Palladium nanoparticles confined pore engineered urethane linked thiol functionalized covalent organic framework: A high-performance catalyst for Suzuki Miyuara cross-coupling reaction

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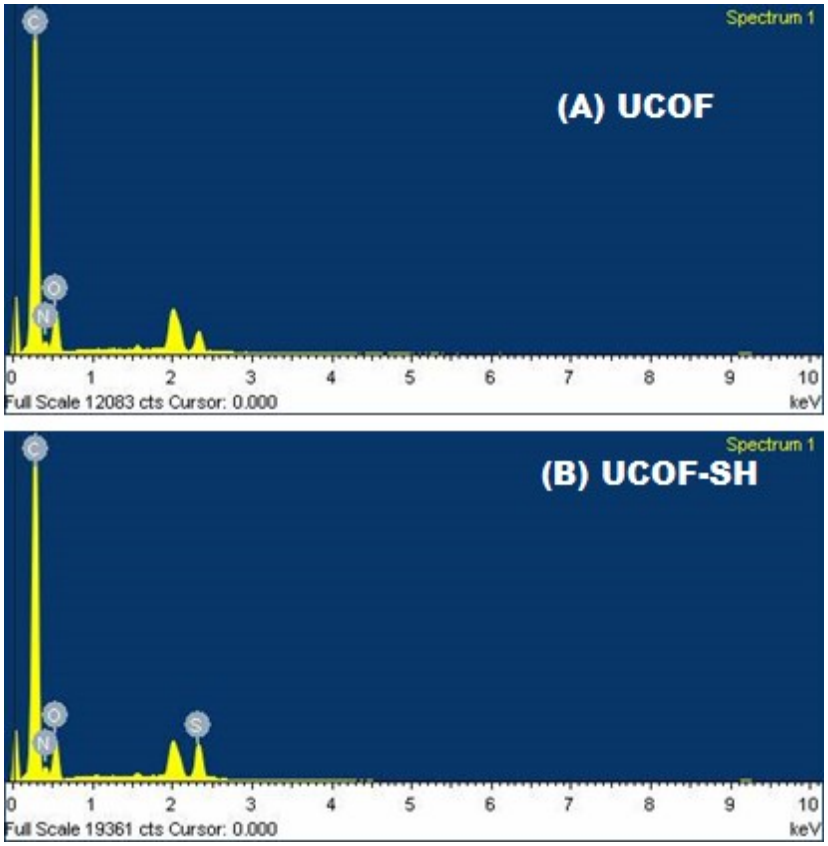

Figure S1: Elemental Mapping of (A) UCOF and (B) UCOF-SH

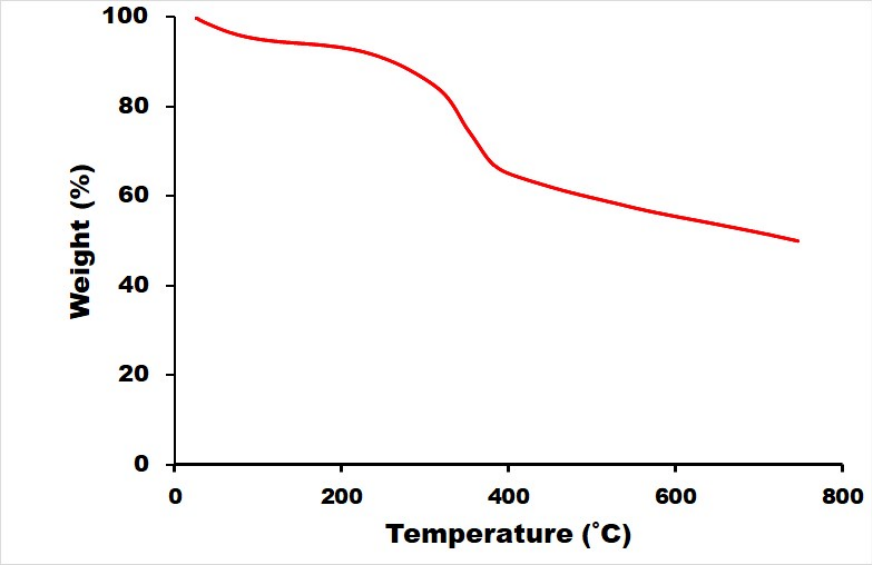

Figure S2: TGA plot of UCOF

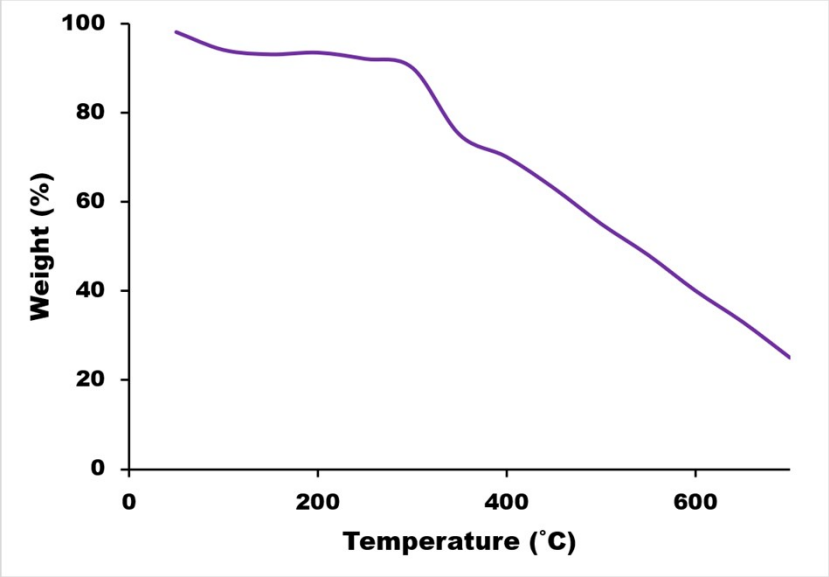

Figure S3: TGA plot of PdNPs@UCOF-SH

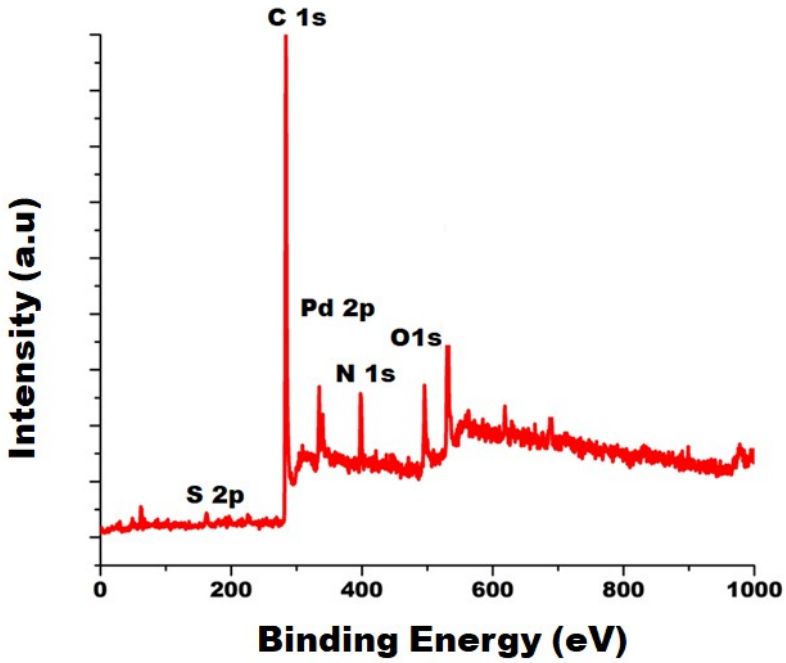

Figure S4: Full scan XPS spectrum of PdNPs@UCOF-SH catalyst

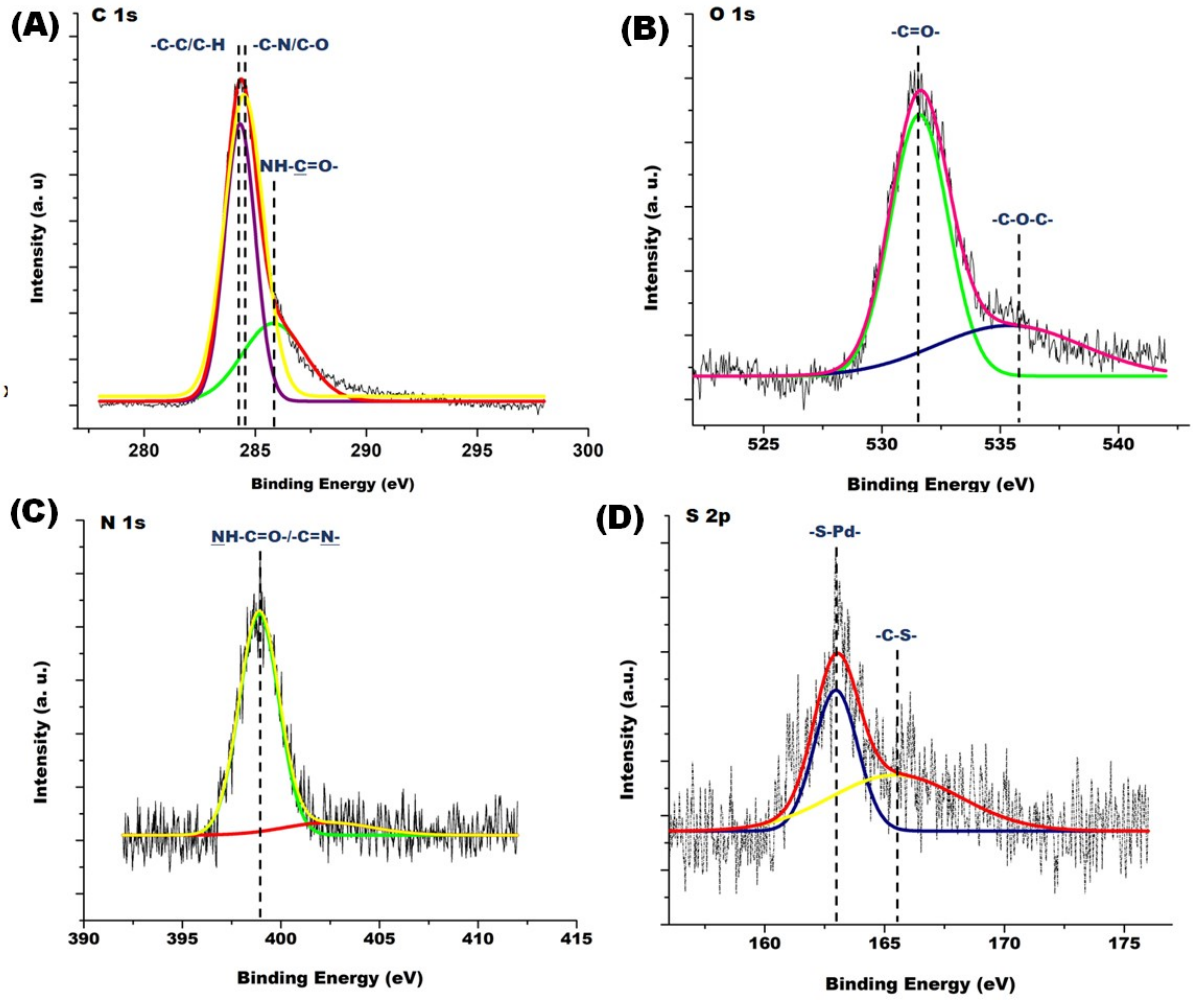

Figure S5: Deconvulated XPS spectra of (A) C 1s (B) O 1s (C) N 1s and (D) S2p

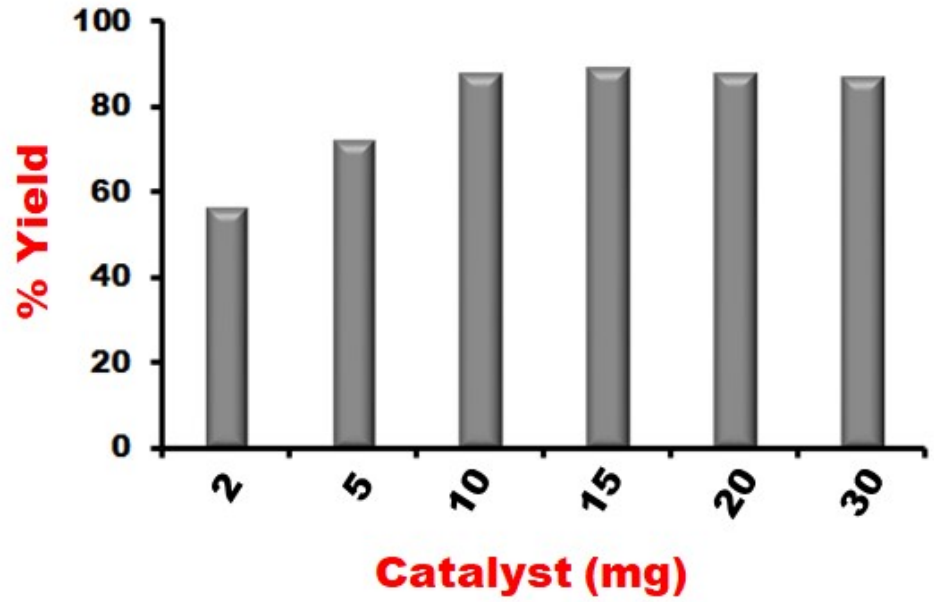

Figure S6: Effect of catalyst loading (Reaction Condition: Bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), 1.0 mmol of Cs_2CO_3, (x mg) PdNPs@UCOF-SH, and solvent EtOH: H_2O 5 mL, Isolated Yield).

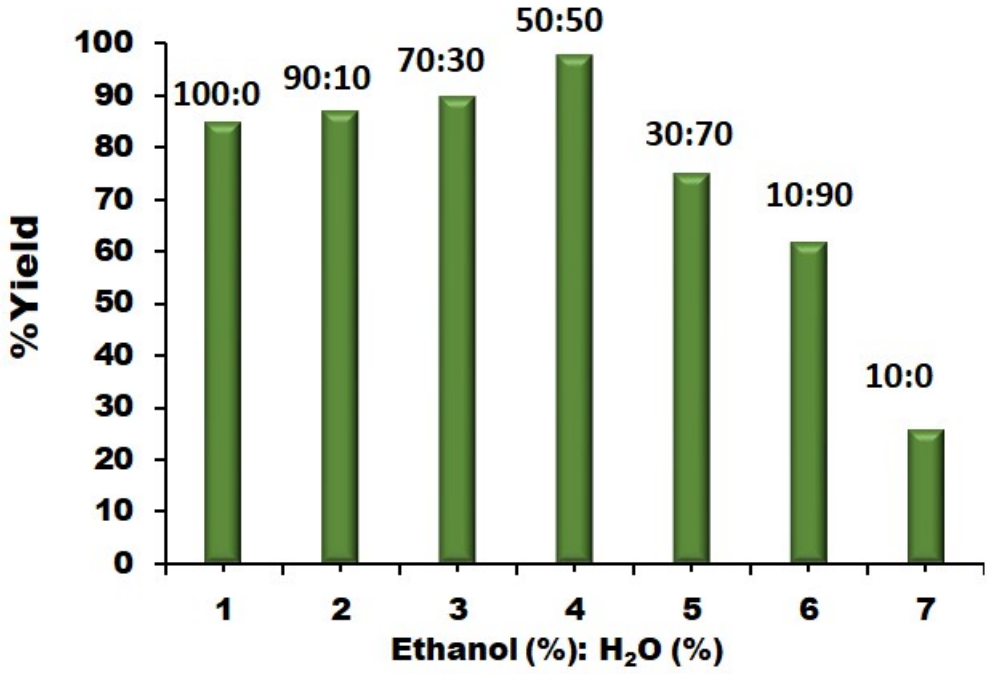

Figure S7: Effect of EtOH: H_2O ratio as a solvent on cross-coupling reaction (Reaction Conditions: Bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), 1.0 mmol of Cs_2CO_3, 0.75 mol % of PdNPs@UCOF-SH, and solvent EtOH: H_2O 5 mL, Isolated Yield).

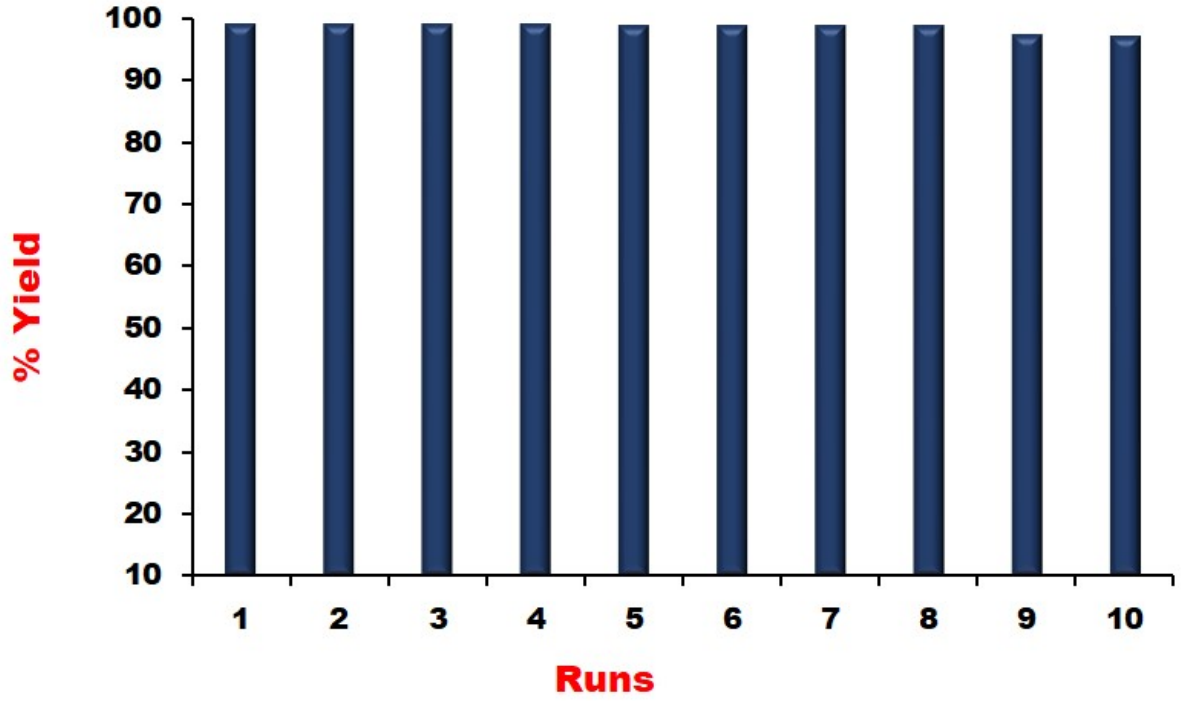

Figure S8: Recycling study (Reaction Conditions: Bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), 1.0 mmol of Cs_2CO_3, 0.75 mol % of PdNPs@UCOF-SH, and solvent EtOH: H_2O 5 mL, Isolated Yield).

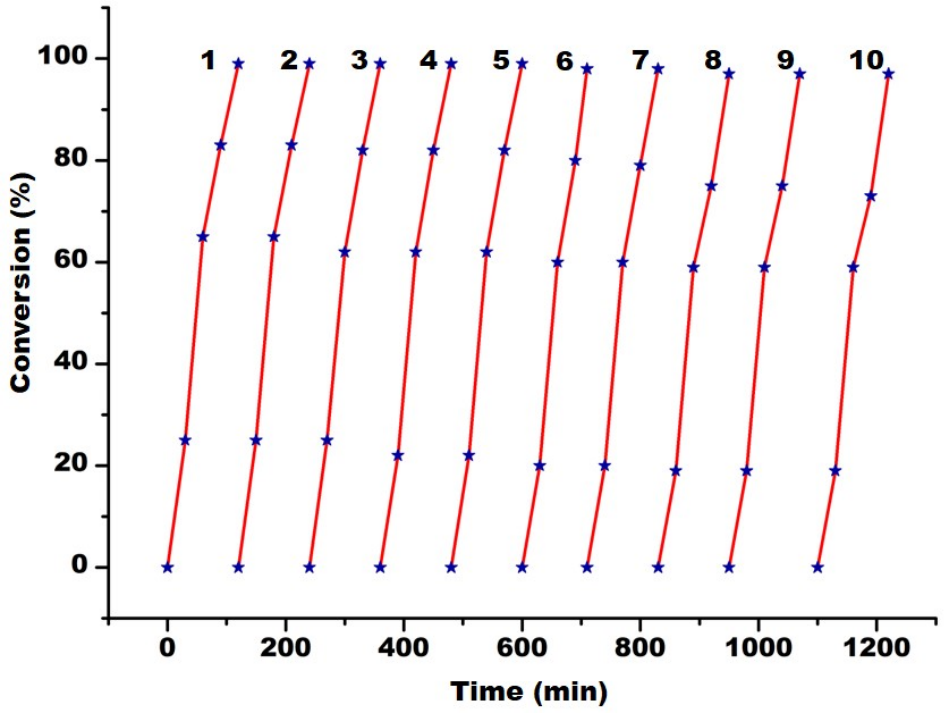

Figure S9: The stability study of PdNPs@UCOF-SH catalyst

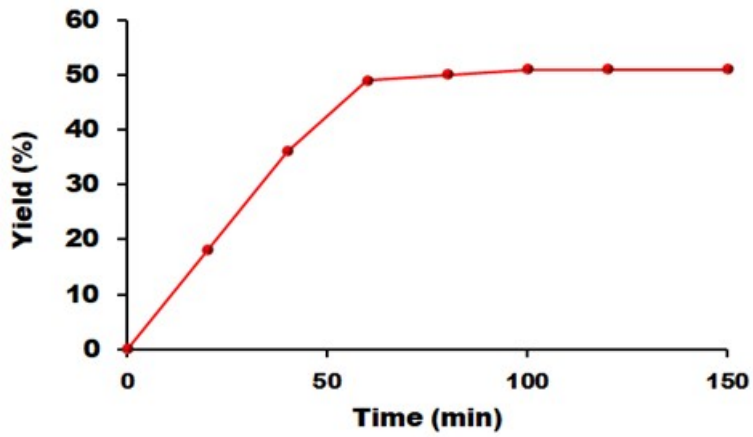

Figure S10: Heterogeneity test (: Bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), 1.0 mmol of Cs_2CO_3, 0.75 mol % of PdNPs@UCOF-SH, and solvent EtOH: H_2O 5 ml).

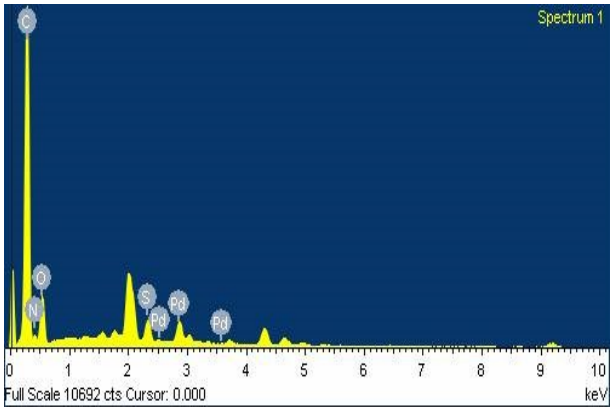

Figure S11: Elemental Mapping of the recycled catalyst after the 10th cycle

NMR Spectra

1,1'-Biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ7.58(t, *J*= 7.8 Hz, 4H), 7.41-7.45 (m, 4H), 7.34 (t, *J*=7.5Hz, 2H) ppm

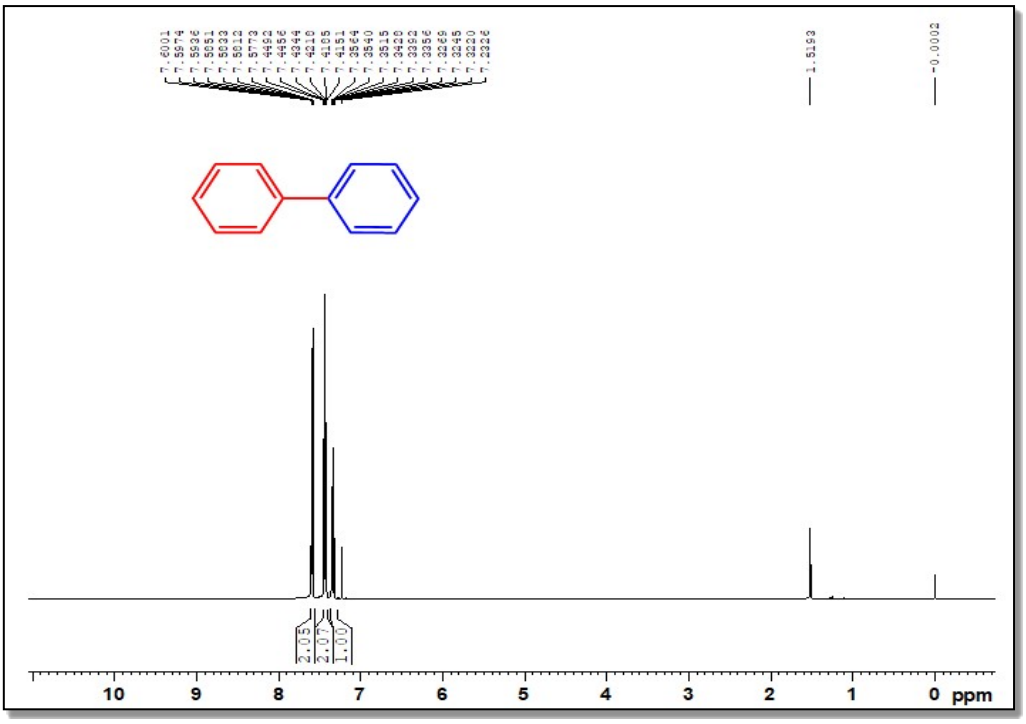

Figure S12:1H NMR of 1,1'-Biphenyl

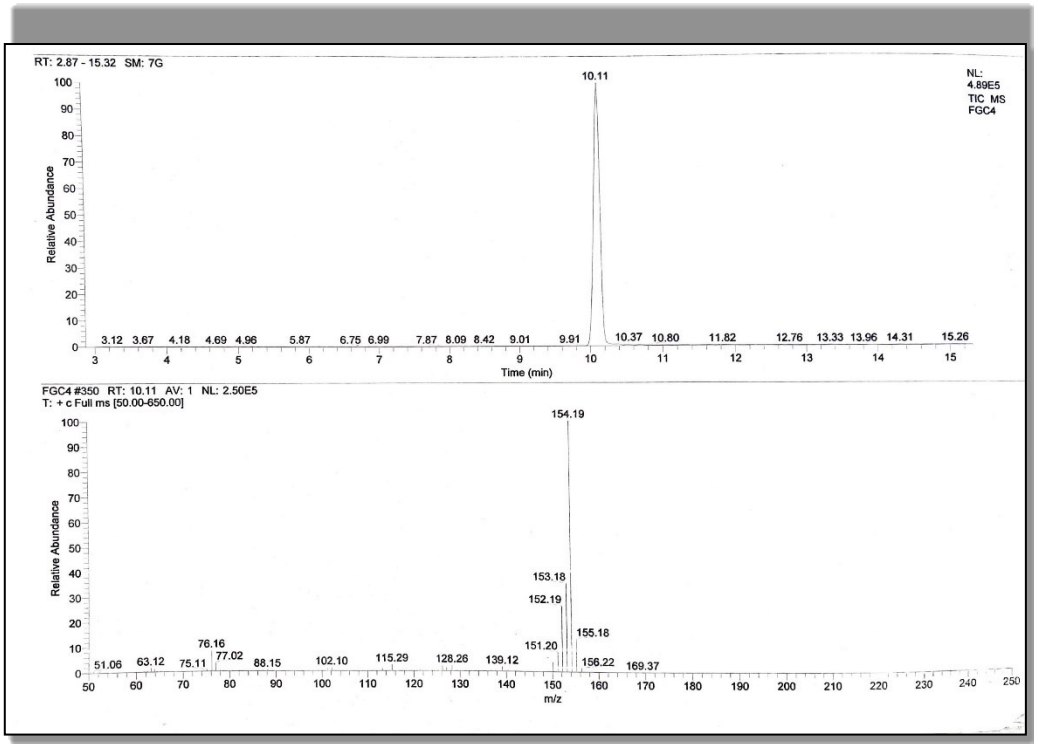

Figure S13: GC-MS spectrum of 1,1'-Biphenyl

4-Methoxy-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.59(m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 6.2 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H) ppm.

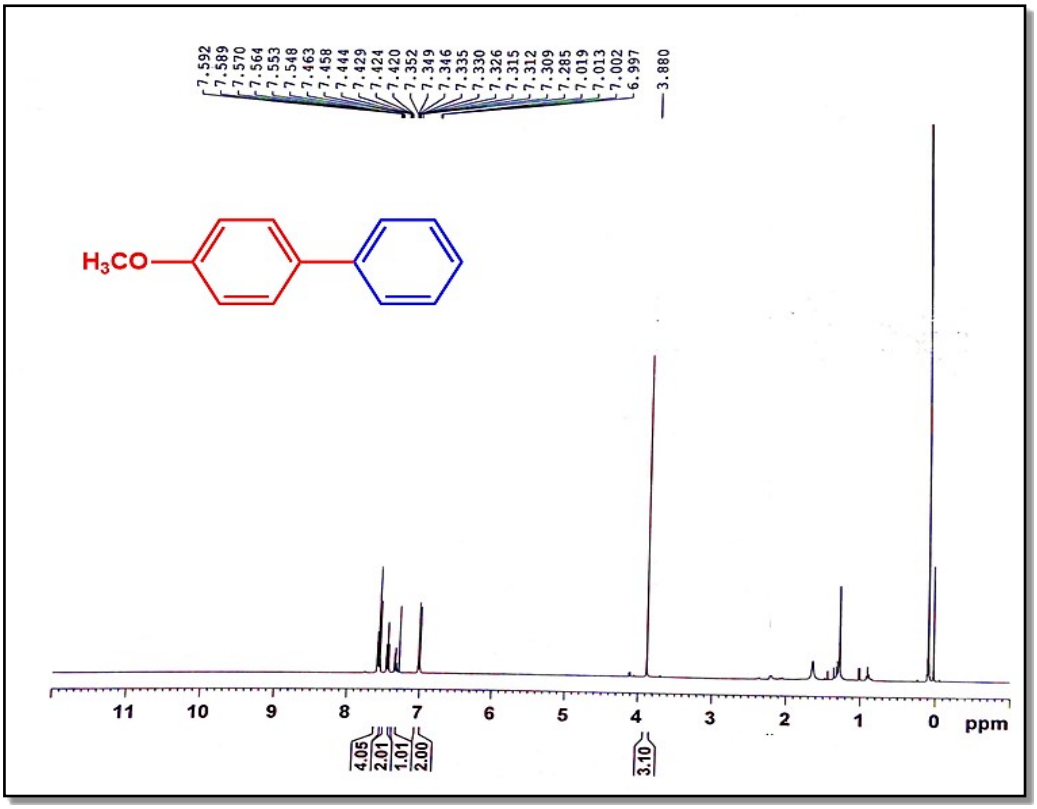

Figure S14: ^{1}H NMR of 4-Methoxy-1,1'-biphenyl

4,4'-Dimethoxy-1,1'-biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 3.71 (s, 3H) ppm

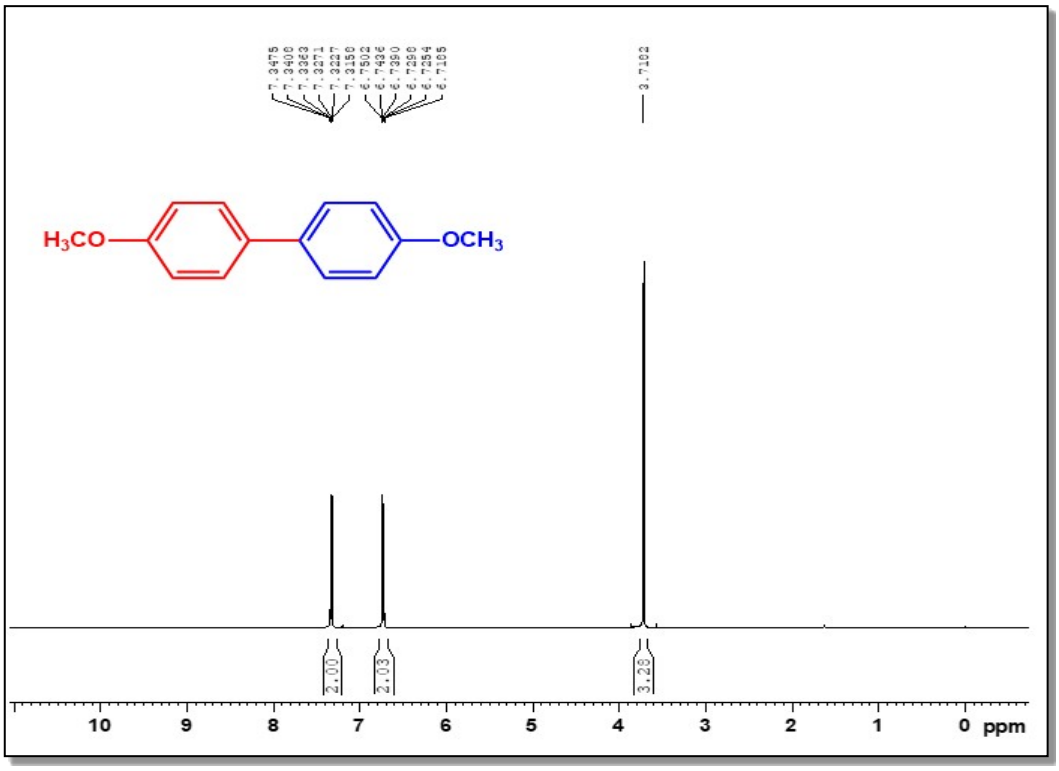

Figure S15: ^{1}H NMR of 4,4'-Dimethoxy-1,1'-biphenyl

4-Acetyl-1,1'-biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 2.63 (s, 3H)ppm.

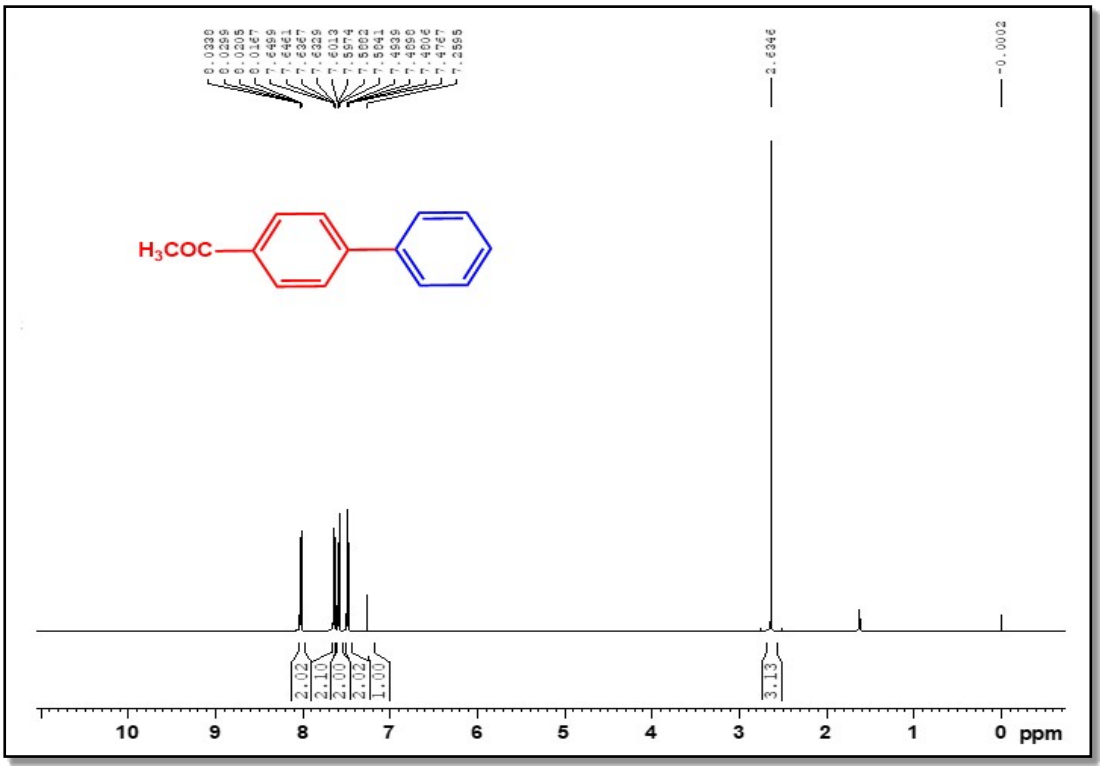

Figure S16: ^{1}H NMR of 4-Acetyl-1,1'-biphenyl

4-Cyano-p-terphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (t, J= 6.15 Hz, 2H), 7.67 (t, J= 6.4 Hz, 1H), 7.55-7.33 (m,10H) ppm.

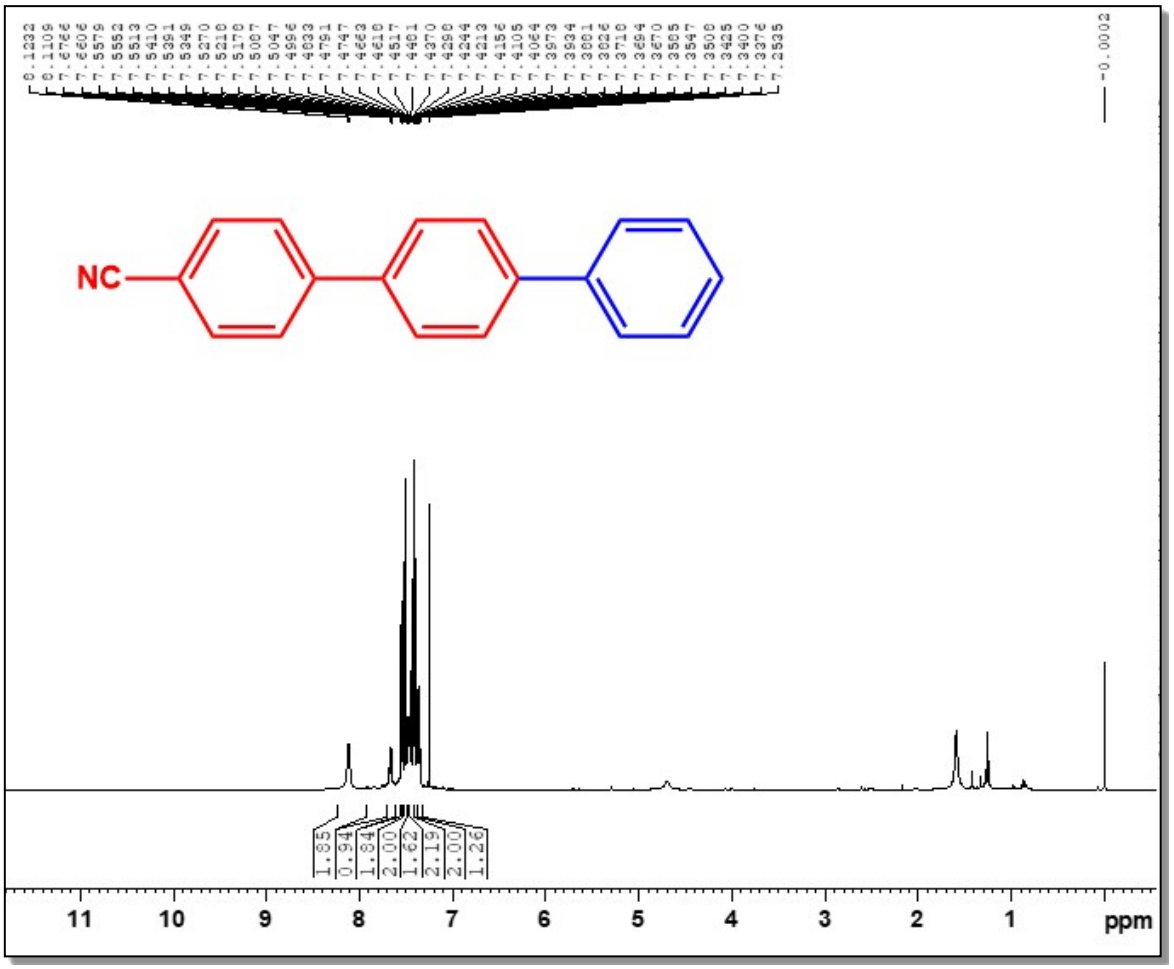

Figure S17: ^{1}H NMR of 4-Cyano-p-terphenyl

3-Flouro-4-nitro-4'-flouro-1,1'-biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J=6.85 Hz, 2 H), 7.73 (s, 1H), 7.59 (d, J=7.1 Hz, 1H), 7.59-7.46 (m, 2H), 7.41-7.38(m, 1H) ppm.

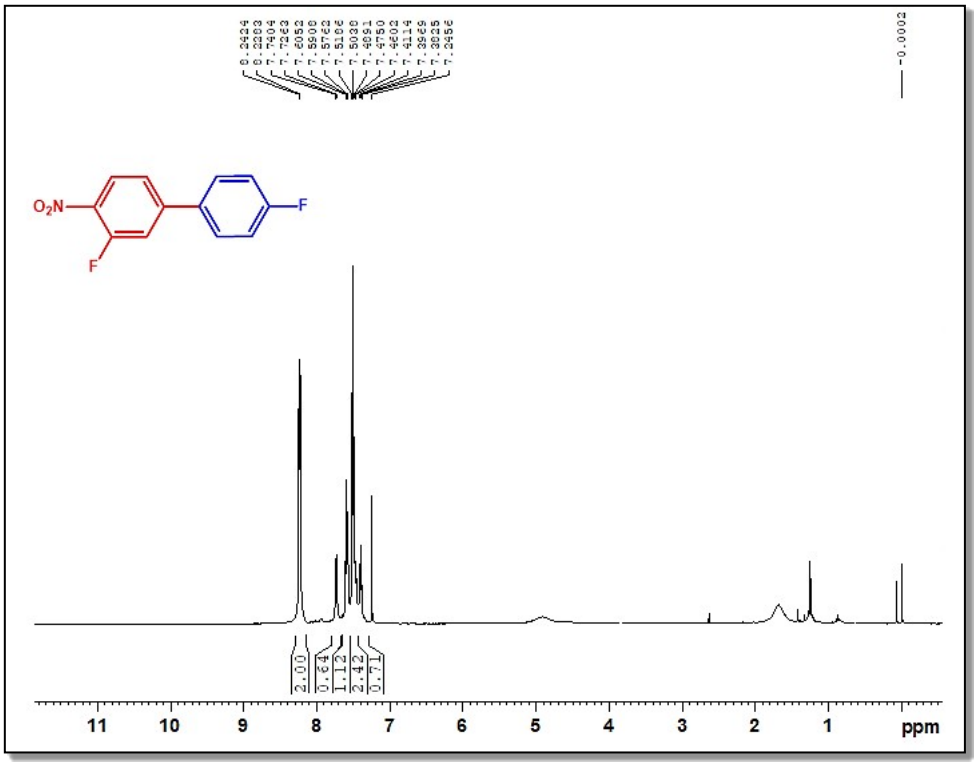

Figure S18: ^{1}H NMR of 3-Flouro-4-nitro-4'-flouro-1,1'-biphenyl

4-Cyano-4’-flouro-1,1’- biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): 7.73-7.64 (m, 4H), 7.49 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H) ppm.

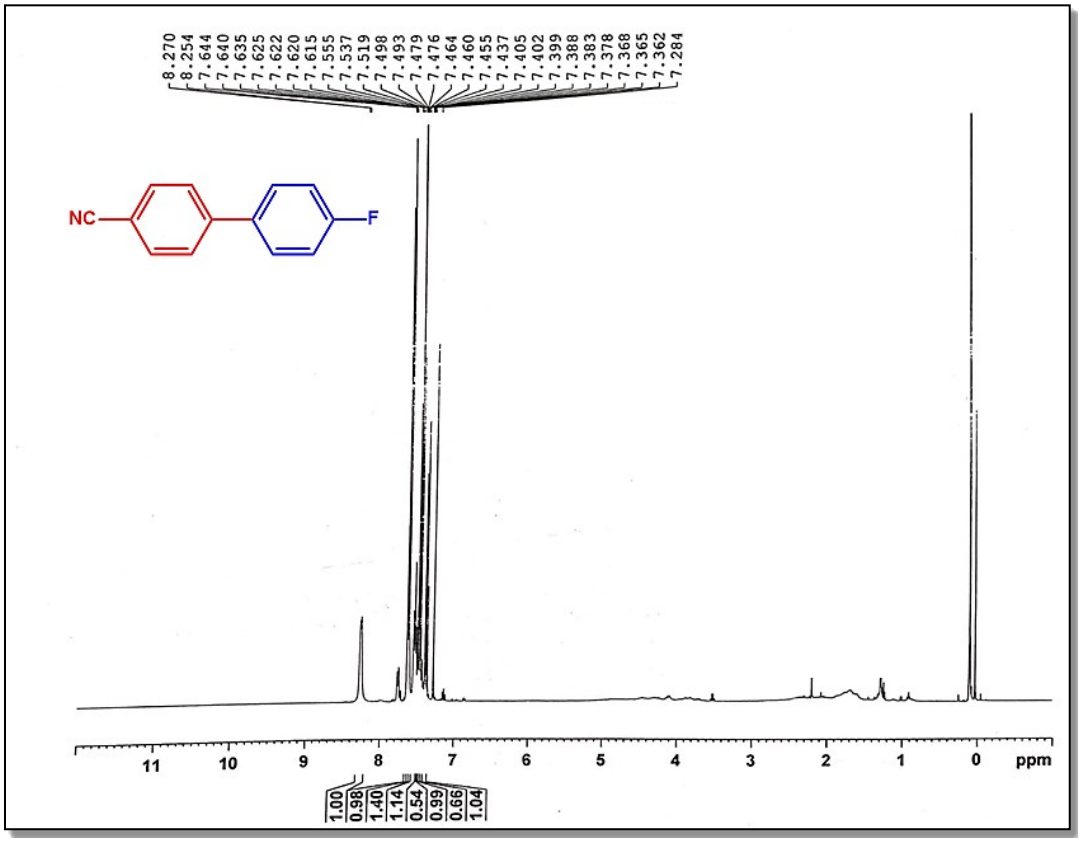

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Figure S19: ^{1}H NMR of 4-Cyano-4’-flouro-1,1’- biphenyl

4-Methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.2 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* =7.8 Hz, 2H),7.51 (m, 4H) ppm.

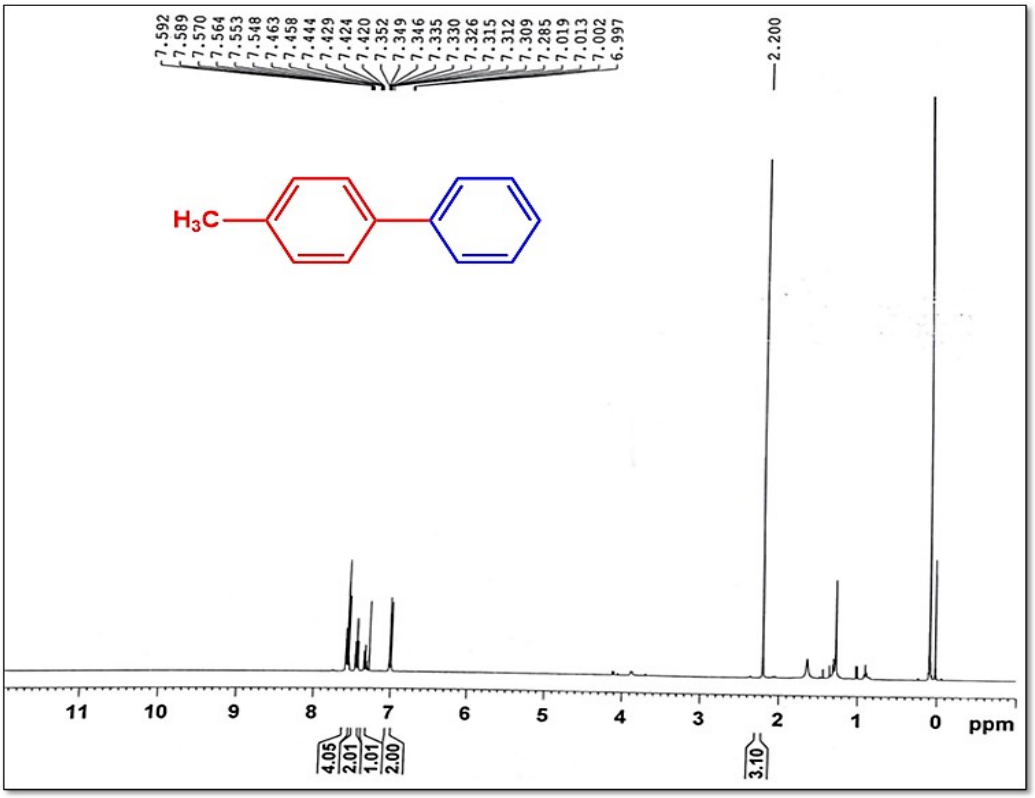

Figure S20: ^{1}H NMR of 4-Methyl-1,1'-biphenyl

4-Flouro-4'-methyl-1,1'- biphenyl

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.63 (s, 3H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H) ppm

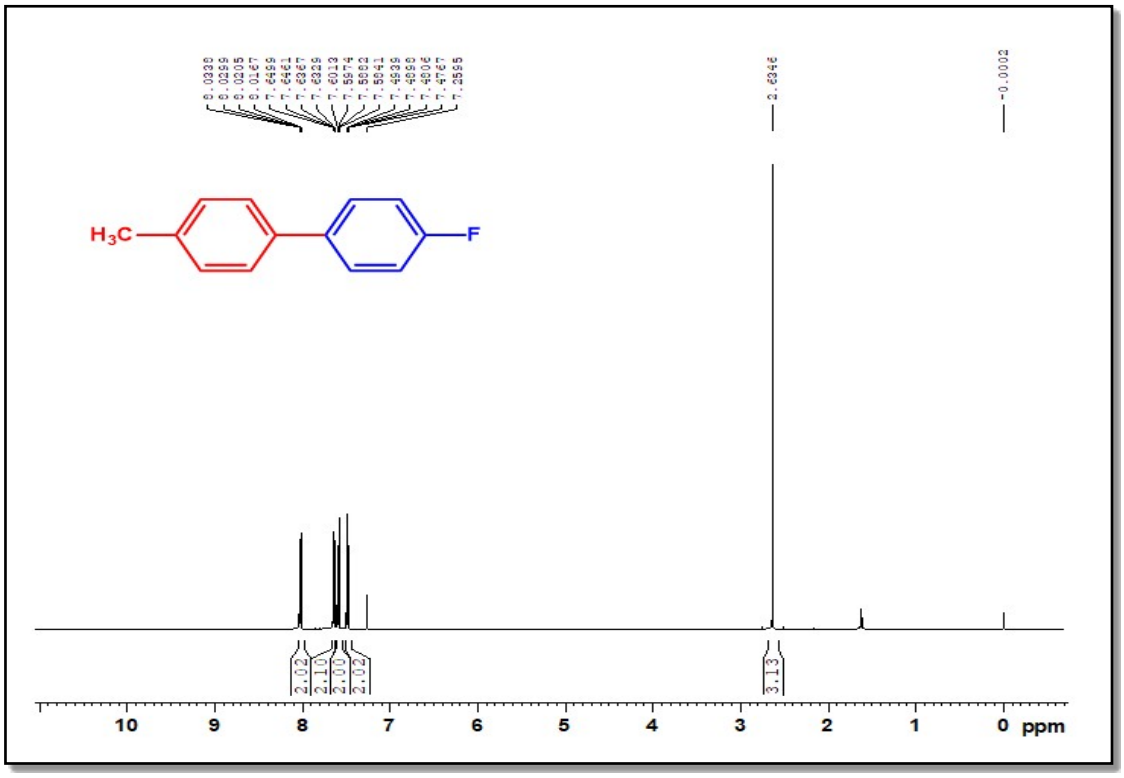

Figure S21: ^{1}H NMR of 4-Flouro-4'-methyl-1,1'- biphenyl

References:

1. Y. Jiang, C. Liu and A. Huang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 32186–32191.
2. J. Yang, Y. Wu, X. Wu, W. Liu, Y. Wang and J. Wang, *Green Chem.*, 2019, **21**, 5267–5273.
3. *S.* Scott*, ACS Catal*. 2018, **8**, 8597.
4. R. Yun, W. Ma, S. Wang, W. Jia and B. Zheng., *Inorg. Chem*. 2019, **58**, 6137