Supporting Information

Catalysis of a Bis-Caffeine Palladium(II) NHC-Pincer Complex

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Keywords: caffeine; NHC; palladium; catalysis

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Experimental data

Synthesis of biphenyl:

The coupling of iodobenzene (35 mg) and phenyl boronic acid (60 mg) afforded a colorless solid (25 mg, 94%).

^{1}H-NMR ($CDCl_3$): δ = 7.62 (m, 2H), 7.47 (m, 2H), 7.37 (m, 1H) ppm.

Synthesis of 4-methoxy-biphenyl:

The cross-coupling of 4-iodoanisole (32 mg) and phenyl boronic acid (60 mg) afforded a colorless solid (24 mg, 96%).

^{1}H-NMR ($CDCl_3$): δ = 7.57 (m, 2H), 7.54 (AB, 2H, ^2J = 8.85 Hz), 7.44 (m, 2H), 7.33 (m, 1H), 7.02 (BA, 2H, ^2J = 8.85 Hz), 3.87 (s, 3H) ppm.

Synthesis of 4-nitro-biphenyl:

The cross-coupling of 4-iodonitrobenzene (38 mg) and phenyl boronic acid (60 mg) afforded a yellow solid (29 mg, 97%).

^{1}H-NMR ($CDCl_3$): δ = 7.57 (m, 2H), 7.54 (AB, 2H, ^2J = 8.85 Hz), 7.44 (m, 2H), 7.33 (m, 1H), 7.02 (BA, 2H, ^2J = 8.85 Hz), 3.87 (s, 3H) ppm.

Synthesis of methyl cinnamate:

The cross-coupling of iodobenzene (35 mg) and methyl acrylate (60 mg) afforded a yellow solid (26 mg, 97%).

^{1}H-NMR ($CDCl_3$): δ = 7.33 (d, 1H, ^2J = 16 Hz), 7.18 (m, 2H), 7.03 (m, 3H), 6.11 (d, 1H, ^2J= 16 Hz), 3.43 (s, 3H) ppm.

Synthesis of methyl 4-methoxycinnamate:

The cross-coupling of 4-iodoanisole (32 mg) and methyl acrylate (60 mg) afforded a colorless solid (27 mg, 98%).

^{1}H-NMR ($CDCl_3$): δ = 7.69 (d, 1H, ^2J = 16 Hz), 7.50 (AB, 2H, ^2J = 8.66 Hz), 6.93 (BA, 2H, ^2J = 8.66 Hz), 6.34 (d, 1H, ^2J = 16 Hz), 3.84 (s, 3H), 3.80 (s, 3H) ppm.

Synthesis of methyl 4-nitrocinnamate:

The cross-coupling of 4-iodonitrobenzene (38 mg) and methyl acrylate (60 mg) afforded a colorless solid (27 mg, 96%).

^{1}H-NMR ($CDCl_3$): δ = 8.27 (AB, 2H, ^2J = 8.75 Hz), 7.75 (d, 1H, ^2J = 16 Hz), 7.69 (BA, 2H, ^2J = 8.75 Hz), 6.59 (d, 1H, ^2J = 16 Hz), 3.84 (s, 3H) ppm.

Synthesis of diphenylethylene:

The cross-coupling of iodobenzene (35 mg) and phenylacetylene (60 mg) afforded a colorless solid (29 mg, 97%).

^{1}H-NMR ($CDCl_3$): δ = 7.55 (m, 2H), 7.36 (m, 3H) ppm.

Synthesis of 1-methoxy-4-(phenylethynyl)benzene:

The cross-coupling of 4-iodoanisole (32 mg) and phenylacetylene (60 mg) afforded a colorless solid (27 mg, 96%).

^{1}H-NMR ($CDCl_3$): δ = 7.51 (m, 2H) 7.49 (AB, 2H, ^2J = 8.94 Hz), 7.34 (m, 4H), 6.90 (BA, 2H, ^2J = 8.94 Hz), 3.84 (s, 3H), ppm.

Synthesis of 1-nitro-4-(phenylethynyl)benzene:

The cross-coupling of 4-iodonitrobenzene (38 mg) and phenylacetylene (60 mg) afforded a yellow solid (33 mg, 98%).

^{1}H-NMR ($CDCl_3$): δ = 8.25 (AB, 2H, ^2J = 8.94 Hz), 7.69 (BA, 2H, ^2J = 8.94 Hz), 7.55 (m, 2H), 7.40 (m, 1H) ppm.

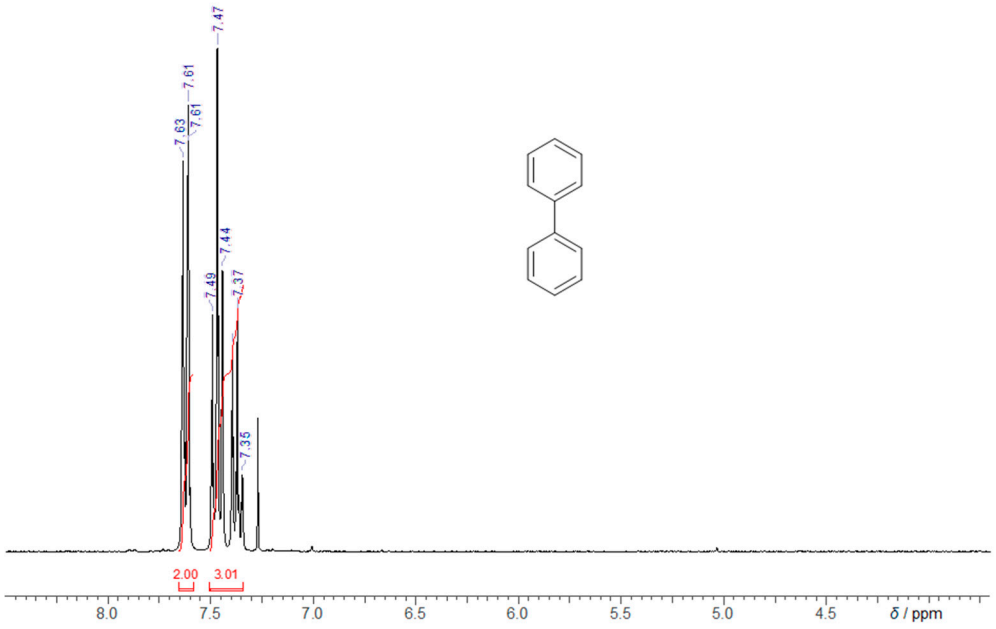

Figure S 1: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of biphenyl.

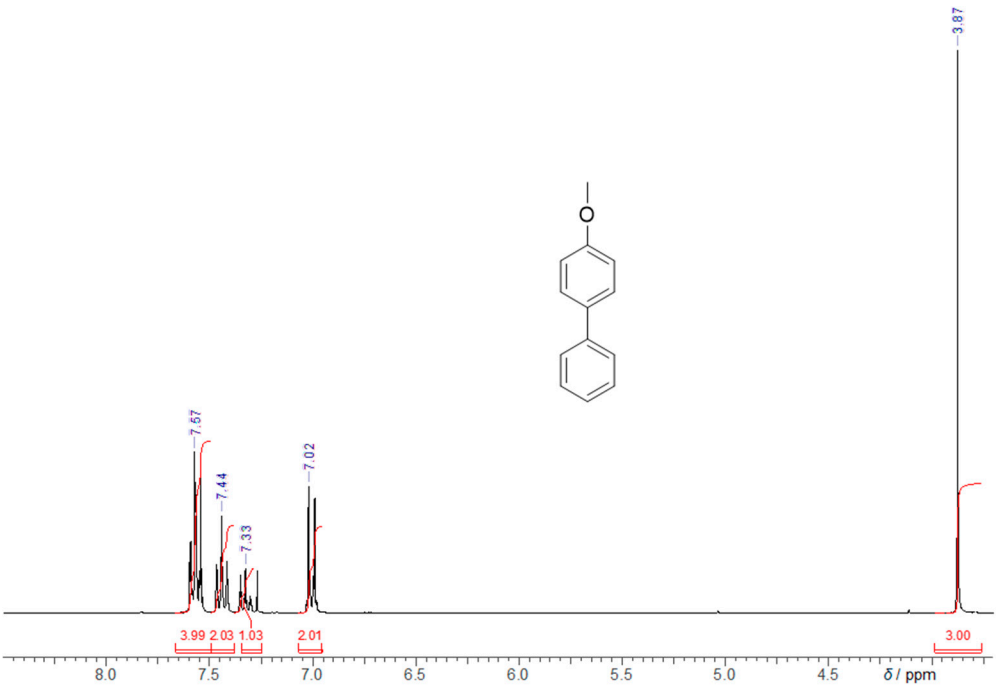

Figure S 2: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 4-methoxy-biphenyl.

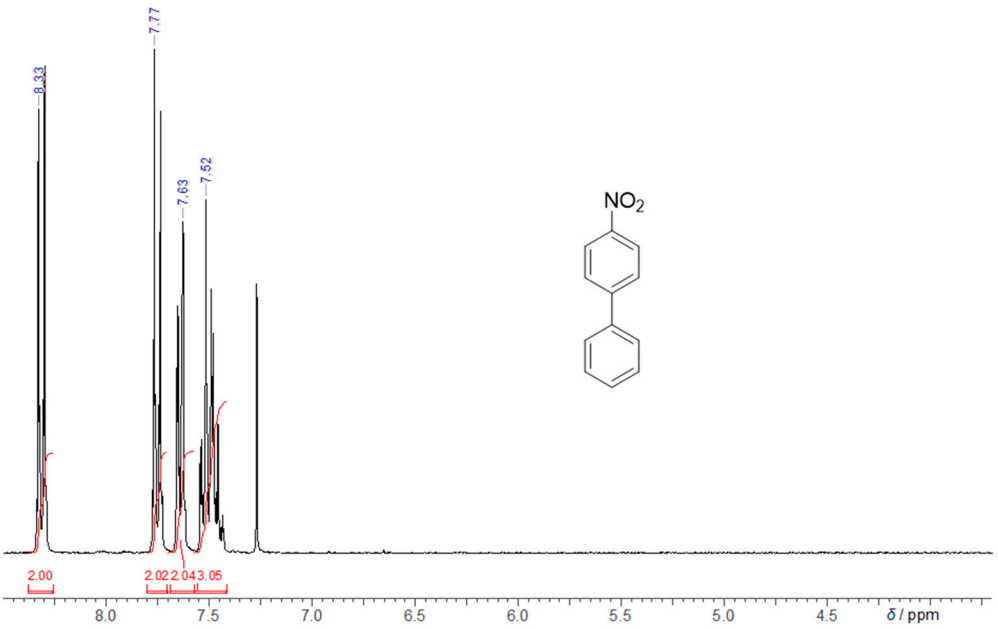

Figure S 3: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 4-nitro-biphenyl.

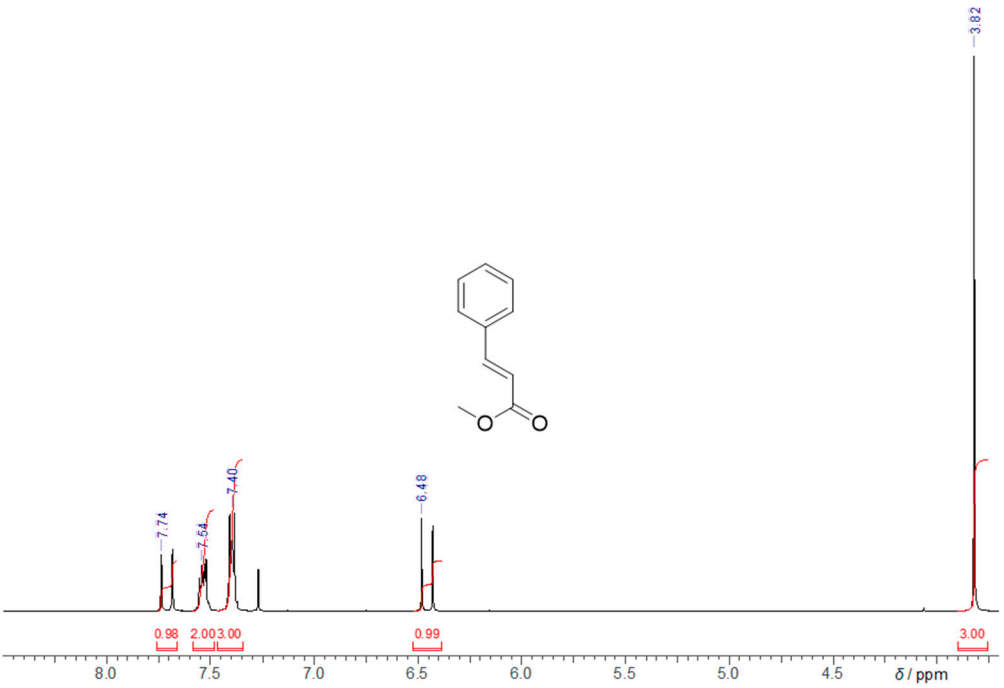

Figure S 4: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of methyl cinnamate.

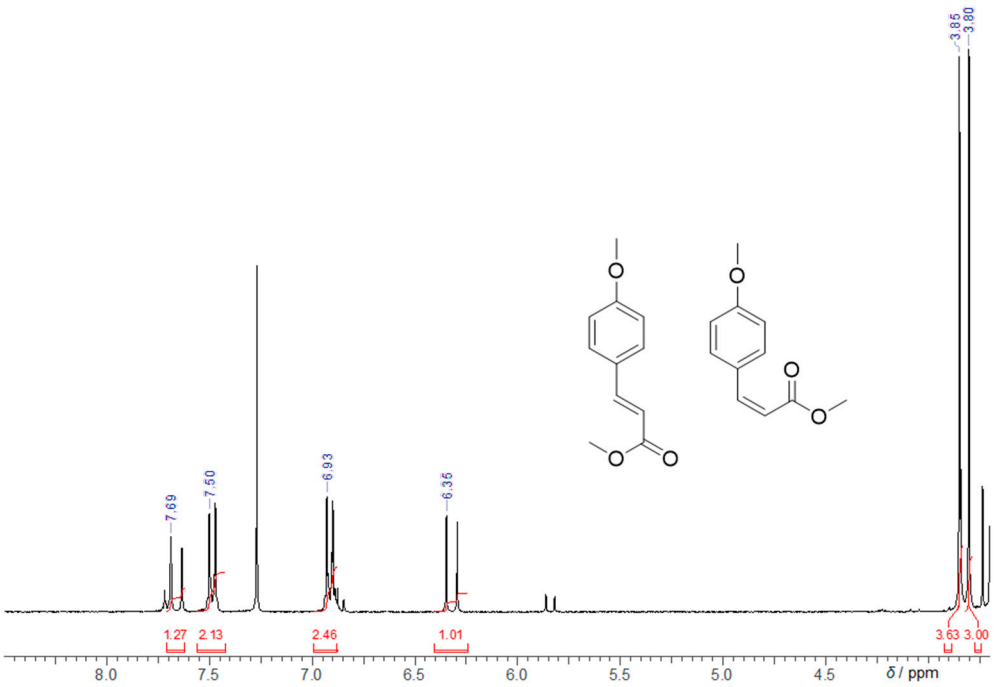

Figure S 5: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of methyl 4-methoxycinnamate.

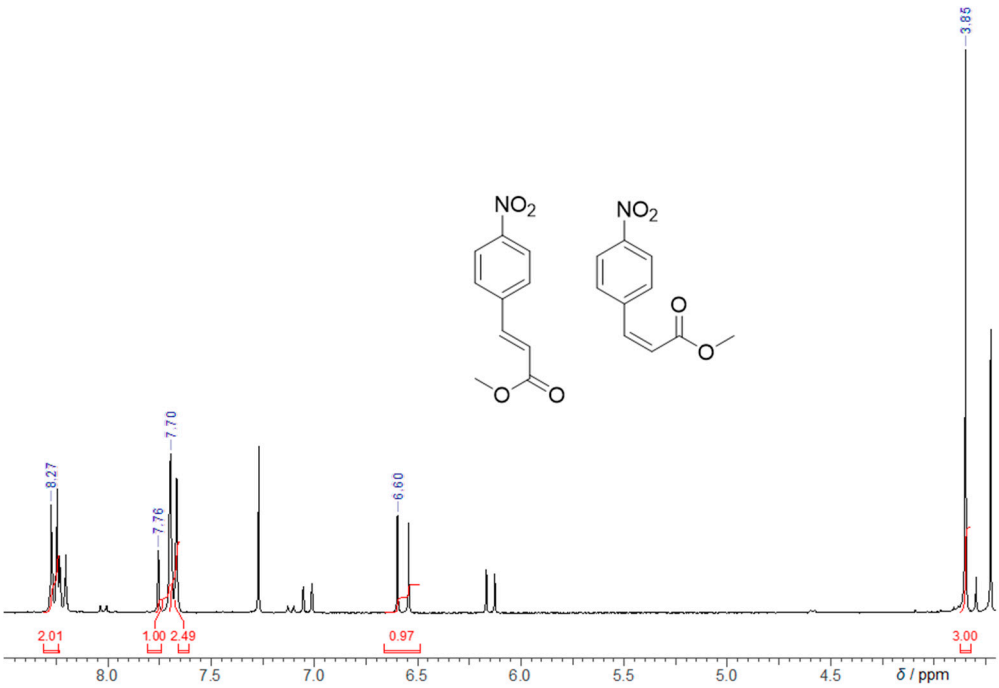

Figure S 6: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of methyl 4-nitrocinnamate.

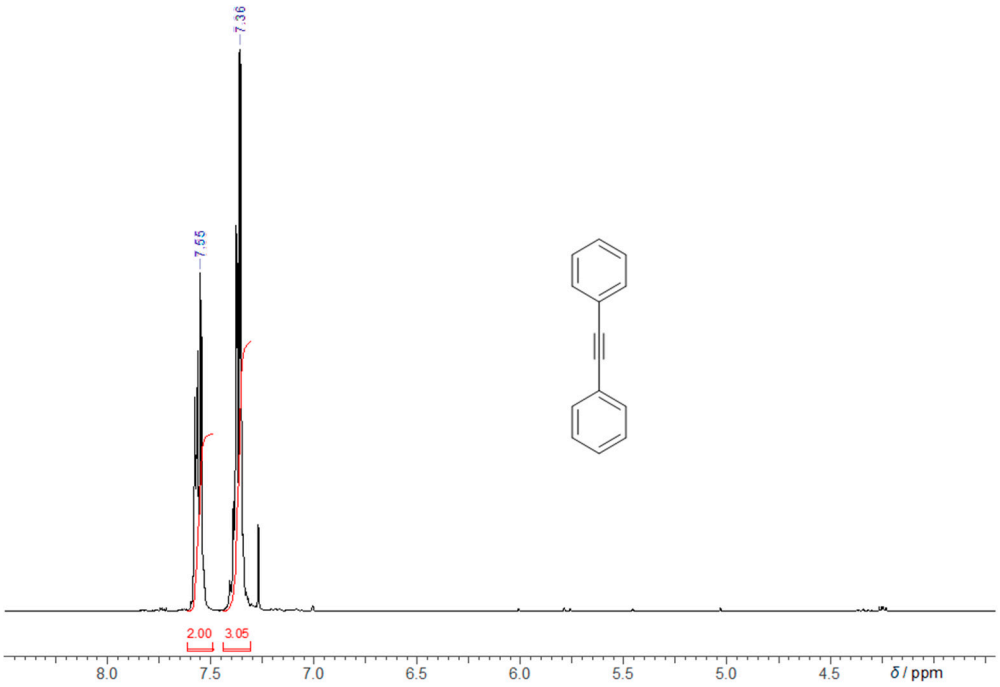

Figure S 7: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of diphenylethylene.

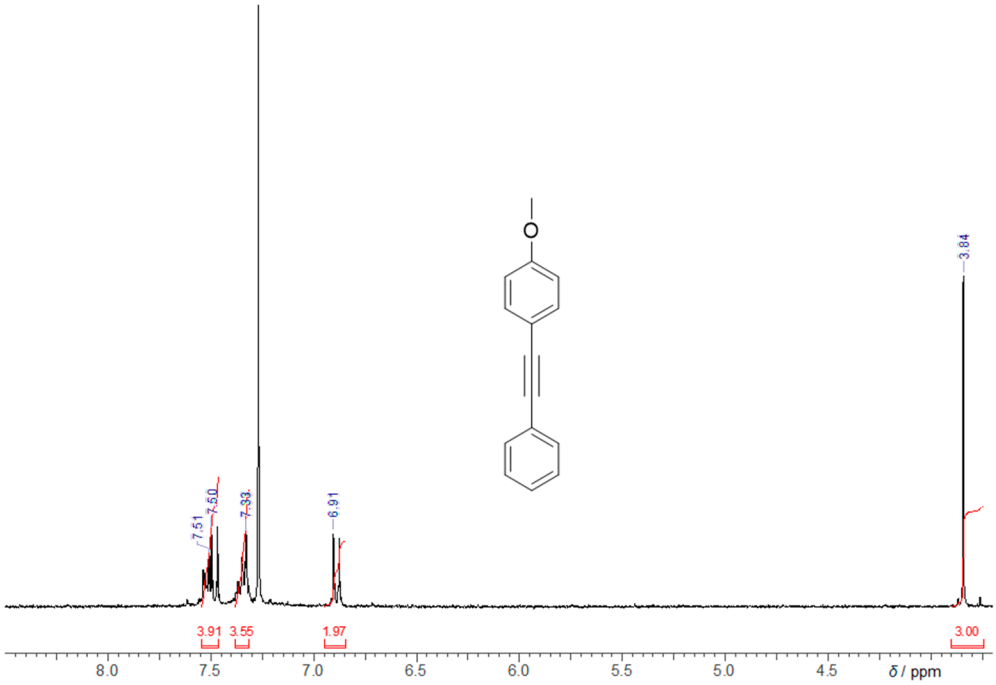

Figure S 8: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 1-methoxy-4-(phenylethynyl)benzene.

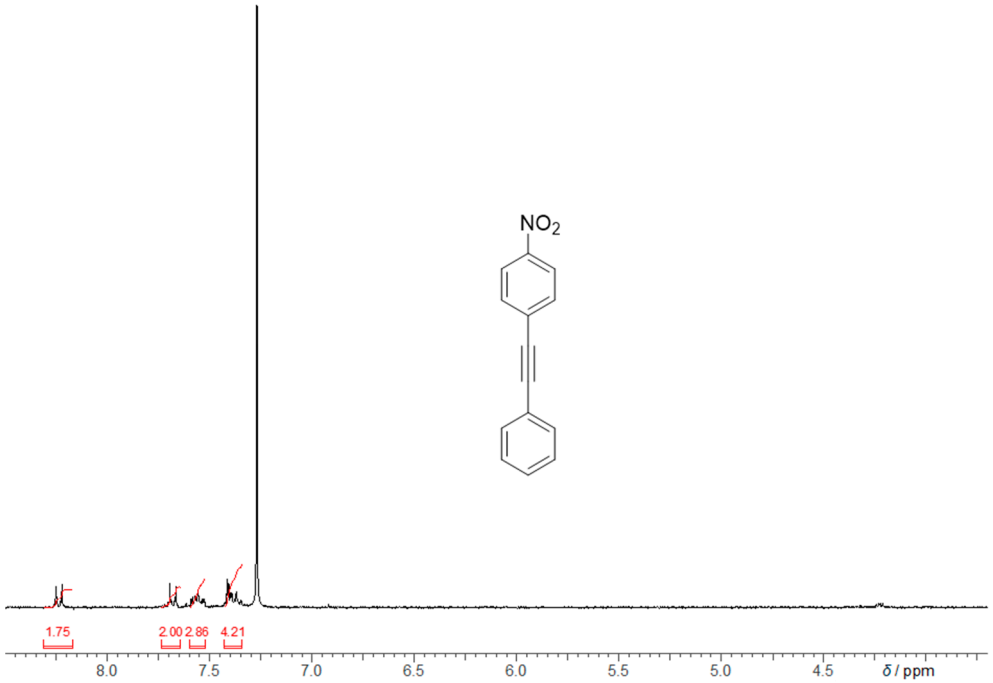

Figure S 9: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 1-nitro-4-(phenylethynyl)benzene.

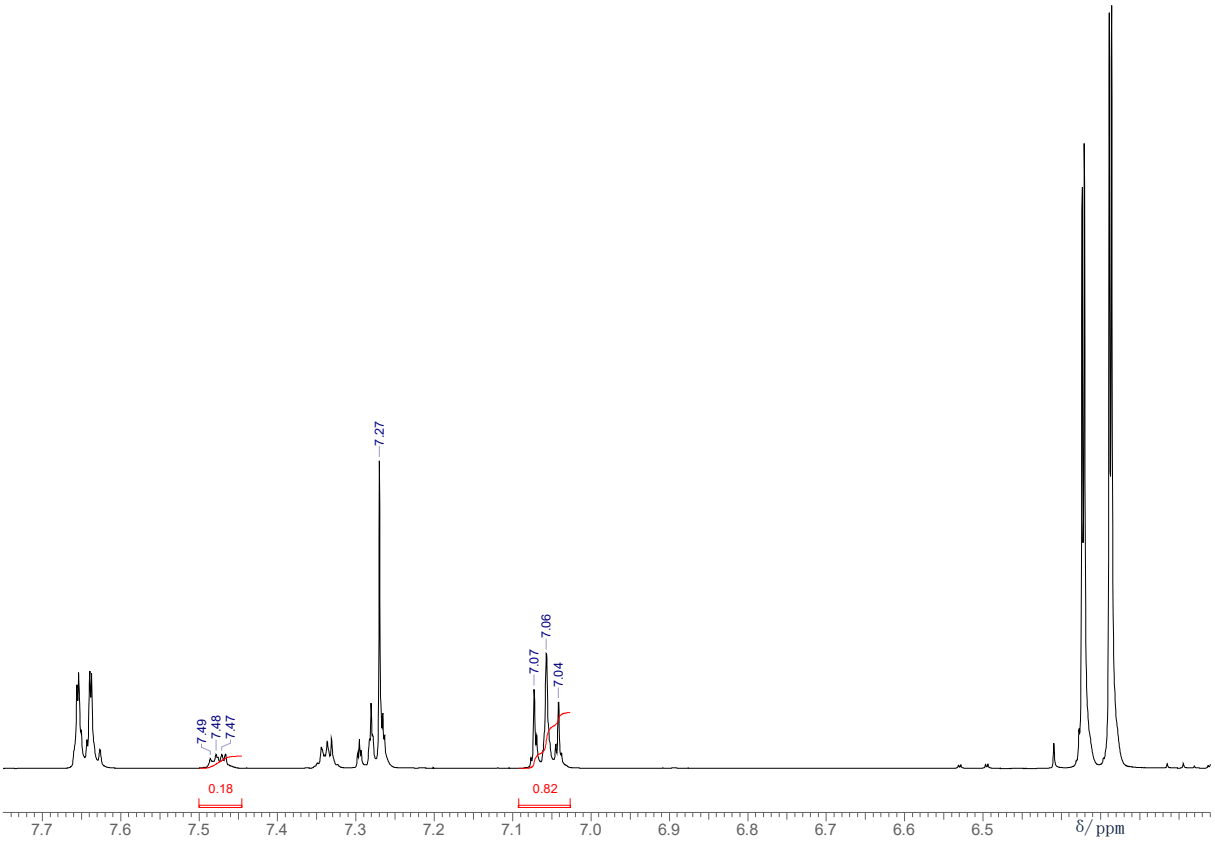

Figure S 10: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of ppm catalysis after 4 hours.

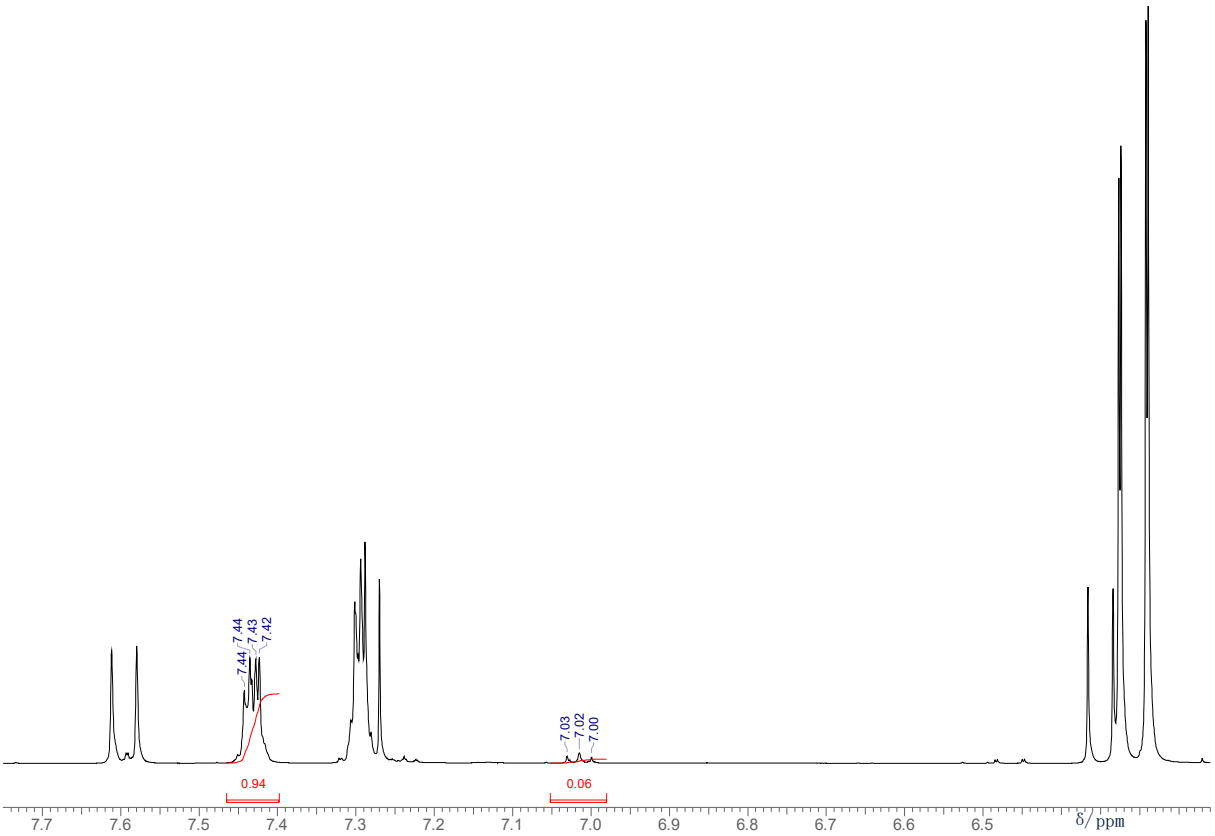

Figure S 11: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of ppm catalysis after 24 hours.

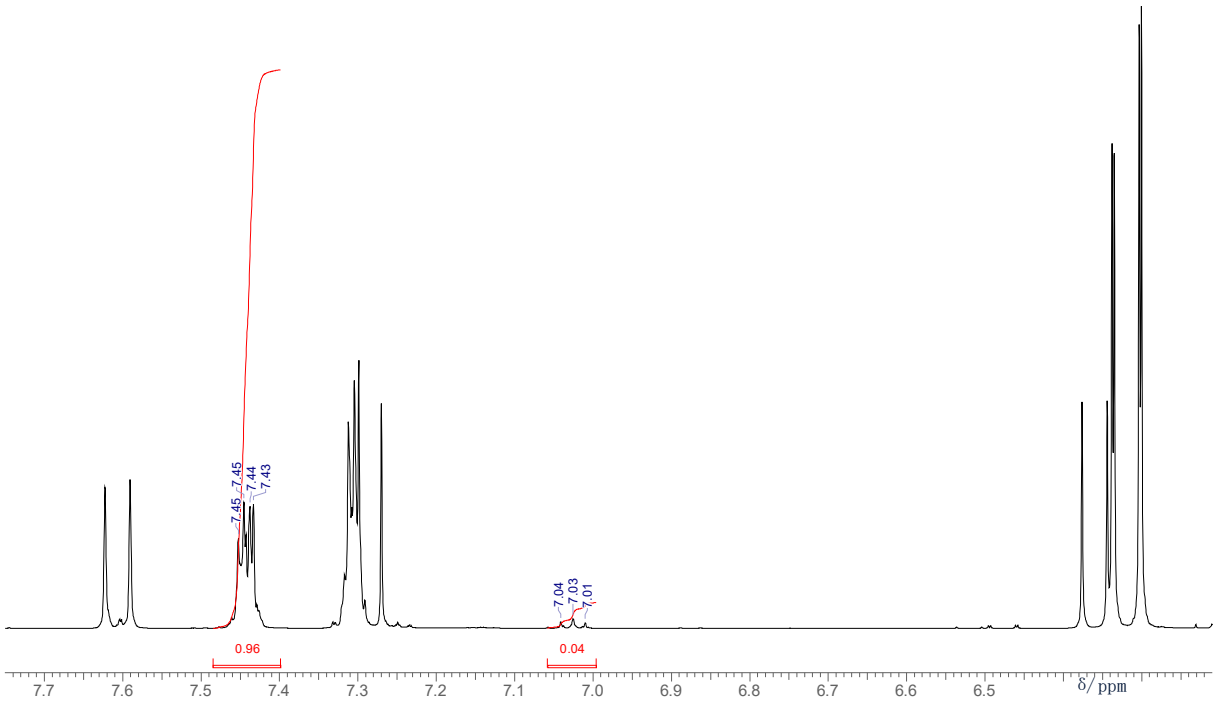

Figure S 12: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of ppm catalysis after 26 hours.

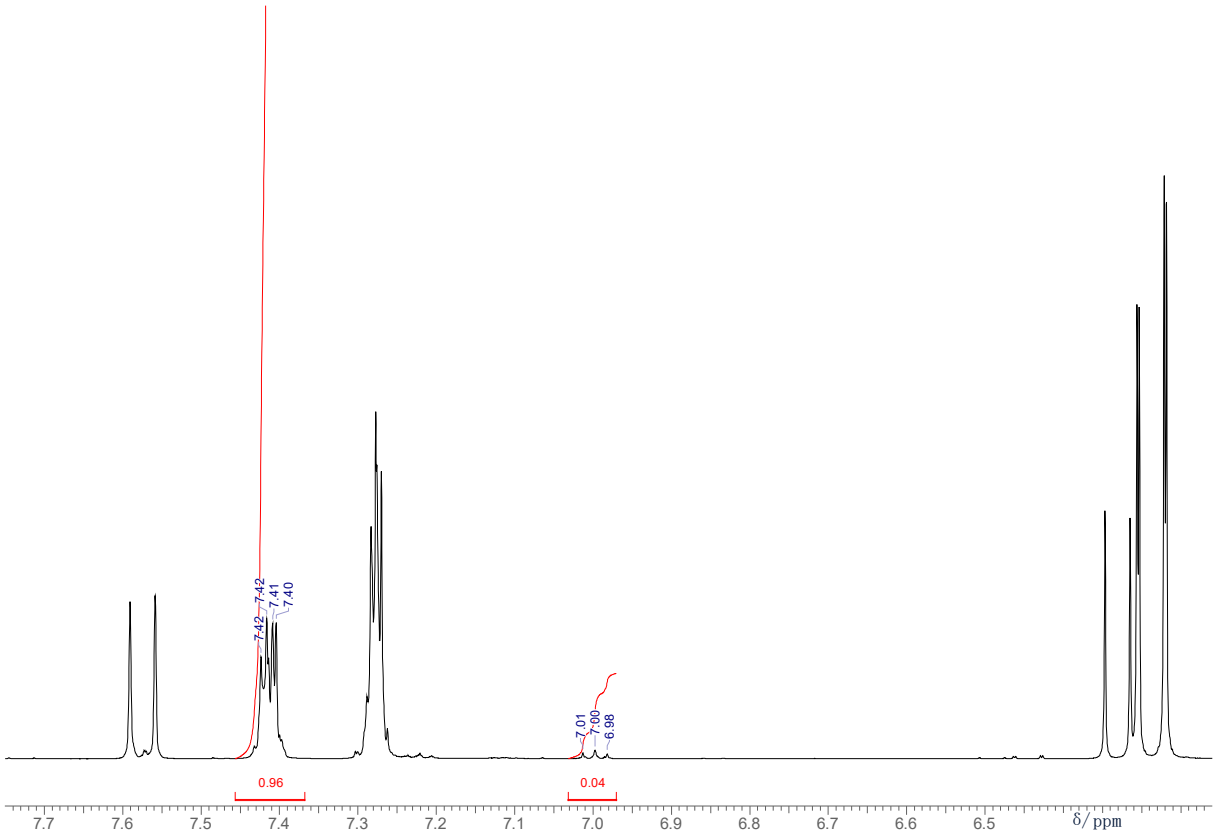

Figure S 13: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of ppm catalysis after 28 hours.

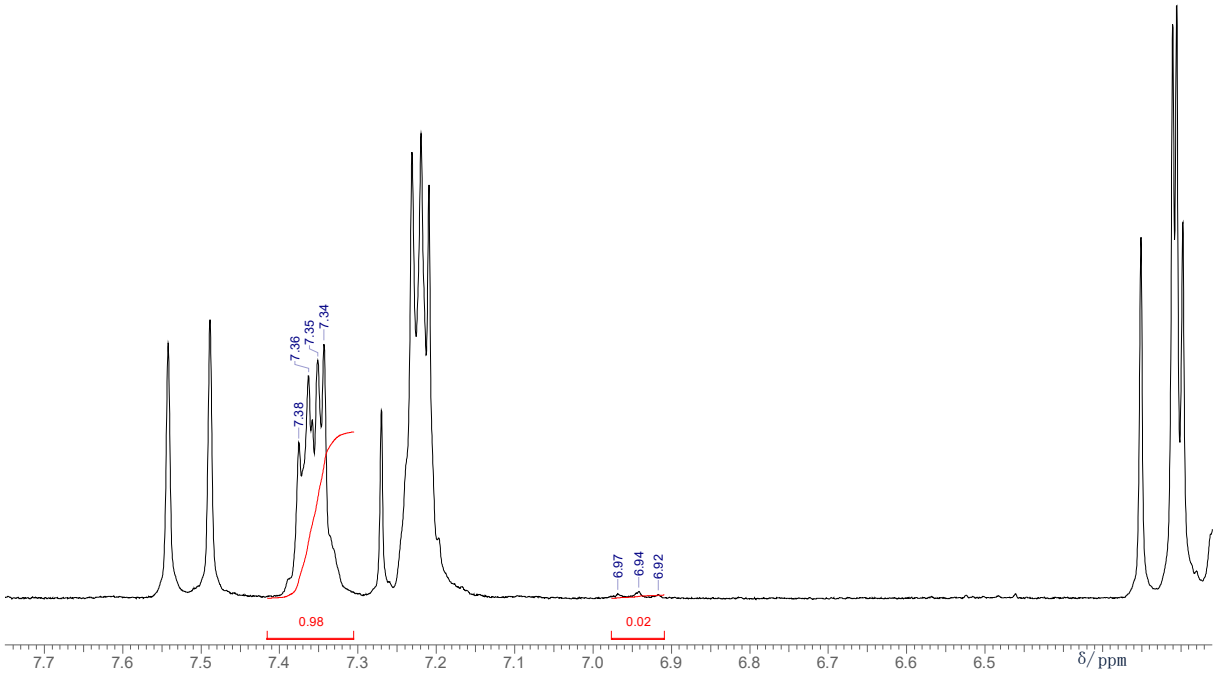

Figure S 14: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of ppm catalysis after 30 hours.