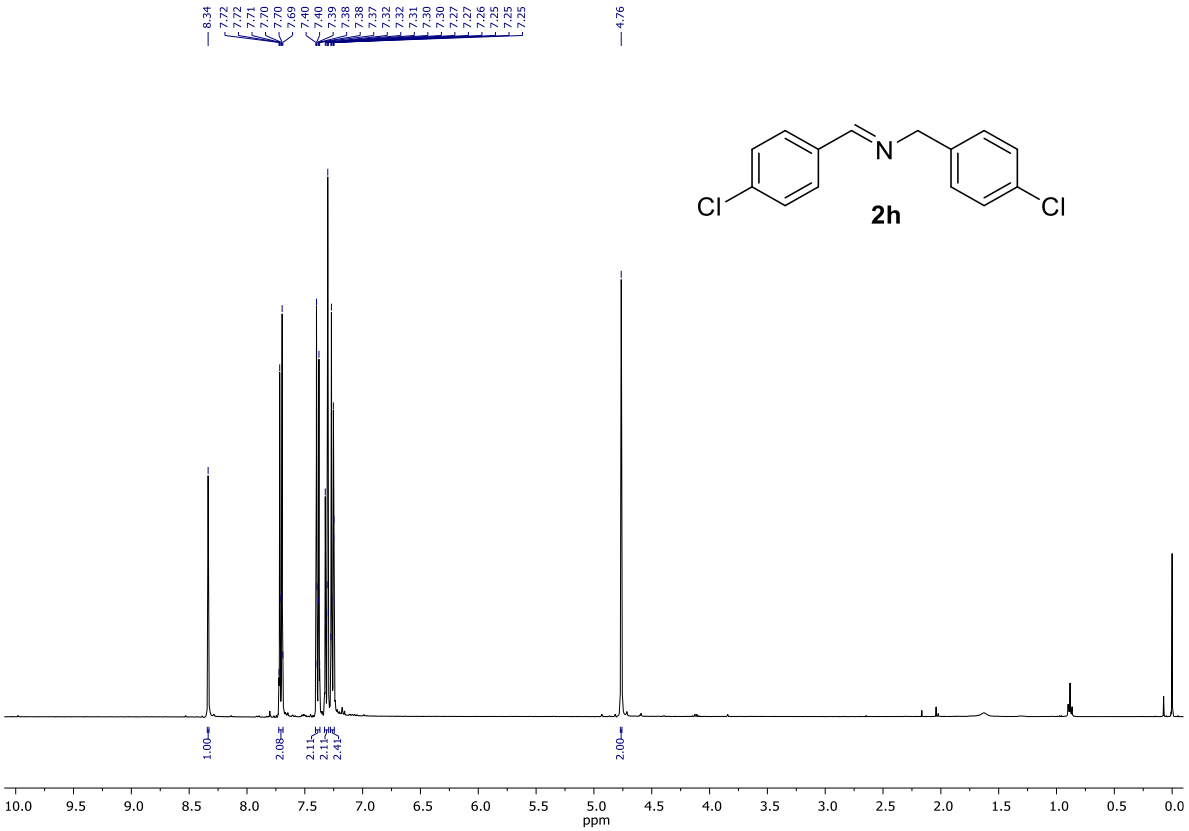

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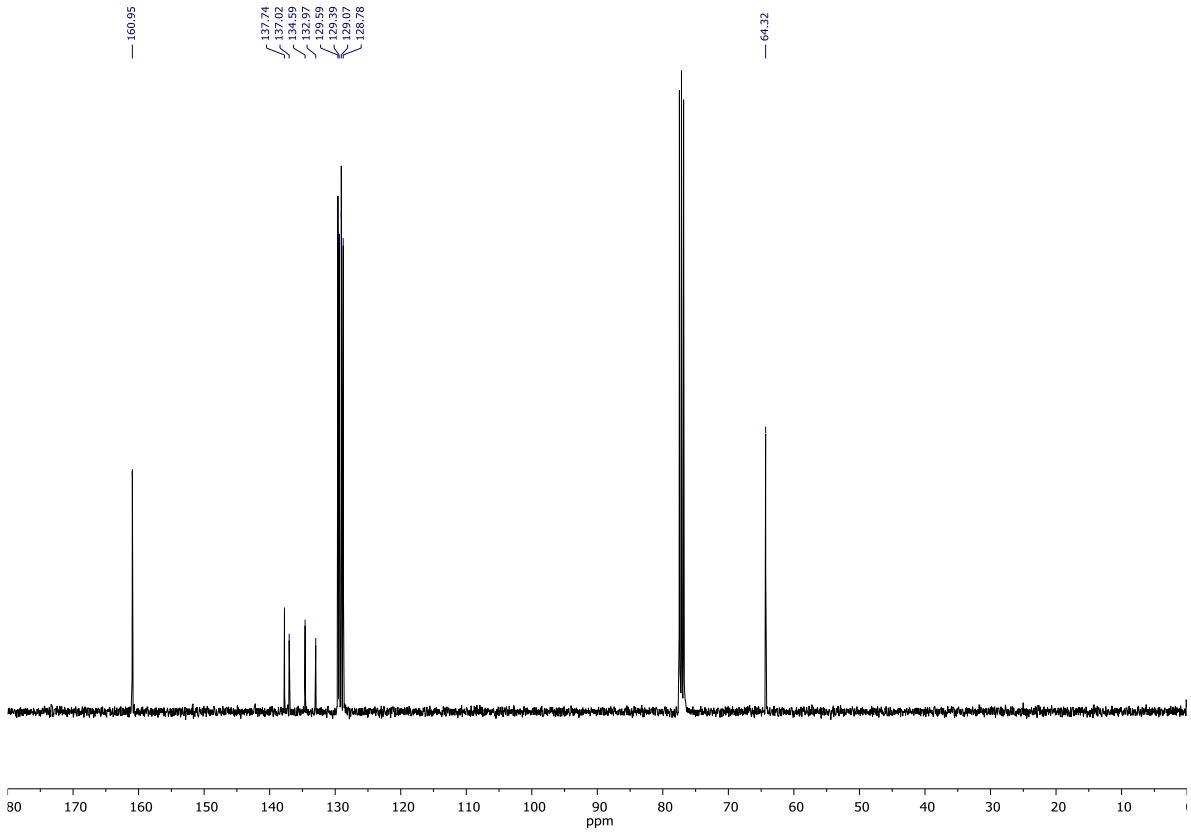

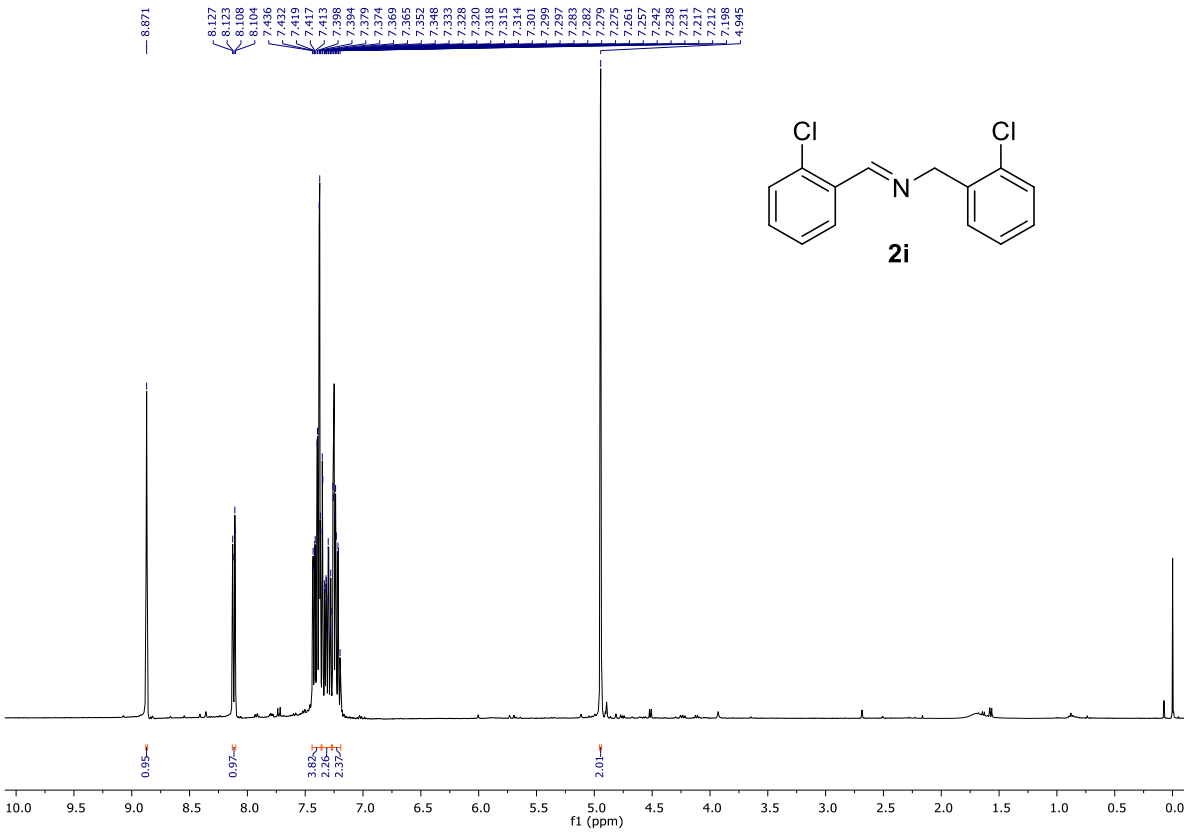

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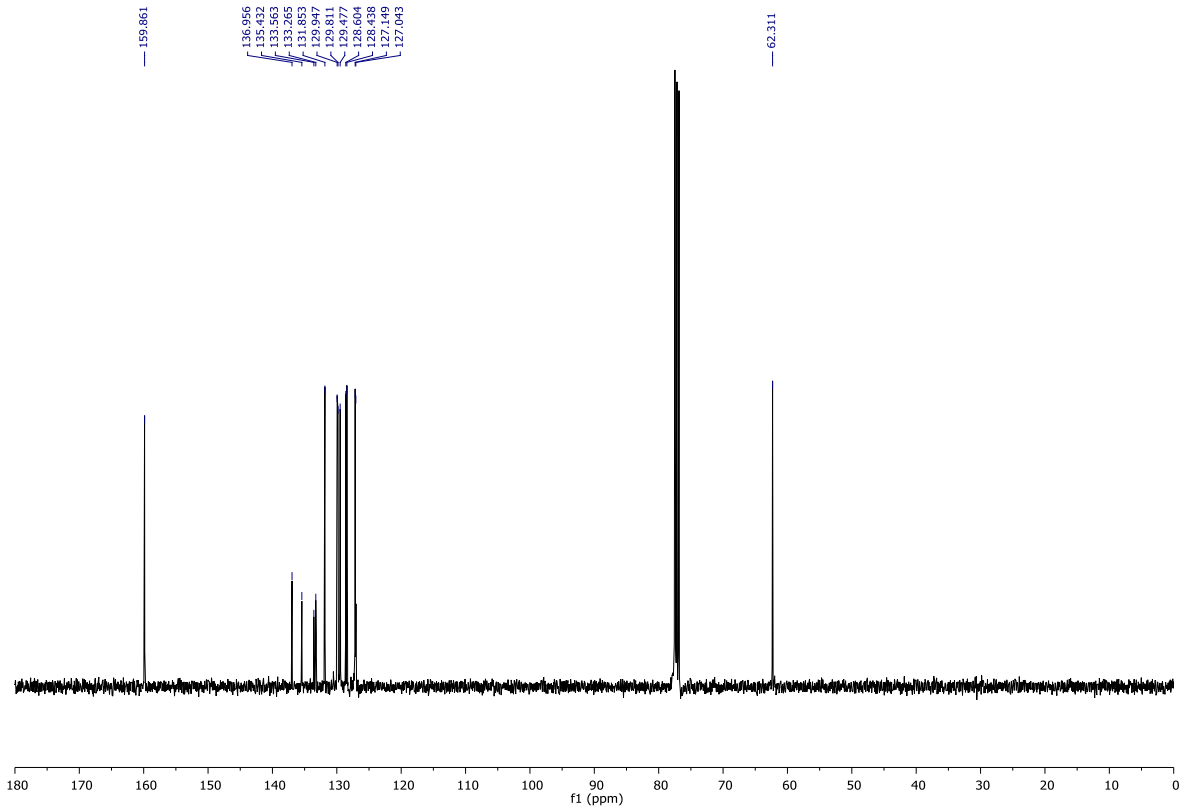

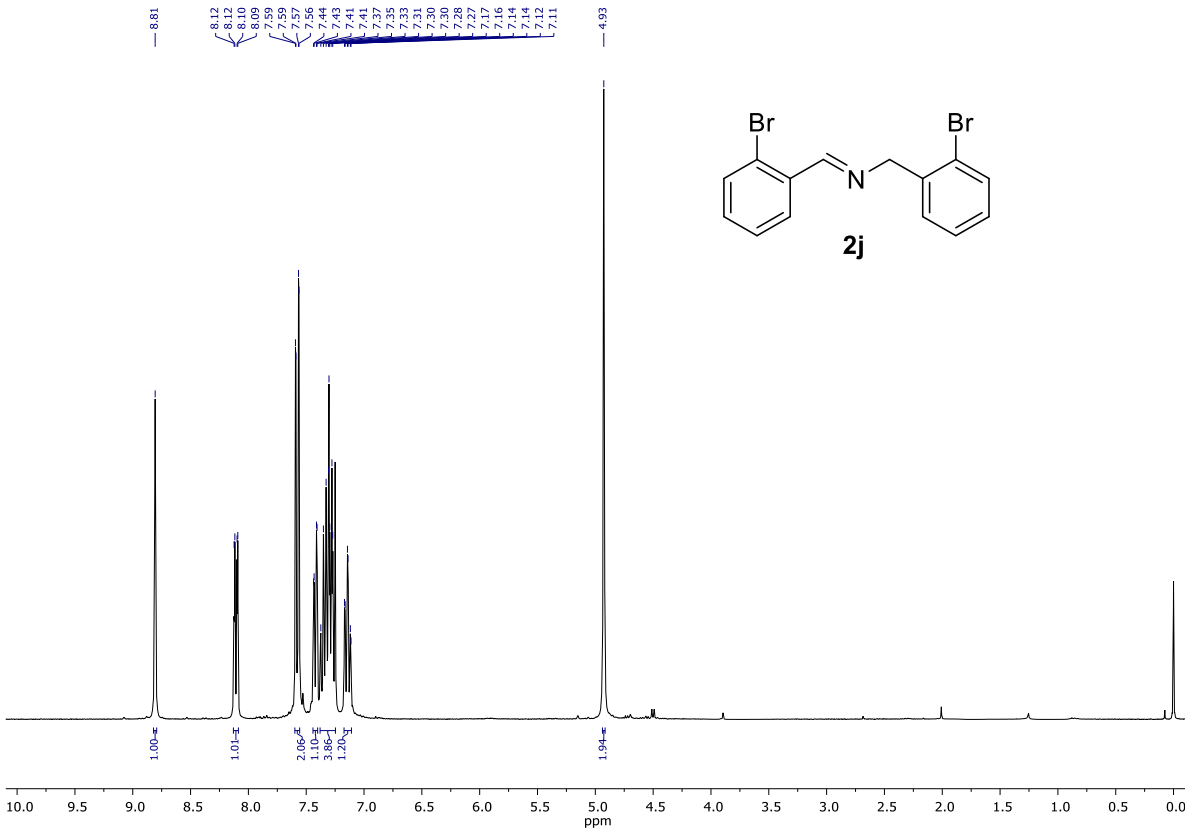

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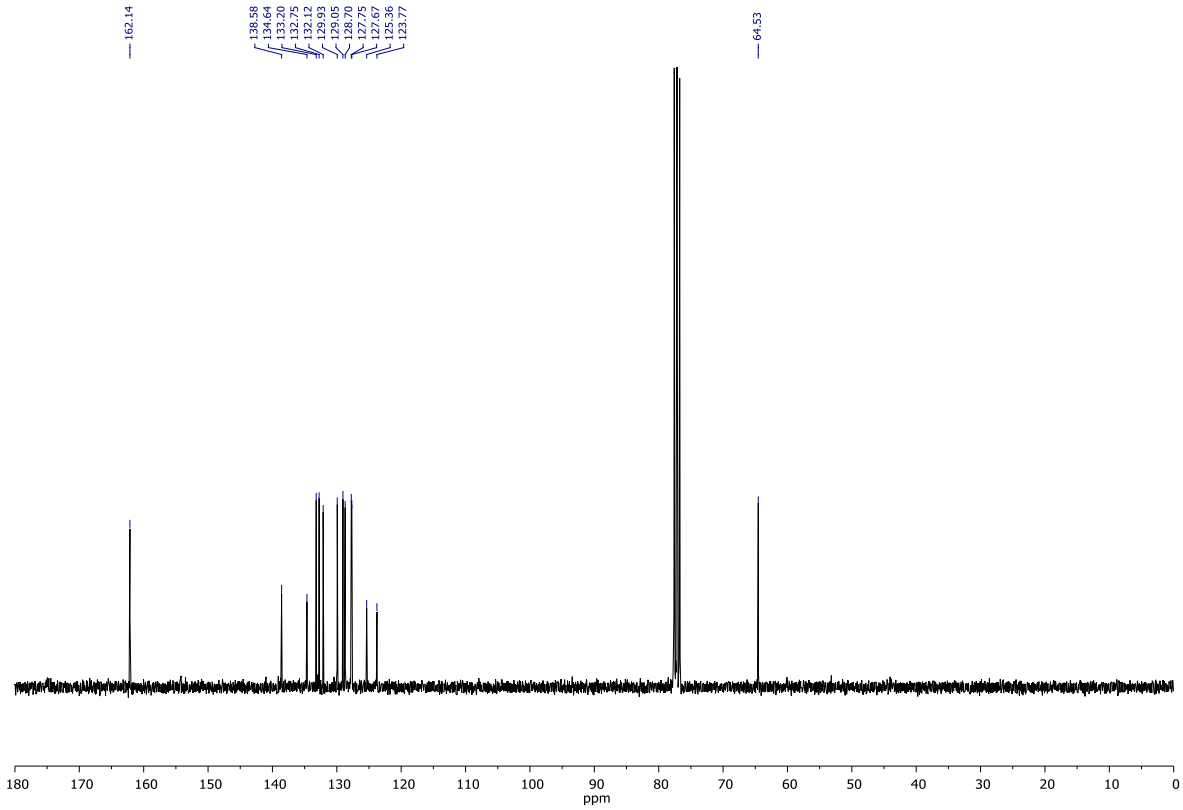

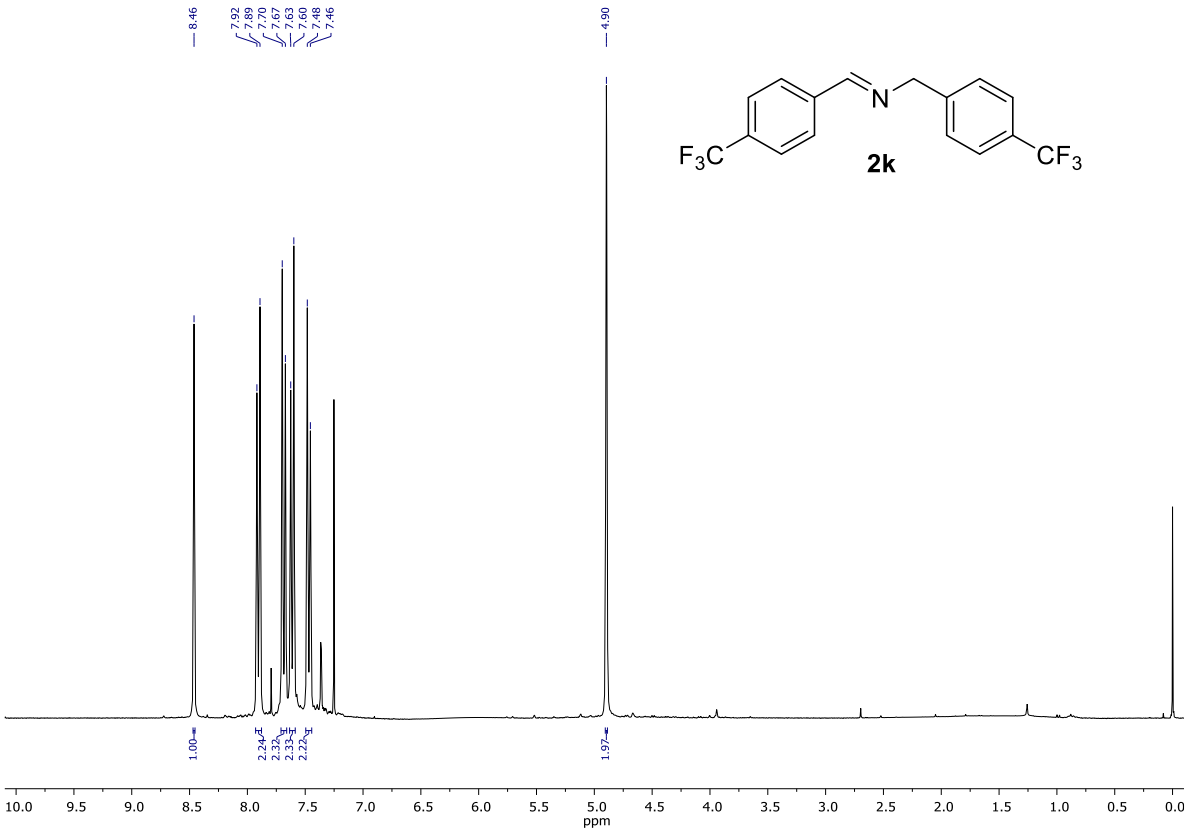

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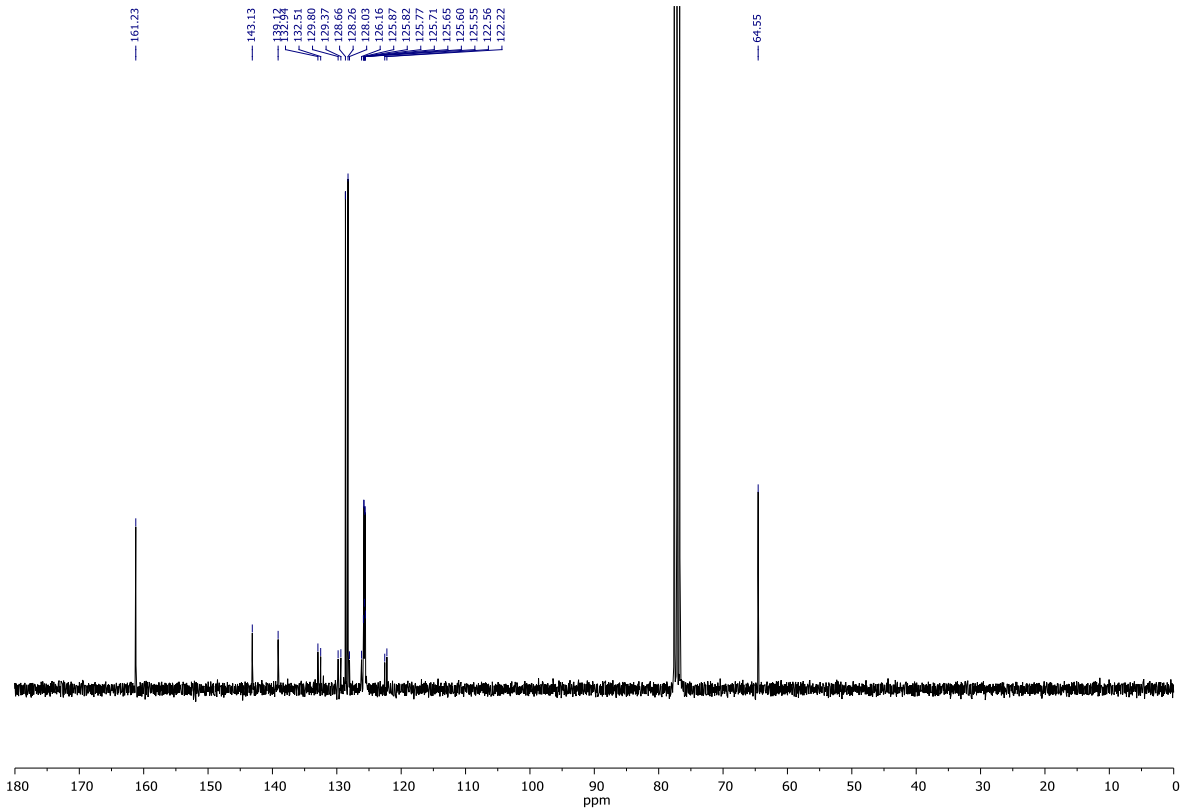

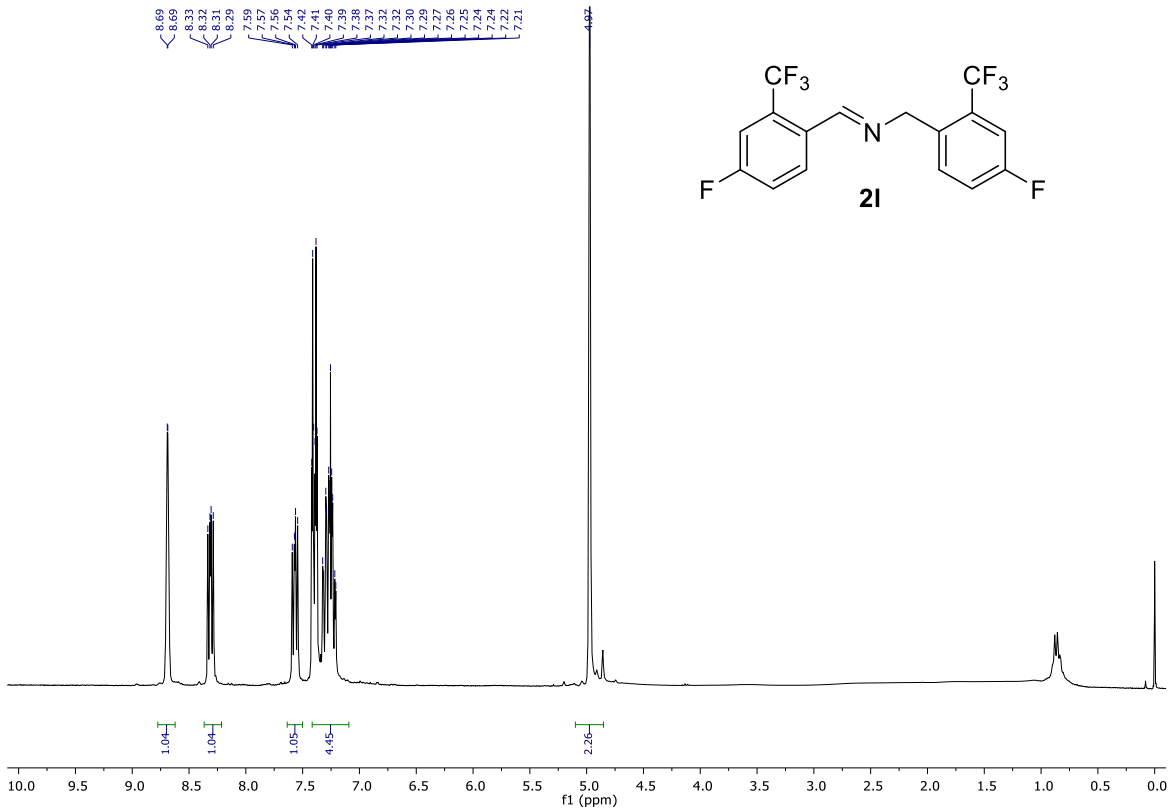

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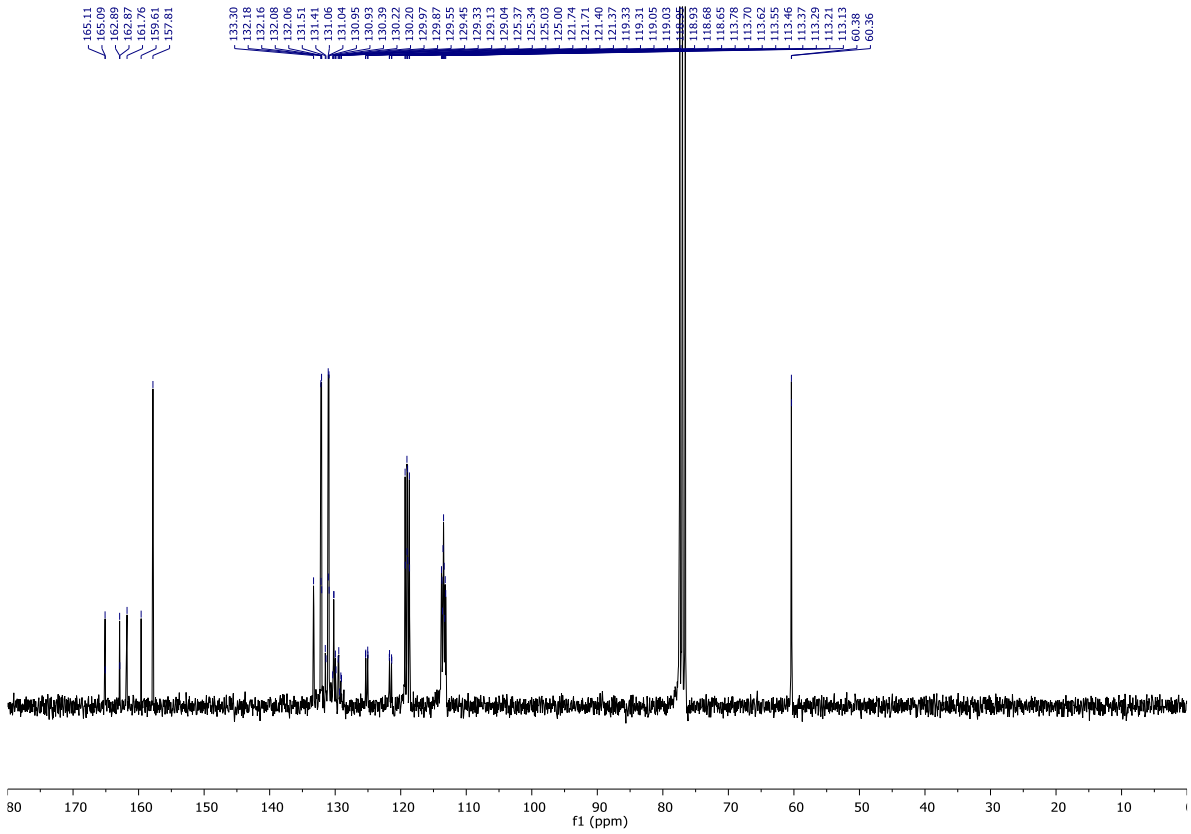

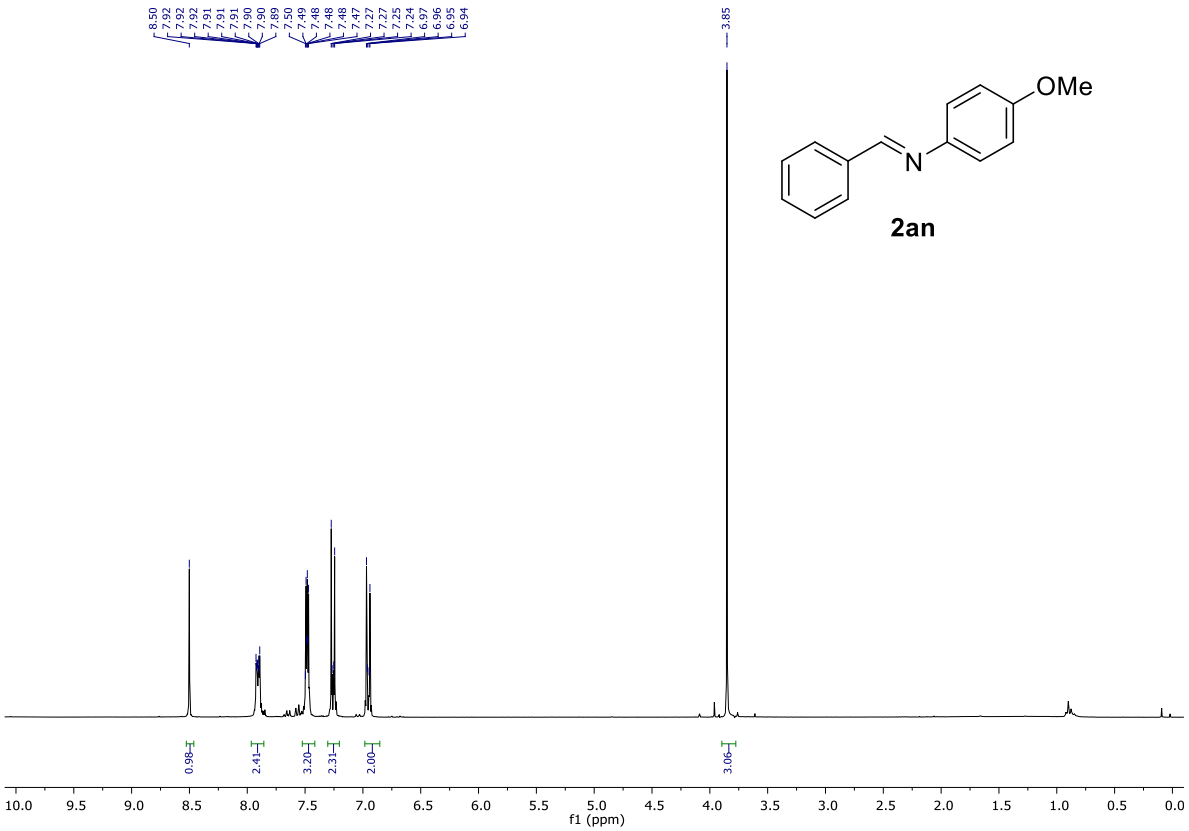

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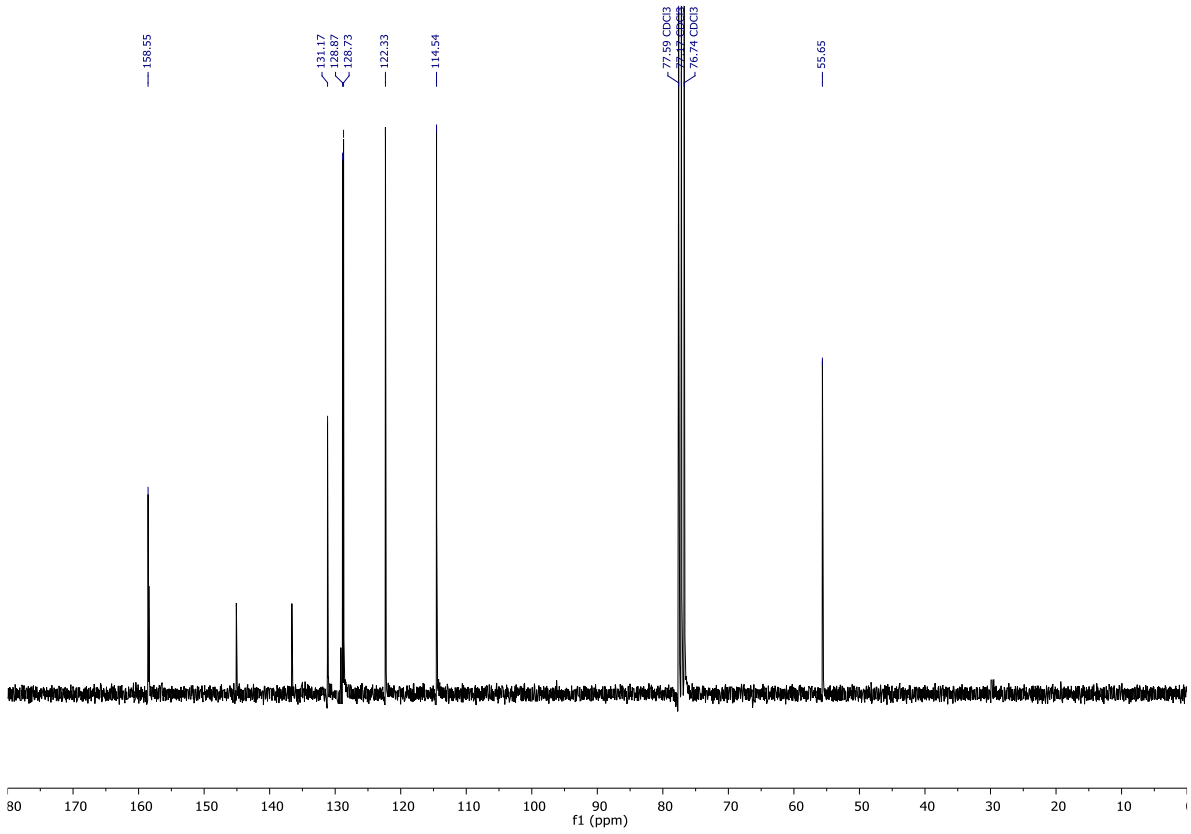

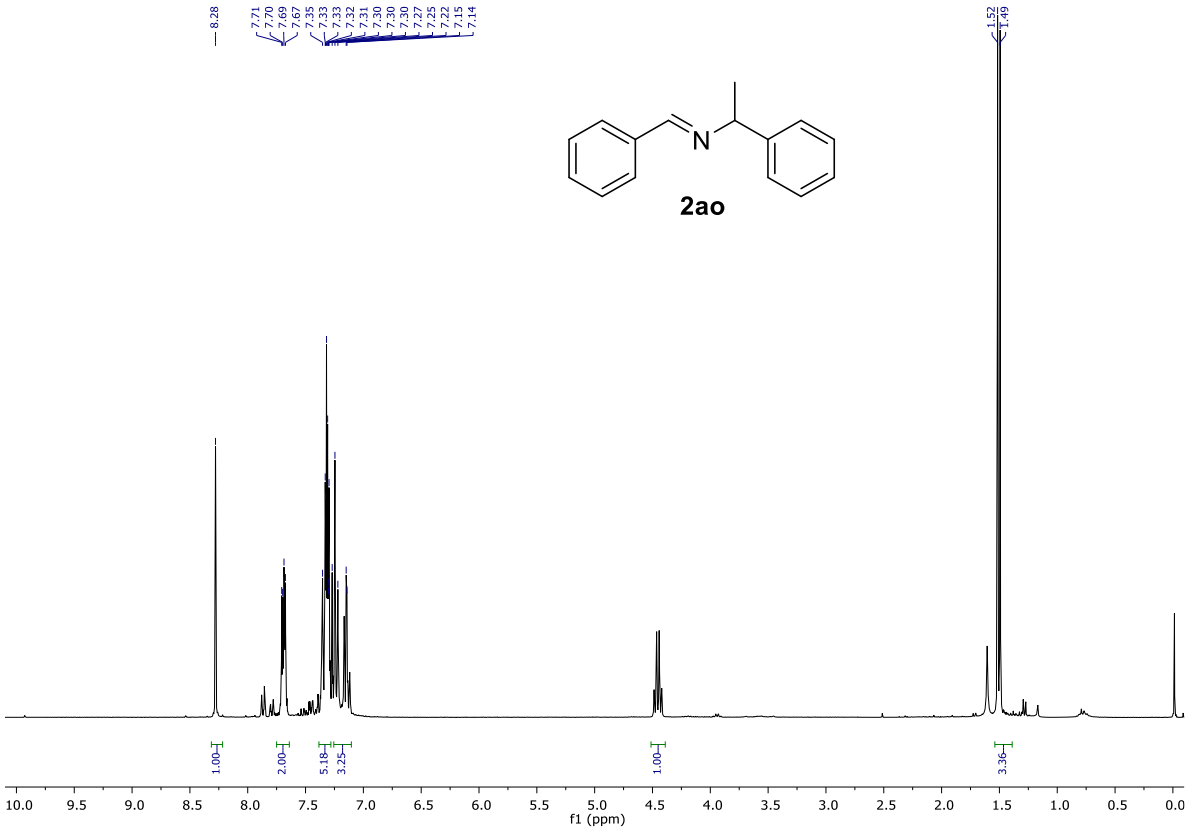

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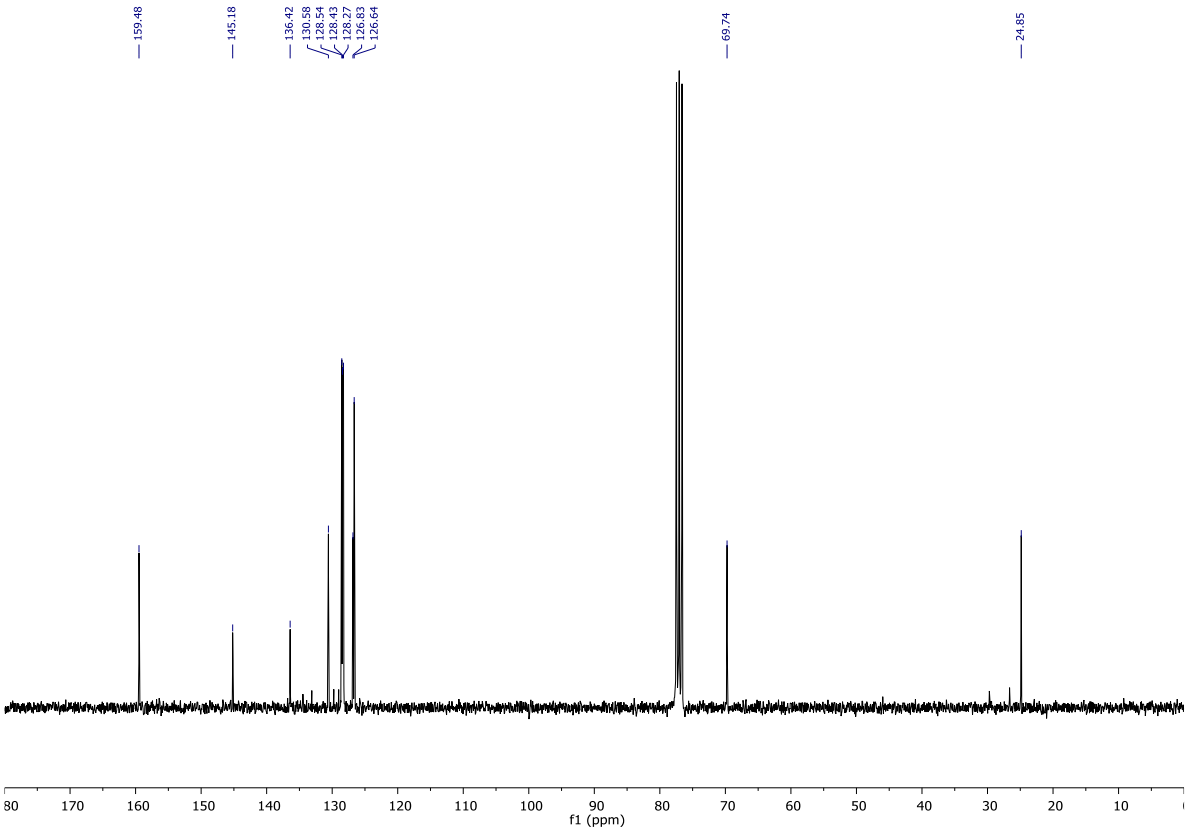


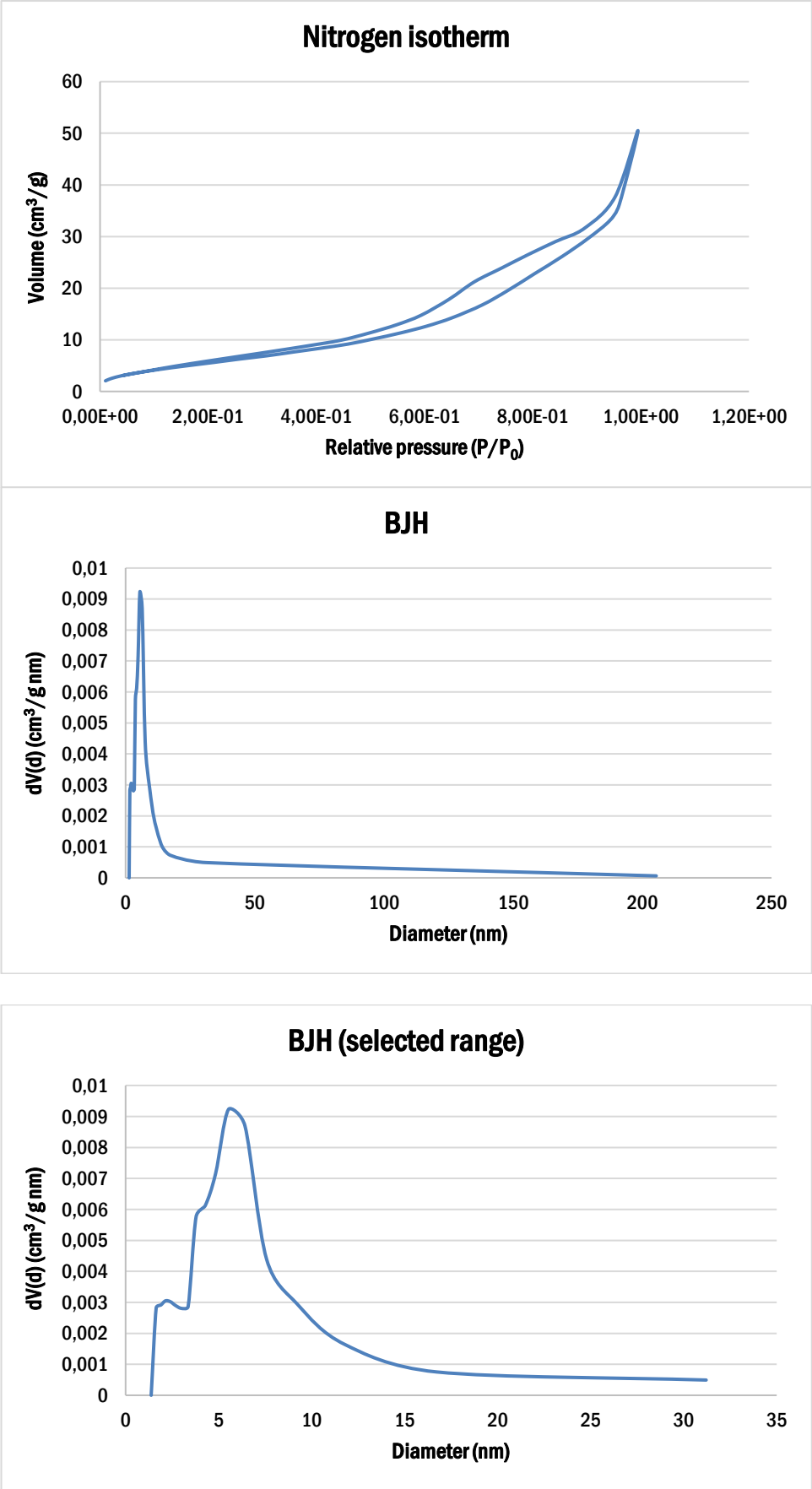


Figure S1. Physisorption study on Cu_2ONPs/S_8.

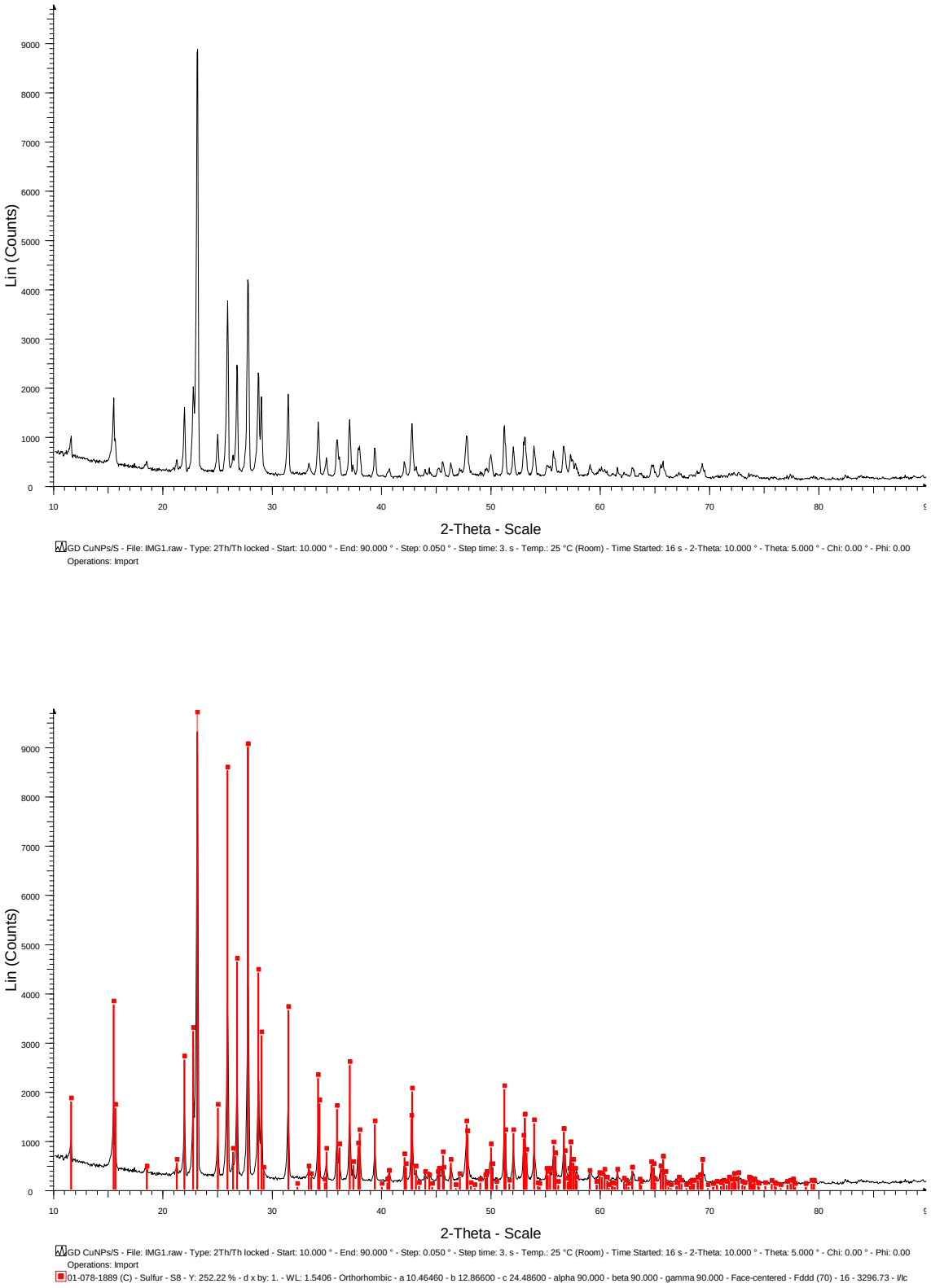


Figure S2. XRD spectra of Cu_2ONPs/S_8.

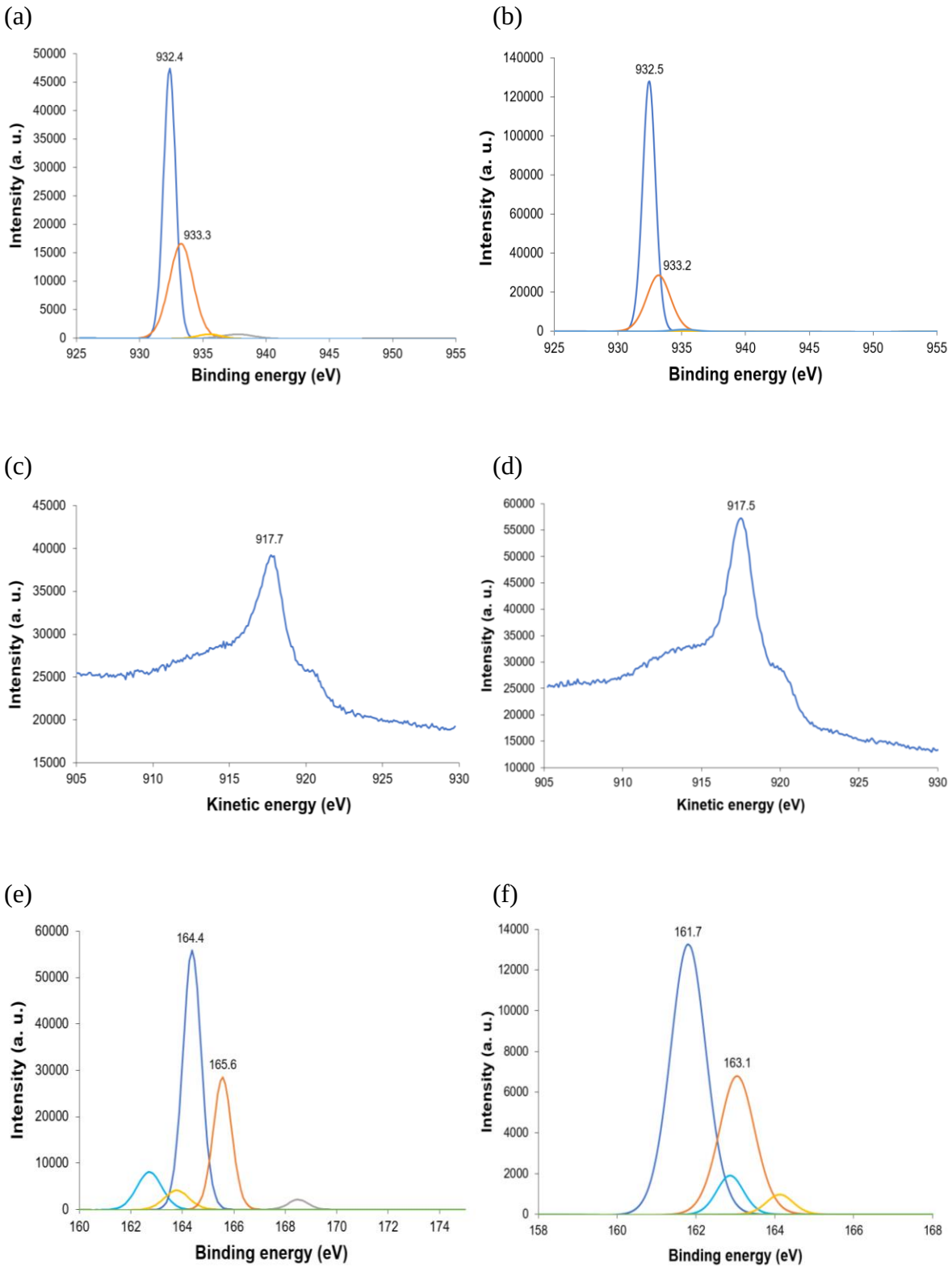


Figure S3. (a) XPS spectrum at the Cu $2p_{3/2}$ level of Cu_2ONPs/S_8. (b) XPS spectrum at the Cu $2p_{3/2}$ level of Cu_2S. (c) Auger spectrum of Cu_2ONPs/S_8 (Cu LMM line). (d) Auger spectrum of Cu_2S (Cu LMM line). (e) XPS spectrum at the S $2p_{3/2}$ (blue) and S $2p_{1/2}$ (orange) levels of Cu_2ONPs/S_8. (f) XPS spectrum at the S $2p_{3/2}$ (blue) and S $2p_{1/2}$ (orange) levels of Cu_2S.

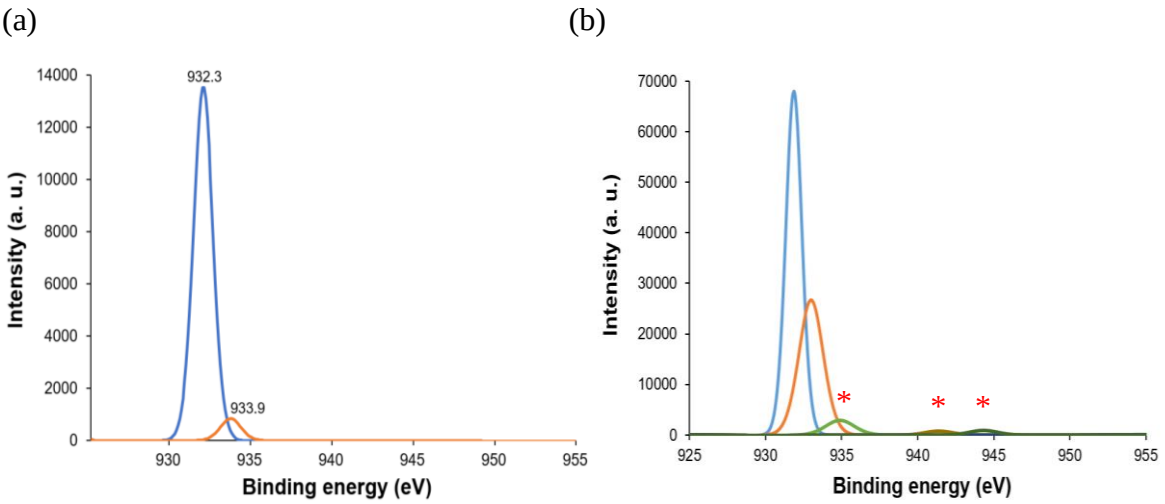


Figure S4. XPS spectra at the Cu $2p_{3/2}$ level of Cu_2ONPs/S_8: (a) original sample prepared four years ago; (b) the same sample kept in air for four years (* denotes CuO).

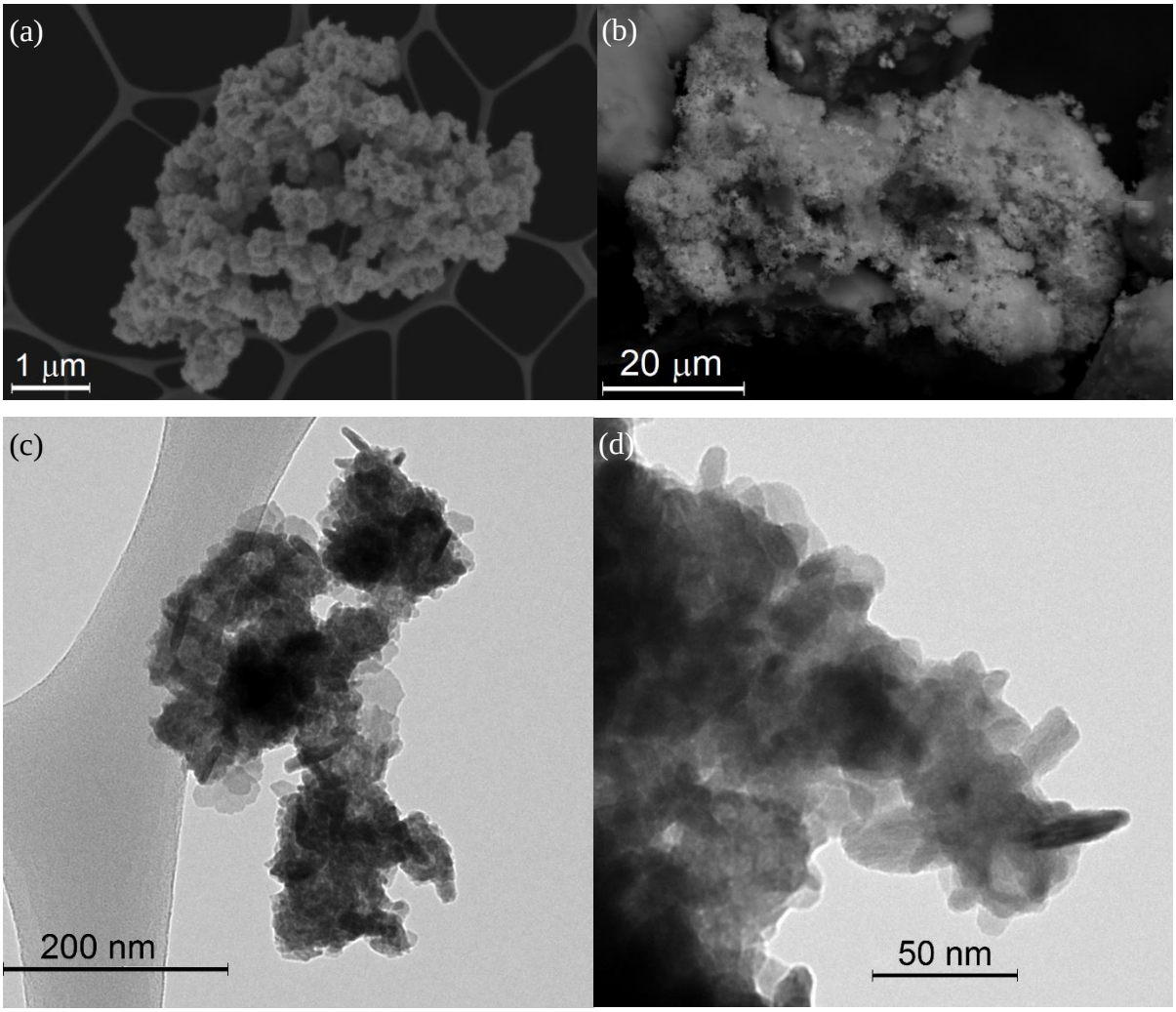


Figure S5. (a) FE-SEM, (b) SEM and (c, d) TEM micrographs of Cu_2ONPs/S_8.

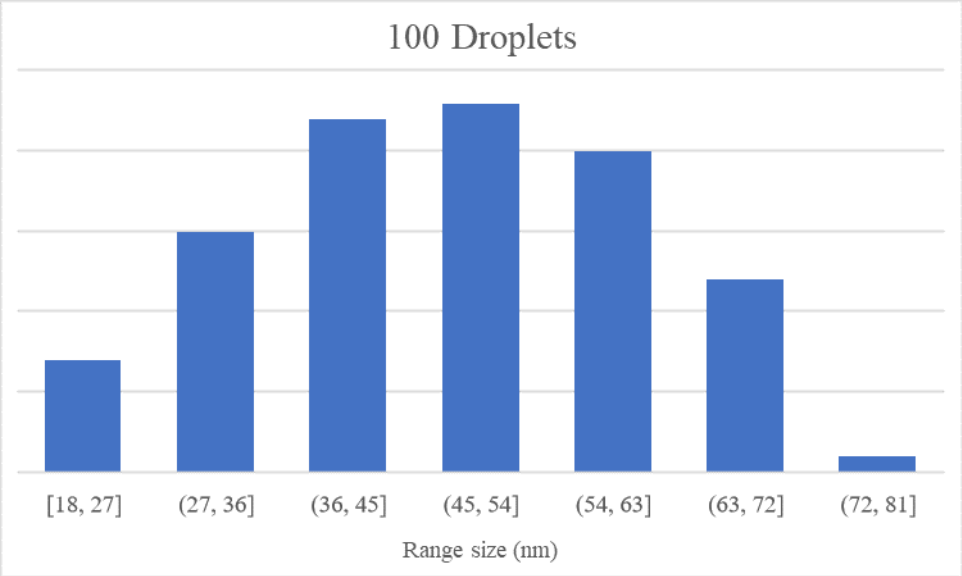


Figure S6. Droplet-size distribution of Cu_2ONPs/S_8 in ethanol determined by Cryo-EM for 100 droplets.

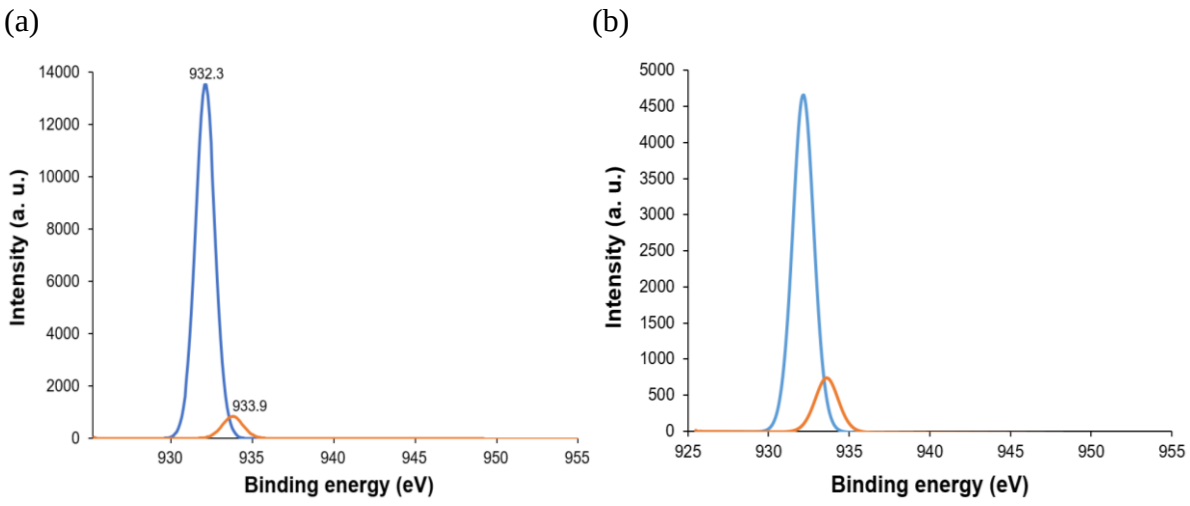
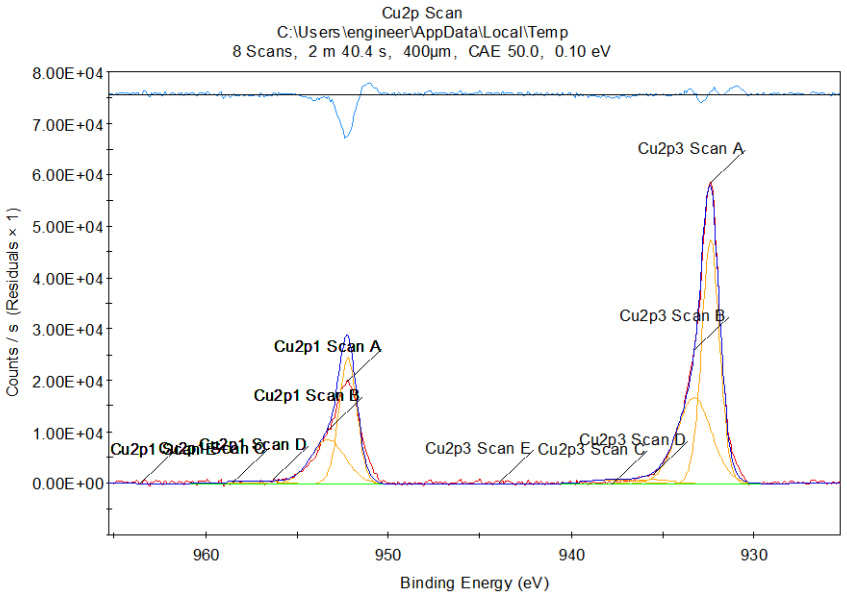


Figure S7. XPS spectra at the Cu 2$p_{3/2}$ level of Cu_2ONPs/S_8: (a) original sample; (b) recovered sample after use in the title reaction.

(a)



(b)

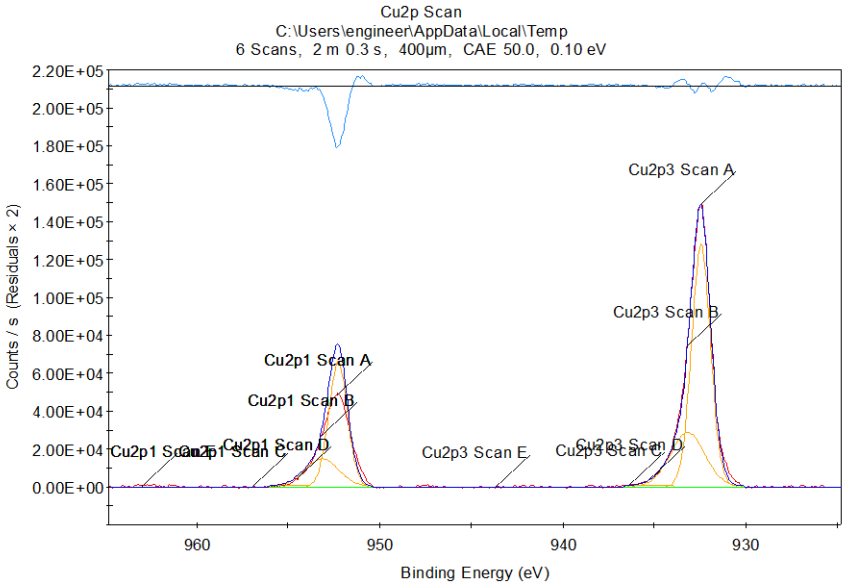
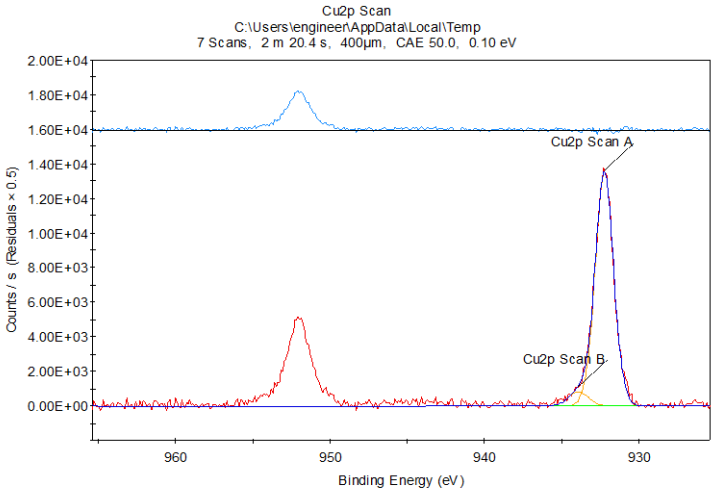


Figure S8. (a) XPS spectrum at the Cu 2*p* level of Cu_2ONPs/S_8. (b) XPS spectrum at the Cu 2*p* level of Cu_2S.

(a)



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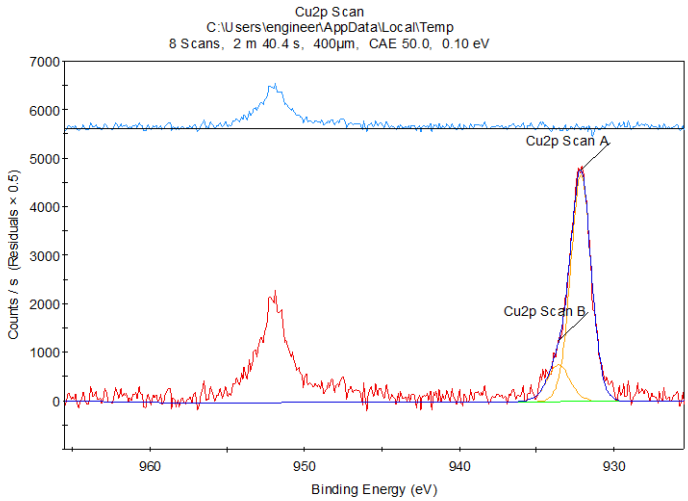

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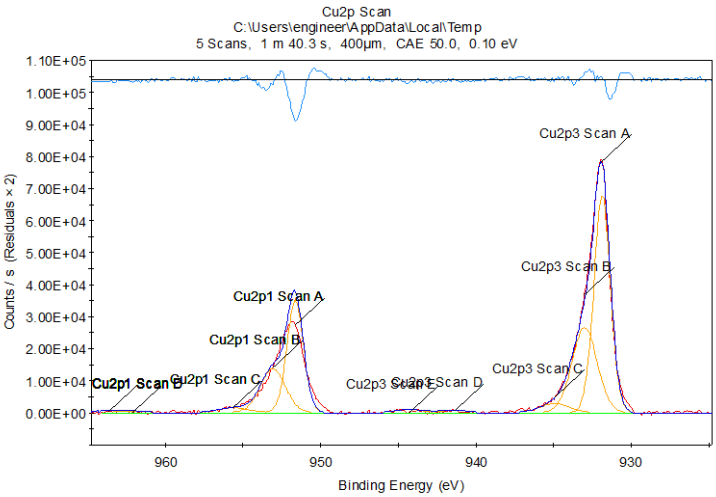

Figure S9. XPS spectra at the Cu 2*p* level of Cu_2ONPs/S_8: (a) original sample prepared four years ago; (b) recovered sample after use in the title reaction; (c) the same sample as in (a) but kept in air for four years.