Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information for

Dual role of Cu_2O nanocubes as templates and networking catalysts for hollow and microporous Fe-porphyrin networks

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Experimental Sections

SEM and TEM images were obtained using a FE-SEM (JSM6700F) and a JEOL 2100F unit operated at 200kV, respectively. The N_2 adsorption-desorption isotherm (77 K) was measured using a BELSORP II-mini equipment. Pore size analysis was performed by the DFT method. PXRD patterns were obtained using a Rigaku MAX-2200 operating with filtered Cu-Ka radiation. Infrared absorption spectra were recorded using a Bruker VERTEX 70 FT-IR spectrometer. The absorption spectra were obtained from diffuse reflectance spectroscopy using a SHIMADZU UN-3600. The solid phase ^{13}C-NMR spectroscopy (CPTOSS) was conducted using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University utilizing a 4 mm magic angle spinning probe. X-ray photoelectron spectroscopy was conducted using a Thermo VG spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a 500 MHz Varian spectrometer. Elemental analysis was performed using a CE EA1110 elemental analyzer. Inductively coupled plasma mass spectroscopy was performed using a Shimadzu ICPS-1000IV.

Synthetic procedure for H-MFePN

Cu_2O nanocubes were prepared by the synthetic procedures in the literature.[1] In our work, Cu_2O nanocubes were prepared by the following procedures. In a 500 mL flask, trisodium citrate dehydrate aqueous solution (0.90 M, 2.0 mL) was added to water (400 mL). This solution was stirred for 20 min. $CuSO_4$ aqueous solution (1.2 M, 2.0 mL) was added to the solution. After stirring for 5 min, NaOH aqueous solution (4.8 M, 2.0 mL) was added to form $Cu(OH)_2$ precipitates. After stirring for 5 min, ascorbic acid aqueous solution (1.2 M, 2.0 mL) was added to induce color change from turbid blue to orange. After stirring for 30 min, Cu_2O nanocubes were retrieved by centrifugation, washed with water and methanol, and dried under vacuum.

Fe(III)Cl-5,10,15,20-tetrakis(4-ethynylphenyl)porphyrin was prepared by the synthetic procedure in the literature.[2] In our work, the following procedures were applied. 5,10,15,20-Tetrakis(4-ethynylphenyl)porphyrin (0.23 g, 0.32 mmol) and $FeCl_3$•$6H_2O$ (0.43 g, 1.6 mmol) were added to DMF (50 mL). The mixture was stirred for 12 h at 180 ^{o}C. After being cooled room temperature, the reaction mixture was added to 6 N HCl solution (100 mL). The mixture was stirred for 3 min to remove excess $FeCl_3$•$6H_2O$. The precipitates were retrieved by centrifugation and dissolved in methylene chloride. The solution was washed with 1 N HCl and water and dried with $MgSO_4$. After

solvent evaporation, the obtained solid was dissolved in a small amount of methylene chloride. The solution was poured into hexane to precipitates and the powder was retrieved by centrifugation and dried under vacuum.

1,4-Diazidobenzene was prepared by the synthetic procedures in the literature.[3] In our work, the following synthetic procedures were applied. In a flame dried Schlenk flask equipped with a condenser, 1,4-diiodobenzene (1.0 g, 3.0 mmol), NaN_3 (0.47 g, 7.3 mmol), $CuSO_4$ (48 mg, 0.30 mmol), L-ascorbic acid (0.11 g, 0.61 mmol), Na_2CO_3 (0.21 g, 2.0 mmol), and L-proline (0.23 g, 2.0 mmol) were added to a mixture of DMSO (9 ml) and H_2O (1 ml) under argon. The reaction mixture was heated at 65 ^oC for 24 h. After being cooled to room temperature, the product was extracted with EtOAc (200 ml), washed with H_2O (100 ml), and dried over $MgSO_4$. After evaporating solvent, the product was purified by a flash column chromatography. The 1,4-diazidobenzene is light-sensitive and should be kept in the dark.

For the preparation of Cu_2O@MFePN, Cu_2O nanocubes (0.15 g) were added to a mixture of DMSO (31 mL) and water (4 mL) in a flame-dried 50 mL Schlenk flask under argon. The reaction mixture was sonicated for 1 h. Fe(III)Cl-5,10,15,20-tetrakis(4-ethynylpheyl)porphyrin (21 mg, 0.026 mmol) and 1,4-diazidobenzene (8.3 mg, 0.052 mmol) were dissolved in DMSO (4 mL) and added to the reaction mixture. The reaction mixture was heated at 85 ^oC for 20 h. After being cooled to room temperature, the solid was retrieved by centrifugation, washed with acetone, THF, and hexane, and dried under vacuum. For the preparation of H-MFePN, Cu_2O@MFePN (0.15 g) was added to 1 N HCl solution (30 mL). Then, the reaction mixture was stirred for 30 min at room temperature. The resultant products were retrieved by centrifugation, washed with water, MeOH, DMF, and methylene chloride, and dried under vacuum.

Procedure for catalytic reactions and recycle tests

H-MFePN (7.0 mg, 4.8 μmol of Fe-porphyrin based on ICP-AES analysis, 0.68 mmol Fe/g of H-MFePN), amine (0.48 mmol), 1.4-dimethoxybenzene (13 mg, 0.096 mmol, internal standard), and acetone (3 mL) were added to a flame-dried 20 mL tube Schlenk flask under argon. Then, ethyl diazoacetate (0.48 mmol, 0.41 mL, 15% solution in toluene) was added to the reaction mixture. After stirring for 3 min at room temperature, the solution was filtered to remove H-MFePN catalysts and analyzed by 500 MHz ^1H and ^{13}C NMR spectroscopy. To obtain isolated yields, the products were purified by flash column chromatography. For the recycling tests, the catalysts were recovered by centrifugation, washed with acetone, methylene chloride, and hexane, dried under vacuum, and used for the next run. All products in Table 1 are known compounds in the literature.[4] ^1H and ^{13}C NMR spectra for the products obtained in our work are as follows. (Also, refer to Figure S3 in the ESI)

$C_5H_{10}NCH_2CO_2Et$ *(Entry 1~3 in Table 1)*: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, 3H, J = 7.1 Hz), 1.44 (m, 2H), 1.63 (m, 4H), 2.50 (m, 4H), 3.17 (s, 2H), 4.18 (q, 2H, J = 7.1 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3, 23.9, 25.8, 54.3, 60.4, 60.5, 170.6 ppm.

$Et_2NCH_2CO_2Et$ *(Entry 4 in Table 1)*: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (t, 6H, J = 7.2 Hz), 1.27 (t, 3H, J = 7.2 Hz), 2.66 (q, 4H, J = 7.2 Hz), 3.31 (s, 2H), 4.18 (q, 2H, J = 7.1 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.1, 14.2, 47.7, 54.2, 60.3, 171.5 ppm.

4-$MeOC_6H_4NHCH_2CO_2Et$ *(Entry 5 in Table 1)*: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, 3H, J = 7.1 Hz), 3.73 (s,

3H), 3.84 (s, 2H), 4.21 (q, 2H, J = 7.1 Hz), 6.57 (d, 2H, J = 8.3 Hz), 6.77 (d, 2H, J = 8.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 46.8, 55.7, 61.1, 114.4, 114.8, 141.2, 152.6, 171.4 ppm.

4-MeC$_6$H$_5$NHCH$_2$CO$_2$Et *(Entry 6 in Table 1)*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, 3H, J = 7.2 Hz), 2.55 (s, 3H), 3.89 (s, 2H), 4.17 (brs, 1H), 4.24 (q, 2H, J = 7.2 Hz), 6.55 (d, 2H, J = 8.3 Hz), 7.01 (d, 2H, J = 8.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 20.4, 46.3, 61.2, 113.0, 127.5, 129.8, 144.8, 171.3 ppm.

C$_6$H$_5$NHCH$_2$CO$_2$Et *(Entry 7-11 in Table 1)*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, 3H, J = 7.2 Hz), 3.88 (s, 2H), 4.23 (q, 2H, J = 7.2 Hz), 4.25 (broad s, 1H), 6.60 (d, 2H, J = 8.5 Hz), 6.74 (t, 1H, J = 8.5 Hz), 7.18 (t, 2H, J = 8.5 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 45.9, 61.3, 113.0, 118.2, 129.3, 147.1, 171.2 ppm.

4-BrC$_6$H$_4$NHCH$_2$CO$_2$Et *(Entry 12 in Table 1)*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, 3H, J = 7.0 Hz), 3.84 (s, 2H), 4.24 (q, 2H, J = 7.0 Hz), 4.33 (brs, 1H), 6.46 (d, 2H, J = 8.3 Hz), 7.25 (d, 2H, J = 8.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 45.7, 61.5, 109.9, 114.5, 132.0, 146.1, 170.8 ppm.

4-NCC$_6$H$_4$NHCH$_2$CO$_2$Et *(Entry 13 in Table 1)*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, 3H, J = 7.1 Hz), 3.92 (s, 2H), 4.26 (q, 2H, J = 7.0 Hz), 4.95 (brs, 1H), 6.57 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.4 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 44.8, 61.8, 99.7, 112.5, 120.2, 133.7, 150.2, 170.1 ppm.

4-NO$_2$C$_6$H$_4$NHCH$_2$CO$_2$Et *(Entry 14 in Table 1)*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, 3H, J = 7.1 Hz), 3.98 (s, 2H), 4.29 (q, 2H, J = 7.2 Hz), 5.12 (brs, 1H), 6.56 (d, 2H, J = 9.2 Hz), 8.12 (d, 2H, J = 9.2 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 44.9, 62.0, 111.5, 126.4, 138.8, 151.9, 169.8 ppm.

Reference

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Figure S1. Low magnification SEM and TEM images of Cu_2O nanocubes (a) and H-MFePN (b).

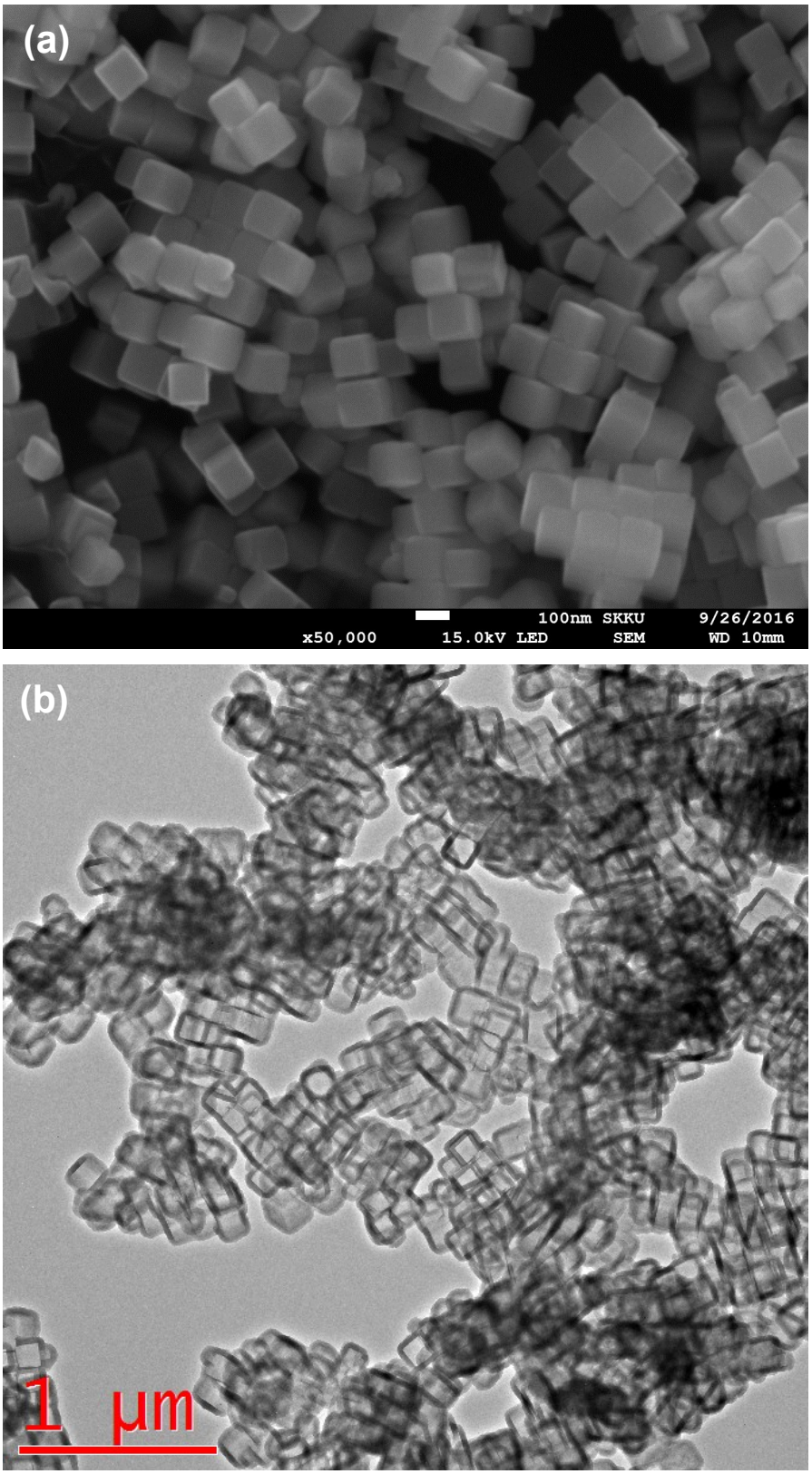


Figure S2. Magnified SEM images of Cu_2O@MFePN.

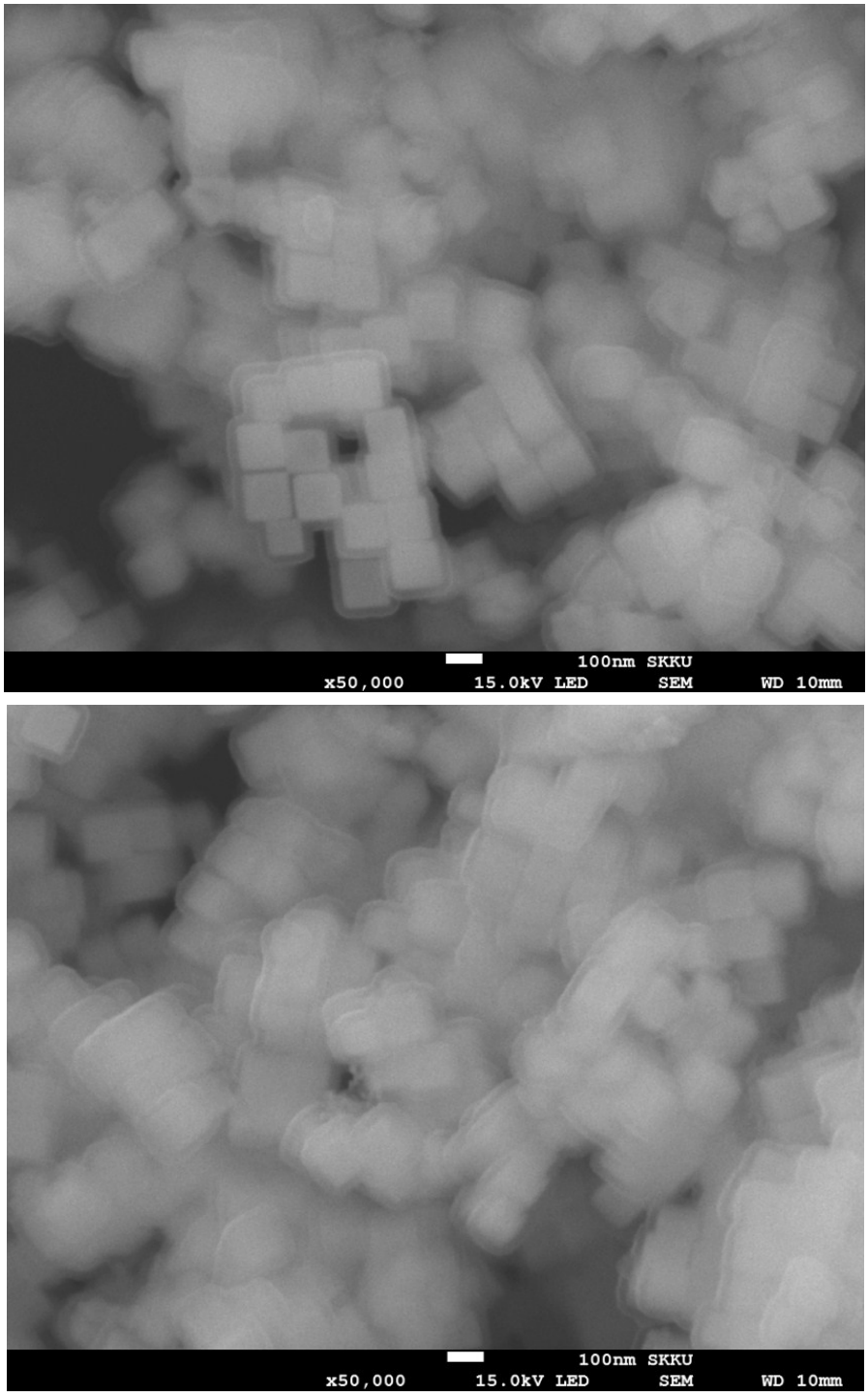
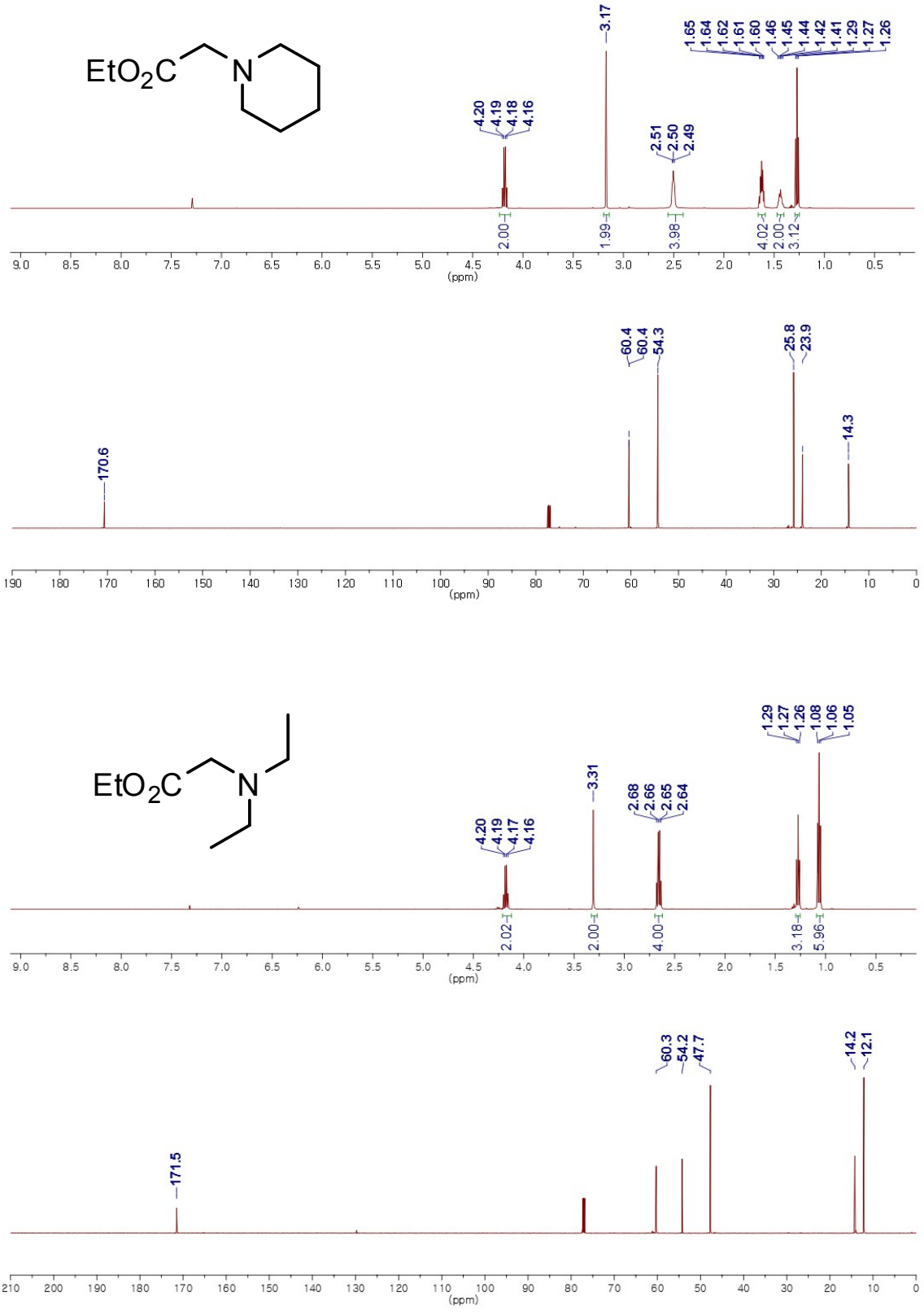
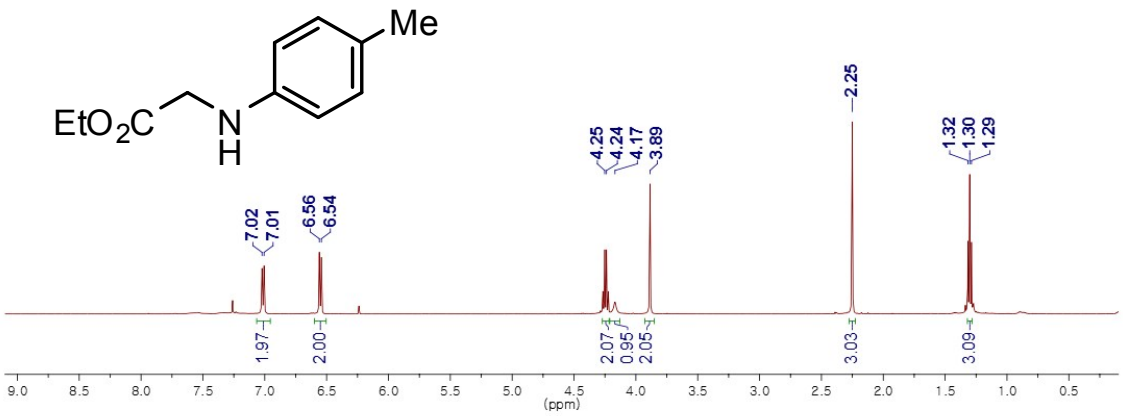
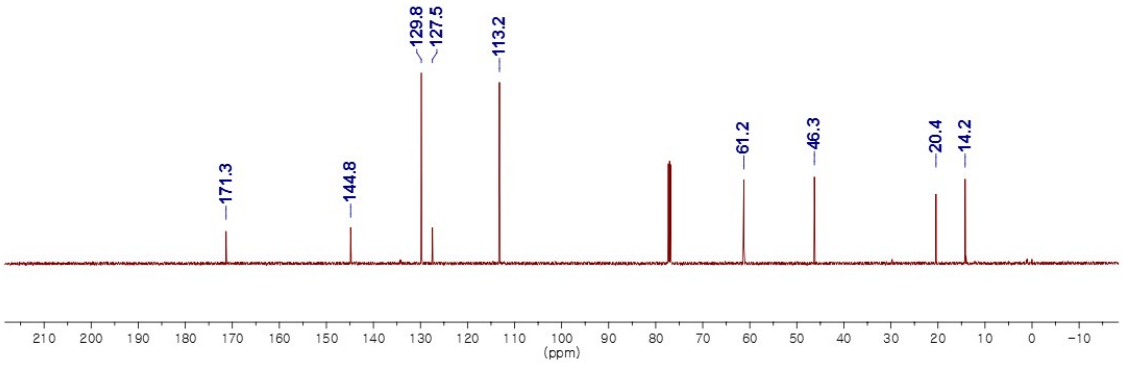
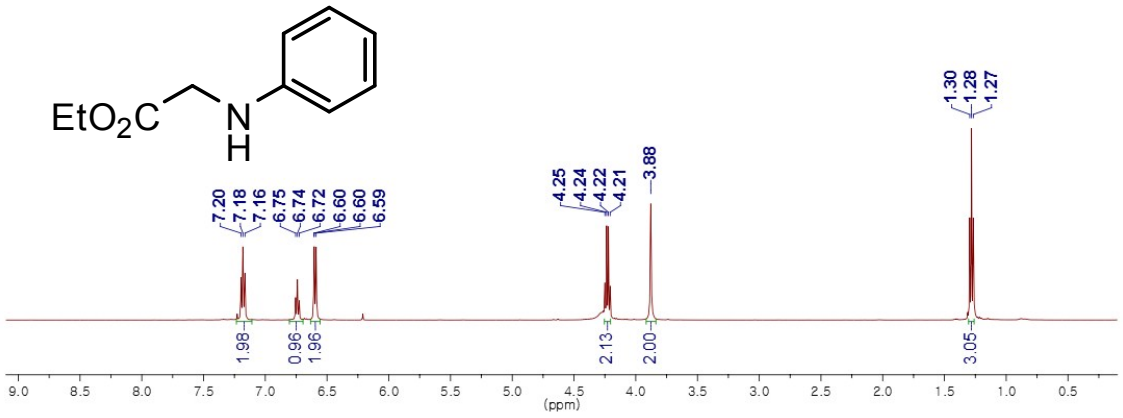


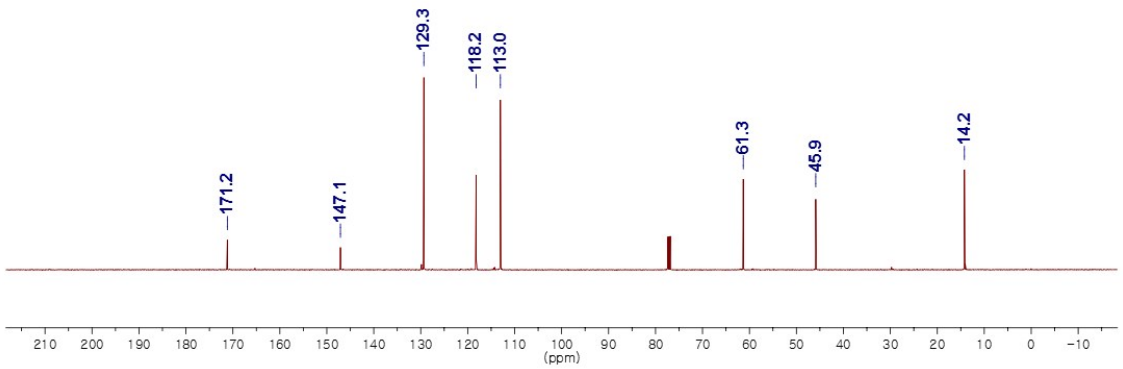
Figure S3. ^{1}H and ^{13}C NMR spectra of the isolated products in Table 1.

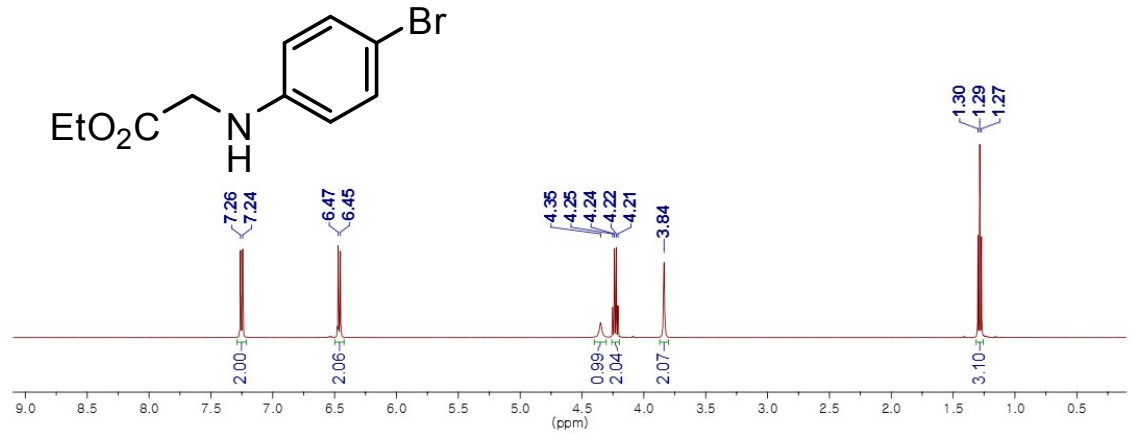


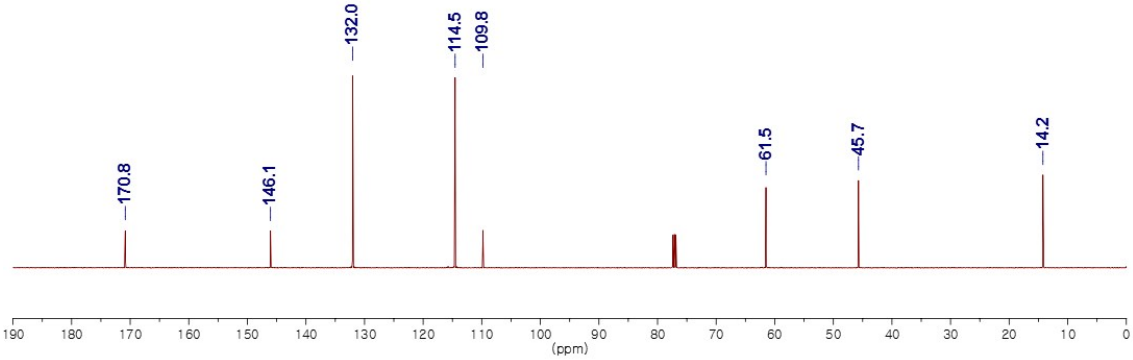

Me
EtO2C
N
H
7.02
7.01
6.56
6.54
4.25
4.24
4.17
3.89
2.25
1.32
1.30
1.29
1.97
2.00
2.07
0.95
2.05
3.03
3.09
(ppm)

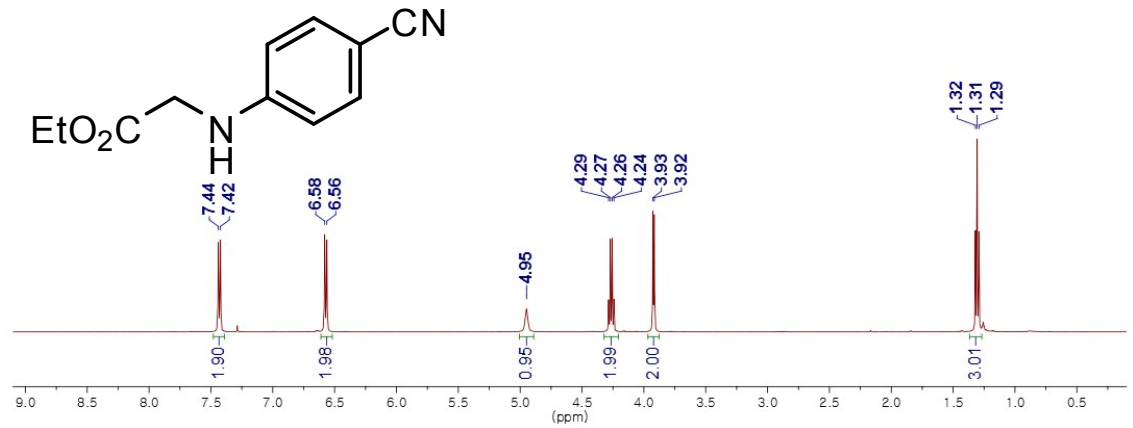

129.8
127.5
113.2
171.3
144.8
61.2
46.3
20.4
14.2
(ppm)

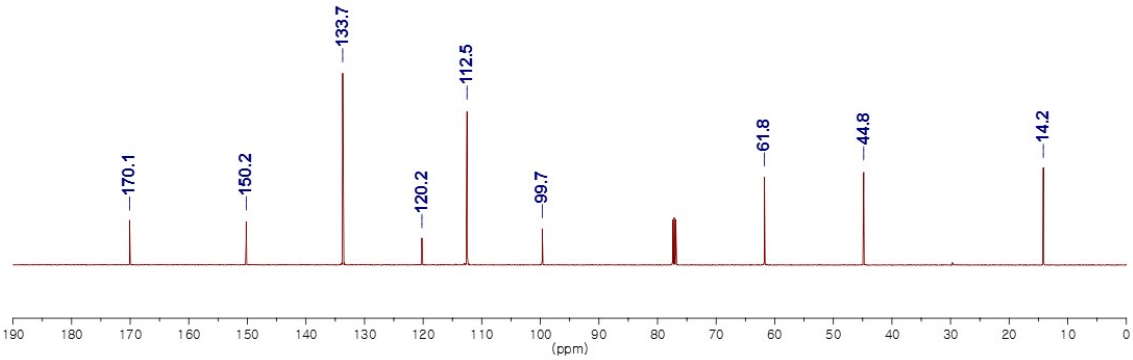

EtO2C
N
H
7.20
7.18
7.16
6.75
6.74
6.72
6.60
6.60
6.59
4.25
4.24
4.22
4.21
3.88
1.30
1.28
1.27
1.98
0.96
1.96
2.13
2.00
3.05
(ppm)

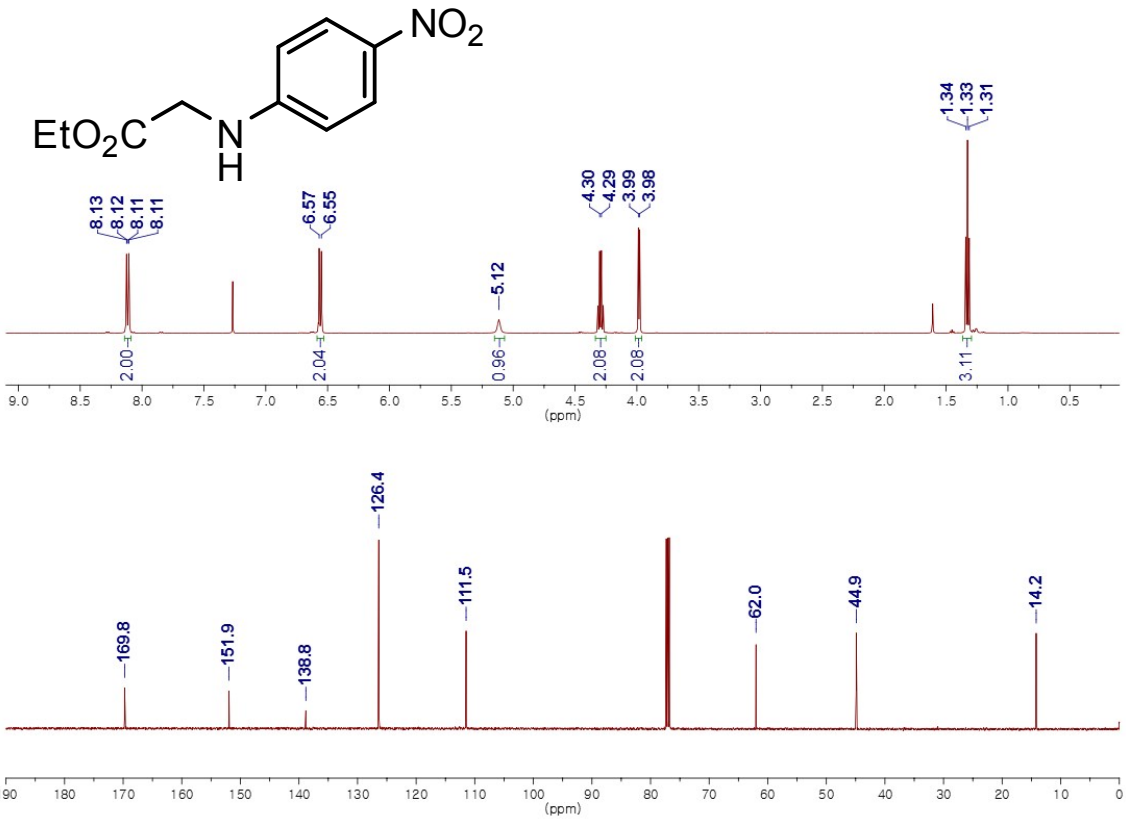

129.3
118.2
113.0
171.2
147.1
61.3
45.9
14.2
(ppm)


Br
EtO2C
N
H
7.26
7.24
6.47
6.45
4.35
4.25
4.24
4.22
4.21
3.84
1.30
1.29
1.27
2.00
2.06
0.99
2.04
2.07
3.10
(ppm)


132.0
114.5
109.8
170.8
146.1
61.5
45.7
14.2
(ppm)


CN
EtO2C
N
H
7.44
7.42
6.58
6.56
4.95
4.29
4.27
4.26
4.24
3.93
3.92
1.32
1.31
1.29
1.90
1.98
0.95
1.99
2.00
3.01
(ppm)


133.7
112.5
170.1
150.2
120.2
99.7
61.8
44.8
14.2
(ppm)


NO2
EtO2C
N
H
8.13
8.12
8.11
8.11
6.57
6.55
5.12
4.30
4.29
3.99
3.98
1.34
1.33
1.31
2.00
2.04
0.96
2.08
2.08
3.11
(ppm)
169.8
151.9
138.8
126.4
111.5
62.0
44.9
14.2
(ppm)