

Supporting Information

Palladium nanoparticles supported on carbazole functionalized mesoporous organic polymer: synthesis and their application as efficient catalysts for Suzuki–Miyaura cross coupling reaction

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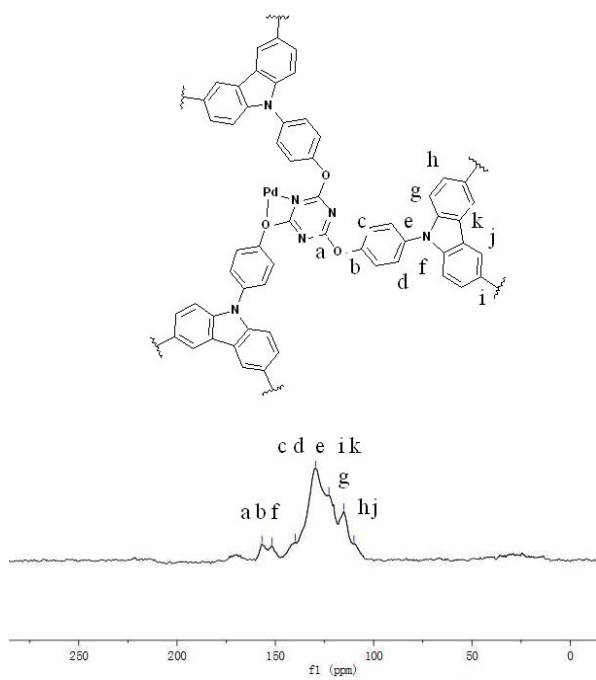
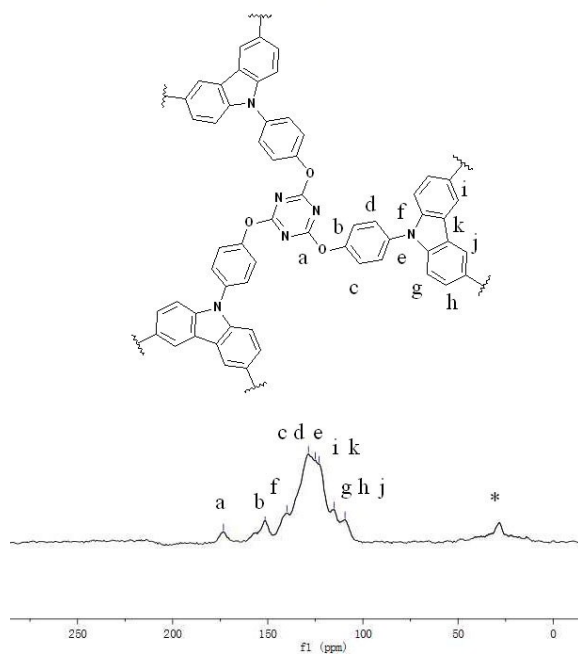


Fig. S1 ^{13}C CP-MAS NMR of CzMOP (top) and Pd@CzMOP (bottom).

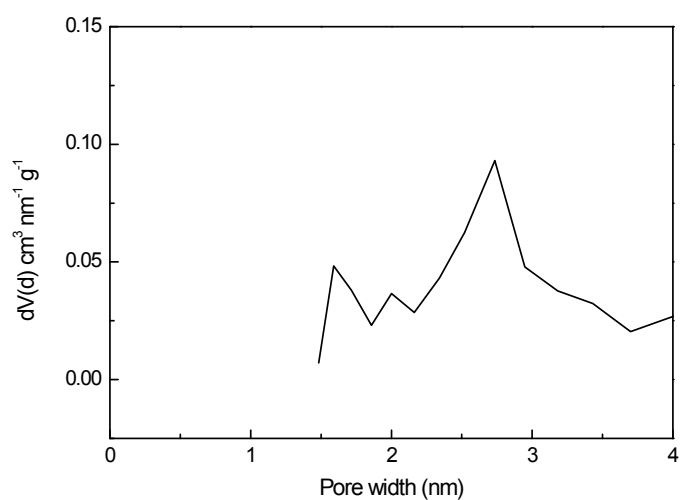


Fig. S2 Pore size distribution of Pd@CzMOP.

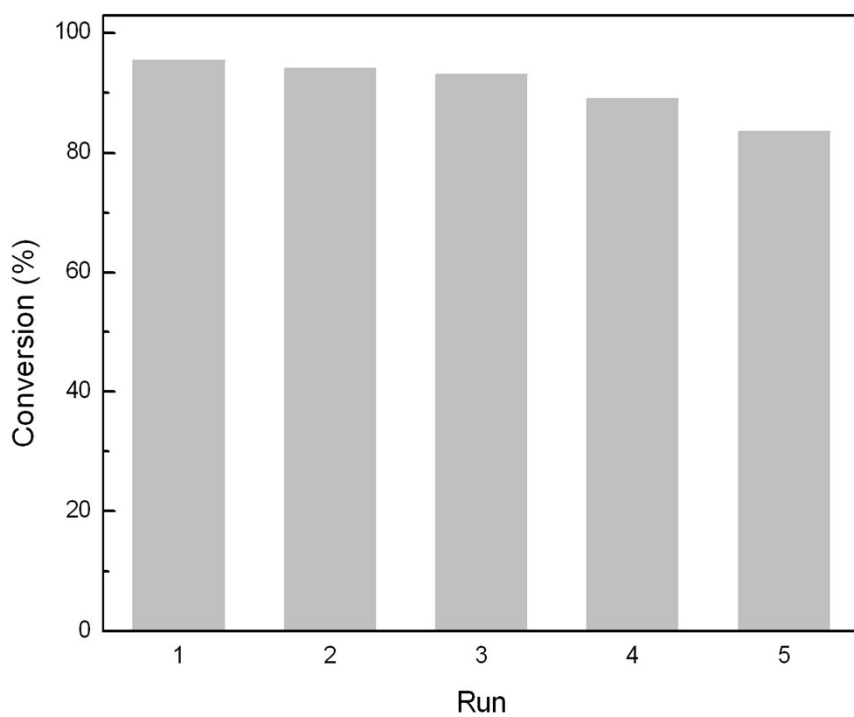


Fig. S3 Reusability of Pd@CzMOP for Suzuki coupling reaction.

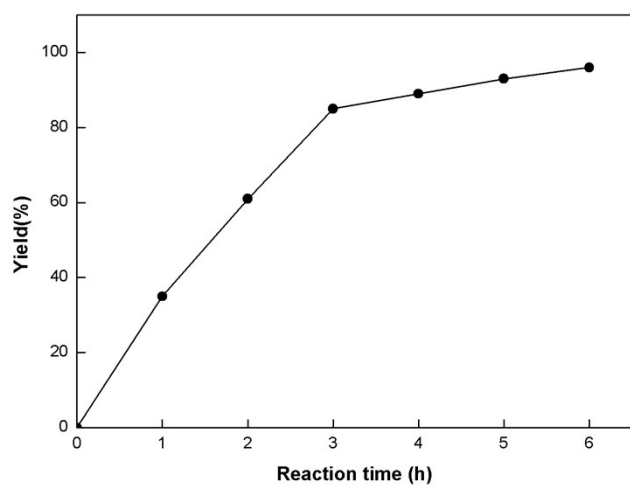
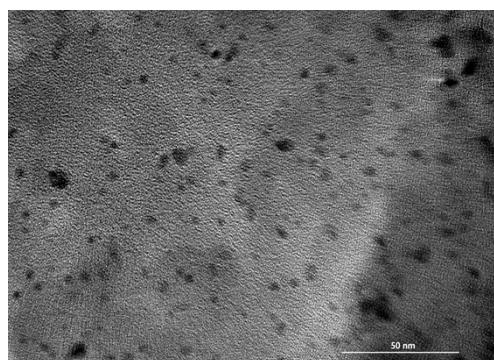
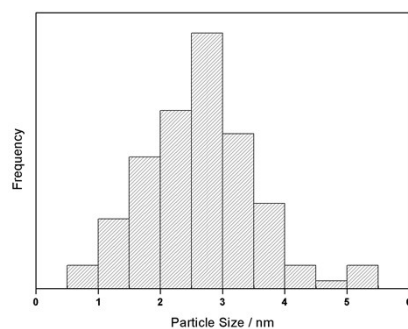


Fig. S4 Effect of reaction time on the percentage conversion in the Pd@CzMOP catalyzed reaction.



a



b

Fig. S5 HR-TEM images of Pd@CzMOP after five cycles (a). Pd NPs size distribution of Pd@CzMOP after five cycles (b).

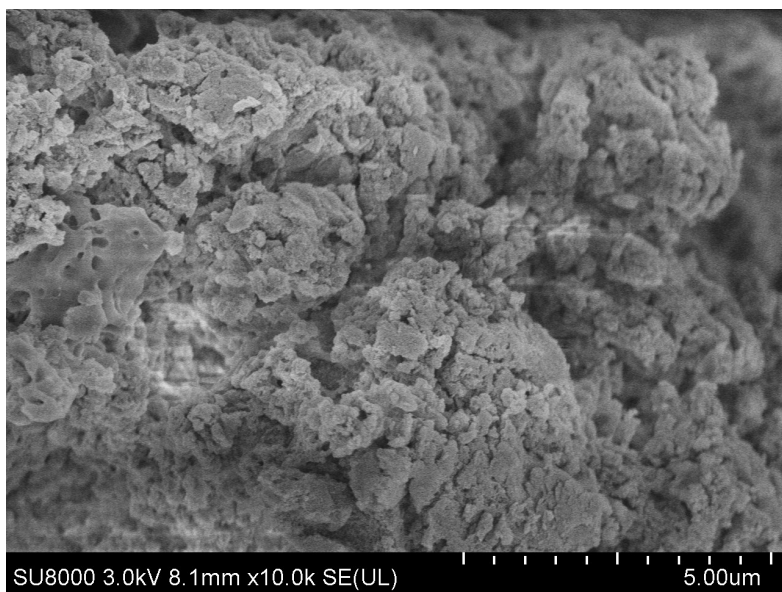


Fig. S6 SEM image of Pd@CzMOP for Suzuki coupling reaction after five cycles.

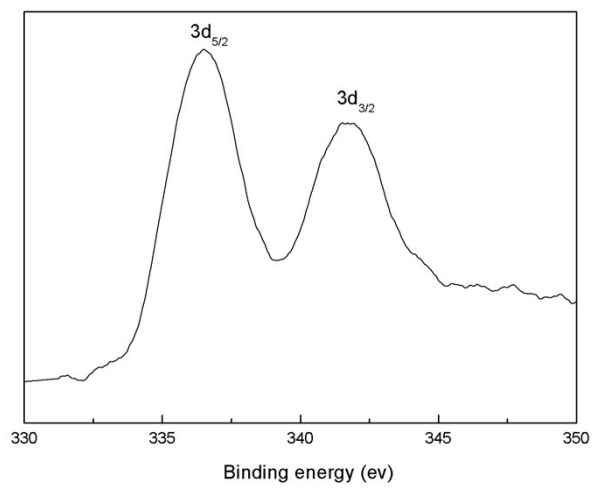


Fig. S7 XPS spectra of Pd@CzMOP (metallic Pd) after five cycles.

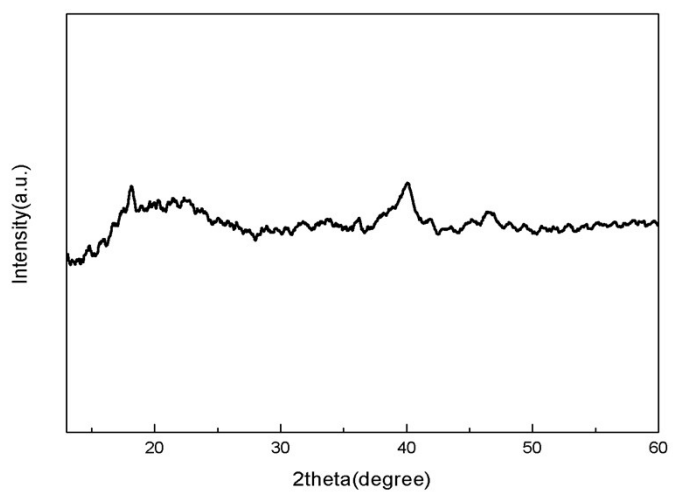
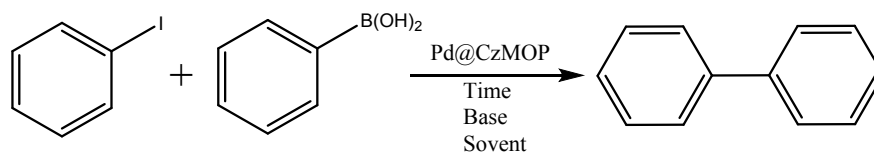


Fig. S8 XRD patterns of Pd@CzMOP for Suzuki coupling reaction after five cycles.

Table S1 Effect of the reaction condition on Suzuki coupling reaction using Pd@CzMOP^a.

| Entry | Solvent | Time (h) | Base | Yield(%) ^b |
|-------|---------|----------|---------------------------------|-----------------------|
| 1 | DMF | 6 | K ₂ CO ₃ | 96 |
| 2 | THF | 6 | K ₂ CO ₃ | 94 |
| 3 | EtOH | 6 | K ₂ CO ₃ | 96 |
| 4 | toluene | 6 | K ₂ CO ₃ | 91 |
| 5 | dioxane | 6 | K ₂ CO ₃ | 88 |
| 6 | DMF | 6 | Na ₂ CO ₃ | 90 |
| 7 | DMF | 6 | KOH | 85 |
| 8 | DMF | 3 | K ₂ CO ₃ | 85 |
| 9 | DMF | 1 | K ₂ CO ₃ | 35 |

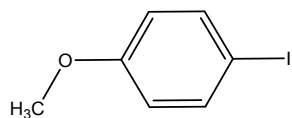
^a PhI (0.5 mmol), phenylboronic acid (0.75 mmol), K₂CO₃ (1.5 equiv), Solvent (5 mL), and Pd@CzMOP (5 mg). ^b Isolated yield based on PhI.

Table S2 Hot filtration test^a

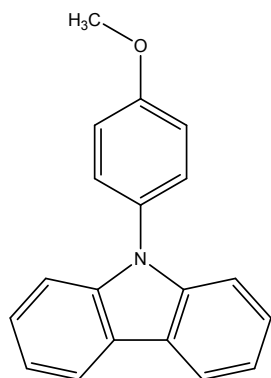
| Catalyst | Yield(%) ^b | |
|----------|-----------------------|---------|
| | 3 h | (3+3) h |
| Pd@CzMOP | 85 | 85 |

^a PhI (0.5 mmol), phenylboronic acid (0.75 mmol), K₂CO₃ (1.5 equiv), Solvent (5 mL), and Pd@CzMOP (5 mg). ^b Isolated yield based on PhI.

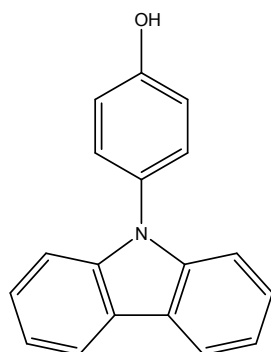
Spectral Data



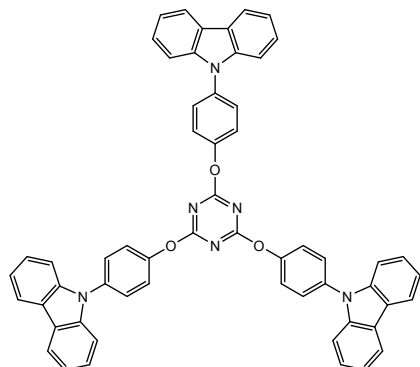
1-iodo-4-methoxybenzene: White solid (yield, 97 %). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56$ (d, $J = 4$ Hz, 2H), 6.78 (d, $J = 8$ Hz, 2H), 3.78 (s, 3H) ppm.



9-(4-methoxyphenyl)-9H-carbazole: White solid (yield, 90%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.13$ (d, $J = 8$ Hz, 2H), 7.48 – 7.28 (m, 8H), 7.12 (d, $J = 4$ Hz, 2H), 3.92 (s, 3H) ppm.

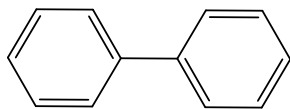


4-(9H-carbazol-9-yl)phenol: White solid (yield, 93%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.14$ (d, $J = 8$ Hz, 2H), 7.42 – 7.26 (m, 8H), 7.04 (d, $J = 8$ Hz, 2H), 5.01 (s, 1H) ppm.

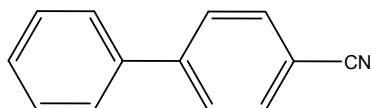


2,4,6-tris(4-(9H-carbazol-9-yl)phenoxy)-1,3,5-triazine: White solid (yield, 86%). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.10$ (d, $J = 4$ Hz, 6H), 7.63 (d, $J = 8$ Hz, 6H), 7.49

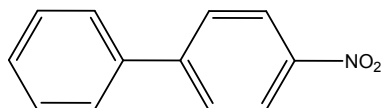
(d, $J = 8$ Hz, 6H), 7.38 (d, $J = 12$ Hz, 6H), 7.26–7.20 (m, 12H) ppm.



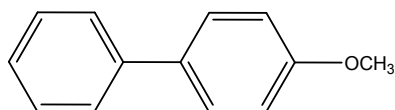
1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.63$ (d, $J = 4$ Hz, 4H), 7.50–7.44 (t, $J = 8$ Hz, 4H), 7.40–7.35 (t, $J = 8$ Hz, 2H) ppm.



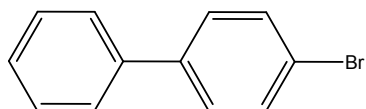
[1,1'-biphenyl]-4-carbonitrile: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.75$ –7.66 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.45 (m, 2H), 7.45–7.40 (m, 1H) ppm.



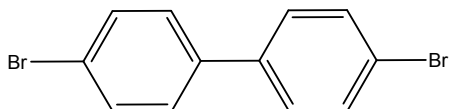
4-nitro-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 8.32$ –8.28 (m, 2H), 7.76–7.72 (m, 2H), 7.65–7.61 (m, 2H), 7.53–7.42 (m, 3H) ppm.



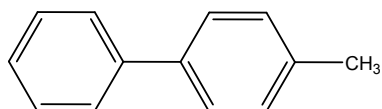
4-methoxy-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.57$ –7.51 (m, 4H), 7.44–7.38 (t, $J = 8$ Hz, 2H), 7.33–7.27 (t, $J = 8$ Hz, 1H), 6.98 (d, $J = 8$ Hz, 2H), 3.85 (s, 3H) ppm.



4-bromo-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.58$ –7.53 (m, 4H), 7.48–7.41 (m, 4H), 7.39–7.33 (t, $J = 8$ Hz, 1H) ppm.

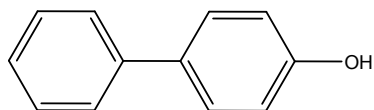


4,4'-dibromo-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.59$ –7.53 (d, $J = 8$ Hz, 4H), 7.44–7.38 (d, $J = 8$ Hz, 4H) ppm.

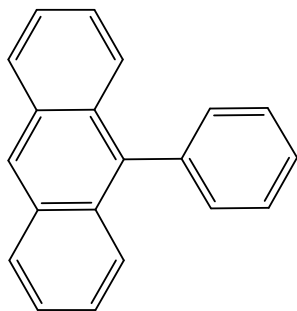


4-methyl-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.60$ –7.55 (d, $J = 8$ Hz, 2H), 7.52–7.46 (d, $J = 8$ Hz, 2H), 7.45–7.39 (t, $J = 8$ Hz, 2H), 7.35–7.29 (t, $J = 8$ Hz, 1H),

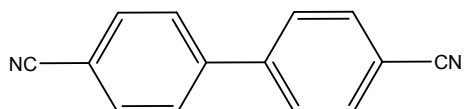
7.27–7.23 (d, $J = 8$ Hz, 2H), 2.40 (s, 3H) ppm.



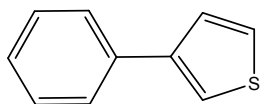
[1,1'-biphenyl]-4-ol: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.62\text{--}7.57$ (d, $J = 4$ Hz, 2H), 7.54–7.49 (d, $J = 8$ Hz, 2H), 7.47–7.41 (t, $J = 8$ Hz, 2H), 7.38–7.31 (t, $J = 8$ Hz, 1H), 6.65–6.59 (d, $J = 8$ Hz, 2H), 4.82 (s, 1H) ppm.



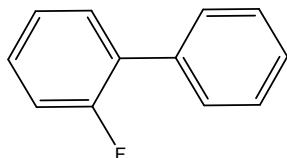
9-phenylanthracene: ^1H NMR (400 MHz, CDCl_3): $\delta = 8.51$ (s, 1H), 8.05 (d, $J = 8$ Hz, 2H), 7.69–7.65 (d, $J = 8$ Hz, 2H), 7.61–7.53 (m, 3H), 7.49–7.42 (m, 4H), 7.38–7.32 (m, 2H) ppm.



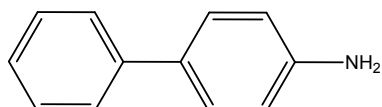
[1,1'-biphenyl]-4,4'-dicarbonitrile: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.85$ (d, $J = 8$ Hz, 4H), 7.37 (d, $J = 8$ Hz, 4H) ppm.



3-phenylthiophene: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.60$ (d, $J = 8$ Hz, 2H), 7.47–7.36 (m, 5H), 7.32–7.26 (t, $J = 8$ Hz, 1H) ppm.

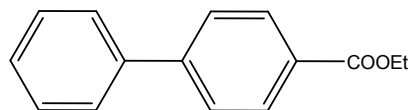


2-fluoro-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49\text{--}7.35$ (m, 7H), 7.35–7.31 (m, 1H), 7.31–7.26 (m, 1H) ppm.

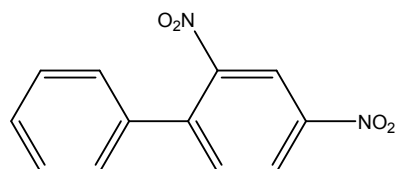


[1,1'-biphenyl]-4-amine: ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56\text{--}7.50$ (d, $J = 8$ Hz, 2H), 7.44–7.35 (q, 4H), 7.29–7.22 (d, $J = 16$ Hz, 1H), 6.78–6.72 (d, $J = 8$ Hz, 2H), 3.72 (s,

2H) ppm.



ethyl [1,1'-biphenyl]-4-carboxylate: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.13\text{--}8.09$ (d, $J = 8$ Hz, 2H), $7.68\text{--}7.60$ (q, 4H), $7.50\text{--}7.43$ (t, $J = 8$ Hz, 2H), $7.42\text{--}7.36$ (t, $J = 8$ Hz, 1H), $4.44\text{--}4.36$ (q, 2H), $1.44\text{--}1.39$ (t, $J = 8$ Hz, 3H) ppm.



2,4-dinitro-1,1'-biphenyl: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.69$ (d, $J = 2.7$ Hz, 1H), $8.26\text{--}8.21$ (m, 2H), 8.19 (d, $J = 2.7$ Hz, 1H), $7.64\text{--}7.55$ (m, 1H), $7.54\text{--}7.46$ (m, 2H), 7.00 (d, $J = 9.5$ Hz, 1H).

