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Formation of C-C, C-S and C-N bonds catalysed by supported copper nanoparticles

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General

Copper(II) chloride (97%, Aldrich), lithium powder (MEDALCHEMY S.L.), 4,4′-di-*tert*-butylbiphenyl (DTBB, Sigma-Aldrich), sodium Y zeolite (Sigma-Aldrich), activated charcoal (Norit CA1, Sigma-Aldrich), TiO_2 (anatasa nanopowder, Alfa Aesar) and montmorillonite K-10 (Sigma-Aldrich), all aryl halides, alkynes, thiols and heteroaromatic starting materials were commercially available of the best grade (Aldrich, Acros, Alfa Aesar, Fluorochem) and were used without further purification. Infrared analysis was performed with a FT-IR-4100 (ATR) spectrophotometer; wavenumbers 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 and coupling constants (*J*) in Hertz. The ^{1}H NMR yields were determined from the reaction crudes using mesitylene as the internal standard. Mass spectra (EI) were obtained at 70 eV on an Agilent 5973 spectrometer; fragment ions in *m/z* with relative intensities (%) in parentheses. HRMS analyses were carried out on Finnigan MAT95S and Agilent 7200 (Q-TOF) spectrometers. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with a Youling 6100 instrument equipped with a flame ionization detector and a 30 m capillary column (0.25 mm diameter, 0.25 μm film thickness), using nitrogen (1 mL/min) as the carrier gas, $T_{injector}$ = 270 ºC, T_{column} = 60 ºC (3 min) and 60–270 ºC (15 ºC/min); retention times (t_r) are given in min. Thin layer chromatography was carried out on TLC plastic sheets with silica gel 60 F_{254} (Merck). Column and preparative chromatography was performed using silica gel 60 of 40–60 microns and P/UV254, respectively (hexane/EtOAc as eluent).

Characterisation of CuNPs/C

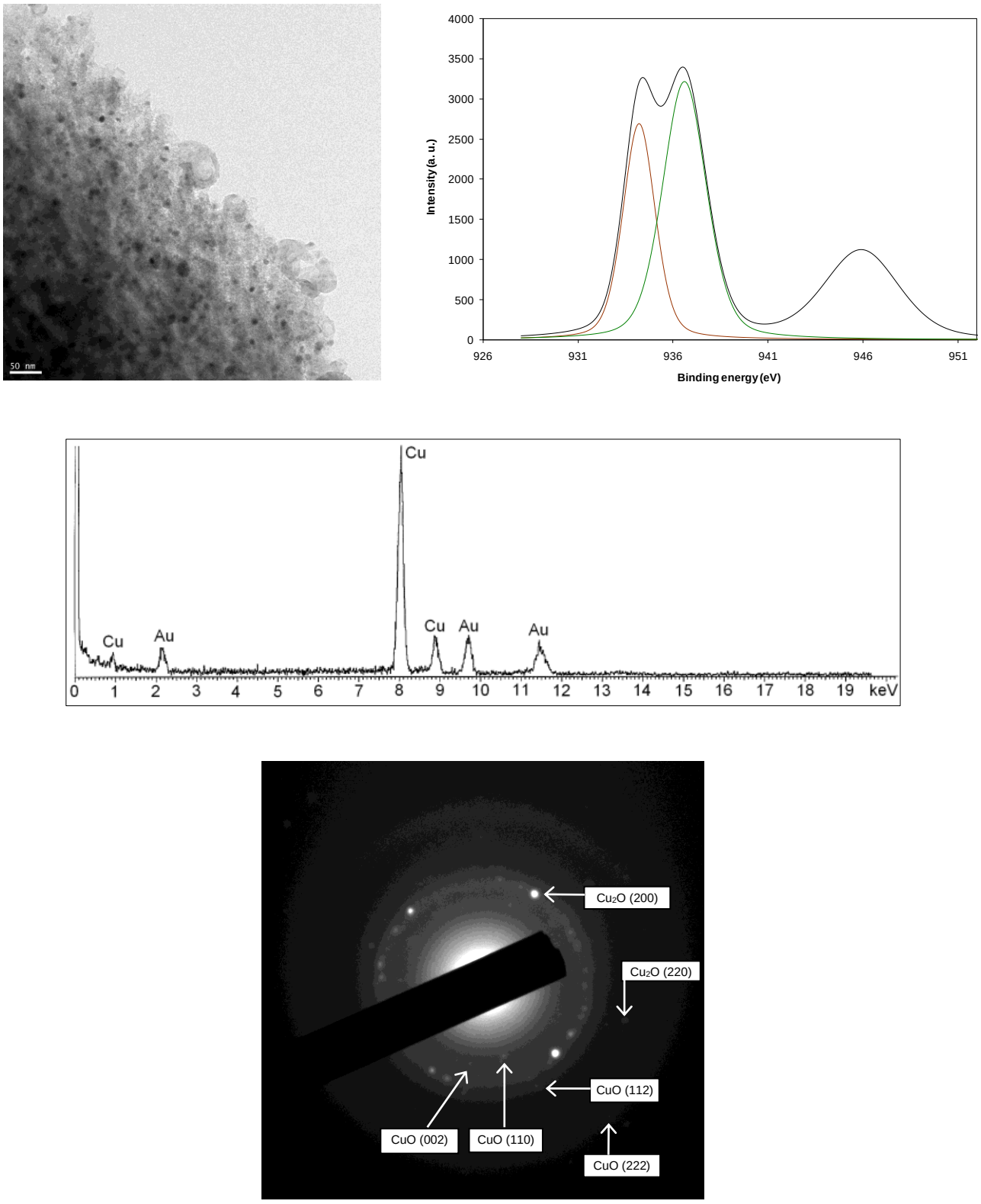


Figure S1. TEM micrograph, XPS spectrum at the Cu $2p_{3/2}$ level, EDX spectrum and selected area electron diffraction (SAED) pattern of CuNPs/C. Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.

Characterisation of CuNPs/ZY

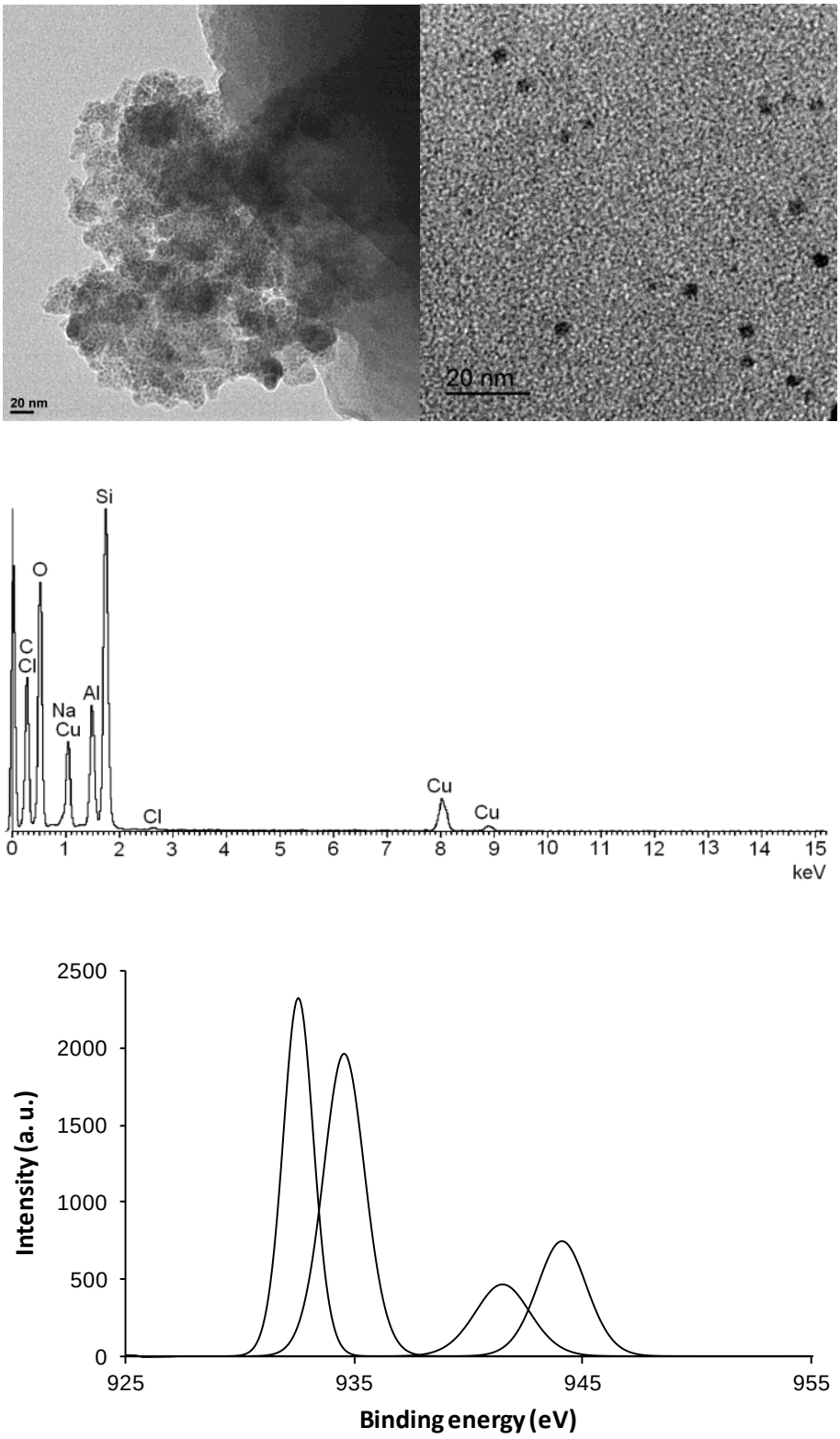
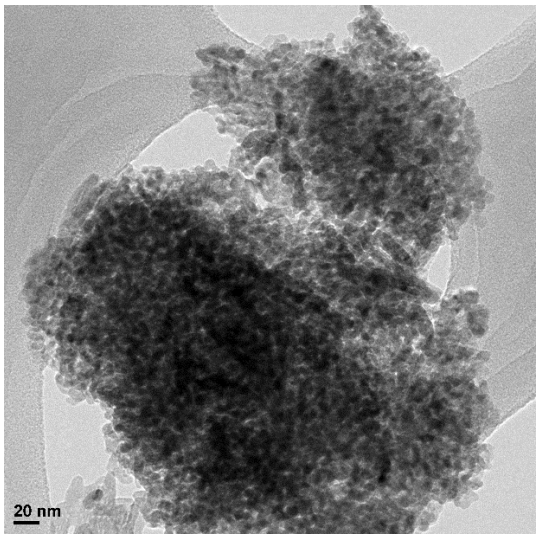
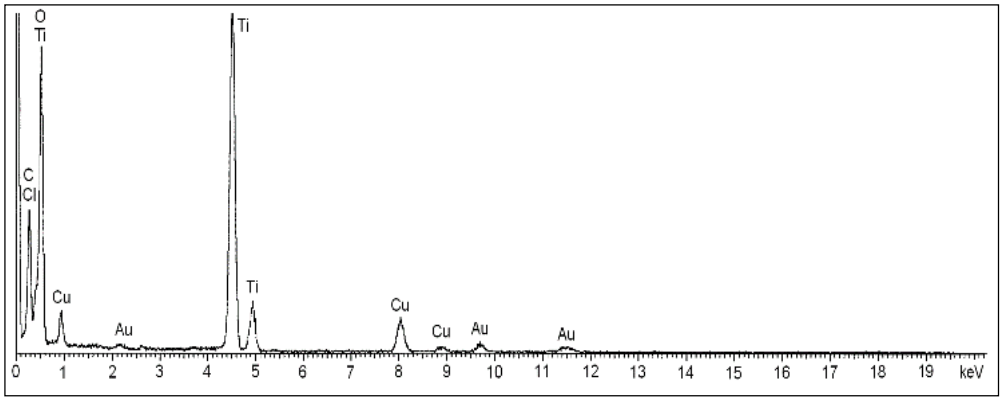


Figure S2. TEM micrographs, EDX spectrum and XPS spectrum at the Cu $2p_{3/2}$ level of CuNPs/ZY. Reproduced from Ref. 2 with permission. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Characterisation of CuNPs/TiO_2





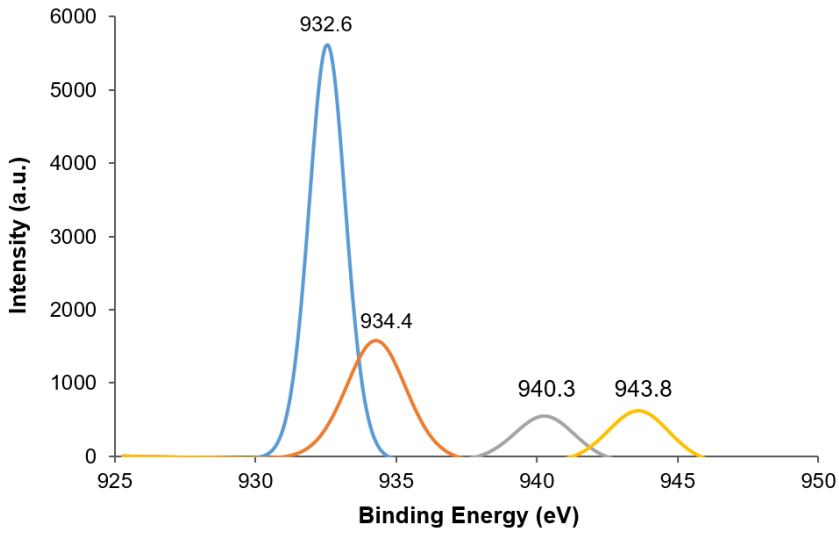
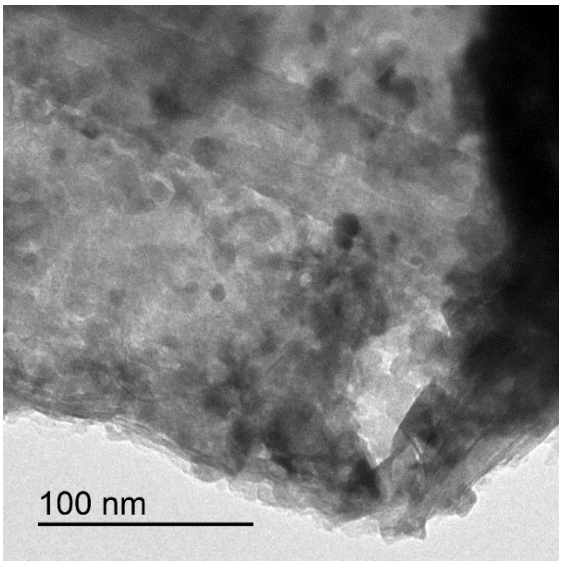
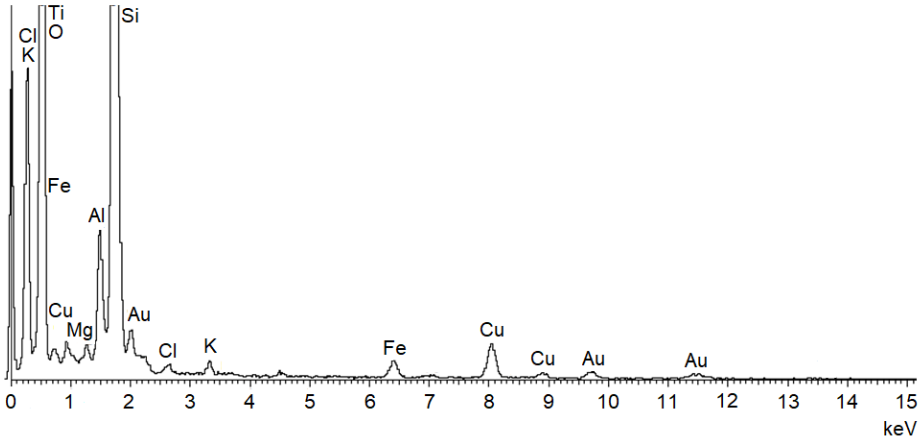


Figure S3. TEM micrograph, EDX spectrum and XPS spectrum at the Cu $2p_{3/2}$ level of CuNPs/TiO_2.

Characterisation of CuNPs/MK-10





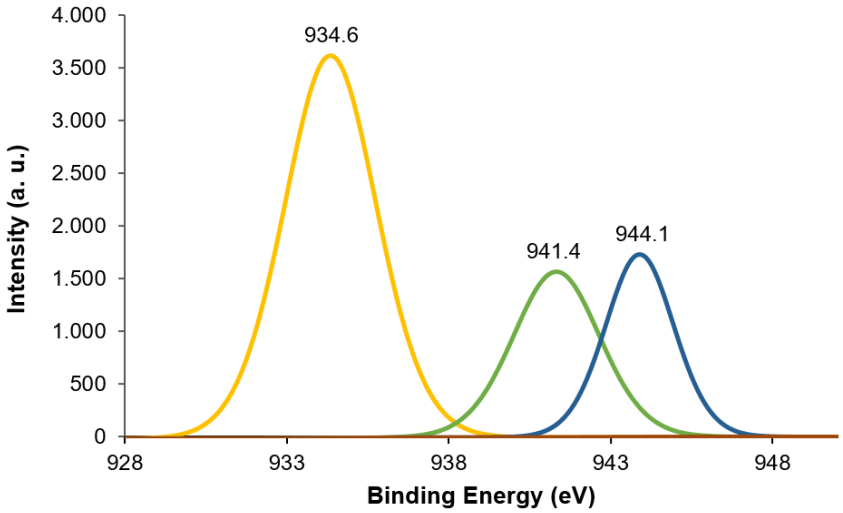


Figure S4. TEM micrograph, EDX spectrum and XPS spectrum at the Cu $2p_{3/2}$ level of CuNPs/MK-10.

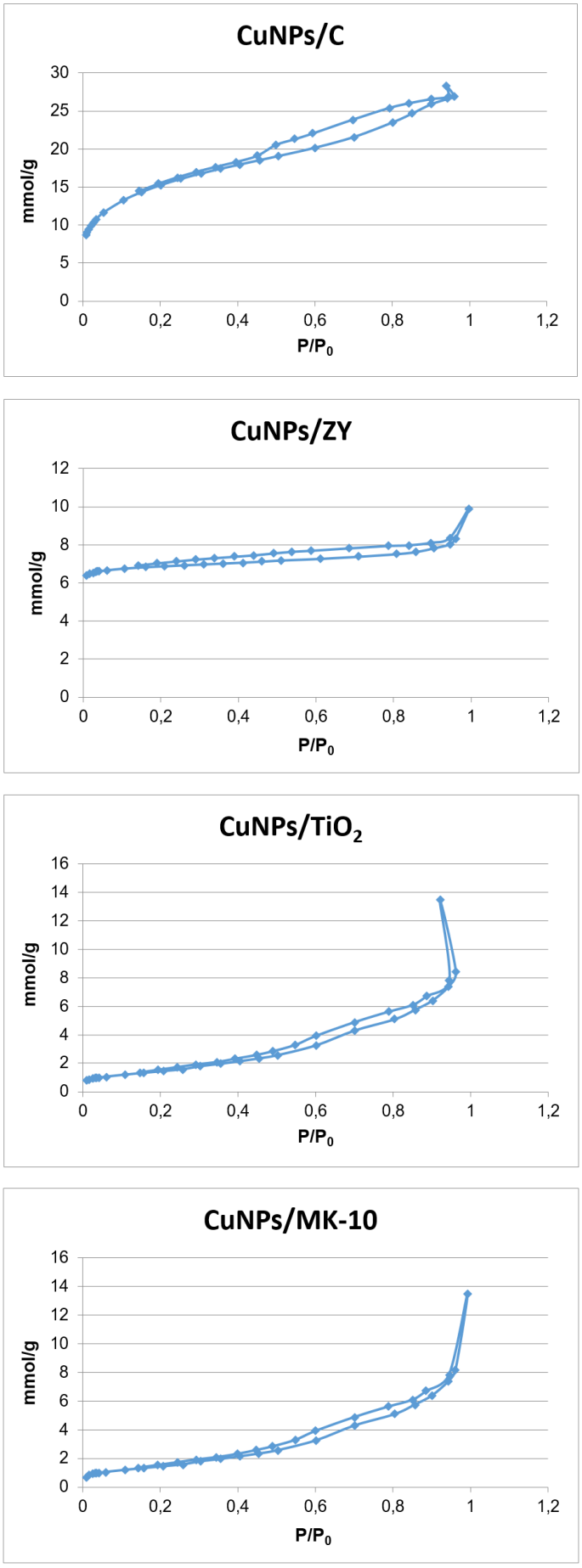
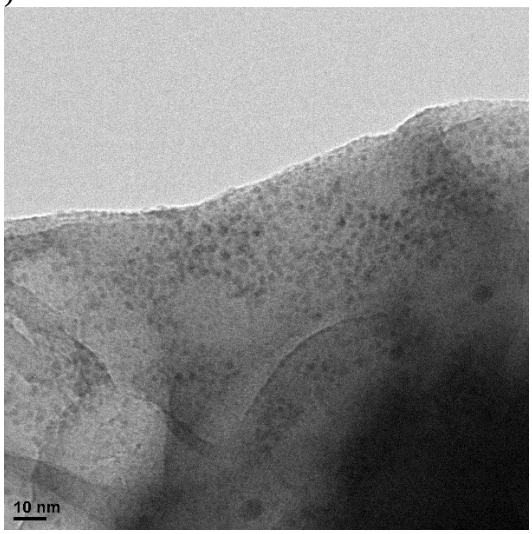
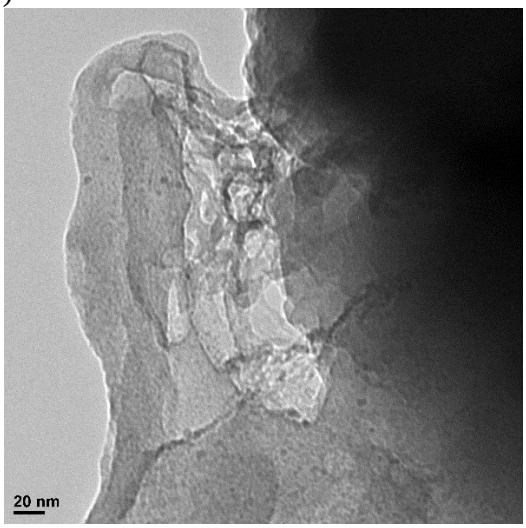


Figure S5. Adsorption isotherms of the catalysts.

(a)



(b)



(c)

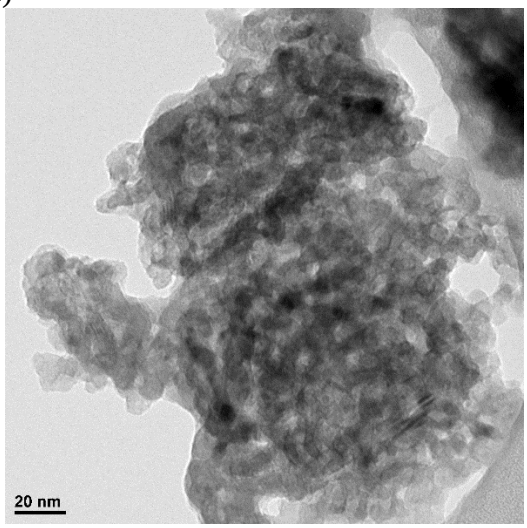


Figure S6. TEM micrographs of (a) CuNPs/ZY after the fourth cycle in the Sonogashira reaction, (b) CuNPs/ZY after the fourth cycle in the thiol arylation reaction and (c) CuNPs/TiO_2 after the second cycle in the azole arylation reaction.

Cross coupling of 1a and 2a catalysed by CuNPs on different supports

4-Iodoanisole (**1a**, 58.5 mg, 0.25 mmol), phenylacetylene (**2a**, 41.2 μL, 0.375 mmol, 1.5 equiv.), the catalyst (5 mol% Cu), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.), and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for 4 or 8 h (Figure 1). The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and to ^{1}H NMR analysis (mesitylene as the internal standard).

General procedure for the cross coupling of aryl iodides with arylacetylenes catalysed by CuNPs/ZY (Table 1). The aryl halide (**1**, 0.25 mmol), arylacetylene (**2**, 0.375 mmol, 1.5 equiv.), CuNPs/ZY (26.7 mg, *ca.* 4 mol%), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.) and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for the specified time in Table 1. The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and to ^{1}H NMR analysis (mesitylene as the internal standard) for products **3aa**-**3ka** or to purification by column chromatography (silica gel, hexane/EtOAc) for products **3cb**-**3cd**.

All compounds **3** were characterised by comparison of their physical and spectroscopic data with those described in the literature: **3aa**,[3] **3ba**,[4] **3ca**,[5] **3da**,[6] **3ea**,[7] **3fa**,[8] **3ga**,[6] **3ha**,[9] **3ka**,[6] **3cb**,[10] **3cc**[11] and **3cd**.[12]

Cross coupling of 1a and 2a catalysed by commercial copper catalysts

4-Iodoanisole (**1a**, 58.5 mg, 0.25 mmol), phenylacetylene (**2a**, 41.2 μL, 0.375 mmol, 1.5 equiv.), the catalyst (5 mol%), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.), and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for 8 h. The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and to GLC analysis.

Cross coupling of 1c and 4a catalysed by CuNPs on different supports

4-Iodobenzonitrile (**1c**, 57 mg, 0.25 mmol), thiophenol (**4a**, 38 μL, 0.375 mmol, 1.5 equiv.), the catalyst (1 mol% Cu), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.) and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 80 ºC under Ar and stirred for 2 or 4 h (Figure 3). The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and ^{1}H NMR analysis (mesitylene as the internal standard).

General procedure for the cross coupling of aryl halides (1) with thiophenol (4a) catalysed by CuNPs/ZY (Table 3).

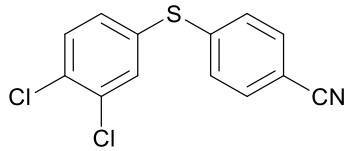
The aryl halide (**1**, 0.25 mmol), thiophenol (**4a**, 38 μL, 0.375 mmol, 1.5 equiv.), CuNPs/ZY (5.3 mg, 0.7 mol%), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.) and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for the specified time in Table 3. The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and ^{1}H NMR analysis (mesitylene as the internal standard).

Compounds **5aa**-**5ra** were characterised by comparison of their physical and spectroscopic data with those described in the literature: **5aa**,[13] **5ba**,[14] **5ca**,[15] **5fa**,[15] **5ga**,[16] **5oa**,[17] **5pa**,[15] **5qa**[14] and **5ra**.[14]

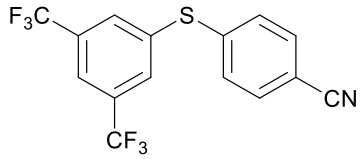
General procedure for the cross coupling of 4-iodobenzonitrile (1c) with thiols (4) catalysed by CuNPs/ZY (Table 4).

4-Iodobenzonitrile (**1c**, 114.5 mg, 0.5 mmol), the thiol (**4**, 0.75 mmol, 1.5 equiv.), CuNPs/ZY (10.6 mg, 0.7 mol%), K_2CO_3 (138 mg, 1.0 mmol) or KOH (56 mg, 1.0 mmol) and DMF (2 mL) were added to a reactor tube. The mixture was warmed to 70 or 100 ºC under Ar and stirred for 4 h. The reaction crude was diluted with EtOAc (6 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 6 mL) to remove the DMF and washing with brine (8 mL). The resulting organic phase was subjected to solvent evaporation under vacuum and purification by column chromatography (silica gel, hexane/EtOAc).

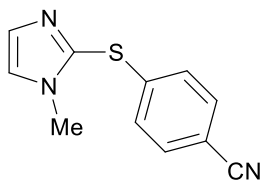
Compounds **5cb**,[18] **5cg**,[19] **5ch**,[20] **5ci**[21] and **5cj**,[22] were characterised by comparison of their physical and spectroscopic data with those described in the literature. Data for the new compounds **5** follows:



4-[(3,4-Dichlorophenyl)thio]benzonitrile (5cc): Yellow solid; 63 g (45% yield); m.p. 108.6–109.0 ºC; t_r 16.99 min; R_f 0.83 (hexane/EtOAc, 1:1). IR (neat) ν = 3035, 2925, 2225, 869, 629, 615 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24, 7.54 (AA'XX' system, *J* = 8.6 Hz, 4H), 7.30 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 109.9, 118.4, 128.4, 131.6, 131.7, 132.6, 132.7, 133.7, 133.8, 135.0, 143.4. GC-MS (EI): *m/z* (%) = 283 (15) [M$^+$+4], 282 (11) [M$^+$+3], 281 (71) [M$^+$+2], 280 (18) [M$^+$+1], 279 (100) [M$^+$], 243 (18), 210 (11), 209 (68), 208 (13), 142 (11). HRMS (EI): *m/z* calcd. for $C_{13}H_7Cl_2N_2$ 278.9676, found 278.9671.

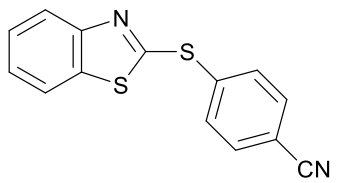


4-{[3,5-Bis(trifluoromethyl)phenyl]thio}benzonitrile (5cd): Yellow oil; 141 mg (81% yield); t_r 13.09 min; R_f 0.54 (hexane/EtOAc, 9:1). IR (neat) ν = 3104, 3030, 2230, 1592, 1486, 1350, 1275, 1130, 822, 681 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD) δ = 7.49, 7.74 (AA'XX' system, *J* = 8.3 Hz, 4H), 7.73–7.97 (m, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ = 111.1, 117.7, 118.8, 121.5, 122.9 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 130.5, 131.6 (q, $^3J_{C\text{-}F}$ = 2.9 Hz), 132.6 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 132.9, 137.5, 140.8. GC-MS (EI) *m/z* (%) = 348 (16) [M$^+$+1], 347 (100) [M$^+$], 328 (11), 326 (13), 258 (22). HRMS (EI): *m/z* calcd. for $C_{15}H_7F_6NS$ 347.0203, found 347.0205.

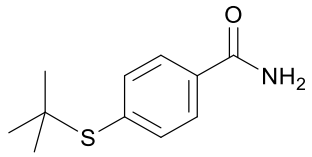


4-[(1-Methyl-1*H*-imidazol-2-yl)thio]benzonitrile (5ce): Yellow solid; 56 mg (52% yield); m.p. 104.0–104.6 ºC; t_r 15.49 min; R_f 0.25 (hexane/EtOAc, 1:1). IR (neat) ν = 3045, 3194, 2761, 2223, 658, 618 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.68 (s, 3H), 7.11, 7.51 (AA'XX' system, *J* = 8.5 Hz, 4H), 7.17 (s, 1H), 7.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 33.9, 109.7, 118.4, 124.6,

126.8, 127.6, 130.9, 132.7, 142.7 ppm. GC-MS (EI) *m/z* (%) = 216 (13) [M^++1], 215 (63) [M^+], 214 (100), 208 (10), 207 (34), 182 (12), 116 (11), 72 (10). HRMS (EI): *m/z* calcd. for $C_{11}H_9N_3S$ 215.0517, found 215.0501.



4-(Benzo[*d*]thiazol-2-ylthio)benzonitrile (5cf): Yellow solid; 85 mg (63% yield); m.p. 91.3–91.8 ºC; t_r 18.13 min; R_f 0.82 (hexane/EtOAc, 1:1). IR (neat) ν = 3070, 2917, 2850, 2225, 1455, 1423, 1006, 829, 758, 727 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.39 (m, 1H), 7.44–7.49 (m, 1H), 7.67–7.78 (m, 5H), 7.94–7.96 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 112.9, 118.0, 121.1, 122.7, 125.4, 126.6, 133.0, 133.1, 136.0, 137.6, 153.4, 163.6. GC-MS (EI): *m/z* (%) = 269 (21) [M^++1], 268 (67) [M^+], 267 (100), 208 (12), 207 (35). HRMS (EI): *m/z* calcd. for $C_{14}H_8N_2S_2$ 268.0129, found 268.0153.



4-(*tert*-Butylthio)benzamide (5si): Yellow solid; 63 mg (60% yield); m.p. 138.9–139.1 ºC; t_r 14.49 min; R_f 0.25 (hexane/EtOAc, 1:1). IR (neat) ν = 3398, 3199, 2922, 2854, 1645, 1612, 1456, 1400, 1361, 1300, 1149, 1086, 848, 781 cm^{-1}. ^1H NMR (300 MHz, DMSO) δ = 1.20 (s, 9H), 7.38 (s, 1H), 7.50, 7.80 (AA'XX' system, *J* = 8.3 Hz, 4H), 7.98 (s, 1H). ^{13}C NMR [75 MHz, $(CD_3)_2SO$] δ = 30.2, 45.7, 127.3, 134.0, 135.3, 135.8, 166.9. GC-MS (EI) *m/z* (%) = 209 (15) [M^+], 153 (100), 137 (41), 136 (15), 57 (41). HRMS (EI) *m/z*: calcd. for $C_{11}H_{15}NOS$ 209.0874, found 209.0870.

Cross coupling of 1c and 4a catalysed by commercial copper catalysts

4-Iodobenzonitrile (**1c**, 57 mg, 0.25 mmol), thiophenol (**4a**, 38 μL, 0.375 mmol, 1.5 equiv.), the catalyst (1 mol%), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.) and DMF (1 mL) were added to a reactor tube. The mixture was warmed to 100 ºC under Ar and stirred for 4 h (Table 5). The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the

DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and to GLC analysis.

General procedure for the cross coupling of 4-iodobenzonitrile (1c) with azoles (6)

4-Iodobenzonitrile (**1c**, 57.3 mg, 0.25 mmol), the corresponding azole (**6**, 0.3 mmol, 1.2 equiv.), CuNPs catalyst (5 mol% Cu), K_2CO_3 (69 mg, 0.5 mmol, 2 equiv.) and DMF (1 ml) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for 16 h. The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and ^{1}H NMR analysis (mesitylene as the internal standard). All compounds **7** were characterised by comparison of their physical and spectroscopic data with those described in the literature: **7ca**,[23] **7cb**,[23] **7cc**,[24] and **7cd**.[25]

Cross coupling of 1c and 6a catalysed by commercial copper catalysts

4-Iodobenzonitrile (**1c**, 57.3 mg, 0.25 mmol), imidazole (**6a**, 17 μL, 0.3 mmol, 1.2 equiv.), the catalyst (1.6 mol%), Cs_2CO_3 (163 mg, 0.5 mmol) and DMF (1 ml) were added to a reactor tube. The mixture was warmed to 120 ºC under Ar and stirred for 16 h. The reaction crude was diluted with EtOAc (3 mL) and filtered through a pad with Celite, followed by extraction of the filtrate with water (3 × 3 mL) to remove the DMF, washing with brine (4 mL) and drying with anhydrous $MgSO_4$. The resulting organic phase was subjected to solvent evaporation under vacuum and GLC analysis.

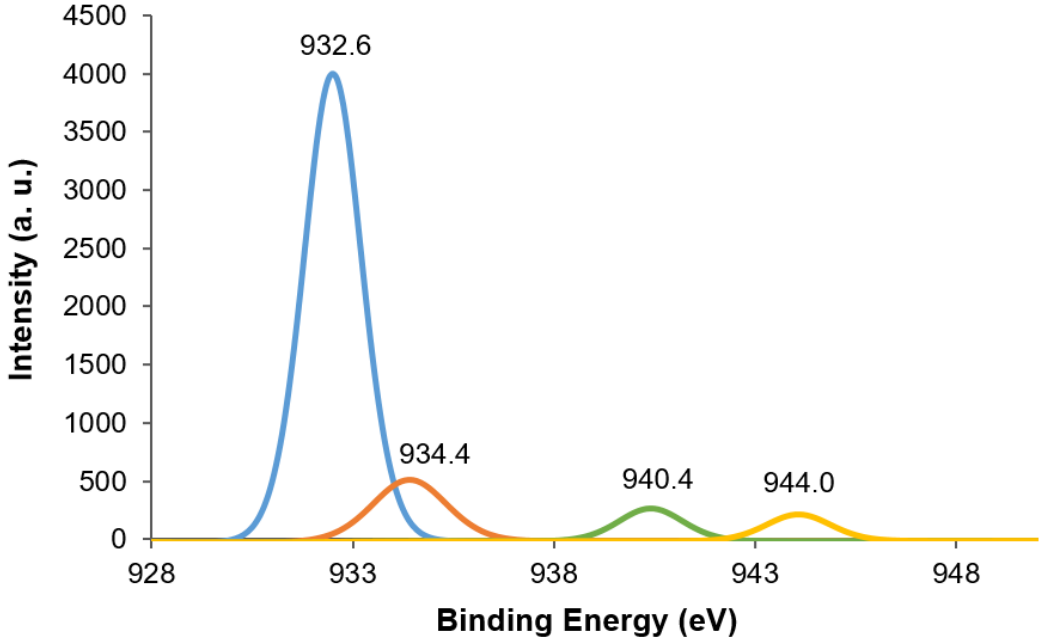


Figure S7. XPS spectrum at the Cu 2$p_{3/2}$ level of reused CuNPs/TiO_2.

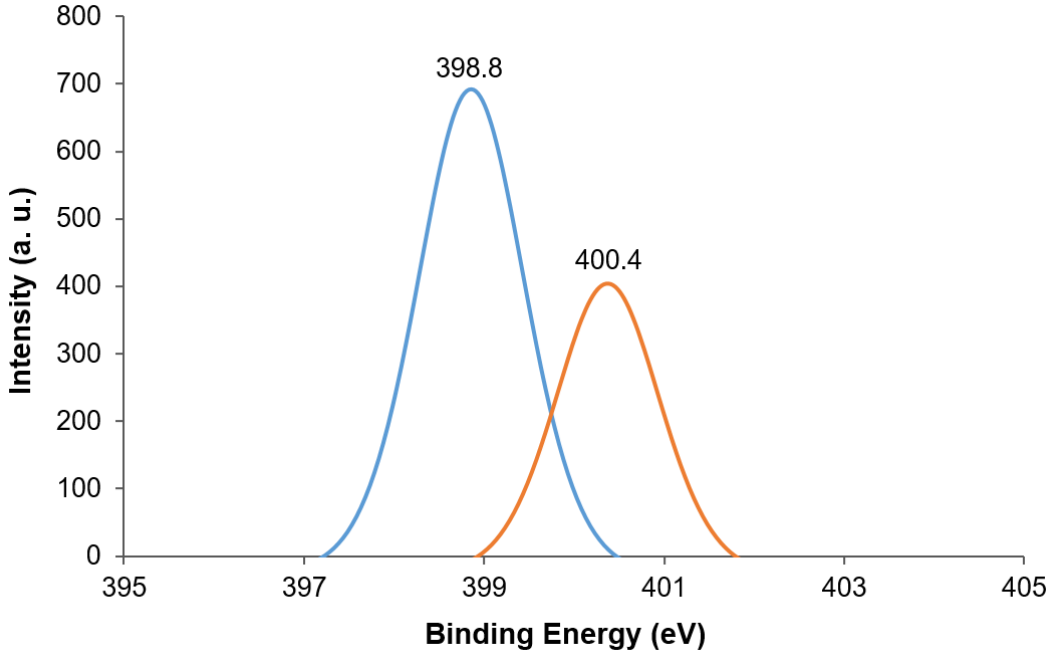


Figure S8. XPS spectrum at the N *1s* level of fresh CuNPs/TiO_2 impregnated with 4-iodobenzonitrile (**1c**).

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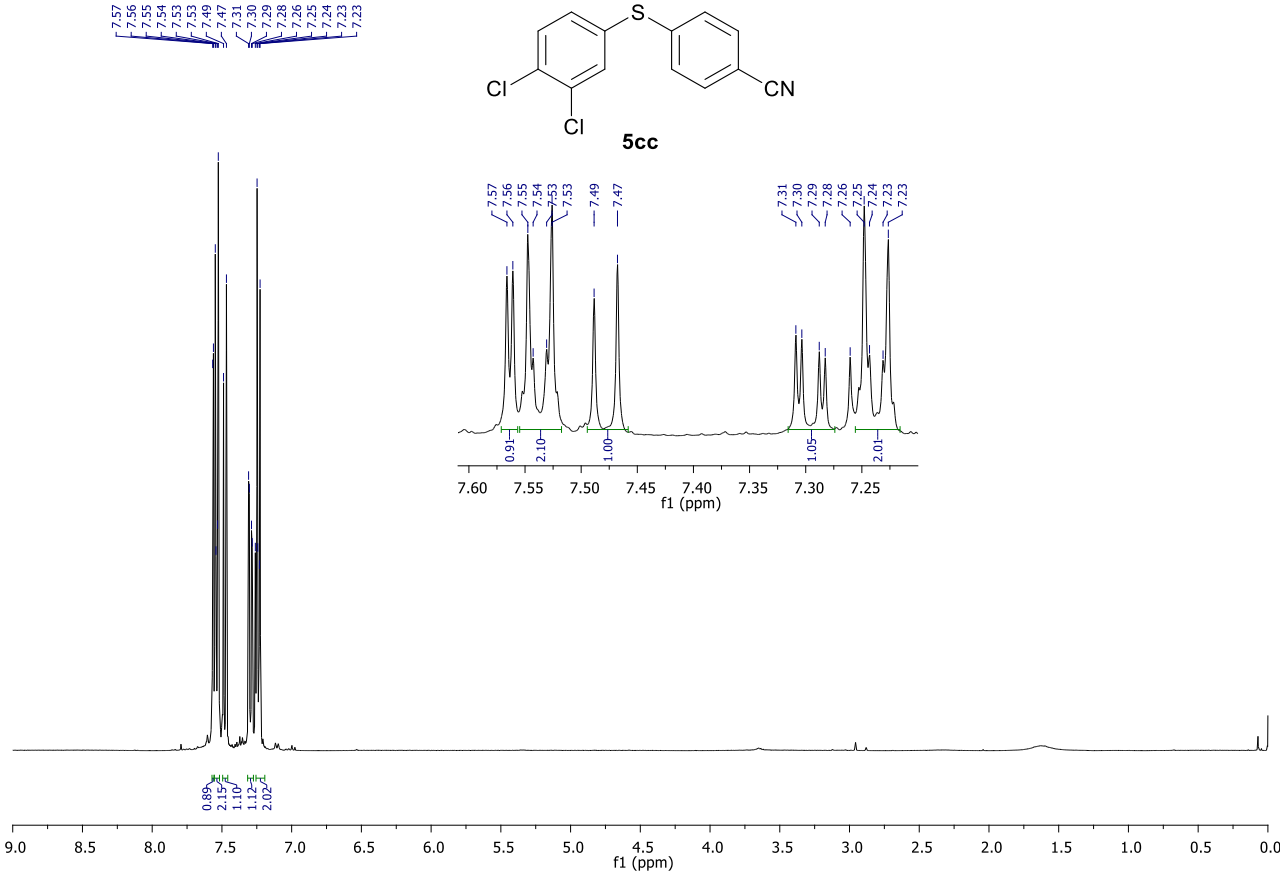
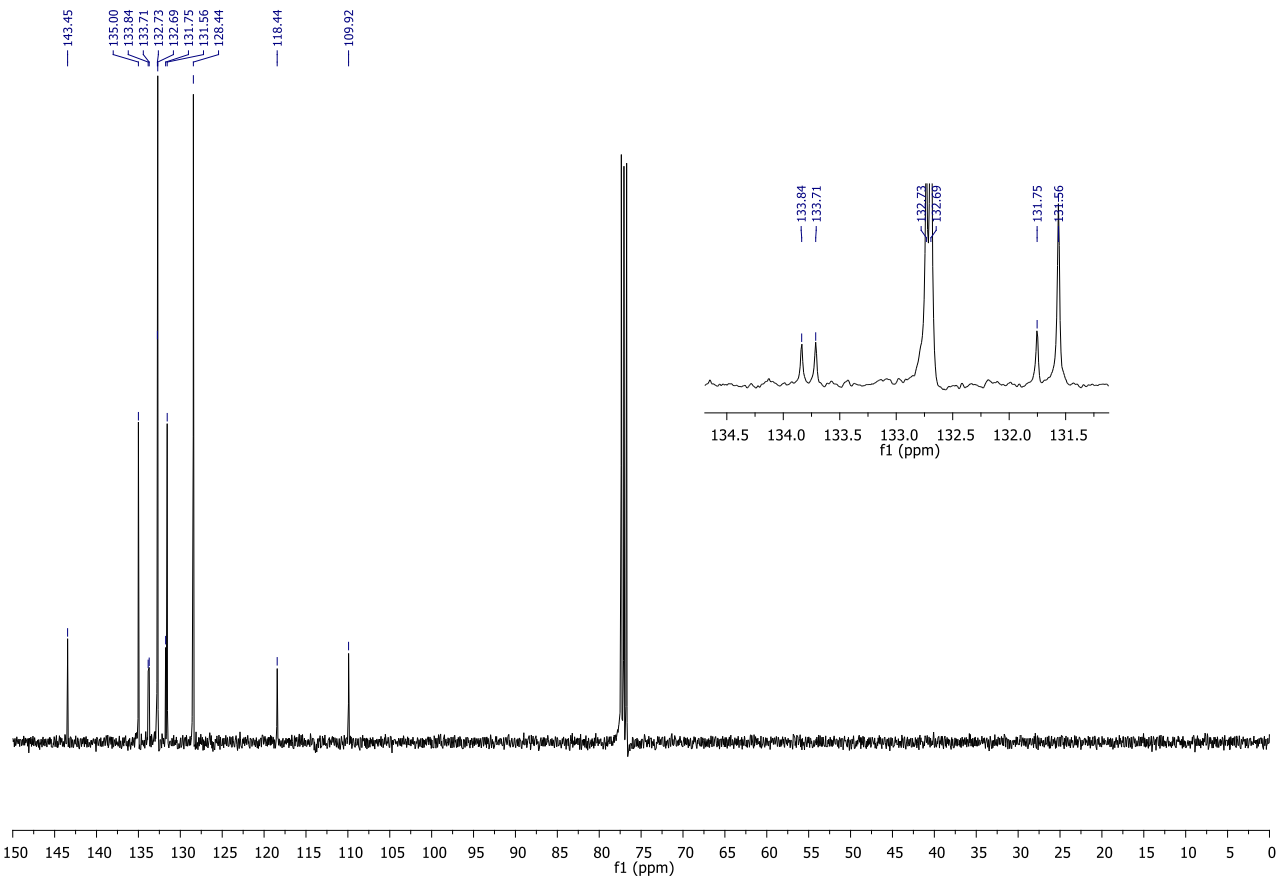
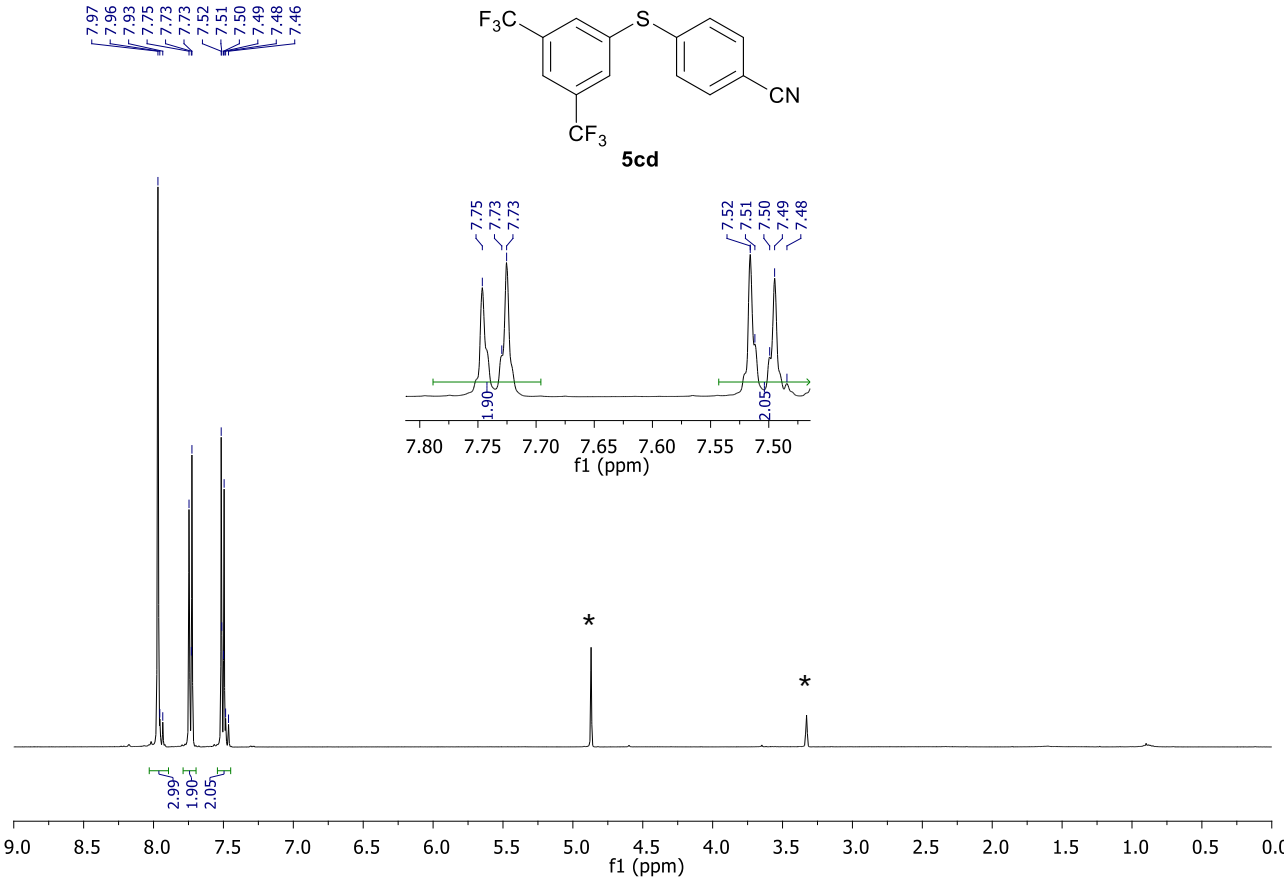
NMR spectra of new compounds 5





(In CD_3OD*)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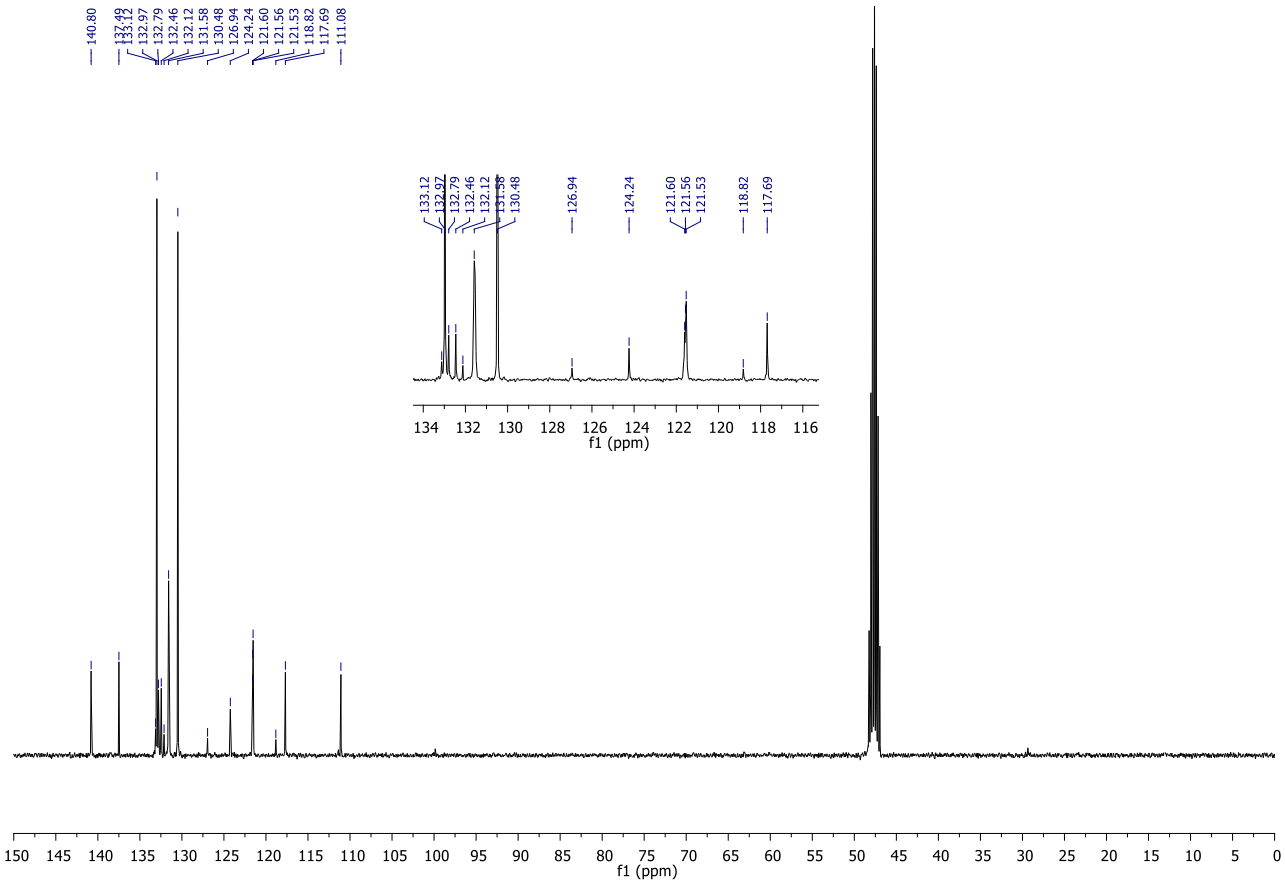
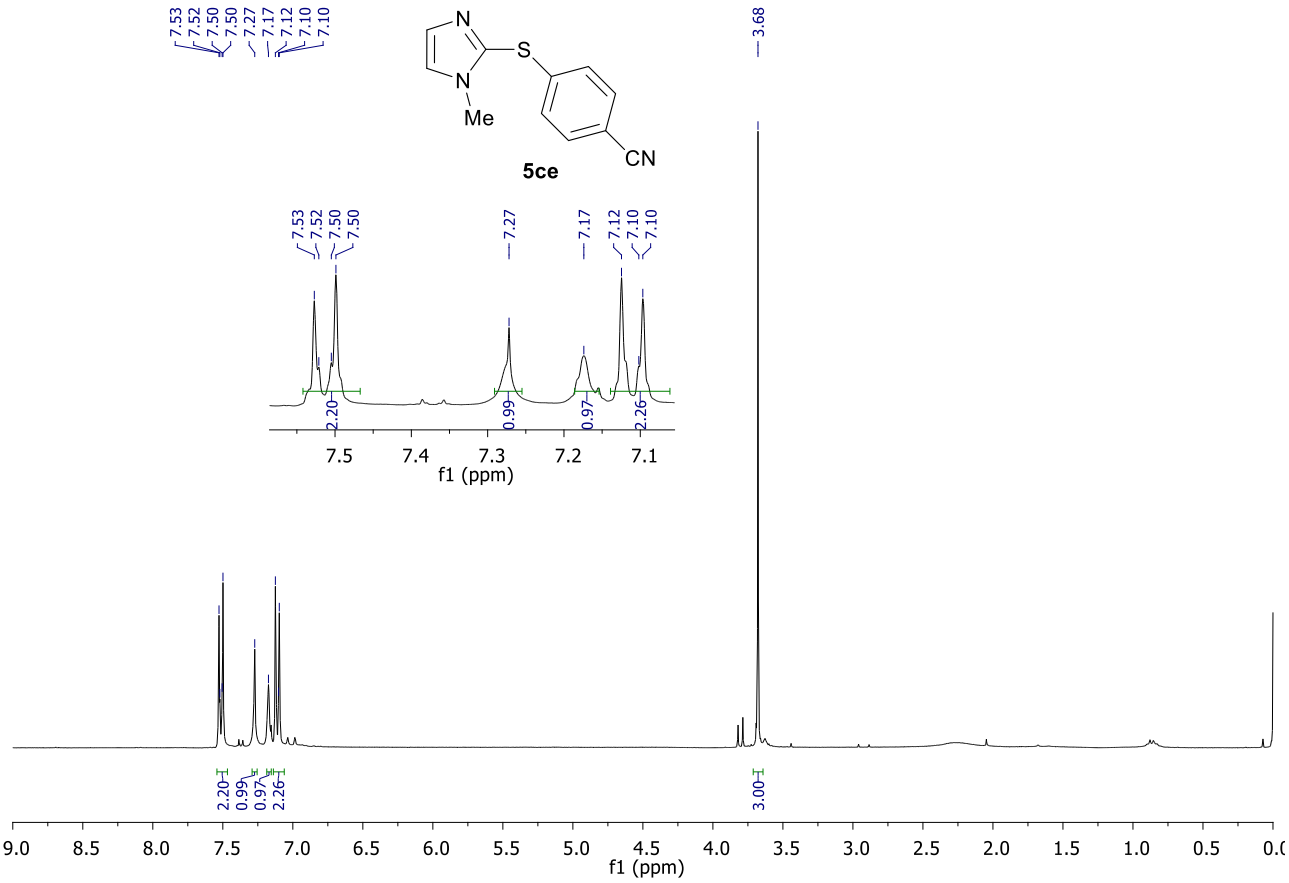
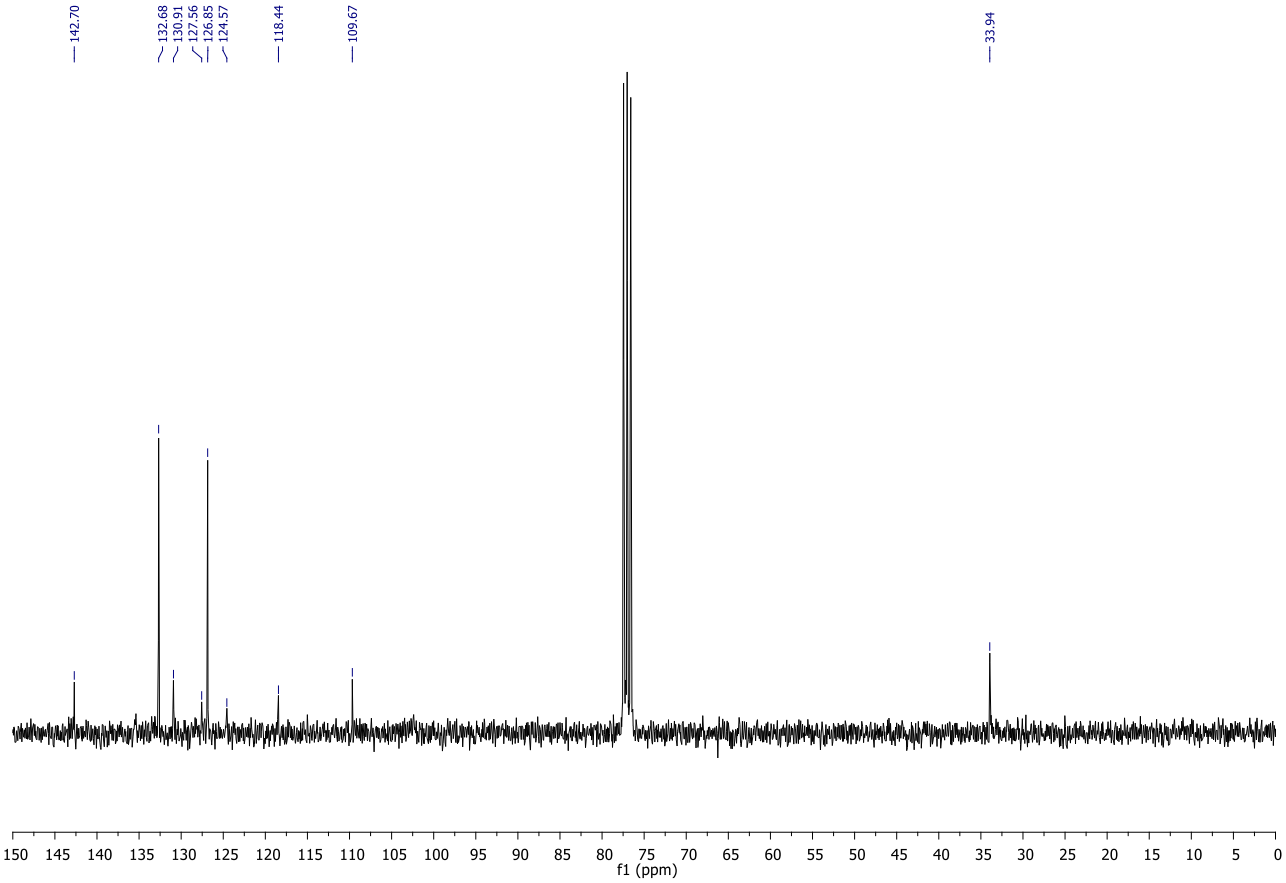
7.96
7.93
7.75
7.73
7.52
7.51
7.50
7.49
7.48
7.46
F3C
S
CN
CF3
5cd
7.75
7.73
7.73
7.52
7.51
7.50
7.49
7.48
1.90
2.05
7.80 7.75 7.70 7.65 7.60 7.55 7.50
f1 (ppm)
*
*
2.99
1.90
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


140.80
137.49
133.12
132.97
132.79
132.46
132.12
131.58
130.48
126.94
124.24
121.60
121.56
121.53
118.82
117.69
111.08
133.12
132.97
132.79
132.46
132.12
131.58
130.48
126.94
124.24
121.60
121.56
121.53
118.82
117.69
134 132 130 128 126 124 122 120 118 116
f1 (ppm)
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.53
7.52
7.50
7.50
7.27
7.17
7.12
7.10
7.10
3.68
N
S
N
Me
CN
5ce
2.20
0.99
0.97
2.26
3.00
f1 (ppm)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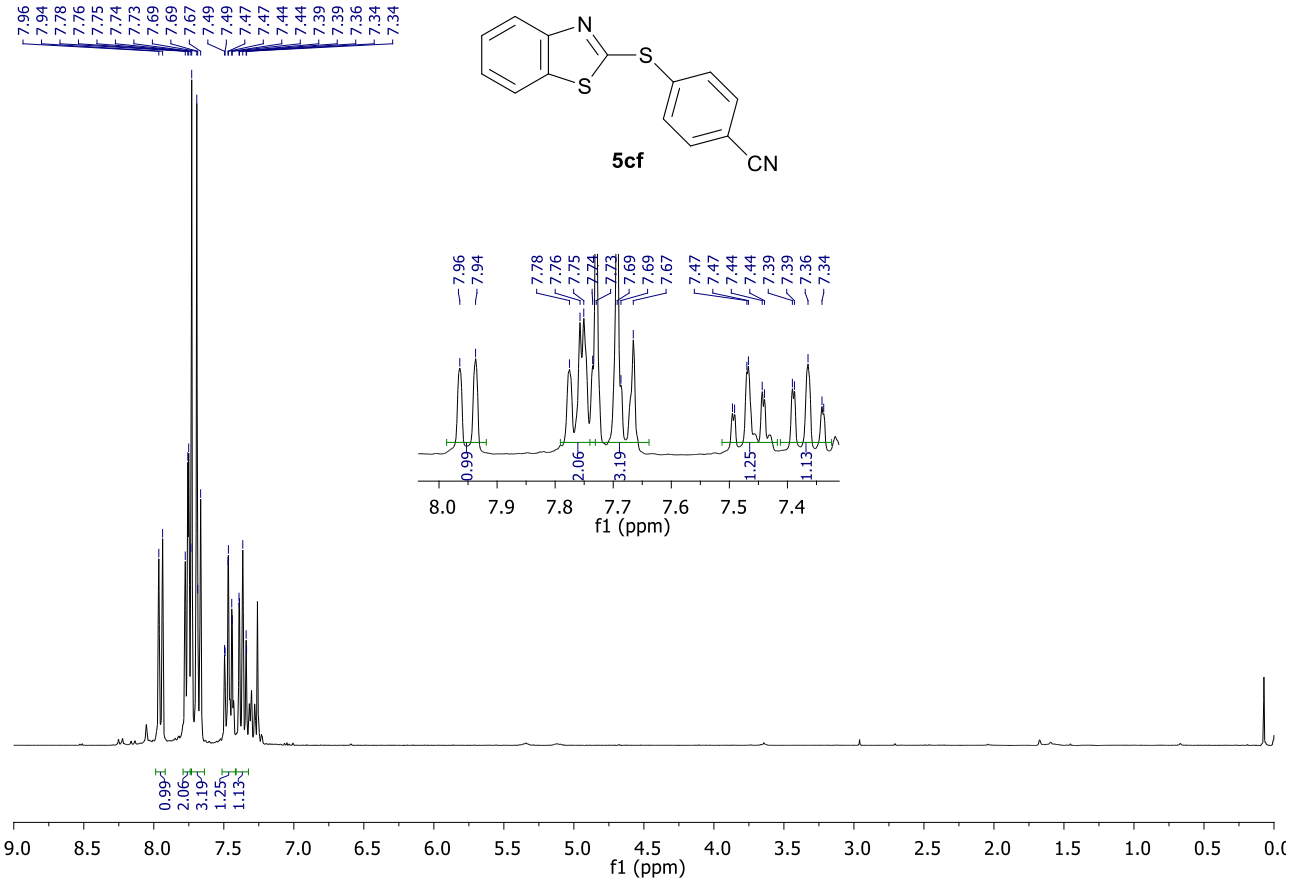
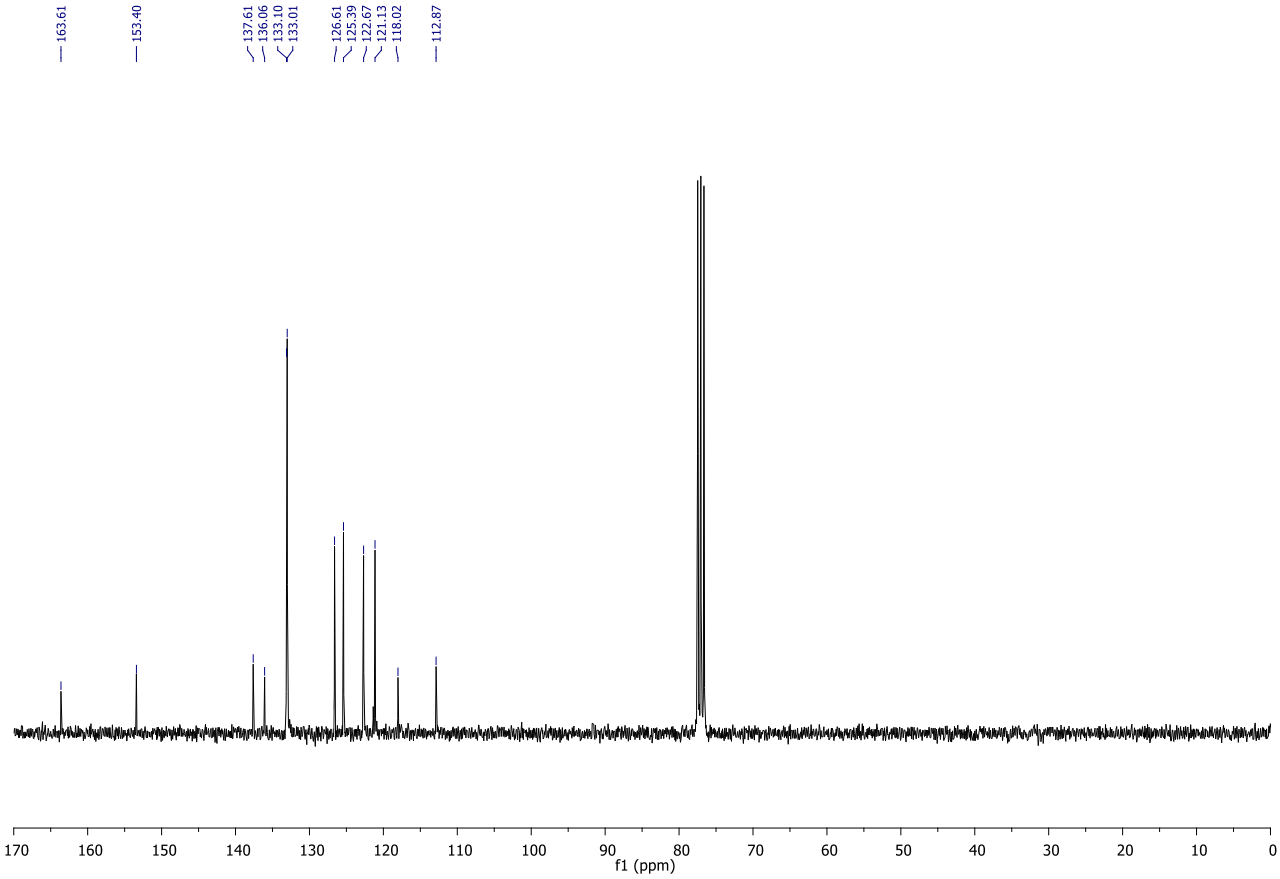
132.68
130.91
127.56
126.85
124.57
118.44
109.67
33.94
f1 (ppm)


7.96
7.94
7.78
7.76
7.75
7.74
7.73
7.69
7.69
7.67
7.49
7.49
7.47
7.47
7.44
7.44
7.39
7.39
7.36
7.34
7.34
N
S
S
CN
5cf
0.99
2.06
3.19
1.25
1.13
f1 (ppm)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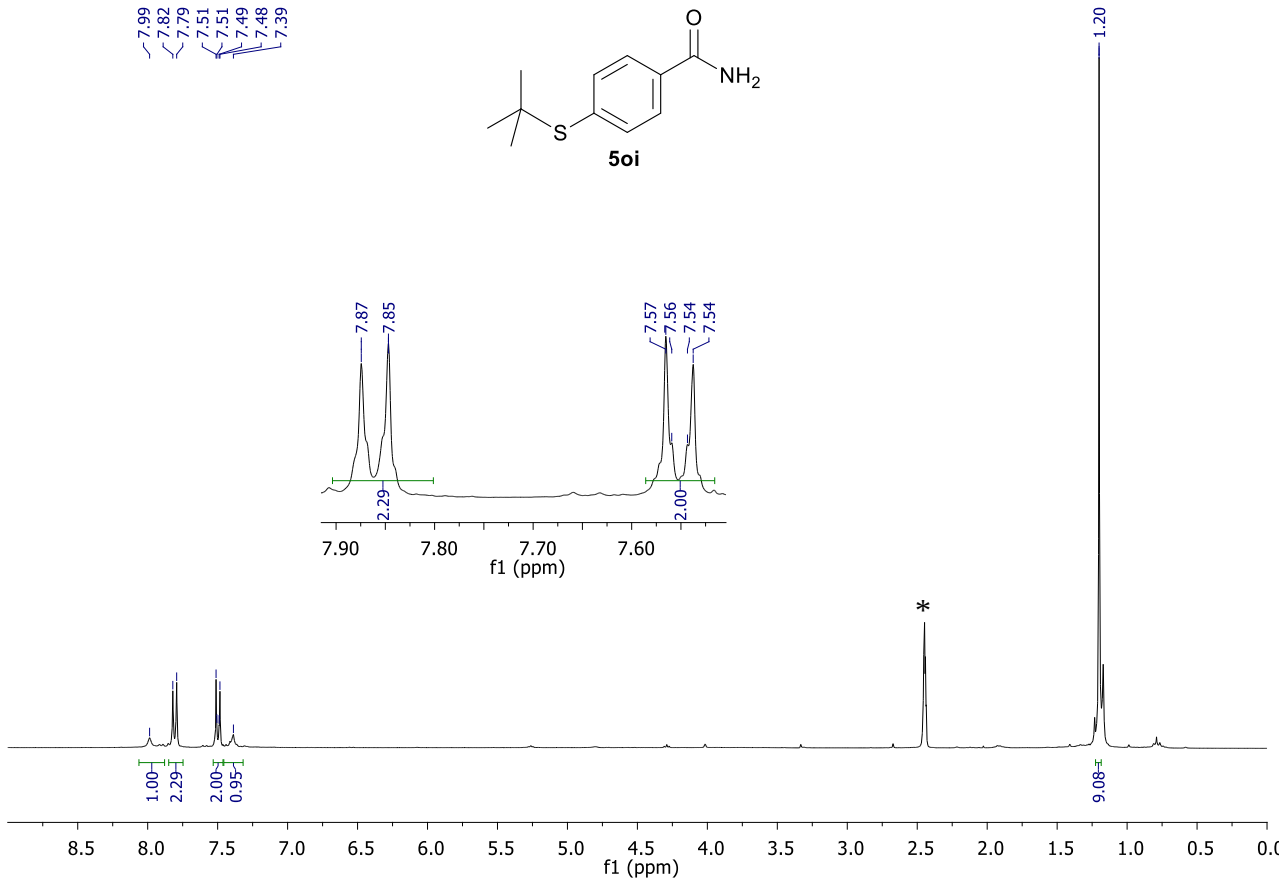
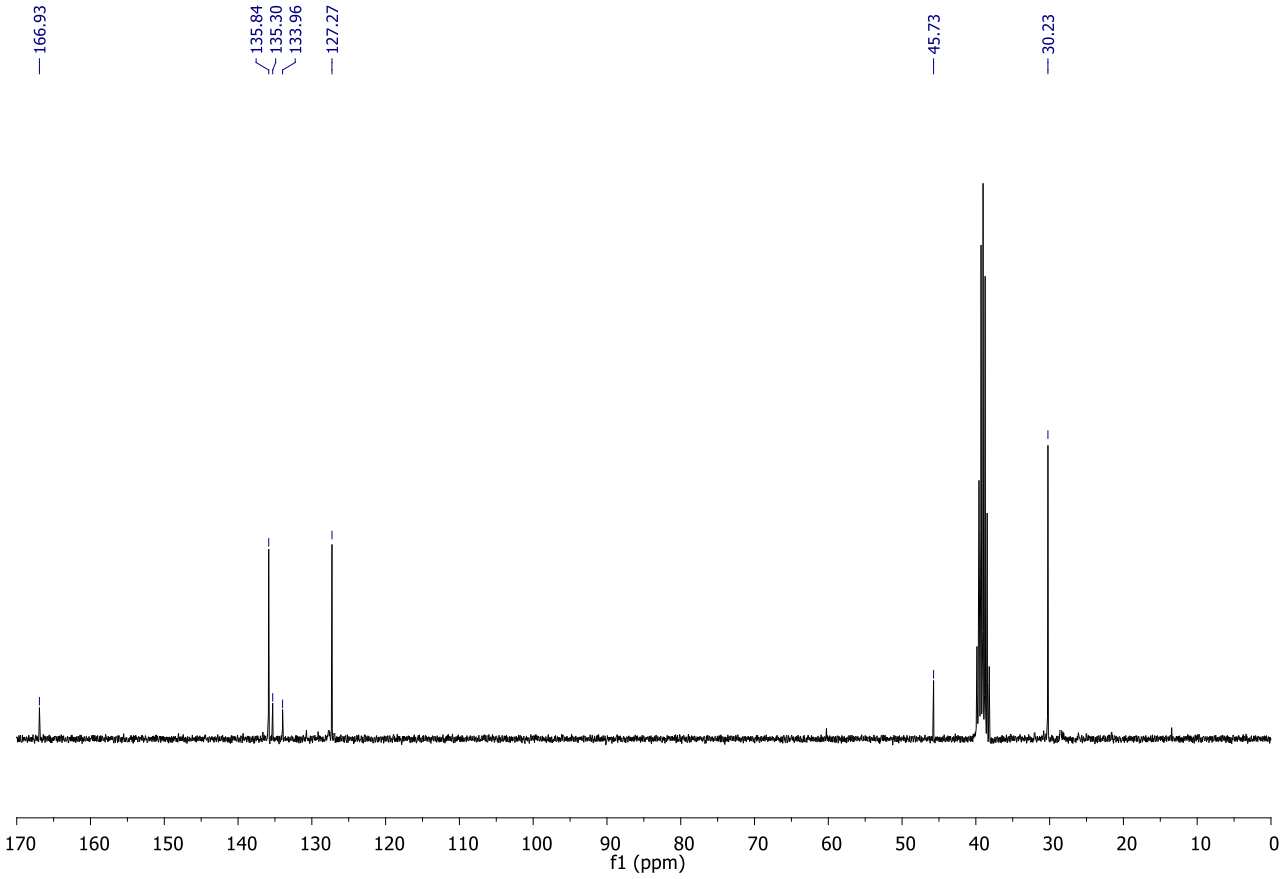
153.40
137.61
136.06
133.10
133.01
126.61
125.39
122.67
121.13
118.02
112.87
f1 (ppm)

[In $(CD_3)_2SO$*]


7.99
7.82
7.79
7.51
7.51
7.49
7.48
7.39
O
NH2
S
5oi
1.20
7.87
7.85
7.57
7.56
7.54
7.54
2.29
2.00
7.90
7.80
7.70
7.60
f1 (ppm)
*
1.00
2.29
2.00
0.95
9.08
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)


166.93
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135.30
133.96
127.27
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30.23
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)