Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPORTING INFORMATION

Efficient and robust superparamagnetic copper ferrite nanoparticles-catalyzed sequential methylation and C-H activation: aldehyde-free propargylamine synthesis

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Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich, Acros, and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Quantachrome 2200e system. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer. Elemental analysis with atomic absorption spectrometry (AAS) was performed on an AA-6800 Shimadzu. Magnetic properties were measured with a EV11 vibrating sample magnetometer (VSM) at room temperature. Scanning electron microscopy studies were conducted on a JSM 7401F Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 100 kV.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC2010 Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis kept samples at 80 ^{o}C in 0.5 min; then heated samples from 80 to 100 ^{o}C at 20 ^{o}C/min and held them at 100 ^{o}C for 1.4 min; then heated them from 100 to 280 ^{o}C at 50 ^{o}C/min and held them at 280 ^{o}C for 2.5 min. Inlet and detector temperatures were set constant at 280 ^{o}C. Diphenyl ether was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μm). The temperature program for GC-MS analysis heated samples from 60 to 280 ^{o}C at 10 ^{o}C/min and held them at 280 ^{o}C for 10 min. Inlet temperature was set constant at 280 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library. The

^{1}H and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

Catalysts content

Experimental copper content = 27.72%

Experimental iron content = 49.9 %

Theoretical (copper: iron) molar ratio = 1:2

Experimental (copper: iron) molar ratio = $= \frac{Experimental\ iron\ content}{Theoretical\ iron\ content} =$ 1:2.1

Note: H was not found in the elemental analysis

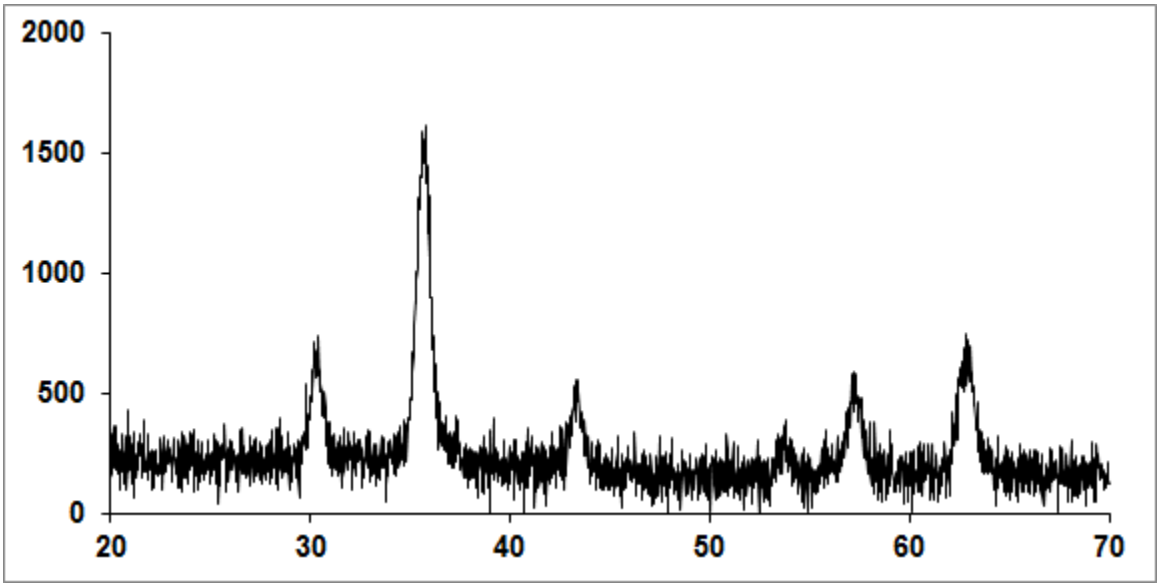


Fig. S1. X-ray powder diffractograms of the $CuFe_2O_4$

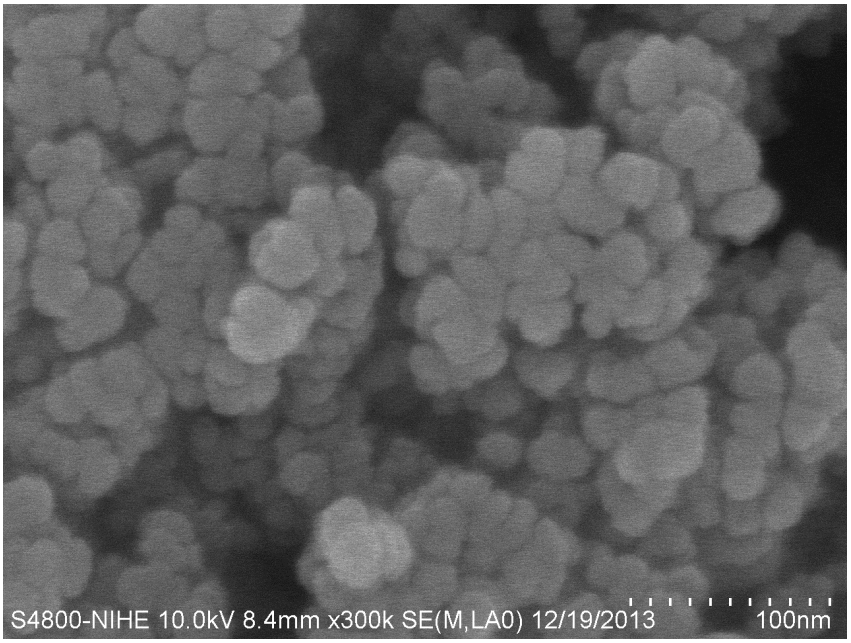


Fig. S2. SEM micrograph of the fresh $CuFe_2O_4$

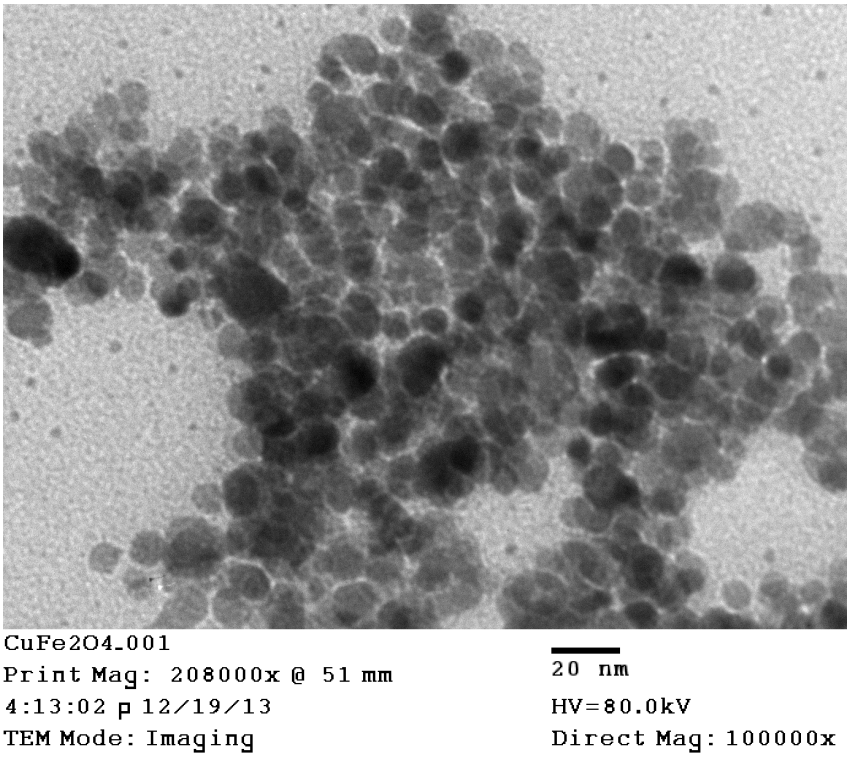


Fig. S3. TEM micrograph of the fresh $CuFe_2O_4$

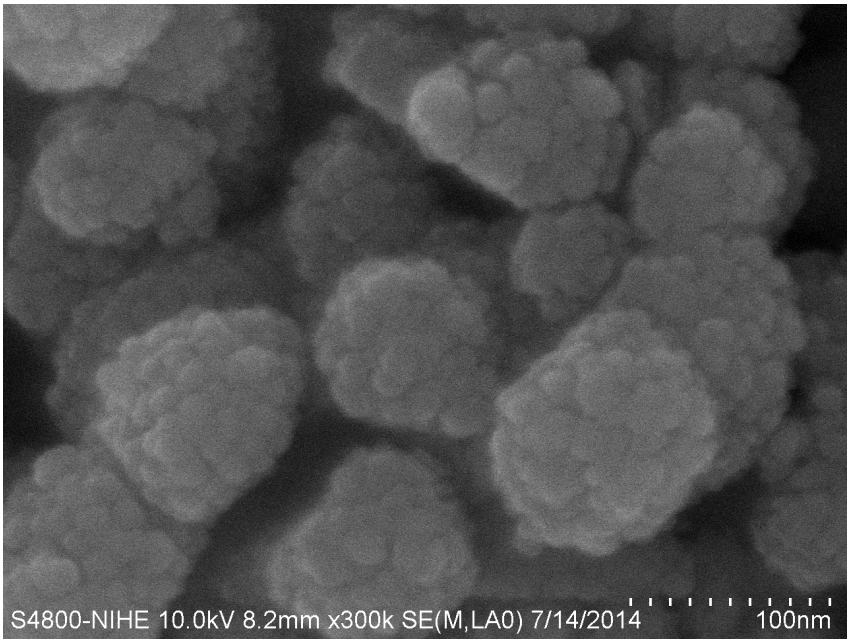


Fig. S4. SEM micrograph of the reused $CuFe_2O_4$ after 6th run

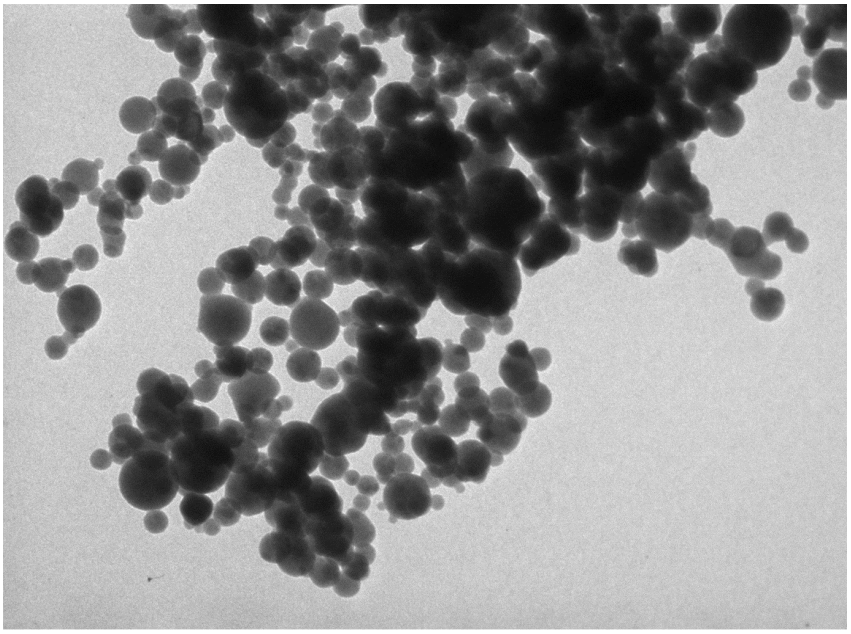


Fig. S5. TEM micrograph of the reused $CuFe_2O_4$ after 6th run

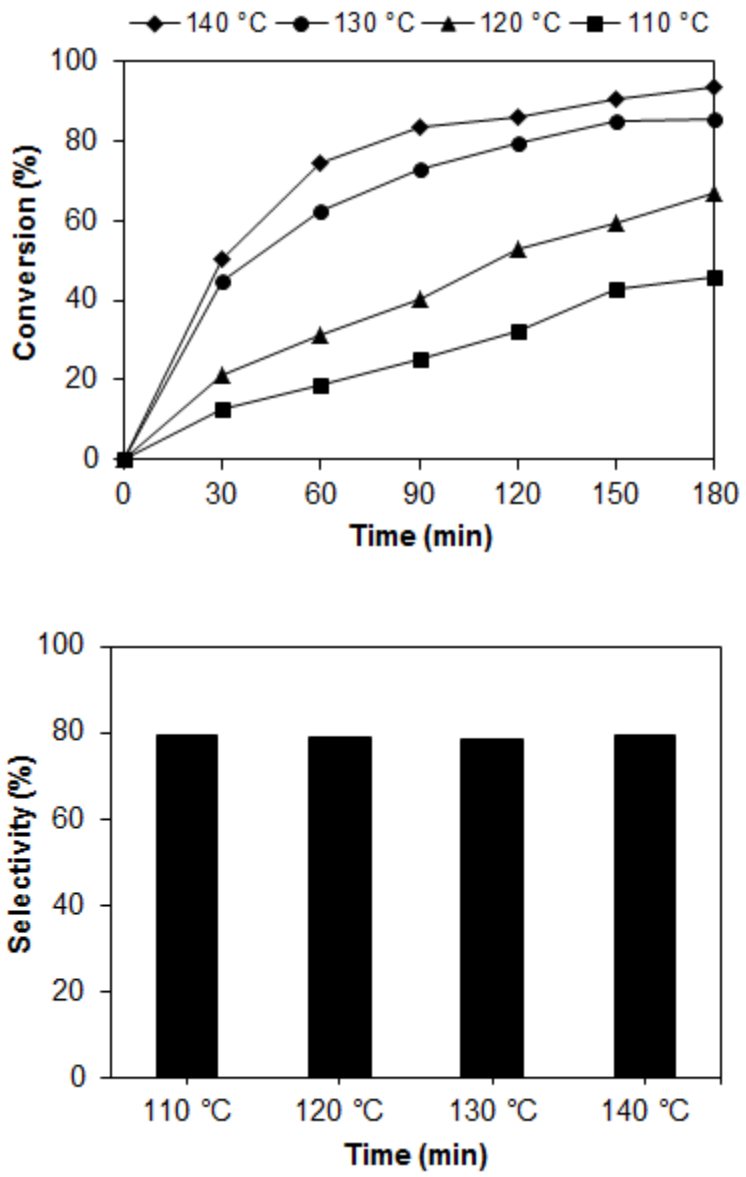


Fig. S6. Effects of different temperatures on the reaction conversion and selectivity

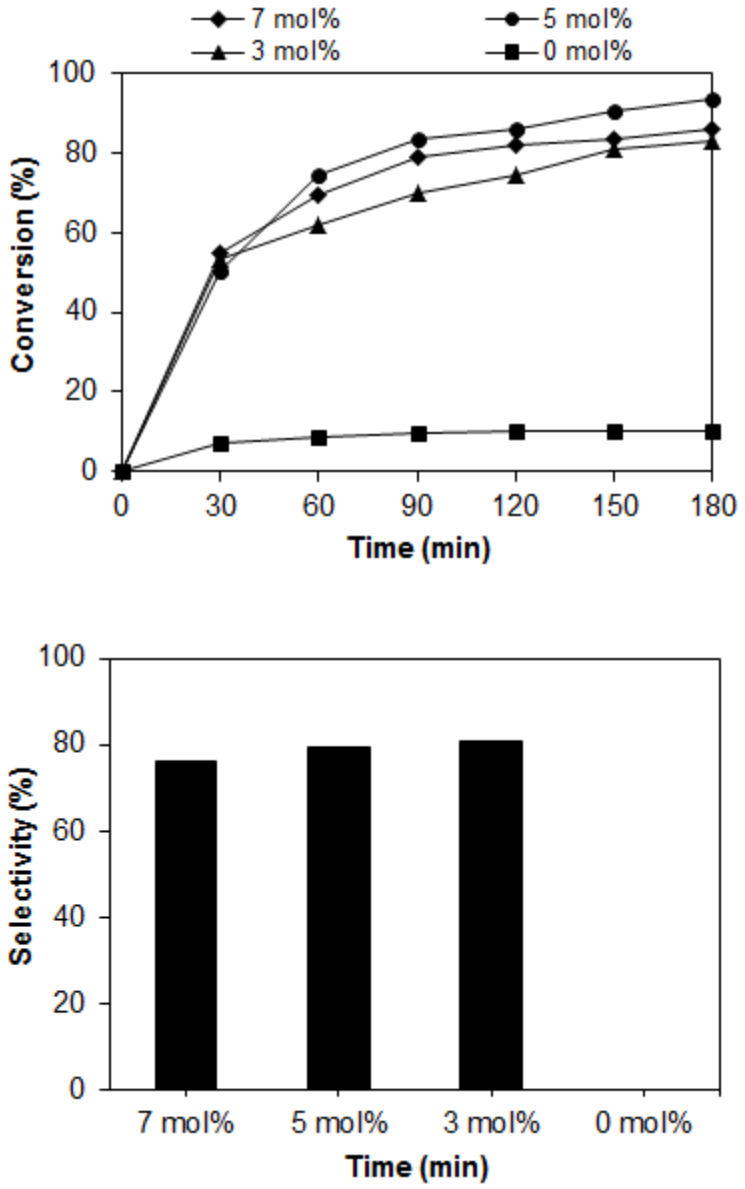


Fig. S7. Effects of amounts of catalyst on the reaction conversion and selectivity

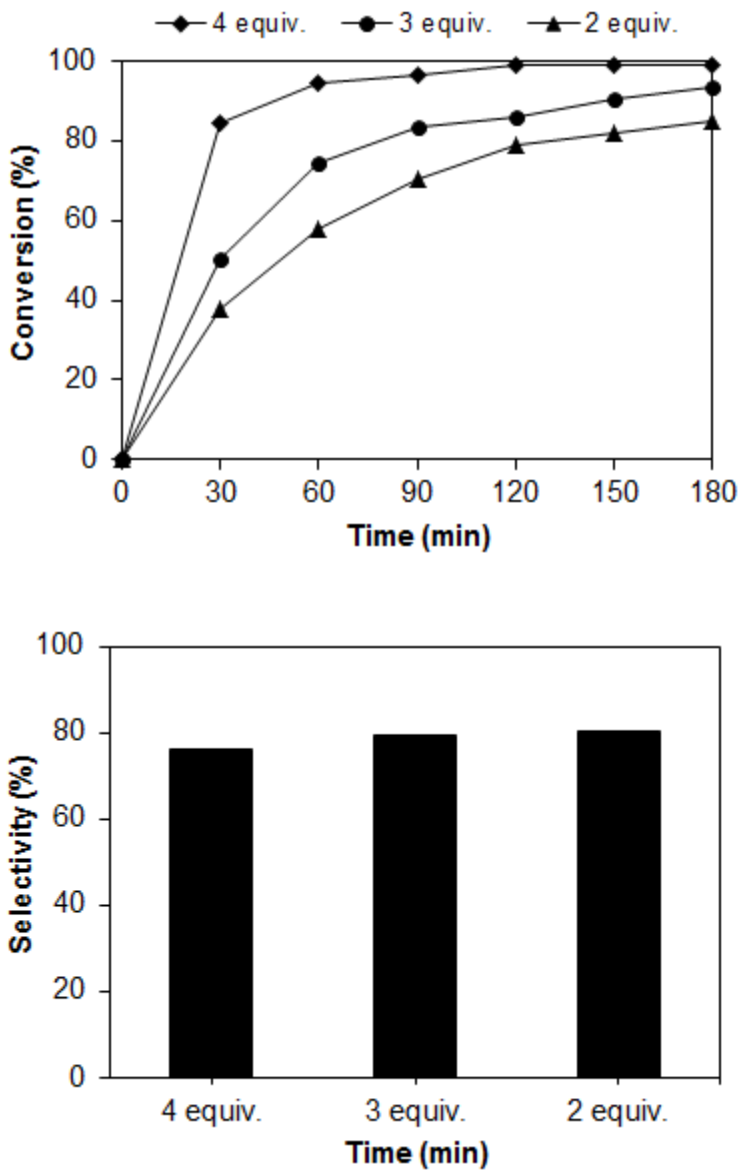


Fig. S8. Effects of amounts of oxidant on the reaction conversion and selectivity

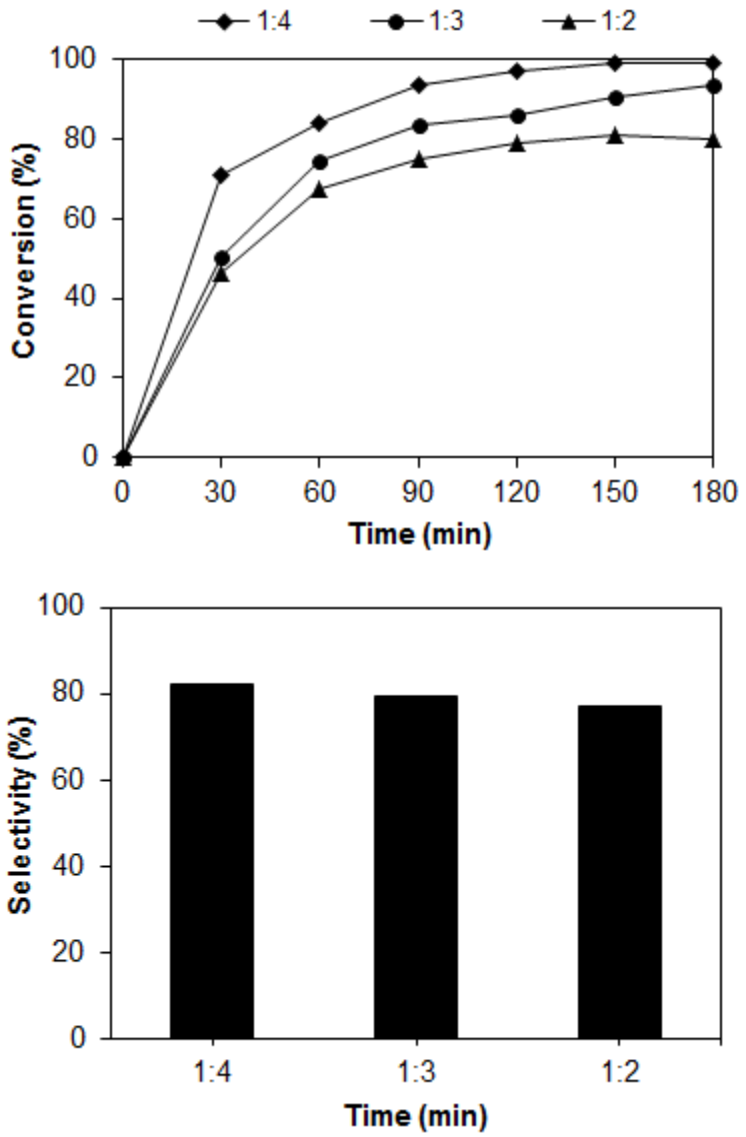


Fig. S9. Effects of phenylacetylene:N-methylanline molar ratio on the reaction conversion and selectivity

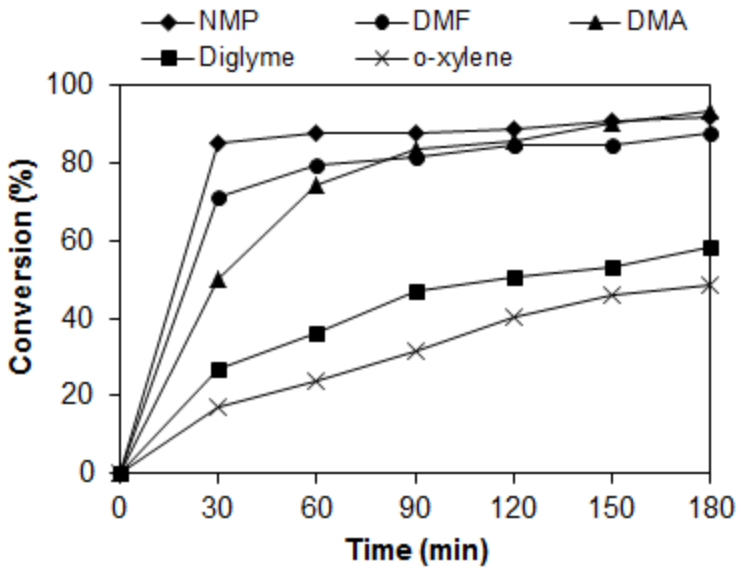


Fig. S10. Effects of different solvents on the reaction conversion to major product

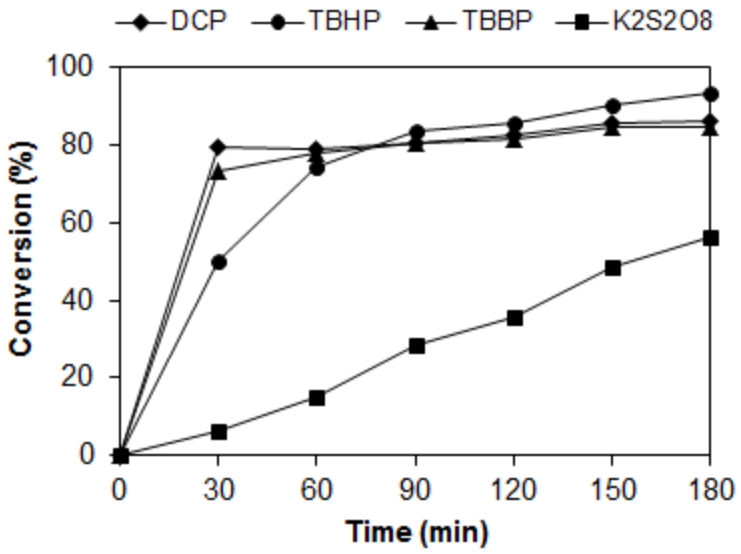
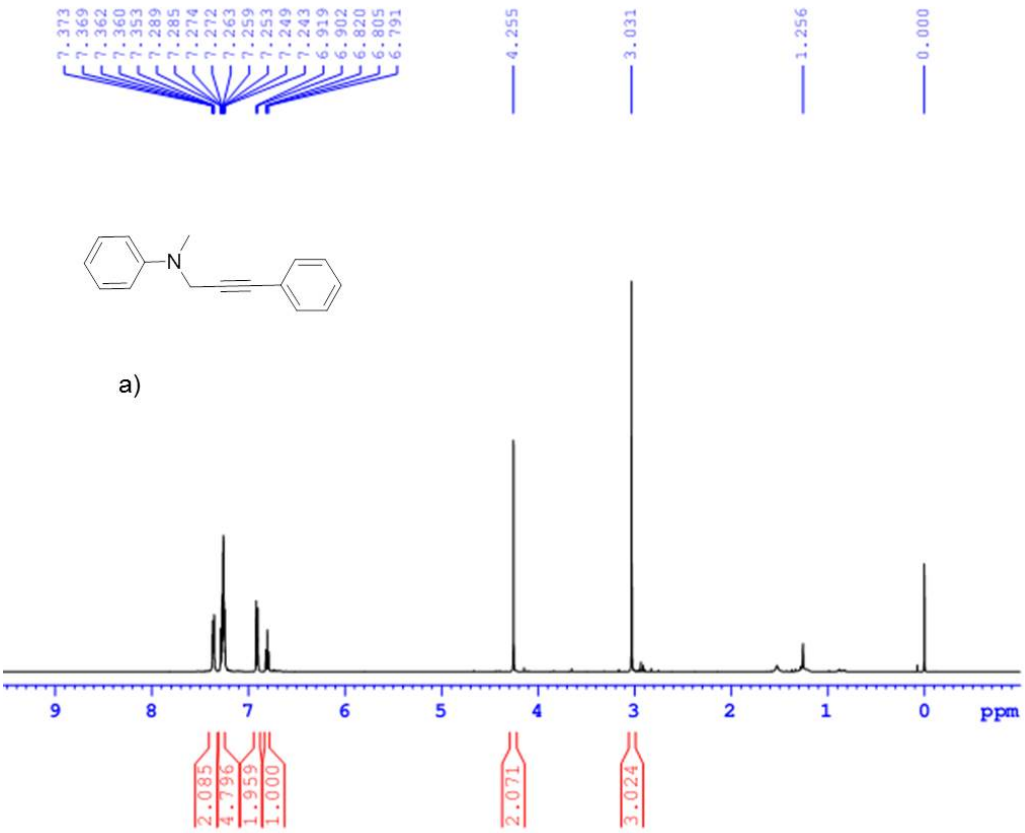


Fig. S11. Effects of different oxidants on the reaction conversion to major product

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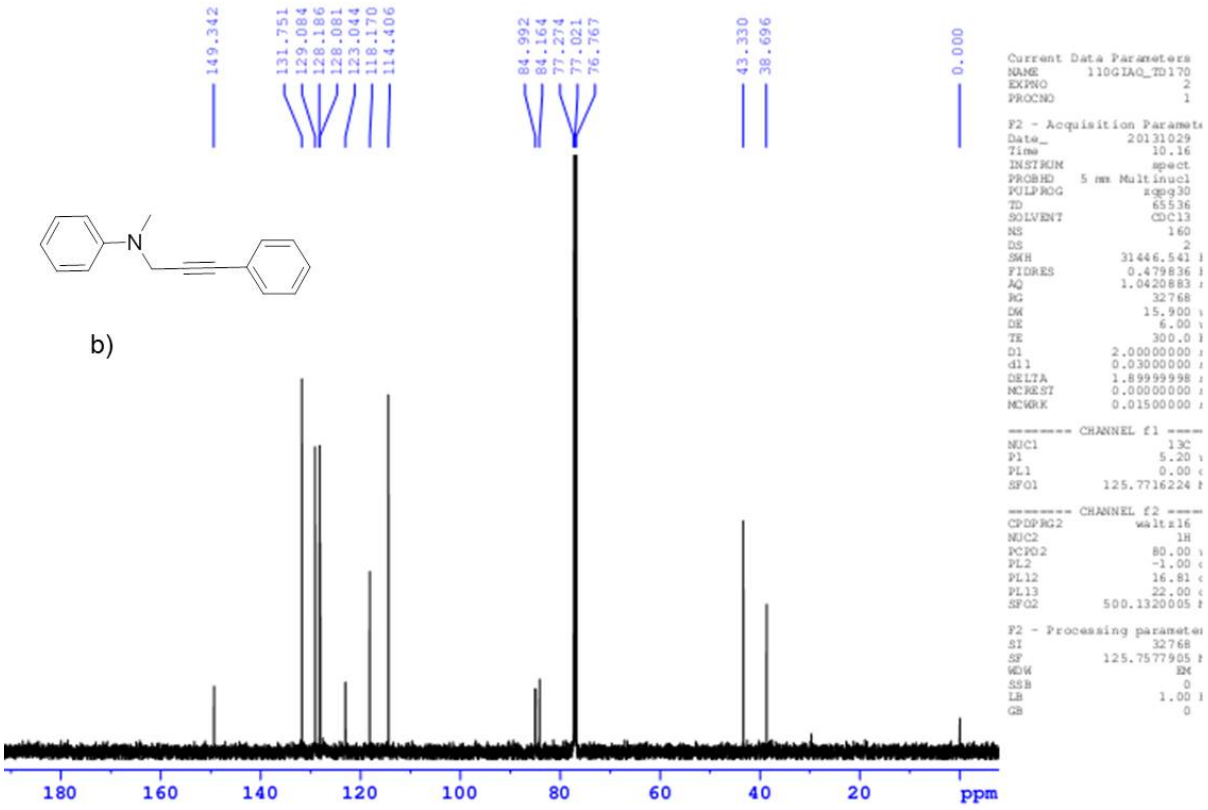
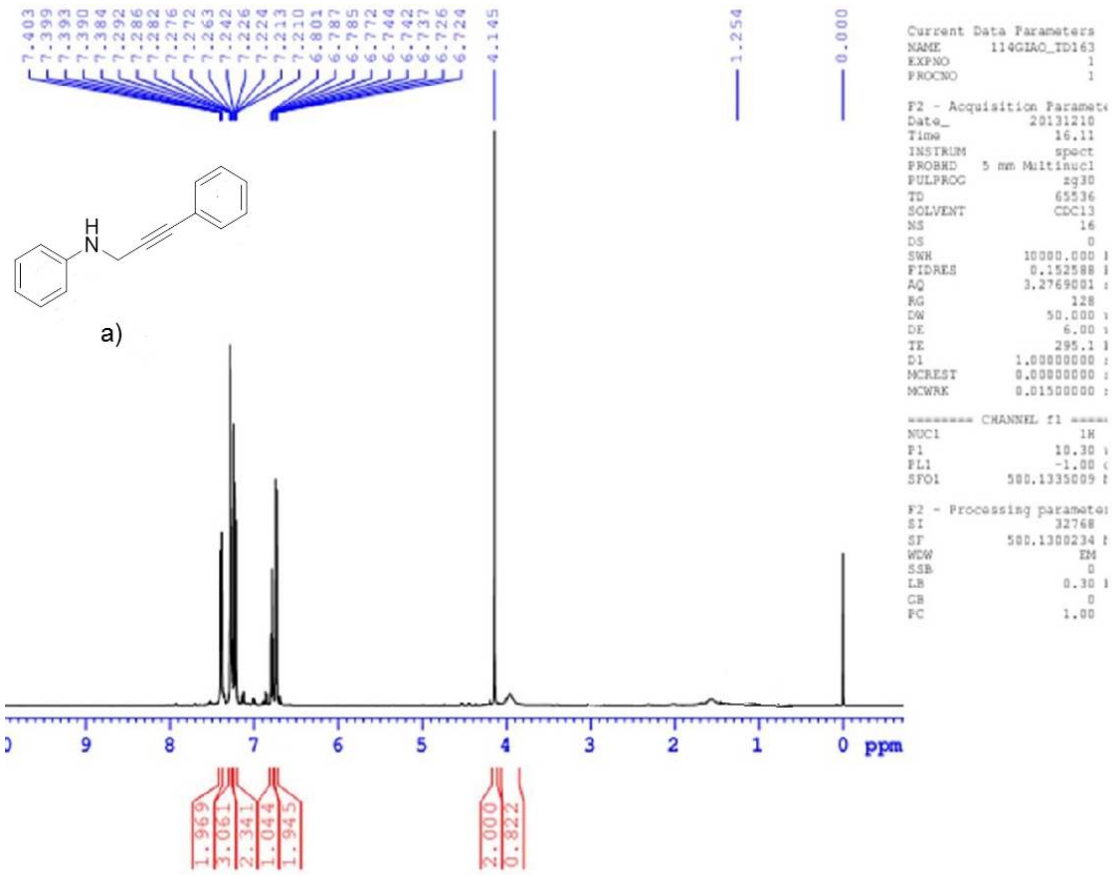


Fig. S12. ^{1}H NMR spectra a) and ^{13}C NMR b) of *N*-methyl-*N*-(3-phenylprop-2-nyl)benzenamine in $CDCl_3$

***N*-methyl-*N*-(3-phenylprop-2-ynyl)benzenamine (A)**. Phenylacetylene (0.11 mL, 1.0 mmol), *N*-Methylaniline (0.22 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (diethyl ether/hexane = 1:20), 144 mg yellow oil was obtained (70%). R_f = 0.30. This compound is known.[1] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.37-7.35 (m, 2H), 7.29-7.24 (m, 5H), 6.91 (d, *J*=8.5 Hz, 2H), 6.81 (t, *J*=7.3, 1H), 4.26 (s, 2H), 3.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): *δ* = 149.3, 131.8, 129.1, 128.2, 128.1, 123.0, 118.1, 114.4, 85.0, 84.2, 43.3, 38.7.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H
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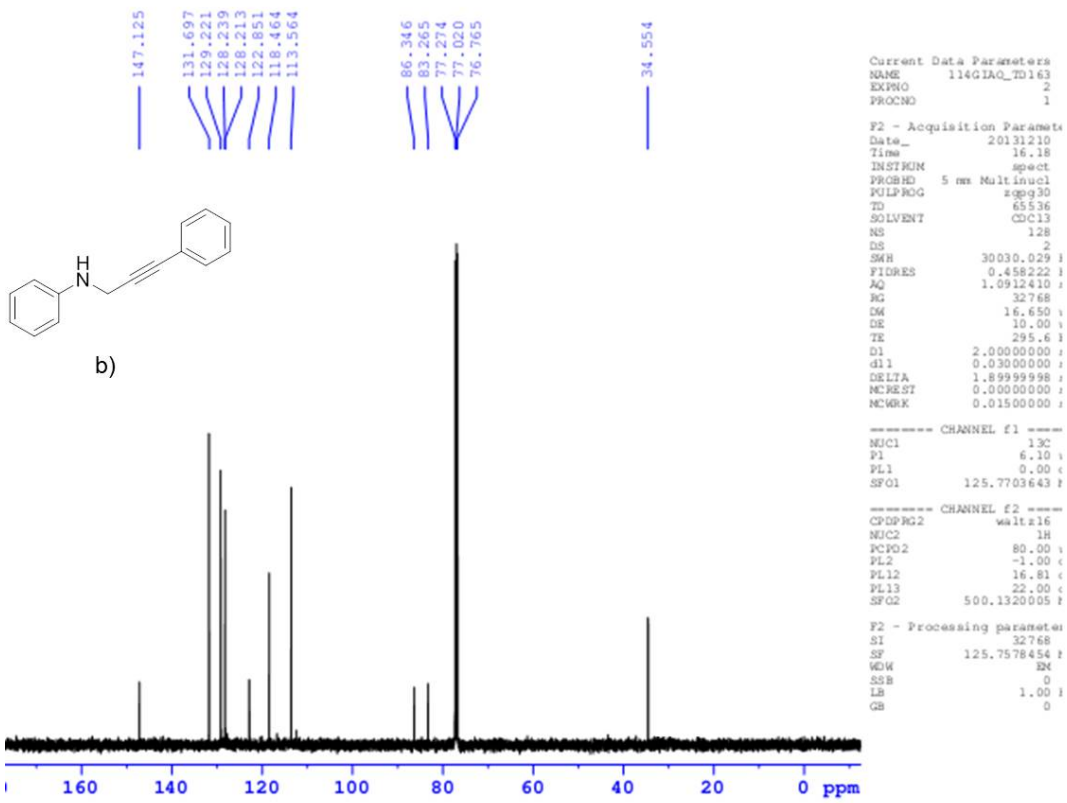
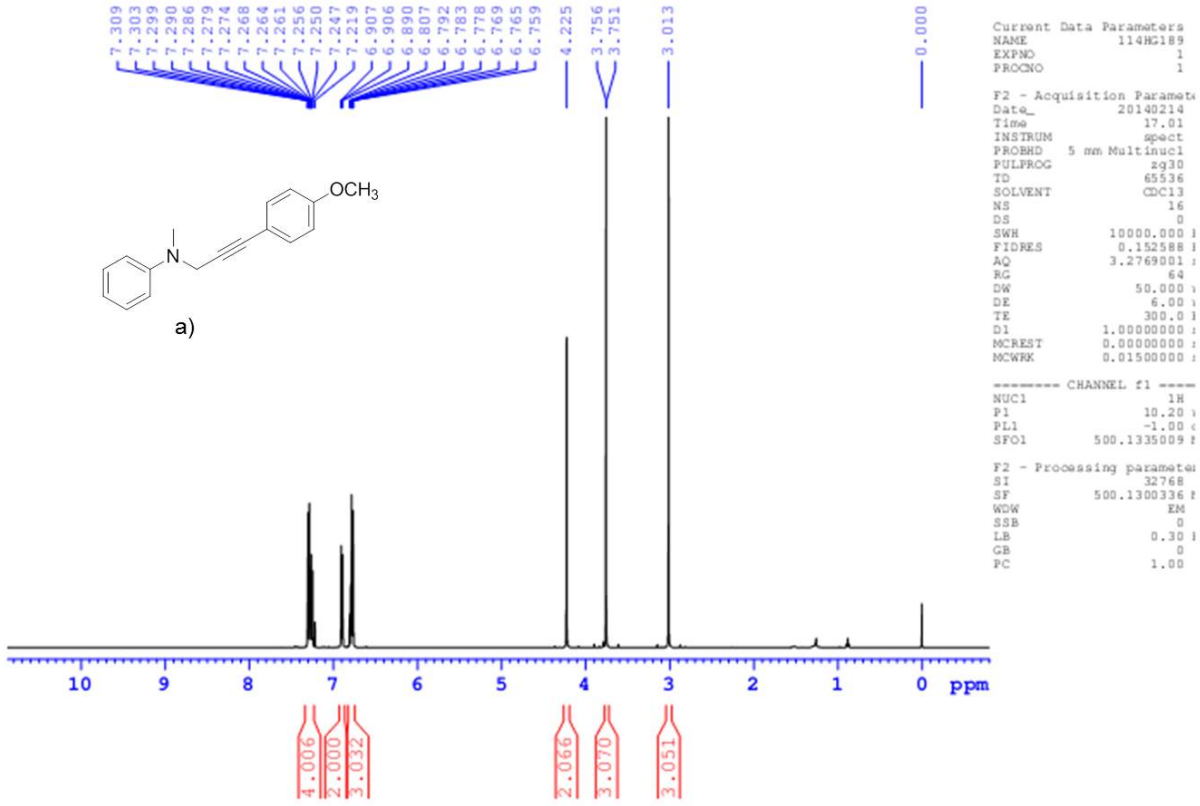


Fig. S13. ^{1}H NMR spectra a) and ^{13}C NMR b) of *N*-(3-phenylprop-2-nyl)benzenamine in $CDCl_3$

***N*-(3-phenylprop-2-ynyl)benzenamine (B)**. Phenylacetylene (0.11 mL, 1.0 mmol), *N*-Methylaniline (0.22 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (diethyl ether/hexane = 1:20), 29 mg yellow oil was obtained (10 %). R_f = 0.27. This compound is known.[2] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.40-7.38 (m, 2H), 7.29-7.27 (m, 3H), 7.24-7.21 (m, 2H), 6.80-6.77 (m, 1H), 6.74-6.72 (m, 1H), 4.15 (s, 2H), 4.00-3.90 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 147.1, 131.7, 129.2, 128.2, 128.2, 122.9, 118.5, 113.6, 86.3, 83.3, 34.6.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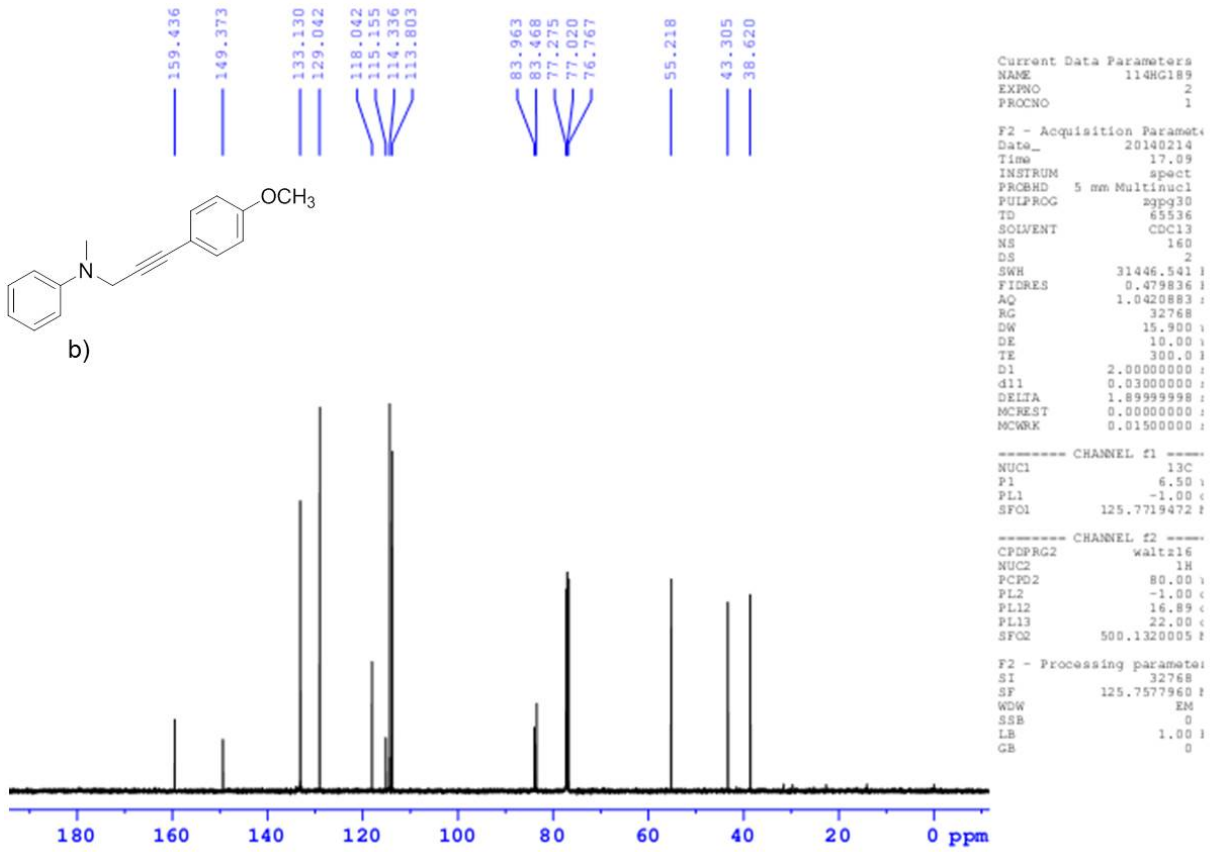
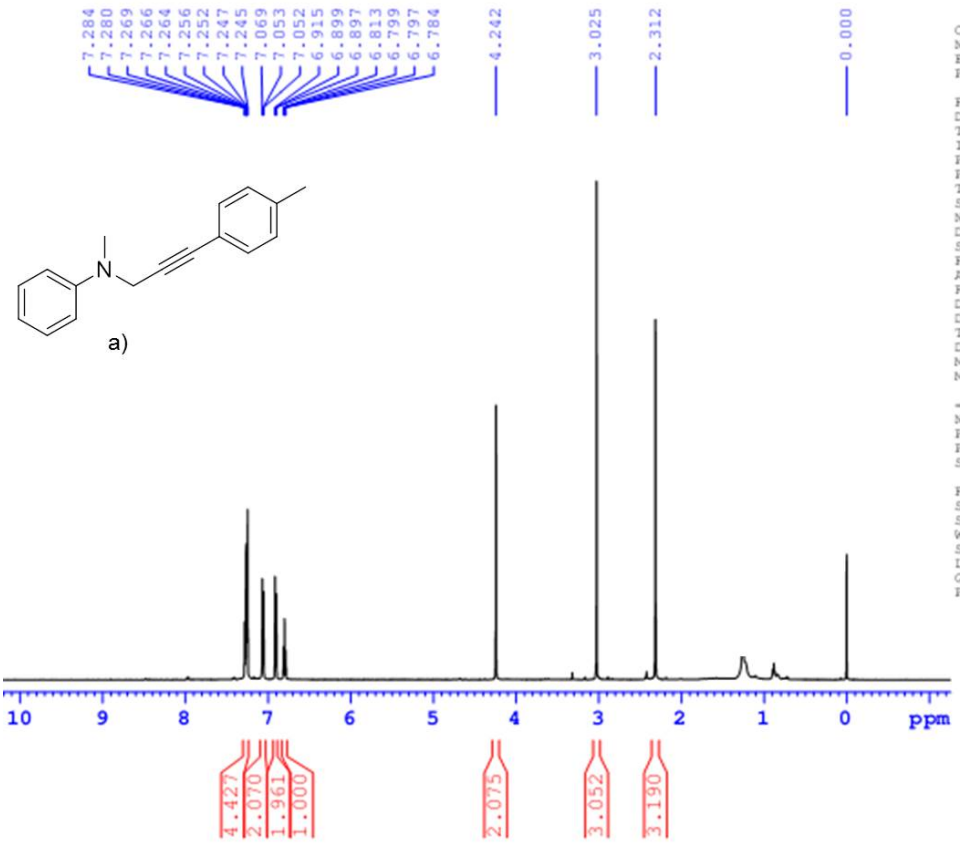


Fig. S14. ^{1}H NMR spectra a) and ^{13}C NMR b) of *N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-*N*-methylaniline in $CDCl_3$

***N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-*N*-methylaniline**. 4-ethynylanisole (0.13 mL, 1.0 mmol), *N*-Methylaniline (0.22 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (diethyl ether/hexane = 1:20), 186 mg pale white solid was obtained (74 %). R_f = 0.26. This compound is known.[1] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.31-7.24 (m, 4H), 6.90 (dd, *J*=8.0 Hz, *J*=1.0 Hz, 2H), 6.86-6.76 (m, 3H), 4.23 (s, 2H), 3.76 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 159.4, 149.4, 133.1, 129.0, 118.0, 115.2, 114.3, 113.8, 84.0, 83.5, 55.2, 43.3, 38.6.

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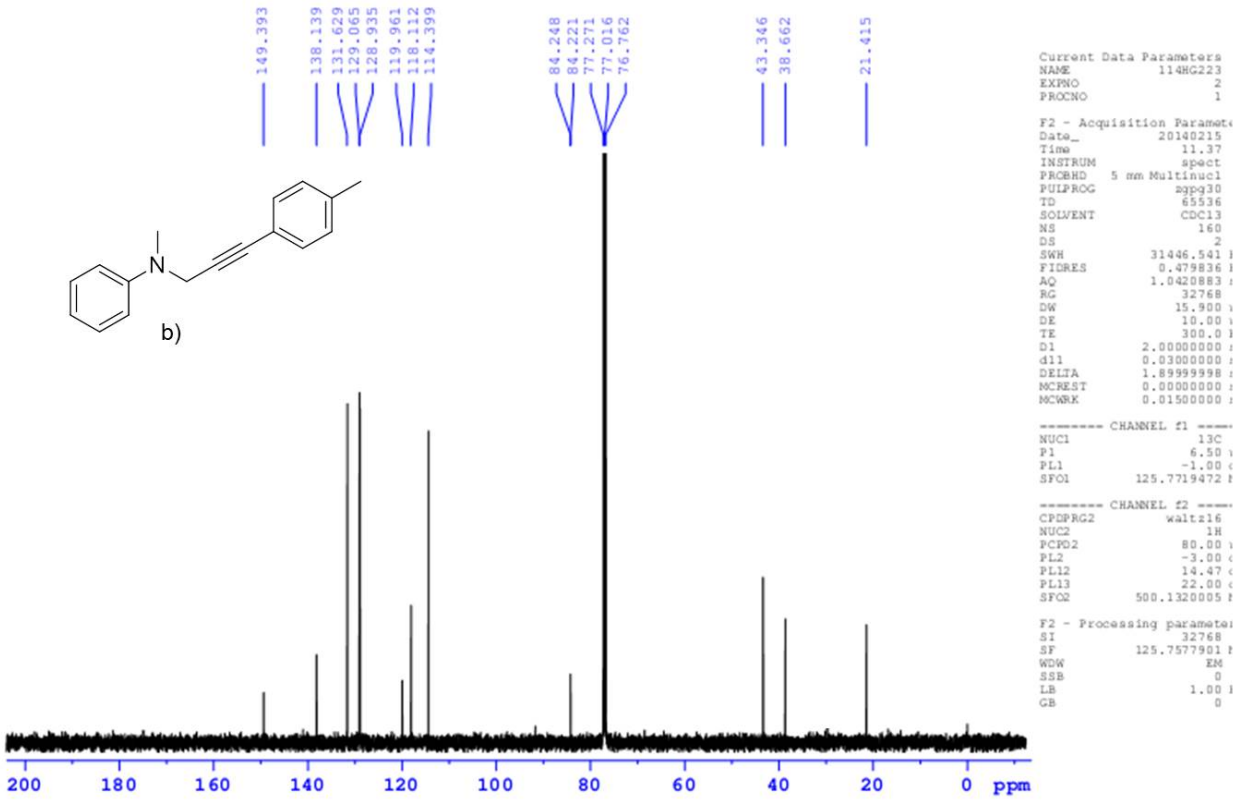
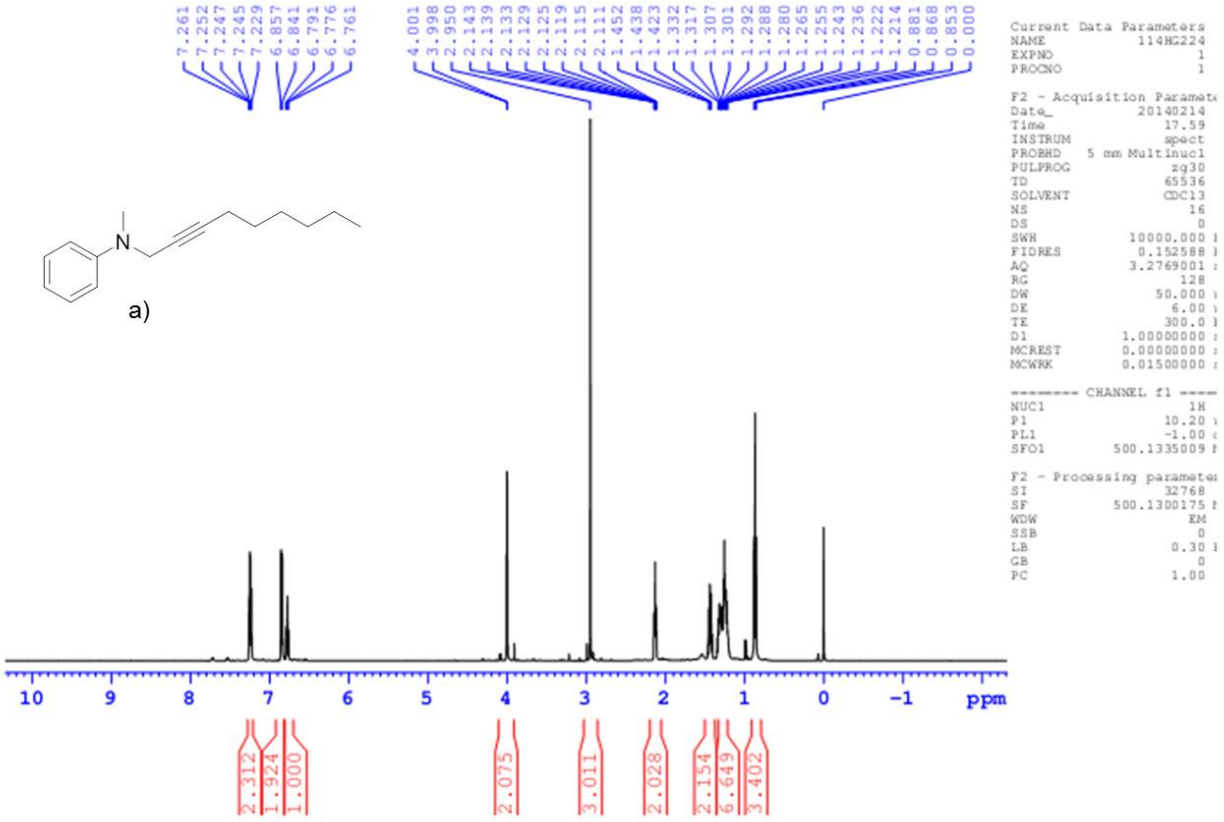


Fig. S15. ^{1}H NMR spectra a) and ^{13}C NMR b) of *N*-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)aniline in $CDCl_3$

***N*-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)aniline.** p-Tolylacetylene (0.11 mL, 1.0 mmol), *N*-Methylaniline (0.22 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (diethyl ether/hexane = 1:15), 172 mg yellow oil was obtained (73 %). R_f = 0.43. This compound is known.[1] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.28-7.25 (m, 4H), 7.06 (d, *J*=8.0 Hz, 2H), 6.90 (dd, *J*=8.0 Hz, *J*=1.0 Hz, 2H), 6.80 (t, *J*=7.8 Hz, 1H), 4.24 (s, 2H), 3.03 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 149.4, 138.1, 133.6, 129.1, 128.9, 120.0, 118.1, 114.4, 84.3, 84.2, 43.3, 38.7, 21.4.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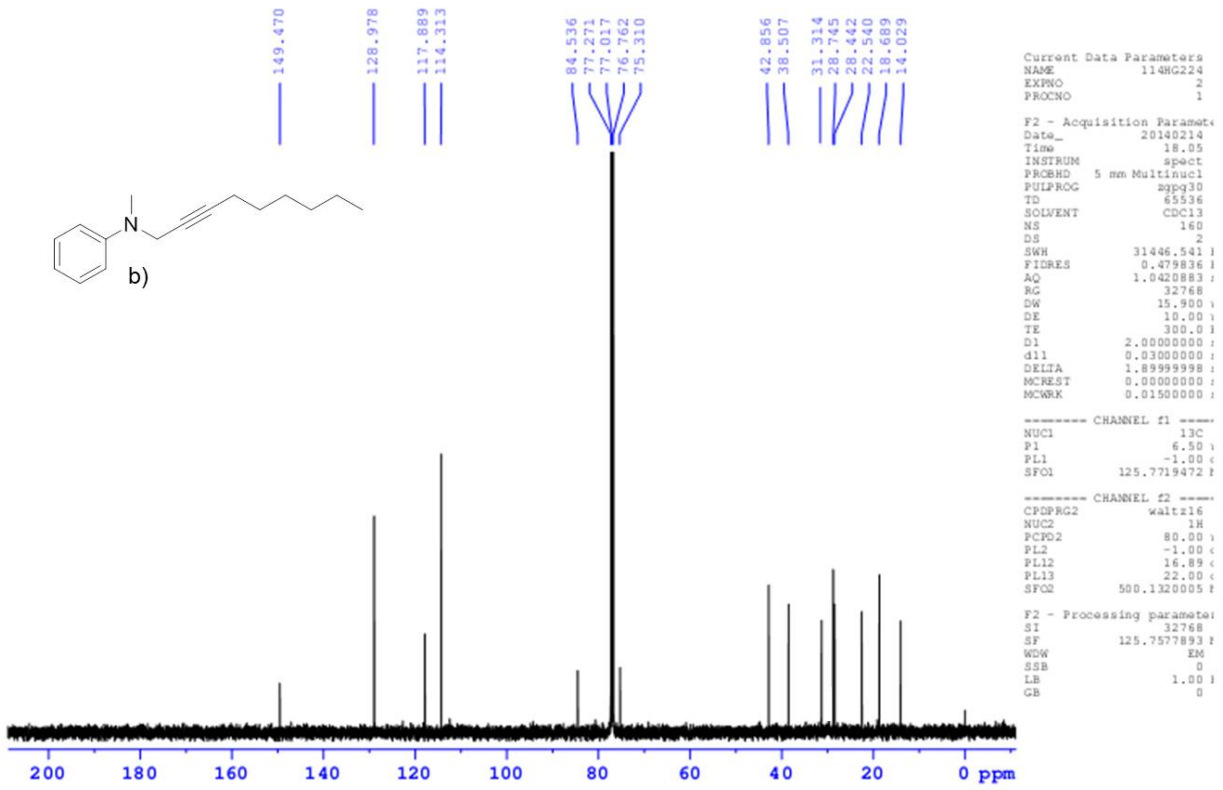

Fig. S16. ^{1}H NMR spectra a) and ^{13}C NMR b) of *N*-methyl-*N*-(non-2-yn-1-yl)aniline in $CDCl_3$

***N*-methyl-*N*-(non-2-yn-1-yl)aniline.** 1-octyne (0.15 mL, 1.0 mmol), *N*-Methylaniline (0.22 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (used hexane as eluent), 126 mg yellow oil was obtained (55 %). R_f = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.26-7.25 (m, 2H), 6.85 (d, J=8.0 Hz, 2H), 6.78 (t, *J*=7.5 Hz, 1H), 4.00 (s, 2H), 2.95 (s, 3H), 2.14-2.11 (m, 2H), 1.45-1.42 (m, 2H), 1.33-1.21 (m, 6H), 0.86 (t, *J*=7.0 Hz , 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 149.5, 129.0, 117.9, 114.3, 84.5, 75.3, 42.9, 38.5, 31.3, 28.7, 28.4, 22.5, 18.7, 14.0.

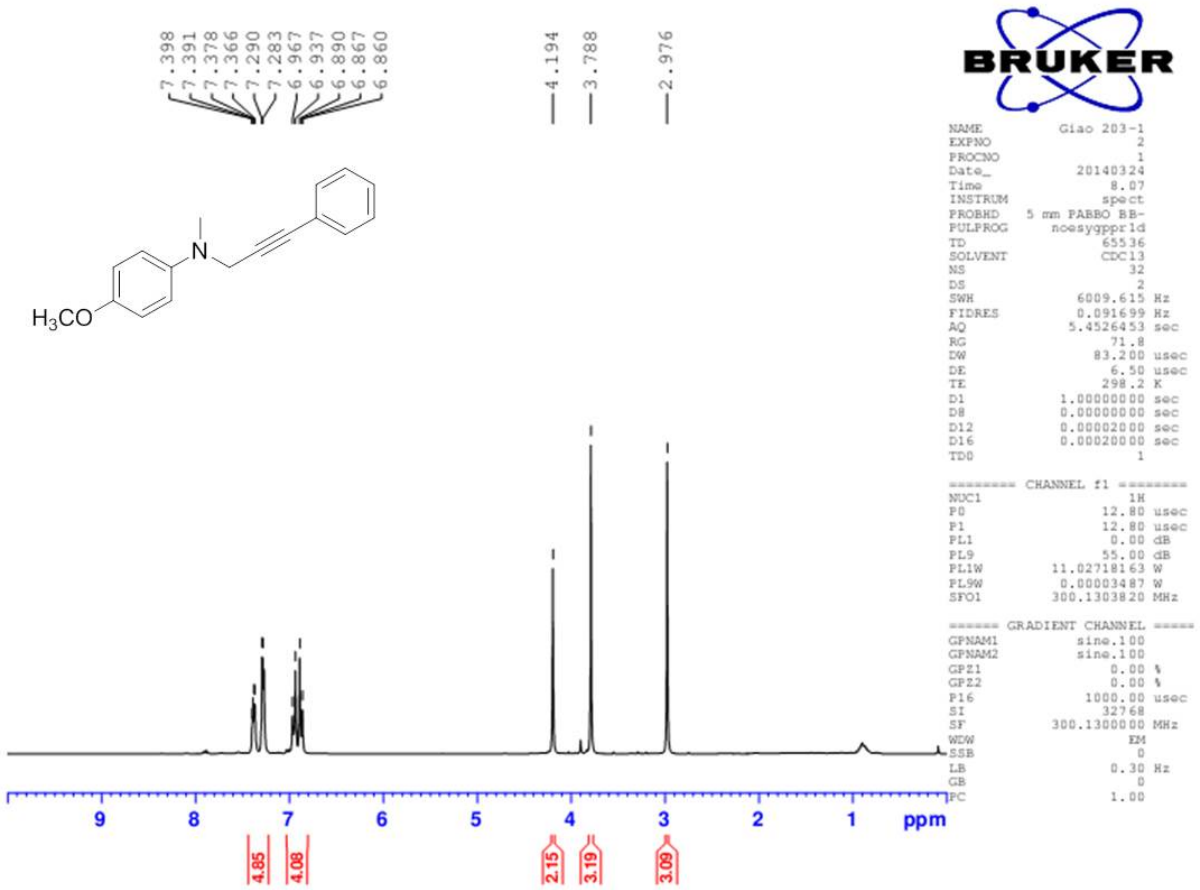

Fig. S17. ^{1}H NMR spectra of 4-methoxy-*N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline in $CDCl_3$

4-methoxy-*N*-methyl-N-(3-phenylprop-2-yn-1-yl)aniline. Phenylacetylene (0.11 mL, 1.0 mmol), *N*-methyl-p-anisidine (0.274g, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (ethyl acetate/hexane = 1: 9), 179 mg yellow oil was obtained (76 %). R_f =0.27. This compound is known.[3] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.40-7.28 (m, 5H), 6.97-6.86 (m, 4H), 4.19 (s, 2H), 3.79 (s, 3H), 2.98 (s, 3H).

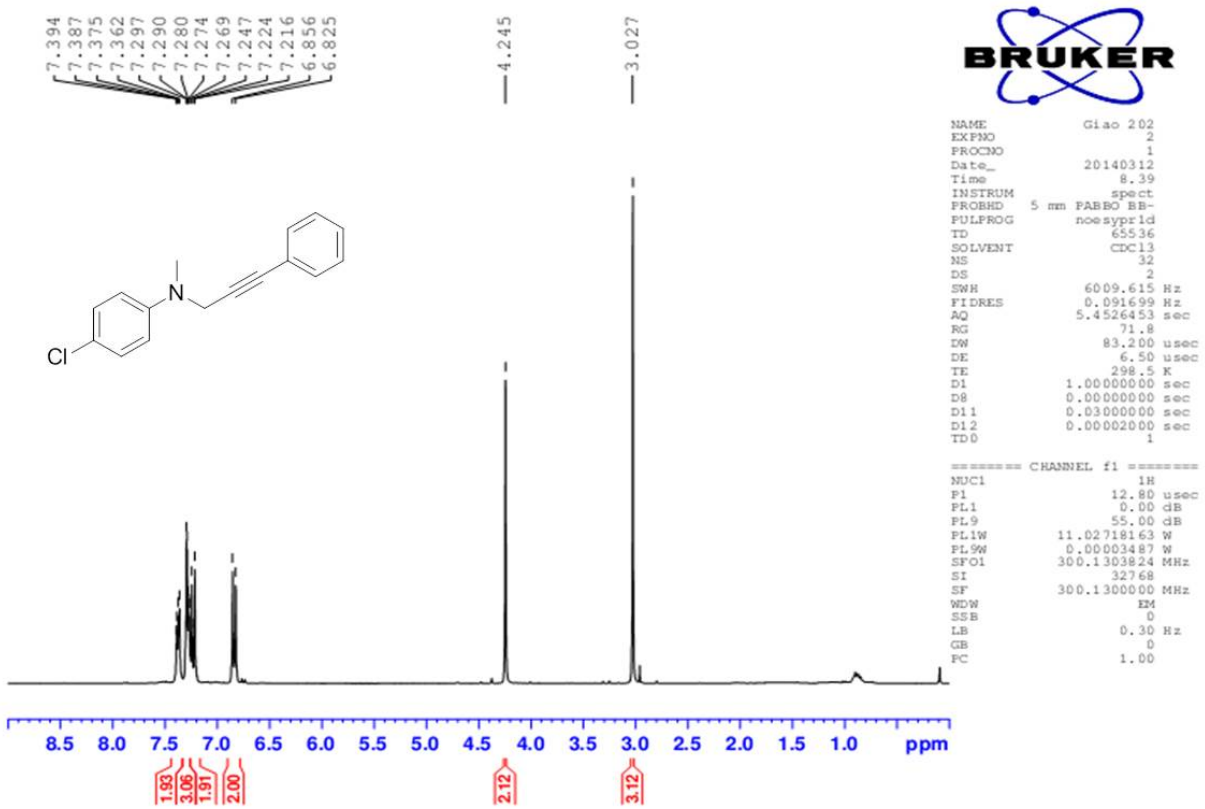

Fig. S18. ^{1}H NMR spectra of 4-chloro-N-methyl-N-(3-phenylprop-2-yn-1-yl)aniline in $CDCl_3$

4-chloro-*N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline. Phenylacetylene (0.11 mL, 1.0 mmol), 4-cloro-*N*-Methylaniline (0.24 mL, 2.0 mmol), CuFe2O4 (0.012g, 5 mol%), *tert*-butyl hydroperoxide (0.41 mL, 3.0 mmol), *N,N*-Dimethylacetamide (4 mL). After chromatography (diethyl ether/ hexane = 1: 15), 222 mg yellow oil was obtained (87 %). R_f = 0.43. This compound is known.[2] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.38 (dd, *J*=6.6 Hz, *J*=3.0 Hz, 2H), 7.29 -7.22 (m, 5H), 6.84 (d, *J*=9.3 Hz, 2H), 4.25 (s, 2H), 3.03 (s, 3H).

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